Supporting Information

From ferrocene to 1,2,3,4,5-pentafluoroferrocene: halogen effect on the properties of metallocenes

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General Considerations. All reactions were performed under an argon atmosphere with anhydrous solvents using Schlenk technics. THF was distilled over sodium/benzophenone. Unless otherwise stated, all reagents were used without prior purification. All organolithium reagents were titrated before use.[1] PE refers to petroleum ether, rt refers to room temperature (25 °C). Column chromatography separations were achieved on silica gel (40-63 μm). All Thin Layer Chromatographies (TLC) were performed on aluminum backed plates pre-coated with silica gel (Merck, Silica Gel 60 F254). They were visualized by exposure to UV light. Melting points were measured on a Kofler bench. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer. ^{1}H, ^{13}C and ^{19}F Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance III HD at 500 MHz, 126 MHz and 470 MHz, respectively. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ^{13}C chemical shifts are relative to the central peak of the solvent signal. Cp refers to the unsubstituted cyclopentadienyl ring of ferrocene. HRMS were recorded on a Bruker MaXis 4G mass spectrometer at the Centre Régional de Mesures Physiques de l'Ouest. **Caution**: As polyfluoroferrocenes **3**, **4** and **5** sublimates under vacuum at rt, it is not recommended to keep them for long period under high vacuum. Pentafluoroferrocene (**5**) is also slowly volatile at rt under air pressure.

Safety Considerations. Due to their pyrophoric character, BuLi reagents (and in particular *t*BuLi) need to be used only under inert conditions (anhydrous, nitrogen or argon atmosphere) and by people well-trained to the manipulation of reactive organometallics. Due to the inherent dangers of using cryogenic temperatures, experiments should be performed by well-trained people.

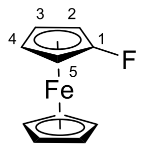
DFT calculations. DFT calculations were carried out using the Gaussian 09 program set,[2] and results visualized using GaussView 5.0. Results were further analyzed using GaussSum3.0.[3] Structures of ferrocene and the various fluorinated derivatives **1** – **5** were optimized without constraints from staggered (D_{5d}) starting geometries using the ωB97X-D functional[4] with the SDD basis set[5] for Fe, and LANL2DZ[6] on C, H and F in CH_2Cl_2 solution modellined by the SMD method.[7] Redox potentials were calculated from differences in single point energies of the ferrocene and ferricenium forms of each compound according to the thermochemical cycles described by other authors.[8-10]

Electrochemical study. Measurements were performed in dry, oxygen-free dichloromethane or acetonitrile, at a concentration of 1 mM, with $n\text{Bu}_4\text{NPF}_6$ (0.1 M) as the supporting electrolyte. For all the experiments, the working electrode was a glassy carbon disk (diameter 1.5 mm) which was polished (5 μm grain size) with a slurry of alumina and ethanol and rinsed with dichloromethane before to use. The reference electrode was Ag/AgCl separated from the solution by a glass frit, while the counter electrode was a glassy carbon rod.

Experimental section: procedures and compounds analyses

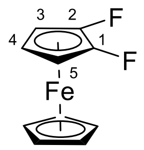
Fluoroferrocene – 1: *t*BuLi (1.6 M, 100 mL, 160 mmol, 2.00 equiv) was added dropwise to a solution of ferrocene (14.9 g, 80.0 mmol, 1.00 equiv) and *t*BuOK (897 mg, 8.00 mmol, 0.10 equiv) in THF (600 mL) at -80 °C. After addition, the reaction was stirred at -80 °C for 1 h. The reaction mixture was cannulated onto a solution of NFSI (50.5 g, 160 mmol, 2.00 equiv) in THF (300 mL) at -20 °C. After addition, the reaction mixture was stirred for 10 min before PE (500 mL) was added. The reaction mixture was poured onto alumina (1 kg), eluting with PE. The combined filtrates were concentration under vacuum to give the crude product. This was purified by column chromatography over SiO_2, using CH_2Cl_2/PE (3:1) to give a fraction containing ferrocene and fluoroferrocene after evaporation. This was dissolved into pentane (400 mL) which was washed with a $FeCl_3$ aqueous solution (0.2 M) until all unreacted ferrocene has been removed (monitoring by ^{1}H NMR). The organic layer was washed with water (5 x 100 mL), brine (100 mL), dried over $MgSO_4$, filtrated and concentrated under vacuum to give the title product as an orange solid (8.22 g, 50%). Analytical data analogous to those reported previously.[11-13]

R_f (eluent: PE-CH_2Cl_2 90:10) = 0.83. Mp 117-118 °C. ν_{max} (film)/cm^{-1} 3100, 1468, 1408, 1369, 1240, 1104, 1018, 999, 927, 803. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.30 (dt, $^{3}J_{HH}$ = 2.0 Hz, $^{3}J_{HF}$ = 3.0 Hz, 2H, FcCH, H2 and H5), 4.26 (s, 5H, Cp), 3.79 (td, $^{4}J_{HF}$ = 1.3 Hz, $^{3}J_{HH}$ = 2.0 Hz, 2H, FcCH, H3 and H4). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 135.8 (d, $^{1}J_{CF}$ = 267.6 Hz, FcC, C1), 69.4 (s, Cp), 61.2 (d, $^{3}J_{CF}$ = 3.8 Hz, 2xFcCH, C3 and C4), 56.2 (d, $^{2}J_{CF}$ = 15.3 Hz, 2xFcCH, C2 and C5). ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -181.8 (dt, $^{4}J_{HF}$ = 1.6 Hz, $^{3}J_{HF}$ = 3.0 Hz).



1,2-Difluoroferrocene – 2: *s*BuLi (1.1 M, 19.7 mL, 21.6 mmol, 1.2 equiv) was added to a solution of fluoroferrocene (**1**; 3.66 g, 18.0 mmol, 1.00 equiv) in THF (30 mL) at -80 °C. After addition, the reaction was stirred at -80 °C for 1 h. It was cannulated onto a solution of NFSI (6.81 g, 21.6 mmol, 1.20 equiv) in THF (40 mL) at -80 °C. The flask was washed with THF (5 mL) for a quantitative transfer. The reaction was warmed to rt, water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under vacuum to give the crude product. This was purified by column chromatography over silica, eluting with PE-CH_2Cl_2 (80:20) to give a mixture of compounds **1** and **2** (10:90). This was dissolved in pentane which was washed with a $FeCl_3$ aqueous solution (1.2 M) until all unreacted fluoroferrocene (**1**) has been removed (monitoring by ^{1}H or ^{19}F NMR). The organic layer was washed with water (5 times), brine, dried over $MgSO_4$, filtrated and concentrated under vacuum to give the title product as an orange solid (2.89 g, 72%). Analytical data analogous to those reported previously.[13-14]

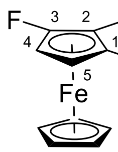
R_f (eluent: PE-CH_2Cl_2 90:10) = 0.86. Mp 115-116 °C. ν_{max} (film)/cm^{-1} 3104, 1509, 1462, 1410, 1377, 1287, 1104, 1014, 1000, 845, 823, 797. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.35 (s, 5H, Cp), 4.07 (dt, $^{3}J_{HF}$ = 1.5 Hz, $^{3}J_{HH}$ = 3.0 Hz, 2H, FcCH, H3 and H5), 3.46 (tt, $^{4}J_{HF}$ = 1.2 Hz, $^{3}J_{HH}$ = 2.9 Hz, 1H, FcCH, H4). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 123.6 (dd, $^{2}J_{CF}$ = 13.4 Hz, $^{1}J_{CF}$ = 272.0 Hz, 2xFcC, C1 and C2), 70.9 (s, Cp), 51.6 (t, $^{4}J_{CF}$ = 2.8 Hz, FcCH, C4), 51.0 (dd, $^{3}J_{CF}$ = 4.8 Hz, $^{2}J_{CF}$ = 9.0 Hz, 2xFcCH, C3 and C5). ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -202.3 (q, J = 1.4 Hz).



1,2,3-Trifluoroferrocene – 3: *s*BuLi (1.1 M, 16.4 mL, 18.0 mmol, 1.2 equiv) was added to a solution of 1,2-difluoroferrocene (**2**; 3.33 g, 15.0 mmol, 1.00 equiv) in THF (30 mL) at -80 °C. After addition, the reaction was stirred at -80 °C for 1 h. It was cannulated onto a solution of

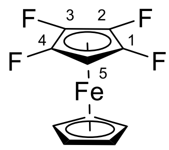
NFSI (5.67 g, 18.0 mmol, 1.20 equiv) in THF (30 mL) at -80 °C. The flask was washed with THF (5 mL) for a quantitative transfer. The reaction was warmed to rt, water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under vacuum to give the crude product. This was purified by column chromatography over silica, eluting with PE-CH_2Cl_2 (80:20) to give a mixture of compounds **2**, **3** and **4** (7:82:11). This was dissolved in pentane which was washed with a $FeCl_3$ aqueous solution (3 M) until all unreacted fluoroferrocene (**2**) has been removed (monitoring by ^{1}H or ^{19}F NMR). The organic layer was washed with water (5 times), brine, dried over $MgSO_4$, filtrated and concentrated under vacuum to give the crude product. This was purified by column chromatography over silica, eluting with PE-CH_2Cl_2 (90:10) to give 1,2,3-trifluoroferrocene (**3**) as a light orange solid (2.27 g, 63%) and 1,2,3,4-tetrafluoroferrocene (**4**) as a yellow solid (183 mg, 5%). Analytical data analogous to those reported previously.[13]

R_f (eluent: PE-CH_2Cl_2 90:10) = 0.82. Mp 112-113 °C. ν_{max} (film)/cm^{-1} 1527, 1516, 1493, 1450, 1411, 1306, 1179, 1149, 1106, 1000, 985, 824, 791, 711. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.44 (s, 5H, Cp), 3.81 (t, $^3J_{HF}$ = 1.6 Hz, 2H, FcCH, H4 and H5). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 119.0 (ddd, $^3J_{CF}$ = 3.0 Hz, $^2J_{CF}$ = 10.6 Hz, $^1J_{CF}$ = 276.9 Hz, 2xFcC, C1 and C3), 113.5 (dt, $^2J_{CF}$ = 12.9 Hz, $^1J_{CF}$ = 274.7 Hz, FcC, C2), 72.5 (s, Cp), 42.3 (dd, $^3J_{CF}$ = 10.0 Hz, $^4J_{CF}$ = 5.9 Hz, 2xFcCH, C4 and C5). ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -203.4 (dt, $^3J_{CF}$ = 1.6 Hz, $^3J_{FF}$ = 21.5 Hz, 2xF, F-C_1 and F-C_3), -214.2 (t, $^3J_{FF}$ = 21.5 Hz, 1F, F-C_2). HRMS (ASAP, *m/z*): calcd. for $C_{10}H_7F_3{}^{56}Fe$ 239.9844, found 239.9847 (1 ppm) $[M]^{+\cdot}$.

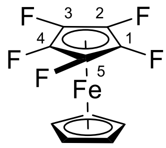


1,2,3,4-Tetrafluoroferrocene – **4**: *s*BuLi (1.1 M, 7.65 mL, 8.40 mmol, 1.2 equiv) was added to a solution of 1,2,3-trifluoroferrocene (**3**; 1.68 g, 7.00 mmol, 1.00 equiv) in THF (15 mL) at -80 °C. After addition, the reaction was stirred at -80 °C for 1 h. It was cannulated onto a solution of NFSI (2.65 g, 8.40 mmol, 1.20 equiv) in THF (15 mL) at -80 °C. The flask was washed with THF (2 mL) for a quantitative transfer. The reaction was warmed to rt, water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under vacuum to give the crude product. This was purified by column chromatography over silica, eluting with PE-CH_2Cl_2 (80:20) to give a mixture of compounds **3**, **4** and **5** (17:76:7). This was purified by column chromatography over silica, eluting with PE-CH_2Cl_2 (90:10) to give 1,2,3-trifluoroferrocene (**3**) as a light orange solid (170 mg, 10%), 1,2,3,4-tetrafluoroferrocene (**4**) as a yellow solid (650 mg, 36%) and 1,2,3,4,5-pentafluoroferrocene (**5**) as a light yellow solid (72 mg, 4%).[13]

R_f (eluent: PE-CH_2Cl_2 90:10) = 0.89. Mp 109-110 °C. ν_{max} (film)/cm^{-1} 3114, 1530, 1509, 1475, 1446, 1413, 1107, 1123, 1072, 1054, 1001, 891, 827, 725. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.54 (s, 5H, Cp), 4.26 (tt, $^4J_{HF}$ = 1.4 Hz, $^3J_{HF}$ = 4.5 Hz, 1H, FcH, H5). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 112.7 (ddt, $^3J_{CF}$ = 4.2 Hz, $^2J_{CF}$ = 8.0 Hz, $^1J_{CF}$ = 283.4 Hz, 2xFcC, C1 and C4), 109.7 (dddd, $^3J_{CF}$ = 4.9 Hz, $^2J_{CF}$ = 8.8 Hz, $^2J_{CF}$ = 13.9 Hz, $^1J_{CF}$ = 282.7 Hz), 74.3 (s, Cp), 35.1 (t, $^3J_{CF}$ = 15.5 Hz, FcCH, C5). ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -210.7 (td, $^3J_{HF}$ = 4.5 Hz, $^3J_{FF}$ = 26.6 Hz, 2xF, F-C_1 and F-C_4), -217.3 (td, $^4J_{HF}$ = 1.4 Hz, $^3J_{FF}$ = 26.6 Hz, 2xF, F-C_2 and F-C_3). HRMS (ASAP, *m/z*): calcd. for $C_{10}H_6F_4{}^{56}Fe$ 257.9755, found 257.9750 (0 ppm) $[M]^{+\cdot}$.



1,2,3,4,5-Pentafluoroferrocene – **5**: *s*BuLi (1.1 M, 2.20 mL, 2.40 mmol, 1.2 equiv) was added to a solution of 1,2,3,4-tetrafluoroferrocene (**4**; 530 mg, 2.00 mmol, 1.00 equiv) in THF (5 mL) at -80 °C. After addition, the reaction was stirred at -80 °C for 1 h. It was cannulated onto a solution of NFSI (757 mg, 2.40 mmol, 1.20 equiv) in THF (5 mL) at -80 °C. The flask was washed with THF (1 mL) for a quantitative transfer. The reaction was warmed to rt, water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under vacuum to give the crude product. This was purified by column chromatography over silica, eluting with PE-CH_2Cl_2 (90:10) to give 1,2,3,4-tetrafluoroferrocene (**4**) as a yellow solid (55 mg, 10%) and 1,2,3,4,5-pentafluoroferrocene (**5**) as a light yellow solid (282 mg, 51%).[13]

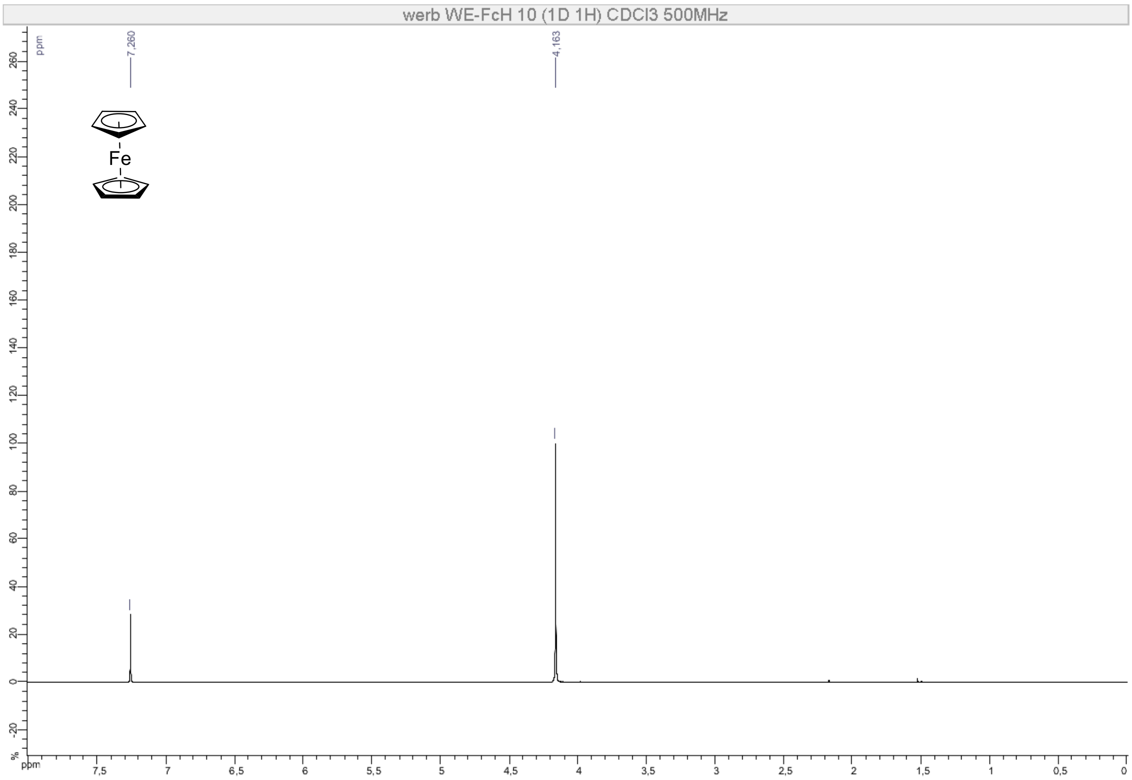


R_f (eluent: PE-CH_2Cl_2 90:10) = 0.91. ν_{max} (film)/cm^{-1} 1508, 1458, 1414, 1024, 1003, 939, 907, 832. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.64 (s, 5H, Cp). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 105.6 (dm, J = 300 Hz, C_5F_5), 76.2 (s, Cp). ^{19}F NMR (470 MHz, $CDCl_3$): δ (ppm) -222.3 (s).

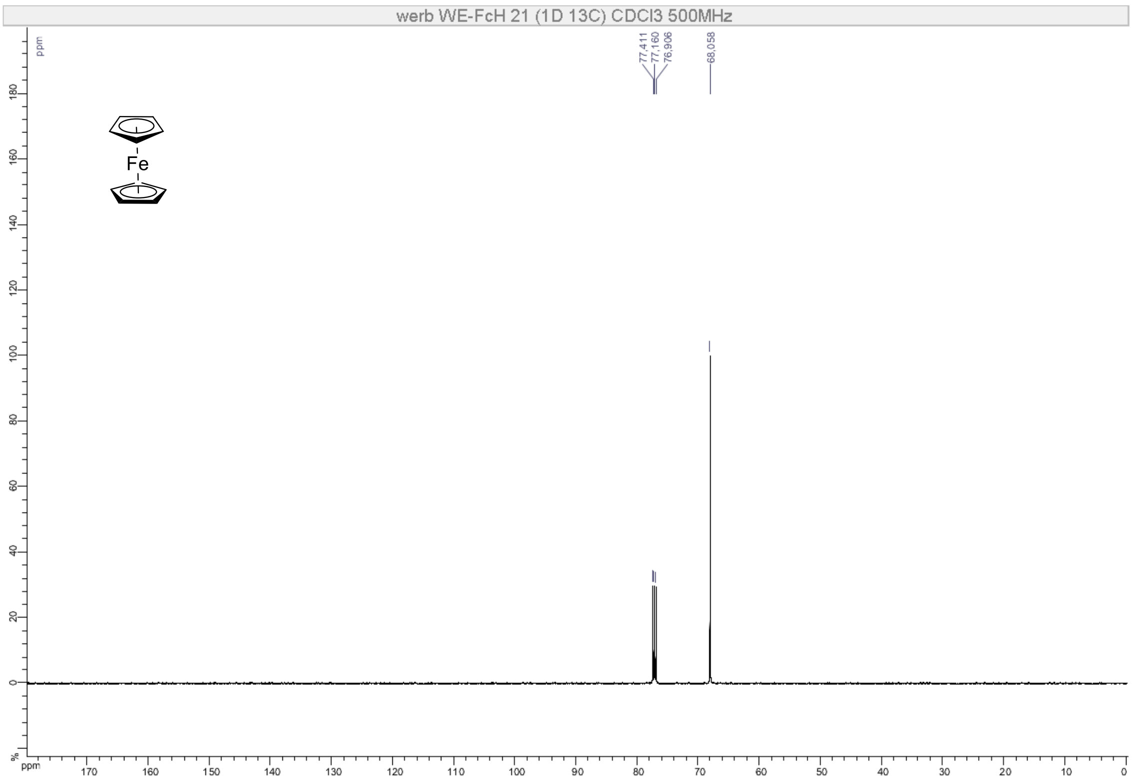
NMR Spectra

<u>Ferrocene</u>

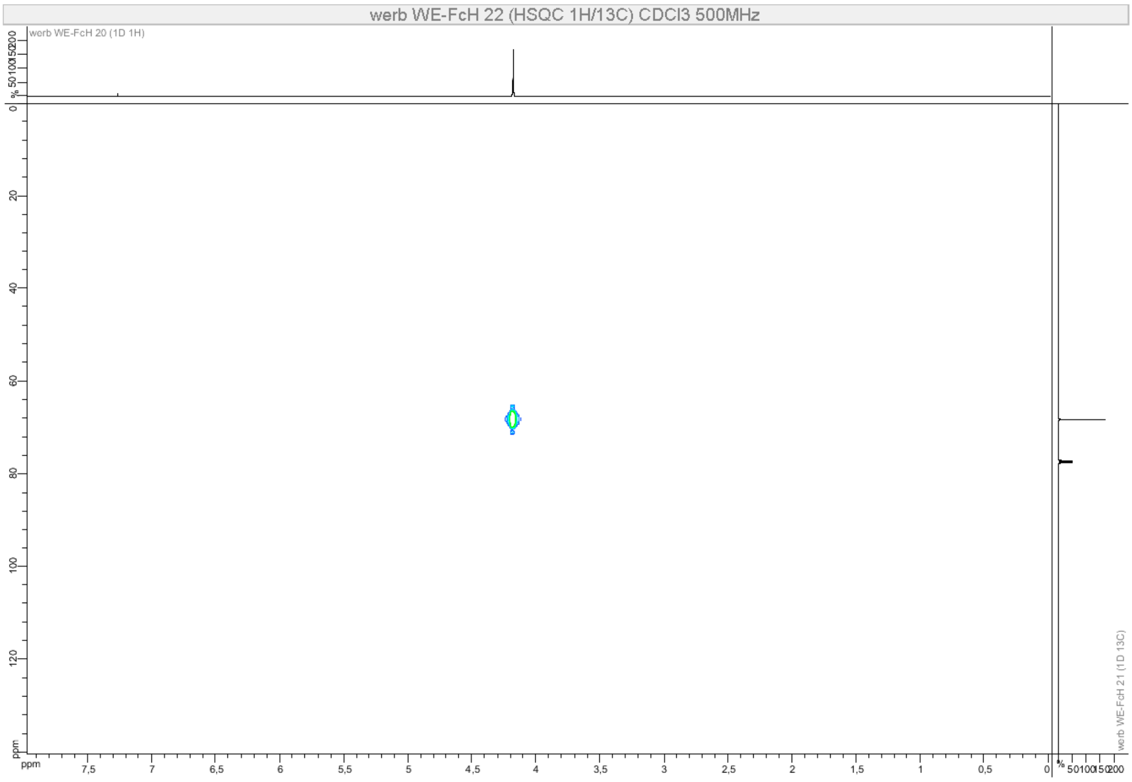
^{1}H (500 MHz, $CDCl_3$) – Full spectrum



^{13}C{^{1}H} (125 MHz, $CDCl_3$) – Full spectrum

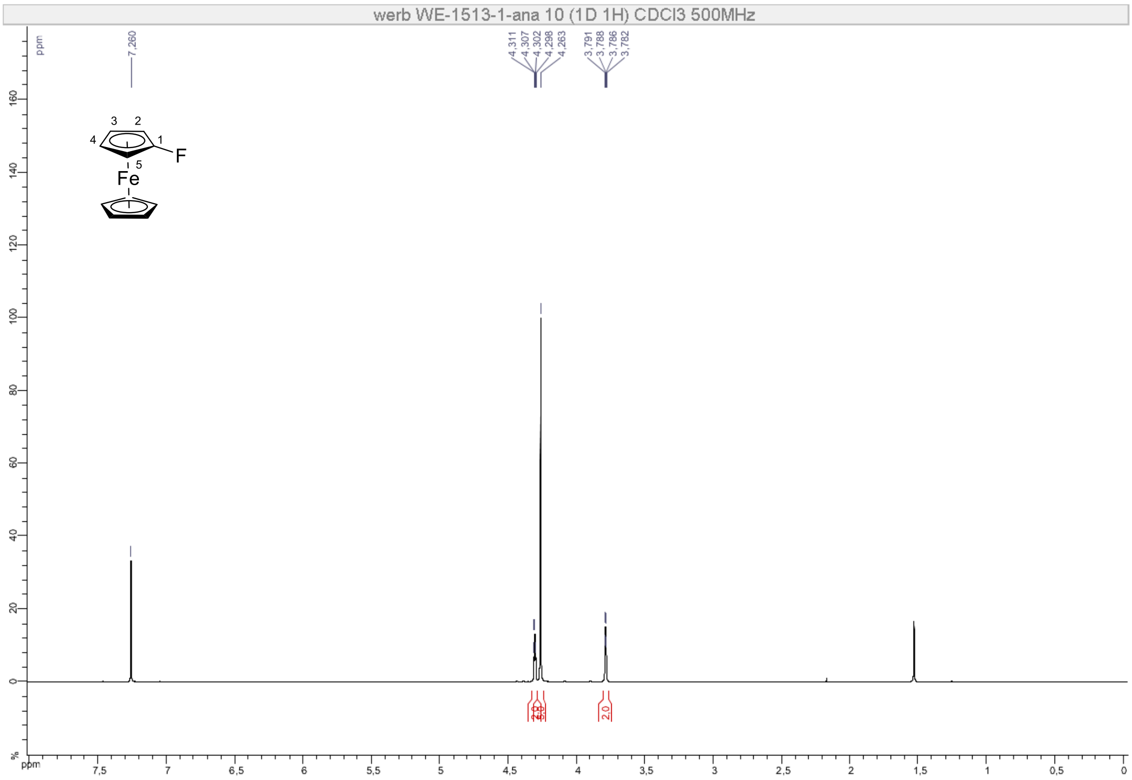


HSQC (500 MHz, $CDCl_3$)

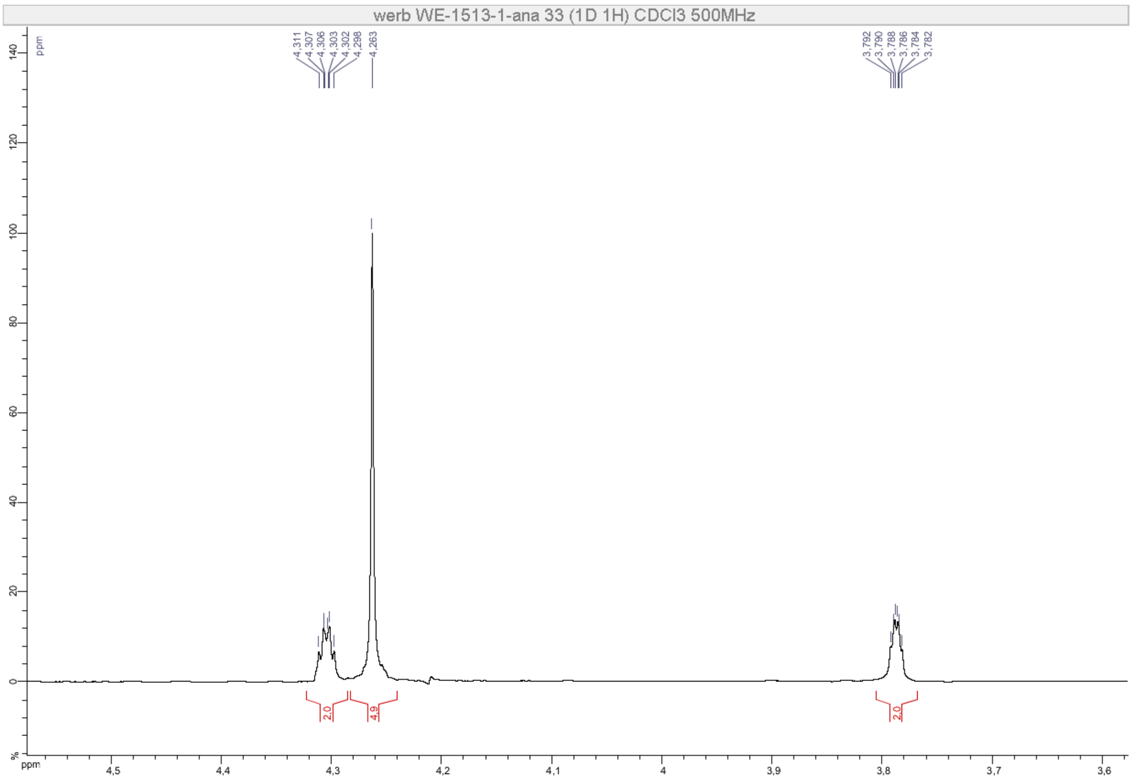


Compound 1

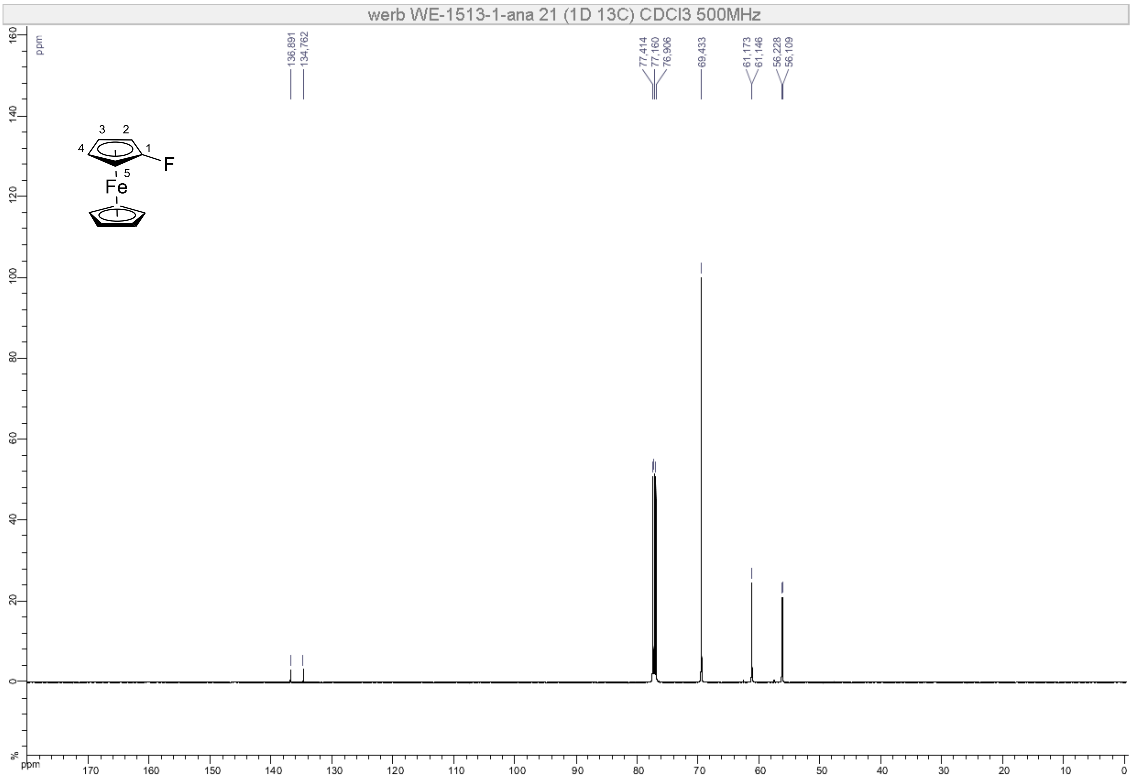
^{1}H (500 MHz, CDCl$_3$) – Full spectrum



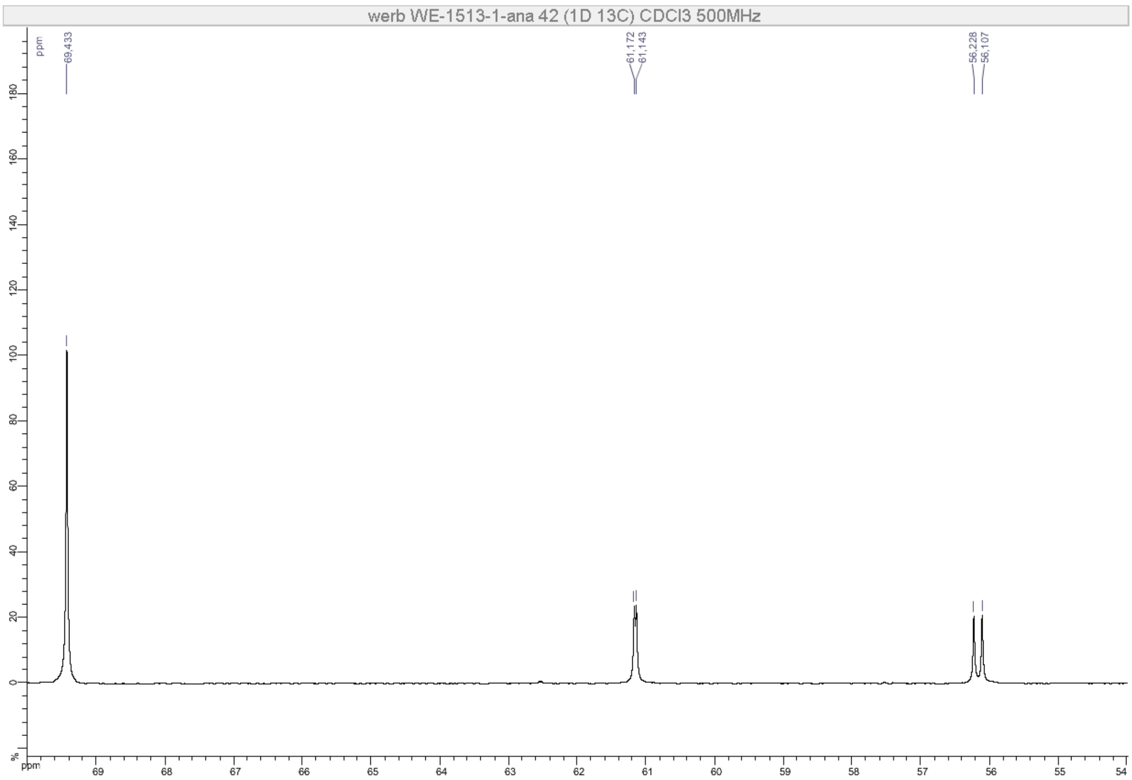
^{1}H (500 MHz, CDCl$_3$) – 3.6 to 4.6 ppm area



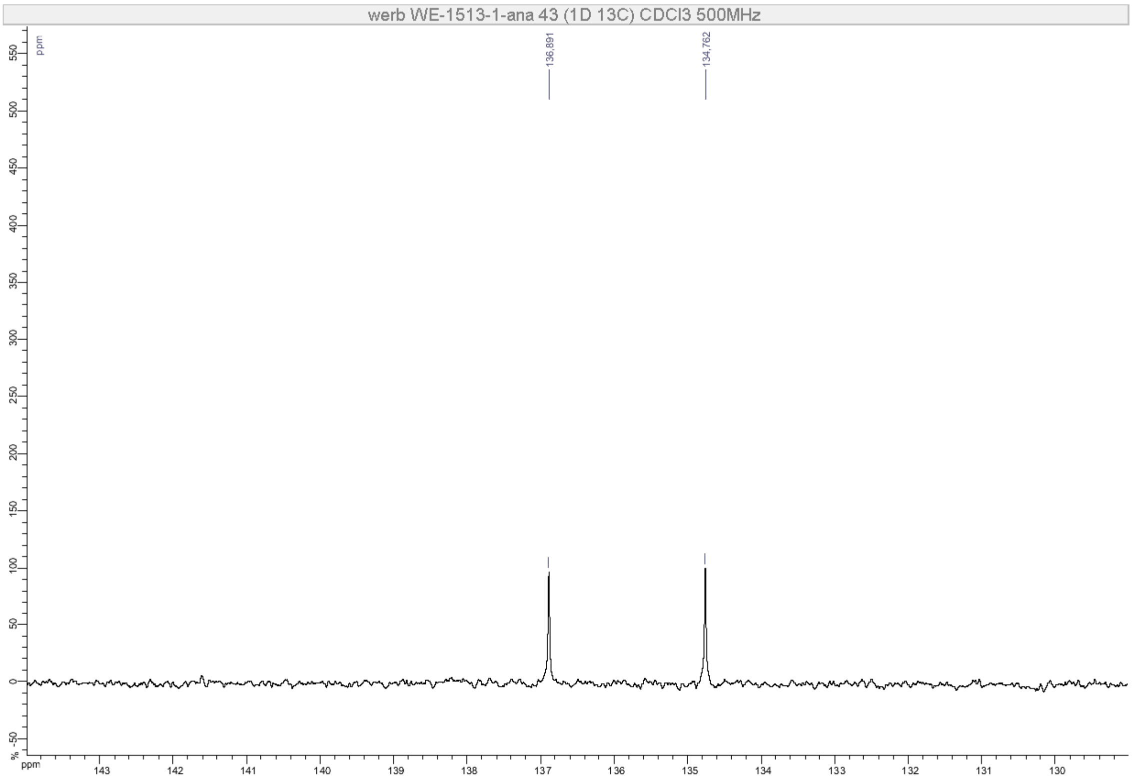
$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) – Full spectrum



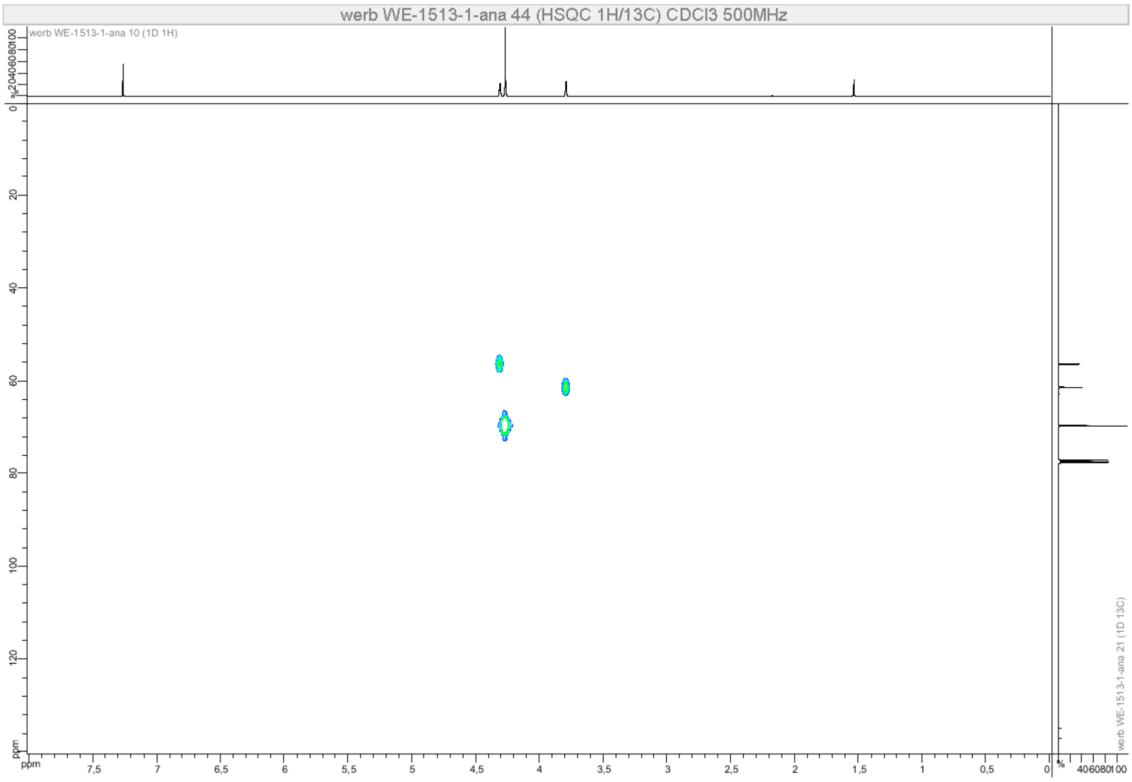
$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) – 54 to 70 ppm area



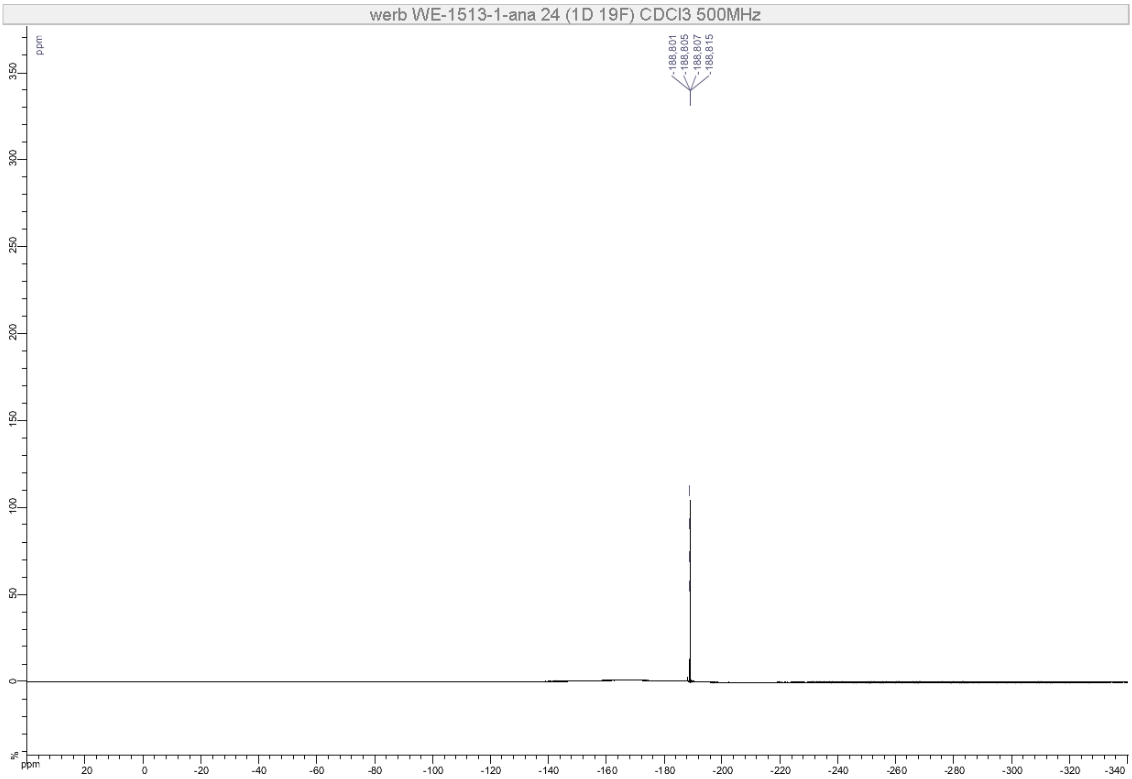
$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) – 125 to 145 ppm area



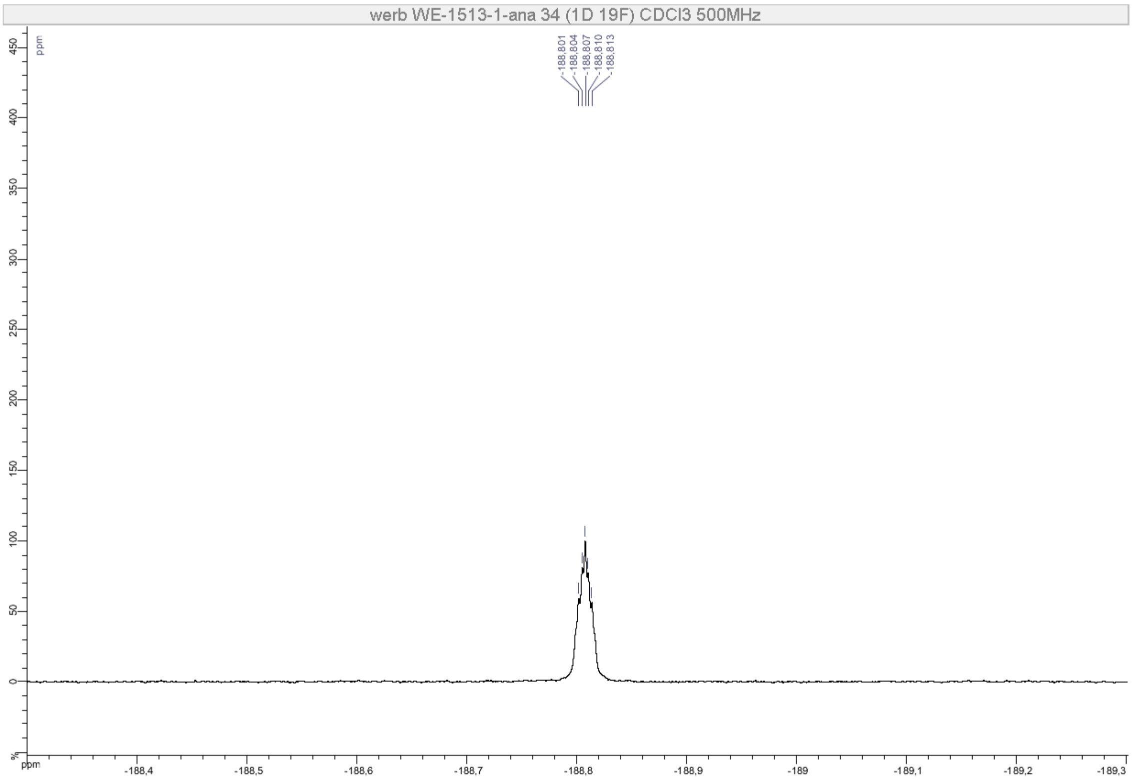
HSQC (500 MHz, $CDCl_3$)



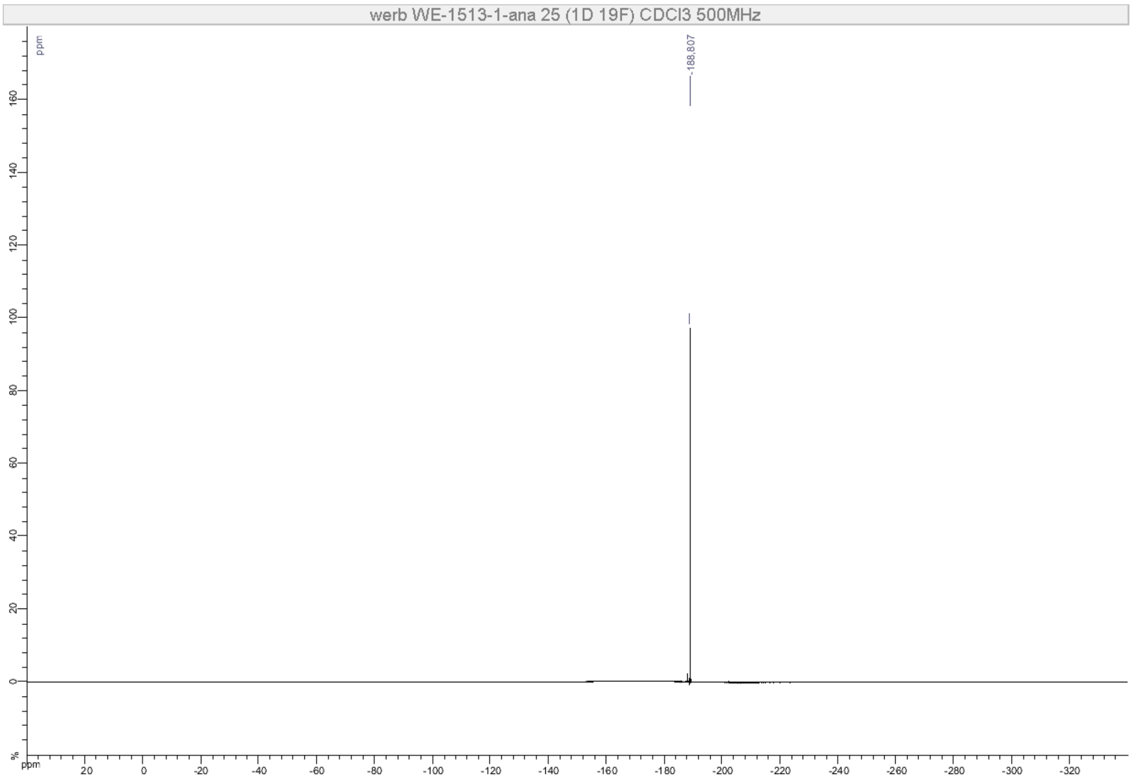
^{19}F (470 MHz, $CDCl_3$) – Full spectrum



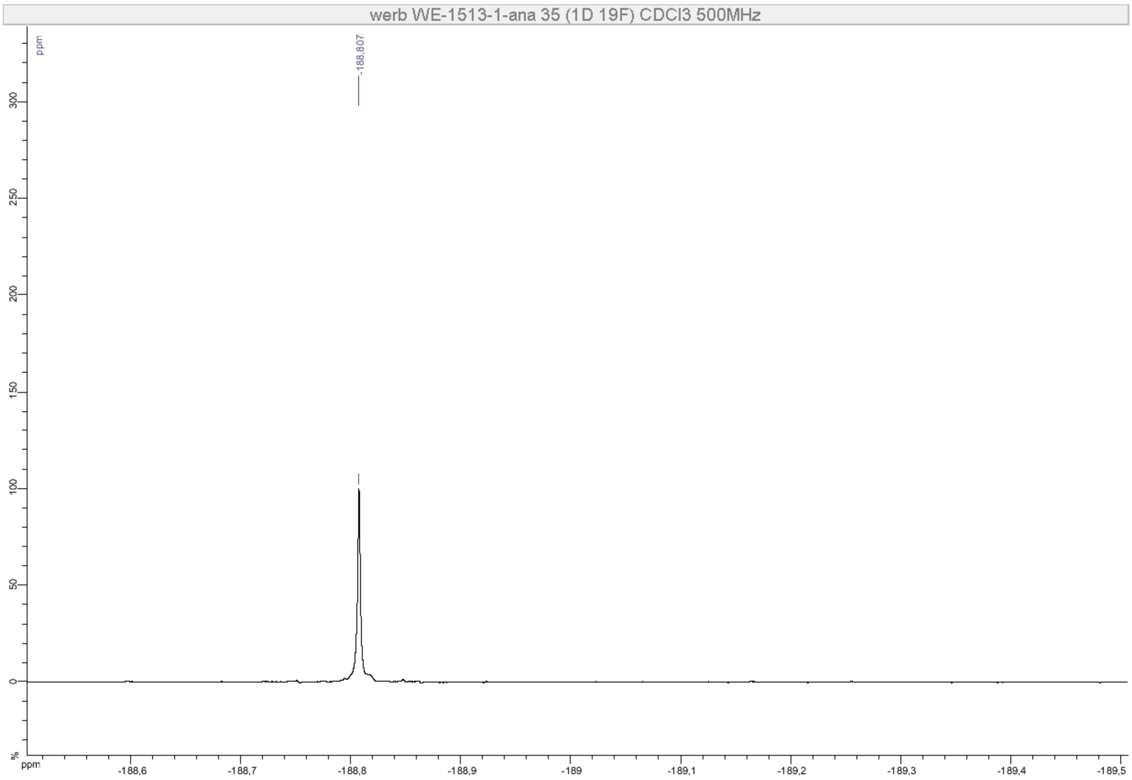
^{19}F (470 MHz, $CDCl_3$) – -184 to -194 ppm area



$^{19}F\{^{1}H\}$ (470 MHz, $CDCl_3$) – Full spectrum

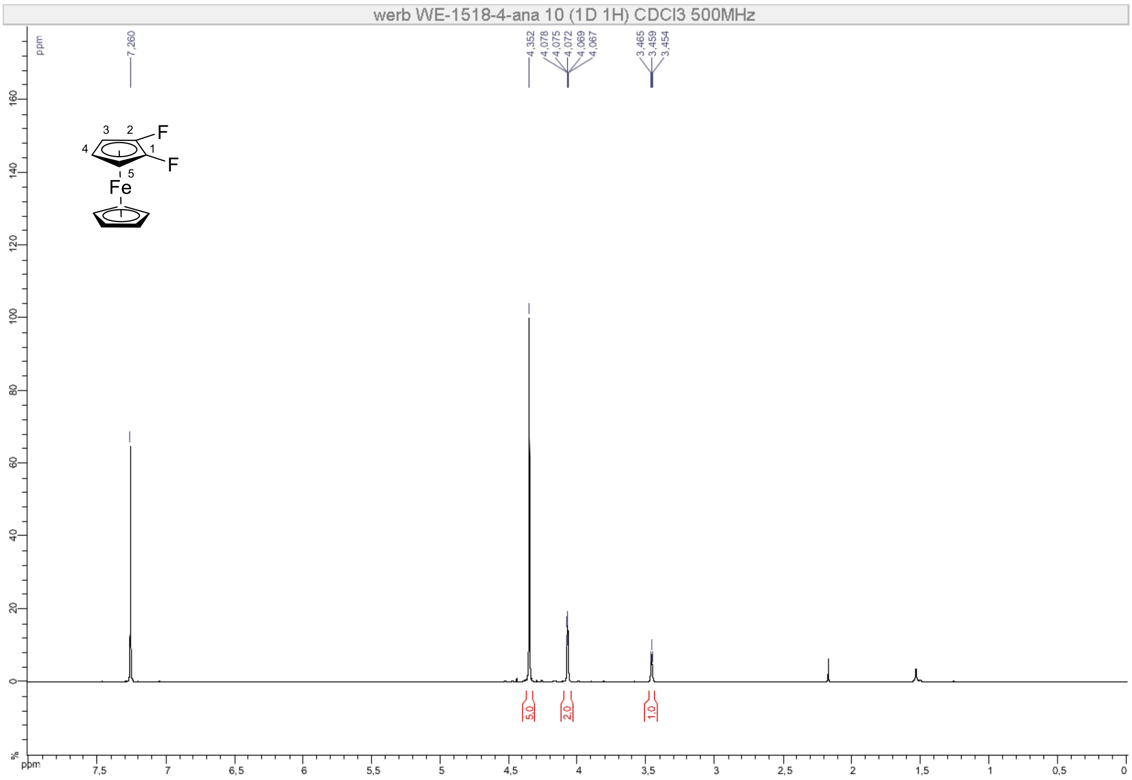


$^{19}F\{^{1}H\}$ (470 MHz, $CDCl_3$) – -188 to -189 ppm area

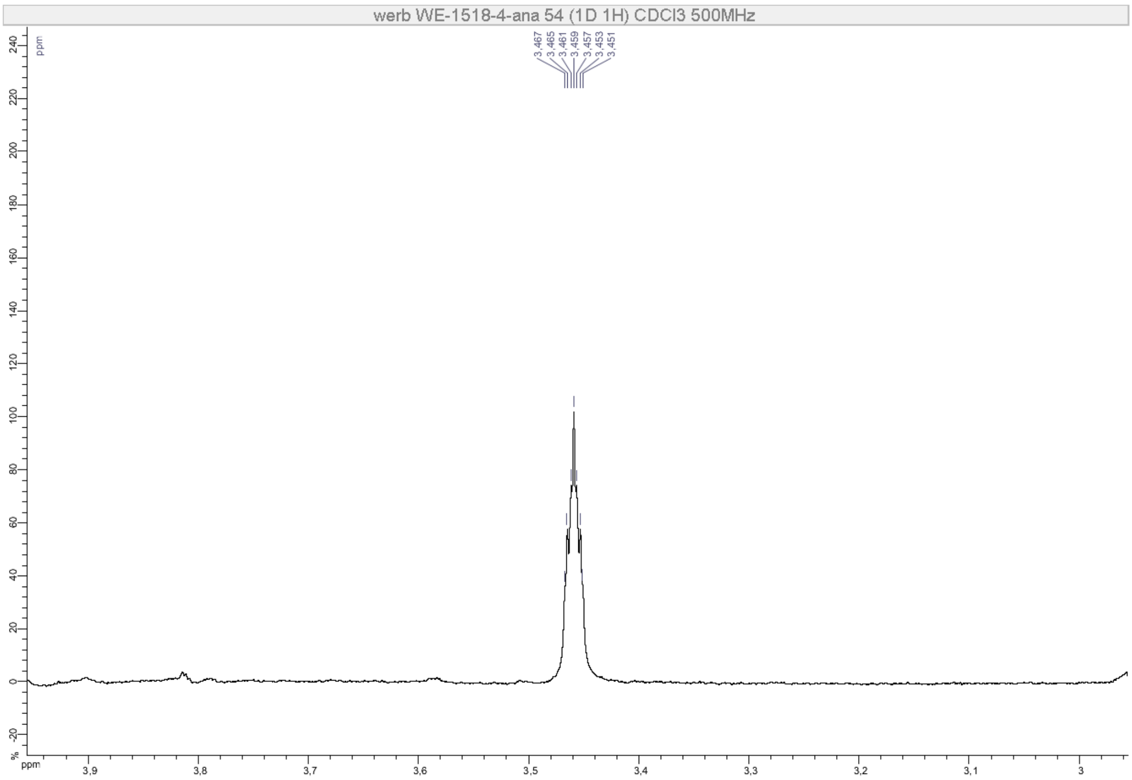


Compound 2

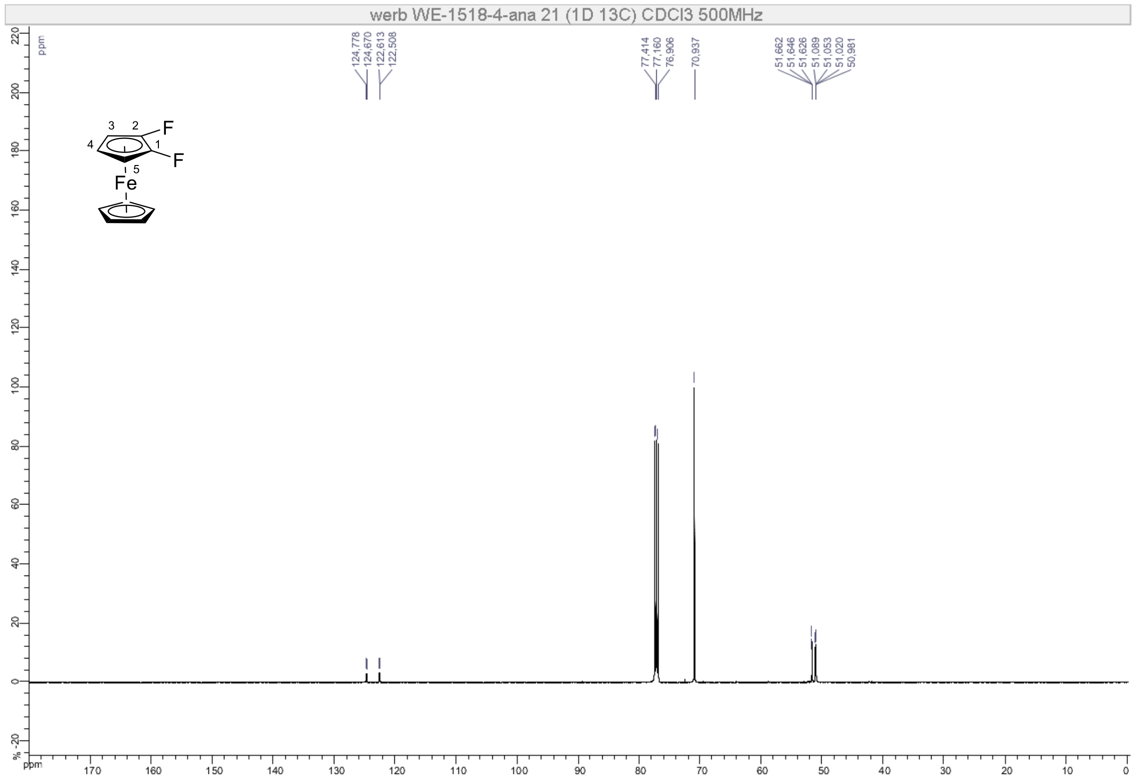
^{1}H (500 MHz, $CDCl_3$) – Full spectrum



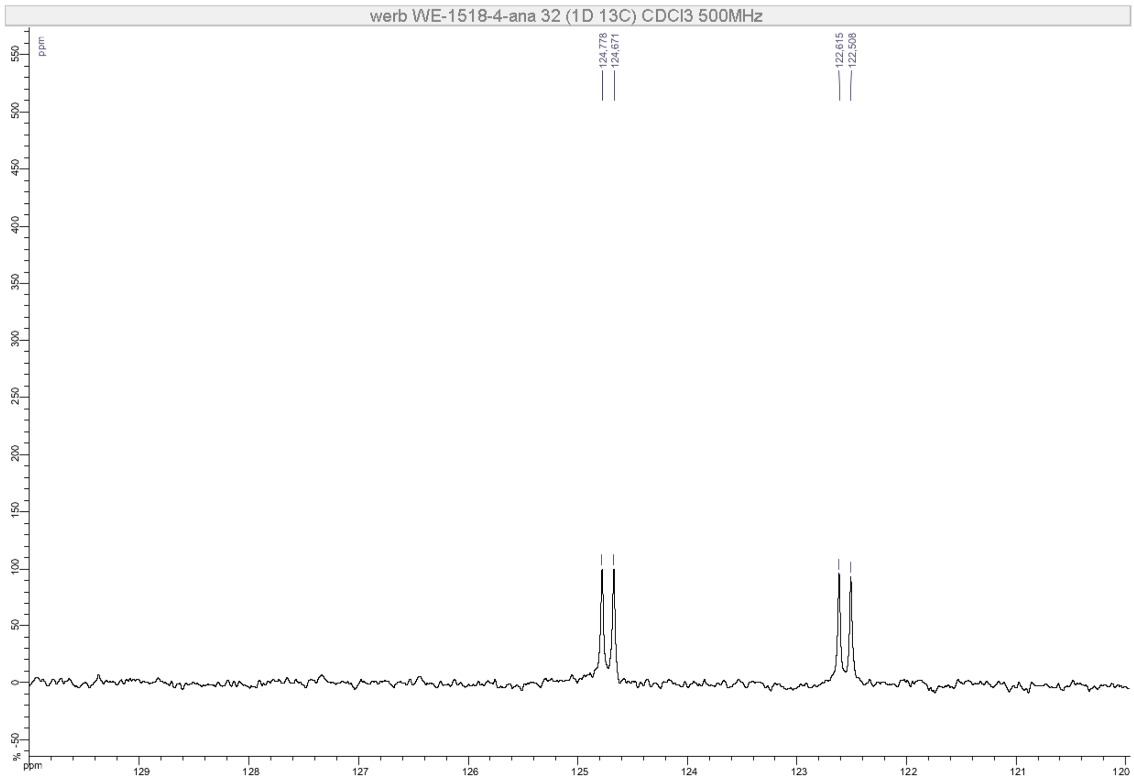
^{1}H (500 MHz, $CDCl_3$) – 3 to 4 ppm area



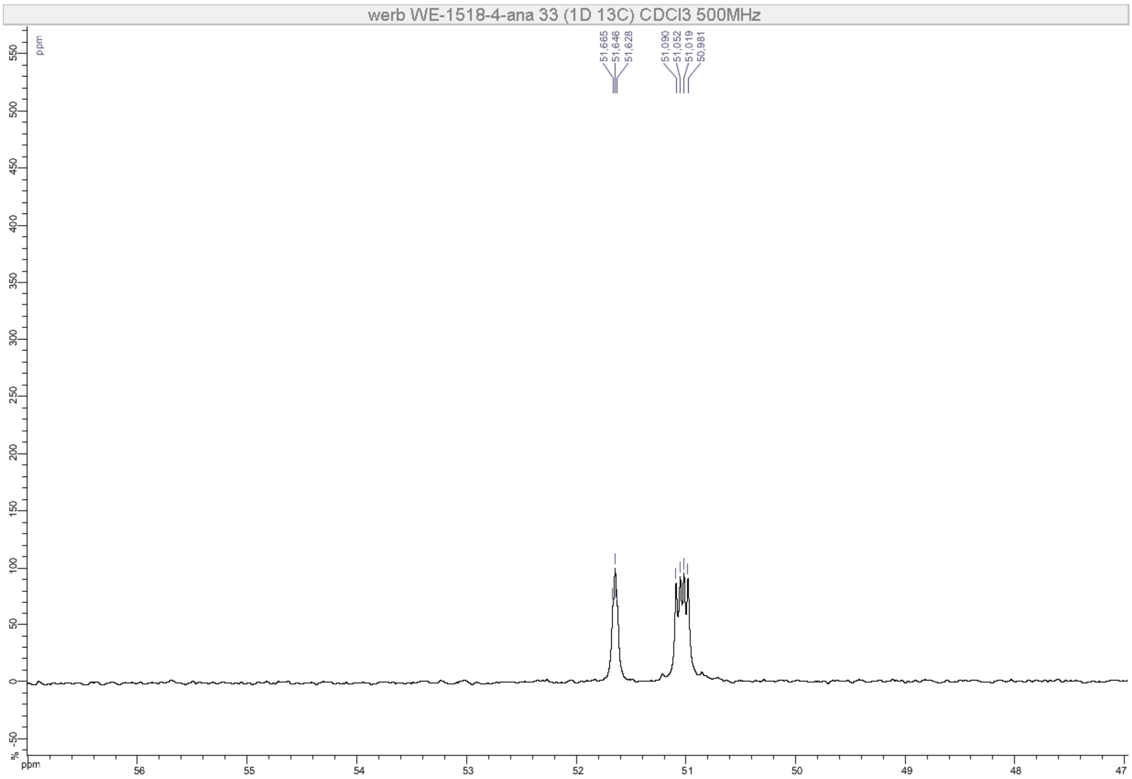
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) – Full spectrum



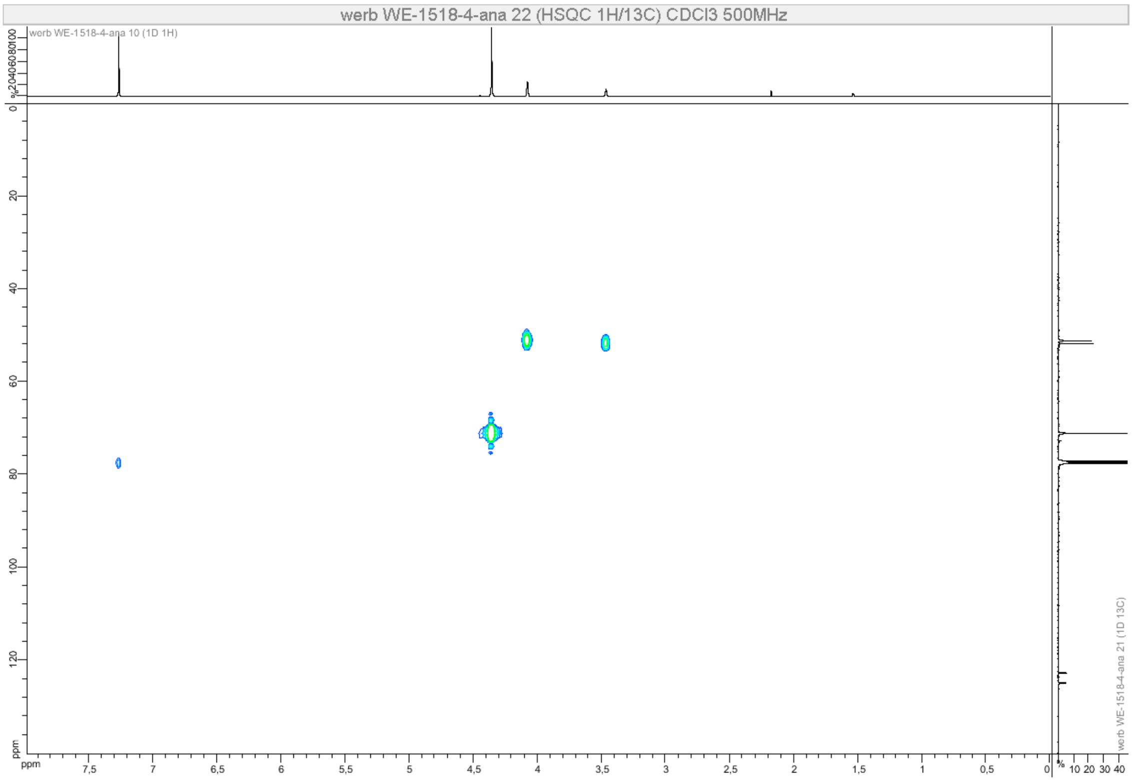
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) – 120 to 130 ppm area



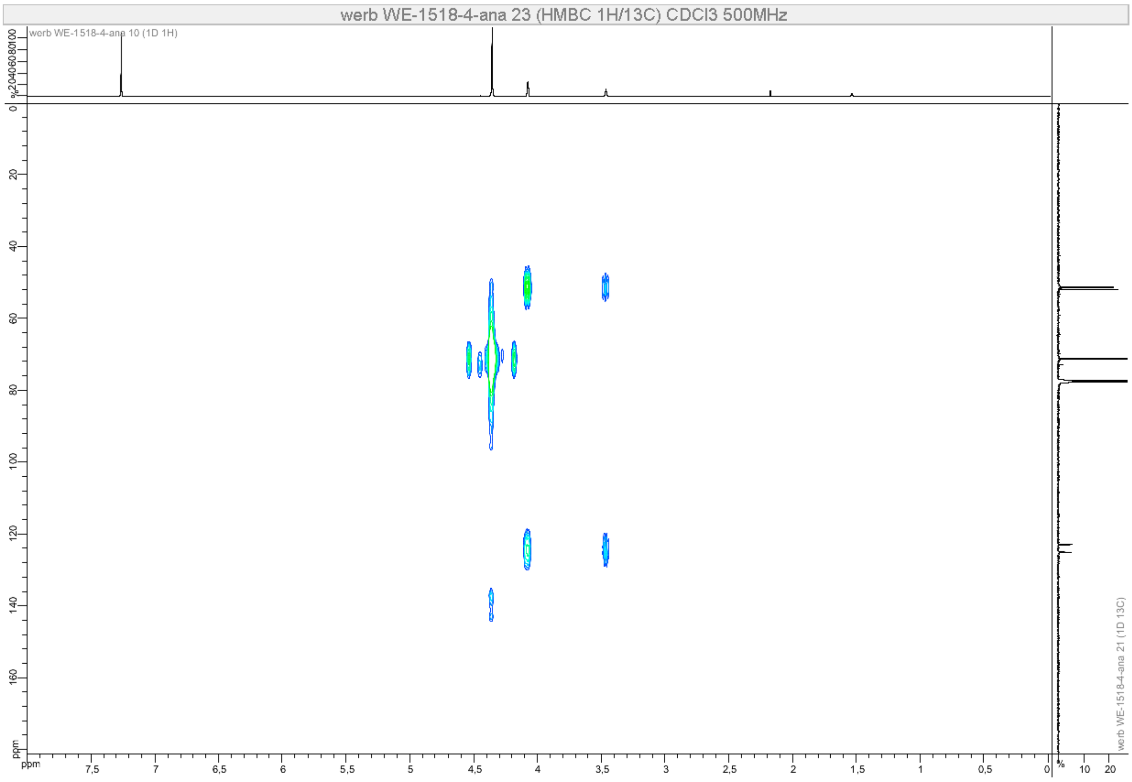
$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) – 47 to 57 ppm area



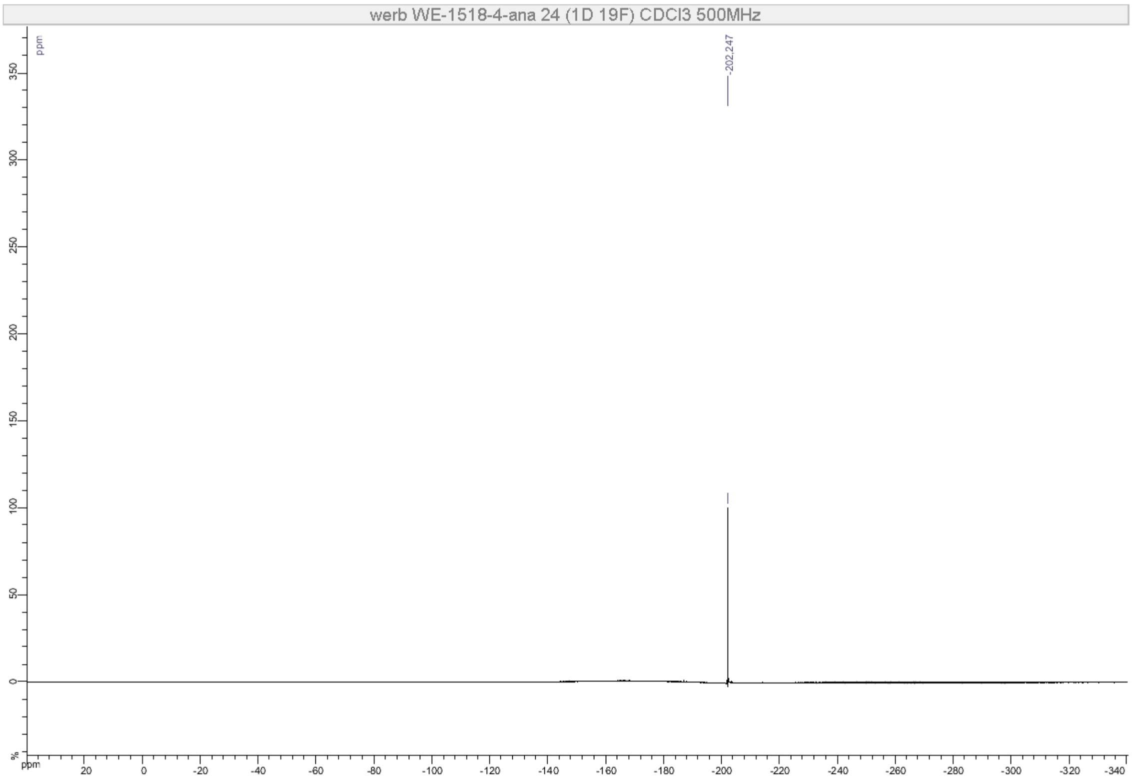
HSQC (500 MHz, $CDCl_3$)



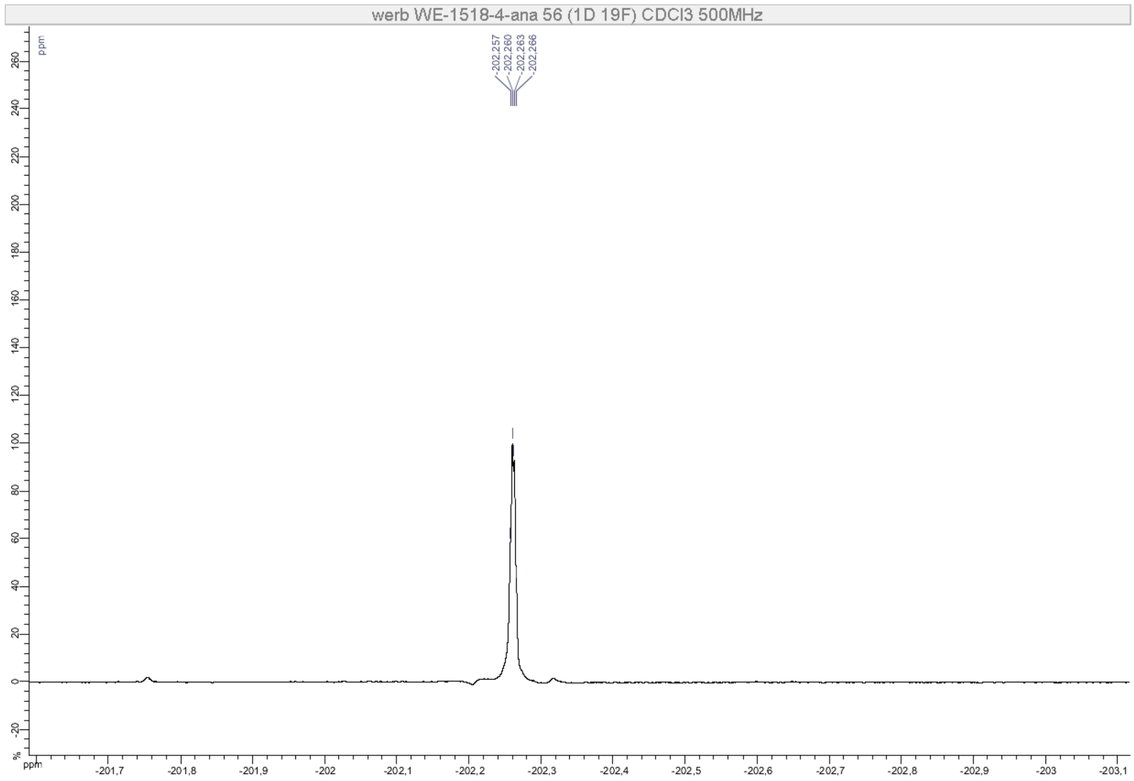
HMBC (500 MHz, $CDCl_3$)



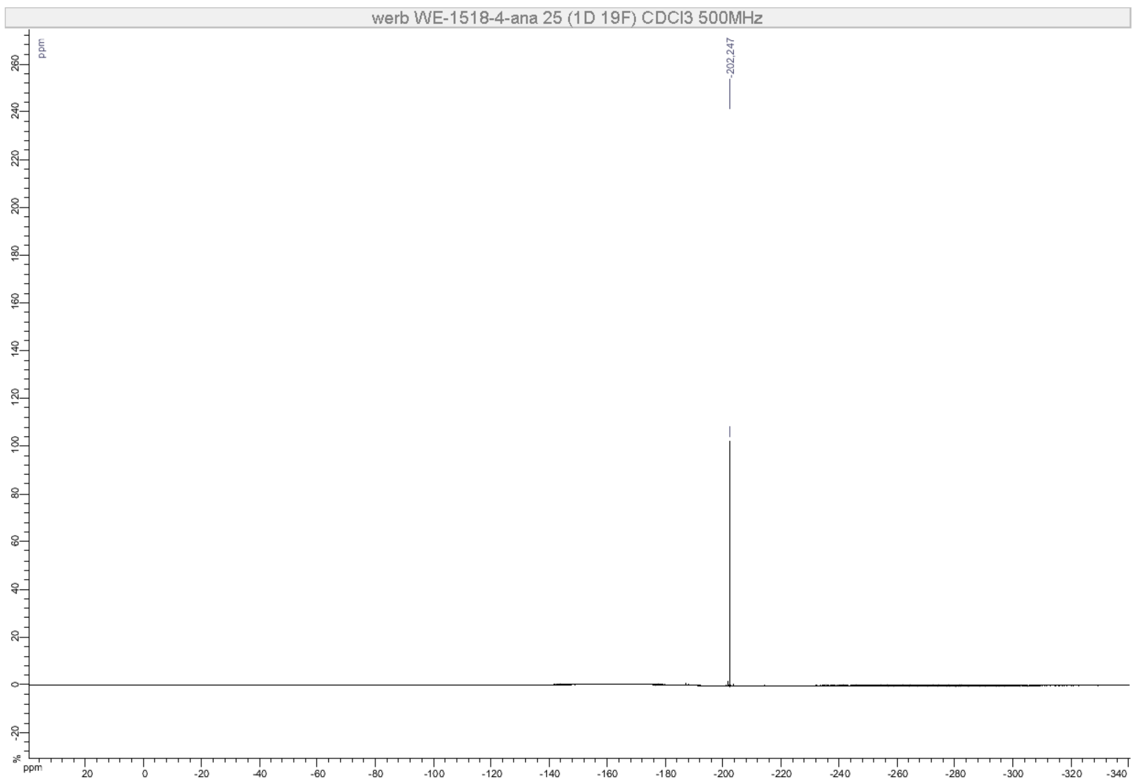
^{19}F (470 MHz, $CDCl_3$) – Full spectrum



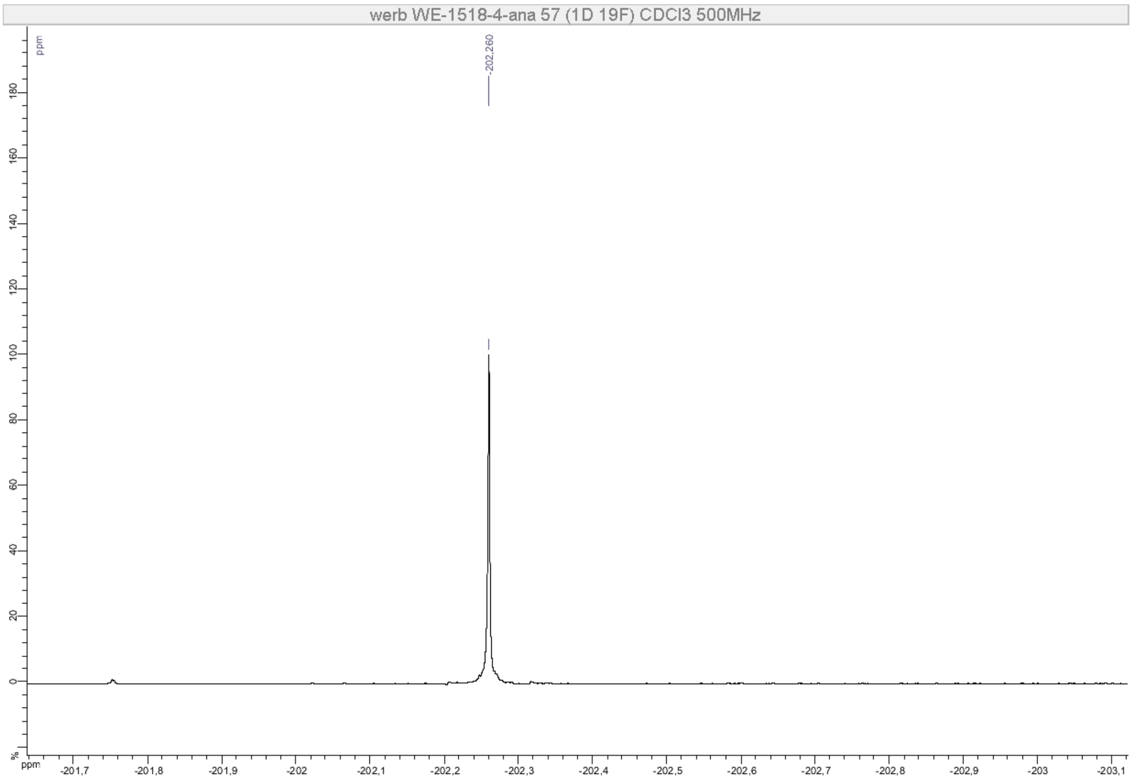
^{19}F (470 MHz, $CDCl_3$) – -203 to -201 ppm area



$^{19}F\{^1H\}$ (470 MHz, $CDCl_3$) – Full spectrum

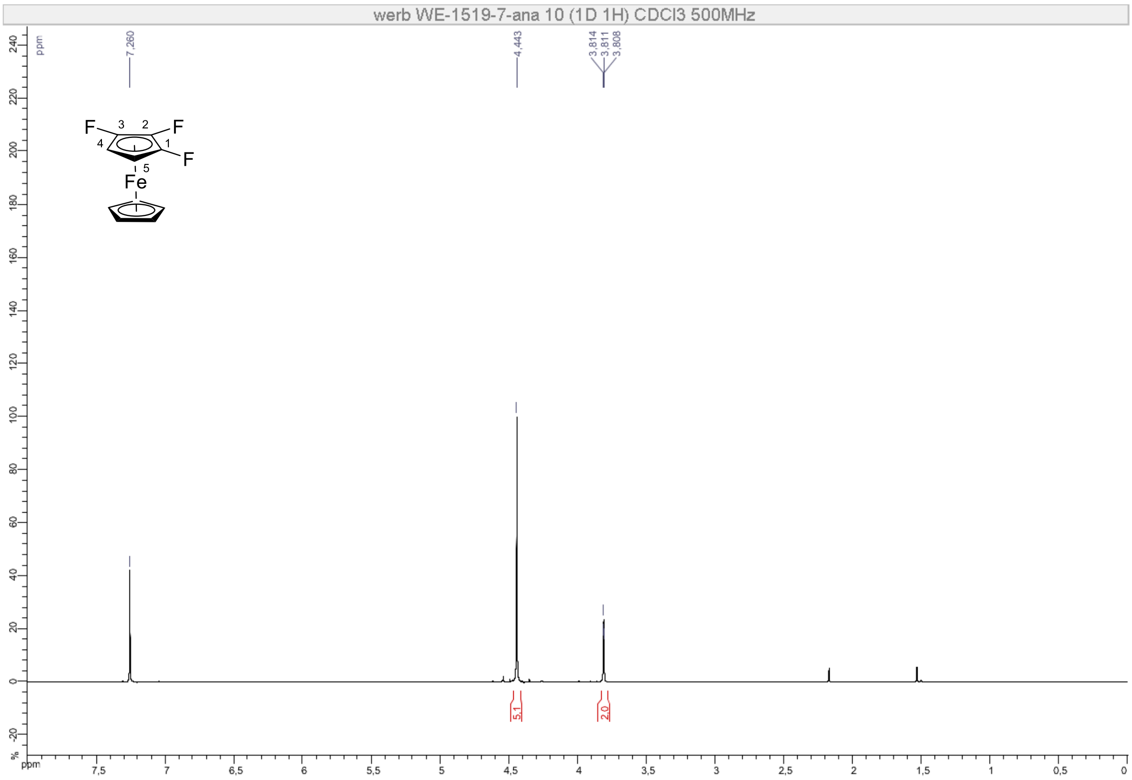


$^{19}F\{^{1}H\}$ (470 MHz, $CDCl_3$) – -203 to -202 ppm area

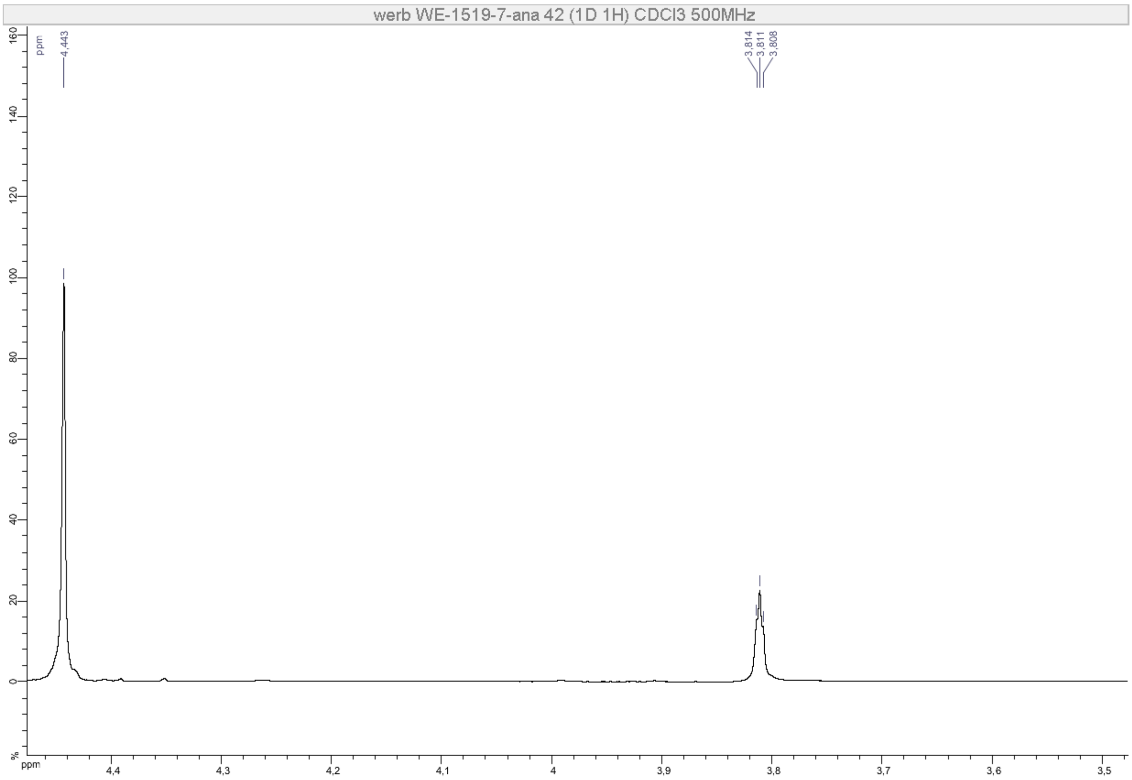


Compound 3

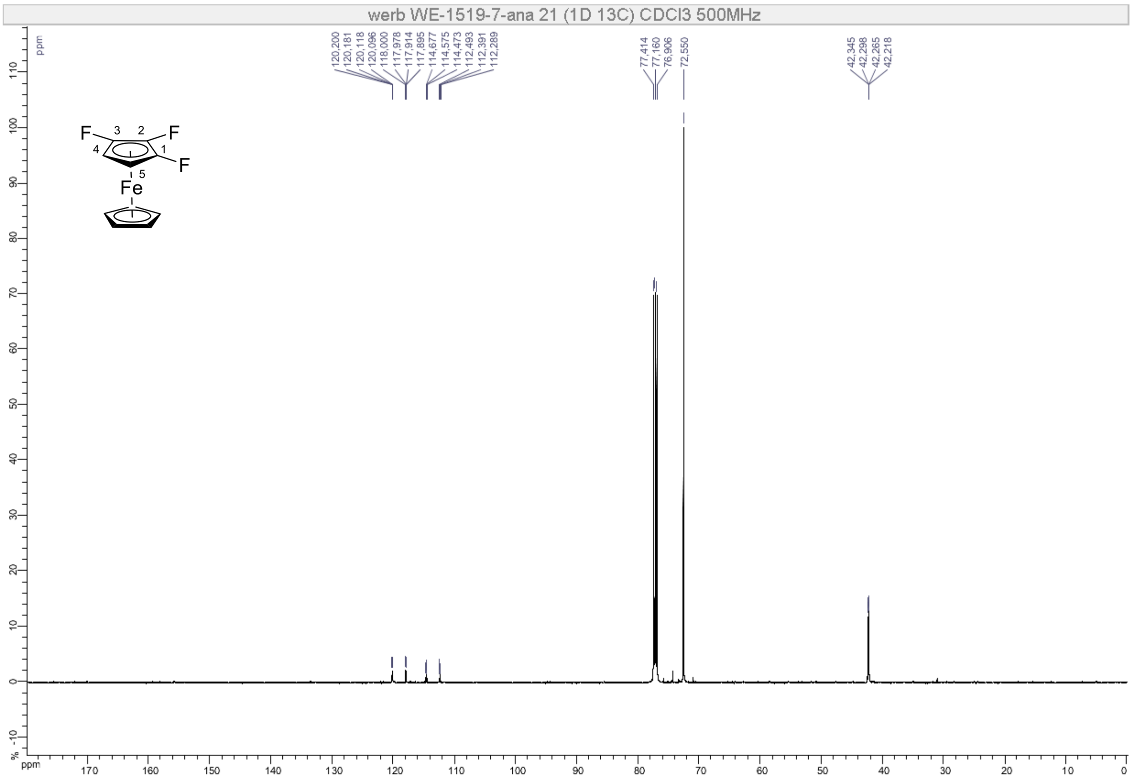
^{1}H (500 MHz, $CDCl_3$) – Full spectrum



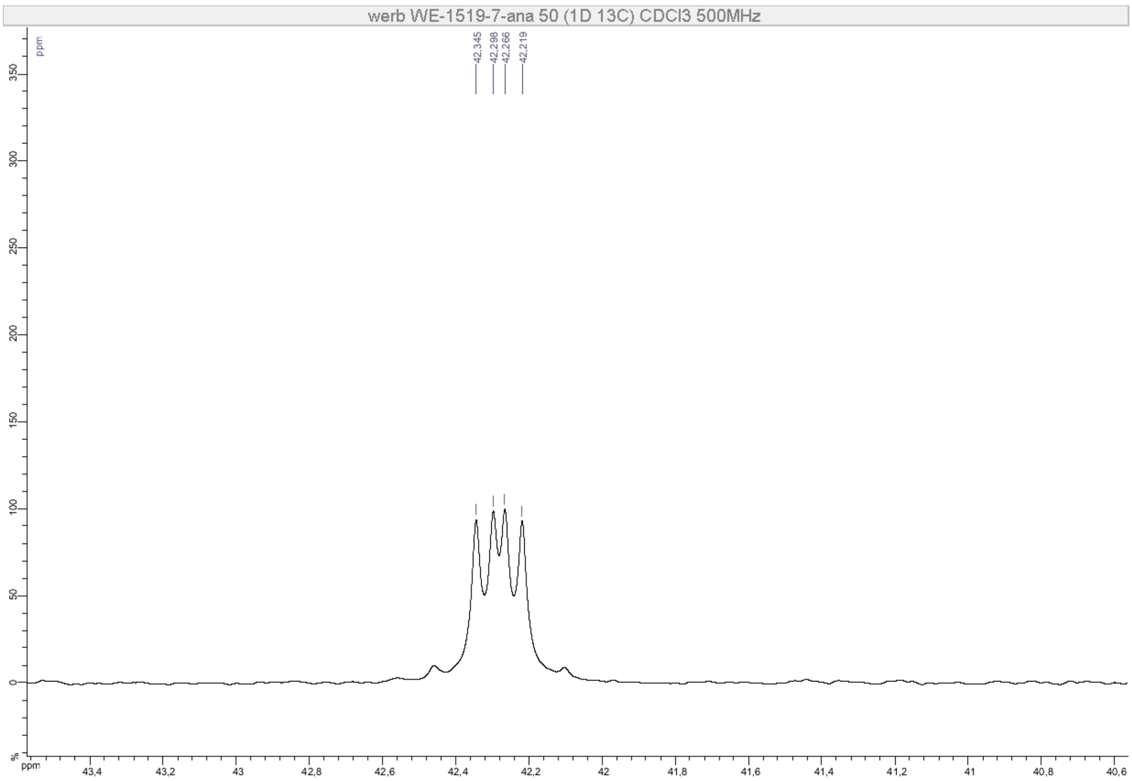
^{1}H (500 MHz, $CDCl_3$) – 3.5 to 4.5 ppm area



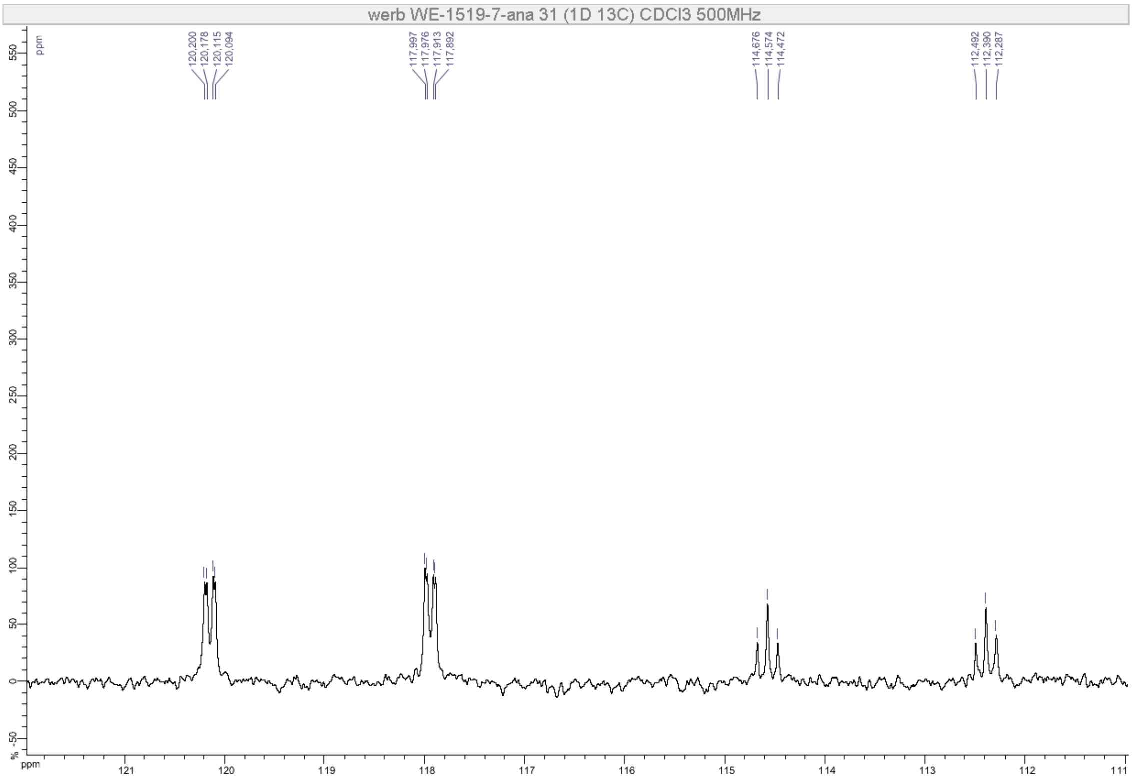
$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) – Full spectrum



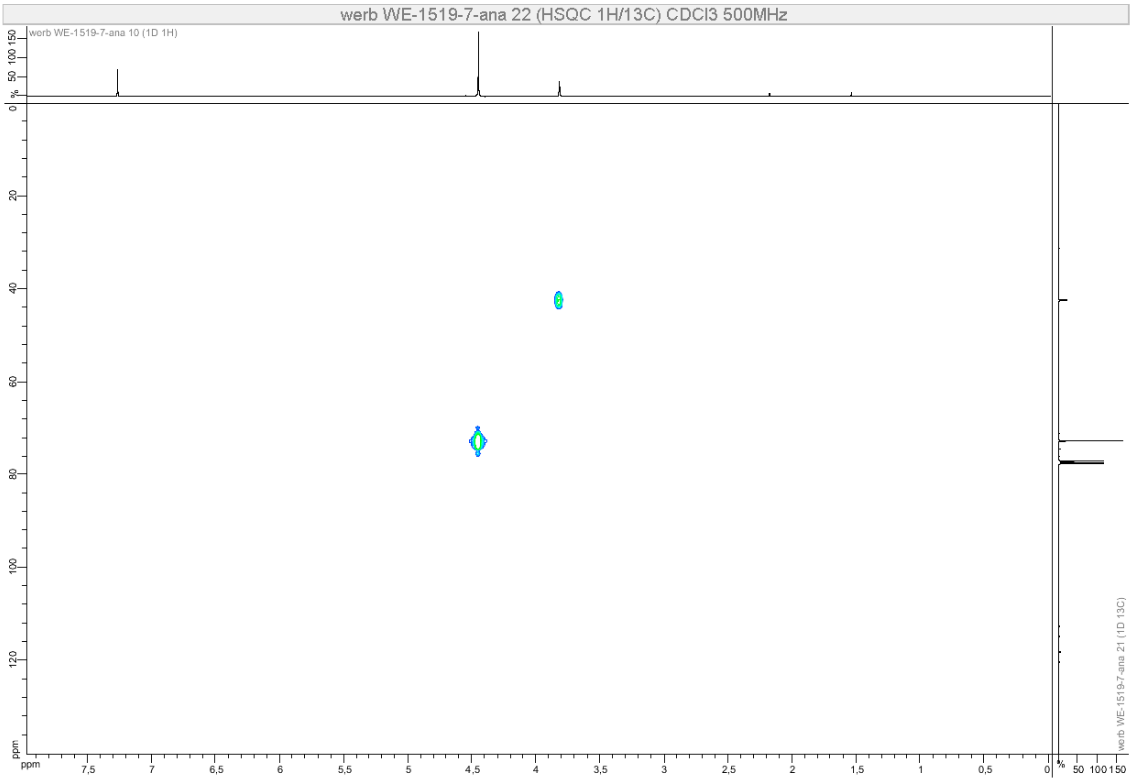
$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) – 40 to 44 ppm area



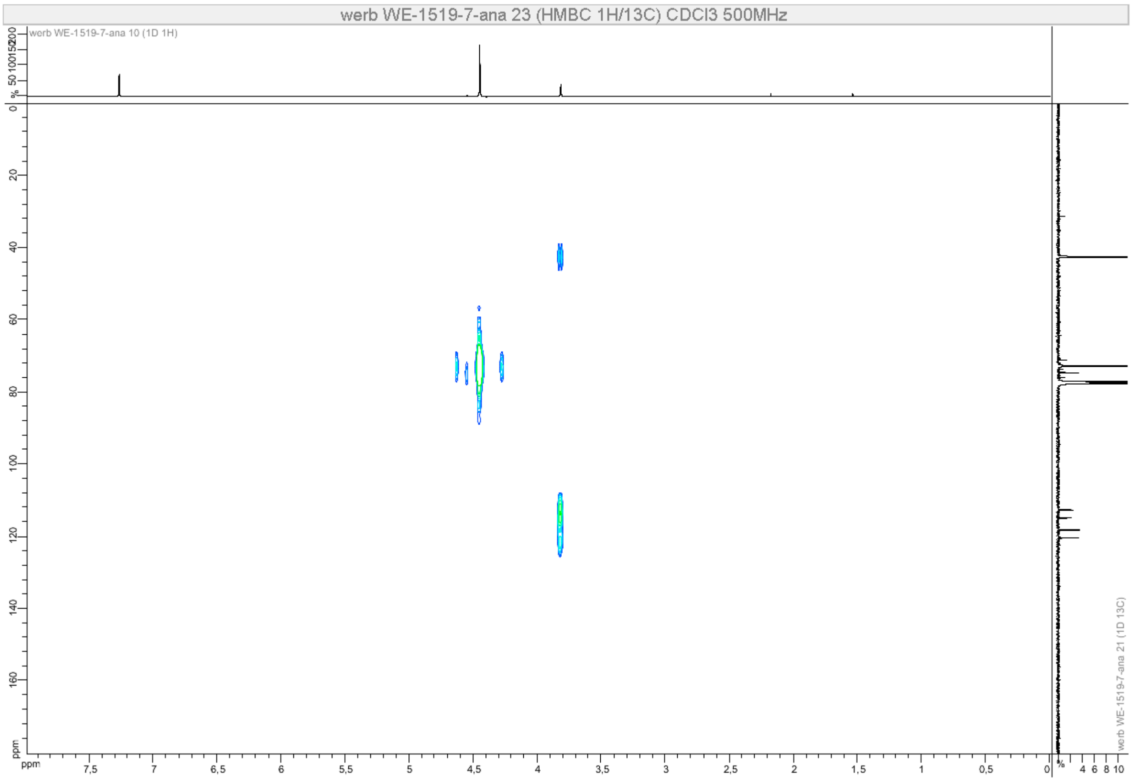
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) – 111 to121 ppm area



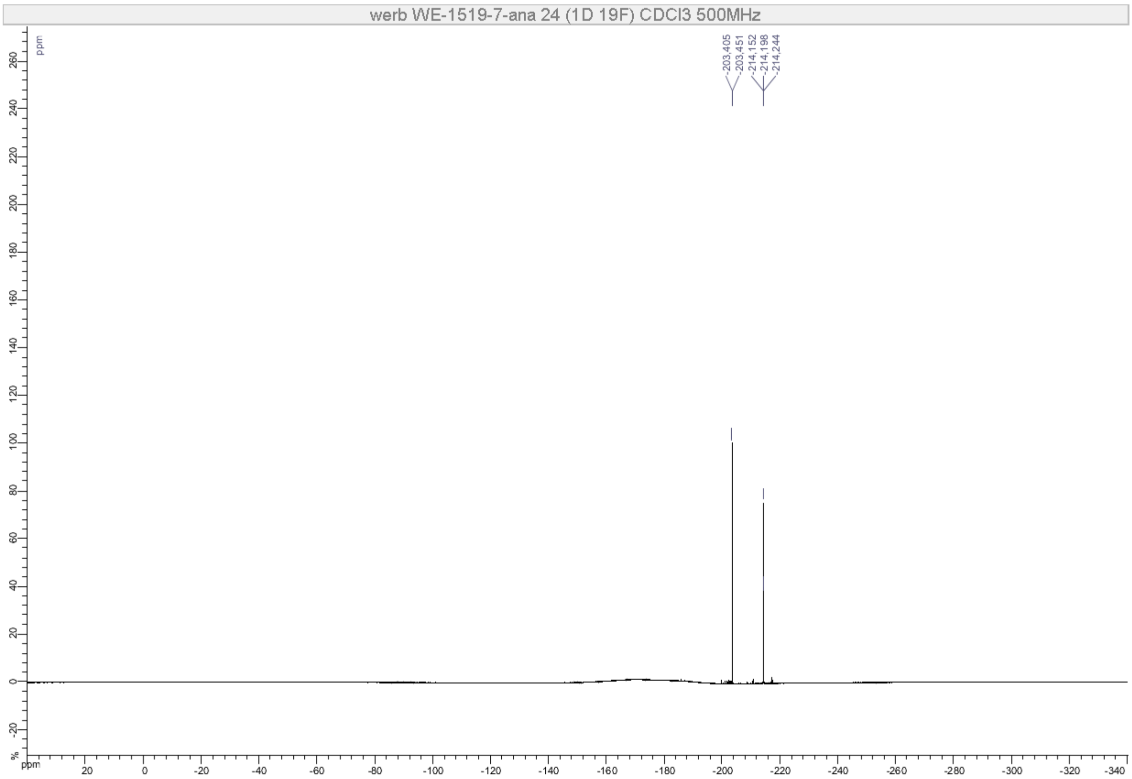
HSQC (500 MHz, $CDCl_3$)



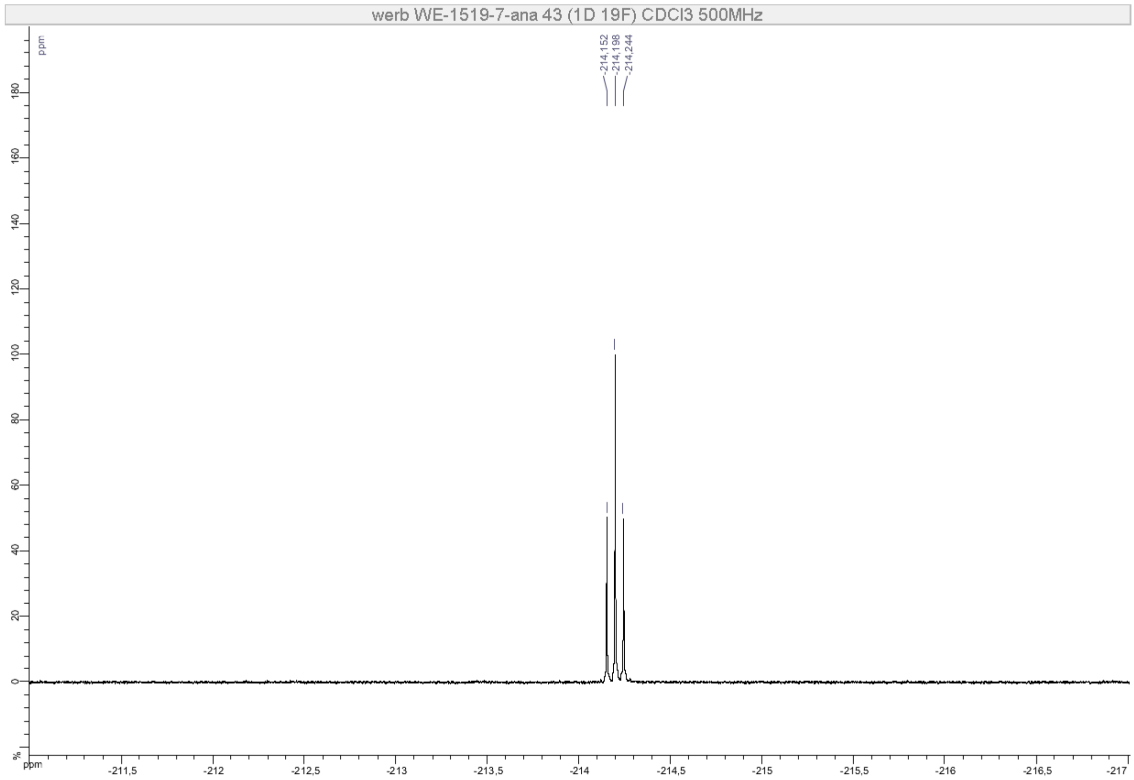
HMBC (500 MHz, $CDCl_3$)



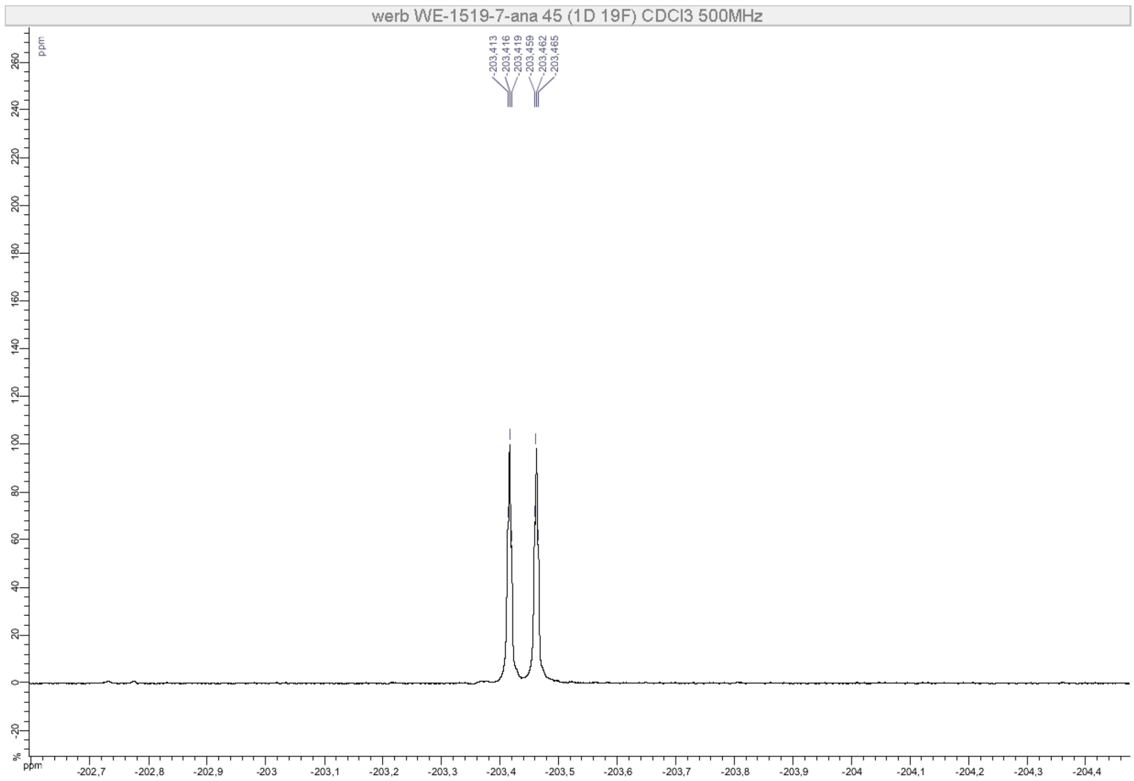
^{19}F (470 MHz, $CDCl_3$) – Full spectrum



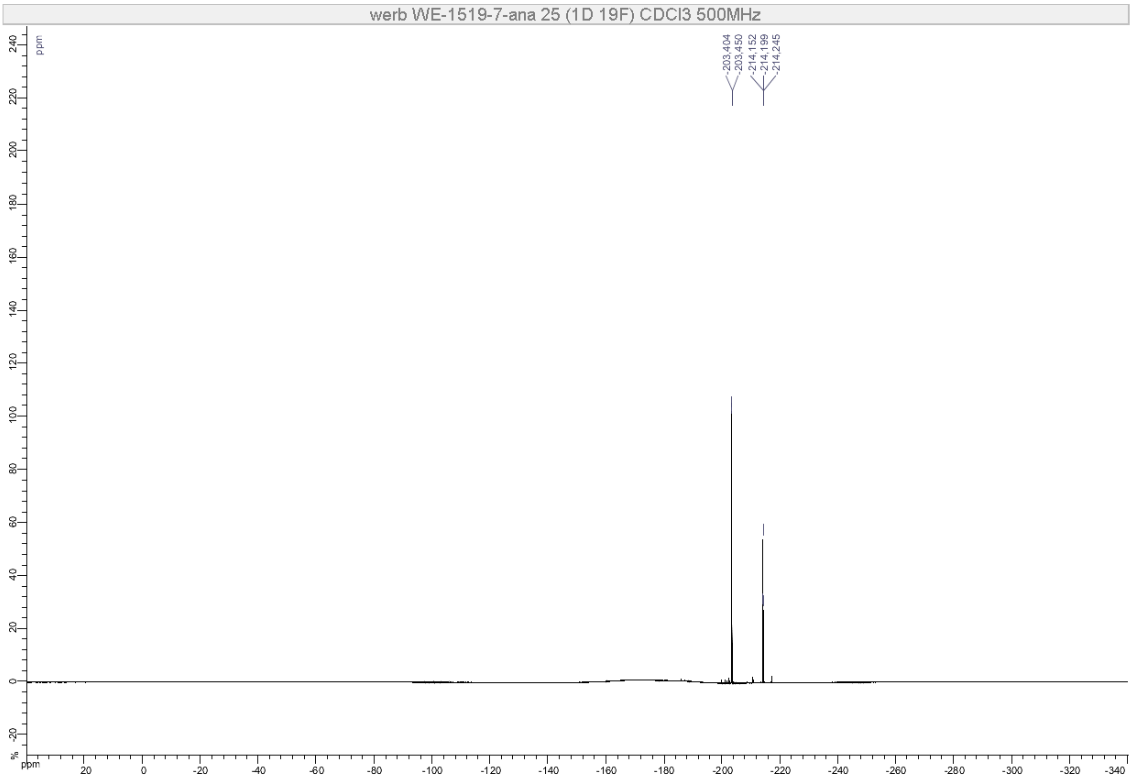
^{19}F (470 MHz, $CDCl_3$) – -217 to -211 ppm area



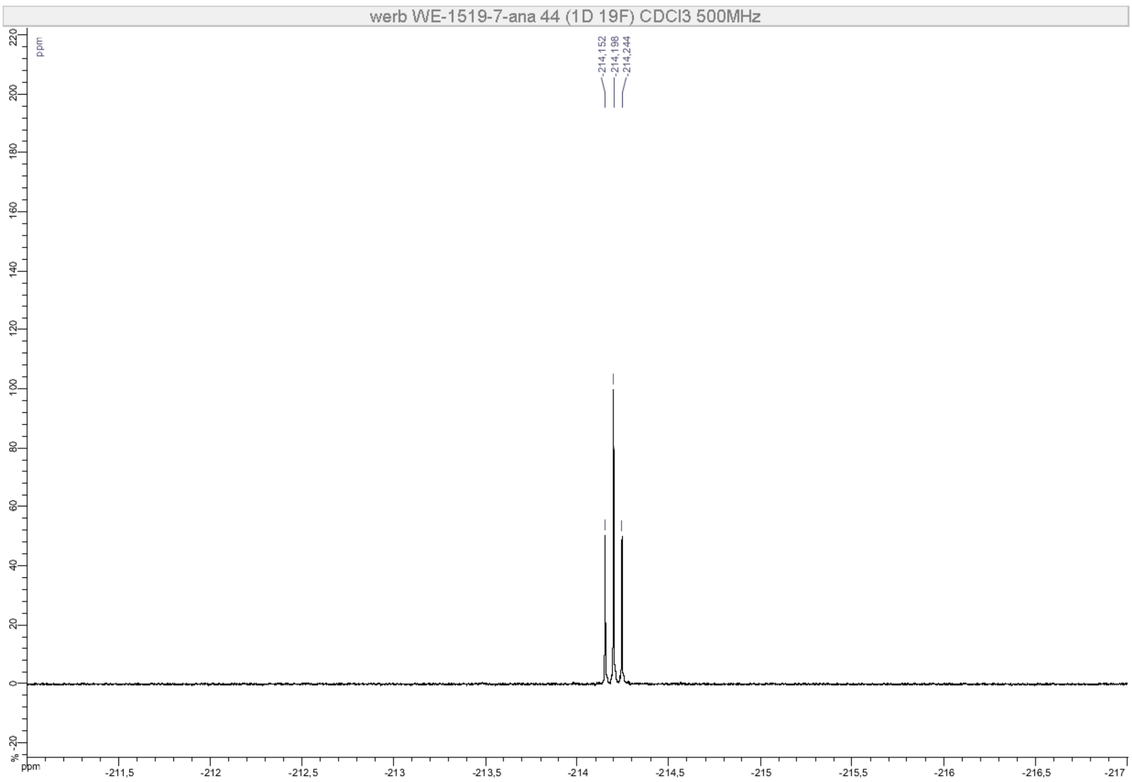
^{19}F (470 MHz, $CDCl_3$) – -204 to -202 ppm area



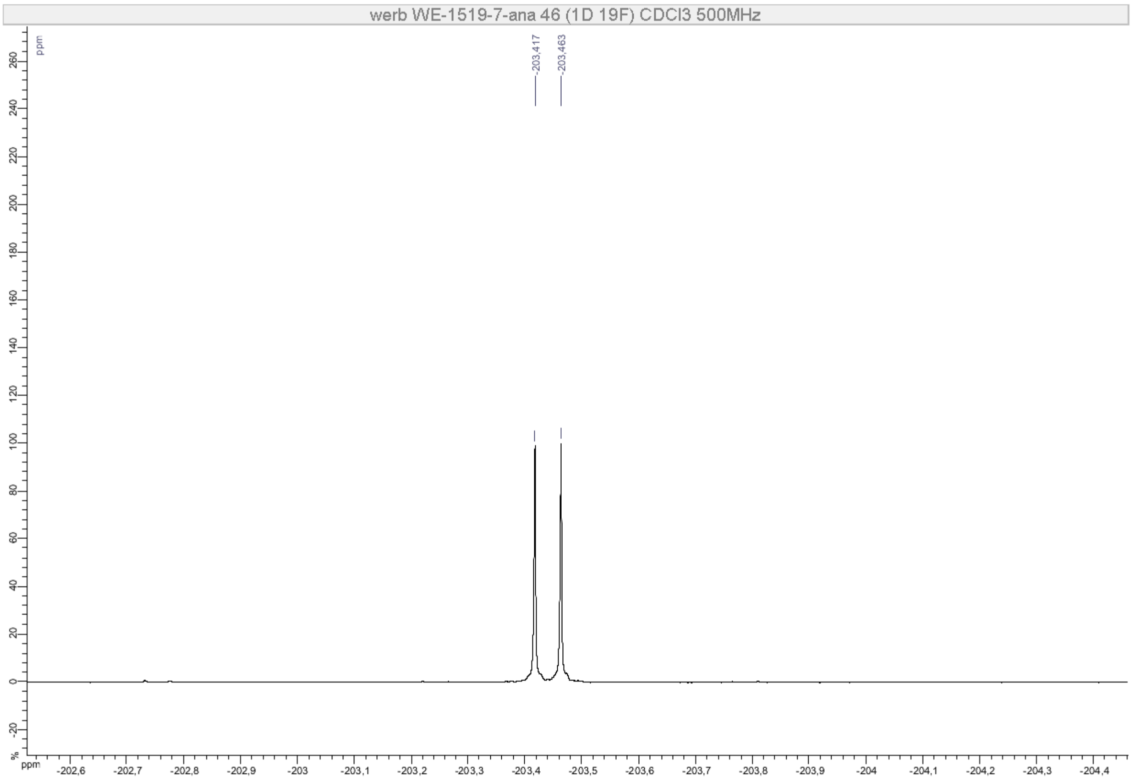
$^{19}F\{^{1}H\}$ (470 MHz, $CDCl_3$) – Full spectrum



$^{19}F\{^{1}H\}$ (470 MHz, $CDCl_3$) – -217 to -211 ppm area

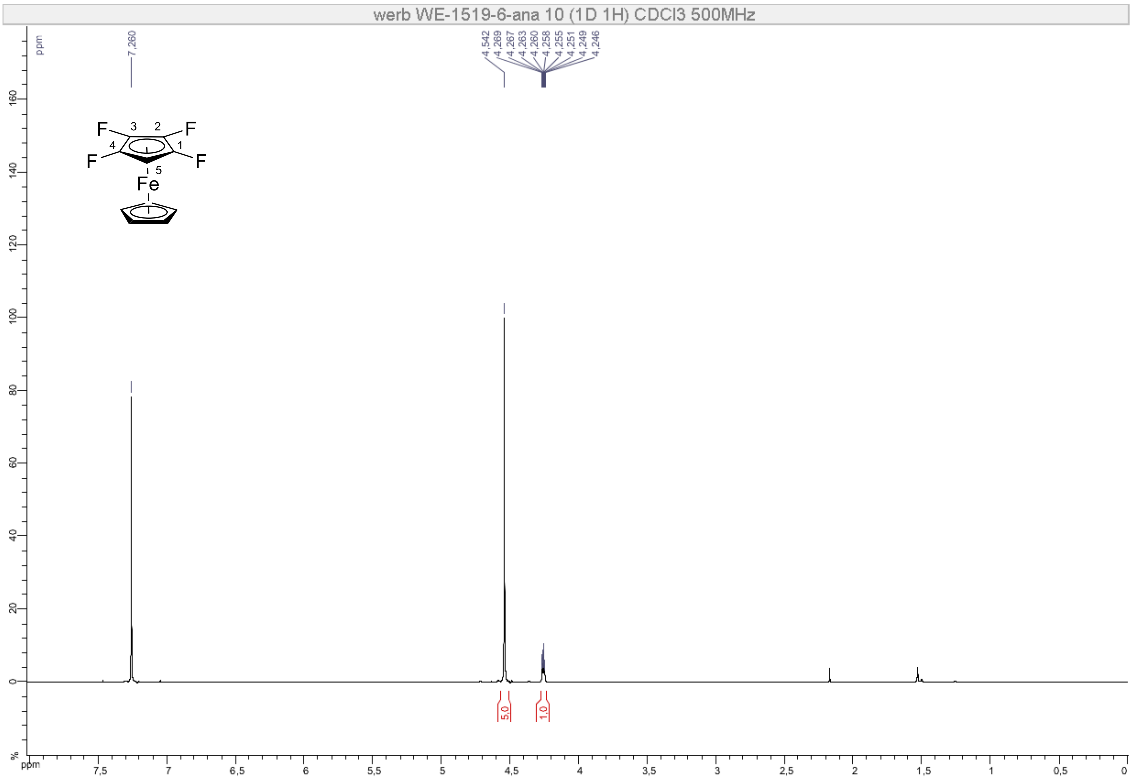


$^{19}F\{^1H\}$ (470 MHz, $CDCl_3$) – -204 to -202 ppm area

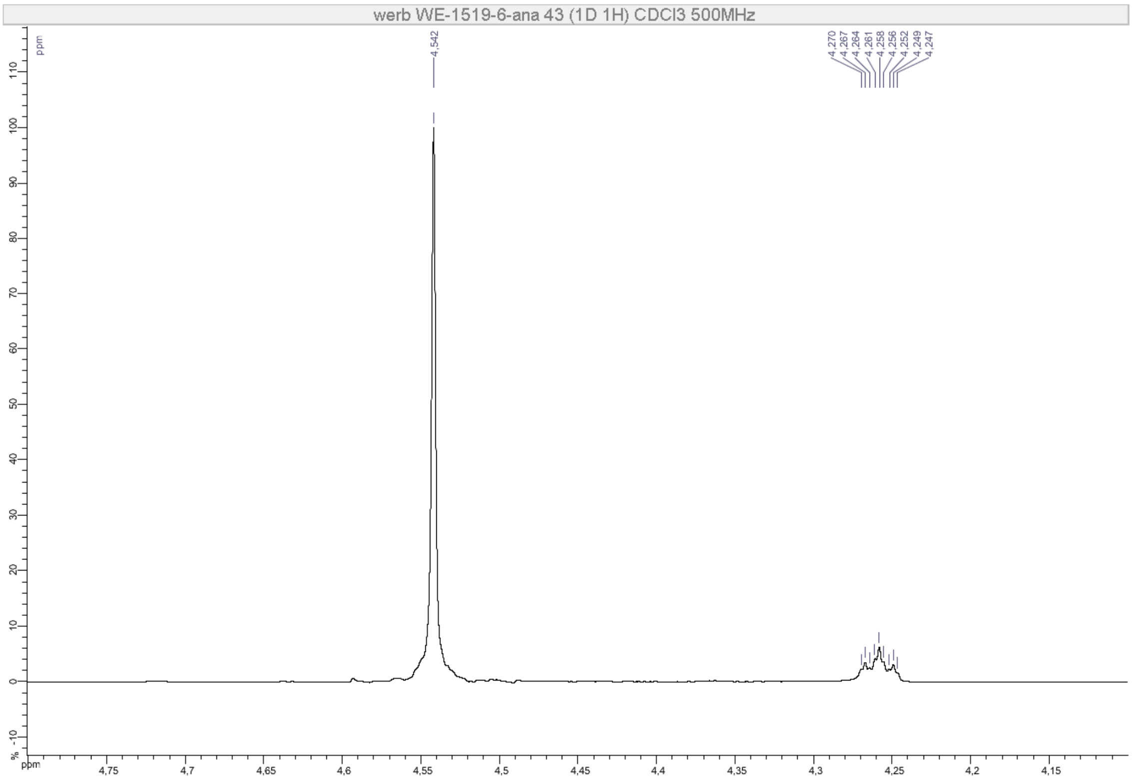


Compound 4

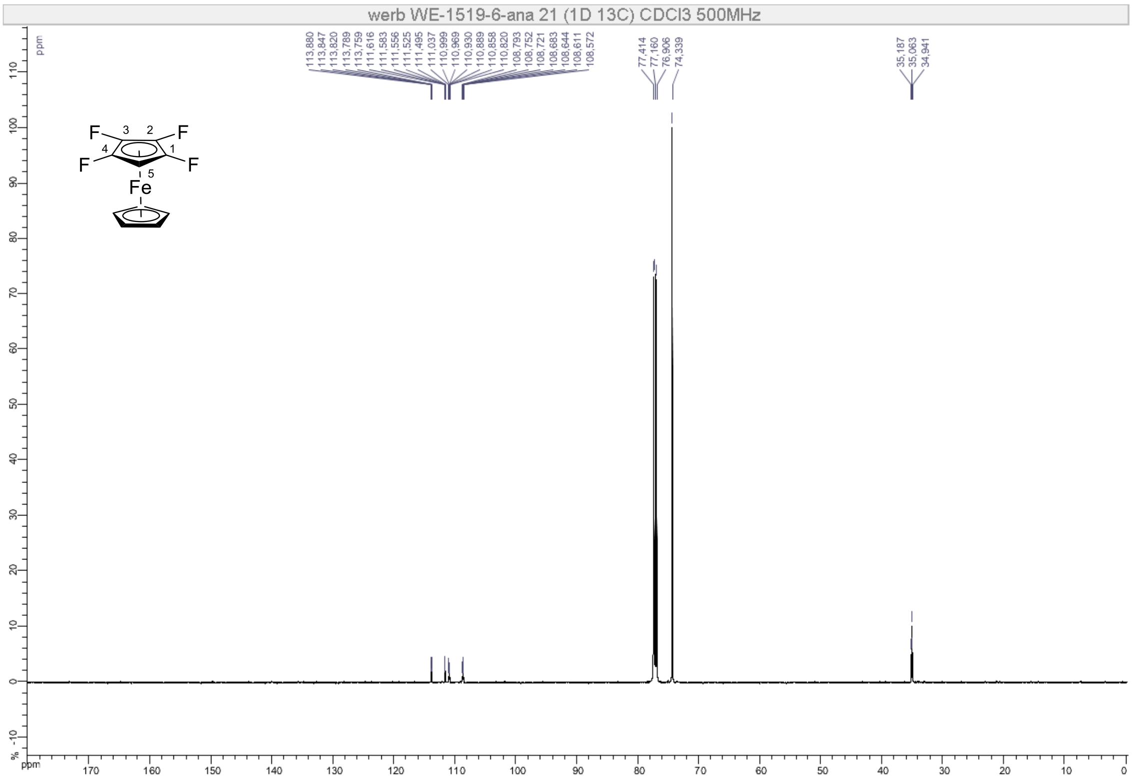
^{1}H (500 MHz, $CDCl_3$) – Full spectrum



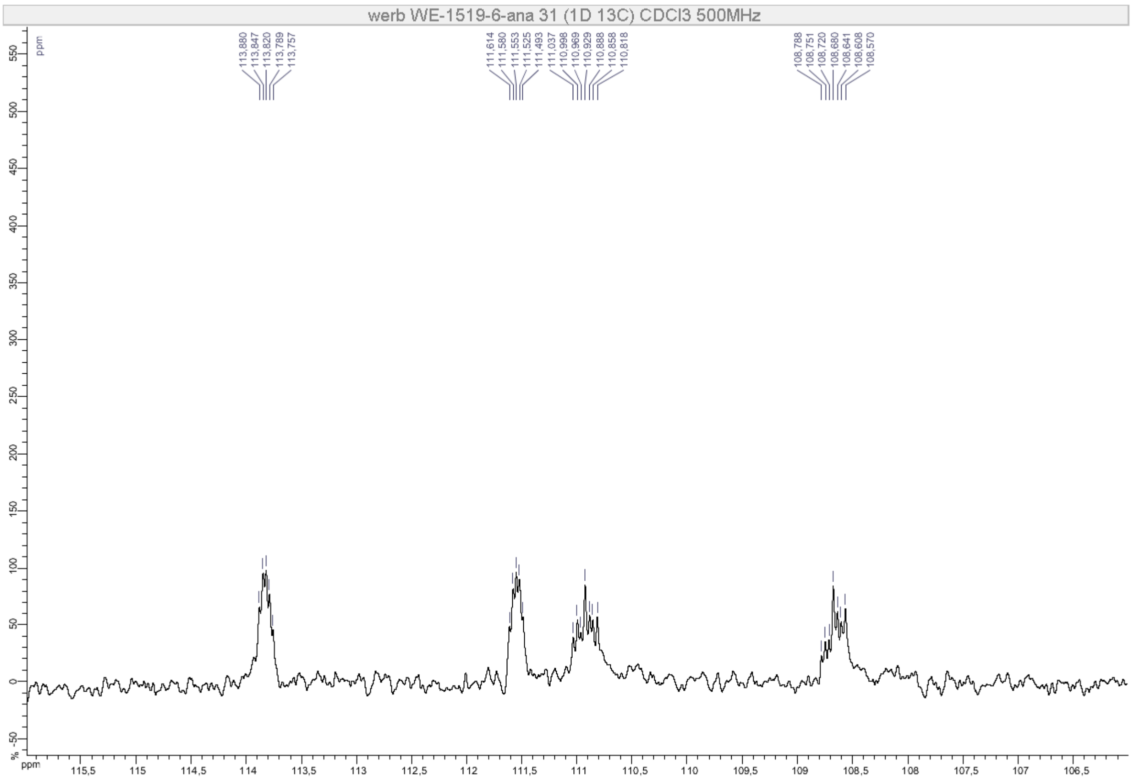
^{1}H (500 MHz, $CDCl_3$) – 4 to 5 ppm area



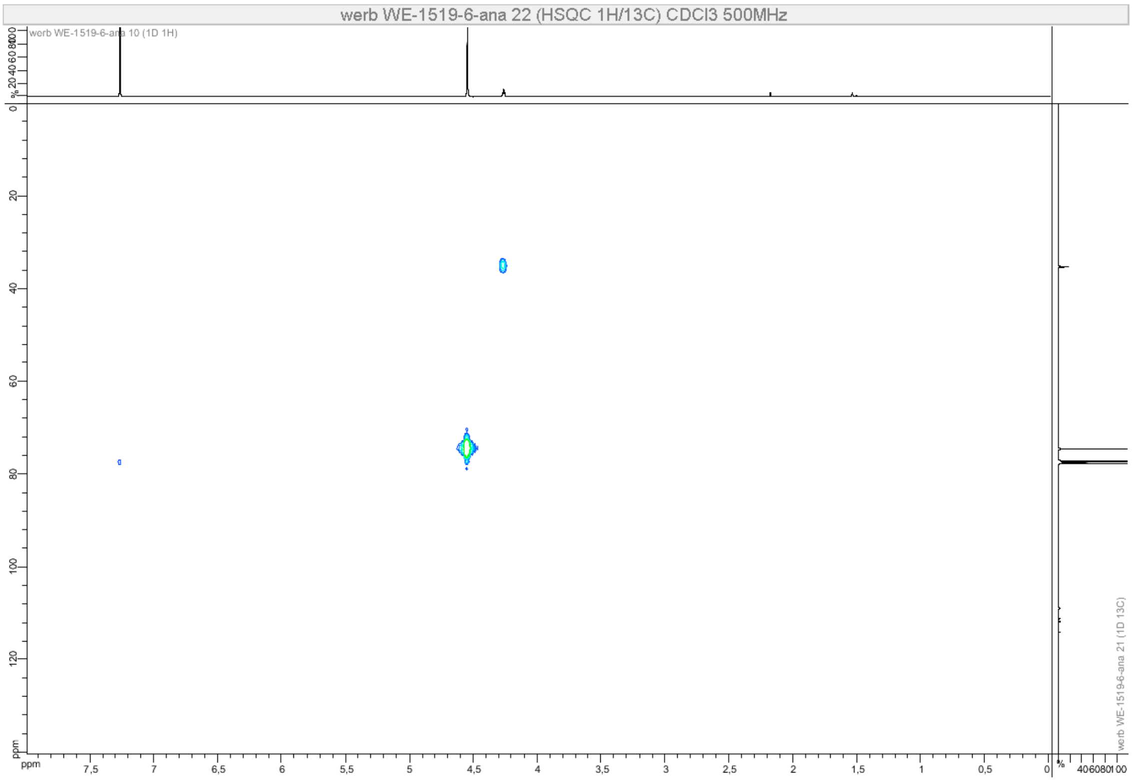
$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) – Full spectrum



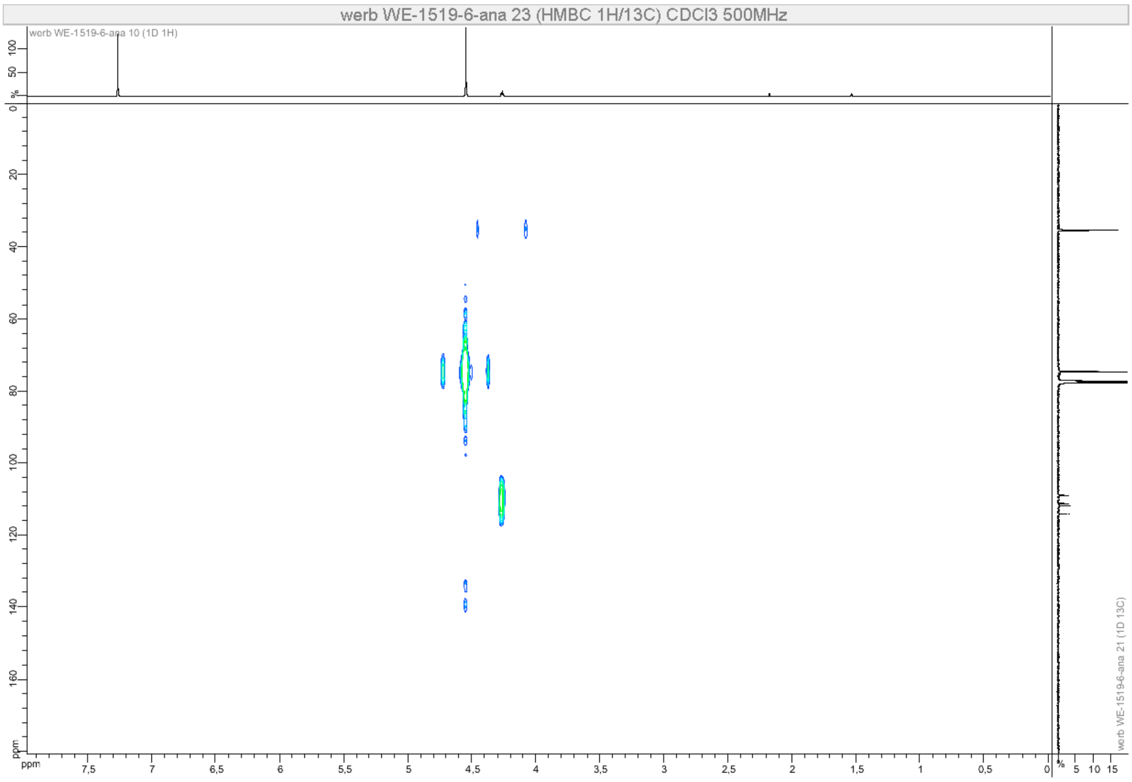
$^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) – 106 to 115 ppm area



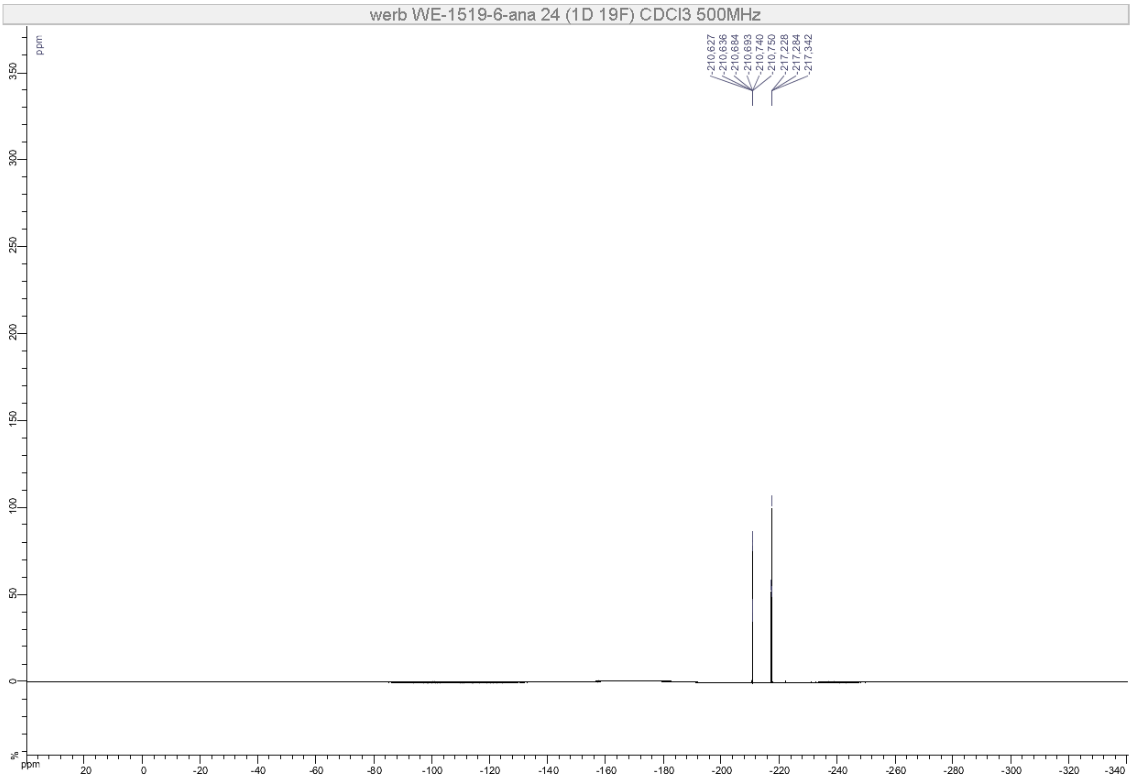
HSQC (500 MHz, $CDCl_3$)



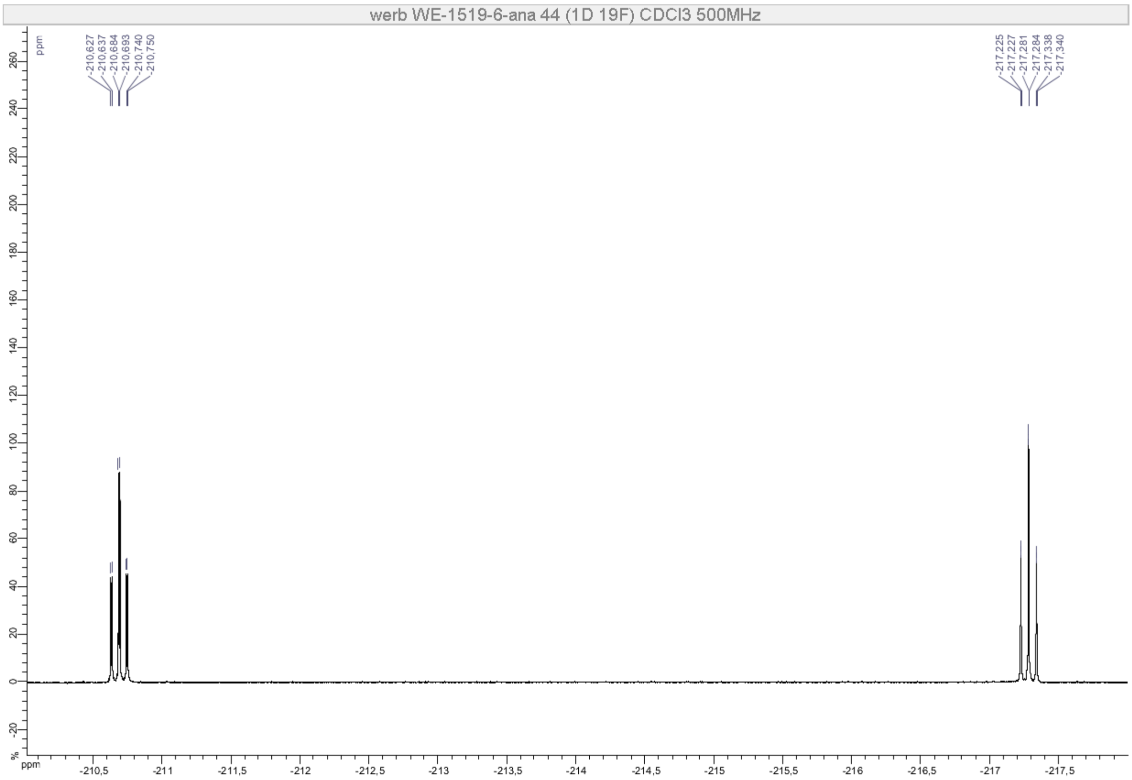
HMBC (500 MHz, $CDCl_3$)



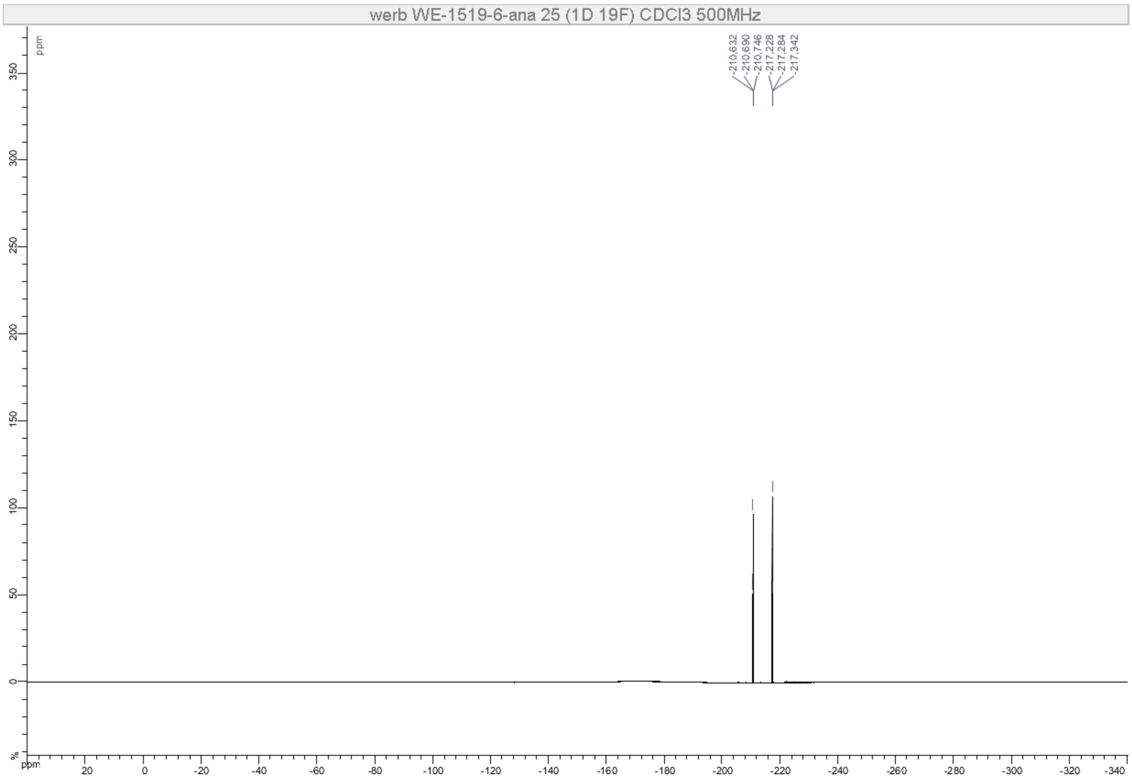
^{19}F (470 MHz, $CDCl_3$) – Full spectrum



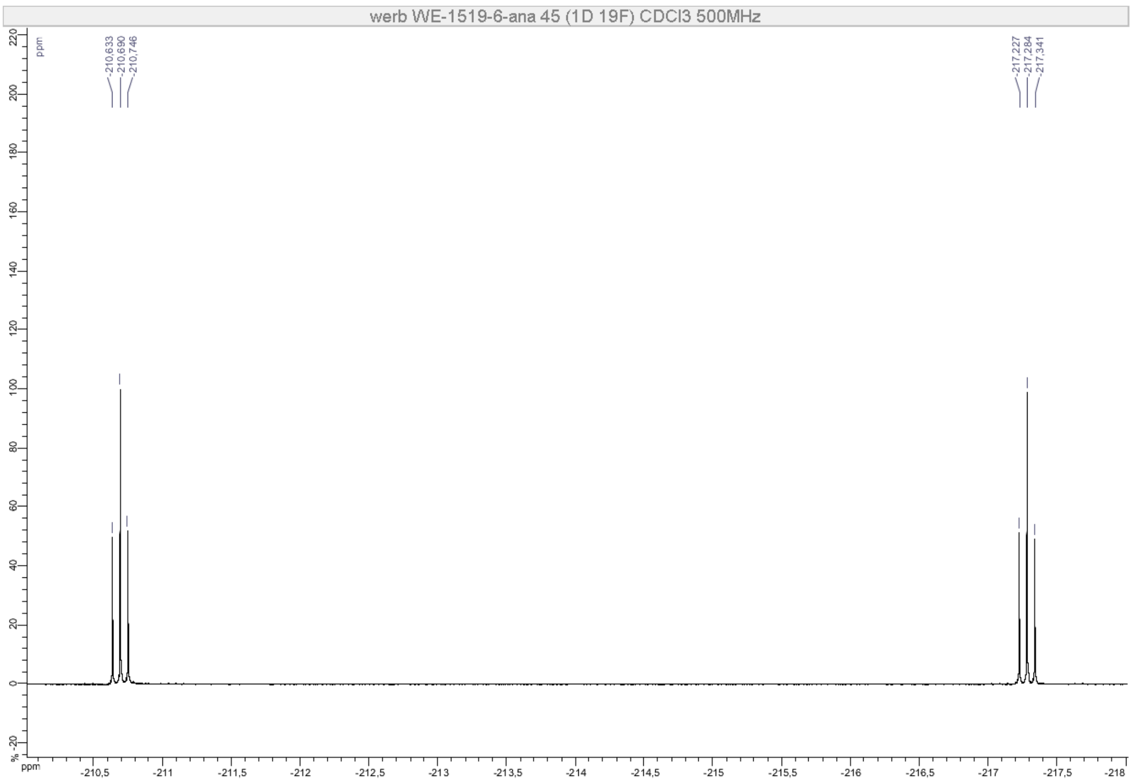
^{19}F (470 MHz, $CDCl_3$) – -210 to -217 ppm area



$^{19}F\{^1H\}$ (470 MHz, $CDCl_3$) – Full spectrum

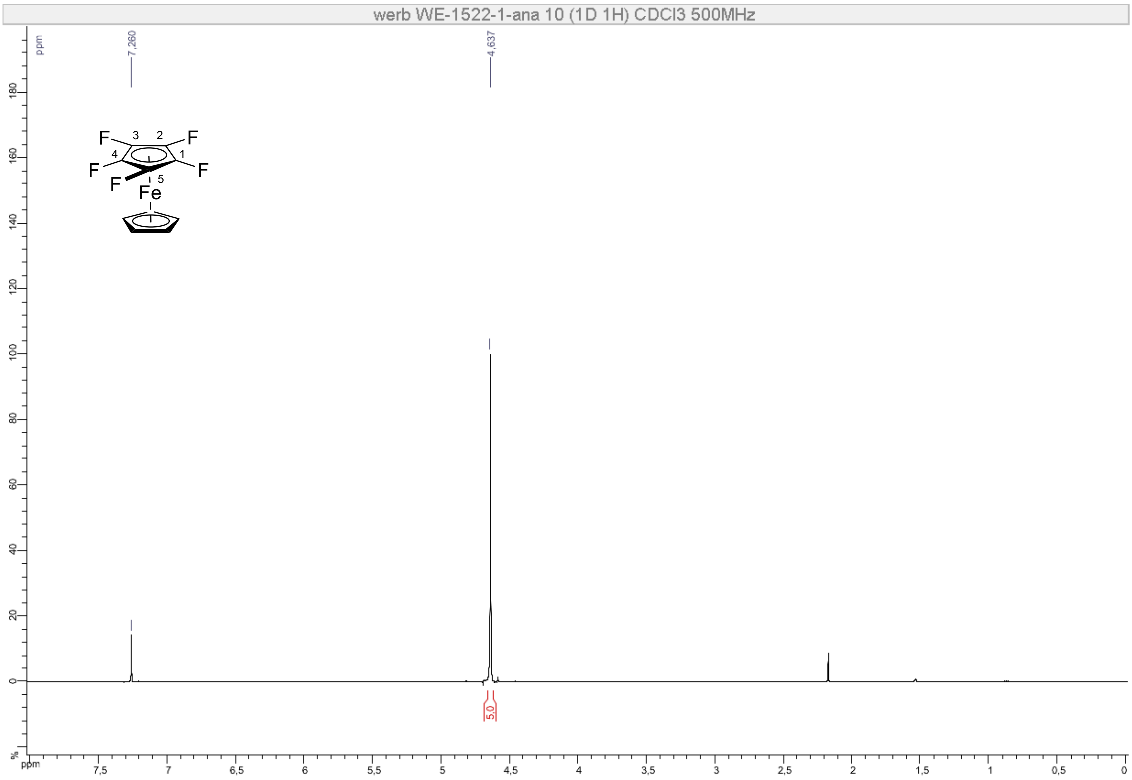


$^{19}F\{^1H\}$ (470 MHz, $CDCl_3$) – -210 to -218 ppm area

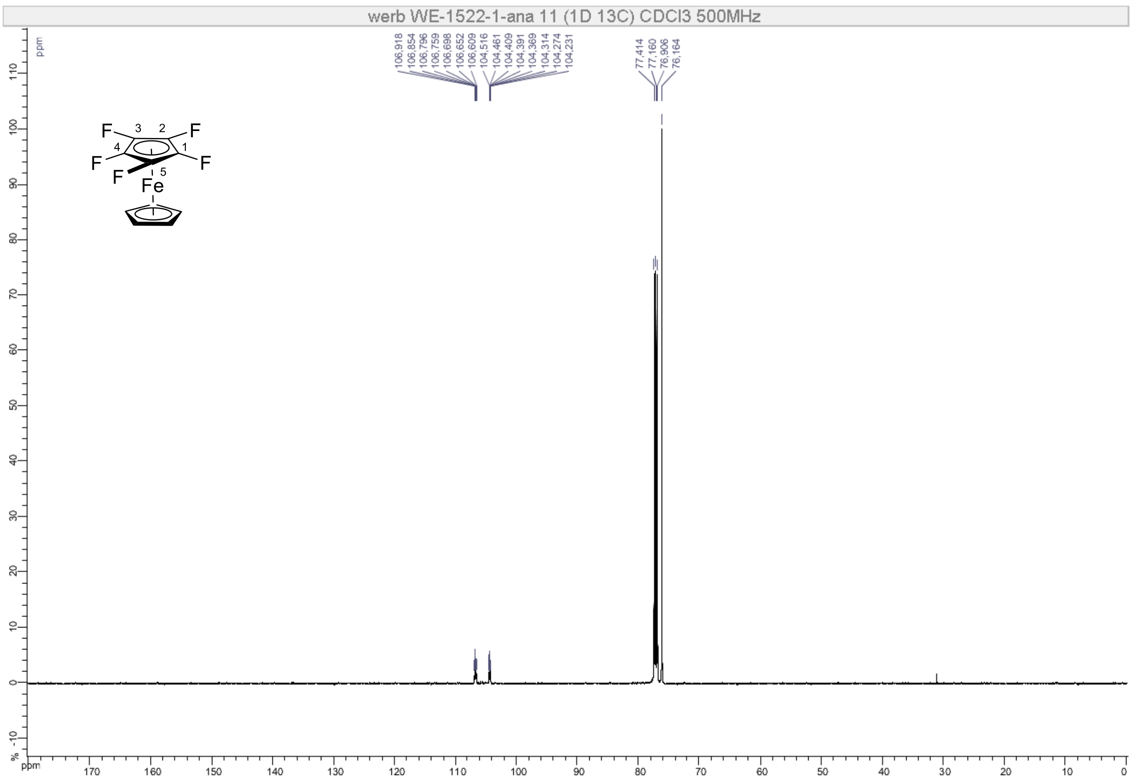


Compound 5

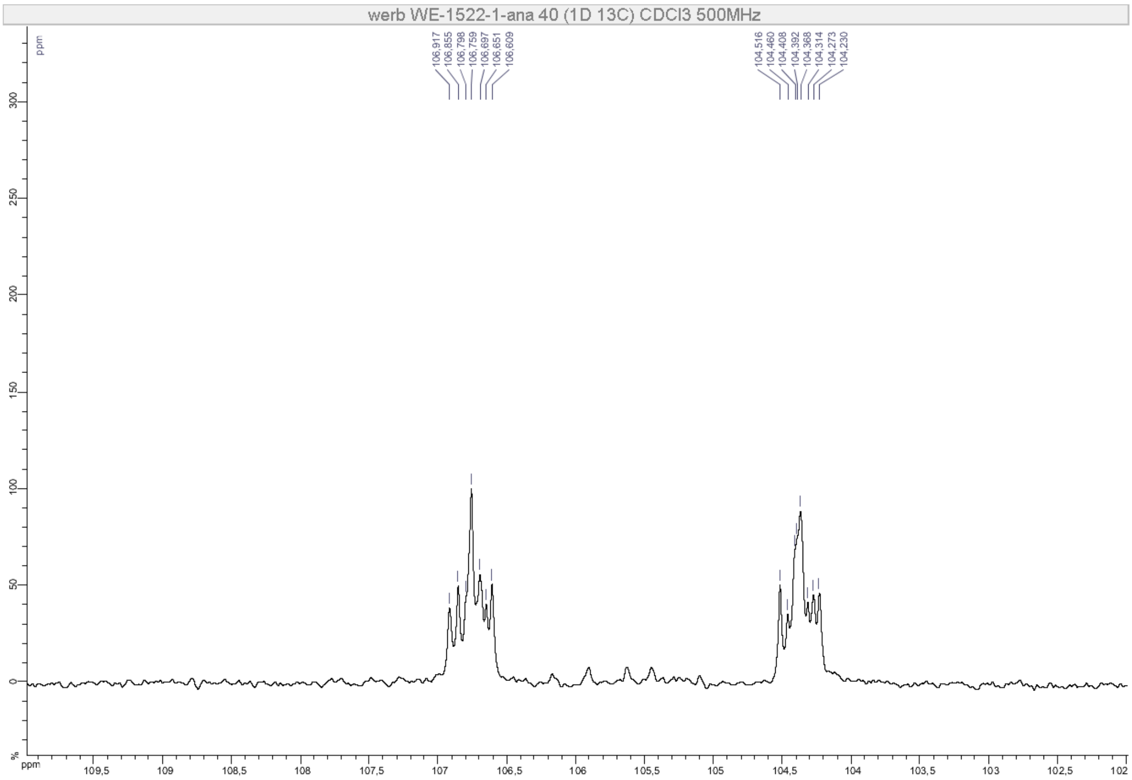
^{1}H (500 MHz, $CDCl_3$) – Full spectrum



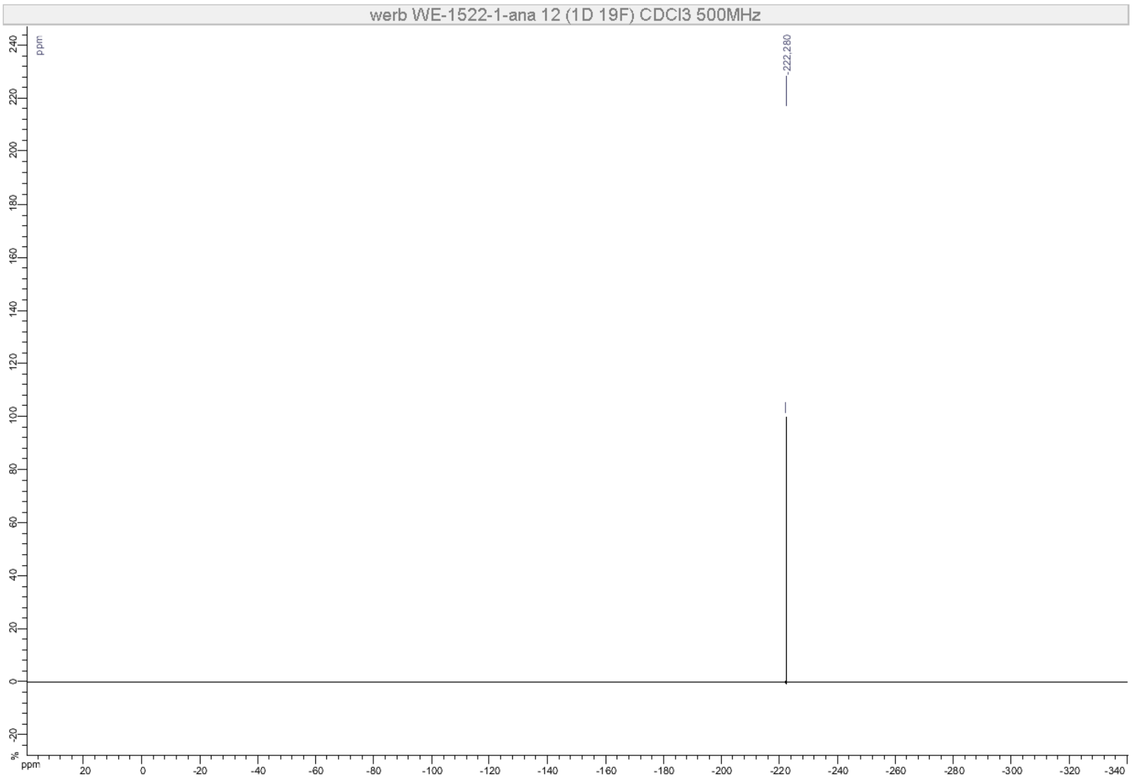
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) – Full spectrum



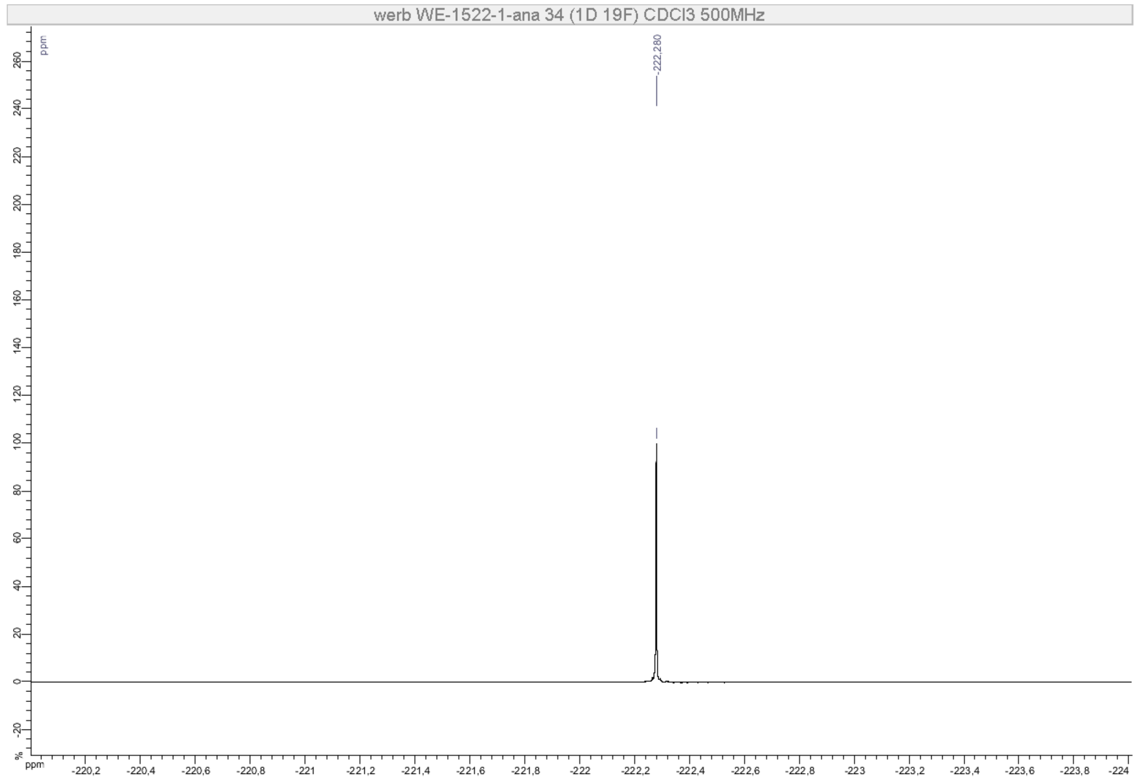
$^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) – 102 to 110 ppm area



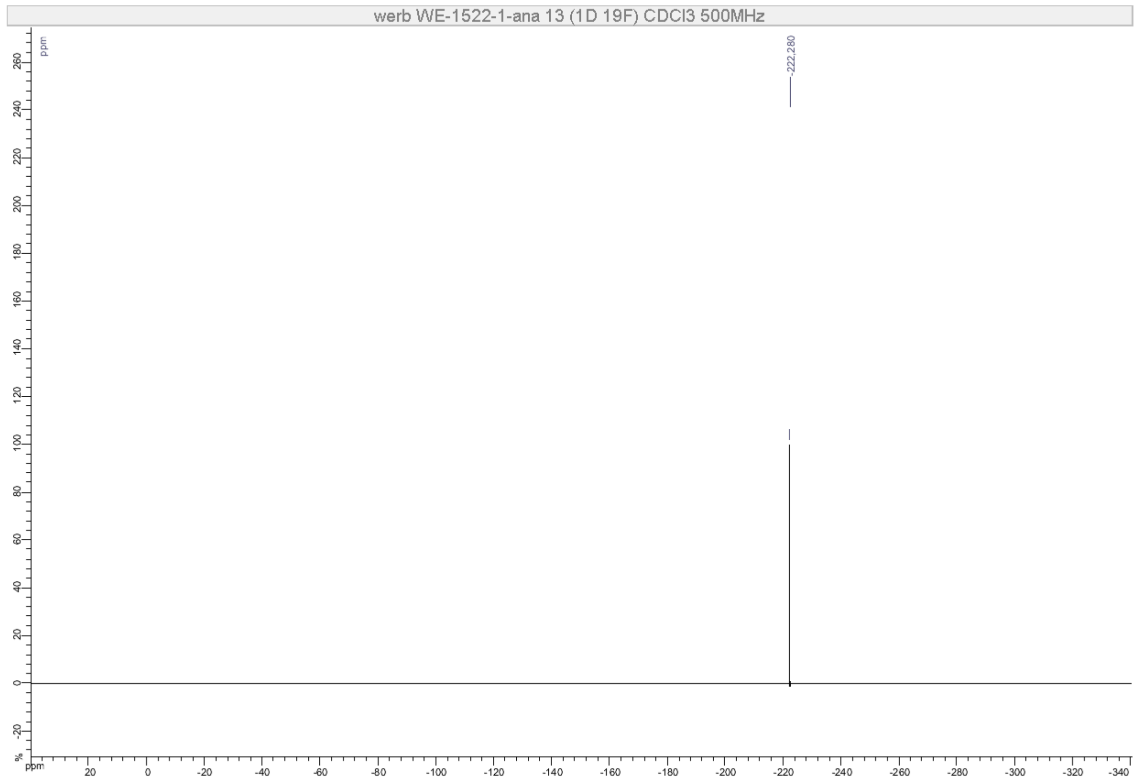
^{19}F (470 MHz, $CDCl_3$) – Full spectrum



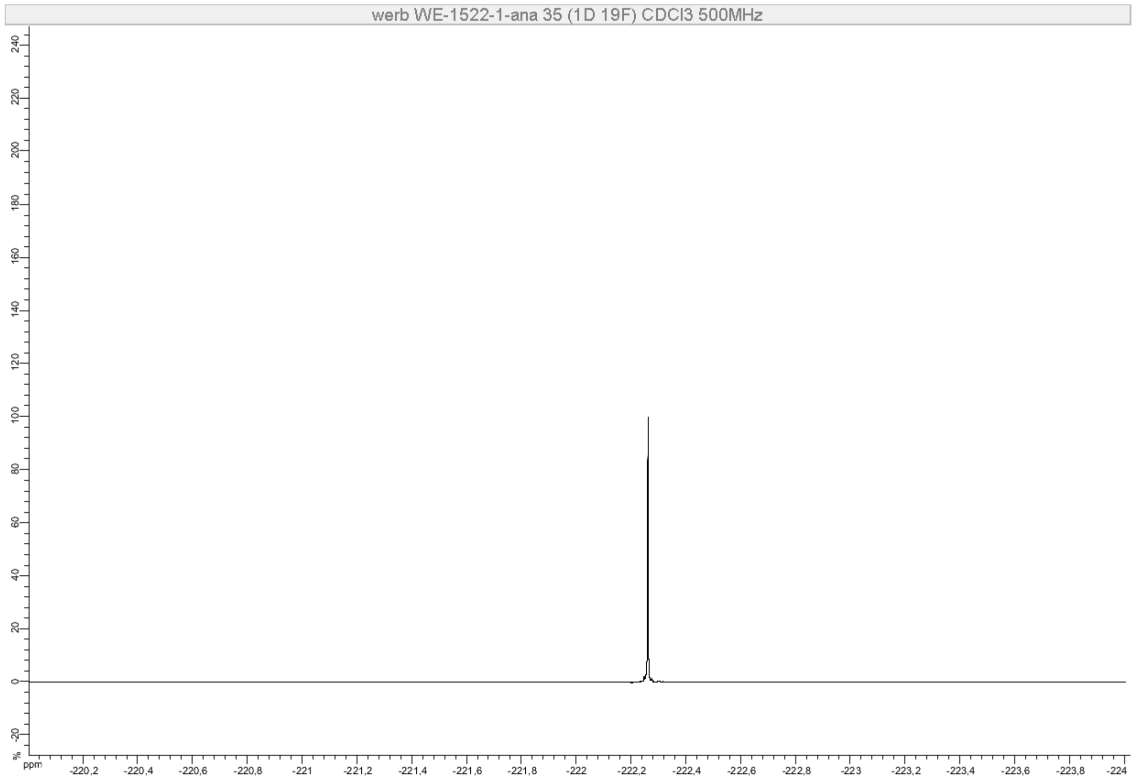
^{19}F (470 MHz, $CDCl_3$) – -224 to -220 ppm area



$^{19}F\{^1H\}$ (470 MHz, $CDCl_3$) – Full spectrum

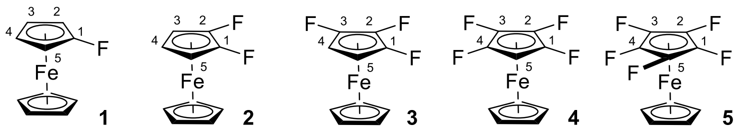


$^{19}F\{^{1}H\}$ (470 MHz, $CDCl_3$) – -224 to -220 ppm area



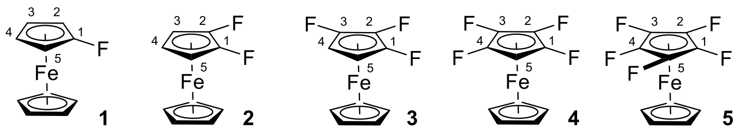
NMR chemical shifts and increments

Table SI1. ^{1}H Chemical shifts and chemical shifts increments (Δδ) of ferrocene and fluoroferrocenes **1**-**5** at 300 K in $CDCl_3$.



Compound	δ (ppm)						Chemical shifts increments (Δδ) due to fluorine		
	H^1	H^2	H^3	H^4	H^5	Cp	α/α’	β/β’	Cp
Ferrocene	4.16	4.16	4.16	4.16	4.16	4.16	/	/	/
1	/	4.30	3.79	3.79	4.30	4.26	+0.14 / +.014	-0.37 / -0.37	+0.10
2	/	/	4.07	3.46	4.07	4.35	+0.28 / -	-0.33 / -0.23	+0.09
3	/	/	/	3.81	3.81	4.44	+0.35 / -	-0.26 / -	+0.09
4	/	/	/	/	4.26	4.54	+0.45 / -	- / -	+0.10
5	/	/	/	/	/	4.64	- / -	- / -	+0.10

Table SI2. ^{13}C Chemical shifts and chemical shifts increments (Δδ) of ferrocene and fluoroferrocenes **1**-**5** at 300 K in $CDCl_3$.

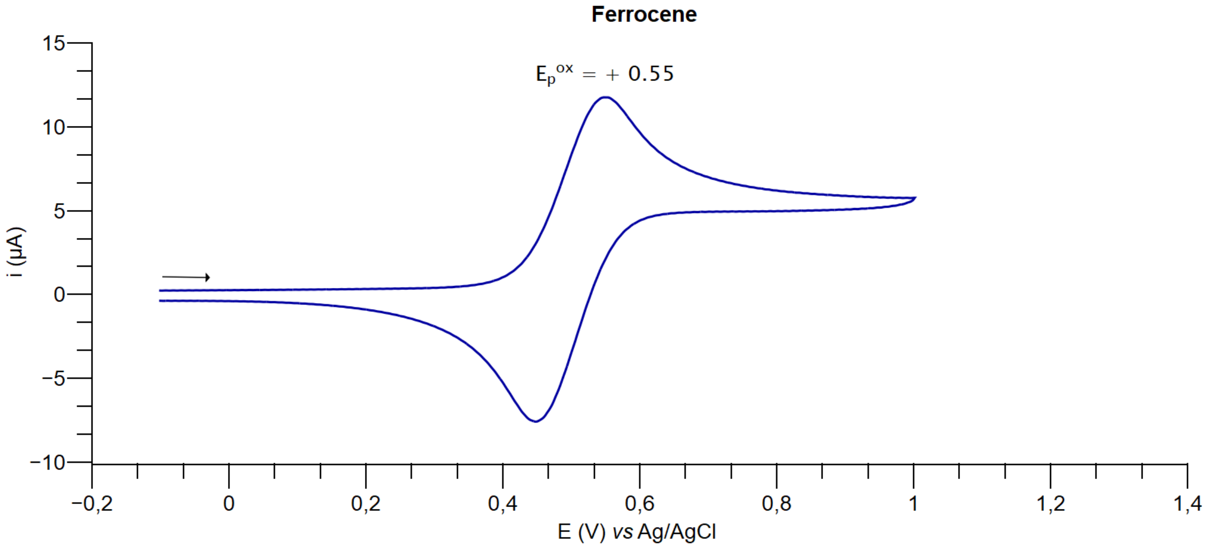


Compound	δ (ppm)						Chemical shifts increments (Δδ) due to fluorine			
	C^1	C^2	C^3	C^4	C^5	Cp	α/α’	β/β’	C_{ipso}	Cp
Ferrocene	68.1	68.1	68.1	68.1	68.1	68.1	/	/	/	/
1	135.8	56.2	61.2	61.2	56.2	69.4	-11.9 / -11.9	-6.9 / -6.9	+67.7	+1.3
2	123.6	123.6	51.0	51.6	51.0	70.9	-10.2 / -12.2	-9.6 / -5.2	+67.4	+1.5
3	119.0	113.5	119.0	42.3	42.3	72.5	-9.3 / -10.1	-8.7 / -4.6	+68.0	+1.6
4	112.7	109.7	109.7	112.7	35.1	74.3	-7.2 / -9.3	-6.3 / -3.8	+70.4	+1.8
5	105.6	105.6	105.6	105.6	105.6	76.2	-7.1 / -7.1	-4.1 / -4.1	+70.5	+1.9

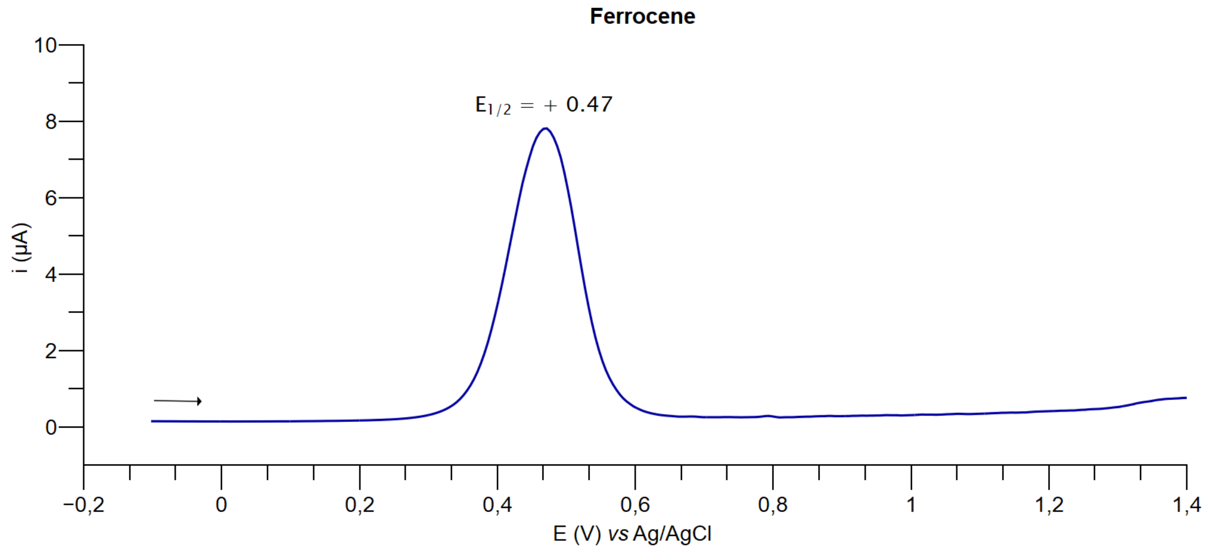
Voltammograms

<u>Ferrocene</u>

Cyclic voltammetry in CH_2Cl_2

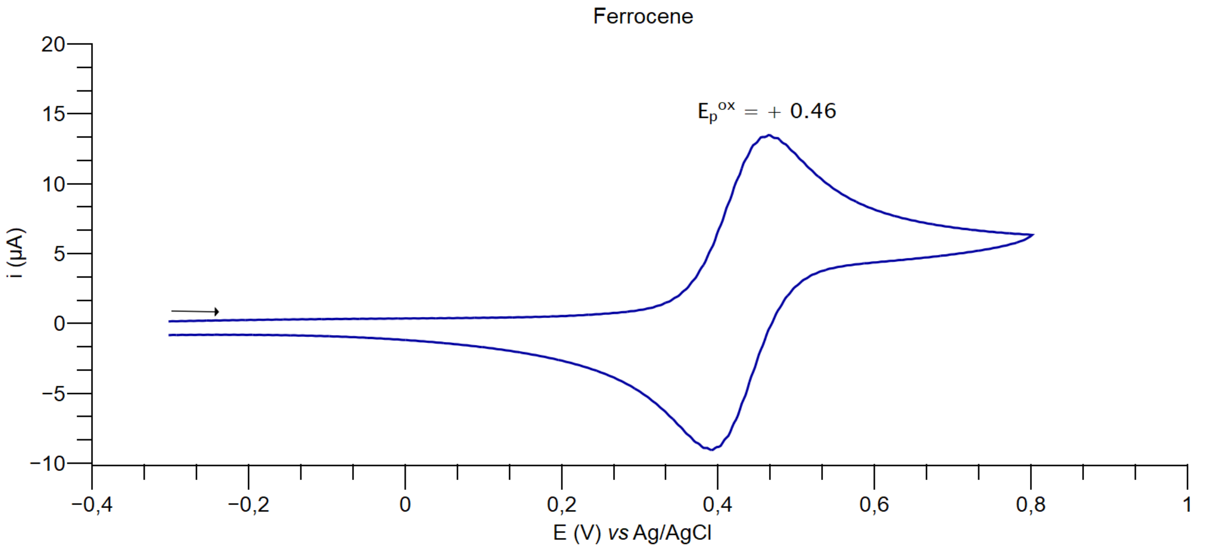


Differential pulse voltammetry in CH_2Cl_2

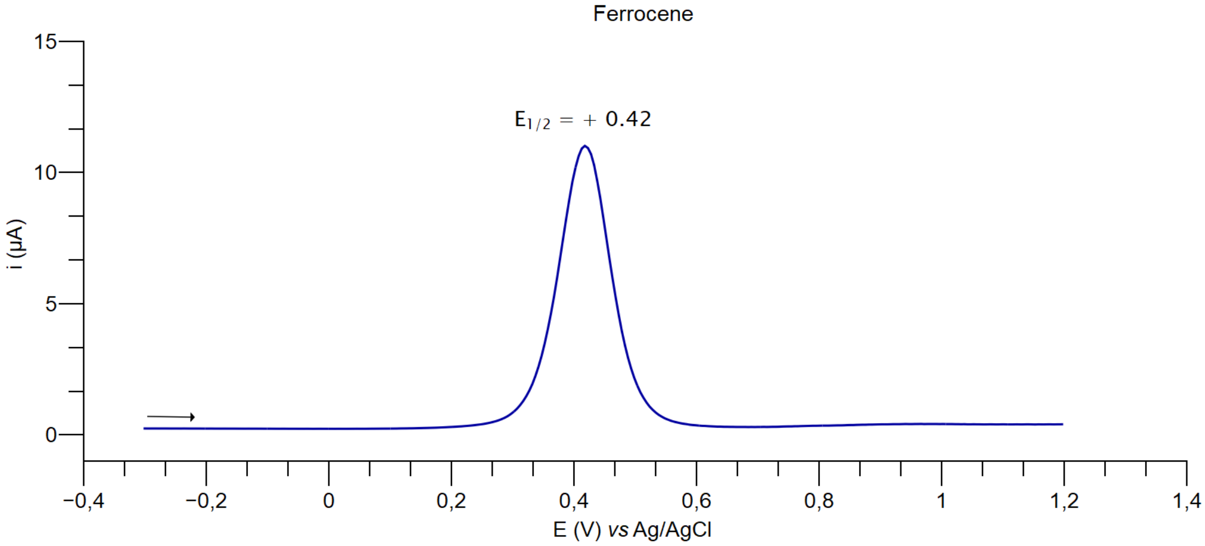


Ferrocene

Cyclic voltammetry in CH_3CN

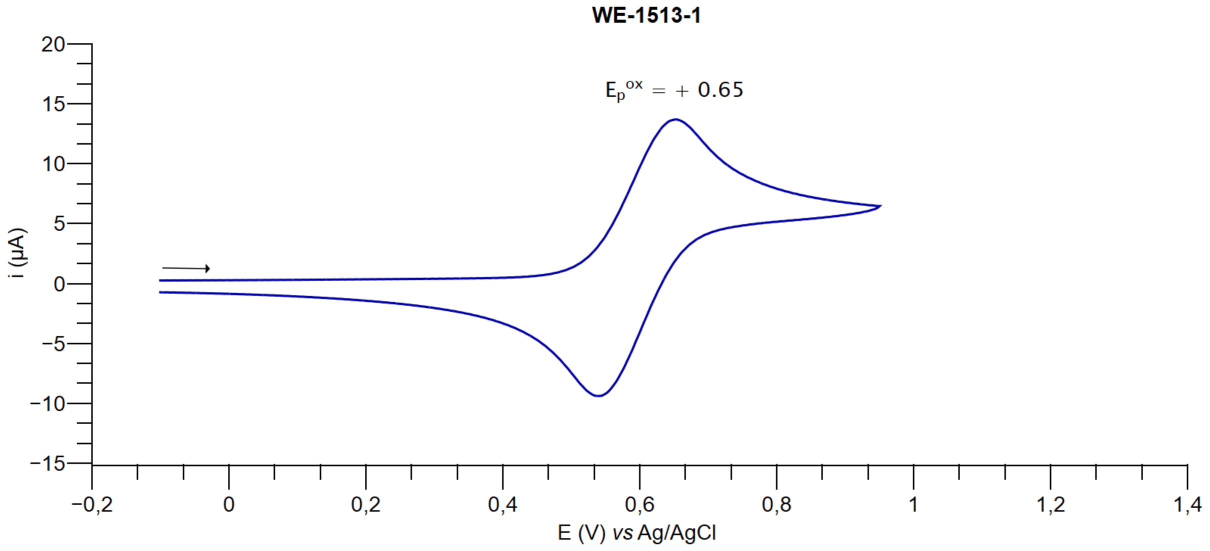


Differential pulse voltammetry in CH_3CN

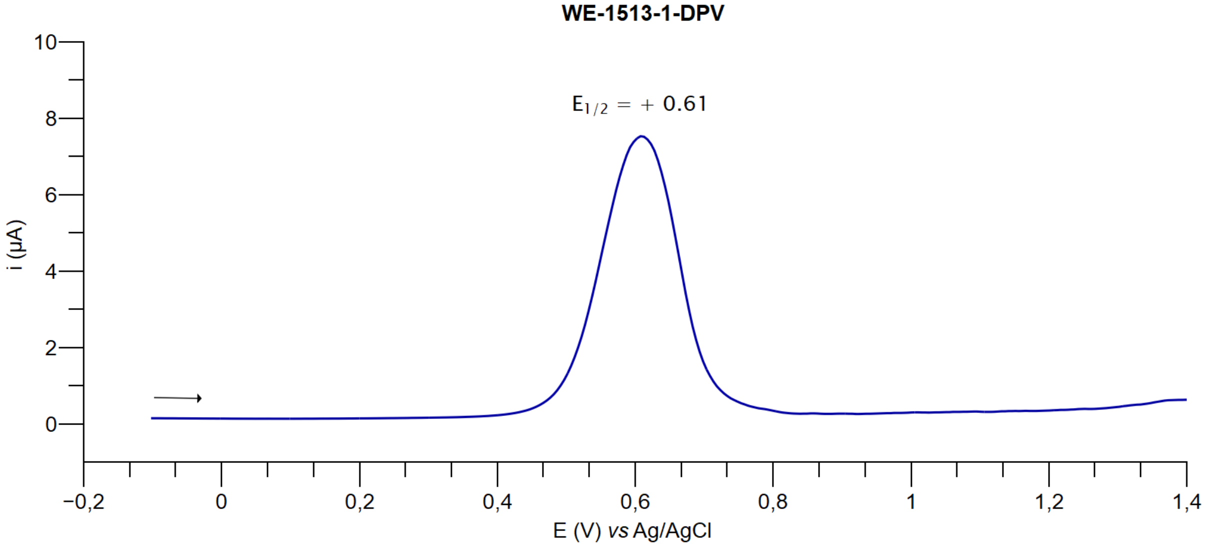


Compound 1

Cyclic voltammetry in CH_2Cl_2

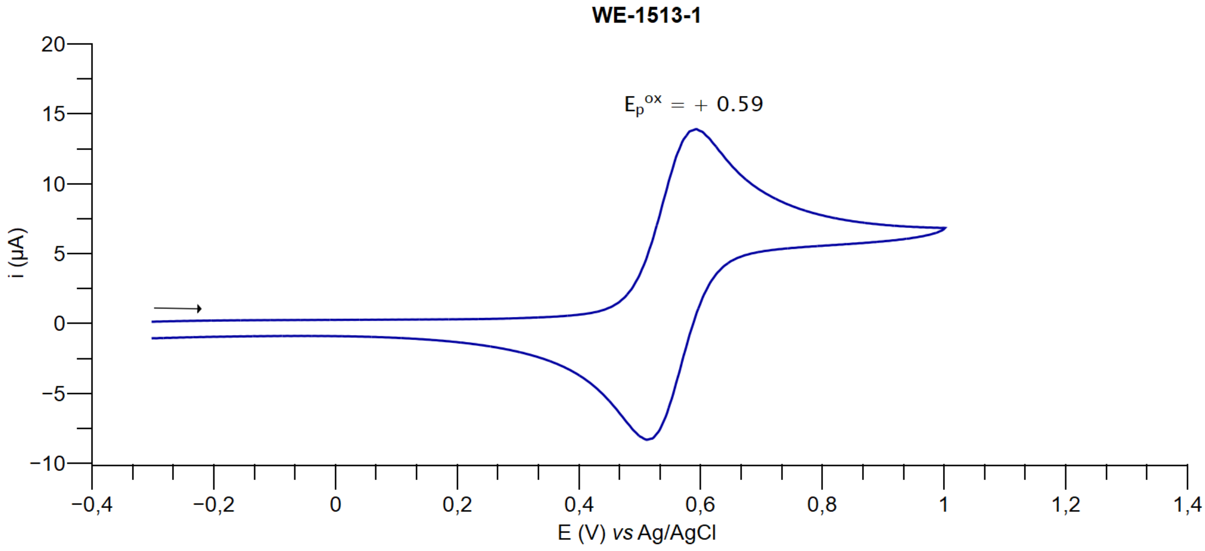


Differential pulse voltammetry in CH_2Cl_2

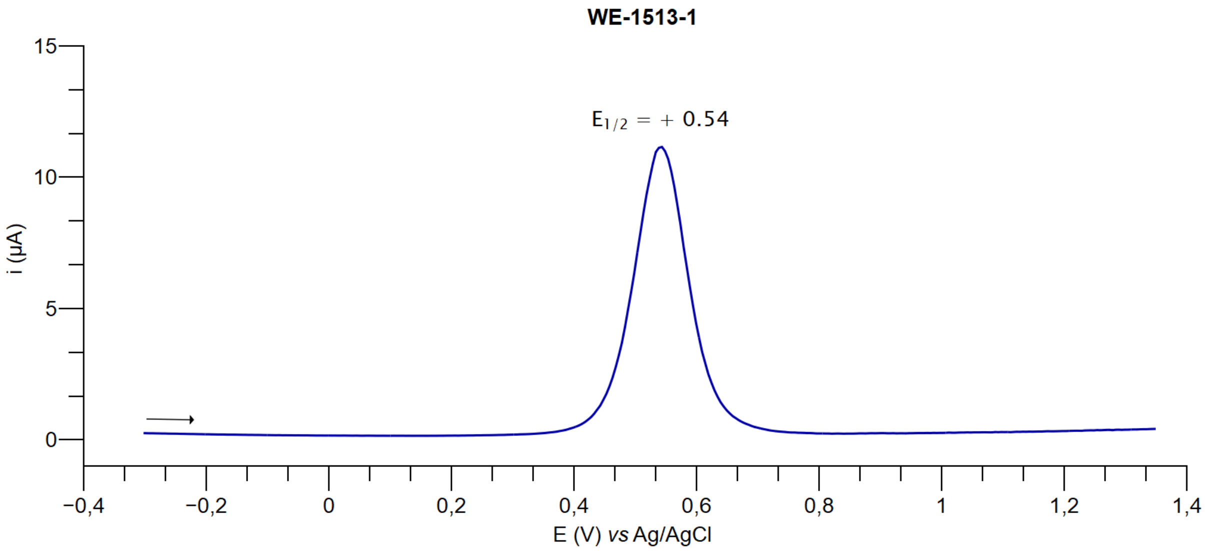


Compound 1

Cyclic voltammetry in CH_3CN

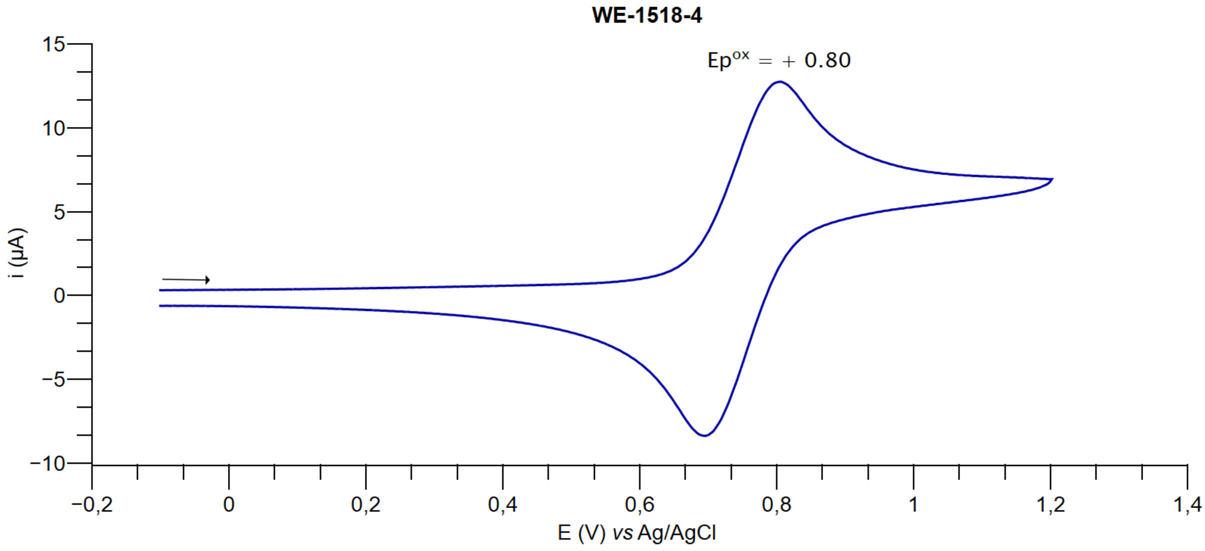


Differential pulse voltammetry in CH_3CN

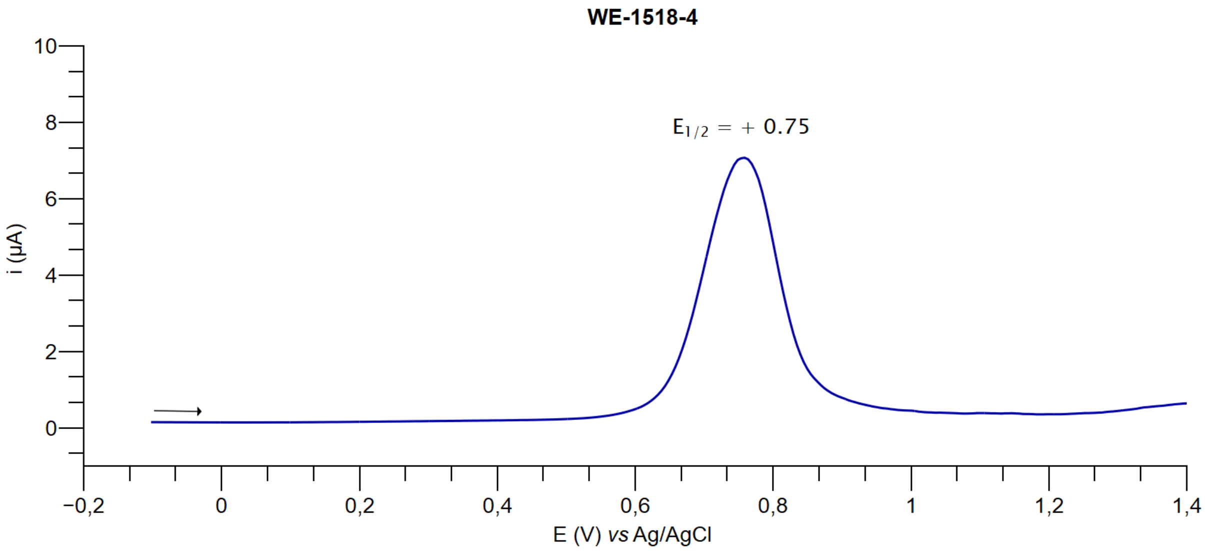


Compound 2

Cyclic voltammetry in CH_2Cl_2

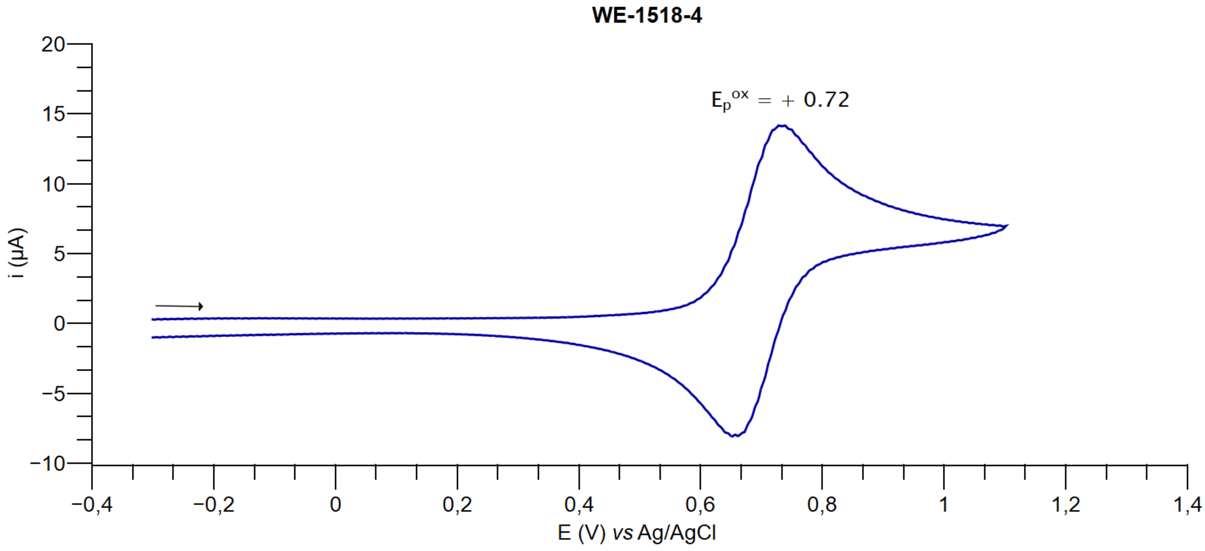


Differential pulse voltammetry in CH_2Cl_2

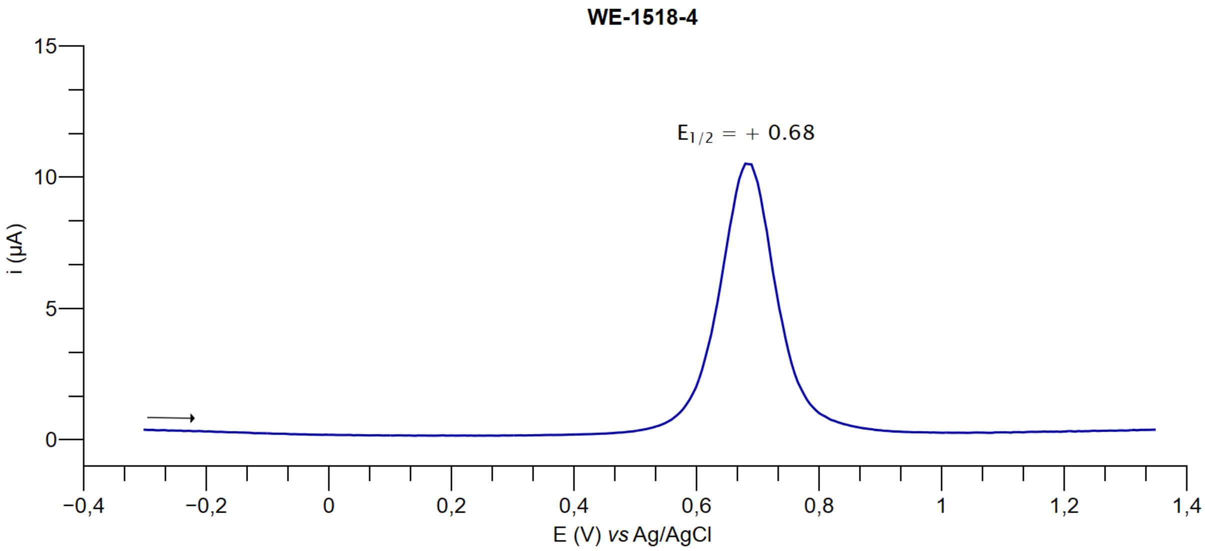


Compound 2

Cyclic voltammetry in CH_3CN

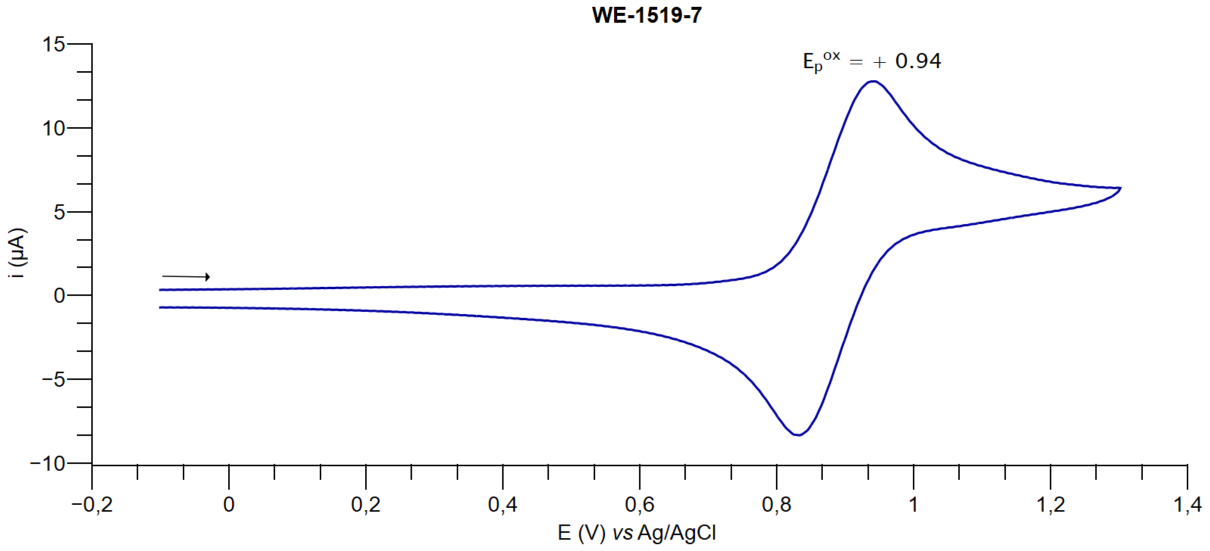


Differential pulse voltammetry in CH_3CN

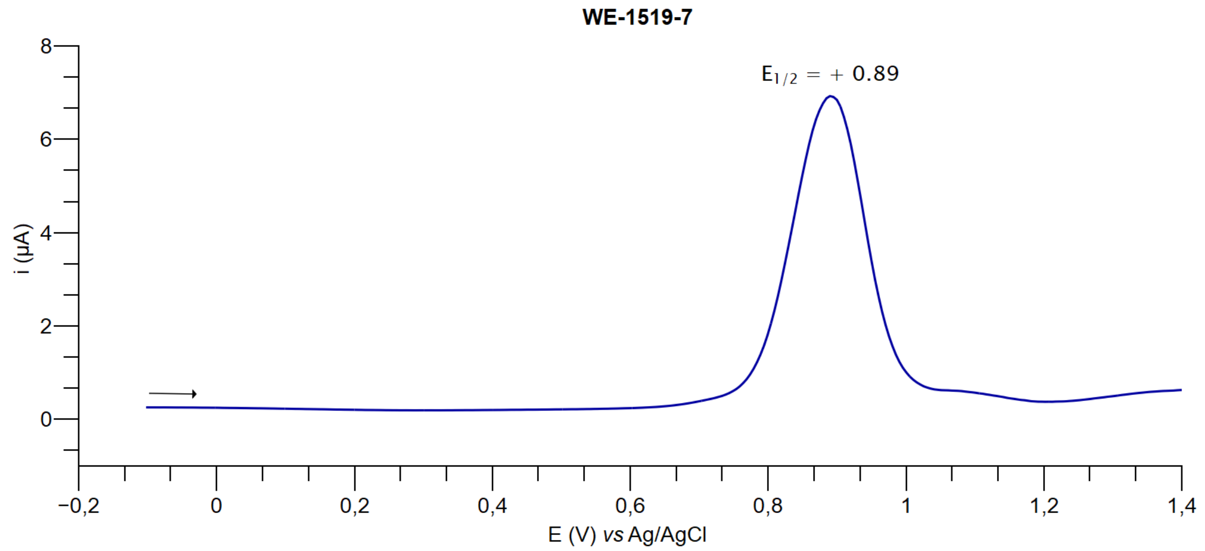


Compound 3

Cyclic voltammetry in CH_2Cl_2

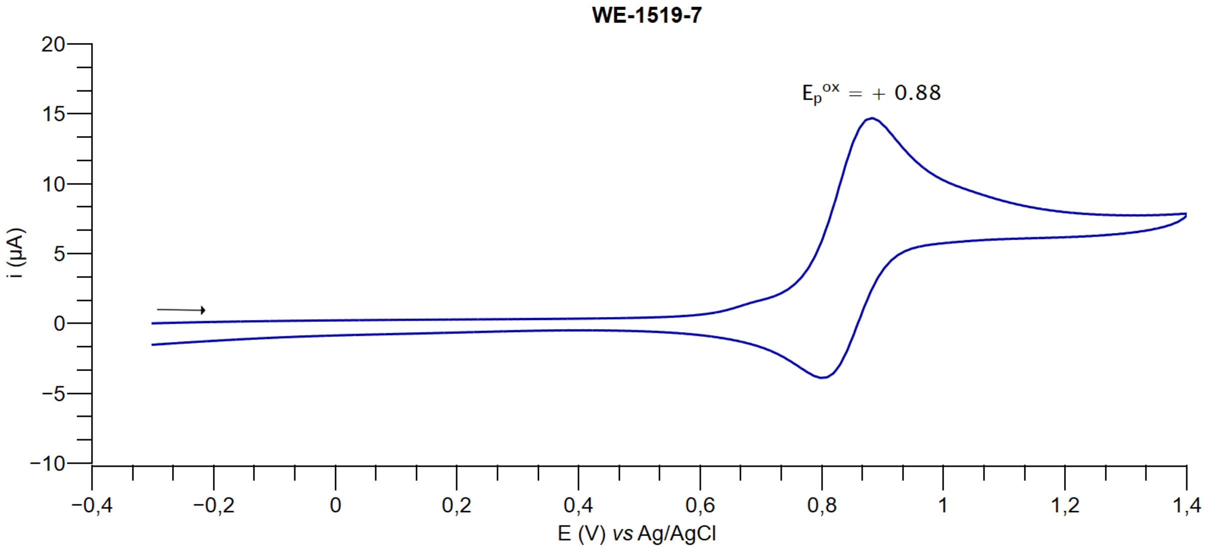


Differential pulse voltammetry in CH_2Cl_2

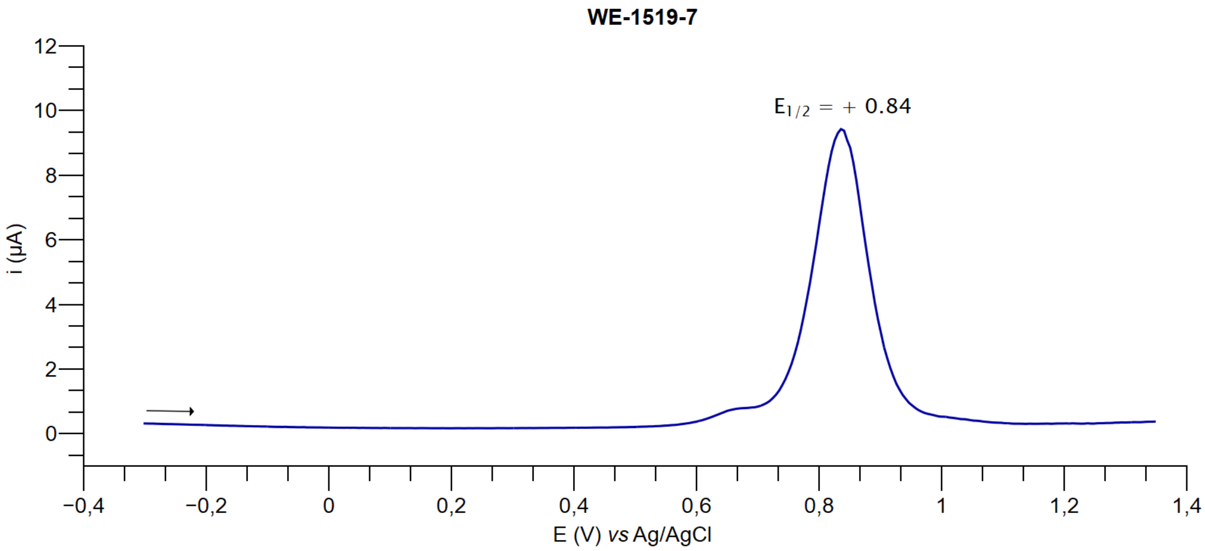


Compound 3

Cyclic voltammetry in CH_3CN

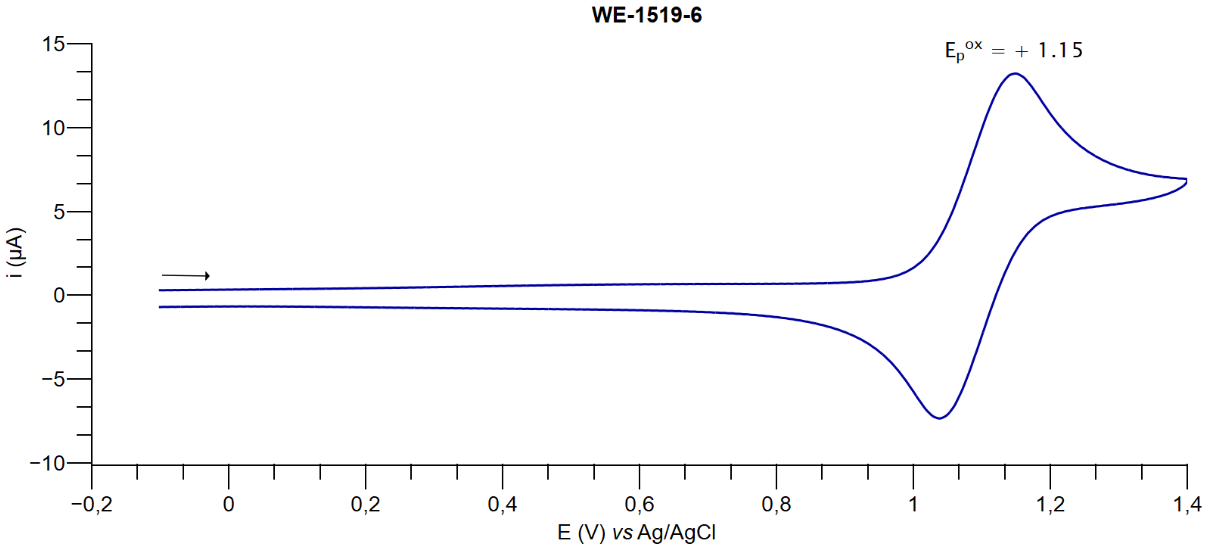


Differential pulse voltammetry in CH_3CN

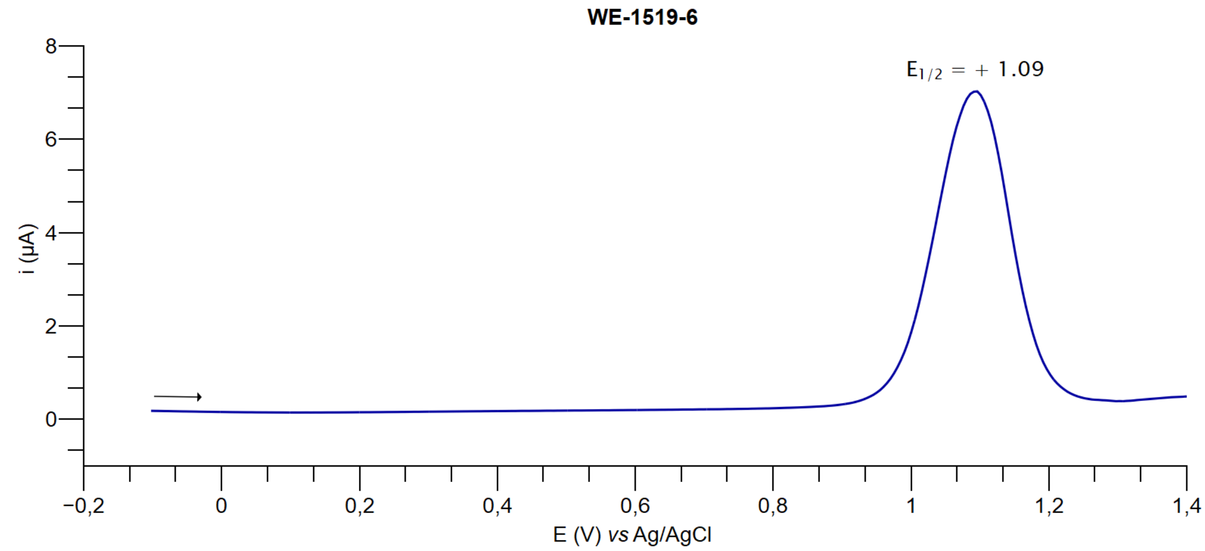


Compound 4

Cyclic voltammetry in CH_2Cl_2

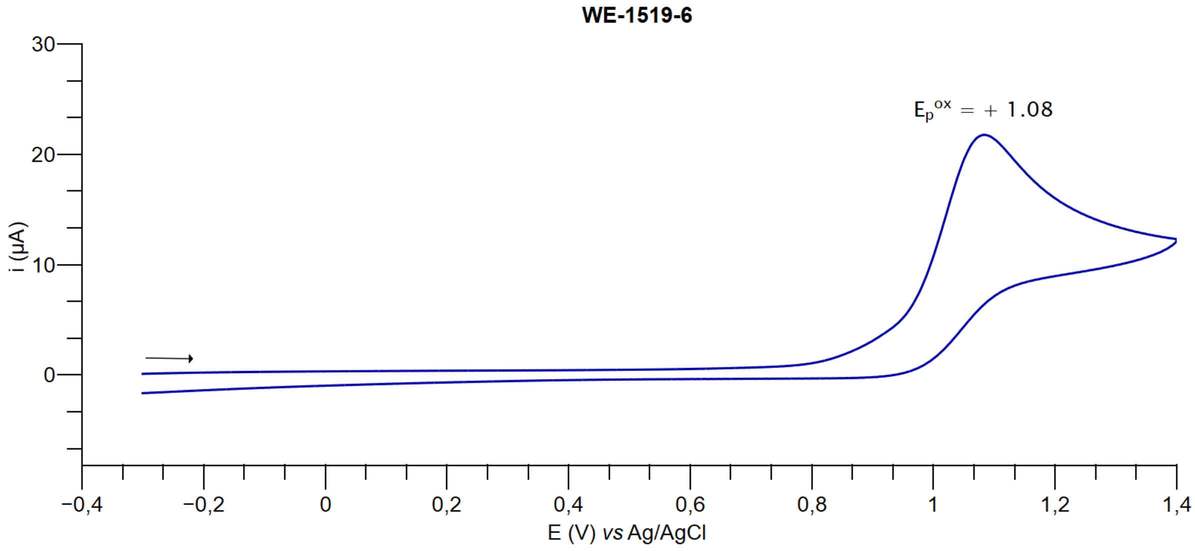


Differential pulse voltammetry in CH_2Cl_2

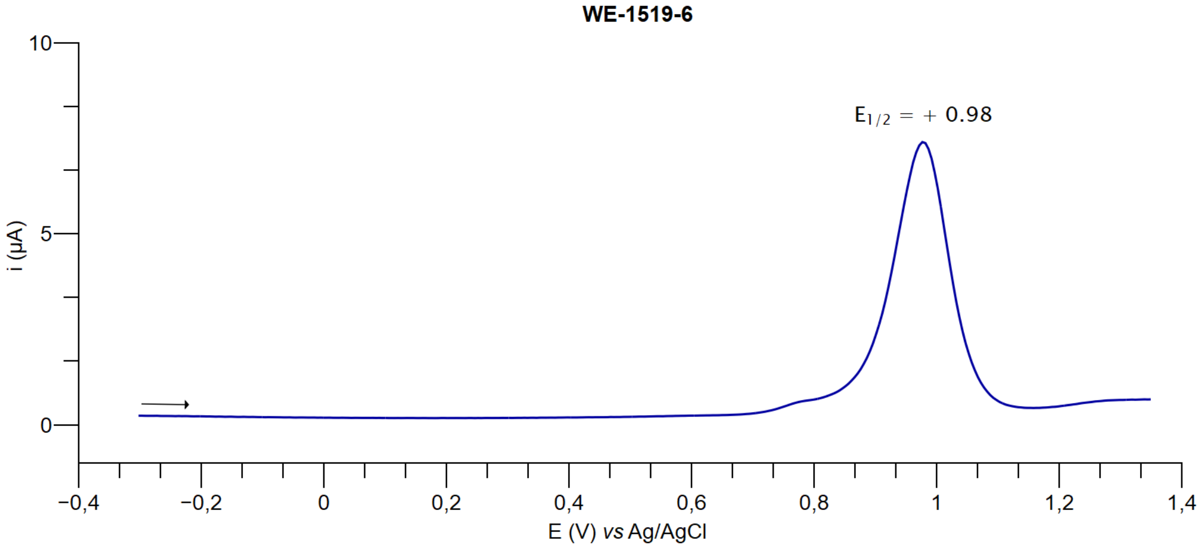


Compound 4

Cyclic voltammetry in CH_3CN

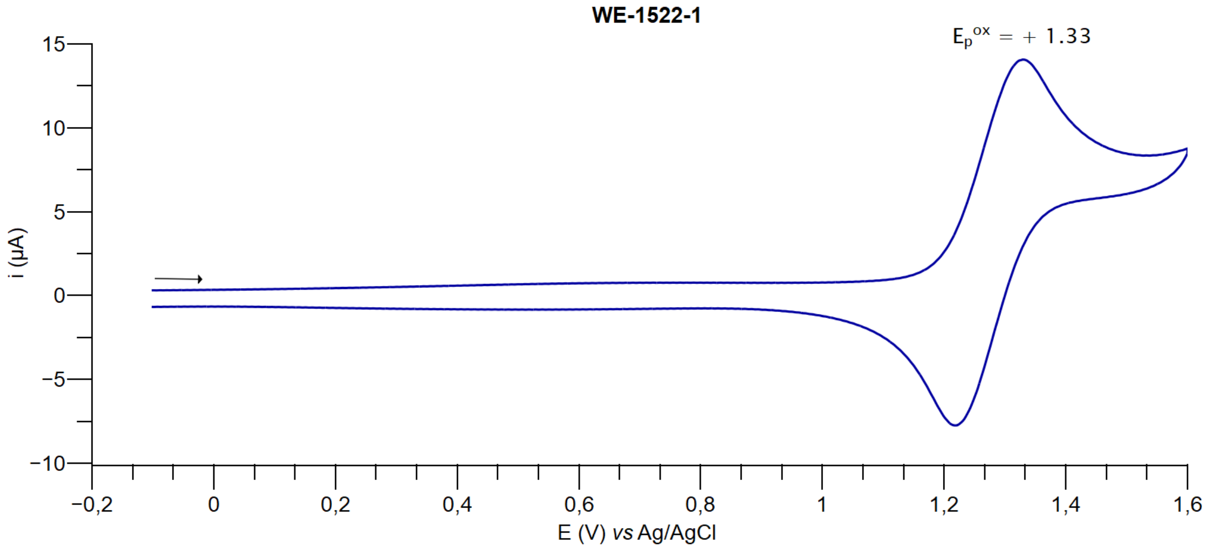


Differential pulse voltammetry in CH_3CN

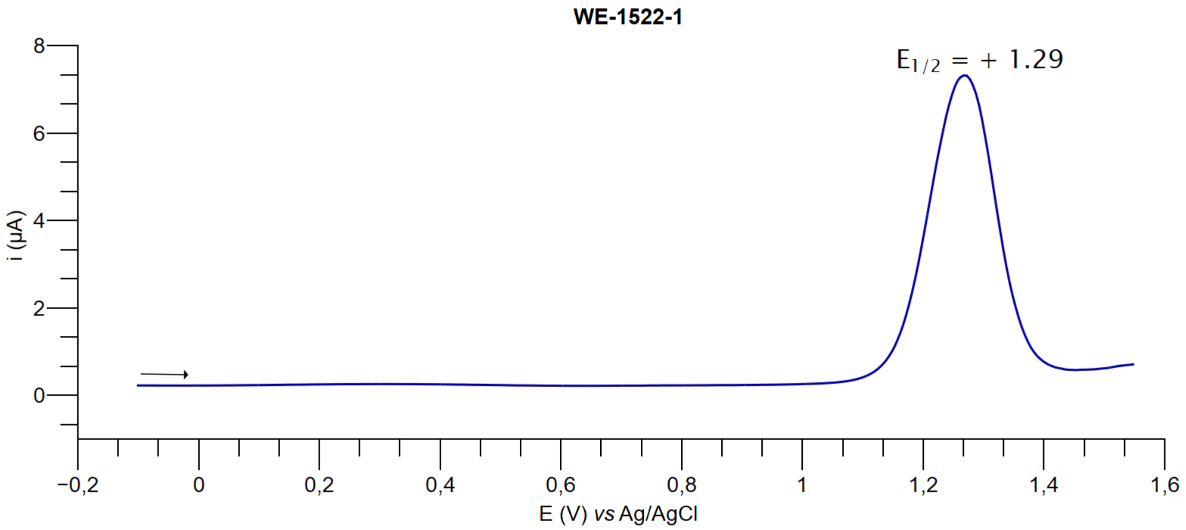


Compound 5

Cyclic voltammetry in CH_2Cl_2

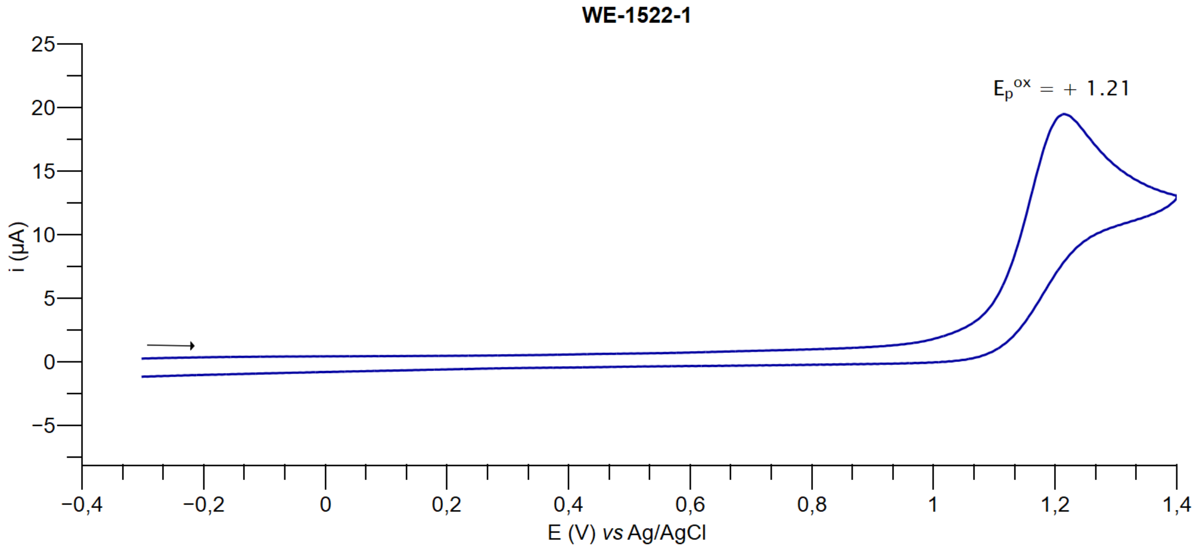


Differential pulse voltammetry in CH_2Cl_2

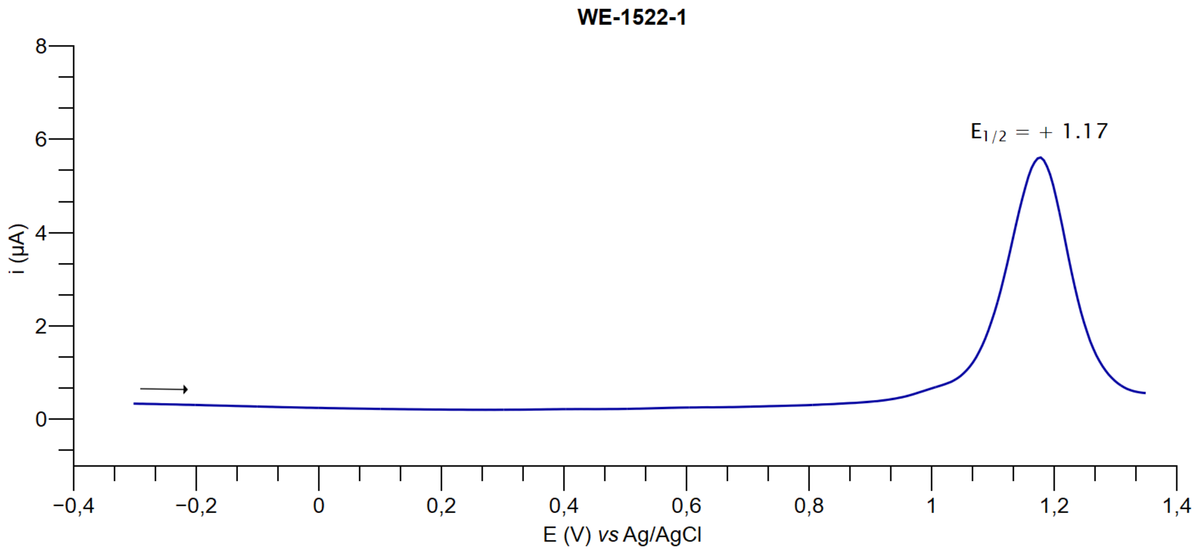


Compound 5

Cyclic voltammetry in CH_3CN



Differential pulse voltammetry in CH_3CN



Superposition of DPV voltammograms.

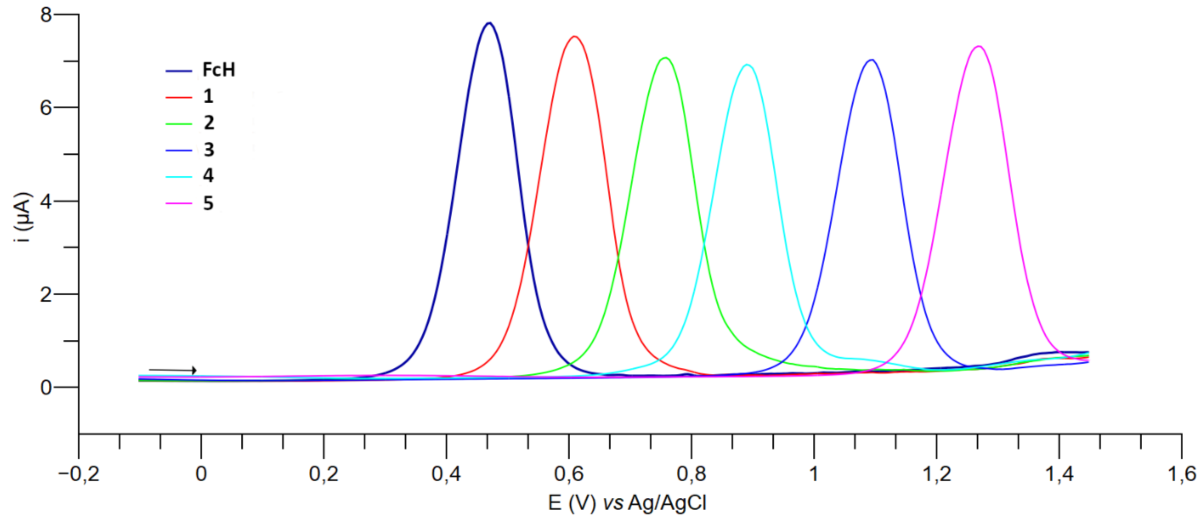


Figure S1. Superposition of DPV voltammograms of ferrocene and compounds **1-5** in CH_2Cl_2.

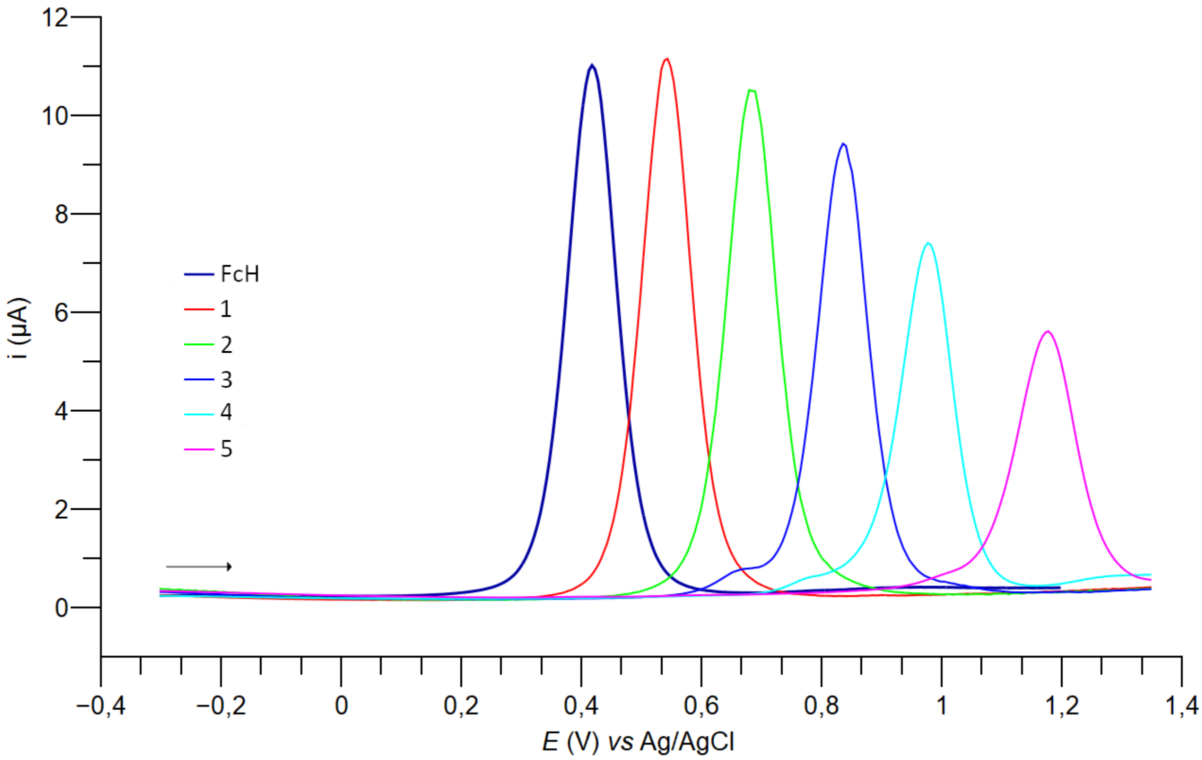


Figure S2. Superposition of DPV voltammograms of ferrocene and compounds **1-5** in CH_3CN.

Calculated electrode potentials

Compound	Cation energy (Ha)	Neutral energy (Ha)	Cation-Neutral energy difference (Ha)	Cation-Neutral energy difference (eV)	*ΔE* (eV)
Ferrocene (staggered)	- 510.704627	- 510.8969113	- 0.19228424	5.232322088	0
1	- 609.90048	- 610.0974289	- 0.19694891	5.359255373	0.126933285
2	- 709.0914881	- 709.2933222	- 0.20183416	5.49218986	0.259867772
3	- 808.2807975	- 808.4882274	- 0.20742992	5.644458318	0.41213623
4	- 907.4676549	- 907.681774	- 0.2141191	5.826480264	0.594158176
5	- 1006.648629	- 1006.868847	- 0.22021795	5.992438504	0.760116416

Cartesian coordinates of DFT optimized structures

Ferrocene

Ferrocene			
Atom	**X**	**Y**	**Z**
Fe	0	-0.0004	-0.0026
C	-1.6651	-0.5503	1.0795
H	-1.642	-1.0419	2.0434
C	-1.6665	-1.1976	-0.1896
H	-1.647	-2.2659	-0.3583
C	-1.6688	-0.1899	-1.1973
H	-1.6528	-0.3593	-2.2655
C	-1.6675	1.0798	-0.5503
H	-1.6482	2.0436	-1.0412
C	-1.6666	0.8566	0.8569
H	-1.6431	1.6215	1.622
C	1.661	0.1884	1.1995
C	1.6648	-1.0804	0.5506
H	1.6421	-2.0447	1.0402
C	1.6728	-0.855	-0.8562
H	1.6581	-1.6188	-1.6227
C	1.6715	0.5521	-1.0767
H	1.6575	1.0451	-2.04
C	1.6642	1.1976	0.1933
H	1.6416	2.2655	0.3637

Ferrocene$^+$			
Atom	**X**	**Y**	**Z**
Fe	-0.0001	-0.0008	-0.003
C	1.6676	0.9189	0.7932
H	1.6213	1.737	1.4988
C	1.6718	1.0378	-0.6279
H	1.6287	1.9615	-1.1879
C	1.6744	-0.2774	-1.1803
H	1.6341	-0.5241	-2.2319
C	1.6717	-1.2089	-0.0999
H	1.6294	-2.2854	-0.1903
C	1.6677	-0.4694	1.1194
H	1.6213	-0.8877	2.1157
C	-1.6661	0.2798	1.1822
C	-1.669	1.2097	0.1003
H	-1.624	2.2862	0.1887
C	-1.6741	0.4683	-1.1178
H	-1.6342	0.8849	-2.1151
C	-1.6743	-0.9195	-0.7895
H	-1.6347	-1.7387	-1.4942
C	-1.6694	-1.0363	0.6317
H	-1.624	-1.9593	1.1928

Compound 1

Compound 1			
Atom	X	Y	Z
Fe	0.1814	-0.1564	-0.0001
C	-1.1275	-1.5668	0.7127
H	-0.8524	-2.3982	1.3472
C	-1.1276	-1.5668	-0.7126
H	-0.853	-2.3985	-1.3471
C	-1.513	-0.269	-1.1647
C	-1.7505	0.502	0
C	-1.5128	-0.2689	1.1648
H	-1.5951	0.074	2.1865
H	-1.596	0.0737	-2.1865
F	-2.1372	1.7883	0
C	1.8735	-0.0211	1.1541
C	2.1265	-0.8231	0.004
H	2.4183	-1.8649	0.0077
C	1.876	-0.0284	-1.1516
H	1.9502	-0.3589	-2.179
C	1.4734	1.2686	-0.7154
H	1.1832	2.0924	-1.354
C	1.4717	1.273	0.7089
H	1.1804	2.1009	1.3417

Compound 1^+			
Atom	X	Y	Z
Fe	0.1878	-0.1452	-0.0002
C	1.4966	1.2807	-0.7116
H	1.1911	2.0996	-1.3483
C	1.8861	-0.0215	-1.1525
H	1.9322	-0.3538	-2.1804
C	2.134	-0.8232	0.0003
H	2.3964	-1.8722	0.0007
C	1.8862	-0.021	1.1527
H	1.9324	-0.3527	2.1809
C	1.4964	1.2809	0.7116
H	1.1908	2.1001	1.3478
C	-1.7992	0.4883	-0.0001
C	-1.5243	-0.276	-1.1644
H	-1.5891	0.0717	-2.1859
C	-1.108	-1.5645	-0.7135
H	-0.8015	-2.3838	-1.3484
C	-1.1081	-1.5644	0.7139
H	-0.8017	-2.3838	1.3488
C	-1.5248	-0.2759	1.1643
H	-1.5901	0.0716	2.1858

Compound 2

Compound 2			
Atom	**X**	**Y**	**Z**
Fe	0.3318	0.1956	0.0001
C	-1.0626	1.1554	-1.1636
H	-0.926	1.4461	-2.1955
C	-0.7596	1.9258	-0.0005
H	-0.3414	2.9227	-0.0008
C	-1.0628	1.1561	1.163
C	-1.5529	-0.0944	0.7088
C	-1.5529	-0.0948	-0.7088
H	-0.9261	1.4472	2.1947
F	-1.9693	-1.1123	-1.4722
F	-1.9695	-1.1115	1.4727
C	1.7153	-0.7846	-1.1519
C	2.2365	0.4684	-0.7151
H	2.5431	1.2858	-1.354
C	2.2381	0.4723	0.7095
H	2.5457	1.2933	1.3433
C	1.7178	-0.7784	1.1543
H	1.5589	-1.0703	2.1838
C	1.3945	-1.5552	0.0036
H	0.9461	-2.5398	0.0068

Compound 2^{+}			
Atom	**X**	**Y**	**Z**
Fe	-0.3502	0.1892	0.0002
C	1.6046	-0.0936	-0.7112
C	1.0626	1.1326	-1.1742
C	0.7442	1.9097	-0.0184
H	0.3	2.8946	-0.0276
C	1.0667	1.1558	1.1513
H	0.9107	1.4475	2.1802
C	1.607	-0.0794	0.7109
H	0.9031	1.4037	-2.2083
F	2.0198	-1.0739	1.4731
F	2.0149	-1.1034	-1.4544
C	-1.7436	-0.7966	-1.1457
H	-1.5632	-1.0933	-2.1699
C	-2.2569	0.4659	-0.7182
H	-2.5353	1.2884	-1.3625
C	-2.2597	0.4795	0.7069
H	-2.5403	1.3146	1.3339
C	-1.7484	-0.7745	1.1607
H	-1.5721	-1.0514	2.1911
C	-1.4326	-1.5636	0.0155

Compound 3

Compound 3			
Atom	**X**	**Y**	**Z**
Fe	-0.4015	-0.0007	-0.1661
C	1.2692	1.1407	-0.3323
C	0.8514	0.7156	-1.6184
H	0.5651	1.3606	-2.4366
C	0.8525	-0.7156	-1.6181
C	1.2709	-1.1396	-0.3319
C	1.5265	0.0009	0.4734
H	0.5674	-1.3613	-2.4362
F	1.9672	0.0014	1.7324
F	1.4251	-2.4034	0.075
F	1.421	2.4048	0.0743
C	-1.645	0.7101	1.2967
C	-2.0866	1.1538	0.0167
H	-2.1631	2.1832	-0.3071
C	-2.361	0.0029	-0.778
H	-2.6811	0.0059	-1.8113
C	-2.089	-1.1527	0.0108
H	-2.1681	-2.1803	-0.3183
C	-1.6466	-0.7166	1.2931
H	-1.3296	-1.3551	2.1068

Compound 3^+			
Atom	**X**	**Y**	**Z**
Fe	-0.4284	-0.0376	-0.1024
C	1.2648	1.1667	-0.3594
C	0.7499	0.7025	-1.5971
H	0.3762	1.3205	-2.401
C	0.8144	-0.7286	-1.5784
C	1.3754	-1.1156	-0.3348
C	1.6453	0.0482	0.4319
H	0.4949	-1.3968	-2.3652
F	2.1506	0.0857	1.6456
F	1.5978	-2.3479	0.0763
F	1.3716	2.4231	0.0253
C	-1.7903	0.7911	1.2187
C	-2.1458	1.0844	-0.1305
H	-2.1914	2.0682	-0.5768
C	-2.3446	-0.1559	-0.8118
H	-2.576	-0.274	-1.8613
C	-2.1161	-1.2116	0.1222
H	-2.1403	-2.2702	-0.0983
C	-1.7714	-0.6261	1.3728
H	-1.4836	-1.1632	2.2663

Compound 4

Compound 4			
Atom	**X**	**Y**	**Z**
Fe	0.4363	-0.0073	-0.0702
C	1.9587	-1.1681	0.6597
H	1.8425	-2.1948	0.9799
C	1.7755	-0.0099	1.4737
H	1.5038	-0.0049	2.5207
C	1.9726	1.1396	0.6525
H	1.8657	2.1697	0.9651
C	2.271	0.6928	-0.6664
H	2.434	1.324	-1.5296
C	2.2619	-0.7335	-0.6619
H	2.418	-1.372	-1.521
C	-1.0926	-1.127	-0.7888
C	-1.3682	-0.6983	0.5349
C	-1.3519	0.7248	0.5328
C	-1.0672	1.1438	-0.7923
C	-0.8985	0.0057	-1.6259
H	-0.661	0.001	-2.6798
F	-1.0501	-2.4029	-1.1789
F	-1.601	1.5118	1.5787
F	-0.9901	2.4175	-1.1841

Compound 4^+			
Atom	**X**	**Y**	**Z**
Fe	0.4663	-0.0682	-0.0175
C	1.9985	-1.1711	0.8449
H	1.8456	-2.1328	1.3158
C	1.8815	0.0977	1.4828
H	1.6333	0.2655	2.522
C	2.0747	1.1089	0.4947
H	1.9925	2.1757	0.6533
C	2.2983	0.4637	-0.7576
H	2.4265	0.9551	-1.7122
C	2.2501	-0.9488	-0.5391
H	2.3288	-1.7116	-1.3018
C	-1.1857	-1.0854	-0.7923
C	-1.52	-0.6109	0.5031
C	-1.3889	0.8067	0.4878
C	-0.9722	1.1825	-0.8185
C	-0.8255	0.0137	-1.6188
H	-0.5239	-0.0261	-2.6562
F	-1.2034	-2.351	-1.1558
F	-1.6252	1.6109	1.4999
F	-0.7813	2.4214	-1.2223

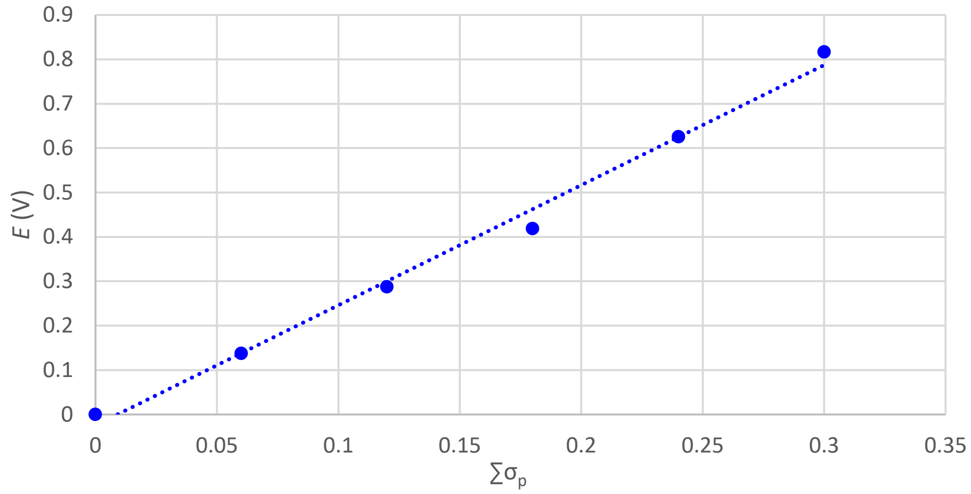
Compound 5

Compound 5			
Atom	**X**	**Y**	**Z**
Fe	0.4925	-0.0035	-0.0298
C	2.1175	-0.9735	0.7419
H	2.0779	-1.8226	1.4094
C	2.1371	0.407	1.1308
H	2.0945	0.7721	2.1431
C	2.1242	1.1848	-0.0556
H	2.0959	2.2728	-0.0962
C	2.1207	0.3083	-1.1672
H	2.0848	0.6077	-2.2181
C	2.1109	-1.0212	-0.6847
H	2.0707	-1.9255	-1.2871
C	-1.1558	-1.1968	0.0616
C	-1.1292	-0.3234	1.1751
C	-1.1249	1.0191	0.6892
C	-1.1393	0.9602	-0.7319
C	-1.1529	-0.4079	-1.116
F	-1.2062	-2.5337	0.1077
F	-1.1258	2.1241	1.4261
F	-1.1665	2.0084	-1.5594
F	-1.1483	-0.6843	2.4585

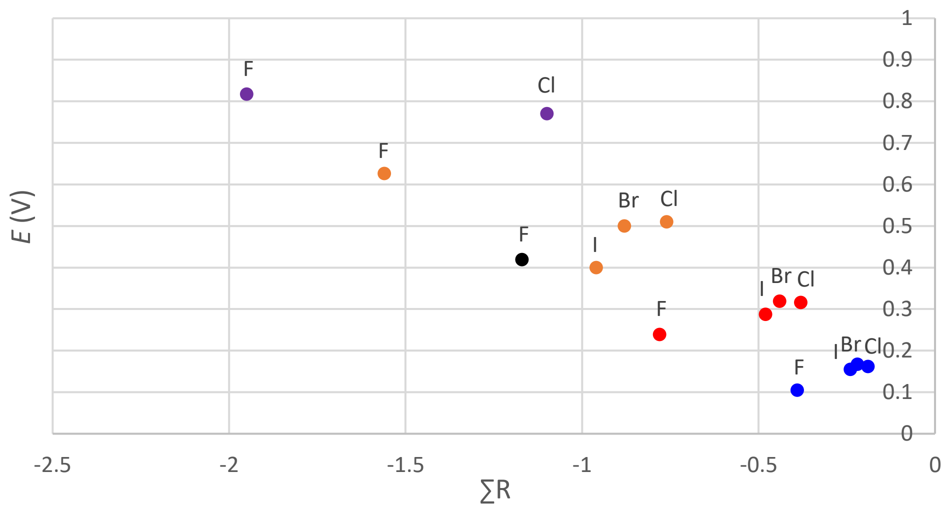
Compound 5^{+}			
Atom	**X**	**Y**	**Z**
Fe	-0.5204	-0.0036	-0.1044
C	-2.173	-0.4891	-1.2661
H	-2.0968	-0.9213	-2.2546
C	-2.1771	0.9018	-0.9615
H	-2.1069	1.7083	-1.679
C	-2.1957	1.0438	0.4578
H	-2.1478	1.976	1.0041
C	-2.2029	-0.2647	1.0314
H	-2.165	-0.4959	2.0872
C	-2.1878	-1.2116	-0.0376
H	-2.1288	-2.2862	0.0693
C	1.2519	-1.1087	-0.3672
C	1.3565	0.1132	-1.0857
C	1.2151	1.1829	-0.1589
C	1.0263	0.6239	1.1372
C	1.0489	-0.7959	1.0082
F	1.3503	-2.3147	-0.8782
F	1.2729	2.4635	-0.4458
F	0.9096	1.2952	2.2604
F	1.5532	0.2339	-2.3784

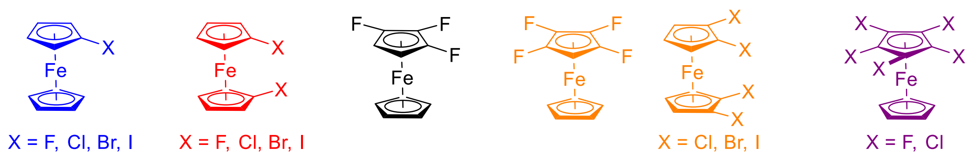
Additional plots

Plot SI1: *E* (V) *vs.* $\sum\sigma_p$ for fluoroferrocenes.

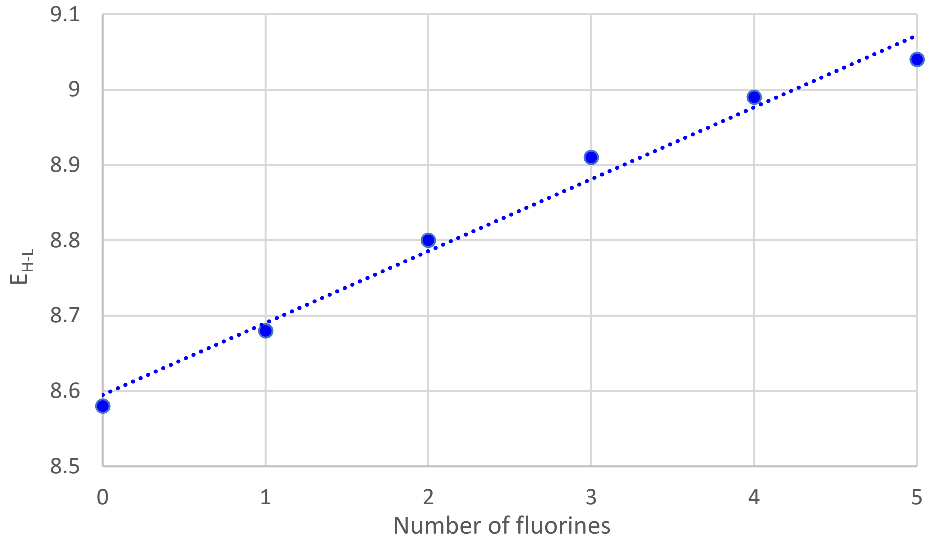


Plot SI2: top: *E* (V) *vs.* ∑*R* for mono- (blue circles), homo-1,1'-di- (red circles), homo-tri- (black circles), homo-tetra- (orange circles) and homo-pentahalogenoferrocenes (purple circles); bottom: structures of compounds reported in plot S2.

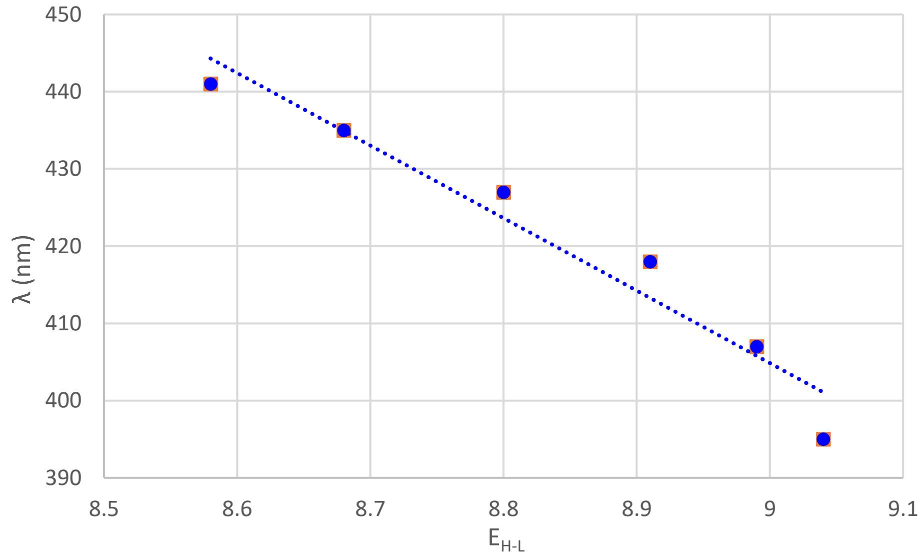




Plot SI3: $E_{H\text{-}L}$ (eV) *vs.* number of fluorines.



Plot SI4: λ_{max} (nm) *vs.* $E_{H\text{-}L}$ (eV).



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