

Supporting Information

The chemistry of ferrocenesulfonyl fluoride revealed

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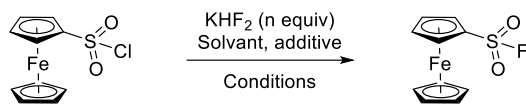
EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all reactions were performed under an argon atmosphere with anhydrous solvents using Schlenk techniques. THF and Et₂O were distilled over sodium/benzophenone under argon. Acetonitrile, dichloromethane and toluene were distilled over CaH₂ under argon. Dimethylsulfoxide was distilled over CaH₂ under vacuum. Unless otherwise stated, all reagents were used without prior purification. 2,2,6,6-Tetramethylpiperidine (TMPH) was distilled under vacuum over CaH₂ 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. ¹H, ¹³C and ¹⁹F 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. ¹H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ¹³C 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 ZnCl₂·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 ₂ O-MeCN (6:4)	2	<i>n</i> Bu ₄ NBr (1 mol%)	25	14 h	32
2 ^a	MeCN-Acetone (1:1)	3	<i>n</i> Bu ₄ NBr (5 mol%)	60	48 h	63
3 ^a	AcOH	3	/	25	14 h	52
4 ^b	AcOH	3	/	60	30 min	63

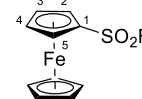
[a] On a 10 mmol scale. [b] On a 100 mmol scale.

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 flask 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. ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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). $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3): δ (ppm) 68.2. Anal. Calcd for $\text{C}_{10}\text{H}_9\text{FFeO}_2\text{S}$: C, 44.80; H, 3.38; S, 11.96. Found: C, 44.91; H, 3.53; S, 12.09.



Crystal data for 2. $\text{C}_{10}\text{H}_9\text{FFeO}_2\text{S}$, $M = 268.08$, $T = 150$ K; monoclinic $P 2_1/n$ (I.T.#14), $a = 7.6335(6)$, $b = 10.0261(10)$, $c = 13.0870(11)$ Å, $\beta = 97.978(4)^\circ$, $V = 991.91(15)$ Å³. $Z = 4$, $d = 1.795$ g.cm⁻³, $\mu = 1.718$ mm⁻¹. A final refinement on F^2 with 2254 unique intensities and 137 parameters converged at $\omega R_F^2 = 0.0631$ ($R_F = 0.0265$) for 1990 observed reflections with $I > 2\sigma(I)$. CCDC 2110433.

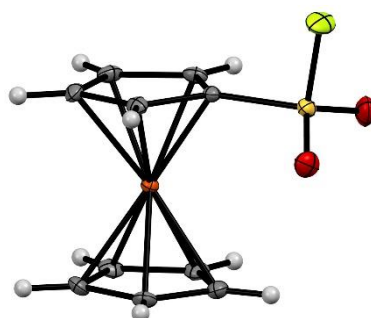
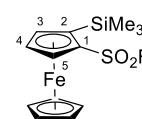


Figure 1. Molecular structure of compound 2 (thermal ellipsoids shown at the 30% probability level).

2-(Trimethylsilyl)ferrocenesulfonyl fluoride – 3a

$n\text{BuLi}$ (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. ^1H 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, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ 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, $\text{Si}(\text{CH}_3)_3$). $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz,



CDCl₃): δ (ppm) 69.8. Anal. Calcd for C₁₃H₁₇FFeO₂SSi: C, 45.89; H, 5.04; S, 9.42. Found: C, 45.96; H, 5.16; S, 9.47.

Crystal data for 3a. C₁₃H₁₇FFeO₂SSi, $M = 340.26$, $T = 150$ K; monoclinic $P 2_1/n$ (I.T.#14), $a = 9.0861(5)$, $b = 13.3795(6)$, $c = 12.8394(7)$ Å, $\beta = 110.418(2)^\circ$, $V = 1462.79(13)$ Å³. $Z = 4$, $d = 1.545$ g.cm⁻³, $\mu = 1.260$ mm⁻¹. A final refinement on F^2 with 3333 unique intensities and 175 parameters converged at $\omega R_F^2 = 0.0815$ ($R_F = 0.0372$) for 2688 observed reflections with $I > 2\sigma(I)$. CCDC 2110434.

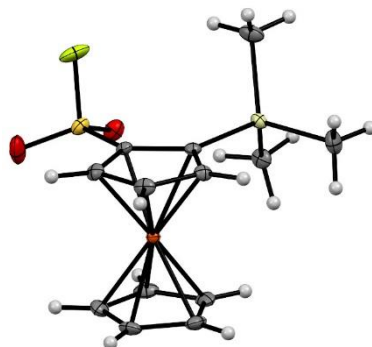
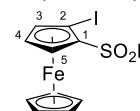


Figure 2. Molecular structure of compound **3a** (thermal ellipsoids shown at the 30% probability level).

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 Na₂S₂O₃ (sat., 10 mL) was added and the reaction mixture was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, 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. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 67.4. Anal. Calcd for C₁₀H₈FFeIO₂S: C, 30.49; H, 2.05; S, 8.14. Found: C, 30.64; H, 2.09; S, 8.18.



Crystal data for 3b. C₁₀H₈FFeIO₂S, $M = 393.97$, $T = 150$ K; monoclinic $P 2_1/c$ (I.T.#14), $a = 15.0316(7)$, $b = 10.8408(6)$, $c = 15.2542(6)$ Å, $\beta = 112.104(2)^\circ$, $V = 2303.04(19)$ Å³. $Z = 8$, $d = 2.273$ g.cm⁻³, $\mu = 4.164$ mm⁻¹. A final refinement on F^2 with 5275 unique intensities and 309 parameters converged at $\omega R_F^2 = 0.1092$ ($R_F = 0.0552$) for 4345 observed reflections with $I > 2\sigma(I)$. CCDC 2110435.

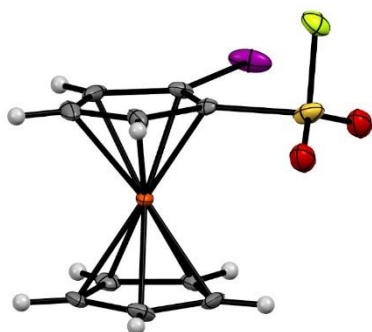
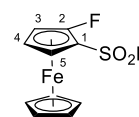


Figure 3. Molecular structure of compound **3b** (thermal ellipsoids shown at the 30% probability level).

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*-Fluorobenzenesulfonyl fluoride (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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, 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. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 69.3 (SO₂F), -186.5 (F). Anal. Calcd for C₁₀H₈F₂FeO₂S: C, 41.98; H, 2.82; S, 11.21. Found: C, 42.02; H, 3.04; S, 11.30.



Crystal data for 3c. C₁₀H₈F₂FeO₂S, 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) Å³. 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.

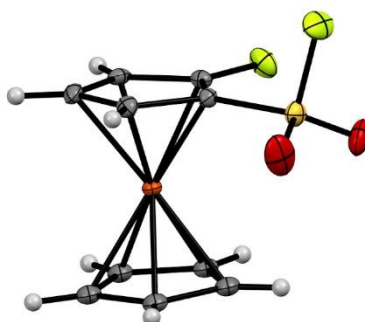
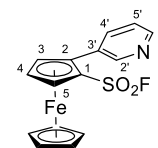


Figure 4. Molecular structure of compound **3c** (thermal ellipsoids shown at the 30% probability level).

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. ZnCl₂·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), PdCl₂ (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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (70:30 to 50:50) with 2% of NEt₃ to give the title product as an orange solid (442 mg, 64%).

R_f (eluent: PE-EtOAc 60:40 with 2% of NEt₃) = 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. ¹H NMR (500 MHz, CDCl₃): 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).



$^{13}\text{C}\{^1\text{H}\}$ 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). $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3): δ (ppm) 70.4. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{FFeNO}_2\text{S}$: 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. $\text{C}_{15}\text{H}_{12}\text{FFeNO}_2\text{S}$, $M = 345.17$, $T = 150$ K; monoclinic Cc (I.T.#9), $a = 10.5249(9)$, $b = 11.3803(6)$, $c = 22.8382(14)$ Å, $\beta = 91.681(3)^\circ$, $V = 2734.3(3)$ Å³. $Z = 8$, $d = 1.677$ g.cm⁻³, $\mu = 1.269$ mm⁻¹. A final refinement on F^2 with 6210 unique intensities and 321 parameters converged at $\omega R_F^2 = 0.1323$ ($R_F = 0.0536$) for 5568 observed reflections with $I > 2\sigma(I)$. CCDC 2110437.

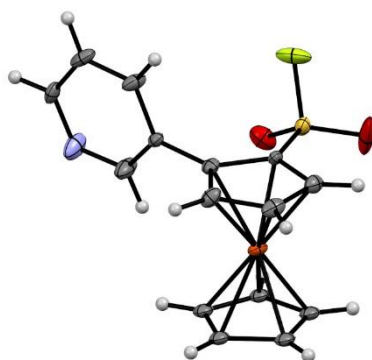
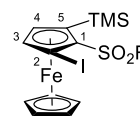


Figure 5. Molecular structure of compound **3d** (thermal ellipsoids shown at the 30% probability level).

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 $\text{Na}_2\text{S}_2\text{O}_3$ (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 $68-72^\circ\text{C}$. 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, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ 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, $\text{Si}(\text{CH}_3)_3$). $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3): δ (ppm) 69.3. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{FFeIO}_2\text{SSi}$: C, 33.50; H, 3.46; S, 6.88. Found: C, 33.55; H, 3.58; S, 6.92.



Crystal data for 4. $\text{C}_{13}\text{H}_{16}\text{FFeIO}_2\text{SSi}$, $M = 466.16$, $T = 150$ K; monoclinic $P2_1/n$ (I.T.#14), $a = 8.4866(5)$, $b = 16.5058(8)$, $c = 12.0171(6)$ Å, $\beta = 99.517(3)^\circ$, $V = 1660.16(15)$ Å³. $Z = 4$, $d = 1.865$ g.cm⁻³, $\mu = 2.973$ mm⁻¹. A final refinement on F^2 with 4356 unique intensities and 184 parameters converged at $\omega R_F^2 = 0.0688$ ($R_F = 0.0313$) for 3691 observed reflections with $I > 2\sigma(I)$. CCDC 2110438.

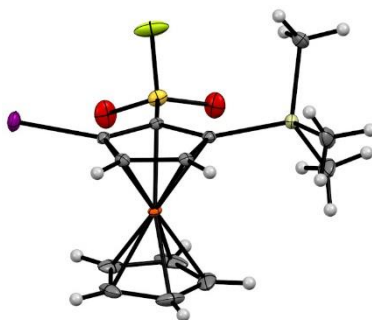
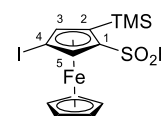


Figure 6. Molecular structure of compound **4** (thermal ellipsoids shown at the 30% probability level).

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 μ L, 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (15:1) to give the title product as an orange solid (1.48 g, 63%).

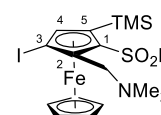
R_f (eluent: PE-EtOAc 15:1) = 0.68. Mp 74-75 °C. ν_{\max} (film)/cm⁻¹ 3111, 2956, 2899, 1399, 1272, 1246, 1214, 1182, 1054, 1006, 979, 879, 841, 829, 760, 738. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 5.26 (s, 1H, FcCH, H5), 4.69 (s, 1H, FcCH, H3), 4.44 (s, 5H, Cp), 0.35 (s, 9H, Si(CH₃)₃). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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(CH₃)₃). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 69.7. Anal. Calcd for C₁₃H₁₆FFeIO₂SSi: 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 μ L, 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 K₂CO₃ solution (sat., 10 mL) was added and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (90:10 to 80:20) to give the title product as an orange oil (899 mg, 68%).

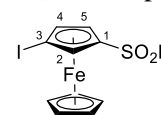
R_f (eluent: PE-EtOAc 80:20) = 0.65. ν_{\max} (film)/cm⁻¹ 2947, 2818, 2769, 1457, 1394, 1247, 1196, 1177, 1122, 1018, 930, 827, 752. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.76 (s, 1H, FcCH, H4), 4.34 (s, 5H, cp), 3.98 (d, *J* = 13.0 Hz, 1H, CHH), 3.32 (d, *J* = 13.0 Hz, 1H, CHH), 2.26 (s, 6H, N(CH₃)₂), 0.34 (s, 9H, Si(CH₃)₃). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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, CH₂), 49.5 (FcC, C3), 45.5 (s, N(CH₃)₂), 0.5 (s, Si(CH₃)₃). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 68.4. Anal. Calcd for C₁₆H₂₃FFeINO₂SSi: 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (90:10) to give the title product as an orange oil (1.34 g, 85%).

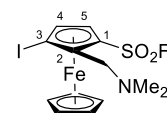
R_f (eluent: PE-EtOAc 70:30) = 0.66. ν_{\max} (film)/cm⁻¹ 3108, 1400, 1368, 1219, 1178, 1108, 1046, 1034, 1003, 904, 875, 828, 745. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 5.11 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 4.86 (dd, *J* = 1.2, 2.6 Hz, 1H, FcCH, H5), 4.82 (dd, *J* = 1.2, 2.6 Hz, 1H, FcCH, H4), 4.47 (s, 5H, Cp). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 68.2. Anal. Calcd for C₁₀H₈FFeIO₂S: 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (80:20 to 70:30) to give the title product as a yellow solid (363 mg, 80%).

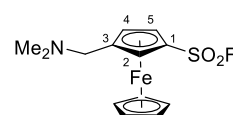
R_f (eluent: PE-EtOAc 80:20) = 0.47. Mp 117-118 °C. ν_{\max} (film)/cm⁻¹ 2975, 2943, 2819, 2767, 1389, 1380, 1256, 1234, 1191, 1153, 1123, 1091, 1047, 1029, 1003, 976, 831, 811, 764, 745. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.96 (d, *J* = 2.7 Hz, 1H, FcCH, H5), 4.85 (d, *J* = 2.7 Hz, 1H, FcCH, H4), 4.36 (s, 5H, Cp), 3.87 (d, *J* = 13.1 Hz, 1H, CHH), 3.32 (d, *J* = 13.1 Hz, 1H, CHH), 2.25 (s, 6H, N(CH₃)₂). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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, CH₂), 47.1 (s, FcC, C3), 45.4 (s, N(CH₃)₂). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 67.2. Anal. Calcd for C₁₃H₁₅FFeINO₂S: 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 K₂CO₃ 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (30:70 to 0:100) with 2% of NEt₃ to give the title product as an orange oil (222 mg, 68%).

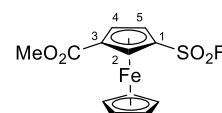
R_f (eluent: PE-EtOAc 30:70 with 2% of NEt₃) = 0.17. ν_{\max} (film)/cm⁻¹ 2943, 2859, 2820, 2772, 1457, 1398, 1357, 1253, 1191, 1170, 1091, 1023, 1004, 829, 740. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.86 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 4.82 (dd, *J* = 1.2, 2.5 Hz, 1H, FcCH, H5), 4.58 (dd, *J* = 1.6, 2.5 Hz, 1H, FcCH, H4), 4.39 (s, 5H, Cp), 3.28 (d, *J* = 13.4 Hz, 1H, CHH), 3.26 (d, *J* = 13.4 Hz, 1H, CHH), 2.20 (s, 6H, N(CH₃)₂). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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, CH₂), 45.0 (s, N(CH₃)₂). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 68.1. Anal. Calcd for C₁₃H₁₆FFeNO₂S: 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (80:20) with 2% of NEt₃ 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. ¹H NMR (500 MHz, CDCl₃): 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, CH₃). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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, CH₃). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 67.7.

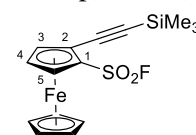


Anal. Calcd for C₁₂H₁₁FFeO₄S: C, 44.20; H, 3.40; S, 9.83. Found: C, 44.34; H, 3.45; S, 9.91.

2-(Trimethylsilylethynyl)ferrocenesulfonyl fluoride – 8a

Compound **3b** (788 mg, 2.00 mmol, 1.00 equiv), Pd(PtBu₃)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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (10:1) with 1% of NEt₃ to give the title product as an orange oil (659 mg, 90%).

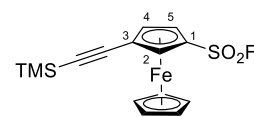
R_f (eluent: PE-EtOAc 90:10) = 0.38. ν_{max} (film)/cm⁻¹ 2960, 2157, 1437, 1406, 1381, 1248, 1206, 1166, 1001, 836, 755, 731. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.88 (dd, *J* = 1.4, 2.8 Hz, 1H, FcCH, H5), 4.79 (dd, *J* = 1.4, 2.6 Hz, 1H, FcCH, H3), 4.54 (t, *J* = 2.8 Hz, 1H, FcCH, H4), 4.46 (s, 5H, Cp), 0.25 (s, 9H, Si(CH₃)₃). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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(CH₃)₃). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 67.5. Anal. Calcd for C₁₅H₁₇FFeO₂SSi: 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(PtBu₃)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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (95:5) with 1% of NEt₃ to give the title product as a red solid (613 mg, 84%).

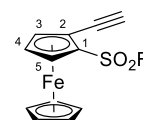
R_f (eluent: PE-EtOAc 95:5) = 0.67. Mp 59-60 °C. ν_{max} (film)/cm⁻¹ 3112, 2967, 2901, 2160, 1402, 1387, 1266, 1249, 1200, 1180, 1092, 1039, 1004, 940, 829, 746, 730. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 5.09 (t, *J* = 1.2 Hz, 1H, FcCH, H2), 4.84 (dd, *J* = 1.2, 2.7 Hz, 1H, FcCH, H5), 4.77 (dd, *J* = 1.2, 2.7 Hz, 1H, FcCH, H4), 4.47 (s, 5H, Cp), 0.23 (s, 9H, Si(CH₃)₃). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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(CH₃)₃). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 68.0. Anal. Calcd for C₁₅H₁₇FFeO₂SSi: 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, 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. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ (ppm) 79.8 (d, *J* = 38.2 Hz, FcC, C1), 79.3 (s,

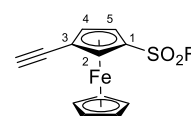


C≡CH), 77.1 (s, C≡CH), 76.8 (s, FcCH, C3), 73.7 (s, Cp), 71.6 and 71.5 (s, FcCH, C4 and C5), 66.2 (s, FcC, C2). $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3): δ (ppm) 67.8. Anal. Calcd for $\text{C}_{12}\text{H}_9\text{FFeO}_2\text{S}$: C, 49.34; H, 3.11; S, 10.98. Found: C, 49.53; H, 3.18; S, 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. ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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≡CH), 75.6 and 70.2 (s, C4 and C5), 73.6 (s, Cp), 72.6 (s, FcCH, C2), 69.4 (s, FcC, C3). $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3): δ (ppm) 67.9. Anal. Calcd for $\text{C}_{12}\text{H}_9\text{FFeO}_2\text{S}$: C, 49.34; H, 3.11; S, 10.98. Found: C, 49.36; H, 3.23; S, 11.06.



Crystal data for 9b. $\text{C}_{12}\text{H}_9\text{FFeO}_2\text{S}$, $M = 292.10$, $T = 150$ K; triclinic $P\bar{1}$ (I.T.#2), $a = 6.9415(12)$, $b = 9.1569(18)$, $c = 9.4381(18)$ Å, $\alpha = 81.337(6)$, $\beta = 74.314(6)$, $\gamma = 84.801(6)$ °, $V = 570.19(19)$ Å³. $Z = 2$, $d = 1.701$ g.cm⁻³, $\mu = 1.502$ mm⁻¹. A final refinement on F^2 with 2602 unique intensities and 154 parameters converged at $\omega R_F^2 = 0.0682$ ($R_F = 0.0264$) for 2386 observed reflections with $I > 2\sigma(I)$. CCDC 2110439.

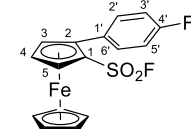


Figure 7. Molecular structure of compound **9b** (thermal ellipsoids shown at the 30% probability level).

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), $\text{Pd}(\text{dba})_2$ (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. ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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). $^{19}\text{F}\{^1\text{H}\}$ NMR (470 MHz, CDCl_3): δ (ppm) 70.0 (SO_2F), -113.8 (F). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{F}_2\text{FeO}_2\text{S}$: C, 53.06; H, 3.34; S, 8.85. Found: C, 53.04; H, 3.17; S, 8.76.



Crystal data for 10a. C₁₆H₁₂F₂FeO₂S, *M* = 362.17, *T* = 150 K; monoclinic *P* 2₁/*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) Å³. *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 ω*R*_{*F*}² = 0.1594 (*R*_{*F*} = 0.0634) for 2725 observed reflections with *I* > 2σ(*I*). CCDC 2110440.

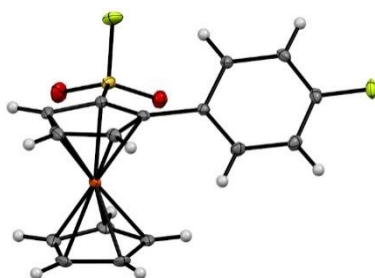
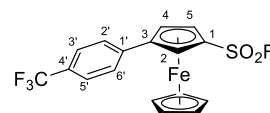


Figure 8. Molecular structure of compound **10a** (thermal ellipsoids shown at the 30% probability level).

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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, 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. *v*_{max} (film)/cm⁻¹ 1618, 1402, 1322, 1207, 1164, 1121, 1107, 1067, 1020, 830, 748. ¹H NMR (500 MHz, CDCl₃): 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). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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, CF₃), 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). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 68.2 (SO₂F), -62.6 (CF₃). Anal. Calcd for C₁₇H₁₂F₄FeO₂S: C, 49.54; H, 2.93; S, 7.78. Found: C, 49.69; H, 3.09; S, 7.73.

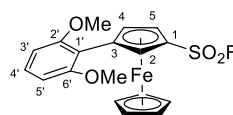


3-(2,5-Dimethoxyphenyl)ferrocenesulfonyl fluoride – 10c

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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, 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. *v*_{max} (film)/cm⁻¹ 2939, 2839, 1586, 1473, 1434, 1396, 1285, 1246, 1202, 1178, 1134, 1102, 1034, 895, 824, 781, 728.

¹H NMR (500 MHz, CDCl₃): 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, OCH₃). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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

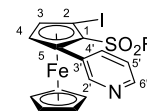


(s, FcCH, C5), 55.8 (s, OCH₃). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 68.5. Anal. Calcd for C₁₈H₁₇FFeO₄S: C, 53.48; H, 4.24; S, 7.93. Found: C, 53.65; H, 4.16; S, 7.86.

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 ZnCl₂·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), PdCl₂ (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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (60:40 to 50:50) with 2% of NEt₃ to give the title product as an orange solid (194 mg, 41%).

R_f (eluent: PE-EtOAc 60:40 with 2% of NEt₃) = 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, CDCl₃): 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). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 71.2. Anal. Calcd for C₁₅H₁₁FFeINO₂S: 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. C₁₅H₁₁FFeINO₂S, *M* = 471.06, *T* = 150 K; monoclinic *P* 2₁/*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) Å³. *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 ω*R*_{*F*}² = 0.0752 (*R*_{*F*} = 0.0337) for 3246 observed reflections with *I* > 2σ(*I*). CCDC 2110441.

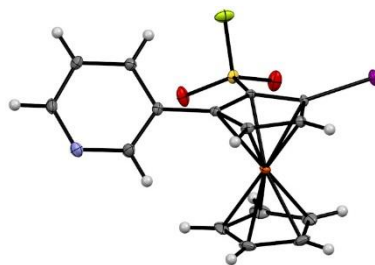


Figure 9. Molecular structure of compound **11** (thermal ellipsoids shown at the 30% probability level).

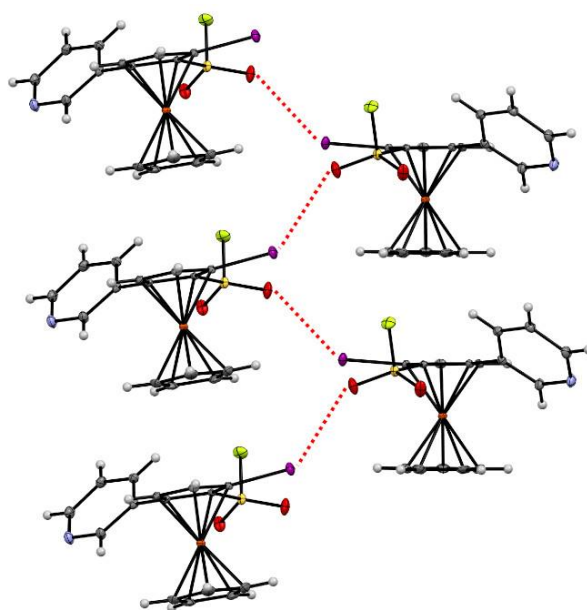
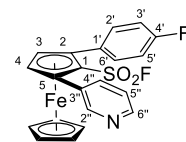


Figure 10. Intermolecular halogen bonds observed at the solid state for compound **11** (thermal ellipsoids shown at the 30% probability level).

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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, 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 NEt₃) = 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, CDCl₃): 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). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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). ¹⁹F{¹H} NMR (470 MHz, CDCl₃): δ (ppm) 72.9 (SO₂F), -113.4 (F). Anal. Calcd for C₂₁H₁₅F₂FeNO₂S: 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. C₂₁H₁₅F₂FeNO₂S, *M* = 439.25, *T* = 150 K; tetragonal *I*4₁/*a* (I.T.#88), *a* = 13.8079(7), *c* = 36.167(2) Å, *V* = 6895.5(8) Å³. *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* > 2σ(*I*). CCDC 2110442.

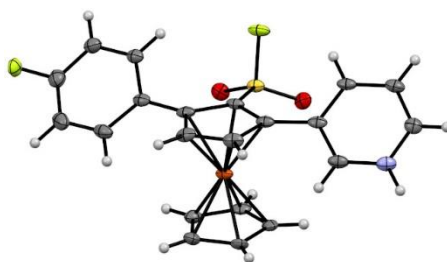
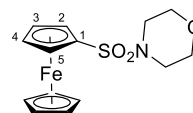


Figure 11. Molecular structure of compound **12** (thermal ellipsoids shown at the 30% probability level).

(N-Morpholino)sulfonylferrocene – 13a

A solution of HOBt (203 mg, 1.50 mmol, 1.50 equiv) and Et₃SiH (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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, 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

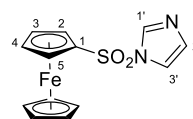
¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.57 (t, *J* = 1.9 Hz, 2H, FcH, H2 and H5), 4.42 (s, 5H, Cp), 4.42 (t, *J* = 1.9 Hz, 2H, FcH, H3 and H4), 3.71 (t, *J* = 4.7 Hz, 4H, CH₂O), 2.91 (t, *J* = 4.7 Hz, 4H, CH₂N).



(N-Imidazolino)sulfonylferrocene – 13b

Compound **2** (268 mg, 1.00 mmol, 1.00 equiv), imidazole (136 mg, 2.00 mmol, 2.00 equiv) and caesium 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (70:30 to 60:40) with 1% of NEt₃ to give the title product as an orange solid (288 mg, 91%). Analytical data analogous to those reported previously.⁶

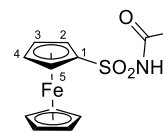
R_f (eluent: PE-EtOAc 70:30) = 0.16. Mp 197-198 °C. ν_{max} (film)/cm⁻¹ 3094, 1460, 1377, 1206, 1156, 1144, 1091, 1052, 1020, 864, 829, 763. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.90 (s, 1H, ArCH, H1'), 7.21 (s, 1H, ArCH, H3'), 7.03 (s, 1H, ArCH, H2'), 4.74 (t, *J* = 1.9 Hz, 2H, FcCH, H2 and H5), 4.51 (t, *J* = 1.9 Hz, 2H, FcH, H3 and H4), 4.49 (s, 5H, Cp). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (60:40 to 50:50) to give the title product as a yellow solid (193 mg, 63%).

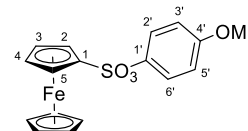
R_f (eluent: PE-EtOAc 70:30) = 0.24. Mp 145-146 °C. ν_{\max} (film)/ cm^{-1} 3334, 3221, 3114, 1698, 1446, 1403, 1343, 1218, 1194, 1131, 1041, 1024, 992, 829, 814. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.18 (br s, 1H, NH), 4.84 (t, $J = 1.8$ Hz, 2H, FcH, H2 and H5), 4.47 (t, $J = 1.8$ Hz, 2H, FcH, H3 and H4), 4.42 (s, 5H, Cp), 2.07 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{12}\text{H}_{13}\text{FeNO}_3\text{S}$: 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 caesium 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. ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{17}\text{H}_{16}\text{FeO}_4\text{S}$: C, 54.86; H, 4.33; S, 8.61. Found: C, 54.88; H, 4.40; S, 8.69.



Crystal data for 13d. $\text{C}_{17}\text{H}_{16}\text{FeO}_4\text{S}$, $M = 372.21$, $T = 150$ K; monoclinic $P2_1/c$ (I.T.#14), $a = 16.7313(11)$, $b = 7.4199(5)$, $c = 12.4538(8)$ Å, $\beta = 96.042(3)$ °, $V = 1537.48(18)$ Å³. $Z = 4$, $d = 1.608$ g. cm^{-3} , $\mu = 1.134$ mm⁻¹. A final refinement on F^2 with 3490 unique intensities and 209 parameters converged at $\omega R_F^2 = 0.0824$ ($R_F = 0.0303$) for 3115 observed reflections with $I > 2\sigma(I)$. CCDC 2110443.

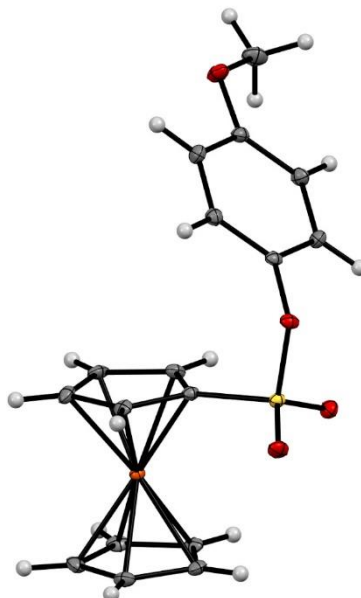
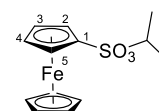


Figure 12. Molecular structure of compound **13d** (thermal ellipsoids shown at the 30% probability level).

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

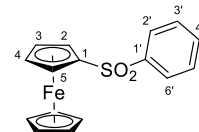
^1H NMR (400 MHz, CDCl_3): δ (ppm) 4.71 (t, $J = 1.8$ Hz, 2H, FcH, H2 and H5), 4.70 (sept, $J = 6.3$ Hz, 1H, CH), 4.42 (t, $J = 1.8$ Hz, 2H, FcH, H3 and H4), 4.41 (s, 5H, Cp), 1.24 (d, $J = 6.3$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$).



Phenylsulfonylferrocene – 13f

A solution of phenyllithium in Et_2O (prepared by adding dropwise $n\text{BuLi}$ (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 $^\circ\text{C}$ 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 $^\circ\text{C}$. The reaction mixture was stirred at 0 $^\circ\text{C}$ 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

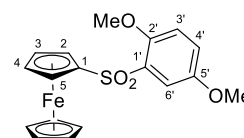
^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.84 (d, $J = 7.6$ Hz, 2H, ArCH, H2' and H6'), 7.50 (t, $J = 7.1$ Hz, 1H, ArCH, H4'), 7.43 (t, $J = 7.5$ Hz, 2H, ArCH, H3' and H4'), 4.68 (s, 2H, FcCH, H2 and H5), 4.49 (s, 5H, Cp), 4.40 (s, 2H, FcCH, H3 and H4). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): 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 $^\circ\text{C}$. 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. ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{18}\text{H}_{18}\text{FeO}_4\text{S}$: C, 55.97; H, 4.70; S, 8.30. Found: C, 55.03; H, 4.61; S, 8.37.

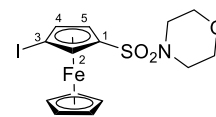


3-Iodo-(N-morpholino)sulfonylferrocene – 13h

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 $^\circ\text{C}$ 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, using PE-EtOAc (80:20) to give the title product as an orange solid (177 mg, 76%).

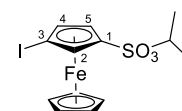
R_f (eluent: PE-EtOAc 70:30) = 0.45. Mp. 129-130 °C. ν_{\max} (film)/cm⁻¹ 3082, 2974, 2848, 1453, 1344, 1328, 1295, 1260, 1149, 1109, 1071, 938, 874, 829, 724. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.83 (t, J = 1.3 Hz, 1H, FcCH, H2), 4.67 (dd, J = 1.3, 2.5 Hz, 1H, FcCH, H4), 4.57 (dd, J = 1.3, 2.5 Hz, 1H, FcCH, H5), 4.44 (s, 5H, Cp), 3.72 (m, 4H, CH₂O), 2.93 (m, 4H, CH₂N). ¹³C{¹H} NMR (126 MHz, CDCl₃): 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, CH₂O), 46.0 (s, CH₂N), 38.8 (s, FcC, C3). Anal. Calcd for C₁₄H₁₆FeINO₃S: C, 36.47; H, 3.50; S, 6.95. Found: C, 36.51; H, 3.70; S, 7.03.



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

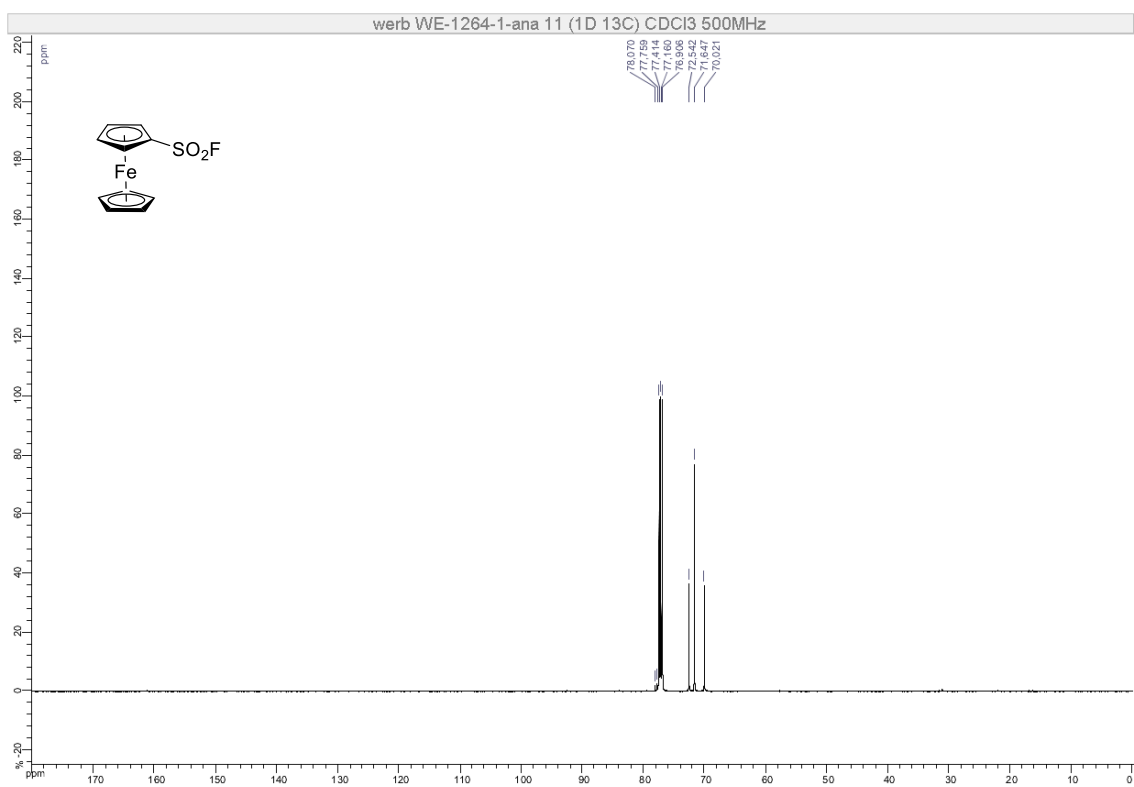
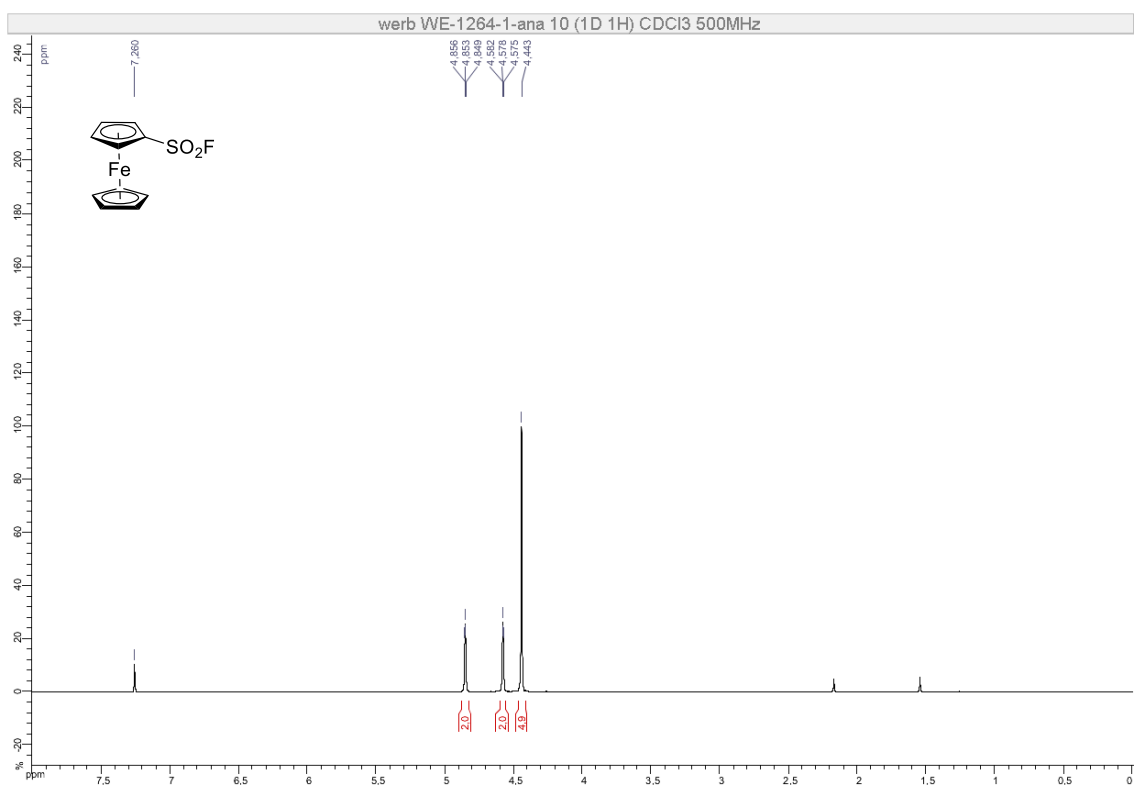
Isopropanol (230 μ L, 180 mg, 3.00 mmol, 6.00 equiv) was added dropwise to a suspension of sodium hydride (60% dispersion in oil, 65.2 mg, 1.50 mmol, 3.00 equiv) in THF (2 mL) and the reaction mixture was stirred at rt for 15 min. Compound **6a** (197 mg, 0.50 mmol, 1.00 equiv) was added in one portion 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 MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. This was purified by column chromatography over SiO₂, 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

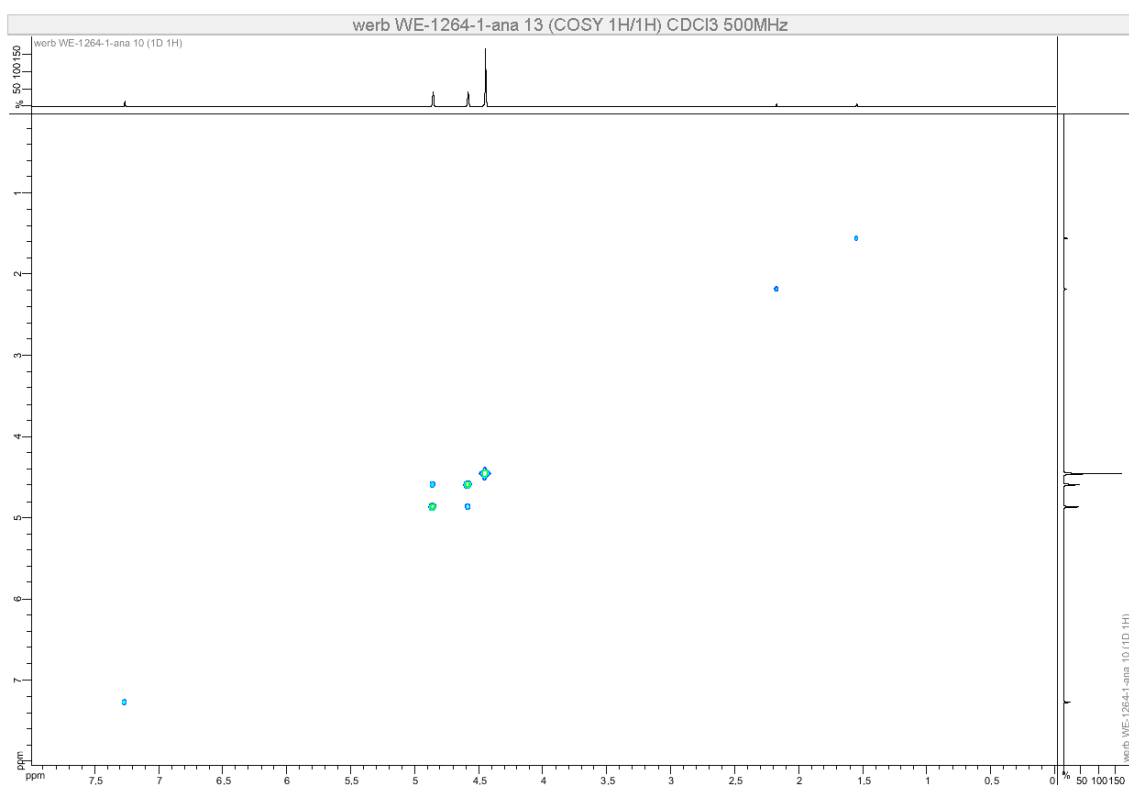
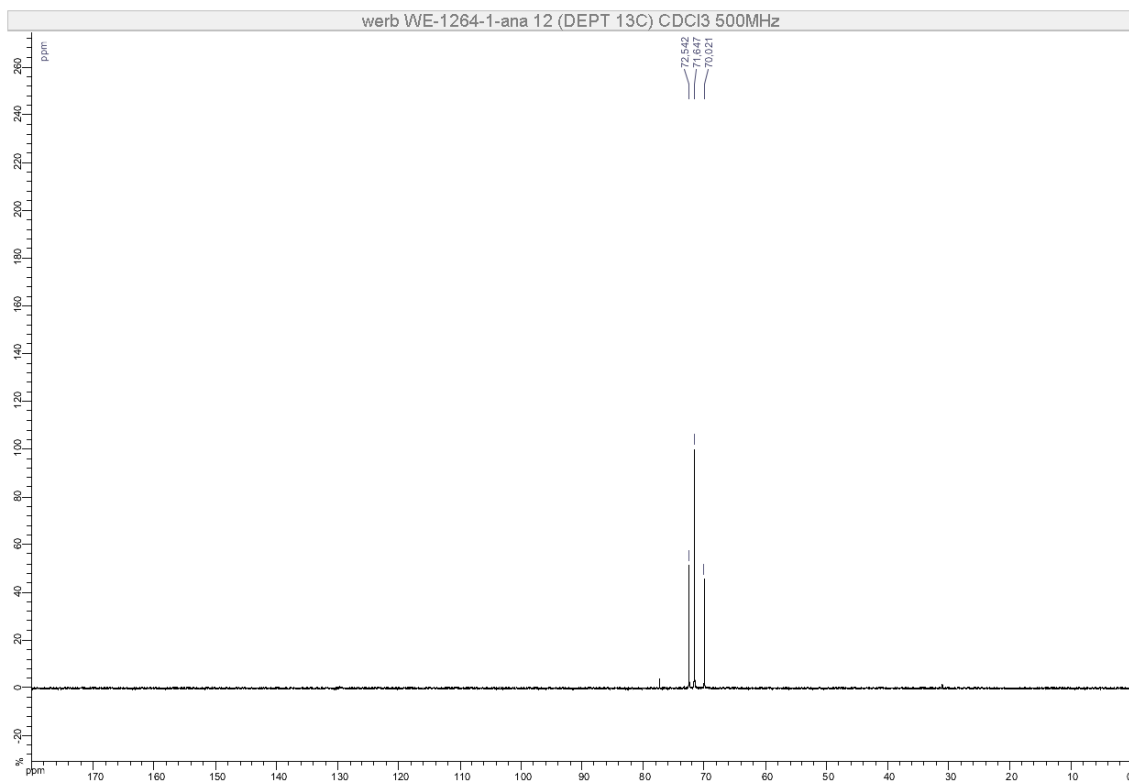
R_f (eluent: PE-EtOAc 90:10) = 0.55. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 4.97 (t, J = 1.3 Hz, 1H, FcCH, H2), 4.73 (q, J = 6.2 Hz, 1H, CH), 4.71 (dd, J = 1.3, 2.6 Hz, 1H, FcCH, H5), 4.67 (dd, J = 1.3, 2.6 Hz, 1H, FcCH, H4), 4.43 (s, 5H, Cp), 1.27 (d, J = 6.2 Hz, 3H, CH₃), 1.26 (d, J = 6.2 Hz, 3H, CH₃).

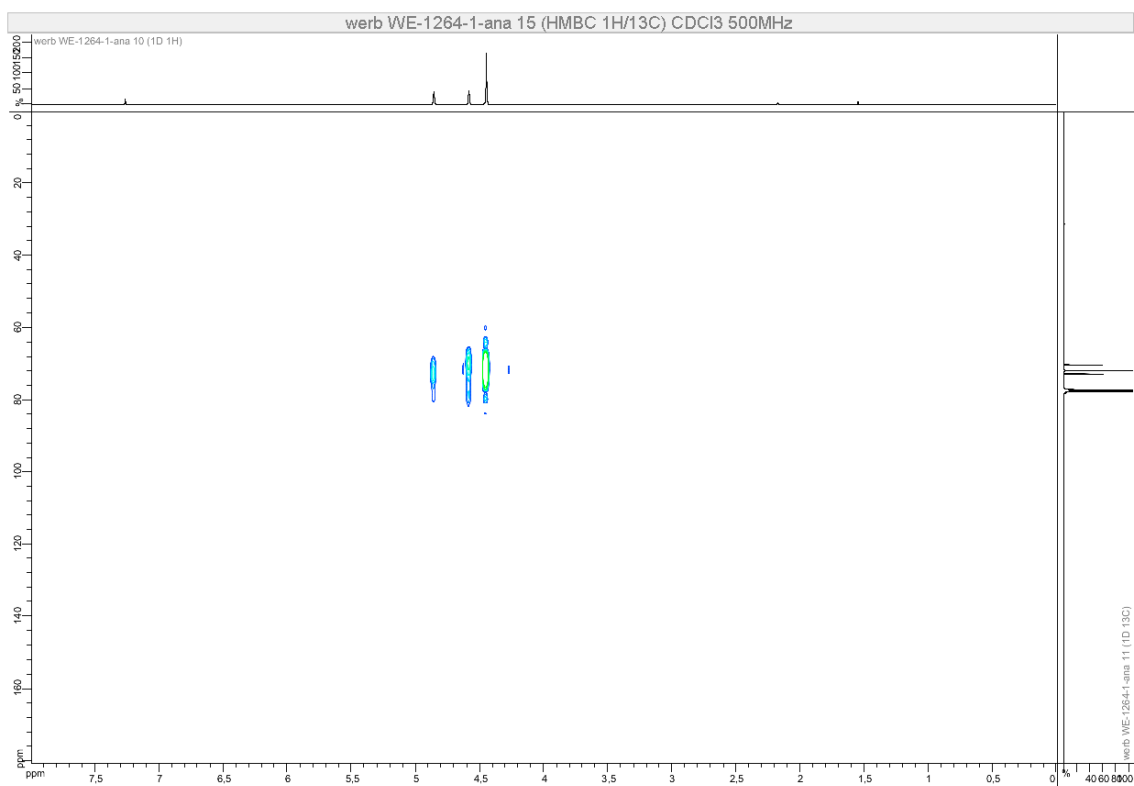
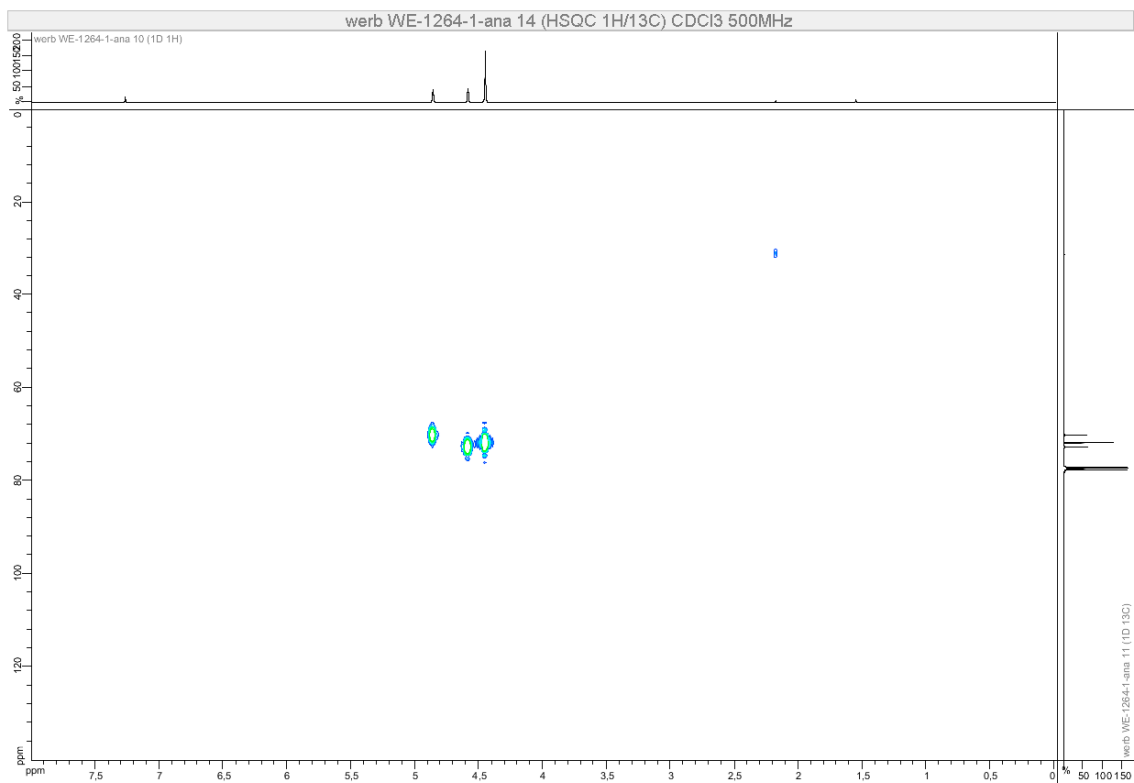


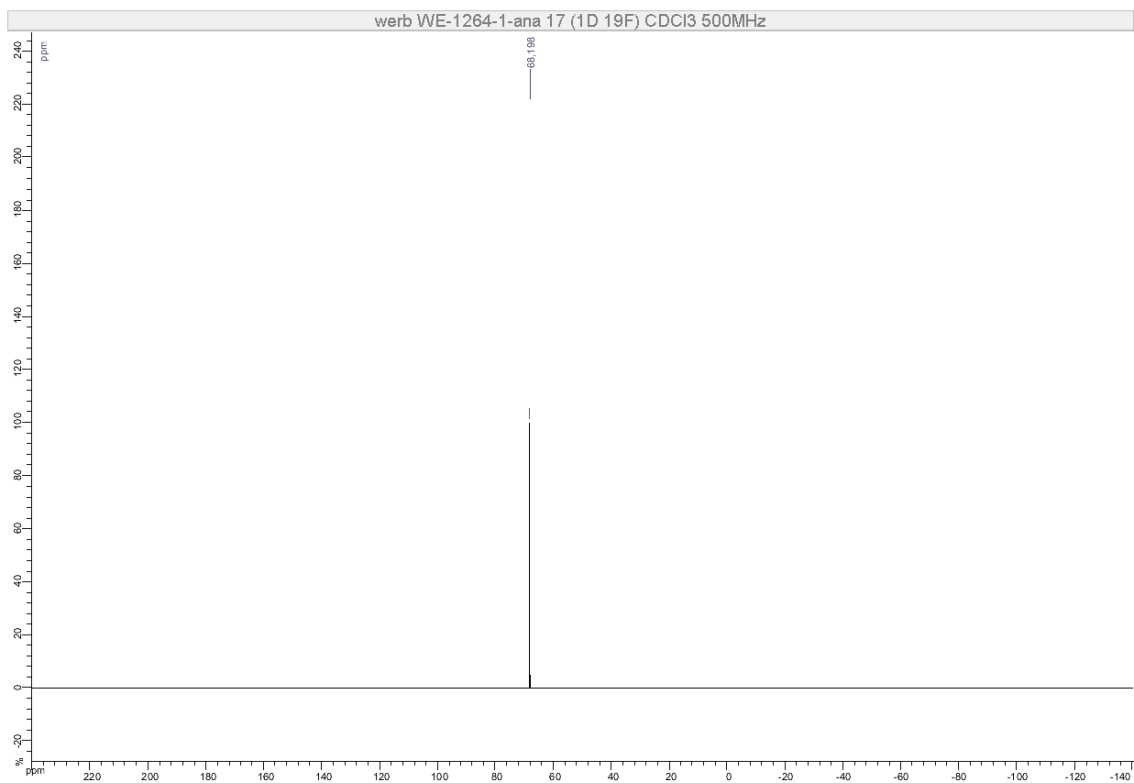
NMR Spectra

Compound 2

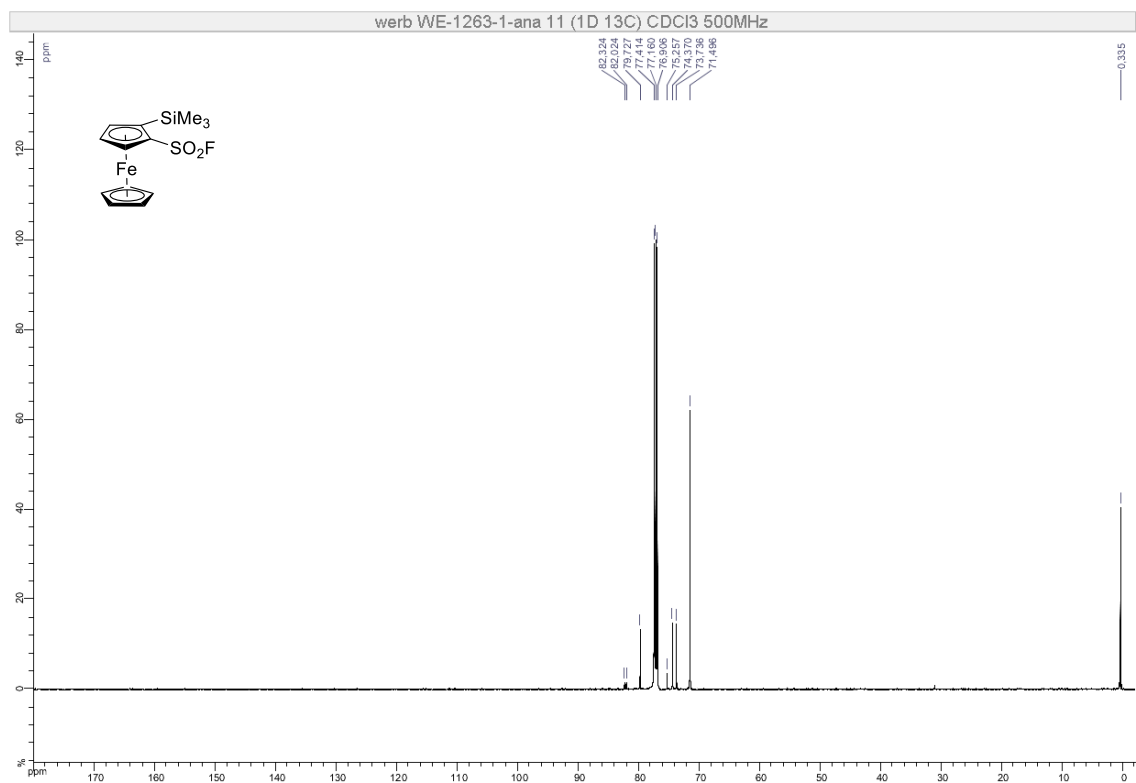
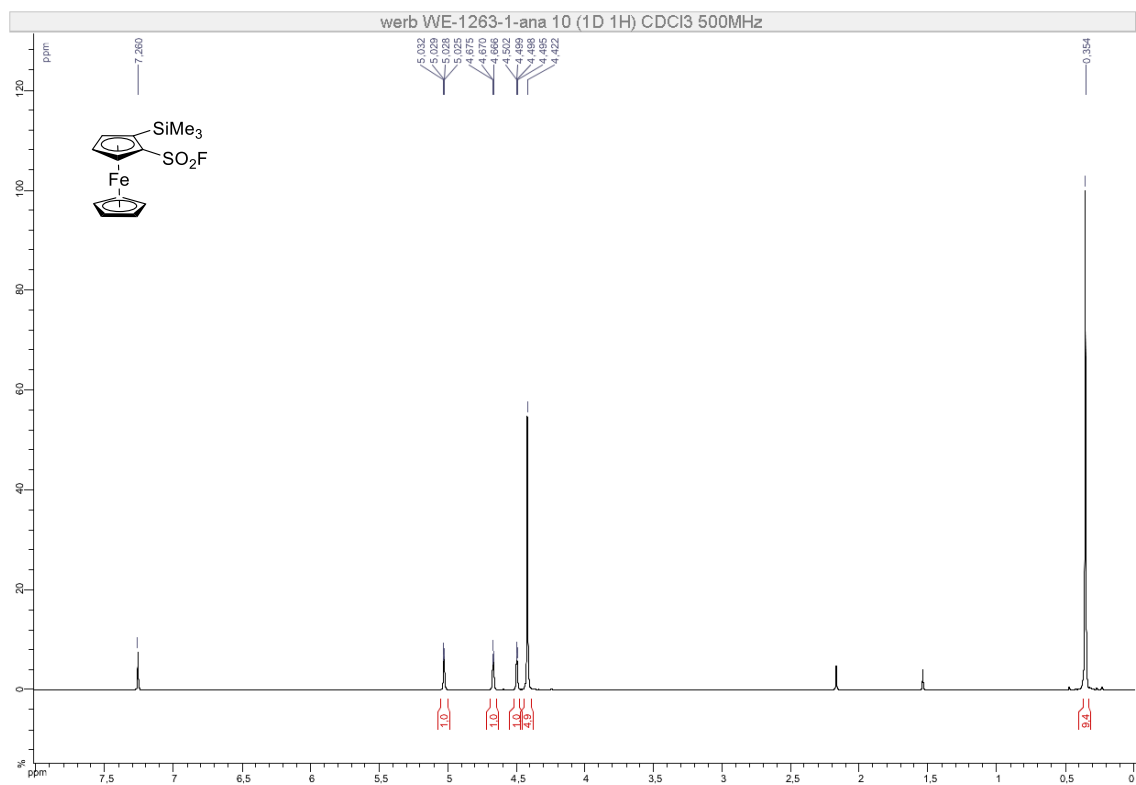


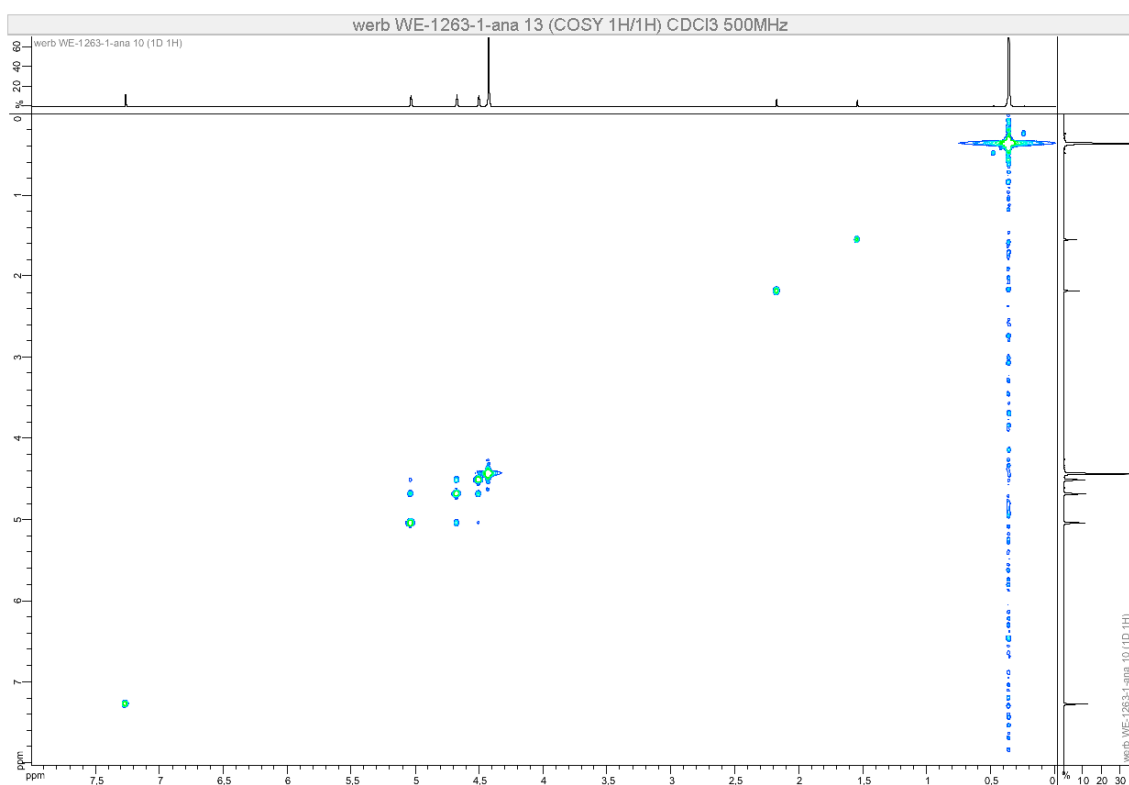
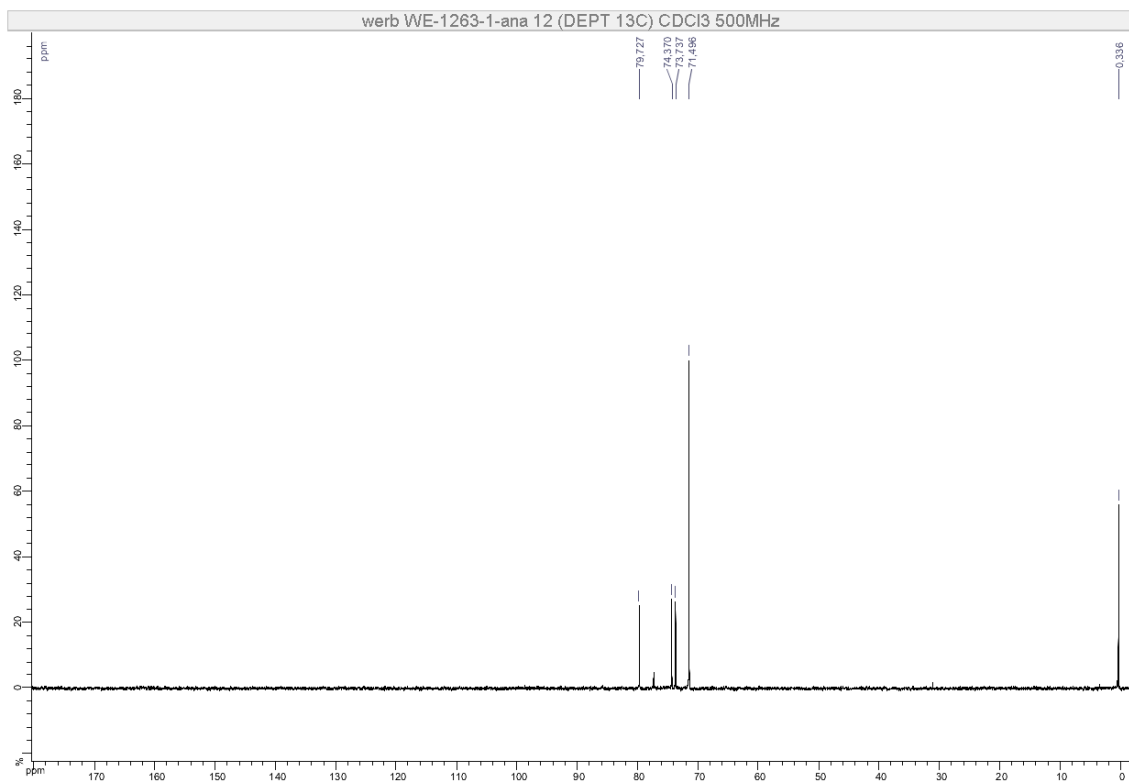


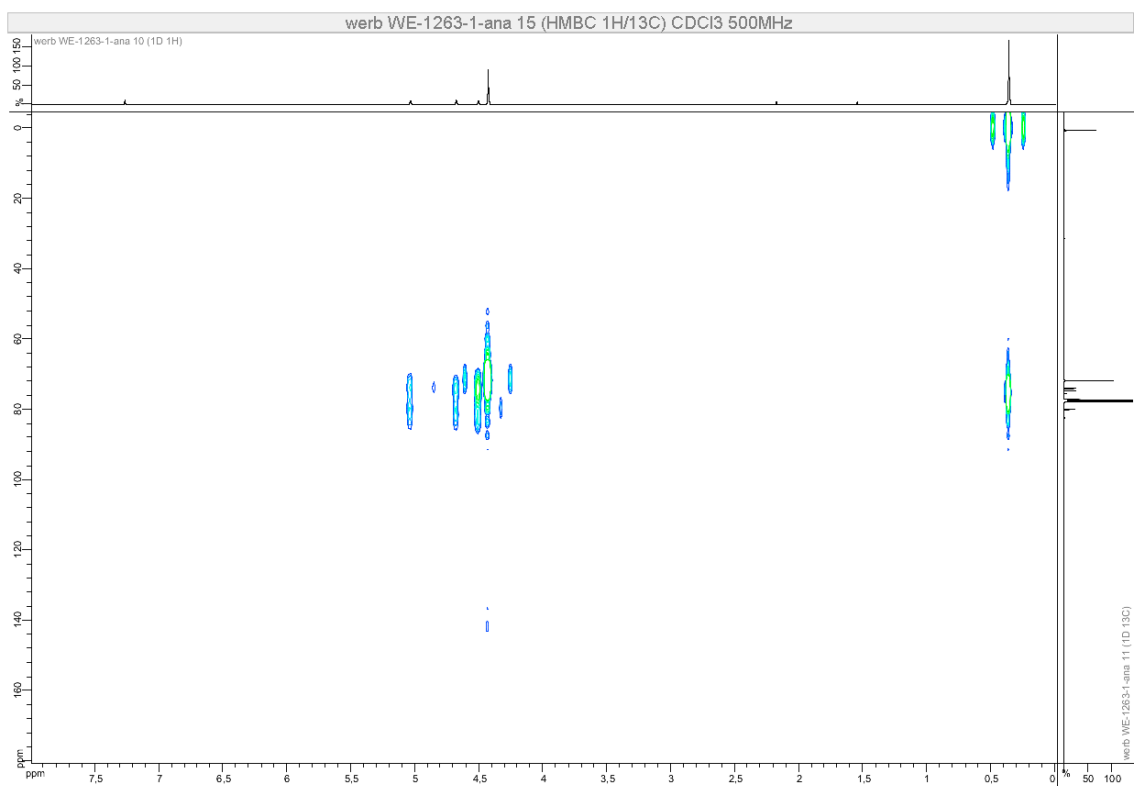
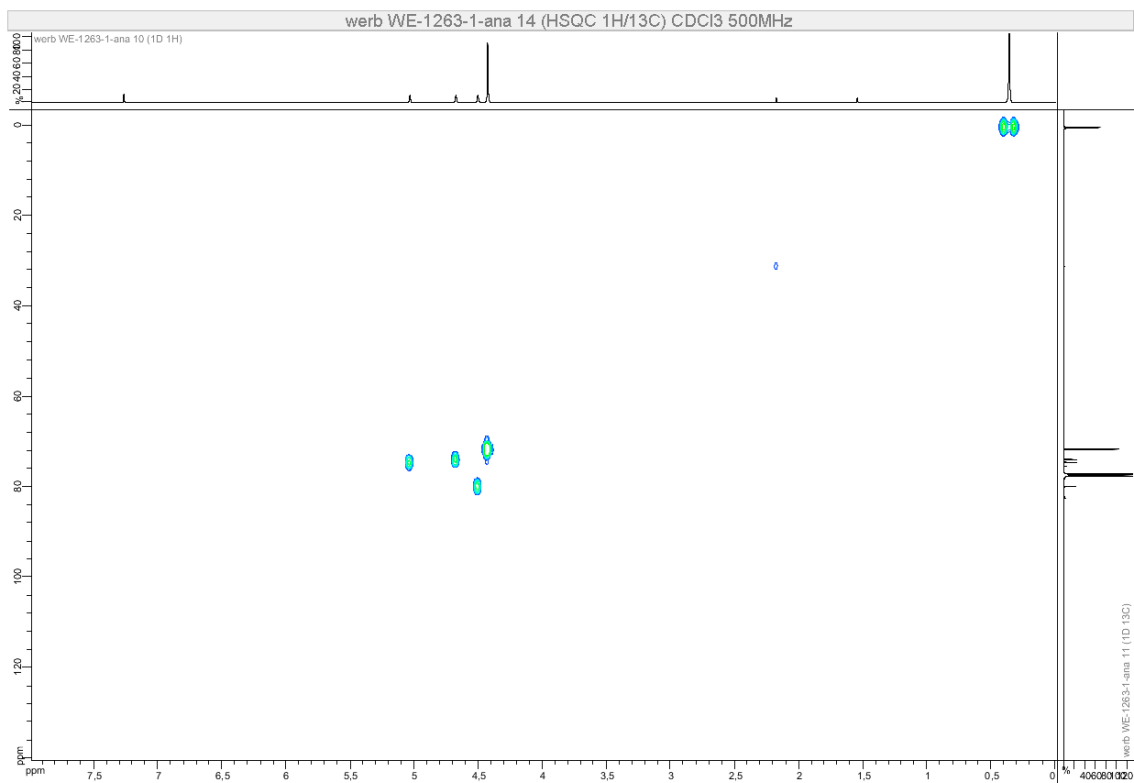


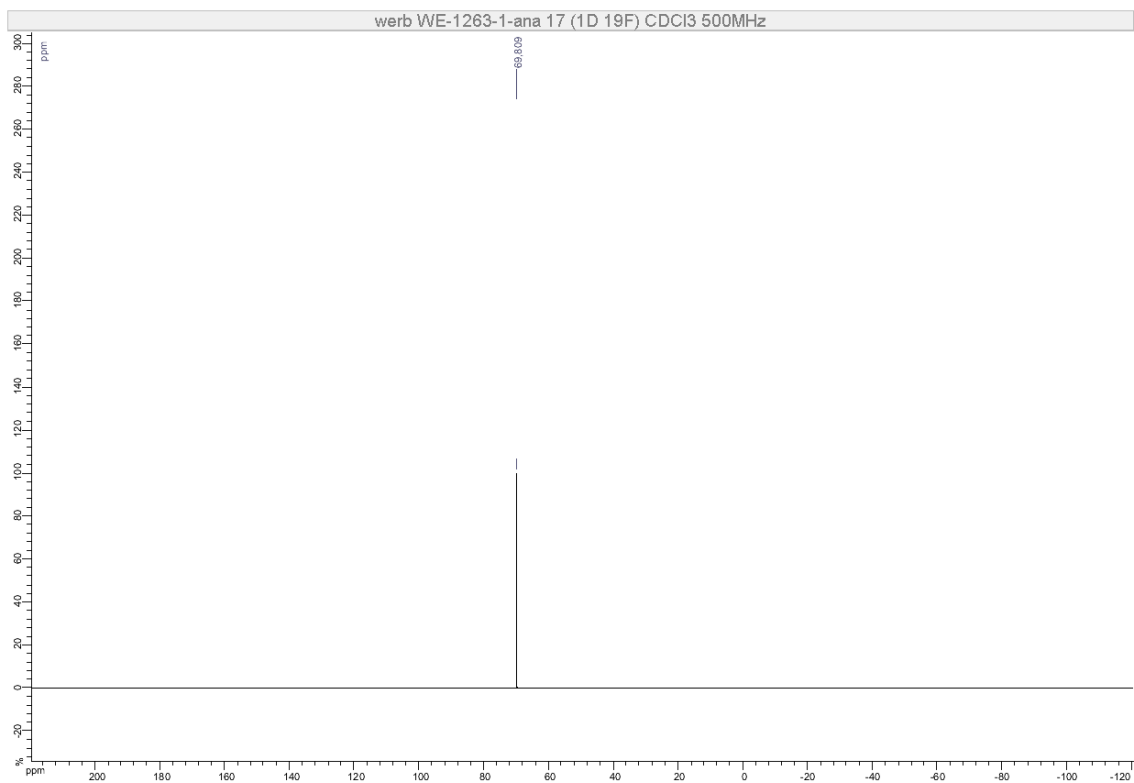


Compound 3a

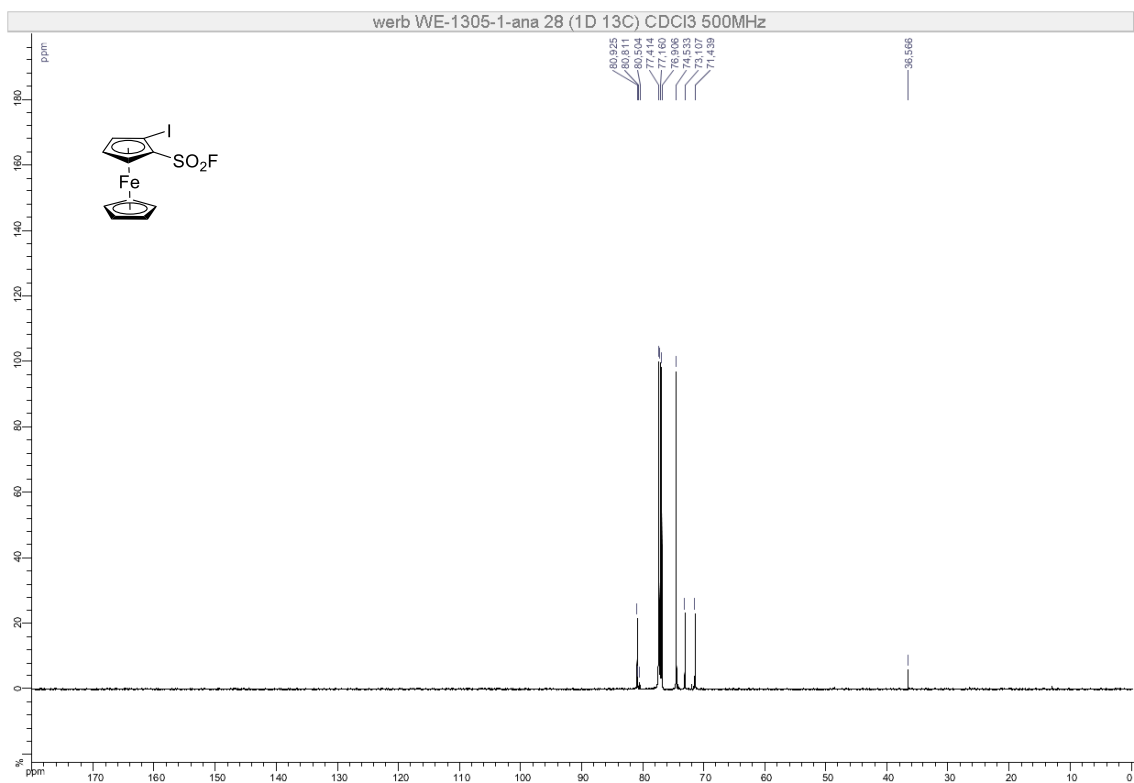
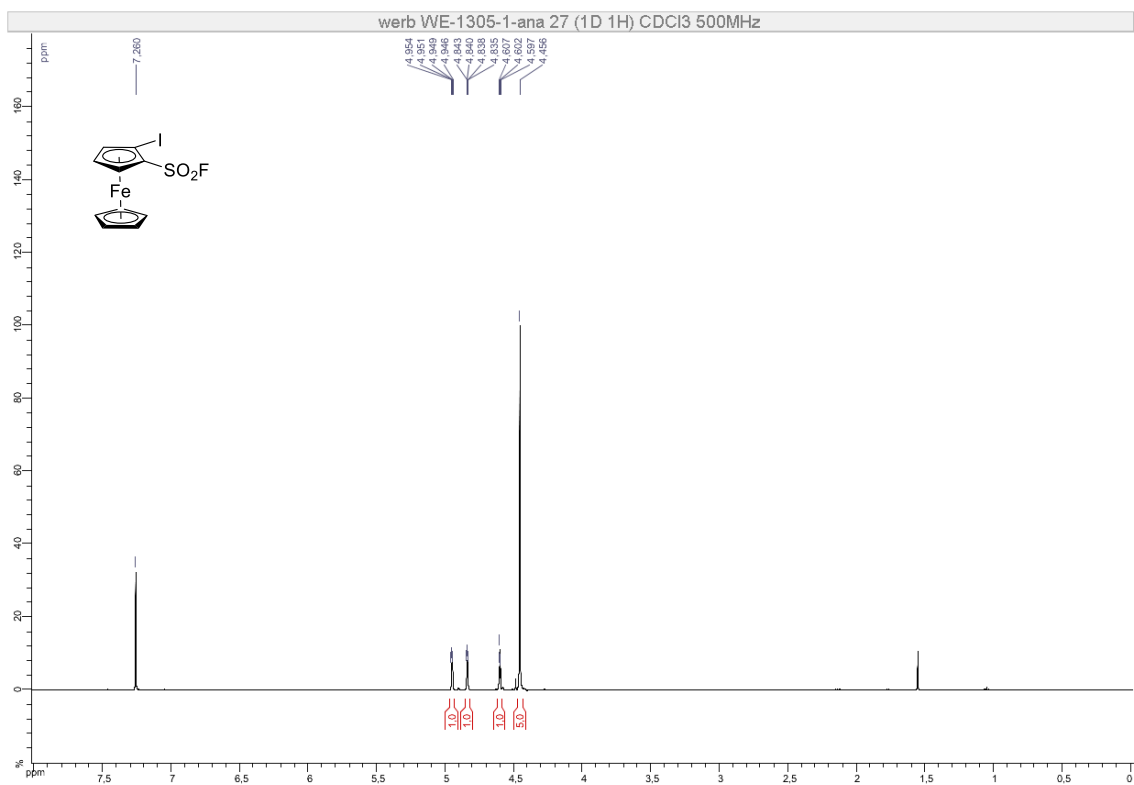


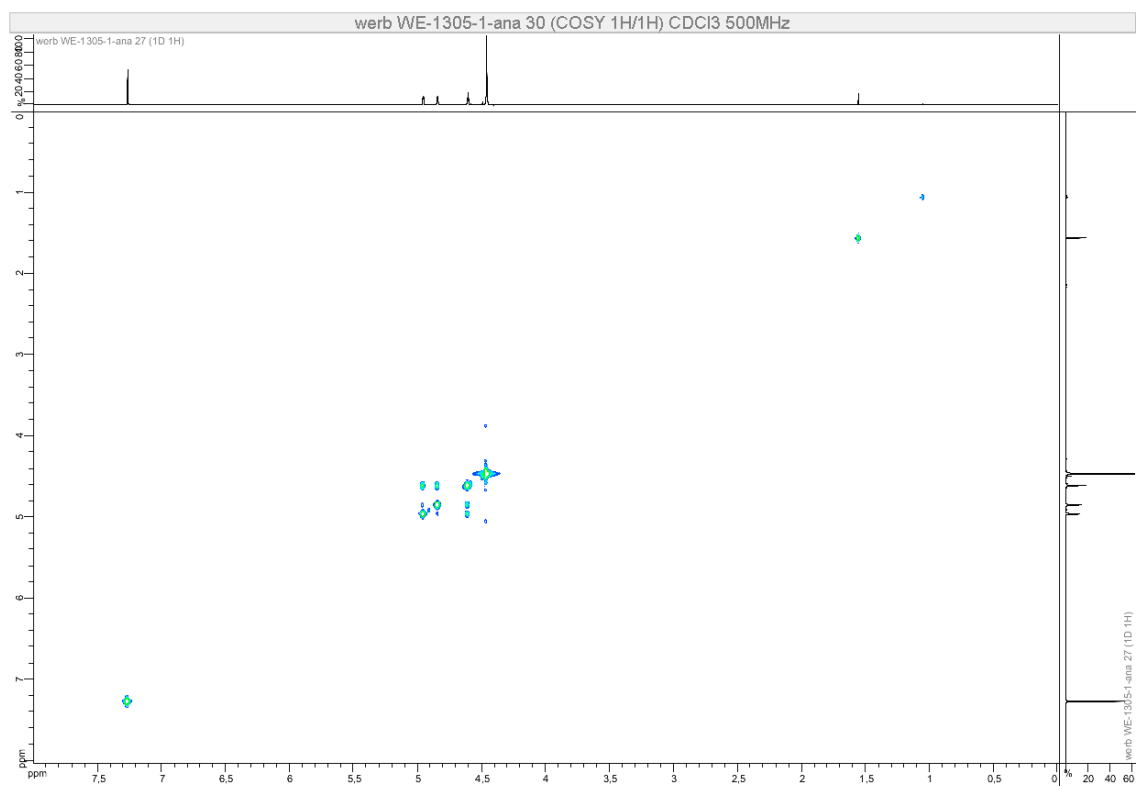
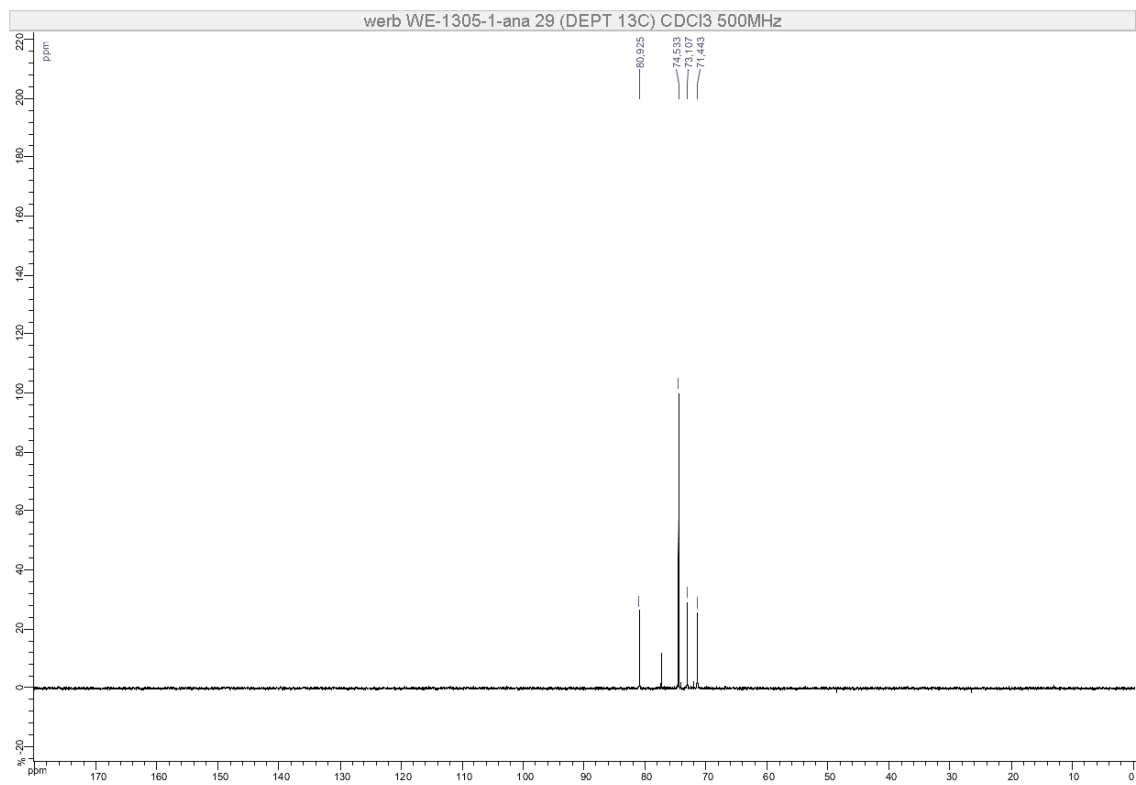


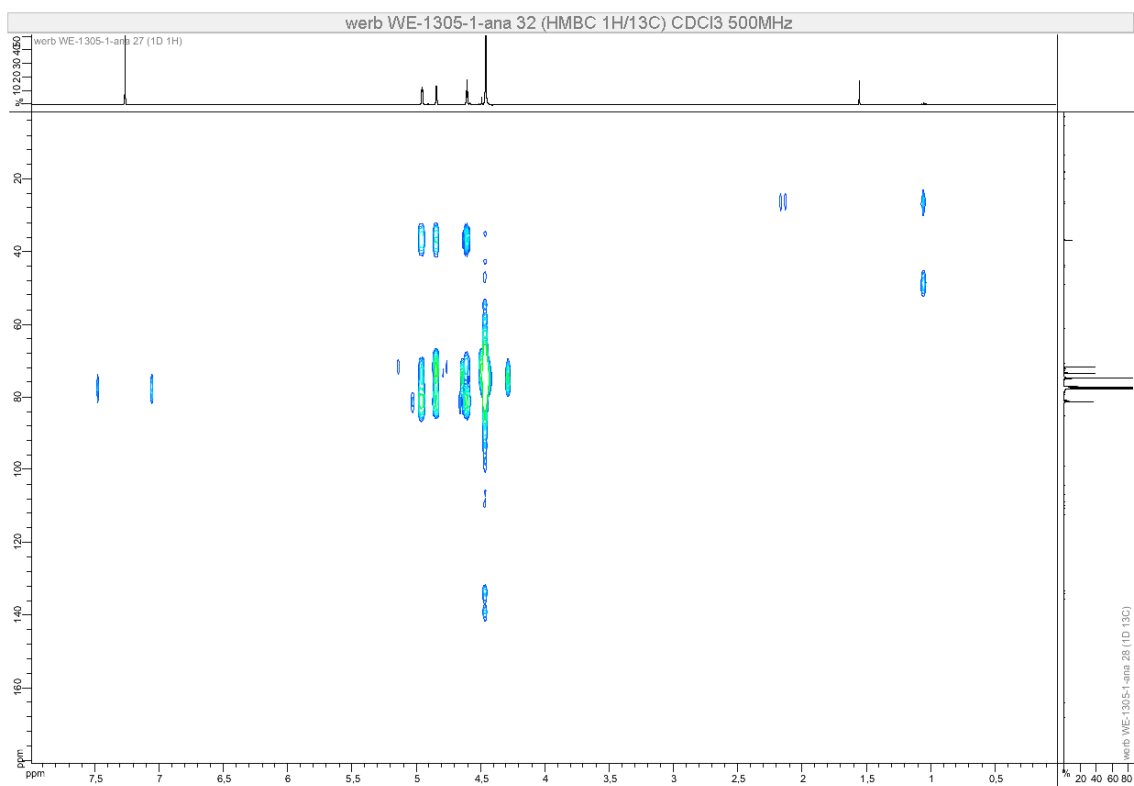
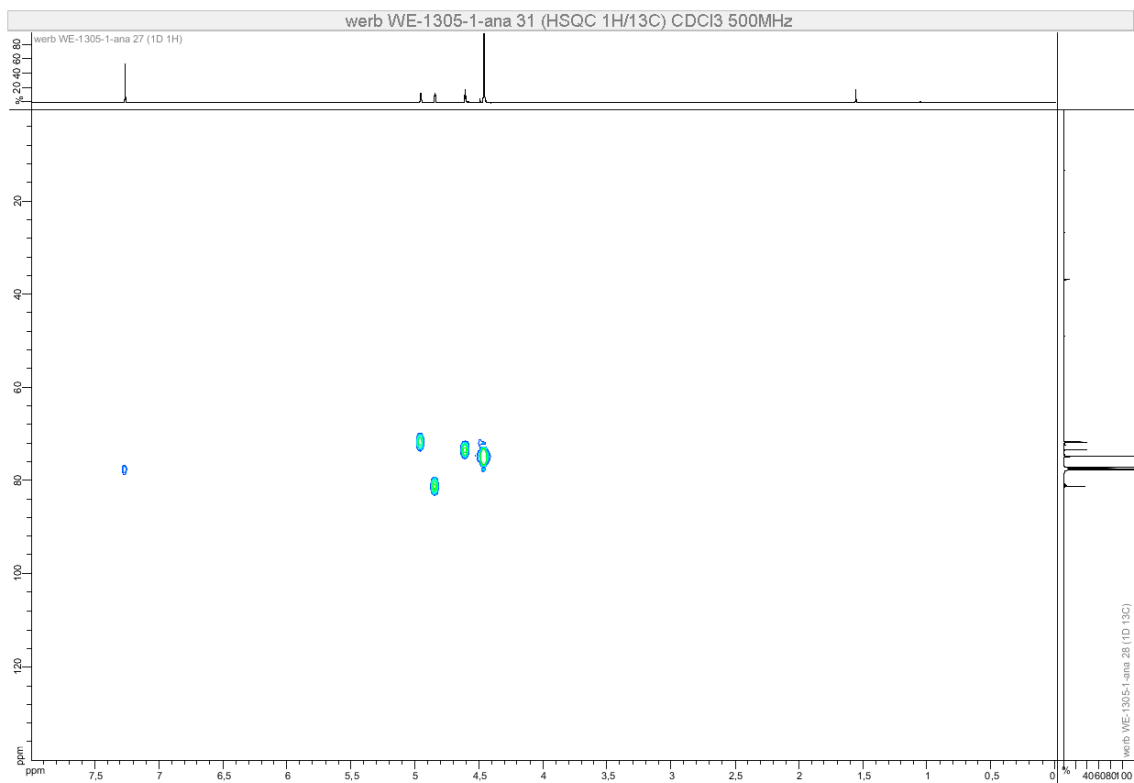


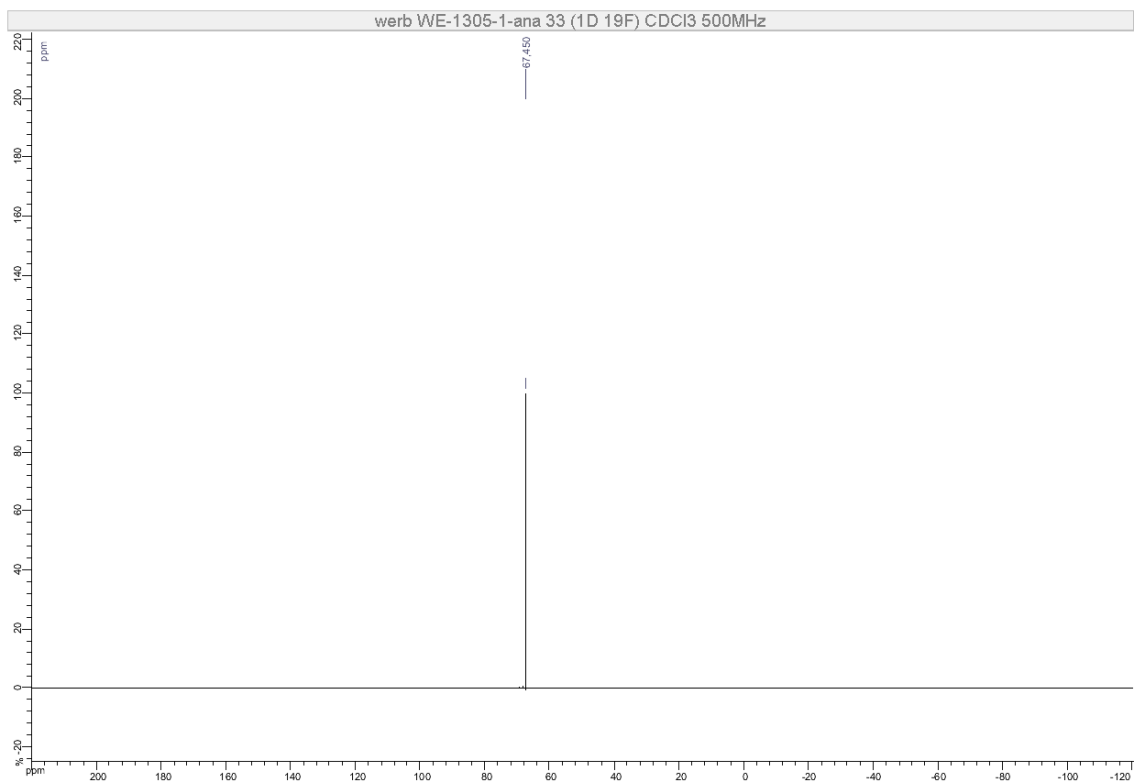


Compound 3b

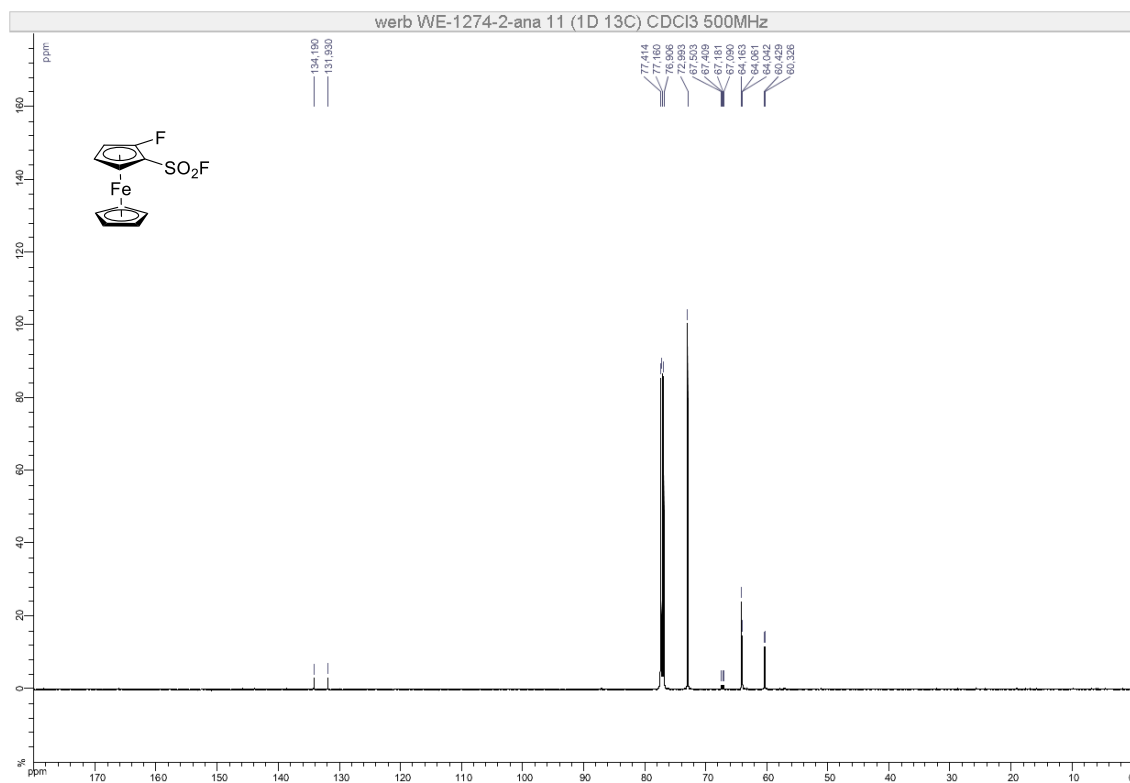
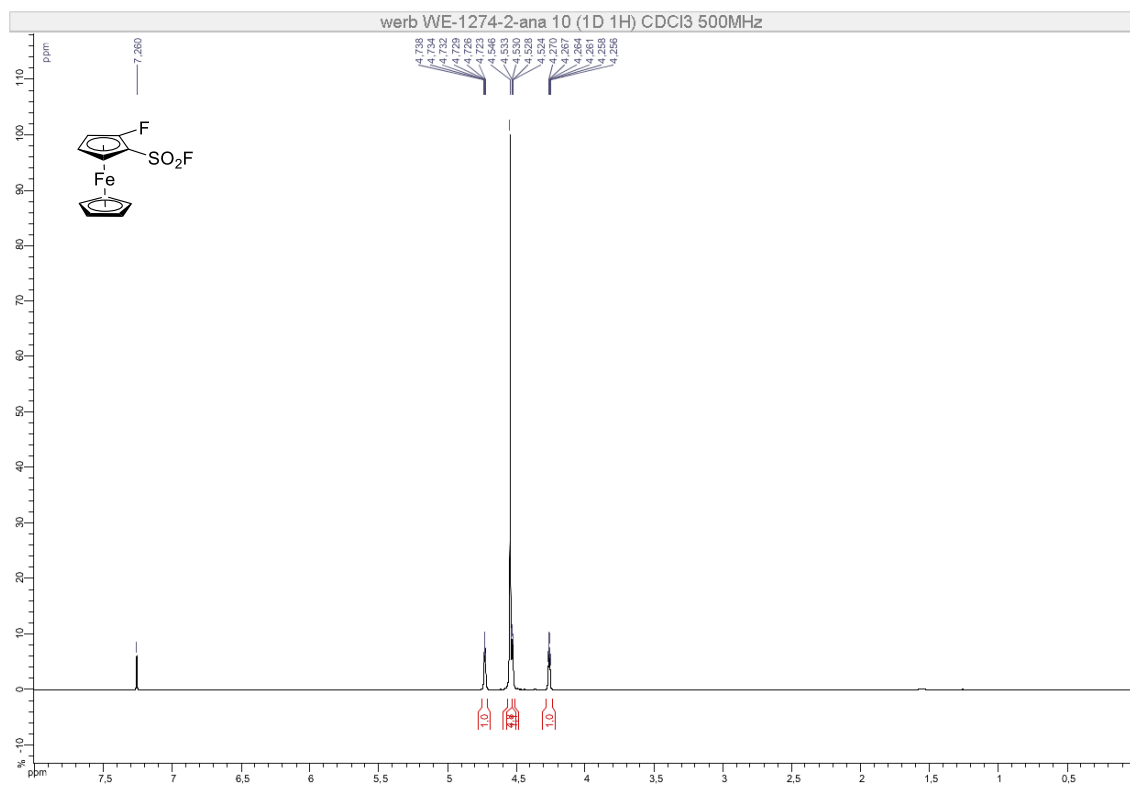


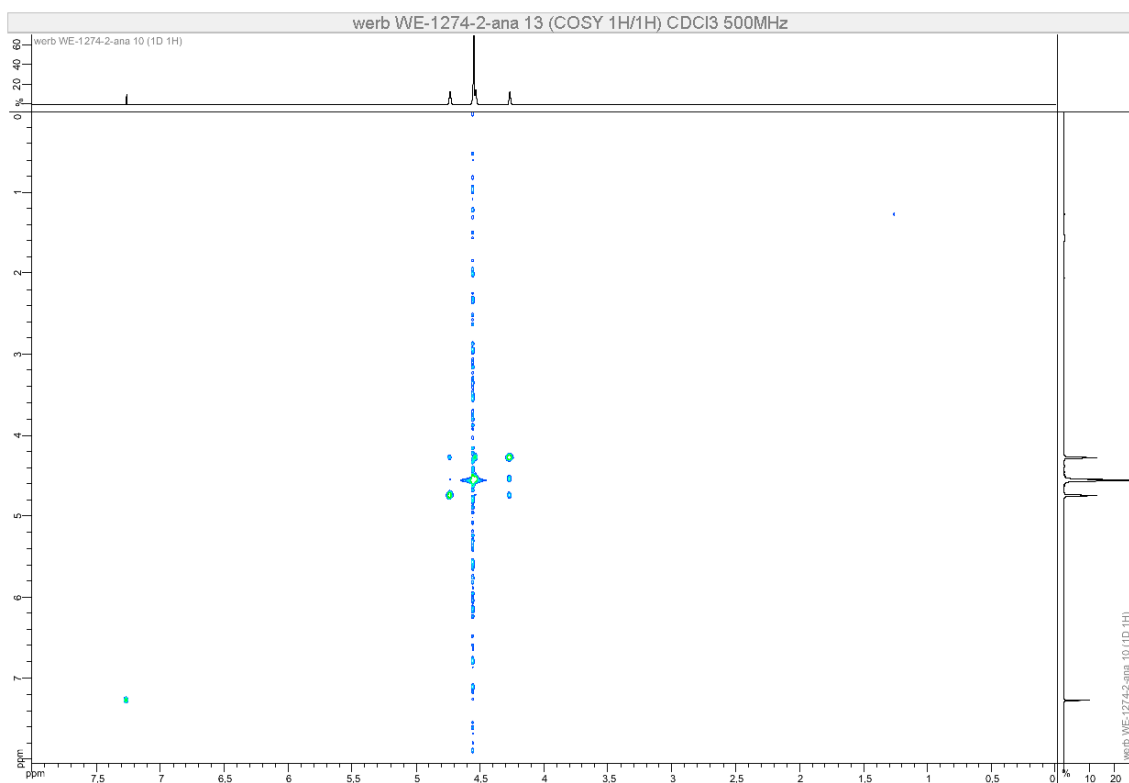
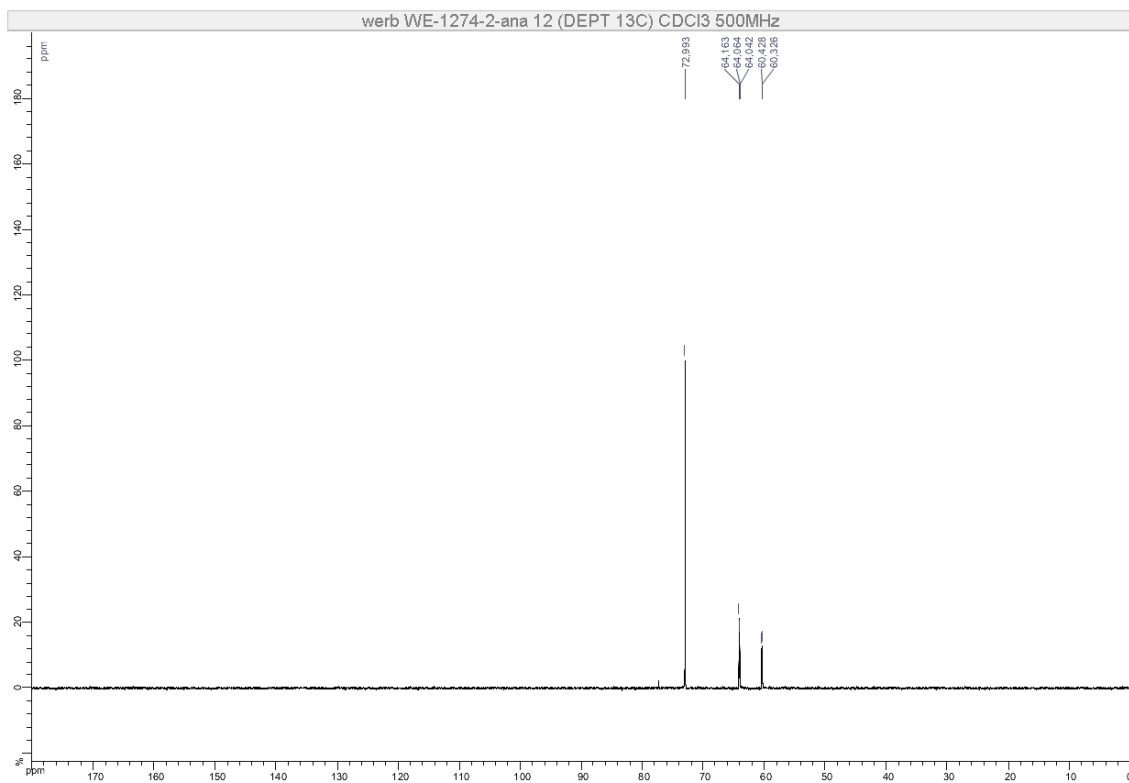


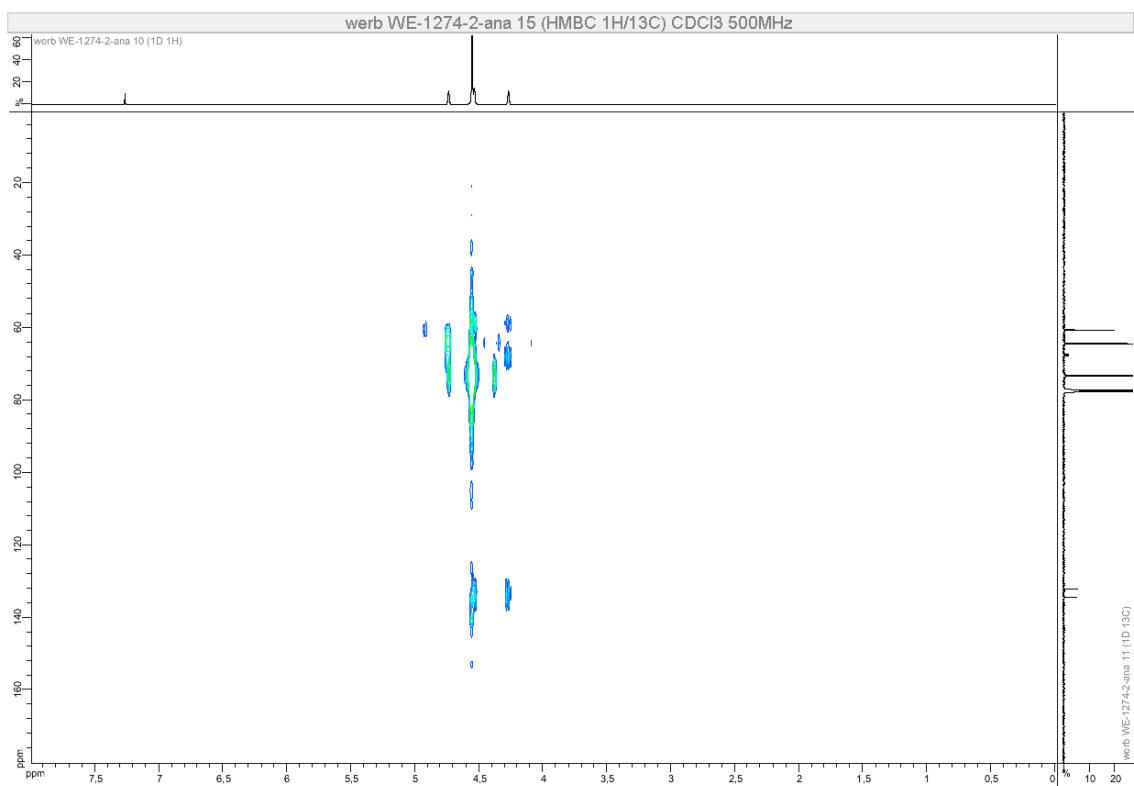
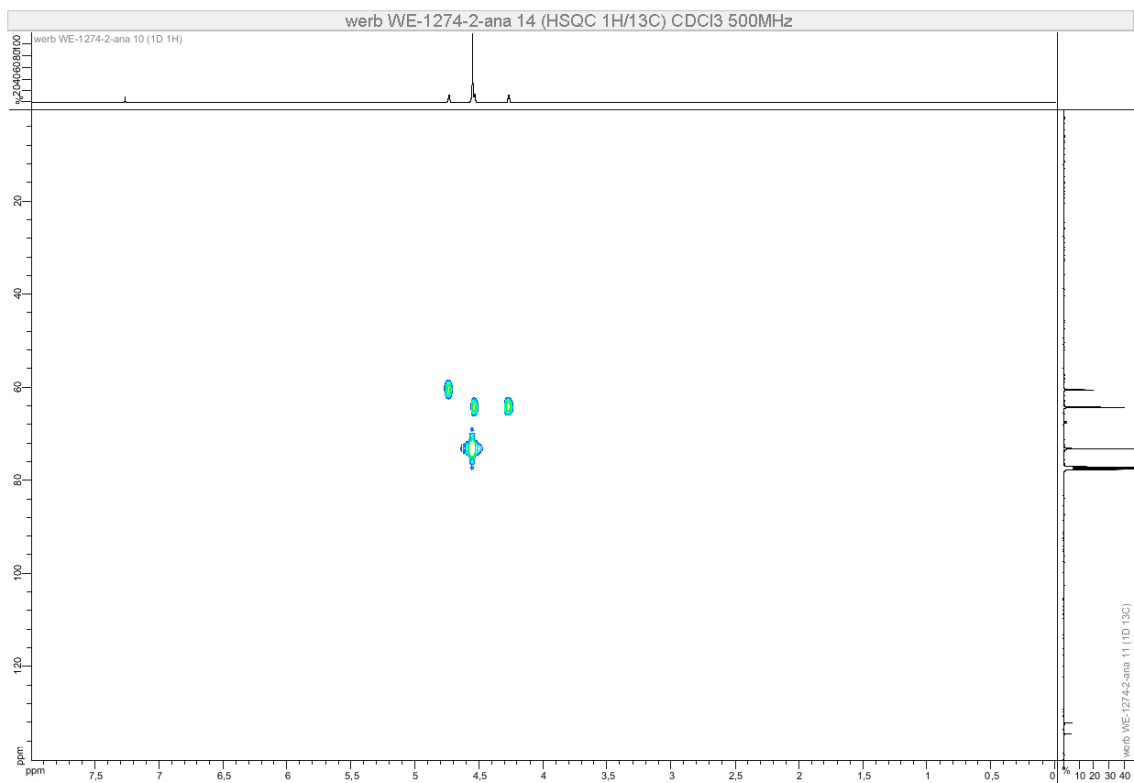


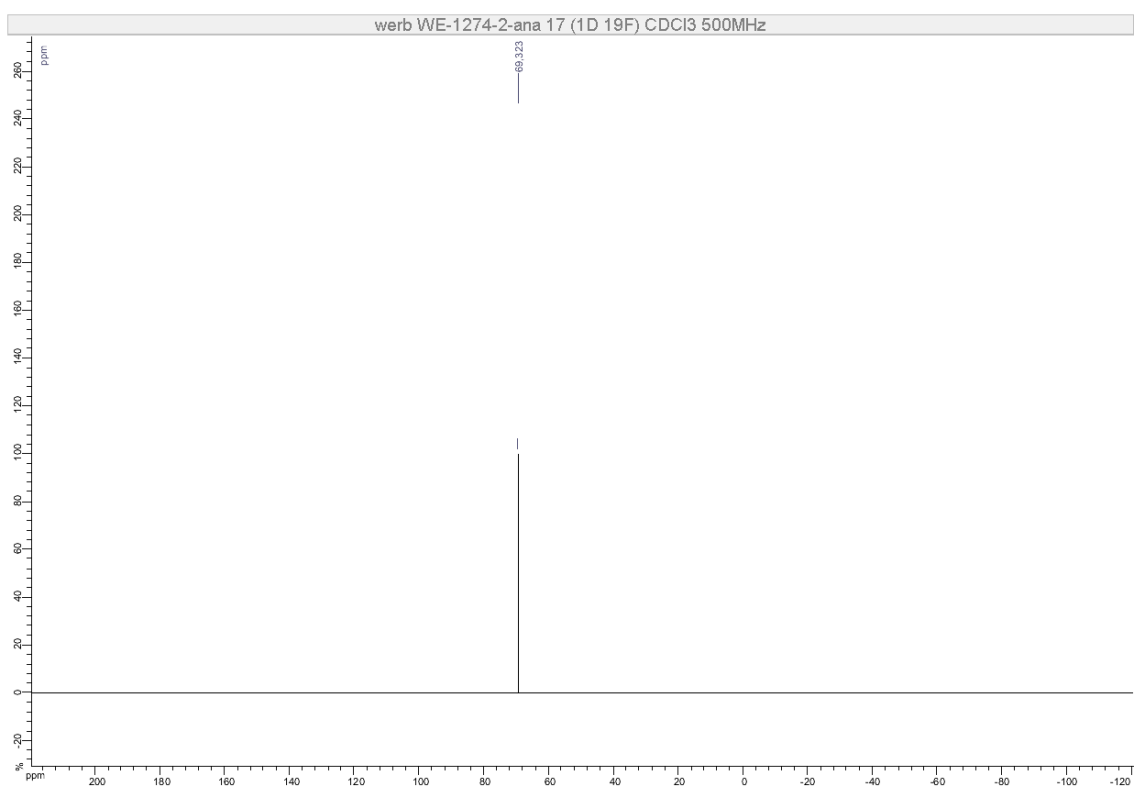
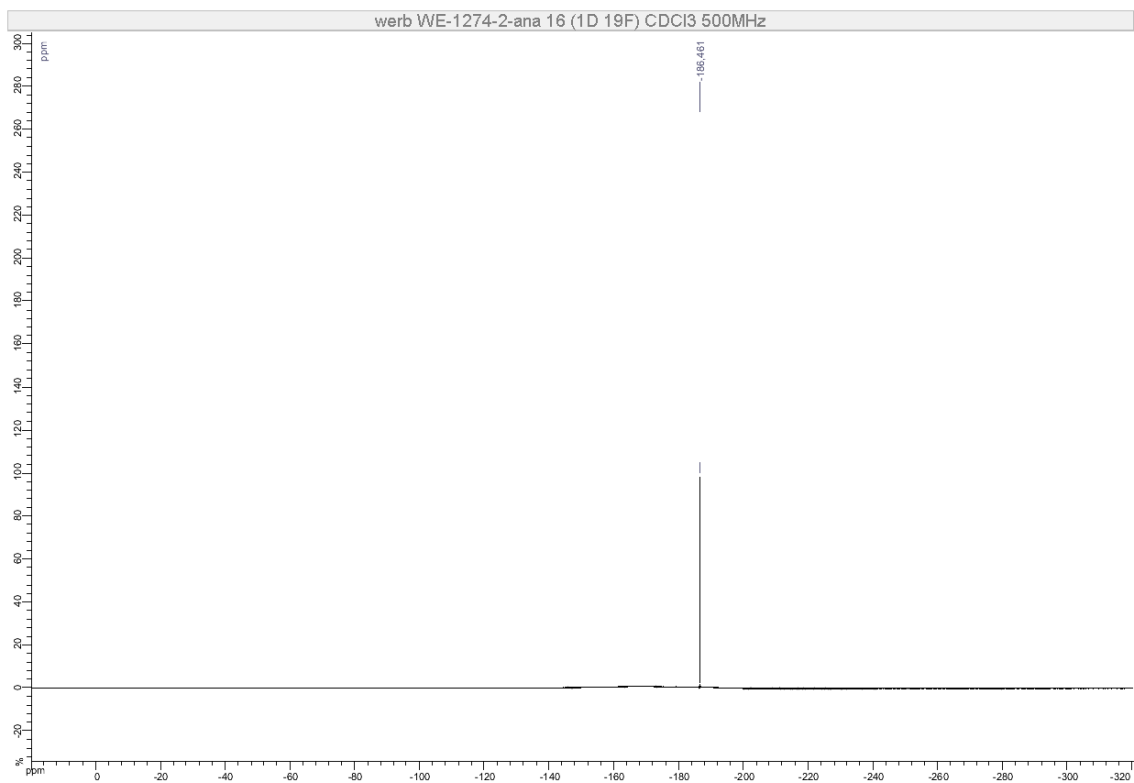


Compound 3c

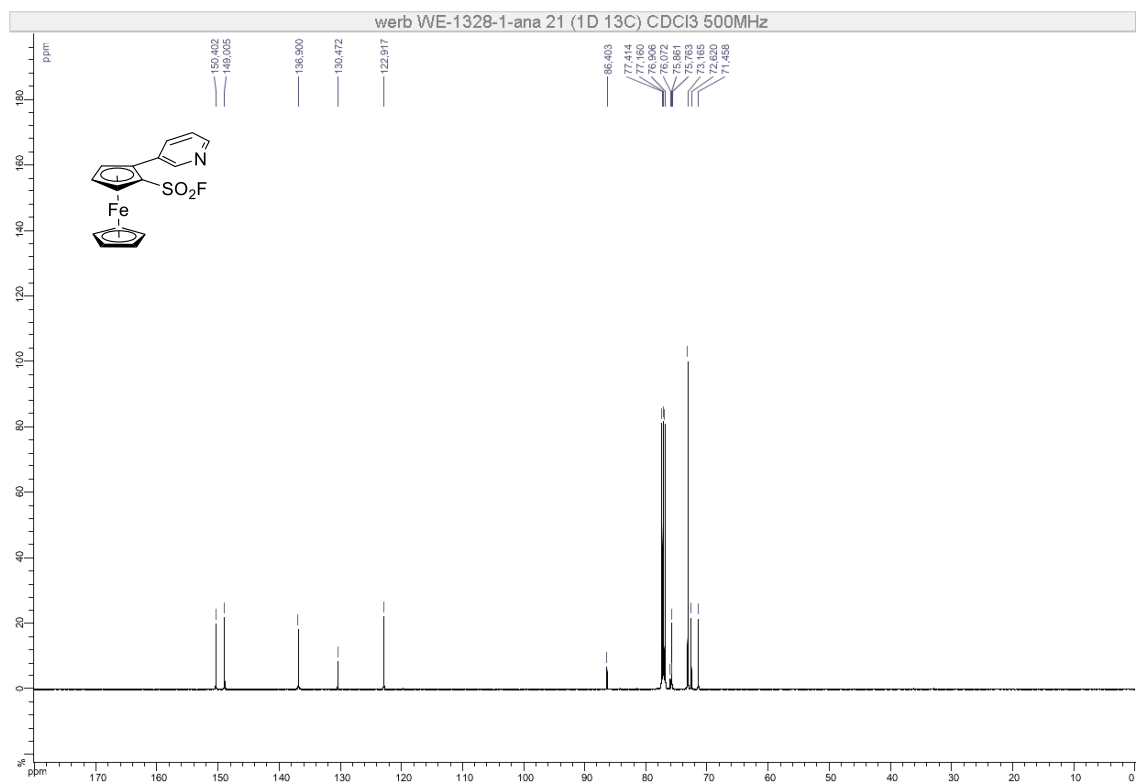
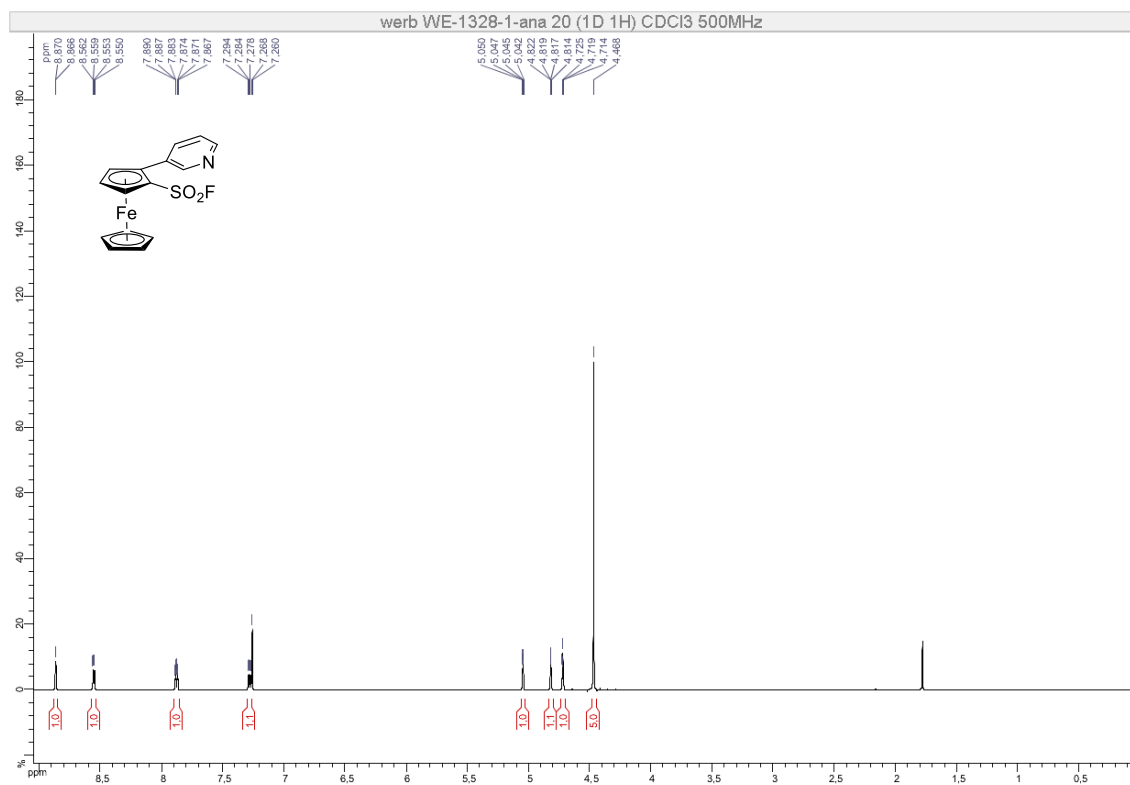


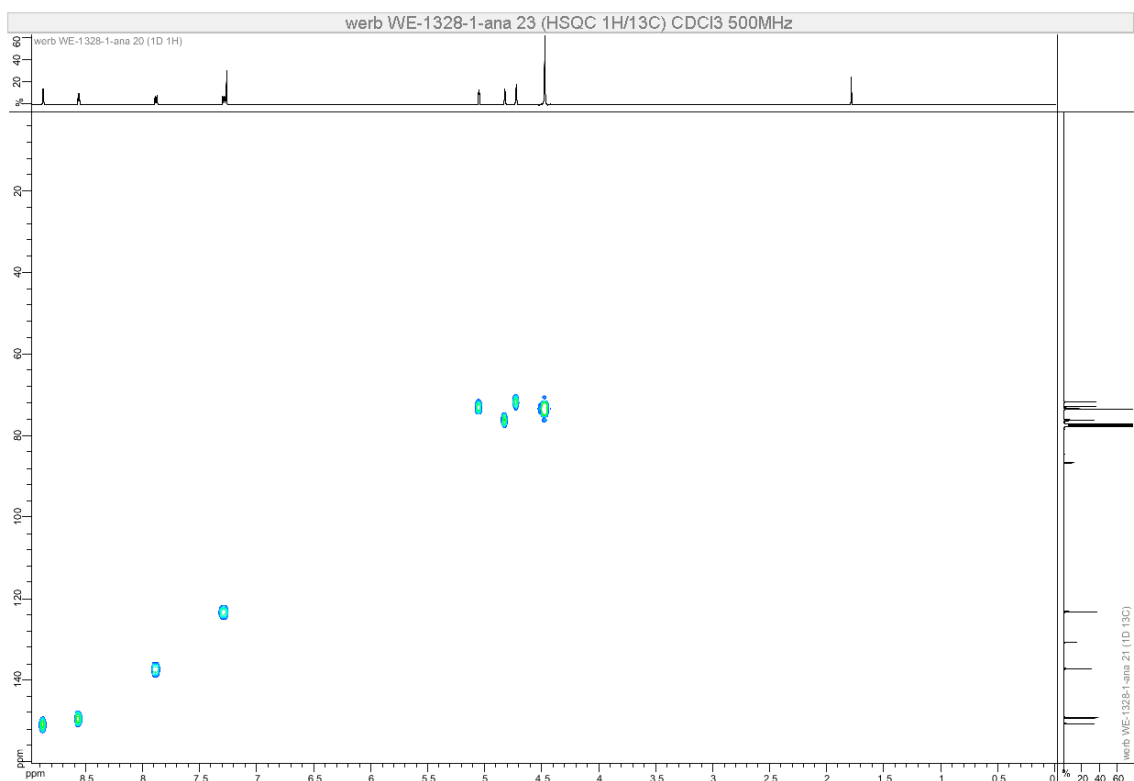
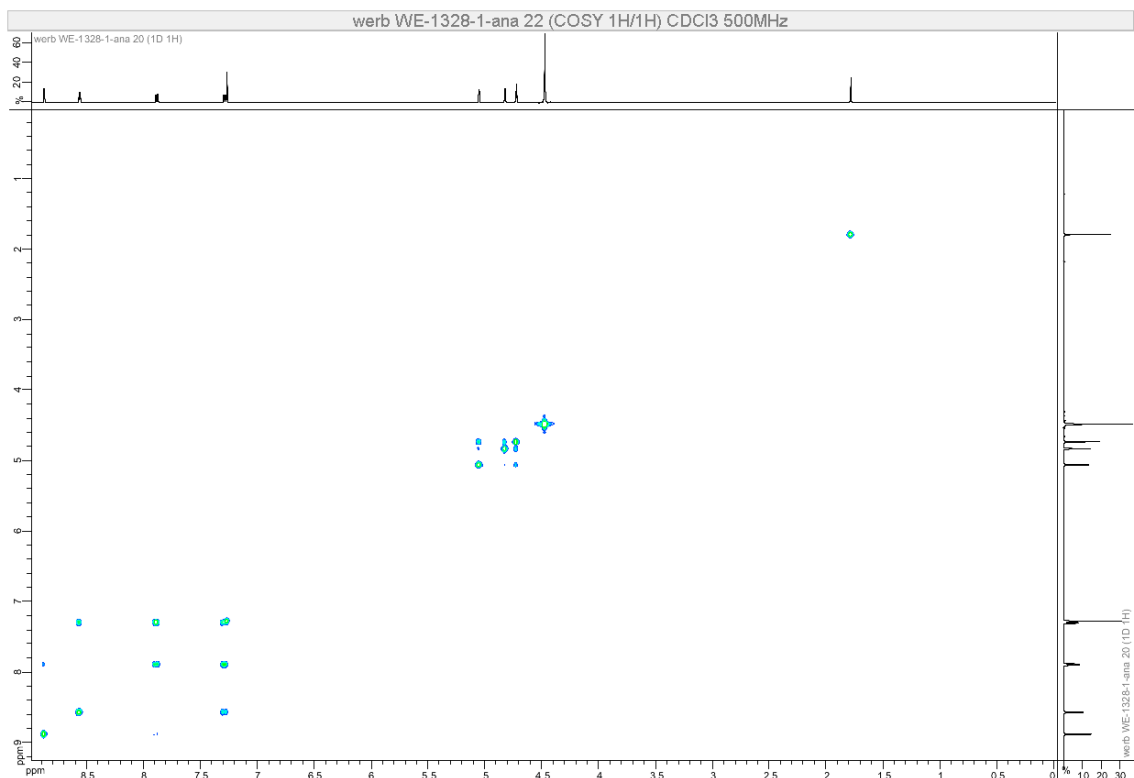


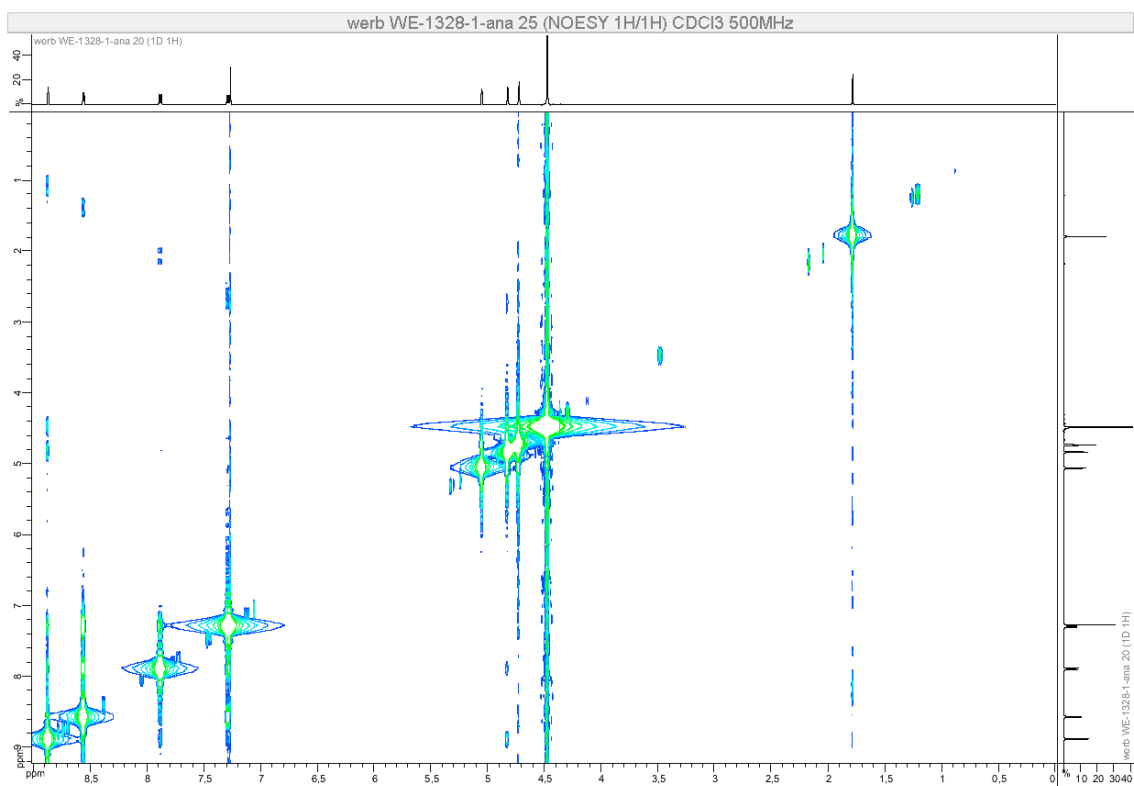
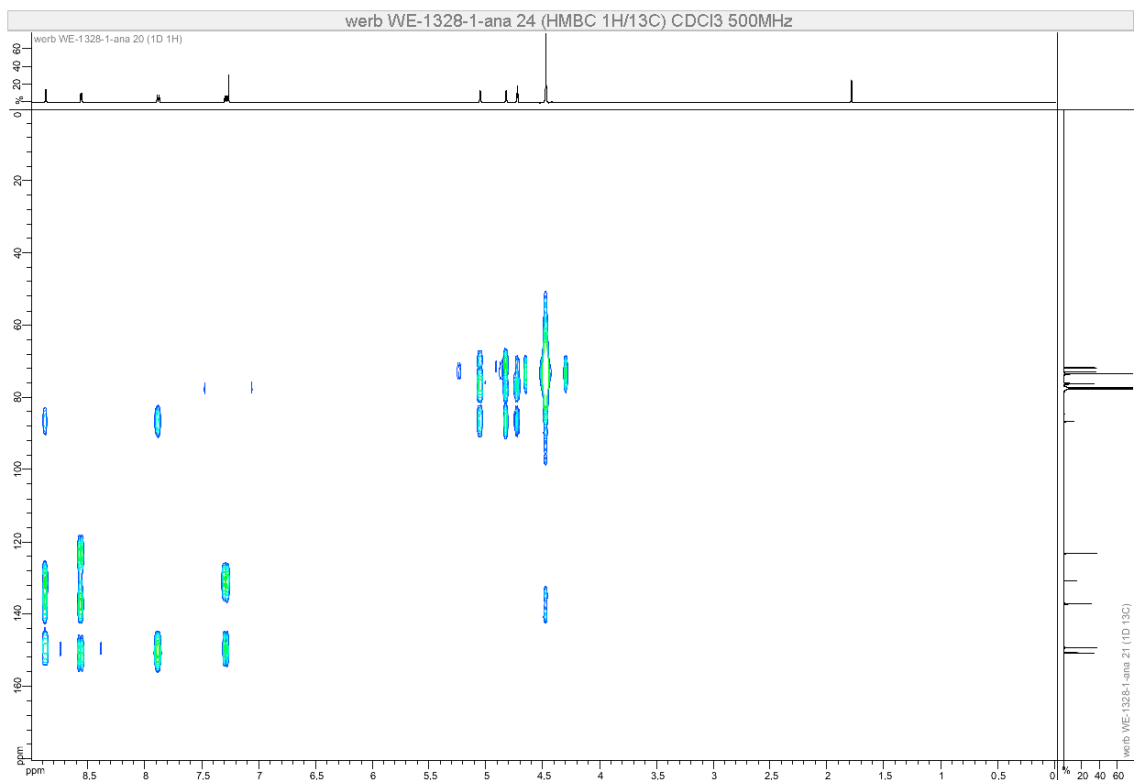


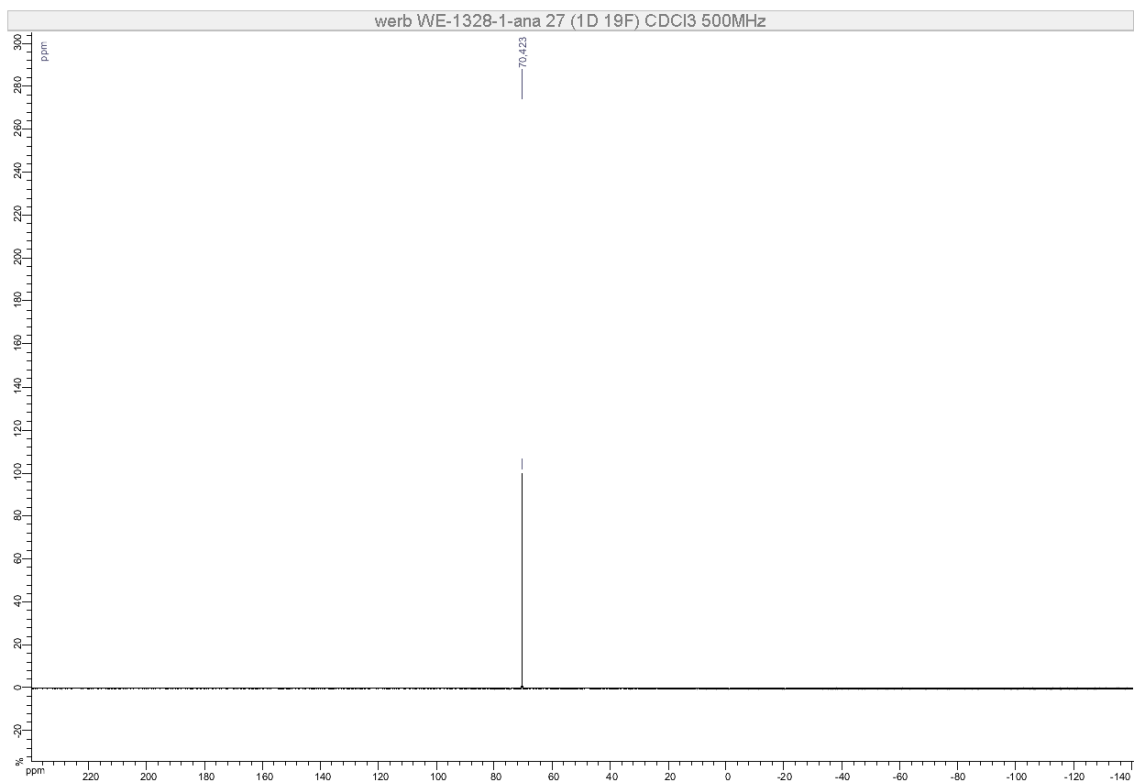


Compound 3d

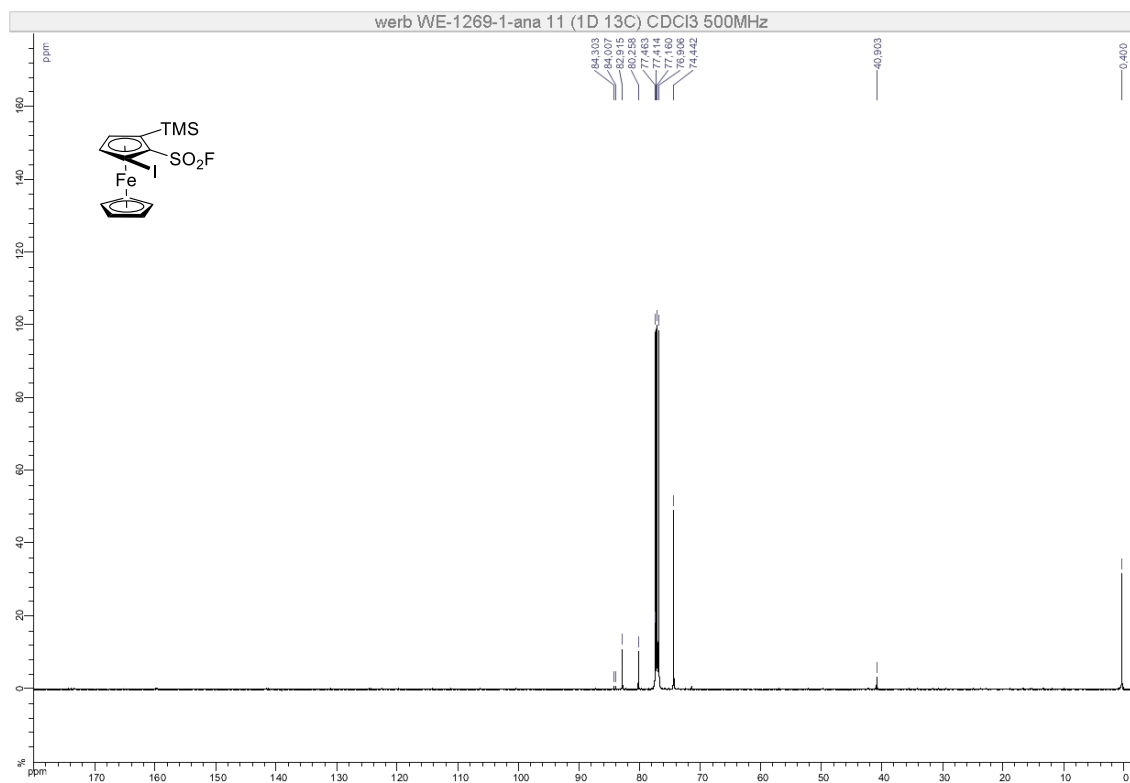
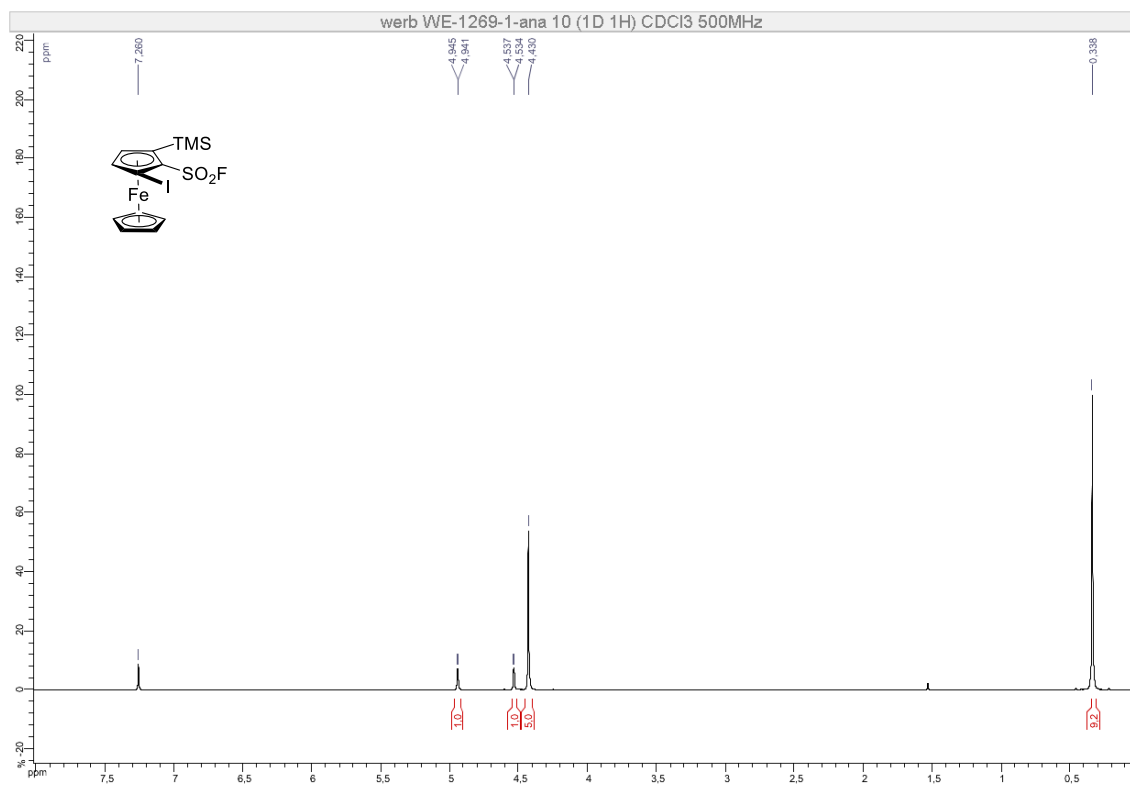


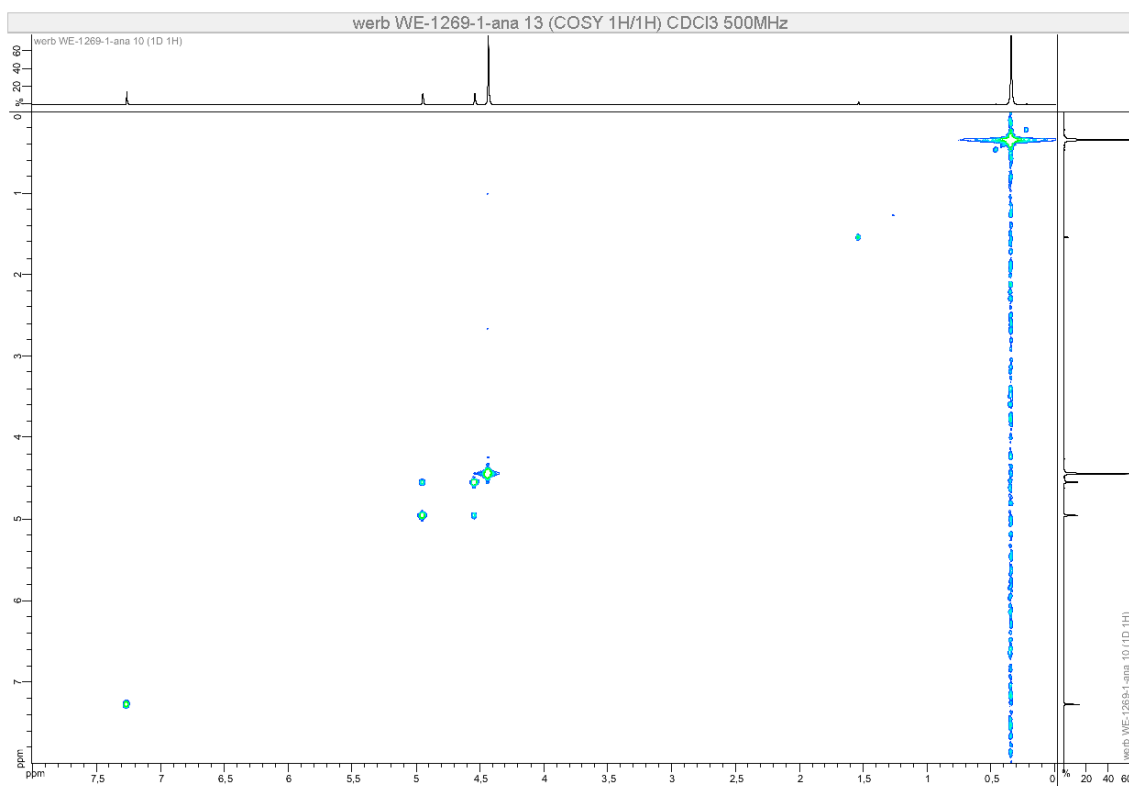
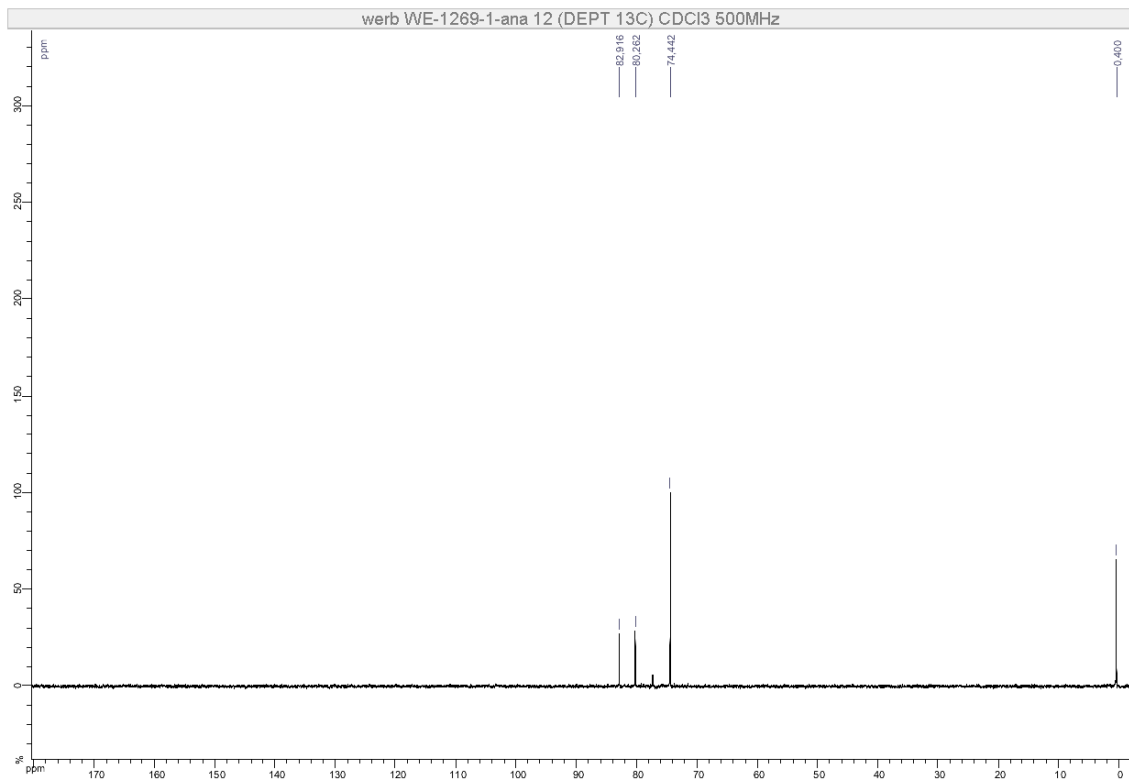


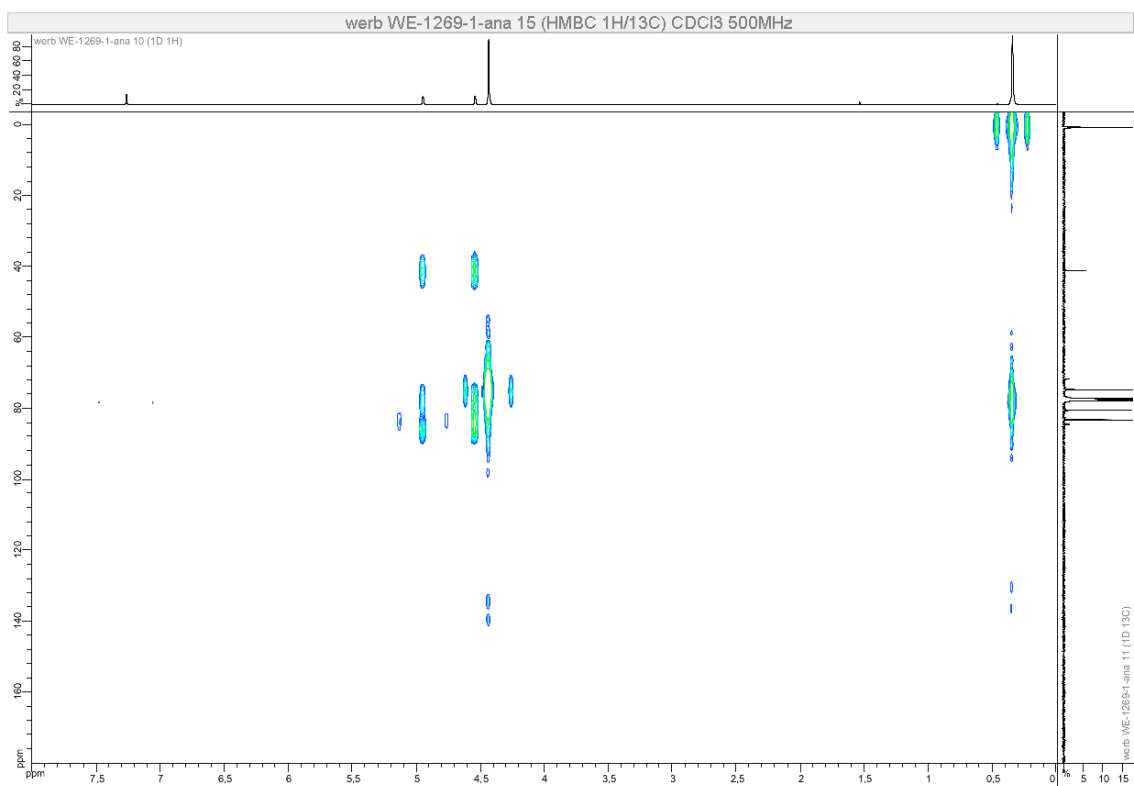
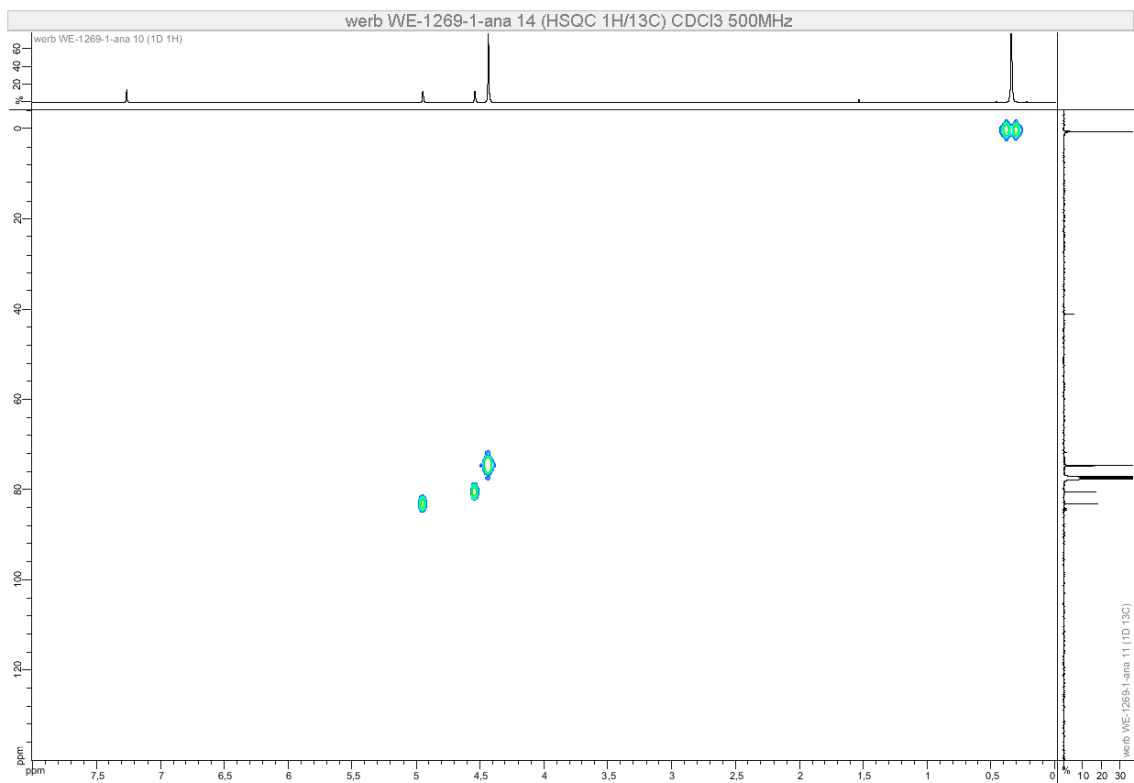


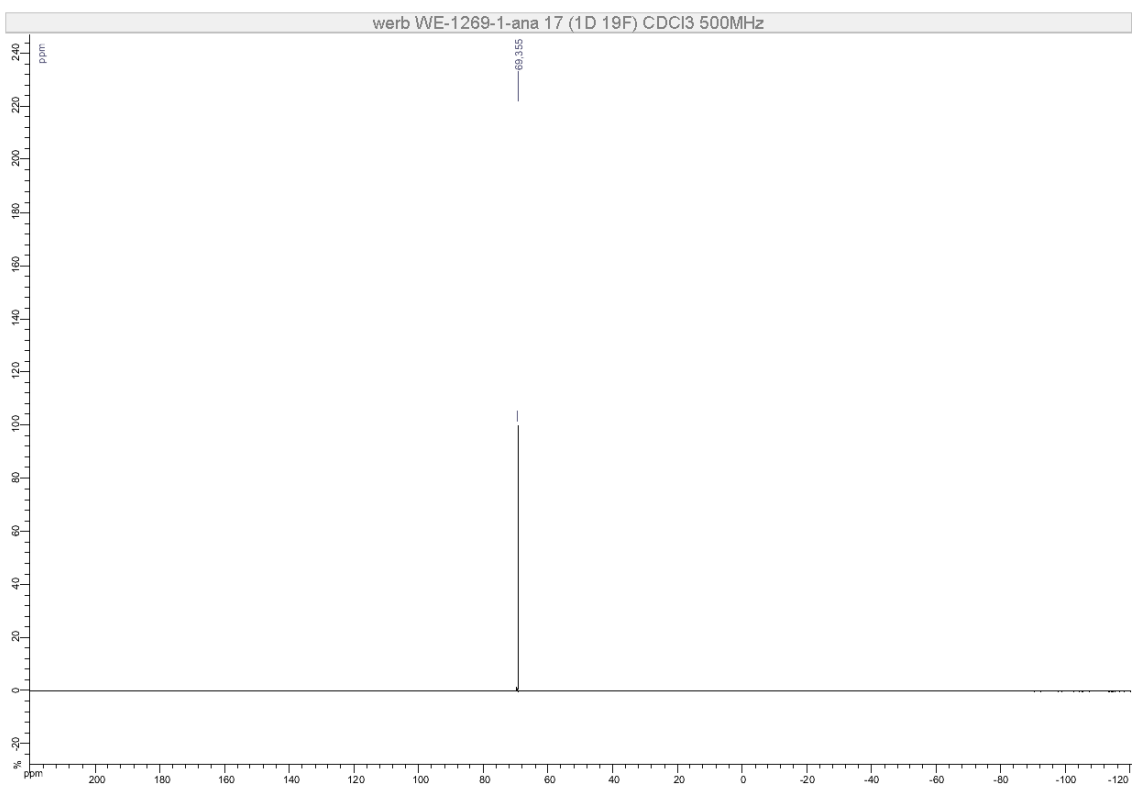
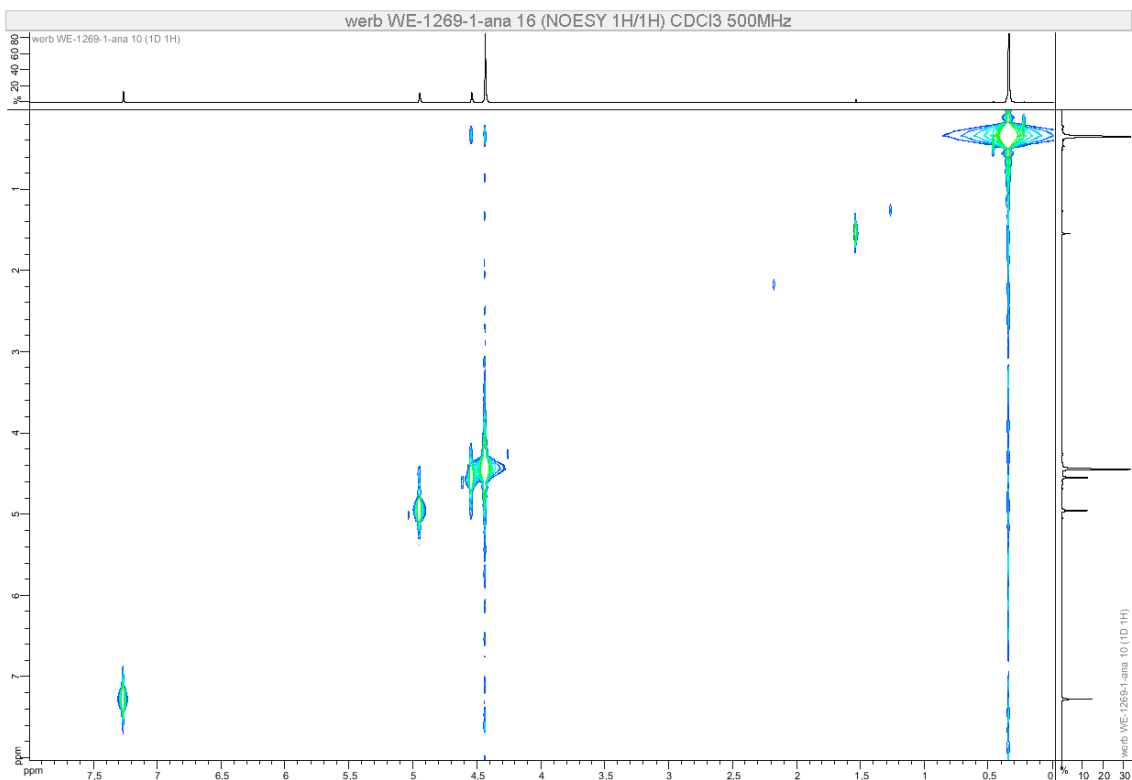


Compound 4

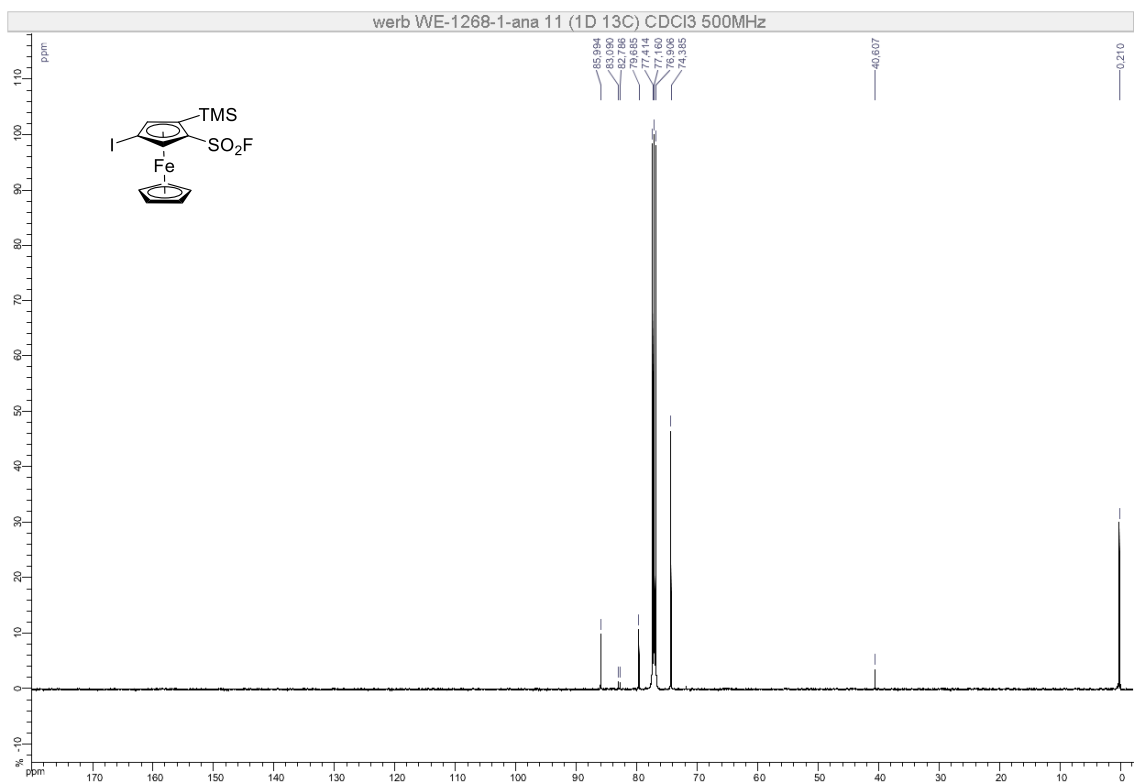
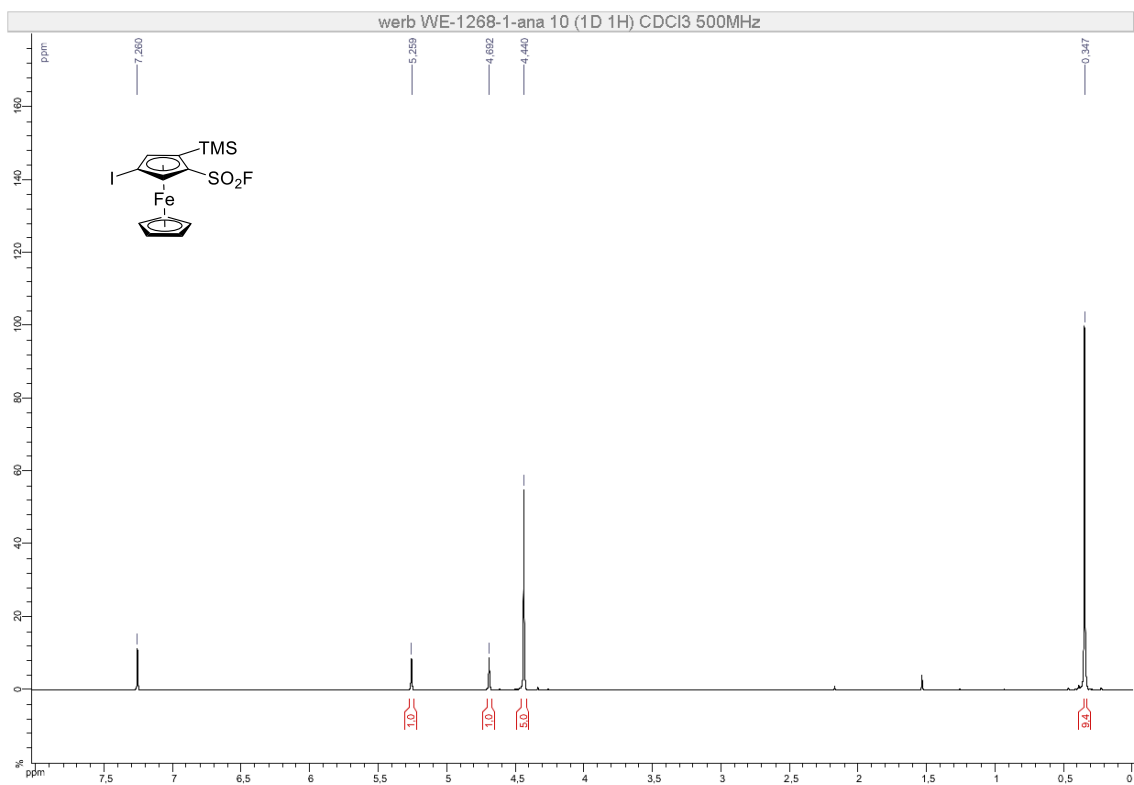


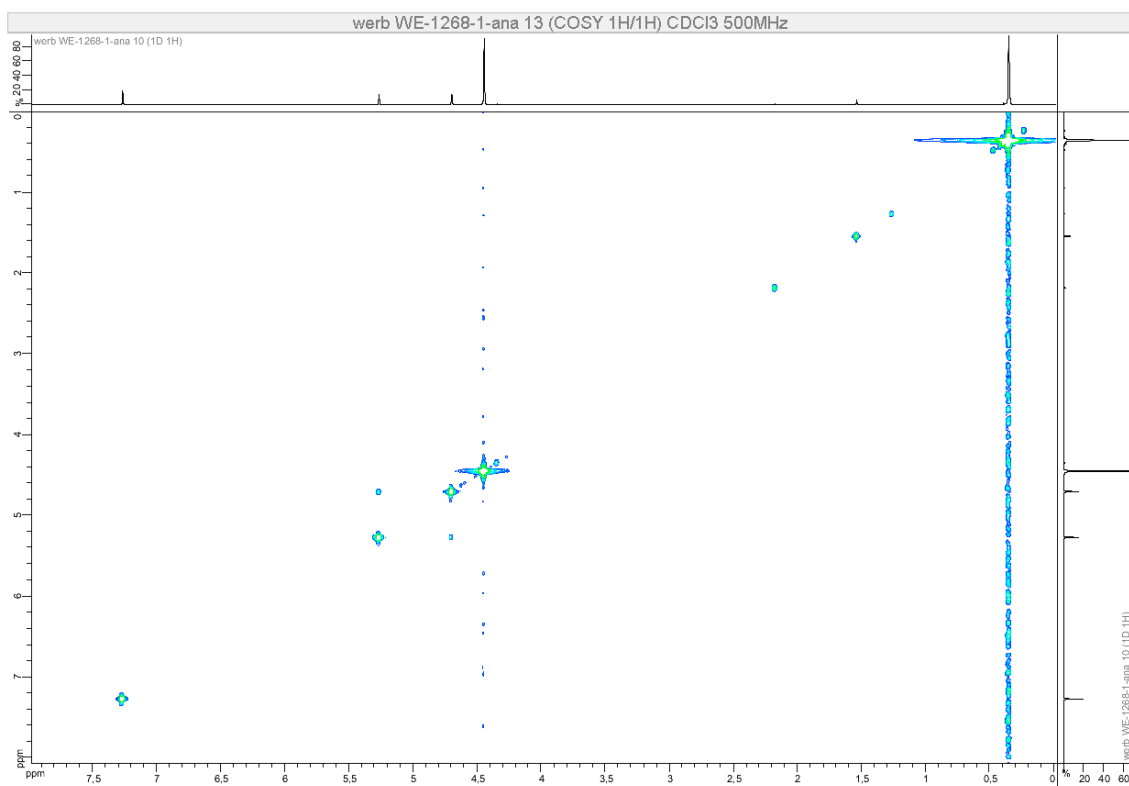
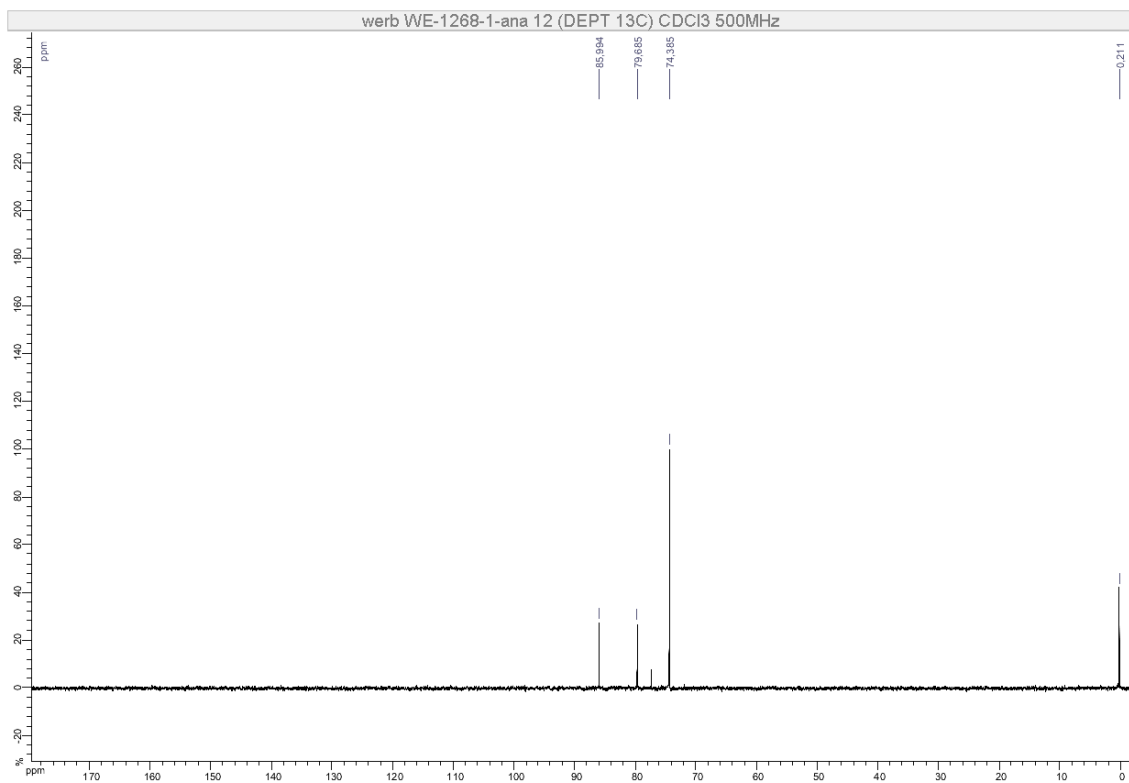


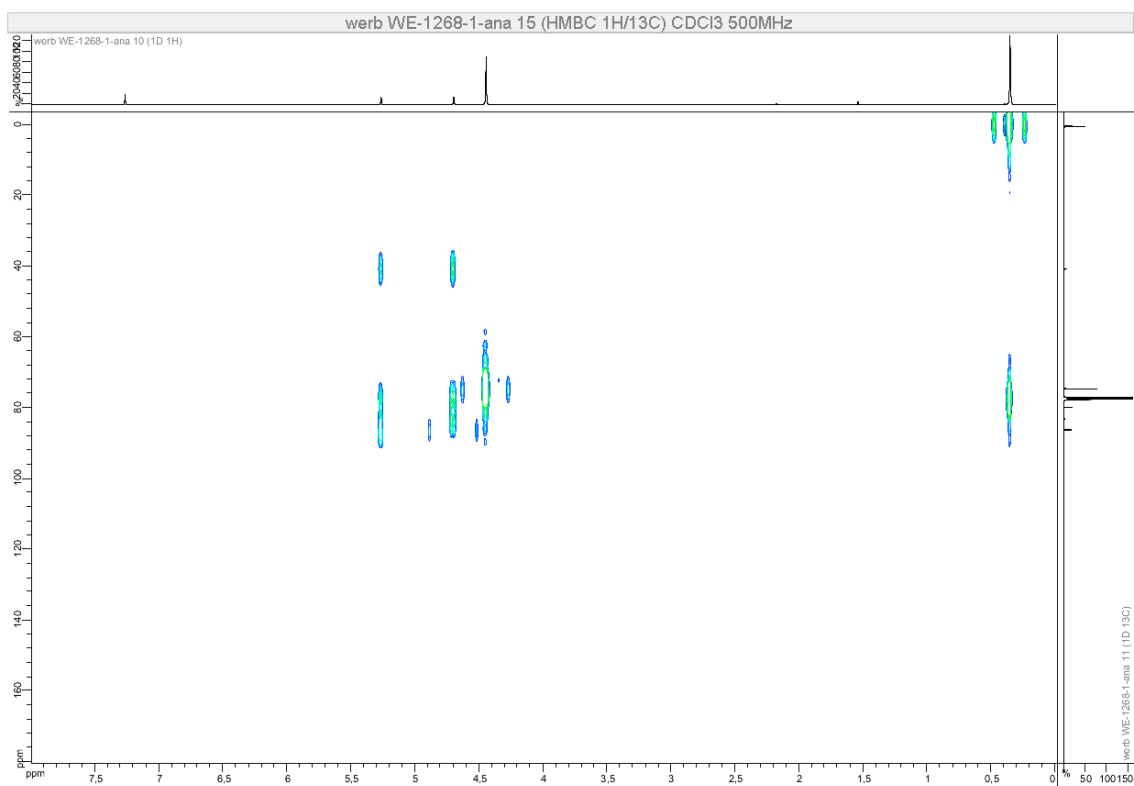
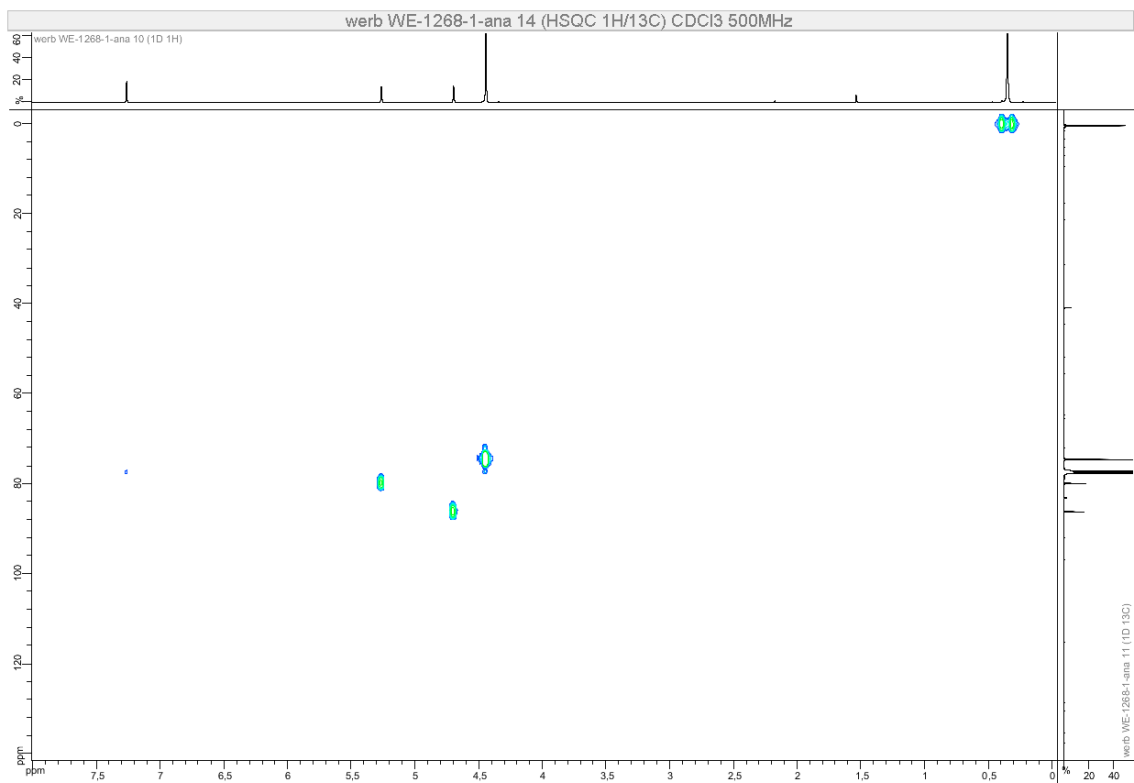


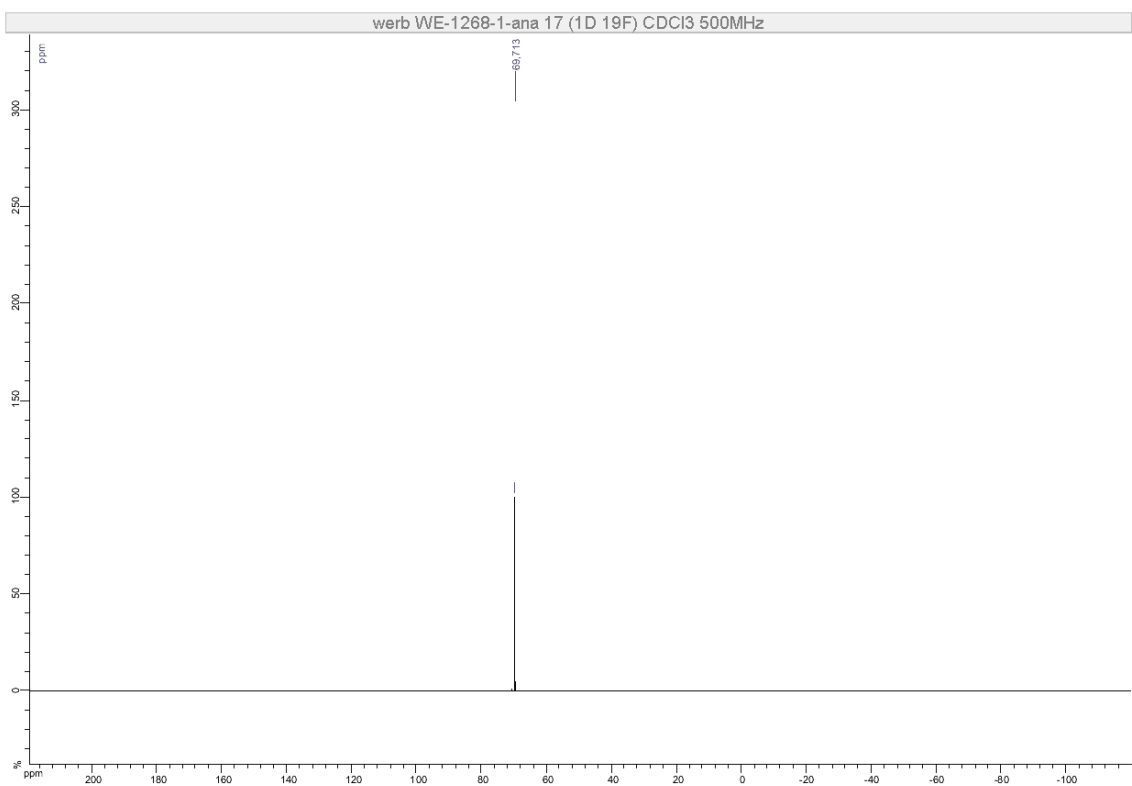
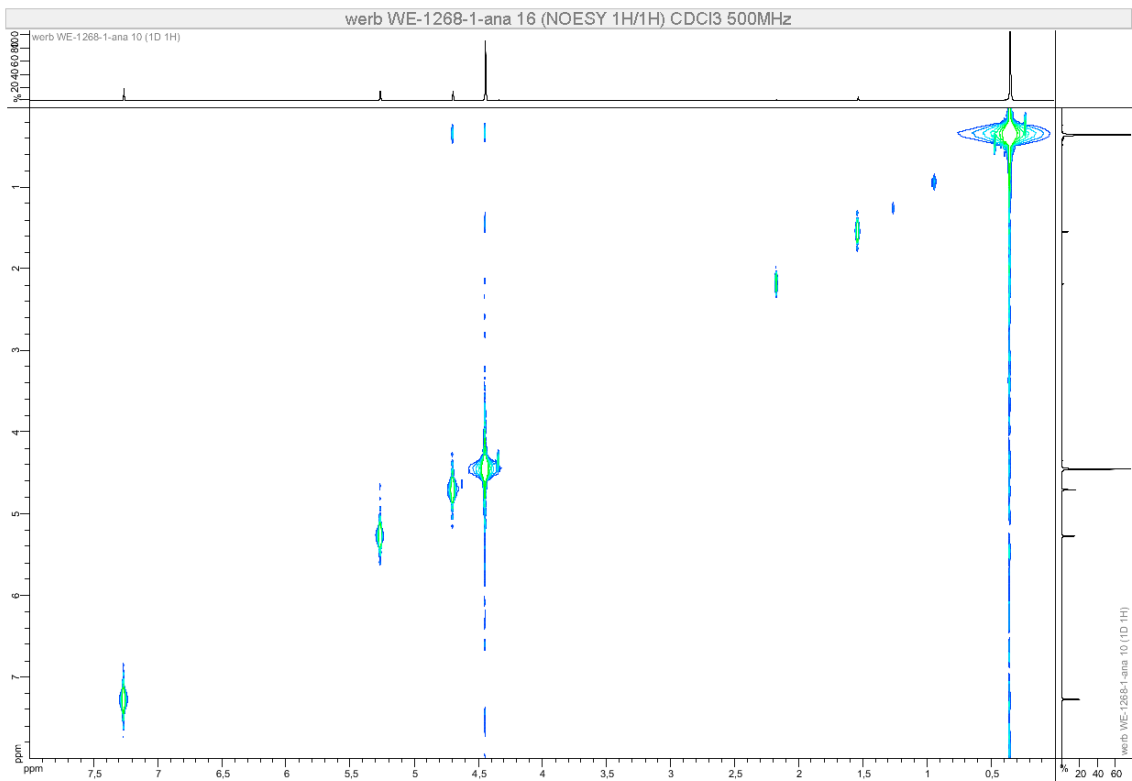


Compound 5a

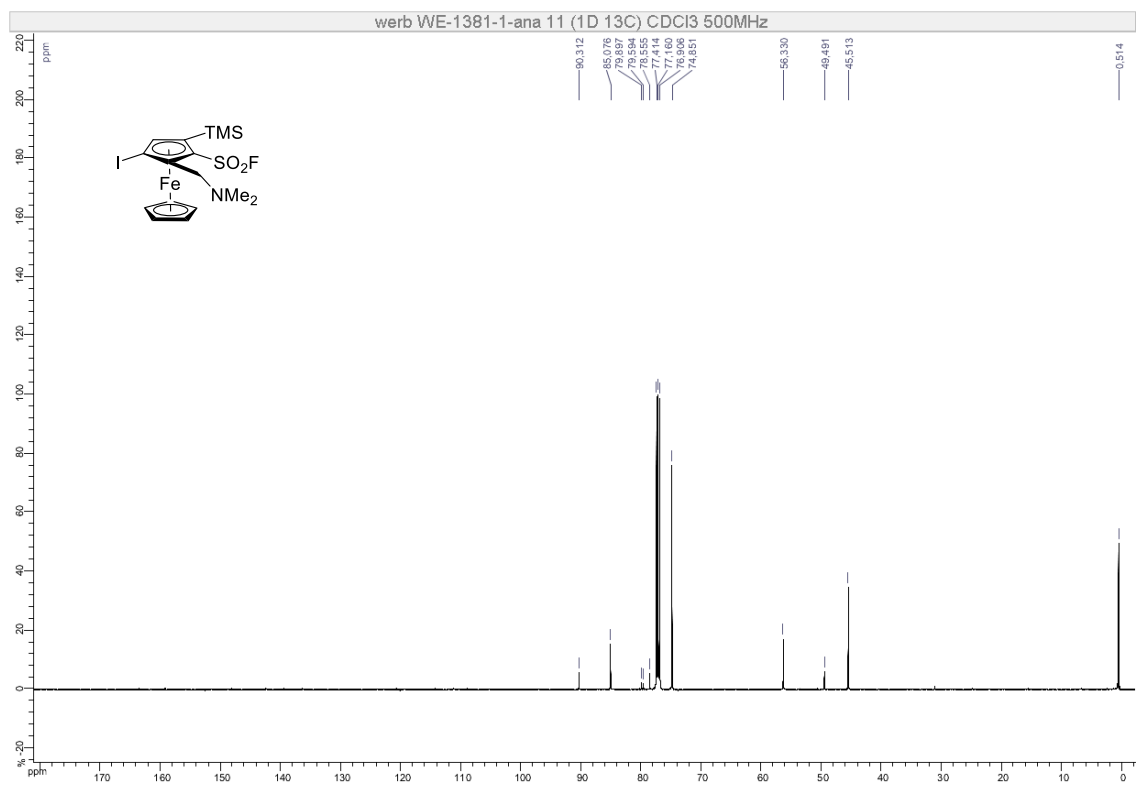
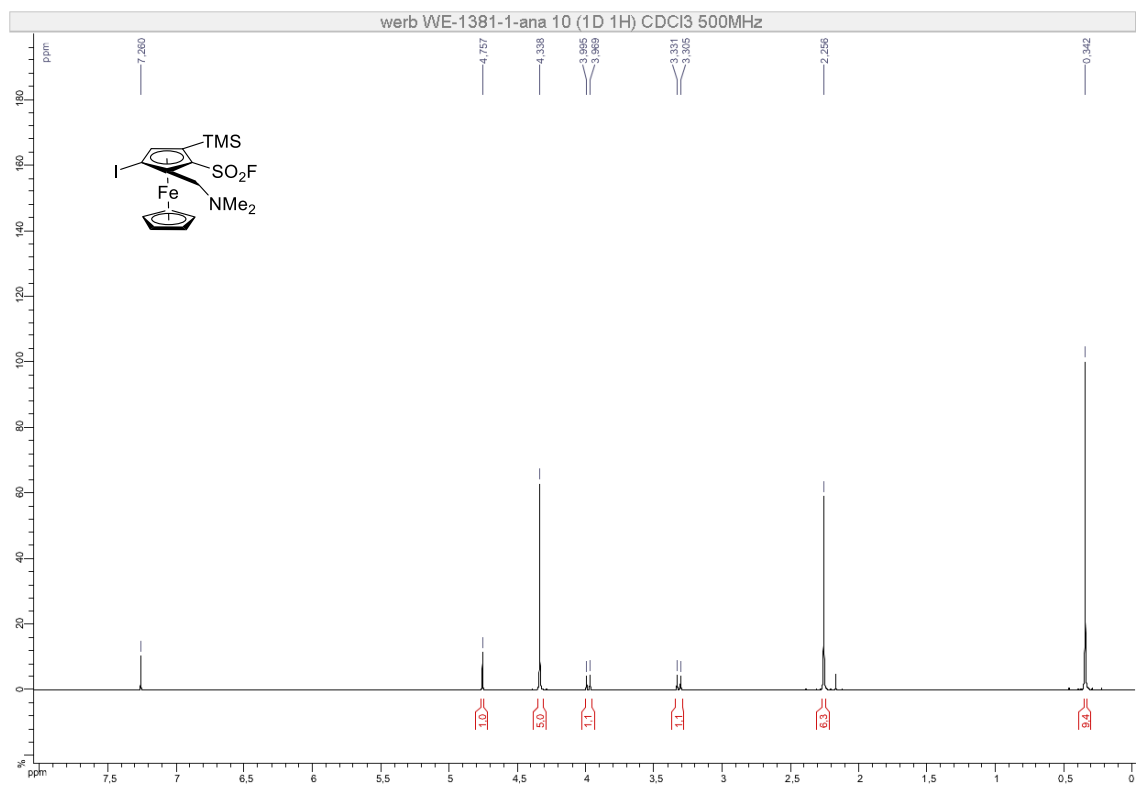


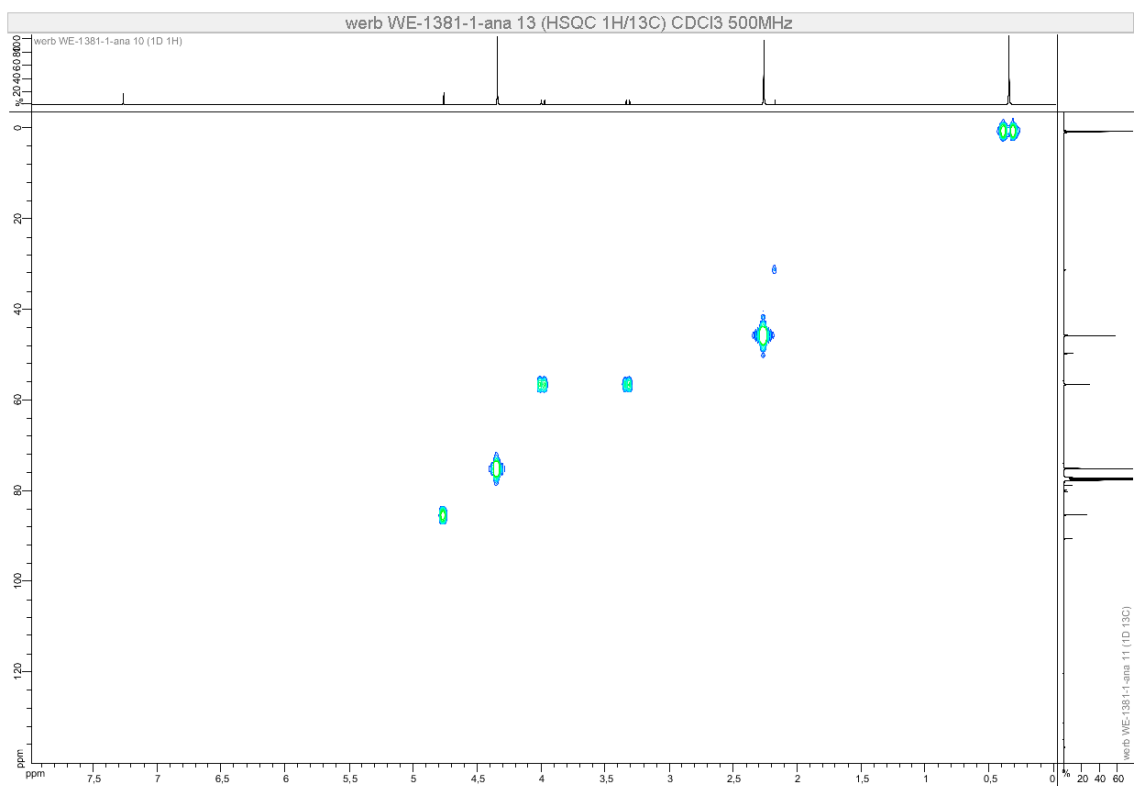
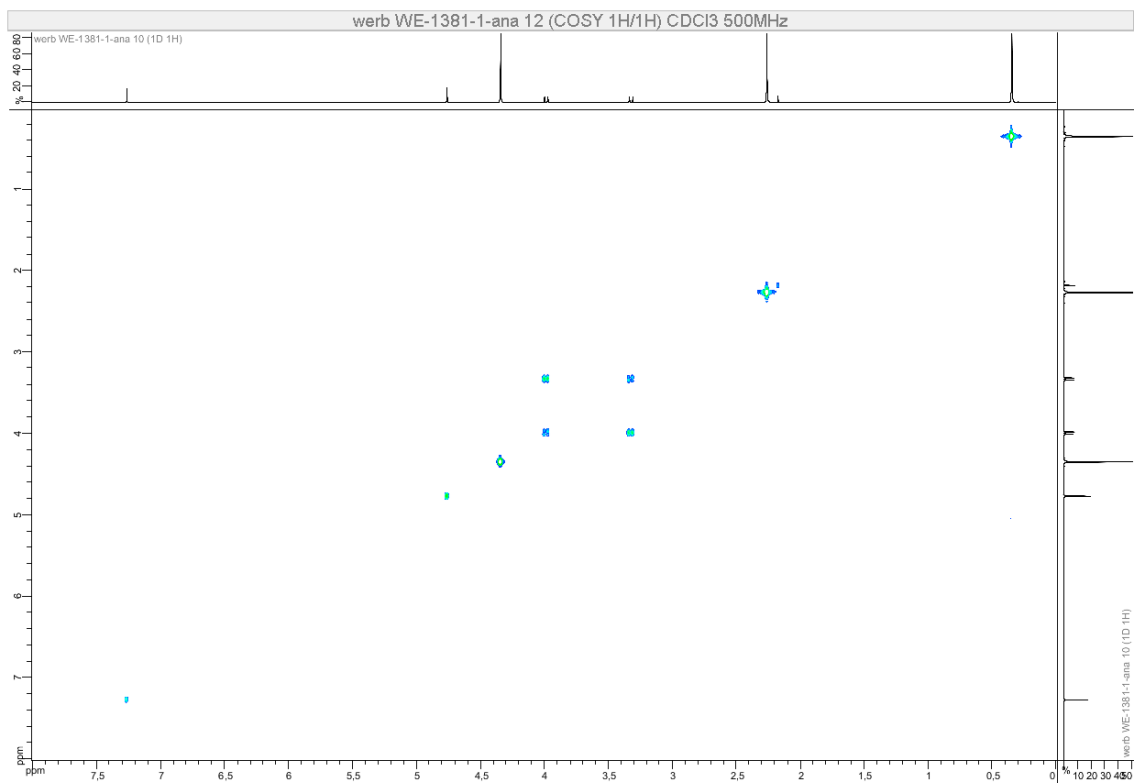


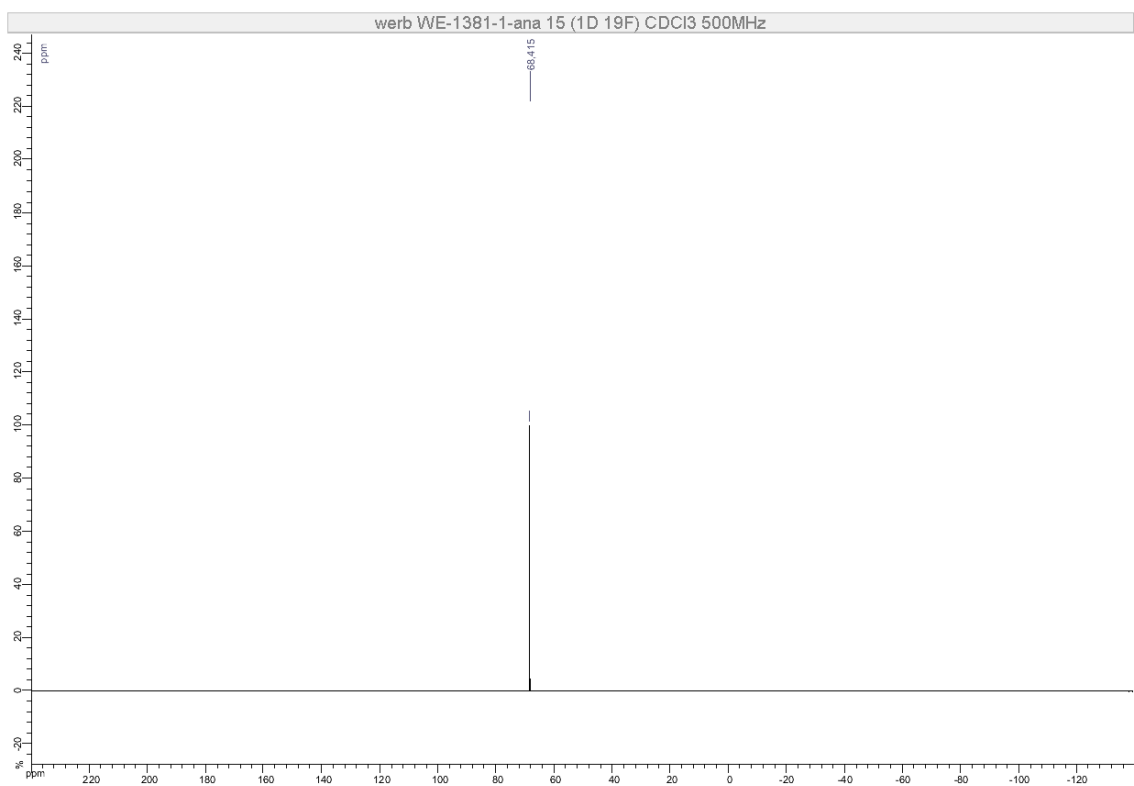
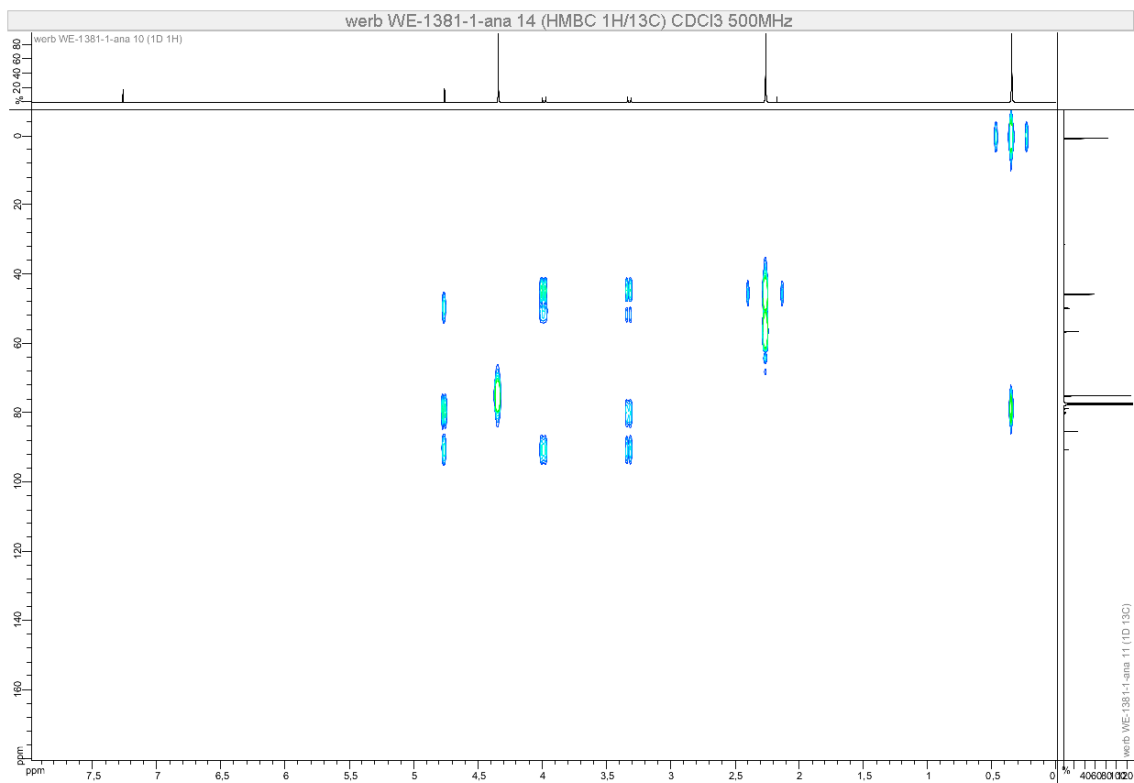




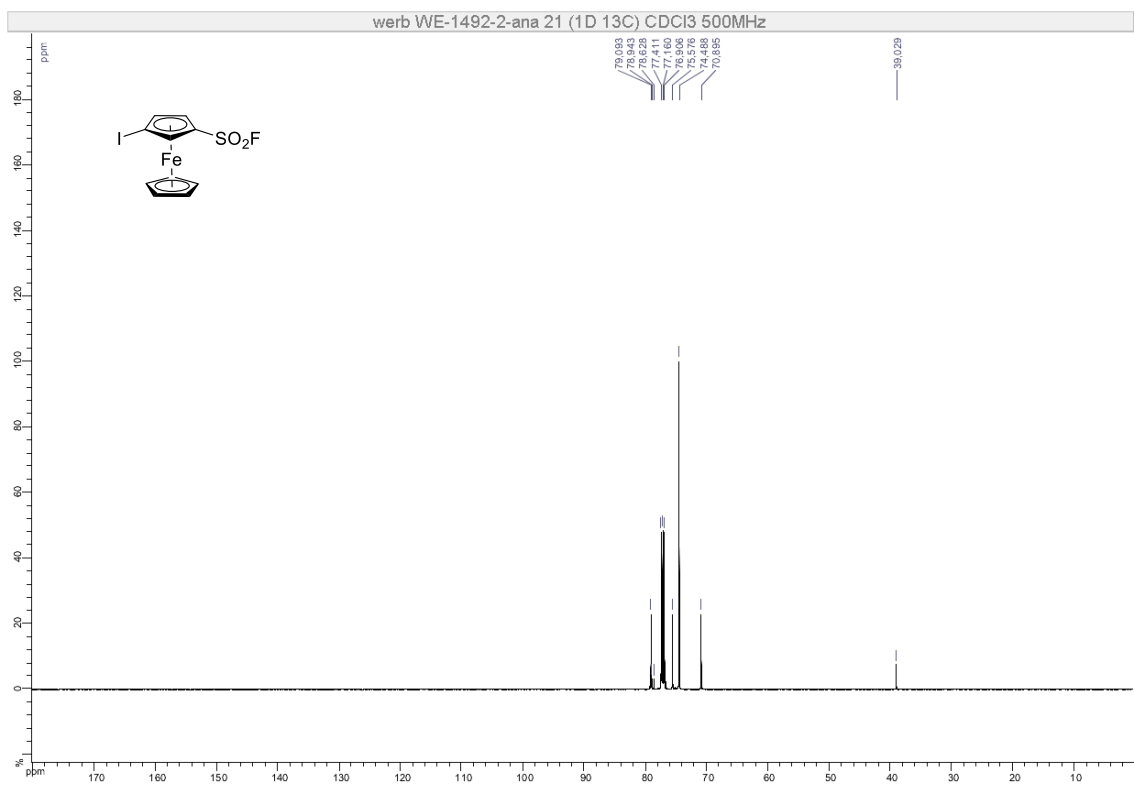
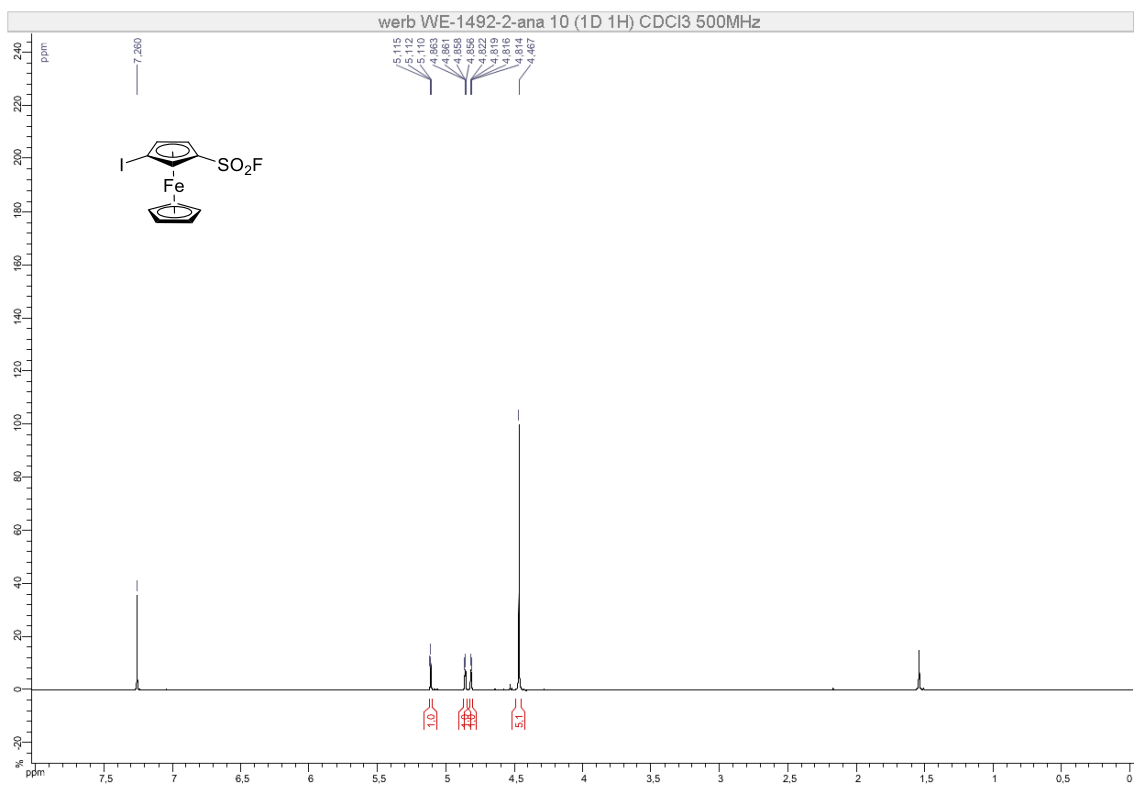
Compound 5b

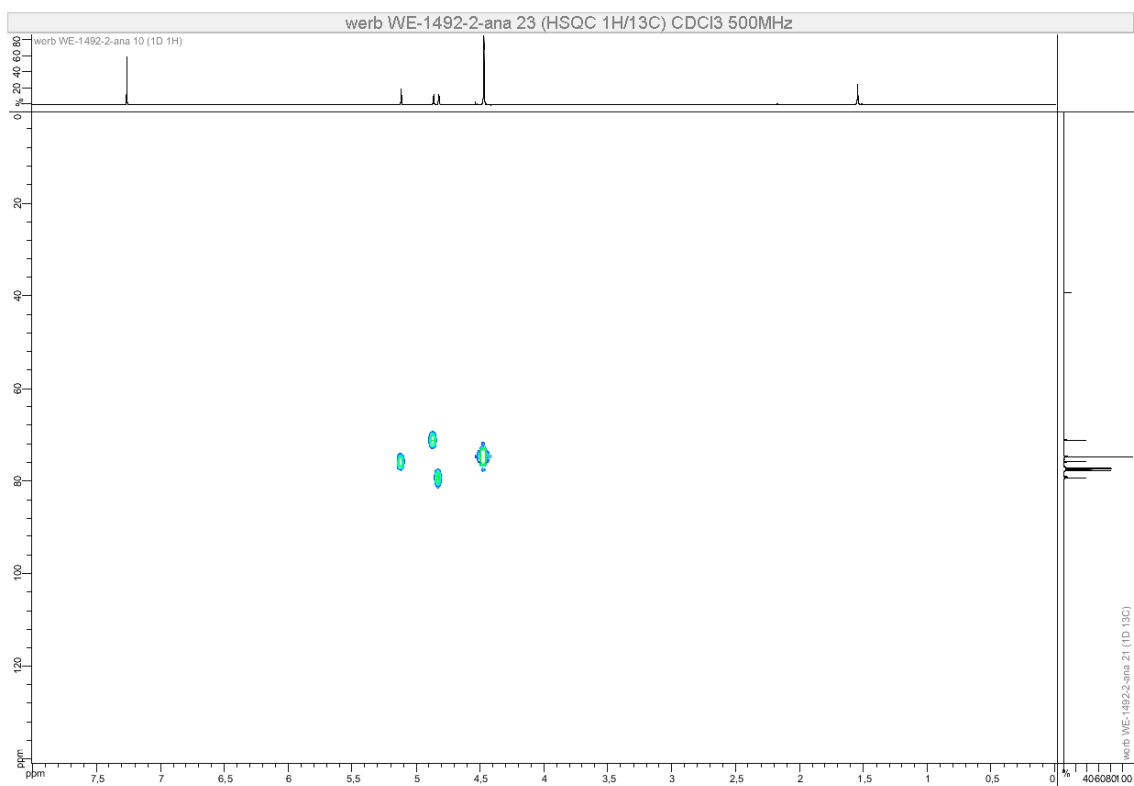
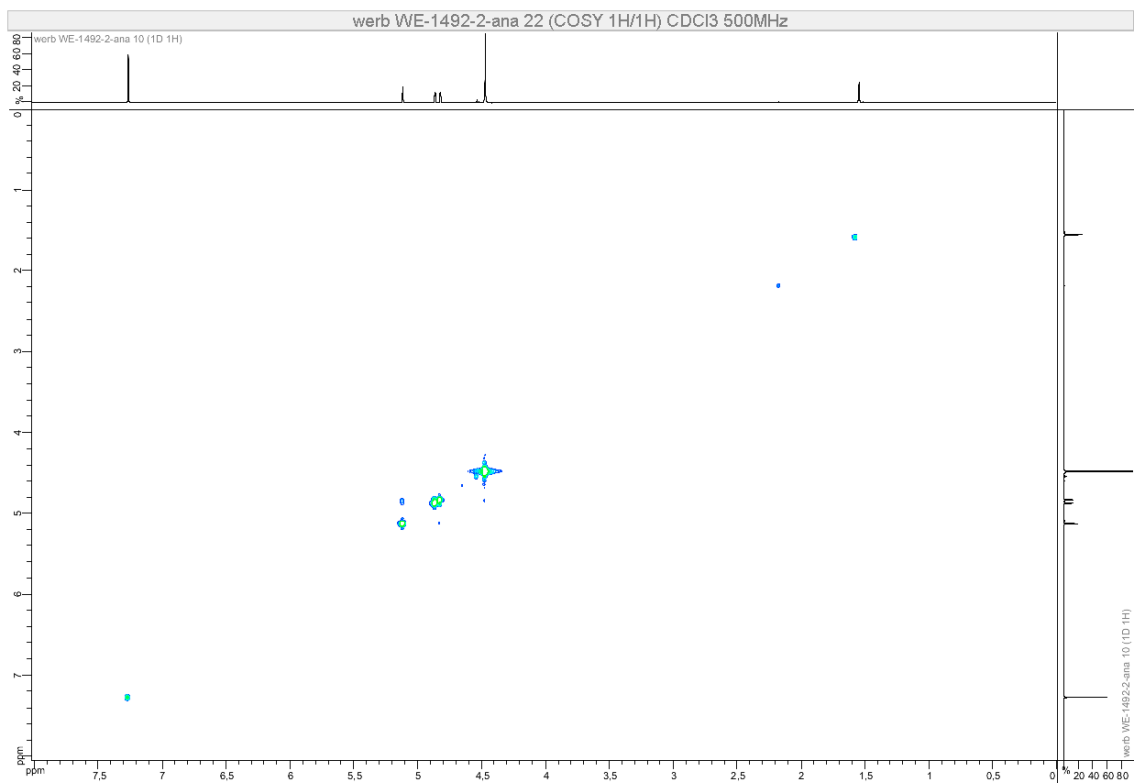


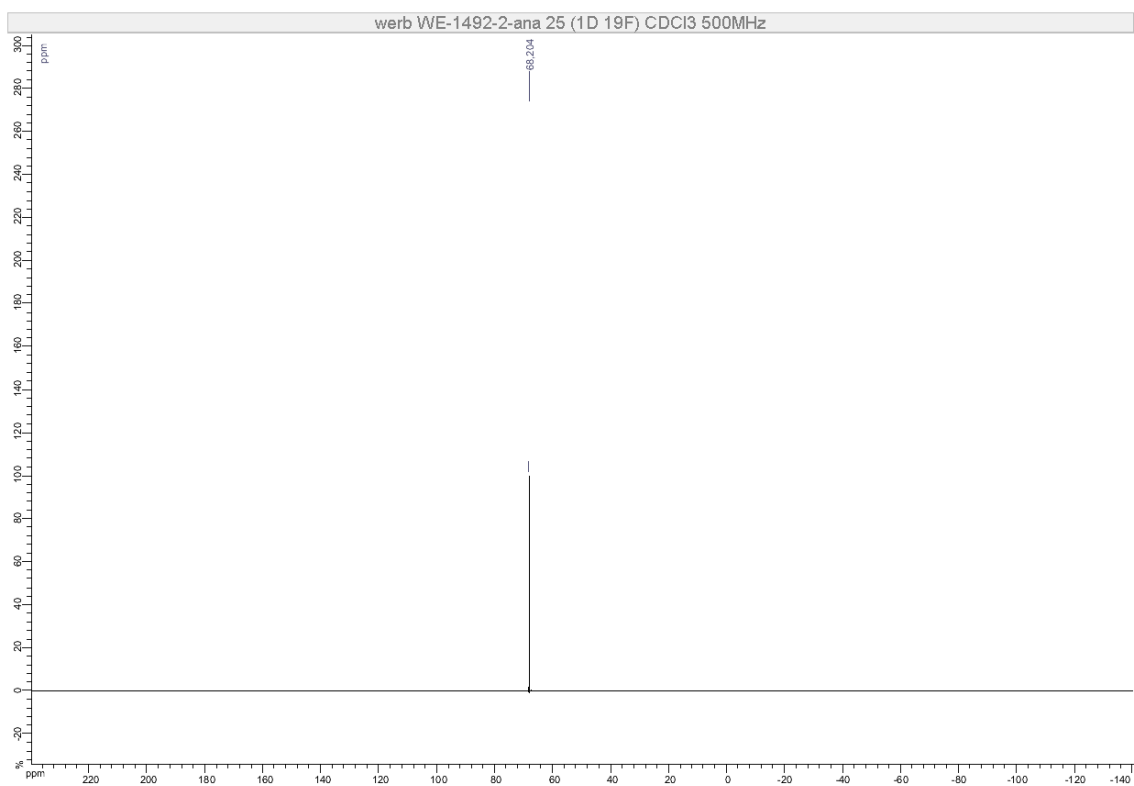
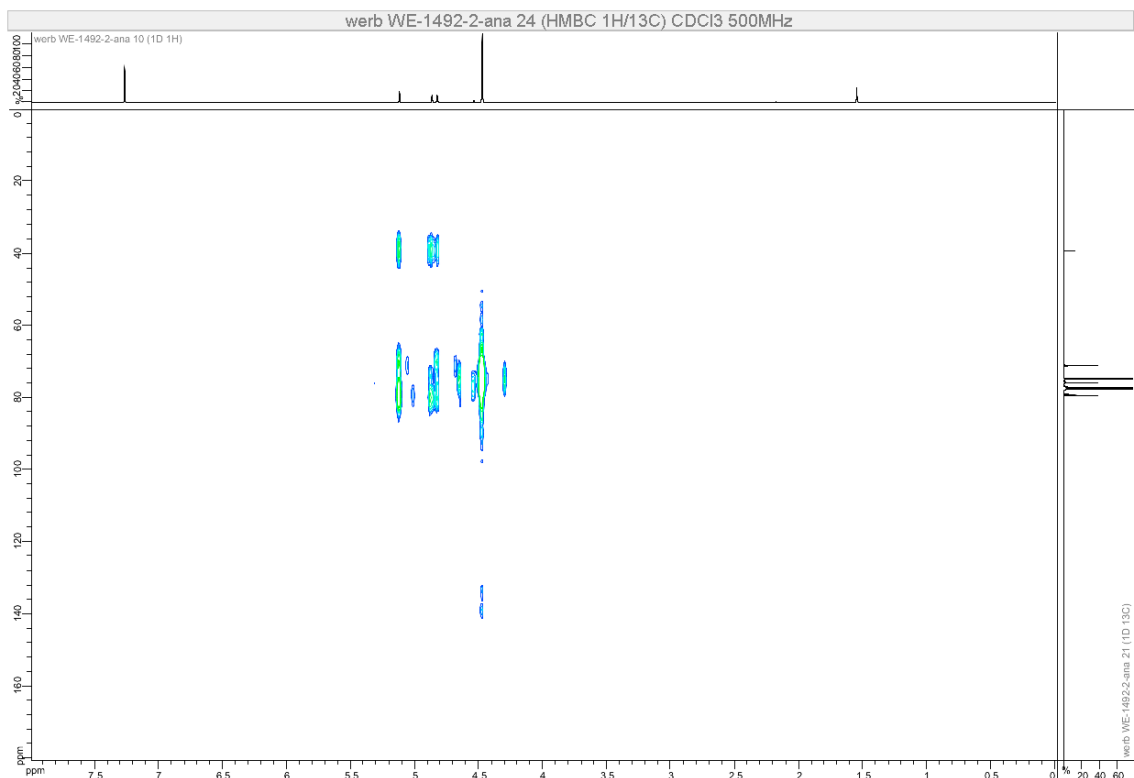




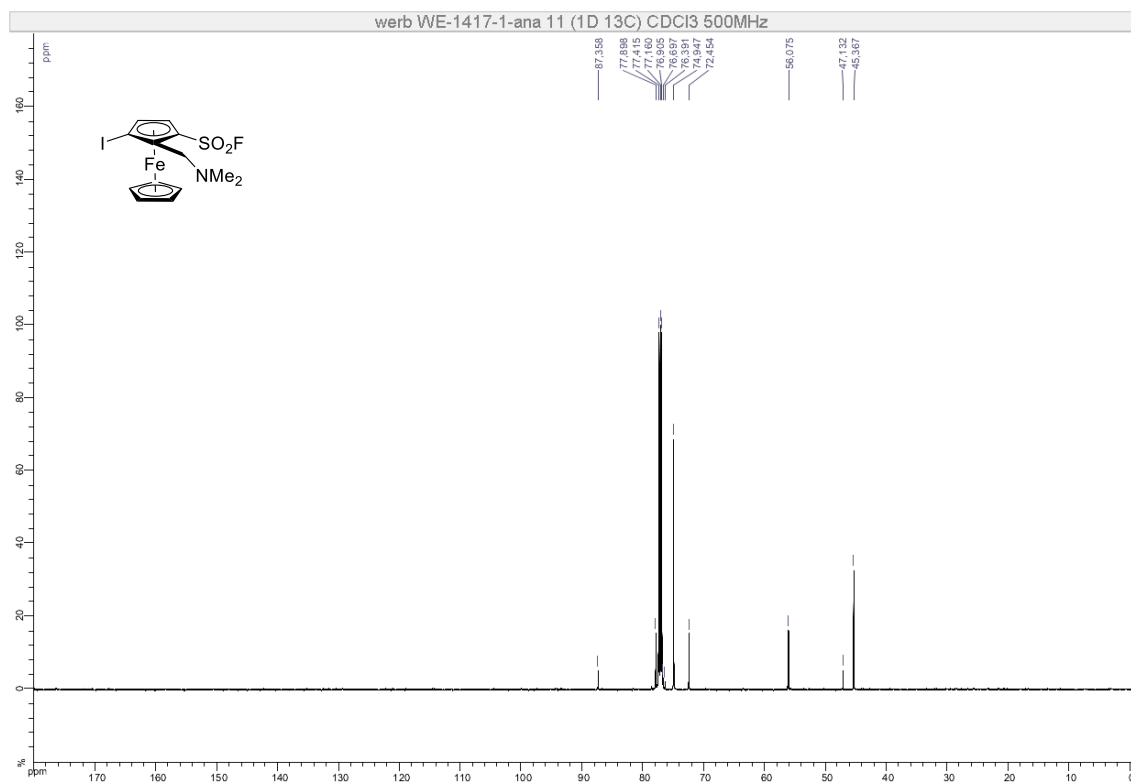
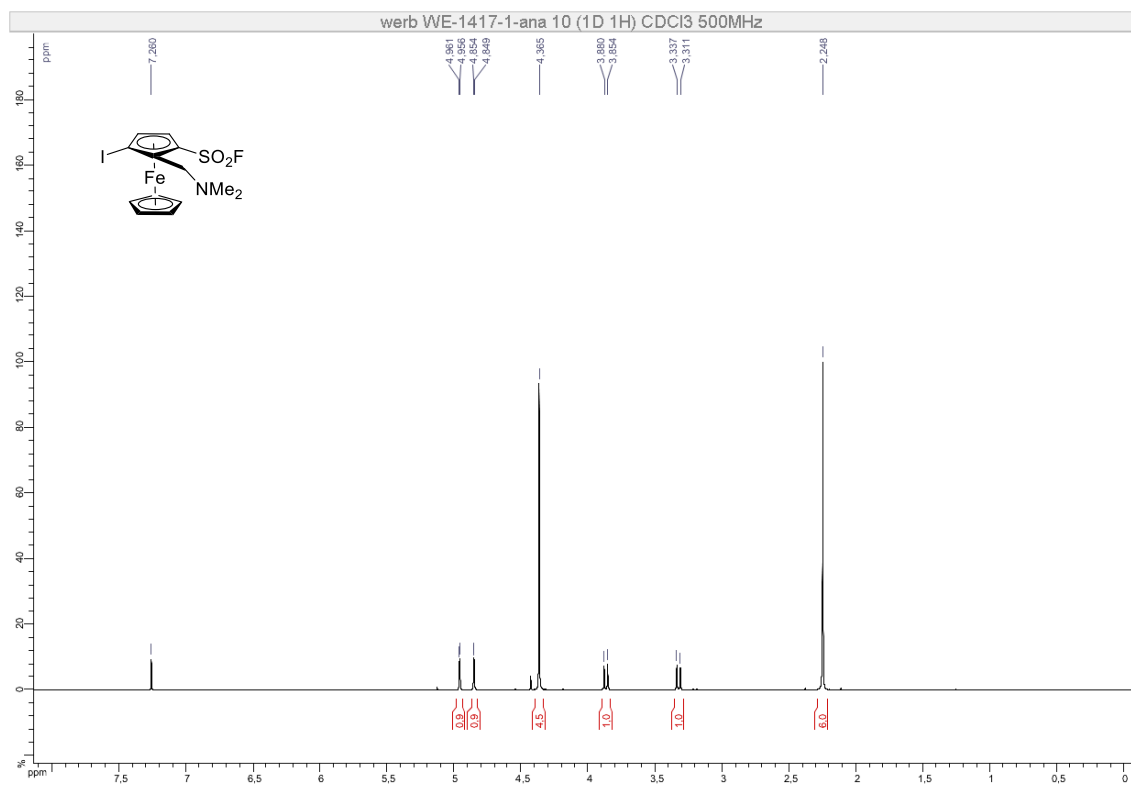
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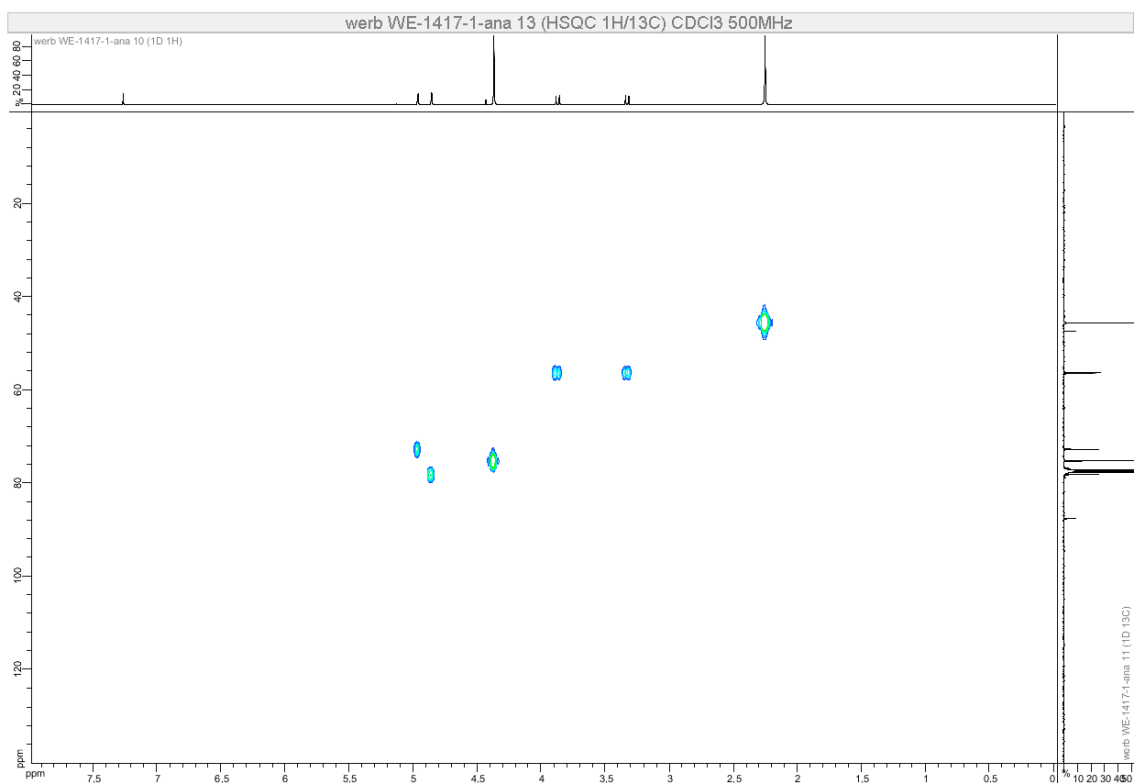
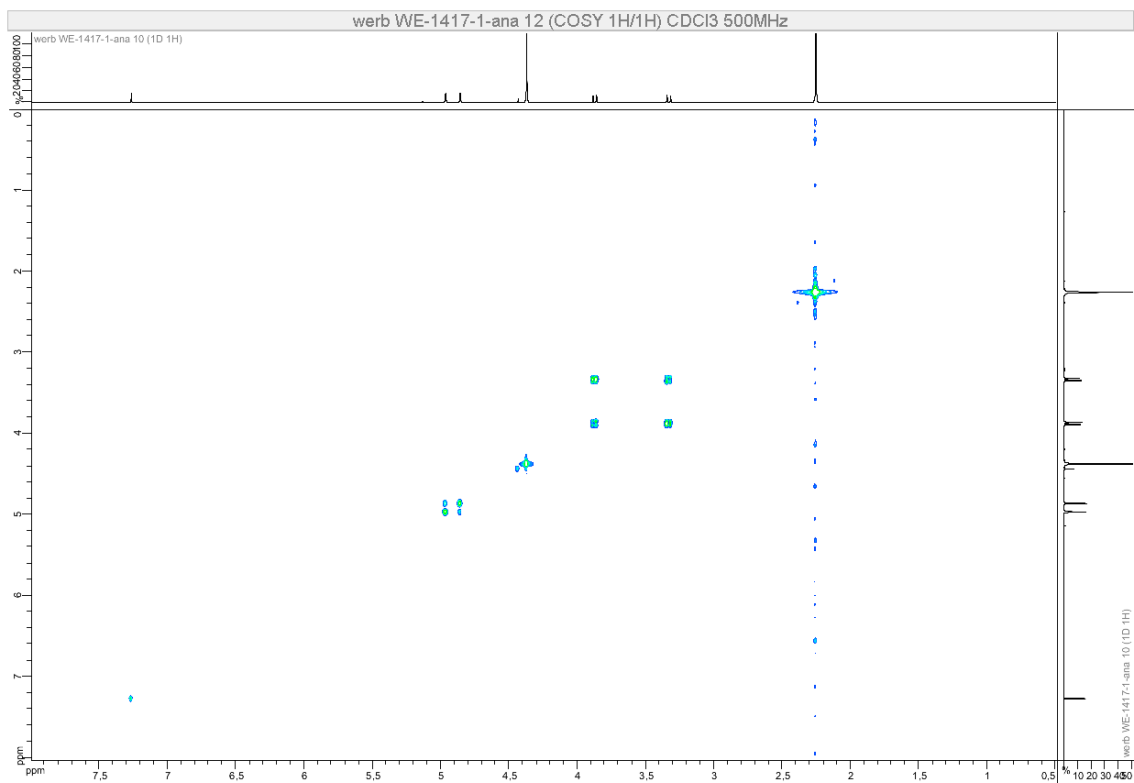


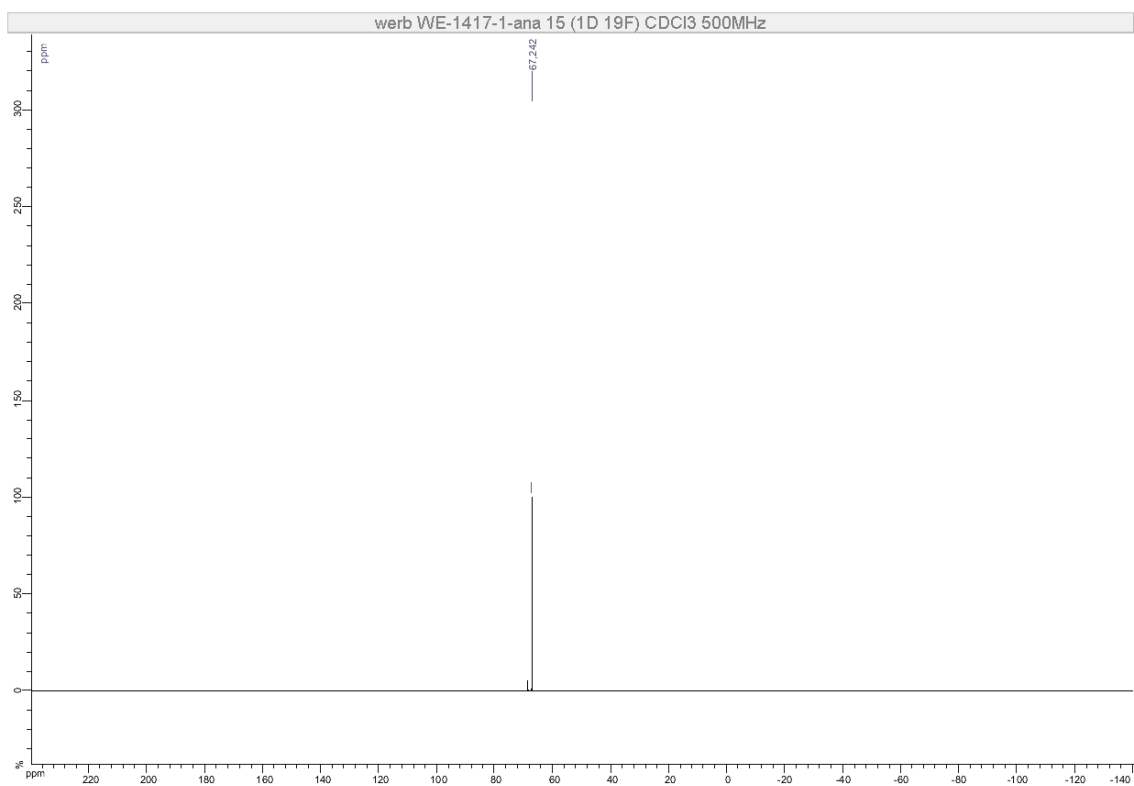
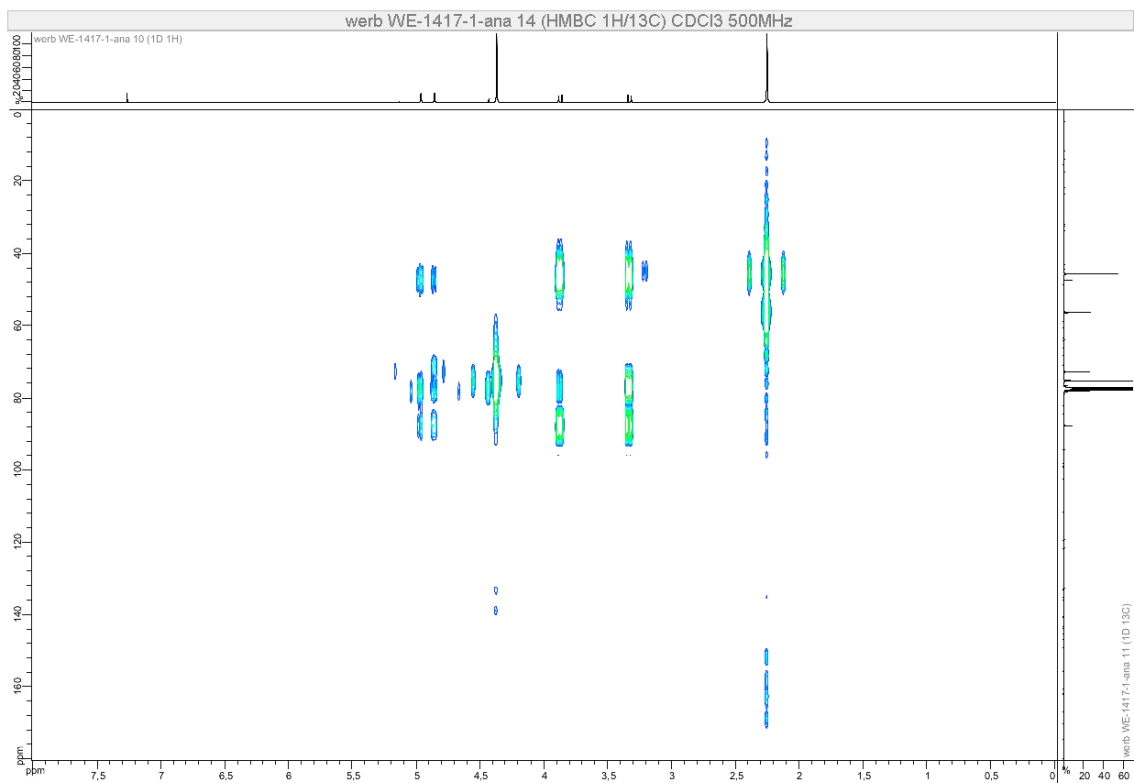




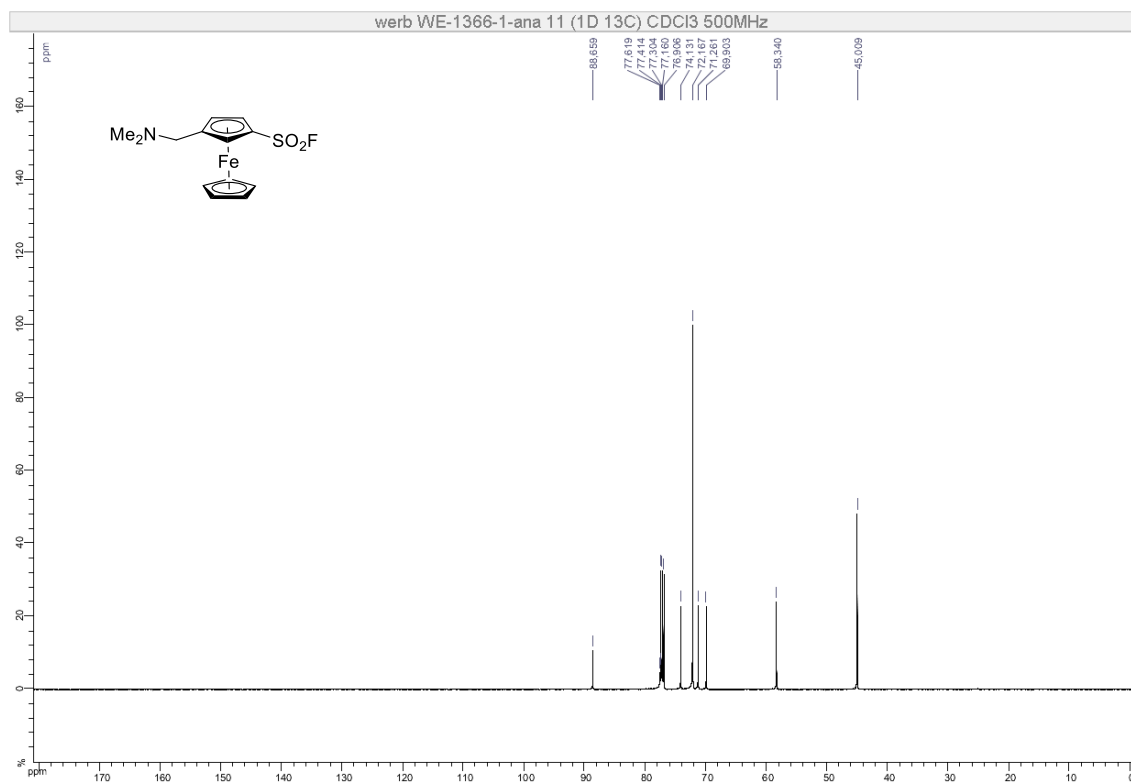
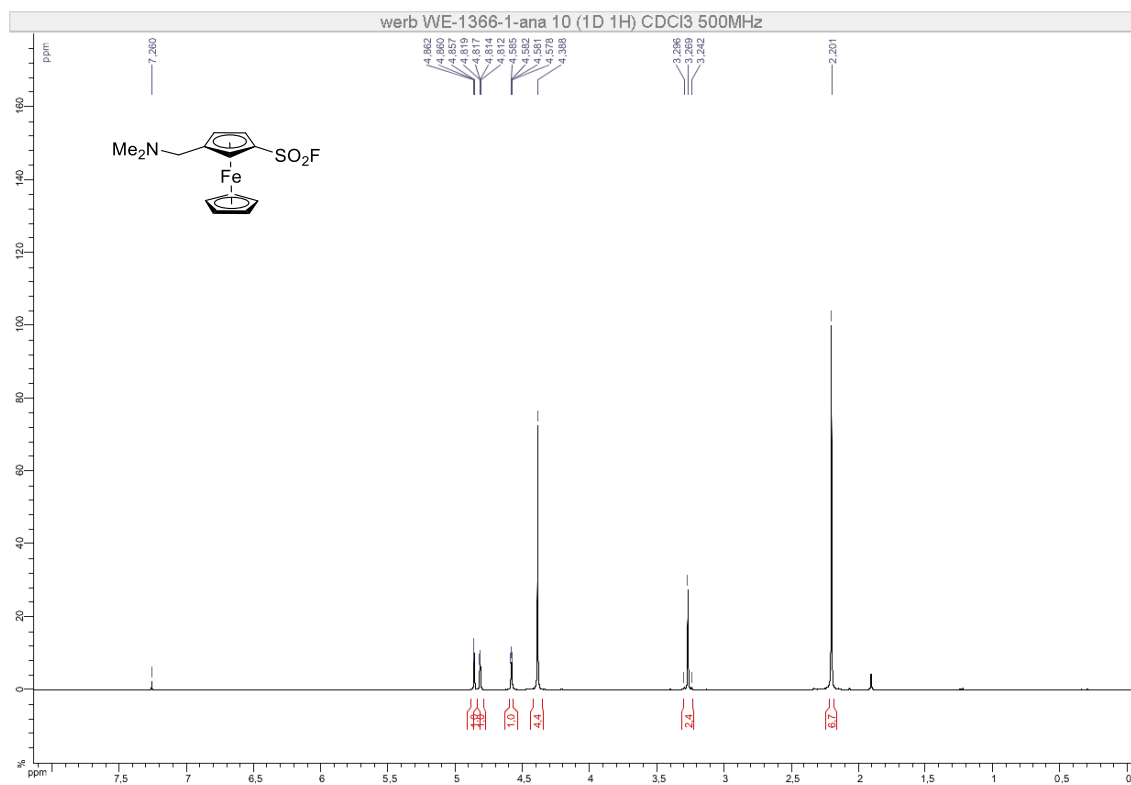
Compound 6b

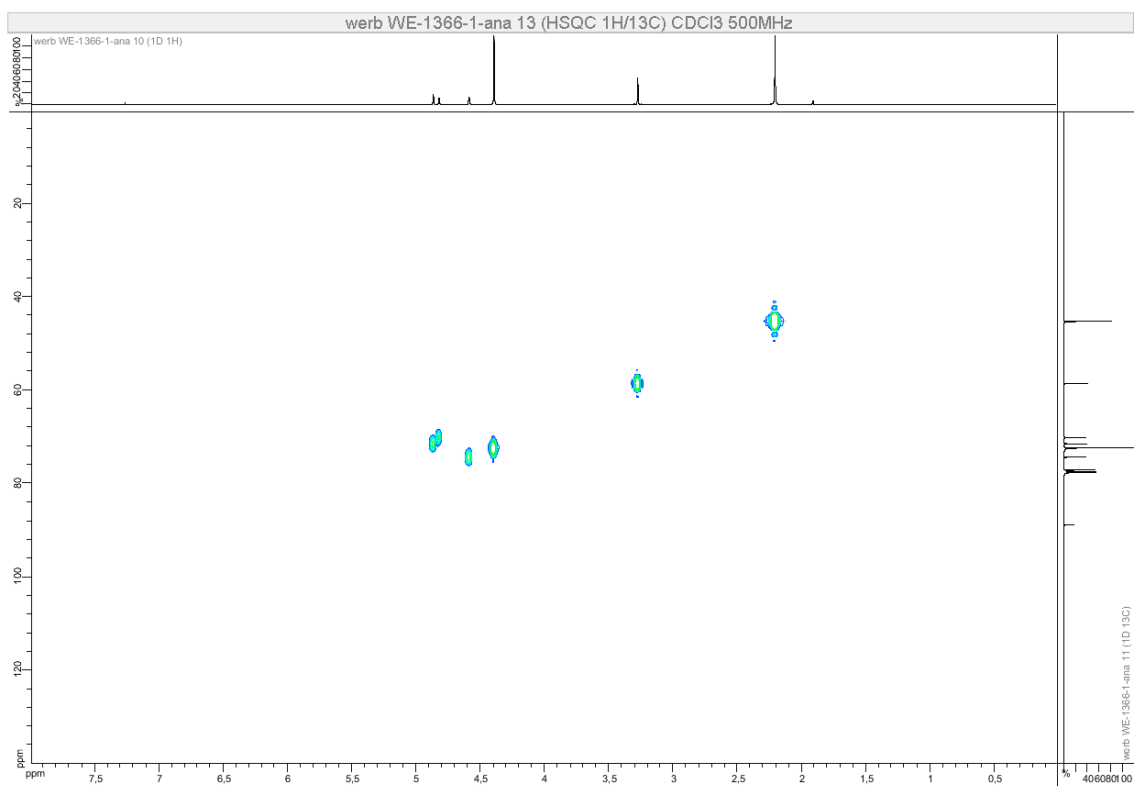
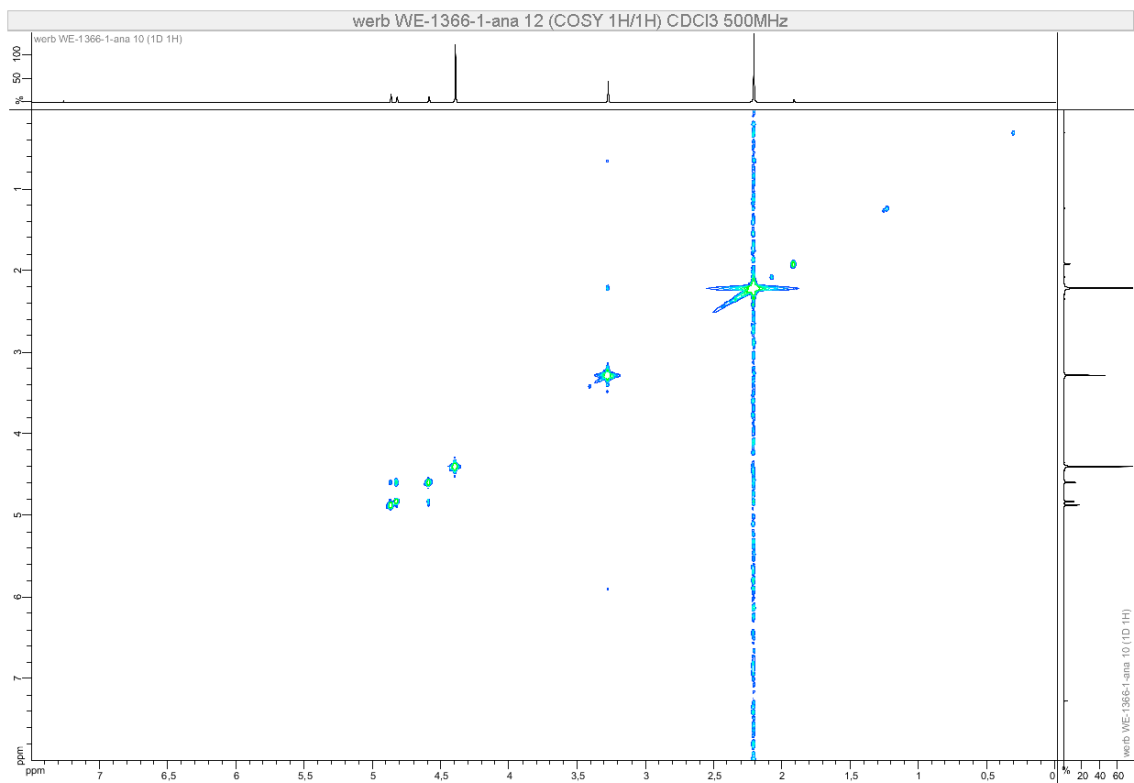


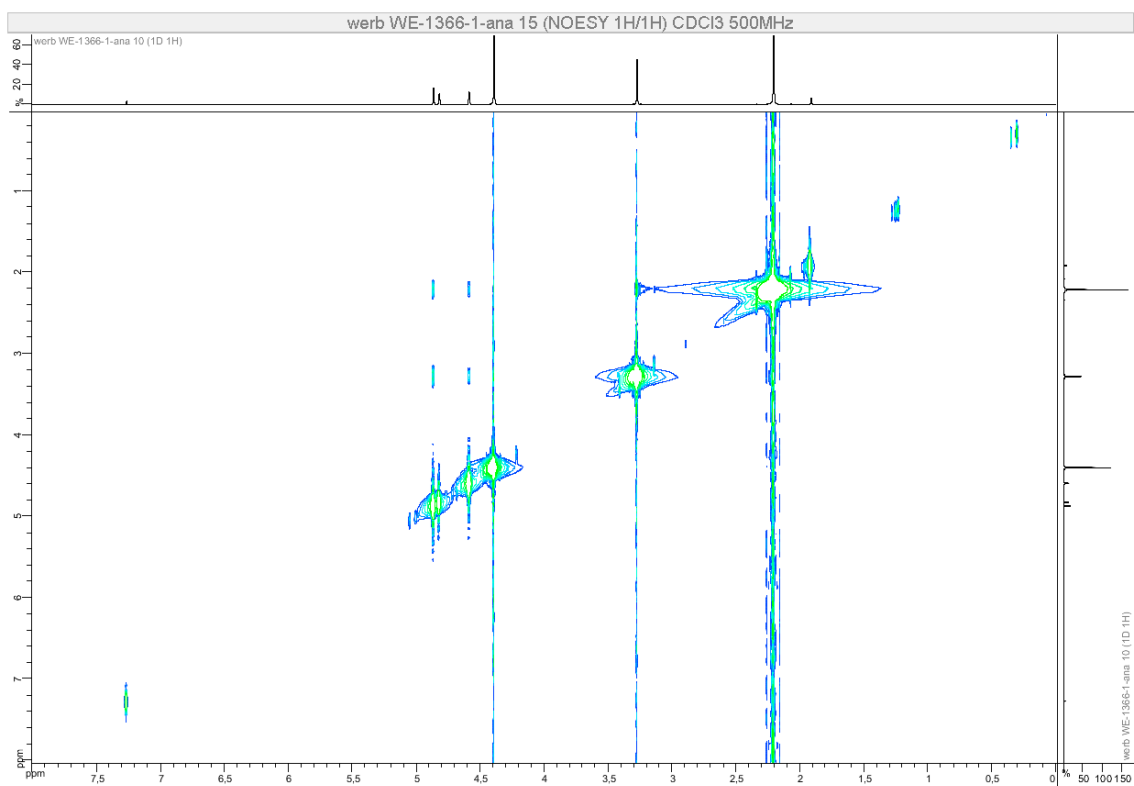
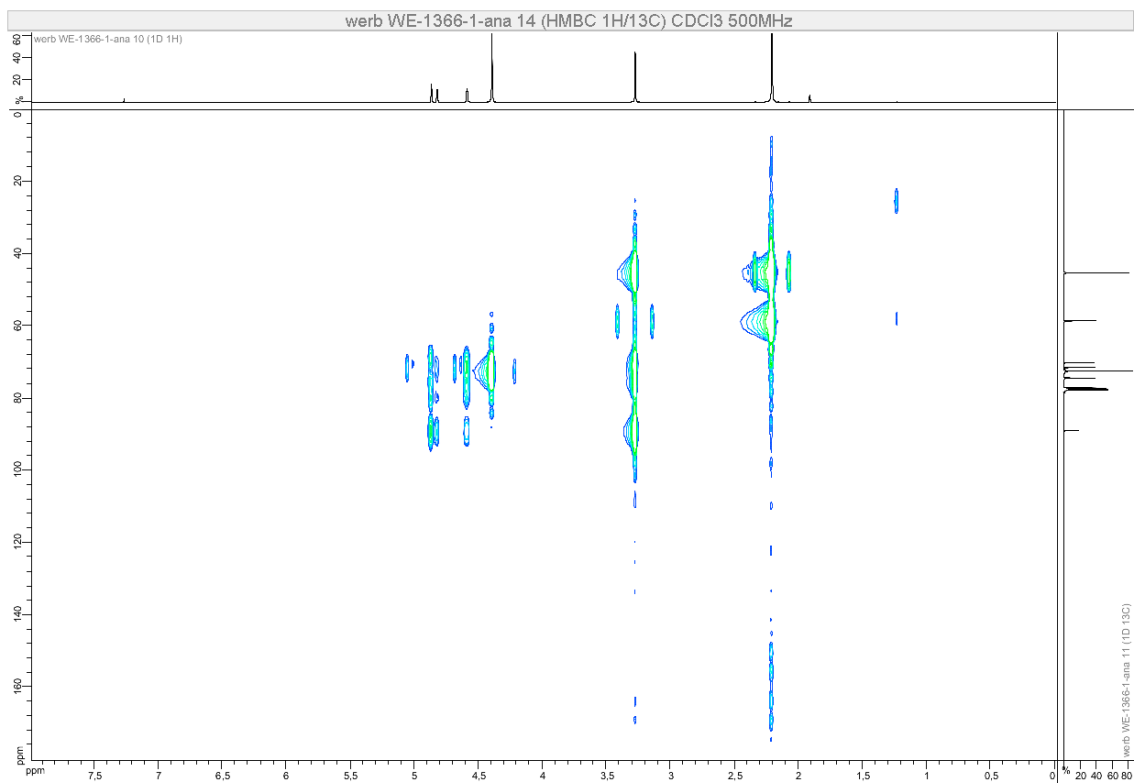


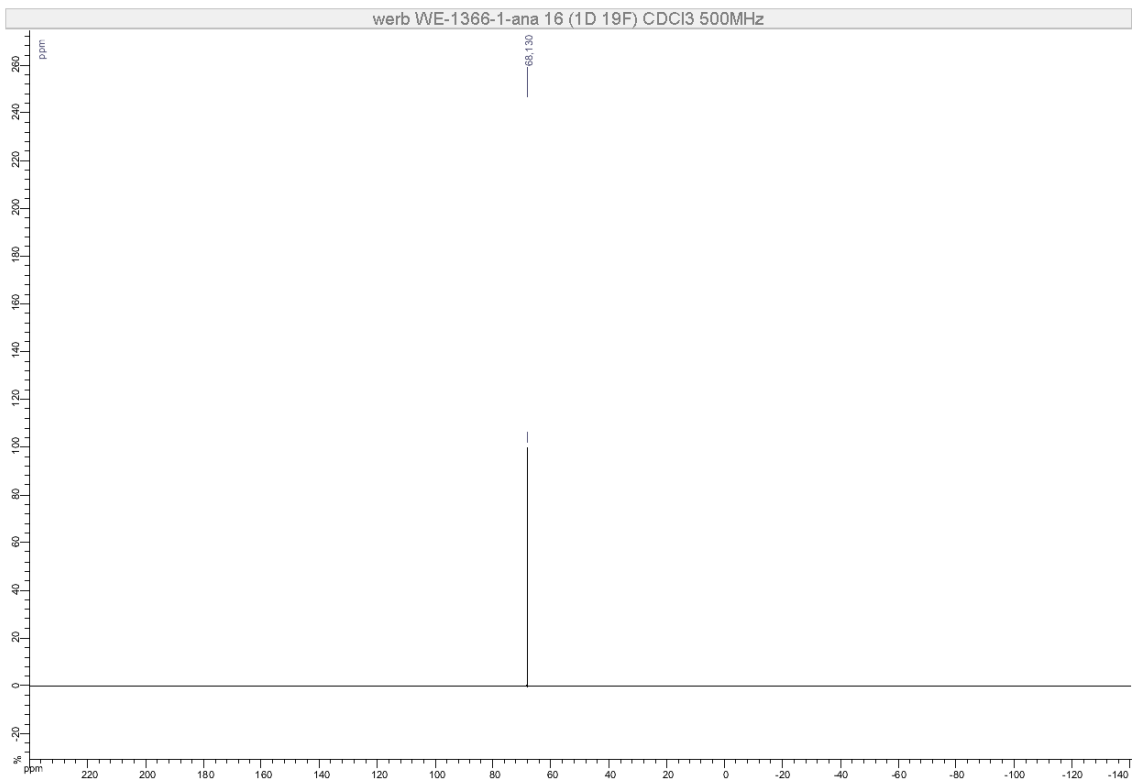


Compound 7a

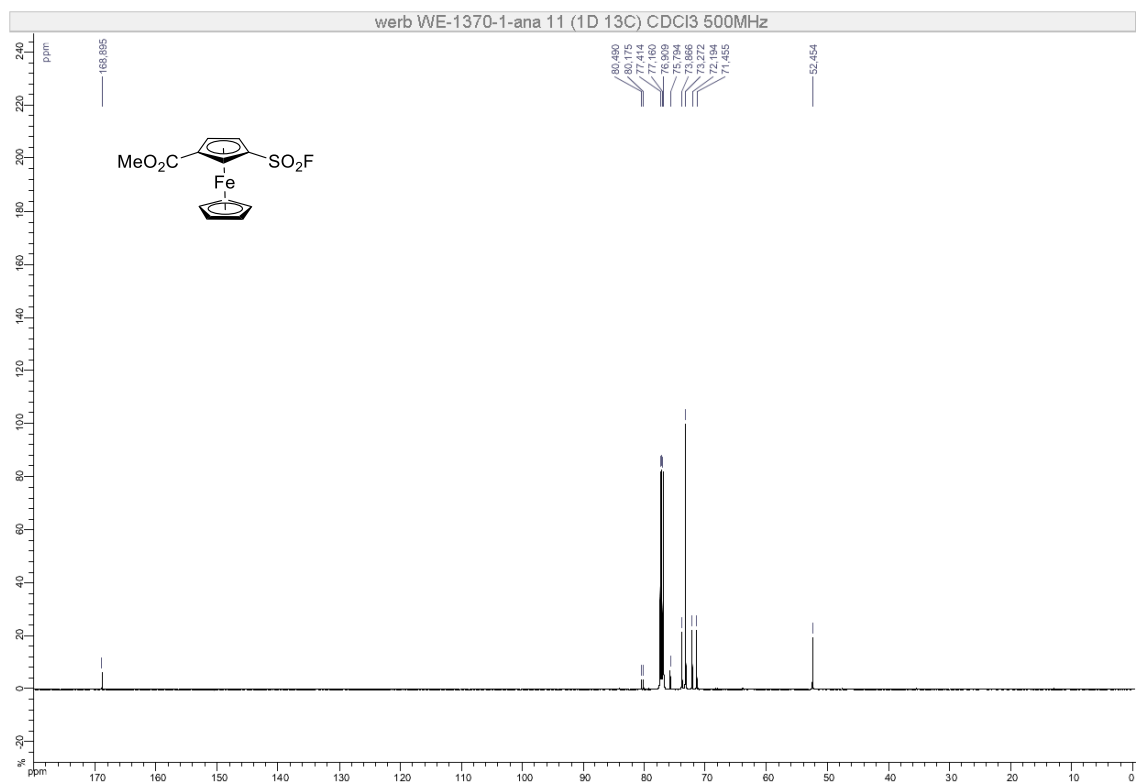
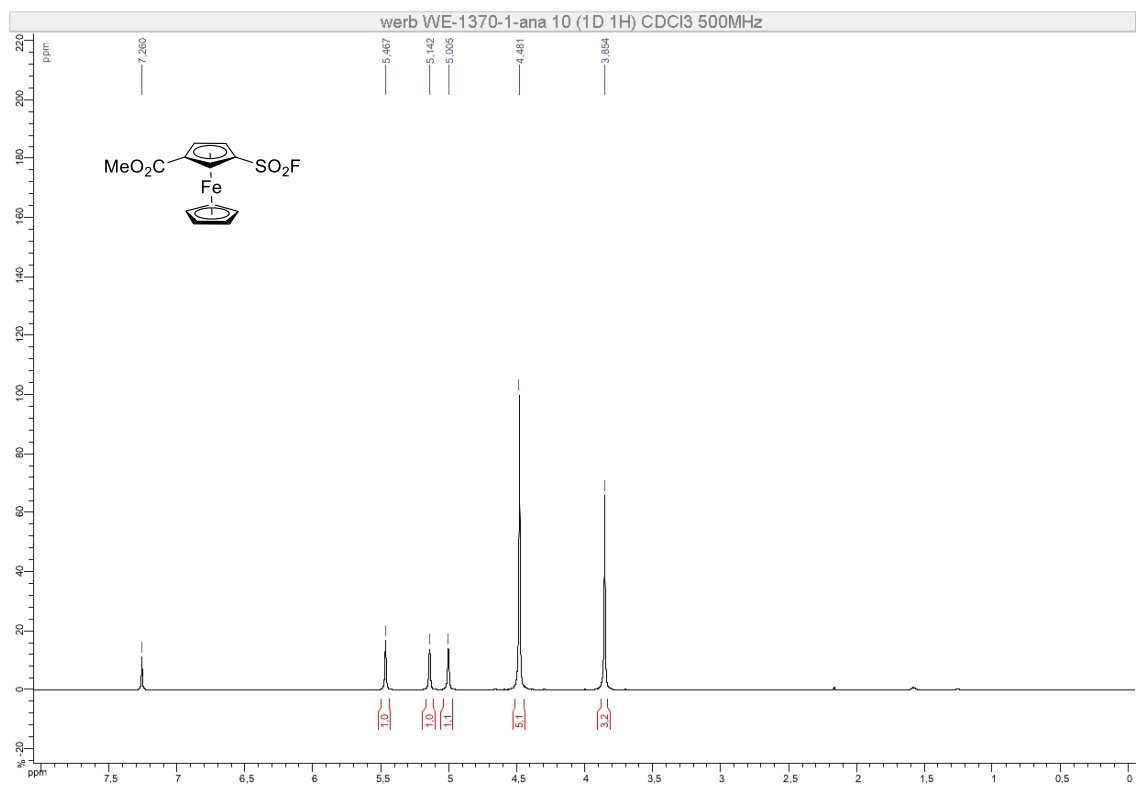


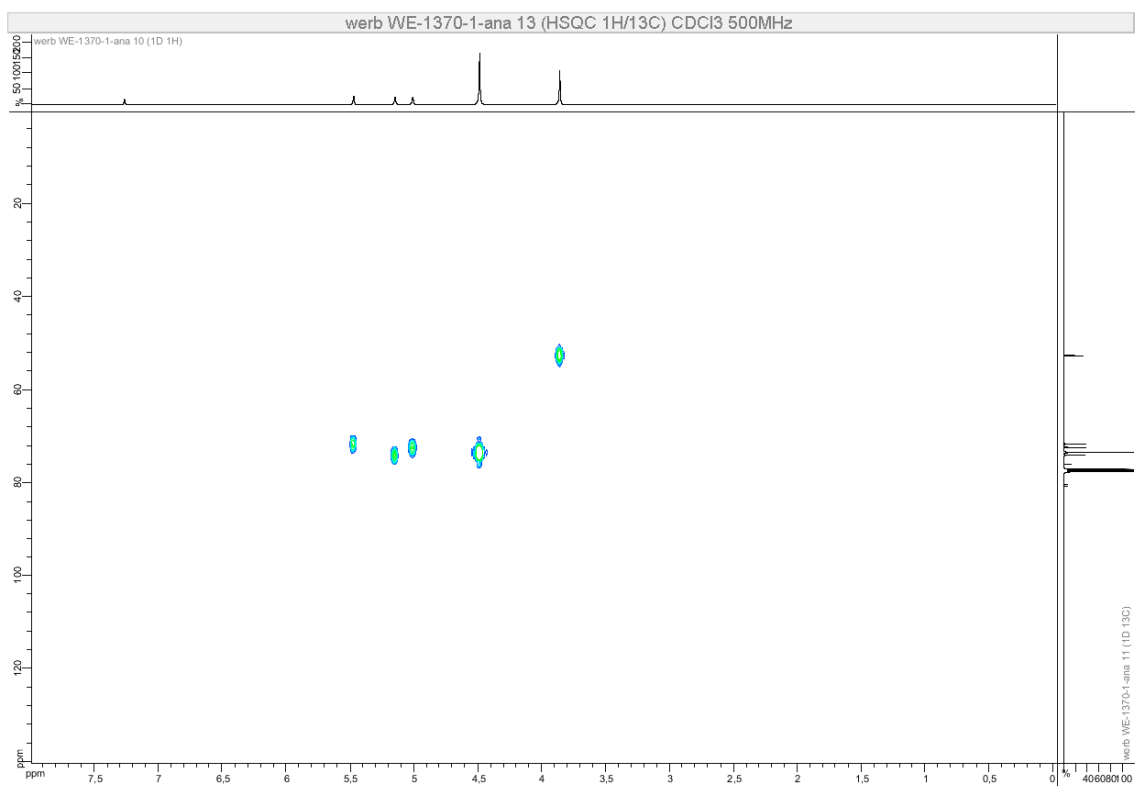
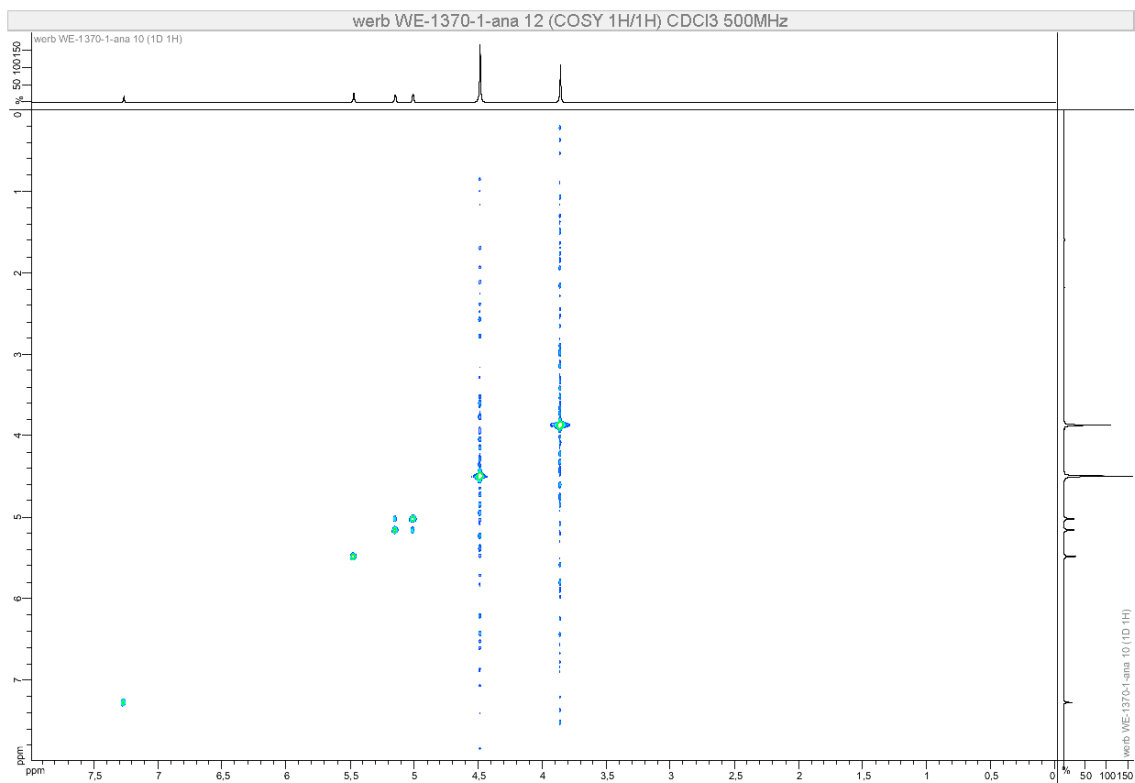


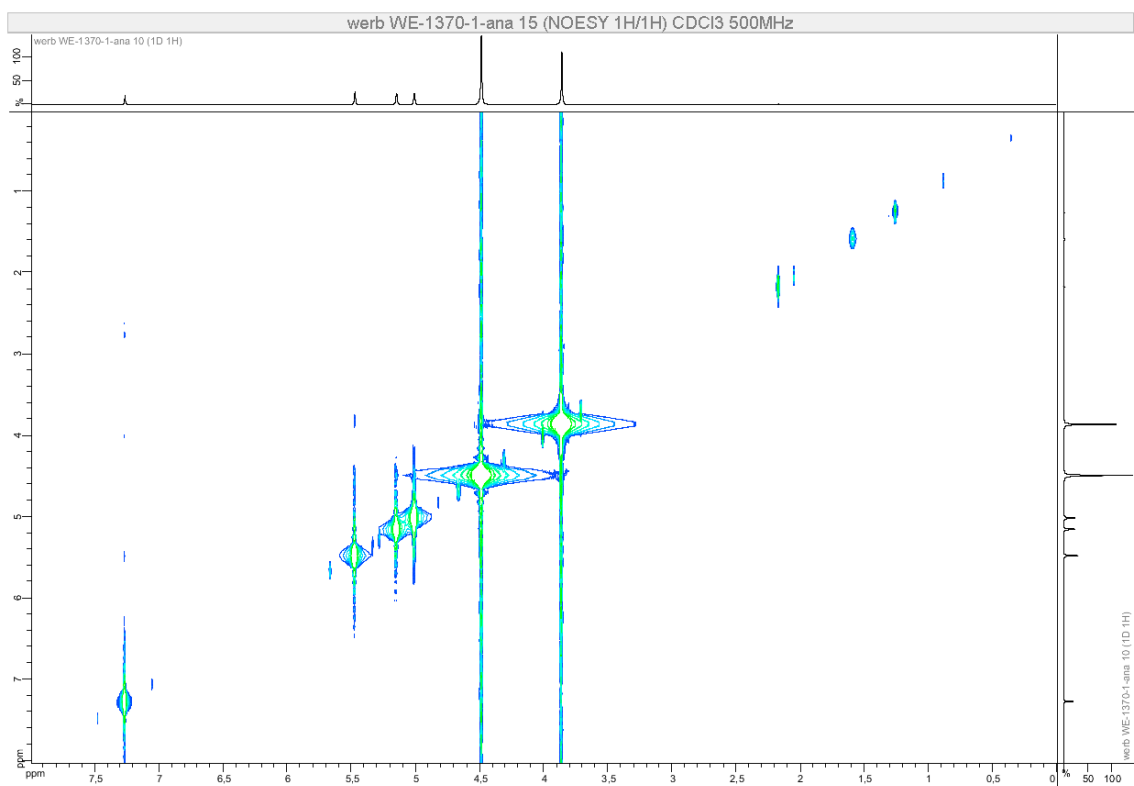
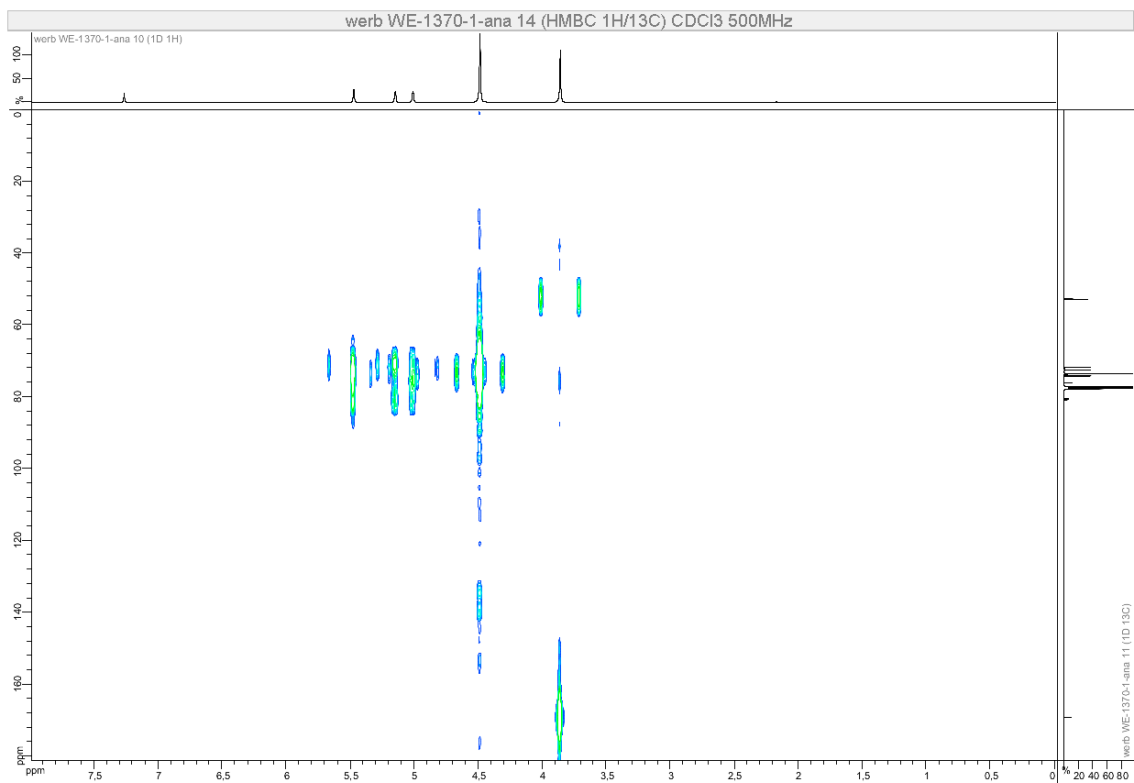


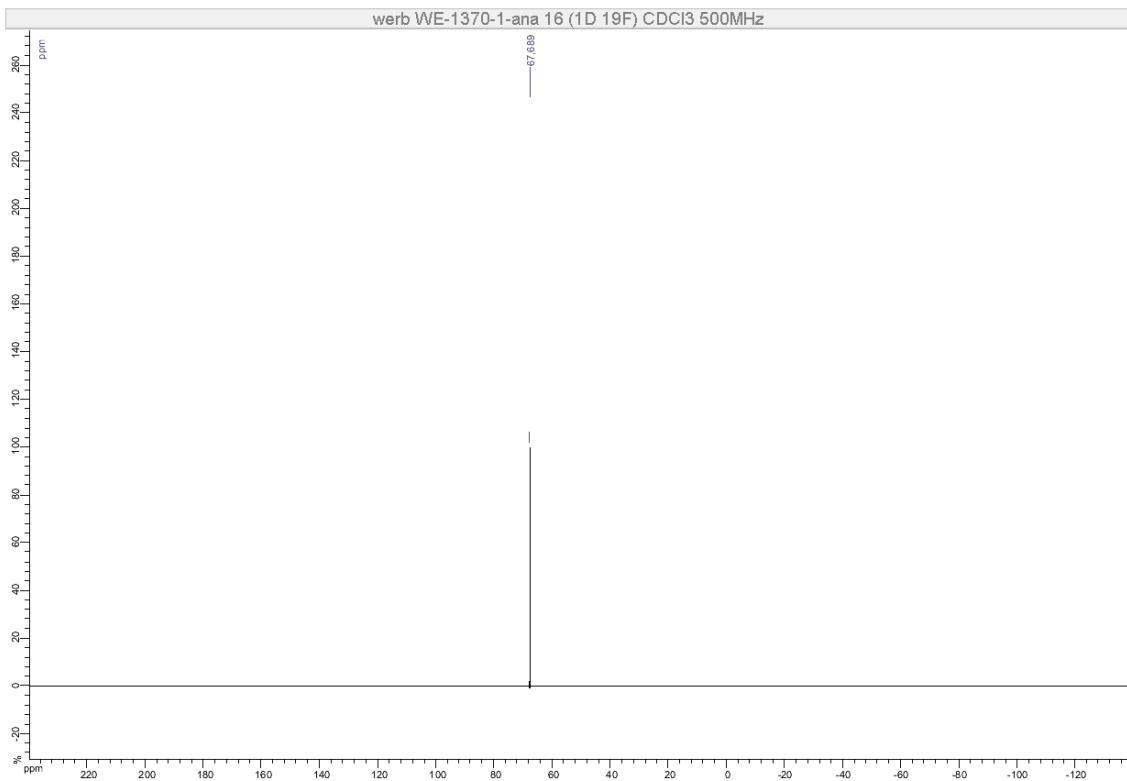


Compound 7b

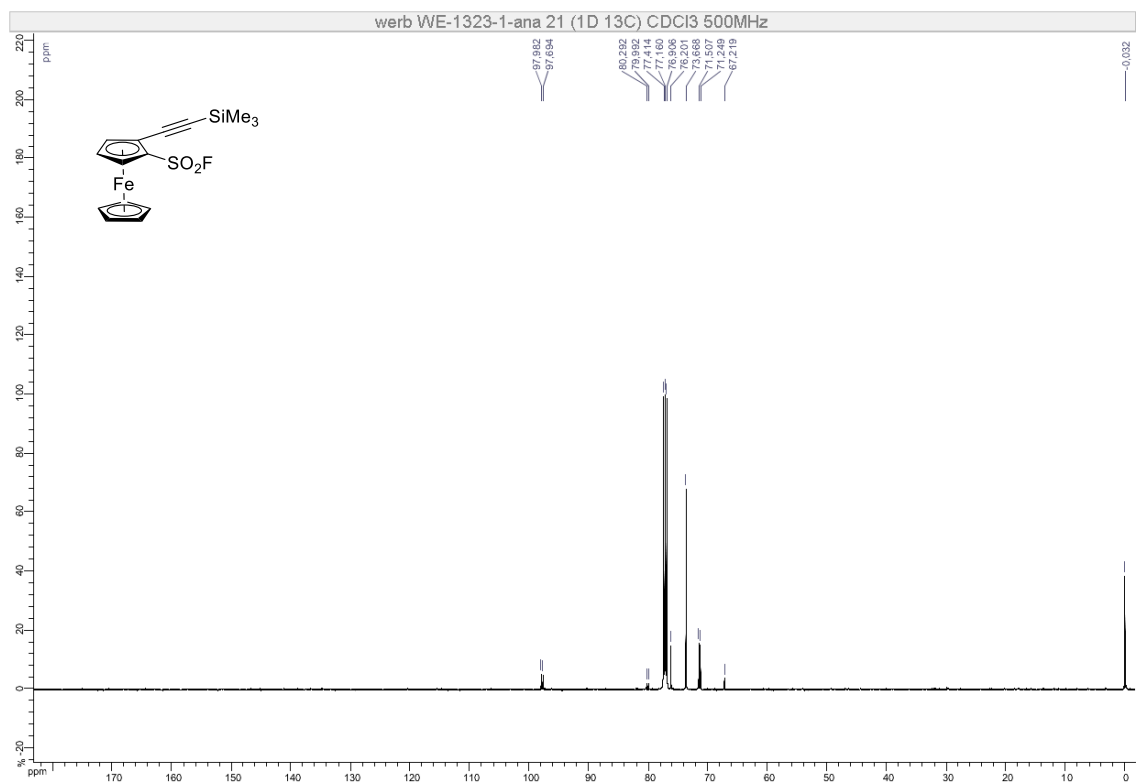
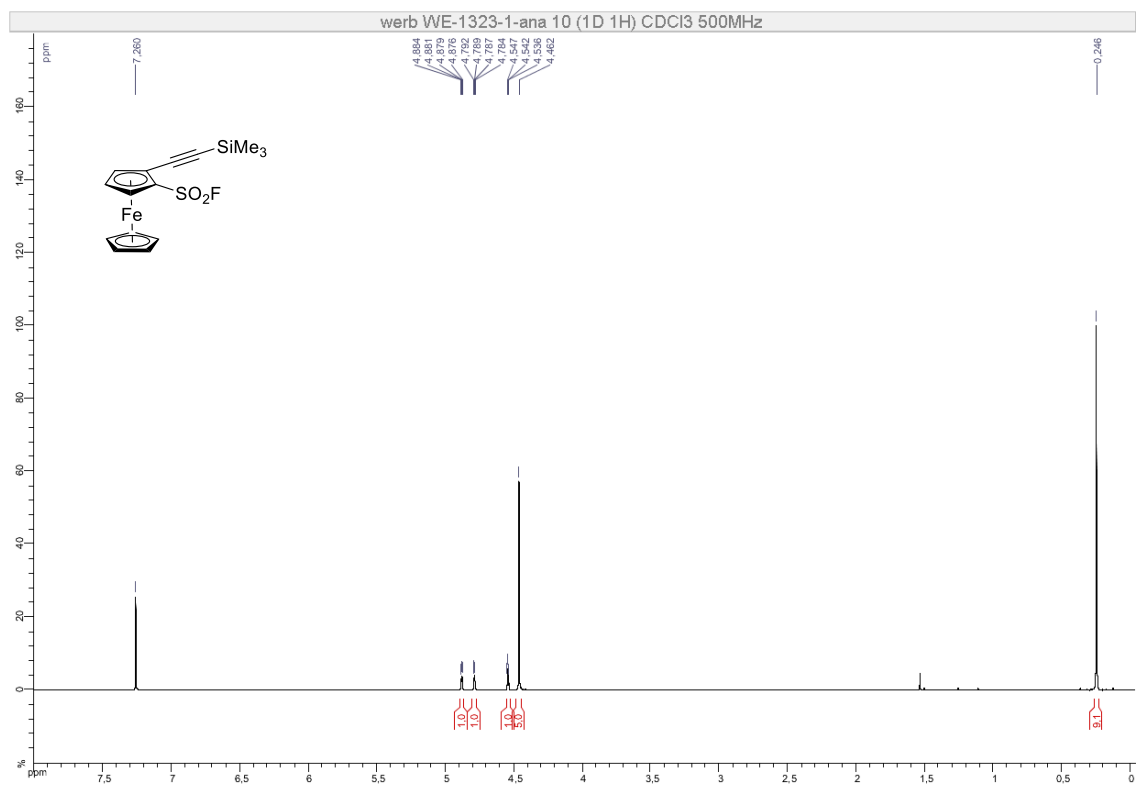


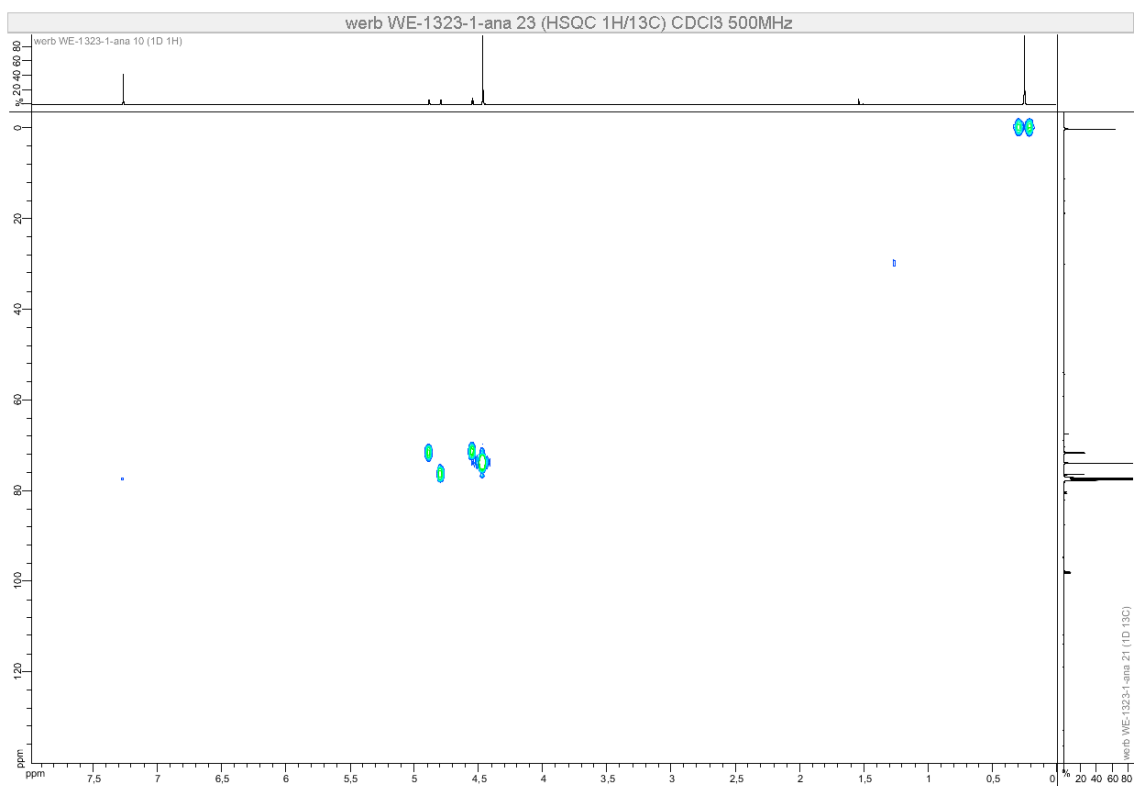
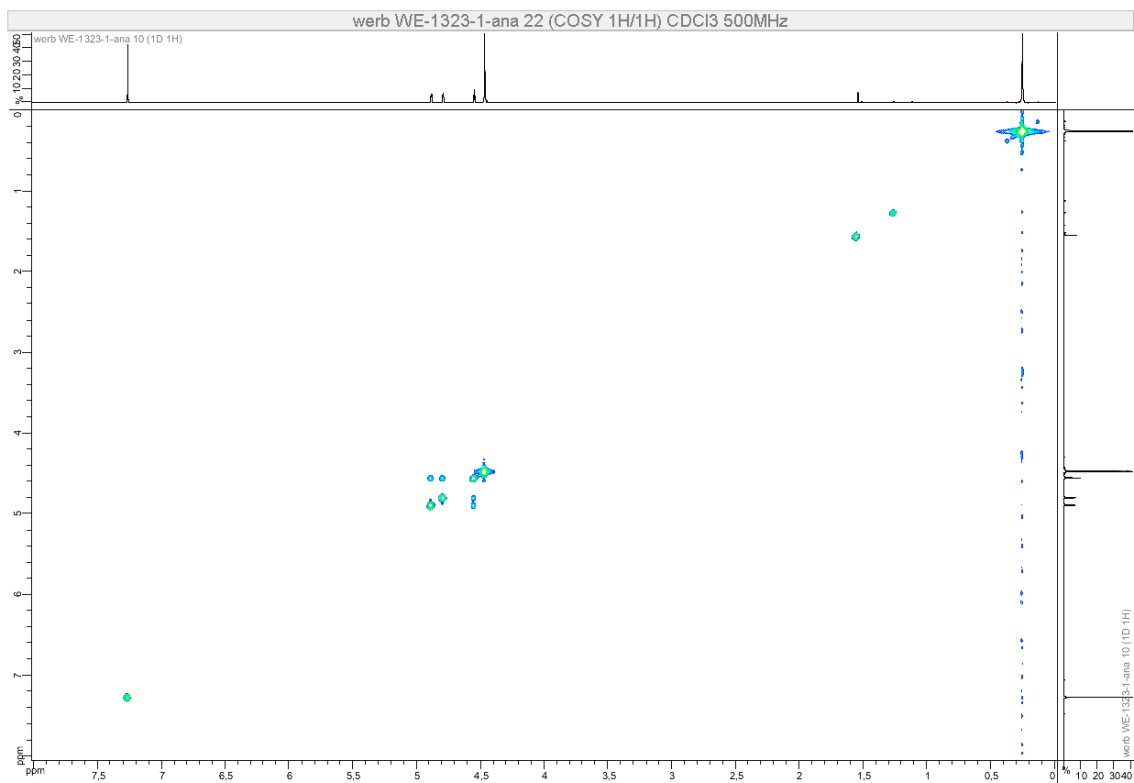


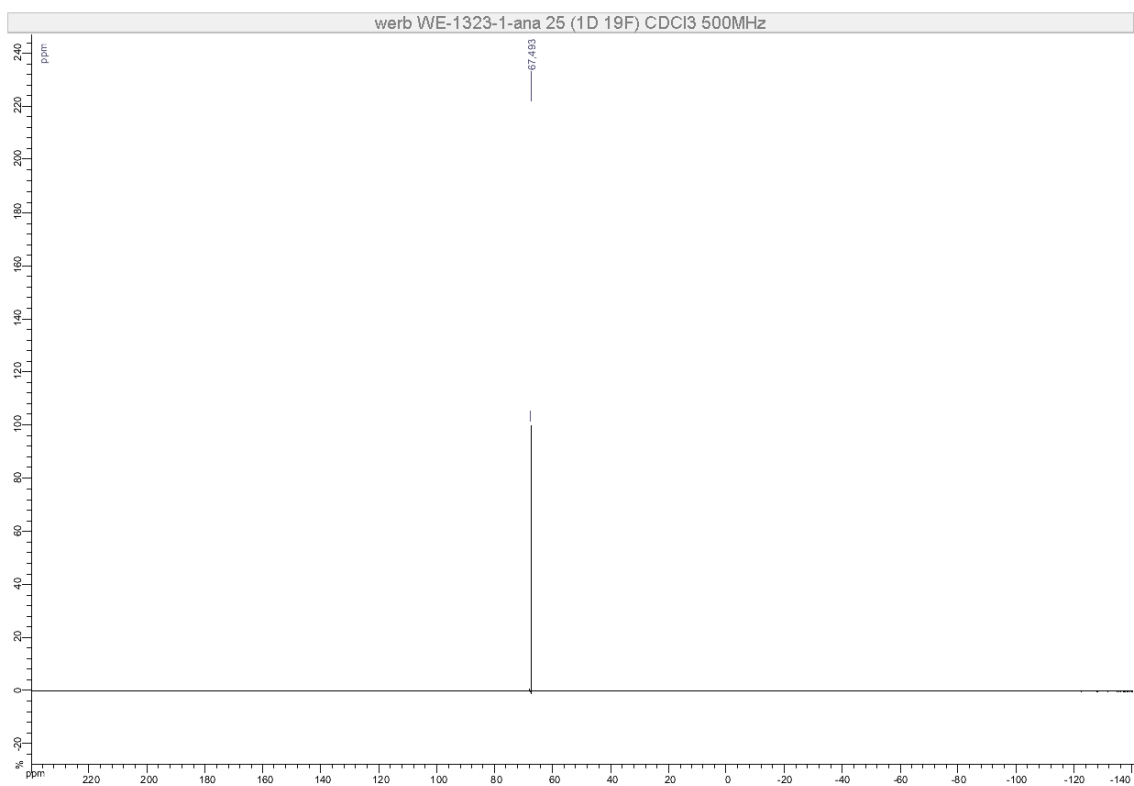
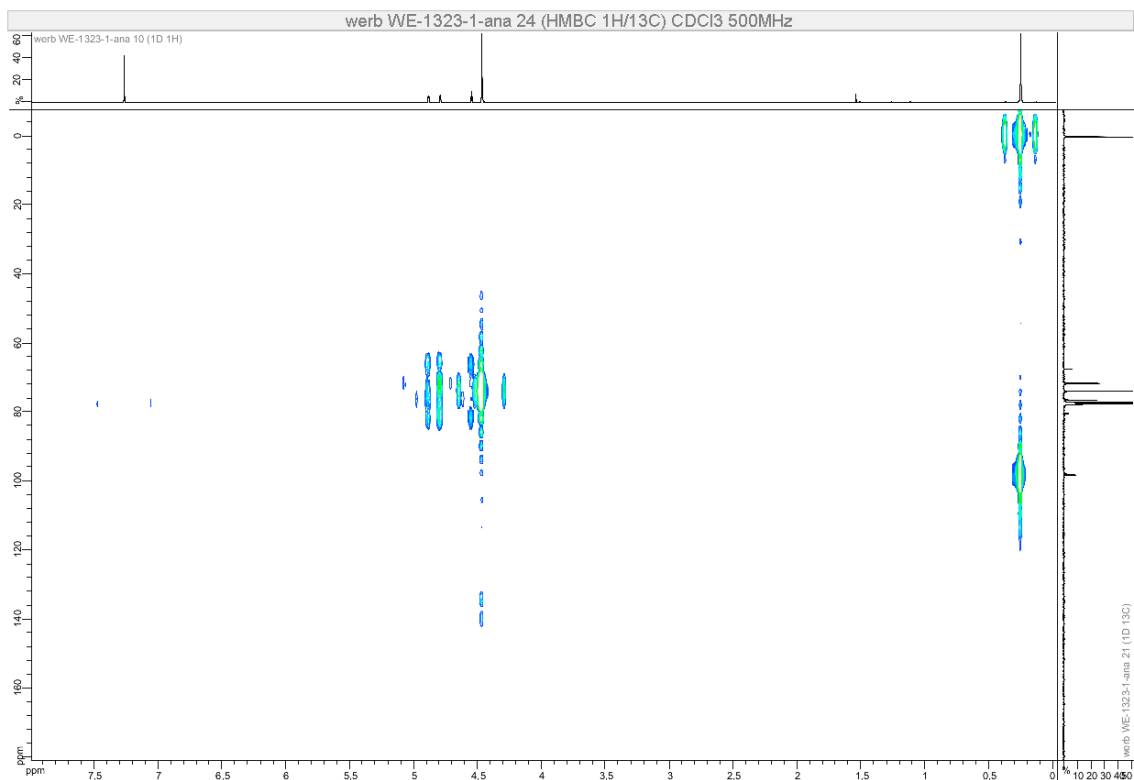




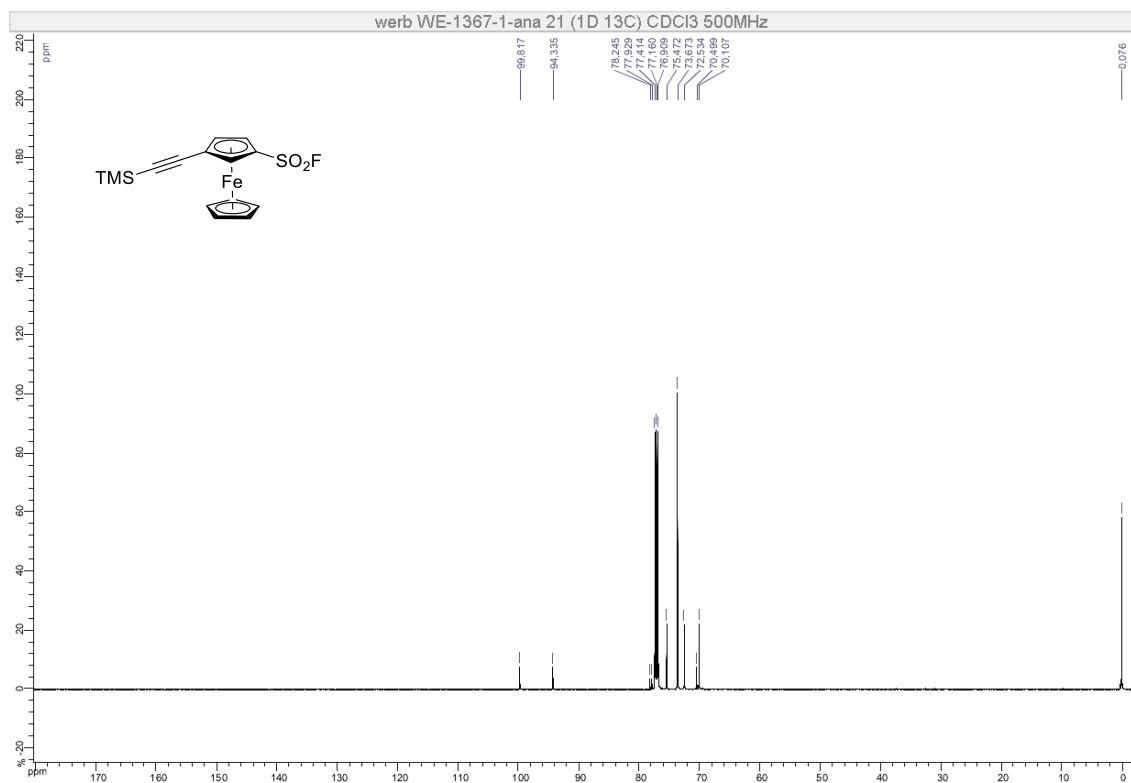
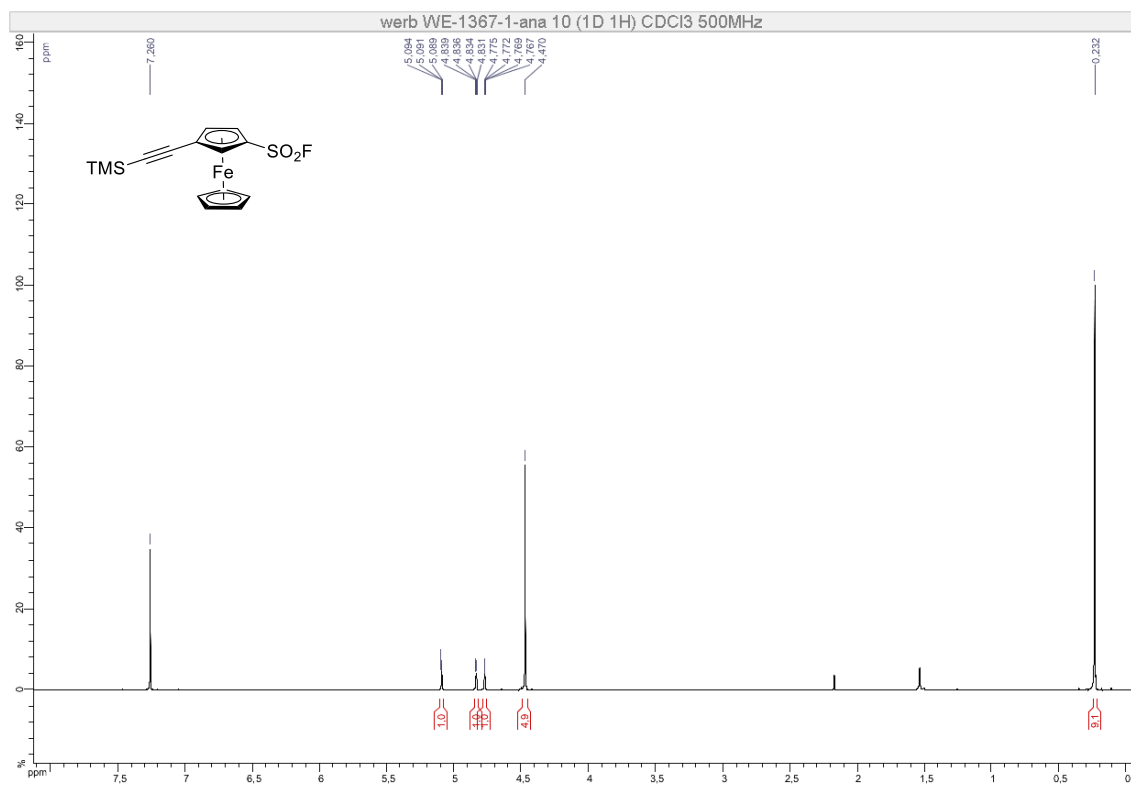
Compound 8a

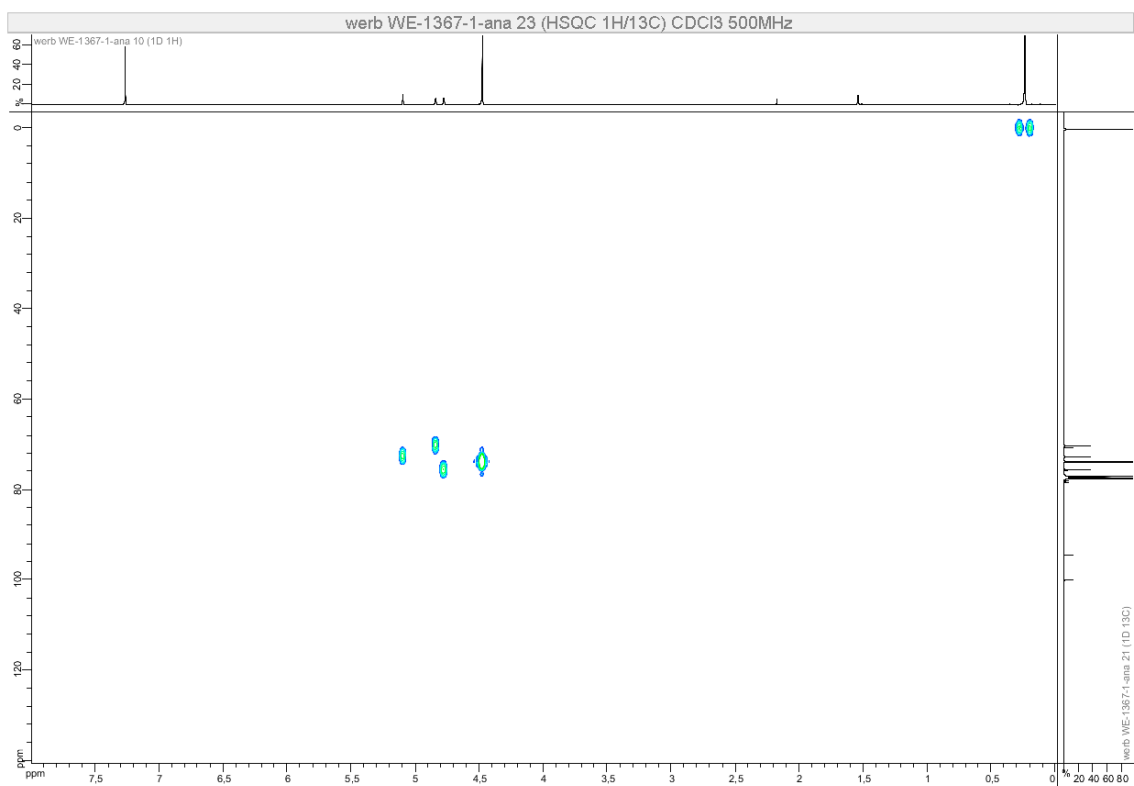
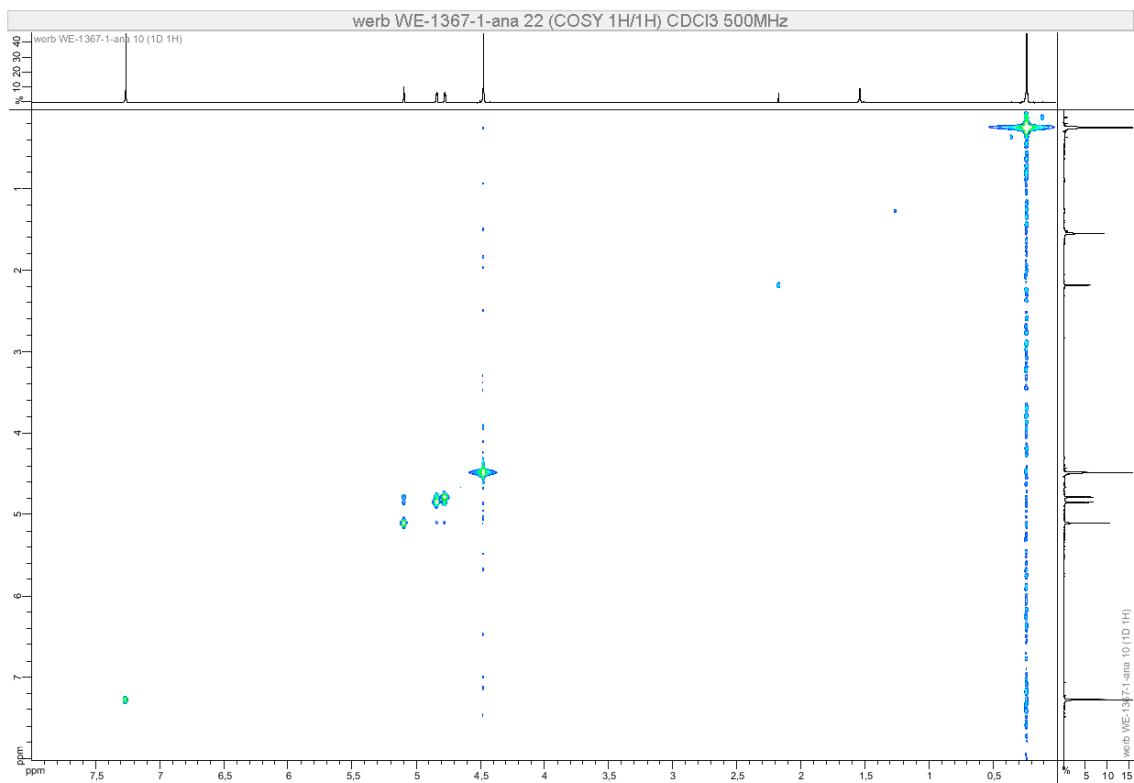


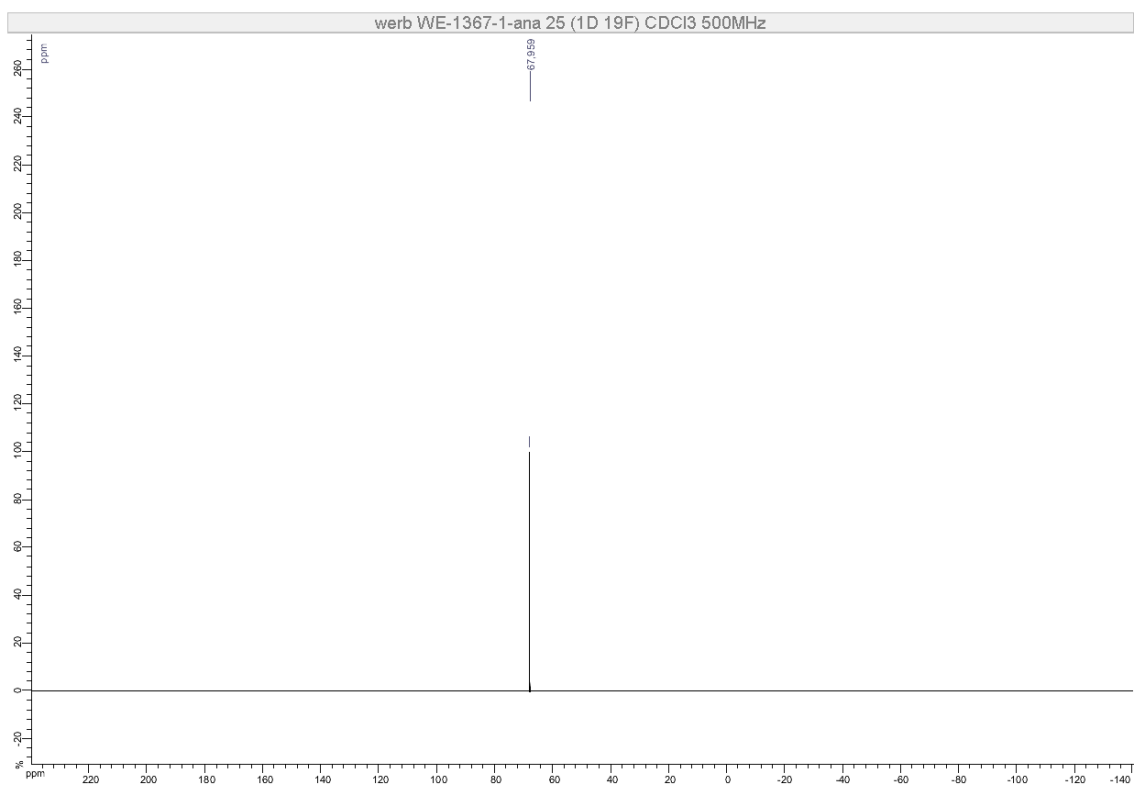
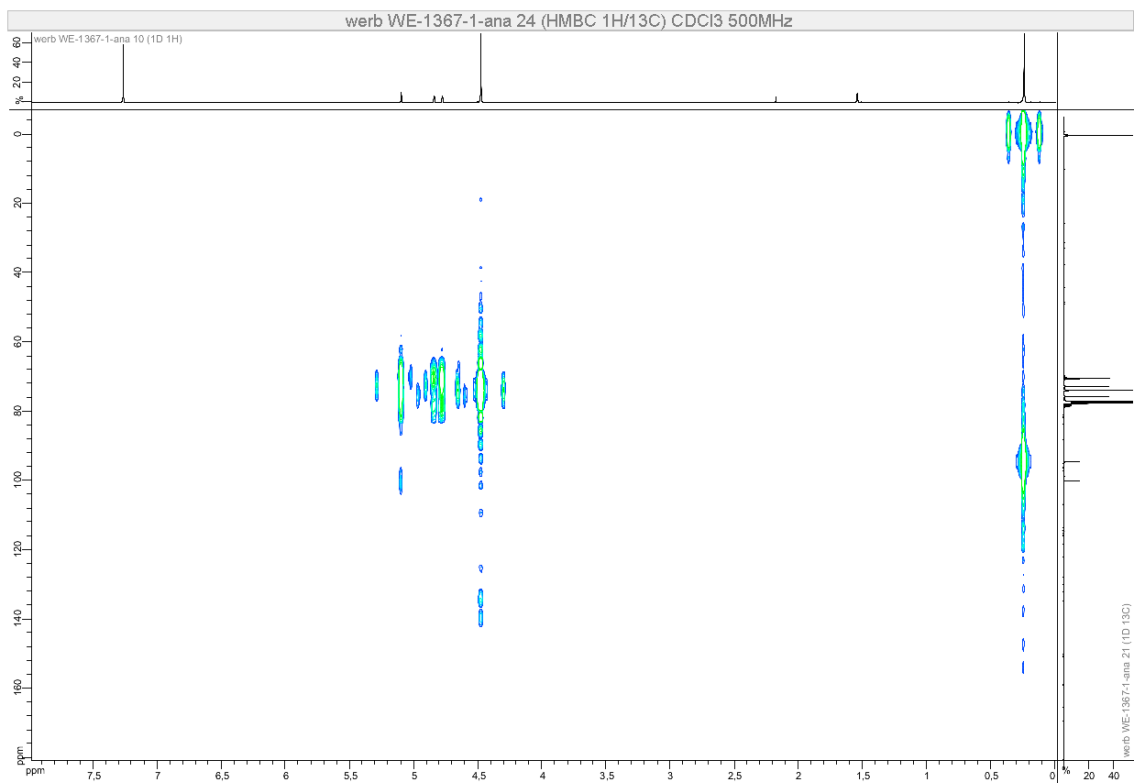




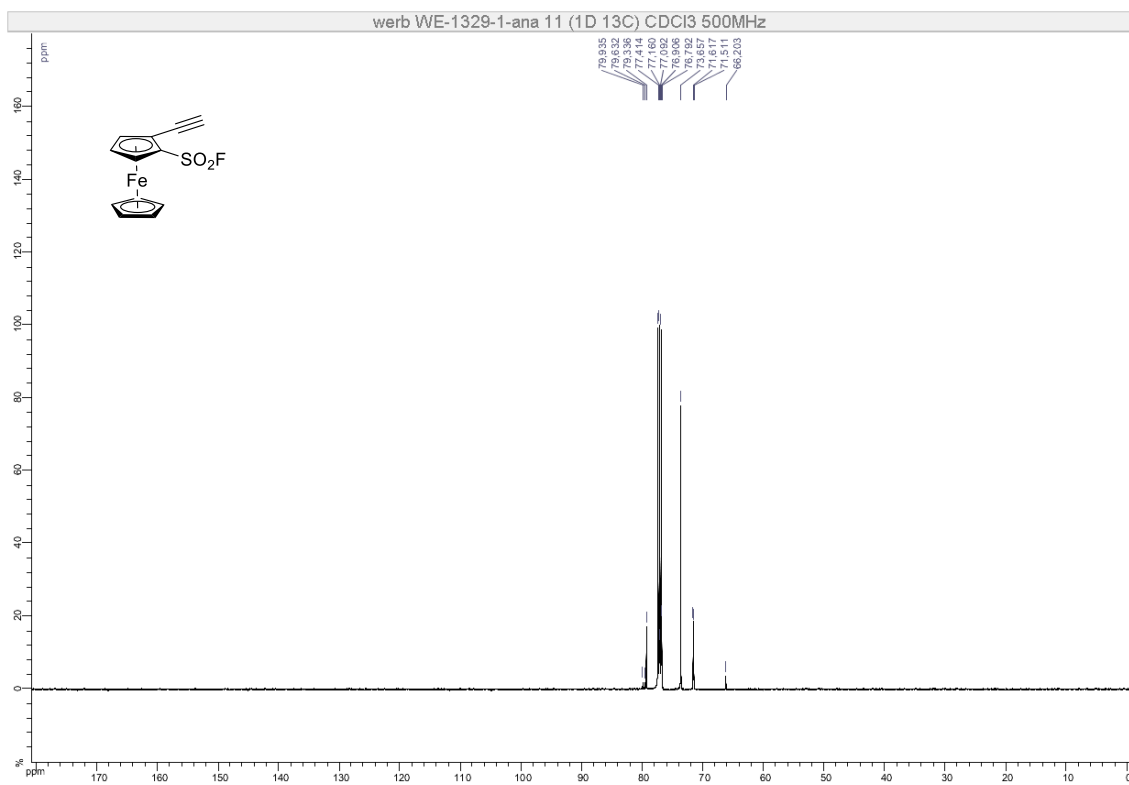
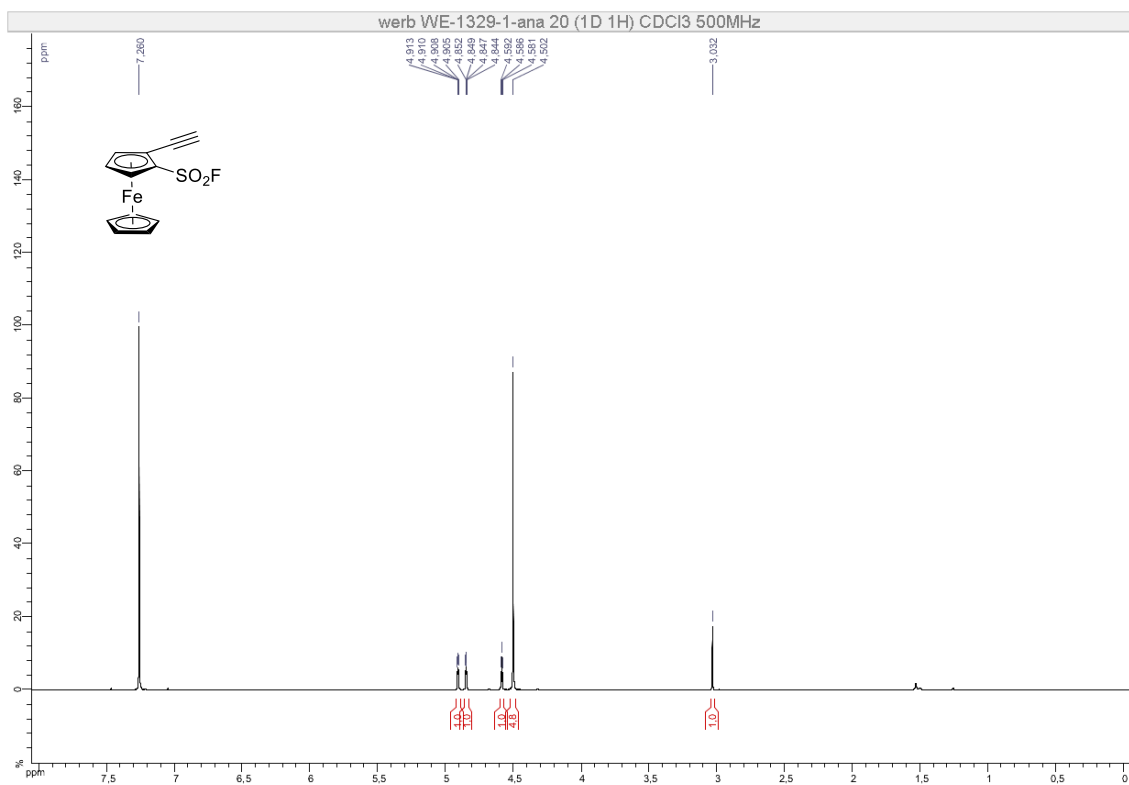
Compound 8b

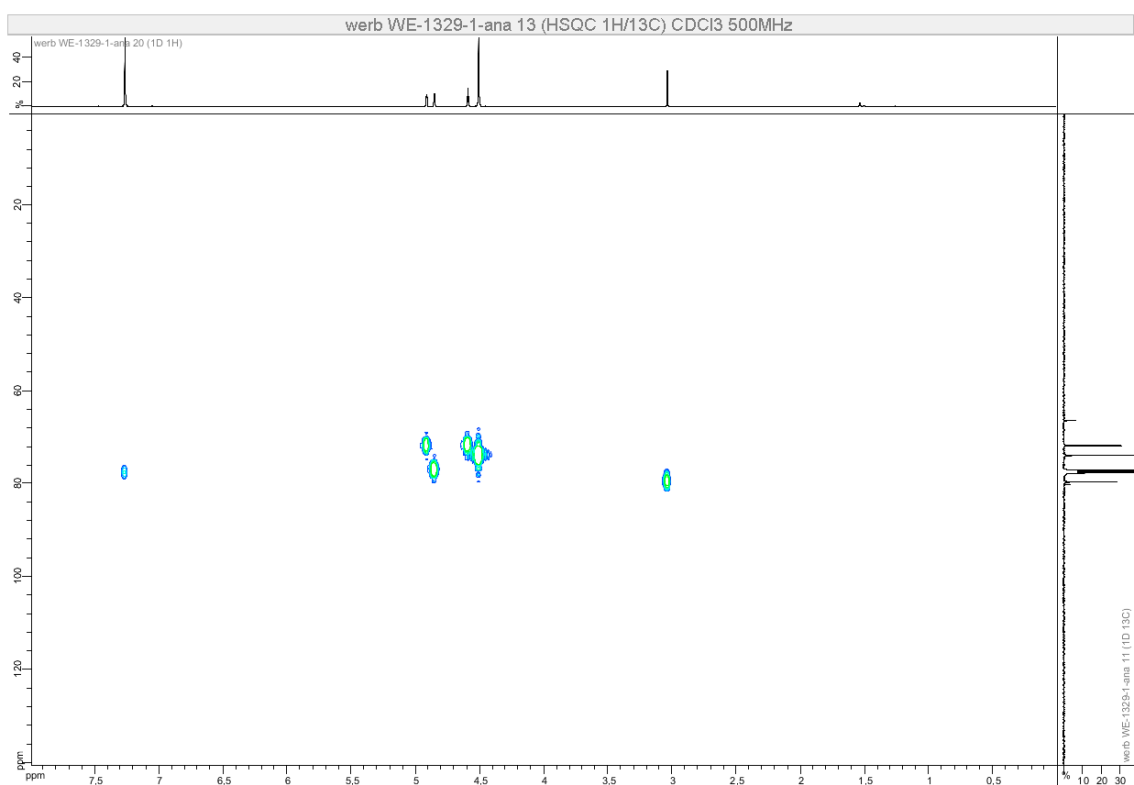
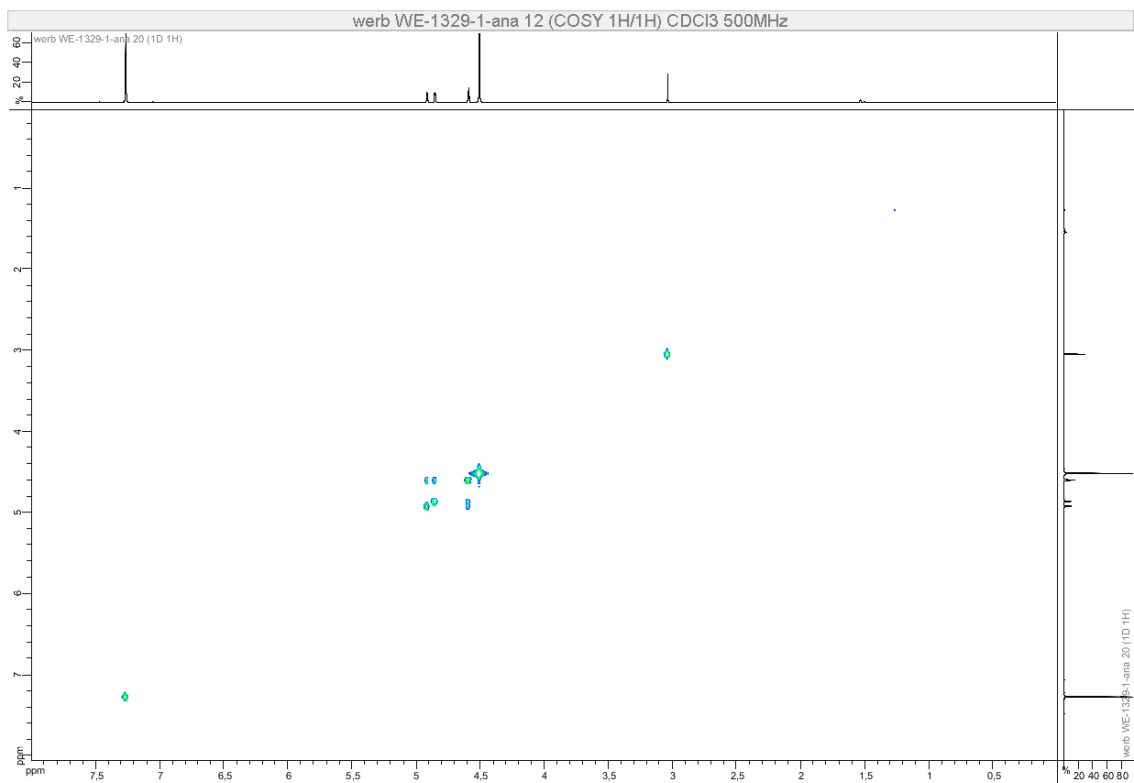


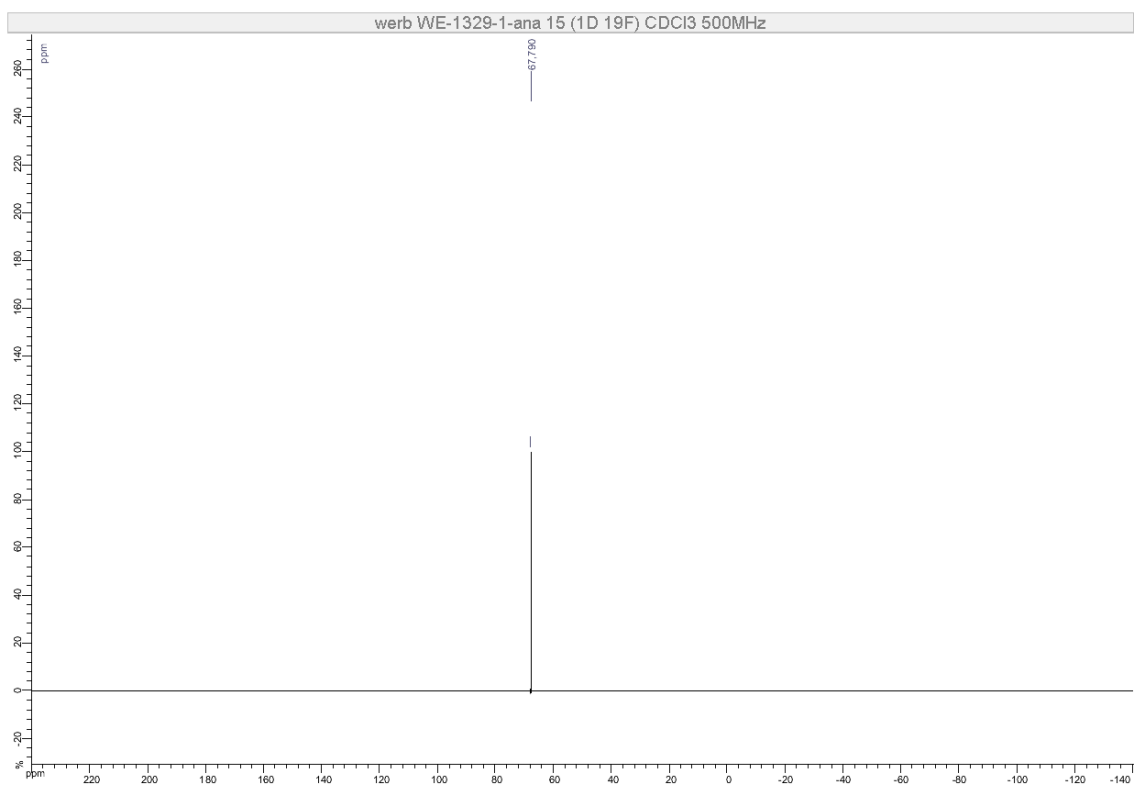
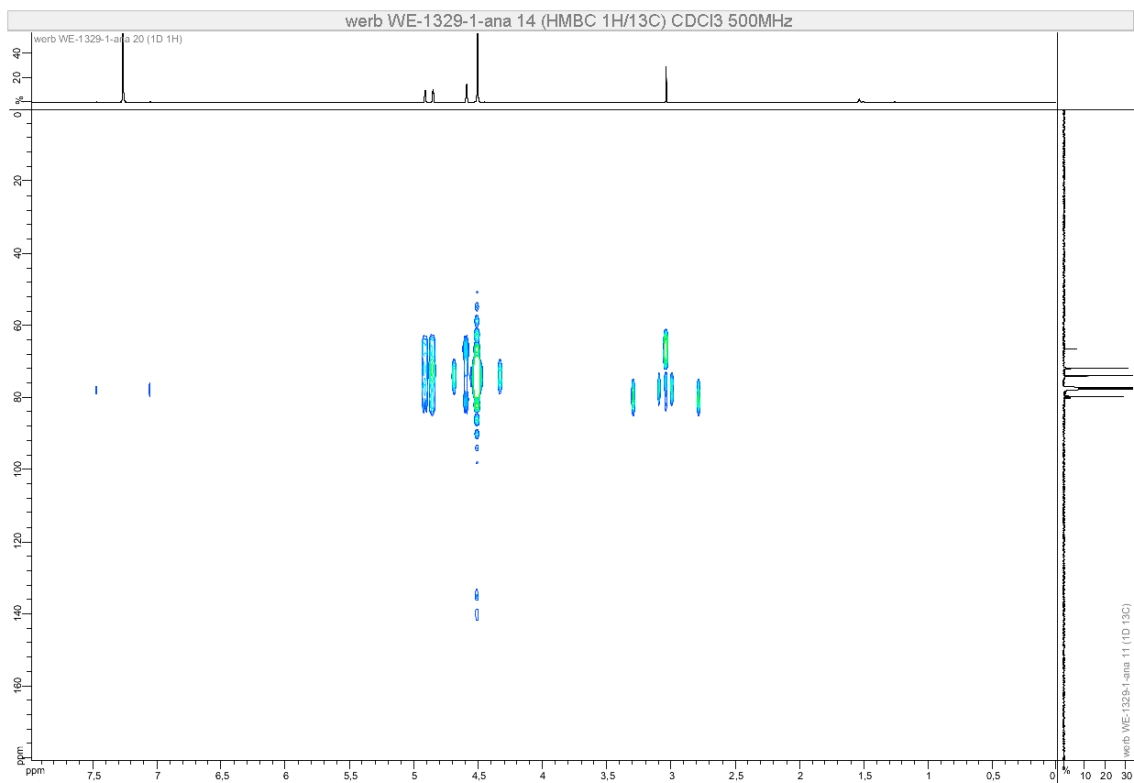




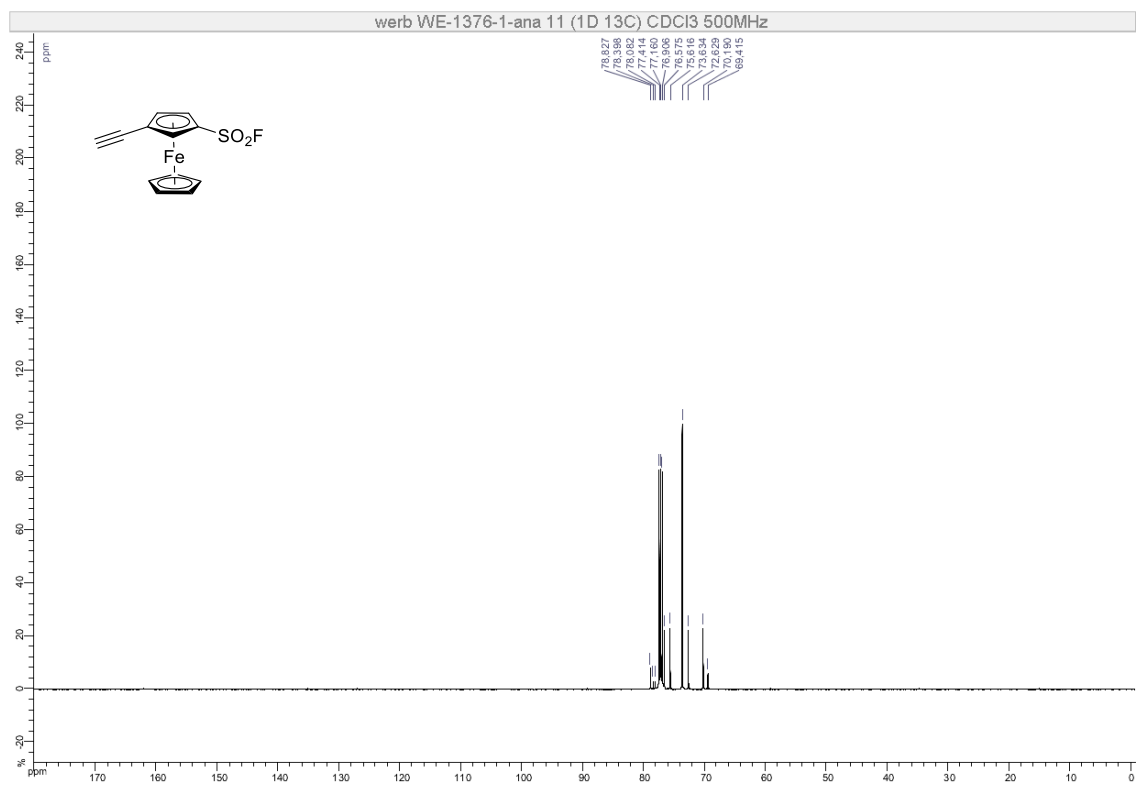
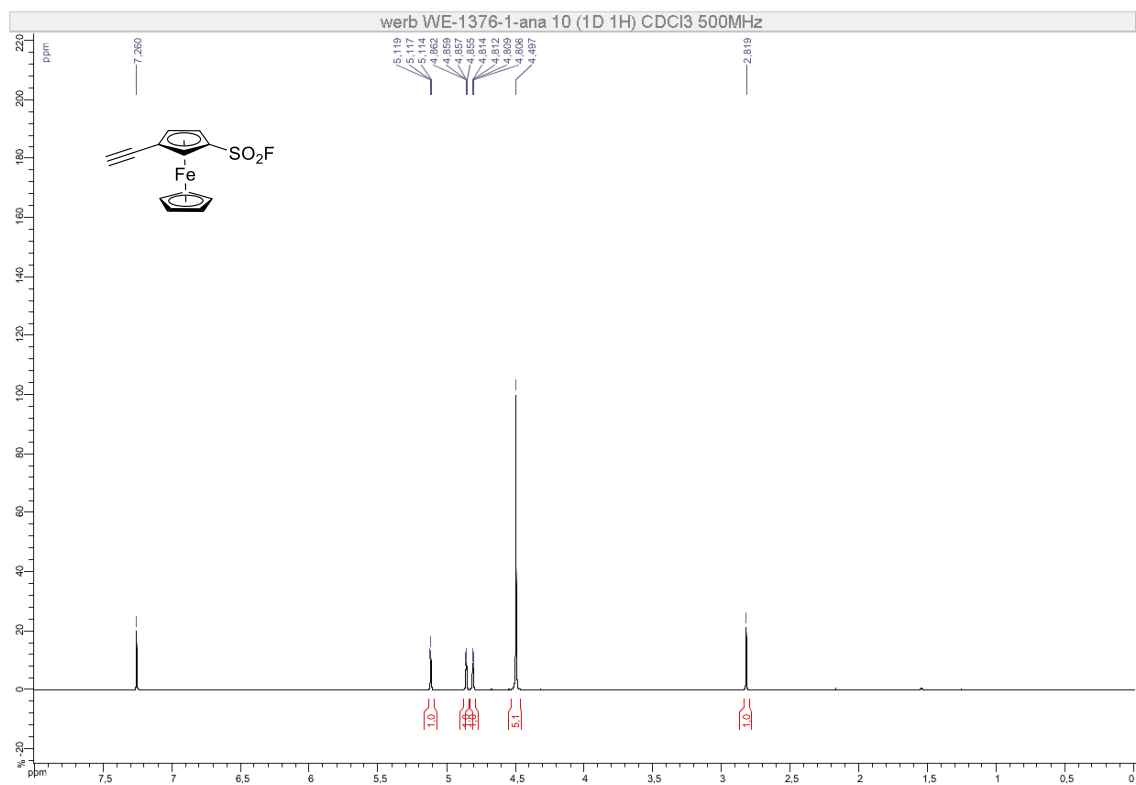
Compound 9a

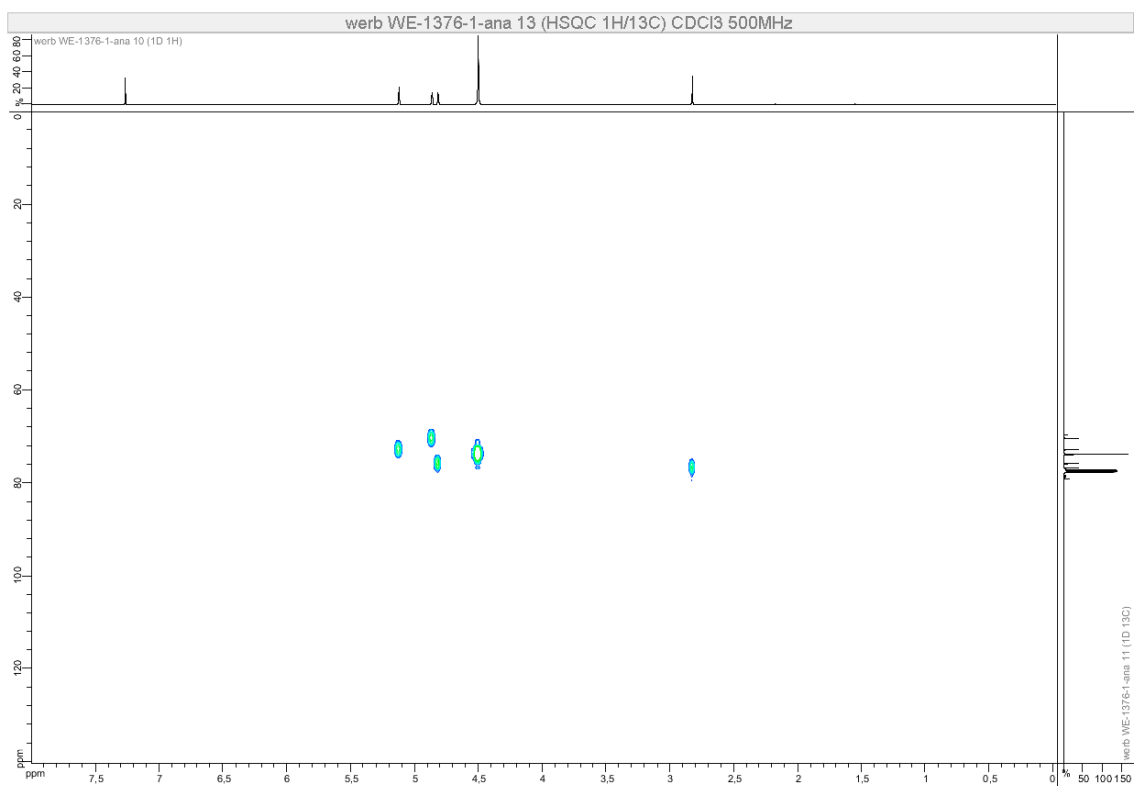
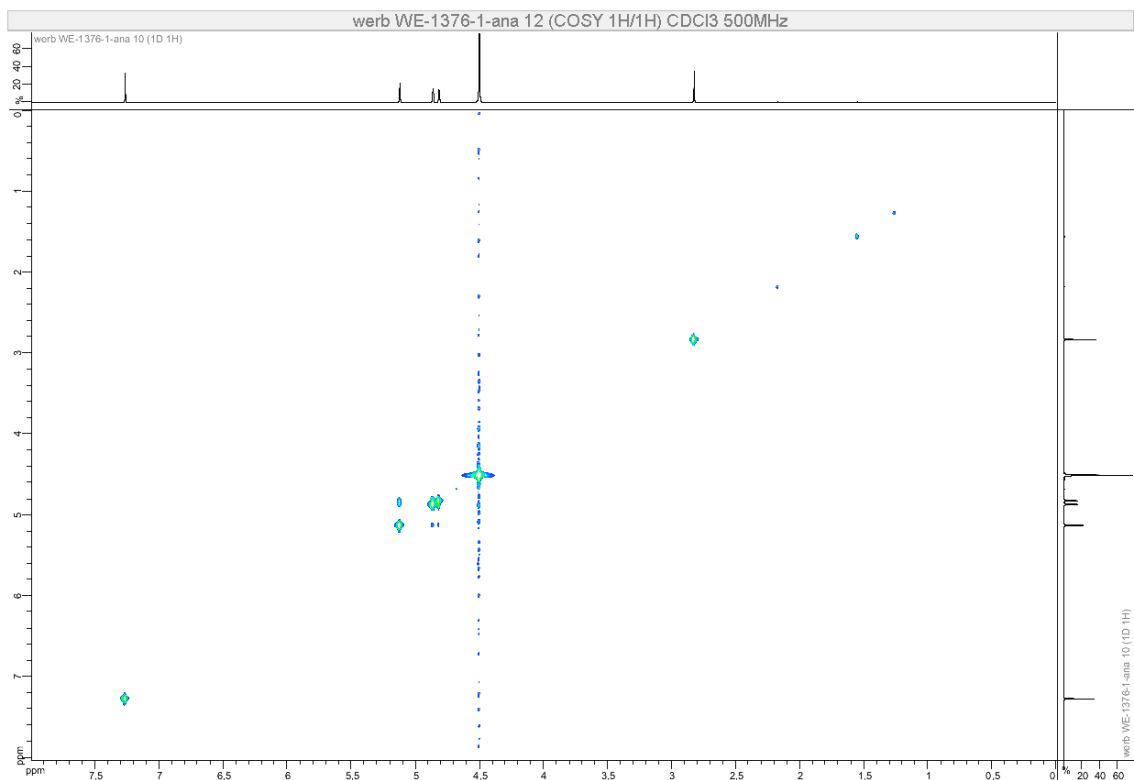


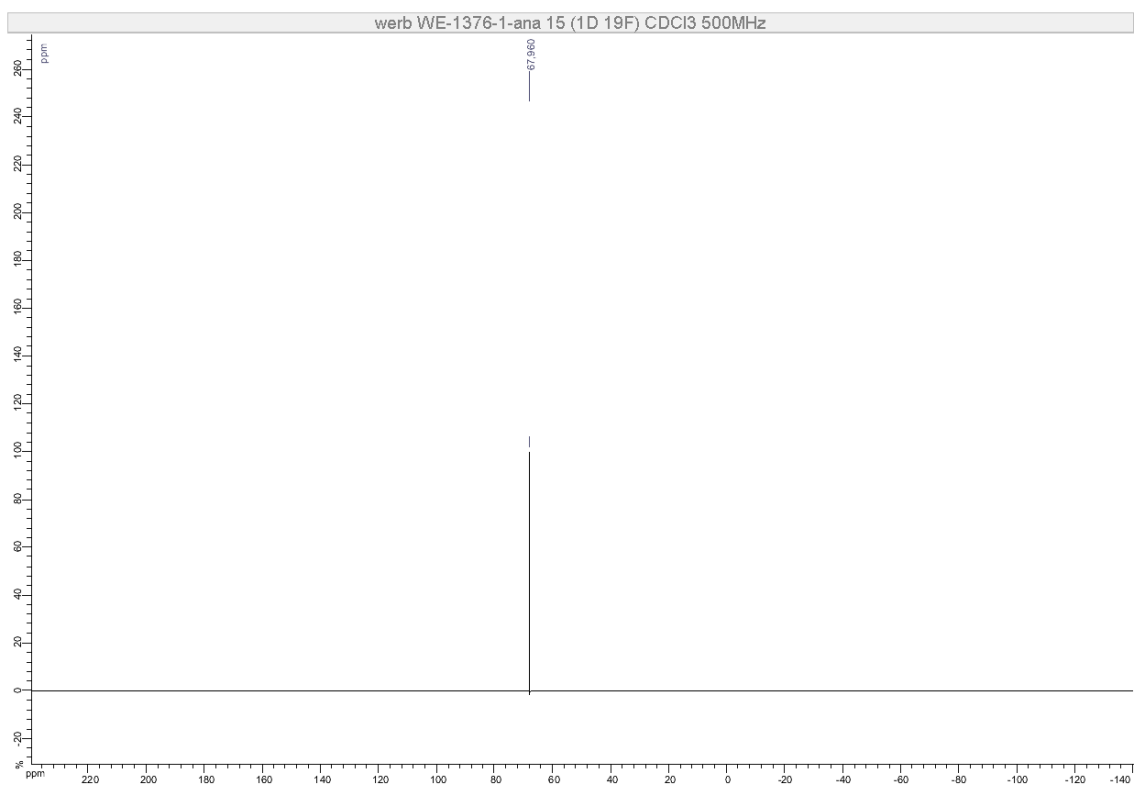
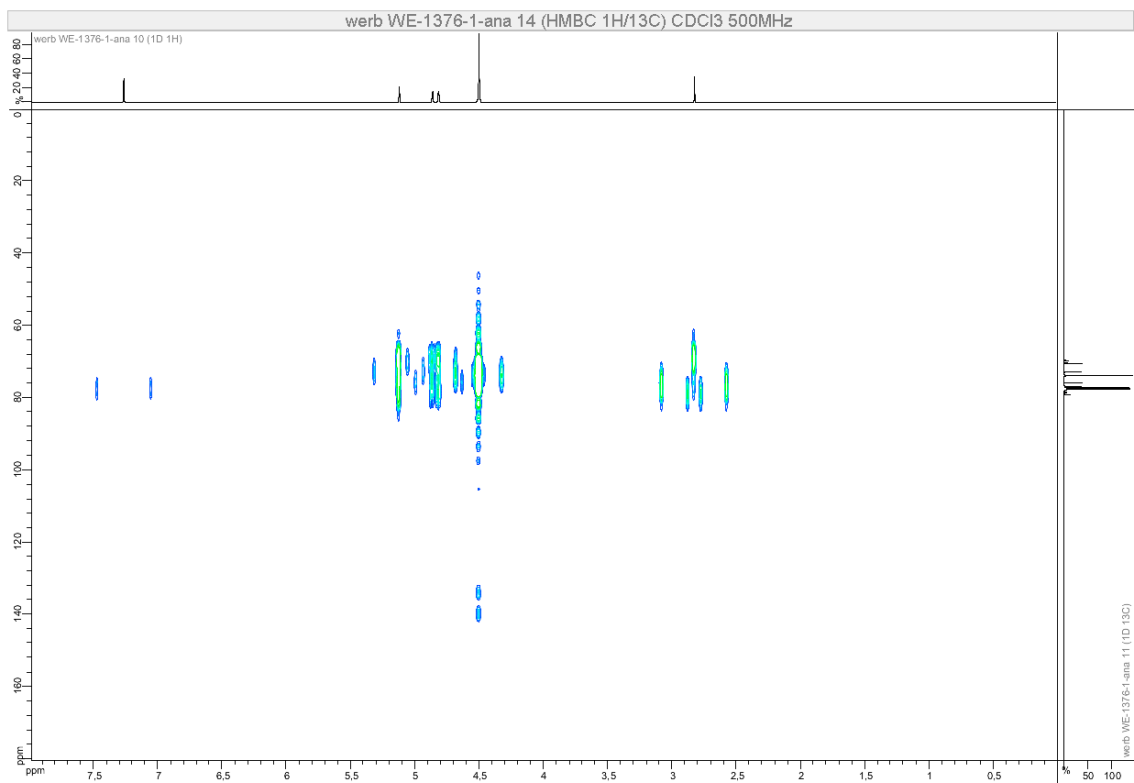




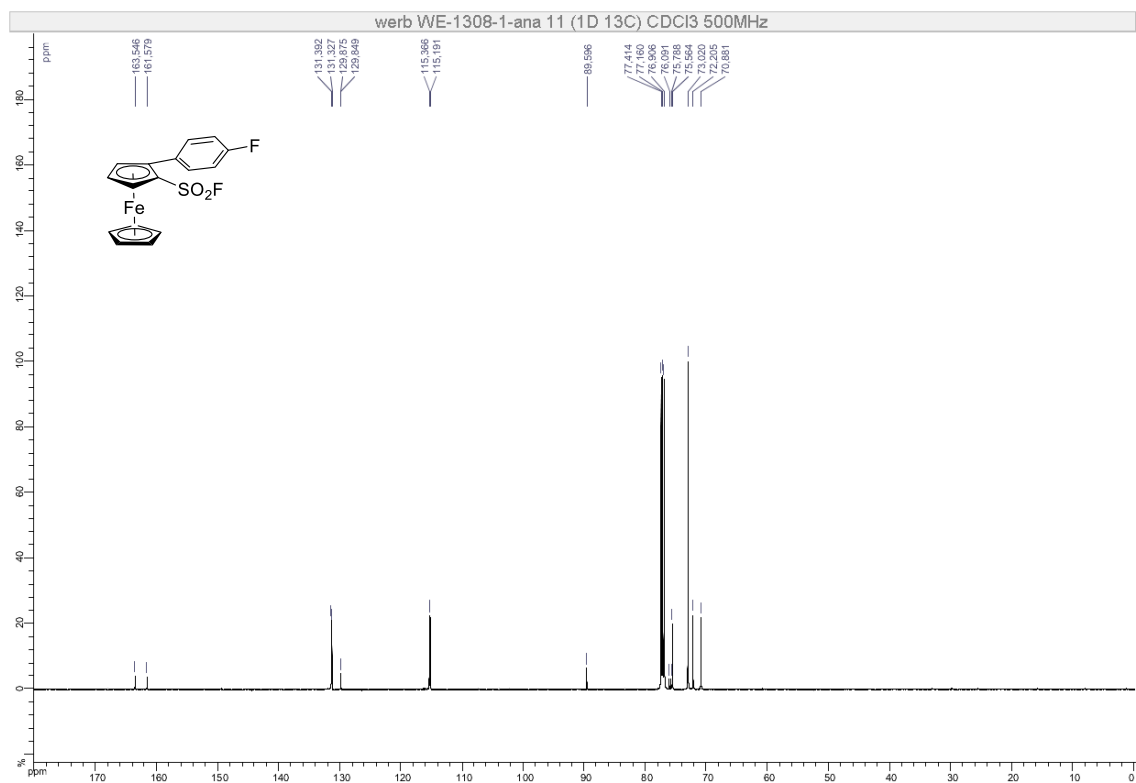
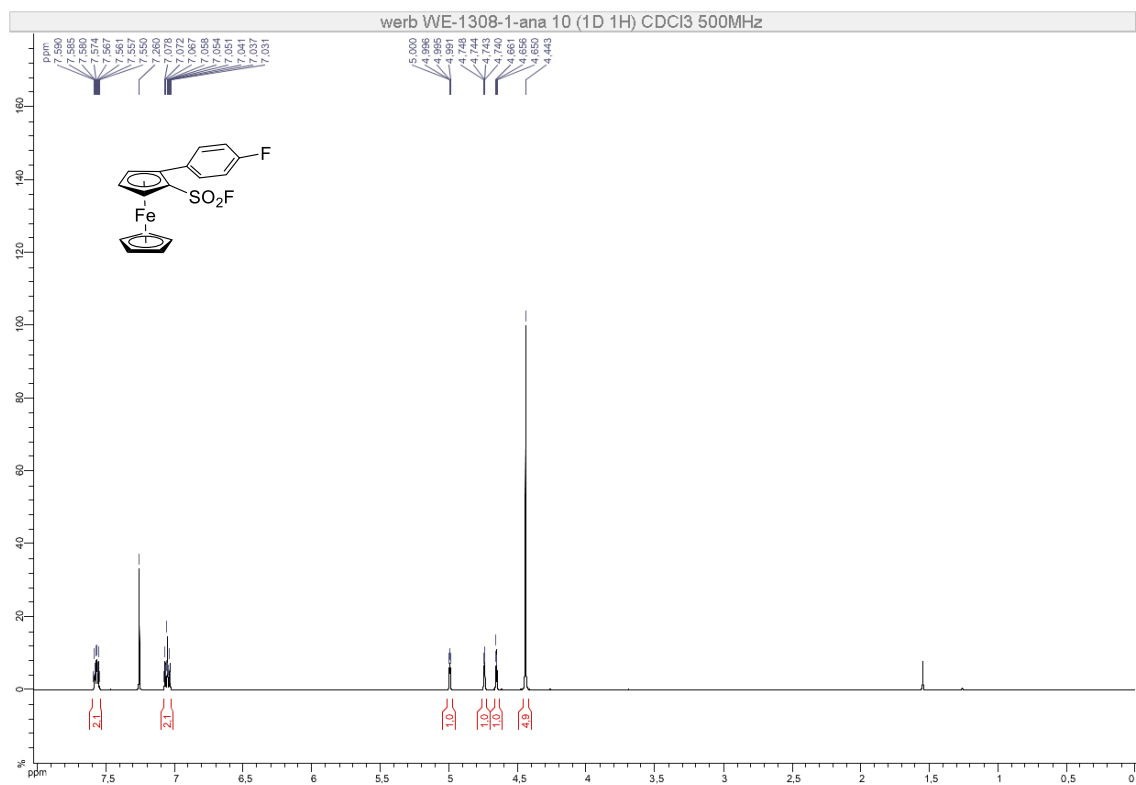
Compound 9b

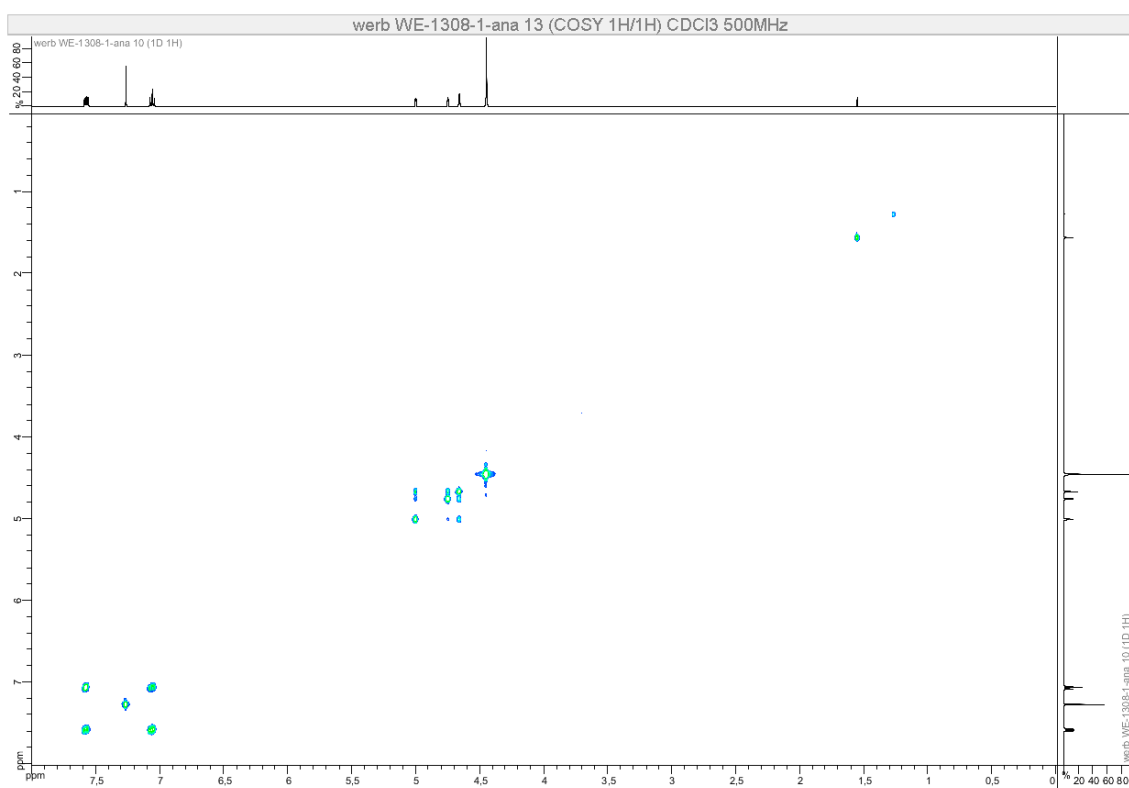
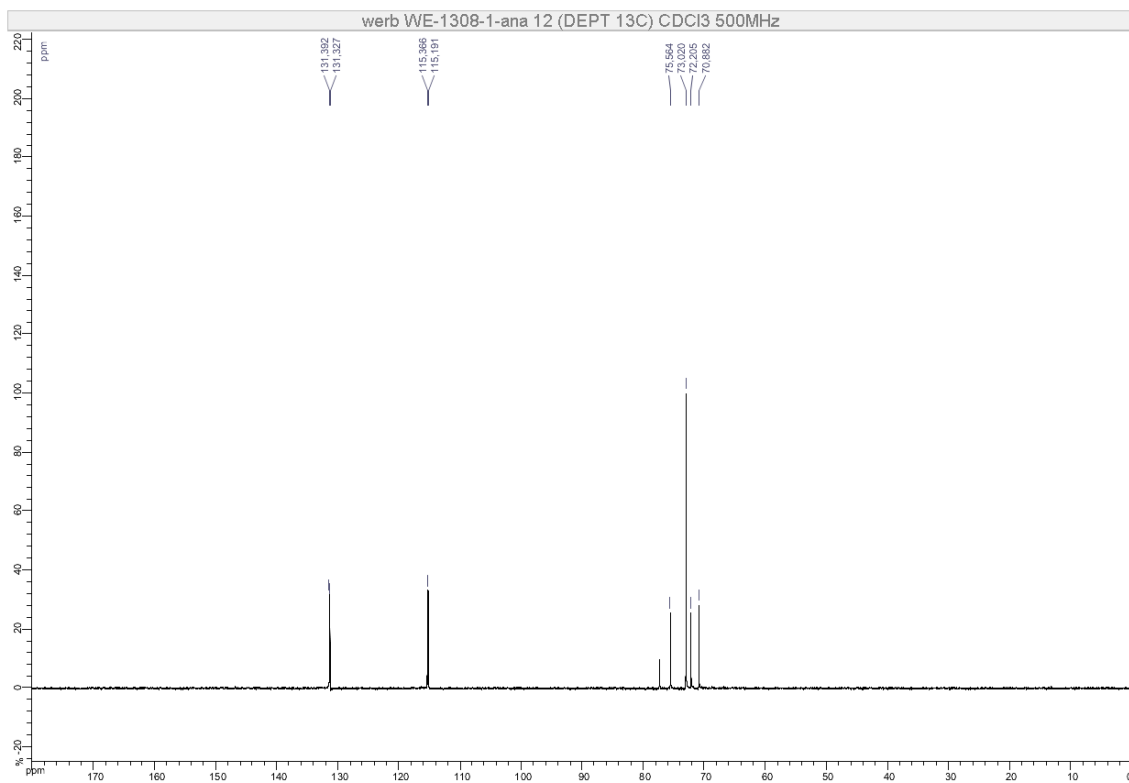


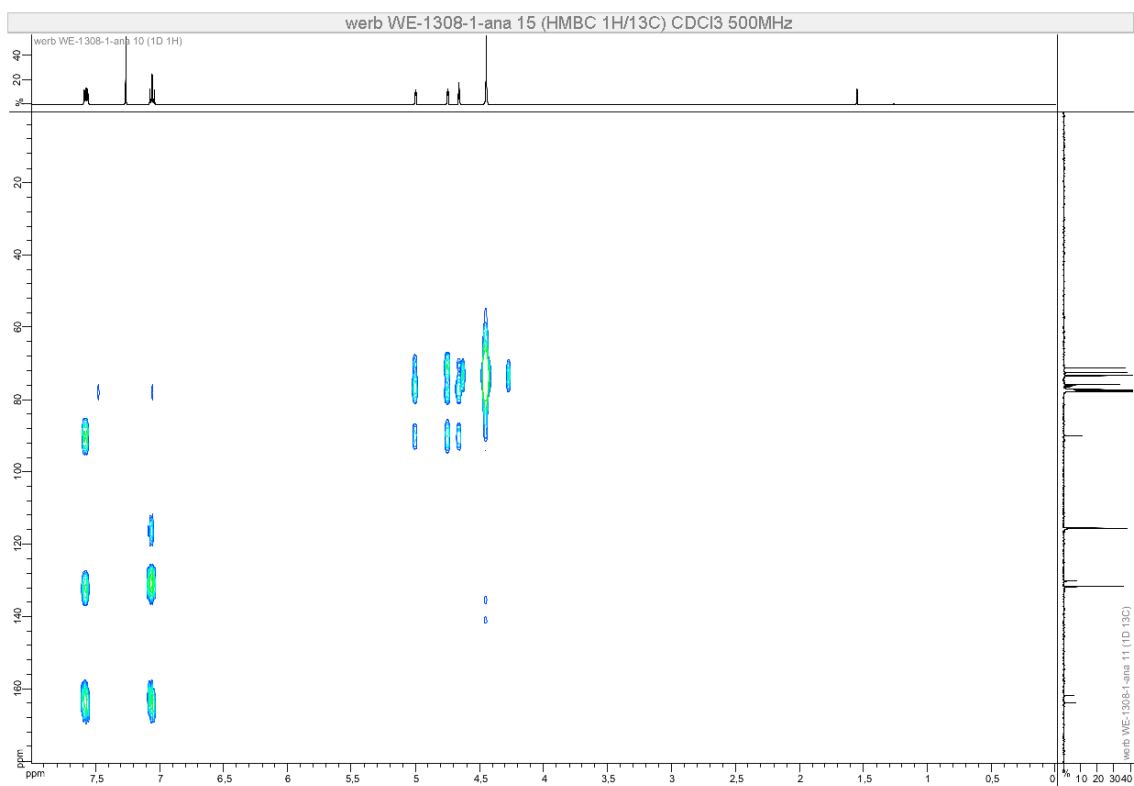


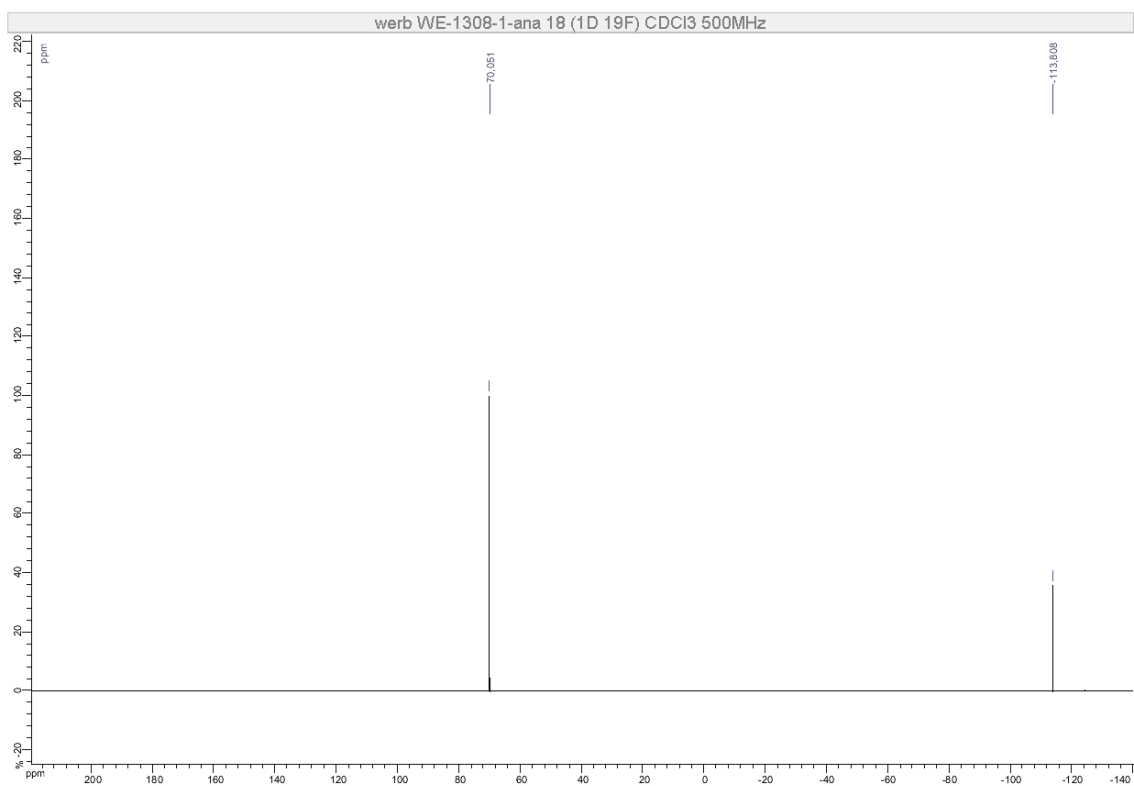
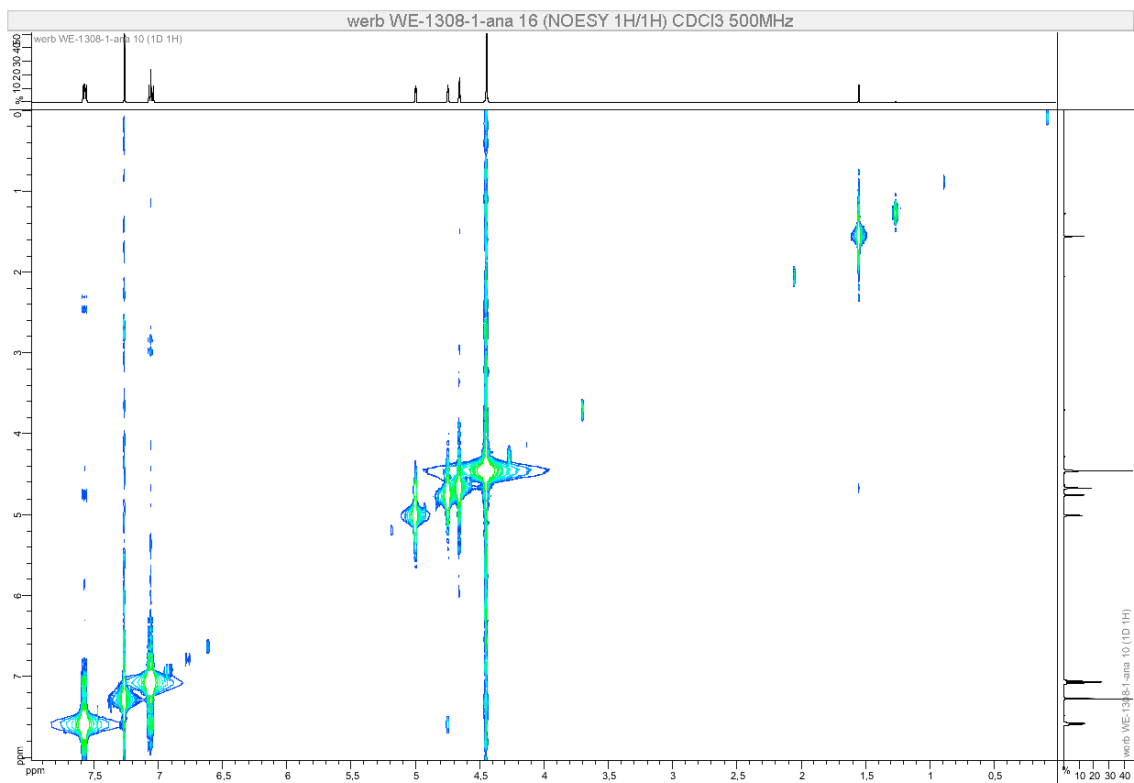


Compound 10a

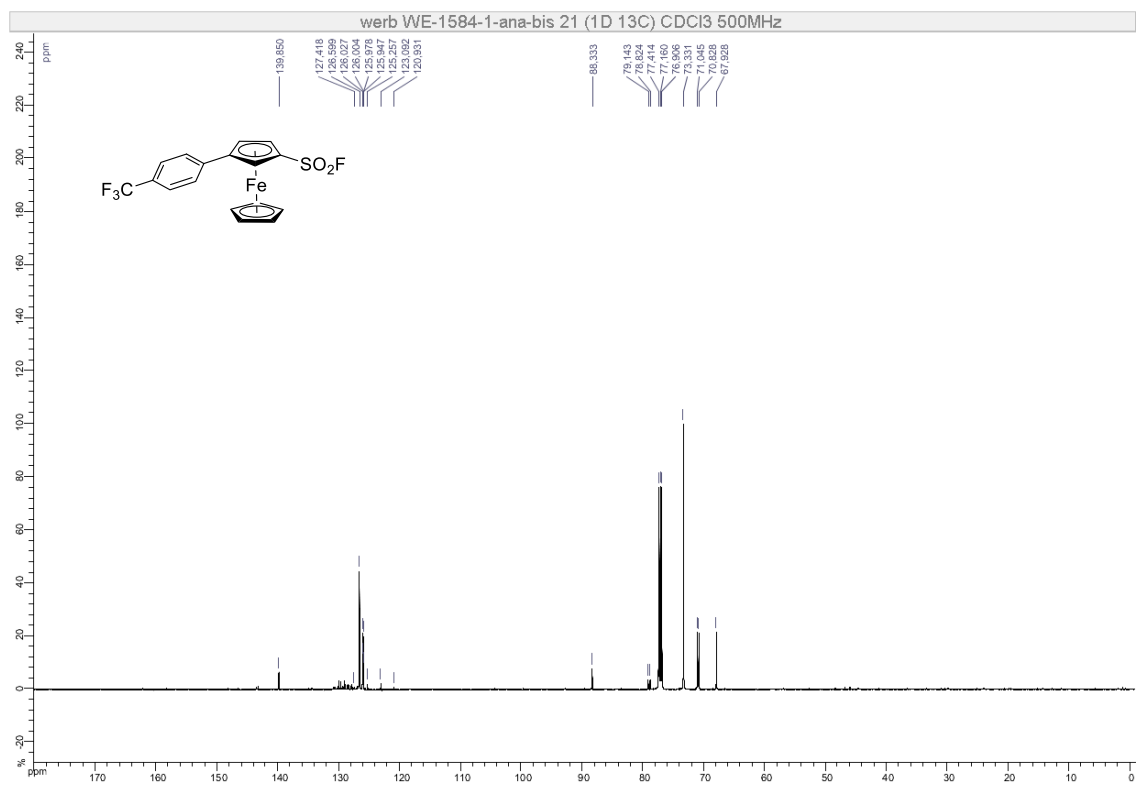
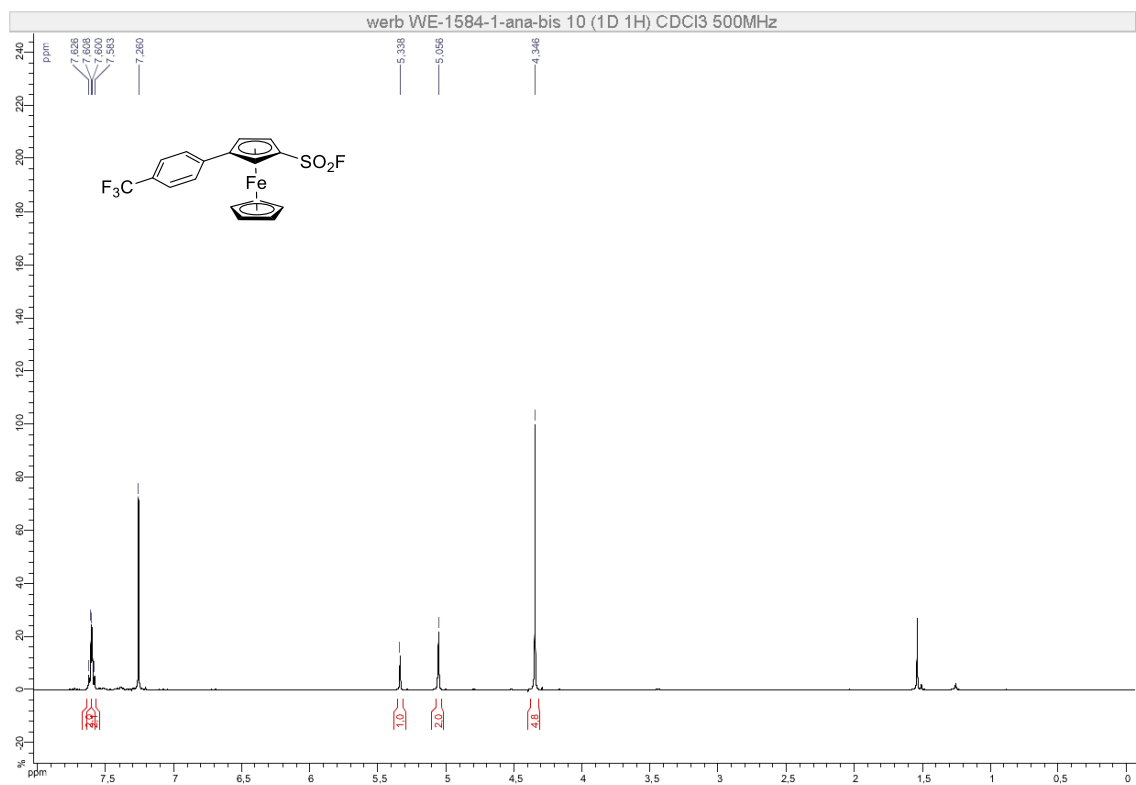


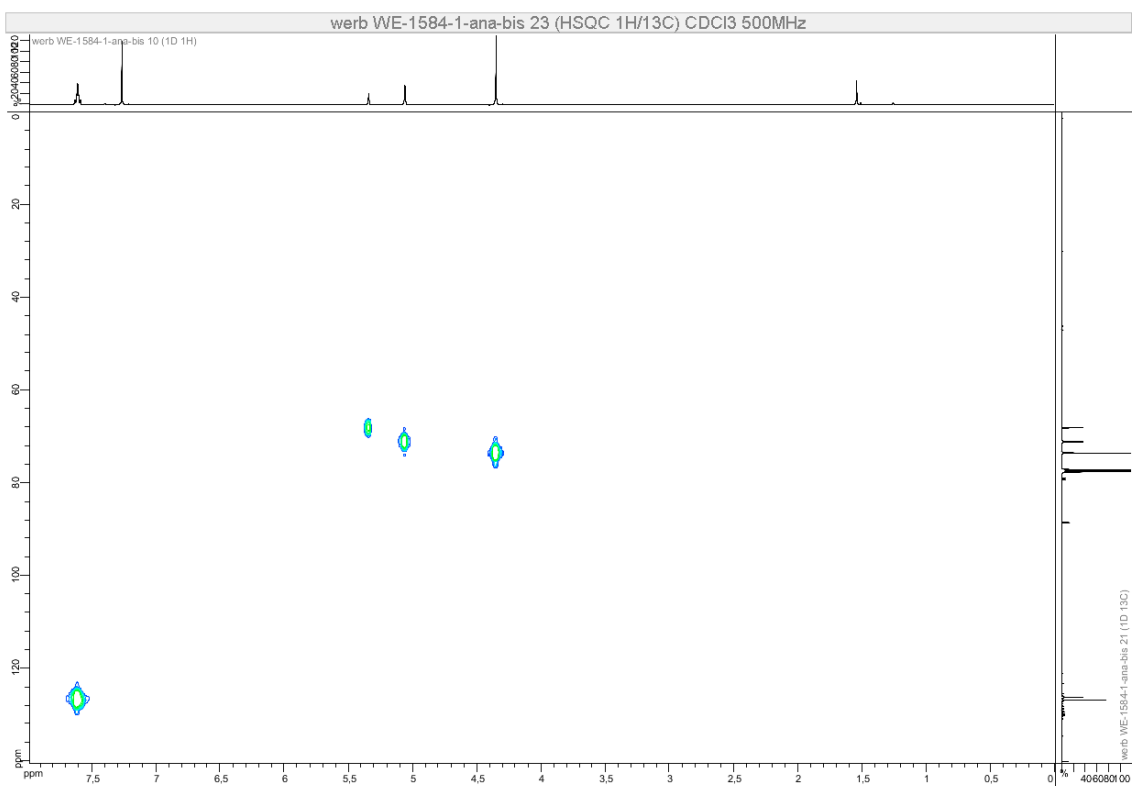
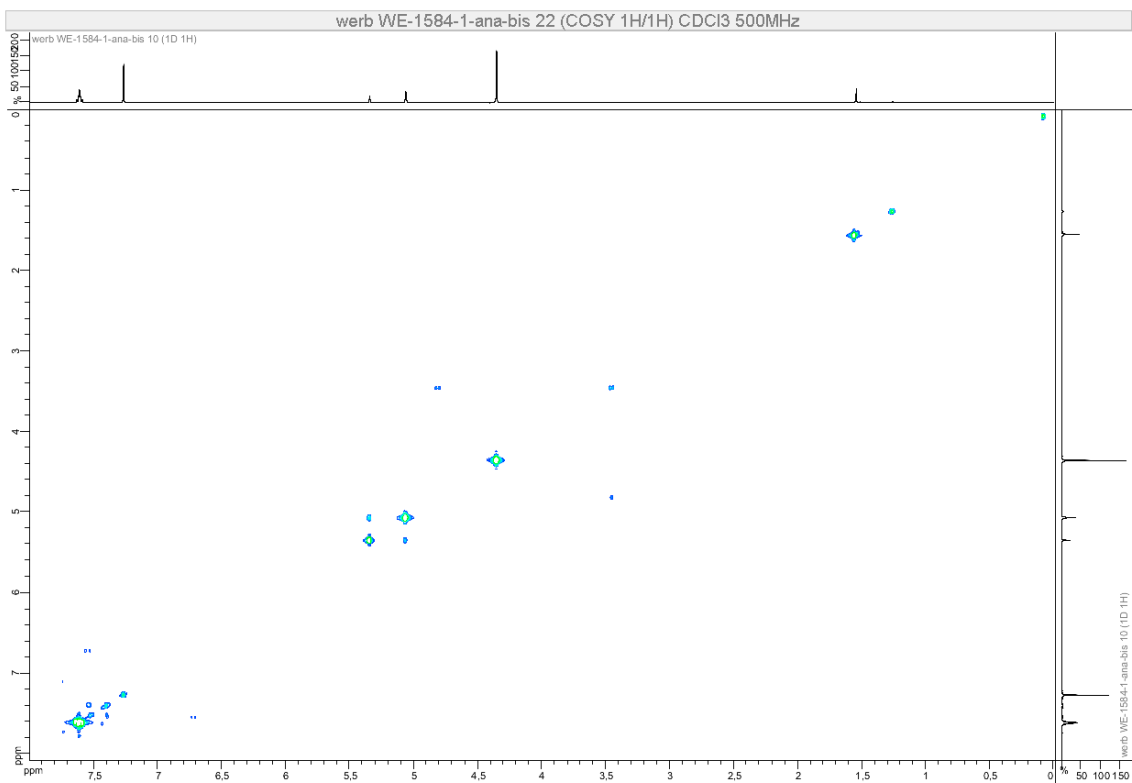


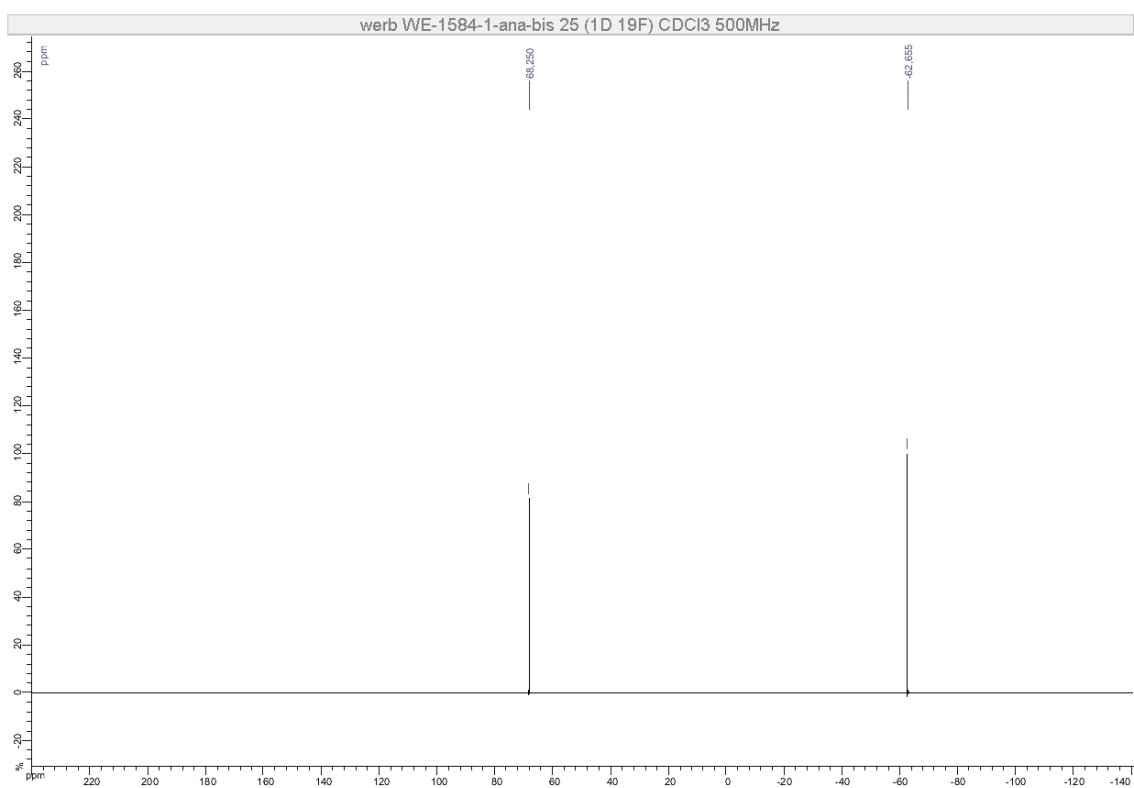
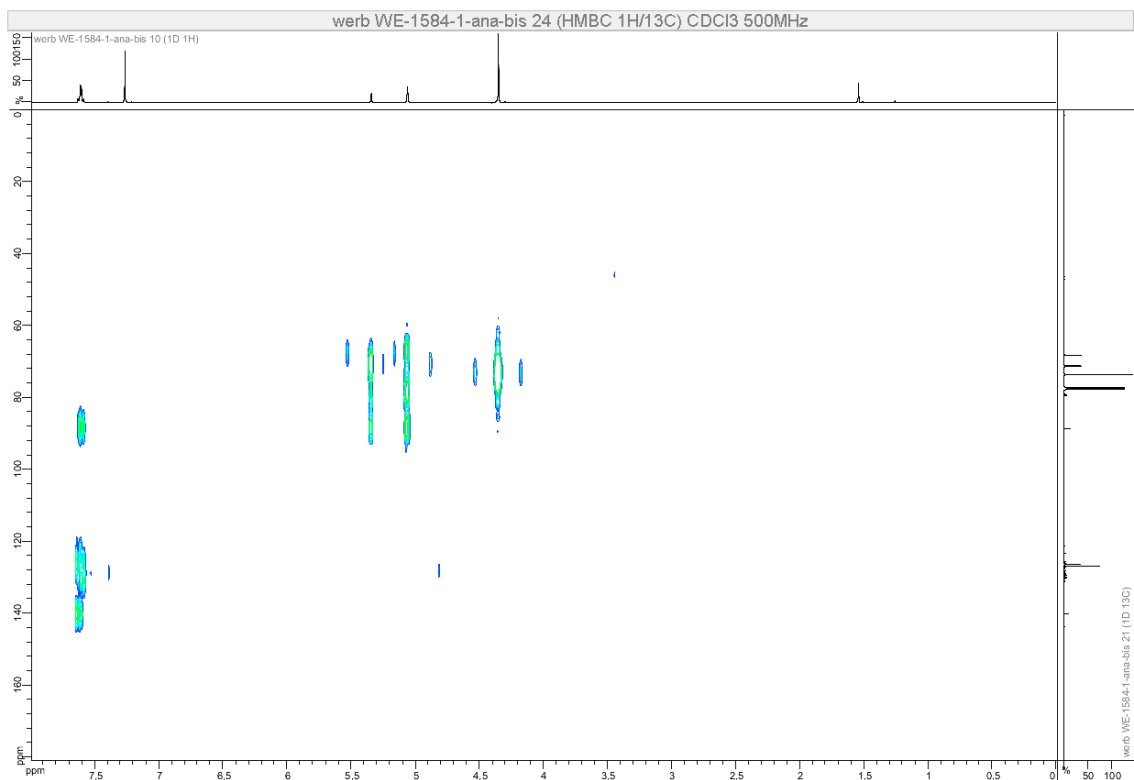




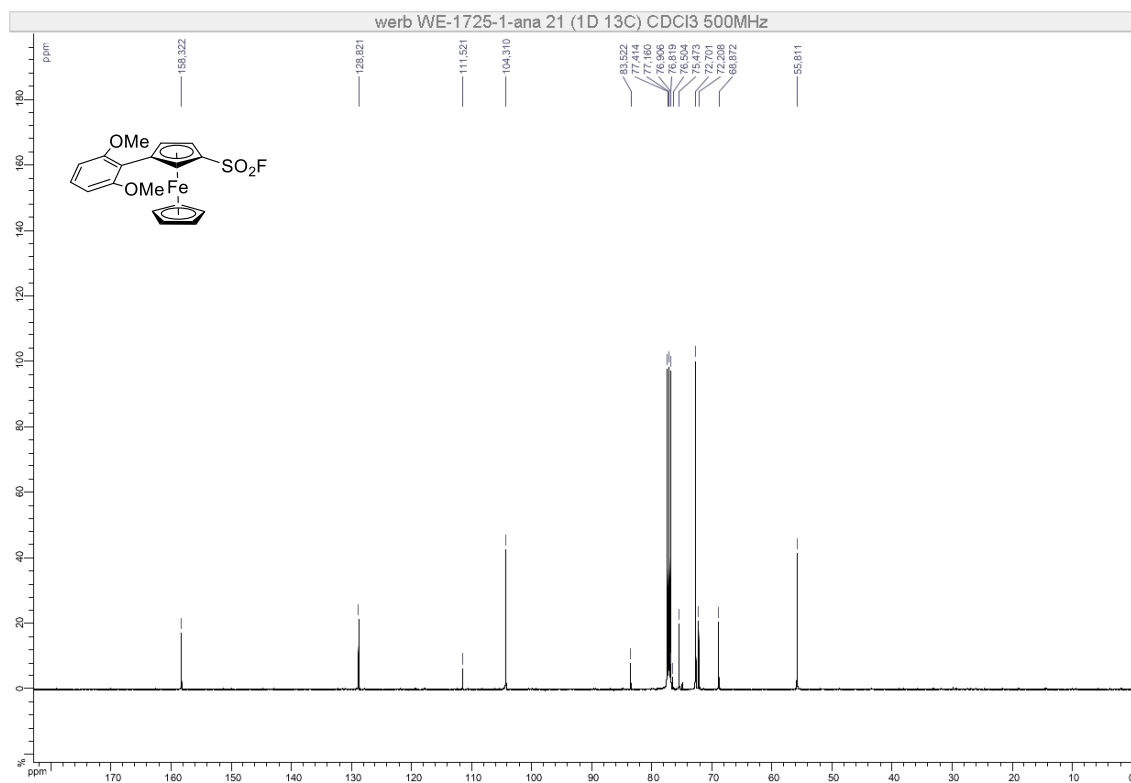
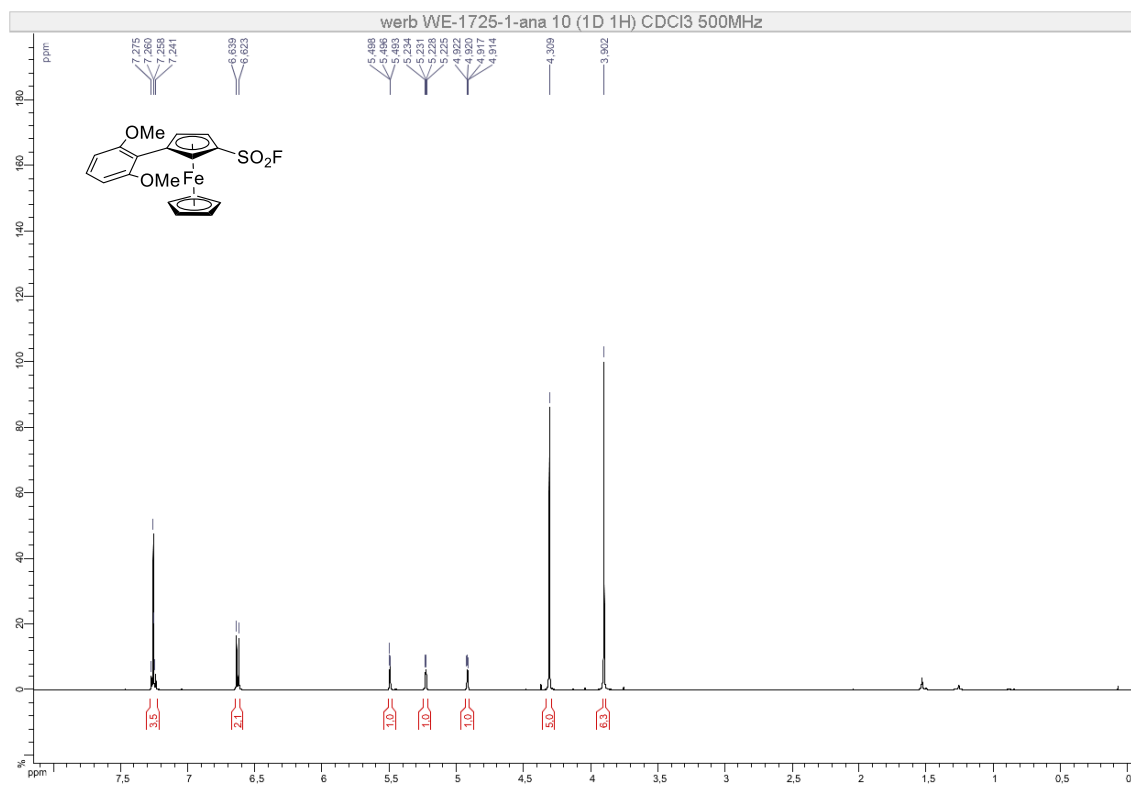
Compound 10b

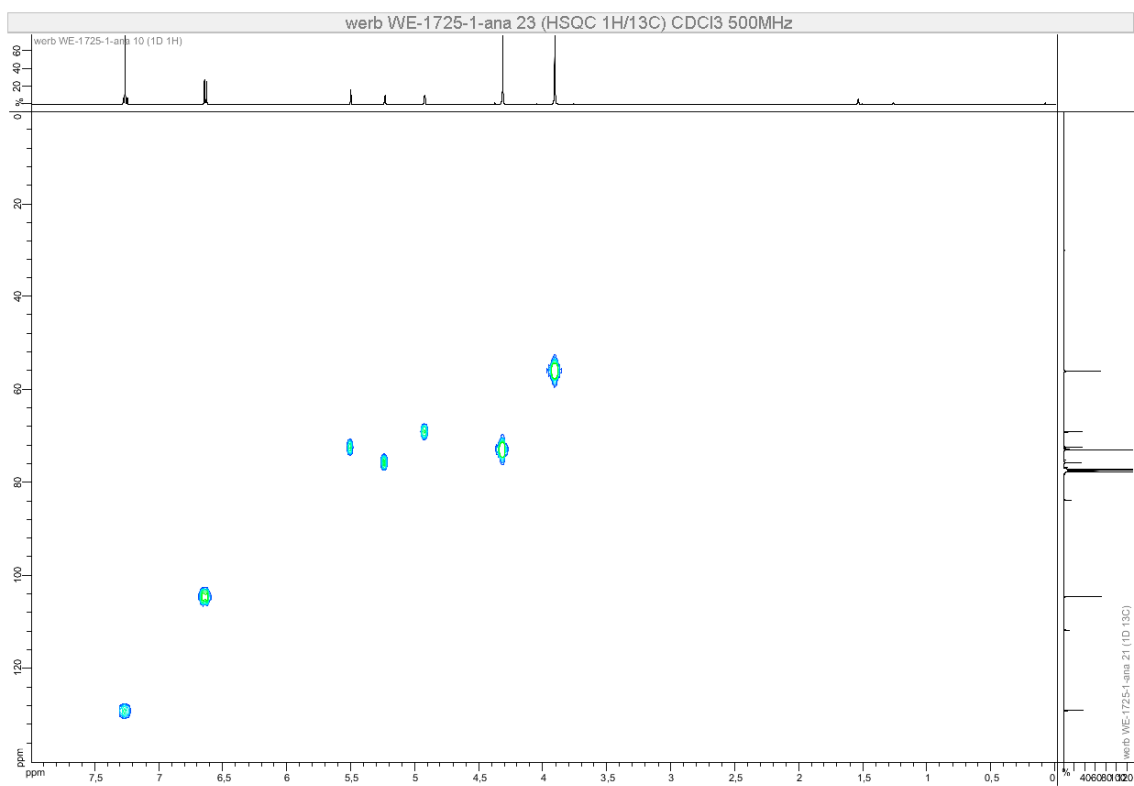
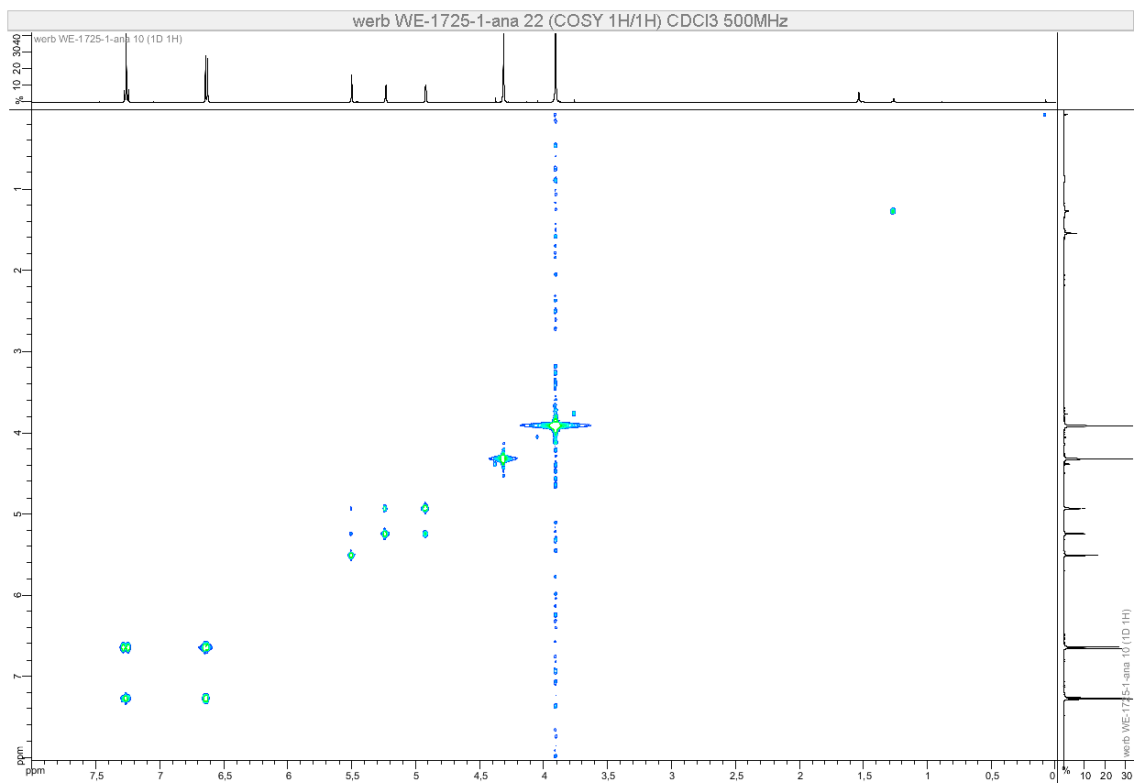


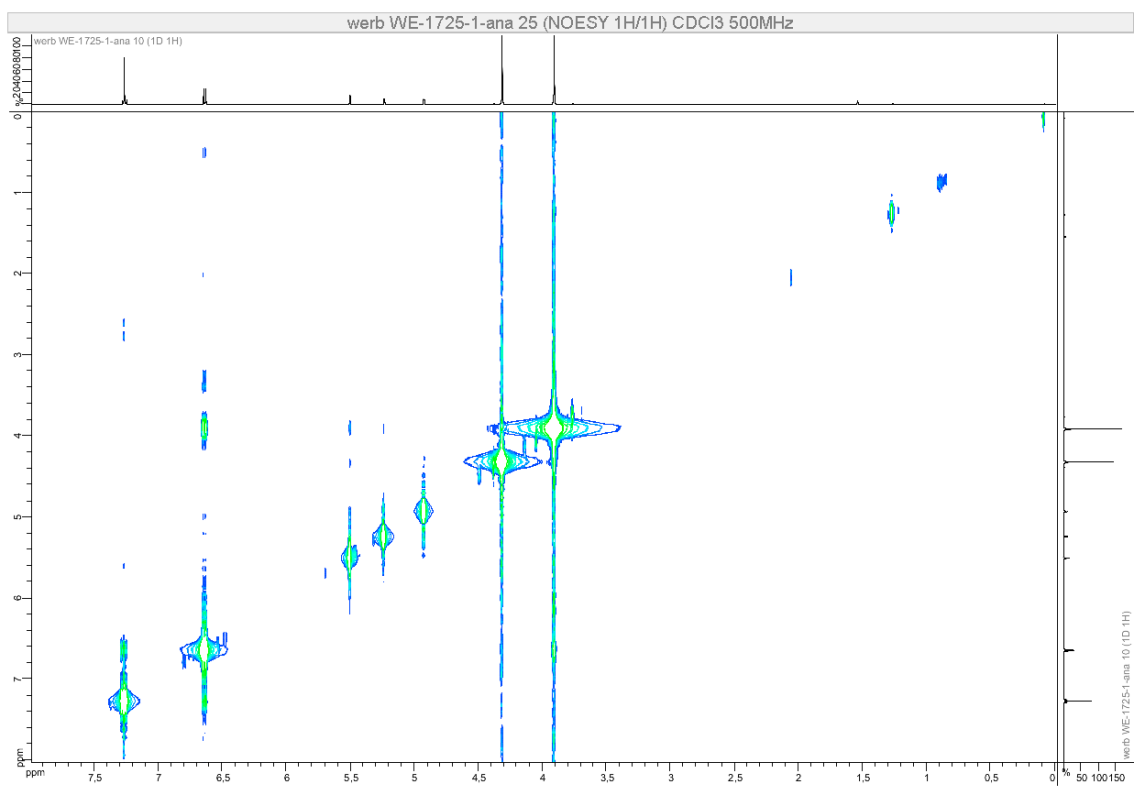
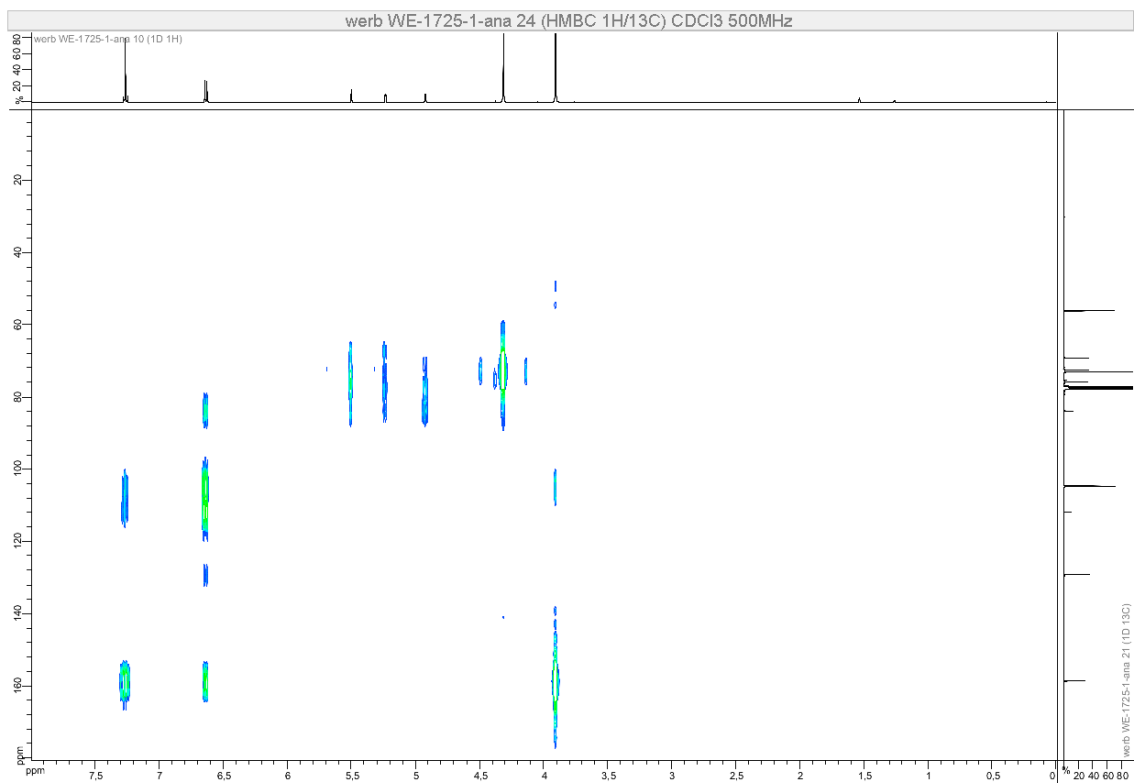


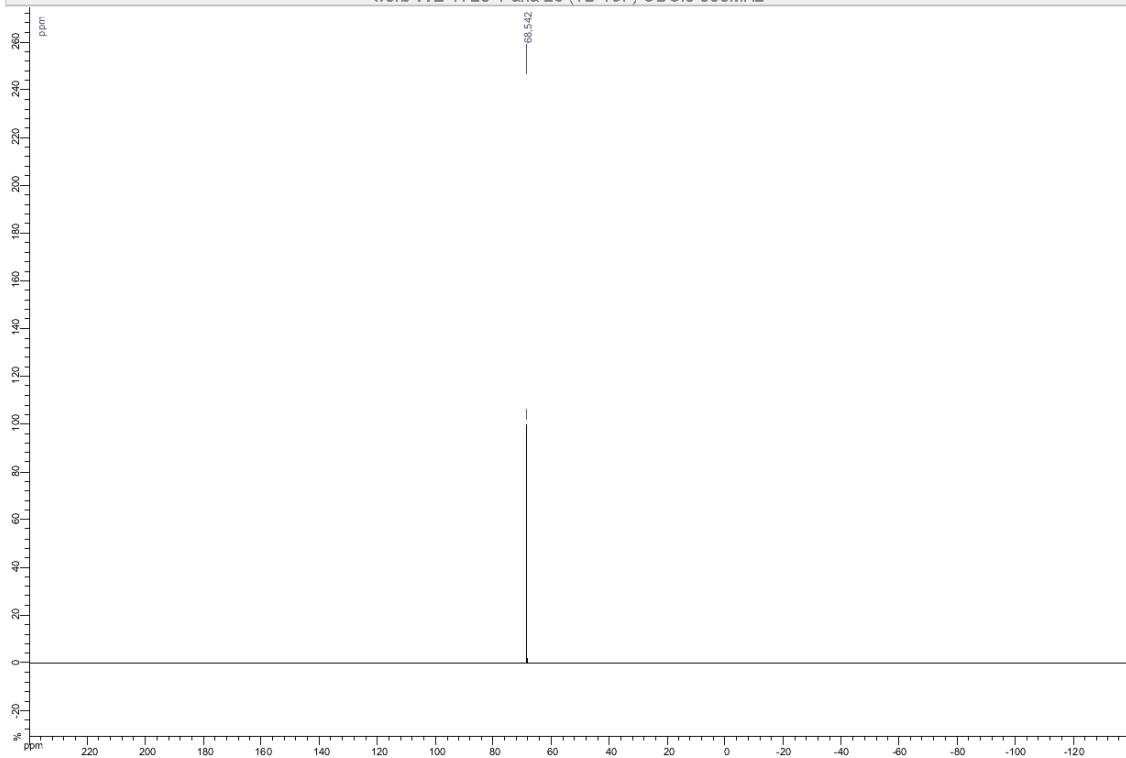


Compound 10c

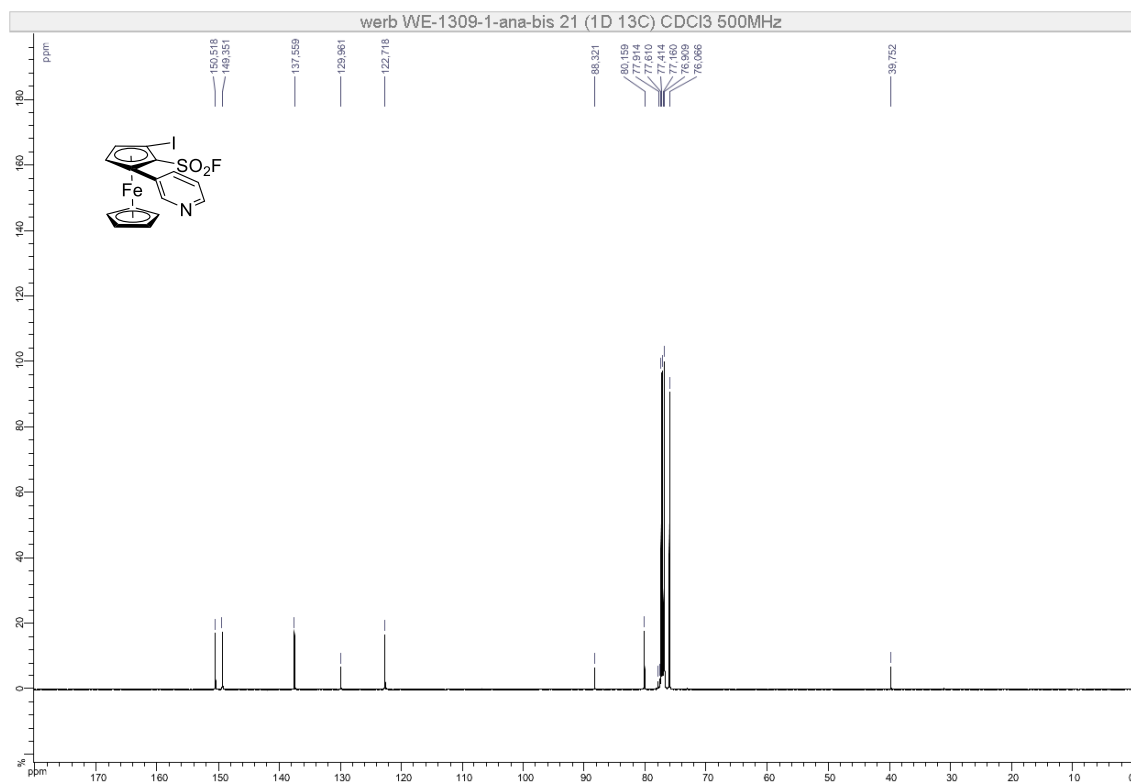
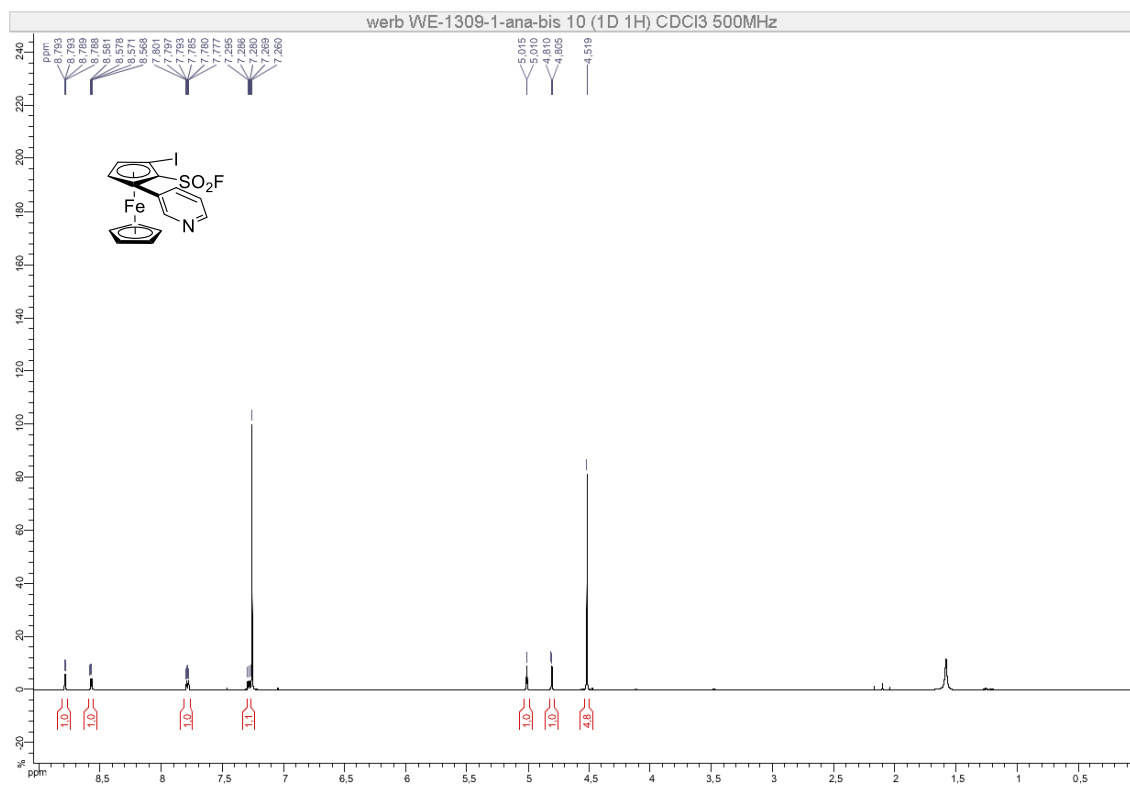


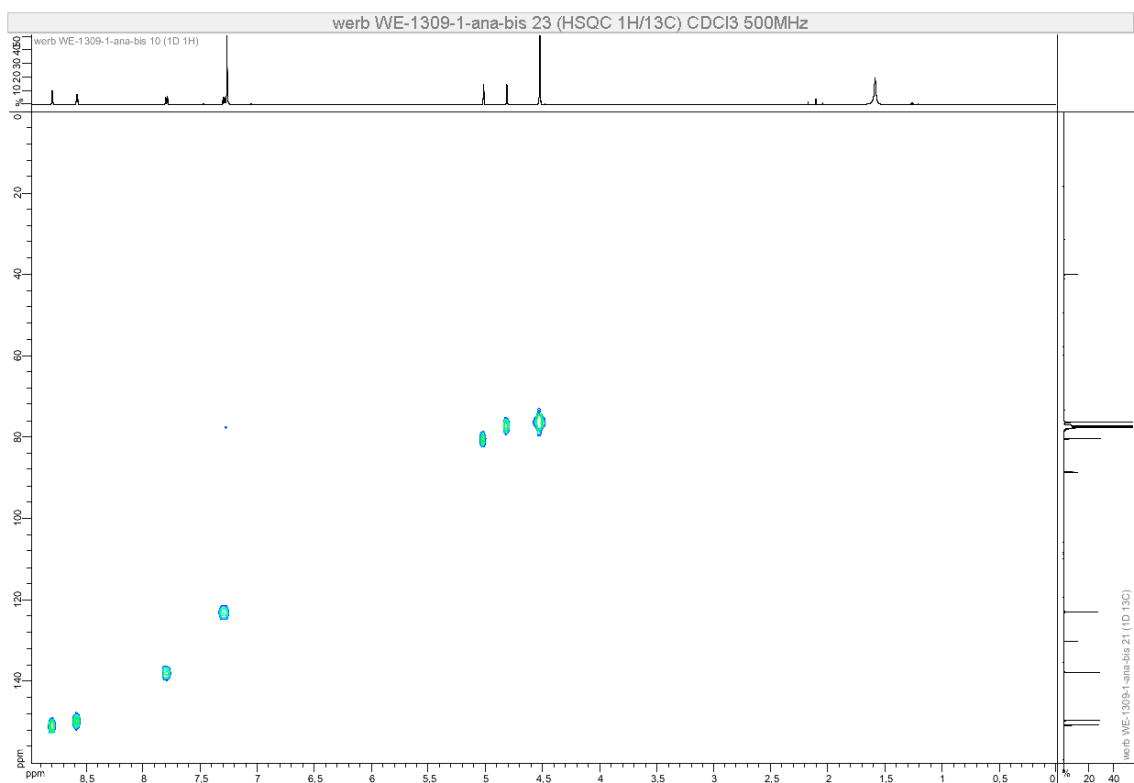
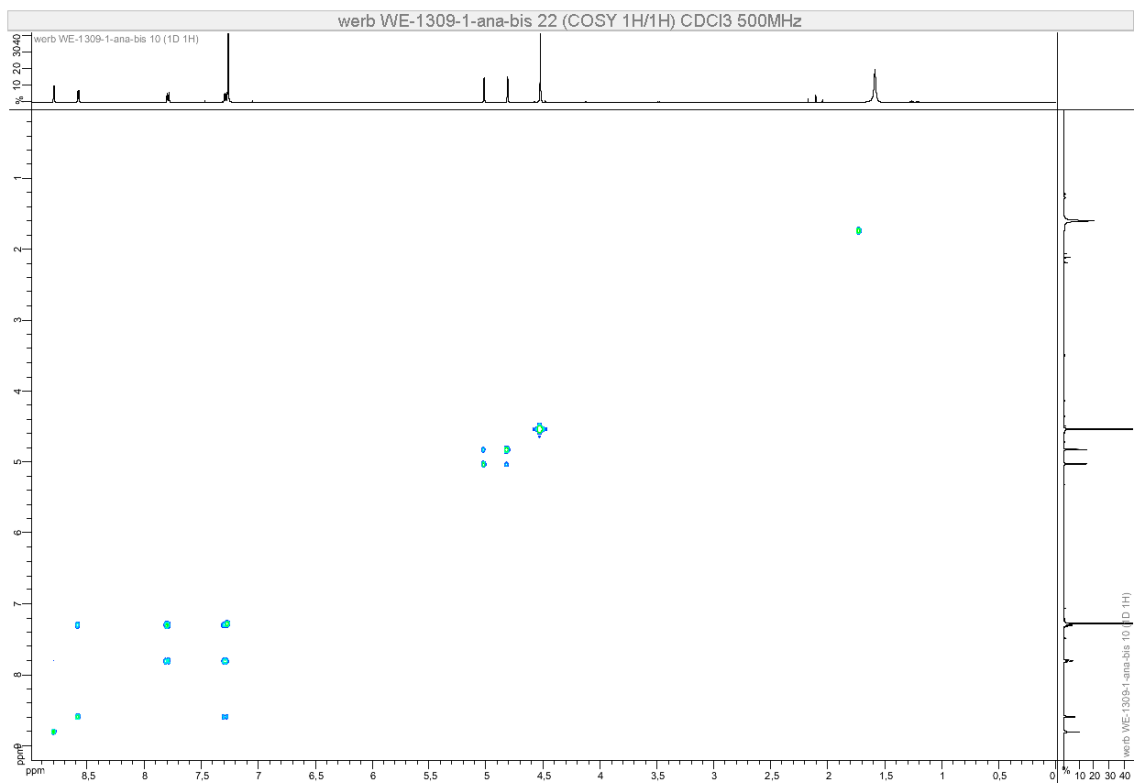


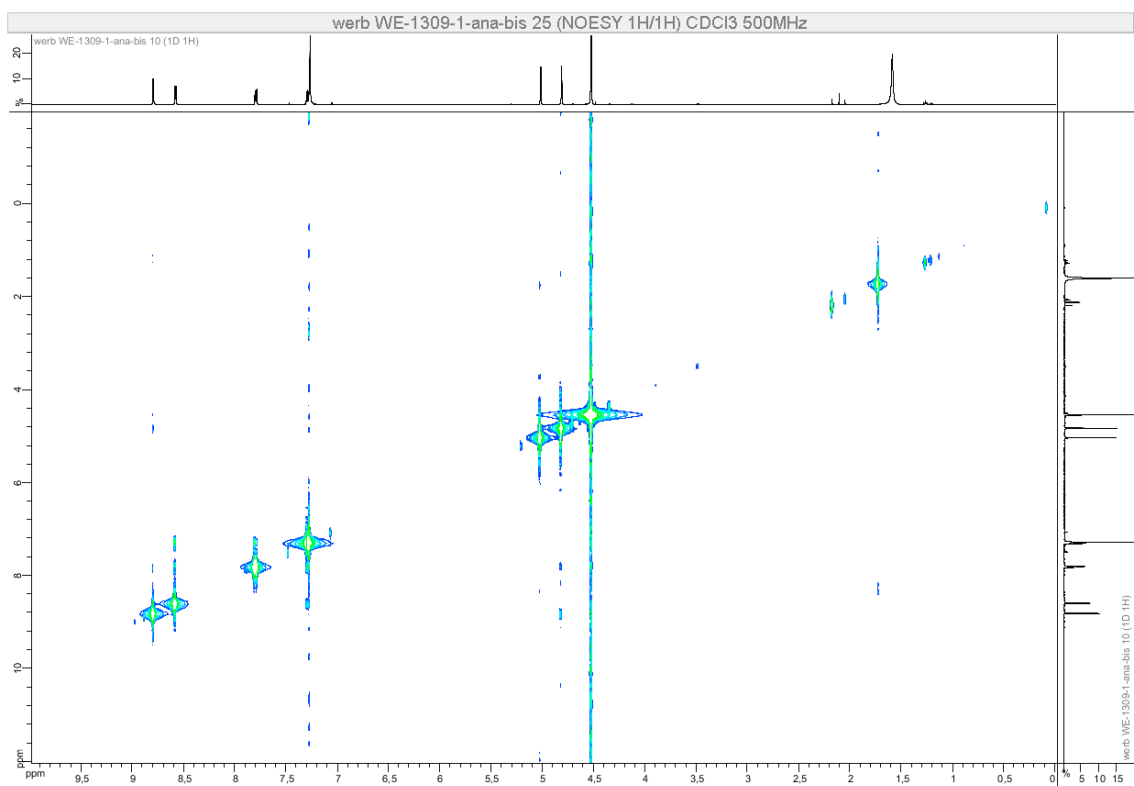
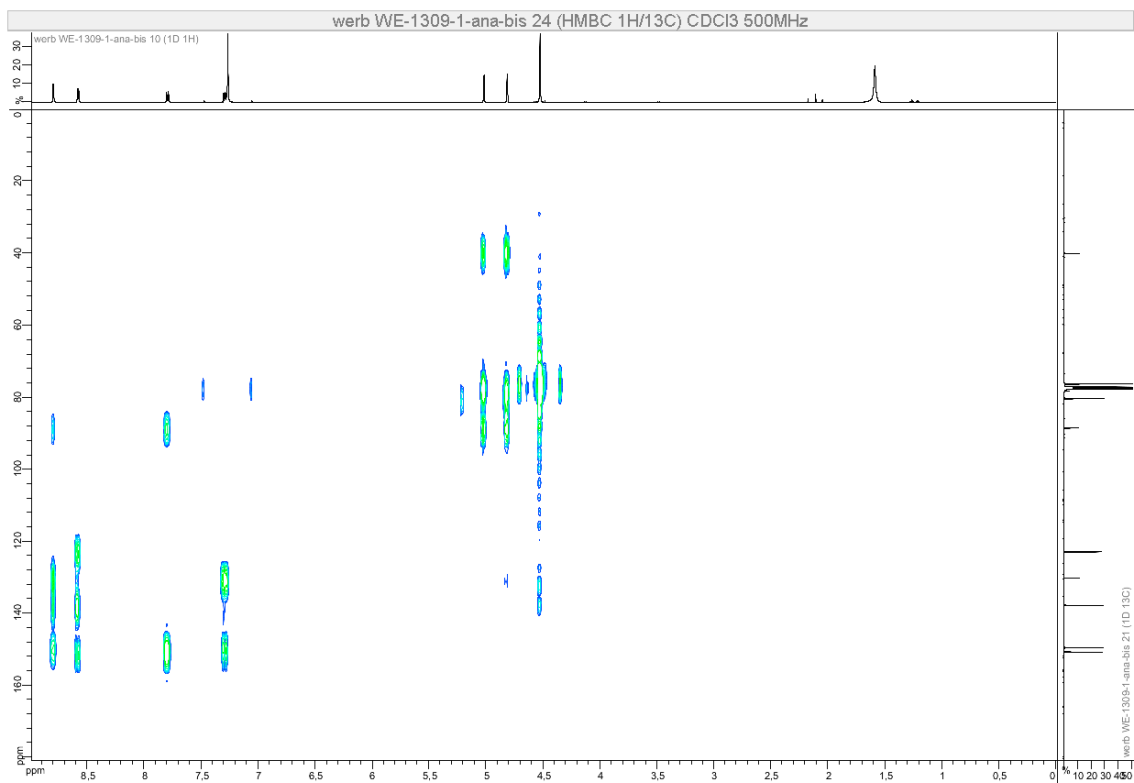


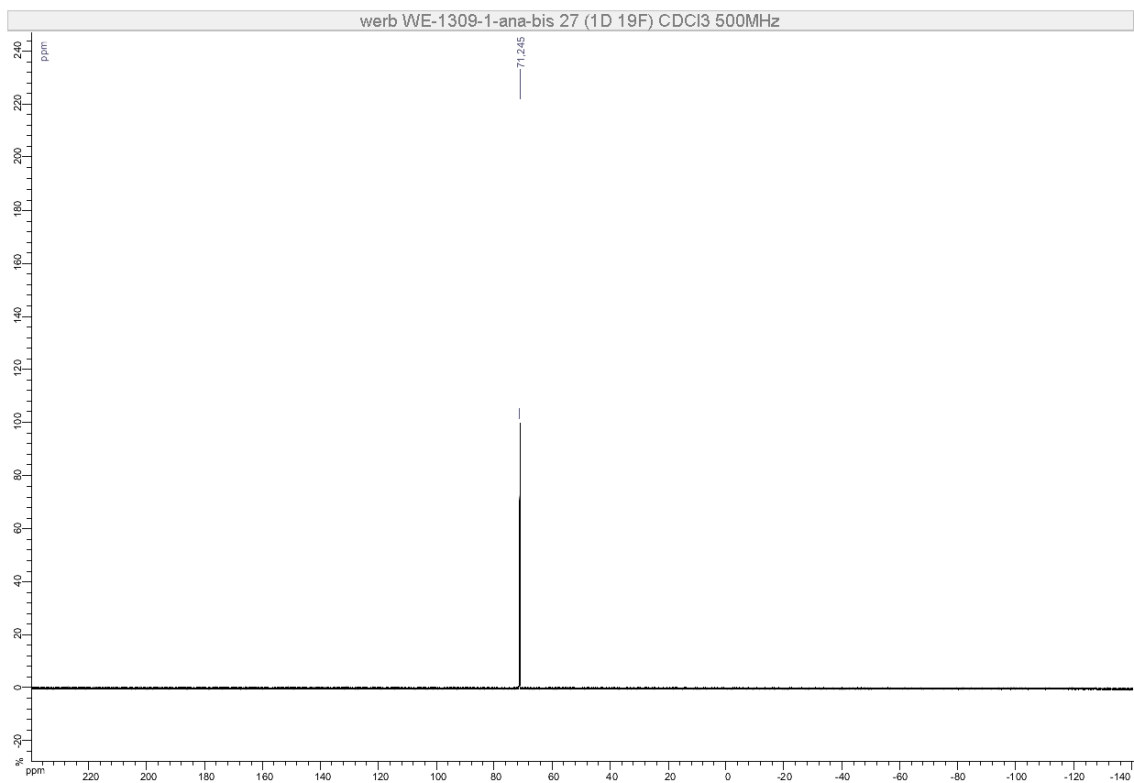


Compound 11

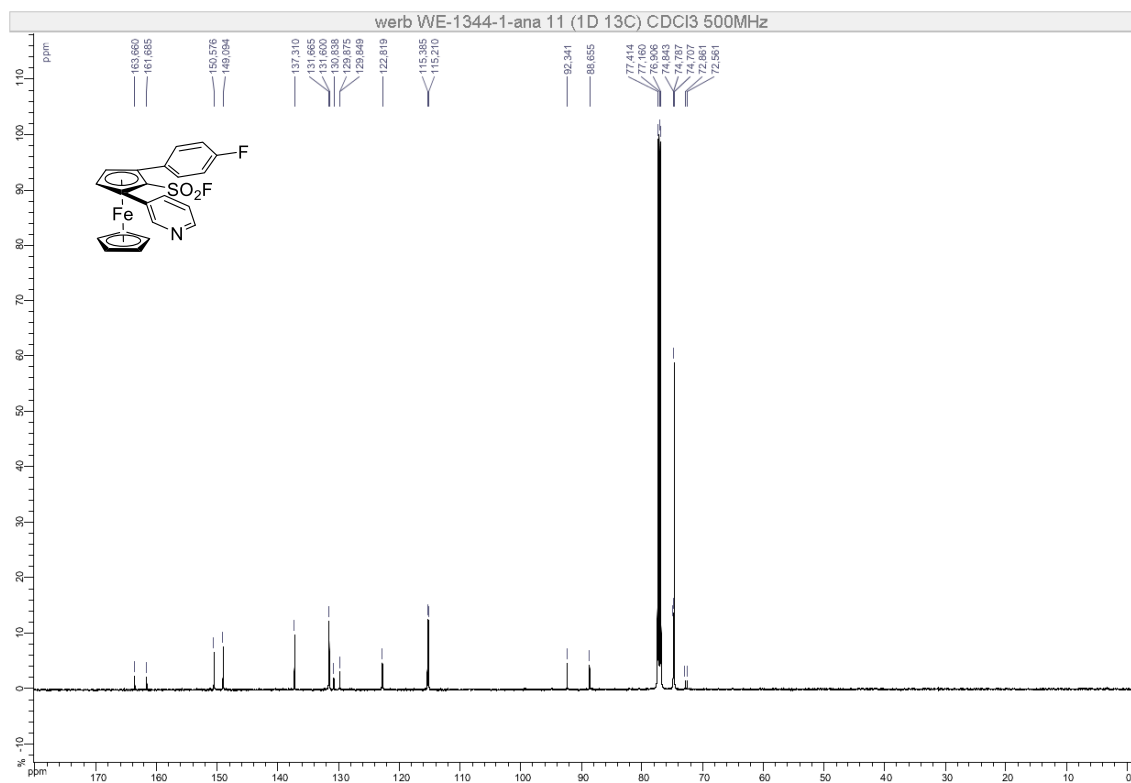
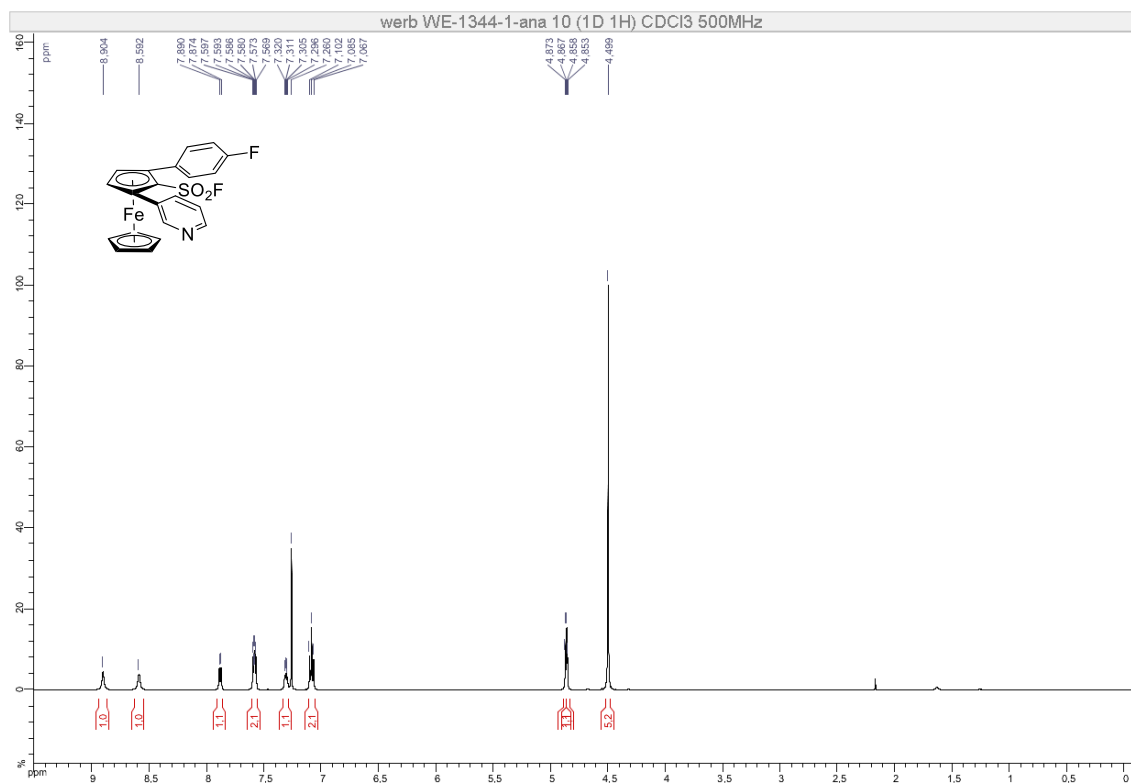


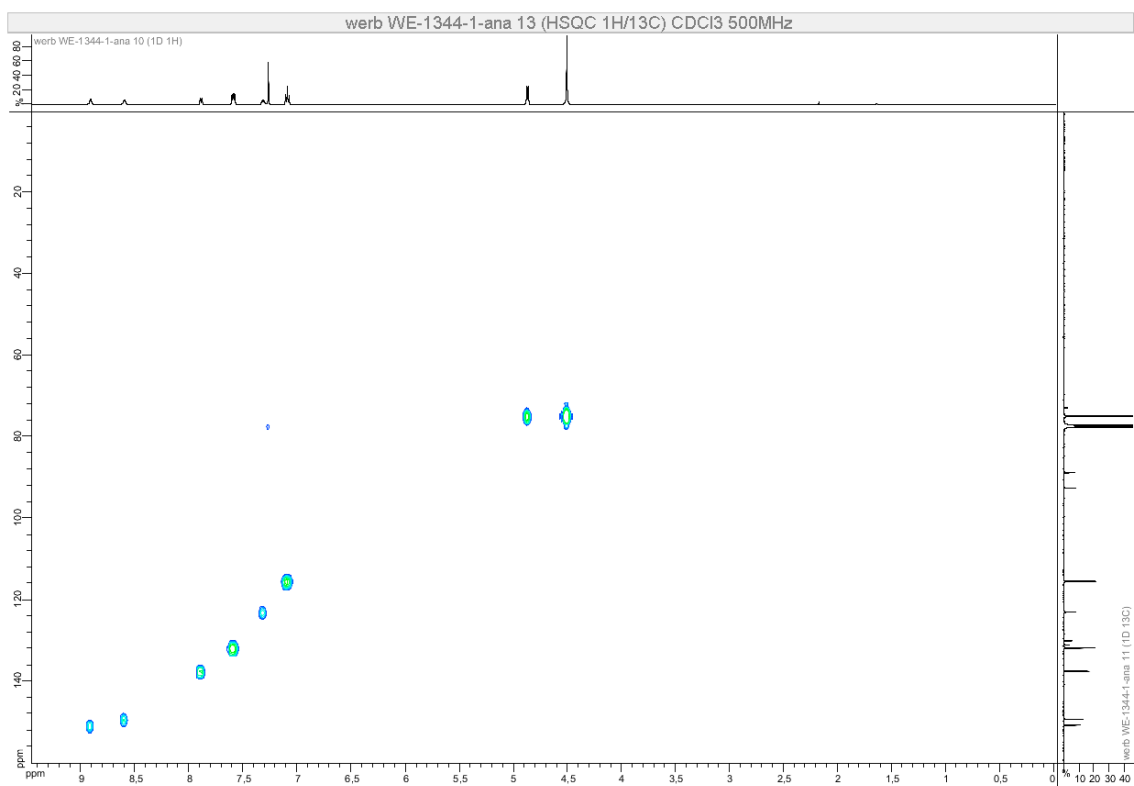
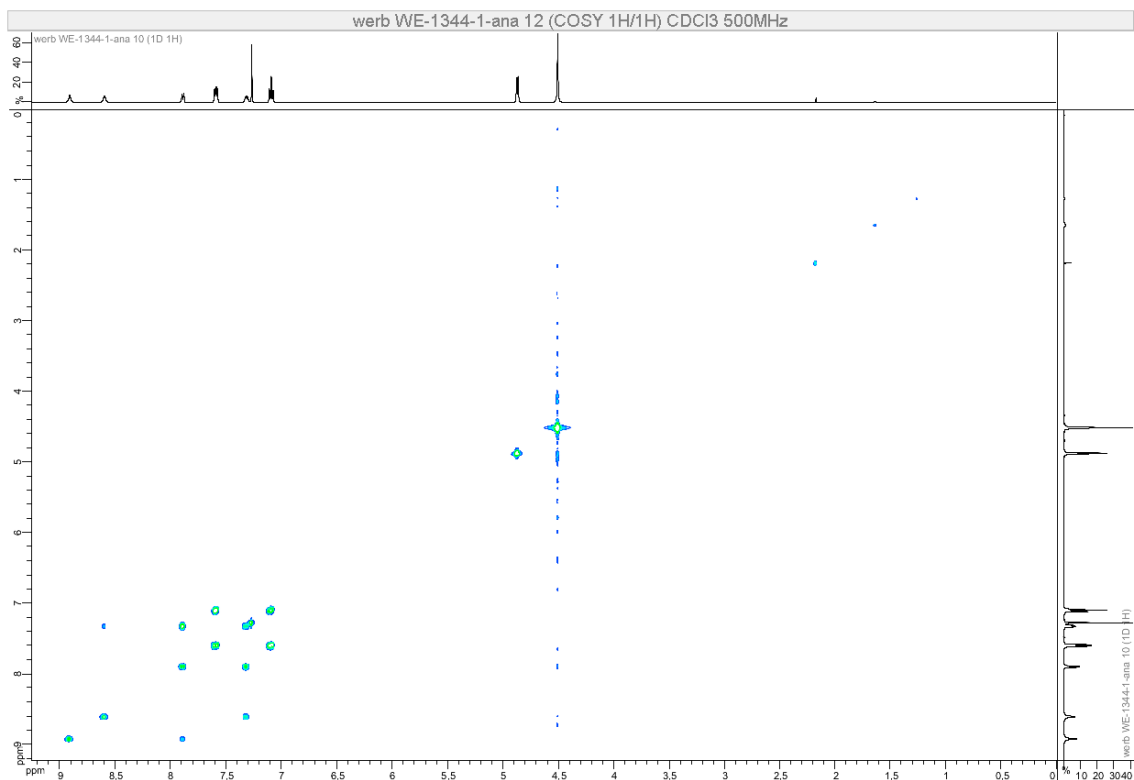


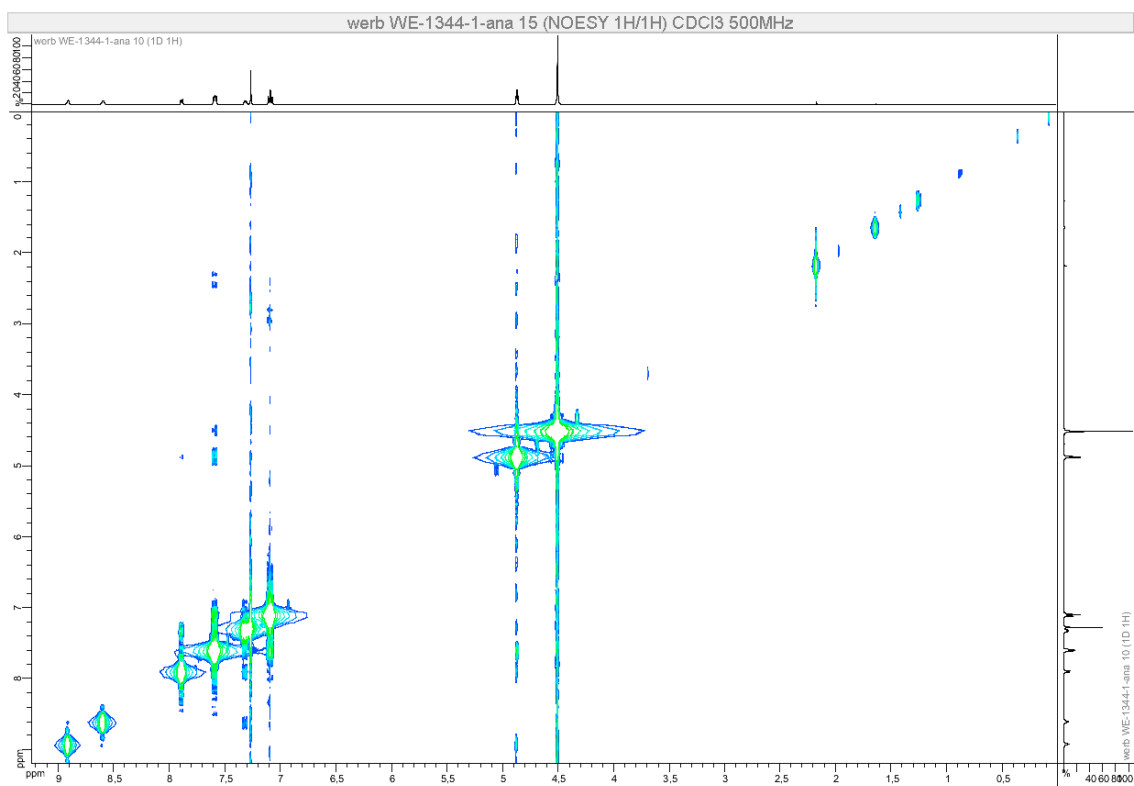
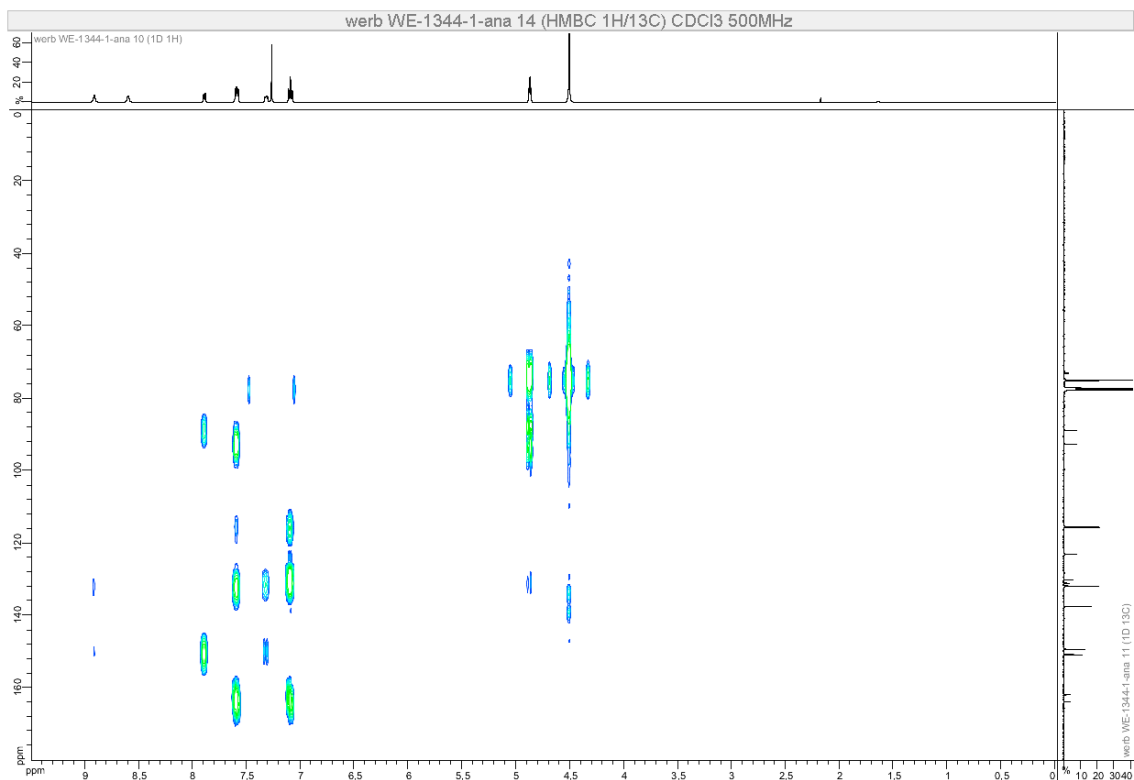


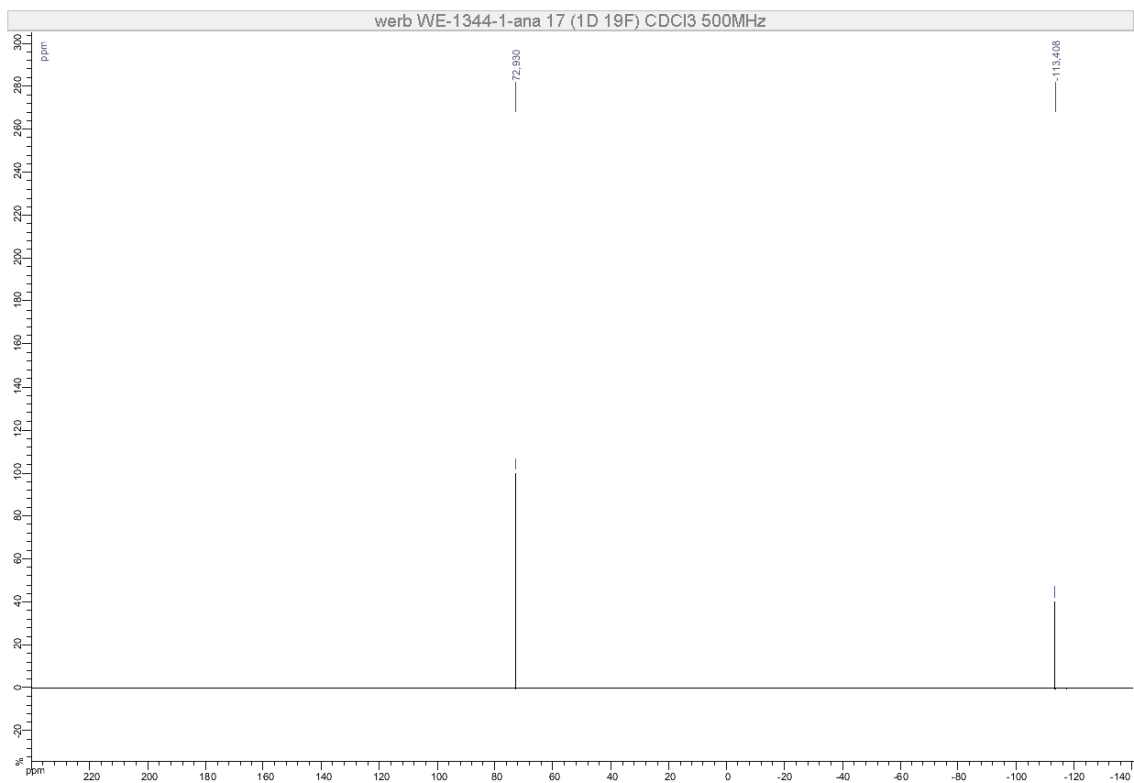


Compound 12

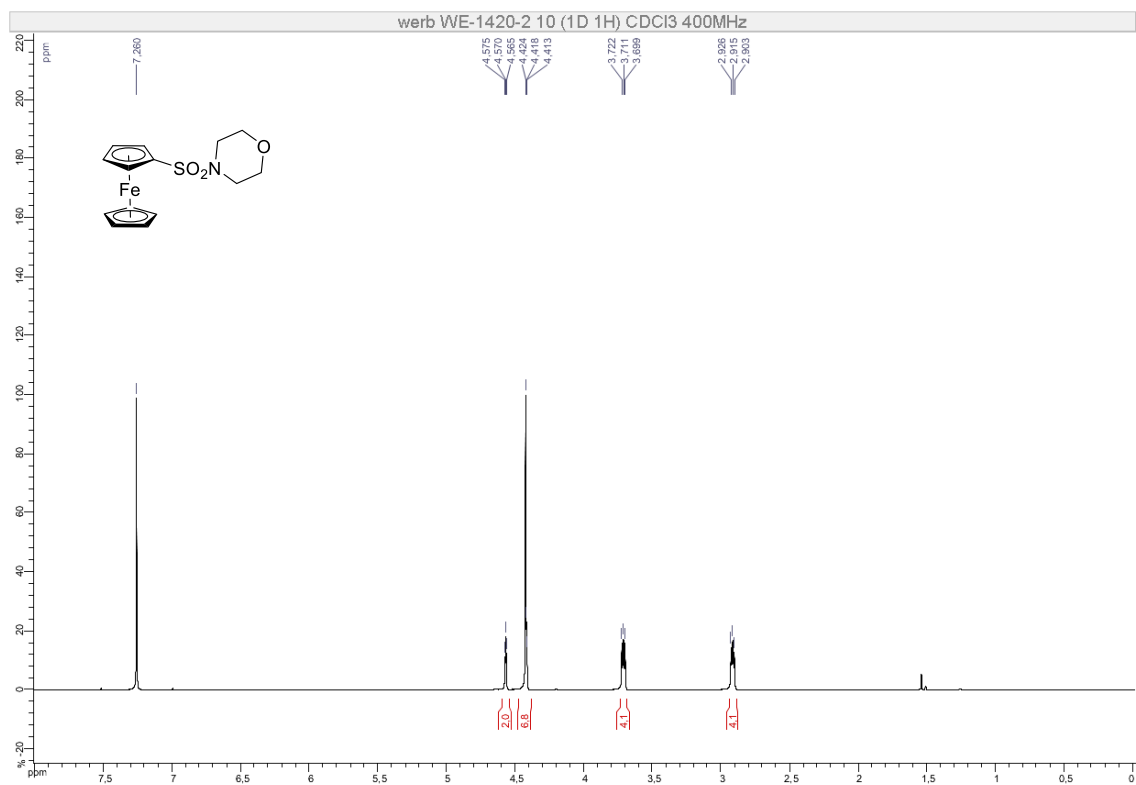




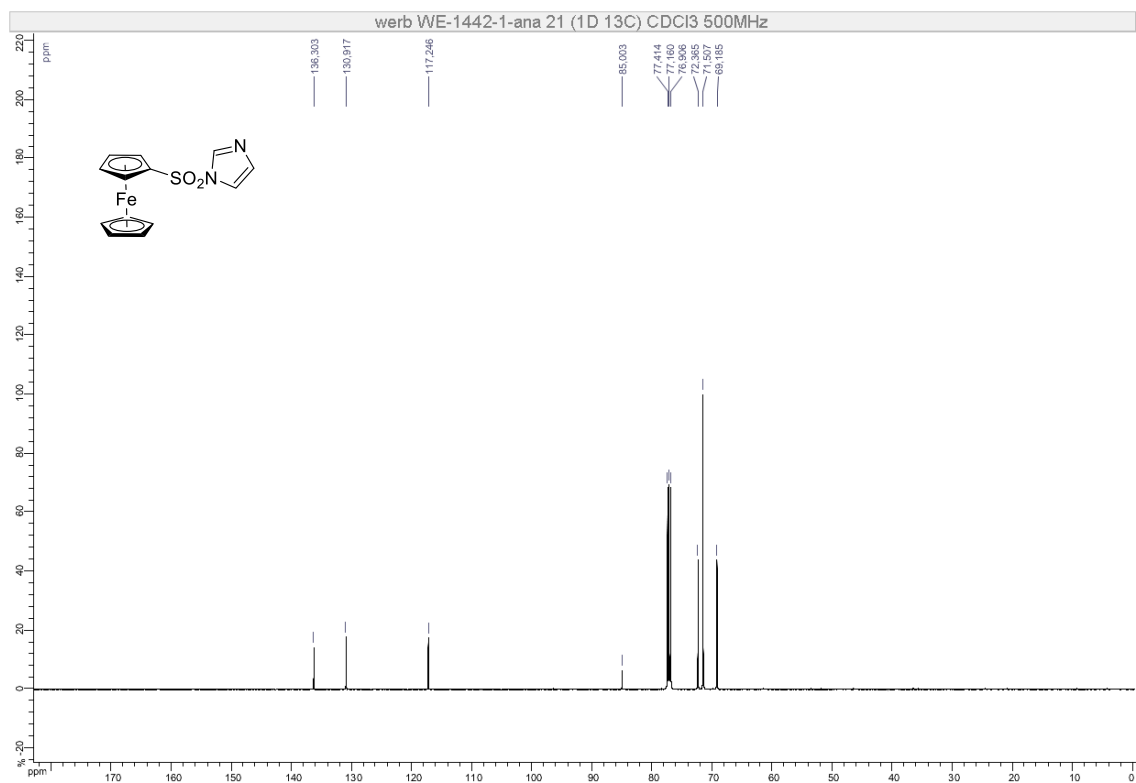
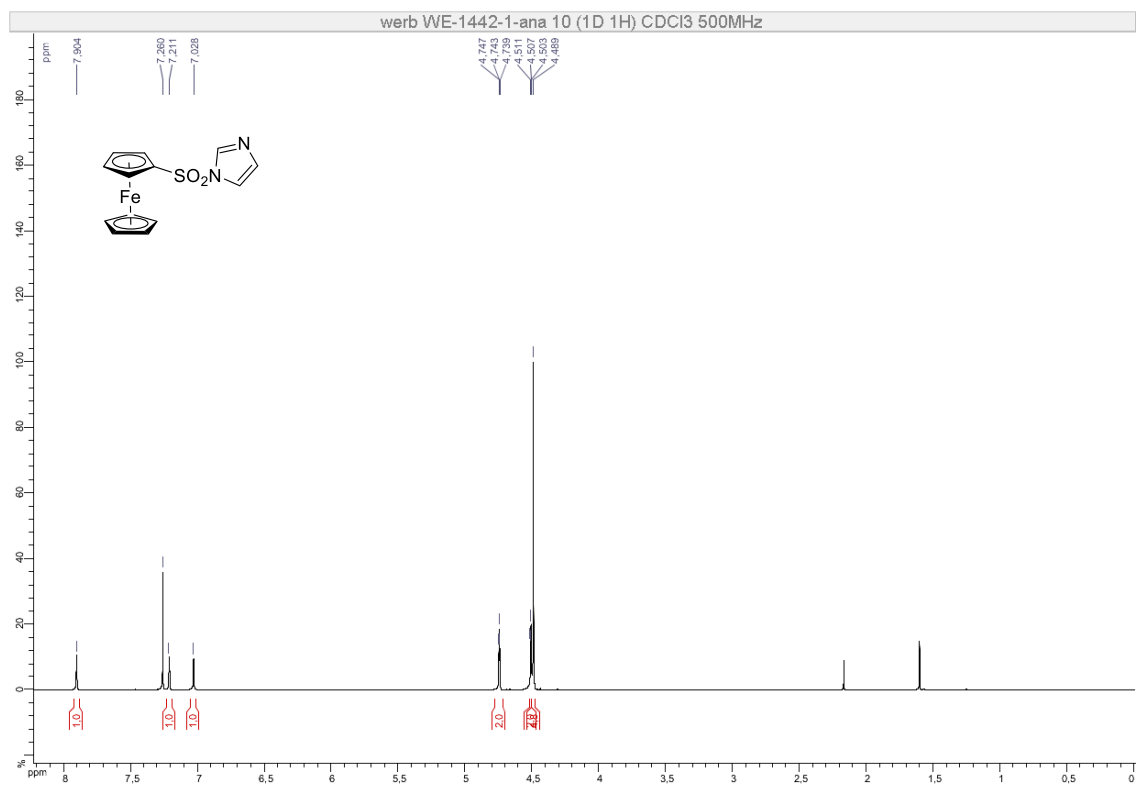


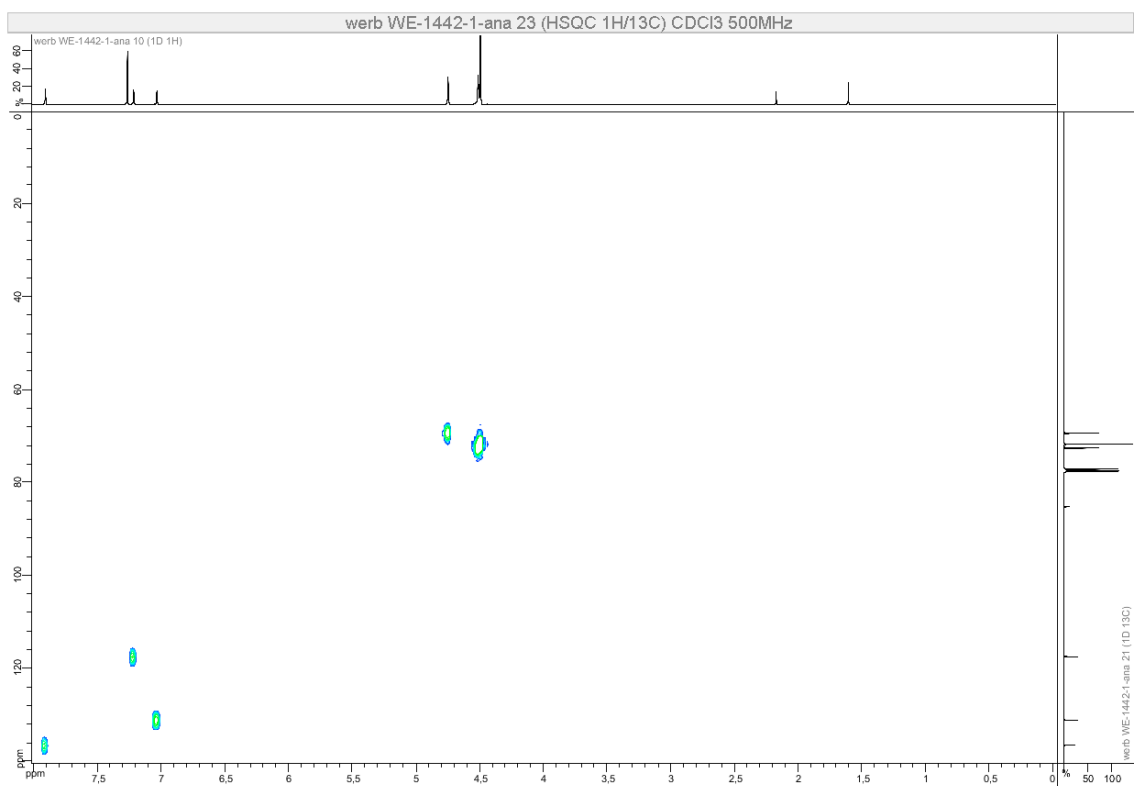
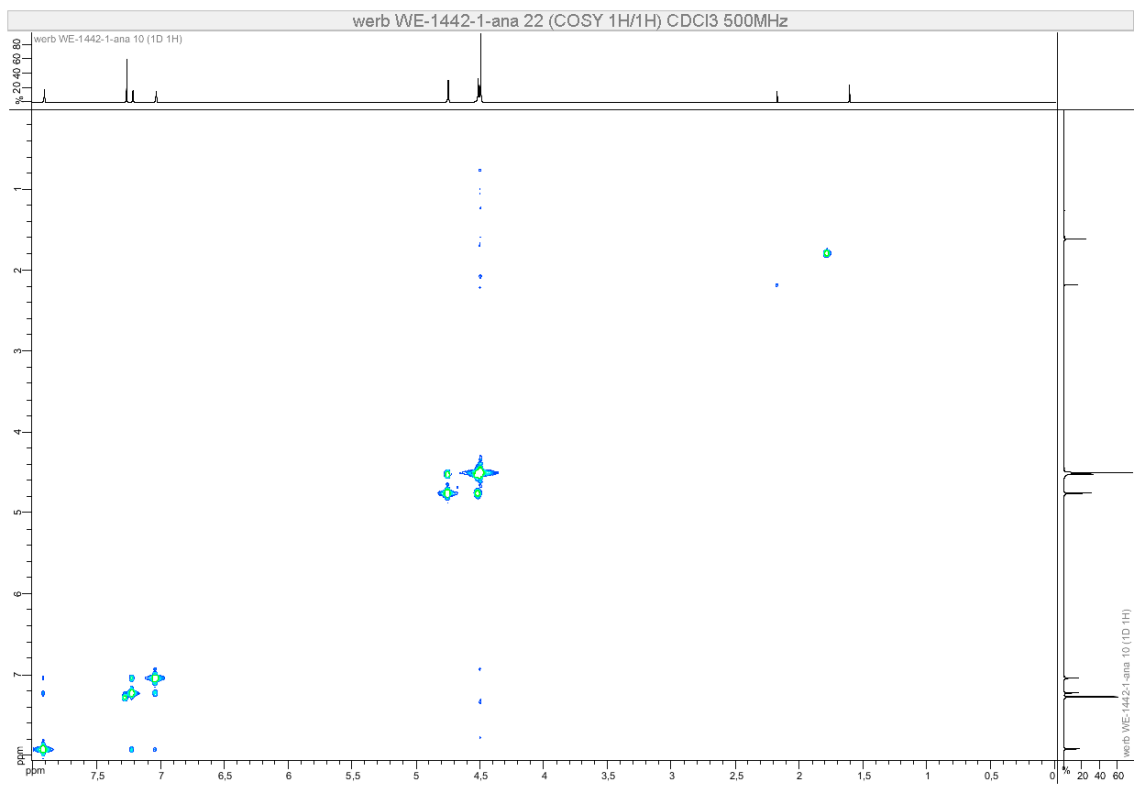


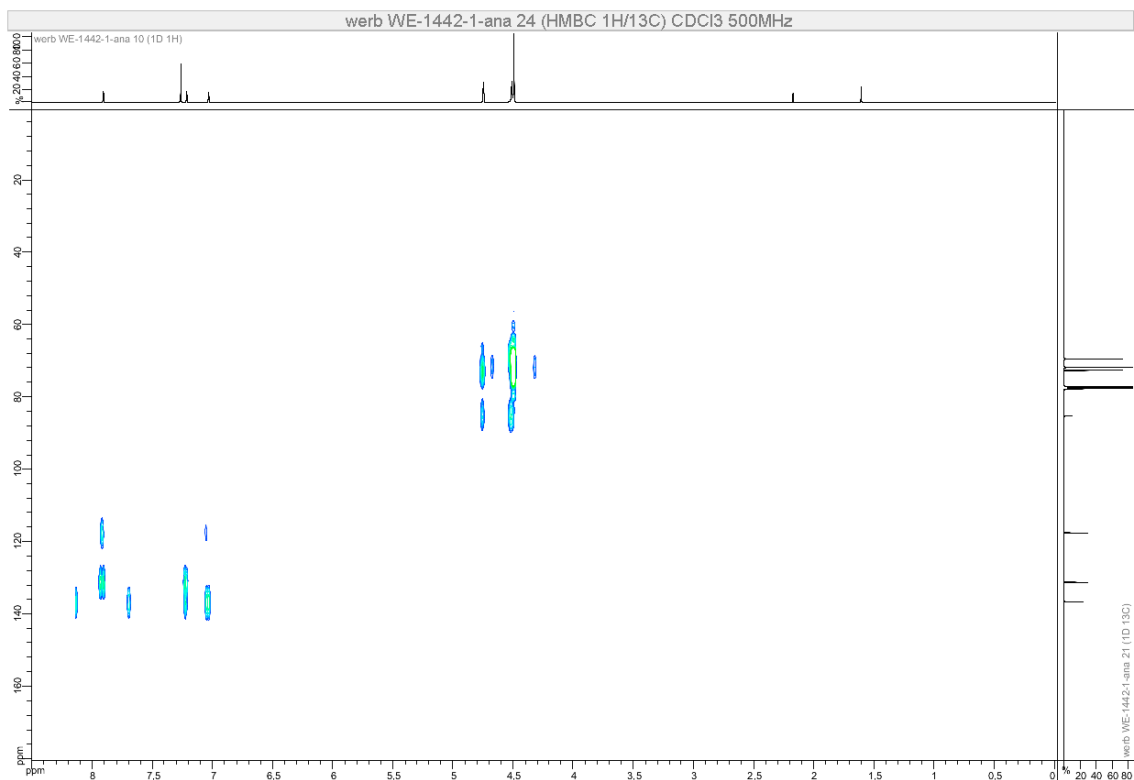
Compound 13a



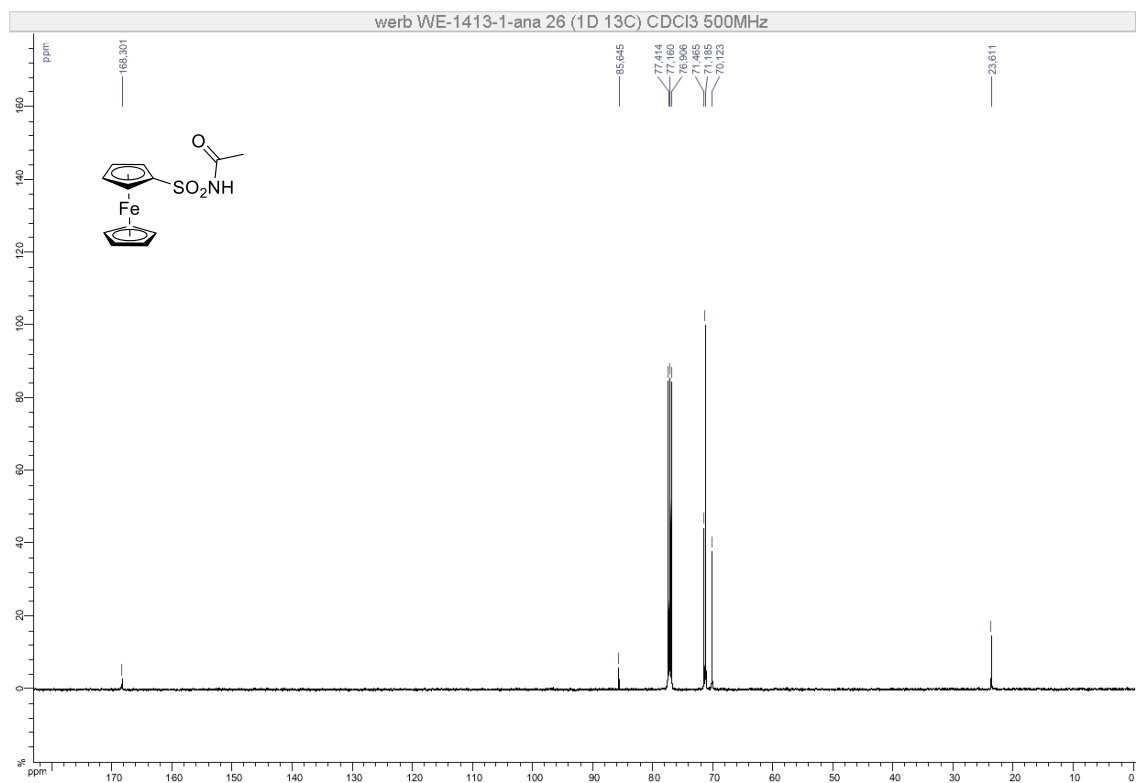
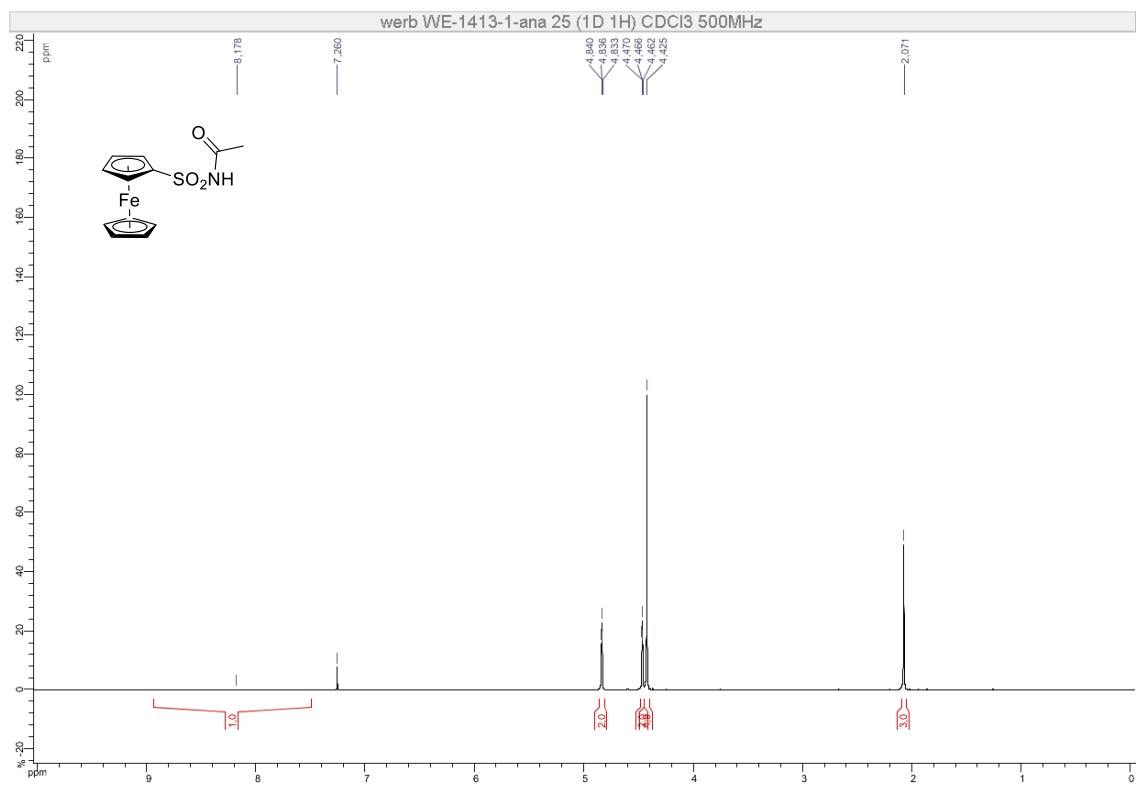
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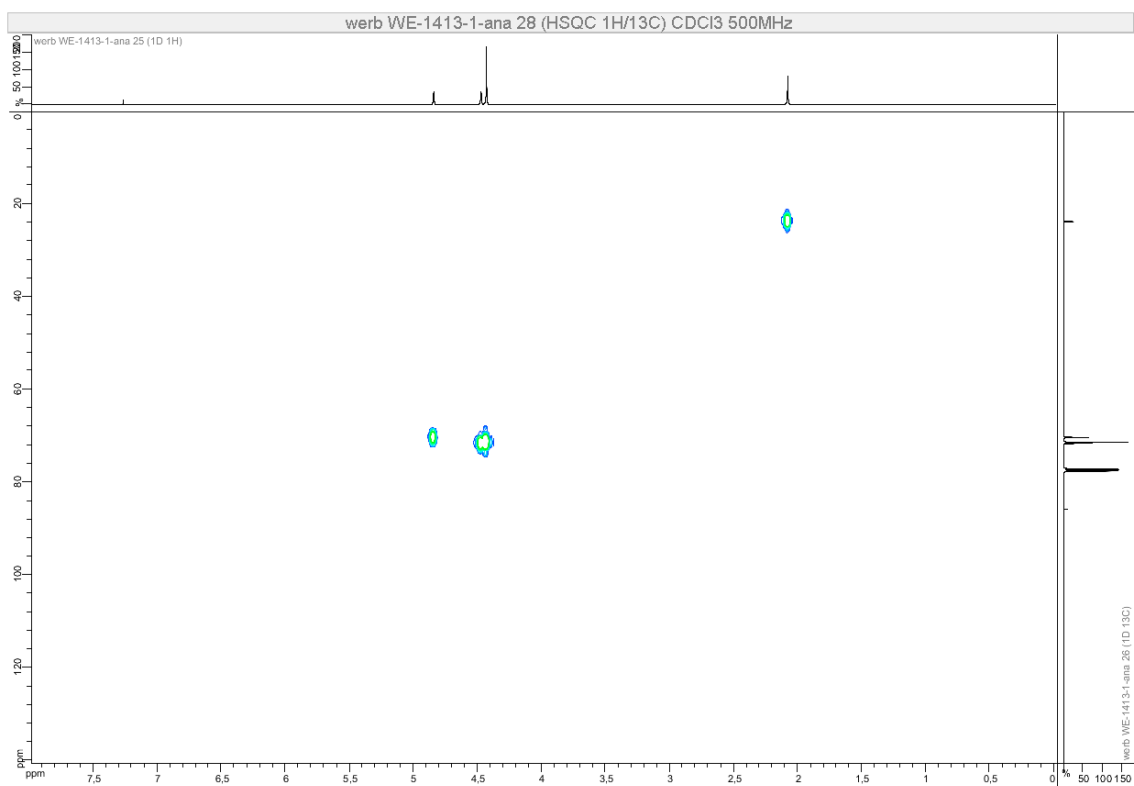
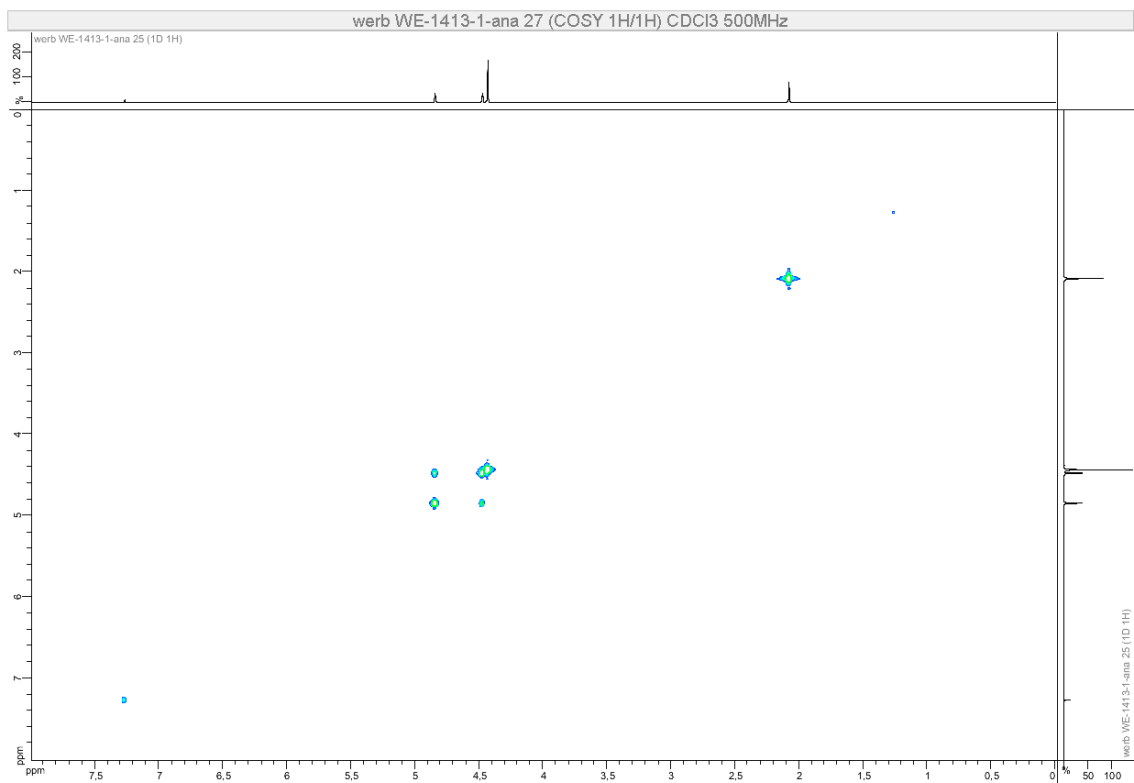


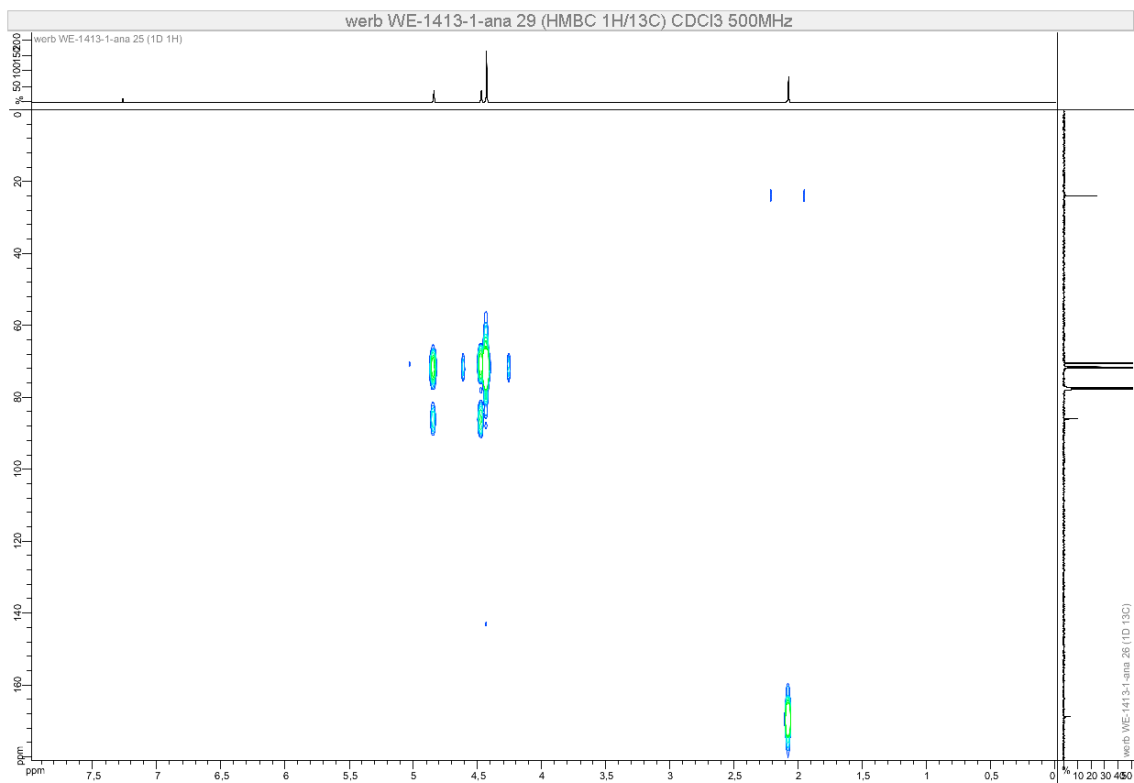




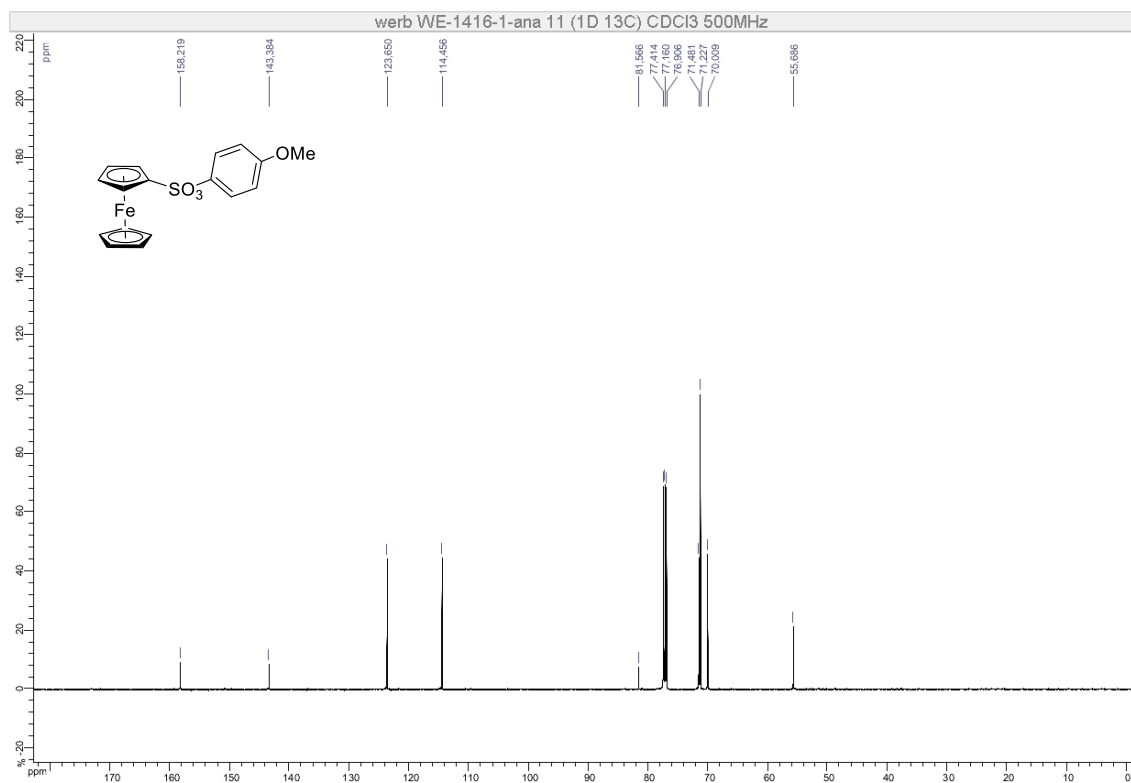
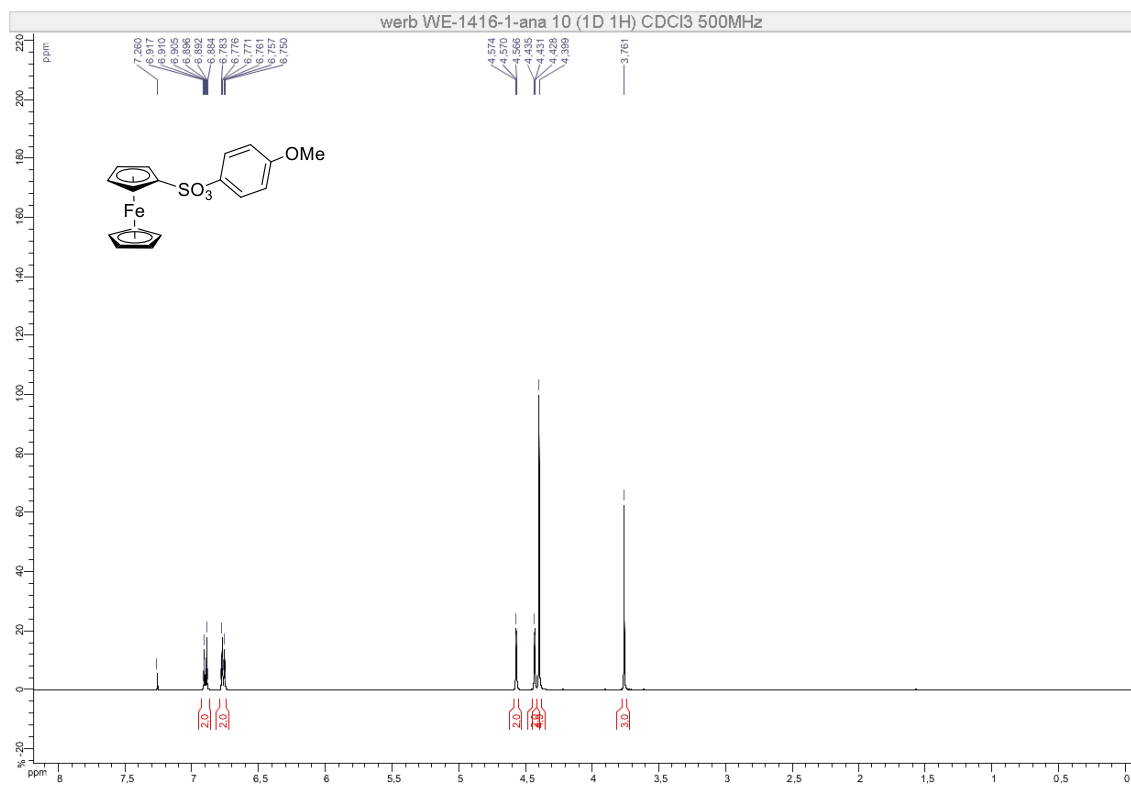
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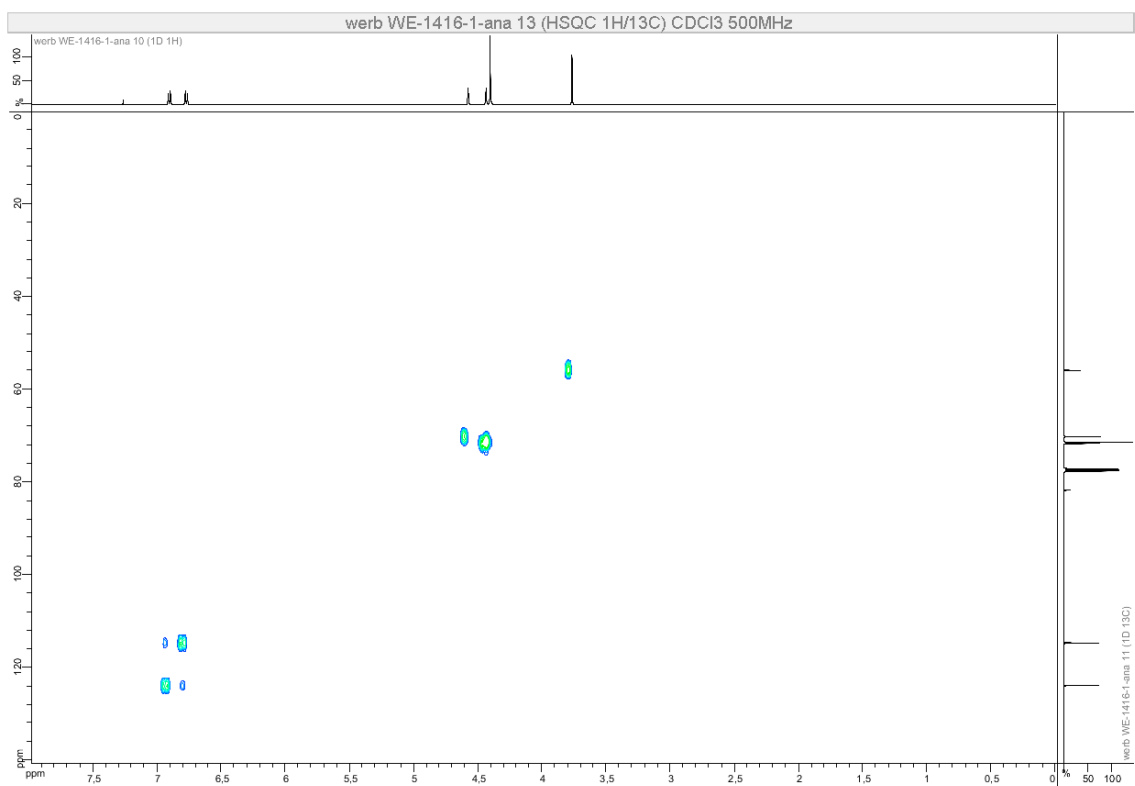
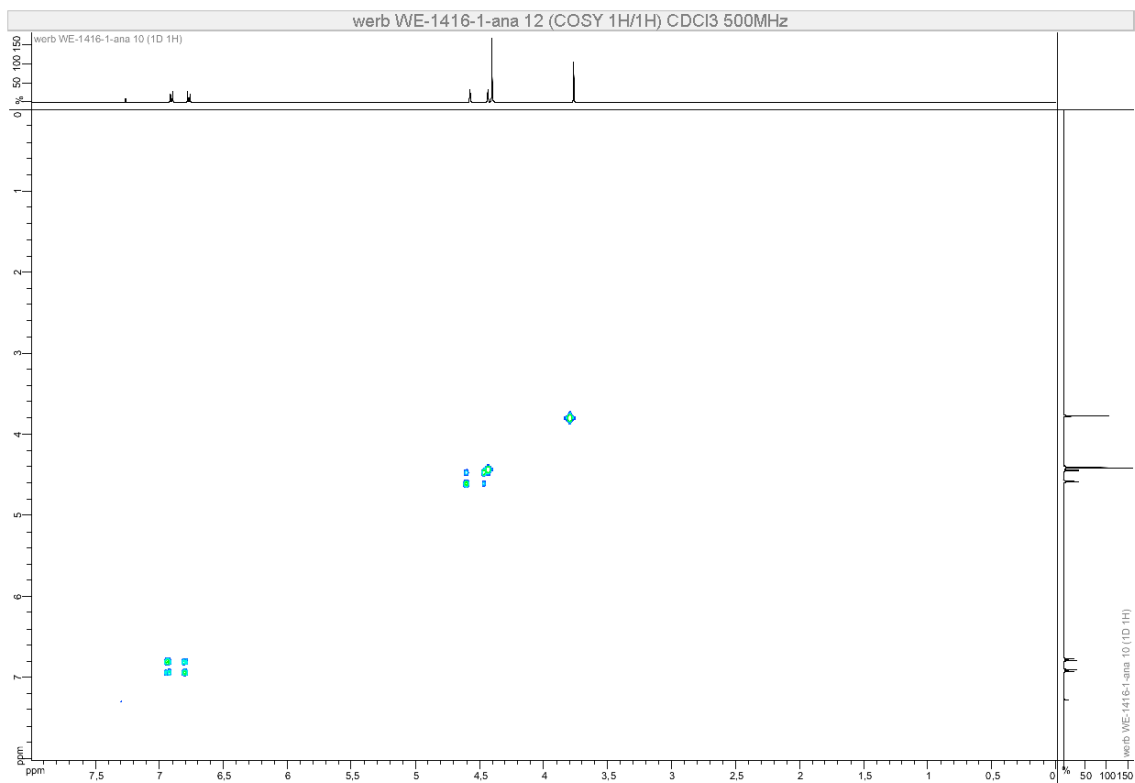


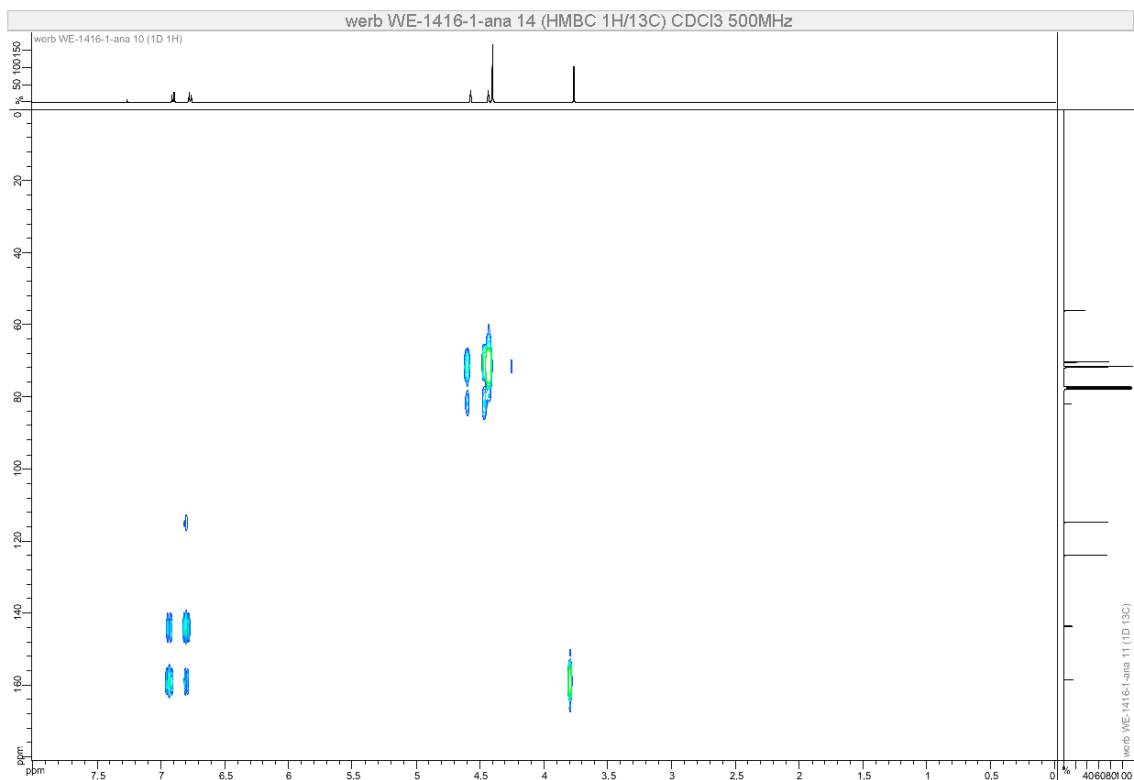




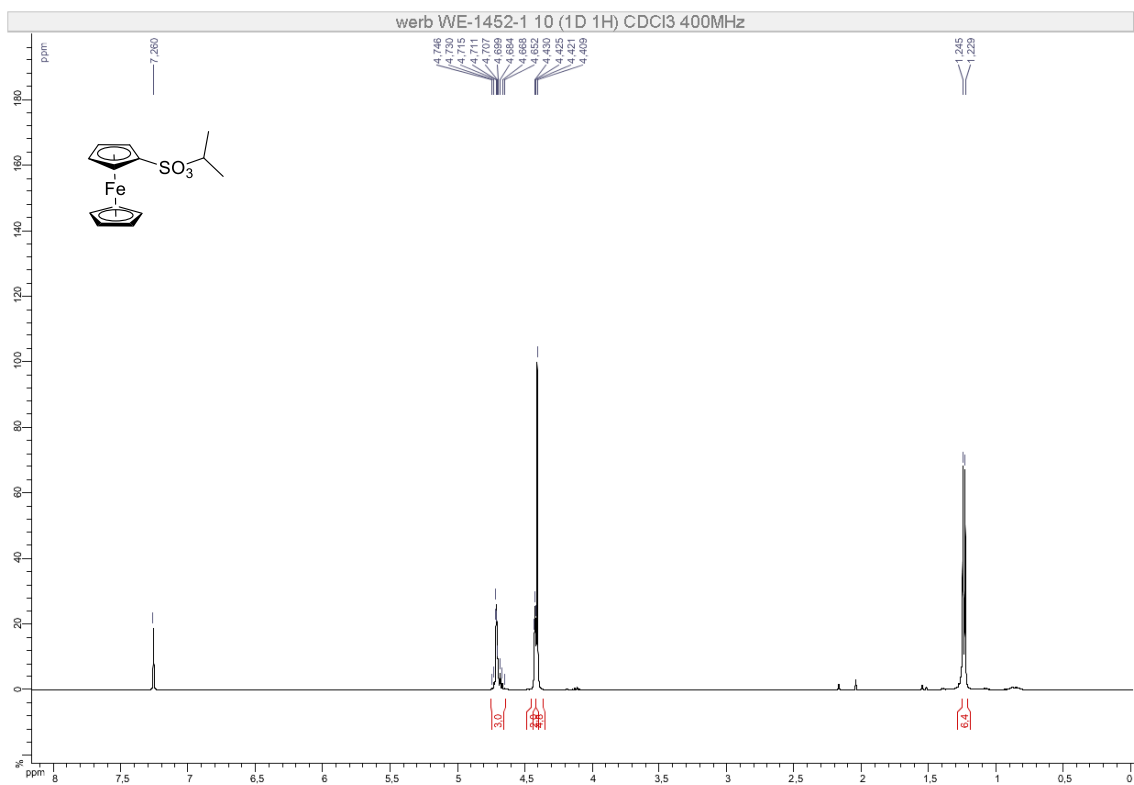
Compound 13d



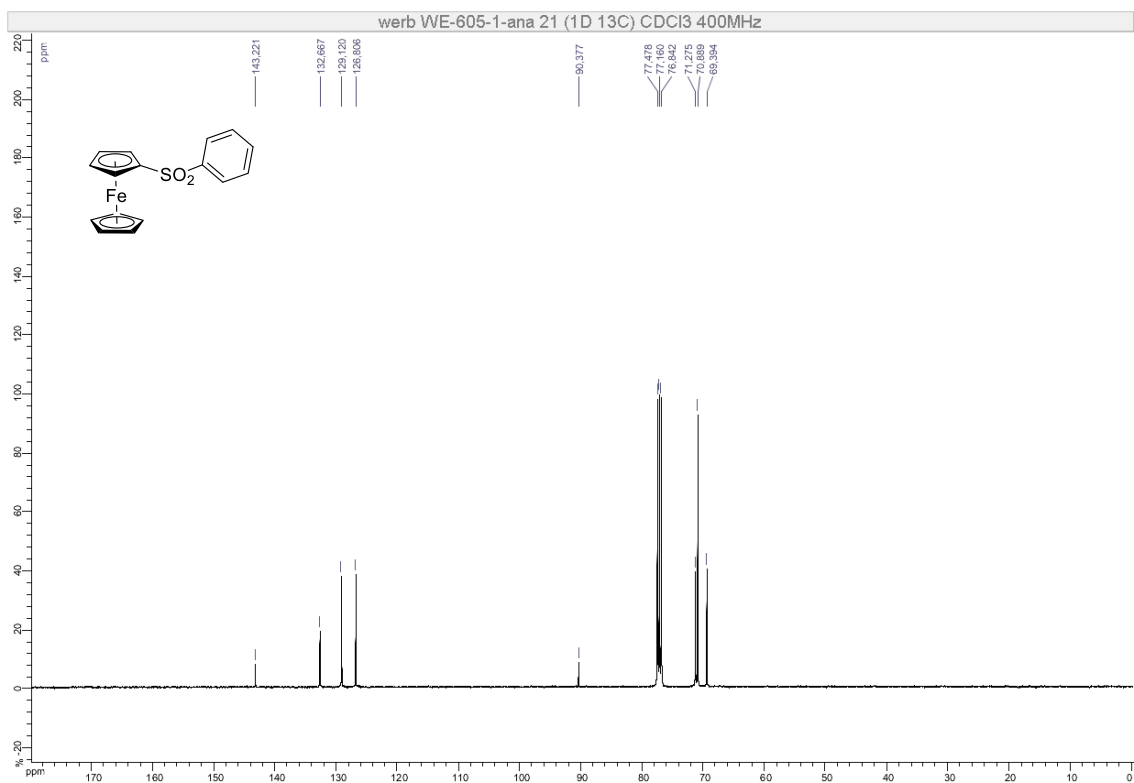
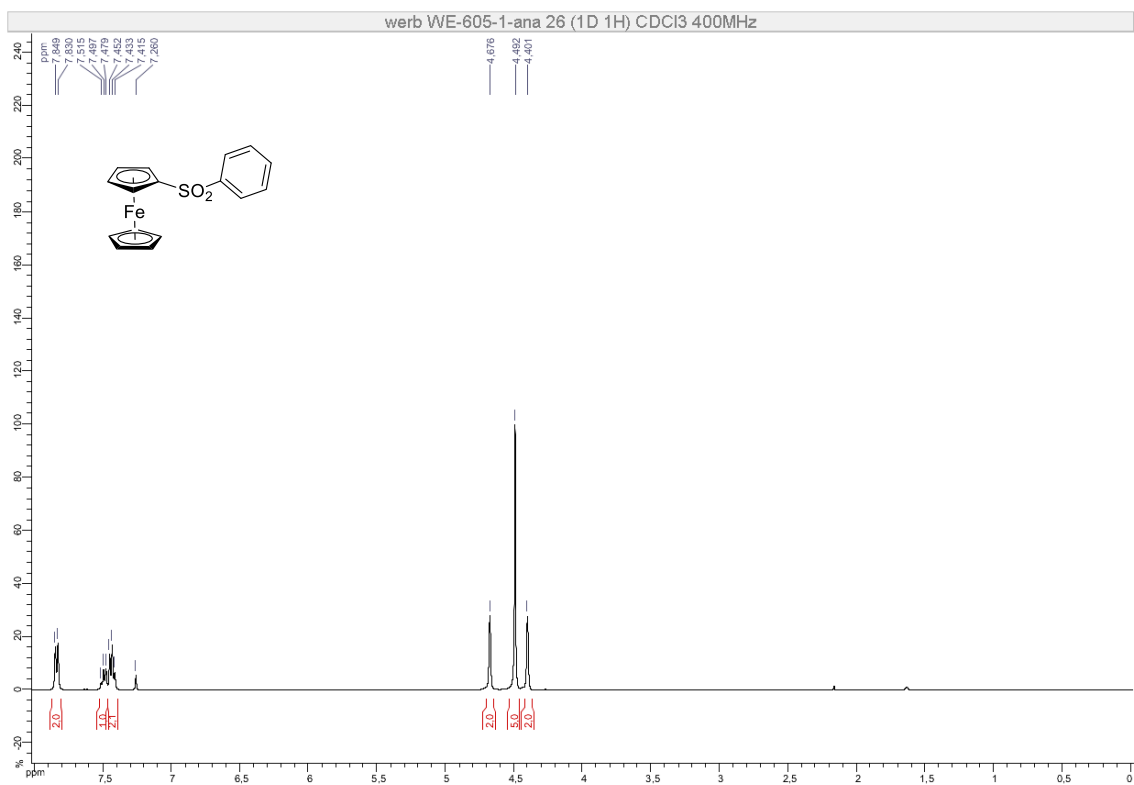


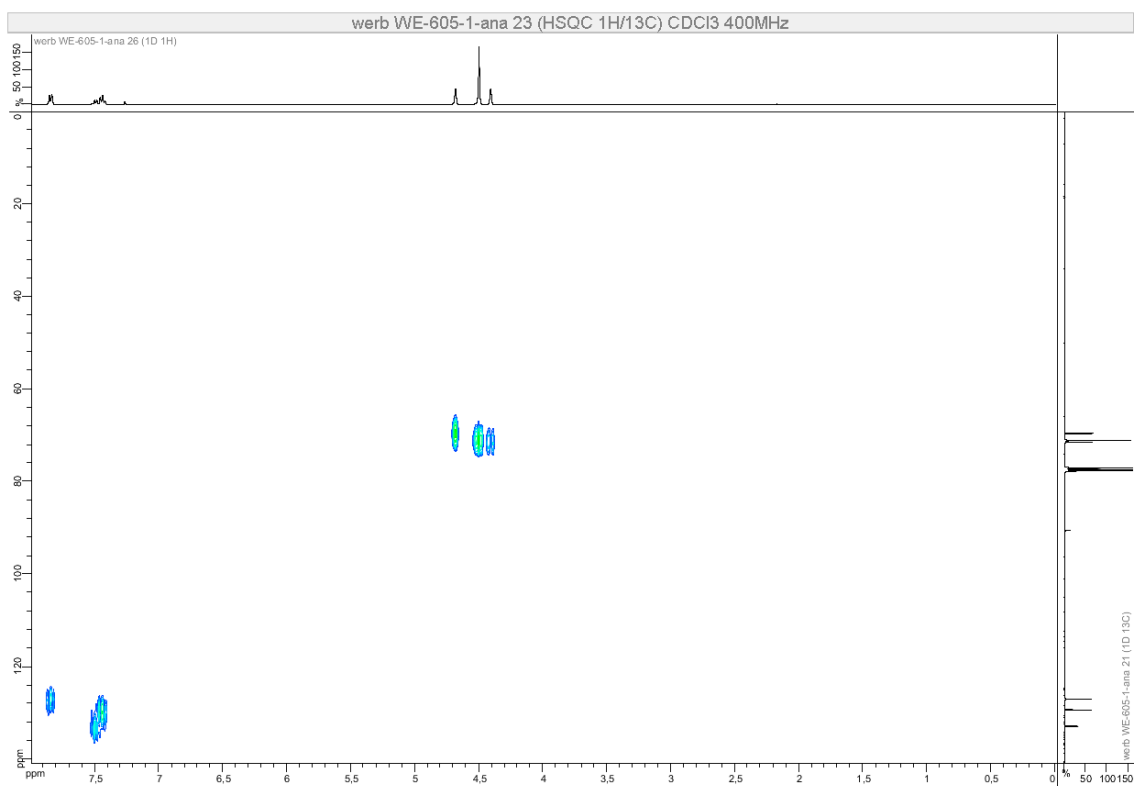
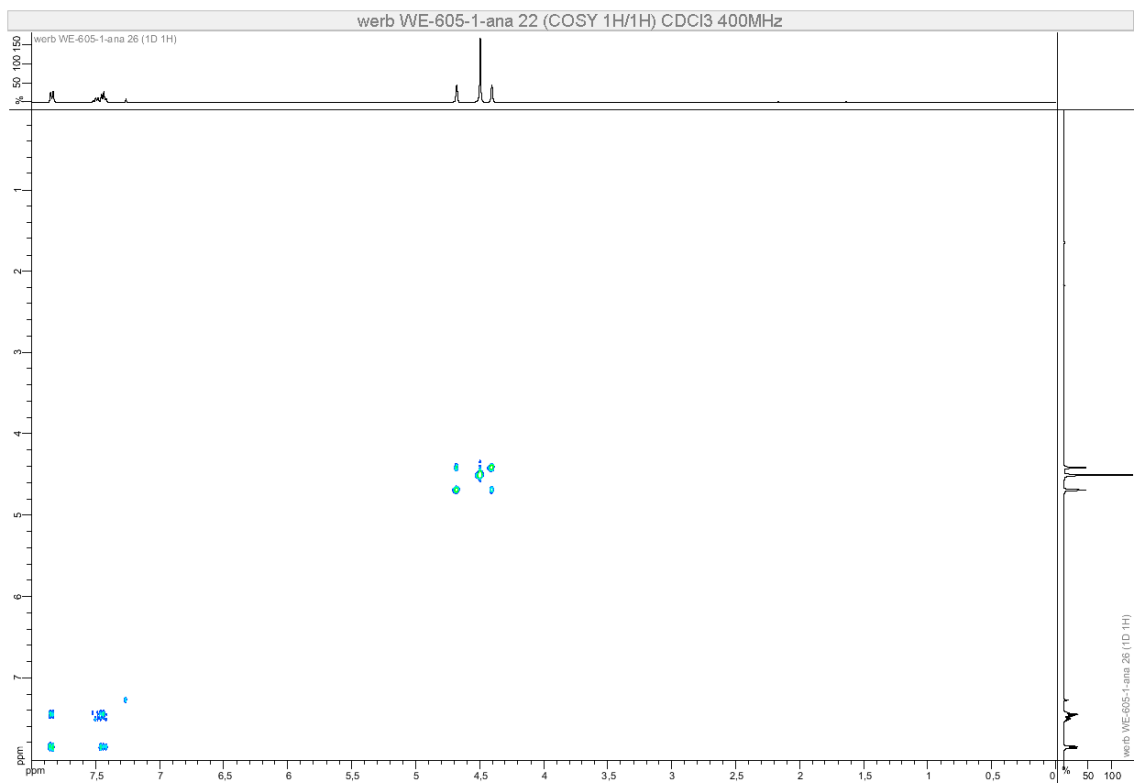


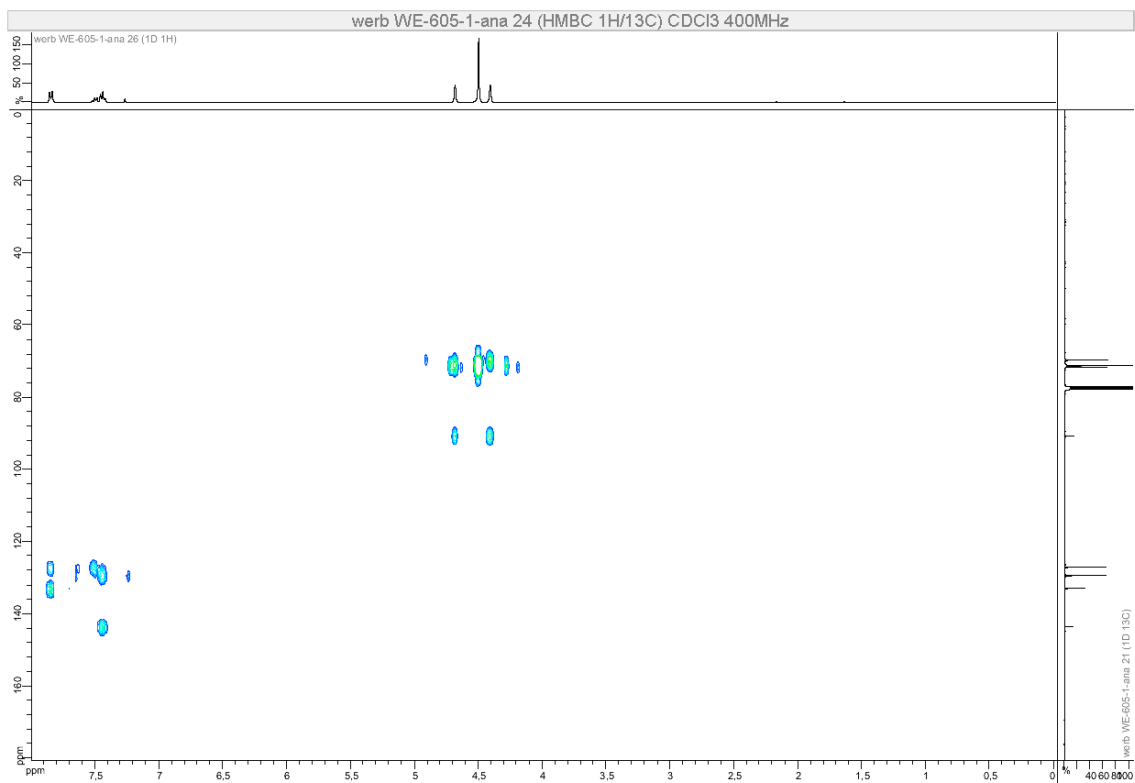
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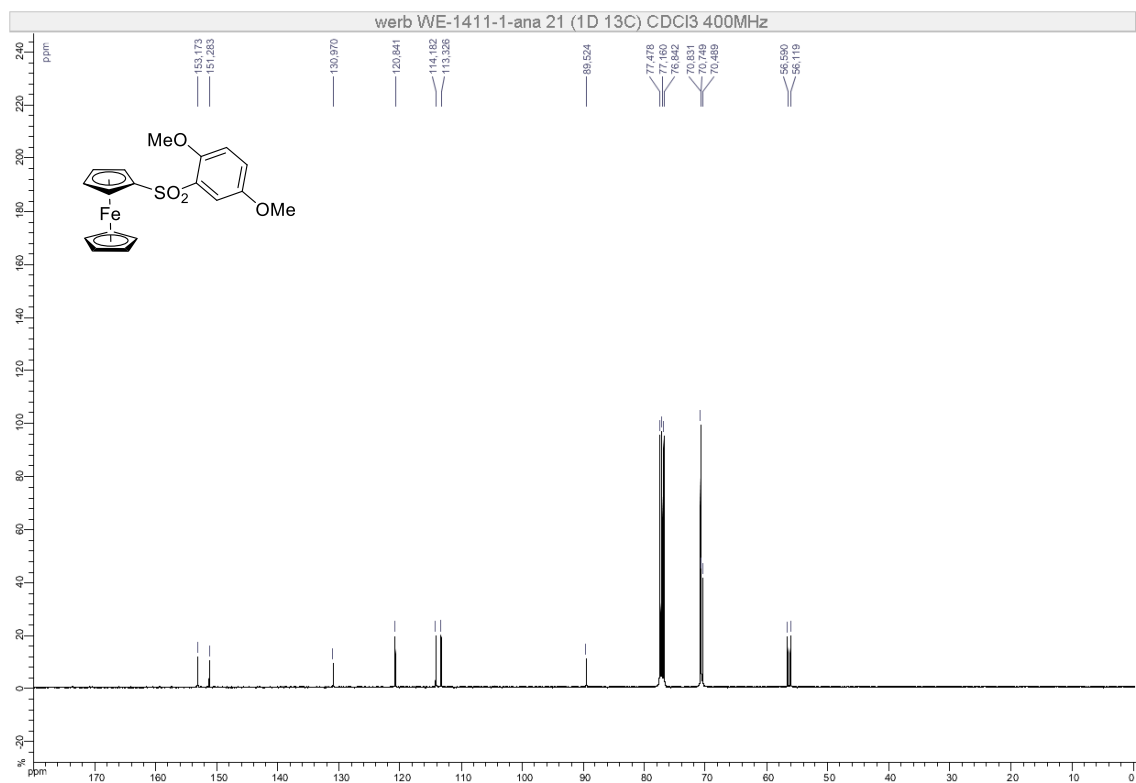
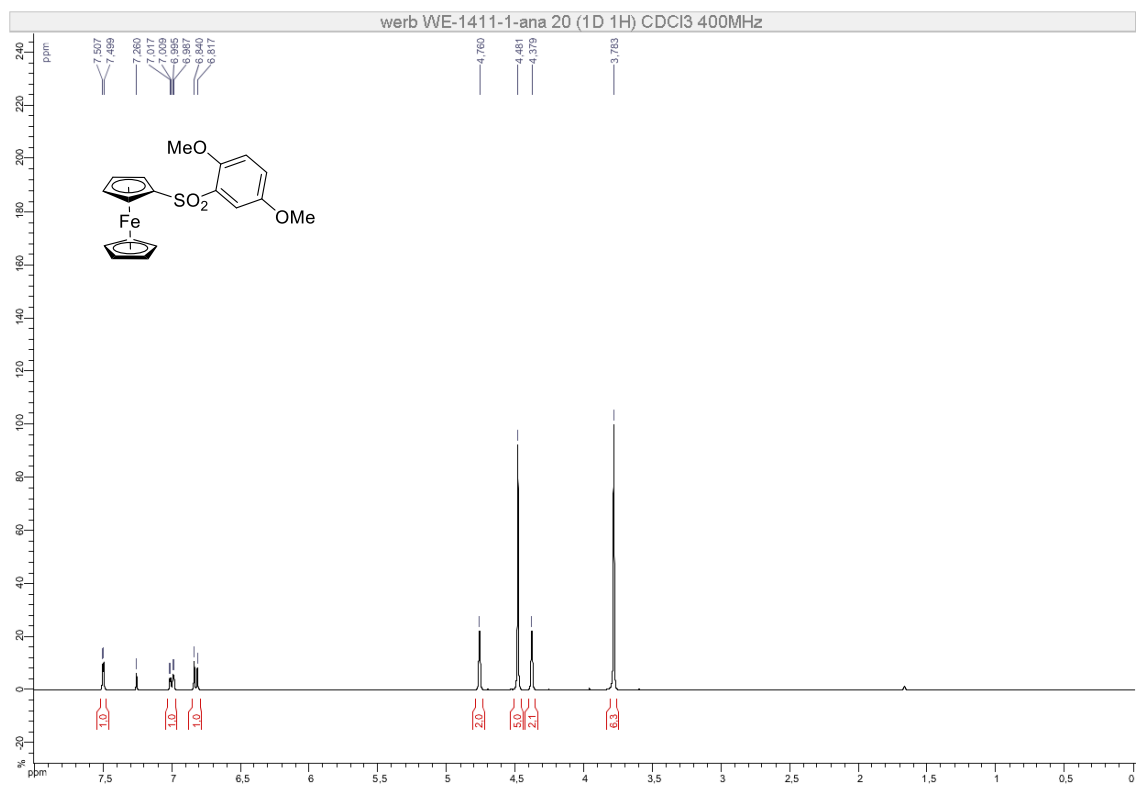
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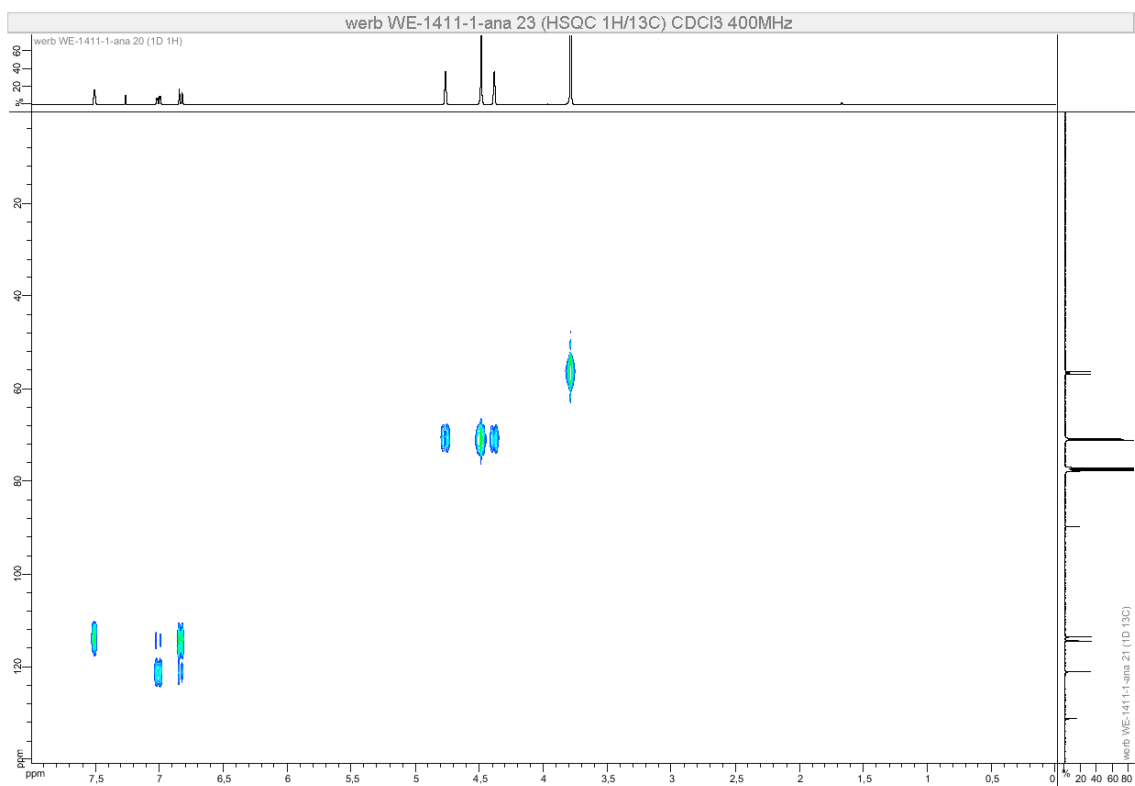
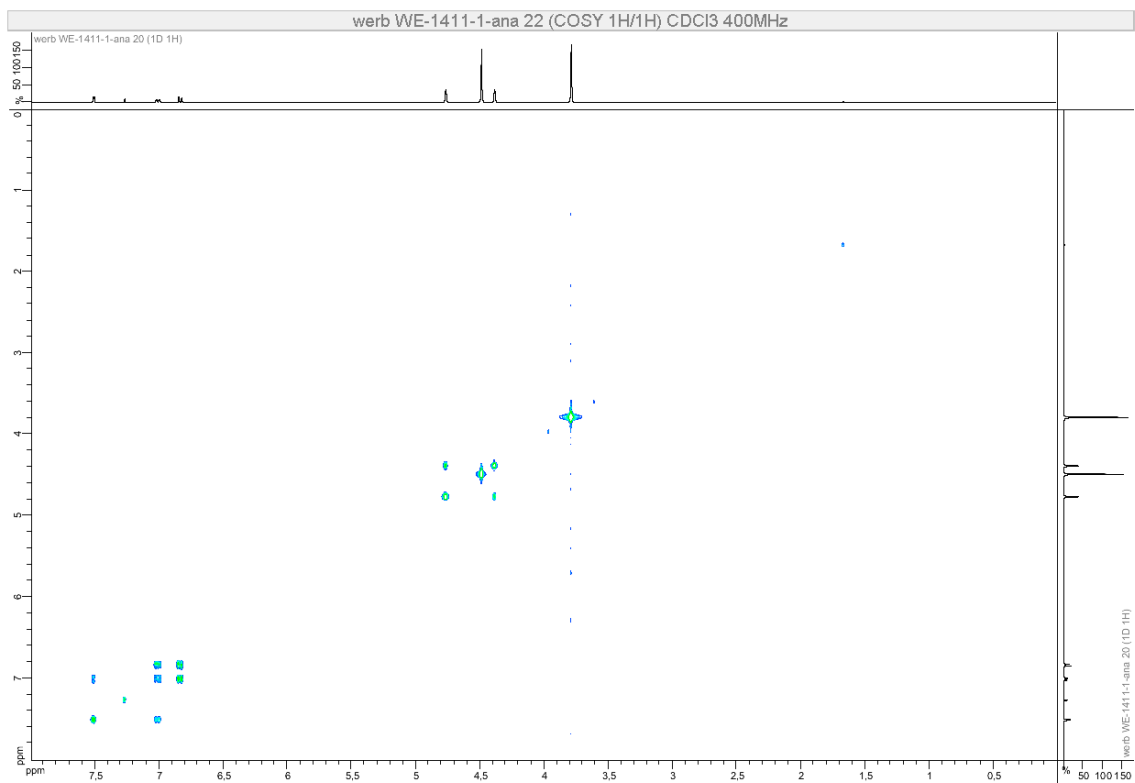


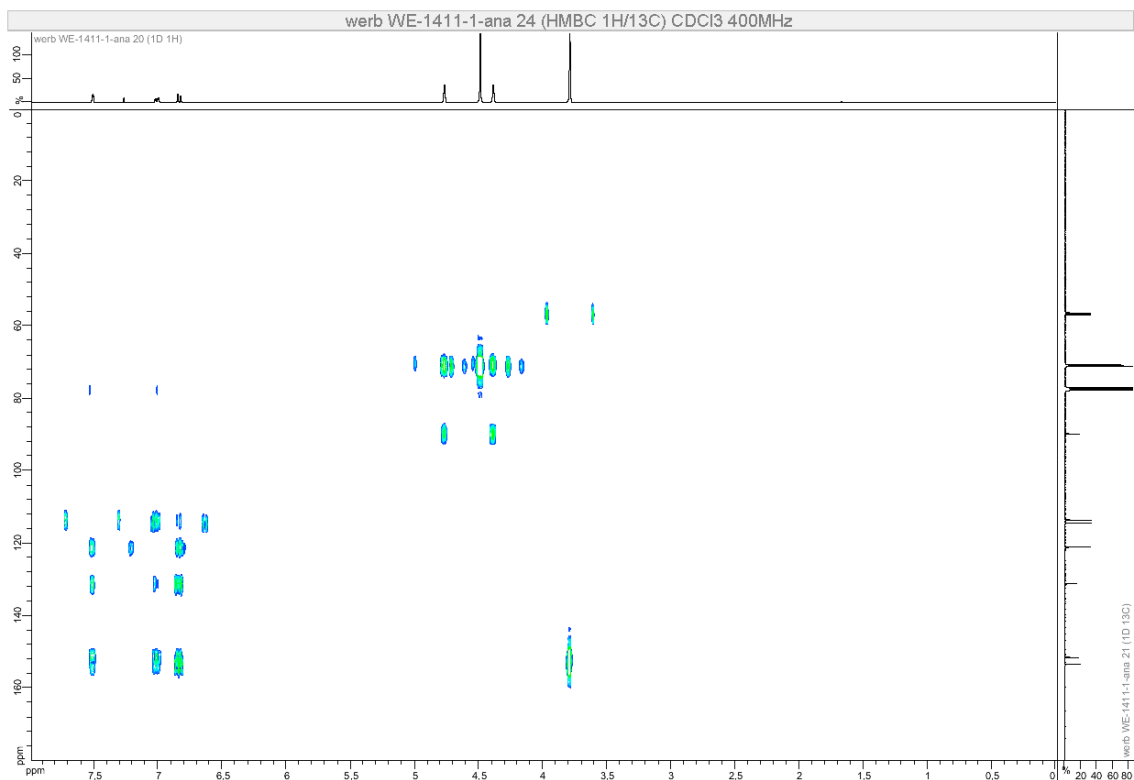




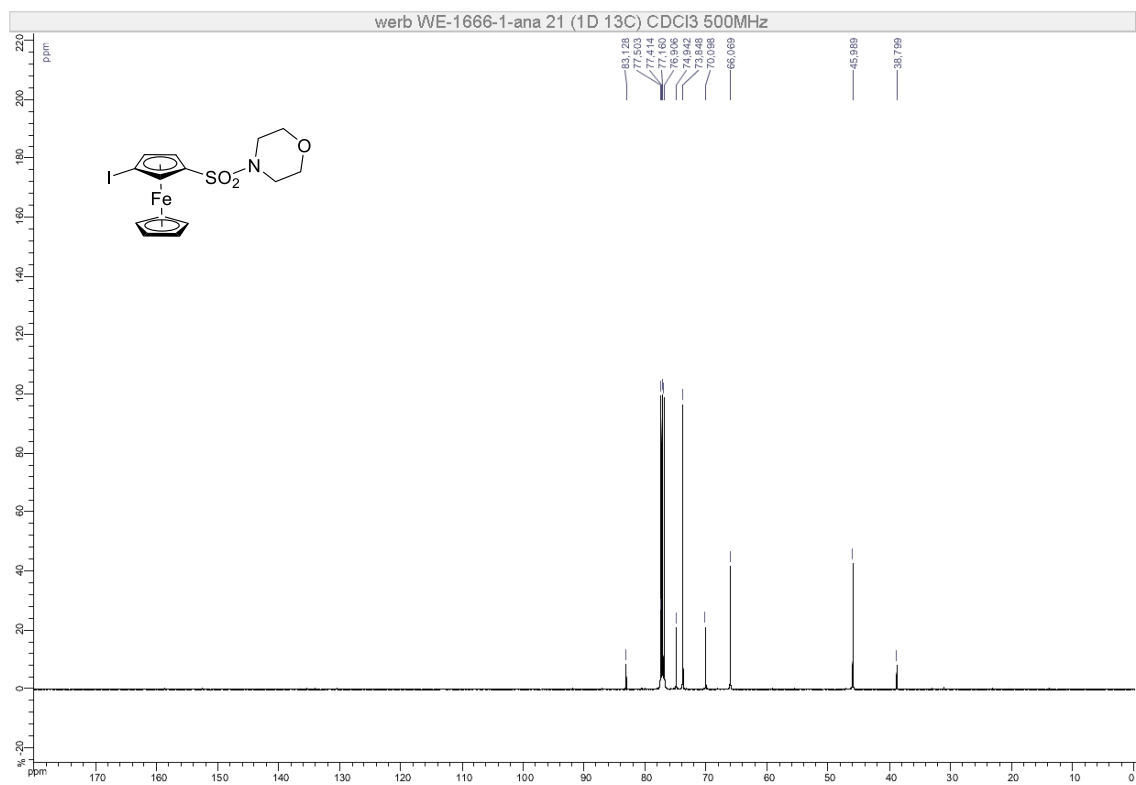
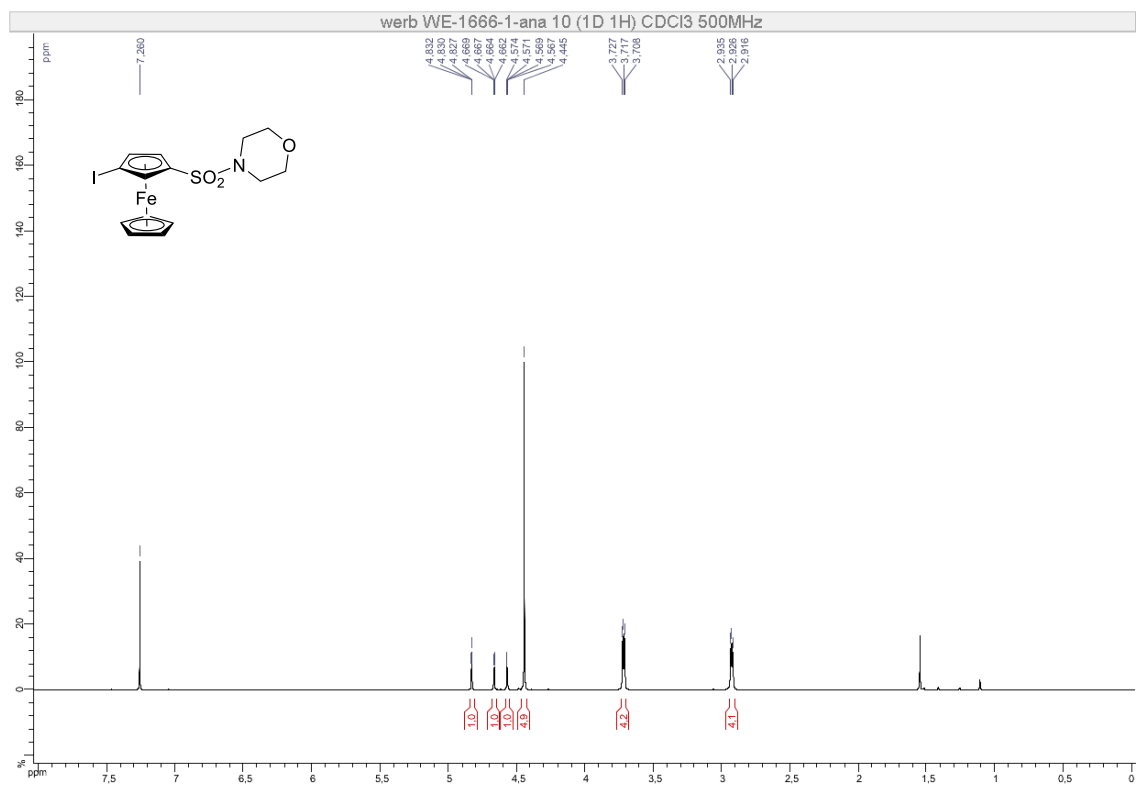
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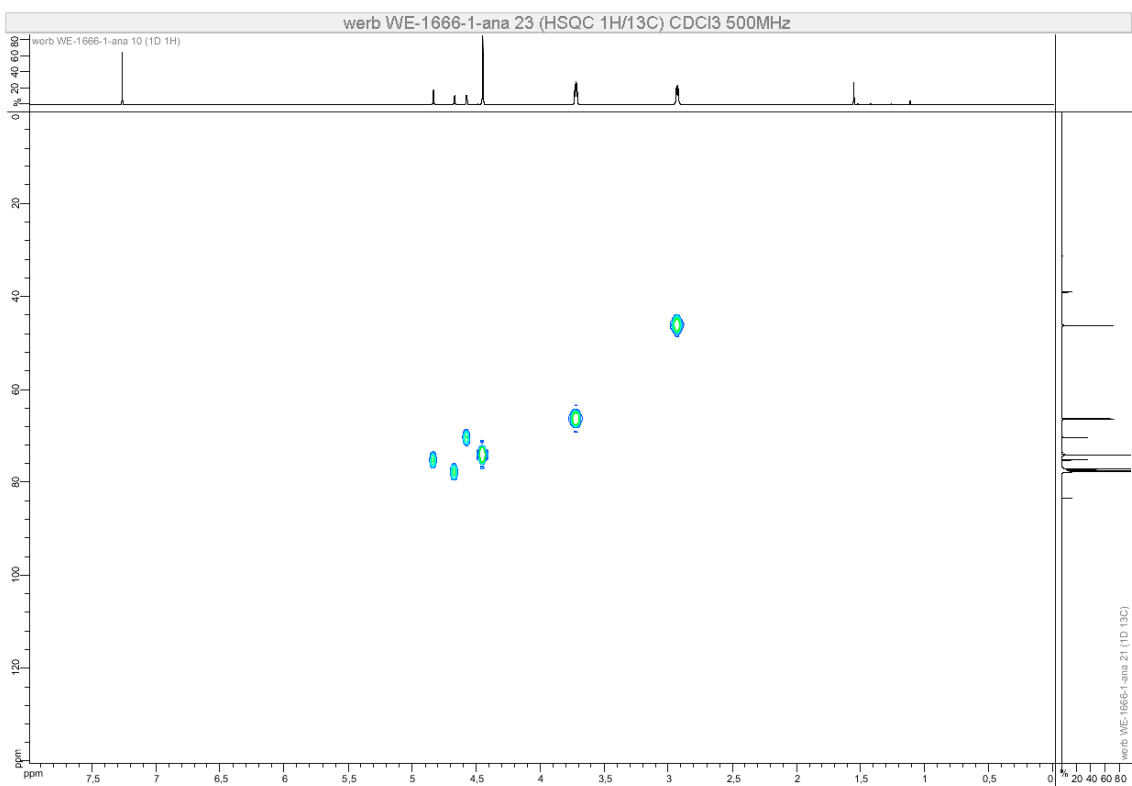
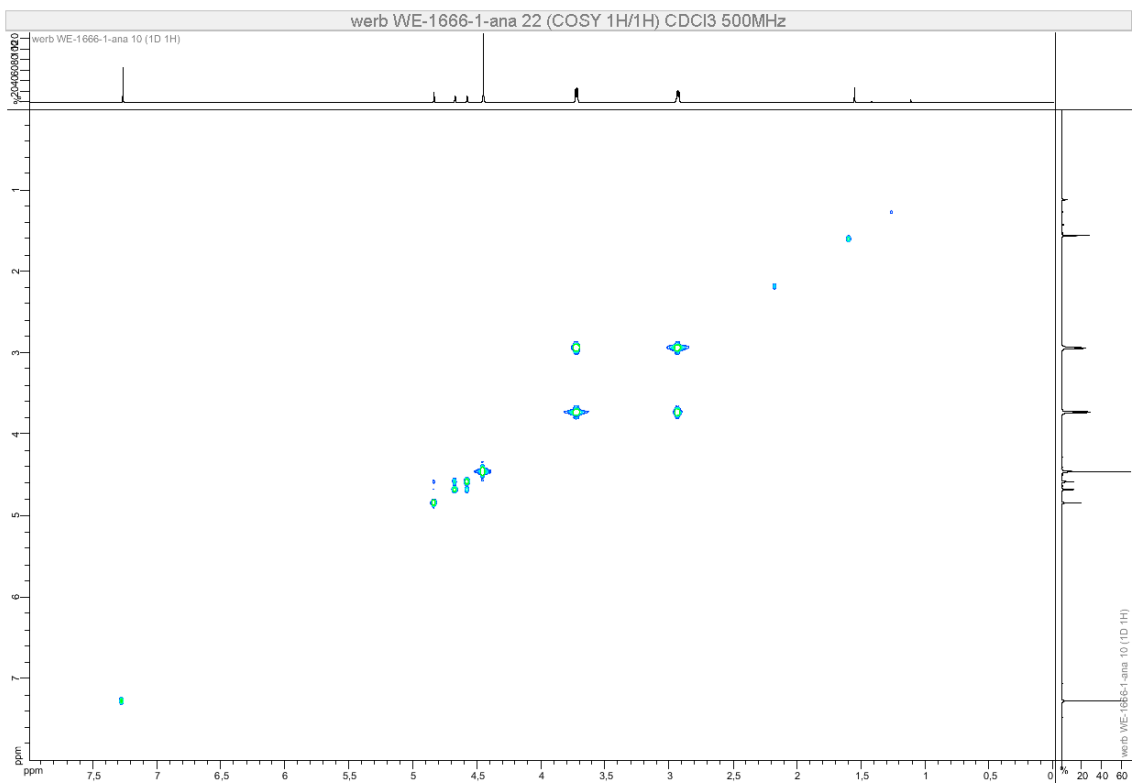


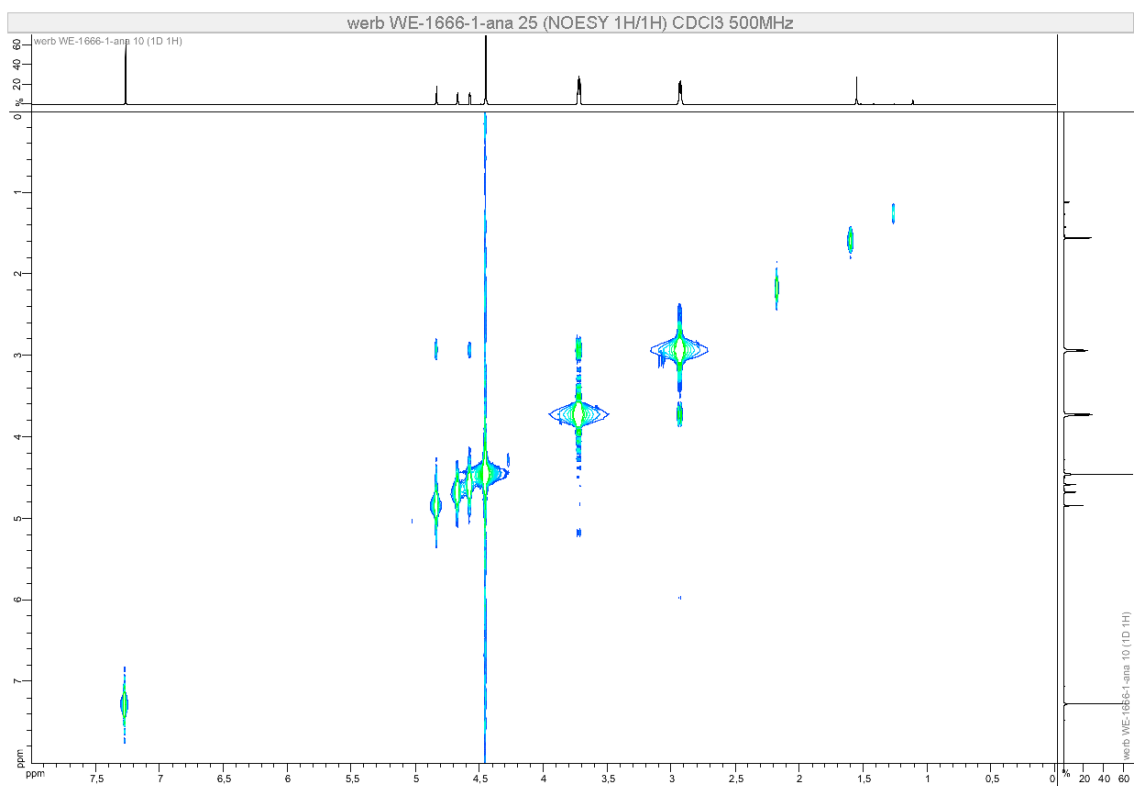
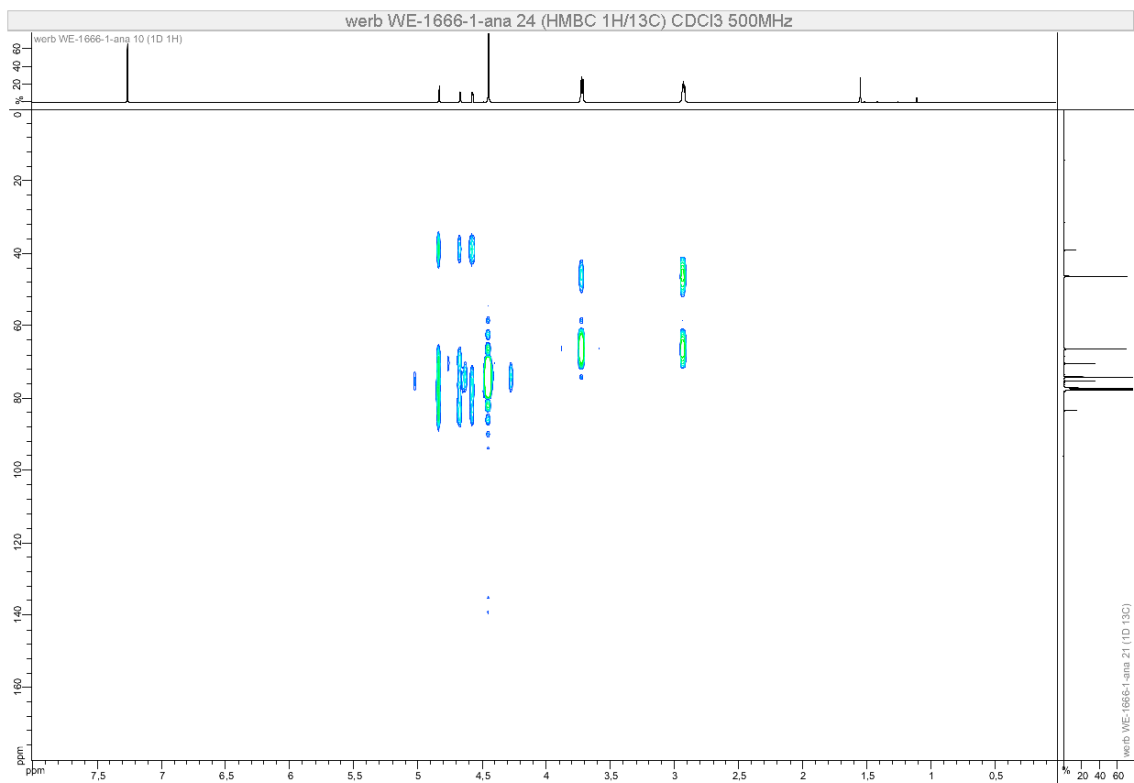




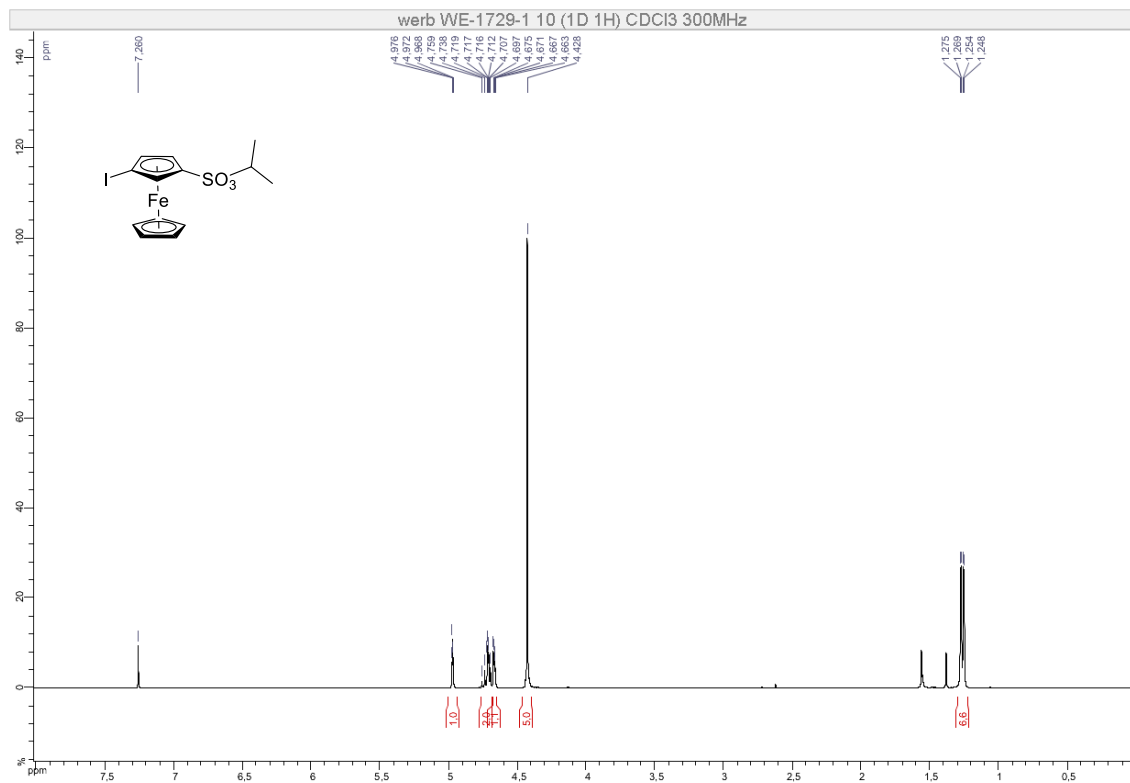
Compound 13h





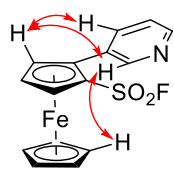


Compound 13i

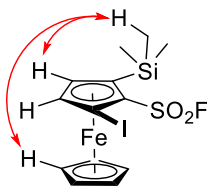


Selected NOESY correlations

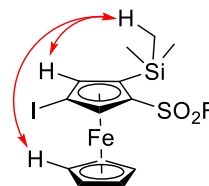
Compound 3d



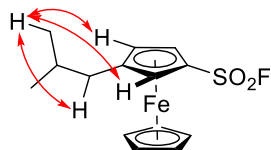
Compound 4



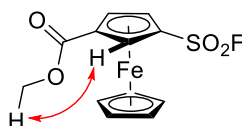
Compound 5a



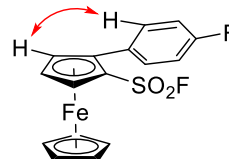
Compound 7a



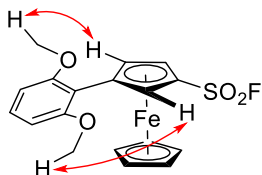
Compound 7b



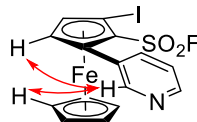
Compound 10a



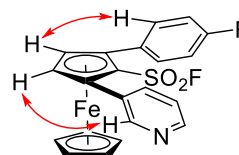
Compound 10c



Compound 11



Compound 12



References

1. A. F. Burchat, J. M. Chong and N. Nielsen, *J. Organomet. Chem.*, 1997, **542**, 281.
2. W. Erb, M. Wen, T. Roisnel and F. Mongin, *Synthesis*, 2021, **53**, 2612.
3. K. Snégaroff, S. Komagawa, F. Chevallier, P. C. Gros, S. Golhen, T. Roisnel, M. Uchiyama and F. Mongin, *Chem. Eur. J.*, 2010, **16**, 8191.
4. G. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **71**, 3.
5. G. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3.
6. M. Jonek, A. Makhloufi, P. Rech, W. Frank and C. Ganter, *J. Organomet. Chem.*, 2014, **750**, 140.
7. W. Erb, M. Wen, J. Pierre Hurvois, F. Mongin, Y. S. Halauko, O. A. Ivashkevich, V. E. Matulis and T. Roisnel, *Eur. J. Inorg. Chem.*, 2021, **2021**, 3165.
8. P. Diter, S. Taudien, O. Samuel and H. B. Kagan, *J. Org. Chem.*, 1994, **59**, 370.