Supporting Information

The chemistry of ferrocenesulfonyl fluoride revealed

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Table of contents

General considerations, safety considerations, crystallography	S2
Optimization of synthesis of ferrocenesulfonyl fluoride (**2**)	S3
Experimental section: procedures, compound analyses and X-ray crystallographic details	S4
NMR Spectra	S19
Selected NOESY correlations	S116
References	S117

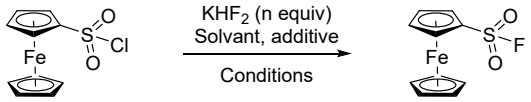
EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all reactions were performed under an argon atmosphere with anhydrous solvents using Schlenk technics. THF and Et_2O 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 (TMPH) 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 Avance III at 300 MHz, on a (ii) Bruker Avance III HD at 400 MHz, 100 MHz and 376 MHz, respectively, or (iii) on a Bruker Avance III HD spectrometer at 500 MHz, 126 MHz and 470 MHz, respectively. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ^{13}C chemical shifts are relative to the central peak of the solvent signal. Cp refers to the unsubstituted cyclopentadienyl ring of ferrocene. Ferrocenesulfonyl chloride was prepared according to Erb.[2] $ZnCl_2$·TMEDA was prepared according to Mongin.[3]

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 **2**, **3a**, **3b**, **3c**, **4**, **9b** and **13d**, the X-ray diffraction data were collected using APEXII Kappa-CCD (Bruker-AXS) diffractometer equipped with a CCD plate detector. For **3d**, **10a**, **11** and **12**, 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,[4] and then refined with full-matrix least-square methods based on F^2 (*SHELXL*).[5] 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 (version 3.9).

Optimization of synthesis of ferrocenesulfonyl fluoride (2).



Entry	Solvent	KHF_2 (equiv)	Additives	T (°C)	Time	Yield (%)
1[a]	H_2O-MeCN (6:4)	2	nBu$_4$NBr (1 mol%)	25	14 h	32
2[a]	MeCN-Acetone (1:1)	3	nBu$_4$NBr (5 mol%)	60	48 h	63
3[a]	AcOH	3	/	25	14 h	52
4[b]	AcOH	3	/	60	30 min	63

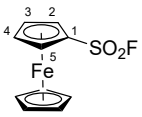
[a] On a 10 mmol scale. [b] On a 100 mmol scale.

Experimental section.

Ferrocenesulfonyl fluoride - 2

Ferrocenesulfonyl chloride (28.6 g, 100 mmol, 1.00 equiv) and KHF_2 (23.4 g, 300 mmol, 3.00 equiv) was placed in a flask under air and 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 poured onto cyclohexane (200 mL) in a 1 L round-bottom flaks and volatiles were removed under vacuum. Cyclohexane (200 mL) was added, volatiles were removed under vacuum and this step was repeated three more times. The residue was dissolved in EtOAc (500 mL) and water (300 mL) and layers were separated. The aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with aqueous NaOH (5%, 3 x 100 mL), water (2 x 100 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 column chromatography over SiO_2, using PE-EtOAc (70:30) to give the title product as an orange solid (17 g, 63%).

R_f (eluent: PE-EtOAc 80:20) = 0.53. Mp 79-80 °C. ν_{max} (film)/cm^{-1} 3121, 1416, 1396, 1214, 1161, 1028, 1018, 899, 868, 826, 813, 722. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.85 (t, J = 1.8 Hz, 2H, FcCH, H2 and H5), 4.58 (t, J = 1.8 Hz, 2H, FcCH, H3 and H4), 4.44 (s, 5H, Cp). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 77.9 (d, J = 39.2 Hz, FcC, C1), 72.5 (s, FcCH, C3 and C4), 71.6 (s, Cp), 70.0 (s, FcH, C2 and C5). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.2. Anal. Calcd for $C_{10}H_9FFeO_2S$: C, 44.80; H, 3.38; S, 11.96. Found: C, 44.91; H, 3.53; S, 12.09.



Crystal data for 2. $C_{10}H_9FFeO_2S$, M = 268.08, T = 150 K; monoclinic P $2_1/n$ (I.T.#14), a = 7.6335(6), b = 10.0261(10), c = 13.0870(11) Å, β = 97.978(4) °, V = 991.91(15) Å^3. Z = 4, d = 1.795 g.cm^{-3}, μ = 1.718 mm^{-1}. A final refinement on F^2 with 2254 unique intensities and 137 parameters converged at ωR_F^2 = 0.0631 (R_F = 0.0265) for 1990 observed reflections with $I > 2\sigma(I)$. CCDC 2110433.

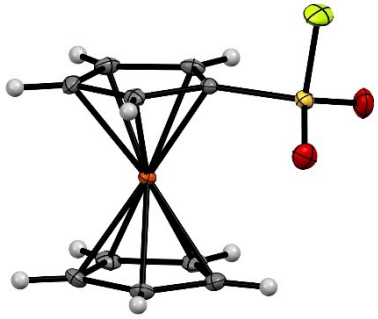
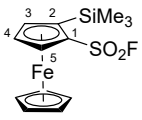


Figure 1. Molecular structure of compound **2** (thermal ellipsoids shown at the 30% probability level).

2-(Trimethylsilyl)ferrocenesulfonyl fluoride – 3a

*n*BuLi (1.4 M in hexane, 8.60 mL, 12.0 mmol, 1.20 equiv) was added dropwise to a solution of compound **2** (2.65 g, 10.0 mmol, 1.00 equiv) in THF (70 mL) at -95 °C and the reaction mixture was stirred at the same temperature for 15 min. Trimethylsilyl chloride (1.50 mL, 1.30 g, 12.0 mmol, 1.20 equiv) was added to the reaction mixture which was warmed to rt. Aqueous NH_4Cl (sat., 20 mL) was added and the reaction mixture was extracted with EtOAc (2 x 25 mL). 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 (10:1) to give the title product as an orange solid (2.74 g, 80%).

R_f (eluent: PE-EtOAc 10:1) = 0.54. Mp 69-70 °C. ν_{max} (film)/cm^{-1} 2964, 2903, 1395, 1351, 1278, 1247, 1210, 1170, 1144, 1039, 856, 827, 759, 738. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.03 (dd, J = 1.5, 2.1 Hz, 1H, FcCH, H5), 4.67 (t, J = 2.1 Hz, 1H, FcCH, H4), 4.50 (dd, J = 1.5, 2.1 Hz, 1H, FcCH, H3), 4.42 (s, 5H, Cp), 0.35 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 82.2 (d, J = 37.7 Hz, FcC, C1), 79.7 (s, FcCH, C3), 75.3 (s, FcC, C2), 74.4 (s, FcCH, C5), 73.7 (s, FcCH, C4), 71.5 (s, Cp), 0.3 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz,



$CDCl_3$): δ (ppm) 69.8. Anal. Calcd for $C_{13}H_{17}FFeO_2SSi$: C, 45.89; H, 5.04; S, 9.42. Found: C, 45.96; H, 5.16; S, 9.47.

Crystal data for 3a. $C_{13}H_{17}FFeO_2SSi$, M = 340.26, T = 150 K; monoclinic $P\,2_1/n$ (I.T.#14), a = 9.0861(5), b = 13.3795(6), c = 12.8394(7) Å, β = 110.418(2) °, V = 1462.79(13) Å^3. Z = 4, d = 1.545 g.cm^{-3}, μ = 1.260 mm^{-1}. A final refinement on F^2 with 3333 unique intensities and 175 parameters converged at ωR_F^2 = 0.0815 (R_F = 0.0372) for 2688 observed reflections with $I > 2\sigma(I)$. CCDC 2110434.

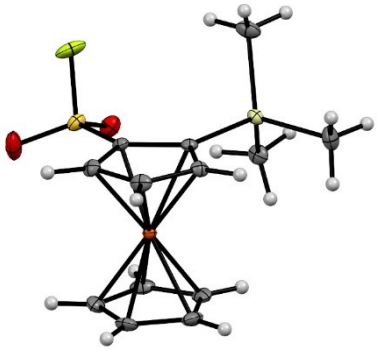
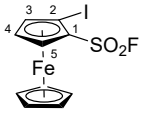


Figure 2. Molecular structure of compound **3a** (thermal ellipsoids shown at the 30% probability level).

2-Iodoferrocenesulfonyl fluoride – 3b

*n*BuLi (1.4 M in hexane, 1.70 mL, 2.40 mmol, 1.20 equiv) was added dropwise to a solution of compound **2** (536 mg, 2.00 mmol, 1.00 equiv) in THF (14 mL) at -95 °C and the reaction mixture was stirred at the same temperature for 15 min. Iodine (609 mg, 2.40 mmol, 1.20 equiv) in THF (3 mL) was added in one portion to the reaction mixture which was warmed to rt. Aqueous $Na_2S_2O_3$ (sat., 10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 (10:1) to give the title product as an orange solid (597 mg, 76%).

R_f (eluent: PE-EtOAc 90:10) = 0.39. Mp 78-80 °C. ν_{max} (film)/cm^{-1} 3105, 1404, 1338, 1303, 1212, 1174, 1108, 1030, 1001, 927, 841, 815, 733. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.95 (dd, J = 1.4, 2.7 Hz, 1H, FcCH, H5), 4.84 (dd, J = 1.5, 2.5 Hz, 1H, FcCH, H3), 4.60 (t, J = 2.7 Hz, 1H, FcCH, H4), 4.46 (s, 5H, Cp). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 80.9 (s, FcCH, C3), 80.7 (d, J = 38.6 Hz, FcC, C1), 74.5 (s, Cp), 73.1 (s, FcCH, C4), 71.4 (s, FcCH, C5), 36.6 (s, FcC, C2). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 67.4. Anal. Calcd for $C_{10}H_8FFeIO_2S$: C, 30.49; H, 2.05; S, 8.14. Found: C, 30.64; H, 2.09; S, 8.18.



Crystal data for 3b. $C_{10}H_8FFeIO_2S$, M = 393.97, T = 150 K; monoclinic $P\,2_1/c$ (I.T.#14), a = 15.0316(7), b = 10.8408(6), c = 15.2542(6) Å, β = 112.104(2) °, V = 2303.04(19) Å^3. Z = 8, d = 2.273 g.cm^{-3}, μ = 4.164 mm^{-1}. A final refinement on F^2 with 5275 unique intensities and 309 parameters converged at ωR_F^2 = 0.1092 (R_F = 0.0552) for 4345 observed reflections with $I > 2\sigma(I)$. CCDC 2110435.

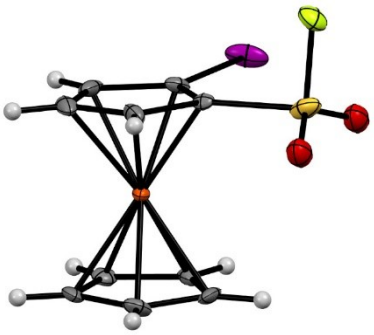
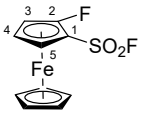


Figure 3. Molecular structure of compound **3b** (thermal ellipsoids shown at the 30% probability level).

2-Fluoroferrocenesulfonyl fluoride – 3c

*n*BuLi (1.4 M in hexane, 1.70 mL, 2.40 mmol, 1.20 equiv) was added dropwise to a solution of compound **2** (536 mg, 2.00 mmol, 1.00 equiv) in THF (14 mL) at -95 °C and the reaction mixture was stirred at the same temperature for 15 min. *N*-Fluorobenzenesulfonimide (757 mg, 2.40 mmol, 1.20 equiv) in THF (3 mL) was added in one portion to the reaction mixture which was warmed -20 °C and stirred for 1 h. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 as an orange solid (274 mg, 48%).

R_f (eluent: PE-EtOAc 90:10) = 0.22. Mp 69-71 °C. ν_{max} (film)/cm^{-1} 3121, 1471, 1400, 1380, 1258, 1208, 1171, 1108, 1087, 1025, 1006, 809, 753. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.73 (m, 1H, FcCH, H3), 4.55 (s, 5H, Cp), 4.53 (dd, J = 1.5, 2.9 Hz, 1H, FcCH, H5), 4.26 (m, 1H, FcCH, H4). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 133.1 (d, J = 284.1 Hz, FcC, C2), 73.0 (s, Cp), 67.3 (dd, J = 11.5, 40.2 Hz, FcC, C1), 64.2 (s, FcCH, C5), 64.0 (d, J = 2.6 Hz, FcCH, C4), 60.4 (d, J = 12.8 Hz, FcCH, C3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.3 (SO_2F), -186.5 (F). Anal. Calcd for $C_{10}H_8F_2FeO_2S$: C, 41.98; H, 2.82; S, 11.21. Found: C, 42.02; H, 3.04; S, 11.30.



Crystal data for 3c. $C_{10}H_8F_2FeO_2S$, M = 286.07, T = 150 K; monoclinic P $2_1/c$ (I.T.#14), a = 6.8825(7), b = 11.9649(14), c = 12.3895(12) Å, β = 90.433(4) °, V = 1020.23(19) Å^3. Z = 4, d = 1.862 g.cm^{-3}, μ = 1.690 mm^{-1}. A final refinement on F^2 with 2319 unique intensities and 149 parameters converged at ωR_F^2 = 0.0846 (R_F = 0.0319) for 2050 observed reflections with $I > 2\sigma(I)$. CCDC 2110436.

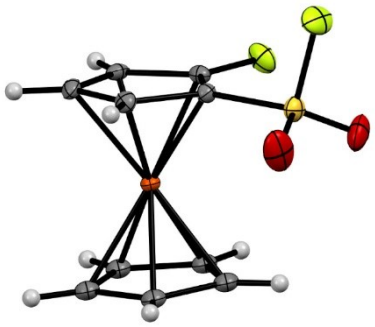
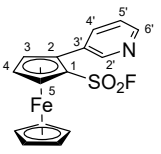


Figure 4. Molecular structure of compound **3c** (thermal ellipsoids shown at the 30% probability level).

2-(3-Pyridinyl)ferrocenesulfonyl fluoride – 3d

*n*BuLi (1.4 M in hexane, 1.70 mL, 2.40 mmol, 1.20 equiv) was added dropwise to a solution of compound **2** (536 mg, 2.00 mmol, 1.00 equiv) in THF (14 mL) at -95 °C and the reaction mixture was stirred at the same temperature for 15 min. $ZnCl_2$·TMEDA (606 mg, 2.40 mmol, 1.20 equiv) was added in one portion and the reaction mixture was warmed 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 (10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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% of NEt_3 to give the title product as an orange solid (442 mg, 64%).

R_f (eluent: PE-EtOAc 60:40 with 2% of NEt_3) = 0.19. Mp 109-110 °C. ν_{max} (film)/cm^{-1} 1591, 1569, 1488, 1441, 1405, 1316, 1264, 1200, 1165, 1125, 1108, 1030, 1004, 940, 823, 810. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.87 (d, J = 2.2 Hz, 1H, ArCH, H2'), 8.56 (dd, J = 1.6, 4.8 Hz, 1H, ArCH, H6'), 7.88 (dt, J = 1.9, 7.9 Hz, 1H, ArCH, H4'), 7.28 (dd, J = 4.8, 7.9 Hz, 1H, ArCH, H5'), 5.05 (dd, J = 1.6, 2.8 Hz, 1H, FcCH, H5), 4.82 (dd, J = 1.6, 2.7 Hz, 1H, FcCH, H3), 4.72 (t, J = 2.7 Hz, 1H, FcCH, H4), 4.47 (s, 5H, Cp).



$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ (ppm) 150.4 (s, ArCH, C2'), 149.0 (s, ArCH, C6'), 136.9 (s, ArC, C4'), 130.5 (s, ArCH, C3'), 122.9 (s, ArCH, C5'), 86.4 (s, FcC, C2), 75.9 (d, J = 38.9 Hz, FcC, C1), 75.8 (s, FcCH, C3), 73.2 (s, Cp), 72.6 (FcCH, C5), 71.5 (FcCH, C4). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 70.4. Anal. Calcd for $C_{15}H_{12}FFeNO_2S$: C, 52.20; H, 3.50; N, 4.06; S, 9.29. Found: C, 52.29; H, 3.40; N, 4.08; S, 9.26.

Crystal data for 3d. $C_{15}H_{12}FFeNO_2S$, M = 345.17, T = 150 K; monoclinic $C\,c$ (I.T.#9), a = 10.5249(9), b = 11.3803(6), c = 22.8382(14) Å, β = 91.681(3) °, V = 2734.3(3) Å^3. Z = 8, d = 1.677 g.cm^{-3}, μ = 1.269 mm^{-1}. A final refinement on F^2 with 6210 unique intensities and 321 parameters converged at ωR_F^2 = 0.1323 (R_F = 0.0536) for 5568 observed reflections with $I > 2\sigma(I)$. CCDC 2110437.

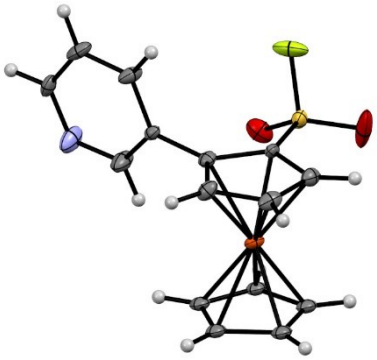
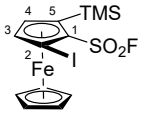


Figure 5. Molecular structure of compound **3d** (thermal ellipsoids shown at the 30% probability level).

2-Iodo-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 4

*n*BuLi (1.4 M in hexane, 1.30 mL, 1.80 mmol, 1.50 equiv) was added dropwise to a solution of compound **3a** (408 mg, 1.20 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 (457 mg, 1.80 mmol, 1.50 equiv) in THF (4 mL) was added in one portion to the reaction mixture which was warmed to rt. Aqueous $Na_2S_2O_3$ (sat., 5 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 solid (481 mg, 86%).

R_f (eluent: PE-EtOAc 15:1) = 0.55. Mp 68-72 °C. ν_{max} (film)/cm^{-1} 3106, 2955, 2901, 1397, 1243, 1212, 1186, 1132, 1108, 1073, 1003, 963, 879, 840, 827, 749. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.94 (d, J = 1.7 Hz, 1H, FcCH, H3), 4.54 (d, J = 1.7 Hz, 1H, FcCH, H4), 4.43 (s, 5H, Cp), 0.34 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ (ppm) 84.2 (d, J = 37.1 Hz, FcC, C1), 82.9 (s, FcCH, C3), 80.3 (s, FcCH, C4), 77.5 (s, FcC, C5), 74.4 (s, Cp), 40.9 (s, FcC, C2), 0.4 (s, $Si(CH_3)_3$). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 69.3. Anal. Calcd for $C_{13}H_{16}FFeIO_2SSi$: C, 33.50; H, 3.46; S, 6.88. Found: C, 33.55; H, 3.58; S, 6.92.



Crystal data for 4. $C_{13}H_{16}FFeIO_2SSi$, M = 466.16, T = 150 K; monoclinic $P\,2_1/n$ (I.T.#14), a = 8.4866(5), b = 16.5058(8), c = 12.0171(6) Å, β = 99.517(3) °, V = 1660.16(15) Å^3. Z = 4, d = 1.865 g.cm^{-3}, μ = 2.973 mm^{-1}. A final refinement on F^2 with 4356 unique intensities and 184 parameters converged at ωR_F^2 = 0.0688 (R_F = 0.0313) for 3691 observed reflections with $I > 2\sigma(I)$. CCDC 2110438.

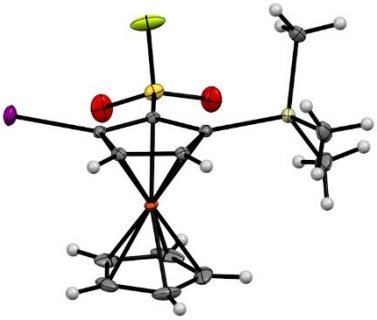
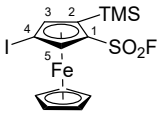


Figure 6. Molecular structure of compound **4** (thermal ellipsoids shown at the 30% probability level).

4-Iodo-2-(trimethylsilyl)ferrocenesulfonyl fluoride – 5a

*n*BuLi (1.4 M in hexane, 3.90 mL, 5.50 mmol, 1.10 equiv) was added dropwise to a solution of TMPH (930 µL, 777 mg, 5.50 mmol, 1.10 equiv) in THF (10 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, compound **4** (2.33 g, 5.00 mmol, 1.00 equiv) was added in one portion and the reaction mixture was stirred at -50 °C for 1 h. Methanol (1 mL), followed by aqueous HCl (1 M, 10 mL), were sequentially added, the reaction mixture was warmed to rt and directly extracted with EtOAc (2 x 10 mL). 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 (15:1) to give the title product as an orange solid (1.48 g, 63%).

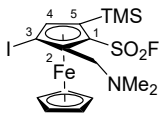
R_f (eluent: PE-EtOAc 15:1) = 0.68. Mp 74-75 °C. ν_{max} (film)/cm^{-1} 3111, 2956, 2899, 1399, 1272, 1246, 1214, 1182, 1054, 1006, 979, 879, 841, 829, 760, 738. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.26 (s, 1H, FcCH, H5), 4.69 (s, 1H, FcCH, H3), 4.44 (s, 5H, Cp), 0.35 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 86.0 (s, FcCH, C3), 82.9 (d, J = 38.1 Hz, FcC, C1), 79.7 (s, FcCH, C5), 77.2 (s, FcC, C2), 74.4 (s, Cp), 40.6 (s, FcC, C4), 0.2 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 69.7. Anal. Calcd for $C_{13}H_{16}FFeIO_2SSi$: C, 33.50; H, 3.46; S, 6.88. Found: C, 33.46; H, 3.37; S, 6.90.



2-(Dimethylaminomethyl)-3-iodo-5-(trimethylsilyl)ferrocenesulfonyl fluoride – 5b

*n*BuLi (1.4 M in hexane, 2.00 mL, 2.75 mmol, 1.10 equiv) was added dropwise to a solution of TMPH (464 µL, 388 mg, 2.75 mmol, 1.10 equiv) in THF (5 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, compound **4** (1.16 g, 2.50 mmol, 1.00 equiv) was added in one portion and the reaction mixture was stirred at -50 °C for 1 h. Eschenmoser's salt (299 mg, 2.75 mmol, 1.10 equiv) was added in one portion and the reaction mixture was warmed to rt. Aqueous K_2CO_3 solution (sat., 10 mL) 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 as an orange oil (899 mg, 68%).

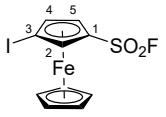
R_f (eluent: PE-EtOAc 80:20) = 0.65. ν_{max} (film)/cm^{-1} 2947, 2818, 2769, 1457, 1394, 1247, 1196, 1177, 1122, 1018, 930, 827, 752. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.76 (s, 1H, FcCH, H4), 4.34 (s, 5H, cp), 3.98 (d, J = 13.0 Hz, 1H, C*H*H), 3.32 (d, J = 13.0 Hz, 1H, CH*H*), 2.26 (s, 6H, $N(CH_3)_2$), 0.34 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 90.3 (s, FcC, C2), 85.1 (s, FcCH, C4), 79.7 (d, J = 38.3 Hz, FcC, C1), 78.6 (s, FcC, C5), 74.8 (s, Cp), 56.3 (s, CH_2), 49.5 (FcC, C3), 45.5 (s, $N(CH_3)_2$), 0.5 (s, $Si(CH_3)_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.4. Anal. Calcd for $C_{16}H_{23}FFeINO_2SSi$: C, 36.73; H, 4.43; N, 2.68; S, 6.13. Found: C, 36.85; H, 4.49; N, 2.73; S, 6.07.



3-Iodoferrocenesulfonyl fluoride – 6a

Tetrabutylammonium fluoride (1.0 M, 6.00 mL, 6.00 mmol, 1.50 equiv) was added to a solution of compound **5a** (1.86 g, 4.00 mmol, 1.00 equiv) in THF (16 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 (2 x 10 mL). 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 as an orange oil (1.34 g, 85%).

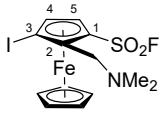
R_f (eluent: PE-EtOAc 70:30) = 0.66. ν_{max} (film)/cm^{-1} 3108, 1400, 1368, 1219, 1178, 1108, 1046, 1034, 1003, 904, 875, 828, 745. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.11 (t, J = 1.2 Hz, 1H, FcCH, H2), 4.86 (dd, J = 1.2, 2.6 Hz, 1H, FcCH, H5), 4.82 (dd, J = 1.2, 2.6 Hz, 1H, FcCH, H4), 4.47 (s, 5H, Cp). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 79.1 (s, FcCH, C4), 78.8 (d, J = 39.6 Hz, FcC, C1), 75.6 (s, FcCH, C2), 74.5 (s, Cp), 70.9 (s, FcCH, C5), 39.1 (s, FcC, C3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.2. Anal. Calcd for $C_{10}H_8FFeIO_2S$: C, 30.49; H, 2.05; S, 8.14. Found: C, 30.53; H, 2.15; S, 8.16.



2-(Dimethylaminomethyl)-3-iodoferrocenesulfonyl fluoride – 6b

Tetrabutylammonium fluoride (1.0 M, 1.50 mL, 1.50 mmol, 1.50 equiv) was added to a solution of compound **5b** (523 mg, 1.00 mmol, 1.00 equiv) in THF (4 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 (2 x 10 mL). 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 70:30) to give the title product as a yellow solid (363 mg, 80%).

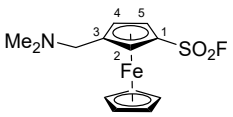
R_f (eluent: PE-EtOAc 80:20) = 0.47. Mp 117-118 °C. ν_{max} (film)/cm^{-1} 2975, 2943, 2819, 2767, 1389, 1380, 1256, 1234, 1191, 1153, 1123, 1091, 1047, 1029, 1003, 976, 831, 811, 764, 745. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.96 (d, *J* = 2.7 Hz, 1H, FcCH, H5), 4.85 (d, *J* = 2.7 Hz, 1H, FcCH, H4), 4.36 (s, 5H, Cp), 3.87 (d, *J* = 13.1 Hz, 1H, C*H*H), 3.32 (d, *J* = 13.1 Hz, 1H, CH*H*), 2.25 (s, 6H, $N(CH_3)_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 87.4 (s, FcC, C2), 77.9 (s, FcCH, C4), 76.5 (d, *J* = 38.9 Hz, FcC, C1), 74.9 (s, Cp), 72.4 (s, FcCH, C5), 56.1 (s, CH_2), 47.1 (s, FcC, C3), 45.4 (s, $N(CH_3)_2$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 67.2. Anal. Calcd for $C_{13}H_{15}FFeINO_2S$: C, 34.62; H, 3.35; N, 3.11; S, 7.11. Found: C, 34.56; H, 3.39; N, 3.15; S, 7.13.



3-(Dimethylaminomethyl)ferrocenesulfonyl fluoride – 7a

*t*BuLi (1.6 M, 1.25 mL, 2.00 mmol, 2.00 equiv) was added dropwise to a solution of compound **6a** (394 mg, 1.00 mmol, 1.00 equiv) in THF (5 mL) at –90 °C. After addition, the reaction mixture was stirred at the same temperature for 15 min. Eschenmoser's salt (370 mg, 2.00 mmol, 2.00 equiv) was added in one portion and the reaction mixture was warmed to rt. Aqueous K_2CO_3 solution (sat., 10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 (30:70 to 0:100) with 2% of NEt_3 to give the title product as an orange oil (222 mg, 68%).

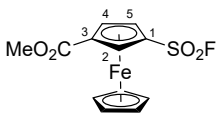
R_f (eluent: PE-EtOAc 30:70 with 2% of NEt_3) = 0.17. ν_{max} (film)/cm^{-1} 2943, 2859, 2820, 2772, 1457, 1398, 1357, 1253, 1191, 1170, 1091, 1023, 1004, 829, 740. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.86 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 4.82 (dd, *J* = 1.2, 2.5 Hz, 1H, FcCH, H5), 4.58 (dd, *J* = 1.6, 2.5 Hz, 1H, FcCH, H4), 4.39 (s, 5H, Cp), 3.28 (d, *J* = 13.4 Hz, 1H, C*H*H), 3.26 (d, *J* = 13.4 Hz, 1H, CH*H*), 2.20 (s, 6H, $N(CH_3)_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 88.7 (s, FcC, C3), 77.5 (d, *J* = 39.5 Hz, FcC, C1), 74.1 (s, FcCH, C4), 72.2 (s, Cp), 71.2 (s, FcCH, C2), 69.9 (s, FcCH, C5), 58.3 (s, CH_2), 45.0 (s, $N(CH_3)_2$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.1. Anal. Calcd for $C_{13}H_{16}FFeNO_2S$: C, 48.02; H, 4.96; N, 4.31; S, 9.86. Found: C, 48.17; H, 5.11; N, 4.54; S, 9.91.



3-(Methoxycarbonyl)ferrocenesulfonyl fluoride – 7b

*t*BuLi (1.6 M, 1.25 mL, 2.00 mmol, 2.00 equiv) was added dropwise to a solution of compound **6a** (394 mg, 1.00 mmol, 1.00 equiv) in THF (5 mL) at –90 °C. After addition, the reaction mixture was stirred at the same temperature for 15 min. Methyl chloroformate (472 mg, 5.00 mmol, 5.00 equiv) was added in one portion and the reaction mixture was warmed to rt. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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) with 2% of NEt_3 to give the title product as an orange solid (239 mg, 73%).

R_f (eluent: PE-EtOAc 70:30) = 0.54. Mp 98-99 °C. ν_{max} (film)/cm^{-1} 3110, 1714, 1473, 1400, 1335, 1297, 1216, 1190, 1169, 1067, 1051, 967, 842, 831, 794, 762. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.47 (s, 1H, FcCH, H2), 5.14 (s, 1H, FcCH, H4), 5.00 (s, 1H, FcCH, H5), 4.48 (s, 5H, Cp), 3.85 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 168.9 (s, C=O), 80.3 (d, *J* = 39.8 Hz, FcC, C1), 75.8 (s, FcC, C3), 73.9 (s, FcCH, C4), 73.3 (s, Cp), 72.2 (s, FcCH, C5), 71.4 (s, FcCH, C2), 52.4 (s, CH_3). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 67.7.

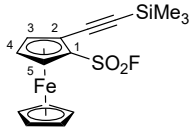


Anal. Calcd for $C_{12}H_{11}FFeO_4S$: C, 44.20; H, 3.40; S, 9.83. Found: C, 44.34; H, 3.45; S, 9.91.

2-(Trimethylsilylethynyl)ferrocenesulfonyl fluoride – 8a

Compound **3b** (788 mg, 2.00 mmol, 1.00 equiv), Pd(P*t*Bu$_3$)$_2$ (30.7 mg, 0.06 mmol, 0.03 equiv) and CuI (11.5 mg, 0.06 mmol, 0.03 equiv) were placed in a dried Schlenk tube which was subjected to three cycles of vacuum/argon. THF (2.25 mL), diisopropylamine (0.75 mL) and trimethylsilylacetylene (554 µL, 393 mg, 4.00 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 (10:1) with 1% of NEt_3 to give the title product as an orange oil (659 mg, 90%).

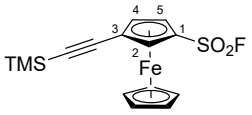
R_f (eluent: PE-EtOAc 90:10) = 0.38. ν_{max} (film)/cm^{-1} 2960, 2157, 1437, 1406, 1381, 1248, 1206, 1166, 1001, 836, 755, 731. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.88 (dd, *J* = 1.4, 2.8 Hz, 1H, FcCH, H5), 4.79 (dd, *J* = 1.4, 2.6 Hz, 1H, FcCH, H3), 4.54 (t, *J* = 2.8 Hz, 1H, FcCH, H4), 4.46 (s, 5H, Cp), 0.25 (s, 9H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 98.0 and 97.7 (s, C≡C, C7 and C8), 80.1 (d, *J* = 37.7 Hz, FcC, C1), 76.2 (s, FcCH, C3), 73.7 (s, Cp), 71.5 (s, FcCH, C5), 71.2 (s, FcCH, C4), 67.2 (s, FcC, C2), 0.0 (s, Si(CH$_3$)$_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 67.5. Anal. Calcd for $C_{15}H_{17}FFeO_2SSi$: C, 49.46; H, 4.70; S, 8.80. Found: C, 49.36; H, 4.68; S, 8.78.



3-(Trimethylsilylethynyl)ferrocenesulfonyl fluoride – 8b

Compound **6a** (788 mg, 2.00 mmol, 1.00 equiv), Pd(P*t*Bu$_3$)$_2$ (30.7 mg, 0.06 mmol, 0.03 equiv) and CuI (11.5 mg, 0.06 mmol, 0.03 equiv) were placed in a dried Schlenk tube which was subjected to three cycles of vacuum/argon. THF (2.25 mL), diisopropylamine (0.75 mL) and trimethylsilylacetylene (554 µL, 393 mg, 4.00 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) with 1% of NEt_3 to give the title product as a red solid (613 mg, 84%).

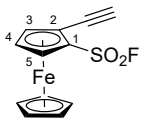
R_f (eluent: PE-EtOAc 95:5) = 0.67. Mp 59-60 °C. ν_{max} (film)/cm^{-1} 3112, 2967, 2901, 2160, 1402, 1387, 1266, 1249, 1200, 1180, 1092, 1039, 1004, 940, 829, 746, 730. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.09 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 4.84 (dd, *J* = 1.2, 2.7 Hz, 1H, FcCH, H5), 4.77 (dd, *J* = 1.2, 2.7 Hz, 1H, FcCH, H4), 4.47 (s, 5H, Cp), 0.23 (s, 9H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 99.8 (s, C≡*C*-C3), 94.3 (s, Si-*C*≡C), 78.1 (d, *J* = 39.7 Hz, FcC, C1), 75.5 (s, FcCH, C4), 73.7 (s, Cp), 72.5 (s, FcCH, C2), 70.5 (s, FcC, C3), 70.1 (FcCH, C5), 0.1 (s, Si(CH$_3$)$_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.0. Anal. Calcd for $C_{15}H_{17}FFeO_2SSi$: C, 49.46; H, 4.70; S, 8.80. Found: C, 49.52; H, 4.73; S, 8.75.



2-Ethynylferrocenesulfonyl fluoride – 9a

Tetrabutylammonium fluoride (1.0 M, 2.00 mL, 2.00 mmol, 2.00 equiv) was added to a solution of compound **8a** (364 mg, 1.00 mmol, 1.00 equiv) in THF (3 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 (2 x 10 mL). 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 as an orange solid (244 mg, 83%).

R_f (eluent: PE-EtOAc 90:10) = 0.41. Mp 78-79 °C. ν_{max} (film)/cm^{-1} 3280, 3116, 2115, 1431, 1398, 1378, 1315, 1236, 1201, 1165, 1109, 1083, 1033, 1003, 993, 837, 816, 742. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.91 (dd, *J* = 1.6, 2.8 Hz, 1H, FcCH, H5), 4.85 (dd, *J* = 1.6, 2.6 Hz, 1H, FcCH, H3), 4.59 (t, *J* = 2.8 Hz, 1H, FcCH, H4), 4.50 (s, 5H, Cp), 3.03 (s, 1H, C≡CH). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 79.8 (d, *J* = 38.2 Hz, FcC, C1), 79.3 (s, C≡*C*H), 77.1 (s,

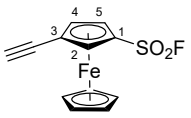


C≡CH), 76.8 (s, FcCH, C3), 73.7 (s, Cp), 71.6 and 71.5 (s, FcCH, C4 and C5), 66.2 (s, FcC, C2). $^{19}F\{^{1}H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 67.8. Anal. Calcd for $C_{12}H_9FFeO_2S$: C, 49.34; H, 3.11; S, 10.98. Found: C, 49.53; H, 3.18; S, 11.03.

3-Ethynylferrocenesulfonyl fluoride – 9b

Tetrabutylammonium fluoride (1.0 M, 2.00 mL, 2.00 mmol, 2.00 equiv) was added to a solution of compound **8b** (364 mg, 1.00 mmol, 1.00 equiv) in THF (3 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 (2 x 10 mL). 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 70:30) to give the title product as an orange solid (171 mg, 58%).

R_f (eluent: PE-EtOAc 90:10) = 0.45. Mp 94-95 °C. ν_{max} (film)/cm^{-1} 3289, 3107, 1402, 1260, 1197, 1110, 1085, 1039, 1005, 829, 757. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.12 (t, *J* = 1.4 Hz, 1H, FcCH, H2), 4.86 and 4.81 (dd, *J* = 1.3, 2.7 Hz, 1H each, FcCH, H4 and H5), 4.50 (s, 5H, Cp), 2.82 (s, 1H, C≡CH). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ (ppm) 78.8 (s, *C*≡CH), 78.2 (d, *J* = 39.9 Hz, FcC, C1), 76.6 (s, C≡*C*H), 75.6 and 70.2 (s, C4 and C5), 73.6 (s, Cp), 72.6 (s, FcCH, C2), 69.4 (s, FcC, C3). $^{19}F\{^{1}H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 67.9. Anal. Calcd for $C_{12}H_9FFeO_2S$: C, 49.34; H, 3.11; S, 10.98. Found: C, 49.36; H, 3.23; S, 11.06.



Crystal data for 9b. $C_{12}H_9FFeO_2S$, *M* = 292.10, *T* = 150 K; triclinic $P\bar{1}$ (I.T.#2), *a* = 6.9415(12), *b* = 9.1569(18), *c* = 9.4381(18) Å, *α* = 81.337(6), *β* = 74.314(6), *γ* = 84.801(6) °, *V* = 570.19(19) Å^3. *Z* = 2, *d* = 1.701 g.cm^{-3}, *μ* = 1.502 mm^{-1}. A final refinement on F^2 with 2602 unique intensities and 154 parameters converged at ωR_F^2 = 0.0682 (R_F = 0.0264) for 2386 observed reflections with $I > 2\sigma(I)$. CCDC 2110439.

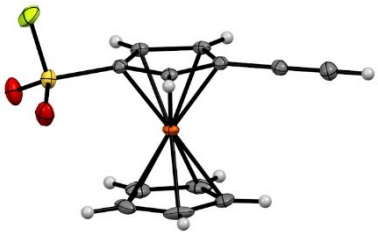
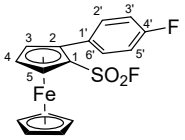


Figure 7. Molecular structure of compound **9b** (thermal ellipsoids shown at the 30% probability level).

2-(4-Fluorophenyl)ferrocenesulfonyl fluoride – 10a

Compound **3b** (197 mg, 0.50 mmol, 1.00 equiv), 4-fluorophenylboronic acid (280 mg, 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 (10 mL) was added. The reaction mixture was extracted with EtOAc (2 x 10 mL) 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 (90:10) to give the title product as an orange solid (157 mg, 86%).

R_f (eluent: PE-EtOAc 90:10) = 0.50. Mp 117-119 °C. ν_{max} (film)/cm^{-1} 1605, 1520, 1443, 1415, 1395, 1325, 1206, 1162, 1124, 1025, 1003, 836, 812, 751, 720. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.57 (m, 2H, 2xArCH, H2' and H6'), 7.05 (m, 2H, 2xArCH, H3' and H5'), 5.00 (dd, *J* = 1.7, 2.7 Hz, 1H, FcCH, H5), 4.74 (dd, *J* = 1.7, 2.5 Hz, 1H, FcCH, H3), 4.66 (t, *J* = 2.7 Hz, 1H, FcCH, H4), 4.44 (s, 5H, Cp). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ (ppm) 162.6 (d, *J* = 247.3 Hz, ArC, C4'), 131.4 (d, *J* = 8.2 Hz, 2xArCH, C2' and C6'), 129.9 (d, *J* = 3.3 Hz, ArC, C1'), 115.3 (d, *J* = 22.1 Hz, 2xArCH, C3' and C5'), 89.6 (s, FcC, C2), 75.9 (d, *J* = 38.3 Hz, FcC, C1), 75.6 (s, FcCH, C3), 73.0 (s, Cp), 72.2 (s, FcCH, C5), 70.9 (s, FcCH, C4). $^{19}F\{^{1}H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 70.0 (SO_2F), -113.8 (F). Anal. Calcd for $C_{16}H_{12}F_2FeO_2S$: C, 53.06; H, 3.34; S, 8.85. Found: C, 53.04; H, 3.17; S, 8.76.



Crystal data for 10a. $C_{16}H_{12}F_2FeO_2S$, M = 362.17, T = 150 K; monoclinic $P\,2_1/c$ (I.T.#14), a = 11.9437(7), b = 7.5335(4), c = 15.7854(7) Å, β = 90.465(3) °, V = 1420.29(13) Å^3. Z = 4, d = 1.694 g.cm^{-3}, μ = 1.234 mm^{-1}. A final refinement on F^2 with 3196 unique intensities and 199 parameters converged at $\omega R_F^2 = 0.1594$ ($R_F = 0.0634$) for 2725 observed reflections with $I > 2\sigma(I)$. CCDC 2110440.

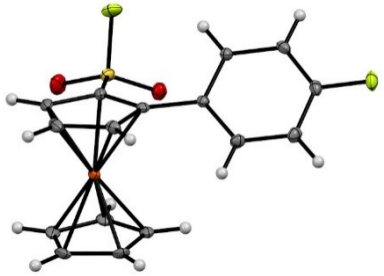
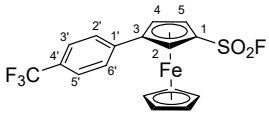


Figure 8. Molecular structure of compound **10a** (thermal ellipsoids shown at the 30% probability level).

3-(4-Trifluoromethylphenyl)ferrocenesulfonyl fluoride – 10b

Compound **6a** (197 mg, 0.50 mmol, 1.00 equiv), 4-trifluoromethylphenylboronic acid (380 mg, 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 (10 mL) was added. The reaction mixture was extracted with EtOAc (2 x 10 mL) 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 (15:1) to give the title product as an orange oil (163 mg, 79%).

R_f (eluent: PE-EtOAc 15:1) = 0.27. ν_{max} (film)/cm^{-1} 1618, 1402, 1322, 1207, 1164, 1121, 1107, 1067, 1020, 830, 748. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.62 (d, J = 8.7 Hz, 2H, ArCH, H3' and H5'), 7.59 (d, J = 8.7 Hz, 2H, ArCH, H2' and H6'), 5.34 (t, J = 1.3 Hz, 1H, FcCH, H2), 5.06 (m, 2H, FcCH, H4 and H5), 4.35 (s, 5H, Cp). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 139.8 (s, ArC, C1'), 126.6 (s, ArCH, C2' and C3' and C5' and C6'), 126.0 (q, J = 3.6 Hz, ArC, C4'), 124.2 (q, J = 271.9 Hz, CF_3), 88.3 (s, FcC, C3), 79.0 (d, J = 39.9 Hz, FcC, C1), 73.3 (s, Cp), 71.0 and 70.8 (s, FcCH, C4 and C5), 67.9 (s, FcCH, C2). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ (ppm) 68.2 (SO_2F), -62.6 (CF_3). Anal. Calcd for $C_{17}H_{12}F_4FeO_2S$: C, 49.54; H, 2.93; S, 7.78. Found: C, 49.69; H, 3.09; S, 7.73.

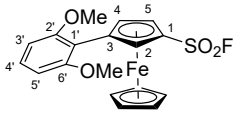


3-(2,5-Dimethoxyphenyl)ferrocenesulfonyl fluoride – 10c

Compound **6a** (197 mg, 0.50 mmol, 1.00 equiv), 2,6-dimethoxyphenylboronic acid (364 mg, 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 (10 mL) was added. The reaction mixture was extracted with EtOAc (2 x 10 mL) 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 (90:10) to give the title product as an orange oil (190 mg, 94%).

R_f (eluent: PE-EtOAc 95:5) = 0.19. ν_{max} (film)/cm^{-1} 2939, 2839, 1586, 1473, 1434, 1396, 1285, 1246, 1202, 1178, 1134, 1102, 1034, 895, 824, 781, 728.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.26 (t, J = 8.2 Hz, 1H, ArCH, H4'), 6.63 (d, J = 8.2 Hz, 2H, ArCH, H3' and H4'), 5.50 (t, J = 1.4 Hz, 1H, FcCH, H2), 5.23 (dd, J = 1.4, 2.8 Hz, 1H, H4), 4.92 (dd, J = 1.4, 2.8 Hz, 1H, FcCH, H5), 4.31 (s, 5H, Cp), 3.90 (s, 6H, OCH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 158.3 (s, ArC, C2' and C6'), 128.8 (s, ArCH, C4'), 111.5 (s, ArC, C1'), 104.3 (s, ArCH, C3' and C5'), 83.5 (s, FcC, C3), 76.7 (d, J = 39.6 Hz, C1), 75.5 (s, FcCH, C4), 72.7 (s, Cp), 72.2 (s, FcCH, C2), 68.9

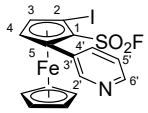


(s, FcCH, C5), 55.8 (s, OCH_3). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 68.5. Anal. Calcd for $C_{18}H_{17}FFeO_4S$: C, 53.48; H, 4.24; S, 7.93. Found: C, 53.65; H, 4.16; S, 7.86.

2-Iodo-5-(3-pyridinyl)ferrocenesulfonyl fluoride – 11

*n*BuLi (1.4 M in hexane, 1.10 mL, 1.50 mmol, 1.50 equiv) was added dropwise to a solution of TMPH (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 **3b** (394 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 (10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 to 50:50) with 2% of NEt_3 to give the title product as an orange solid (194 mg, 41%).

R_f (eluent: PE-EtOAc 60:40 with 2% of NEt_3) = 0.19. Mp 138-136 °C. ν_{max} (film)/cm^{-1} 3111, 3033, 1565, 1490, 1413, 1397, 1337, 1288, 1261, 1200, 1160, 1109, 1066, 1022, 1004, 946, 876, 838, 811, 763, 737. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.79 (dd, *J* = 0.9, 2.3 Hz, 1H, ArCH, H2'), 8.57 (dd, *J* = 1.6, 4.9 Hz, 1H, ArCH, H6'), 7.79 (dt, *J* = 2.0, 8.0 Hz, 1H, ArCH, H4'), 7.28 (ddd, *J* = 0.5, 4.9, 8.0 Hz, 1H, ArCH, H5'), 5.01 (d, *J* = 2.7 Hz, 1H, FcCH, H3), 4.81 (d, *J* = 2.7 Hz, 1H, FcCH, H4), 4.52 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ (ppm) 150.5 (s, ArCH, C2'), 149.3 (s, ArCH, C6'), 137.6 (s, ArCH, C4'), 129.9 (s, ArC, C3'), 122.7 (s, ArCH, C5'), 88.3 (s, FcC, C5), 80.2 (s, FcCH, C3, 77.8 (d, *J* = 38.1 Hz, FcC, C1), 76.9 (s, FcCH, C4), 76.1 (s, Cp), 39.7 (s, FcC, C2). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 71.2. Anal. Calcd for $C_{15}H_{11}FFeINO_2S$: C, 38.25; H, 2.35; N, 2.97; S, 6.81. Found: C, 38.21; H, 2.40; N, 3.01; S, 6.87.



Crystal data for 11. $C_{15}H_{11}FFeINO_2S$, *M* = 471.06, *T* = 150 K; monoclinic *P* $2_1/c$ (I.T.#14), *a* = 15.0556(16), *b* = 6.8264(7), *c* = 15.1425(14) Å, *β* = 92.999(4) °, *V* = 1554.1(3) Å^3. *Z* = 4, *d* = 2.013 g.cm^{-3}, *µ* = 3.106 mm^{-1}. A final refinement on F^2 with 3722 unique intensities and 200 parameters converged at $\omega R_F^2 = 0.0752$ ($R_F = 0.0337$) for 3246 observed reflections with $I > 2\sigma(I)$. CCDC 2110441.

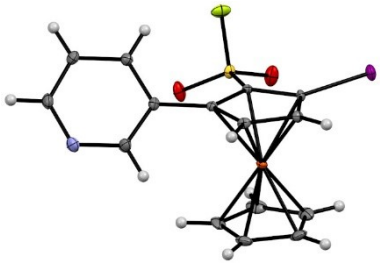


Figure 9. Molecular structure of compound **11** (thermal ellipsoids shown at the 30% probability level).

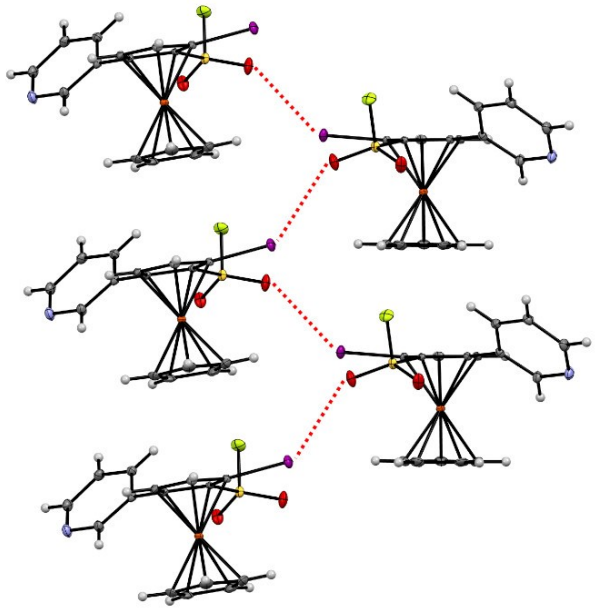
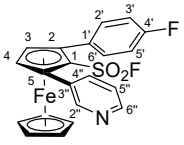


Figure 10. Intermolecular halogen bonds observed at the solid state for compound **11** (thermal ellipsoids shown at the 30% probability level).

2-(4-Fluorophenyl)-5-(3-pyridinyl)ferrocenesulfonyl fluoride – 12

Compound **11** (189 mg, 0.40 mmol, 1.00 equiv), 4-fluorophenylboronic acid (224 mg, 1.60 mmol, 4.00 equiv), $Pd(dba)_2$ (11.5 mg, 20.0 µmol, 0.05 equiv), SPhos (32.8 mg, 0.08 mmol, 0.20 equiv) and CsF (122 mg, 0.08 mmol, 2.00 equiv) were placed in a dried Schlenk tube, subjected to three cycles of vacuum/argon. Toluene (4 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 (10 mL) was added. The reaction mixture was extracted with EtOAc (2 x 10 mL) 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 (60:40 to 50:50) to give the title product as a yellow solid (132 mg, 75%).

R_f (eluent: PE-EtOAc 50:50 with 2% of NEt_3) = 0.57 after 2 developments. Mp 208-209 °C. ν_{max} (film)/cm^{-1} 1516, 1435, 1392, 1320, 1226, 1198, 1160, 1116, 1103, 1009, 951, 833, 809, 728. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.90 (br s, 1H, ArCH, H2"), 8.59 (br s, 1H, ArCH, H6"), 7.88 (d, J = 7.9 Hz, 1H, ArCH, H4"), 7.58 (m, 2H, ArCH, H2' and H6'), 7.31 (dd, J = 4.9, 7.6 Hz, 1H, ArCH, H5"), 7.08 (t, J = 8.5 Hz, 2H, ArCH, H3' and H5'), 4.87 (d, J = 2.7 Hz, 1H, FcCH, H4), 4.86 (d, J = 2.7 Hz, 1H, FcCH, H3), 4.50 (s, 5H, Cp). $^{13}C\{^1H\}$0 NMR (126 MHz, $CDCl_3$): δ (ppm) 162.7 (d, J = 248.0 Hz, ArC, C4'), 150.6 (s, ArCH, C2"), 149.1 (s, ArCH, C6"), 137.3 (s, ArCH, C4"), 131.6 (d, J = 8.2 Hz, ArCH, C2' and C6'), 130.8 (s, ArC, C3"), 129.9 (d, J = 3.2 Hz, ArC, C1'), 122.8 (s, ArCH, C5"), 115.3 (d, J = 21.7 Hz, ArCH, C3' and C5'), 92.3 (s, FcC, C2), 88.6 (s, FcC, C5), 74.9 and 74.8 (s, FcCH, C3 and C4), 74.7 (s, Cp), 72.7 (d, J = 37.8 Hz, FcC, C1). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ (ppm) 72.9 (SO_2F), -113.4 (F). Anal. Calcd for $C_{21}H_{15}F_2FeNO_2S$: C, 57.42; H, 3.44; N, 3.19; S, 7.30. Found: C, 57.56; H, 3.53; N, 3.22, S, 7.31.

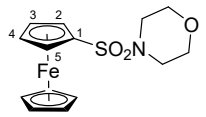


Crystal data for 12. $C_{21}H_{15}F_2FeNO_2S$, M = 439.25, T = 150 K; tetragonal $I4_1/a$ (I.T.#88), a = 13.8079(7), c = 36.167(2) Å, V = 6895.5(8) $Å^3$. Z = 16 d = 1.692 $g.cm^{-3}$, μ = 1.035 mm^{-1}. A final refinement on F^2 with 3956 unique intensities and 258 parameters converged at ωR_F^2 = 0.0540 (R_F = 0.1090) for 3188 observed reflections with $I > 2\sigma(I)$. CCDC 2110442.

Figure 11. Molecular structure of compound **12** (thermal ellipsoids shown at the 30% probability level).

(*N*-Morpholino)sulfonylferrocene – 13a

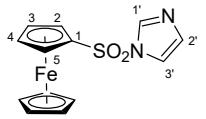
A solution of HOBt (203 mg, 1.50 mmol, 1.50 equiv) and Et_3SiH (203 mg, 1.50 mmol, 1.50 equiv) in DMSO (1.8 mL) was added to compound **2** (268 mg, 1.00 mmol, 1.00 equiv) and morpholine (262 µL, 261 mg, 3.00 mmol, 3.00 equiv) under argon in a pre-dried Schlenk tube. The reaction mixture stirred at 60 °C in an oil-bath for 72 h. The reaction mixture was cooled to rt and water (10 mL) was added. The reaction mixture was extracted with EtOAc (2 x 10 mL) 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 (80:20 to 70:30) to give the title product as an orange solid (205 mg, 61%). Analytical data analogous to those reported previously.[2]



^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.57 (t, J = 1.9 Hz, 2H, FcH, H2 and H5), 4.42 (s, 5H, Cp), 4.42 (t, J = 1.9 Hz, 2H, FcH, H3 and H4), 3.71 (t, J = 4.7 Hz, 4H, CH_2O), 2.91 (t, J = 4.7 Hz, 4H, CH_2N).

(*N*-Imidazolino)sulfonylferrocene – 13b

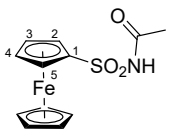
Compound **2** (268 mg, 1.00 mmol, 1.00 equiv), imidazole (136 mg, 2.00 mmol, 2.00 equiv) and cæsium carbonate (977 mg, 3.00 mmol, 3.00 equiv) were placed under argon in a pre-dried Schlenk tube. Acetonitrile (5 mL) was added and the reaction mixture was stirred at rt for 14 h. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 1% of NEt_3 to give the title product as an orange solid (288 mg, 91%). Analytical data analogous to those reported previously.[6]



R_f (eluent: PE-EtOAc 70:30) = 0.16. Mp 197-198 °C. ν_{max} (film)/cm^{-1} 3094, 1460, 1377, 1206, 1156, 1144, 1091, 1052, 1020, 864, 829, 763. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.90 (s, 1H, ArCH, H1'), 7.21 (s, 1H, ArCH, H3'), 7.03 (s, 1H, ArCH, H2'), 4.74 (t, J = 1.9 Hz, 2H, FcCH, H2 and H5), 4.51 (t, J = 1.9 Hz, 2H, FcH, H3 and H4), 4.49 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ (ppm) 136.3 (s, ArCH, C1'), 130.9 (s, ArCH, C2'), 117.2 (s, ArCH, C3'), 85.0 (s, FcC, C1), 72.4 (s, FcCH, C3 and C4), 71.5 (s, Cp), 69.2 (s, FCH, C2 and C5).

(*N*-Acetamido)sulfonylferrocene – 13c

Compound **2** (268 mg, 1.00 mmol, 1.00 equiv), acetamide (119 mg, 2.00 mmol, 2.00 equiv) and sodium hydride (60% dispersion in oil, 174 mg, 4.00 mmol, 4.00 equiv) were placed under argon in a pre-dried Schlenk tube. THF (8 mL) was added and the reaction mixture was stirred at 50 °C for 14 h. The reaction mixture was cooled to 0 °C, water (10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 to 50:50) to give the title product as a yellow solid (193 mg, 63%).



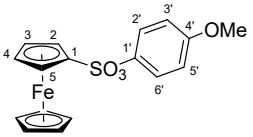
R_f (eluent: PE-EtOAc 70:30) = 0.24. Mp 145-146 °C. ν_{max} (film)/cm^{-1} 3334, 3221, 3114, 1698, 1446, 1403, 1343, 1218, 1194, 1131, 1041, 1024, 992, 829, 814. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.18 (br s, 1H, NH), 4.84 (t, J = 1.8 Hz, 2H, FcH, H2 and H5), 4.47 (t, J = 1.8 Hz, 2H, FcH, H3 and H4), 4.42 (s, 5H, Cp), 2.07 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ

(ppm) 168.3 (s, C=O), 85.6 (s, FcC, C1), 71.5 (s, FcCH, C3 and C4), 71.2 (s, Cp), 70.1 (s, FcCH, C2 and C5), 23.6 (CH_3). Anal. Calcd for $C_{12}H_{13}FeNO_3S$: C, 46.93; H, 4.27; N, 4.56; S, 10.44. Found: C, 47.07; H, 4.40; N, 4.61; S, 10.31.

***O*-(4-Methoxyphenyl)ferrocenesulfonate – 13d**

Compound **2** (536 mg, 2.00 mmol, 1.00 equiv), 4-methoxyphenol (497 mg, 4.00 mmol, 2.00 equiv) and cæsium carbonate (1.95 g, 6.00 mmol, 3.00 equiv) were placed under argon in a pre-dried Schlenk tube. Acetonitrile (10 mL) was added and the reaction mixture was stirred at rt for 14 h. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed four times with aqueous 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 PE-EtOAc (80:20) to give the title product as a yellow solid (697 mg, 93%).

R_f (eluent: PE-EtOAc 80:20) = 0.50. Mp. 98-99 °C. ν_{max} (film)/cm^{-1} 2970, 1497, 1364, 1251, 1207, 1182, 1138, 1104, 1029, 1022, 1055, 856, 834, 822, 785, 729. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.90 (m, 2H, ArCH, H2' and H6'), 6.77 (m, 2H, ArCH, H3' and H5'), 4.57 (t, J = 1.9 Hz, 2H, FcCH, H2 and H5), 4.43 (t, J = 1.9 Hz, 2H, FcCH, H3 and H4), 4.40 (s, 5H, Cp), 3.76 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 158.2 (s, ArC, C4'), 143.4 (s, ArC, C1'), 123.6 (s, ArCH, C2' and C6'), 114.5 (s, ArCH, C3' and C5'), 81.6 (s, FcC, C1), 71.5 (s, FcCH, C3 and C4), 71.2 (s, Cp), 70.0 (s, FcCH, C2 and C5), 55.7 (s, CH_3). Anal. Calcd for $C_{17}H_{16}FeO_4S$: C, 54.86; H, 4.33; S, 8.61. Found: C, 54.88; H, 4.40; S, 8.69.



Crystal data for 13d. $C_{17}H_{16}FeO_4S$, M = 372.21, T = 150 K; monoclinic $P\,2_1/c$ (I.T.#14), a = 16.7313(11), b = 7.4199(5), c = 12.4538(8) Å, β = 96.042(3) °, V = 1537.48(18) Å^3. Z = 4, d = 1.608 g.cm^{-3}, μ = 1.134 mm^{-1}. A final refinement on F^2 with 3490 unique intensities and 209 parameters converged at ωR_F^2 = 0.0824 (R_F = 0.0303) for 3115 observed reflections with $I > 2\sigma(I)$. CCDC 2110443.

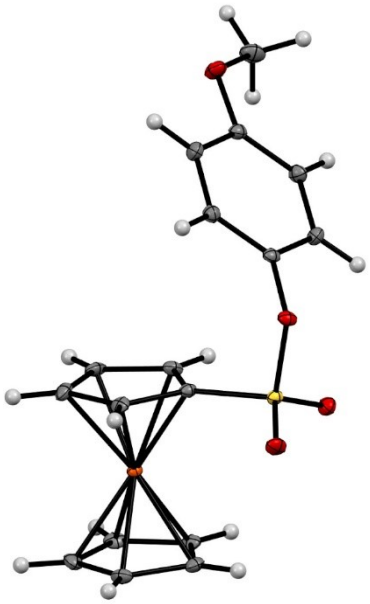
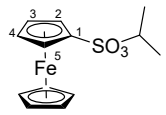


Figure 12. Molecular structure of compound **13d** (thermal ellipsoids shown at the 30% probability level).

***O*-Isopropylferrocenesulfonate – 13e**

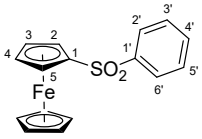
Isopropanol (689 µL, 541 mg, 9.00 mmol, 6.00 equiv) was added dropwise to a suspension of sodium hydride (60% dispersion in oil, 196 mg, 4.60 mmol, 3.00 equiv) in THF (5 mL) and the reaction mixture was stirred at rt for 15 min. Compound **2** (402 mg, 1.50 mmol, 1.00 equiv) was added in one portion and the reaction mixture was stirred for 30 min. Water (20 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 as an orange solid (461 mg, 99%). Analytical data analogous to those reported previously.[7]



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.71 (t, *J* = 1.8 Hz, 2H, FcH, H2 and H5), 4.70 (sept, *J* = 6.3 Hz, 1H, CH), 4.42 (t, *J* = 1.8 Hz, 2H, FcH, H3 and H4), 4.41 (s, 5H, Cp), 1.24 (d, *J* = 6.3 Hz, 6H, $CH(CH_3)_2$).

Phenylsulfonylferrocene – 13f

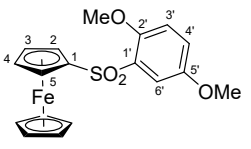
A solution of phenyllithium in Et_2O (prepared by adding dropwise *n*BuLi (1.6 M, 3.60 mL, 5.00 equiv) to a solution of bromobenzene (685 µL, 1.02 g, 6.50 mmol, 1.30 equiv) in Et_2O (20 mL) at 0 °C and stirring for 30 min, 0.25 M, 6.00 mL, 1.50 mmol, 1.50 equiv) was added to a solution of compound **2** (268 mg, 1.00 mmol, 1.00 equiv) in Et_2O (2 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and water (10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 as an orange solid (234 mg, 72%). Analytical data analogous to those reported previously.[8]



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 7.6 Hz, 2H, ArCH, H2' and H6'), 7.50 (t, *J* = 7.1 Hz, 1H, ArCH, H4'), 7.43 (t, *J* = 7.5 Hz, 2H, ArCH, H3' and H4'), 4.68 (s, 2H, FcCH, H2 and H5), 4.49 (s, 5H, Cp), 4.40 (s, 2H, FcCH, H3 and H4). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 143.2 (s, ArC, C1'), 132.7 (ArCH, C4'), 129.1 (s, ArCH, C3' and C5'), 126.8 (s, ArCH, C2' and C6'), 90.4 (s, FcC, C1), 71.3 (s, FcCH, C3 and C4), 70.9 (s, FcC, C1), 69.4 (s, FcCH, C2 and C5).

(2,5-Dimethoxyphenyl)sulfonylferrocene – 13g

$AlCl_3$ (200 mg, 1.50 mmol, 1.50 equiv) was added portionwise to a solution of compound **2** (268 mg, 1.00 mmol, 1.00 equiv) and 1,4-dimethoxybenzene (1.38 g, 10.0 mmol, 10.0 equiv) in CH_2Cl_2 (5 mL) at 0 °C. After addition, the reaction mixture was warmed to rt and stirred for 1 h. Water (10 mL) was added dropwise and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 as an orange solid (351 mg, 91%).



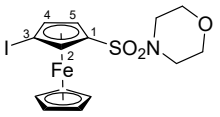
R_f (eluent: PE-EtOAc 70:30) = 0.30. ν_{max} (film)/cm^{-1} 3001, 1488, 1451, 1302, 1272, 1222, 1191, 1127, 1055, 1036, 1011, 865, 820. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50 (d, *J* = 3.1 Hz, 1H, ArCH, H6'), 7.00 (dd, *J* = 3.1, 8.9 Hz, 1H, ArCH, H4'), 6.83 (d, *J* = 8.9 Hz, 1H, ArCH, H3'), 4.76 (s, 2H, FcCH, H2 and H5), 4.48 (s, 5H, Cp), 4.38 (s, 2H, FcCH, H3 and H4), 3.78 (s, 6H, 2 x CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 153.2 (s, ArC, C5'), 151.3 (s, ArC, C2'), 131.0 (s, ArC, C1'), 120.8 (s, ArCH, C4'), 114.2 (s, ArCH, C3'), 113.3 (s, ArCH, C6'), 89.5 (s, FcC, C1), 70.8 (s, Cp), 70.7 (s, FcCH, C3 and C4), 70.5 (s, FcCH, C2 and C5), 56.6 and 56.1 (s, CH_3). Anal. Calcd for $C_{18}H_{18}FeO_4S$: C, 55.97; H, 4.70; S, 8.30. Found: C, 55.03; H, 4.61; S, 8.37.

3-Iodo-(*N*-morpholino)sulfonylferrocene – 13h

A solution of HOBt (101 mg, 0.75 mmol, 1.50 equiv) and Et_3SiH (160 µL, 116 mg, 1.00 mmol, 2.00 equiv) in DMSO (0.9 mL) was added to compound **6a** (197 mg, 0.50 mmol, 1.00 equiv) and morpholine (131 µL, 131 mg, 1.50 mmol, 3.00 equiv) under argon in a pre-dried Schlenk tube. The reaction mixture stirred at 60 °C in an oil-bath for 16 h. The reaction mixture was cooled to rt and water (10 mL) was

added. The reaction mixture was extracted with EtOAc (2 x 10 mL) 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 (80:20) to give the title product as an orange solid (177 mg, 76%).

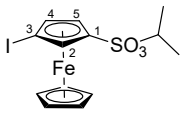
R_f (eluent: PE-EtOAc 70:30) = 0.45. Mp. 129-130 °C. ν_{max} (film)/cm^{-1} 3082, 2974, 2848, 1453, 1344, 1328, 1295, 1260, 1149, 1109, 1071, 938, 874, 829, 724. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.83 (t, *J* = 1.3 Hz, 1H, FcCH, H2), 4.67 (dd, *J* = 1.3, 2.5 Hz, 1H, FcCH, H4), 4.57 (dd, *J* = 1.3, 2.5 Hz, 1H, FcCH, H5), 4.44 (s, 5H, Cp), 3.72 (m, 4H, CH_2O), 2.93 (m, 4H, CH_2N). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 83.1 (s, FcC, C1), 77.5 (s, FcCH, C4), 74.9 (s, FcCH, C2), 73.8 (s, Cp), 70.1 (s, FcCH, C5), 66.1 (s, CH_2O), 46.0 (s, CH_2N), 38.8 (s, FcC, C3). Anal. Calcd for $C_{14}H_{16}FeINO_3S$: C, 36.47; H, 3.50; S, 6.95. Found: C, 36.51; H, 3.70; S, 7.03.



3-Iodo-*O*-isopropylferrocenesulfonate – 13i

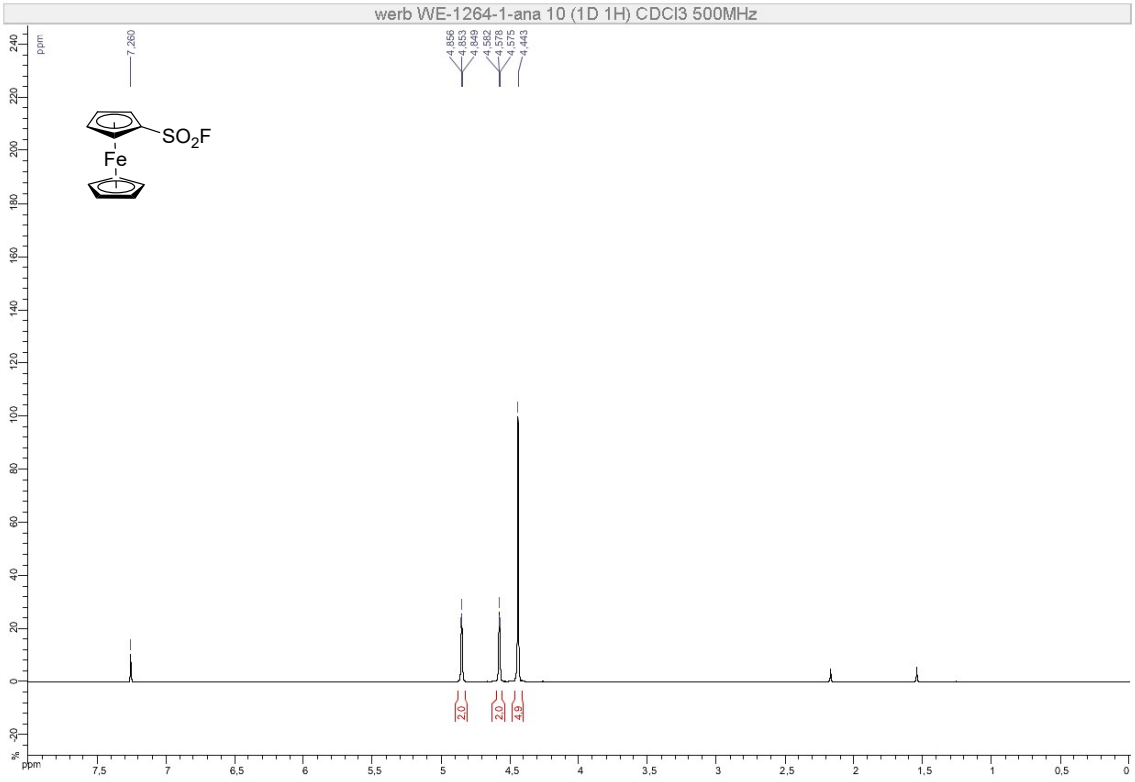
Isopropanol (230 µL, 180 mg, 3.00 mmol, 6.00 equiv) was added dropwise to a suspension of sodium hydride (60% dispersion in oil, 65.2 mg, 1.50 mmol, 3.00 equiv) in THF (2 mL) and the reaction mixture was stirred at rt for 15 min. Compound **6a** (197 mg, 0.50 mmol, 1.00 equiv) was added in one portion and the reaction mixture was stirred for 30 min. Water (10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). 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 as an orange oil (195 mg, 89%). Analytical data analogous to those reported previously.[7]

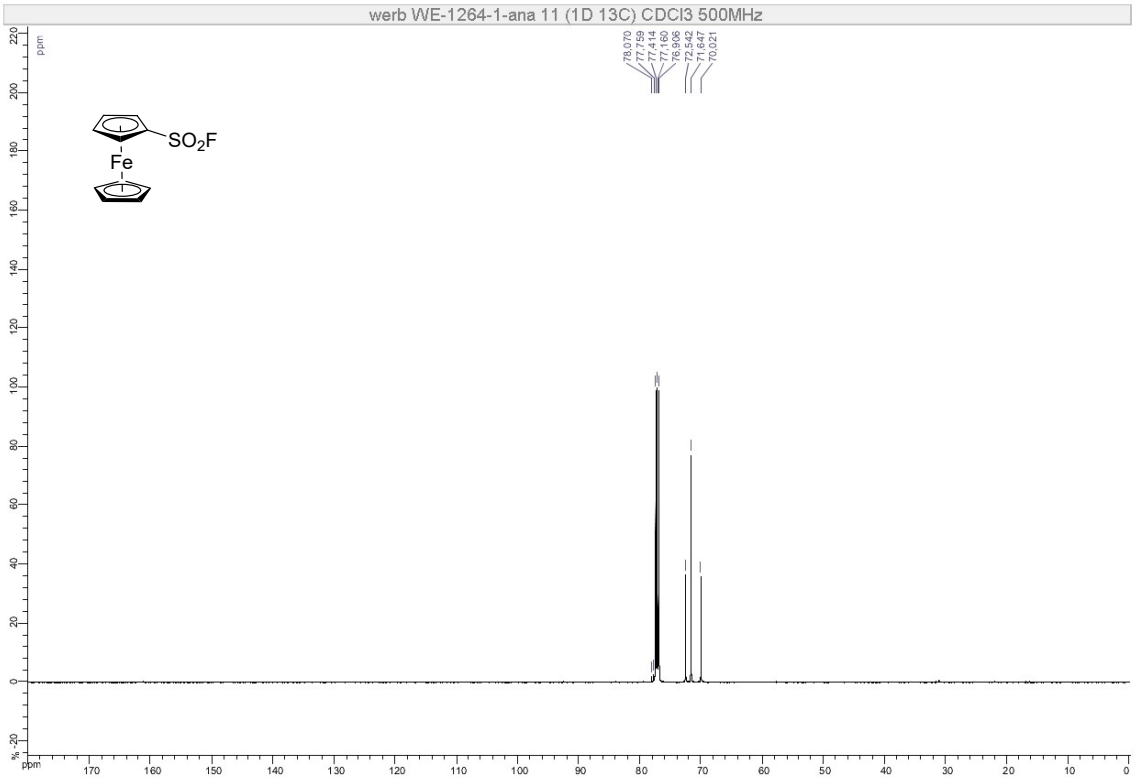
R_f (eluent: PE-EtOAc 90:10) = 0.55. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.97 (t, *J* = 1.3 Hz, 1H, FcCH, H2), 4.73 (q, *J* = 6.2 Hz, 1H, CH), 4.71 (dd, *J* = 1.3, 2.6 Hz, 1H, FcCH, H5), 4.67 (dd, *J* = 1.3, 2.6 Hz, 1H, FcCH, H4), 4.43 (s, 5H, Cp), 1.27 (d, *J* = 6.2 Hz, 3H, CH_3), 1.26 (d, *J* = 6.2 Hz, 3H, CH_3).

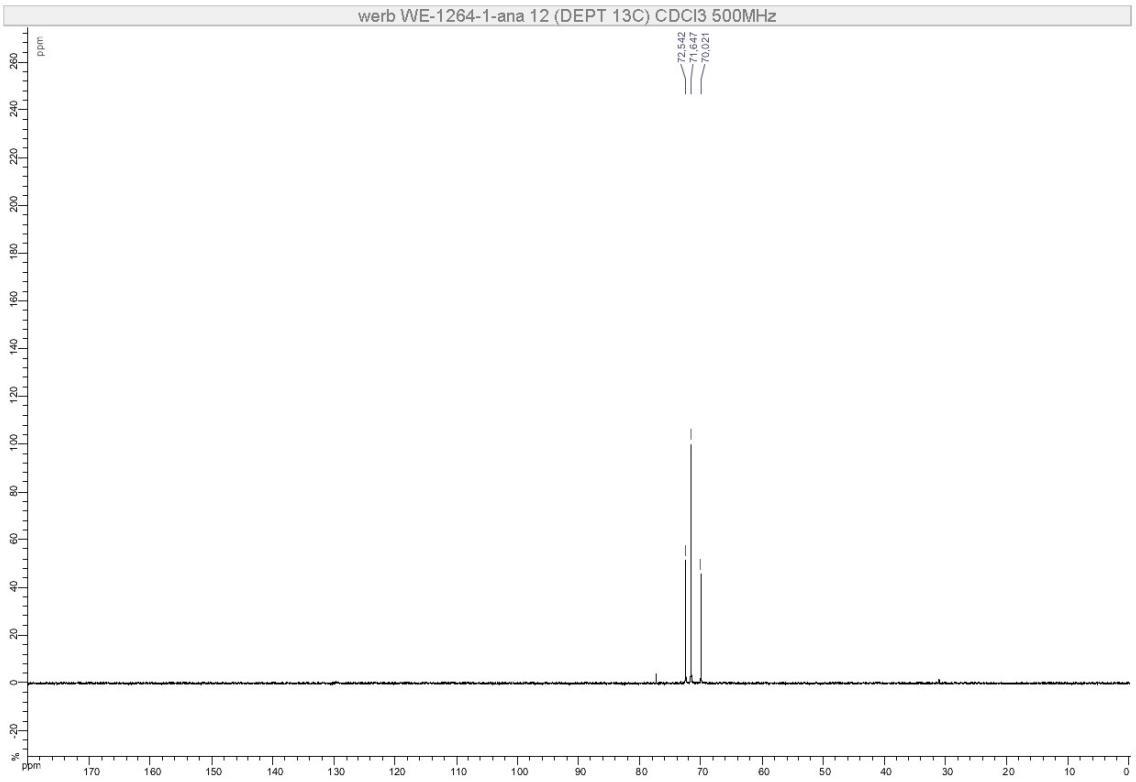


NMR Spectra

Compound 2



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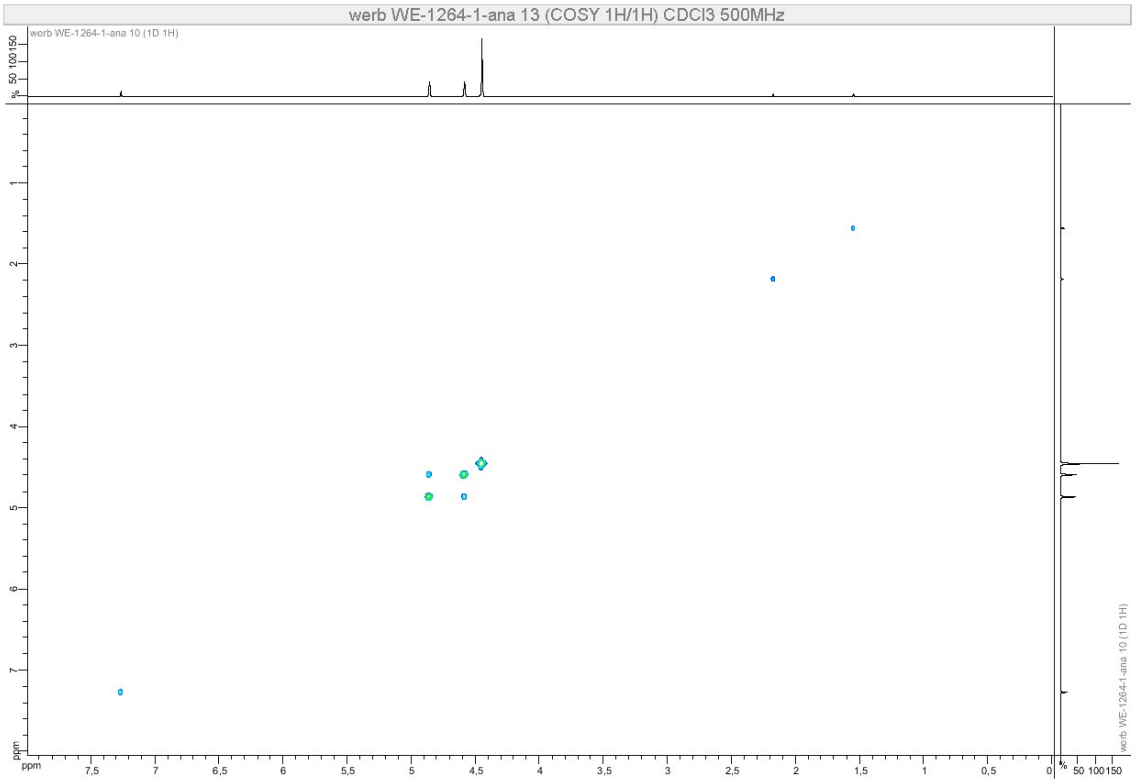
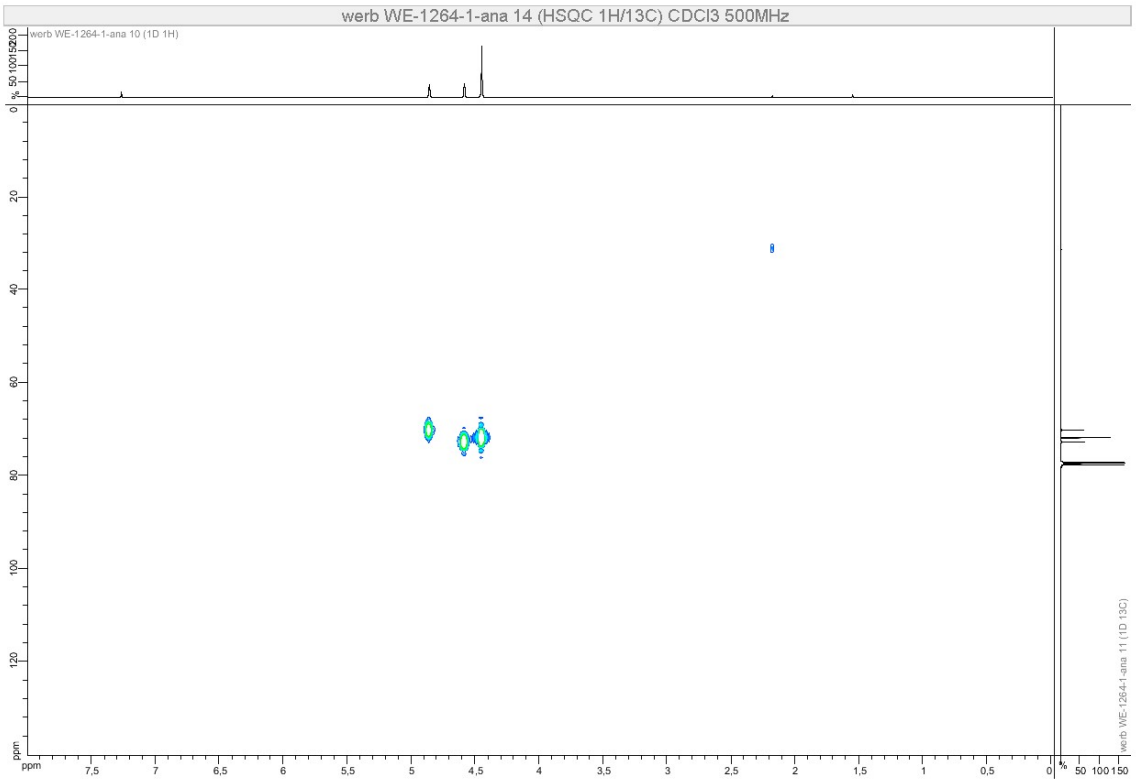
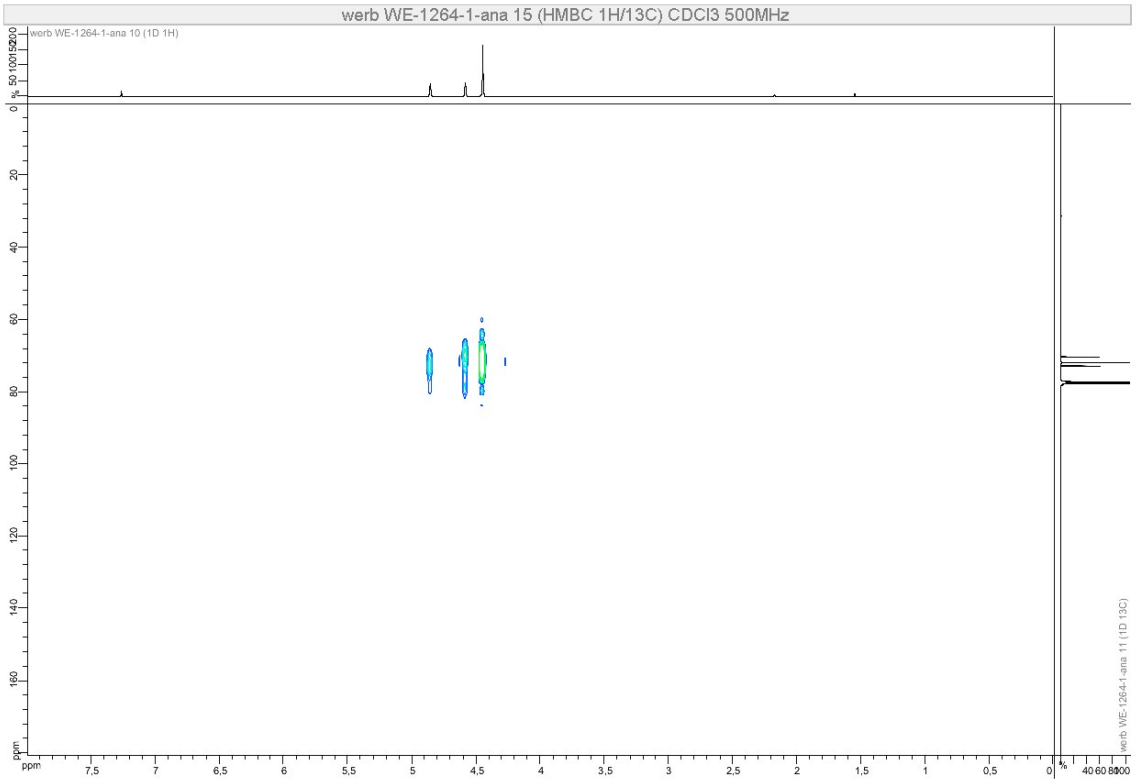
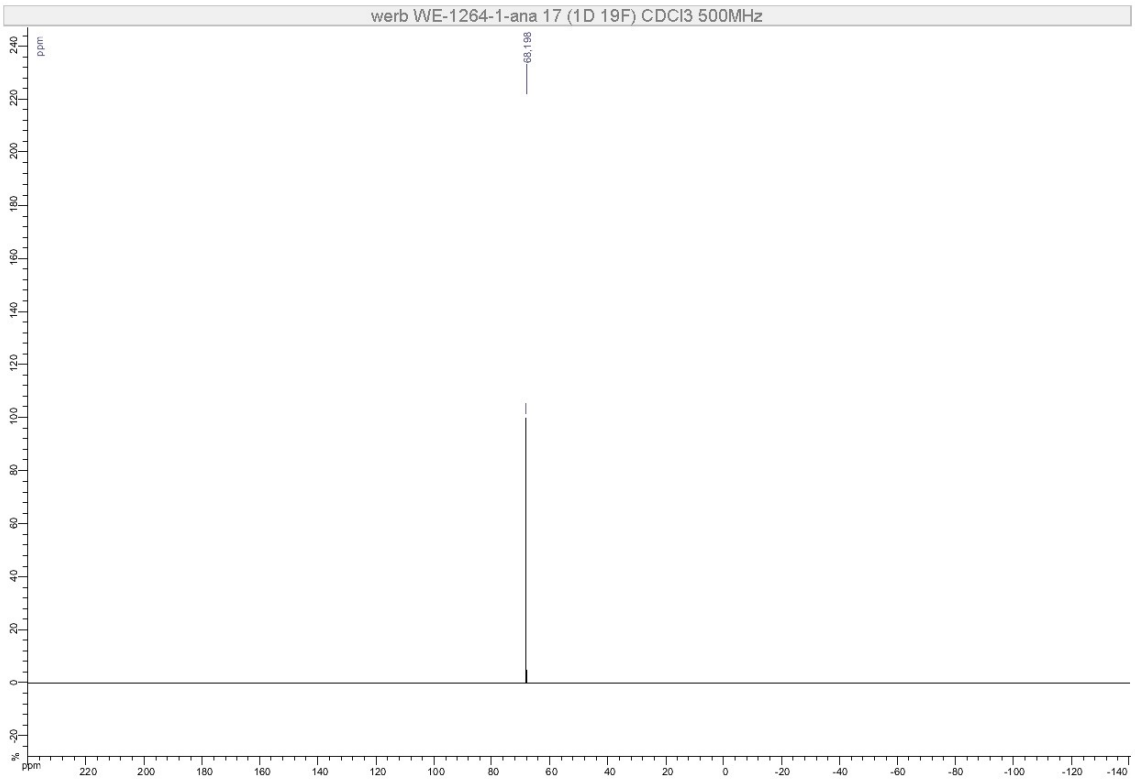
72.542
71.647
70.021
ppm

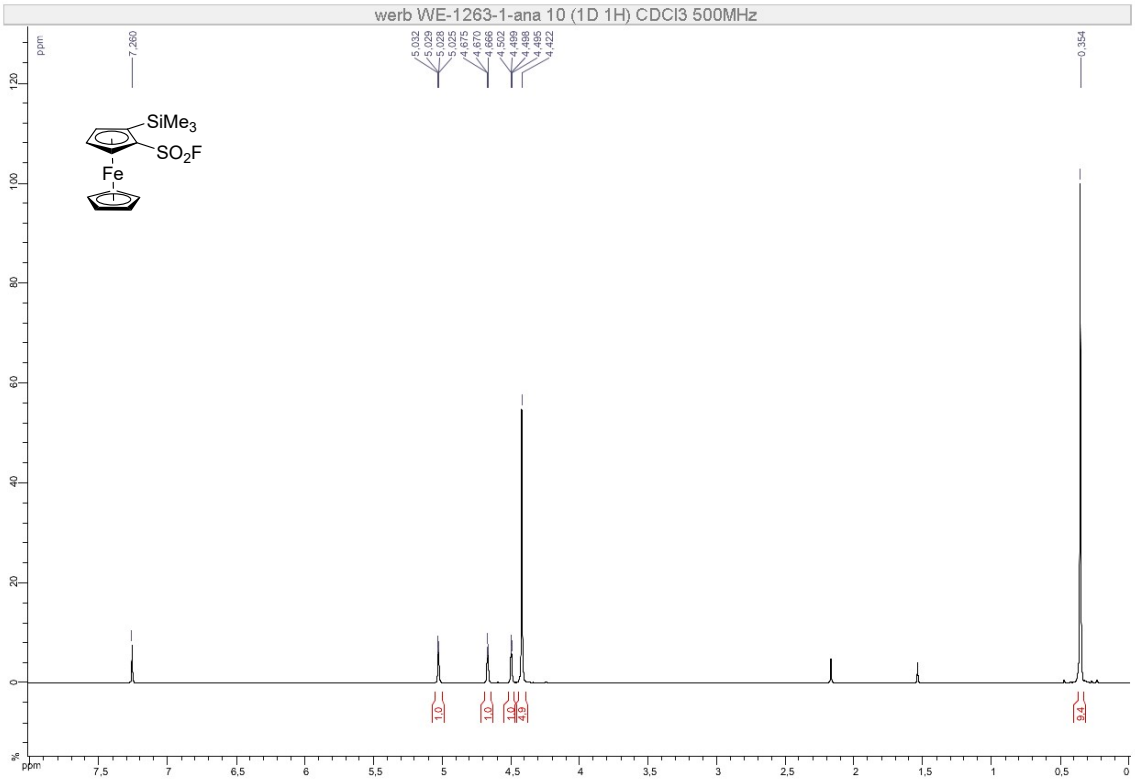

werb WE-1264-1-ana 13 (COSY 1H/1H) CDCl3 500MHz
werb WE-1264-1-ana 10 (1D 1H)
ppm

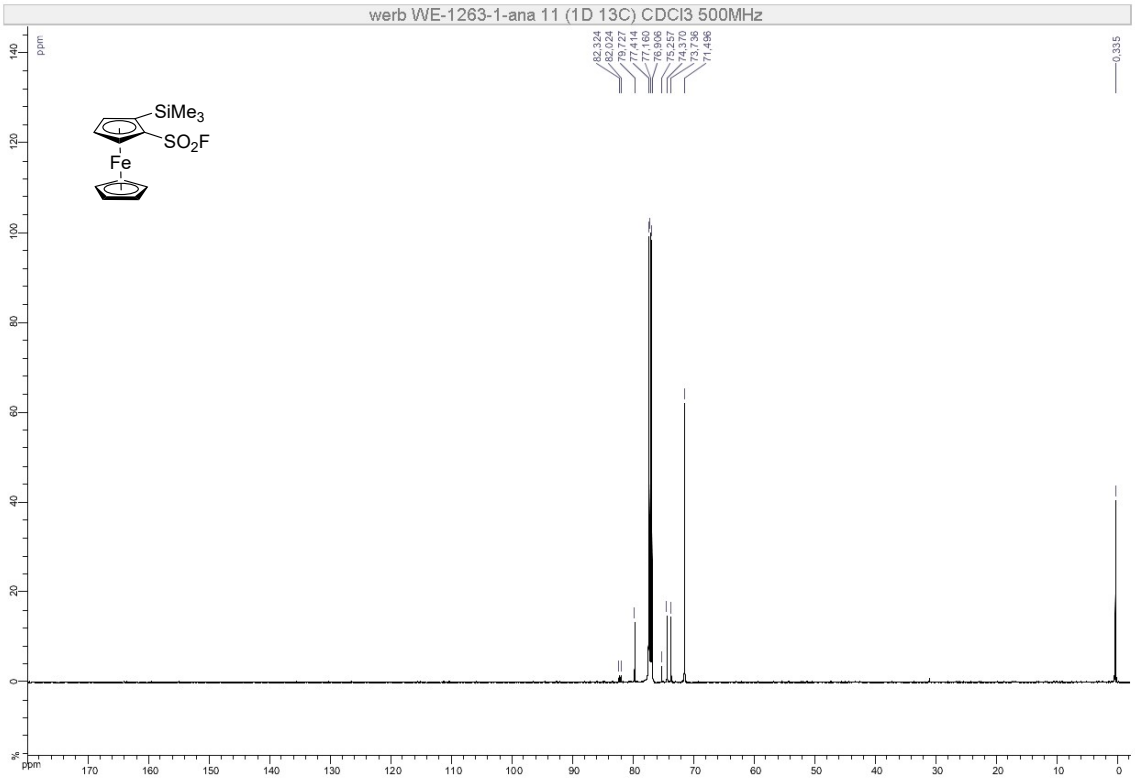

werb WE-1264-1-ana 14 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1264-1-ana 10 (1D 1H)
werb WE-1264-1-ana 11 (1D 13C)
ppm

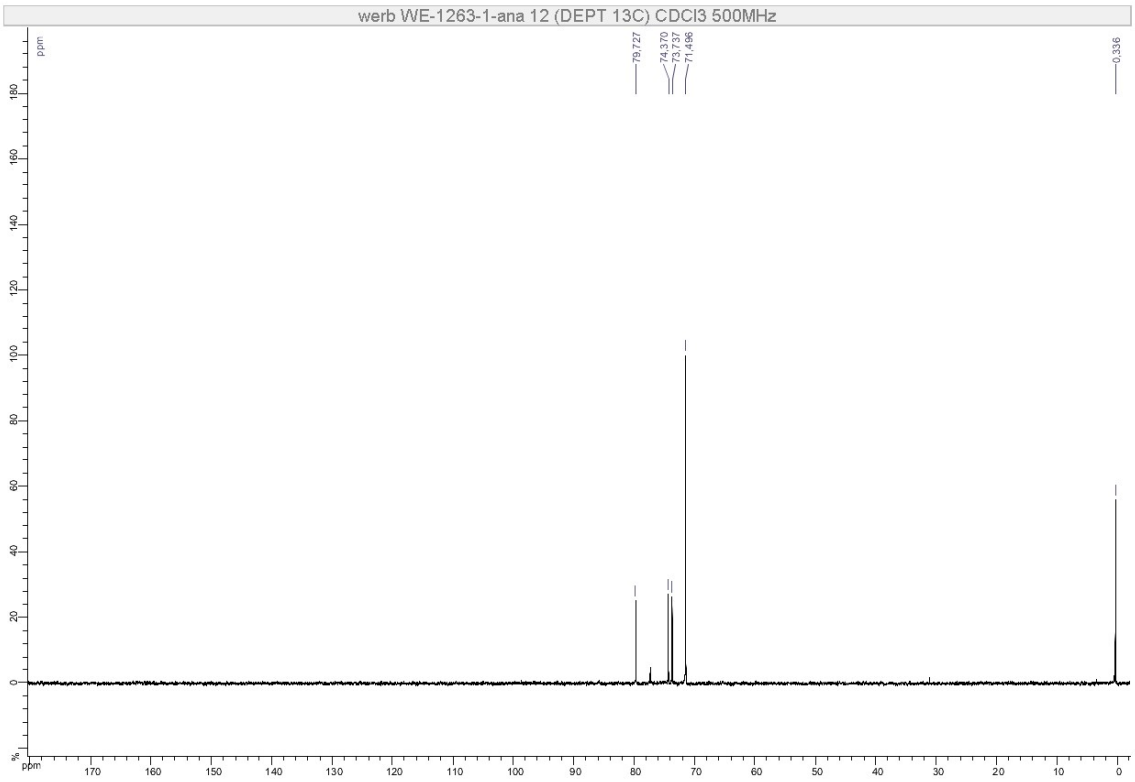

werb WE-1264-1-ana 15 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1264-1-ana 10 (1D 1H)
werb WE-1264-1-ana 11 (1D 13C)
ppm

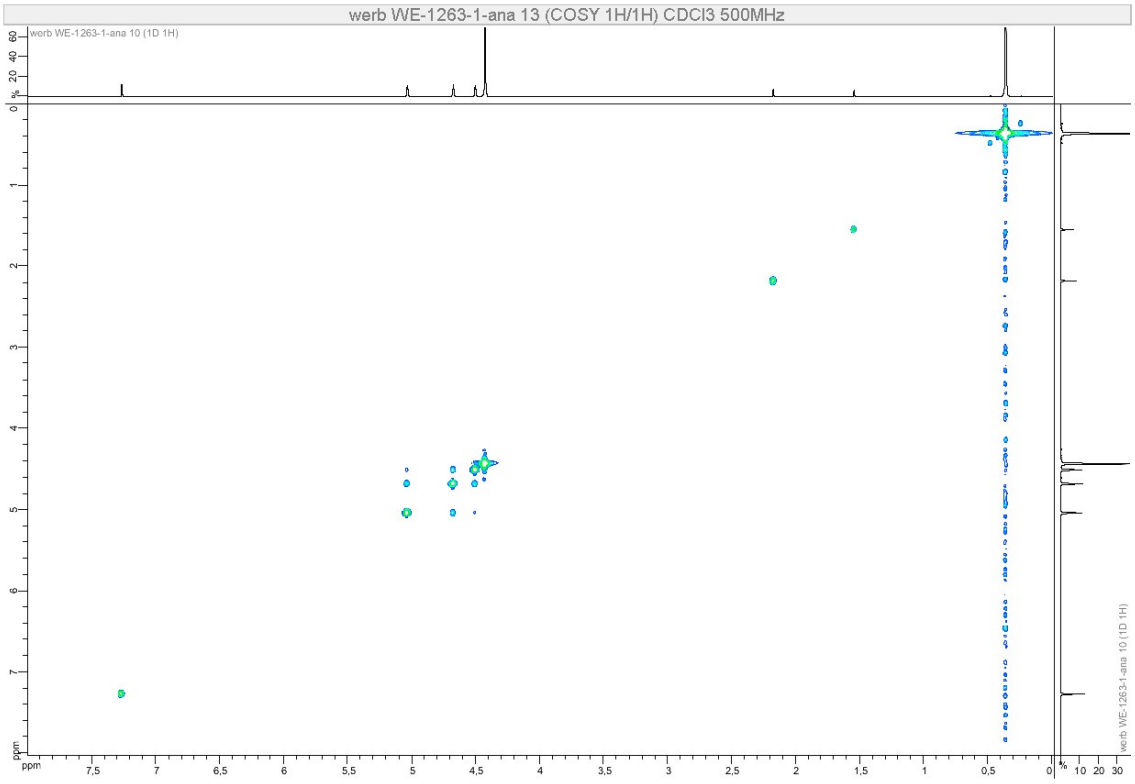

werb WE-1264-1-ana 17 (1D 19F) CDCl3 500MHz
ppm
68,198
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140

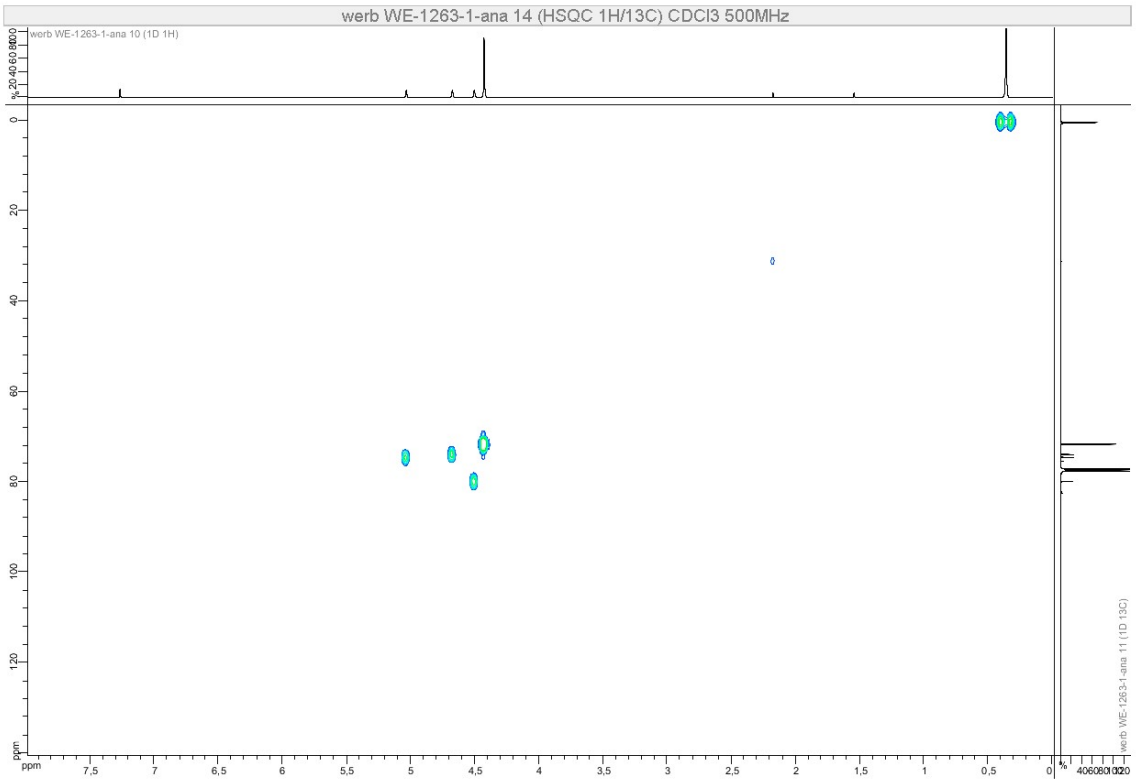
Compound 3a

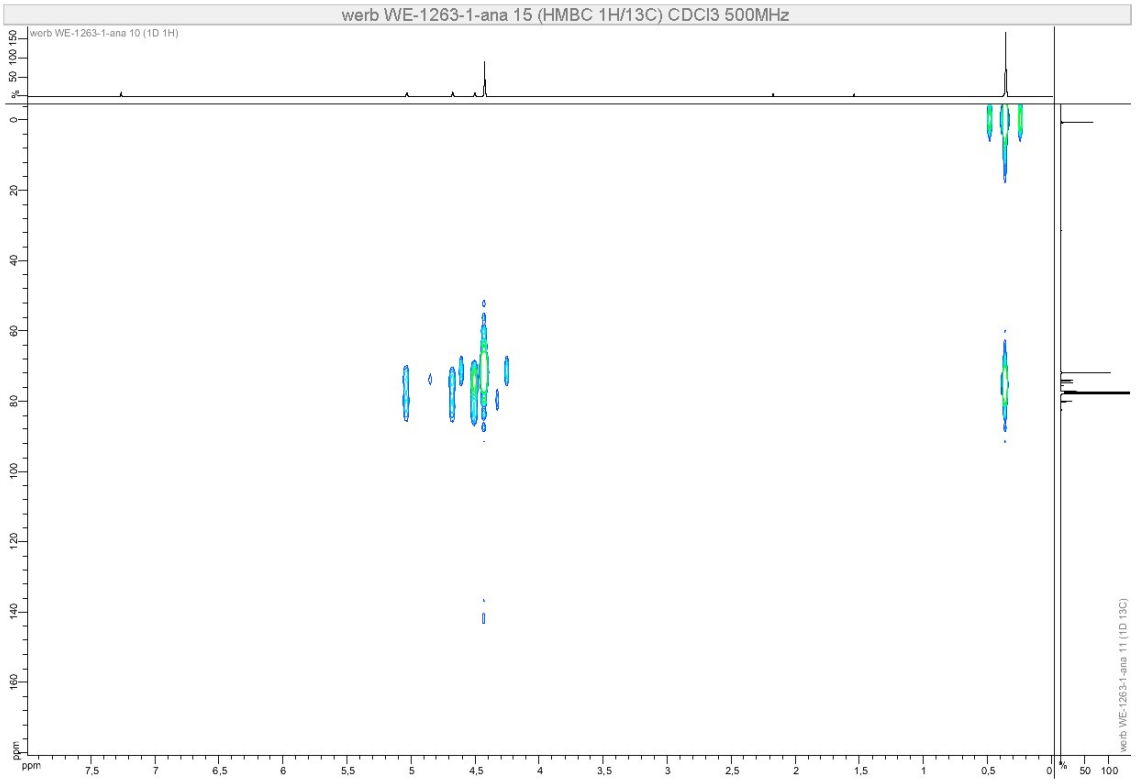

werb WE-1263-1-ana 10 (1D 1H) CDCl3 500MHz
SiMe3
SO2F
Fe

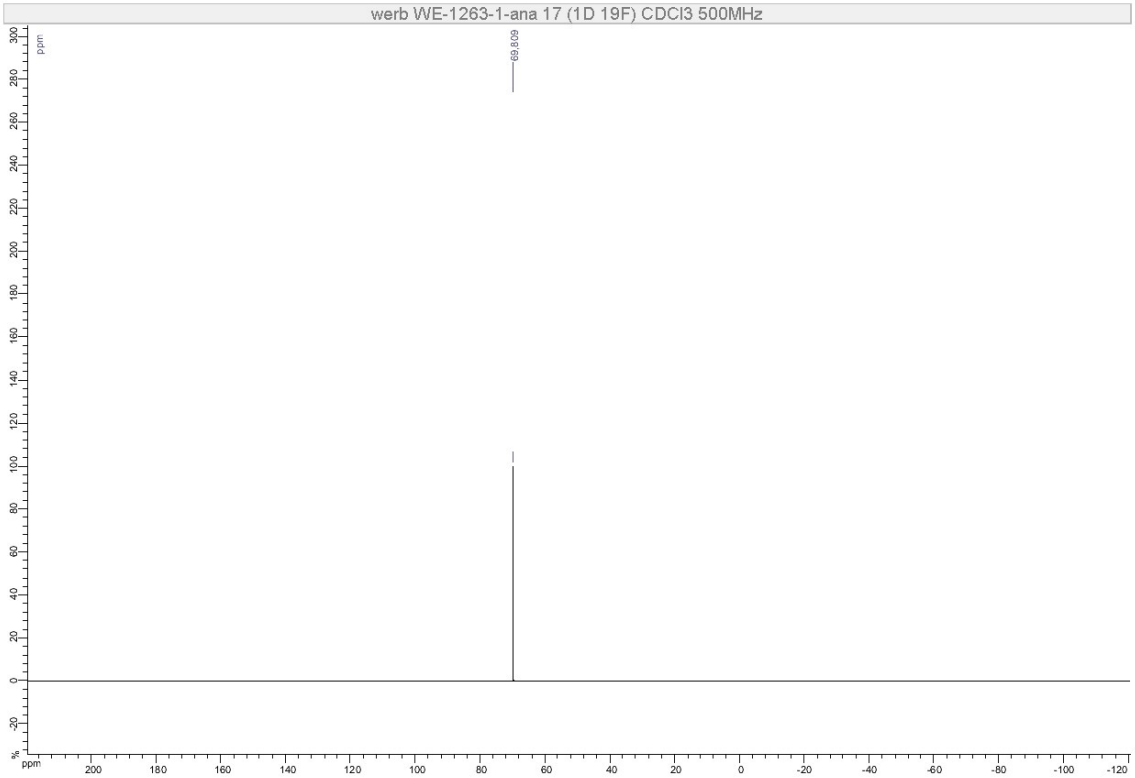

werb WE-1263-1-ana 11 (1D 13C) CDCl3 500MHz
SiMe3
SO2F
Fe


werb WE-1263-1-ana 12 (DEPT 13C) CDCl3 500MHz
79,727
74,370
73,737
71,496
0,336
ppm

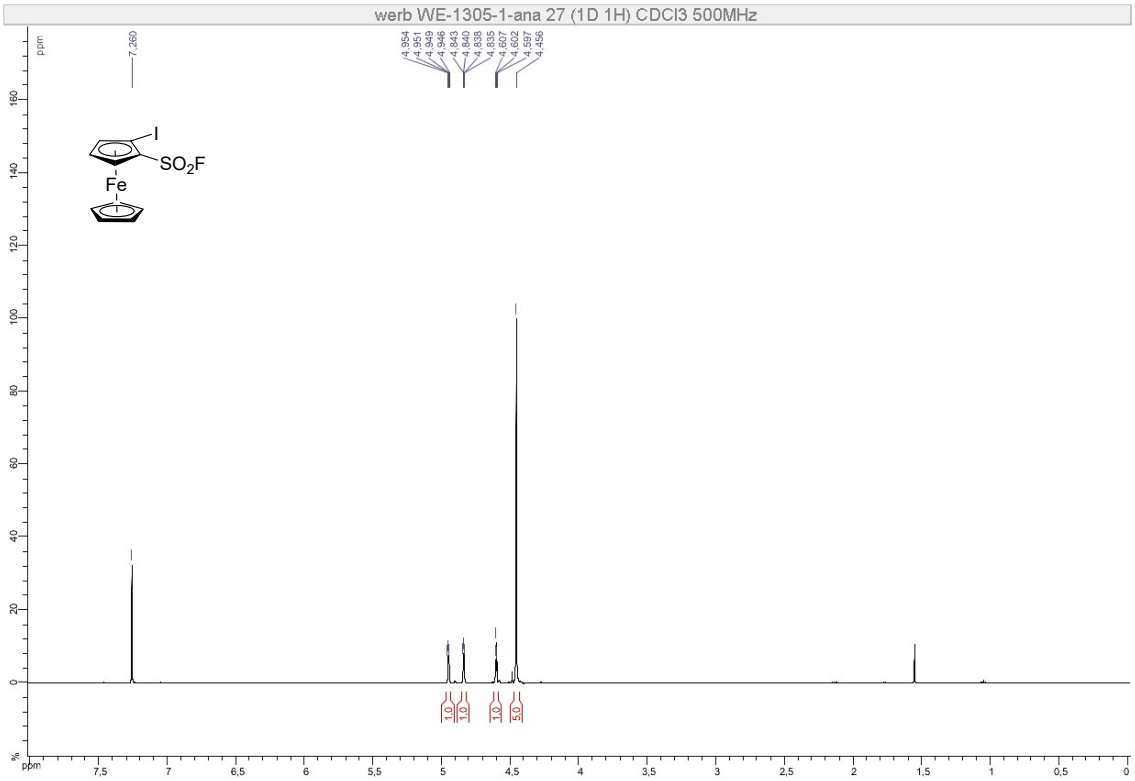

werb WE-1263-1-ana 13 (COSY 1H/1H) CDCl3 500MHz
werb WE-1263-1-ana 10 (1D 1H)
ppm

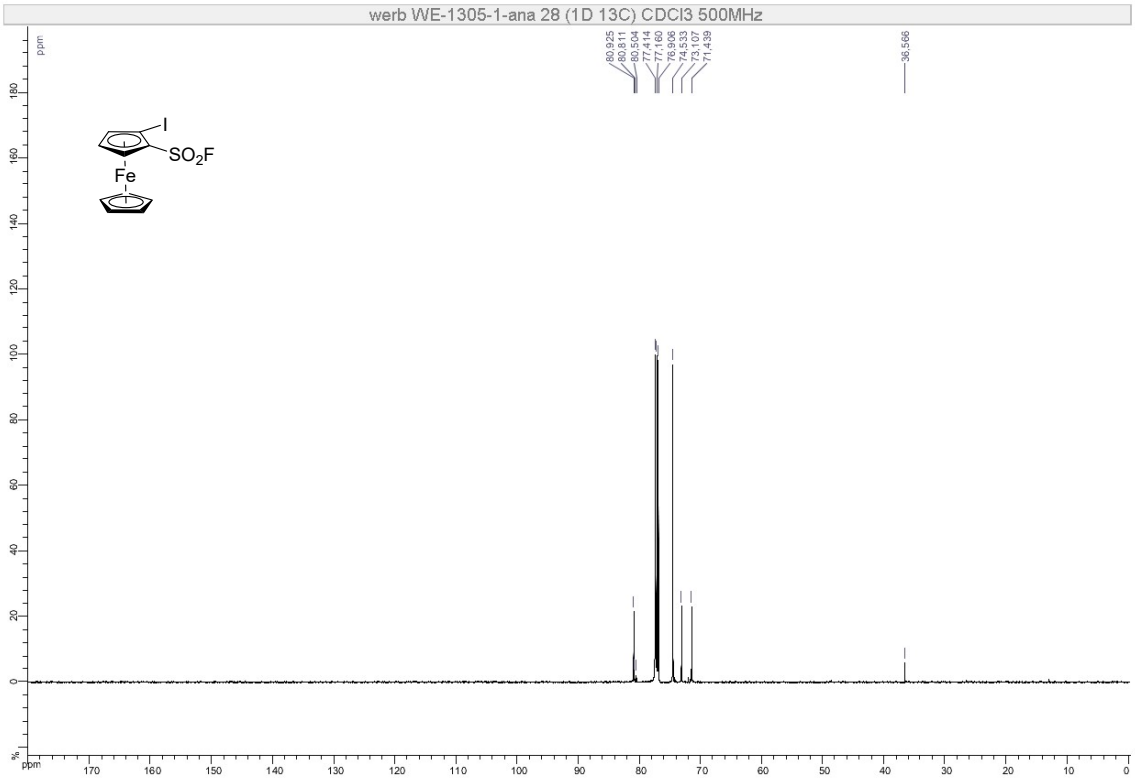

werb WE-1263-1-ana 14 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1263-1-ana 10 (1D 1H)
werb WE-1263-1-ana 11 (1D 13C)
ppm

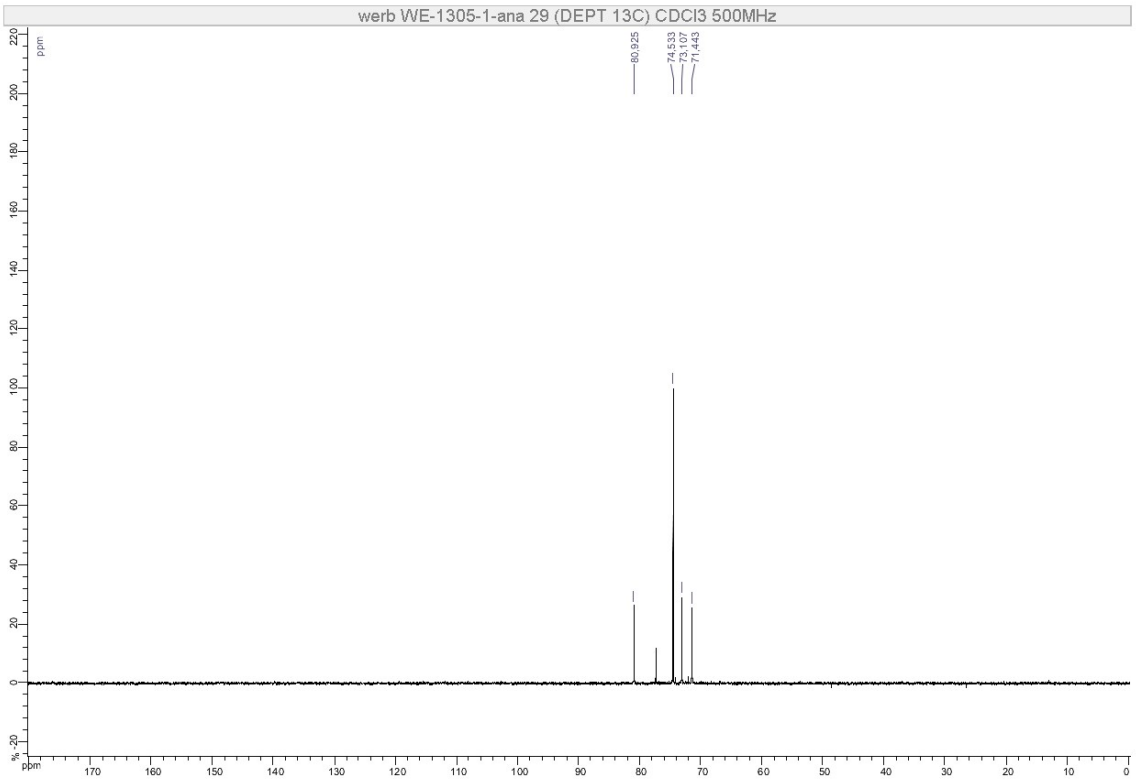

werb WE-1263-1-ana 15 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1263-1-ana 10 (1D 1H)
werb WE-1263-1-ana 11 (1D 13C)
ppm

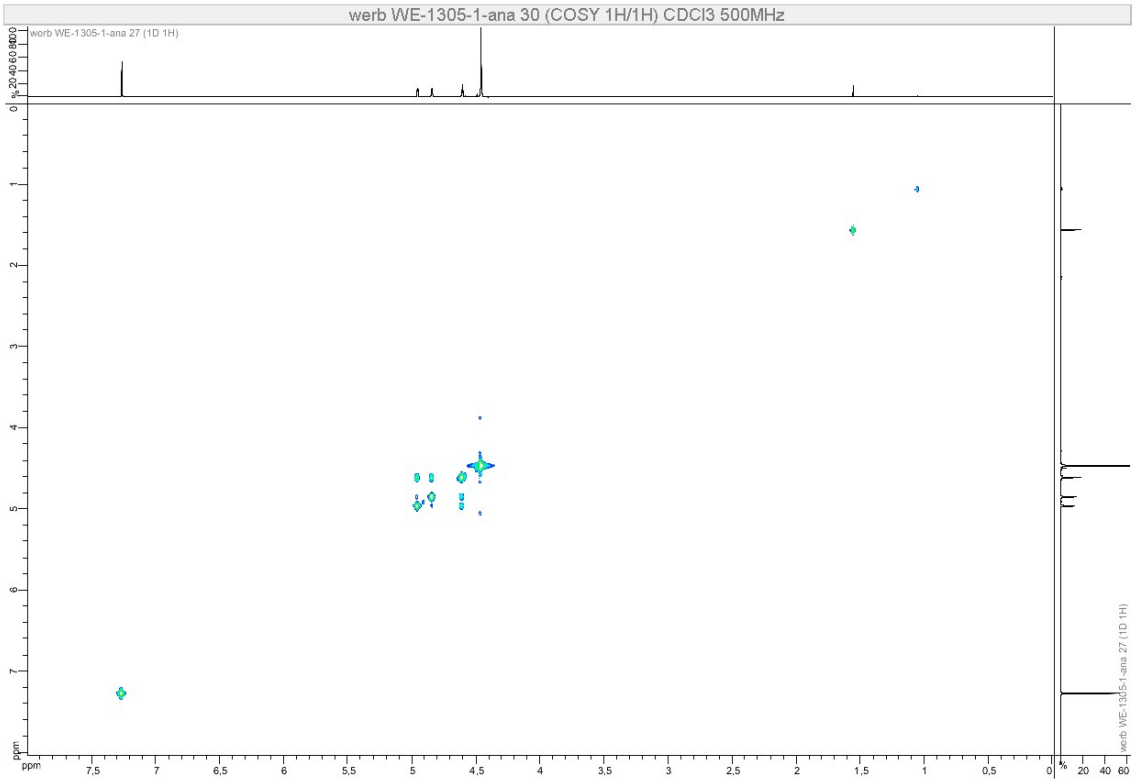

werb WE-1263-1-ana 17 (1D 19F) CDCl3 500MHz
ppm
69.809
ppm
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120

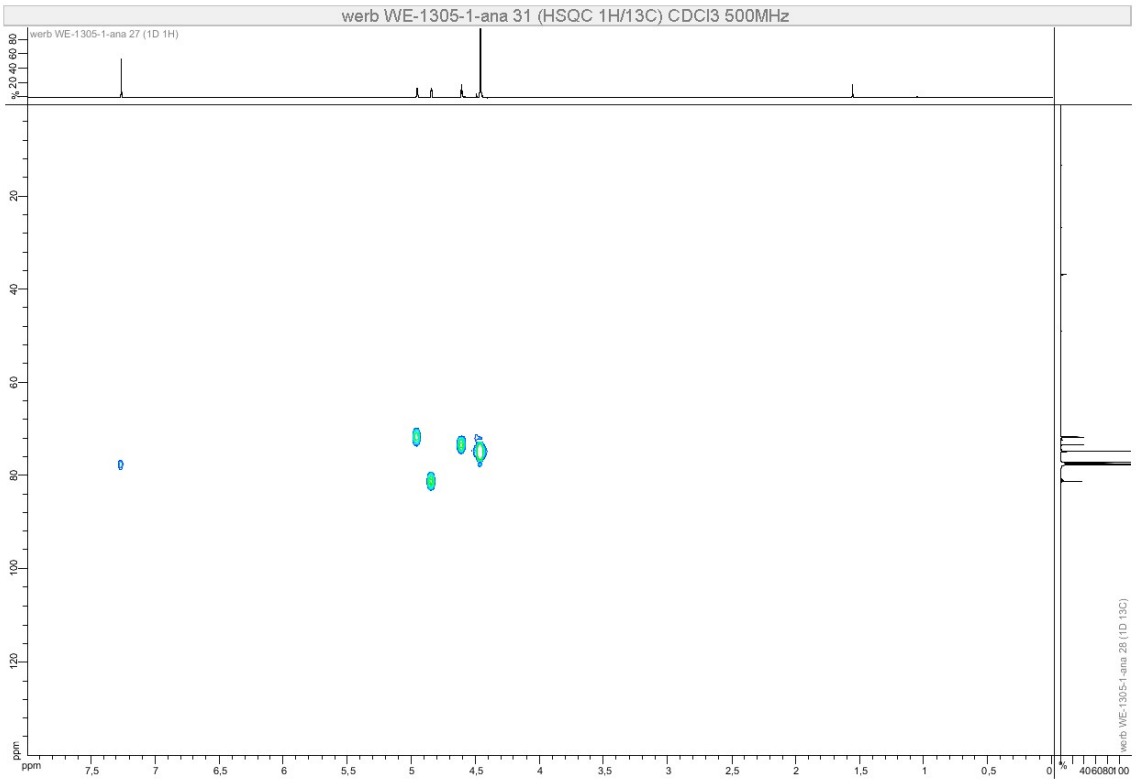
Compound 3b

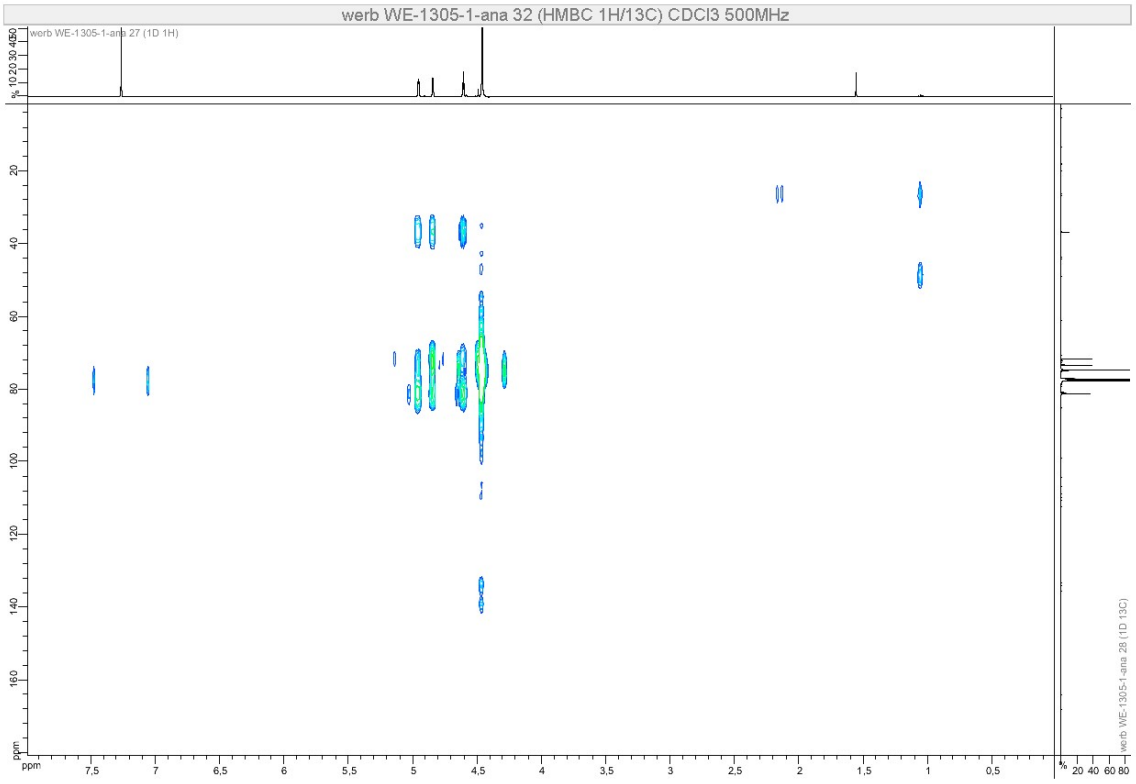

werb WE-1305-1-ana 27 (1D 1H) CDCl3 500MHz
7.260
4.954
4.951
4.949
4.946
4.843
4.840
4.838
4.835
4.607
4.602
4.597
4.456
I
SO2F
Fe
1.0
1.0
1.40
5.0
ppm

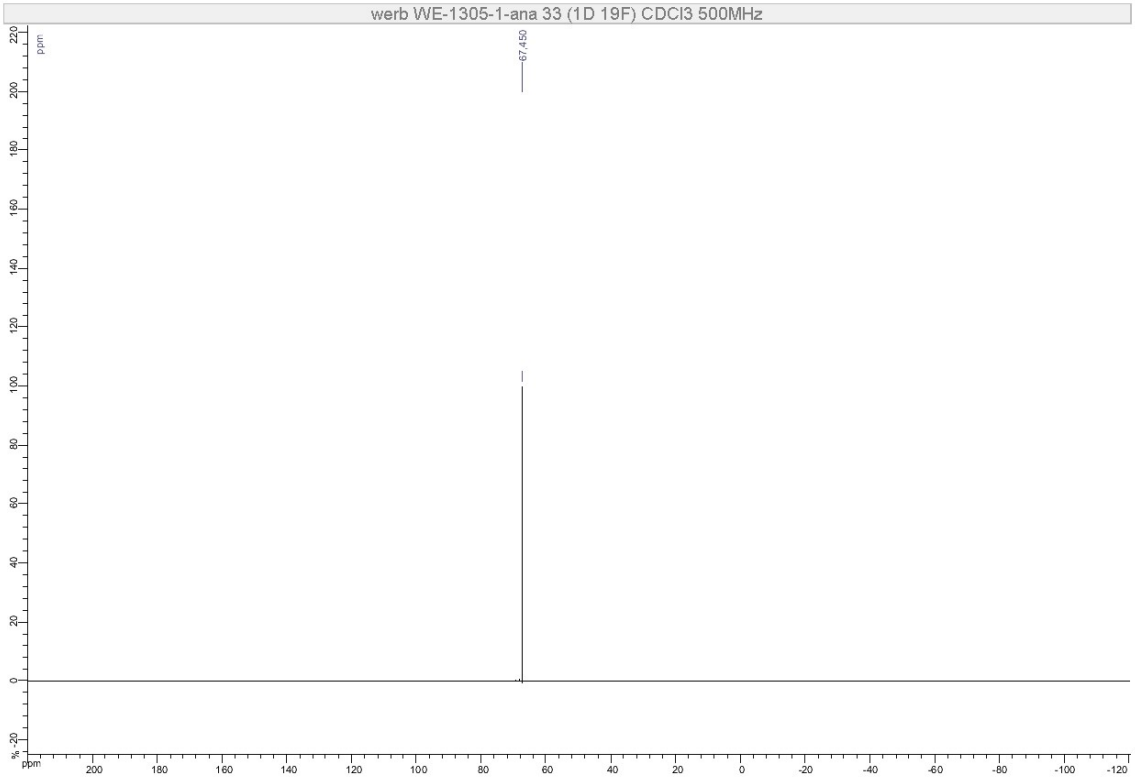

werb WE-1305-1-ana 28 (1D 13C) CDCl3 500MHz
80.925
80.811
80.504
77.414
77.160
76.906
74.533
73.107
71.439
36.566
I
SO2F
Fe
ppm


werb WE-1305-1-ana 29 (DEPT 13C) CDCl3 500MHz
80,925
74,533
73,107
71,443
ppm

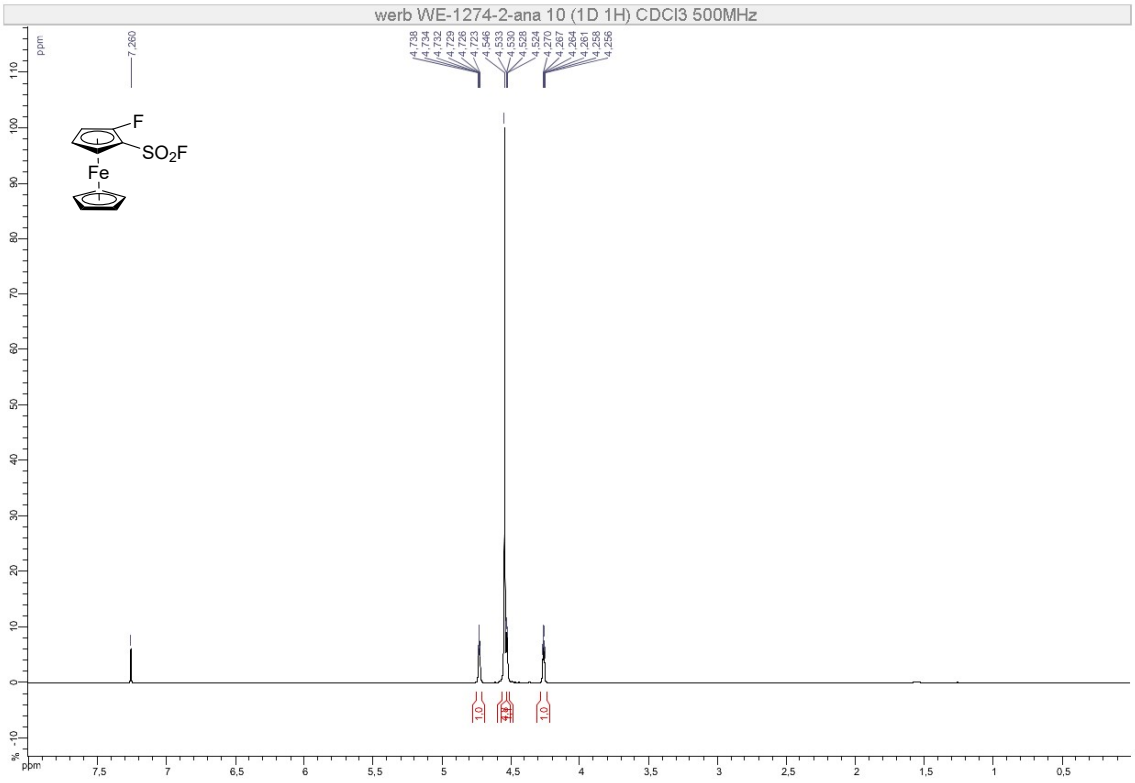

werb WE-1305-1-ana 30 (COSY 1H/1H) CDCl3 500MHz
werb WE-1305-1-ana 27 (1D 1H)
ppm

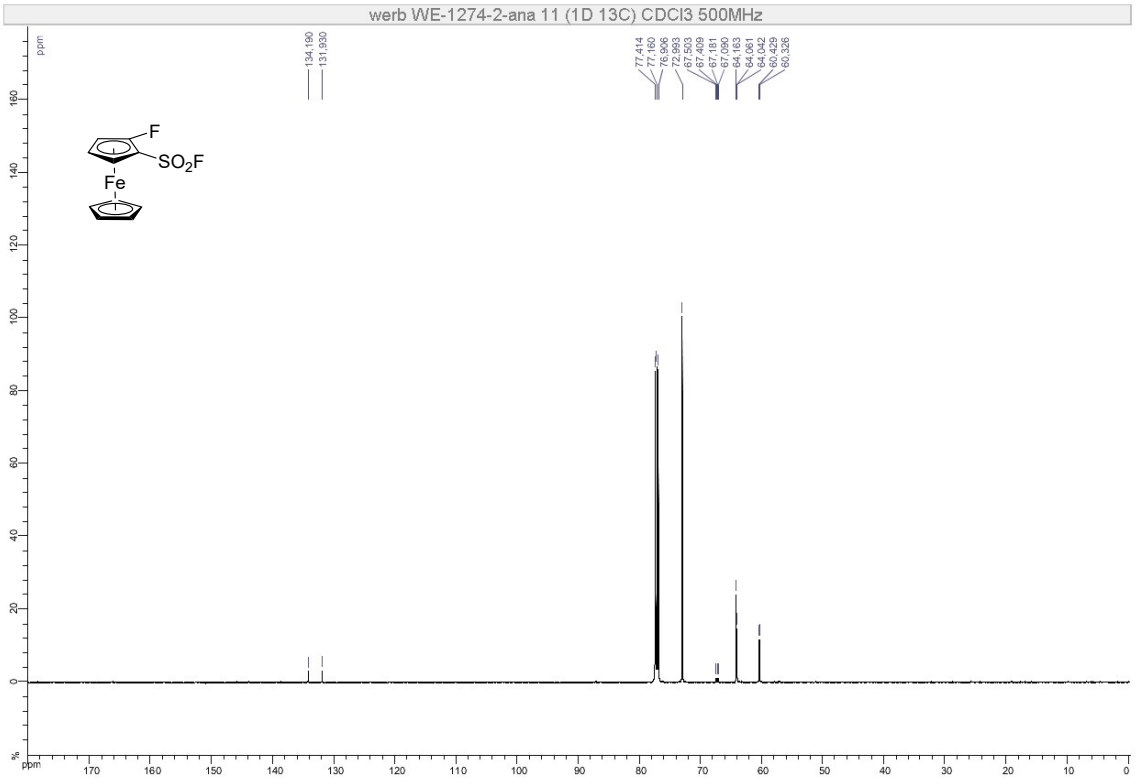

werb WE-1305-1-ana 31 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1305-1-ana 27 (1D 1H)
werb WE-1305-1-ana 28 (1D 13C)
ppm

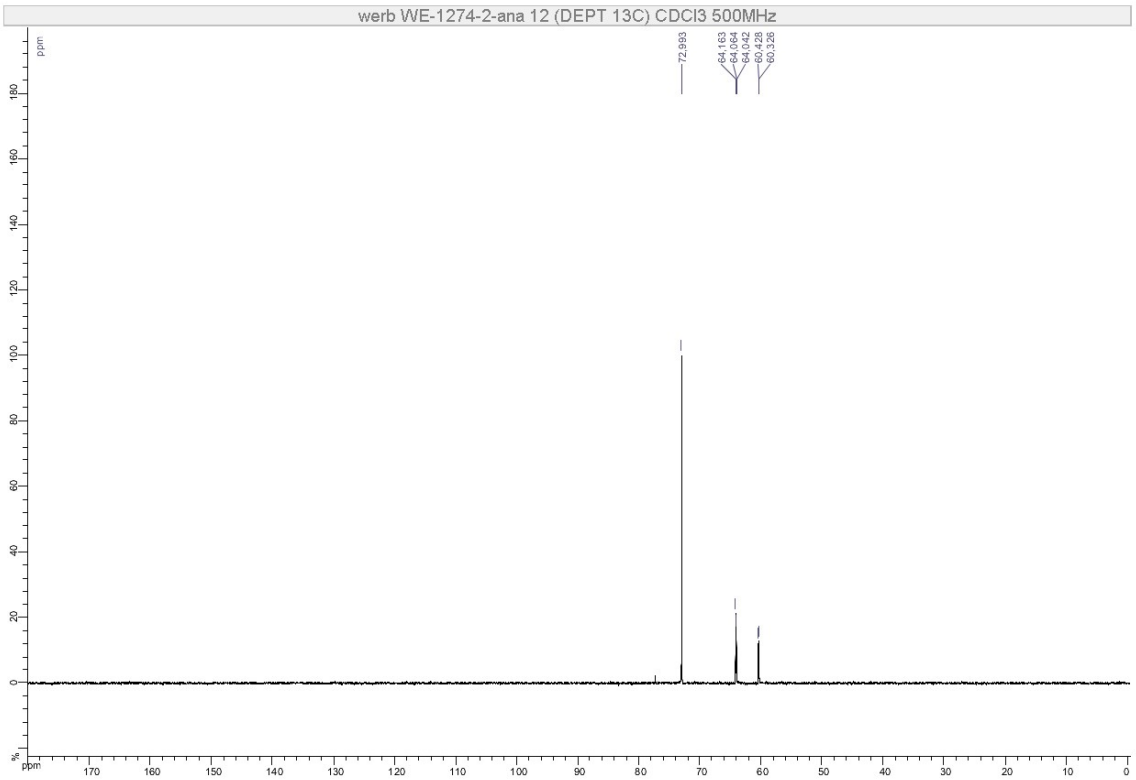

werb WE-1305-1-ana 32 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1305-1-ana 27 (1D 1H)
werb WE-1305-1-ana 28 (1D 13C)
ppm

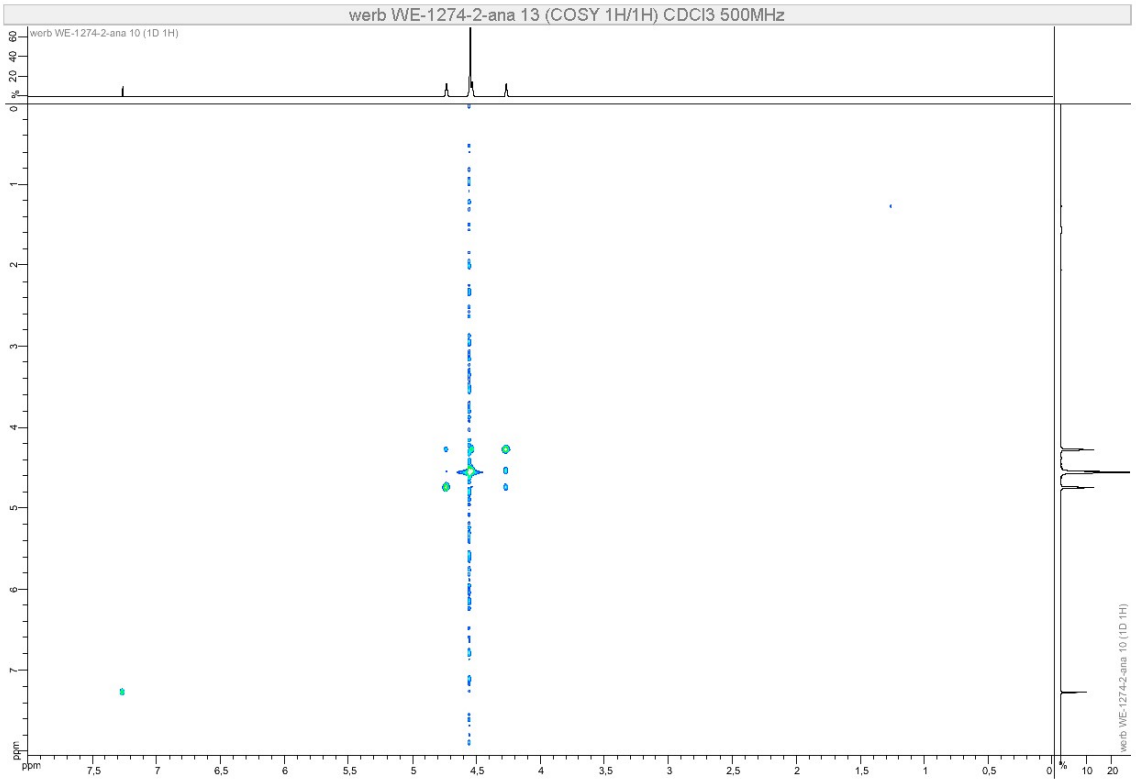

werb WE-1305-1-ana 33 (1D 19F) CDCl3 500MHz
ppm
67.450
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120

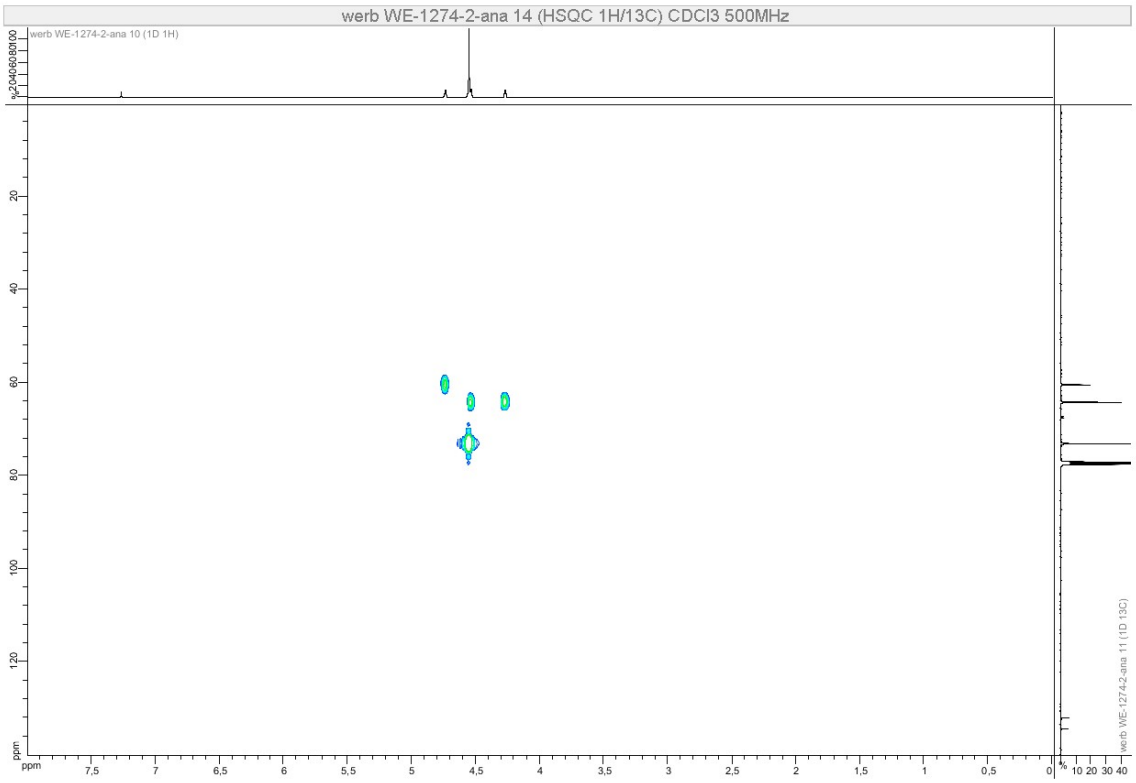
Compound 3c

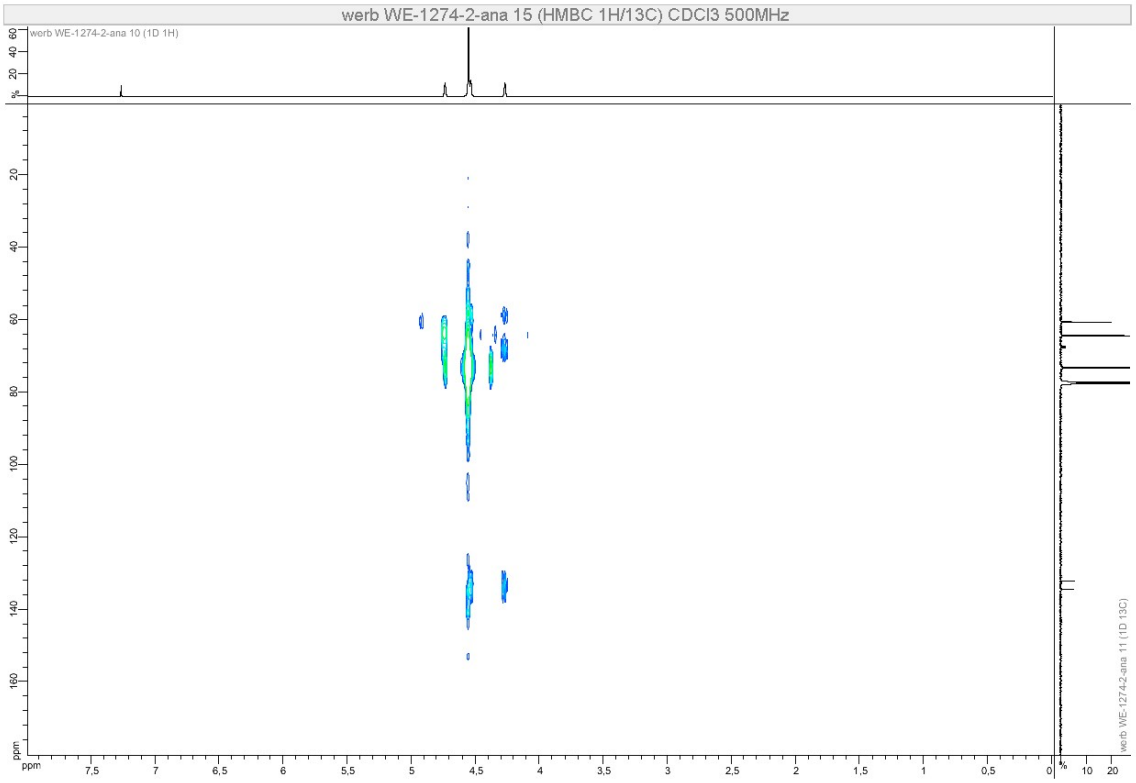

werb WE-1274-2-ana 10 (1D 1H) CDCl3 500MHz
F
SO2F
Fe

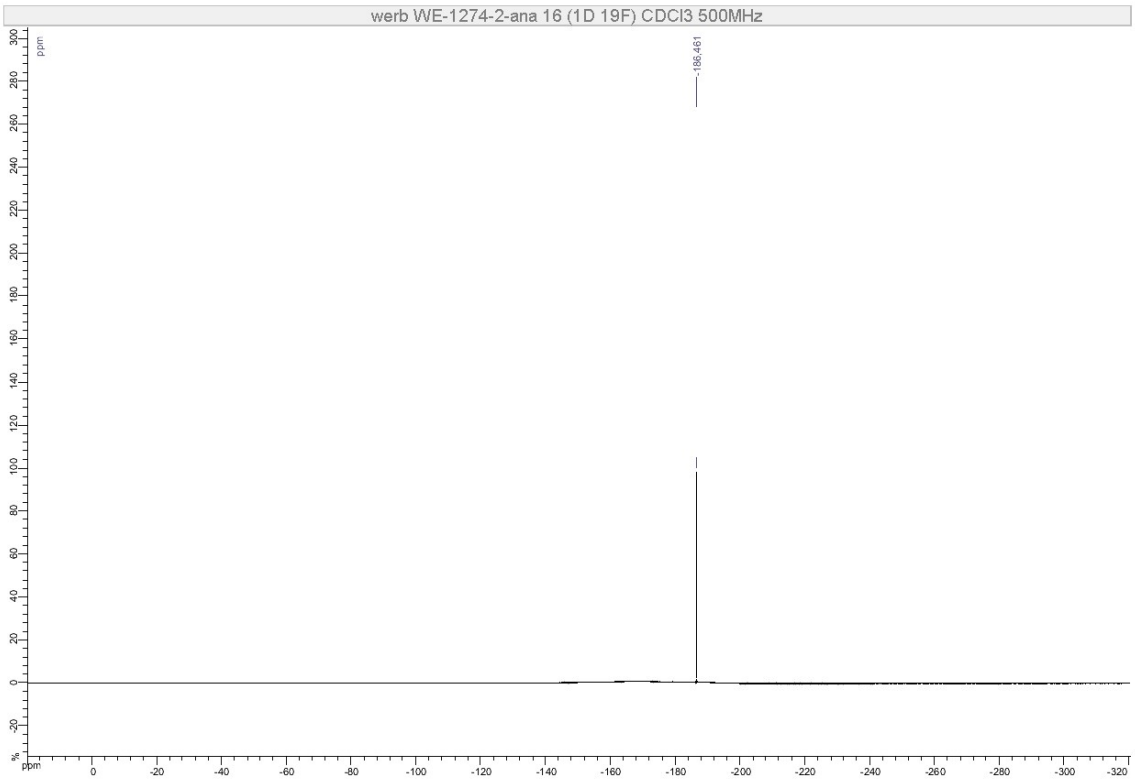

werb WE-1274-2-ana 11 (1D 13C) CDCl3 500MHz
F
SO2F
Fe

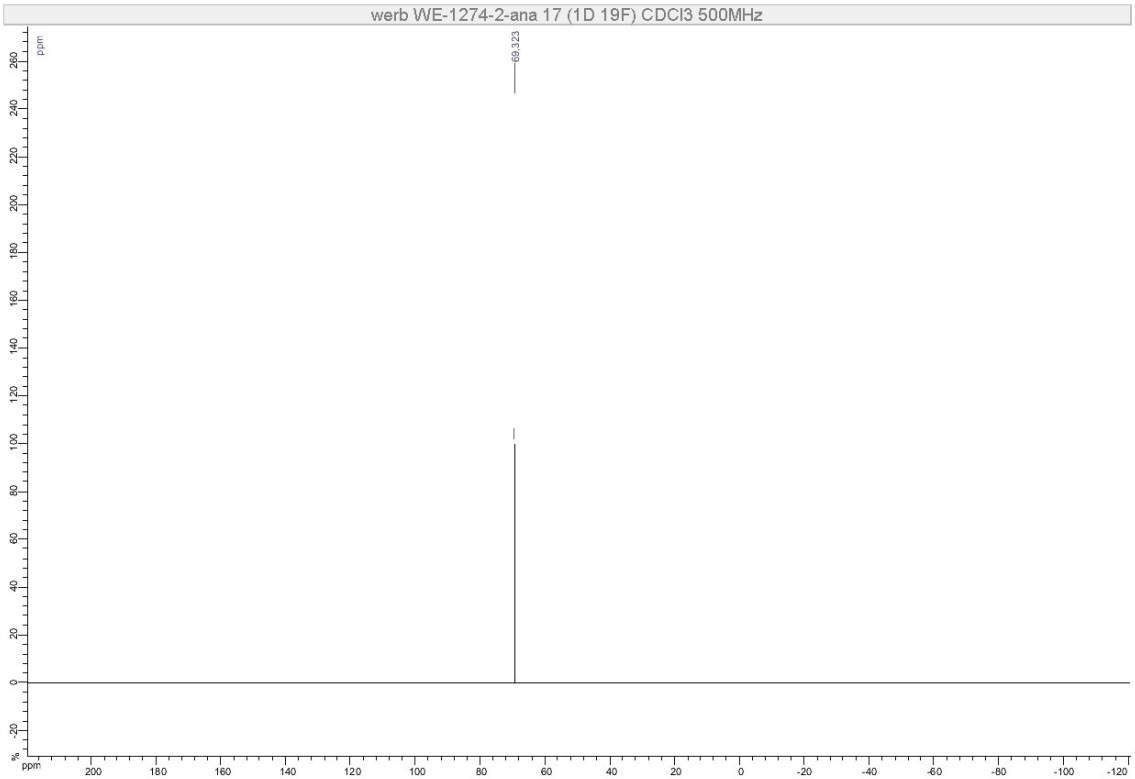

werb WE-1274-2-ana 12 (DEPT 13C) CDCl3 500MHz
72,993
64,163
64,064
64,042
60,428
60,326
ppm


werb WE-1274-2-ana 13 (COSY 1H/1H) CDCl3 500MHz
werb WE-1274-2-ana 10 (1D 1H)
ppm

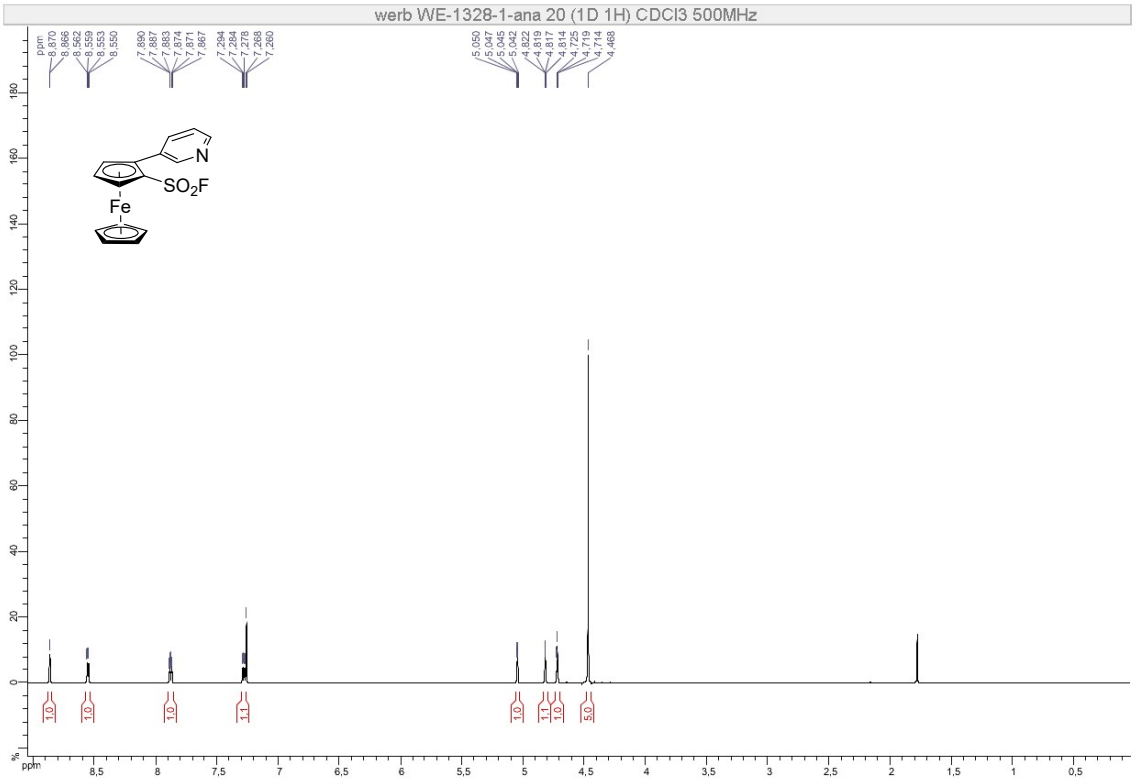

werb WE-1274-2-ana 14 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1274-2-ana 10 (1D 1H)
werb WE-1274-2-ana 11 (1D 13C)
ppm

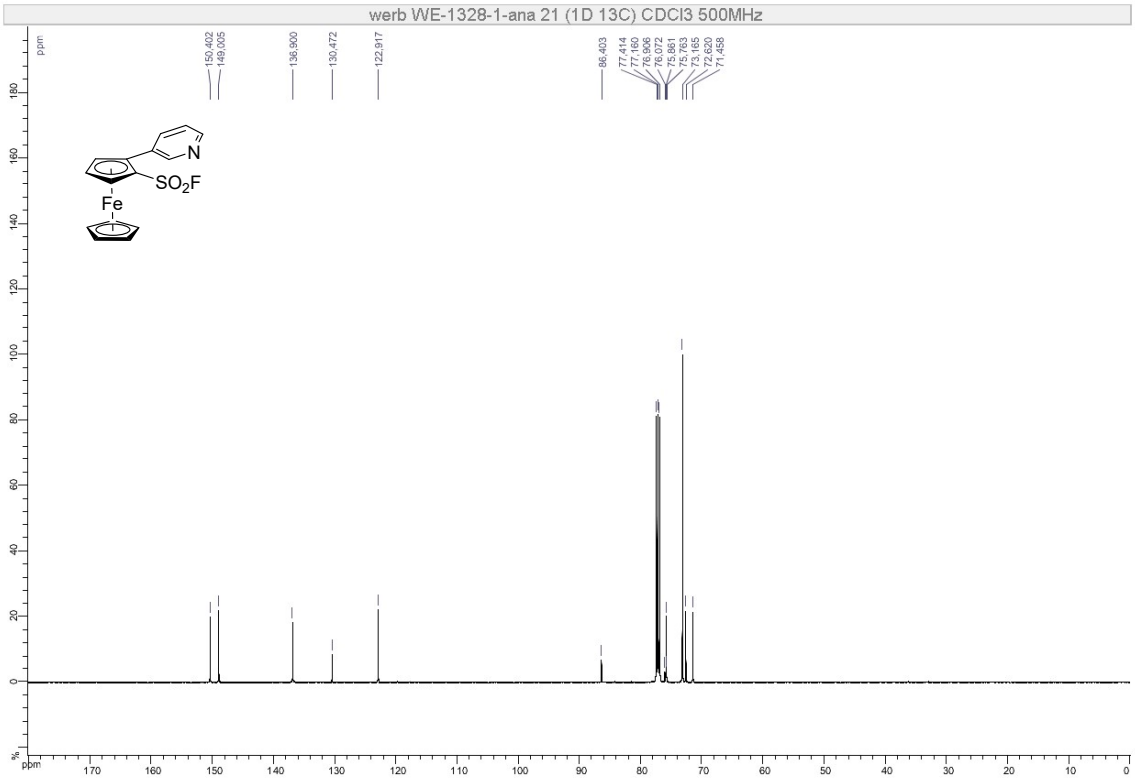

werb WE-1274-2-ana 15 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1274-2-ana 10 (1D 1H)
werb WE-1274-2-ana 11 (1D 13C)
ppm

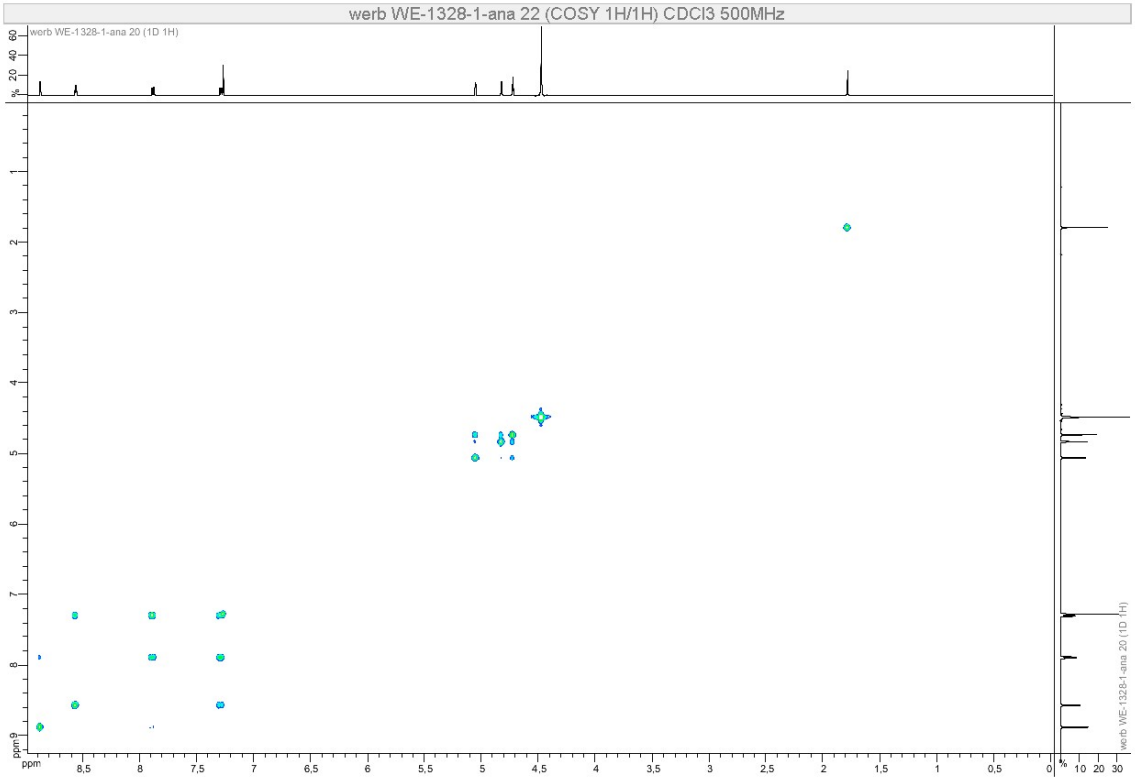

werb WE-1274-2-ana 16 (1D 19F) CDCl3 500MHz
-186.461
ppm
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
-320

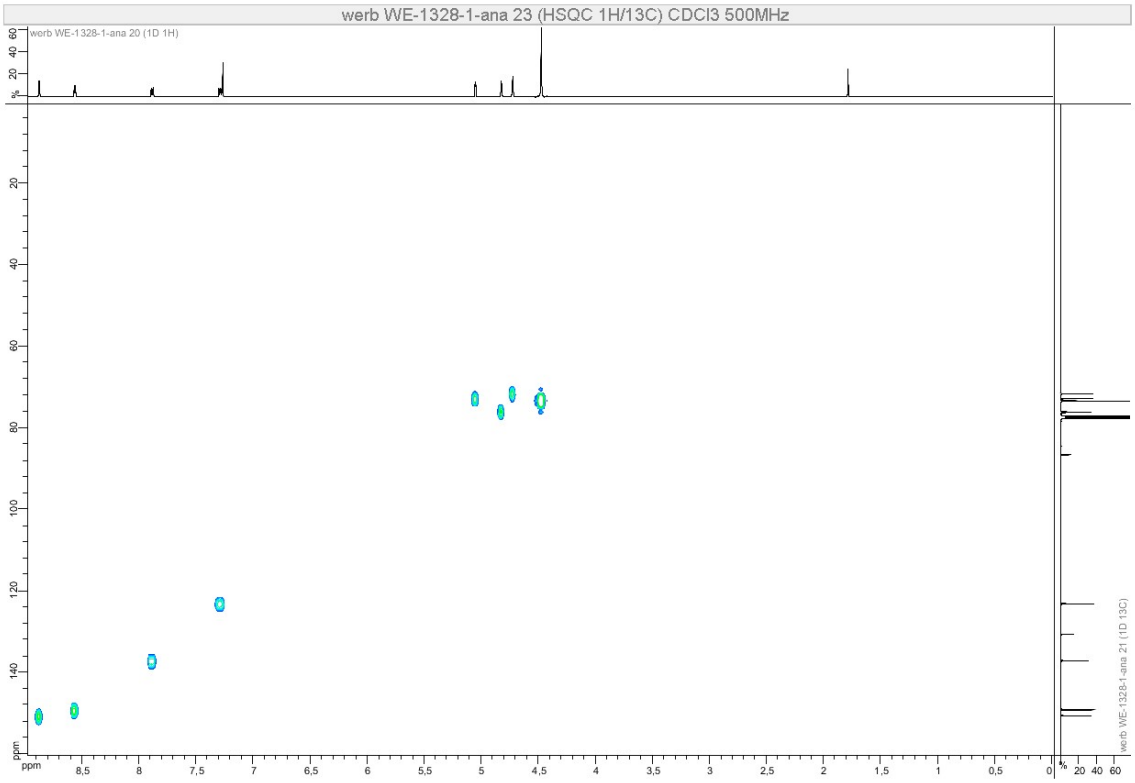

werb WE-1274-2-ana 17 (1D 19F) CDCl3 500MHz
69.323
ppm
ppm
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120

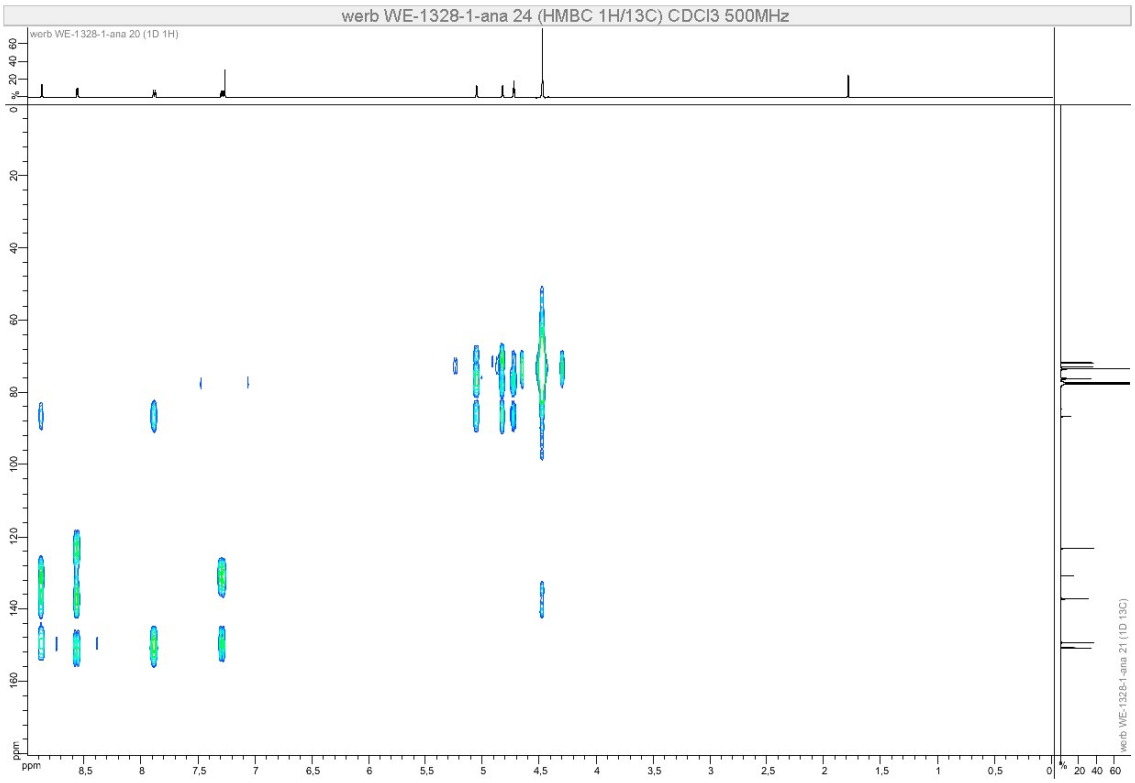
Compound 3d

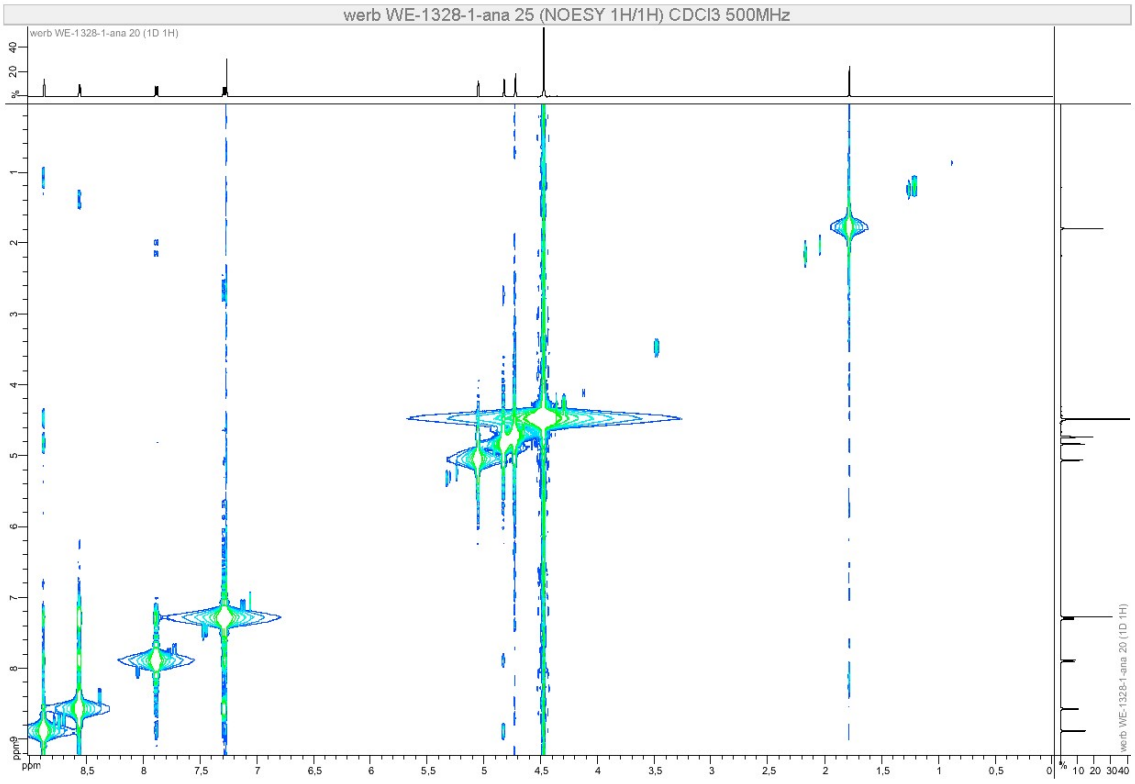

werb WE-1328-1-ana 20 (1D 1H) CDCl3 500MHz
ppm
8,870
8,866
8,562
8,559
8,553
8,550
7,890
7,887
7,883
7,874
7,871
7,867
7,294
7,284
7,278
7,268
7,260
5,059
5,047
5,045
5,042
4,822
4,819
4,817
4,814
4,725
4,719
4,714
4,468
N
SO2F
Fe
1,0
1,0
1,0
4,1
1,0
1,1
1,0
5,0
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5

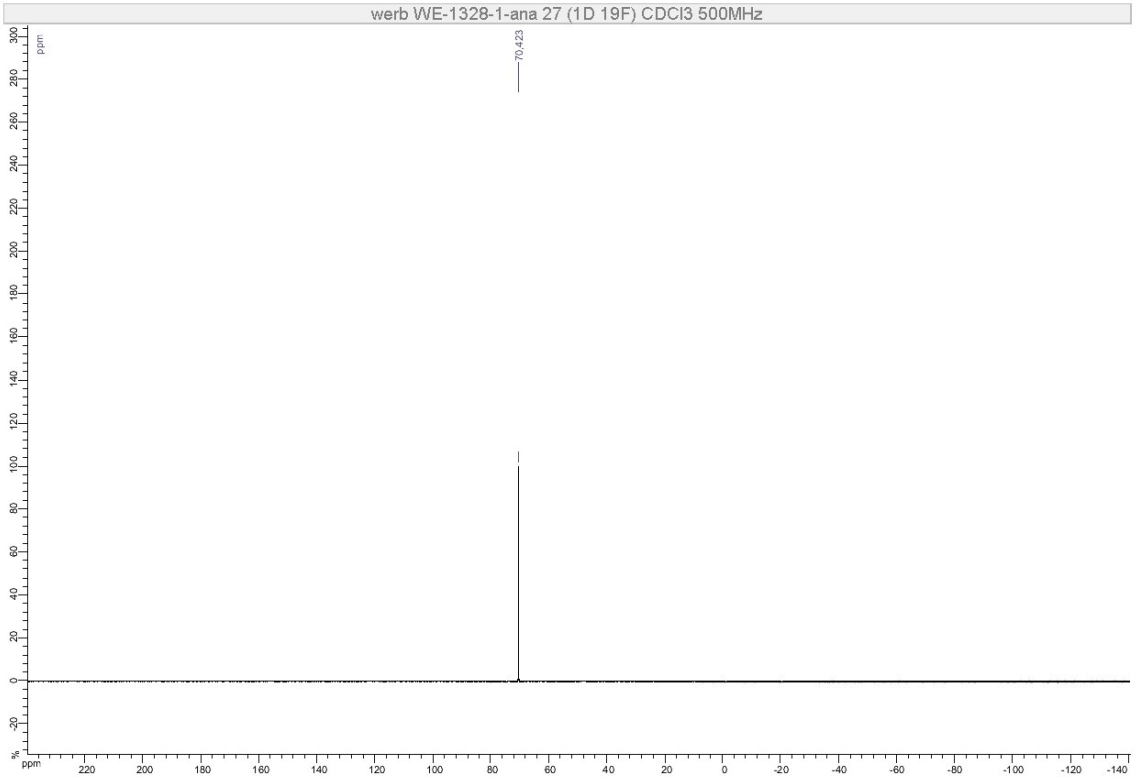

werb WE-1328-1-ana 21 (1D 13C) CDCl3 500MHz
ppm
150,402
149,005
136,900
130,472
122,917
86,403
77,414
77,160
76,906
76,072
75,661
75,363
73,165
72,620
71,458
N
SO2F
Fe
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


werb WE-1328-1-ana 22 (COSY 1H/1H) CDCl3 500MHz
werb WE-1328-1-ana 20 (1D 1H)
ppm
werb WE-1328-1-ana 20 (1D 1H)

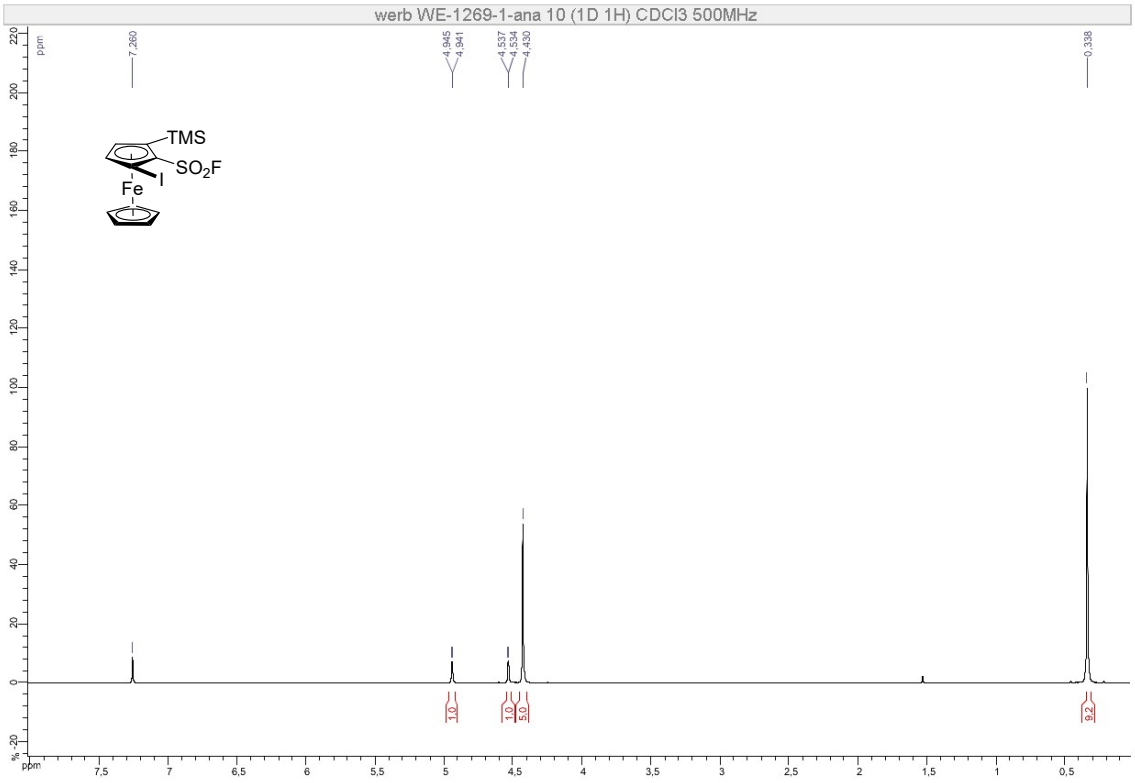

werb WE-1328-1-ana 23 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1328-1-ana 20 (1D 1H)
ppm
werb WE-1328-1-ana 21 (1D 13C)

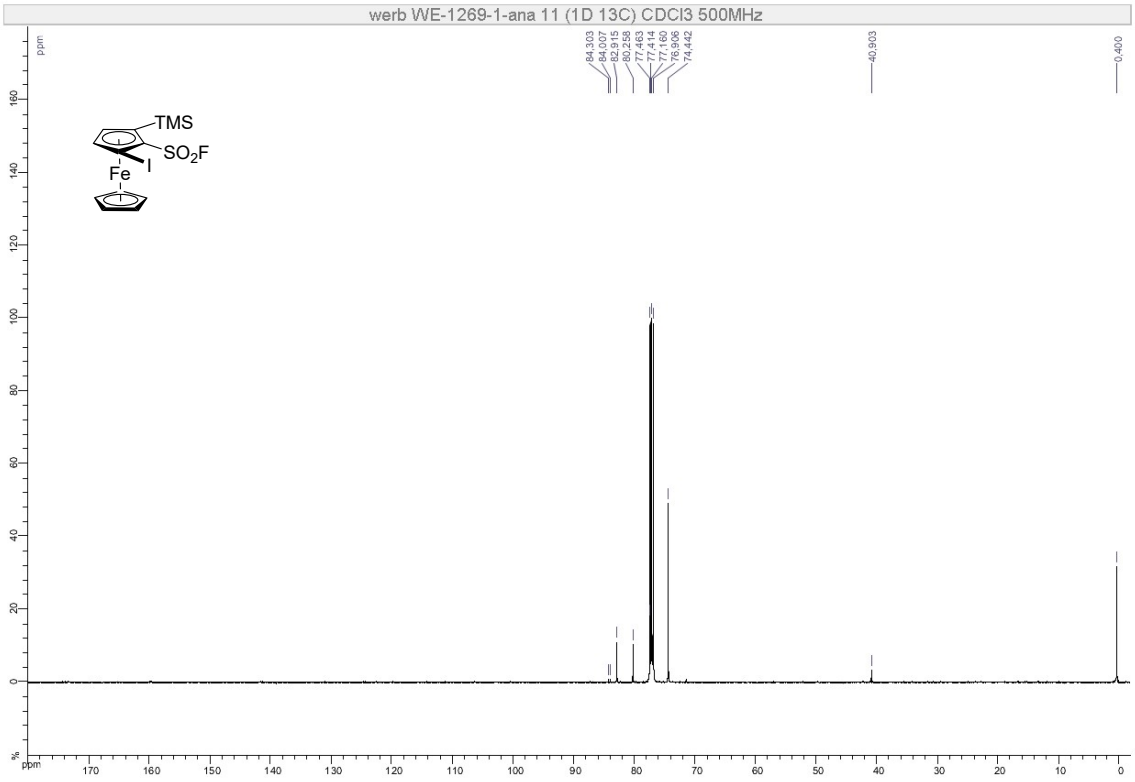

werb WE-1328-1-ana 24 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1328-1-ana 20 (1D 1H)
werb WE-1328-1-ana 21 (1D 13C)
ppm
%

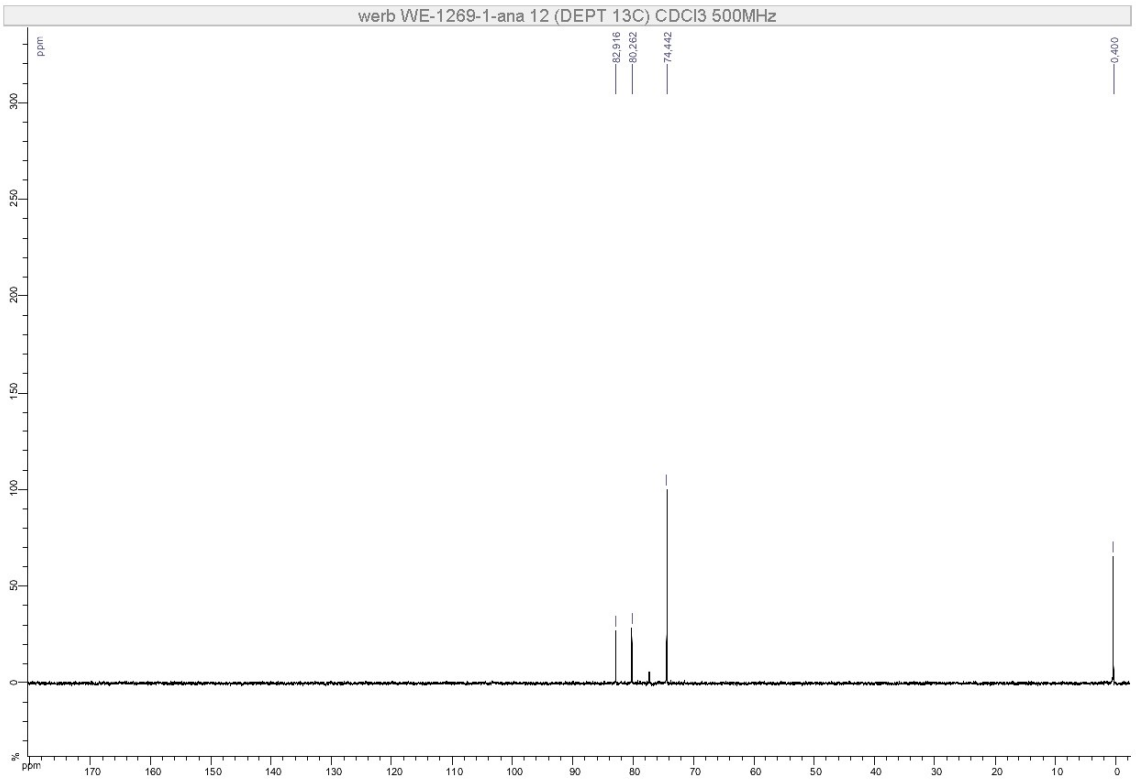

werb WE-1328-1-ana 25 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1328-1-ana 20 (1D 1H)
werb WE-1328-1-ana 20 (1D 1H)
ppm
%

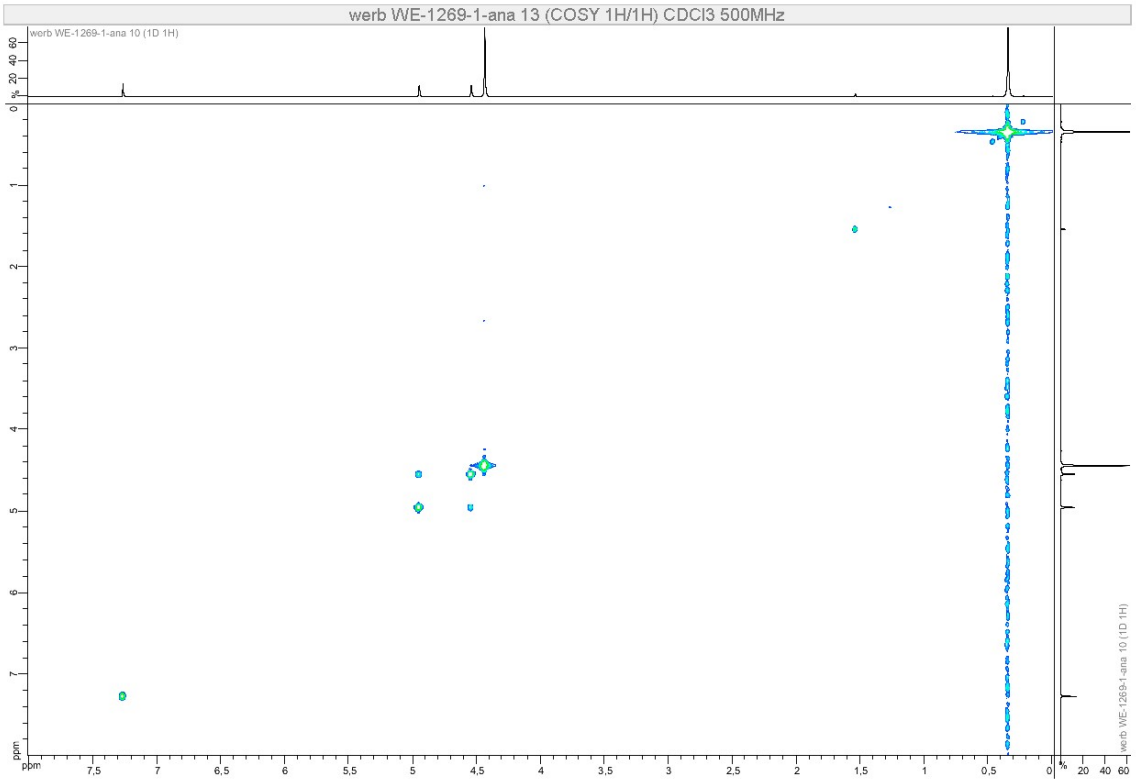

werb WE-1328-1-ana 27 (1D 19F) CDCl3 500MHz
ppm
70.423
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140

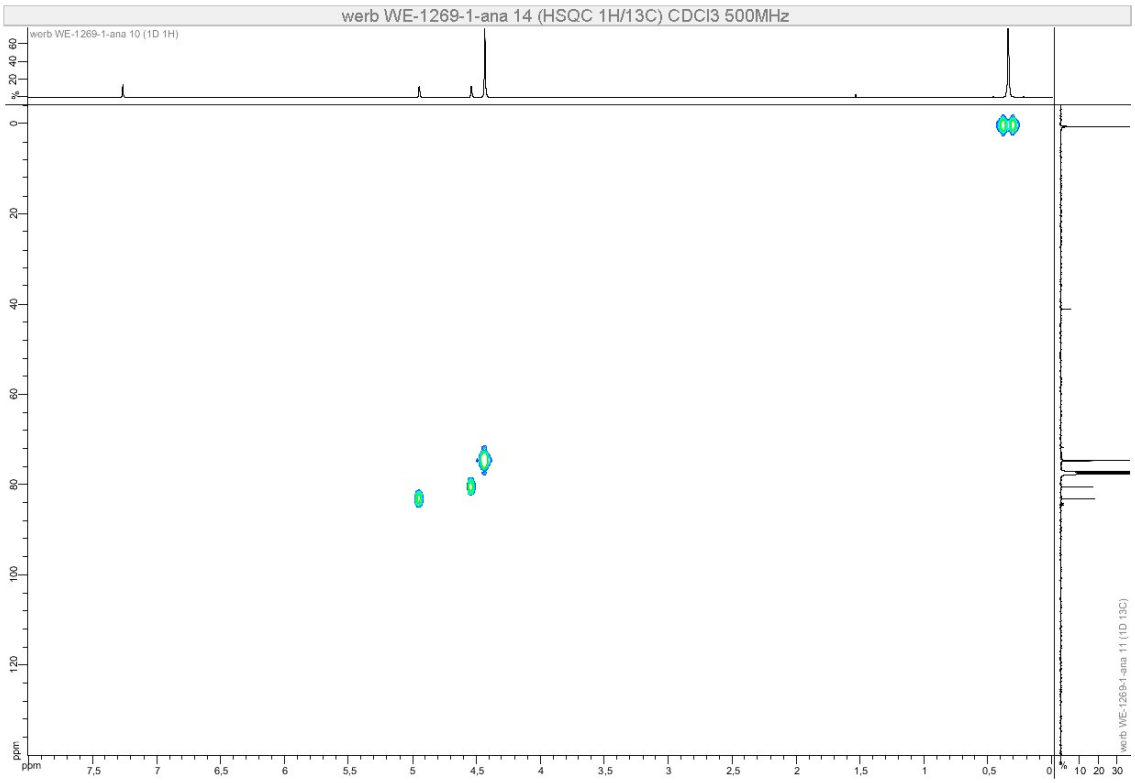
Compound 4

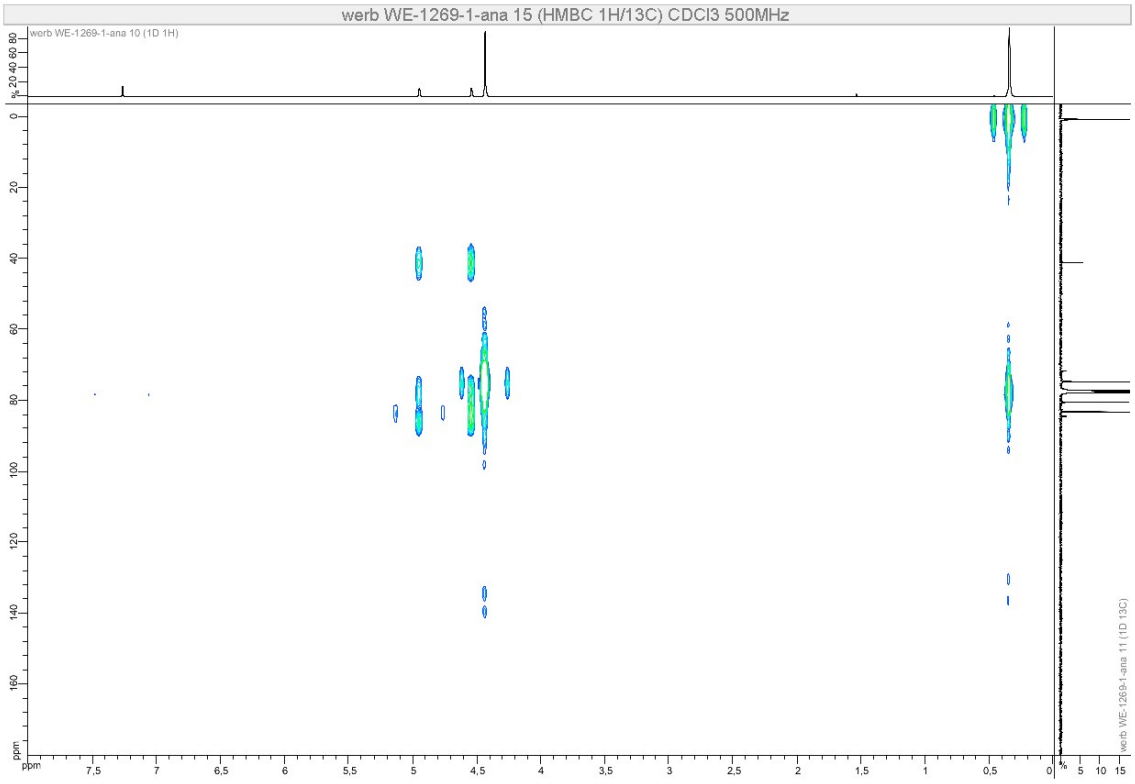

werb WE-1269-1-ana 10 (1D 1H) CDCl3 500MHz
TMS
SO2F
Fe

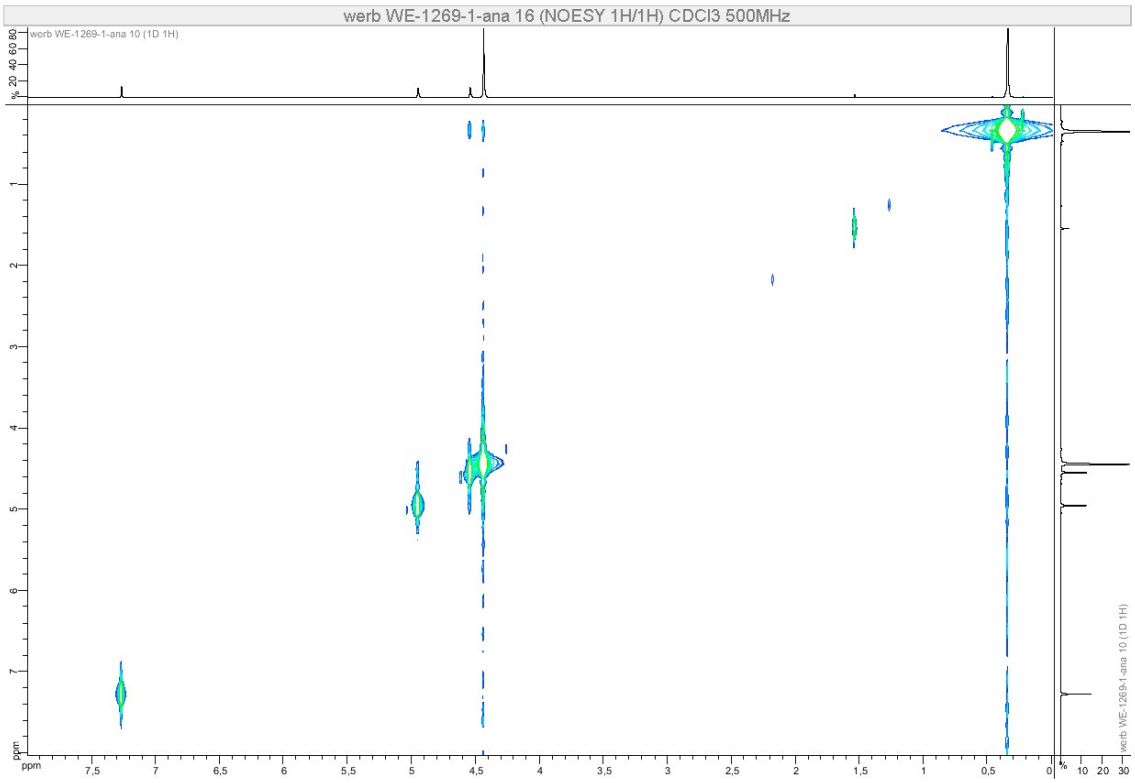

werb WE-1269-1-ana 11 (1D 13C) CDCl3 500MHz
TMS
SO2F
Fe

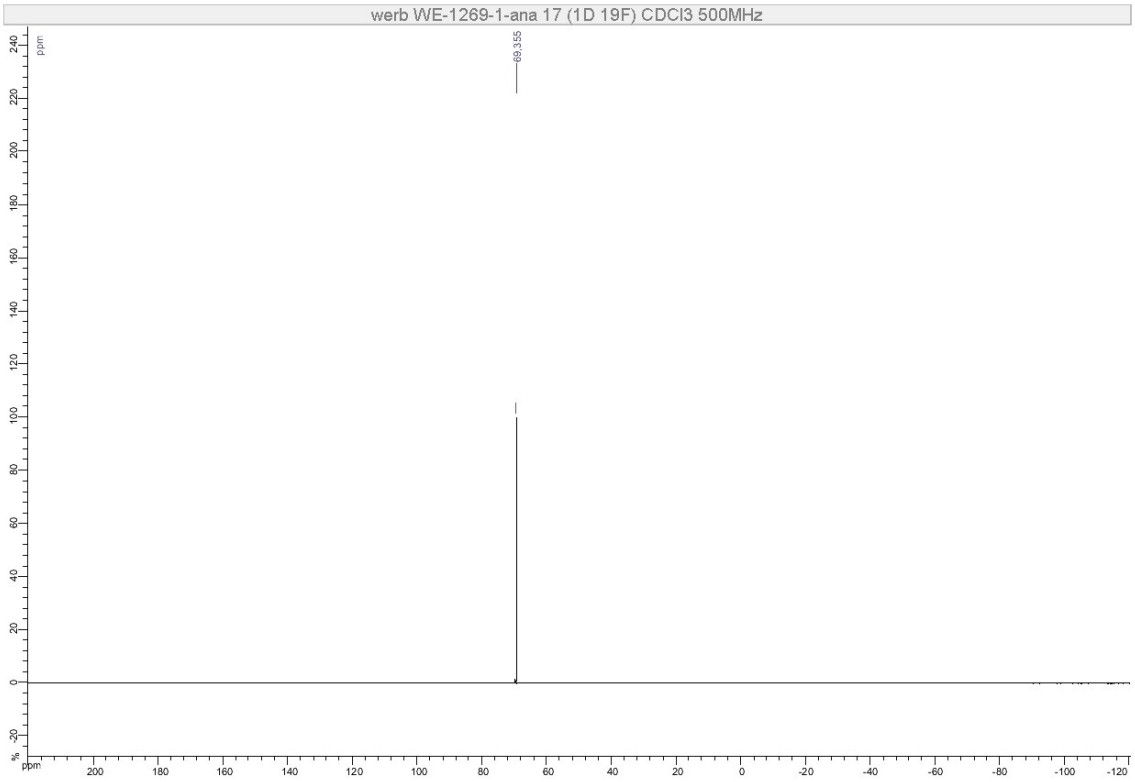

werb WE-1269-1-ana 12 (DEPT 13C) CDCl3 500MHz
82,916
80,262
74,442
0,400
ppm


werb WE-1269-1-ana 13 (COSY 1H/1H) CDCl3 500MHz
werb WE-1269-1-ana 10 (1D 1H)
ppm

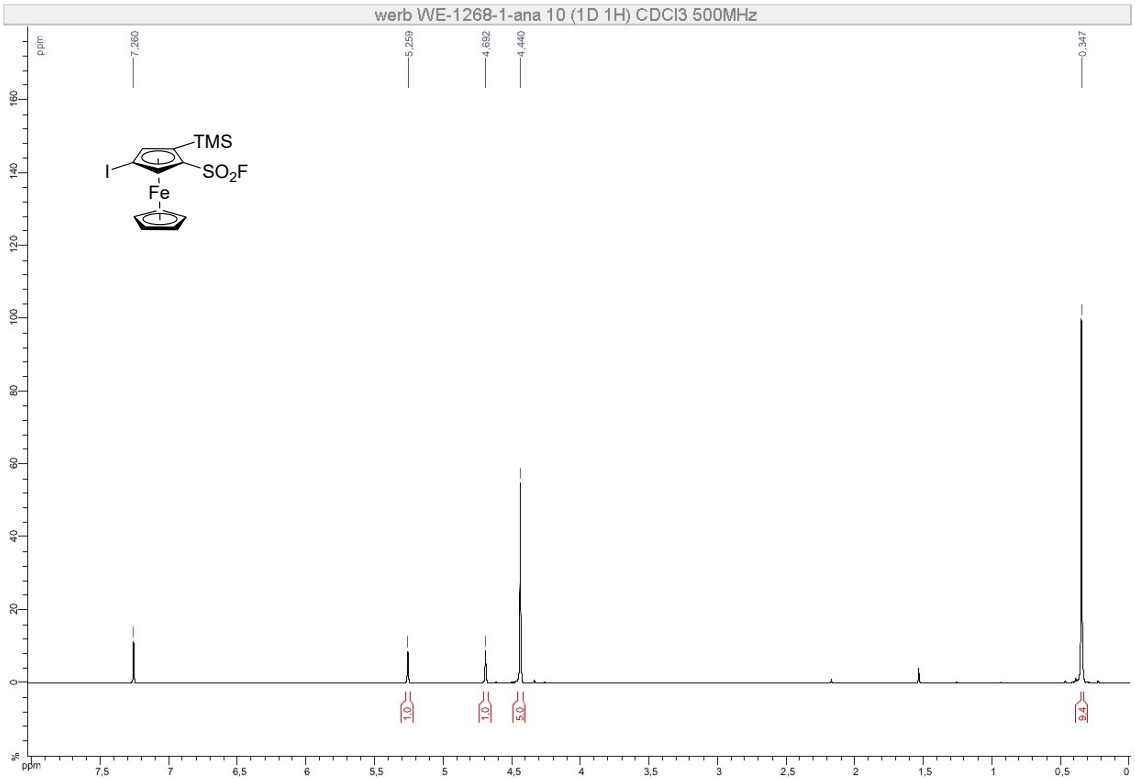

werb WE-1269-1-ana 14 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1269-1-ana 10 (1D 1H)
werb WE-1269-1-ana 11 (1D 13C)
ppm
%

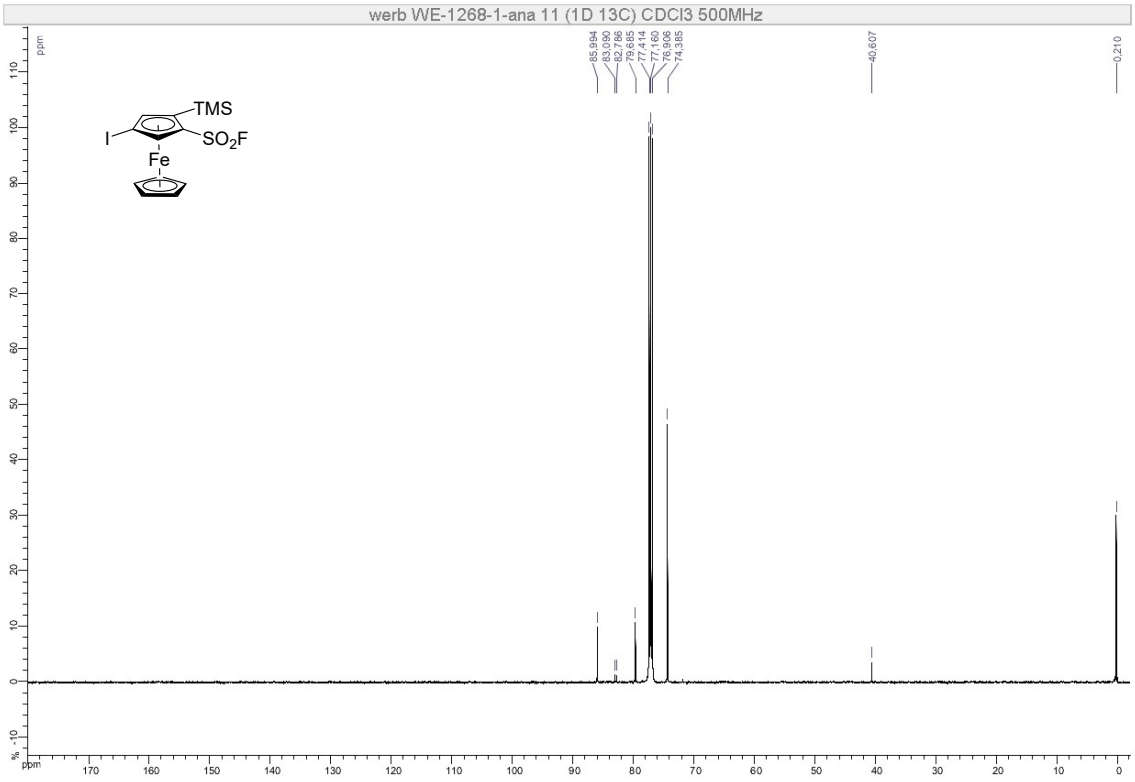

werb WE-1269-1-ana 15 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1269-1-ana 10 (1D 1H)
werb WE-1269-1-ana 11 (1D 13C)
ppm
%

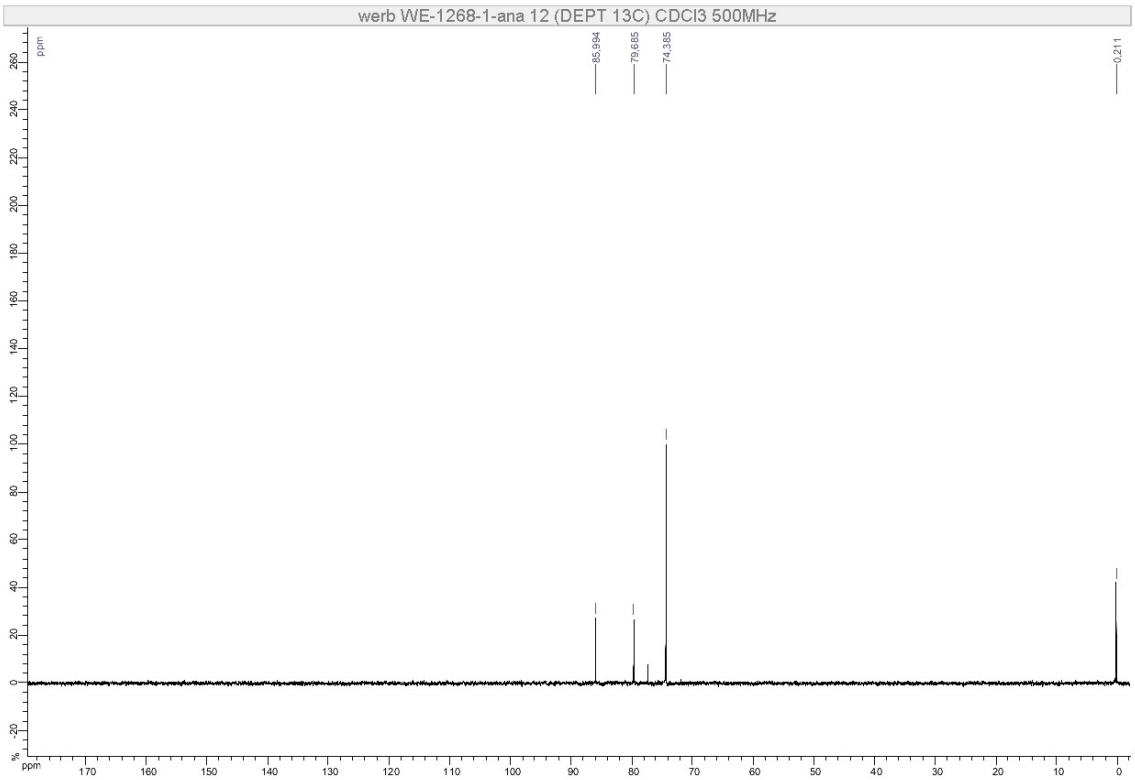

werb WE-1269-1-ana 16 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1269-1-ana 10 (1D 1H)
ppm
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
%
10
20
30

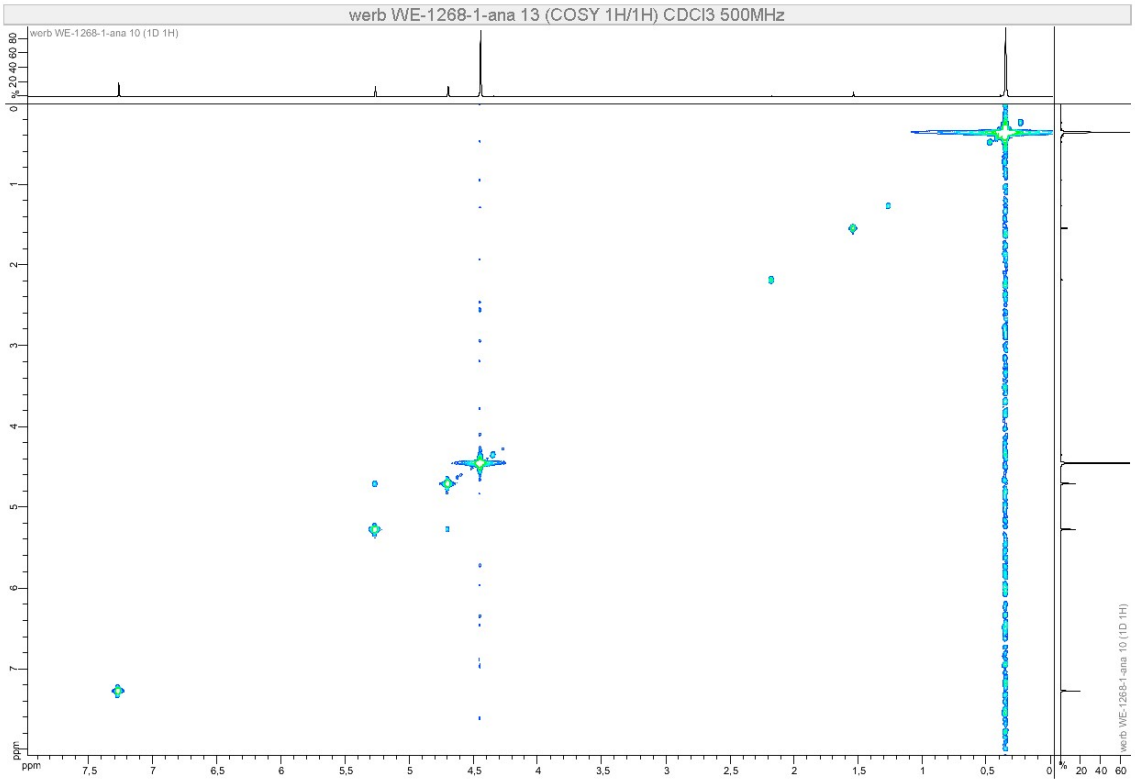

werb WE-1269-1-ana 17 (1D 19F) CDCl3 500MHz
ppm
-69,355
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120

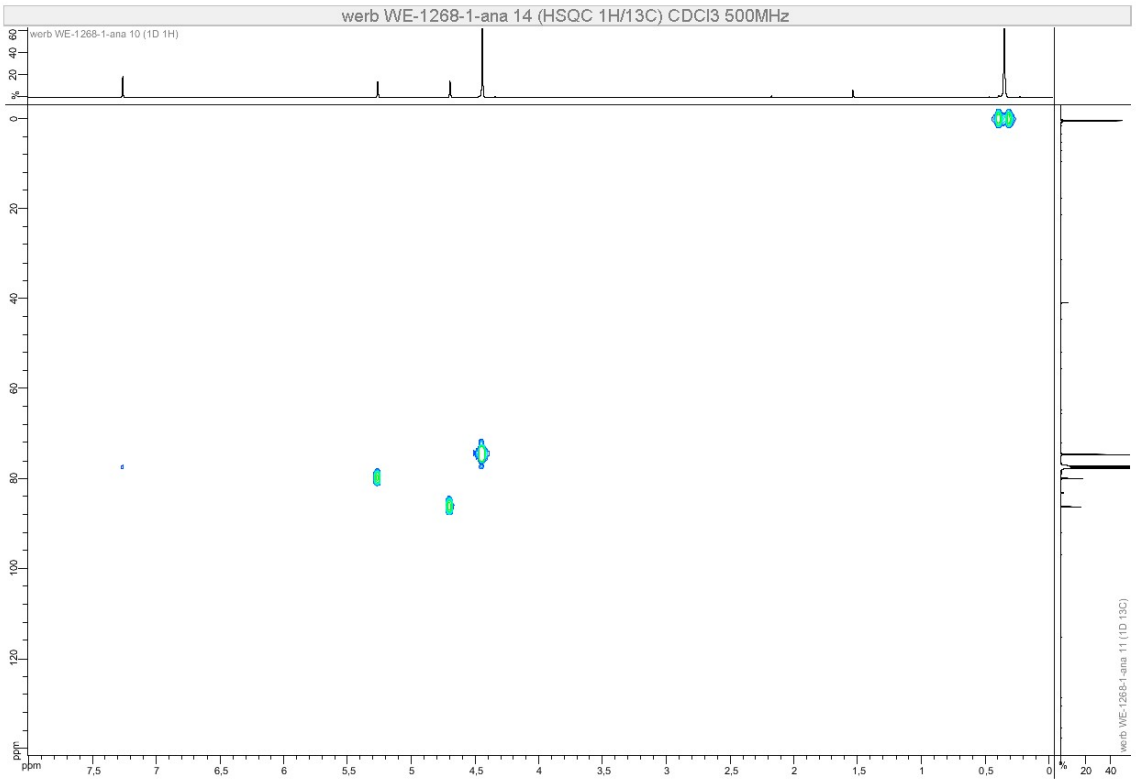
Compound 5a

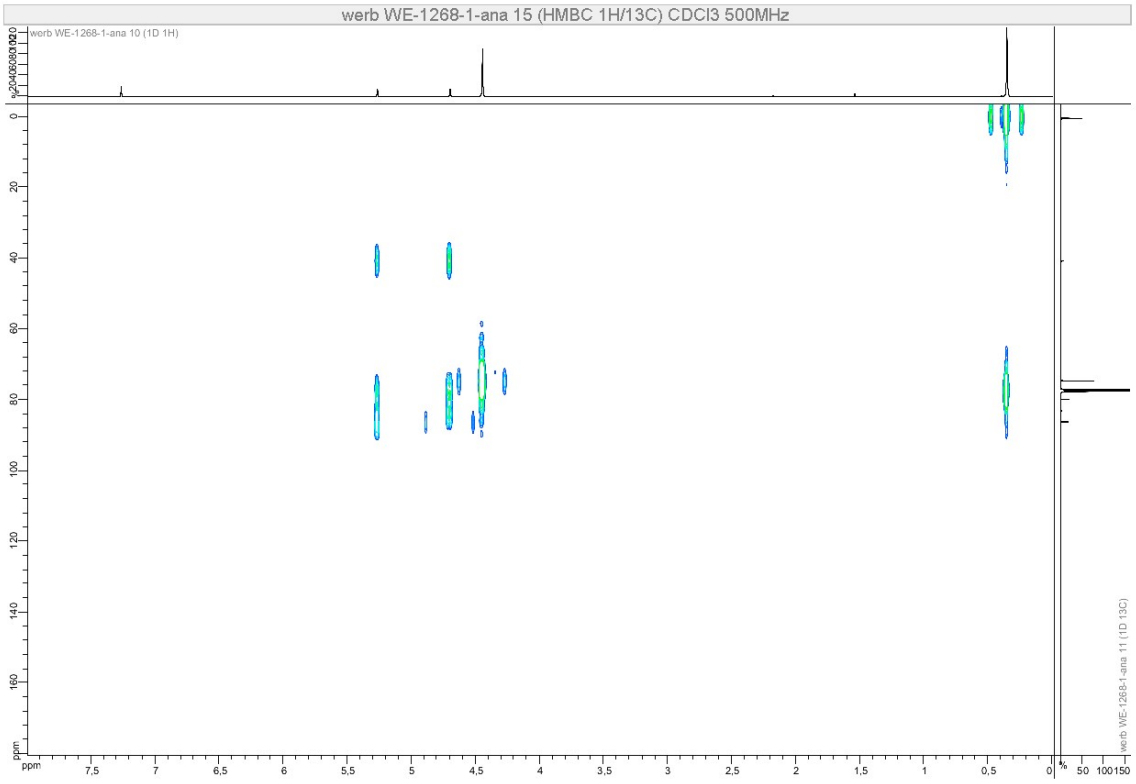

werb WE-1268-1-ana 10 (1D 1H) CDCl3 500MHz
TMS
I
SO2F
Fe

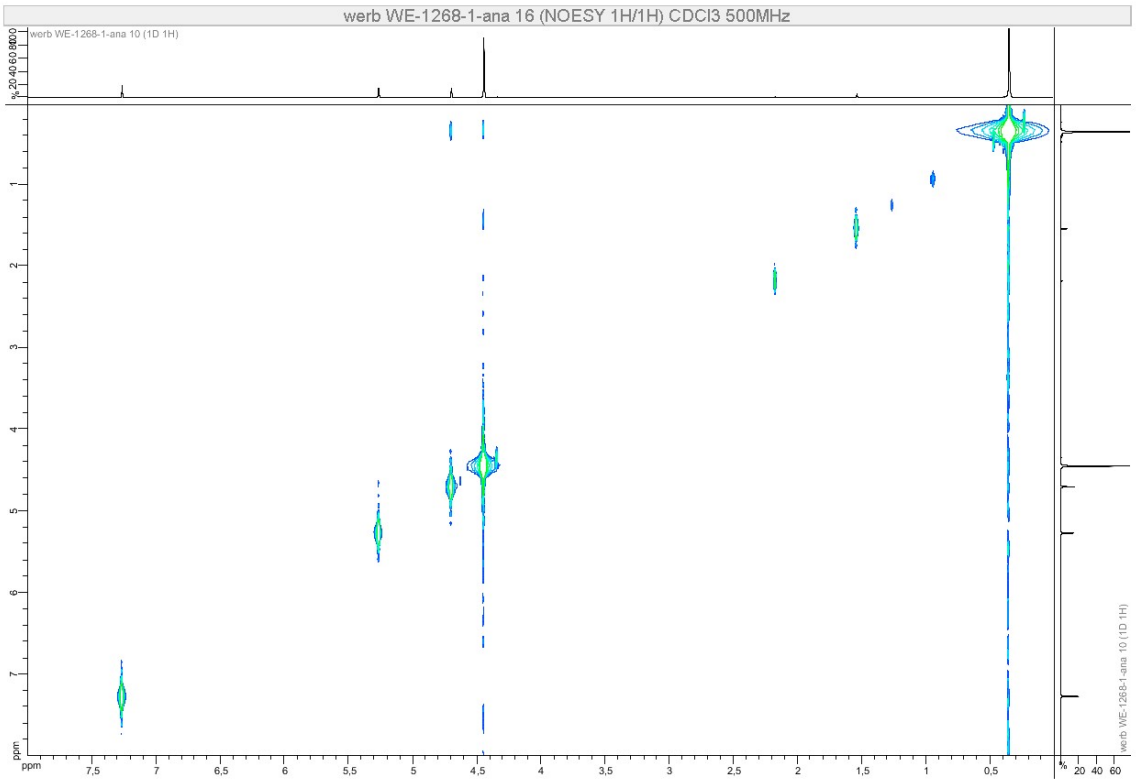

werb WE-1268-1-ana 11 (1D 13C) CDCl3 500MHz
TMS
I
SO2F
Fe

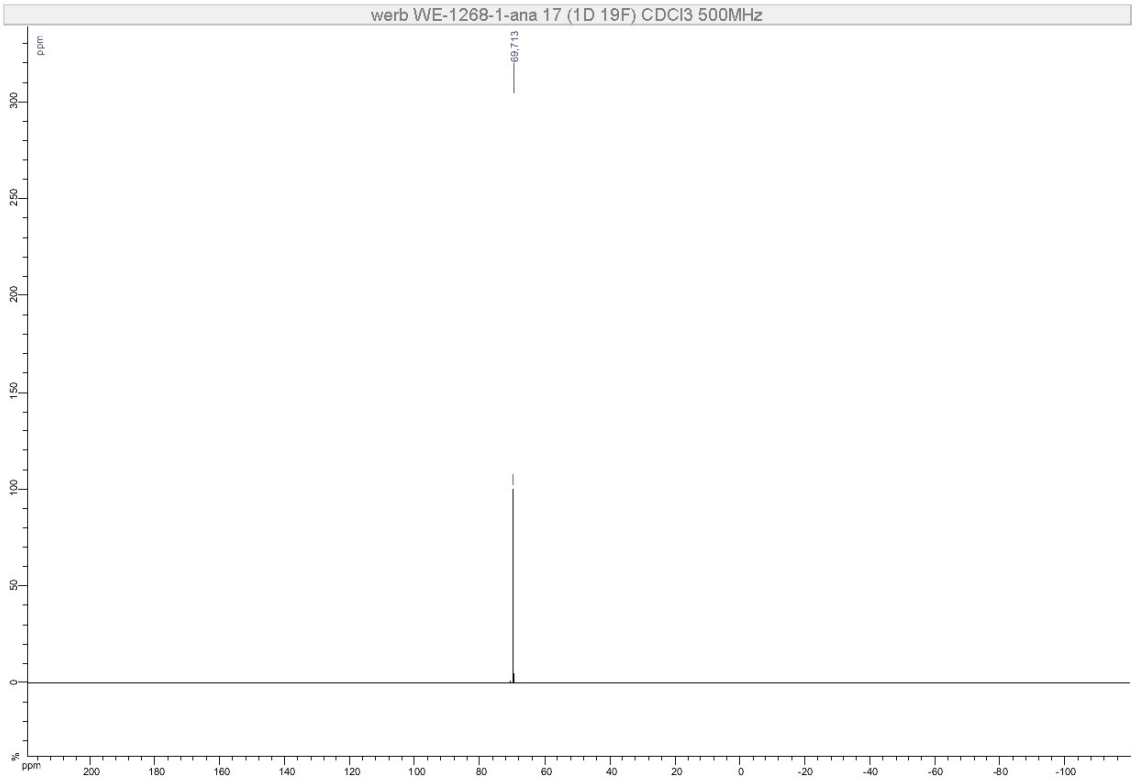

werb WE-1268-1-ana 12 (DEPT 13C) CDCl3 500MHz
85,994
79,685
74,385
0,211
ppm


werb WE-1268-1-ana 13 (COSY 1H/1H) CDCl3 500MHz
werb WE-1268-1-ana 10 (1D 1H)
ppm

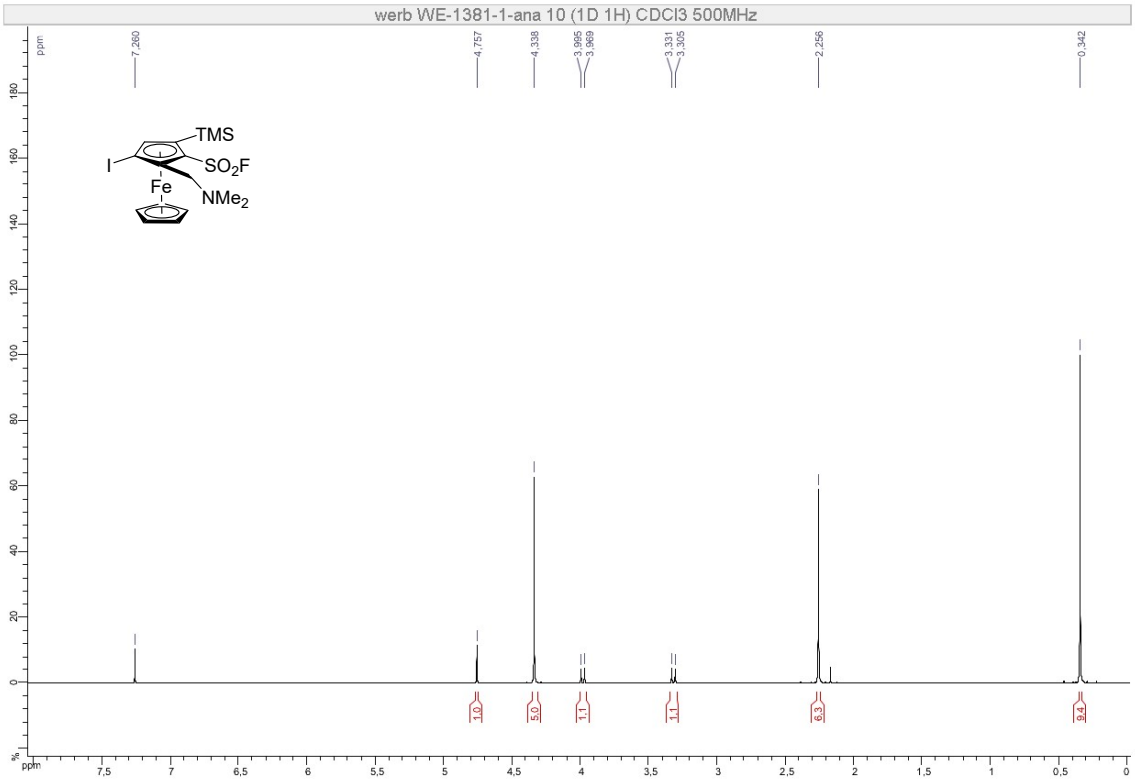

werb WE-1268-1-ana 14 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1268-1-ana 10 (1D 1H)
ppm
werb WE-1268-1-ana 11 (1D 13C)

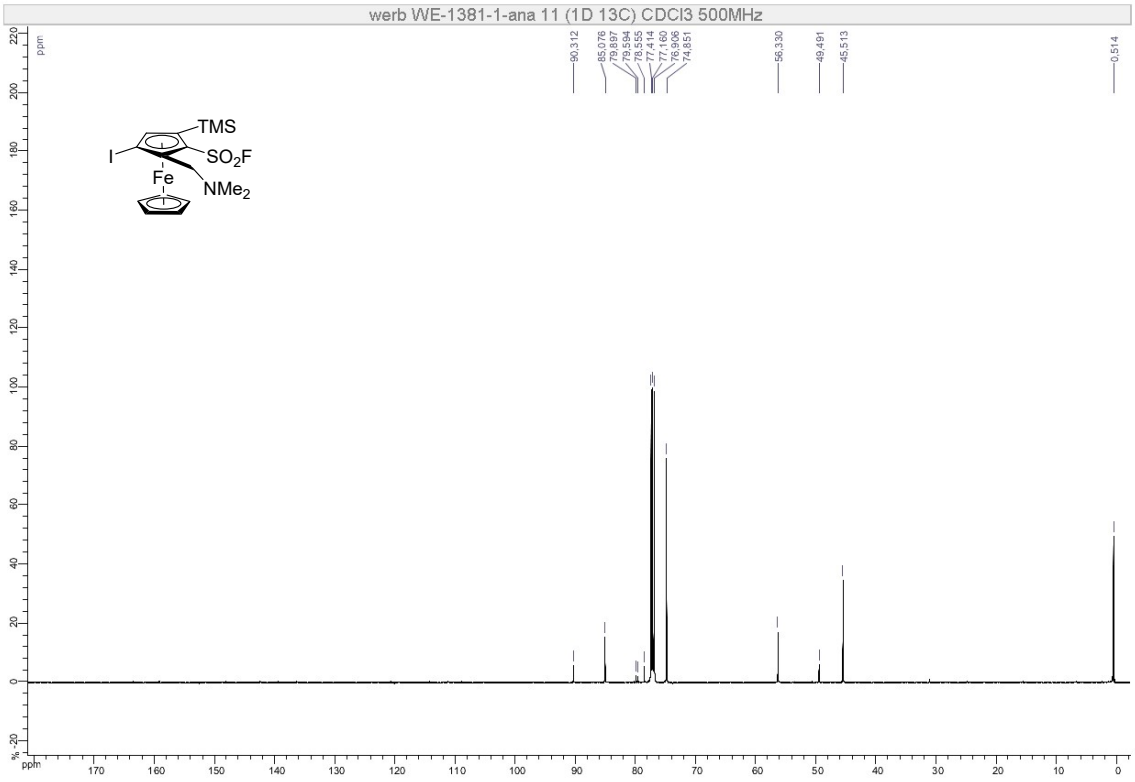

werb WE-1268-1-ana 15 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1268-1-ana 10 (1D 1H)
ppm
werb WE-1268-1-ana 11 (1D 13C)

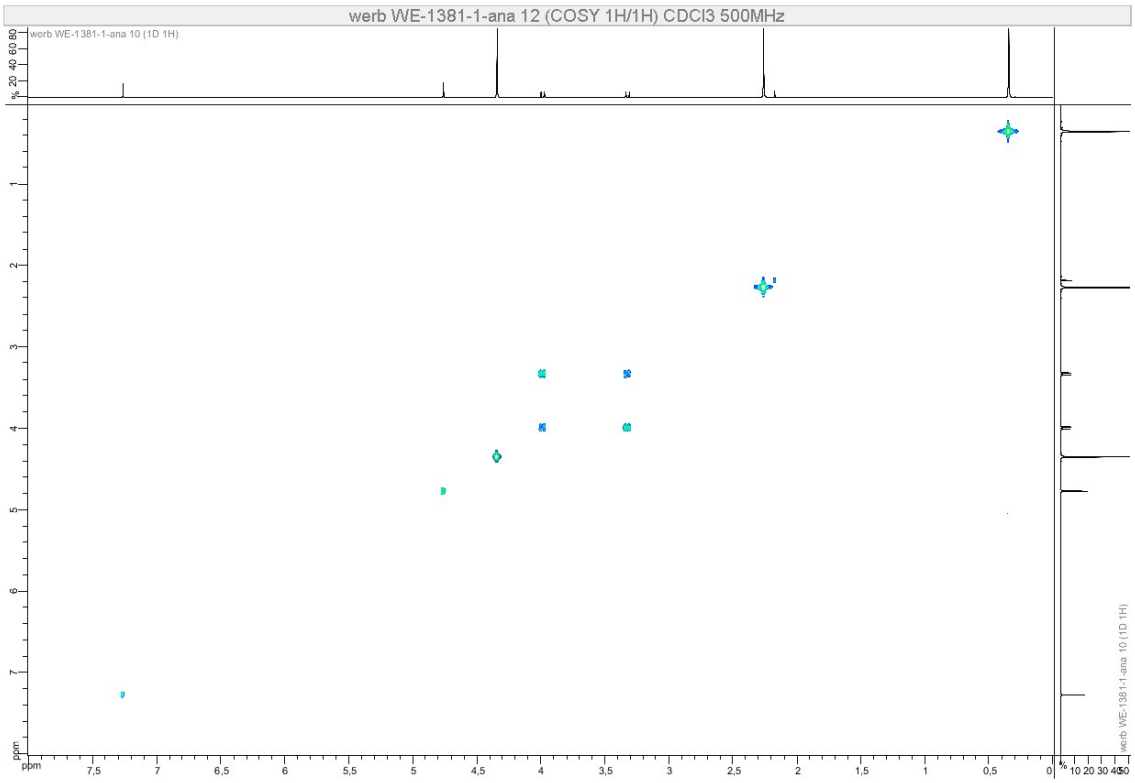

werb WE-1268-1-ana 16 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1268-1-ana 10 (1D 1H)
ppm
werb WE-1268-1-ana 10 (1D 1H)

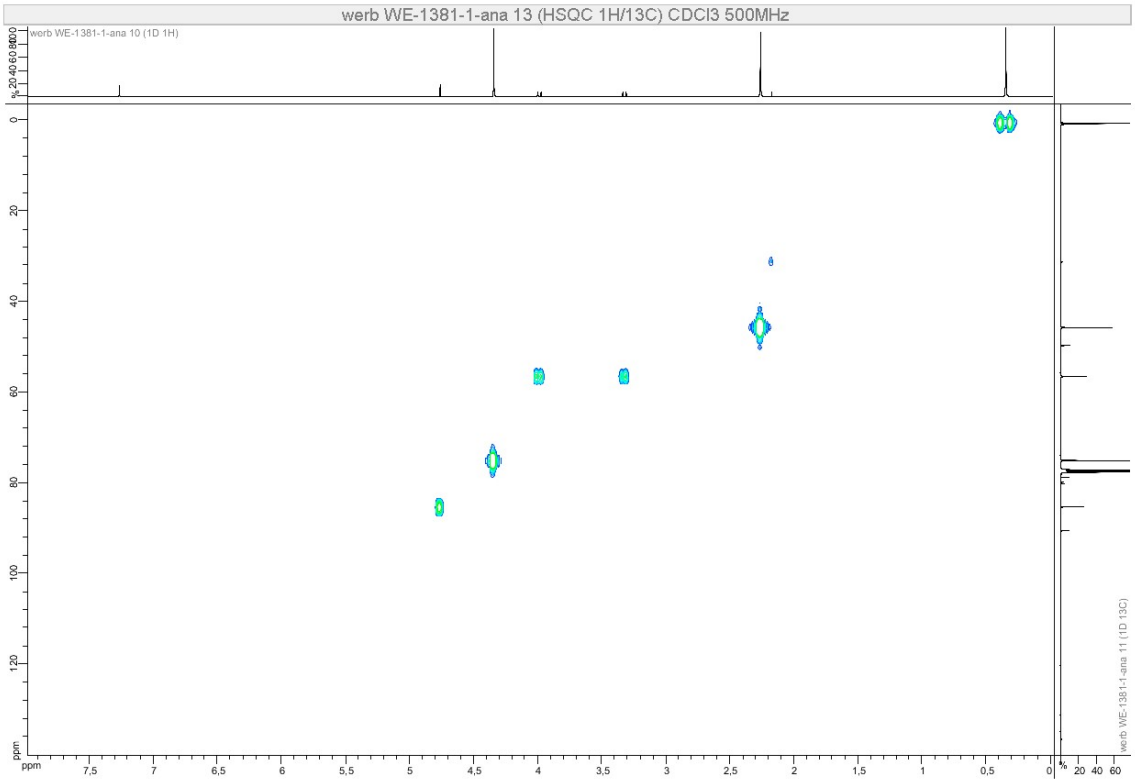

werb WE-1268-1-ana 17 (1D 19F) CDCl3 500MHz
ppm
69.713

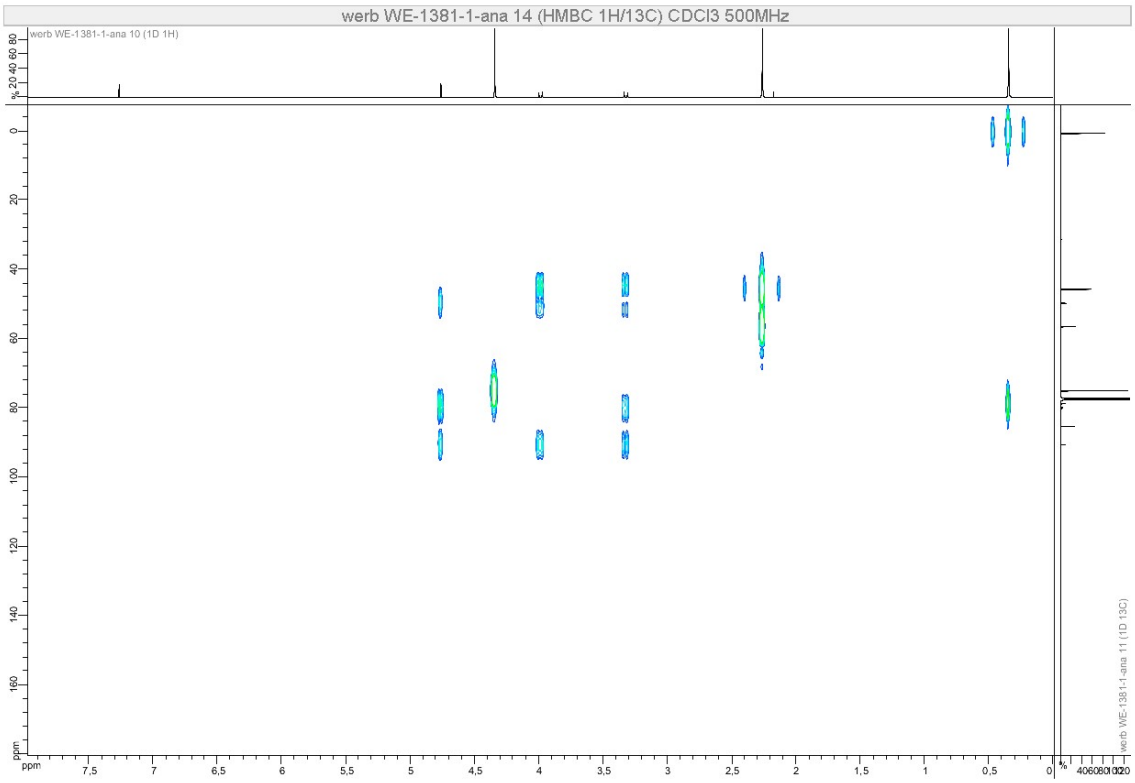
Compound 5b

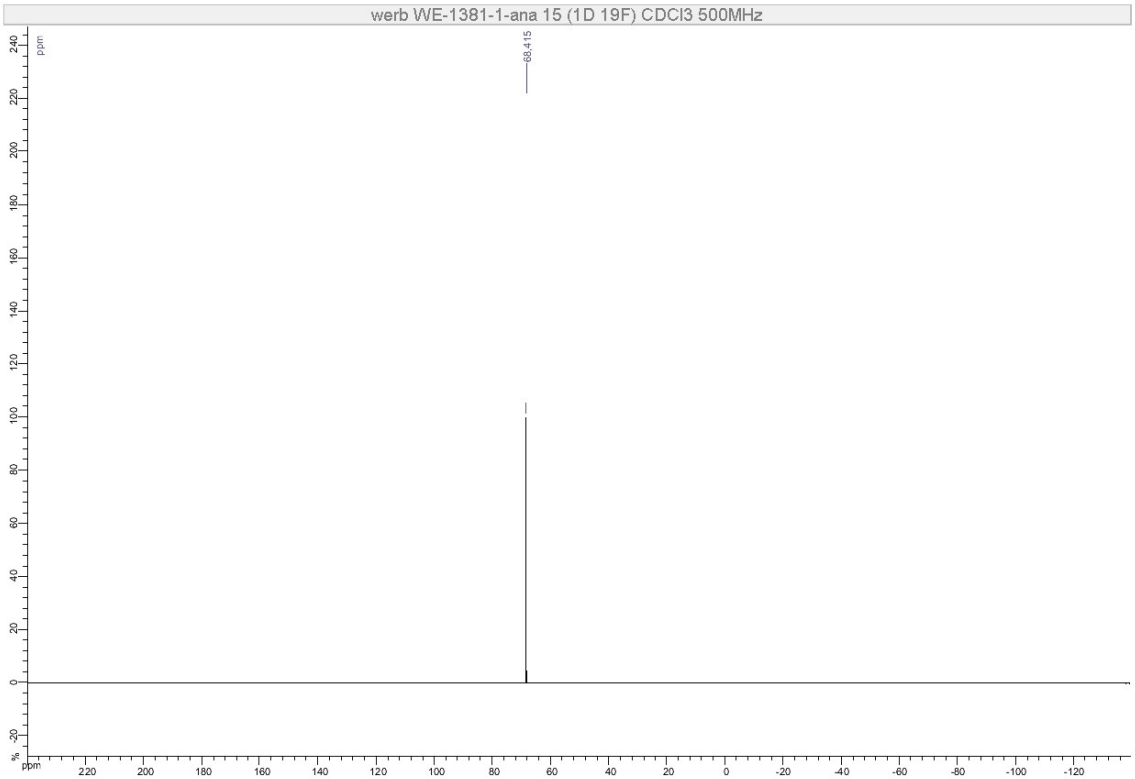

werb WE-1381-1-ana 10 (1D 1H) CDCl3 500MHz
ppm
7,260
4,757
4,338
3,995
3,969
3,331
3,305
2,256
0,342
TMS
I
SO2F
Fe
NMe2
1,0
5,0
1,1
1,1
6,3
9,4


werb WE-1381-1-ana 11 (1D 13C) CDCl3 500MHz
ppm
90,312
85,078
79,897
79,594
78,555
77,414
77,160
76,906
74,851
56,330
49,491
45,513
0,514
TMS
I
SO2F
Fe
NMe2

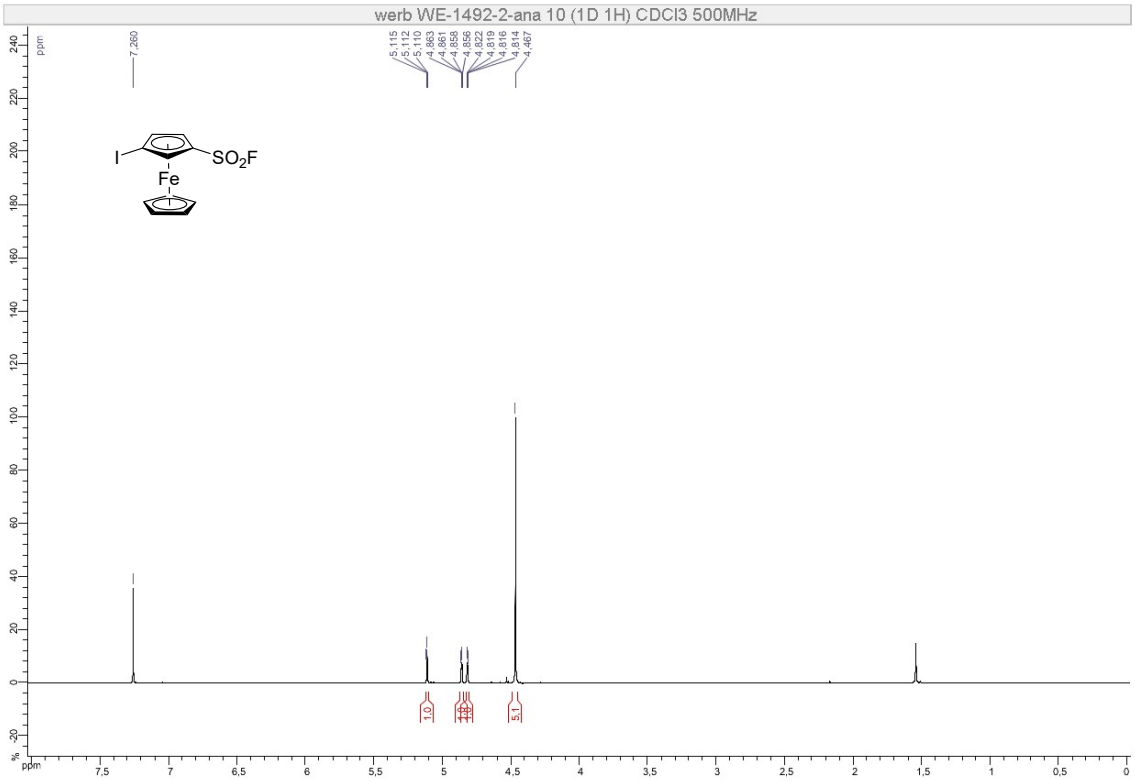

werb WE-1381-1-ana 12 (COSY 1H/1H) CDCl3 500MHz
werb WE-1381-1-ana 10 (1D 1H)
ppm
werb WE-1381-1-ana 10 (1D 1H)

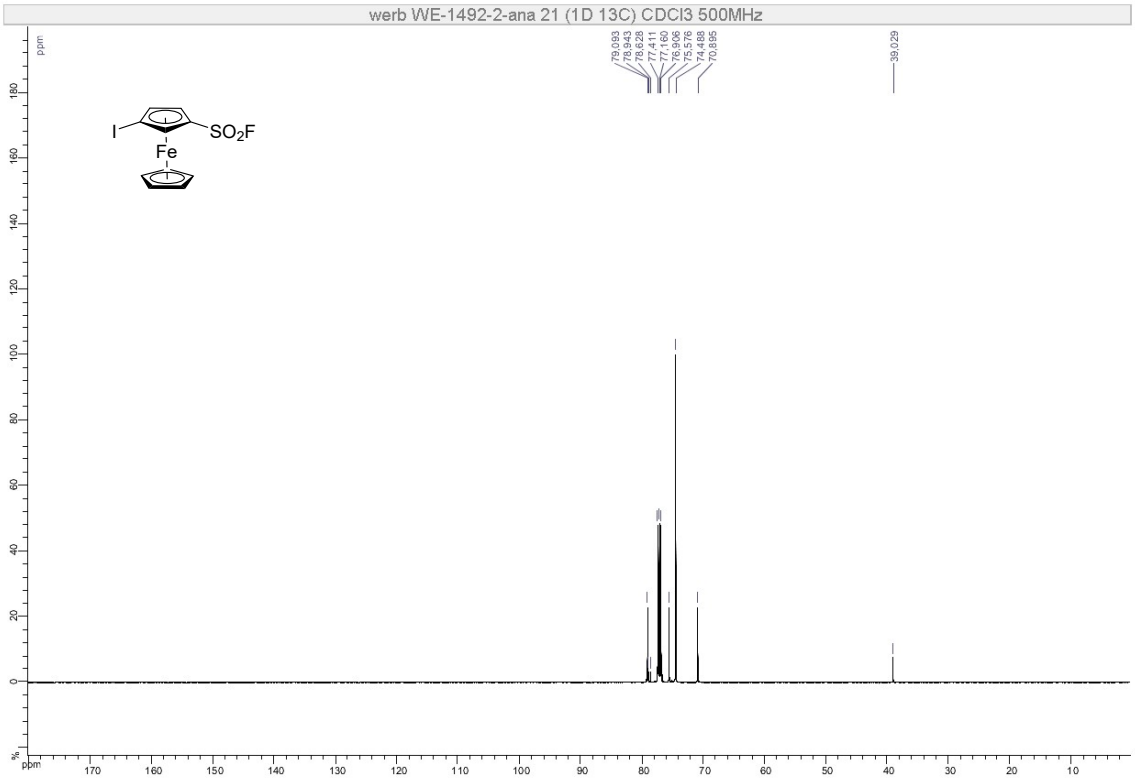

werb WE-1381-1-ana 13 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1381-1-ana 10 (1D 1H)
ppm
werb WE-1381-1-ana 11 (1D 13C)

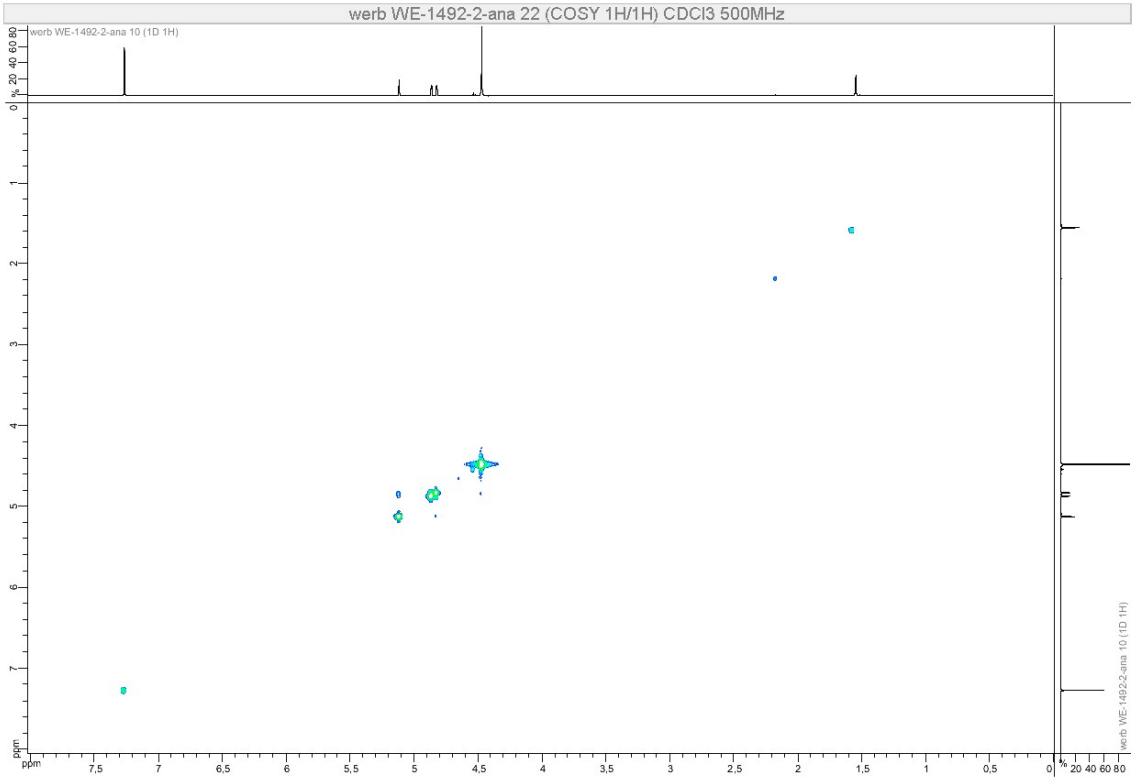

werb WE-1381-1-ana 14 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1381-1-ana 10 (1D 1H)
werb WE-1381-1-ana 11 (1D 13C)
ppm
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

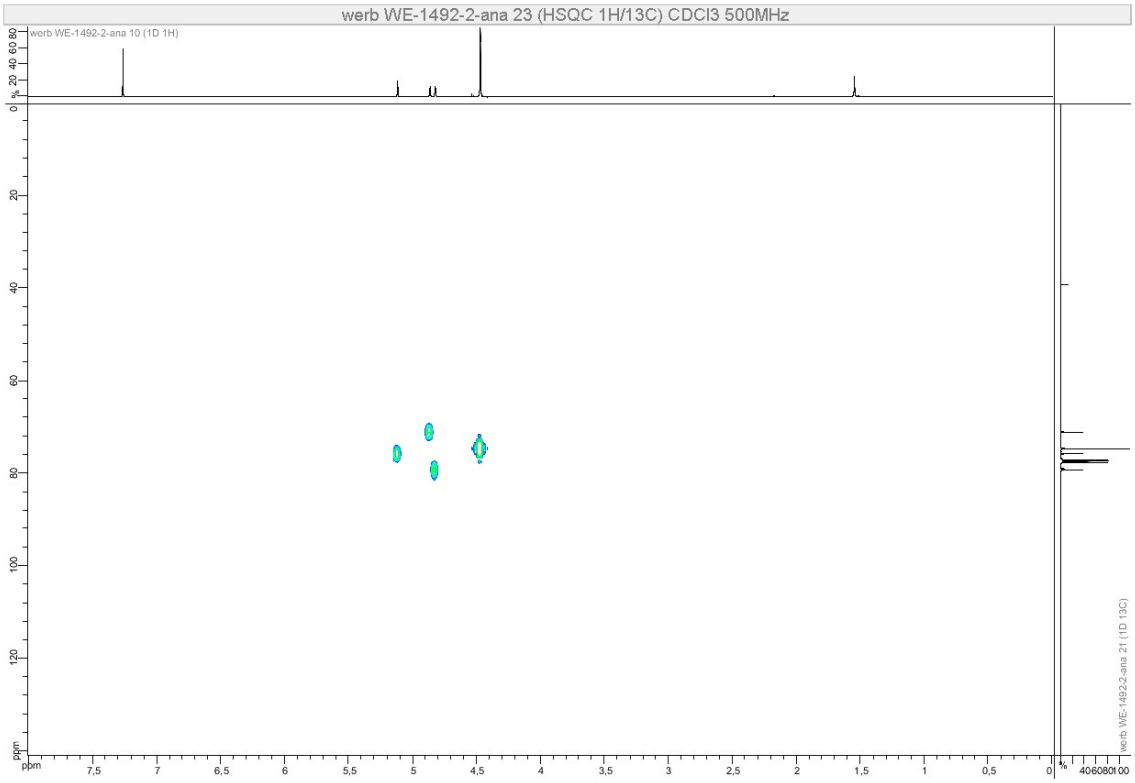

werb WE-1381-1-ana 15 (1D 19F) CDCl3 500MHz
ppm
-68,415
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120

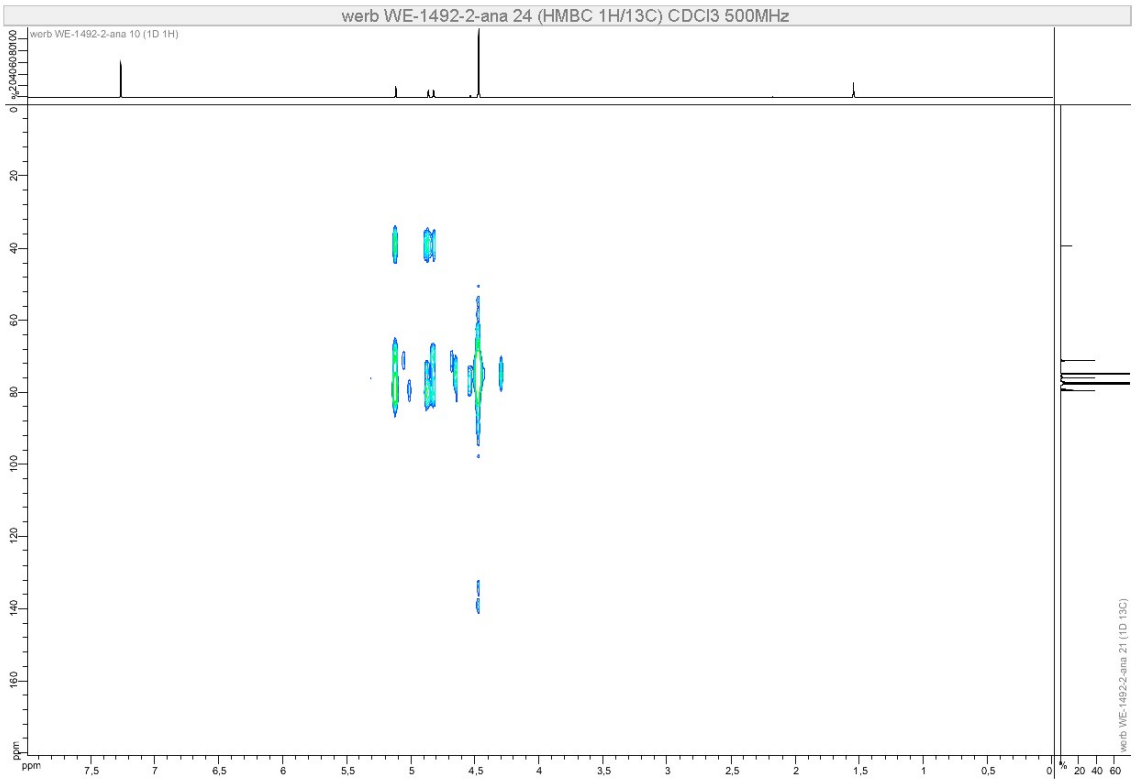
Compound 6a

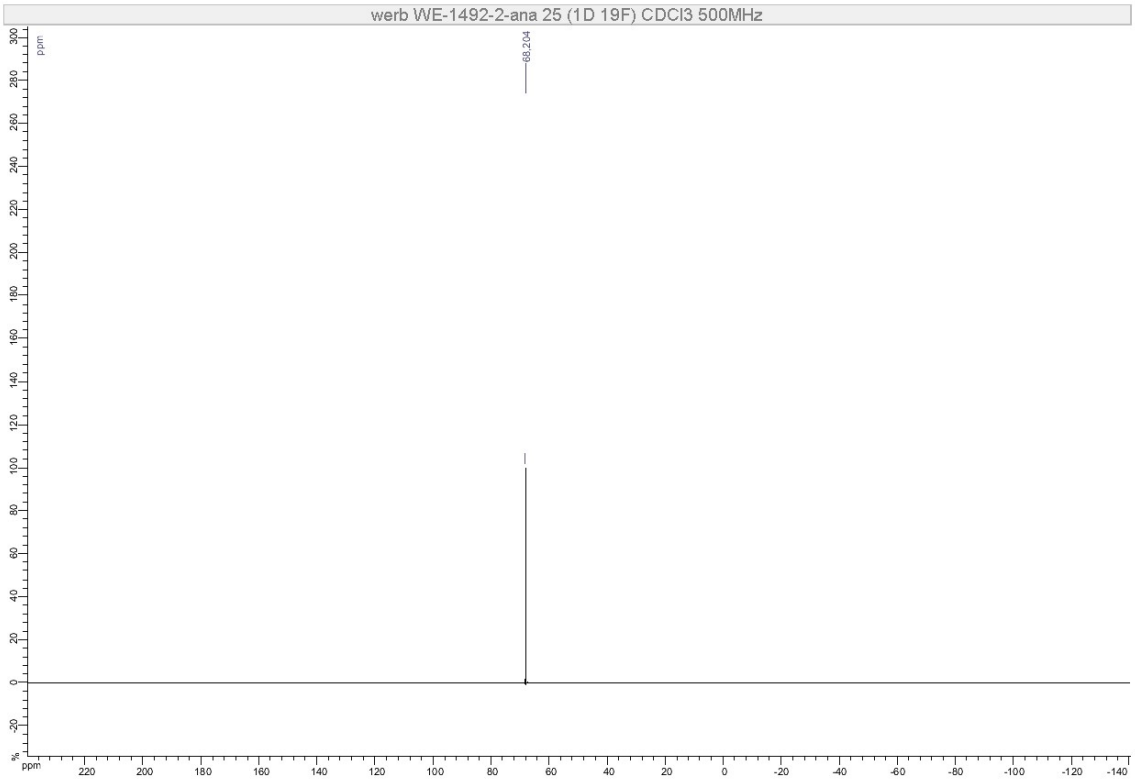

werb WE-1492-2-ana 10 (1D 1H) CDCl3 500MHz
7.260
5.115
5.112
5.110
4.863
4.861
4.858
4.856
4.822
4.819
4.816
4.814
4.467
I
SO2F
Fe
1.0
5.11
ppm


werb WE-1492-2-ana 21 (1D 13C) CDCl3 500MHz
79.093
78.943
78.628
77.411
77.160
76.906
75.576
74.488
70.885
39.029
I
SO2F
Fe
ppm

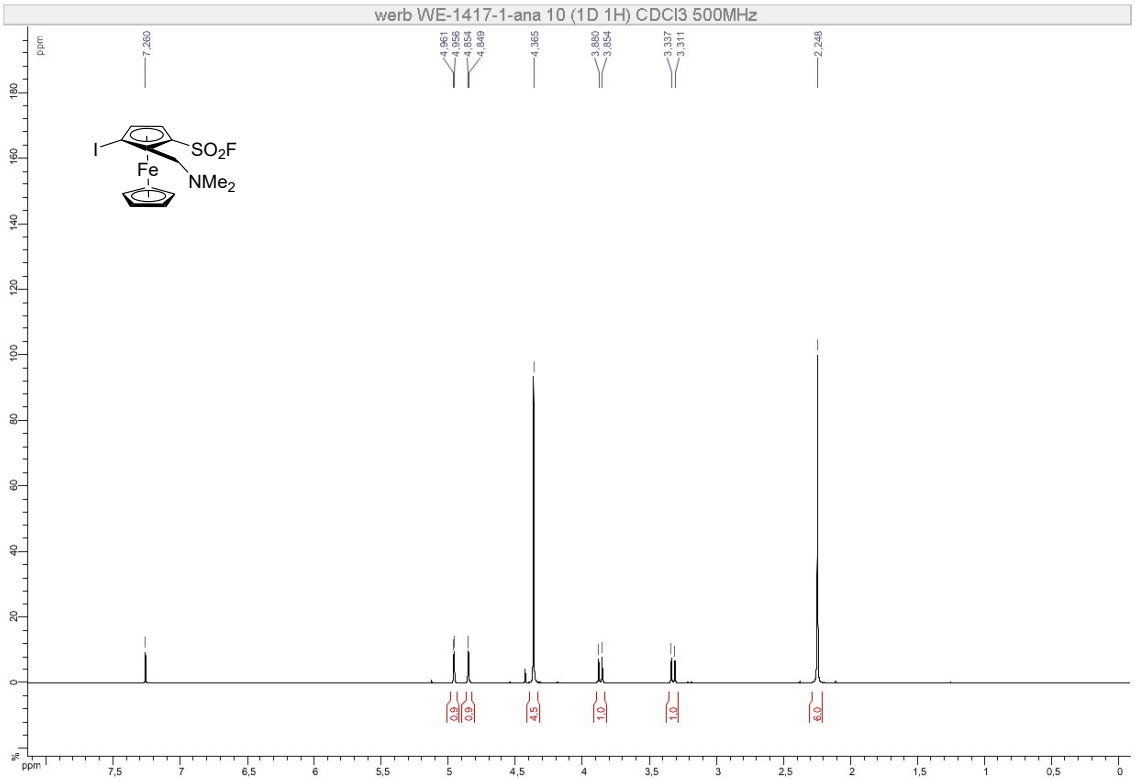

werb WE-1492-2-ana 22 (COSY 1H/1H) CDCl3 500MHz
werb WE-1492-2-ana 10 (1D 1H)
ppm
7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0
werb WE-1492-2-ana 10 (1D 1H)

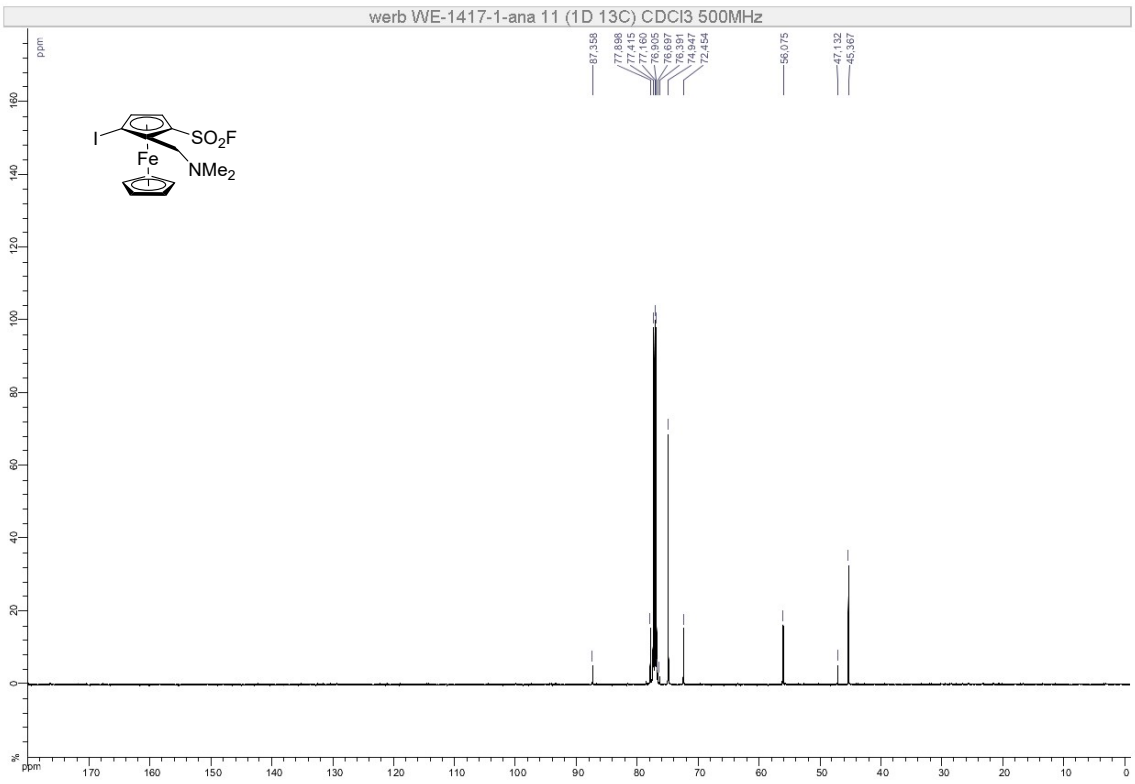

werb WE-1492-2-ana 23 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1492-2-ana 10 (1D 1H)
ppm
7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0
werb WE-1492-2-ana 21 (1D 13C)

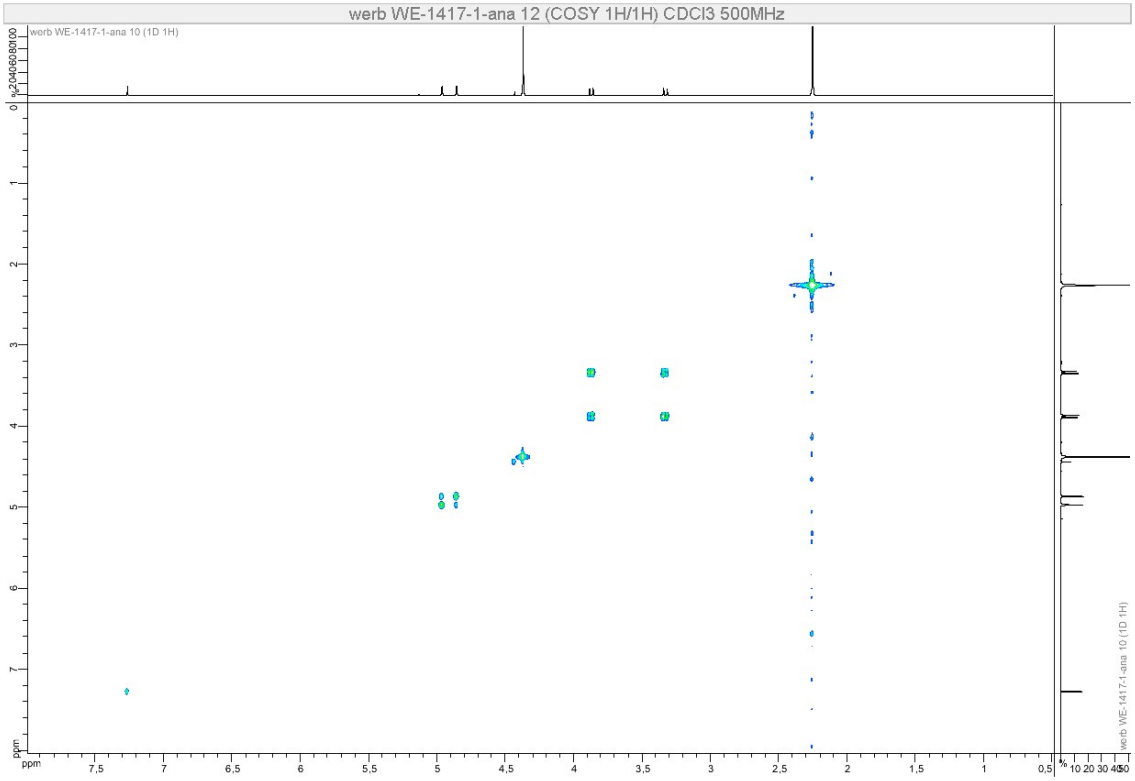

werb WE-1492-2-ana 24 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1492-2-ana 10 (1D 1H)
werb WE-1492-2-ana 21 (1D 13C)
ppm
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
%
20
40
60

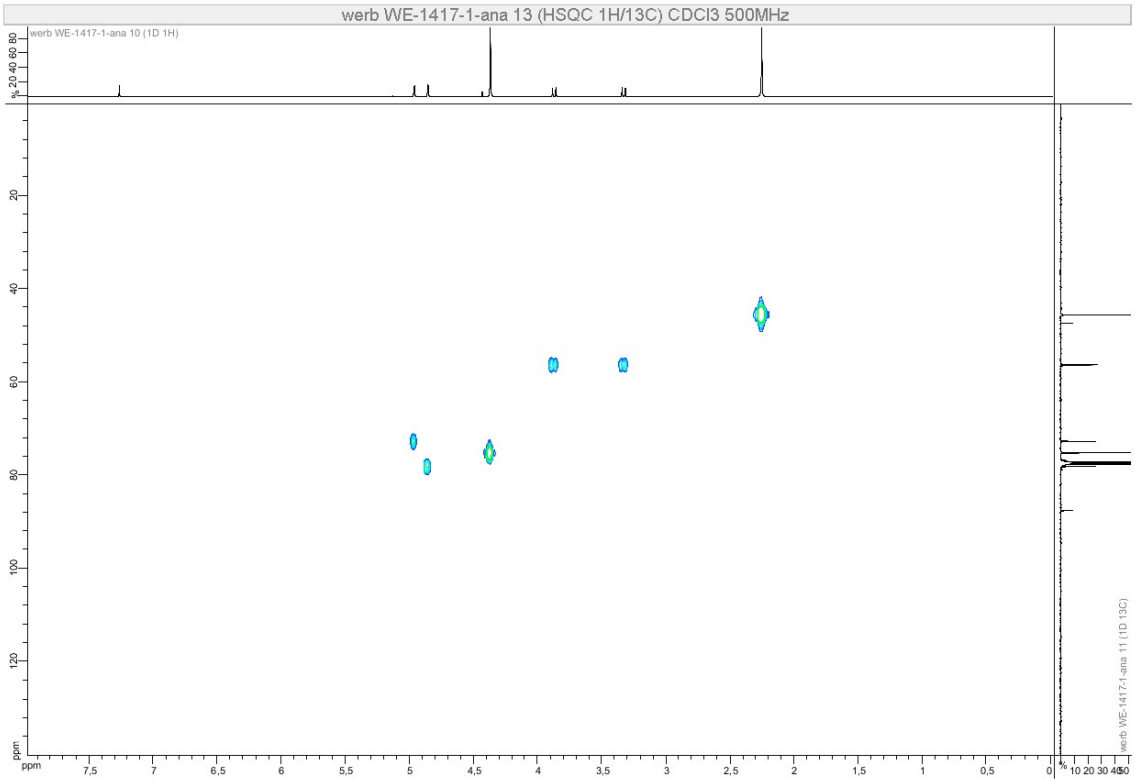

werb WE-1492-2-ana 25 (1D 19F) CDCl3 500MHz
ppm
-68,204
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140

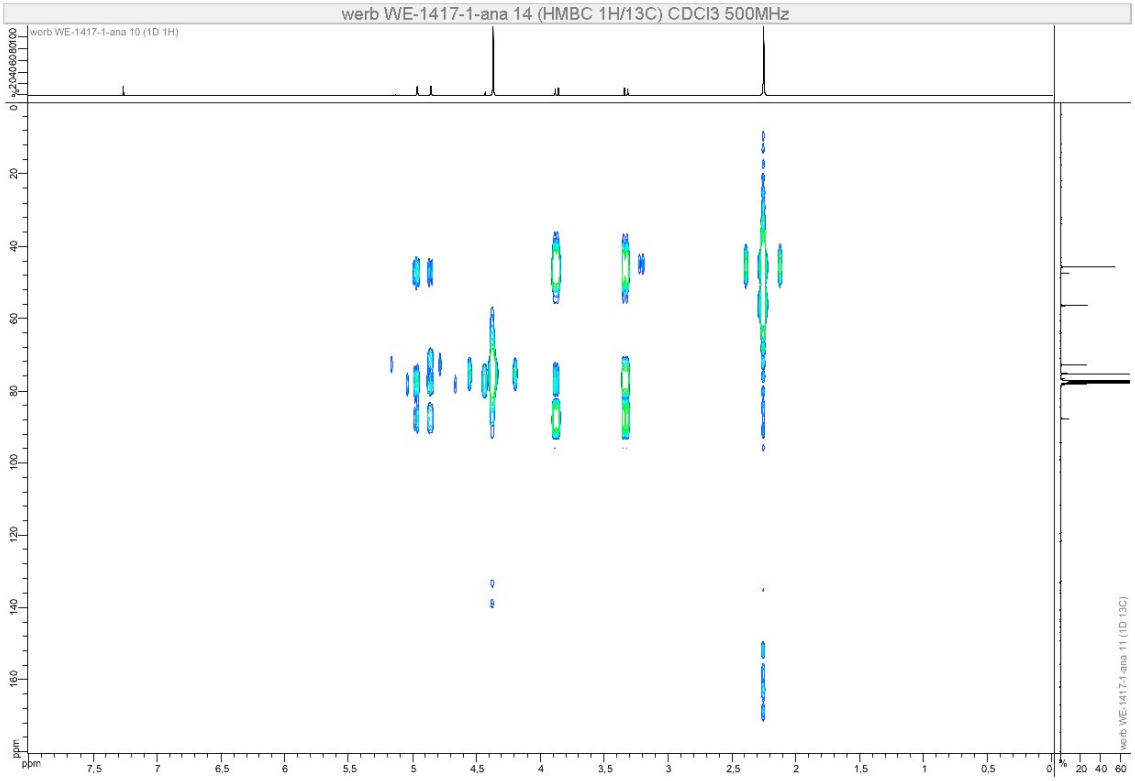
Compound 6b

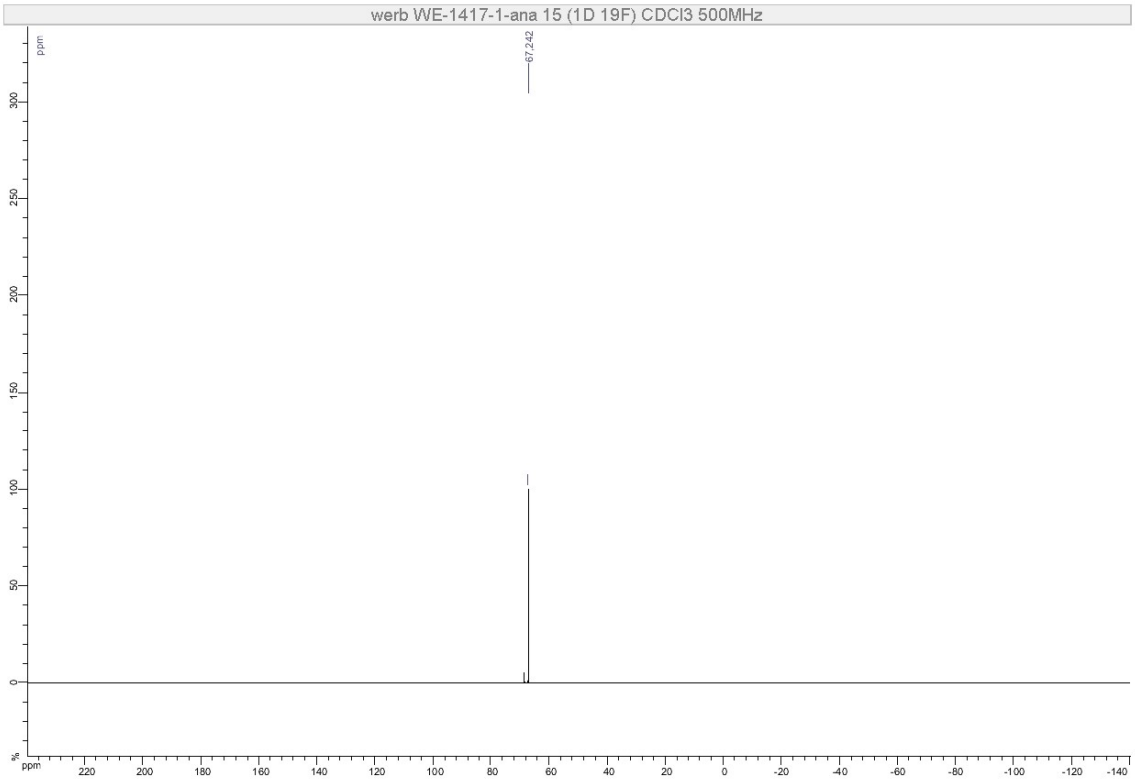

werb WE-1417-1-ana 10 (1D 1H) CDCl3 500MHz
ppm
7.260
4.961
4.956
4.854
4.849
4.365
3.880
3.854
3.337
3.311
2.248
I
SO2F
Fe
NMe2
0.9
0.9
4.5
1.0
1.0
6.0


werb WE-1417-1-ana 11 (1D 13C) CDCl3 500MHz
ppm
87.358
77.898
77.415
77.163
76.905
76.697
76.391
74.947
72.454
56.075
47.132
45.367
I
SO2F
Fe
NMe2

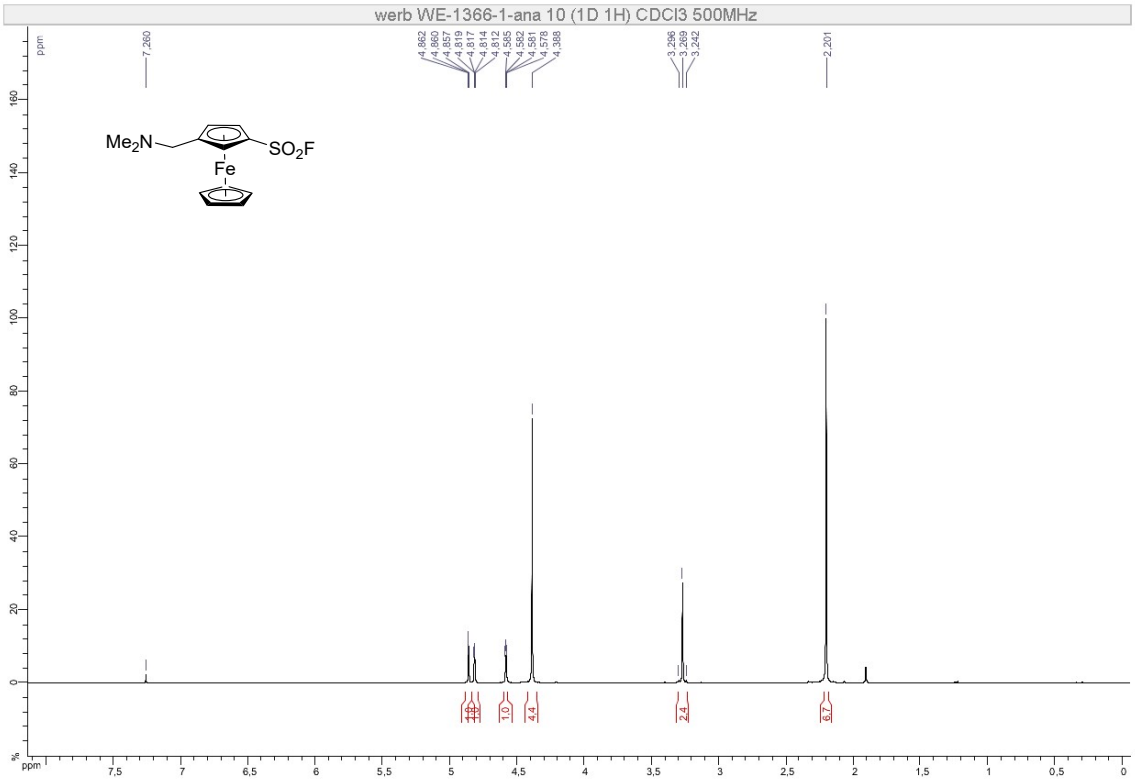

werb WE-1417-1-ana 12 (COSY 1H/1H) CDCl3 500MHz
werb WE-1417-1-ana 10 (1D 1H)
ppm
werb WE-1417-1-ana 10 (1D 1H)

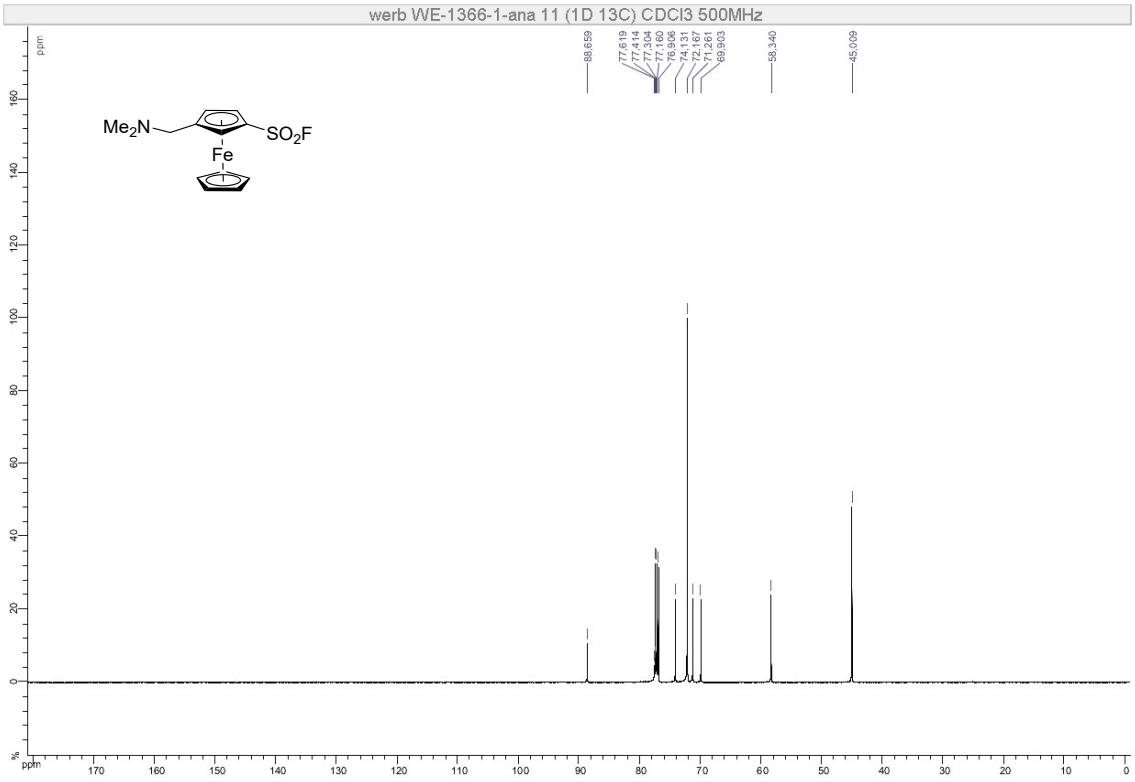

werb WE-1417-1-ana 13 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1417-1-ana 10 (1D 1H)
ppm
werb WE-1417-1-ana 11 (1D 13C)

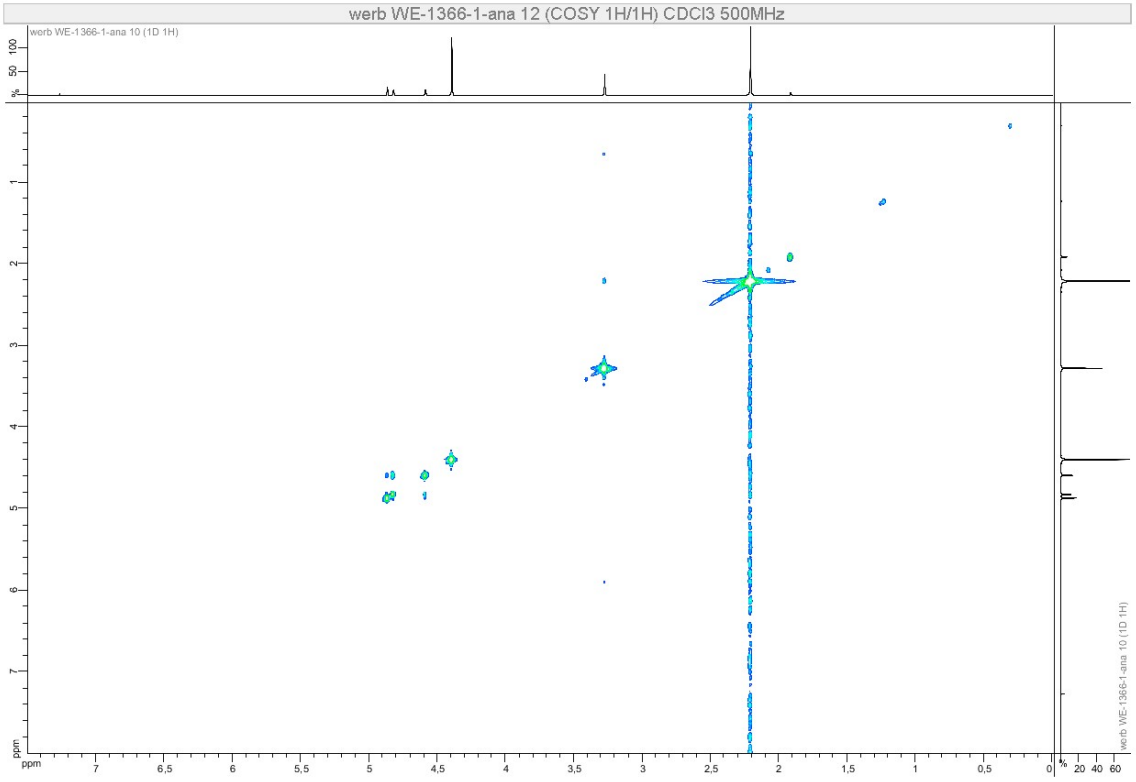

werb WE-1417-1-ana 14 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1417-1-ana 10 (1D 1H)
werb WE-1417-1-ana 11 (1D 13C)
ppm
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
20
40
60
80
100
120
140
160

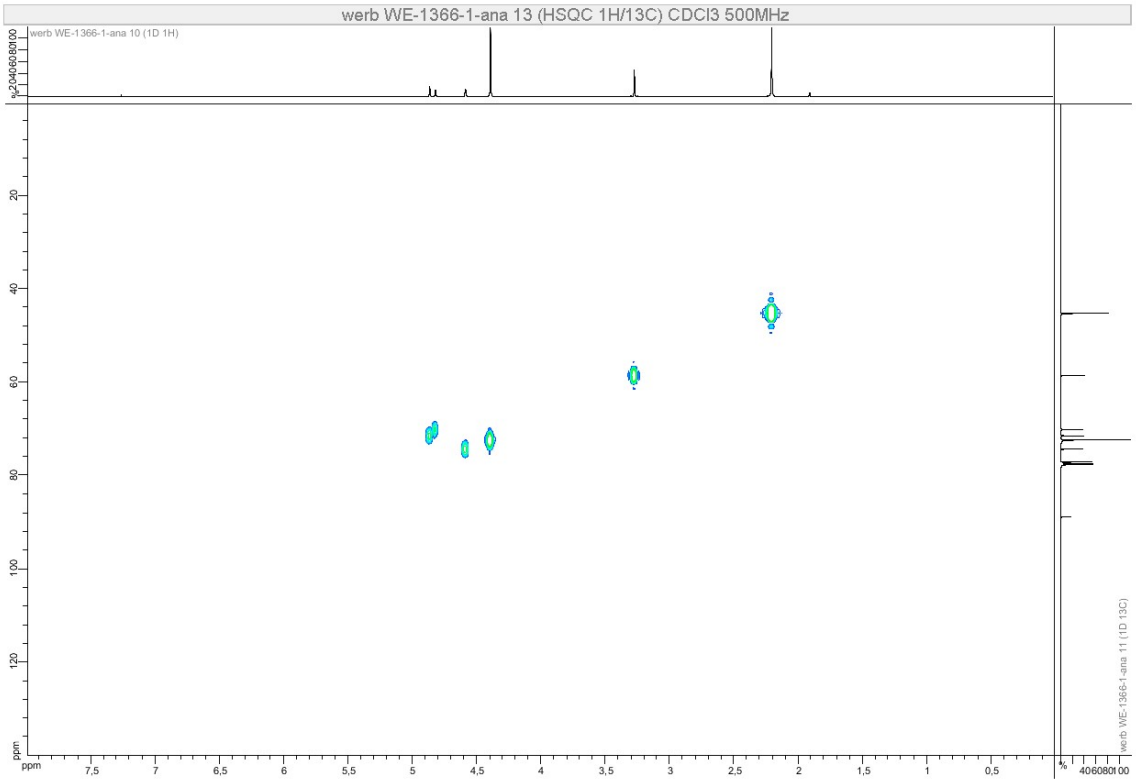

werb WE-1417-1-ana 15 (1D 19F) CDCl3 500MHz
ppm
67,242
300
250
200
150
100
50
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140

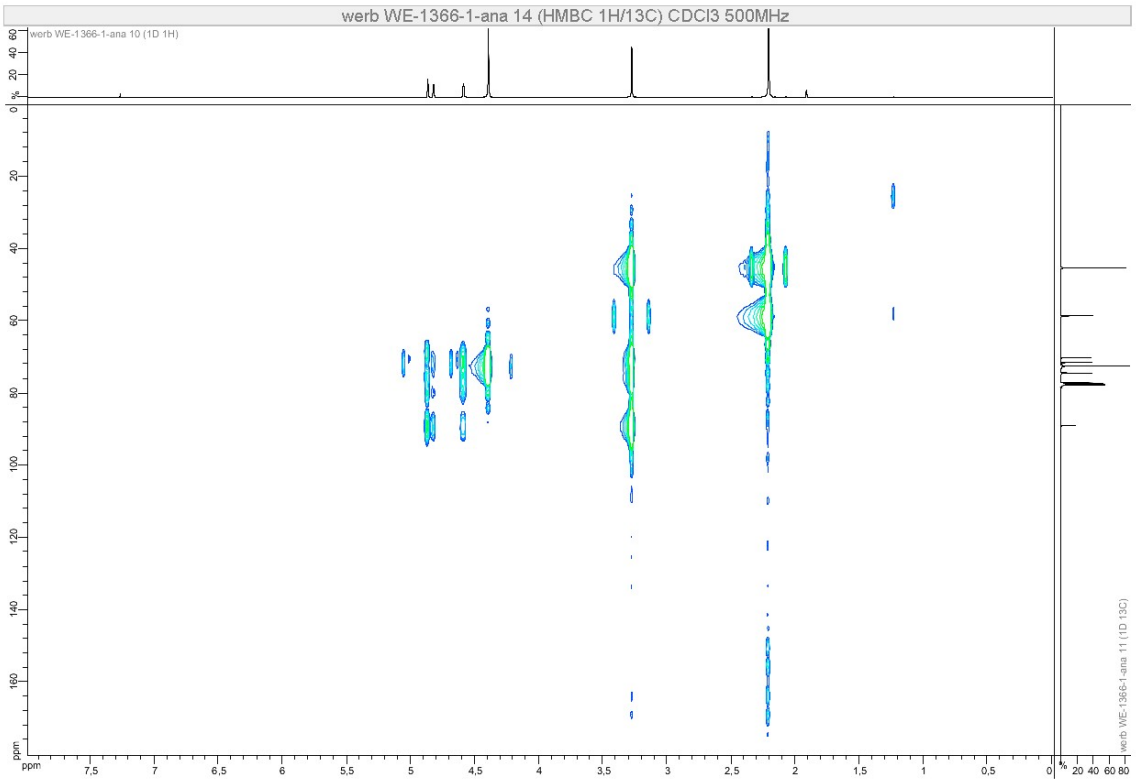
Compound 7a

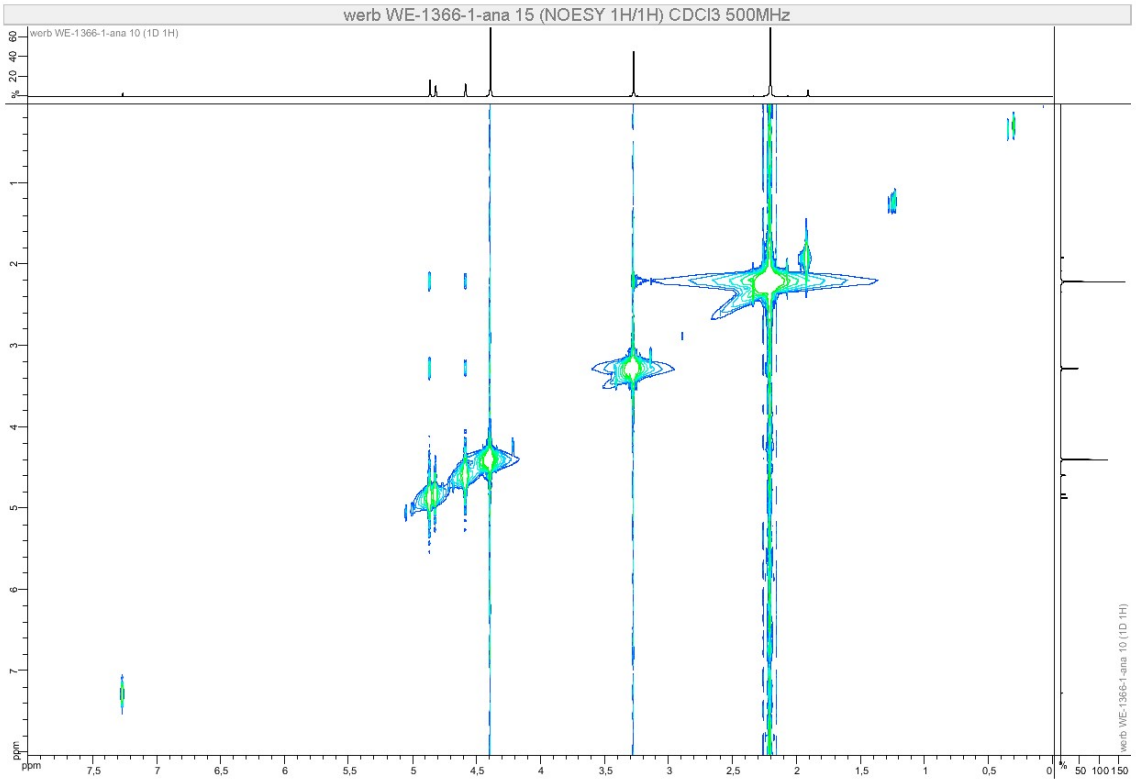

werb WE-1366-1-ana 10 (1D 1H) CDCl3 500MHz
Me2N
SO2F
Fe

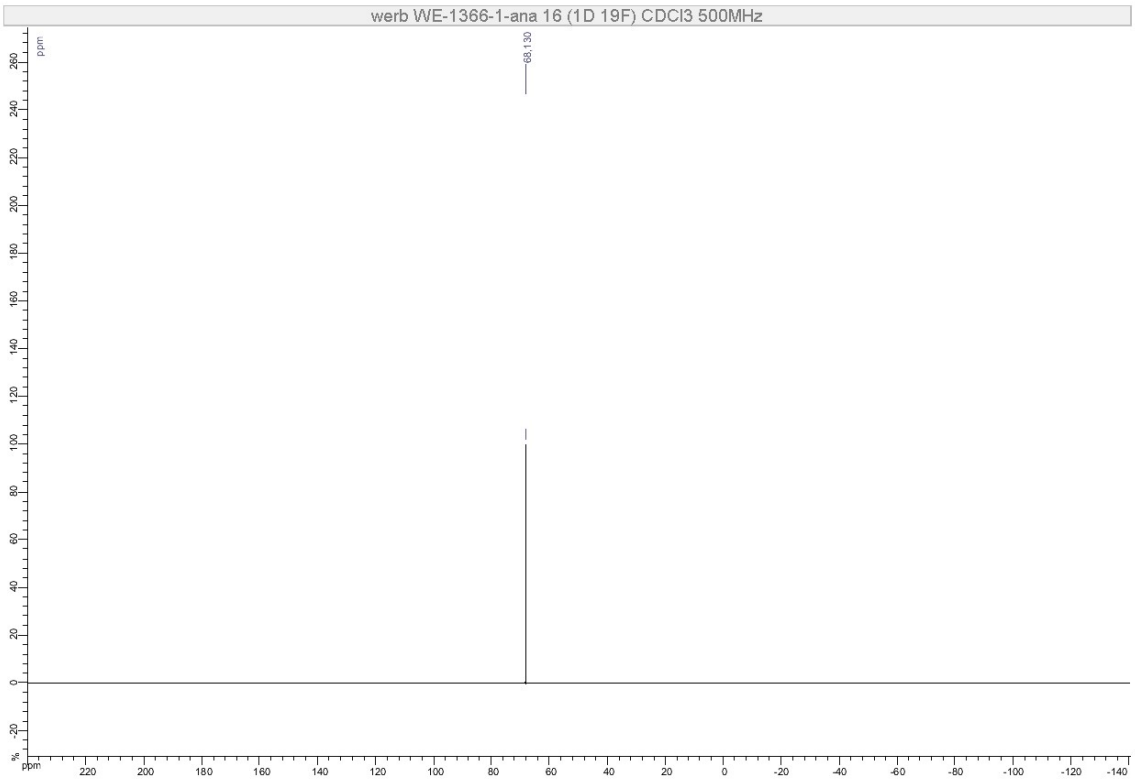

werb WE-1366-1-ana 11 (1D 13C) CDCl3 500MHz
Me2N
SO2F
Fe


werb WE-1366-1-ana 12 (COSY 1H/1H) CDCl3 500MHz
werb WE-1366-1-ana 10 (1D 1H)
ppm
werb WE-1366-1-ana 10 (1D 1H)

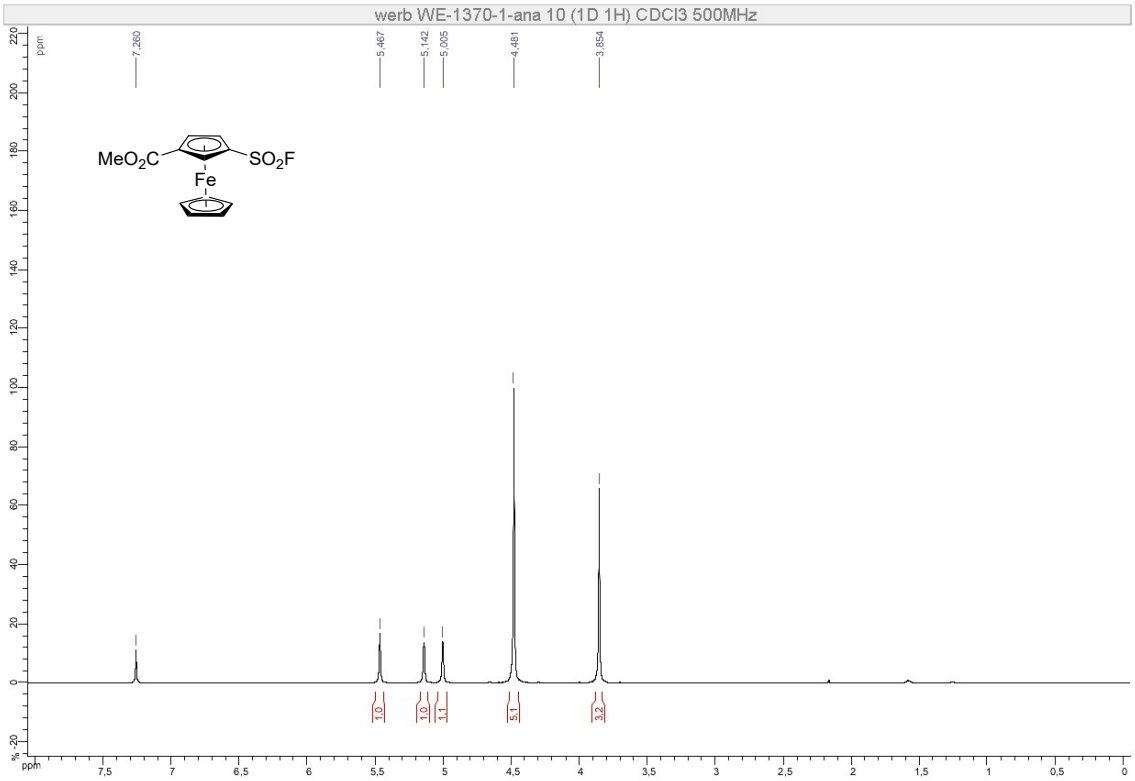

werb WE-1366-1-ana 13 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1366-1-ana 10 (1D 1H)
ppm
werb WE-1366-1-ana 11 (1D 13C)

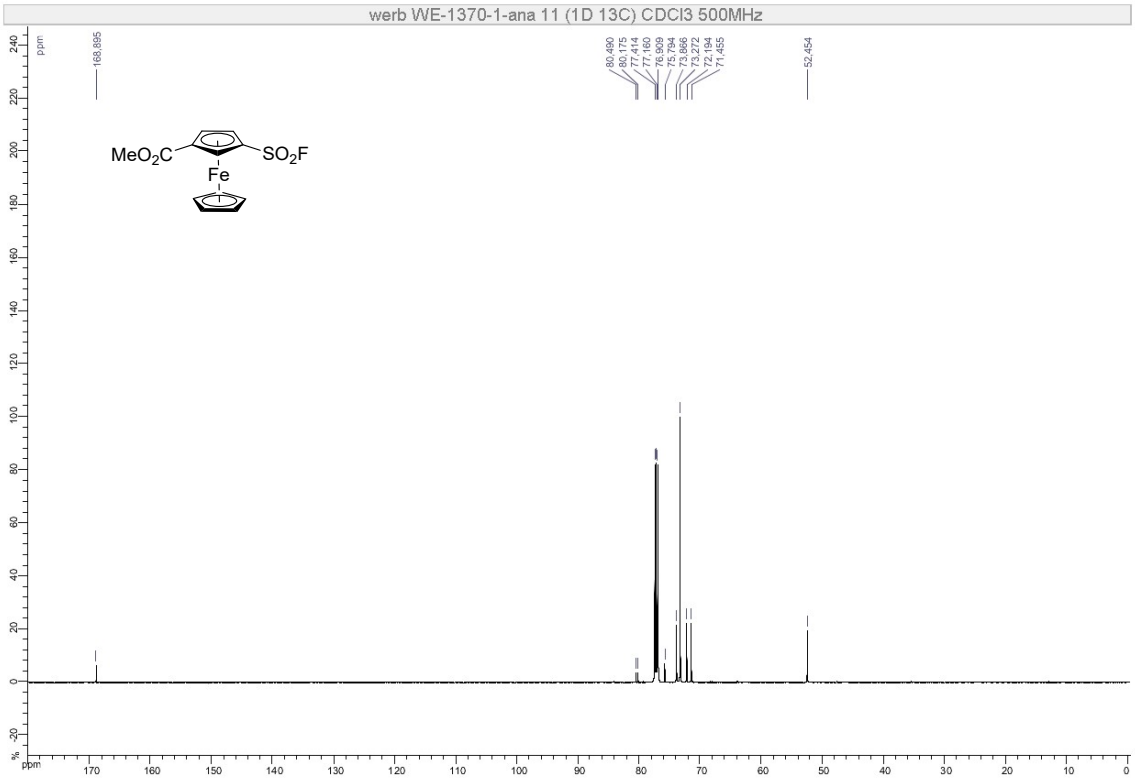

werb WE-1366-1-ana 14 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1366-1-ana 10 (1D 1H)
werb WE-1366-1-ana 11 (1D 13C)
ppm
%

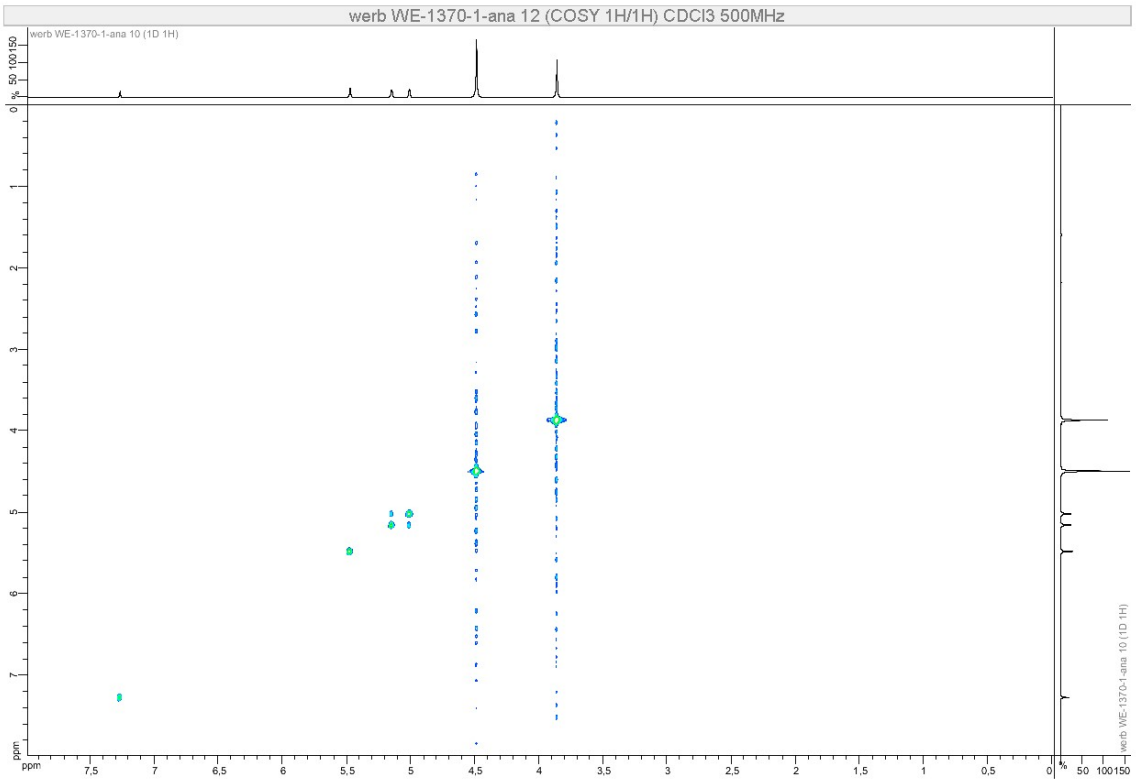

werb WE-1366-1-ana 15 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1366-1-ana 10 (1D 1H)
werb WE-1366-1-ana 10 (1D 1H)
ppm
%

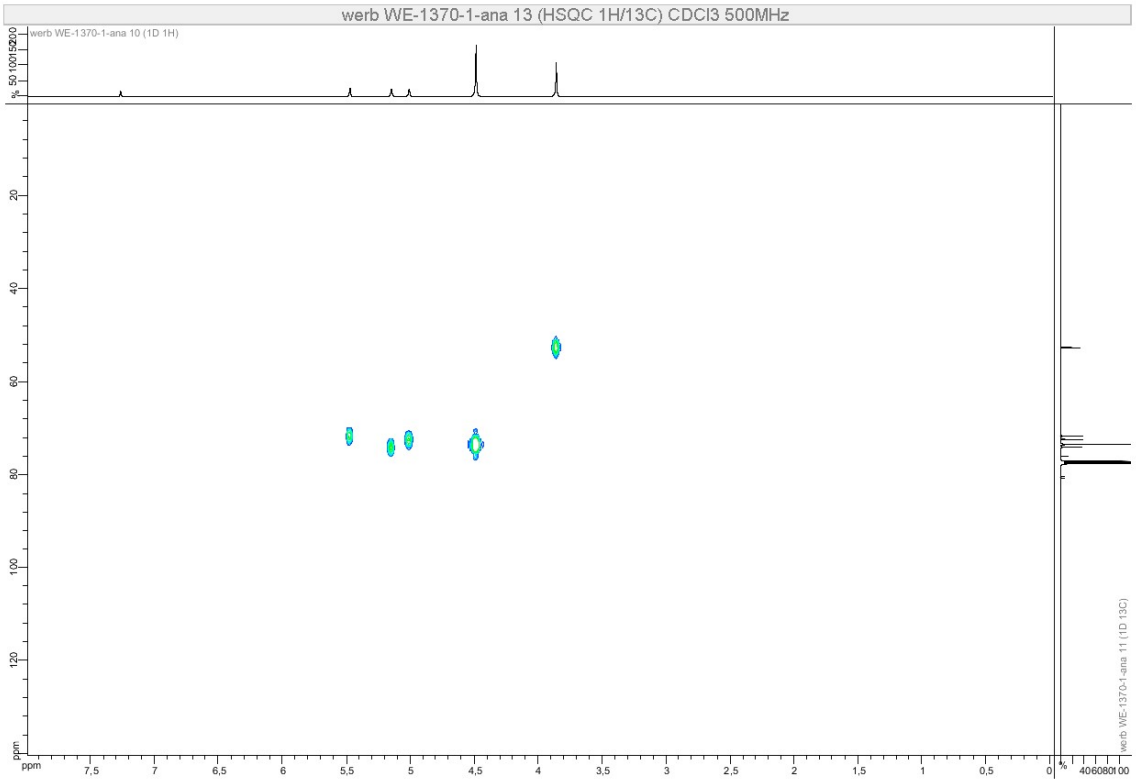

werb WE-1366-1-ana 16 (1D 19F) CDCl3 500MHz
ppm
68.130
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140

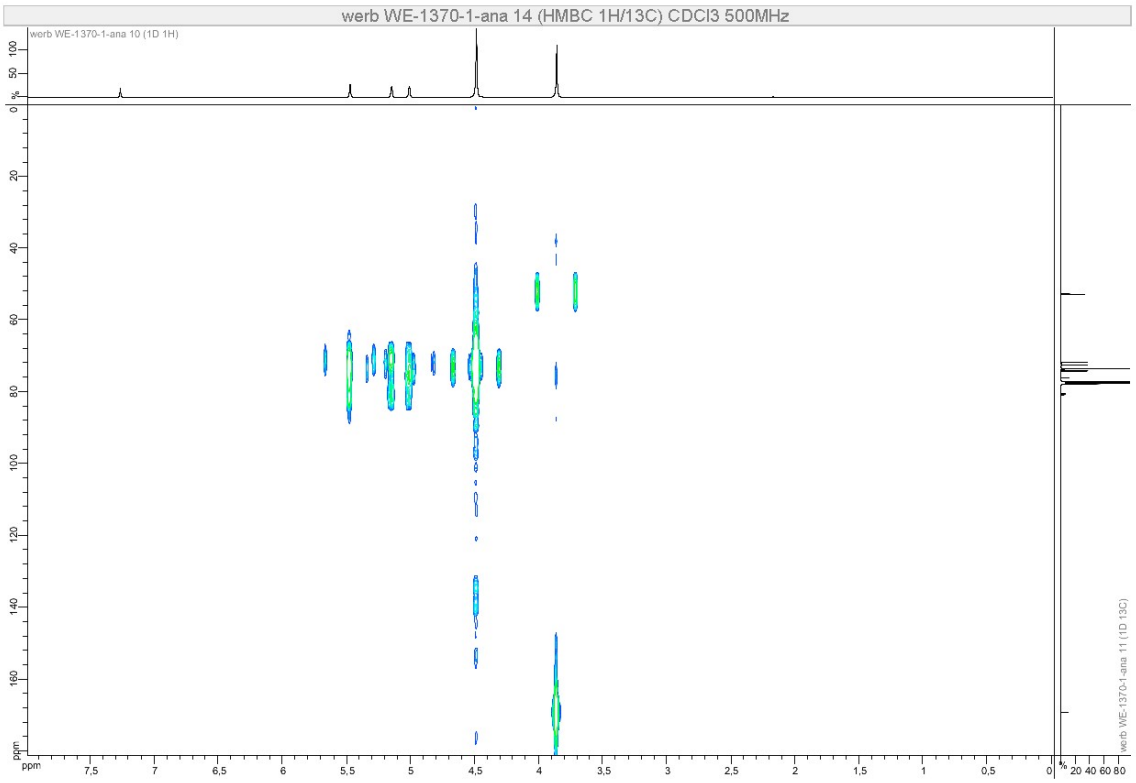
Compound 7b

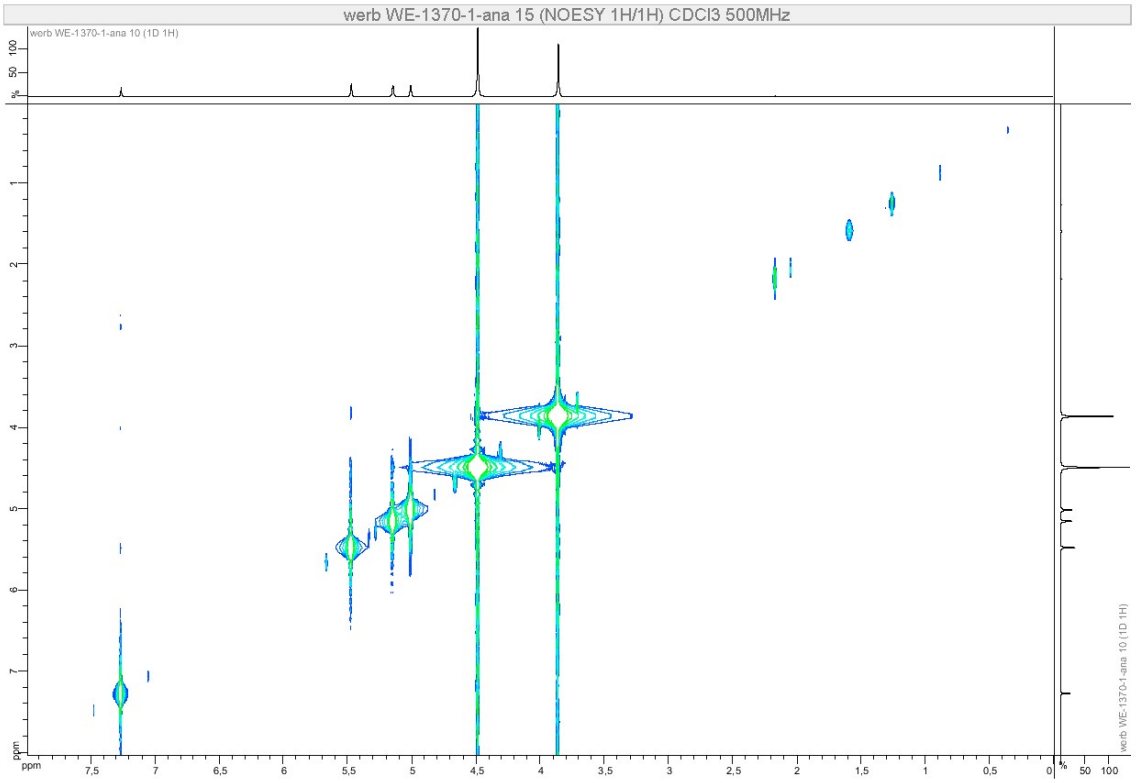

werb WE-1370-1-ana 10 (1D 1H) CDCl3 500MHz
ppm
7.260
5.467
5.142
5.005
4.481
3.854
MeO2C
SO2F
Fe
1.0
1.0
1.1
5.1
3.2

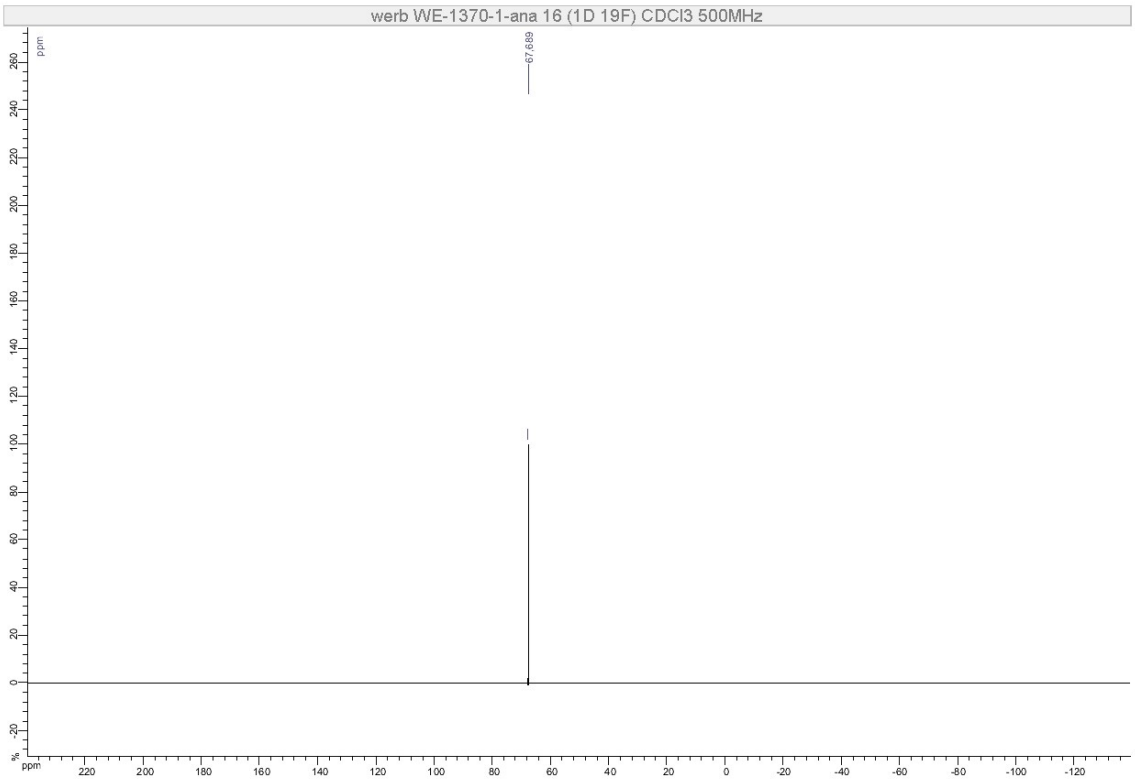

werb WE-1370-1-ana 11 (1D 13C) CDCl3 500MHz
ppm
168.895
80.490
80.175
77.414
77.160
76.909
75.794
73.886
73.272
72.194
71.455
52.454
MeO2C
SO2F
Fe


werb WE-1370-1-ana 12 (COSY 1H/1H) CDCl3 500MHz
werb WE-1370-1-ana 10 (1D 1H)
ppm
werb WE-1370-1-ana 10 (1D 1H)

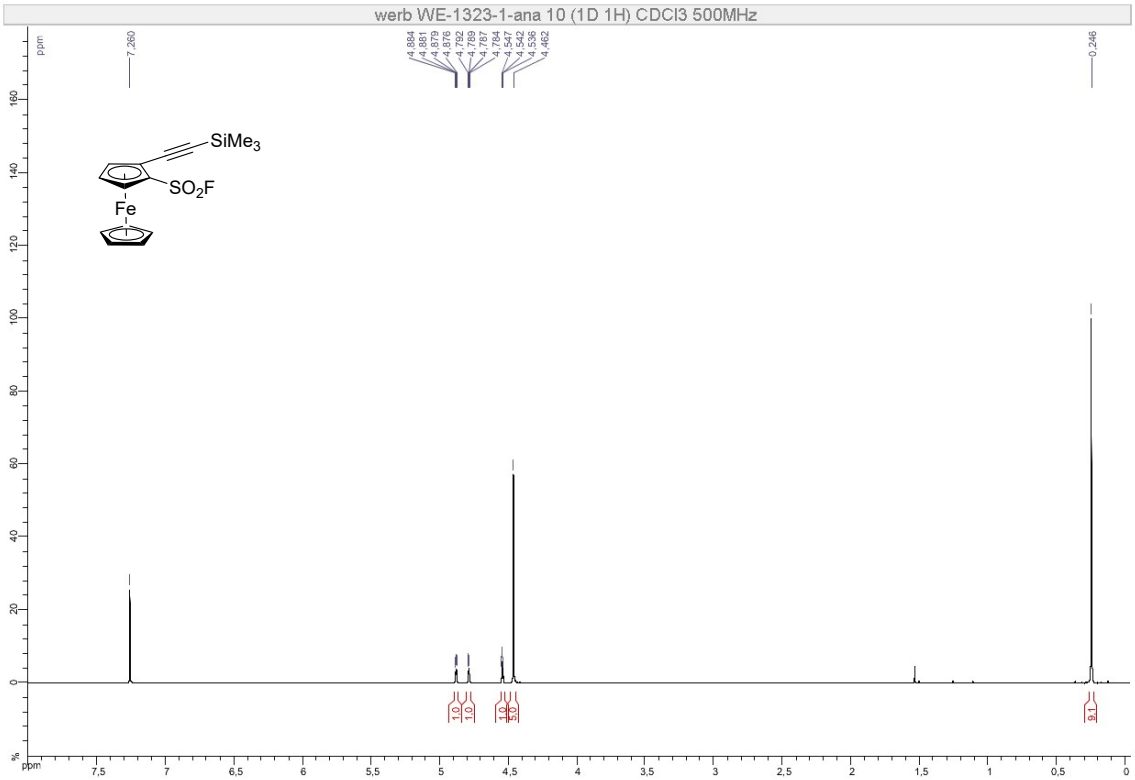

werb WE-1370-1-ana 13 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1370-1-ana 10 (1D 1H)
ppm
werb WE-1370-1-ana 11 (1D 13C)

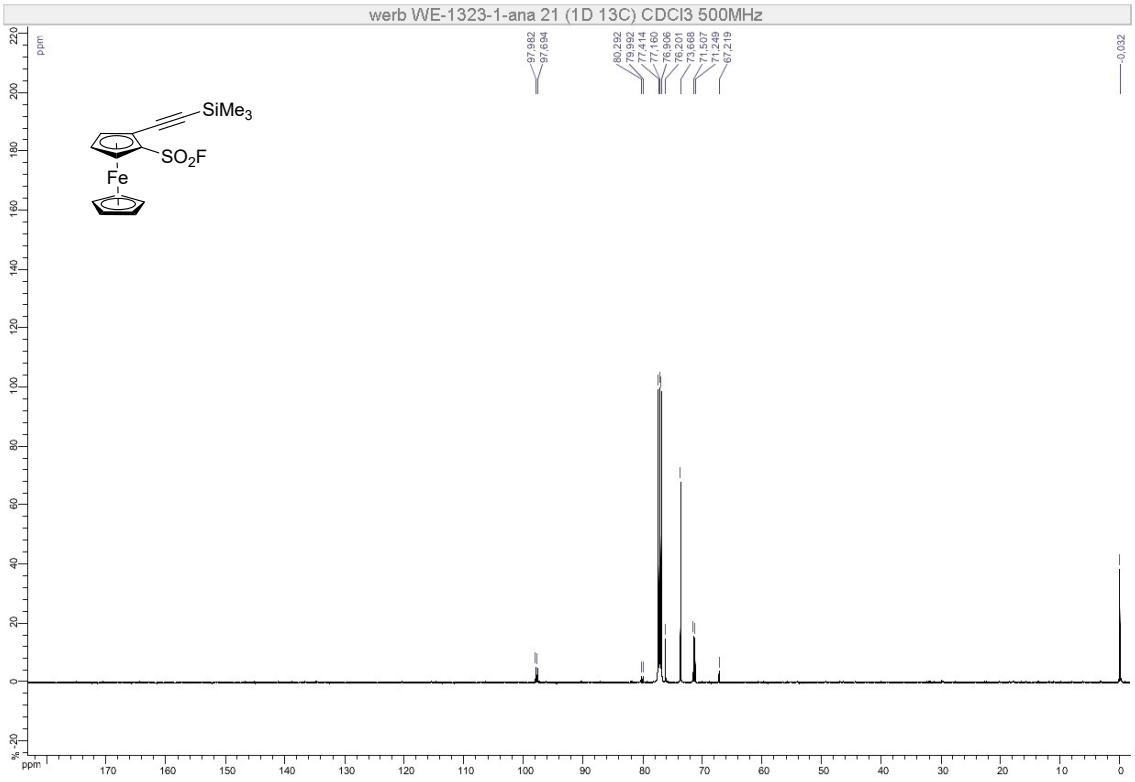

werb WE-1370-1-ana 14 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1370-1-ana 10 (1D 1H)
werb WE-1370-1-ana 11 (1D 13C)
ppm
%

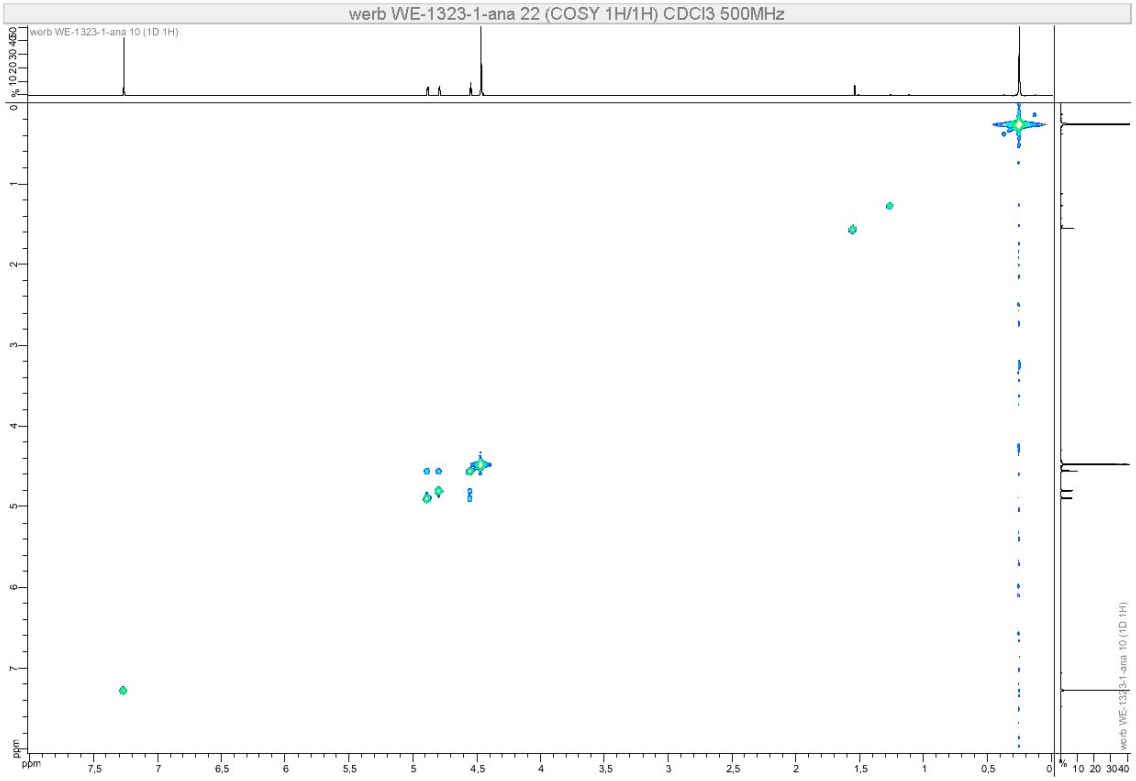

werb WE-1370-1-ana 15 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1370-1-ana 10 (1D 1H)
werb WE-1370-1-ana 10 (1D 1H)
ppm
%

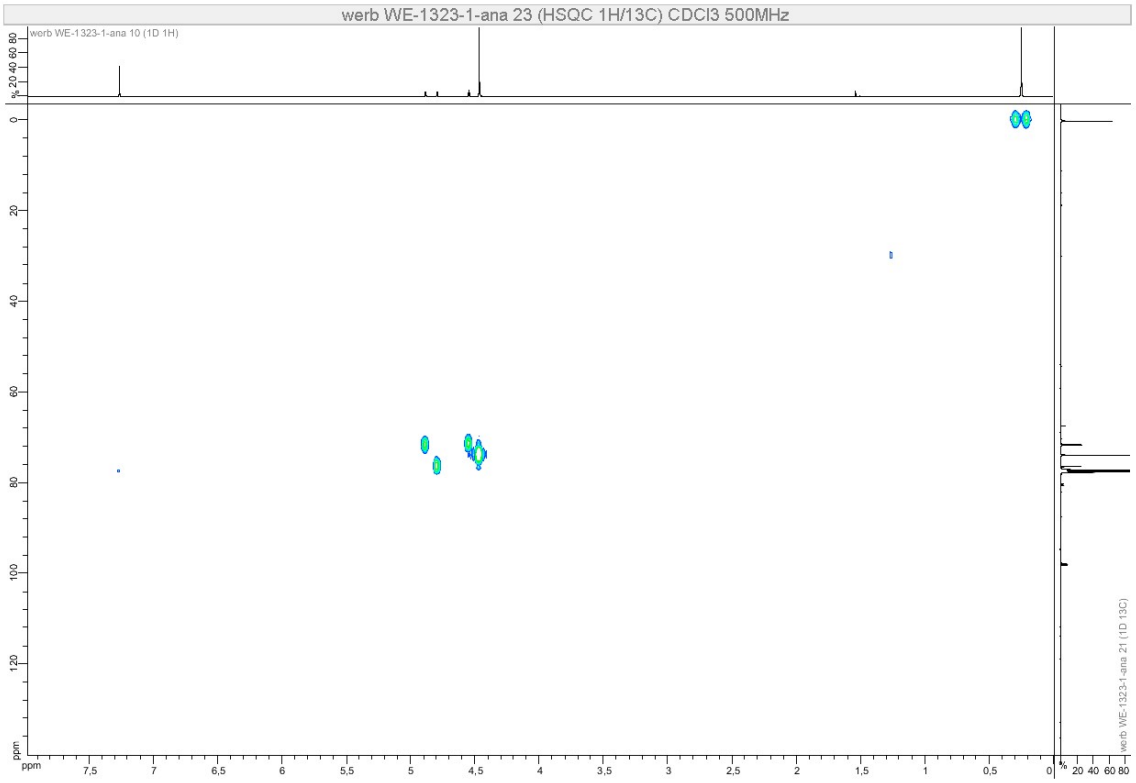

werb WE-1370-1-ana 16 (1D 19F) CDCl3 500MHz
ppm
-67.689
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120

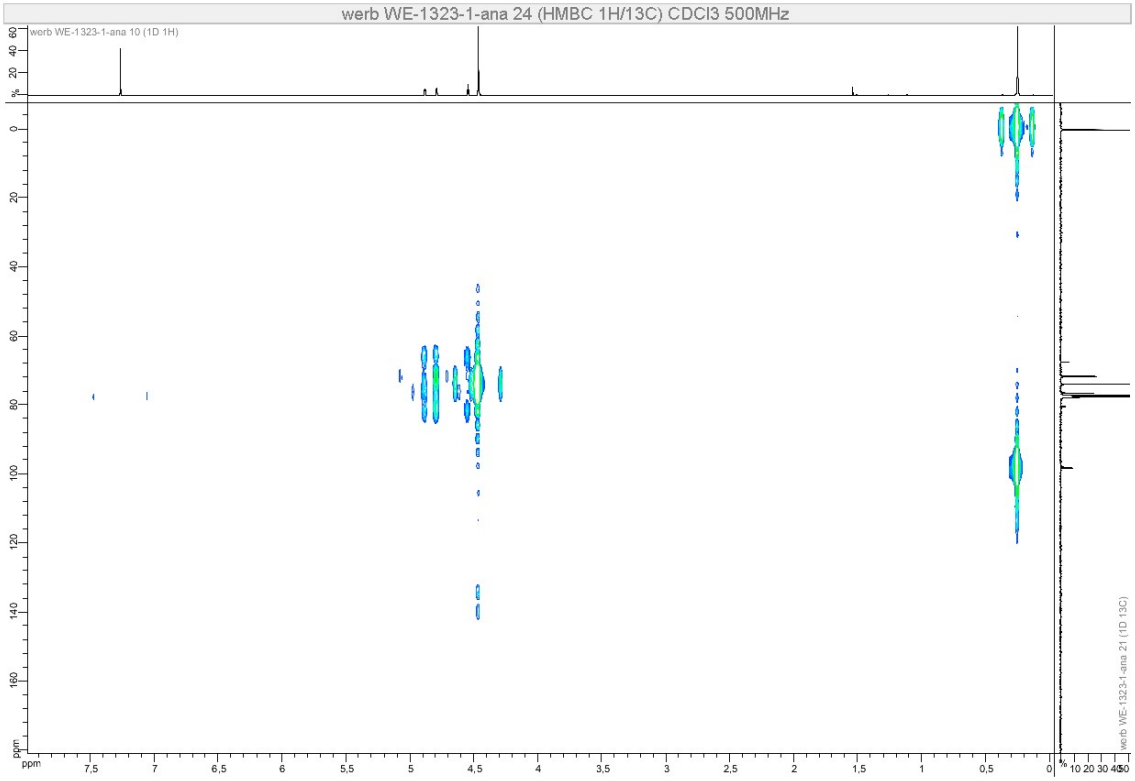
Compound 8a

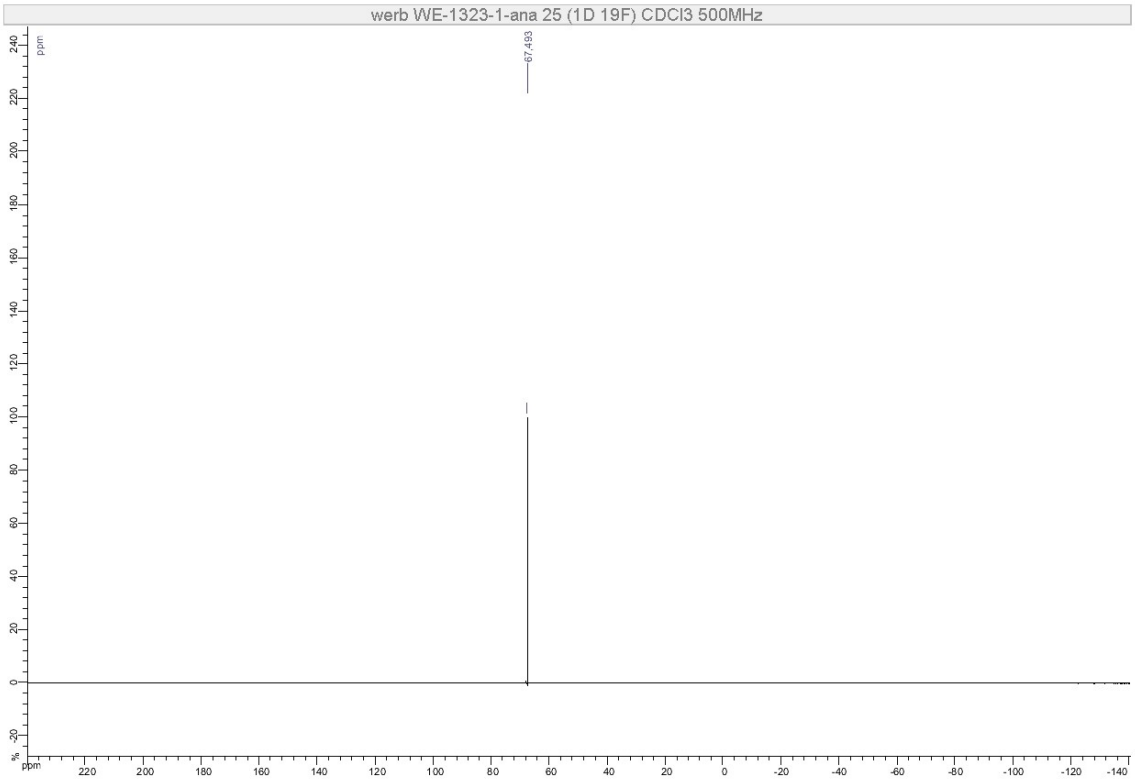

werb WE-1323-1-ana 10 (1D 1H) CDCl3 500MHz
SiMe3
SO2F
Fe


werb WE-1323-1-ana 21 (1D 13C) CDCl3 500MHz
SiMe3
SO2F
Fe

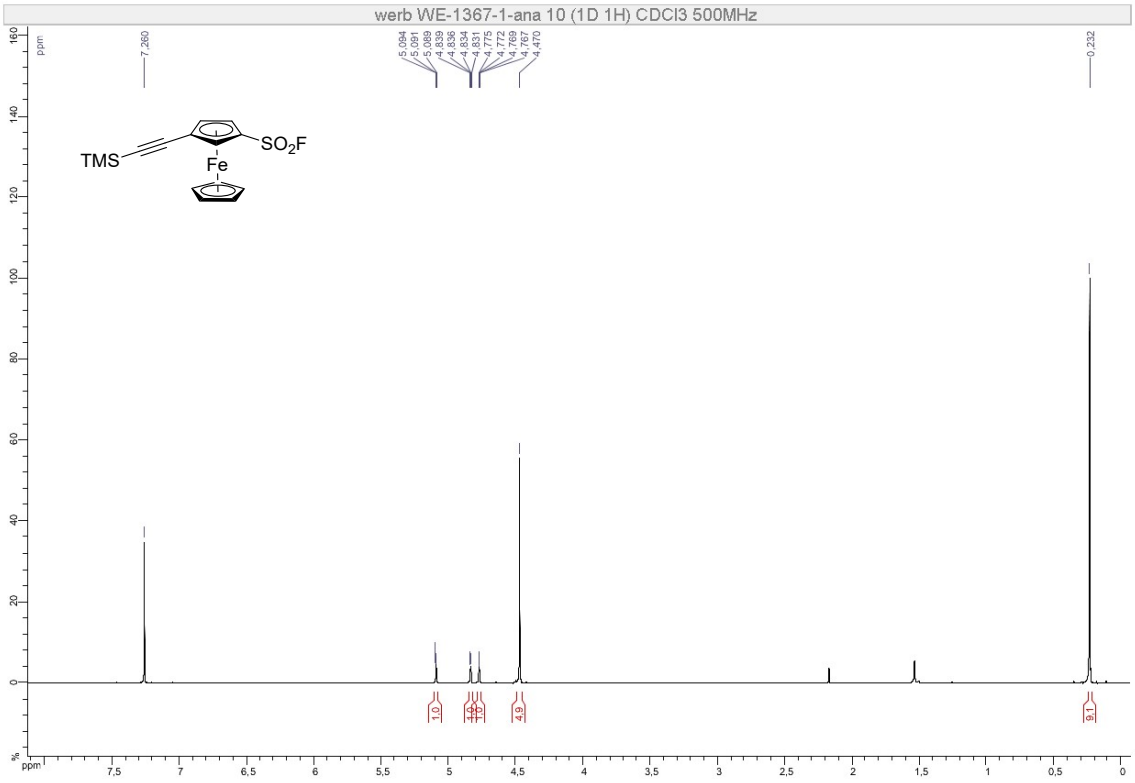

werb WE-1323-1-ana 22 (COSY 1H/1H) CDCl3 500MHz
werb WE-1323-1-ana 10 (1D 1H)
ppm
werb WE-1323-1-ana 10 (1D 1H)

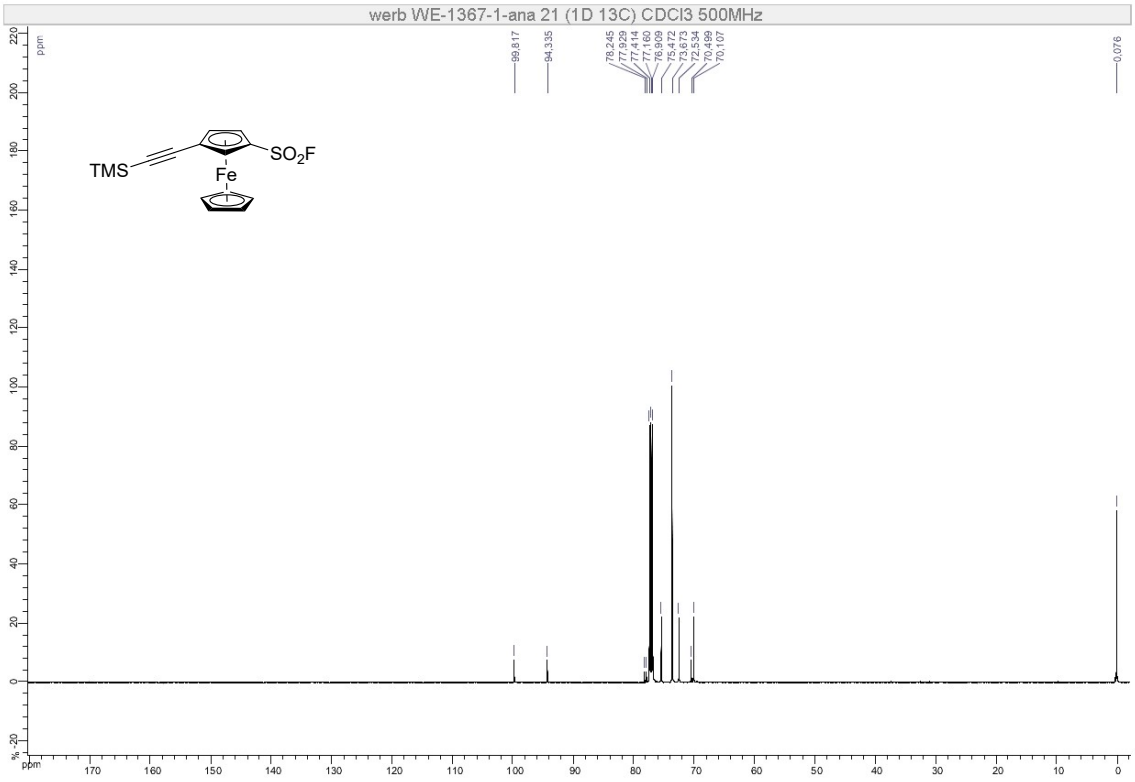

werb WE-1323-1-ana 23 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1323-1-ana 10 (1D 1H)
ppm
werb WE-1323-1-ana 21 (1D 13C)

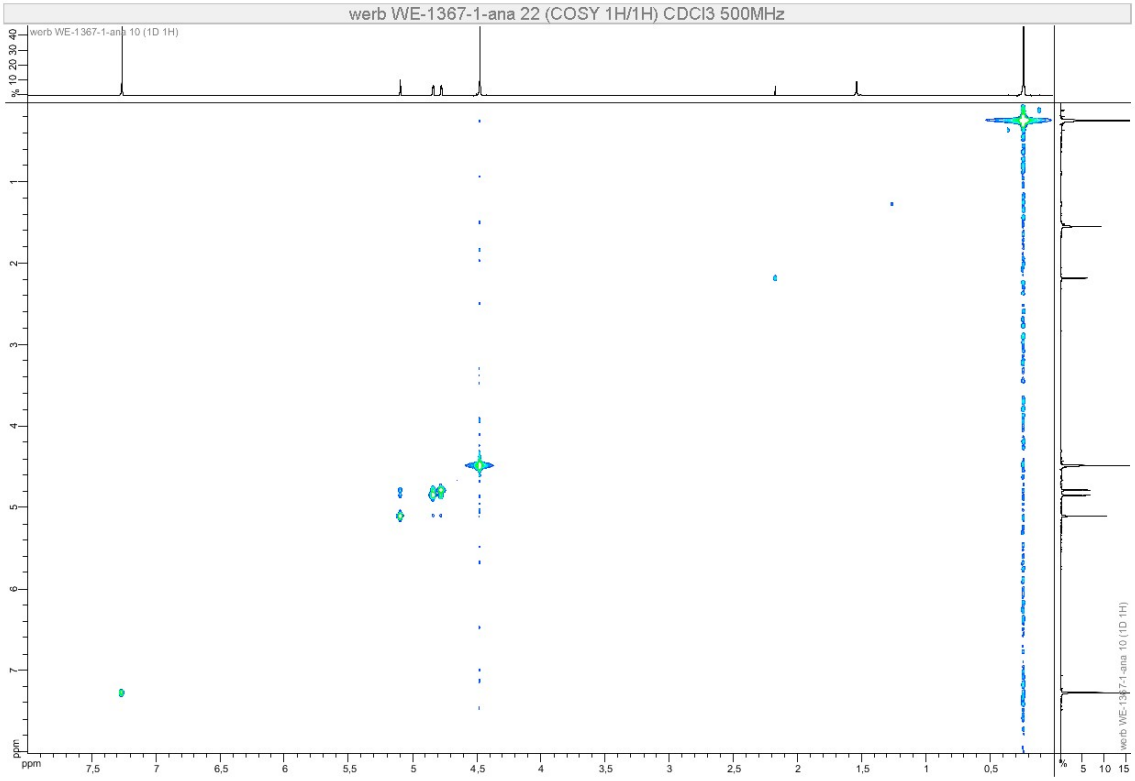

werb WE-1323-1-ana 24 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1323-1-ana 10 (1D 1H)
werb WE-1323-1-ana 21 (1D 13C)
ppm
%

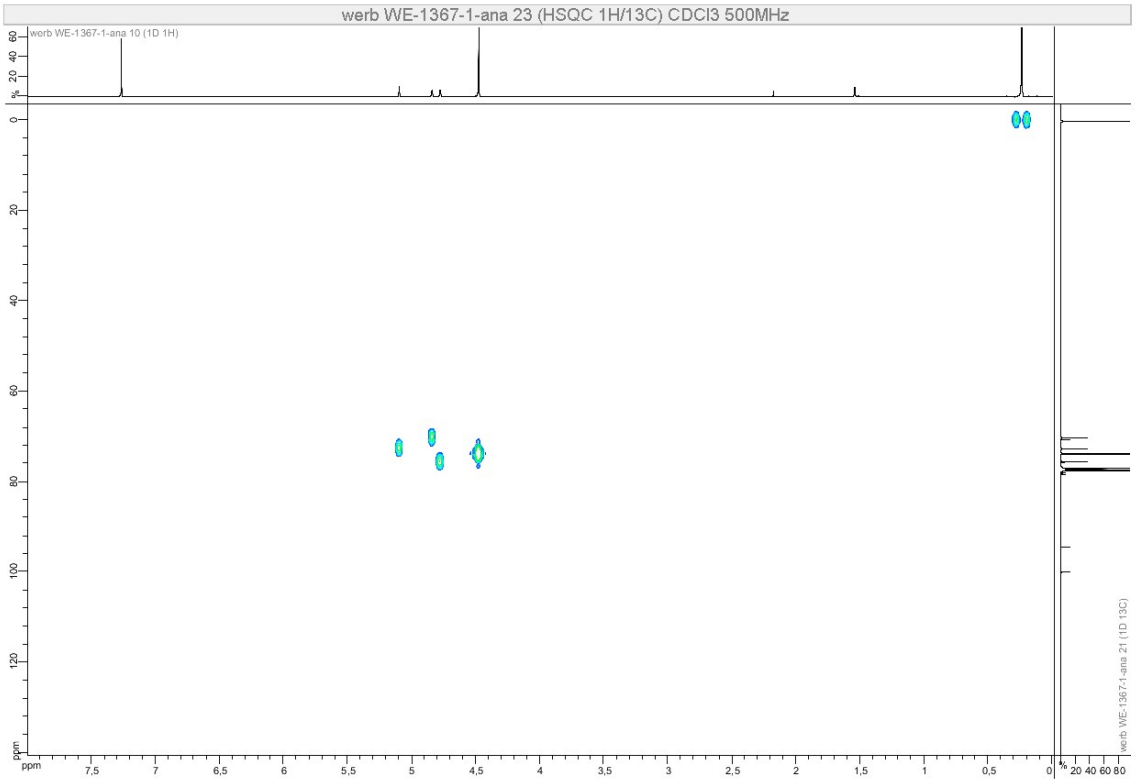

werb WE-1323-1-ana 25 (1D 19F) CDCl3 500MHz
67,493
ppm
%

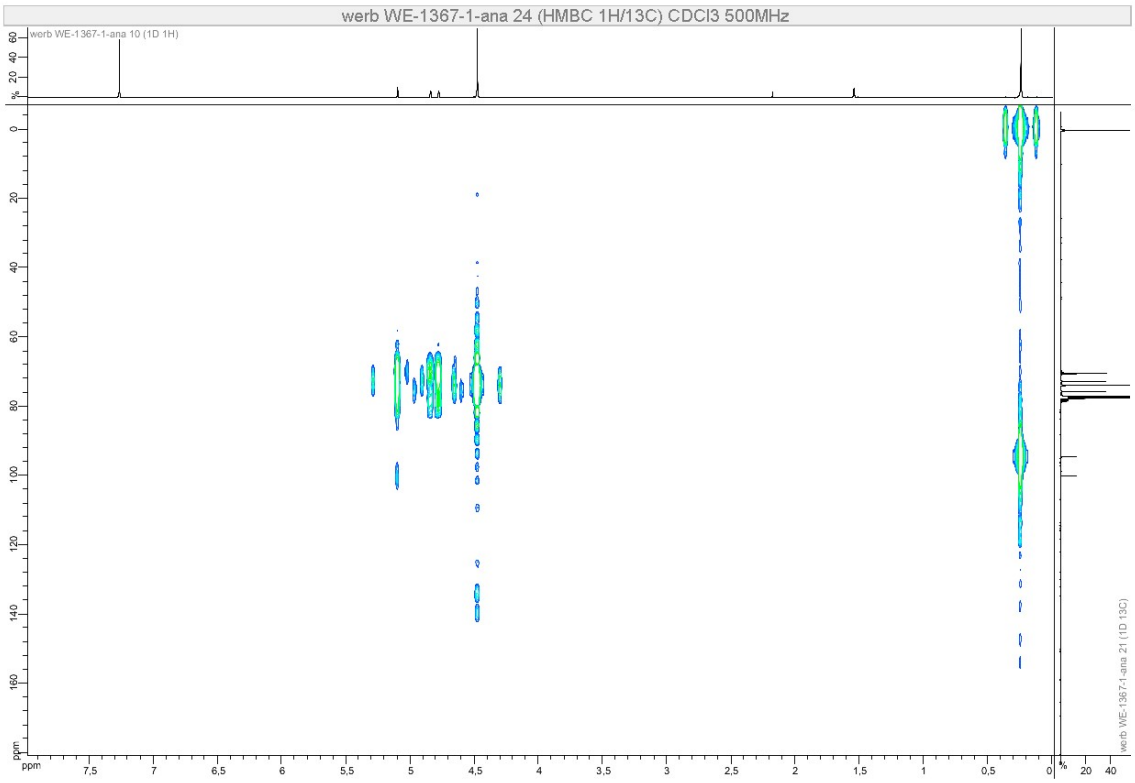
Compound 8b

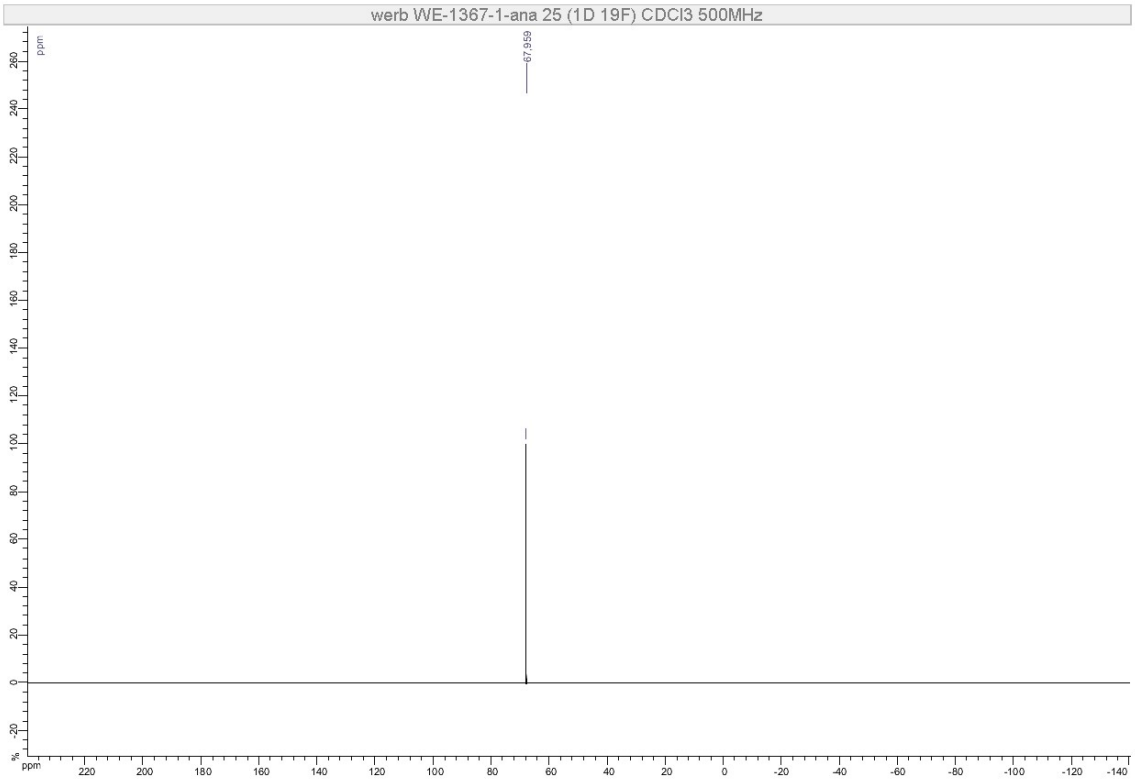

werb WE-1367-1-ana 10 (1D 1H) CDCl3 500MHz
TMS
Fe
SO2F


werb WE-1367-1-ana 21 (1D 13C) CDCl3 500MHz
TMS
Fe
SO2F

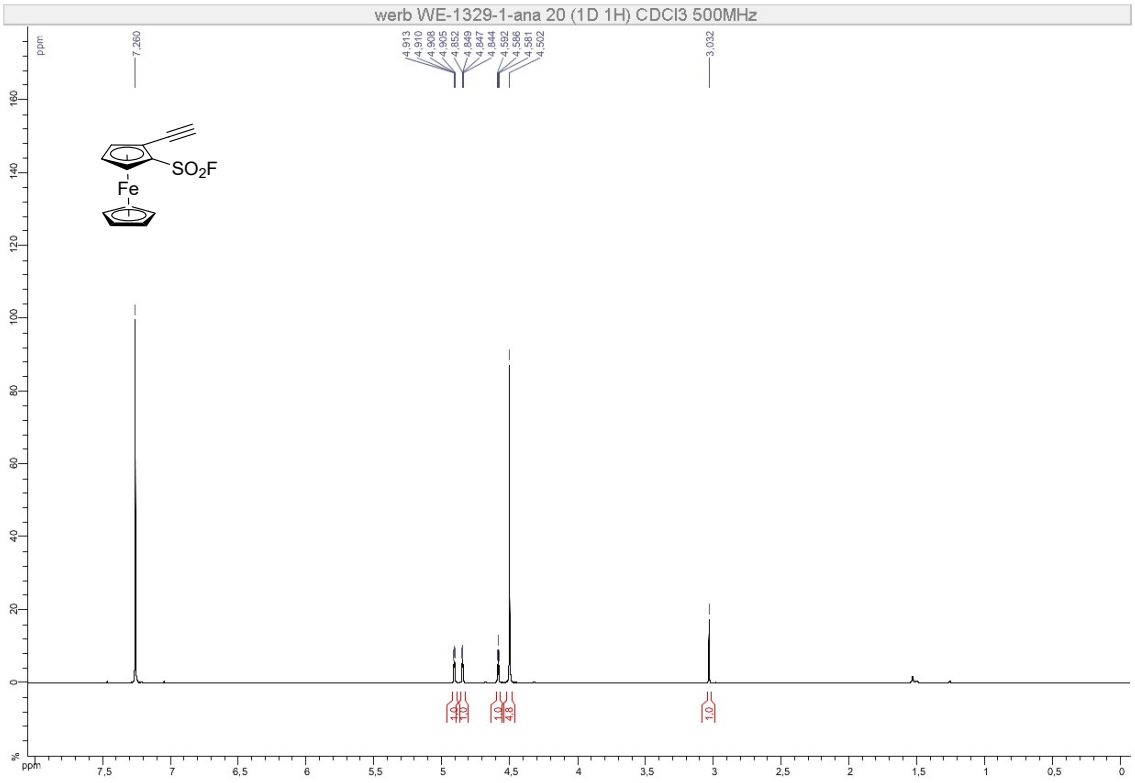

werb WE-1367-1-ana 22 (COSY 1H/1H) CDCl3 500MHz
werb WE-1367-1-ana 10 (1D 1H)
ppm
werb WE-1367-1-ana 10 (1D 1H)

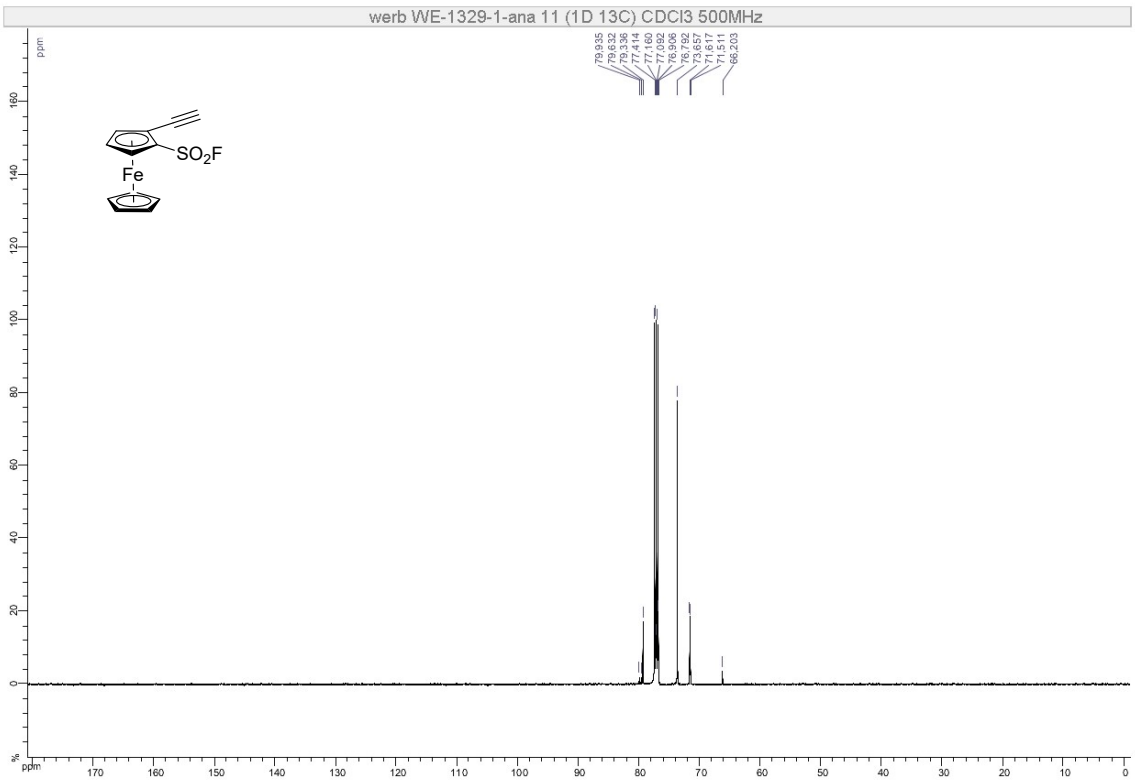

werb WE-1367-1-ana 23 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1367-1-ana 10 (1D 1H)
ppm
werb WE-1367-1-ana 21 (1D 13C)

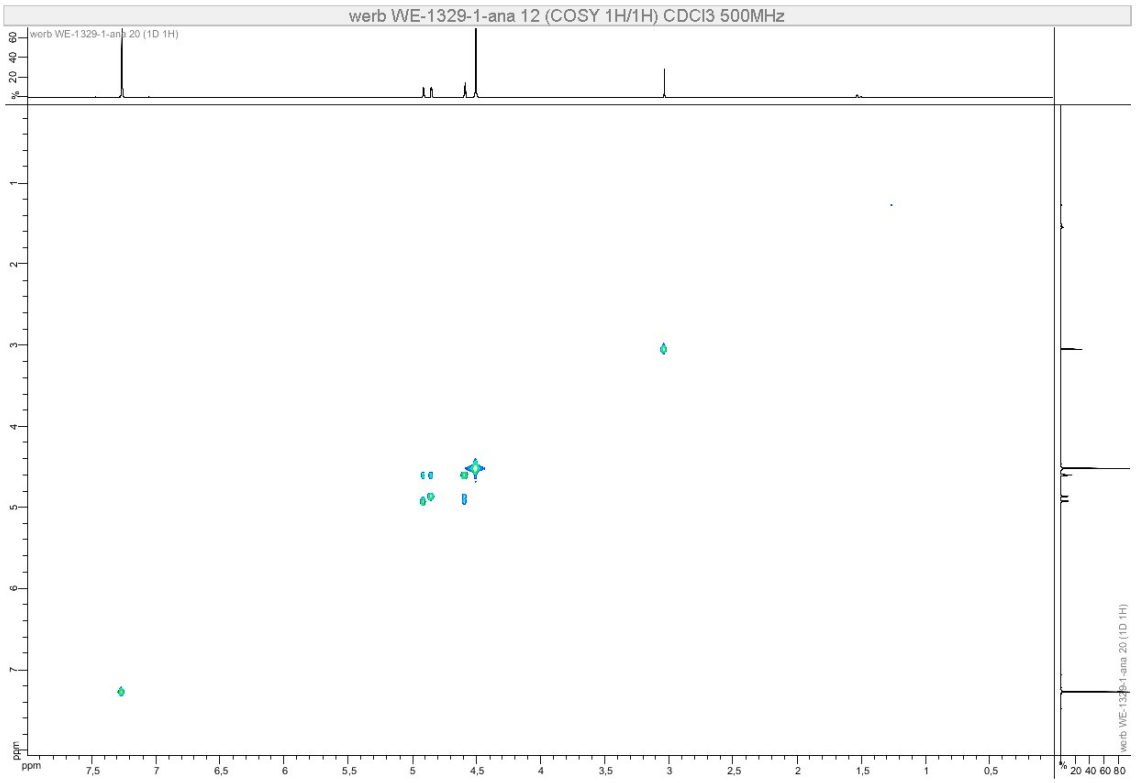

werb WE-1367-1-ana 24 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1367-1-ana 10 (1D 1H)
werb WE-1367-1-ana 21 (1D 13C)
ppm
%

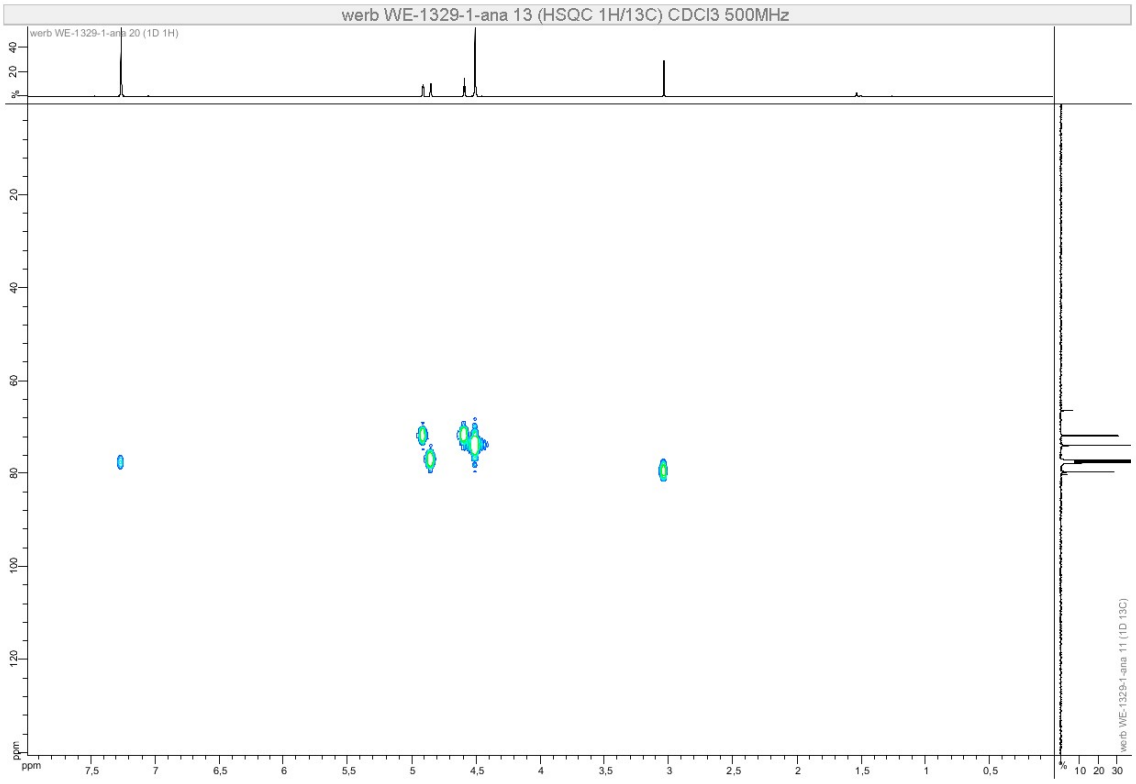

werb WE-1367-1-ana 25 (1D 19F) CDCl3 500MHz
67,959
ppm
%

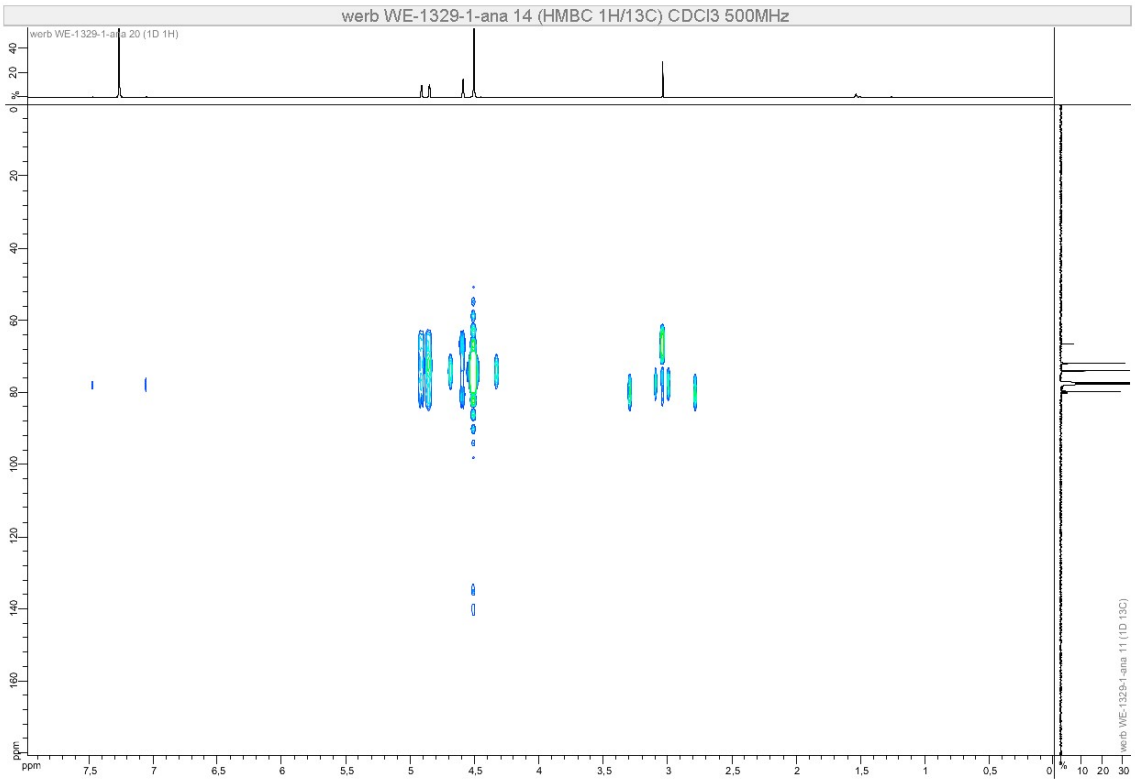
Compound 9a

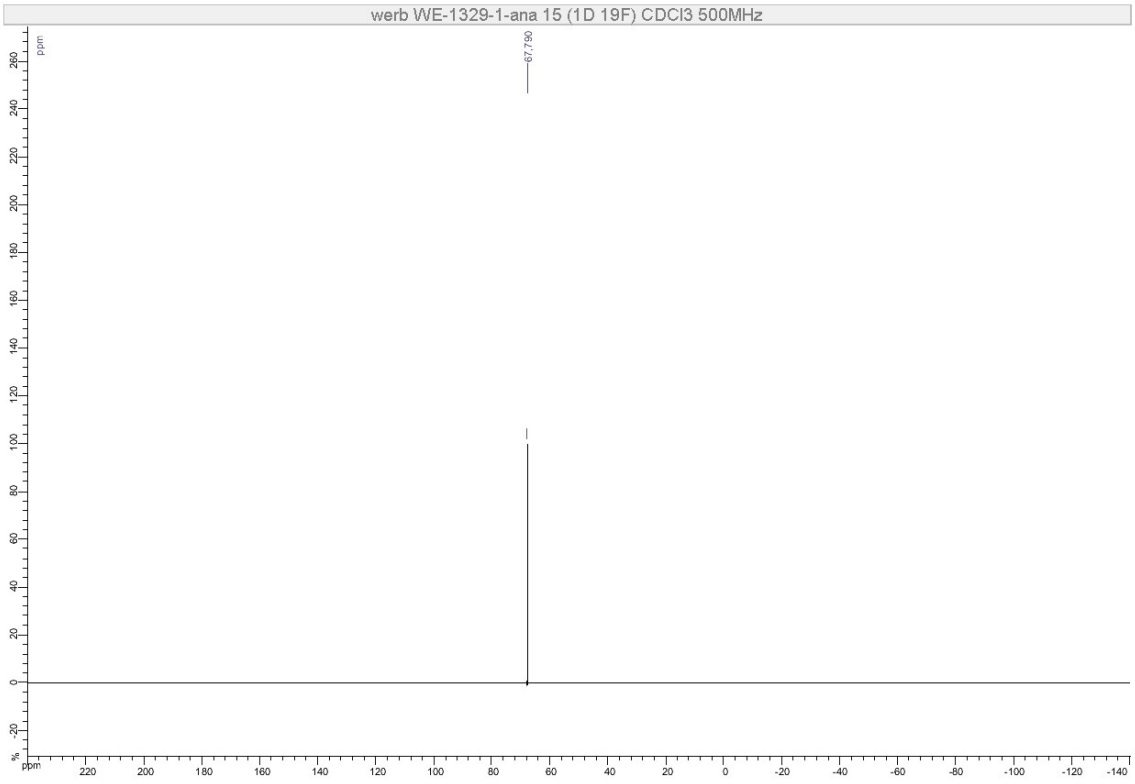

werb WE-1329-1-ana 20 (1D 1H) CDCl3 500MHz
7.260
4.913
4.910
4.908
4.905
4.852
4.849
4.847
4.844
4.592
4.588
4.581
4.502
3.032
SO2F
Fe
1.48
1.46
1.00


werb WE-1329-1-ana 11 (1D 13C) CDCl3 500MHz
79.935
79.632
79.336
77.414
77.160
77.082
76.906
75.857
73.657
71.617
71.511
66.203
SO2F
Fe

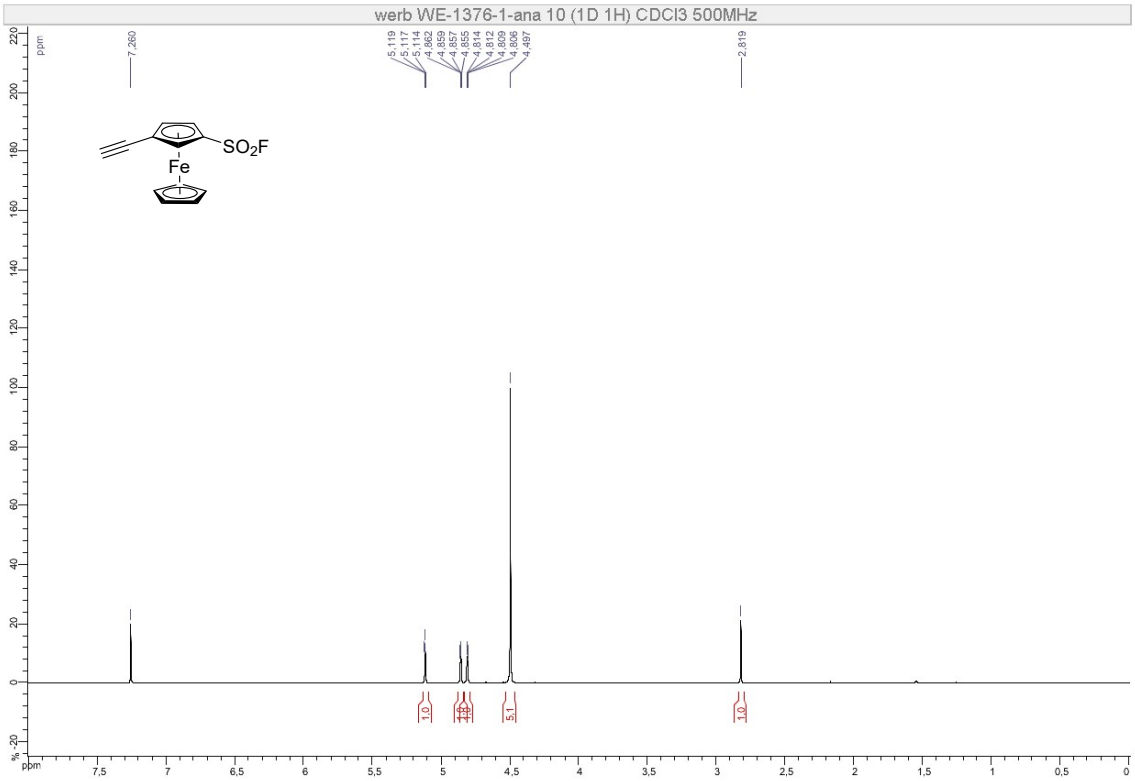

werb WE-1329-1-ana 12 (COSY 1H/1H) CDCl3 500MHz
werb WE-1329-1-ana 20 (1D 1H)
ppm
7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5
% 20 40 60 80
werb WE-1329-1-ana 20 (1D 1H)

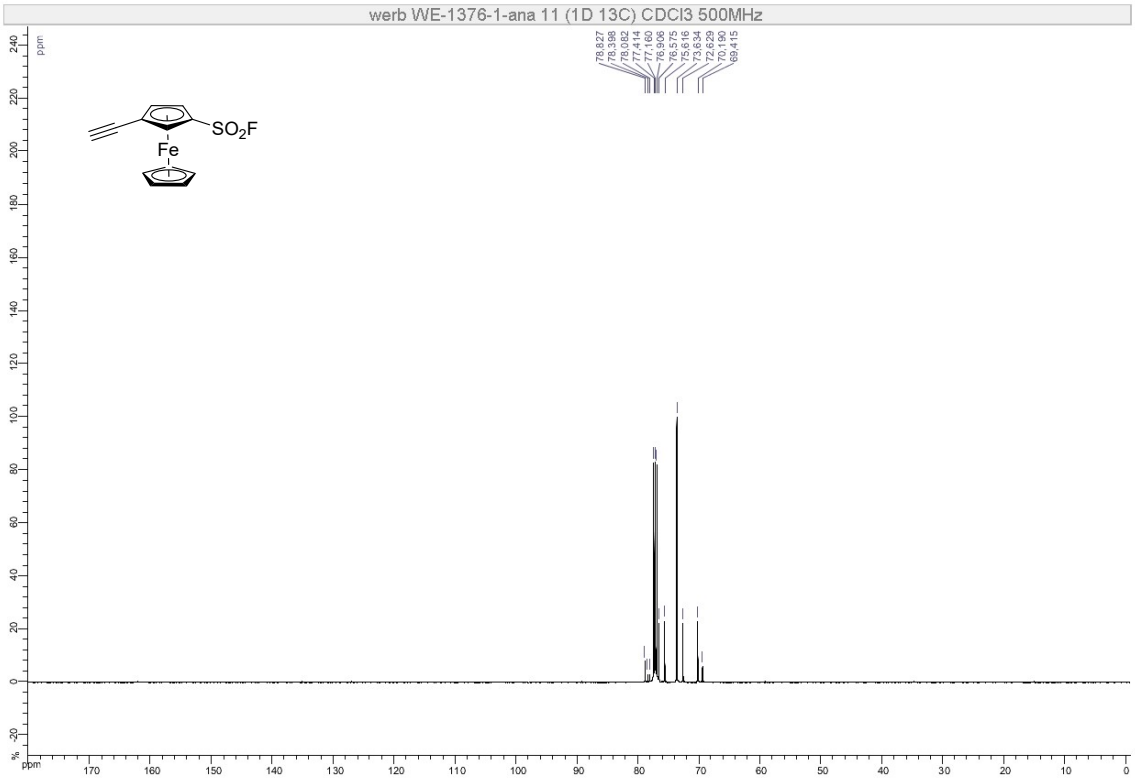

werb WE-1329-1-ana 13 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1329-1-ana 20 (1D 1H)
ppm
7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5
% 10 20 30
werb WE-1328-1-ana 11 (1D 13C)

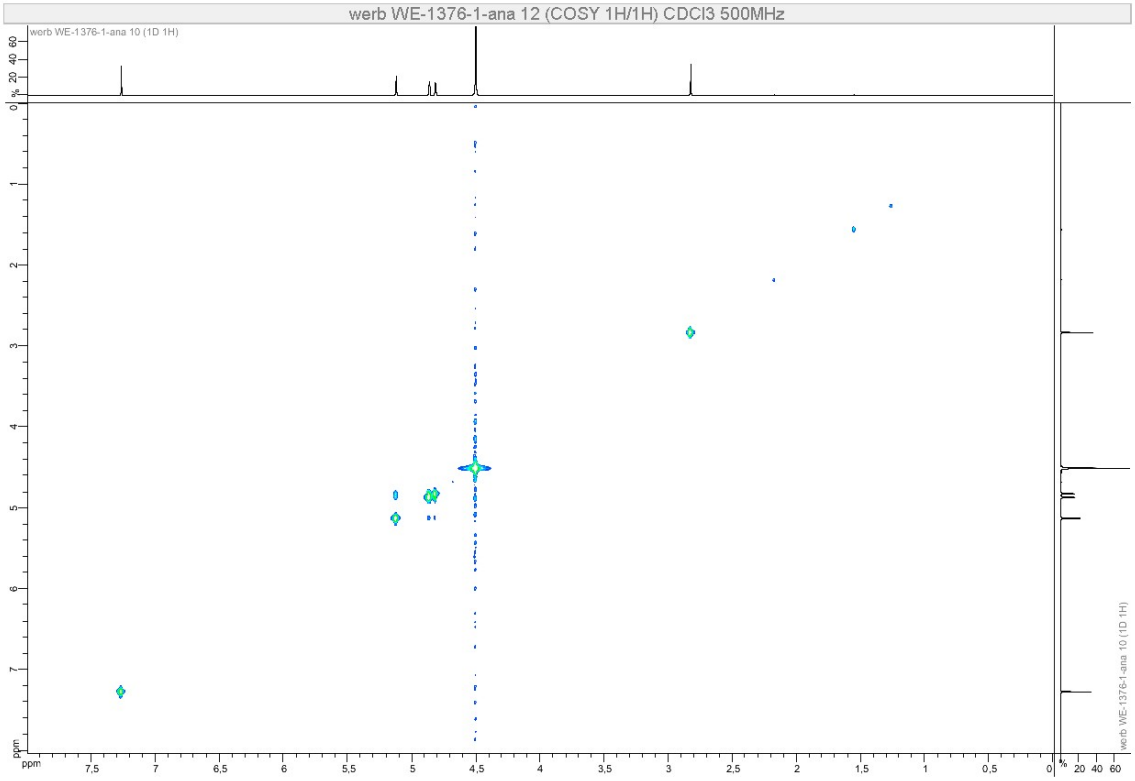

werb WE-1329-1-ana 14 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1329-1-ana 20 (1D 1H)
werb WE-1329-1-ana 11 (1D 13C)
ppm
%

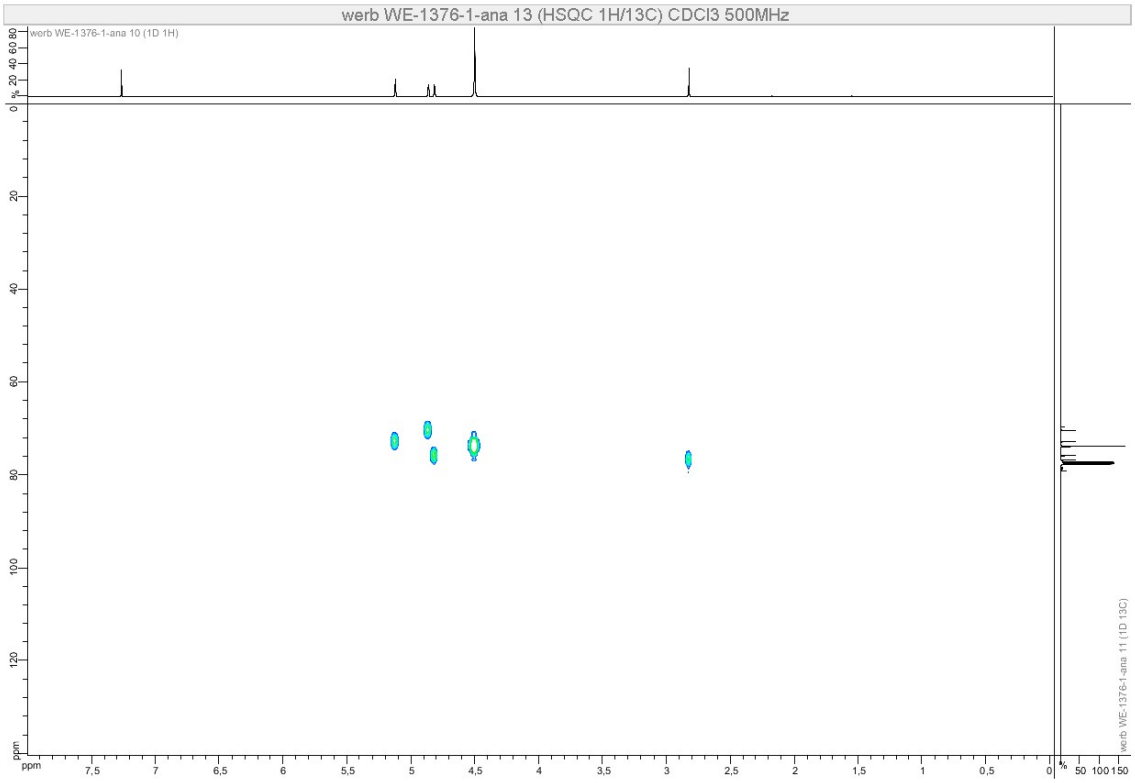

werb WE-1329-1-ana 15 (1D 19F) CDCl3 500MHz
67,790
ppm
%

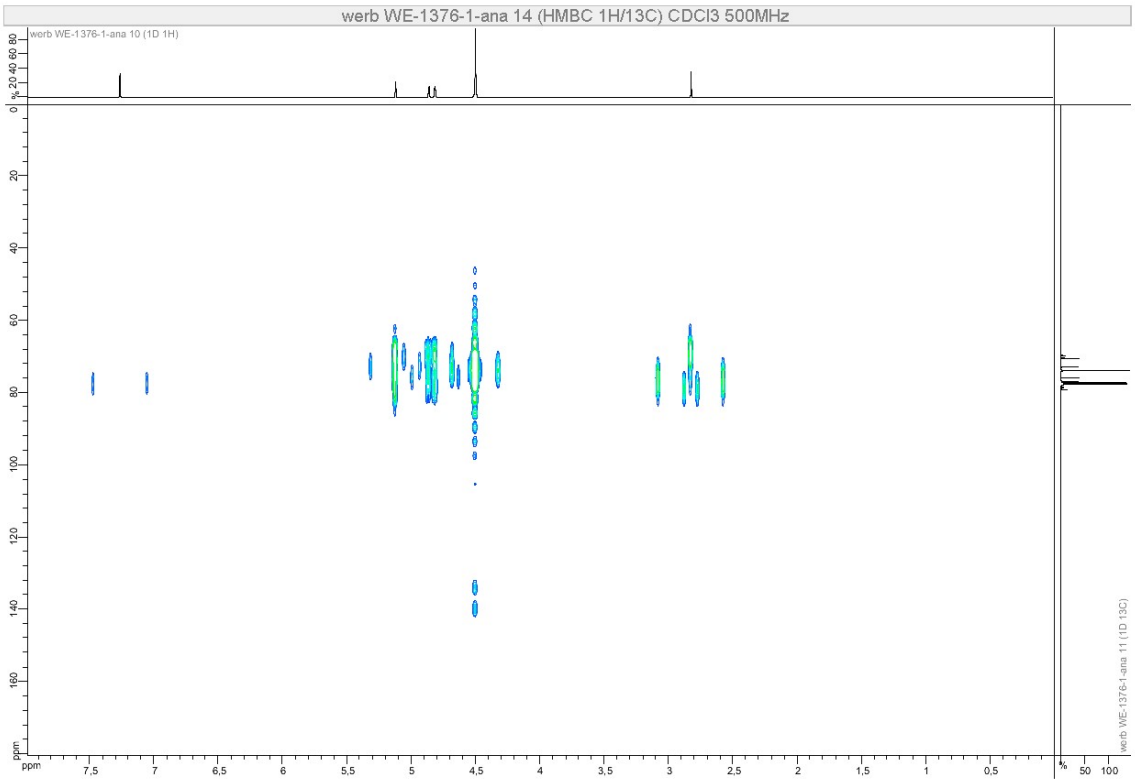
Compound 9b

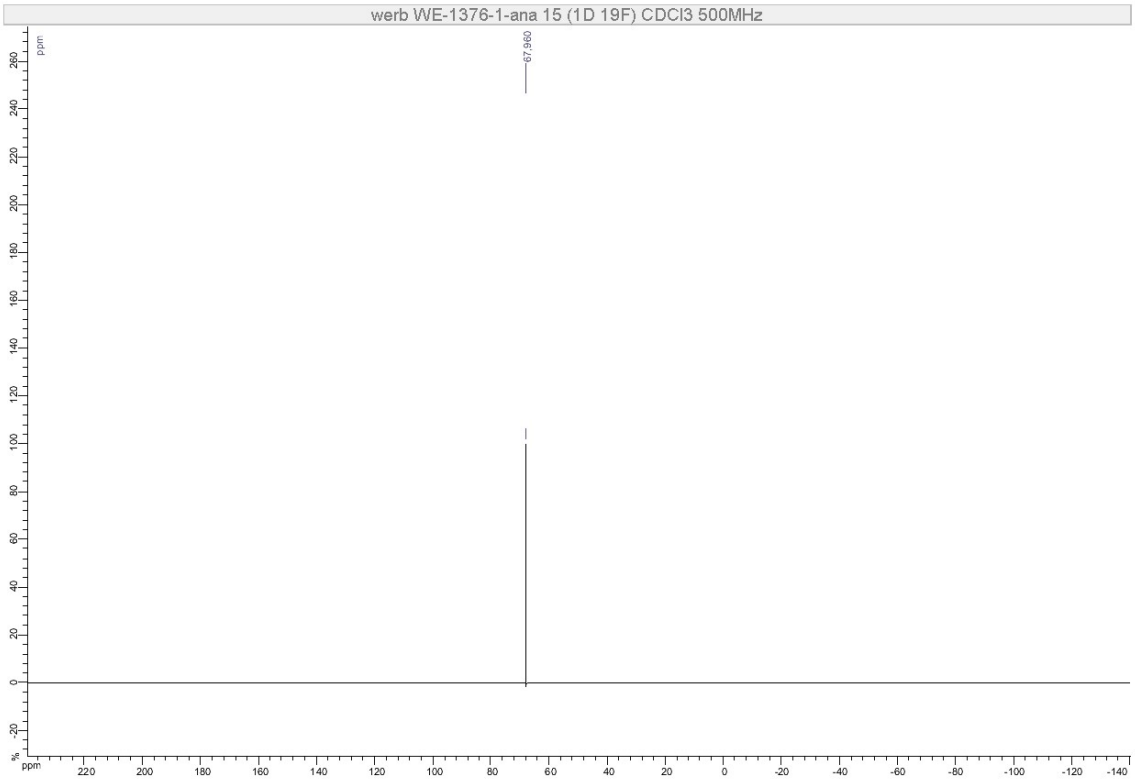

werb WE-1376-1-ana 10 (1D 1H) CDCl3 500MHz
ppm
7.260
5.119
5.117
5.114
4.862
4.859
4.857
4.855
4.814
4.812
4.809
4.806
4.497
2.819
SO2F
Fe
1.0
1.8
5.1
1.0


werb WE-1376-1-ana 11 (1D 13C) CDCl3 500MHz
ppm
78.827
78.398
78.082
77.414
77.160
76.906
76.575
75.516
73.534
72.629
70.190
69.415
SO2F
Fe

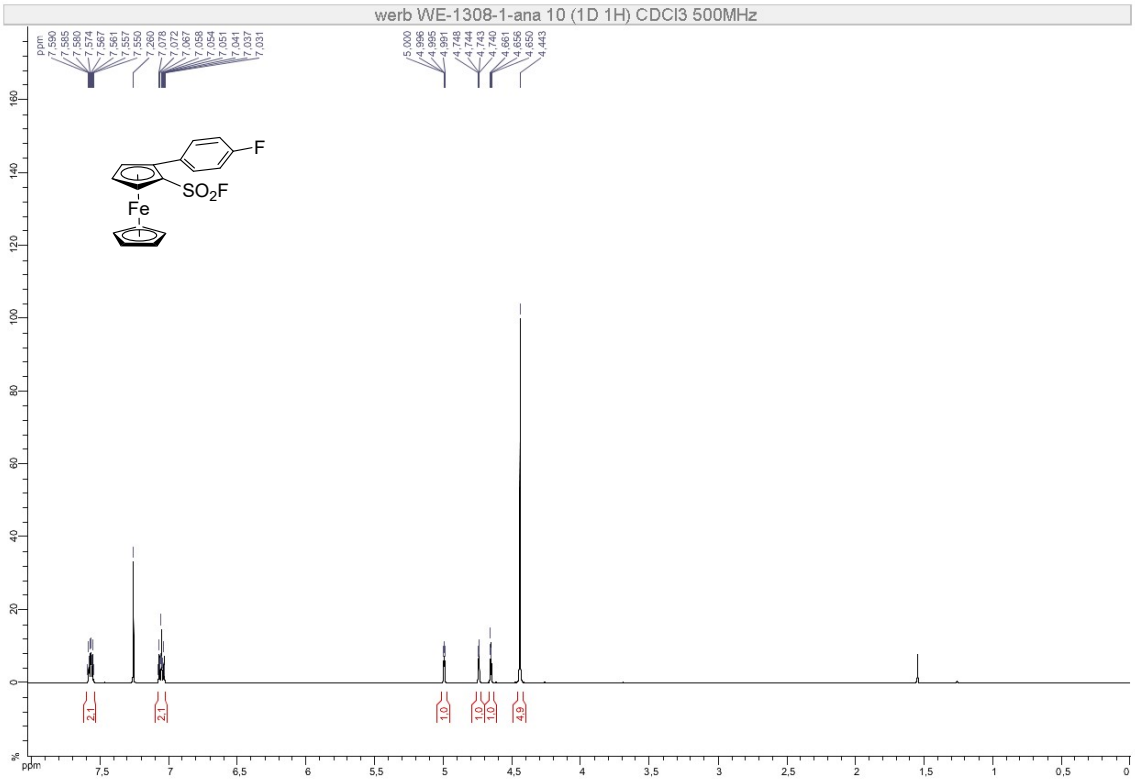

werb WE-1376-1-ana 12 (COSY 1H/1H) CDCl3 500MHz
werb WE-1376-1-ana 10 (1D 1H)
ppm
werb WE-1376-1-ana 10 (1D 1H)

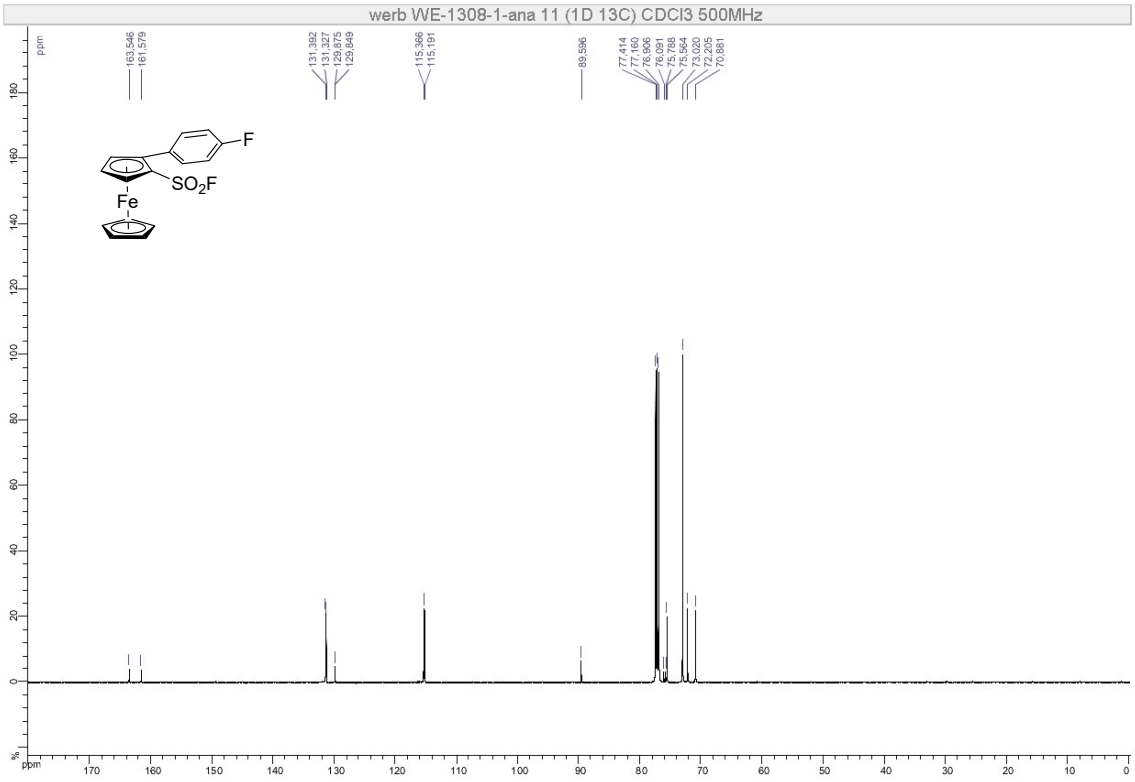

werb WE-1376-1-ana 13 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1376-1-ana 10 (1D 1H)
ppm
werb WE-1376-1-ana 11 (1D 13C)

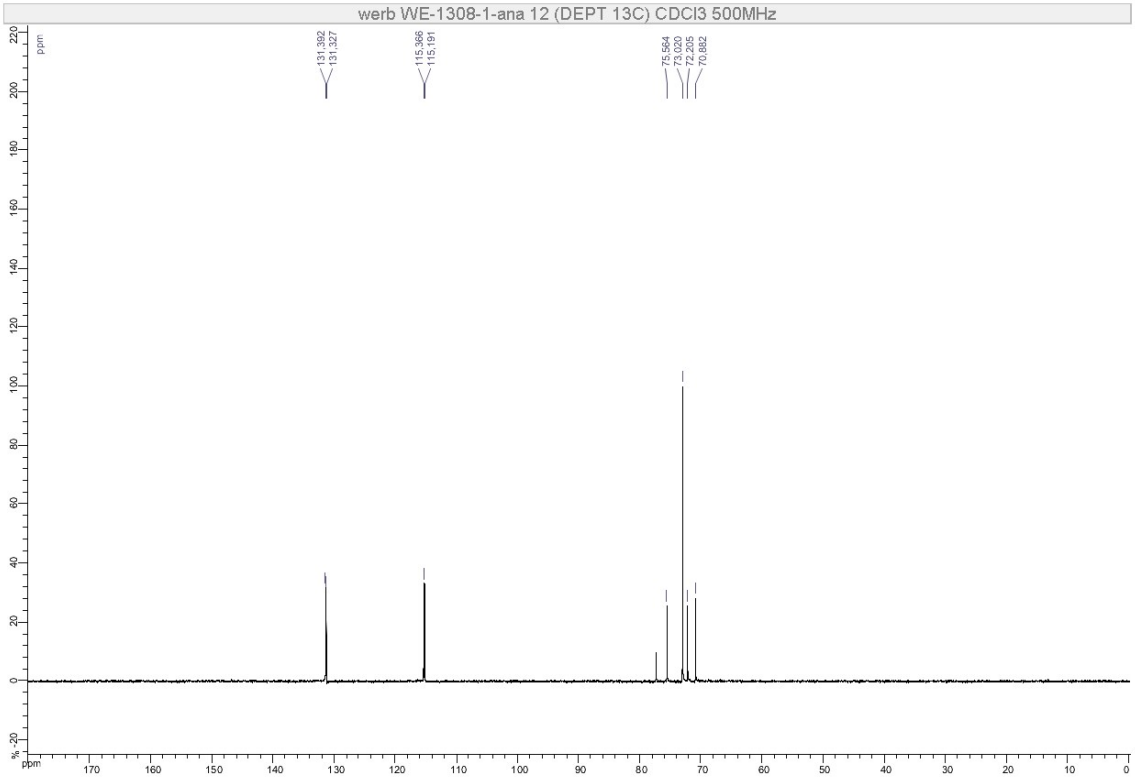

werb WE-1376-1-ana 14 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1376-1-ana 10 (1D 1H)
werb WE-1376-1-ana 11 (1D 13C)
ppm
%

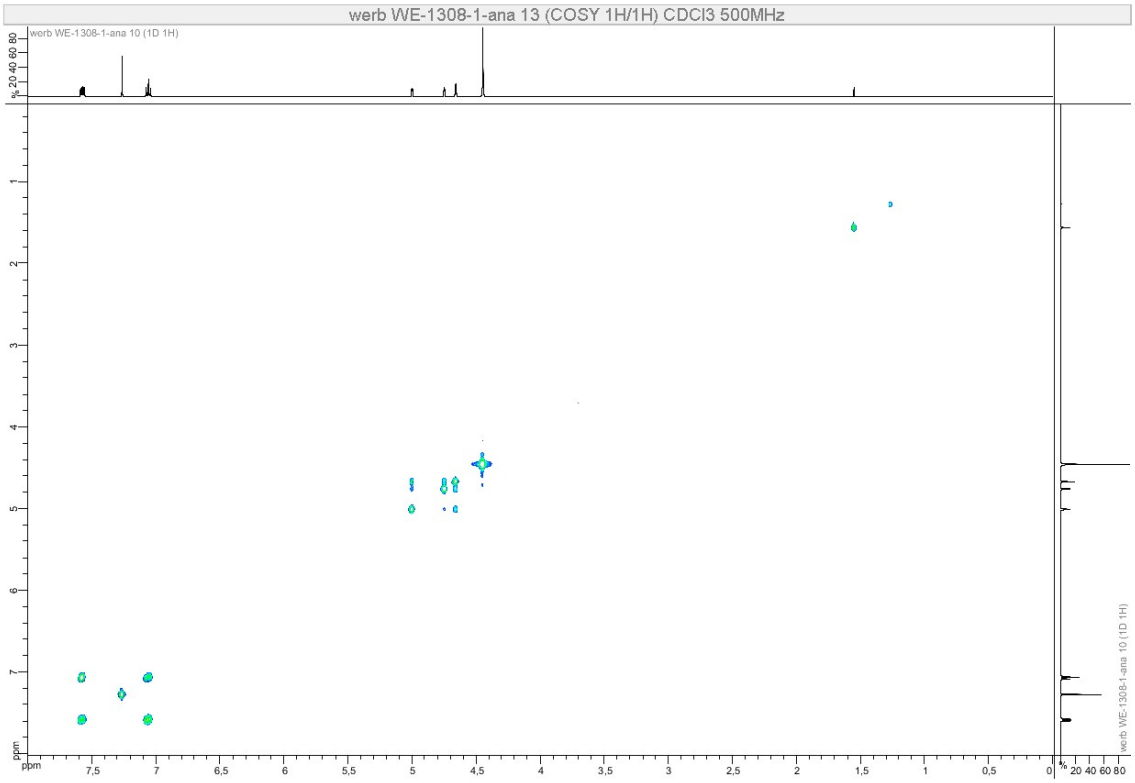

werb WE-1376-1-ana 15 (1D 19F) CDCl3 500MHz
67,960
ppm
%

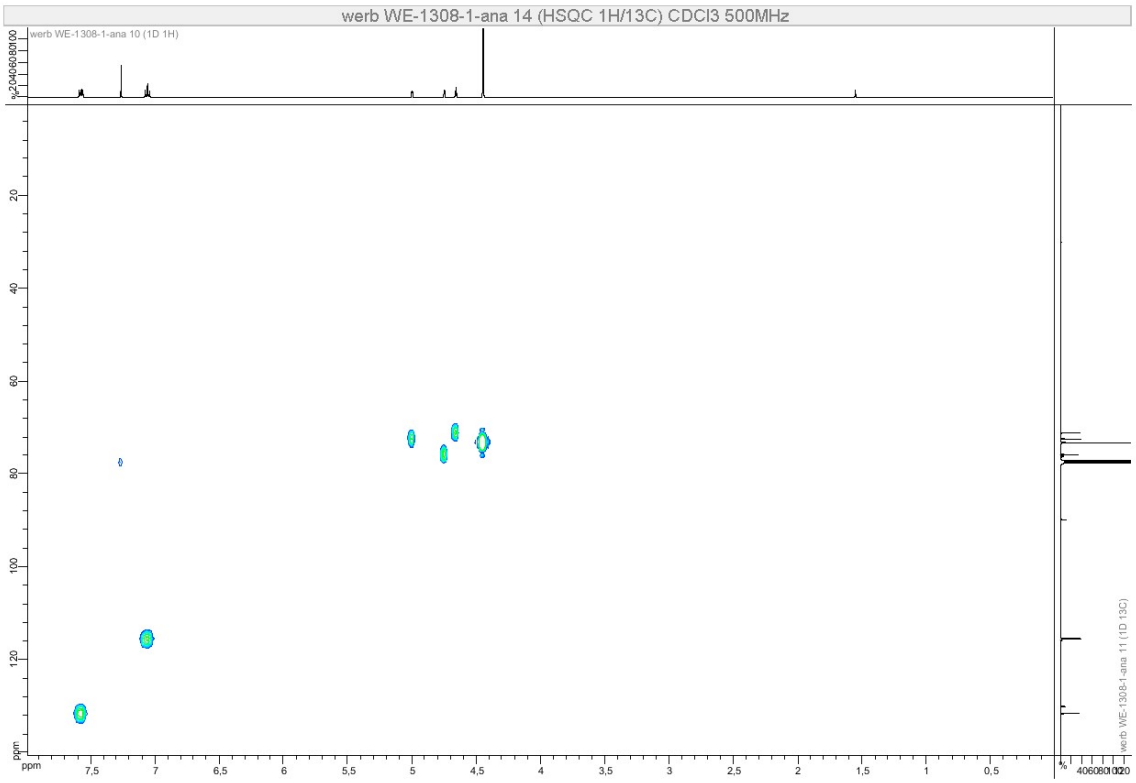
Compound 10a

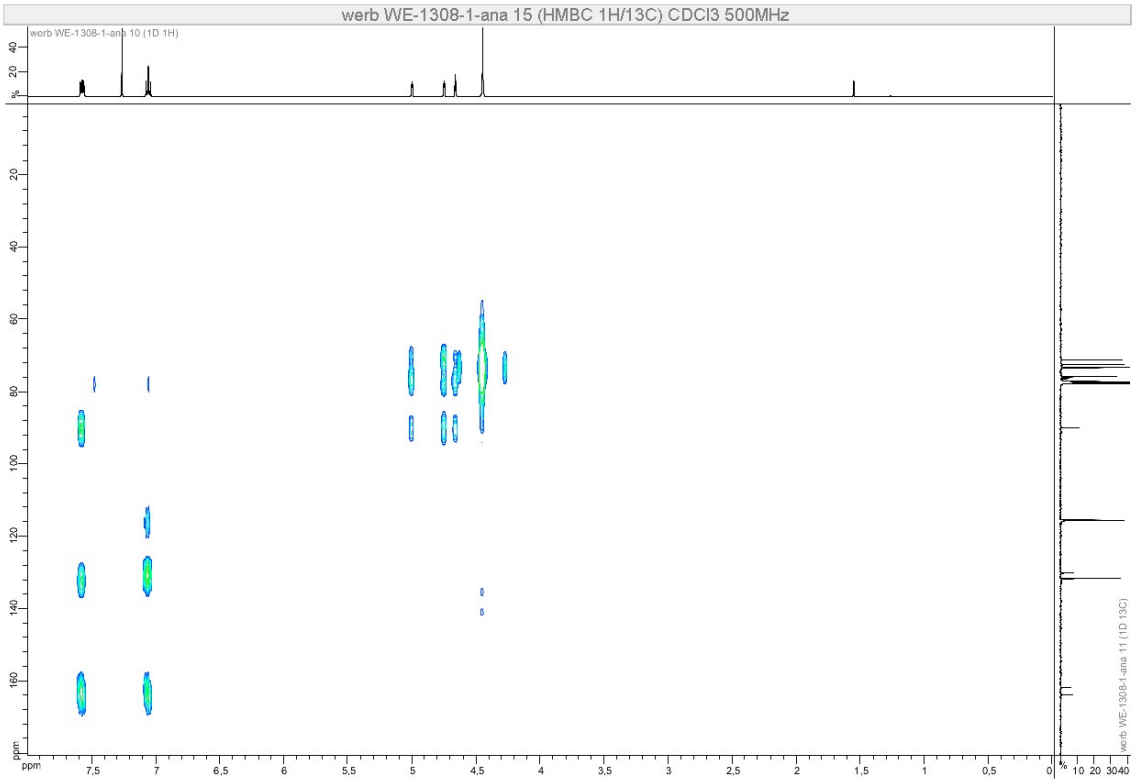


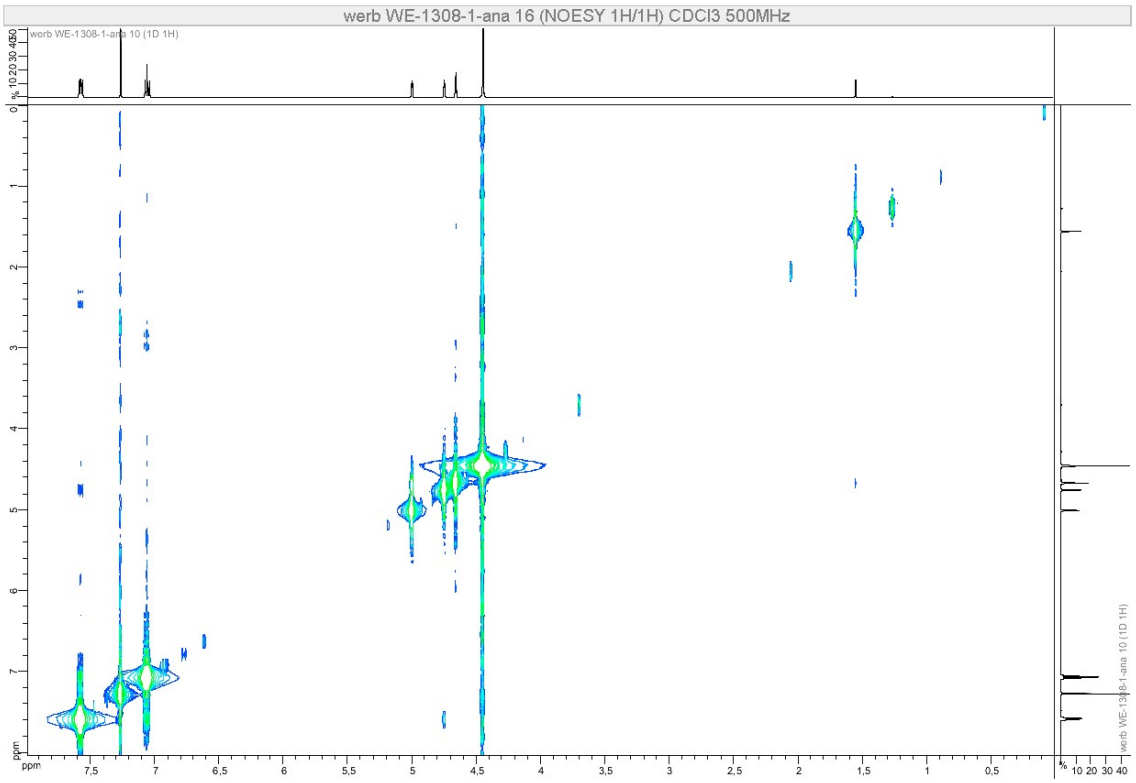


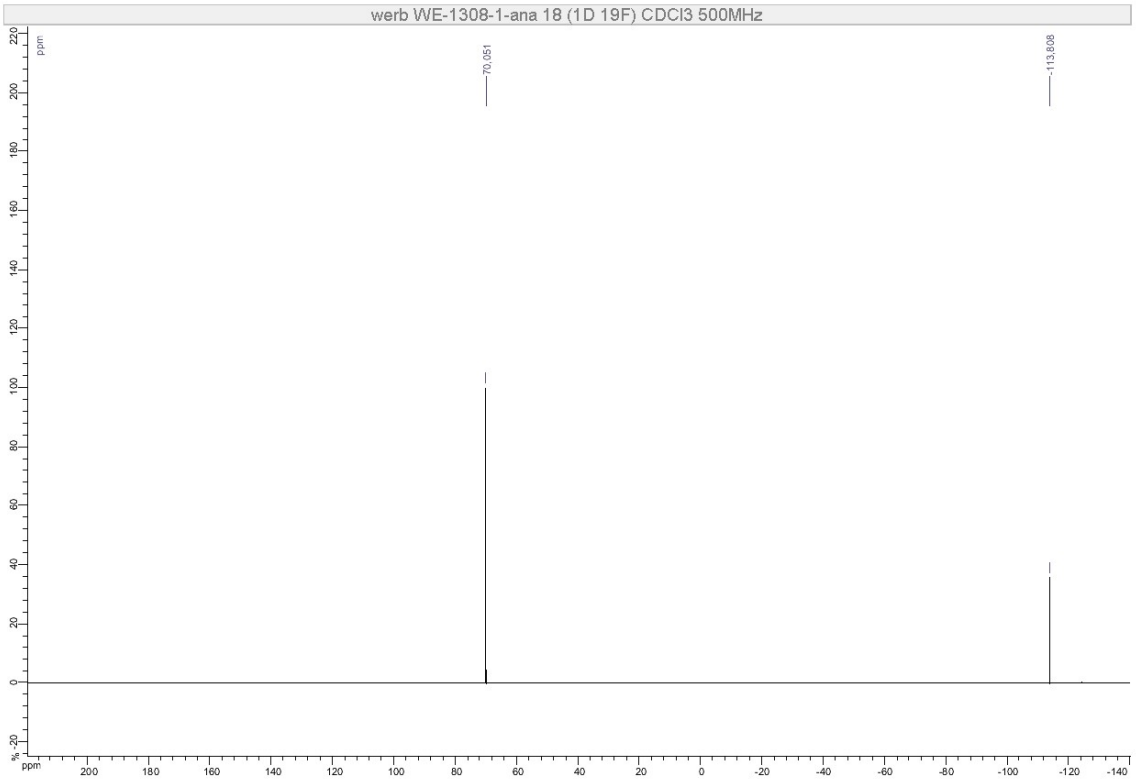

werb WE-1308-1-ana 12 (DEPT 13C) CDCl3 500MHz
131,392
131,327
115,366
115,191
75,564
73,020
72,205
70,882
ppm


werb WE-1308-1-ana 13 (COSY 1H/1H) CDCl3 500MHz
werb WE-1308-1-ana 10 (1D 1H)
ppm

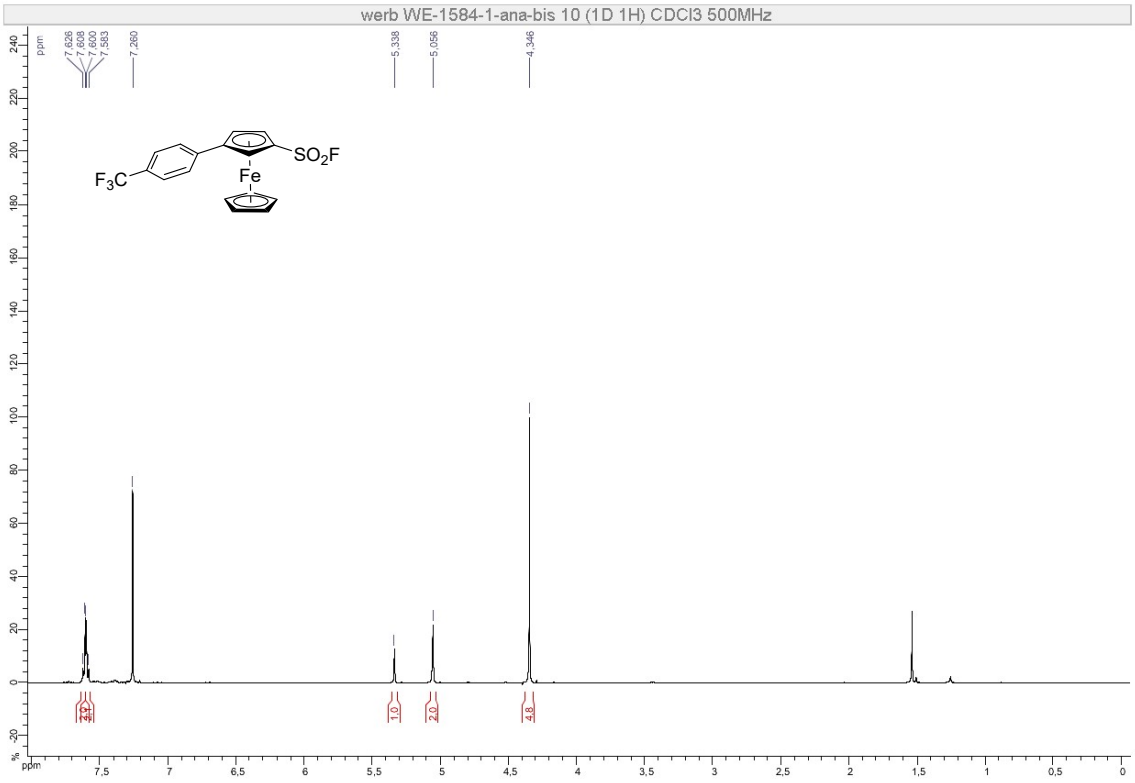

werb WE-1308-1-ana 14 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1308-1-ana 10 (1D 1H)
werb WE-1308-1-ana 11 (1D 13C)
ppm

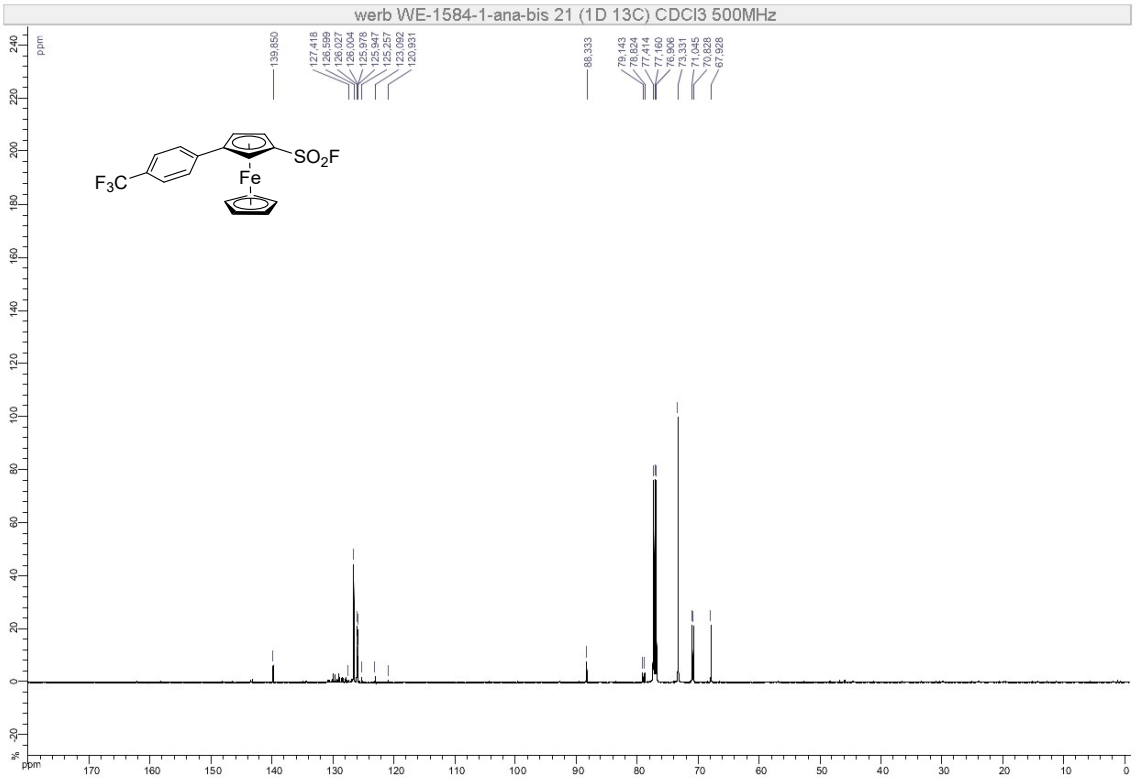

werb WE-1308-1-ana 15 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1308-1-ana 10 (1D 1H)
werb WE-1308-1-ana 11 (1D 13C)
ppm

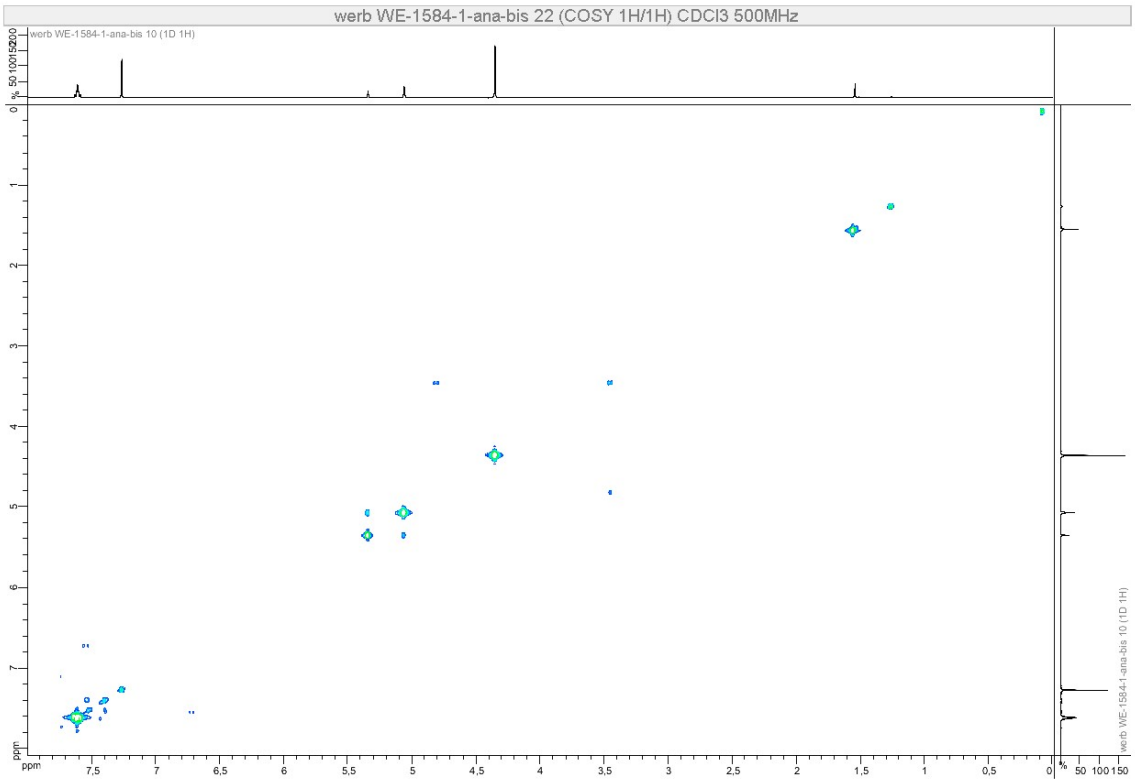

werb WE-1308-1-ana 16 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1308-1-ana 10 (1D 1H)
ppm
werb WE-1308-1-ana 10 (1D 1H)

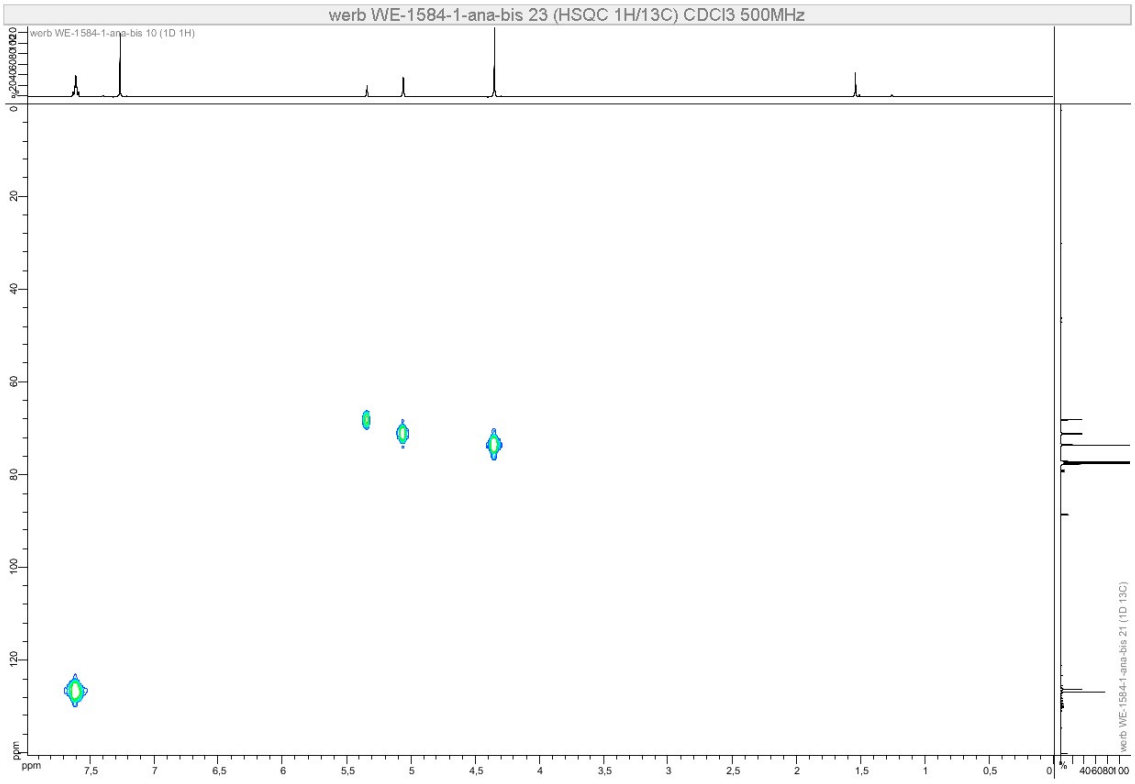

werb WE-1308-1-ana 18 (1D 19F) CDCl3 500MHz
ppm
-70,051
-113,808

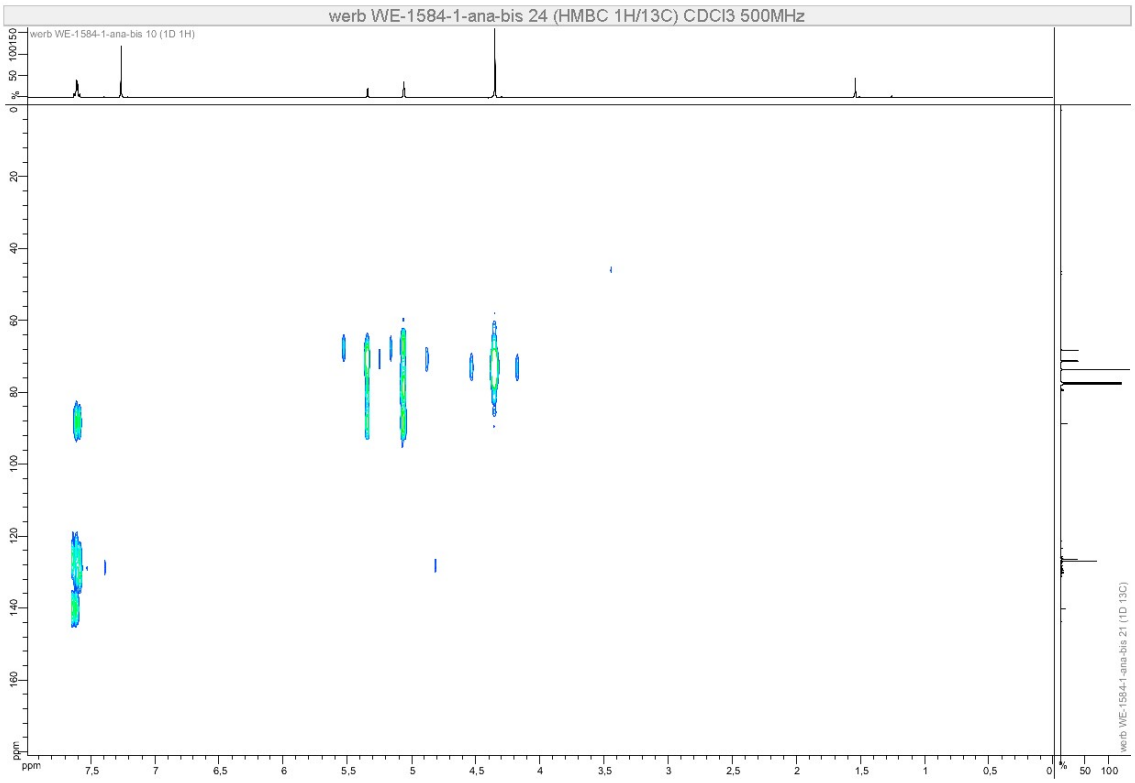
Compound 10b

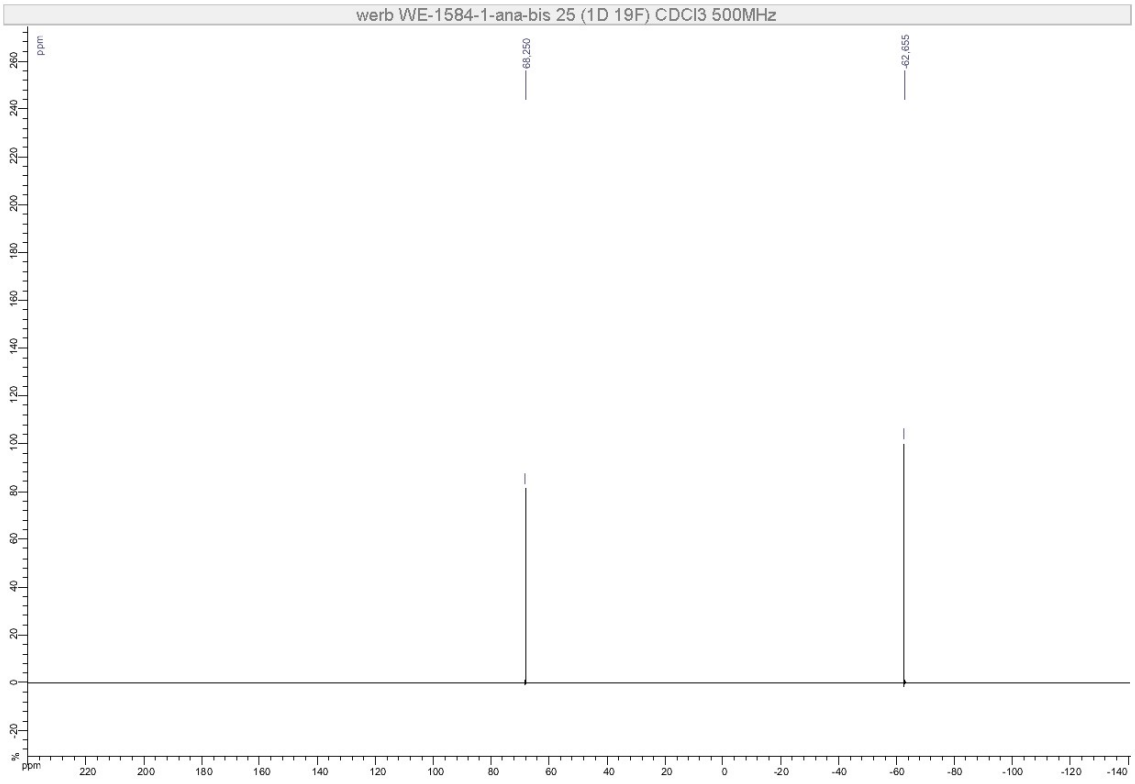




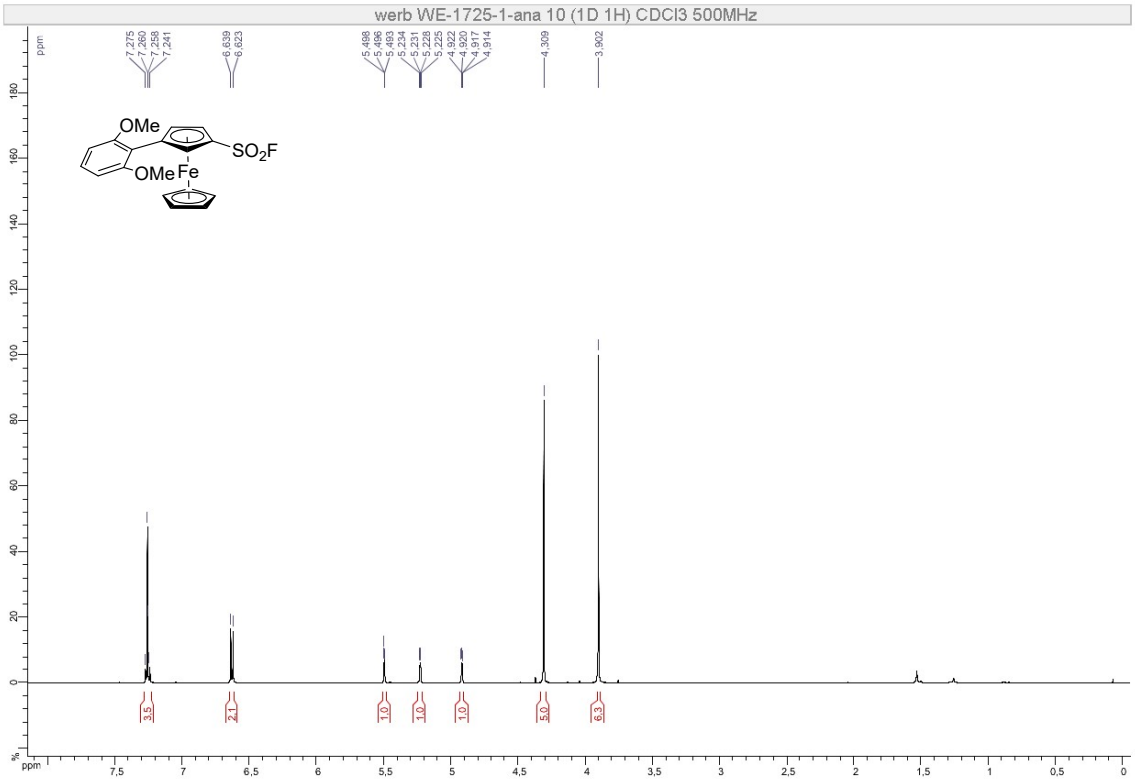

werb WE-1584-1-ana-bis 22 (COSY 1H/1H) CDCl3 500MHz
werb WE-1584-1-ana-bis 10 (1D 1H)
ppm
werb WE-1584-1-ana-bis 10 (1D 1H)

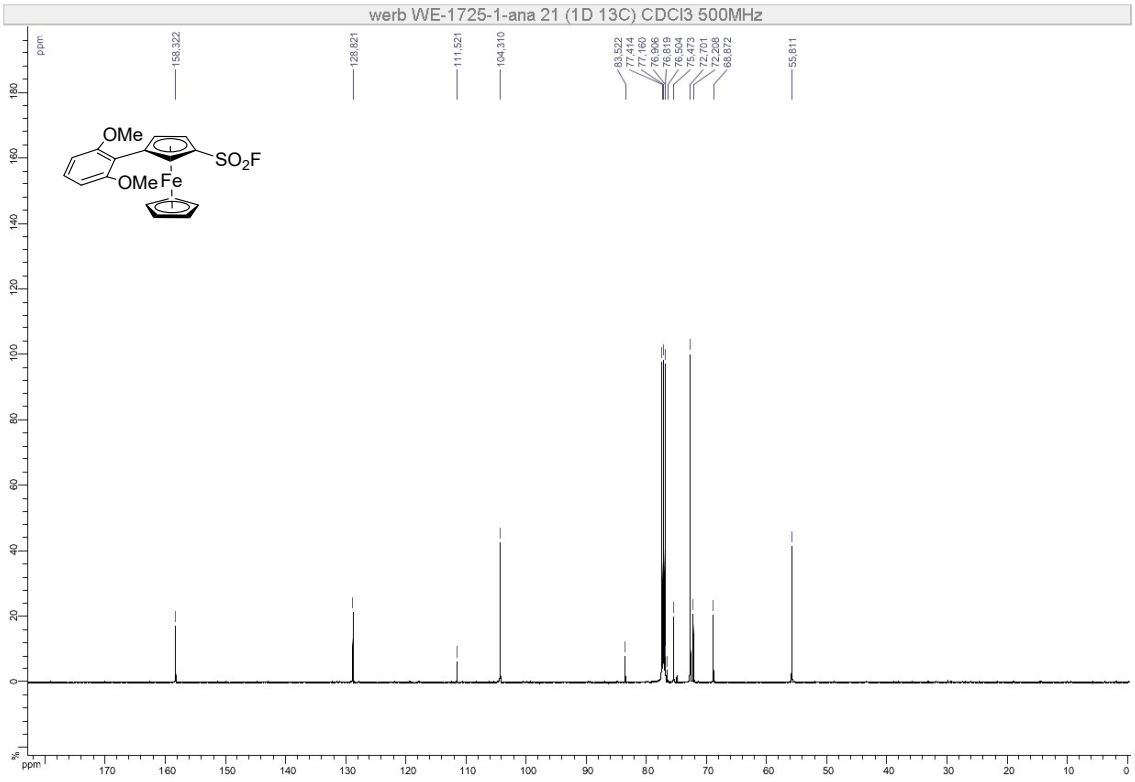

werb WE-1584-1-ana-bis 23 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1584-1-ana-bis 10 (1D 1H)
ppm
werb WE-1584-1-ana-bis 21 (1D 13C)

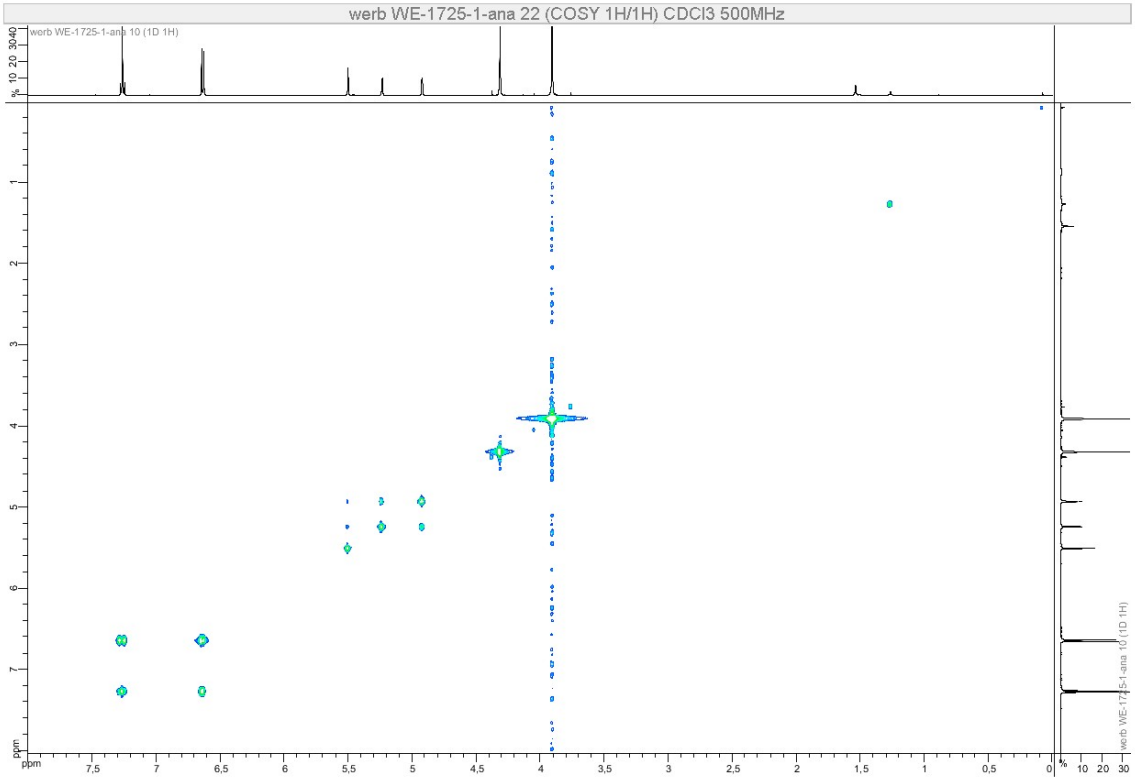

werb WE-1584-1-ana-bis 24 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1584-1-ana-bis 10 (1D 1H)
werb WE-1584-1-ana-bis 21 (1D 13C)
ppm

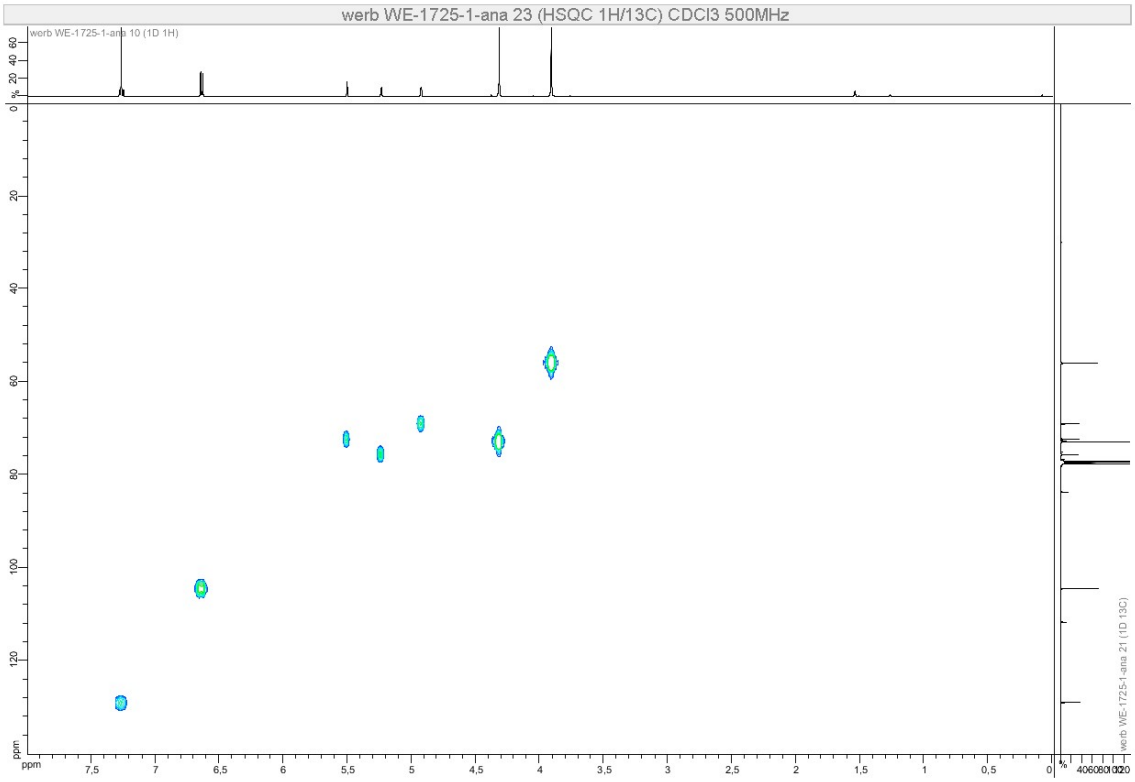

werb WE-1584-1-ana-bis 25 (1D 19F) CDCl3 500MHz
ppm
68.250
-62.655

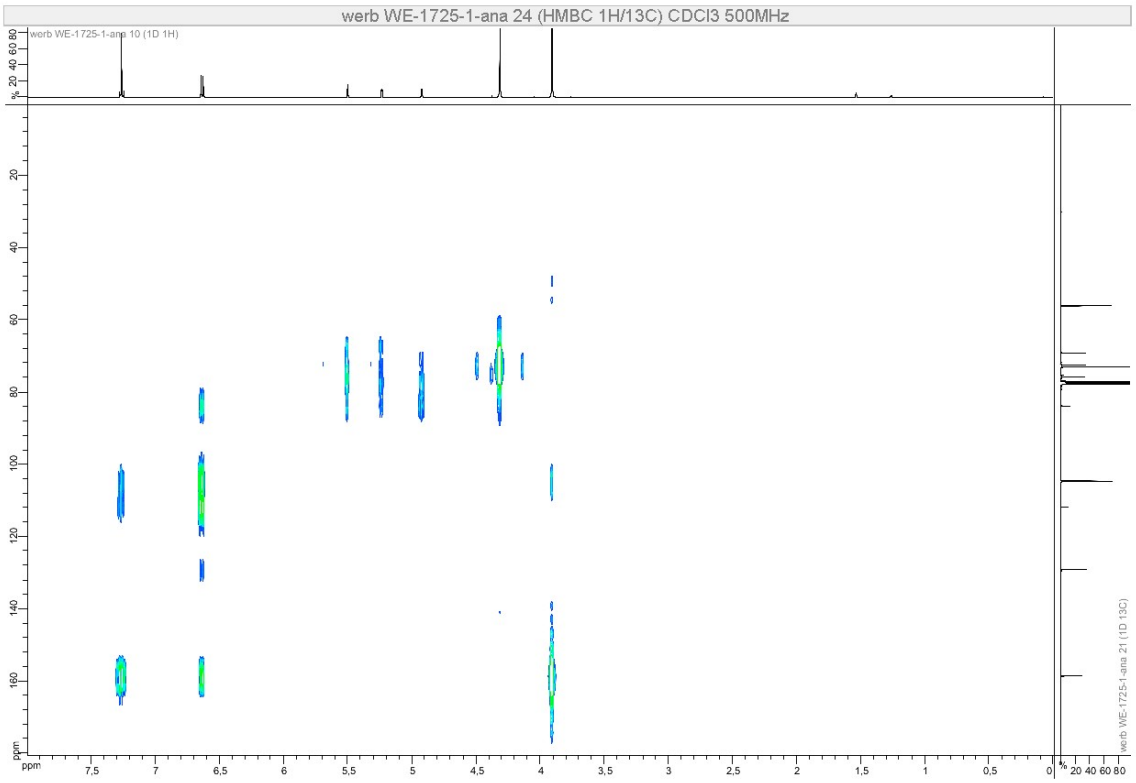
Compound 10c

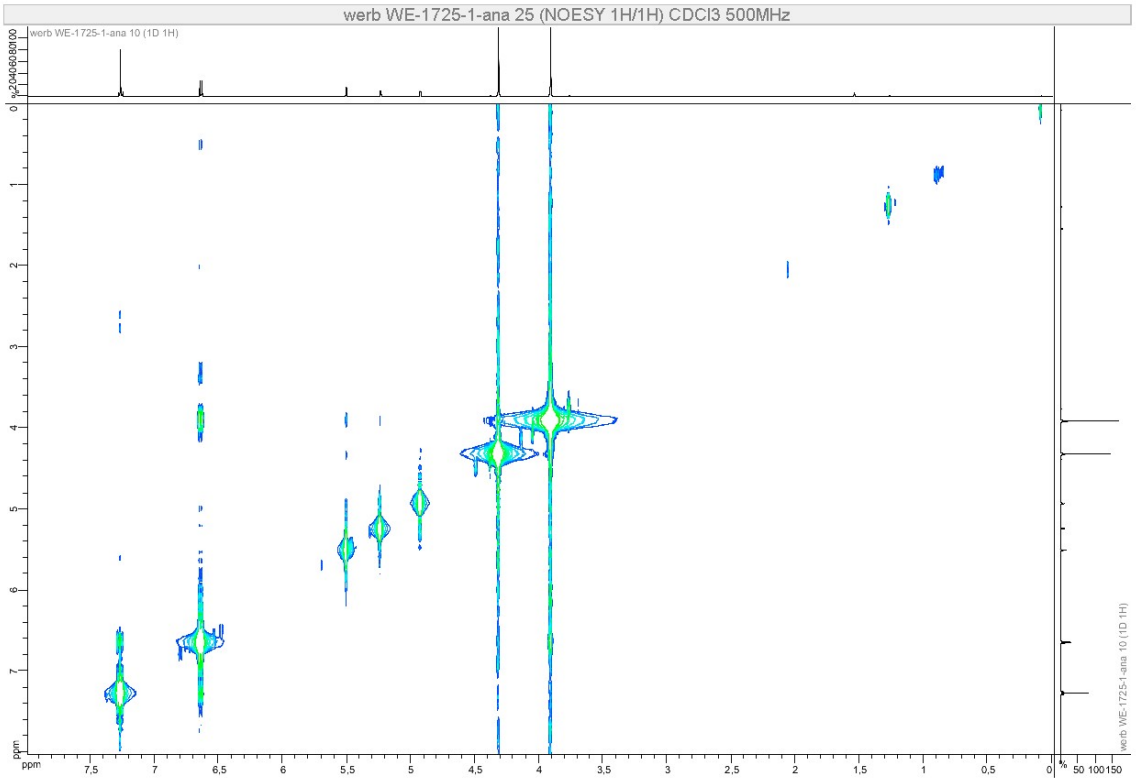


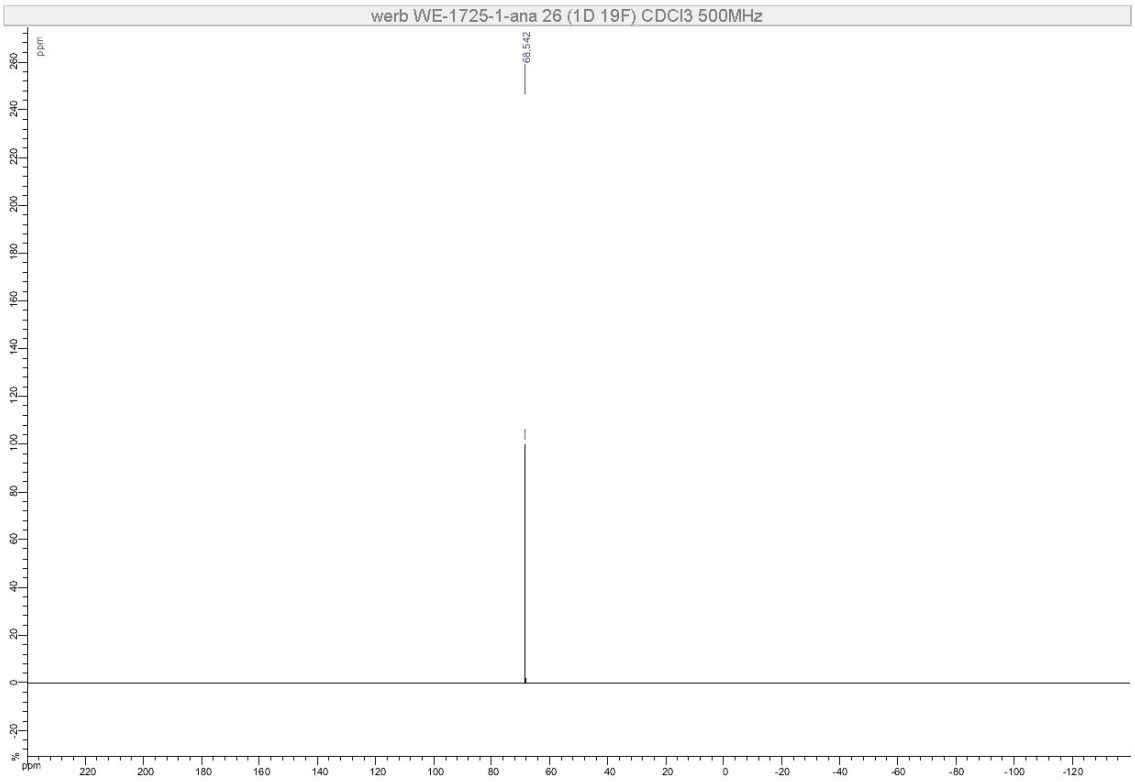



werb WE-1725-1-ana 22 (COSY 1H/1H) CDCl3 500MHz
werb WE-1725-1-ana 10 (1D 1H)
ppm
werb WE-1725-1-ana 10 (1D 1H)

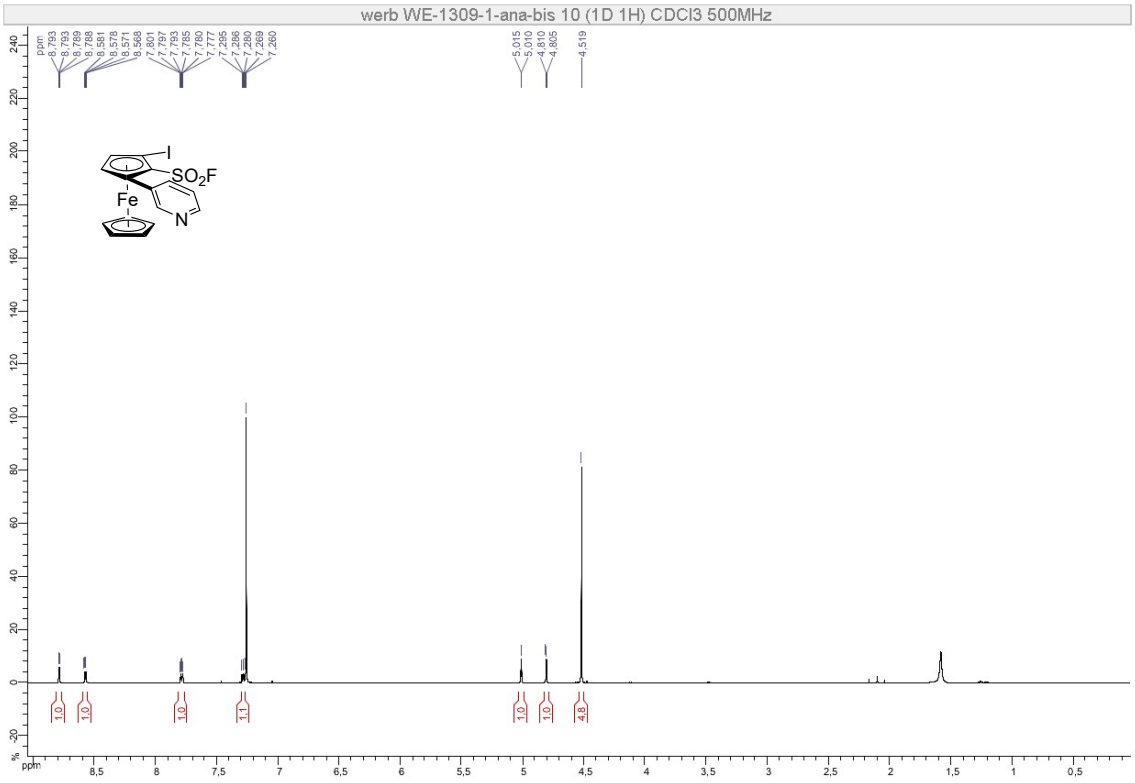

werb WE-1725-1-ana 23 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1725-1-ana 10 (1D 1H)
ppm
werb WE-1725-1-ana 21 (1D 13C)

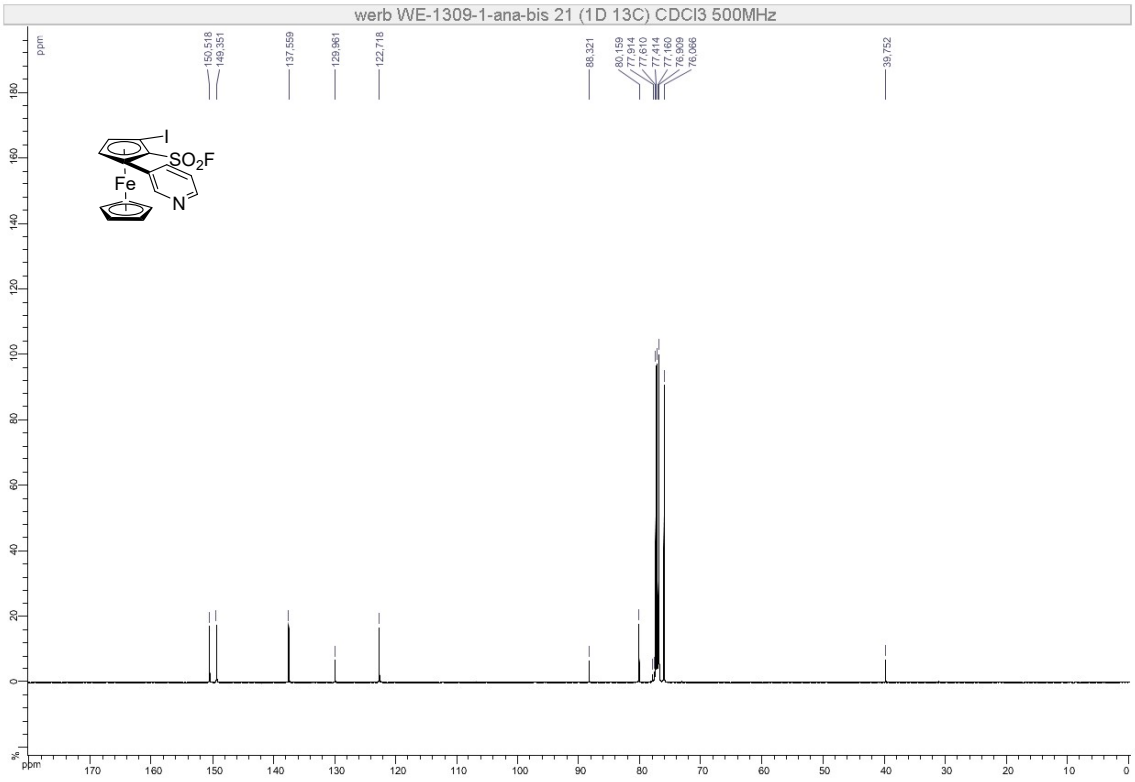

werb WE-1725-1-ana 24 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1725-1-ana 10 (1D 1H)
werb WE-1725-1-ana 21 (1D 13C)
ppm

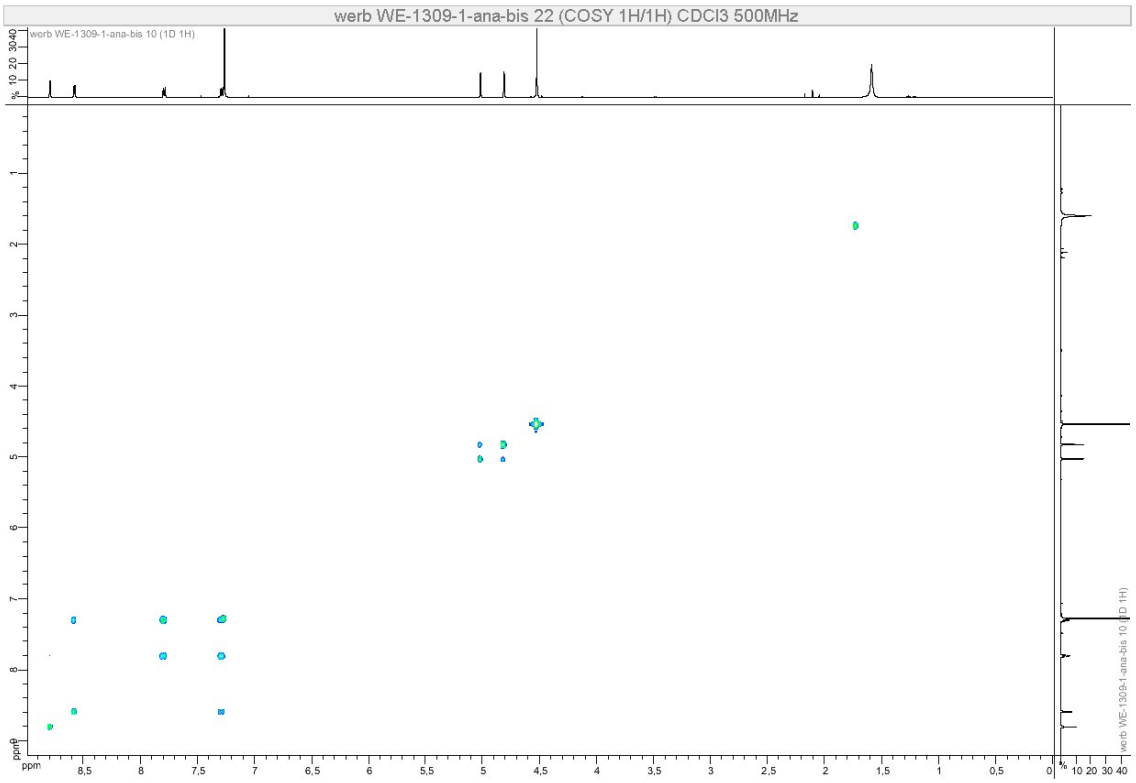

werb WE-1725-1-ana 25 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1725-1-ana 10 (1D 1H)
werb WE-1725-1-ana 10 (1D 1H)
ppm

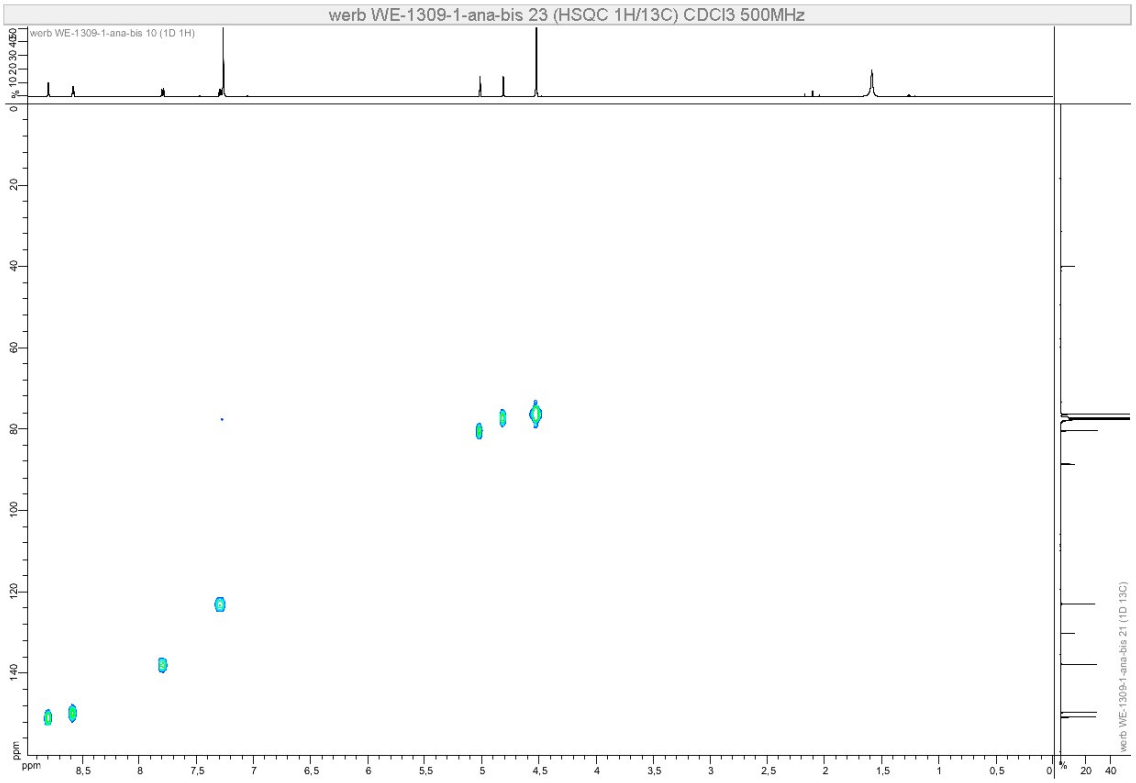

werb WE-1725-1-ana 26 (1D 19F) CDCl3 500MHz
68.542
ppm
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120

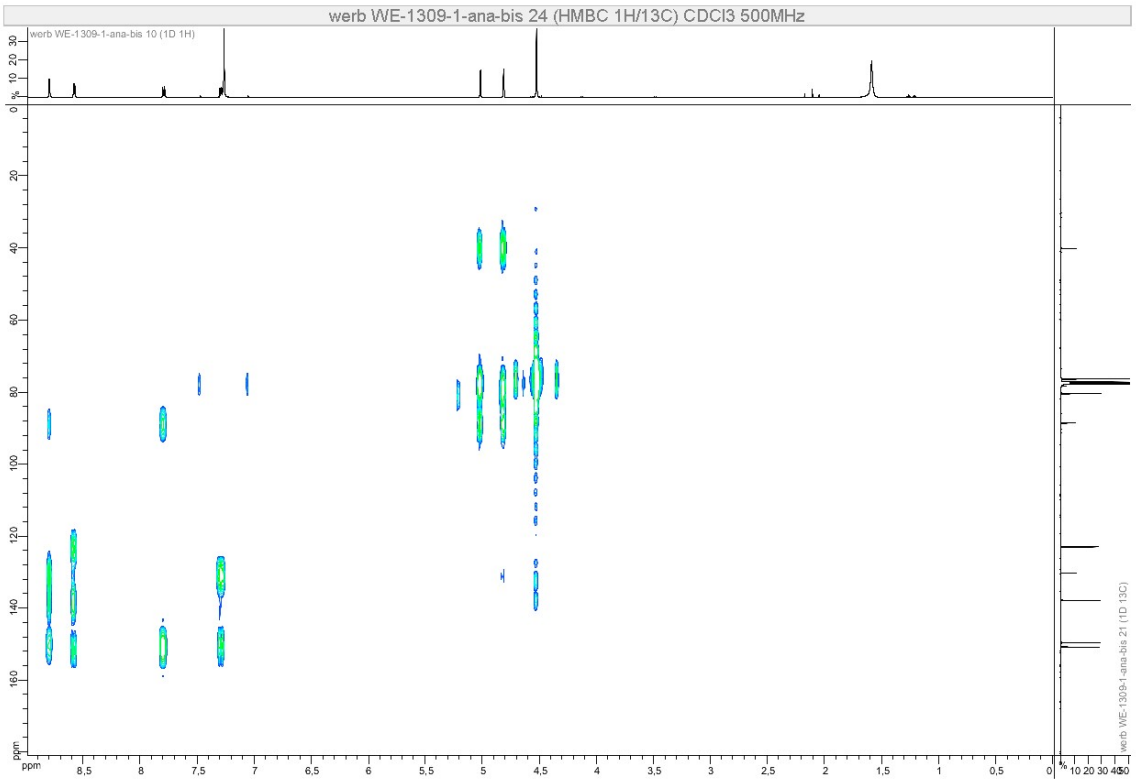
Compound 11

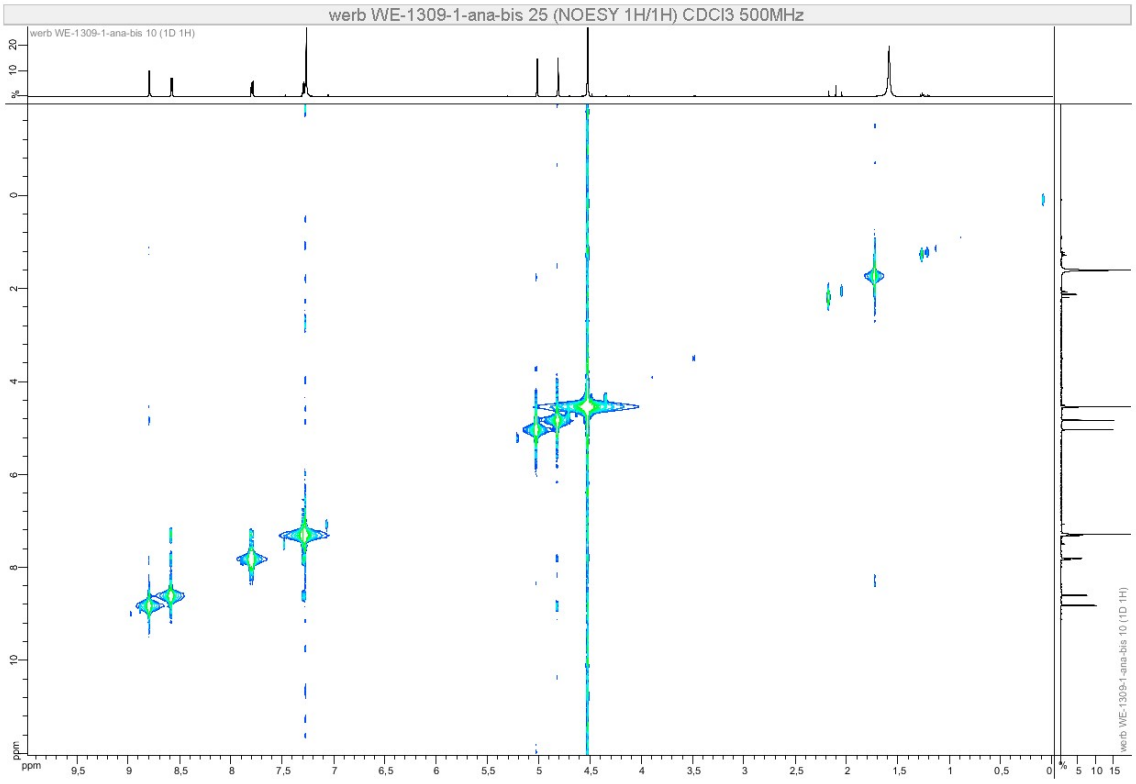

werb WE-1309-1-ana-bis 10 (1D 1H) CDCl3 500MHz
I
SO2F
Fe
N

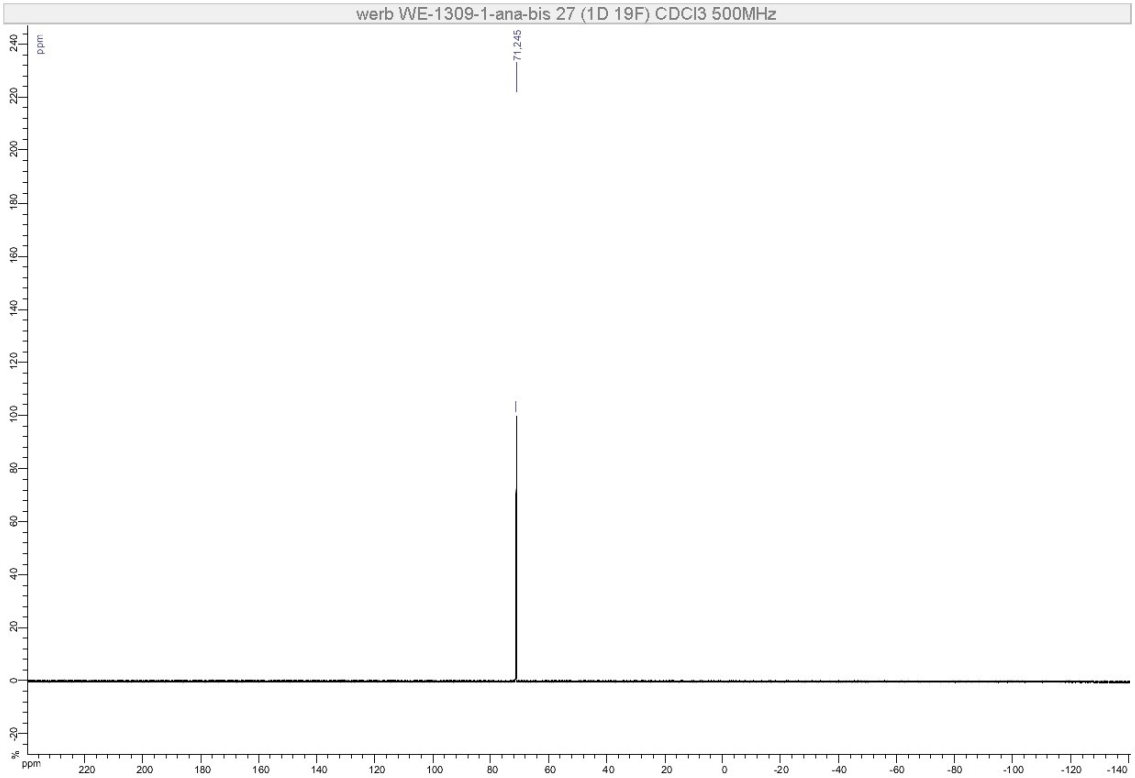

werb WE-1309-1-ana-bis 21 (1D 13C) CDCl3 500MHz
I
SO2F
Fe
N


werb WE-1309-1-ana-bis 22 (COSY 1H/1H) CDCl3 500MHz
werb WE-1309-1-ana-bis 10 (1D 1H)
ppm
werb WE-1309-1-ana-bis 10 (1D 1H)

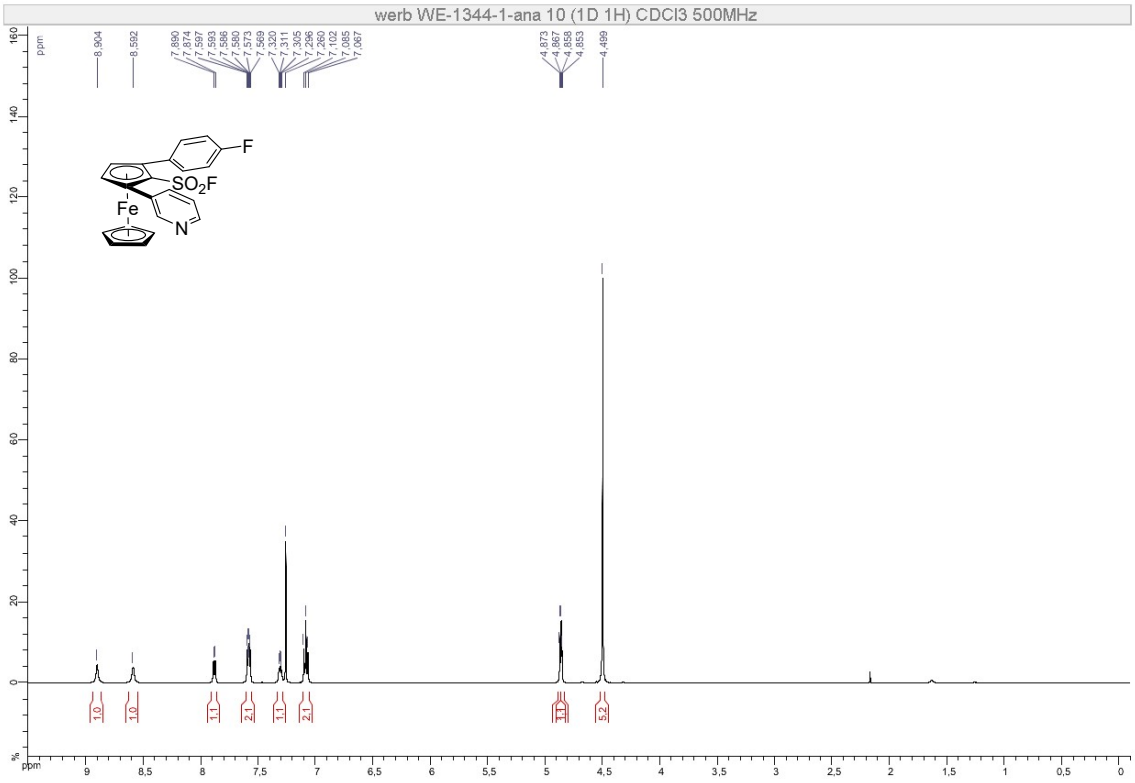

werb WE-1309-1-ana-bis 23 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1309-1-ana-bis 10 (1D 1H)
ppm
werb WE-1309-1-ana-bis 21 (1D 13C)

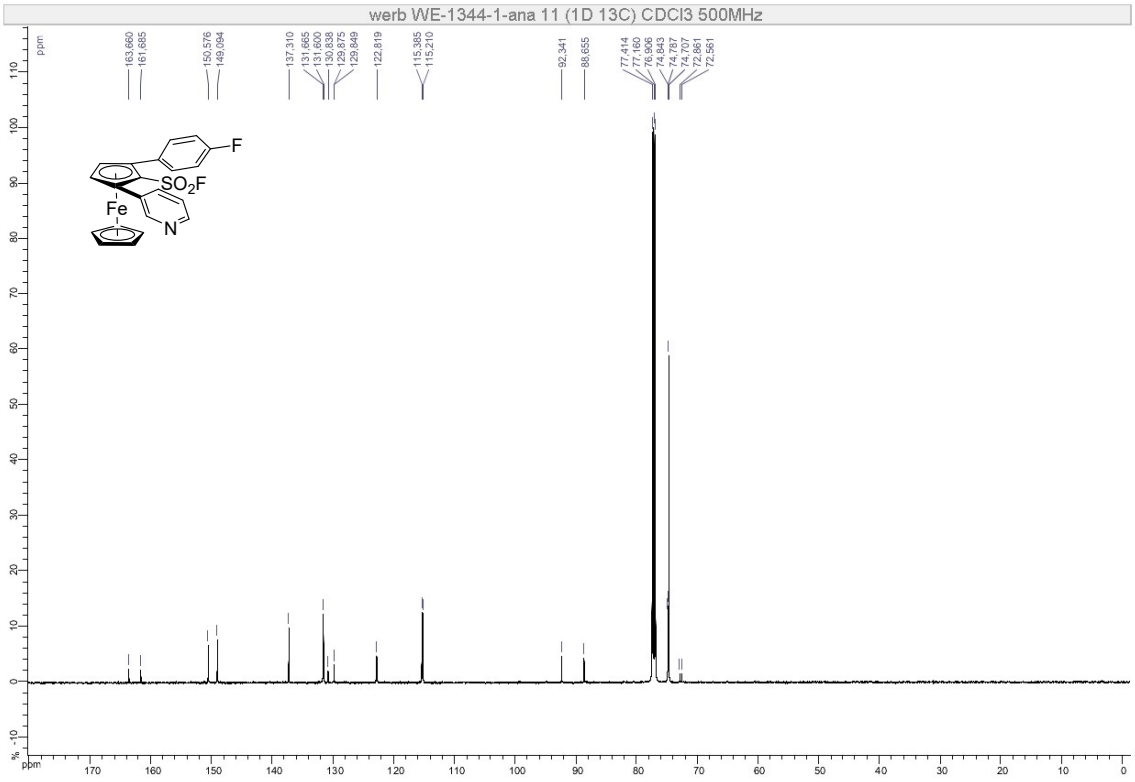

werb WE-1309-1-ana-bis 24 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1309-1-ana-bis 10 (1D 1H)
werb WE-1309-1-ana-bis 21 (1D 13C)
ppm

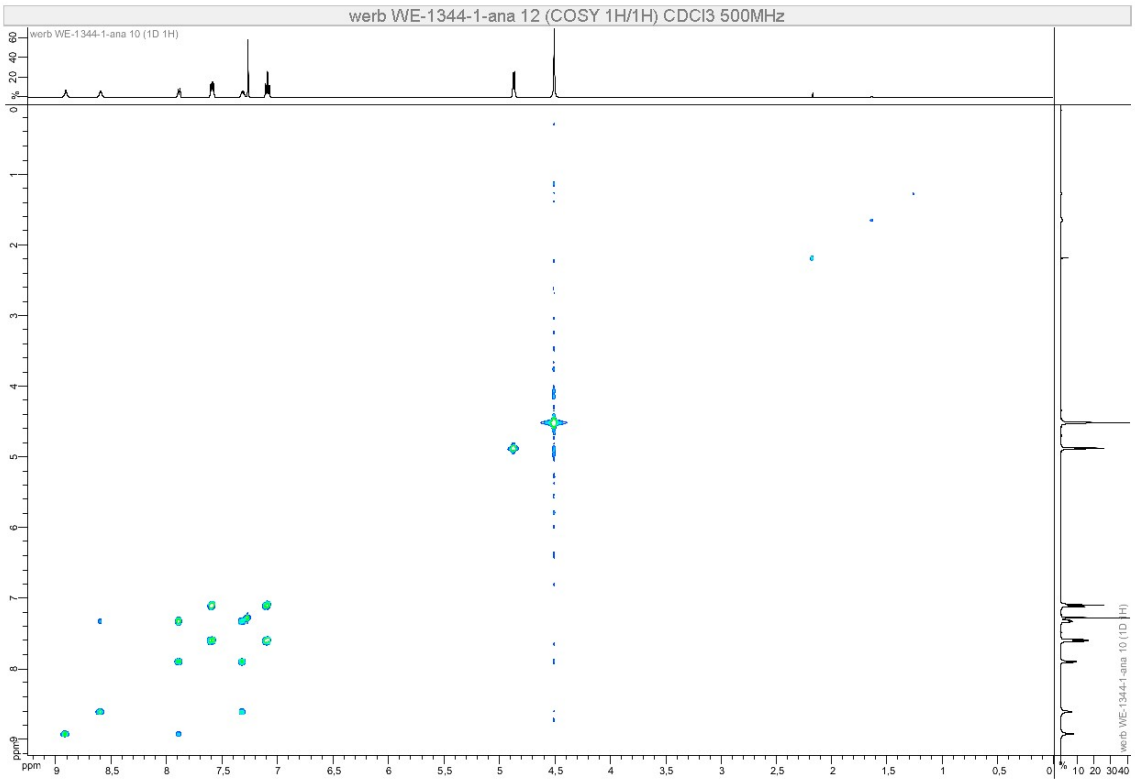

werb WE-1309-1-ana-bis 25 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1309-1-ana-bis 10 (1D 1H)
werb WE-1309-1-ana-bis 10 (1D 1H)
ppm

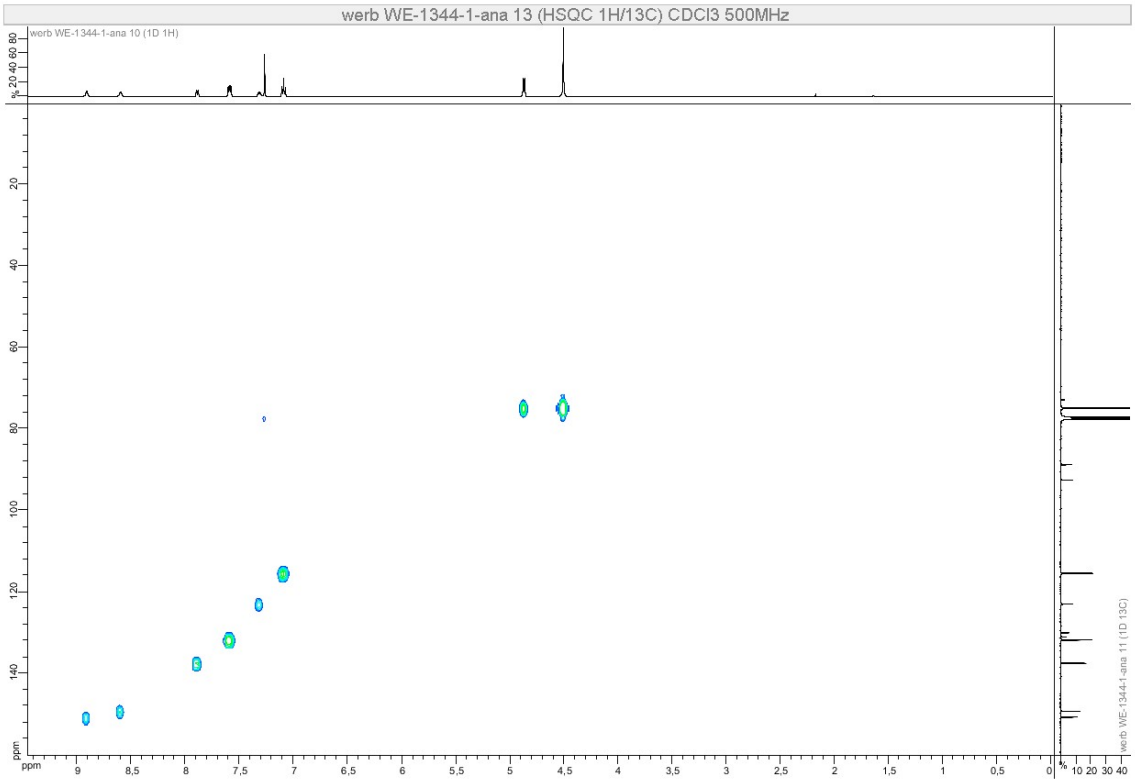

werb WE-1309-1-ana-bis 27 (1D 19F) CDCl3 500MHz
71.245
ppm
%
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140

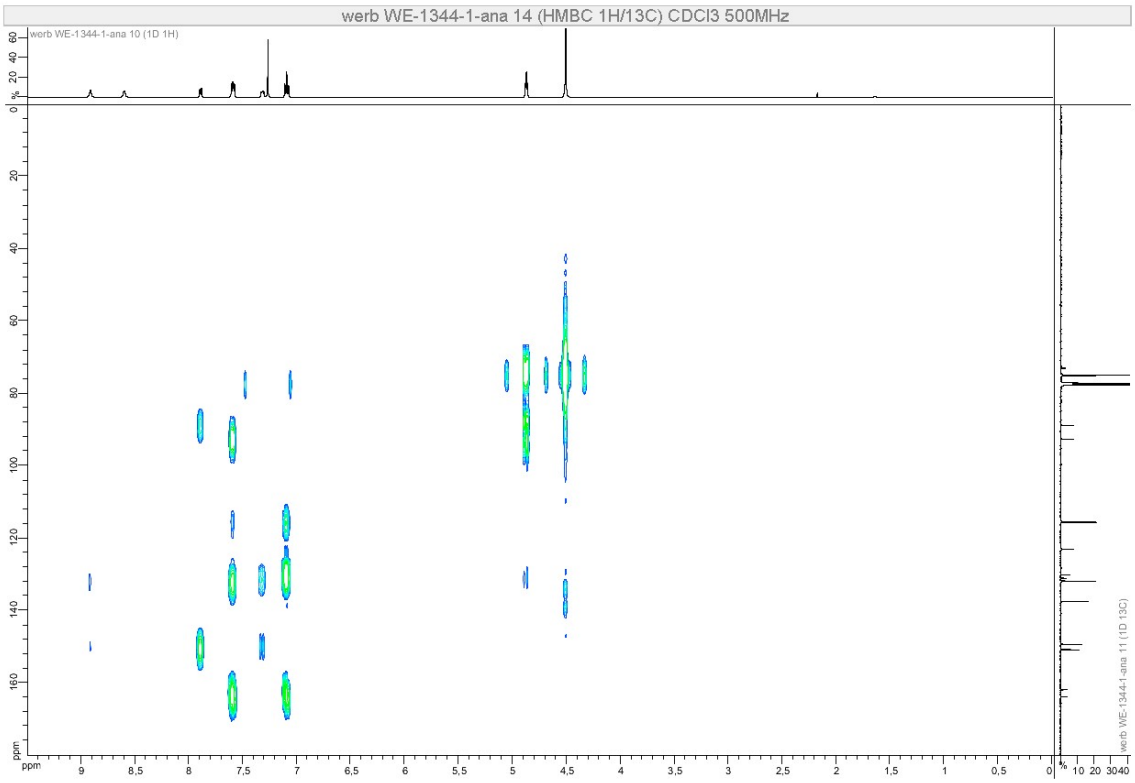
Compound 12

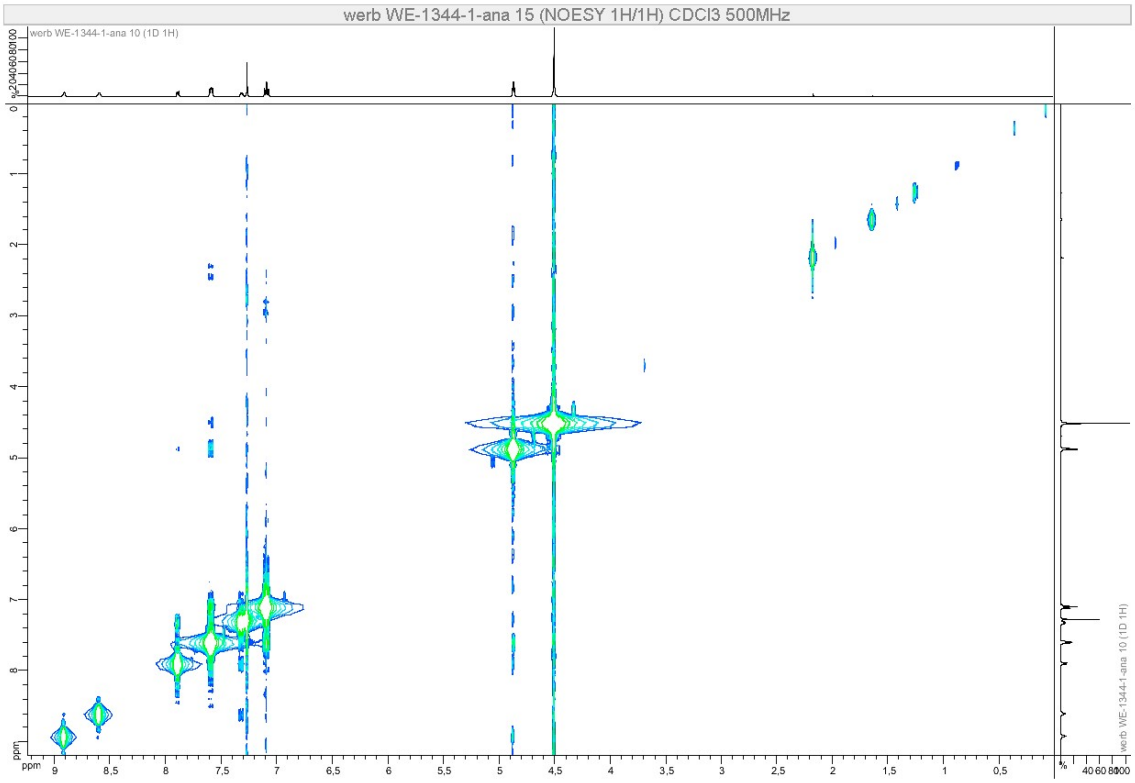

werb WE-1344-1-ana 10 (1D 1H) CDCl3 500MHz
F
SO2F
Fe
N

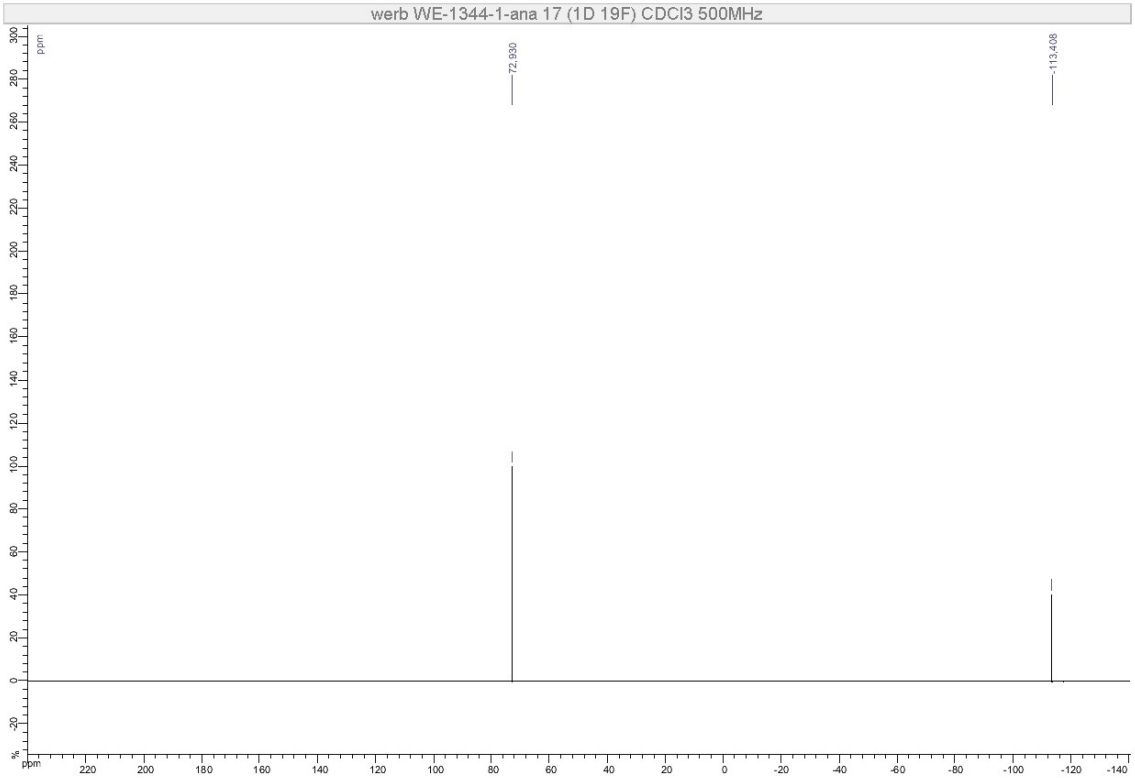

werb WE-1344-1-ana 11 (1D 13C) CDCl3 500MHz
F
SO2F
Fe
N


werb WE-1344-1-ana 12 (COSY 1H/1H) CDCl3 500MHz
werb WE-1344-1-ana 10 (1D 1H)
ppm
werb WE-1344-1-ana 10 (1D 1H)

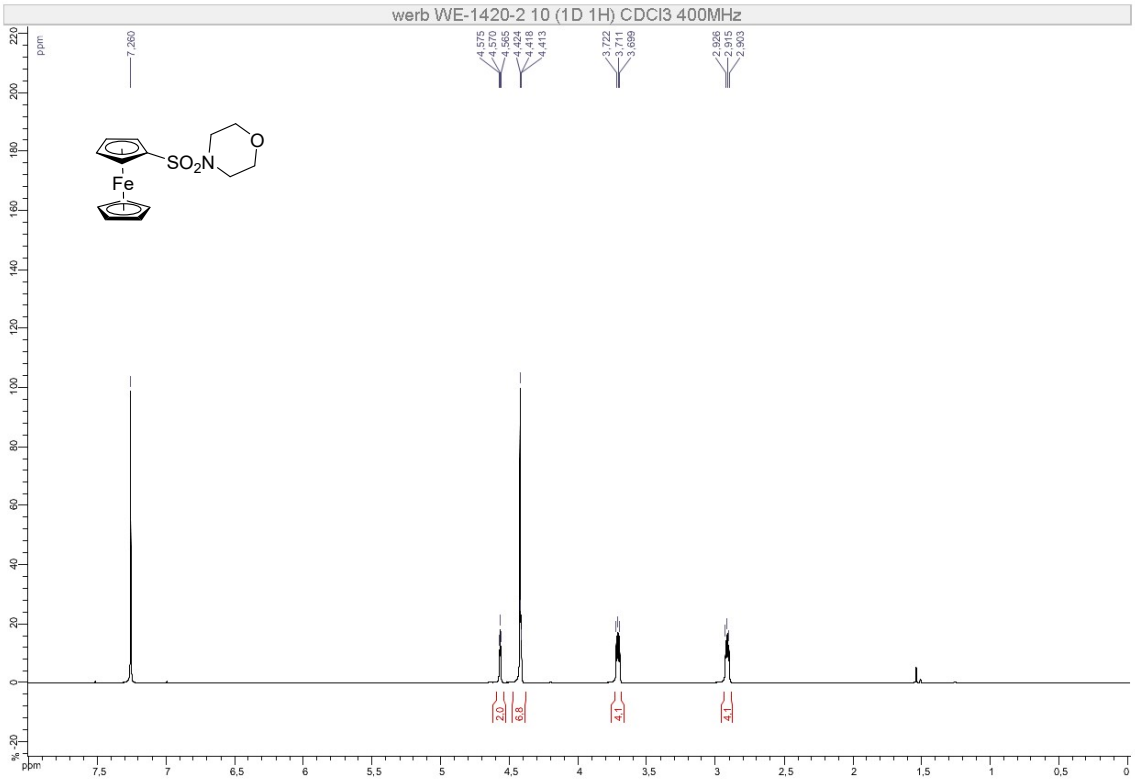

werb WE-1344-1-ana 13 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1344-1-ana 10 (1D 1H)
ppm
werb WE-1344-1-ana 11 (1D 13C)


werb WE-1344-1-ana 14 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1344-1-ana 10 (1D 1H)
werb WE-1344-1-ana 11 (1D 13C)
ppm

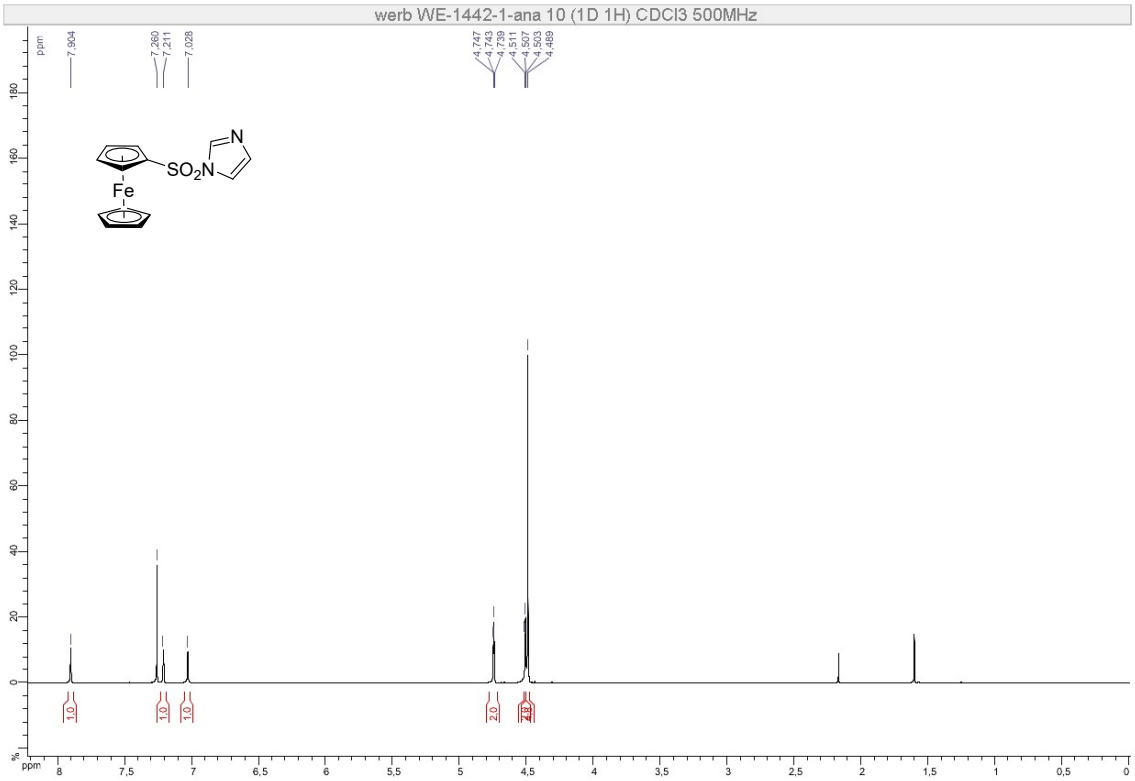

werb WE-1344-1-ana 15 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1344-1-ana 10 (1D 1H)
werb WE-1344-1-ana 10 (1D 1H)
ppm

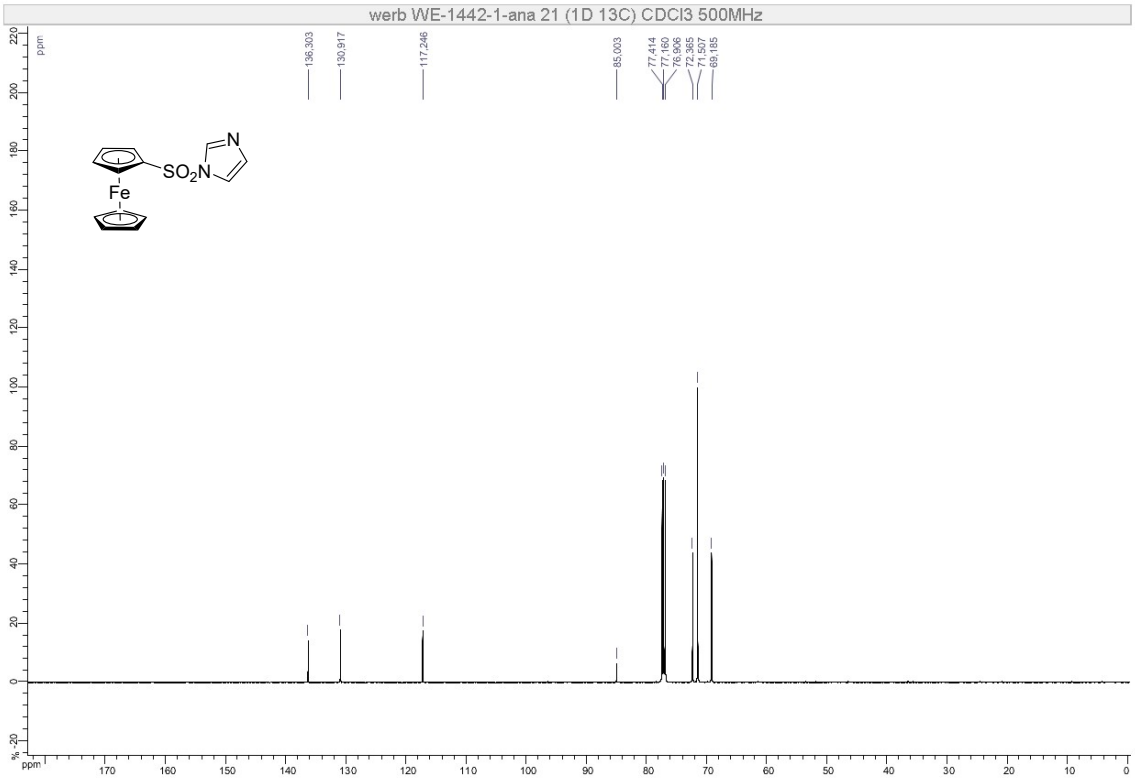

werb WE-1344-1-ana 17 (1D 19F) CDCl3 500MHz
ppm
72,930
-113,408
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140

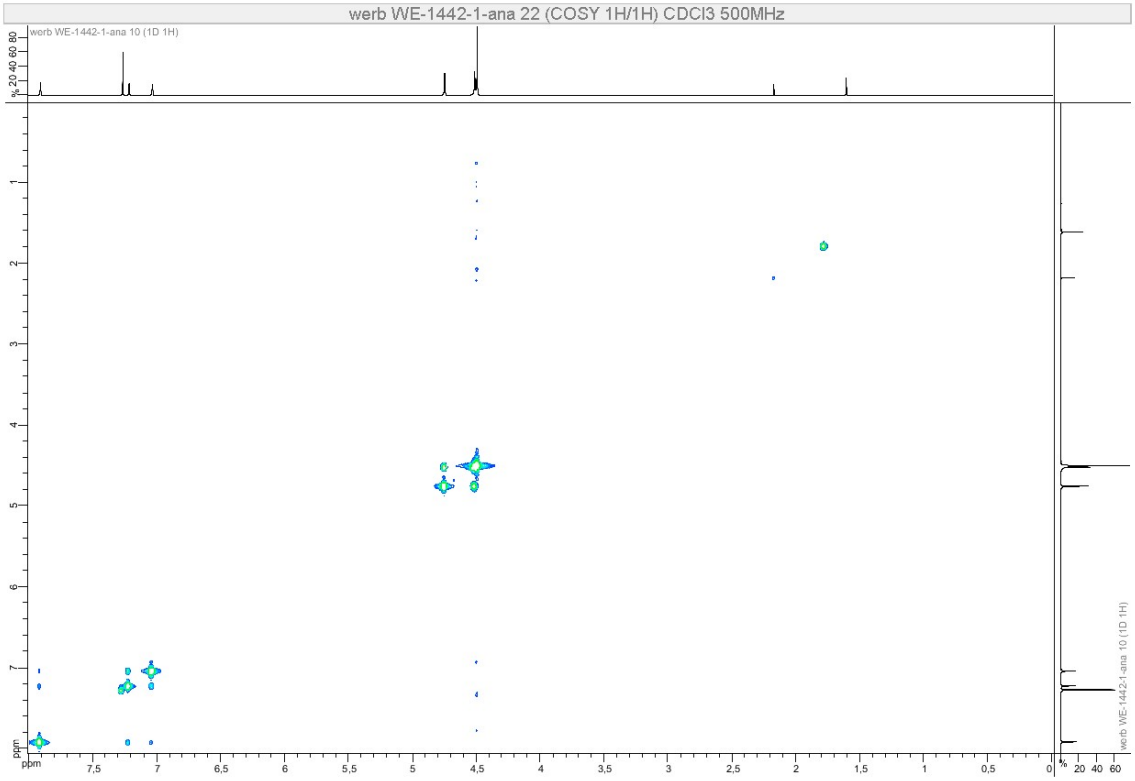
Compound 13a

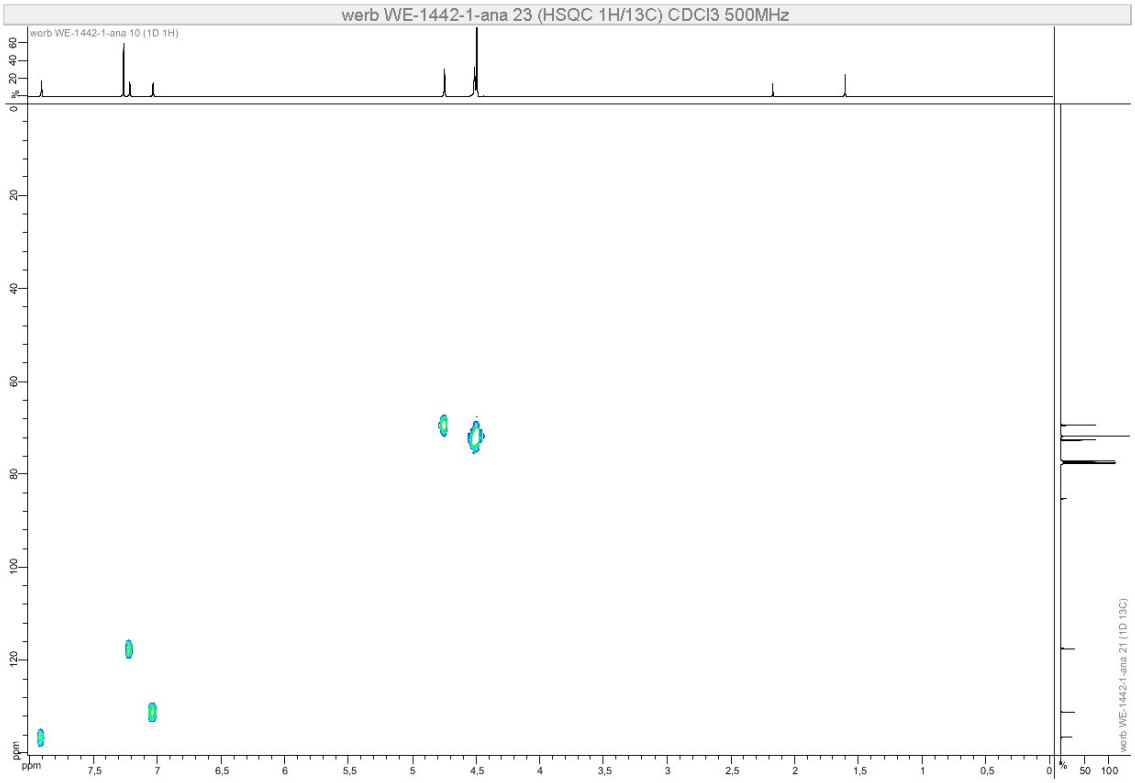


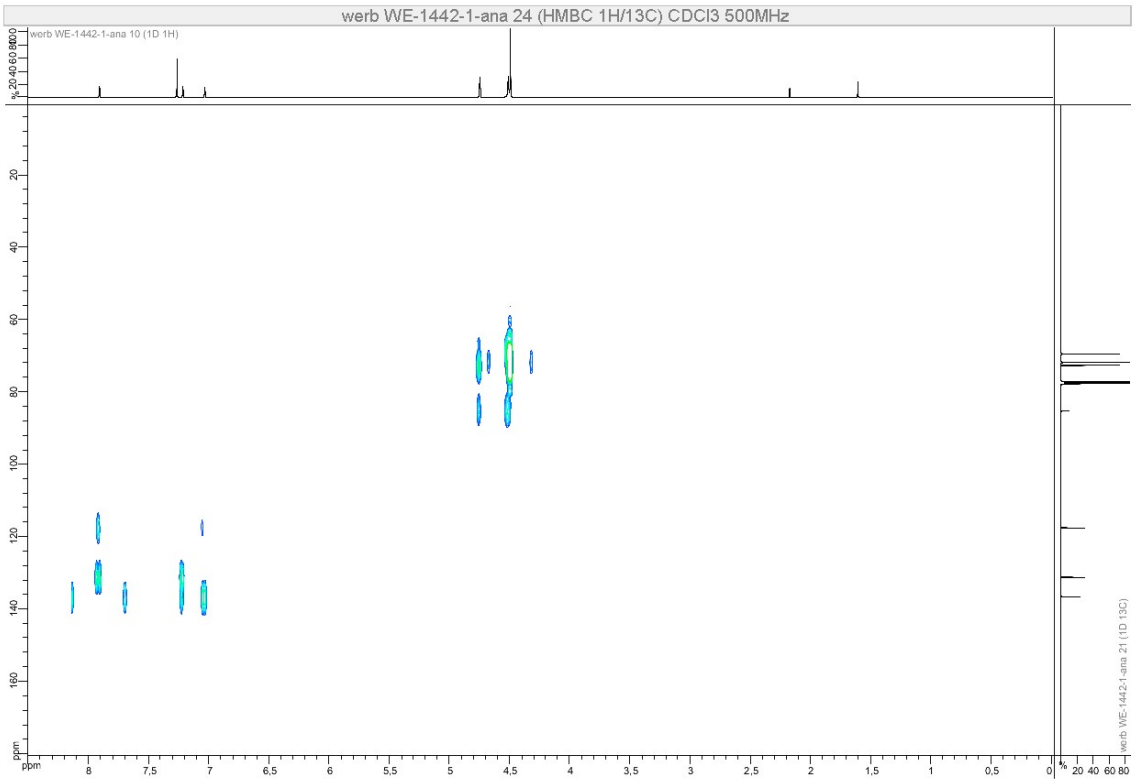
Compound 13b



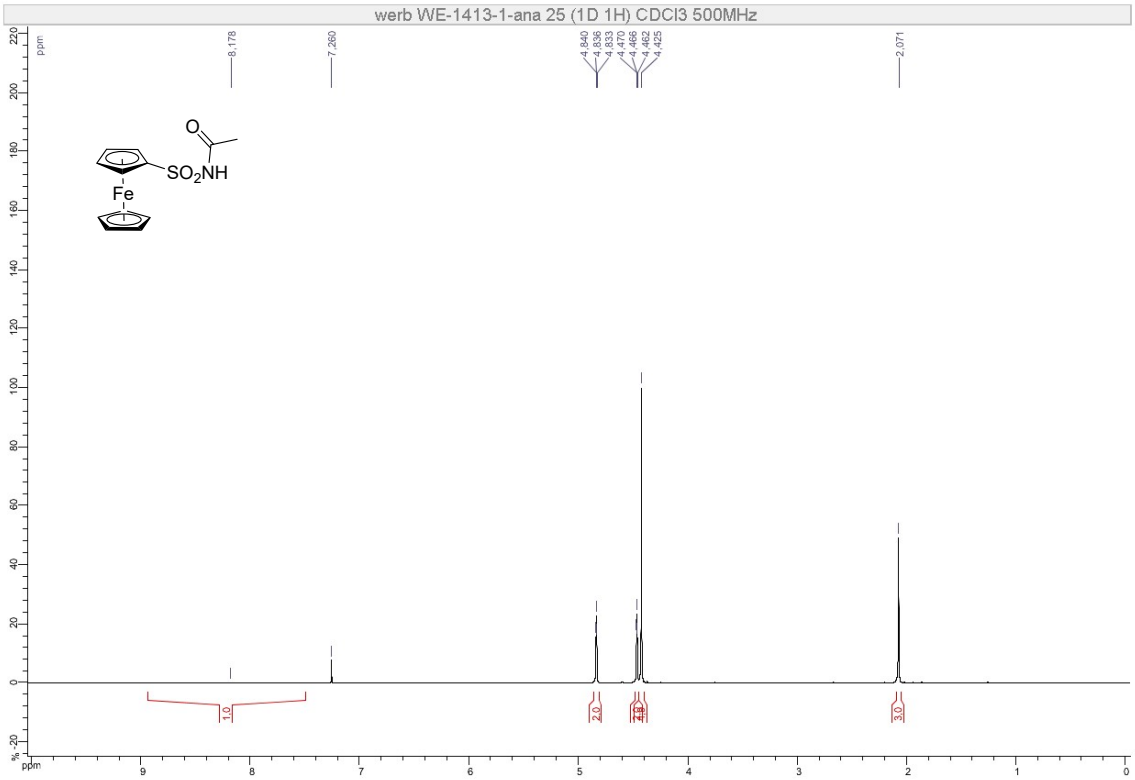


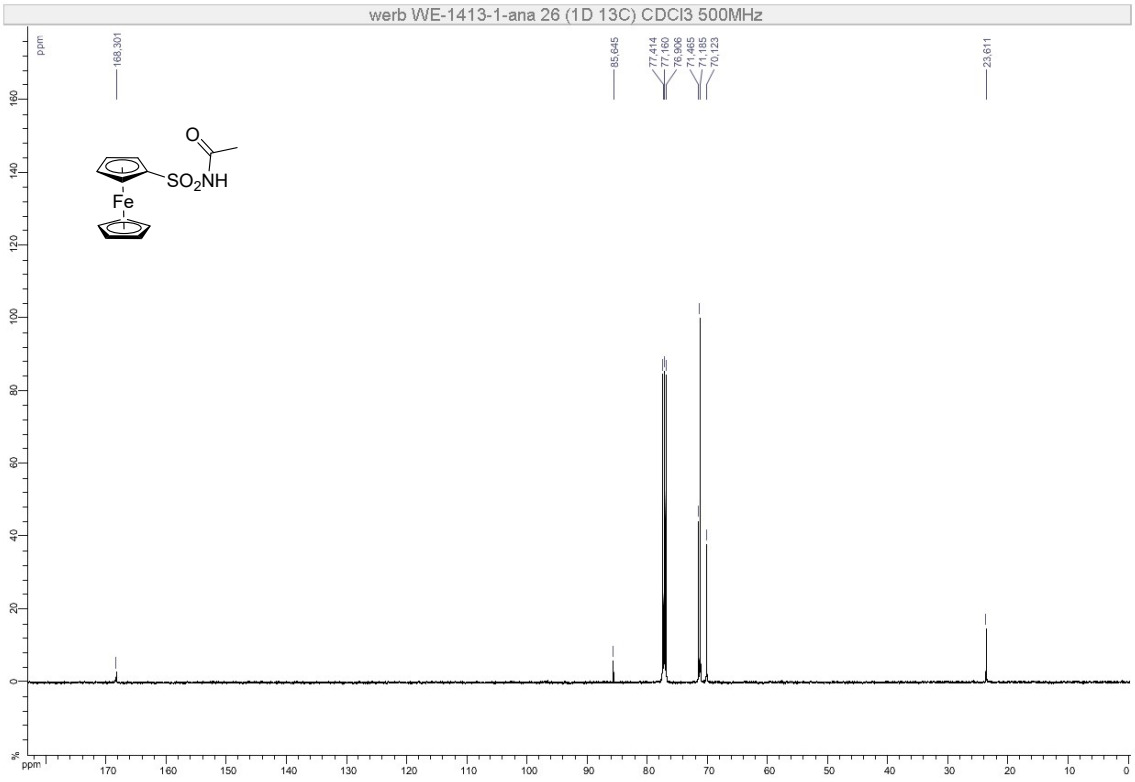

werb WE-1442-1-ana 22 (COSY 1H/1H) CDCl3 500MHz
werb WE-1442-1-ana 10 (1D 1H)
ppm
werb WE-1442-1-ana 10 (1D 1H)

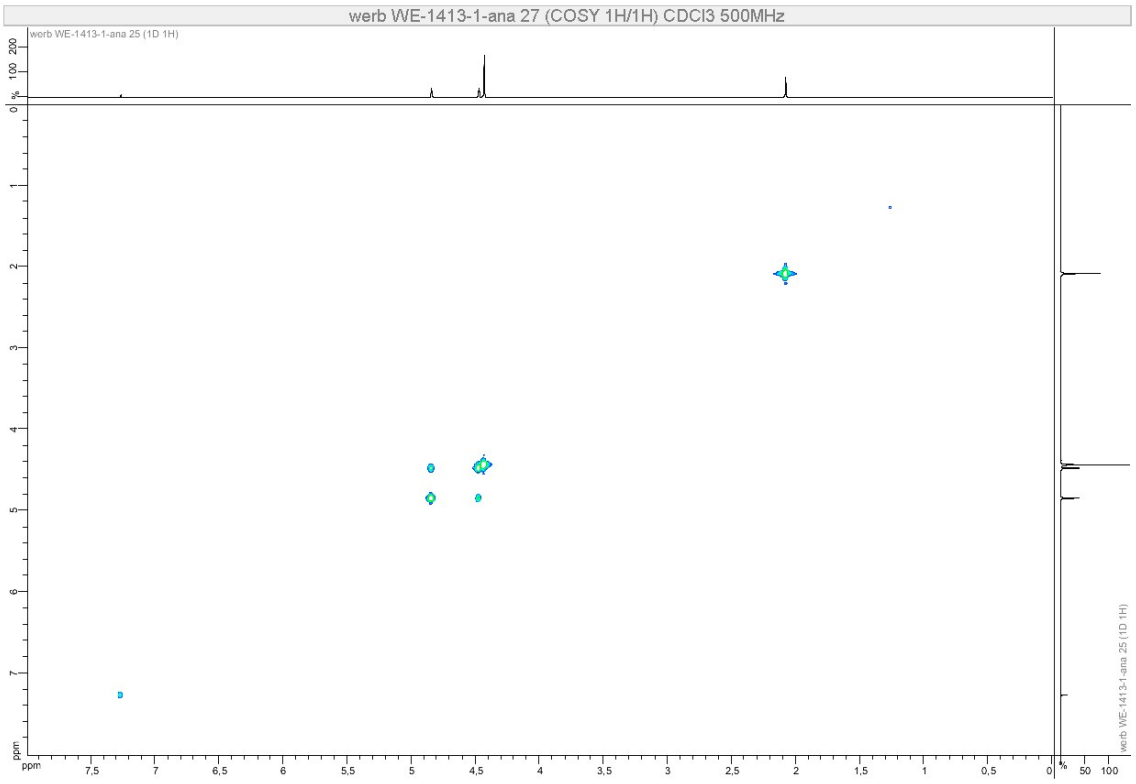

werb WE-1442-1-ana 23 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1442-1-ana 10 (1D 1H)
ppm
werb WE-1442-1-ana 21 (1D 13C)

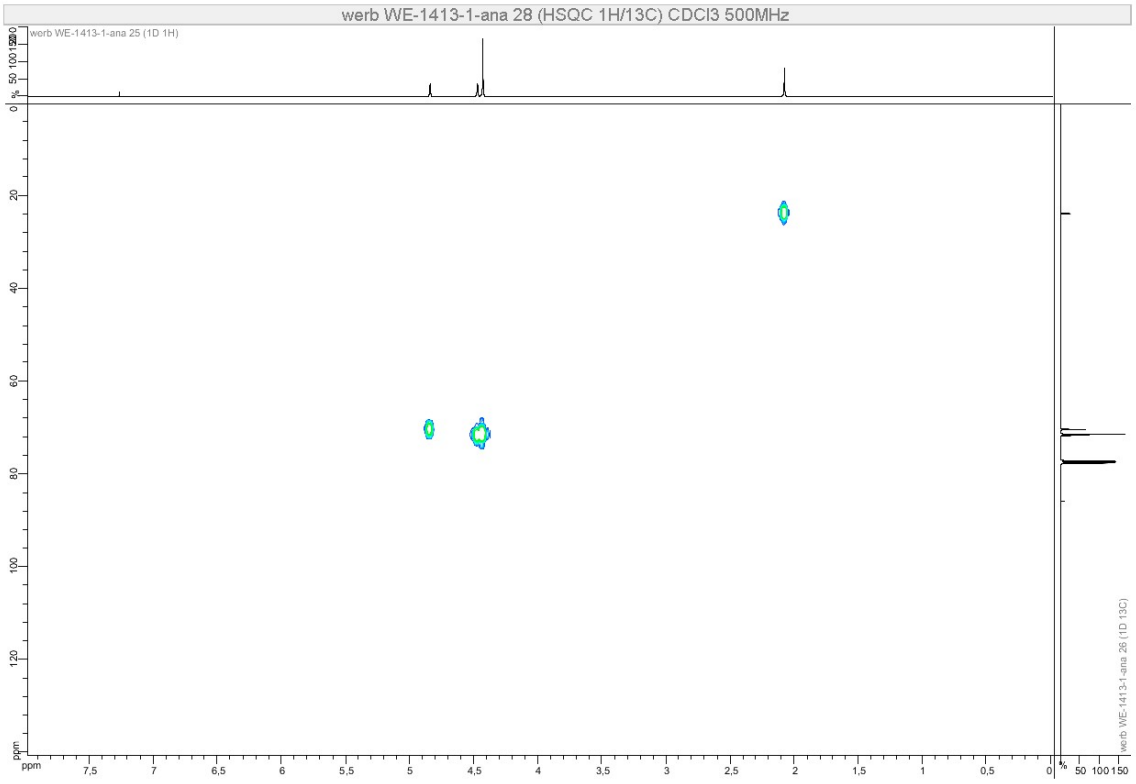

werb WE-1442-1-ana 24 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1442-1-ana 10 (1D 1H)
werb WE-1442-1-ana 21 (1D 13C)
ppm
%

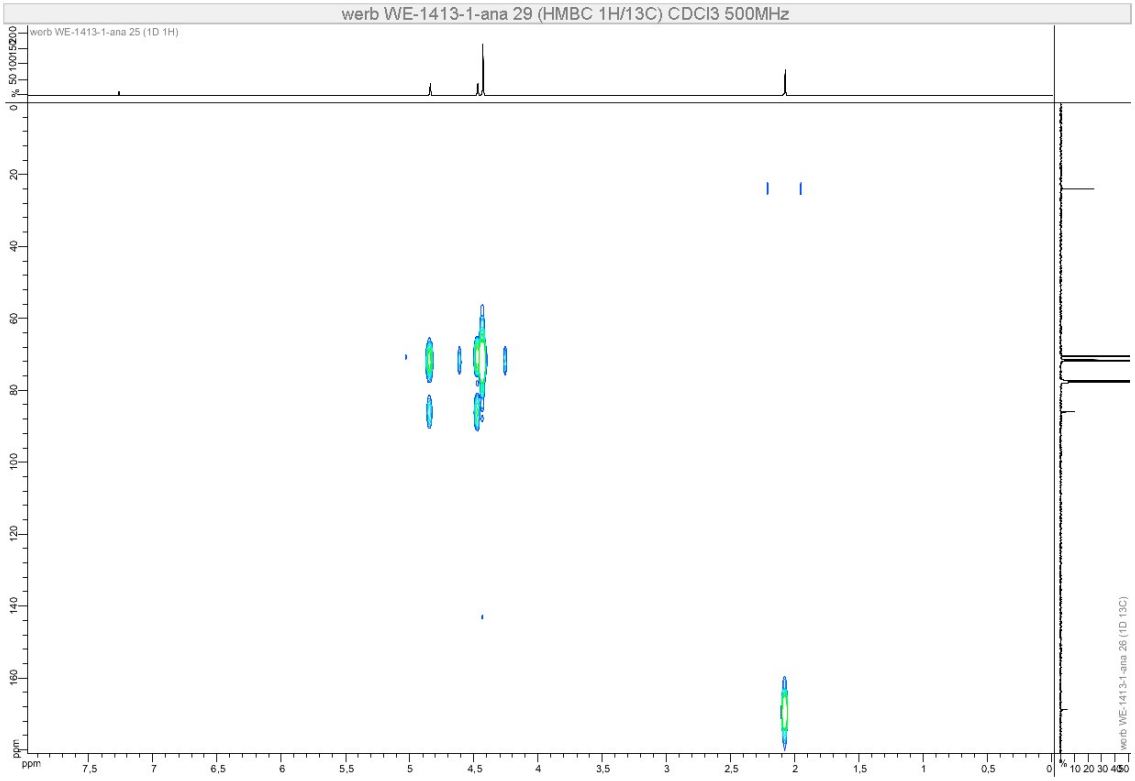
Compound 13c



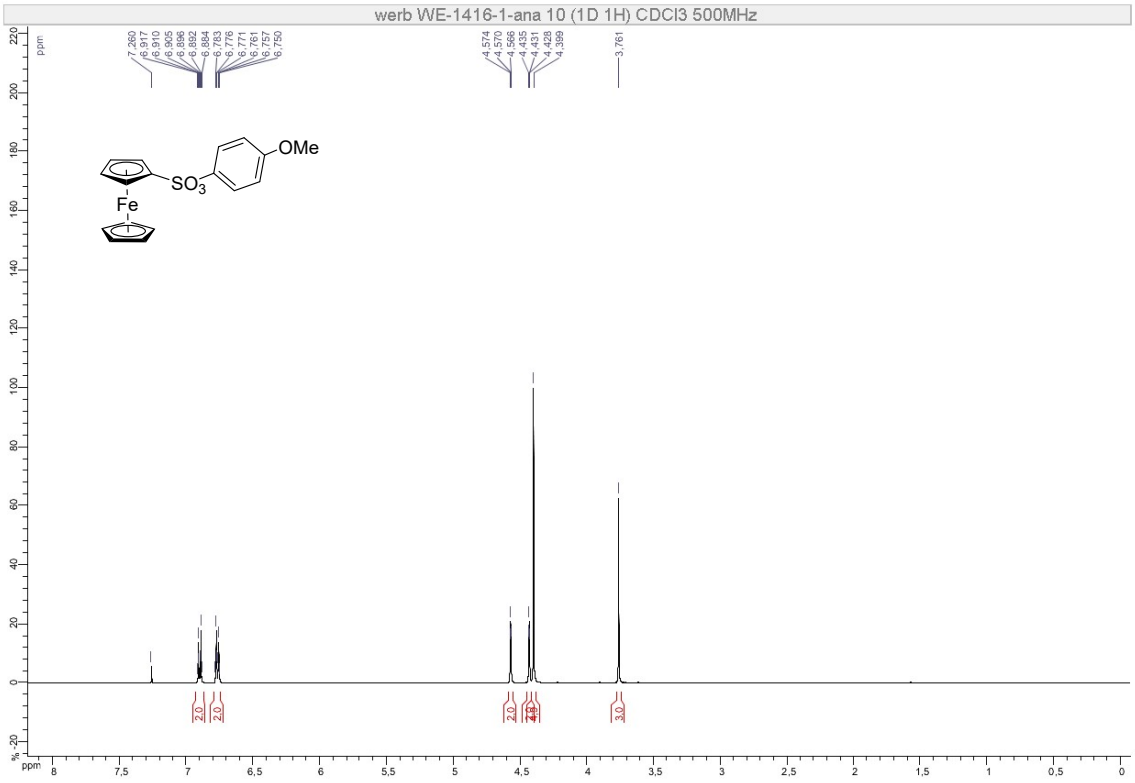


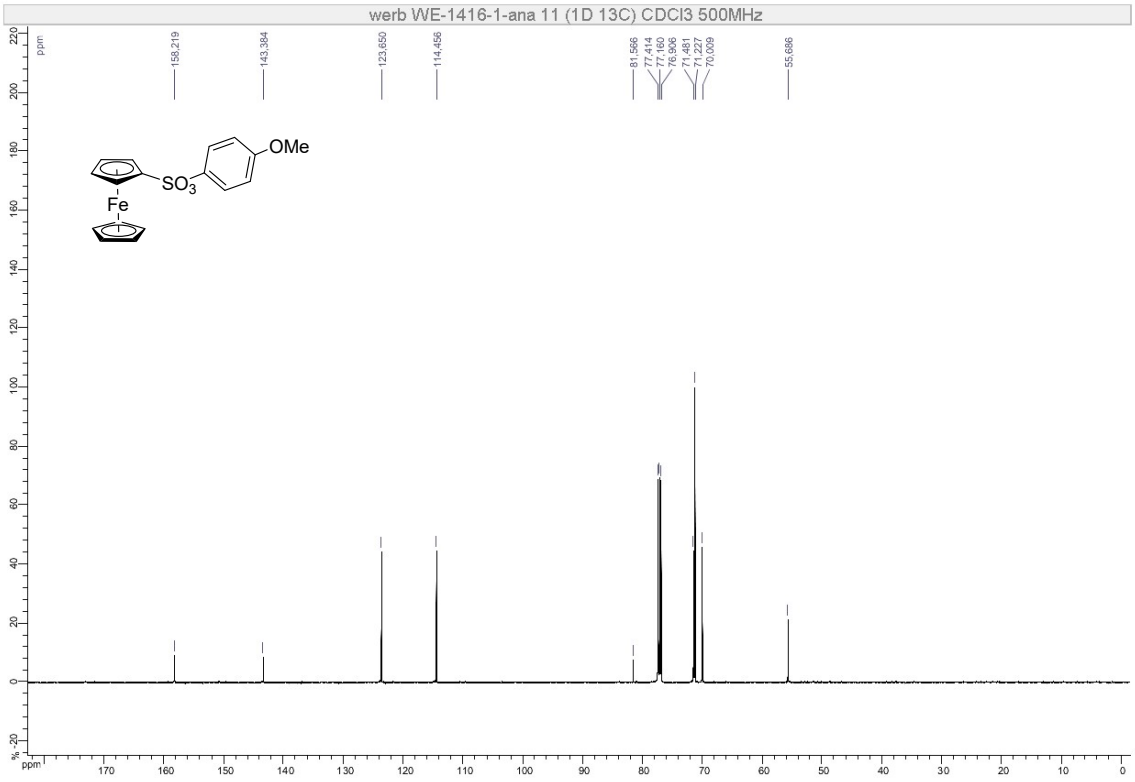

werb WE-1413-1-ana 27 (COSY 1H/1H) CDCl3 500MHz
werb WE-1413-1-ana 25 (1D 1H)
ppm
werb WE-1413-1-ana 25 (1D 1H)

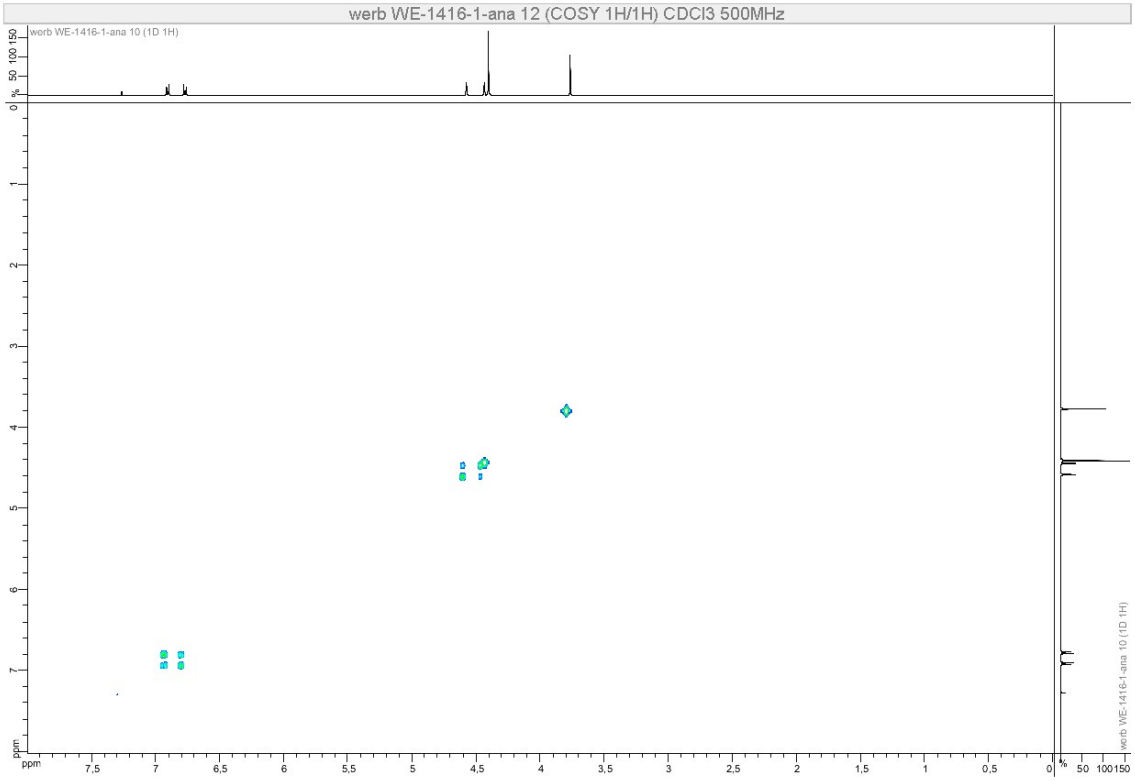

werb WE-1413-1-ana 28 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1413-1-ana 25 (1D 1H)
ppm
werb WE-1413-1-ana 26 (1D 13C)

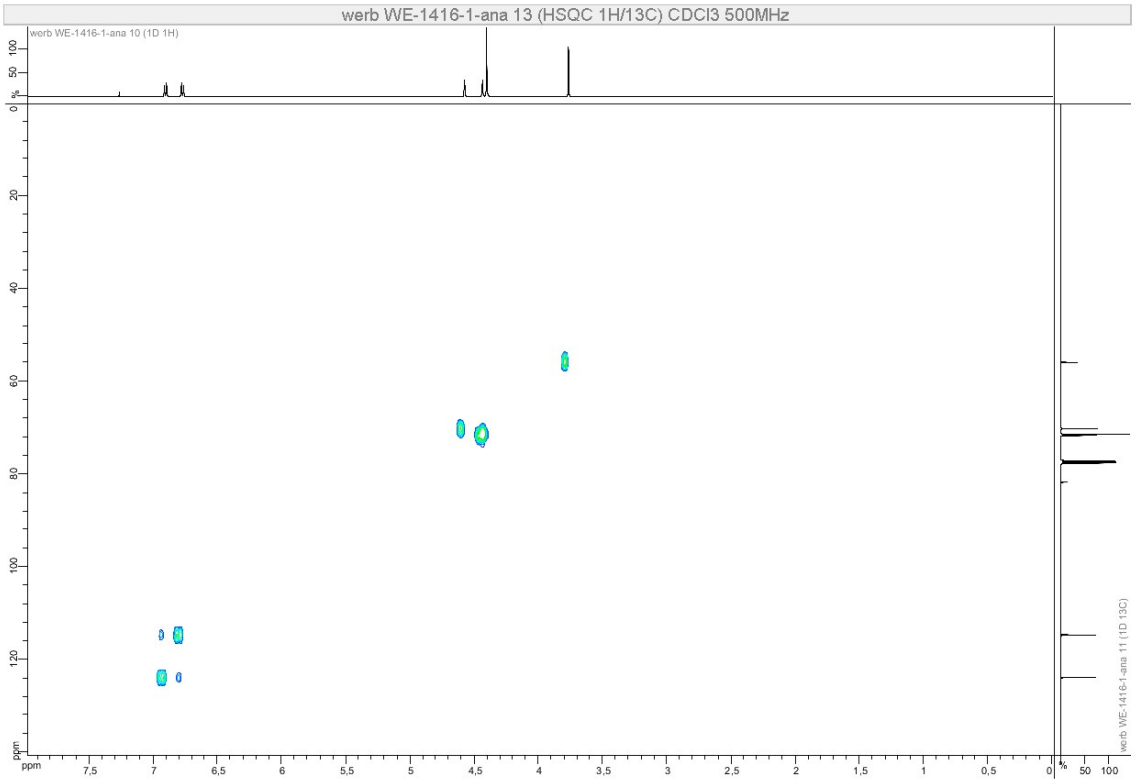

werb WE-1413-1-ana 29 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1413-1-ana 25 (1D 1H)
werb WE-1413-1-ana 26 (1D 13C)
ppm
%

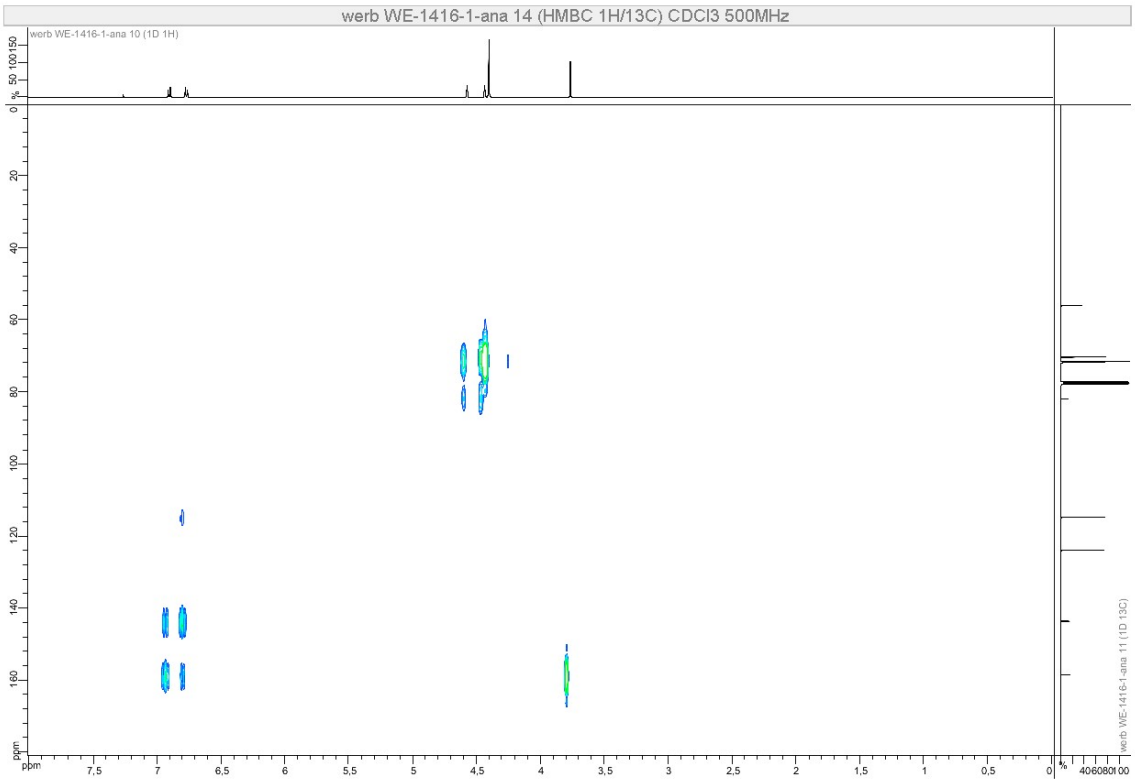
Compound 13d



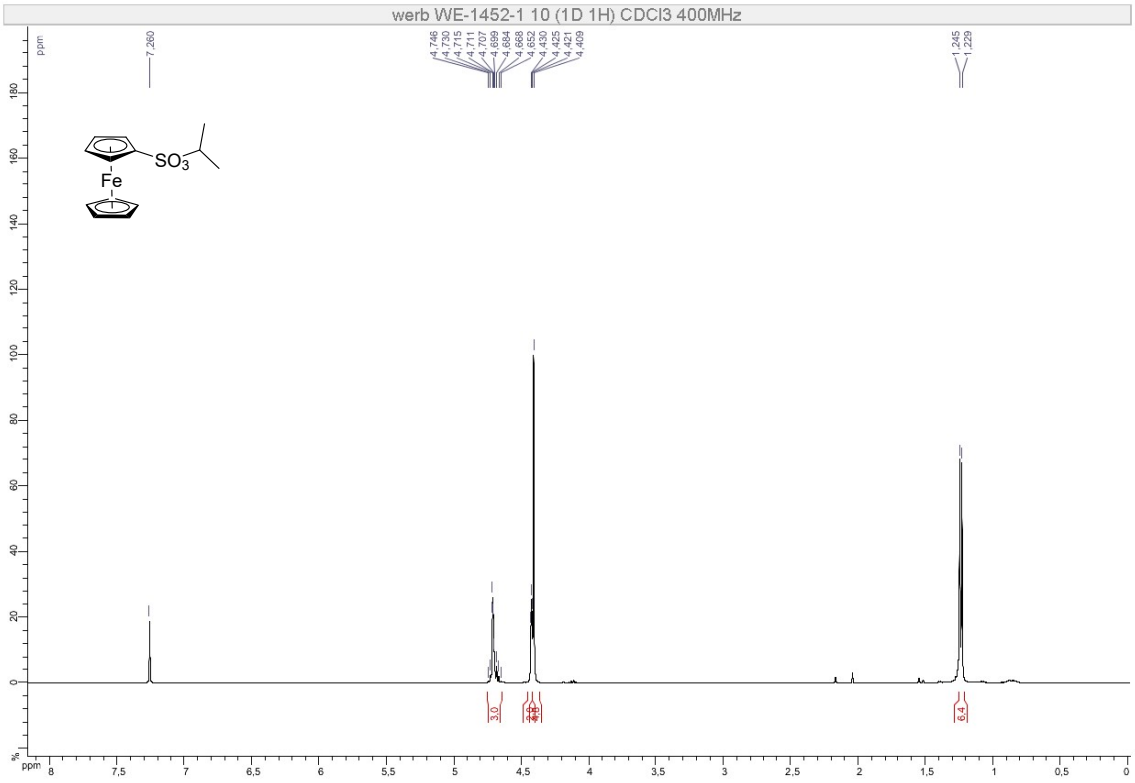



werb WE-1416-1-ana 12 (COSY 1H/1H) CDCl3 500MHz
werb WE-1416-1-ana 10 (1D 1H)
ppm
%
werb WE-1416-1-ana 10 (1D 1H)

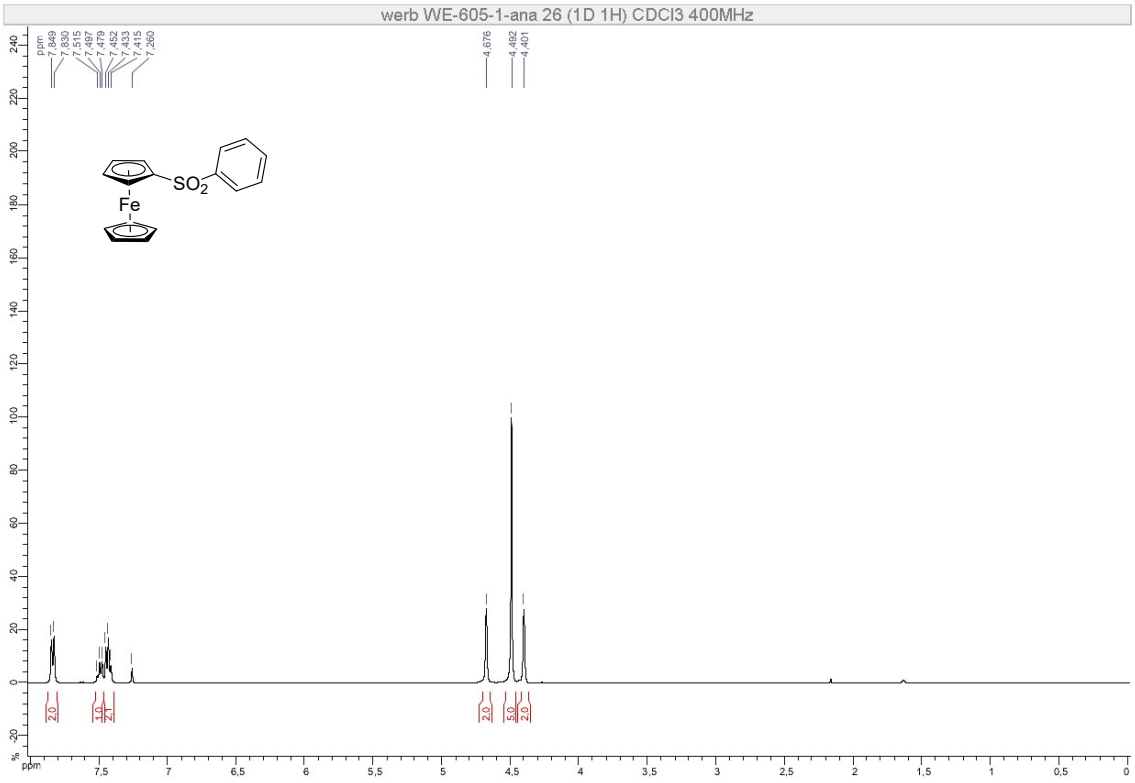

werb WE-1416-1-ana 13 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1416-1-ana 10 (1D 1H)
ppm
%
werb WE-1416-1-ana 11 (1D 13C)

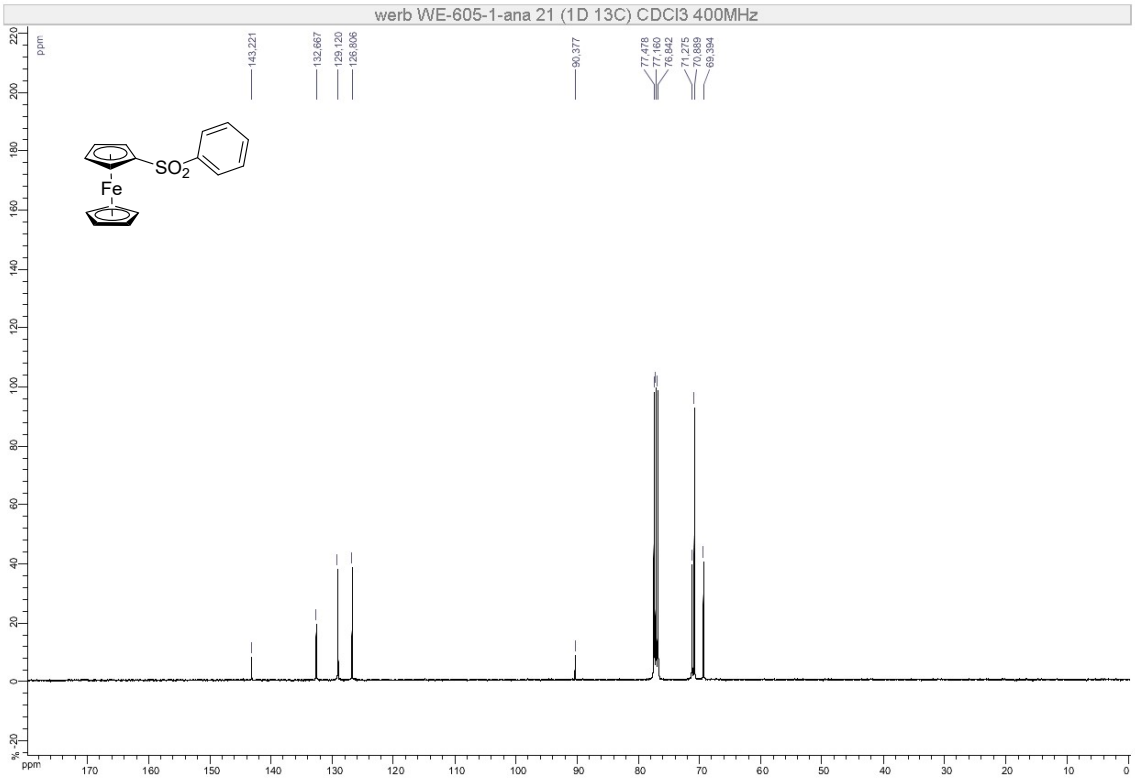

werb WE-1416-1-ana 14 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1416-1-ana 10 (1D 1H)
werb WE-1416-1-ana 11 (1D 13C)
ppm
%

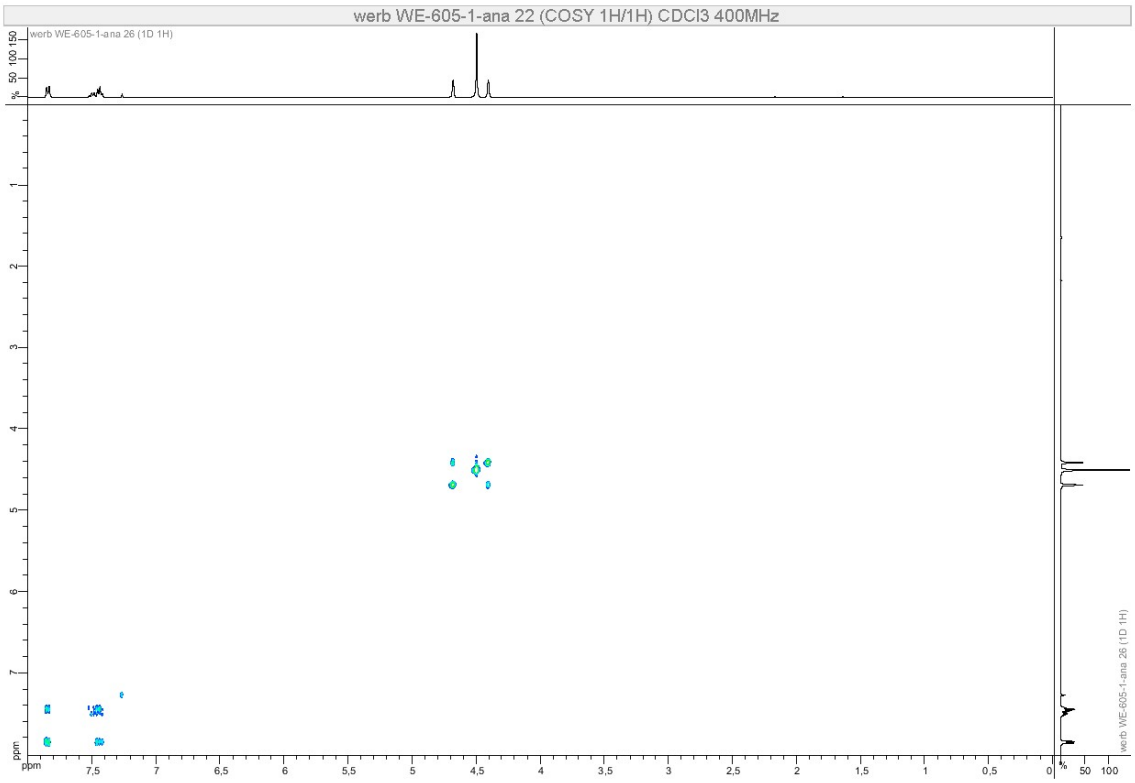
Compound 13e

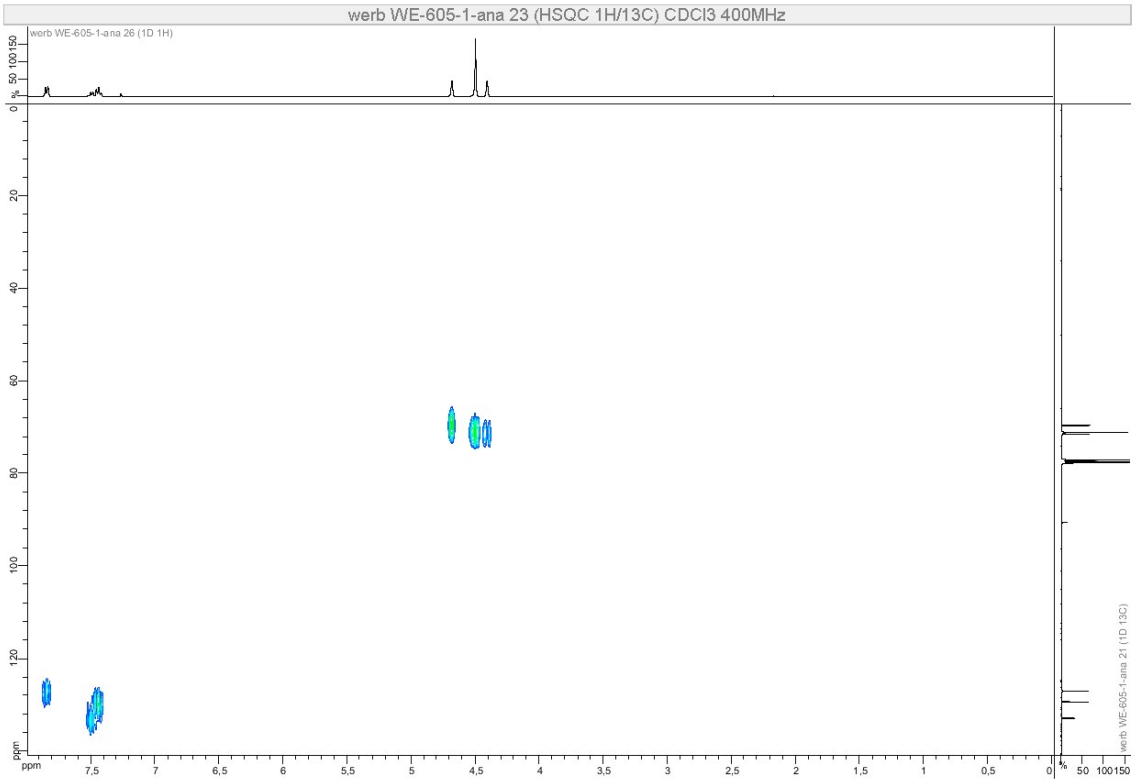


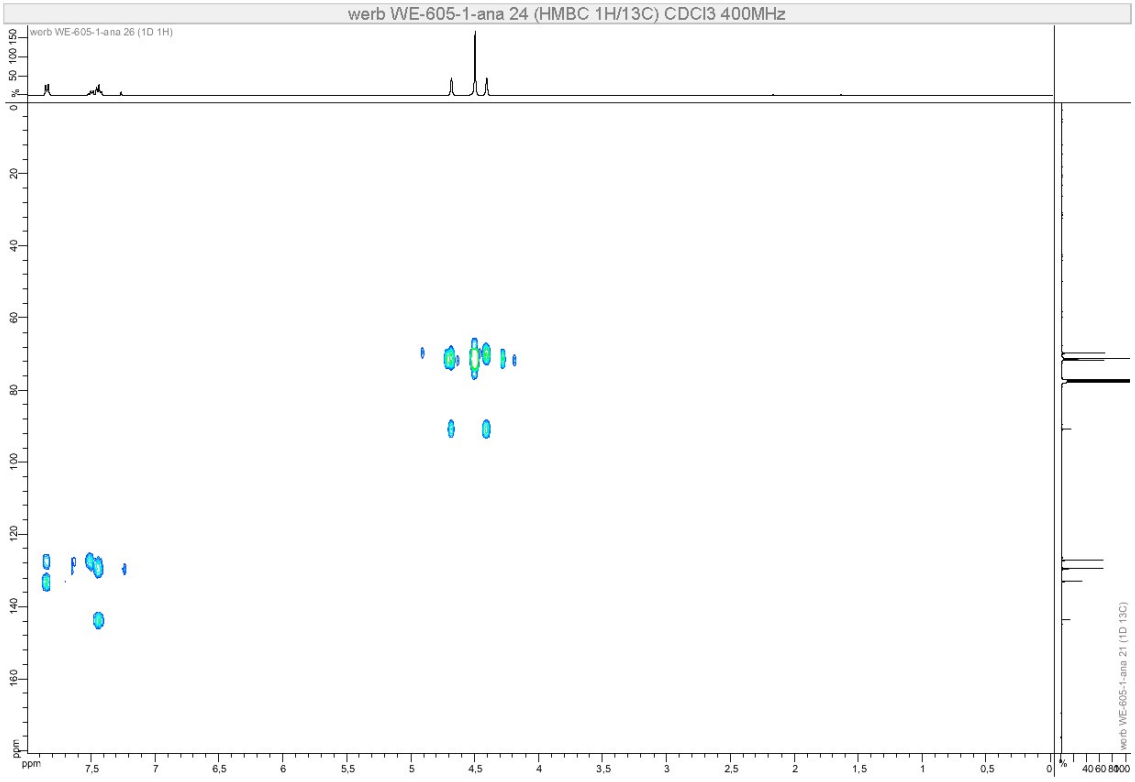
Compound 13f



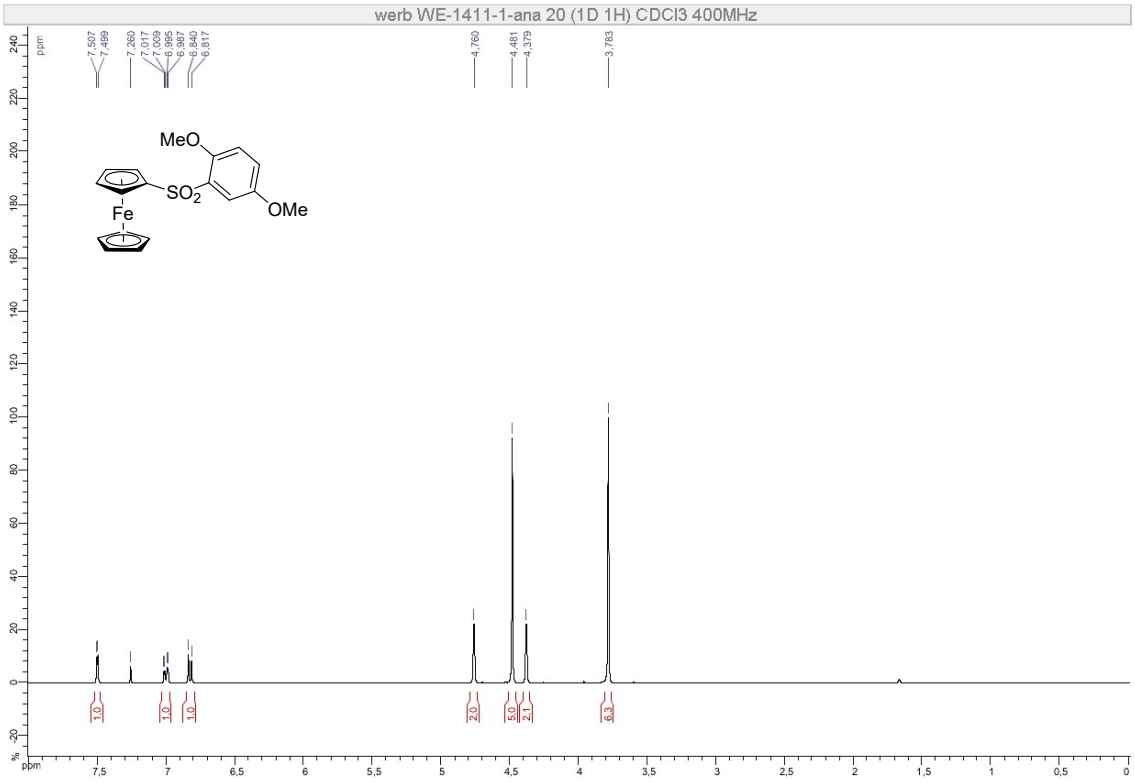


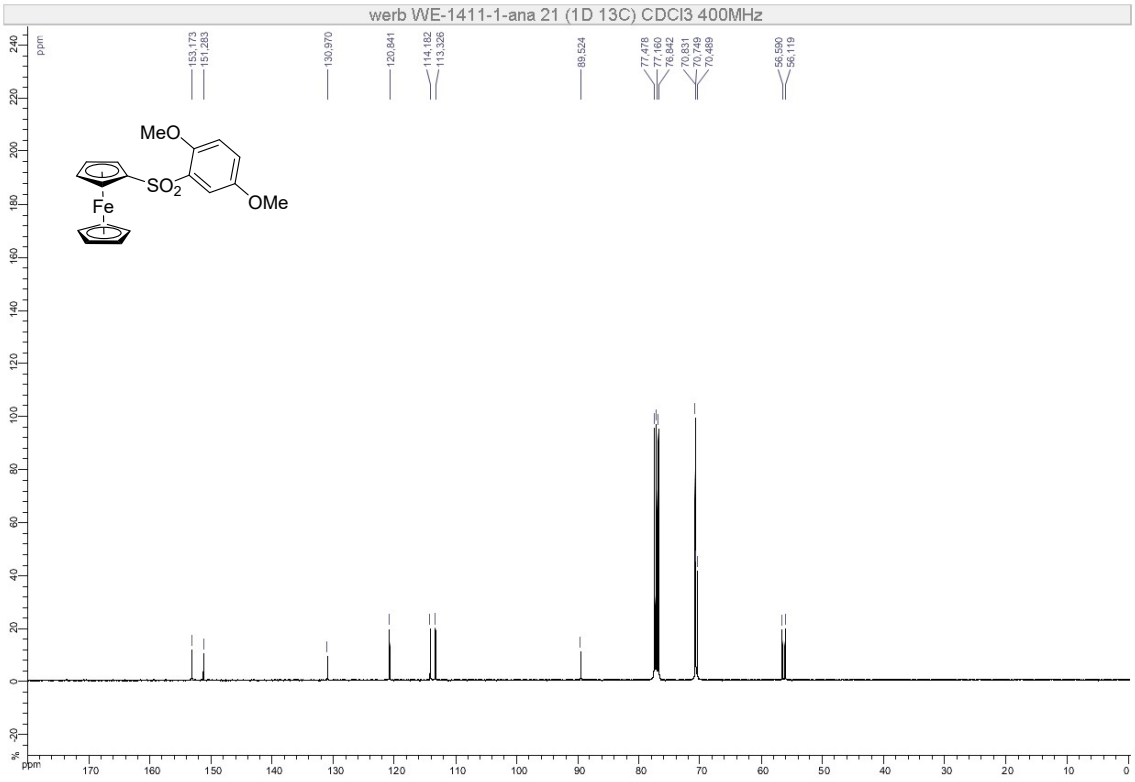

werb WE-605-1-ana 22 (COSY 1H/1H) CDCl3 400MHz
werb WE-605-1-ana 26 (1D 1H)
ppm
werb WE-605-1-ana 26 (1D 1H)

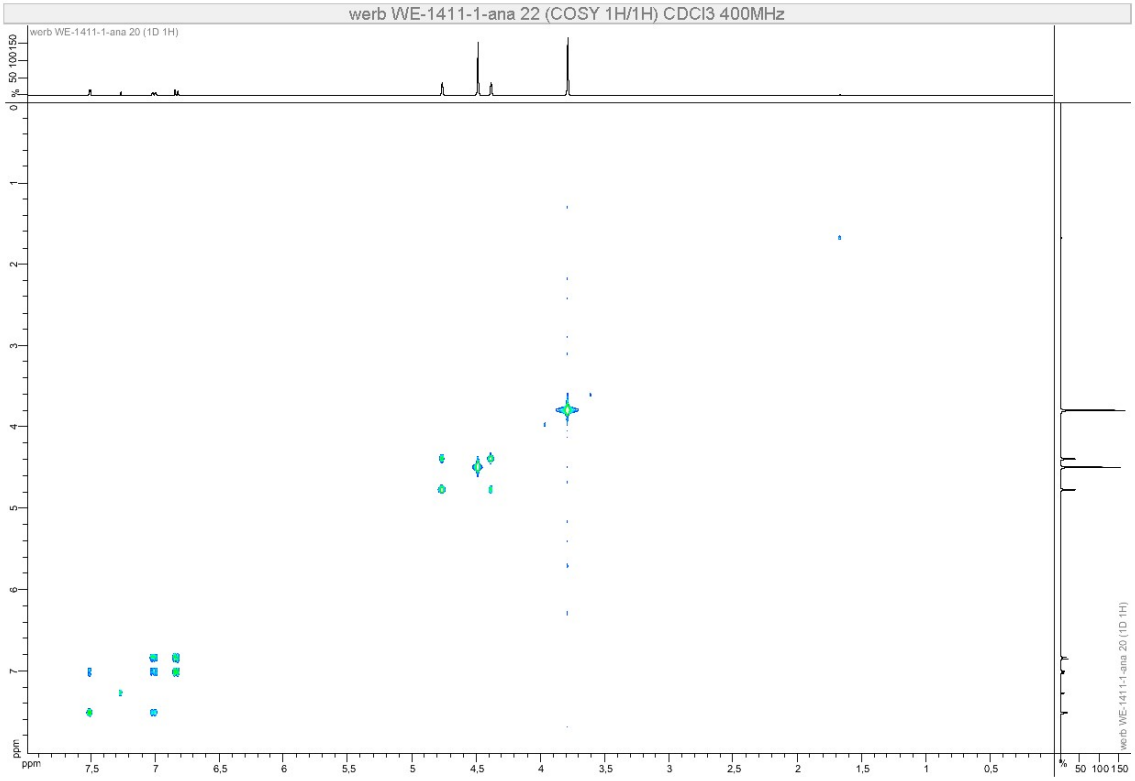

werb WE-605-1-ana 23 (HSQC 1H/13C) CDCl3 400MHz
werb WE-605-1-ana 26 (1D 1H)
ppm
werb WE-605-1-ana 21 (1D 13C)

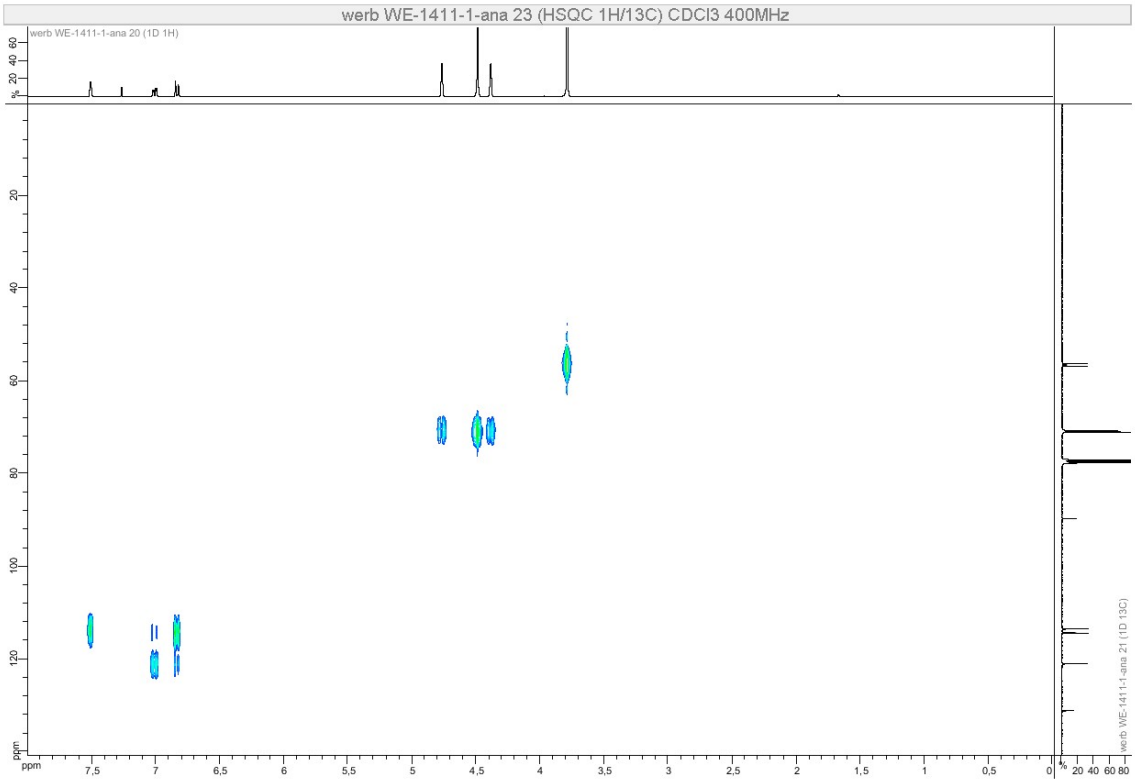

werb WE-605-1-ana 24 (HMBC 1H/13C) CDCl3 400MHz
werb WE-605-1-ana 26 (1D 1H)
werb WE-605-1-ana 21 (1D 13C)
ppm
%

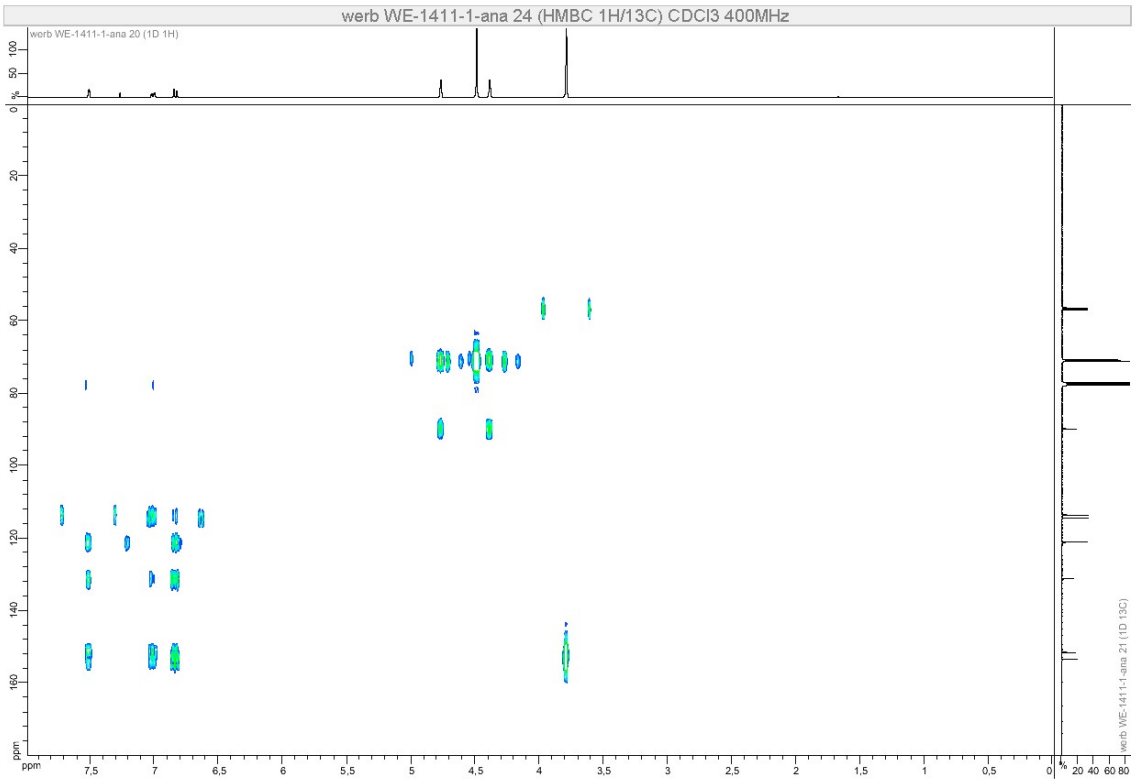
Compound 13g



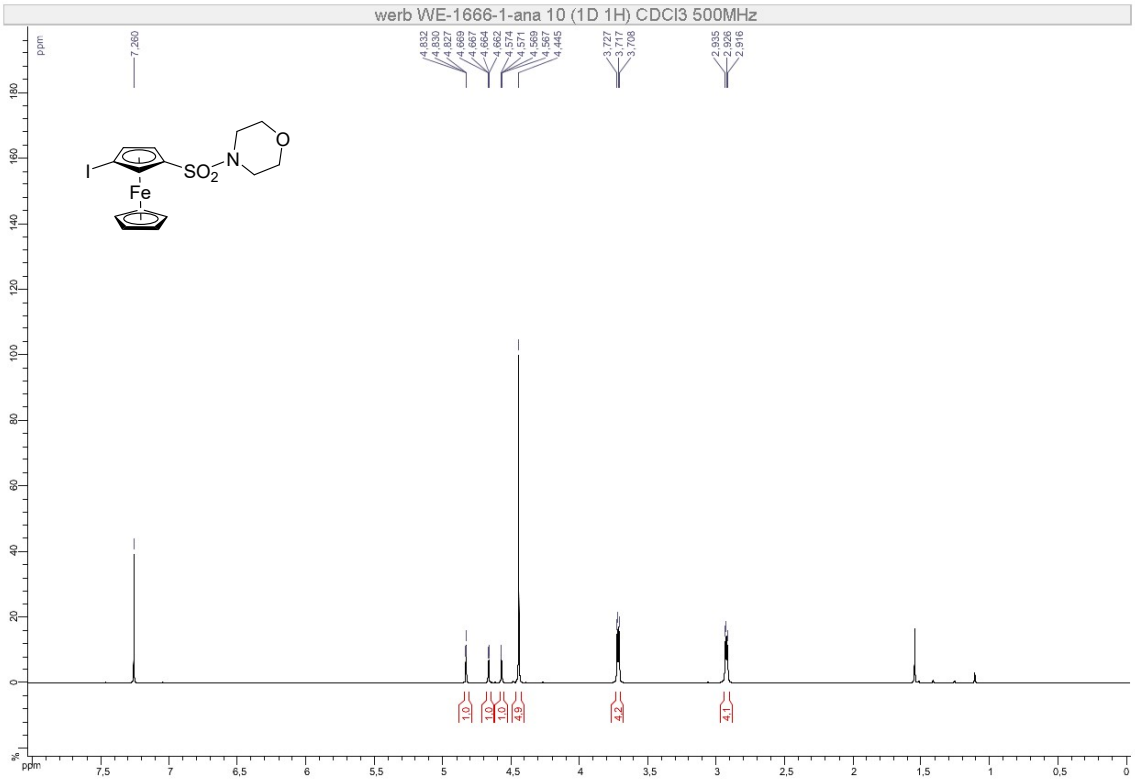


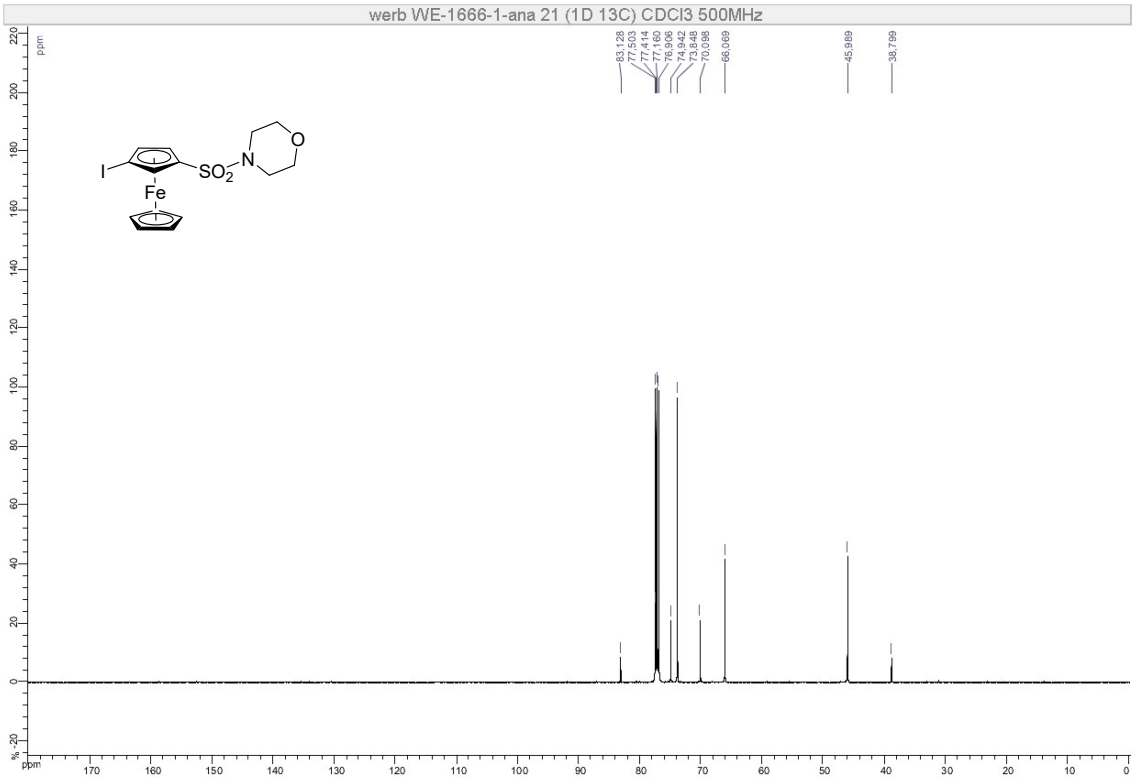

werb WE-1411-1-ana 22 (COSY 1H/1H) CDCl3 400MHz
werb WE-1411-1-ana 20 (1D 1H)
ppm
werb WE-1411-1-ana 20 (1D 1H)

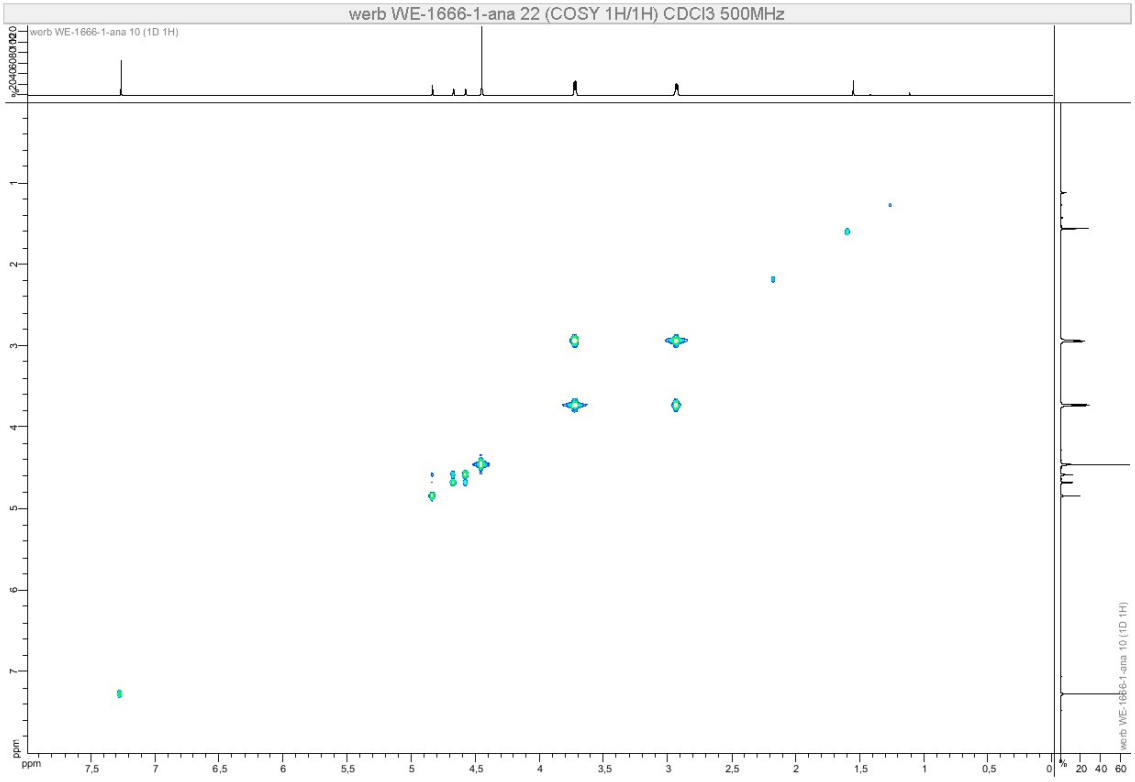

werb WE-1411-1-ana 23 (HSQC 1H/13C) CDCl3 400MHz
werb WE-1411-1-ana 20 (1D 1H)
ppm
werb WE-1411-1-ana 21 (1D 13C)

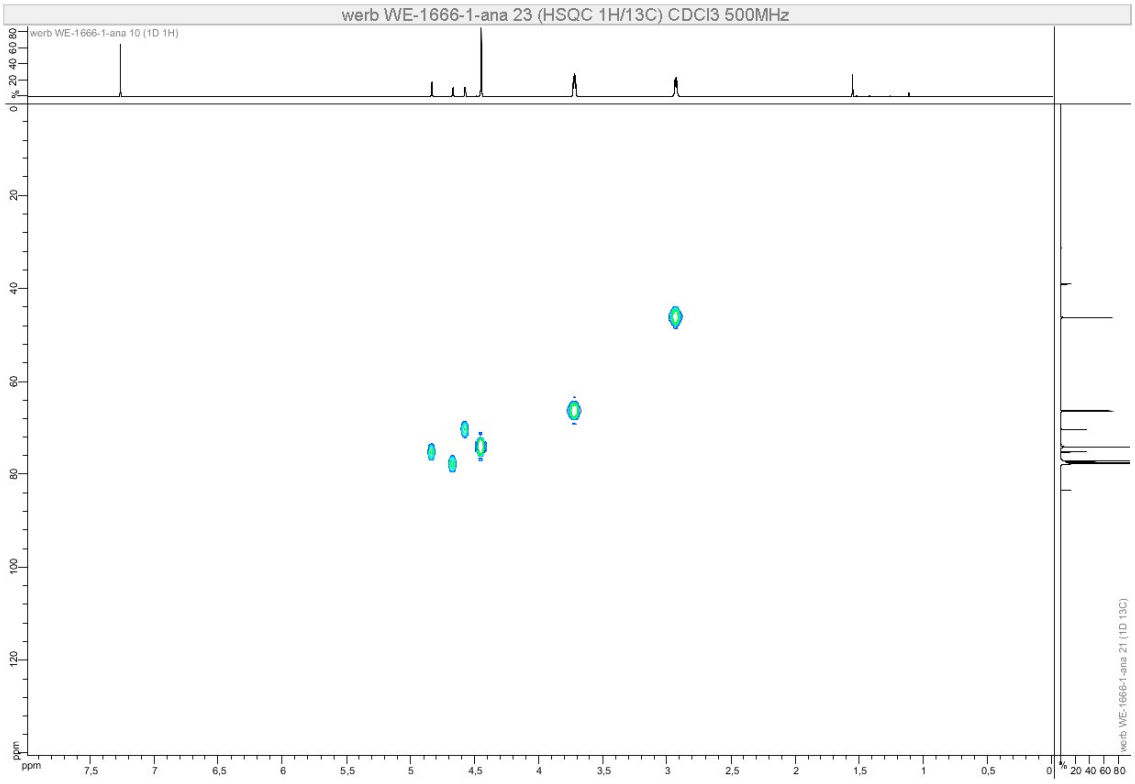

werb WE-1411-1-ana 24 (HMBC 1H/13C) CDCl3 400MHz
werb WE-1411-1-ana 20 (1D 1H)
werb WE-1411-1-ana 21 (1D 13C)
ppm
%

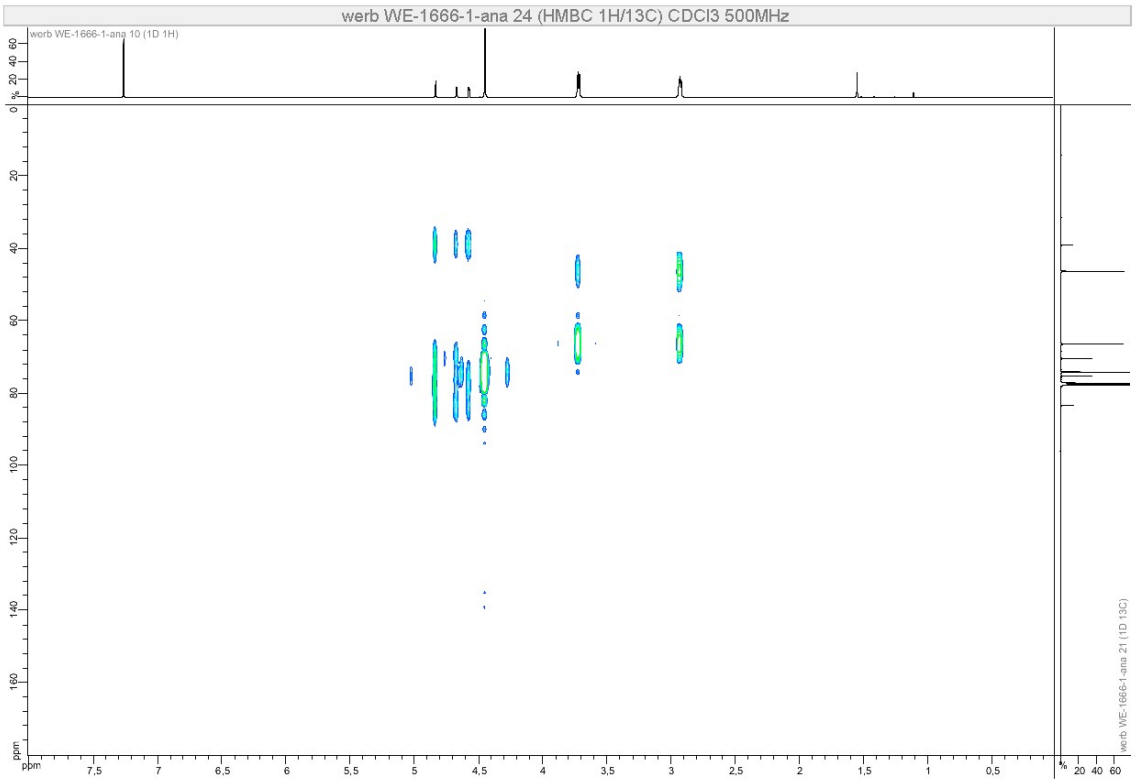
Compound 13h

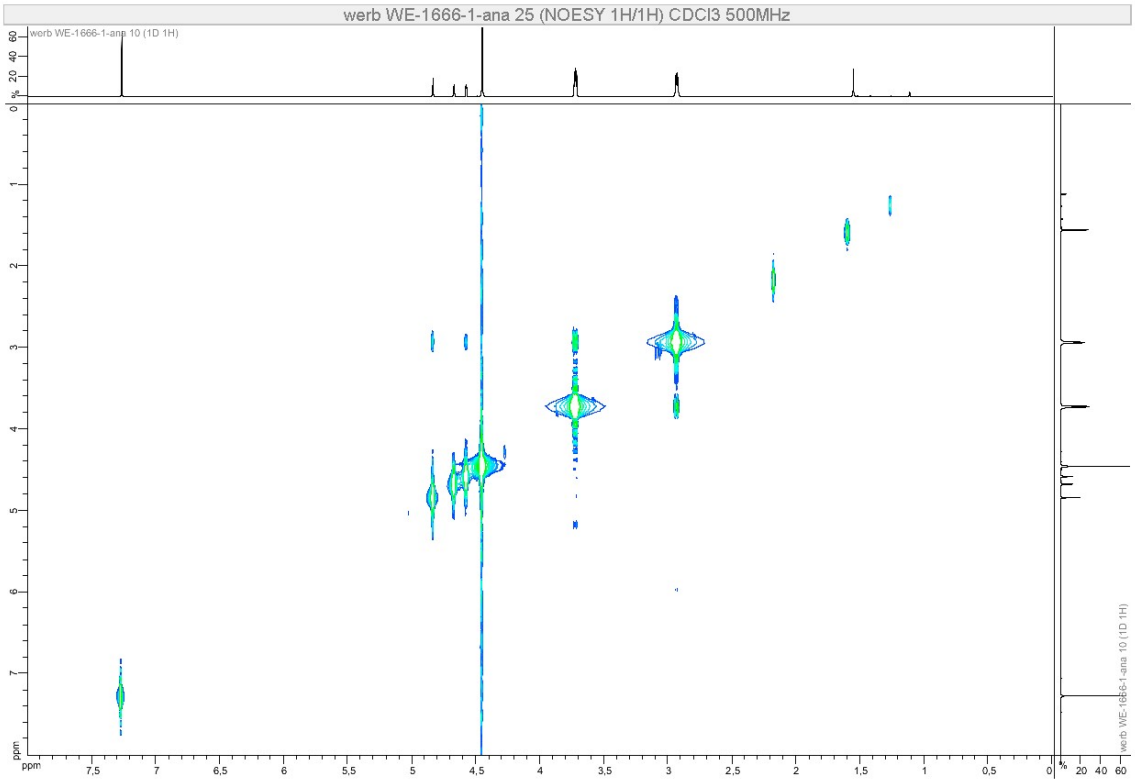




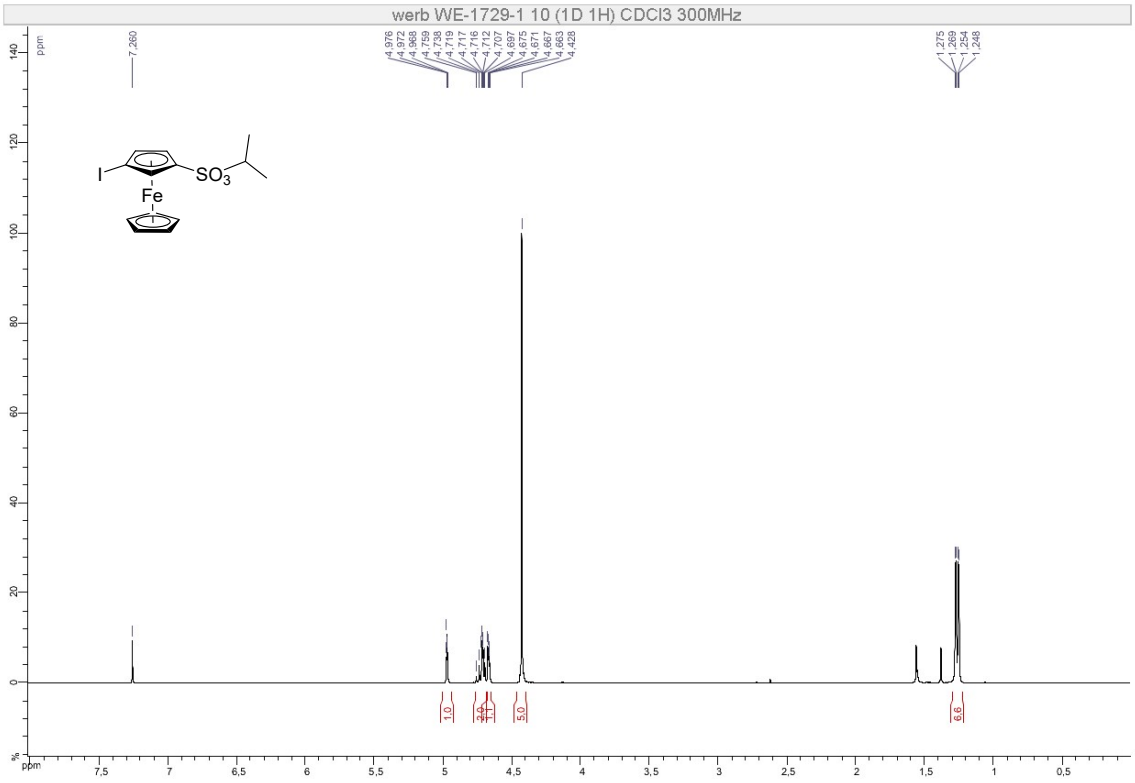

werb WE-1666-1-ana 22 (COSY 1H/1H) CDCl3 500MHz
werb WE-1666-1-ana 10 (1D 1H)
ppm
7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0
% 20 40 60
werb WE-1666-1-ana 10 (1D 1H)


werb WE-1666-1-ana 23 (HSQC 1H/13C) CDCl3 500MHz
werb WE-1666-1-ana 10 (1D 1H)
ppm
7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0
% 20 40 60 80
werb WE-1666-1-ana 21 (1D 13C)


werb WE-1666-1-ana 24 (HMBC 1H/13C) CDCl3 500MHz
werb WE-1666-1-ana 10 (1D 1H)
werb WE-1666-1-ana 21 (1D 13C)
ppm

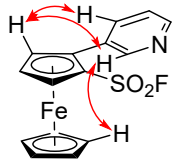

werb WE-1666-1-ana 25 (NOESY 1H/1H) CDCl3 500MHz
werb WE-1666-1-ana 10 (1D 1H)
werb WE-1666-1-ana 10 (1D 1H)
ppm

Compound 13i

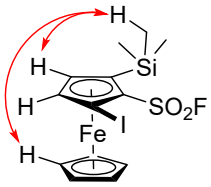


Selected NOESY correlations

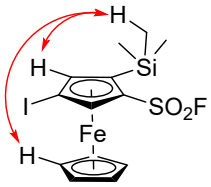
Compound 3d



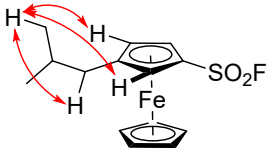
Compound 4



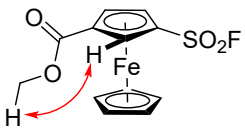
Compound 5a



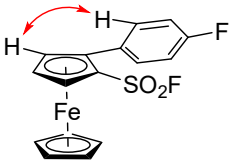
Compound 7a



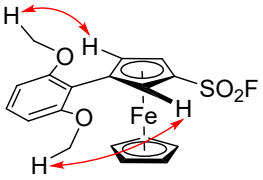
Compound 7b



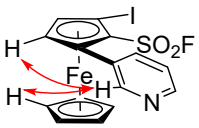
Compound 10a



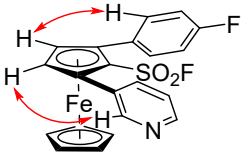
Compound 10c



Compound 11



Compound 12



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