Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Exploring the boundaries of ferrocenesulfonyl fluoride chemistry

William Erb,[a] Jean-Pierre Hurvois,*[a] Yury S. Halauko,*[b] Vadim E. Matulis[b] and Thierry Roisnel[a]*

[a] *Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France.*
[b] *Belarusian State University, 4, Nezavisimosti Avenue, 220030 Minsk, Belarus.*

Table of contents

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all reactions were performed under an argon atmosphere with anhydrous solvents using Schlenk technics. THF, Et_2O and dioxane were distilled over sodium/benzophenone under argon. Acetonitrile, dichloromethane and toluene were distilled over CaH_2 under argon. Dimethylsulfoxide was distilled over CaH_2 under vacuum. Unless otherwise stated, all reagents were used without prior purification. 2,2,6,6-Tetramethylpiperidine (HTMP) was distilled under vacuum over CaH_2 and was stored over KOH pellets. 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 either on a (i) Bruker AV III 300 MHz spectrometer fitted with a BBFO probe at 300 MHz, 75 MHz and 282 MHz or on a (ii) Bruker AV III HD 500 MHz spectrometer fitted with a BBFO probe 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.[2] Cp refers to the unsubstituted cyclopentadienyl ring of ferrocene. Ferrocenesulfonyl chloride **1** was prepared according to Erb.[3] $ZnCl_2$·TMEDA was prepared according to Mongin.[4] Compounds **3a**, **3e**, **3f**, **3j**, **5b**, **6a**, **6b**, **19a**, **19b**, **20c**, **20d**, **27c**, **28a**, **28b**, **30b**, **31**, **32a**, **32b**, **33a**, **33b**, **35a**, **35b**, **36a**, **37a**, **38a**, **38b**, **38c**, **39b**, **40a** were already reported and fully characterized in our preliminary communication.[5]

Safety Considerations. Due to their pyrophoric character, BuLi reagents 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, the experiments should be performed by well-trained people.

Crystallography. For **3b**, **3k**, **5g**, **15**, **17**, **18**, **29b** and **34a**, the X-ray diffraction data were collected using APEXII Kappa-CCD (Bruker-AXS) diffractometer equipped with a CCD-LDI-APEX2 detector. For **5c**, **5f**, **6e**, **8a**, **10**, **11**, **36b**, the X-ray diffraction data were collected using D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 70 detector. For **6d**, **22a**, **27a**, **27b**, **38d**, the X-ray diffraction data were collected using D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector. The structure was solved by dual-space algorithm using the *SHELXT* program,[6] and then refined with full-matrix least-square methods based on F^2 (*SHELXL*).[7] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The molecular diagrams were generated by MERCURY 2020.3.0.

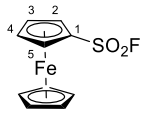
Electrochemical measurements. Measurements were performed in dry, oxygen-free dichloromethane at a concentration of 1 mM, with nBu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte. For all the experiments, the working electrode was a glassy carbon disk (diameter 1.5 mm) which was polished (5 μm grain 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.

Ferrocenesulfonyl fluoride - 2

Ferrocenesulfonyl chloride **1** (28.6 g, 100 mmol, 1.00 equiv) and KHF_2 (23.4 g, 300 mmol, 3.00 equiv) were placed in a flask under air, acetic acid (100 mL) was added and the reaction mixture was stirred at 60 °C in a pre-heated oil bath for 30 min. The reaction mixture was cooled to rt and was poured into a 1 L round-bottom flask. Cyclohexane (200 mL) was added and volatiles were removed under vacuum. The same procedure was repeated four more times. Aqueous NaOH (10%, 350 mL) and EtOAc (350 mL) were added and the solution was stirred at rt until dissolution of almost all solids. The solution was filtrated over cotton wool under vacuum to break the emulsion. The layers were separated and the aqueous layer was extracted with EtOAc (3 x 150 mL). The combined organic layers were washed with water (3 x 150 mL), brine (100 mL), dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by filtration on a pad of SiO_2 (20 cm height, 8 cm large), using PE-EtOAc (80:20) to give the title product **2** as an orange solid (17 g, 63%).

On a larger scale, ferrocenesulfonyl chloride (85.9 g, 300 mmol, 1.00 equiv) and KHF_2 (70.3 g, 900 mmol, 3.00 equiv) were placed in a flask under air. Acetic acid (300 mL) was added and the reaction mixture was stirred at 60 °C in a pre-heated oil bath for 30 min. The reaction mixture was cooled to rt and was poured into a 2 L round-bottom flask. Cyclohexane (400 mL) was added and volatiles were removed under vacuum. The same procedure was repeated five more times. Aqueous NaOH (10%, 900 mL) and EtOAc (900 mL) were added and the solution was stirred at rt until dissolution of almost all solids. The resulting emulsion was filtrated over cotton wool under vacuum. The two layers were separated and the aqueous layer was extracted with EtOAc (4 x 250 mL). The combined organic layers were washed with water (4 x 250 mL), brine (100 mL), dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by filtration on a pad of SiO_2 (25 cm height, 8 cm large), using PE-EtOAc (80:20) to give the title product **2** as an orange solid (51.9 g, 64%).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.85 (t, *J* = 1.9 Hz, 2H, FcCH, H2 and H5), 4.58 (t, *J* = 1.9 Hz, 2H, FcCH, H3 and H4), 4.44 (s, 5H, Cp). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm) 68.2. The ^{1}H NMR data are as reported previously.[5, 8]

Deprotolithiation of ferrocenesulfonyl fluoride 2 with *s*BuLi·(+)-sparteine by using chlorotrimethylsilane as electrophile (Table 2, entry 3).

*s*BuLi (1.1 M in hexane, 2.20 mL, 2.40 mmol, 1.20 equiv) was added dropwise to a solution of (+)-sparteine (0.55 mL, 562 mg, 2.40 mmol, 1.20 equiv) in Et_2O (7 mL) at -80 °C. After 30 min at this temperature, the reaction mixture was cooled to -90 °C and a solution of ferrocenesulfonyl fluoride **2** (536 mg, 2.00 mmol, 1.00 equiv) in Et_2O (7 mL) was added dropwise. After addition, the reaction mixture was stirred at the same temperature for 15 min. Chlorotrimethylsilane (0.30 mL, 2.4 mmol, 1.20 equiv) was added and the reaction mixture was warmed to 0 °C. Saturated aqueous NH_4Cl was added, and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography, eluting with EtOAc/PE (10:1) to give the title product **3a*** as an orange solid (413 mg, 61%). The er (54:46) was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 99:1, 1.0 mL·min^{-1}, 25 °C, λ = 220 nm, t (major) = 6.09 min, t (minor) = 6.65 min. Starting material was also recovered in 24% yield (130 mg). Its analyses were comparable with the ones of the racemic product.[5]

Deprotolithiation of ferrocenesulfonyl fluoride 2 with (*R*)-PEALi by using chlorotrimethylsilane as *in situ* trap (Table 2, entry 7).

*n*BuLi (1.4 M in hexane, 2.90 mL, 4.00 mmol, 2.00 equiv) was added dropwise to a solution of (*R*)-PEAH (0.91 mL, 902 mg, 4.00 mmol, 2.00 equiv) in THF (6 mL) at -15 °C. After 5 min at this temperature, the reaction mixture was cooled to -80 °C and was transferred by cannula to a solution of ferrocenesulfonyl fluoride **2** (536 mg, 2.00 mmol, 1.00 equiv) and chlorotrimethylsilane (0.51 mL, 435 mg, 4.00 mmol, 2.00 equiv) in THF (6 mL) at -80 °C. After addition, the reaction mixture was stirred at

-80 °C for 30 min. Saturated aqueous NH_4Cl was added, and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography, eluting with EtOAc/PE (10:1) to give the title product **3a*** as an orange solid (286 mg, 42%). The er (57:43) was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 99:1, 1.0 mL·min^{-1}, 25 °C, λ = 220 nm, t (major) = 6.09 min, t (minor) = 6.65 min. Its analyses were comparable with the ones of the racemic product.[5] Starting material was also recovered in 43% yield (232 mg).

Deprotolithiation of ferrocenesulfonyl fluoride 2 with (*R*)-PEALi by using [{(*R*)-PEA}$_2$Zn] as *in situ* trap (Table 2, entry 11).

*n*BuLi (1.4 M in hexane, 1.70 mL, 2.40 mmol, 2.00 equiv) was added dropwise to a solution of (*R*)-PEAH (0.55 mL, 540 mg, 2.40 mmol, 2.00 mmol) in THF (7 mL) at −15 °C. After 5 min at this temperature, $ZnCl_2$·TMEDA (0.30 g, 1.20 mmol, 1.00 mmol) was added in one portion and the reaction mixture was stirred for 15 min. Ferrocenesulfonyl fluoride **2** (0.32 g, 1.20 mmol, 1.00 equiv) was added in one portion at the same temperature and the reaction mixture was cooled to -80 °C. A cooled (-80 °C) solution of (*R*)-PEALi (prepared by adding *n*BuLi (1.70 mL, 2.40 mmol, 2.00 equiv) dropwise to a solution of (*R*)-PEAH (0.55 mL, 2.40 mmol, 2.00 equiv) in THF (7 mL) at −15 °C and stirring for 5 min) was then added at -80 °C by cannula. After addition, the reaction mixture was stirred at -80 °C for 30 min before a solution of I_2 (1.22 g, 4.80 mmol, 4.00 equiv) in THF (5 mL) was added and the reaction mixture was warmed to 0 °C. A saturated aqueous solution of $Na_2S_2O_3$ was added to the reaction mixture which was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography, eluting with EtOAc/PE (10:1) to give the title product **3f*** as an orange solid (157 mg, 33%). The er (29:71) was determined by HPLC analysis on a Daicel ODH column, hexane-isopropanol 99:1, 0.5 mL·min^{-1}, 5 °C, λ = 220 nm, t (major) = 37.27 min, t (minor) = 35.72 min. Its analyses were comparable with the ones of the racemic product. Starting material was also recovered in 22% yield (122 mg).

General procedure A: deprotometallation-electrophilic trapping from 2.

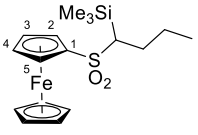
*n*BuLi (1.4 M in hexane, 1.20 equiv) was added dropwise to a solution of compound **2** (1.00 equiv) in THF (0.14 M) at -90 °C and the reaction mixture was stirred at the same temperature for 15 min. The required electrophile (1.20 equiv), neat or in solution for solids, was added to the reaction mixture which was warmed to 0 °C. Unless overwise stated, aqueous NH_4Cl was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (proportions given in the product description) to give the title product.

2-(Trimethylsilyl)ferrocenesulfonyl fluoride – 3a

By following the general procedure A, compound **2** (536 mg, 2.00 mmol, 1.00 equiv) was reacted with the *n*BuLi·TMEDA chelate (prepared by adding *n*BuLi (1.70 mL, 2.40 mmol, 1.20 equiv) dropwise to a solution of TMEDA (0.36 mL, 2.40 mmol, 1.20 equiv) in Et_2O (7 mL) at −80 °C and stirring for 30 min), before chlorotrimethylsilane (305 µL, 261 mg, 2.40 mmol, 1.20 equiv) was added as the electrophile. The title product **3a** was obtained after column chromatography (eluent PE-EtOAc 10:1) as an orange solid (465 mg, 68%). Its analyses were comparable with the ones reported previously.[5]

1-(Trimethylsilyl)butylsulfonylferrocene (**4a**) was also isolated as an orange solid (50 mg, 6%).

R_f (eluent: PE-EtOAc 10:1) = 0.49. Mp 104-105 °C. ν_{max} (film)/cm^{-1} 3103, 2958, 2871, 1461, 1408, 1301, 1280, 1248, 1181, 1115, 1067, 1012, 841, 820, 771, 732. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.66 (dt, *J* = 1.4, 2.6 Hz, 1H, FcCH, H2 or H4), 4.57 (dt, *J* = 1.4, 2.5 Hz, 1H, FcCH, H2 or H5), 4.43 (s, 5H, Cp), 4.39 (m, 2H, FcCH, H3 and H4), 2.34 (dd, *J* = 4.4, 5.6 Hz, 1H, CH), 1.73-1.66 (m, 1H, CH-C*H*H), 1.62-1.55 (m, 1H, CH-CH*H*), 1.20-1.10 (m, 1H, CH-CH$_2$-C*H*H), 1.05-0.95 (m, 1H, CH-CH$_2$-CH*H*), 0.69 (t, *J* = 7.3 Hz, 3H, CH_3), 0.24 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 90.0 (s, FcC, C1), 71.0 (s, FcCH, C3 or C4), 70.7 (s, Cp), 70.6 (s, FcCH, C2 or C5), 70.5 (s, FcCH, C3 or C4), 69.2 (s,

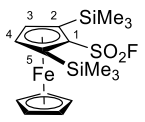


FcCH, , C2 or C5), 57.2 (s, CH), 28.9 (s, CH-*C*H2), 22.9 (s, CH-CH_2-*C*H_2), 13.9 (s, CH_3), -0.9 (s, $Si(CH_3)_3$).

By following the general procedure A, compound **2** (5.36 g, 20.0 mmol, 1.00 equiv) was reacted with *s*BuLi (1.1 M in hexane, 22.0 mL, 24.0 mmol, 1.20 equiv) before chlorotrimethylsilane (3.00 mL, 2.61 g, 24.0 mmol, 1.20 equiv) was added as the electrophile. The title product **3a** was obtained after column chromatography (eluent PE-EtOAc 10:1) as an orange solid (5.58 g, 82%). Its analyses were comparable with the ones reported previously.[5]

2,5-Bis-(trimethylsilyl)ferrocenesulfonyl fluoride (**5a**) was also isolated as an orange solid (797 mg, 10%).

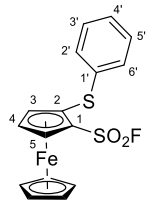
R_f (eluent: PE-EtOAc 10:1) = 0.77. Mp 140-142 °C. ν_{max} (film)/cm^{-1} 2953, 1385, 1242, 1208, 1184, 1131, 1004, 911, 892, 820, 768, 748. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.60 (s, 2H, FcCH, H3 and H4), 4.40 (s, 5H, Cp), 0.37 (s, 18H, 2 x $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 86.0 (d, J = 36.1 Hz, FcC, C1), 81.4 (s, FcCH, C3 and C4), 79.5 (s, FcC, C2 and C5), 71.5 (s, Cp), 0.55 (s, 2 x $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 71.6. Anal. Calcd for $C_{16}H_{25}FFeO_2SSi_2$: C, 46.59; H, 6.11; S, 7.77. Found: C, 46.53; H, 6.14; S, 7.63.



2-(Phenylthio)ferrocenesulfonyl fluoride – 3b

By following the general procedure A, compound **2** (536 mg, 2.00 mmol, 1.00 equiv) was reacted with diphenyldisulfide (524 mg, 2.4 mmol, 1.20 equiv) in THF (3 mL) as the electrophile. After addition of saturated NH_4Cl and extraction with EtOAc, the combined organic layers were washed three times with aqueous sodium hydroxide (10%), water, and brine before being dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. The title product **3b** was obtained after column chromatography (eluent PE-EtOAc 90:10) as a yellow solid (509 mg, 67%). Similarly, starting from 12 mmol of compound **2**, the title product **3b** was isolated in 64% yield (2.91 g).

R_f (eluent: PE-EtOAc 90:10) = 0.33. Mp 145-146 °C. ν_{max} (film)/cm^{-1} 3100, 1581, 1480, 1438, 1397, 1361, 1295, 1219, 1184, 1071, 1024, 962, 833, 751, 741. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.24-7.21 (m, 2H, ArCH, H3' and H5'), 7.18-7.14 (m, 3H, ArCH, H2', H4' and H6'), 5.03 (dd, J = 1.6, 2.7 Hz, 1H, FcCH, H5), 4.77 (dd, J = 1.6, 2.5 Hz, 1H, FcCH, H3), 4.66 (t, J = 2.7 Hz, 1H, FcCH, H4), 4.53 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 137.7 (s, ArC, C1'), 129.1 (s, ArCH, H3' and H5'), 128.5 (s, ArCH, H2' and H6'), 126.6 (ArCH, H4'), 80.8 (d, J = 37.4 Hz, FcC, C1), 80.6 (s, FcC, C2), 80.2 (s, FcCH, C3), 73.3 (s, Cp), 7.3.1 (s, FcCH, C5), 72.2 (s, FcCH, C4). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.3. Anal. Calcd for $C_{16}H_{13}FFeO_2S_2$: C, 51.08; H, 3.48; S, 17.04. Found: C, 51.16; H, 3.54; S, 17.07.



Crystal data for 3b. $C_{16}H_{13}FFeO_2S_2$, M = 376.23, T = 150(2) K; monoclinic P $2_1/n$ (I.T.#14), a = 9.4238(7), b = 14.4798(10), c = 11.2622(7) Å, β = 99.638(3) °, V = 1515.09(18) Å^3. Z = 4, d = 1.649 g.cm^{-3}, μ = 1.284 mm^{-1}. A final refinement on F^2 with 3482 unique intensities and 199 parameters converged at $\omega R(F)^2$ = 0.0664 (R_F = 0.0285) for 3013 observed reflections with $I > 2\sigma$. CCDC 2189751.

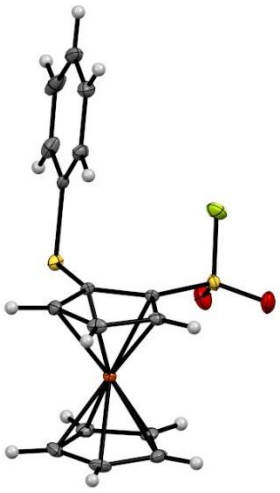
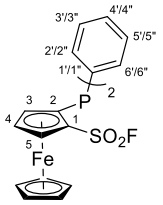


Figure 1. Molecular structure of compound **3b** (thermal ellipsoids shown at the 30% probability level).

2-(Diphenylphosphino)ferrocenesulfonyl fluoride – 3c

By following the general procedure A, compound **2** (536 mg, 2.00 mmol, 1.00 equiv) was reacted with chlorodiphenylphosphine (445 µL, 529 mg, 2.40 mmol, 1.20 equiv) as the electrophile. After warming to 0 °C, methanol (0.1 mL) was added dropwise and the reaction mixture was concentrated under vacuum to give the crude product. The title product **3c** was obtained after column chromatography (eluent PE-EtOAc 90:10 to 80:20 with 2% of NEt_3) as an orange solid (570 mg, 63%).

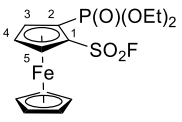
R_f (eluent: PE-EtOAc 90:10) = 0.24. Mp 187-188 °C. ν_{max} (film)/cm^{-1} 3085, 1434, 1406, 1390, 1215, 1176, 1153, 834, 747, 731. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.54-7.50 (m, 2H, ArCH, H2' and H6'), 7.43-7.40 (m, 3H, ArCH, 3', H4' and H5'), 7.30-7.27 (m, 3H, ArCH, H3", H4" and H5"), 7.21-7.18 (m, 2H, ArCH, H2" and H6"), 5.09-5.08 (m, 1H, FcCH, H5), 4.53 (t, *J* = 2.7 Hz, 1H, FcCH, H2), 4.40 (s, 5H, Cp), 3.98 (t, *J* = 1.9 Hz, 1H, FcCH, H3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 137.7 (d, *J* = 12.1 Hz, ArC, C1"), 136.5 (d, *J* = 12.6 Hz, ArC, C1'), 135.0 (d, *J* = 22.1 Hz, ArCH, C2' and C6'), 132.8 (d, *J* = 20.0 Hz, ArCH, C2" and C6"), 129.8 (s, ArCH, C4'), 128.8 (s, ArCH, C4"), 128.7 (d, *J* = 7.6 Hz, ArCH, C3" and C5"), 128.5 (d, *J* = 6.7 Hz, ArCH, C3' and C5'), 82.8 (dd, *J* = 19.8, 37.3 Hz, FcC, C1), 80.3 (d, *J* = 22.8 Hz, FcC, C2), 76.6 (d, *J* = 4.0 Hz, FcH, C3), 74.3 (s, FcCH, C5), 72.8 (s, FcCH, C4), 72.7 (Cp). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.3 (d, *J* = 7.8 Hz). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ (ppm) -21.6 (d, *J* = 7.8 Hz). Anal. Calcd for $C_{22}H_{18}FFeO_2PS$: C, 58.43; H, 4.01; S, 7.09. Found: C, 58.62; H, 4.18; S, 7.15.



2-(*O,O*-Diethoxyphosphonyl)ferrocenesulfonyl fluoride – 3d

By following the general procedure A, compound **2** (536 mg, 2.00 mmol, 1.00 equiv) was reacted with chlorodiethylphosphate (347 µL, 414 mg, 2.40 mmol, 1.20 mmol) as the electrophile. The title product **3d** was obtained after column chromatography (eluent PE-EtOAc 50:50 to 10:90) as an orange oil (433 mg, 53%).

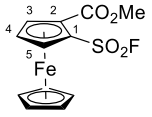
R_f (eluent: PE-EtOAc 50:50) = 0.22. ν_{max} (film)/cm^{-1} 2984, 1406, 1250, 1215, 1186, 1161, 1077, 1019, 967, 831, 750. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.09 (dd, *J* = 2.1, 3.9 Hz, 1H, FcCH, H5), 5.02 (dd, *J* = 2.4, 4.2 Hz, 1H, FcCH, H3), 4.73 (q, *J* = 2.4 Hz, 1H, FcCH, H4), 4.58 (5H, Cp), 4.32-4.25 (m, 2H, CH_2'), 4.18-4.07 (m, 2H, CH_2), 1.42 (t, *J* = 7.0 Hz, 3H, CH_3'), 1.32 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 80.4 (dd, *J* = 12.5, 37.9 Hz, FcC, C1), 79.9 (d, *J* = 13.0 Hz, FcCH, C3), 75.7 (d, *J* = 9.4 Hz, FcCH, C5), 73.5 (s, Cp), 73.0 (d, *J* = 12.6 Hz, FcCH, C4), 69.9 (d, *J* = 216.8 Hz, FcC, C2), 63.1 (d, *J* = 6.5 Hz, CH_2'), 62.9 (d, *J* = 5.7 Hz, CH_2), 16.4 (d, *J* = 7.6 Hz, CH_3 or CH_3'), 16.3 (d, *J* = 7.1 Hz, CH_3 or CH_3'). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.1. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ (ppm) 18.7. Anal. Calcd for $C_{14}H_{18}FFeO_5PS$: C, 41.60; H, 4.49; S, 7.90. Found: C, 41.54; H, 4.31; S, 7.93.



2-(Methoxycarbonyl)ferrocenesulfonyl fluoride – 3g

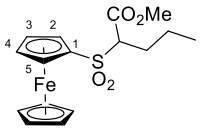
By following the general procedure A, compound **2** (536 mg, 2.00 mmol, 1.00 equiv) was reacted with methyl chloroformate (618 µL, 756 mg, 8.00 mmol, 4.00 equiv) as the electrophile. The title product **3g** was obtained after column chromatography (eluent PE-EtOAc 80:20) as an orange solid (390 mg, 60%). Similarly, starting from 10 mmol of compound **2**, the title product **3g** was isolated in 66% yield (2.17 g).

R_f (eluent: PE-EtOAc 80:20) = 0.33. Mp 82-83 °C. ν_{max} (film)/cm^{-1} 3119, 2964, 1726, 1451, 1399, 1374, 1254, 1207, 1162, 1110, 1075, 1039, 1010, 834, 798, 771, 748. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.19 (dd, *J* = 1.7, 2.6 Hz, 1H, FcCH, H3), 5.10 (dd, *J* = 1.8, 2.6 Hz, 1H, FcCH, H5), 4.71 (t, *J* = 2.7 Hz, 1H, FcCH, H4), 4.52 (s, 5H, Cp), 3.89 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 168.4 (s, C=O), 79.1 (d, *J* = 37.6 Hz, FcC, C1), 77.2 (s, FcCH, C3), 75.9 (s, FcCH, C5), 73.5 (s, Cp), 73.3 (s, FcC, C2), 72.2 (s, FcCH, C4), 52.6 (s, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 65.6. Anal. Calcd for $C_{12}H_{11}FFeO_4S$: C, 44.20; H, 3.40; S, 9.83. Found: C, 44.30; H, 3.51; S, 9.86.



On large scale, 1-(methoxycarbonyl)butylsulfonylferrocene (**4b**) was also isolated as an orange solid (219 mg, 6%).

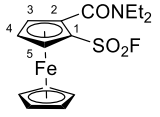
R_f (eluent: PE-EtOAc 80:20) = 0.35. Mp 64-66 °C. ν_{max} (film)/cm^{-1} 3123, 2961, 2876, 1734, 1440, 1410, 1341, 1312, 1296, 1240, 1209, 1190, 1167, 1124, 1105, 1027, 920, 842, 824, 757, 713. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.64 (dt, *J* = 1.3, 2.6 Hz, 1H, FcCH, H2 or H5), 4.61 (dt, *J* = 1.4, 2.6 Hz, 1H, FcCH, H2 or H5), 4.48-4.47 (m, 2H, FcCH, H3 and H4), 4.44 (s, 5H, Cp), 3.87-3.82 (m, 1H, CH), 3.69 (s, 3H, OCH_3), 1.94-1.86 (m, 2H, CH-CH_2), 1.37-1.24 (m, 2H, CH_2-CH_3), 0.89 (t, *J* = 7.3 Hz, 3H, CH_2-CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 167.0 (s, C=O), 84.8 (s, FcC, C1), 73.2, 71.6, 71.5 and 71.0 (s, FcCH, C2, C3, C4 and C5), 70.9 (s, Cp), 70.6 (s, CH), 52.8 (s, OCH_3), 29.2 (s, CH-*C*H_2), 20.4 (s, *C*H_2-CH_3), 13.6 (s, CH_2-*C*H_3).



2-(*N*,*N*-Diethylcarbamoyl)ferrocenesulfonyl fluoride – 3h

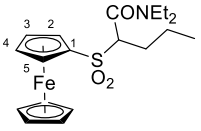
By following the general procedure A, compound **2** (1.34 g, 5.00 mmol, 1.00 equiv) was reacted with *N*,*N*-diethylcarbamoyl chloride (2.50 mL, 2.71 g, 20.0 mmol, 4.00 equiv) as the electrophile. The title product **3h** was obtained after column chromatography (eluent PE-EtOAc 75:25 to 70:30 with 2% NEt_3) as a brown solid (816 mg, 44%). Ferrocenesulfonyl fluoride **2** (525 mg, 39%) was recycled.

R_f (eluent: PE-EtOAc 70:30) = 0.32. Mp 104-105 °C. ν_{max} (film)/cm^{-1} 3111, 2972, 2935, 1641, 1477, 1407, 1379, 1279, 1233, 1200, 837, 737. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.85 (s, 1H, FcCH, H5), 4.74 (s, 1H, FcCH, H3), 4.62 (s, 5H, Cp), 4.60 (t, *J* = 2.5 Hz, 1H, FcCH, H4), 3.81 (dq, *J* = 6.8, 13.7 Hz, 1H, C*H*H-CH_3), 3.16 (dq, *J* = 6.8, 13.7 Hz, 1H, CH*H*-CH_3), 3.08 (q, *J* = 7.0 Hz, 2H, CH_2-CH_3), 1.19 (t, *J* = 6.8 Hz, CHH-CH_3), 0.98 (t, *J* = 7.0 Hz, 3H, CH_2-CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 163.6 (s, C=O), 89.5 (s, FcC, C2), 76.5 (d, *J* = 38.1 Hz, FcC, C1), 73.6 (s, Cp), 73.3 (s, FcCH, C3), 70.7 (s, FcCH, C4), 69.9 (s, FcCH, C5), 42.0 (*C*H_2-CH_3), 39.7 (*C*HH-CH_3), 14.0 (CH_2-*C*H_3), 12.5 (CHH-*C*H_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.5. Anal. Calcd for $C_{15}H_{18}FFeNO_3S$: C, 49.06; H, 4.94; N, 3.81; S, 8.73. Found: C, 49.15; H, 4.73; N, 3.76; S 8.80.



1-(*N*,*N*-Diethylcarbamoyl)butylsulfonylferrocene (**4c**) was also isolated as an orange solid (134 mg, 6%).

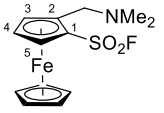
R_f (eluent: PE-EtOAc 70:30) = 0.34. Mp 91-93 °C. ν_{max} (film)/cm^{-1} 3116, 2967, 2934, 2873, 1635, 1464, 1434, 1309, 1262, 1185, 1121, 1096, 1025, 1003, 824. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.60 (s, 2H, FcCH, H2 and H5), 4.45 (s, 2H, H3 and H4), 4.41 (s, 5H, Cp), 4.07 (dd, *J* = 4.2, 10.2 Hz, 1H, CH), 3.72-3.60 (dq, *J* = 7.2, 14.6 Hz, 1H, N-C*H*H), 3.51-3.40 (dq, *J* = 7.2, 14.6 Hz, 1H, N-CH*H*), 3.33-3.14 (m, 2H, N-CH_2), 1.94-1.78 (m, 2H, CH-CH_2), 1.31-1.21 (m, 2H, CH_2-CH_3), 1.18 (t, *J* = 7.1 Hz, 3H, N-CHH-CH_3), 1.01 (t, *J* = 7.0 Hz, 3H, N-CH_2-CH_3), 0.87 (t, *J* = 7.3 Hz, 3H, CH_2-CH_3).



2-(*N*,*N*-Dimethylaminomethyl)ferrocenesulfonyl fluoride – 3i

By following the general procedure A, compound **2** (536 mg, 2.00 mmol, 1.00 equiv) was reacted with *N*,*N*-dimethylmethyleneiminium iodide (444 mg, 2.4 mmol, 1.20 equiv) as the electrophile. After warming to 0 °C, water is added instead of NH_4Cl. The title product **3i** was obtained after column chromatography (eluent PE-EtOAc 50:50 to 20:80 with 2% NEt_3) as an orange oil (487 mg, 75%). Similarly, starting from 10 mmol of compound **2**, the title product **3i** was isolated in 70% yield (2.37 g).

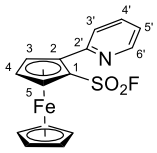
R_f (eluent: PE-EtOAc 50:50 with 2% NEt_3) = 0.22. ν_{max} (film)/cm^{-1} 2944, 2819, 2770, 1456, 1398, 1239, 1202, 1181, 1035, 1004, 831, 759, 738. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.84 (dd, *J* = 1.5, 2.3 Hz, 1H, FcCH, H5), 4.63 (dd, *J* = 1.5, 2.3 Hz, 1H, FcCH, H3), 4.54 (t, *J* = 2.6 Hz, 1H, FcCH, H4), 4.38 (s, 5H, Cp), 3.77 (d, *J* = 13.5 Hz, 1H, C*H*H), 3.37 (d, *J* = 13.5 Hz, 1H, CH*H*), 2.22 (s, 6H, $N(CH_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 86.2 (s, FcC, C2), 77.0 (d, *J* = 38.4 Hz, FcC, C1), 75.1 (s, FcCH, C3), 72.2 (s, Cp), 71.4 (s, FcCH, C5), 71.0 (s, FcCH, C4), 56.0 (s, CH_2), 45.1 (s, $N(CH_3)_2$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.3. Anal. Calcd for $C_{13}H_{16}FFeNO_2S$: C, 48.02; H, 4.96; N, 4.31; S, 9.86. Found: C, 47.81; H, 4.76; S, 9.72.



2-(2-Pyridyl)ferrocenesulfonyl fluoride – 3k

By following the general procedure A, compound **2** (536 mg, 2.00 mmol, 1.00 equiv) was reacted with $ZnCl_2$·TMEDA (606 mg, 2.4 mmol, 1.20 equiv) as the electrophile. After warming to 0 °C, 2-chloropyridine (757 µL, 908 mg, 8.00 mmol, 4.00 equiv), $PdCl_2$ (28.4 mg, 0.16 mmol, 0.08 equiv) and dppf (88.7 mg, 0.16 mmol, 0.08 equiv) were added and the reaction mixture was stirred at 80 °C for 14 h in a pre-heated oil bath. The reaction mixture was cooled to rt, water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30) to give the title product **3k** as an orange solid (292 mg, 42%).

R_f (eluent: PE-EtOAc 70:30) = 0.27. Mp 124-126 °C. ν_{max} (film)/cm^{-1} 3089, 1591, 1564, 1498, 1424, 1392, 1338, 1207, 1170, 1156, 1145, 1107, 1046, 993, 952, 826, 784, 744. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.60 (dt, *J* = 1.4, 4.7 Hz, 1H, ArCH, H6'), 7.66-7.65 (m, 2H, H3' and H4'), 7.21 (ddd, *J* = 2.9, 4.8, 5.7 Hz, 1H, H5'), 5.16 (dd, *J* = 1.6, 2.7 Hz, 1H, FcCH, H3), 5.04 (dd, *J* = 1.6, 2.7 Hz, 1H, FcCH, H5), 4.72 (t, *J* = 2.7 Hz, 1H, FcCH, H4), 4.44 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 154.3 (s, ArC, C2'), 149.5 (s, ArCH, C6'), 136.0 (s, ArCH, C4'), 123.6 (s, ArCH, C3'), 122.4 (s, ArCH, C5'), 88.3 (s, FcC, C2), 76.2 (s, FcCH, C3), 75.8 (d, *J* = 38.3 Hz, FcC, C1), 73.4 (s, FcCH, C5), 73.3 (s, Cp), 71.5 (s, FcCH, C4). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.3. Anal. Calcd for $C_{15}H_{12}FFeNO_2S$: C, 52.20; H, 3.50; N, 4.06; S, 9.29. Found: C, 52.17; H, 3.57; N, 4.05; S, 9.14.



Crystal data for 3k. $C_{15}H_{12}FFeNO_2S$, *M* = 345.17, *T* = 150(2) K; orthorhombic *P* 2_1 2_1 2_1 (I.T.#19), *a* = 6.8514(7), *b* = 9.7058(8), *c* = 20.4257(18) Å, *V* = 1358.3(2) Å^3. *Z* = 4, *d* = 1.688 g.cm^{-3}, μ = 1.278 mm^{-1}. A final refinement on F^2 with 3108 unique intensities and 167 parameters converged at $\omega R(F^2)$ = 0.1159 (R_F = 0.0522) for 2820 observed reflections with $I > 2\sigma$. CCDC 2189752.

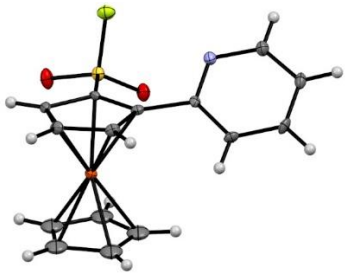


Figure 2. Molecular structure of compound **3k** (thermal ellipsoids shown at the 30% probability level).

General procedure B: deprotometallation-electrophilic trapping from 3a, 3b and 3i.

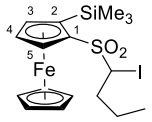
*s*BuLi (1.1 M in hexane, 1.50 equiv) or *n*BuLi (1.4 M in hexane, 1.50 equiv) was added dropwise to a solution of compound **3a**, **3b** or **3i** (1.00 equiv) in THF (0.3 M) at -90 °C and the reaction mixture was stirred at the same temperature for 15 min. The required electrophile (1.50 equiv), neat or in solution for solids, was added to the reaction mixture which was warmed to 0 °C. Unless overwise stated, aqueous NH_4Cl was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (proportions given in the product description) to give the title product.

2-Iodo-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 5b

By following the general procedure B, compound **3a** (408 mg, 1.20 mmol, 1.00 equiv) was reacted with *n*BuLi (1.30 mL, 1.80 mmol, 1.50 equiv) before the addition of iodine (457 mg, 1.80 mmol, 1.50 equiv) in THF (4 mL). The title product **5b** was obtained after column chromatography (eluent PE-EtOAc 50:3) as an orange solid (481 mg, 85%). Its analyses were comparable with the ones reported previously.[5]

2-(Trimethylsilyl)-1-(1-iodobutylsulfonyl)ferrocene **4d** was also isolated as an orange oil (39 mg, 6%) and was identified by ^{1}H NMR.

R_f (eluent: PE-EtOAc 15:1) = 0.57. ν_{max} (film)/cm^{-1} 2958, 2873, 1321, 1244, 1188, 1145, 1123, 1067, 1039, 1033, 955, 822, 755. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.88 (dd, *J* = 1.4, 2.5 Hz, 1H, FcCH, H5), 4.76 (dd, *J* = 3.0, 11.1 Hz, CH), 4.63 (t, *J* = 2.5 Hz, 1H, FcCH, H4), 4.45-4.40 (m, 6H, Cp and FcCH, Cp and H3), 1.92-1.83 (m, 1H, CH-C*H*H), 1.79-1.69 (m, 1H, CH-CH*H*), 1.68-1.58 (m, 1H, C*H*H-CH_3), 1.34-1.20 (m, 1H, CH*H*-CH_3), 0.83 (t, *J* = 7.40 Hz, 3H, CHH-C*H*$_3$), 0.34 (s, 9H, $(CH_3)_3$).

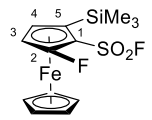


By following the general procedure B, compound **3a** (680 mg, 2.00 mmol, 1.00 equiv) was reacted with *s*BuLi (2.70 mL, 3.00 mmol, 1.50 equiv) before the addition of iodine (761 mg, 3.00 mmol, 1.50 equiv) in THF (4 mL). The title product **5b** was obtained after column chromatography (eluent PE-EtOAc 50:3) as an orange solid (845 mg, 90%). When the reaction was performed on a larger scale (compound **3a**, 6.81 g, 20.0 mmol), the title product **5b** was obtained as an orange solid (8.83 g, 95%).

2-Fluoro-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 5c

By following the general procedure B, compound **3a** (1.70 g, 5.00 mmol, 1.00 equiv) was reacted with *N*-fluorobenzenesulfonimide (2.36 g, 7.50 mmol, 1.50 equiv) in THF (5 mL) as the electrophile. The title product **5c** was obtained after column chromatography (eluent PE-EtOAc 95:5) as an orange solid (1.15 g, 63%).

R_f (eluent: PE-EtOAc 10:1) = 0.53. Mp 96-97 °C. ν_{max} (film)/cm^{-1} 2959, 1468, 1398, 1246, 1197, 1139, 1070, 1020, 921, 826, 750, 698, 682. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.85 (t, *J* = 2.9 Hz, 1H, FcCH, H3), 4.52 (s, 5H, Cp), 4.18 (t, *J* = 2.9 Hz, 1H, FcCH, H4), 0.33 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 135.5 (d, *J* = 286.7 Hz, FcC, C2), 72.8 (s, Cp), 71.3 (dd, *J* = 8.0, 38.5 Hz, FcC, C1), 70.4 (d, *J* = 3.9 Hz, FcCH, C4), 69.6 (d, *J* = 3.7 Hz, FcC, C5), 62.0 (d, *J* = 13.6 Hz, FcCH, C3), 0.2 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.9 (d, *J* = 2.1 Hz, SO_2F), -182.0 (d, *J* = 2.1 Hz, F). Anal. Calcd for $C_{13}H_{16}F_2FeO_2SSi$: C, 43.58; H, 4.50; S, 8.95. Found: C, 43.39; H, 4.51; S, 8.82.



Crystal data for 5c. $C_{13}H_{16}F_2FeO_2SSi$, *M* = 358.26, *T* = 150(2) K; monoclinic *P* 2$_1$/*n* (I.T.#14), *a* = 8.9485(5), *b* = 11.4607(6), *c* = 14.4020(5) Å, *β* = 98.087(2) °, *V* = 1462.32(12) Å^3. *Z* = 4, *d* = 1.627 g.cm^{-3}, *μ* = 1.275 mm^{-1}. A final refinement on F^2 with 3215 unique intensities and 185 parameters converged at $\omega R(F)^2$ = 0.0962 (R_F = 0.0292) for 3024 observed reflections with $I > 2\sigma$. CCDC 2189753.

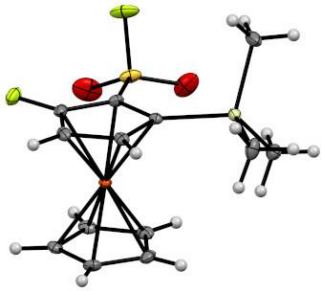
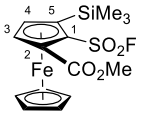


Figure 3. Molecular structure of compound **5c** (thermal ellipsoids shown at the 30% probability level).

2-Methoxycarbonyl-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 5d

By following the general procedure B, compound **3a** (2.55 g, 7.50 mmol, 1.00 equiv) was reacted with methyl chloroformate (1.90 mL, 3.54 g, 37.5 mmol, 5.00 equiv) in THF (25 mL) as the electrophile in reverse addition. The title product **5d** was obtained after column chromatography (eluent PE-EtOAc 90:10 to 80:20) as an orange solid (2.48 g, 83%).

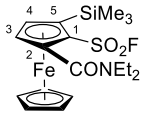
R_f (eluent: PE-EtOAc 80:20) = 0.56. Mp 107-108 °C. ν_{max} (film)/cm^{-1} 2962, 1724, 1450, 1417, 1389, 1350, 1273, 1250, 1240, 1198, 1167, 1080, 1026, 1005, 836, 795, 771, 753. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.24 (d, *J* = 2.7 Hz, 1H, FcCH, H3), 4.63 (d, *J* = 2.7 Hz, 1H, FcCH, H4), 4.49 (s, 5H, Cp), 3.88 (s, 3H, CH_3), 0.35 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 168.4 (s, C=O), 82.0 (s, FcC, C5), 81.5 (d, *J* = 37.0 Hz, FcC, C1), 79.2 (s, FcCH, C4), 78.7 (s, FcCH, C3), 77.9 (s, FcC, C2), 73.5 (s, Cp), 52.7 (s, CH_3), 0.6 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 67.6. Anal. Calcd for $C_{15}H_{19}FFeO_4SSi$: C, 45.23; H, 4.81; S, 8.05. Found: C, 45.30; H, 4.90; S, 8.04.



2-(*N*,*N*-Diethylcarbamoyl)-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 5e

By following the general procedure B, compound **3a** (2.55 g, 7.50 mmol, 1.00 equiv) was reacted with *N*,*N*-diethylcarbamoyl chloride (4.80 mL, 5.08 g, 37.5 mmol, 5.00 equiv) in THF (25 mL) as the electrophile in reverse addition. The title product **5e** was obtained after column chromatography (eluent PE-EtOAc 80:20 to 70:30) as a brown solid (3.00 g, 91%).

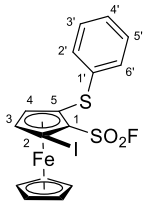
R_f (eluent: PE-EtOAc 80:20) = 0.32. Mp 92-94 °C. ν_{max} (film)/cm^{-1} 2961, 1632, 1474, 1461, 1441, 1400, 1383, 1248, 1193, 1143, 1065, 824, 760, 752, 739. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.80 (d, *J* = 2.5 Hz, 1H, FcCH, H3), 4.61 (s, 5H, Cp), 4.51 (d, *J* = 2.5 Hz, 1H, FcCH, H4), 3.84 (dq, *J* = 7.2, 14.2 Hz, 1H, C*H*H-CH_3), 3.12 (dq, *J* = 7.2, 14.2 Hz, 1H, CH*H*-CH_3), 3.01 (q, *J* = 7.2 Hz, 2H, CH_2-CH_3), 1.18 (t, *J* = 7.2 Hz, 3H, CHH-CH_3), 0.97 (t, *J* = 7.2 Hz, 3H, CH_2-CH_3), 0.36 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 164.0 (s, C=O), 93.6 (s, FcC, C2), 80.3 (d, *J* = 36.9 Hz, FcC, C1), 77.9 (s, FcCH, C4), 74.8 (s, FcC, C5), 74.5 (s, FcCH, C3), 73.5 (s, Cp), 42.8 (CH_2-CH_3), 39.5 (s, *C*HH-CH_3), 13.9 (s, CHH-CH_3), 12.4 (CH_2-CH_3), 0.4 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.5. Anal. Calcd for $C_{18}H_{26}FFeNO_3SSi$: C, 49.20; H, 5.96; N, 3.19; S, 7.30. Found: C, 49.18; H, 6.00; N, 3.24; S, 7.38.



2-Iodo-5-(phenylthio)ferrocenesulfonyl fluoride – 5f

By following the general procedure B, compound **3b** (1.20 g, 3.20 mmol, 1.00 equiv) was reacted with iodine (1.22 g, 4.80 mmol, 1.50 equiv) in THF (10 mL) as the electrophile. After warming to 0 °C, saturated aqueous $Na_2S_2O_3$ was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. The title product **5f** was obtained after column chromatography (eluent PE-EtOAc 95:5 to 90:10) as an orange solid (1.42 g, 88%).

R_f (eluent: PE-EtOAc 90:10) = 0.36. Mp 124-125 °C. ν_{max} (film)/cm^{-1} 3107, 1580, 1477, 1438, 1405, 1296, 1267, 1218, 1194, 1067, 963, 842, 761, 748, 738. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.28-7.25 (m, 2H, ArCH, H3' and H5'), 7.23-7.20 (m, 3H, ArCH, H2', H4' and H6'), 4.93 (d, J = 2.4 Hz, 1H, FcCH, H3), 4.75 (d, J = 2.4 Hz, 1H, FcCH, H4), 4.52 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.4 (s, ArC, C1'), 129.5 (s, ArCH, C2' and C6'), 129.2 (s, ArCH, C3' and C5'), 127.2 (s, ArCH, C4'), 83.3 (s, FcC, C5), 81.4 (d, J = 36.9 Hz, FcC, C1), 80.7 (s, FcCH, C3), 79.9 (s, FcCH, C4), 76.1 (s, Cp), 38.8 (s, FcC, C2). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.1. Anal. Calcd for $C_{16}H_{12}FFeIO_2S_2$: C, 38.27; H, 2.41; S, 12.77. Found: C, 38.21; H, 2.52; S, 12.95.



Crystal data for 5f. $C_{16}H_{12}FFeIO_2S_2$, M = 502.13, T = 150(2) K; monoclinic C 2/c (I.T.#15), a = 20.540(3), b = 10.7796(13), c = 15.5376(17) Å, β = 90.036(4) °, V = 3440.2(7) Å^3. Z = 8, d = 1.939 g.cm^{-3}, μ = 2.928 mm^{-1}. A final refinement on F^2 with 3935 unique intensities and 208 parameters converged at $\omega R(F)^2$ = 0.0457 (R_F = 0.0195) for 3701 observed reflections with $I > 2\sigma$. CCDC 2189754.

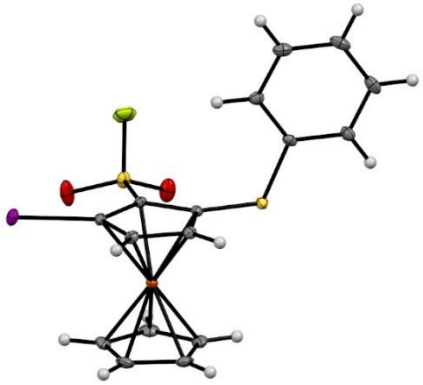
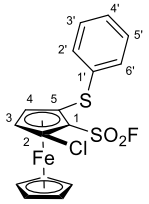


Figure 4. Molecular structure of compound **5f** (thermal ellipsoids shown at the 30% probability level).

2-Chloro-5-(phenylthio)ferrocenesulfonyl fluoride – 5g

By following the general procedure B, compound **3b** (2.44 g, 6.50 mmol, 1.00 equiv) was reacted with hexachloroethane (2.31 g, 9.75 mmol, 1.50 equiv) in THF (17 mL) as the electrophile. The title product **5g** was obtained after column chromatography (eluent PE-EtOAc 90:10 to 80:20) as a yellow solid (2.27 g, 85%).

R_f (eluent: PE-EtOAc 80:20) = 0.57. Mp 113-114 °C. ν_{max} (film)/cm^{-1} 3114, 1473, 1437, 1412, 1318, 1277, 1228, 1199, 1067, 1002, 973, 897, 852, 836, 741. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.28-7.25 (m, 2H, ArCH, H2' and H6'), 7.22-7.19 (m, 3H, ArCH, H3', H4' and H5'), 4.89 (d, J = 2.8 Hz, 1H, FcCH, H3), 4.66 (d, J = 2.8 Hz, 1H, FcCH, H4), 4.57 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.6 (s, ArC, C1'), 129.4 (s, ArCH, C2' and C6' or C3' and C5'), 129.3 (s, ArCH, C2' and C6' or C3' and C5'), 127.2 (s, ArCH, C4'), 93.8 (s, FcC, C2), 81.7 (s, FcC, C5), 78.3 (d, J = 37.0 Hz, FcC, C1), 76.1 (s, FcCH, C4), 75.5 (s, Cp), 73.1 (s, FcCH, C3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.6. Anal. Calcd for $C_{16}H_{12}ClFFeO_2S_2$: C, 46.79; H, 2.95; S, 15.61. Found: C, 46.82; H, 3.01; S, 15.64.



Crystal data for 5g. $C_{16}H_{12}ClFFeO_2S_2$, M = 410.68, T = 150(2) K; monoclinic P 2$_1$/c (I.T.#14), a = 12.426(3), b = 11.340(2), c = 11.384(2) Å, β = 99.083(7) °, V = 1584.0(6) Å^3. Z = 4, d = 1.722 g.cm^{-3}, μ = 1.399 mm^{-1}. A final refinement on F^2 with 3618 unique intensities and 208 parameters converged at $\omega R(F)^2$ = 0.0812 (R_F = 0.0311) for 3041 observed reflections with $I > 2\sigma$. CCDC 2189755.

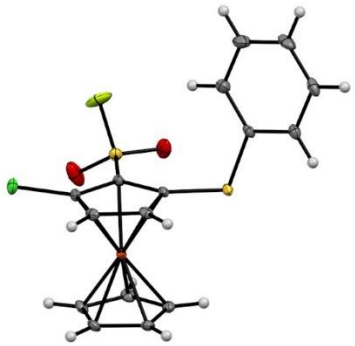
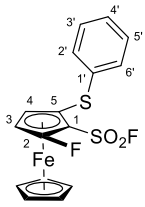


Figure 5. Molecular structure of compound **5g** (thermal ellipsoids shown at the 30% probability level).

2-Fluoro-5-(phenylthio)ferrocenesulfonyl fluoride – 5h

By following the general procedure B, compound **3b** (510 mg, 1.36 mmol, 1.00 equiv) was reacted with *N*-fluorobenzenesulfonimide (643 mg, 2.04 mmol, 1.50 equiv) in THF (4 mL) as the electrophile. An inseparable mixture of the title product **5h** (45%) and the compound **3b** (9.5%) was obtained after column chromatography (eluent PE-EtOAc 80:20) as an orange solid (293 mg). Product **5h** was identified by its ^{1}H and ^{19}F spectra.

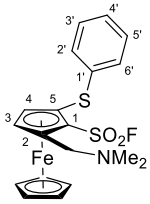


^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.25-7.18 (m, 5H, ArCH, H2', H3', H4', H5' and H6'), 4.84 (t, *J* = 2.8 Hz, 1H, FcCH, H3), 4.61 (s, 5H, Cp), 4.52 (dd, *J* = 2.1, 3.0 Hz, 1H, FcCH, H4). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm) 71.0 (d, *J* = 3.4 Hz, SO_2F), -178.9 (d, *J* = 3.4 Hz, F).

2-(*N*,*N*-Dimethylaminomethyl)-5-(phenylthio)ferrocenesulfonyl fluoride – 5i

By following the general procedure B, compound **3b** (340 mg, 1.00 mmol, 1.00 equiv) was reacted with *N*,*N*-dimethylmethyleneiminium iodide (277 mg, 1.50 mmol, 1.50 equiv) as the electrophile. The title product **5i** was obtained after column chromatography (eluent PE-EtOAc 50:50 to 20:80 with 2% NEt_3) as a yellow solid (283 mg, 65%).

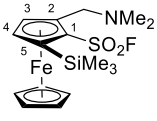
R_f (eluent: PE-EtOAc 80:20 with 2% NEt_3) = 0.18. Mp 119-120 °C. ν_{max} (film)/cm^{-1} 2948, 2857, 2814, 2767, 1579, 1478, 1439, 1398, 1361, 1249, 1200, 1023, 1003, 837, 757, 735. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.34-7.22 (m, 5H, ArCH, H2'-6'), 4.84 (d, *J* = 2.4 Hz, 1H, FcCH, H3), 4.79 (d, *J* = 2.4 Hz, 1H, FcCH, H4), 4.53 (s, 5H, Cp), 3.92 (d, *J* = 13.7 Hz, 1H, C*H*H), 3.44 (d, *J* = 13.7 Hz, 1H, CH*H*), 2.35 (s, 6H, $N(CH_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 137.5 (s, ArC, C1'), 129.1 (s, ArCH, C2' and C6' or C3' and C5'), 128.8 (s, ArCH, C2' and C6' or C3' and C5'), 126.7 (s, ArCH, C5'), 88.5 (s, FcC, C2), 82.7 (s, FcC, C5), 79.0 (d, *J* = 36.4 Hz, FcC, C1), 78.5 (s, FcCH, C4), 74.9 (s, FcCH, C3), 73.9 (s, Cp), 56.5 (s, CH_2), 45.2 (s, $N(CH_3)_2$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.9. Anal. Calcd for $C_{19}H_{20}FFeNO_2S_2$: C, 52.66; H, 4.65; N, 3.23; S, 14.80. Found: C, 52.59; H, 4.69; N, 3.19; S, 14.91.



2-(*N*,*N*-Dimethylaminomethyl)-5-(phenylthio)ferrocenesulfonyl fluoride – 5j

By following the general procedure B, compound **3i** (408 mg, 1.20 mmol, 1.00 equiv) was reacted with chlorotrimethylsilane (229 µL, 195 mg, 1.80 mmol, 1.50 equiv) as the electrophile. The title product **5j** was obtained after column chromatography (eluent PE-EtOAc 90:10 to 10:90 with 2% NEt_3) as an orange solid (95 mg, 20%).

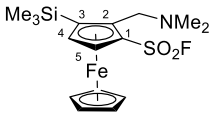
R_f (eluent: PE-EtOAc 70:30 with 2% NEt_3) = 0.23. Mp 61-63 °C. ν_{max} (film)/cm^{-1} 2952, 2814, 2762, 1463, 1403, 1393, 1246, 1194, 1174, 1009, 925, 830, 749, 731. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.76 (d, *J* = 2.5 Hz, 1H, FcCH, H3), 4.47 (d, *J* = 2.5 Hz, 1H, FcCH, H4), 4.36 (s, 5H, Cp), 3.83 (d, *J* = 13.6 Hz, 1H, C*H*H), 3.39 (d, *J* = 13.6 Hz, 1H, CH*H*), 2.24 (s, 6H, $N(CH_3)_2$), 0.34 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 89.9 (s, FcC, C2), 80.5 (d, *J* = 37.5 Hz, FcC, C1), 78.2 (s, FcCH, C4), 77.2 (s, FcC, C5), 77.0 (s, FcCH, C3), 72.1 (s, Cp), 56.6 (s, CH_2), 45.4 (s, $N(CH_3)_2$), 0.6 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz,



$CDCl_3$): δ (ppm) 69.7. Anal. Calcd for $C_{16}H_{24}FFeNO_2SSi$: C, 48.36; H, 6.09; N, 3.53; S, 8.07. Found: C, 48.46; H, 6.11; N, 3.49; S, 8.22.

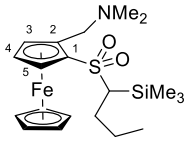
2-(*N*,*N*-Dimethylaminomethyl)-3-(trimethylsilyl)ferrocenesulfonyl fluoride (**5k**) was also isolated as a yellow solid (45 mg, 9%).

R_f (eluent: PE-EtOAc 70:30 with 2% NEt_3) = 0.89. Mp 102-104 °C. ν_{max} (film)/cm^{-1} 2948, 2819, 2767, 1394, 1425, 1228, 1189, 1177, 1129, 1108, 1028, 1005, 831, 821, 768, 732. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.92 (d, *J* = 2.6 Hz, 1H, FcCH, H5), 4.41 (d, *J* = 2.6 Hz, 1H, FcCH, H4), 4.34 (s, 5H, Cp), 3.55 (d, *J* = 13.1 Hz, 1H, C*H*H), 3.39 (d, *J* = 13.1 Hz, 1H, CH*H*), 2.08 (s, 6H, $N(CH_3)_2$), 0.30 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 91.6 (s, FcC, C2), 80.4 (s, FcC, C3), 80.0 (d, *J* = 37.9 Hz, FcC, C1), 76.8 (s, FcCH, C4), 72.7 (s, FcCH, C5), 72.3 (s, Cp), 55.7 (CH_2), 44.7 (s, $N(CH_3)_2$), -0.1 (s, $Si(CH_3)_3$). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 68.9. Anal. Calcd for $C_{16}H_{24}FFeNO_2SSi$: C, 48.36; H, 6.09; N, 3.53; S, 8.07. Found: C, 48.48; H, 6.24; N, 3.70; S, 8.19.



2-(*N*,*N*-Dimethylaminomethyl)-1-(1-(trimethylsilyl)butylsulfonyl)ferrocene (**4e**) was also isolated as an orange solid (90 mg, 17%).

R_f (eluent: PE-EtOAc 70:30 with 2% NEt_3) = 0.42. Mp 72-73 °C. ν_{max} (film)/cm^{-1} 2959, 2825, 2775, 1467, 1457, 1310, 1286, 1245, 1143, 1124, 1106, 1081, 1031, 999, 838, 824, 786, 771, 719. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.64 (t, *J* = 1.9 Hz, 1H, FcCH, H5), 4.35 (s, 5H, Cp), 4.28 (t, *J* = 2.5 Hz, 1H, FcCH, H4), 4.27 (t, *J* = 2.0 Hz, 1H, FcCH, H3), 4.12 (d, *J* = 12.4 Hz, 1H, N-C*H*H), 3.37 (t, *J* = 5.0 Hz, 1H, CH), 2.68 (d, *J* = 12.4 Hz, 1H, N-CH*H*), 2.12 (s, 6H, $N(CH_3)_2$), 1.69-1.62 (m, 1H, CH-C*H*H), 1.56-1.49 (m, 1H, CH-CH*H*), 1.09-1.01 (m, 1H, C*H*H-CH_3), 0.95-0.88 (m, 1H, CH*H*-CH_3), 0.66 (t, *J* = 7.2 Hz, 3H, CHH-C*H*$_3$), 0.26 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 89.4 (s, FcC, C1), 84.6 (s, FcC, C2), 74.0 (s, FcCH, C3), 72.4 (s, FcCH, C5), 71.0 (s, Cp), 67.8 (s, FcCH, C4), 57.0 (s, N-CH_2), 55.1 (s, CH), 45.2 (s, $N(CH_3)_2$), 29.0 (s, CH-*C*H_2), 22.5 (s, *C*H_2-CH_3), 14.0 (s, CH_2-*C*H_3), -0.5 (s, $Si(CH_3)_3$).



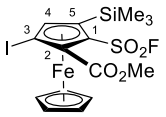
General procedure C: 'Halogen dance' reaction.

*n*BuLi (1.4 M in hexane, 1.10 equiv) was added dropwise to a solution of HTMP (1.10 equiv) in THF (0.55 M) at -15 °C. After addition, the reaction was stirred for 5 min at the same temperature before being cooled to -50 °C. After 2 min, the compound **5b** or **5f** (1.00 equiv) was added in one portion and the reaction mixture was stirred at -50 °C for 1 h. The desired electrophile (1.10 equiv) was added and the reaction mixture was warmed to 0 °C. Water was added to reaction mixture which was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (eluant given in the product description) to give the title product.

<u>3-Iodo-2-(methoxycarbonyl)-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 6c</u>

By following the general procedure C, compound **5b** (1.16 g, 2.50 mmol, 1.00 equiv) was reacted with methyl chloroformate (966 µL, 1.18 g, 12.5 mmol, 5.00 equiv) as the electrophile in THF (15 mL) in reverse addition. The title product **6c** was obtained after column chromatography (eluent PE-EtOAc 80:20) as an orange oil (18 mg, 2%).

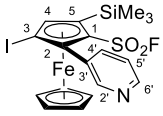
R_f (eluent: PE-EtOAc 10:1) = 0.71. ν_{max} (film)/cm^{-1} 2952, 1729, 1441, 1396, 1266, 1248, 1195, 1173, 1120, 1027, 917, 830, 801, 755. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.79 (s, 1H, FcCH, H3), 4.52 (s, 5H, Cp), 3.93 (s, 3H, CH_3), 0.35 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 166.6 (s, C=O), 86.1 (s, FcCH, H4), 85.0 (s, FcC, C5), 80.8 (s, FcC, C2), 78.9 (d, *J* = 39.2 Hz, FcC, C1), 76.4 (s, Cp), 53.2 (s, CH_3), 44.7 (s, FcC, C3), 0.4 (s, $Si(CH_3)_3$). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 66.9.



3-Iodo-2-(3-pyridyl)-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 6d

By following the general procedure C, compound **5b** (932 mg, 2.00 mmol, 1.00 equiv) was reacted with $ZnCl_2$·TMEDA (555 mg, 2.2 mmol, 1.10 equiv) as the electrophile. After warming to 0 °C, 3-iodopyridine (820 mg, 4.00 mmol, 2.00 equiv), $PdCl_2$ (28.4 mg, 0.16 mmol, 0.08 equiv) and dppf (88.7 mg, 0.16 mmol, 0.08 equiv) were added and the reaction mixture was stirred at 80 °C for 14 h in a pre-heated oil bath. The reaction mixture was cooled to rt, water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (80:20 to 50:50) to give the title product **6d** as an orange solid (298 mg, 27%).

R_f (eluent: PE-EtOAc 80:20 with 2% NEt_3) = 0.40. Mp 160-161 °C. ν_{max} (film)/cm^{-1} 3663, 2955, 2901, 1566, 1488, 1393, 1265, 1249, 1200, 1185, 1149, 1066, 980, 911, 829, 754. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.88 (br s, 1H, ArCH, H2'), 8.66 (dd, *J* = 1.6, 4.8 Hz, 1H, ArCH, H6'), 7.85 (d, *J* = 7.3 Hz, 1H, ArCH, H4'), 7.35 (dd, *J* = 5.0, 7.8 Hz, 1H, ArCH, H5'), 4.89 (s, 1H, FcCH, H4), 4.54 (s, 5H, Cp), 0.41 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 152.2 (s, ArCH, C2'), 149.7 (s, ArCH, C6'), 139.1 (s, ArCH, C4'), 129.2 (s, ArC, C3'), 122.6 (s, ArCH, C5'), 92.9 (s, FcC, C2), 85.0 (s, FcCH, C4), 80.3 (d, *J* = 37.5 Hz, FcC, C1), 78.5 (s, FcC, C5), 75.2 (s, Cp), 49.4 (s, FcC, C3), 0.5 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 71.5. Anal. Calcd for $C_{18}H_{19}FFeINO_2SSi$: C, 39.82; H, 3.53; N, 2.58; S, 5.90. Found: C, 39.70; H, 3.59; N, 2.66; S, 5.95.



Crystal data for 6d. $C_{18}H_{19}FFeINO_2SSi$, *M* = 543.24, *T* = 150(2) K; triclinic *P* $\bar{1}$ (I.T.#2), *a* = 8.2515(9), *b* = 9.8647(10), *c* = 13.6336(15) Å, *α* = 69.547(3), *β* = 75.439(4), *γ* = 81.881(3) °, *V* = 1004.65(19) Å^3. *Z* = 2, *d* = 1.796 g.cm^{-3}, *μ* = 2.472 mm^{-1}. A final refinement on F^2 with 4593 unique intensities and 238 parameters converged at $\omega R(F)^2$ = 0.0766 (R_F = 0.0330) for 4139 observed reflections with $I > 2\sigma$. CCDC 2189756.

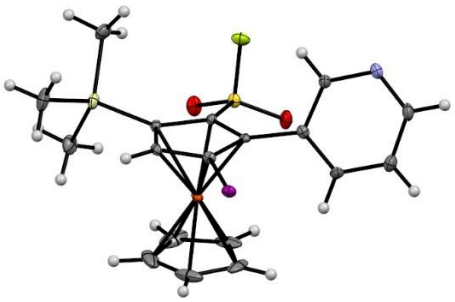
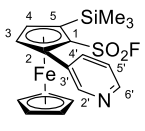


Figure 6. Molecular structure of compound **6d** (thermal ellipsoids shown at the 30% probability level).

4-Iodo-2-(trimethylsilyl)ferrocenesulfonyl fluoride (**6a**) was also isolated in 9% yield (88 mg). Its analyses were comparable with the ones reported previously.[5]

2-(3-Pyridyl)-5-(trimethylsilyl)ferrocenesulfonyl fluoride (**6d'**) was also isolated in 6% yield (49 mg) as an orange oil and was identified by ^{1}H and ^{19}F NMR spectroscopy.

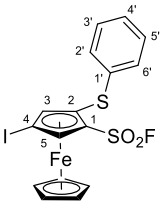
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.87 (br s, 1H, ArCH, H2'), 8.56 (d, *J* = 4.4 Hz, 1H, ArCH, H6'), 7.88 (dt, *J* = 1.6, 8.0 Hz, 1H, ArCH, H4'), 7.28 (dd, *J* = 4.7, 8.0 Hz, 1H, ArCH, H5'), 4.86 (d, *J* = 2.7 Hz, 1H, FcCH, H3 or H4), 4.64 (d, *J* = 2.7 Hz, 1H, FcCH, H3 or H4), 4.47 (s, 5H, Cp), 0.40 (s, 9H, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm) 71.9.



4-Iodo-2-(phenylthio)ferrocenesulfonyl fluoride – 6e

By following the general procedure C, compound **5f** (653 mg, 1.30 mmol, 1.00 equiv) was reacted with methanol (0.5 mL) instead of an electrophile. The title product **6e** was obtained after column chromatography (eluent PE-EtOAc 95:5) as an orange solid (247 mg, 38%).

R_f (eluent: PE-EtOAc 95:5) = 0.59. Mp 118-119 °C. ν_{max} (film)/cm^{-1} 3107, 1580, 1478, 1437, 1399, 1370, 1224, 1191, 1072, 1023, 1002, 965, 859, 834, 760, 744, 693. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.29-7.25 (m, 2H, ArCH, H3' and H5'), 7.24-7.19 (m, 3H, ArCH, H2', H4' and H6'), 5.27 (d, *J* = 1.5 Hz, 1H, FcCH, H5), 4.98 (d, *J* = 1.5 Hz, 1H, FcCH, H3), 4.53 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.5 (s, ArC, C1'), 129.5 (s, ArCH, C2' and C6' or C3' and C5'), 129.3 (s, ArCH, C2' and C6' or C3' and C5'), 127.3 (s, ArCH, C4'), 85.5 (s, FcCH, C3), 82.6 (s, FcC, C2), 81.6 (d, *J* = 37.7 Hz, FcC, C1), 78.6 (s, FcCH, C5), 76.1 (s, Cp), 38.1 (s, FcC, C4). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.3. Anal. Calcd for $C_{16}H_{12}FFeIO_2S_2$: C, 38.27; H, 2.41; S, 12.77. Found: C, 38.39; H, 2.62; S, 12.73.



Crystal data for 6e. $C_{16}H_{12}FFeIO_2S_2$, *M* = 502.13, *T* = 150(2) K; monoclinic *P* 2$_1$/*c* (I.T.#14), *a* = 7.2866(6), *b* = 18.0595(16), *c* = 12.8343(13) Å, *β* = 99.140(3) °, *V* = 1667.5(3) Å^3. *Z* = 4, *d* = 2.000 g.cm^{-3}, *μ* = 3.021 mm^{-1}. A final refinement on F^2 with 3807 unique intensities and 208 parameters converged at $\omega R(F)^2$ = 0.0518 (R_F = 0.0209) for 3643 observed reflections with $I > 2\sigma$. CCDC 2189757.

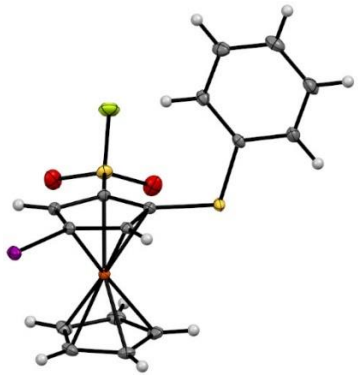
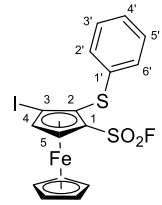


Figure 7. Molecular structure of compound **6e** (thermal ellipsoids shown at the 30% probability level).

Compounds **3b** (80 mg, 16%) and **5f** (39 mg, 6%) were also isolated and identified by their ^{1}H and ^{19}F NMR spectra. 3-Iodo-2-(phenylthio)ferrocenesulfonyl fluoride (**6f**) was also isolated as an orange solid (87 mg, 13%).

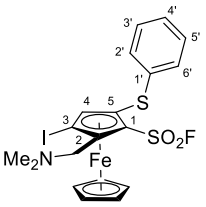
R_f (eluent: PE-EtOAc 95:5) = 0.37. Mp 169-170 °C. ν_{max} (film)/cm^{-1} 1582, 1480, 1401, 1288, 1219, 1191, 1025, 1004, 985, 873, 835, 740, 689. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.22 (t, *J* = 7.4 Hz, 2H, ArCH, H3' and H5'), 7.17-7.14 (m, 3H, ArCH, H2', H4' and H6'), 5.17 (d, *J* = 2.6 Hz, 1H, FcCH, H5), 5.03 (d, *J* = 2.6 Hz, 1H, FcCH, H4), 4.52 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.7 (s, ArC, C1'), 129.1 (s, ArCH, C3' and C5'), 128.2 (s, ArCH, C2' and C6'), 126.7 (s, ArCH, C4'), 82.8 (s, FcC, C2), 81.1 (d, *J* = 37.7 Hz, FcC, C1), 79.1 (s, FcCH, C4), 76.0 (s, Cp), 74.4 (s, FcCH, C5), 55.3 (s, FcC, C3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.0. Anal. Calcd for $C_{16}H_{12}FFeIO_2S_2$: C, 38.27; H, 2.41; S, 12.77. Found: C, 38.34; H, 2.52; S, 12.80.



2-(*N*,*N*-Dimethylaminomethyl)-3-iodo-5-(phenylthio)ferrocenesulfonyl fluoride – 6g

By following the general procedure C, compound **5f** (753 mg, 1.50 mmol, 1.00 equiv) was reacted with *N*,*N*-dimethylmethyleneiminium iodide (333 mg, 1.80 mmol, 1.20 equiv) as the electrophile. After warming to 0 °C, water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were extracted with aqueous HCl (1 M). The combined aqueous layers were washed with Et_2O, basified with K_2CO_3 until pH 12 and were extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30) to give the title product **6g** as a brown solid (100 mg, 12%).

R_f (eluent: PE-EtOAc 70:30) = 0.50. Mp 130-131 °C. ν_{max} (film)/cm^{-1} 2975, 2942, 2813, 1765, 1582, 1398, 1253, 1199, 1177, 1039, 1019, 1003, 834, 761, 737. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.29-7.27 (m, 2H, ArCH, H3' and H5'), 7.25-7.21 (m, 3H, H2', H4' and H6'), 4.97 (s, 1H, FcCH, H4), 4.42 (s, 5H, Cp), 3.92 (d, *J* = 13.0 Hz, 1H, C*H*H), 3.30 (d, *J* = 13.0 Hz, 1H, CH*H*), 2.28 (s, 6H, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.2 (s, ArC, C1'), 129.9 (s, ArCH, C2' and C6'), 129.3 (s, ArCH, C3' and C5'), 127.3 (s, ArCH, C4'), 89.4 (s, FcC, C2), 85.3 (s, FcC, C5), 84.1 (s, FcCH, C4), 78.2 (d, *J* = 36.1 Hz, FcC, C1), 76.5 (s, Cp), 56.4 (s, CH_2), 46.7 (s, FcC, C3), 45.4 (s, N(CH_3)$_2$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.2. Anal. Calcd for $C_{19}H_{19}FFeINO_2S_2$: C, 40.81; H, 3.42; N, 2.50; S, 11.47. Found: C, 40.88; H, 3.49; N, 2.64; S, 11.46.

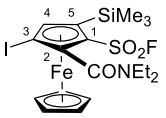


Compound **3b** (64%) and **5f** (21%) were also obtained as an inseparable mixture (522 mg) from the organic layer after extraction with aqueous HCl.

2-(*N*,*N*-Diethylcarbamoyl)-3-iodo-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 7a

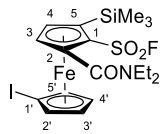
A cooled (-30 °C) solution of LiTMP (prepared by adding *n*BuLi (1.4 M in hexane, 2.15 mL, 3.00 mmol, 2.00 equiv) dropwise to a solution of HTMP (506 µL, 424 mg, 3.00 mmol, 2.00 equiv) in THF (5 mL) at −15 °C and stirring for 5 min) was added dropwise to a solution of compound **5e** (659 mg, 1.50 mmol, 1.00 equiv) and $ZnCl_2$·TMEDA (379 mg, 1.5 mmol, 1.00 equiv) in THF (20 mL) at -30 °C. The reaction mixture was stirred at the same temperature for 30 min and a solution of iodine (762 mg, 3.00 mmol, 2.00 equiv) in THF (10 mL) was added. The reaction mixture was warmed to 0 °C and a saturated aqueous solution of $Na_2S_2O_3$ was added. The reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (80:20) to give the title product **7a** as an orange solid (475 mg, 56%).

R_f (eluent: PE-EtOAc 80:20) = 0.60. Mp 157-158 °C. ν_{max} (film)/cm^{-1} 2952, 1630, 1477, 1462, 1445, 1403, 1383, 1273, 1247, 1194, 1114, 1032, 1005, 851, 835, 842, 822, 755. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.73 (s, 1H, FcCH, H4), 4.61 (s, 5H, Cp), 3.68 (dq, *J* = 7.0, 14.2 Hz, 1H, C*H*H-CH_3), 3.40 (dq, *J* = 7.0, 14.2 Hz, 1H, CH*H*-CH_3), 2.99 (dq, *J* = 1.5, 7.0 Hz, 2H, CH_2-CH_3), 1.22 (t, *J* = 7.0 Hz, 3H, CHH-CH_3), 1.06 (t, *J* = 7.0 Hz, 3H, CH_2-CH_3), 0.36 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 162.7 (s, C=O), 96.9 (s, FcC, C2), 84.3 (s, FcCH, C4), 80.7 (d, *J* = 37.0 Hz, FcC, C1), 76.3 (s, Cp), 76.1 (s, FcC, C5), 43.1 (s, *C*H_2-CH_3), 42.9 (s, FcC, C3), 39.4 (s, *C*HH-CH_3), 14.0 (s, CH_2-*C*H_3), 12.5 (s, CHH-*C*H_3), 0.4 (s, Si(CH_3)$_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.8. Anal. Calcd for $C_{18}H_{25}FFeINO_3SSi$: C, 38.25; H, 4.46; N, 2.48; S, 5.67. Found: C, 38.21; H, 4.57; N, 2.56; S, 5.73.



2-(*N*,*N*-Diethylcarbamoyl)-1'-iodo-5-(trimethylsilyl)ferrocenesulfonyl fluoride (**7b**) was also isolated as a brown oil (57 mg, 7%).

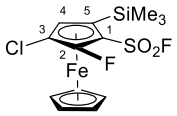
R_f (eluent: PE-EtOAc 80:20) = 0.50. ν_{max} (film)/cm^{-1} 2975, 1634, 1476, 1458, 1404, 1266, 1234, 1194, 1149, 1069, 1023, 919, 839, 824, 741. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.98 (dt, *J* = 1.3, 2.6 Hz, 1H, FcCH, H2'), 4.94 (td, *J* = 1.3, 2.6 Hz, 1H, FcCH, H3'), 4.79 (d, *J* = 2.5 Hz, 1H, FcCH, H3), 4.66 (dt, *J* = 1.3, 2.6 Hz, 1H, FcCH, H5'), 4.57 (td, *J* = 1.3, 2.6 Hz, 1H, FcCH, H4'), 4.30 (d, *J* = 2.5 Hz, 1H, FcCH, H4), 3.84 (dq, *J* = 7.1, 14.1 Hz, 1H, C*H*H-CH_3), 3.13 (dq, *J* = 7.1, 14.1 Hz, 1H, CH*H*-CH_3), 2.99 (qd, *J* = 7.1, 14.1 Hz, 2H, CH_2-CH_3), 1.18 (t, *J* = 7.1 Hz, 3H, CHH-CH_3), 0.99 (t, *J* = 7.1 Hz, 3H, CH_2-CH_3), 0.41 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 164.4 (s, C=O), 94.8 (s, FcC, C2), 84.3 (s, FcCH, C4), 80.8 (d, *J* = 37.2 Hz, FcC, C1), 80.4 (s, FcCH, C2'), 78.3 (s, FcCH, C3), 78.2 (s, FcCH, C5'), 77.1 (s, FcCH, C3'), 76.7 (s, FcC, C5), 74.9 (s, FcCH, C4'), 42.9 (s, *C*H_2-CH_3), 40.6 (s, FcC, C1'), 39.6 (s, *C*HH-CH_3), 14.0 (s, CH_2-*C*H_3), 12.4 (s, CHH-*C*H_3), 0.6 (s, Si(CH_3)$_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.5. Anal. Calcd for $C_{18}H_{25}FFeINO_3SSi$: C, 38.25; H, 4.46; N, 2.48; S, 5.67. Found: C, 38.15; H, 4.48; N, 2.41; S, 5.74.



3-Chloro-2-fluoro-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 8a

*s*BuLi (1.1 M in hexane, 4.9 mL, 5.40 mmol, 1.20 equiv) was added dropwise to a solution of compound **5c** (1.61 g, 4.50 mmol, 1.00 equiv) in THF (18 mL) at -80 °C and the reaction mixture was stirred at the same temperature for 1 h. Hexachloroethane (1.28 g, 5.40 mmol, 1.20 equiv) in THF (9 mL) was added to the reaction mixture which 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 over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (95:5) to give the title product **8a** as an orange solid (1.32 g, 75%).

R_f (eluent: PE-EtOAc 95:5) = 0.77. Mp 88-89 °C. ν_{max} (film)/cm^{-1} 2953, 1475, 1403, 1272, 1246, 1199, 1126, 1074, 1006, 951, 831, 748, 736. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.55 (s, 5H, Cp), 4.48 (s, 1H, FcCH, H4), 0.33 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 131.2 (d, J = 290.2 Hz, FcC, C2), 83.6 (d, J = 13.9 Hz, FcC, C3), 74.9 (s, Cp), 71.0 (s, FcCH, C4), 69.7 (dd, J = 6.8, 39.6 Hz, FcC, C1), 66.3 (d, J = 4.3 Hz, FcC, C5), 0.1 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.9 (d, J = 2.2 Hz, SO_2F), -186.0 (d, J = 2.2 Hz, F). Anal. Calcd for $C_{13}H_{15}ClF_2FeO_2SSi$: C, 39.76; H, 3.85; S, 8.16. Found: C, 39.84; H, 3.91; S, 8.06.



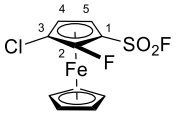
Crystal data for 8a. $C_{13}H_{15}ClF_2FeO_2SSi$, M = 392.70, T = 150(2) K; monoclinic P $2_1/n$ (I.T.#14), a = 7.1087(16), b = 13.056(3), c = 17.190(4) Å, β = 91.972(9) °, V = 1594.5(6) Å^3. Z = 4, d = 1.636 g.cm^{-3}, μ = 1.339 mm^{-1}. A final refinement on F^2 with 3631 unique intensities and 193 parameters converged at $\omega R(F)^2$ = 0.0612 (R_F = 0.0252) for 3440 observed reflections with $I > 2\sigma$. CCDC 2189758.

Figure 8. Molecular structure of compound **8a** (thermal ellipsoids shown at the 30% probability level).

3-Chloro-2-fluoroferrocenesulfonyl fluoride – 9

Tetrabutylammonium fluoride (1 M in THF, 5.3 mL, 5.30 mmol, 1.50 equiv) was added dropwise to a solution of compound **8a** (1.25 g, 3.50 mmol, 1.00 equiv) in THF (10 mL) at 0 °C. After addition, the reaction mixture was stirred at 0 °C for 5 min. Water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (90:10) to give the title product **9** as an orange solid (784 mg, 70%).

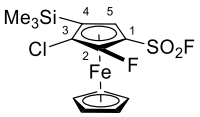
R_f (eluent: PE-EtOAc 95:5) = 0.53. Mp 93-94 °C. ν_{max} (film)/cm^{-1} 3120, 2969, 1471, 1411, 1403, 1382, 1252, 1204, 1147, 1108, 1018, 903, 805, 754. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.59 (s, 6H, Cp and FcCH, Cp and H4 or H5), 4.52 (d, J = 2.9 Hz, 1H, FcCH, H4 or H5). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 129.1 (d, J = 287.9 Hz, FcC, C2), 82.6 (d, J = 13.4 Hz, FcC, C3), 75.2 (s, Cp), 65.8 (dd, J = 10.8, 41.1 Hz, FcC, C1), 65.0 (s, FcCH, C4 or C5), 60.8 (s, FcCH, C4 or C5). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.3 (s, SO_2F), -190.7 (s, F). Anal. Calcd for $C_{10}H_7ClF_2FeO_2S$: C, 37.47; H, 2.20; S, 10.00. Found: C, 37.38; H, 2.09; S, 10.12.



3-Chloro-2-fluoro-4-(trimethylsilyl)ferrocenesulfonyl fluoride – 8b

*s*BuLi (1.1 M in hexane, 440 µL, 0.48 mmol, 1.20 equiv) was added dropwise to a solution of compound **9** (128 mg, 0.40 mmol, 1.00 equiv) in THF (1.5 mL) at -90 °C and the reaction mixture was stirred at the same temperature for 15 min. Chlorotrimethylsilane (61.0 µL, 52.1 mg, 0.48 mmol, 1.20 equiv) was added to the reaction mixture which 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 over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (1000:25 to 1000:50) to give an inseparable mixture (81 mg) of the title product **8b** (25%) and its isomer **8a** (25%). The NMR data are only described for the compound **8b**.

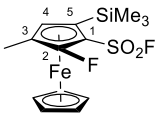
R_f (eluent: PE-EtOAc 95:5) = 0.77. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.54 (s, 5H, Cp), 4.37 (s, 1H, FcCH, C5), 0.36 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 130.4 (d, J = 290.2 Hz, FcC, C2), 87.1 (d, J = 10.9 Hz, FcC, C3), 75.0 (s, Cp), 69.8 (d, J = 3.2 Hz, FcC, C4), 67.2 (dd, J = 11.2, 40.8 Hz, FC, C1), 65.5 (s, FcCH, C5), -0.6 (s, $Si(CH_3)_3$). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 69.5 (s, SO_2F), -187.7 (s, F).



2-Fluoro-3-methyl-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 10

*s*BuLi (1.1 M in hexane, 2.2 mL, 2.40 mmol, 1.20 equiv) was added dropwise to a solution of compound **5c** (716 mg, 2.00 mmol, 1.00 equiv) in THF (8 mL) at -80 °C and the reaction mixture was stirred at the same temperature for 1 h. Iodomethane (150 µL, 340 mg, 2.40 mmol, 1.20 equiv) was added to the reaction mixture which 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 over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (95:5) to give the title product **10** as an orange solid (638 mg, 85%).

R_f (eluent: PE-EtOAc 95:5) = 0.50. Mp 125-126 °C. ν_{max} (film)/cm^{-1} 2965, 1501, 1424, 1401, 1296, 1266, 1248, 1198, 1139, 1125, 1109, 1004, 971, 839, 827, 791, 758, 745. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.42 (s, 5H, Cp), 4.15 (d, J = 2.2 Hz, 1H, FcCH, H4), 2.11 (s, 3H, CH_3), 0.31 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 134.1 (d, J = 285.5 Hz, FcC, C2), 77.5 (d, J = 6.8 Hz, FcC, C3), 73.3 (s, Cp), 72.3 (d, J = 3.4 Hz, FcCH, C4), 70.4 (dd, J = 8.2, 38.8 Hz, FcC, C1), 66.8 (d, J = 3.2 Hz, FcC, C5), 11.1 (s, CH_3), 0.2 (s, $Si(CH_3)_3$). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 71.0 (d, J = 2.3 Hz, SO_2F), -185.9 (d, J = 2.3 Hz, F). Anal. Calcd for $C_{14}H_{18}F_2FeO_2SSi$: C, 45.17; H, 4.87; S, 8.61. Found: C, 45.22; H, 4.98; S, 8.65.



Crystal data for 10. $C_{14}H_{18}F_2FeO_2SSi$, M = 372.28, T = 150(2) K; monoclinic P $2_1/n$ (I.T.#14), a = 9.6910(16), b = 11.7554(19), c = 13.9616(19) Å, β = 96.089(6) °, V = 1581.6(4) Å^3. Z = 4, d = 1.564 g.cm^{-3}, μ = 1.182 mm^{-1}. A final refinement on F^2 with 3597 unique intensities and 194 parameters converged at $\omega R(F)^2$ = 0.0643 (R_F = 0.0258) for 3337 observed reflections with $I > 2\sigma$. CCDC 2189759.

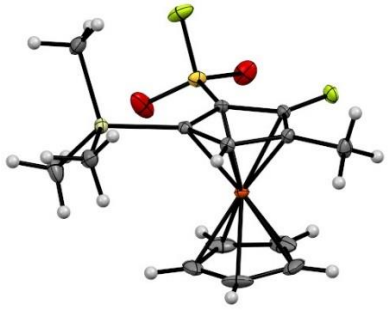


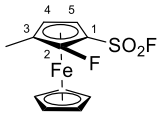
Figure 9. Molecular structure of compound **10** (thermal ellipsoids shown at the 30% probability level).

2-Fluoro-3-methylferrocenesulfonyl fluoride – 11

Tetrabutylammonium fluoride (1 M in THF, 3.0 mL, 3.00 mmol, 1.50 equiv) was added dropwise to a solution of compound **10** (750 mg, 2.00 mmol, 1.00 equiv) in THF (8 mL) at 0 °C. After addition, the reaction mixture was stirred at 0 °C for 5 min. Water was added and the reaction mixture was extracted

with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (90:10 to 80:20) to give the title product **11** as a yellow solid (537 mg, 89%).

R_f (eluent: PE-EtOAc 90:10) = 0.30. Mp 96-97 °C. ν_{max} (film)/cm^{-1} 3112, 2927, 1460, 1432, 1395, 1384, 1203, 1166, 1141, 1108, 1039, 1000, 942, 831, 815, 756, 717. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.45 (s, 5H, Cp), 4.43 (d, J = 3.0 Hz, 1H, FcCH, H5), 4.23 (t, J = 2.5 Hz, 1H, FcCH, H4), 2.11 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 131.8 (d, J = 283.3 Hz, FcC, C2), 75.9 (d, J = 12.0 Hz, FcC, C3), 73.4 (s, Cp), 66.2 (dd, J = 11.9, 40.6 Hz, FcC, C1), 65.8 (d, J = 1.5 Hz, FcCH, C4), 61.9 (s, FcCH, C5), 11.1 (d, J = 2.1 Hz, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.3 (s, SO_2F), -190.8 (s, F). Anal. Calcd for $C_{11}H_{10}F_2FeO_2S$: C, 44.03; H, 3.36; S, 10.68. Found: C, 44.18; H, 3.42; S, 10.85.



Crystal data for 11. $C_{11}H_{10}F_2FeO_2S$, M = 300.10, T = 150(2) K; orthorhombic $P\ n\ a\ 2_1$ (I.T.#33), a = 13.125(3), b = 13.589(3), c = 6.2890(14) Å, V = 1121.6(4) Å^3. Z = 4, d = 1.777 g.cm^{-3}, μ = 1.542 mm^{-1}. A final refinement on F^2 with 2156 unique intensities and 156 parameters converged at $\omega R(F^2)$ = 0.0598 (R_F = 0.0225) for 2084 observed reflections with $I > 2\sigma$. CCDC 2189760.

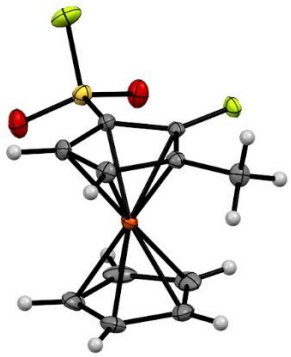
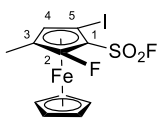


Figure 10. Molecular structure of compound **11** (thermal ellipsoids shown at the 30% probability level).

2-Fluoro-5-iodo-3-methylferrocenesulfonyl fluoride – 12

*s*BuLi (1.1 M in hexane, 2 mL, 2.25 mmol, 1.50 equiv) was added dropwise to a solution of compound **11** (450 mg, 1.50 mmol, 1.00 equiv) in THF (4 mL) at -90 °C and the reaction mixture was stirred at the same temperature for 15 min. Iodine (571 mg, 2.25 mmol, 1.50 equiv) in THF (3 mL) was added to the reaction mixture which was warmed to rt. Saturated aqueous $Na_2S_2O_3$ was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (95:5) to give the title product **12** as a yellow solid (558 mg, 87%).

R_f (eluent: PE-EtOAc 95:50) = 0.30. Mp 124-125 °C. ν_{max} (film)/cm^{-1} 3108, 2926, 1496, 1425, 1403, 1304, 1201, 1142, 1108, 1002, 953, 834, 746. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.62 (d, J = 2.0 Hz, 1H, FcCH, H4), 4.46 (s, 5H, Cp), 2.08 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 130.9 (d, J = 290.1 Hz, FcC, C2), 76.9 (d, J = 12.9 Hz, FcC, C3), 76.4 (s, Cp), 73.9 (s, FcCH, C4), 68.9 (dd, J = 9.3, 39.5 Hz, FcC, C1), 31.4 (s, FcC, C5), 10.9 (d, J = 2.2 Hz, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.1 (d, J = 2.3 Hz, SO_2F), -185.4 (d, J = 2.3 Hz, F). Anal. Calcd for $C_{11}H_9F_2FeIO_2S$: C, 31.01; H, 2.13; S, 7.53. Found: C, 31.14; H, 2.19; S, 7.54.

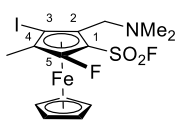


2-(*N*,*N*-Dimethylaminomethyl)-5-fluoro-3-iodo-4-methylferrocenesulfonyl fluoride – 13

*n*BuLi (1.1 M in hexane, 1.1 mL, 1.21 mmol, 1.10 equiv) was added dropwise to a solution of HTMP (204 µL, 171 mg, 1.21 mmol, 1.10 equiv) in THF (2.3 mL) at -15 °C. After addition, the reaction was stirred for 5 min at the same temperature before being cooled to -50 °C. After 2 min, the compound **12** (469 mg, 1.10 mmol, 1.00 equiv) was added in one portion and the reaction mixture was stirred at -50 °C for 1 h. *N*,*N*-dimethylmethyleneiminium iodide (224 mg, 1.21 mmol, 1.10 equiv) was added in one

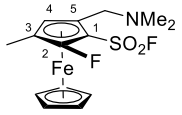
portion and the reaction mixture was warmed to 0 °C. Water was added to reaction mixture which was extracted with EtOAc. The combined organic layers were extracted with aqueous HCl (1 M). The combined aqueous layers were washed with Et_2O, basified with solid K_2CO_3 until pH 12 and were extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (80:20 to 10:90) to give the title product **13** as an orange solid (167 mg, 31%).

R_f (eluent: PE-EtOAc 90:10) = 0.39. Mp 61-62 °C. ν_{max} (film)/cm^{-1} 2943, 2819, 2770, 1481, 1428, 1401, 1378, 1327, 1203, 1176, 1148, 1125, 1019, 1005, 884, 832, 761. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.34 (s, 5H, Cp), 3.75 (d, J = 13.1 Hz, 1H, C*H*H), 3.25 (d, J = 13.1 Hz, 1H, CH*H*), 2.24 (s, 6H, $N(CH_3)_2$), 2.19 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 131.5 (d, J = 290.2 Hz, FcC, C5), 79.8 (s, FcC, C2), 78.2 (d, J = 11.8 Hz, FcC, C4), 76.7 (s, Cp), 66.1 (dd, J = 10.4, 39.1 Hz, FcC, C1), 56.3 (s, CH_2), 48.0 (s, FcC, C3), 45.3 (s, $N(CH_3)_2$), 13.0 (d, J = 2.3 Hz, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.3 (s, SO_2F), -185.6 (s, F). Anal. Calcd for $C_{14}H_{16}F_2FeINO_2S$: C, 34.81; H, 3.34; N, 2.90; S, 6.64. Found: C, 34.70; H, 3.53; N, 3.06; S, 6.72.



5-(*N*,*N*-Dimethylaminomethyl)-2-fluoro-3-methylferrocenesulfonyl fluoride (**14**) was also isolated as an orange solid (85 mg, 21%).

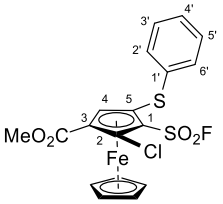
R_f (eluent: PE-EtOAc 90:10) = 0.10. Mp 91-92 °C. ν_{max} (film)/cm^{-1} 2946, 2817, 2769, 1500, 1424, 1398, 1365, 1354, 1325, 1203, 1162, 1139, 1128, 1037, 1011, 870, 836, 750. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.38 (s, 5H, Cp), 4.35 (s, 1H, FcCH, H4), 3.66 (d, J = 13.7 Hz, 1H, C*H*H), 3.17 (d, J = 13.7 Hz, 1H, CH*H*), 2.19 (s, 6H, $N(CH_3)_2$), 2.09 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 132.3 (d, J = 285.7 Hz, FcC, C2), 78.1 (s, FcC, C5), 74.7 (d, J = 12.1 Hz, FcC, C3), 74.0 (s, Cp), 68.3 (s, FcCH, C4), 65.5 (dd, J = 9.7, 39.4 Hz, FcC, C1), 55.8 (s, CH_2), 45.0 (s, $N(CH_3)_2$), 10.9 (s, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.0 (d, J = 1.6 Hz, SO_2F), -188.6 (d, J = 1.6 Hz, F). Anal. Calcd for $C_{14}H_{17}F_2FeNO_2S$: C, 47.08; H, 4.80; N, 3.92; S, 8.98. Found: C, 47.20; H, 4.12; N, 3.84; S, 9.06.



2-Chloro-3-methoxycarbonyl-5-(phenylthio)ferrocenesulfonyl fluoride – 15

*s*BuLi (1.1 M in hexane, 2.2 mL, 2.40 mmol, 1.20 equiv) was added dropwise to a solution of compound **5g** (822 mg, 2.00 mmol, 1.00 equiv) in THF (8 mL) at -80 °C and the reaction mixture was stirred at the same temperature for 1 h. Methyl chloroformate (618 µL, 756 mg, 8.00 mmol, 4.00 equiv) was added to the reaction mixture which was warmed to 0 °C. Water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (80:20) to give the title product **15** as an orange solid (637 mg, 68%).

R_f (eluent: PE-EtOAc 80:20) = 0.47. Mp 135-136 °C. ν_{max} (film)/cm^{-1} 2958, 1716, 1449, 1423, 1410, 1367, 1328, 1202, 1181, 1031, 1007, 924, 835, 764, 755, 706. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.33-7.32 (m, 4H, ArCH, H2', H3', H5' and H6'), 7.30-7.28 (m, 1H, ArCH, H4'), 5.10 (s, 1H, FcCH, H4), 4.57 (s, 5H, Cp), 3.87 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 167.2 (s, C=O), 134.7 (s, ArC, C1'), 131.1 (s, ArCH, C2' and C6' or C3' and C5'), 129.6 (s, ArCH, C2' and C6' or C3' and C5'), 128.2 (s, ArCH, C4'), 93.9 (s, FcC, C2), 85.4 (s, FcC, C3), 80.2 (d, J = 36.8 Hz, FcC, C1), 77.0 (s, Cp), 76.3 (s, FcCH, C4), 72.6 (s, FcC, C5), 52.7 (s, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.9. Anal. Calcd for $C_{18}H_{14}ClFFeO_4S_2$: C, 46.13; H, 3.01; S, 13.68. Found: C,46.16; H, 3.02; S, 13.59.



Crystal data for 15. $C_{18}H_{14}ClFFeO_4S_2$, M = 468.71, T = 150(2) K; monoclinic P 2$_1$/c (I.T.#14), a = 12.4412(13), b = 17.6060(14), c = 8.5001(7) Å, β = 97.985(4) °, V = 1843.8(3) Å^3. Z = 4, d = 1.688 g.cm^{-3}, μ = 1.221 mm^{-1}. A final refinement on F^2 with 4157 unique intensities and 245 parameters converged at $\omega R(F)^2$ = 0.0713 (R_F = 0.0329) for 3318 observed reflections with $I > 2\sigma$. CCDC 2189761.

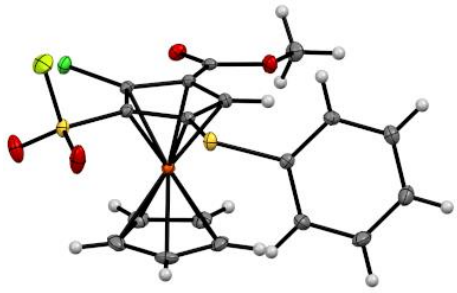
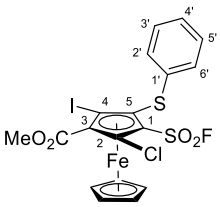


Figure 11. Molecular structure of compound **15** (thermal ellipsoids shown at the 30% probability level).

2-Chloro-4-iodo-3-methoxycarbonyl-5-(phenylthio)ferrocenesulfonyl fluoride – 16

A cooled (-50 °C) solution of LiTMP (prepared by adding *n*BuLi (1.4 M in hexane, 1.40 mL, 2.00 mmol, 2.00 equiv) dropwise to a solution of HTMP (337 µL, 282 mg, 2.00 mmol, 2.00 equiv) in THF (4 mL) at −15 °C and stirring for 5 min) was added dropwise to a solution of compound **15** (469 mg, 1.00 mmol, 1.00 equiv) and $ZnCl_2$·TMEDA (252 mg, 1.00 mmol, 1.00 equiv) in THF (4 mL) at -50 °C. The reaction mixture was stirred at the same temperature for 20 min and a solution of iodine (507 mg, 2.00 mmol, 2.00 equiv) in THF (4 mL) was added. The reaction mixture was warmed to 0 °C and a saturated aqueous solution of $Na_2S_2O_3$ was added. The reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (85:15) to give the title product **16** as a yellow solid (32 mg, 5%).

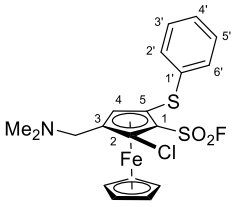


R_f (eluent: PE-EtOAc 80:20) = 0.43. Mp 80-81 °C. ν_{max} (film)/cm^{-1} 1728, 1581, 1478, 1440, 1414, 1317, 1203, 1178, 1022, 994, 937, 840, 816, 769, 741. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.24 (d, *J* = 7.2 Hz, 2H, ArCH, H2' and H6'), 7.20-7.16 (m, 3H, ArCH, H3', H4' and H5'), 4.60 (s, 5H, Cp), 4.00 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 165.6 (s, C=O), 135.8 (s, ArC, C1'), 129.3 (s, ArCH, C2' and C6'), 128.6 (s, ArCH, C3' and C5'), 127.2 (s, ArCH, C4'), 94.1 (s, FcC, C2), 84.2 (s, FcC, C3), 81.7 (d, *J* = 36.3 Hz, C1), 79.7 (s, FcC, C5), 54.7 (s, FcC, C4), 53.2 (s, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.7.

2-Chloro-3-(*N*,*N*-dimethylaminomethyl)-5-(phenylthio)ferrocenesulfonyl fluoride – 17

*s*BuLi (1.1 M in hexane, 2.7 mL, 3.00 mmol, 1.20 equiv) was added dropwise to a solution of compound **5g** (1.03 g, 2.50 mmol, 1.00 equiv) in THF (20 mL) at -80 °C and the reaction mixture was stirred at the same temperature for 1 h. *N*,*N*-Dimethylmethyleneiminium iodide (555 mg, 3.00 mmol, 3.00 equiv) was added in one portion and the reaction mixture which was warmed to 0 °C. Water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (50:50 to 30:70 with 2% NEt_3) to give an inseparable mixture (868 mg) of the title product **17** (64%) and the compound **5i** (10%) as a brown solid.

R_f (eluent: PE-EtOAc 70:30 with 2% NEt_3) = 0.40. ν_{max} (film)/cm^{-1} 2944, 2826, 2777, 1581, 1480, 1458, 1441, 1405, 1360, 1278, 1199, 1178, 1047, 1023, 842, 751, 741. ^{1}H NMR (500 MHz, $CDCl_3$, compound **17**): δ (ppm) 7.26-7.23 (m, 2H, ArCH, H2' and H6'), 7.20-7.12 (m, 3H, ArCH, H3', H4' and H5'), 4.79 (s, 1H, FcCH, H4), 4.49 (s, 5H, Cp), 3.55 (d, *J* = 13.4 Hz, 1H, C*H*H), 3.27 (d, *J* = 13.4 Hz, 1H, CH*H*), 2.25 (s, 6H, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, compound **17**): δ (ppm) 136.7 (s, ArC, C1'), 129.3 (s, ArCH, C2' and C6' or C3' and C5'), 129.2 (s, ArCH, C2' and C6' or C3' and C5'), 127.1 (s, ArCH, C4'), 94.3 (s, FcC, C2), 86.8 (s, FcC, C3), 80.8 (s, FcC, C5), 78.1 (d, *J* = 37.1 Hz, FcC, C1), 77.8 (s, FcCH, C4), 76.0 (s, Cp), 55.7 (s, CH_2), 45.3 (s, N(CH_3)$_2$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.5.



Crystal data for 17. $C_{19}H_{19}ClFFeNO_2S_2$, M = 467.77, T = 150(2) K; monoclinic $P\ 2_1/n$ (I.T.#14), a = 7.9543(7), b = 19.0071(13), c = 12.9401(9) Å, β = 95.730(4) °, V = 1946.6(3) Å^3. Z = 4, d = 1.596 g.cm^{-3}, μ = 1.150 mm^{-1}. A final refinement on F^2 with 4379 unique intensities and 246 parameters converged at $\omega R(F)^2$ = 0.0905 (R_F = 0.0341) for 3591 observed reflections with $I > 2\sigma$. CCDC 2189762.

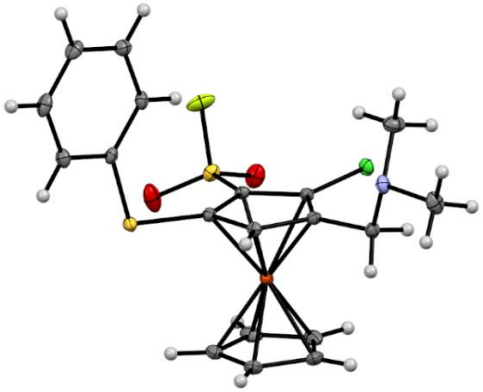
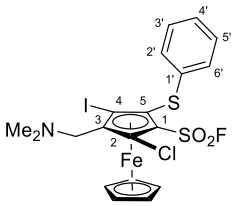


Figure 12. Molecular structure of compound **17** (thermal ellipsoids shown at the 30% probability level).

2-Chloro-3-(*N*,*N*-dimethylaminomethyl)-4-iodo-5-(phenylthio)ferrocenesulfonyl fluoride – 18

*s*BuLi (1.1 M in hexane, 0.87 mL, 0.96 mmol, 1.20 equiv) was added dropwise to a solution of a mixture of compounds **17** and **5i** (370 mg, 0.69 mmol of **17**, 0.11 mmol of **5i**, 1.00 equiv) in THF (4 mL) at -80 °C and the reaction mixture was stirred at the same temperature for 1 h. Iodine (244 mg, 0.96 mmol, 1.20 equiv) in THF (1 mL) was added and the reaction mixture was warmed to 0 °C. A saturated aqueous solution of $Na_2S_2O_3$ was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30 to 30:70) to give the title product **18** as a yellow solid (181 mg, 44%).

R_f (eluent: PE-EtOAc 60:40 with 2% NEt_3) = 0.58. Mp 153-154 °C. ν_{max} (film)/cm^{-1} 2944, 2869, 2812, 2786, 1581, 1477, 1454, 1439, 1412, 1362, 1351, 1316, 1269, 1252, 1201, 1174, 1040, 1026, 996, 837, 759, 739. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.21 (t, J = 7.2 Hz, 2H, ArCH, H3' and H5'), 7.15 (t, J = 7.2 Hz, ArCH, H4'), 7.13 (d, J = 7.8 Hz, ArCH, H2' and H6'), 4.46 (s, 5H, Cp), 3.66 (d, J = 12.8 Hz, 1H, C*H*H), 3.47 (d, J = 12.8 Hz, 1H, CH*H*), 2.34 (s, 6H, $N(CH_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.4 (s, ArC, C1'), 129.2 (s, ArCH, C3' and C5'), 128.1 (s, ArCH, C2' and C6'), 126.8 (s, ArCH, C4'), 94.6 (s, FcC, C2), 90.2 (s, FcC, C3), 82.3 (s, FcC, C5), 80.2 (d, J = 36.2 Hz, FcC, C1), 78.5 (s, Cp), 59.8 (s, FcC, C4), 57.2 (s, CH_2), 46.0 (s, $N(CH_3)_2$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 71.0. Anal. Calcd for $C_{19}H_{18}ClFFeINO_2S_2$: C, 38.44; H, 3.06; N, 2.36; S, 10.80. Found: C, 38.50; H, 3.22; N, 2.29; S, 10.76.



Crystal data for 18. $C_{19}H_{18}ClFFeINO_2S_2$, M = 593.66, T = 150(2) K; orthorhombic $P\ 2_1\ 2_1\ 2_1$ (I.T.#19), a = 11.0942(5), b = 11.5718(6), c = 16.5861(9) Å, V = 2129.32(19) Å^3. Z = 4, d = 1.852 g.cm^{-3}, μ = 2.504 mm^{-1}. A final refinement on F^2 with 4711 unique intensities and 255 parameters converged at $\omega R(F^2)$ = 0.0531 (R_F = 0.0218) for 4557 observed reflections with $I > 2\sigma$. CCDC 2189763.

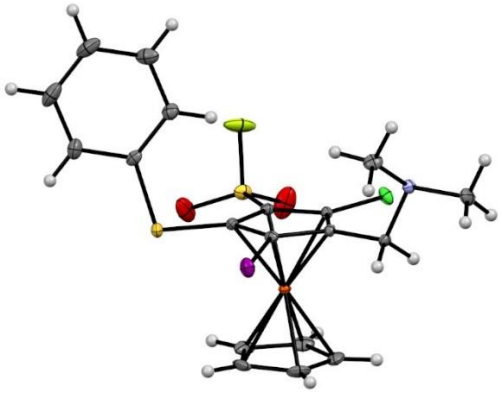
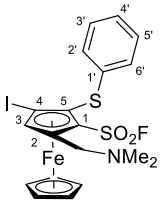


Figure 13. Molecular structure of compound **18** (thermal ellipsoids shown at the 30% probability level).

2-(*N*,*N*-Dimethylaminomethyl)-3-iodo-5-(phenylthio)ferrocenesulfonyl fluoride (**6g**) was also isolated as an orange solid (20 mg, 32%). Its NMR data were identical to the ones recorded for the compound obtained by the 'halogen dance' reaction.

5-(*N*,*N*-Dimethylaminomethyl)-3-iodo-2-(phenylthio)ferrocenesulfonyl fluoride (**6h**) was also isolated as an orange solid (35 mg, 54%).

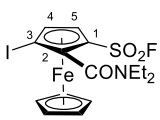
R_f (eluent: PE-EtOAc 60:40 with 2% NEt_3) = 0.28. Mp 123-124 °C. ν_{max} (film)/cm^{-1} 2821, 2773, 1581, 1480, 1456, 1441, 1402, 1256, 1195, 1179, 1034, 1003, 835, 779, 739. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.27-7.24 (m, 2H, ArCH, H3' and H5'), 7.21-7.18 (m, 3H, ArCH, H2', H4' and H6'), 4.93 (s, 1H, FcCH, H4), 4.43 (s, 5H, Cp), 3.45 (d, *J* = 13.4 Hz, 1H, C*H*H), 3.21 (d, *J* = 13.4 Hz, 1H, CH*H*), 2.27 (s, 6H, $N(CH_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.7 (s, ArC, C1'), 129.4 (s, ArCH, C2' and C6' or C3' and C5'), 129.3 (s, ArCH, C2' and C6' or C3' and C5'), 127.1 (s, ArCH, C4'), 91.5 (s, FcC, C5), 83.7 (s, FcC, C2), 81.7 (d, *J* = 36.4 Hz, FcC, C1), 79.9 (s, FcCH, C4), 76.6 (s, Cp), 59.0 (s, CH_2), 45.5 (s, $N(CH_3)_2$), 45.0 (s, FcC, C3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.9.



2-(*N*,*N*-Diethylcarbamoyl)-3-iodoferrocenesulfonyl fluoride – 19c

Tetrabutylammonium fluoride (1.0 M in THF, 0.75 mL, 0.75 mmol, 1.50 equiv) was added to a solution of compound **7a** (283 mg, 0.50 mmol, 1.00 equiv) in THF (2 mL) at 0 °C. The reaction mixture was stirred for 5 min at 0 °C. Water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (90:10 to 80:20) to give the title product **19c** as a light sensitive brown solid (162 mg, 65%).

R_f (eluent: PE-EtOAc 80:20) = 0.49. Mp 130-131 °C. ν_{max} (film)/cm^{-1} 2986, 2940, 1629, 1479, 1402, 1383, 1270, 1231, 1192, 1008, 831, 752. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.90 (d, *J* = 2.5 Hz, 1H, FcCH, H5), 4.86 (d, *J* = 2.5 Hz, 1H, FcCH, H4), 4.63 (s, 5H, Cp), 3.67 (dq, *J* = 7.1, 14.0 Hz, 1H, C*H*H-CH_3), 3.41 (dq, *J* = 7.1, 14.0 Hz, 1H, CH*H*-CH_3), 3.01 (m, 2H, CH_2-CH_3), 1.22 (t, *J* = 7.1 Hz, 3H, CHH-C*H*$_3$), 1.04 (t, *J* = 7.1 Hz, 3H, CH_2-C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 162.2 (s, C=O), 93.2 (s, FcC, C2), 77.3 (s, FcCH, C4), 76.8 (d, *J* = 38.1 Hz, FcC, C1), 76.3 (s, Cp), 70.1 (s, FcCH, C5), 43.1 (s, *C*H_2-CH_3), 41.2 (s, FcC, C3), 39.6 (s, *C*HH-CH_3), 14.0 (s, CH_2-*C*H_3), 12.5 (s, CHH-*C*H_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.0. Anal. Calcd for $C_{15}H_{17}FFeINO_3S$: C, 36.54; H, 3.48; N, 2.84; S, 6.50. Found: C, 36.42; H, 3.46; N, 2.90; S, 6.43.

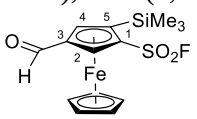


3-Formyl-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 20a

*t*BuLi (1.6 M, 1.25 mL, 2.00 mmol, 2.00 equiv) was added dropwise to a solution of compound **6a** (466 mg, 1.00 mmol, 1.00 equiv) in THF (10 mL) at –90 °C. After addition, the reaction mixture was stirred at the same temperature for 5 min. Dimethylformamide (155 µL, 146 mg, 2.00 mmol, 2.00 equiv) was added and the reaction mixture was warmed to 0 °C. Aqueous HCl (1 M) was added and the reaction

mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (90:10 to 80:20) to give the title product **20a** as a red solid (305 mg, 83%).

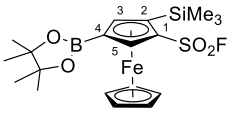
R_f (eluent: PE-EtOAc 70:30) = 0.77. Mp 72-73 °C. ν_{max} (film)/cm^{-1} 3112, 2957, 1689, 1459, 1397, 1371, 1254, 1245, 1194, 1140, 1110, 1092, 1009, 992, 828, 758, 745. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 10.00 (s, 1H, CHO), 5.61 (d, *J* = 1.4 Hz, 1H, FcCH, H2), 5.06 (d, *J* = 1.4 Hz, 1H, FcCH, H4), 4.52 (s, 5H, Cp), 0.39 (s, 9H, Si$(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 191.1 (s, C=O), 85.9 (d, *J* = 38.4 Hz, FcC, C1), 83.5 (s, FcC, C3), 80.6 (s, FcC, C5), 80.1 (s, FcCH, C4), 85.2 (s, FcCH, C2), 72.9 (s, Cp), 0.2 (s, Si$(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.2. Anal. Calcd for $C_{14}H_{17}FFeO_3SSi$: C, 45.66; H, 4.65; S, 8.71. Found: C, 45.80; H, 4.68; S, 8.90.



4-Pinacolboryl-2-(trimethylsilyl)ferrocenesulfonyl fluoride – 20b

*t*BuLi (1.6 M, 1.25 mL, 2.00 mmol, 2.00 equiv) was added dropwise to a solution of compound **6a** (466 mg, 1.00 mmol, 1.00 equiv) in THF (10 mL) at –90 °C. After addition, the reaction mixture was stirred at the same temperature for 5 min. Triisopropyl borate (461 µL, 376 mg, 2.00 mmol, 2.00 equiv) was added and the reaction mixture was warmed to 0 °C. Methanol (2 mL) was added and the reaction mixture was stirred at rt for 1 h. Volatiles were removed under vacuum. Pinacol (236 mg, 2.00 mmol, 2.00 equiv) and THF (10 mL) were added to the reaction mixture which was stirred at rt for 1 h. Volatiles were removed under vacuum, THF (10 mL) was added and the reaction mixture was stirred at rt for 14 h. Volatiles were removed under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (80:20 to 0:100) to give the title product **20b** as an orange solid (327 mg, 70%).

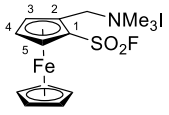
R_f (eluent: PE-EtOAc 15:1) = 0.47. Mp 144-145 °C. ν_{max} (film)/cm^{-1} 2980, 1503, 1484, 1402, 1371, 1345, 1334, 1247, 1204, 1178, 1139, 965, 838, 759, 734. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.28 (d, *J* = 1.3 Hz, 1H, FcCH, H5), 4.70 (d, *J* = 1.3 Hz, 1H, FcCH, H3), 4.39 (s, 5H, Cp), 1.36 (s, 6H, C$(CH_3)_2$), 1.35 (s, 6H, C$(CH_3)_2$), 0.35 (s, 9H, Si$(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 85.2 (d, *J* = 37.6 Hz, FcC, C1), 85.1 (s, FcCH, C3), 84.2 (s, 2 x *C*$(CH_3)_2$), 80.1 (s, FcCH, C5), 78.8 (s, FcC, C2), 71.9 (s, Cp), 25.1 (s, C(*C*$H_3)_2$), 25.0 (s, C(*C*$H_3)_2$), 0.3 (s, Si$(CH_3)_3$). Due to quadrupolar coupling, C4 is not observed. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.5. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ (ppm) 31.8. Anal. Calcd for $C_{19}H_{28}BFFeO_4SSi$: C, 48.95; H, 6.05; S, 6.88. Found: C, 48.82; H, 6.01; S, 6.86.



(2-(Fluorosulfonyl)ferrocenylmethyl)trimethylammonium iodide – 21

Iodomethane (373 µL, 852 mg, 6.00 mmol, 3.00 equiv) was added dropwise to a solution of compound **3i** (680 mg, 2.00 mmol, 1.00 equiv) in acetonitrile (12 mL). The reaction mixture was stirred at rt for 30 min and volatiles were removed under vacuum using a rotary evaporator. Et_2O was added to precipitate the product which was filtrated. The resulting solids were washed with Et_2O and dried under vacuum to afford the title product **21** as a yellow solid (933 mg, quant.).

R_f (eluent: PE-EtOAc 50:50) = 0.00. Mp 189-191 °C (decomposition). ν_{max} (film)/cm^{-1} 3463 (br), 1487, 1464, 1402, 1254, 1204, 1174, 878, 853, 820, 772, 758, 746. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 5.28 (s, 2H, FcCH, H3 and H5), 5.11 (s, 1H, FcCH, H4), 4.88 (d, *J* = 13.9 Hz, 1H, C*H*H), 4.56 (s, 5H, Cp), 4.53 (d, *J* = 13.9 Hz, 1H, CH*H*), 3.03 (s, 9H, N$(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ (ppm) 79.3 (s, FcCH, C5), 76.3 (d, *J* = 37.8 Hz, FcC, C2), 74.5 (s, FcCH, C4), 74.3 (s, FcC, C1), 73.6 (s, FcCH, C3), 73.0 (s, Cp), 62.5 (CH_2), 51.9 (s, N$(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.0. Anal. Calcd for $C_{14}H_{19}FFeINO_2S$: C, 36.00; H, 4.10; N, 3.00; S, 6.86. Found: C, 36.12; H, 4.07; N, 3.07; S, 6.88.

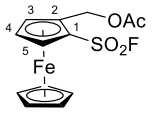


2-(Acetoxymethyl)ferrocenesulfonyl fluoride – 22a

A solution of compound **3i** (170 mg, 0.50 mmol, 1.00 equiv) in acetic anhydride (1.2 mL, 1.27 g, 12.5 mmol, 25.0 equiv) was heated at 120 °C in a pre-heated oil bath for 1 h. The reaction mixture was cooled to rt and was poured onto an ice and water mixture. K_2CO_3 was added until pH 8-9 and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over

cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30 to 60:40 with 2% NEt_3) to give the title product **22a** as an orange oil (89 mg, 52%).

R_f (eluent: PE-EtOAc 70:30) = 0.55. ν_{max} (film)/cm^{-1} 1737, 1398, 1373, 1274, 1241, 1221, 1201, 1172, 1108, 1097, 1040, 1019, 971, 950, 829, 814, 753, 736. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.18 (d, *J* = 12.4 Hz, 1H, C*H*H), 5.13 (d, *J* = 12.4 Hz, 1H, CH*H*), 4.90 (dd, *J* = 1.5, 2.5 Hz, 1H, FcCH, H5), 4.70 (dd, *J* = 1.5, 2.5 Hz, 1H, FcCH, H3), 4.58 (t, *J* = 2.8 Hz, 1H, FcCH, H4), 4.40 (s, 5H, Cp), 2.05 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 82.8 (s, FcC, C2), 77.4 (d, *J* = 38.9 Hz, FcC, C1), 75.2 (s, FcCH, C3), 72.2 (s, Cp), 72.1 (s, FcCH, C5), 71.4 (s, FcCH, C4), 59.8 (s, CH_2), 20.9 (CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.9. Anal. Calcd for $C_{13}H_{13}FFeO_4S$: C, 45.90; H, 3.85; S, 9.43. Found: C, 45.96; H, 3.88; S, 9.47.



Crystal data for 22a. $C_{13}H_{13}FFeO_4S$, *M* = 340.14, *T* = 150(2) K; monoclinic *P* $2_1/c$ (I.T.#14), *a* = 6.809(4), *b* = 7.744(2), *c* = 25.366(10) Å, *β* = 91.69(2) °, *V* = 1337.0(10) Å^3. *Z* = 4, *d* = 1.690 g.cm^{-3}, *μ* = 1.305 mm^{-1}. A final refinement on F^2 with 3047 unique intensities and 162 parameters converged at $\omega R(F)^2$ = 0.1485 (R_F = 0.0651) for 2787 observed reflections with $I > 2\sigma$. CCDC 2189764.

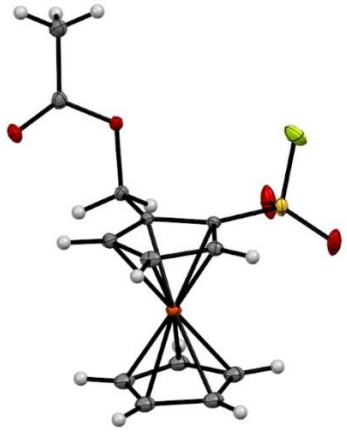
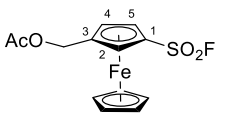


Figure 14. Molecular structure of compound **22a** (thermal ellipsoids shown at the 30% probability level).

3-(Acetoxymethyl)ferrocenesulfonyl fluoride – 22b

A solution of compound **20c** (460 mg, 1.40 mmol, 1.00 equiv) in acetic anhydride (3.3 mL, 3.57 g, 35.0 mmol, 25.0 equiv) was heated at 120 °C in a pre-heated oil bath for 1 h. The reaction mixture was cooled to rt and was poured onto an ice and water mixture. K_2CO_3 was added until pH 8-9 and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (90:10 to 80:20 with 2% NEt_3) to give the title product **22b** as an orange oil (287 mg, 60%).

R_f (eluent: PE-EtOAc 80:20) = 0.62. ν_{max} (film)/cm^{-1} 3113, 1737, 1400, 1223, 1197, 1095, 1024, 939, 911, 831, 731. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.98 (t, *J* = 1.3 Hz, 1H, FcCH, H2), 4.88-4.89 (m, 3H, CH_2 and FcCH, CH_2 and H5), 4.68 (dd, *J* = 1.3, 2.3 Hz, 1H, FcCH, H4), 4.45 (s, 5H, Cp), 2.09 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 170.6 (s, C=O), 86.5 (s, FcC, C3), 78.2 (d, *J* = 39.6 Hz, FcC, C1), 73.3 (s, FcCH, C4), 72.2 (s, Cp), 70.6 (s, FcCH, C2), 70.3 (s, FcCH, C5), 61.1 (s, CH_2), 20.9 (s, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.1. Anal. Calcd for $C_{13}H_{13}FFeO_4S$: C, 45.90; H, 3.85; S, 9.43. Found: C, 45.88; H, 3.90; S, 9.56.

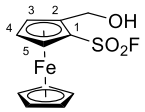


2-(Hydromethyl)ferrocenesulfonyl fluoride – 23

Diisobutylaluminium hydride (1 M in CH_2Cl_2, 1.3 mL, 1.3 mmol, 2.2 equiv) was added dropwise to a solution of compound **3g** (163 mg, 0.5 mmol, 1.00 equiv) in THF (2 mL) at 0 °C. After addition, the reaction mixture was stirred at the same temperature for 10 min. Aqueous HCl (1 M) was added and the reaction mixture was stirred at 0 °C for 10 min. The reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under

vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30 to 50:50 with 2% NEt_3) to give the title product **23** as a brown solid (74 mg, 49%). This compound should not be stored and used right away.

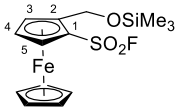
R_f (eluent: PE-EtOAc 70:30) = 0.35. ν_{max} (film)/cm^{-1} 3269 (br), 2969, 1399, 1252, 1201, 1167, 982, 834, 750. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.87 (dd, *J* = 1.4, 2.5 Hz, 1H, FcCH, H5), 4.72 (d, *J* = 13.0 Hz, 1H, C*H*H), 4.678 (dd, *J* = 1.5, 2.3 Hz, 1H, FcCH, H3), 4.55 (t, *J* = 2.7 Hz, 1H, FcCH, H4), 4.55 (d, *J* = 13.0 Hz, 1H, CH*H*), 4.44 (s, 5H, Cp), 2.10 (br s, 1H, OH). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm) 69.9



2-(Trimethylsilyloxy)methylferrocenesulfonyl fluoride – 24a

Diisobutylaluminium hydride (1 M in CH_2Cl_2, 3.9 mL, 3.9 mmol, 2.6 equiv) was added dropwise to a solution of compound **3g** (489 mg, 1.5 mmol, 1.00 equiv) in CH_2Cl_2 (6 mL) at 0 °C. After addition, the reaction mixture was stirred at the same temperature for 10 min. Aqueous HCl (1 M) was added and the reaction mixture was stirred at 0 °C for 10 min. Layers were separated and the aqueous one was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and filtrated over cotton wool. Triethylamine (627 µL, 455 mg, 4.5 mmol, 3.00 equiv) and chlorotrimethylsilane (571 µL, 489 mg, 4.5 mmol, 3.00 equiv) were successively added to the filtrate and the reaction mixture was stirred at rt for 1 h. Volatiles were removed under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30 with 2% NEt_3) to give the title product **24a** as an orange oil (381 mg, 68%). Unstable over long period storage at 0 °C.

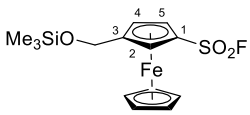
R_f (eluent: PE-EtOAc 70:30) = 0.75. ν_{max} (film)/cm^{-1} 2958, 1399, 1250, 1202, 1169, 1100, 1064, 1015, 870, 834, 747. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.83 (dd, *J* = 1.7, 2.5 Hz, 1H, FcCH, H5), 4.74 (d, *J* = 12.3 Hz, 1H, C*H*H), 4.68 (dd, *J* = 1.7, 2.5 Hz, 1H, FcCH, H3), 4.59 (d, *J* = 12.3 Hz, 1H, CH*H*), 4.51 (t, *J* = 2.6 Hz, 1H, FcCH, H4), 4.39 (s, 5H, Cp), 0.15 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 89.1 (s, FcC, C2), 76.2 (d, *J* = 39.1 Hz, FcC, C1), 73.7 (s, FcCH, C3), 72.0 (s, Cp), 71.5 (s, FcCH, C5), 70.7 (s, FcCH, C4), 58.3 (s, CH_2), - 0.3 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.5.



3-(Trimethylsilyloxy)methylferrocenesulfonyl fluoride – 24b

Diisobutylaluminium hydride (1 M in CH_2Cl_2, 3.9 mL, 3.9 mmol, 2.6 equiv) was added dropwise to a solution of compound **20d** (489 mg, 1.5 mmol, 1.00 equiv) in CH_2Cl_2 (6 mL) at 0 °C. After addition, the reaction mixture was stirred at the same temperature for 10 min. Aqueous HCl (1 M) was added and the reaction mixture was stirred at 0 °C for 10 min. Layers were separated and the aqueous one was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and filtrated over cotton wool. Triethylamine (627 µL, 455 mg, 4.5 mmol, 3.00 equiv) and chlorotrimethylsilane (571 µL, 489 mg, 4.5 mmol, 3.00 equiv) were successively added to the filtrate and the reaction mixture was stirred at rt for 1 h. Volatiles were removed under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30 with 2% NEt_3) to give the title product **24b** as an orange oil (390 mg, 70%). Unstable over long period storage at 0 °C.

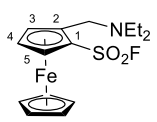
R_f (eluent: PE-EtOAc 70:30) = 0.75. R_f of the intermediate alcohol (eluent: PE-EtOAc 70:30) = 0.22. ν_{max} (film)/cm^{-1} 2957, 1400, 1251, 1197, 1107, 1071, 1037, 1004, 910, 870, 830, 743. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.91 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 4.83 (dd, *J* = 1.1, 2.5 Hz, 1H, FcCH, H5), 4.63 (dd, *J* = 1.3, 2.5 Hz, 1H, FcCH, H4), 4.44 (s, 5H, Cp), 4.41 (s, 2H, CH_2), 0.19 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 92.7 (s, FcC, C3), 72.2 (s, Cp), 72.1 (s, FcCH, C4), 71.9 (d, *J* = 35.8 Hz, FcC, C1), 69.7 (s, FcCH, C5), 69.3 (s, FcCH, C2), 59.7 (s, CH_2), -0.3 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.2.



2-(*N*,*N*-Diethylaminomethyl)ferrocenesulfonyl fluoride – 25

A solution of BH_3·THF (1 M in THF, 5 mL, 5.00 mmol, 5.00 equiv) was added dropwise to a solution of compound **3h** (367 mg, 1.00 mmol, 1.00 equiv) in THF (5 mL) at rt. After addition, the reaction mixture was stirred at rt for 15 min and was heated at 80 °C for 14 h. **Remark**: the use of PTFE sleeve is strongly recommended to avoid blockage of the ground glass joints. The reaction mixture was cooled to 0 °C and a aqueous solution of NaOH (10%) was added dropwise. **Caution**: as a vigorous evolution of gas was noticed, the first drops of NaOH solution should be added slowly. After addition, the reaction mixture was stirred at 80 °C for 1 h. The reaction mixture was cooled to rt and the layers were separated. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with water, brine, dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PET/EtOAc (70:30 with 2% NEt_3) to give the title product **25** as an orange oil (221 mg, 62%). Compound **3h** was also recovered (28 mg, 7%).

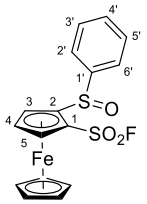
R_f (eluent: PE-EtOAc 70:30 with 2% NEt_3) = 0.25. ν_{max} (film)/cm^{-1} 2970, 2935, 2807, 1453, 1398, 1263, 1233, 1201, 1177, 1108, 1057, 1037, 1003, 829, 755. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.82 (s, 1H, FcCH, H5), 4.72 (s, 1H, FcCH, H3), 4.51 (t, *J* = 2.3 Hz, 1H, FcCH, H4), 4.38 (s, 5H, Cp), 3.84 (d, *J* = 14.0 Hz, 1H, C*H*H), 3.59 (d, *J* = 14.0 Hz, 1H, CH*H*), 2.59-2.47 (m, 4H, C*H*$_2$-CH$_3$), 1.02 (t, *J* = 7.1 Hz, 6H, CH$_2$-C*H*$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 87.2 (s, FcC, C2), 76.7 (d, *J* = 38.7 Hz, FcC, C1), 75.3 (s, FcCH, C3), 72.2 (s, Cp), 71.3 (s, FcCH, C5), 70.7 (s, FcCH, C4), 50.3 (s, CHH), 46.4 (s, *C*H$_2$-CH$_3$), 11.7 (s, CH$_2$-*C*H$_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 67.7. Anal. Calcd for $C_{15}H_{20}FFeNO_2S$: C, 51.00; H, 5.71; N, 3.97; S, 9.08. Found: C, 51.02; H, 5.90; N, 4.07; S, 9.01.



2-(Phenylsulfinyl)ferrocenesulfonyl fluoride – 26

A solution of *m*CPBA (183 mg, 0.75 mmol, 1.00 equiv) in CH_2Cl_2 (2.5 mL) was added dropwise to a solution of compound **3b** (282. mg, 0.75 mmol, 1.00 equiv) in CH_2Cl_2 (2.5 mL) at 0 °C. After addition, the reaction mixture was stirred at 0 °C for 30 min and a saturated aqueous solution of $Na_2S_2O_3$ was added dropwise. Layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with NaOH (5%), dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PET/EtOAc (70:30 to 50:50) to give the title product **26** as a light sensitive orange solid (243 mg, 82%).

R_f (eluent: PE-EtOAc 70:30) = 0.22. Mp 115-116 °C. ν_{max} (film)/cm^{-1} 3100, 1445, 1410, 1360, 1220, 1179, 1082, 1070, 1043, 1023, 817, 749. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.69-7.67 (m, 2H, ArCH, C2' and C6'), 7.43-7.42 (m, 3H, H3', H4' and H5'), 5.23 (dd, *J* = 1.8, 2.5 Hz, 1H, FcCH, H3), 4.95 (dd, *J* = 1.8, 2.5 Hz, 1H, FcCH, H5), 4.74 (t, *J* = 2.7 Hz, 1H, FcCH, H4), 4.68 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 146.2 (s, ArC, C1'), 131.7 (s, ArCH, C4'), 129.5 (s, ArCH, C3' and C5'), 124.5 (s, ArCH, C2' and C6'), 96.4 (s, FcC, C2), 77.6 (d, *J* = 39.8 Hz, FcC, C1), 73.8 (s, Cp), 73.4 (FcCH, C5), 72.5 (FcCH, C4), 69.0 (FcCH, C3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.6. Anal. Calcd for $C_{16}H_{13}FFeO_3S_2$: C, 48.99; H, 3.34; S, 16.35. Found: C, 48.88; H, 3.41; S, 16.49.



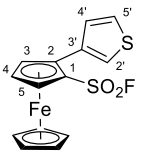
General procedure D for the Suzuki-Miyaura cross-coupling of iodinated ferrocenesulfonyl fluoride.

Compound **3f**, **6a** or **19a** (0.50 mmol, 1.00 equiv), the required boronic acid (2.00 mmol, 4.00 equiv), $Pd(dba)_2$ (14.4 mg, 25.0 µmol, 0.05 equiv), SPhos (41 mg, 0.10 mmol, 0.20 equiv) and CsF (152 mg, 1.00 mmol, 2.00 equiv) were placed in a dried Schlenk tube, subjected to three cycles of vacuum/argon. Toluene (5 mL) was added and the reaction mixture was stirred overnight at 110 °C in a pre-heated oil bath. The reaction mixture was cooled to rt and water was added. The reaction mixture was extracted with EtOAc and the combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (proportions given in the product description) to give the title product.

2-(3-Thienyl)ferrocenesulfonyl fluoride – 27a

By following the general procedure D, compound **3f** (197 mg, 0.50 mmol) was reacted with 3-thienylboronic acid (256 mg, 2.00 mmol). The title product **27a** was obtained after column chromatography (eluent PE-EtOAc 90:10) as an orange solid (136 mg, 77%).

R_f (eluent: PE-EtOAc 90:10) = 0.36. Mp 99-101 °C. ν_{max} (film)/cm^{-1} 3119, 1454, 1402, 1357, 1312, 1254, 1207, 1193, 1164, 1114, 1030, 1005, 848, 835, 797, 756. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.49 (dd, *J* = 1.5, 2.7 Hz, 1H, ArCH, H2'), 7.34-7.31 (m, 2H, H4' and H5'), 4.98 (dd, *J* = 1.6, 2.8 Hz, 1H, FcCH, H5), 4.81 (dd, *J* = 1.6, 2.8 Hz, 1H, FcCH, H3), 4.63 (t, *J* = 2.6 Hz, 1H, FcCH, H4), 4.41 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 133.8 (s, ArC, C3'), 128.7 (s, ArCH, C4' or C5'), 125.5 (s, ArCH, C4' or C5'), 123.9 (s, ArCH, C2'), 83.9 (s, FcC, C2), 76.2 (d, *J* = 37.6 Hz, FcC, C1), 74.4 (s, FcCH, C3), 72.9 (s, Cp), 72.3 (s, FcCH, C5), 70.7 (s, FcCH, C4). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.1. Anal. Calcd for $C_{14}H_{11}FFeO_2S_2$: C, 48.02; H, 3.17; S, 18.31. Found: C, 47.97; H, 3.17; S, 18.34.



Crystal data for 27a. $C_{14}H_{11}FFeO_2S_2$, *M* = 350.20, *T* = 150(2) K; monoclinic *P* 2$_1$/*c* (I.T.#14), *a* = 7.9750(11), *b* = 21.685(4), *c* = 7.7176(12) Å, *β* = 93.869(5) °, *V* = 1331.7(4) Å^3. *Z* = 4, *d* = 1.747 g.cm^{-3}, *μ* = 1.453 mm^{-1}. A final refinement on F^2 with 3038 unique intensities and 181 parameters converged at $\omega R(F)^2$ = 0.0723 (R_F = 0.0299) for 2676 observed reflections with $I > 2\sigma$. CCDC 2189765.

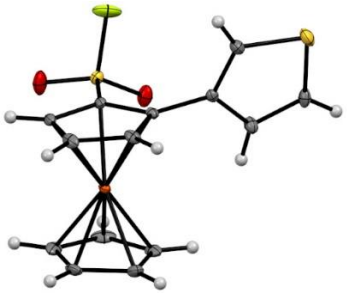
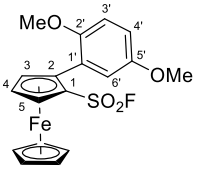


Figure 15. Molecular structure of compound **27a** (thermal ellipsoids shown at the 30% probability level).

2-(2,5-Dimethoxyphenyl)ferrocenesulfonyl fluoride – 27b

By following the general procedure D, compound **3f** (197 mg, 0.50 mmol) was reacted with 2,5-dimethoxyphenylboronic acid (364 mg, 2.00 mmol). The title product **27b** was obtained after column chromatography (eluent PE-EtOAc 90:10 to 70:30) as an orange solid (133 mg, 66%).

R_f (eluent: PE-EtOAc 90:10) = 0.21. Mp 108-110 °C. ν_{max} (film)/cm^{-1} 2961, 1833, 1507, 1466, 1430, 13891, 1301, 1272, 1239, 1216, 1201, 1163, 1140, 1051, 1035, 1005, 978, 863, 836, 812, 743. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.31 (d, *J* = 3.1 Hz, 1H, ArCH, H6'), 6.86 (dd, *J* = 3.1, 8.8 Hz, 1H, ArCH, H4'), 6.80 (d, *J* = 8.8 Hz, 1H, ArCH, H3'), 4.98 (dd, *J* = 1.5, 2.2 Hz, 1H, FcCH, H5), 4.70 (dd, *J* = 1.5, 2.2 Hz, 1H, FcCH, H3), 4.66 (t, *J* = 2.7 Hz, 1H, FcCH, H4), 4.47 (s, 5H, Cp), 3.84 (s, 3H, 5'-OCH_3), 3.72 (s, 3H, 2'-OCH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 152.9 (s, ArC, C5'), 151.7 (s, ArCH, C2'), 123.3 (s, ArC, C1'), 118.8 (s, ArCH, C6'), 113.6 (s, ArCH, C4'), 111.2 (s, ArCH, C3'), 87.6 (s, FcC, C2), 76.8 (d, *J* = 36.4 Hz, FcC, C1), 76.3 (s, FcCH, C3), 73.0 (s, Cp), 71.3 (s, FcCH, C5), 70.3 (s, FcCH, C4), 55.9 (s, 5'-OCH_3), 55.5 (s, 2'-OCH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 64.2. Anal. Calcd for $C_{18}H_{17}FFeO_4S$: C, 53.48; H, 4.24; S, 7.93. Found: C, 53.47; H, 4.31; S, 7.94.



Crystal data for 27b. $C_{18}H_{17}FFeO_4S$, *M* = 404.22, *T* = 150(2) K; monoclinic *P* 2$_1$/*c* (I.T.#14), *a* = 7.9976(8), *b* = 7.6106(7), *c* = 27.200(3) Å, *β* = 94.676(4) °, *V* = 1650.0(3) Å^3. *Z* = 4, *d* = 1.627 g.cm^{-3}, *μ* = 1.072 mm^{-1}. A final refinement on F^2 with 3776 unique intensities and 228 parameters converged at $\omega R(F)^2$ = 0.0726 (R_F = 0.0295) for 3506 observed reflections with $I > 2\sigma$. CCDC 2189766.

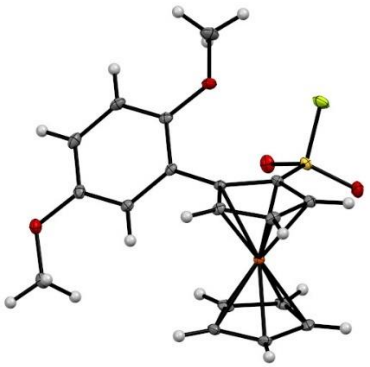
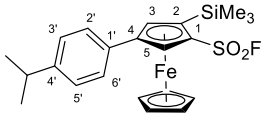


Figure 16. Molecular structure of compound **27b** (thermal ellipsoids shown at the 30% probability level).

4-(4-Isopropylphenyl)-2-(trimethylsilyl)ferrocenesulfonyl fluoride – 29a

By following the general procedure D, compound **6a** (233 mg, 0.50 mmol) was reacted with 4-isopropylphenylboronic acid (328 mg, 2.00 mmol). The title product **29a** was obtained after column chromatography (eluent PE-EtOAc 95:5) as an orange oil (151 mg, 66%).

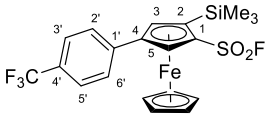
R_f (eluent: PE-EtOAc 95:5) = 0.59. ν_{max} (film)/cm^{-1} 2959, 1459, 1398, 1309, 1248, 1199, 1151, 1003, 990, 825, 747. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.43 (d, J = 8.1 Hz, 2H, ArCH, H2' and H6'), 7.22 (d, J = 8.1 Hz, 2H, ArCH, H3' and H5'), 5.43 (d, J = 1.5 Hz, 1H, FcCH, H5), 4.89 (d, J = 1.5 Hz, 1H, FcCH, H3), 4.30 (s, 5H, Cp), 2.92 (sept, J = 6.9 Hz, 1H, C*H*$(CH_3)_2$), 1.28 (d, J = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 0.40 (s, 9H, Si$(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 148.7 (s, ArC, C4'), 132.6 (s, ArC, C1'), 127.0 (s, ArCH, C3' and C5'), 126.5 (s, ArCH, C2' and C6'), 92.0 (s, FcC, C4), 82.2 (d, J = 38.0 Hz, FcC, C1), 77.5 (s, FcCH, C3), 75.7 (FcC, C2), 73.0 (s, Cp), 71.6 (s, FcCH, C5), 34.0 (s, *C*H$(CH_3)_2$), 24.0 (s, CH(*C*H$_3)_2$), 0.4 (s, Si$(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.9. Anal. Calcd for $C_{22}H_{27}FFeO_2SSi$: C, 57.64; H, 5.94; S, 6.99. Found: C, 57.72; H, 5.90; S, 7.09.



4-(4-(Trifluoromethyl)phenyl)-2-(trimethylsilyl)ferrocenesulfonyl fluoride – 29b

By following the general procedure D, compound **6a** (233 mg, 0.50 mmol) was reacted with 4-(trifluoromethyl)phenylboronic acid (380 mg, 2.00 mmol). The title product **29b** was obtained after column chromatography (eluent PE-EtOAc 15:1) as an orange solid (131 mg, 54%).

R_f (eluent: PE-EtOAc 15:1) = 0.53. Mp 129-130 °C. ν_{max} (film)/cm^{-1} 2970, 2908, 1617, 1395, 1321, 1248, 1203, 1150, 1121, 1107, 1066, 839, 828, 749. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.62 (s, 4H, ArCH, H2', H3', H5' and H6'), 5.50 (d, J = 1.50 Hz, 1H, FcCH, H5), 4.95 (d, J = 1.50 Hz, 1H, FcCH, H3), 4.31 (s, 5H, Cp), 0.41 (s, 9H, Si$(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 139.8 (s, ArC, C1'), 129.7 (q, J = 32.6 Hz, ArC, C4'), 126.6 (s, ArCH, C2' and C6'), 126.0 (q, J = 3.7 Hz, ArCH, C3' and C5'), 124.2 (q, J = 272.3 Hz, Cq, F_3C), 89.2 (s, Fc, C4), 83.1 (d, J = 38.5 Hz, FcC, C1), 77.8 (s, FcCH, C3), 77.2 (s, FcC, C2), 73.2 (s, Cp), 72.1 (s, FcCH, C5), 0.4 (s, Si$(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.8 (s, SO_2F), -62.6 (s, CF_3). Anal. Calcd for $C_{20}H_{20}F_4FeO_2SSi$: C, 49.60; H, 4.16; S, 6.62. Found: C, 49.84; H, 4.24; S, 6.76.



Crystal data for 29b. $C_{20}H_{20}F_4FeO_2SSi$, M = 484.36, T = 150(2) K; triclinic $P\,\bar{1}$ (I.T.#2), a = 8.9209(7), b = 9.9176(8), c = 12.6295(10) Å, α = 88.185(3), β = 75.906(3), γ = 76.235(3) °, V = 1052.21(15) Å^3. Z = 2, d = 1.529 g.cm^{-3}, μ = 0.921 mm^{-1}. A final refinement on F^2 with 4724 unique intensities and 239 parameters converged at $\omega R(F)^2$ = 0.1324 (R_F = 0.0492) for 3882 observed reflections with $I > 2\sigma$. CCDC 2189767.

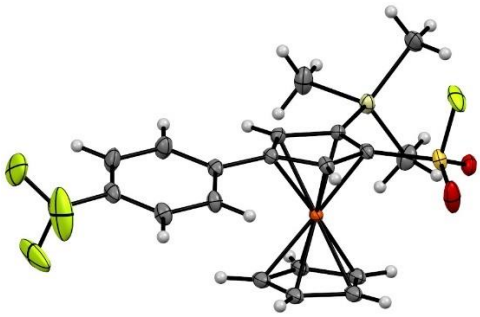
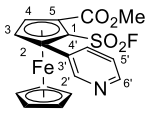


Figure 17. Molecular structure of compound **29b** (thermal ellipsoids shown at the 30% probability level).

2-Methoxycarbonyl-5-(3-pyridyl)ferrocenesulfonyl fluoride – 30a

*n*BuLi (1.4 M in hexane, 1.10 mL, 1.50 mmol, 1.50 equiv) was added dropwise to a solution of HTMP (253 µL, 212 mg, 1.50 mmol, 1.50 equiv) in THF (3 mL) at -15 °C. After addition, the reaction was stirred for 5 min at the same temperature before being cooled to -50 °C. After 2 min, this LiTMP solution was cannulated onto a solution of compound **3g** (326 mg, 1.00 mmol, 1.00 equiv) and $ZnCl_2$·TMEDA (253 mg, 1.00 mmol, 1.00 equiv) in THF (3 mL) at -50 °C. After addition, the reaction mixture was warmed to 0 °C. 3-Iodopyridine (307 mg, 1.50 mmol, 1.50 equiv), $PdCl_2$ (14.2 mg, 0.08 mmol, 0.08 equiv) and dppf (44.4 mg, 0.08 mmol, 0.08 equiv) were added and the reaction mixture was stirred at 80 °C for 14 h in a pre-heated oil bath. The reaction mixture was cooled to rt, water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (60:40) with 2% of NEt_3 to give the title product **30a** as an orange solid (147 mg, 36%).

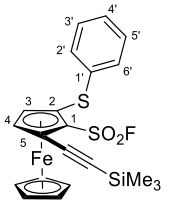
R_f (eluent: PE-EtOAc 60:40 with 2% of NEt_3) = 0.16. Mp 129-130 °C. ν_{max} (film)/cm^{-1} 3070, 1717, 1448, 1416, 1386, 1281, 1236, 1204, 1158, 1099, 1023, 1011, 834, 814, 800, 748, 714. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.76 (d, *J* = 1.7 Hz, 1H, ArCH, H2'), 8.58 (dd, *J* = 0.9, 4.6 Hz, 1H, ArCH, H6'), 7.87 (dt, *J* = 1.7, 7.9 Hz, 1H, ArCH, H4'), 7.30 (dd, *J* = 4.8, 7.8 Hz, 1H, ArCH, H5'), 5.17 (d, *J* = 2.7 Hz, 1H, FcCH, H3), 4.90 (d, *J* = 2.7 Hz, 1H, FcCH, H4), 4.55 (s, 5H, Cp), 3.84 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 167.3 (s, C=O), 150.2 (s, ArCH, C2'), 149.4 (s, ArCH, C6'), 136.9 (s, ArCH, C4'), 130.5 (s, ArC, C3'), 123.0 (s, ArCH, C5'), 92.4 (s, FcC, C5), 77.7 (d, *J* = 39.5 Hz, FcC, C1), 76.1 (s, FcC, C2), 75.0 (s, Cp), 73.3 (s, FcCH, C4), 72.2 (s, FcCH, C3), 53.0 (s, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 65.4. Anal. Calcd for $C_{17}H_{14}FFeNO_4S$: C, 50.64; H, 3.50; N, 3.47; S, 7.95. Found: C, 50.61; H, 3.52; N, 3.57; S, 8.09.



2-(Phenylthio)-5-(trimethylsilylethynyl)ferrocenesulfonyl fluoride – 32c

Compound **5f** (502 mg, 1.00 mmol, 1.00 equiv), Pd(P*t*Bu$_3$)$_2$ (15.3 mg, 0.03 mmol, 0.03 equiv) and CuI (5.71 mg, 0.03 mmol, 0.03 equiv) were placed in a dried Schlenk tube which was subjected to three cycles of vacuum/argon. THF (1.12 mL), diisopropylamine (0.38 mL) and trimethylsilylacetylene (277 µL, 196 mg, 2.00 mmol, 2.00 equiv) were added and the reaction mixture was stirred at rt for 14 h. It was filtrated over Celite® which was washed with EtOAc until colorless. The combined filtrates were washed with aqueous HCl (1 M), water, brine, dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (95:5) to give the title product **32c** as an orange solid (364 mg, 77%).

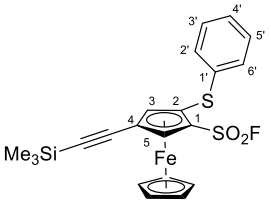
R_f (eluent: PE-EtOAc 95:5) = 0.50. Mp 113-114 °C. ν_{max} (film)/cm^{-1} 2955, 2160, 1581, 1480, 1406, 1292, 1248, 1200, 1074, 1005, 832, 736. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.26-7.22 (m, 2H, ArCH, H3' and H5'), 7.19-7.16 (m, 3H, ArCH, H2', H4' and H6'), 4.86 (d, *J* = 2.7 Hz, 1H, FcCH, H3), 4.69 (d, *J* = 2.7 Hz, 1H, FcCH, H4), 4.53 (s, 5H, Cp), 0.24 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 137.0 (s, ArC, C1'), 129.2 (s, ArCH, C2' and C6' or C3' and C5'), 129.1 (s, ArCH, C2' and C6' or C3' and C5'), 127.0 (s, ArCH, C4'), 98.6 (s, C≡*C*-Si), 97.8 (s, *C*≡C-Si), 83.0 (s, FcC, C2), 82.0 (d, *J* = 35.1 Hz, FcC, C1), 78.5 (s, FcCH, C4), 75.8 (s, FcCH, C3), 75.3 (s, Cp), 69.7 (s, FcC, C5), -0.1 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.9. Anal. Calcd for $C_{21}H_{21}FFeO_2S_2Si$: C, 53.39; H, 4.48; S, 13.57. Found: C, 53.48; H, 4.60; S, 13.62.



2-(Phenylthio)-4-(trimethylsilylethynyl)ferrocenesulfonyl fluoride – 32d

Compound **6e** (100 mg, 0.20 mmol, 1.00 equiv), Pd(P*t*Bu$_3$)$_2$ (3.00 mg, 6.00 µmol, 0.03 equiv) and CuI (1.15 mg, 6.00 µmol, 0.03 equiv) were placed in a dried Schlenk tube which was subjected to three cycles of vacuum/argon. THF (0.75 mL), diisopropylamine (0.15 mL) and trimethylsilylacetylene (55.5 µL, 39.3 mg, 0.40 mmol, 2.00 equiv) were added and the reaction mixture was stirred at rt for 14 h. It was filtrated over Celite® which was washed with EtOAc until colorless. The combined filtrates were washed with aqueous HCl (1 M), water, brine, dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (95:5) to give the title product **32d** as an orange oil (69 mg, 73%).

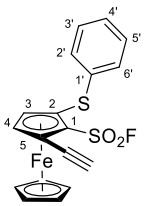
R_f (eluent: PE-EtOAc 95:5) = 0.60. ν_{max} (film)/cm^{-1} 2959, 2159, 1582, 1407, 1315, 1269, 1249, 1201, 952, 839, 757, 735. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.26-7.23 (m, 2H, ArCH, H3' and H5'), 7.22-7.18 (m, 3H, ArCH, H2', H4' and H6'), 5.24 (d, *J* = 1.6 Hz, 1H, FcCH, H5), 4.94 (d, *J* = 1.6 Hz, 1H, FcCH, H3), 4.54 (s, 5H, Cp), 0.22 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.8 (s, ArC, C1'), 129.3 (s, ArCH, C2' and C6' or C3' and C5'), 129.2 (s, ArCH, C2' and C6' or C3' and C5'), 127.1 (s, ArCH, C4'), 98.8 (s, *C*≡C-Si), 95.4 (s, C≡*C*-Si), 82.2 (s, FcCH, C3), 81.7 (s, FcC, C2), 80.6 (d, *J* = 37.9 Hz, FcC, C1), 75.2 (s, Cp and FcCH, Cp and C5), 70.1 (s, FcC, C4), -0.0 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.1. Anal. Calcd for $C_{21}H_{21}FFeO_2S_2Si$: C, 53.39; H, 4.48; S, 13.57. Found: C, 53.27; H, 4.42; S, 13.70.



2-Ethynyl-5-(phenylthio)ferrocenesulfonyl fluoride – 33c

Tetrabutylammonium fluoride (1.0 M in THF, 0.80 mL, 0.80 mmol, 2.00 equiv) was added to a solution of compound **32c** (189 mg, 0.40 mmol, 1.00 equiv) in THF (2 mL) at 0 °C. The reaction mixture was stirred for 5 min at 0 °C. Water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (95:5 to 90:10) to give the title product **33c** as a brown solid (145 mg, 90%).

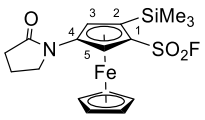
R_f (eluent: PE-EtOAc 95:5) = 0.21. Mp 99-100 °C. ν_{max} (film)/cm^{-1} 3308, 3282, 1581, 1478, 1427, 1406, 1396, 1293, 1249, 1197, 1073, 998, 827, 772, 731. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.27-7.24 (m, 2H, ArCH, H3' and H5'), 7.22-7.18 (m, 3H, ArCH, H2', H4' and H6'), 4.91 (d, *J* = 2.7 Hz, 4H, FcCH, H3), 4.72 (d, *J* = 2.7 Hz, 1H, FcCH, H4), 4.56 (s, 5H, Cp), 3.07 (s, 1H, Fc-C≡CH). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.6 (s, ArC, C1'), 129.4 (s, ArCH, C2' and C6' or C3' and C5'), 129.3 (s, ArCH, C2' and C6' or C3' and C5'), 127.2 (s, ArCH, C4'), 83.6 (s, FcC, C5), 81.4 (d, *J* = 36.1 Hz, FcC, C1), 80.1 (s, Fc-C≡*C*H), 78.5 (s, FcCH, C4), 77.0 (s, Fc-*C*≡CH), 76.4 (s, FcCH, C3), 75.3 (s, Cp), 68.6 (FcC, C2). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.9. Anal. Calcd for $C_{18}H_{13}FFeO_2S_2$: C, 54.01; H, 3.27; S, 16.02. Found: C, 54.11; H, 3.34; S, 16.11.



4-(2-Oxo-*N*-pyrrolidyl)-2-trimethylsilylferrocenesulfonyl fluoride – 34a

The compound **6a** (465 mg, 1.00 mmol, 1.00 equiv), CuI (190 mg, 1.00 mmol, 1.00 equiv) and K_3PO_4 (424 mg, 2.00 mmol, 2.00 equiv) were introduced in a degassed (argon) Schlenk tube then subjected to three vacuum/argon cycles. Dioxane (2 mL), pyrrolidinone (83.5 µL, 93.6 mg, 1.10 mmol, 1.10 equiv) and *N*,*N*'-dimethylethylenediamine (108 µL, 88.2 mg, 1.00 mmol, 1.00 equiv) were next introduced under argon, and the mixture was heated at 90 °C for 14 h in a pre-heated oil bath. The reaction mixture was cooled to rt before addition of water and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30) to give the title product **34a** as an orange solid (186 mg, 44%). The compounds **6a** (65 mg, 14%) and **3a** (96 mg, 28%) were also isolated.

R_f (eluent: PE-EtOAc 70:30) = 0.26. Mp 153-154 °C. ν_{max} (film)/cm^{-1} 2963, 1698, 1503, 1389, 1371, 1303, 1239, 1193, 1157, 1090, 986, 845, 830, 761, 729. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.47 (s, 1H, FcCH, H5), 5.13 (s, 1H, FcCH, H3), 4.40 (s, 5H, Cp), 3.73-3.63 (m, 2H, CH_2-CH_2-CH_2-N), 2.51 (t, J = 8.1 Hz, 2H, CH_2-CH_2-CH_2-N), 2.18 (quint, J = 7.6 Hz, 2H, CH_2-CH_2-CH_2-N), 0.35 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 174.2 (s, C=O), 100.9 (s, FcC, C4), 78.8 (d, J = 38.2 Hz, FcC, C1), 72.2 (s, Cp), 72.0 (s, FcC, C2), 70.6 (s, FcCH, C3), 64.6 (s, FcCH, C5), 48.3 (s, CH_2-CH_2-CH_2-N), 32.1 (s, CH_2-CH_2-CH_2-N), 18.3 (s, CH_2-CH_2-CH_2-N), 0.3 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 70.1. Anal. Calcd for $C_{17}H_{22}FFeNO_3SSi$: C, 48.23; H, 5.24; N, 3.31; S, 7.57. Found: C, 48.24; H, 5.27; N, 3.37; S, 7.59.



Crystal data for 34a. $C_{17}H_{22}FFeNO_3SSi$, M = 423.35, T = 150(2) K; monoclinic P $2_1/c$ (I.T.#14), a = 6.8130(4), b = 18.7277(9), c = 29.0696(15) Å, β = 94.188(2) °, V = 3699.1(3) Å^3. Z = 8, d = 1.520 g.cm^{-3}, μ = 1.019 mm^{-1}. A final refinement on F^2 with 8464 unique intensities and 458 parameters converged at $\omega R(F)^2$ = 0.1223 (R_F = 0.0632) for 7123 observed reflections with $I > 2\sigma$. CCDC 2189768.

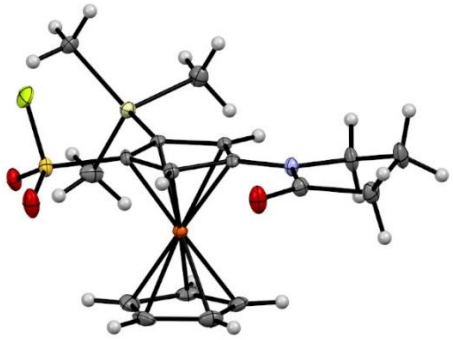
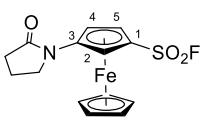


Figure 18. Molecular structure of compound **34a** (thermal ellipsoids shown at the 30% probability level).

3-(2-Oxo-*N*-pyrrolidyl)ferrocenesulfonyl fluoride – 34b

The compound **19a** (394 mg, 1.00 mmol, 1.00 equiv), CuI (190 mg, 1.00 mmol, 1.00 equiv) and K_3PO_4 (424 mg, 2.00 mmol, 2.00 equiv) were introduced in a degassed (argon) Schlenk tube then subjected to three vacuum/argon cycles. Dioxane (2 mL), pyrrolidinone (83.5 µL, 93.6 mg, 1.10 mmol, 1.10 equiv) and *N*,*N*'-dimethylethylenediamine (108 µL, 88.2 mg, 1.00 mmol, 1.00 equiv) were next introduced under argon, and the mixture was heated at 110 °C for 14 h in a pre-heated oil bath. The reaction mixture was cooled to rt before addition of water and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30) to give the title product **34b** as a brown solid (69 mg, 19%). The compounds **19a** (128 mg, 32%) and **2** (74 mg, 27%) were also isolated.

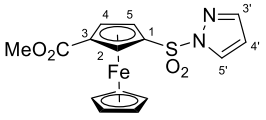
R_f (eluent: PE-EtOAc 70:30) = 0.13. Mp 139-140 °C. ν_{max} (film)/cm^{-1} 3091, 1692, 1495, 1395, 1382, 1302, 1248, 1203, 1153, 1073, 826, 773. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.29 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 5.23 (dd, *J* = 1.2, 2.3 Hz, 1H, FcCH, H4), 4.76 (dd, *J* = 1.2, 2.3 Hz, 1H, FcCH, H5), 4.41 (s, 5H, Cp), 3.70-3.60 (m, 2H, CH_2-CH_2-C*H*$_2$-N), 2.50 (t, *J* = 8.1 Hz, 2H, C*H*$_2$-CH_2-CH_2-N), 2.18 (quint, *J* = 8.1 Hz, 2H, CH_2-C*H*$_2$-CH_2-N). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 174.2 (s, C=O), 99.7 (s, FcC, C3), 74.4 (d, *J* = 39.6 Hz, FcC, C1), 72.3 (s, Cp), 69.9 (s, FcCH, C5), 64.3 (s, FcCH, C4), 60.2 (s, FcCH, C2), 48.2 (s, CH_2-CH_2-*C*H_2-N), 32.1 (s, *C*H_2-CH_2-CH_2-N), 18.2 (s, CH_2-*C*H_2-CH_2-N). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.5. Anal. Calcd for $C_{14}H_{14}FFeNO_3S$: C, 47.88; H, 4.02; N, 3.99; S, 9.13. Found: C, 47.97; H, 4.15; N, 4.13; S, 9.14.



3-Methoxycarbonyl-1-(*N*-pyrazolyl)sulfonylferrocene – 36b

Compound **20d** (217 mg, 0.66 mmol, 1.00 equiv), pyrazole (89.9 mg, 1.32 mmol, 2.00 equiv) and cesium carbonate (643 mg, 1.98 mmol, 3.00 equiv) were placed under argon in a pre-dried Schlenk tube. Acetonitrile (4 mL) was added and the reaction mixture was stirred at rt for 14 h. Water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30 to 60:40) with 2% of NEt_3 to give the title product **36b** as an orange solid (216 mg, 87%).

R_f (eluent: PE-EtOAc 60:40) = 0.54. Mp 180-181 °C. ν_{max} (film)/cm^{-1} 3110, 2958, 1703, 1469, 1381, 1360, 1296, 1208, 1196, 1179, 1162, 1070, 1056, 1036, 971, 922, 906, 842, 775. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.01 (d, *J* = 2.7 Hz, 1H, ArCH, H5'), 7.71 (d, *J* = 1.1 Hz, 1H, ArCH, H3'), 6.36 (dd, *J* = 1.7, 2.7 Hz, 1H, ArCH, H4'), 5.41 (t, *J* = 1.3 Hz, 1H, FcCH, H2), 5.05 (dd, *J* = 1.3, 2.7 Hz, 1H, FcCH, H4), 4.99 (dd, *J* = 1.3, 2.7 Hz, 1H, FcCH, H5), 4.53 (s, 5H, Cp), 3.81 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 169.3 (s, C=O), 144.9 (s, ArCH, C3'), 130.7 (s, ArCH, C5'), 108.6 (s, ArCH, C4'), 86.3 (s, FcC, C1), 75.2 (s, FcC, C3), 73.4 (s, FcCH, C4), 73.0 (s, Cp), 72.1 (s, FcCH, C5), 71.1 (s, FcCH, C2), 52.3 (s, CH_3). Anal. Calcd for $C_{15}H_{14}FeN_2O_4S$: C, 48.15; H, 3.77; N, 7.49; S, 8.57. Found: C, 48.22; H, 3.72; N, 7.53; S, 8.63.



Crystal data for 36b. $C_{15}H_{14}FeN_2O_4S$, *M* = 374.19, *T* = 150(2) K; monoclinic *P* 2$_1$/*c* (I.T.#14), *a* = 19.288(2), *b* = 5.8549(7), *c* = 13.2527(17) Å, *β* = 99.843(5) °, *V* = 1474.5(3) Å^3. *Z* = 4, *d* = 1.686 g.cm^{-3}, *μ* = 1.186 mm^{-1}. A final refinement on F^2 with 3349 unique intensities and 209 parameters converged at $\omega R(F)^2$ = 0.0645 (R_F = 0.0275) for 3110 observed reflections with $I > 2\sigma$. CCDC 2189769.

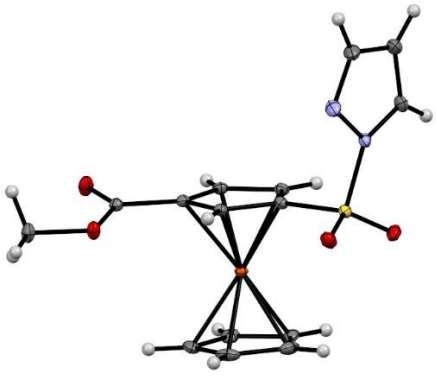


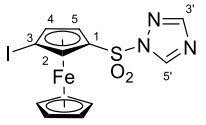
Figure 19. Molecular structure of compound **36b** (thermal ellipsoids shown at the 30% probability level).

3-Iodo-1-(*N1*-1,2,4-triazolyl)sulfonylferrocene – 36c

Compound **19a** (295 mg, 0.75 mmol, 1.00 equiv), 1,2,4-triazole (104 mg, 1.5 mmol, 2.00 equiv) and cesium carbonate (731 mg, 2.25 mmol, 3.00 equiv) were placed under argon in a pre-dried Schlenk tube. Acetonitrile (4 mL) was added and the reaction mixture was stirred at rt for 14 h. Water was added and

the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (95:5 to 90:10 to give the title product **36c** as a yellow solid (82 mg, 25%). The compound **19a** (193 mg, 65%) was also isolated.

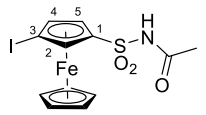
R_f (eluent: PE-EtOAc 80:20) = 0.23. Mp 158-159 °C. ν_{max} (film)/cm^{-1} 3125, 3105, 1499, 1386, 1368, 1324, 1269, 1209, 1155, 1133, 1101, 1034, 983, 877, 828. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.61 (s, 1H, ArCH, H5'), 8.00 (s, 1H, ArCH, H3'), 5.11 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 4.87 (dd, *J* = 1.2, 2.5 Hz, 1H, FcCH, H5), 4.81 (dd, *J* = 1.2, 2.5 Hz, 1H, FcCH, H4), 4.53 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 154.0 (s, ArCH, C3'), 144.1 (s, ArCH, C5'), 82.9 (s, FcC, C1), 79.5 (s, FcCH, C4), 75.7 (s, FcCH, C2), 74.5 (s, Cp), 71.1 (s, FcCH, C5), 39.4 (s, FcC, C3). Anal. Calcd for $C_{12}H_{10}FeIN_3O_2S$: C, 32.53; H, 2.28; N, 9.48; S, 7.24. Found: C, 32.47; H, 2.26; N, 9.61; S, 7.25.



<u>*N*-Acetyl-3-iodoferrocenesulfonamide – 37b</u>

Compound **19a** (197 mg, 0.50 mmol, 1.00 equiv), acetamide (59.1 mg, 1.00 mmol, 2.00 equiv) and sodium hydride (60% dispersion in oil, 87.0 mg, 2.00 mmol, 4.00 equiv) were placed under argon in a pre-dried Schlenk tube. THF (4 mL) was added and the reaction mixture was stirred at 50 °C for 14 h. The reaction mixture was cooled to 0 °C, water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30 to 64:40) to give the title product **37b** as an orange solid (152 mg, 70%).

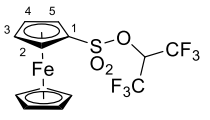
R_f (eluent: PE-EtOAc 70:30) = 0.42. Mp 174-175 °C. ν_{max} (film)/cm^{-1} 3227, 1721, 1431, 1370, 1331, 1221, 1206, 1132, 1040, 993, 908, 870, 846, 824. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.19 (br s, 1H, NH), 5.09 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 4.87 (dd, *J* = 1.2, 2.5 Hz, 1H, FcCH, H5), 4.71 (dd, *J* = 1.2, 2.5 Hz, 1H, FcCH, H4), 4.45 (s 5H, Cp), 2.07 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 168.0 (s, C=O), 86.4 (s, FcC, C1), 78.0 (s, FcCH, C4), 75.6 (s, FcCH, C2), 74.1 (s, Cp), 71.2 (s, FcCH, C5), 39.0 (s, FcC, C3), 23.7 (s, CH_3). Anal. Calcd for $C_{12}H_{12}FeINO_3S$: C, 33.28; H, 2.79; N, 3.23, S, 7.40. Found: C, 33.31; H, 2.88; N, 3.21; S, 7.54.



<u>*O*-(1,1,1,3,3,3-Hexafluoroisopropyl)ferrocenesulfonate – 38d</u>

1,1,1,3,3,3-Hexafluoroisopropanol (210 µL, 336 mg, 2.00 mmol, 2.00 equiv) was added to a suspension of compound **2** (268 mg, 1.00 mmol, 1.00 equiv) and cesium carbonate (977 mg, 3.00 mmol, 3.00 equiv) in acetonitrile (5 mL) and the reaction mixture was stirred at 80 °C for 14 h. The reaction mixture was cooled to rt. Water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (90:10 to 80:20) to give the title product **38d** as a yellow solid (48 mg, 11%). Compound **2** (184 mg, 68%) was also isolated.

R_f (eluent: PE-EtOAc 90:10) = 0.55. Mp 82-83 °C. ν_{max} (film)/cm^{-1} 2964, 1394, 1371, 1356, 1283, 1234, 1202, 1175, 1155, 1108, 1073, 1033, 1013, 895, 785, 828, 784, 726. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.14 (hept, *J* = 5.8 Hz, 1H, CH), 4.77 (t, *J* = 1.9 Hz, 2H, FcCH, H2 and H5), 4.55 (t, *J* = 1.9 Hz, 2H, FcCH, H3 and H4), 4.44 (s, 5H, Cp). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 120.1 (q, *J* = 283.6 Hz, CF_3), 80.7 (s, FcC, C1), 72.3 (s, FcCH, C3 and C4), 71.9 (q, *J* = 35.3 Hz, CH), 71.6 (s, Cp), 69.7 (s, FcCH, C2 and C5). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) -73.1.



Crystal data for 38d. $C_{13}H_{10}F_6FeO_3S$, M = 416.12, T = 150 K; monoclinic $P\,2_1/c$ (I.T.#14), a = 8.8905(8), b = 7.3007(7), c = 22.9465(19) Å, β = 93.063(3) °, V = 1487.3(2) Å^3. Z = 4, d = 1.858 g.cm^{-3}, μ = 1.233 mm^{-1}. A final refinement on F^2 with 3413 unique intensities and 217 parameters converged at $\omega R(F)^2$ = 0.0665 (R_F = 0.0285) for 3096 observed reflections with $I > 2\sigma$. CCDC 2189770.

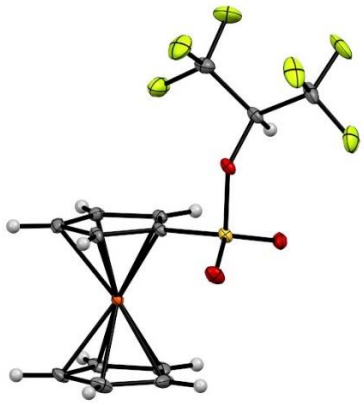
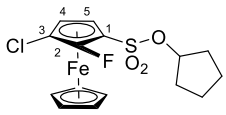


Figure 20. Molecular structure of compound **38d** (thermal ellipsoids shown at the 30% probability level).

3-Chloro-*O*-cyclopentyl-2-fluoroferrocenesulfonate – 38e

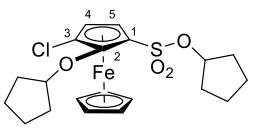
Cyclopentanol (381 µL, 362 mg, 4.20 mmol, 6.00 equiv) was added dropwise to a suspension of sodium hydride (60% dispersion in oil, 91.2 mg, 2.10 mmol, 3.00 equiv) in THF (5 mL) and the reaction mixture was stirred at rt for 15 min. Compound **9** (224 mg, 0.70 mmol, 1.00 equiv) was added in one portion and the reaction mixture was stirred for 30 min. Water was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (95:5) to give the title product as an orange oil (83 mg, 31%).

R_f (eluent: PE-EtOAc 95:5) = 0.32. ν_{max} (film)/cm^{-1} 2966, 1463 ,1369, 1249, 1182, 1163, 1138, 1108, 928, 905, 874, 829. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.06-5.02 (m, 1H, OCH), 4.54 (s, 5H, Cp), 4.43 (d, J = 3.0 Hz, 1H, FcCH, H4), 4.38 (d, J = 3.0 Hz, 1H, FcCH, H5), 1.88-1.83 (m, CH-C*H*H), 1.81-1.78 (m, 3H, CH-CH*H* and CH-CH_2), 1.76-1.68 (m, 2H, CH_2), 1.57-1.54 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 128.9 (d, J = 284.0 Hz, FcC, C2), 86.3 (s, OCH), 81.7 (d, J = 14.4 Hz, FcC, C1 or C3), 74.7 (s, Cp), 71.6 (d, J = 10.9 Hz, FcC, C1 or C3), 63.4 (s, FcCH, C4), 60.3 (s, FcCH, C5), 33.5 (s, CH-*C*HH), 33.3 (s, CH-*C*H_2), 23.3 (s, 2 x CH_2). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) -192.1. Anal. Calcd for $C_{15}H_{16}ClFFeO_3S$: C, 46.60; H, 4.17; S, 8.29. Found: C, 46.75; H, 4.25; S, 8.37.



3-Chloro-*O*-cyclopentyl-2-(cyclopentyloxy)ferrocenesulfonate (**38f**) was also isolated as an orange oil (25 mg, 8%).

R_f (eluent: PE-EtOAc 95:5) = 0.45. ν_{max} (film)/cm^{-1} 2961, 2873, 1444, 1360, 1249, 1181, 1134, 1110, 1013, 958, 930, 898, 872, 825, 753, 732. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.04 (tt, J = 2.9, 5.7 Hz, 1H, OCH), 4.85 (tt, J = 2.6, 5.4 Hz, 1H, OCH), 4.46 (s, 5H, Cp), 4.44 (d, J = 3.0 Hz, 1H, FcCH, H4 or H5), 4.41 (d, J = 3.0 Hz, 1H, FcCH, H4 or H5), 2.09 (m, 1H, C*H*H), 2.02-1.96 (m, 1H, C*H*H), 1.99-1.787 (m, 6H, CH*H*, CH*H* and 2 x CH_2), 1.77-1.68 (m, 4H, 2 x CH_2),1.61-1.54 (m, 4H, 2 x CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 118.4 (s, FcC, C2), 89.5 (s, OCH), 85.7 (s, FcC, C1 or 3), 85.2 (OCH), 74.9 (s, FcC, C1 or C3), 74.0 (s, Cp), 64.5 (s, FcCH, C4 or C5), 62.0 (s, FcCH, C4 or C5), 33.8 (s, CH_2), 35.5 (s, CH_2), 33.3 (s, CH_2), 33.0 (s, CH_2), 23.8 (s, CH_2), 23.7 (s, CH_2), 23.4 (s, CH_2), 23.3 (s, CH_2).



Methylsulfonylferrocene – 39a

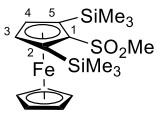
A solution of methyllithium (1.5 M in Et_2O, 0.95 mL, 1.50 mmol, 1.50 equiv) was added dropwise to a solution of compound **2** (268 mg, 1.00 mmol, 1.00 equiv) in THF (2 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and water was added. The reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (70:30) to give the title product **39a** as an orange solid (222 mg, 84%).

R_f (eluent: PE-EtOAc 70:30) = 0.41. Mp 73-74 °C (litt. 73-74 °C).[9] ν_{max} (film)/cm^{-1} 3128, 1420, 1413, 1295, 1191, 1130, 1106, 1019, 969, 906, 845, 812, 760. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.67 (t, *J* = 1.8 Hz, 2H, FcCH, H2 and H5), 4.45 (s, 5H, Cp), 4.44 (t, *J* = 1.8 Hz, 2H, FcCH, H3 and H4), 2.98 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 89.0 (s, FcC, C1), 71.1 (s, FcCH, C3 and C4), 70.7 (s, Cp), 69.3 (s, FcCH, C2 and C5), 45.3 (s, CH_3). Anal. Calcd for $C_{11}H_{12}FeO_2S$: C, 50.02; H, 4.58; S, 12.14. Found: C, 50.06; H, 4.60; S, 12.11.

2,5-Bis(trimethylsilyl)-1-methylsulfonylferrocene – 39c

A solution of methyllithium (1.5 M in Et_2O, 0.95 mL, 1.50 mmol, 1.50 equiv) was added dropwise to a solution of compound **5a** (412.4 mg, 1.00 mmol, 1.00 equiv) in THF (2 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and water was added. The reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (95:5 to 90:10) to give the title product **39c** as an orange solid (270 mg, 66%).

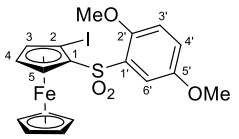
R_f (eluent: PE-EtOAc 95:5) = 0.47. Mp 200-201 °C. ν_{max} (film)/cm^{-1} 2951, 2900, 1409, 1305, 1273, 1242, 1201, 1133, 1109, 950, 908, 890, 820, 758. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.51 (s, 2H, FcCH, H3 and H4), 4.41 (s, 5H, Cp), 2.96 (s, 3H, CH_3), 0.37 (s, 18H, 2 x Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 97.3 (s, FcC, C1), 80.7 (s, FcCH, C3 and C4), 77.8 (s, FcC, C2 and C5), 70.9 (s, Cp), 45.4 (s, CH_3), 1.2 (s, 2 x Si(CH_3)$_3$). Anal. Calcd for $C_{17}H_{28}FeO_2SSi_2$: C, 49.99; H, 6.91; S, 7.85. Found: C, 49.93; H, 6.98; S, 7.95.



2-Iodo-1-(2,5-dimethoxyphenyl)sulfonylferrocene – 40b

$AlCl_3$ (150 mg, 1.13 mmol, 1.50 equiv) was added portionwise to a solution of compound **3f** (295 mg, 0.75 mmol, 1.00 equiv) and 1,4-dimethoxybenzene (1.04 g, 7.50 mmol, 10.0 equiv) in CH_2Cl_2 (4 mL) at 0 °C. After addition, the reaction mixture was warmed to rt and stirred for 1 h. Water was added dropwise and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (80:20 to 60:40) to give the title product **40b** as an orange solid (275 mg, 74%). Compound **2** (30 mg, 15%) was also isolated.

R_f (eluent: PE-EtOAc 80:20) = 0.18. Mp 174-175 °C. ν_{max} (film)/cm^{-1} 2964, 2937, 1488, 1461, 1448, 1473, 1410, 1309, 1271, 1220, 1195, 1182, 1145, 1134, 1042, 1018, 919, 878, 818, 802, 738, 713. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.65 (d, *J* = 3.2 Hz, 1H, ArCH, H6'), 7.04 (dd, *J* = 3.2, 9.0 Hz, 1H, ArCH, H4'), 6.83 (d, *J* = 9.0 Hz, 1H, ArCH, H3'), 5.02 (dd, *J* = 1.5, 2.6 Hz, 1H, FcCH, H5), 4.63 (dd, *J* = 1.6, 2.3 Hz, 1H, FcCH, H3), 4.52 (s, 5H, Cp), 4.45 (t, *J* = 2.6 Hz, 1H, FcCH, H4), 3.82 (s, 3H, 5'-CH_3O), 3.73 (s, 3H, 2'-CH_3O). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 153.0 (s, ArC, C5'), 151.4 (s, ArC, C2'), 129.5 (s, ArC, C1'), 121.5 (s, ArCH, C4'), 114.6 (s, ArCH, C6'), 114.2 (s, ArCH, C3'), 89.3 (s, FcC, C1), 79.1 (s, FcCH, C3), 73.8 (s, Cp), 72.2 (s, FcCH, C5), 71.4 (s, FcCH, C4), 56.7 (s, 2'-CH_3O), 56.2

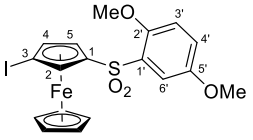


(s, 5'-CH_3O), 38.6 (s, FcC, C2). Anal. Calcd for $C_{18}H_{17}FeIO_4S$: C, 42.21; H, 3.35; S, 6.26. Found: C, 42.37; H, 3.33; S, 6.41.

3-Iodo-1-(2,5-dimethoxyphenyl)sulfonylferrocene – 40c

$AlCl_3$ (150 mg, 1.13 mmol, 1.50 equiv) was added portionwise to a solution of compound **19a** (295 mg, 0.75 mmol, 1.00 equiv) and 1,4-dimethoxybenzene (1.04 g, 7.50 mmol, 10.0 equiv) in CH_2Cl_2 (4 mL) at 0 °C. After addition, the reaction mixture was warmed to rt and stirred for 1 h. Water was added dropwise and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO_2, using PE-EtOAc (80:20 to 60:40) to give the title product **40c** as an orange solid (354 mg, 95%).

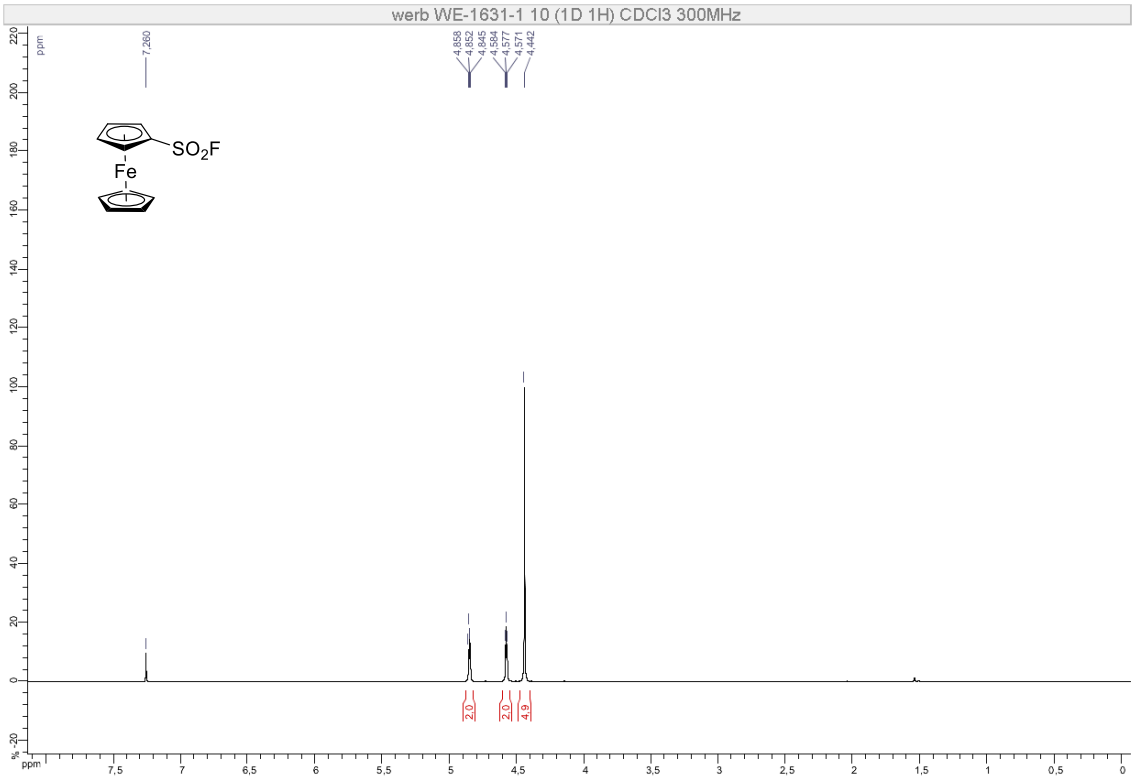
R_f (eluent: PE-EtOAc 80:20) = 0.30. Mp < 50 °C. ν_{max} (film)/cm^{-1} 3105, 2939, 2834, 1490, 1462, 1435, 1410, 1303, 1271, 1220, 1201, 1137, 1037, 1015, 872, 824, 747, 714. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.48 (d, *J* = 3.0 Hz, 1H, ArCH, H6'), 7.03 (dd, *J* = 3.0, 9.1 Hz, 1h, ArCH, H4'), 6.85 (d, *J* = 9.1 Hz, 1H, ArCH, H3'), 5.00 (s, 1H, FcCH, H2), 4.78 (s,1H, FcCH, H5), 4.62 (s, 1H, FcCH, H4), 4.50 (s, 5H, Cp), 3.80 (s, 3H, 2'-CH_3O), 3.79 (s, 3H, 5'-CH_3O). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 153.2 (s, ArC, C2' or C5'), 151.3 (s, ArC, C2' or C5'), 130.4 (s, ArC, C1'), 121.2 (s, ArCH, C4'), 114.2 (s, ArCH, C3'), 113.4 (s, ArCH, C6'), 90.3 (s, FcC, C1), 77.2 (s, FcCH, C4), 76.2 (s, FcCH, C2), 73.8 (s, Cp), 71.3 (s, FcCH, C5), 56.6 (s, 2'-CH_3O or 5'-CH_3O), 56.1 (s, 2'-CH_3O or 5'-CH_3O), 39.1 (s, FcC, C3). Anal. Calcd for $C_{18}H_{17}FeIO_4S$: C, 42.21; H, 3.35; S, 6.26. Found: C, 42.37; H, 3.30; S, 6.30.



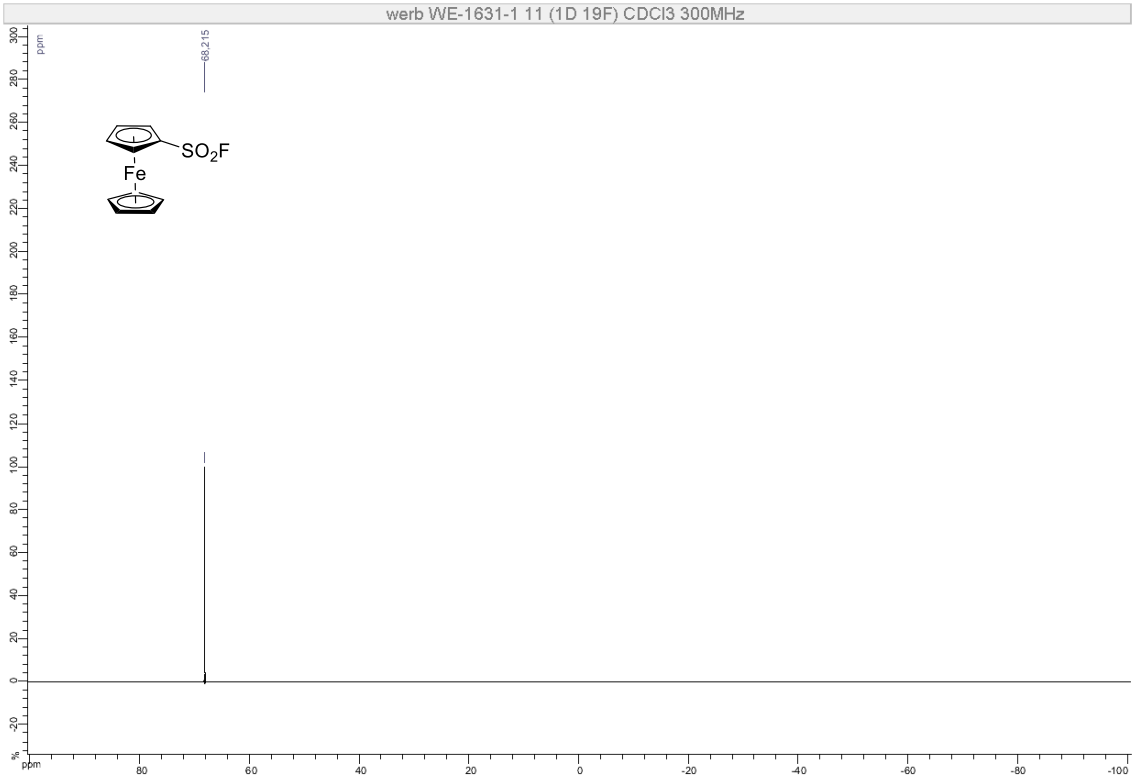
NMR Spectra

Ferrocenesulfonyl fluoride (2)

^{1}H NMR (300 MHz, $CDCl_3$)

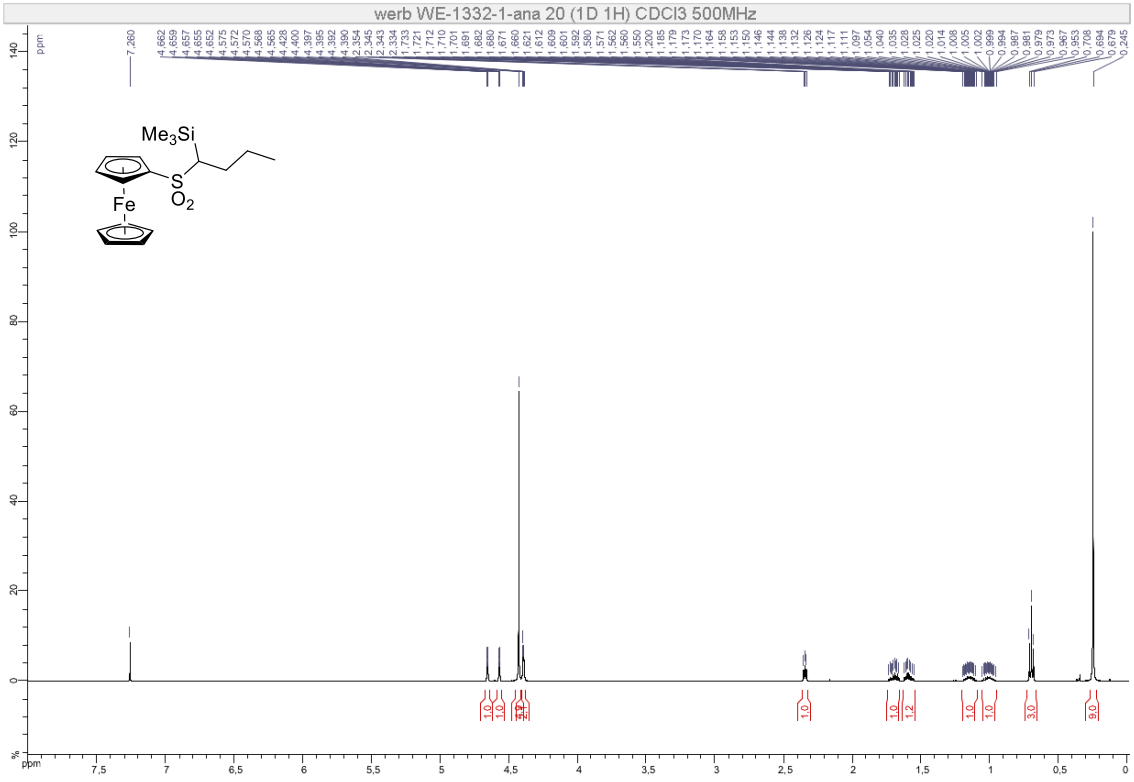


^{19}F NMR (470 MHz, $CDCl_3$)

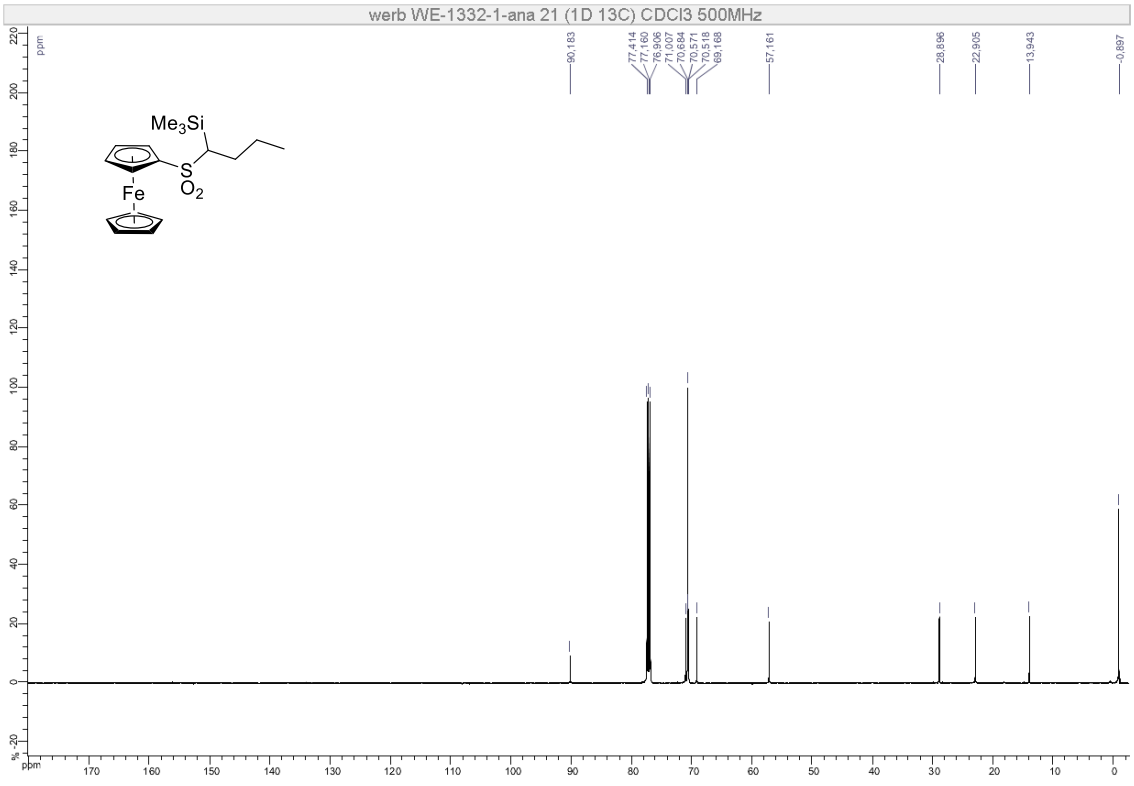


1-(Trimethylsilyl)butylsulfonylferrocene (4a)

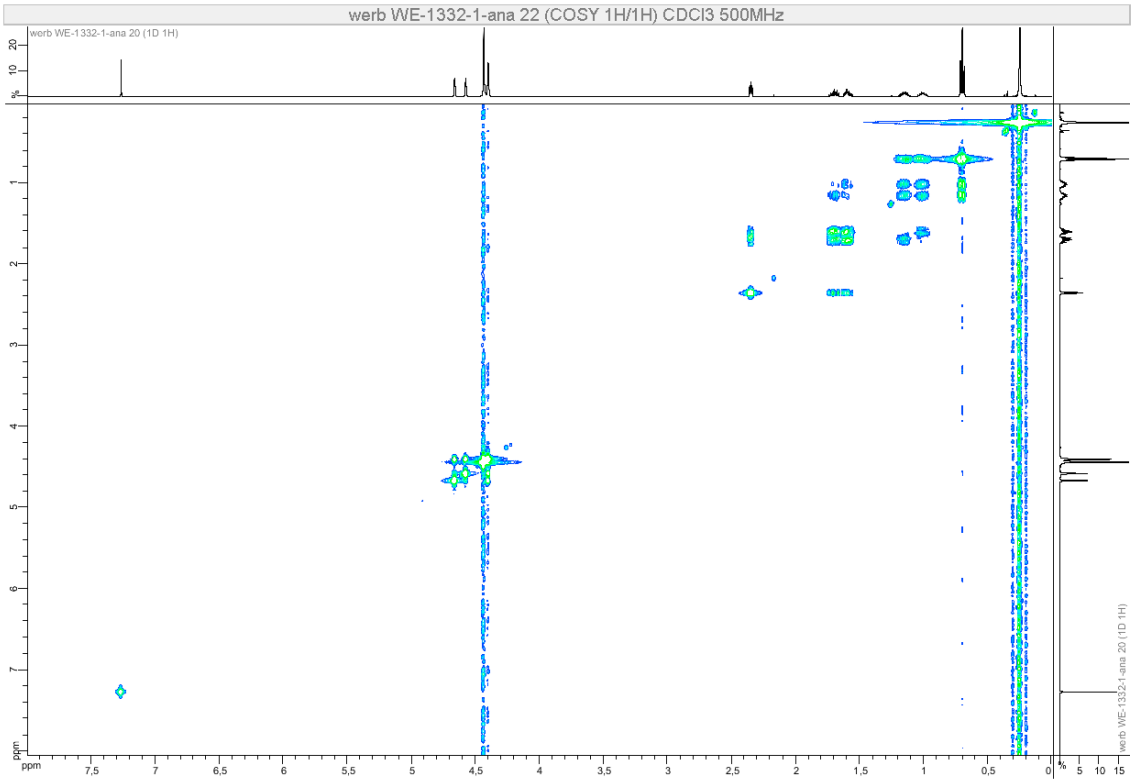
^{1}H NMR (500 MHz, $CDCl_3$)



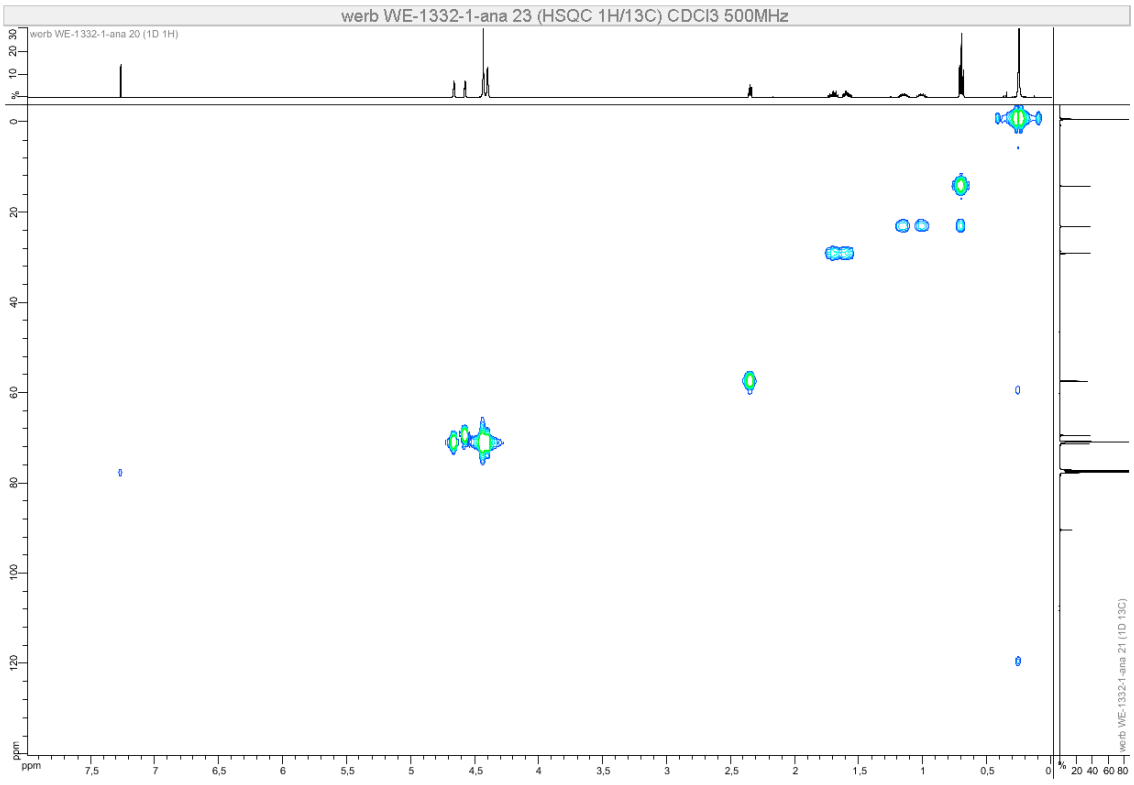
^{13}C NMR (126 MHz, $CDCl_3$)



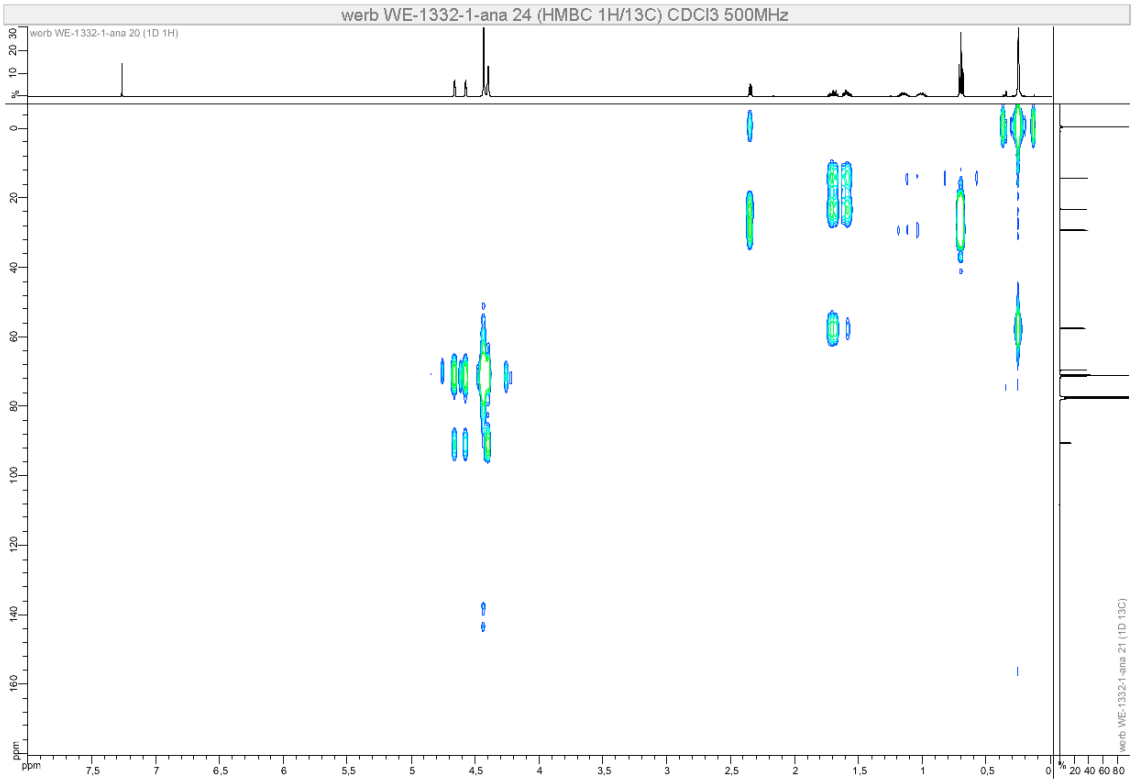
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

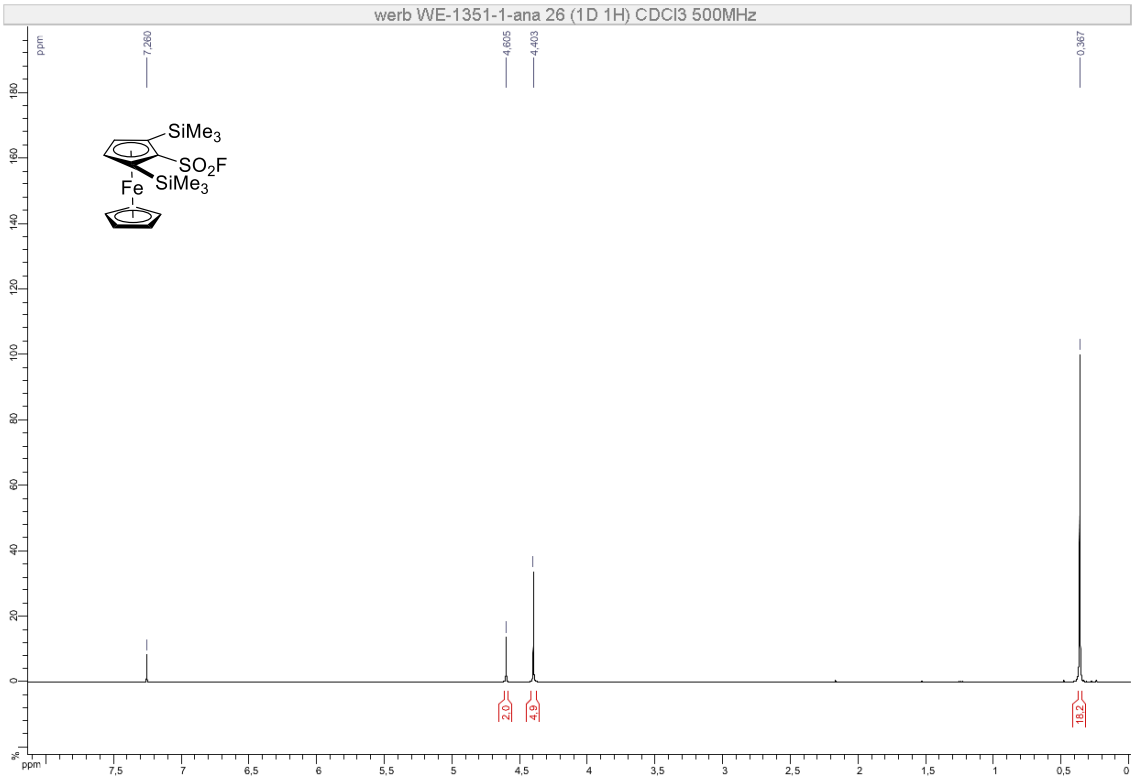


HMBC (500 MHz, $CDCl_3$)

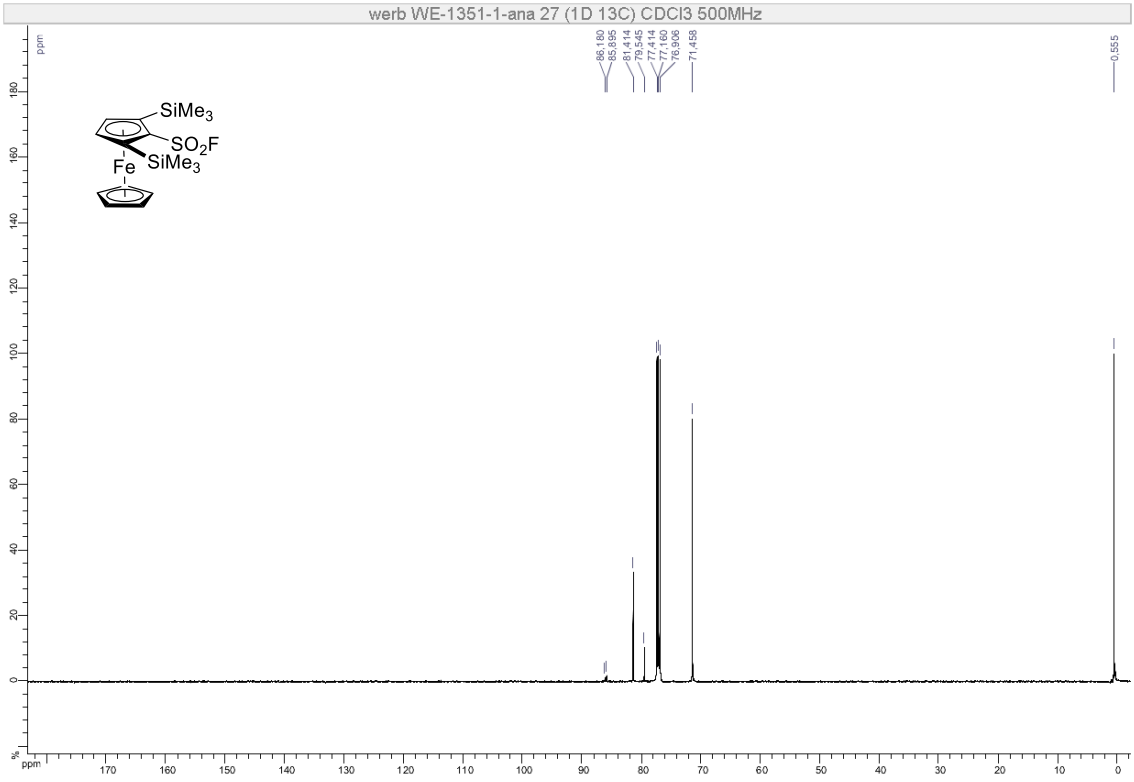


2,5-Bis-(trimethylsilyl)ferrocenesulfonyl fluoride (5a)

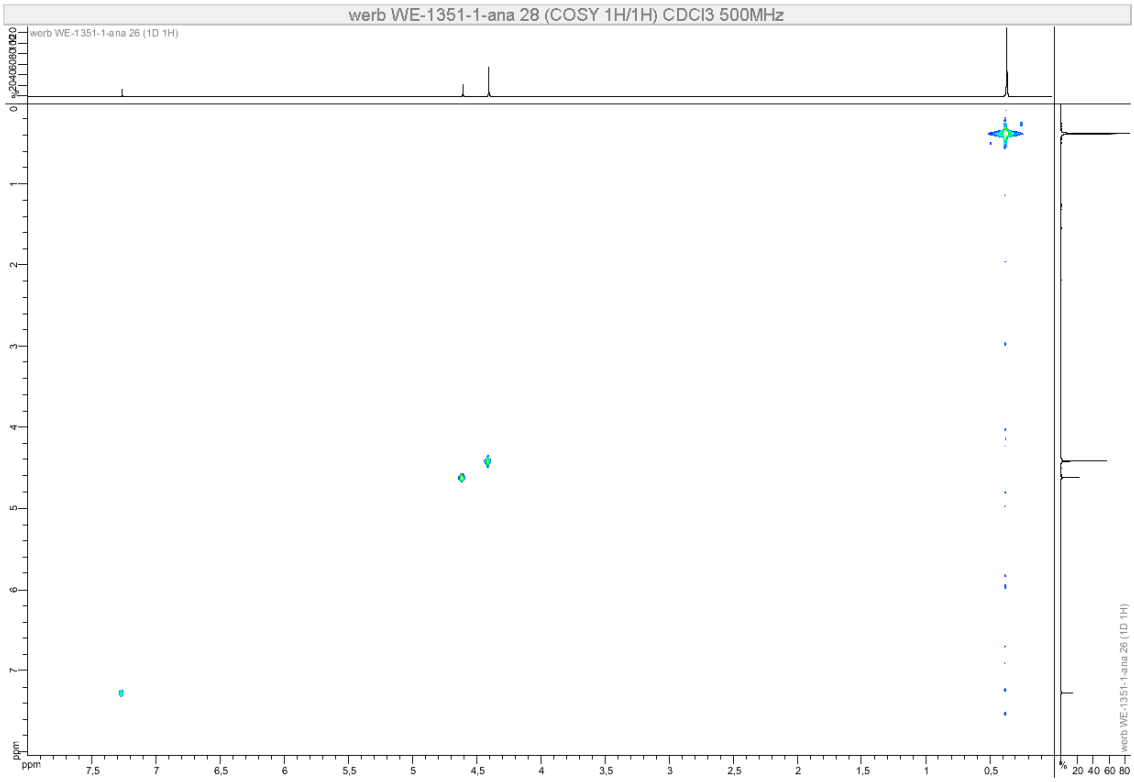
^{1}H NMR (500 MHz, $CDCl_3$)



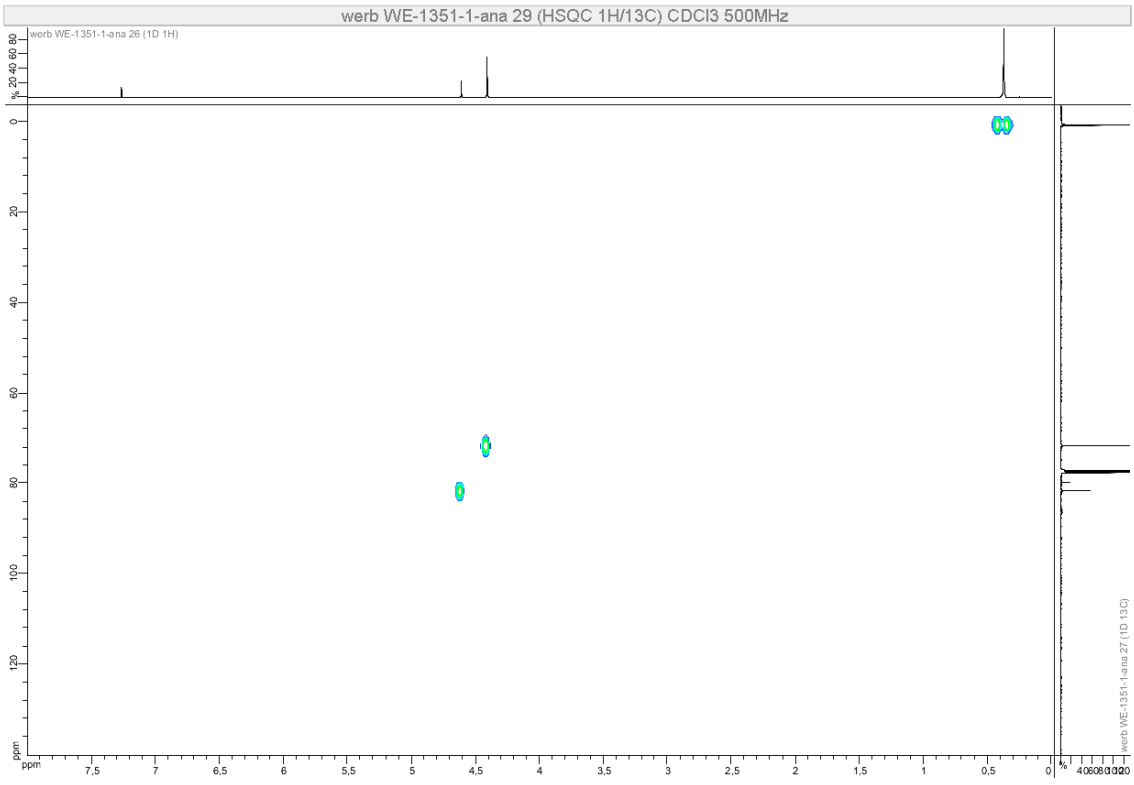
^{13}C NMR (126 MHz, $CDCl_3$)



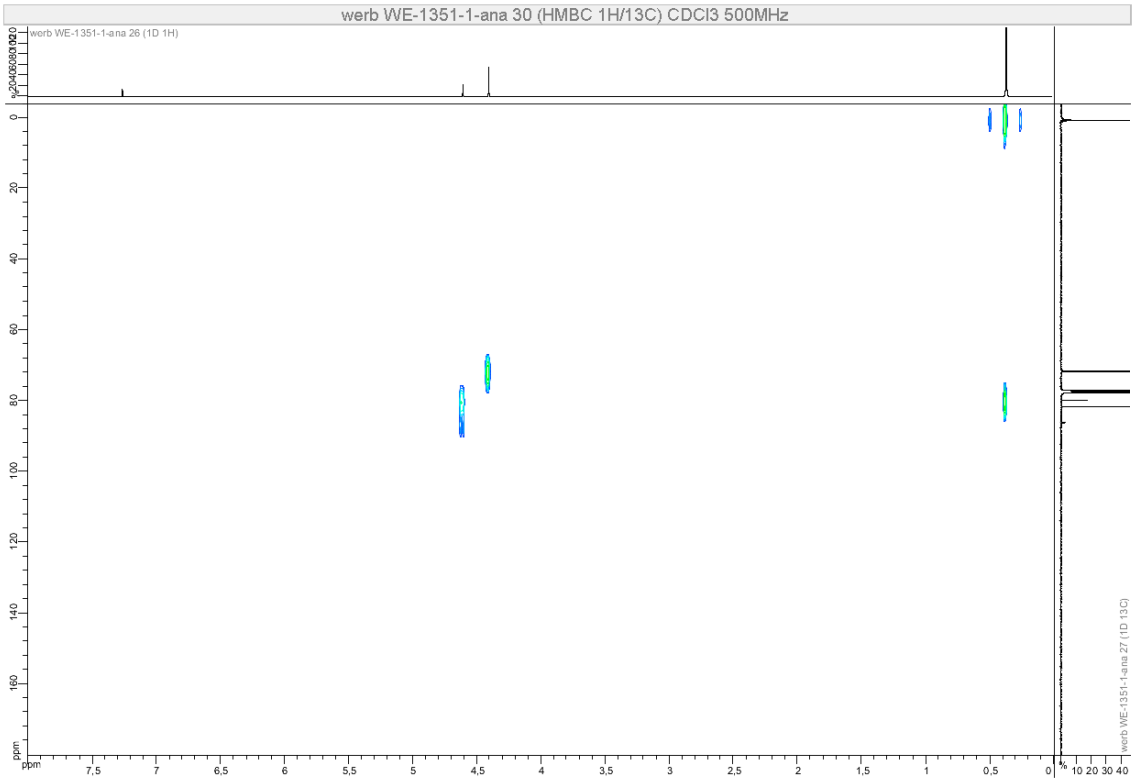
COSY (500 MHz, $CDCl_3$)



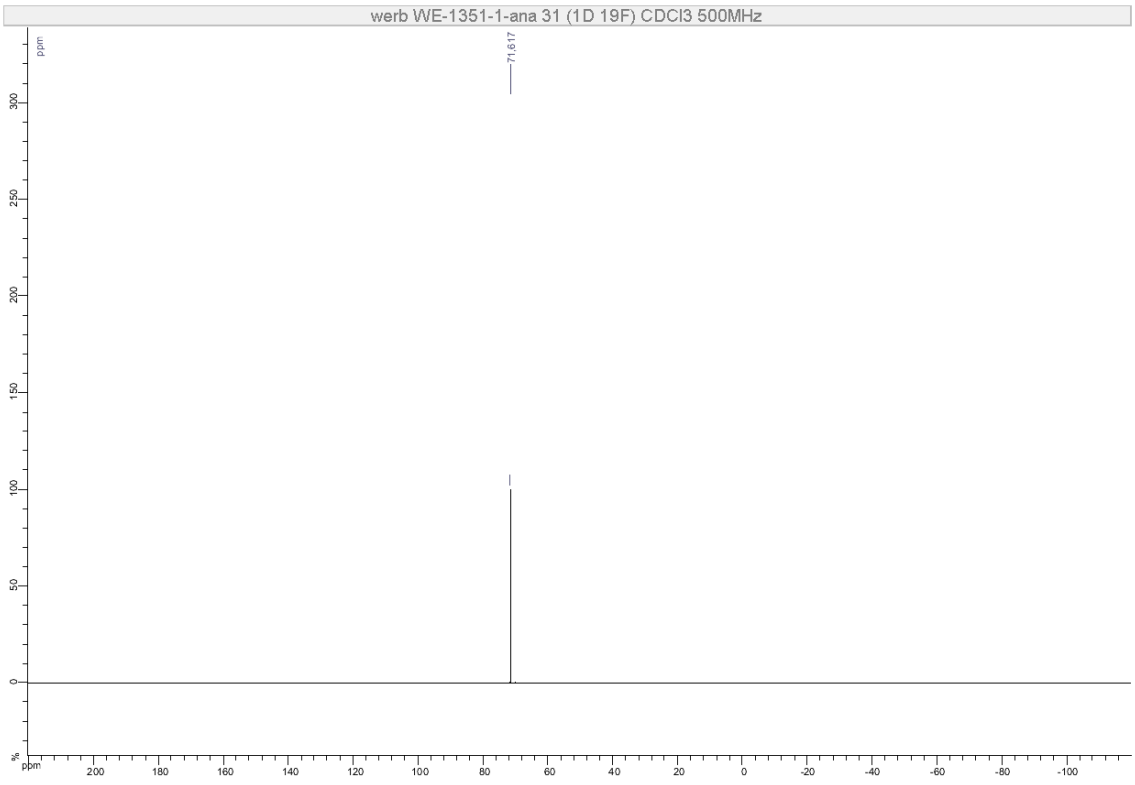
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

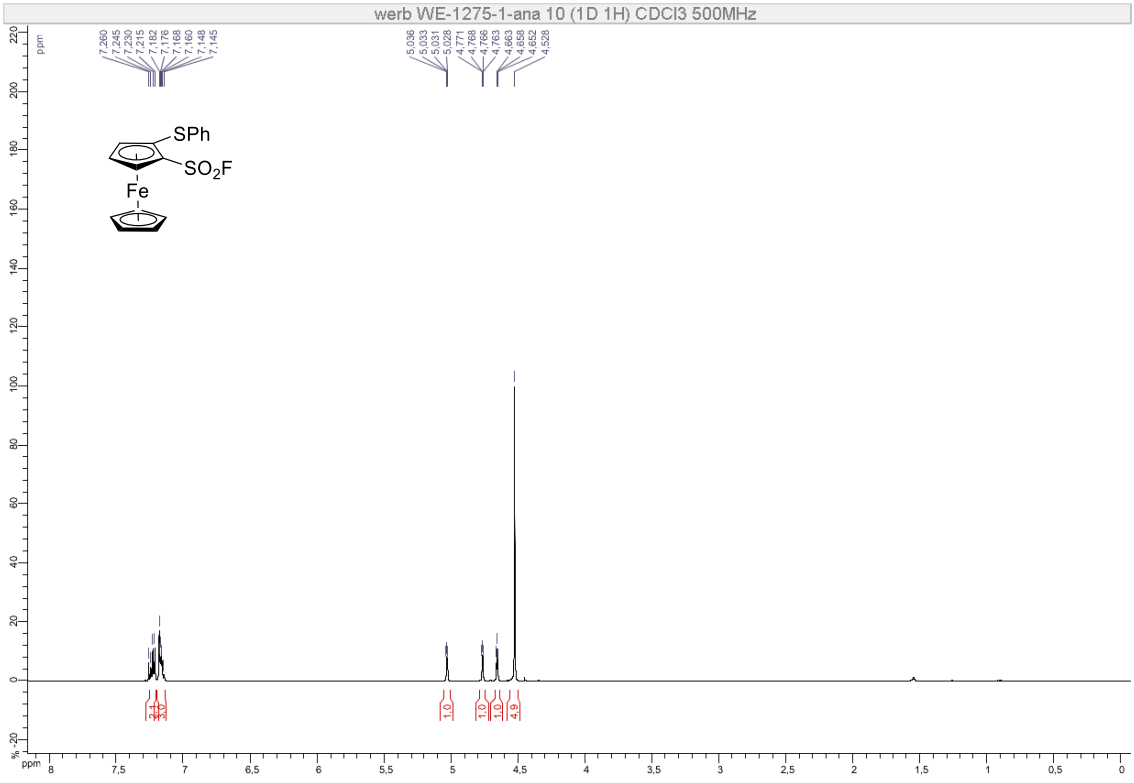


^{19}F NMR (470 MHz, $CDCl_3$)

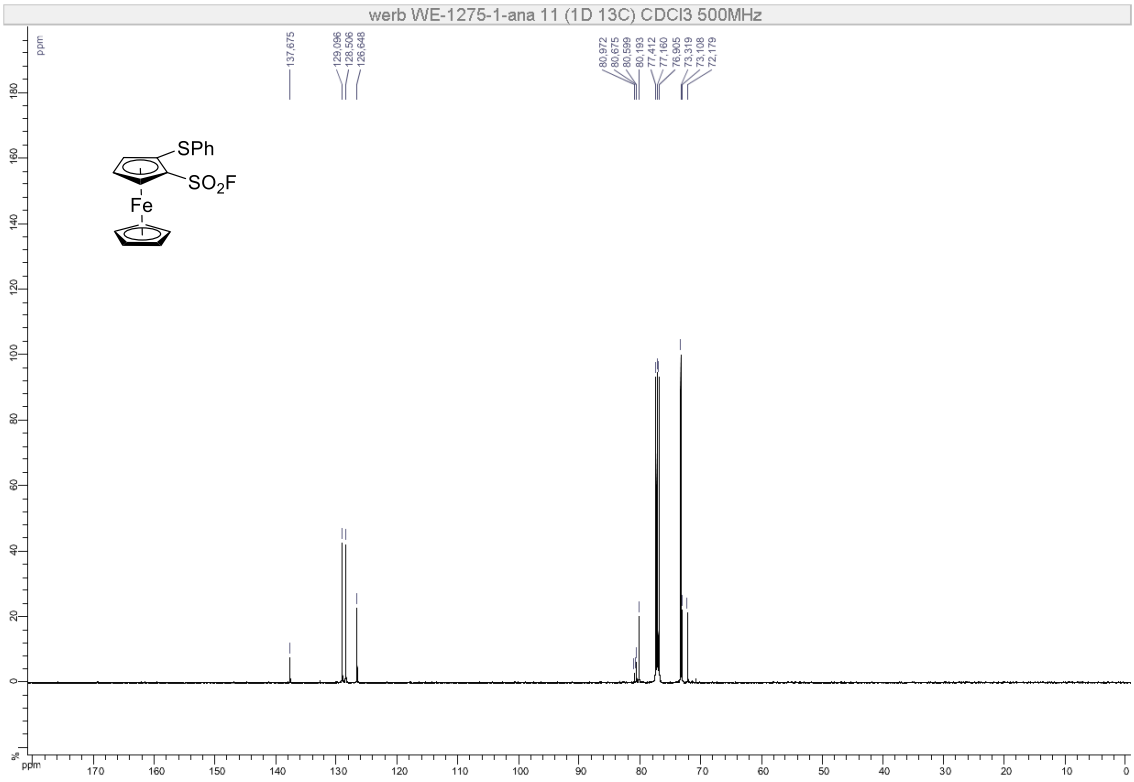


2-(Phenylthio)ferrocenesulfonyl fluoride (3b)

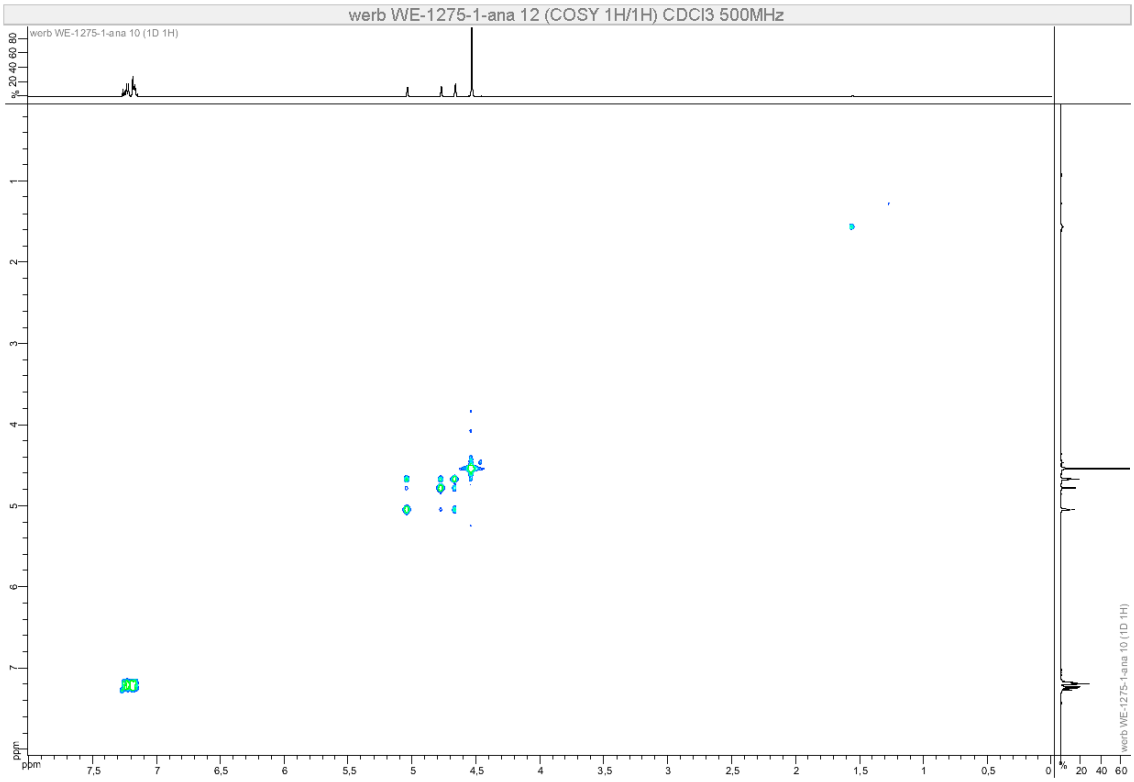
^{1}H NMR (500 MHz, $CDCl_3$)



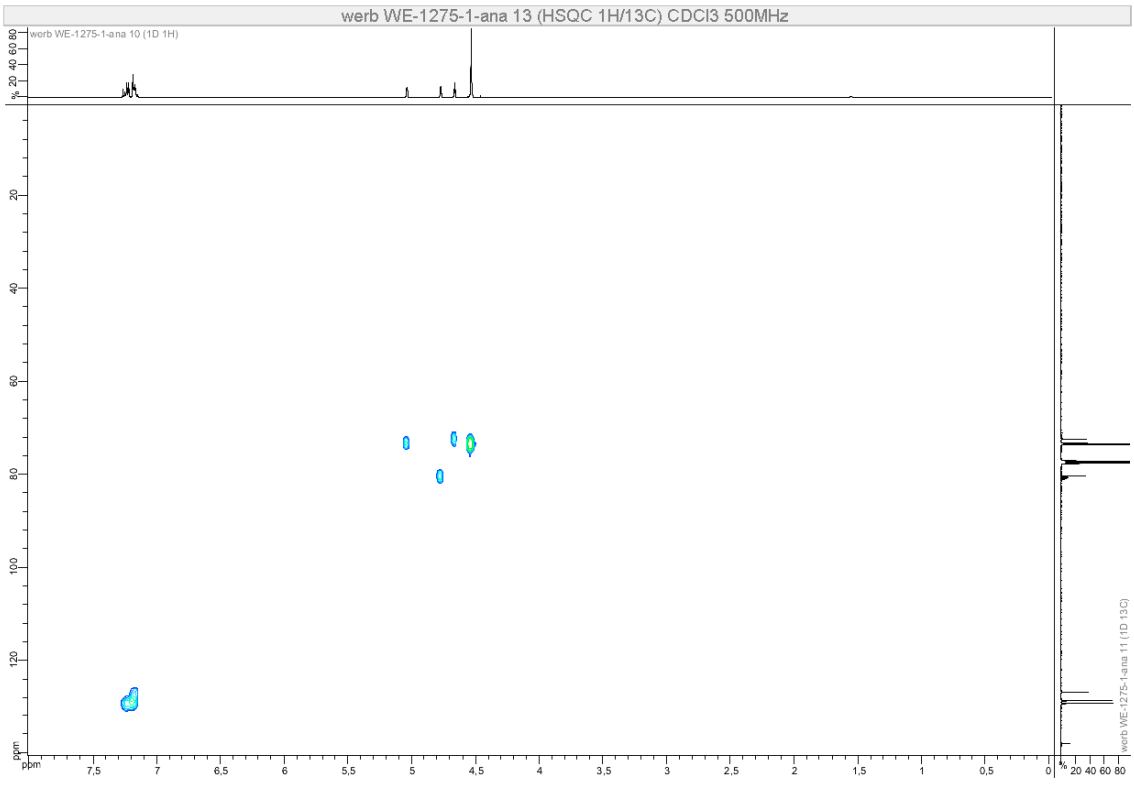
^{13}C NMR (126 MHz, $CDCl_3$)



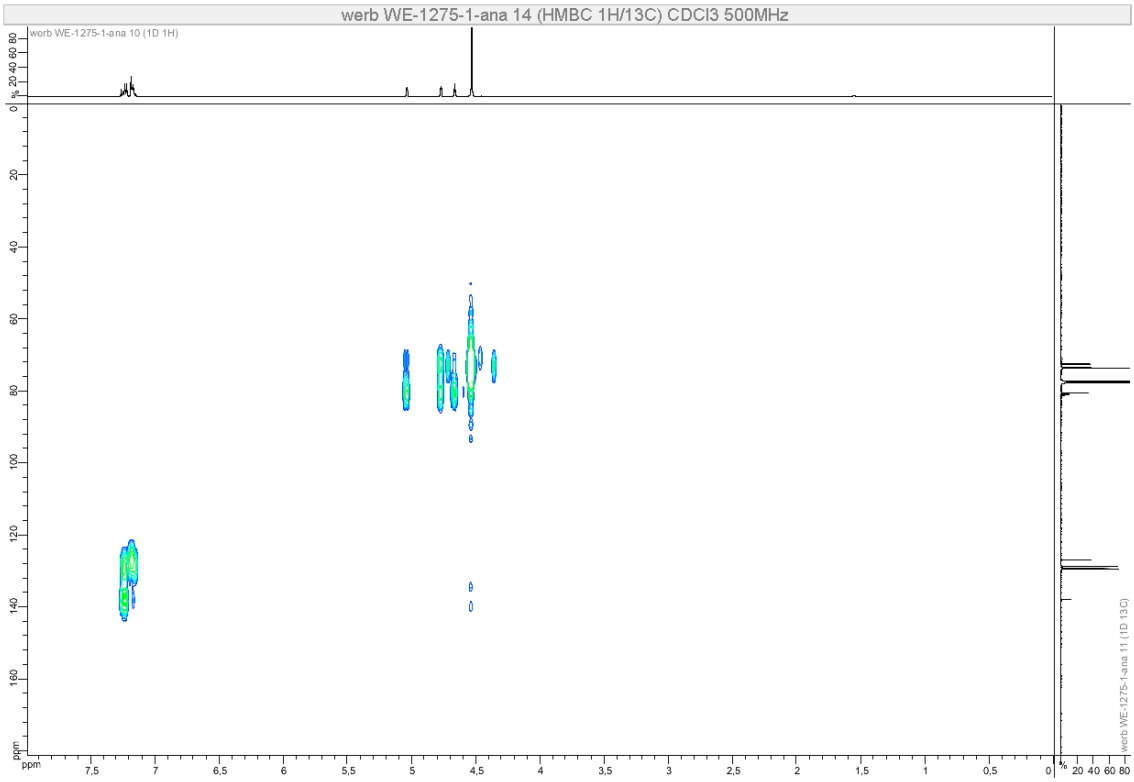
COSY (500 MHz, $CDCl_3$)



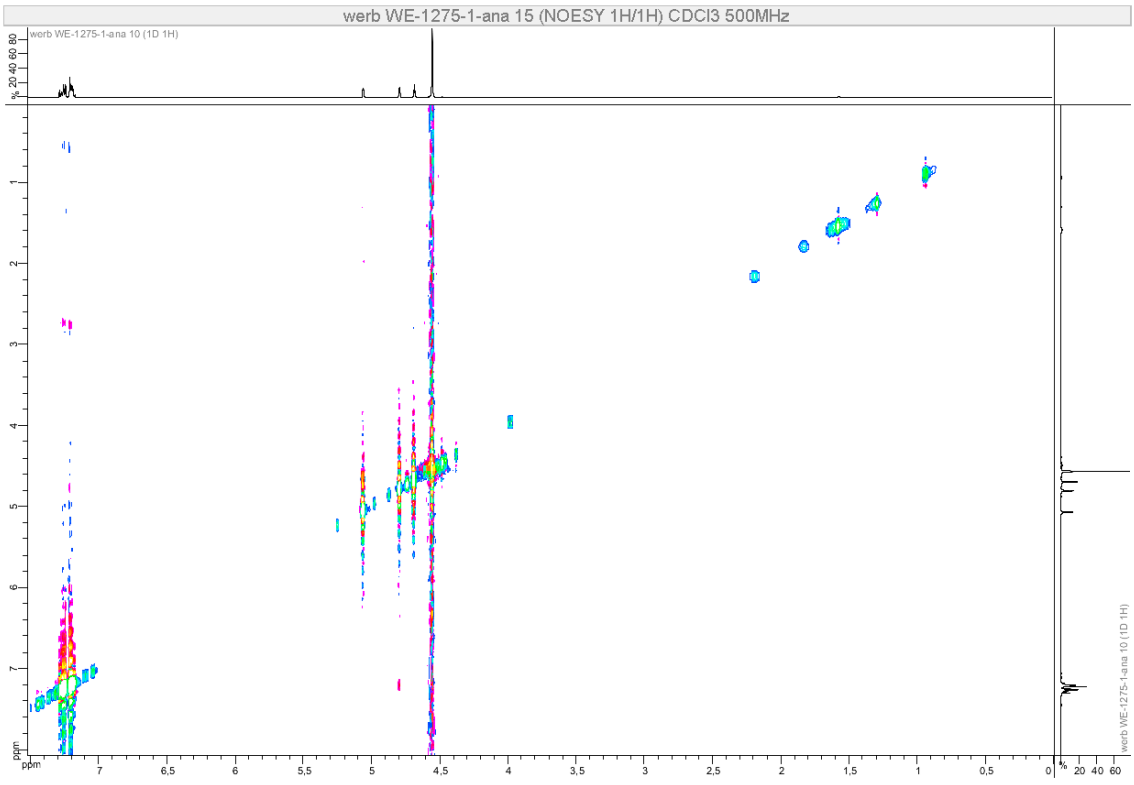
HSQC (500 MHz, $CDCl_3$)



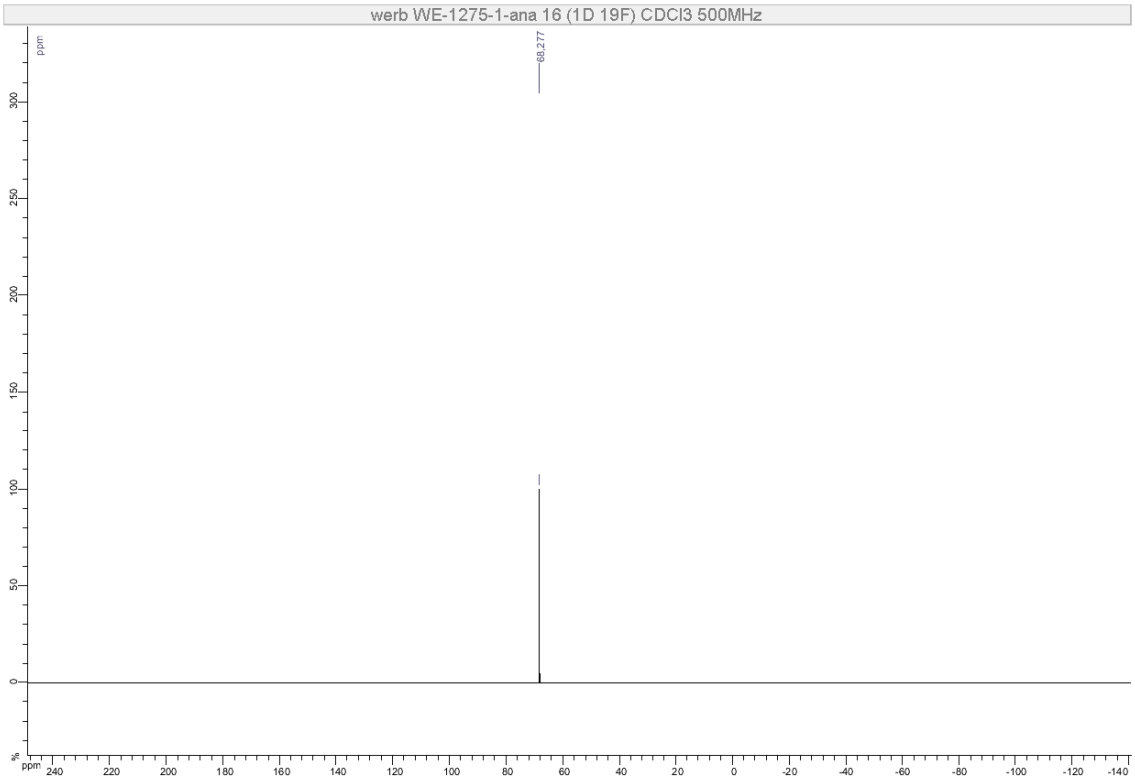
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

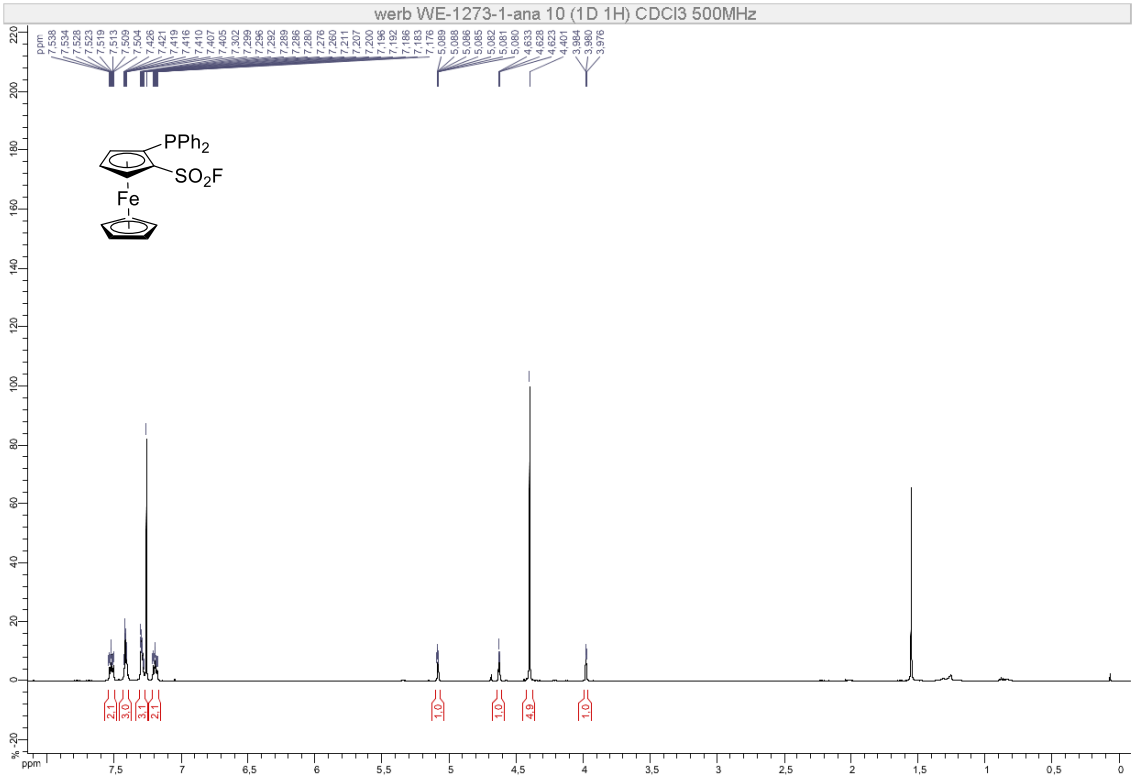


^{19}F NMR (470 MHz, $CDCl_3$)

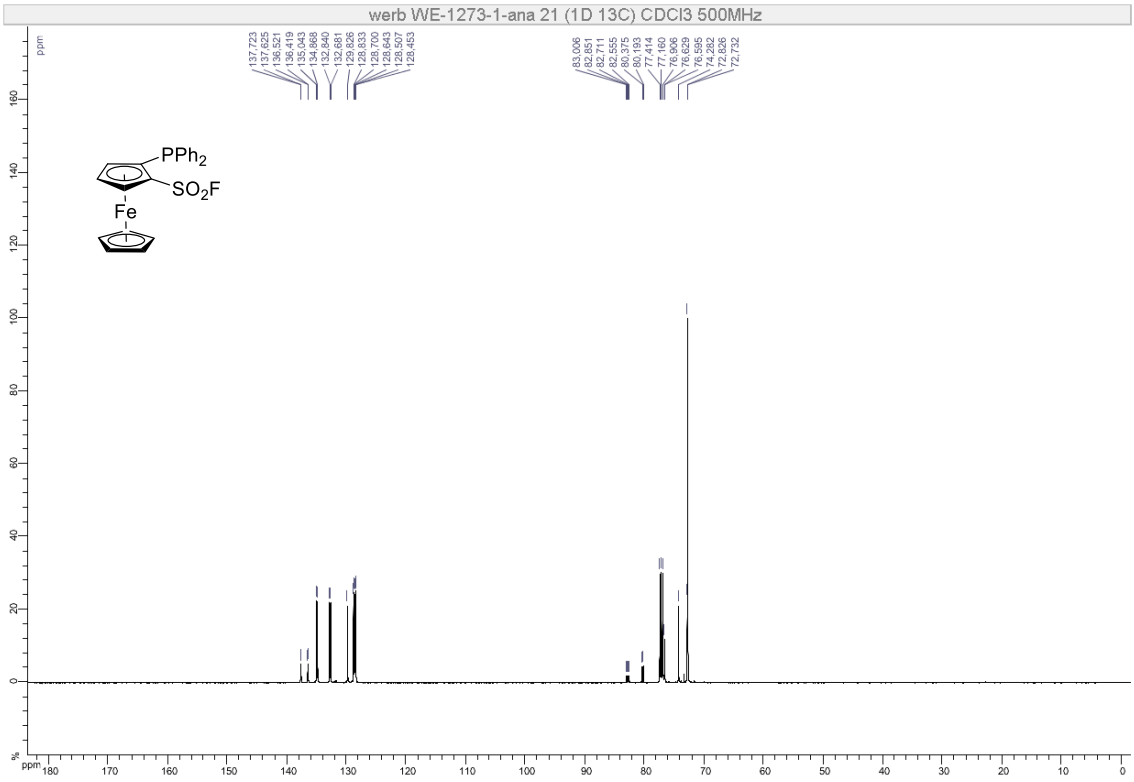


2-(Diphenylphosphino)ferrocenesulfonyl fluoride (3c)

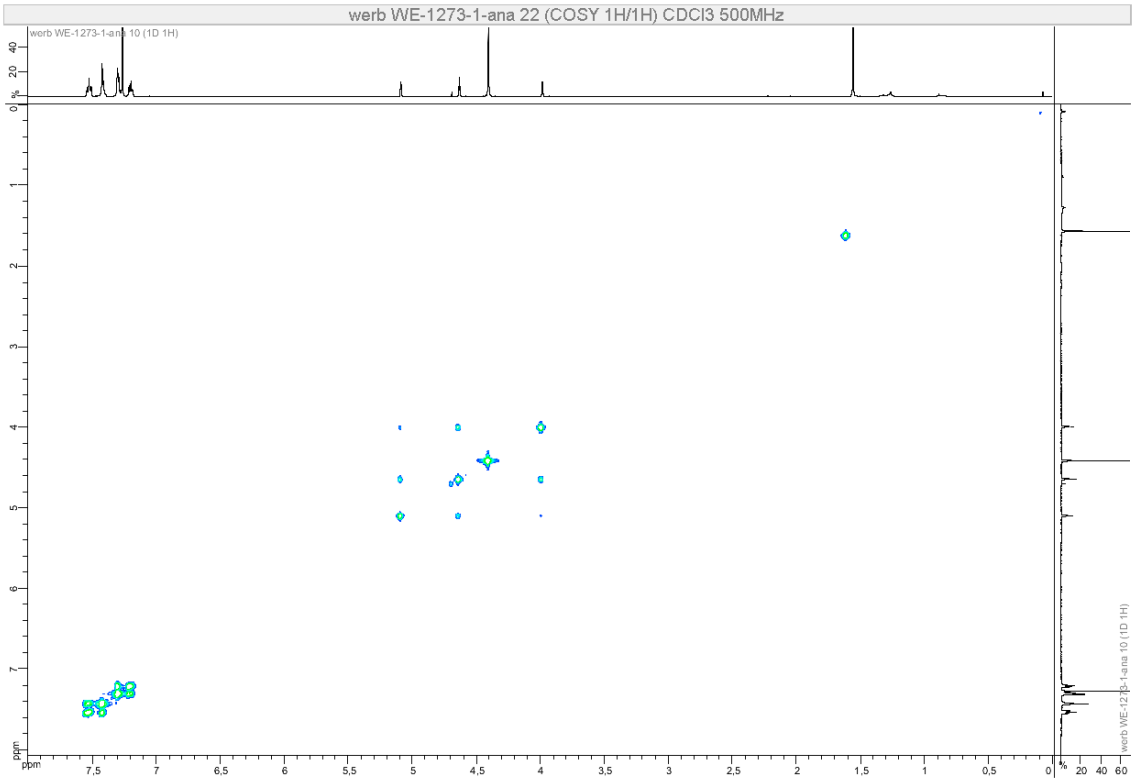
^{1}H NMR (500 MHz, $CDCl_3$)



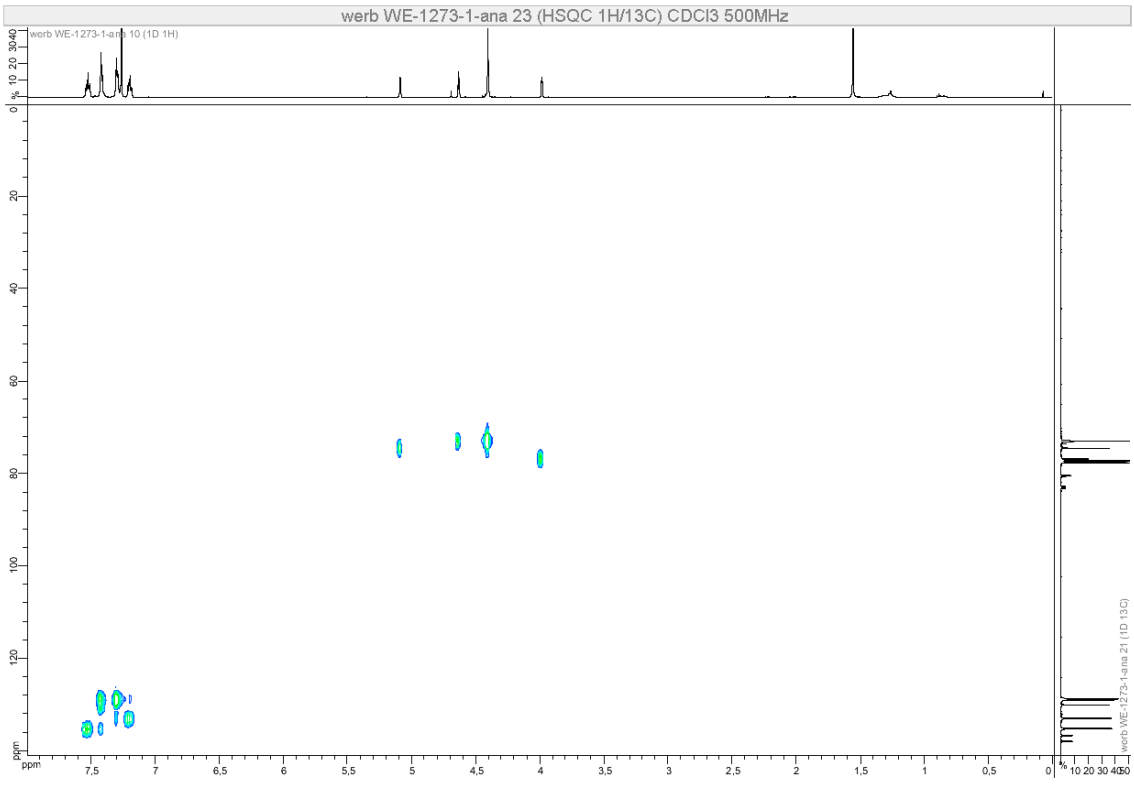
^{13}C NMR (126 MHz, $CDCl_3$)



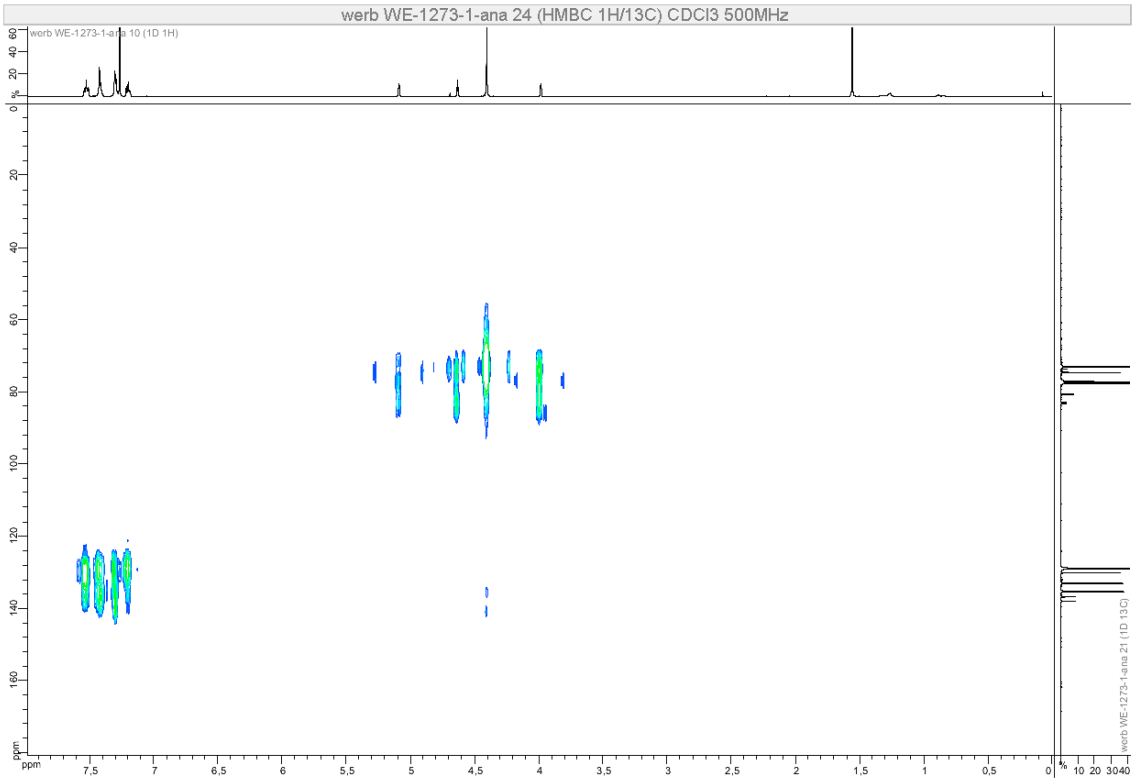
COSY (500 MHz, $CDCl_3$)



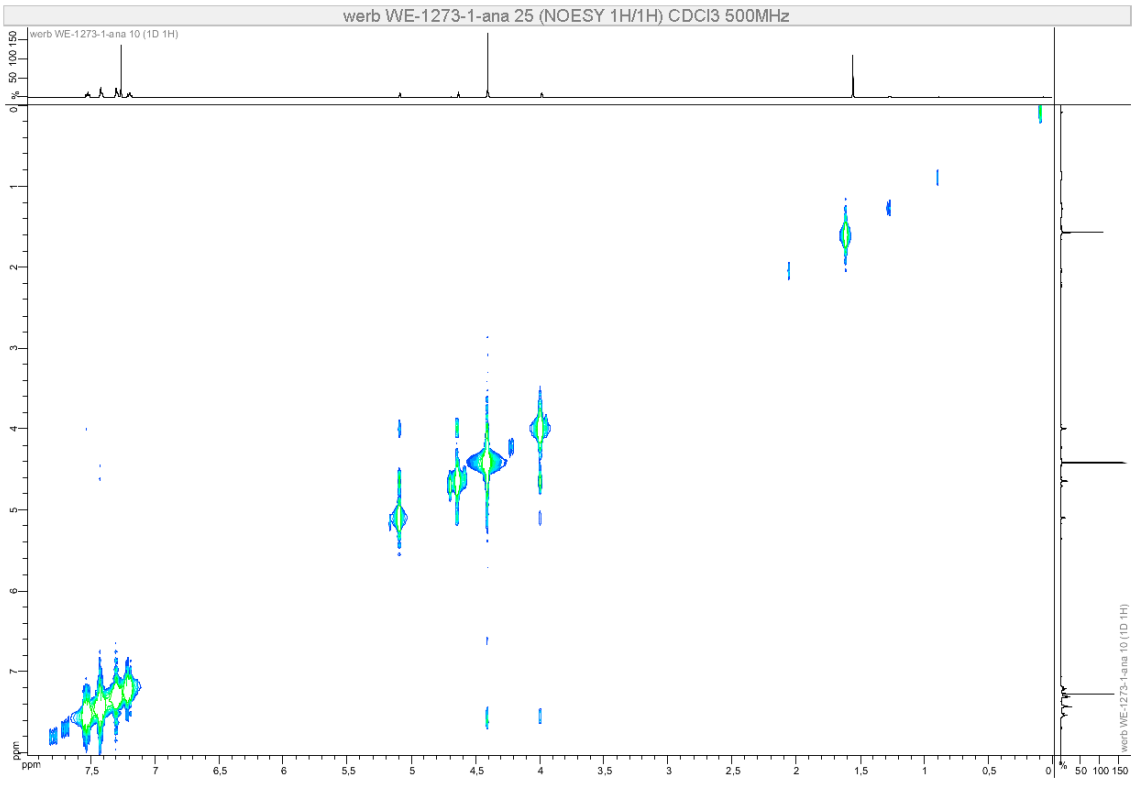
HSQC (500 MHz, $CDCl_3$)



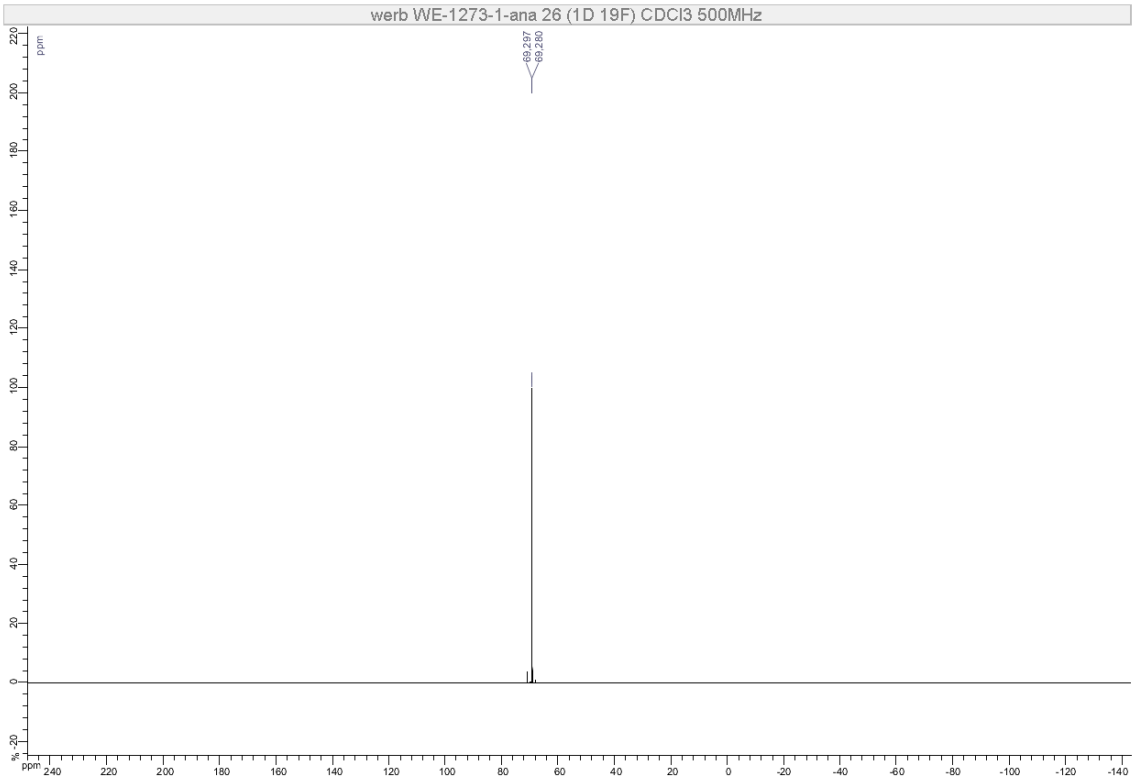
HMBC (500 MHz, $CDCl_3$)



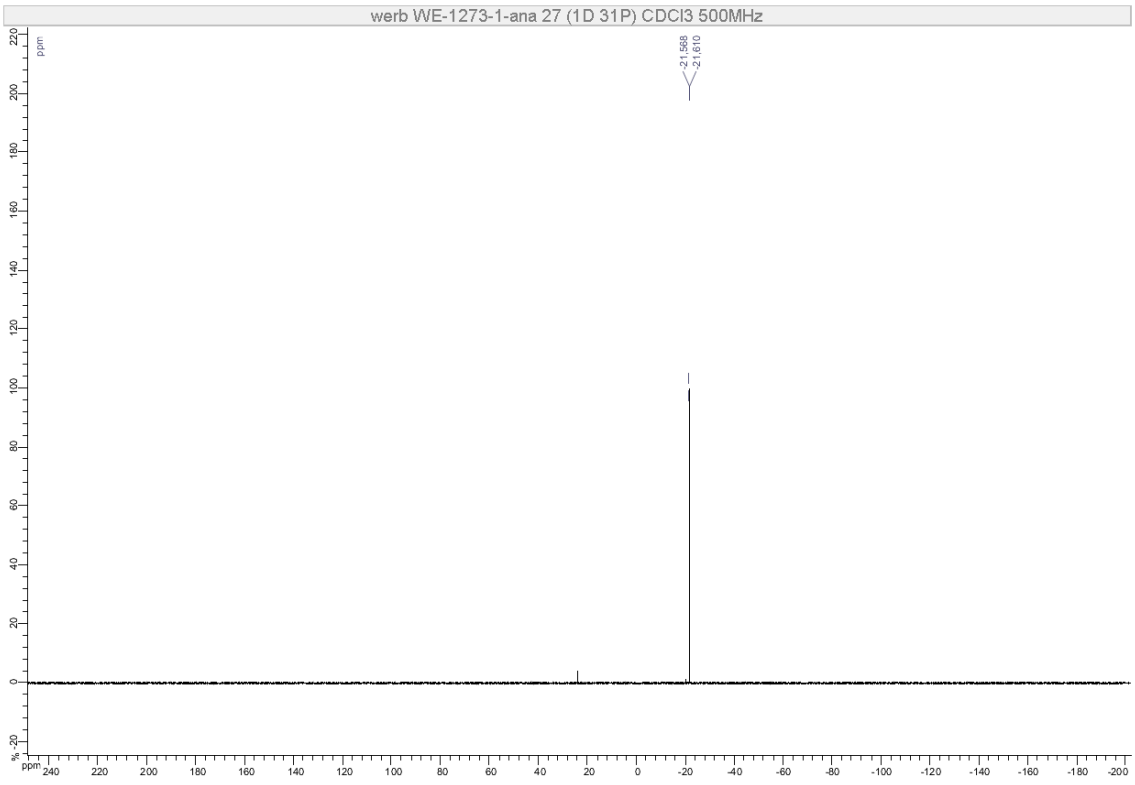
NOESY (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)

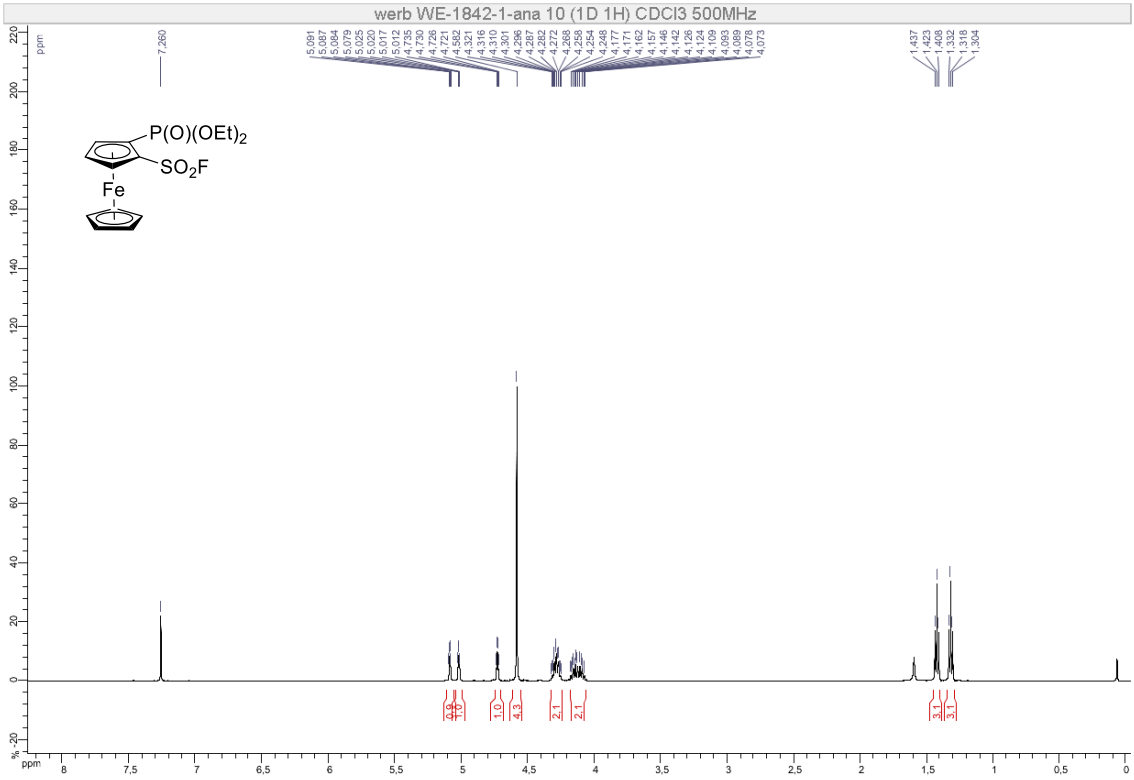


^{31}P NMR (202 MHz, $CDCl_3$)

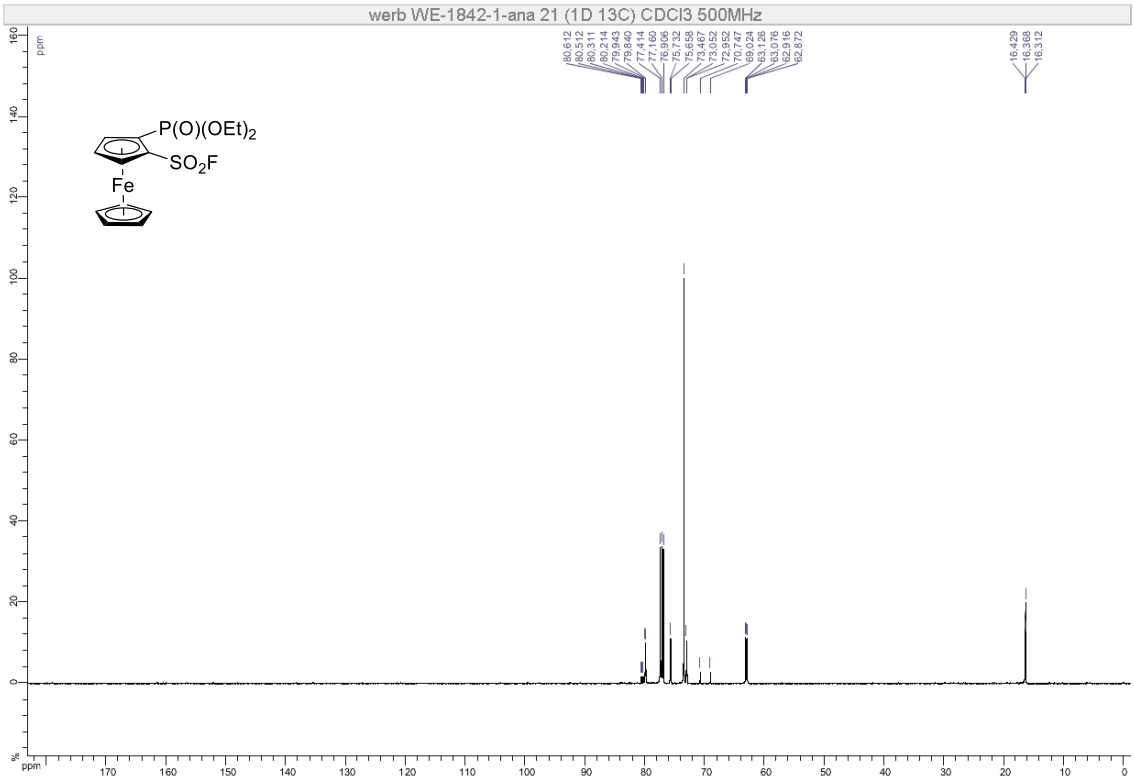


2-(*O,O*-Diethoxyphosphonyl)ferrocenesulfonyl fluoride (3d)

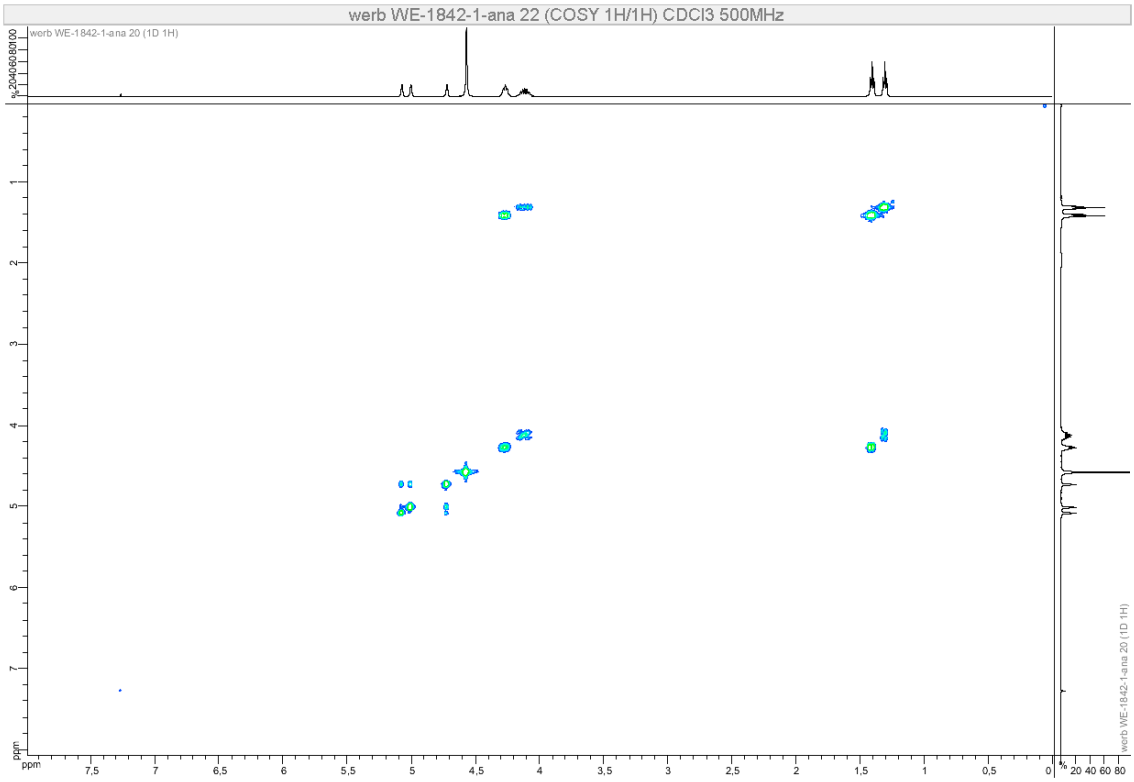
^{1}H NMR (500 MHz, $CDCl_3$)



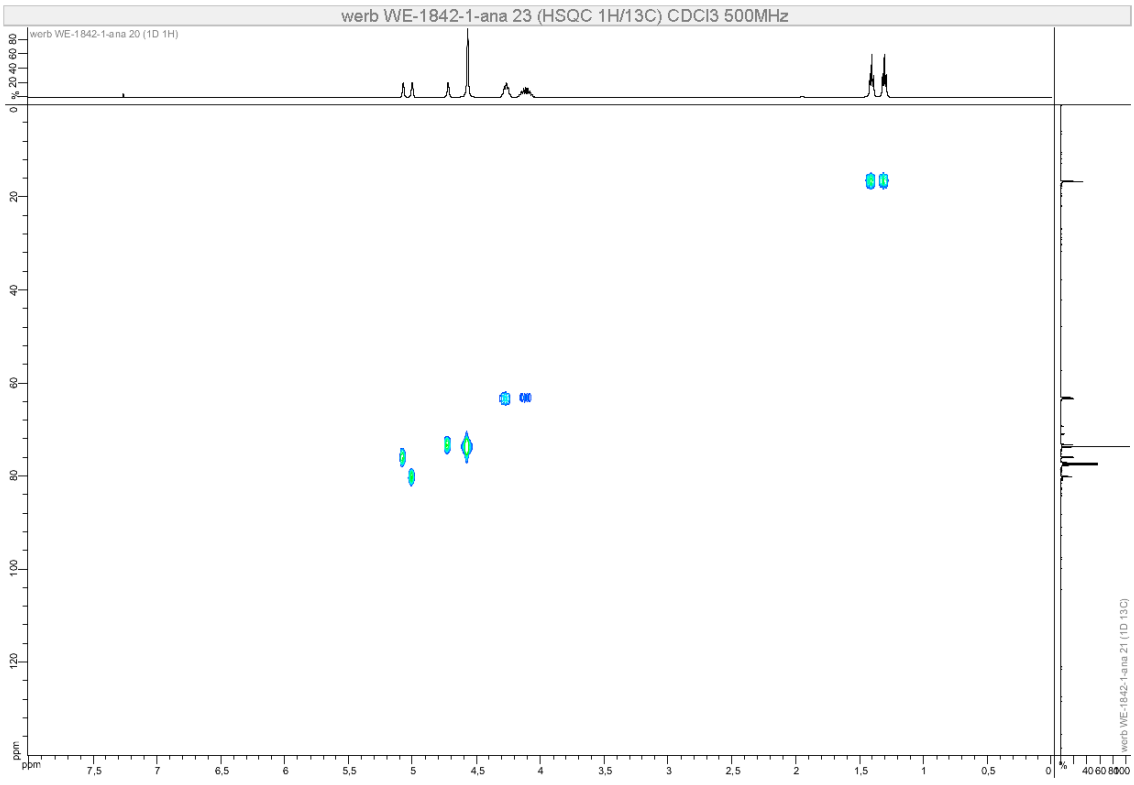
^{13}C NMR (125 MHz, $CDCl_3$)



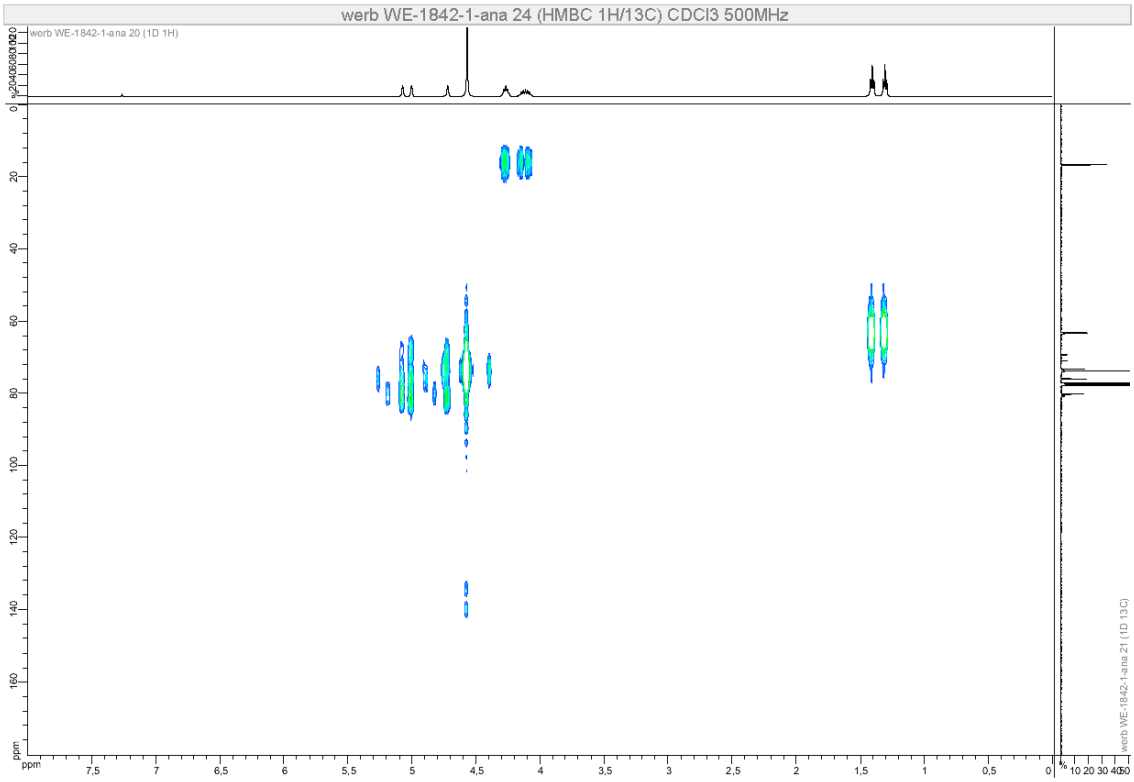
COSY (500 MHz, $CDCl_3$)



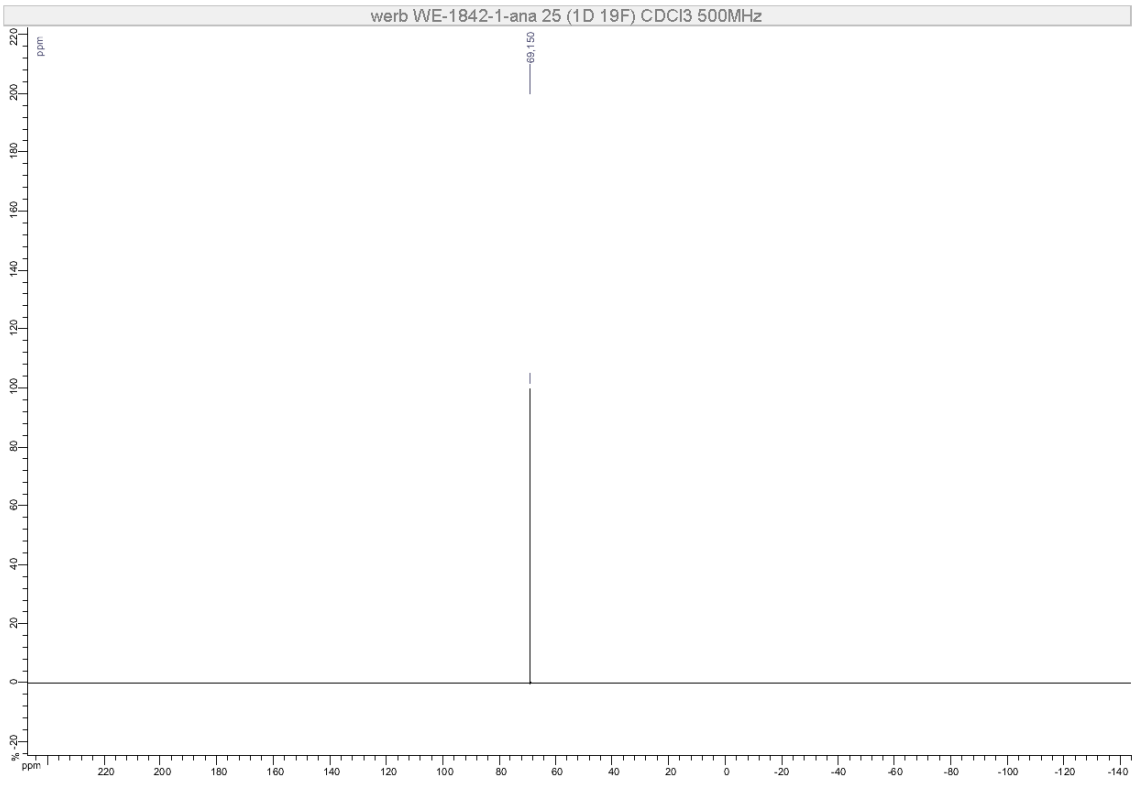
HSQC (500 MHz, $CDCl_3$)



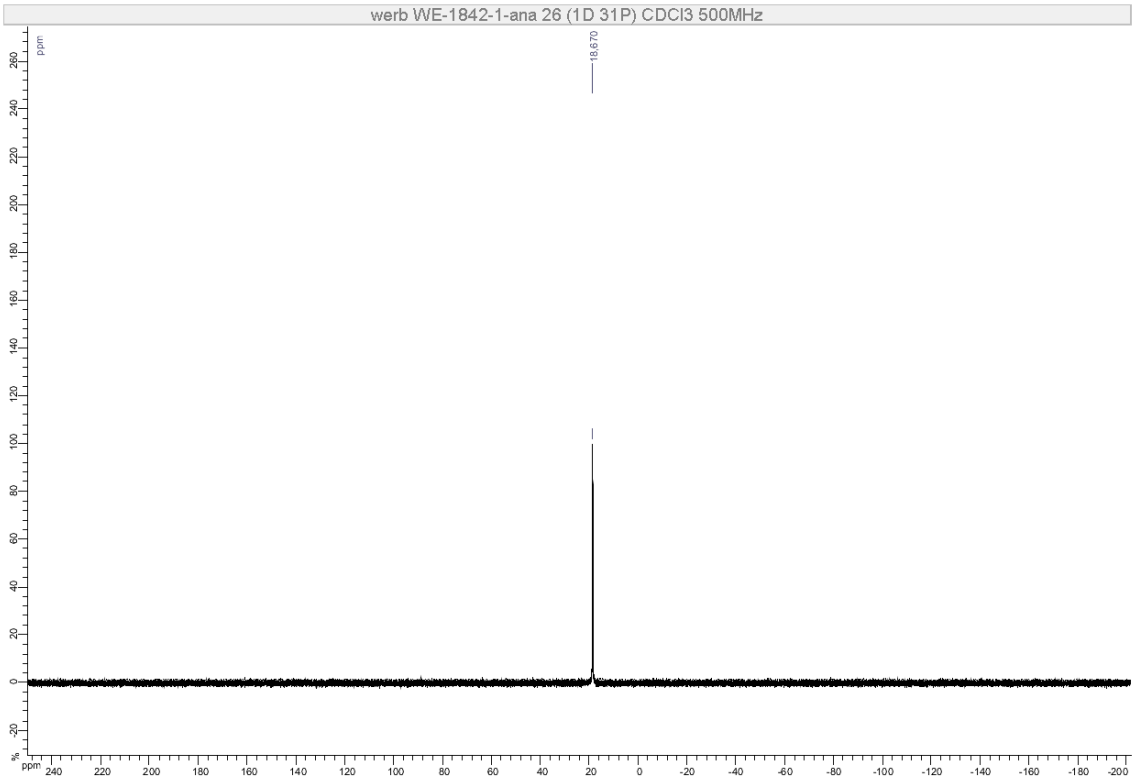
HMBC (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)

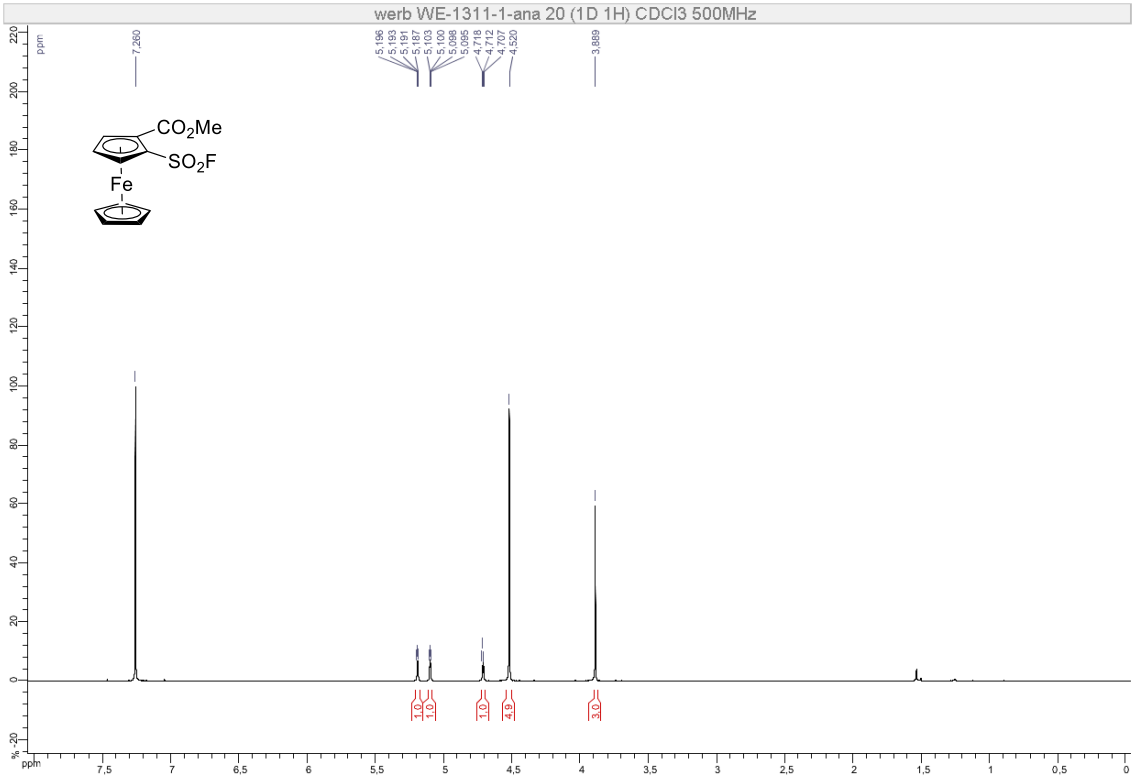


^{31}P NMR (202 MHz, $CDCl_3$)

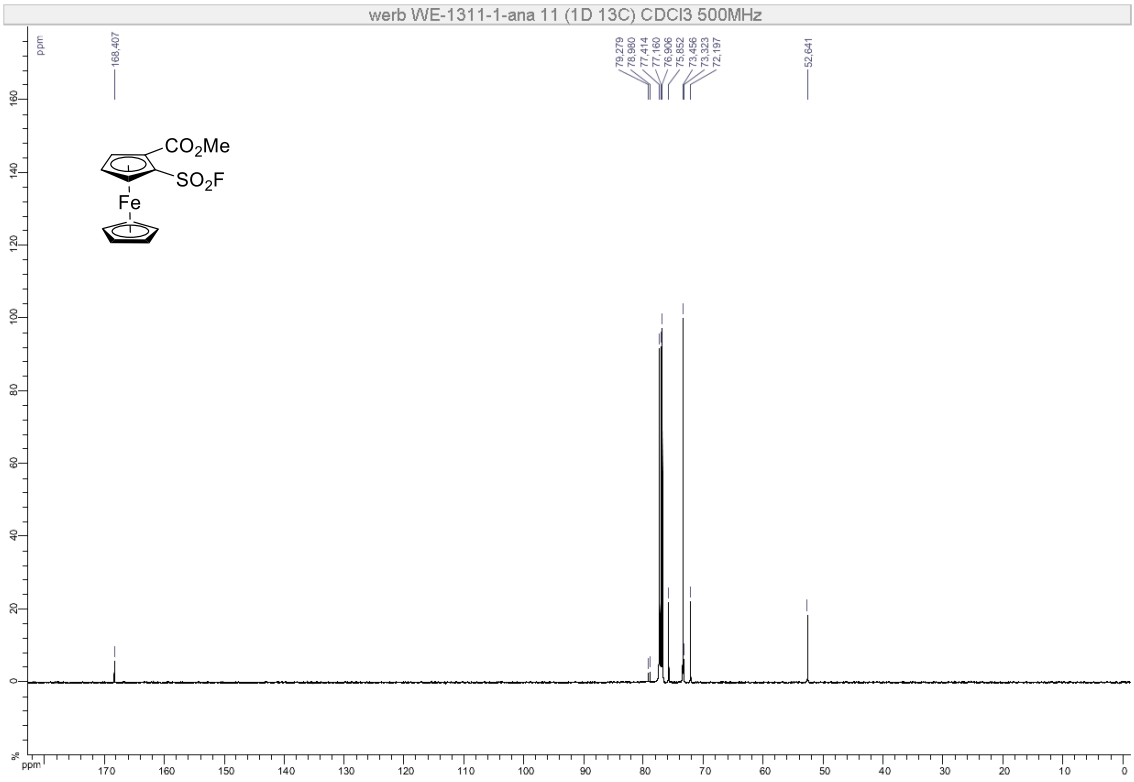


2-(Methoxycarbonyl)ferrocenesulfonyl fluoride (3g)

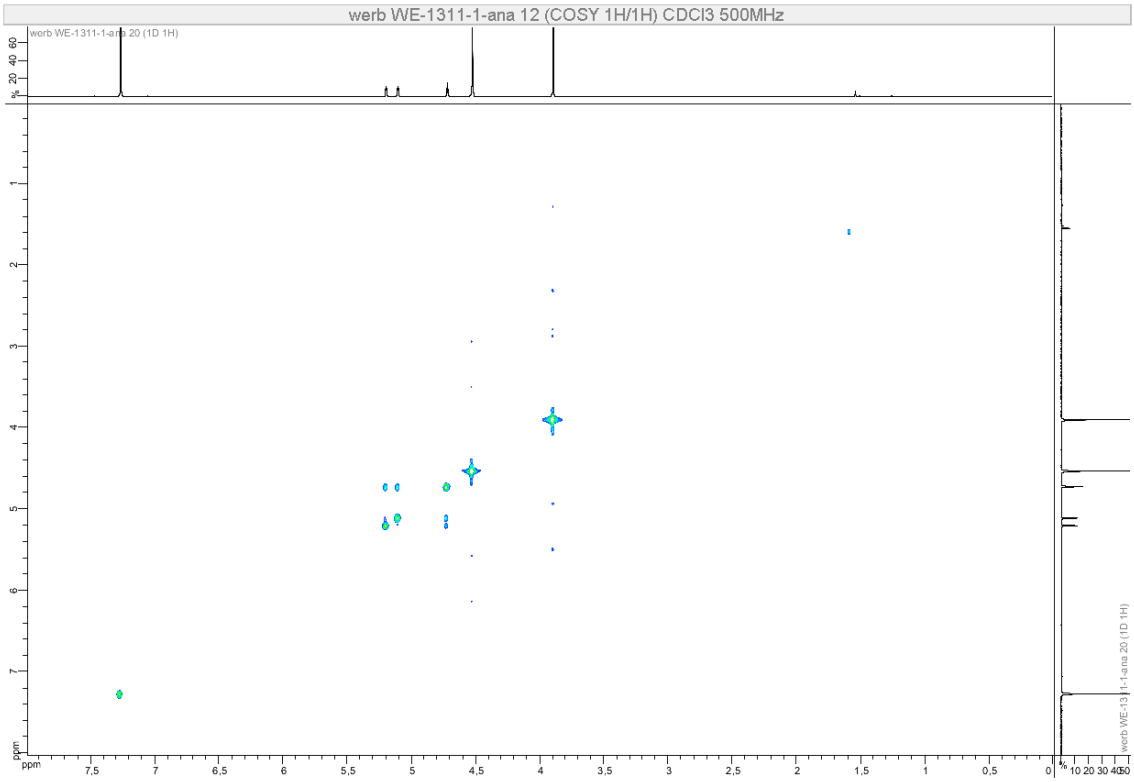
^{1}H NMR (500 MHz, $CDCl_3$)



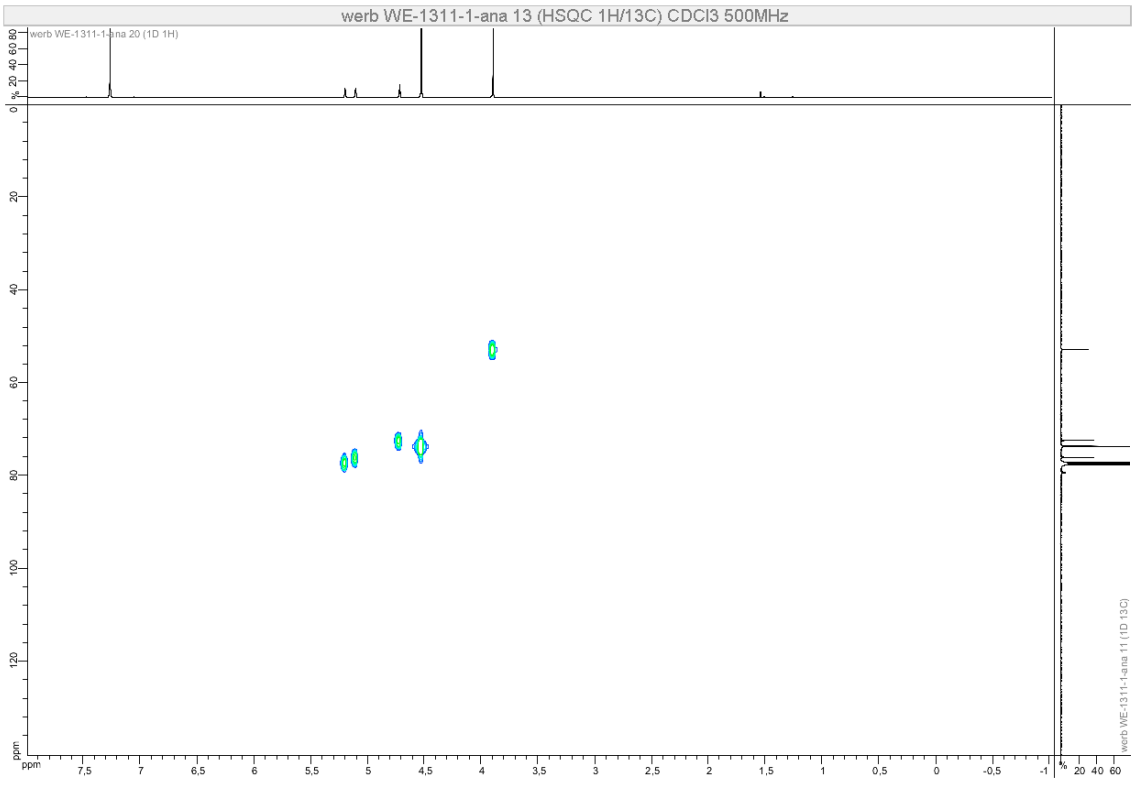
^{13}C NMR (125 MHz, $CDCl_3$)



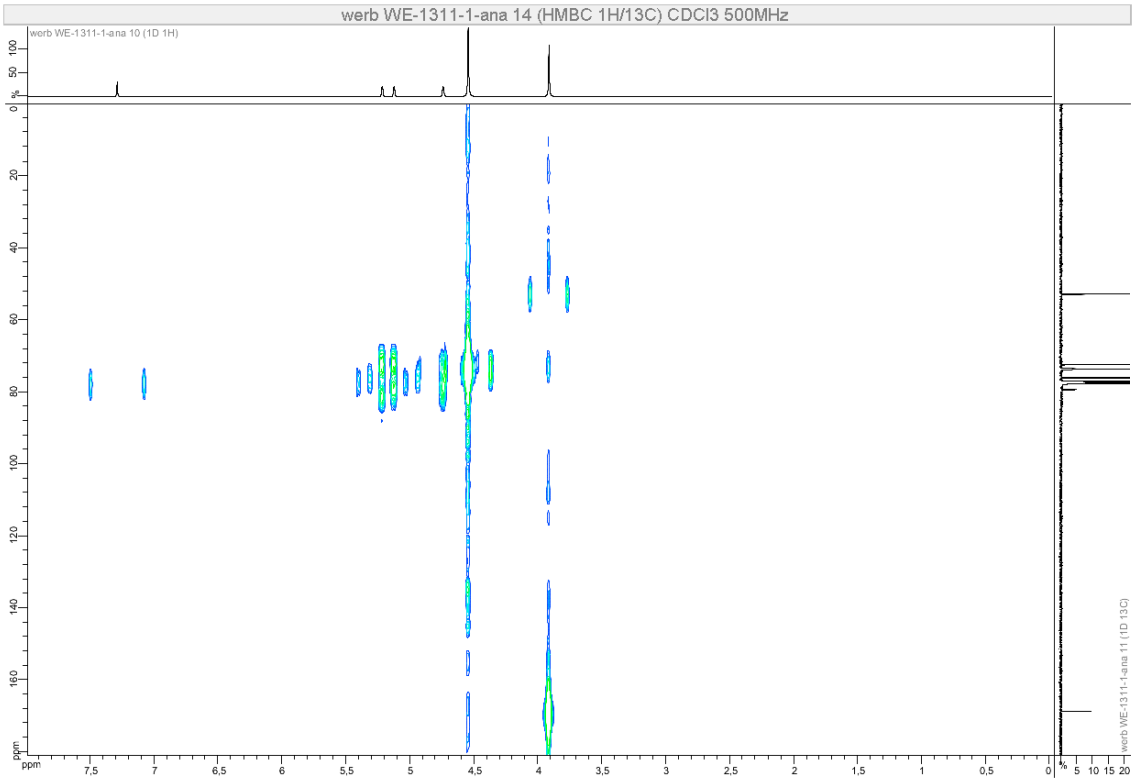
COSY (500 MHz, $CDCl_3$)



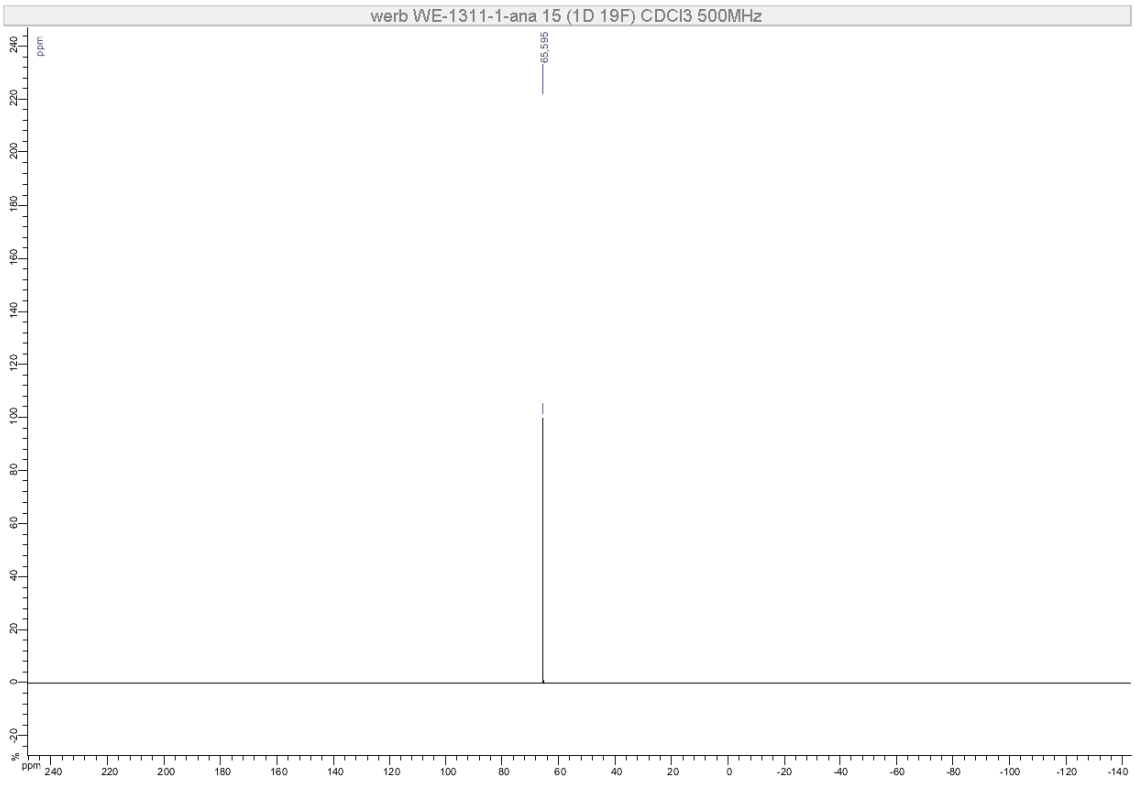
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

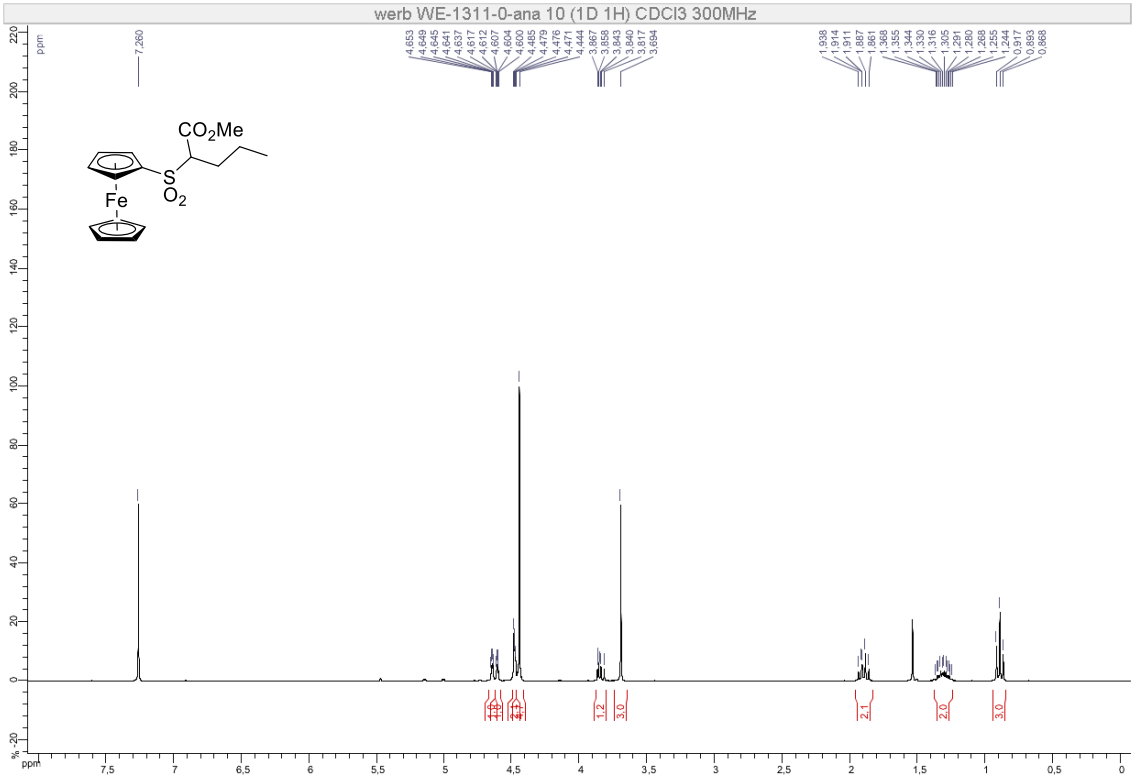


^{19}F NMR (470 MHz, $CDCl_3$)

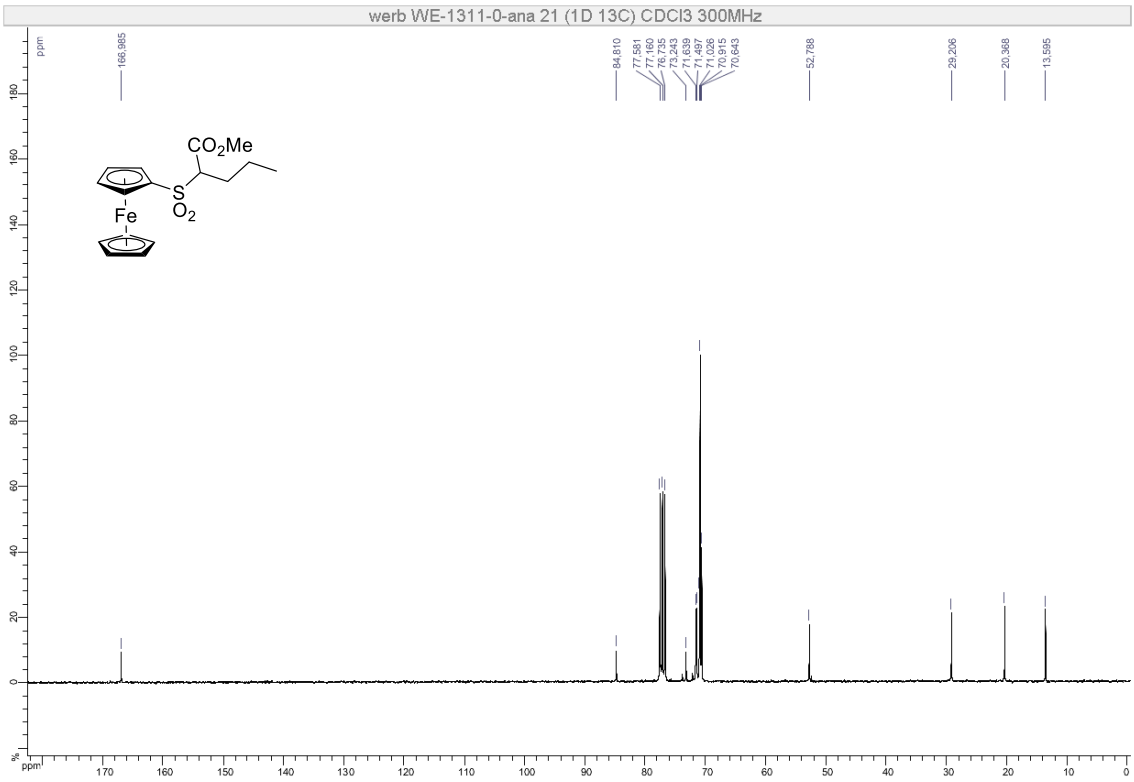


1-(Methoxycarbonyl)butylsulfonylferrocene (4b)

^{1}H NMR (300 MHz, $CDCl_3$)

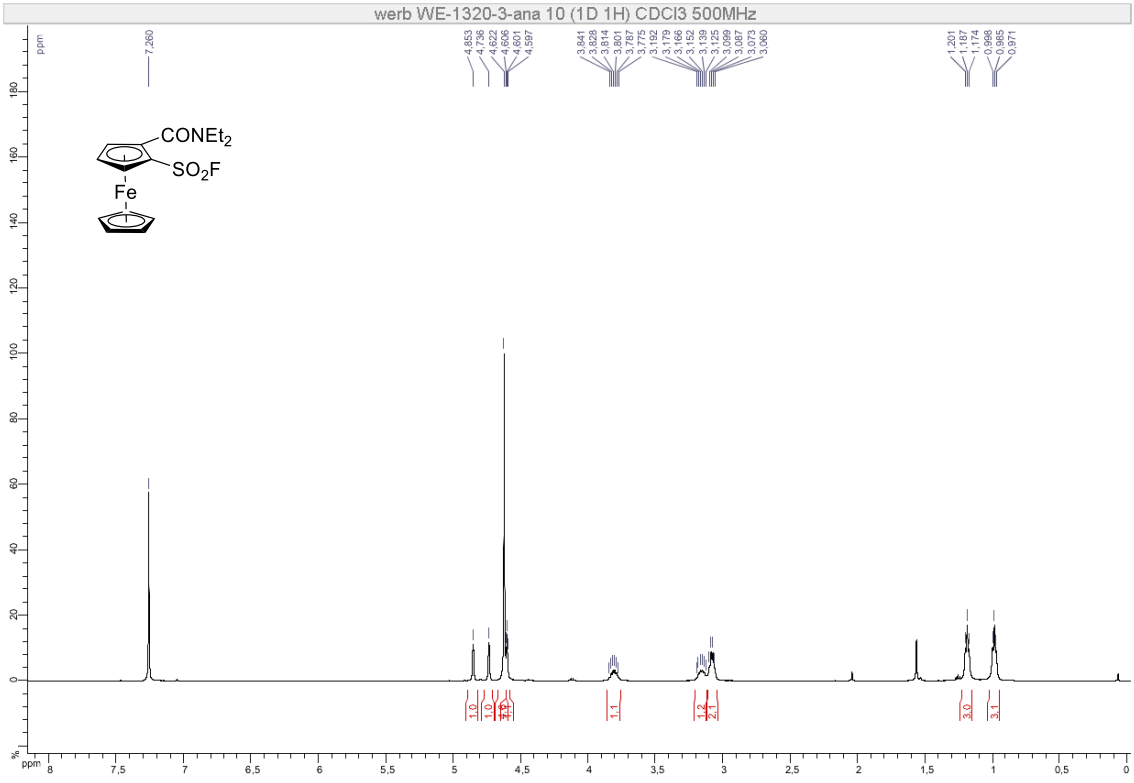


^{13}C NMR (75 MHz, $CDCl_3$)

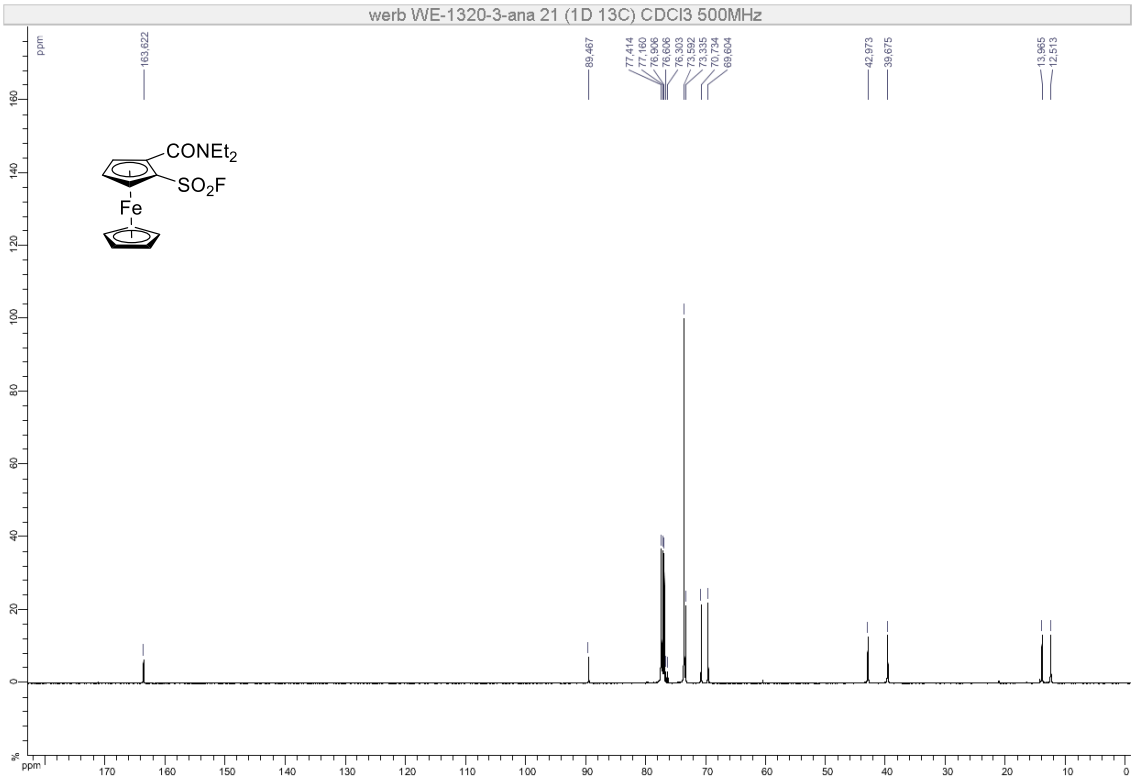


2-(*N*,*N*-Diethylcarbamoyl)ferrocenesulfonyl fluoride (3h)

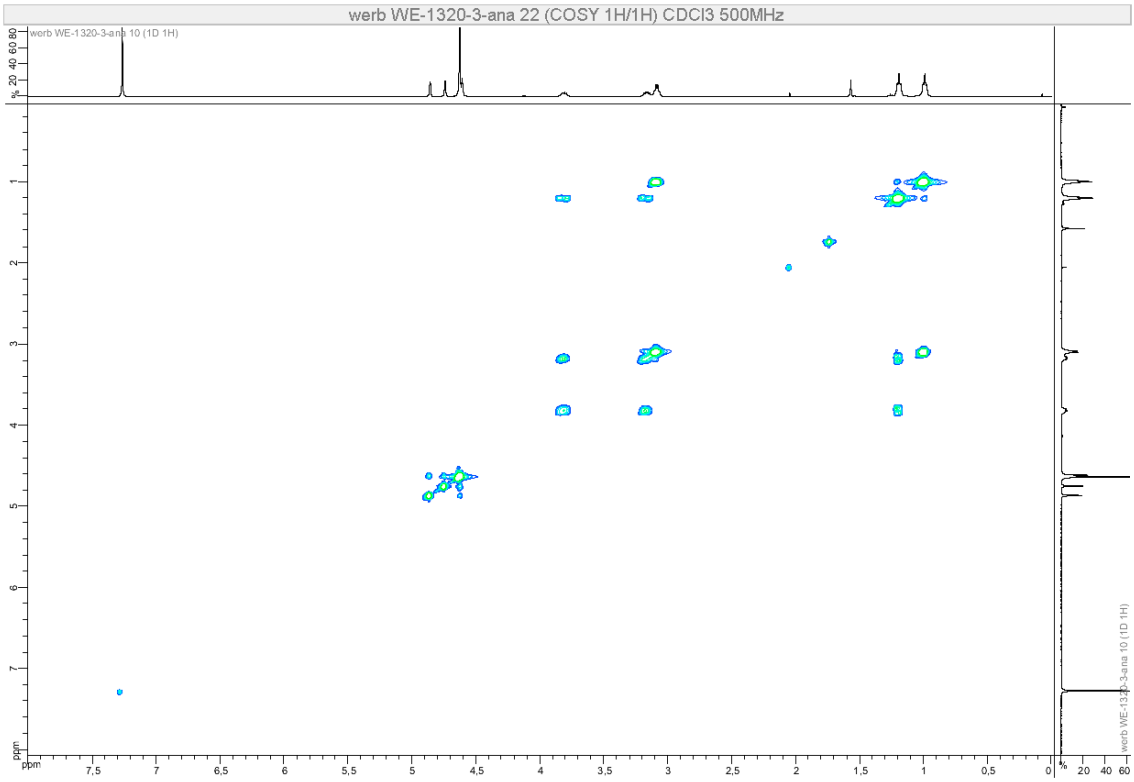
^{1}H NMR (500 MHz, $CDCl_3$)



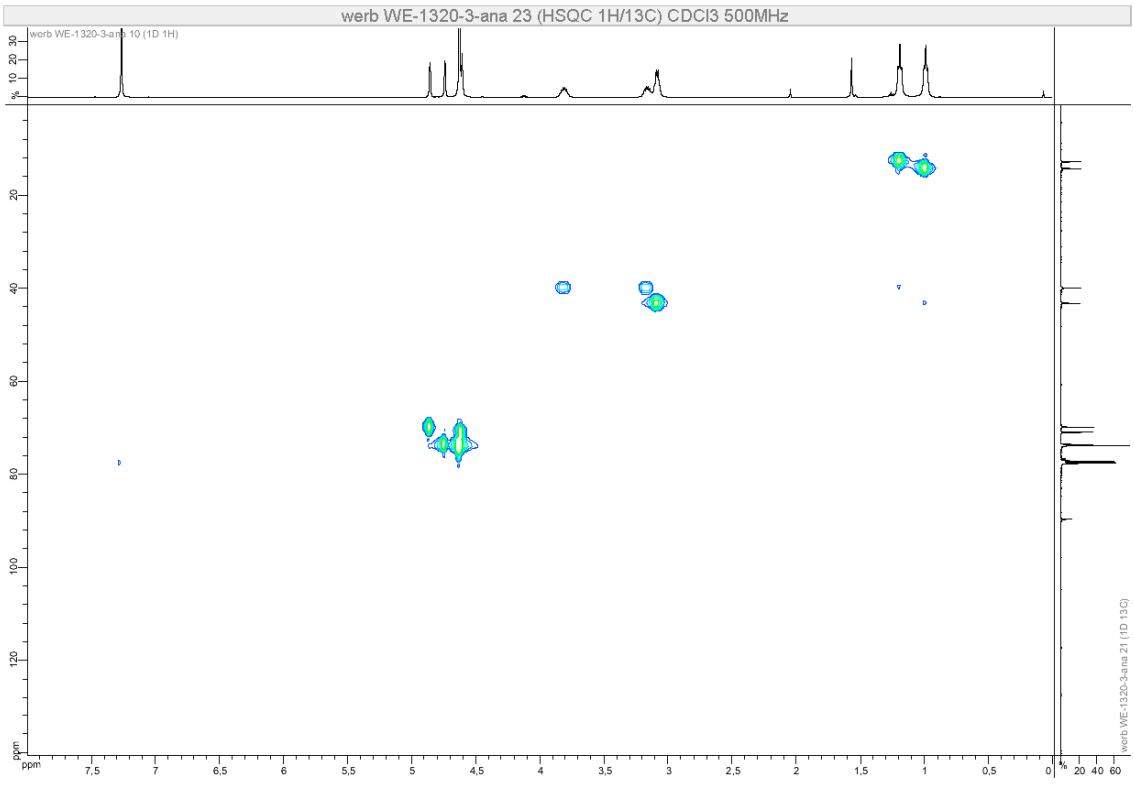
^{13}C NMR (125 MHz, $CDCl_3$)



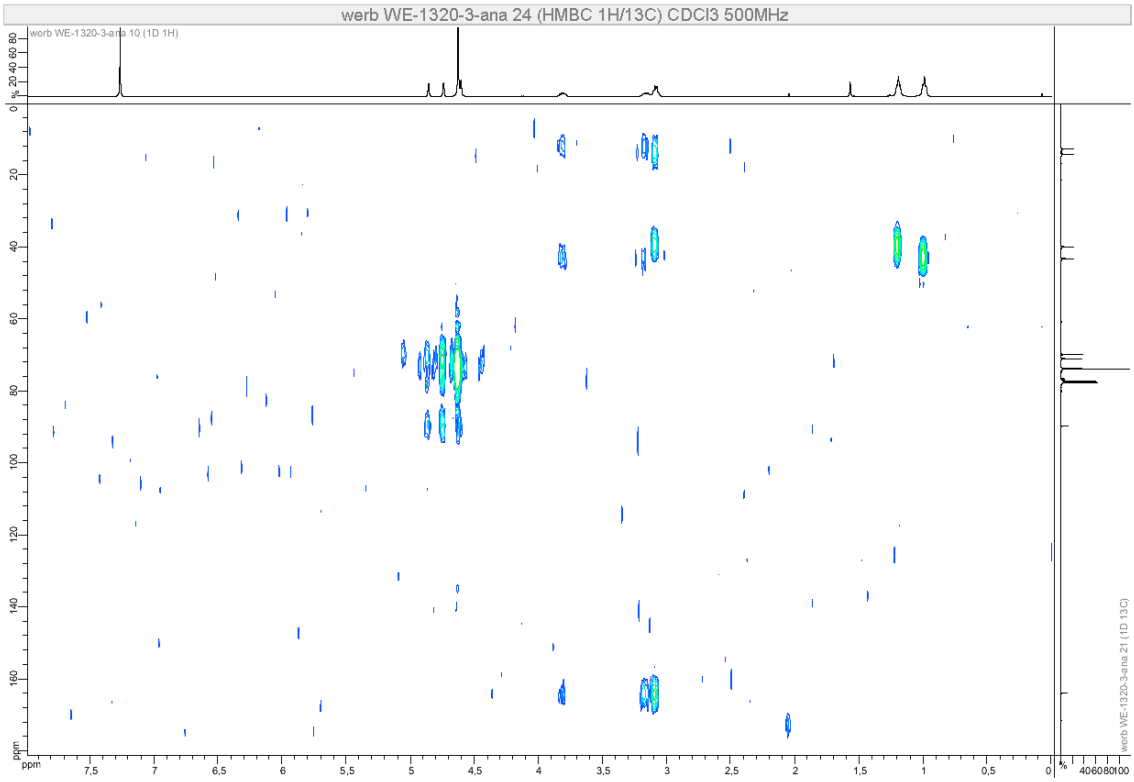
COSY (500 MHz, $CDCl_3$)



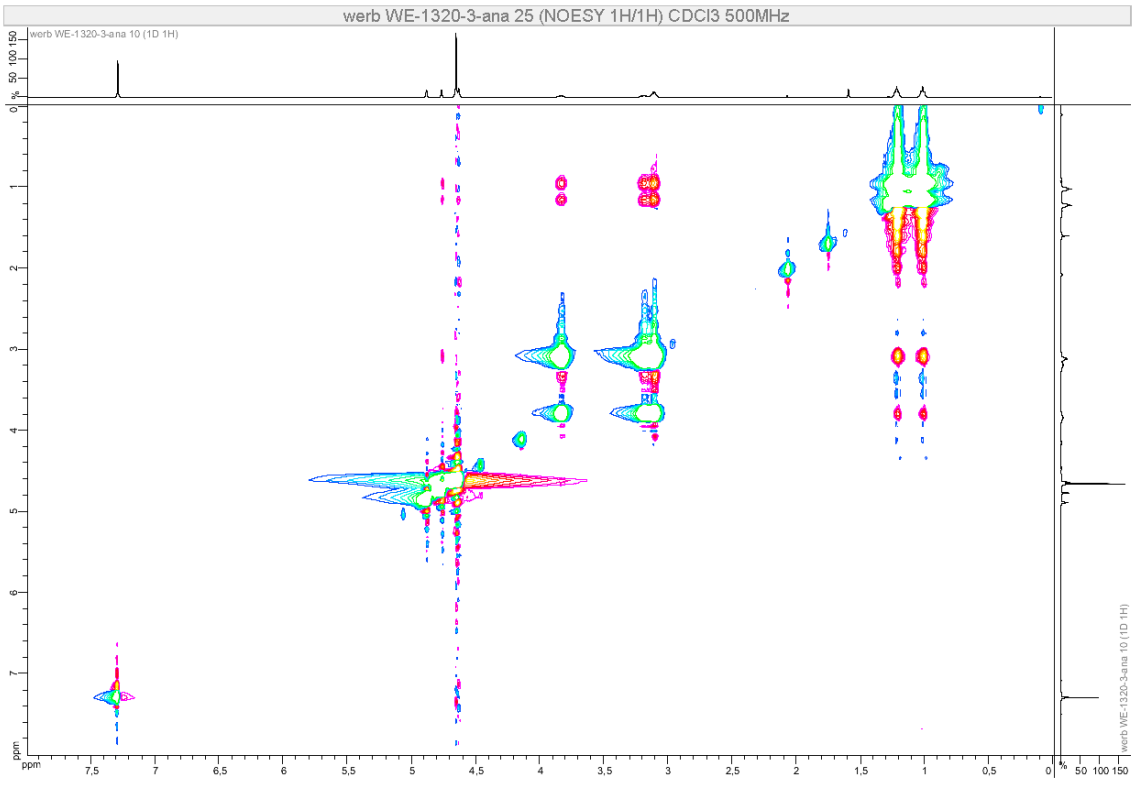
HSQC (500 MHz, $CDCl_3$)



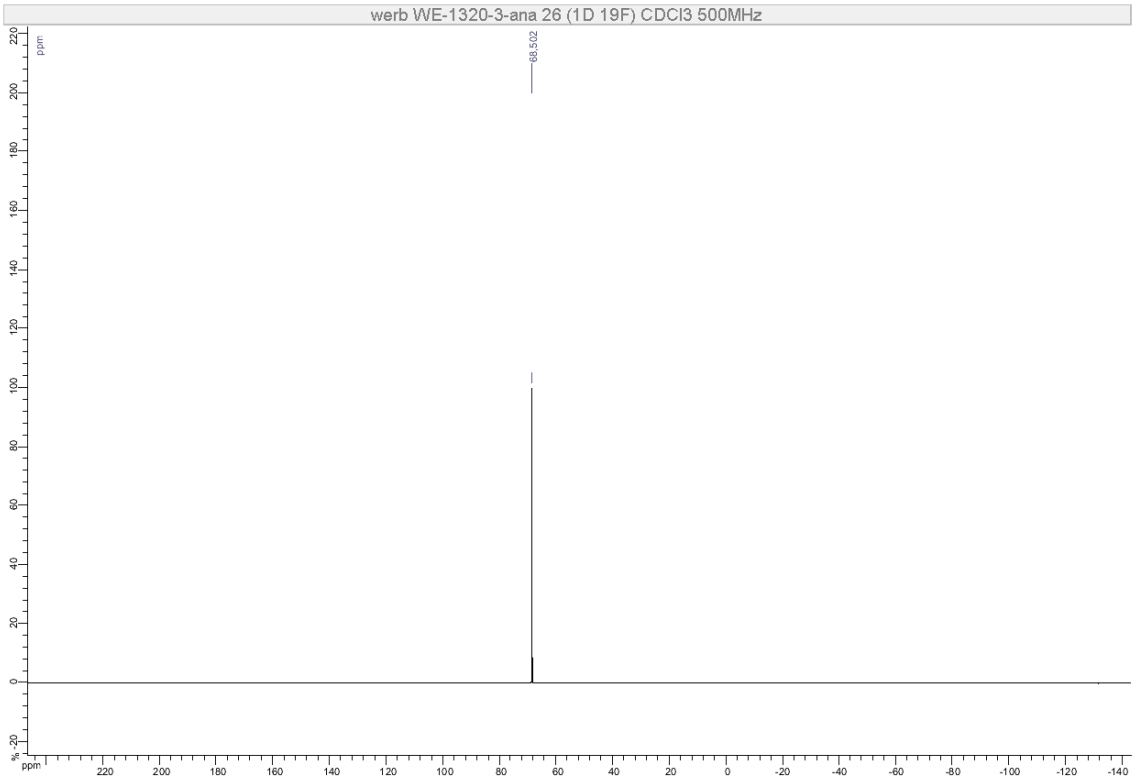
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

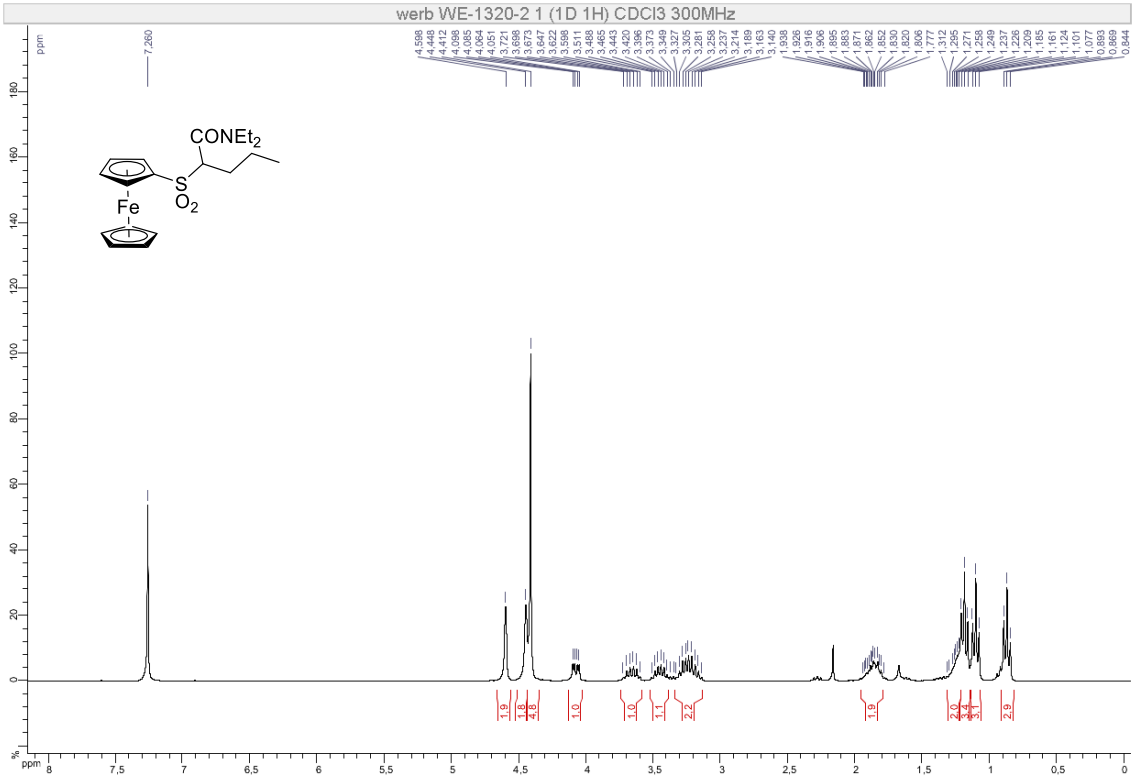


^{19}F NMR (470 MHz, $CDCl_3$)



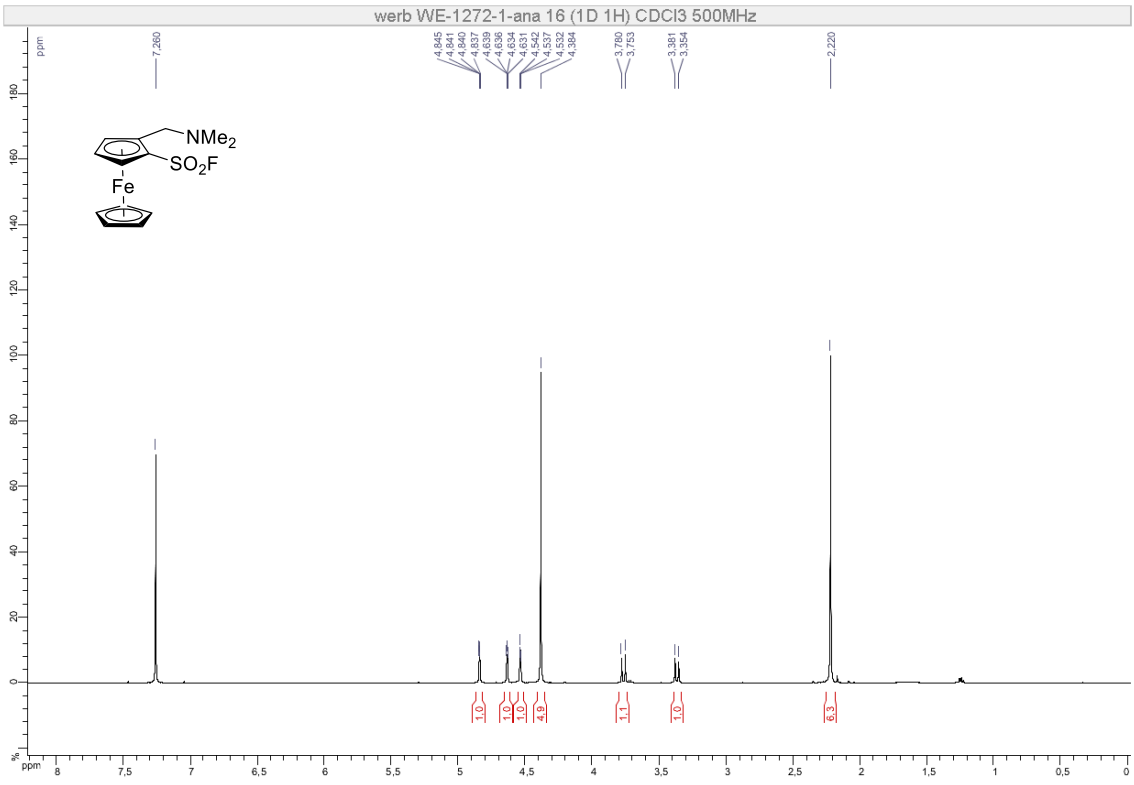
1-(*N*,*N*-Diethylcarbamoyl)butylsulfonylferrocene (4c)

^{1}H NMR (300 MHz, $CDCl_3$)

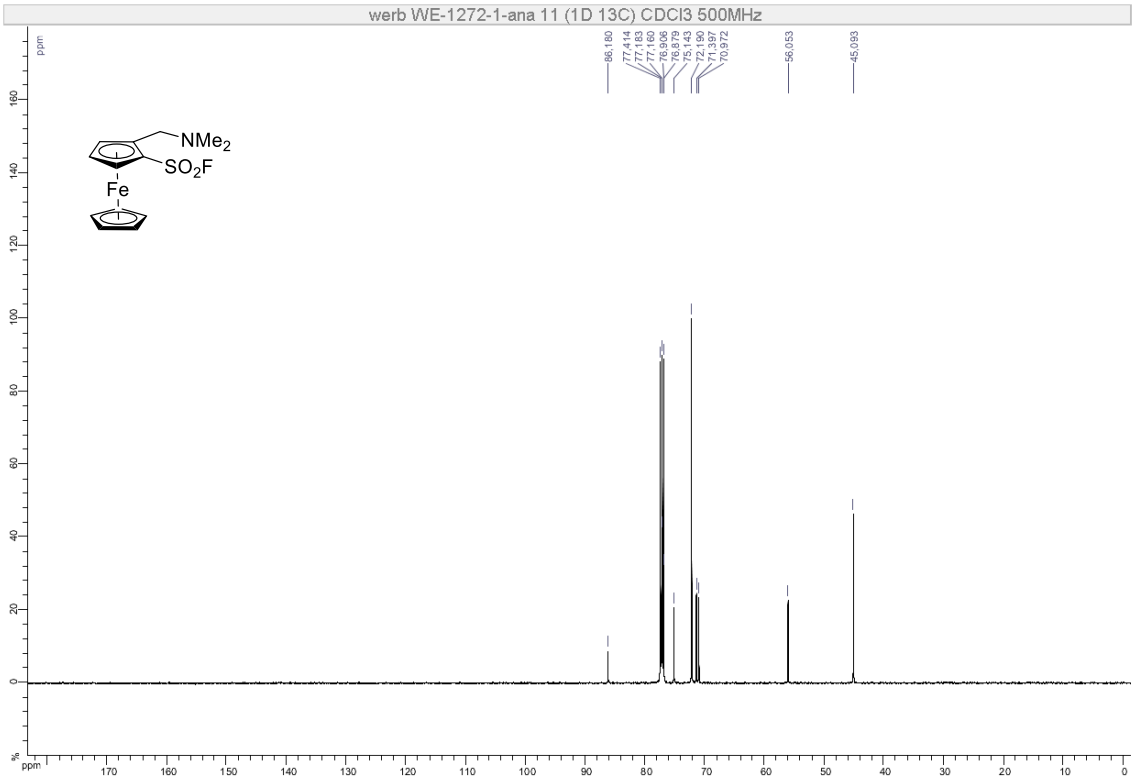


2-(*N*,*N*-Dimethylaminomethyl)ferrocenesulfonyl fluoride (3i)

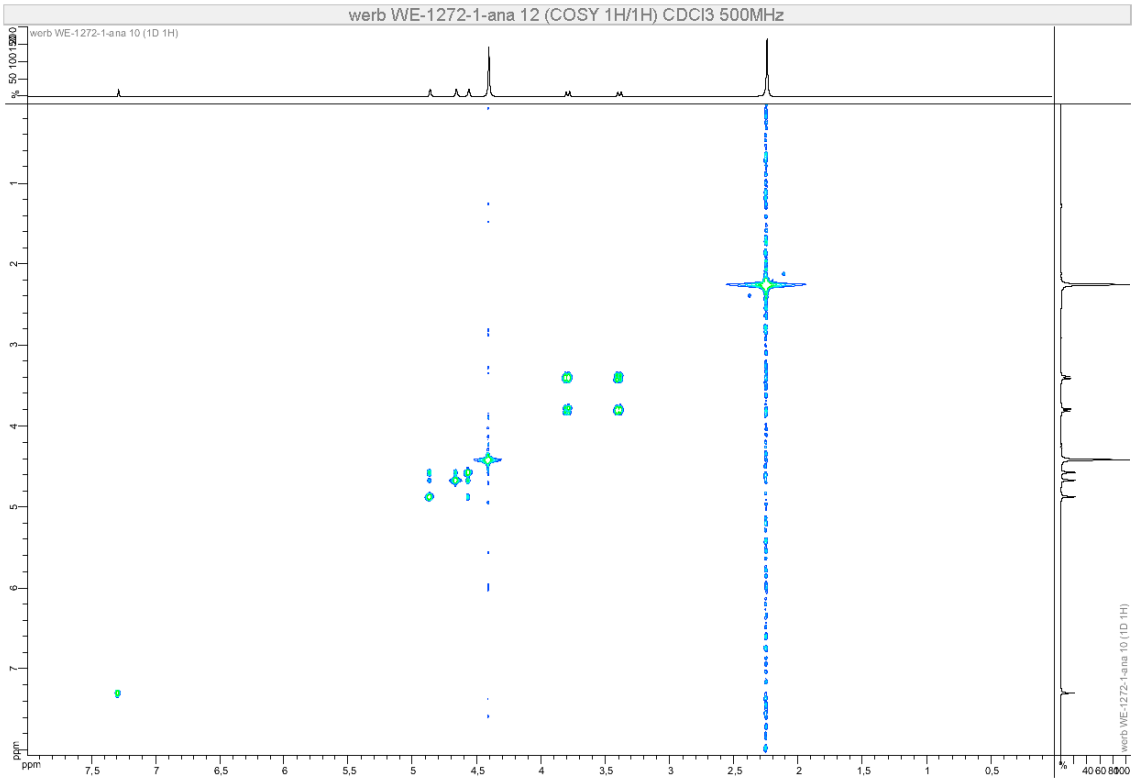
^{1}H NMR (500 MHz, $CDCl_3$)



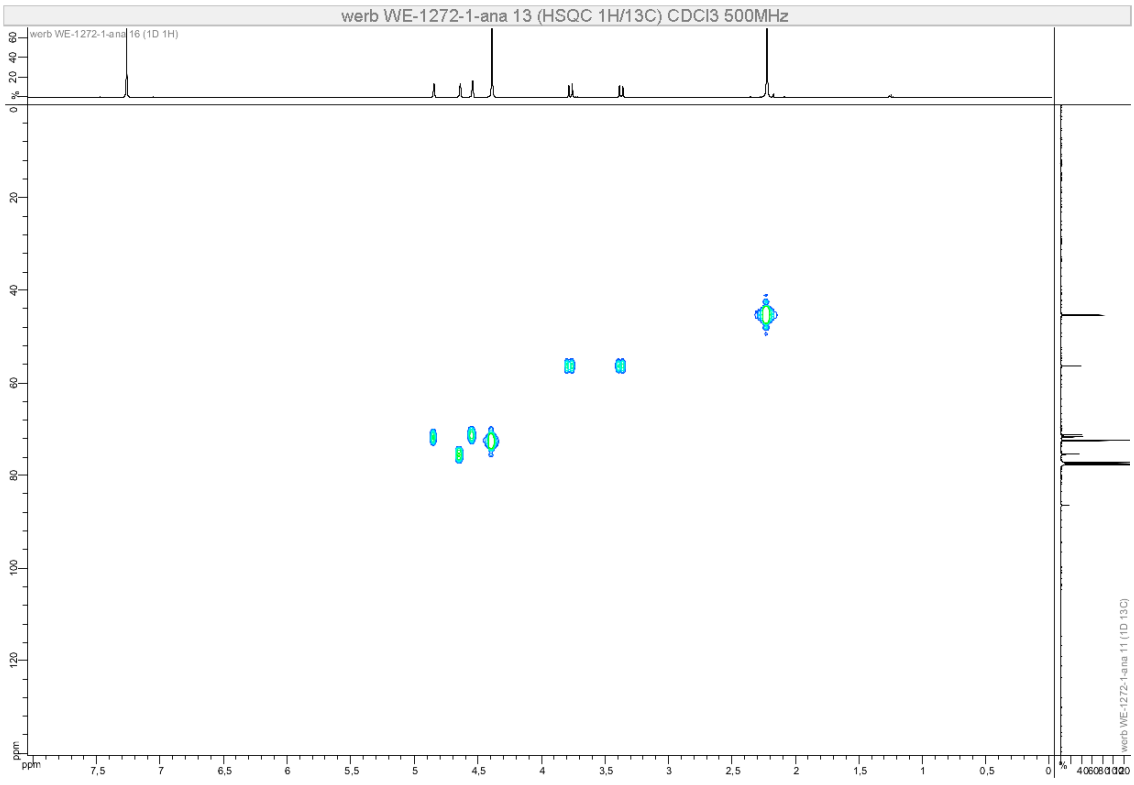
^{13}C NMR (125 MHz, $CDCl_3$)



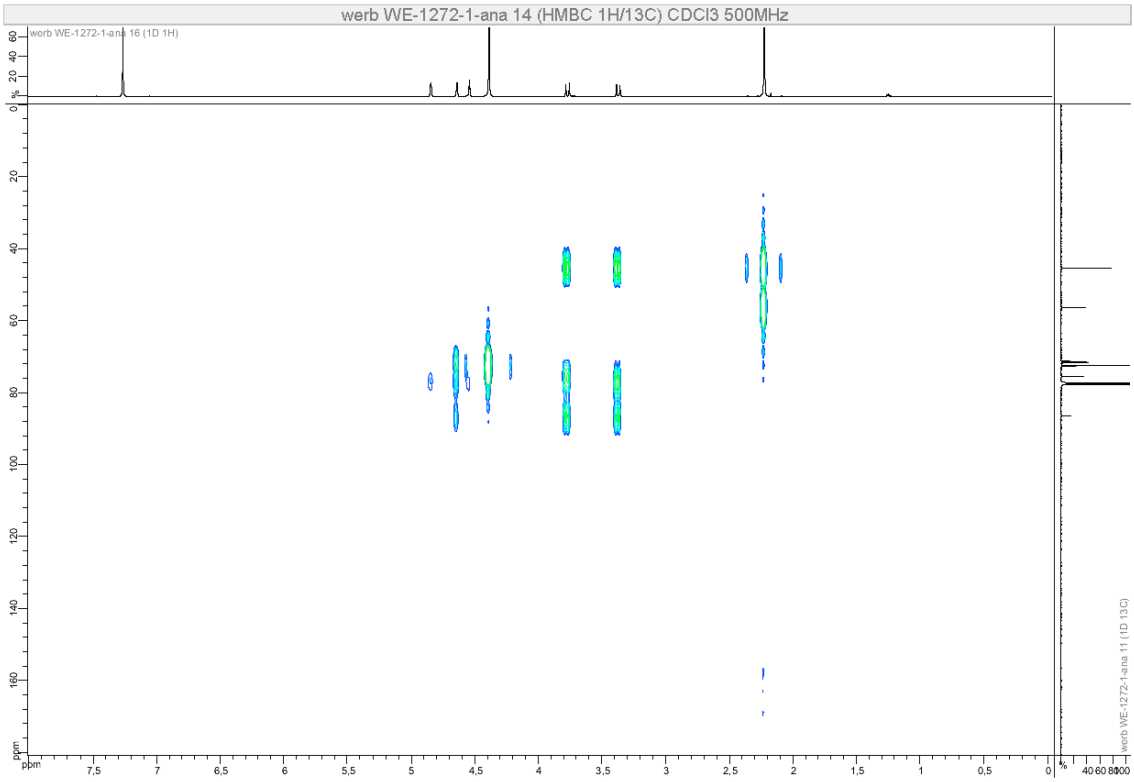
COSY (500 MHz, $CDCl_3$)



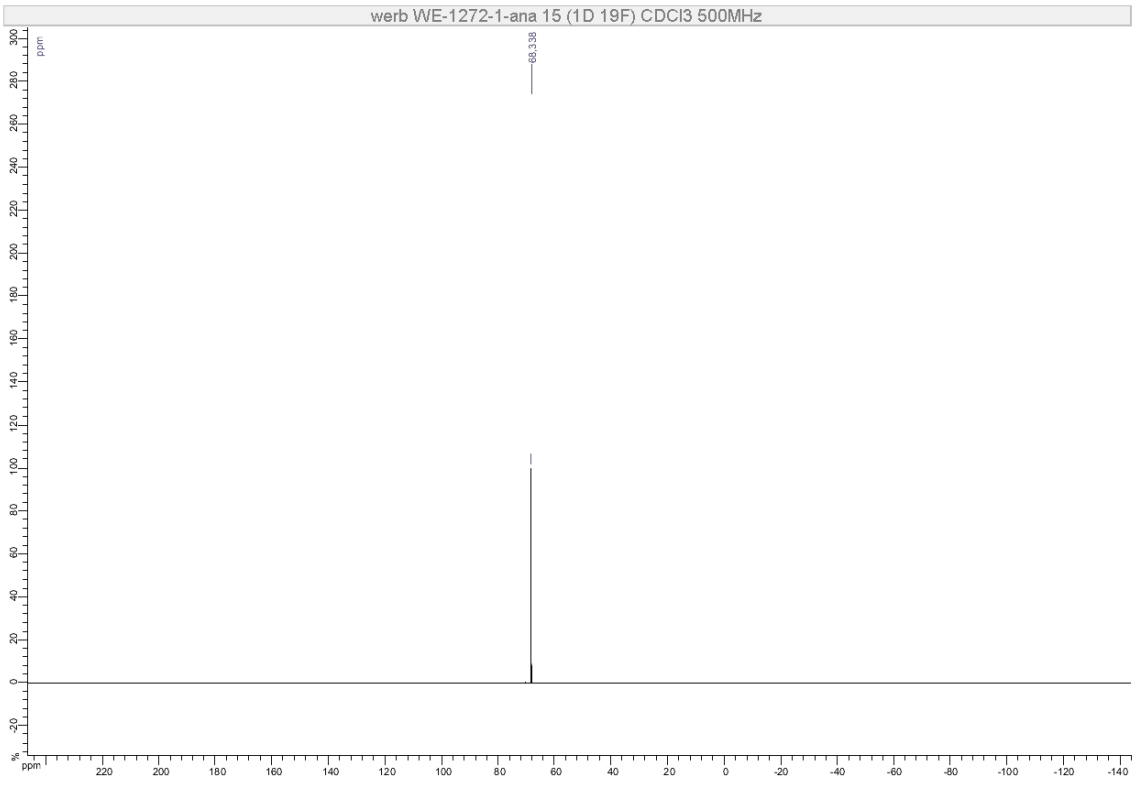
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

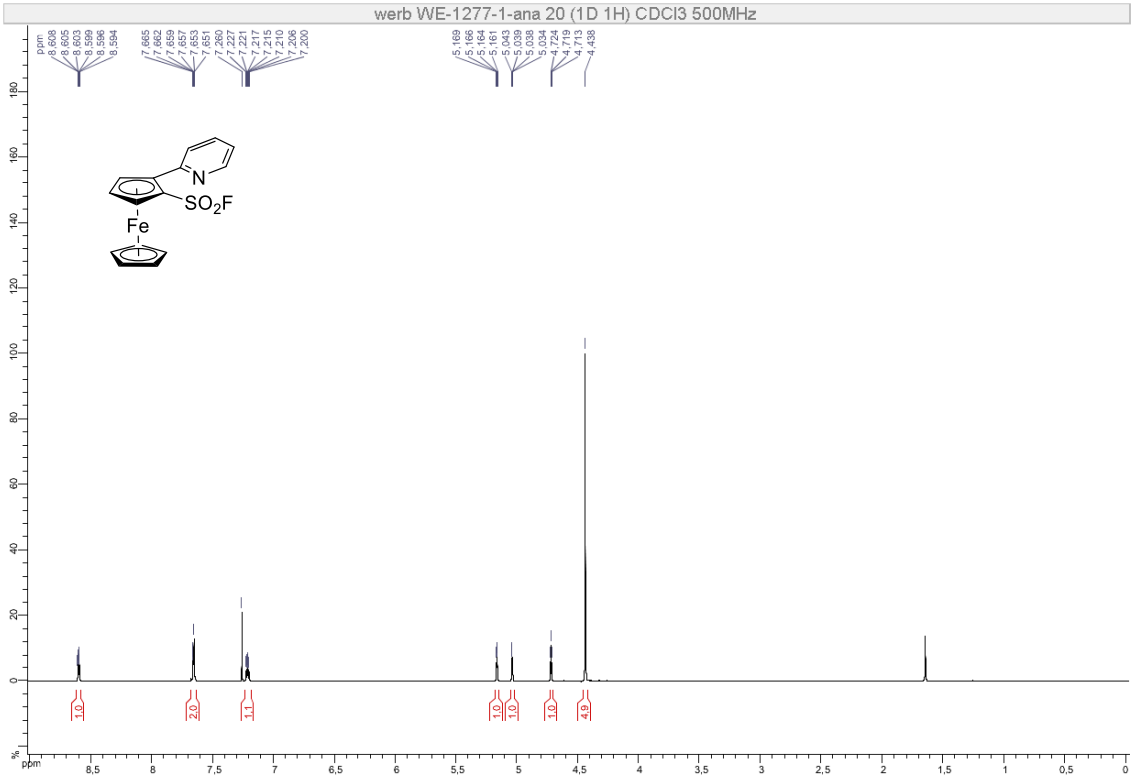


^{19}F NMR (470 MHz, $CDCl_3$)

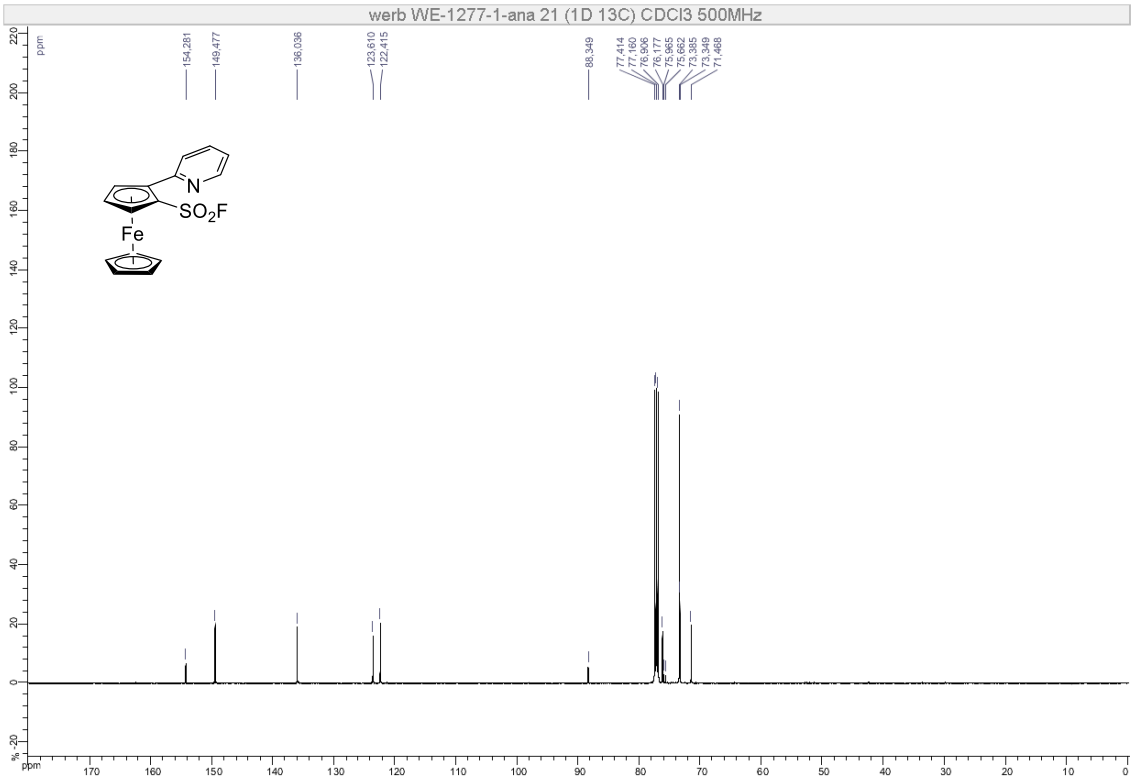


2-(2-Pyridyl)ferrocenesulfonyl fluoride (3k)

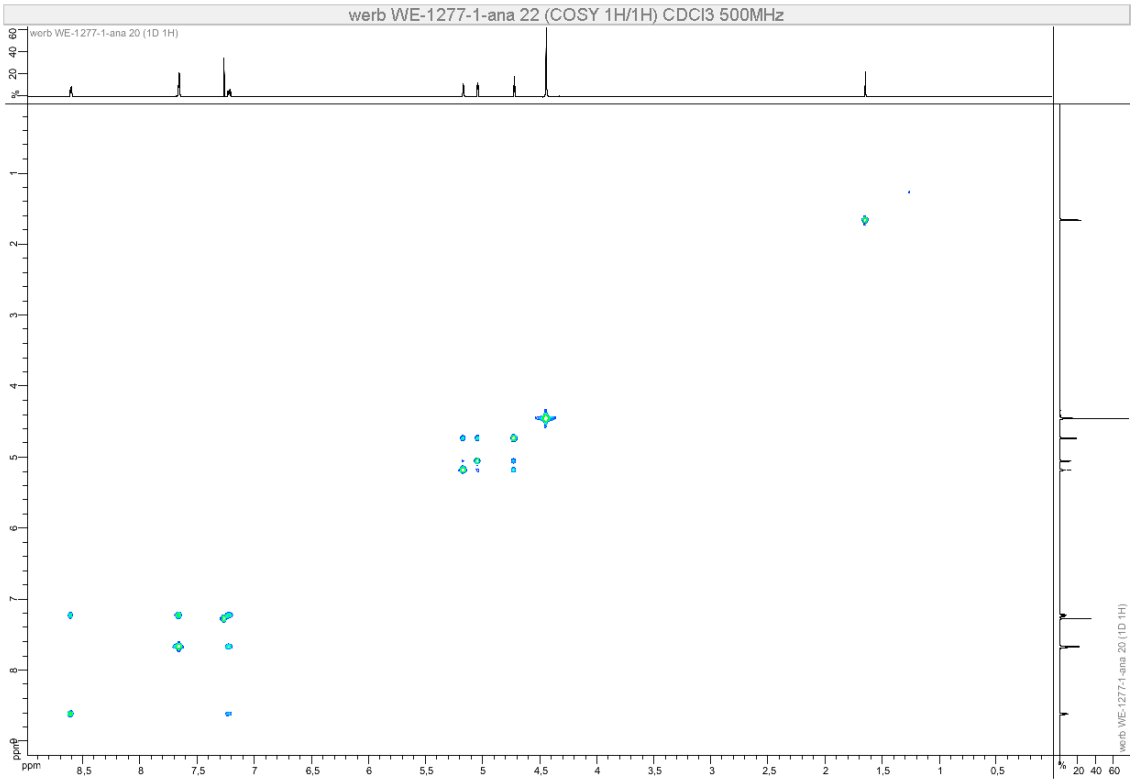
^{1}H NMR (500 MHz, $CDCl_3$)



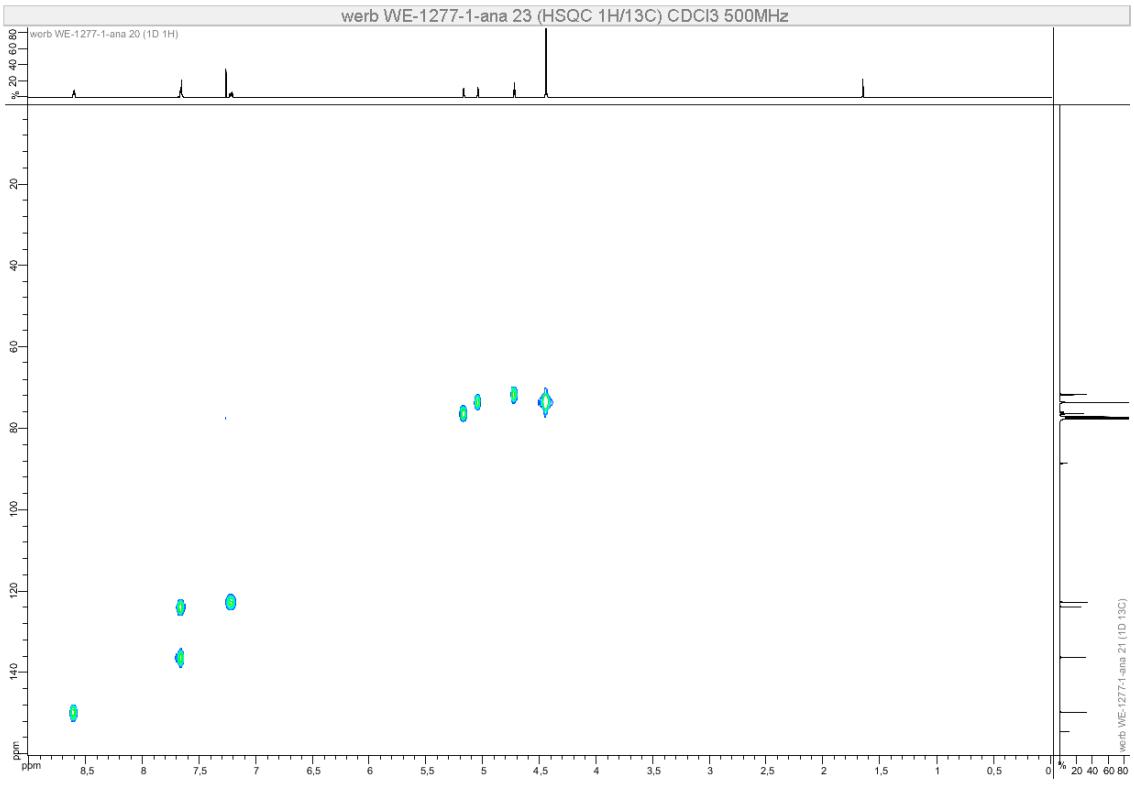
^{13}C NMR (125 MHz, $CDCl_3$)



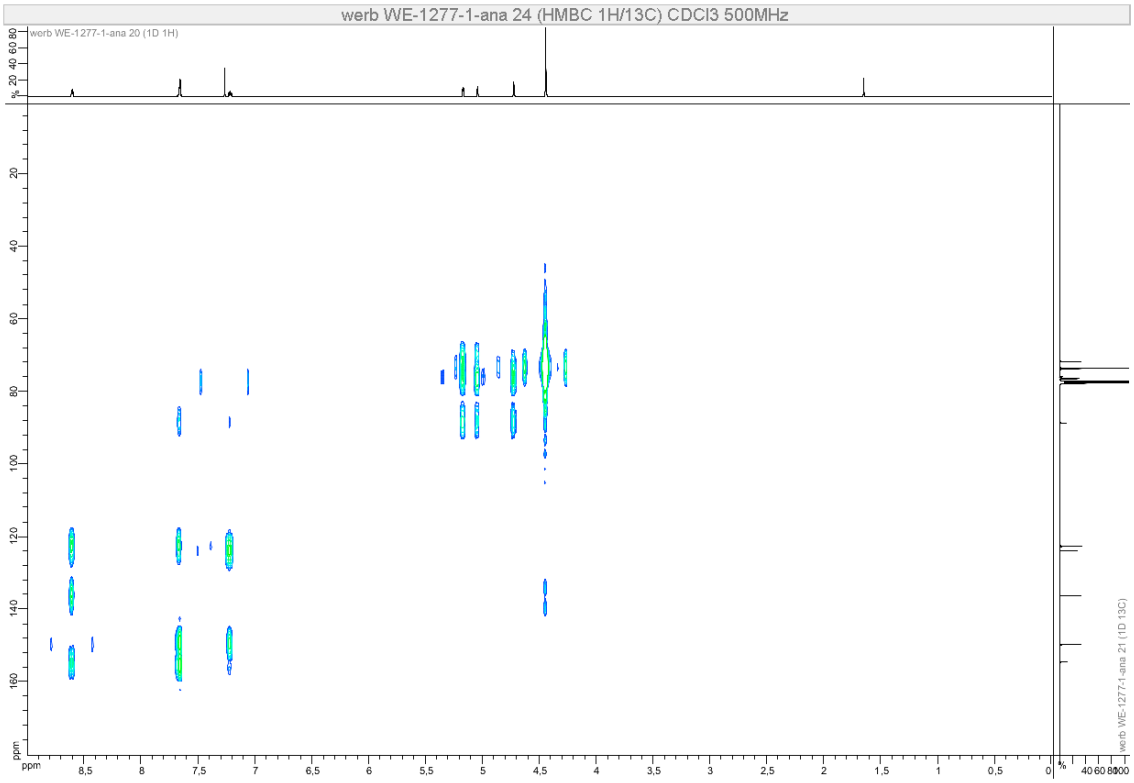
COSY (500 MHz, $CDCl_3$)



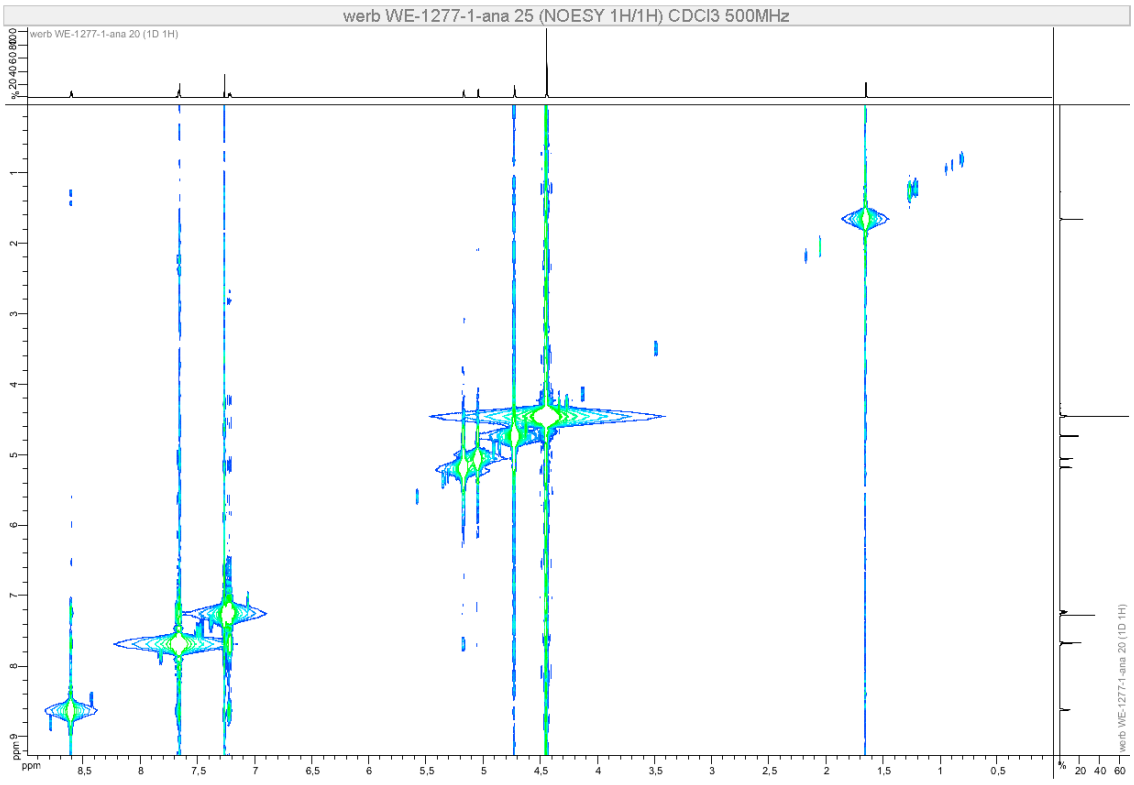
HSQC (500 MHz, $CDCl_3$)



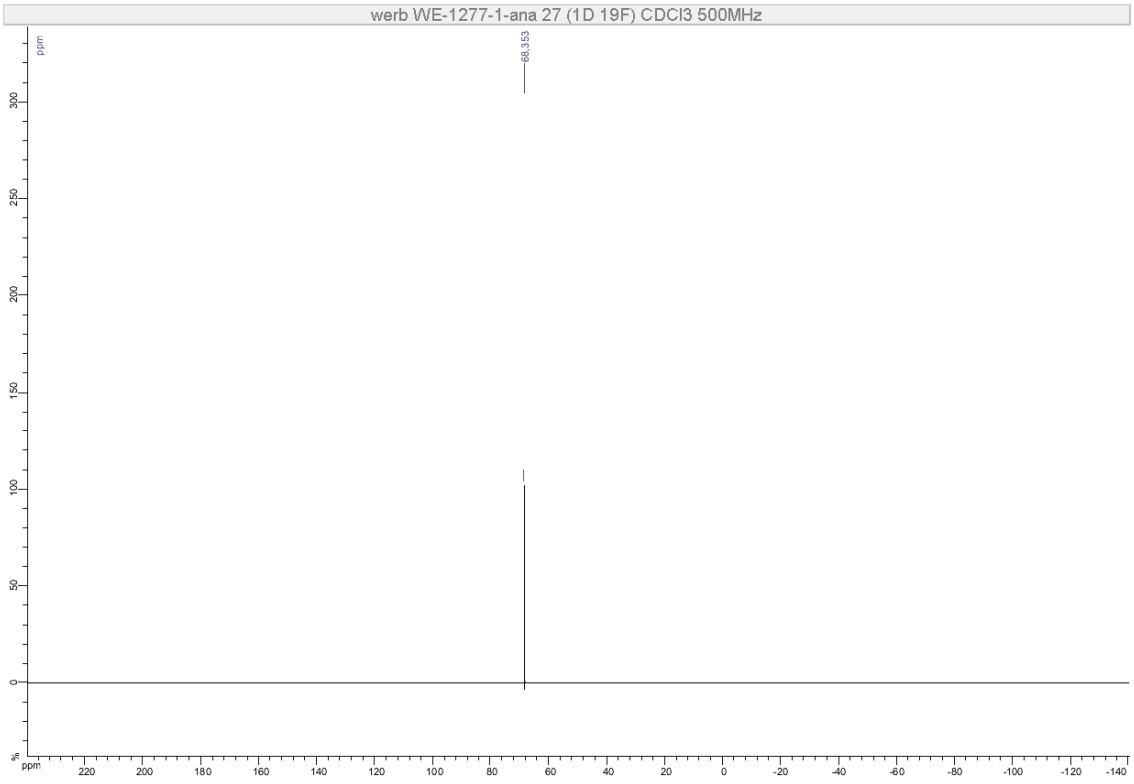
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

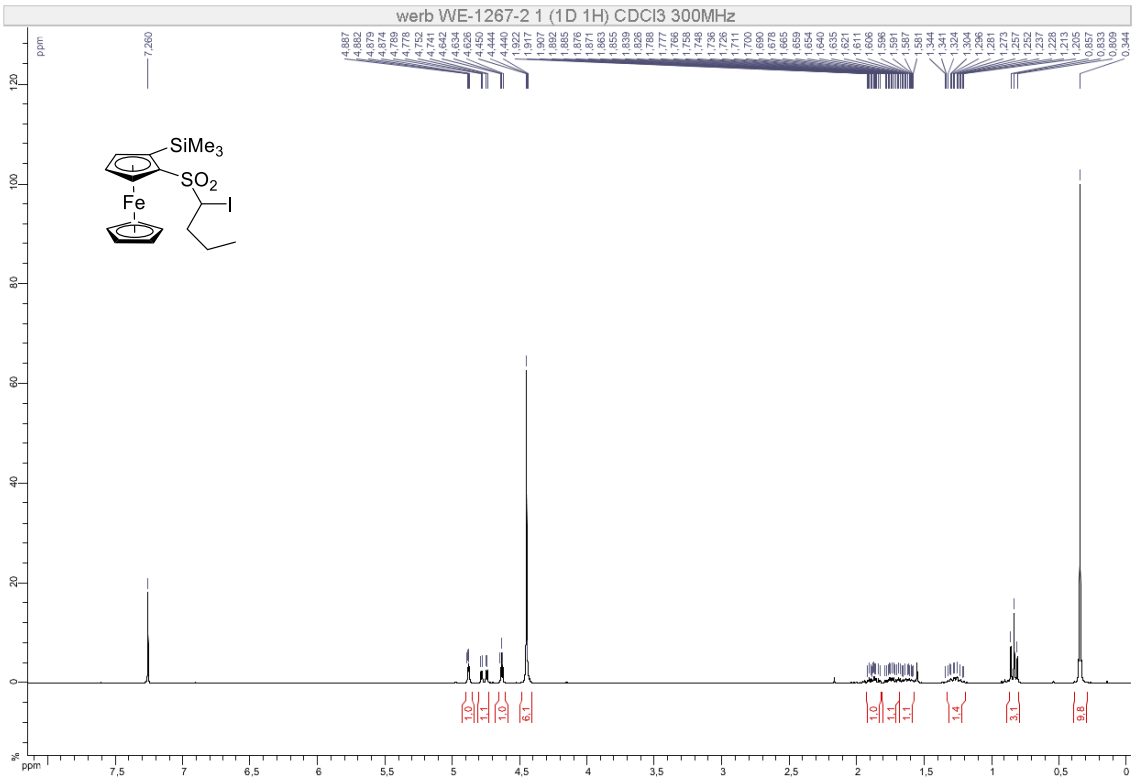


^{19}F NMR (470 MHz, $CDCl_3$)



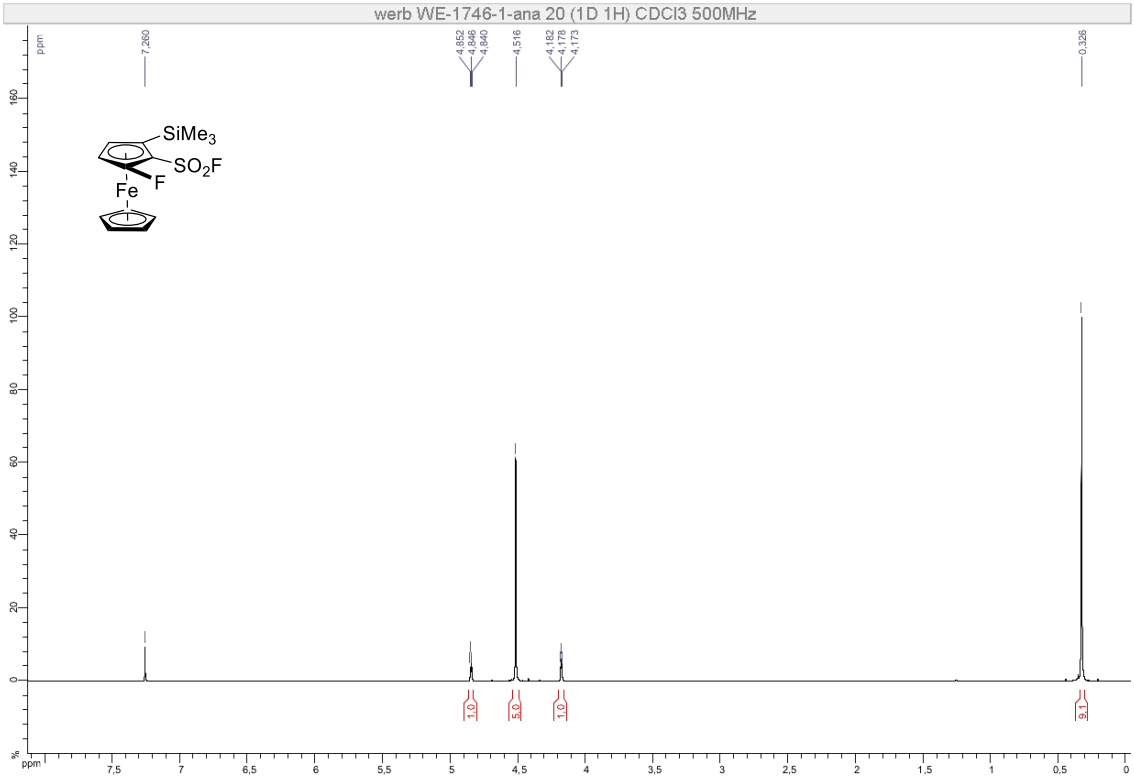
2-(Trimethylsilyl)-1-(1-iodobutylsulfonyl)ferrocene (4d)

^{1}H NMR (300 MHz, $CDCl_3$)

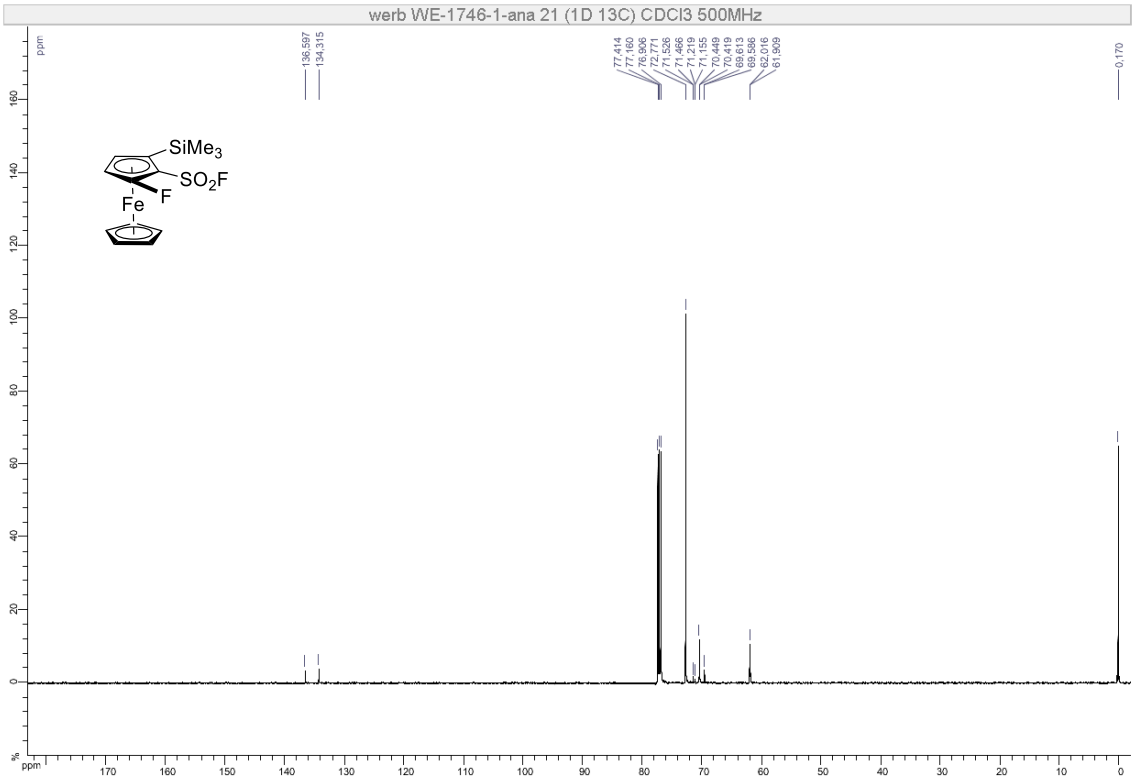


2-Fluoro-5-(trimethylsilyl)ferrocenesulfonyl fluoride (5c)

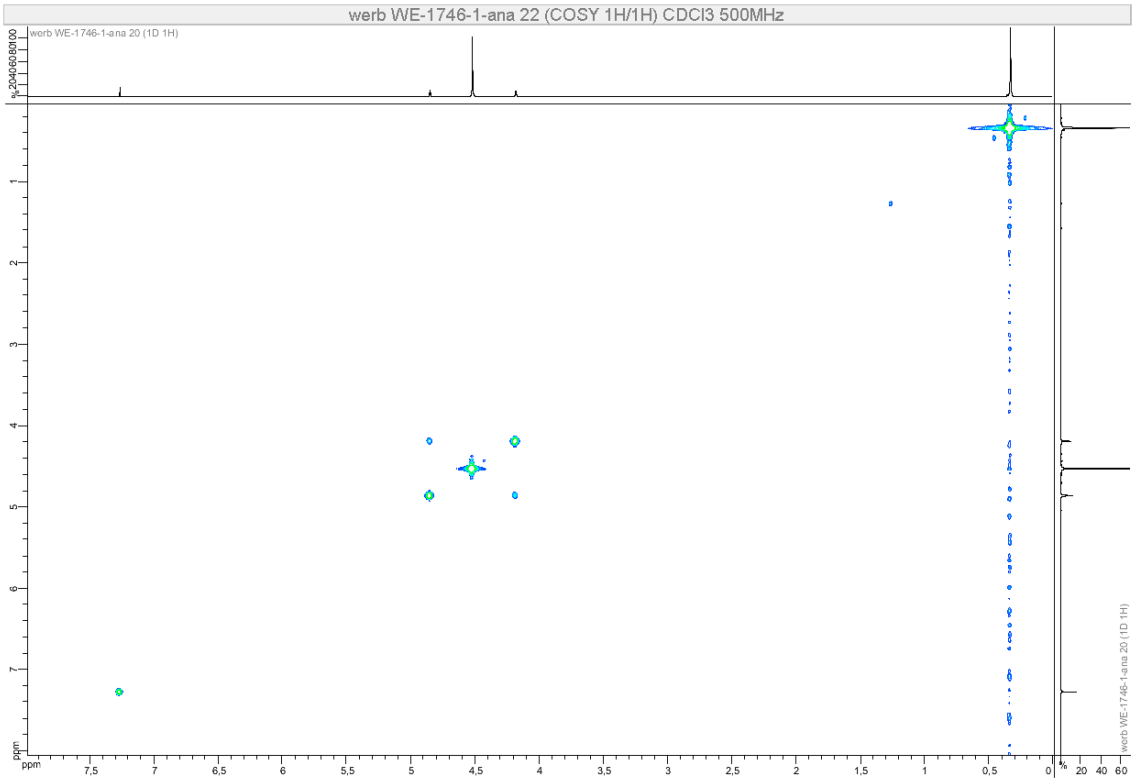
^{1}H NMR (500 MHz, $CDCl_3$)



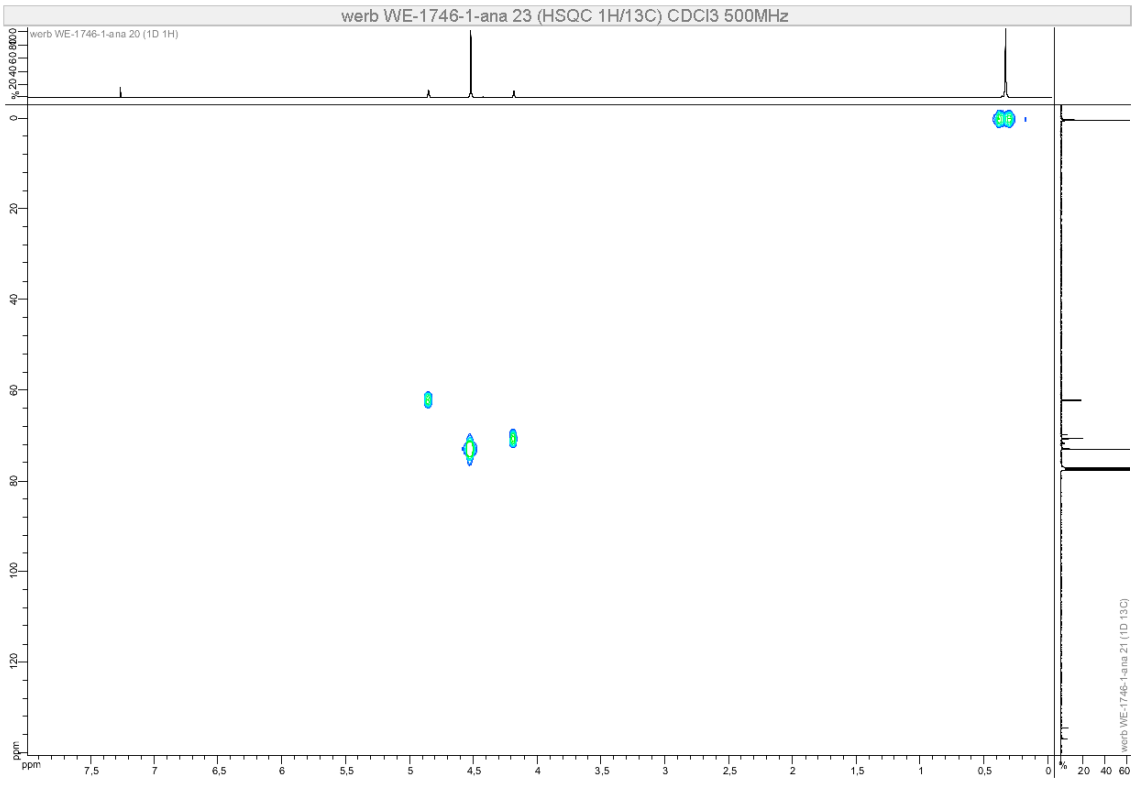
^{13}C NMR (125 MHz, $CDCl_3$)



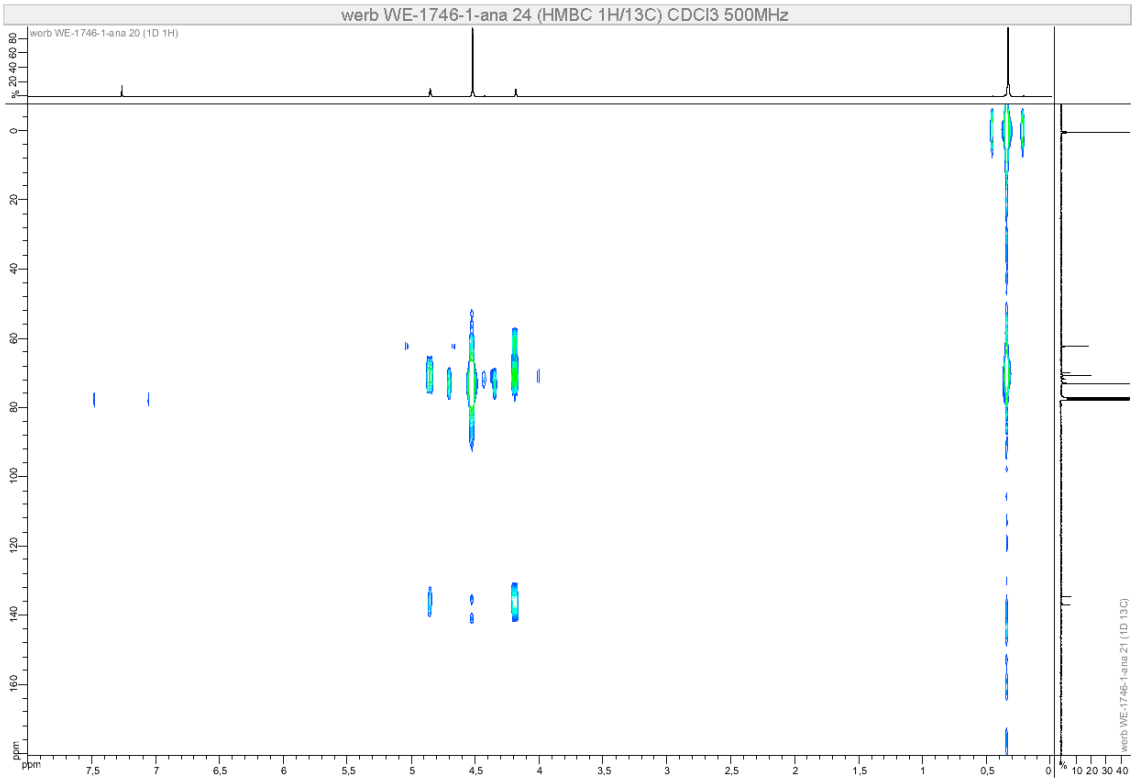
COSY (500 MHz, $CDCl_3$)



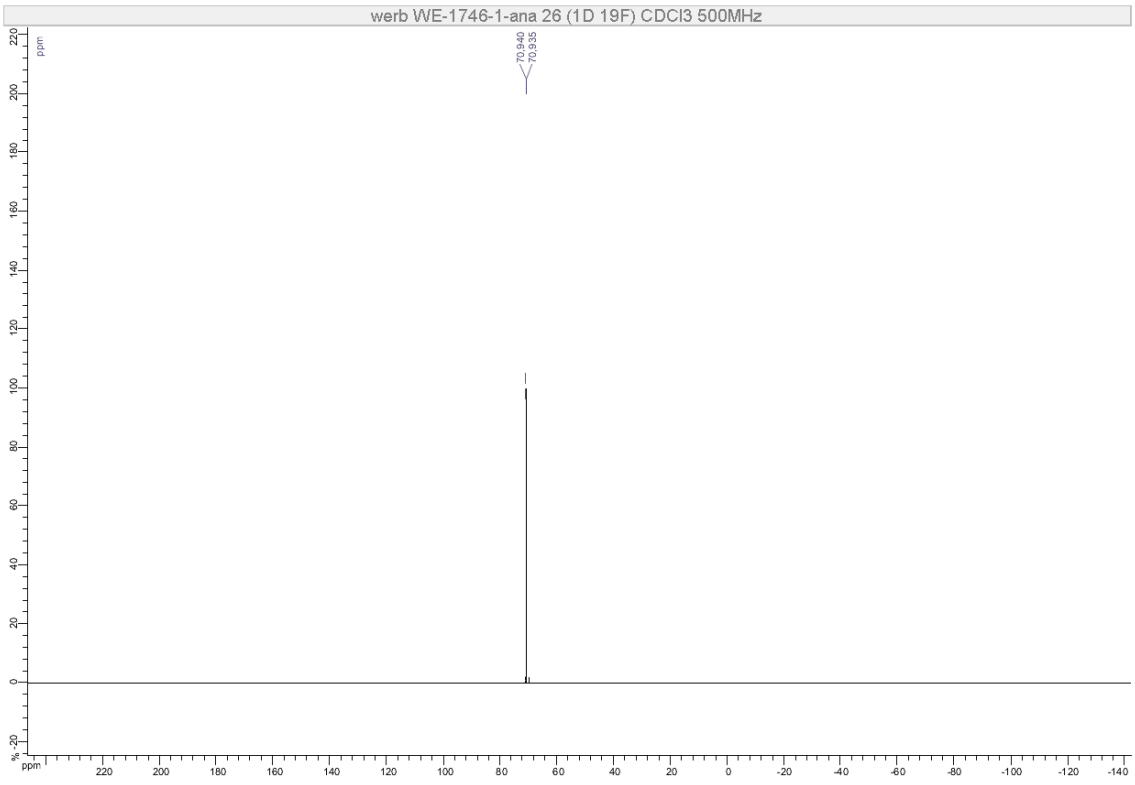
HSQC (500 MHz, $CDCl_3$)



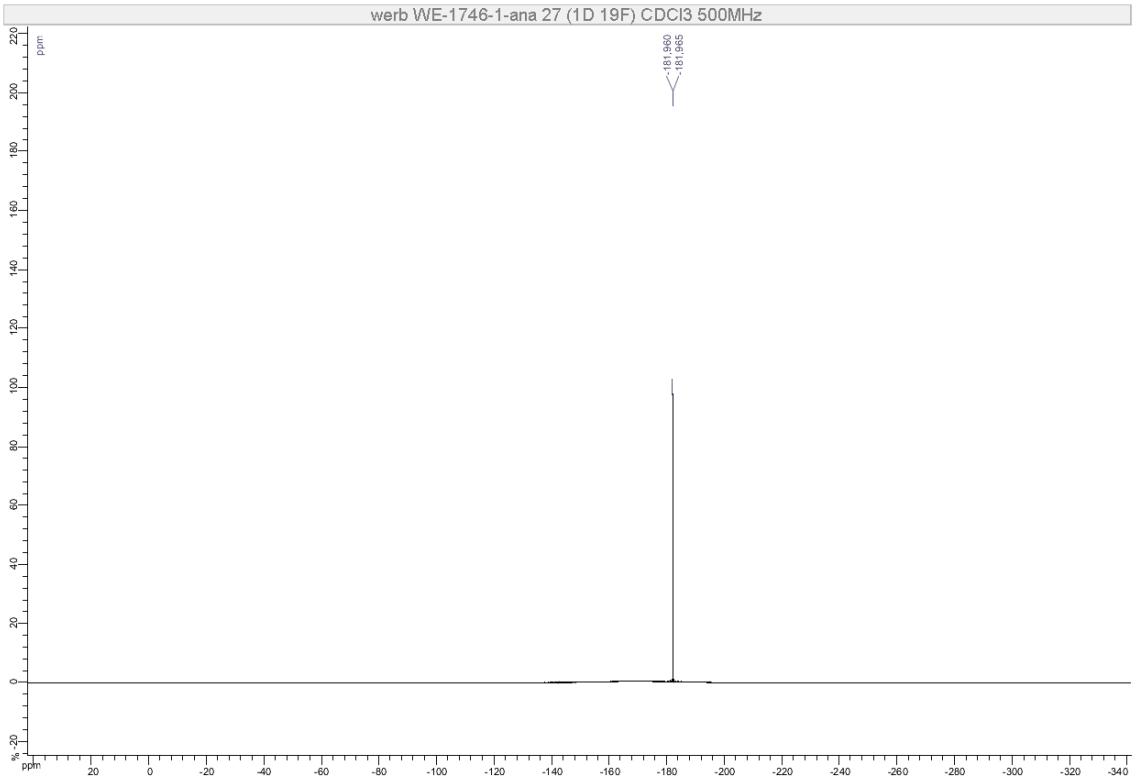
HMBC (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$) – 240 to -140 ppm area

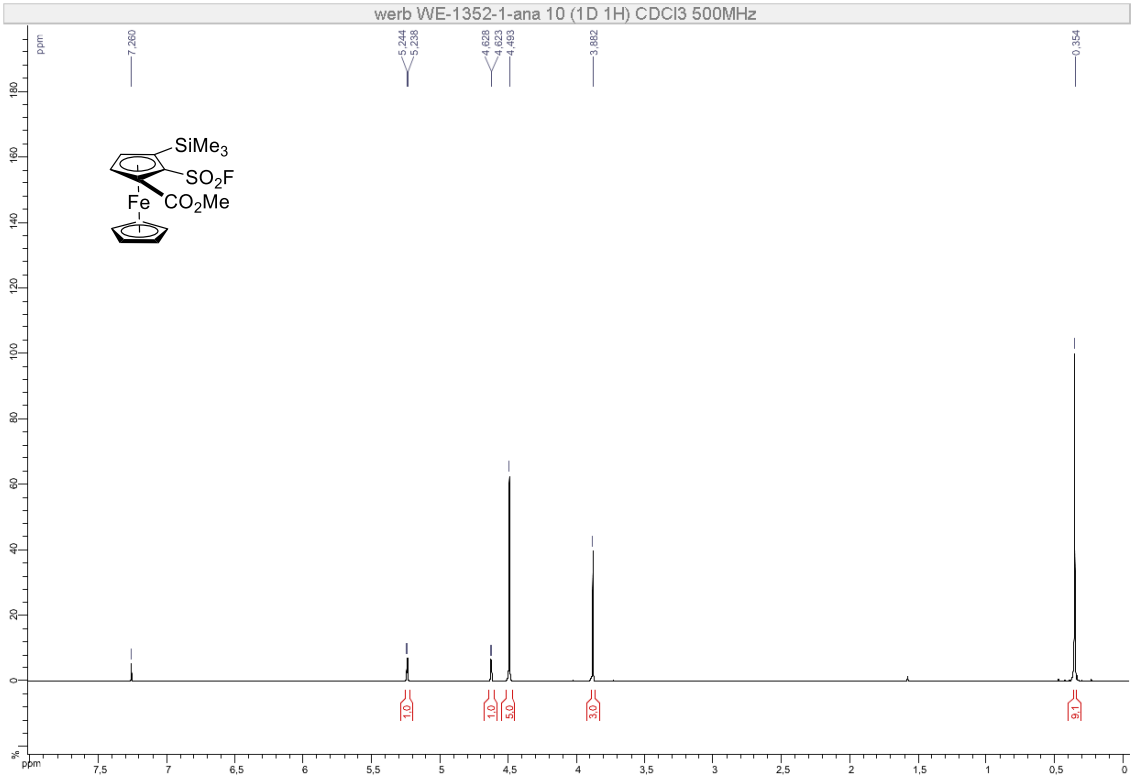


^{19}F NMR (470 MHz, $CDCl_3$) – 40 to -340 ppm area

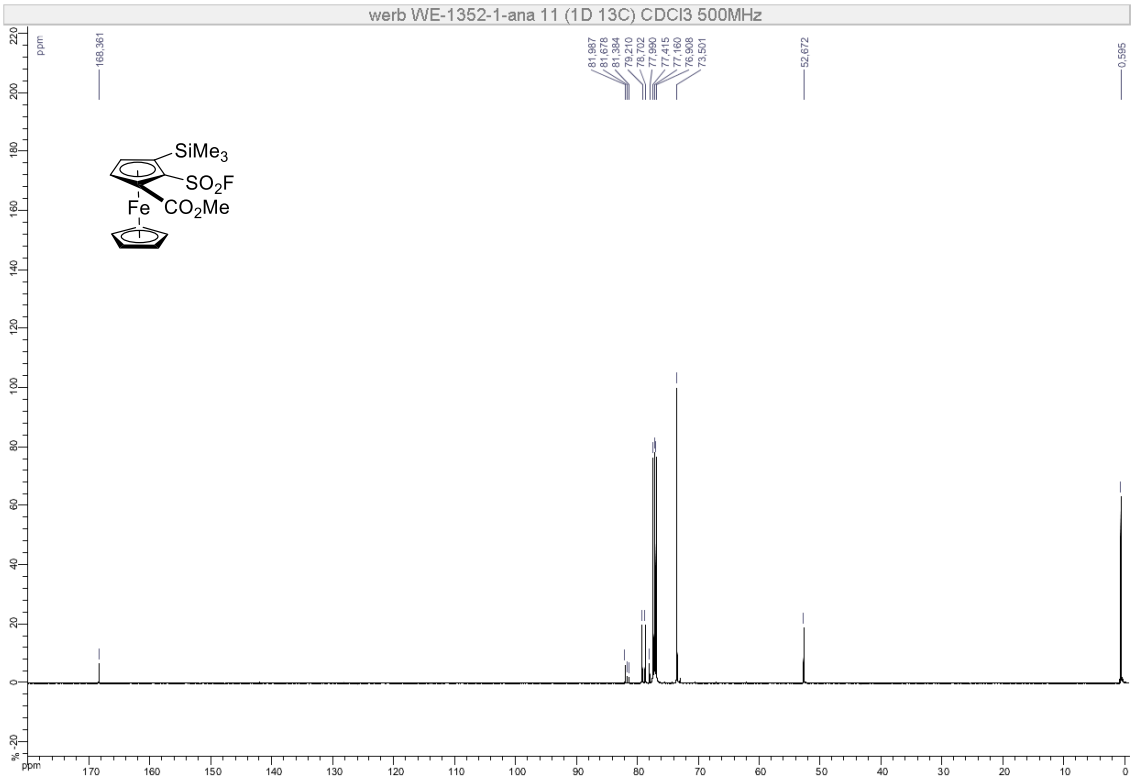


2-Methoxycarbonyl-5-(trimethylsilyl)ferrocenesulfonyl fluoride (5d)

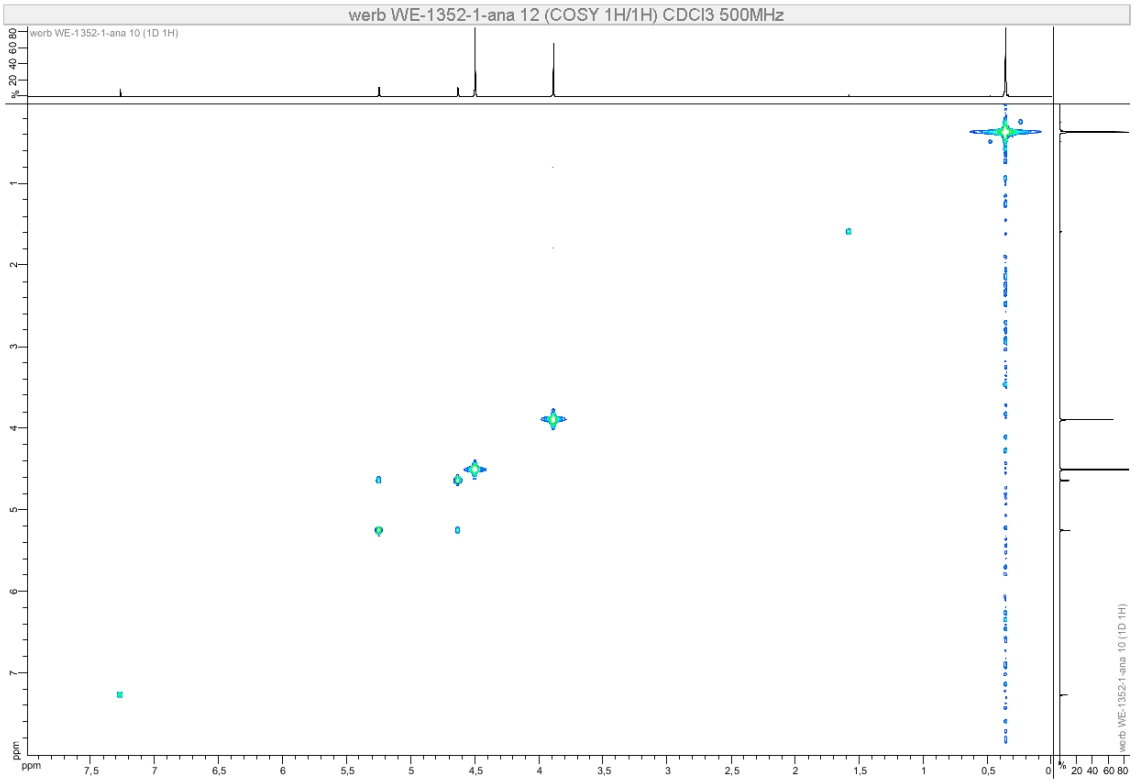
^{1}H NMR (500 MHz, $CDCl_3$)



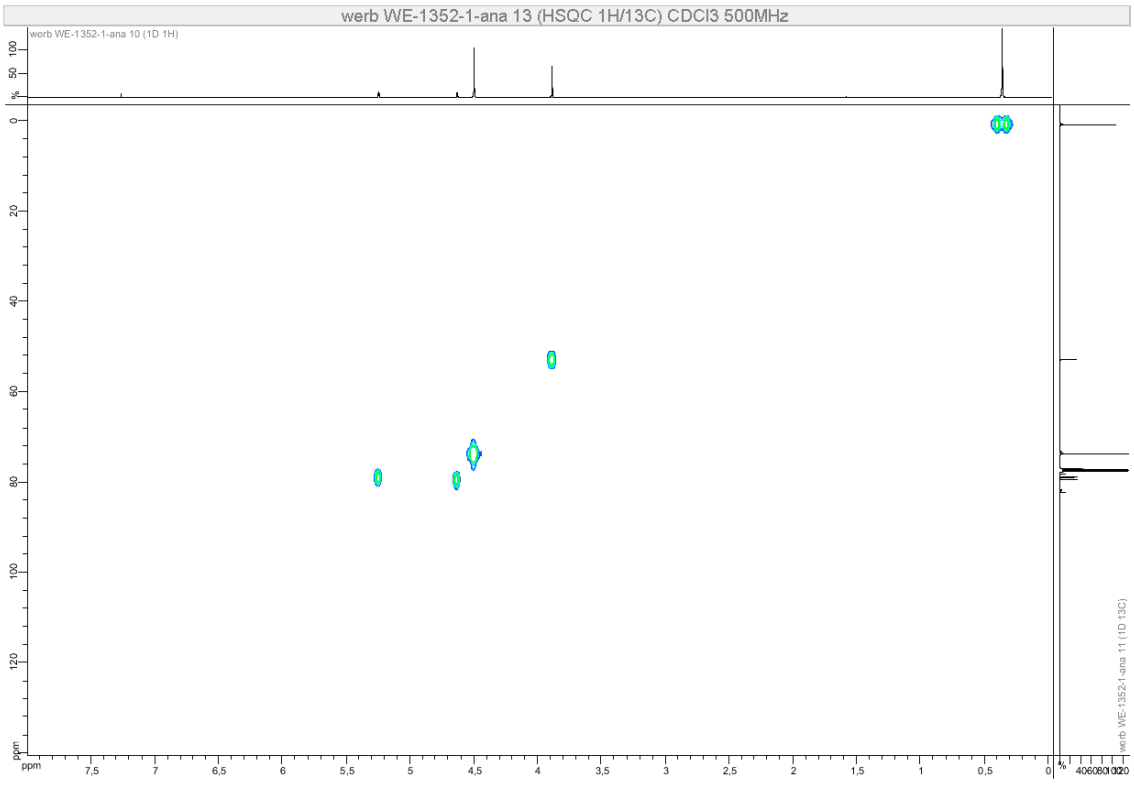
^{13}C NMR (125 MHz, $CDCl_3$)



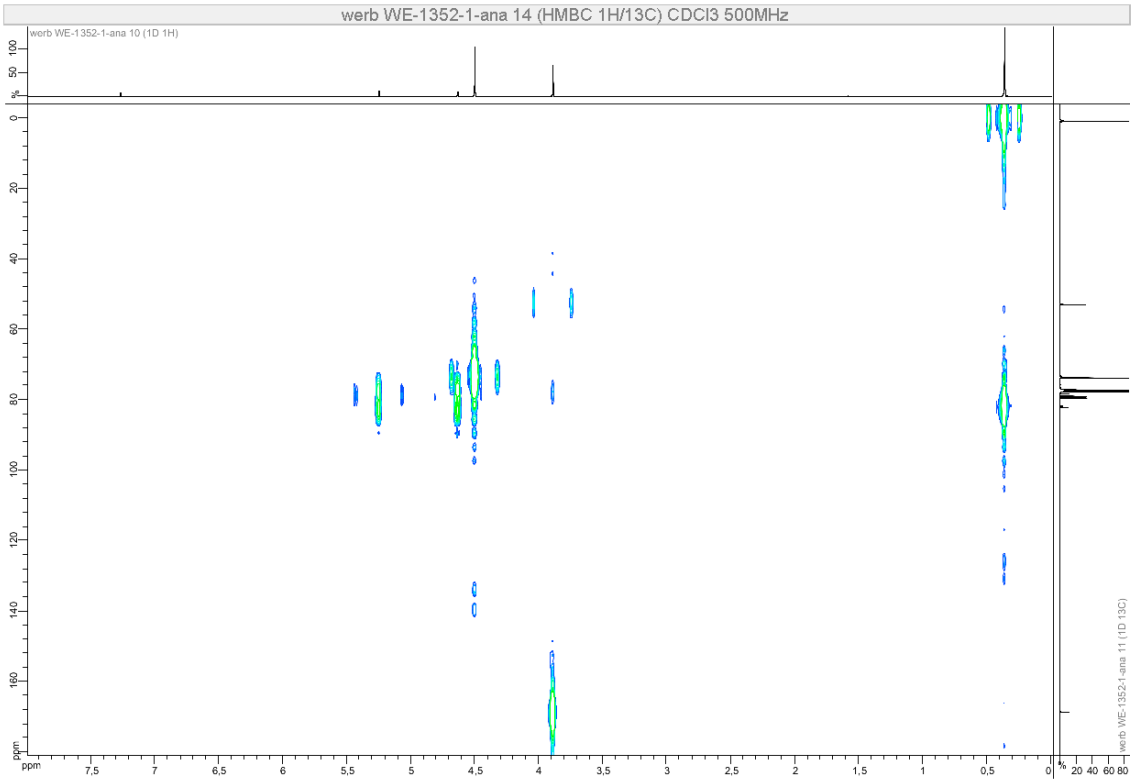
COSY (500 MHz, $CDCl_3$)



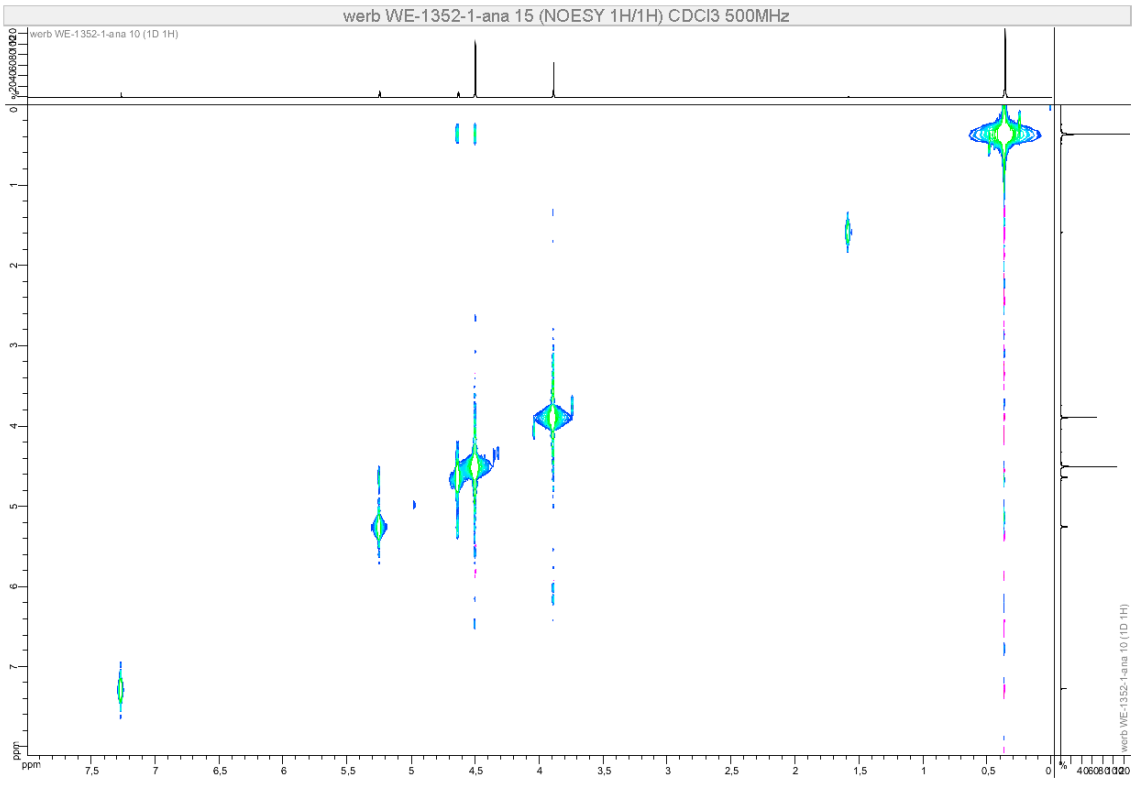
HSQC (500 MHz, $CDCl_3$)



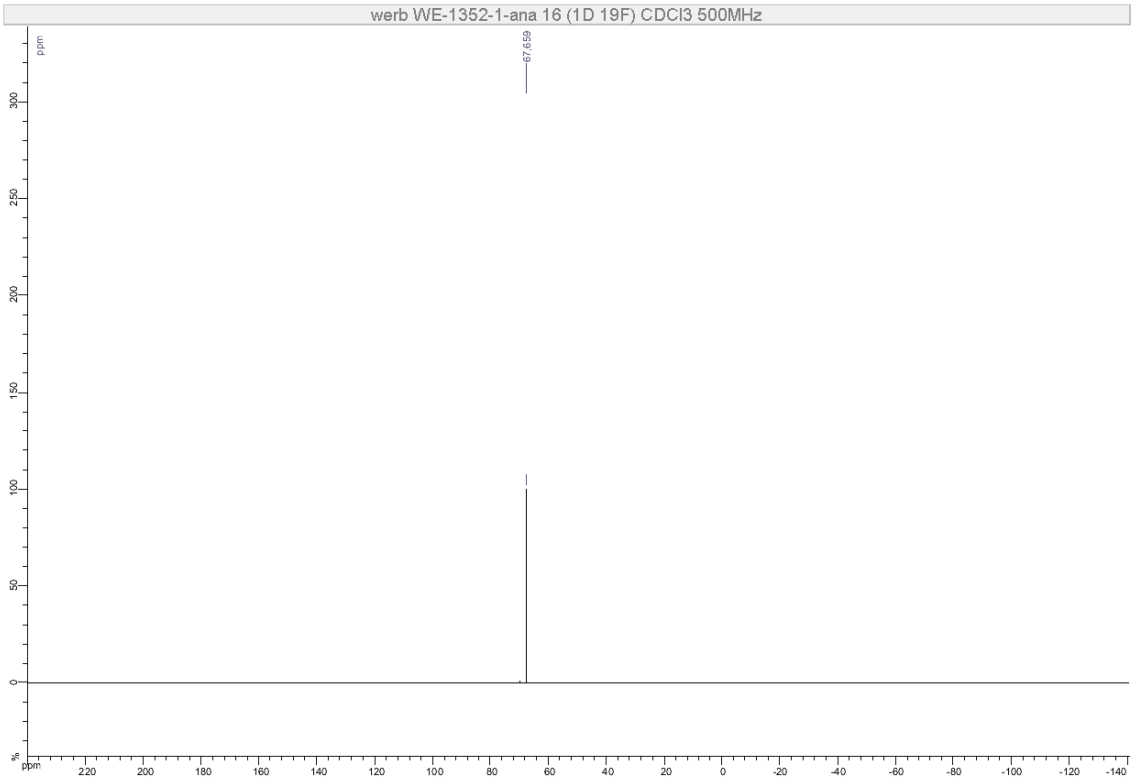
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

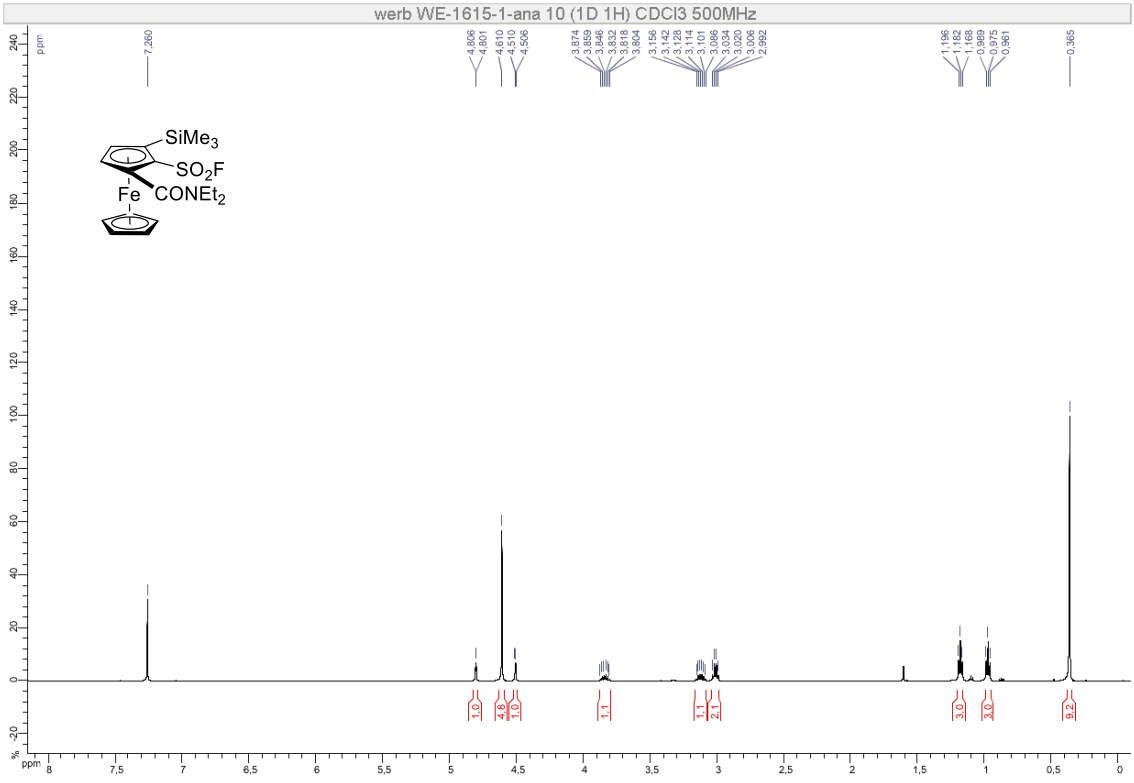


^{19}F NMR (470 MHz, $CDCl_3$)

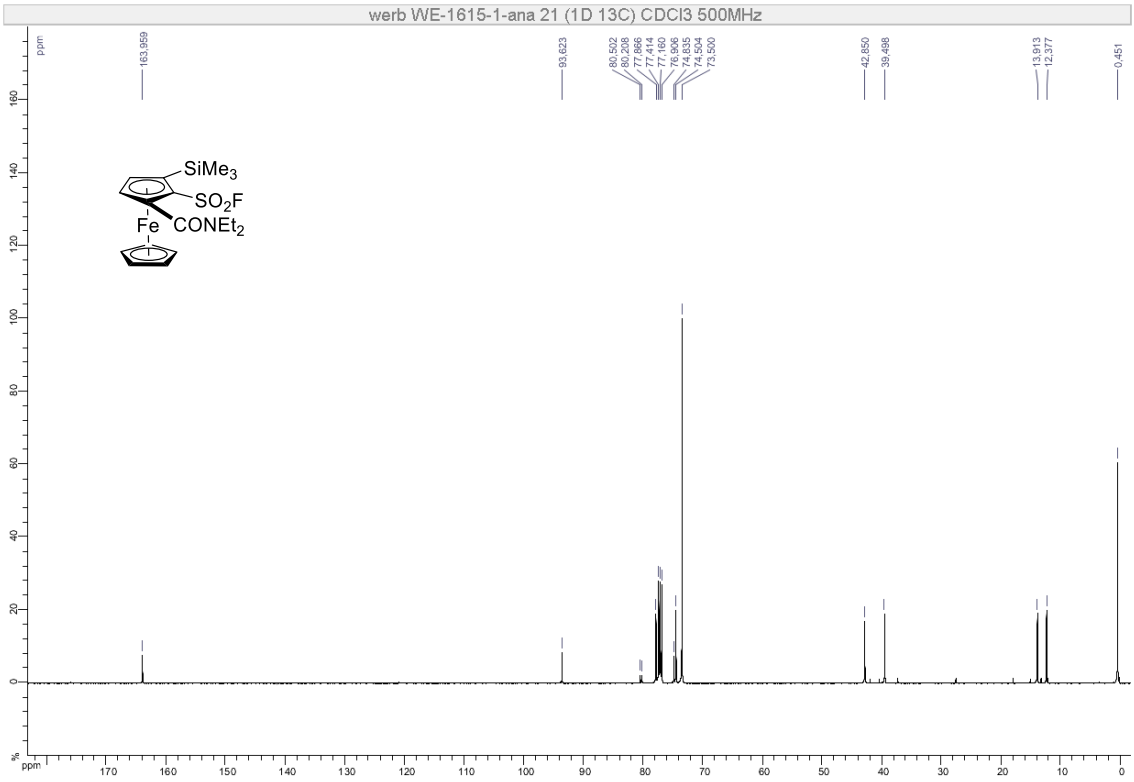


2-(*N*,*N*-Diethylcarbamoyl)-5-(trimethylsilyl)ferrocenesulfonyl fluoride (5e)

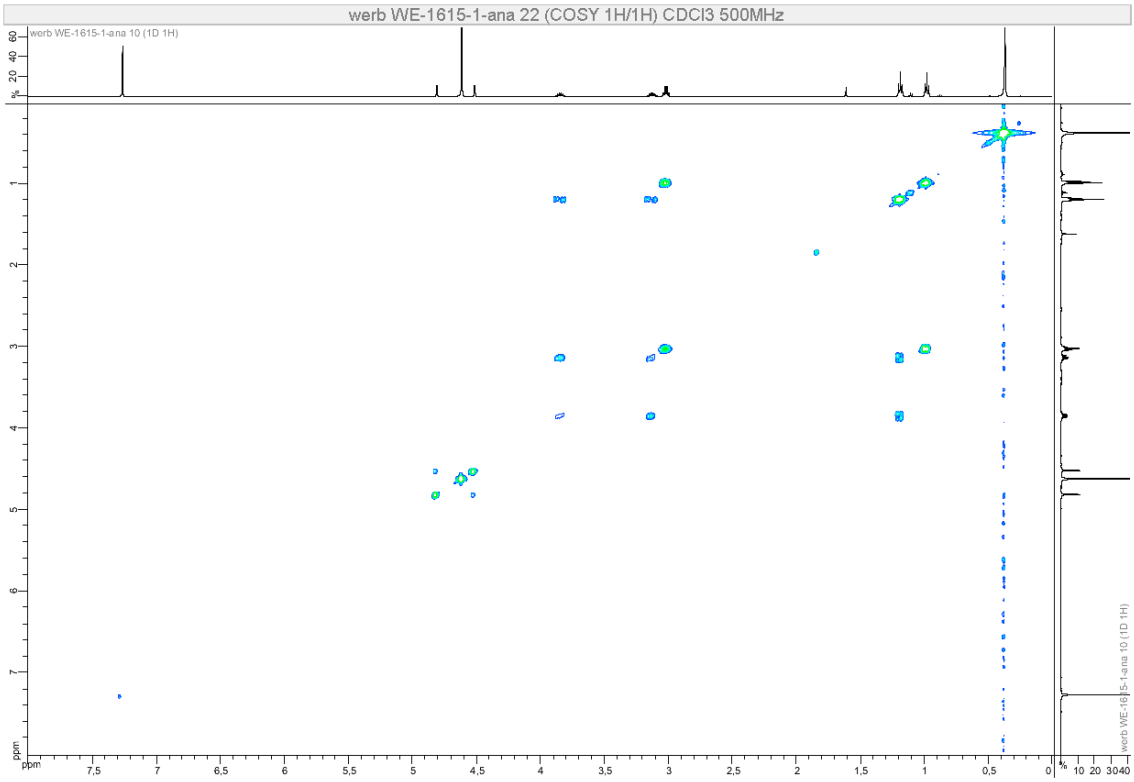
^{1}H NMR (500 MHz, $CDCl_3$)



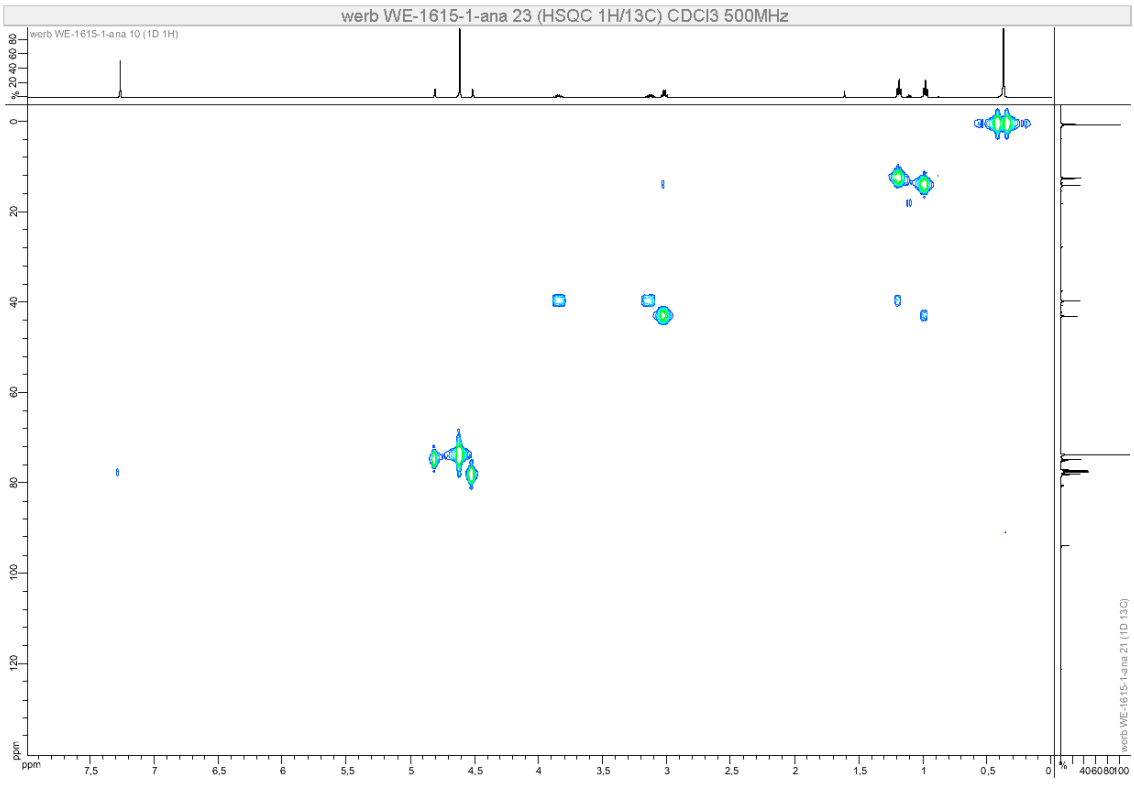
^{13}C NMR (125 MHz, $CDCl_3$)



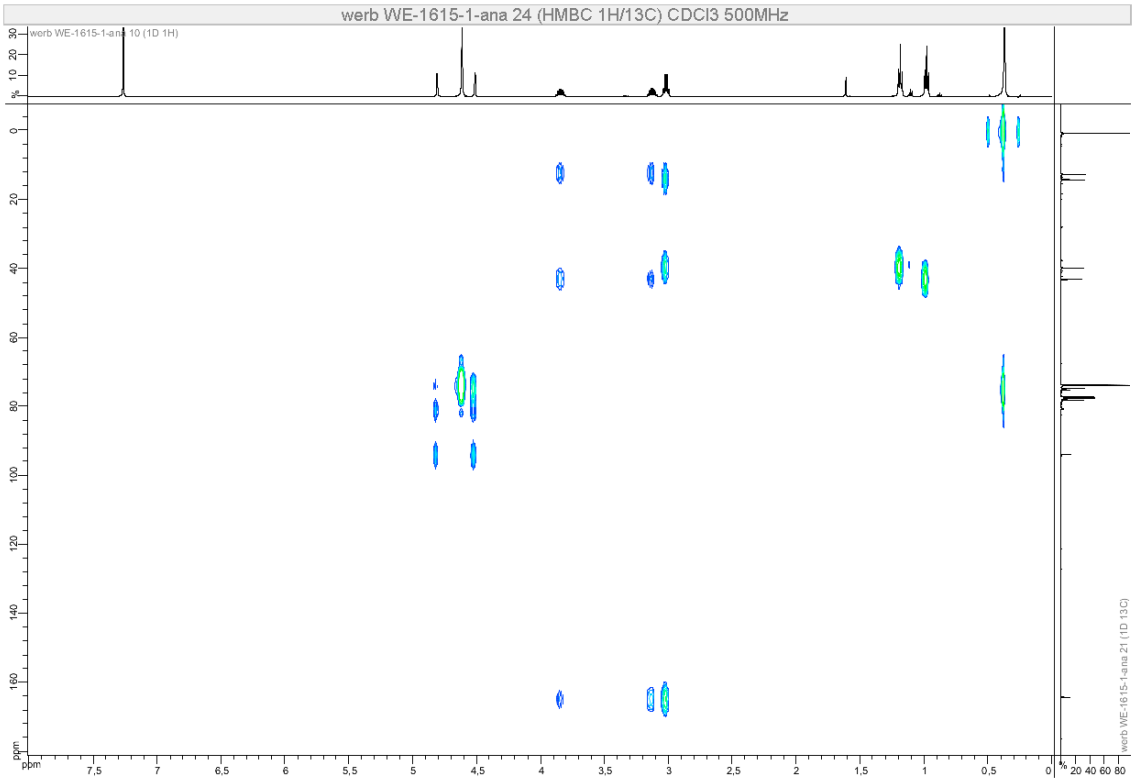
COSY (500 MHz, $CDCl_3$)



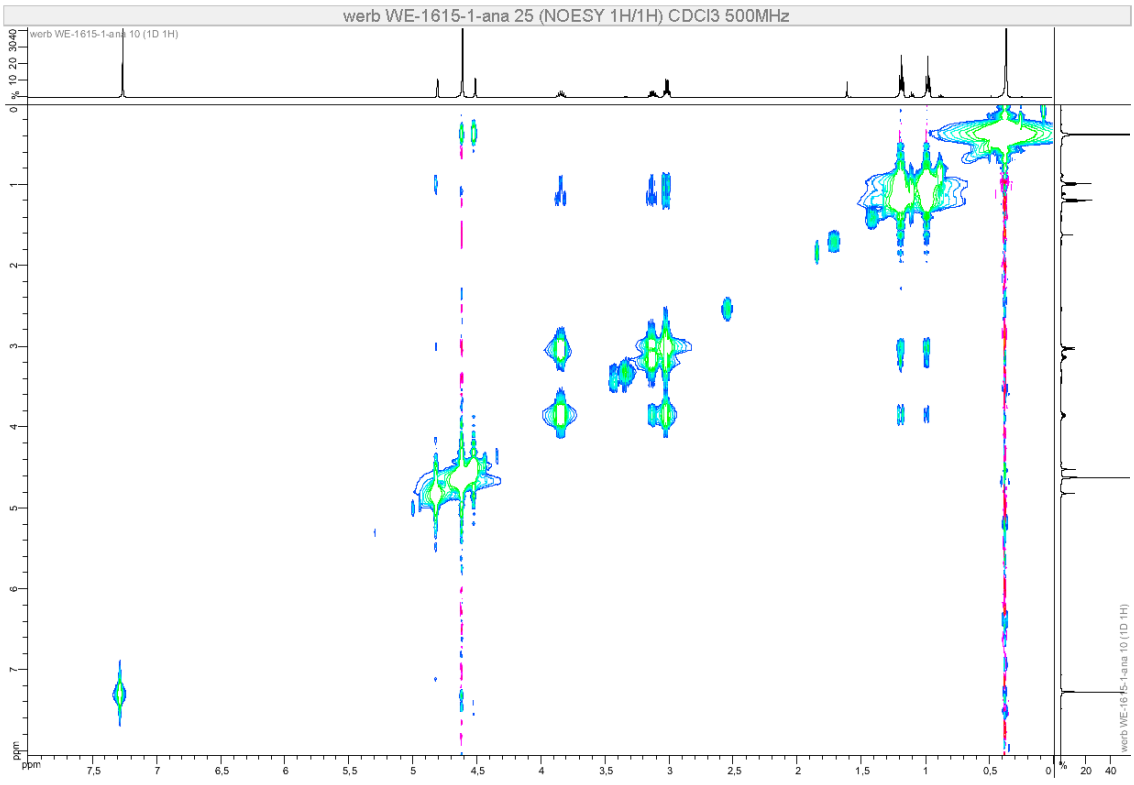
HSQC (500 MHz, $CDCl_3$)



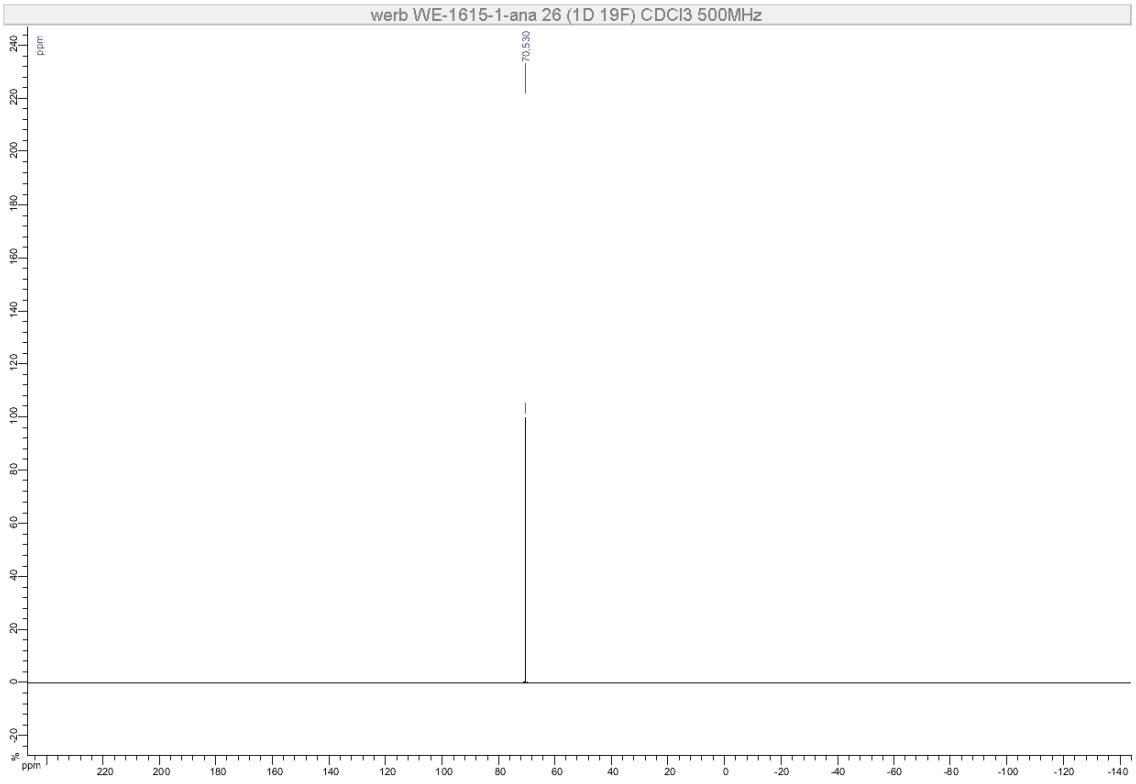
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

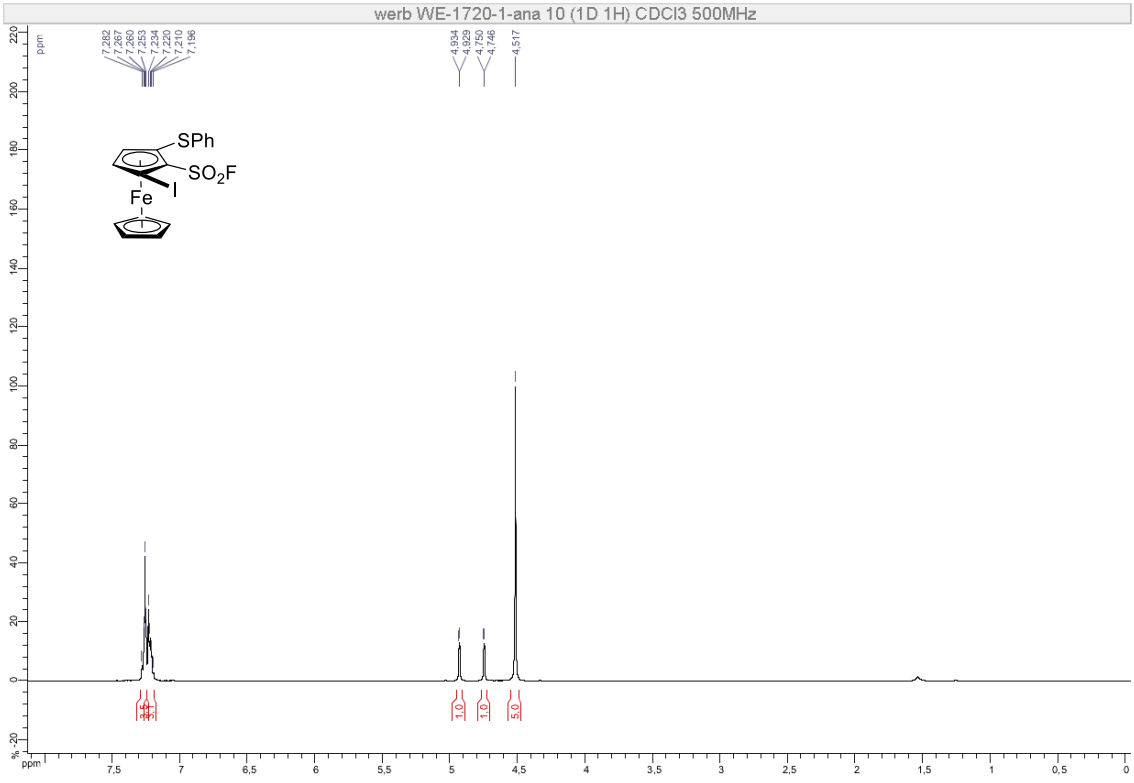


^{19}F NMR (470 MHz, $CDCl_3$)

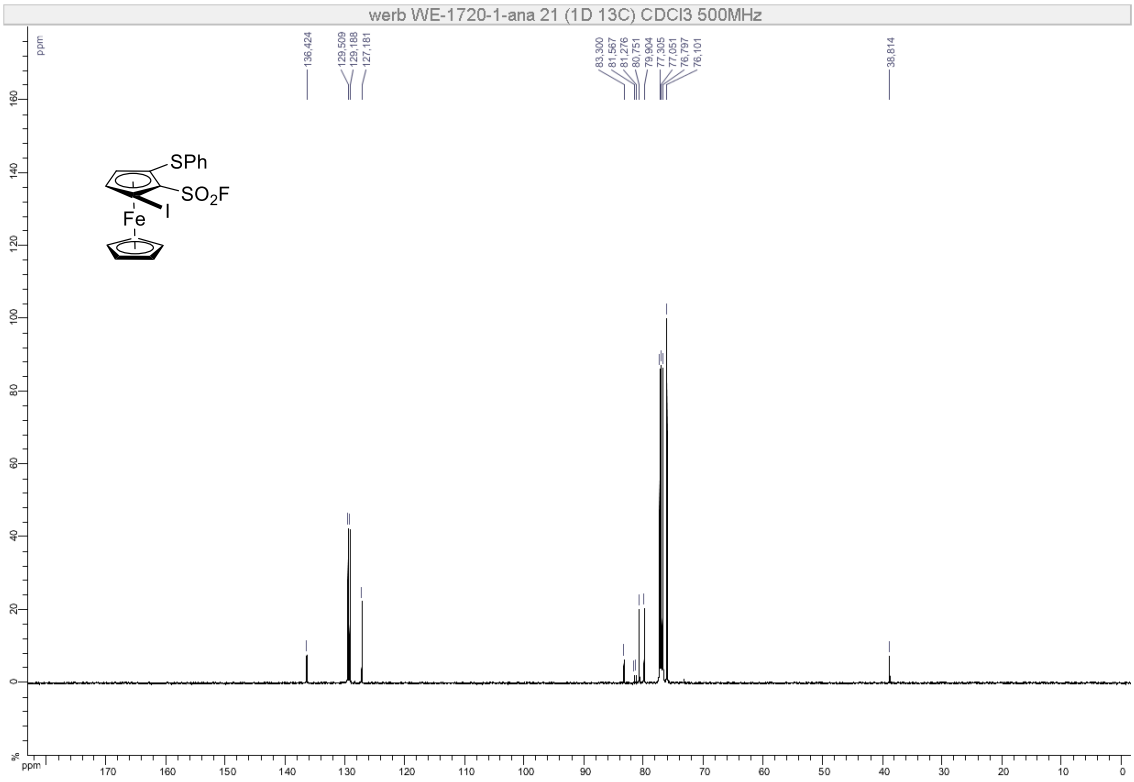


2-Iodo-5-(phenylthio)ferrocenesulfonyl fluoride (5f)

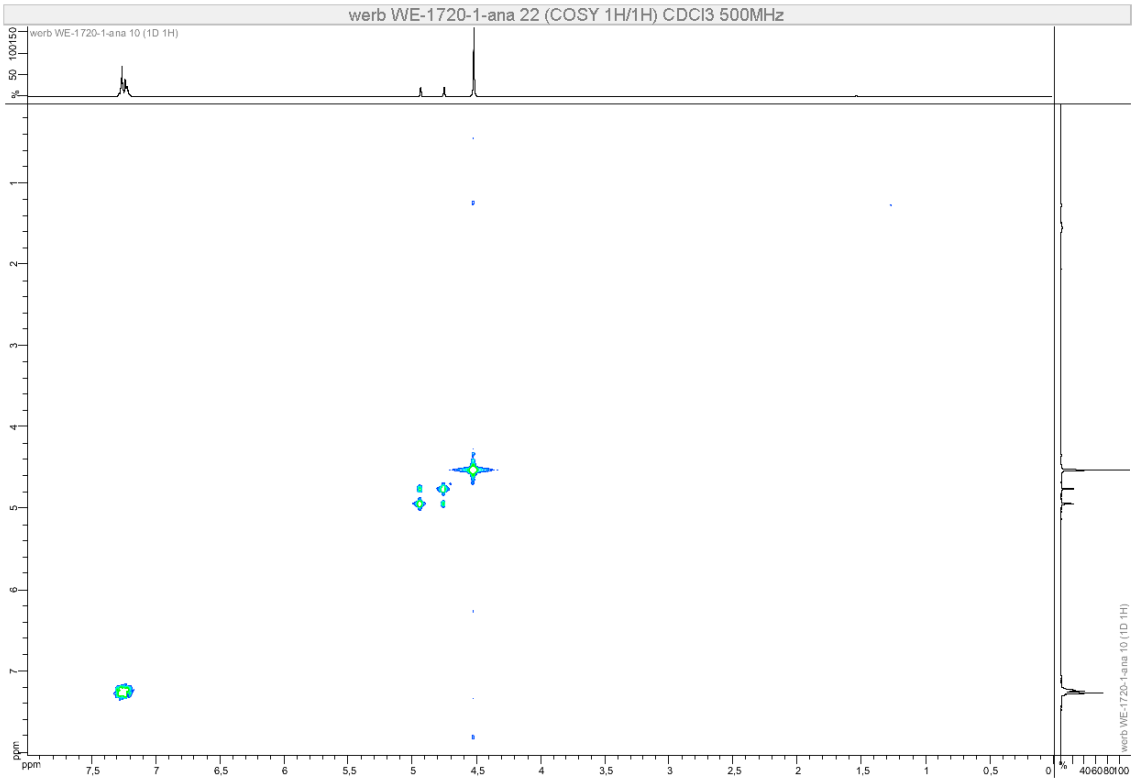
^{1}H NMR (500 MHz, $CDCl_3$)



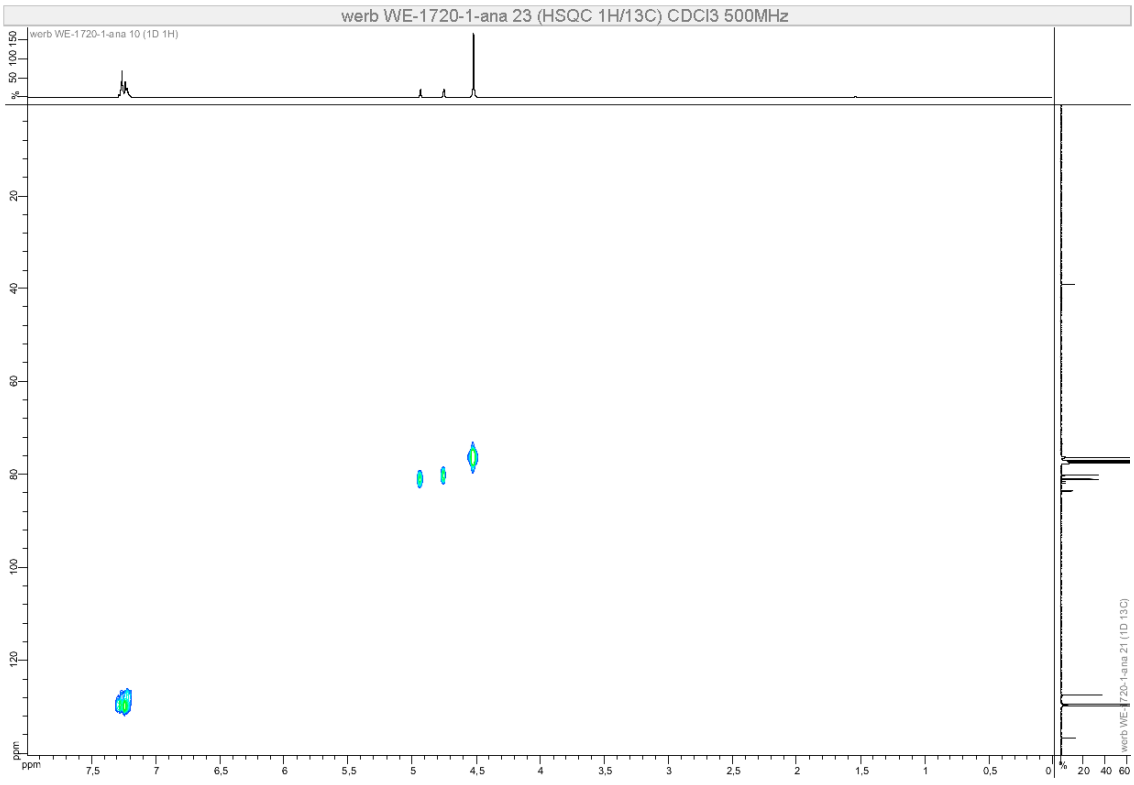
^{13}C NMR (125 MHz, $CDCl_3$)



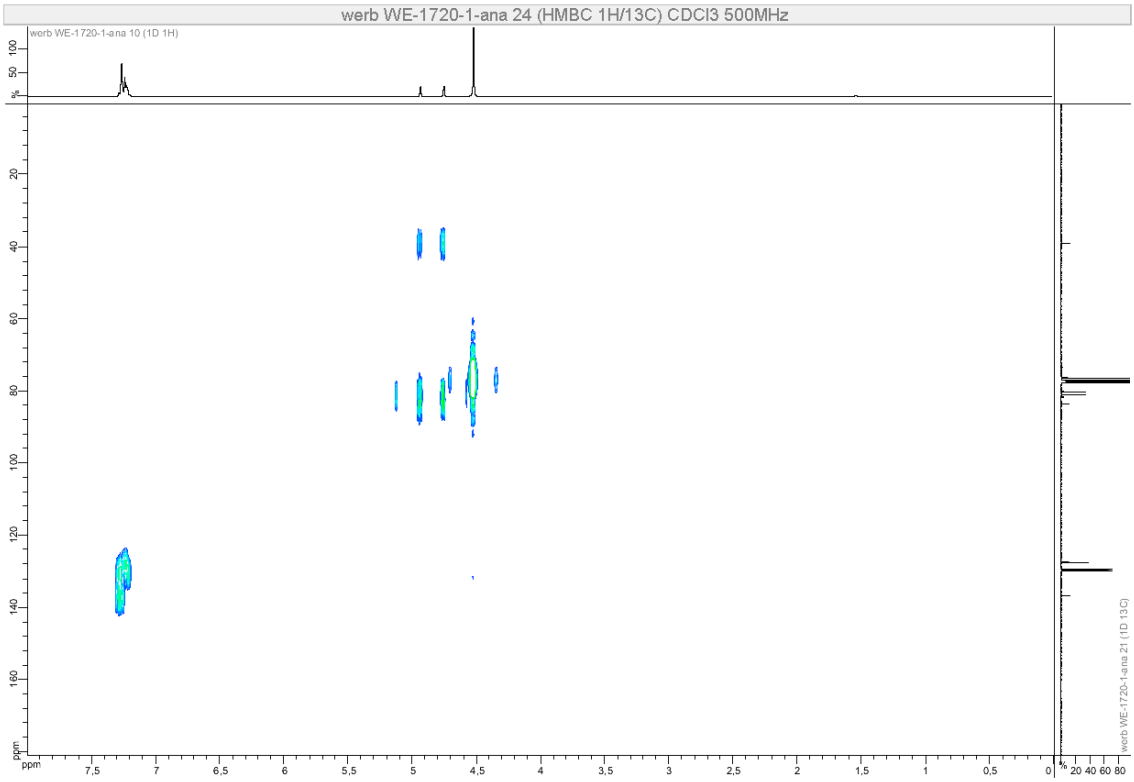
COSY (500 MHz, $CDCl_3$)



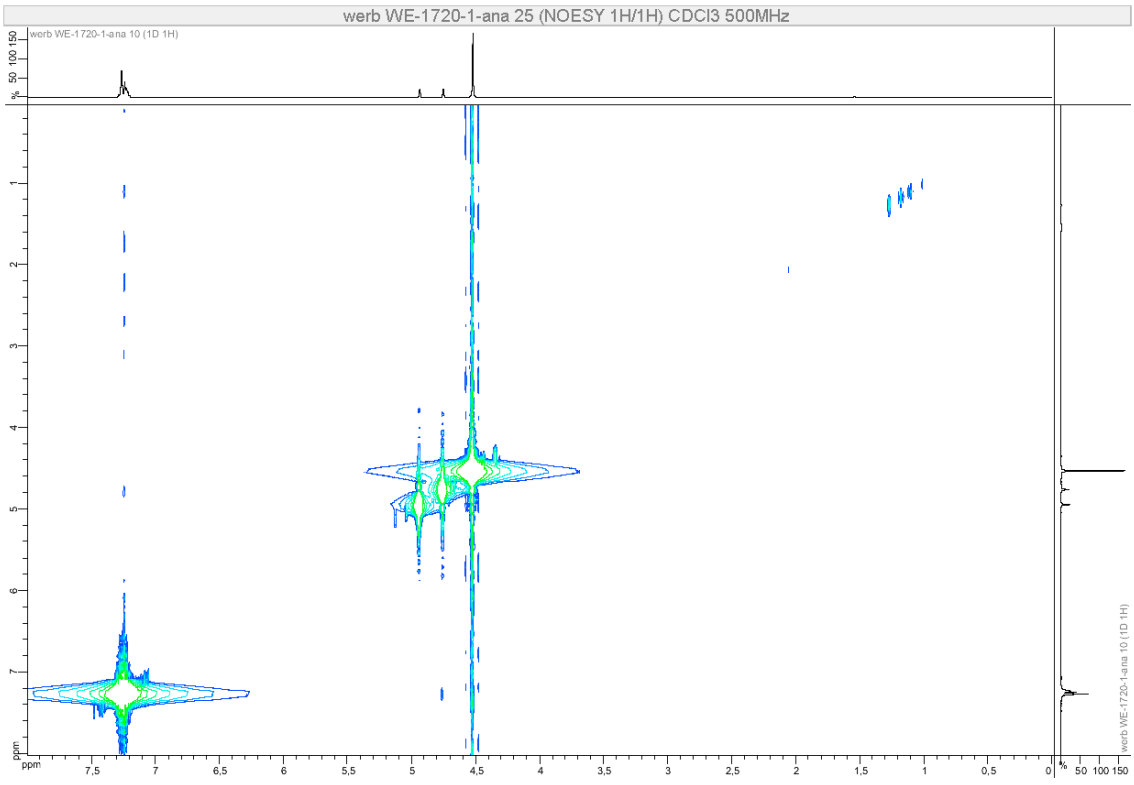
HSQC (500 MHz, $CDCl_3$)



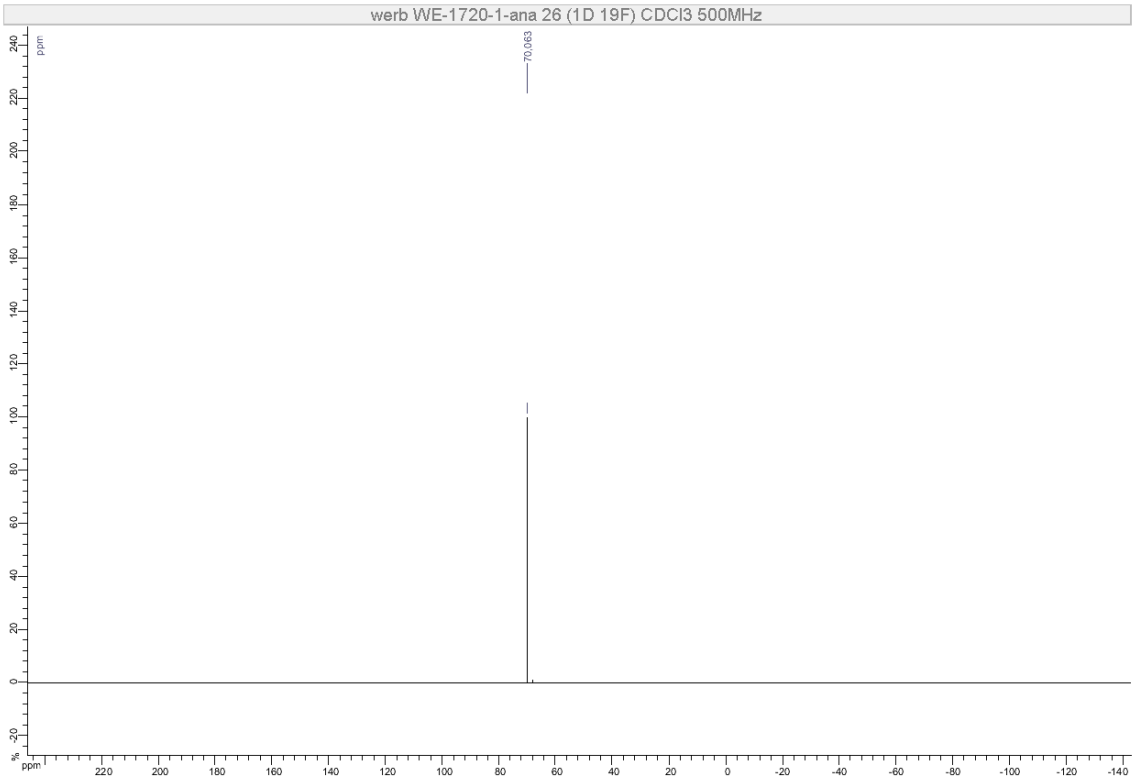
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

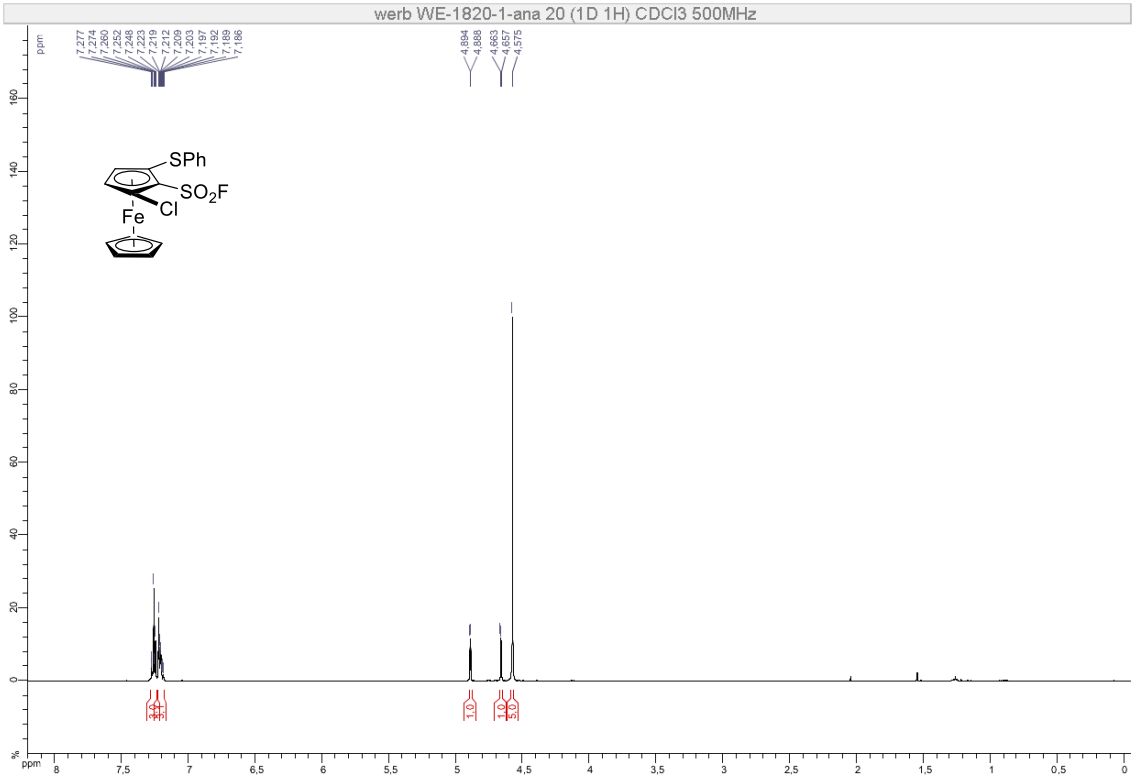


^{19}F NMR (470 MHz, $CDCl_3$)

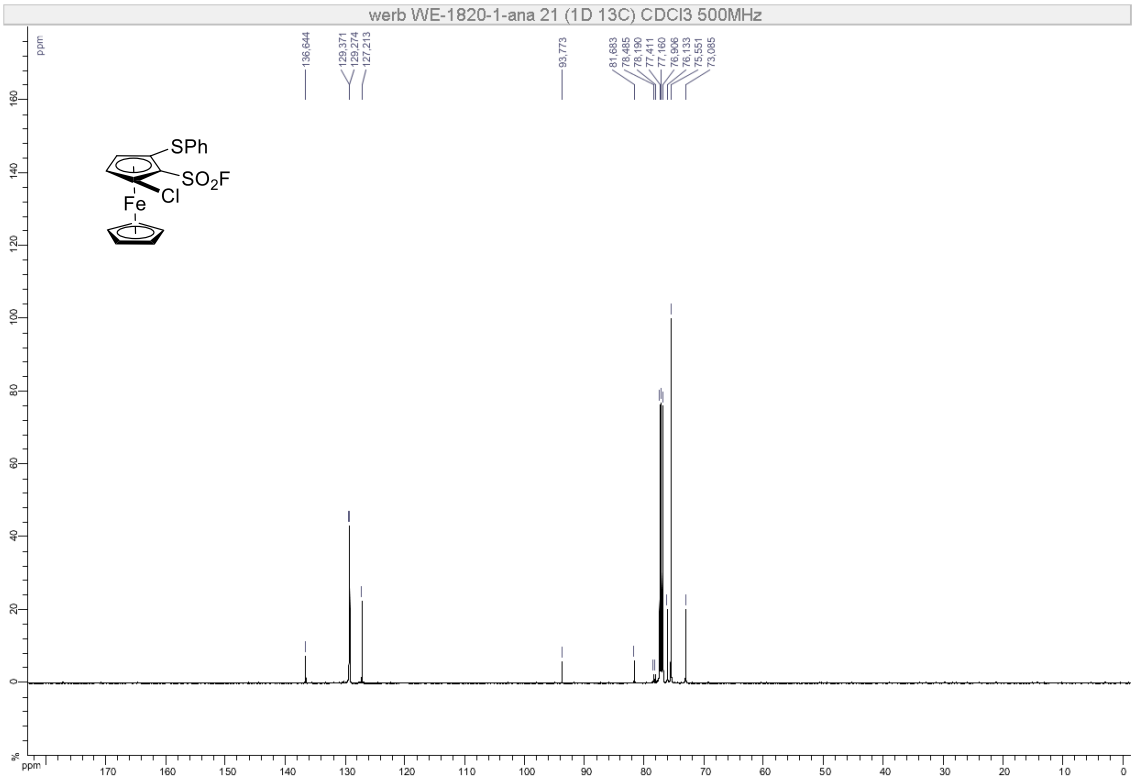


2-Chloro-5-(phenylthio)ferrocenesulfonyl fluoride (5g)

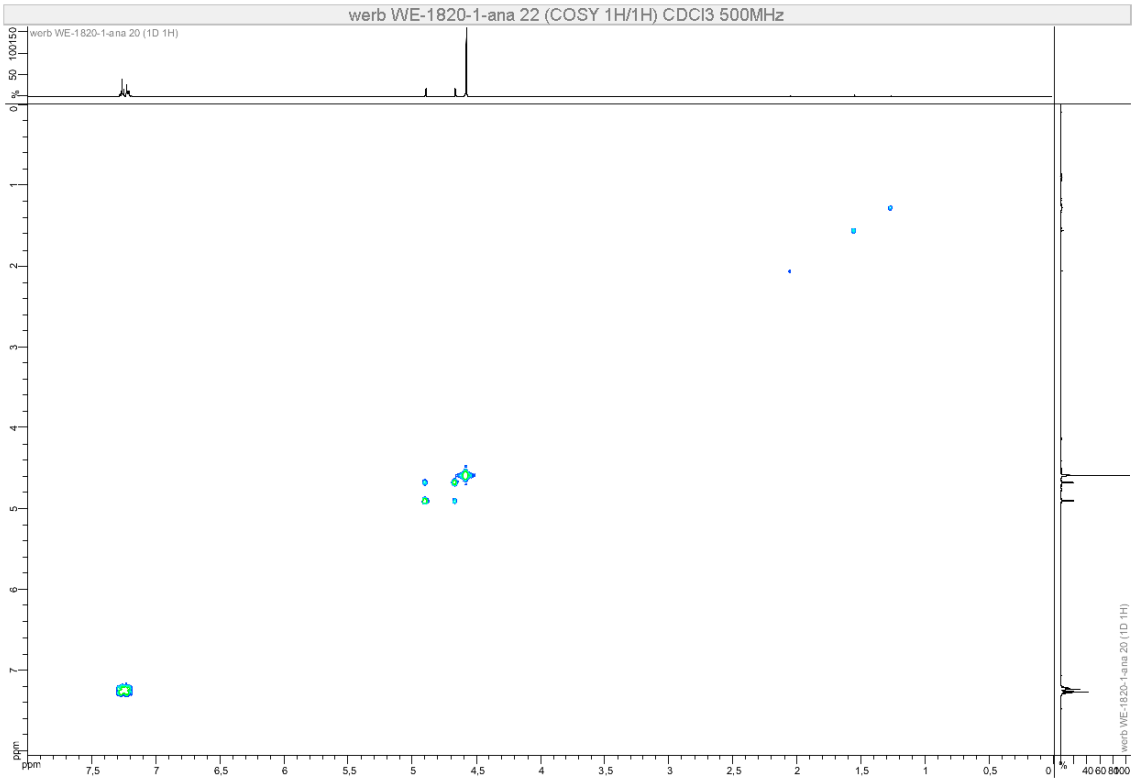
^{1}H NMR (500 MHz, $CDCl_3$)



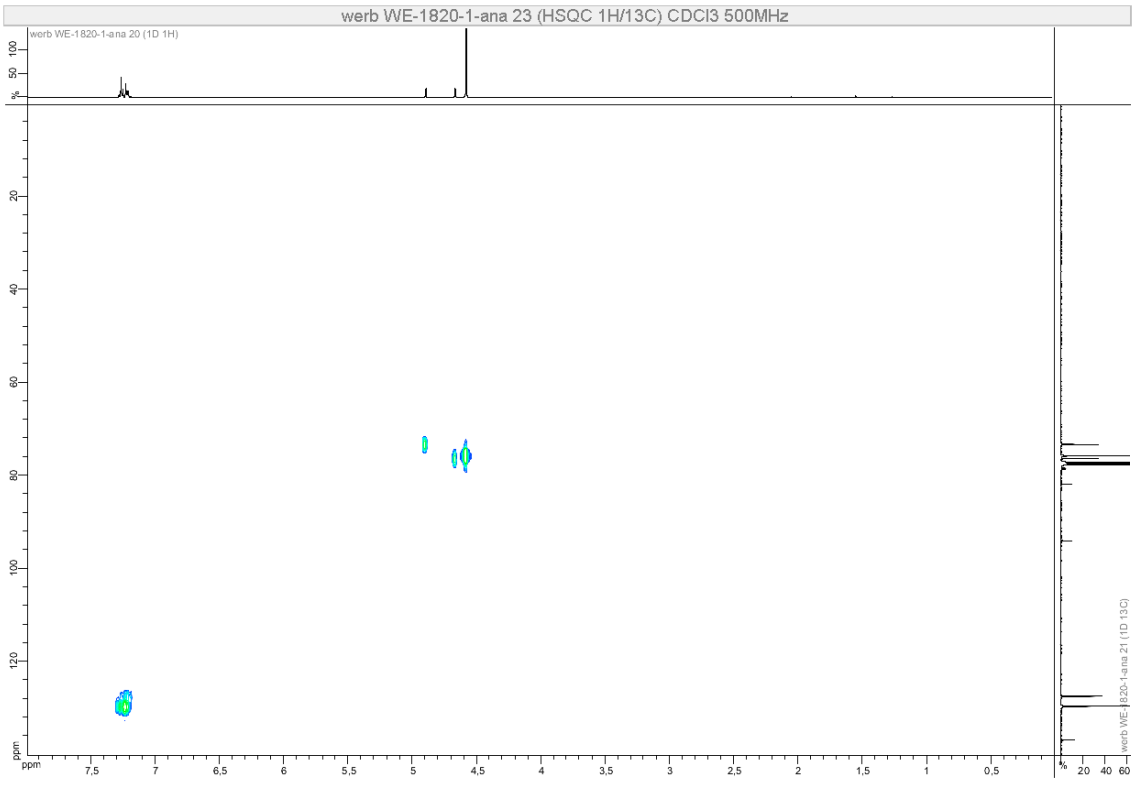
^{13}C NMR (125 MHz, $CDCl_3$)



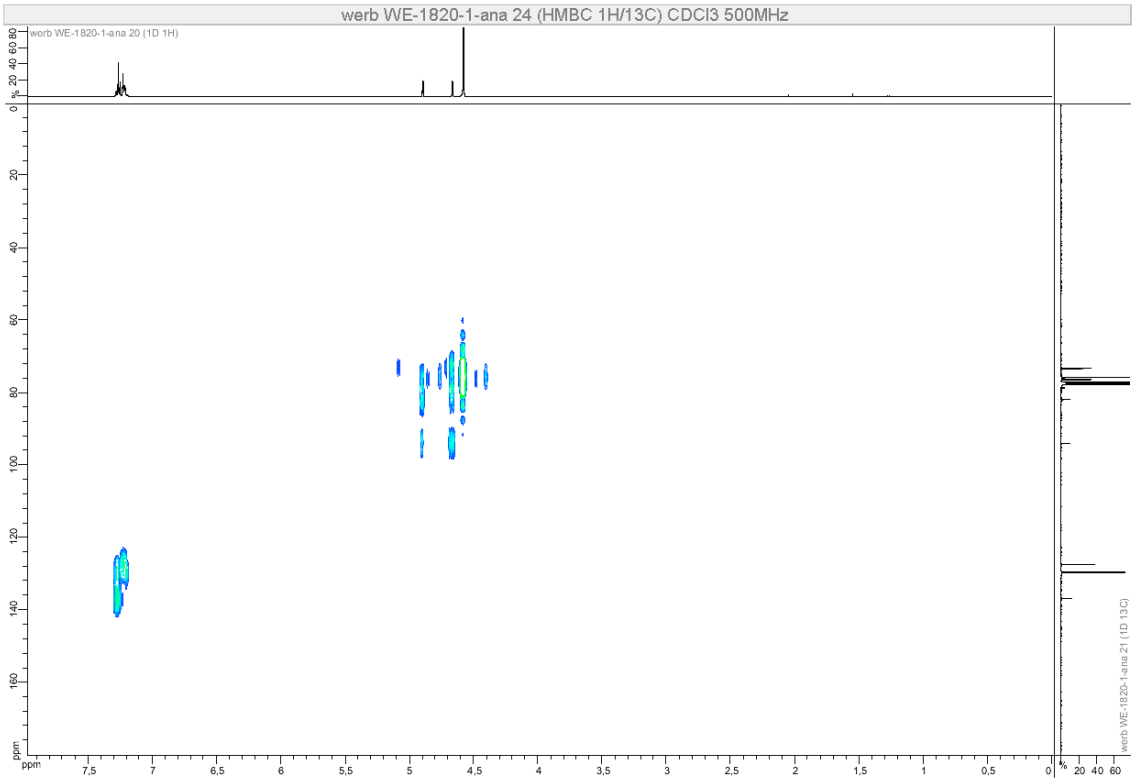
COSY (500 MHz, $CDCl_3$)



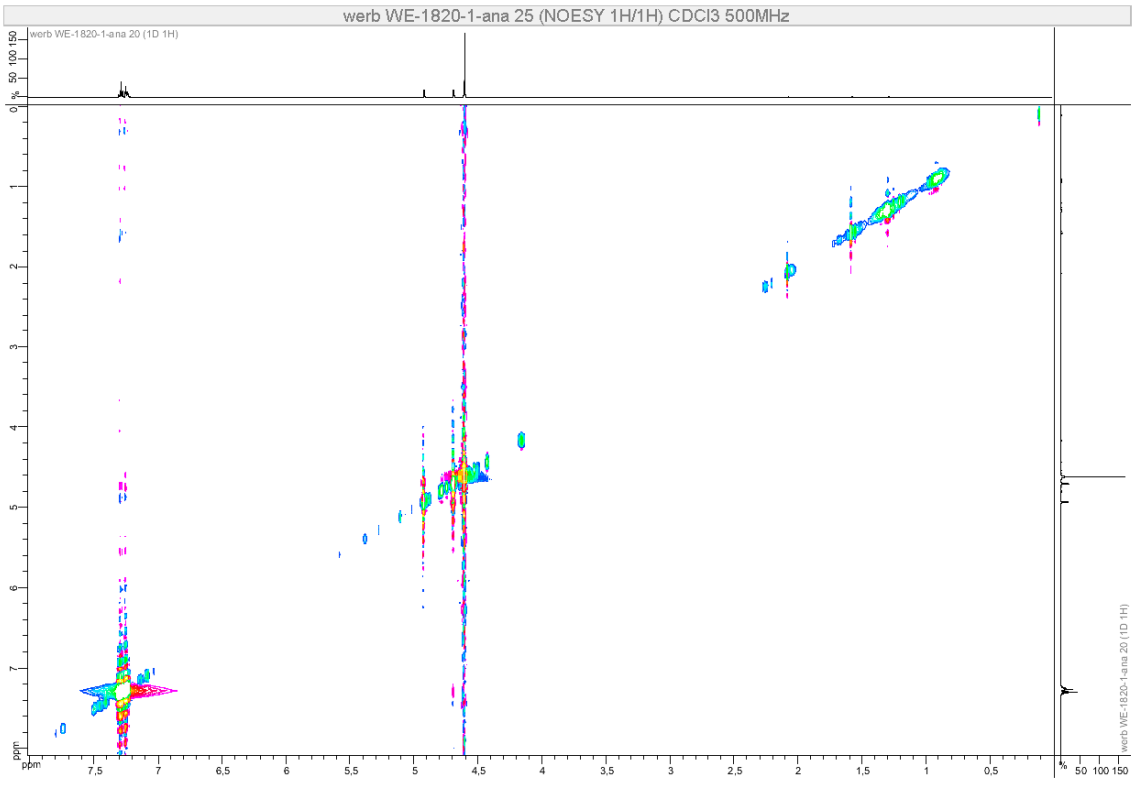
HSQC (500 MHz, $CDCl_3$)



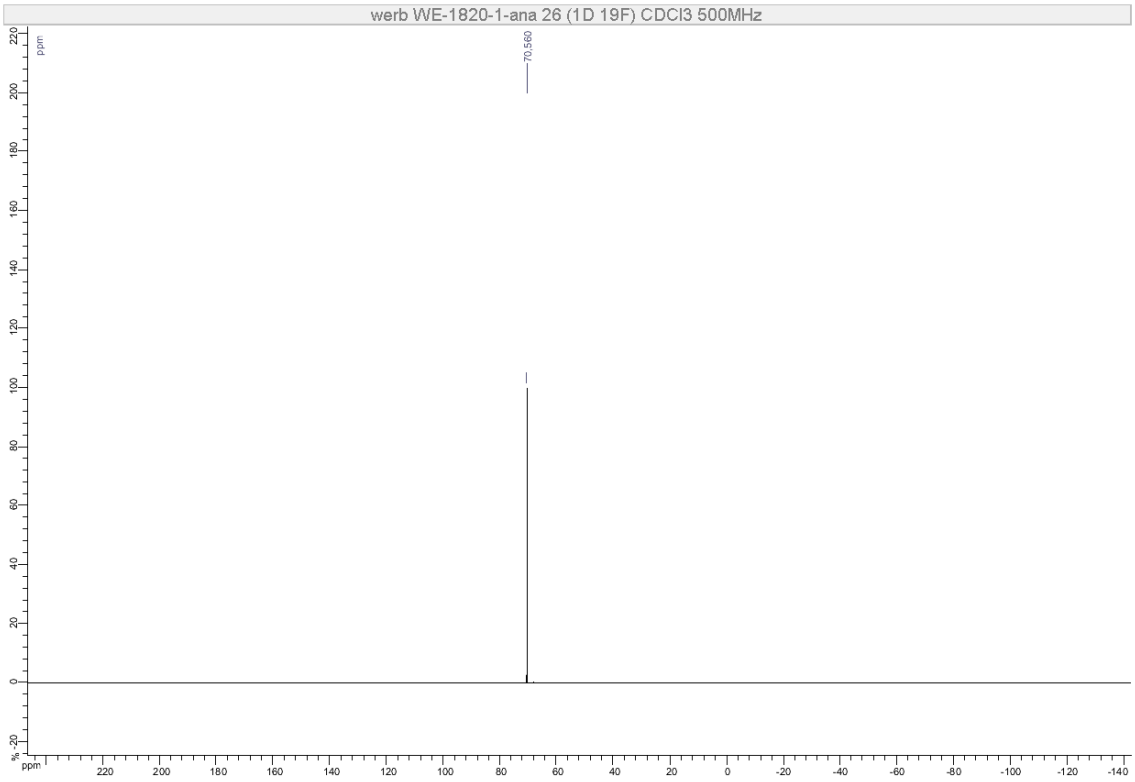
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

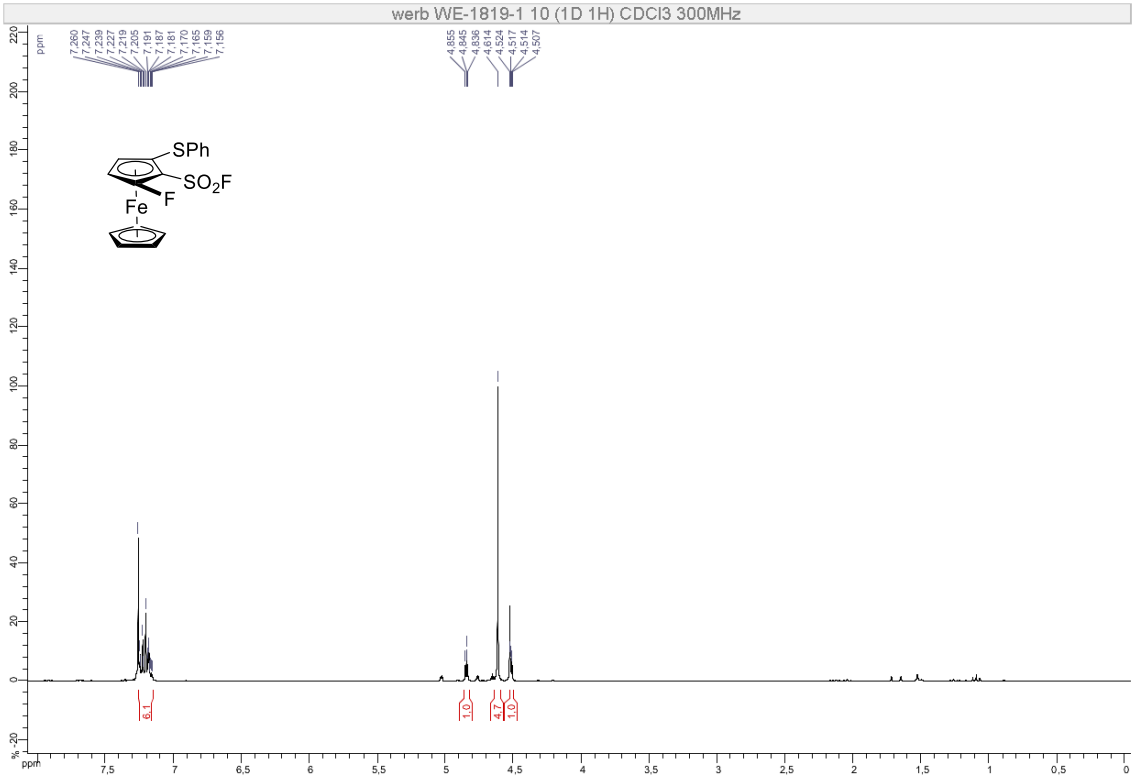


^{19}F NMR (470 MHz, $CDCl_3$)

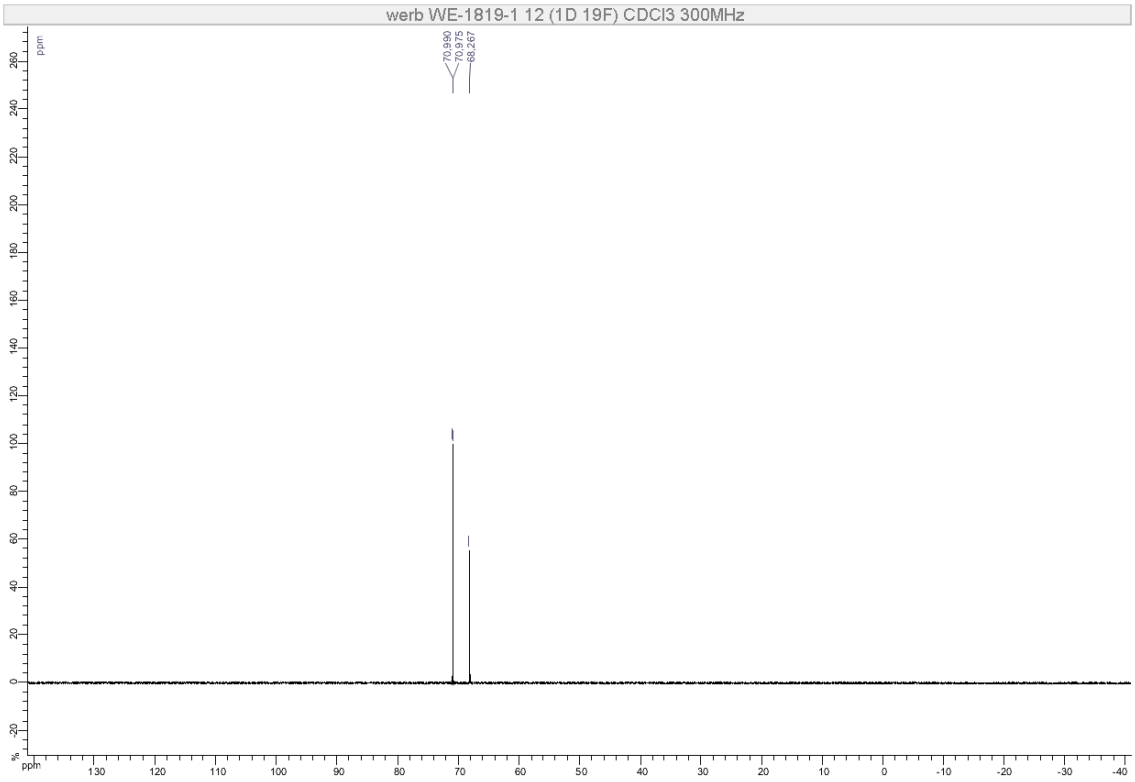


2-Fluoro-5-(phenylthio)ferrocenesulfonyl fluoride (5h)

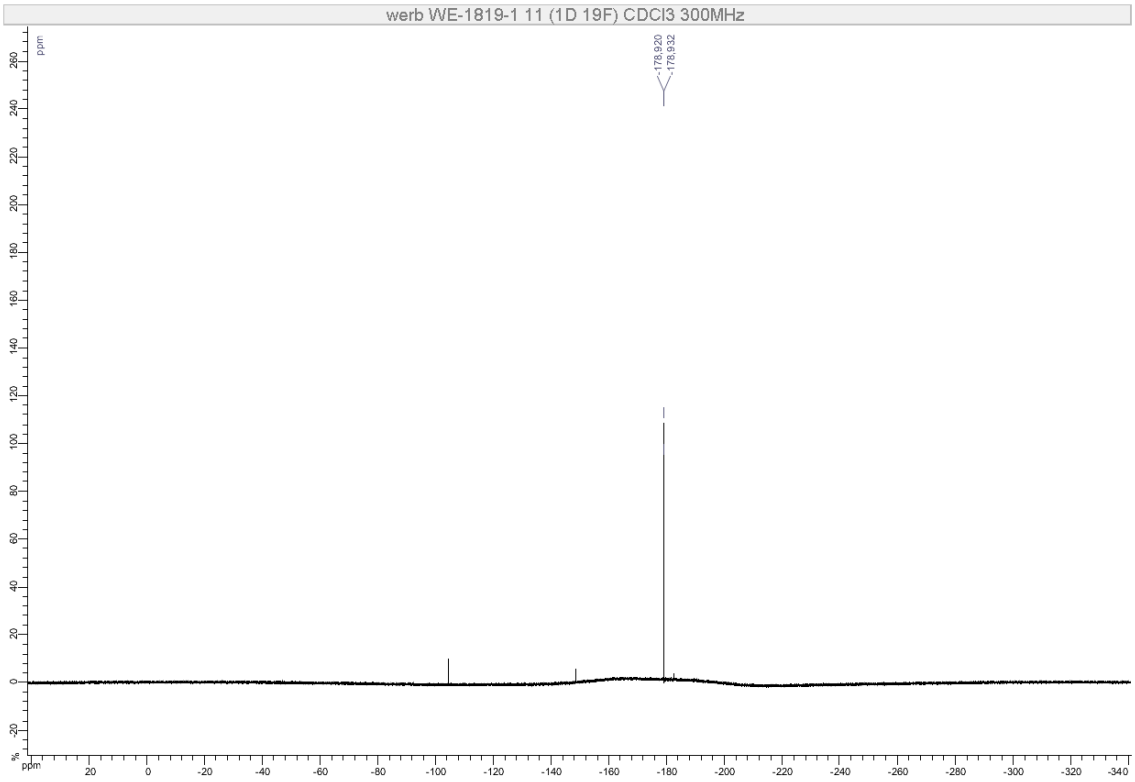
^{1}H NMR (300 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$) – 140 to -40 ppm area

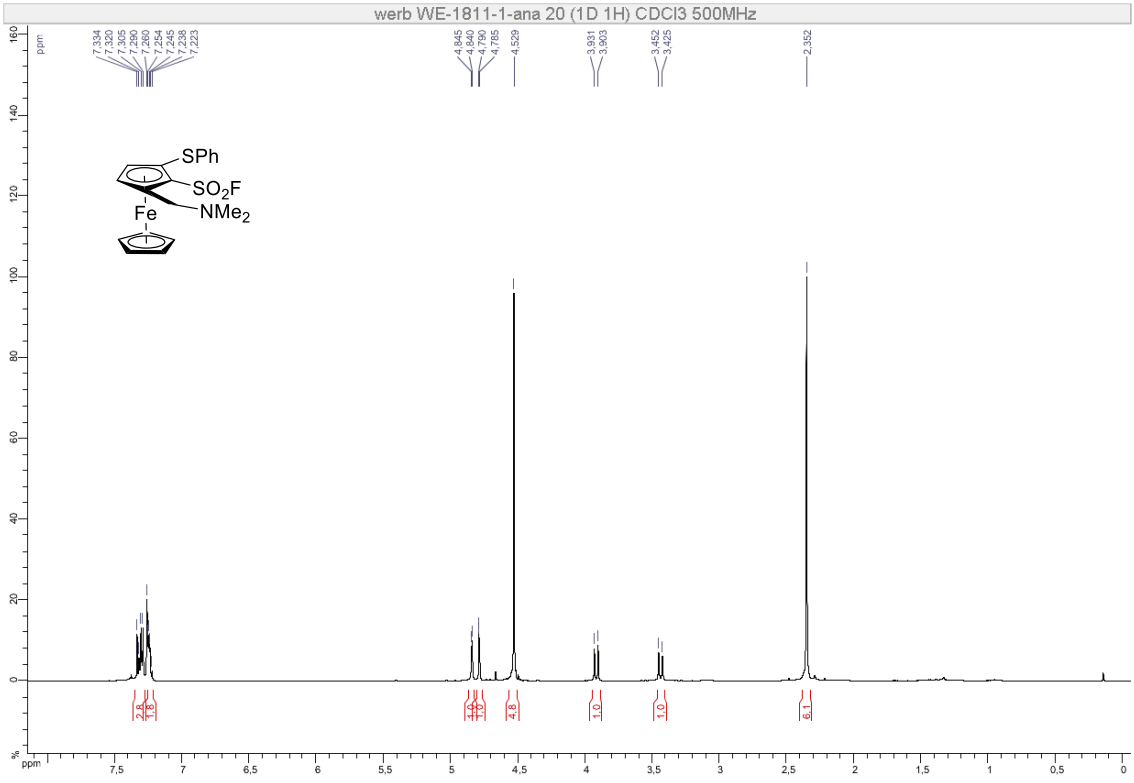


^{19}F NMR (470 MHz, $CDCl_3$) – 40 to -340 ppm area

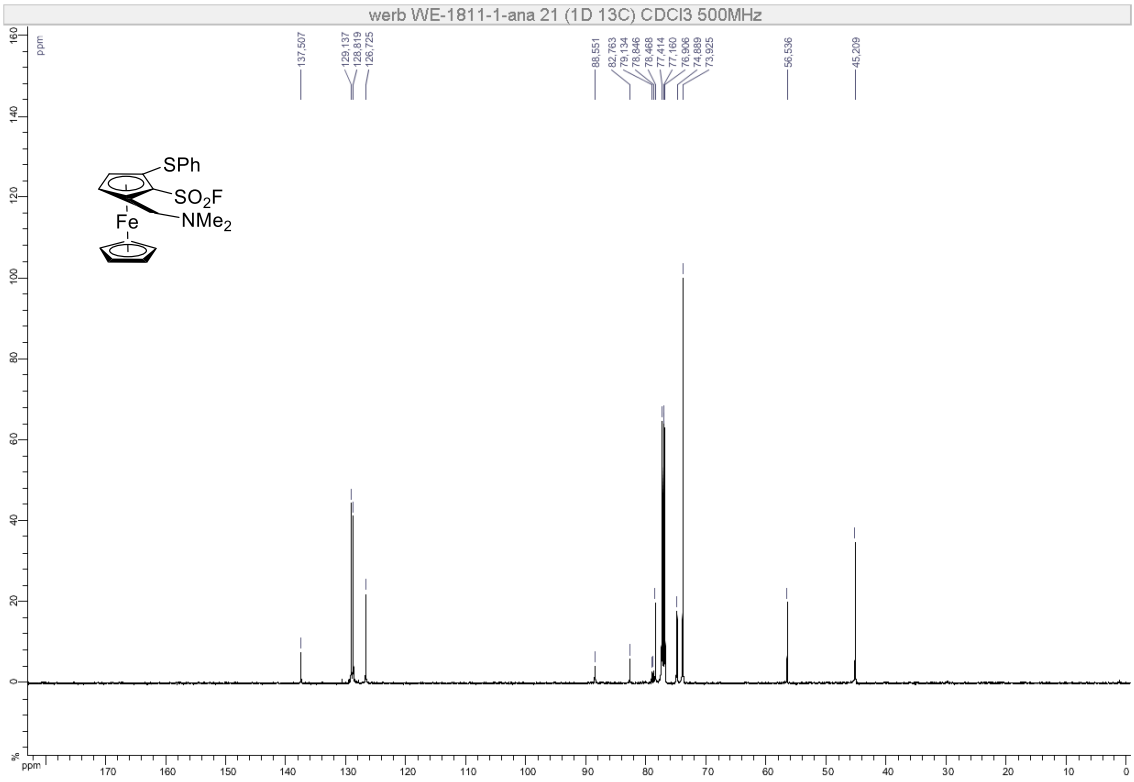


2-(*N*,*N*-Dimethylaminomethyl)-5-(phenylthio)ferrocenesulfonyl fluoride (5i)

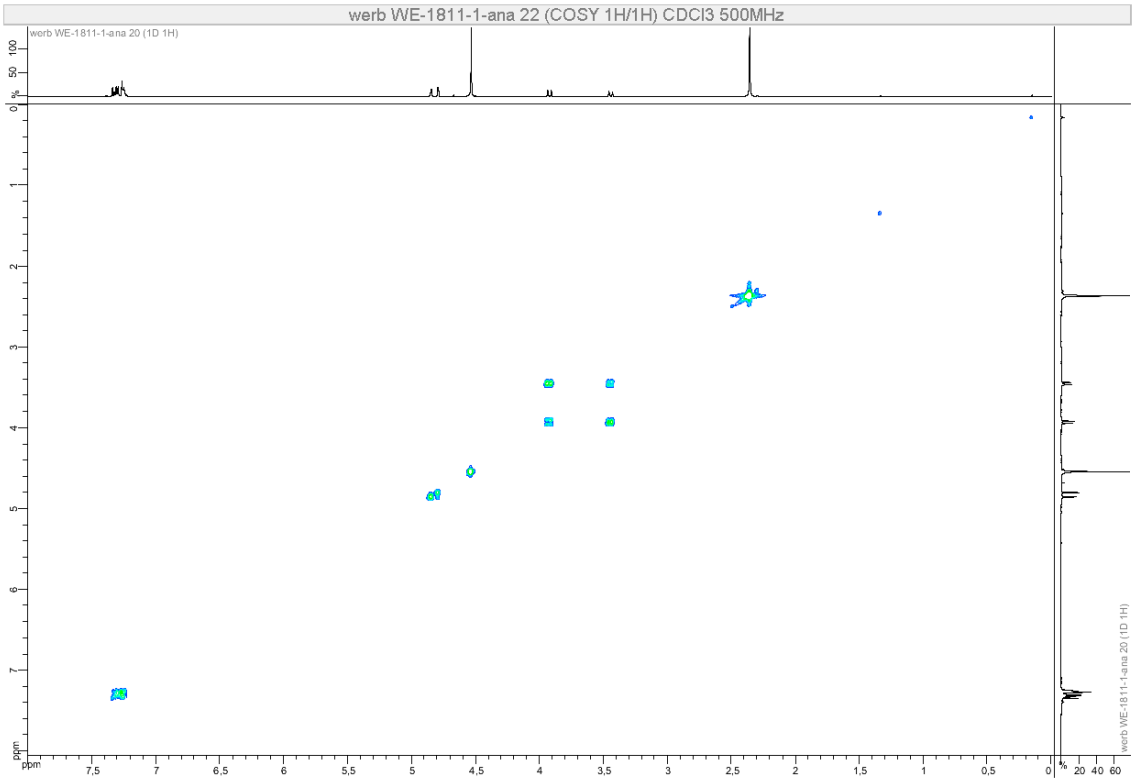
^{1}H NMR (500 MHz, $CDCl_3$)



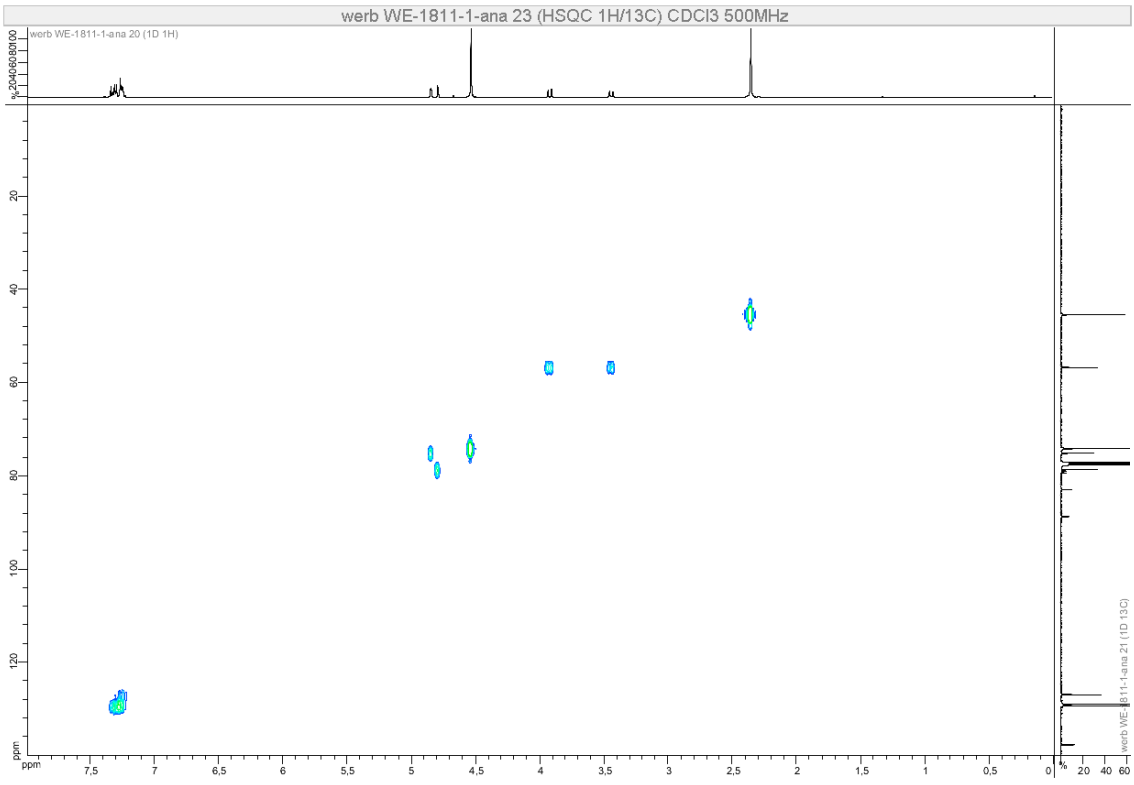
^{13}C NMR (125 MHz, $CDCl_3$)



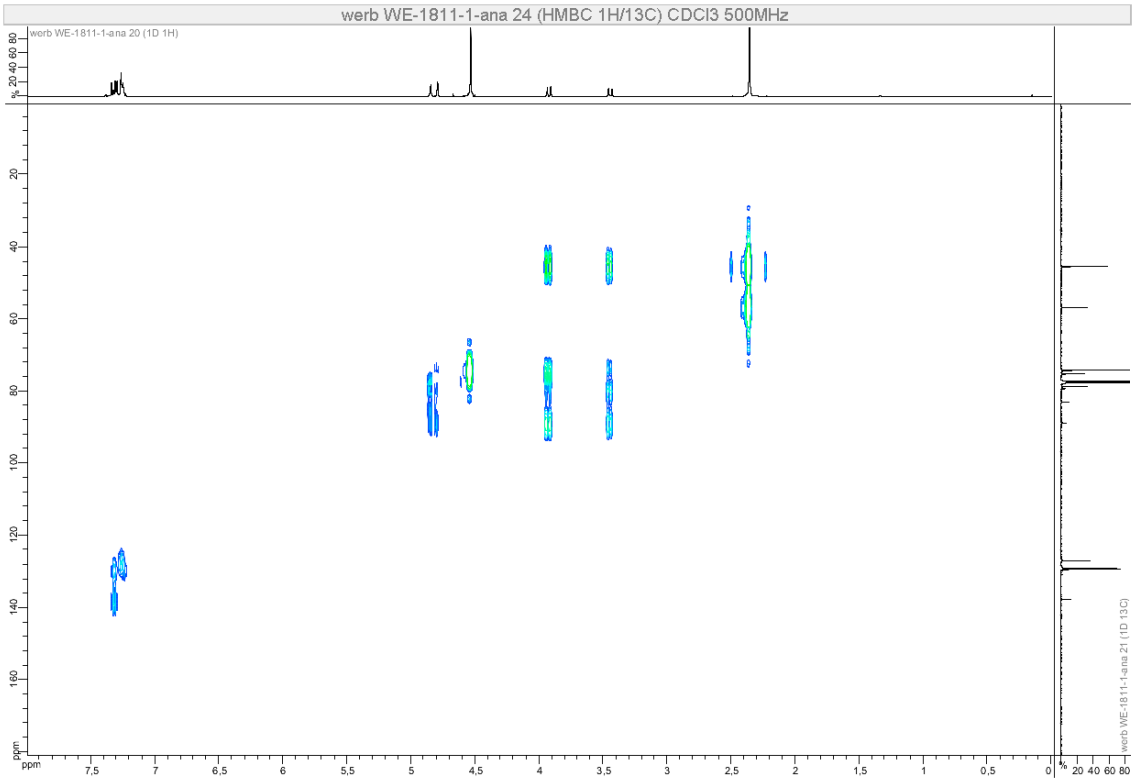
COSY (500 MHz, $CDCl_3$)



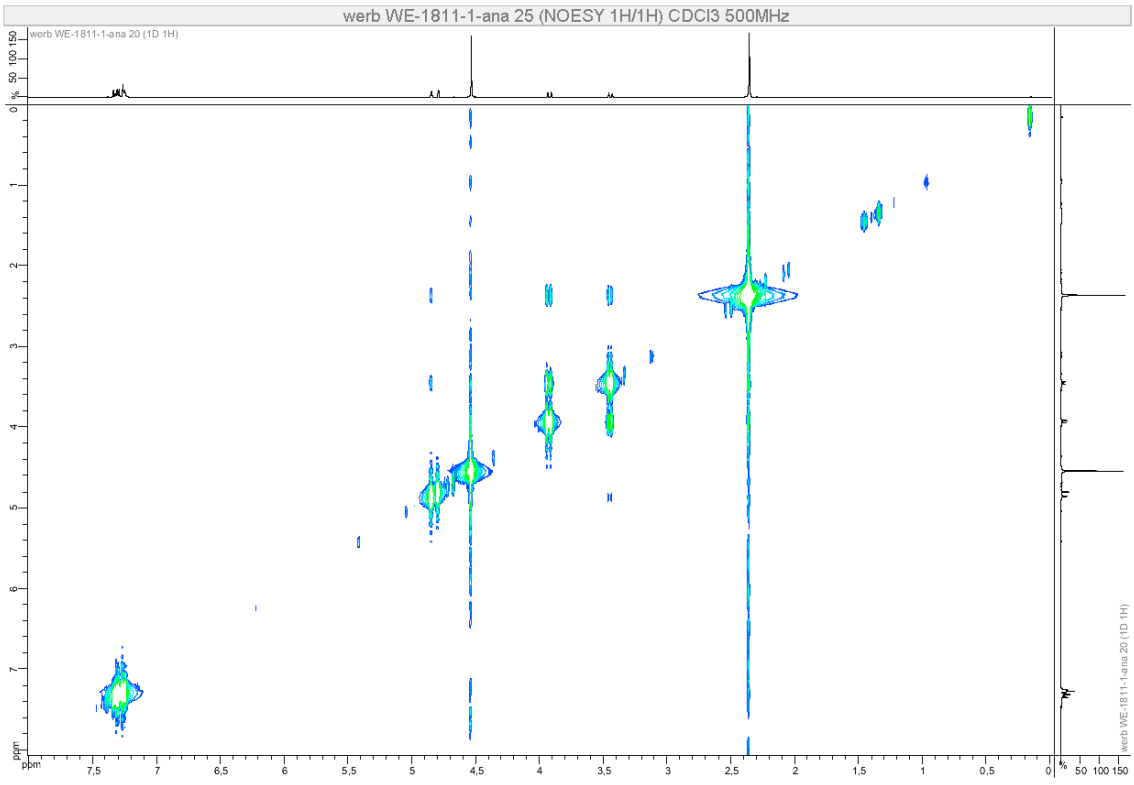
HSQC (500 MHz, $CDCl_3$)



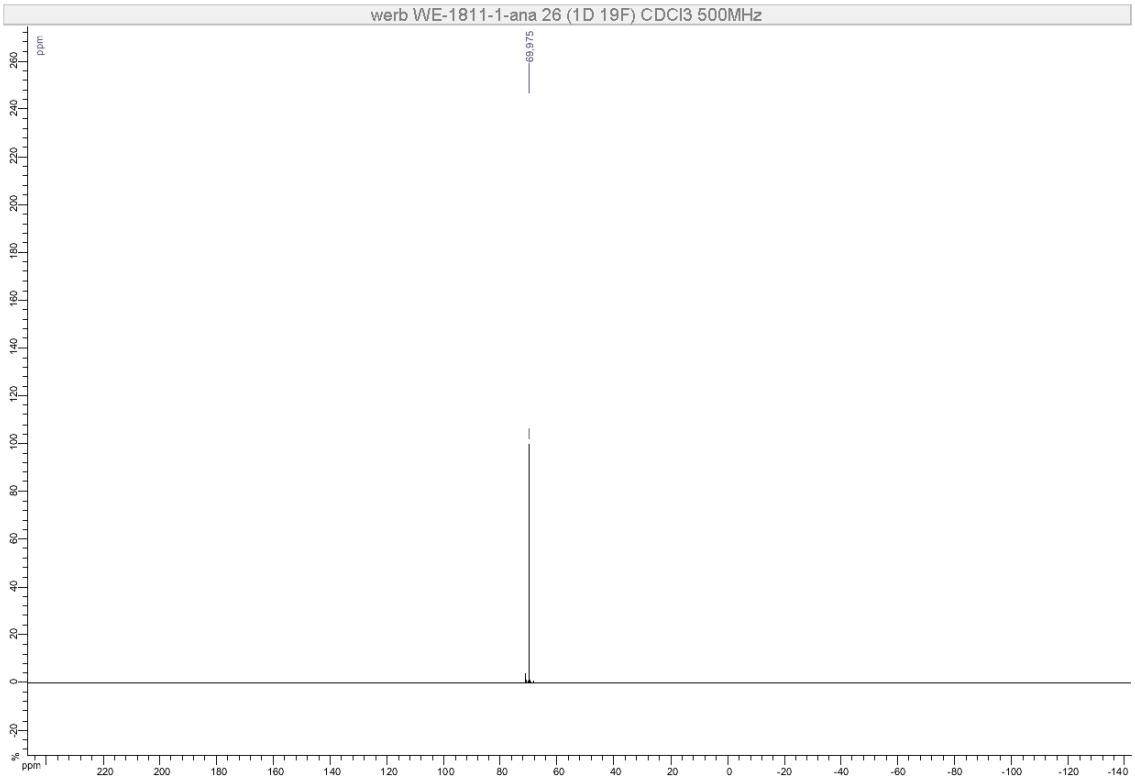
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

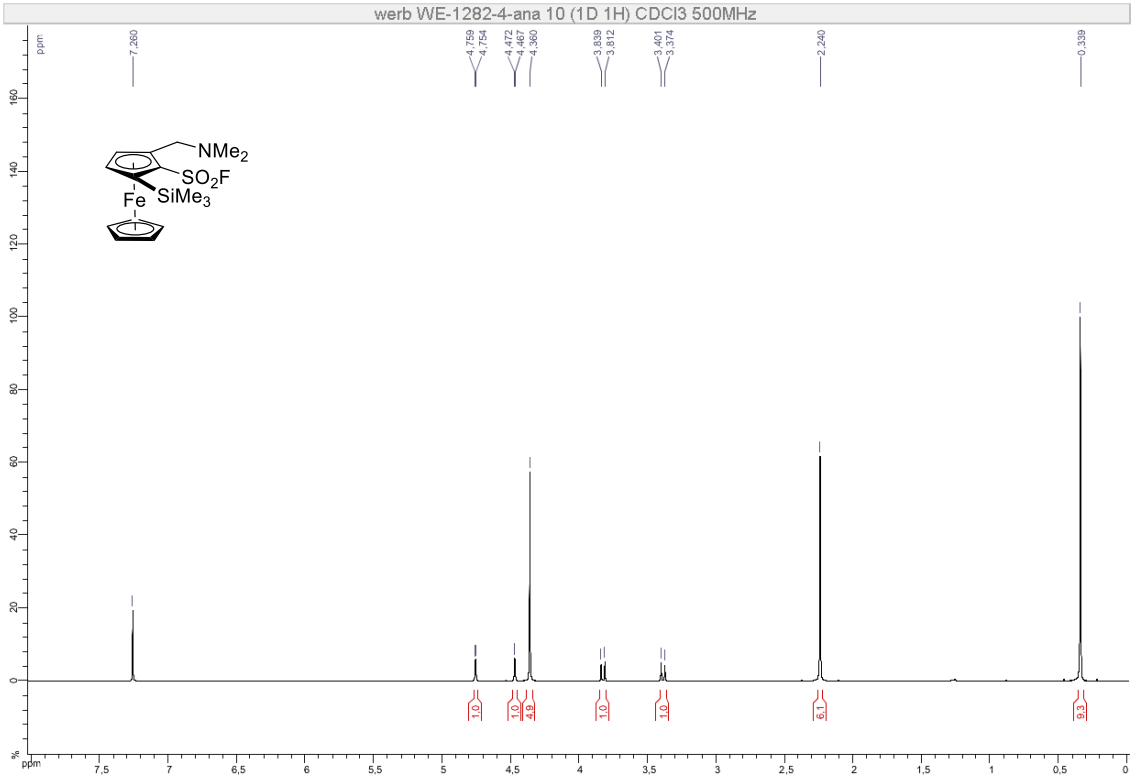


^{19}F NMR (470 MHz, $CDCl_3$)

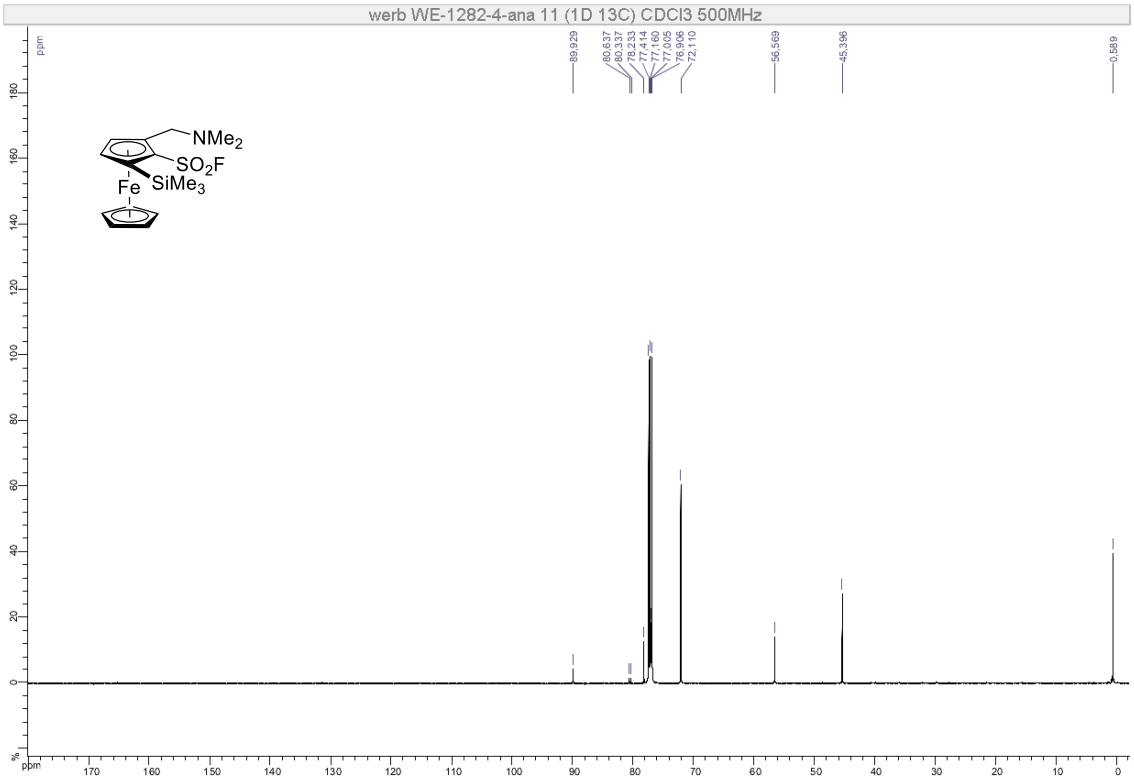


2-(*N*,*N*-Dimethylaminomethyl)-5-(phenylthio)ferrocenesulfonyl fluoride (5j)

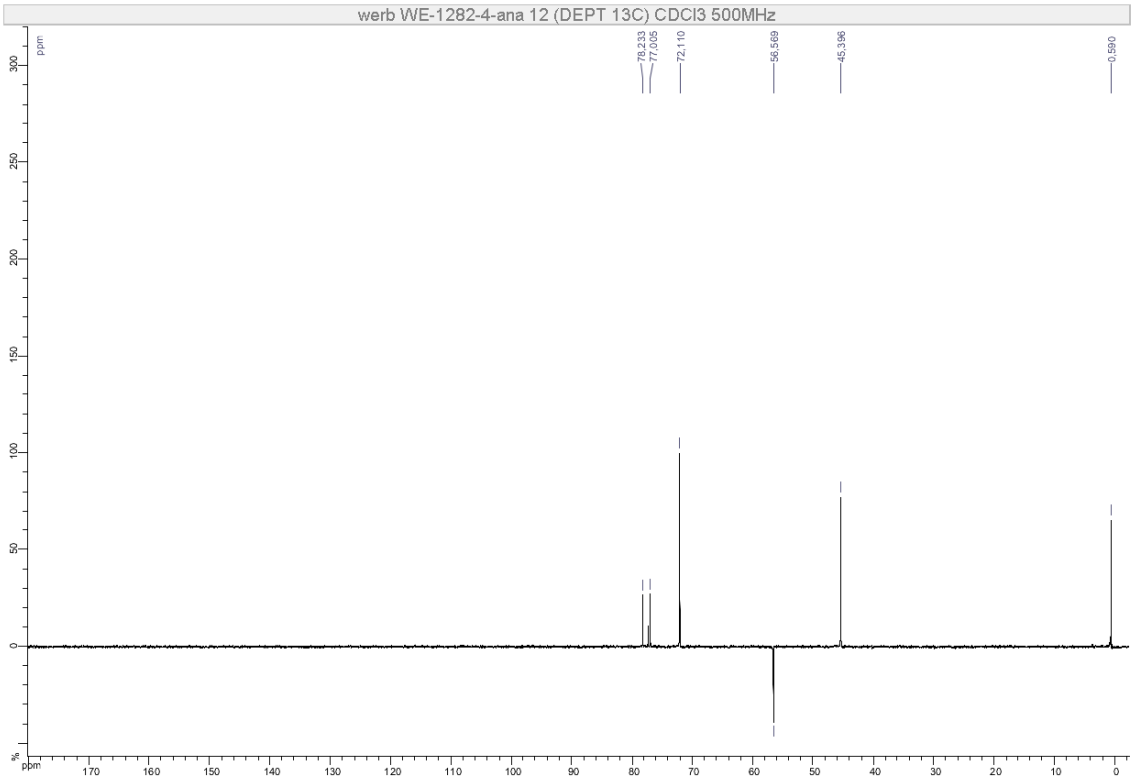
^{1}H NMR (500 MHz, $CDCl_3$)



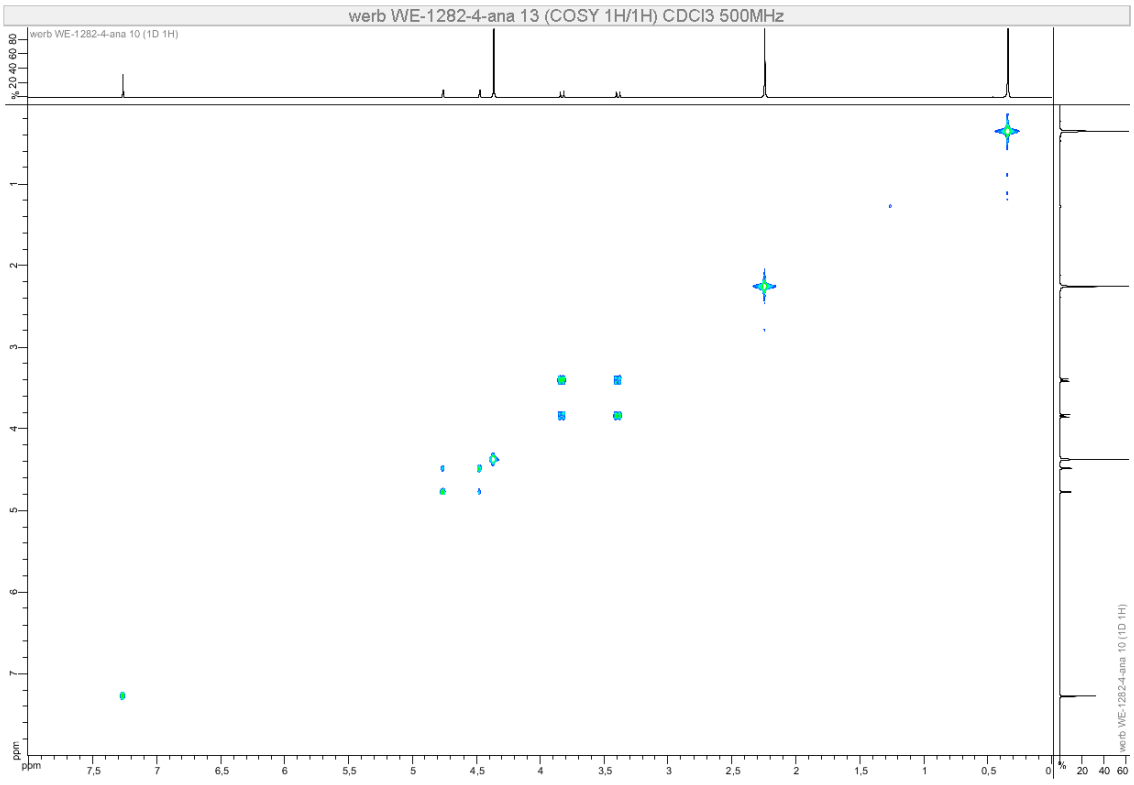
^{13}C NMR (125 MHz, $CDCl_3$)



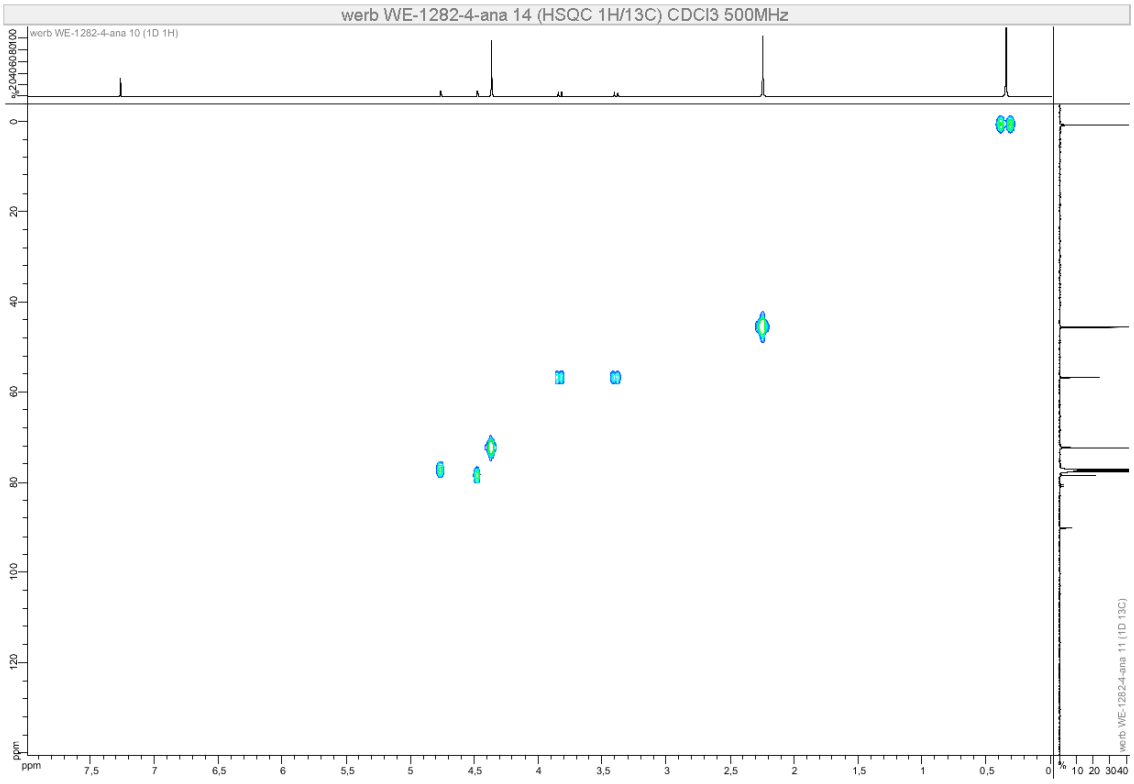
DEPT 135 (500 MHz, $CDCl_3$)



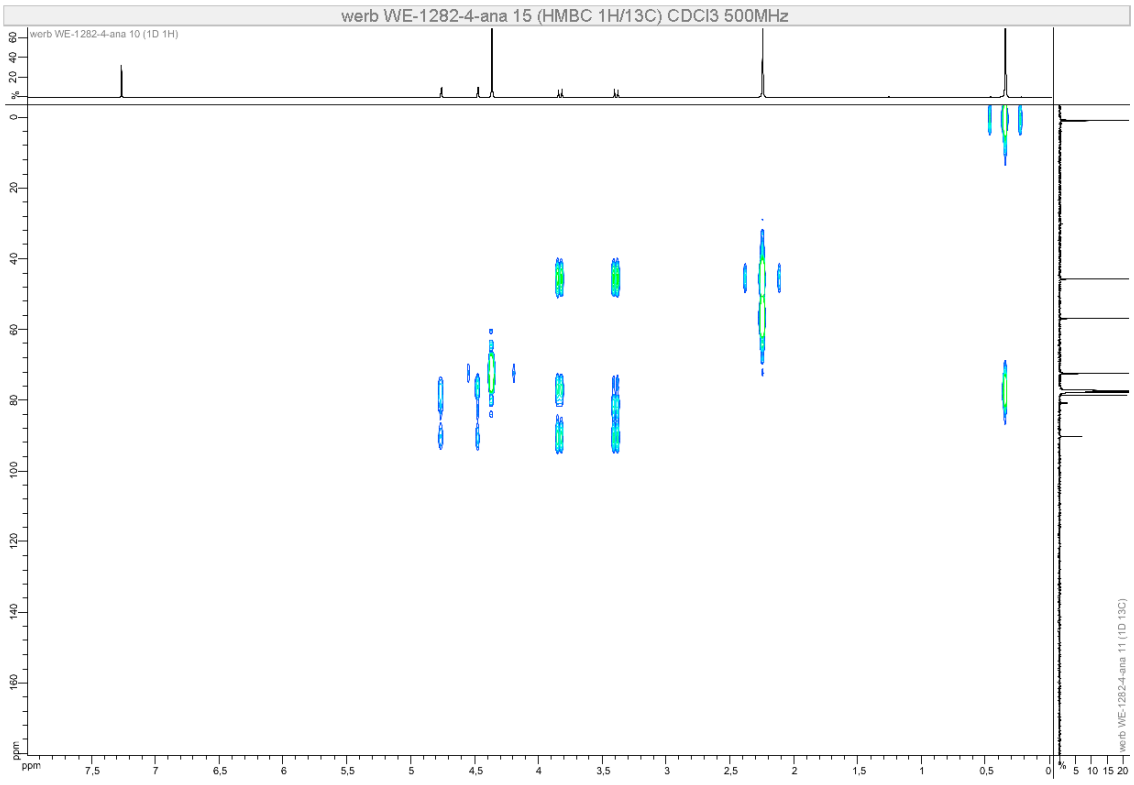
COSY (500 MHz, $CDCl_3$)



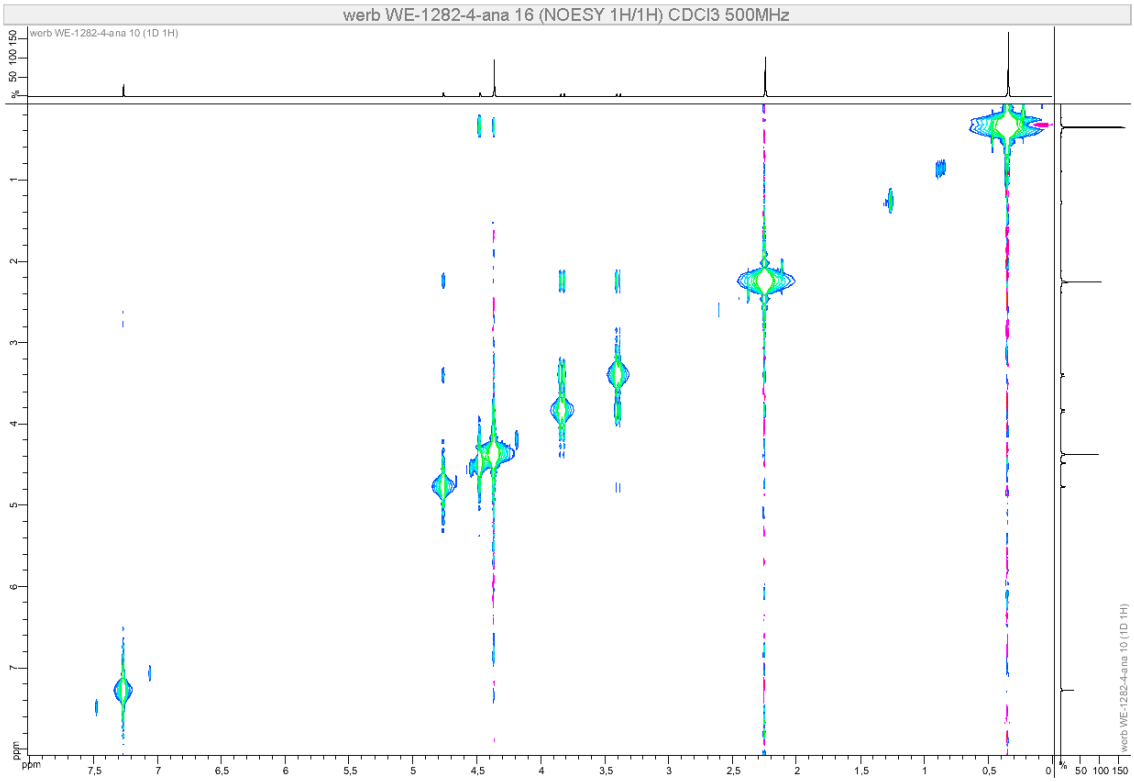
HSQC (500 MHz, $CDCl_3$)



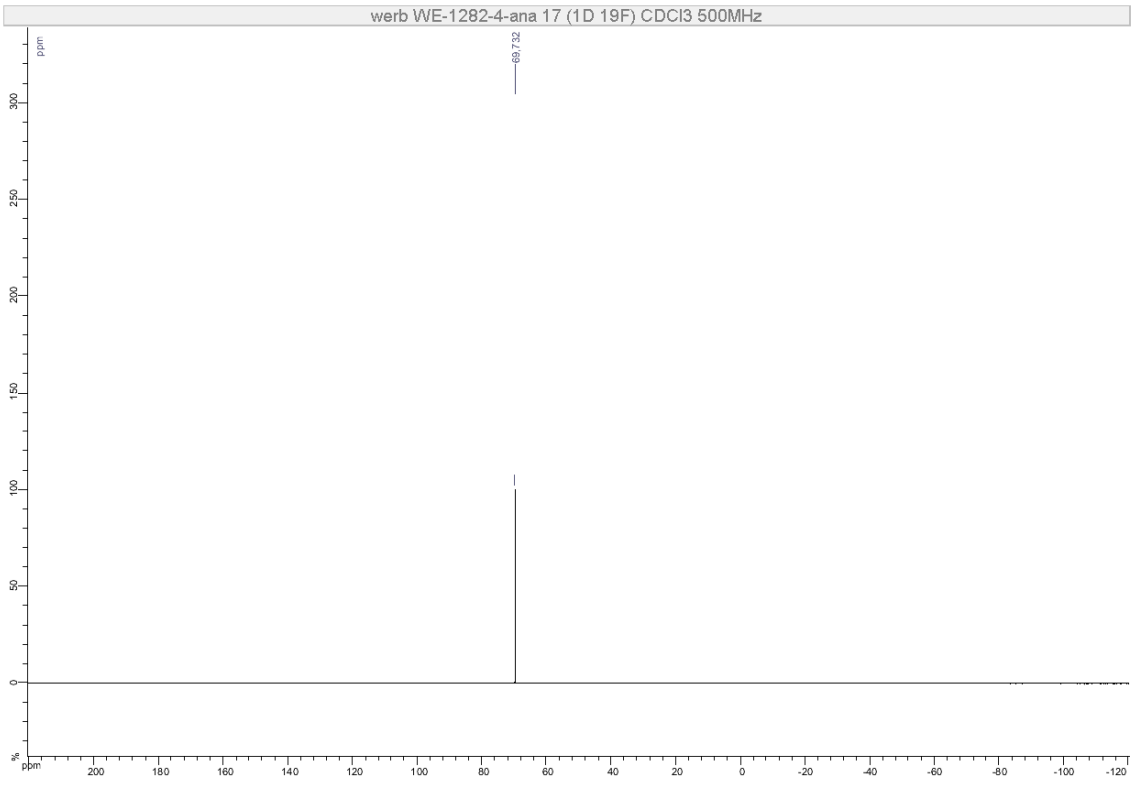
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

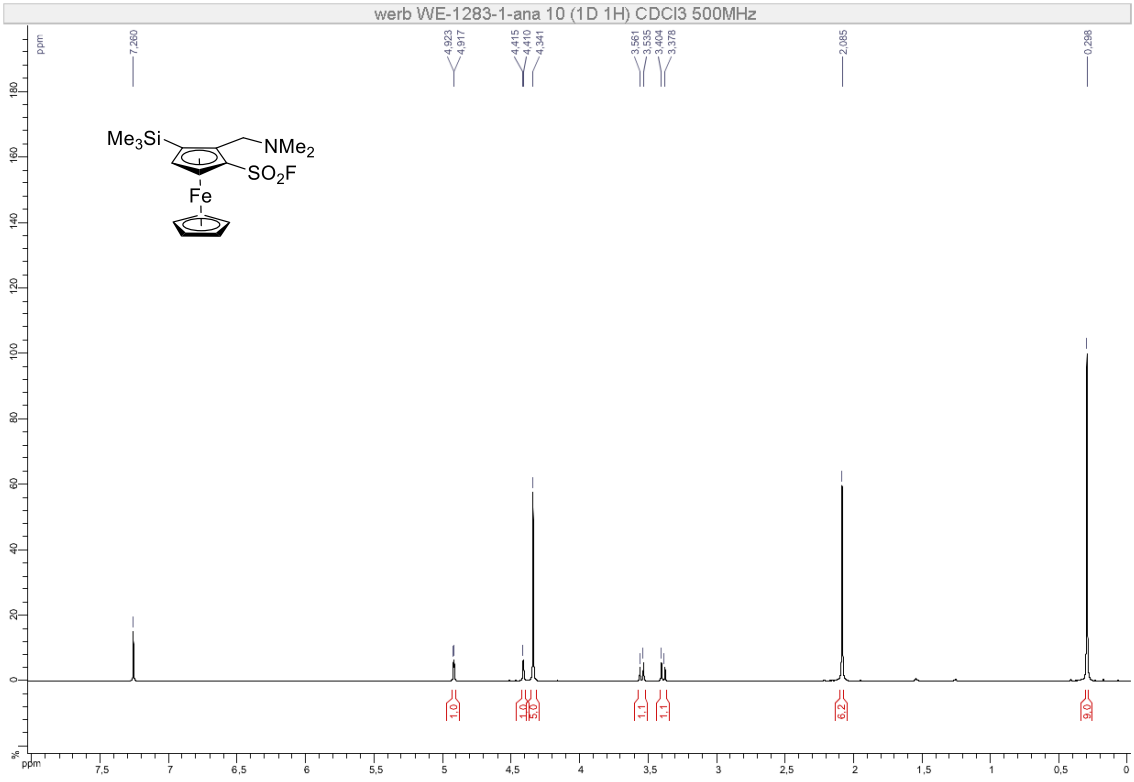


^{19}F NMR (470 MHz, $CDCl_3$)

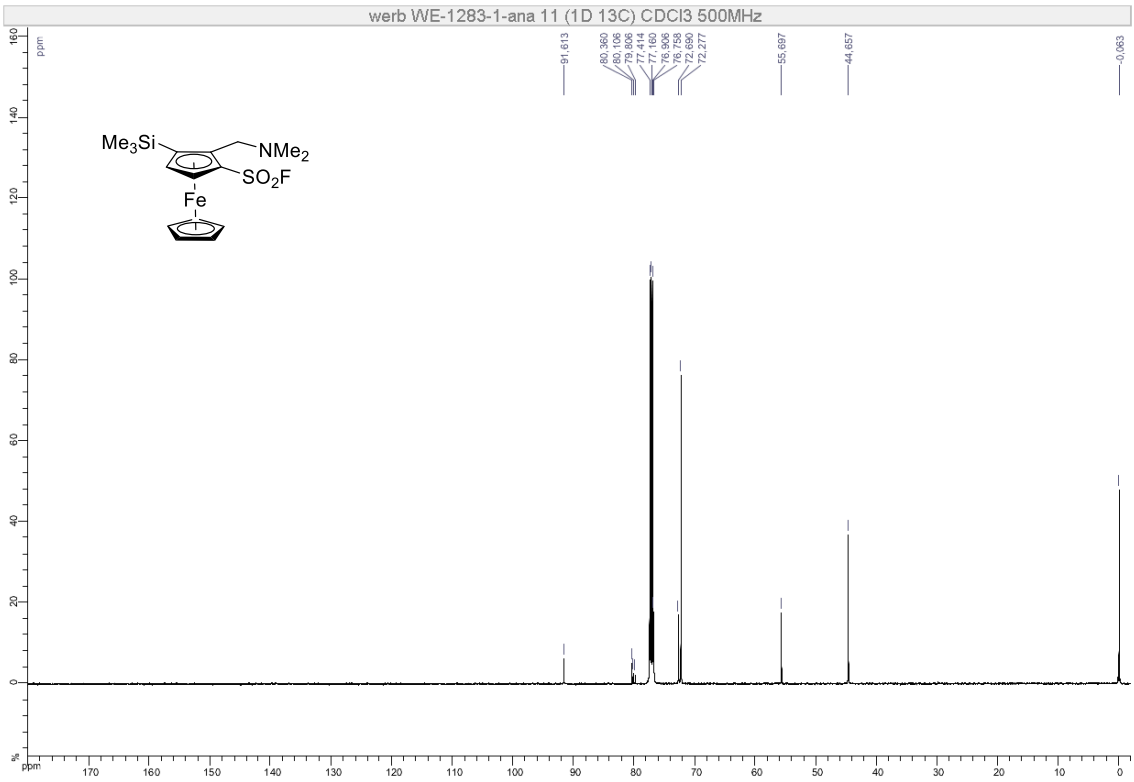


2-(*N*,*N*-Dimethylaminomethyl)-3-(trimethylsilyl)ferrocenesulfonyl fluoride (5k)

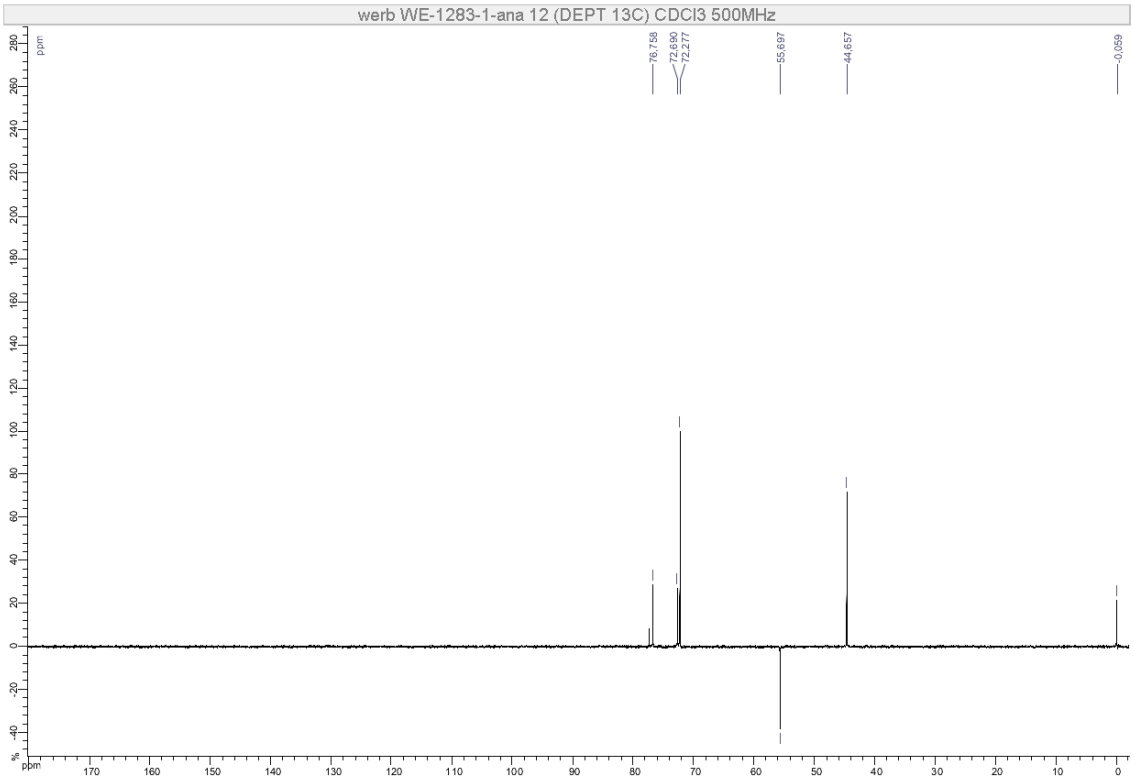
^{1}H NMR (500 MHz, $CDCl_3$)



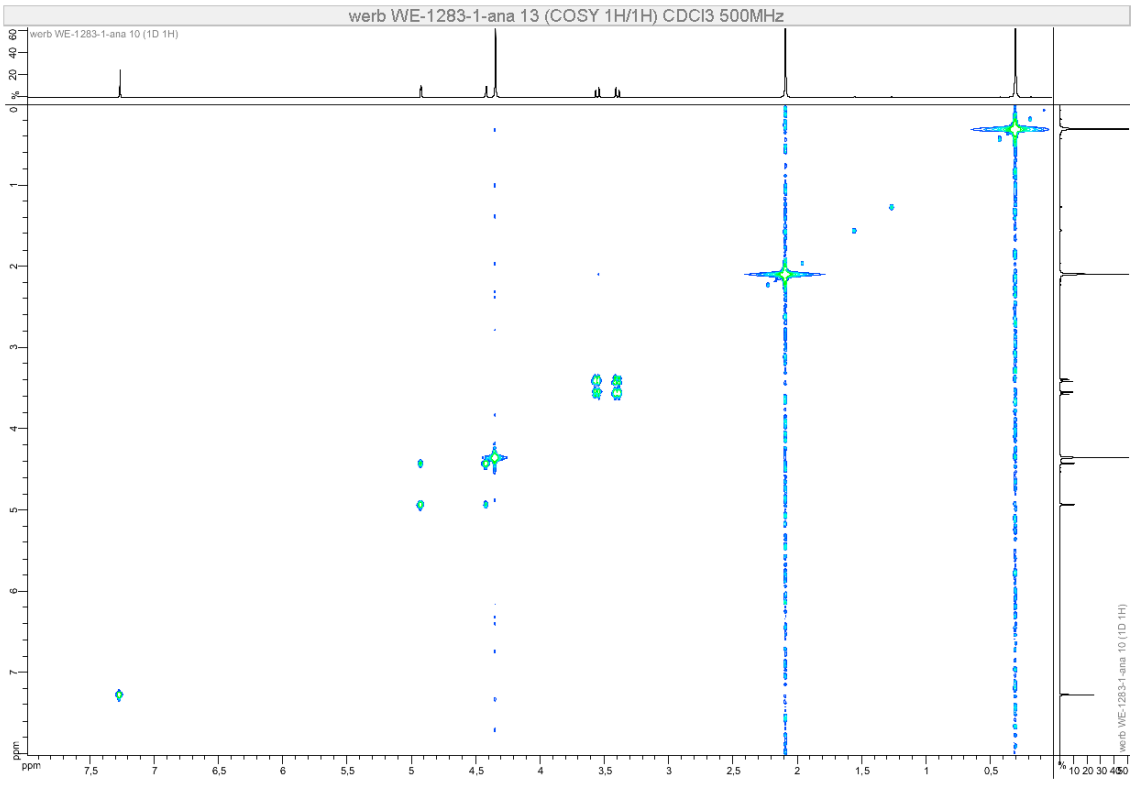
^{13}C NMR (125 MHz, $CDCl_3$)



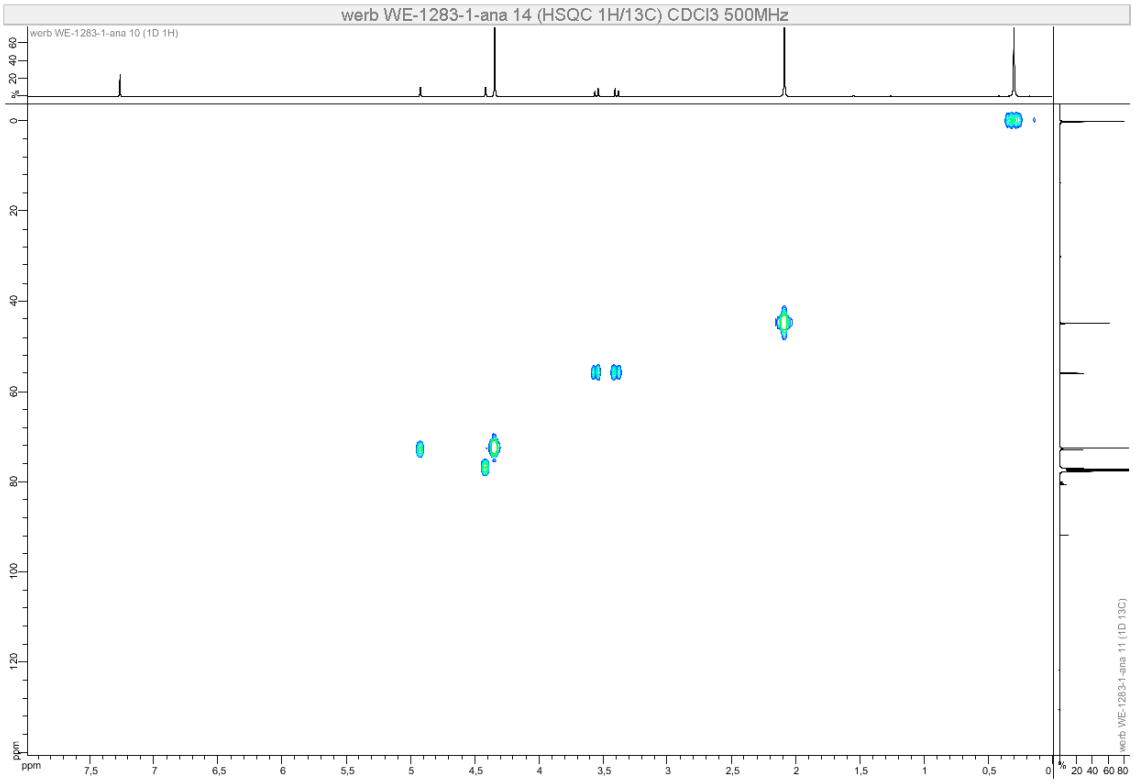
DEPT 135 (500 MHz, $CDCl_3$)



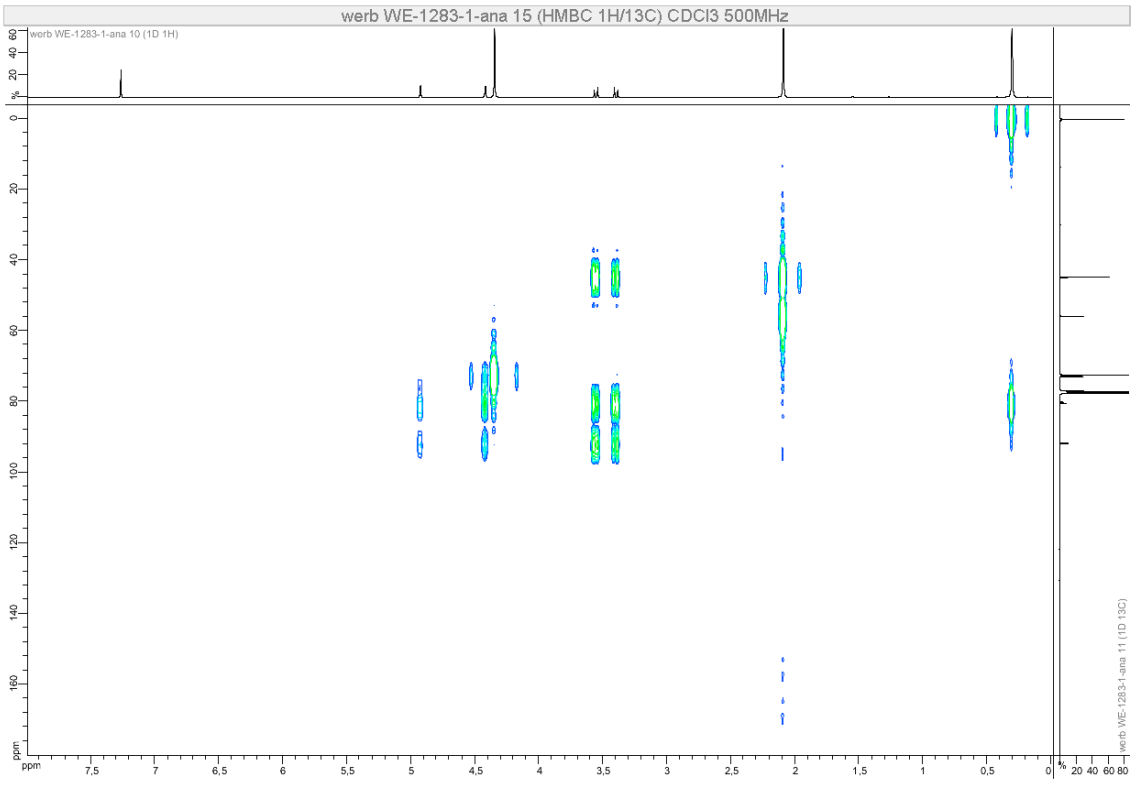
COSY (500 MHz, $CDCl_3$)



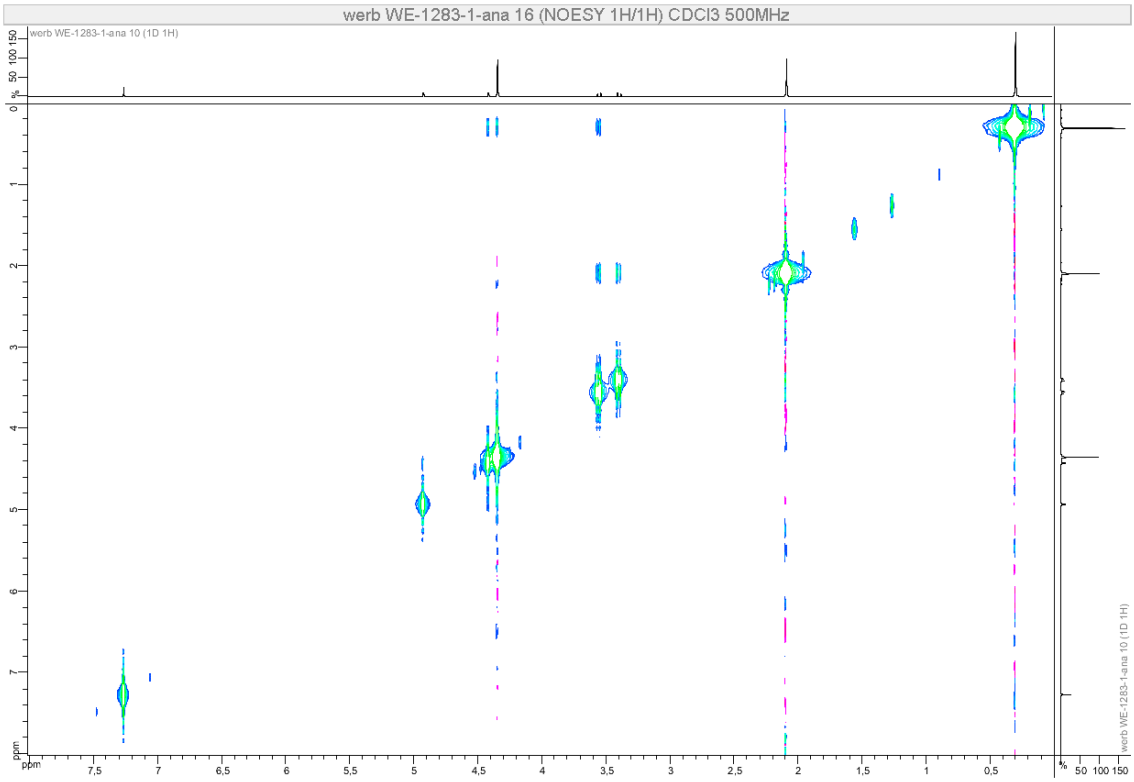
HSQC (500 MHz, $CDCl_3$)



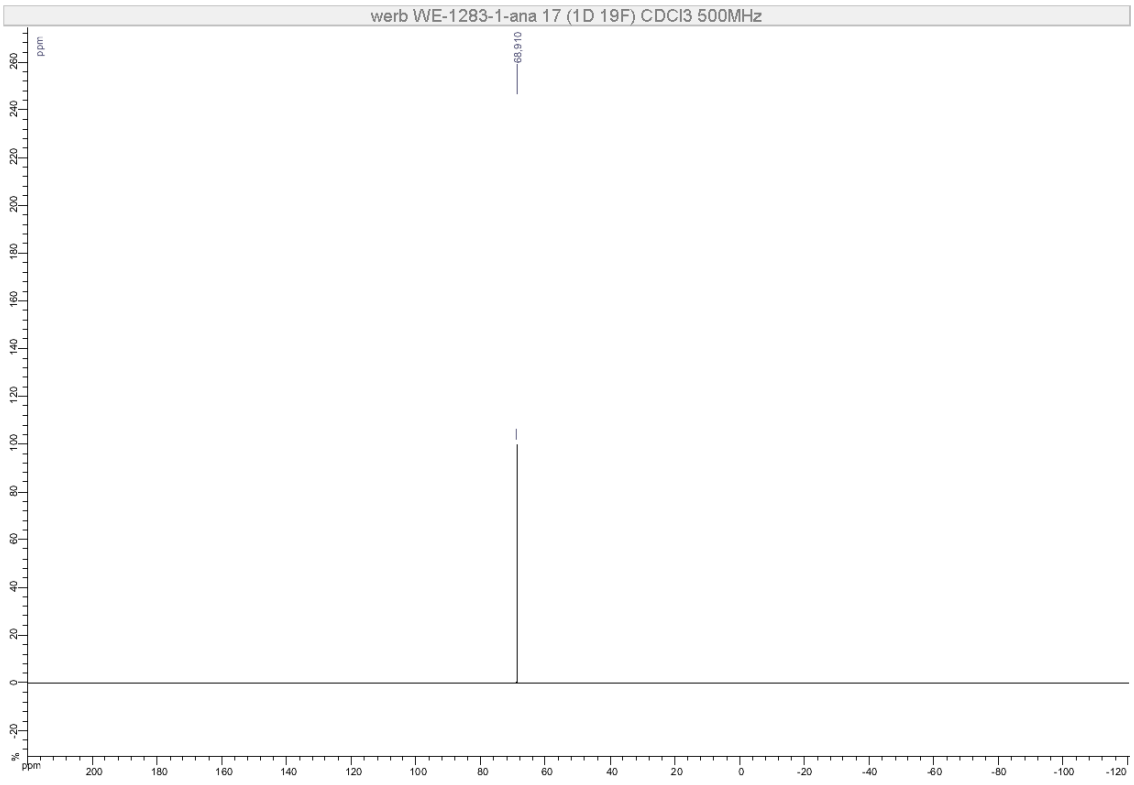
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

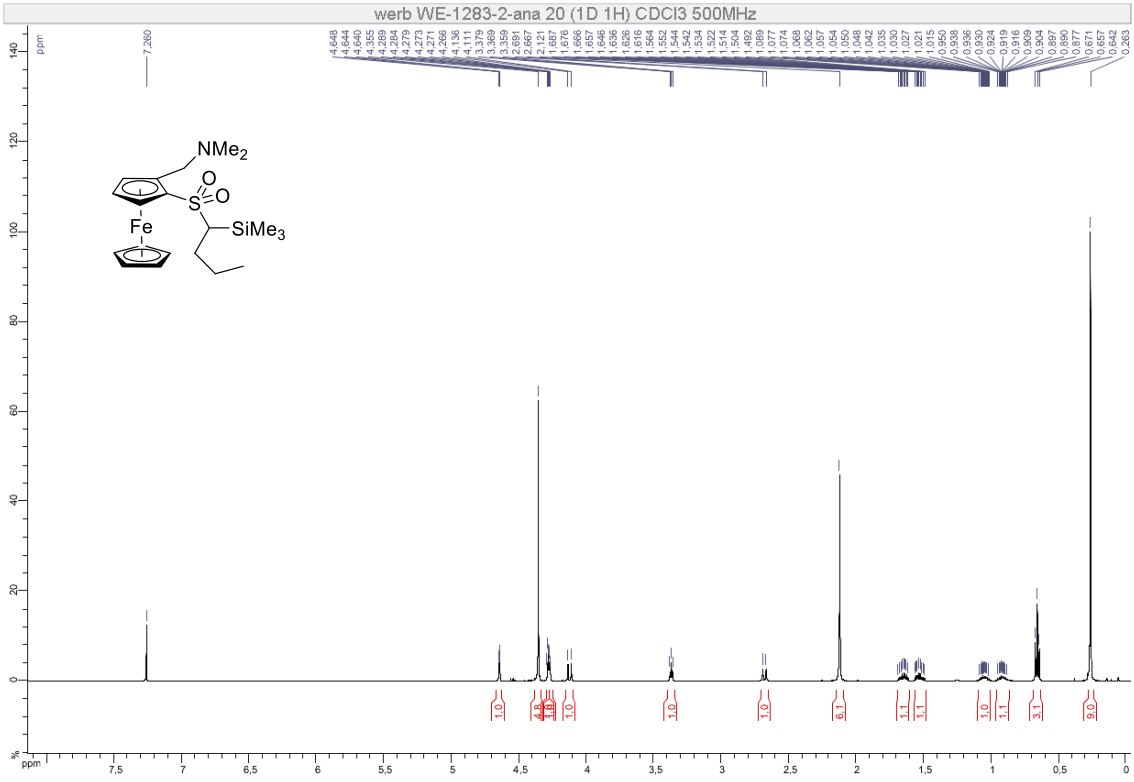


^{19}F NMR (470 MHz, $CDCl_3$)

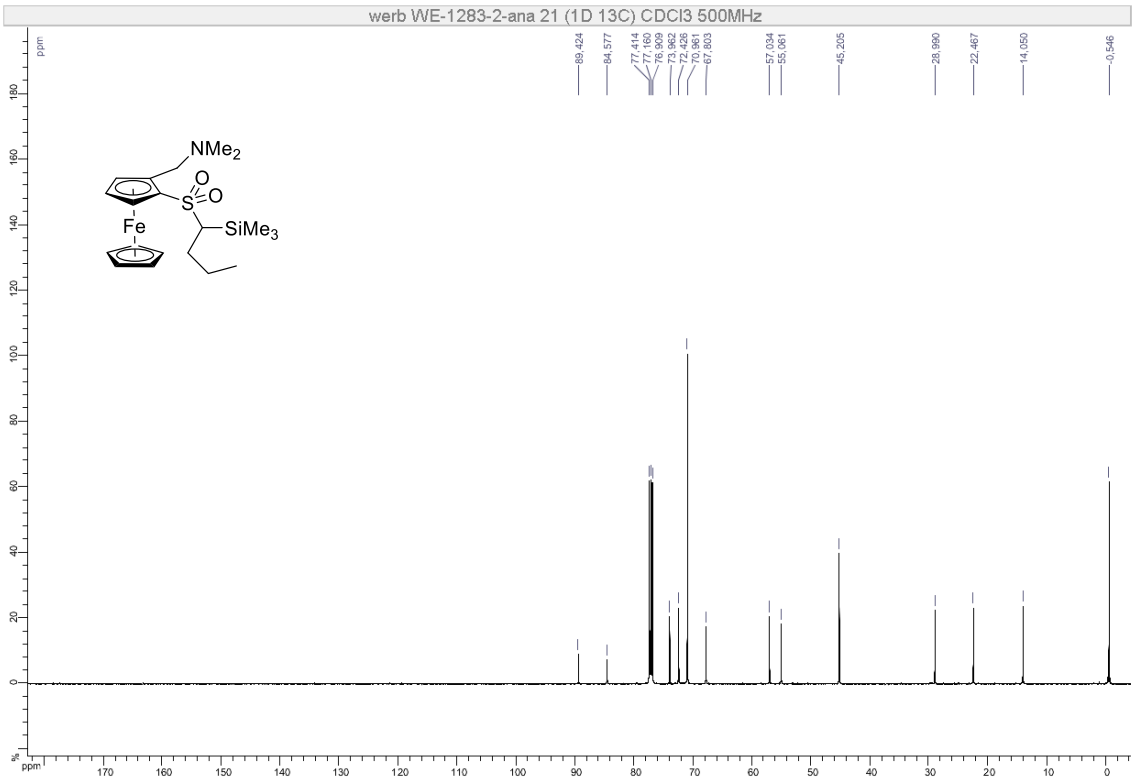


2-(*N*,*N*-Dimethylaminomethyl)-1-(1-(trimethylsilyl)butylsulfonyl)ferrocene (4e)

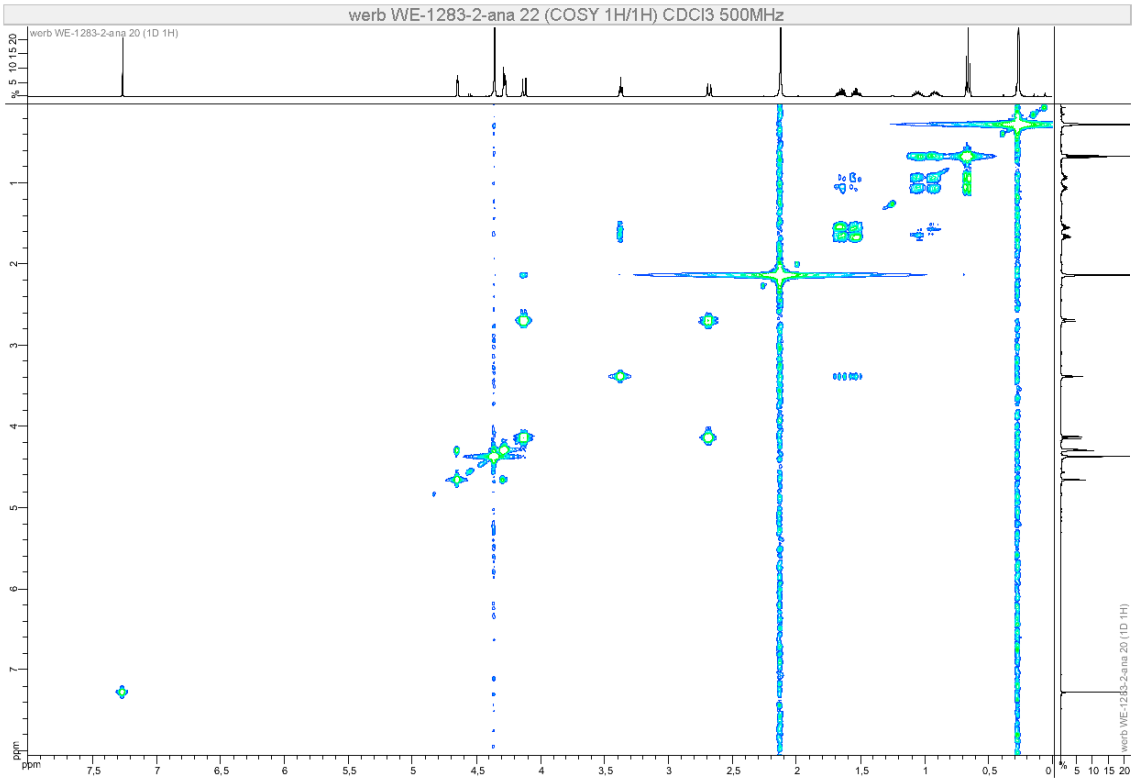
^{1}H NMR (500 MHz, $CDCl_3$)



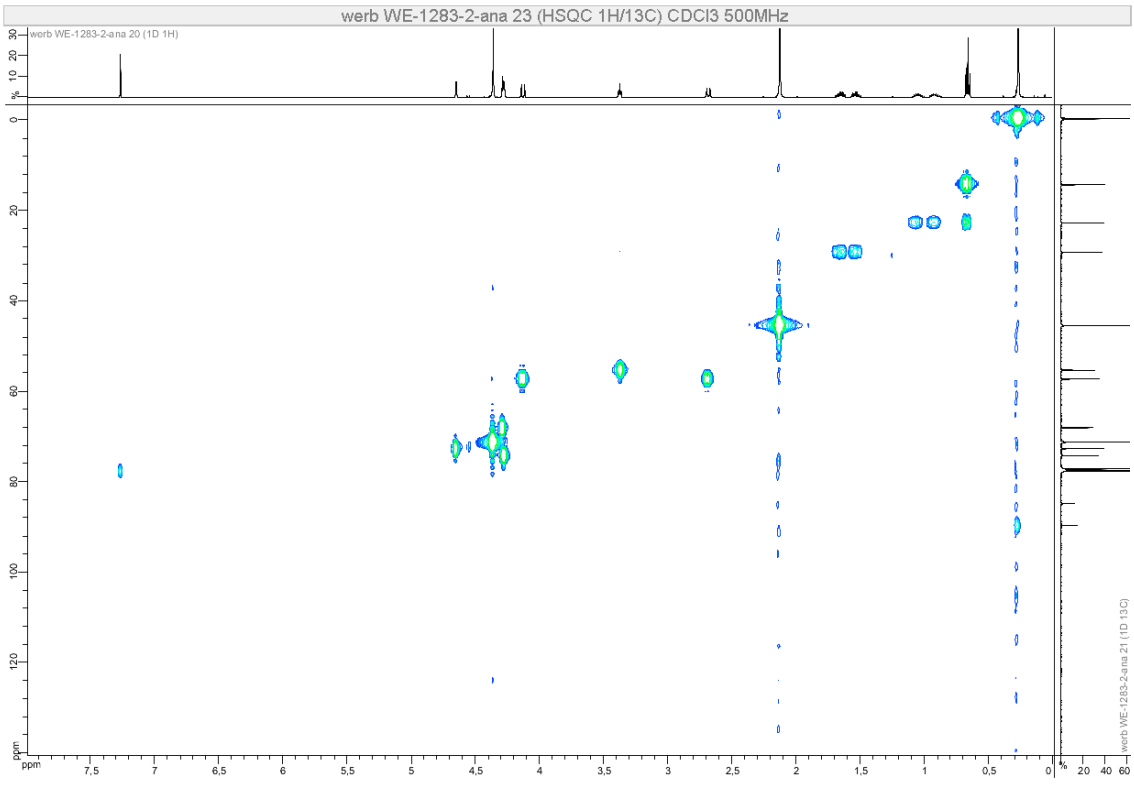
^{13}C NMR (125 MHz, $CDCl_3$)



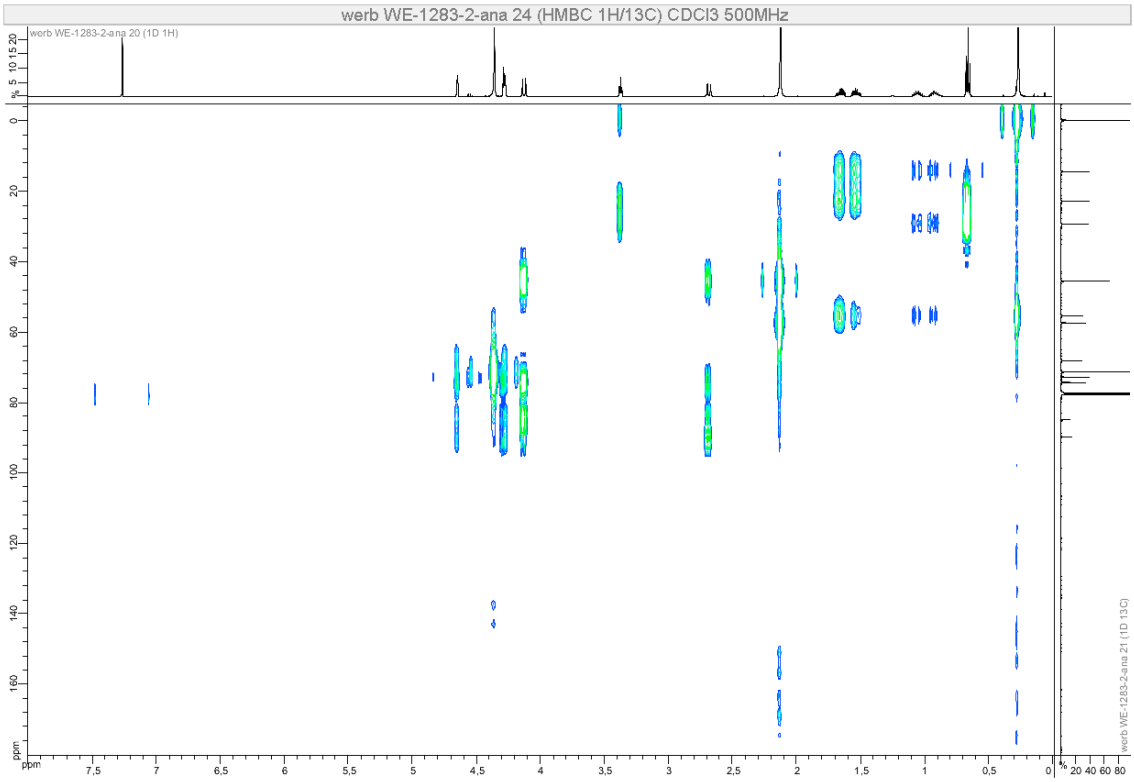
COSY (500 MHz, $CDCl_3$)



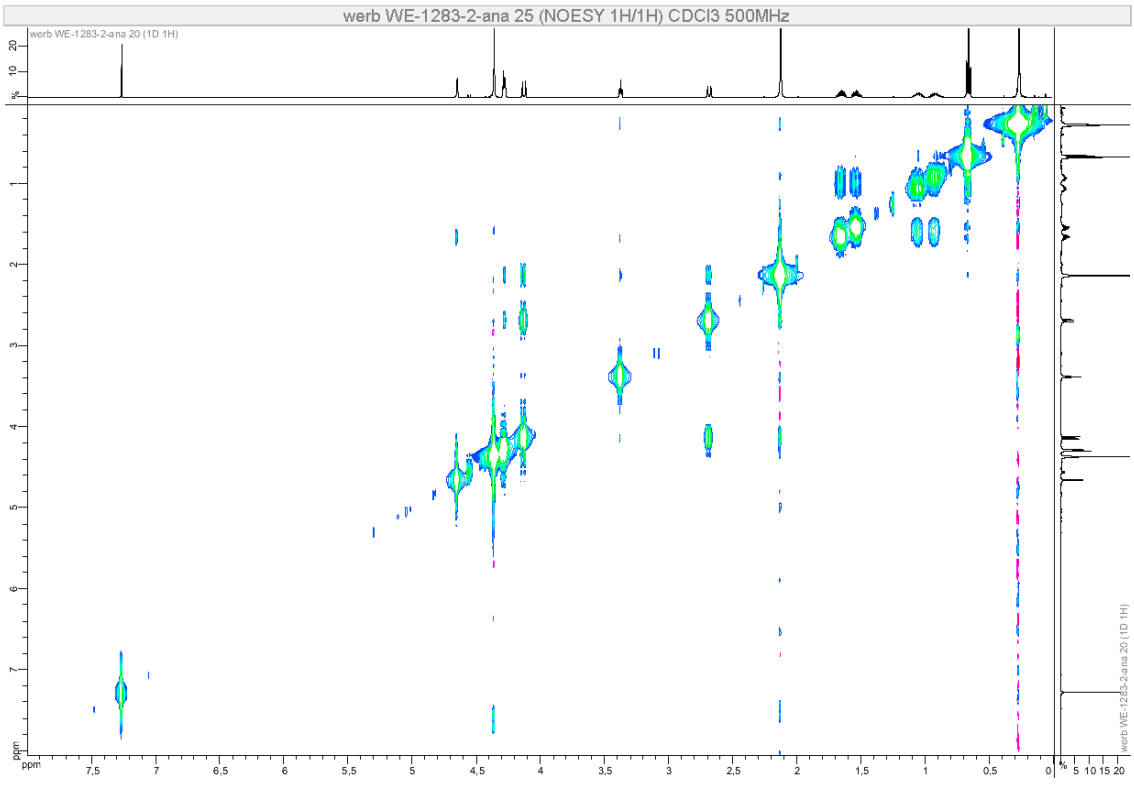
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

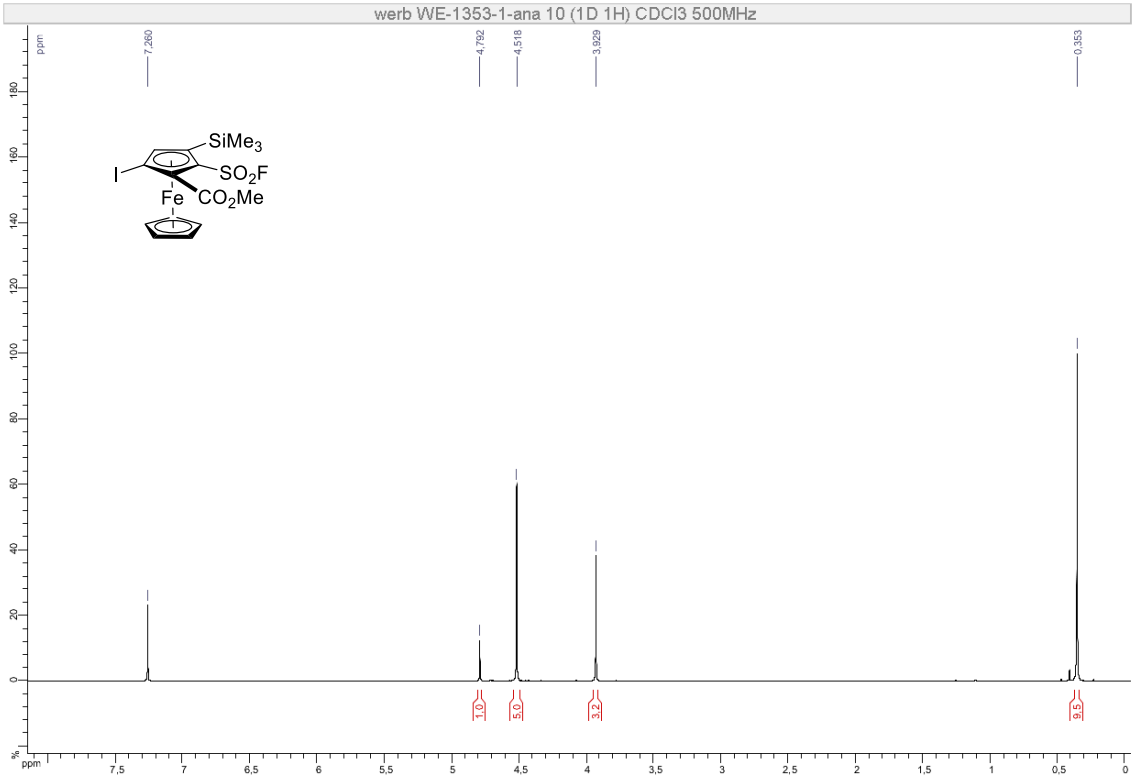


NOESY (500 MHz, $CDCl_3$)

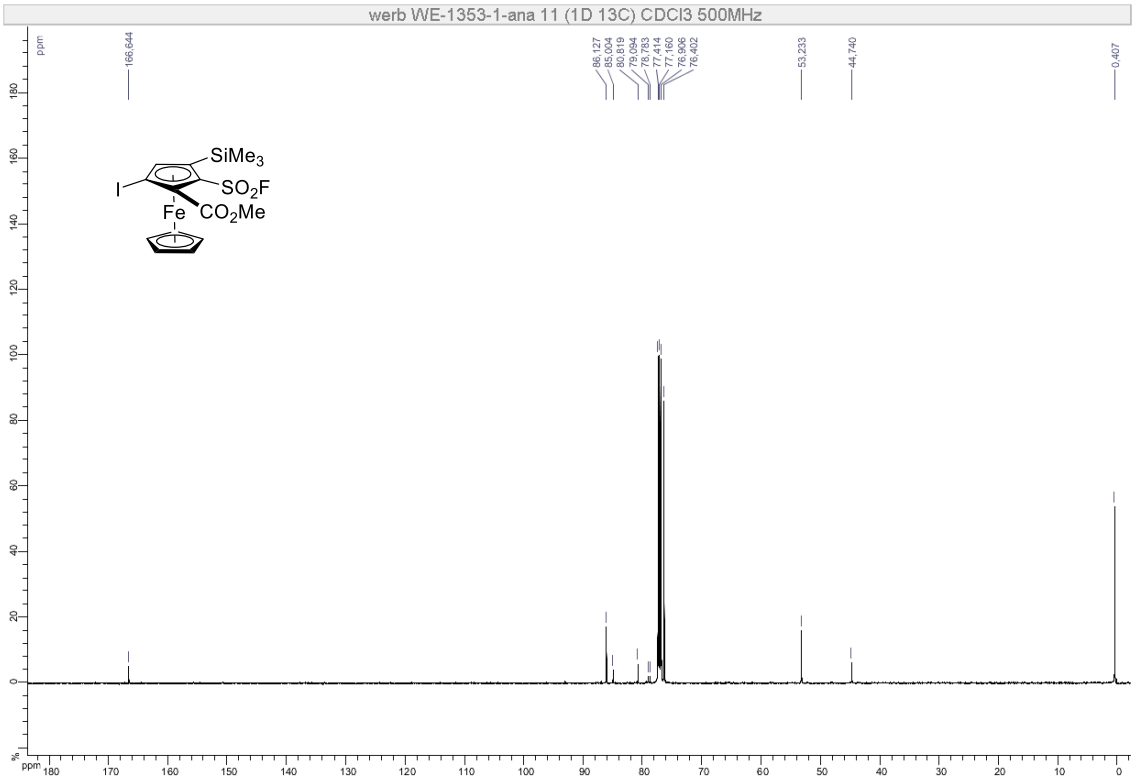


3-Iodo-2-(methoxycarbonyl)-5-(trimethylsilyl)ferrocenesulfonyl fluoride (6c)

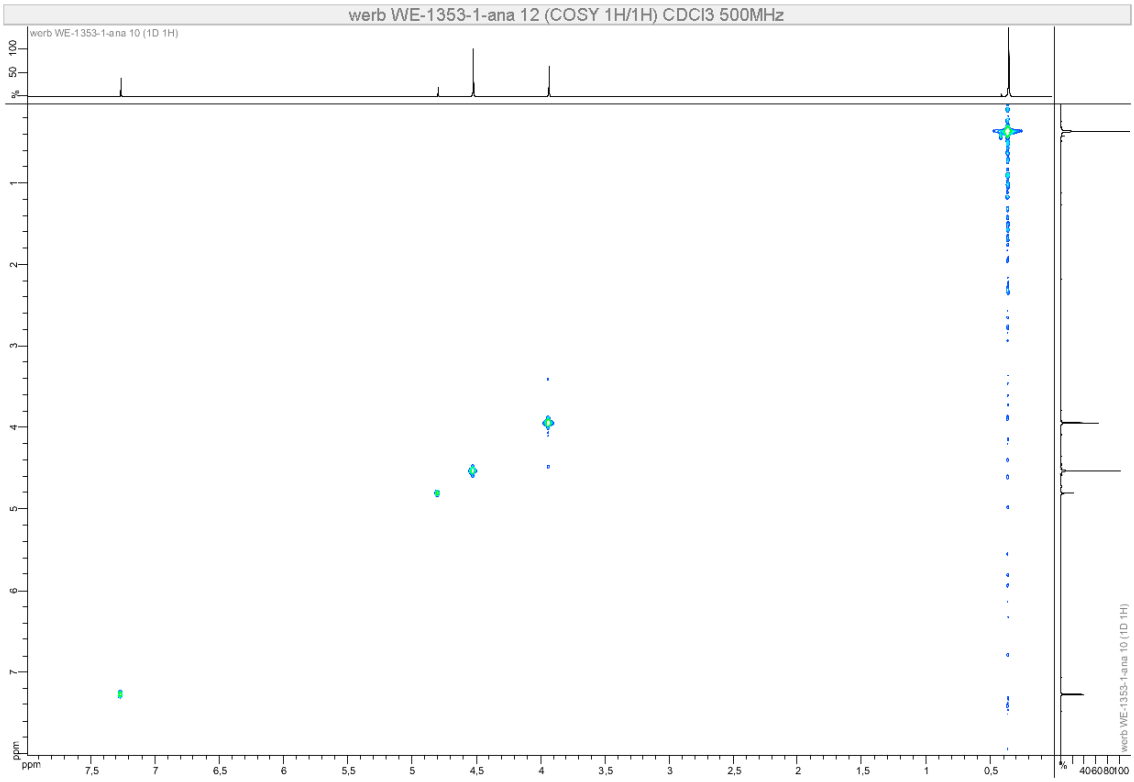
^{1}H NMR (500 MHz, $CDCl_3$)



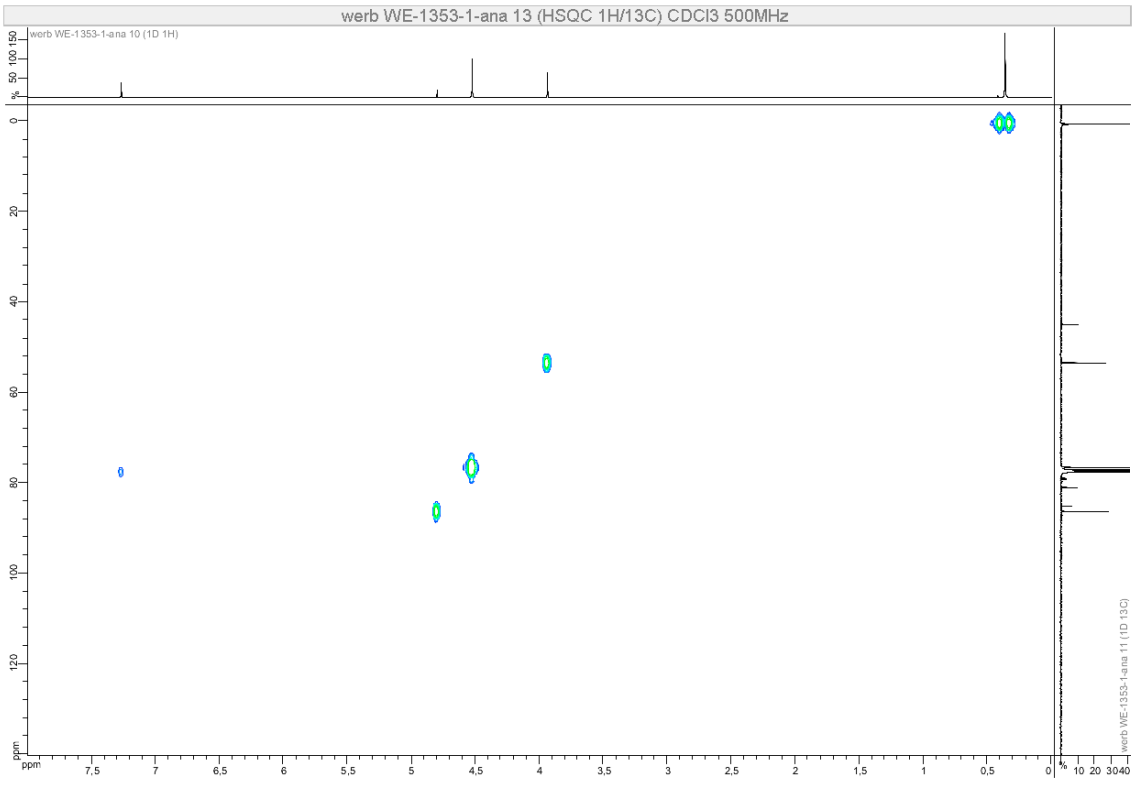
^{13}C NMR (125 MHz, $CDCl_3$)



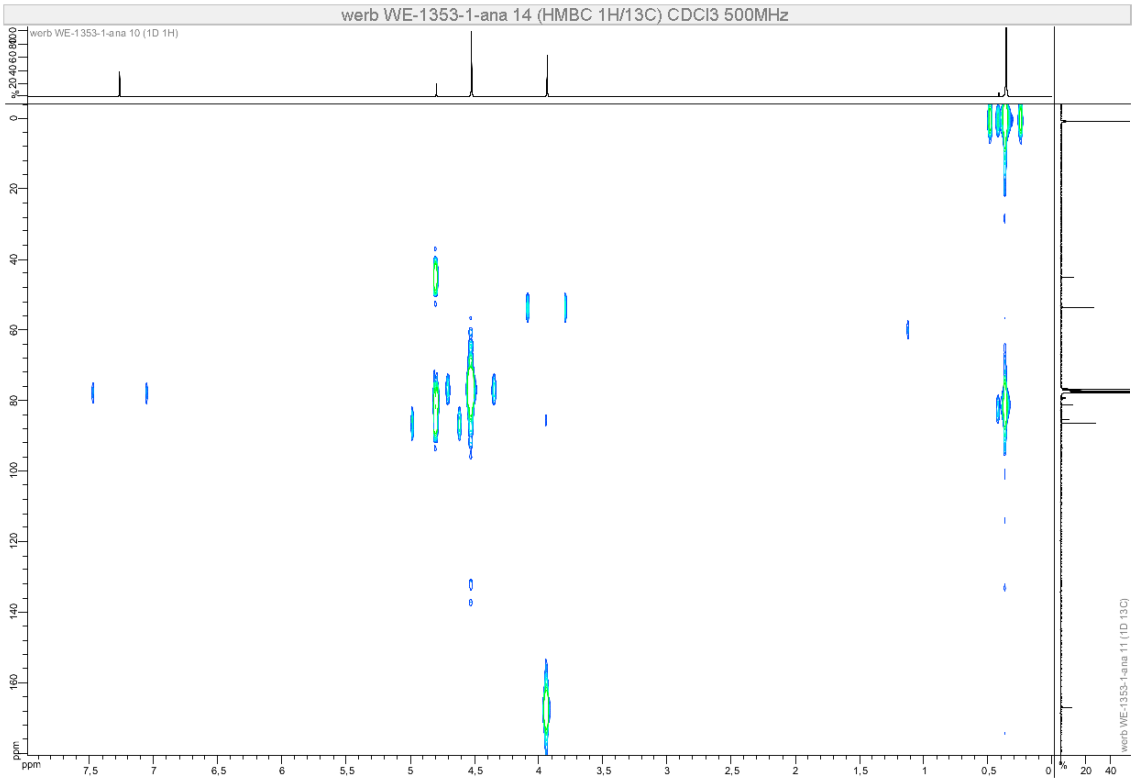
COSY (500 MHz, $CDCl_3$)



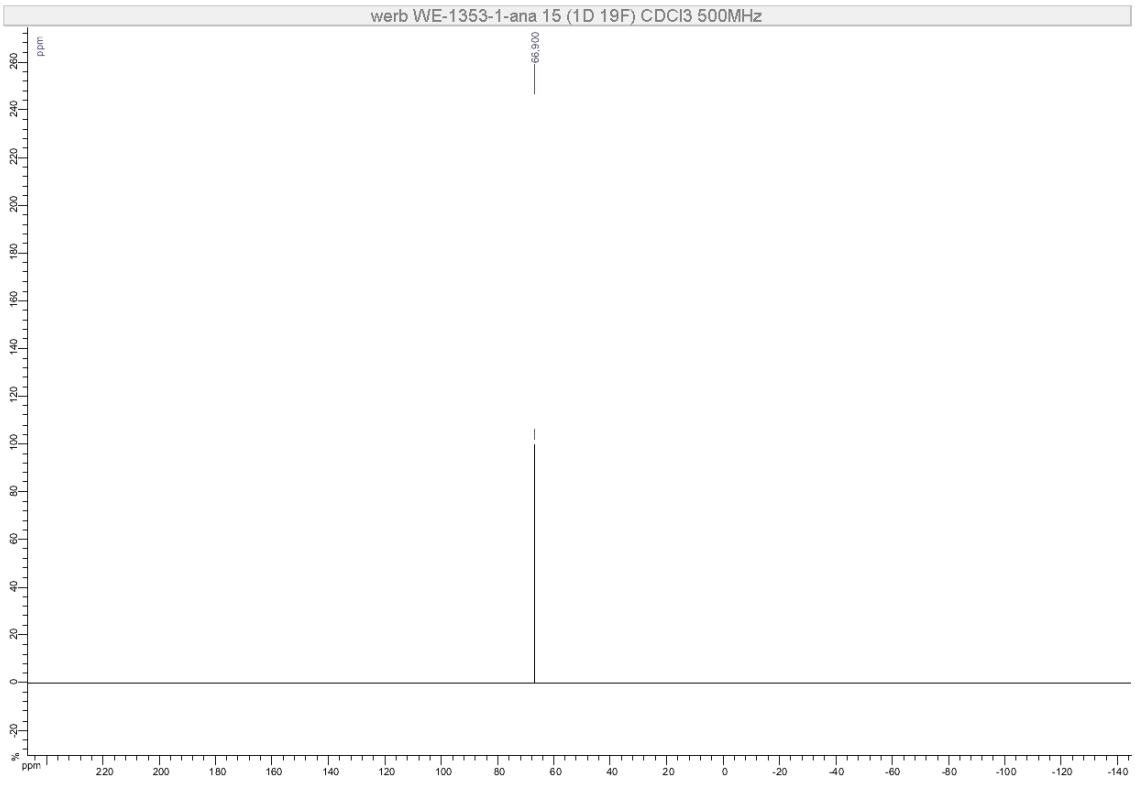
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

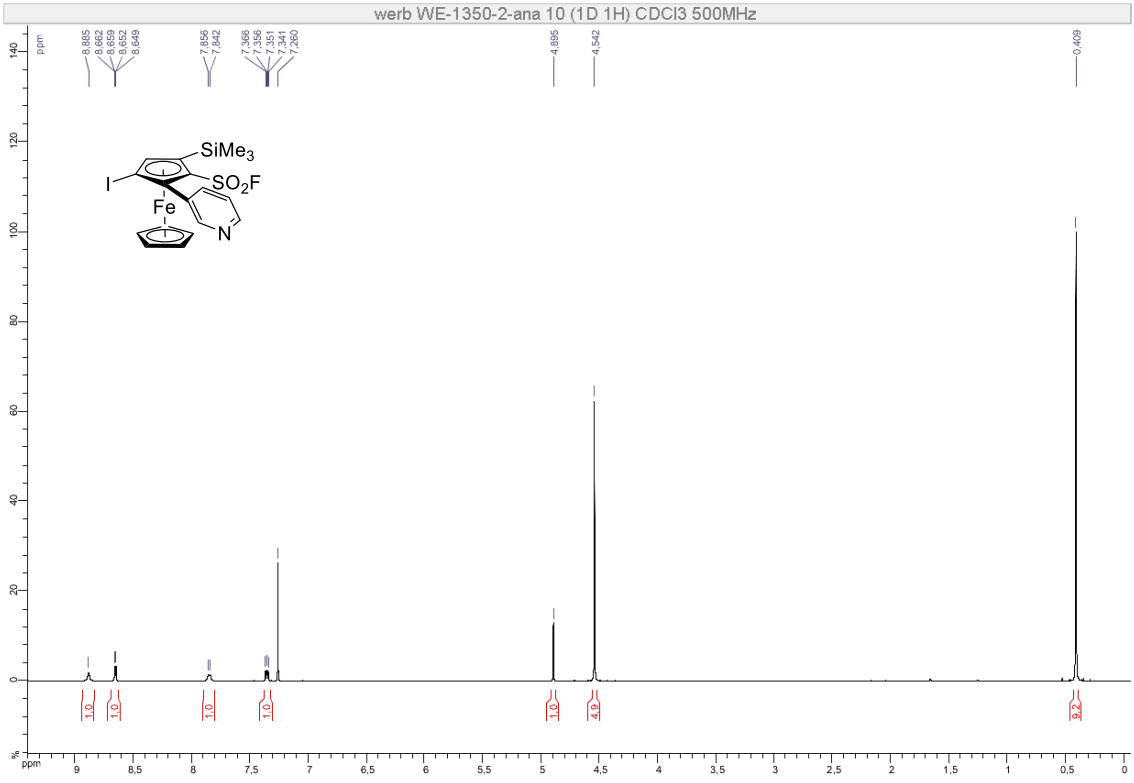


^{19}F NMR (470 MHz, $CDCl_3$)

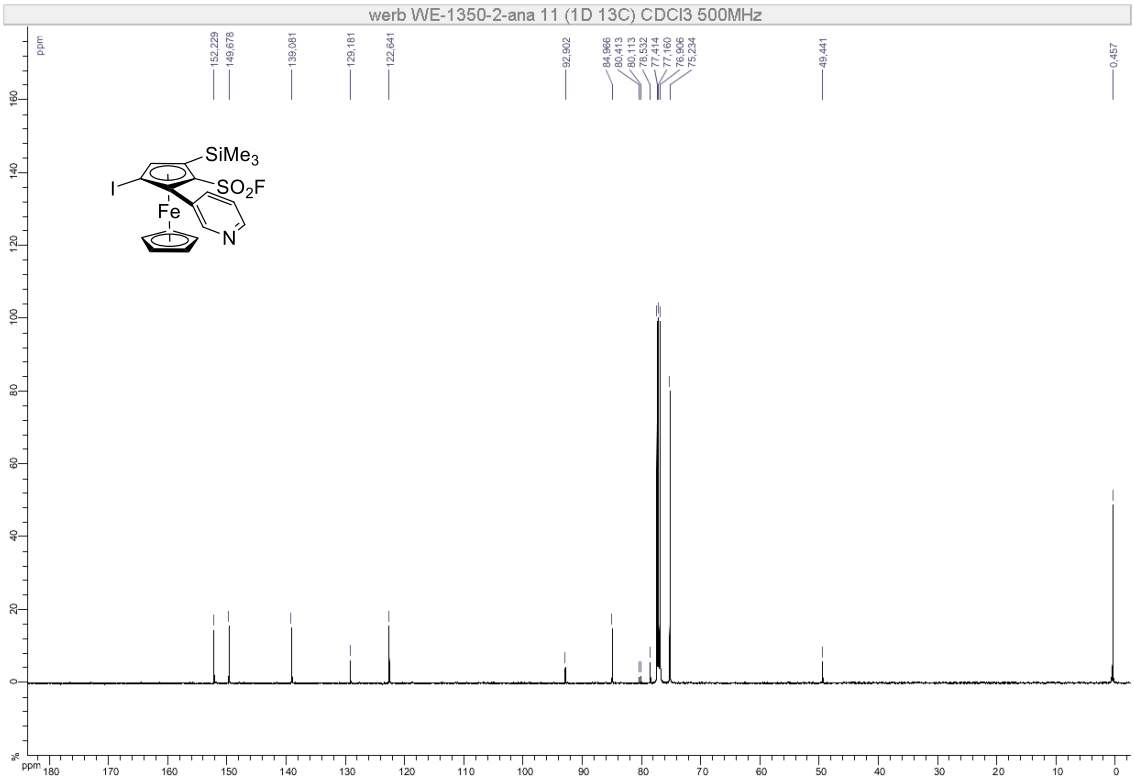


3-Iodo-2-(3-pyridyl)-5-(trimethylsilyl)ferrocenesulfonyl fluoride (6d)

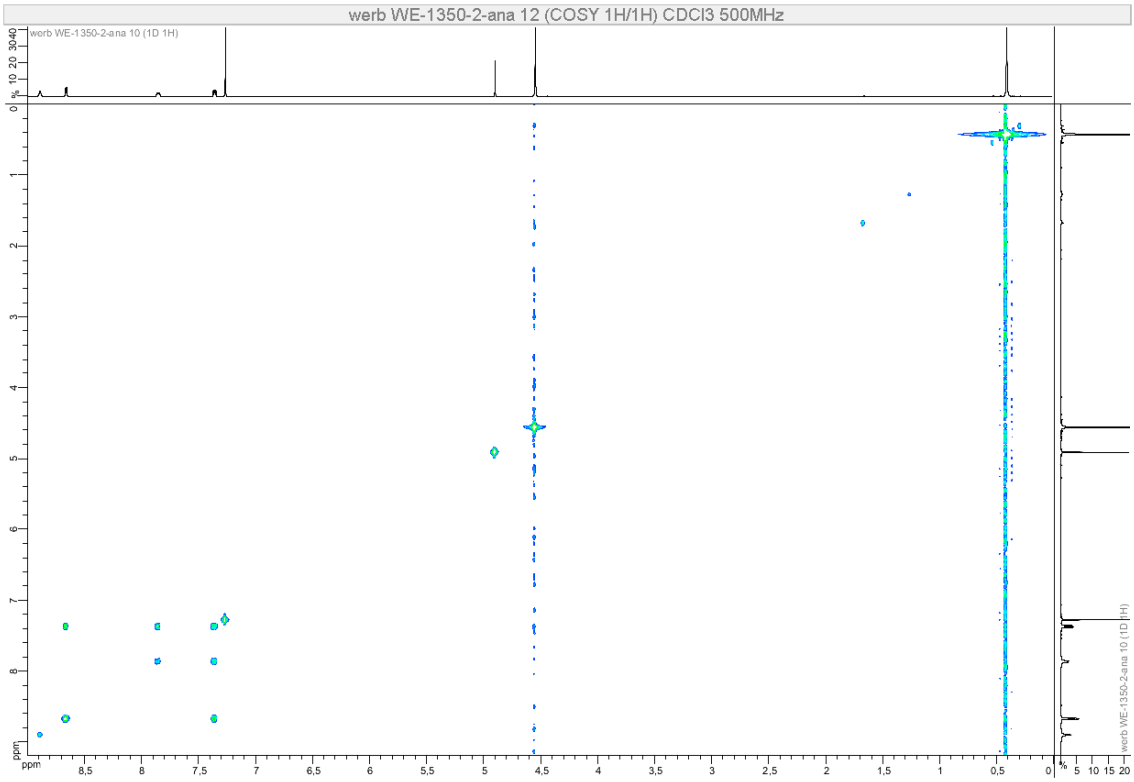
^{1}H NMR (500 MHz, $CDCl_3$)



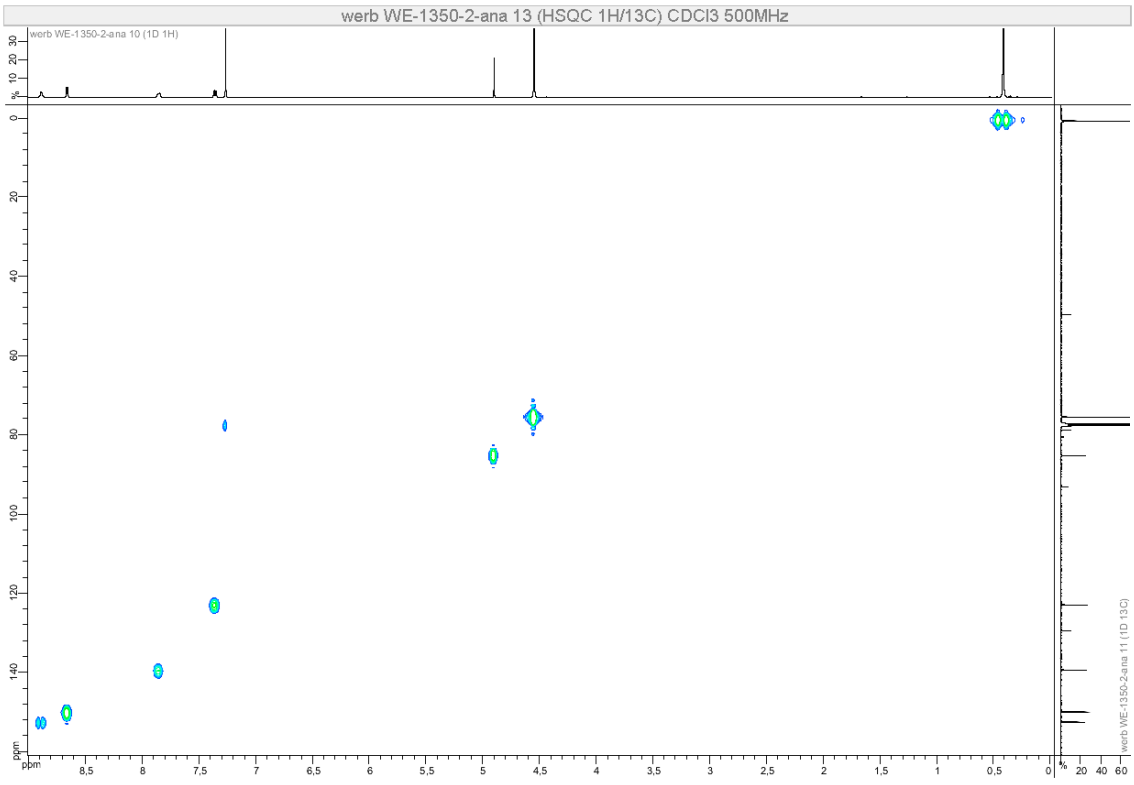
^{13}C NMR (125 MHz, $CDCl_3$)



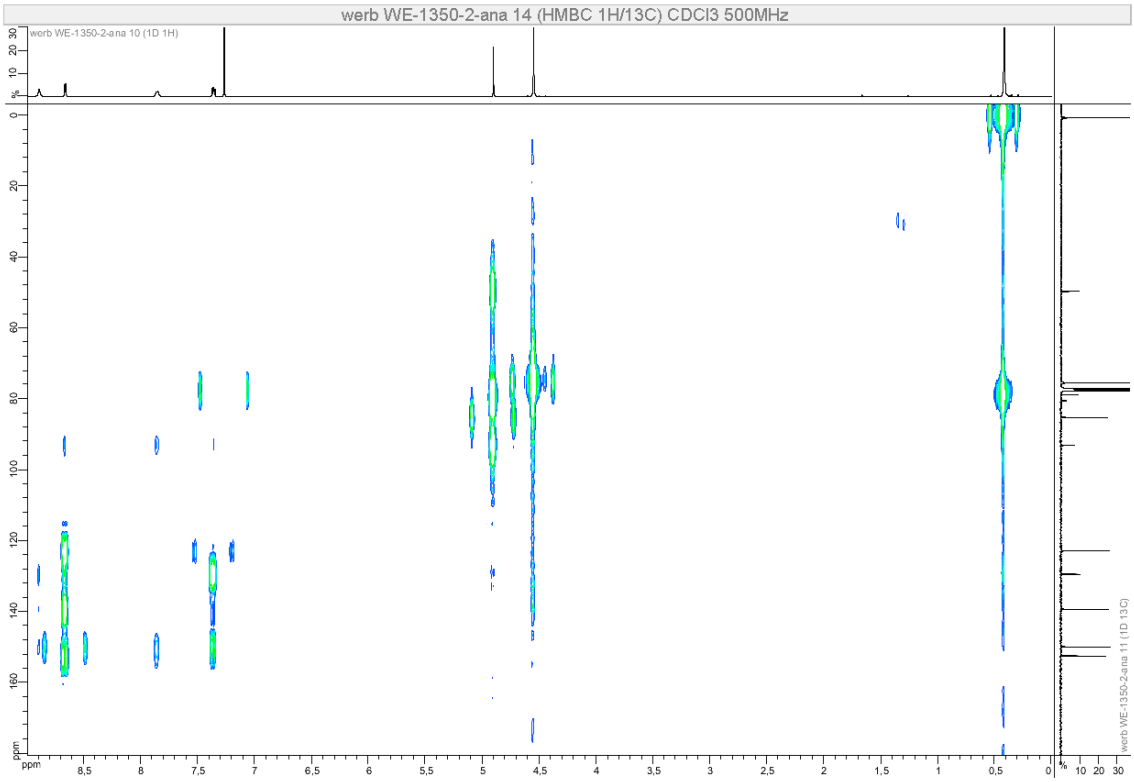
COSY (500 MHz, $CDCl_3$)



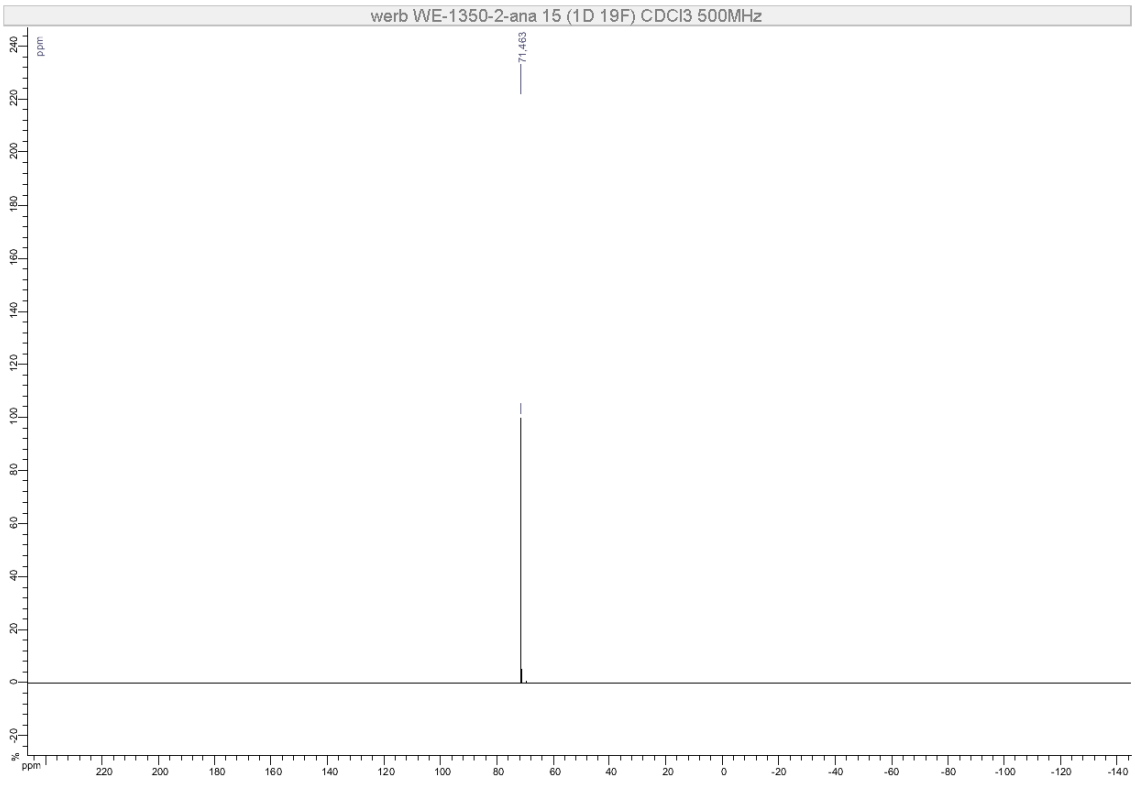
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

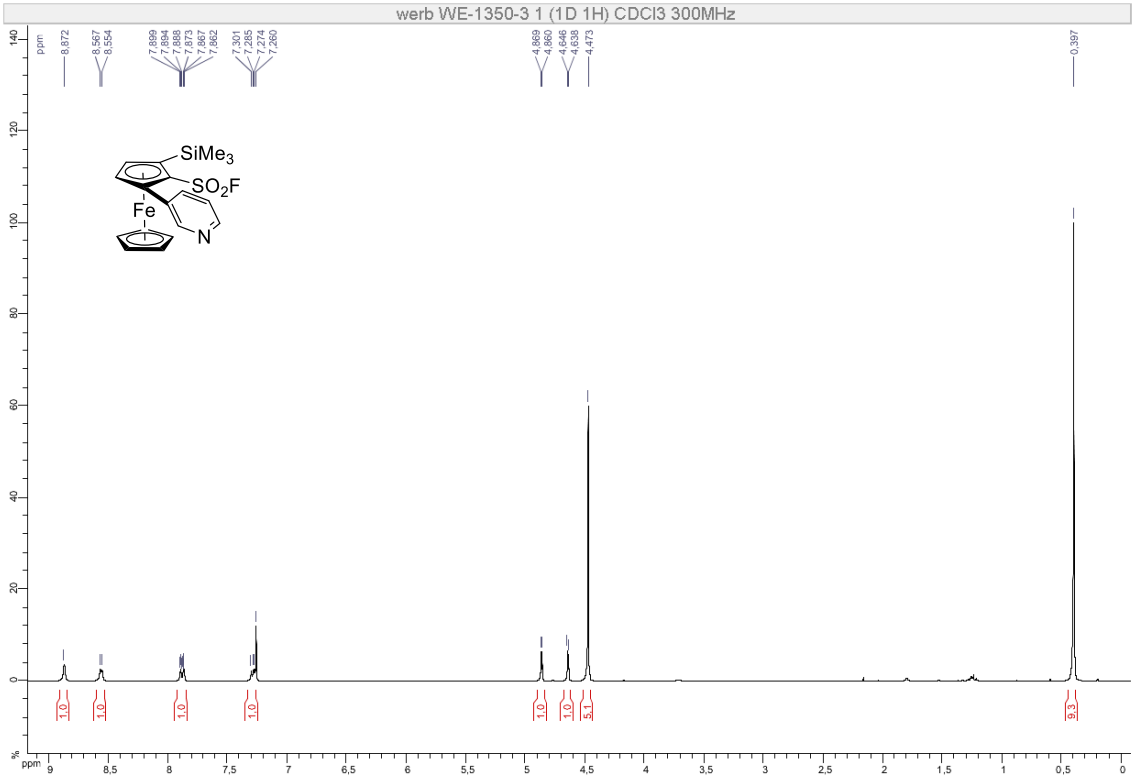


^{19}F NMR (470 MHz, $CDCl_3$)

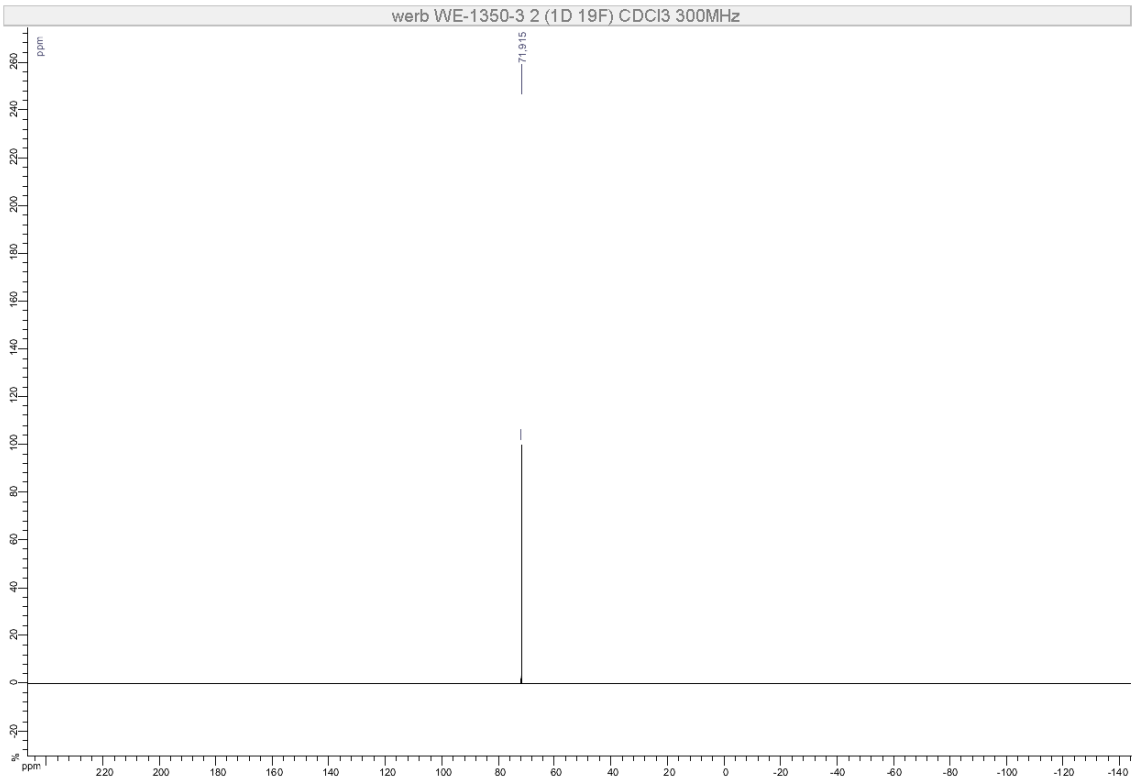


2-(3-Pyridyl)-5-(trimethylsilyl)ferrocenesulfonyl fluoride (6d')

^{1}H NMR (300 MHz, $CDCl_3$)

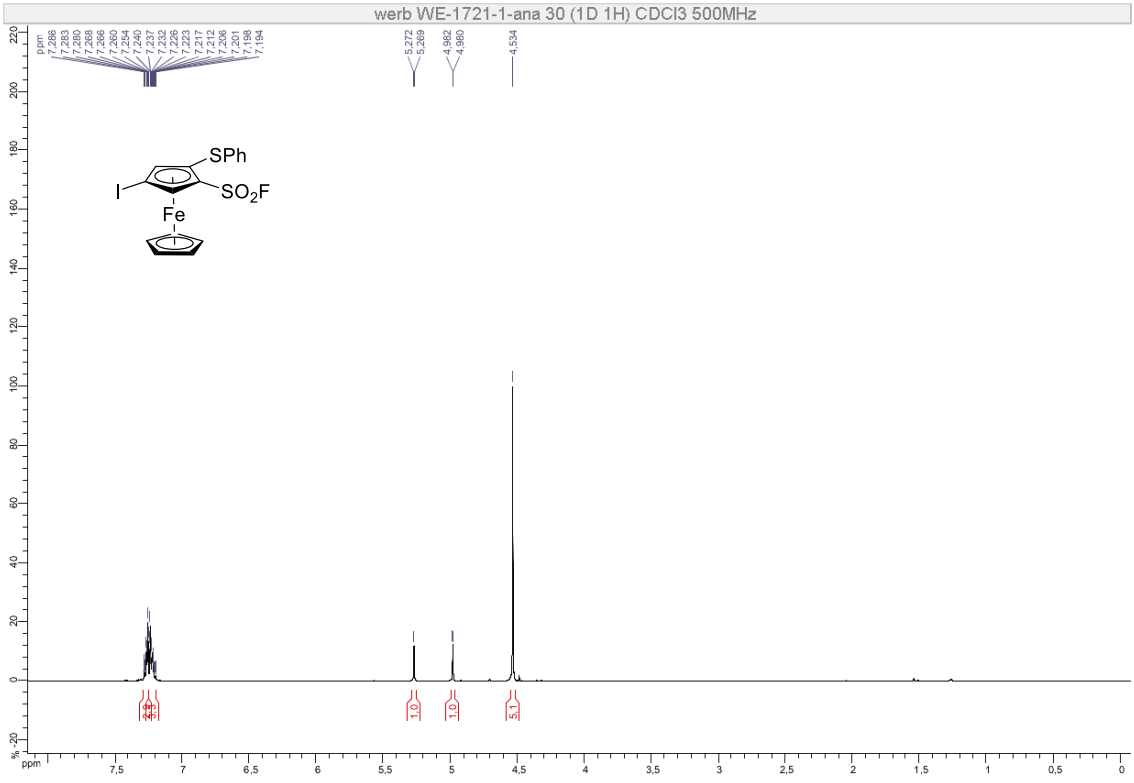


^{19}F NMR (282 MHz, $CDCl_3$)

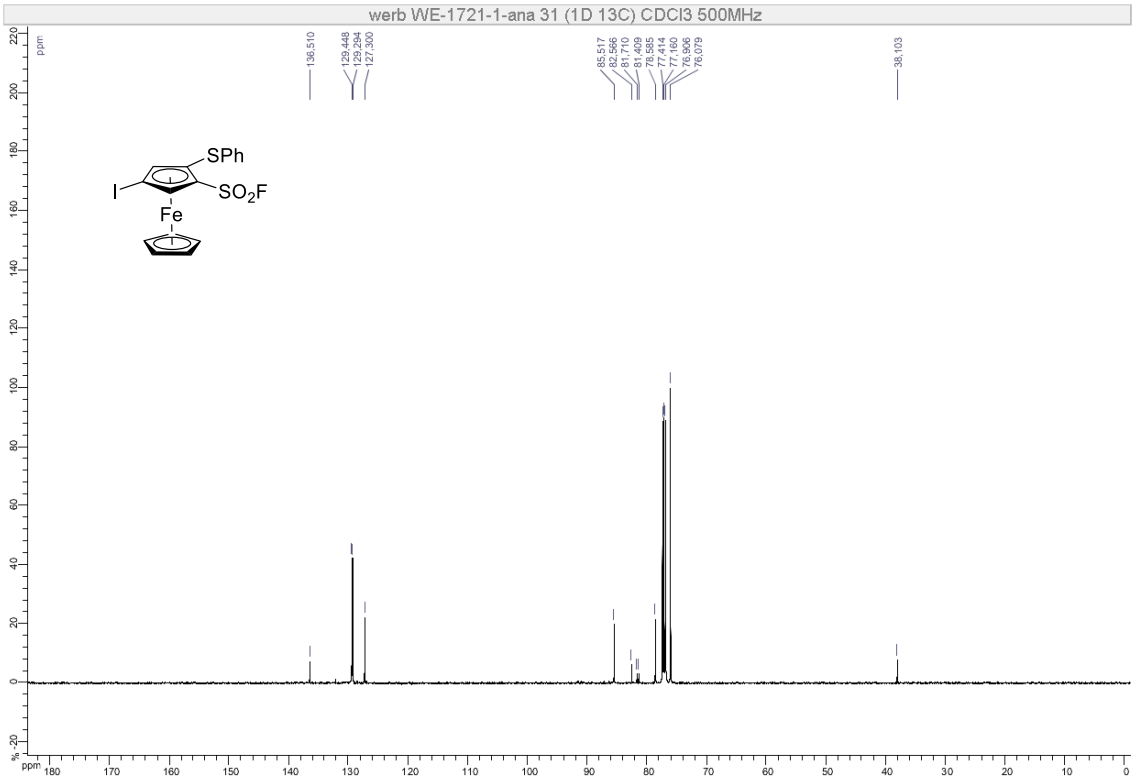


4-Iodo-2-(phenylthio)ferrocenesulfonyl fluoride (6e)

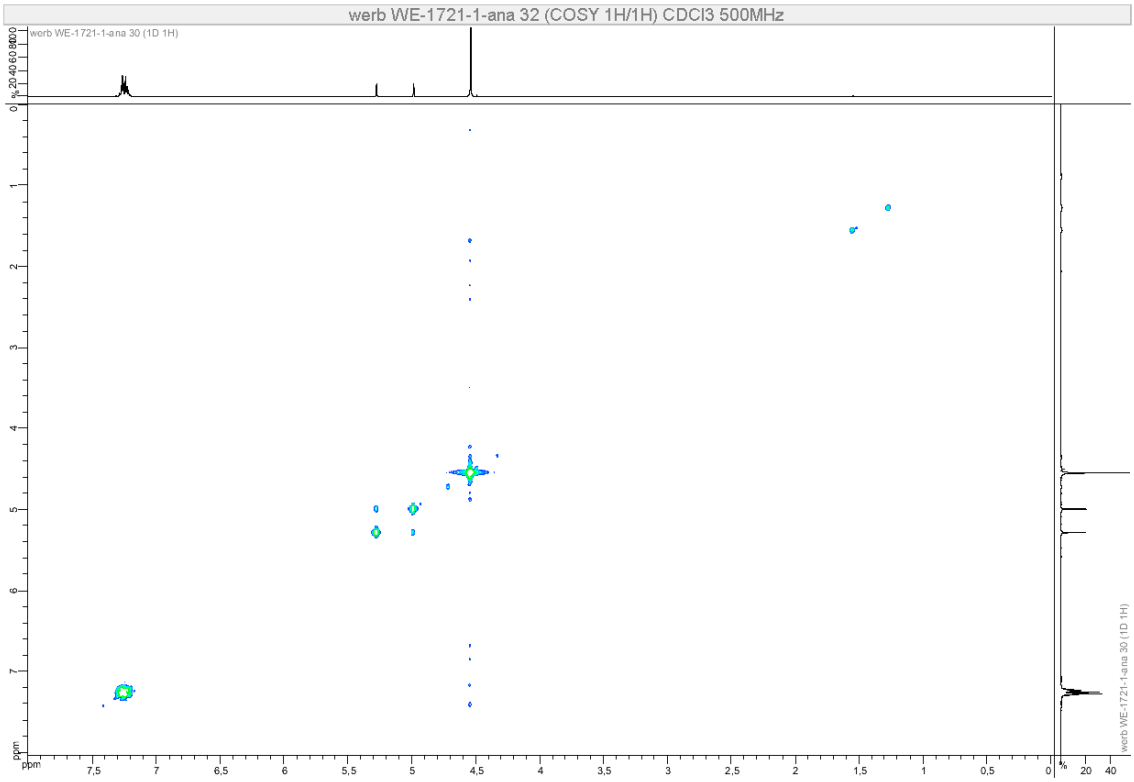
^{1}H NMR (500 MHz, $CDCl_3$)



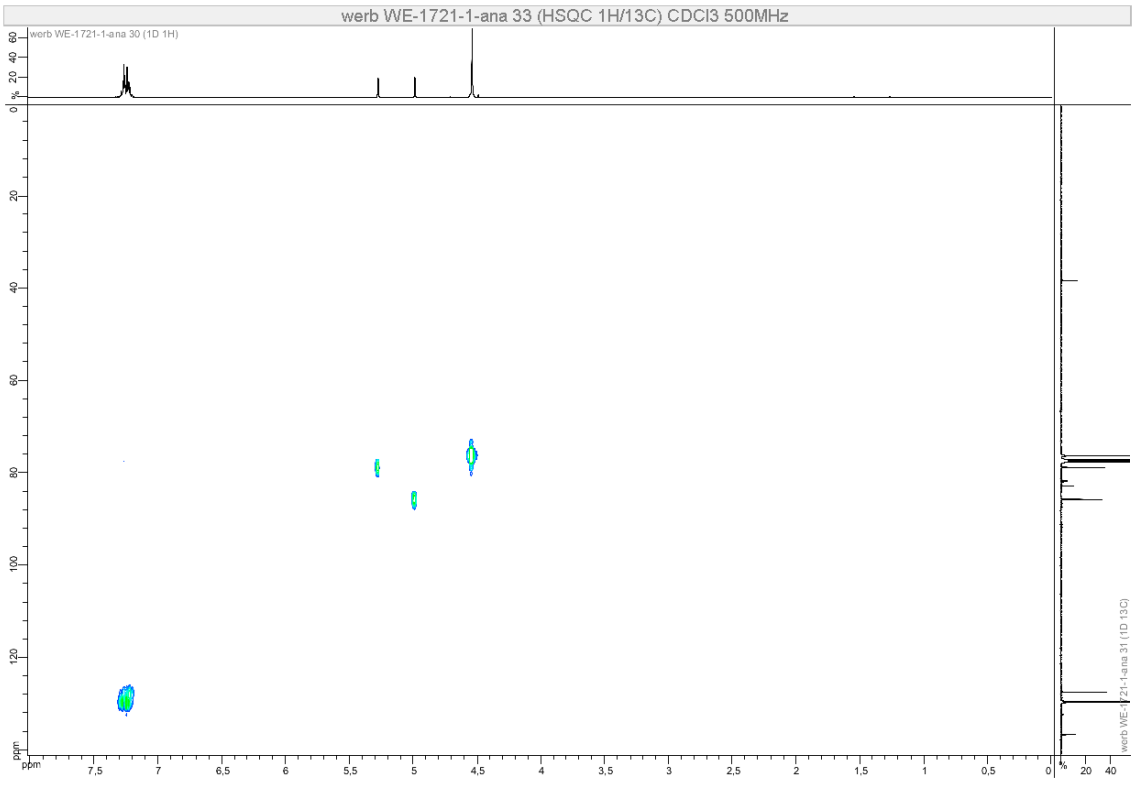
^{13}C NMR (125 MHz, $CDCl_3$)



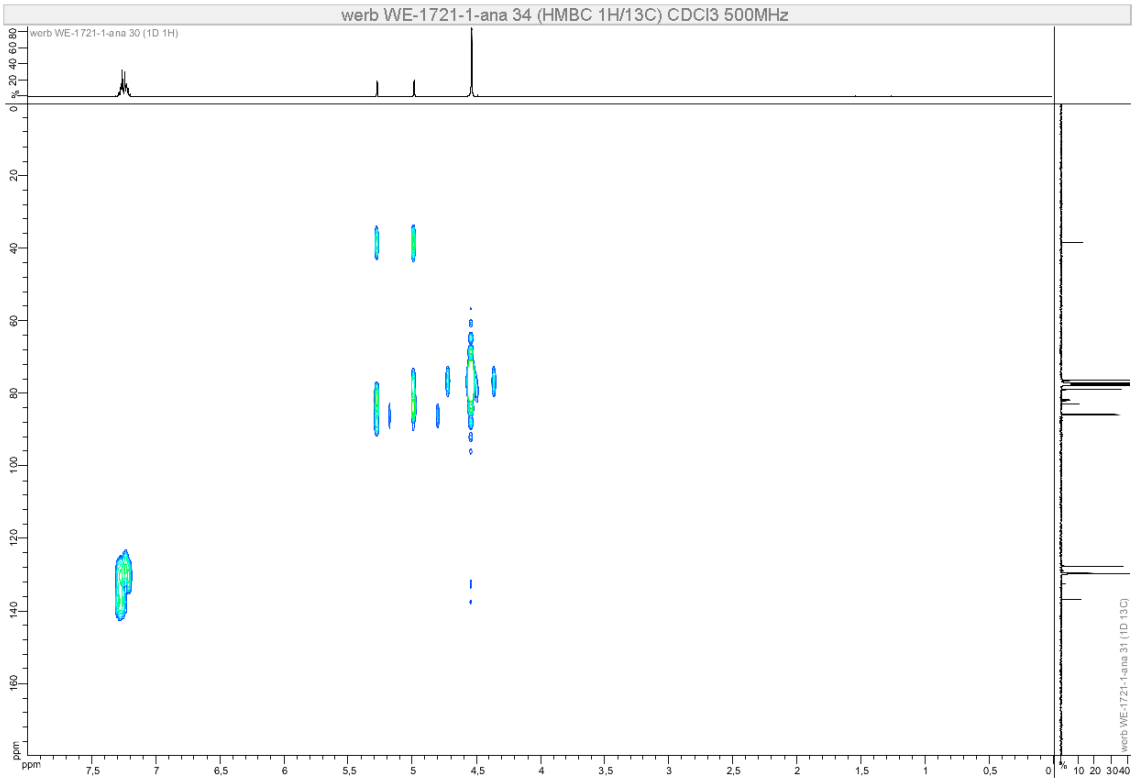
COSY (500 MHz, $CDCl_3$)



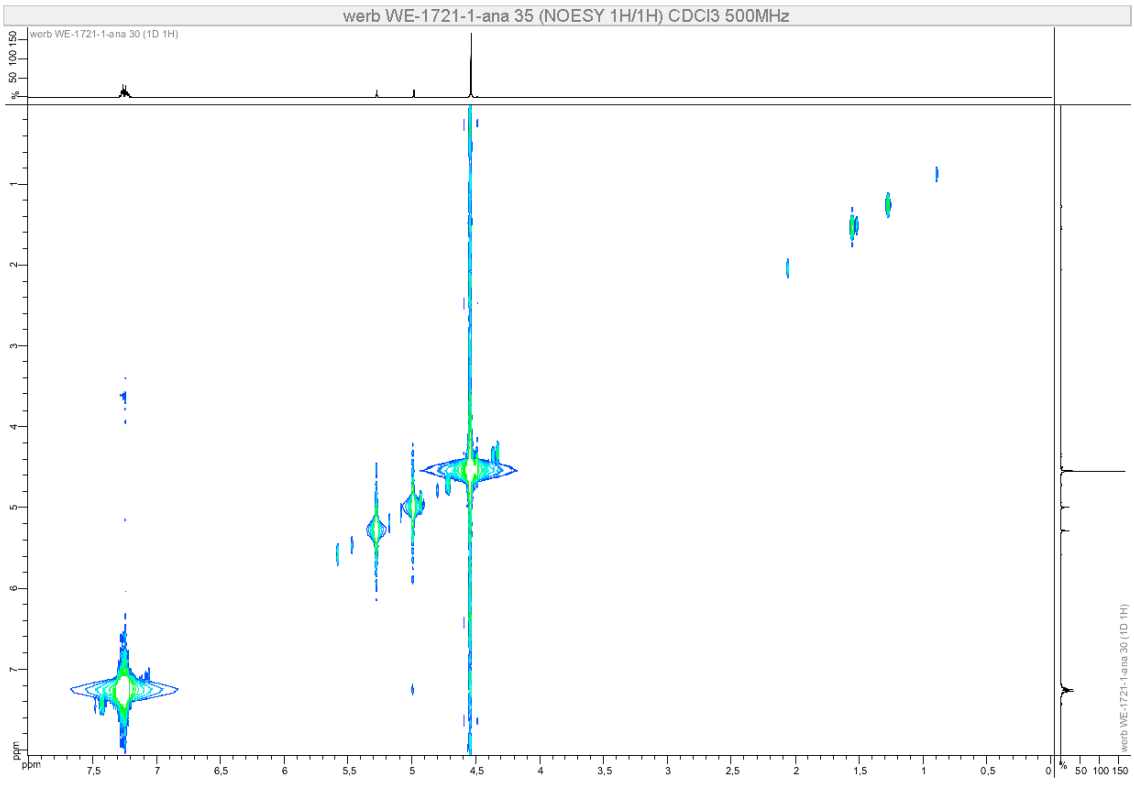
HSQC (500 MHz, $CDCl_3$)



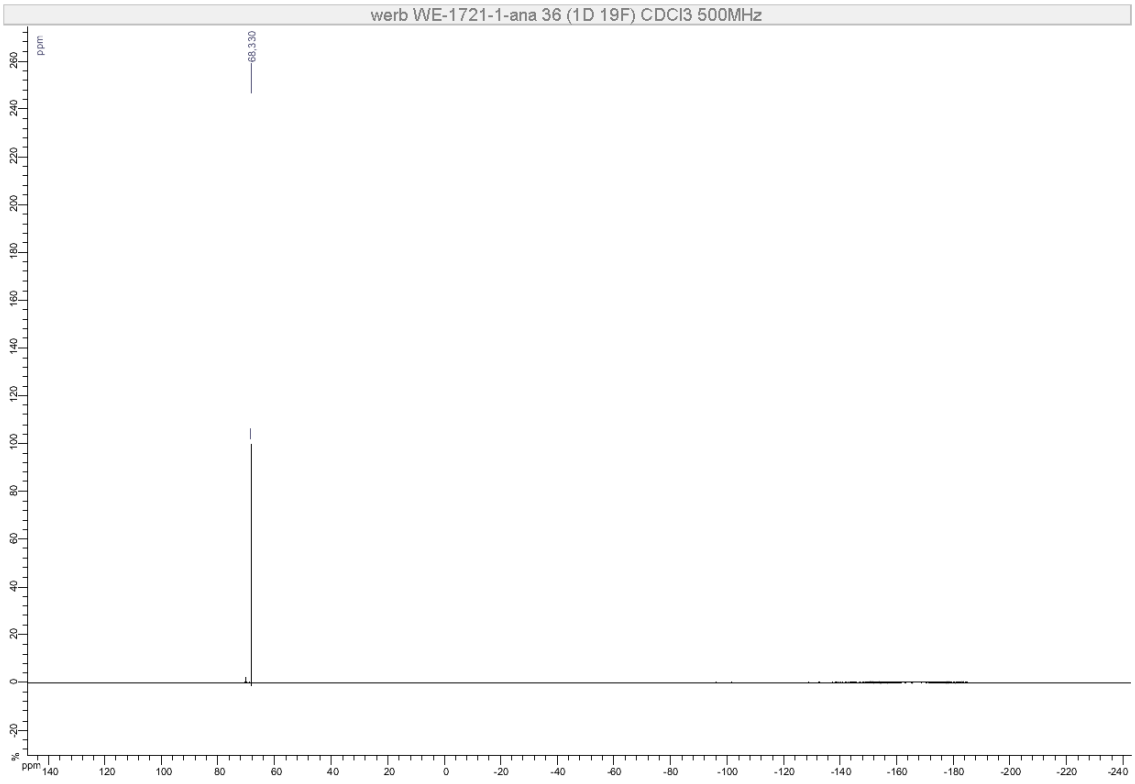
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

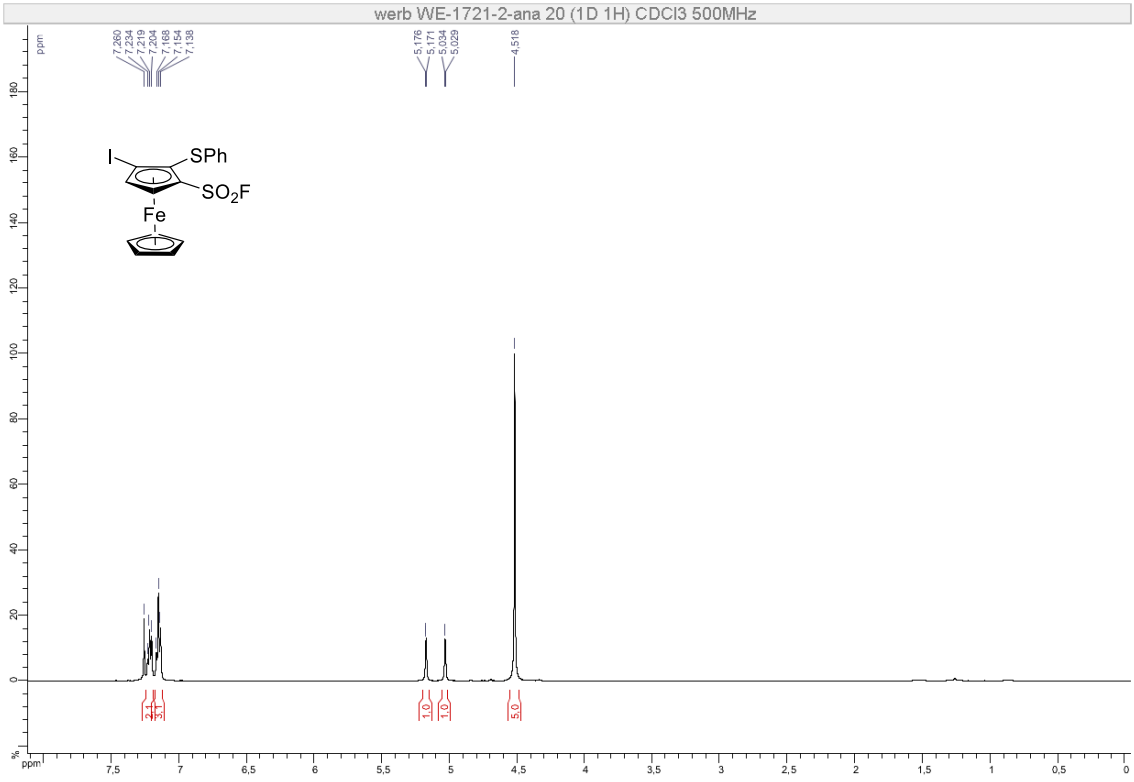


^{19}F NMR (470 MHz, $CDCl_3$)

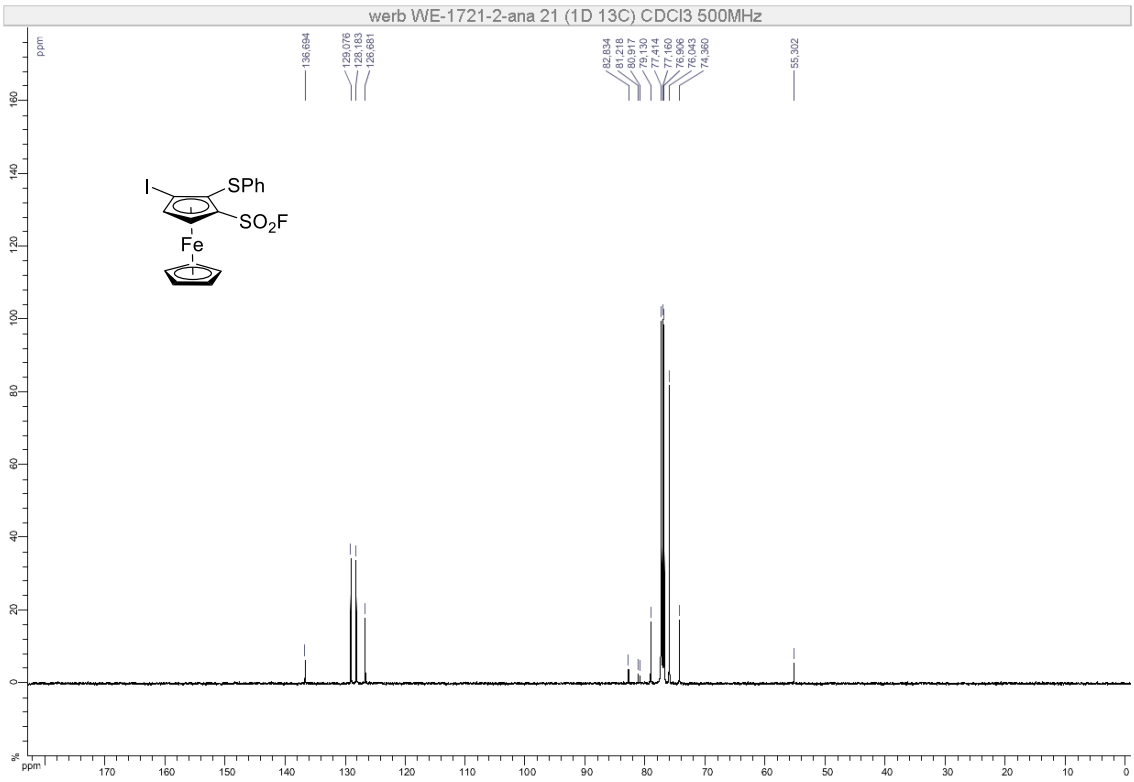


3-Iodo-2-(phenylthio)ferrocenesulfonyl fluoride (6f)

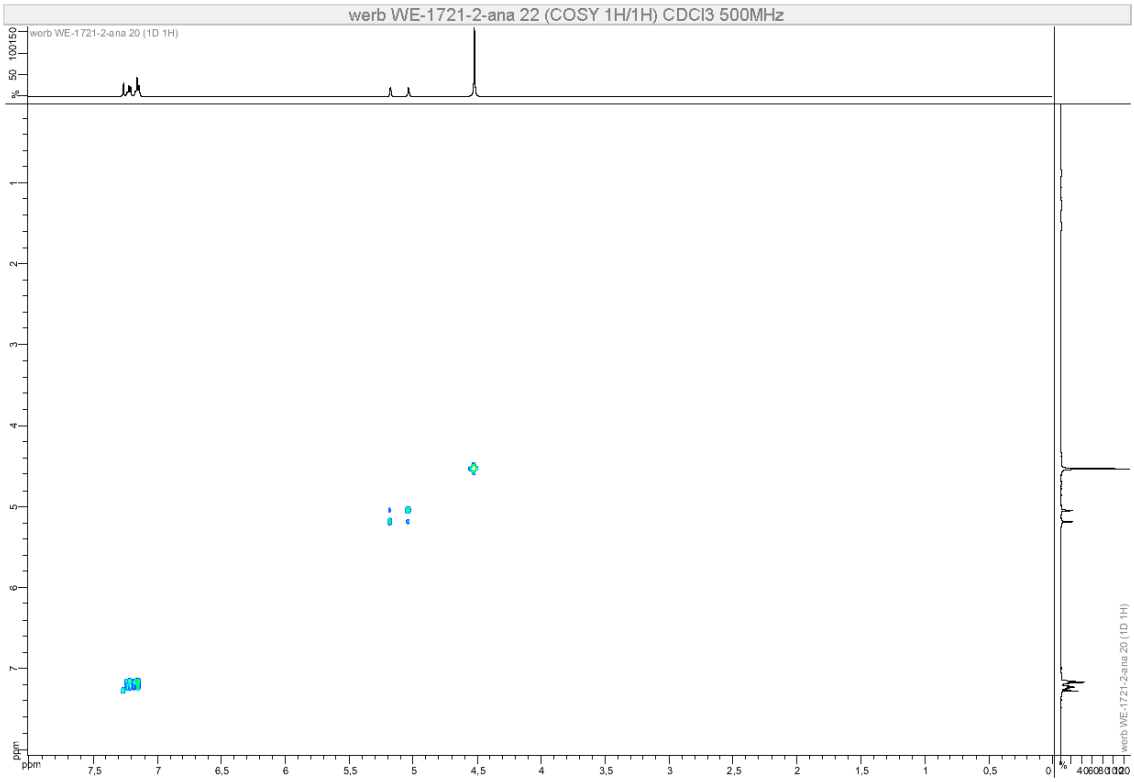
^{1}H NMR (500 MHz, $CDCl_3$)



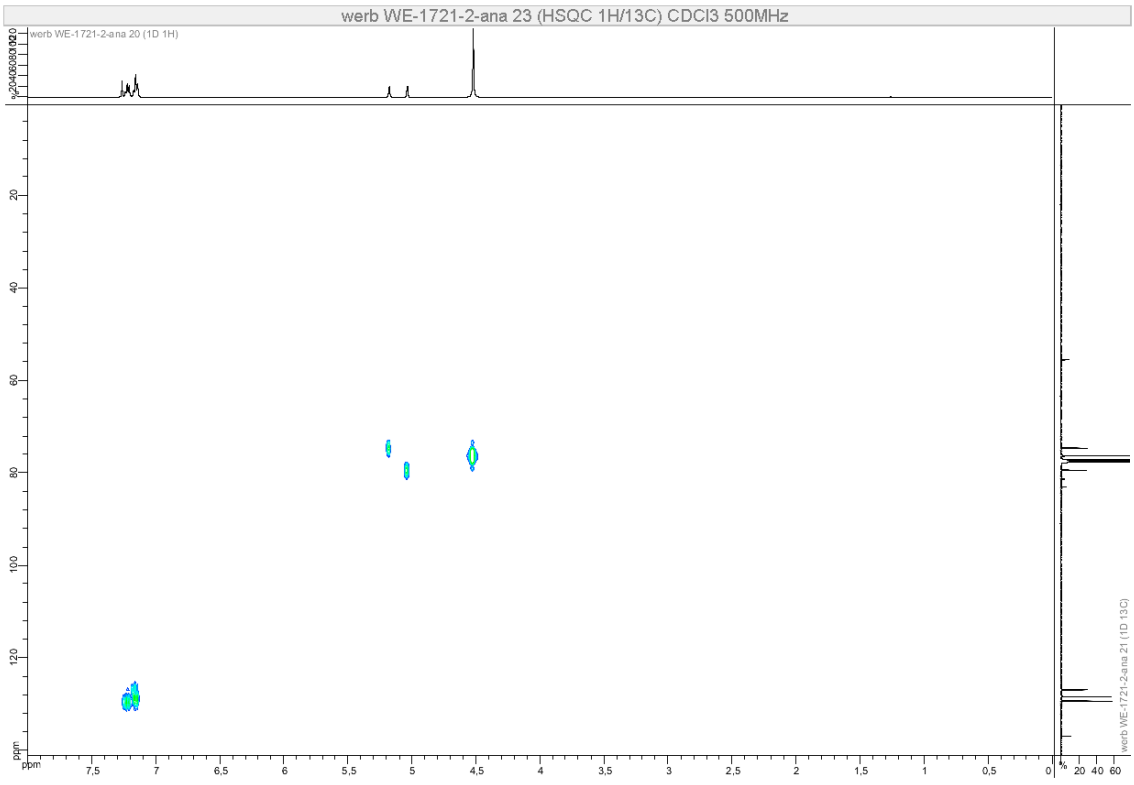
^{13}C NMR (125 MHz, $CDCl_3$)



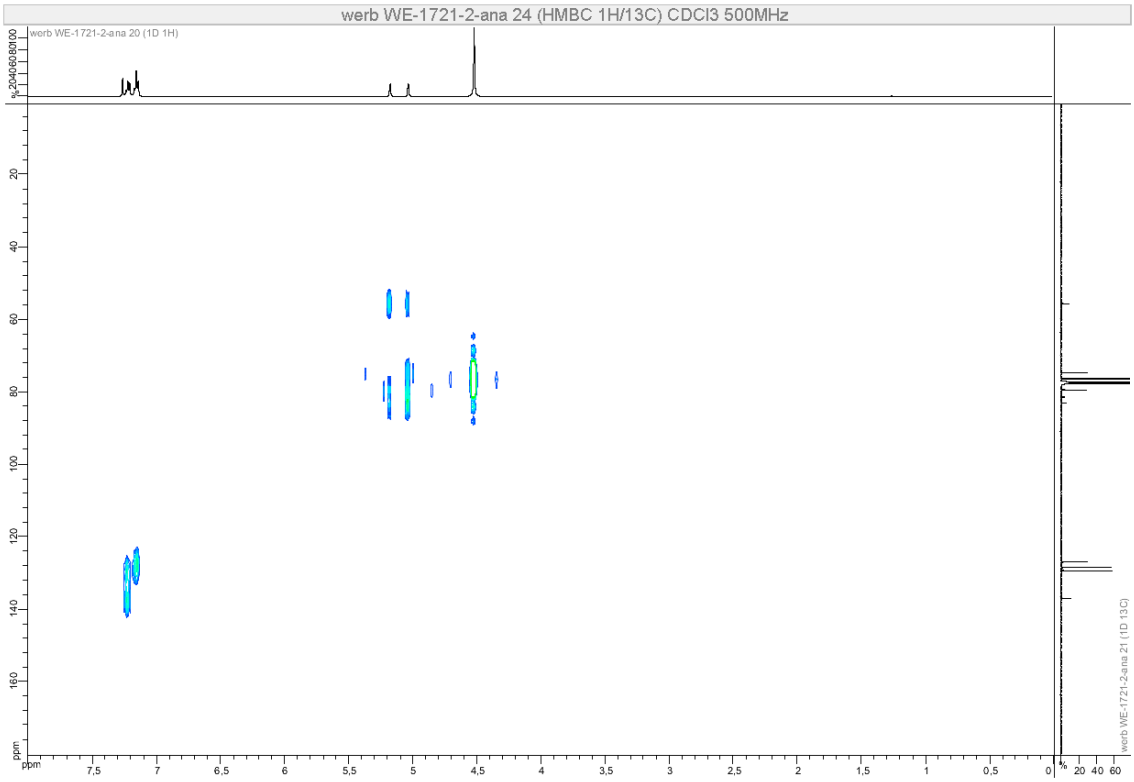
COSY (500 MHz, $CDCl_3$)



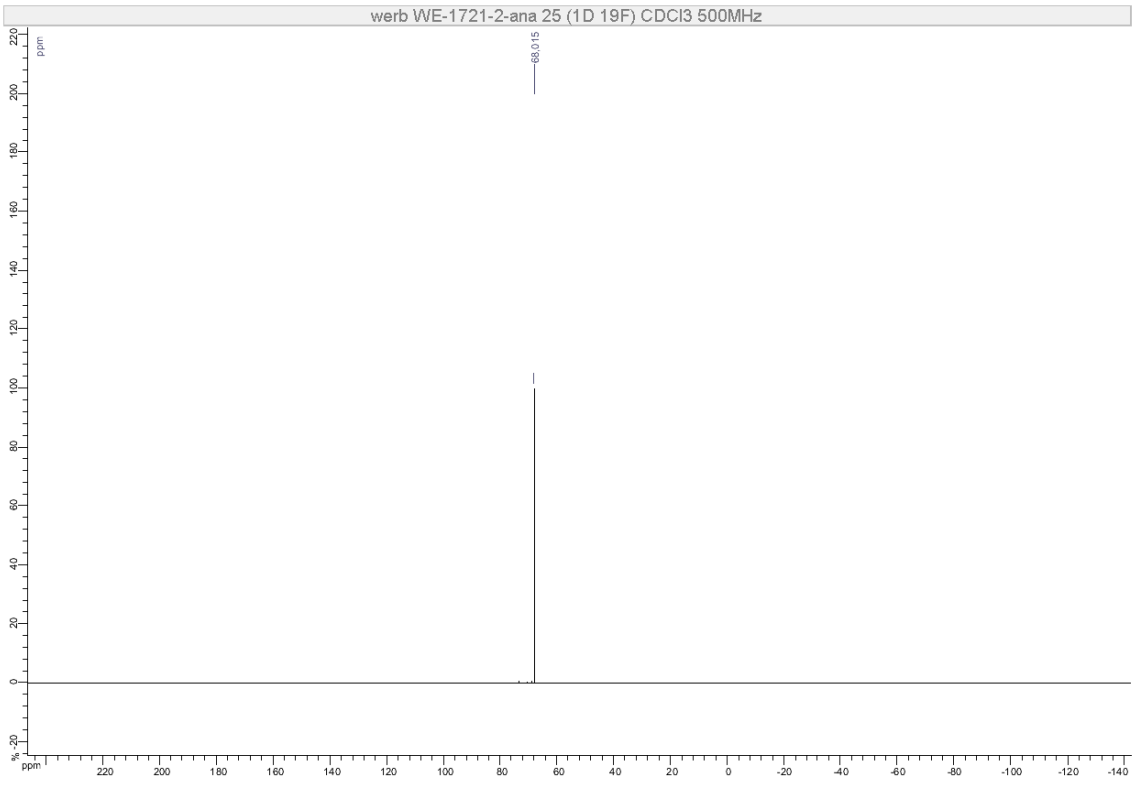
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

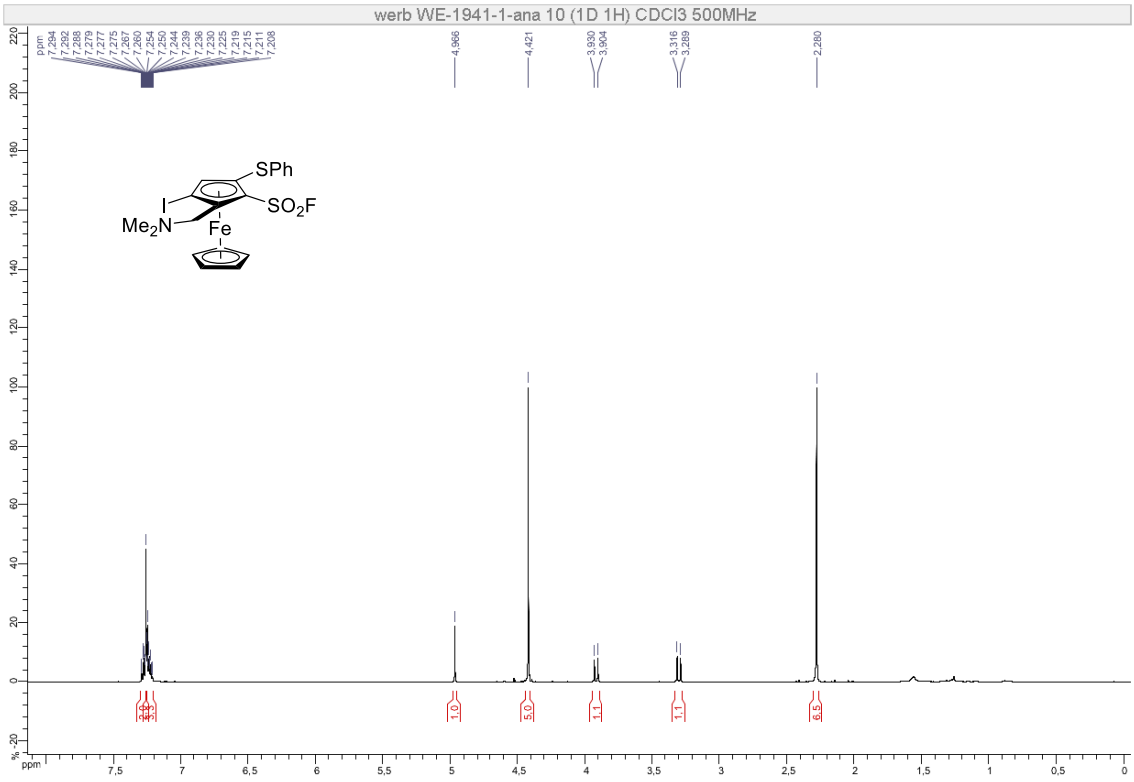


^{19}F NMR (470 MHz, $CDCl_3$)

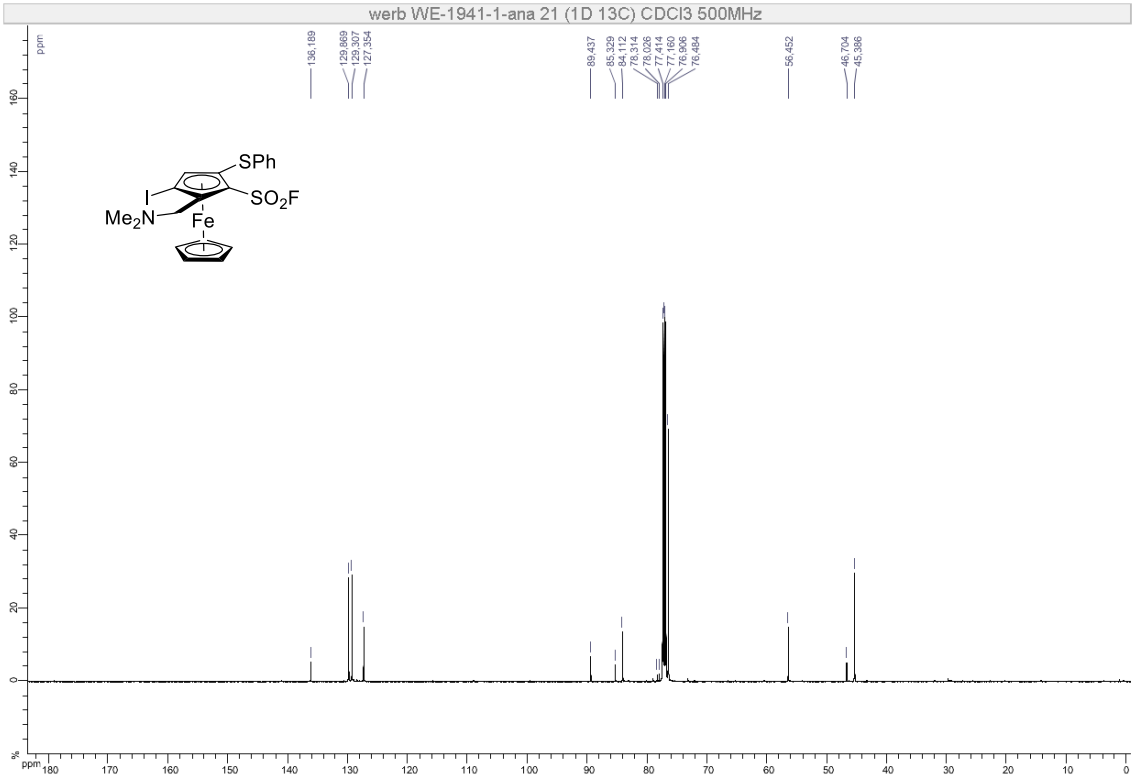


2-(*N*,*N*-Dimethylaminomethyl)-3-iodo-5-(phenylthio)ferrocenesulfonyl fluoride (6g)

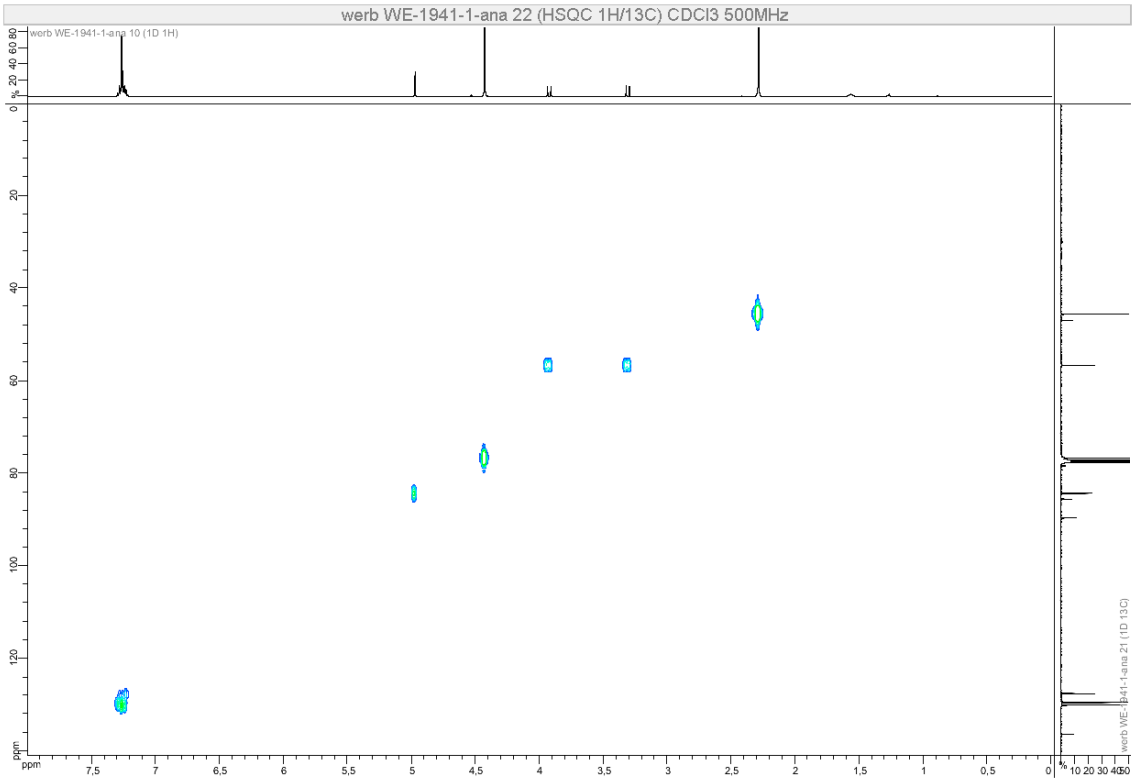
^{1}H NMR (500 MHz, $CDCl_3$)



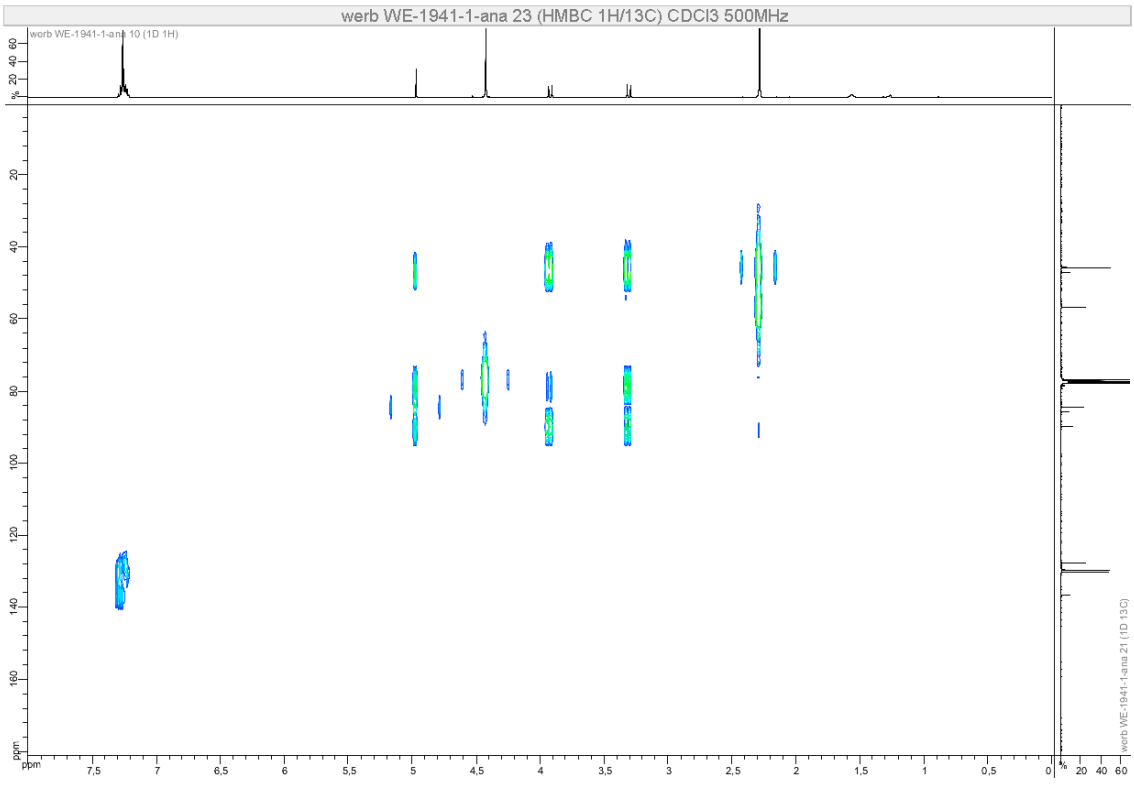
^{13}C NMR (125 MHz, $CDCl_3$)



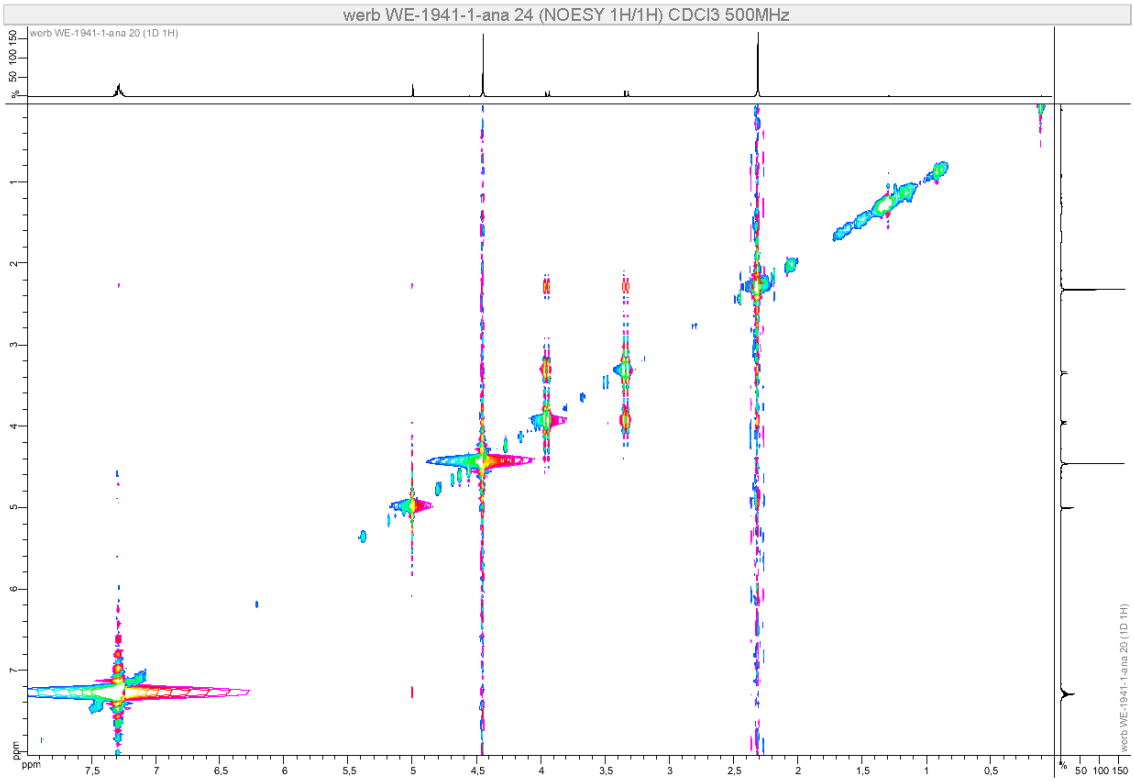
HSQC (500 MHz, $CDCl_3$)



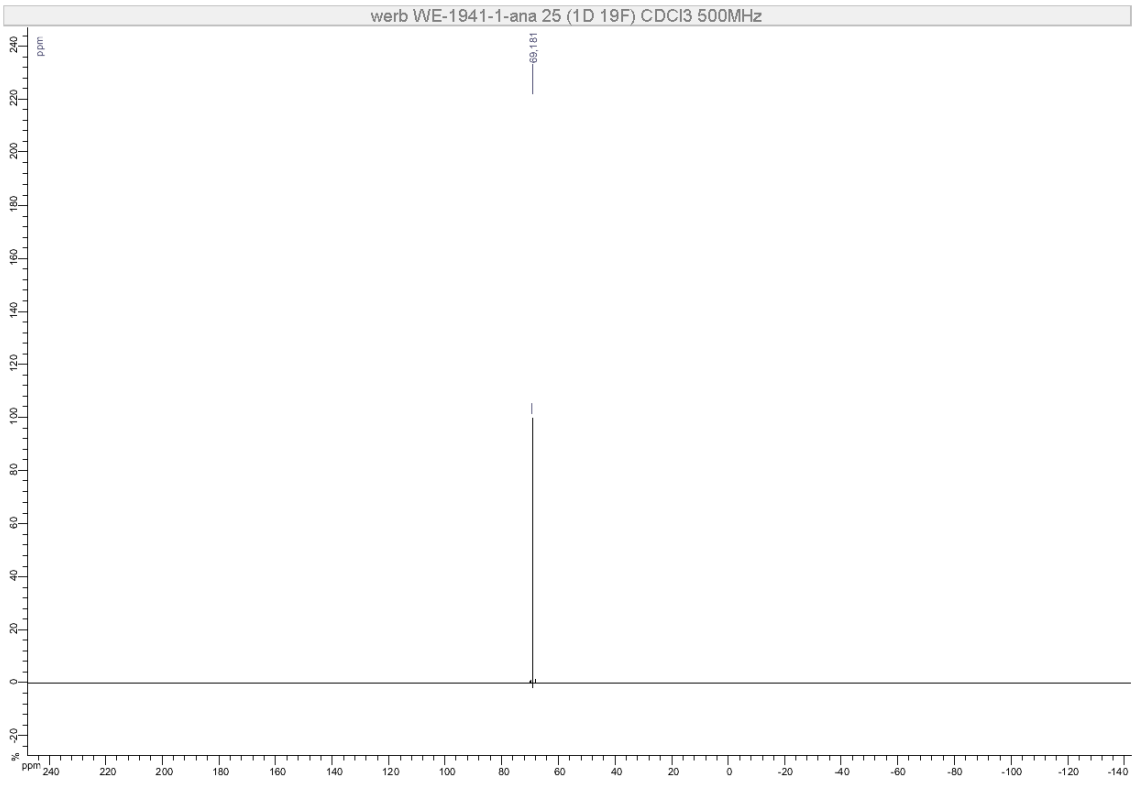
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

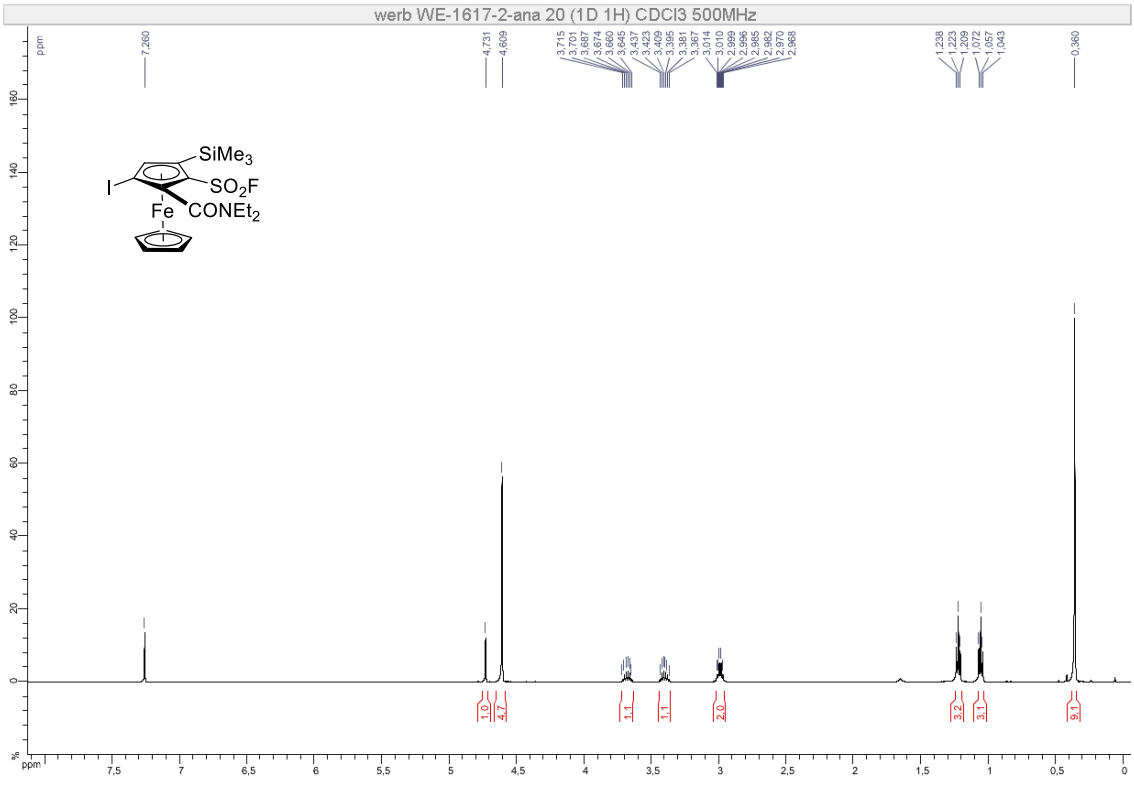


^{19}F NMR (470 MHz, $CDCl_3$)

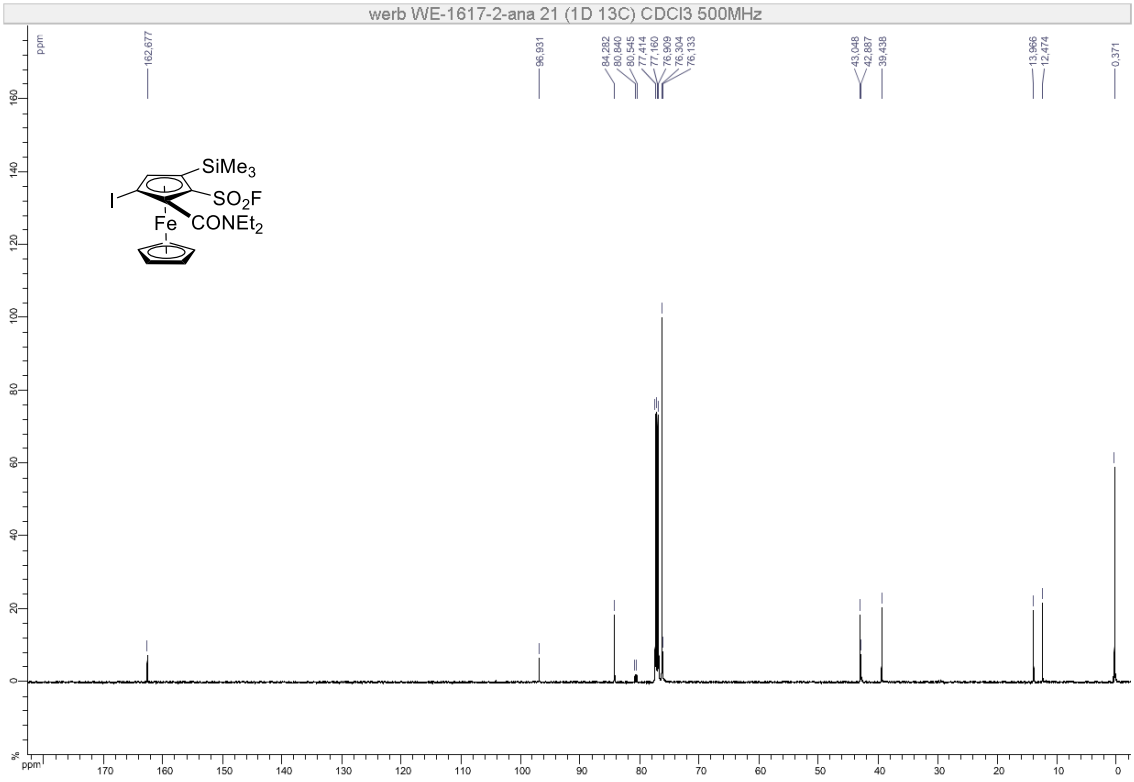


2-(*N*,*N*-Diethylcarbamoyl)-3-iodo-5-(trimethylsilyl)ferrocenesulfonyl fluoride (7a)

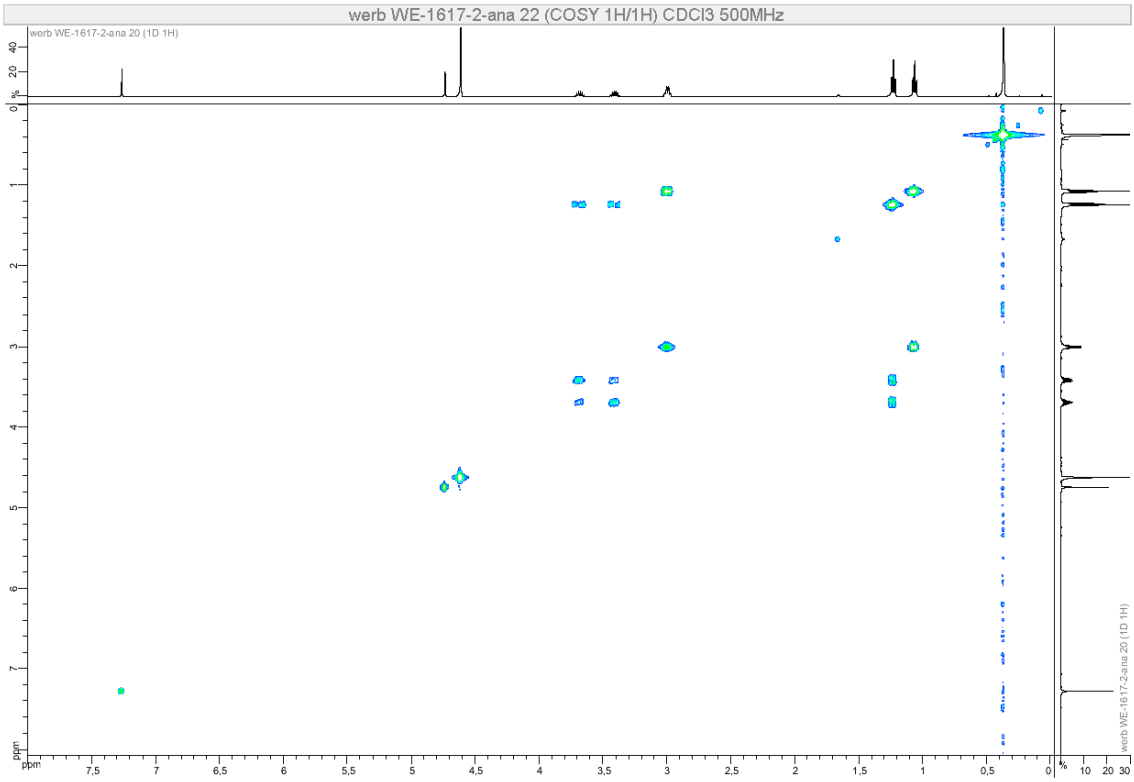
^{1}H NMR (500 MHz, $CDCl_3$)



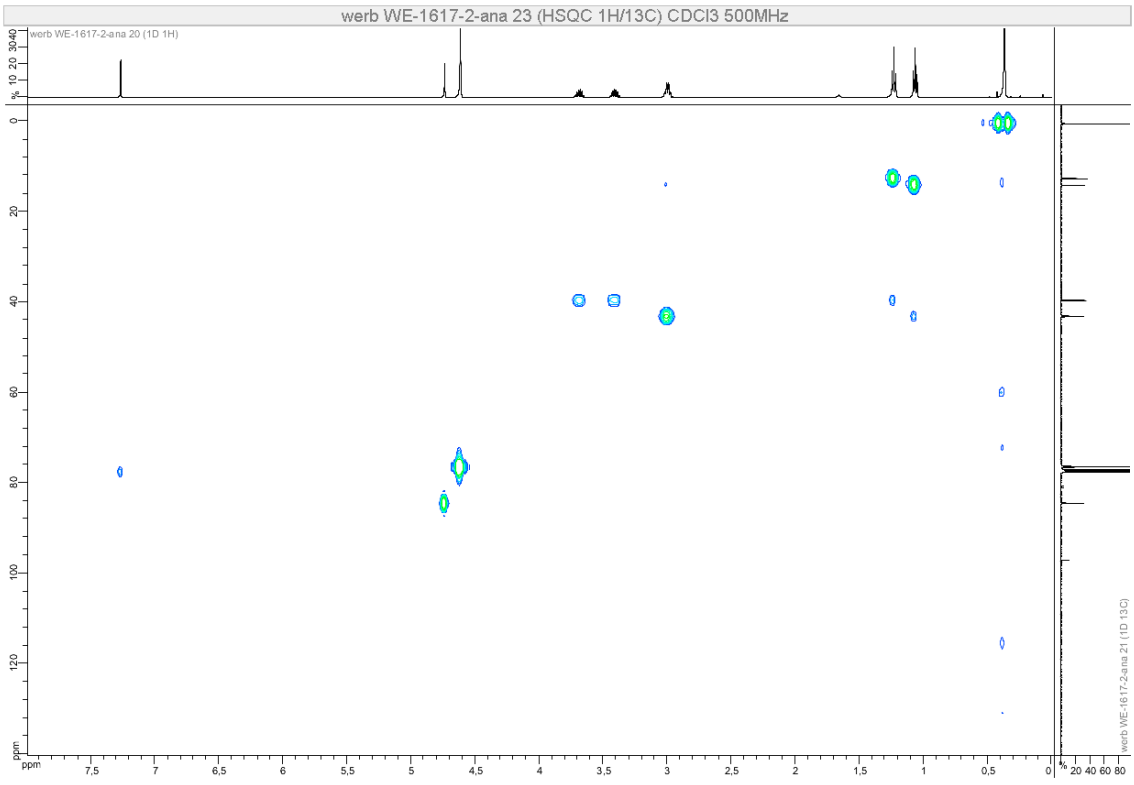
^{13}C NMR (125 MHz, $CDCl_3$)



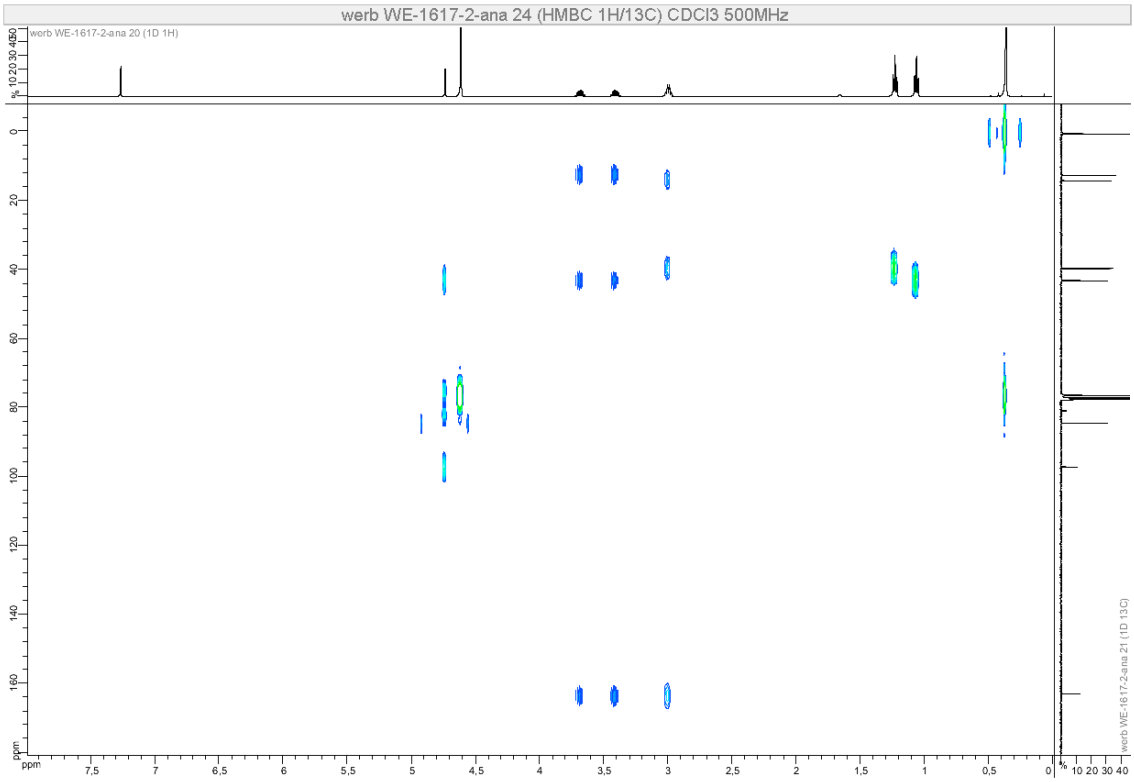
COSY (500 MHz, $CDCl_3$)



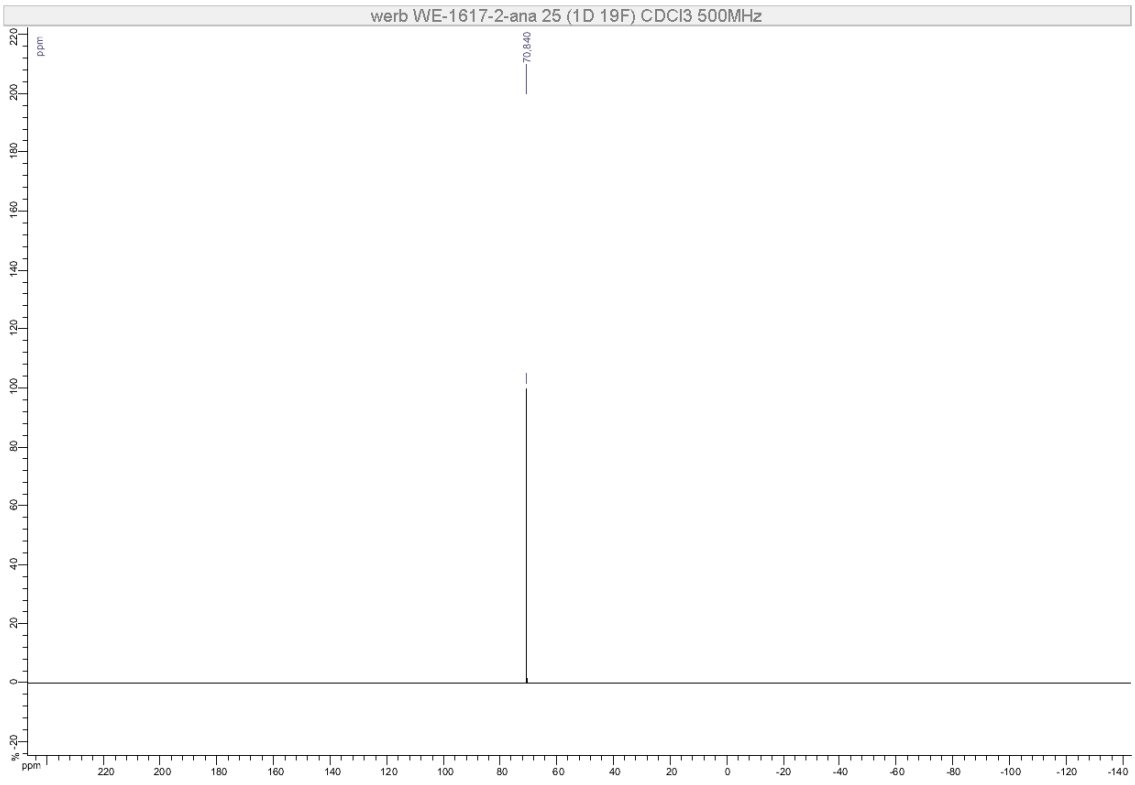
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

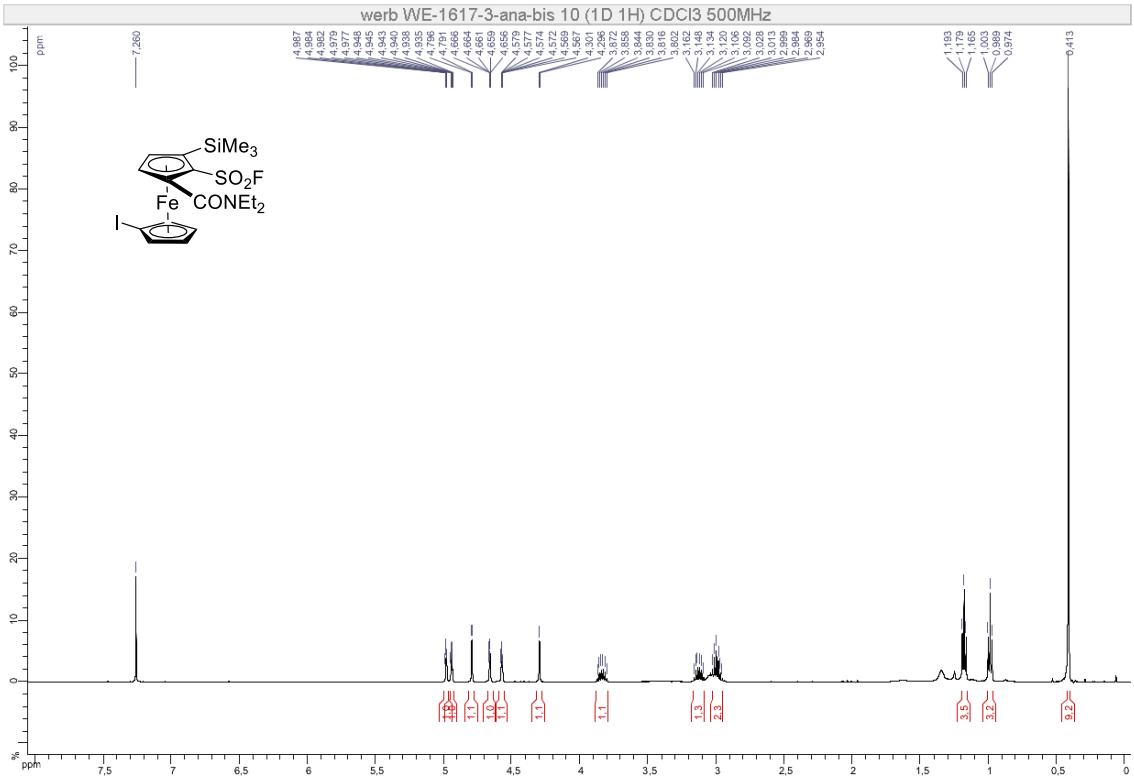


^{19}F NMR (470 MHz, $CDCl_3$)

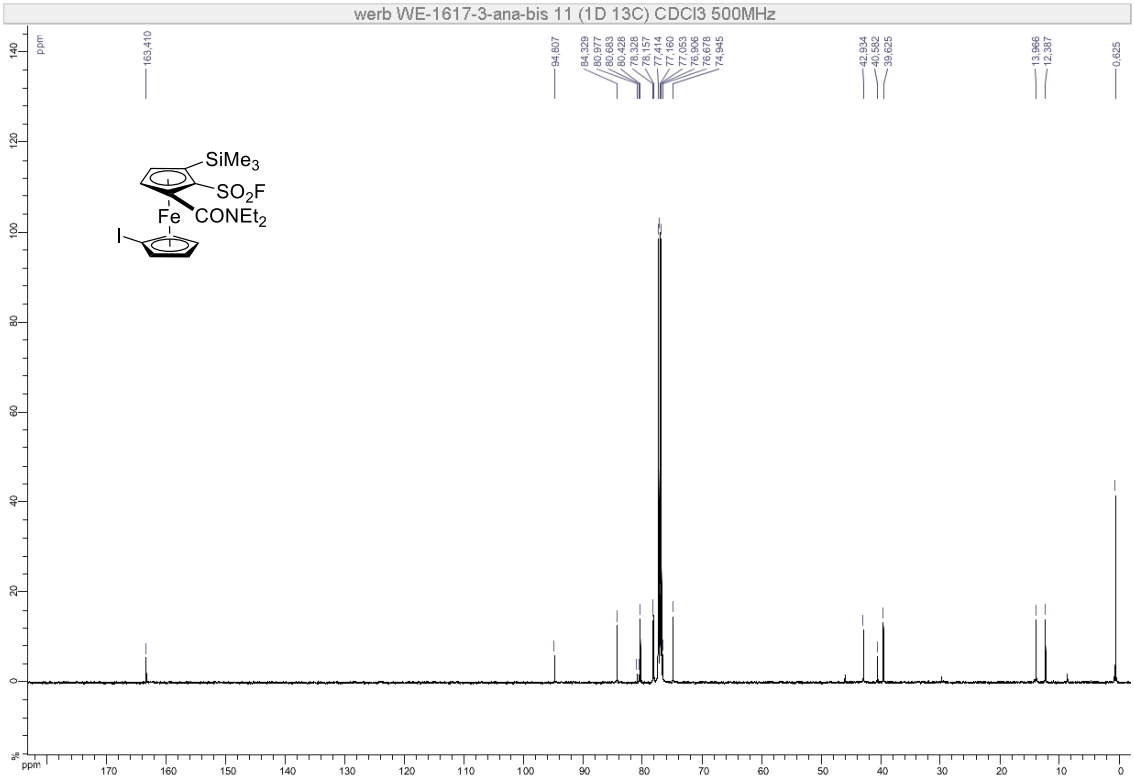


2-(*N*,*N*-Diethylcarbamoyl)-1'-iodo-5-(trimethylsilyl)ferrocenesulfonyl fluoride (7b)

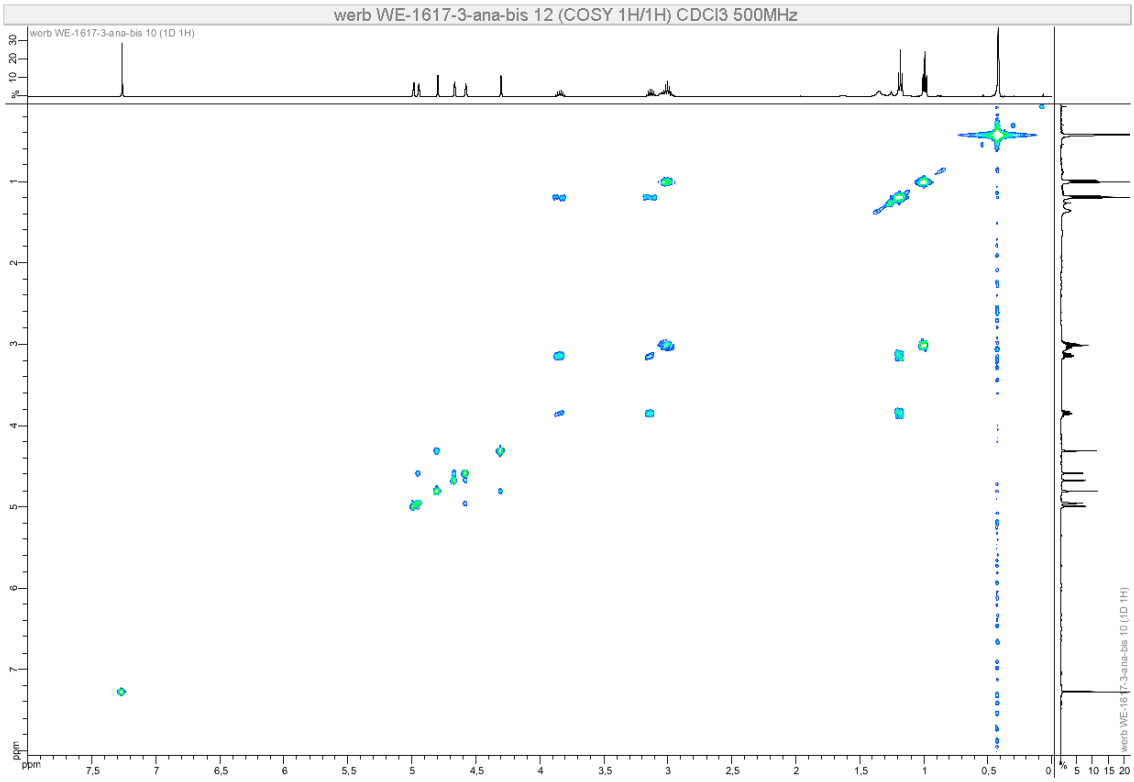
^{1}H NMR (500 MHz, $CDCl_3$)



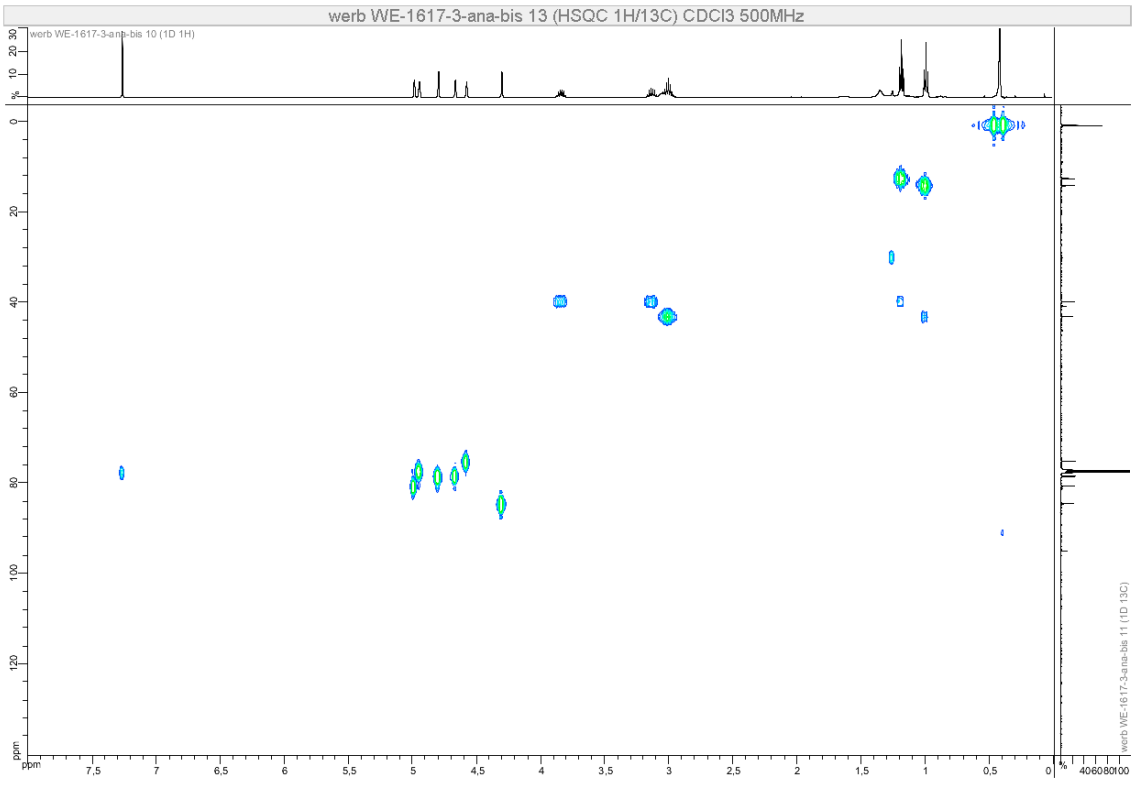
^{13}C NMR (125 MHz, $CDCl_3$)



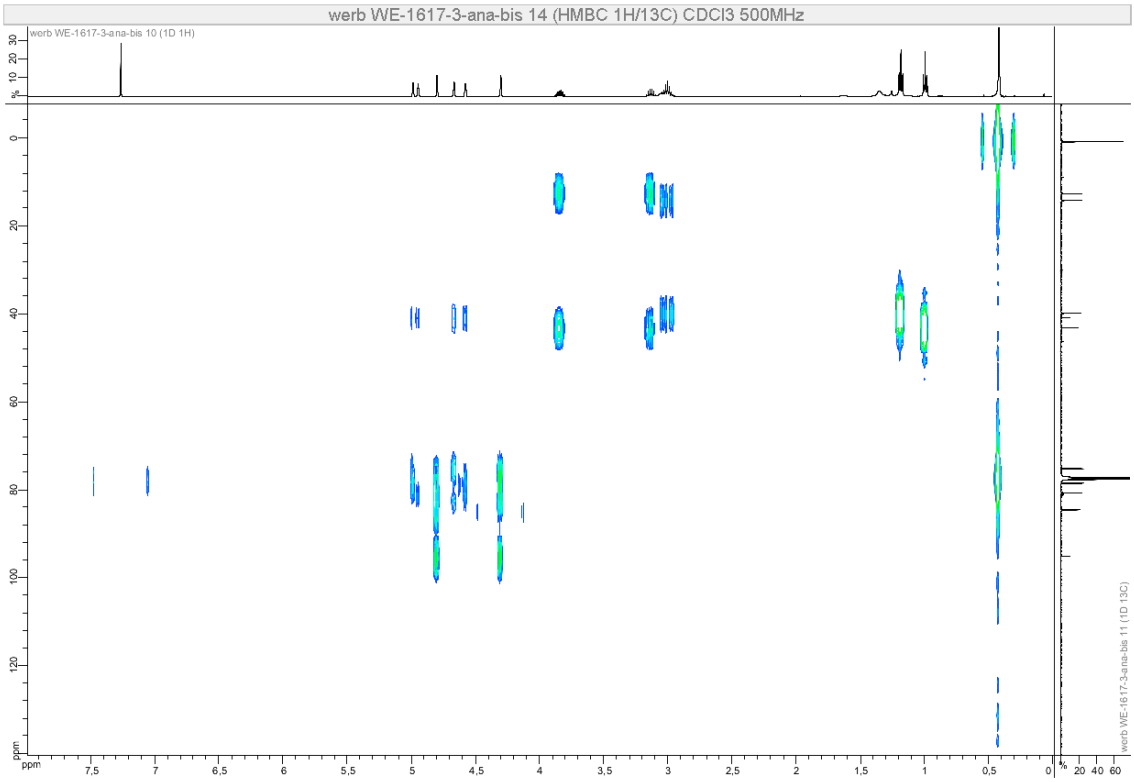
COSY (500 MHz, $CDCl_3$)



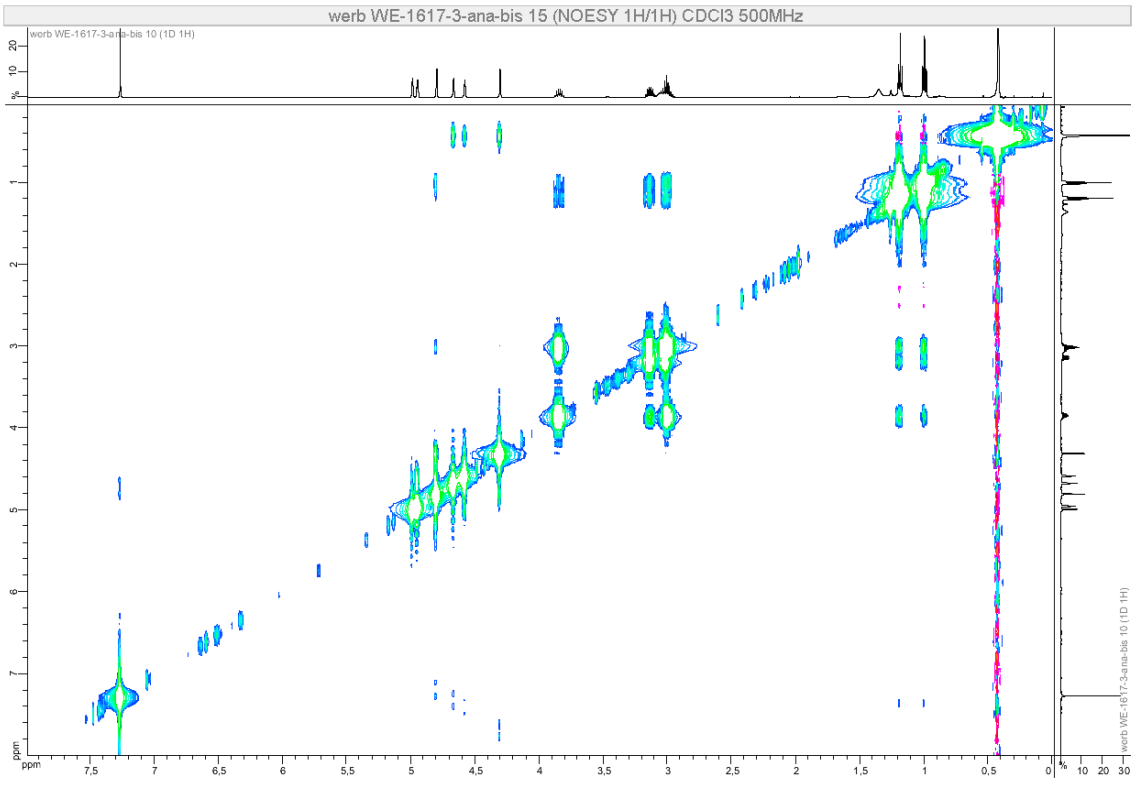
HSQC (500 MHz, $CDCl_3$)



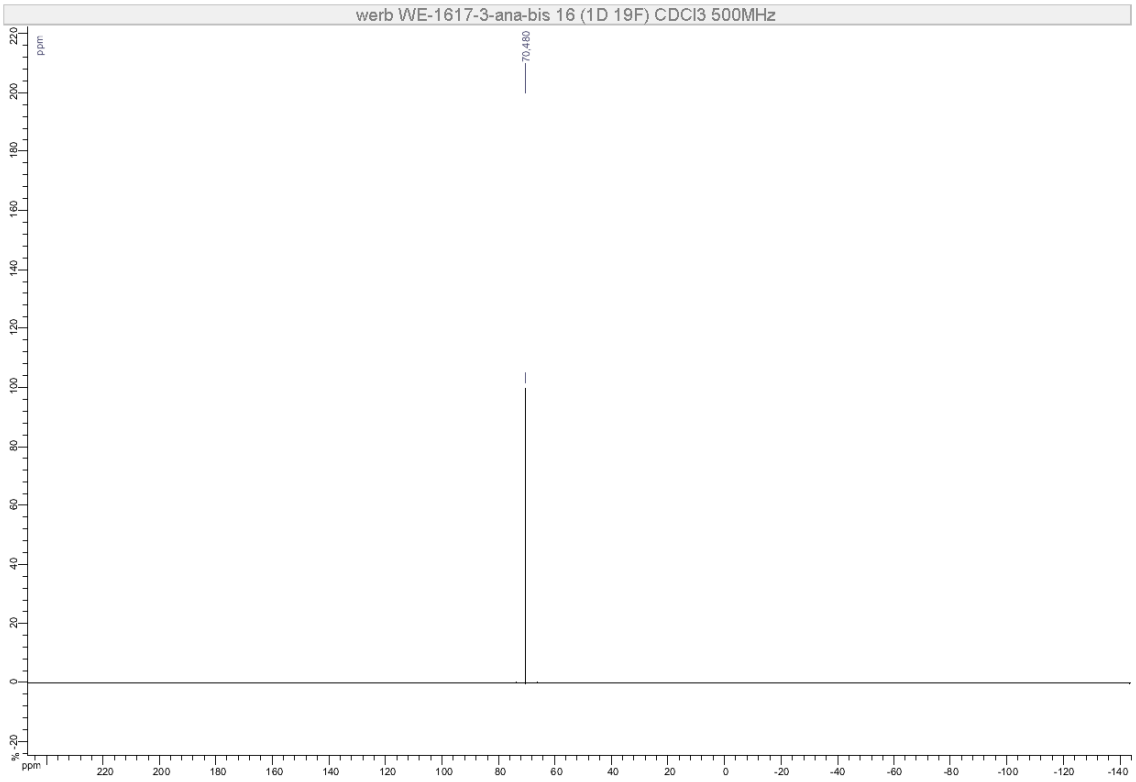
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

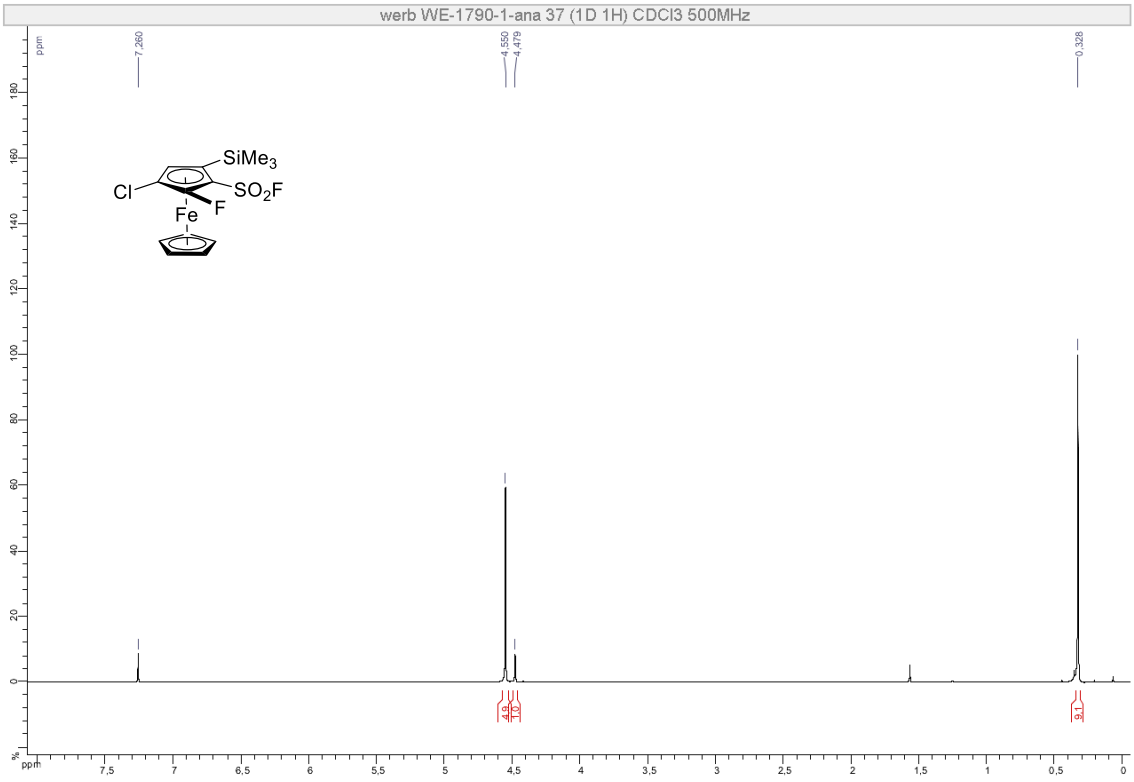


^{19}F NMR (470 MHz, $CDCl_3$)

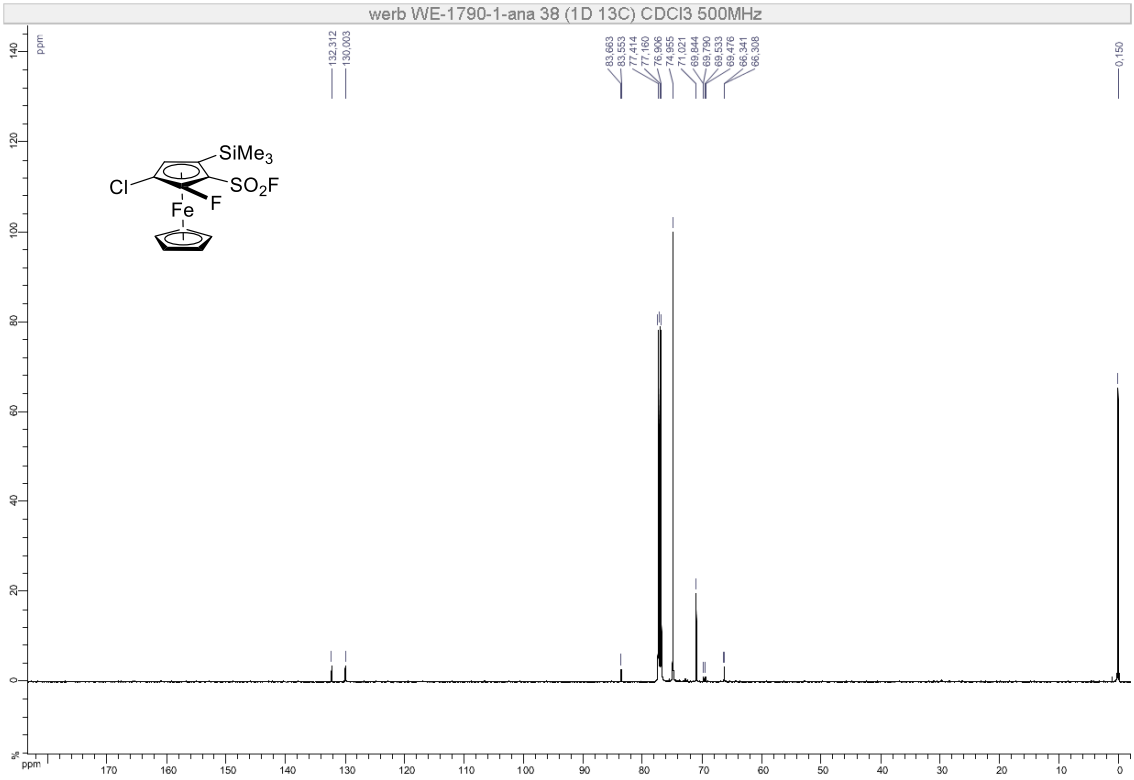


3-Chloro-2-fluoro-5-(trimethylsilyl)ferrocenesulfonyl fluoride (8a)

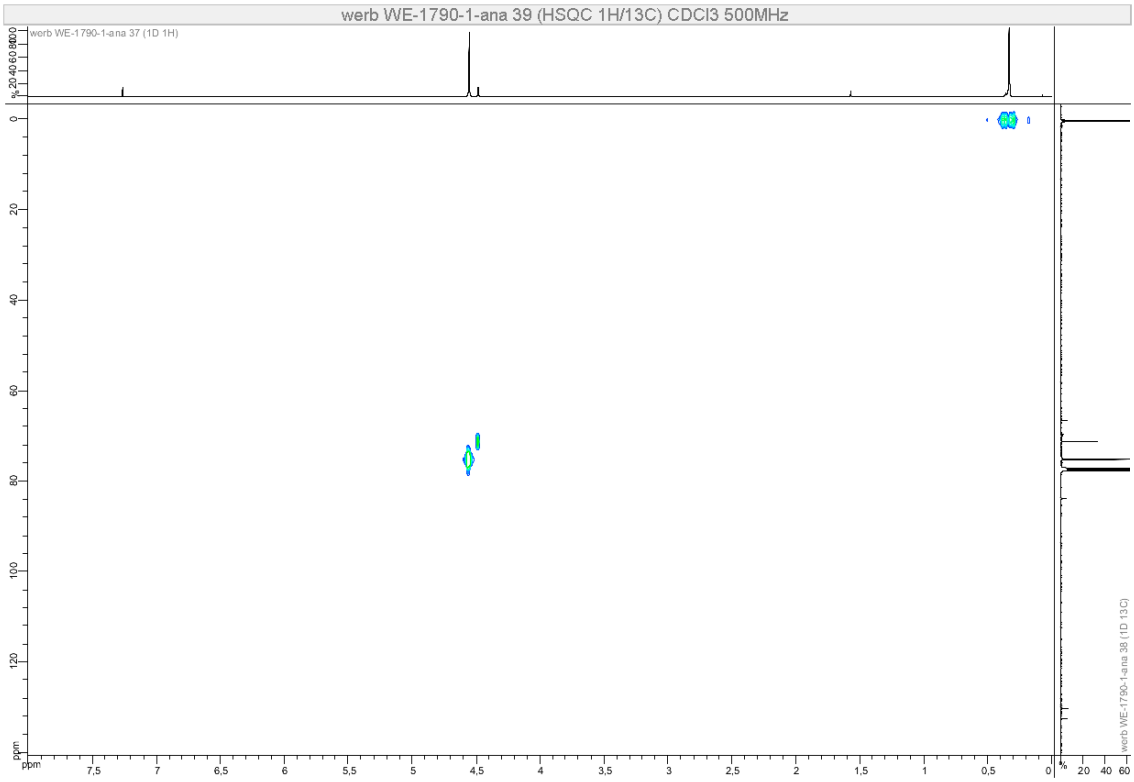
^{1}H NMR (500 MHz, $CDCl_3$)



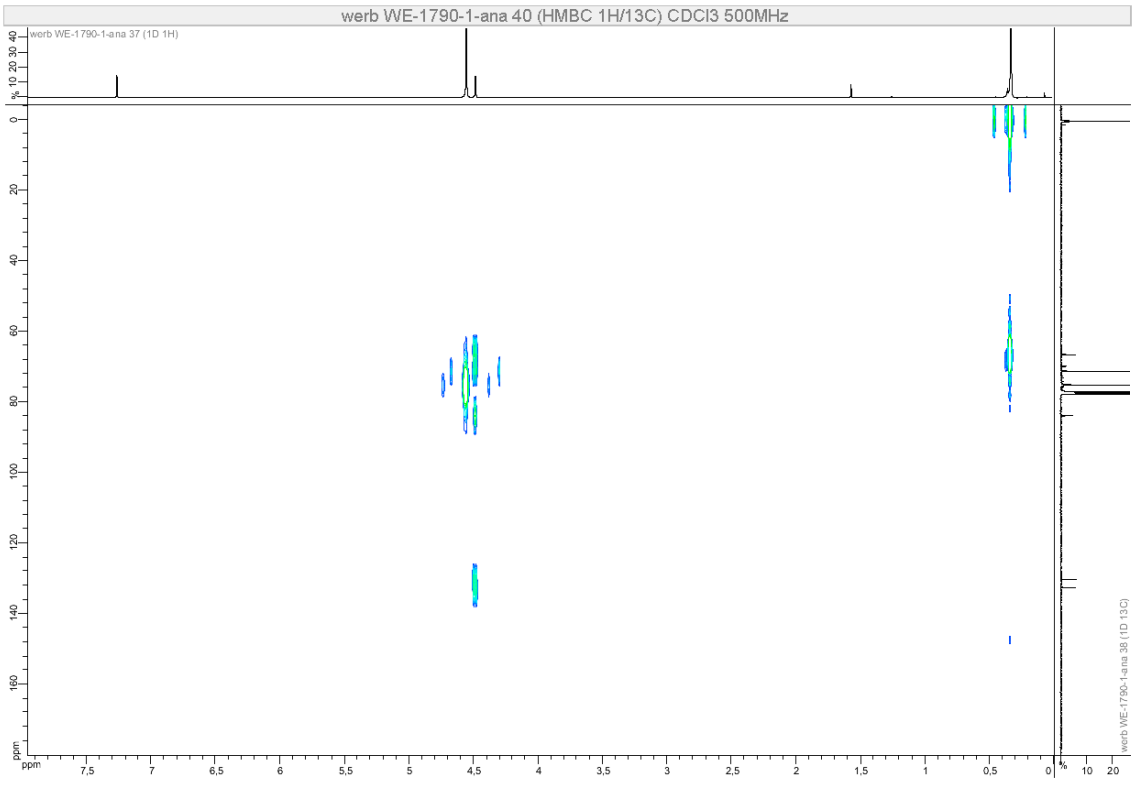
^{13}C NMR (125 MHz, $CDCl_3$)



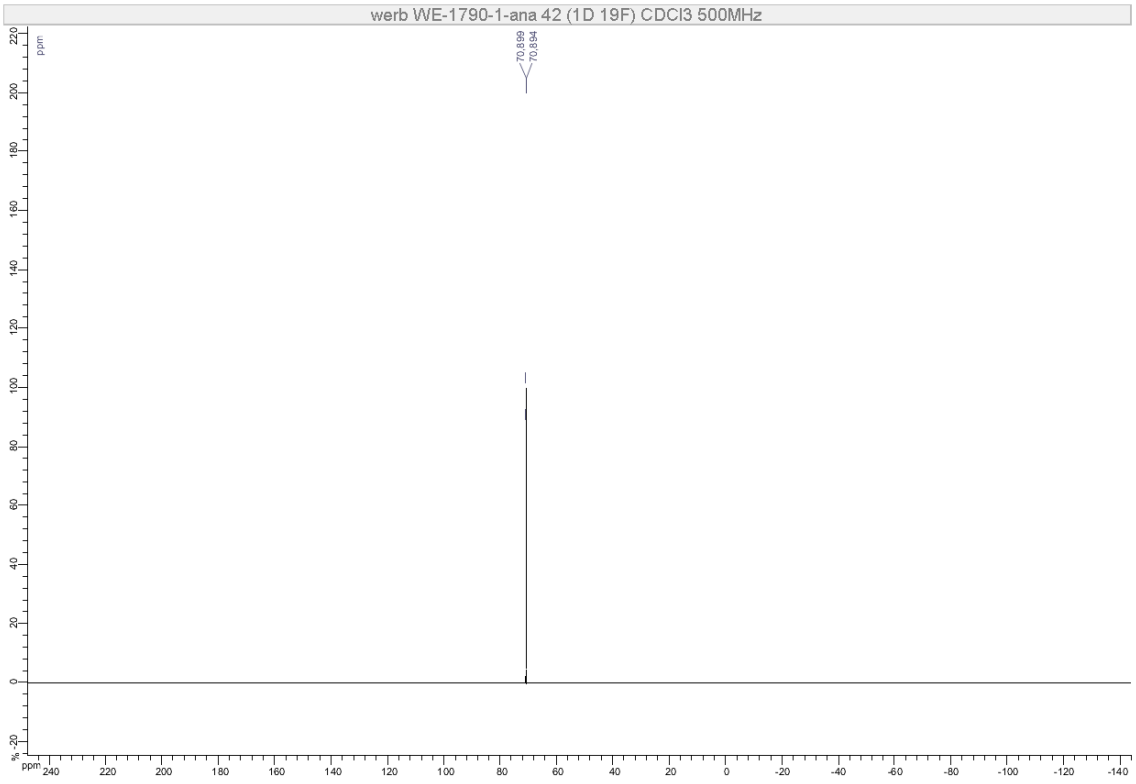
HSQC (500 MHz, $CDCl_3$)



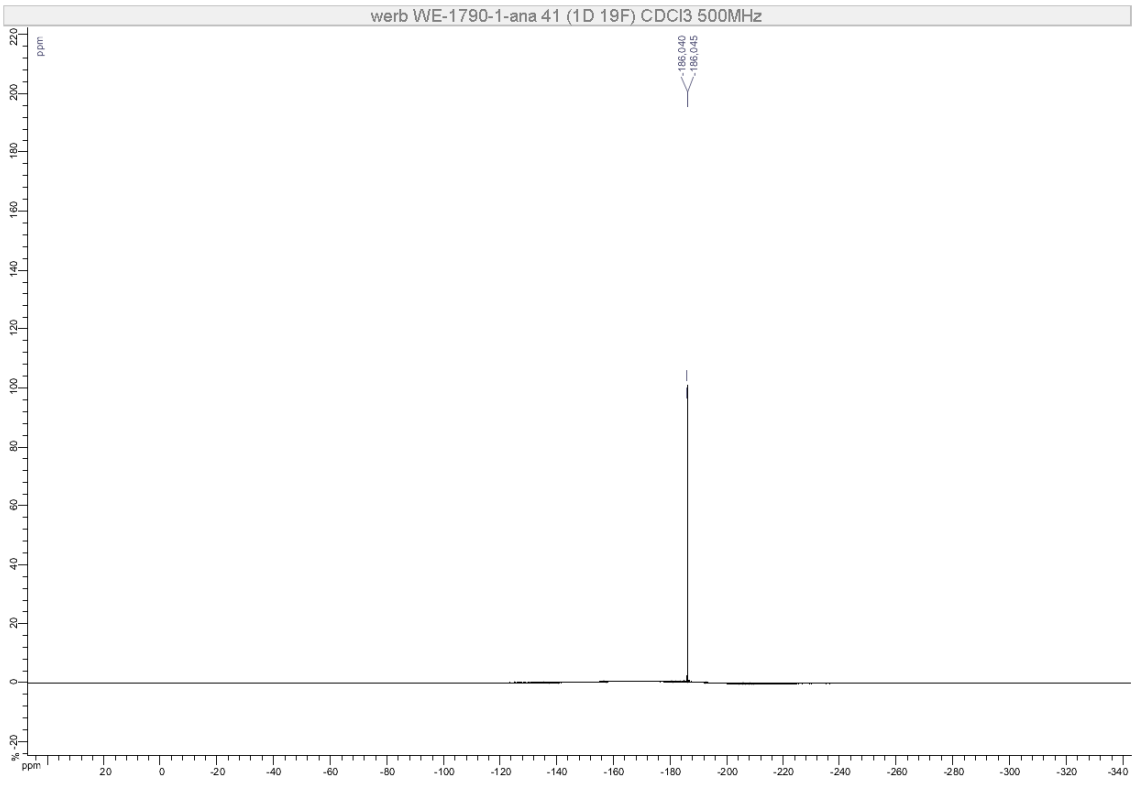
HMBC (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$) – 240 to -140 ppm area

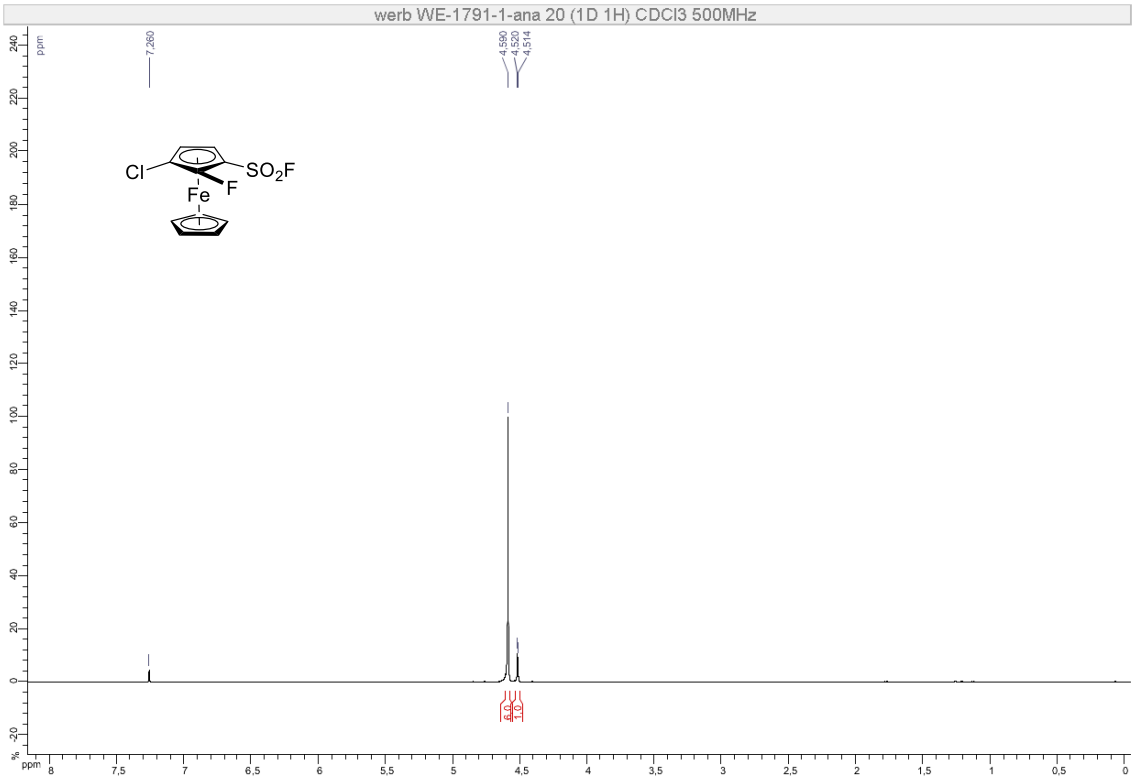


^{19}F NMR (470 MHz, $CDCl_3$) – 40 to -340 ppm area

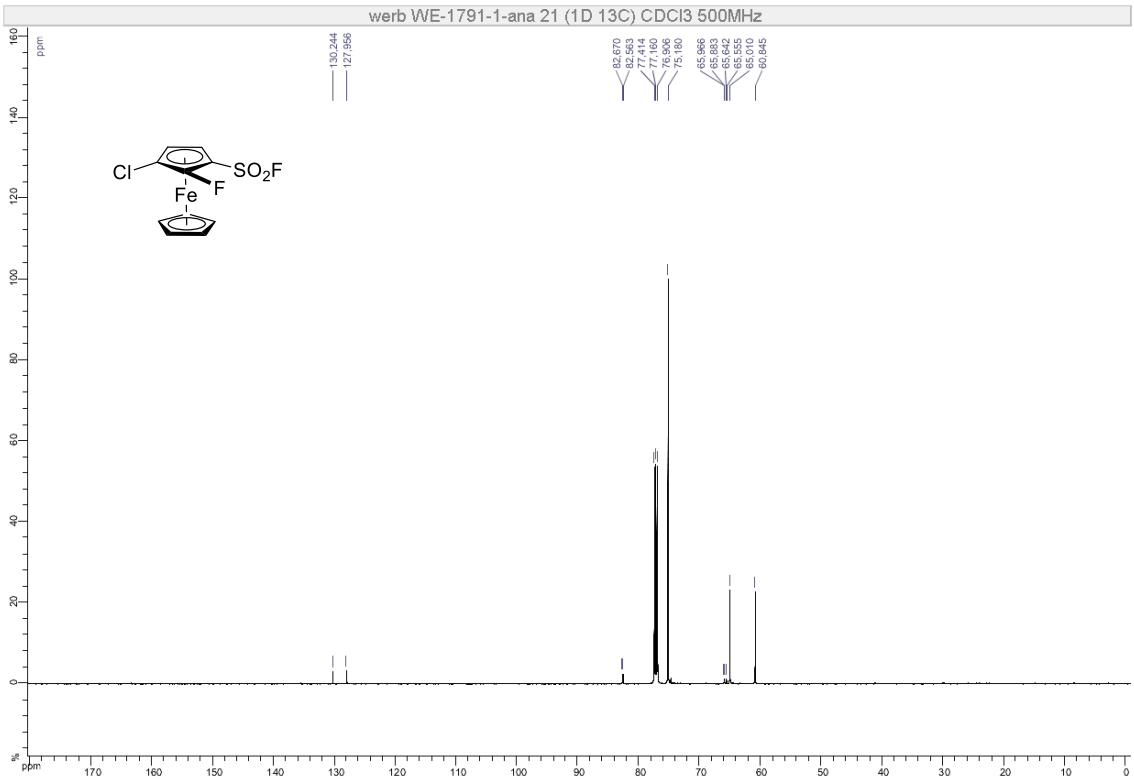


3-Chloro-2-fluoroferrocenesulfonyl fluoride (9)

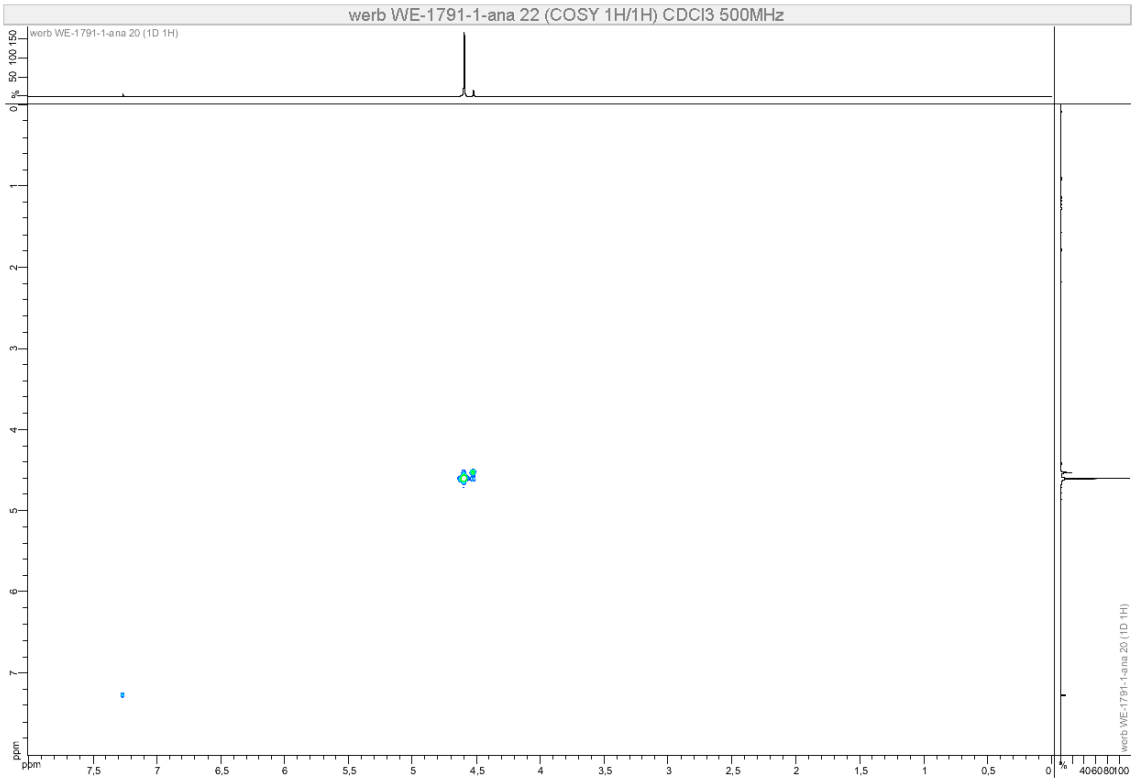
^{1}H NMR (500 MHz, $CDCl_3$)



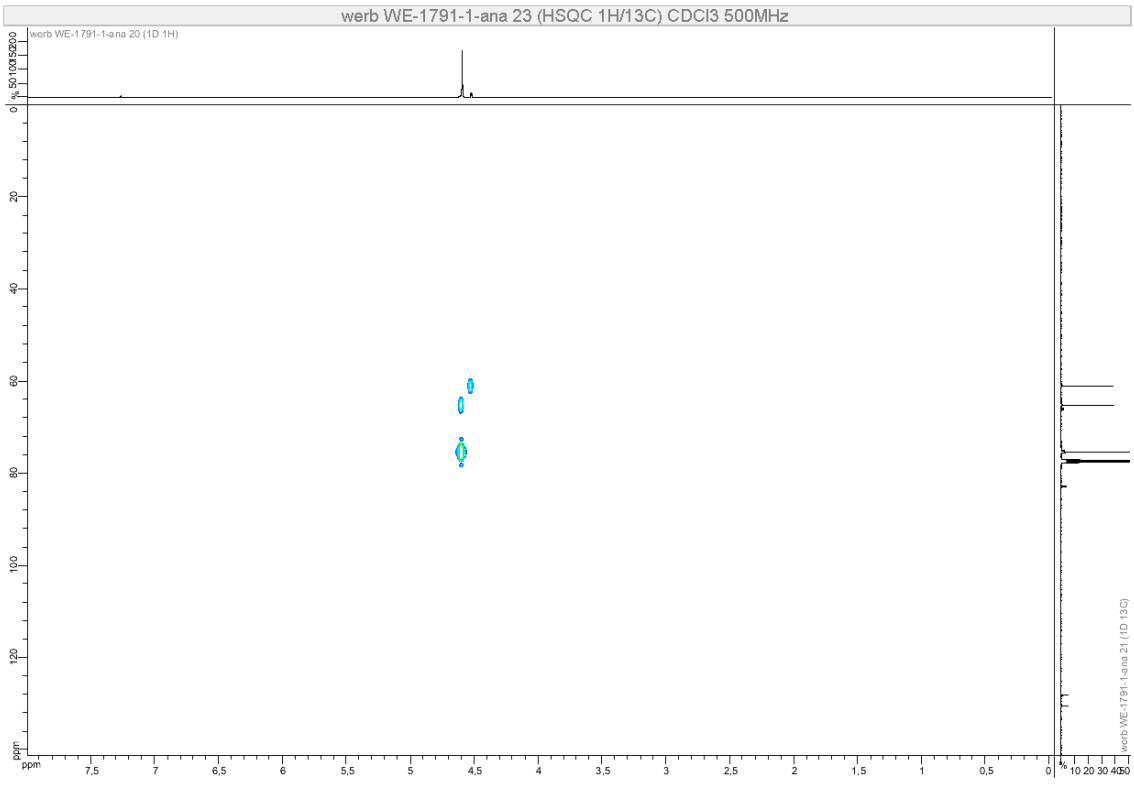
^{13}C NMR (125 MHz, $CDCl_3$)



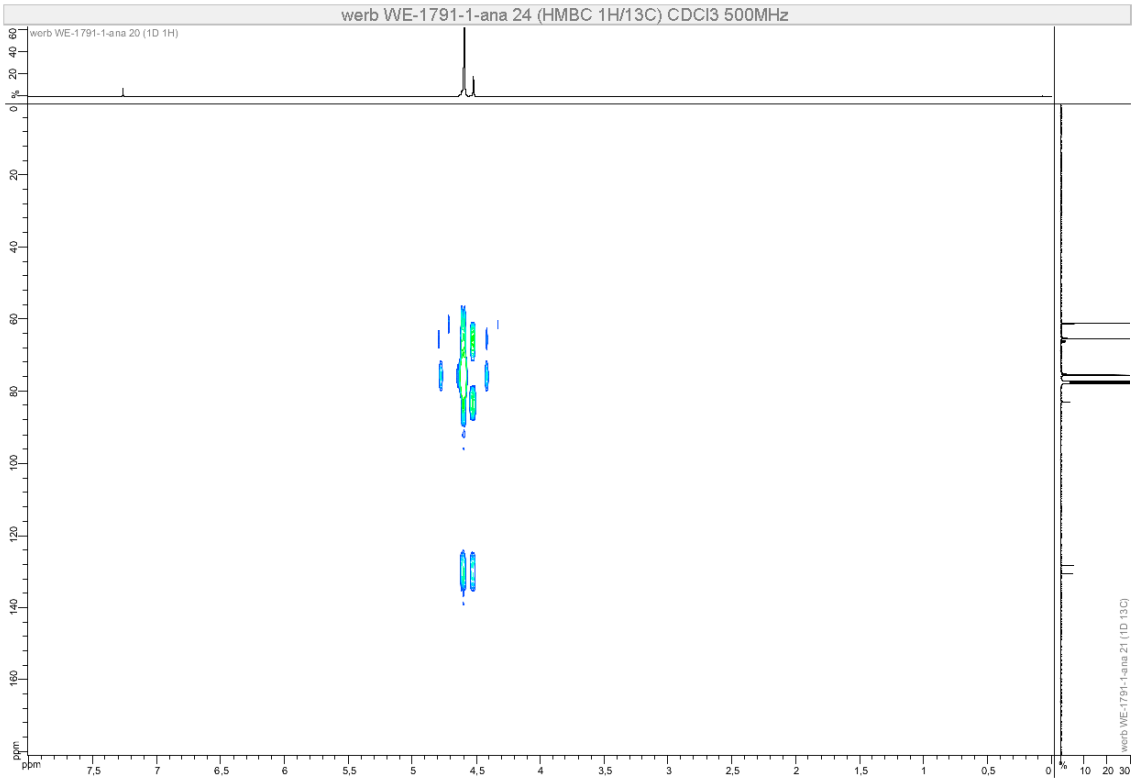
COSY (500 MHz, $CDCl_3$)



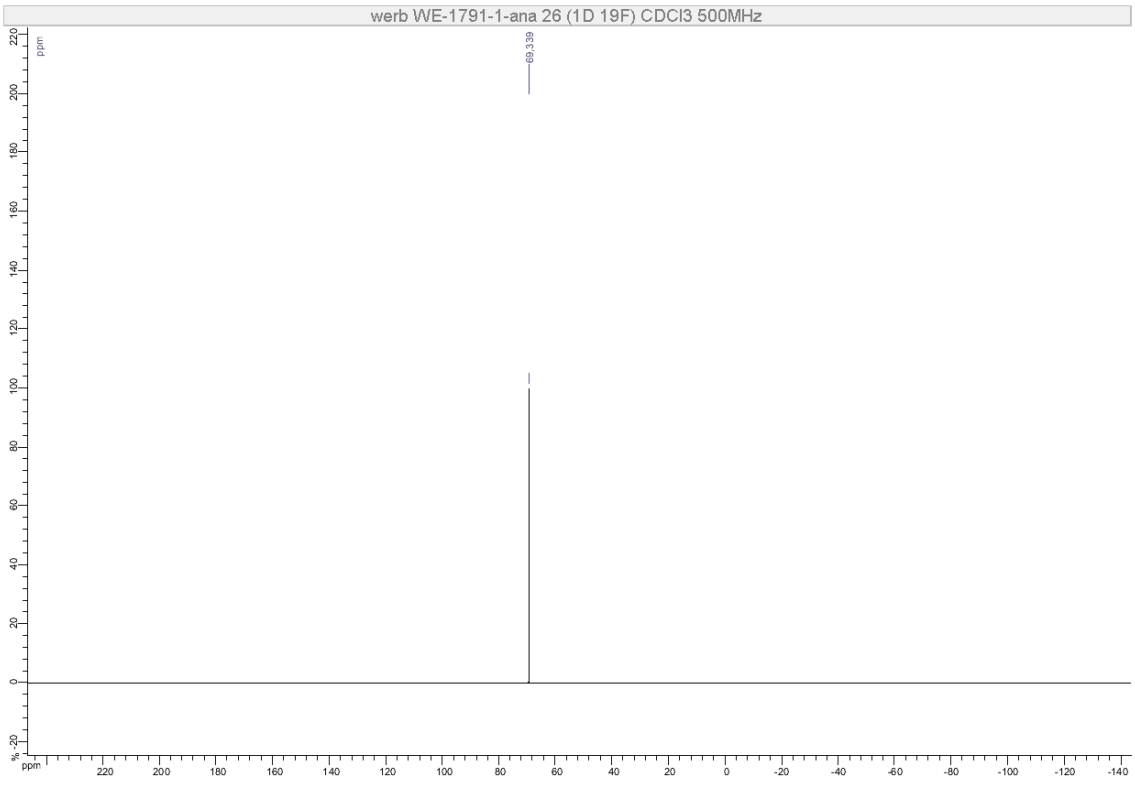
HSQC (500 MHz, $CDCl_3$)



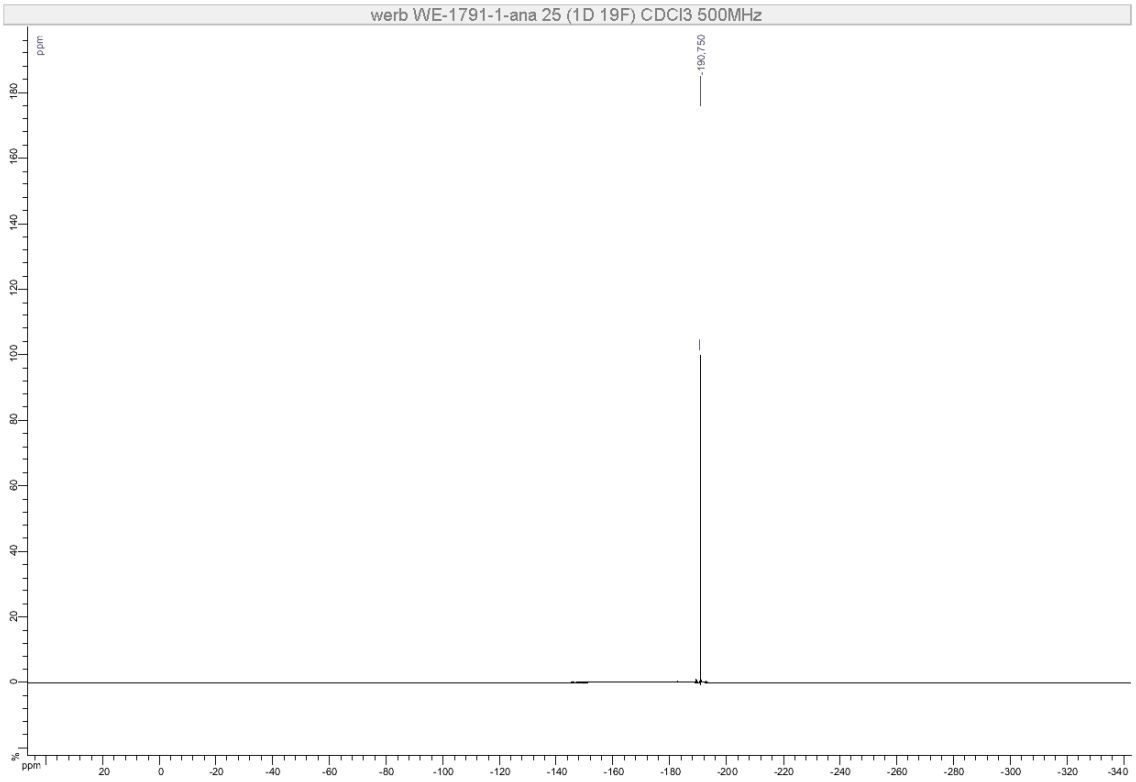
HMBC (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$) – 240 to -140 ppm area

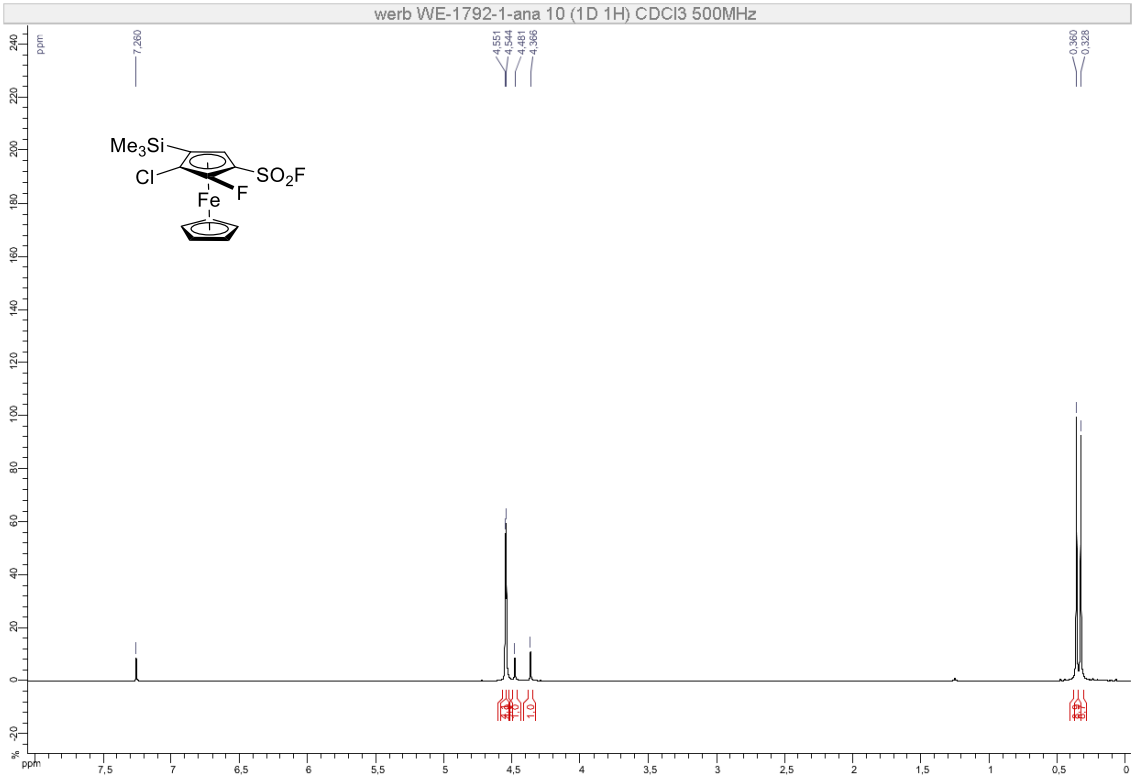


^{19}F NMR (470 MHz, $CDCl_3$) – 40 to -340 ppm area

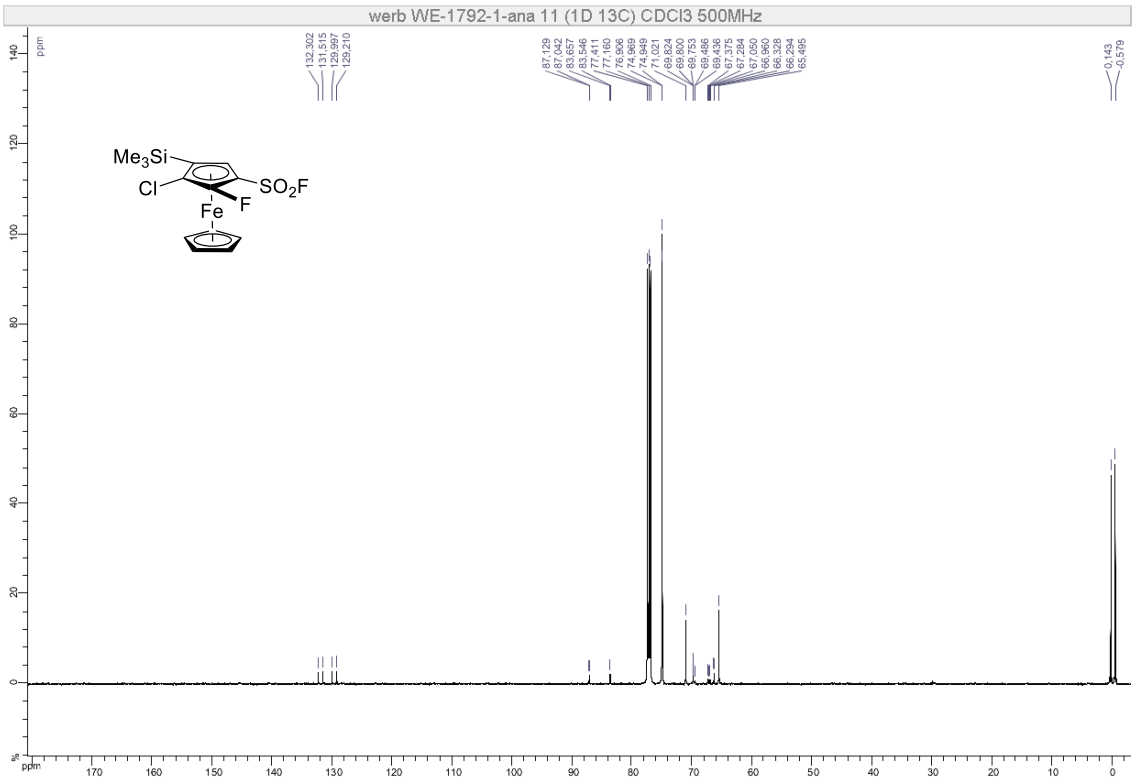


3-Chloro-2-fluoro-4-(trimethylsilyl)ferrocenesulfonyl fluoride (8b)

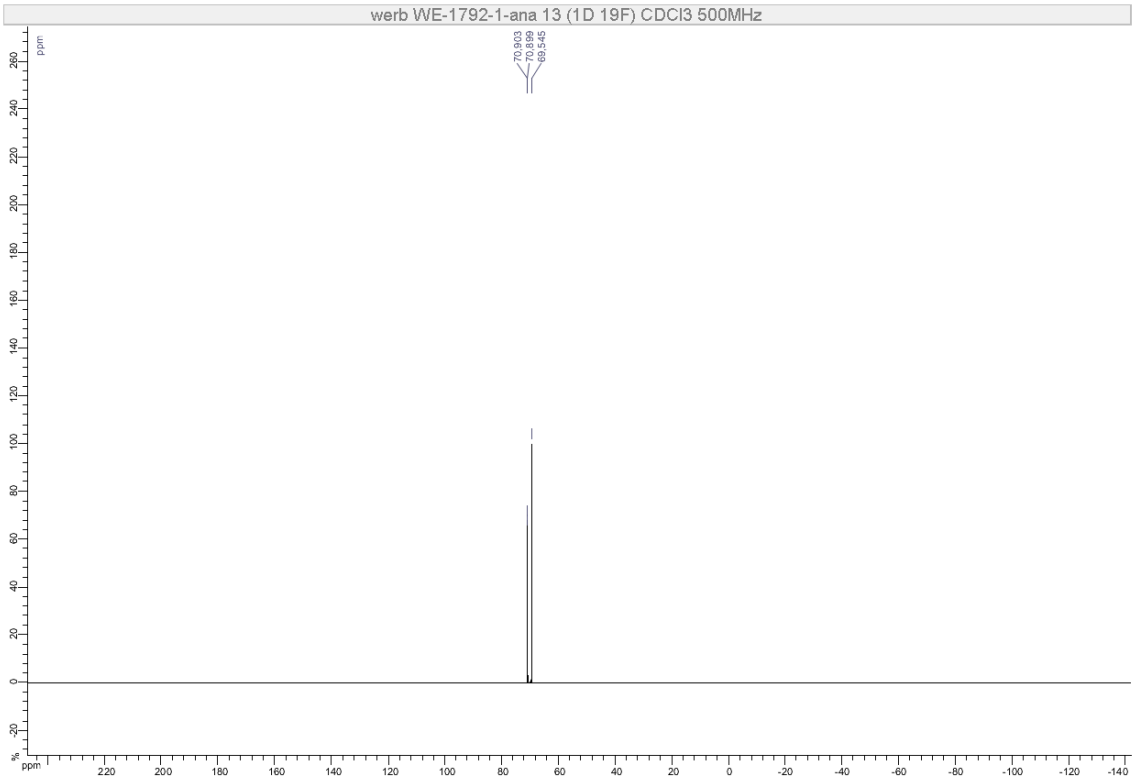
^{1}H NMR (500 MHz, $CDCl_3$)



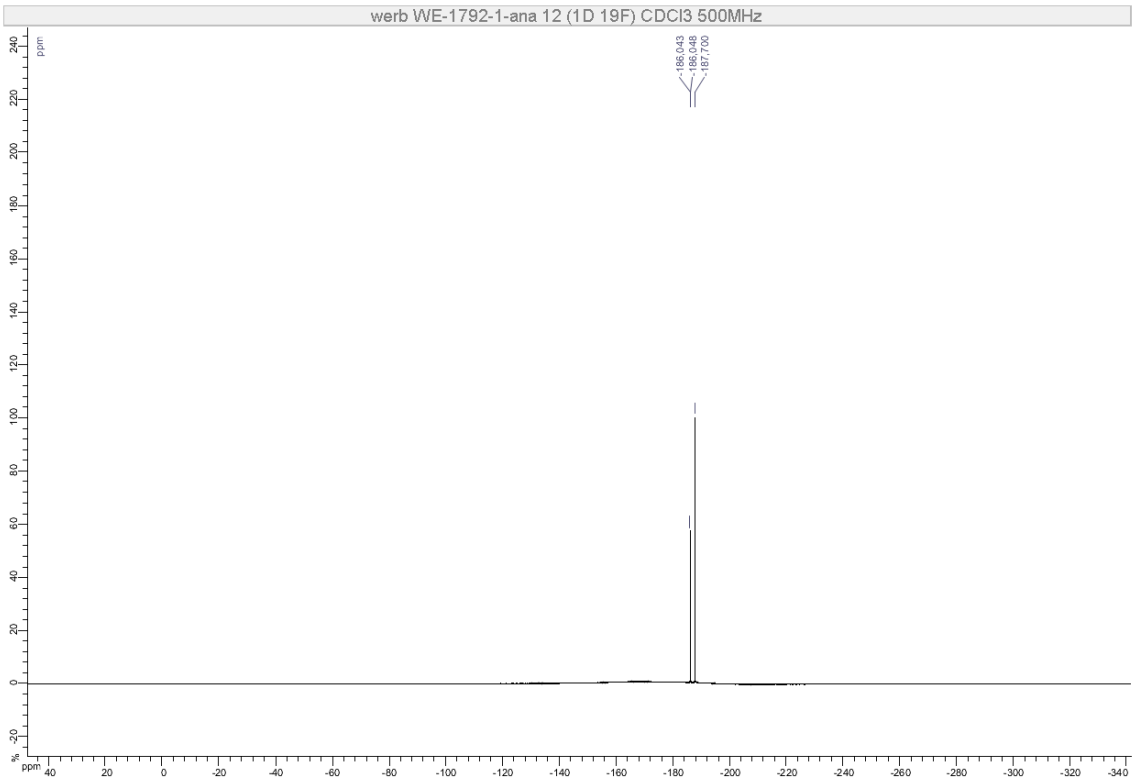
^{13}C NMR (125 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$) – 240 to -140 ppm area

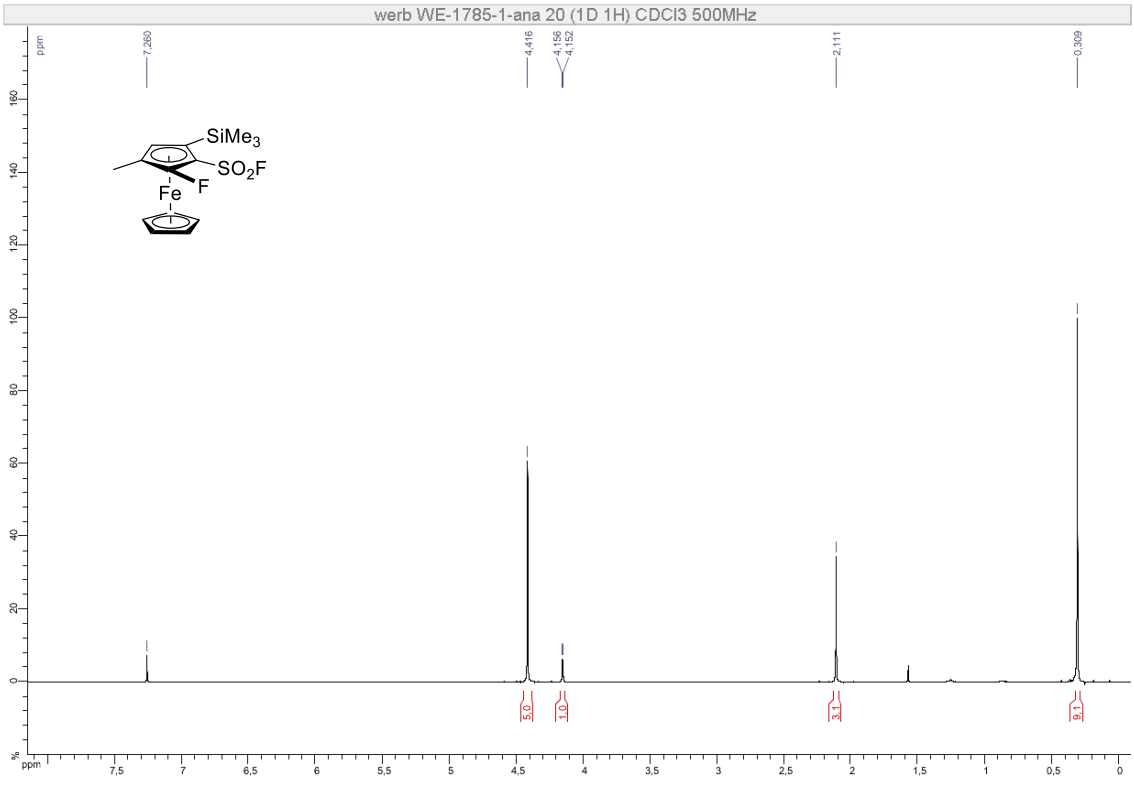


^{19}F NMR (470 MHz, $CDCl_3$) – 40 to -340 ppm area

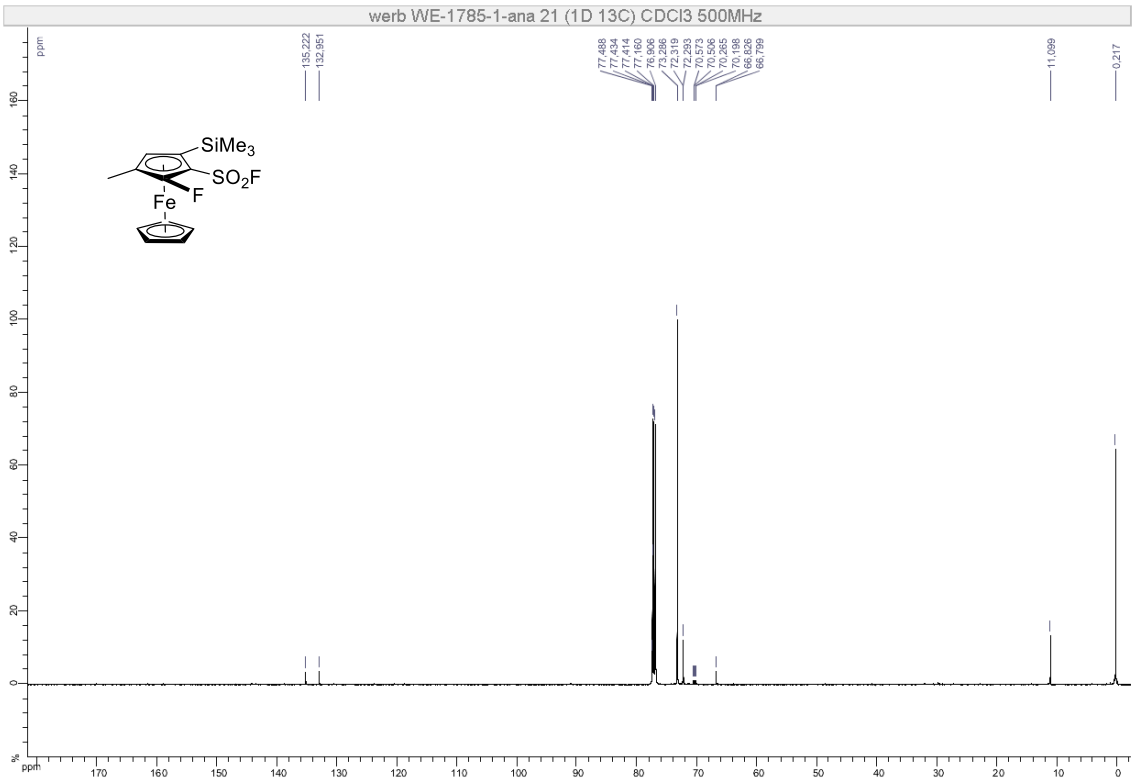


2-Fluoro-3-methyl-5-(trimethylsilyl)ferrocenesulfonyl fluoride (10)

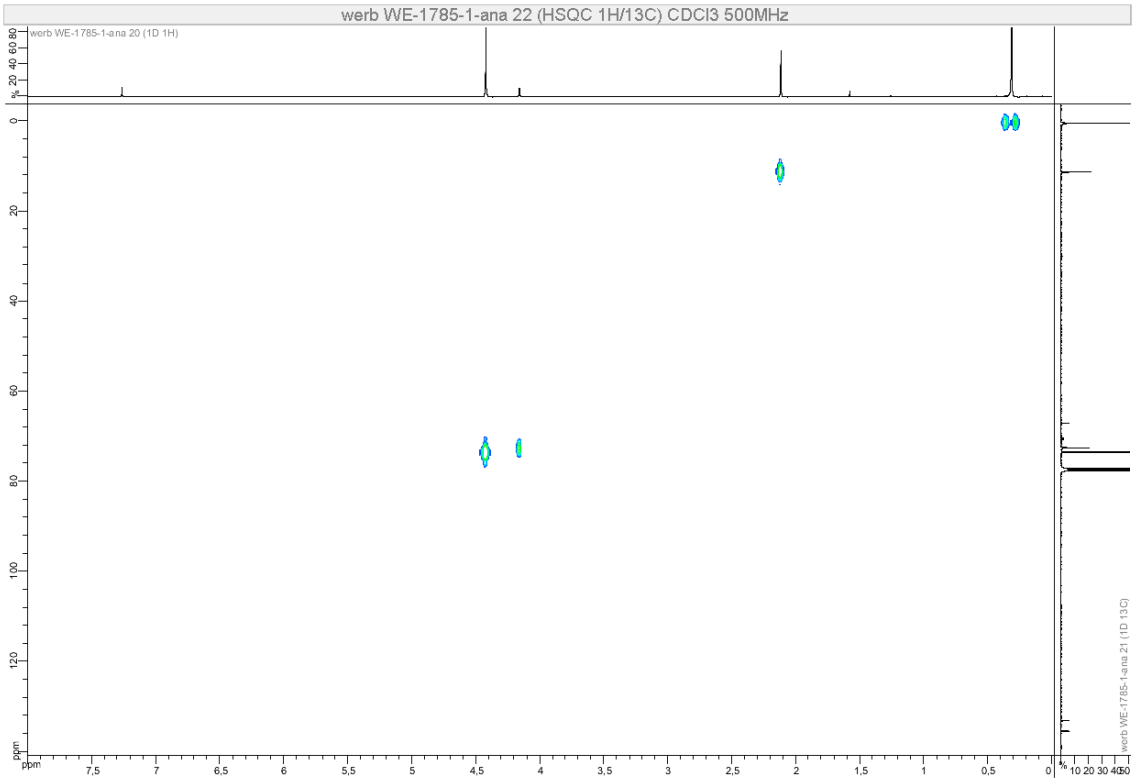
^{1}H NMR (500 MHz, $CDCl_3$)



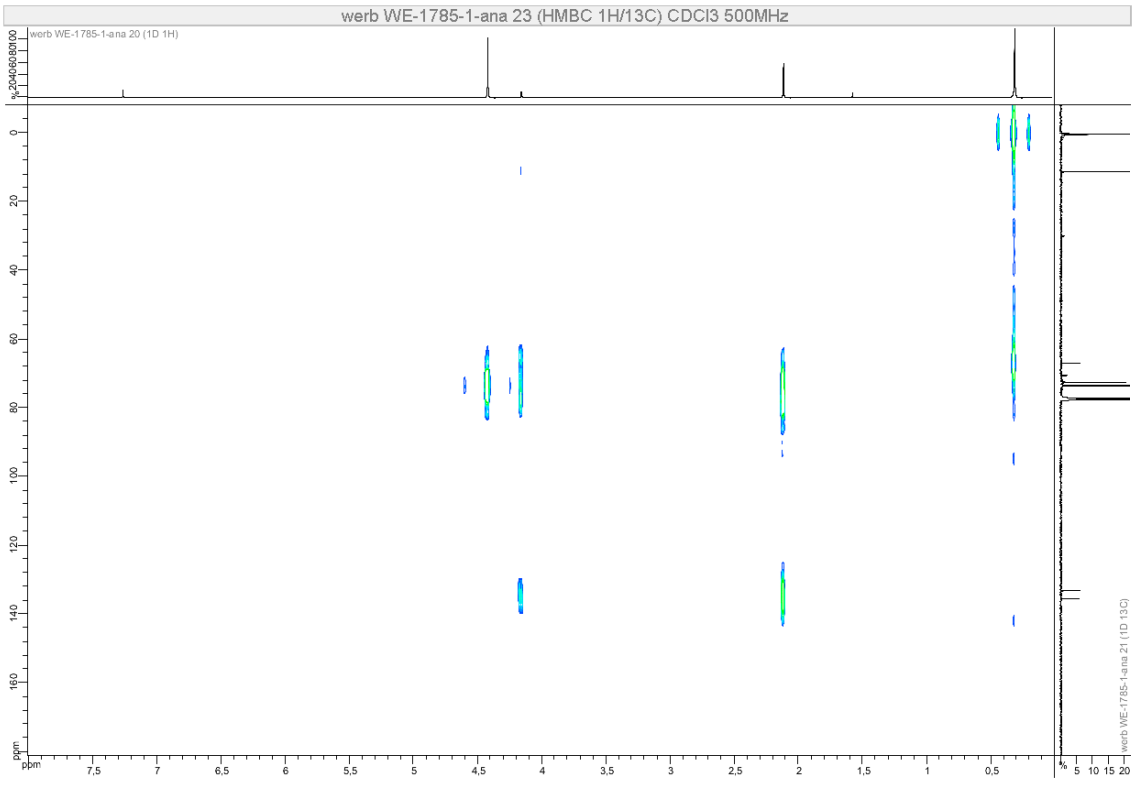
^{13}C NMR (125 MHz, $CDCl_3$)



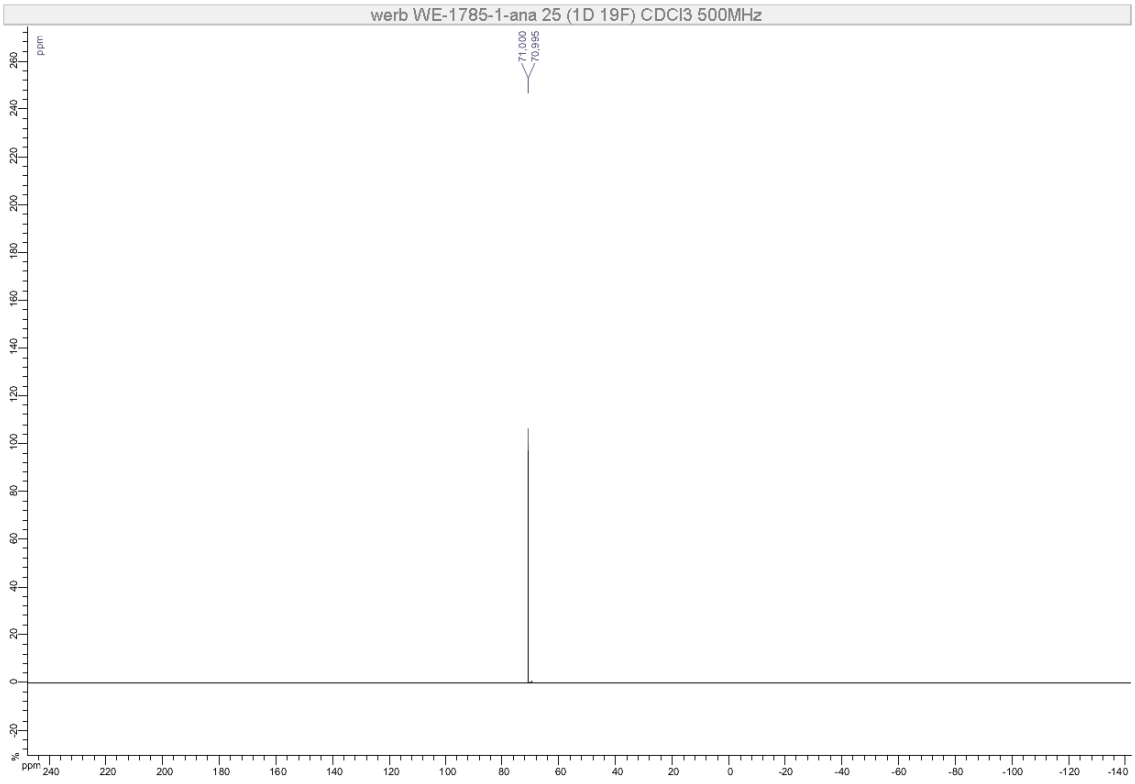
HSQC (500 MHz, $CDCl_3$)



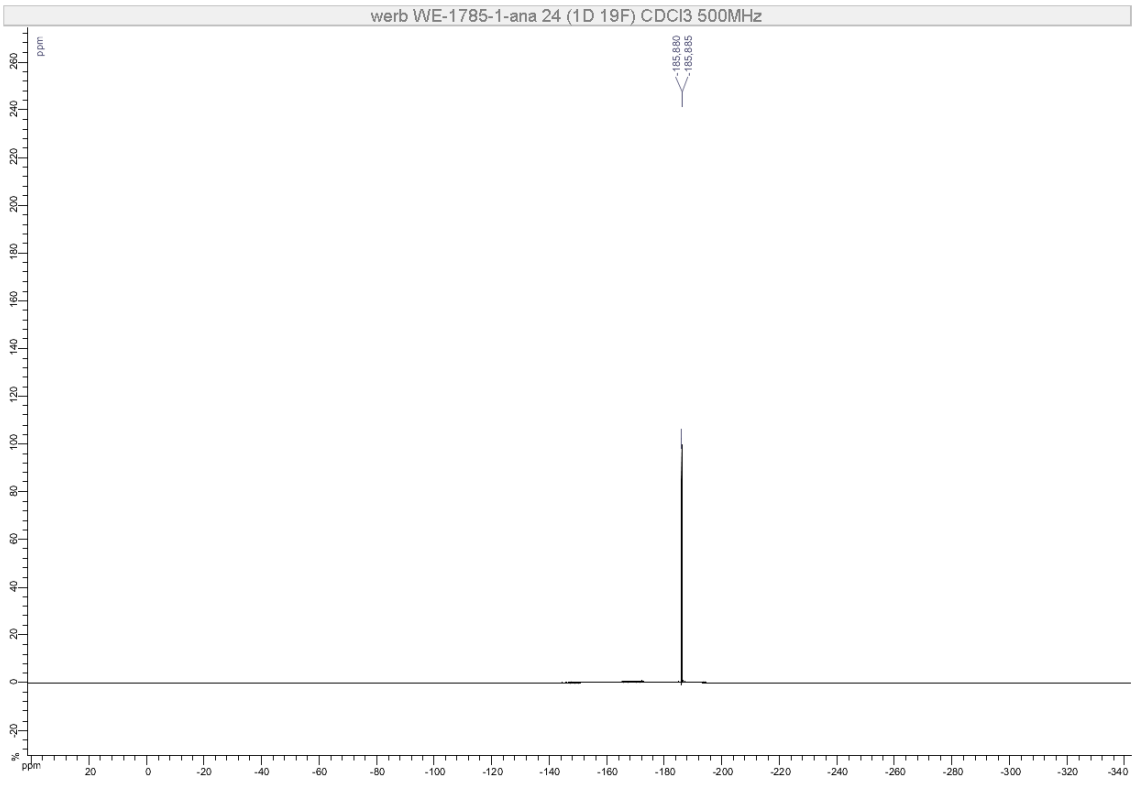
HMBC (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$) – 240 to -140 ppm area

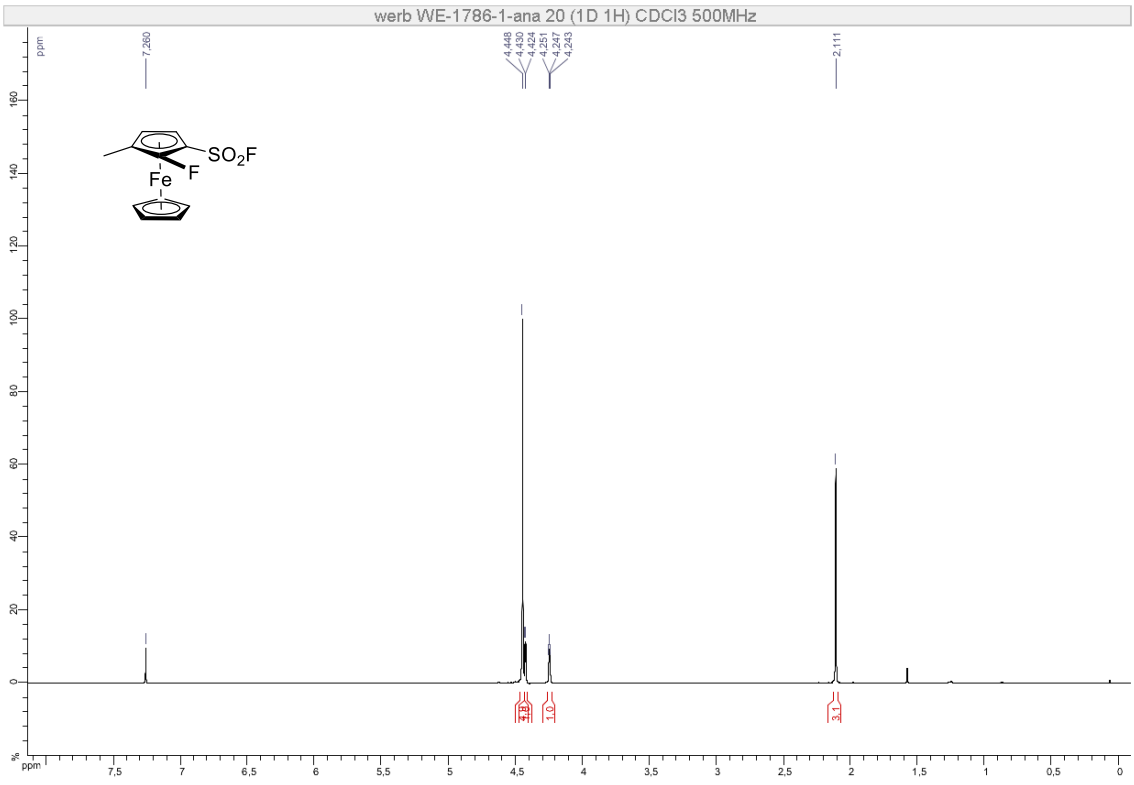


^{19}F NMR (470 MHz, $CDCl_3$) – 40 to -340 ppm area

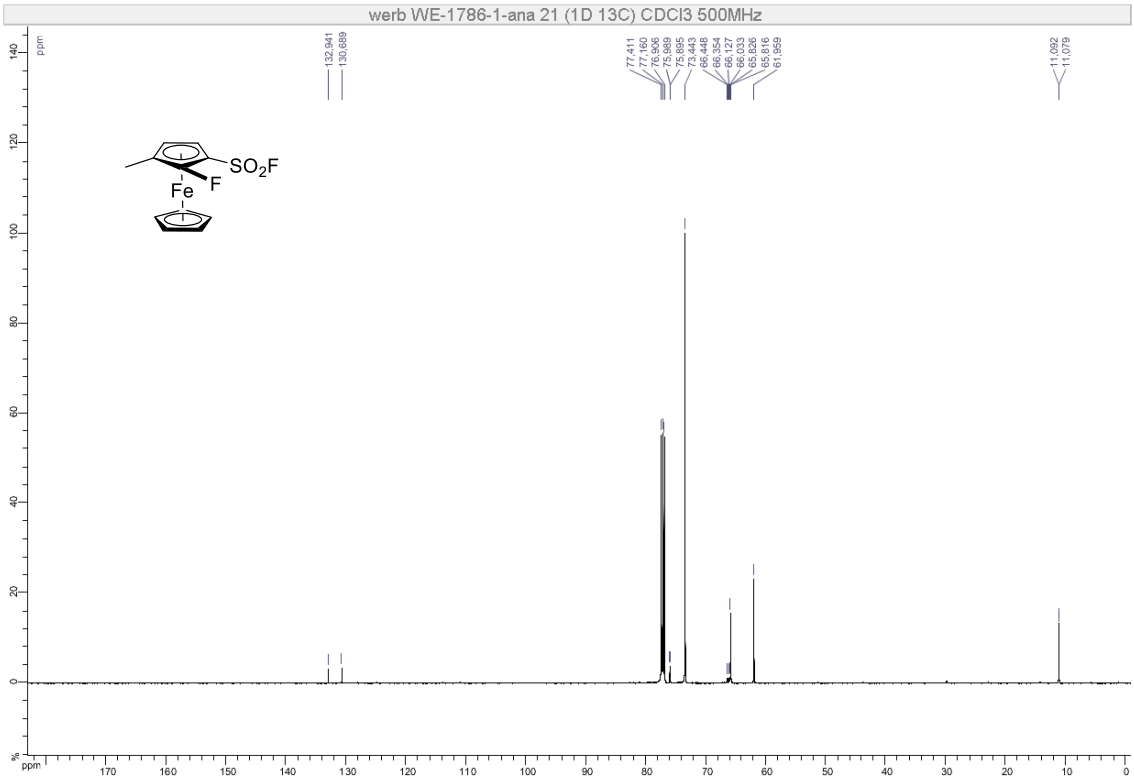


2-Fluoro-3-methylferrocenesulfonyl fluoride (11)

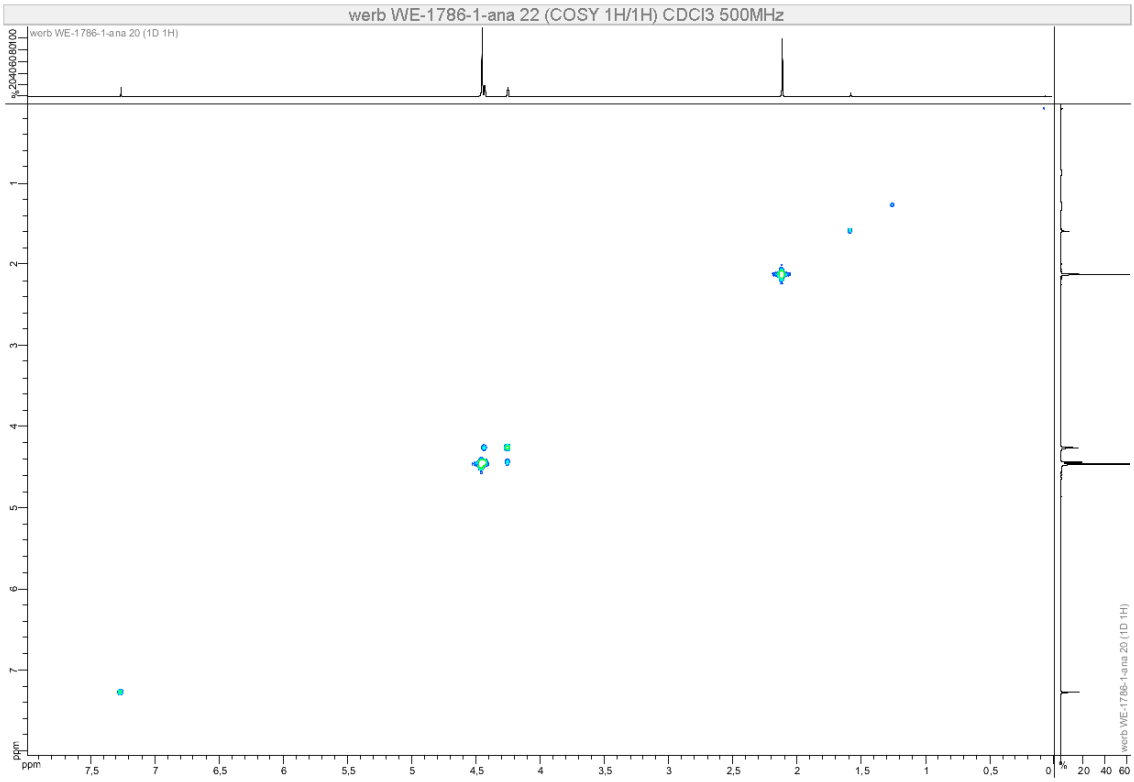
^{1}H NMR (500 MHz, $CDCl_3$)



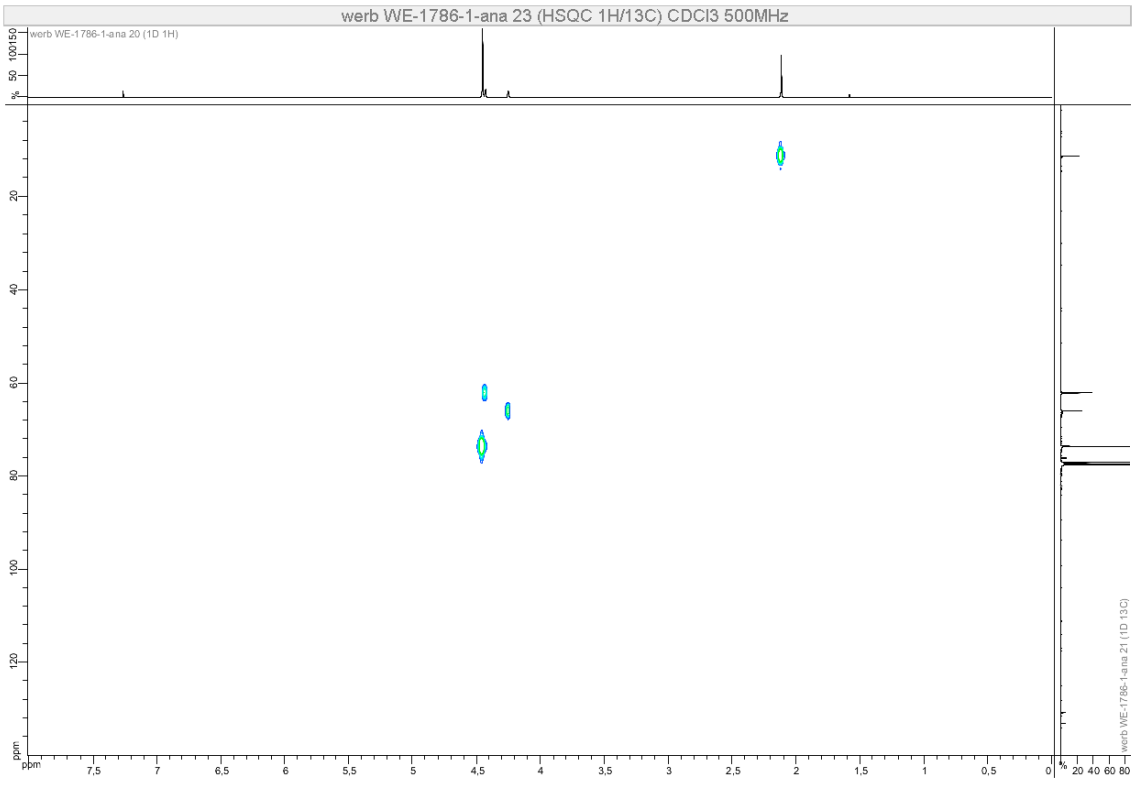
^{13}C NMR (125 MHz, $CDCl_3$)



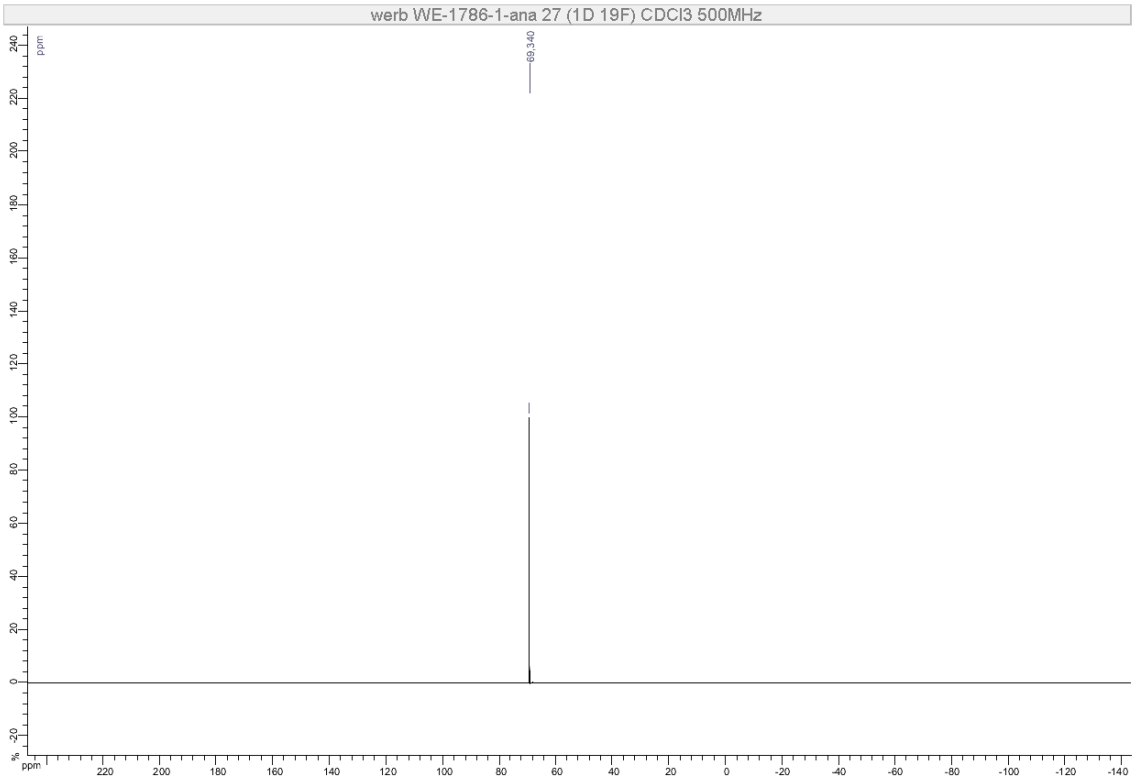
COSY (500 MHz, $CDCl_3$)



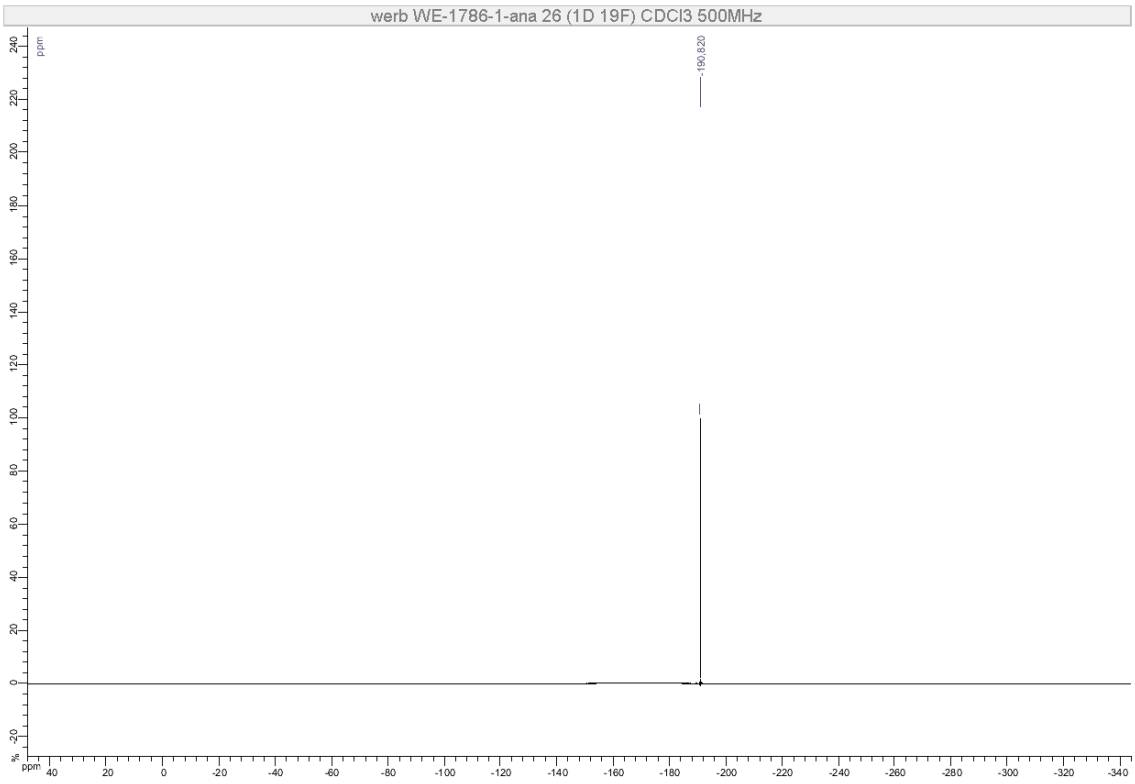
HSQC (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$) – 240 to -140 ppm area

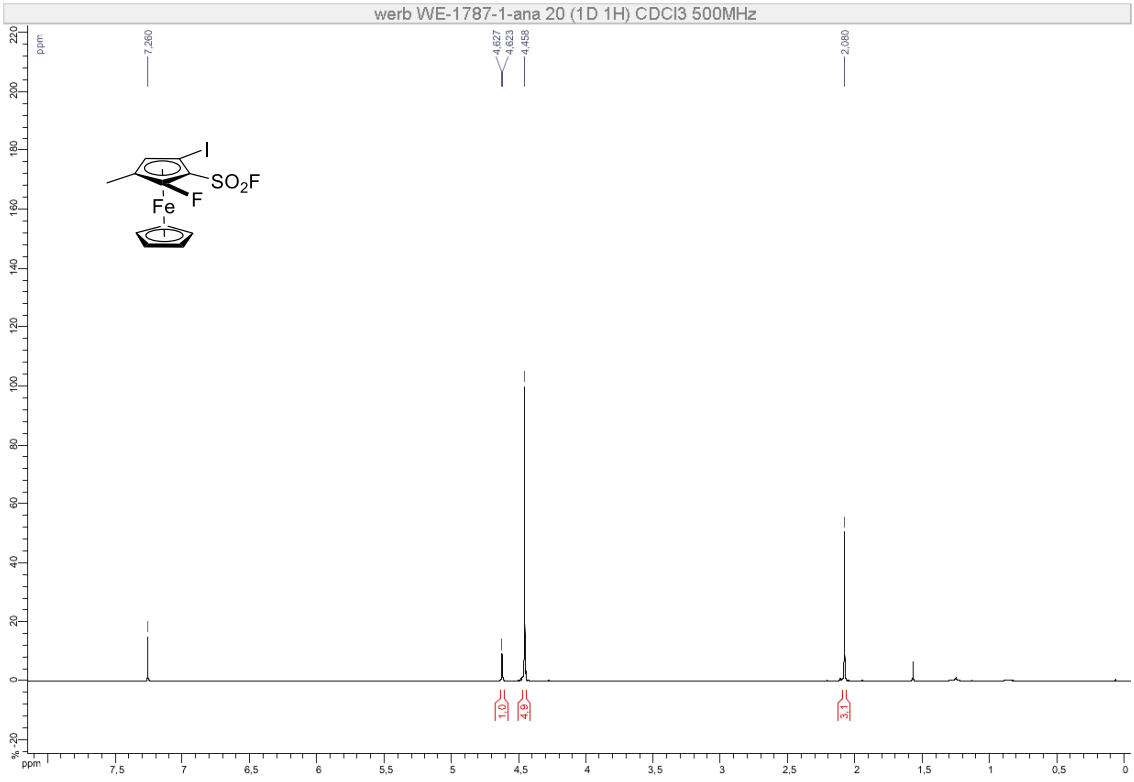


^{19}F NMR (470 MHz, $CDCl_3$) – 40 to -340 ppm area

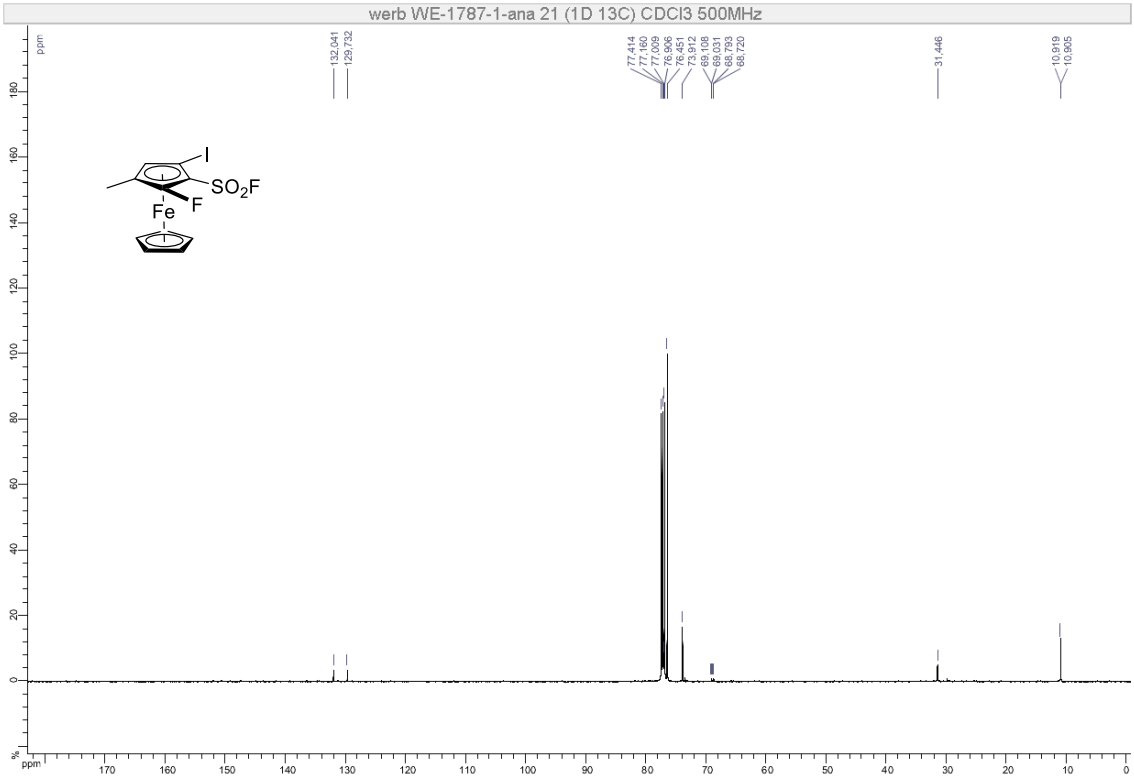


2-Fluoro-5-iodo-3-methylferrocenesulfonyl fluoride (12)

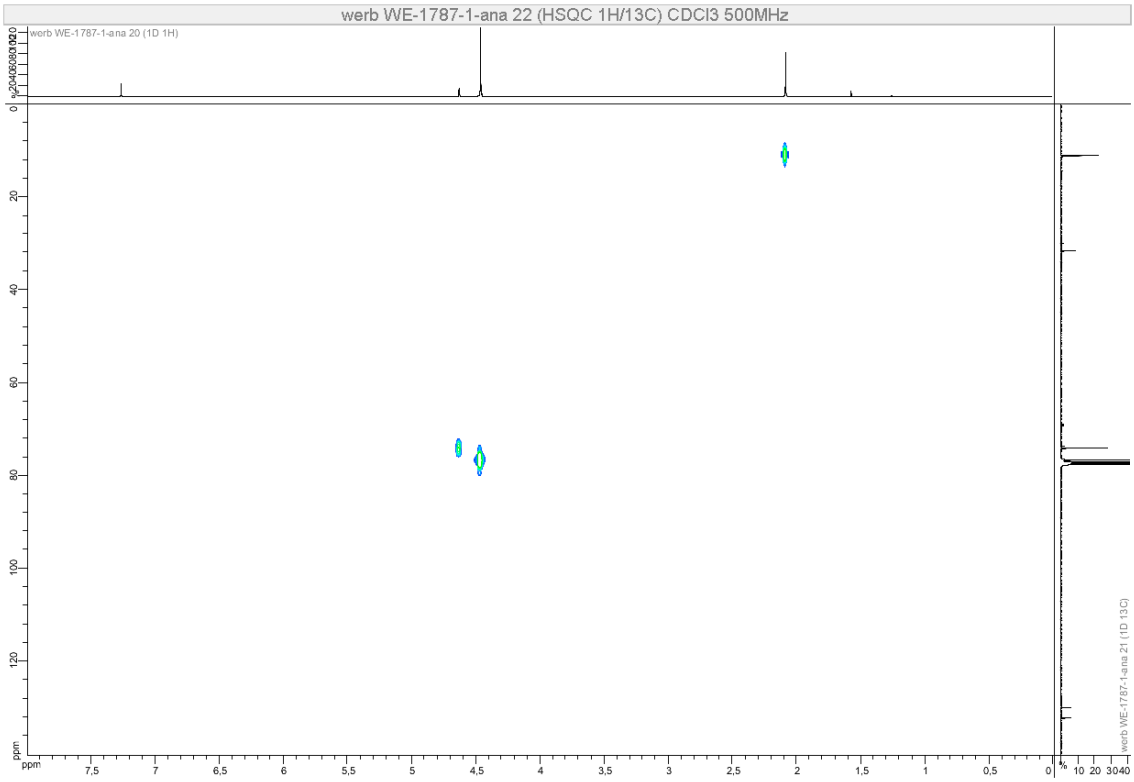
^{1}H NMR (500 MHz, $CDCl_3$)



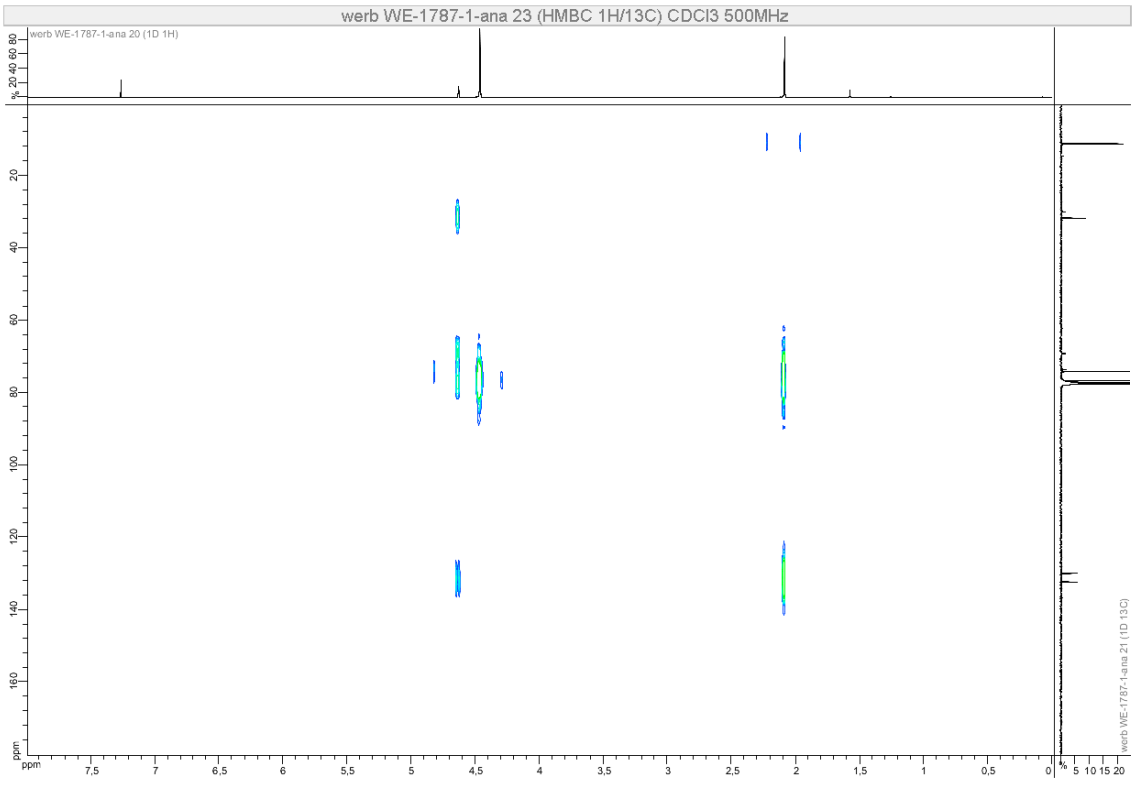
^{13}C NMR (125 MHz, $CDCl_3$)



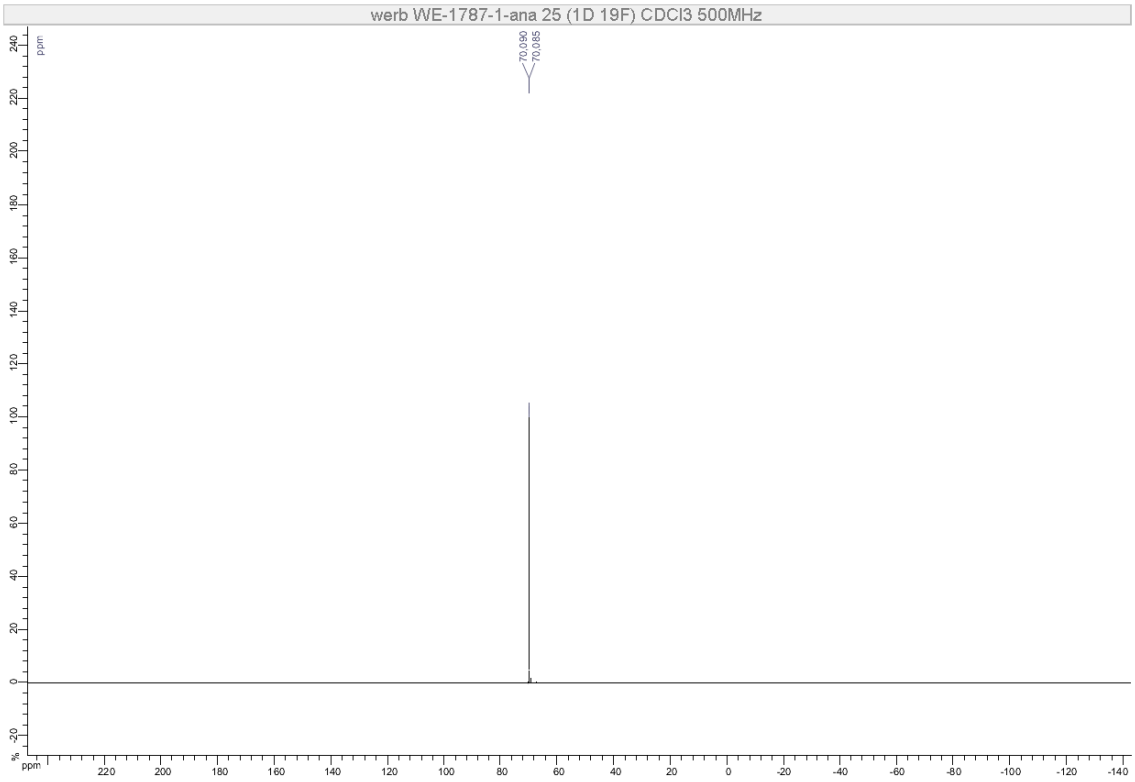
HSQC (500 MHz, $CDCl_3$)



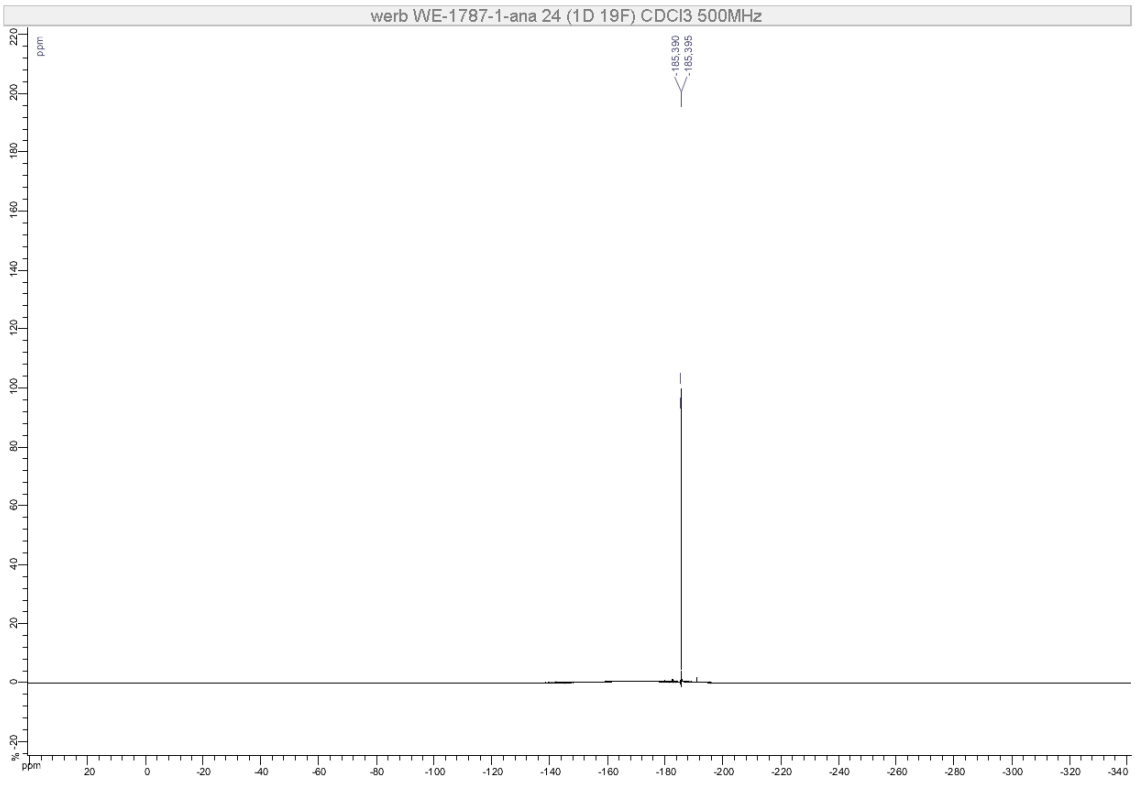
HMBC (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$) – 240 to -140 ppm area

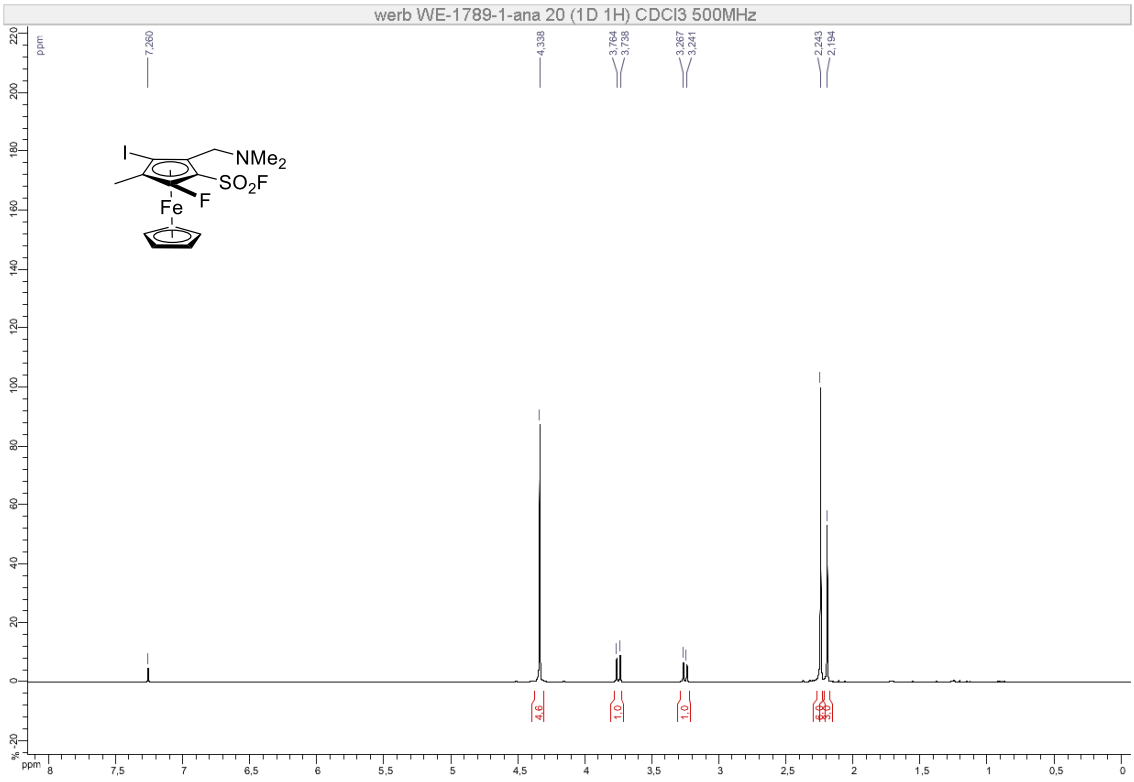


^{19}F NMR (470 MHz, $CDCl_3$) – 40 to -340 ppm area

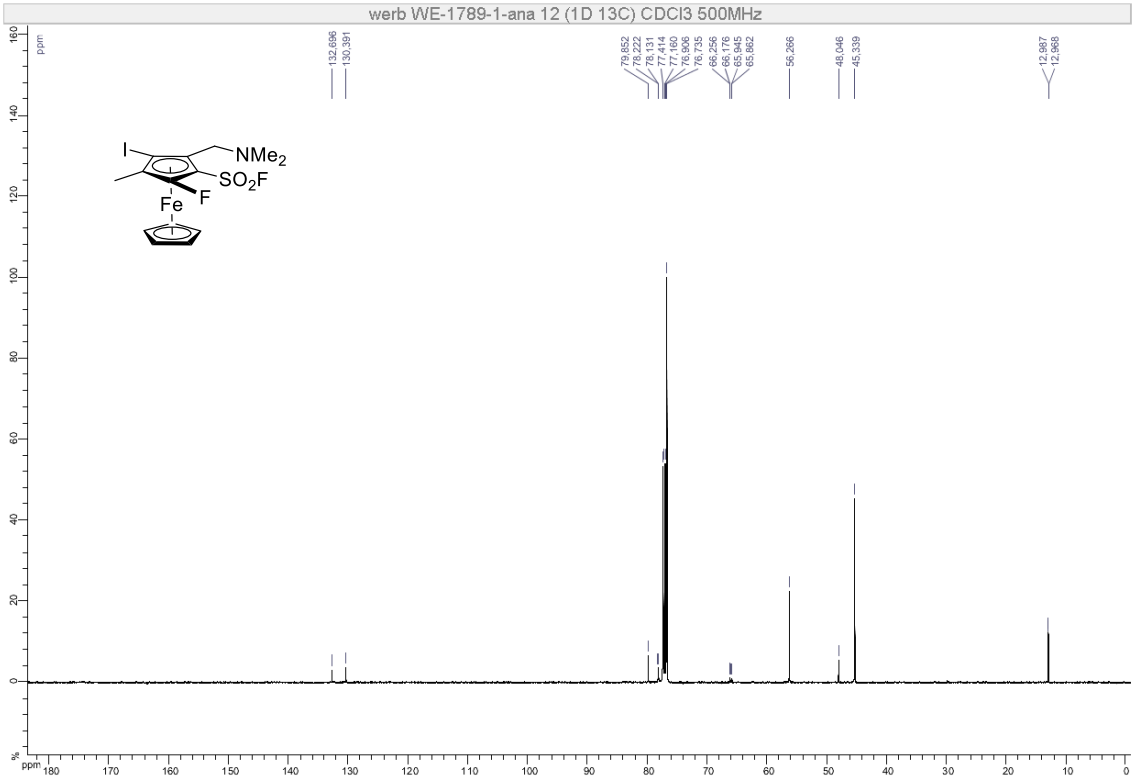


2-(*N*,*N*-Dimethylaminomethyl)-5-fluoro-3-iodo-4-methylferrocenesulfonyl fluoride (13)

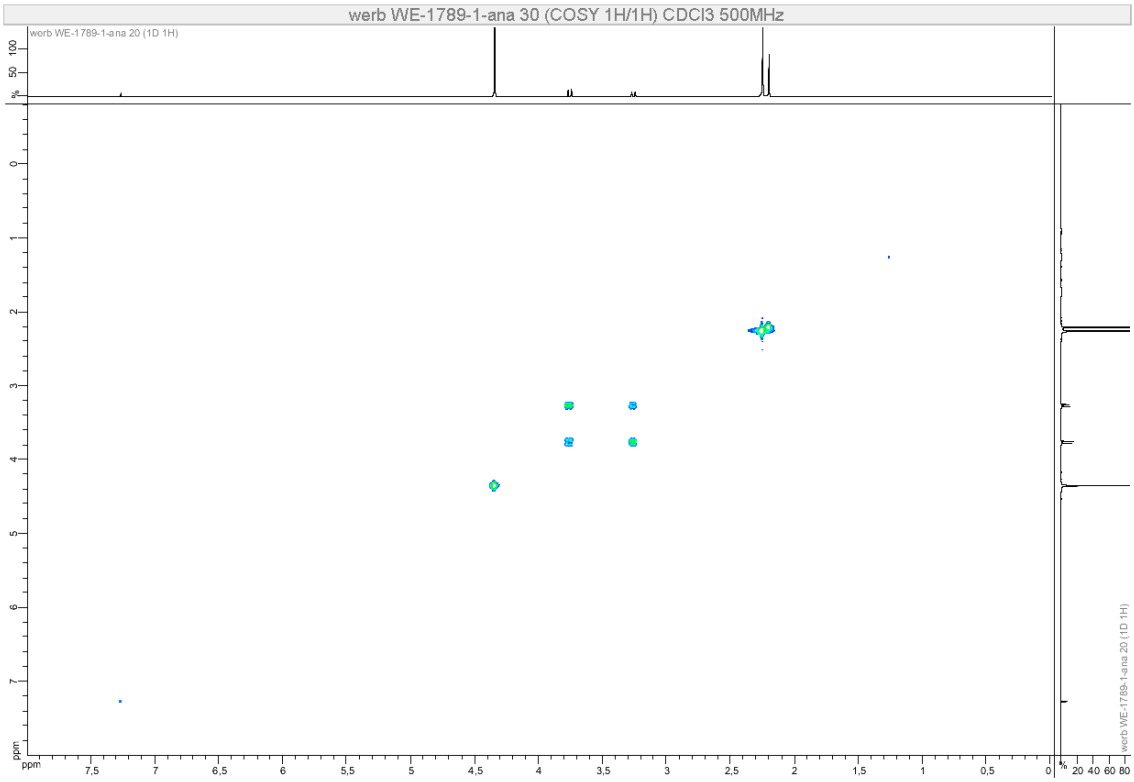
^{1}H NMR (500 MHz, $CDCl_3$)



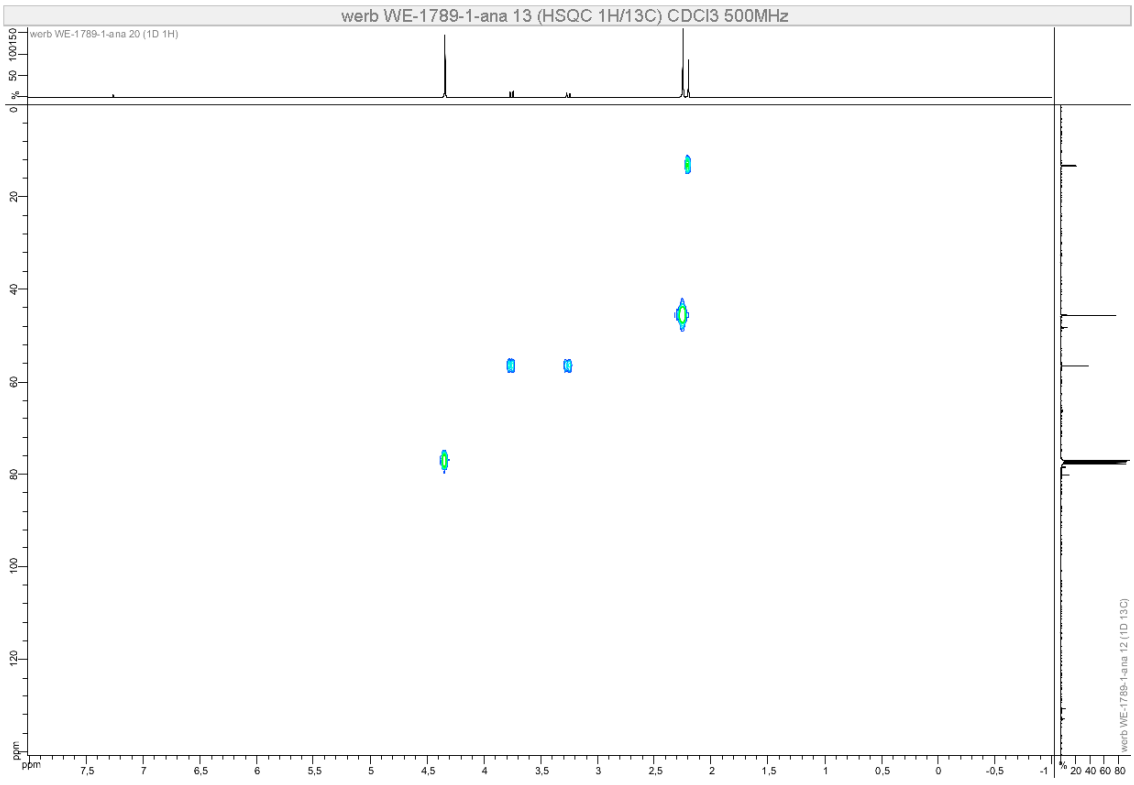
^{13}C NMR (125 MHz, $CDCl_3$)



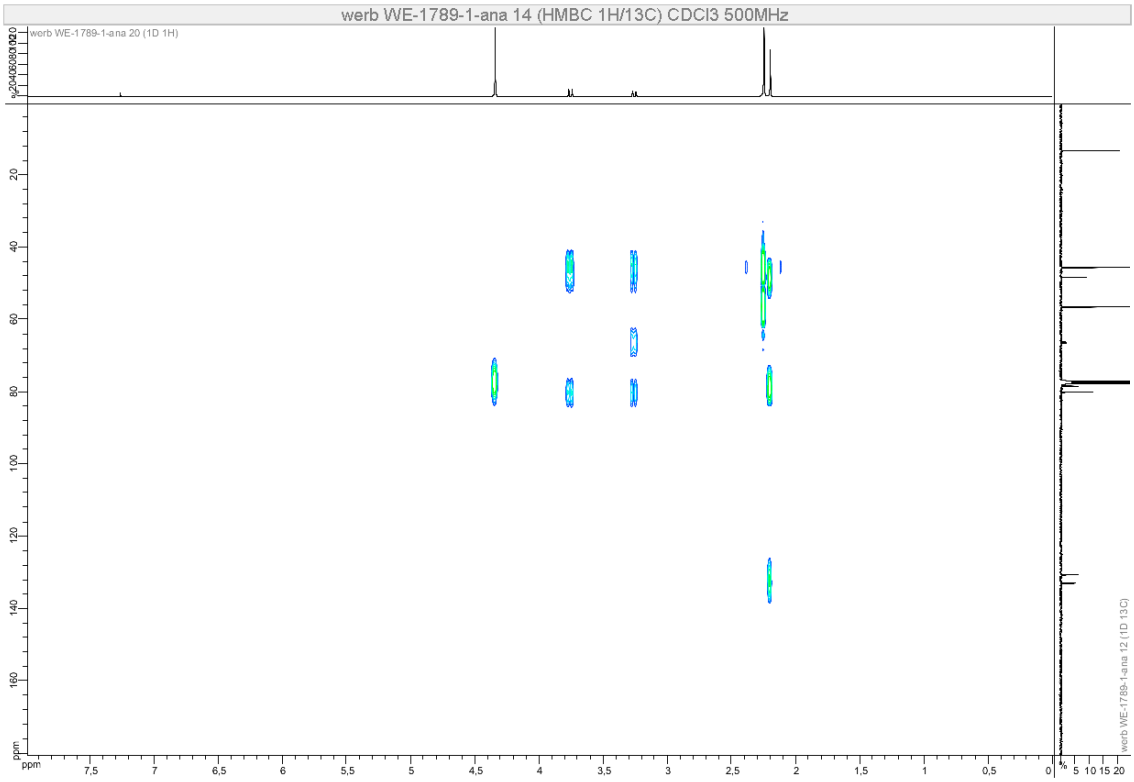
COSY (500 MHz, $CDCl_3$)



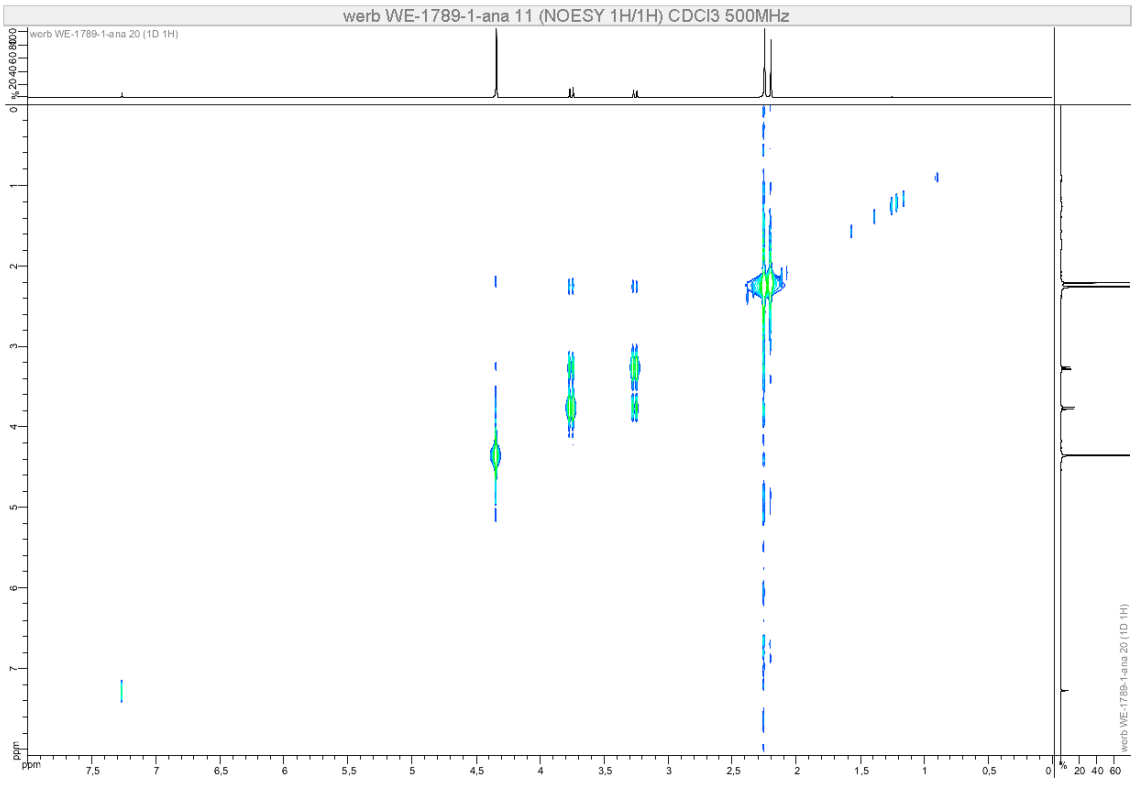
HSQC (500 MHz, $CDCl_3$)



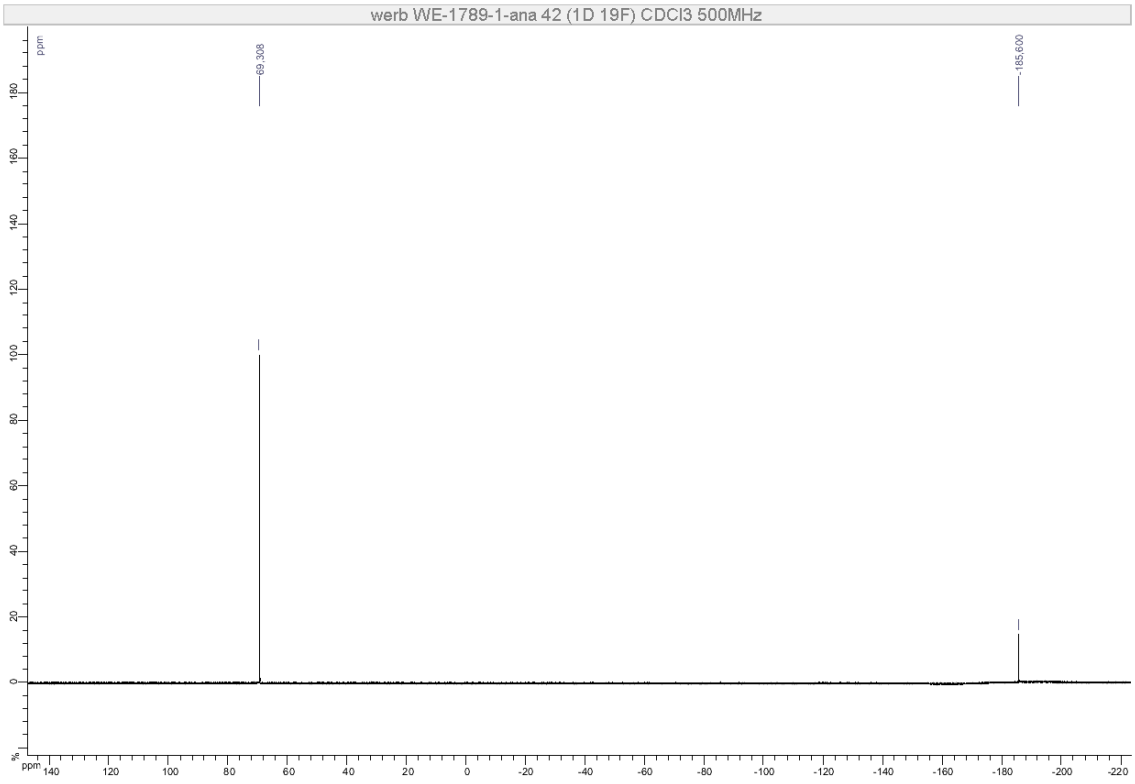
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

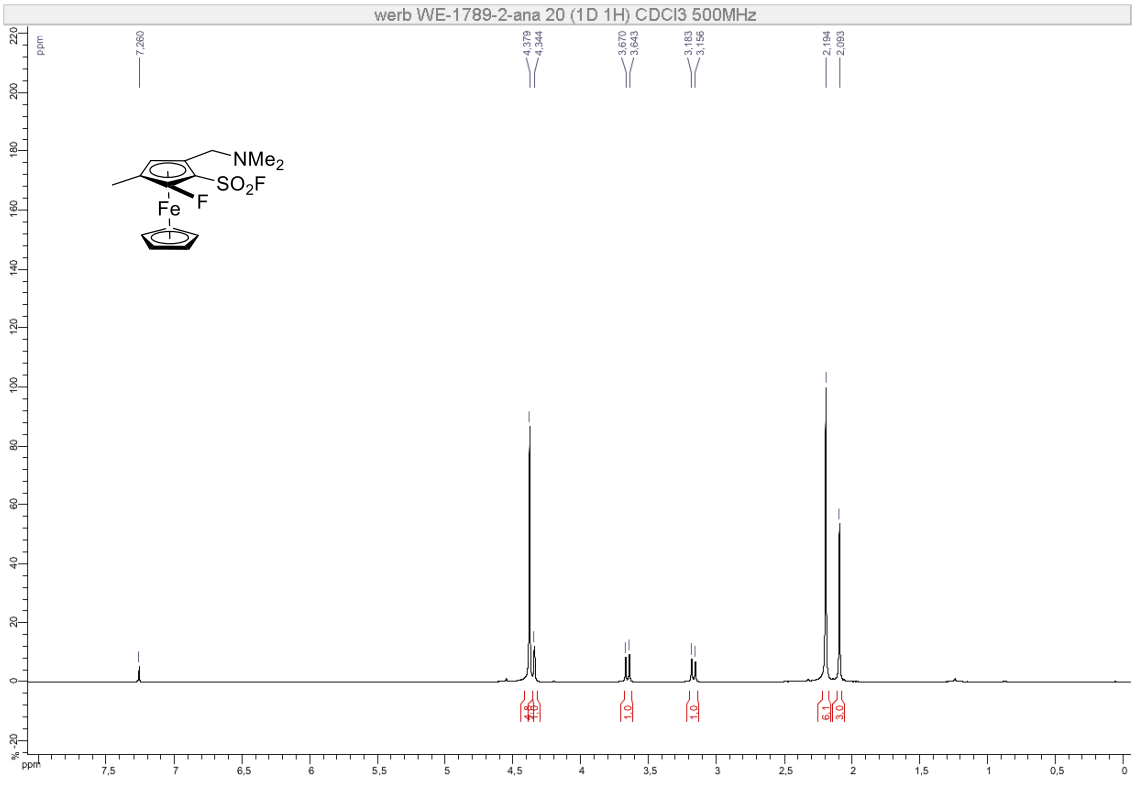


^{19}F NMR (470 MHz, $CDCl_3$)

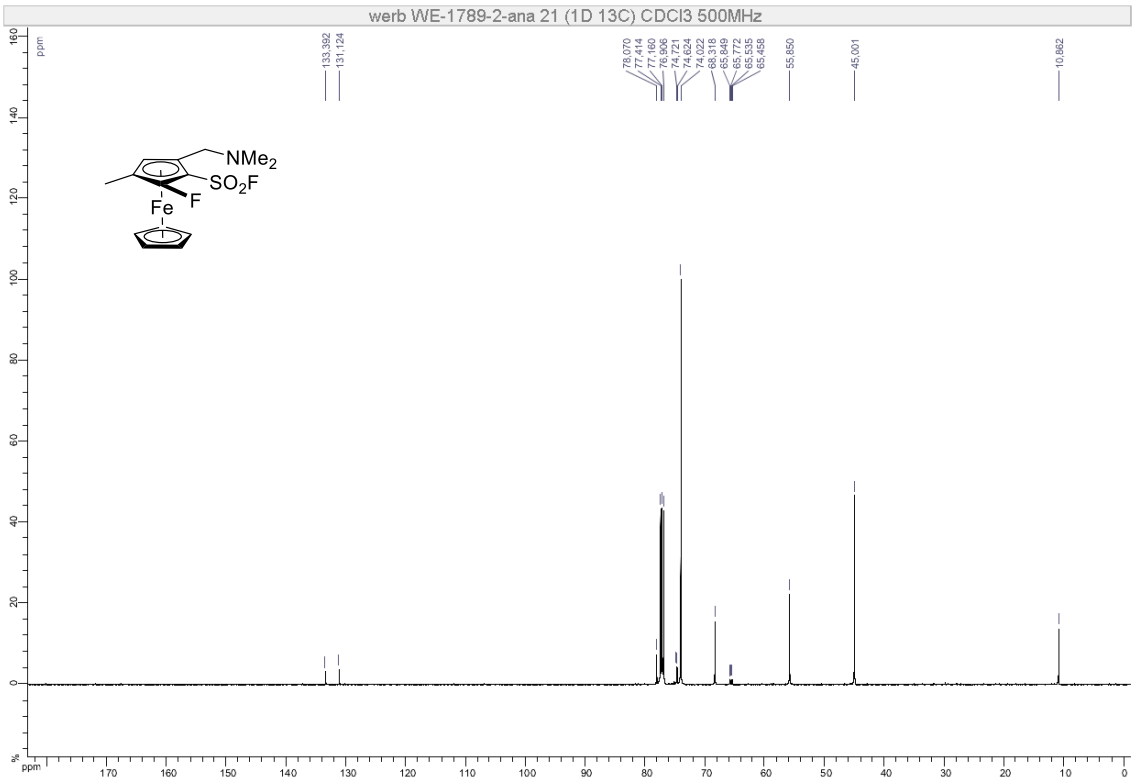


5-(*N*,*N*-Dimethylaminomethyl)-2-fluoro-3-methylferrocenesulfonyl fluoride (14)

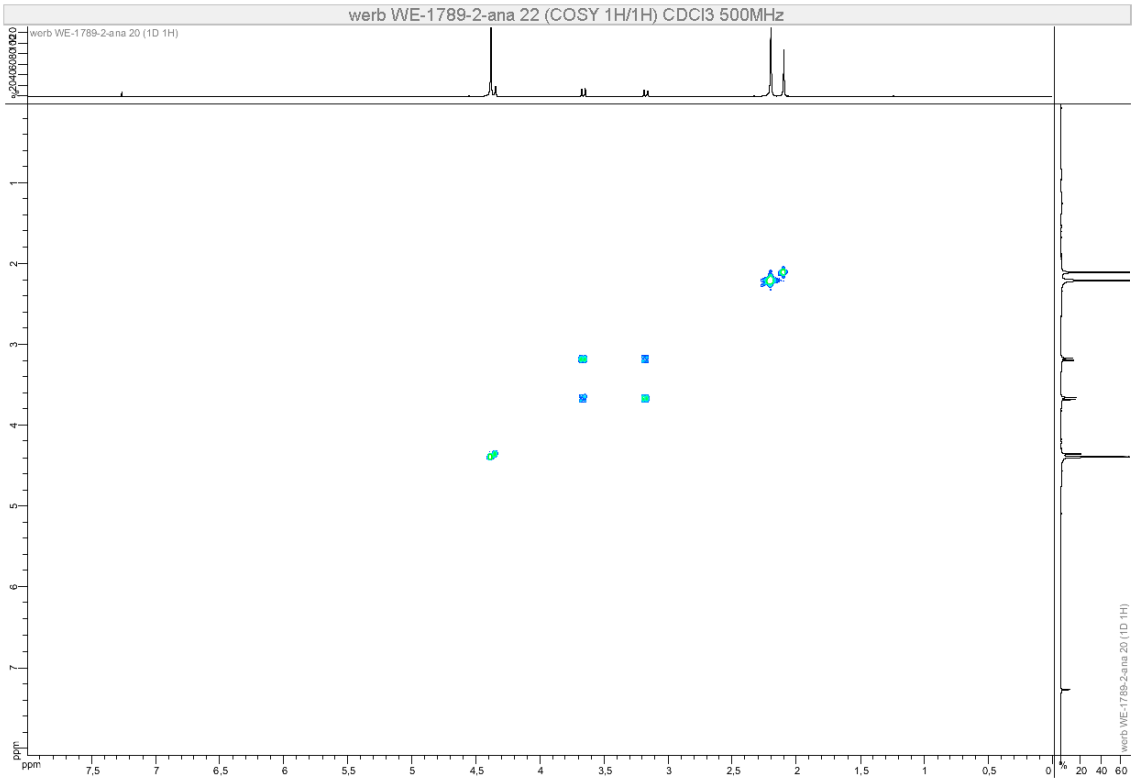
^{1}H NMR (500 MHz, $CDCl_3$)



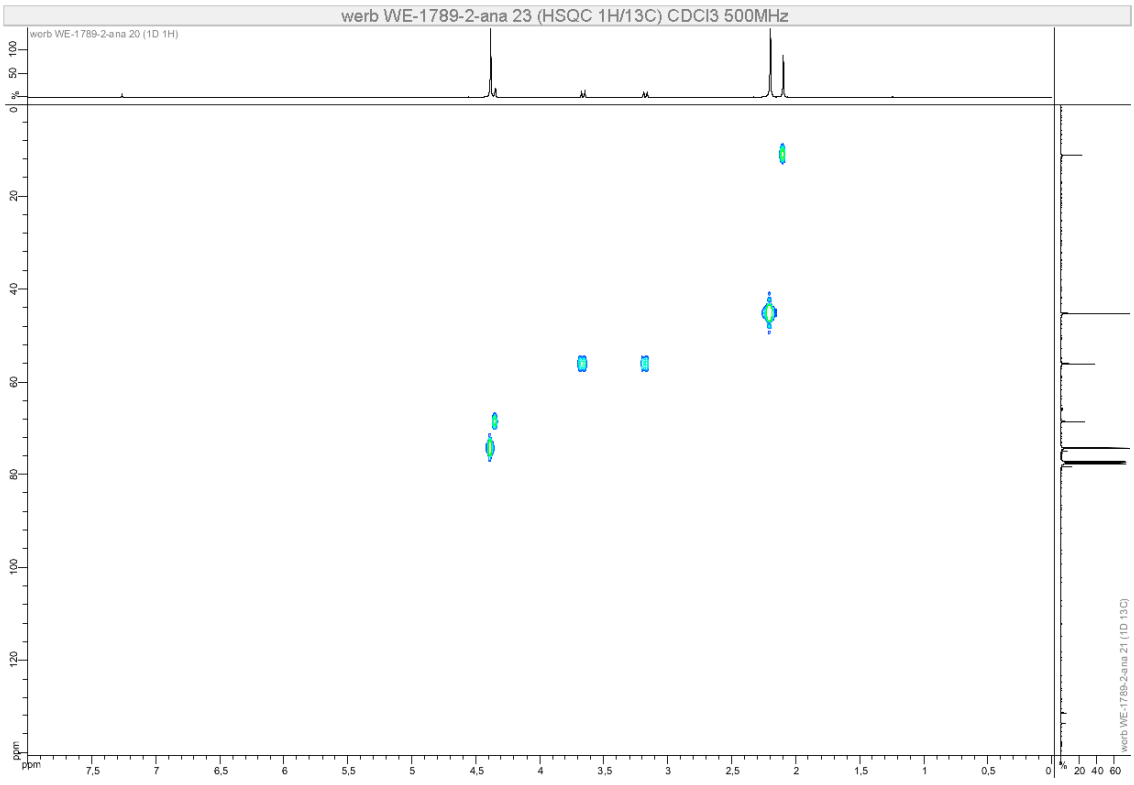
^{13}C NMR (125 MHz, $CDCl_3$)



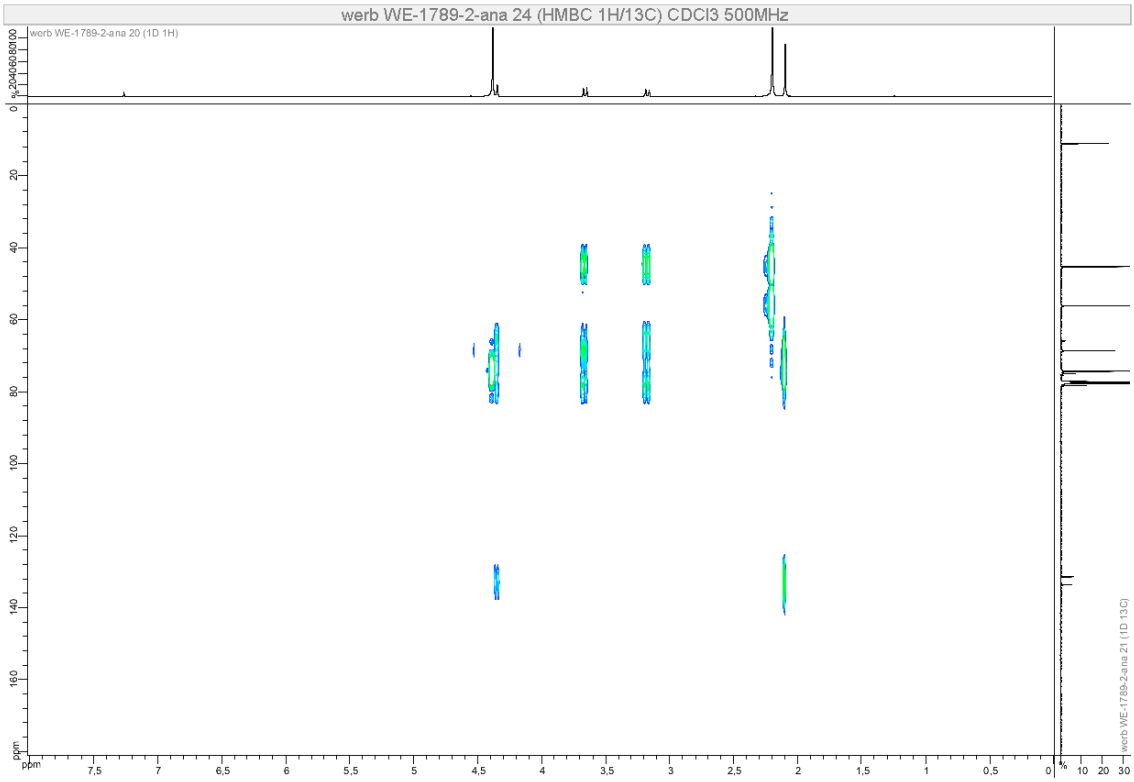
COSY (500 MHz, $CDCl_3$)



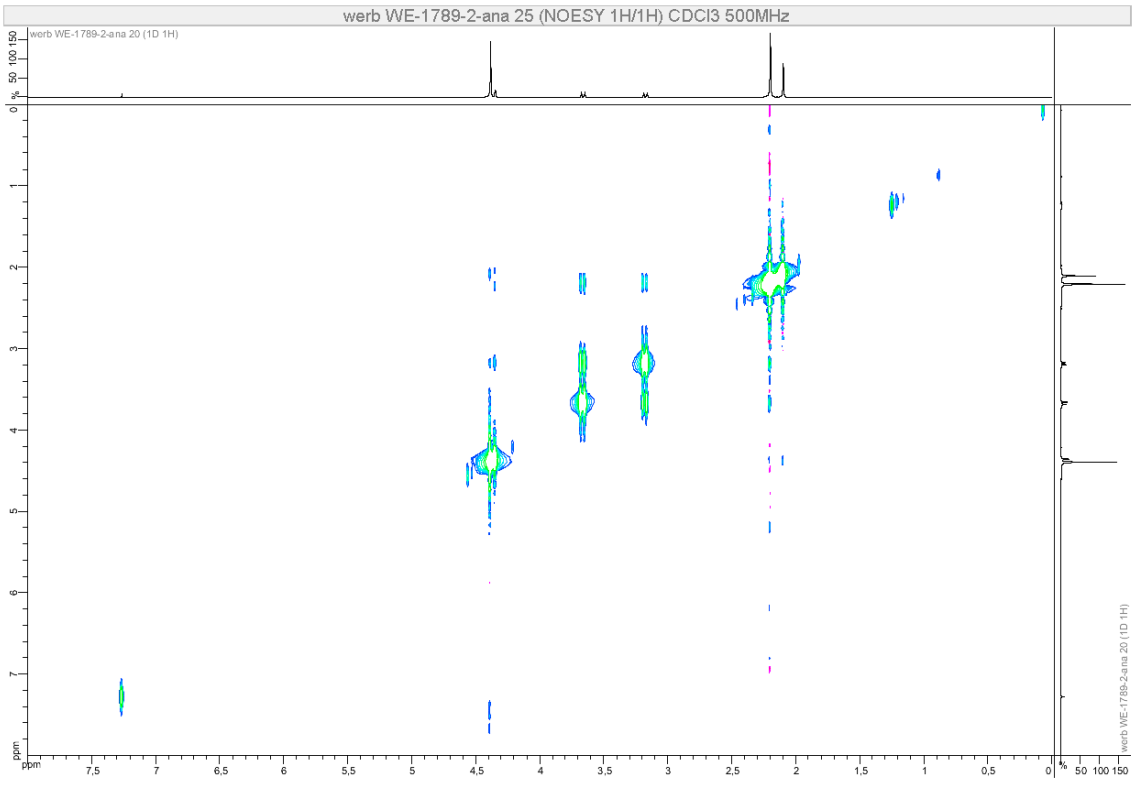
HSQC (500 MHz, $CDCl_3$)



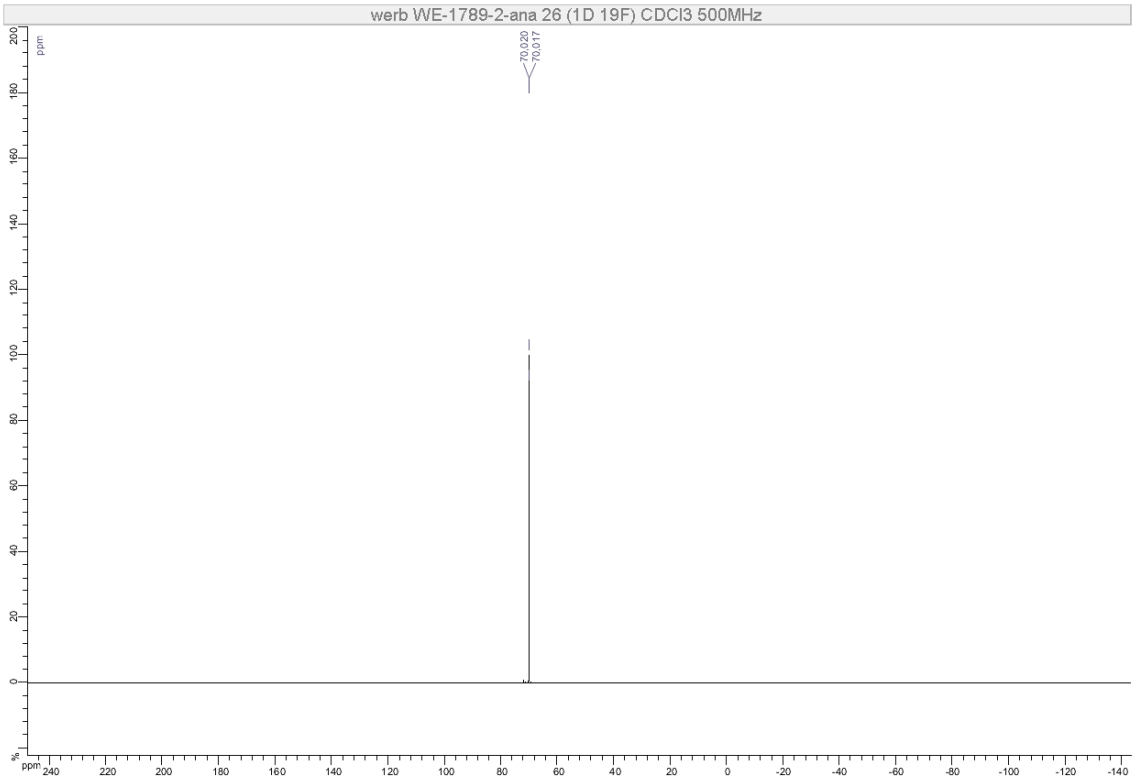
HMBC (500 MHz, $CDCl_3$)



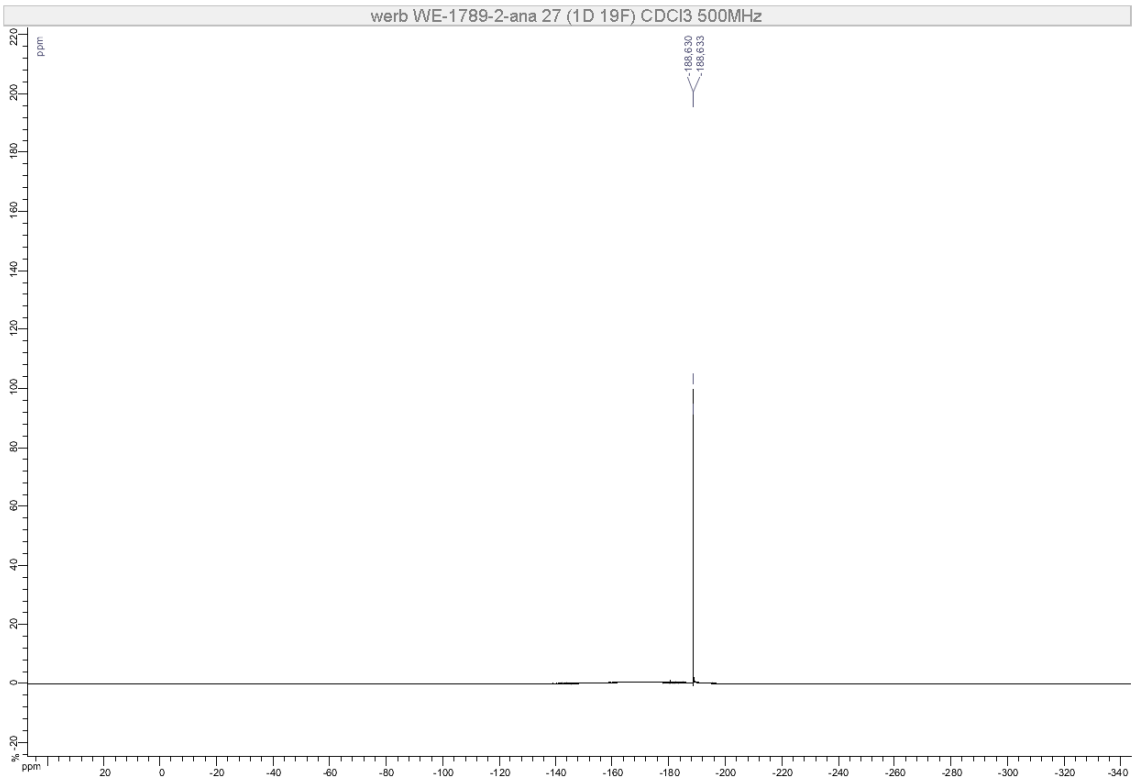
NOESY (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$) – 240 to -140 ppm area

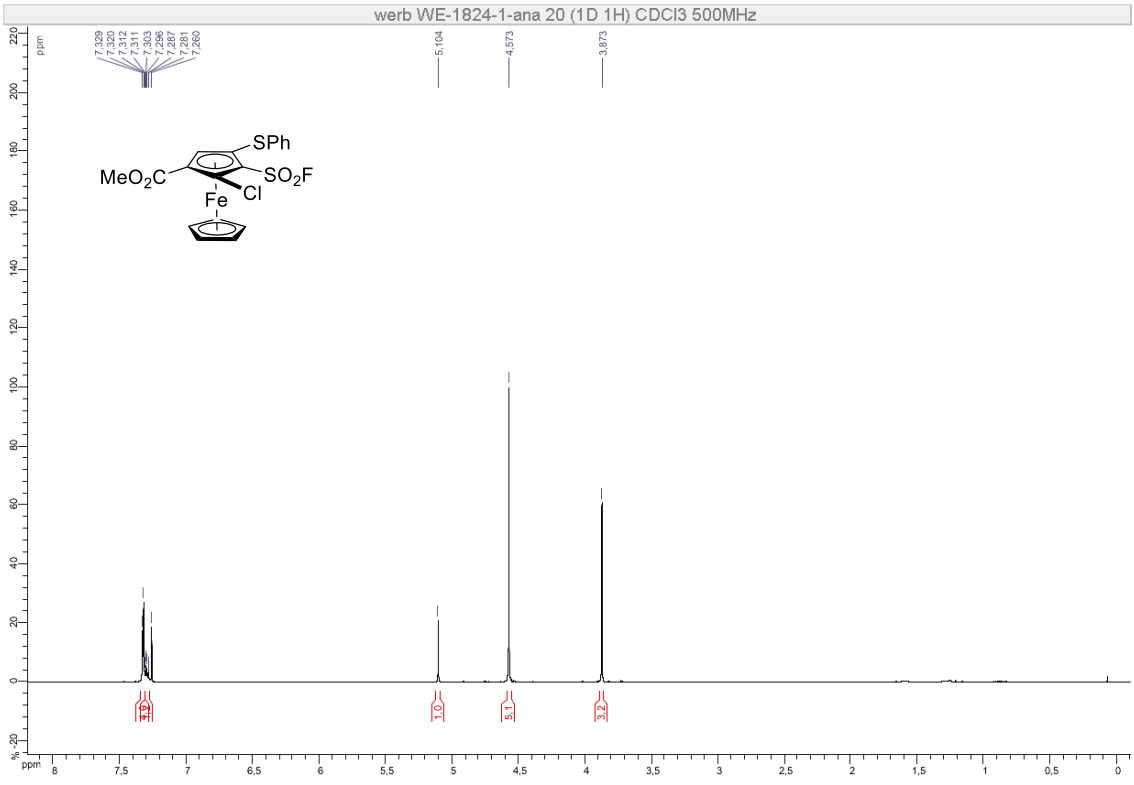


^{19}F NMR (470 MHz, $CDCl_3$) – 40 to -340 ppm area

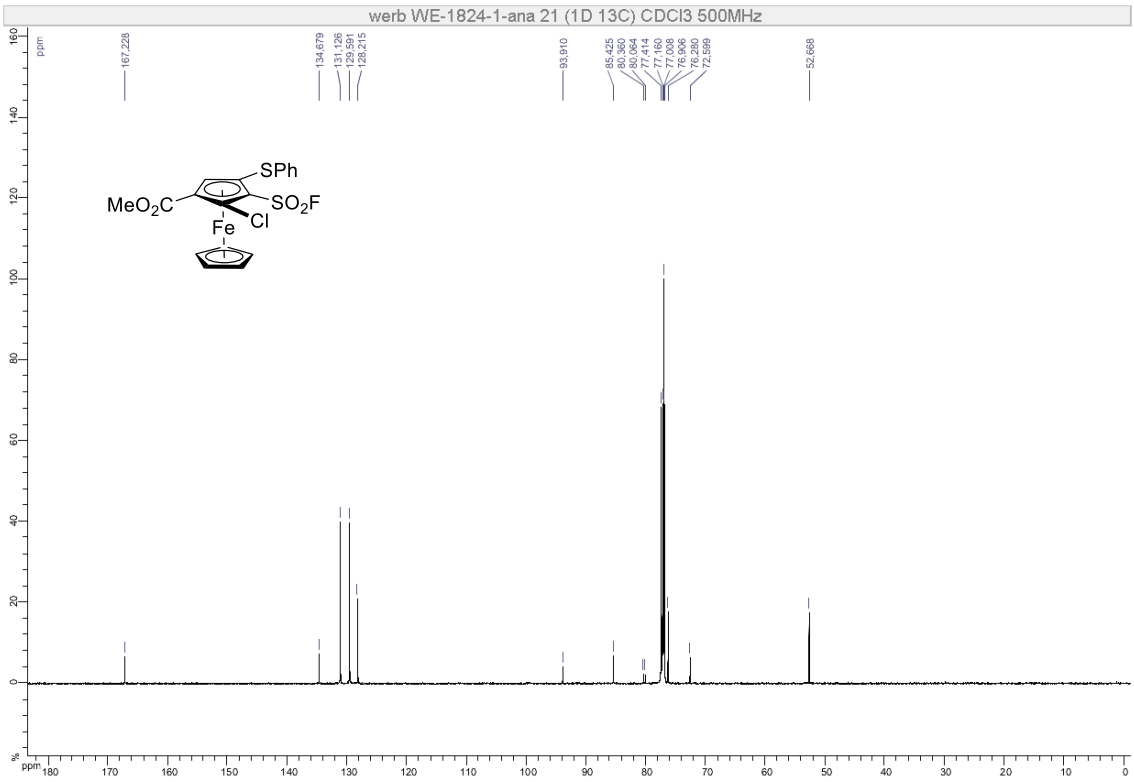


2-Chloro-3-methoxycarbonyl-5-(phenylthio)ferrocenesulfonyl fluoride (15)

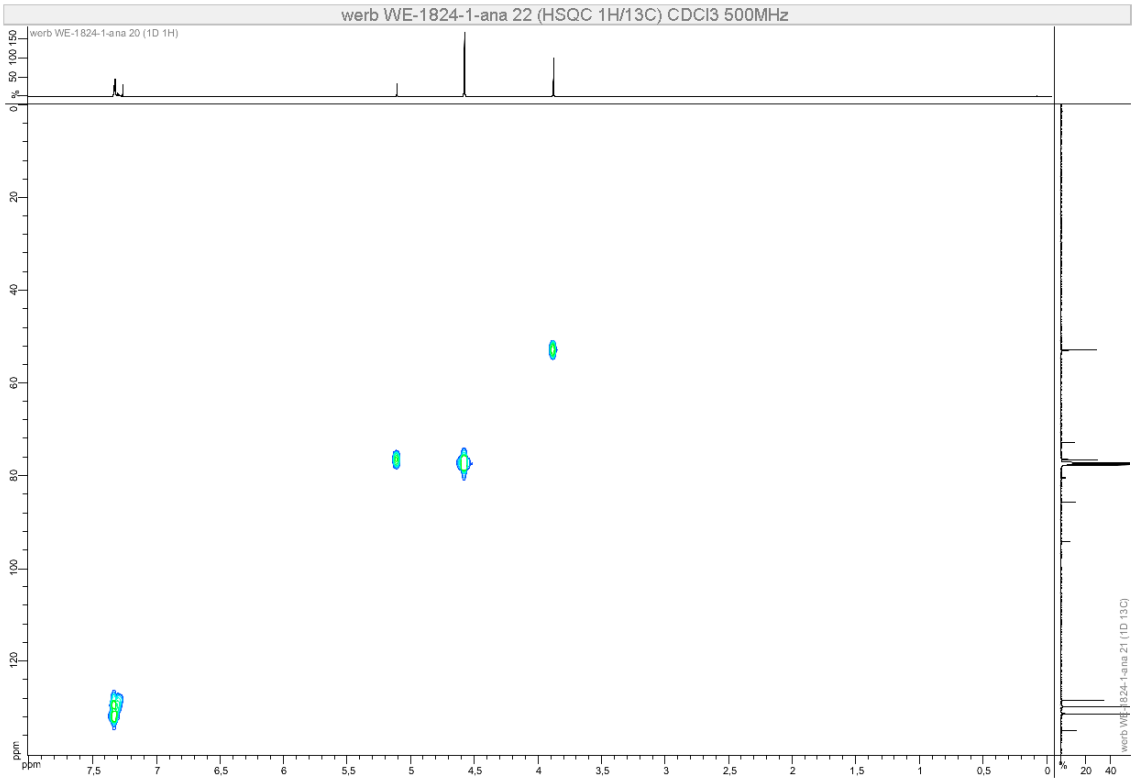
^{1}H NMR (500 MHz, $CDCl_3$)



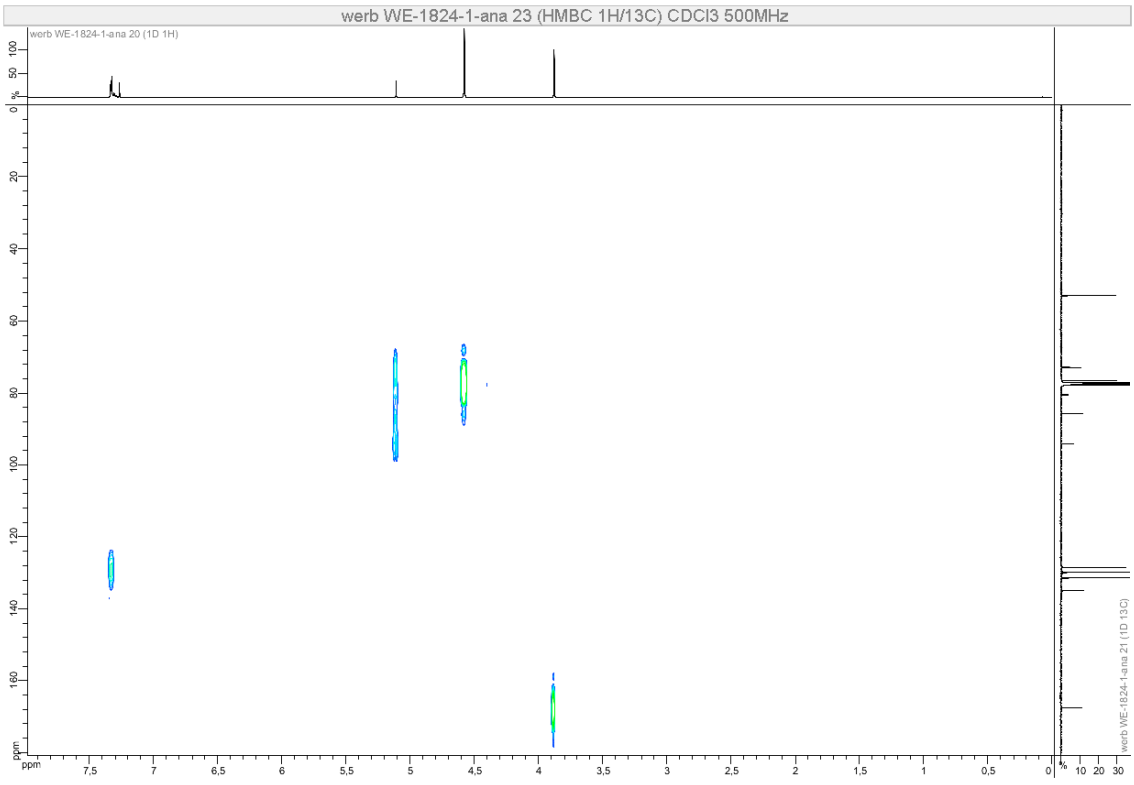
^{13}C NMR (125 MHz, $CDCl_3$)



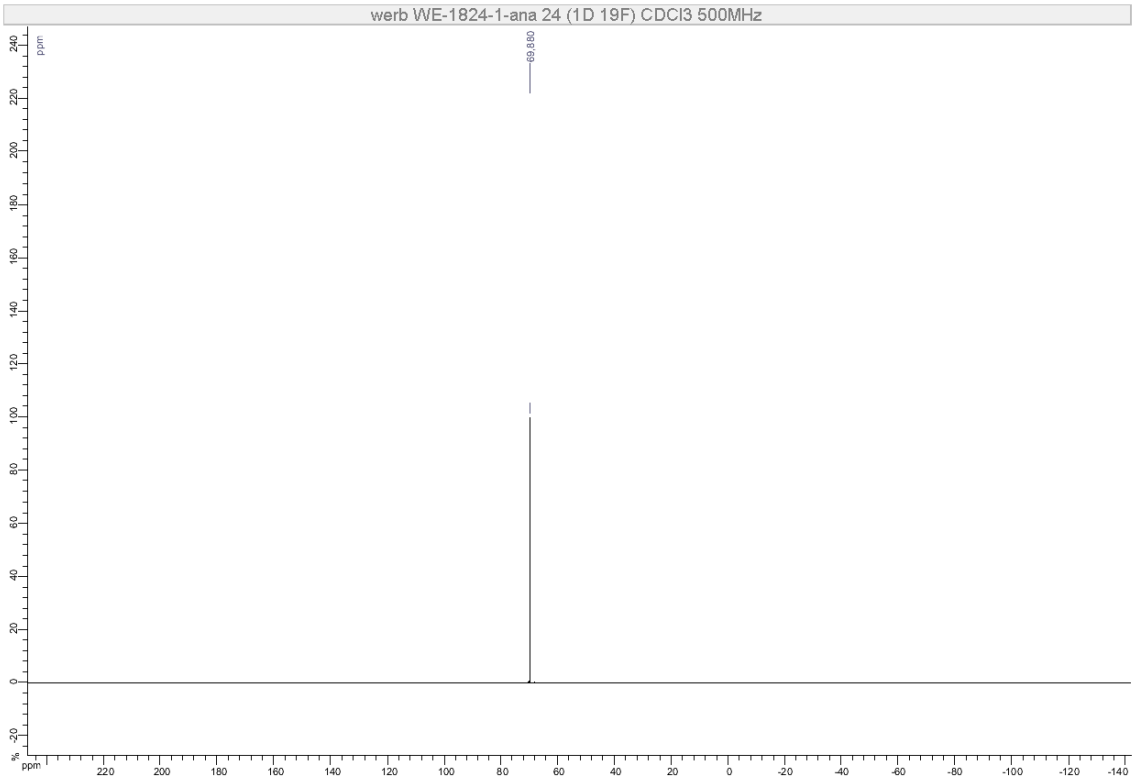
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

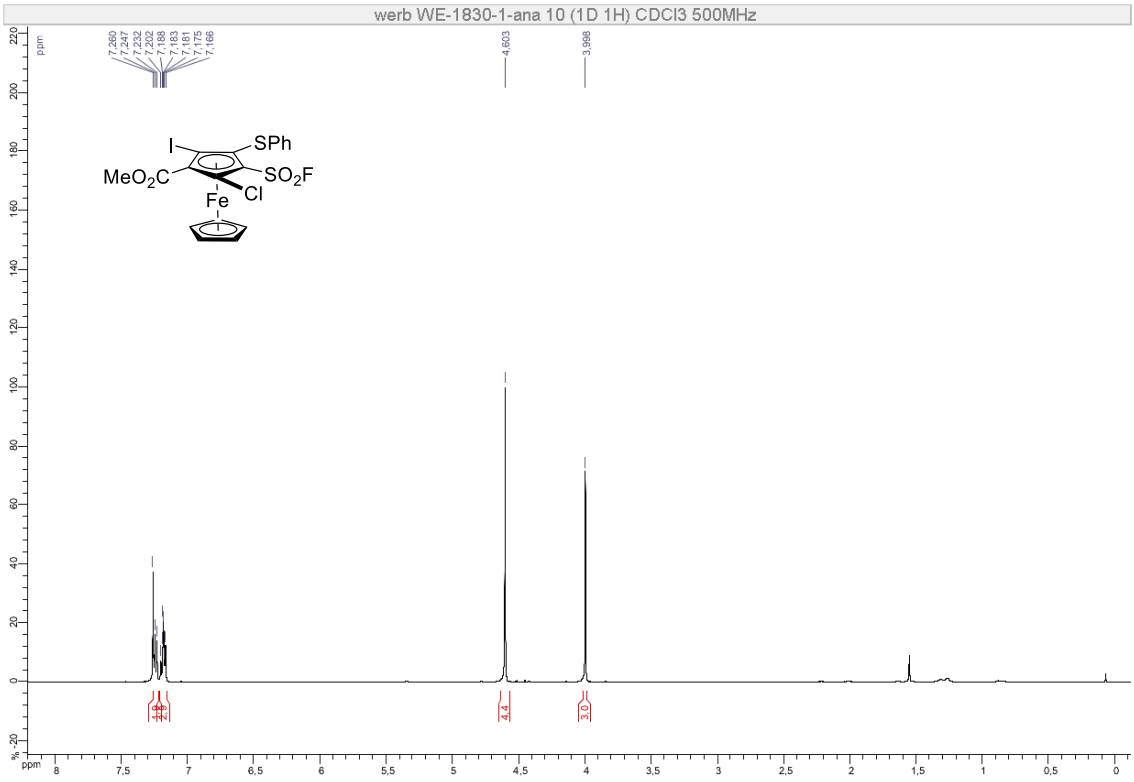


^{19}F NMR (470 MHz, $CDCl_3$)

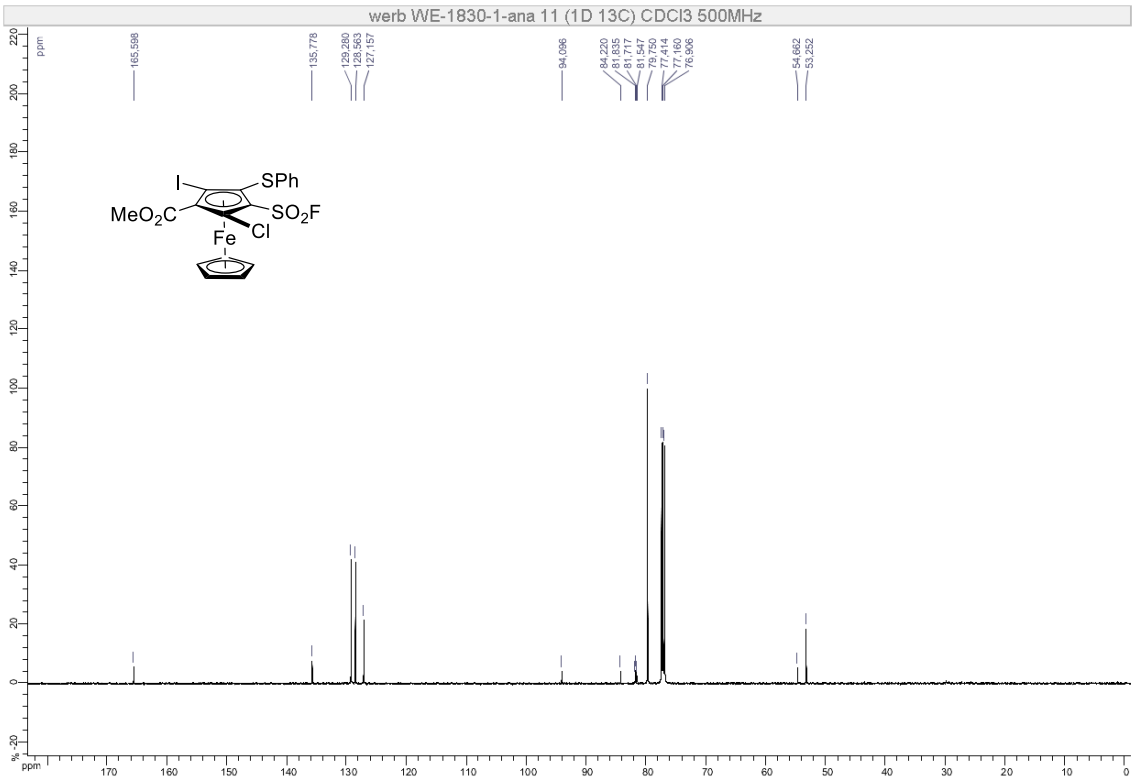


2-Chloro-4-iodo-3-methoxycarbonyl-5-(phenylthio)ferrocenesulfonyl fluoride (16)

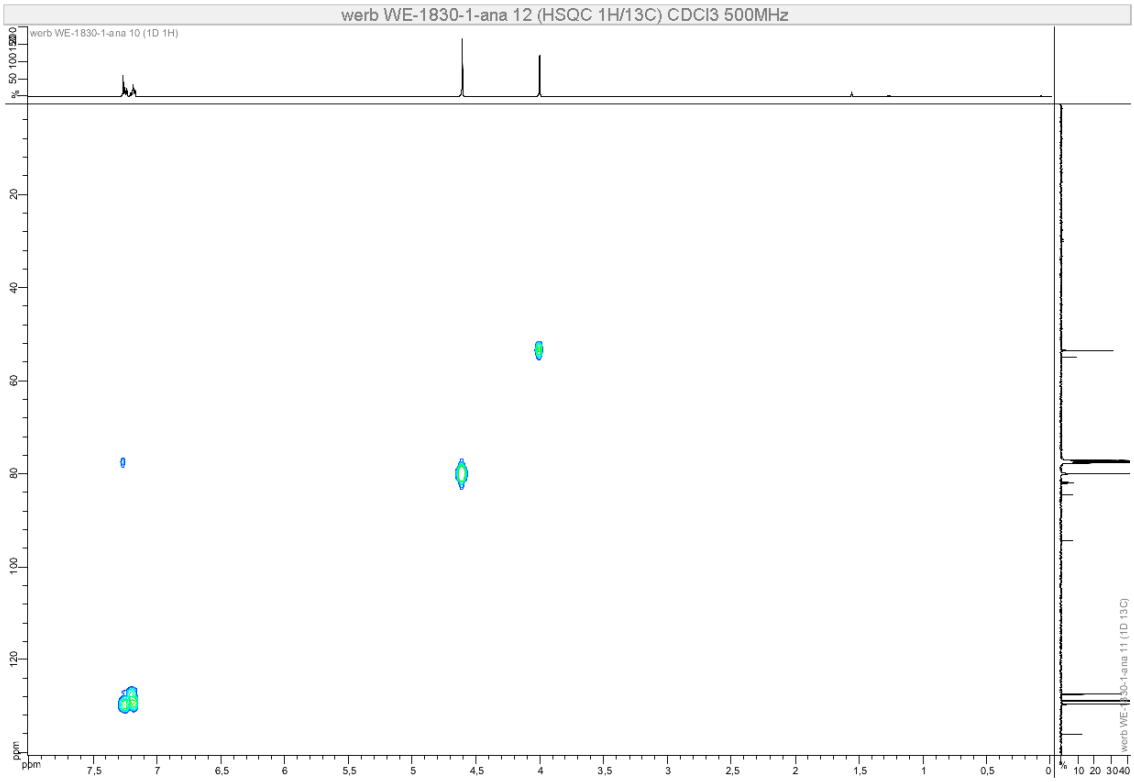
^{1}H NMR (500 MHz, $CDCl_3$)



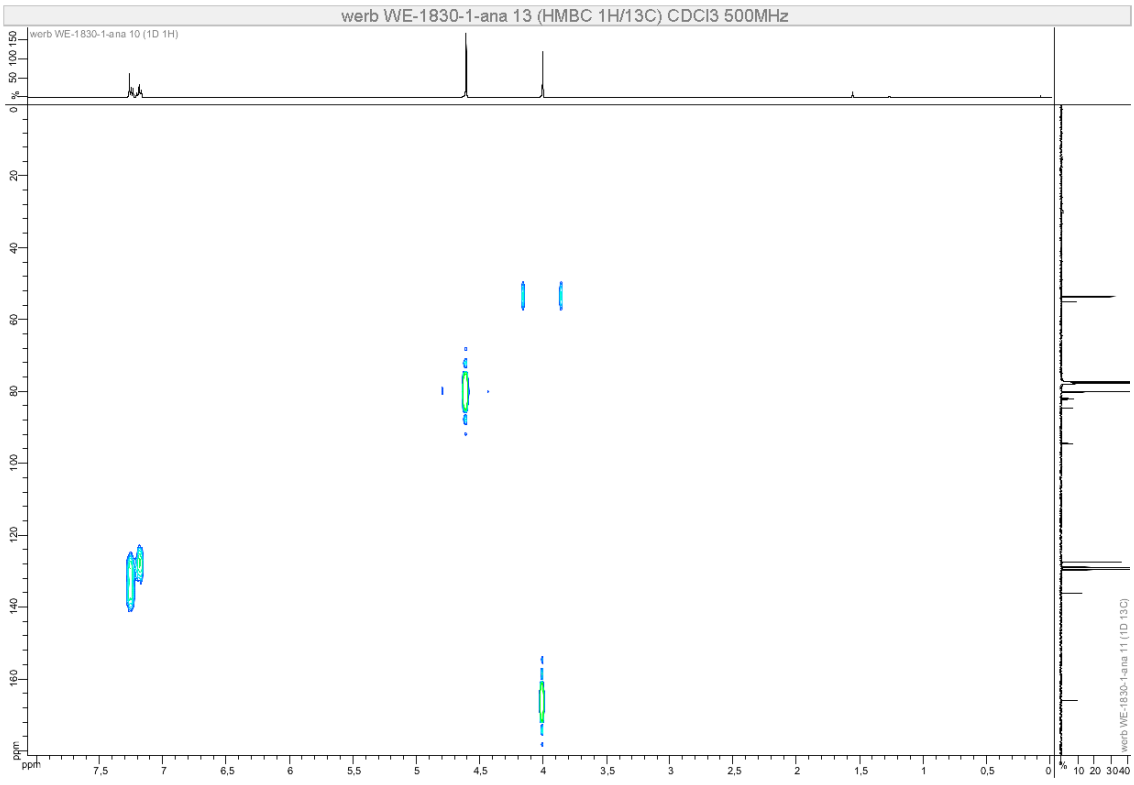
^{13}C NMR (125 MHz, $CDCl_3$)



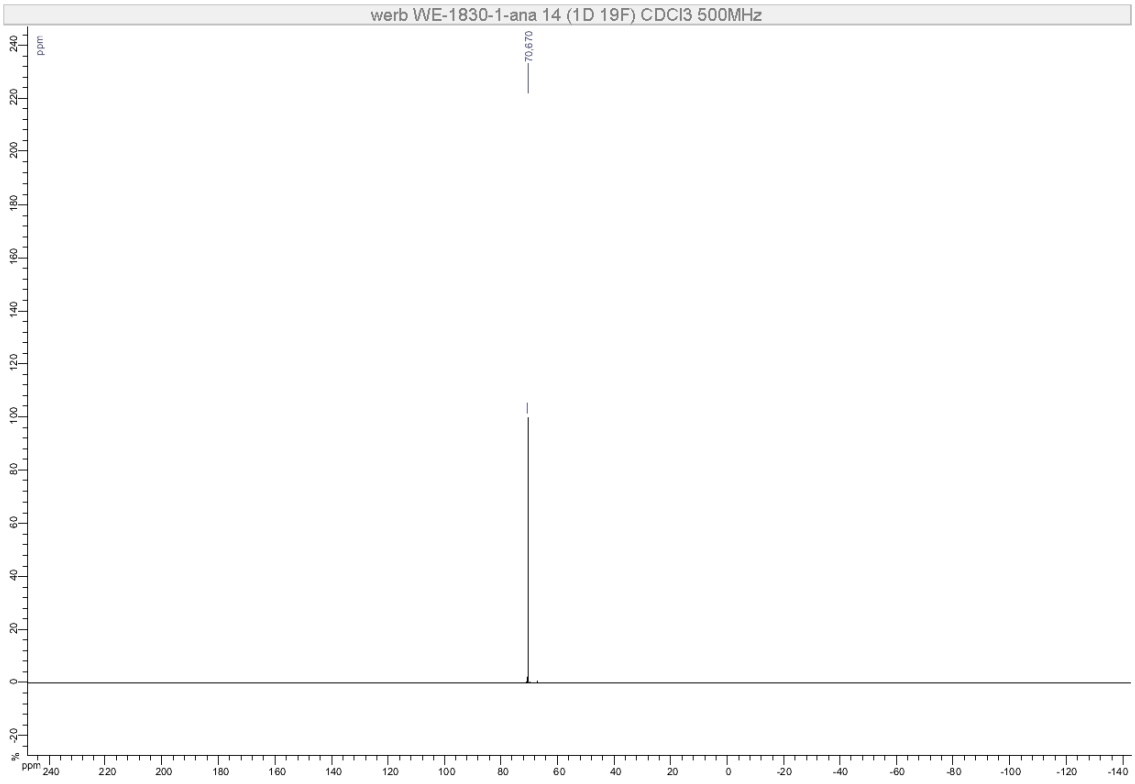
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

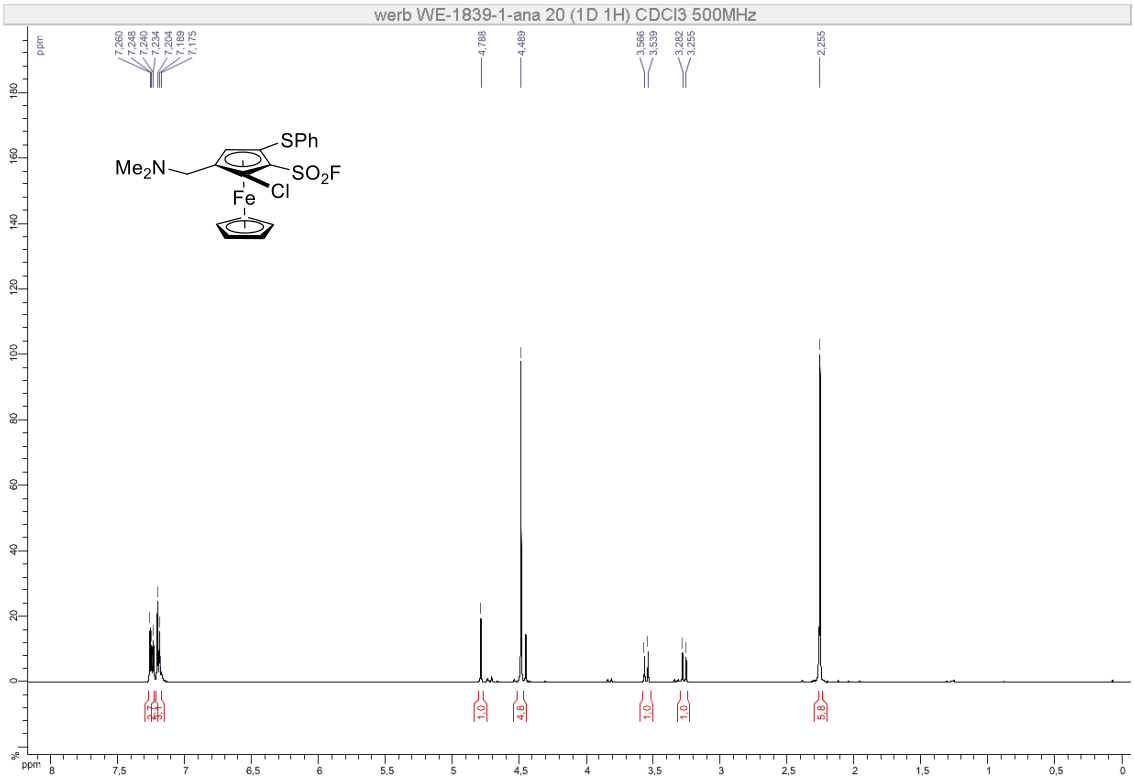


^{19}F NMR (470 MHz, $CDCl_3$)

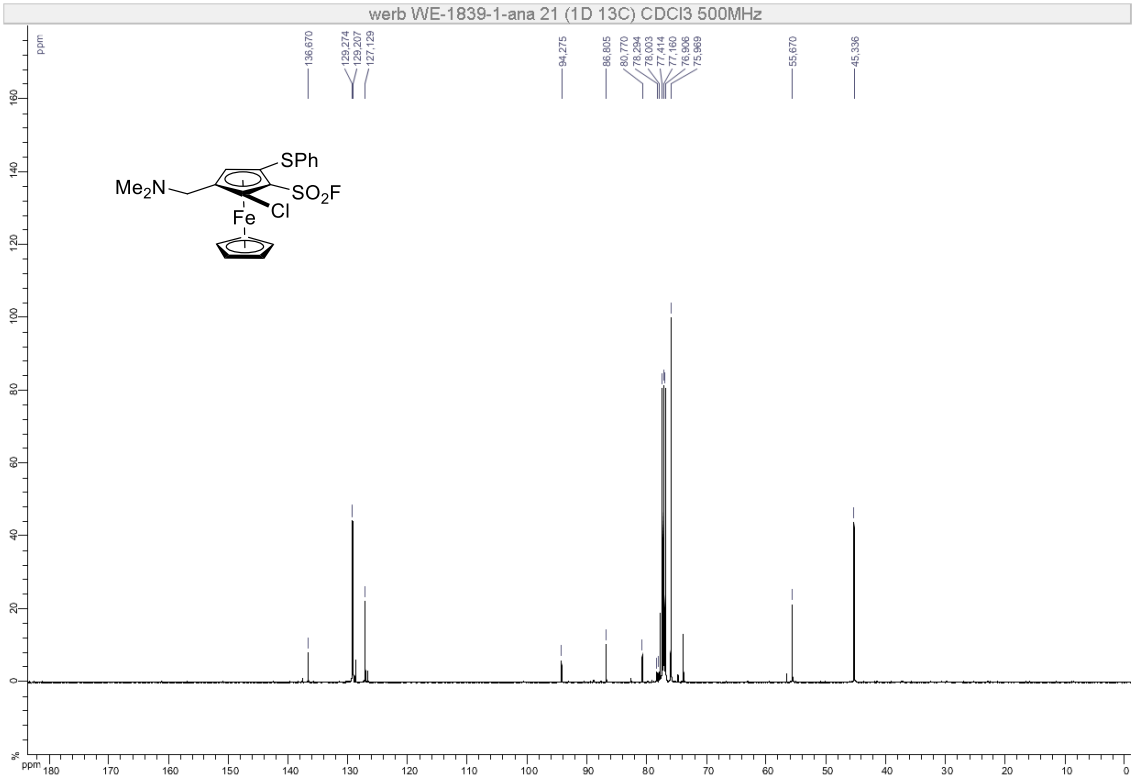


2-Chloro-3-(*N*,*N*-dimethylaminomethyl)-5-(phenylthio)ferrocenesulfonyl fluoride (17)

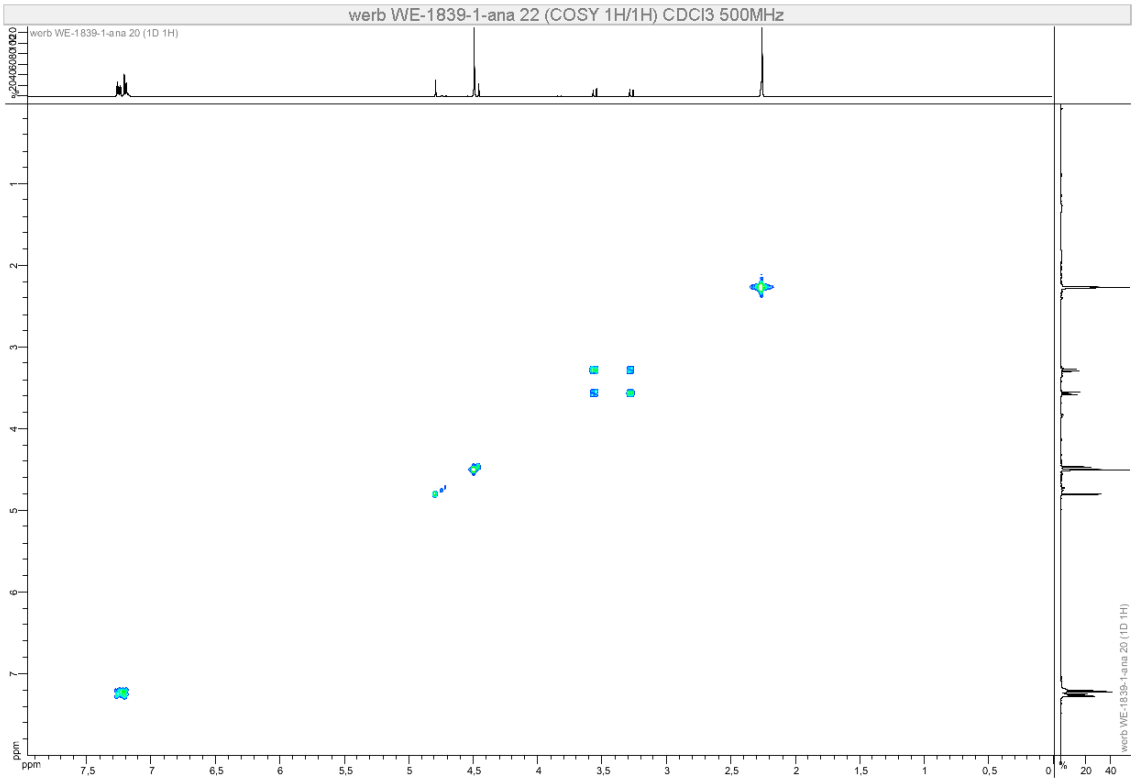
^{1}H NMR (500 MHz, $CDCl_3$)



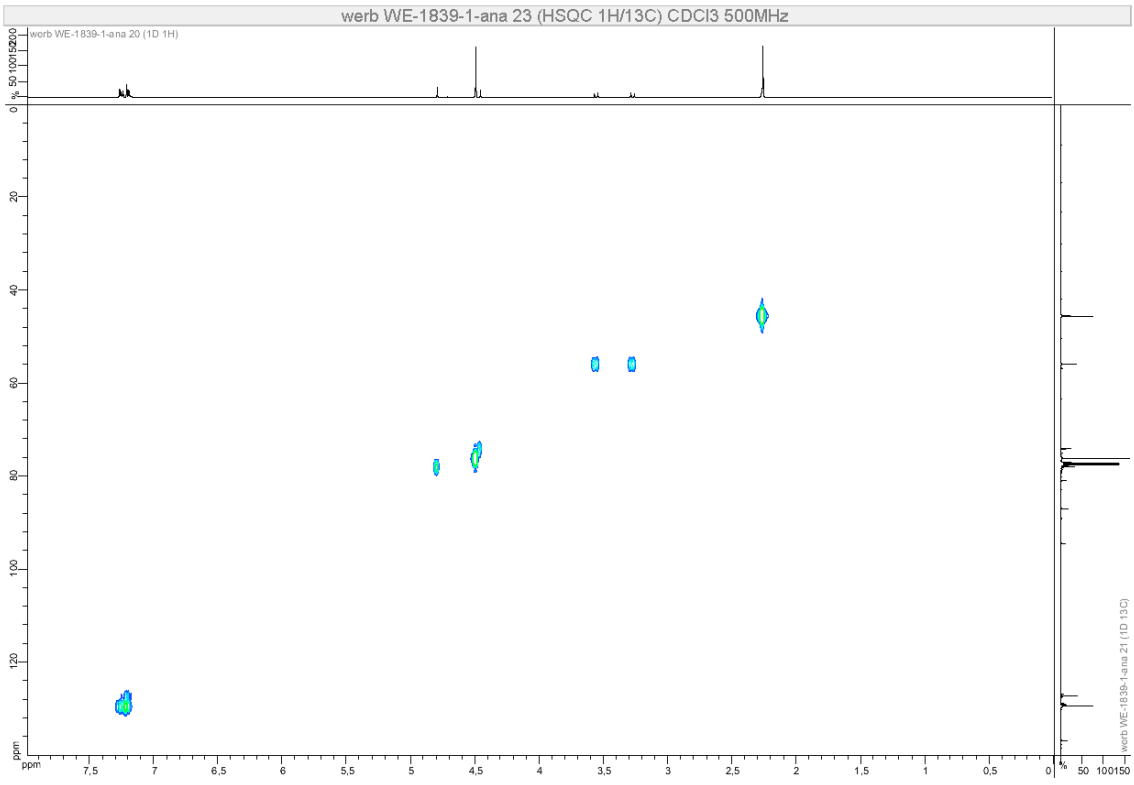
^{13}C NMR (125 MHz, $CDCl_3$)



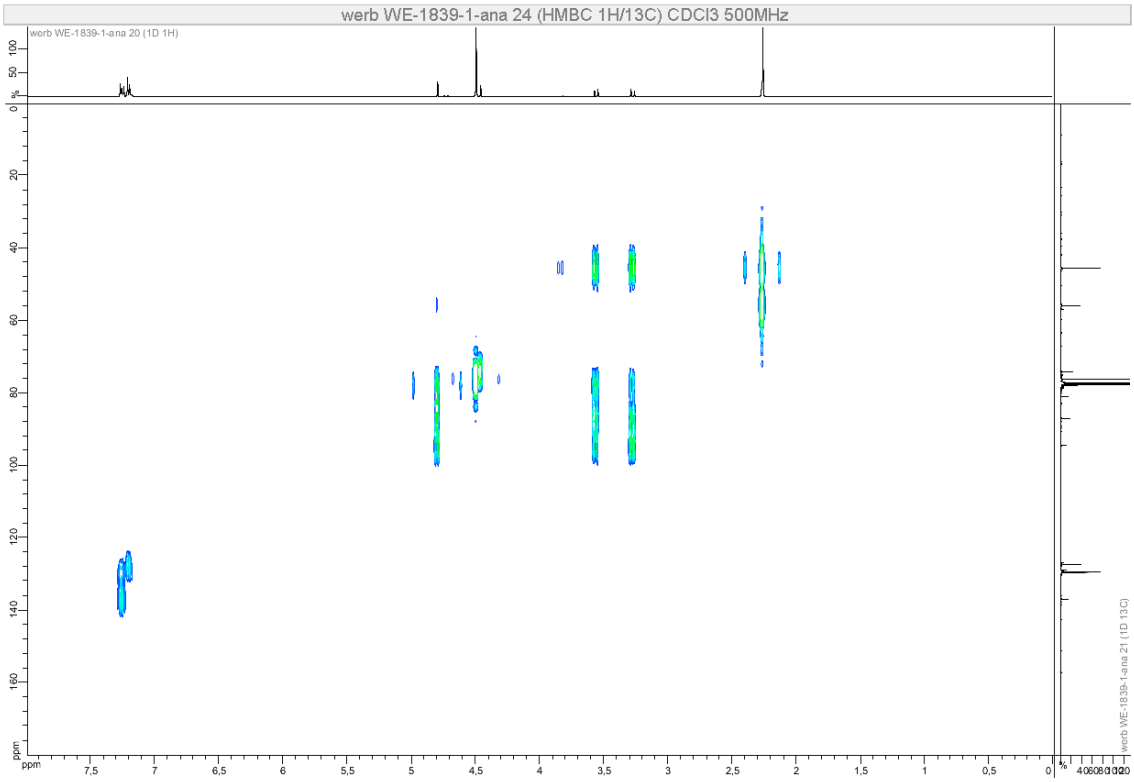
COSY (500 MHz, $CDCl_3$)



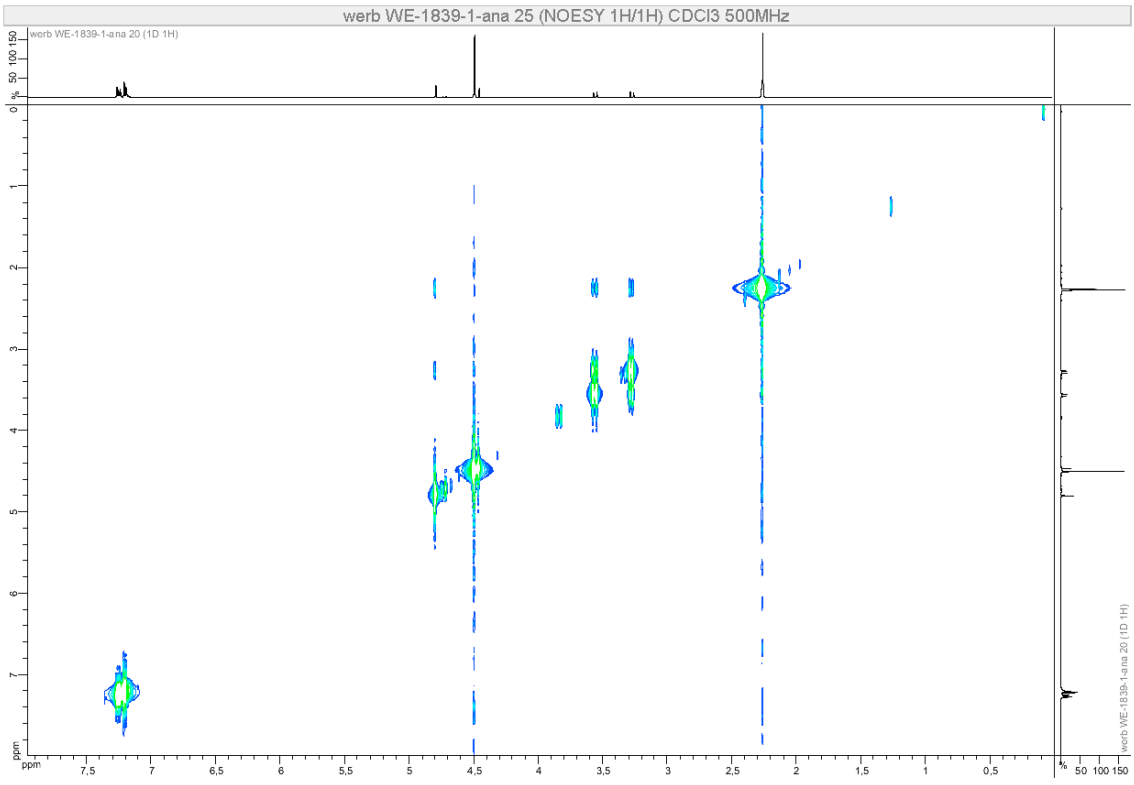
HSQC (500 MHz, $CDCl_3$)



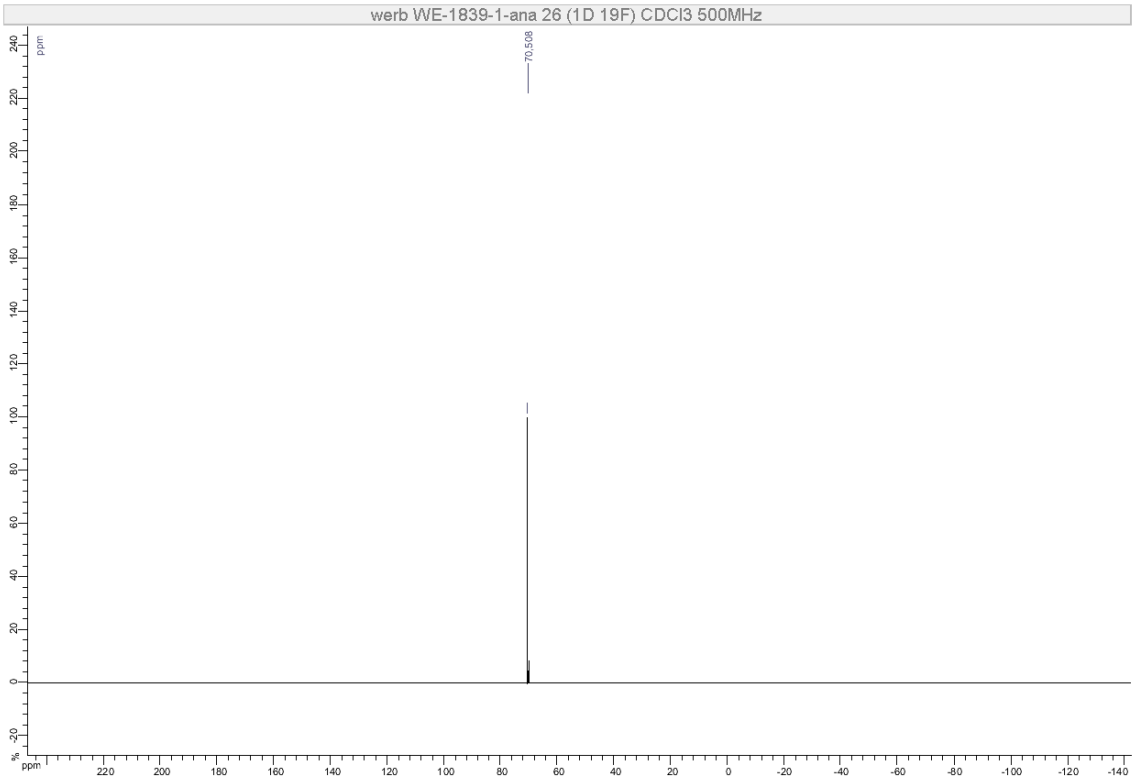
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

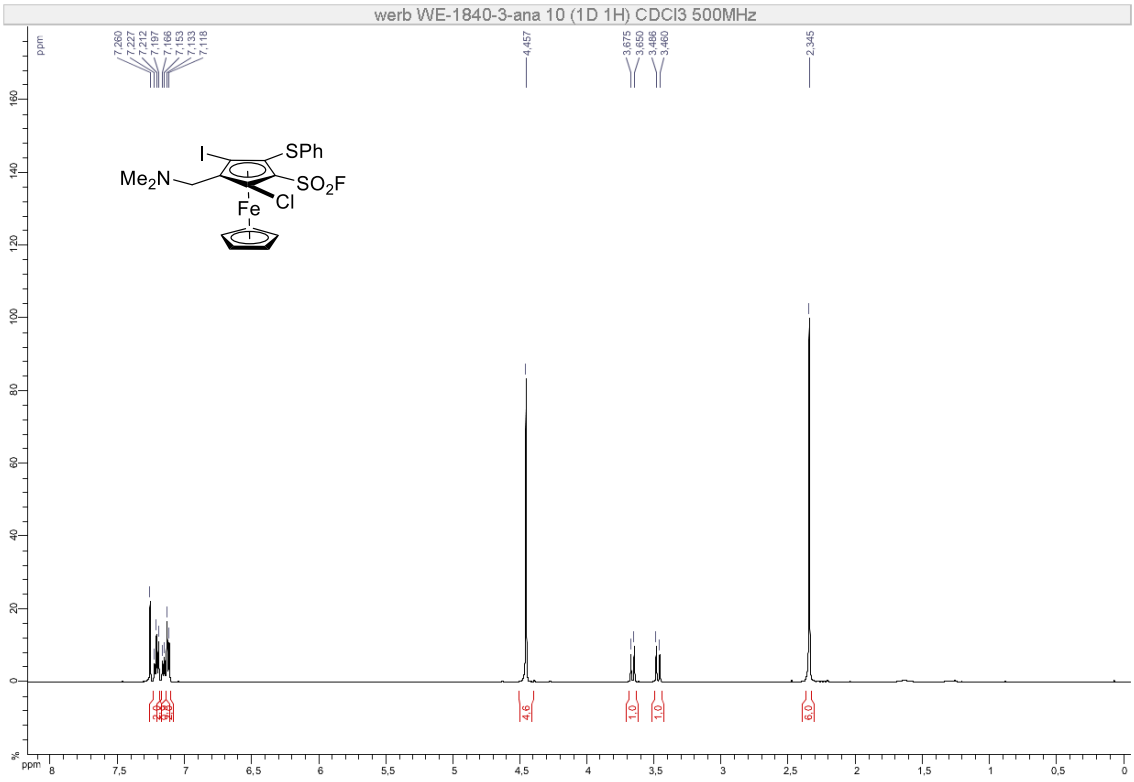


^{19}F NMR (470 MHz, $CDCl_3$)

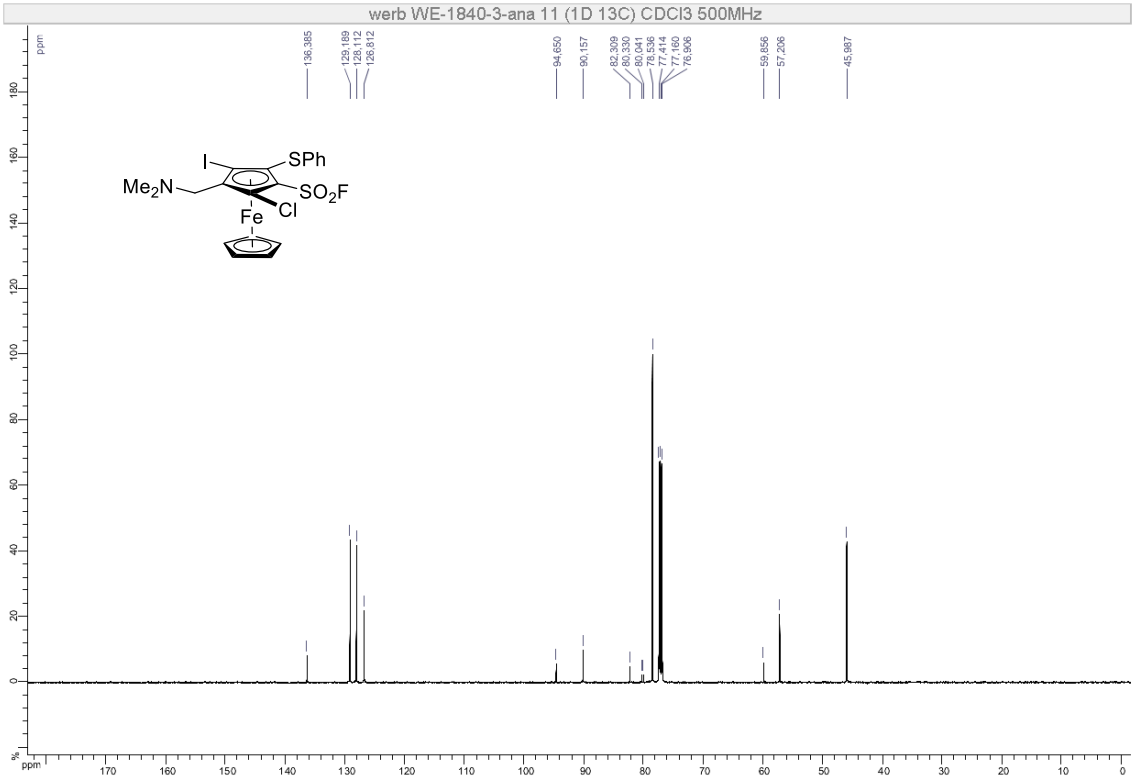


2-Chloro-3-(*N*,*N*-dimethylaminomethyl)-4-iodo-5-(phenylthio)ferrocenesulfonyl fluoride (18)

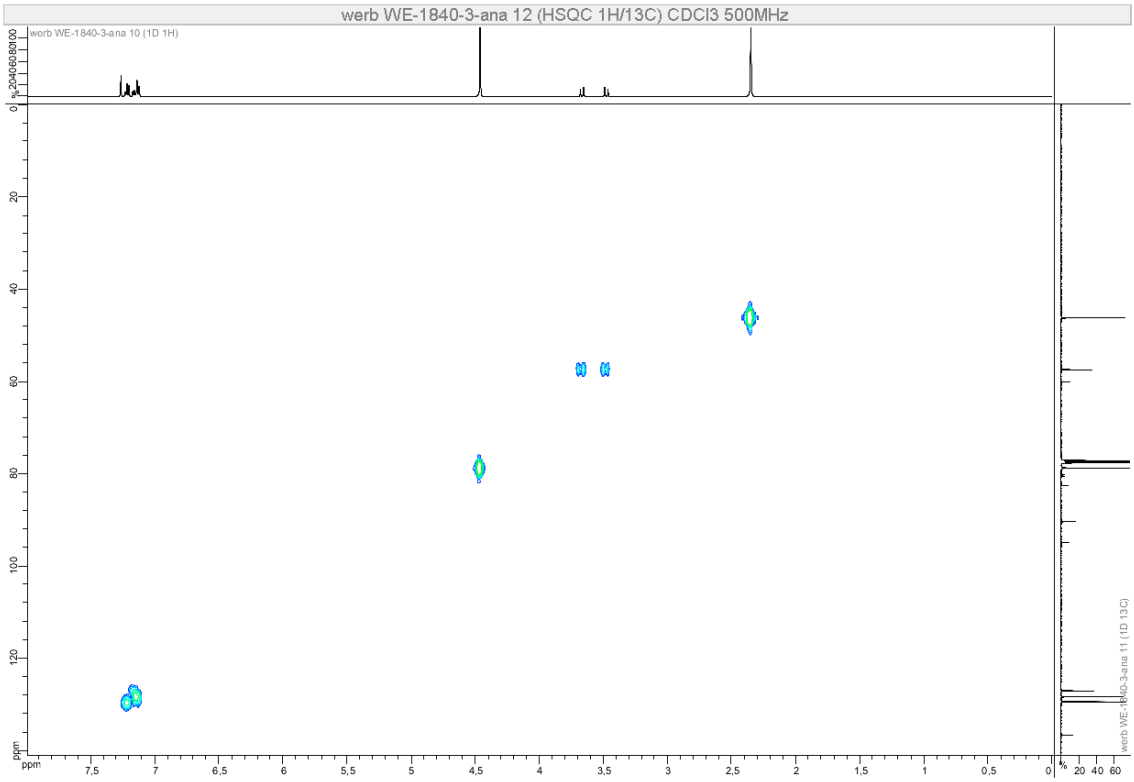
^{1}H NMR (500 MHz, $CDCl_3$)



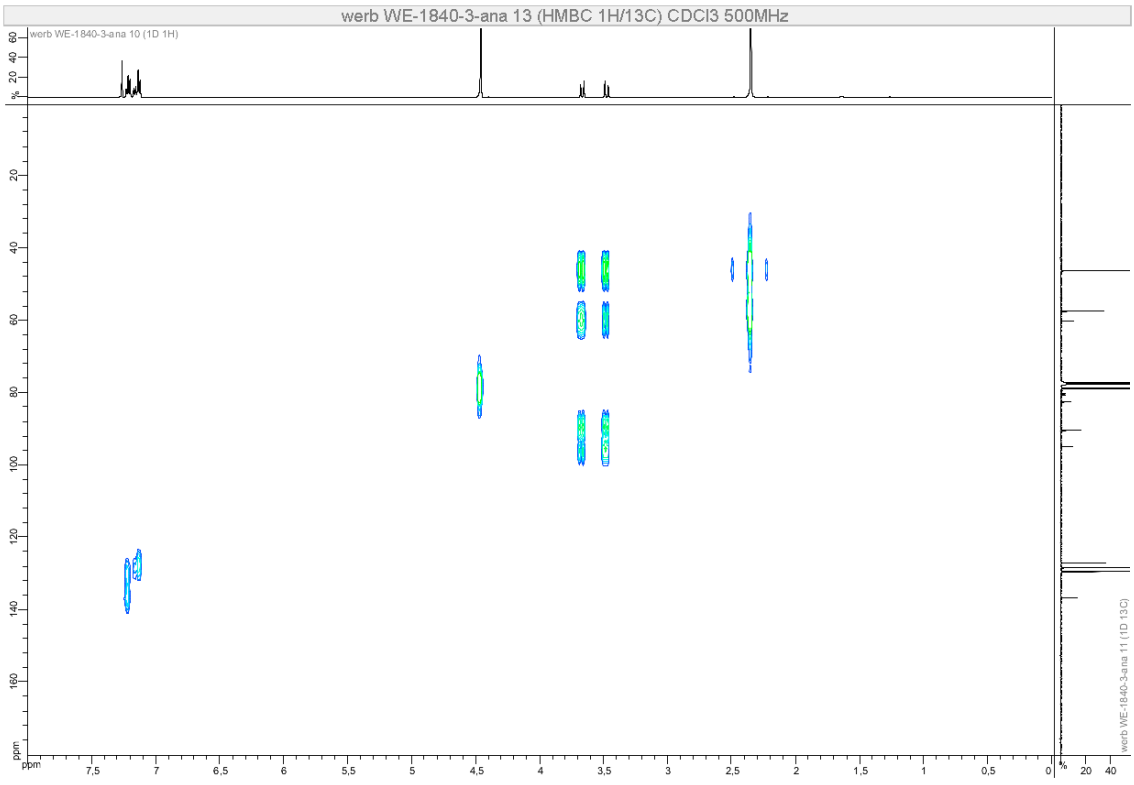
^{13}C NMR (125 MHz, $CDCl_3$)



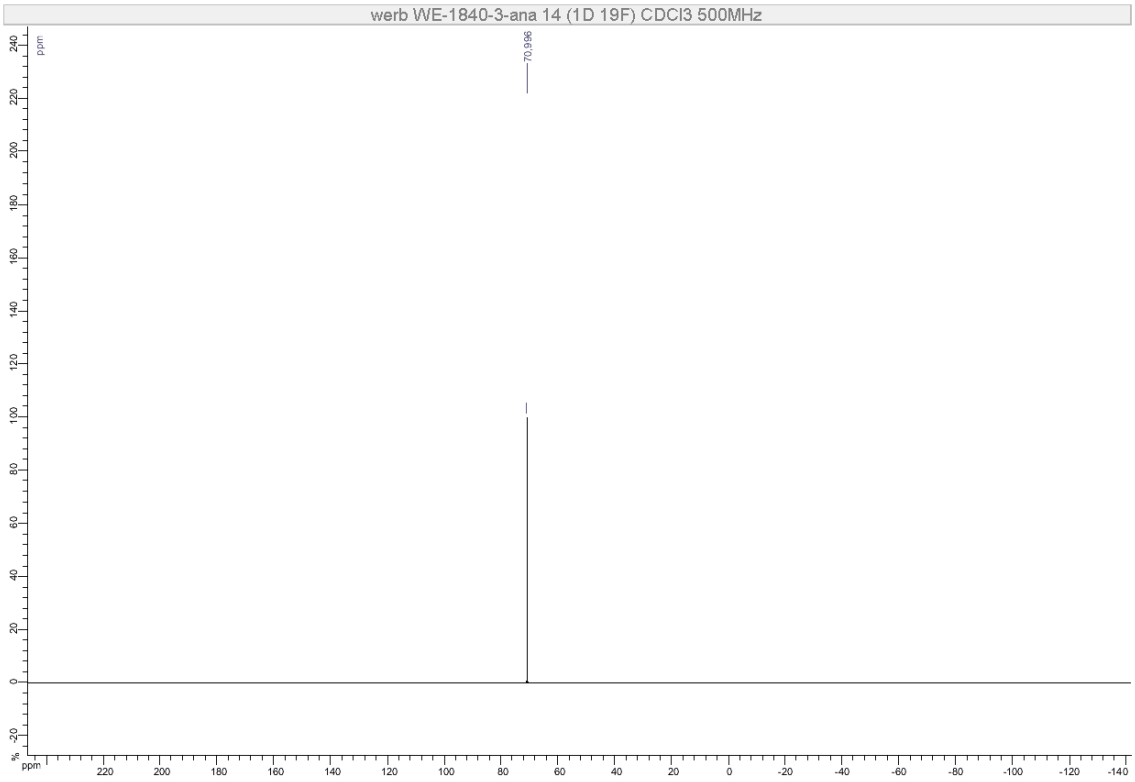
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

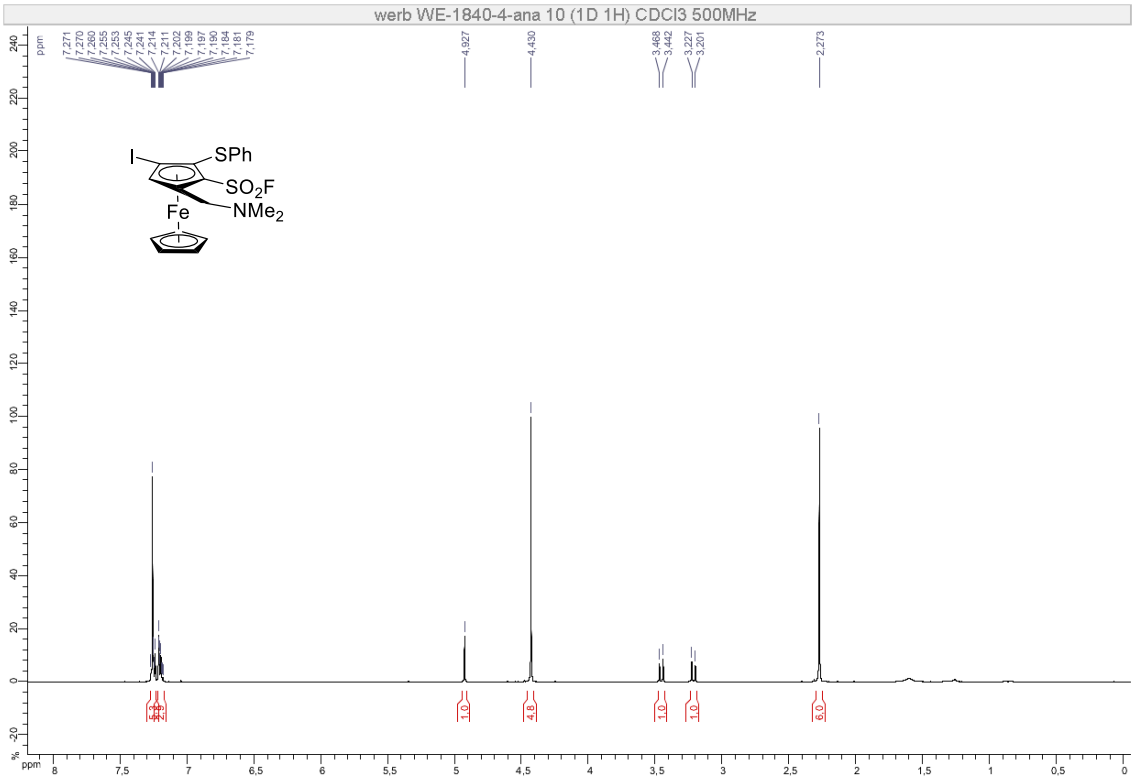


^{19}F NMR (470 MHz, $CDCl_3$)

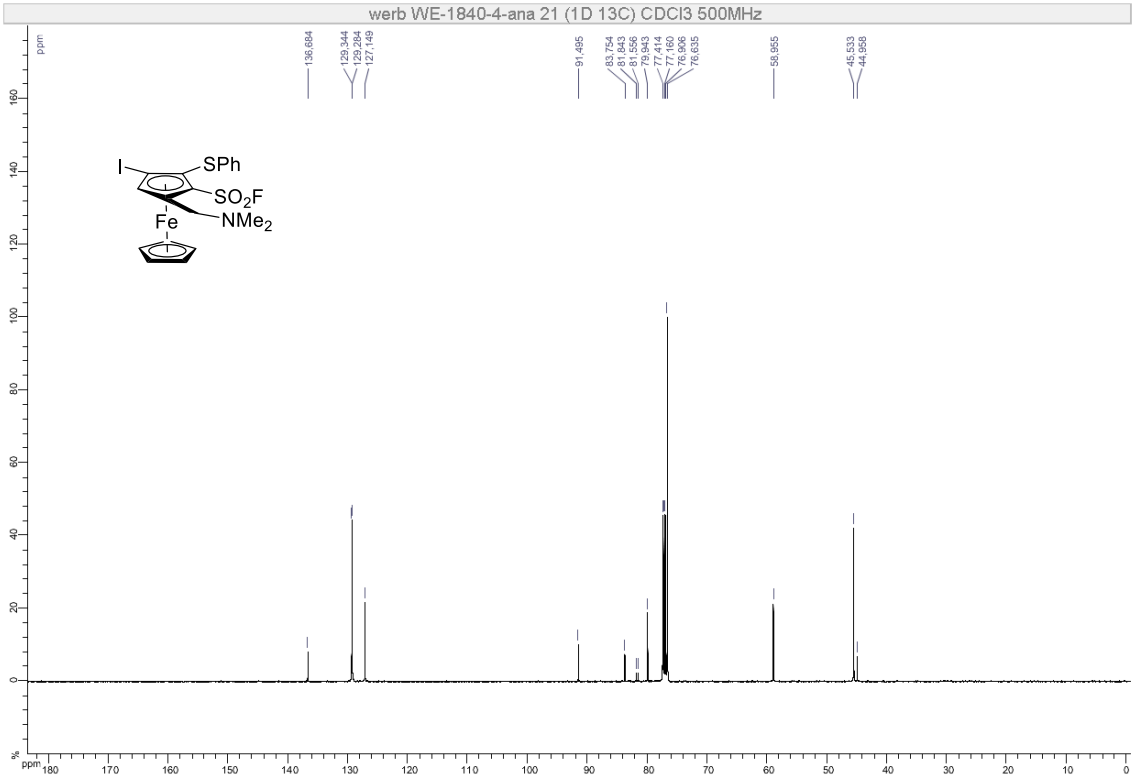


5-(*N*,*N*-Dimethylaminomethyl)-3-iodo-2-(phenylthio)ferrocenesulfonyl fluoride (6h)

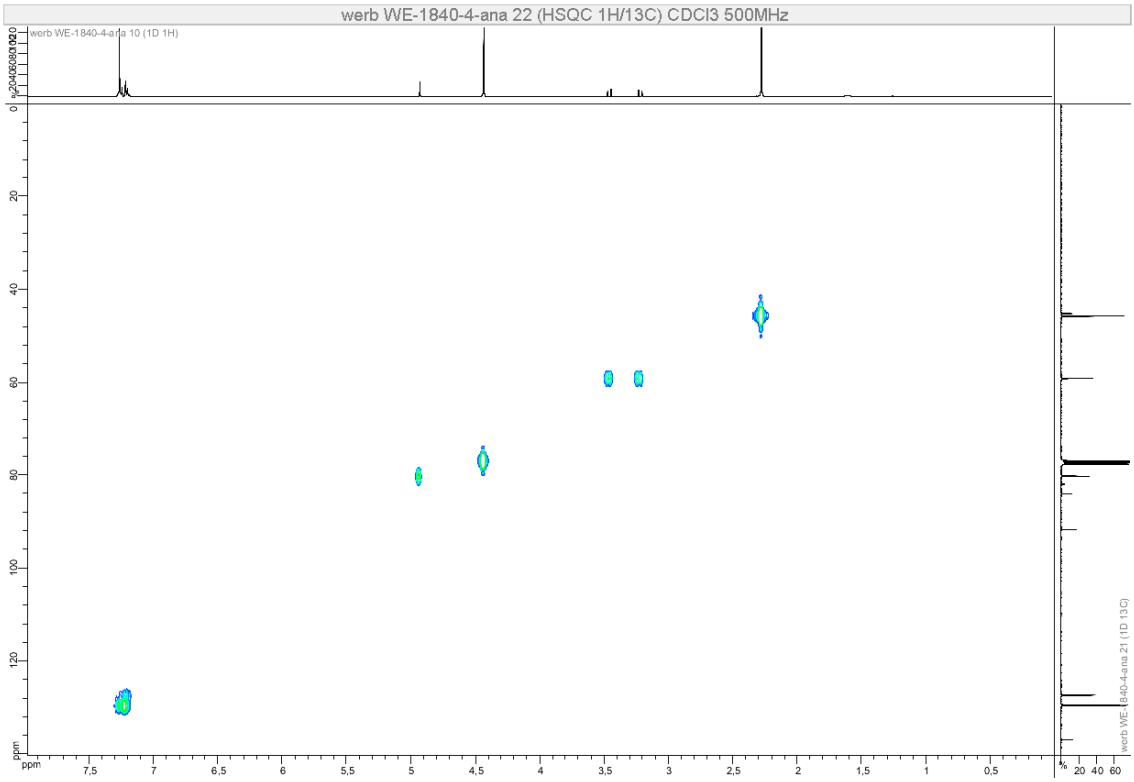
^{1}H NMR (500 MHz, $CDCl_3$)



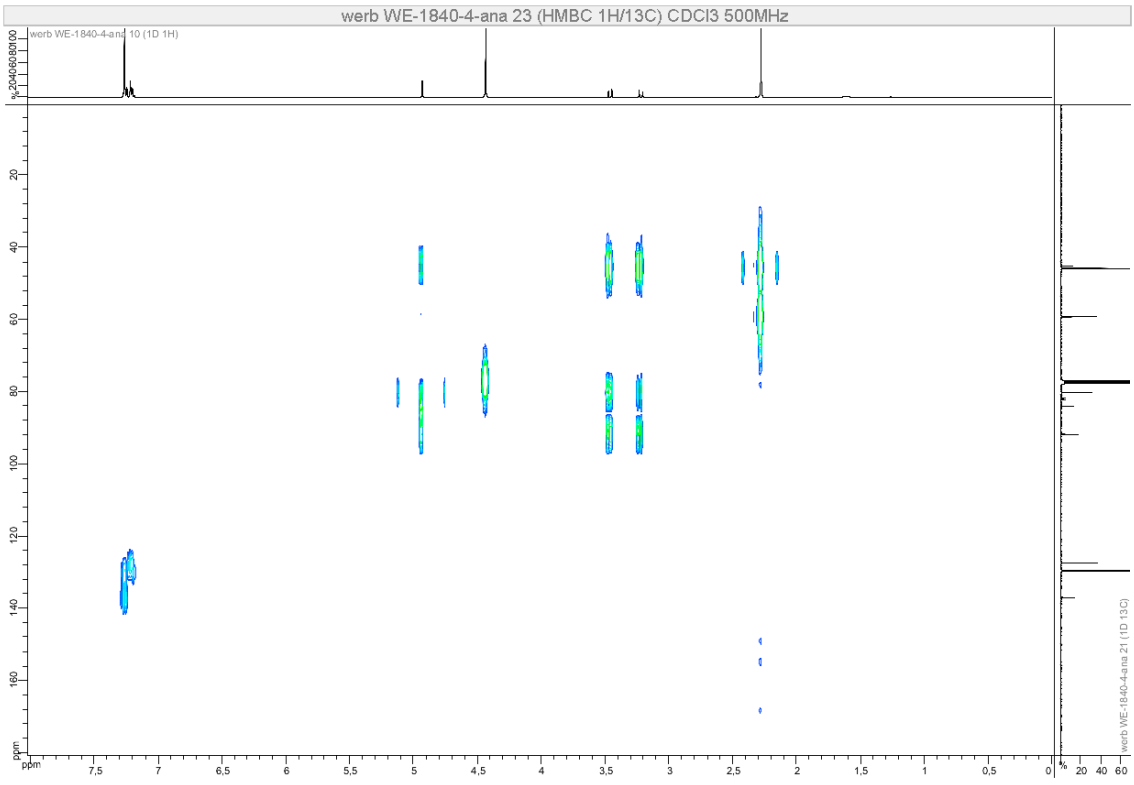
^{13}C NMR (125 MHz, $CDCl_3$)



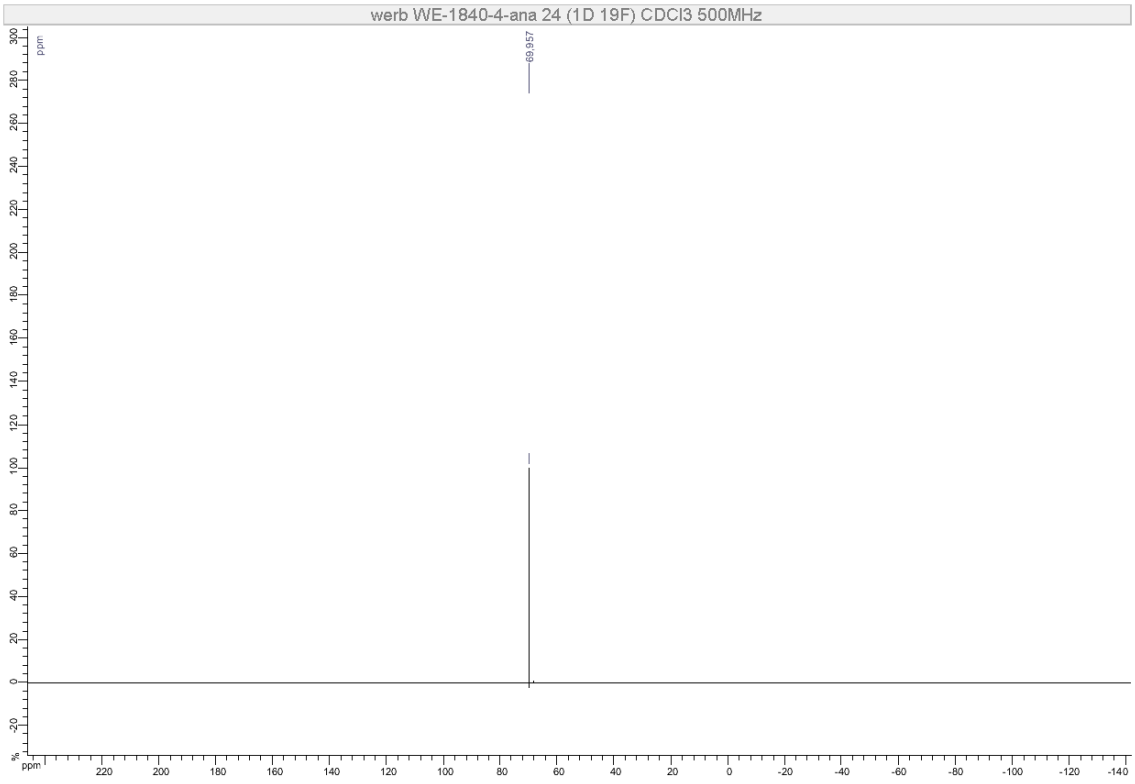
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

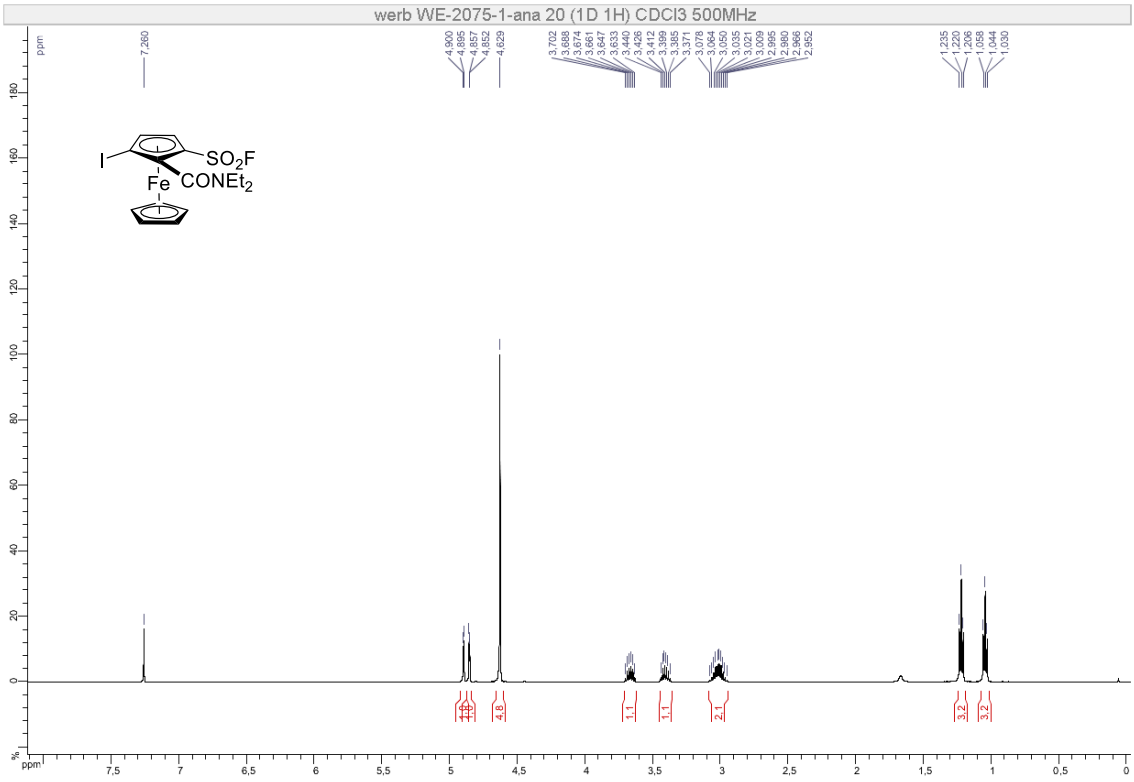


^{19}F NMR (470 MHz, $CDCl_3$)

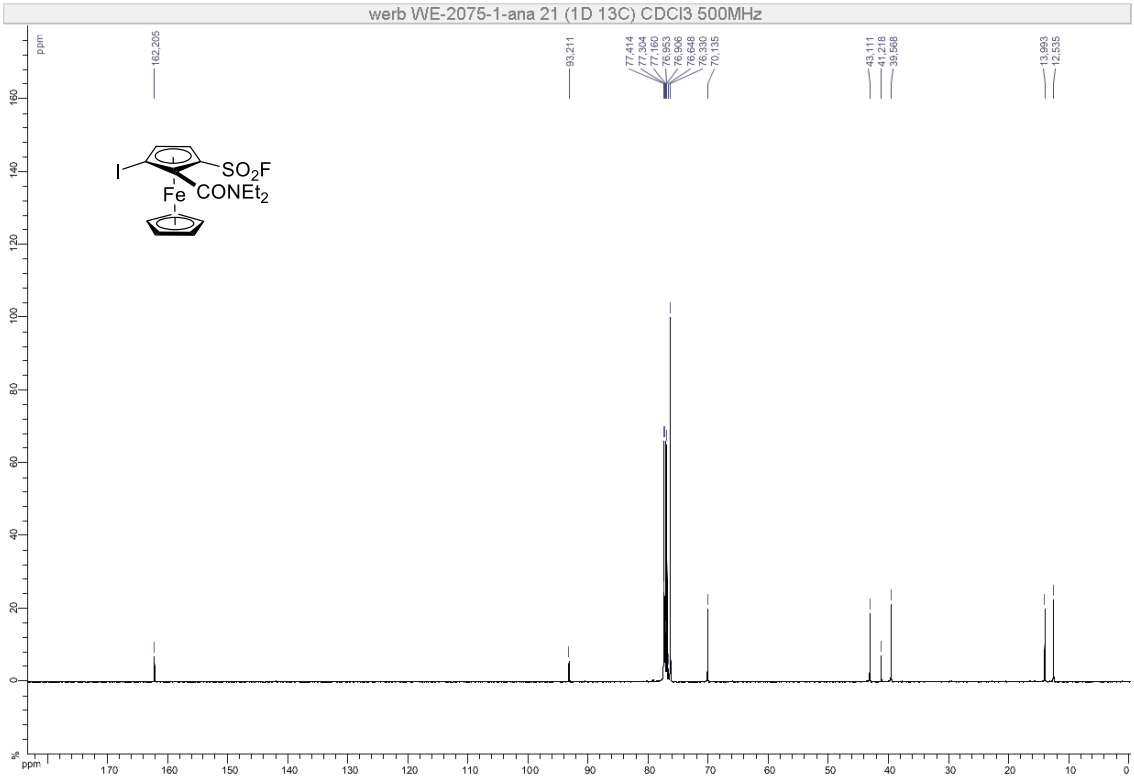


2-(*N*,*N*-Diethylcarbamoyl)-3-iodoferrocenesulfonyl fluoride (19c)

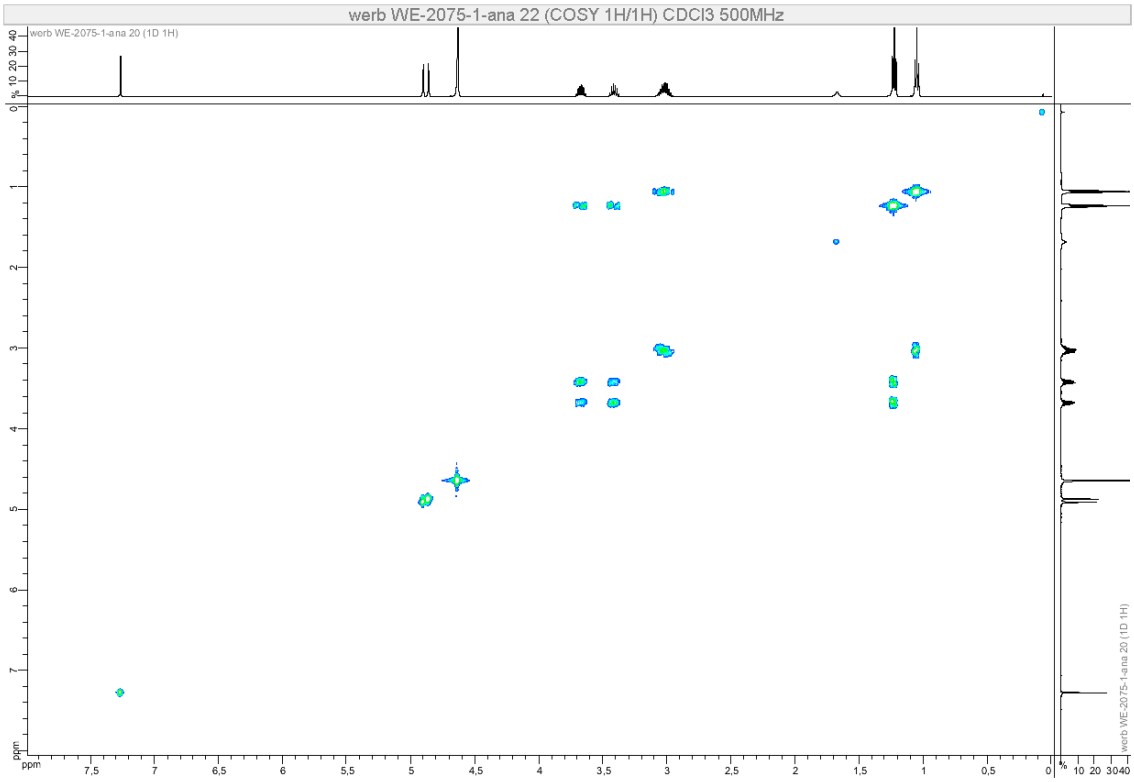
^{1}H NMR (500 MHz, $CDCl_3$)



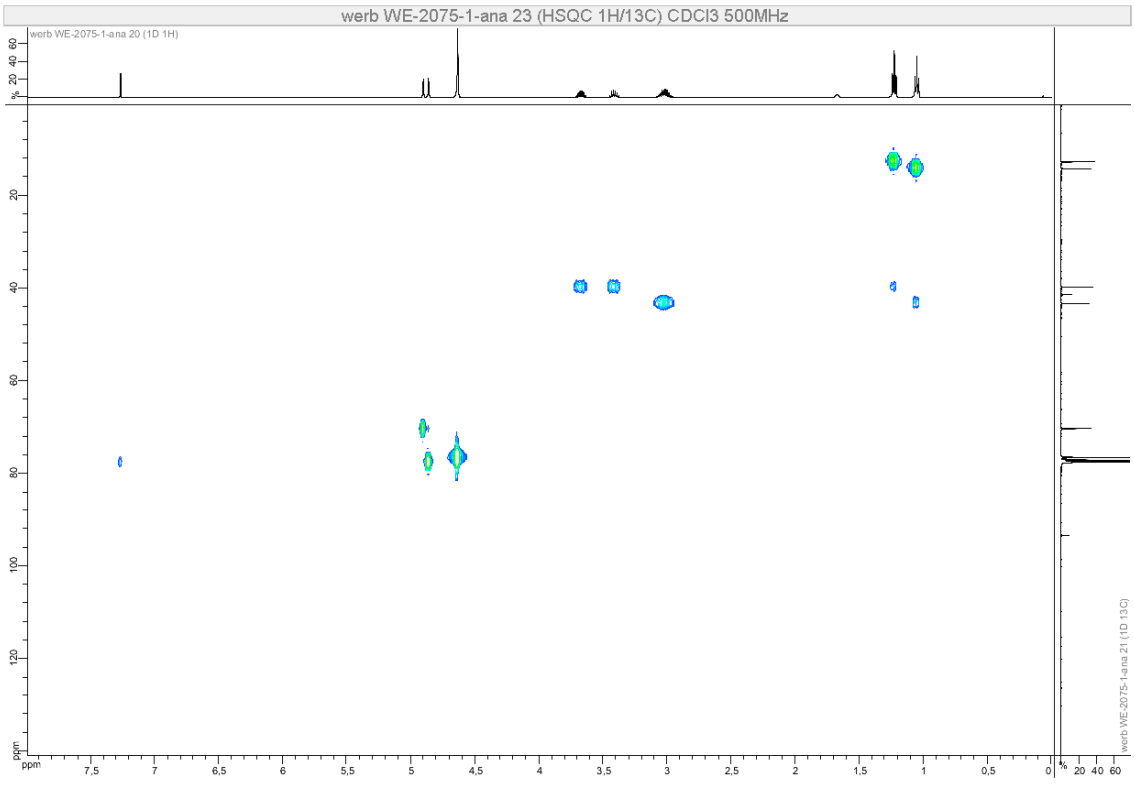
^{13}C NMR (125 MHz, $CDCl_3$)



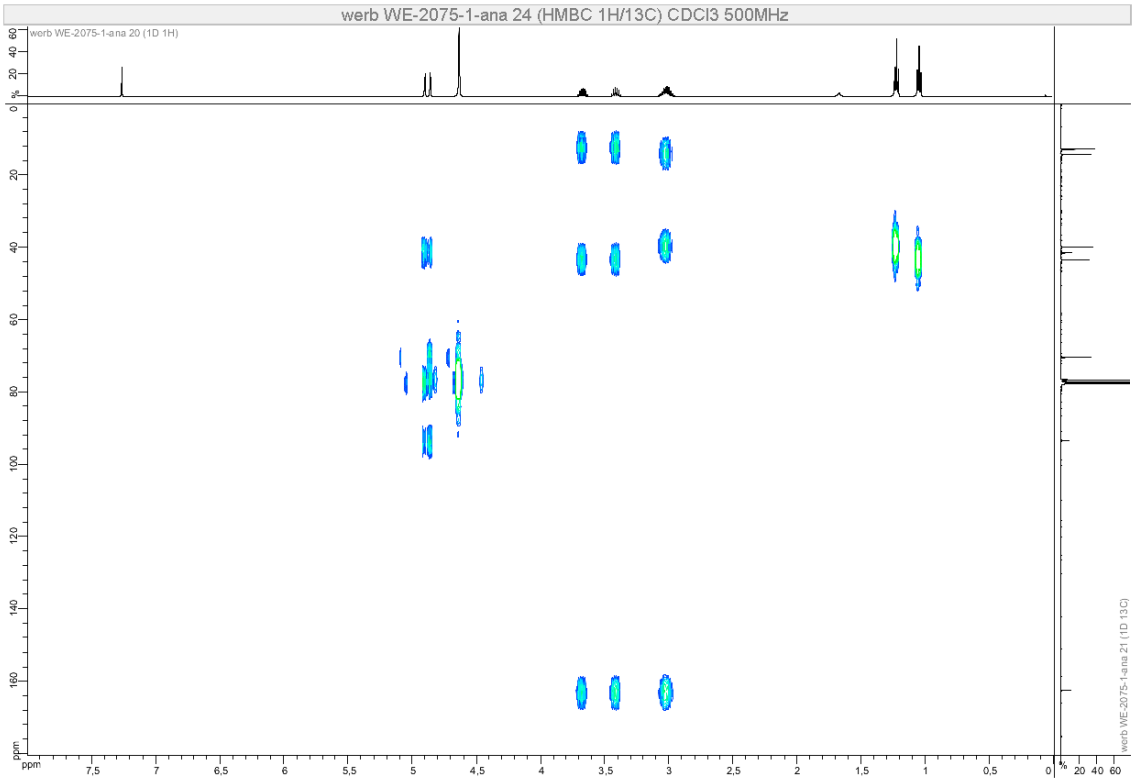
COSY (500 MHz, $CDCl_3$)



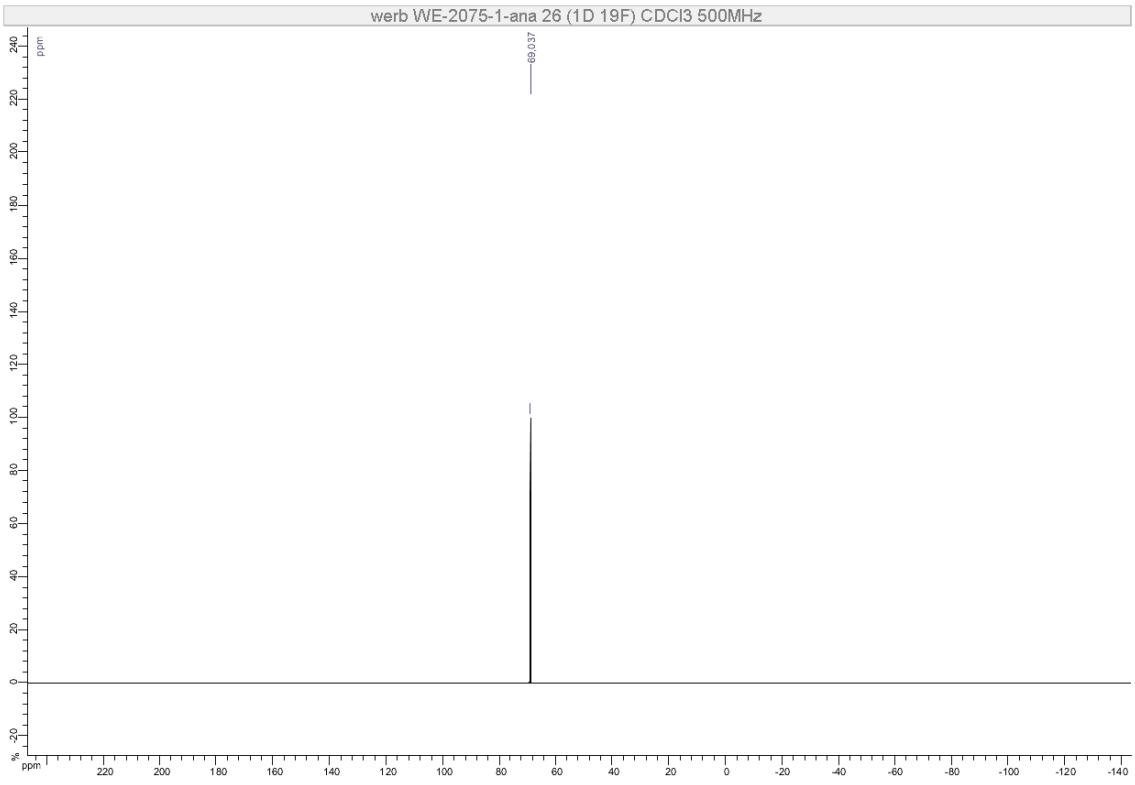
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

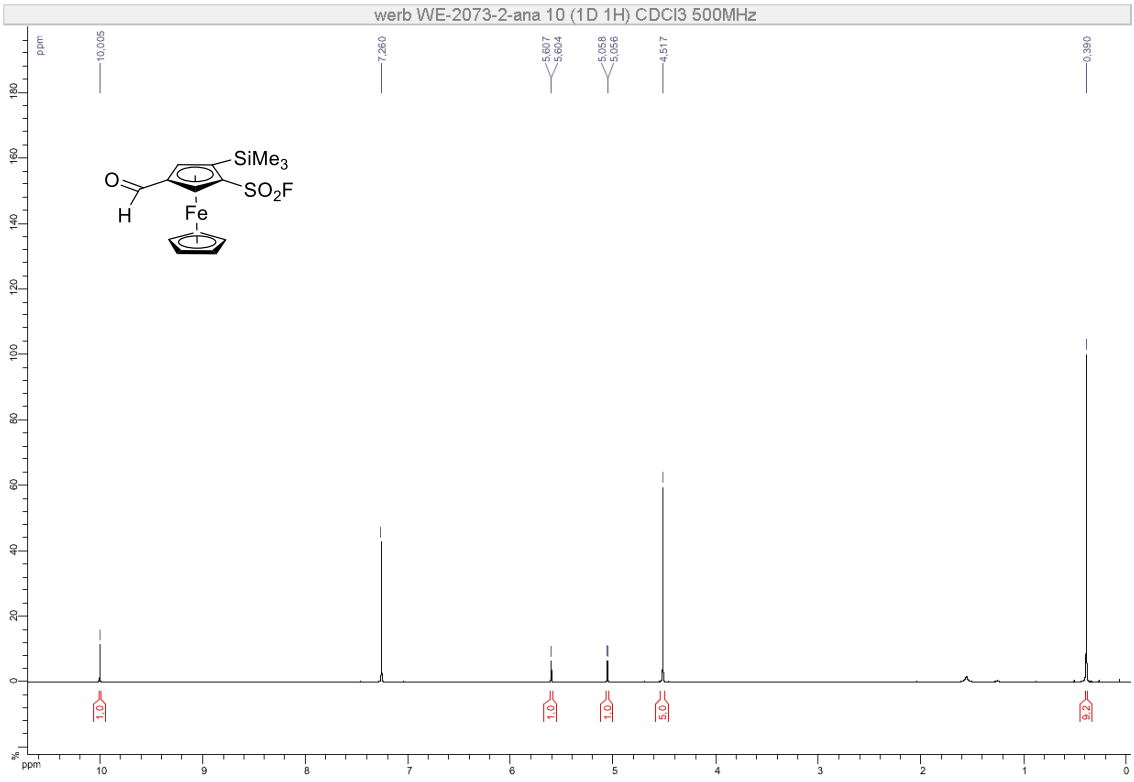


^{19}F NMR (470 MHz, $CDCl_3$)

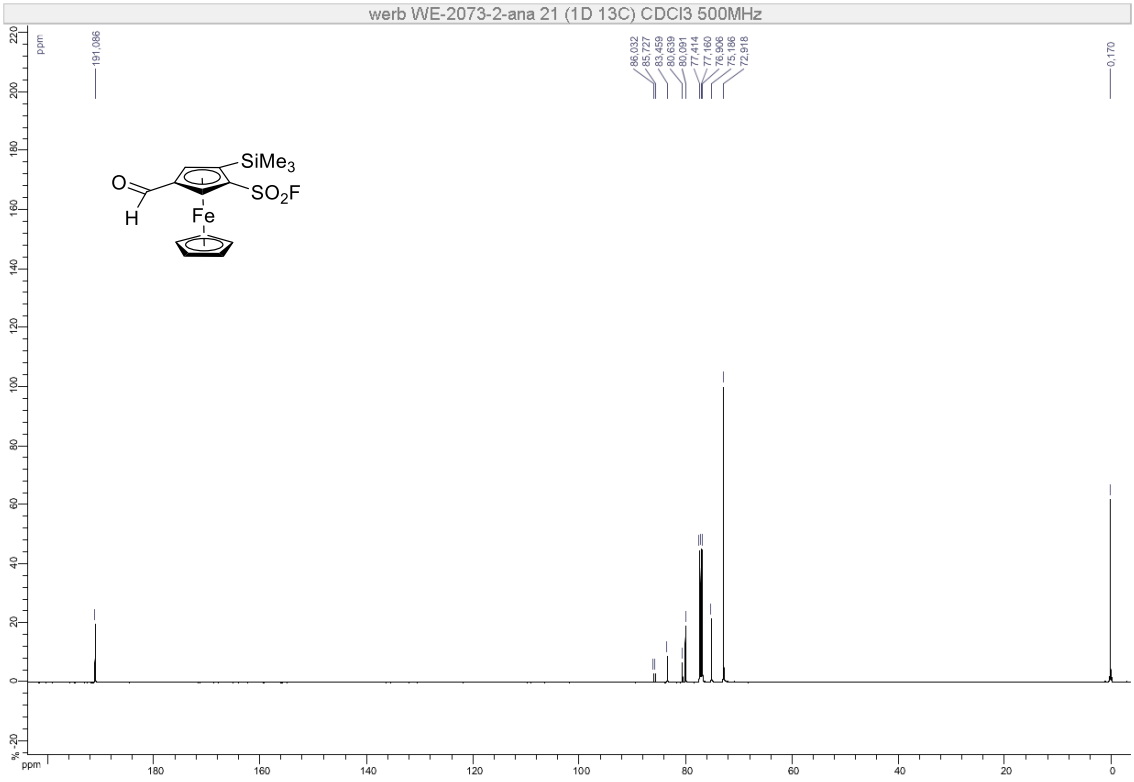


3-Formyl-5-(trimethylsilyl)ferrocenesulfonyl fluoride (20a)

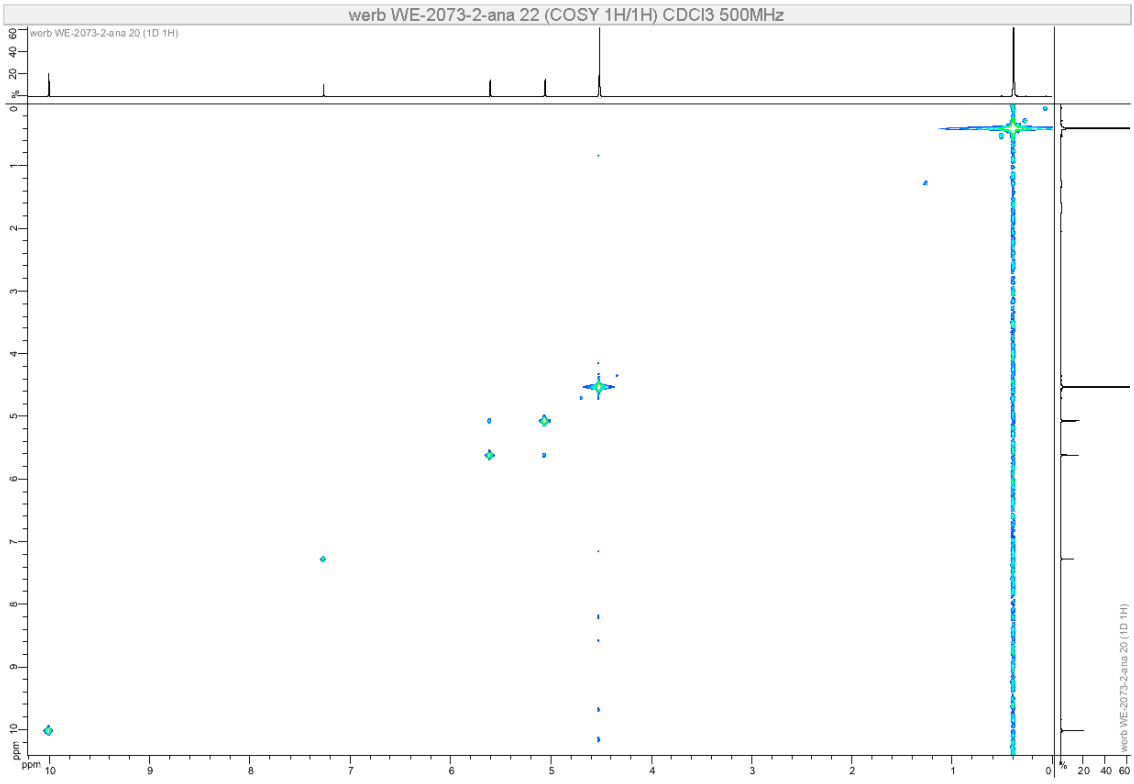
^{1}H NMR (500 MHz, $CDCl_3$)



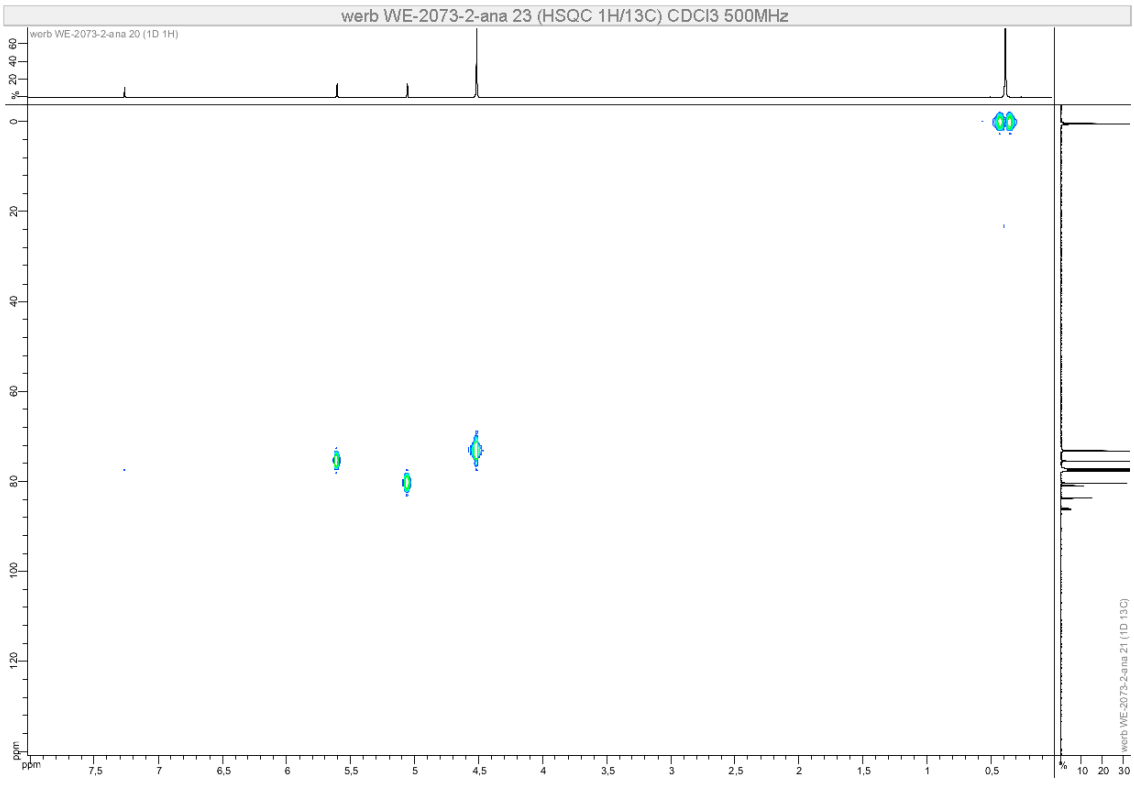
^{13}C NMR (125 MHz, $CDCl_3$)



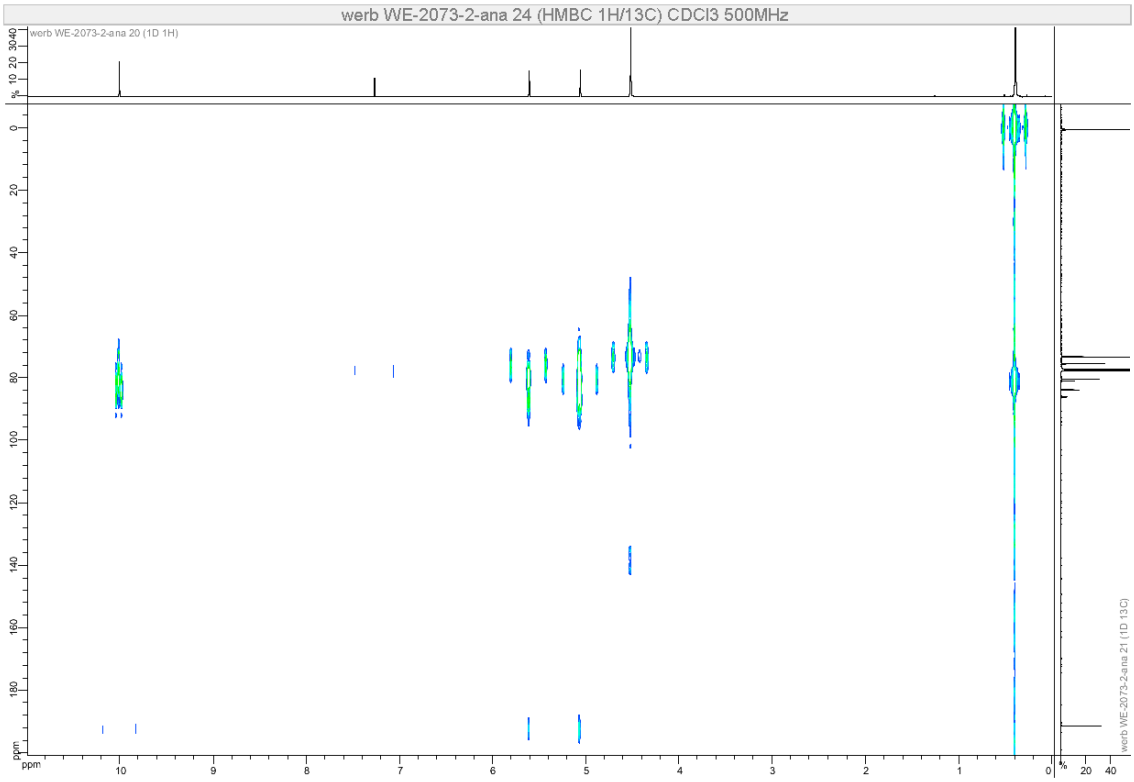
COSY (500 MHz, $CDCl_3$)



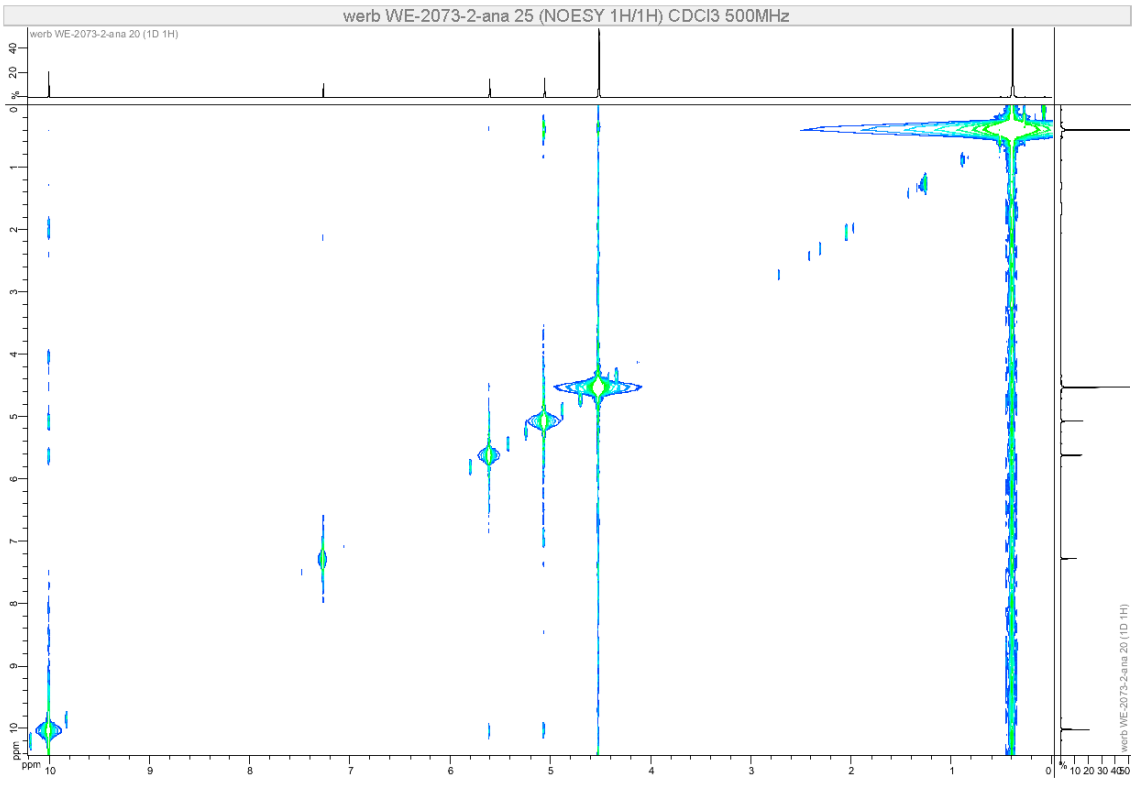
HSQC (500 MHz, $CDCl_3$)



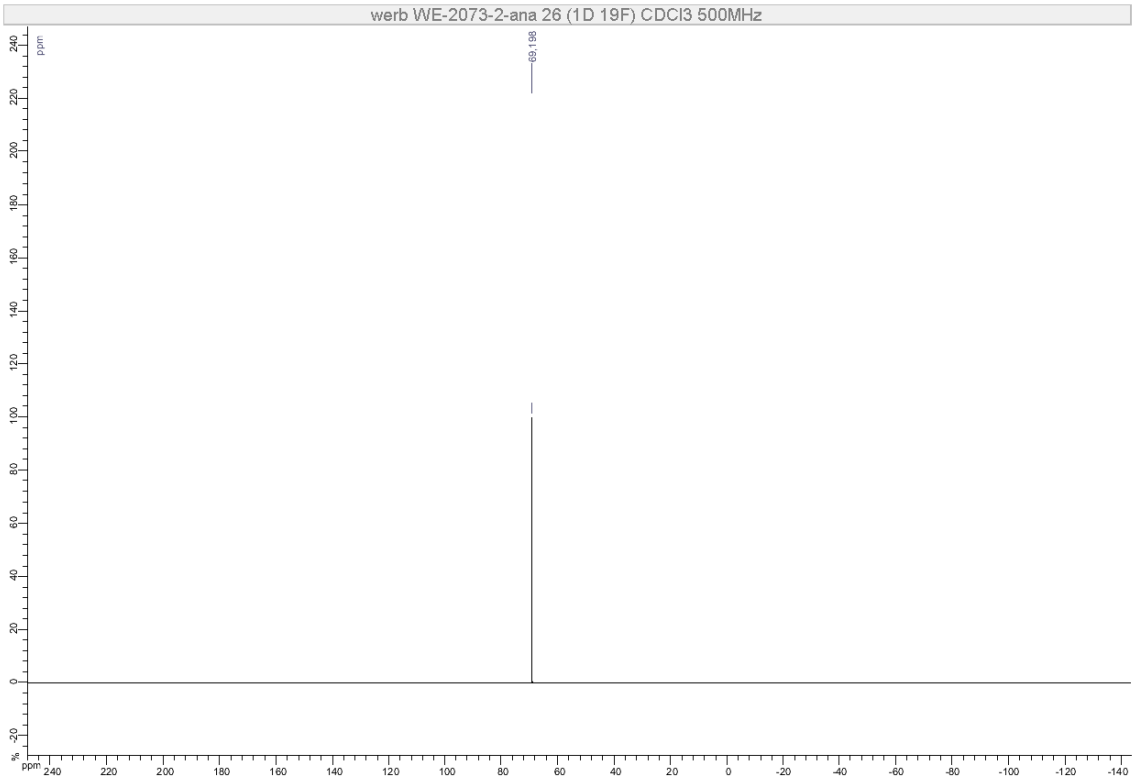
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

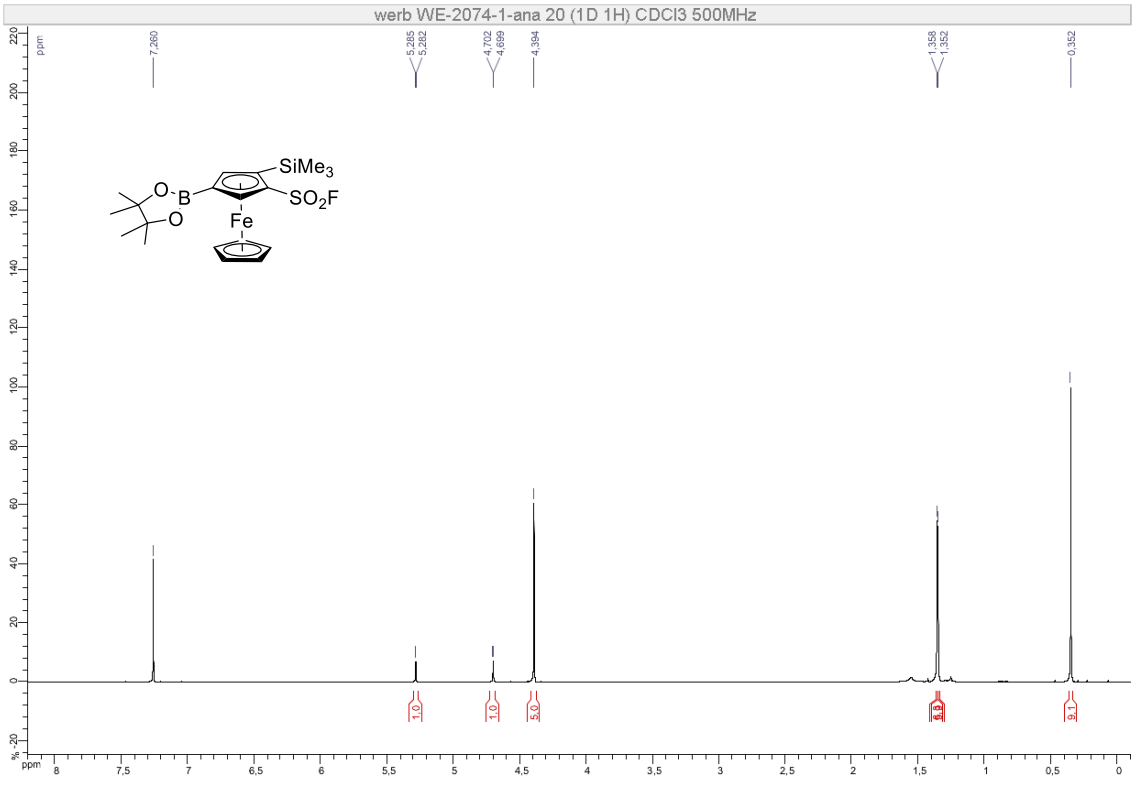


^{19}F NMR (470 MHz, $CDCl_3$)

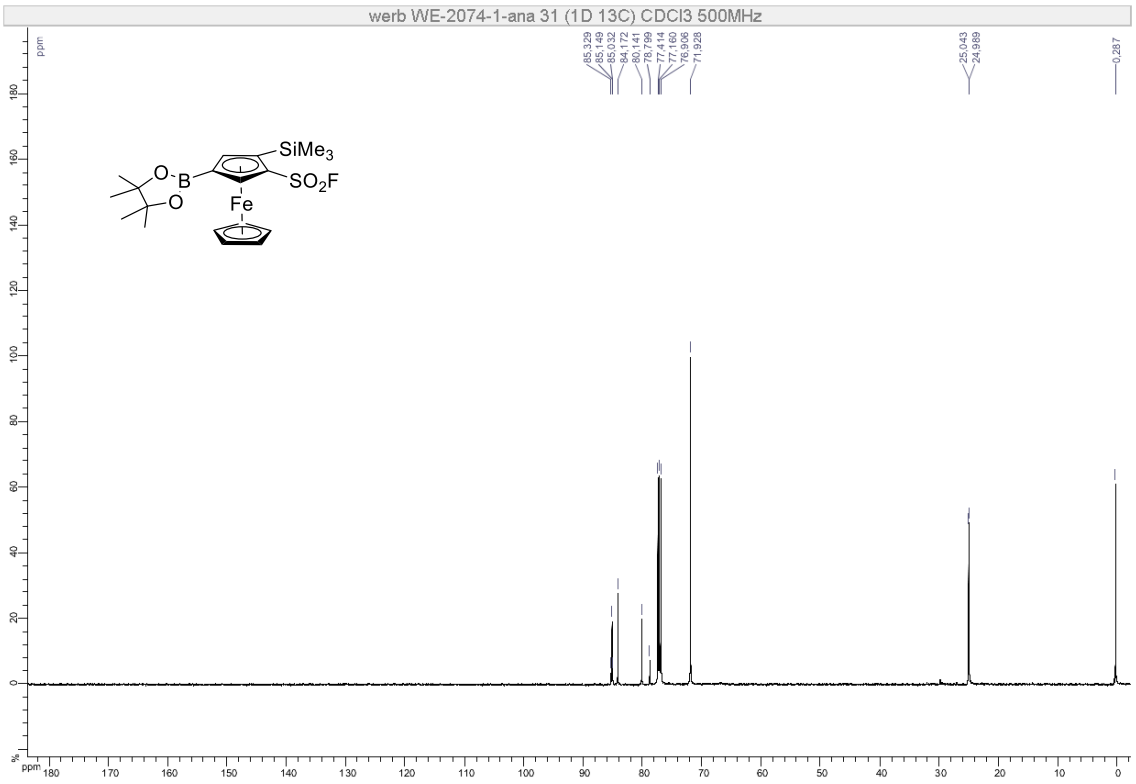


4-Pinacolboryl-2-(trimethylsilyl)ferrocenesulfonyl fluoride (20b)

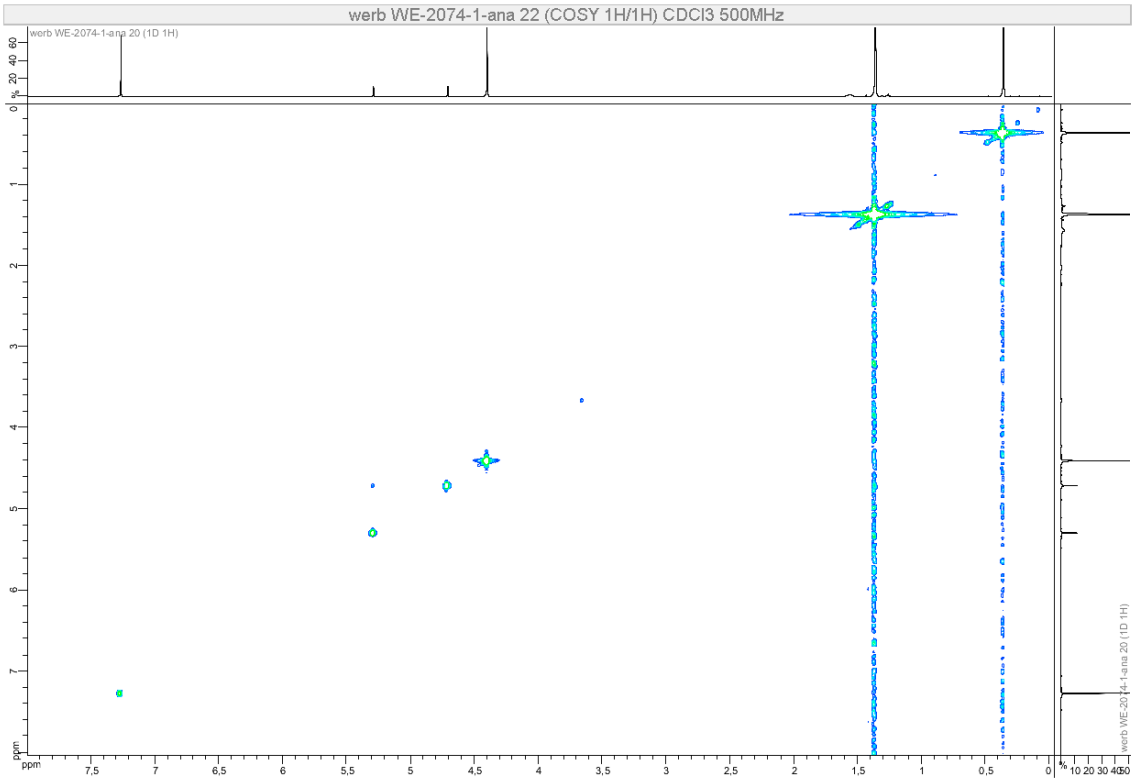
^{1}H NMR (500 MHz, $CDCl_3$)



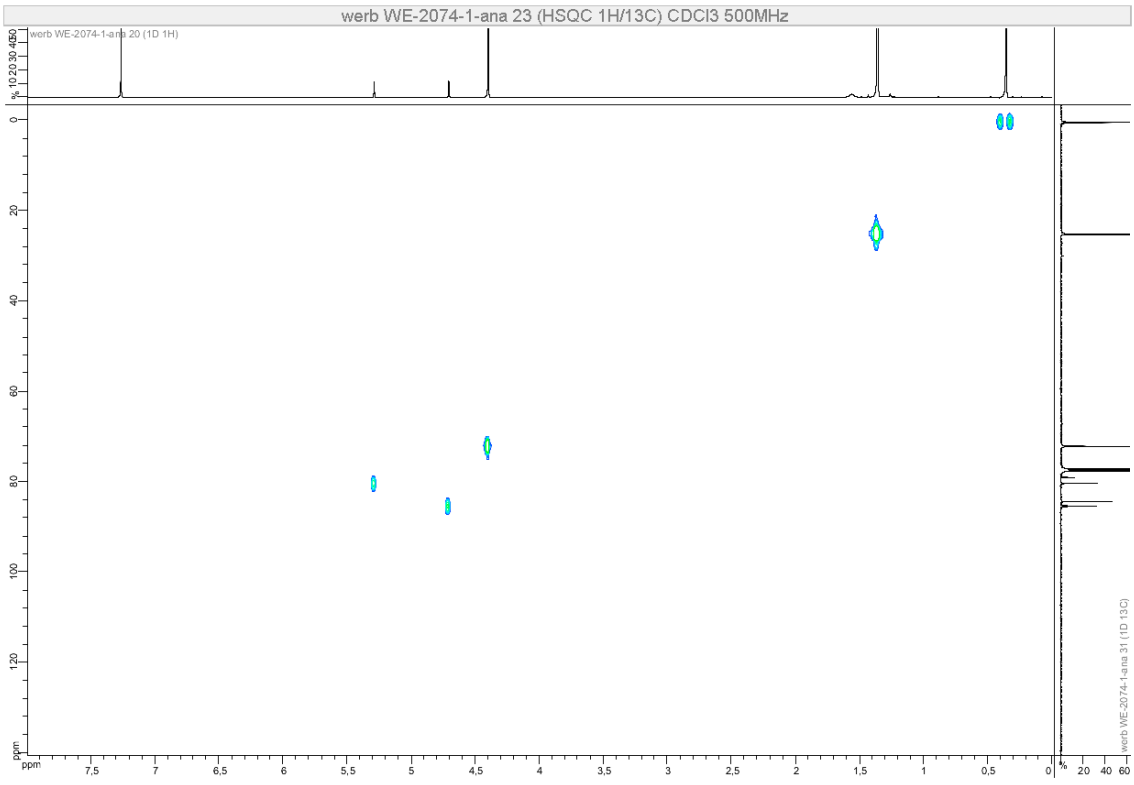
^{13}C NMR (125 MHz, $CDCl_3$)



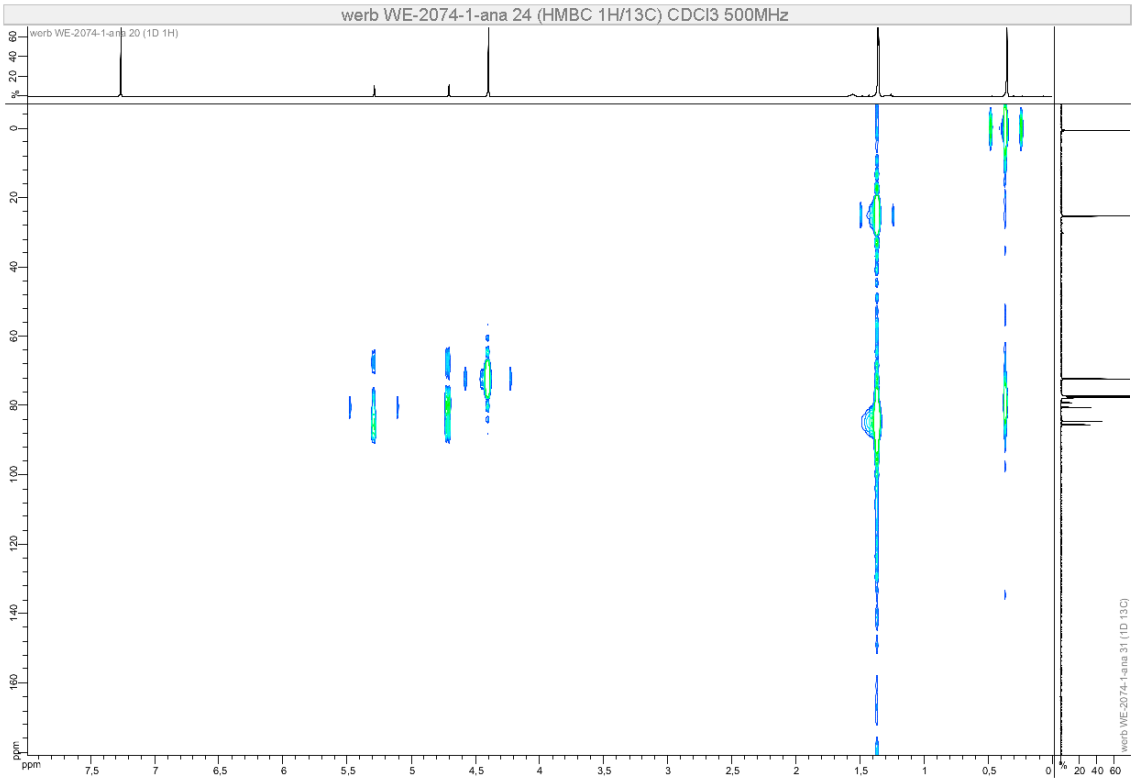
COSY (500 MHz, $CDCl_3$)



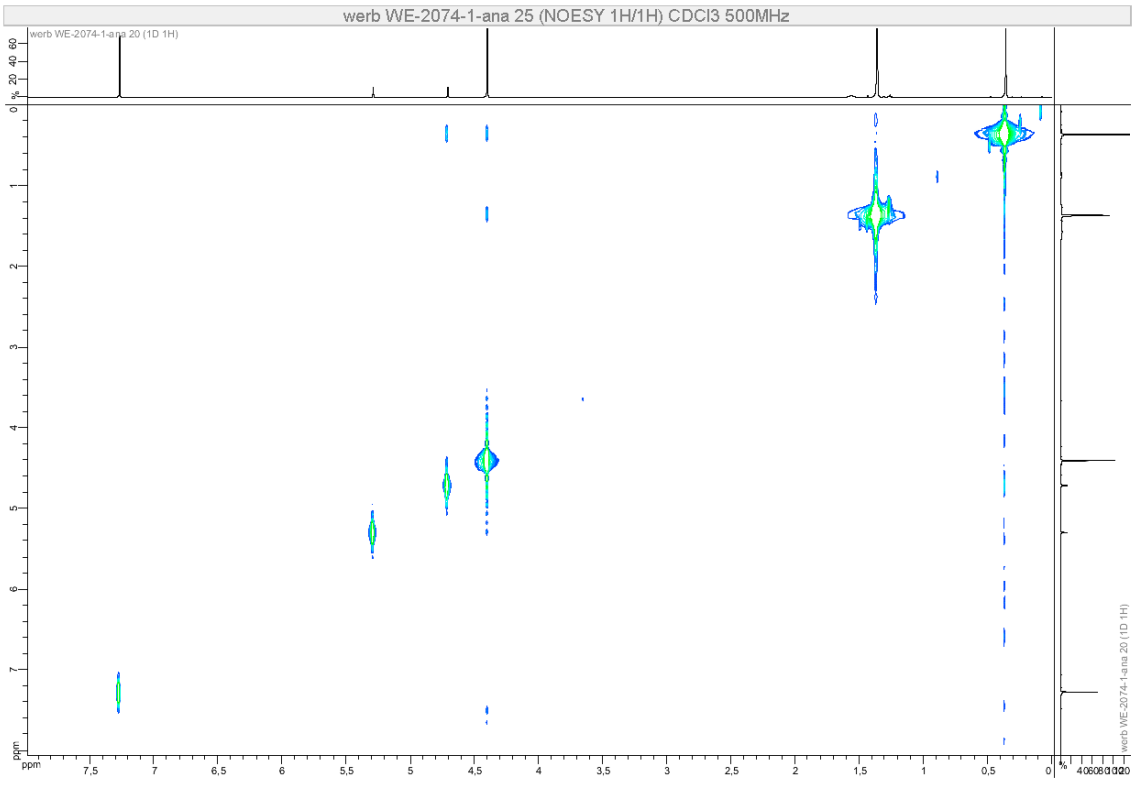
HSQC (500 MHz, $CDCl_3$)



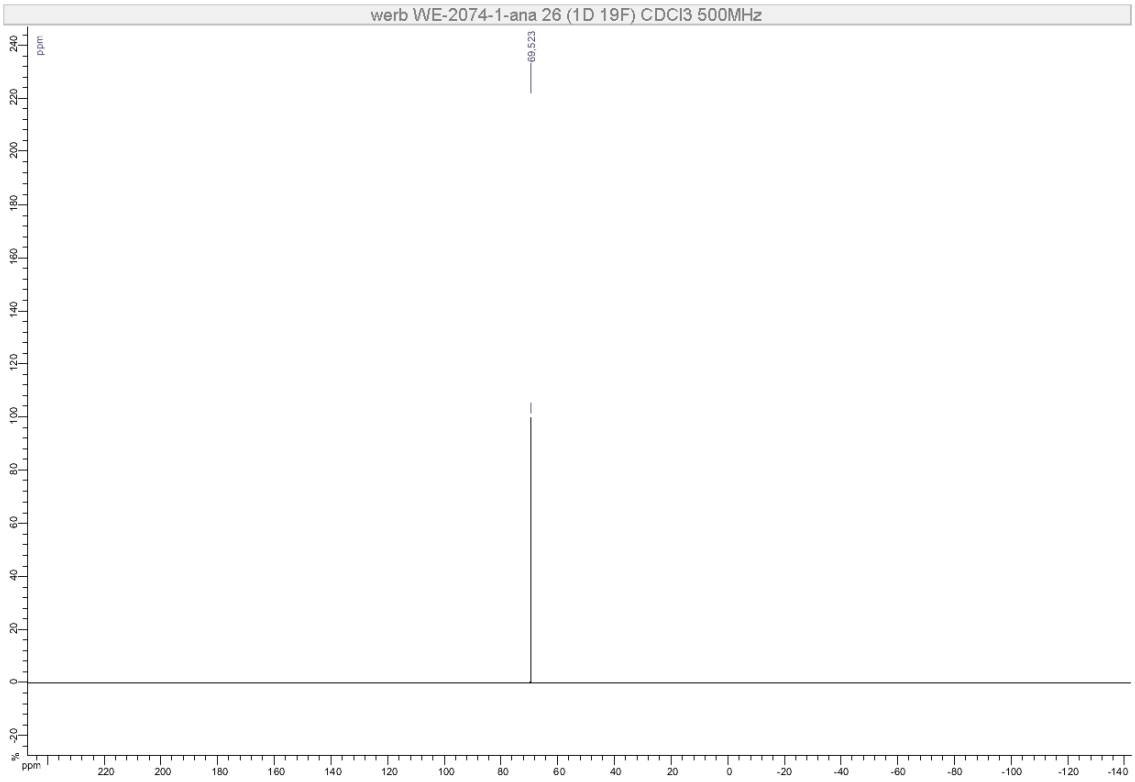
HMBC (500 MHz, $CDCl_3$)



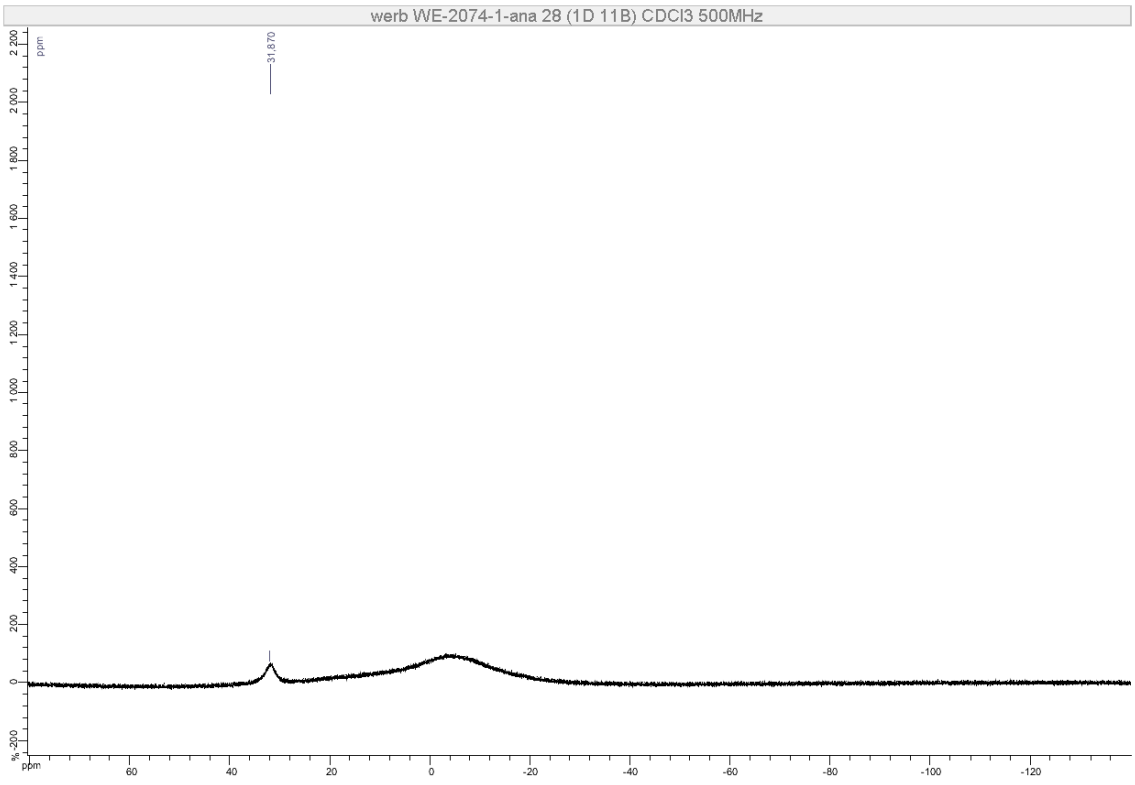
NOESY (500 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)

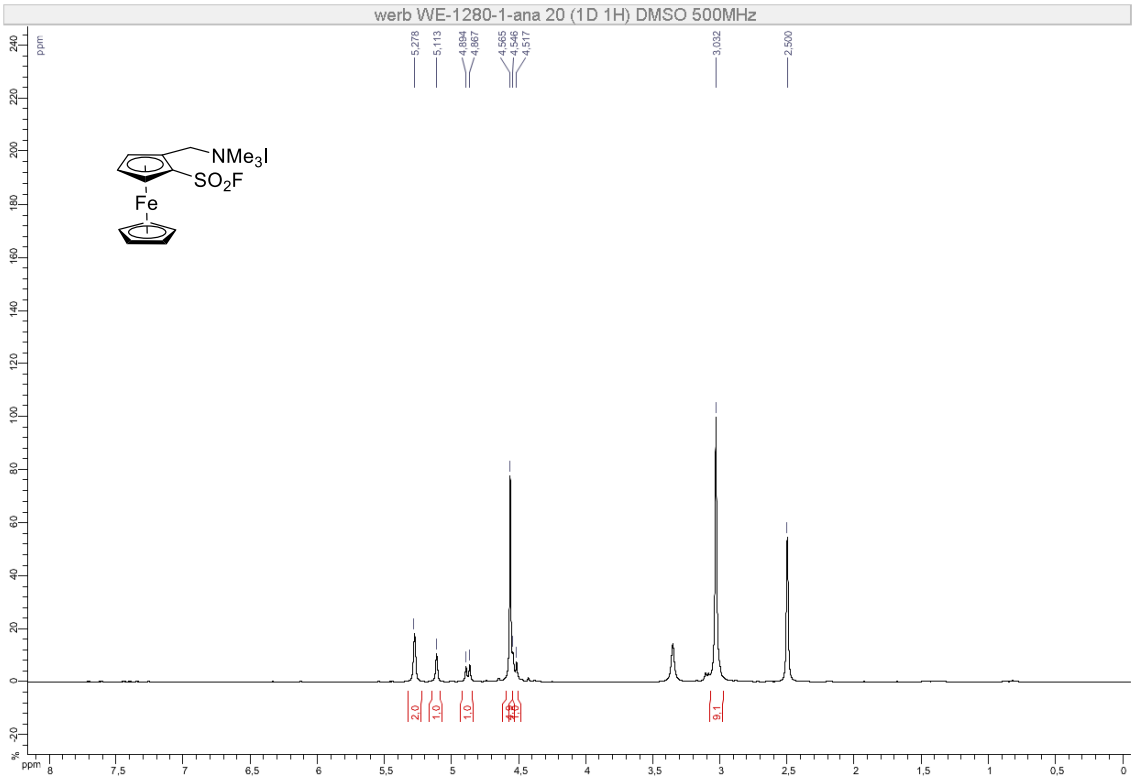


^{11}B NMR (160 MHz, $CDCl_3$)

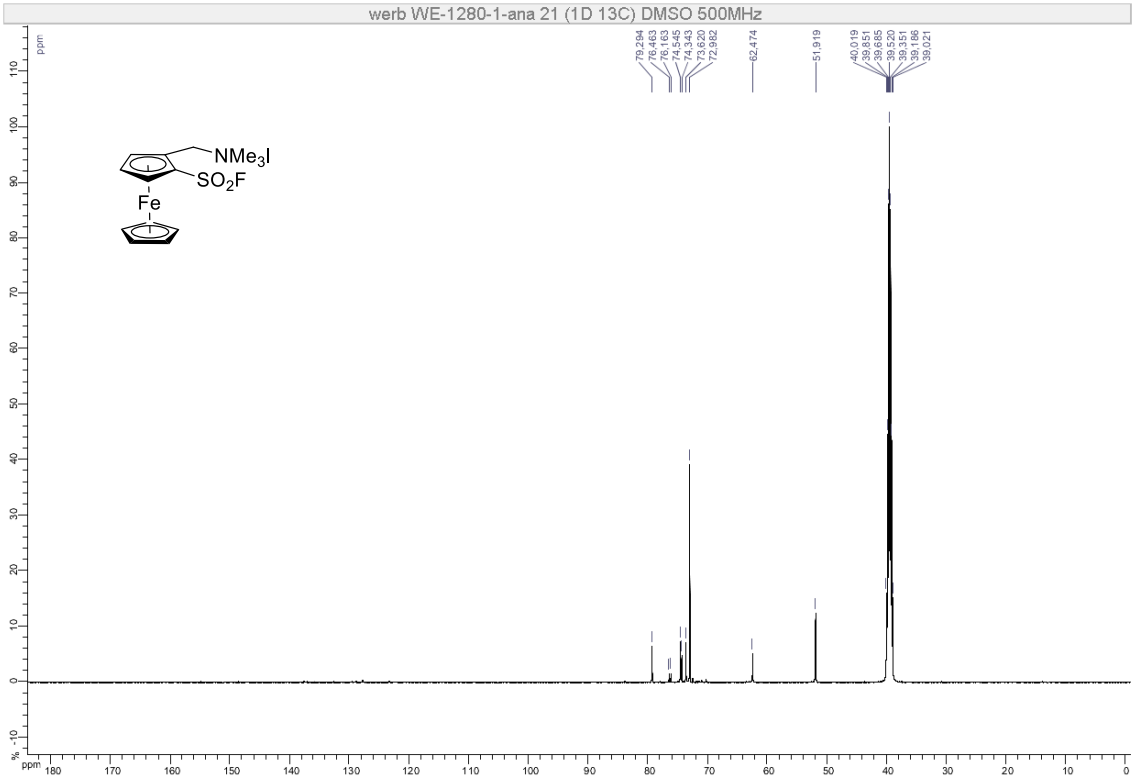


(2-(Fluorosulfonyl)ferrocenylmethyl)trimethylammonium iodide (21)

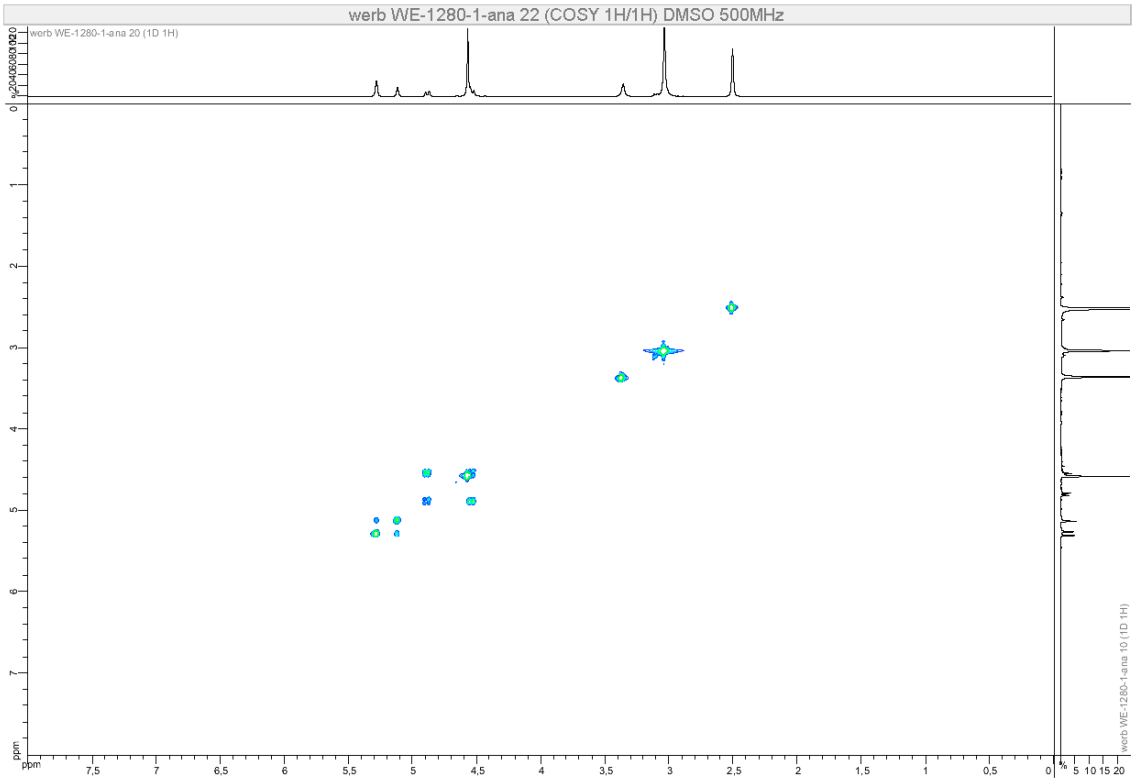
^{1}H NMR (500 MHz, DMSO-d_6)



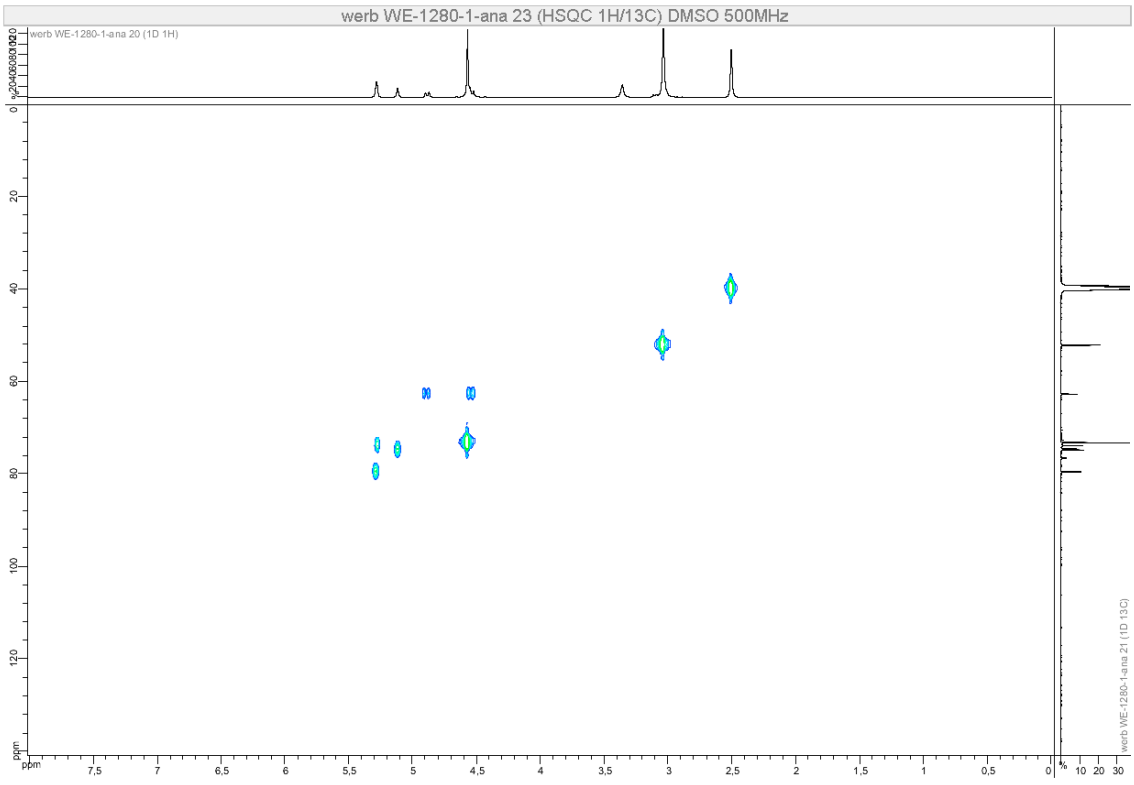
^{13}C NMR (125 MHz, DMSO-d_6)



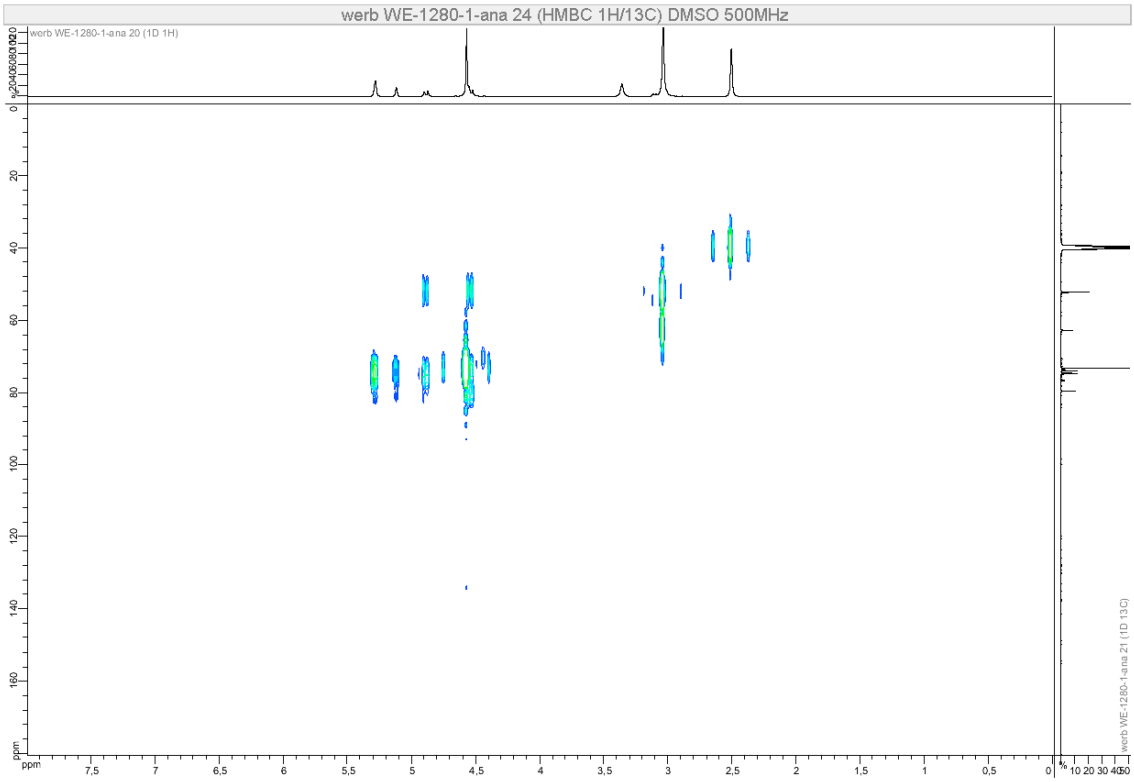
COSY (500 MHz, DMSO-d_6)



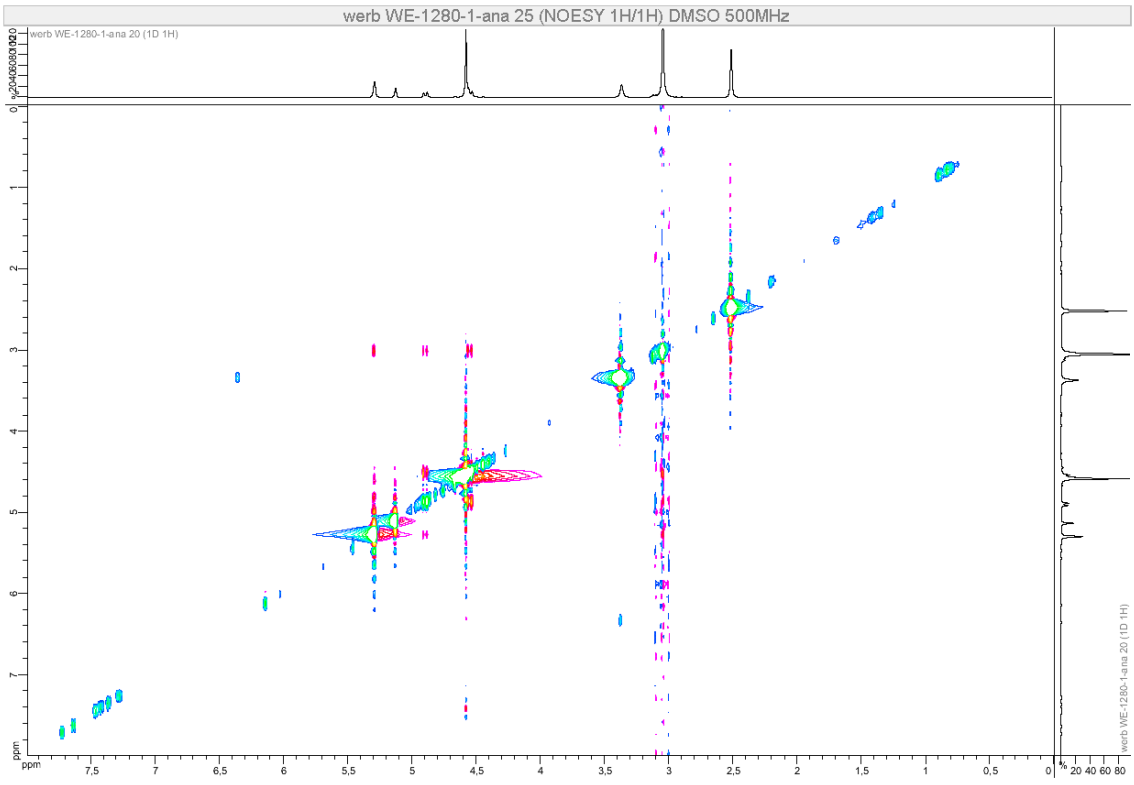
HSQC (500 MHz, DMSO-d_6)



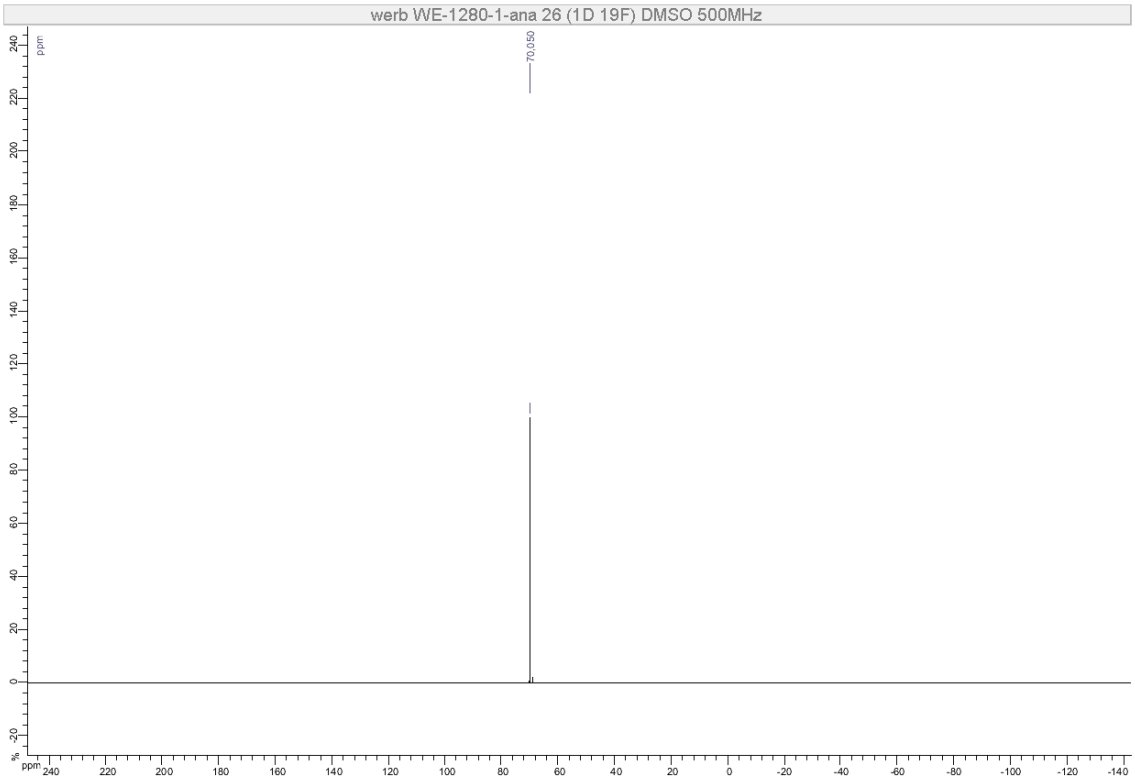
HMBC (500 MHz, DMSO-d_6)



NOESY (500 MHz, DMSO-d_6)

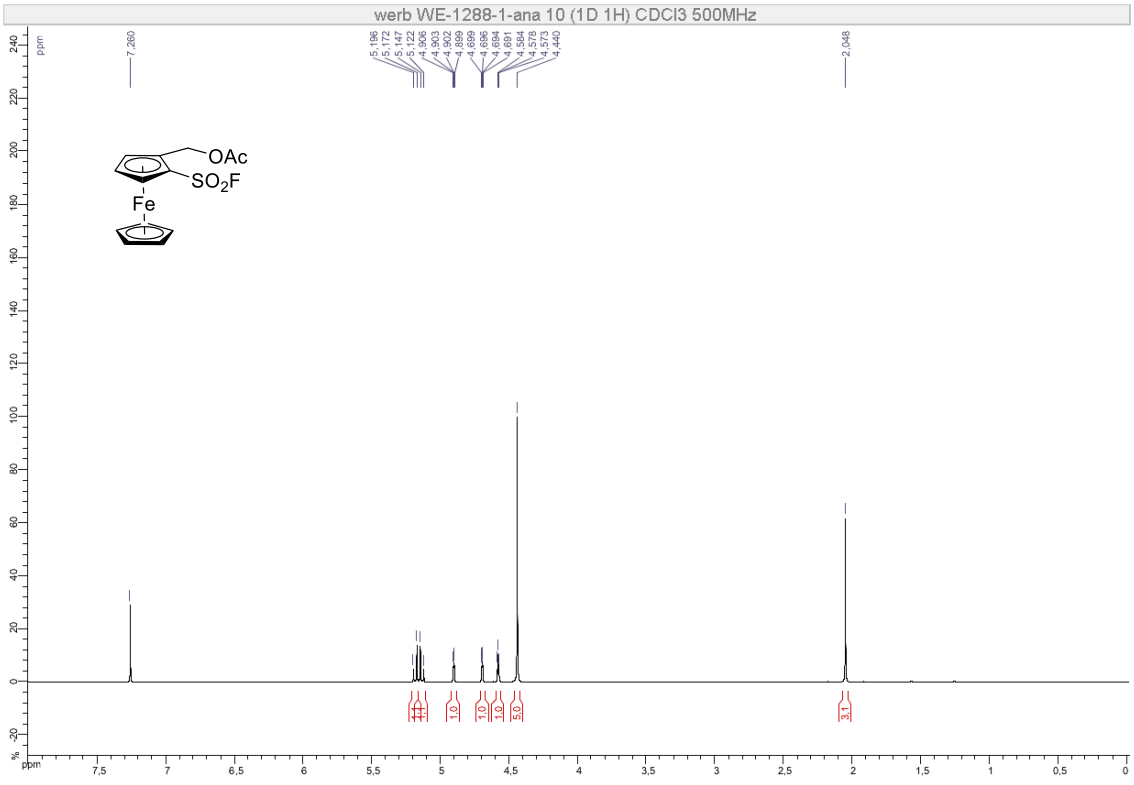


^{19}F NMR (470 MHz, DMSO-d_6)

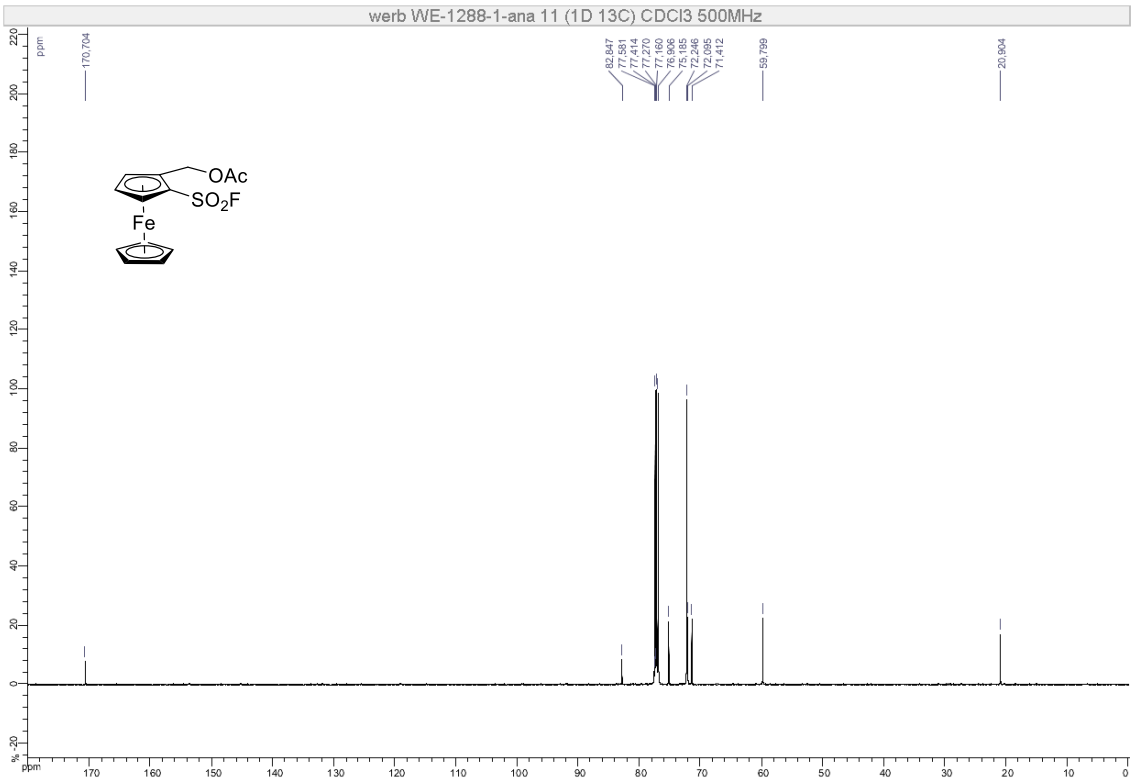


2-(Acetoxymethyl)ferrocenesulfonyl fluoride (22a)

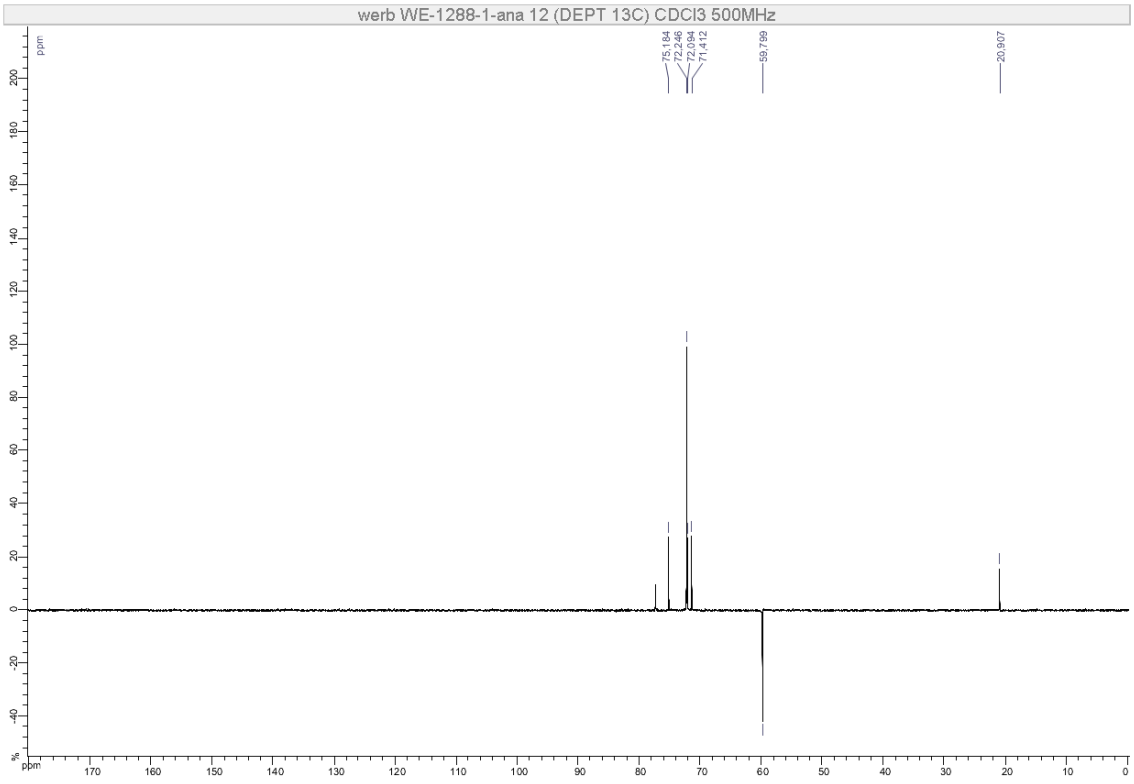
^{1}H NMR (500 MHz, $CDCl_3$)



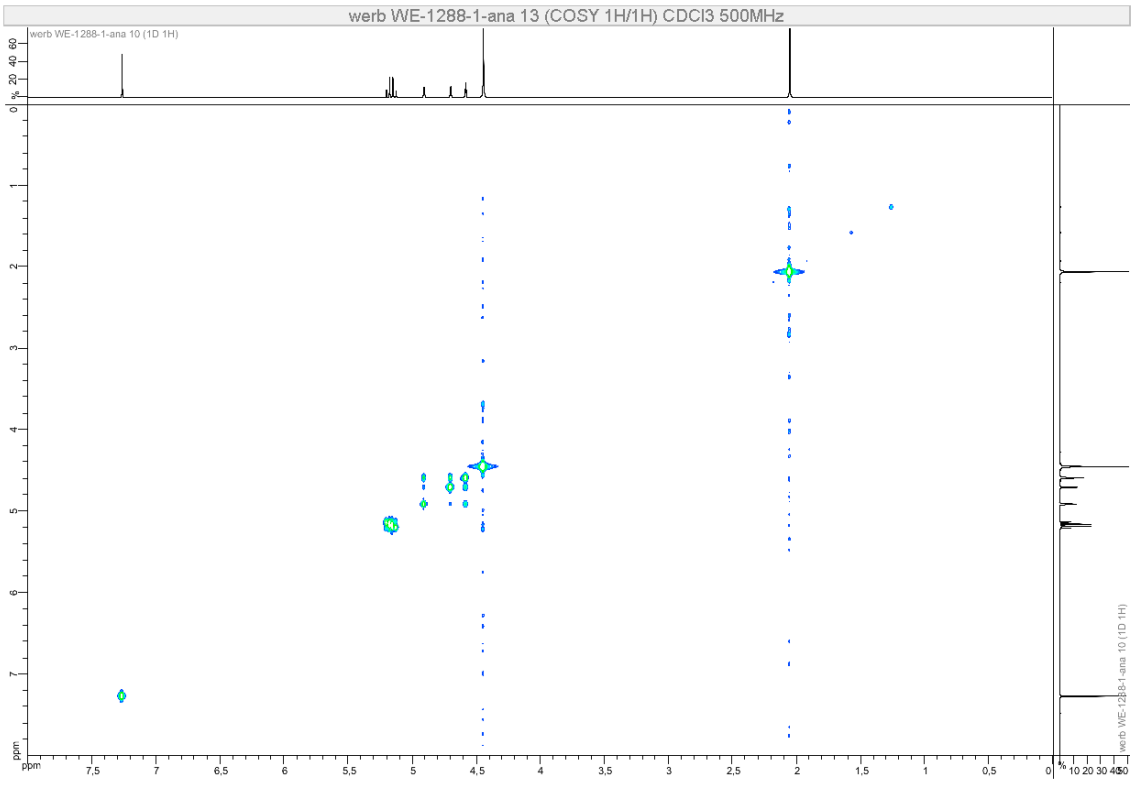
^{13}C NMR (125 MHz, $CDCl_3$)



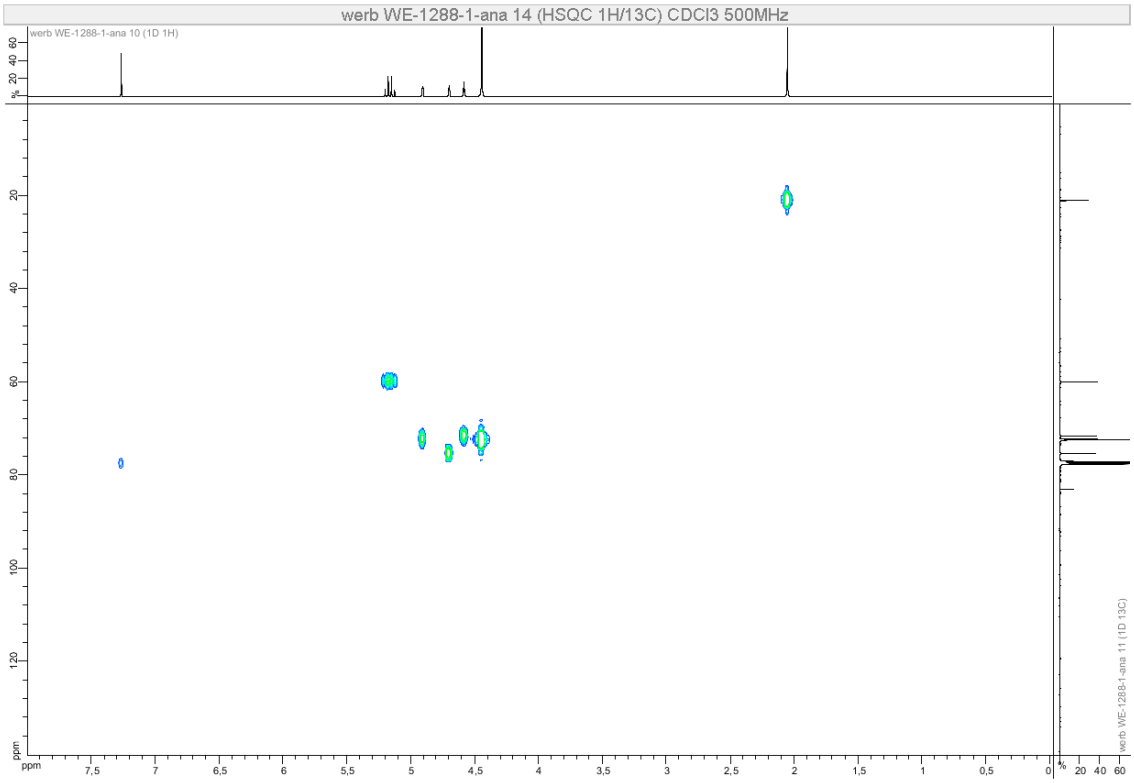
DEPT 135 (125 MHz, $CDCl_3$)



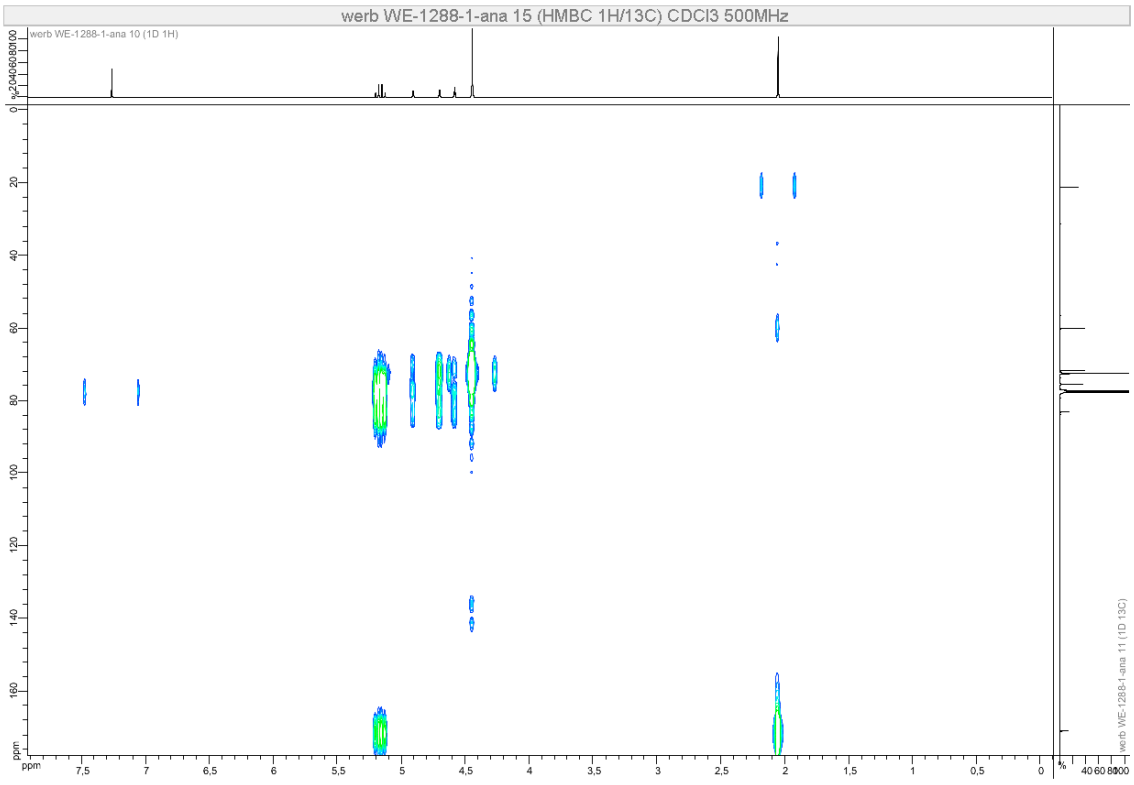
COSY (500 MHz, $CDCl_3$)



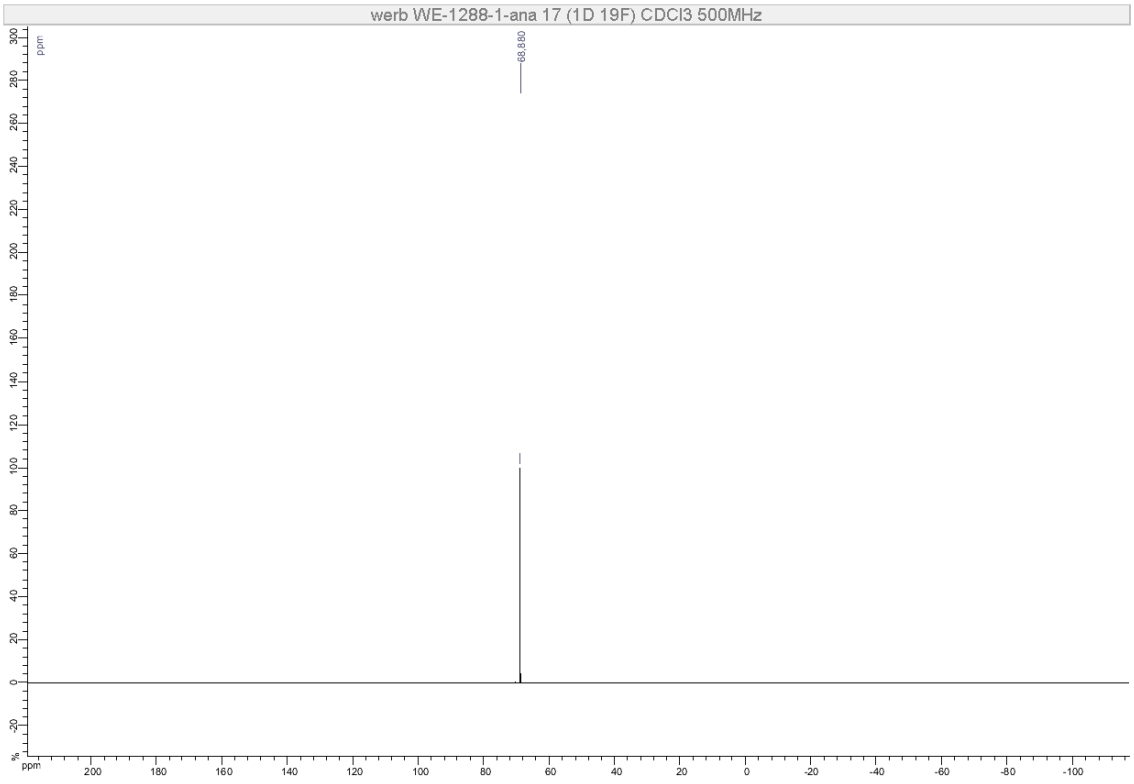
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

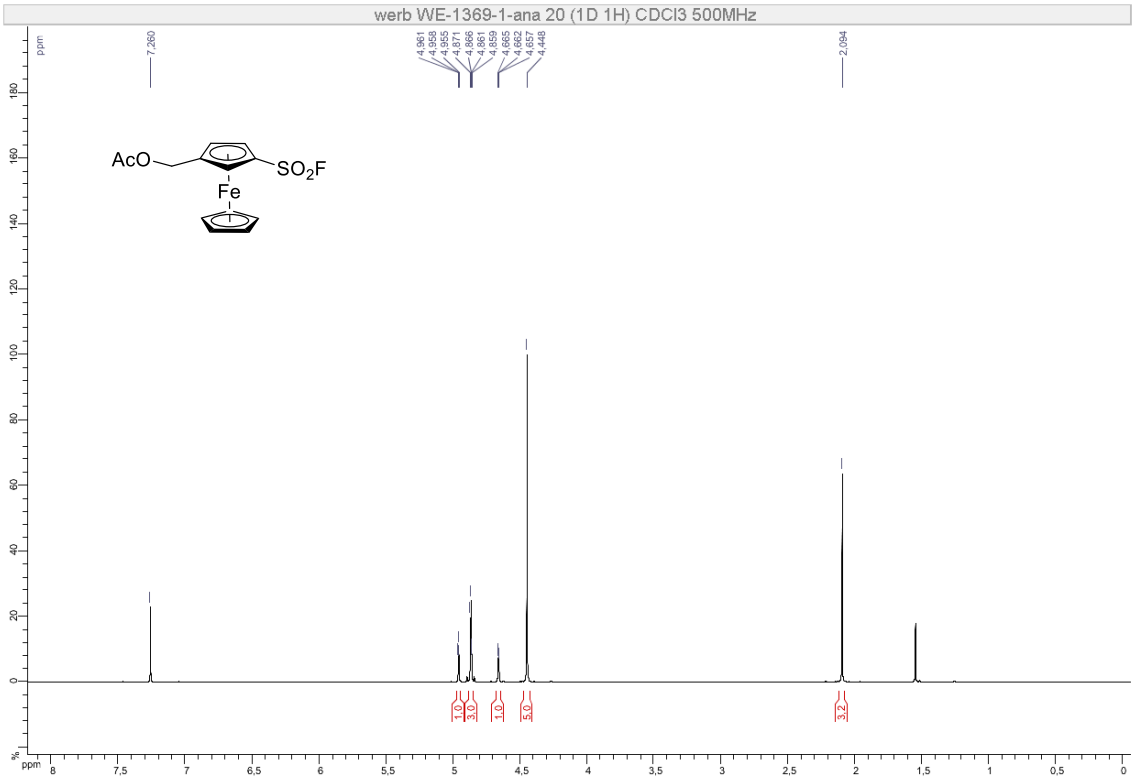


^{19}F NMR (470 MHz, $CDCl_3$)

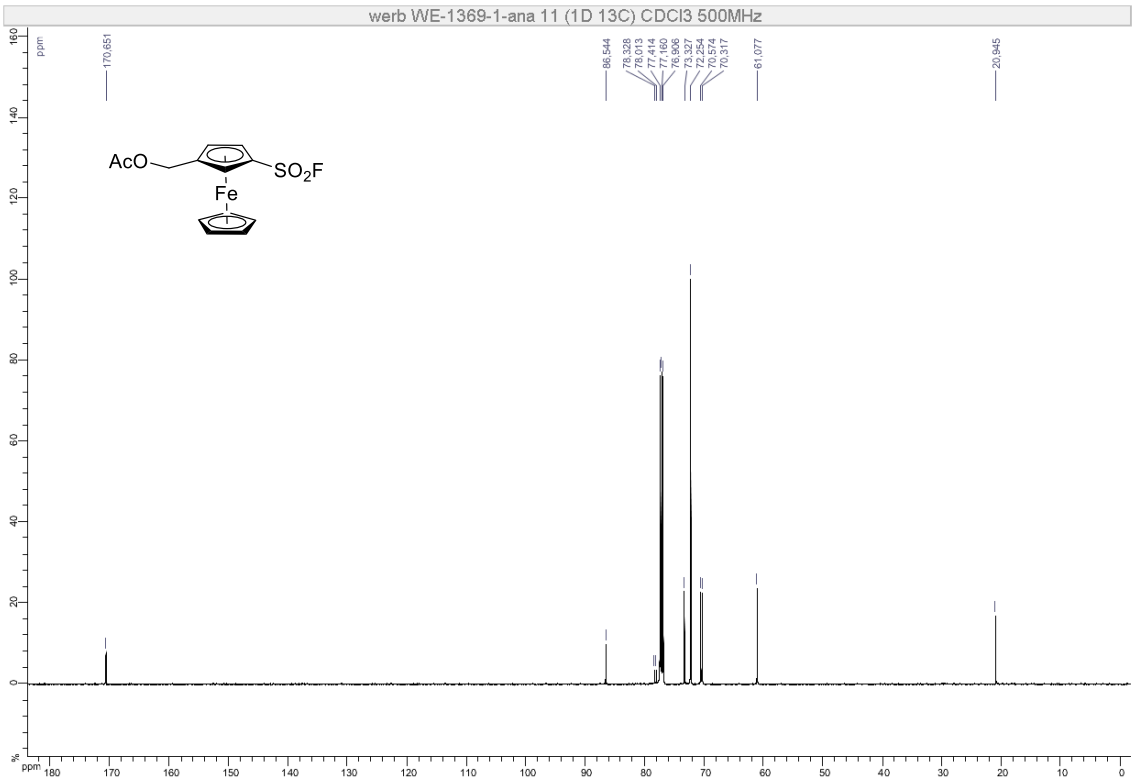


3-(Acetoxymethyl)ferrocenesulfonyl fluoride (22b)

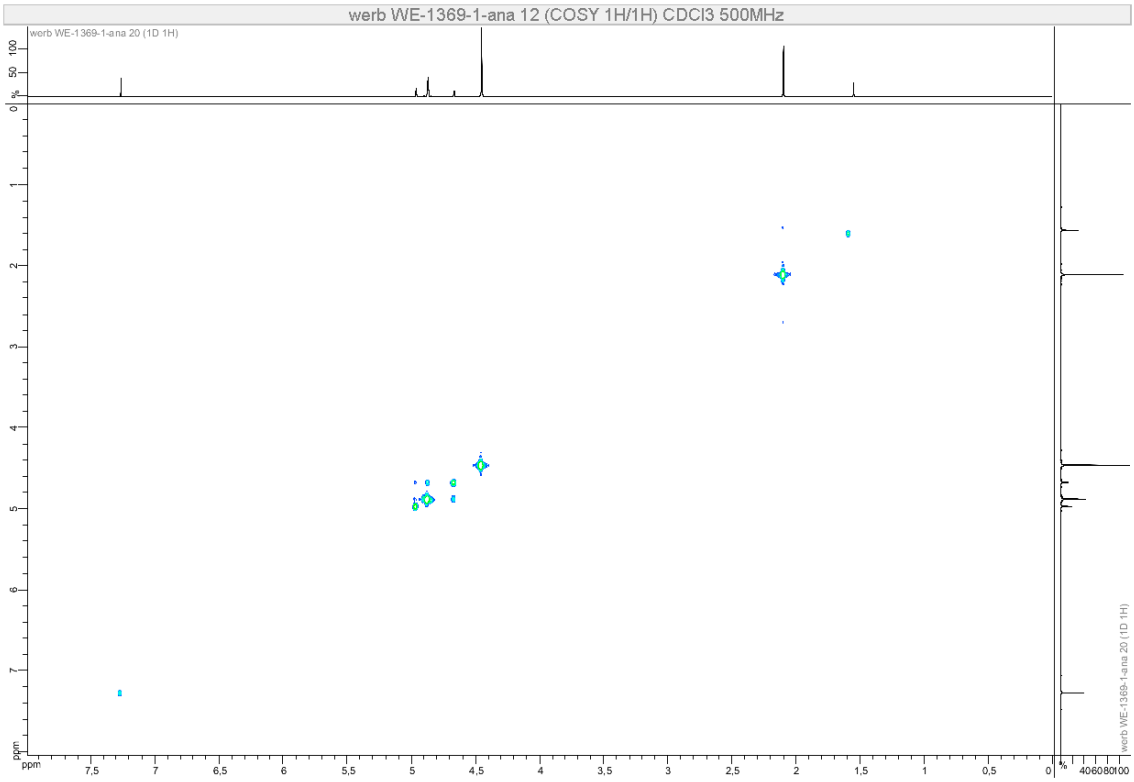
^{1}H NMR (500 MHz, $CDCl_3$)



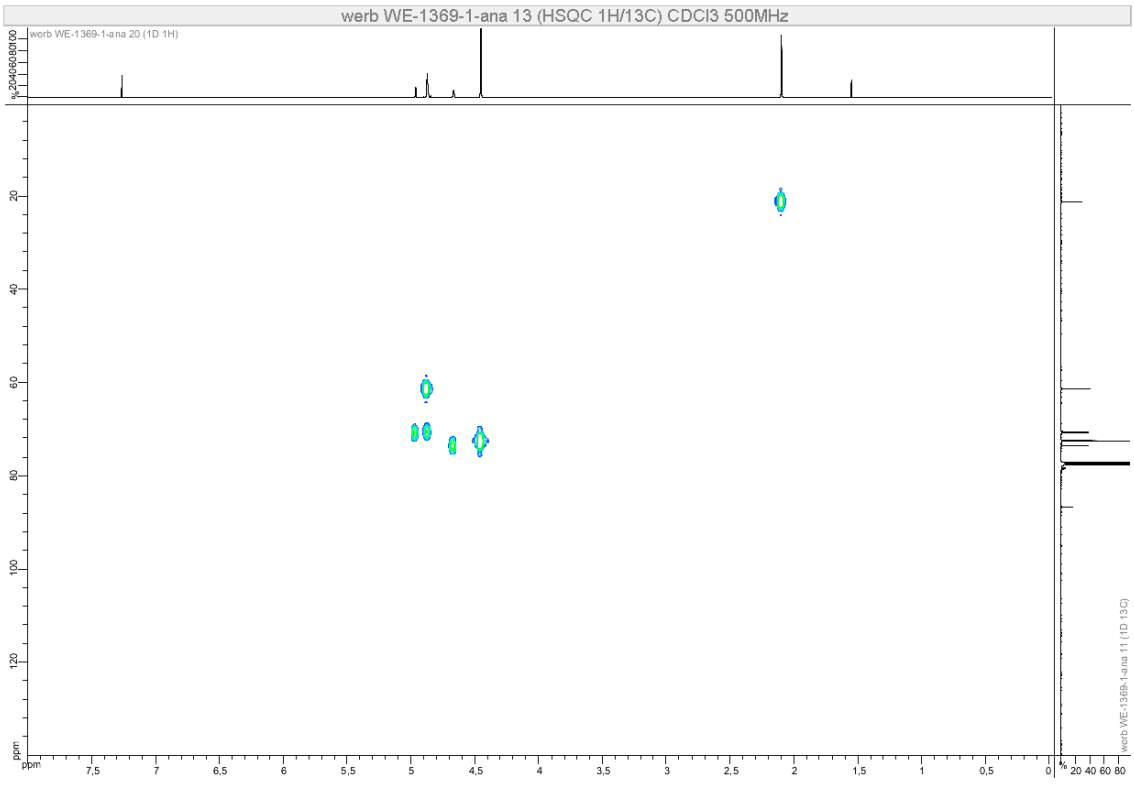
^{13}C NMR (125 MHz, $CDCl_3$)



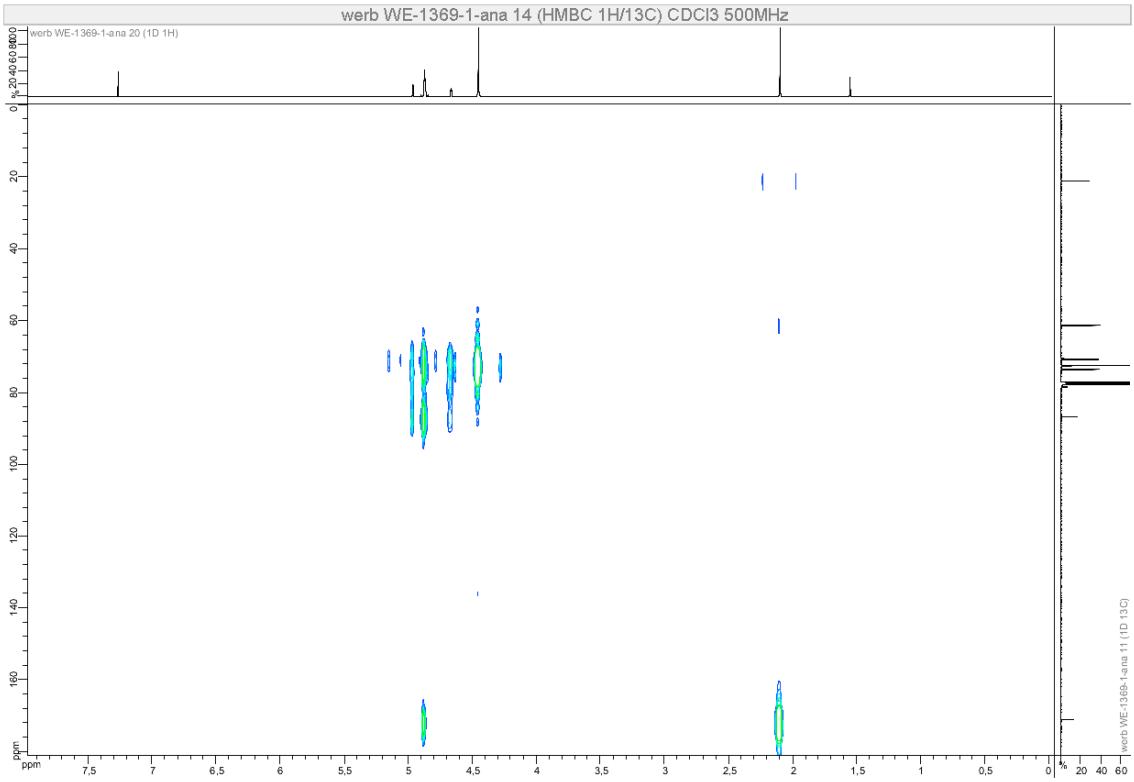
COSY (500 MHz, $CDCl_3$)



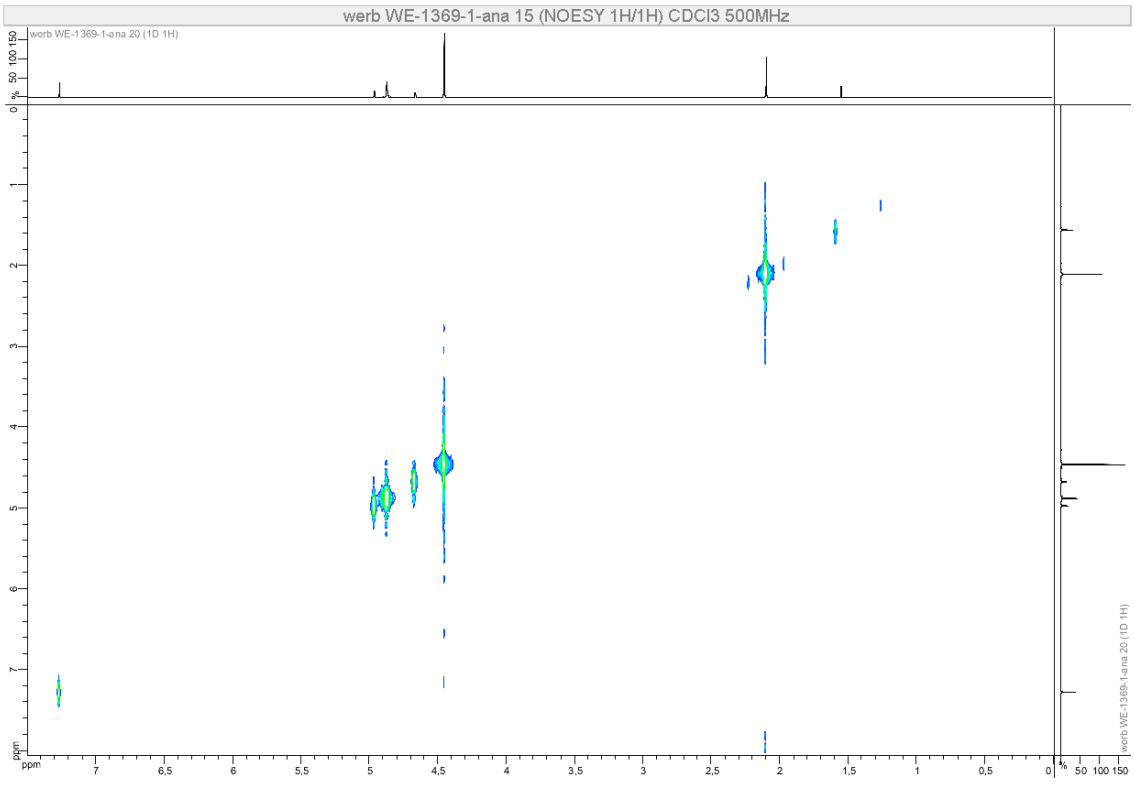
HSQC (500 MHz, $CDCl_3$)



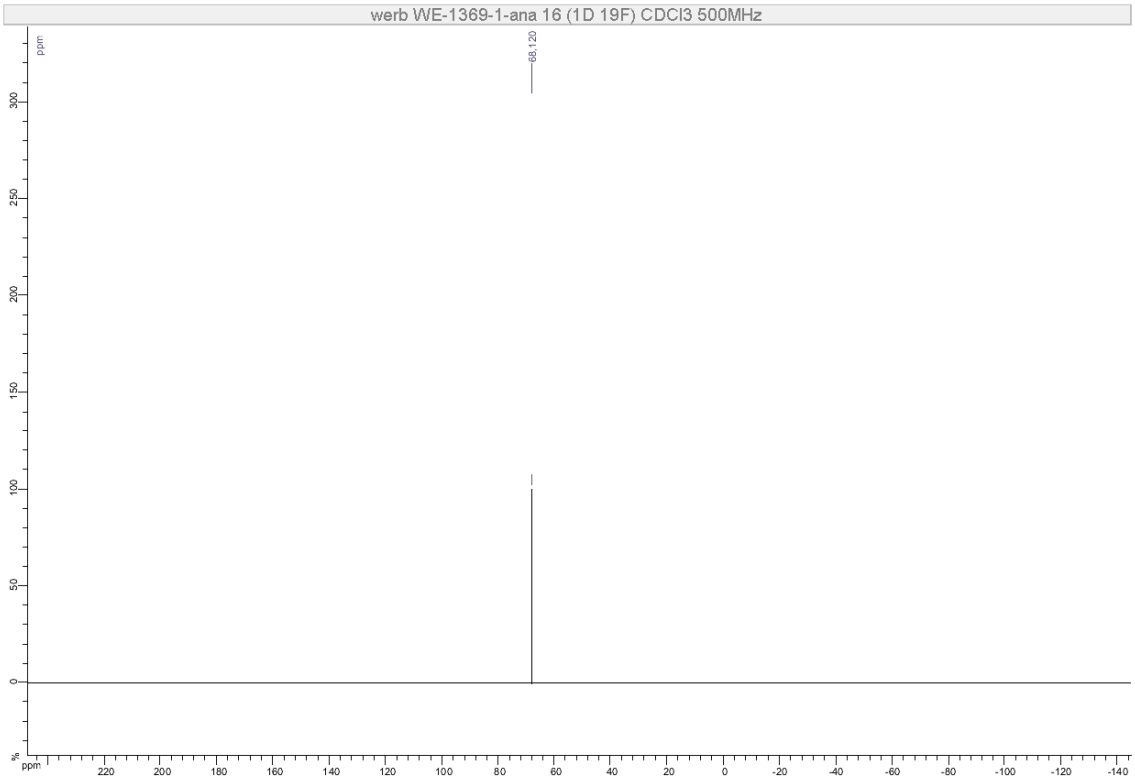
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

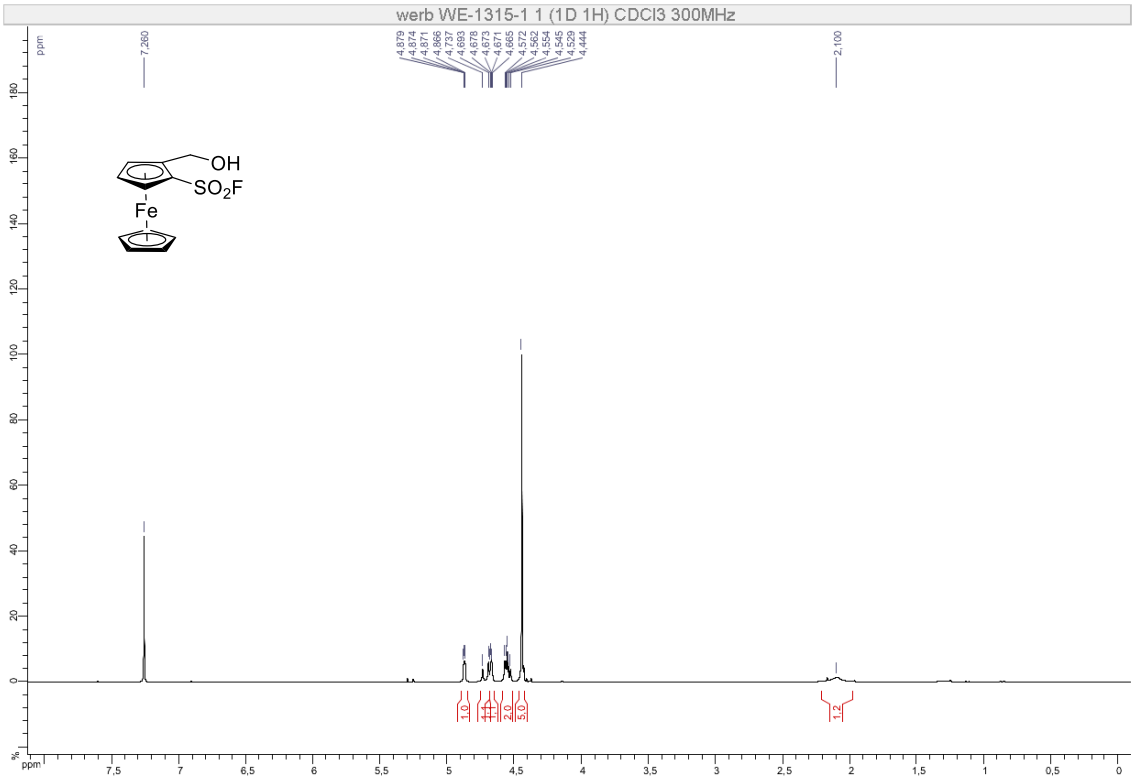


^{19}F NMR (470 MHz, $CDCl_3$)

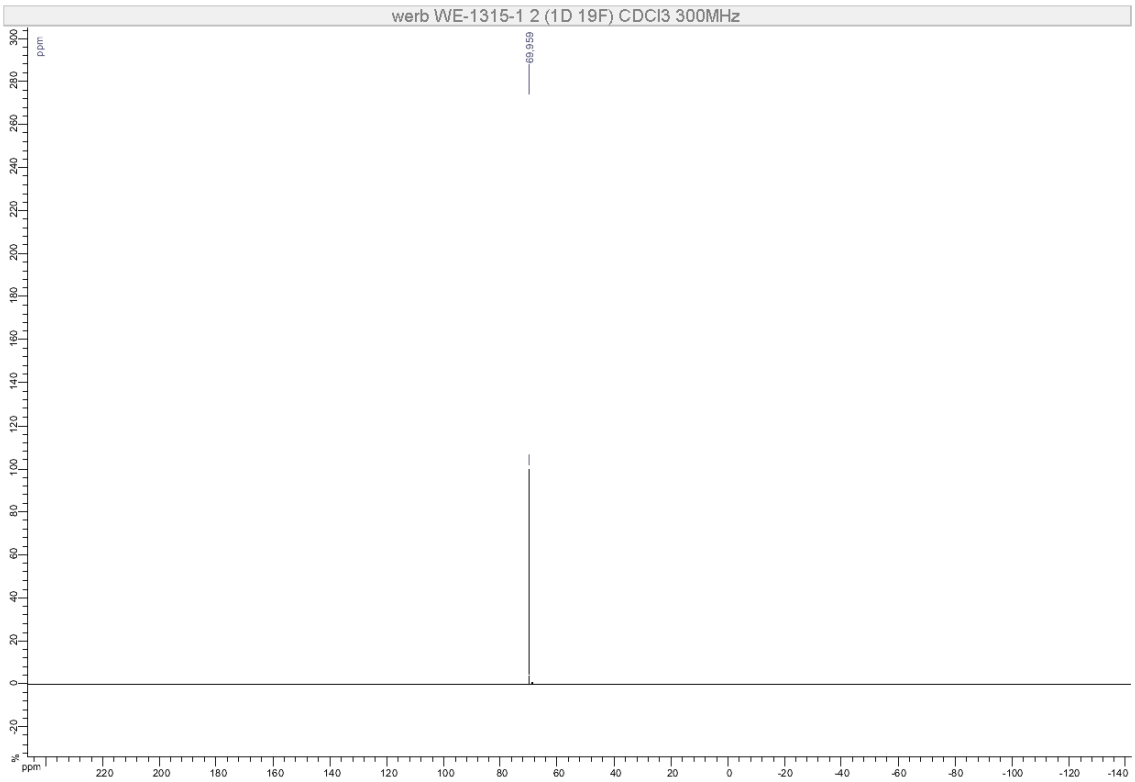


2-(Hydromethyl)ferrocenesulfonyl fluoride (23)

^{1}H NMR (300 MHz, $CDCl_3$)

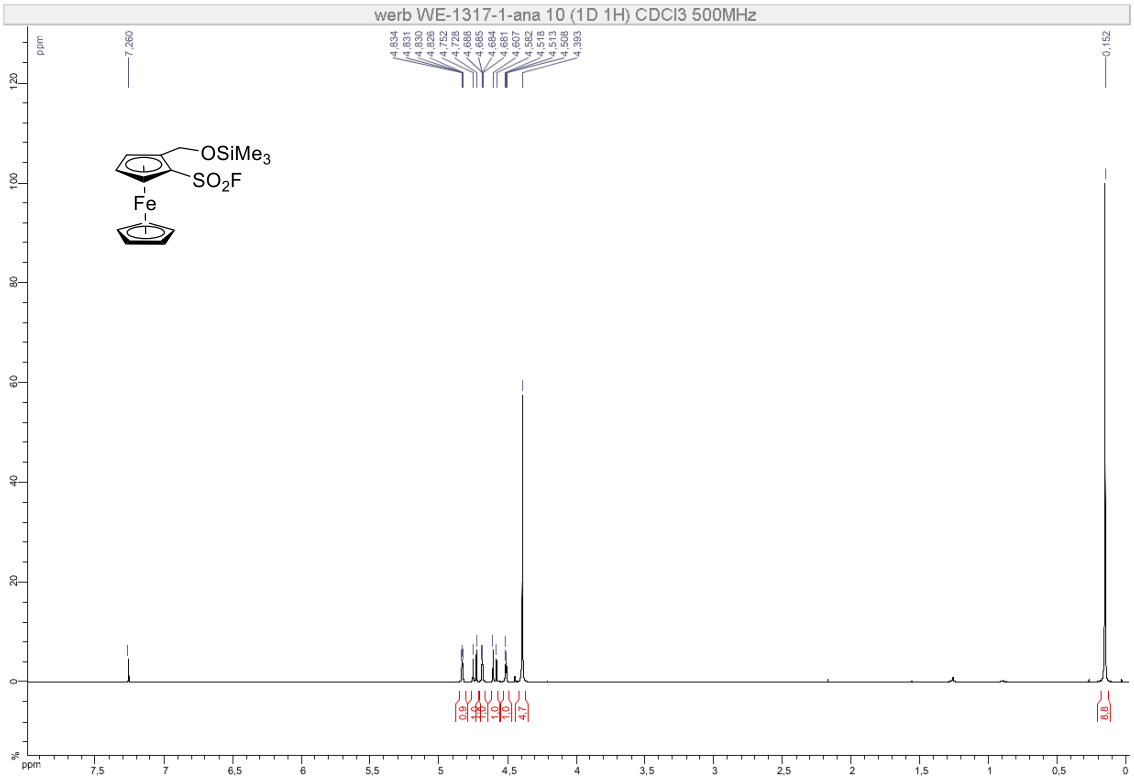


^{19}F NMR (282 MHz, $CDCl_3$)

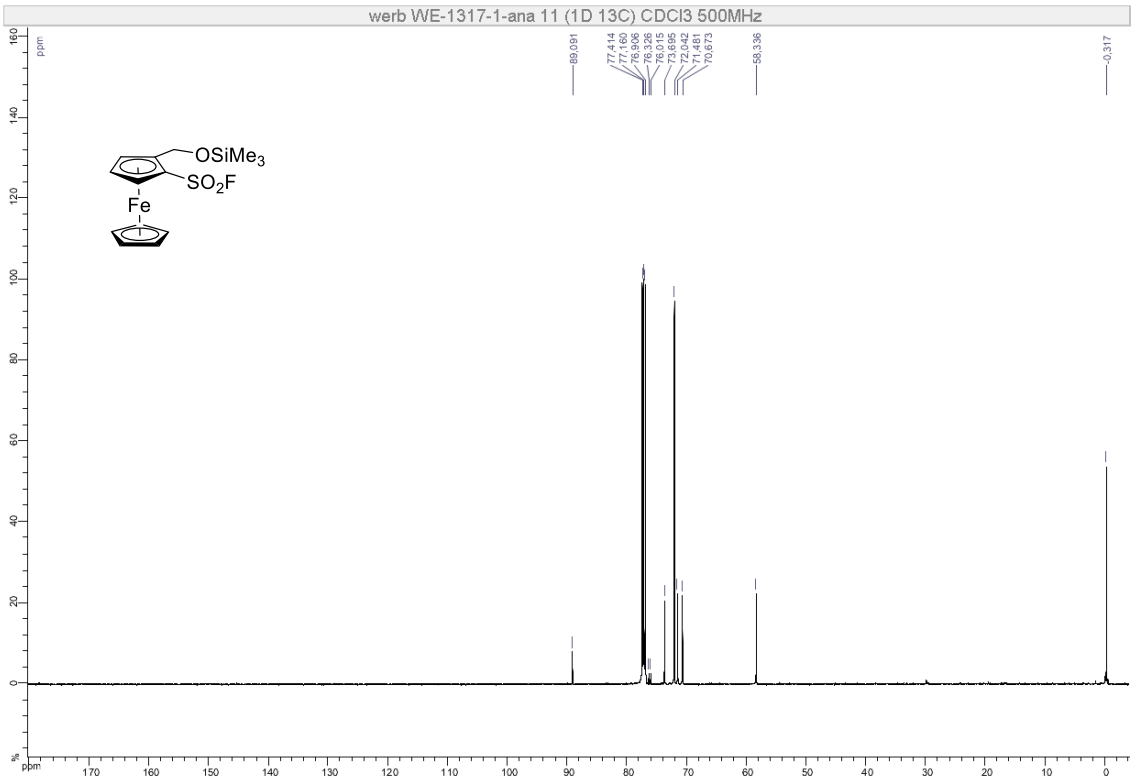


2-(Trimethylsilyloxy)methylferrocenesulfonyl fluoride (24a)

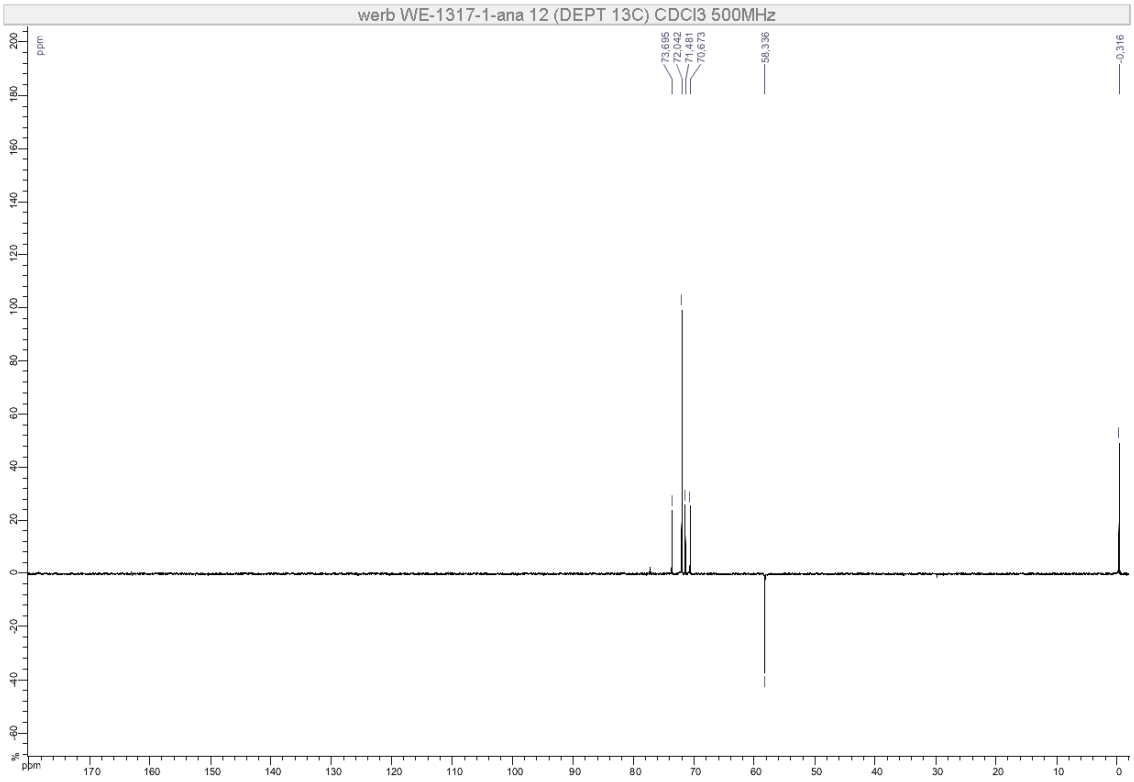
^{1}H NMR (500 MHz, $CDCl_3$)



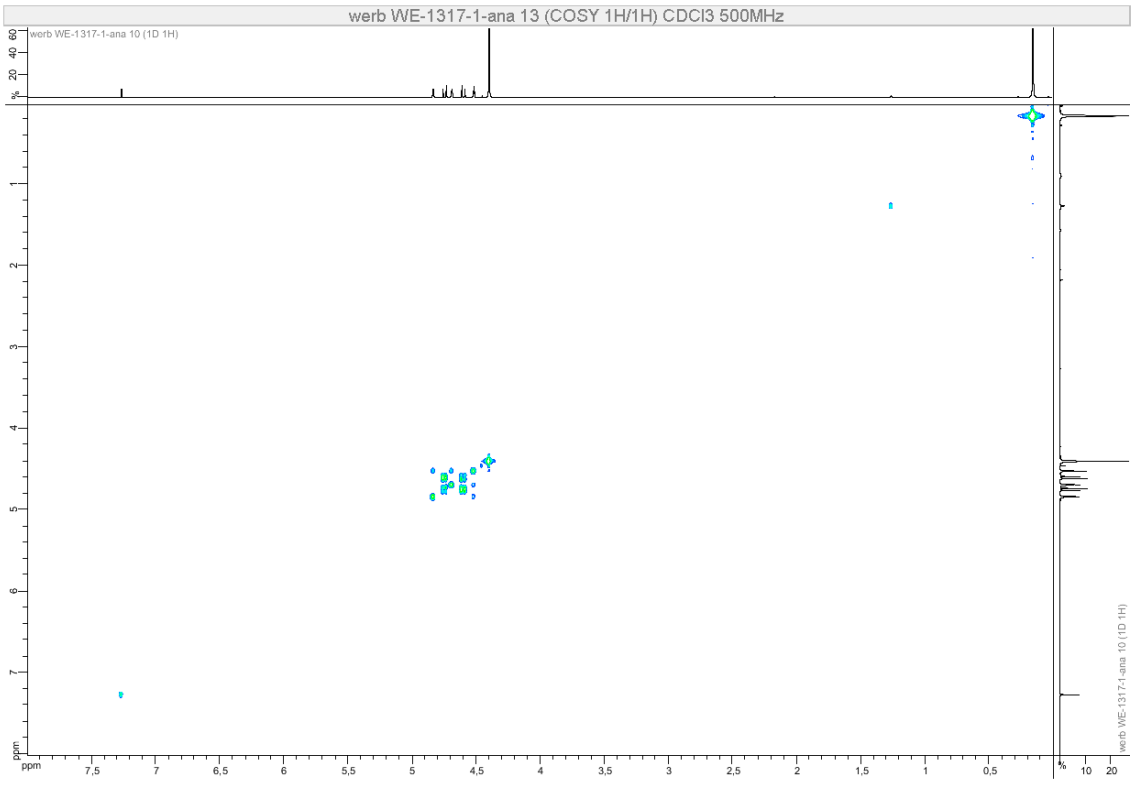
^{13}C NMR (125 MHz, $CDCl_3$)



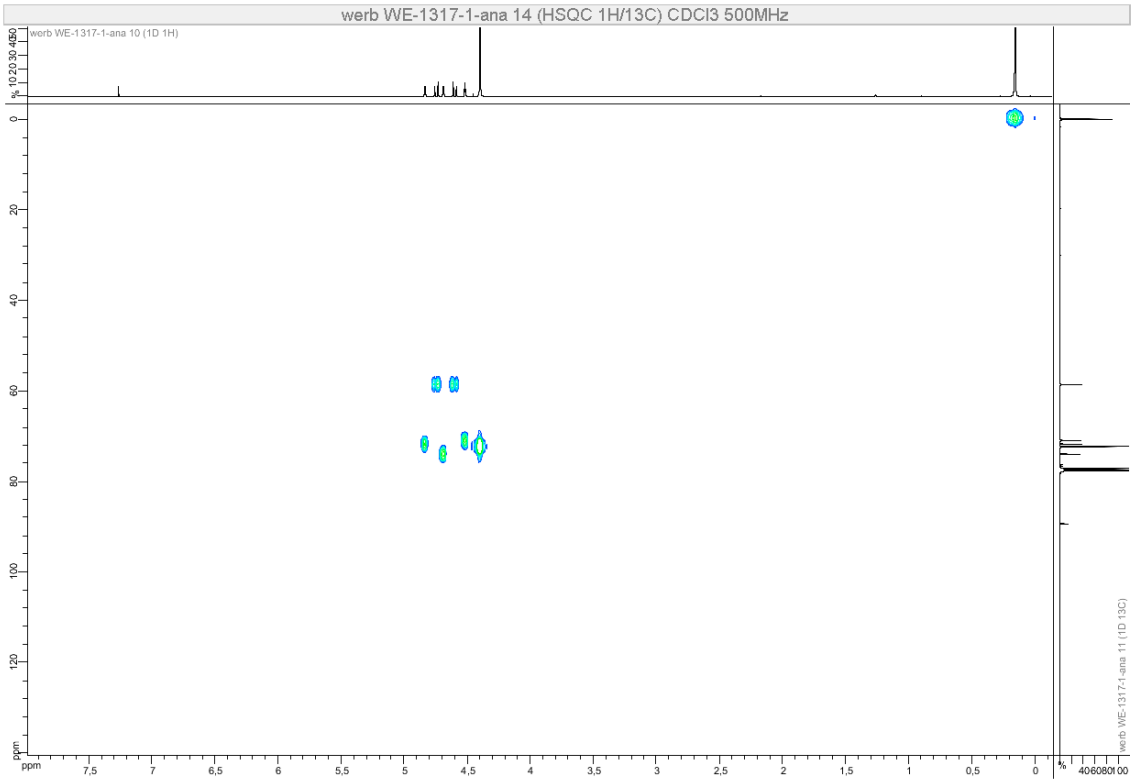
DEPT 135 (125 MHz, $CDCl_3$)



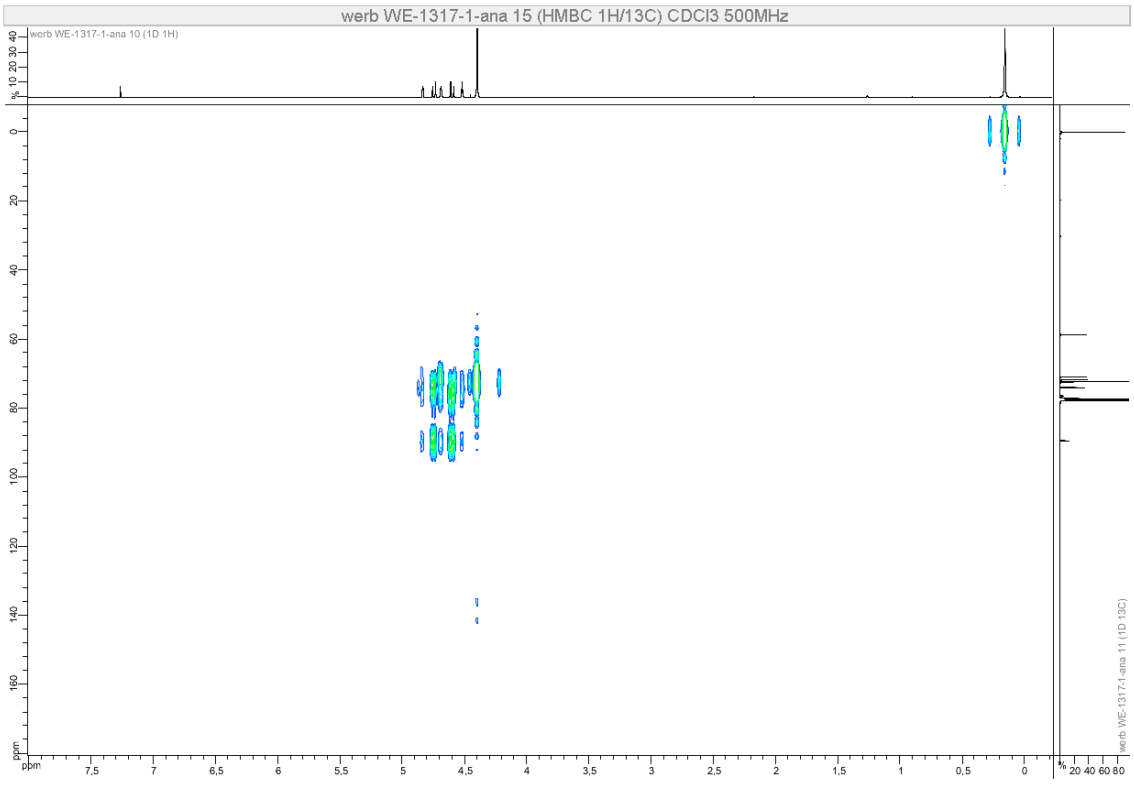
COSY (500 MHz, $CDCl_3$)



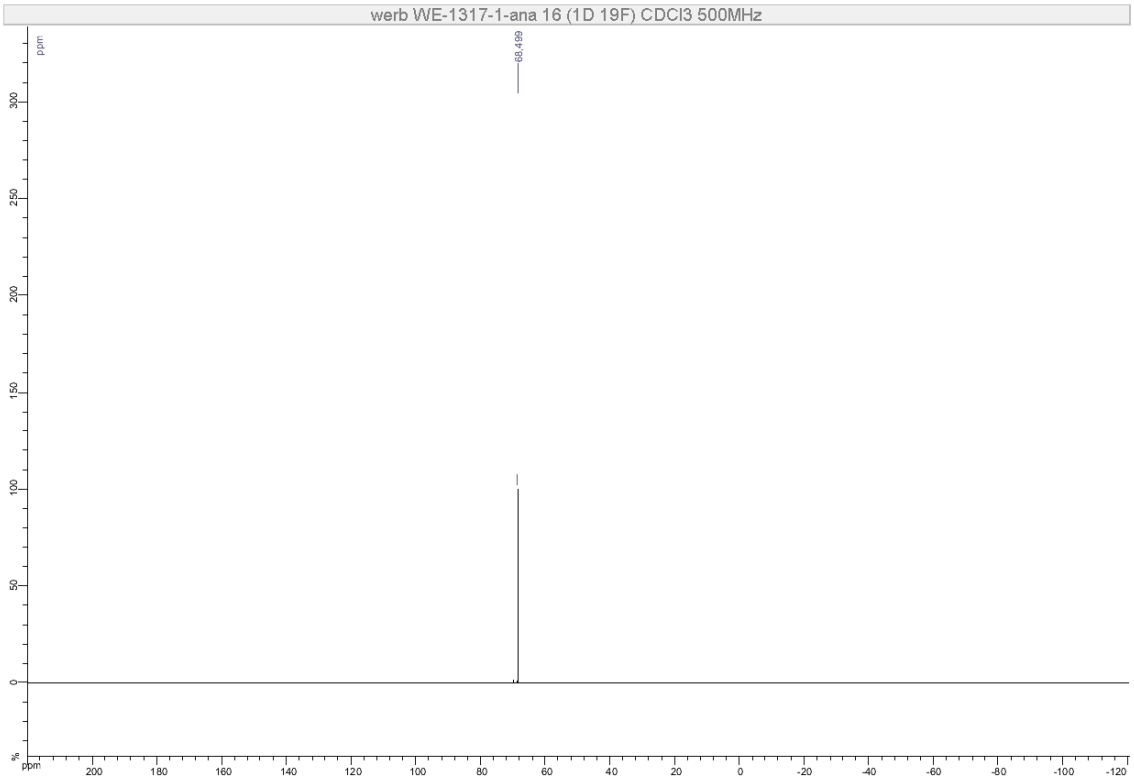
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

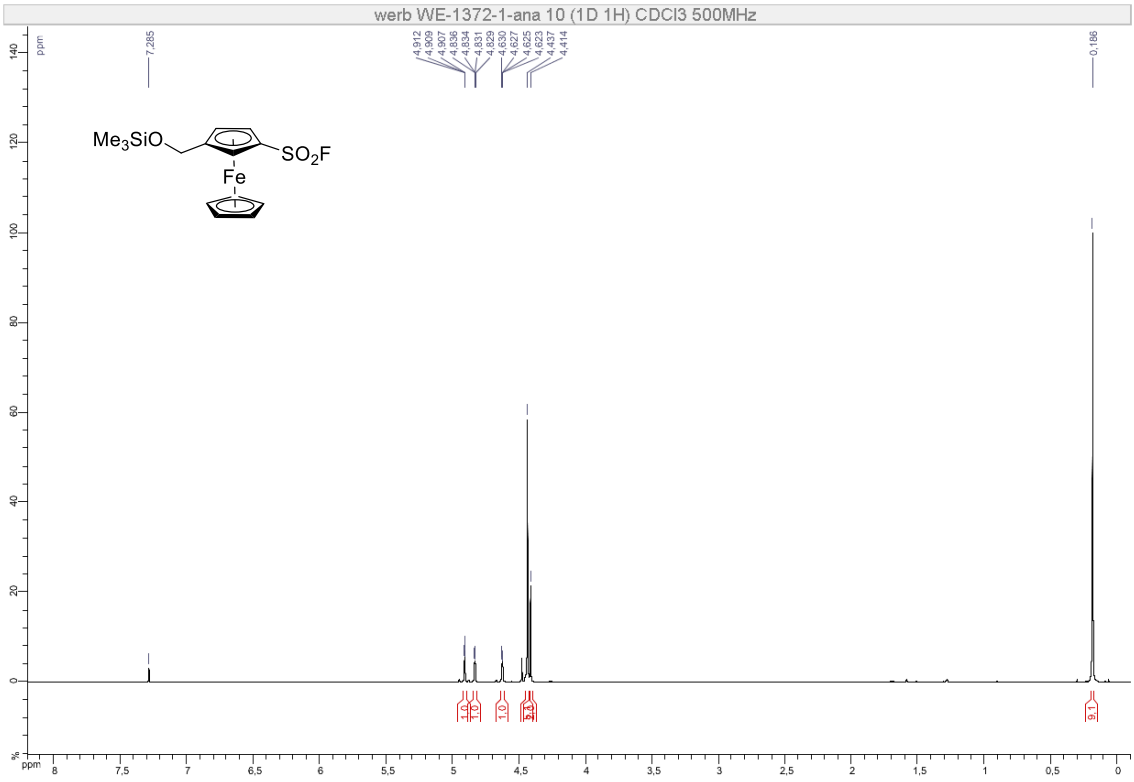


^{19}F NMR (470 MHz, $CDCl_3$)

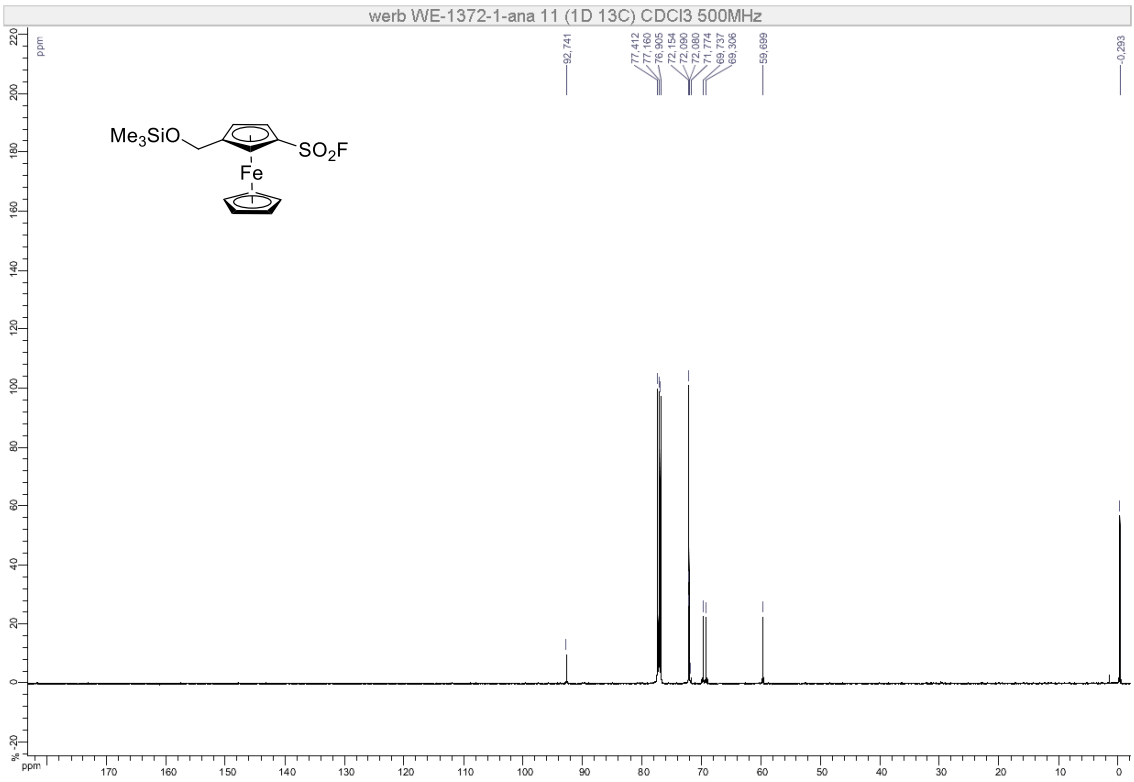


3-(Trimethylsilyloxy)methylferrocenesulfonyl fluoride (24b)

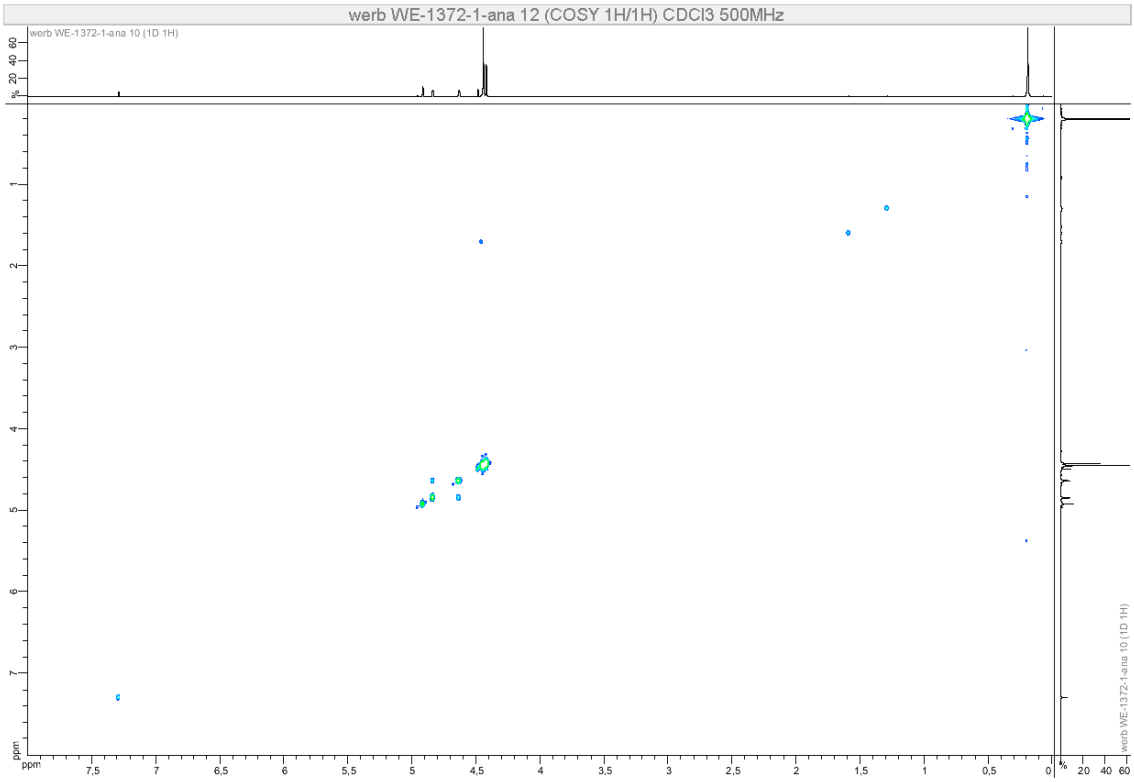
^{1}H NMR (500 MHz, $CDCl_3$)



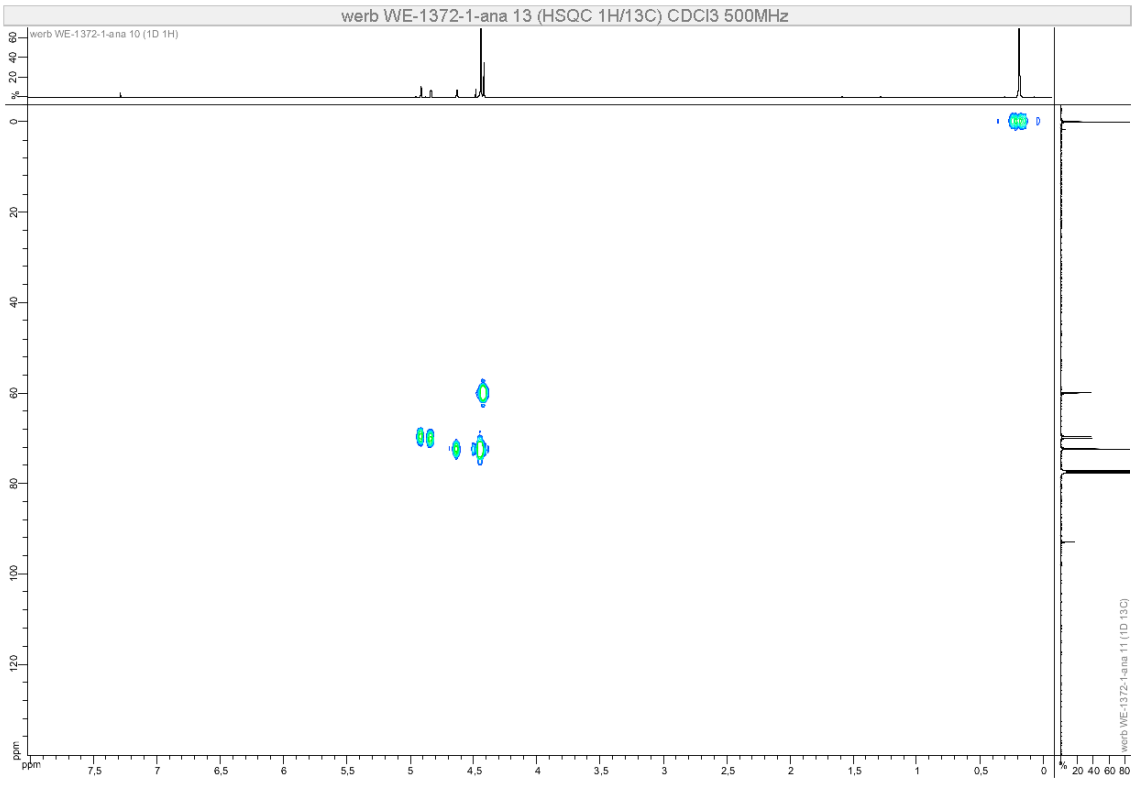
^{13}C NMR (125 MHz, $CDCl_3$)



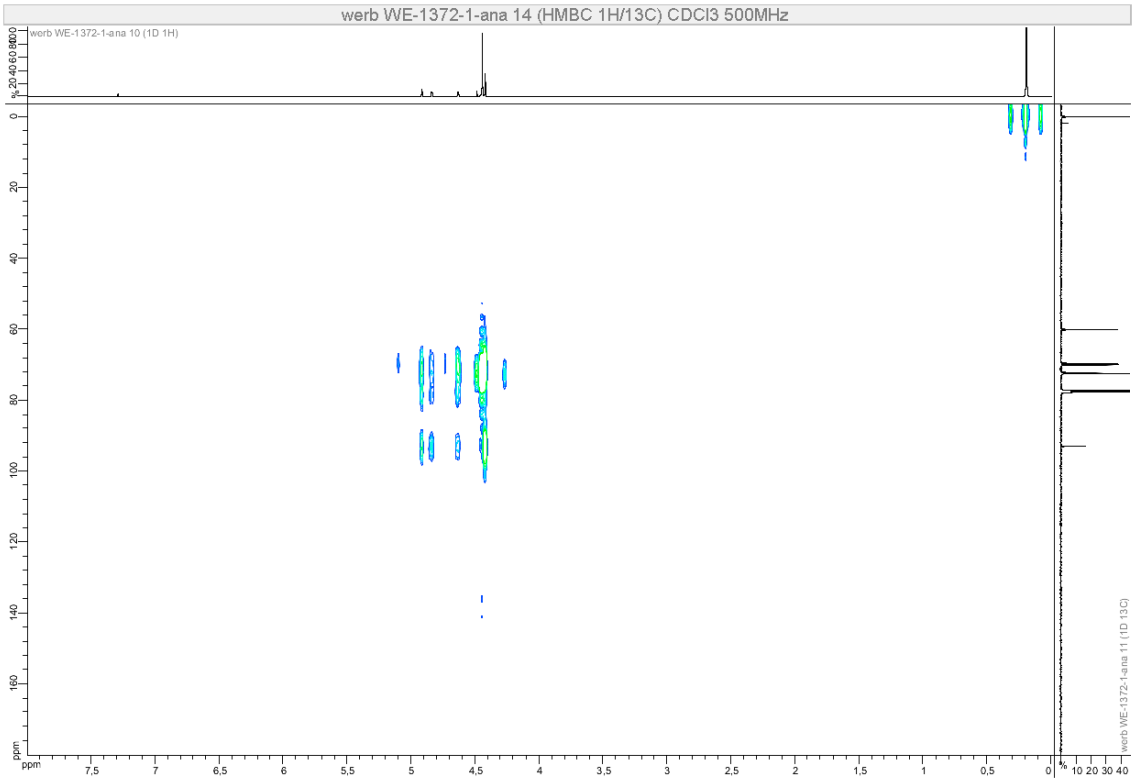
COSY (500 MHz, $CDCl_3$)



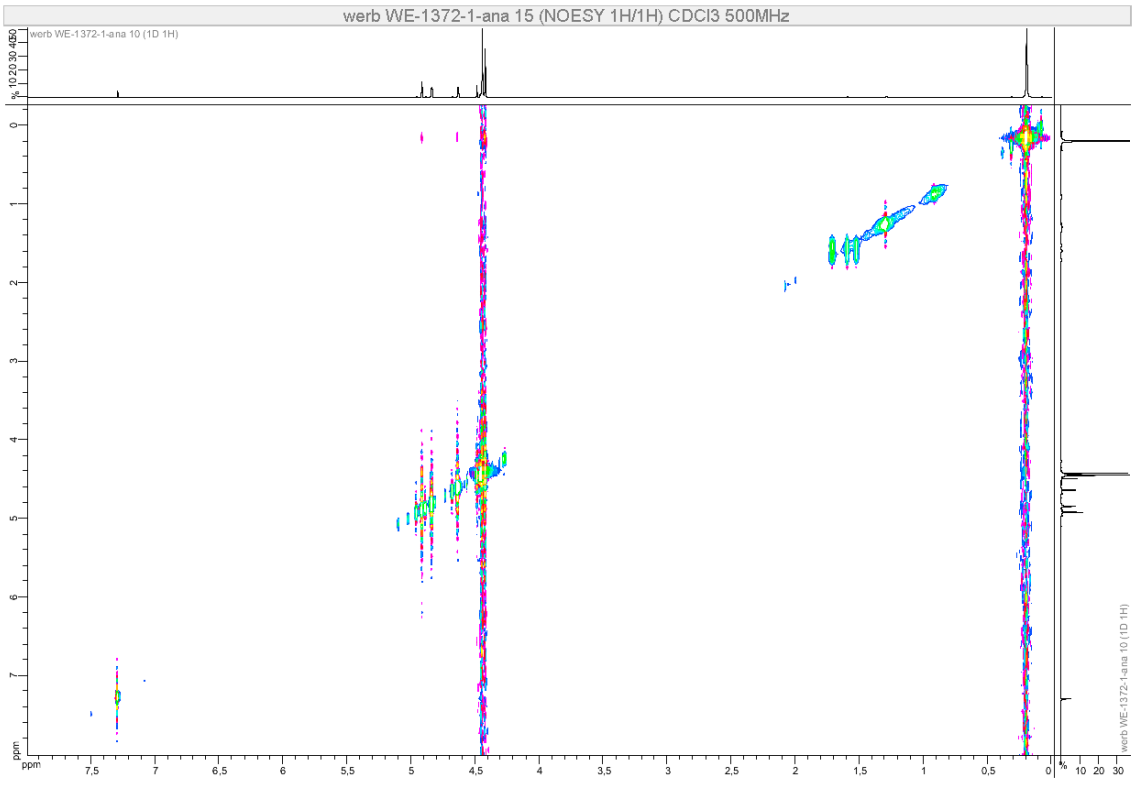
HSQC (500 MHz, $CDCl_3$)



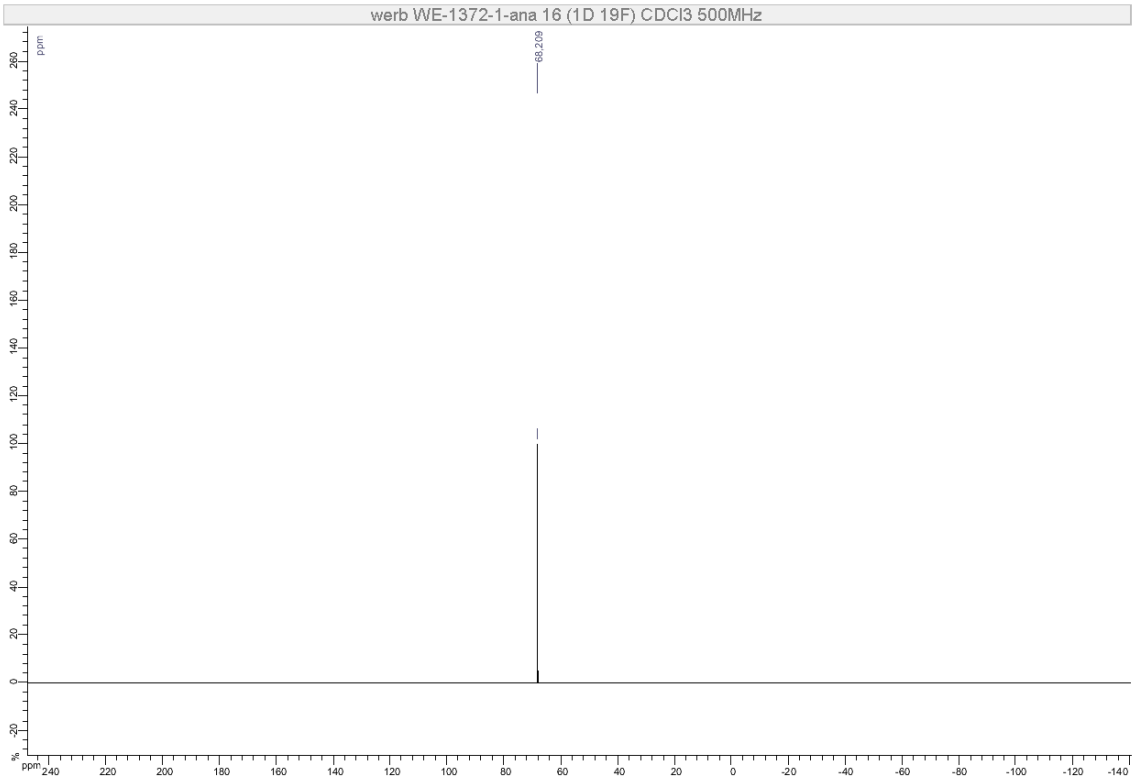
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

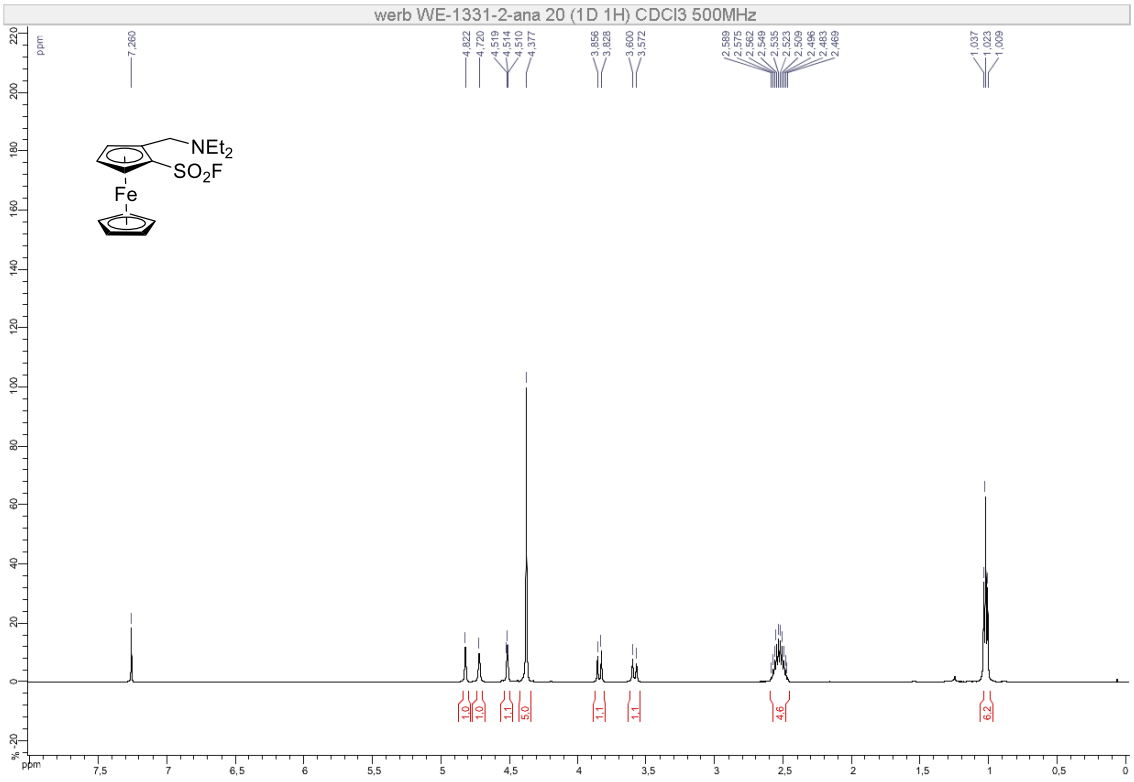


^{19}F NMR (470 MHz, $CDCl_3$)

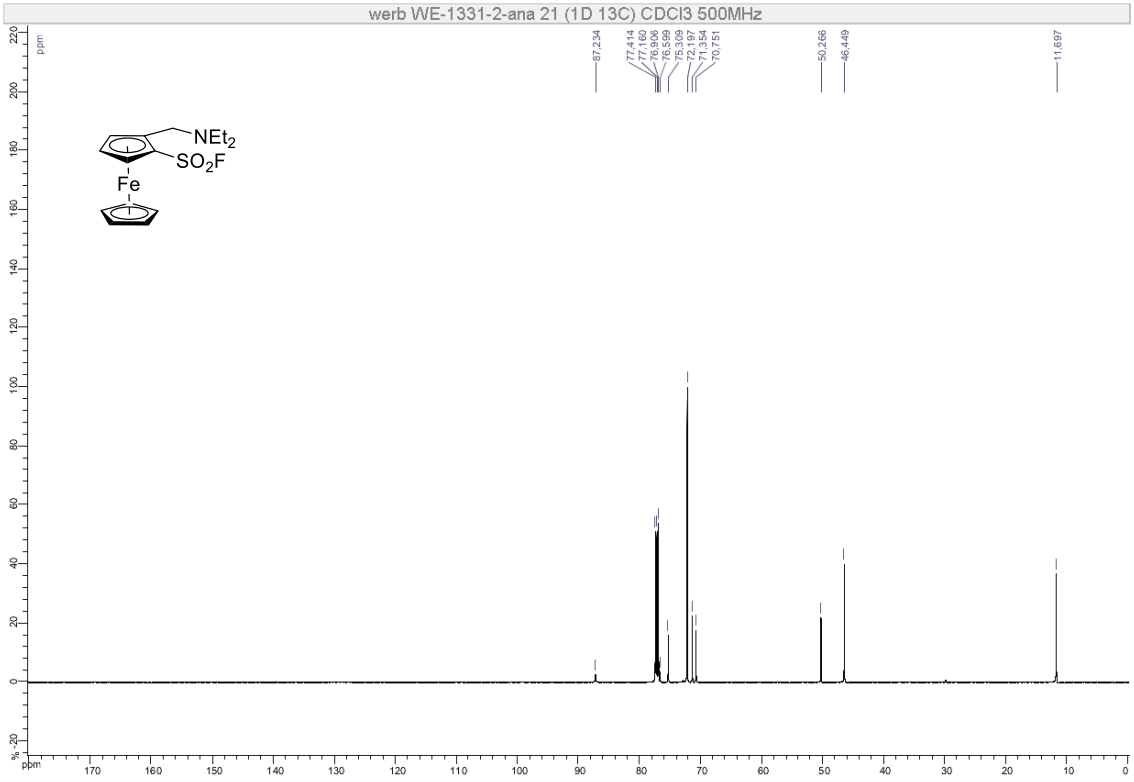


2-(*N*,*N*-Diethylaminomethyl)ferrocenesulfonyl fluoride (25)

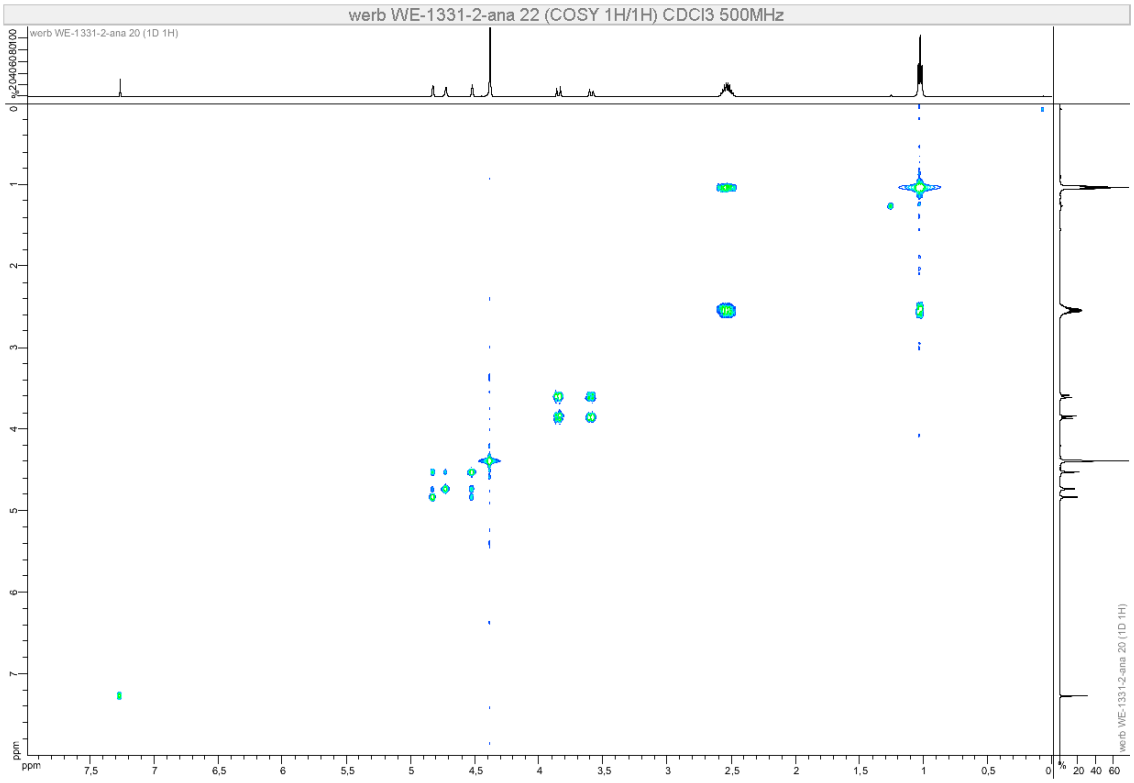
^{1}H NMR (500 MHz, $CDCl_3$)



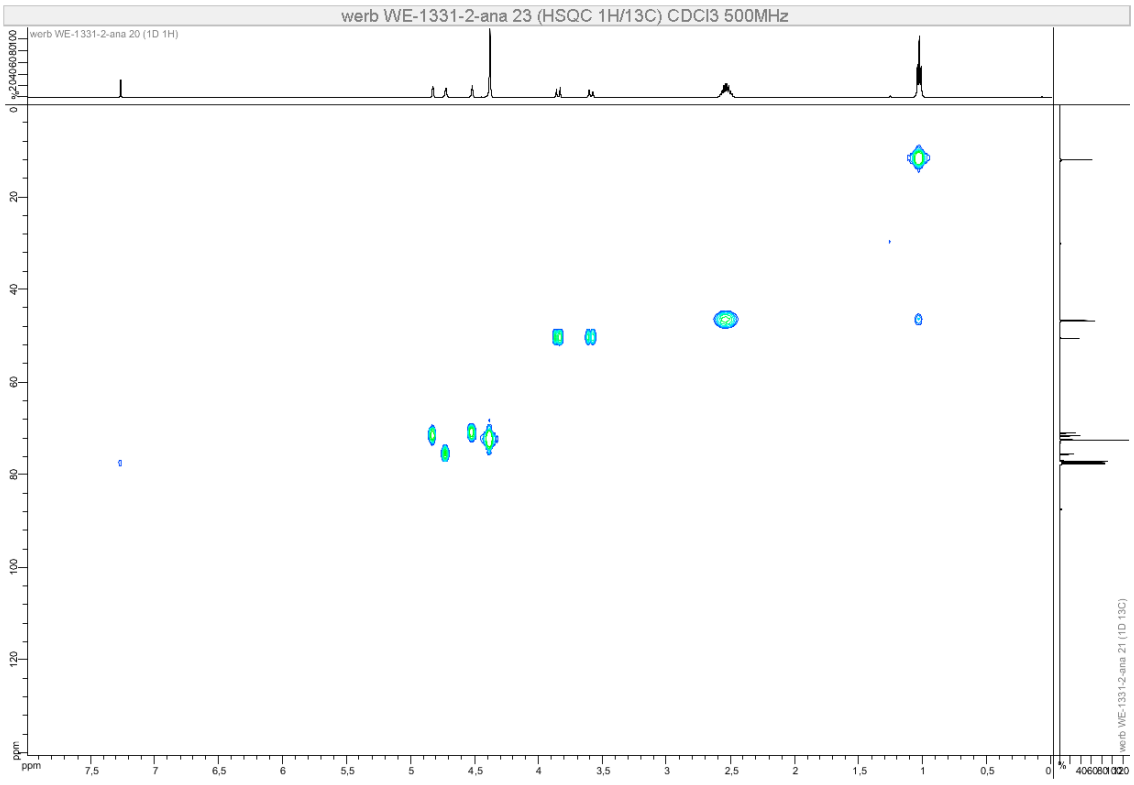
^{13}C NMR (125 MHz, $CDCl_3$)



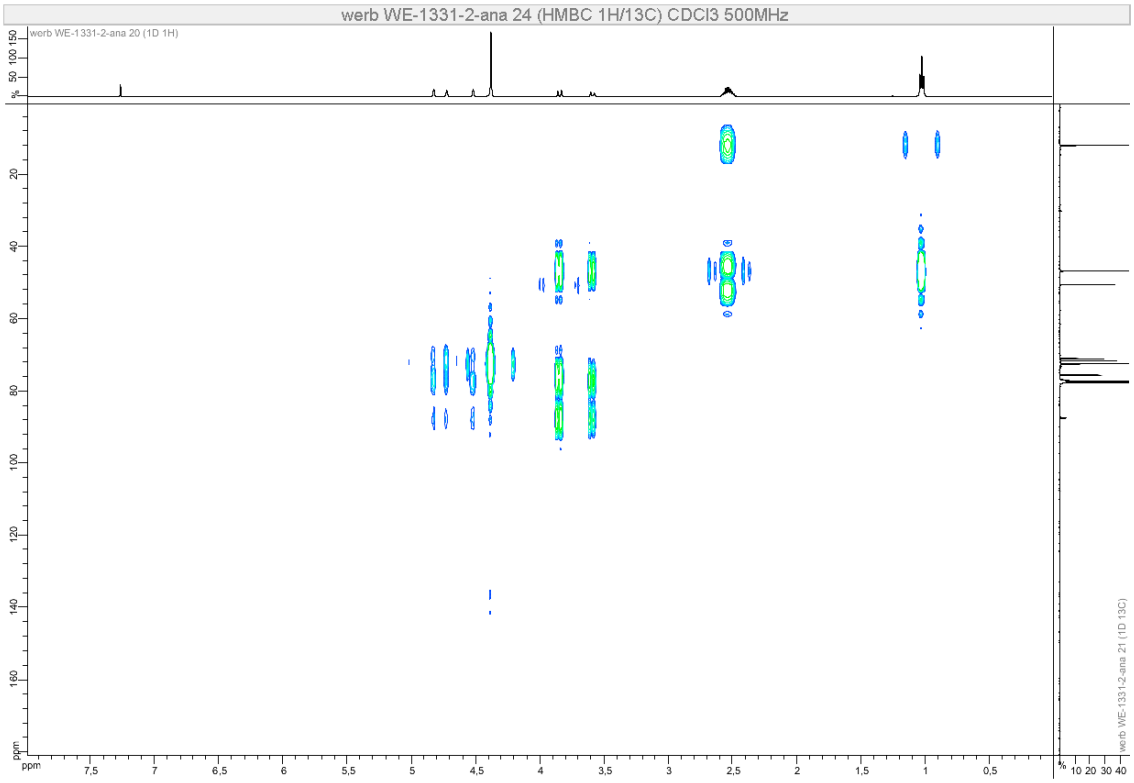
COSY (500 MHz, $CDCl_3$)



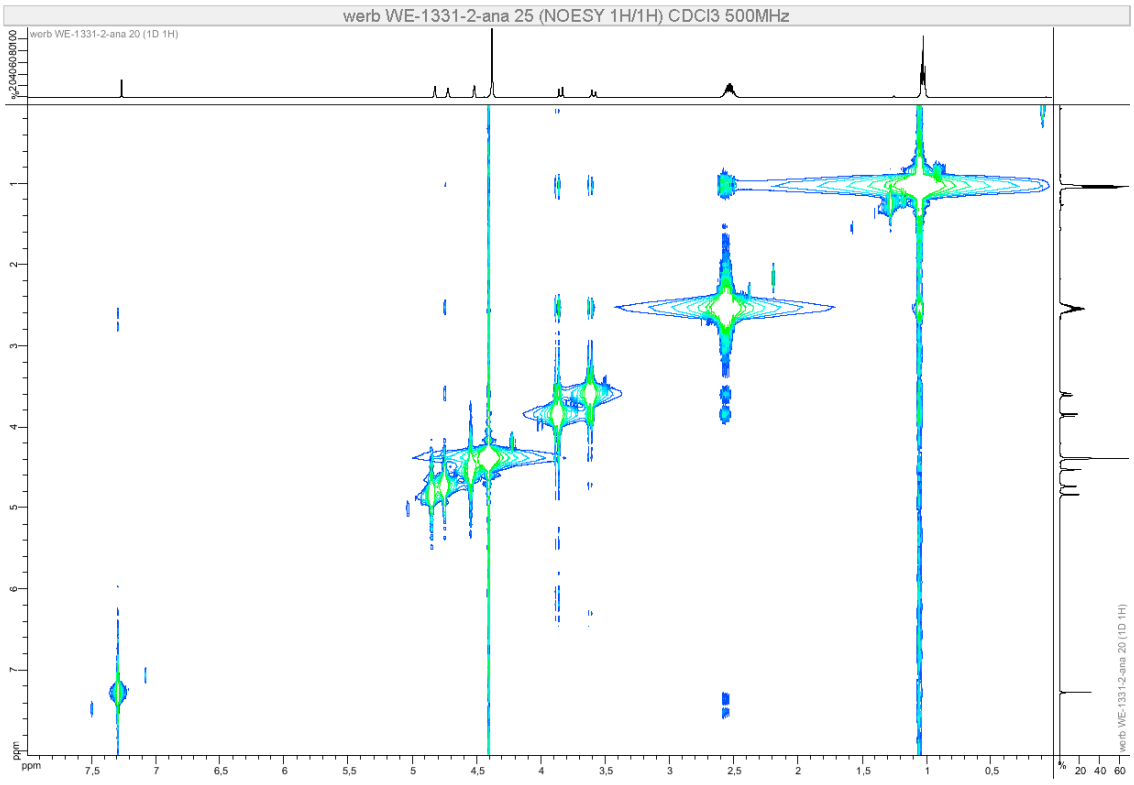
HSQC (500 MHz, $CDCl_3$)



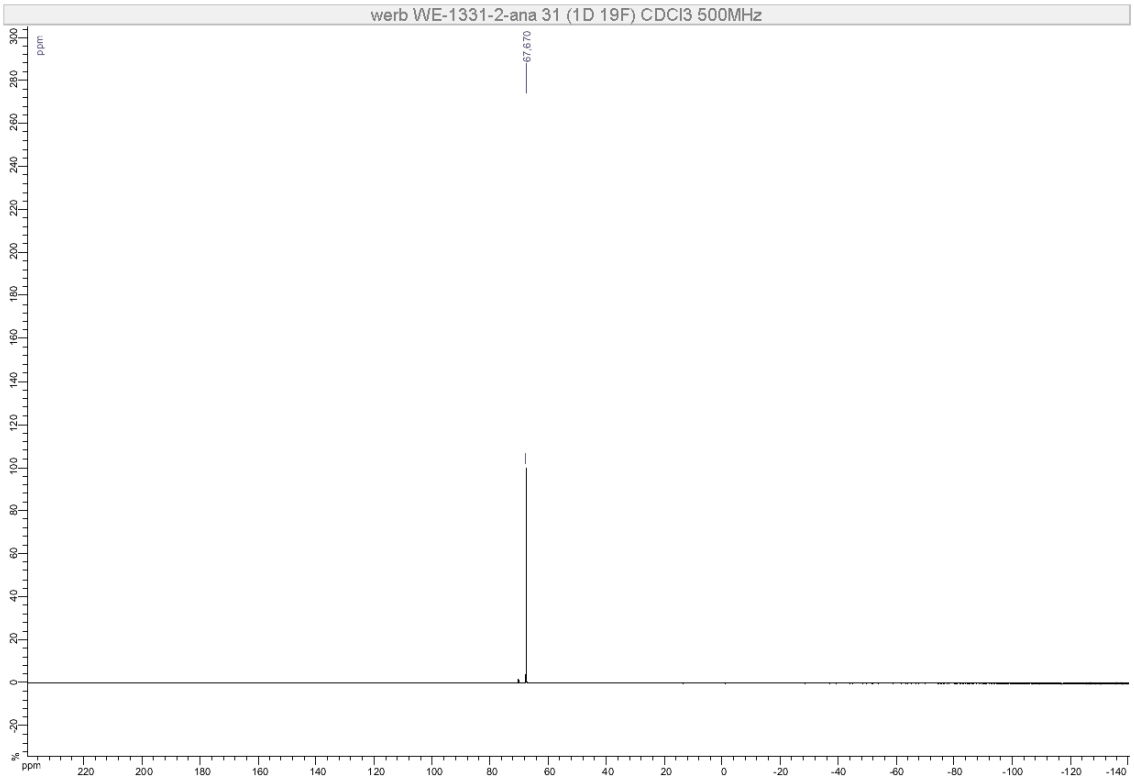
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

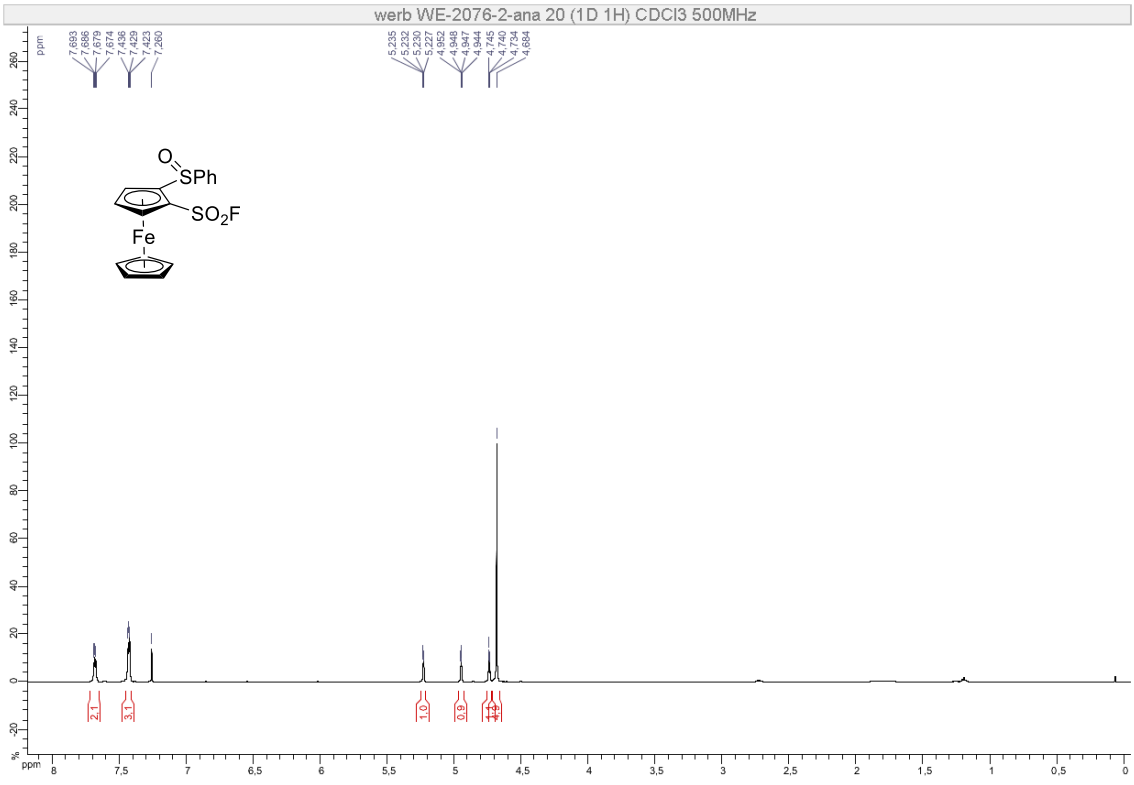


^{19}F NMR (470 MHz, $CDCl_3$)

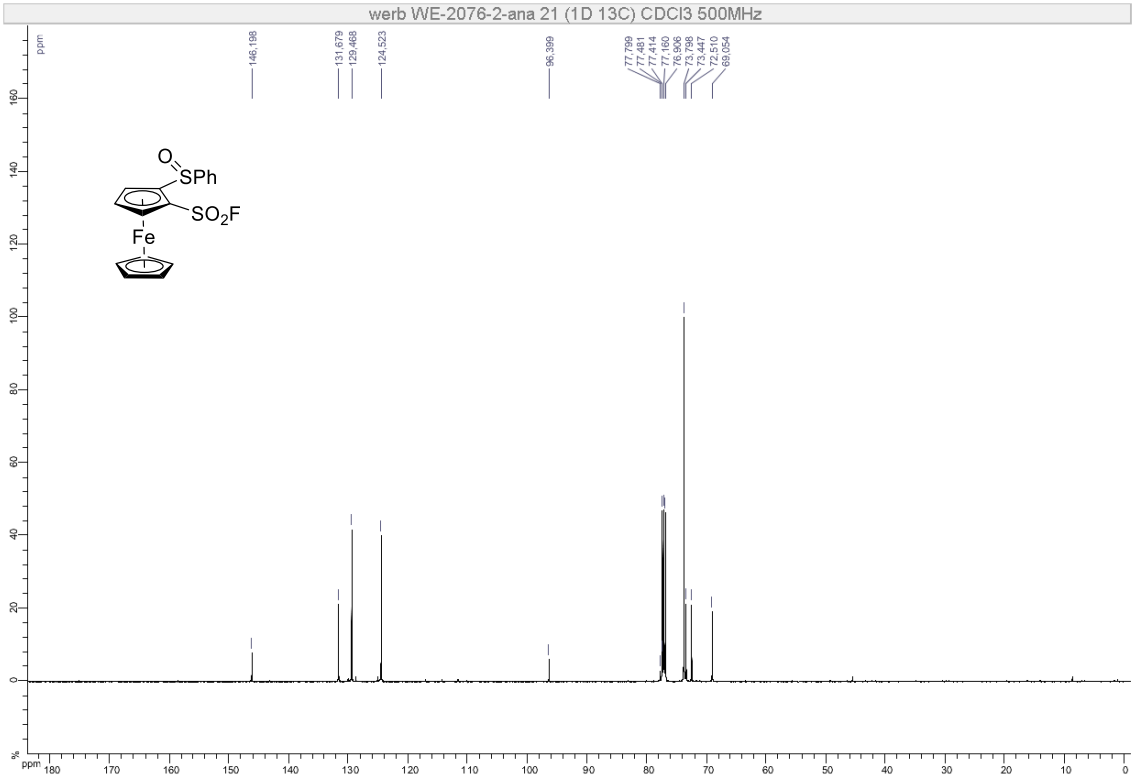


2-(Phenylsulfinyl)ferrocenesulfonyl fluoride (**26**)

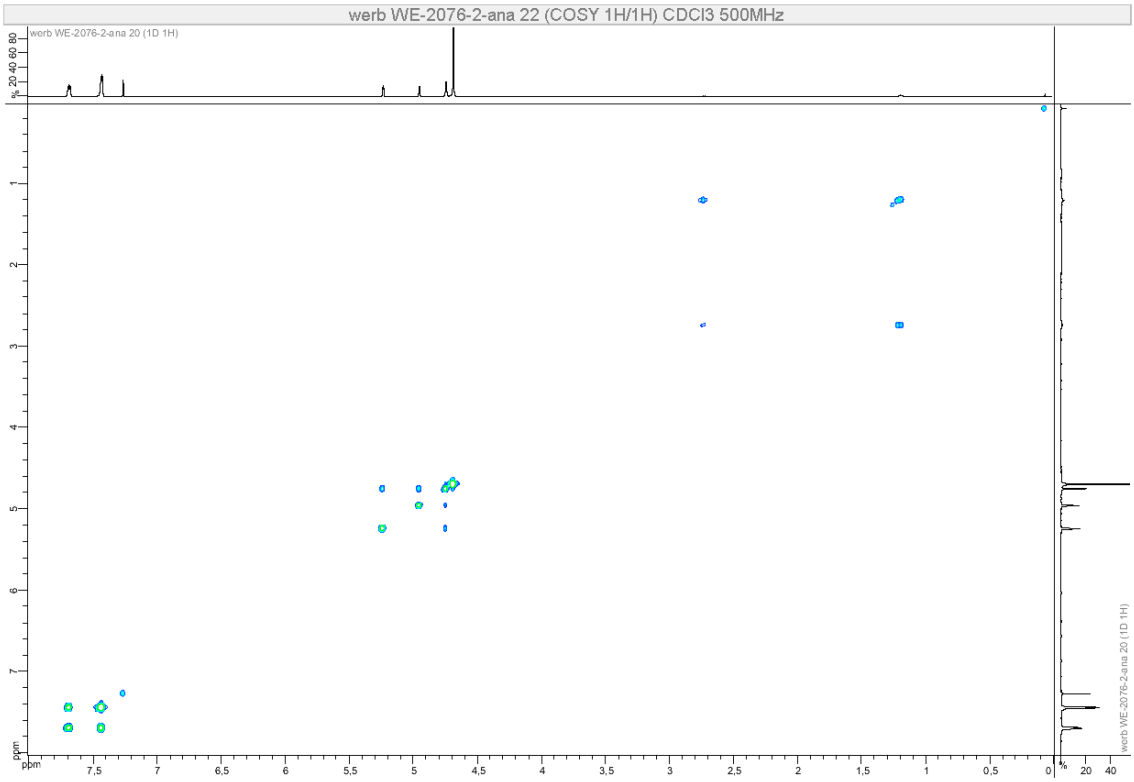
^{1}H NMR (500 MHz, $CDCl_3$)



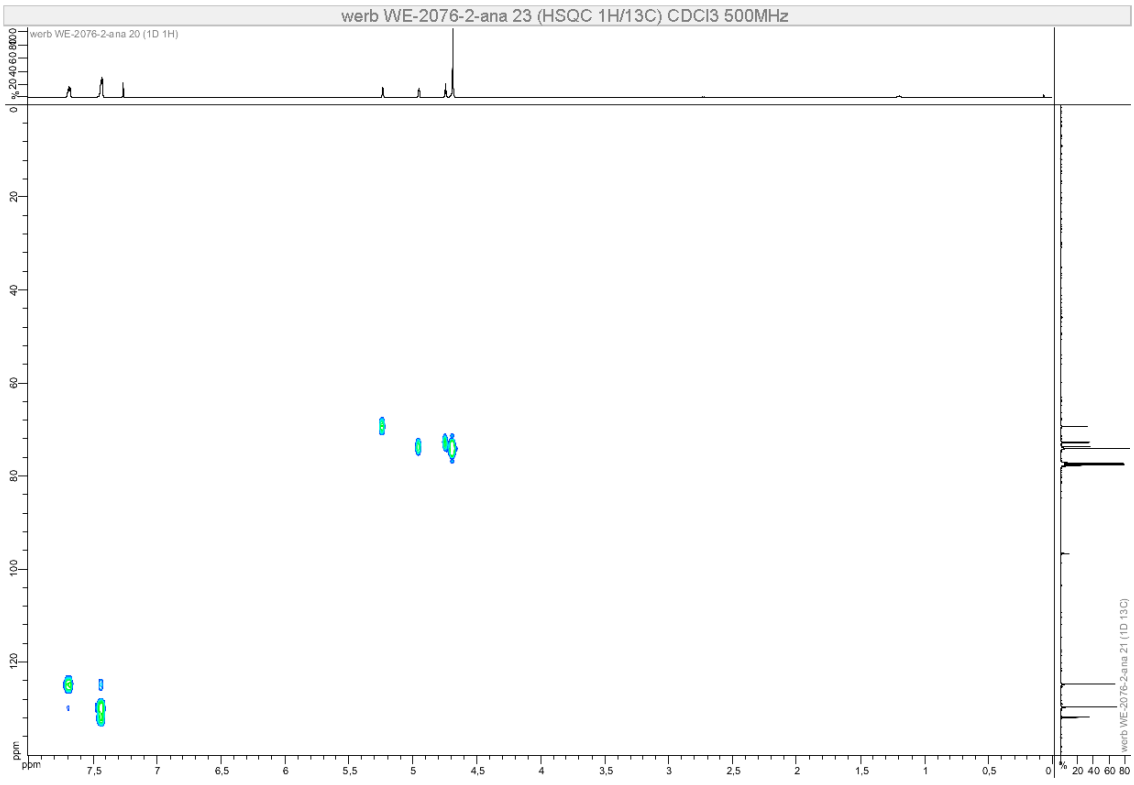
^{13}C NMR (125 MHz, $CDCl_3$)



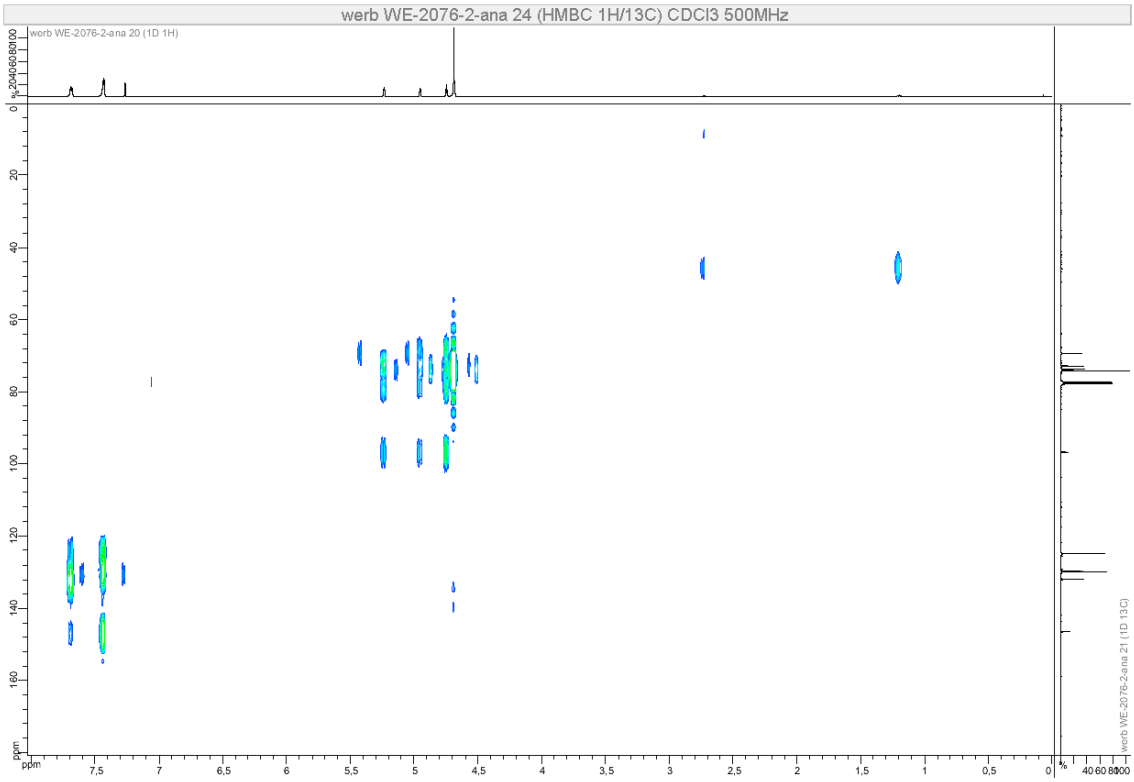
COSY (500 MHz, $CDCl_3$)



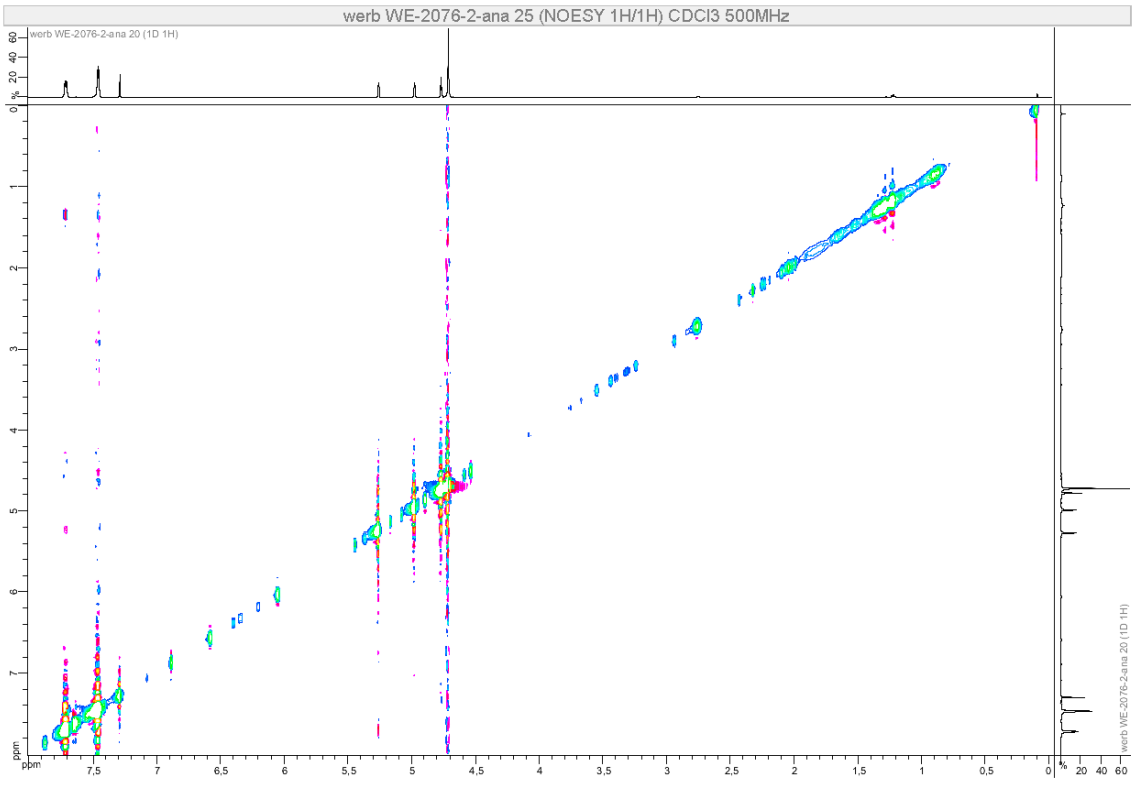
HSQC (500 MHz, $CDCl_3$)



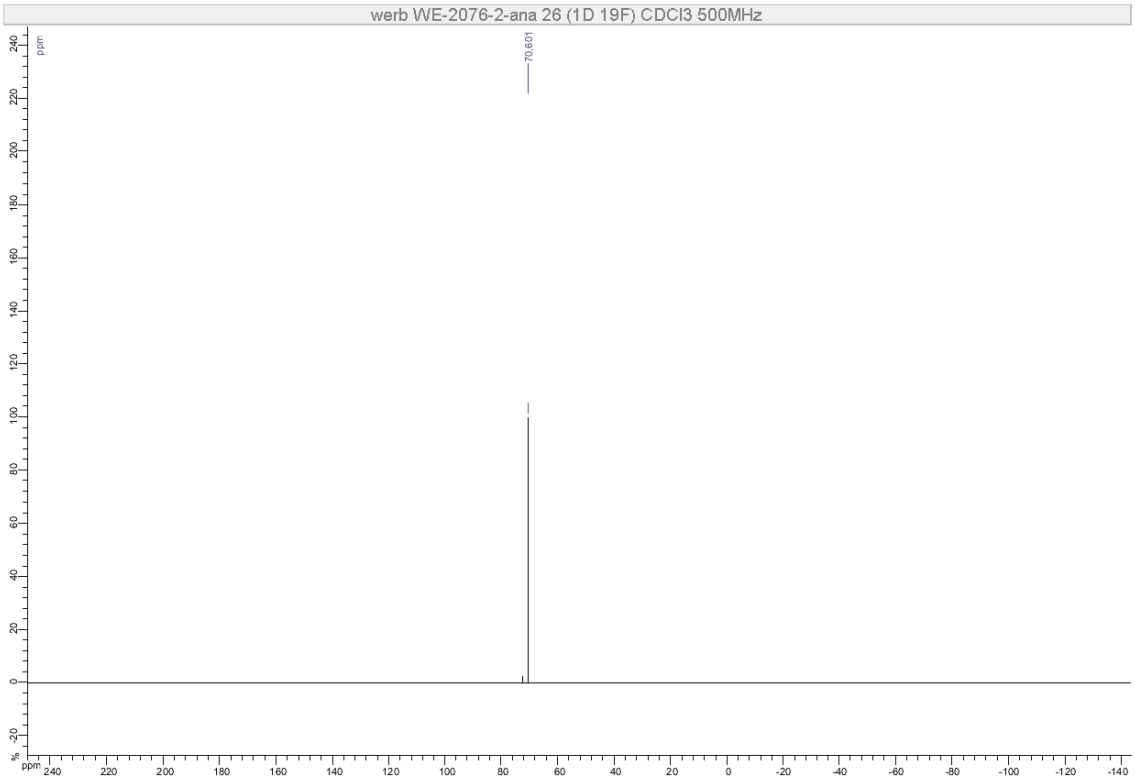
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

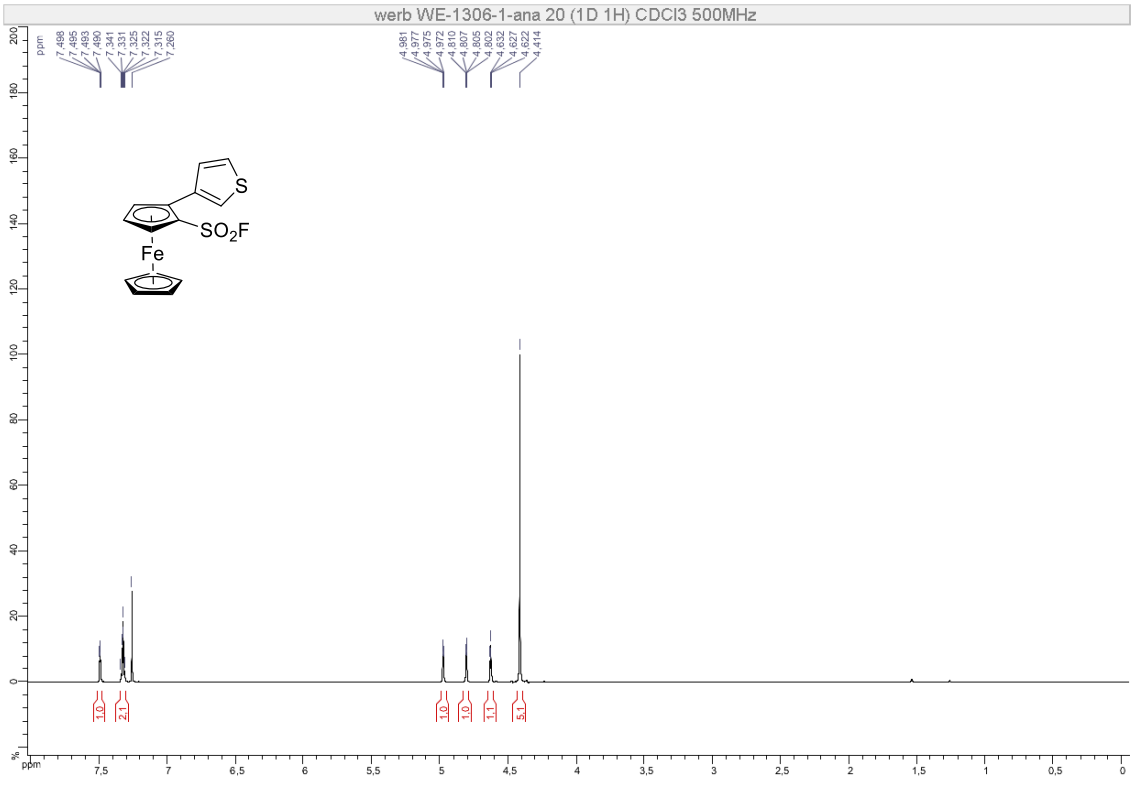


^{19}F NMR (470 MHz, $CDCl_3$)

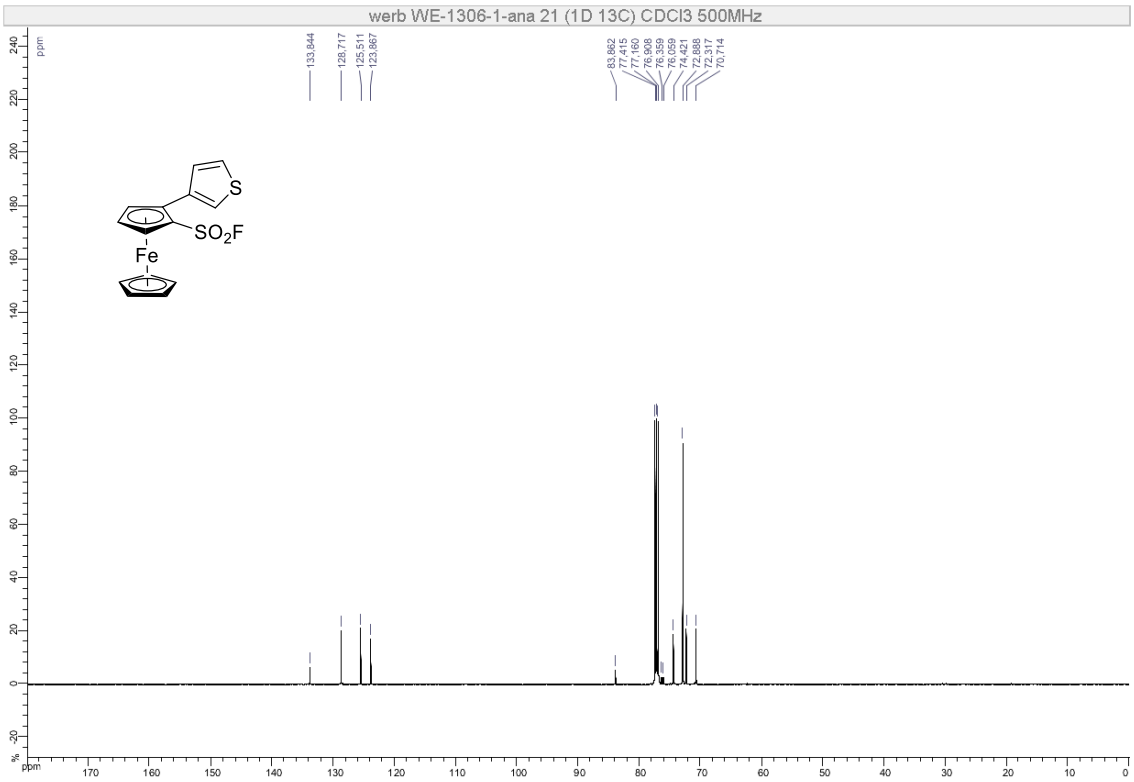


2-(3-Thienyl)ferrocenesulfonyl fluoride (27a)

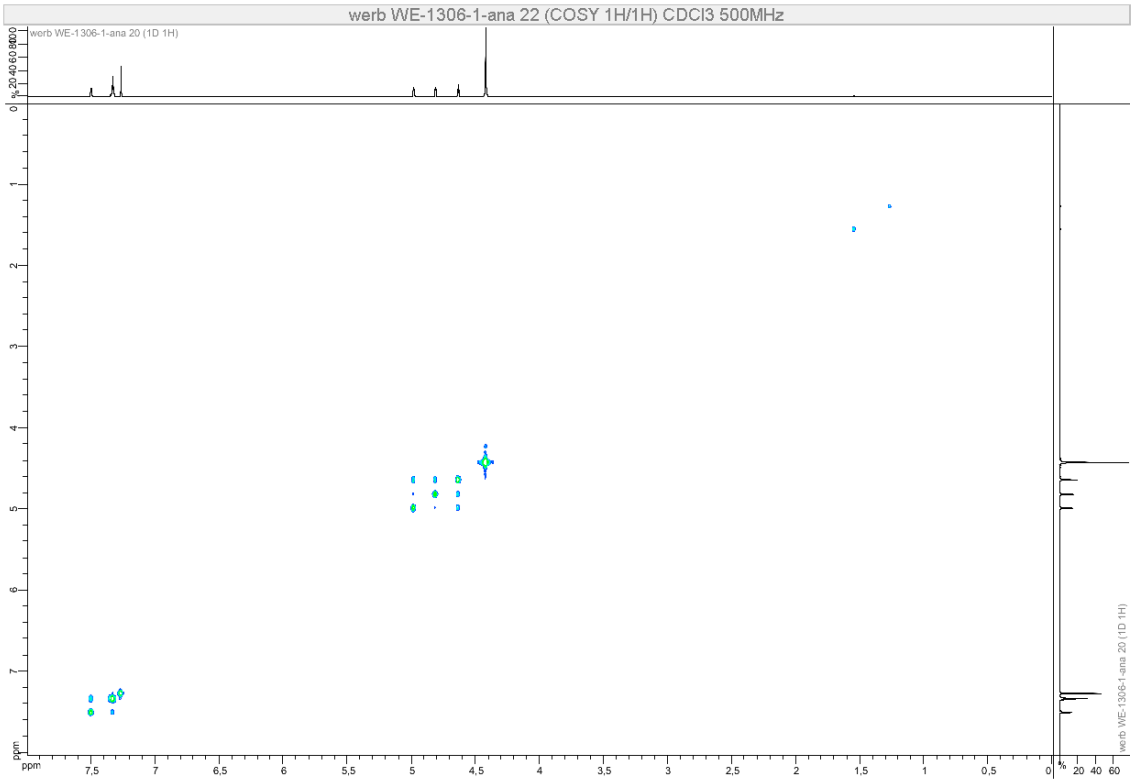
^{1}H NMR (500 MHz, $CDCl_3$)



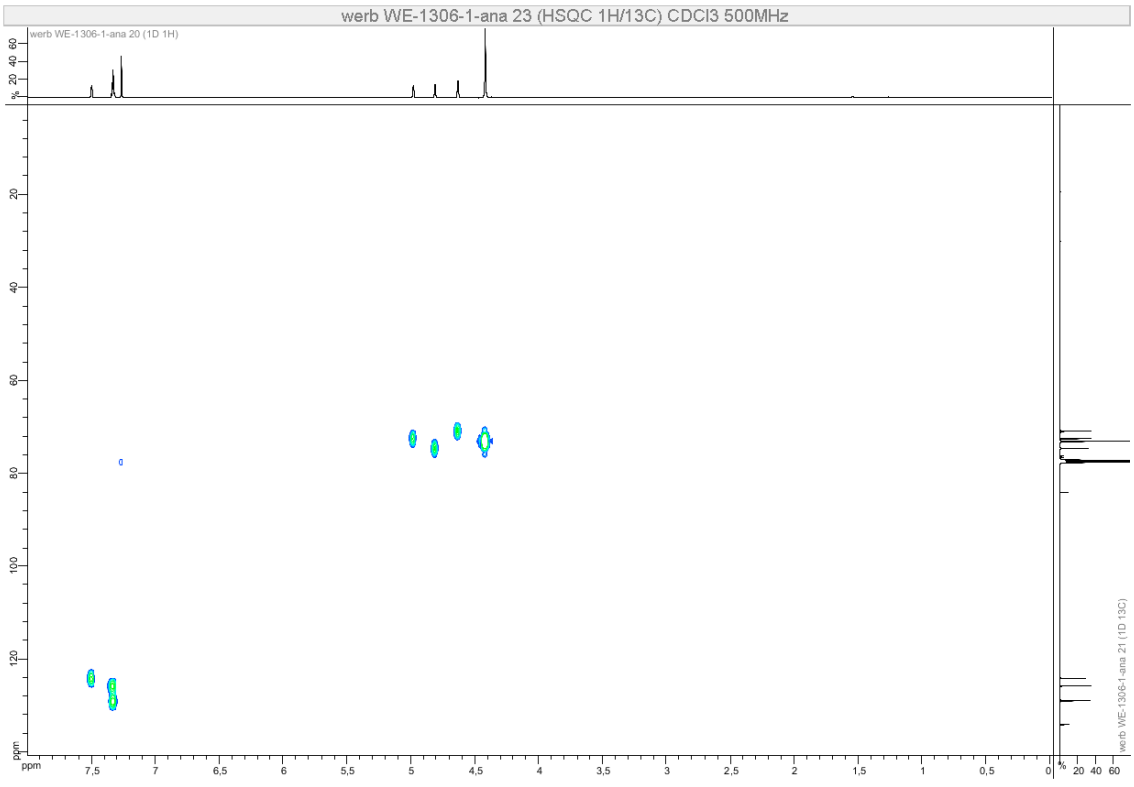
^{13}C NMR (125 MHz, $CDCl_3$)



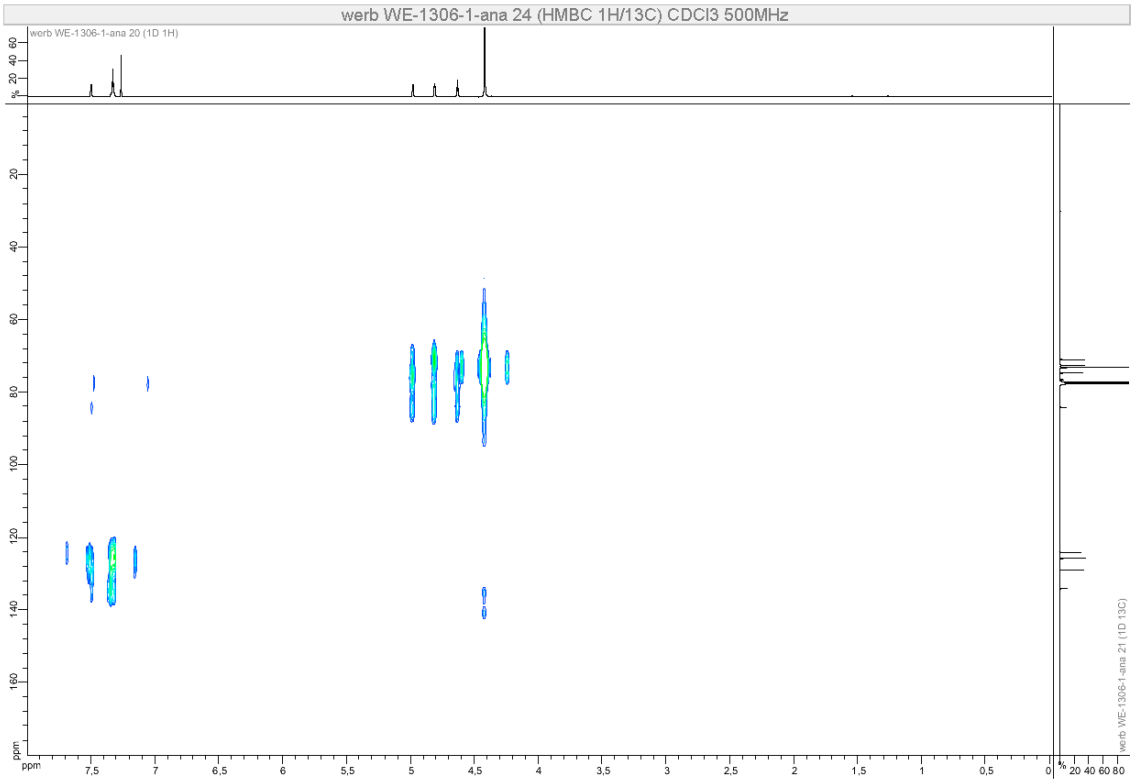
COSY (500 MHz, $CDCl_3$)



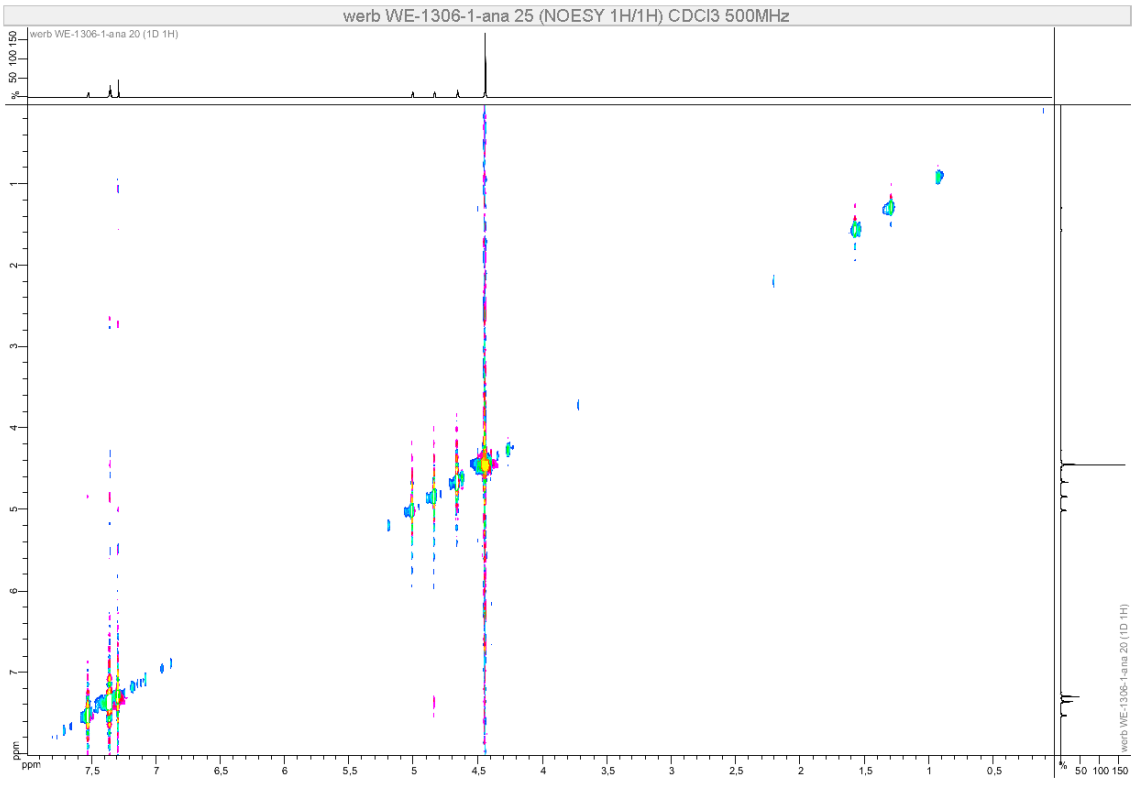
HSQC (500 MHz, $CDCl_3$)



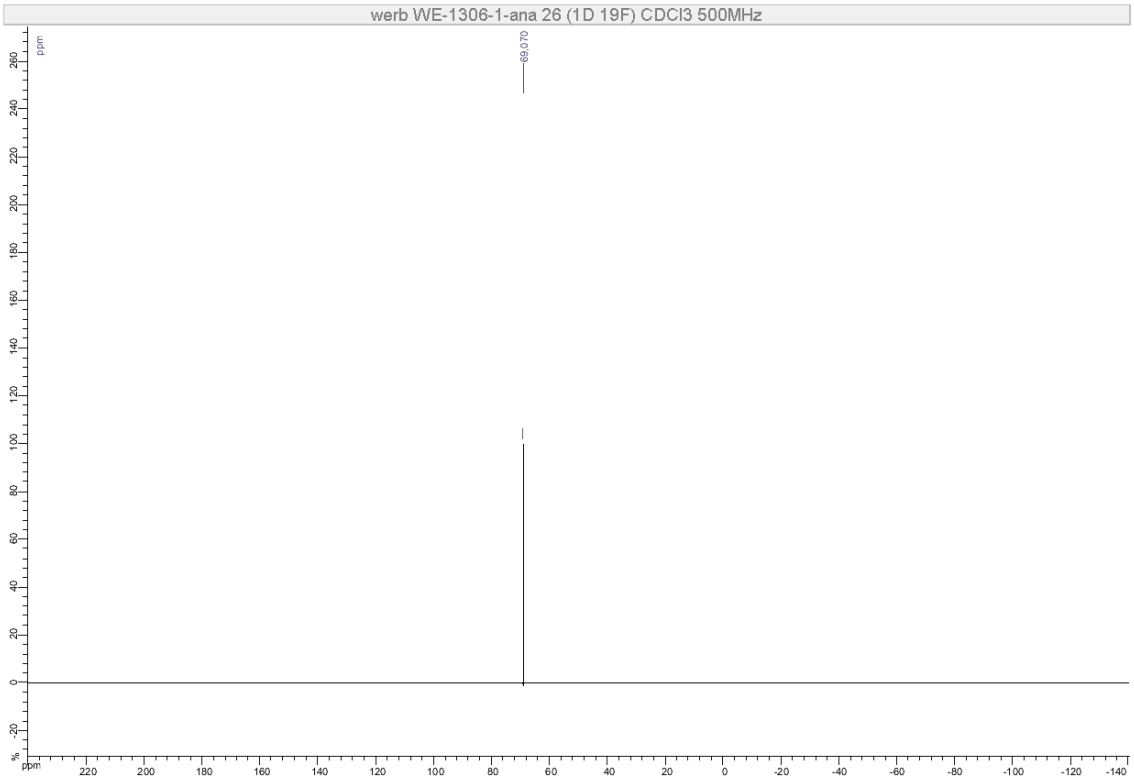
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

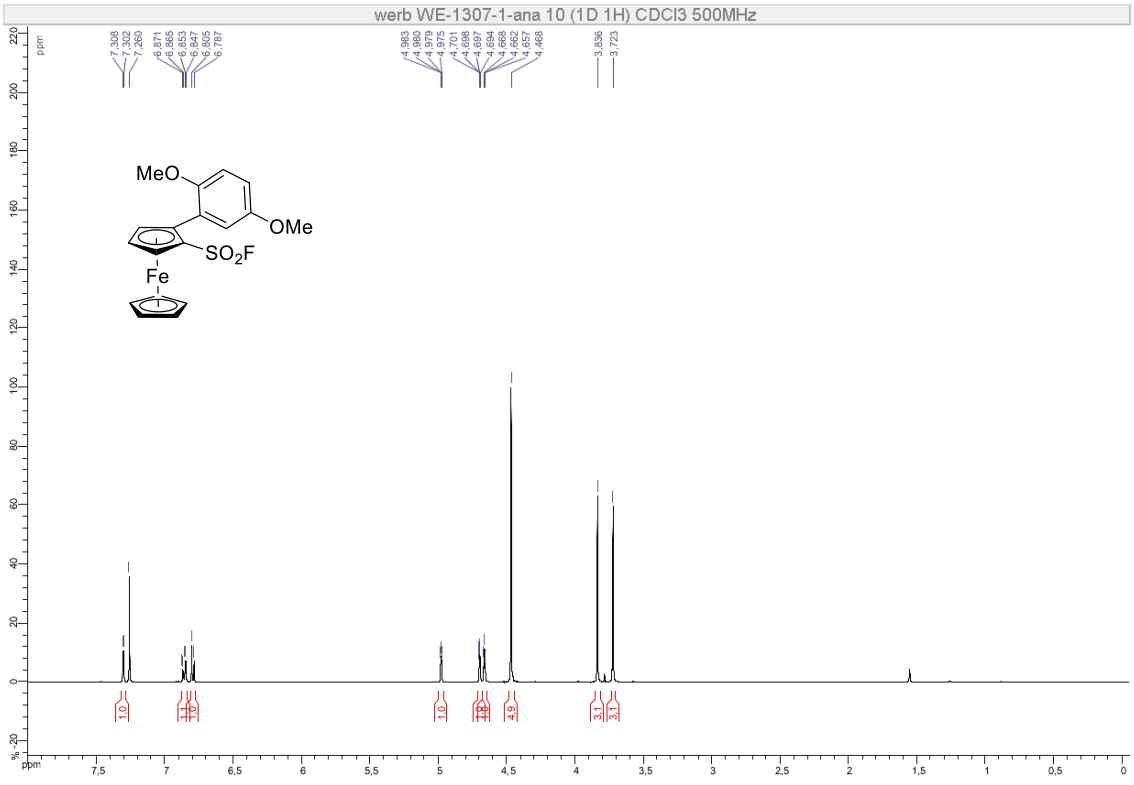


^{19}F NMR (470 MHz, $CDCl_3$)

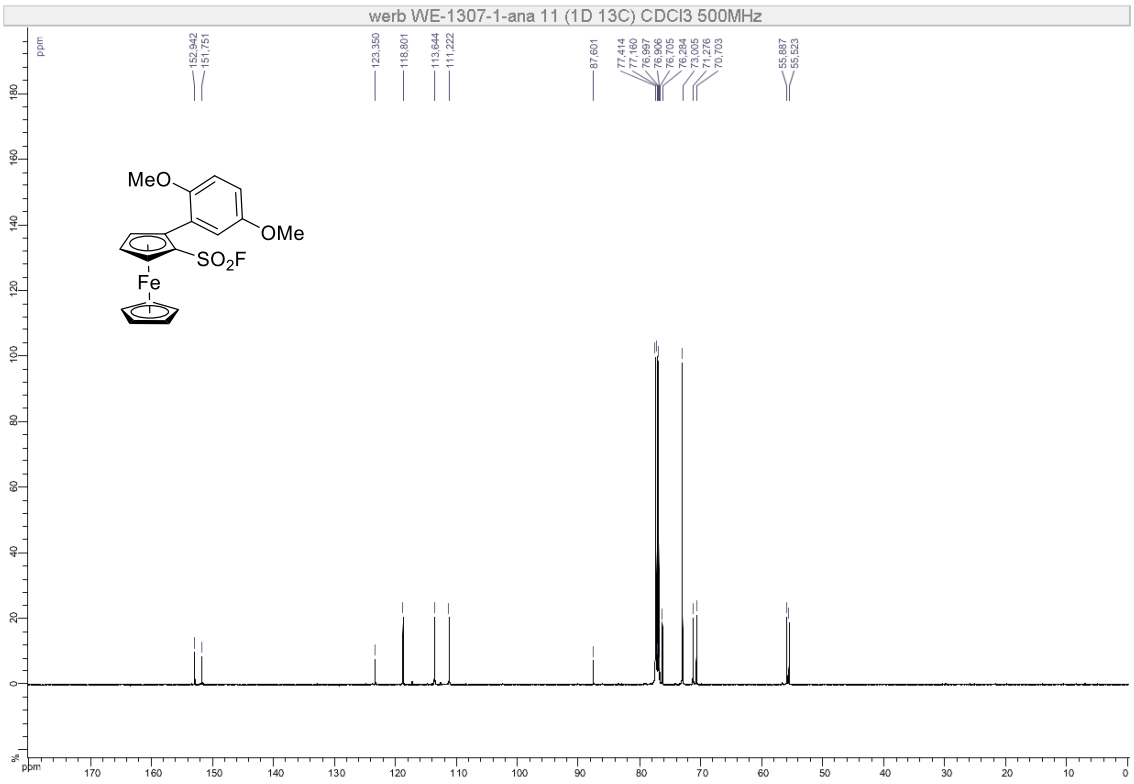


2-(2,5-Dimethoxyphenyl)ferrocenesulfonyl fluoride (27b)

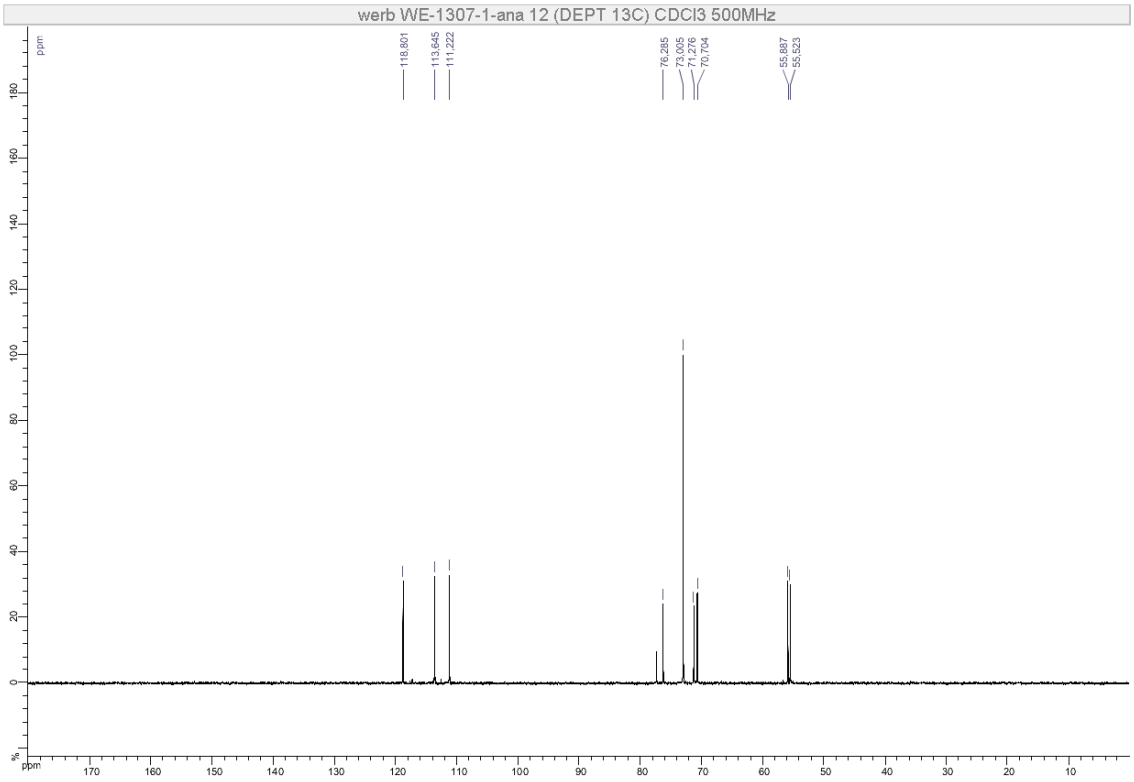
^{1}H NMR (500 MHz, $CDCl_3$)



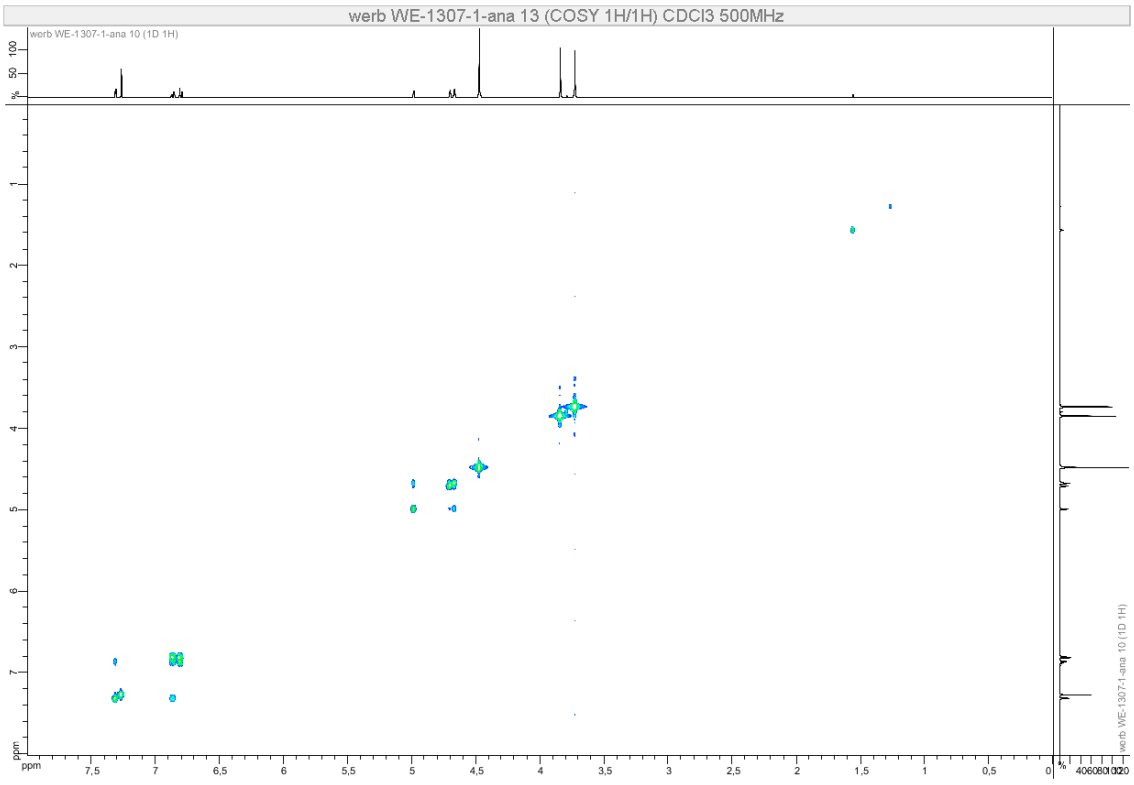
^{13}C NMR (125 MHz, $CDCl_3$)



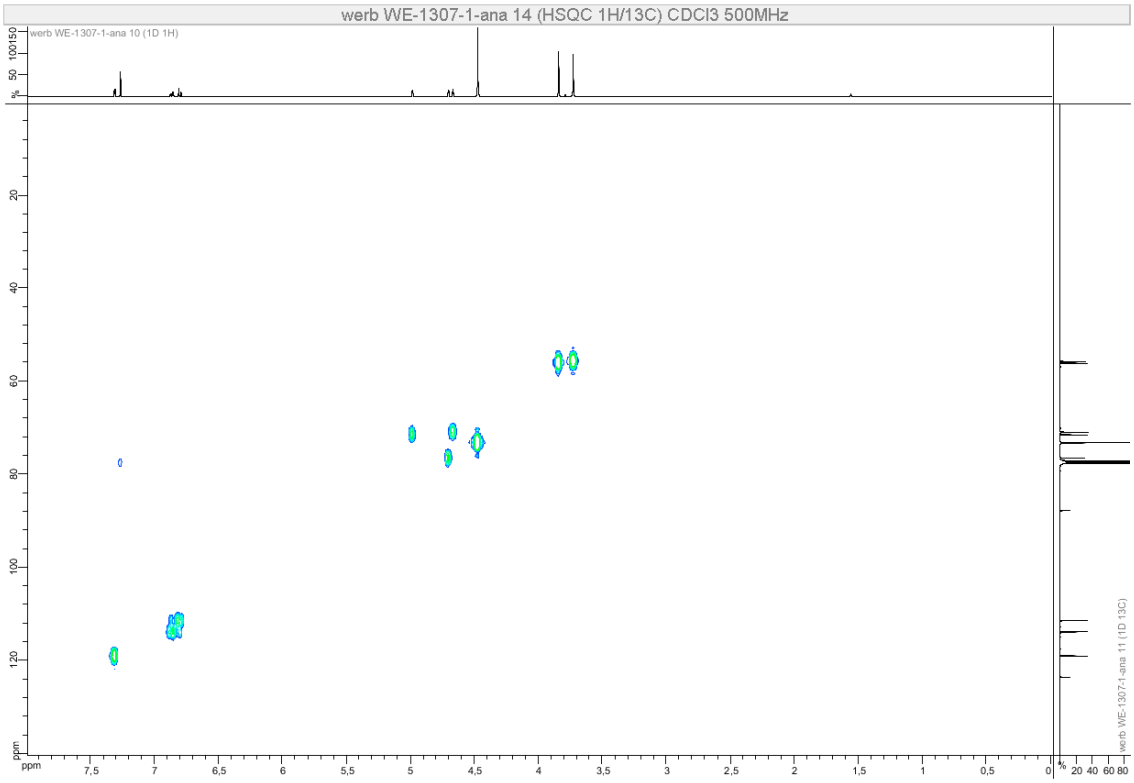
DEPT 135 (125 MHz, $CDCl_3$)



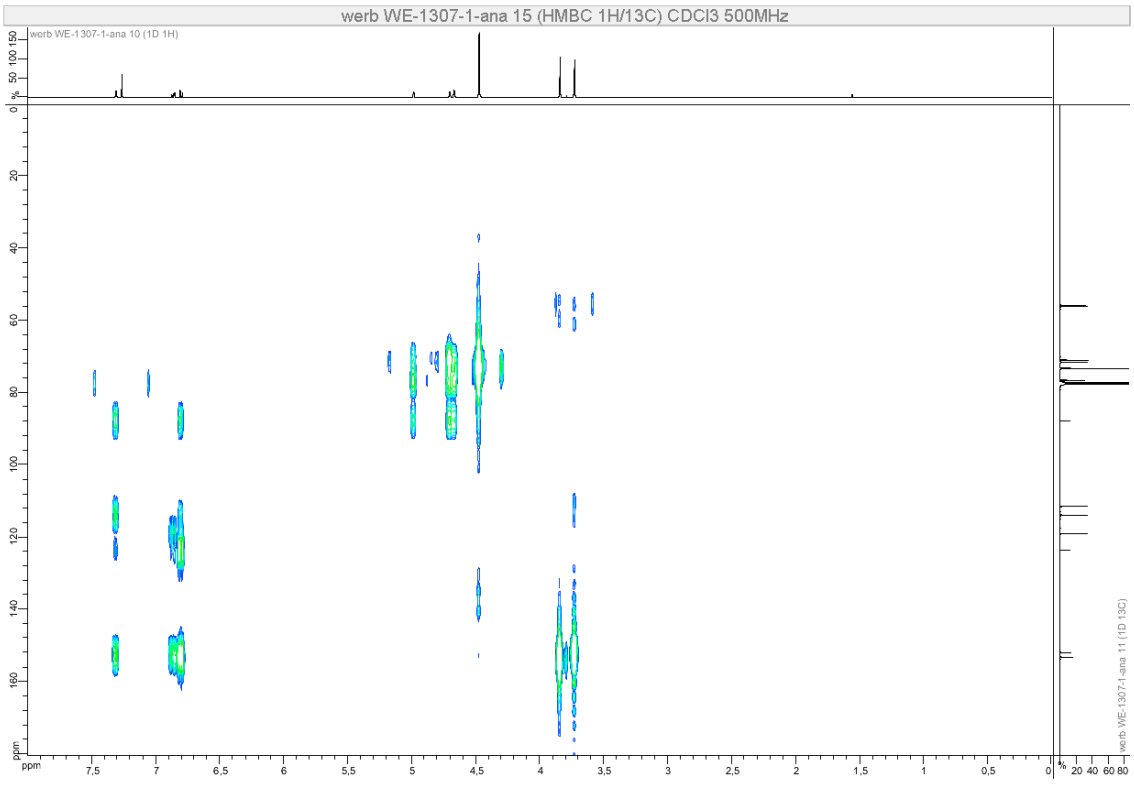
COSY (500 MHz, $CDCl_3$)



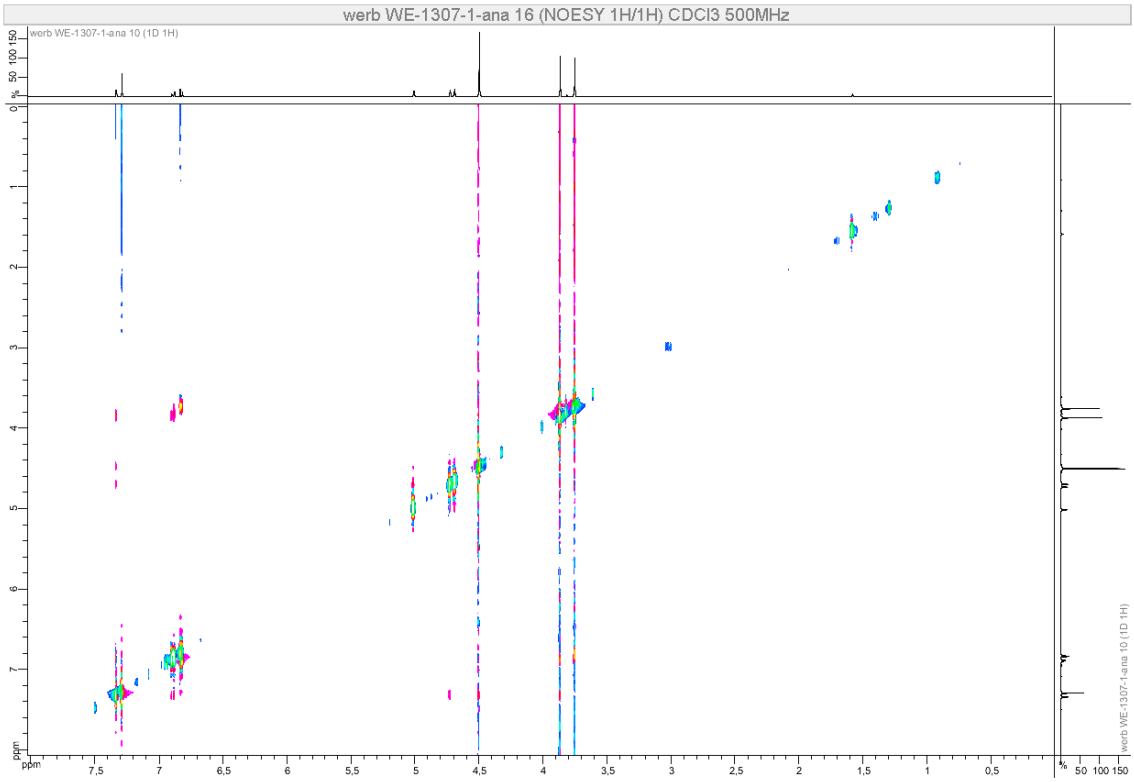
HSQC (500 MHz, $CDCl_3$)



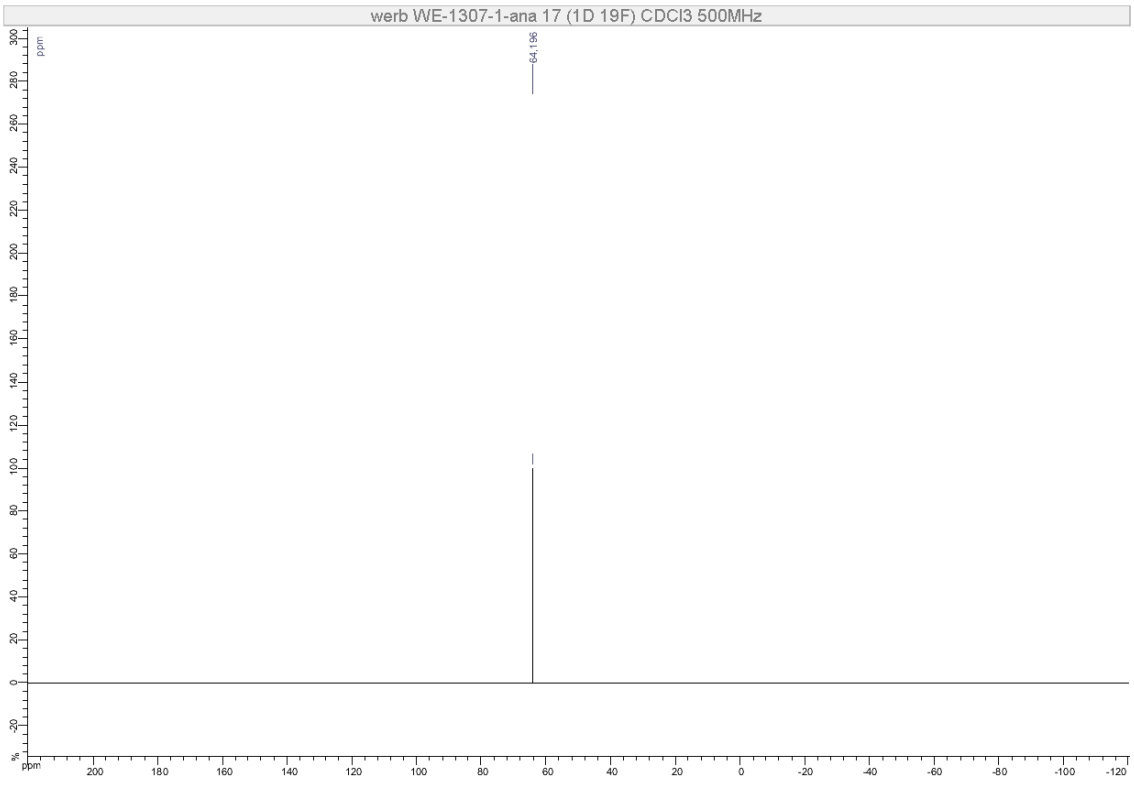
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

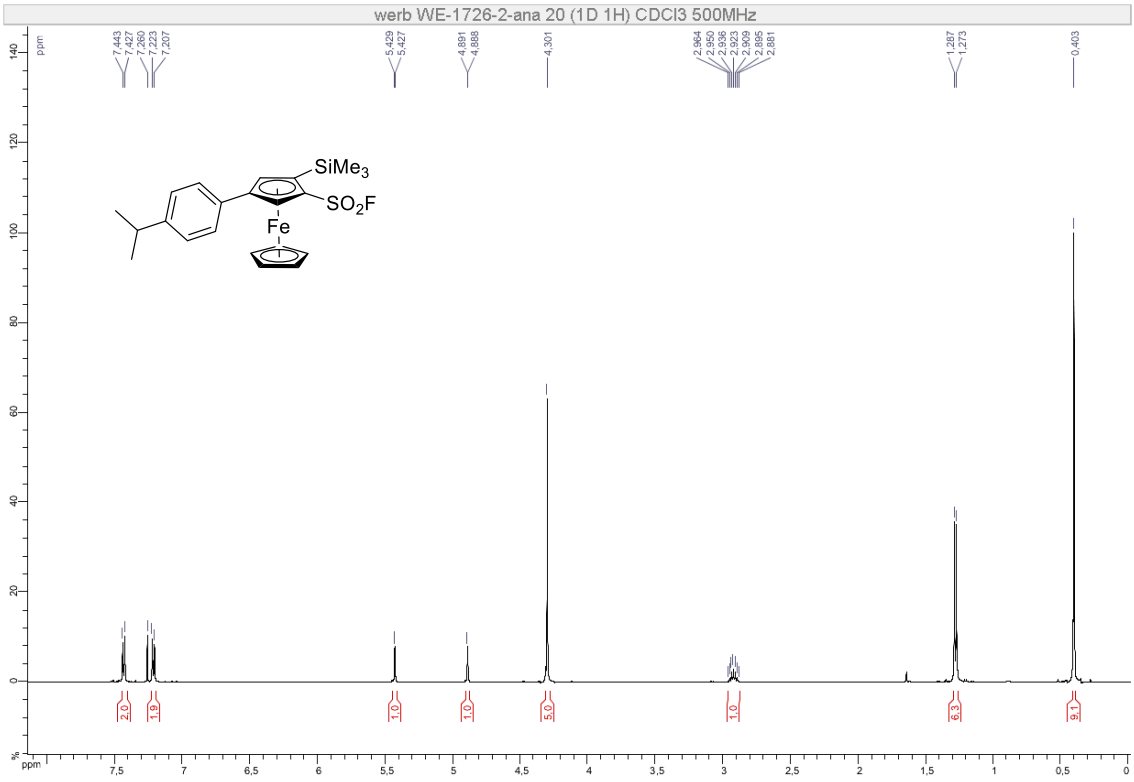


^{19}F NMR (470 MHz, $CDCl_3$)

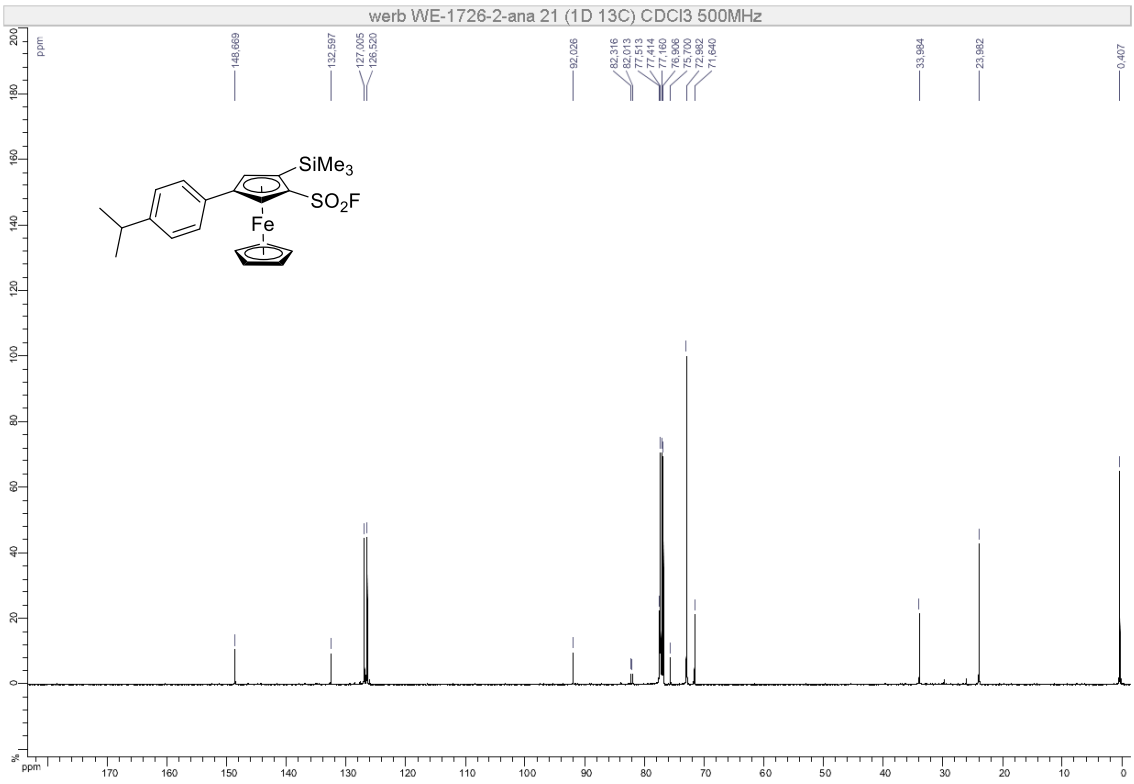


4-(4-Isopropylphenyl)-2-(trimethylsilyl)ferrocenesulfonyl fluoride (29a)

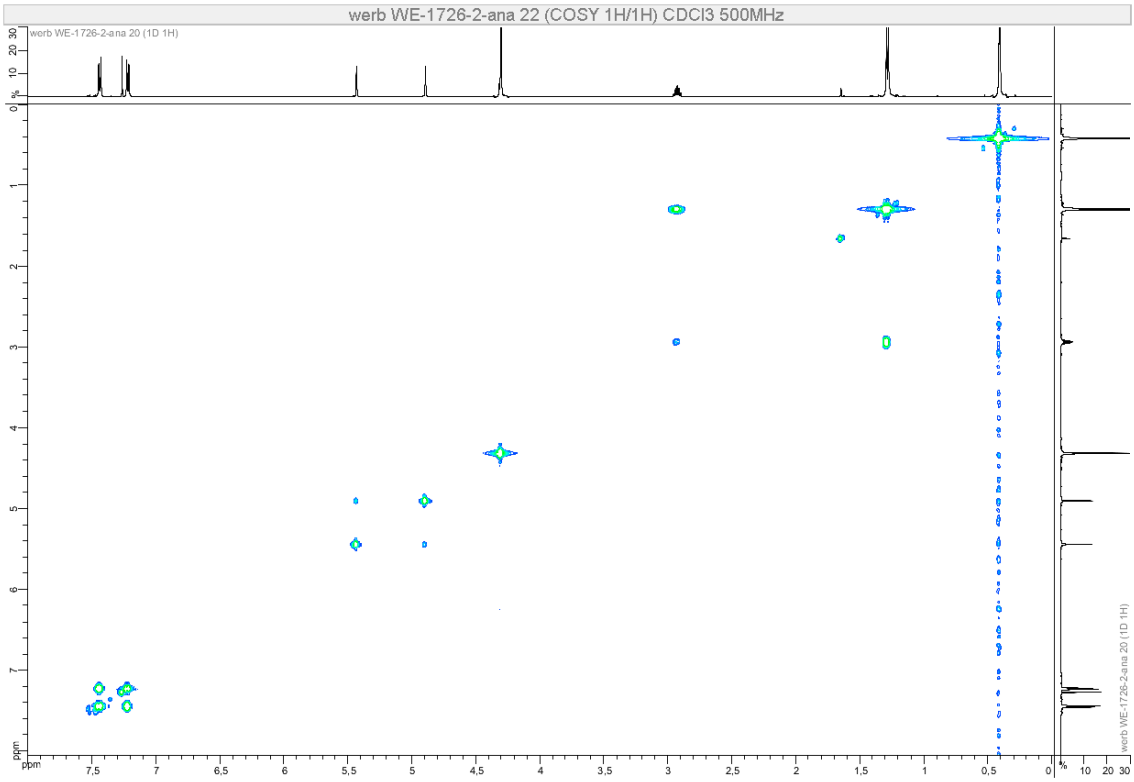
^{1}H NMR (500 MHz, $CDCl_3$)



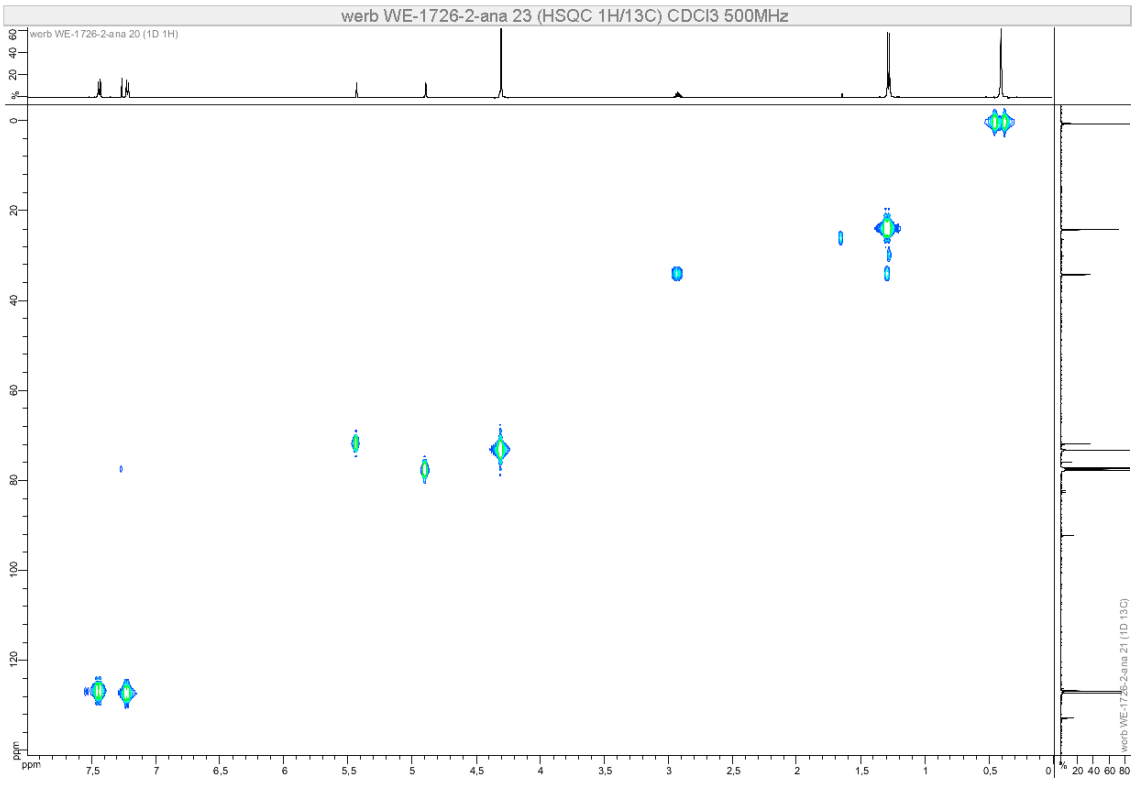
^{13}C NMR (125 MHz, $CDCl_3$)



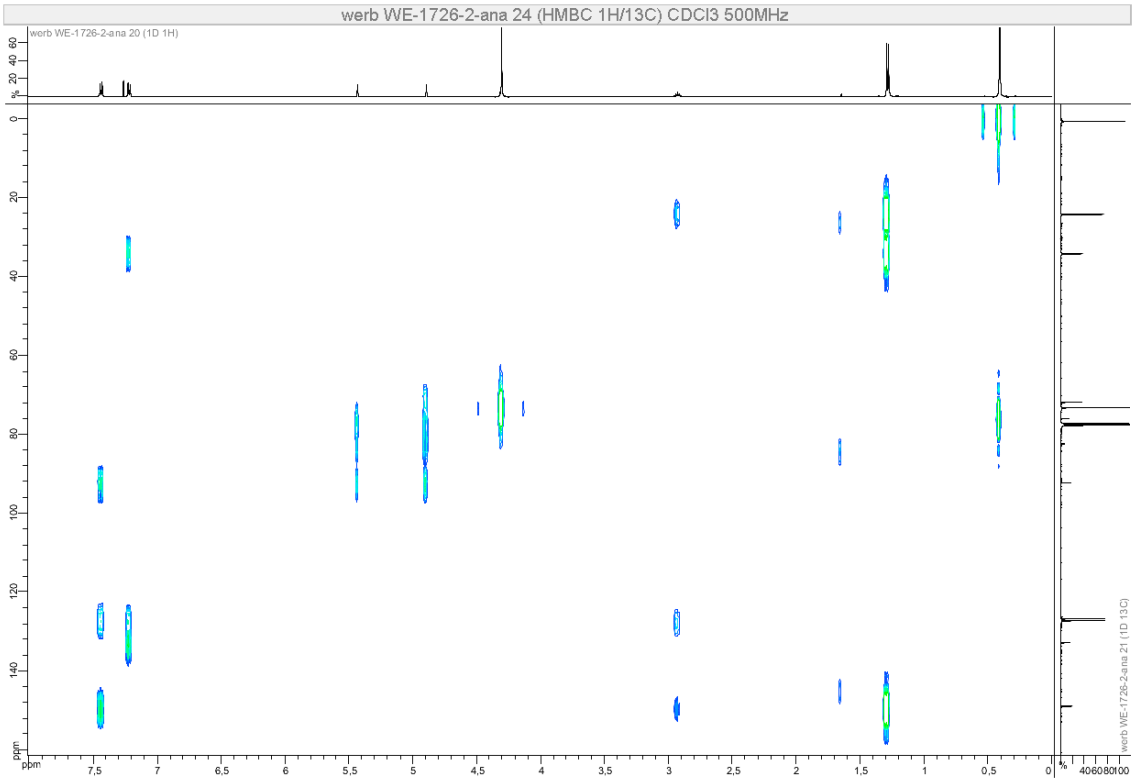
COSY (500 MHz, $CDCl_3$)



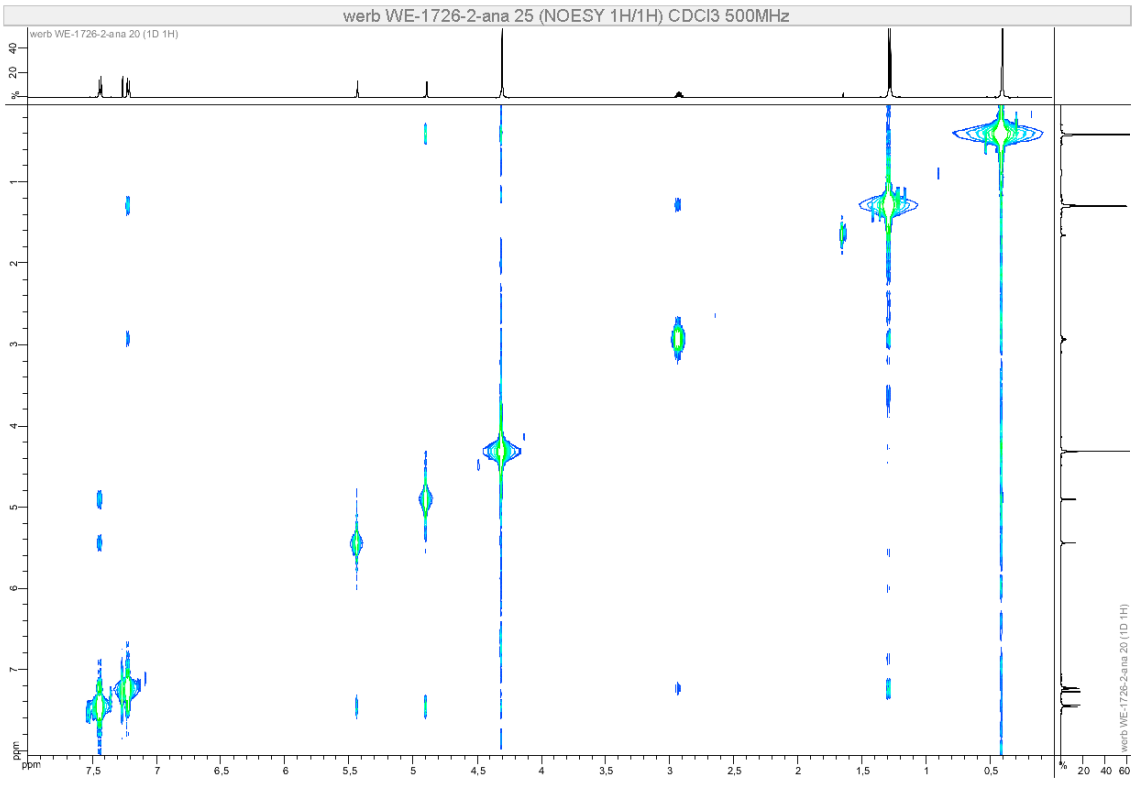
HSQC (500 MHz, $CDCl_3$)



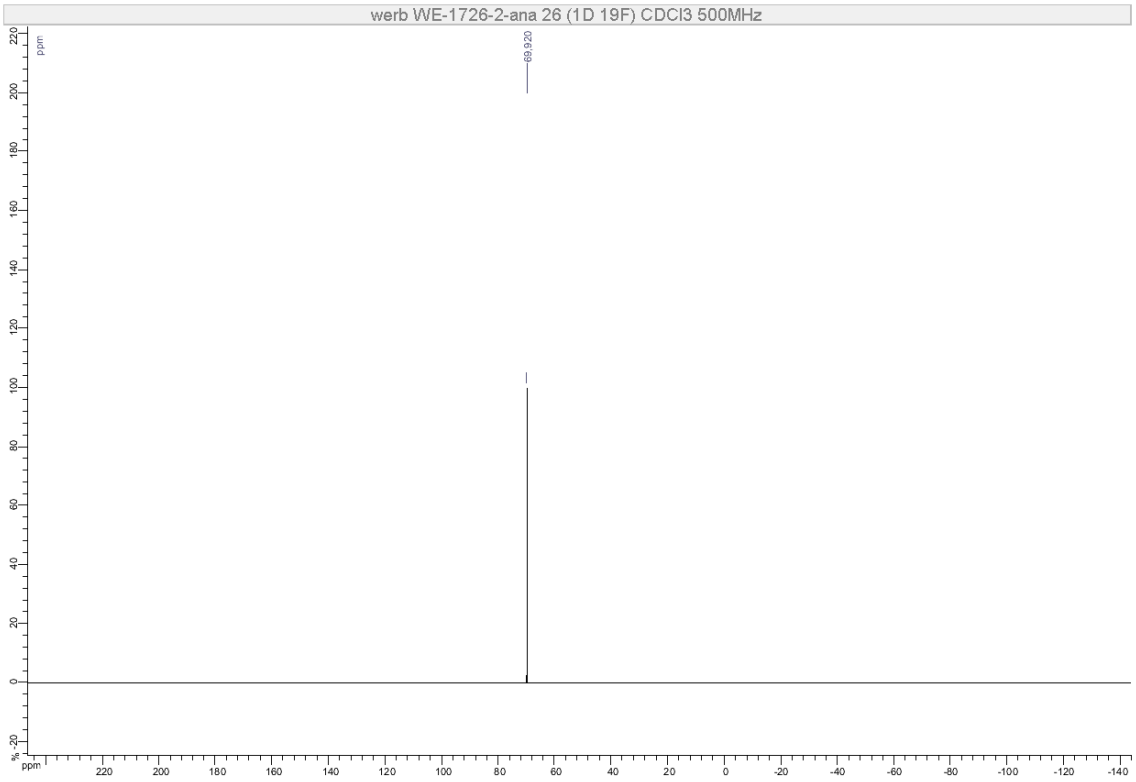
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

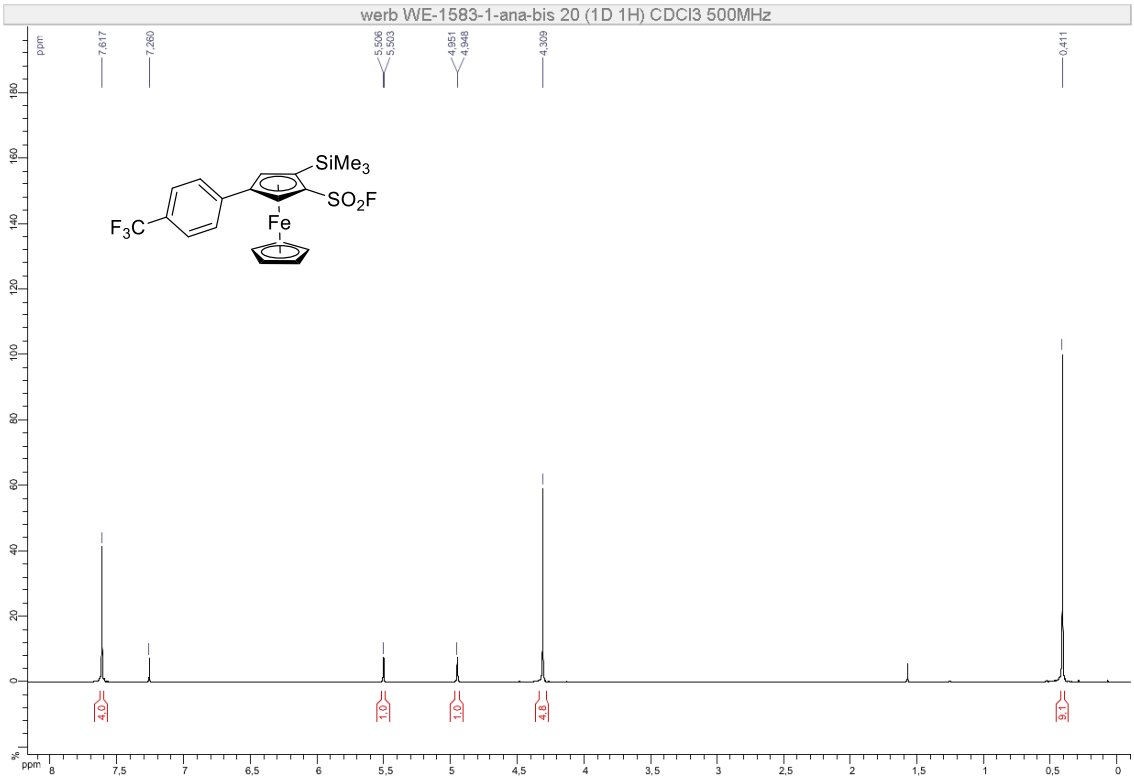


^{19}F NMR (470 MHz, $CDCl_3$)

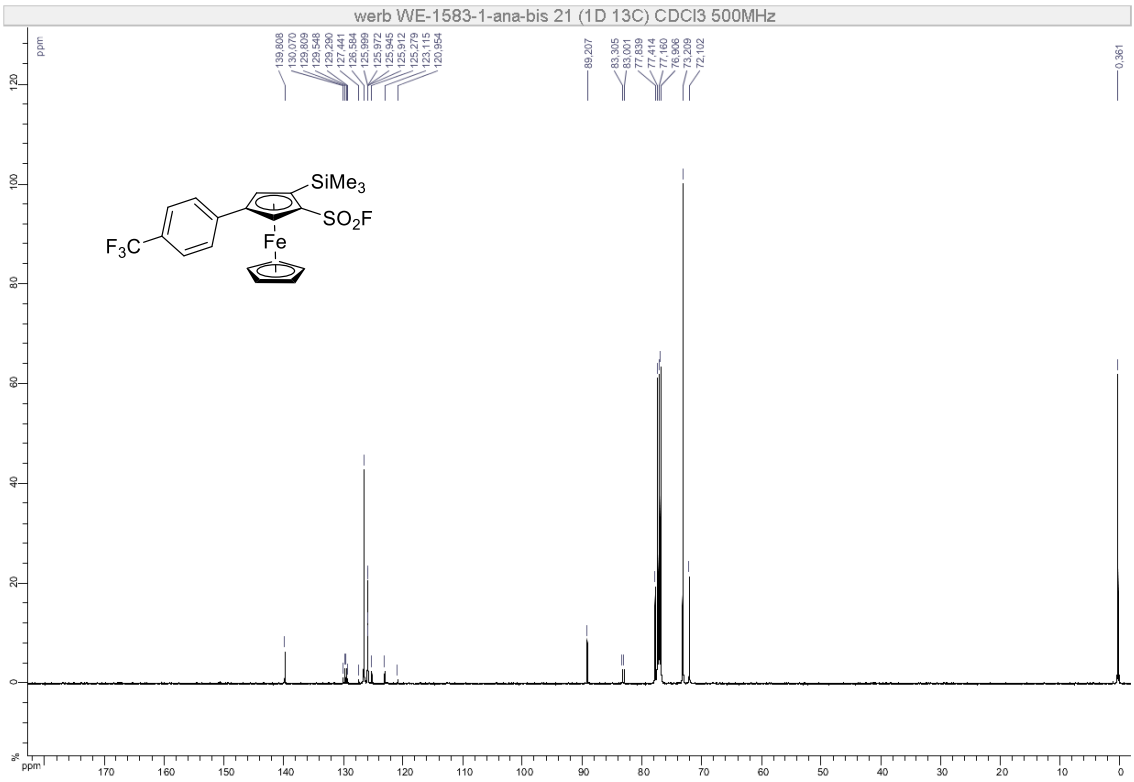


4-(4-(Trifluoromethyl)phenyl)-2-(trimethylsilyl)ferrocenesulfonyl fluoride (29b)

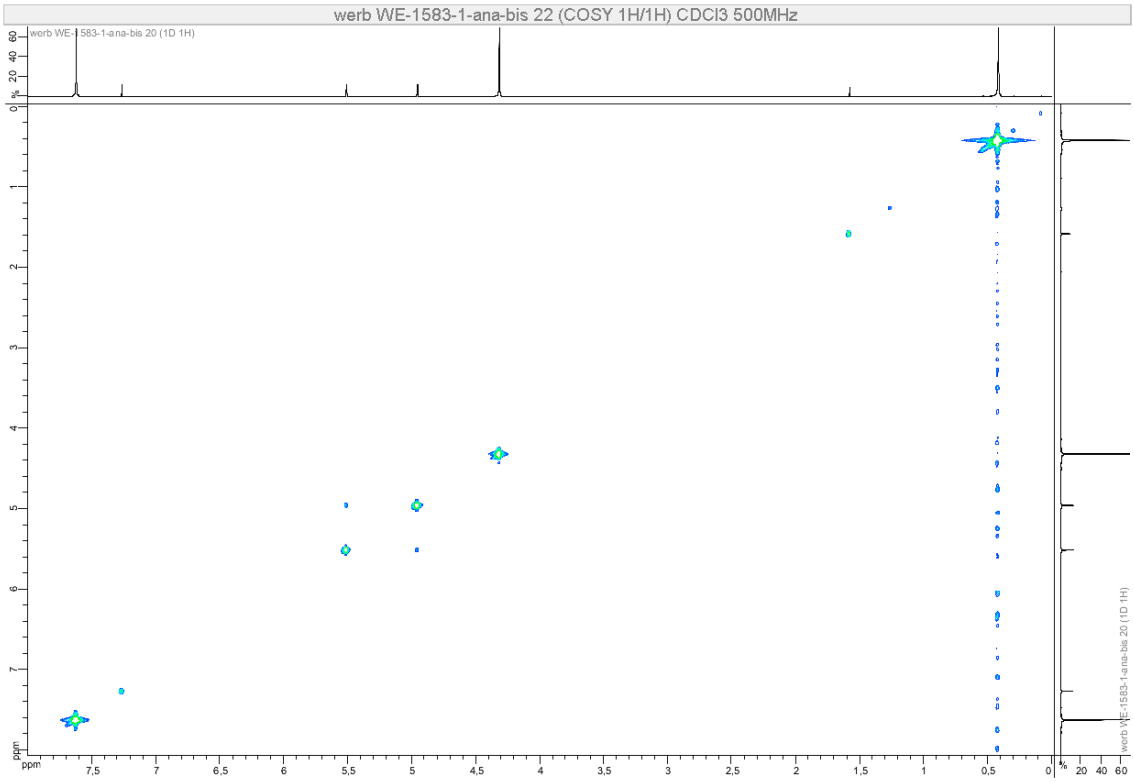
^{1}H NMR (500 MHz, $CDCl_3$)



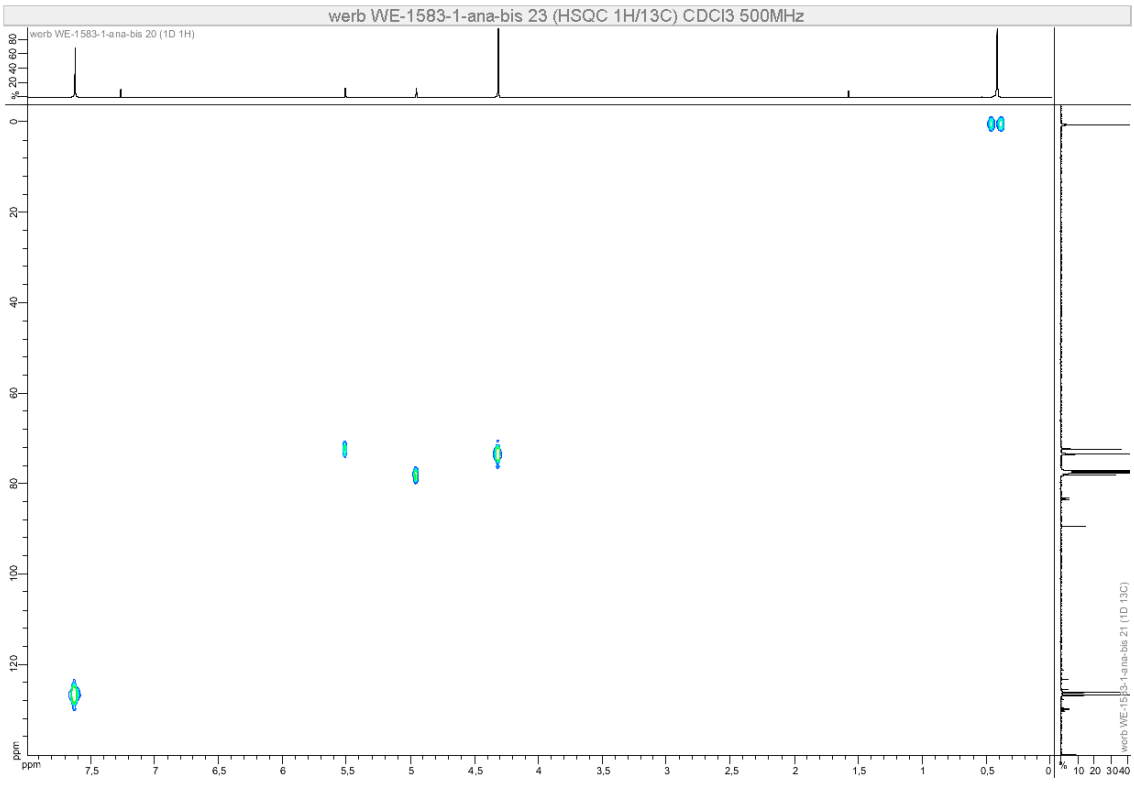
^{13}C NMR (125 MHz, $CDCl_3$)



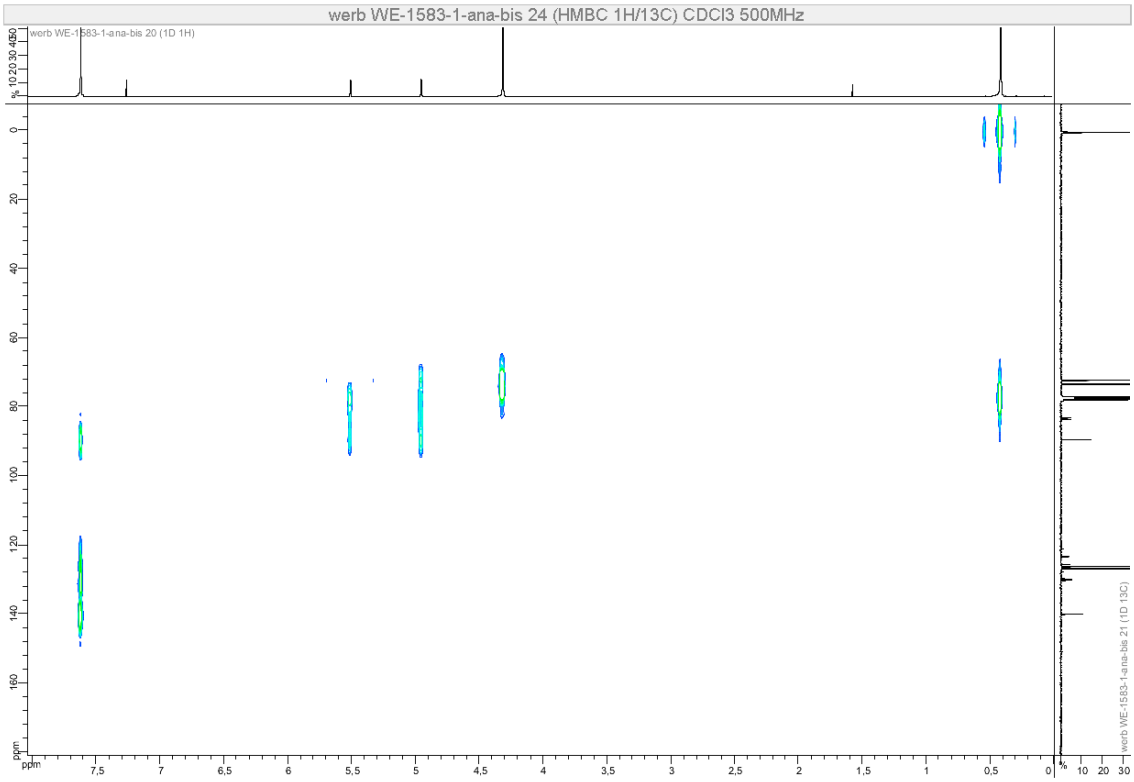
COSY (500 MHz, $CDCl_3$)



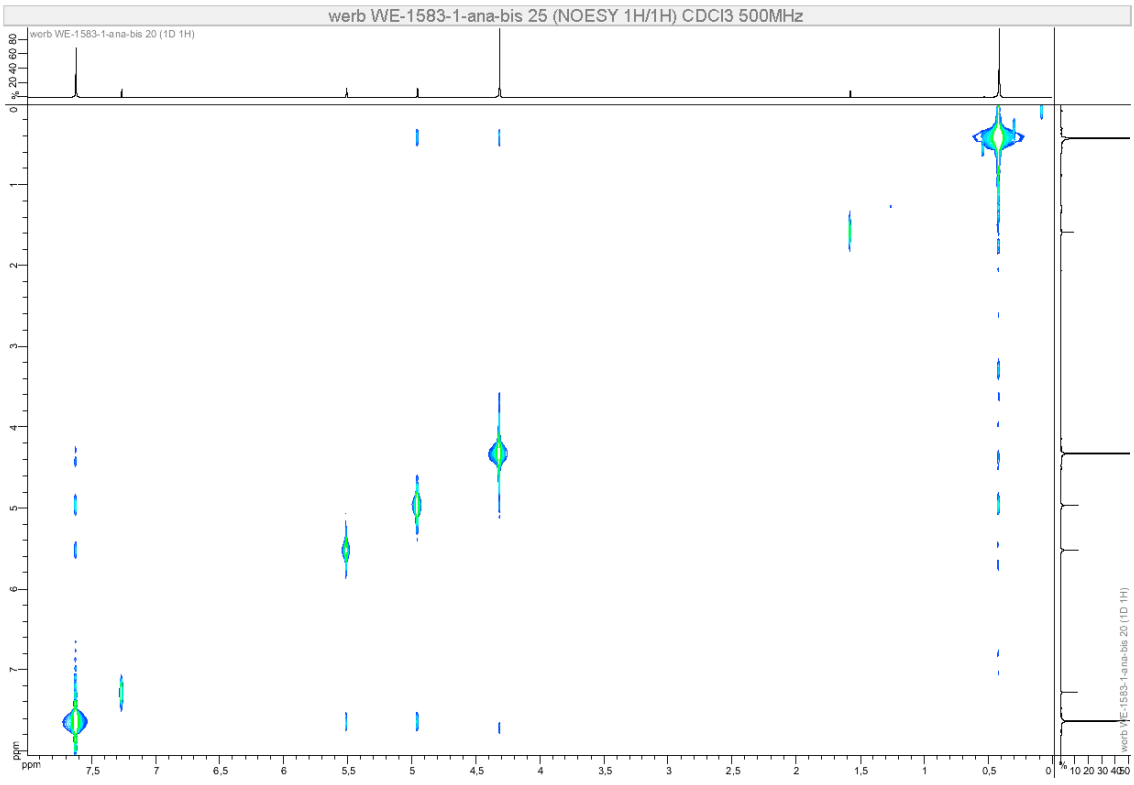
HSQC (500 MHz, $CDCl_3$)



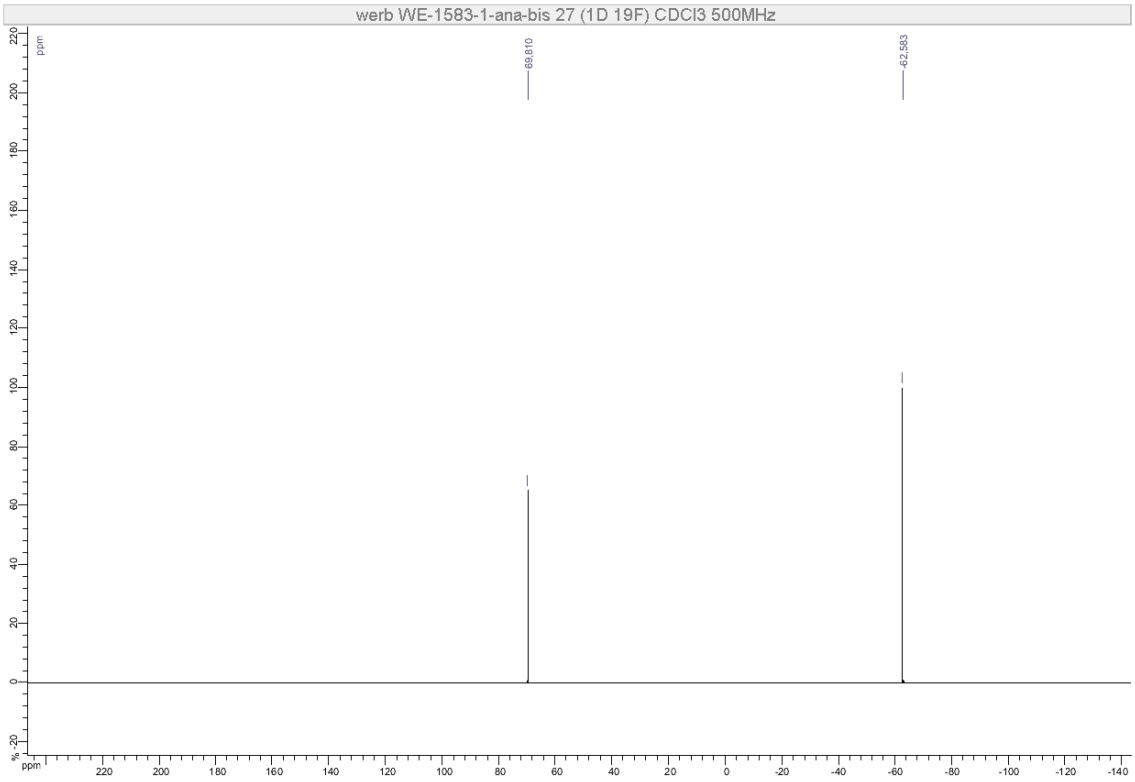
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

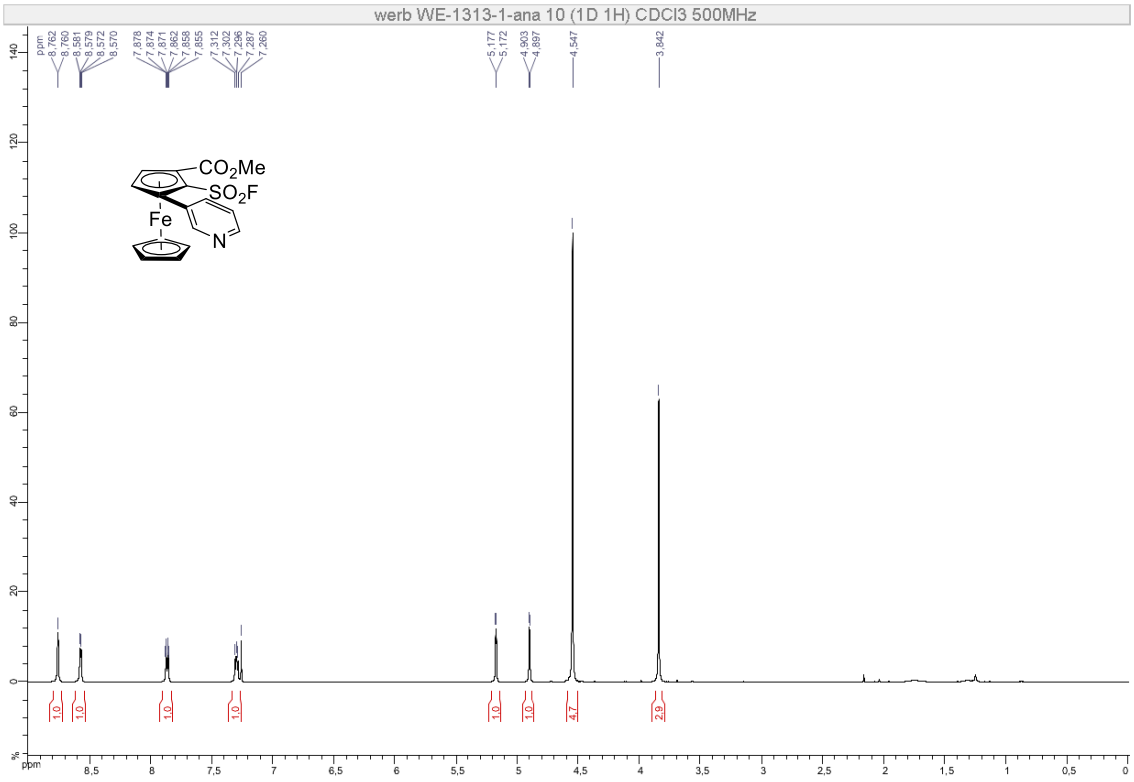


^{19}F NMR (470 MHz, $CDCl_3$)

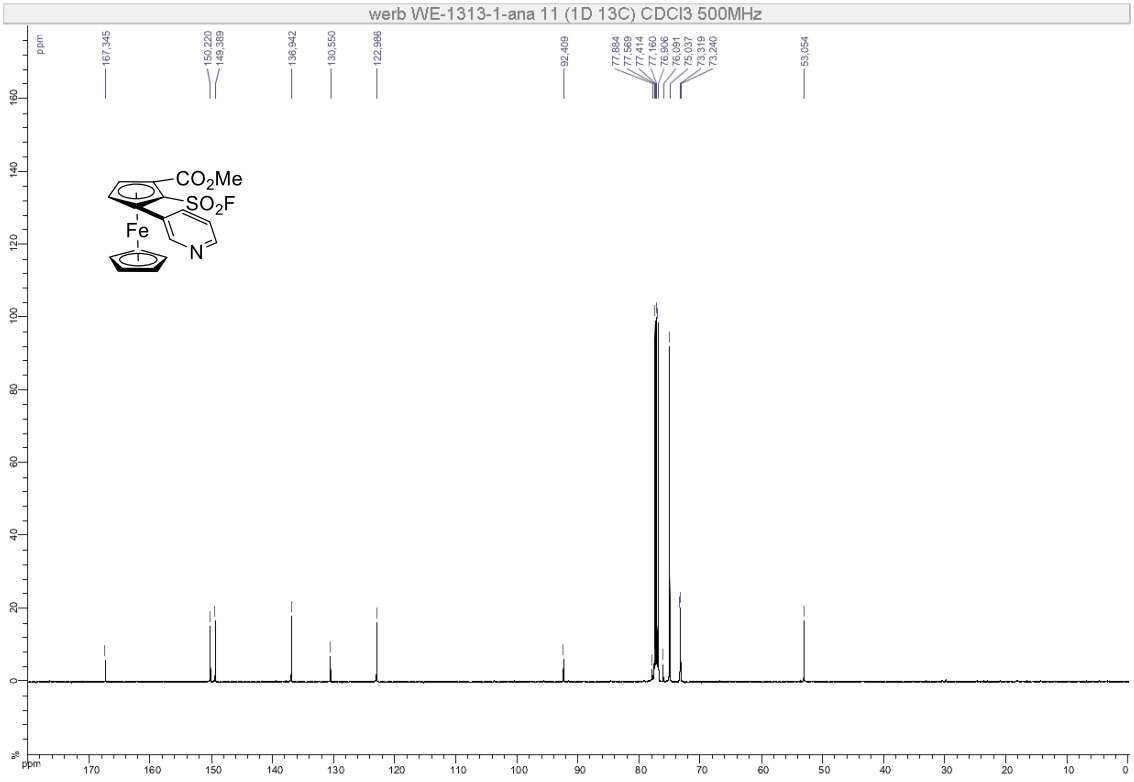


2-Methoxycarbonyl-5-(3-pyridyl)ferrocenesulfonyl fluoride (30a)

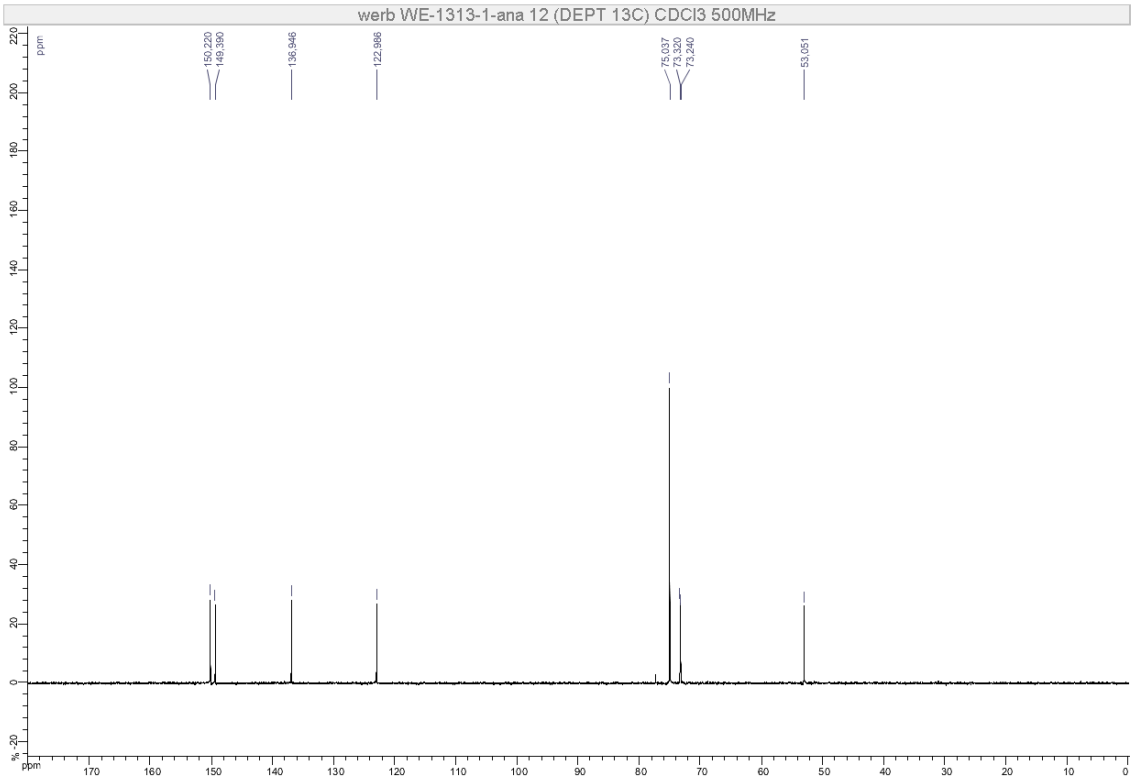
^{1}H NMR (500 MHz, $CDCl_3$)



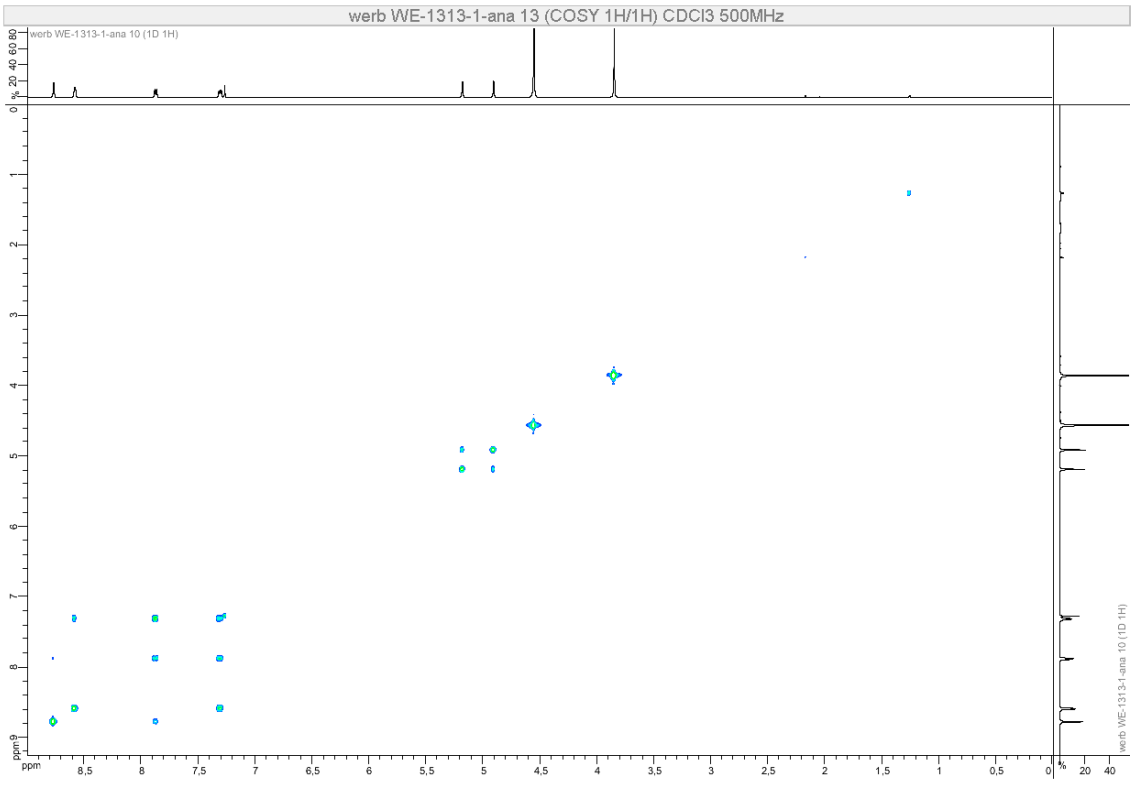
^{13}C NMR (125 MHz, $CDCl_3$)



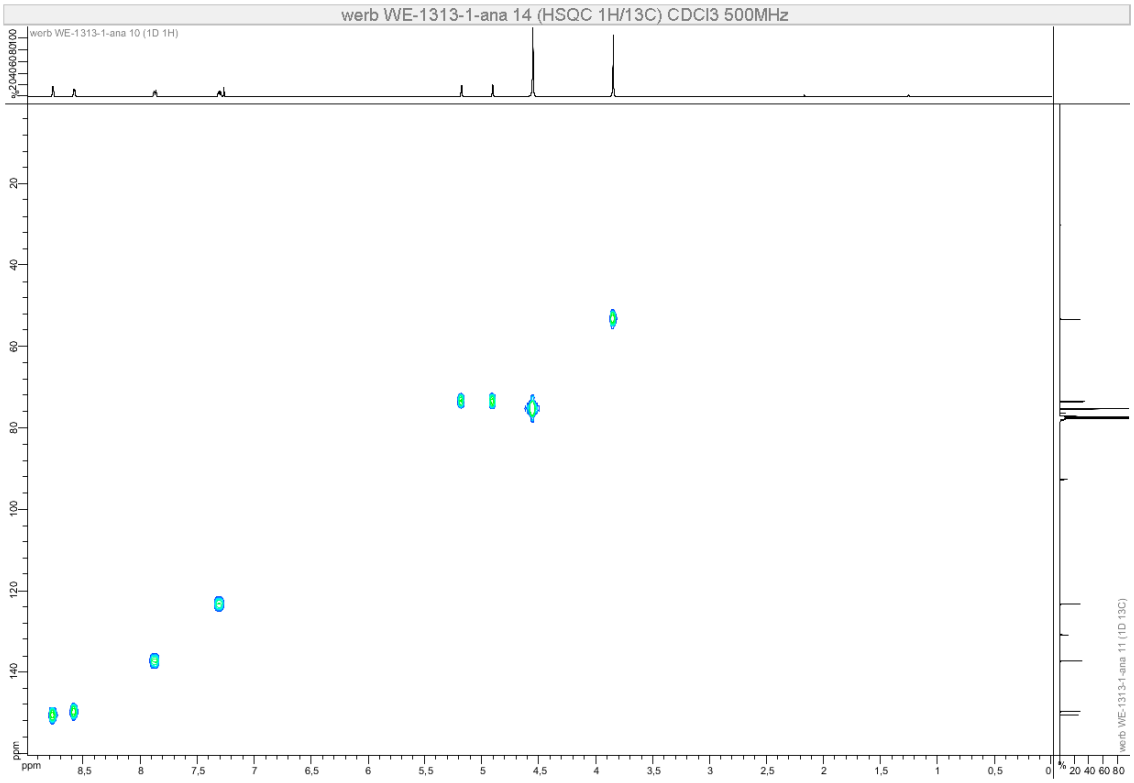
DEPT 135 (125 MHz, $CDCl_3$)



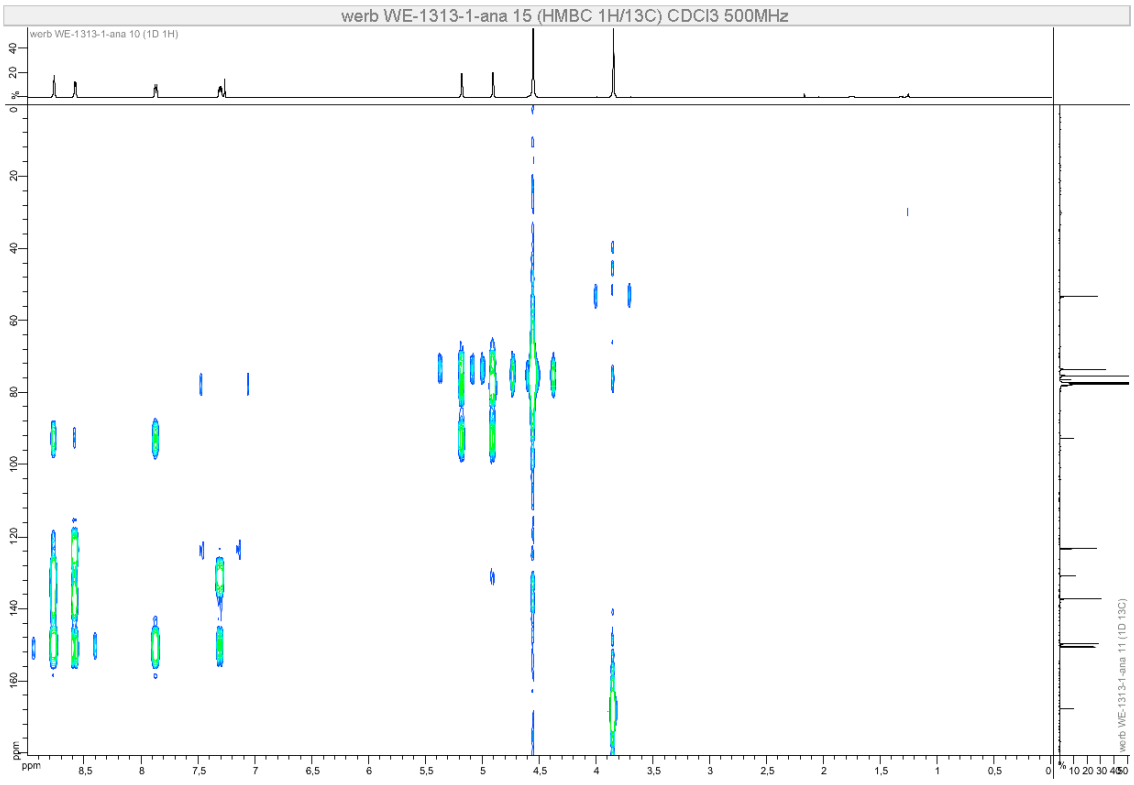
COSY (500 MHz, $CDCl_3$)



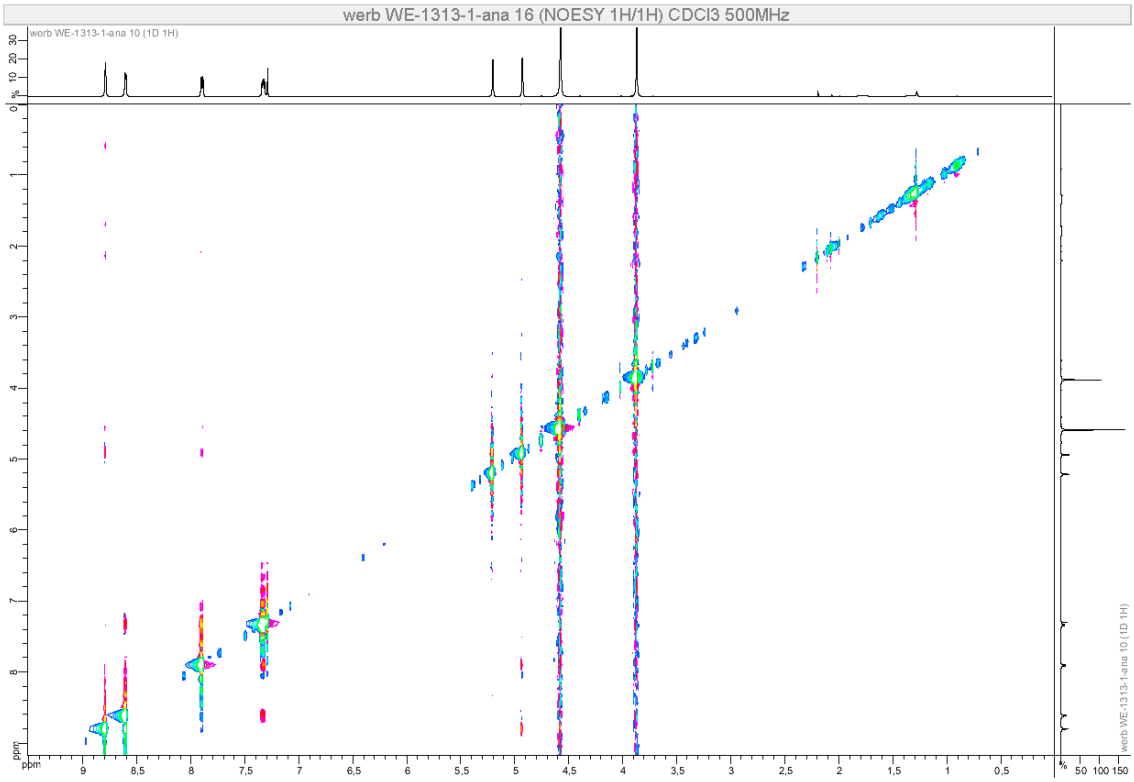
HSQC (500 MHz, $CDCl_3$)



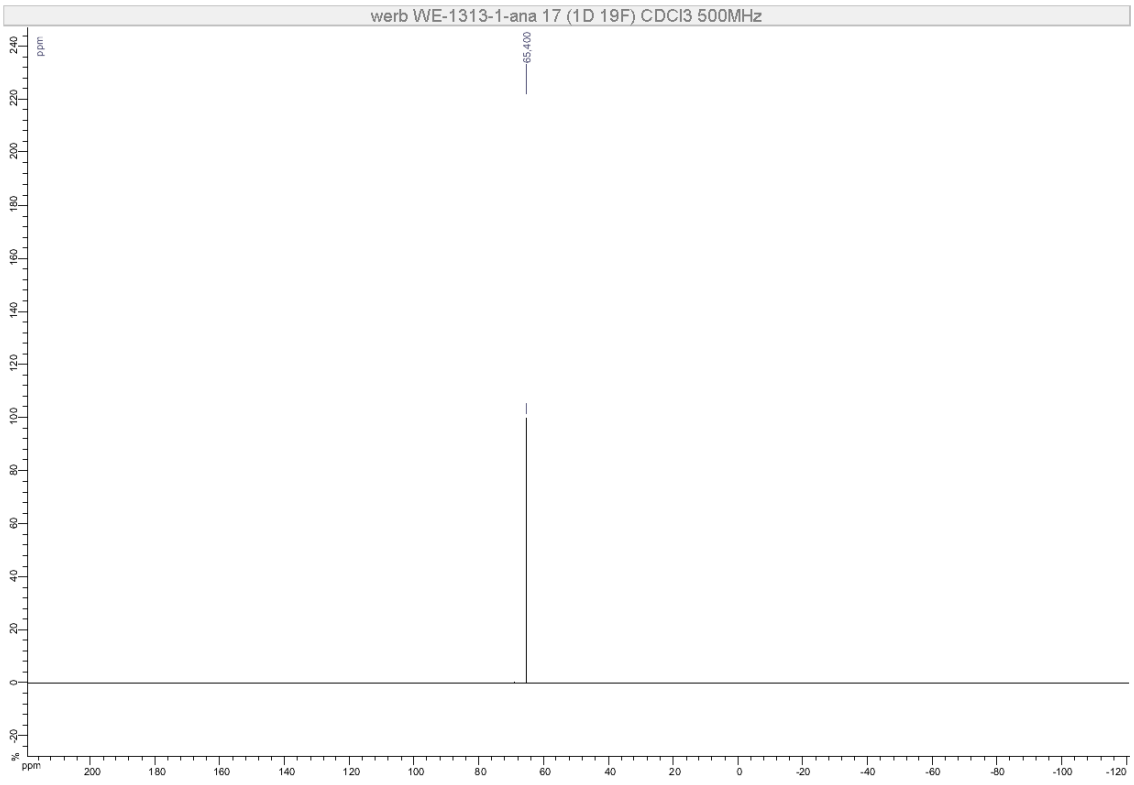
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

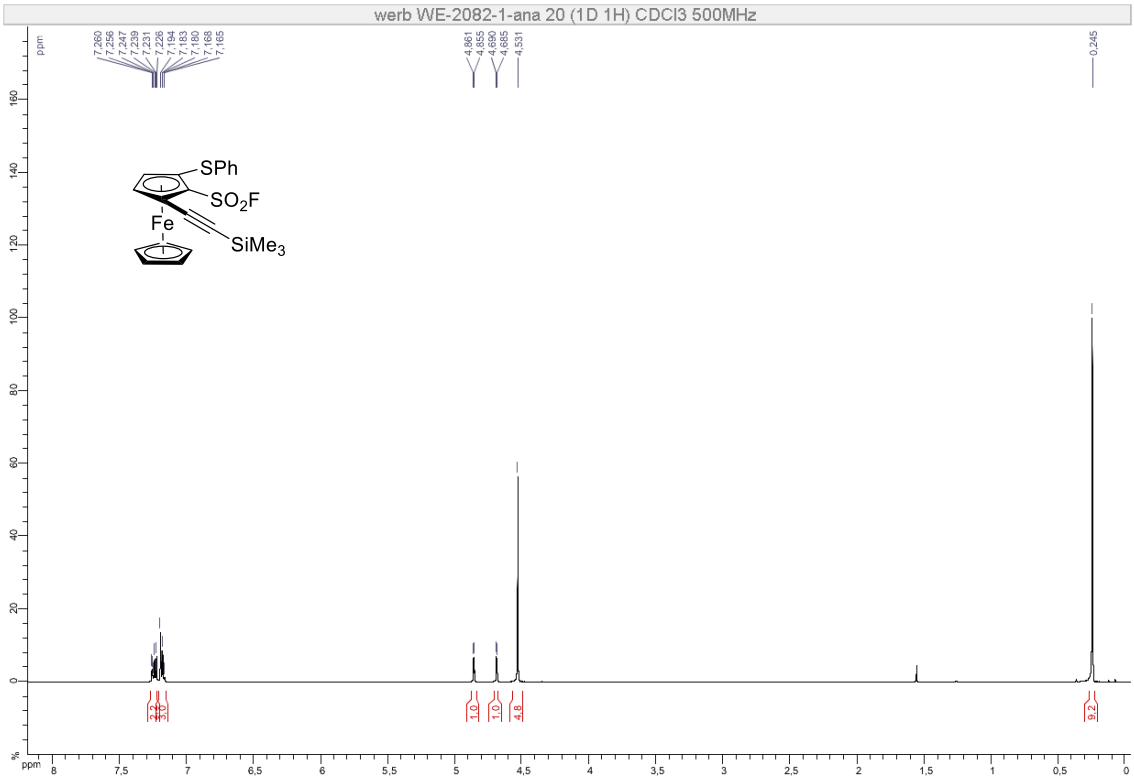


^{19}F NMR (470 MHz, $CDCl_3$)

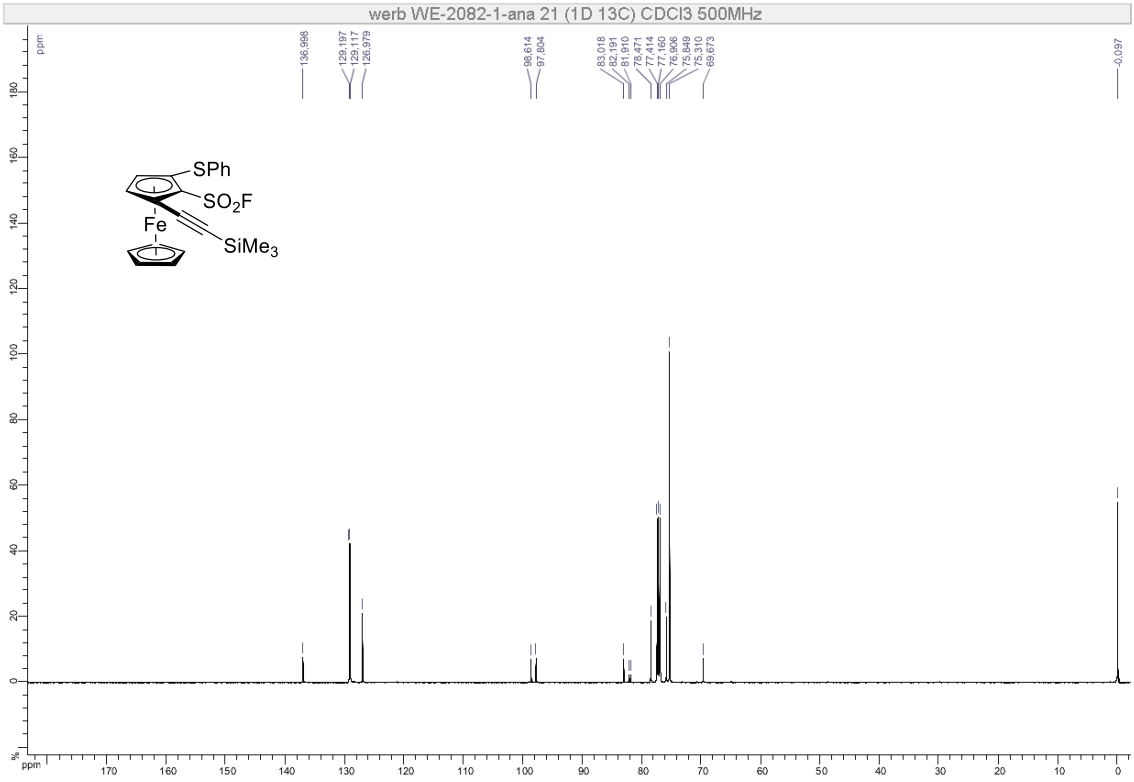


2-(Phenylthio)-5-(trimethylsilylethynyl)ferrocenesulfonyl fluoride (32c)

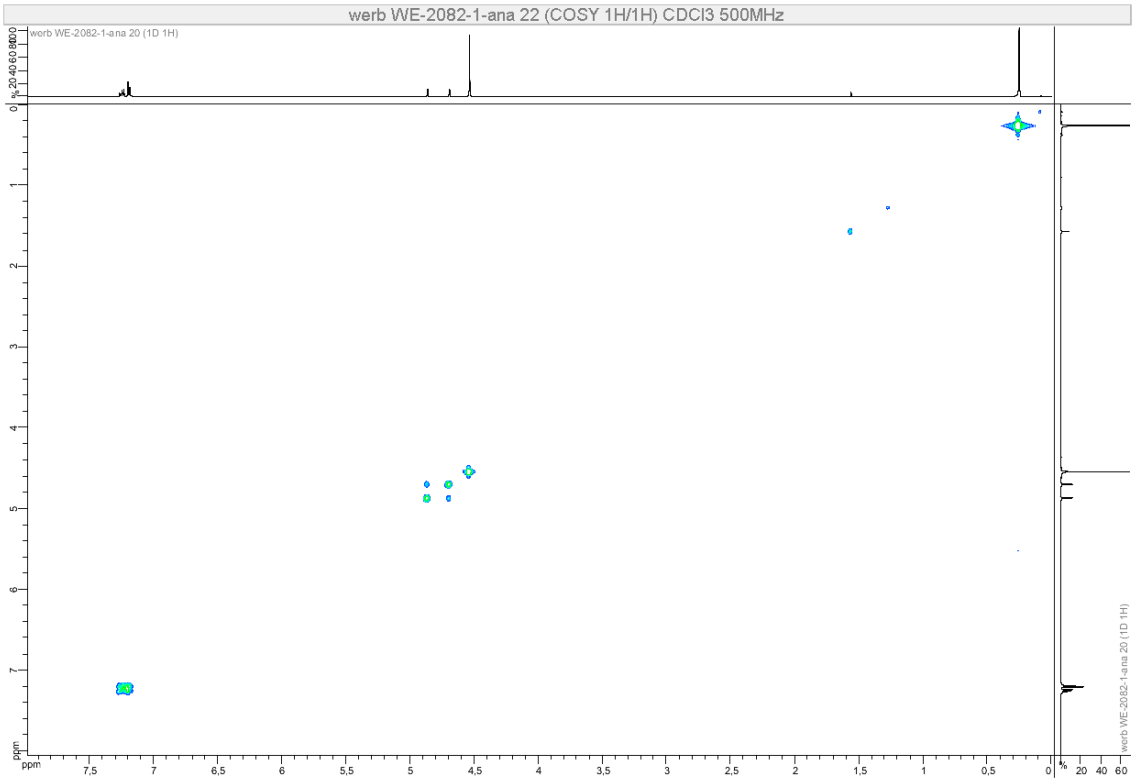
^{1}H NMR (500 MHz, $CDCl_3$)



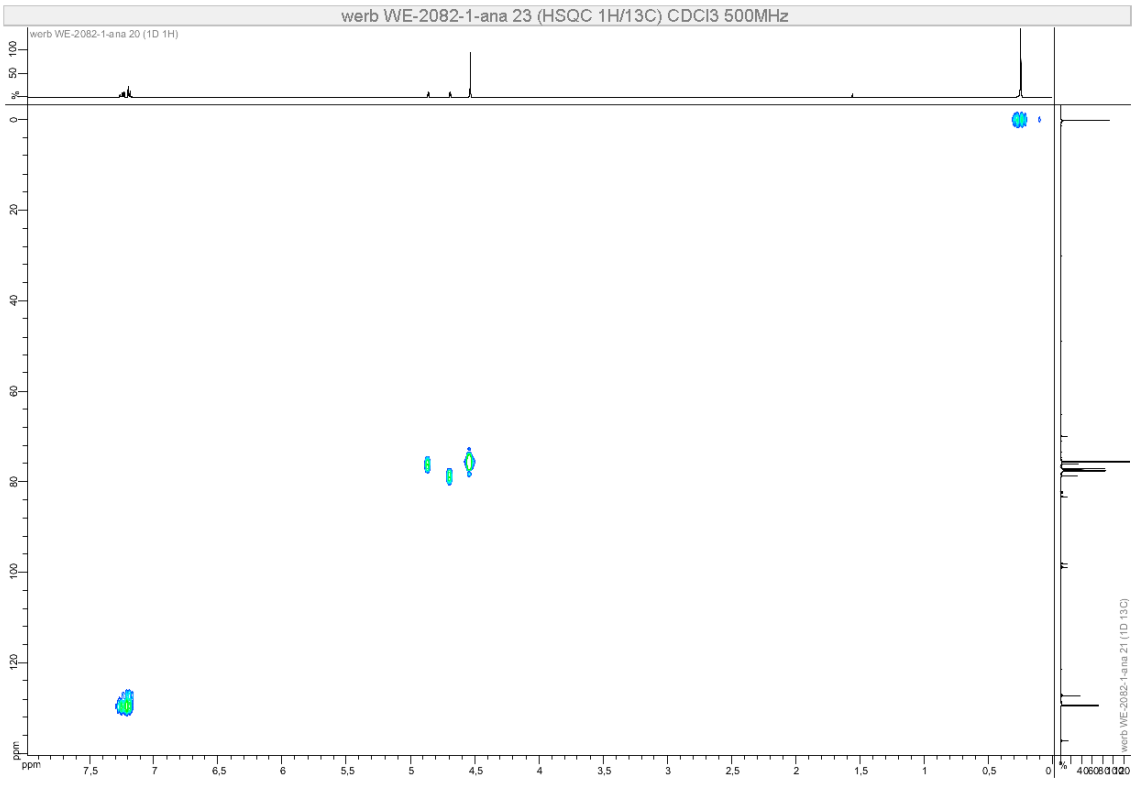
^{13}C NMR (125 MHz, $CDCl_3$)



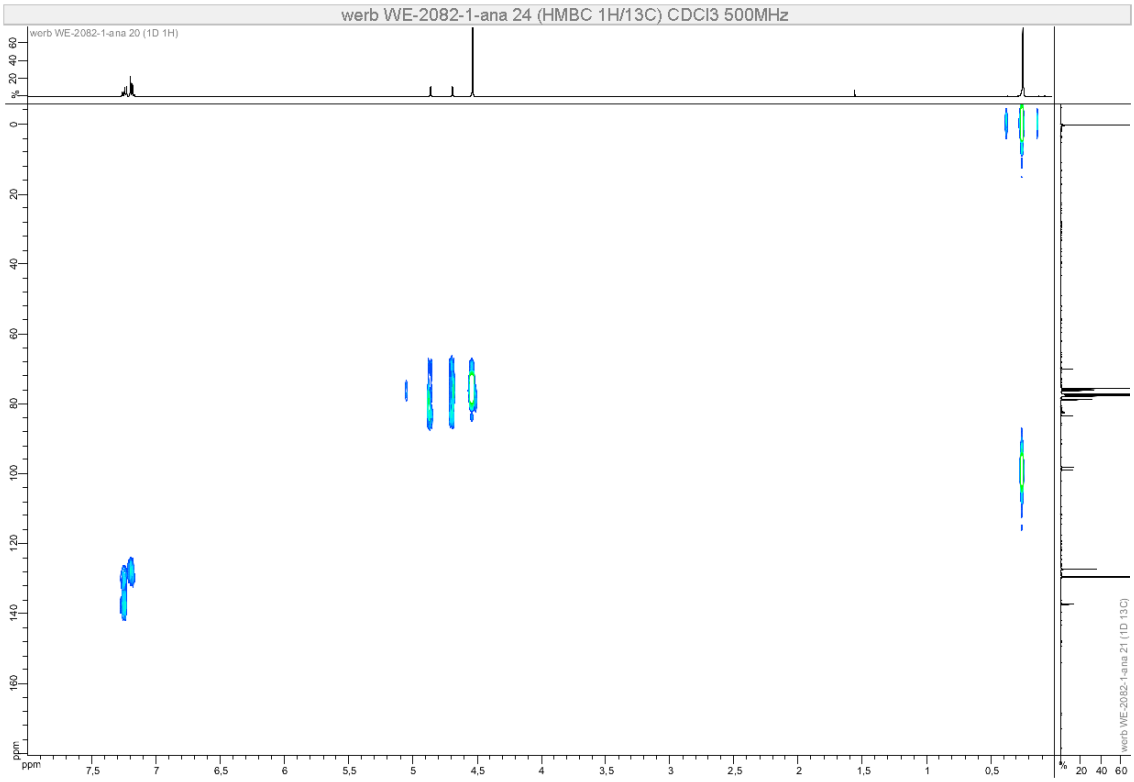
COSY (500 MHz, $CDCl_3$)



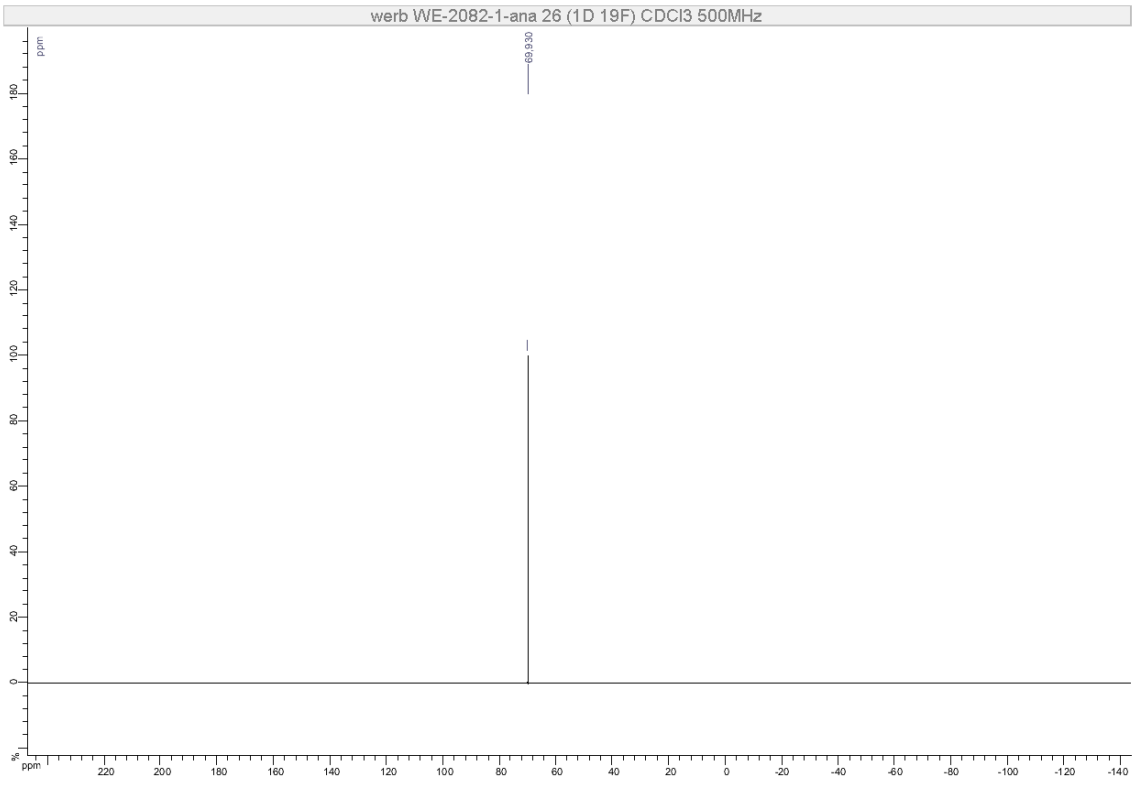
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

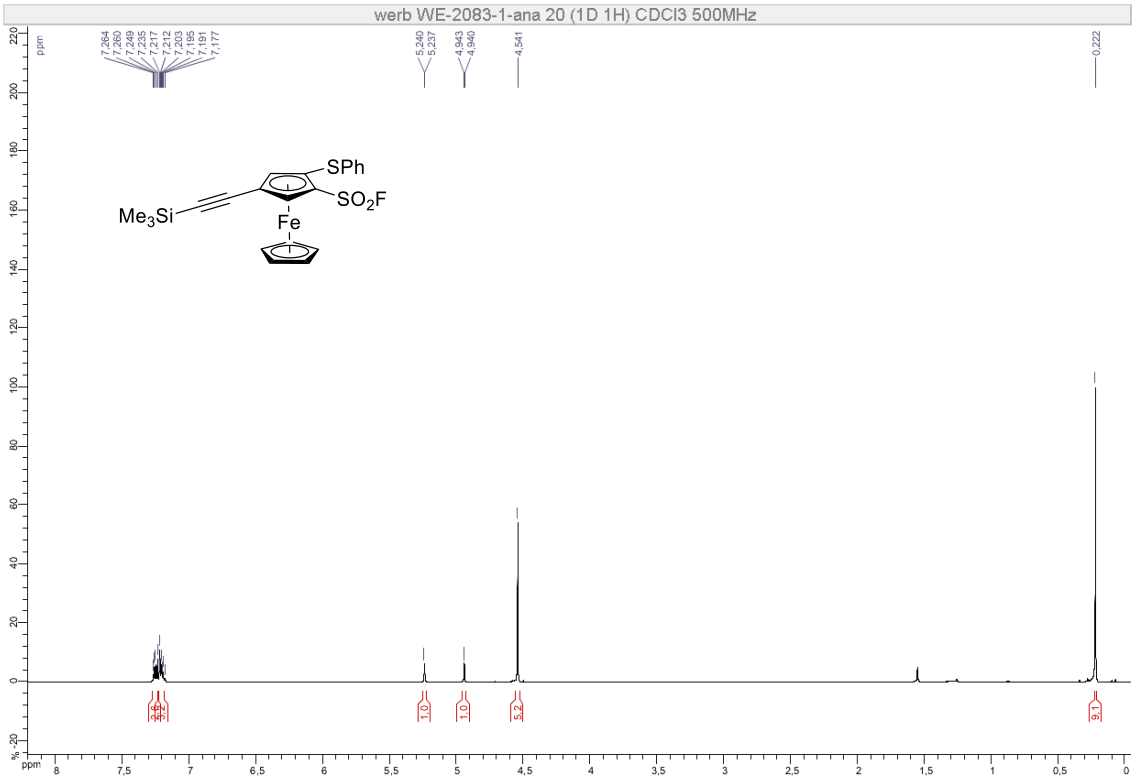


^{19}F NMR (470 MHz, $CDCl_3$)

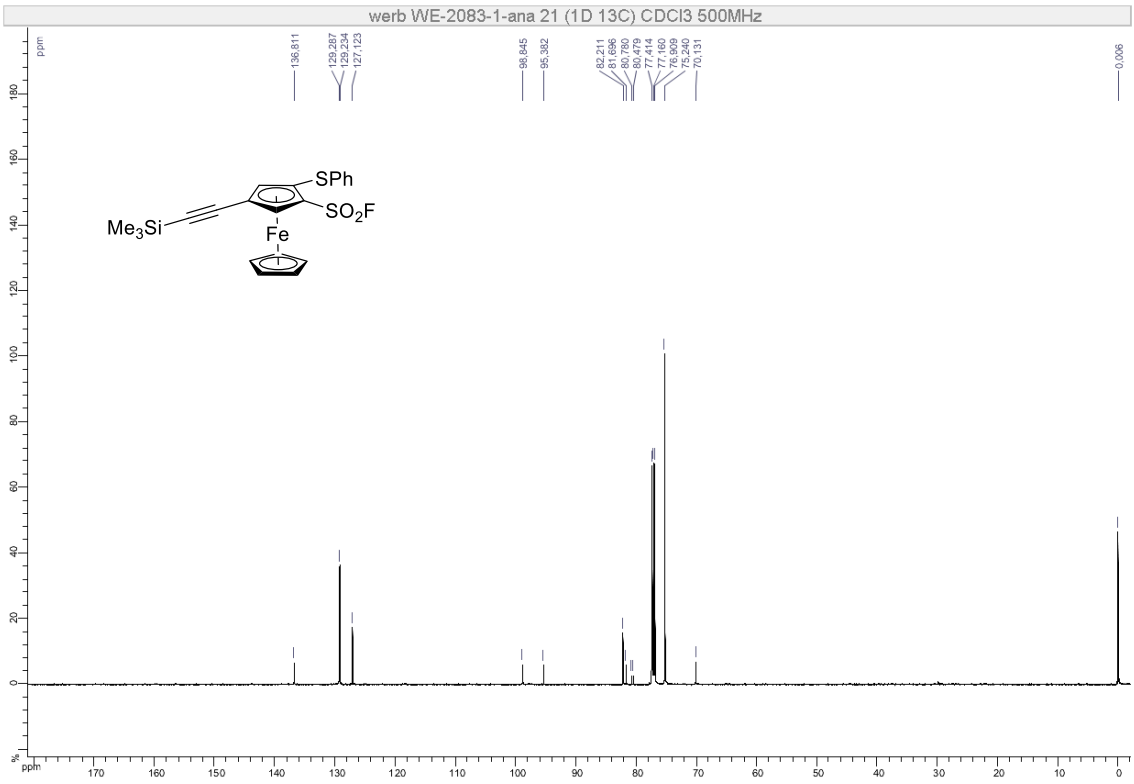


2-(Phenylthio)-4-(trimethylsilylethynyl)ferrocenesulfonyl fluoride (32d)

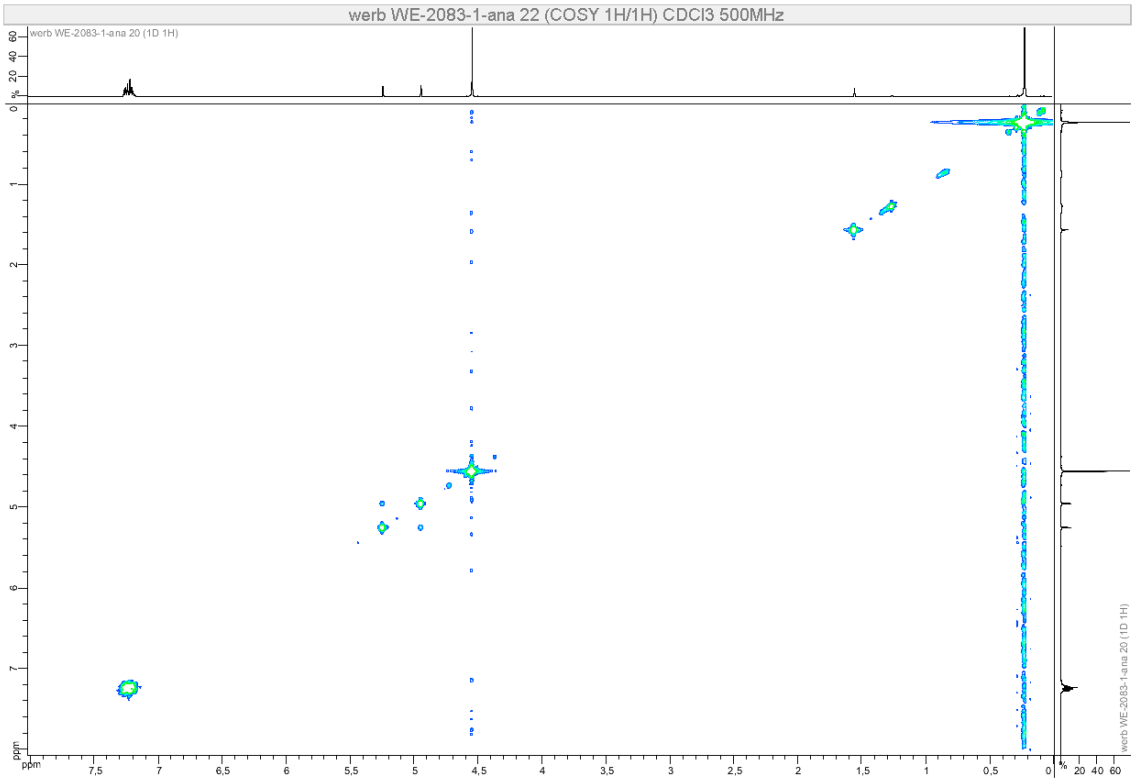
^{1}H NMR (500 MHz, $CDCl_3$)



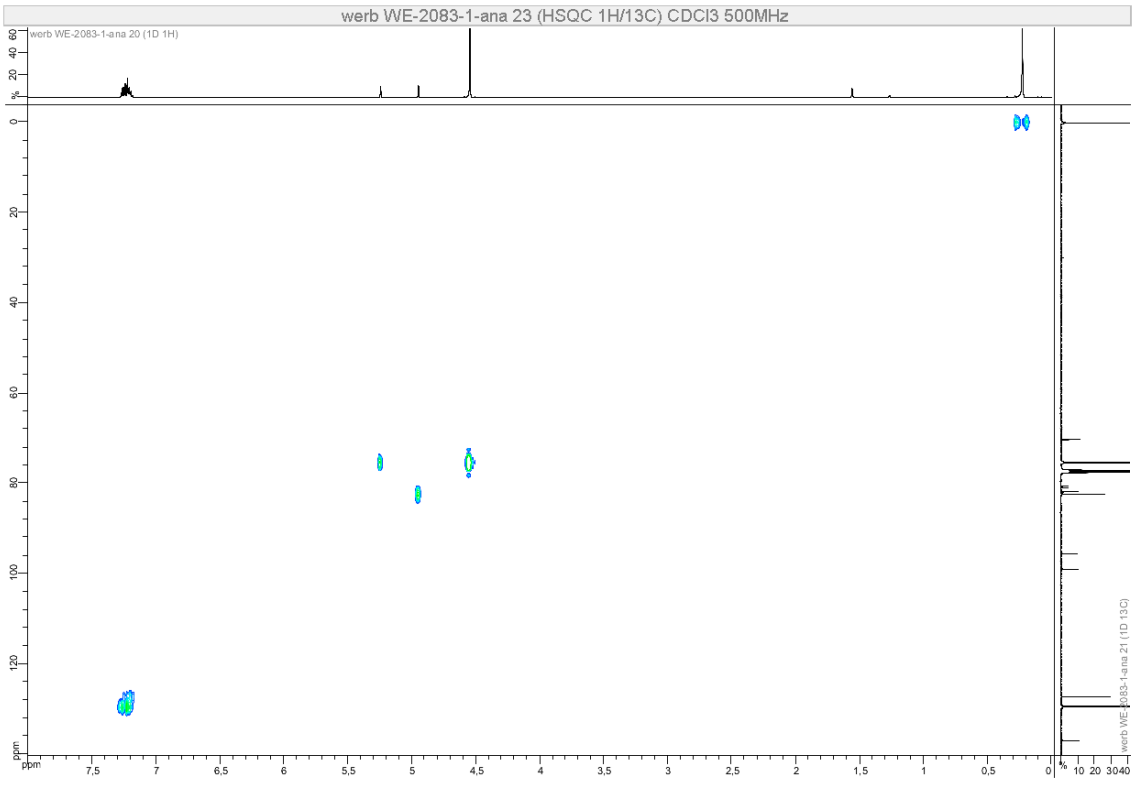
^{13}C NMR (125 MHz, $CDCl_3$)



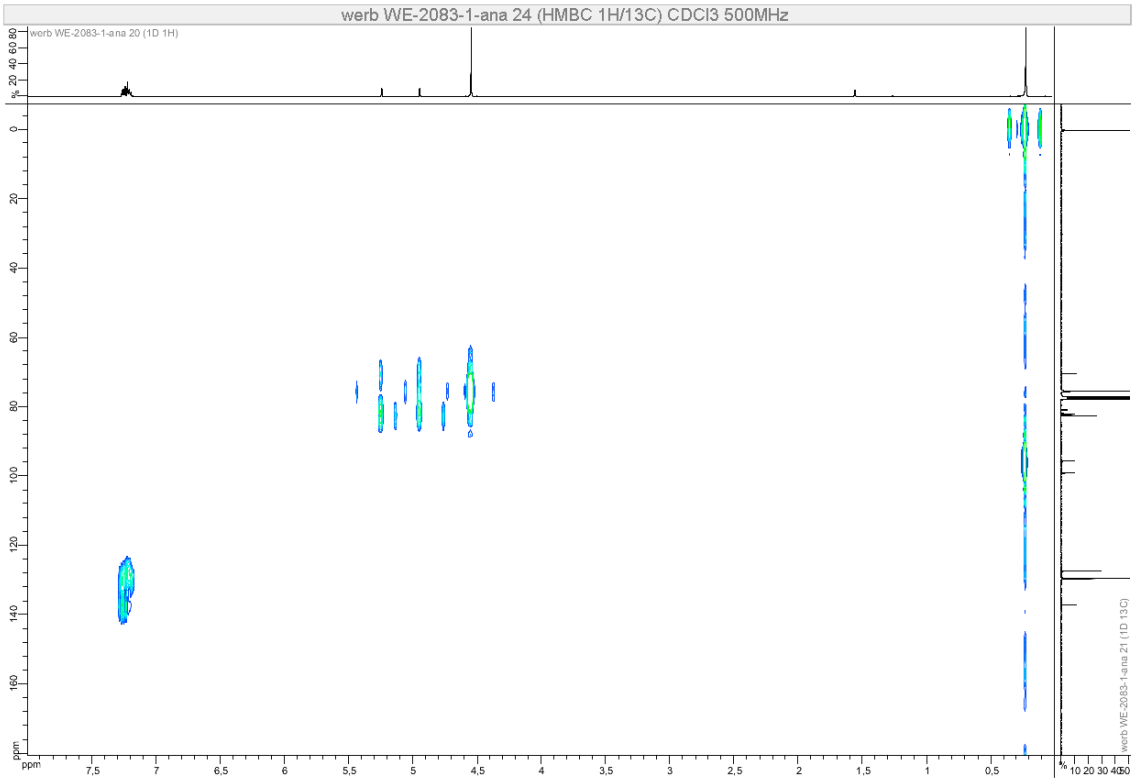
COSY (500 MHz, $CDCl_3$)



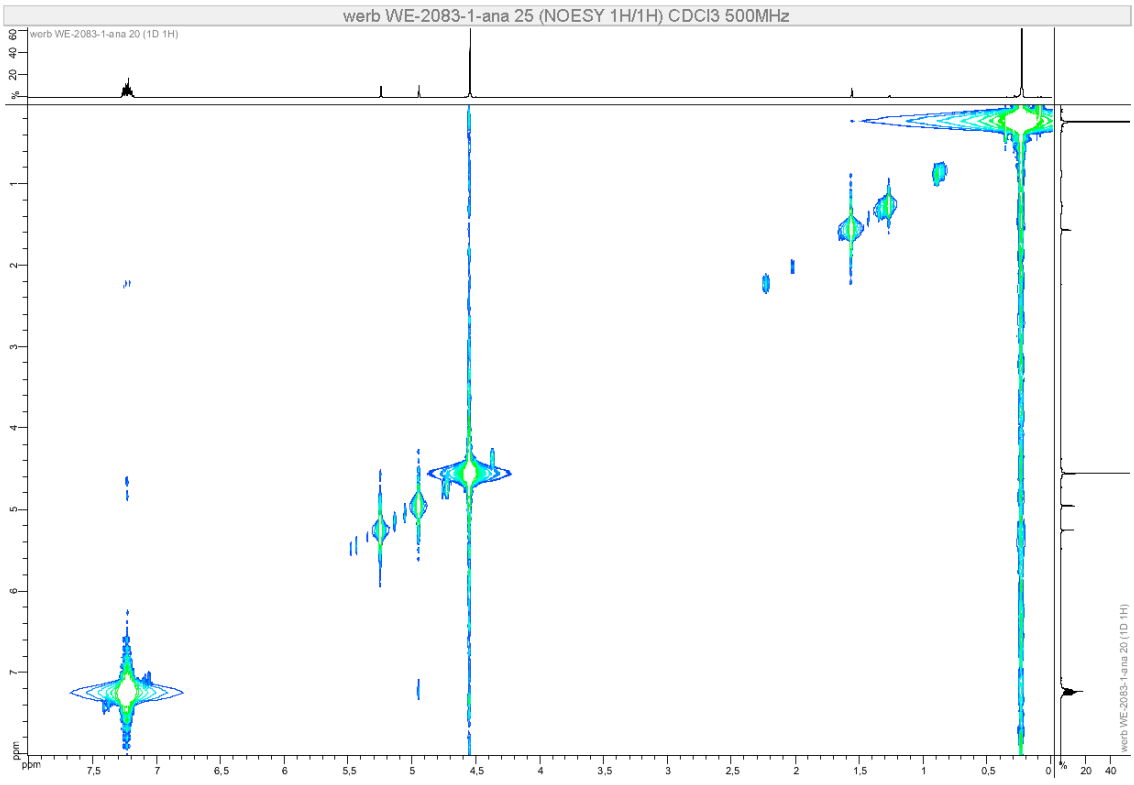
HSQC (500 MHz, $CDCl_3$)



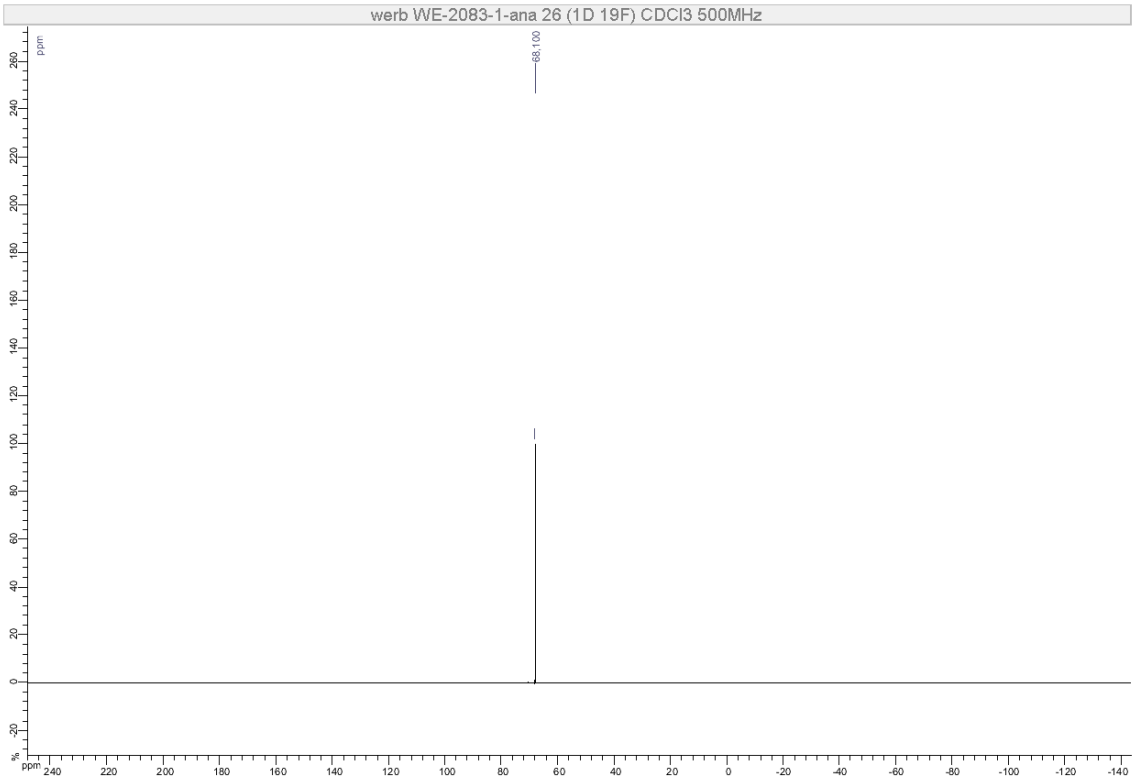
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

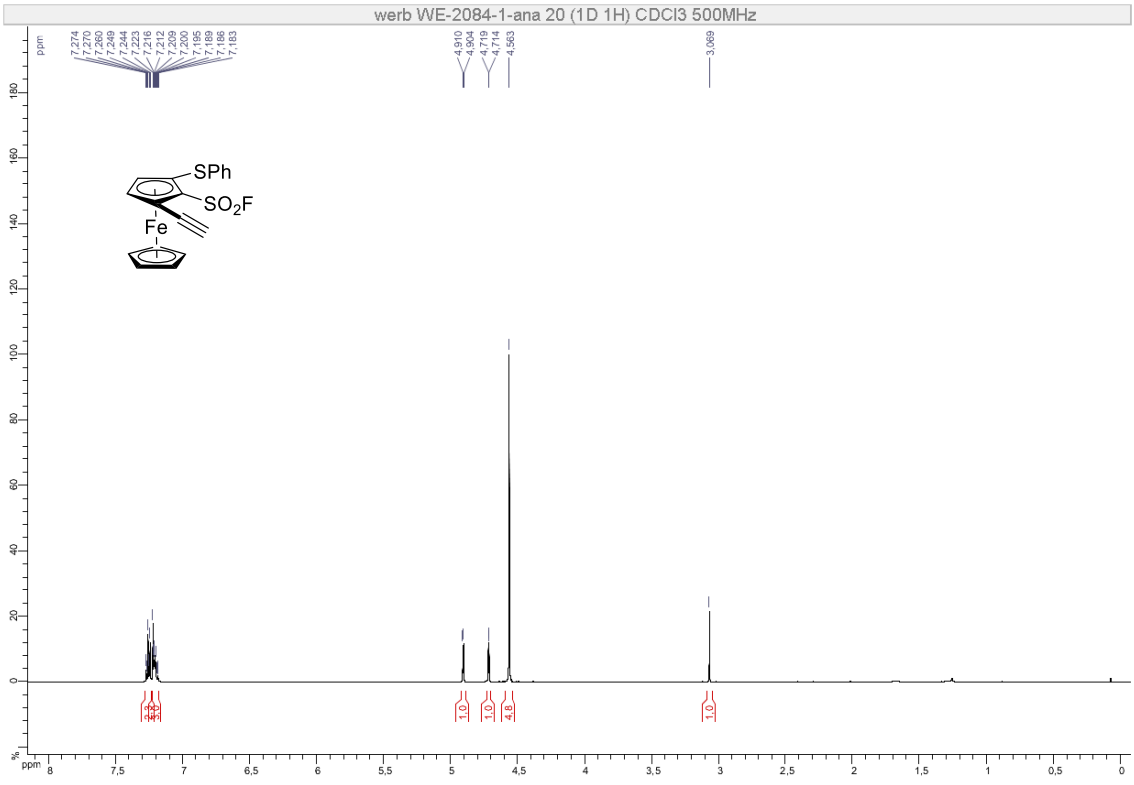


^{19}F NMR (470 MHz, $CDCl_3$)

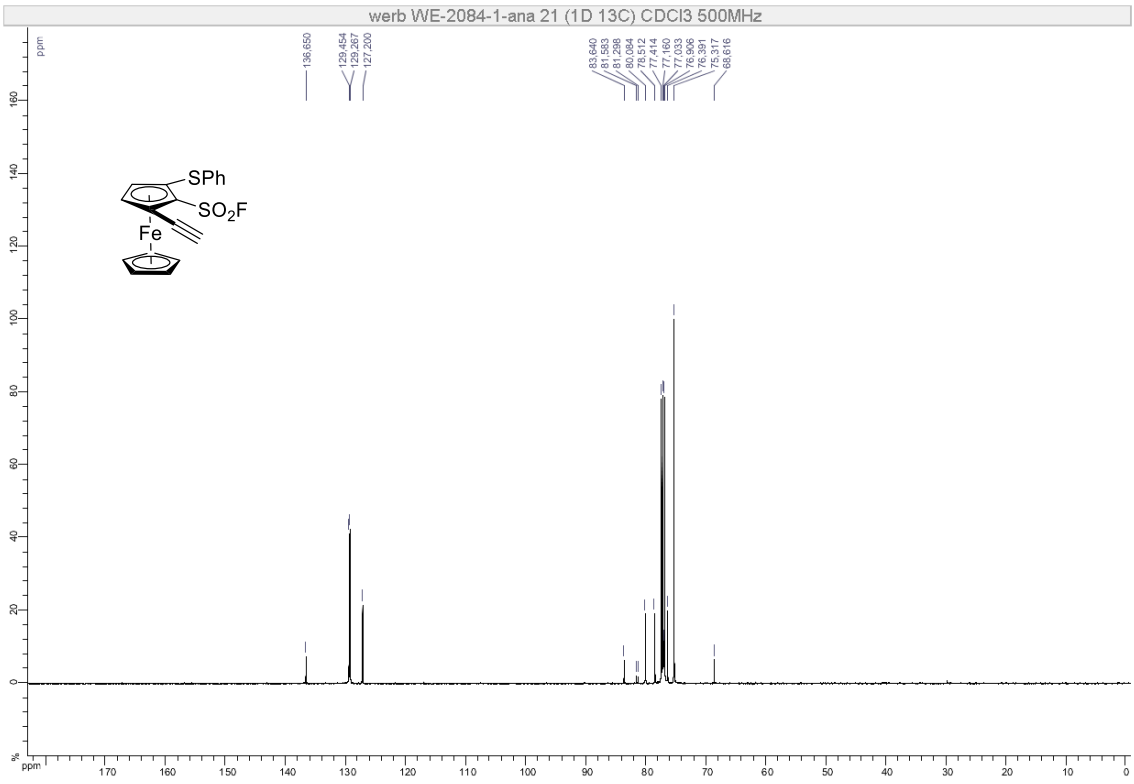


2-Ethynyl-5-(phenylthio)ferrocenesulfonyl fluoride (33c)

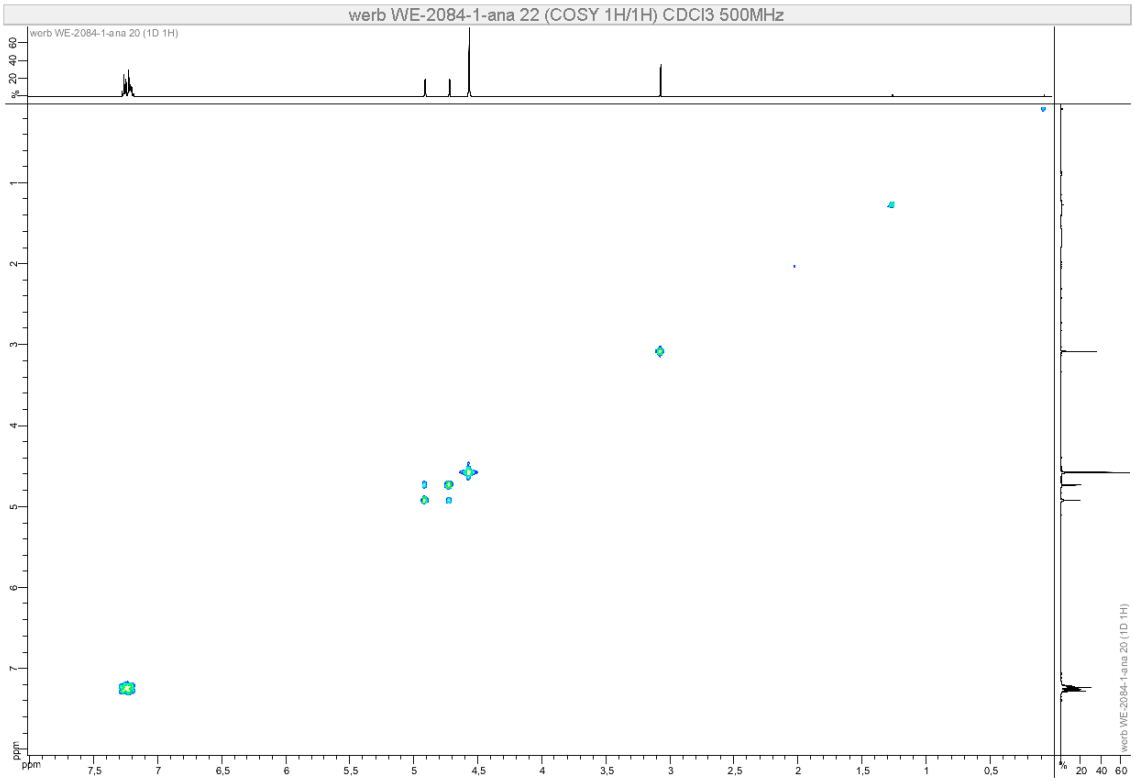
^{1}H NMR (500 MHz, $CDCl_3$)



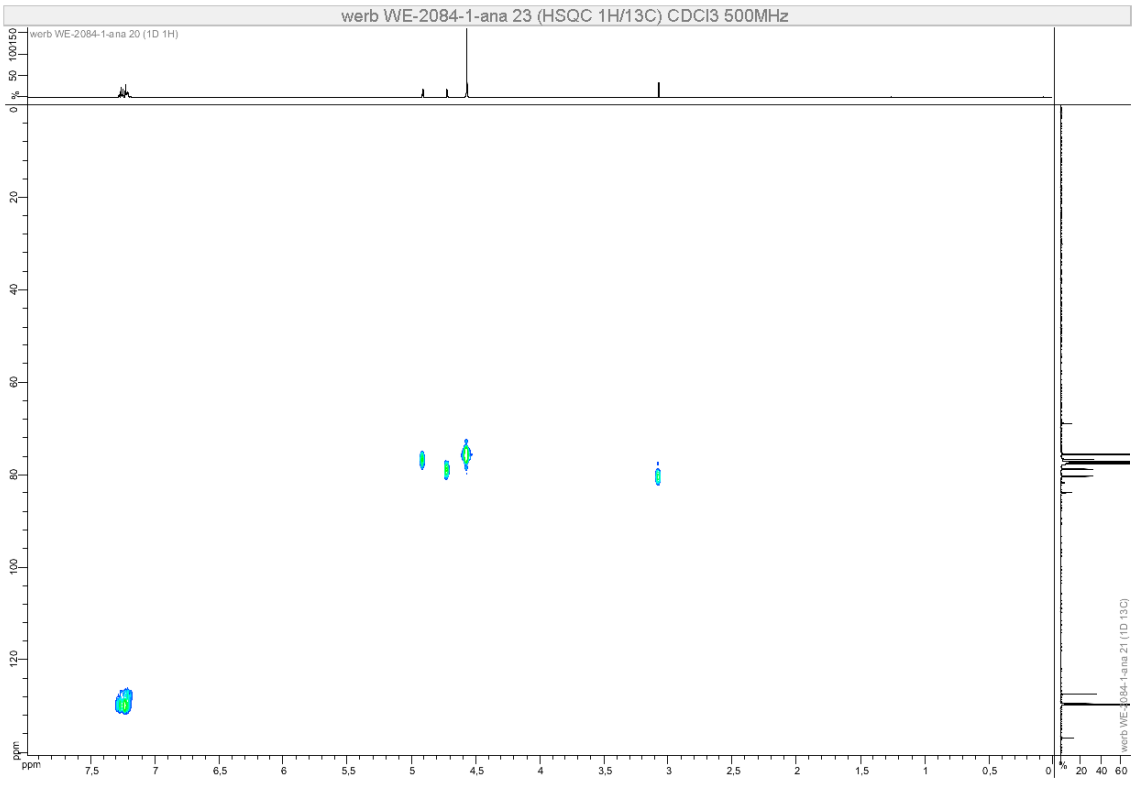
^{13}C NMR (125 MHz, $CDCl_3$)



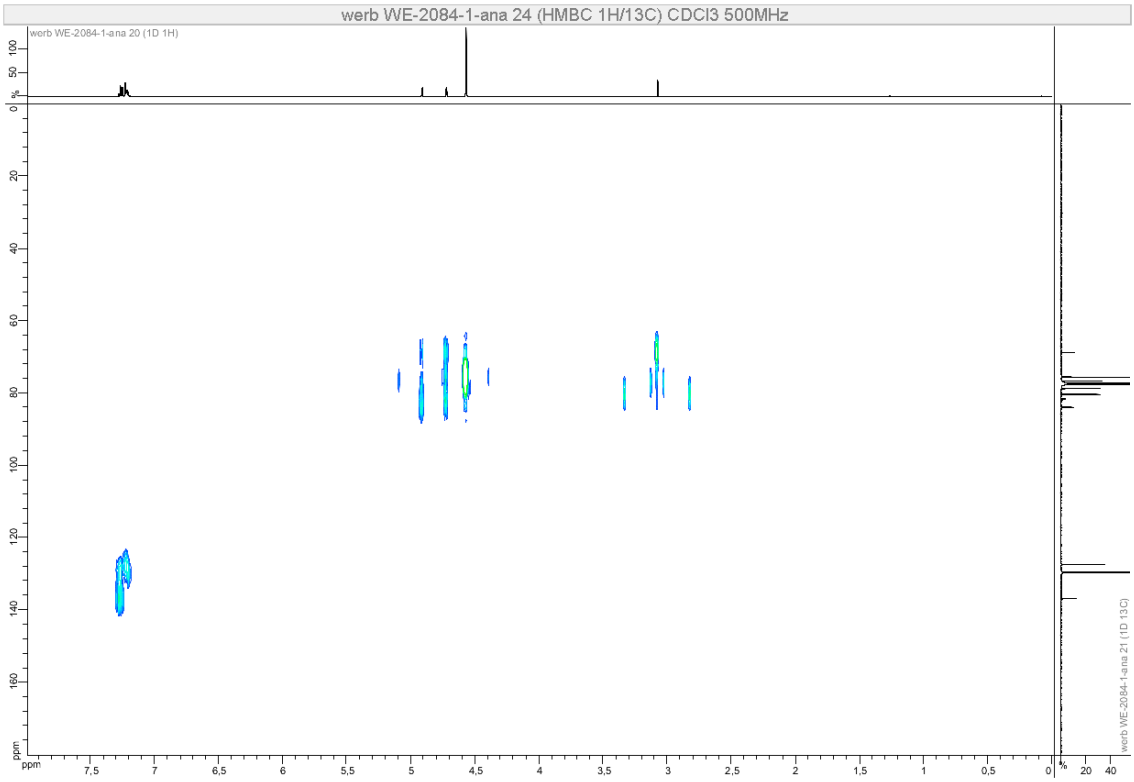
COSY (500 MHz, $CDCl_3$)



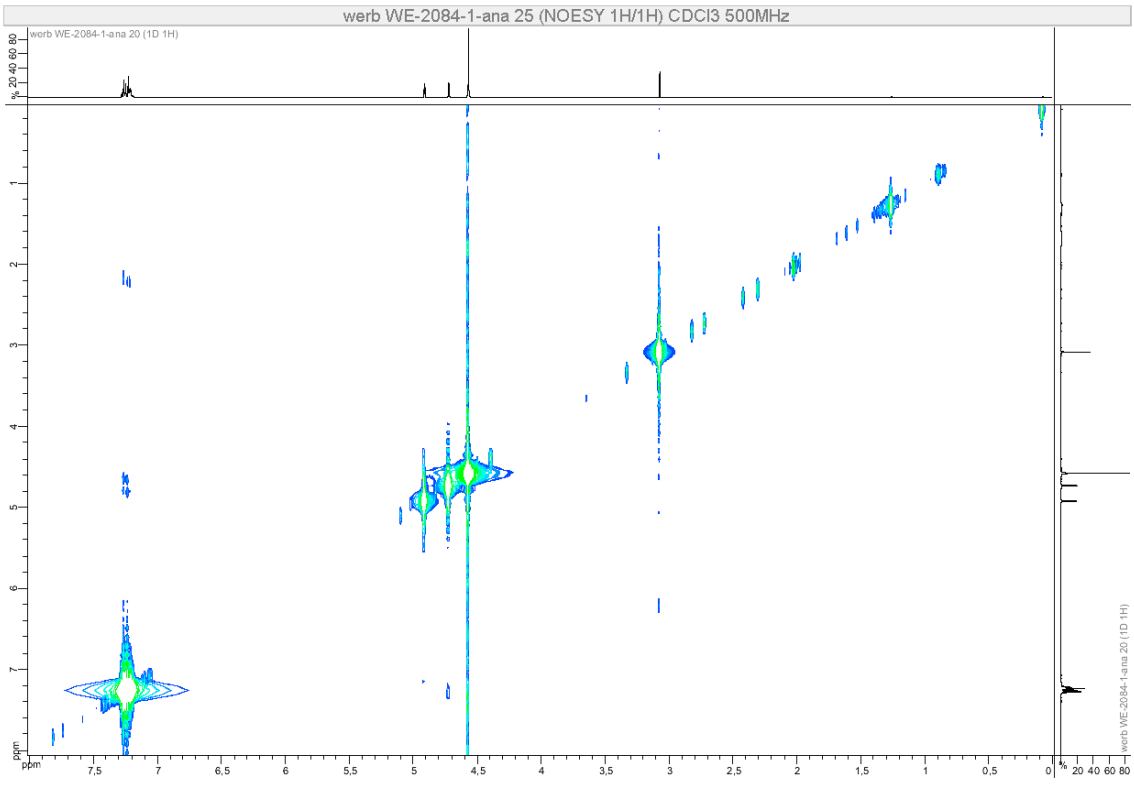
HSQC (500 MHz, $CDCl_3$)



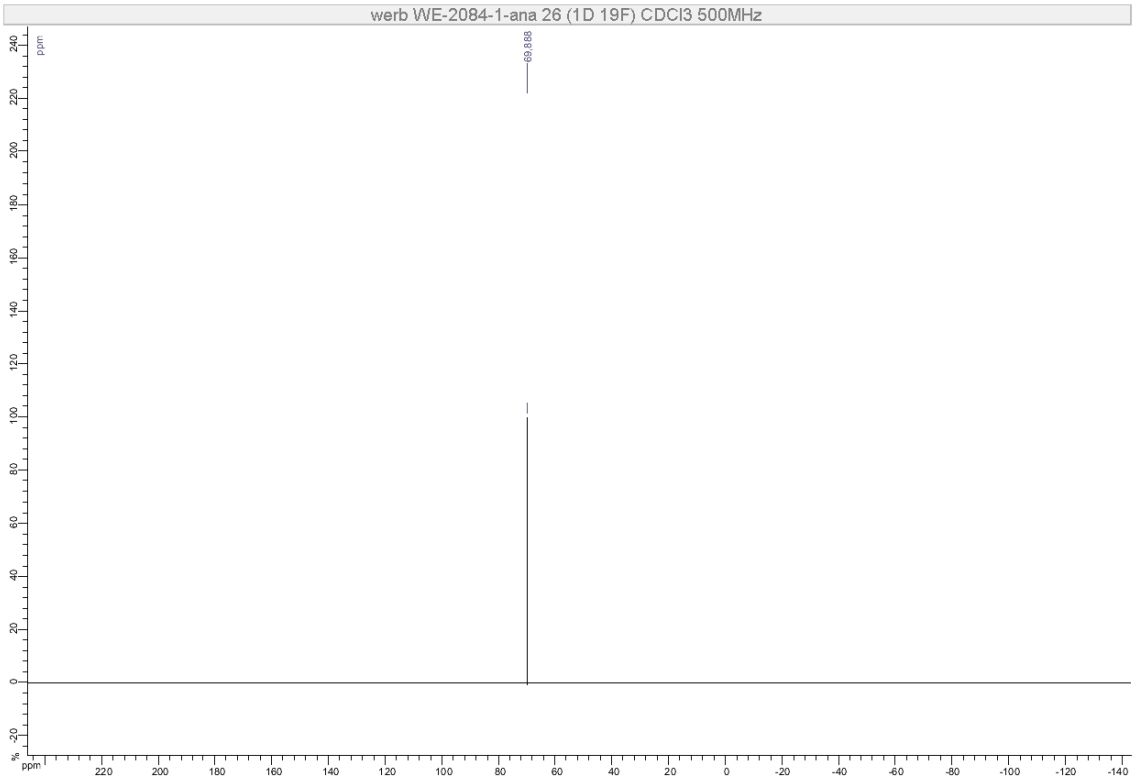
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

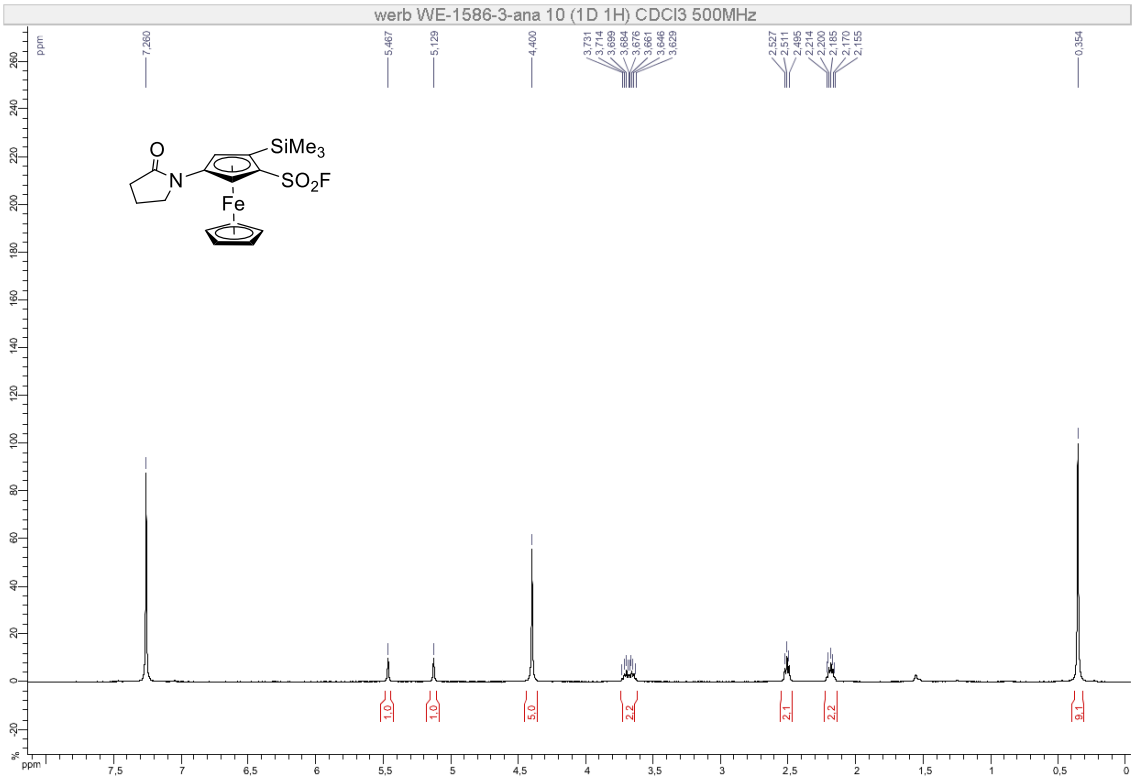


^{19}F NMR (470 MHz, $CDCl_3$)

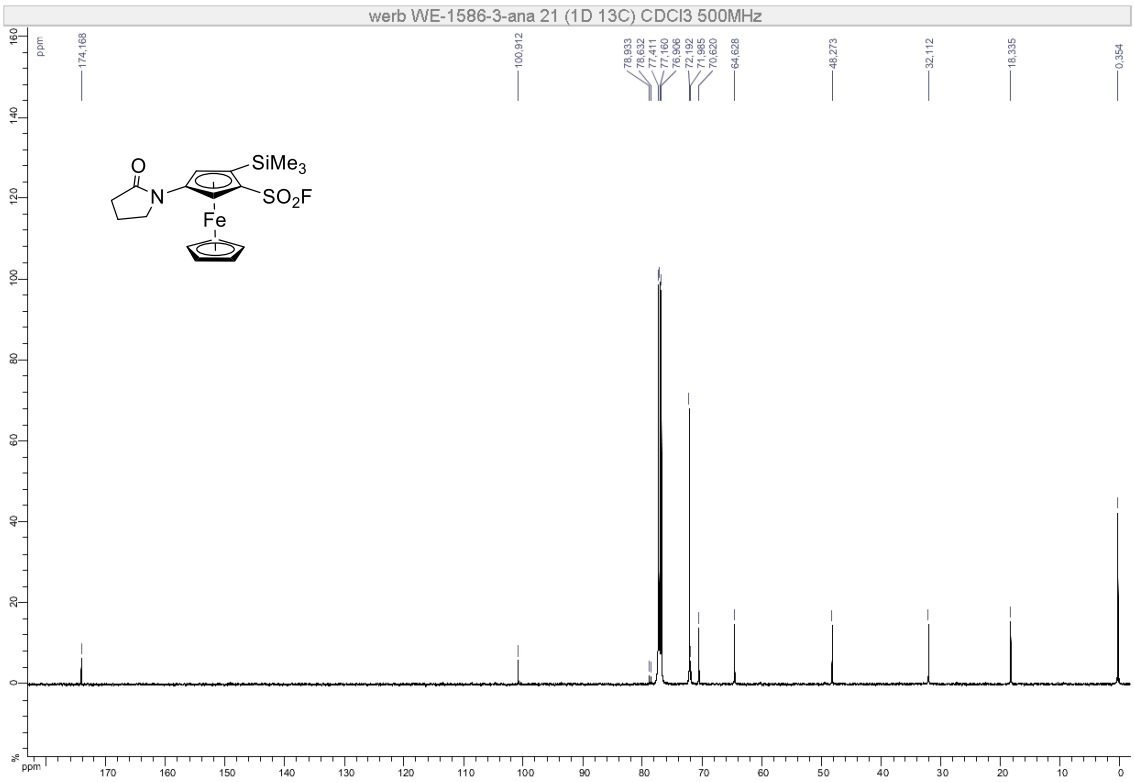


4-(2-Oxo-*N*-pyrrolidyl)-2-trimethylsilylferrocenesulfonyl fluoride (34a)

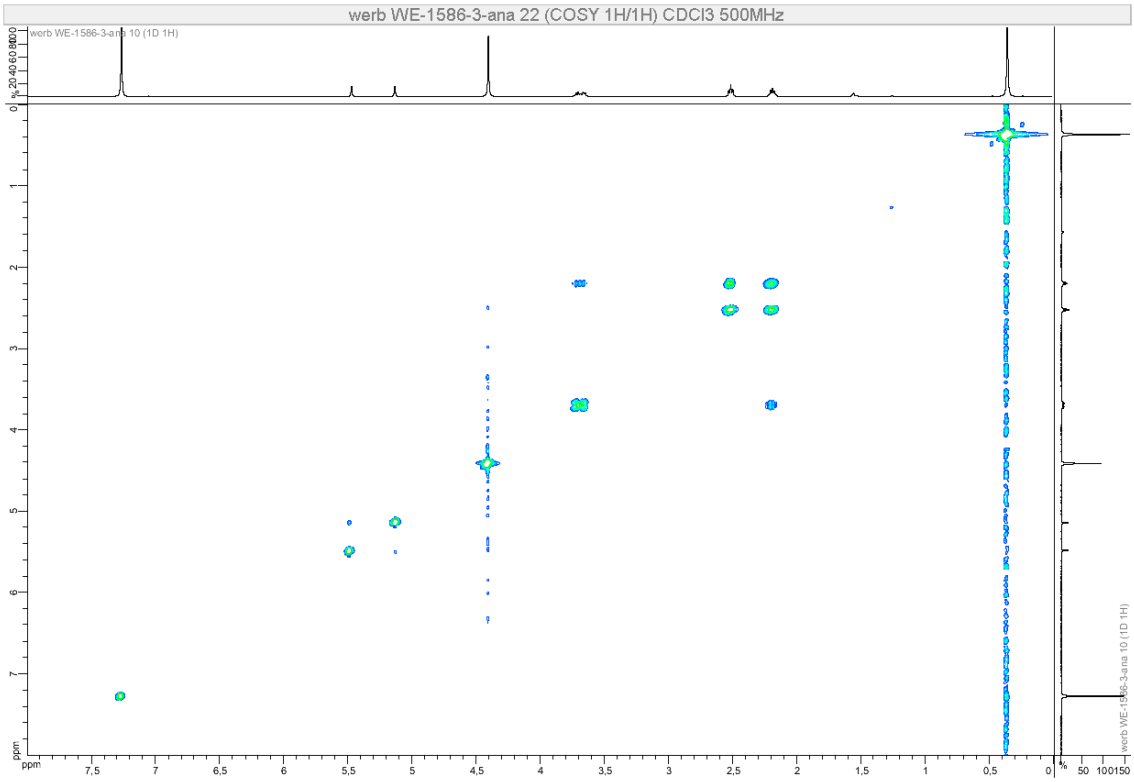
^{1}H NMR (500 MHz, $CDCl_3$)



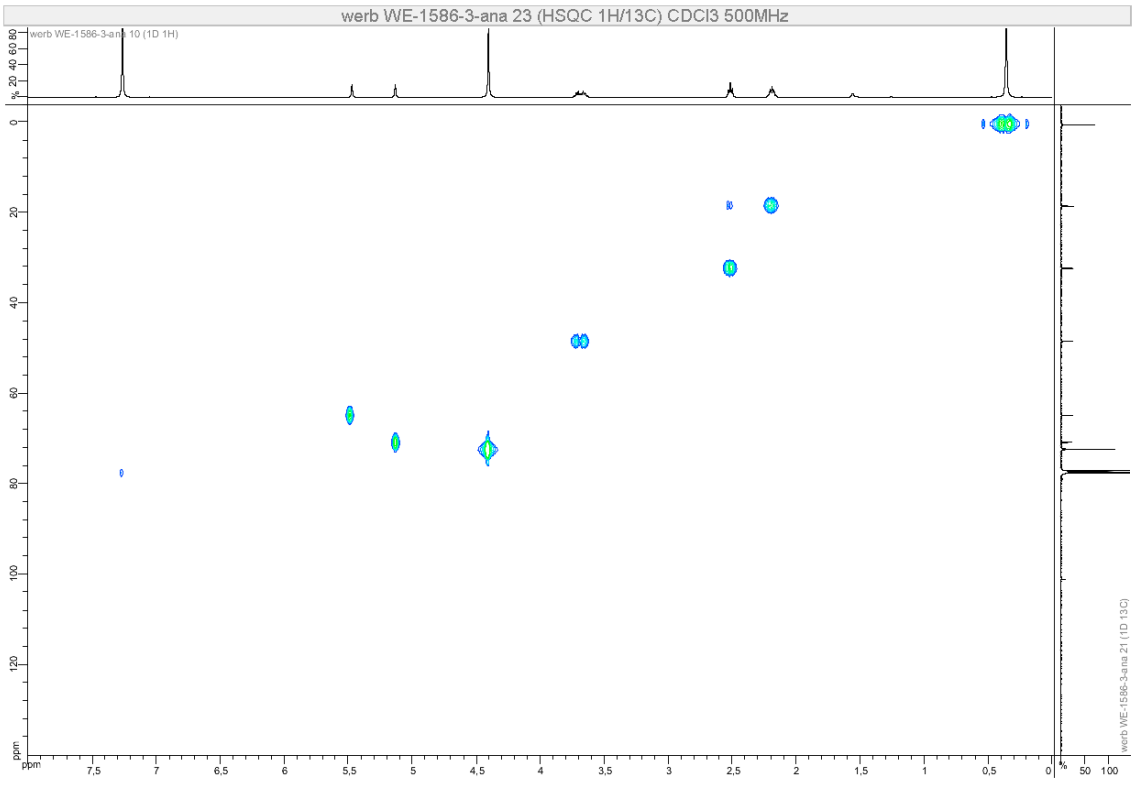
^{13}C NMR (125 MHz, $CDCl_3$)



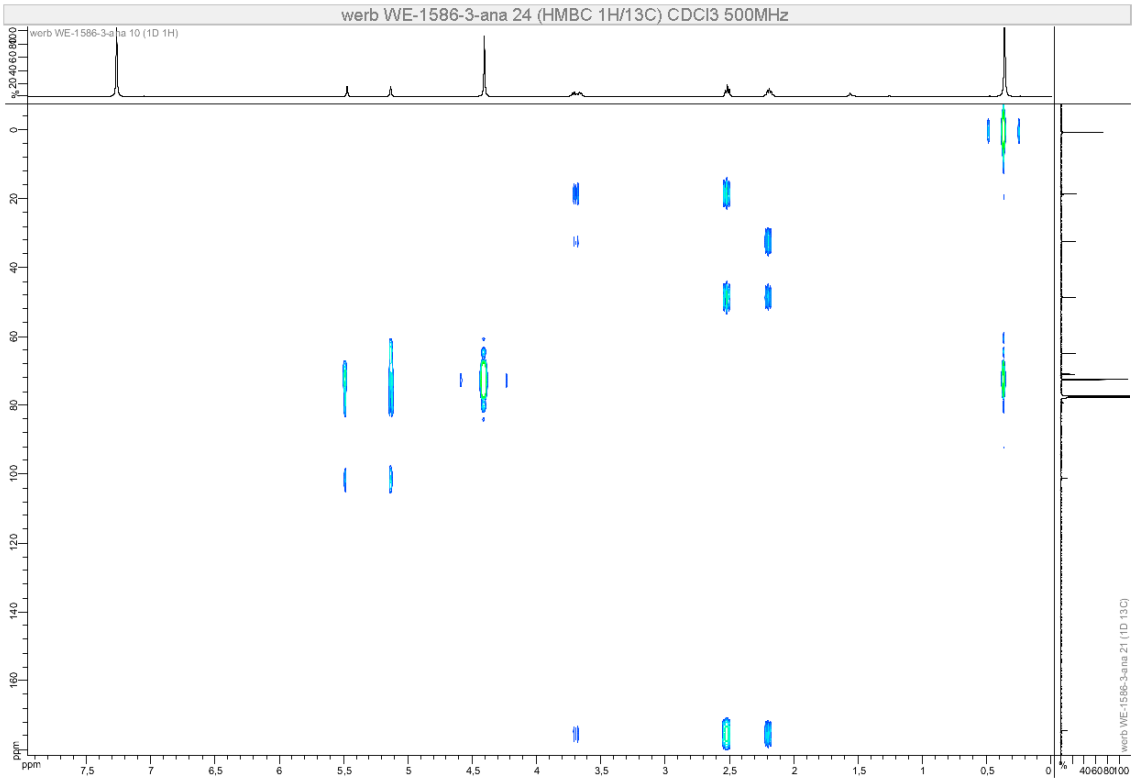
COSY (500 MHz, $CDCl_3$)



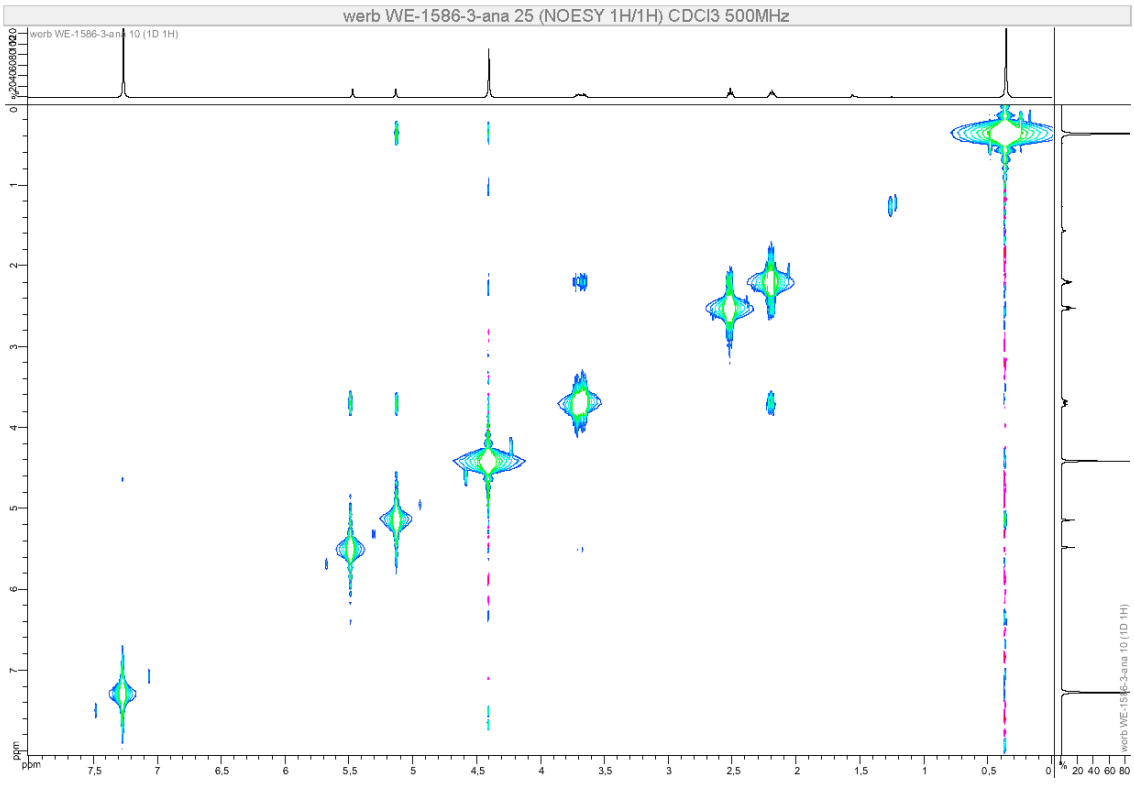
HSQC (500 MHz, $CDCl_3$)



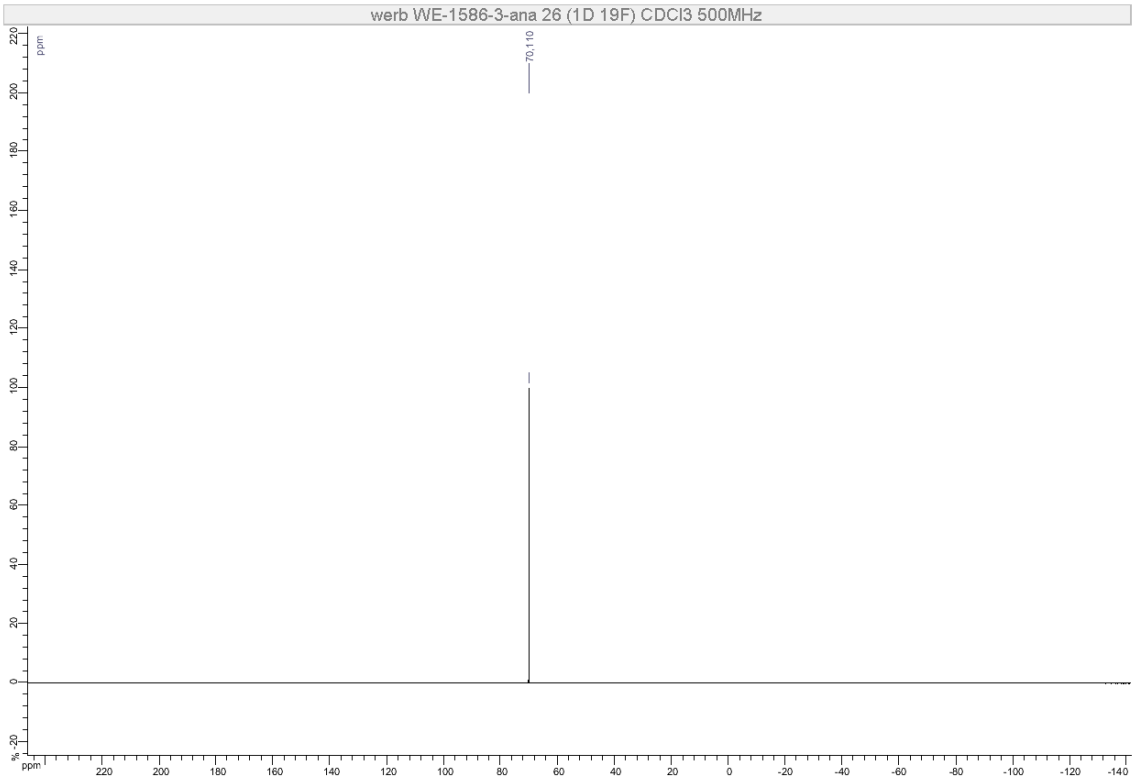
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

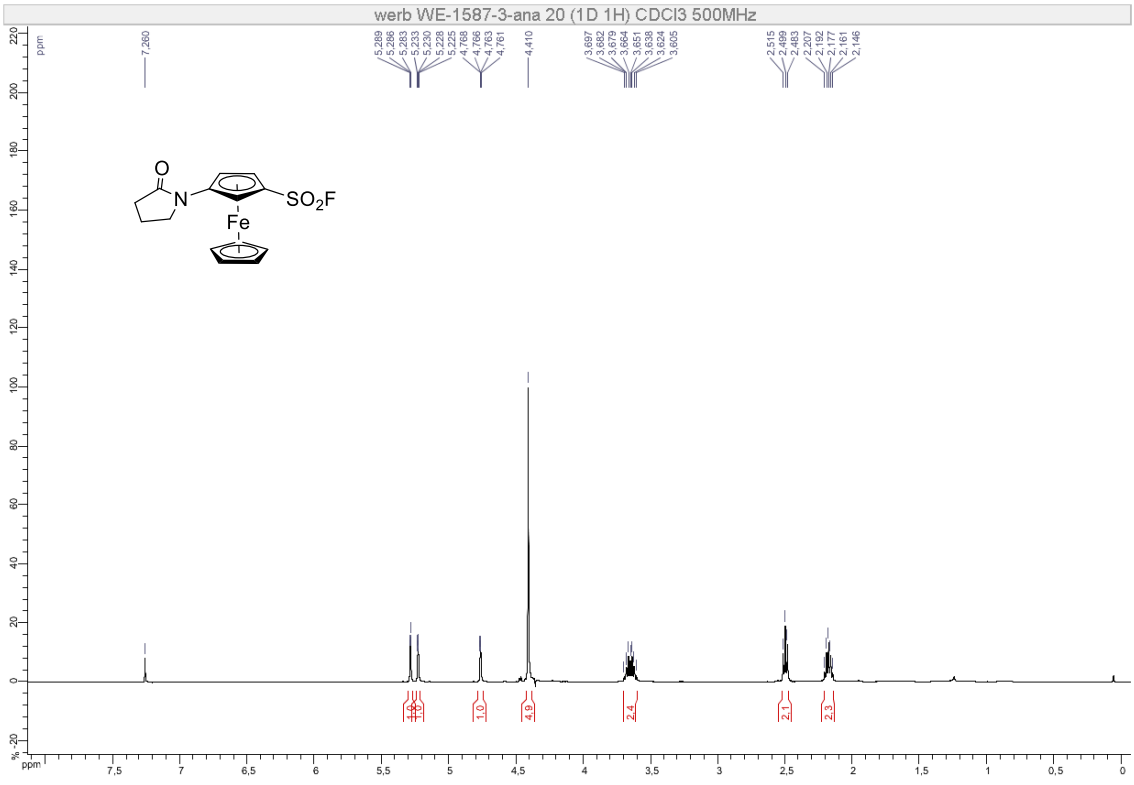


^{19}F NMR (470 MHz, $CDCl_3$)

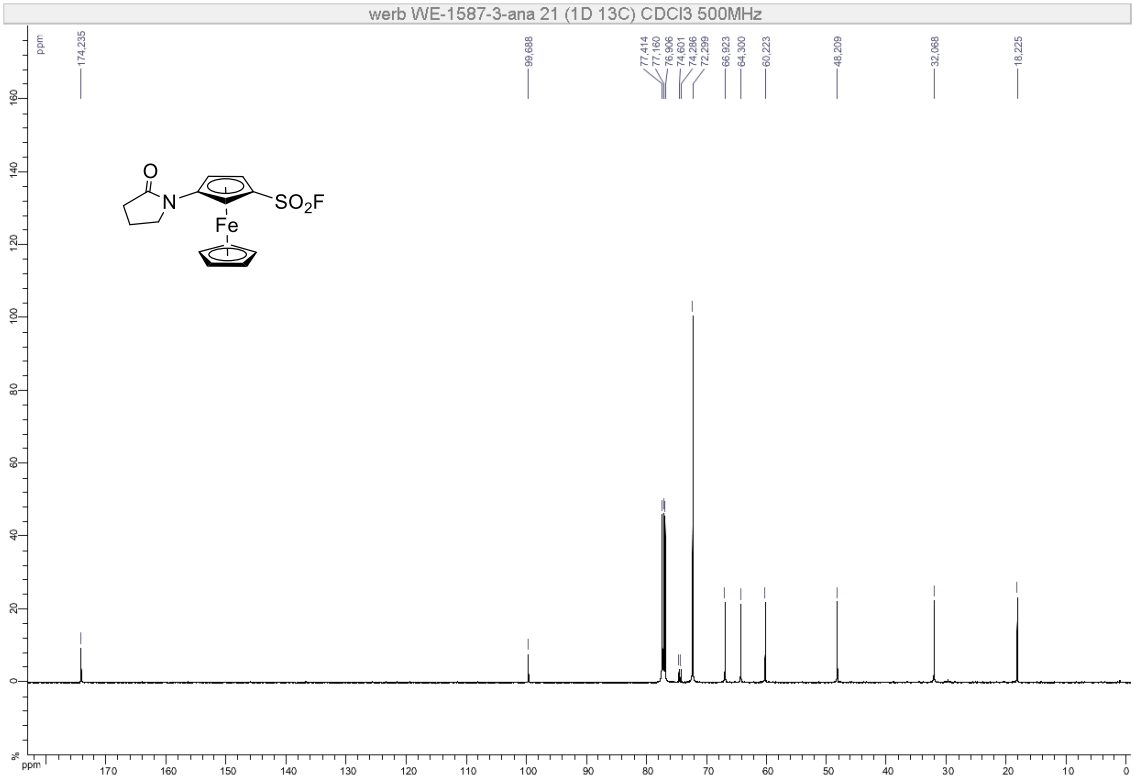


3-(2-Oxo-*N*-pyrrolidyl)ferrocenesulfonyl fluoride (**34b**)

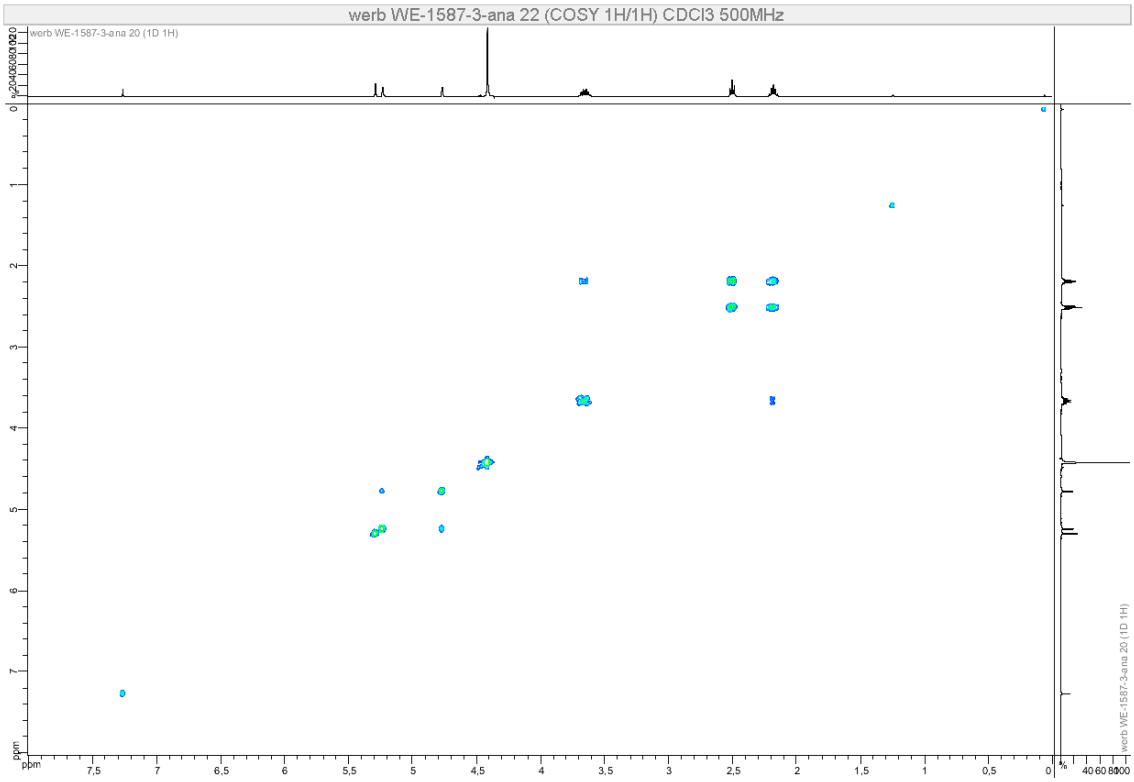
^{1}H NMR (500 MHz, $CDCl_3$)



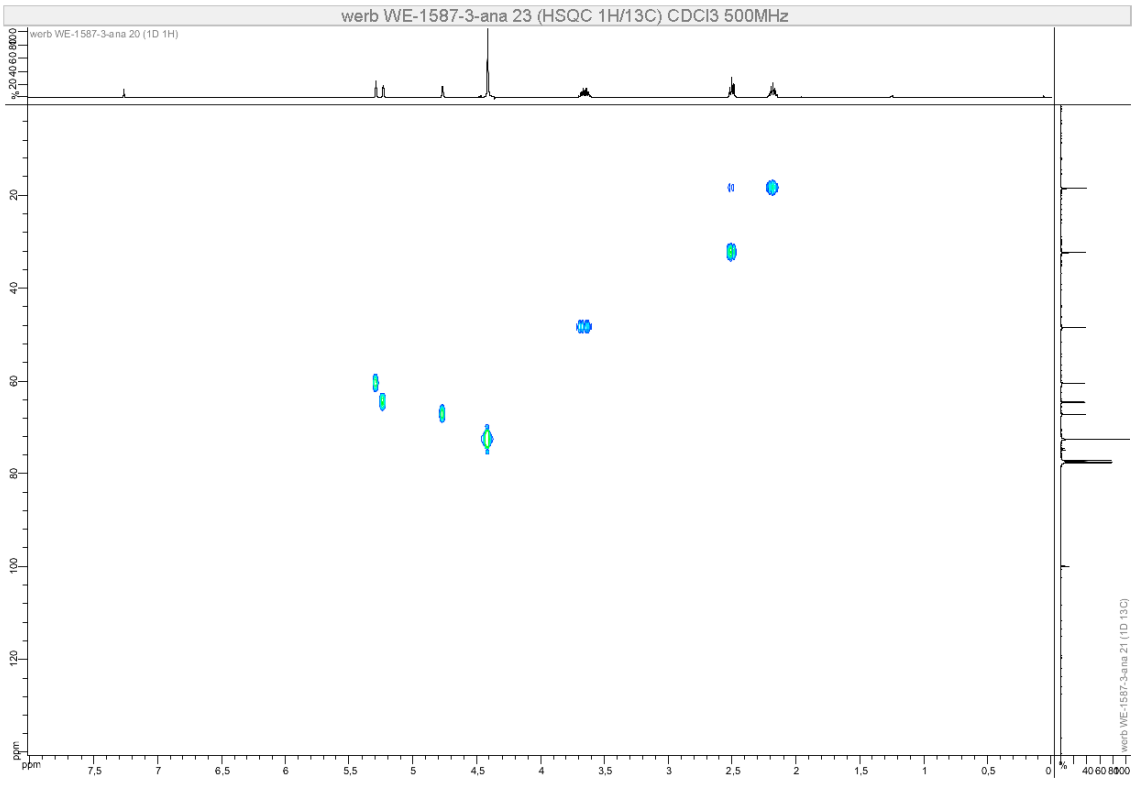
^{13}C NMR (125 MHz, $CDCl_3$)



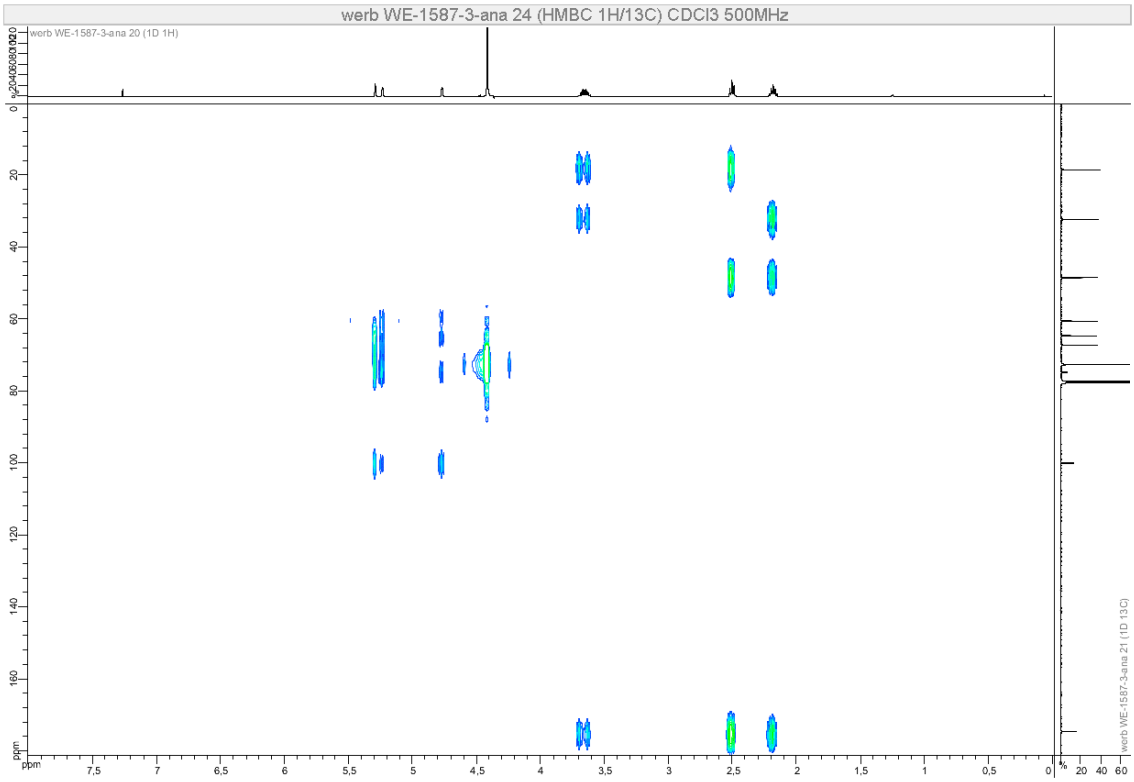
COSY (500 MHz, $CDCl_3$)



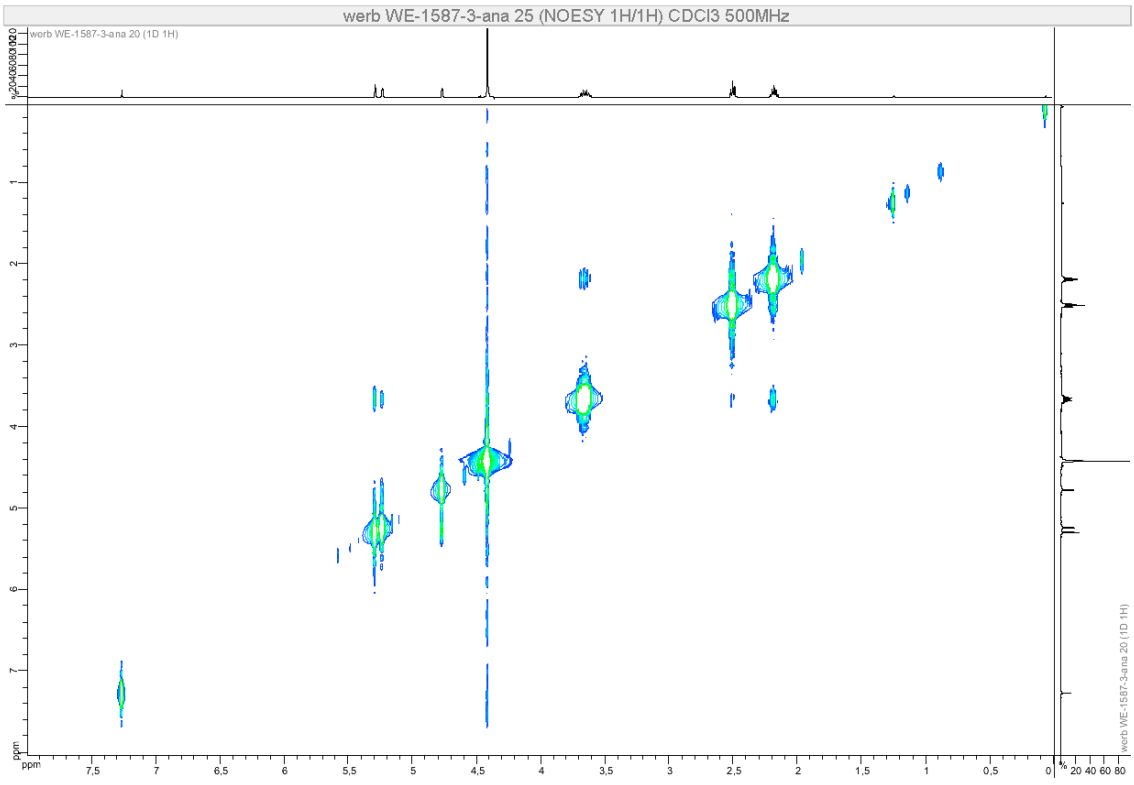
HSQC (500 MHz, $CDCl_3$)



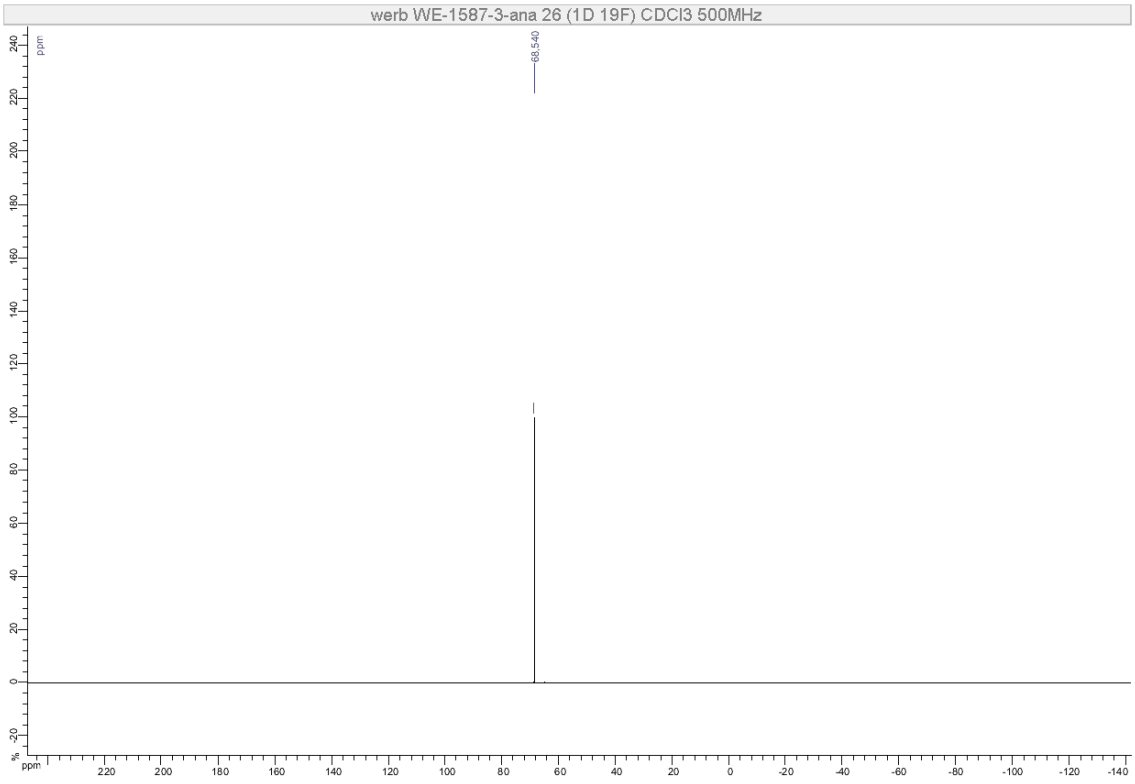
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

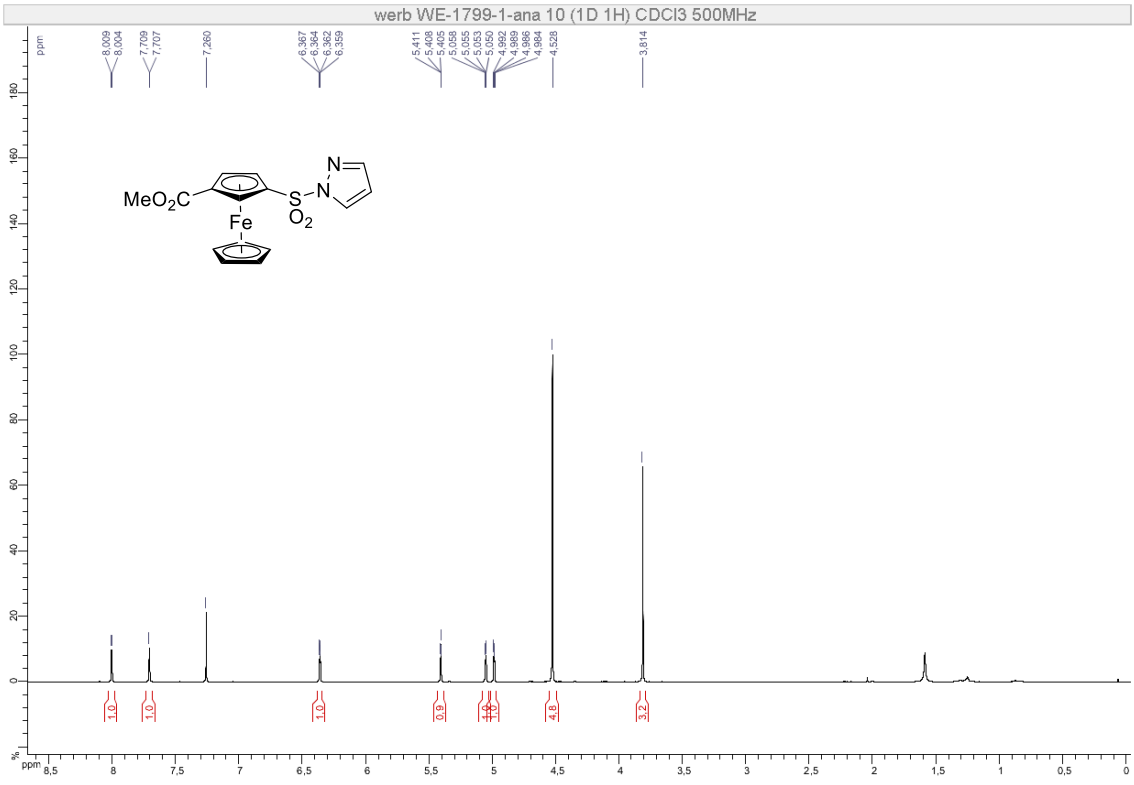


^{19}F NMR (470 MHz, $CDCl_3$)

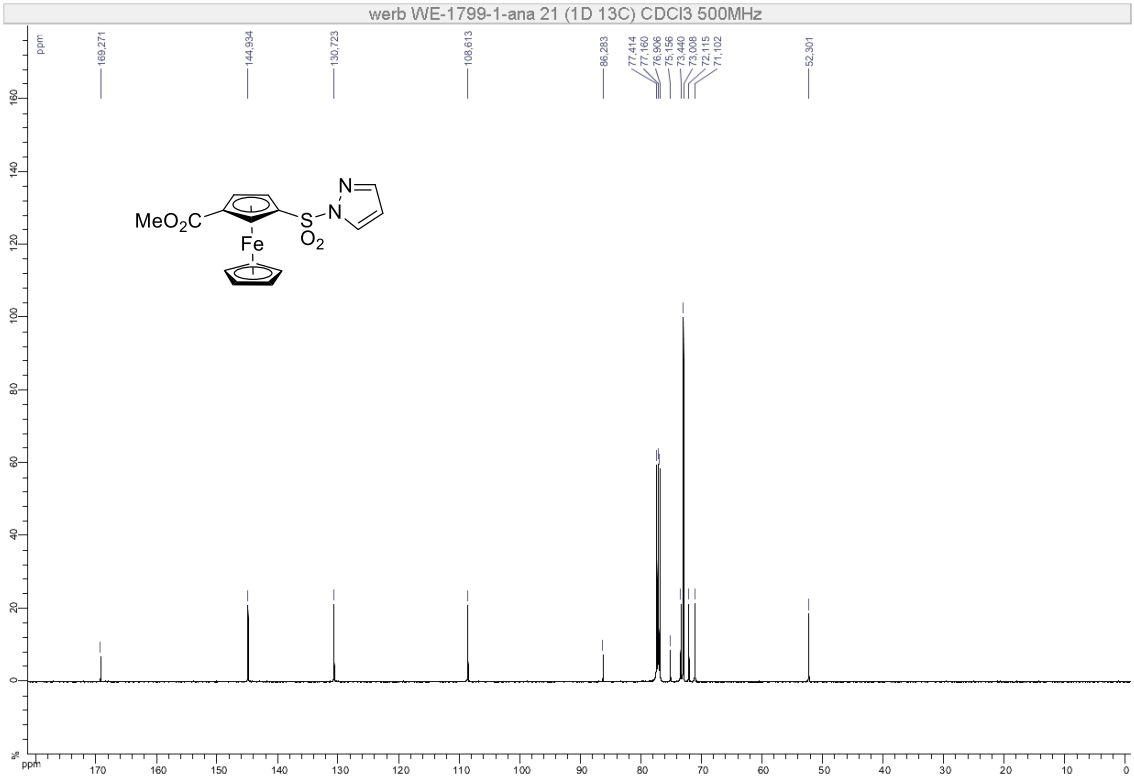


3-Methoxycarbonyl-1-(*N*-pyrazolyl)sulfonylferrocene (36b)

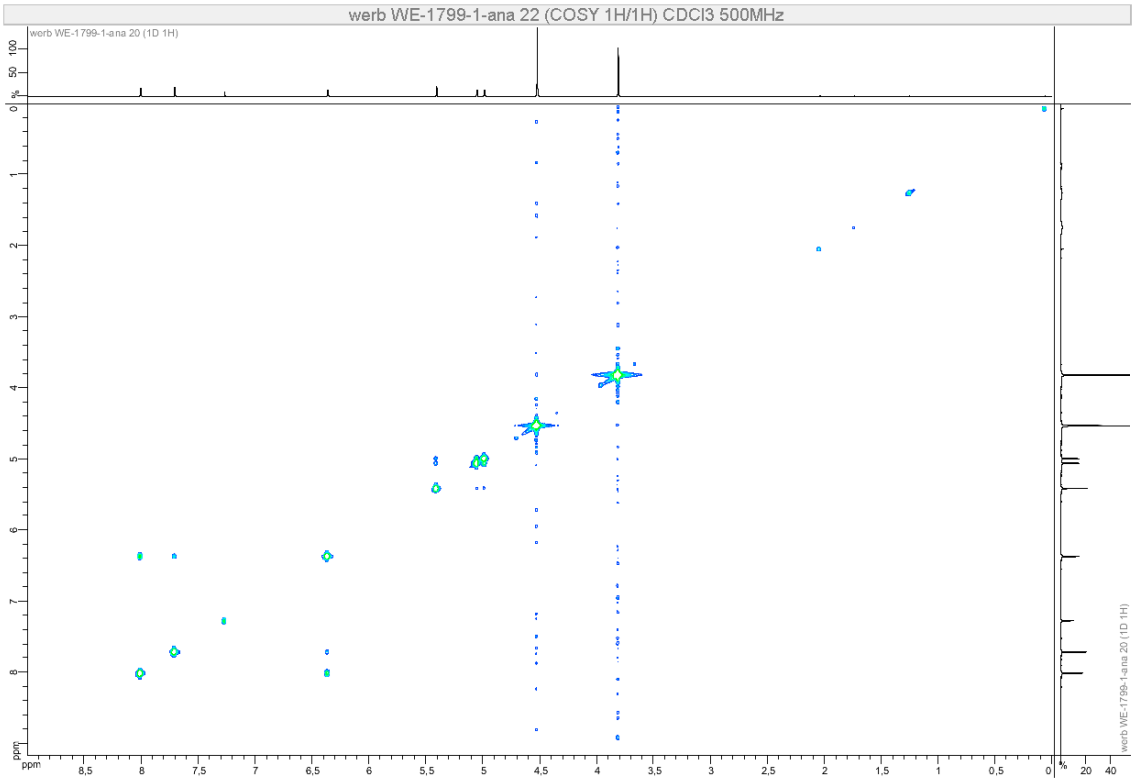
^{1}H NMR (500 MHz, $CDCl_3$)



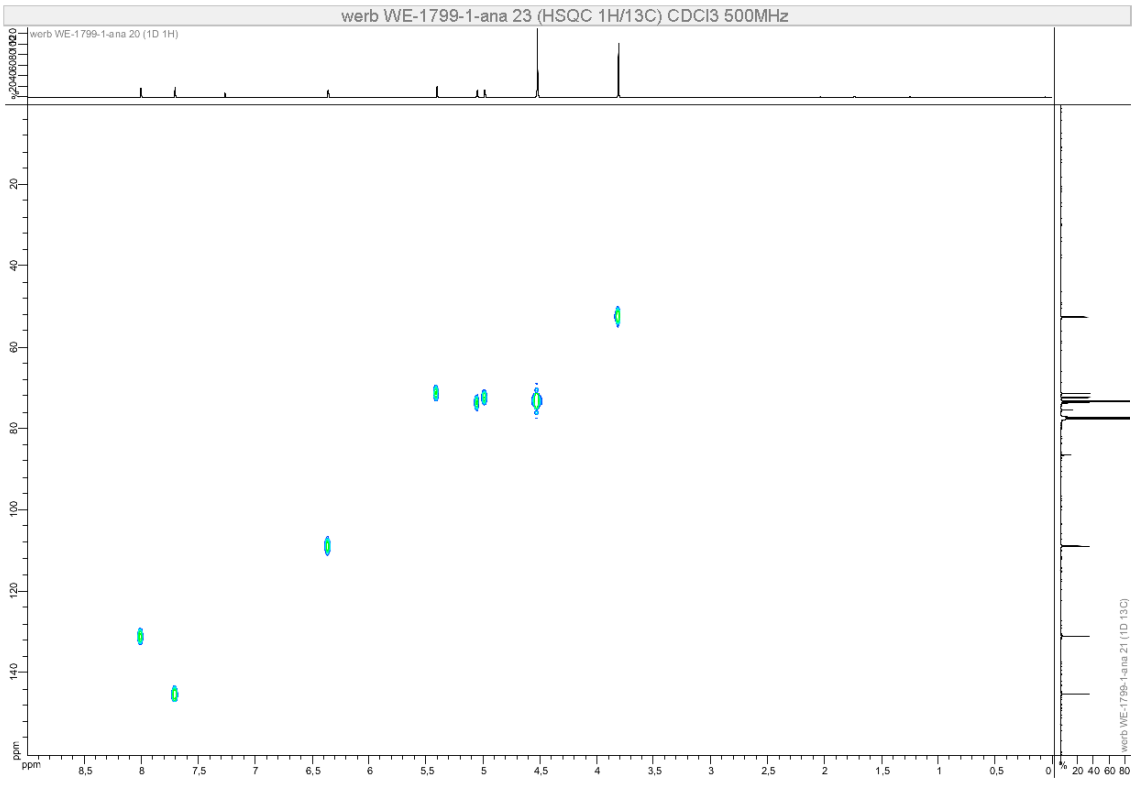
^{13}C NMR (125 MHz, $CDCl_3$)



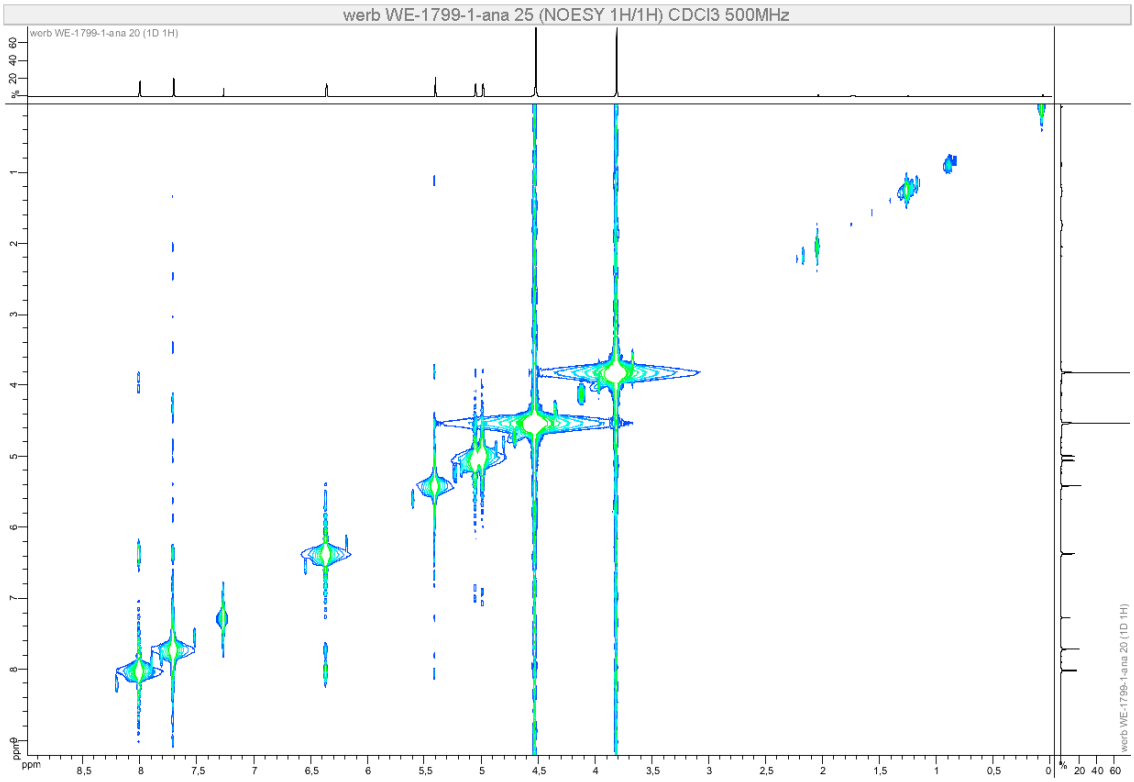
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

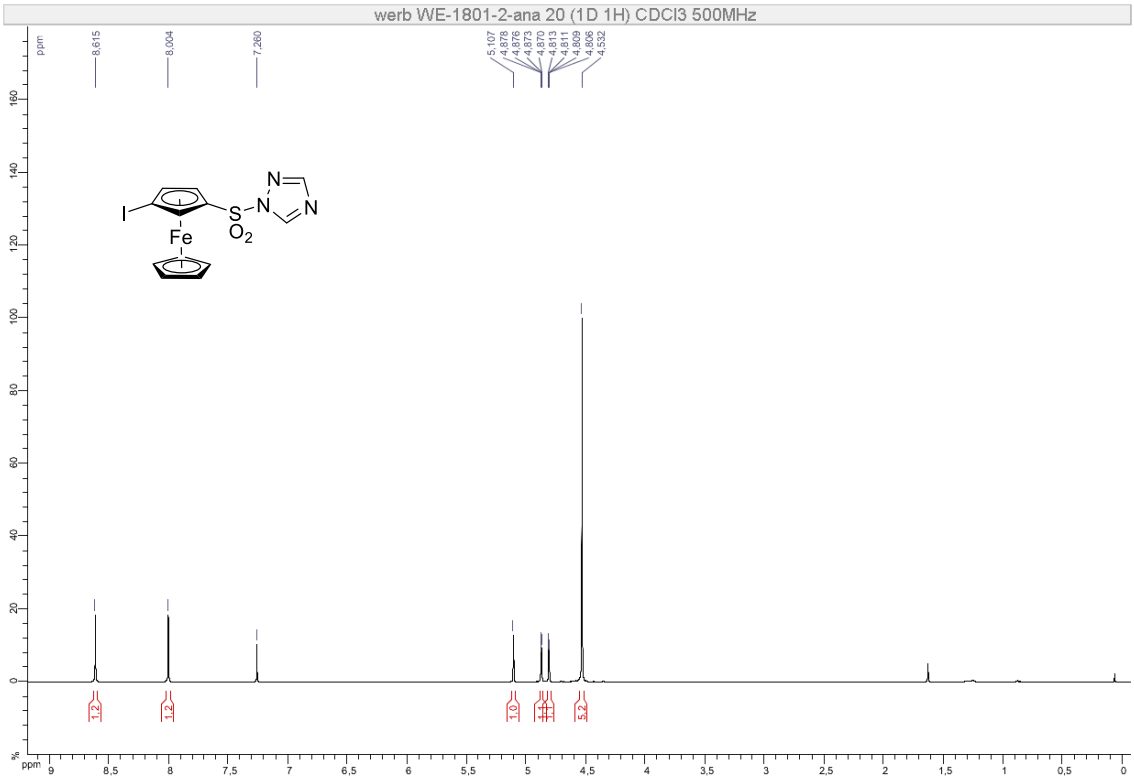


NOESY (500 MHz, $CDCl_3$)

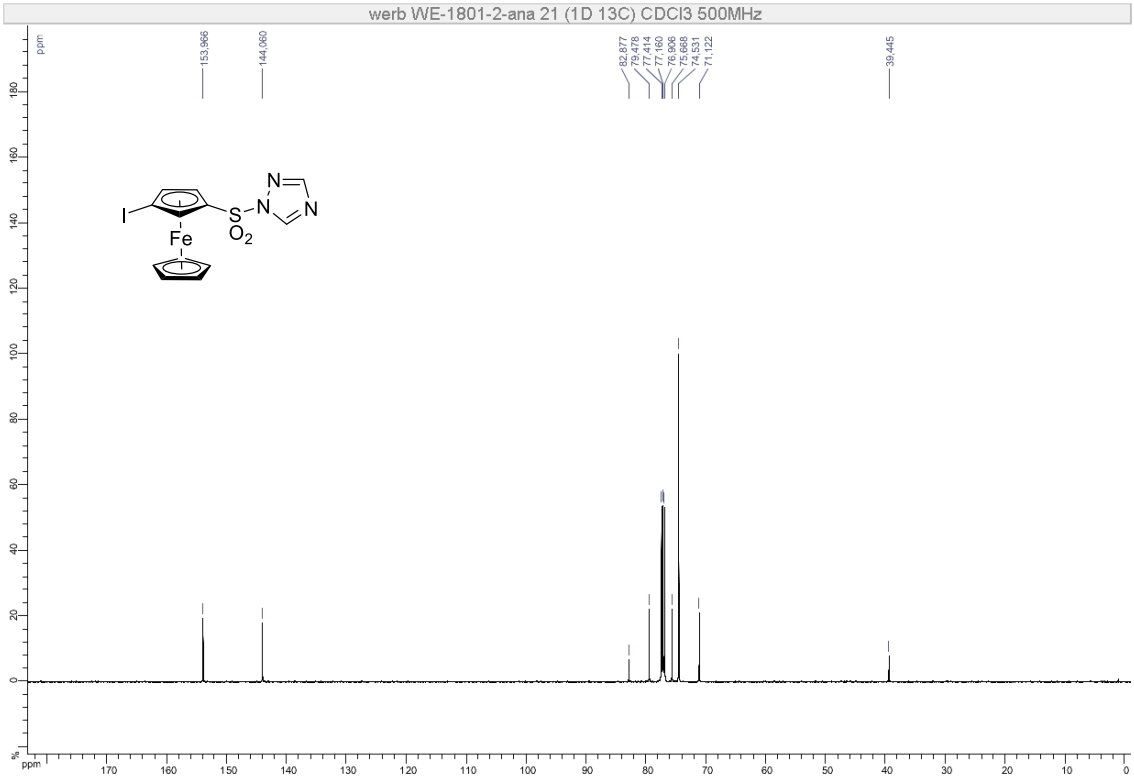


3-Iodo-1-(*N1*-1,2,4-triazolyl)sulfonylferrocene (36c)

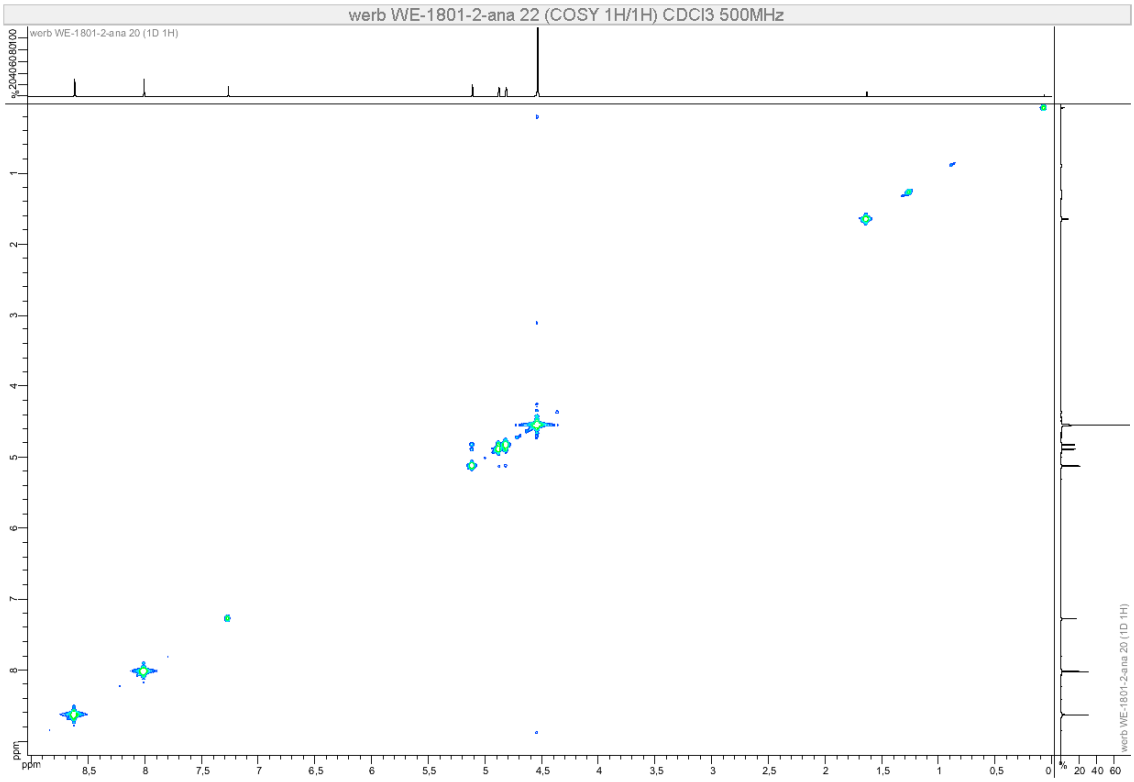
^{1}H NMR (500 MHz, $CDCl_3$)



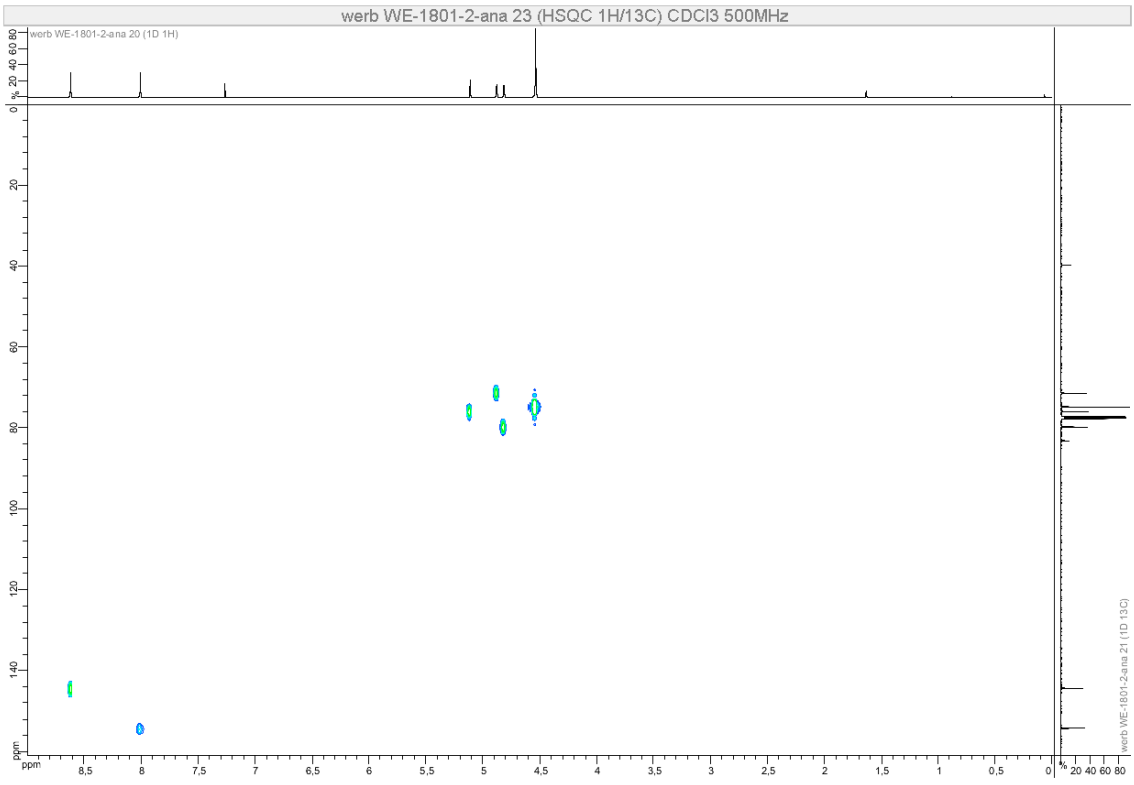
^{13}C NMR (125 MHz, $CDCl_3$)



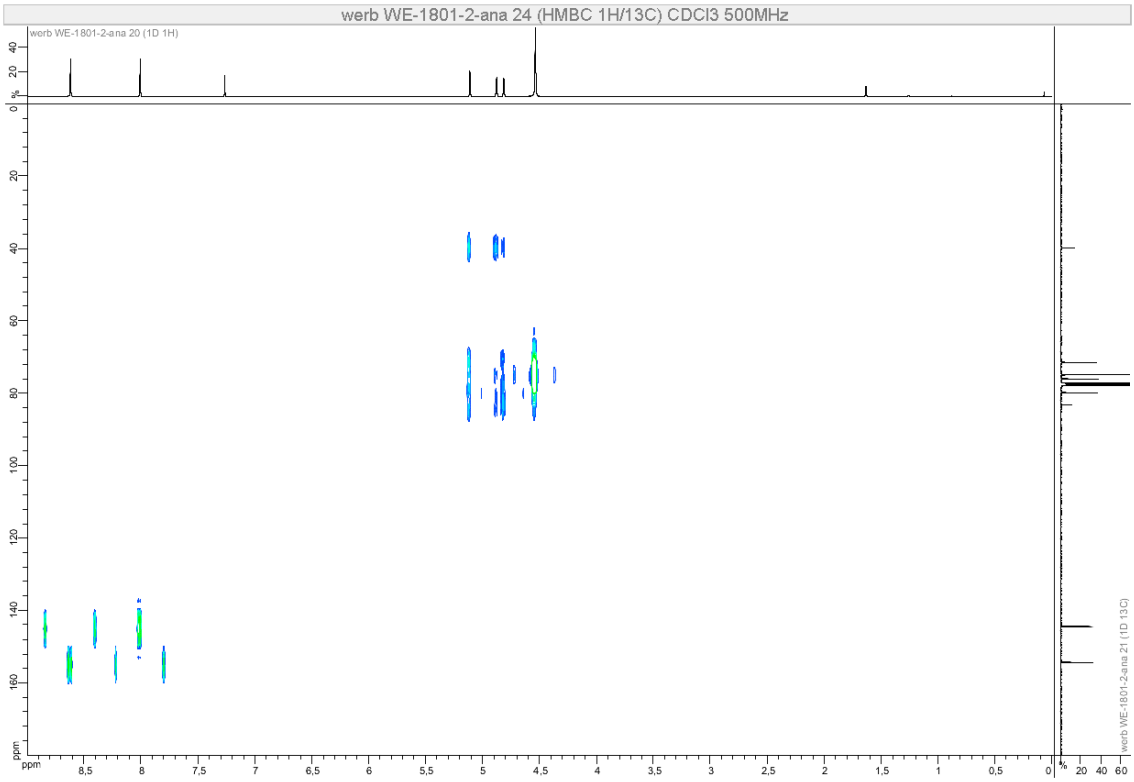
COSY (500 MHz, $CDCl_3$)



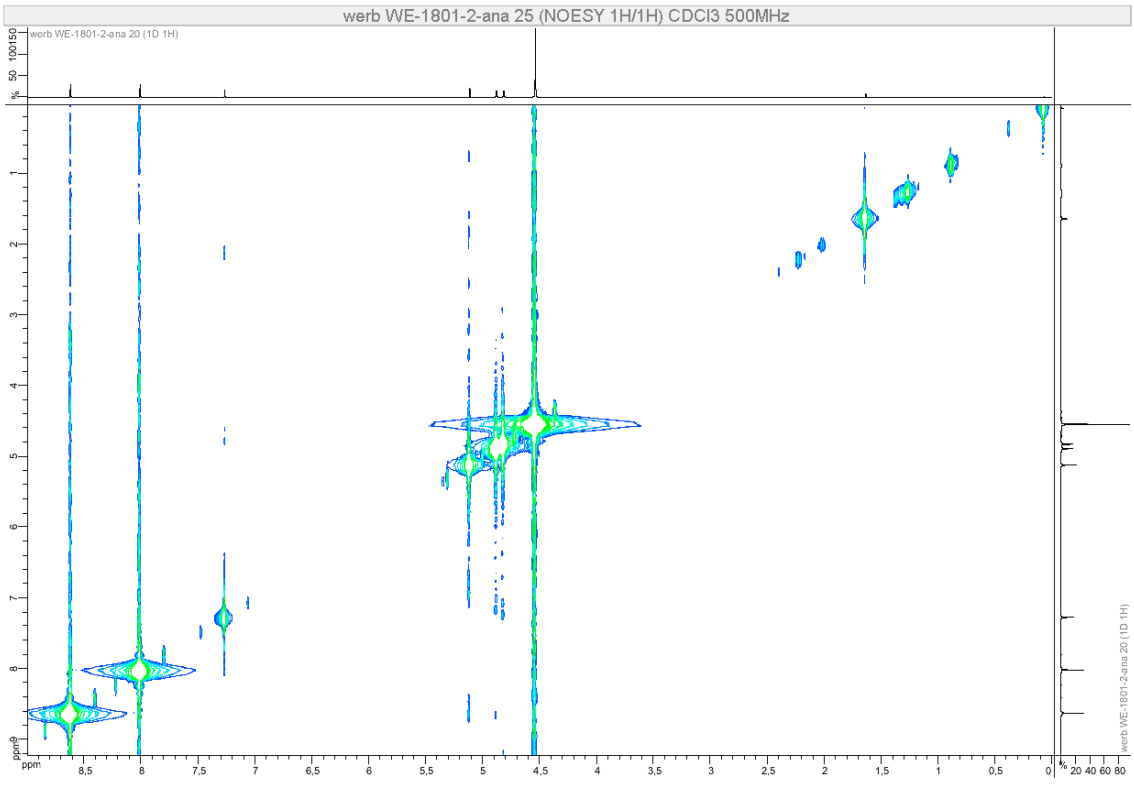
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

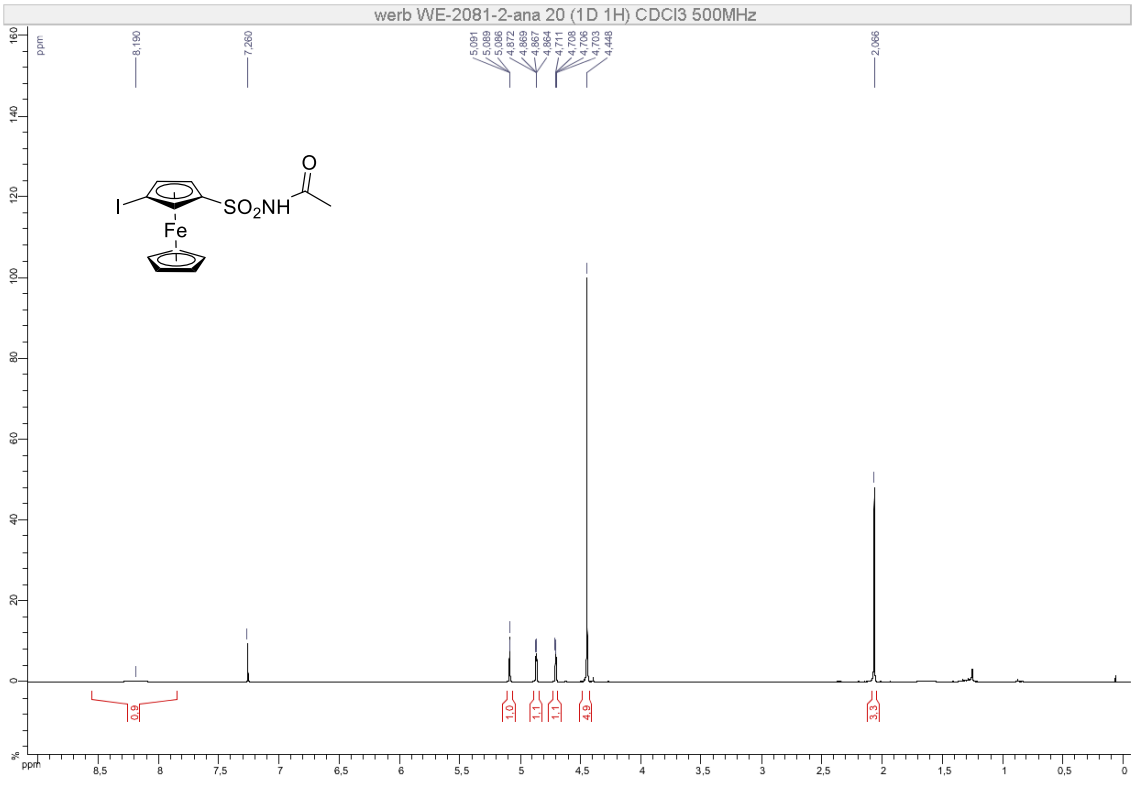


NOESY (500 MHz, $CDCl_3$)

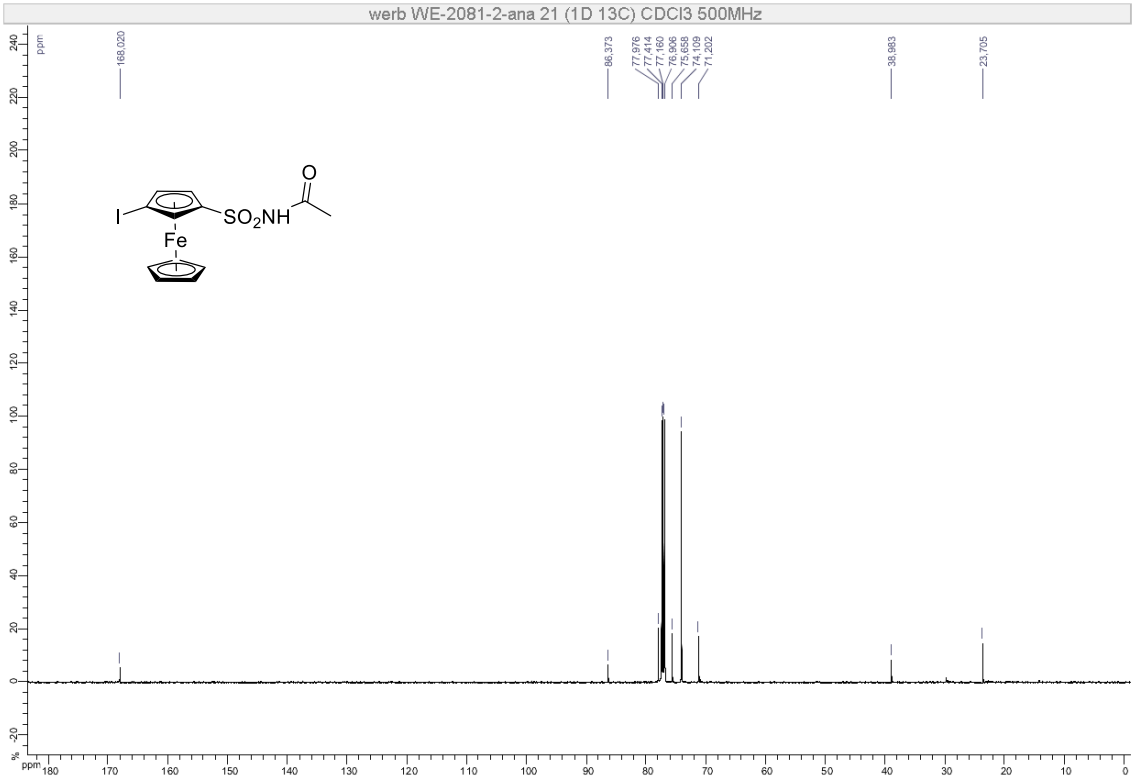


N-Acetyl-3-iodoferrocenesulfonamide (37b)

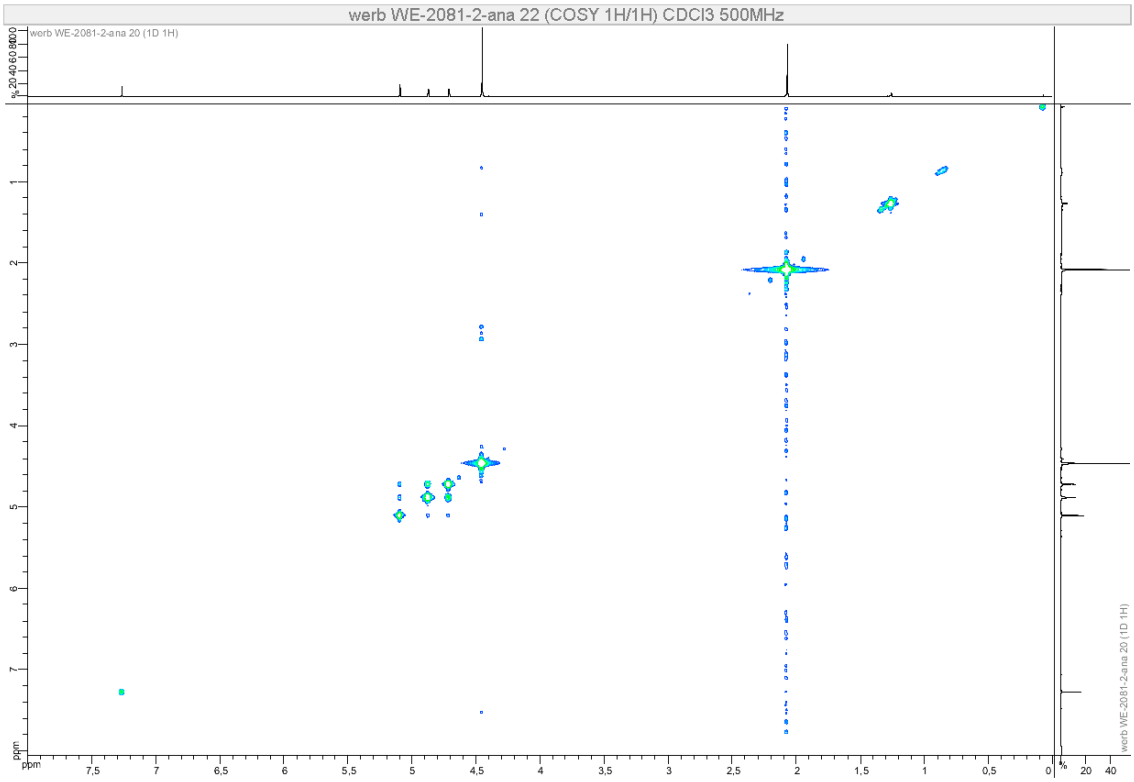
^{1}H NMR (500 MHz, $CDCl_3$)



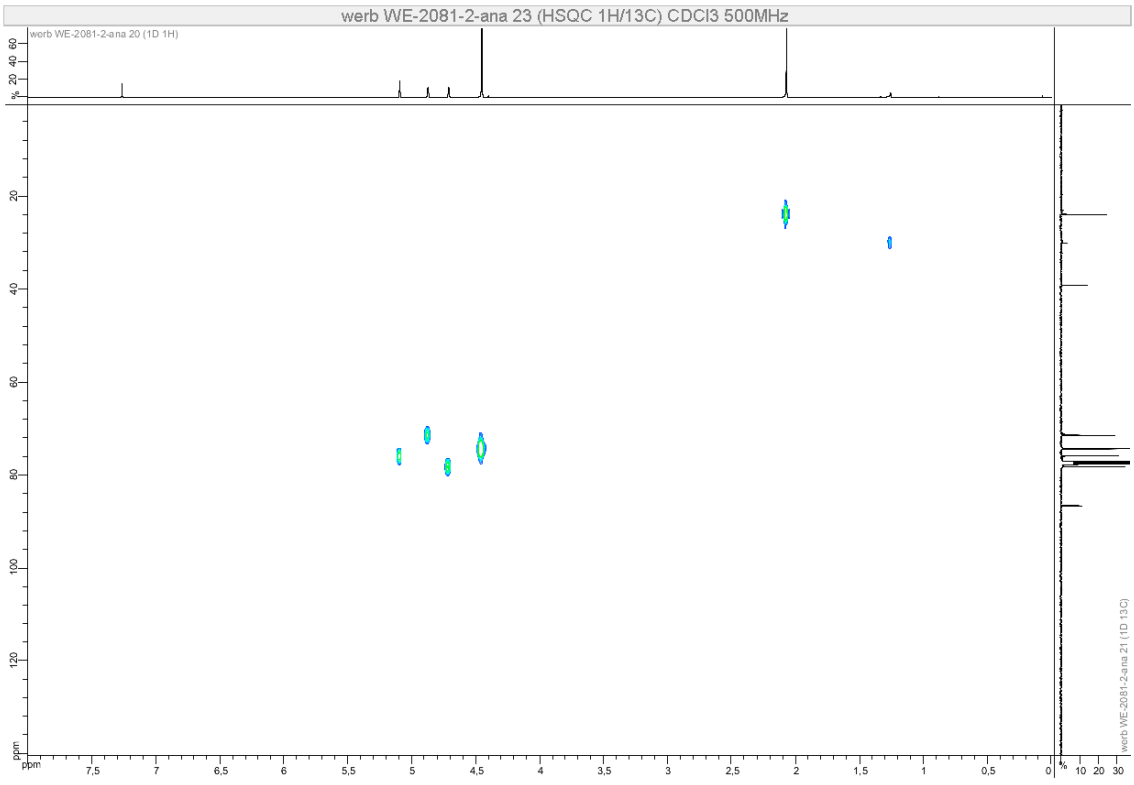
^{13}C NMR (125 MHz, $CDCl_3$)



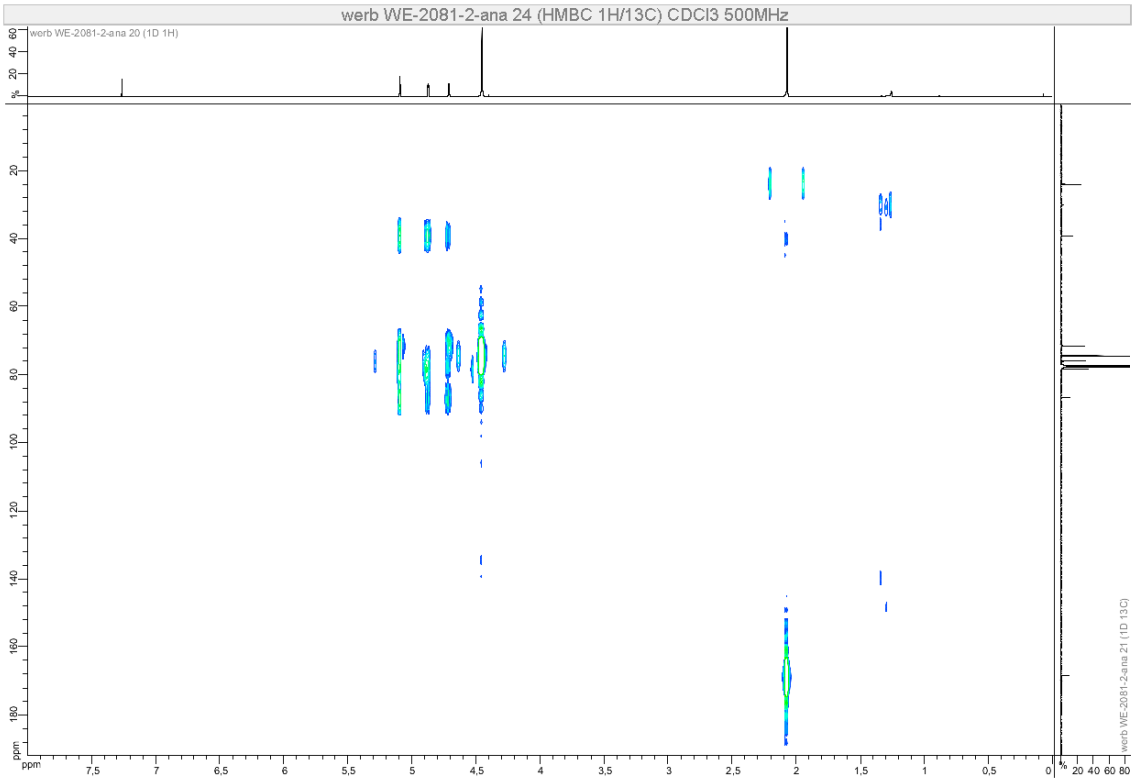
COSY (500 MHz, $CDCl_3$)



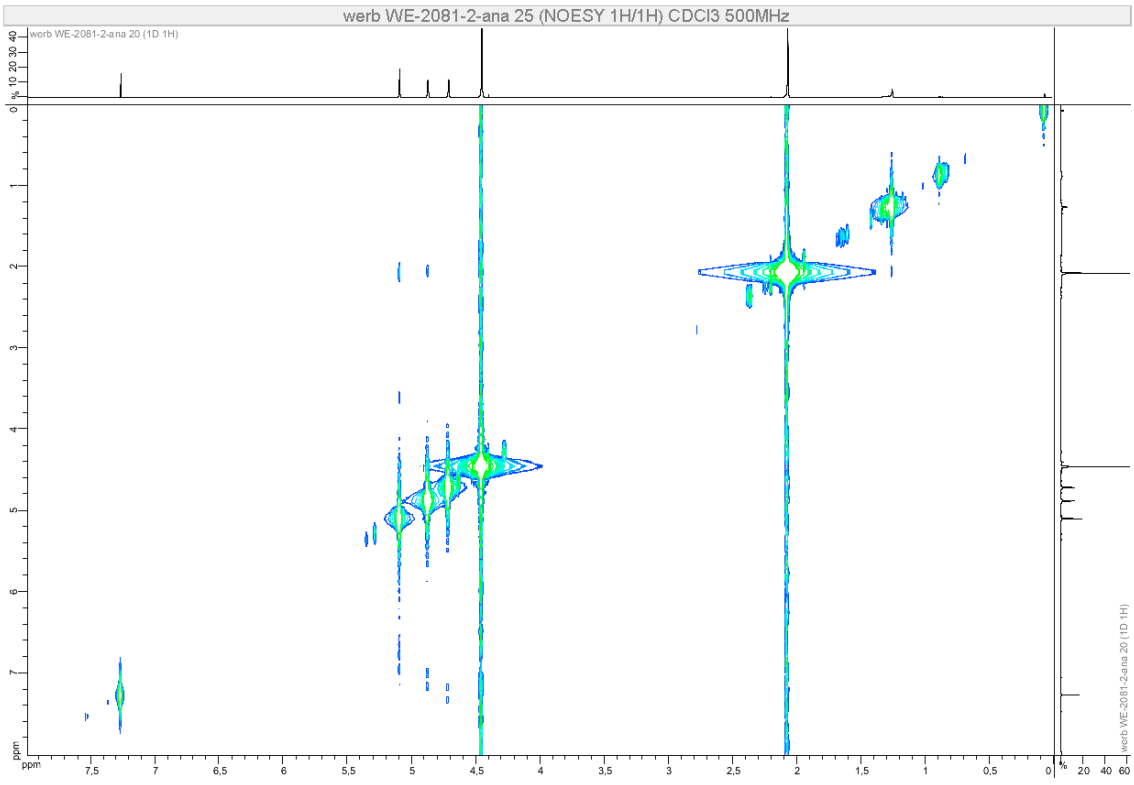
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

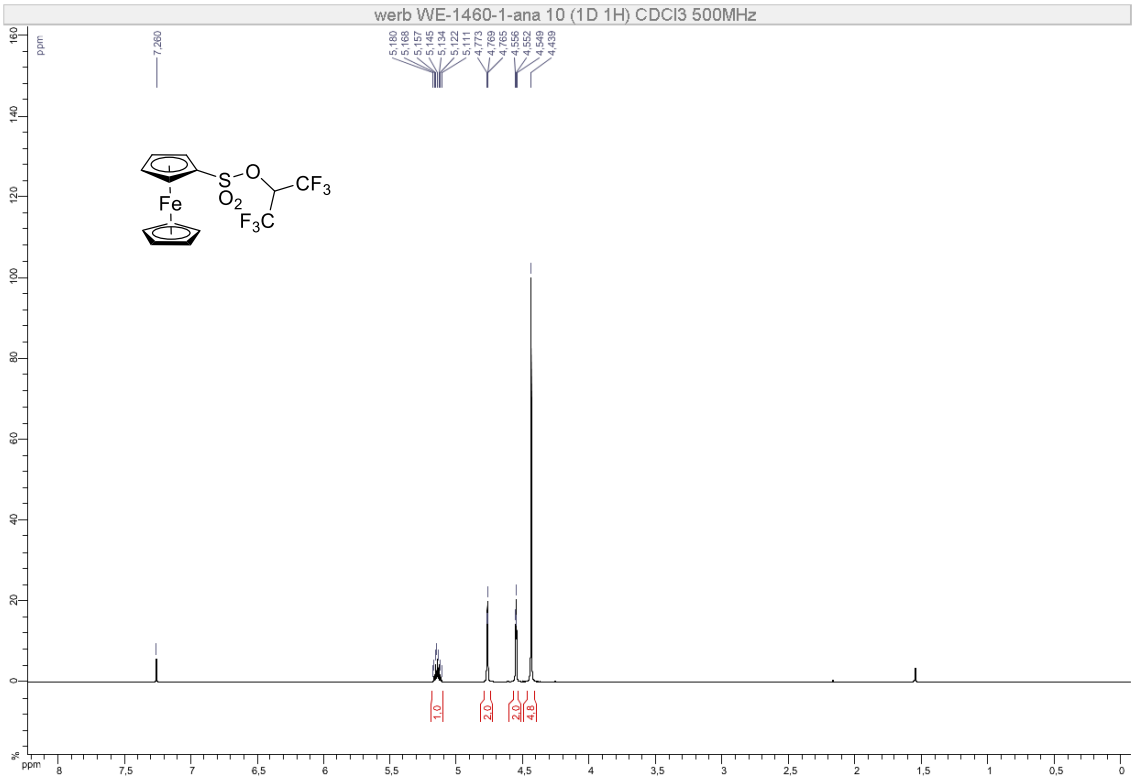


NOESY (500 MHz, $CDCl_3$)

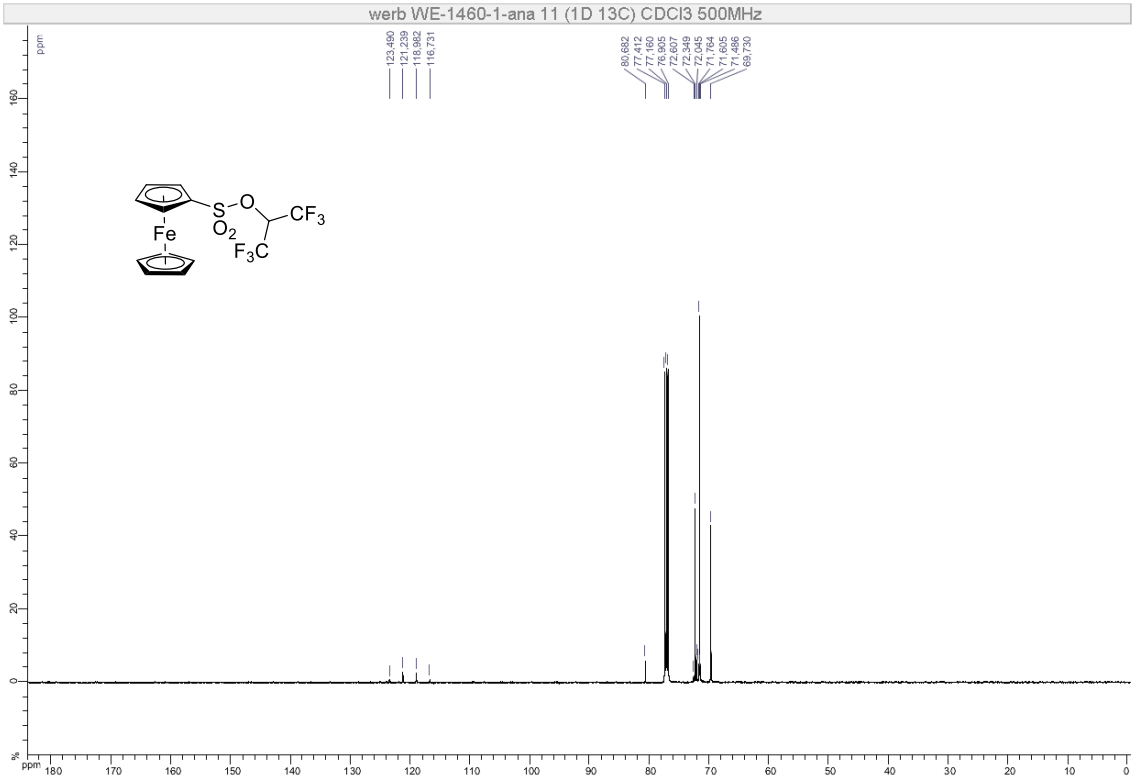


***O*-(1,1,1,3,3,3-Hexafluoroisopropyl)ferrocenesulfonate (38d)**

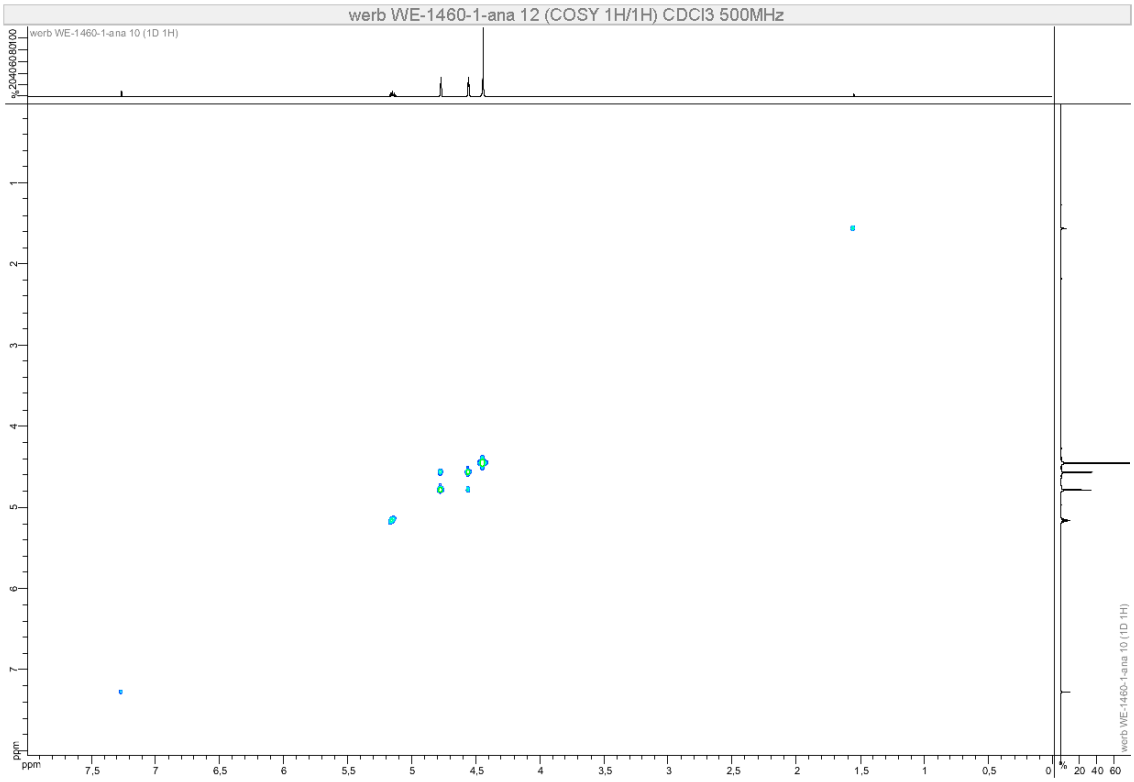
^{1}H NMR (500 MHz, $CDCl_3$)



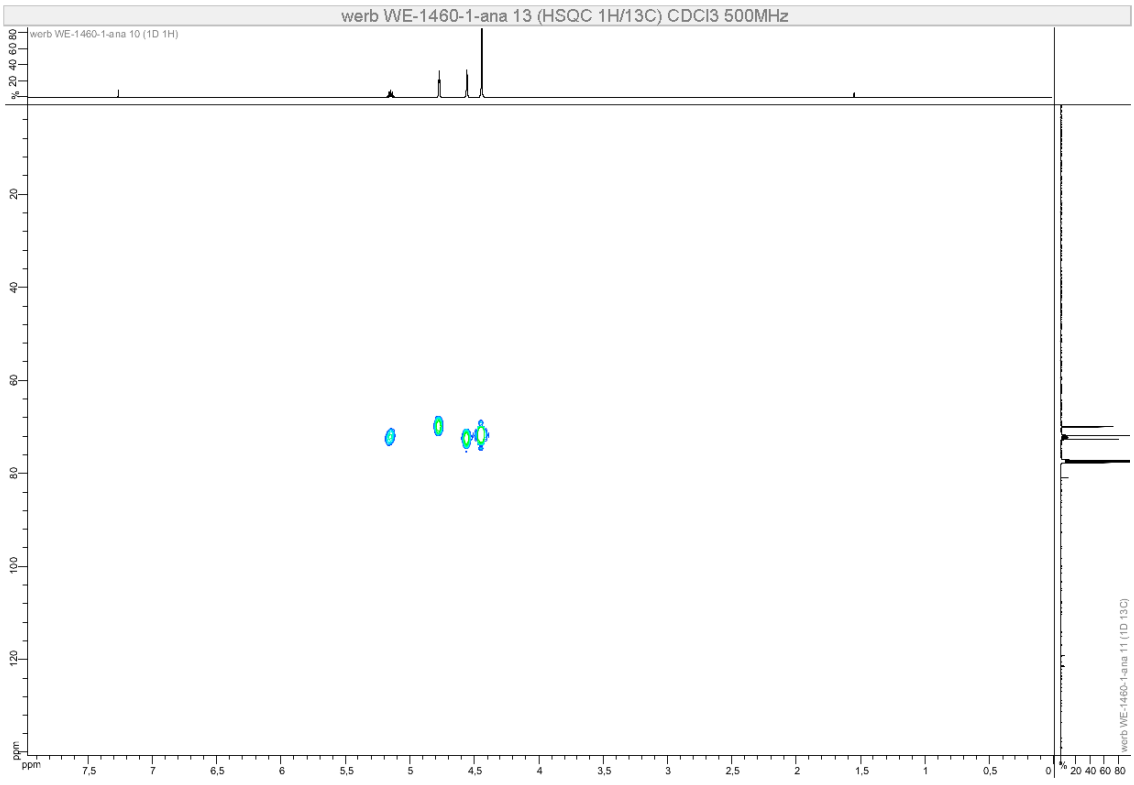
^{13}C NMR (125 MHz, $CDCl_3$)



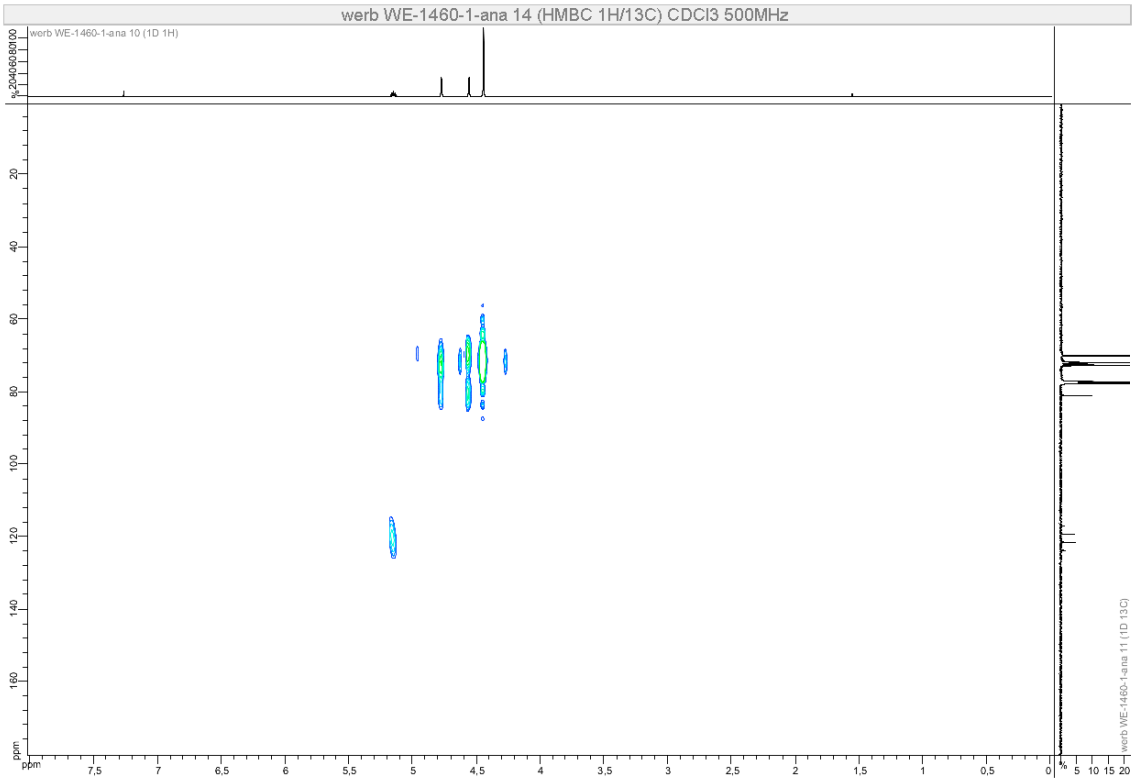
COSY (500 MHz, $CDCl_3$)



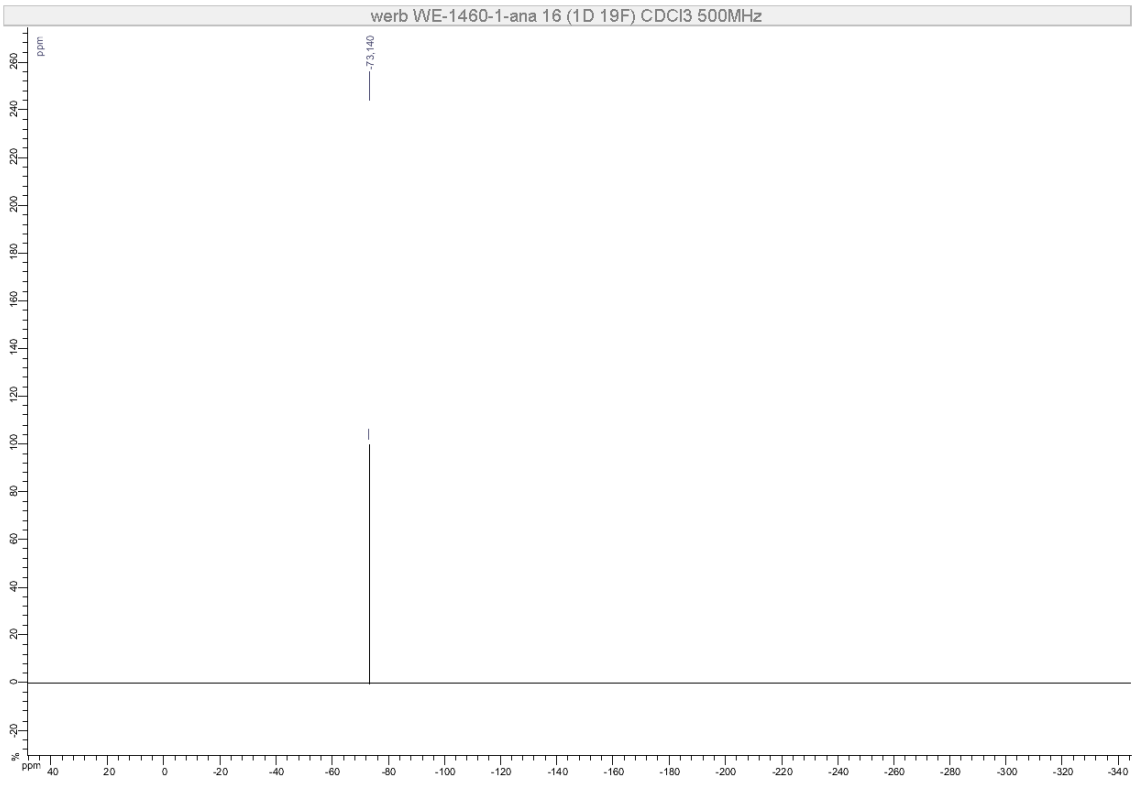
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

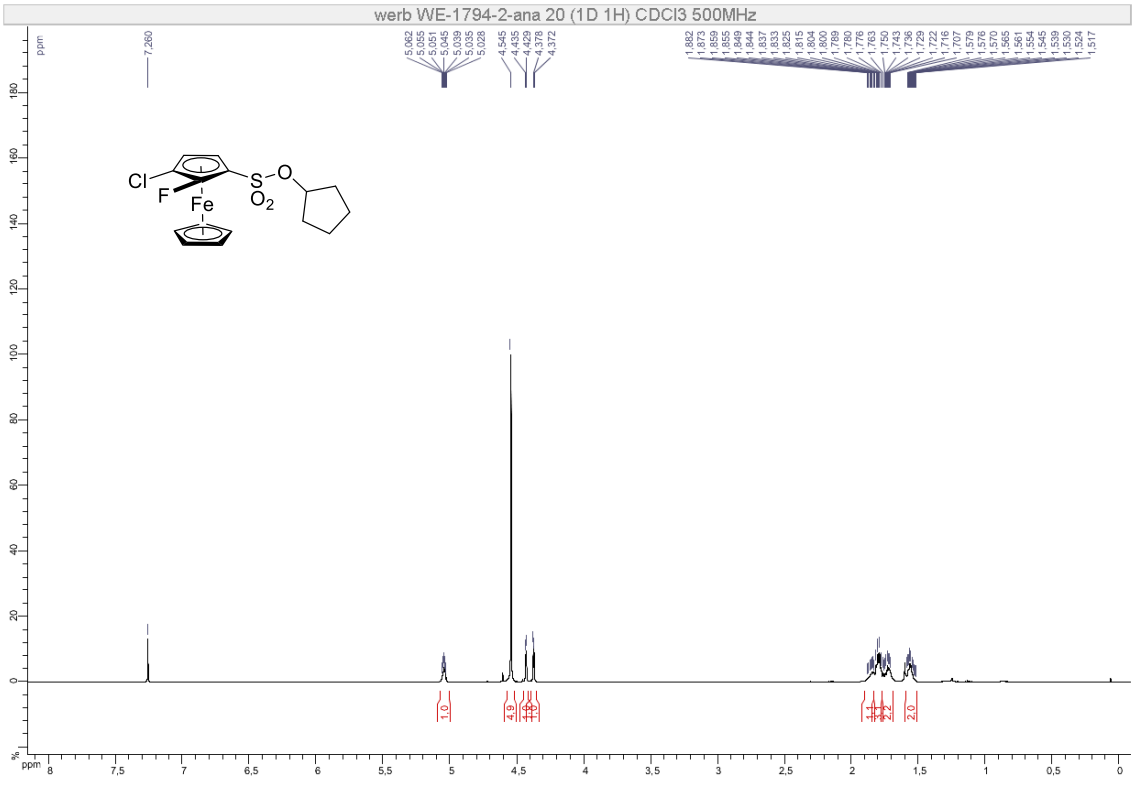


^{19}F NMR (470 MHz, $CDCl_3$)

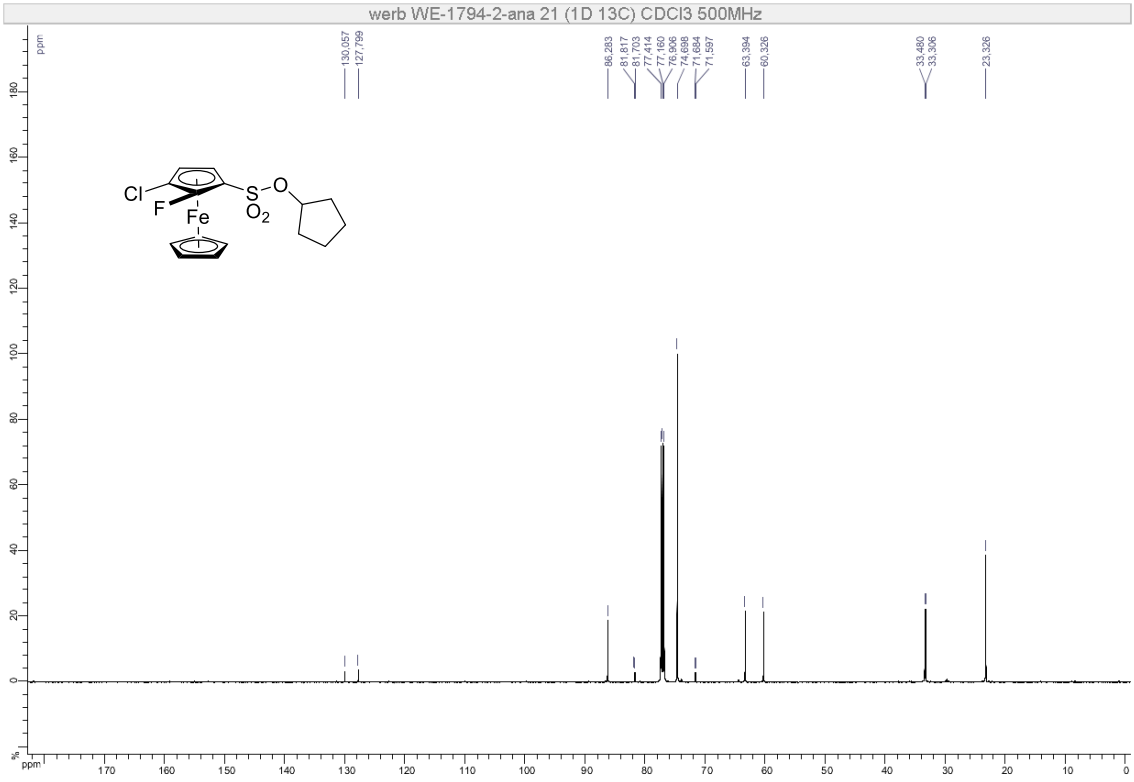


3-Chloro-*O*-cyclopentyl-2-fluoroferrocenesulfonate (38e)

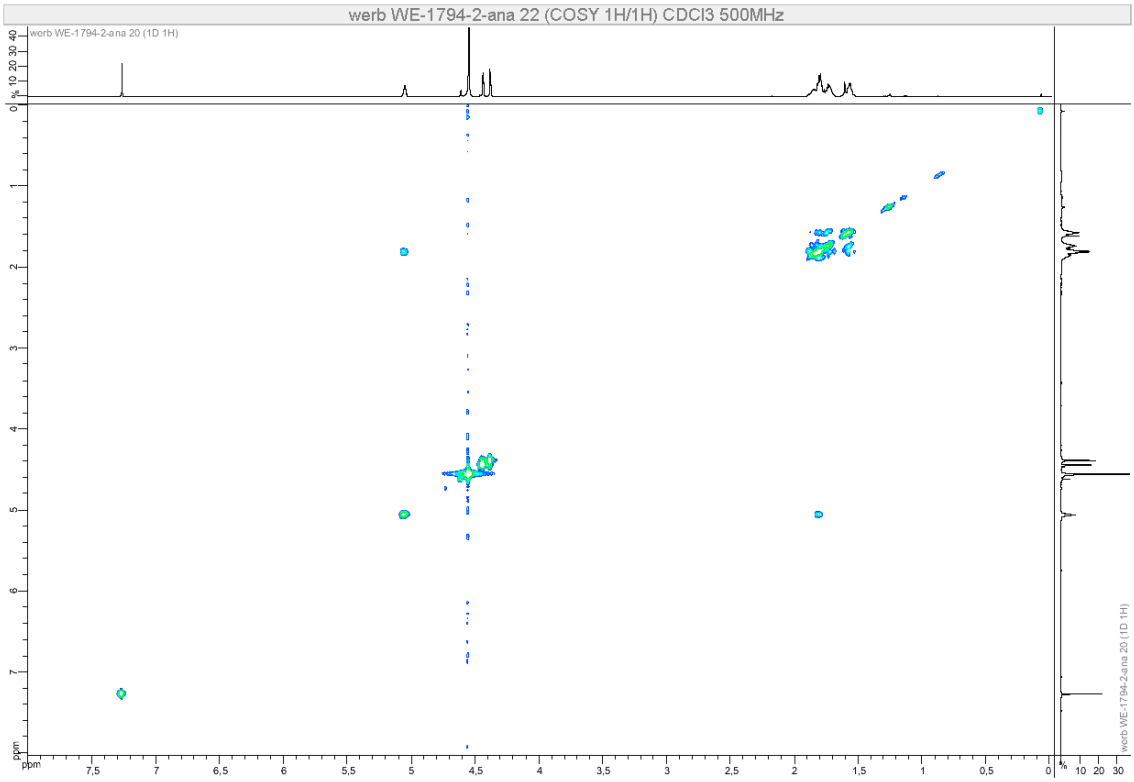
^{1}H NMR (500 MHz, $CDCl_3$)



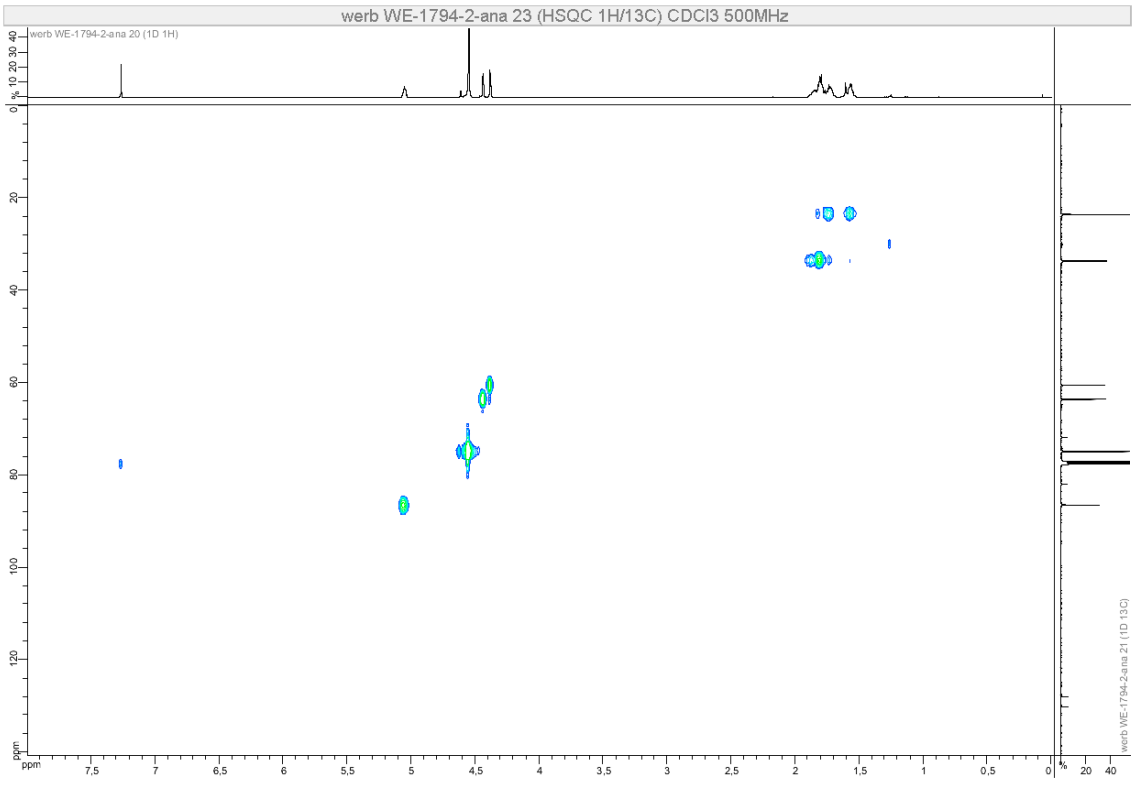
^{13}C NMR (125 MHz, $CDCl_3$)



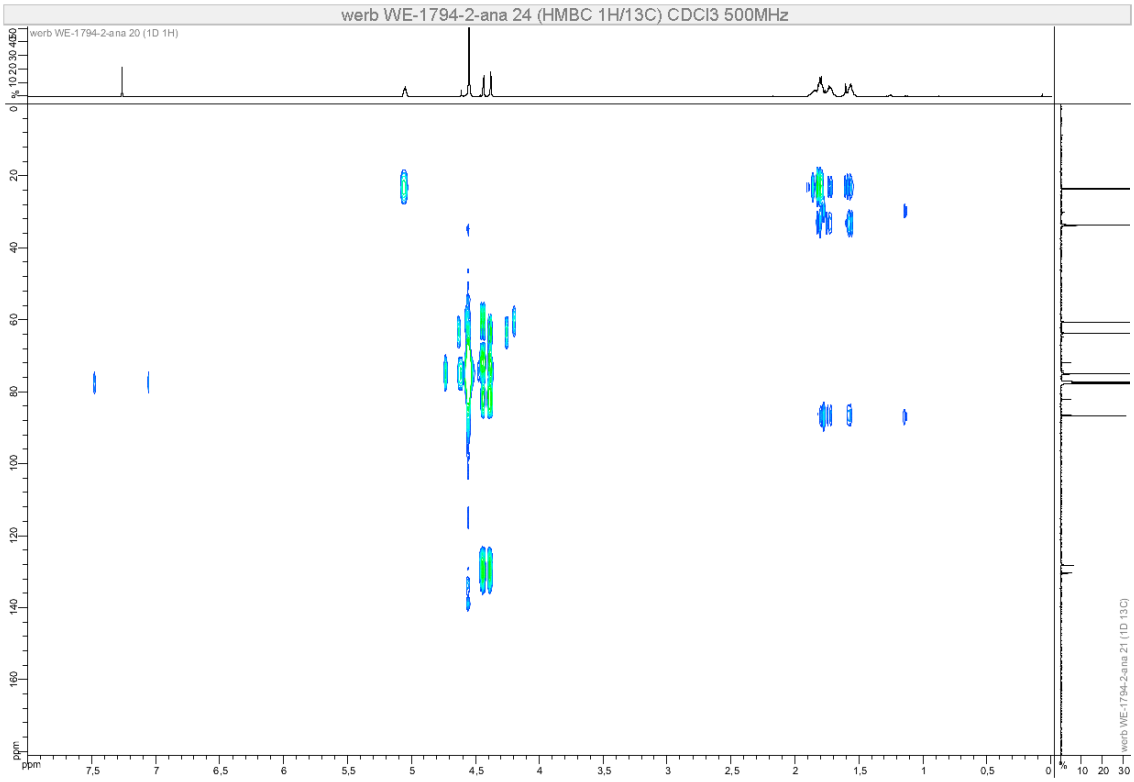
COSY (500 MHz, $CDCl_3$)



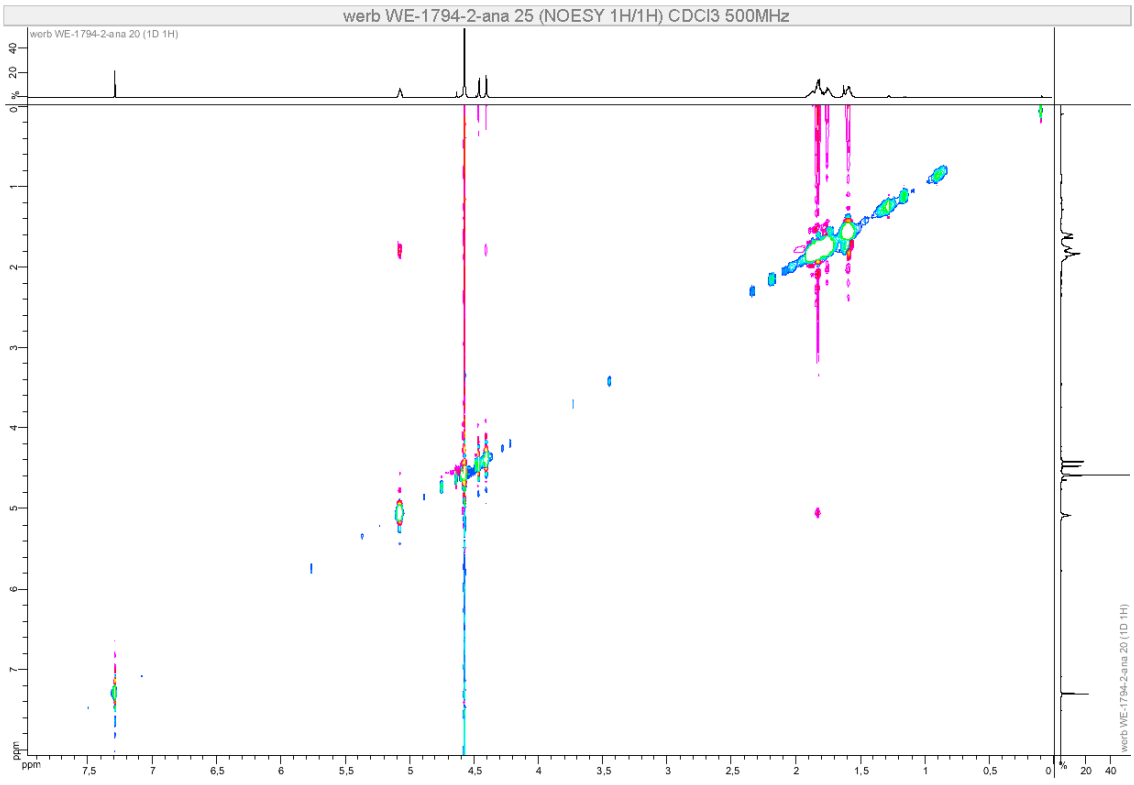
HSQC (500 MHz, $CDCl_3$)



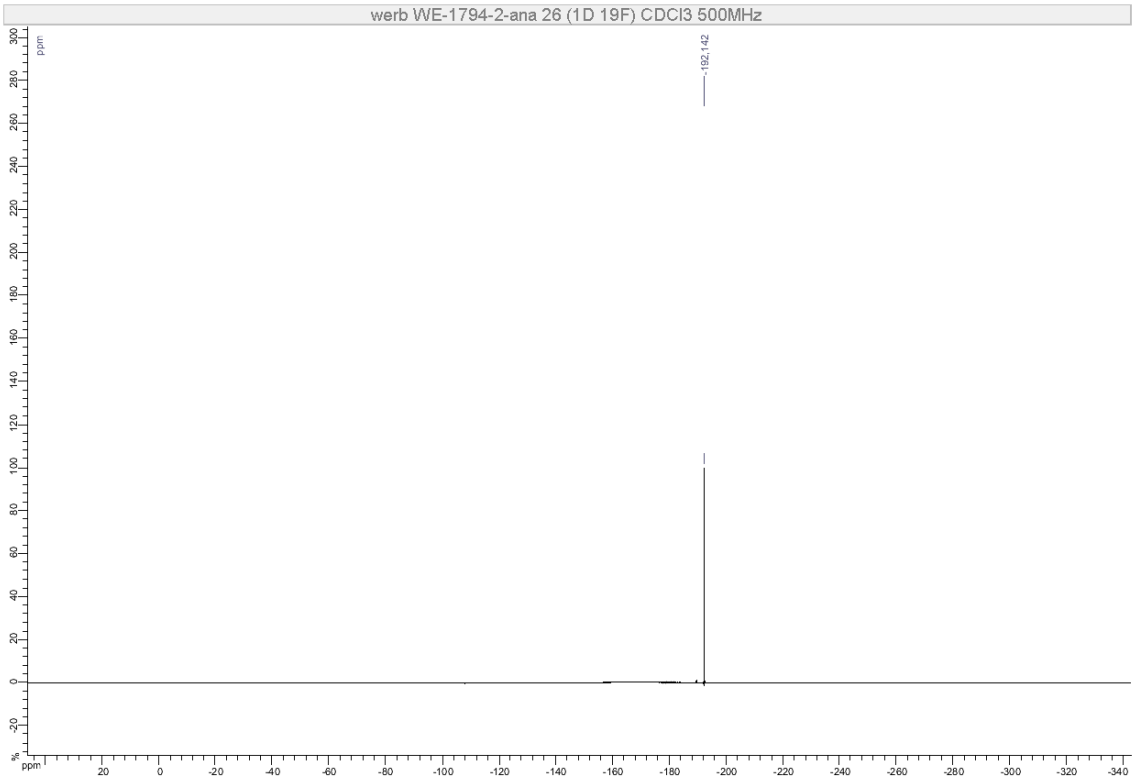
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

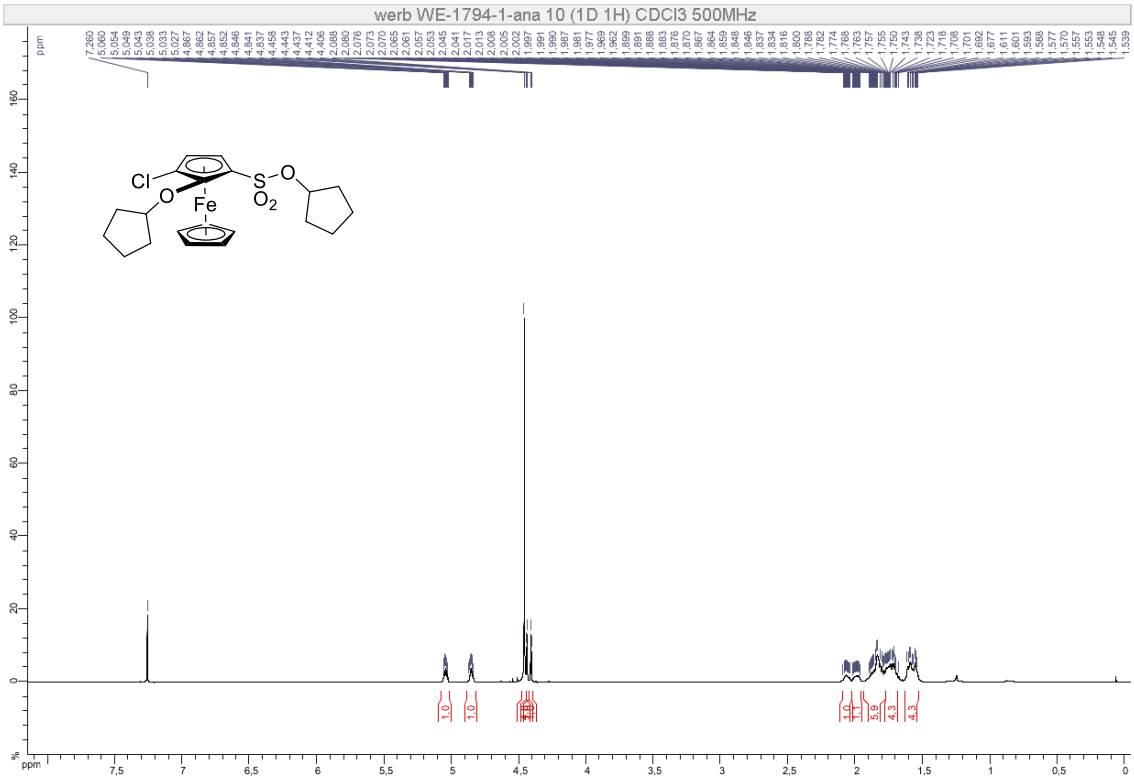


^{19}F NMR (470 MHz, $CDCl_3$)

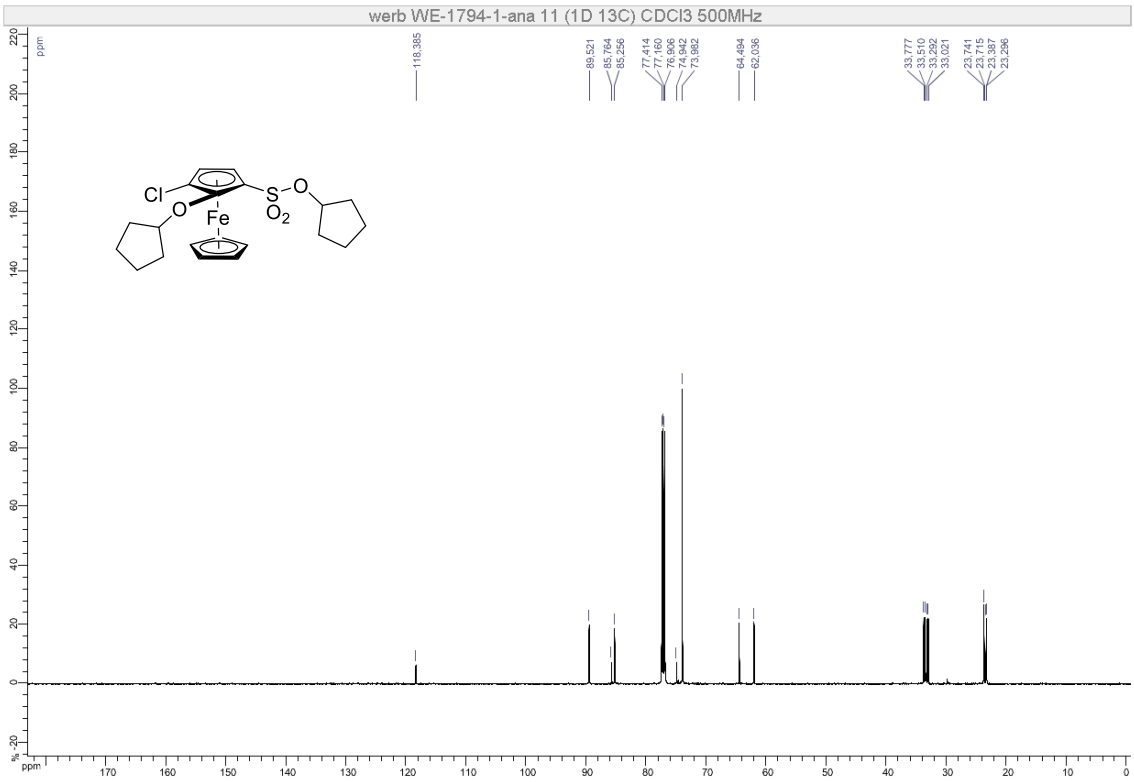


3-Chloro-*O*-cyclopentyl-2-(cyclopentyloxy)ferrocenesulfonate (38f)

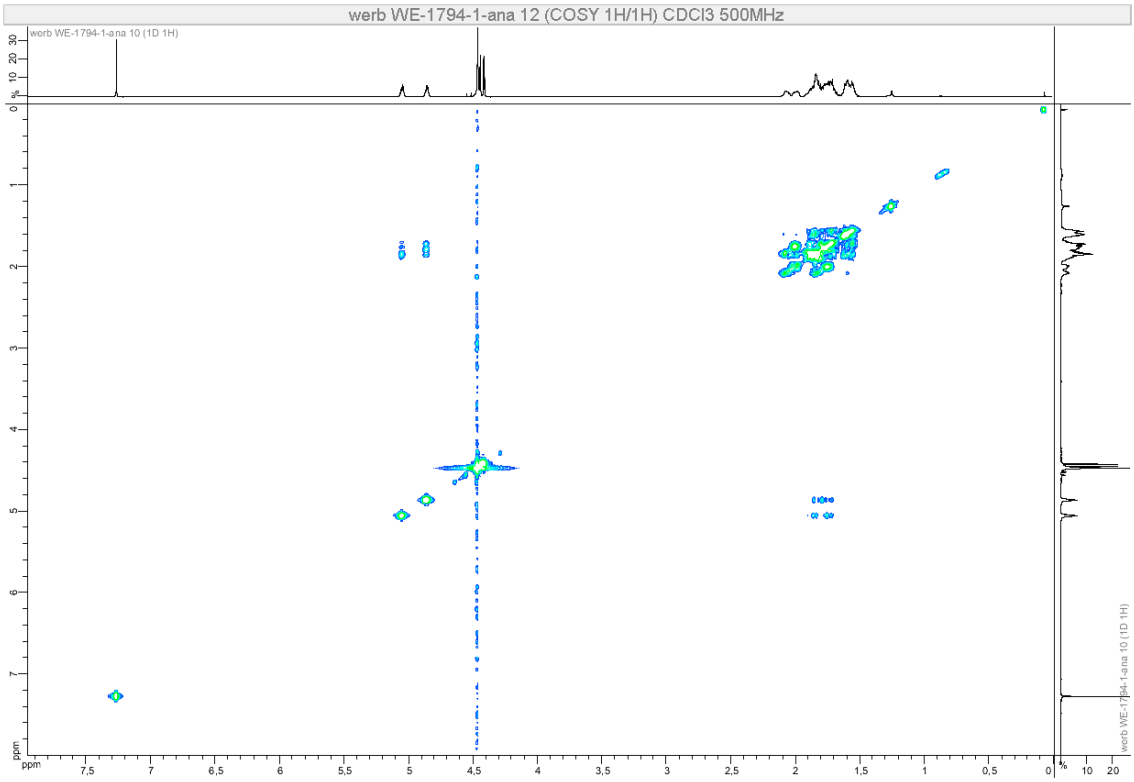
^{1}H NMR (500 MHz, $CDCl_3$)



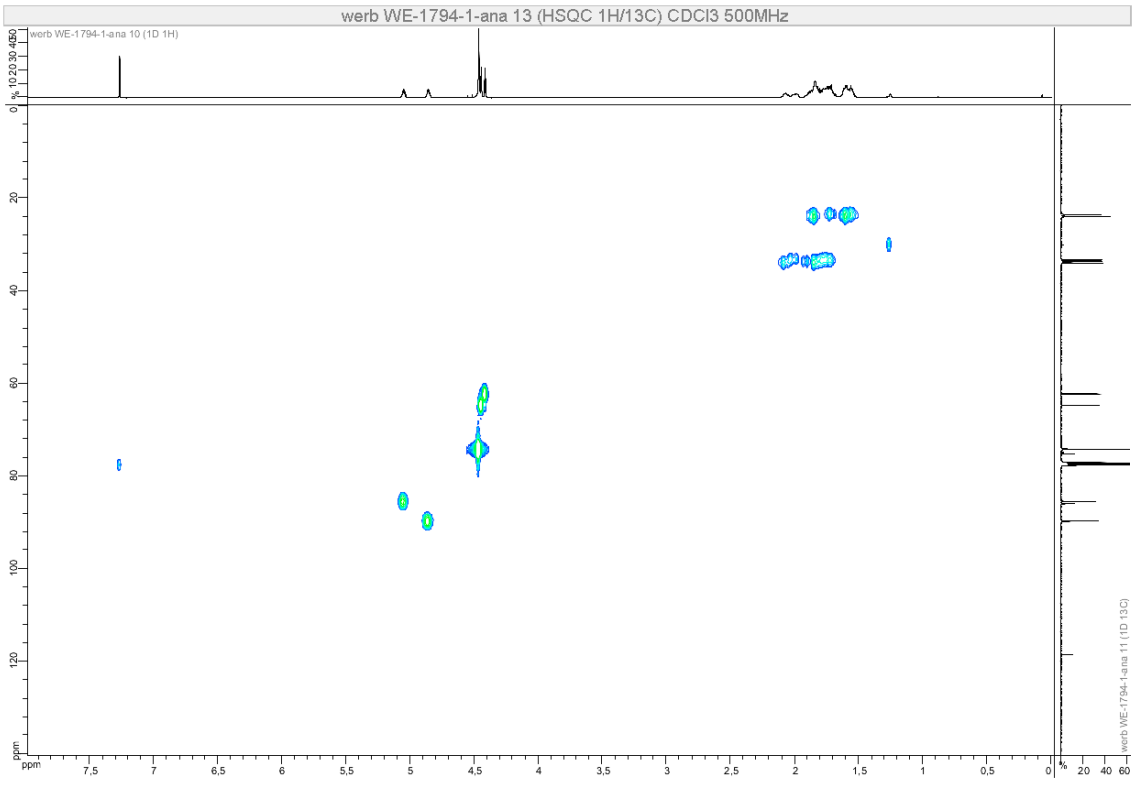
^{13}C NMR (125 MHz, $CDCl_3$)



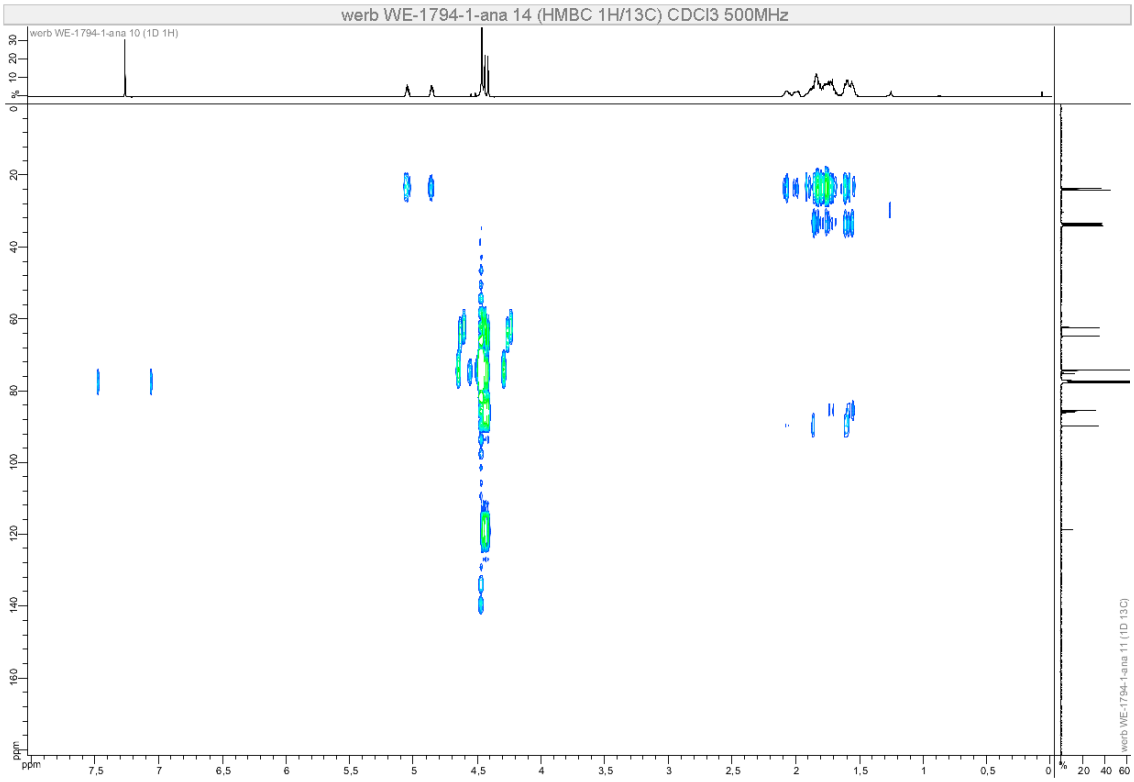
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

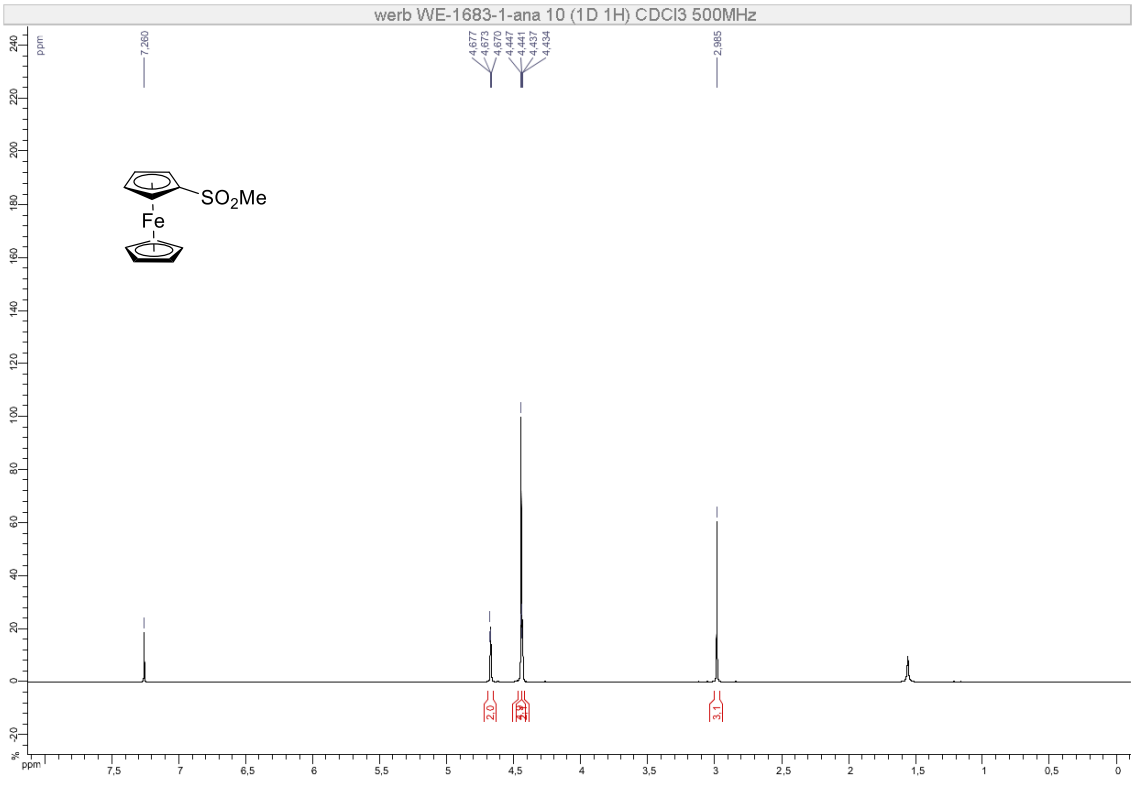


HMBC (500 MHz, $CDCl_3$)

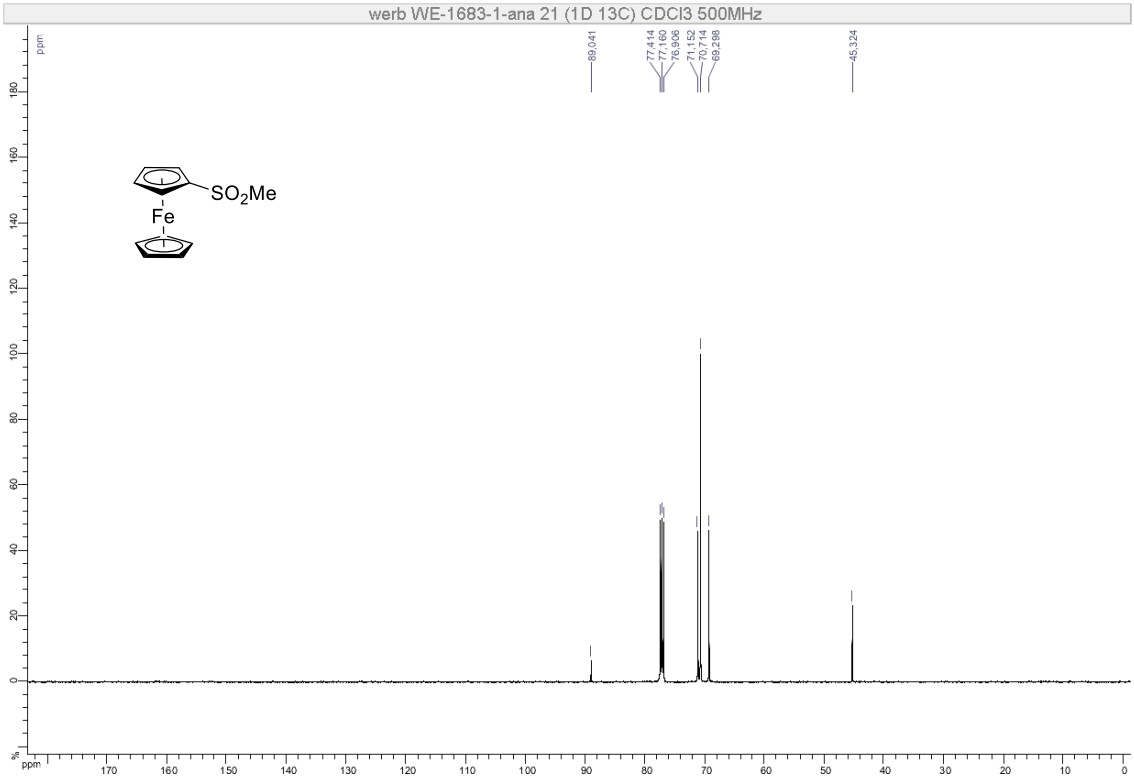


Methylsulfonylferrocene (39a)

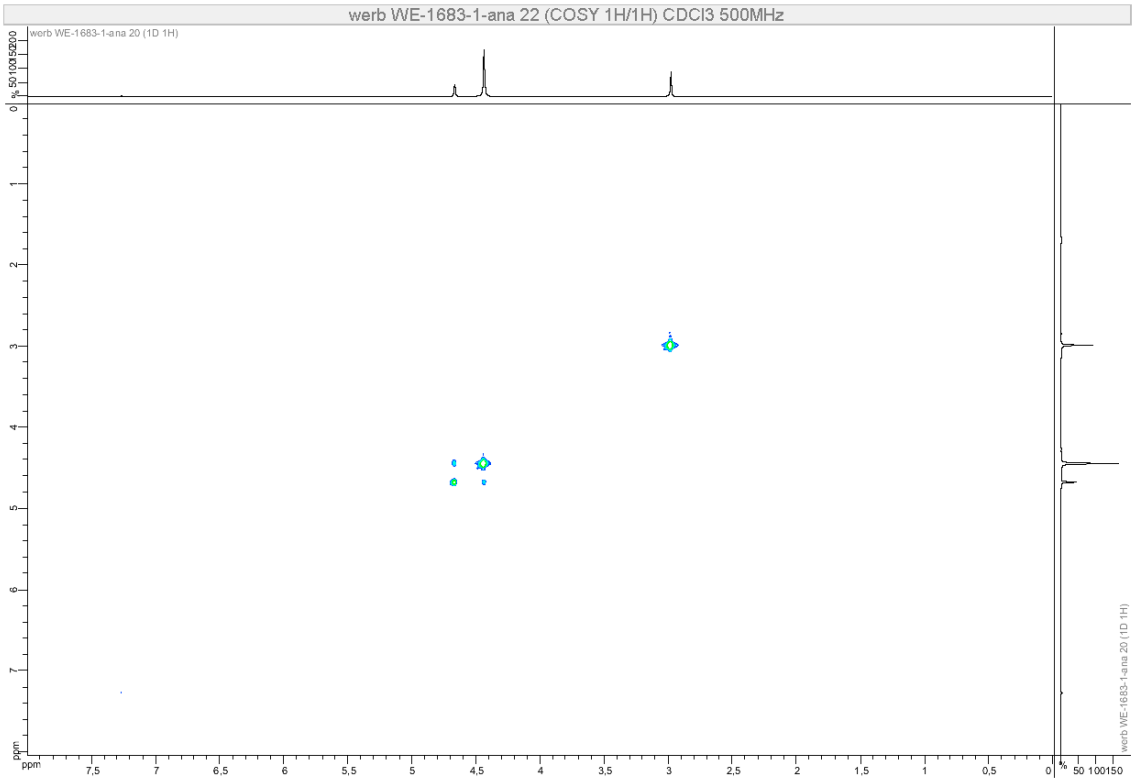
^{1}H NMR (500 MHz, $CDCl_3$)



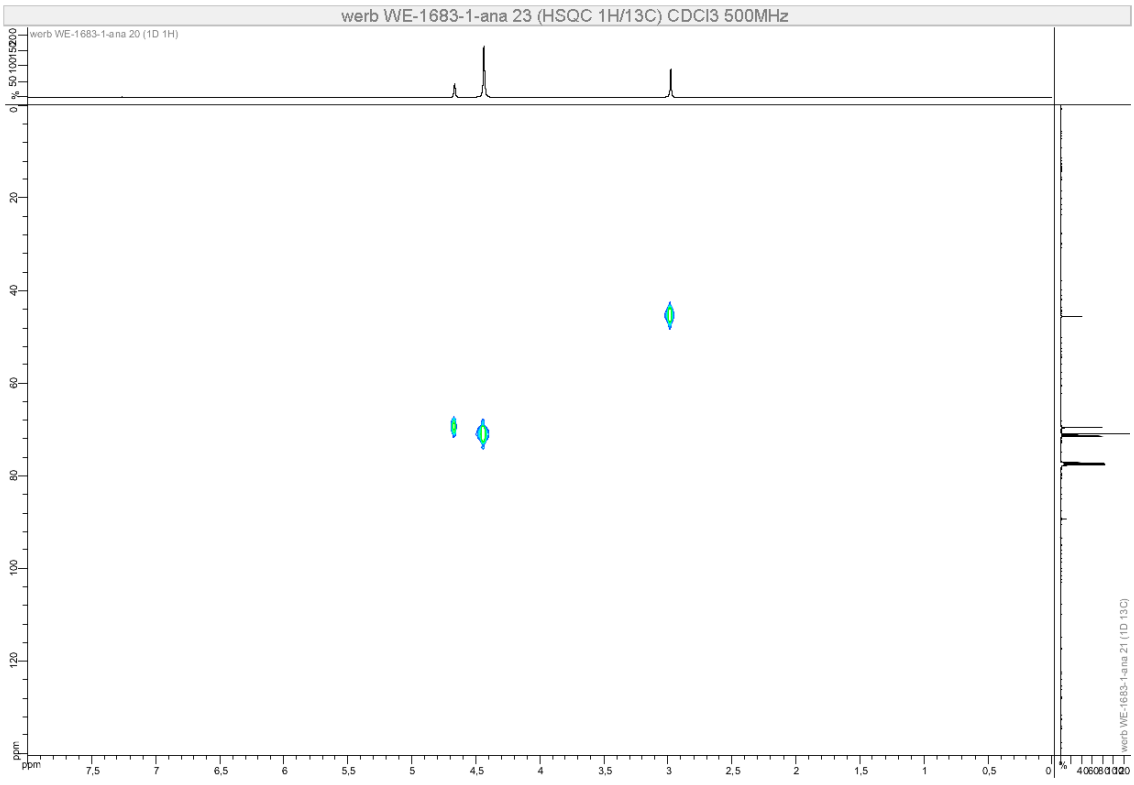
^{13}C NMR (125 MHz, $CDCl_3$)



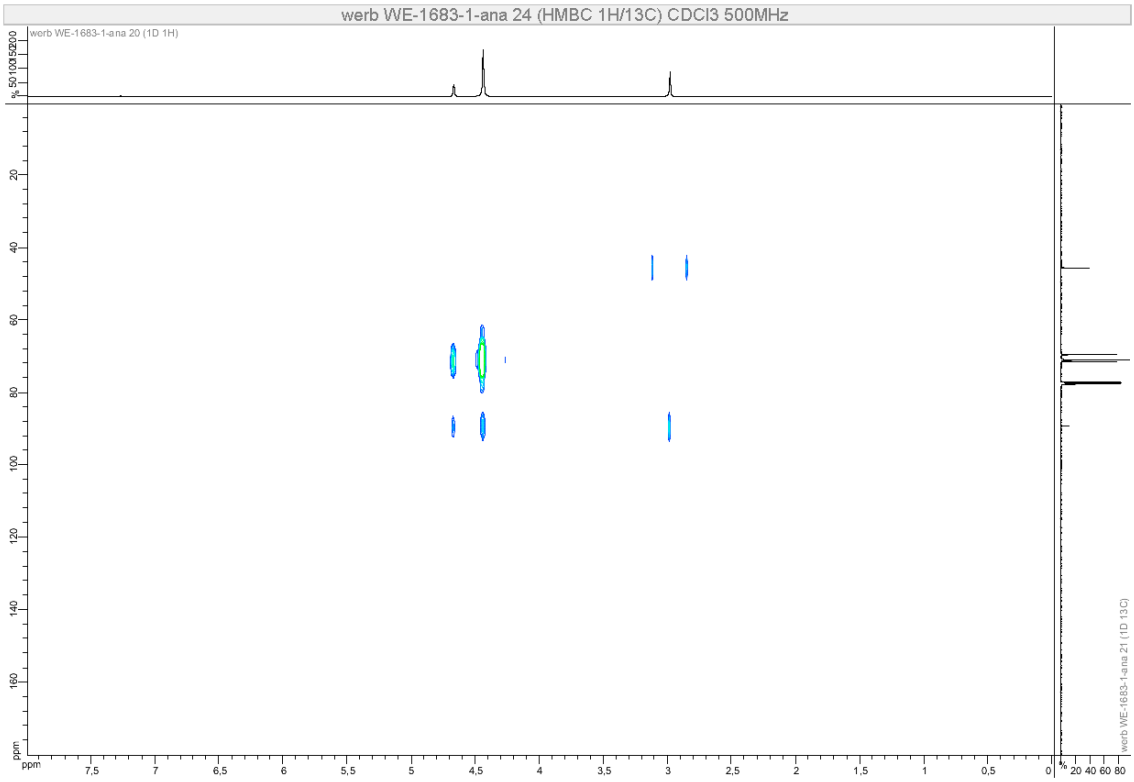
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

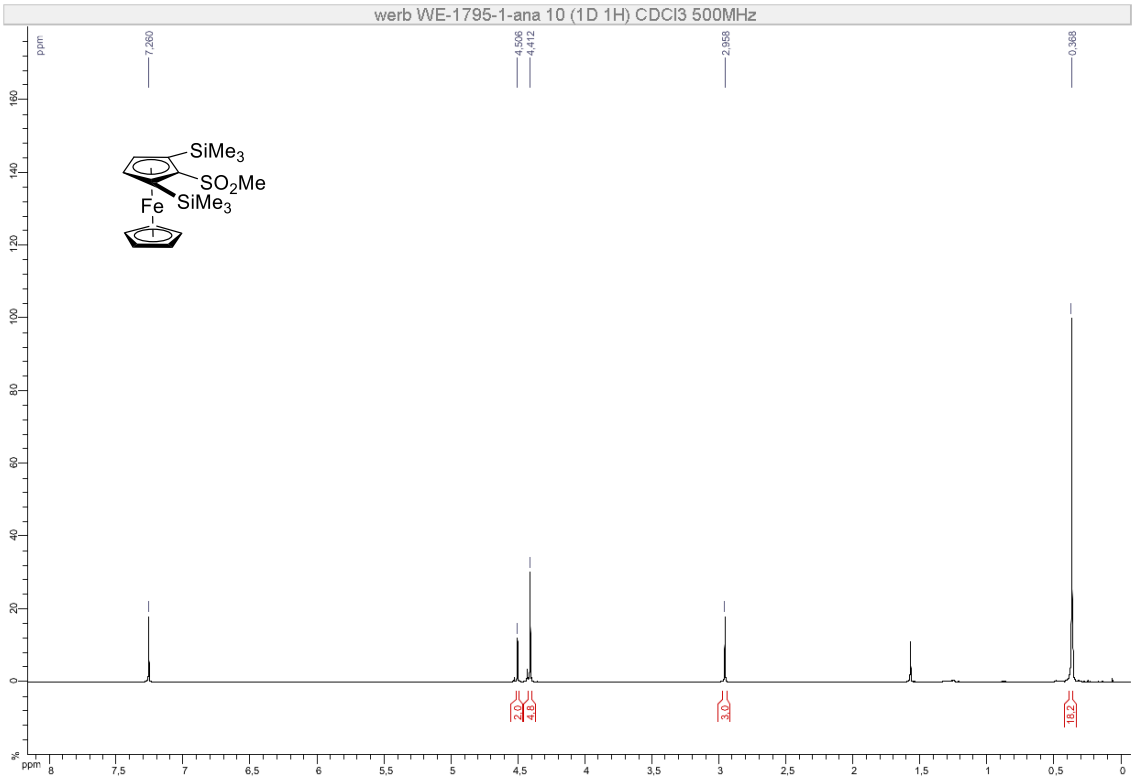


HMBC (500 MHz, $CDCl_3$)

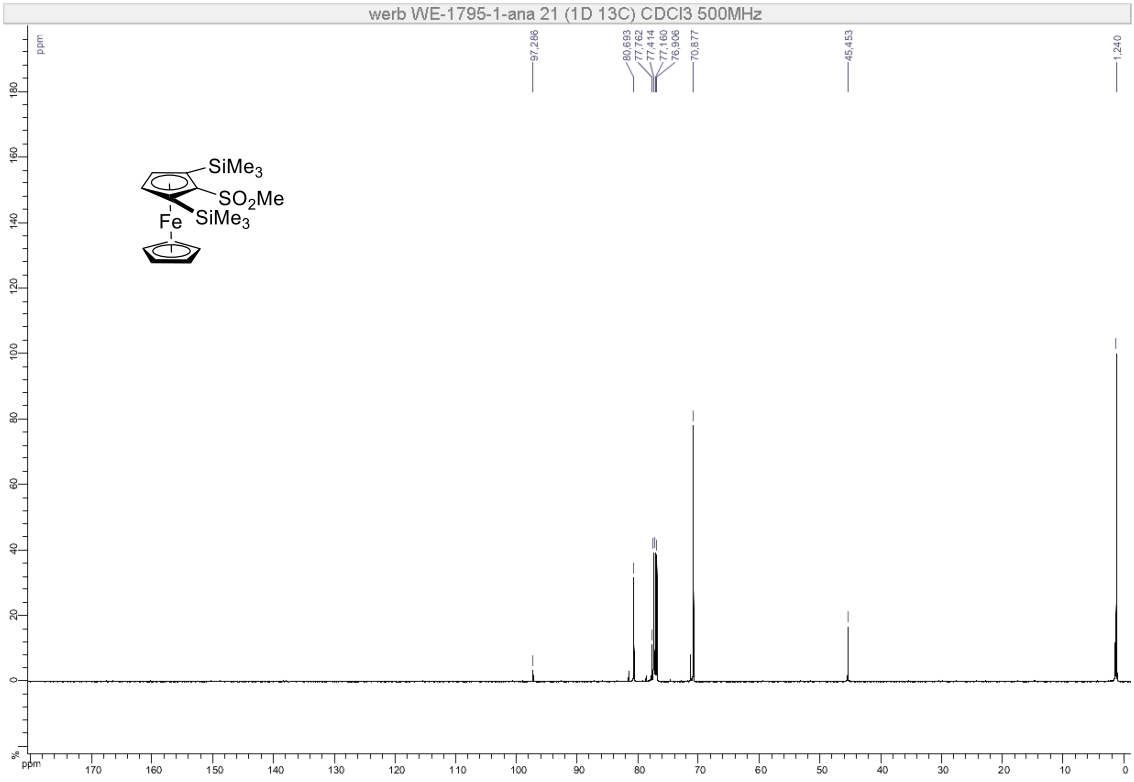


2,5-Bis(trimethylsilyl)-1-methylsulfonylferrocene – 39c

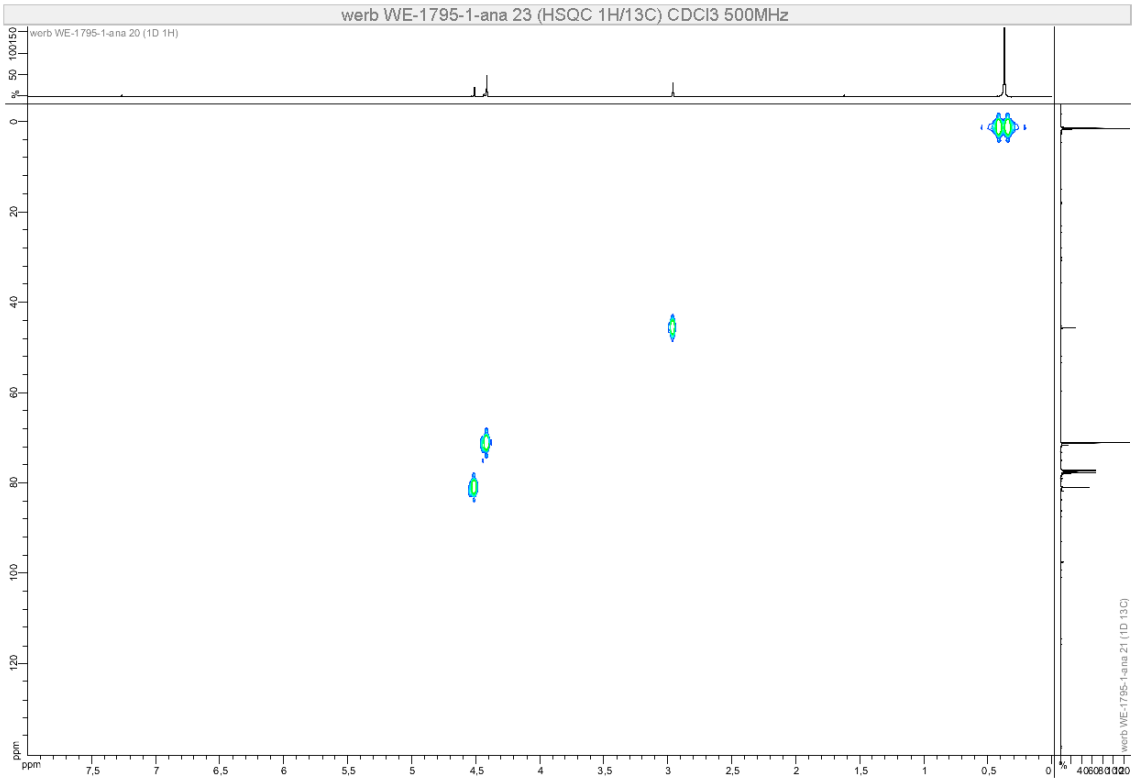
^{1}H NMR (500 MHz, $CDCl_3$)



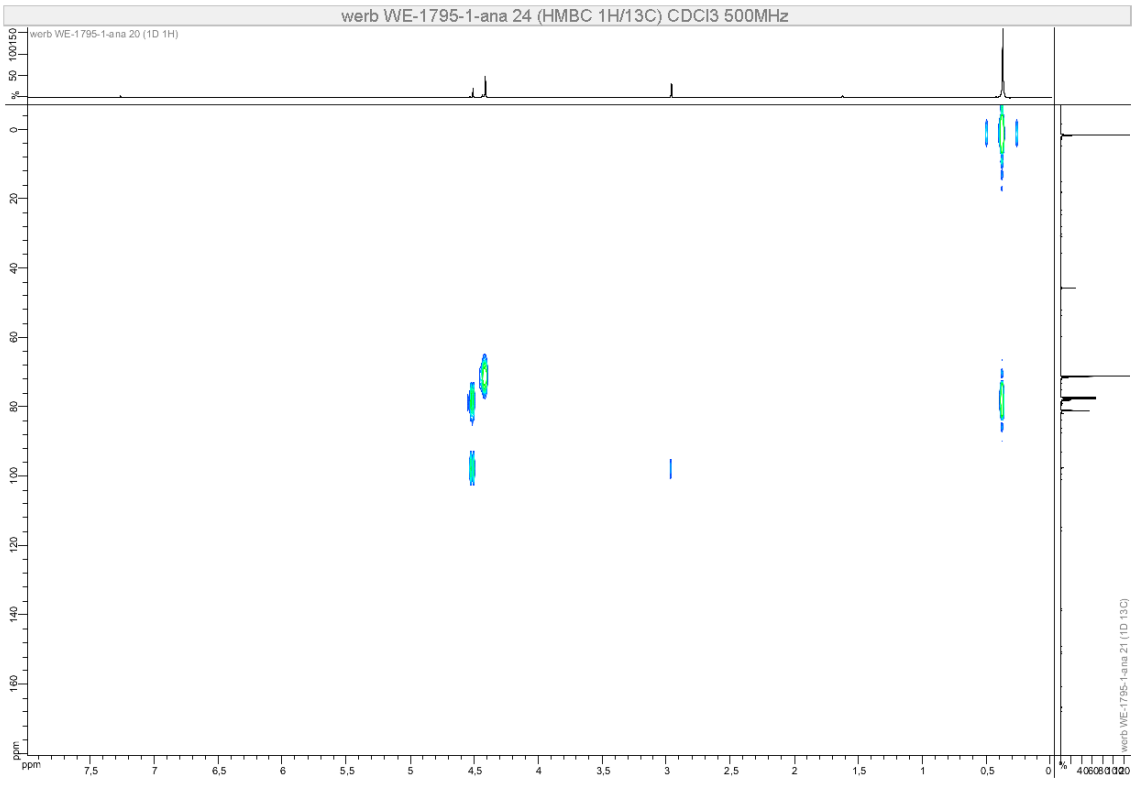
^{13}C NMR (125 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

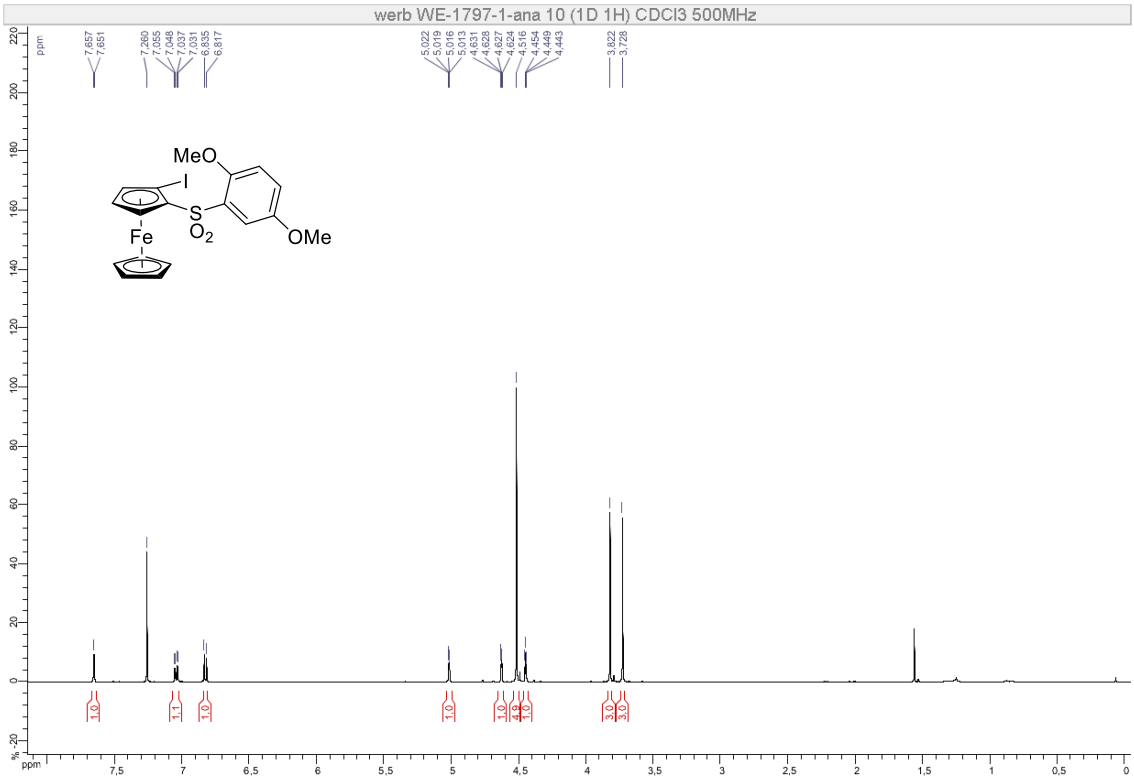


HMBC (500 MHz, $CDCl_3$)

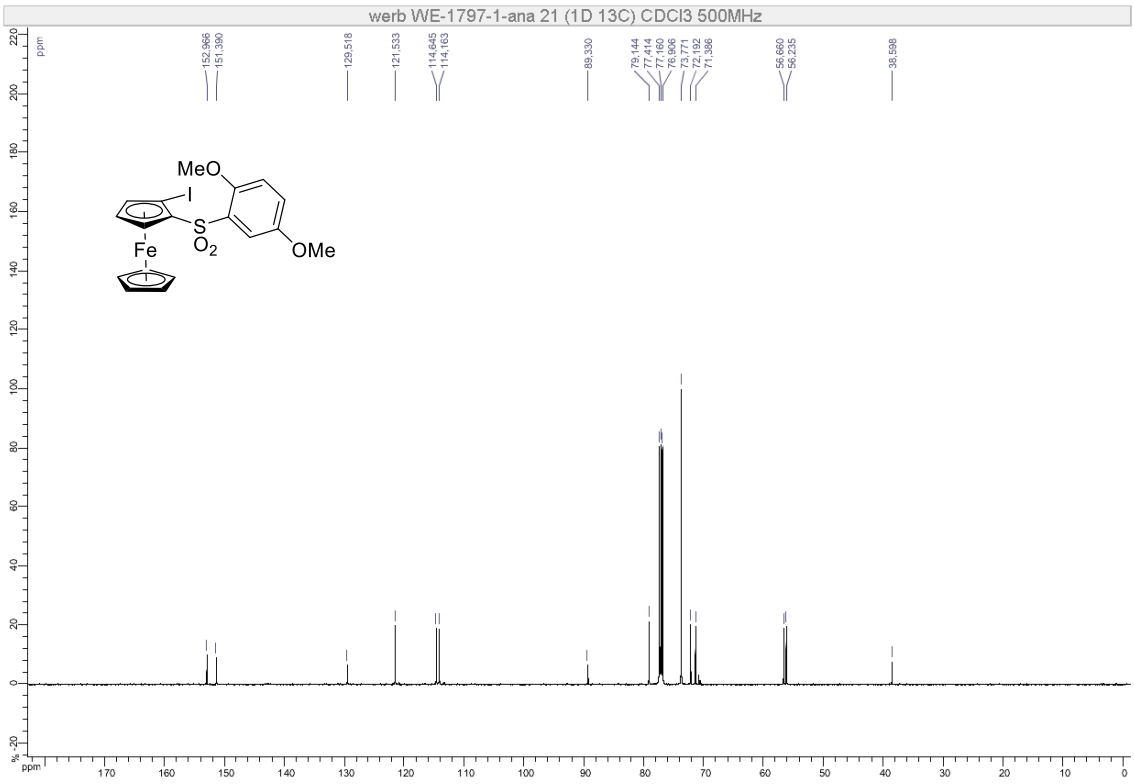


2-Iodo-1-(2,5-dimethoxyphenyl)sulfonylferrocene (40b)

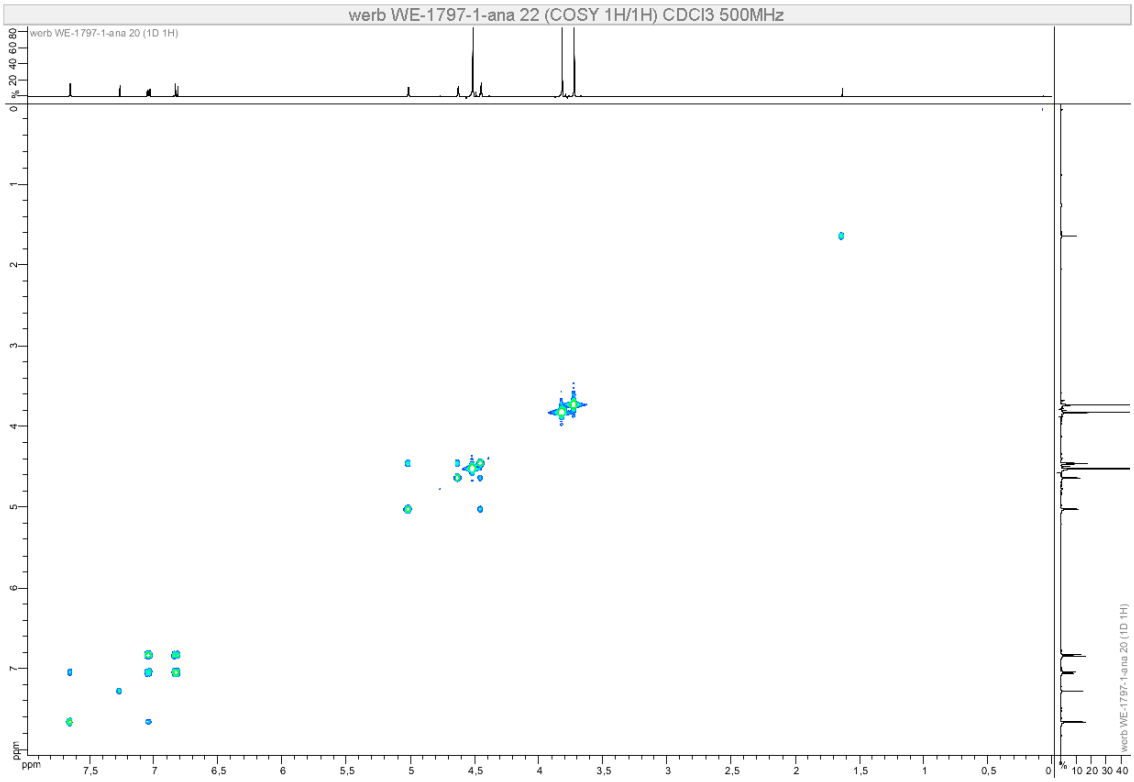
^{1}H NMR (500 MHz, $CDCl_3$)



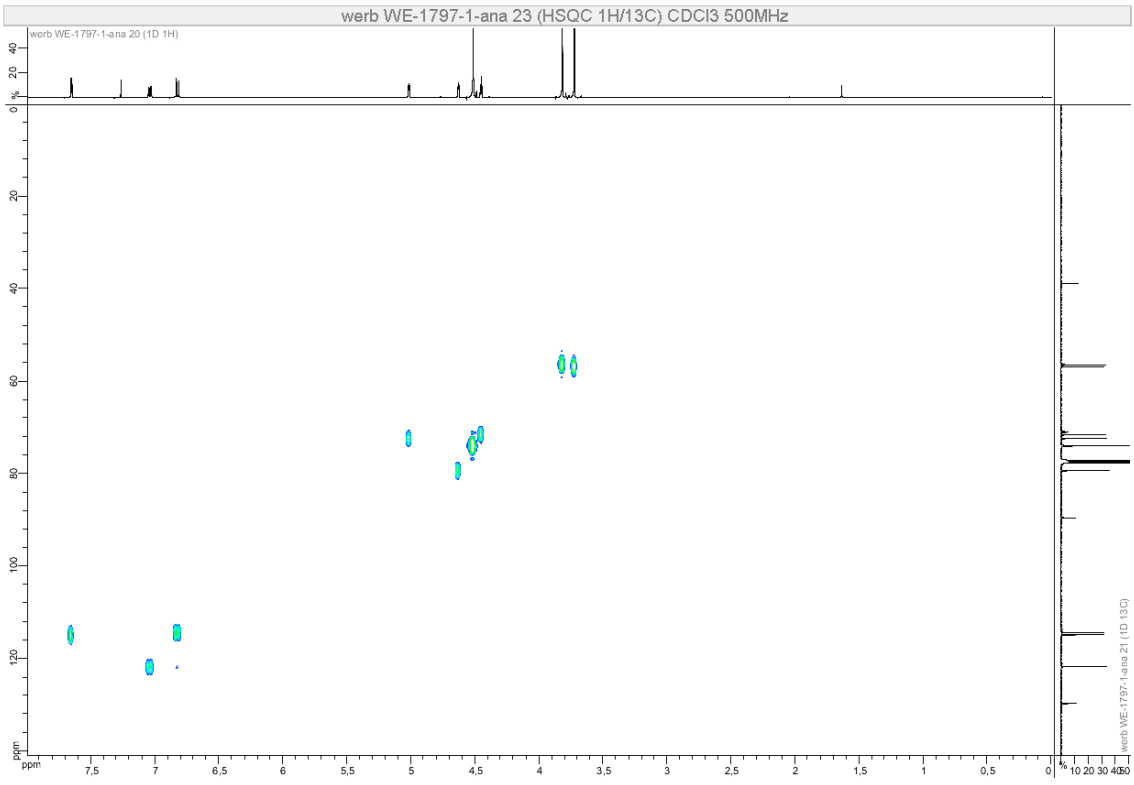
^{13}C NMR (125 MHz, $CDCl_3$)



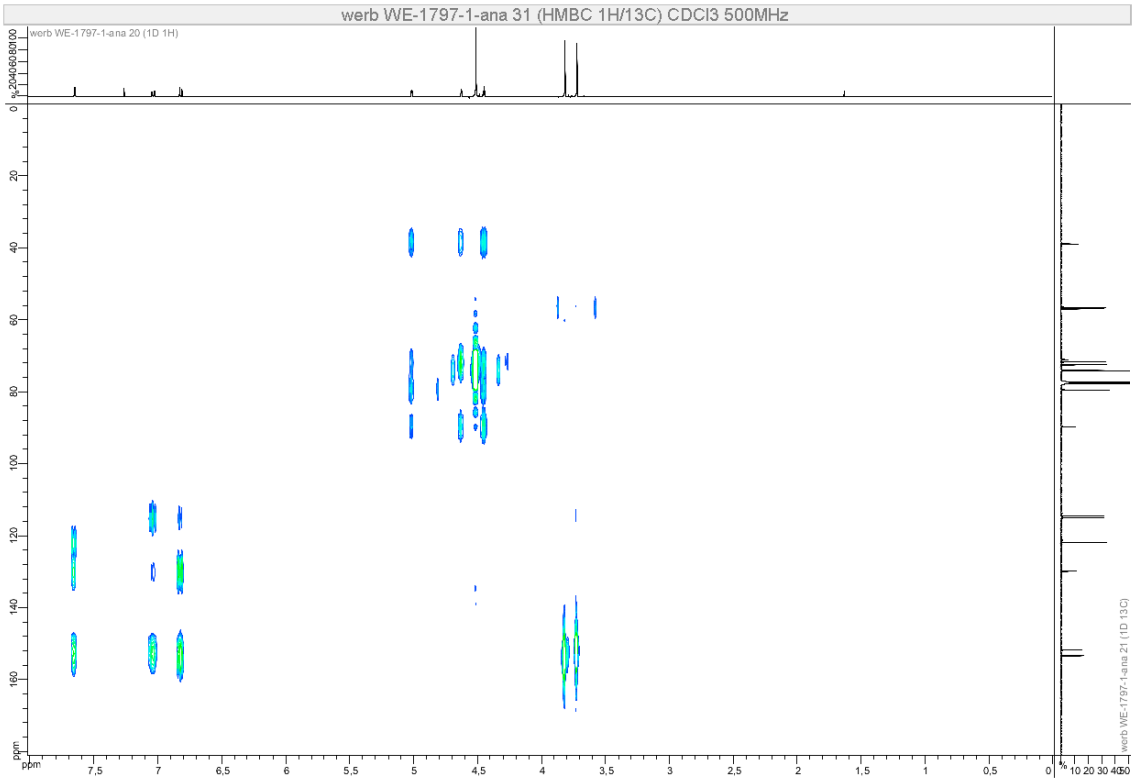
COSY (500 MHz, $CDCl_3$)



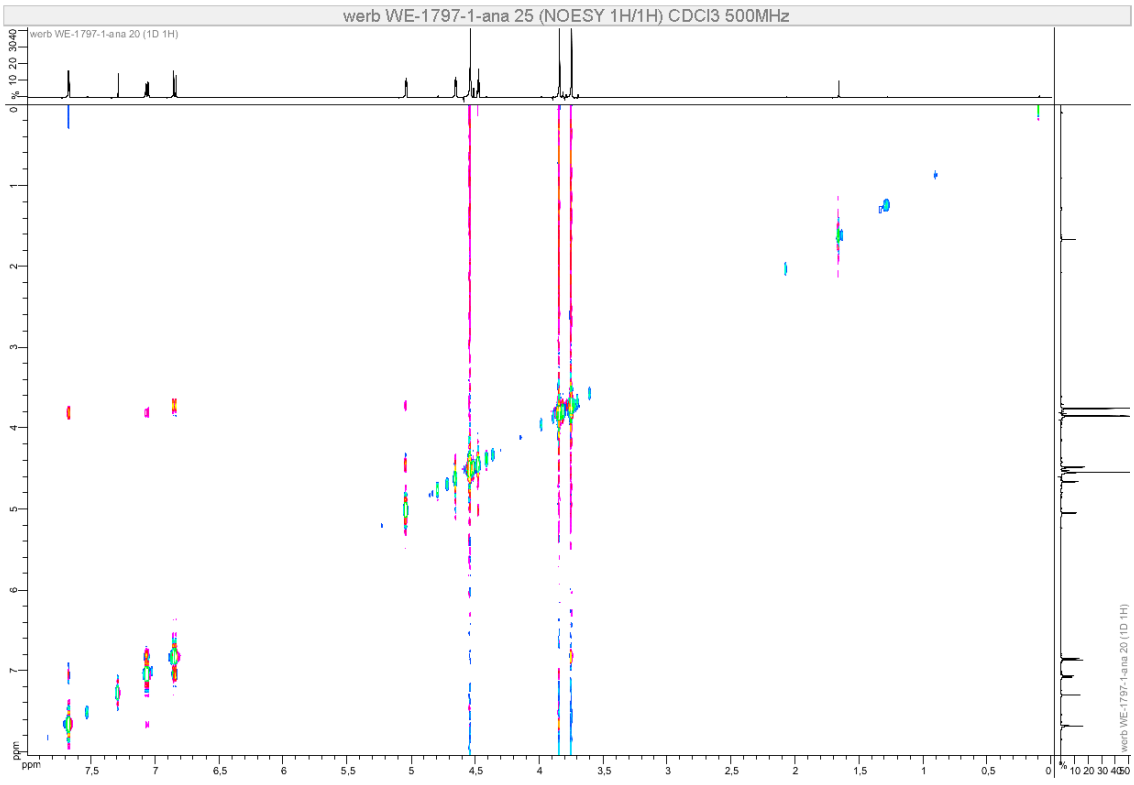
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

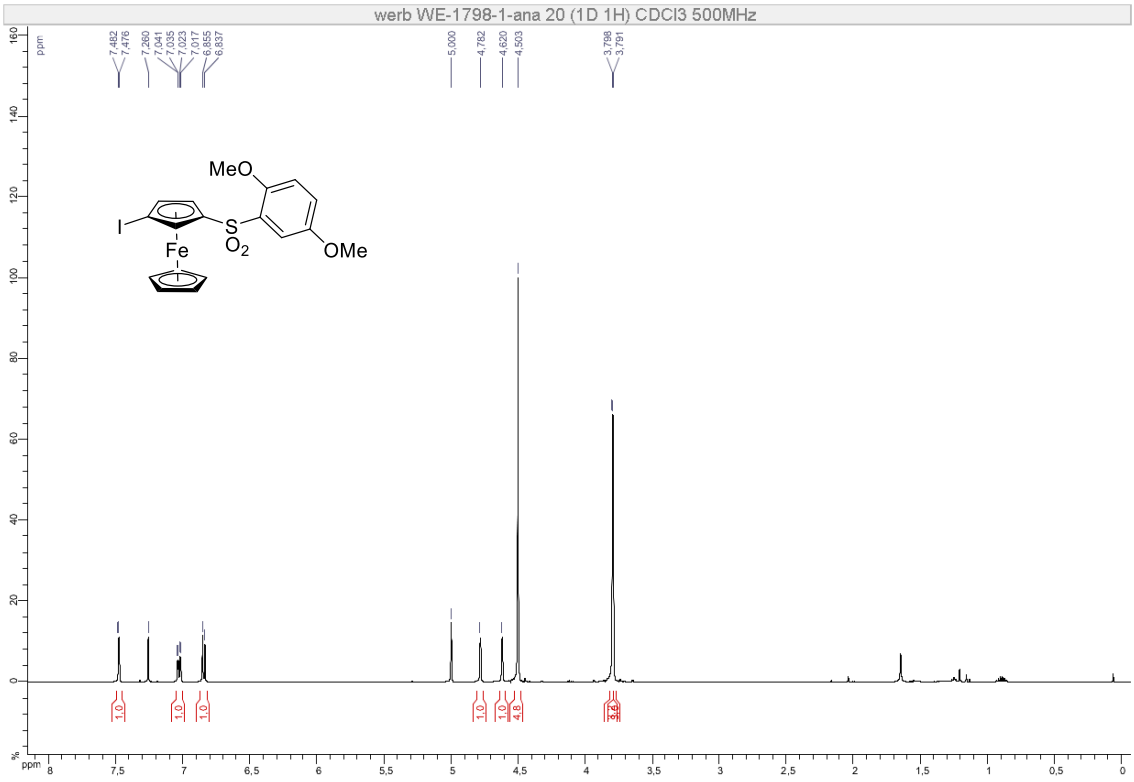


NOESY (500 MHz, $CDCl_3$)

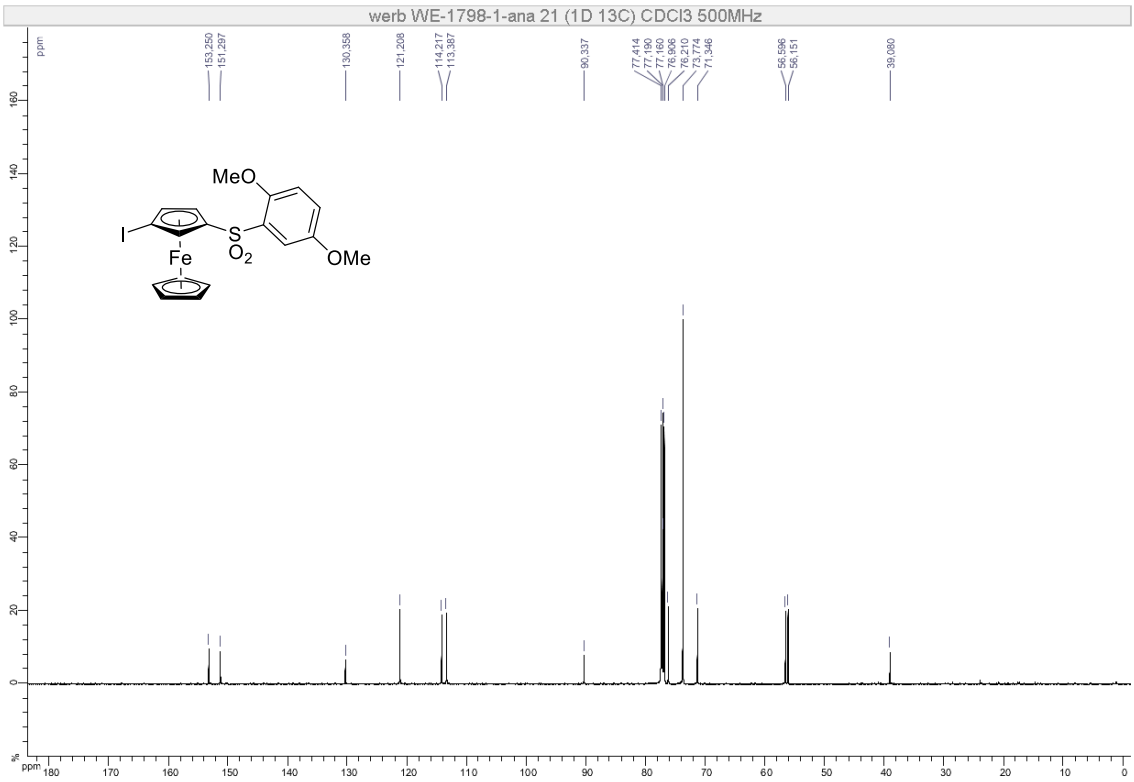


3-Iodo-1-(2,5-dimethoxyphenyl)sulfonylferrocene (40c)

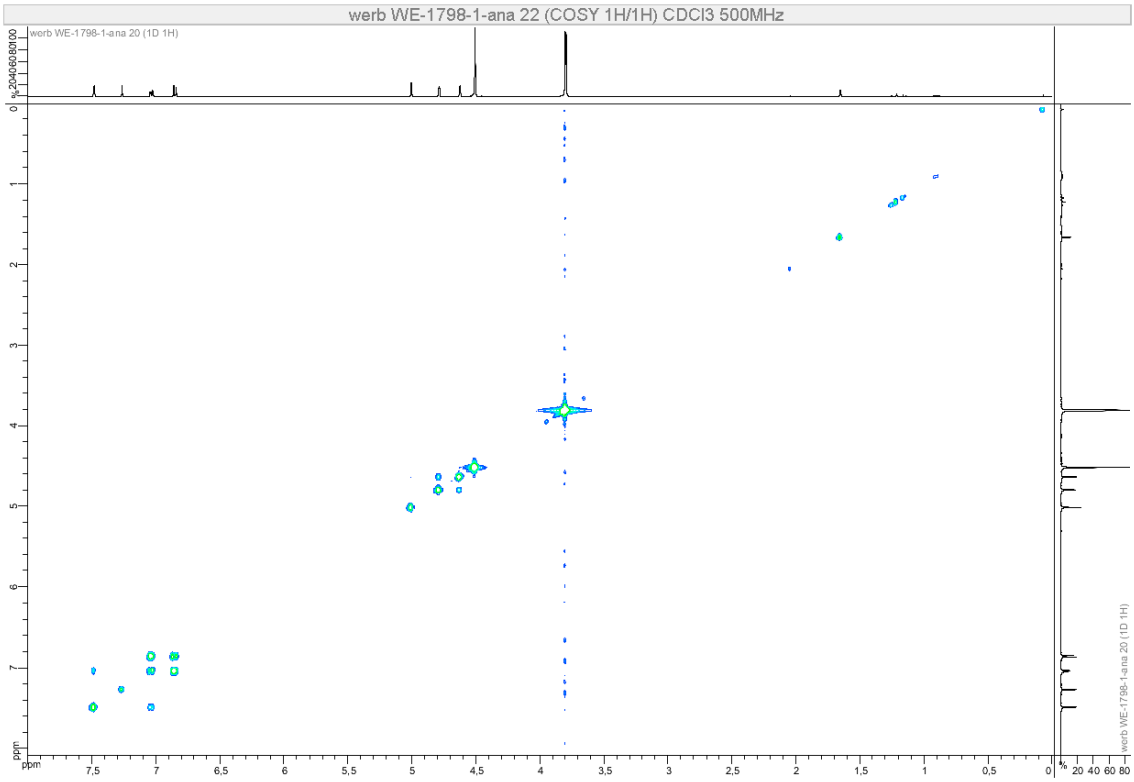
^{1}H NMR (500 MHz, $CDCl_3$)



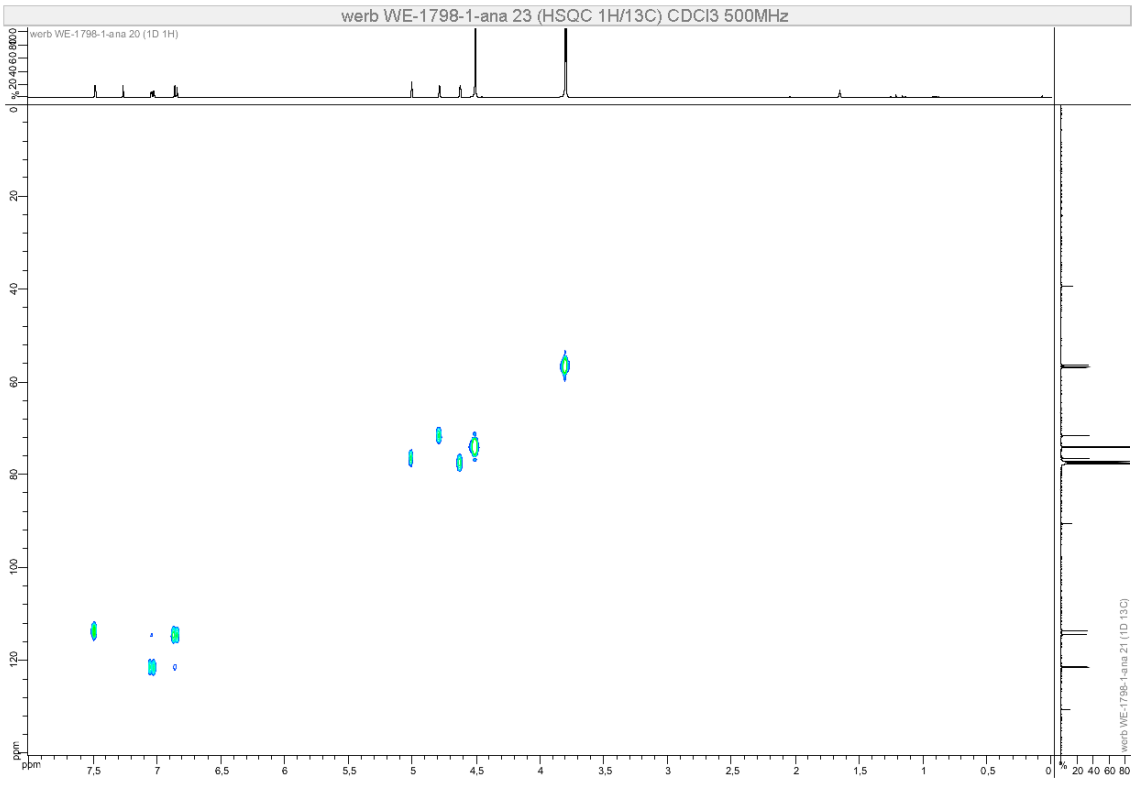
^{13}C NMR (125 MHz, $CDCl_3$)



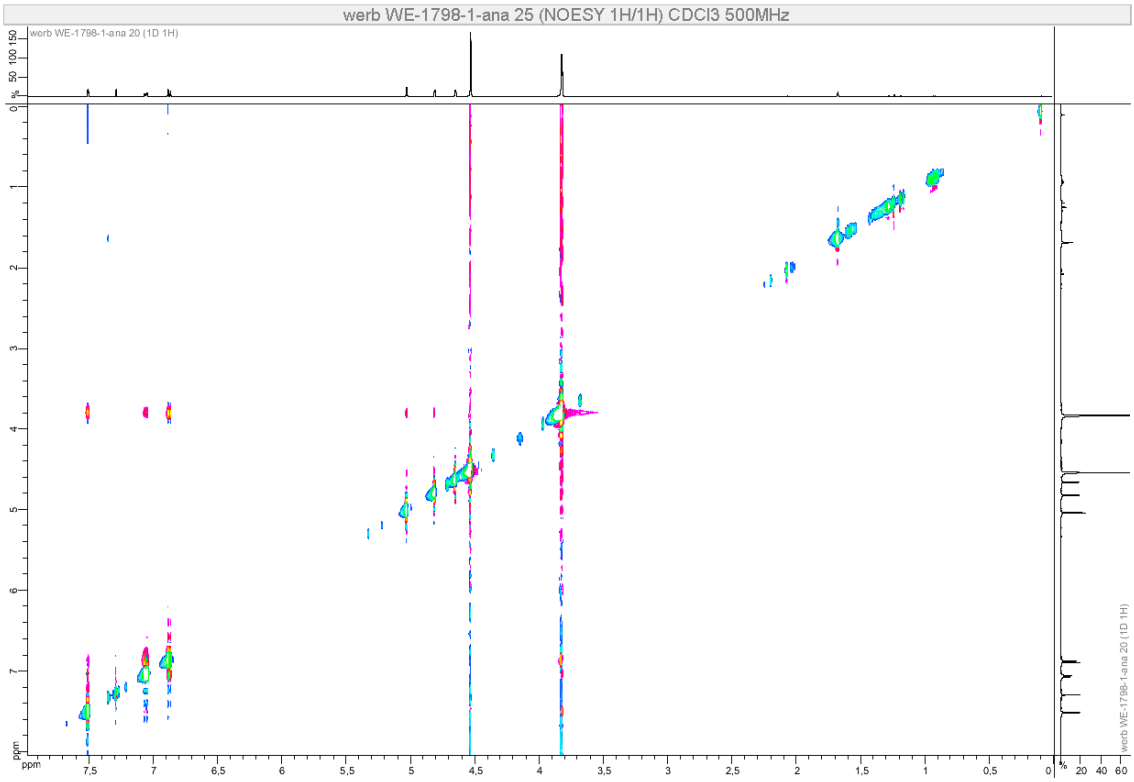
COSY (500 MHz, $CDCl_3$)



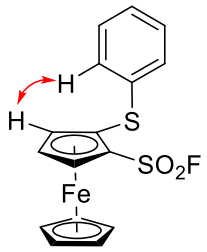
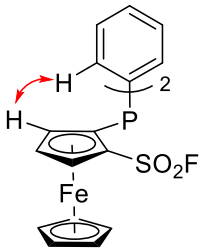
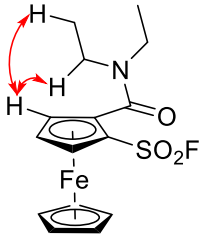
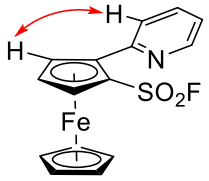
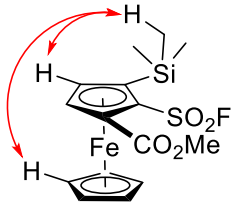
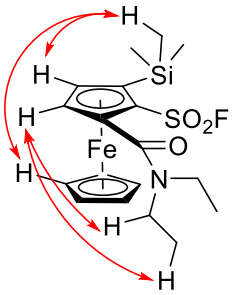
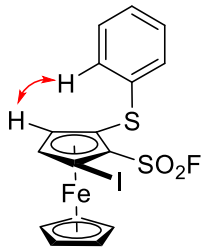
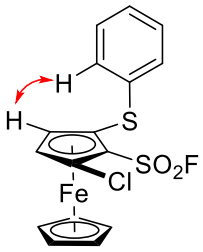
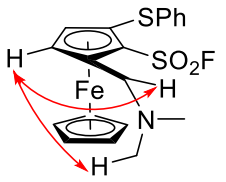
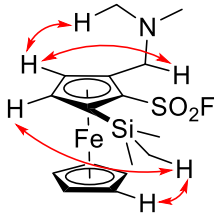
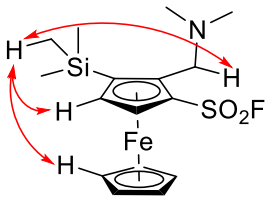
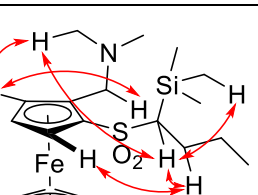
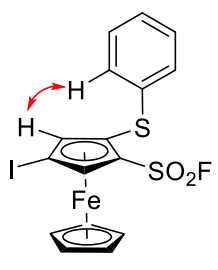
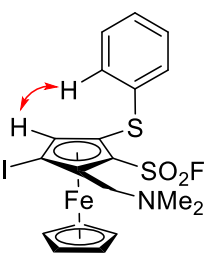
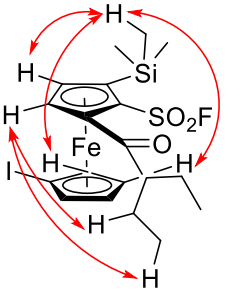
HSQC (500 MHz, $CDCl_3$)

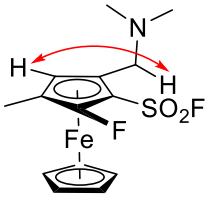
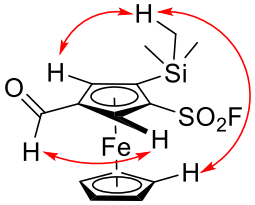
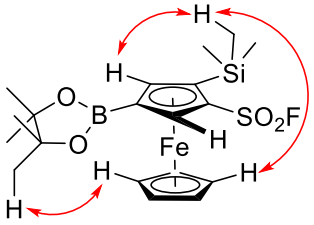
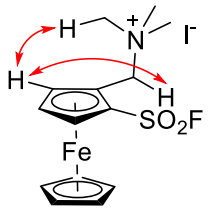
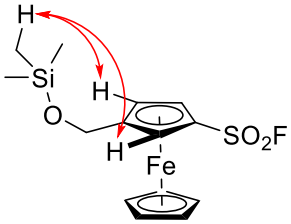
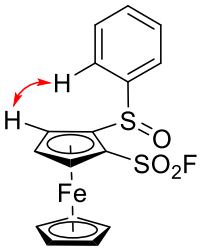
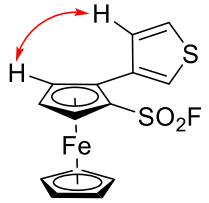
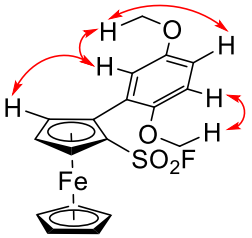
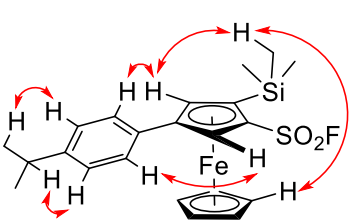
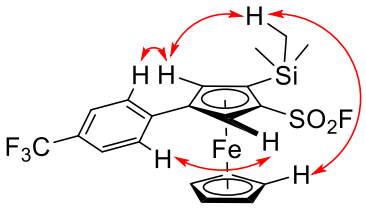
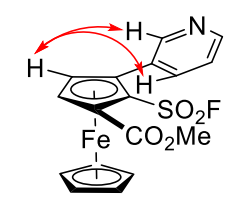
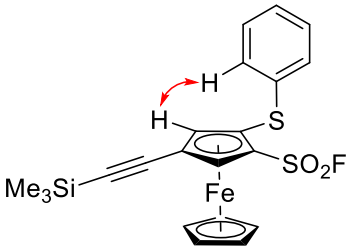
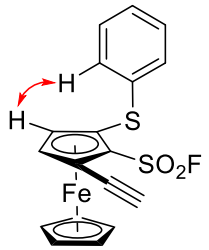
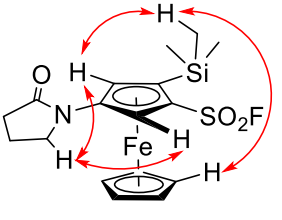
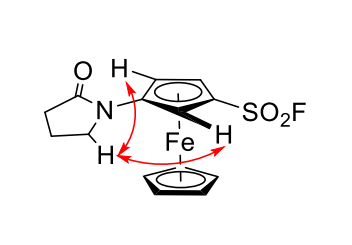


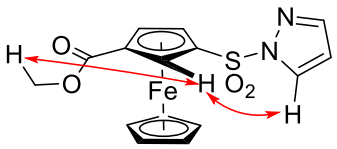
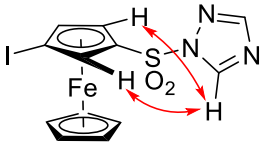
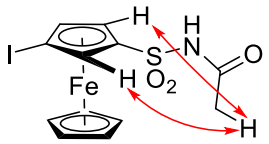
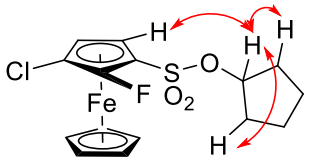
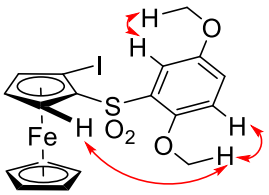
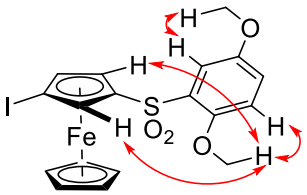
NOESY (500 MHz, $CDCl_3$)



Selected NOESY correlations

		
3b	**3c**	**3h**
		
3k	**5d**	**5e**
		
5f	**5g**	**5i**
		
5j	**5k**	**4e**
		
6e	**6g**	**7b**

		
14	**20a**	**20b**
		
21	**24b**	**26**
		
27a	**27b**	**29a**
		
29b	**30a**	**32d**
		
33c	**34a**	**34b**

		
36b	**36c**	**37b**
		
38e	**40b**	**40c**

DFT calculations.

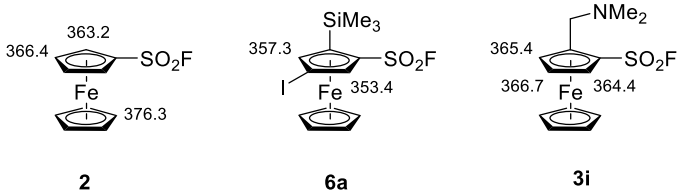
To calculate the CH acidity values, we used the approach developed earlier and applied successfully in ferrocene series.[10-15] In brief, all electronic structure calculations were carried out using standard DFT methods implemented in Gaussian 09 software.[16] We used the CAM-B3LYP hybrid functional.[17] Vibrational frequencies were calculated to prove the nature of the stationary points (no imaginary values). The LANL2DZ basis set[18] with the effective core potential was used to describe Fe and I, while the 6-31G(d) basis set[19] was used to treat the rest of the atoms. The latter was replaced by 6-311+G(d,p) set for single point energy calculations. To develop an acidity scale without solvent influence, it is important to know gas-phase CH acidities, which were defined as the Gibbs free energy of deprotonation of the substance:

$\Delta_{acid}G = G^0_{298}(R^-) + G^0_{298}(H^+) - G^0_{298}(RH)$

While the pK_a values were obtained from the Gibbs energy of the isodesmic reaction between the studied (RH) and a reference compound (HetH):

R–H(solv) + Het$^-$(solv) → R$^-$(solv) + Het–H(solv)

here furane with pK_a(THF) of 35.6[20] was used as the reference compound. The solvent effects for pK_a calculations were treated using polarizable continuum model (IEF-PCM)[21] with the default parameters for THF in order to mimic experimental conditions.

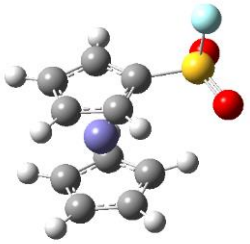


2 **6a** **3i**

Figure 21. Calculated values of the Gibbs energies $\Delta_{acid}G$ [kcal mol^{-1}] for deprotonation at the corresponding positions of the investigated compounds (gas-phase acidities).

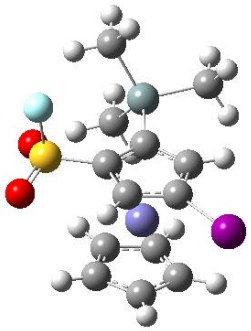
Cartesian coordinates of DFT optimized structures.

Compound 2



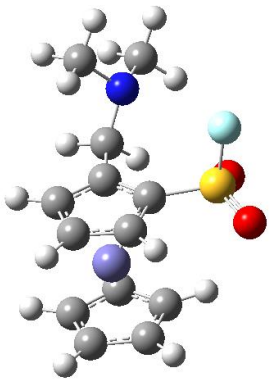
atom	X	Y	Z
Fe	1.02807	0.20563	0.00171
S	-2.17307	-0.43502	-0.00219
C	1.13133	-1.84990	0.03031
C	1.80557	-1.30950	1.15868
C	2.84983	-0.46833	0.68452
C	2.81952	-0.48920	-0.73654
C	1.75671	-1.34318	-1.14129
C	-0.27780	1.28271	-1.16543
C	0.75245	2.14011	-0.71250
C	0.75148	2.14159	0.71181
C	-0.27914	1.28481	1.16541
C	-0.91289	0.75601	0.00003
O	-2.21547	-1.11390	-1.27431
O	-2.19503	-1.14450	1.25372
F	-3.46029	0.52373	0.02087
H	0.26270	-2.49311	0.05962
H	1.54367	-1.48037	2.19342
H	3.52294	0.11587	1.29652
H	3.46513	0.07705	-1.39342
H	1.45040	-1.54338	-2.15845
H	-0.52911	1.03464	-2.18588
H	1.45039	2.67161	-1.34390
H	1.44815	2.67491	1.34308
H	-0.53079	1.03976	2.18654

Compound 6a



atom	X	Y	Z
Fe	-0.22061	-0.51830	0.86346
S	2.04204	-1.54046	-1.27142
Si	2.42192	1.89414	0.22435
C	-0.06228	-2.36465	1.75795
H	0.19014	-3.26072	1.20758
C	-1.36812	-1.83872	1.94845
H	-2.28728	-2.26753	1.57366
C	-1.25043	-0.60849	2.65077
H	-2.06469	0.05408	2.90946
C	0.13016	-0.37593	2.89520
H	0.54907	0.49646	3.37692
C	0.86555	-1.45890	2.34329
H	1.94212	-1.55086	2.31518
C	-0.44111	1.31780	-0.09458
H	-0.73609	2.24174	0.38172
C	-1.34103	0.36181	-0.63792
C	-0.60190	-0.72889	-1.14223
H	-0.98104	-1.63337	-1.59344
C	0.76974	-0.42116	-0.88872
C	0.90001	0.85781	-0.24074
O	1.49223	-2.85337	-1.50351
F	2.47526	-0.98550	-2.71402
O	3.19399	-1.33048	-0.42602
C	3.47993	2.08435	-1.31685
H	2.91341	2.54043	-2.13540
H	3.85967	1.12029	-1.66592
H	4.34280	2.72727	-1.11121
C	3.41982	1.16846	1.63873
H	3.80861	0.18141	1.37991
H	2.82316	1.07943	2.55187
H	4.27020	1.82225	1.86326
C	1.75176	3.57678	0.74580
H	2.58259	4.24494	0.99731
H	1.11134	3.51125	1.63220
H	1.17617	4.05652	-0.05250
I	-3.42686	0.55020	-0.69757

Compound 3i



atom	X	Y	Z
Fe	1.45098	-0.39460	0.16899
S	-0.88190	1.90264	-0.06368
C	2.15786	0.56700	-1.50873
C	1.95313	-0.81217	-1.78262
C	2.77260	-1.56296	-0.89468
C	3.48258	-0.64683	-0.07278
C	3.10199	0.67010	-0.45100
C	0.67286	0.55670	1.81899
C	0.99462	-0.77684	2.15887
C	0.25202	-1.64767	1.31270
C	-0.53813	-0.87731	0.42217
C	-0.26870	0.49364	0.74714
O	-0.08227	3.04790	0.29753
O	-1.21582	1.61720	-1.43867
F	-2.27491	2.09048	0.69532
C	-1.49639	-1.37741	-0.62045
N	-2.87608	-1.09791	-0.25543
C	-3.75931	-1.19090	-1.40176
C	-3.33414	-1.92163	0.84542
H	1.64276	1.38951	-1.98546
H	1.26687	-1.21791	-2.51293
H	2.81818	-2.64125	-0.82997
H	4.16044	-0.90693	0.72843
H	3.43948	1.58874	0.00811
H	1.07877	1.46348	2.24208
H	1.71259	-1.08025	2.90766
H	0.30864	-2.72793	1.30803
H	-1.29432	-0.86508	-1.56244
H	-1.31680	-2.45768	-0.78313
H	-3.79480	-2.20582	-1.84105
H	-4.77511	-0.91857	-1.10151
H	-3.43326	-0.48781	-2.17282
H	-4.34716	-1.62405	1.13006
H	-3.34947	-3.00000	0.59483
H	-2.68627	-1.78313	1.71506

HPLC data

(±)-2-(Trimethylsilyl)ferrocenesulfonyl fluoride (3a)

Chromatogram and Results

General informations

Sequence Name:	2022-06-22
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA3 DAICEL

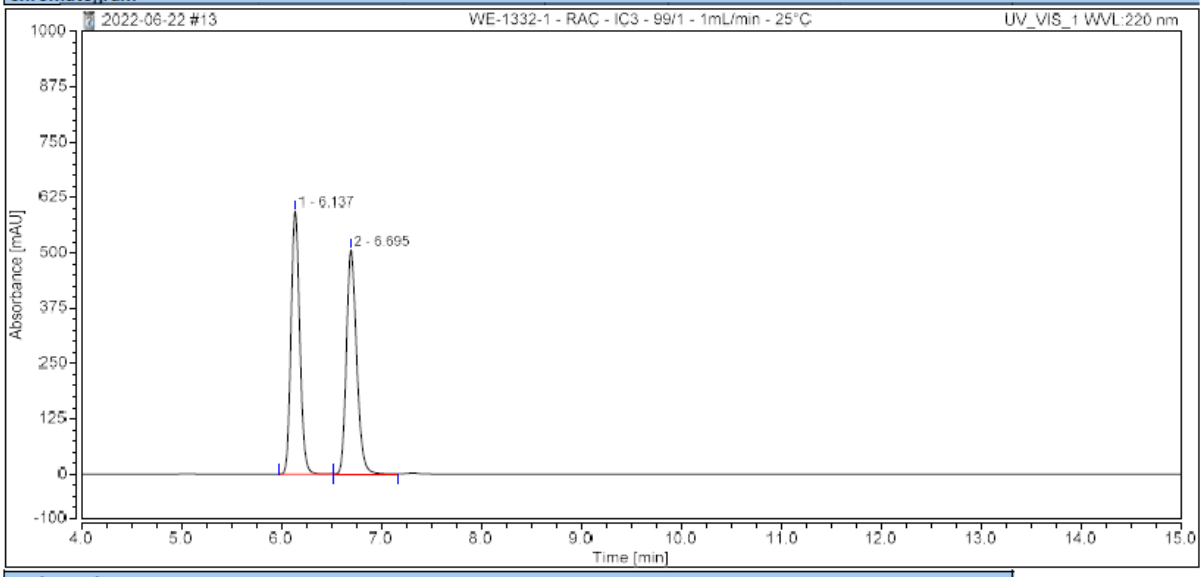
Injection Details

Injection Name:	WE-1332-1 - RAC - IC3 - 99/1 - 1mL/min - 25°C	*Run Time:*	15.00 min
Instrument Method:	Enantio Fc Will	*Injection Volume:*	3.00 µL
Injection Date/Time:	22/juin/22 22:16	*Channel:*	UV_VIS_1
		Wavelength:	220 nm

Instrument Method Details

Instrument Method:	Enantio Fc Will				
%A	iPrOH 10	1 %			
%B	Hexane 90	99 %	*Température du four:*	25.0 °C	
	Débit:	1.000 mL/min	*Pression:*	71 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		6.137	0.093	3.28	1.14	24213
2		6.695	0.108	n.a.	1.24	21214

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		6.137	59.815	593.527	49.91	53.98
2		6.695	60.043	506.045	50.09	46.02
Total:			**119.858**	**1099.571**	**100.00**	**100.00**

Deprotonation of ferrocenesulfonyl fluoride (2) with *s*BuLi·(+)-sparteine using chlorotrimethylsilane as electrophile – Table 2, entry 3

Chromatogram and Results

General informations

Sequence Name:	2022-06-22
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA3 DAICEL

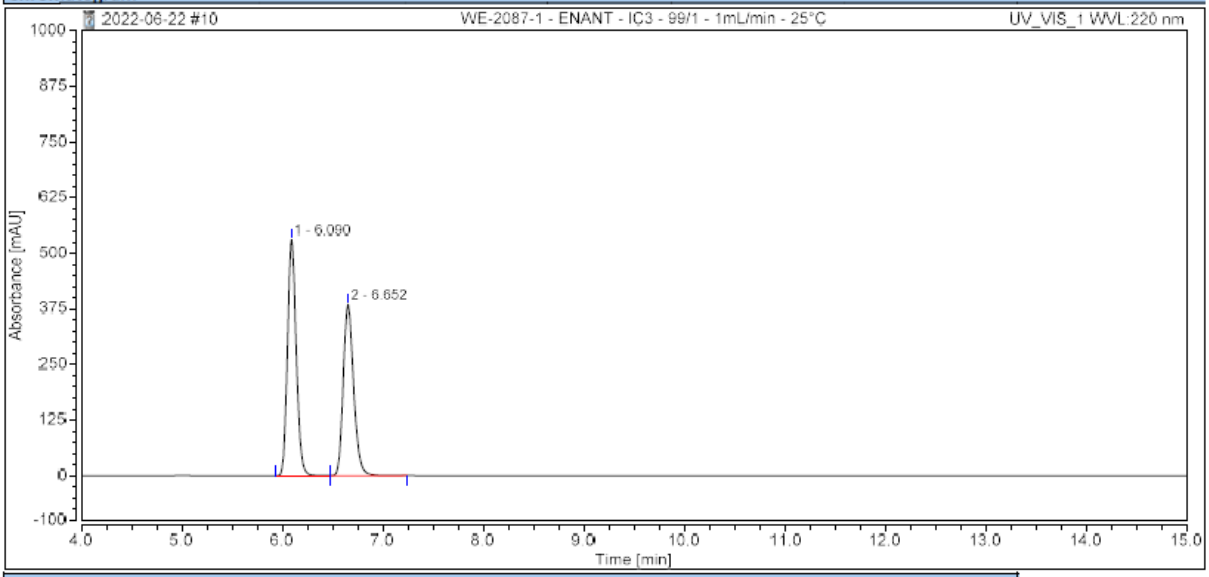
Injection Details

Injection Name:	WE-2087-1 - ENANT - IC3 - 99/1 - 1mL/min - 25°C	*Run Time:*	15.00 min
Instrument Method:	Enantio Fc Will	*Injection Volume:*	3.00 µL
Injection Date/Time:	22/juin/22 21:29	*Channel:*	UV_VIS_1
		Wavelength:	220 nm

Instrument Method Details

Instrument Method:	Enantio Fc Will				
%A	iPrOH 10	1 %			
%B	Hexane 90	99 %	*Température du four:*	25.0 °C	
	Débit:	1.000 mL/min	*Pression:*	71 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		6.090	0.093	3.28	1.16	23903
2		6.652	0.109	n.a.	1.22	20487

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		6.090	53.508	530.844	53.63	57.94
2		6.652	46.269	385.306	46.37	42.06
Total:			**99.776**	**916.150**	**100.00**	**100.00**

Deprotonation of ferrocenesulfonyl fluoride (2) with (*S*)-PEALi using chlorotrimethylsilane as in situ trap – Table 2, entry 8

Chromatogram and Results

General informations

Sequence Name:	2022-06-26
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA3 DAICEL

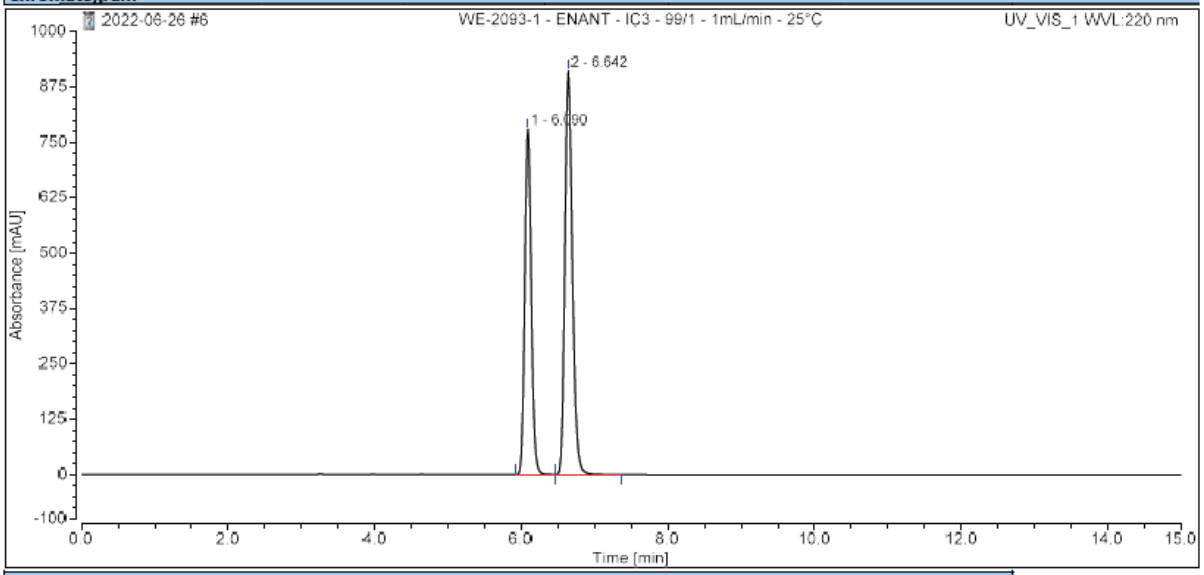
Injection Details

Injection Name:	WE-2093-1 - ENANT - IC3 - 99/1 - 1mL/min - 25°C	*Run Time:*	15.00 min
Instrument Method:	Enantio Fc Will	*Injection Volume:*	2.00 µL
Injection Date/Time:	26/juin/22 12:23	*Channel:*	UV_VIS_1
		Wavelength:	220 nm

Instrument Method Details

Instrument Method:	Enantio Fc Will				
%A	iPrOH 10	1 %			
%B	Hexane 90	99 %	*Température du four:*	25.0 °C	
	Débit:	1.000 mL/min	*Pression:*	71 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		6.090	0.095	3.20	1.12	22979
2		6.642	0.109	n.a.	1.21	20728

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		6.090	80.036	780.181	42.46	46.09
2		6.642	108.470	912.442	57.54	53.91
Total:			**188.505**	**1692.623**	**100.00**	**100.00**

Deprotonation of ferrocenesulfonyl fluoride (2) with (*R*)-PEALi using chlorotrimethylsilane as in situ trap – Table 2, entry 9

Chromatogram and Results

General informations

Sequence Name:	2022-06-26
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA3 DAICEL

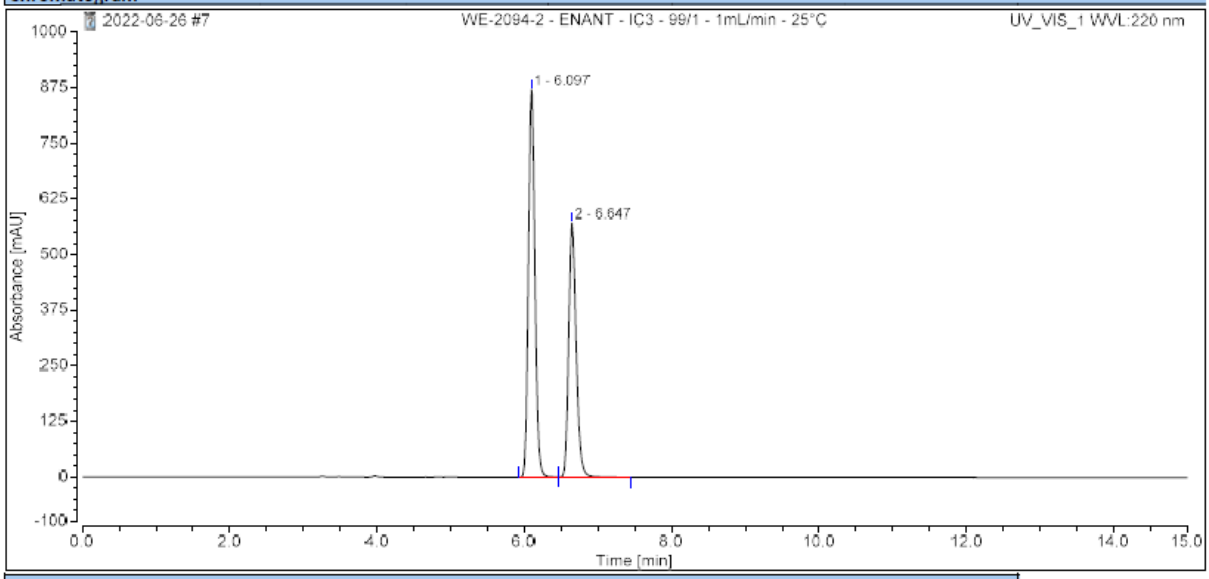
Injection Details

Injection Name:	WE-2094-2 - ENANT - IC3 - 99/1 - 1mL/min - 25°C	*Run Time:*	15.00 min
Instrument Method:	Enantio Fc Will	*Injection Volume:*	3.00 µL
Injection Date/Time:	26/juin/22 12:38	*Channel:*	UV_VIS_1
		Wavelength:	220 nm

Instrument Method Details

Instrument Method:	Enantio Fc Will				
%A	iPrOH 10	1 %			
%B	Hexane 90	99 %	*Température du four:*	25.0 °C	
	Débit:	1.000 mL/min	*Pression:*	70 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		6.097	0.094	3.22	1.13	23235
2		6.647	0.107	n.a.	1.23	21193

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		6.097	88.968	871.435	56.87	60.40
2		6.647	67.487	571.268	43.13	39.60
Total:			**156.455**	**1442.703**	**100.00**	**100.00**

(±)-2-Iodoferrocenesulfonyl fluoride (3f)

Chromatogram and Results

General informations

Sequence Name:	2022-06-26
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA3 DAICEL

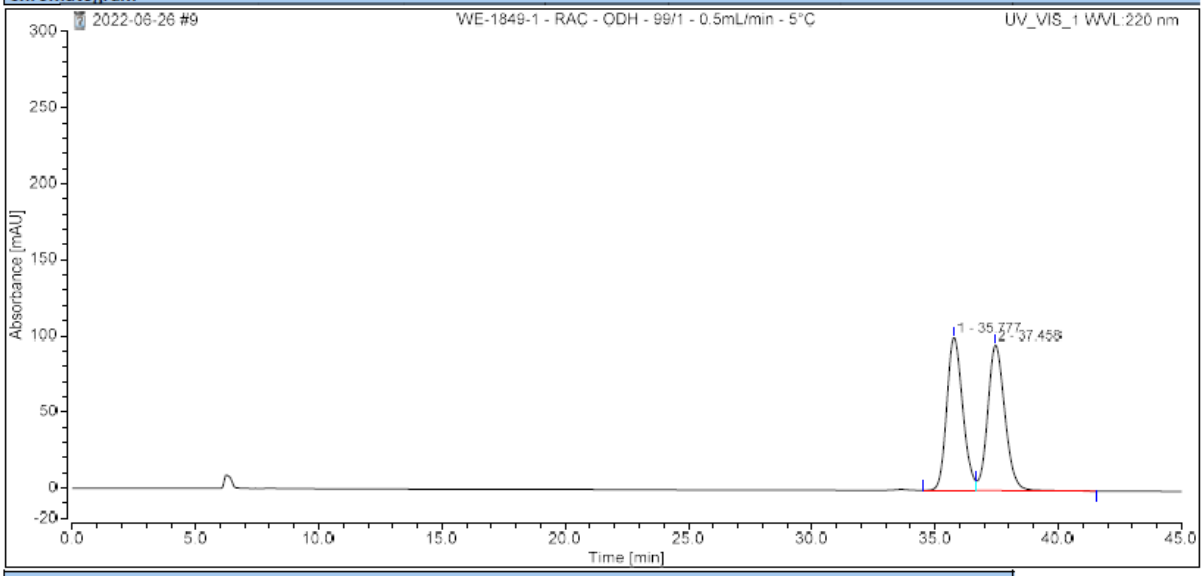
Injection Details

Injection Name:	WE-1849-1 - RAC - ODH - 99/1 - 0.5mL/min - 5°C	*Run Time:*	45.00 min
Instrument Method:	Enantio Fc Will	*Injection Volume:*	2.00 µL
Injection Date/Time:	26/juin/22 14:20	*Channel:*	UV_VIS_1
		Wavelength:	220 nm

Instrument Method Details

Instrument Method:	Enantio Fc Will				
%A	iPrOH 10	1 %			
%B	Hexane 90	99 %	*Température du four:*	5.0 °C	
	Débit:	0.500 mL/min	*Pression:*	22 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		35.777	0.700	1.38	n.a.	14486
2		37.458	0.741	n.a.	n.a.	14160

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		35.777	75.922	100.788	49.49	51.29
2		37.458	77.499	95.702	50.51	48.71
Total:			**153.421**	**196.490**	**100.00**	**100.00**

Deprotonation of ferrocenesulfonyl fluoride (2) with (*R*)-PEALi using [(*R*)-PEA]$_2$Zn as in situ trap – Table 2, entry 11

Chromatogram and Results

General informations

Sequence Name:	2022-06-26
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA3 DAICEL

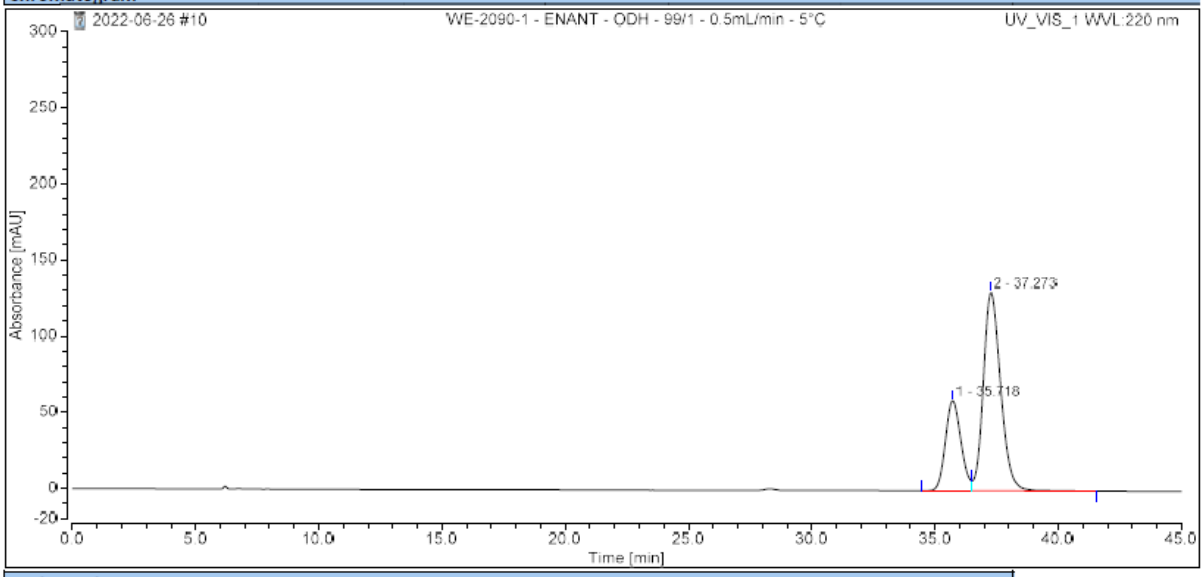
Injection Details

Injection Name:	WE-2090-1 - ENANT - ODH - 99/1 - 0.5mL/min - 5°C	*Run Time:*	45.00 min
Instrument Method:	Enantio Fc Will	*Injection Volume:*	2.00 µL
Injection Date/Time:	26/juin/22 15:06	*Channel:*	UV_VIS_1
		Wavelength:	220 nm

Instrument Method Details

Instrument Method:	Enantio Fc Will				
%A	iPrOH 10	1 %			
%B	Hexane 90	99 %	*Température du four:*	5.0 °C	
	Débit:	0.500 mL/min	*Pression:*	22 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		35.718	0.687	1.28	n.a.	14959
2		37.273	0.747	n.a.	n.a.	13783

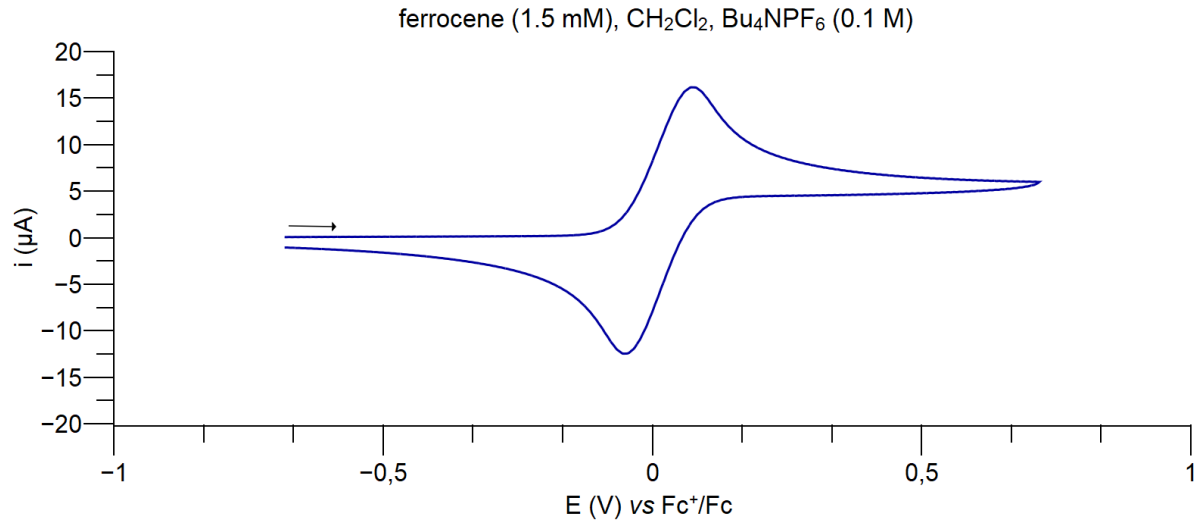
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		35.718	43.571	59.376	28.98	31.29
2		37.273	106.768	130.381	71.02	68.71
Total:			**150.339**	**189.757**	**100.00**	**100.00**

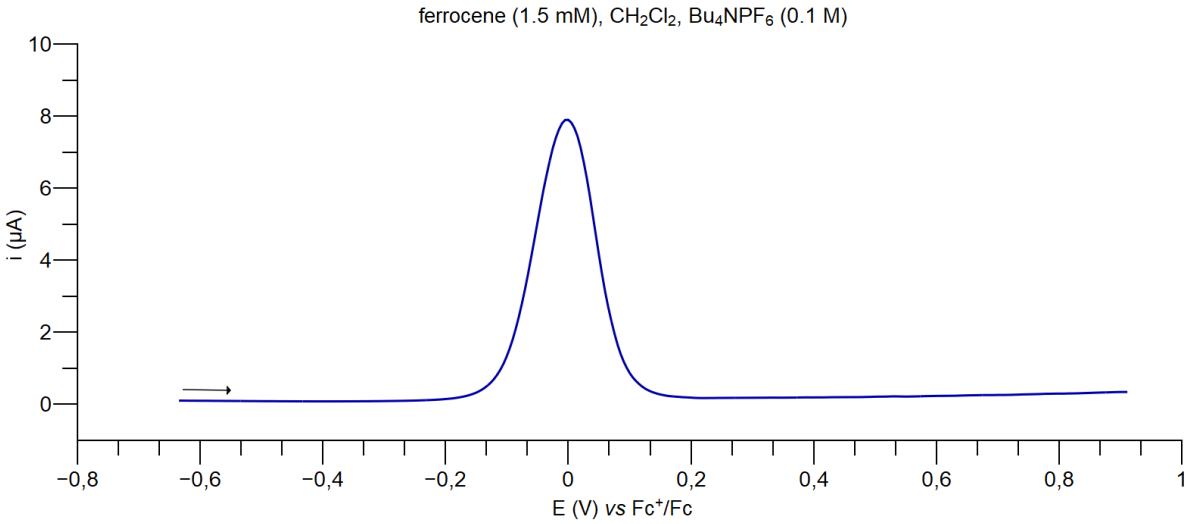
Voltammograms

Ferrocene

Cyclic voltammetry

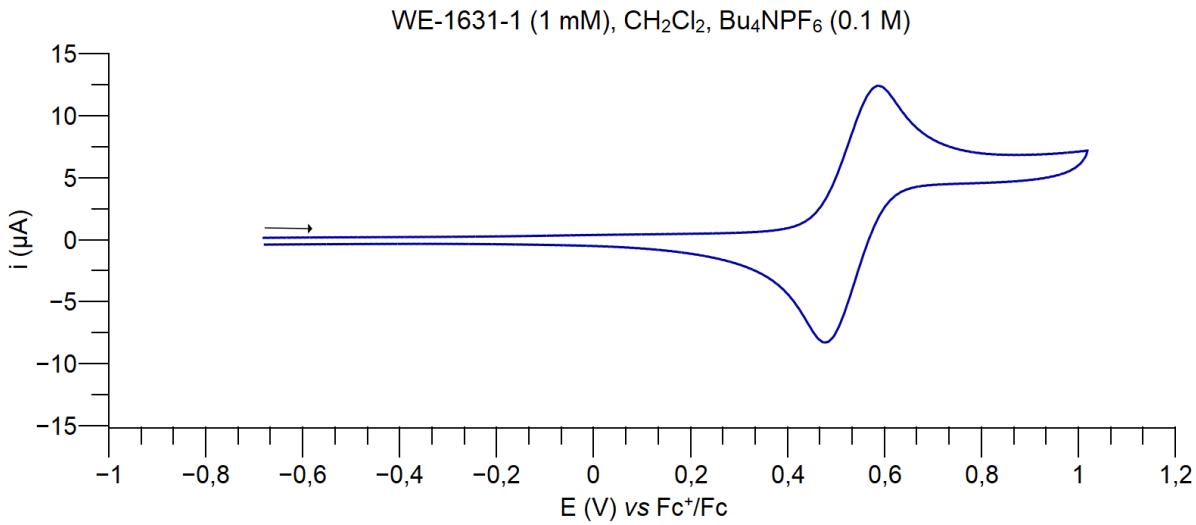


Differential pulse voltammetry

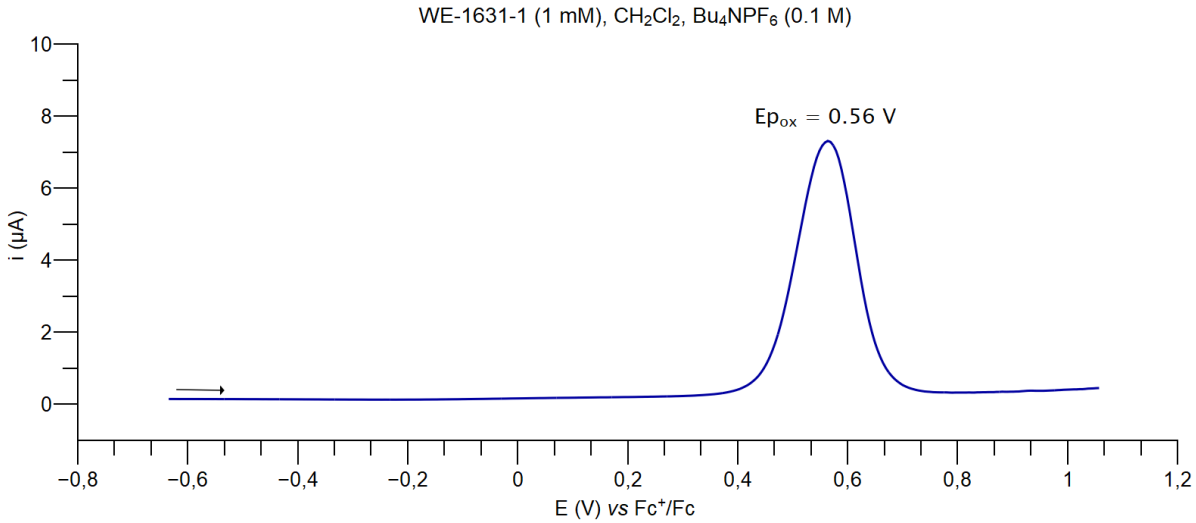


Ferrocenesulfonyl fluoride (2)

Cyclic voltammetry

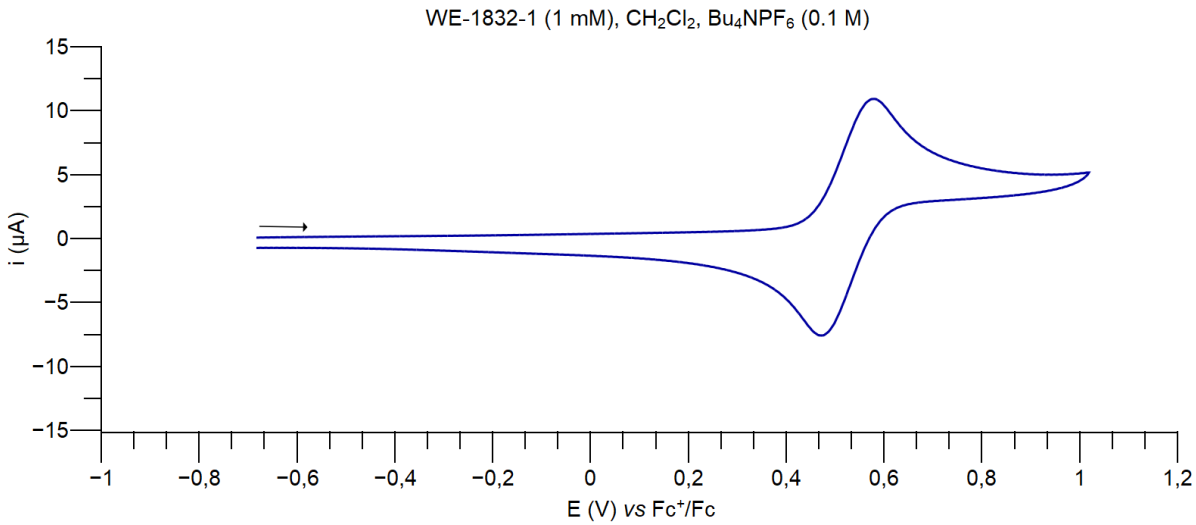


Differential pulse voltammetry

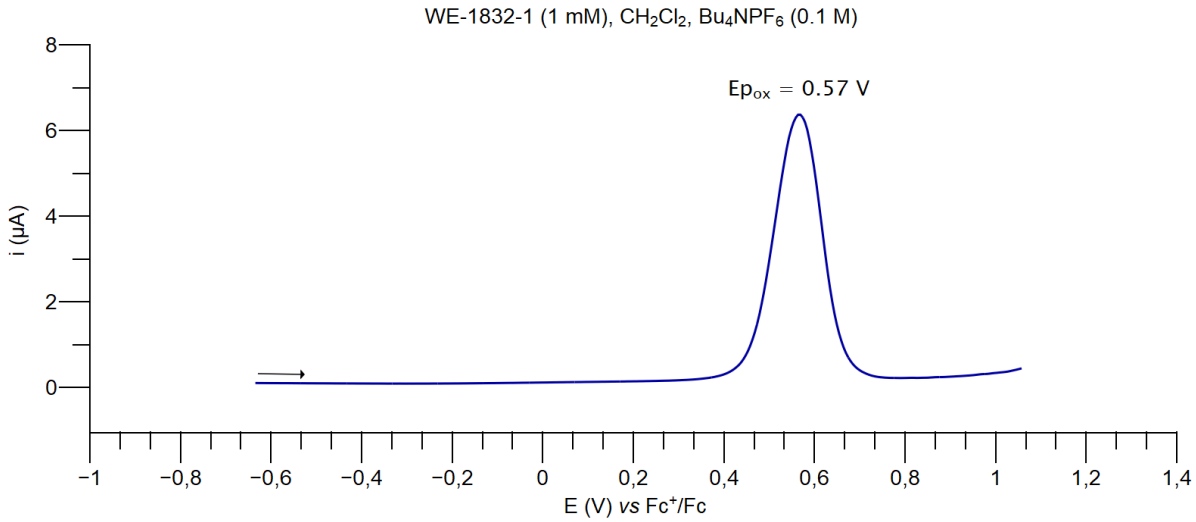


2-(Phenylthio)ferrocenesulfonyl fluoride (3b)

Cyclic voltammetry

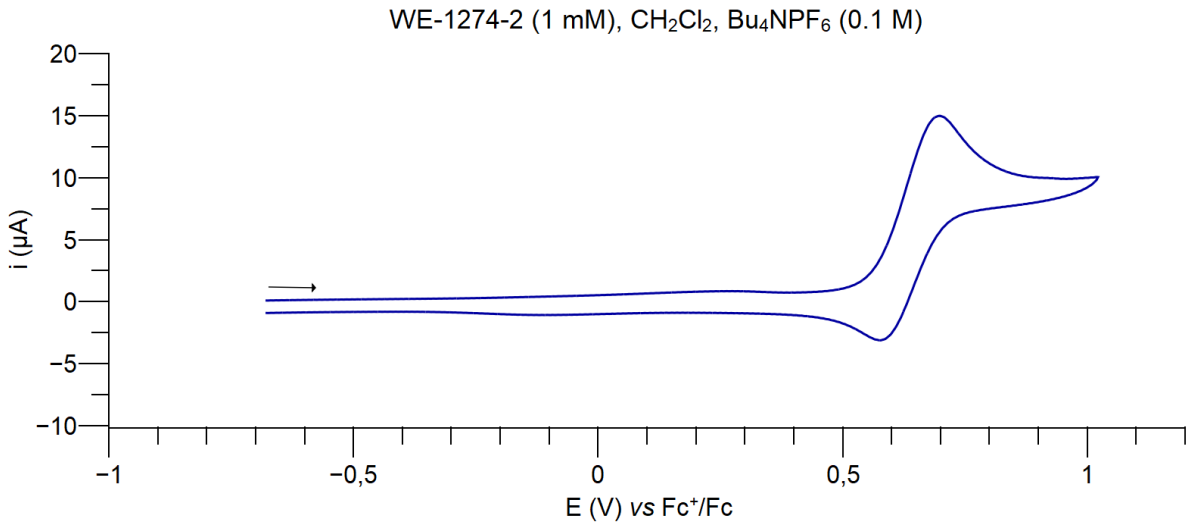


Differential pulse voltammetry

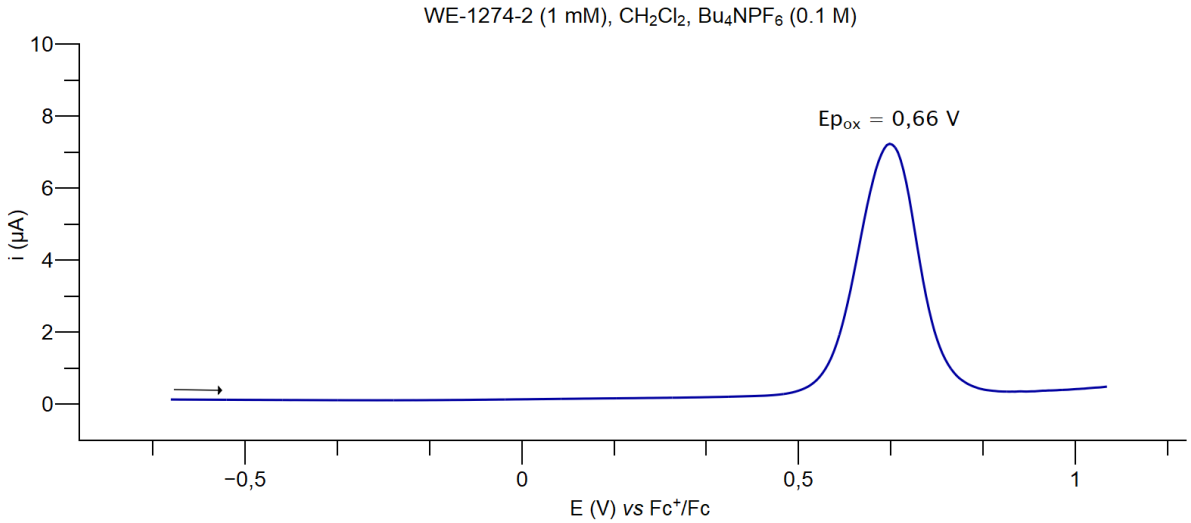


2-Fluoroferrocenesulfonyl fluoride (3e)

Cyclic voltammetry

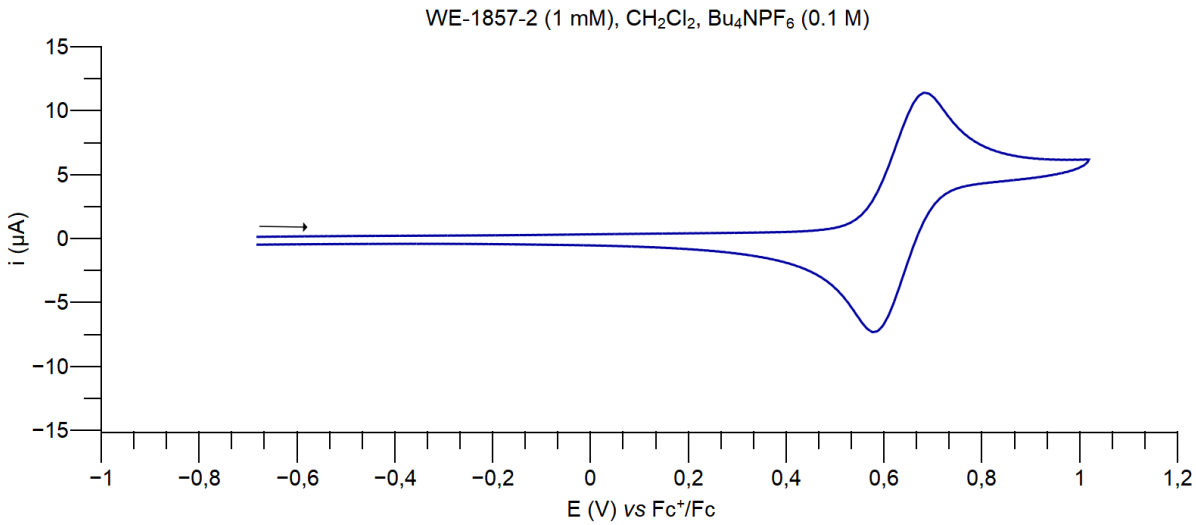


Differential pulse voltammetry

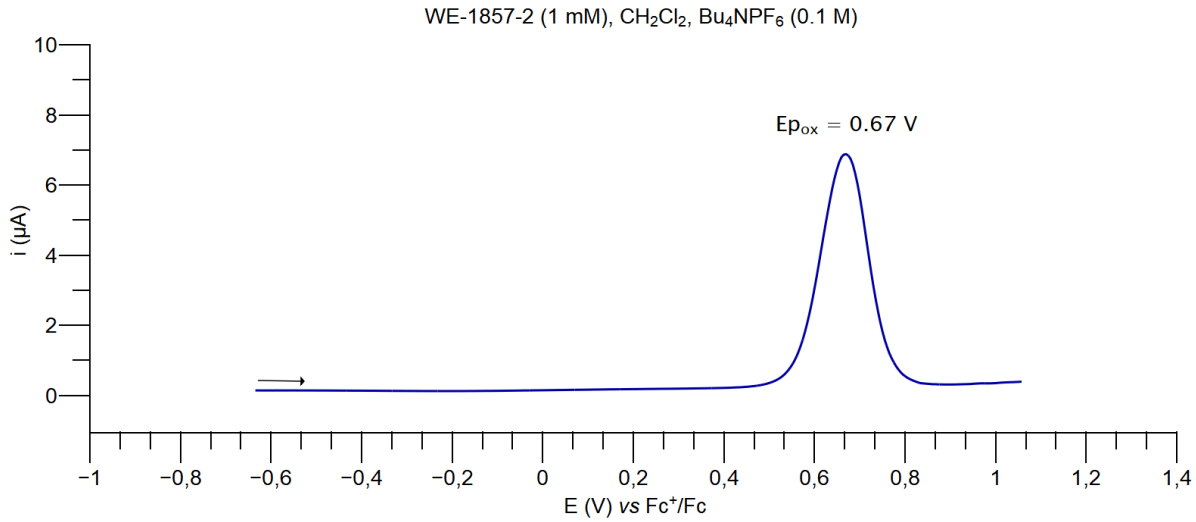


2-Iodoferrocenesulfonyl fluoride (3f)

Cyclic voltammetry

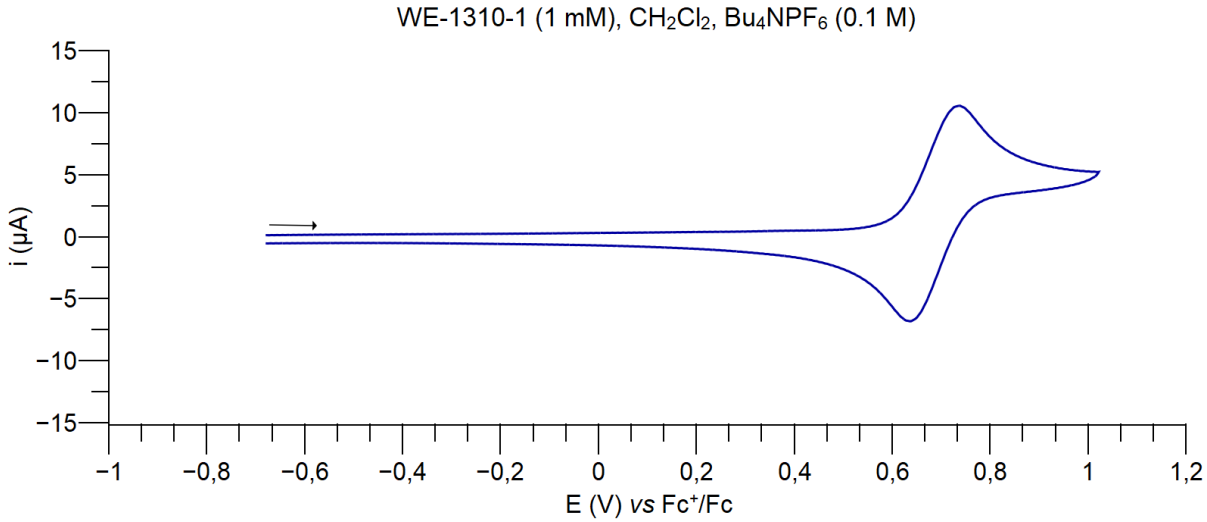


Differential pulse voltammetry

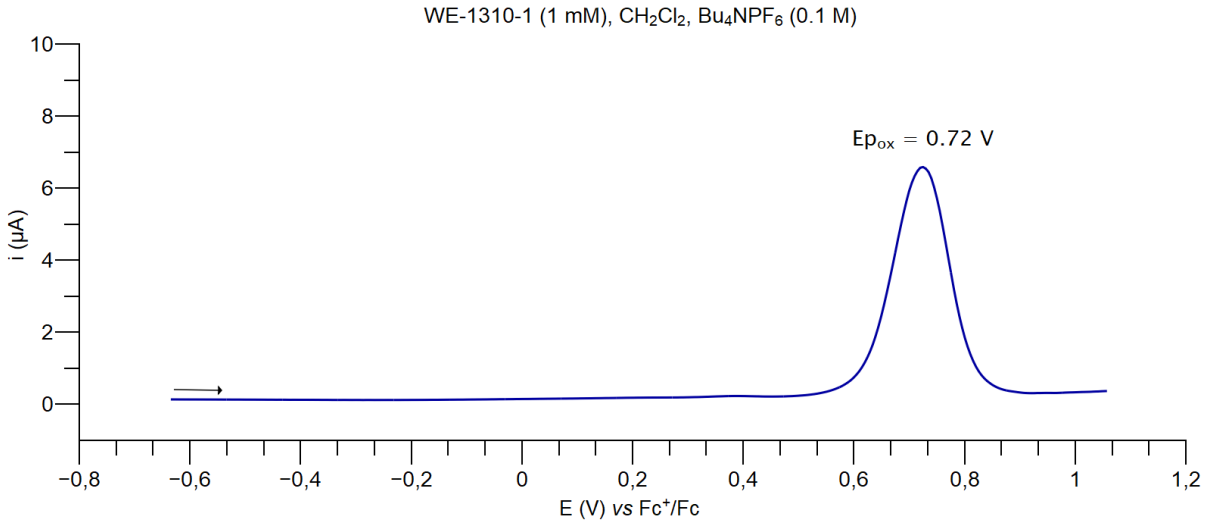


2-(Methoxycarbonyl)ferrocenesulfonyl fluoride (3g)

Cyclic voltammetry

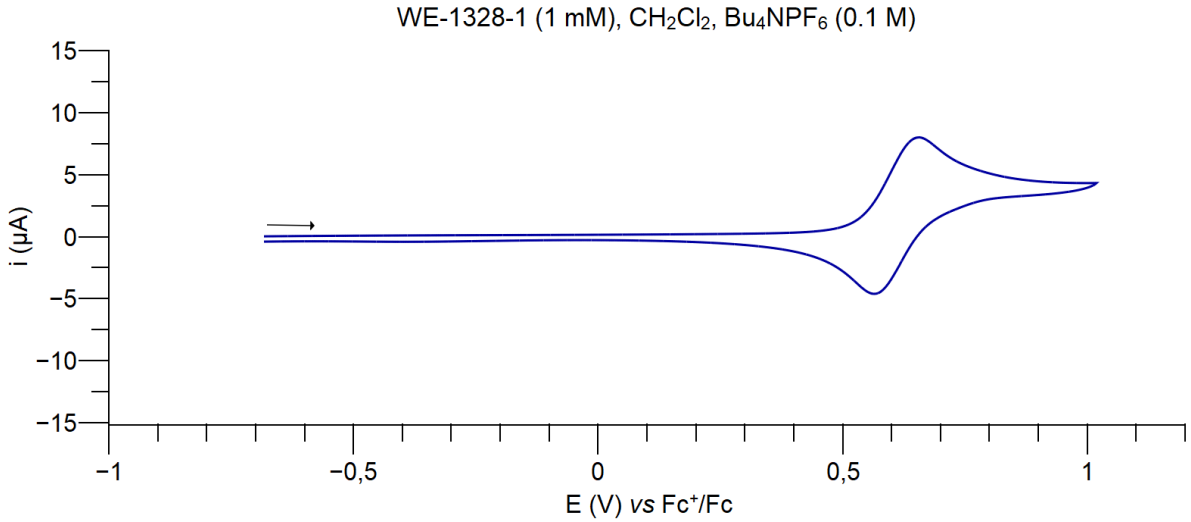


Differential pulse voltammetry

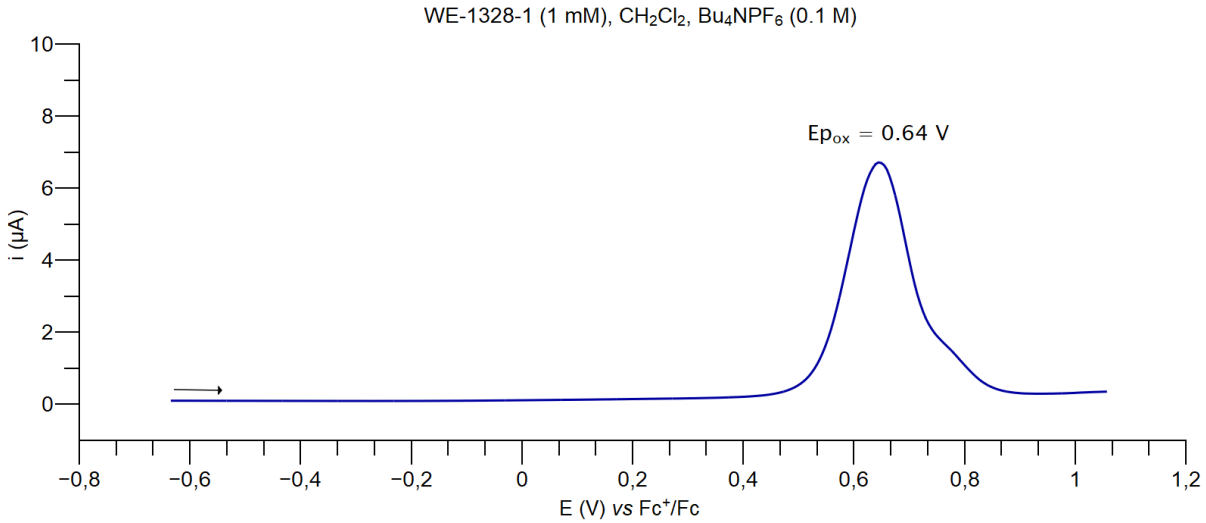


2-(2-Pyridyl)ferrocenesulfonyl fluoride (3k)

Cyclic voltammetry

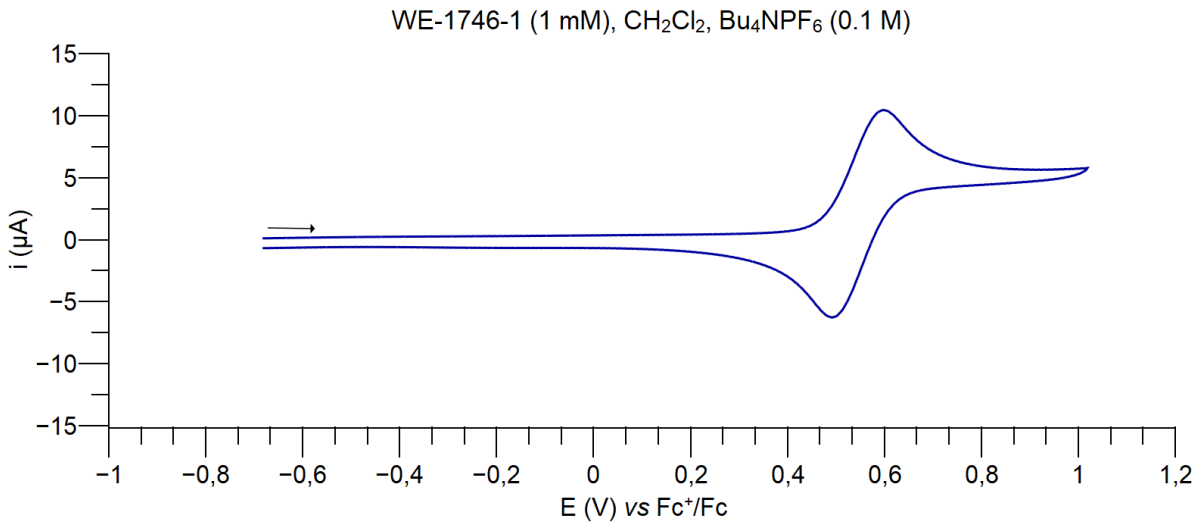


Differential pulse voltammetry

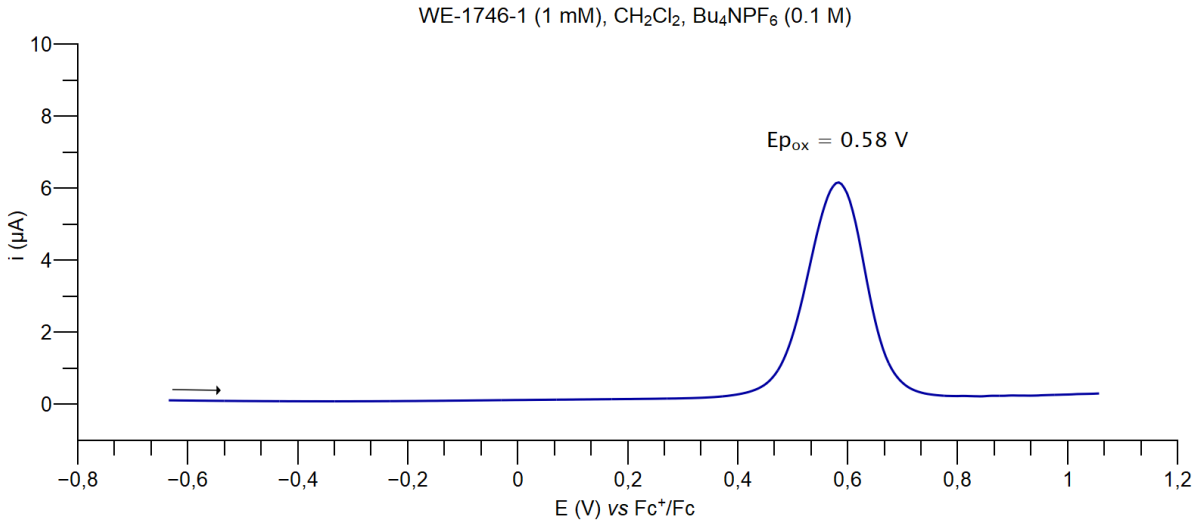


2-Fluoro-5-(trimethylsilyl)ferrocenesulfonyl fluoride (5c)

Cyclic voltammetry

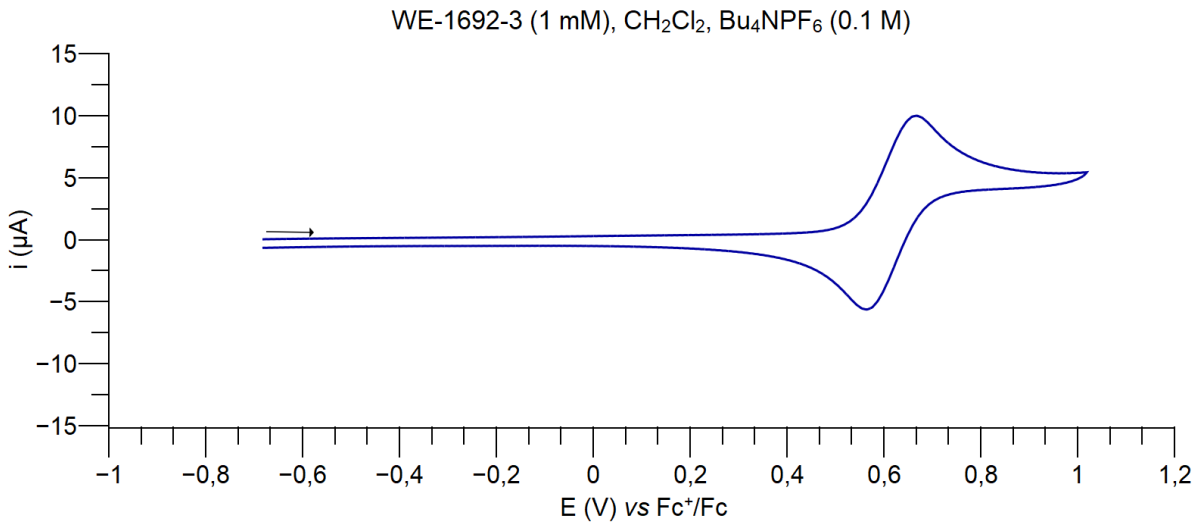


Differential pulse voltammetry

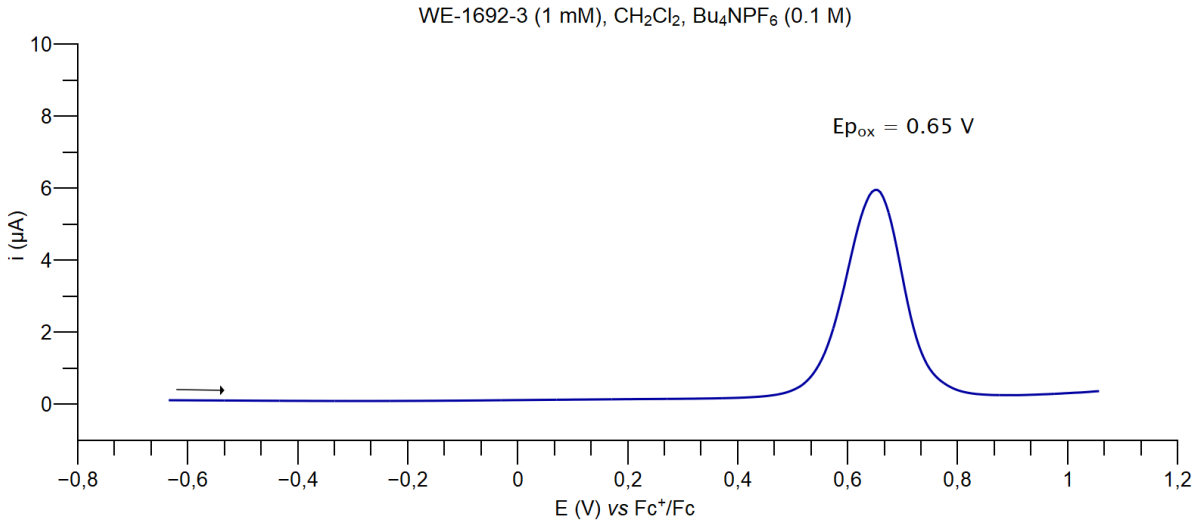


2-Iodo-5-(phenylthio)ferrocenesulfonyl fluoride (5f)

Cyclic voltammetry

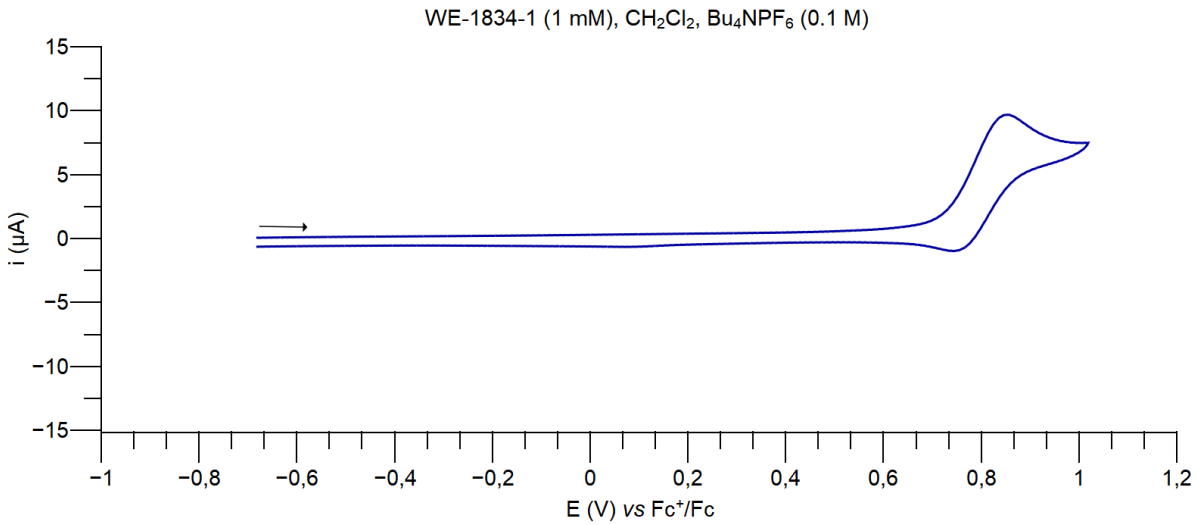


Differential pulse voltammetry

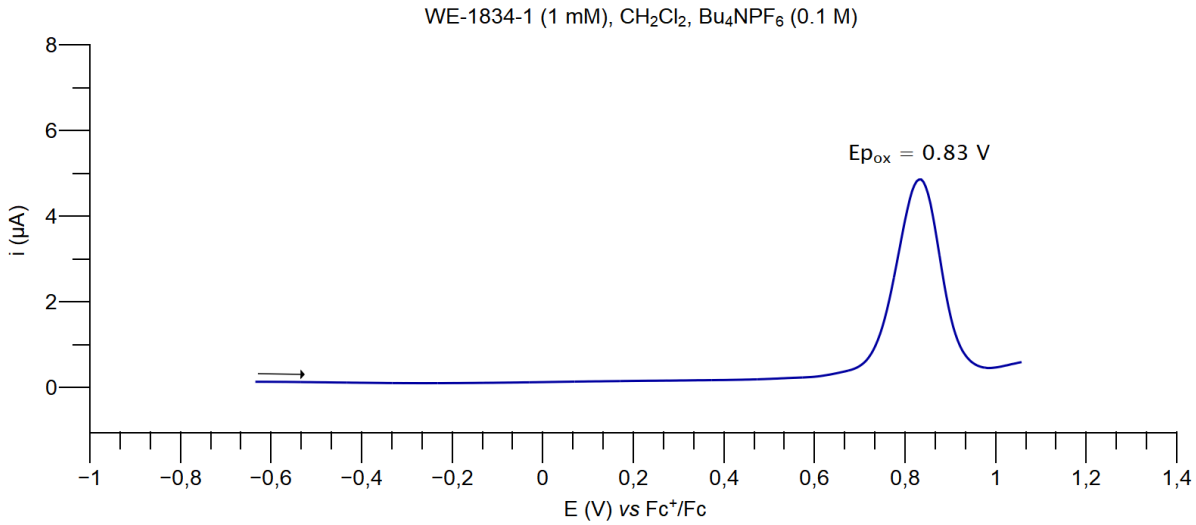


2-Chloro-5-(phenylthio)ferrocenesulfonyl fluoride (5g)

Cyclic voltammetry

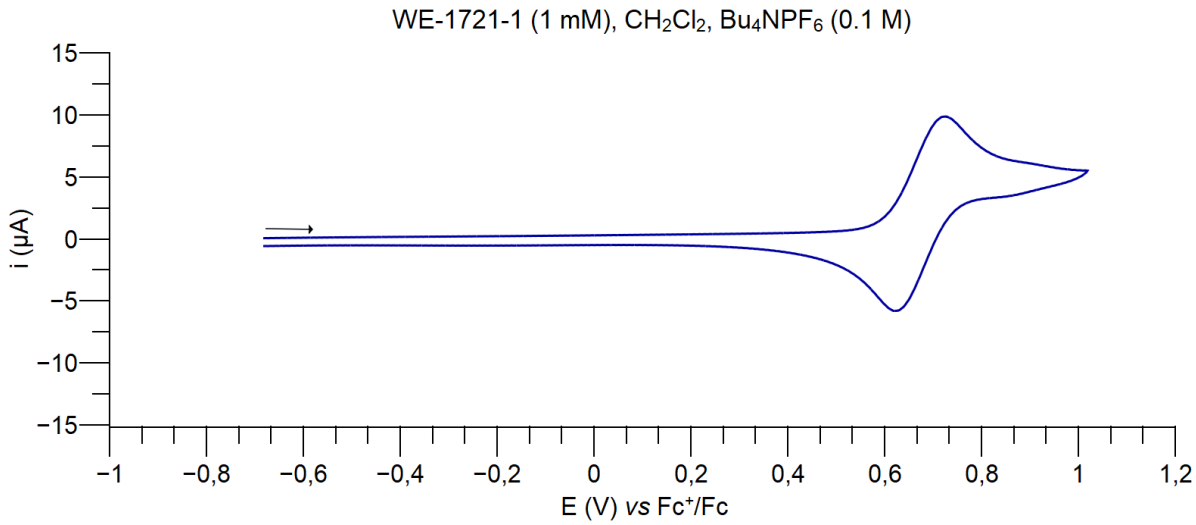


Differential pulse voltammetry

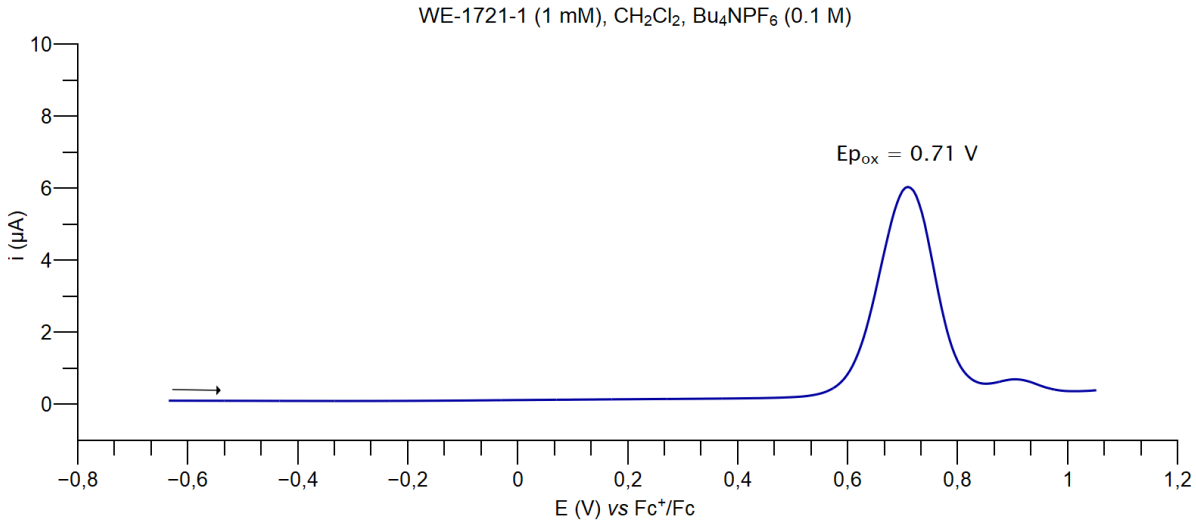


4-Iodo-2-(phenylthio)ferrocenesulfonyl fluoride (6e)

Cyclic voltammetry

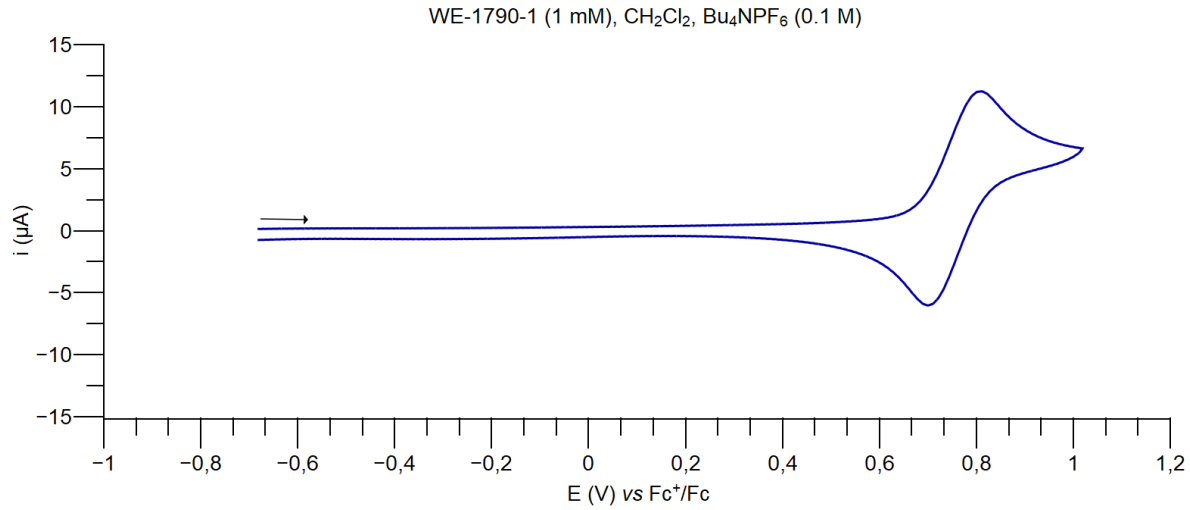


Differential pulse voltammetry

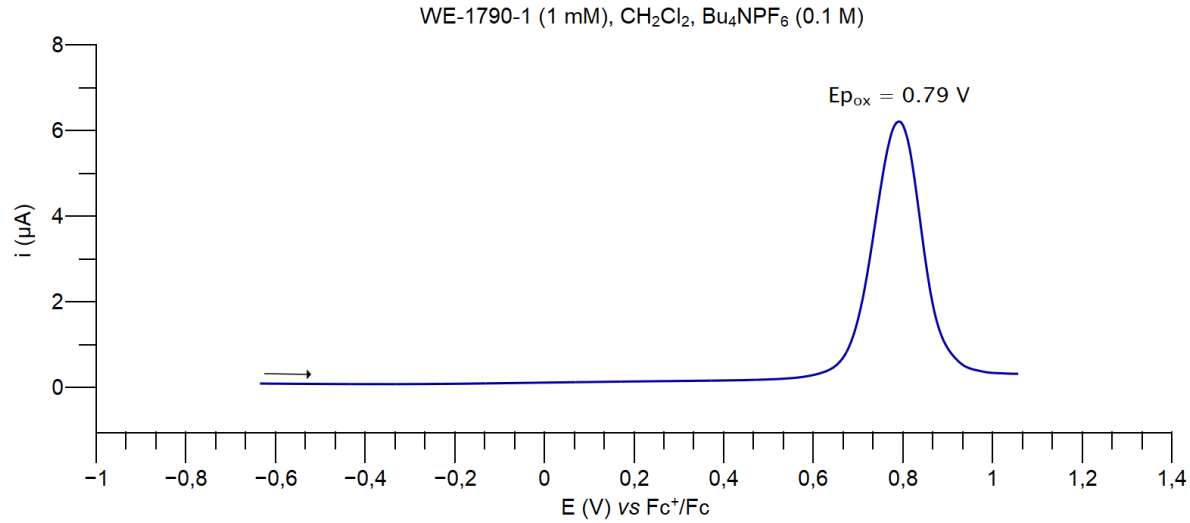


3-Chloro-2-fluoro-5-(trimethylsilyl)ferrocenesulfonyl fluoride (8a)

Cyclic voltammetry

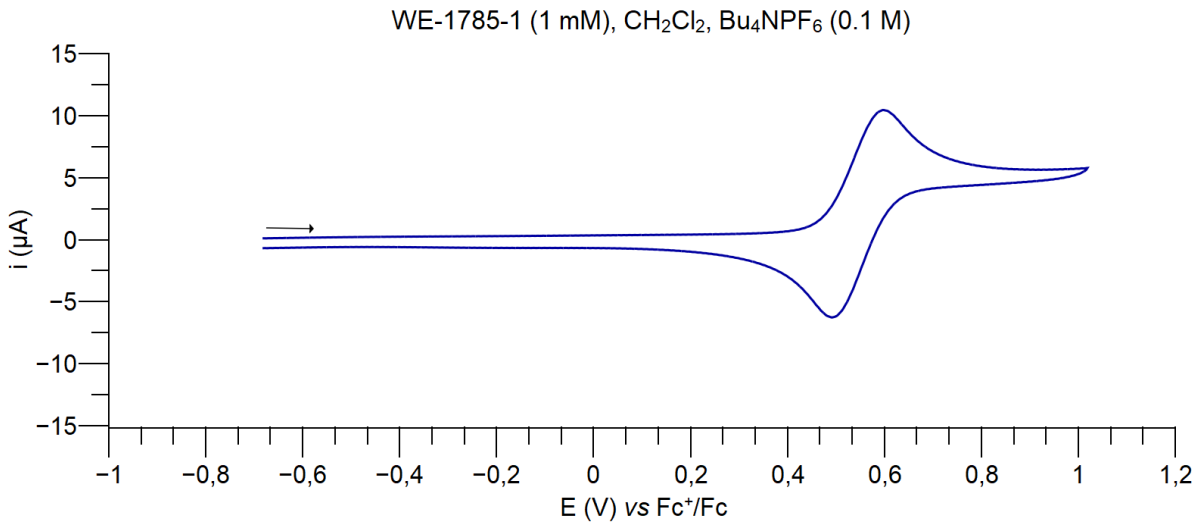


Differential pulse voltammetry

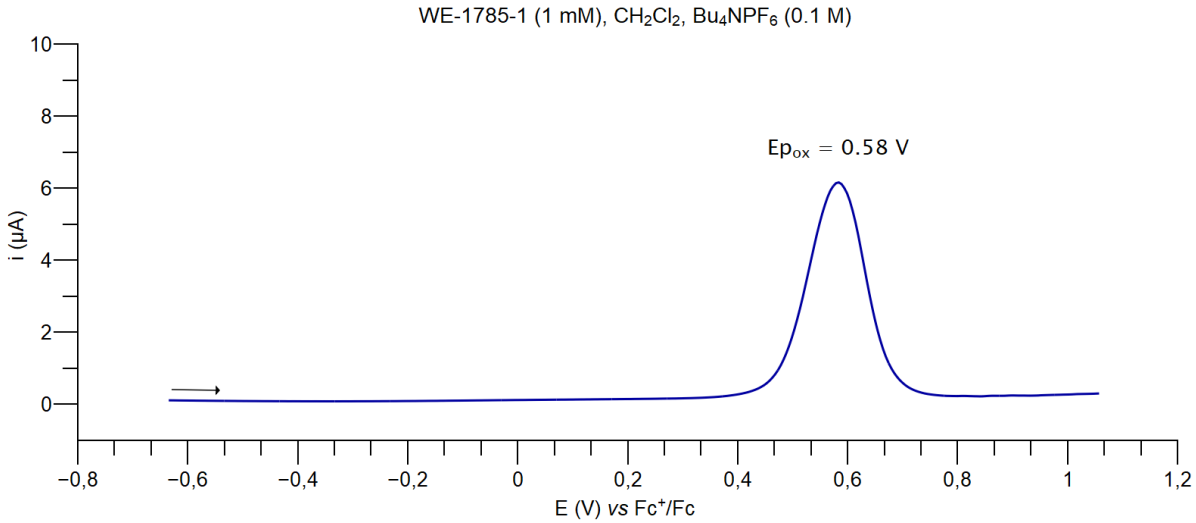


2-Fluoro-3-methyl-5-(trimethylsilyl)ferrocenesulfonyl fluoride (10)

Cyclic voltammetry

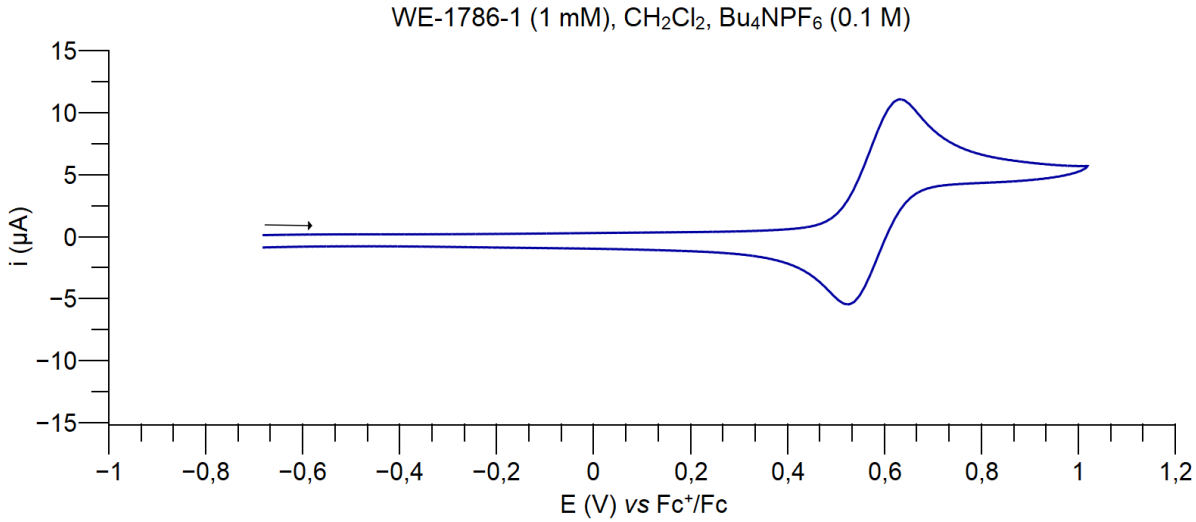


Differential pulse voltammetry

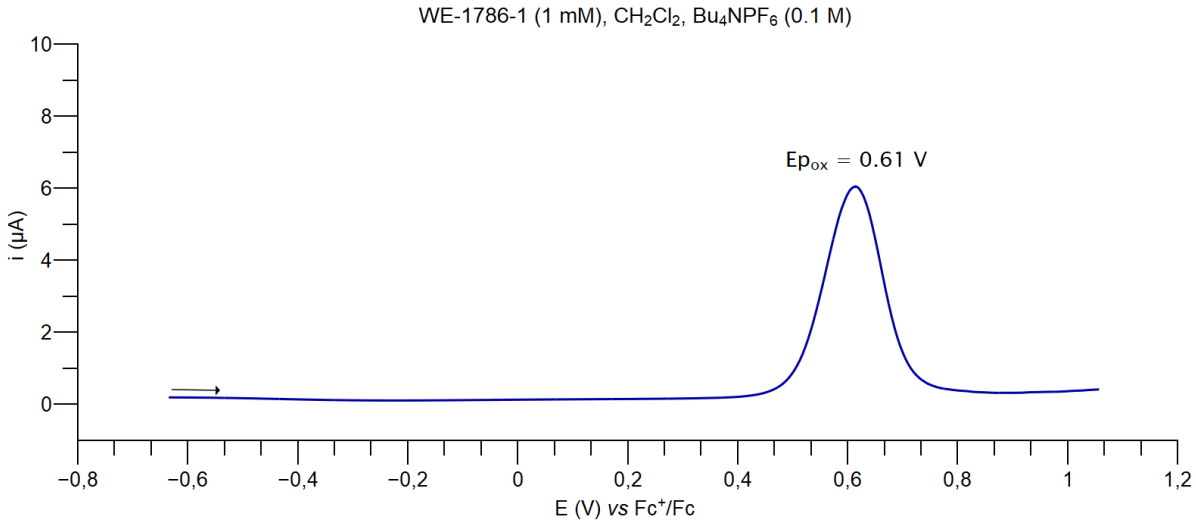


2-Fluoro-3-methylferrocenesulfonyl fluoride (11)

Cyclic voltammetry

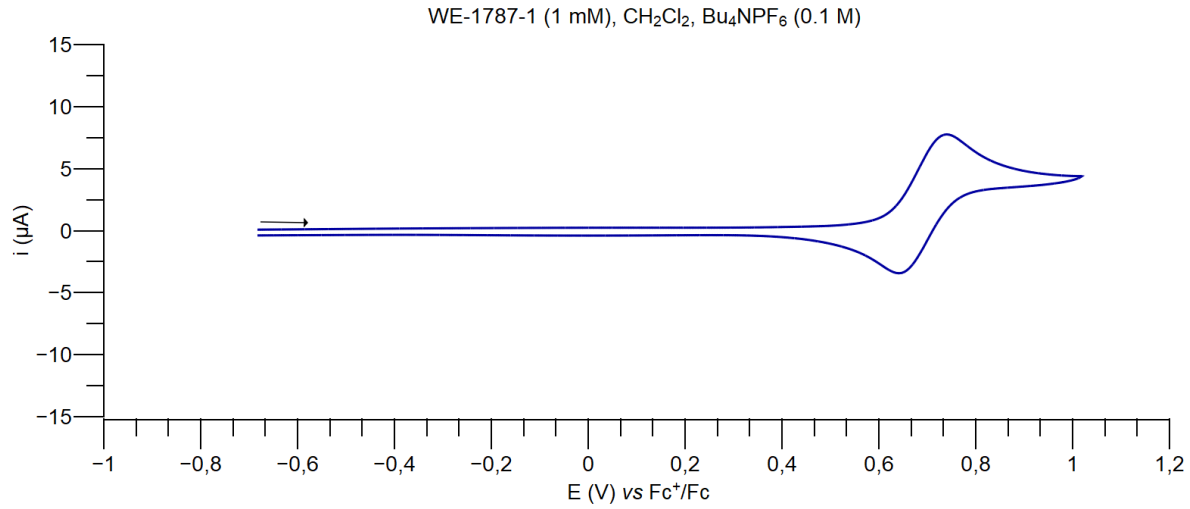


Differential pulse voltammetry

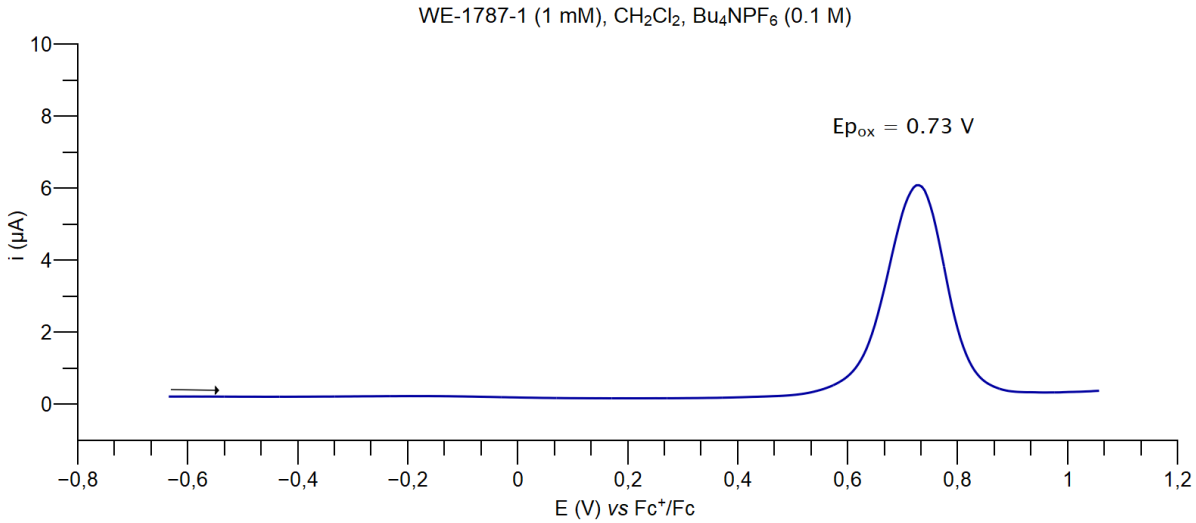


2-Fluoro-5-iodo-3-methylferrocenesulfonyl fluoride (12)

Cyclic voltammetry

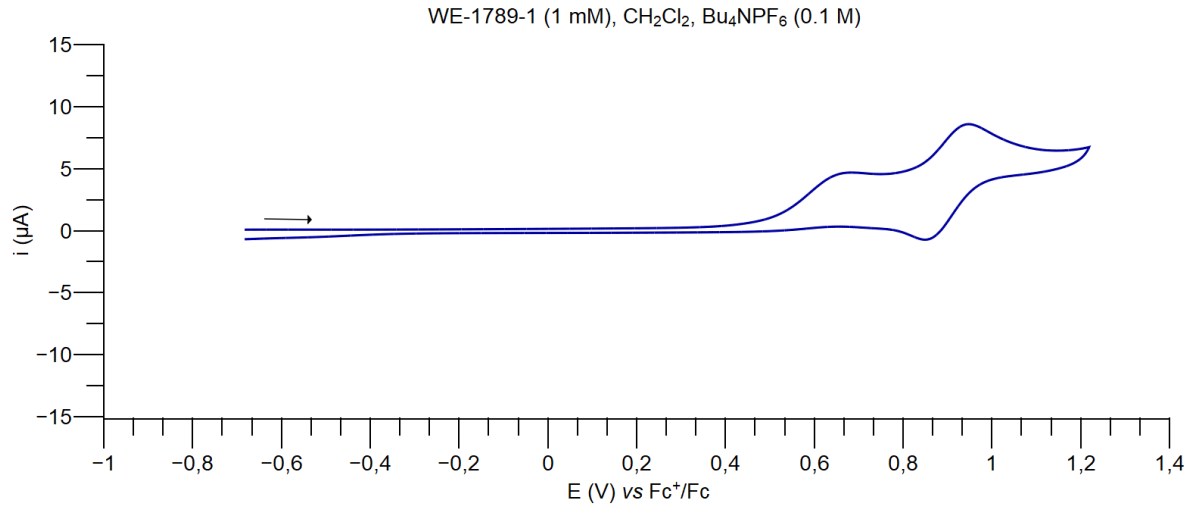


Differential pulse voltammetry

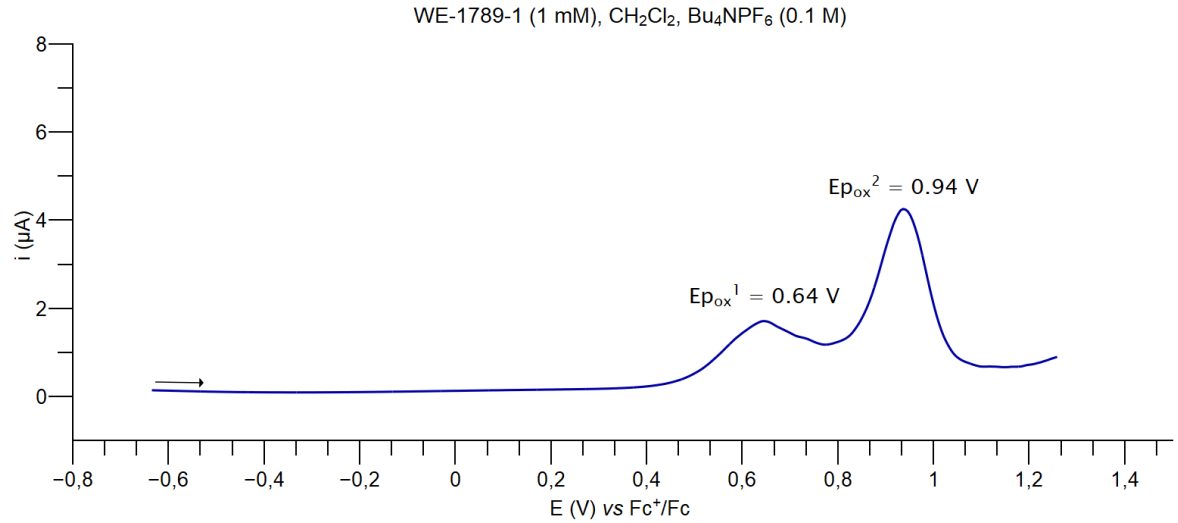


2-(*N*,*N*-Dimethylaminomethyl)-5-fluoro-3-iodo-4-methylferrocenesulfonyl fluoride (13)

Cyclic voltammetry

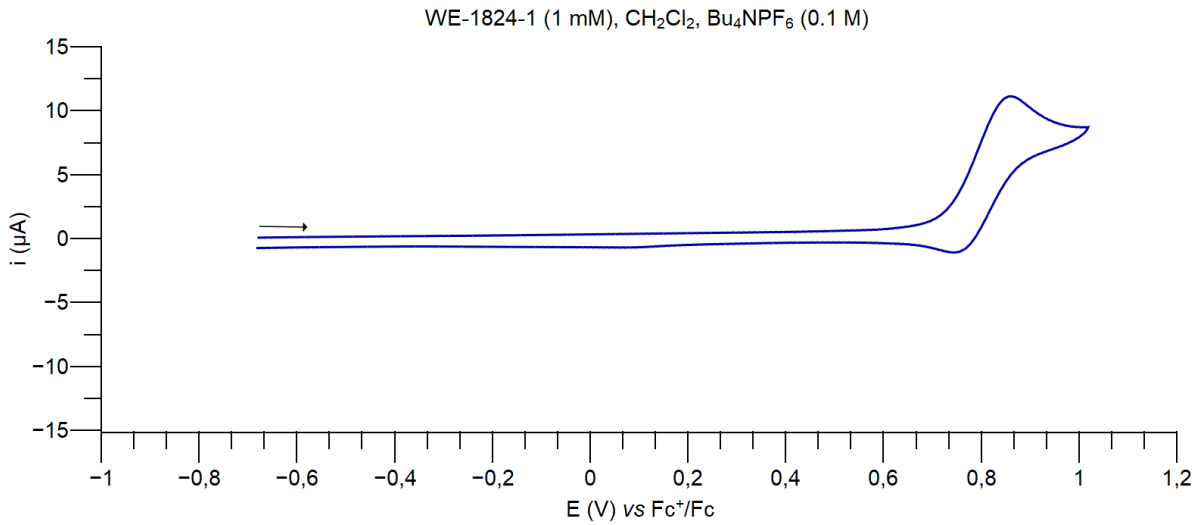


Differential pulse voltammetry

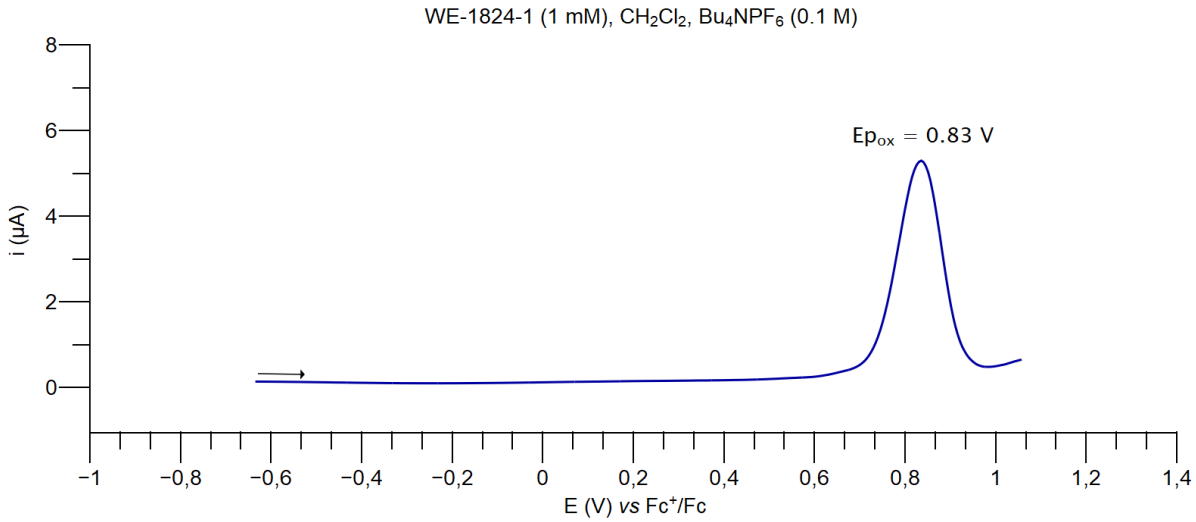


2-Chloro-3-methoxycarbonyl-5-(phenylthio)ferrocenesulfonyl fluoride (15)

Cyclic voltammetry

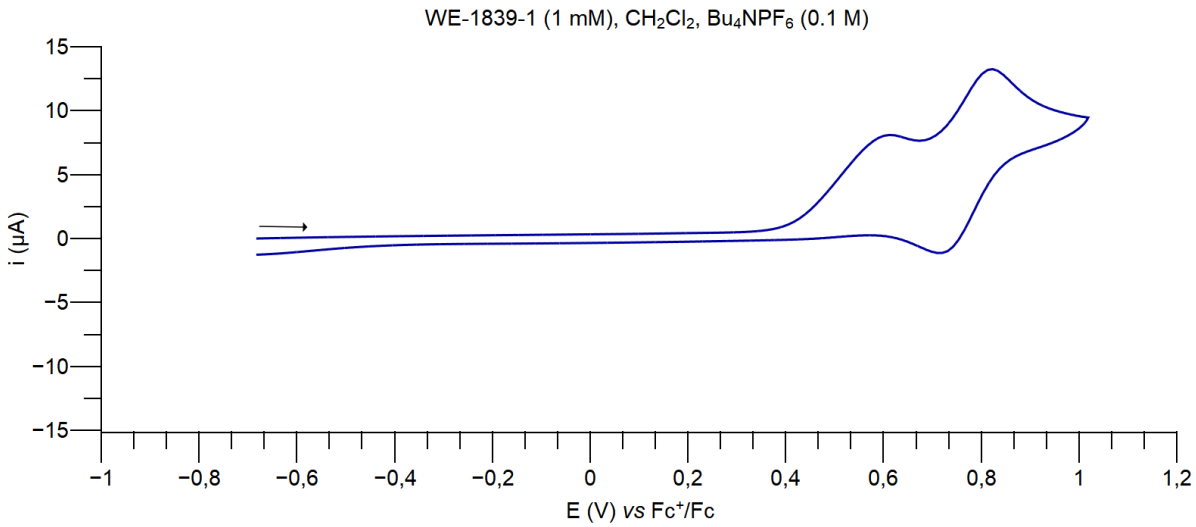


Differential pulse voltammetry

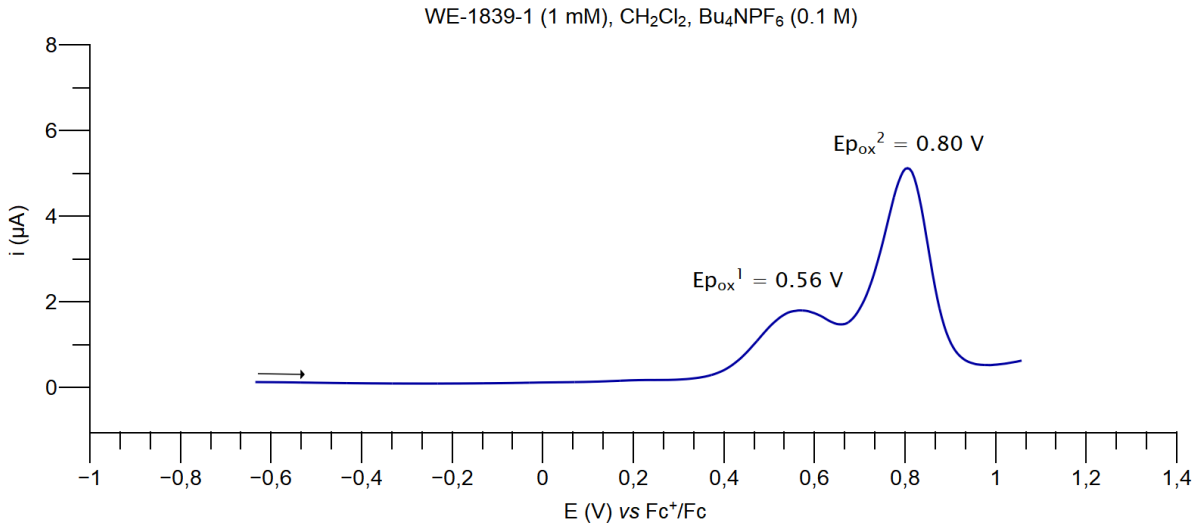


2-Chloro-3-(*N*,*N*-dimethylaminomethyl)-5-(phenylthio)ferrocenesulfonyl fluoride (17)

Cyclic voltammetry

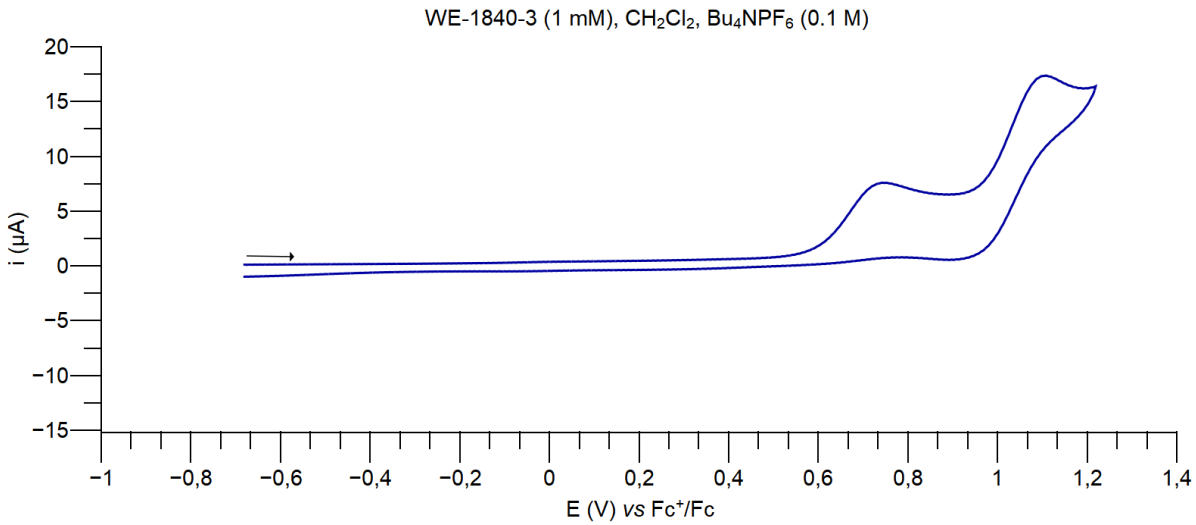


Differential pulse voltammetry

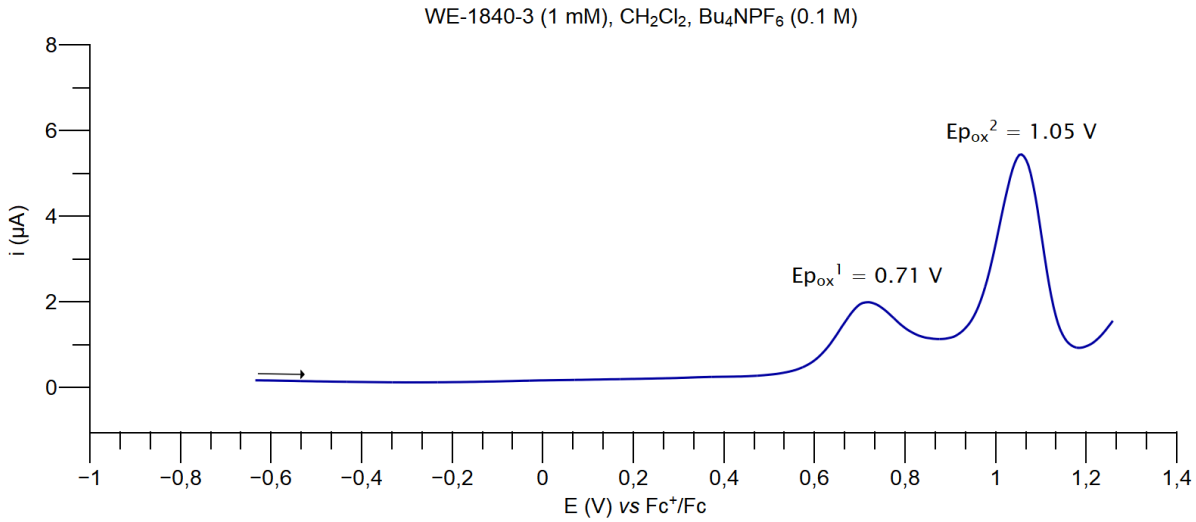


2-Chloro-3-(*N*,*N*-dimethylaminomethyl)-4-iodo-5-(phenylthio)ferrocenesulfonyl fluoride (18)

Cyclic voltammetry

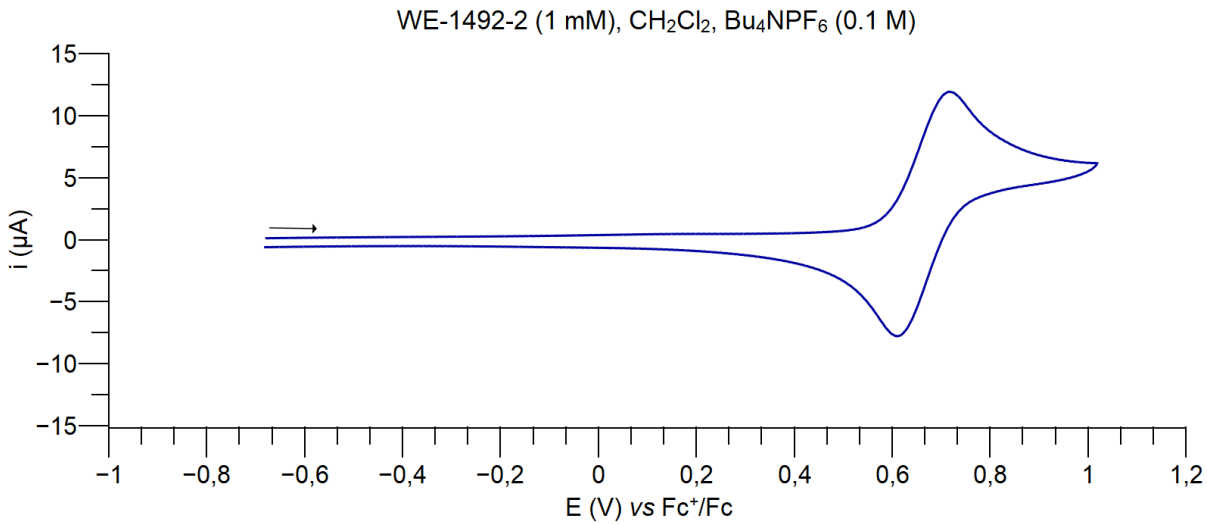


Differential pulse voltammetry

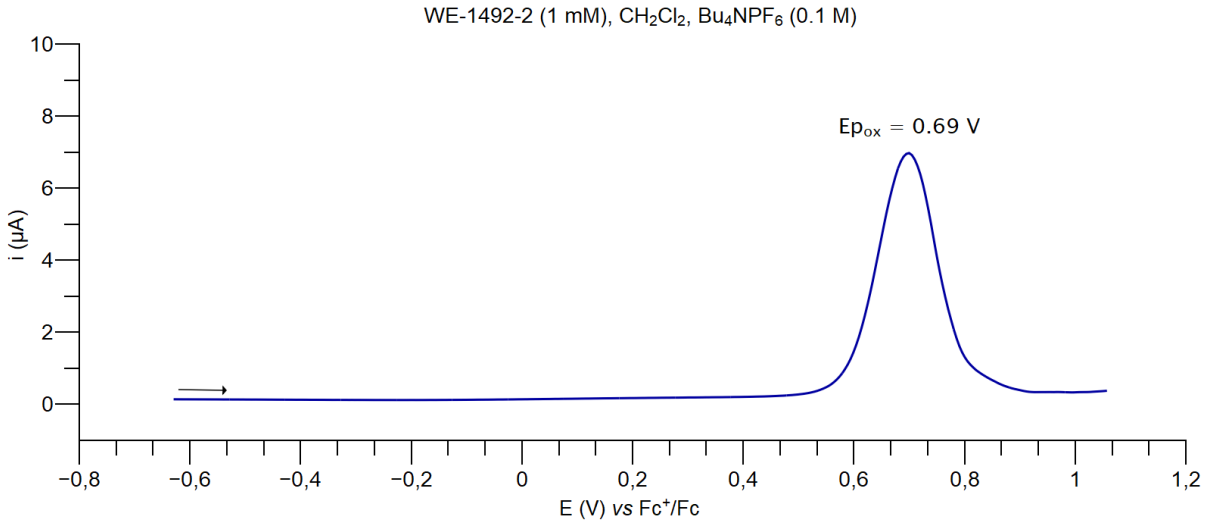


3-Iodoferrocenesulfonyl fluoride (19a)

Cyclic voltammetry

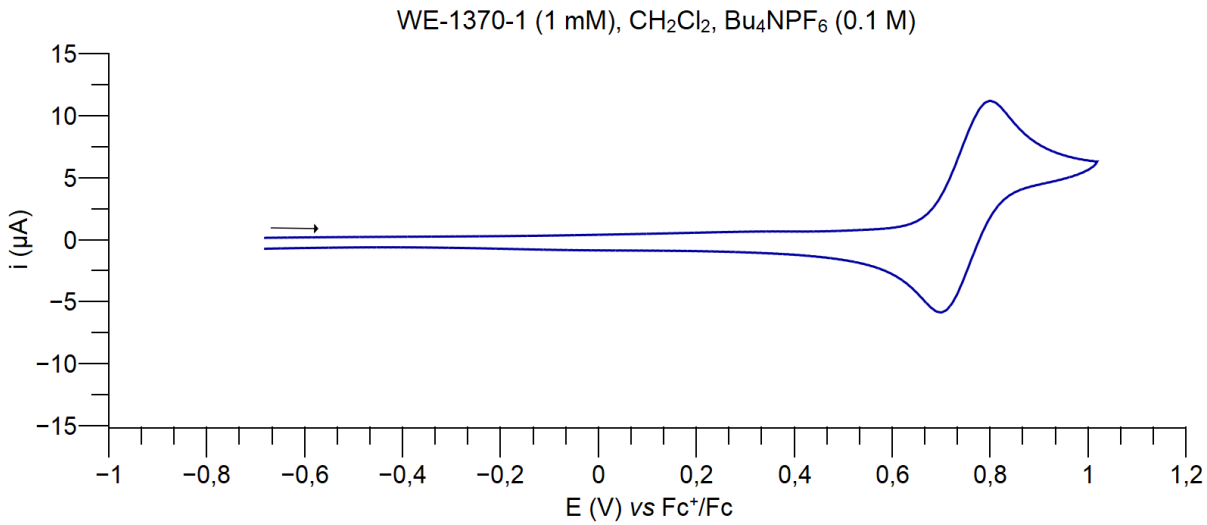


Differential pulse voltammetry

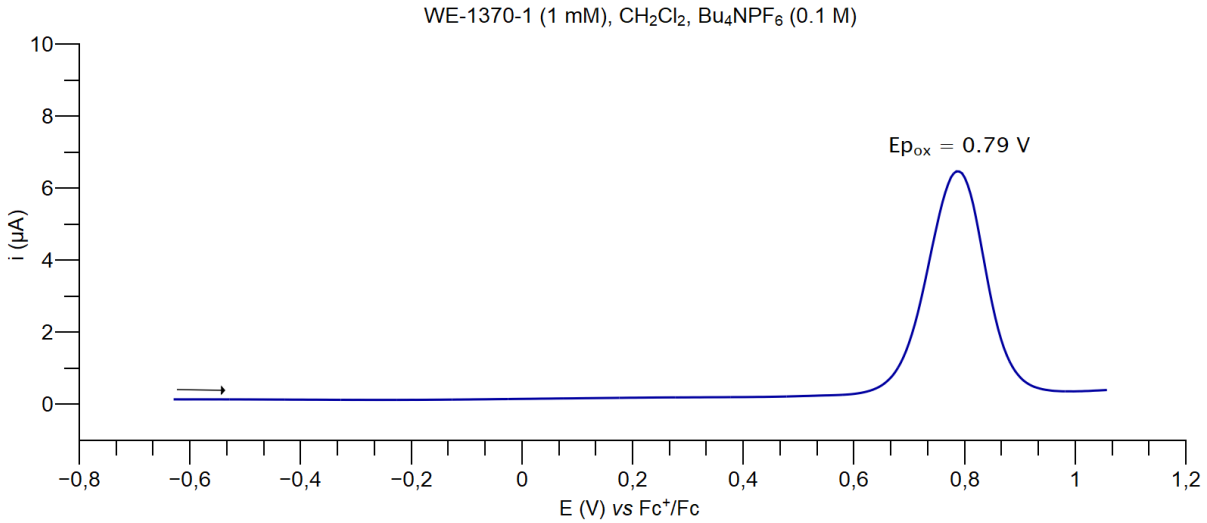


3-(Methoxycarbonyl)ferrocenesulfonyl fluoride (20d)

Cyclic voltammetry

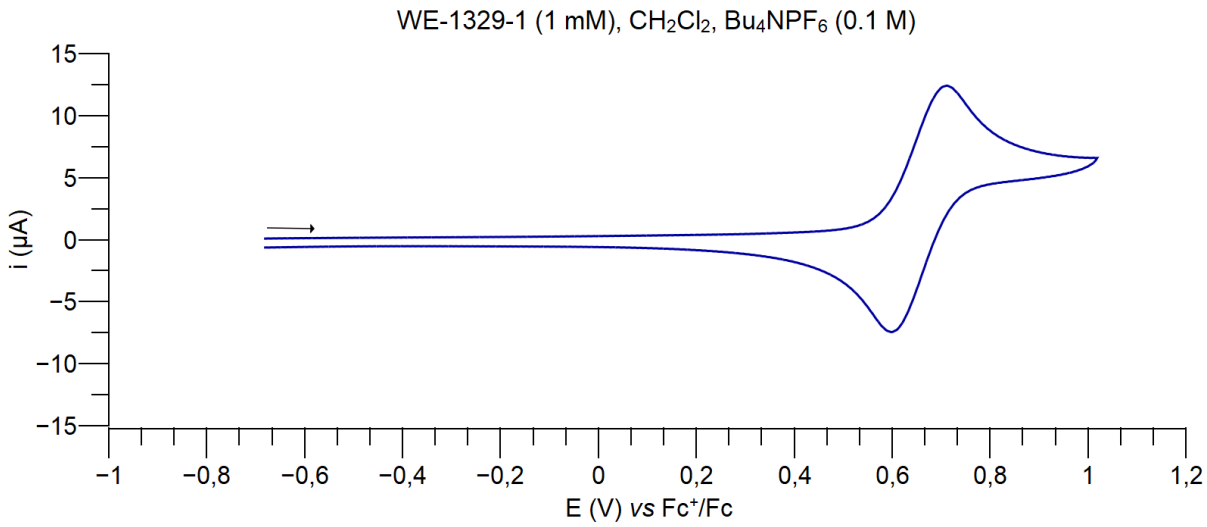


Differential pulse voltammetry

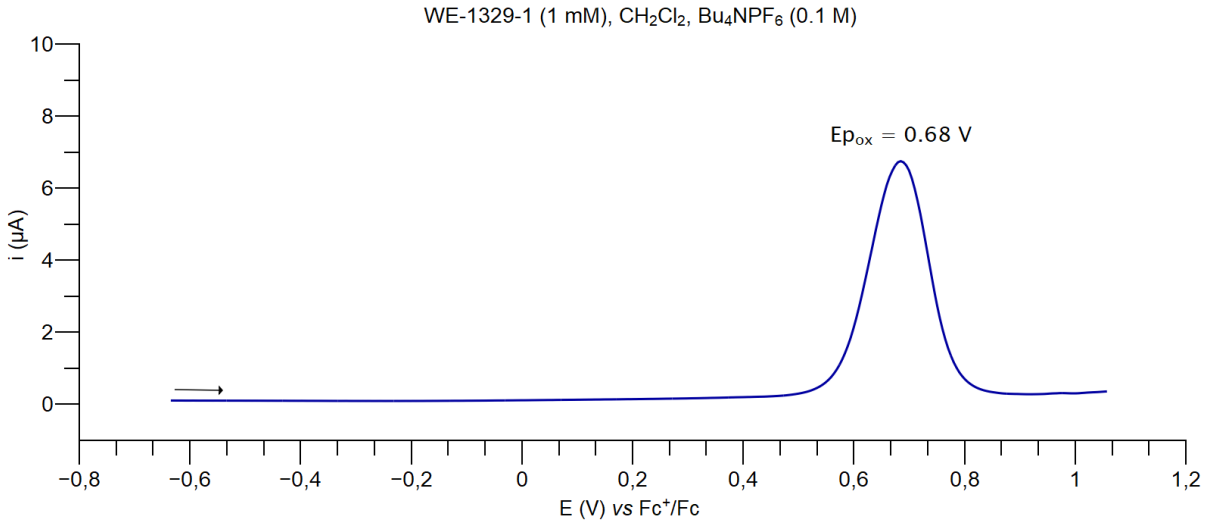


2-Ethynylferrocenesulfonyl fluoride (33a)

Cyclic voltammetry

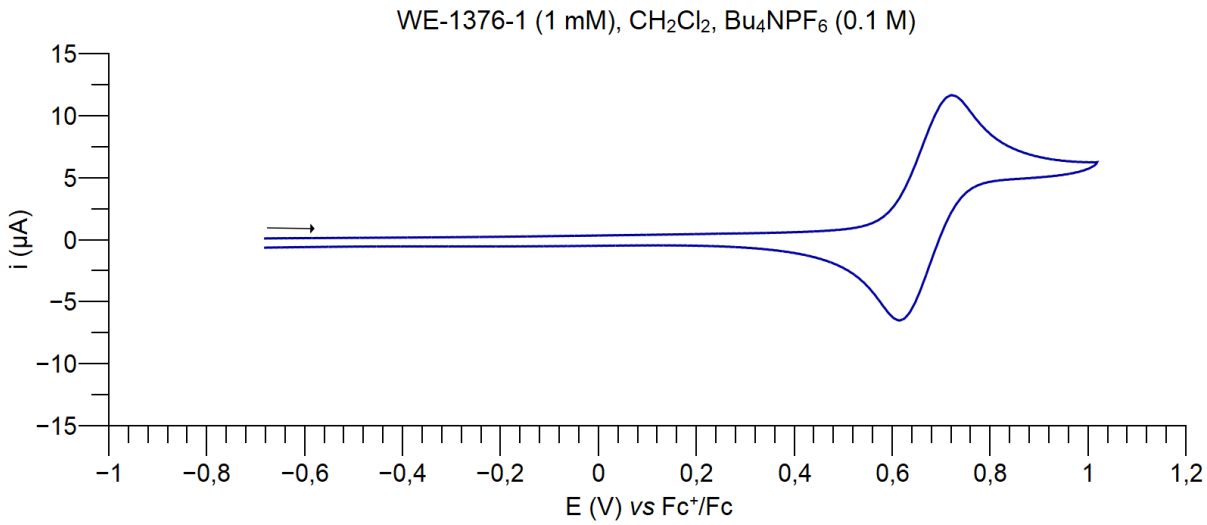


Differential pulse voltammetry

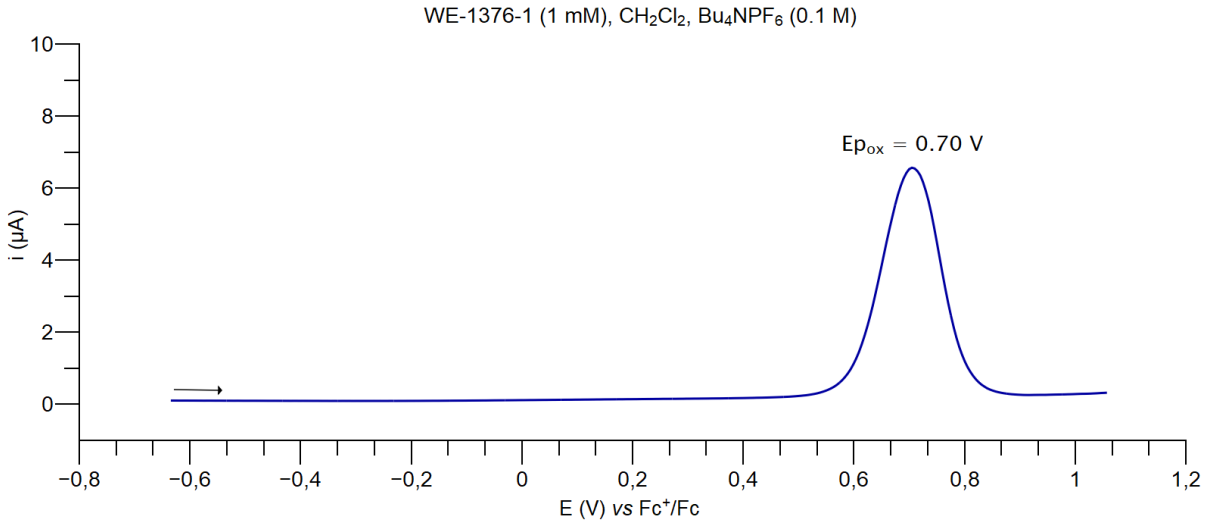


3-Ethynylferrocenesulfonyl fluoride (33b)

Cyclic voltammetry

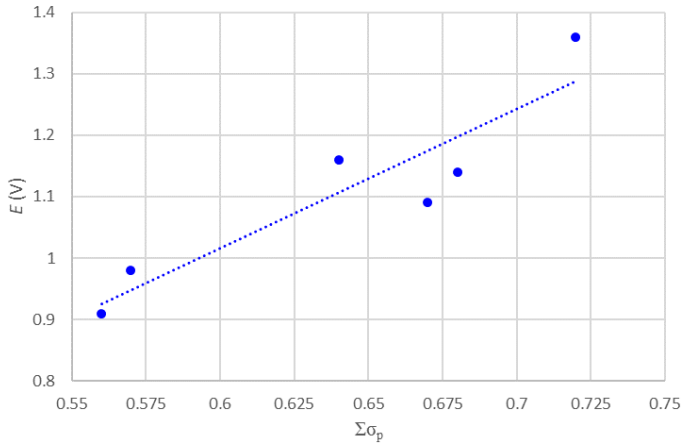


Differential pulse voltammetry

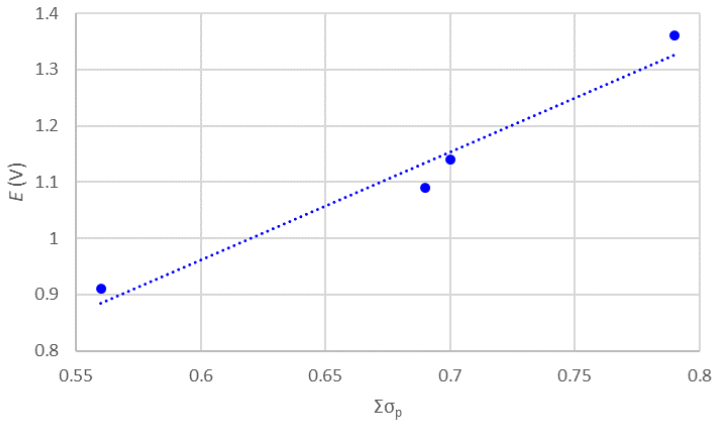


Additional plots

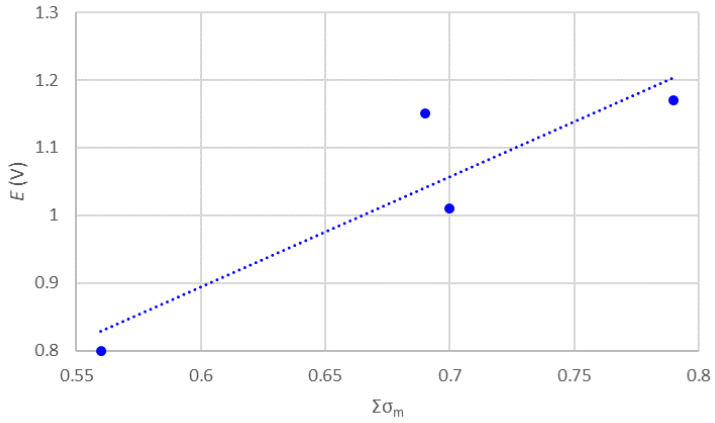
Plot SI1: *E* (V) *vs*. $\Sigma\sigma_P$ for 2-substituted ferrocenesulfonyle fluorides.



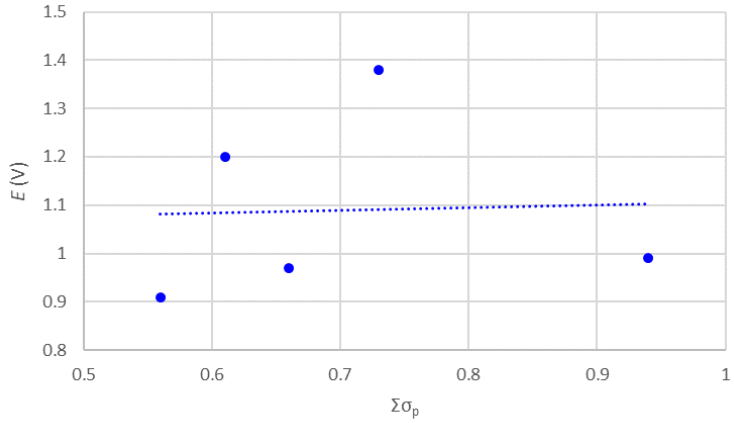
Plot SI2: E (V) *vs* $\Sigma\sigma_P$ for 3-substituted ferrocenesulfonyle fluorides.



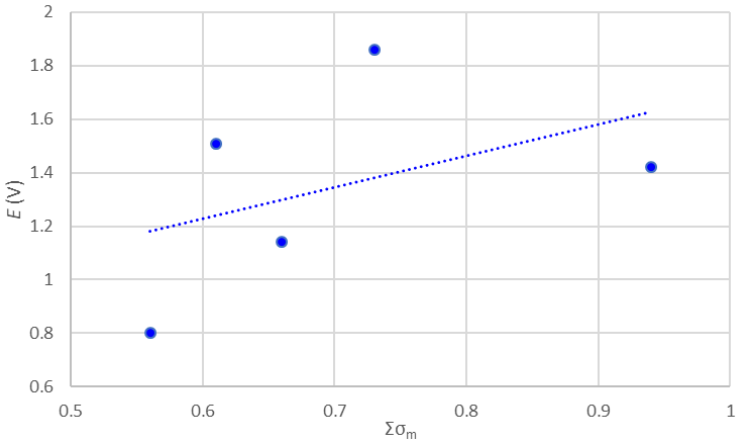
Plot SI3: E (V) *vs* $\Sigma\sigma_m$ for 3-substituted ferrocenesulfonyle fluorides.



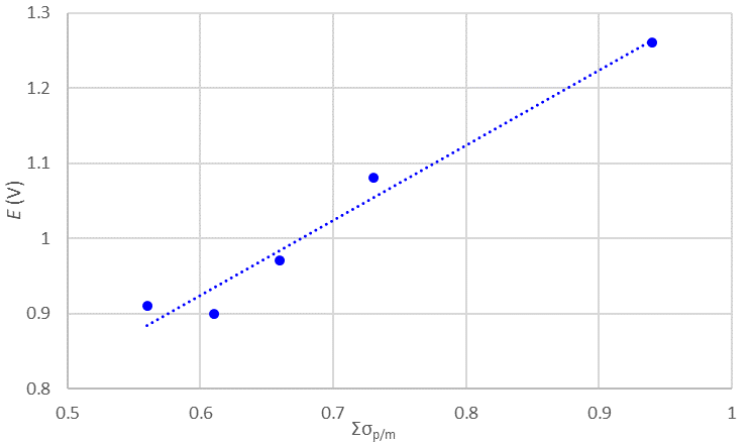
Plot SI4: *E* (V) *vs*. $\Sigma\sigma_P$ for ferrocenes **2**, **3e**, **11**, **12** and **13**.



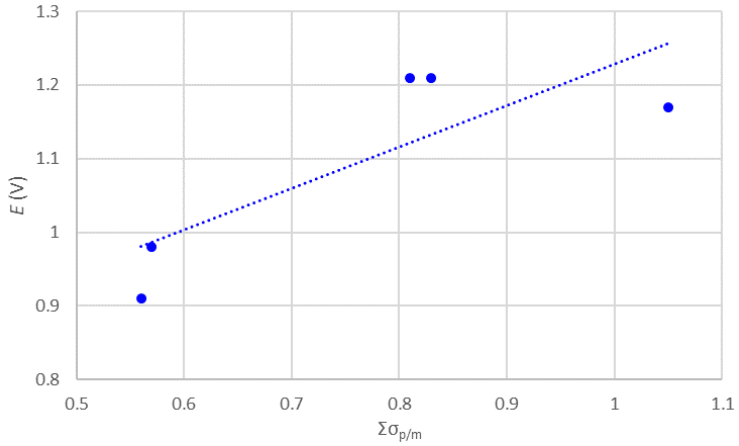
Plot SI5: *E* (V) *vs*. $\Sigma\sigma_m$ for ferrocenes **2**, **3e**, **11**, **12** and **13**.



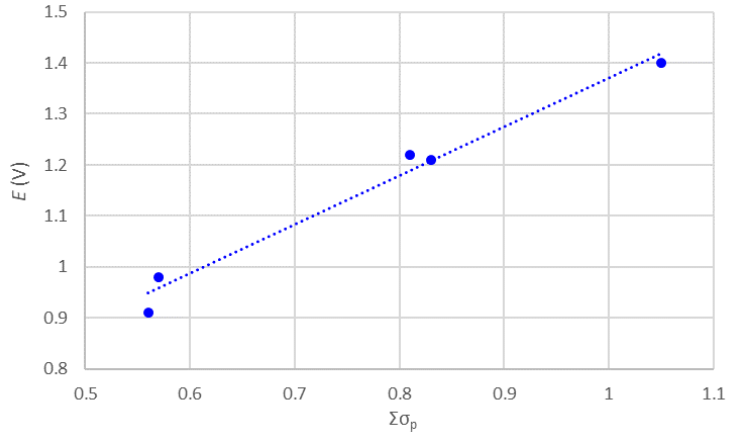
Plot SI6: *E* (V) *vs*. $\Sigma\ \sigma_{p\ SO_2F}+\sigma_{p\ \text{substituent adjacent to } SO_2F}+\sigma_{m\ \text{substituted remote from } SO_2F}$ for ferrocenes **2**, **3e**, **11**, **12** and **13**.



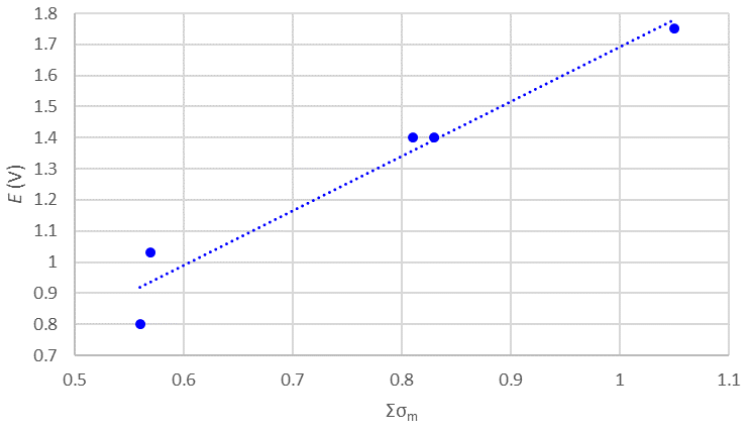
Plot SI7: *E* (V) *vs*. Σ $\sigma_{p\ SO_2F}$+$\sigma_{p\ substituent\ adjacent\ to\ SO_2F}$+$\sigma_{m\ substituted\ remote\ from\ SO_2F}$ for ferrocenes **2**, **3b**, **5g**, **17** and **19**.



Plot SI8: *E* (V) *vs*. Σ σ_p for ferrocenes **2**, **3b**, **5g**, **17** and **19**.



Plot SI9: *E* (V) *vs*. Σ σ_m for ferrocenes **2**, **3b**, **5g**, **17** and **19**.



References

1 A. F. Burchat, J. M. Chong and N. Nielsen, *J. Organomet. Chem.*, 1997, **542**, 281.
2 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.
3 W. Erb, M. Wen, T. Roisnel and F. Mongin, *Synthesis*, 2021, **53**, 2612.
4 K. Snégaroff, S. Komagawa, F. Chevallier, P. C. Gros, S. Golhen, T. Roisnel, M. Uchiyama and F. Mongin, *Chem. Eur. J.*, 2010, **16**, 8191.
5 W. Erb and T. Roisnel, *Dalton Trans.*, 2021, **50**, 16483.
6 G. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **71**, 3.
7 G. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3.
8 G. M. Romero Boston, H. M. Philipp and H. Butenschön, *Eur. J. Inorg. Chem.*, **2021**, 4903.
9 V. A. Nefedov and M. N. Nefedova, *Zh. Obshch. Khim.*, 1966, **36**, 122.
10 M. Tazi, W. Erb, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis, T. Roisnel, V. Dorcet and F. Mongin, *Organometallics*, 2017, **36**, 4770.
11 M. Tazi, M. Hedidi, W. Erb, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis, T. Roisnel, V. Dorcet, G. Bentabed-Ababsa and F. Mongin, *Organometallics*, 2018, **37**, 2207.
12 W. Erb, M. Wen, J. Pierre Hurvois, F. Mongin, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis and T. Roisnel, *Eur. J. Inorg. Chem.*, 2021, **2021**, 3165.
13 L. Kadari, W. Erb, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis, D. Lyakhov, T. Roisnel, P. Radha Krishna and F. Mongin, *Eur. J. Inorg. Chem.*, 2021, **2021**, 377.
14 M. Wen, W. Erb, F. Mongin, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis, T. Roisnel and V. Dorcet, *Organometallics*, 2021, **40**, 1129.
15 M. Wen, W. Erb, F. Mongin, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis and T. Roisnel, *Molecules*, 2022, **27**, 1798.
16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.02, Gaussian Inc., Wallingford, CT, 2009.
17 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.
18 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
19 P. C. Hariharan and J. A. Pople, *Theoretica chimica acta*, 1973, **28**, 213.
20 R. R. Fraser, T. S. Mansour and S. Savard, *Can. J. Chem.*, 1985, **63**, 3505.
21 E. Cancès, B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3032.