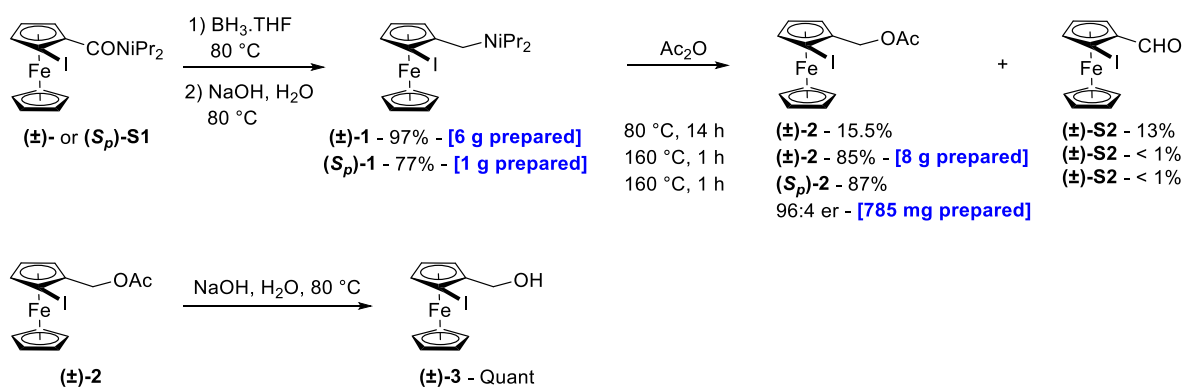


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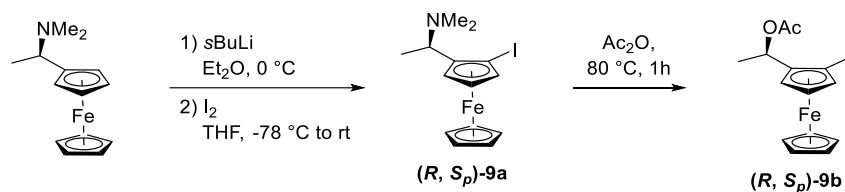
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Synthesis of substrates 1-3 and (*R*, *S_p*)-9a-b

Substrates **1-3** were prepared from (\pm)-**S1** or (*S_p*)-**S1**^[1] by following the route described on scheme S1. The bulky carboxamide was reduced using the borane-tetrahydrofuran (BH₃·THF) complex toward the amino derivatives (\pm)-**1** or (*S_p*)-**1**.^[2] In our hands, yields were almost similar when using commercially available solution of BH₃·THF or when it is prepared *in situ* from sodium borohydride and iodine. However, for practical reasons, we used the commercial solution on small scale (up to 1 g) and preferred to use the *in situ* prepared complex on larger scale. Substitution of similar bulky amines with an adjacent stable substituent was reported by Anderson although no experimental details were provided. Therefore, we set up an overnight reaction with a large excess of acetic anhydride at 80 °C. Surprisingly, only a modest conversion was observed (49.5% on starting material recycled) while we isolated the acetate (\pm)-**2** and the unexpected aldehyde (\pm)-**S2** in low yields (15.5 and 13%, respectively). To increase conversion and reduce the formation of (\pm)-**S2**, we increased the temperature and decrease the reaction time. Pleasingly, after 1 h at 160 °C, full conversion was noticed and the title product was isolated in 83.5% with traces of the aldehyde. Reacting (*S_p*)-**1** in similar conditions afforded (*S_p*)-**2** in 87% yield without erosion of the er (96:4 calculated by chiral HPLC). Other reported synthesis toward the same enantioenriched acetate (*S_p*)-**2** were reported by Ito,^[3] Widhalm^[4] and Nicolosi^[5] in 7, 6 and 4 steps, respectively. Saponification of the acetate using sodium hydroxide in a THF-water mixture finally afforded (\pm)-**3** in a quantitative yield.



Substrates (*R*, *S_p*)-**9a-b** were prepared from (*R*)-Ugi's amine, with a modified protocol from Tucker.^[6]



(\pm)-1-Iodo-2-(*N,N*-diisopropylaminomethyl)iodoferrocene - (\pm)-1**:** A solution of iodine (9.75 g, 38.4 mmol, 2.40 equiv) in THF (60 mL) was added dropwise to a suspension of sodium borohydride (3.03 g, 80.0 mmol, 5.00 equiv) in THF (50 mL) at 0 °C. After addition, the reaction mixture was warmed to rt and stirred for 1 h. Compound (\pm)-**S1** (7.03 g, 16.0 mmol, 1.00 equiv) was added portionwise to the reaction mixture which was then heated at reflux overnight (heating mantel, external temperature 80 °C). **Remark:** the use of PTFE sleeve is strongly recommended to avoid blockage of the ground glass joints. The reaction mixture was cooled to 0 °C and a solution of NaOH (10%, 50 mL) was added dropwise. **Caution:** as a vigorous evolution of gas occurred, the first drops of NaOH solution should be added slowly. After addition, the reaction mixture was stirred at reflux for 1 h (heating mantel, external temperature 80 °C). The reaction mixture was cooled to rt and the layers were separated. The

aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were extracted with aqueous HCl (1.0 M, 3 x 50 mL). The combined aqueous layers were washed with Et₂O (3 x 50 mL) before being basified with solid K₂CO₃ until pH 8-9. **Caution:** as vigorous evolution of gas occurred, only small portions of K₂CO₃ should be added each time. The aqueous layer was extracted with Et₂O (2 x 60 mL). The combined organic layers were washed with water (50 mL), brine (50 mL), dried over MgSO₄, filtrated on cotton wool and concentrated under vacuum using a rotary evaporator to give the pure product as an orange oil (6.63 g, 97%). R_f (eluent: PET/EtOAc 10:1 with 5 drops of NEt₃) = 0.55. ν_{\max} (film)/cm⁻¹ 2961, 1676, 1461, 1380, 1361, 1202, 1181, 1150, 1116, 1000, 952, 818, 804. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 4.37 (dd, *J* = 2.3, 1.4 Hz, 1H, FcCH, H5), 4.33 (br s, 1H, FcCH, H3), 4.14 (t, *J* = 2.3 Hz, 1H, FcCH, H4), 4.10 (s, 5H, Cp), 3.59 (d, *J* = 14.5 Hz, 1H, CHH), 3.39 (d, *J* = 14.5 Hz, 1H, CHH), 3.01 (sept, *J* = 6.7 Hz, 2H, 2 x CH), 1.03 (d, *J* = 6.7 Hz, 6H, 2 x CH₃), 1.02 (d, *J* = 6.7 Hz, 6H, 2 x CH₃). ¹³C NMR (75.4 MHz, CDCl₃): δ (ppm) 89.4 (FcC, C2), 74.1 (FcCH, C5), 71.7 (Cp), 69.1 (FcCH, C3), 68.2 (FcCH, C4), 47.3 (2 x CH), 45.4 (FcC, C1), 44.6 (CH₂), 21.6 (2 x CH₃), 20.6 (2 x CH₃). Mass: 425 [M], 325 [M-NiPr₂].

(S_p)-1-Iodo-2-(N,N-diisopropylaminomethyl)ferrocene - (S_p)-1: By following a similar protocol, starting from **(S_p)-S1** (1.40 g, 3.01 mmol, 1.00 equiv, 96:4 er) and BH₃.THF complex in THF (1.0 M, 15.5 mL, 15.5 mmol, 5.00 equiv), the title product was obtained as an orange oil (1.0 g, 77%). Analytical data analogous to racemic compound. [α]_D +20.5 (*c* 0.01 in CHCl₃).

(±)-1-Iodo-2-(acetoxymethyl)ferrocene - (±)-2: Compound **(±)-1** (10.6 g, 25.0 mmol, 1.00 equiv) was dissolved into acetic anhydride (95.3 mL, 103 g, 1.00 mol, 40.0 equiv) at rt and the resulting solution was stirred at 160 °C (heating mantel, external temperature) for 1 h. The reaction mixture was cooled to 0 °C and EtOAc (100 mL) was added before pouring the reaction mixture onto ice (200 mL). Solid K₂CO₃ was added under stirring until pH 8 was reached. **Caution:** as vigorous evolution of gas occurred, only small portions of K₂CO₃ should be added each time. The layers were separated and the aqueous layers was extracted with EtOAc (50 mL). The combined organic layers were washed with water (2 x 50 mL), brine (1 x 50 mL), dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum using a rotary evaporator to give the crude product. **Remark:** if acetic acid remains at this stage, it can be easily removed by distillation with cyclohexane using a rotary evaporator. The crude product was purified by column chromatography over SiO₂, using PET/EtOAc (10:1) with 1% NEt₃ to give the title product as an orange oil which solidifies upon standing (8.2 g, 85%). Analytical data analogous to those reported previously.^[3b] R_f (eluent: PET/EtOAc 10:1) = 0.48. Mp 47-52 °C. ν_{\max} (film)/cm⁻¹ 3093, 1731, 1438, 1411, 1366, 1220, 1106, 1064, 1019, 999, 943, 823, 809. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 5.03 (d, *J* = 12.1 Hz, 1H, CHH), 4.86 (d, *J* = 12.1 Hz, 1H, CHH), 4.47 (s, 1H, FcCH, H3), 4.35 (s, 1H, FcCH, H5), 4.25 (s, 1H, FcCH, H4), 4.16 (s, 5H, Cp), 2.04 (s, 3H, CH₃). ¹³C NMR (75.4 MHz, CDCl₃): δ (ppm) 170.8 (C=O), 82.8 (FcC, C2), 75.6 (FcCH, C3), 71.6 (Cp), 69.7 (FcCH, C4), 69.2 (FcCH, C5), 63.0 (CH₂), 44.7 (FcC, C1), 21.0 (CH₃). Mass: 384 [M].

(S_p)-1-Iodo-2-(acetoxymethyl)ferrocene - (S_p)-2: By following a similar protocol, starting from **(S_p)-1** (1.00 g, 2.35 mmol, 1.00 equiv, 96:4 er) and acetic anhydride (8.90 mL, 9.70 g, 94.0 mmol, 40.0 equiv), the title product was obtained as an orange oil (785.0 mg, 87%, 96:4 er). Analytical data analogous to racemic compound. [α]_D -4.75 (*c* 0.01 in CHCl₃). The enantiomeric ratio was determined on Chiralpak IC-3 column, hexane/iPrOH: 99:1, 0.9 mL/min, 5 °C, λ = 254 nm, *t* (major) = 16.76 min, *t* (minor) = 17.35 min).

(±)-1-Iodo-2-(hydromethyl)ferrocene - (±)-3: NaOH (240 mg, 6.00 mmol, 3.00 equiv) was dissolved in H₂O (6.5 mL) and THF (3.5 mL) at rt. Compound **(±)-2** (750 mg, 2.00 mmol, 1.00 equiv) was added and the reaction mixture was heated overnight (heating mantel, external temperature 80 °C). The reaction mixture was cooled to rt, water (10 mL), followed by EtOAc

(10 mL) were added. The layers were separated and the aqueous layer was extracted with EtOAc (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 PET/EtOAc (80:20 to 70:30) to give the title product as an orange solid (682 mg, quant). Analytical data analogous to those reported previously.^[3b,5] R_f (eluent: PET/EtOAc 70:30) = 0.57. Mp 89-90 °C. ν_{\max} (film)/cm⁻¹ 3250 (br), 1365, 1308, 1246, 1103, 1060, 996, 972, 940, 815, 752. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.49 (dd, J = 3.4, 12.3 Hz, 1H, CHH), 4.47 (dd, J = 1.2, 2.1 Hz, 1H, FcCH, H5), 4.38 (dd, J = 3.4, 12.3 Hz, 1H, CHH), 4.32 (dd, J = 1.2, 2.1 Hz, 1H, FcCH, H3), 4.24 (t, J = 2.4 Hz, 1H, FcCH, H4), 4.17 (s, 5H, Cp), 1.64 (br t, J = 4.5 Hz, 1H, OH). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 88.3 (FcC, C2), 75.2 (FcCH, C5), 71.5 (Cp), 69.2 (FcCH, C4), 67.8 (FcCH, C3), 61.5 (CH₂), 43.9 (FcC, C1).

(R,S_p)-1-Iodo-2-(α ,N,N-trimethylaminomethyl)ferrocene - (R, S_p)-9a: *s*BuLi (1.1 M in cyclohexane-hexane (92:8), 3.80 mL, 4.20 mmol, 1.40 equiv) was added dropwise to a solution of (*R*)-Ugi's amine (772 mg, 3.00 mmol, 1.00 equiv) in Et₂O (11 mL) at 0 °C. After addition, the reaction was stirred for 1 h at the same temperature before being cooled to -78 °C. After 5 min, a solution of iodine (1.07 g, 4.20 mmol, 1.40 equiv) in THF (10 mL) was added and the reaction mixture was stirred at the same temperature for 15 min before being warmed to rt. Aqueous Na₂S₂O₃ solution (sat., 15 mL) was added and the reaction mixture was extracted with EtOAc (3 x 20 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 neutralized SiO₂, using PET-EtOAc (80:20) with 2% of NEt₃ to give the title product as an orange oil (993 mg, 86%). Analytical data analogous to those reported previously.^[6] R_f (TLC plate dipped in NEt₃ and dried prior to use, eluent: PET/EtOAc 80:20 with 5 drops of NEt₃) = 0.50. $[\alpha]_D$ -8.32 (*c* 0.01 in CHCl₃). ν_{\max} (film)/cm⁻¹ 3093, 2970, 2933, 2855, 2815, 2771, 1449, 1372, 1260, 1192, 1106, 1088, 1071, 1000, 918, 818. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 4.46 (dd, J = 1.3, 2.3 Hz, 1H, FcCH, H5), 4.24 (t, J = 2.5 Hz, 1H, FcCH, H4), 4.15 (dd, J = 1.3, 2.5 Hz, 1H, FcCH, H3), 4.12 (s, 5H, Cp), 3.62 (q, J = 6.8 Hz, 1H, CH), 2.14 (s, 6H, N(CH₃)₂), 1.50 (d, J = 6.8 Hz, 3H, CH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 90.4 (FcC, C2), 74.5 (FcCH, C5), 71.8 (Cp), 68.3 (FcCH, C4), 65.7 (FcCH, C3), 57.7 (CH), 45.6 (FcC, C1), 41.3 N(CH₃)₂, 16.1 (CH₃).

(R,S_p)-1-Iodo-2-(acetoxyethyl)ferrocene - (R,S_p)-9b: a solution of (*R, S_p*)-9a (693 mg, 1.80 mmol, 1.00 equiv) in acetic anhydride (6.90 mL, 7.40 g, 72.0 mmol, 40.0 equiv) was heated at 80 °C for 1 h in a pre-heated oil bath. The reaction mixture was cooled to rt, cyclohexane (50 mL) was added and volatiles were removed under vacuum using a rotary evaporator. Cyclohexane (50 mL) was added and removed under vacuum. The same procedure was repeated until all acetic anhydride is removed. The crude reaction mixture was purified by column chromatography over neutralized SiO₂, using PET-EtOAc (90:10) with 2% of NEt₃ to give the title product as an orange solid (547 mg, 76%). Analytical data analogous to those reported previously.^[6] R_f (eluent: PET/EtOAc 90:10 with 5 drops of NEt₃) = 0.59. $[\alpha]_D$ -98.9 (*c* 0.01 in CHCl₃). Mp 66-67 °C. ν_{\max} (film)/cm⁻¹ 3093, 2986, 1731, 1718, 1366, 1227, 1107, 1045, 1018, 1000, 949, 928, 840, 821. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 5.89 (q, J = 6.5 Hz, 1H, CH), 4.54 (dd, J = 1.3, 2.2, 1H, FcCH, H5), 4.33 (dd, J = 1.3, 2.4 Hz, 1H, FcCH, H3), 4.28 (t, J = 2.5 Hz, 1H, FcCH, H4), 4.15 (s, 5H, Cp), 2.01 (s, 3H, CH₃CO), 1.66 (s, 3H, CH₃). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 170.4 (C=O), 87.7 (FcC, C2), 75.8 (FcCH, C5), 71.9 (Cp), 69.8 (CH), 69.1 (FcCH, C4), 65.9 (FcCH, C3), 44.2 (FcC, C1), 21.8 (CH₃CO), 18.8 (CH₃).

Solid-state structures of compounds (\pm)-4a, (\pm)-4n, (\pm)-4r, (\pm)-4u, (\pm)-4v, (\pm)-7a, (\pm)-7b, 8a, (*R,S*)-10 and (\pm)-11b.

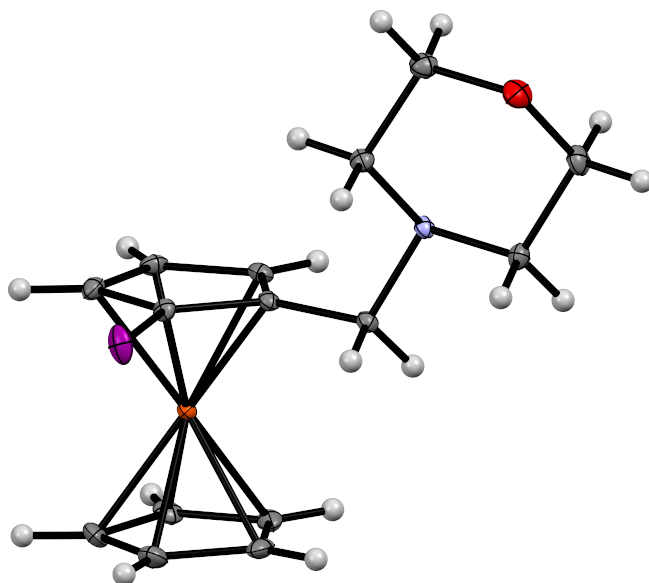


Figure S1. Molecular structure of compound (\pm)-4a (thermal ellipsoids shown at the 30% probability level). CCDC 2090455.

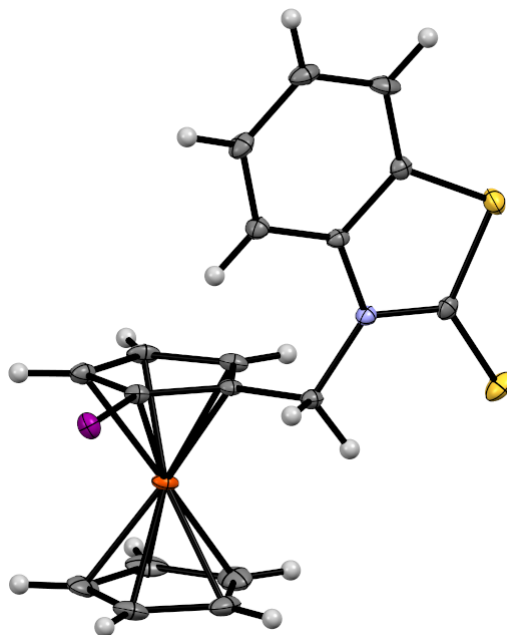


Figure S2. Molecular structure of compound (\pm)-4n (thermal ellipsoids shown at the 30% probability level). CCDC 2090456.

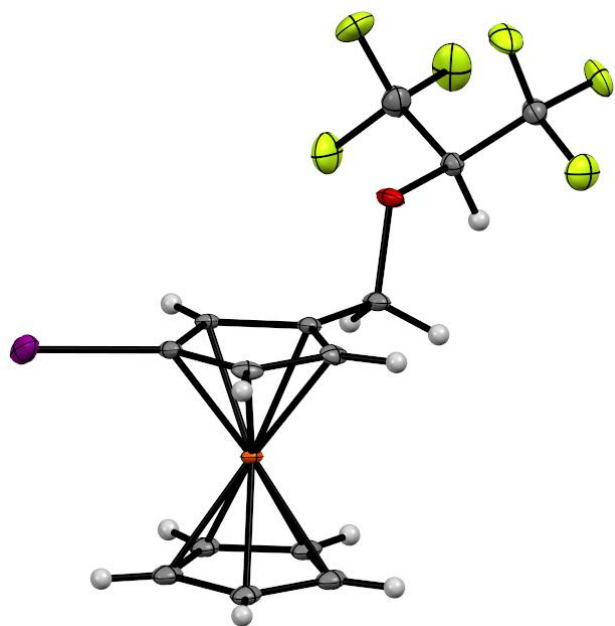


Figure S3. Molecular structure of compound (±)-4r (thermal ellipsoids shown at the 30% probability level). CCDC 1898629.

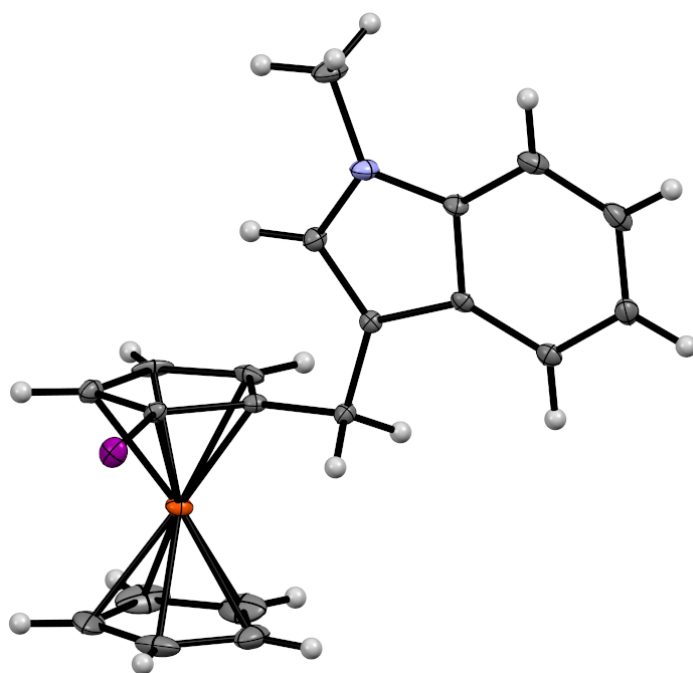


Figure S4. Molecular structure of compound (±)-4u (thermal ellipsoids shown at the 30% probability level). CCDC 2090457.

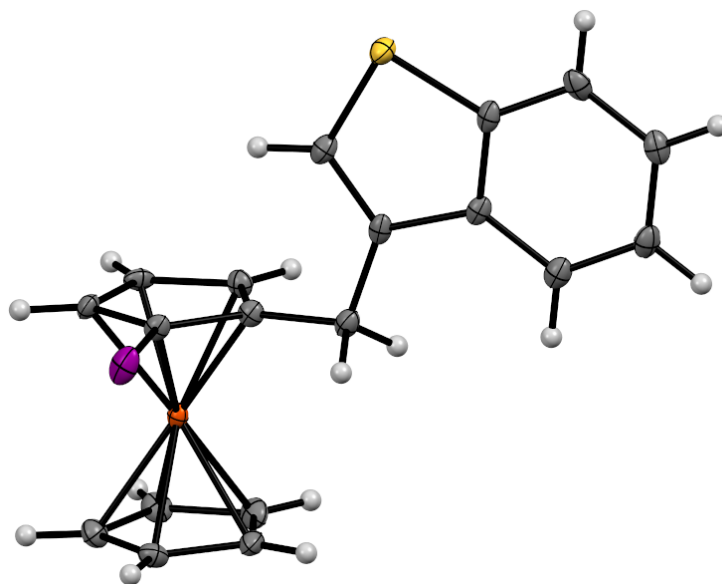


Figure S5. Molecular structure of compound (±)-4v (thermal ellipsoids shown at the 30% probability level). CCDC 2090458.

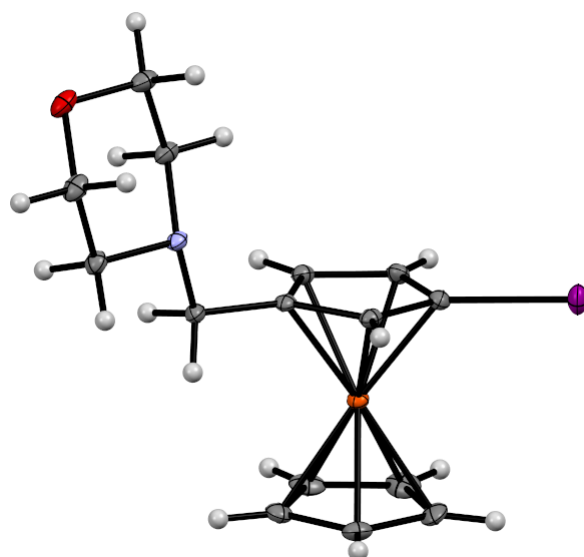


Figure S6. Molecular structure of compound (±)-7a (thermal ellipsoids shown at the 30% probability level). CCDC 2090459.

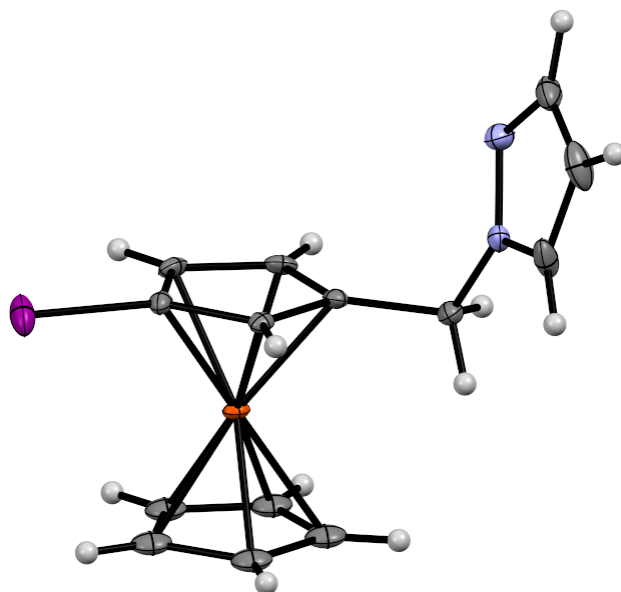


Figure S7. Molecular structure of compound (±)-7b (thermal ellipsoids shown at the 30% probability level). CCDC 1898630.

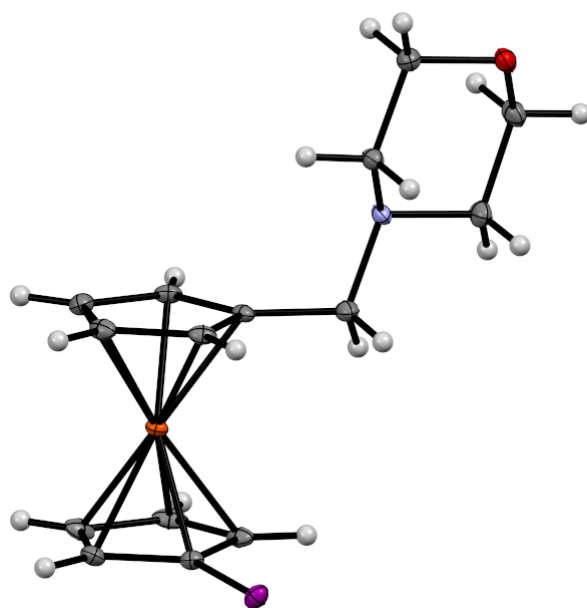


Figure S 8. Molecular structure of compound 8a (thermal ellipsoids shown at the 30% probability level). CCDC 2090460.

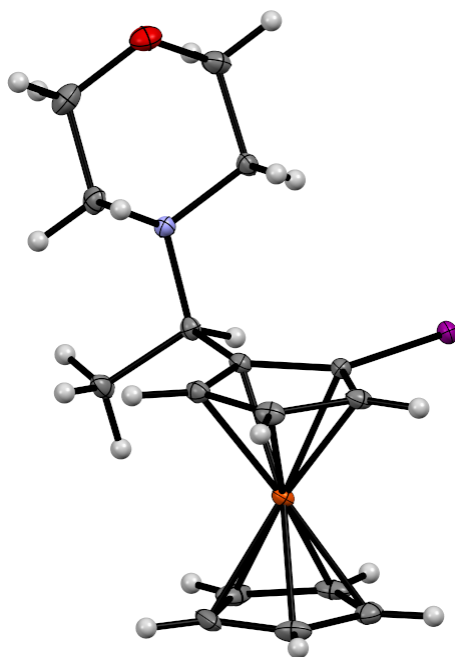


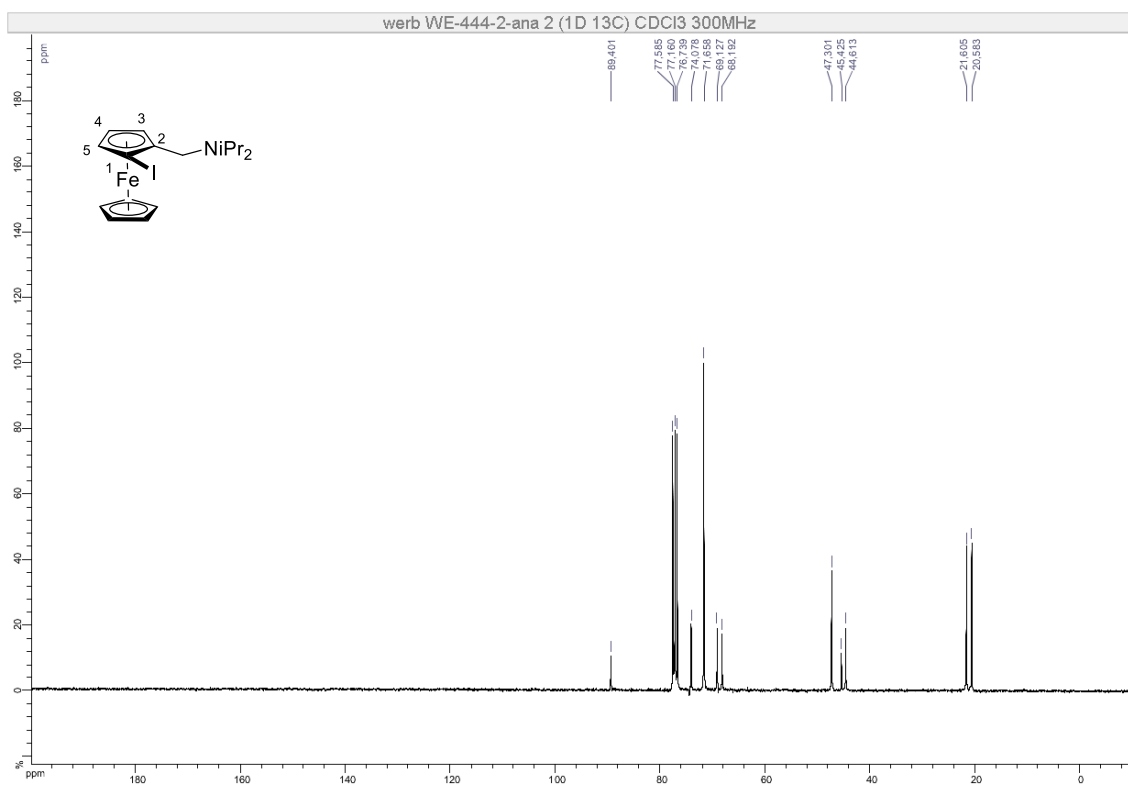
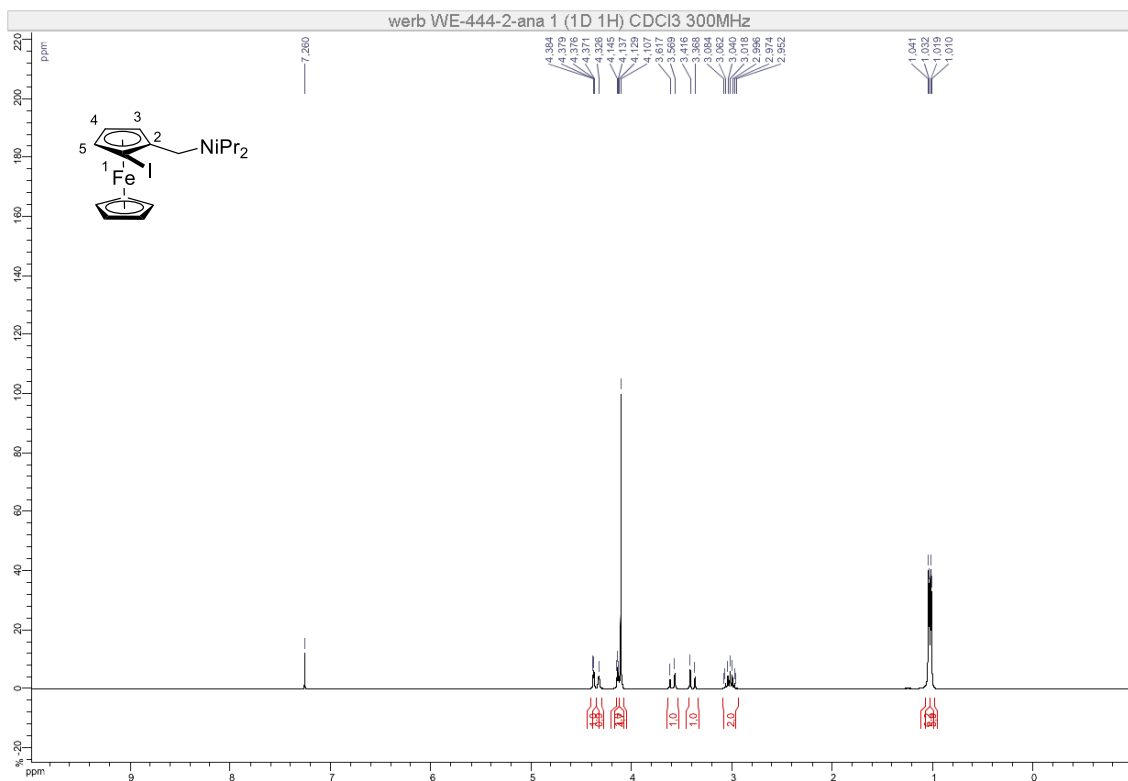
Figure S9. Molecular structure of compound (*R,S_p*)-**10** (thermal ellipsoids shown at the 30% probability level). CCDC 2090461.

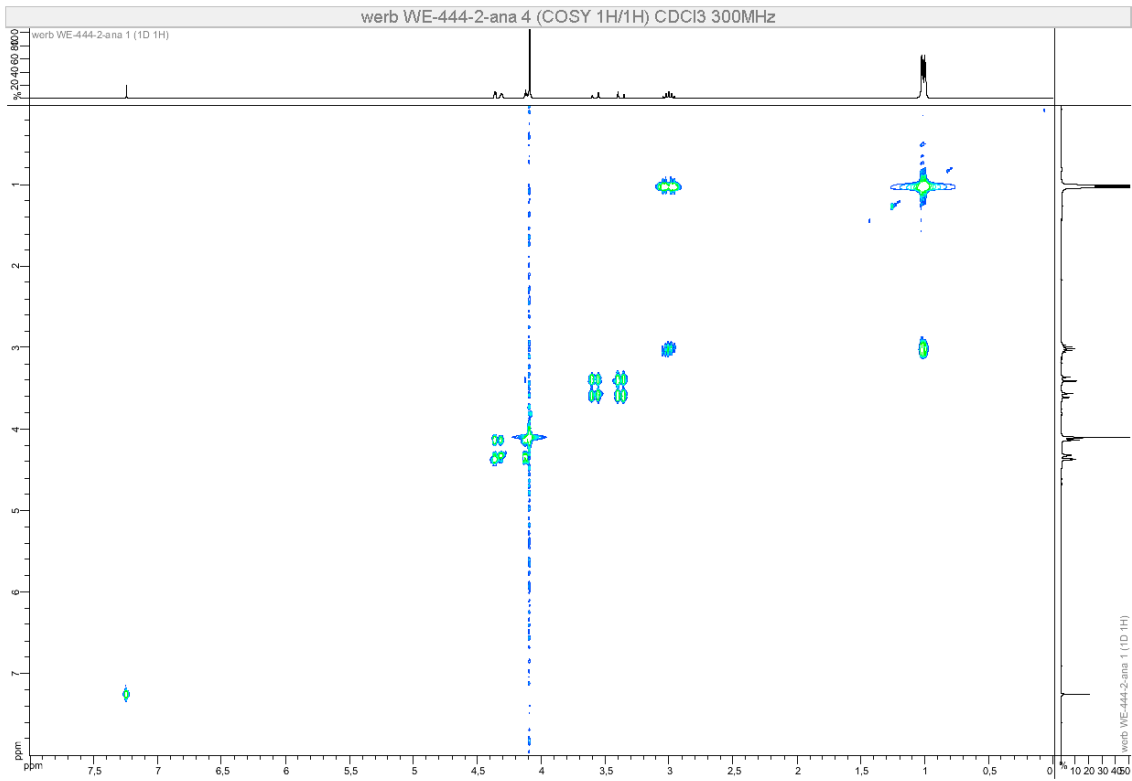
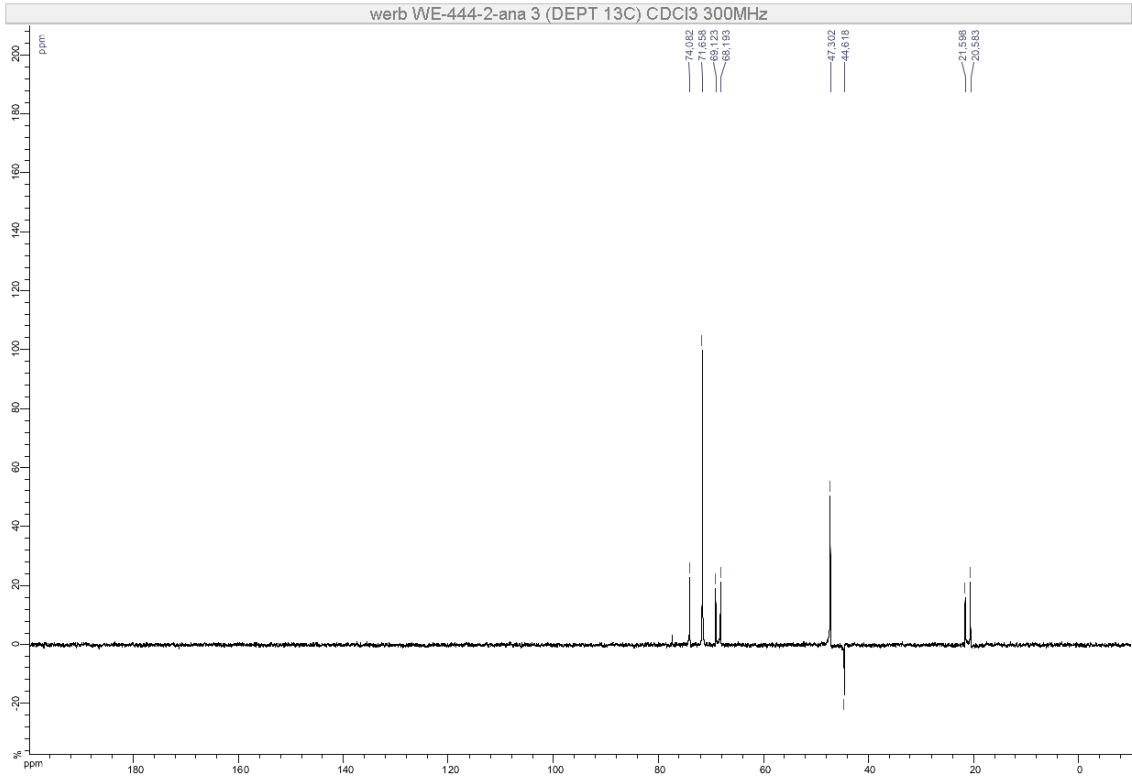


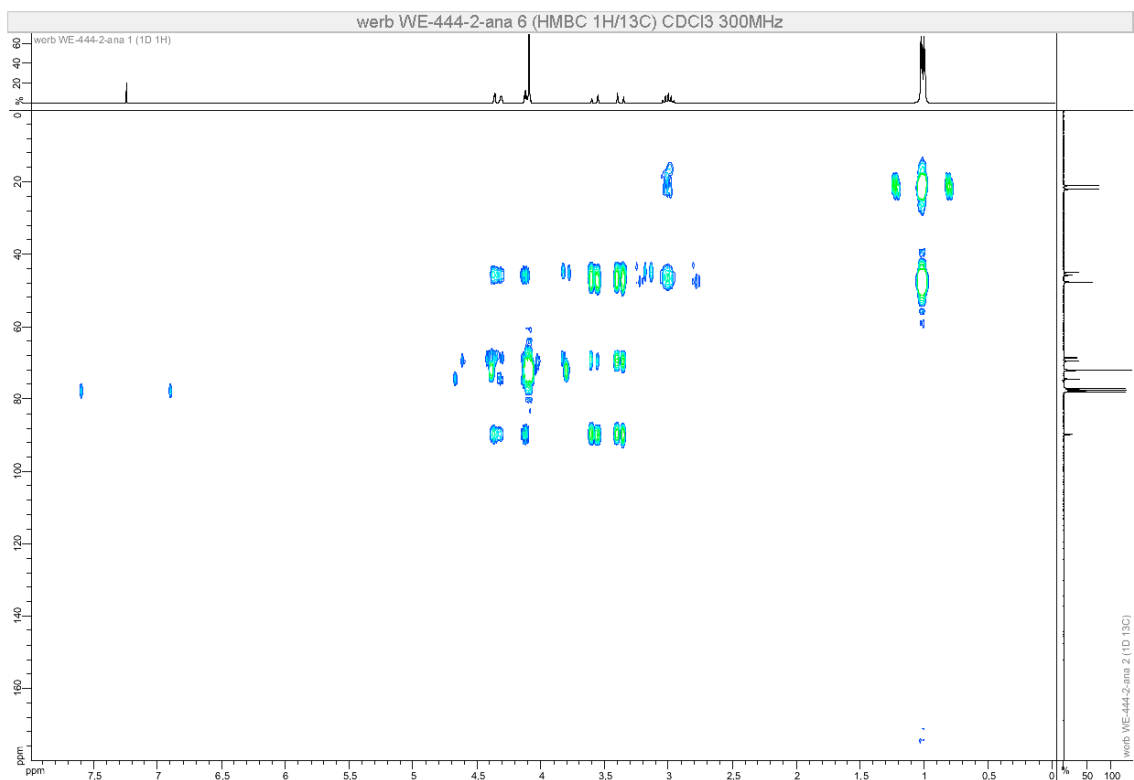
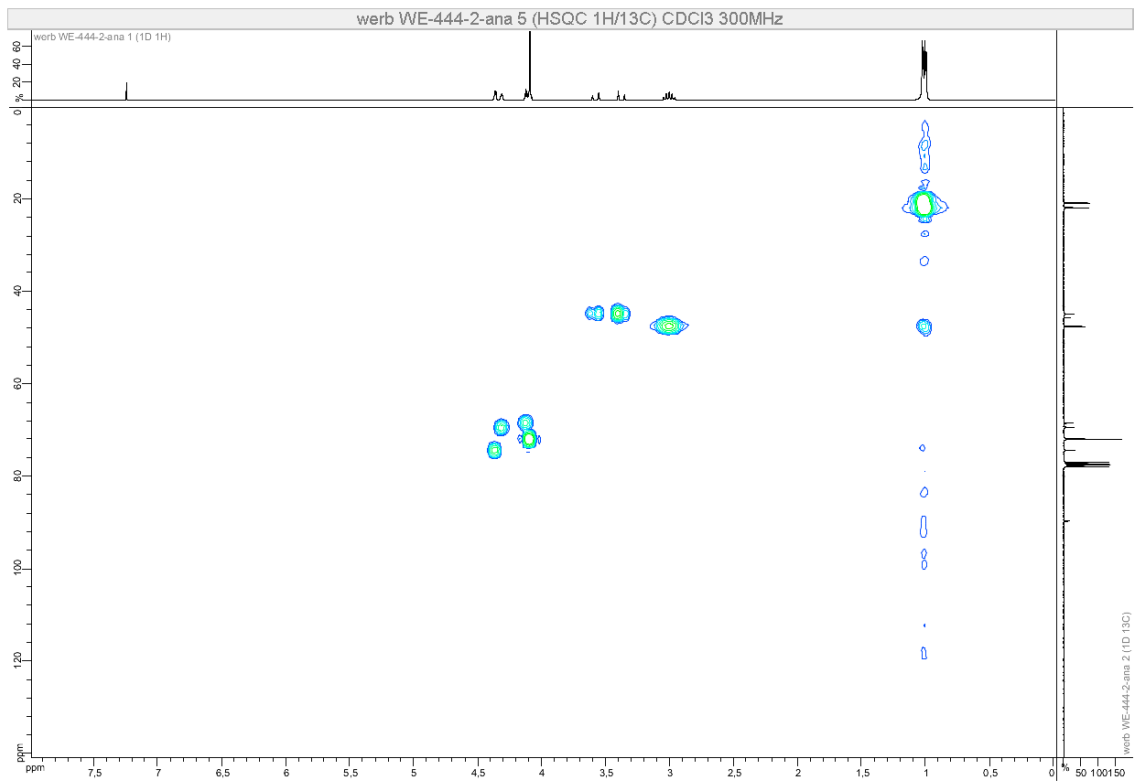
Figure S10. Molecular structure of compound (\pm)-**11b** (thermal ellipsoids shown at the 30% probability level). CCDC 2090462.

NMR Spectra

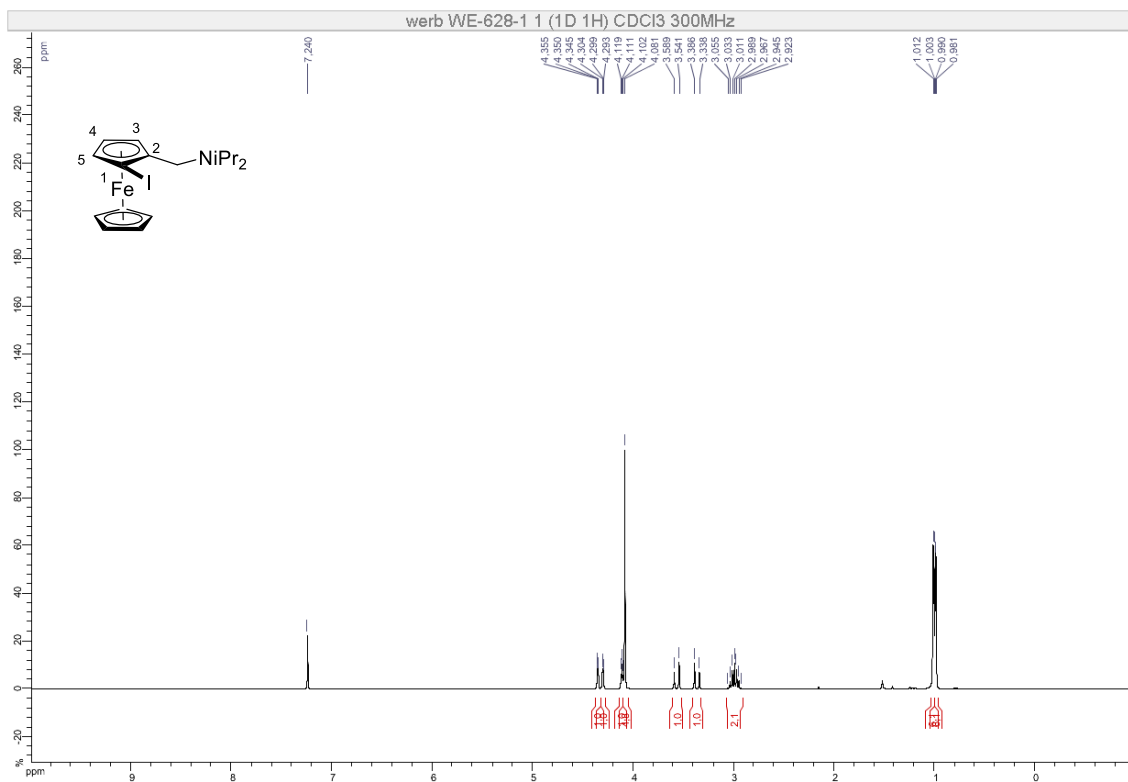
Compound (\pm)-1



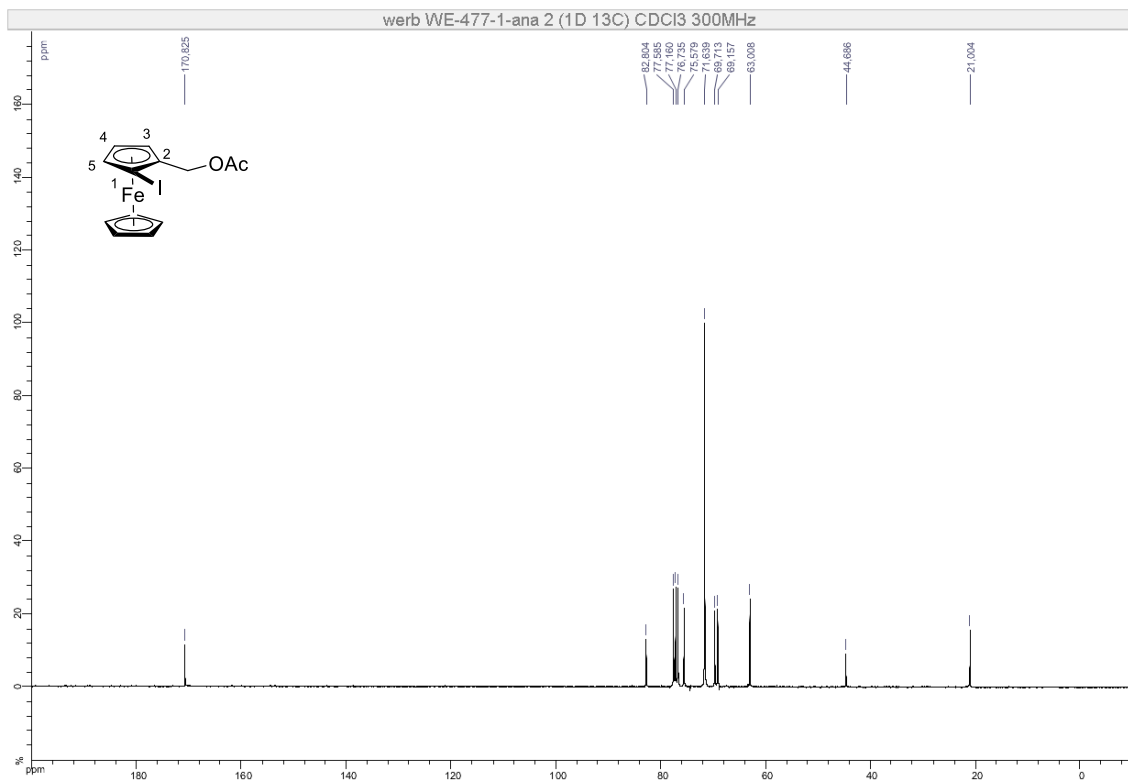
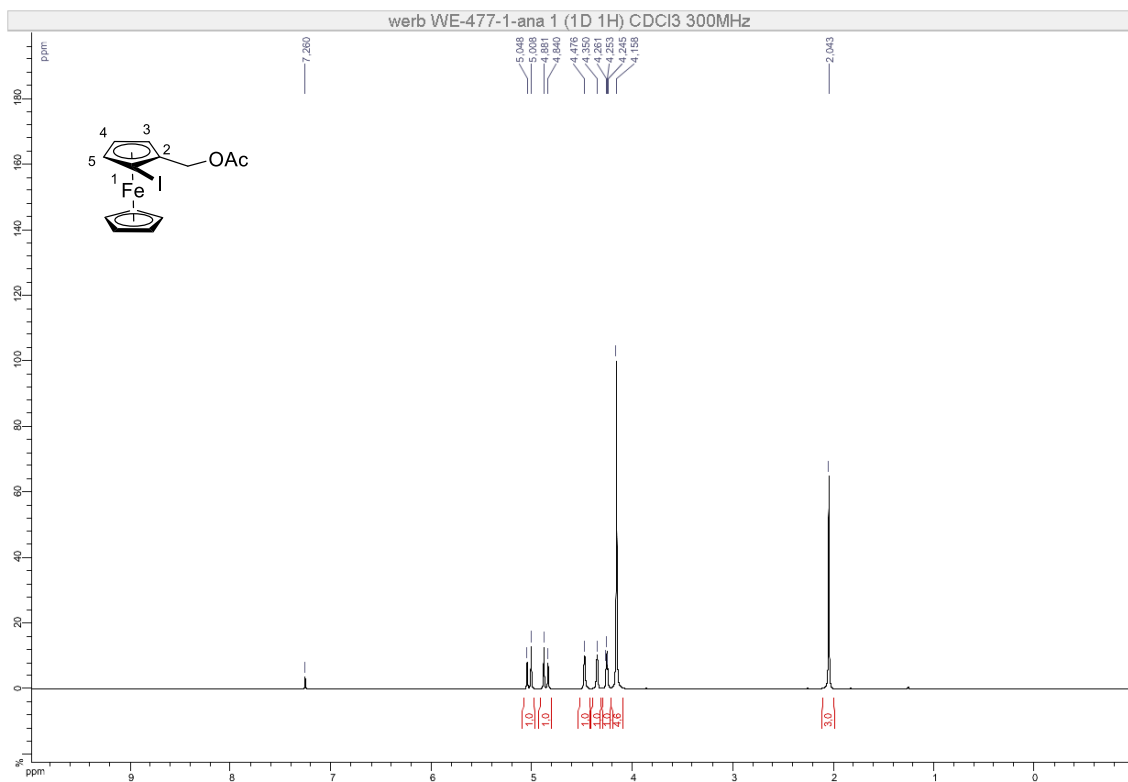


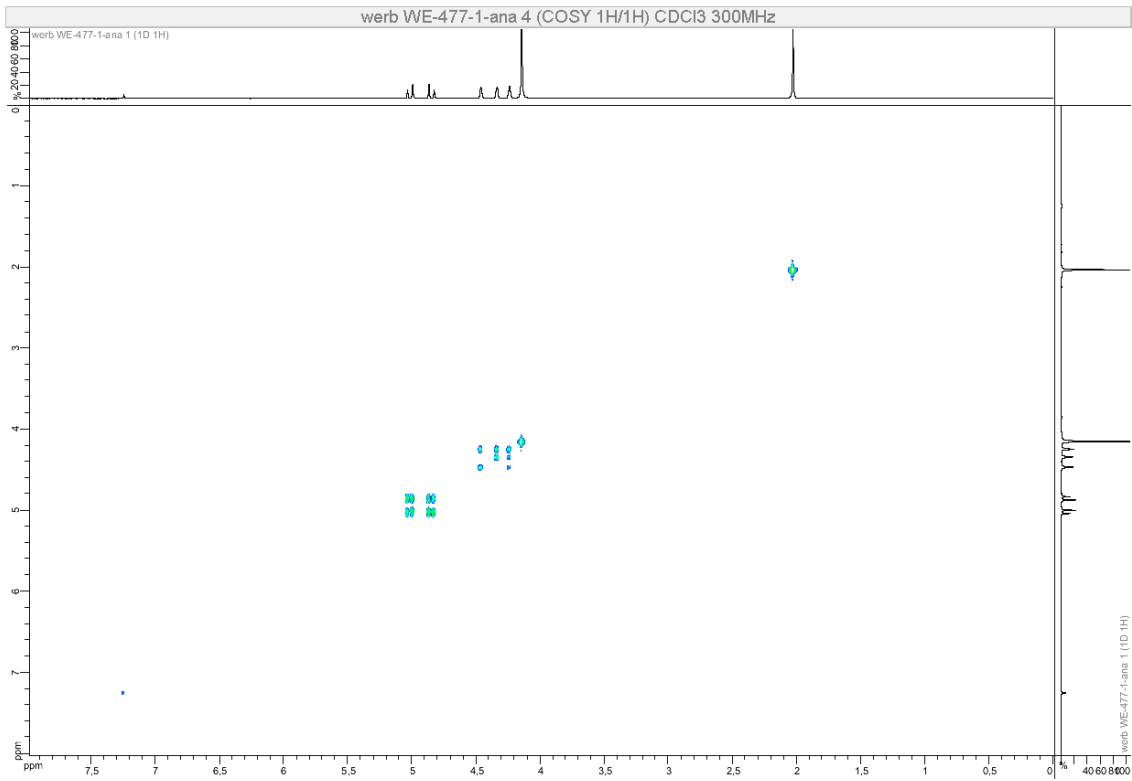
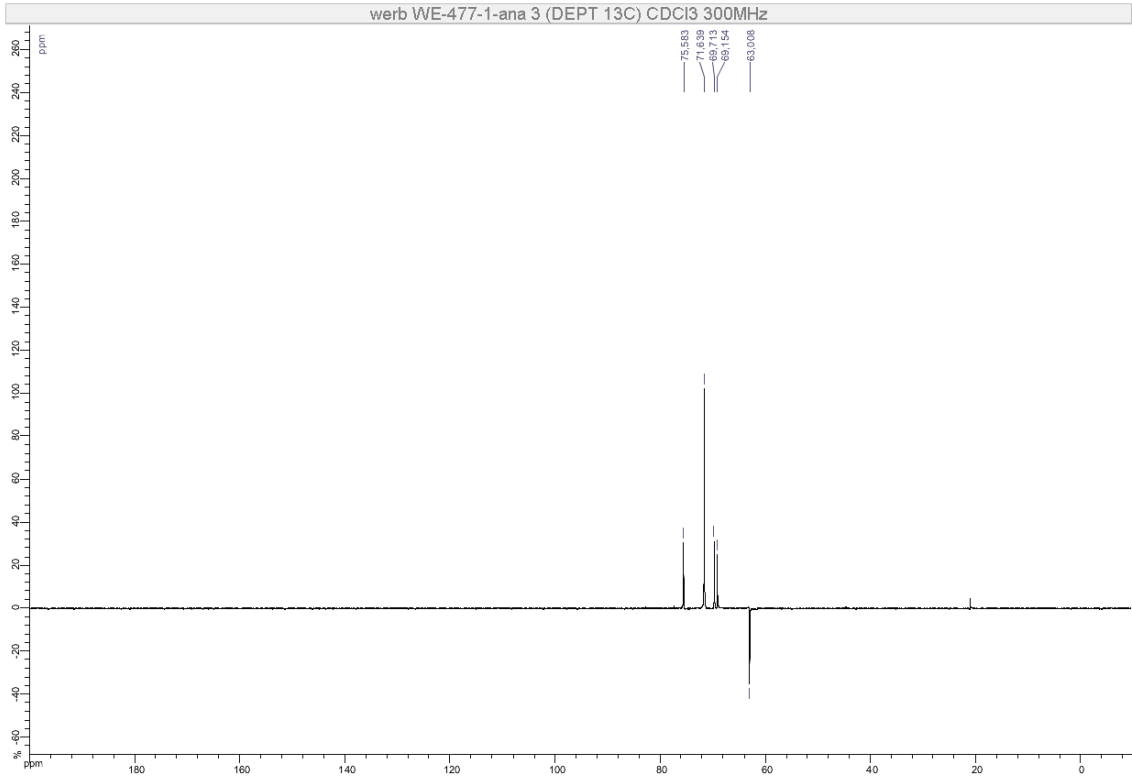


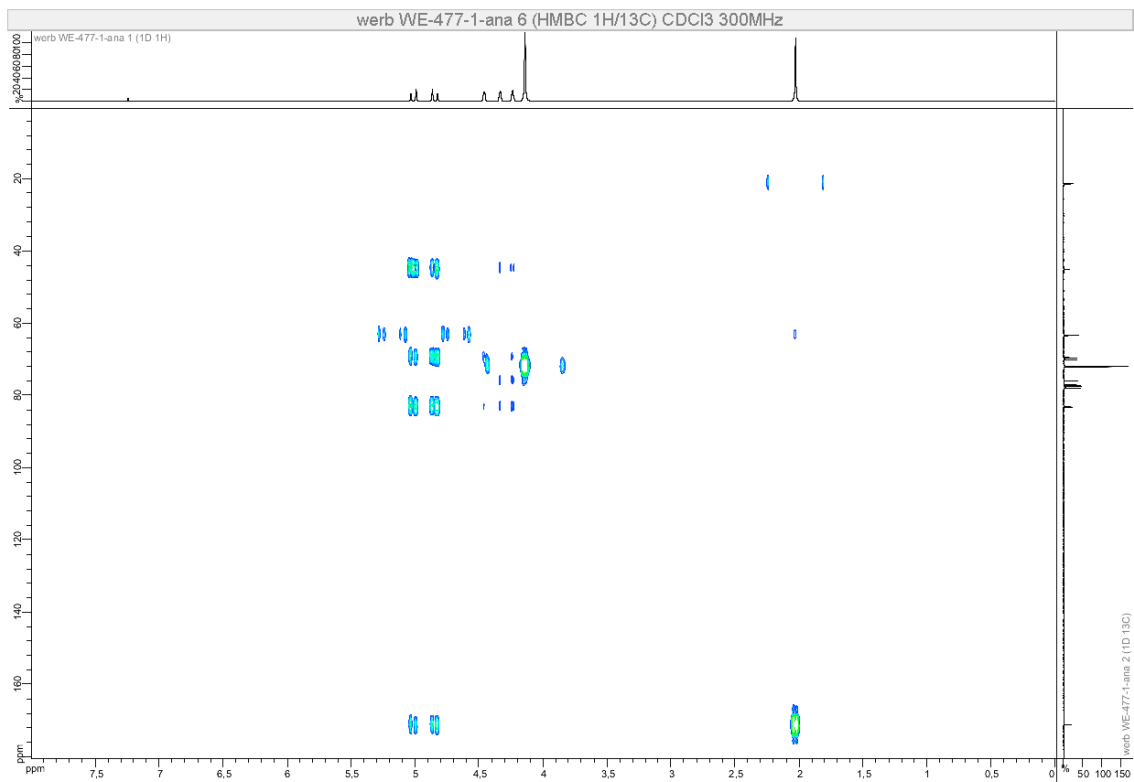
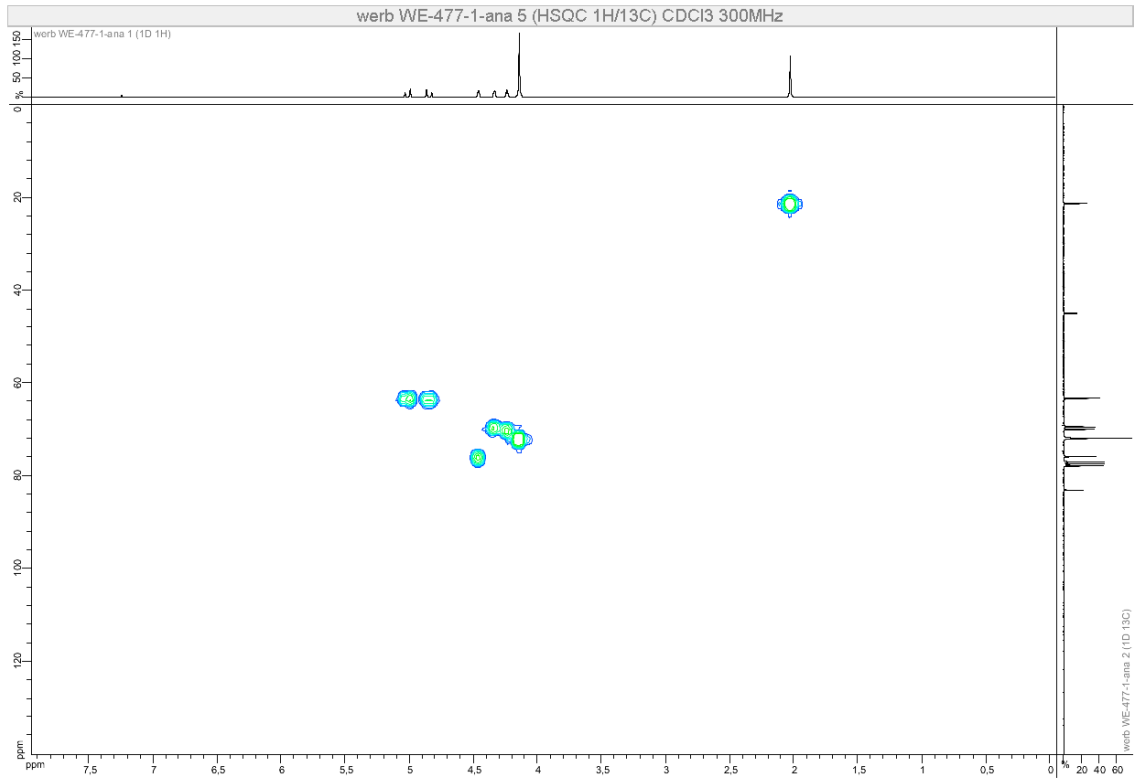
Compound (*S_p*)-1



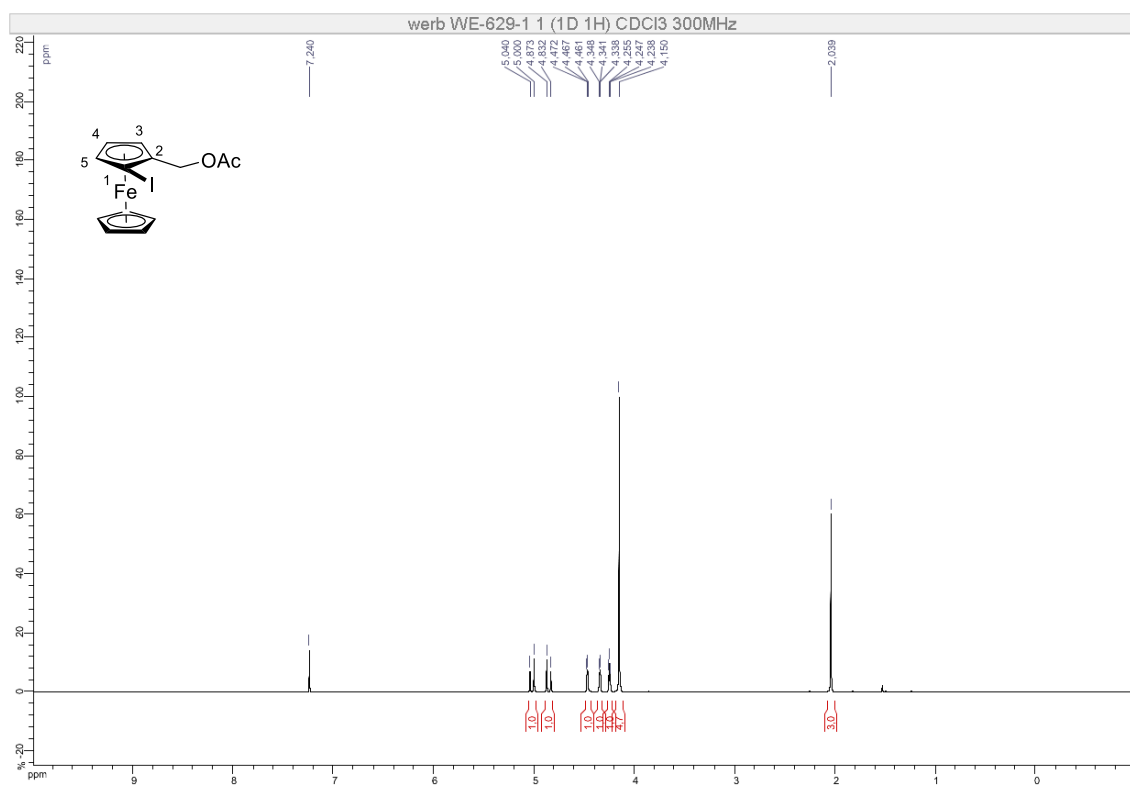
Compound (\pm)-2



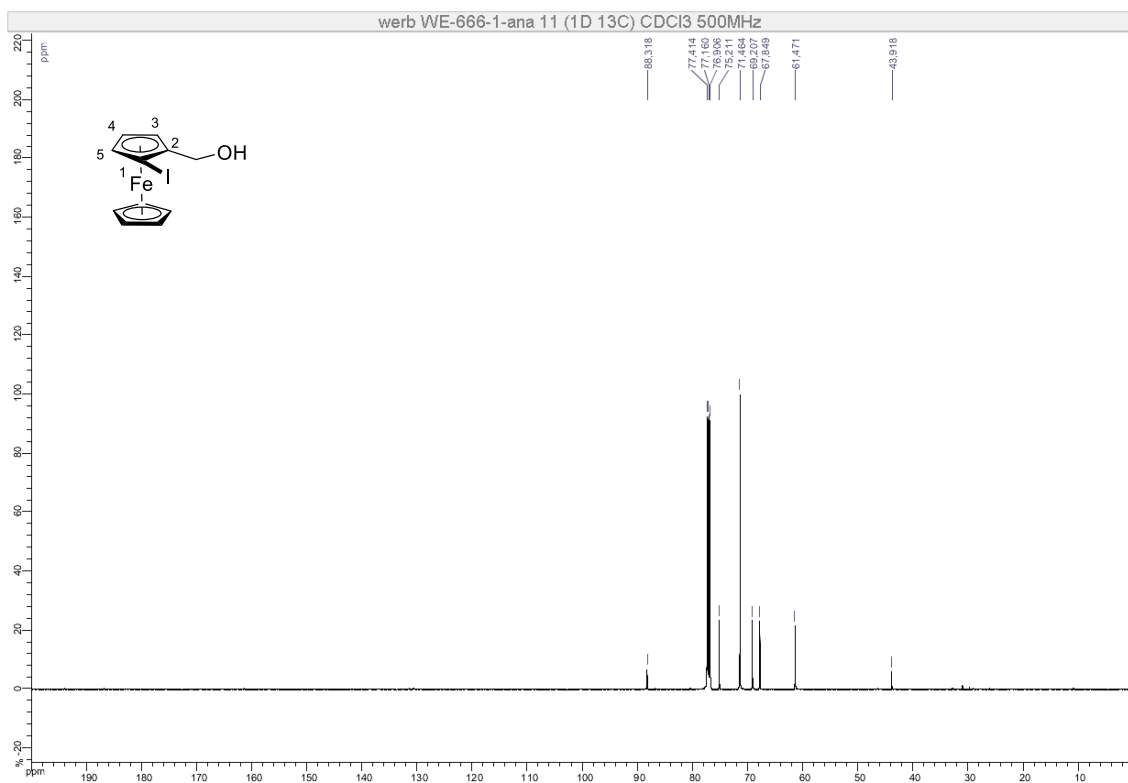
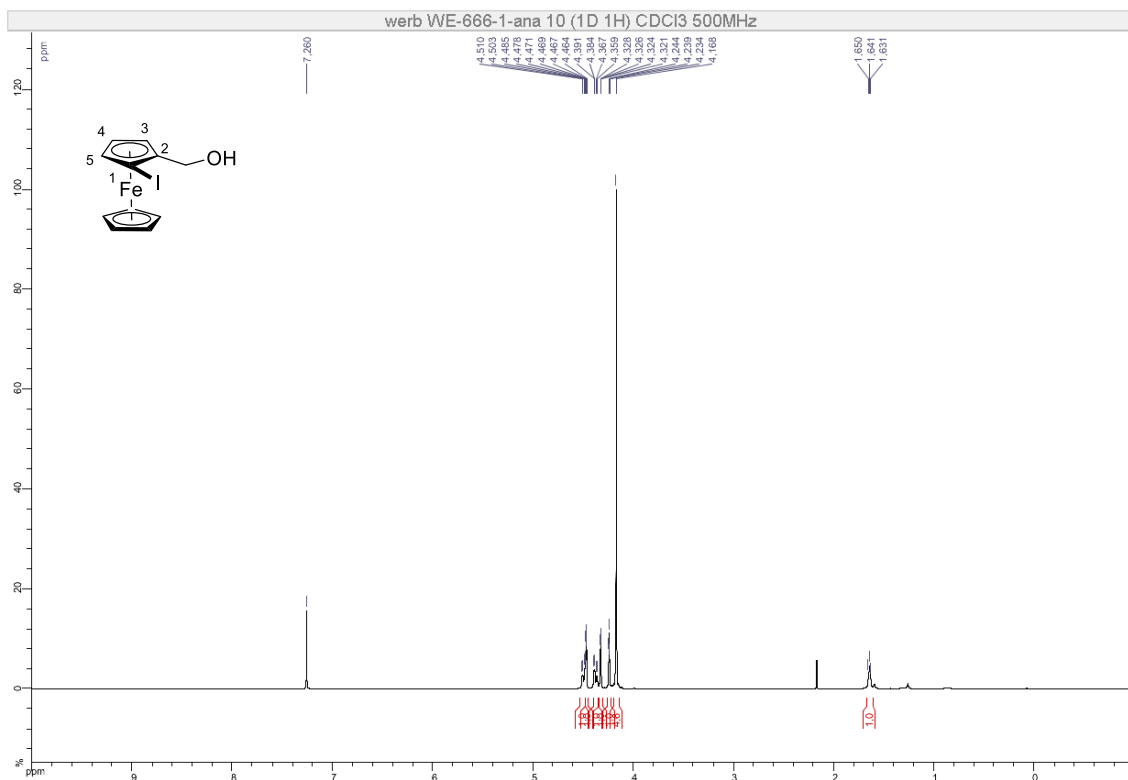


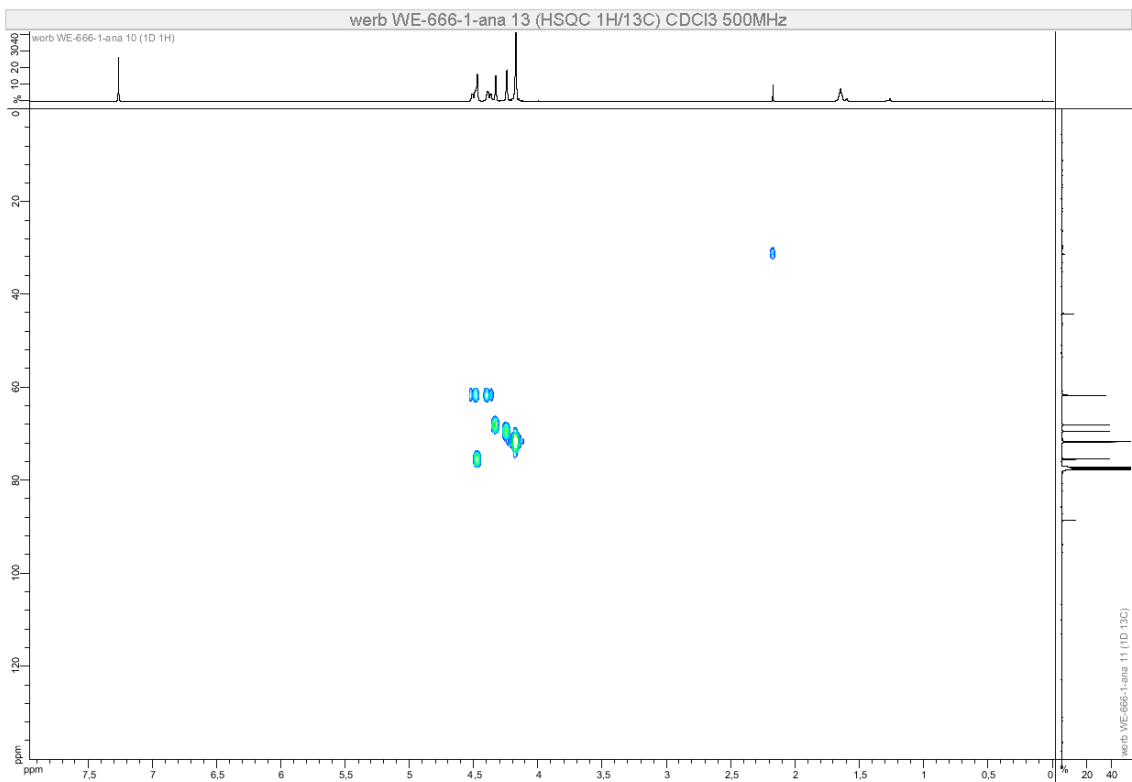
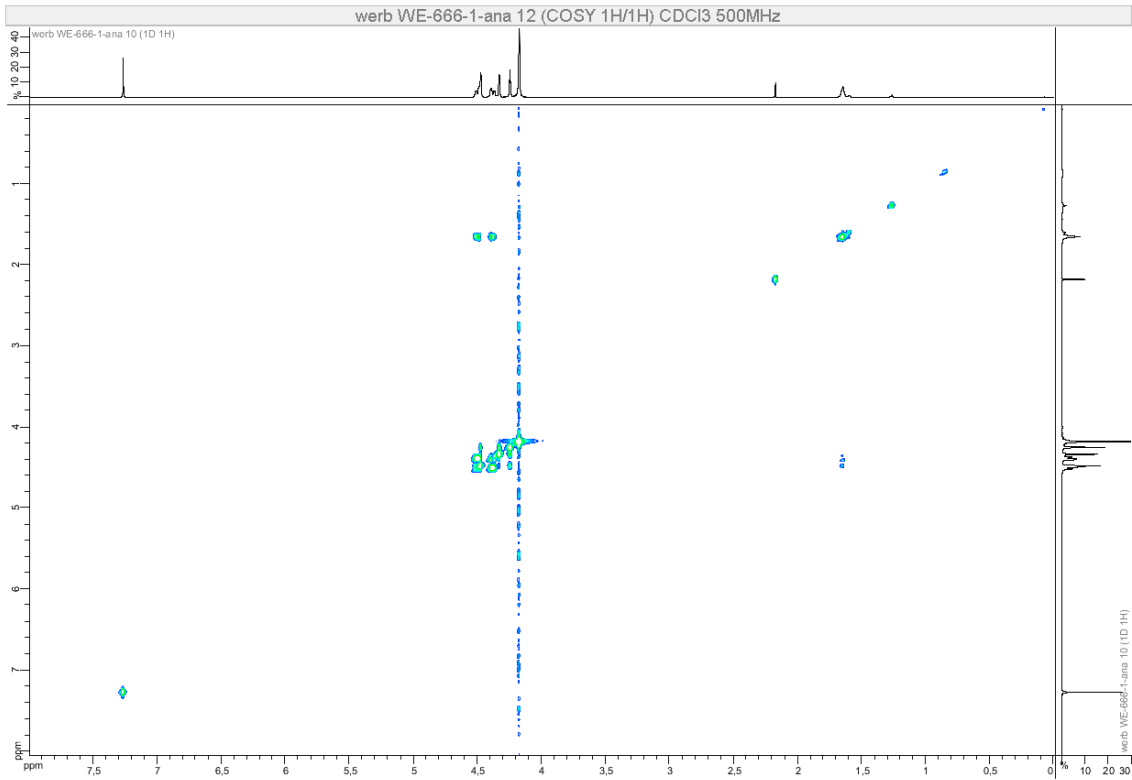


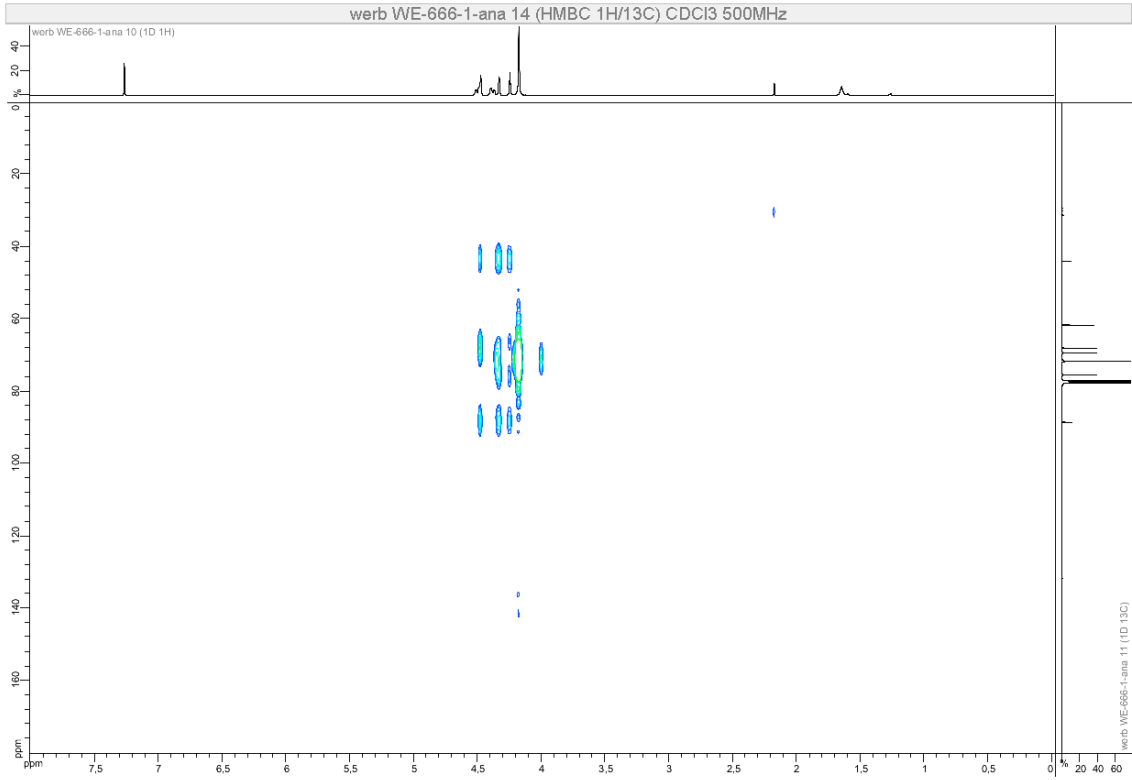
Compound (*S_p*)-2



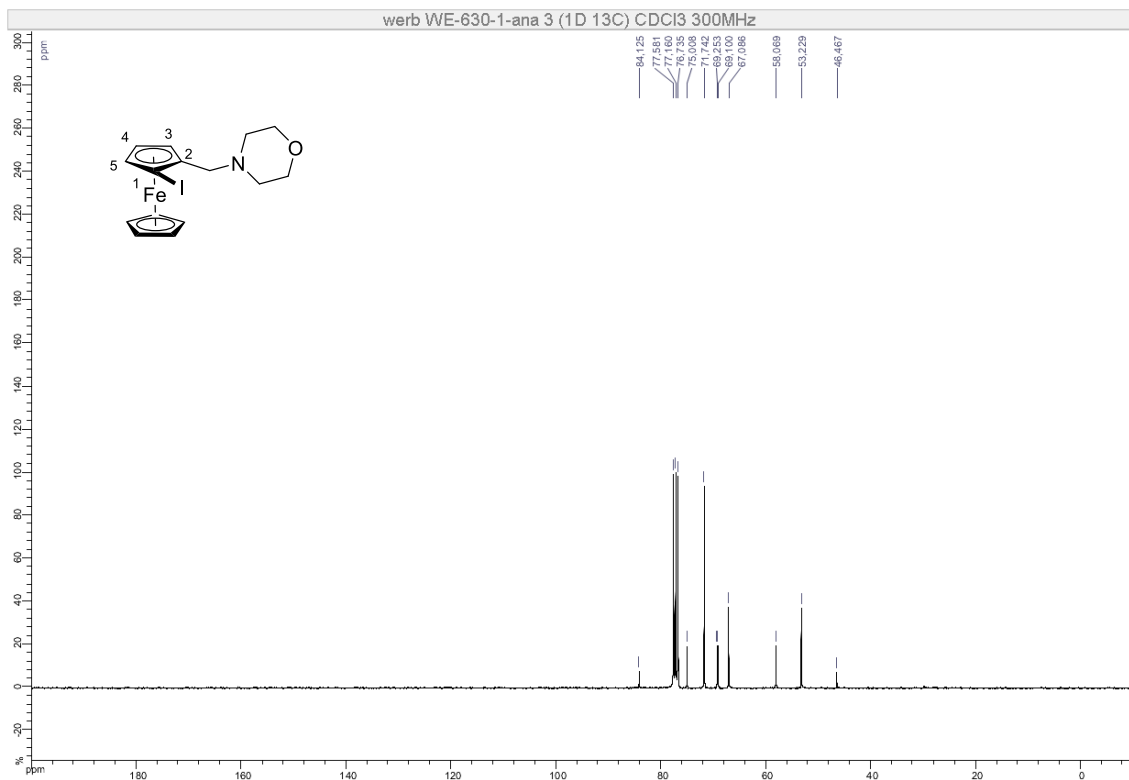
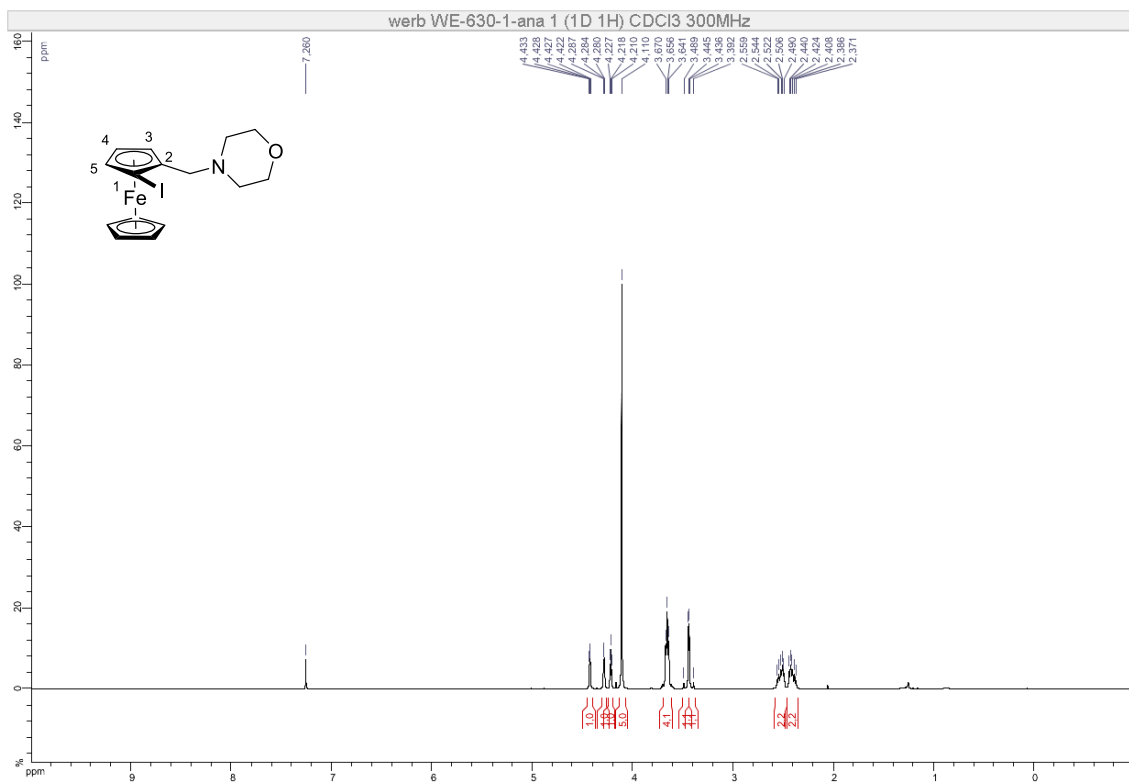
Compound (\pm)-3

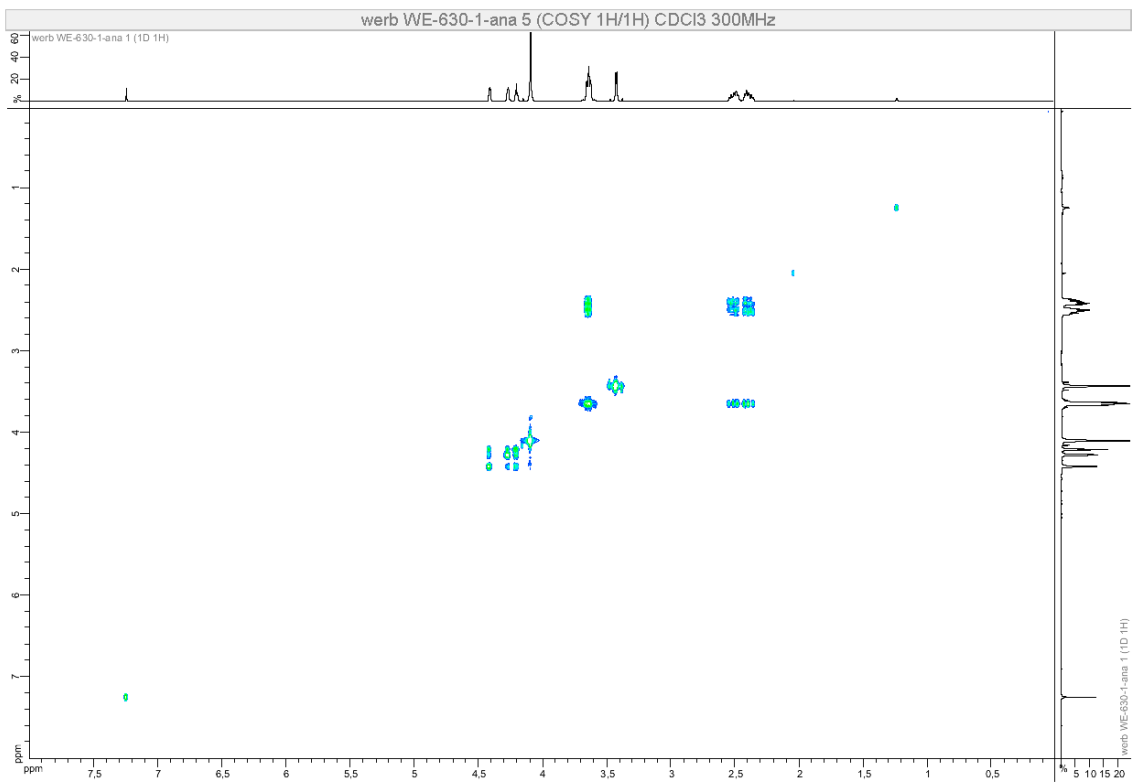
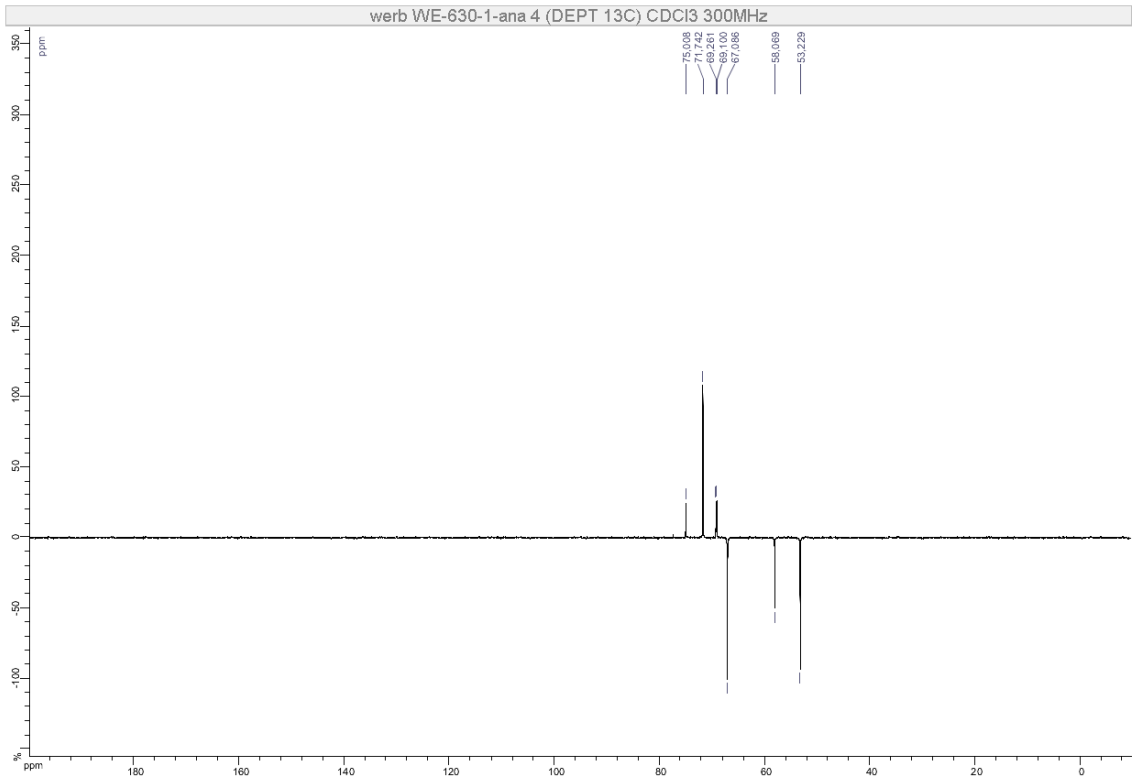


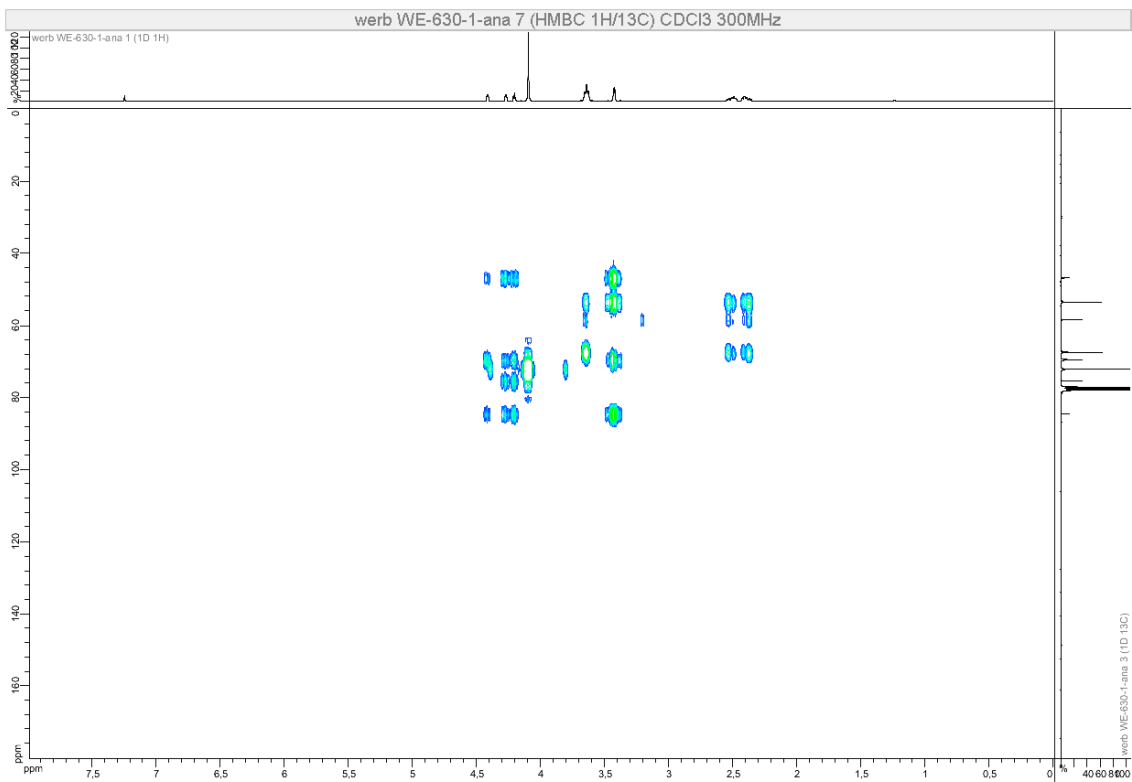
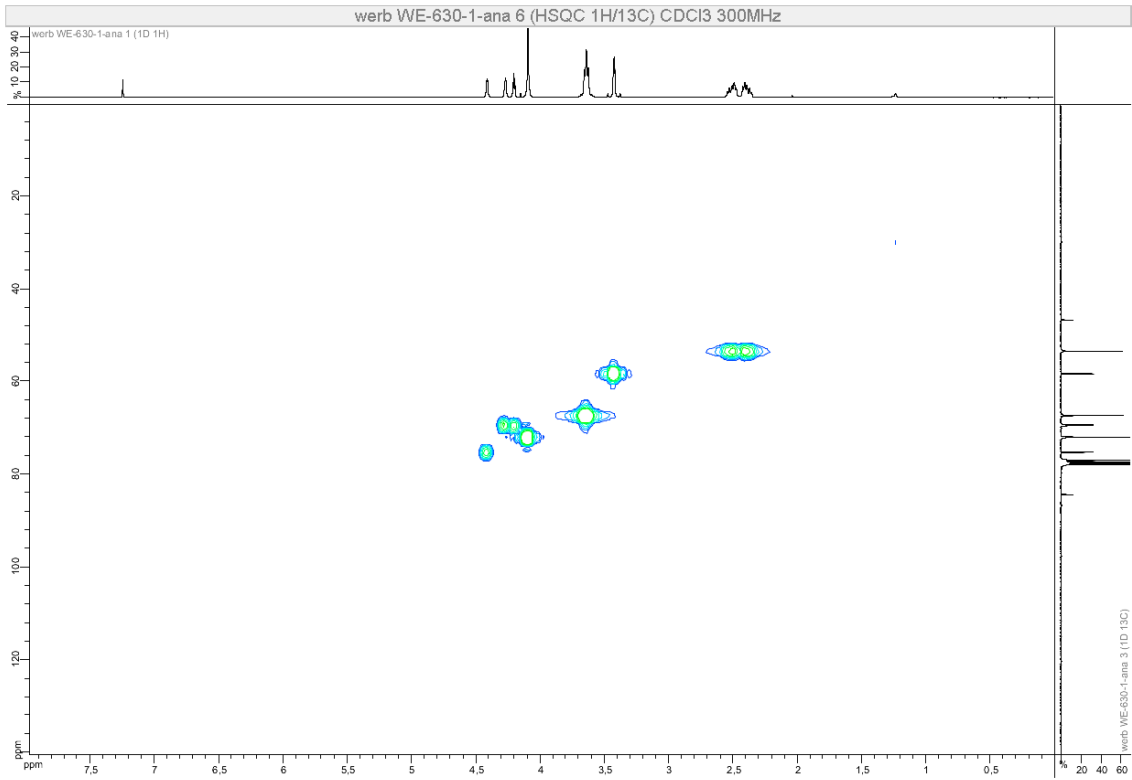




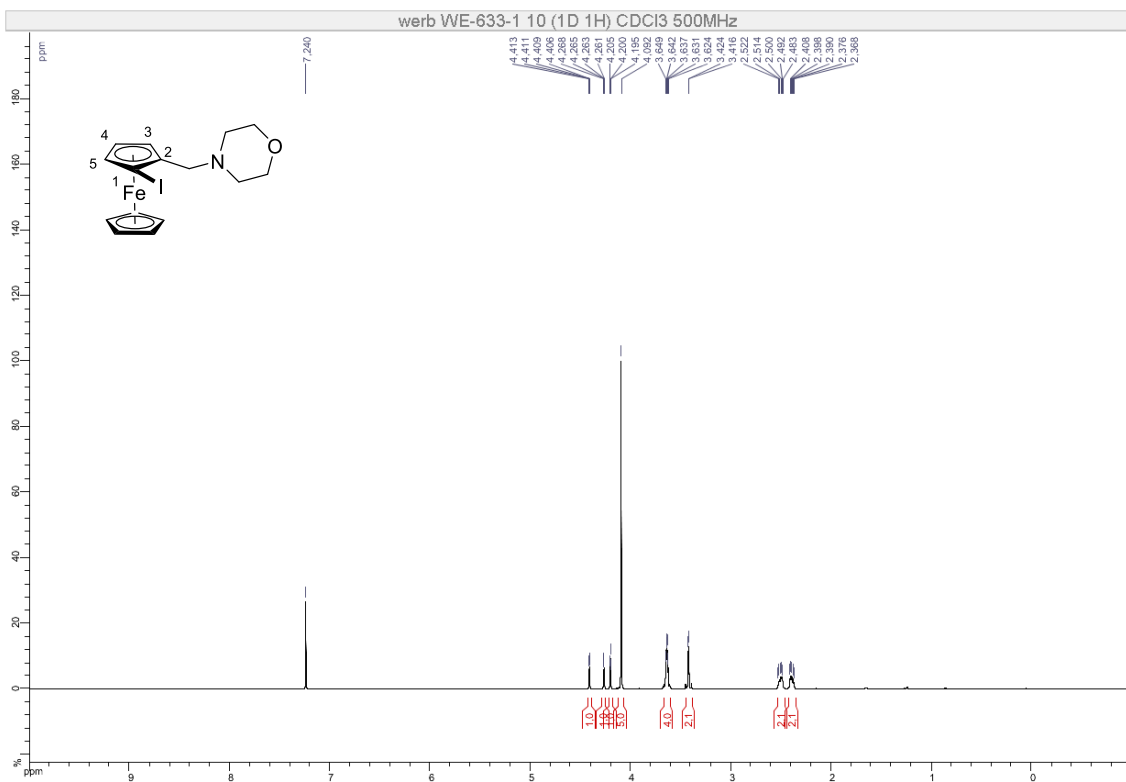
Compound (\pm)-4a



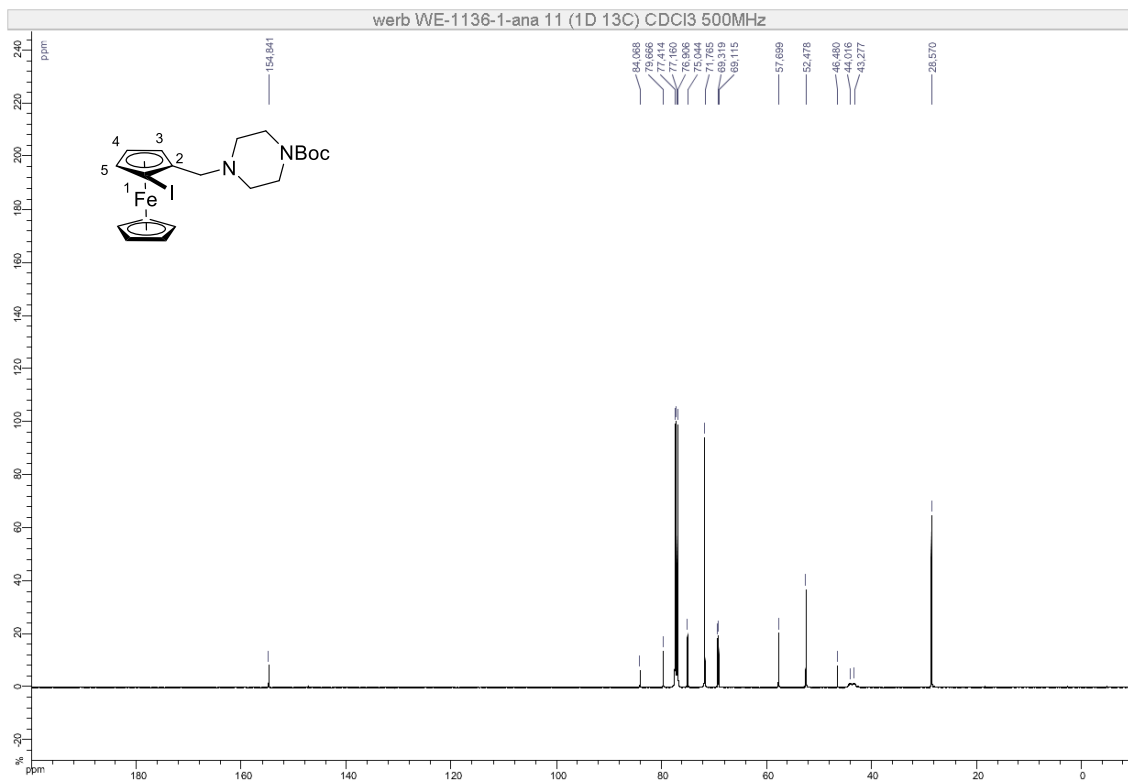
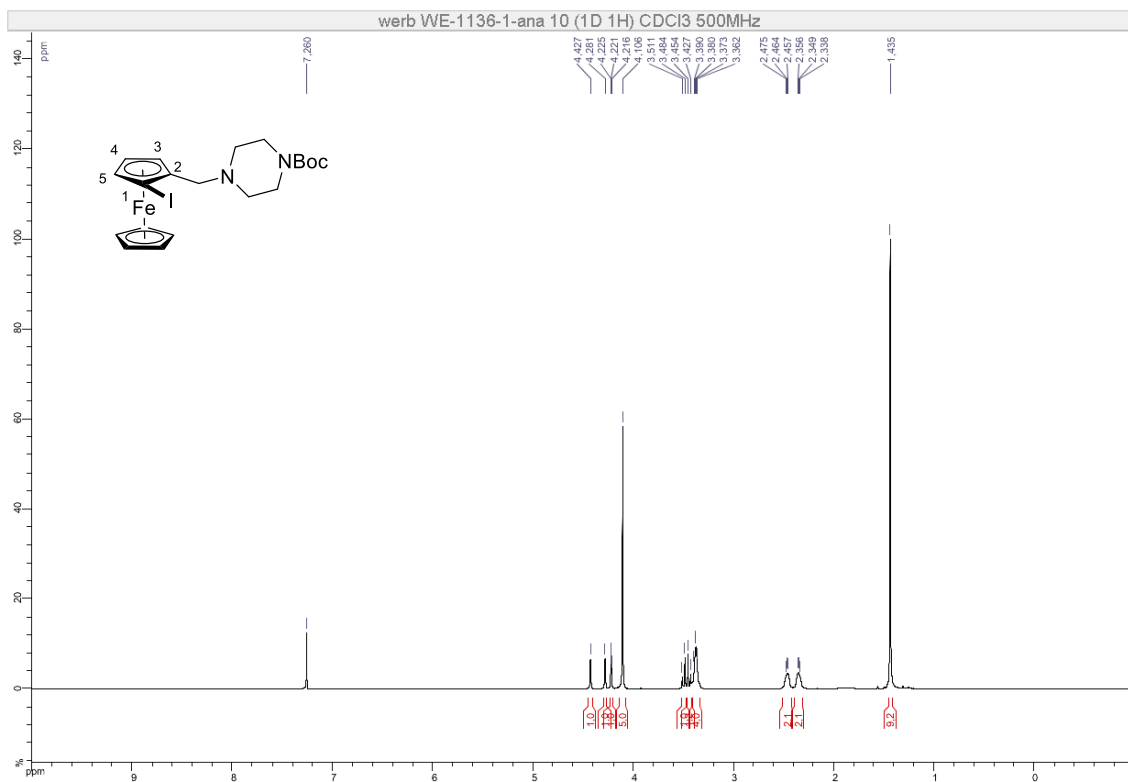


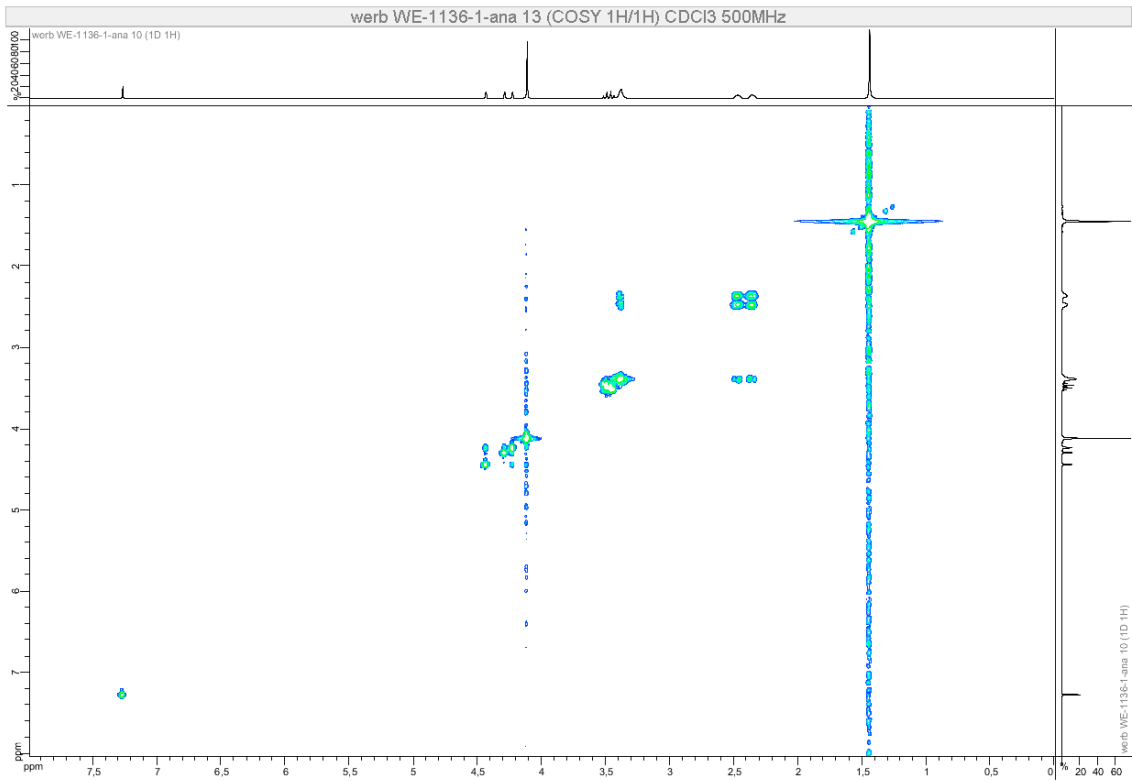
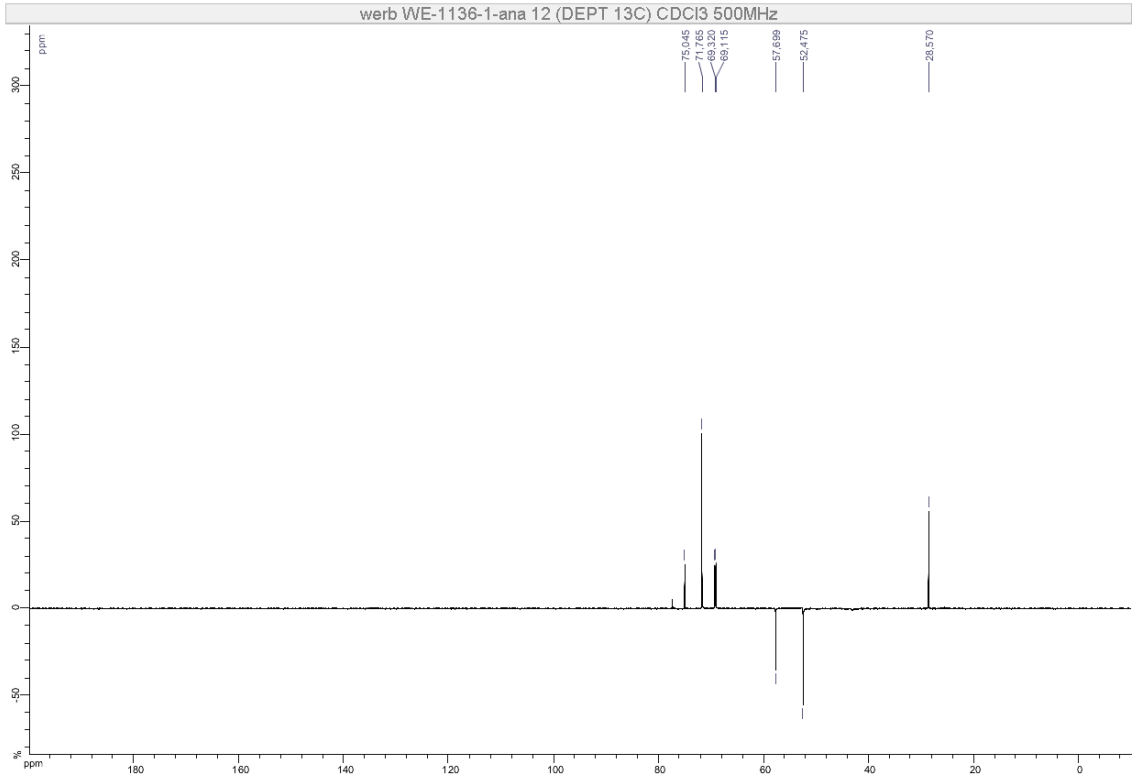


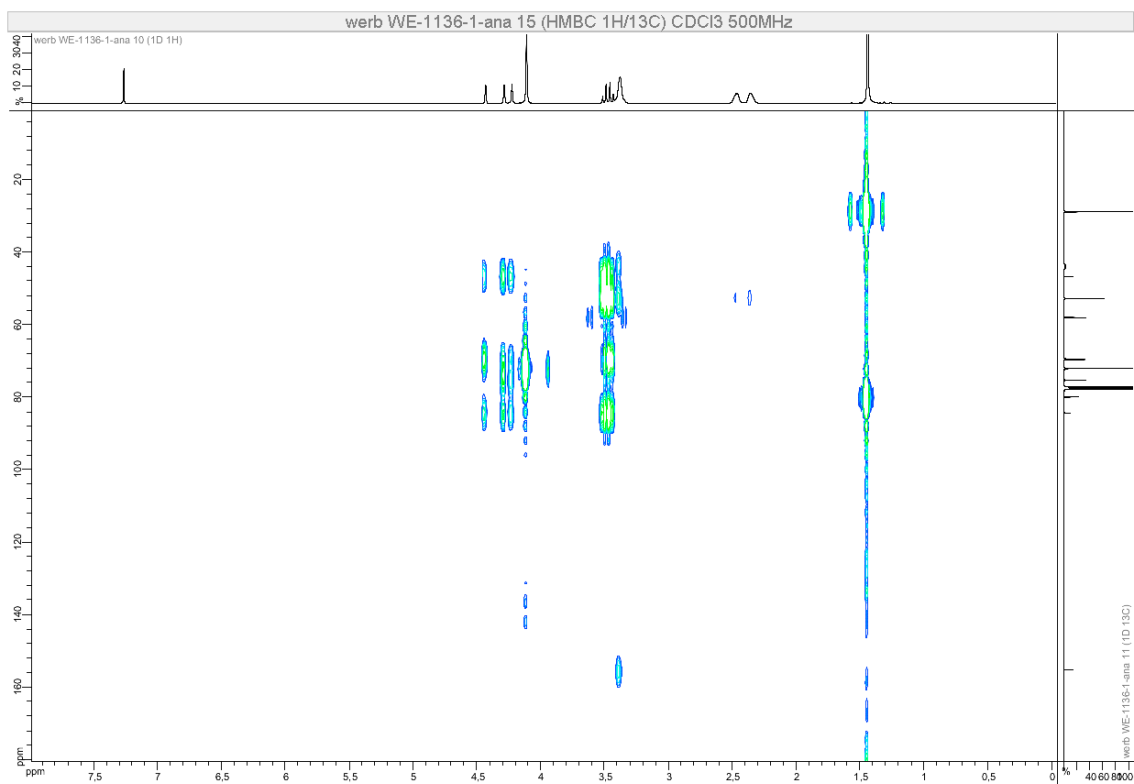
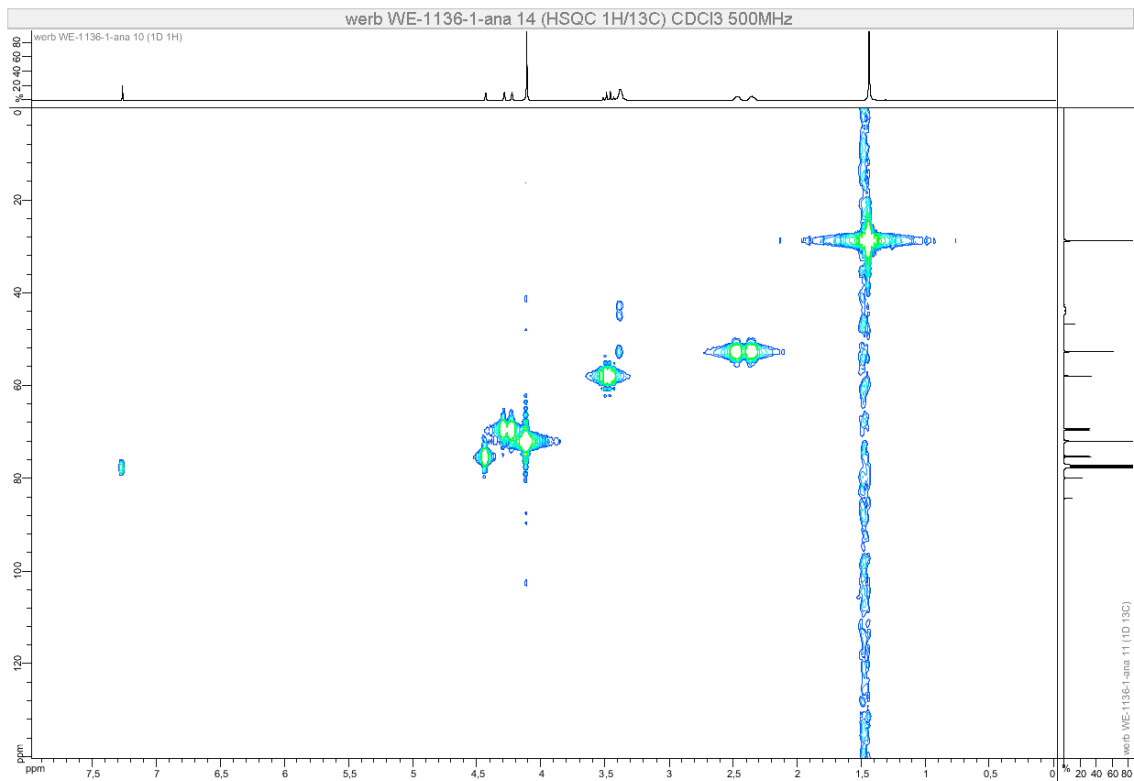
Compound (*S_p*)-4a

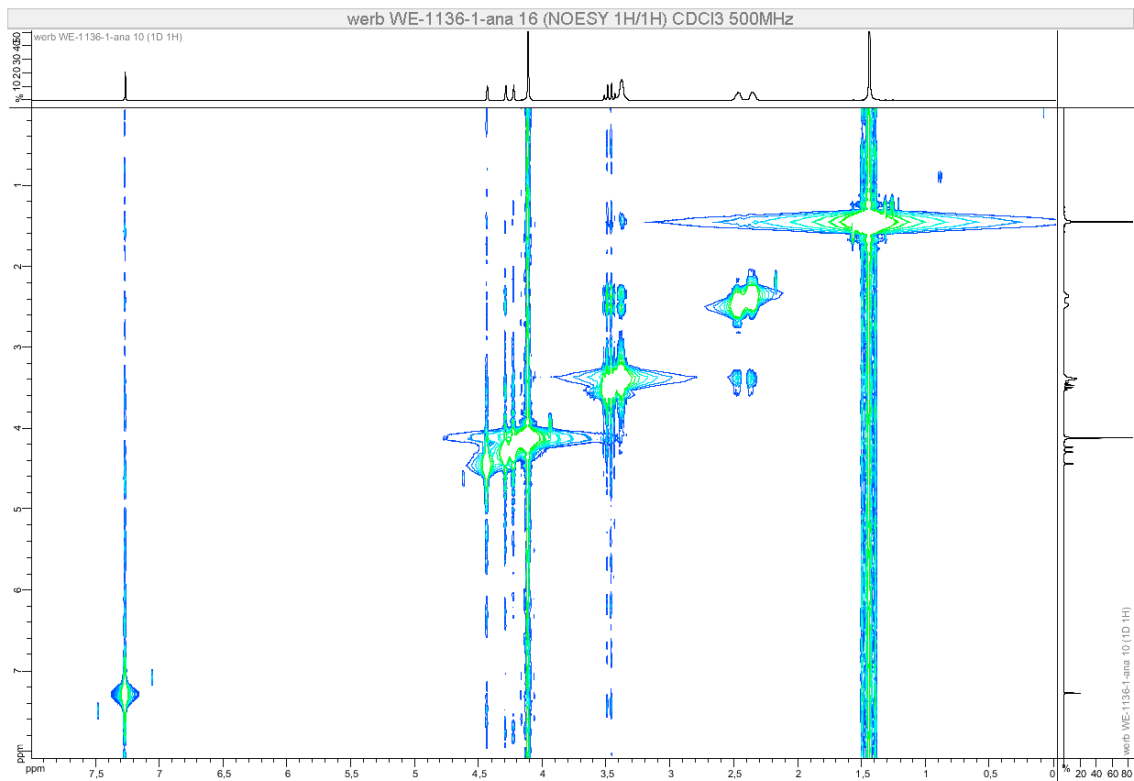


Compound (\pm)-4b

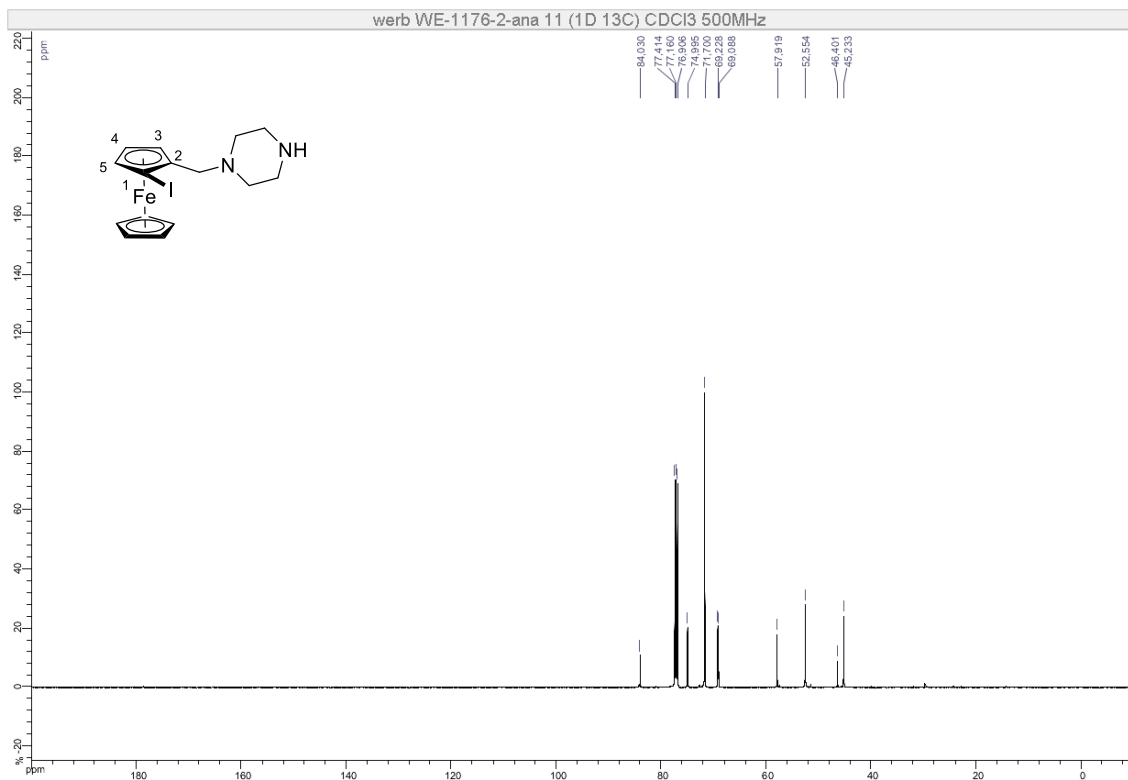
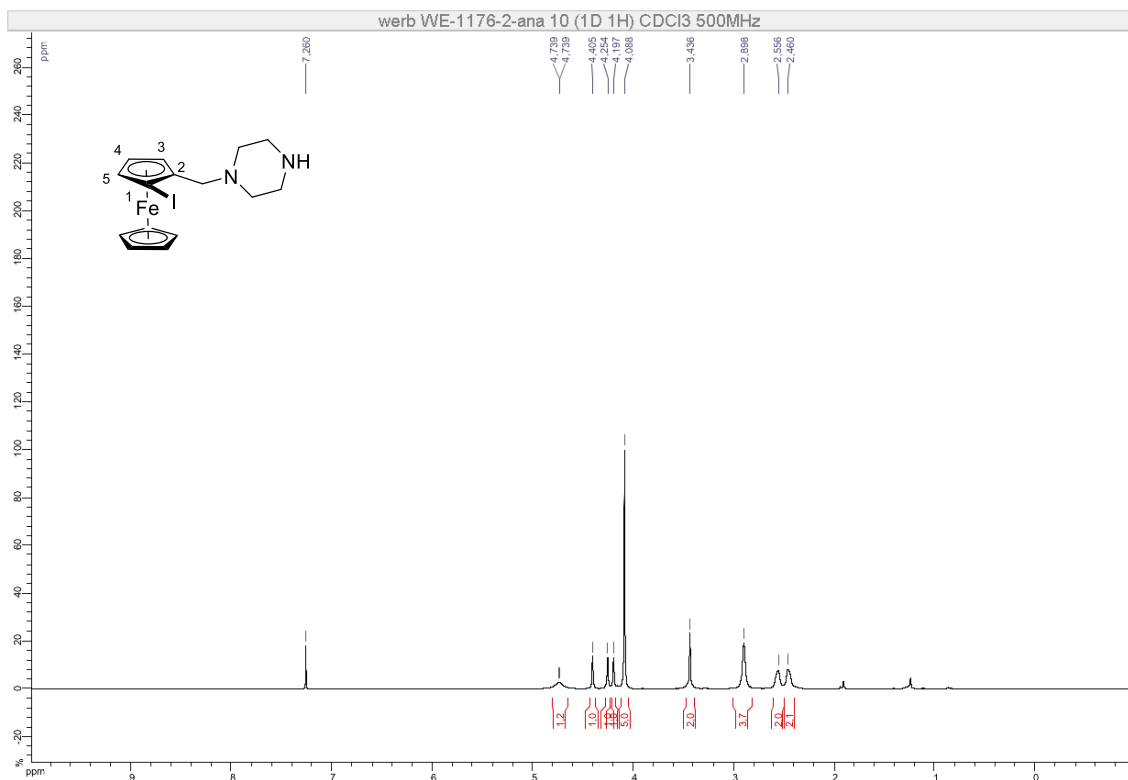


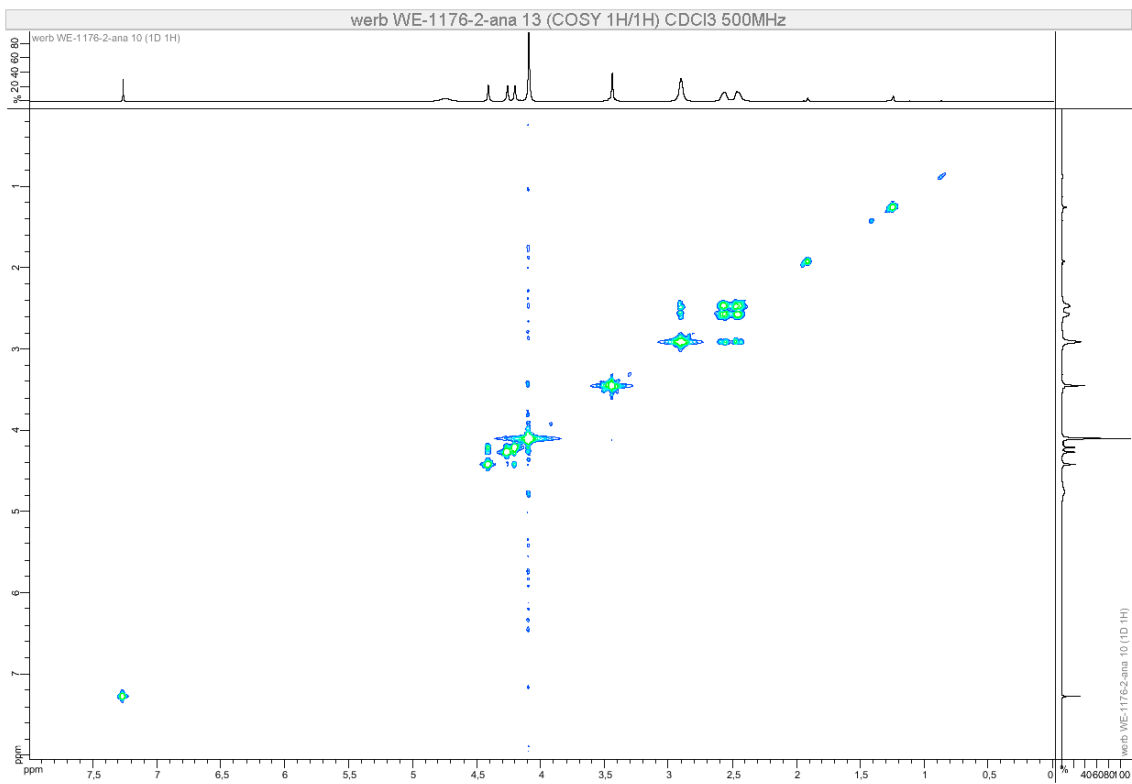
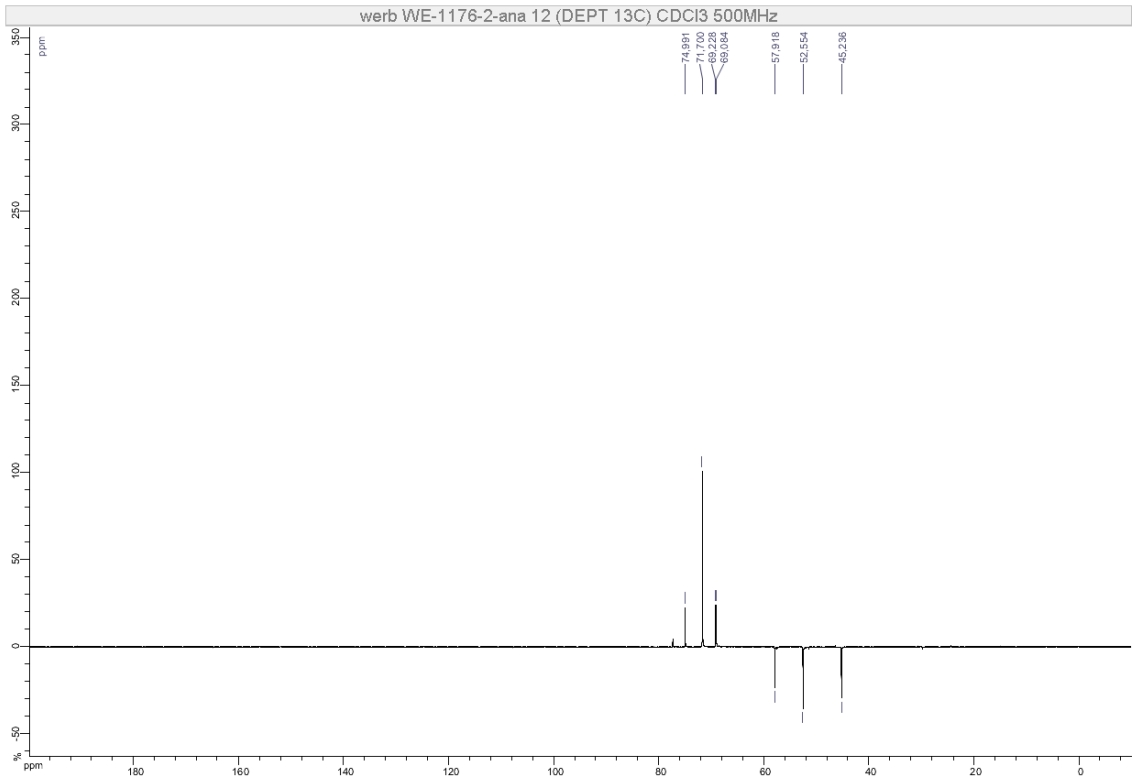


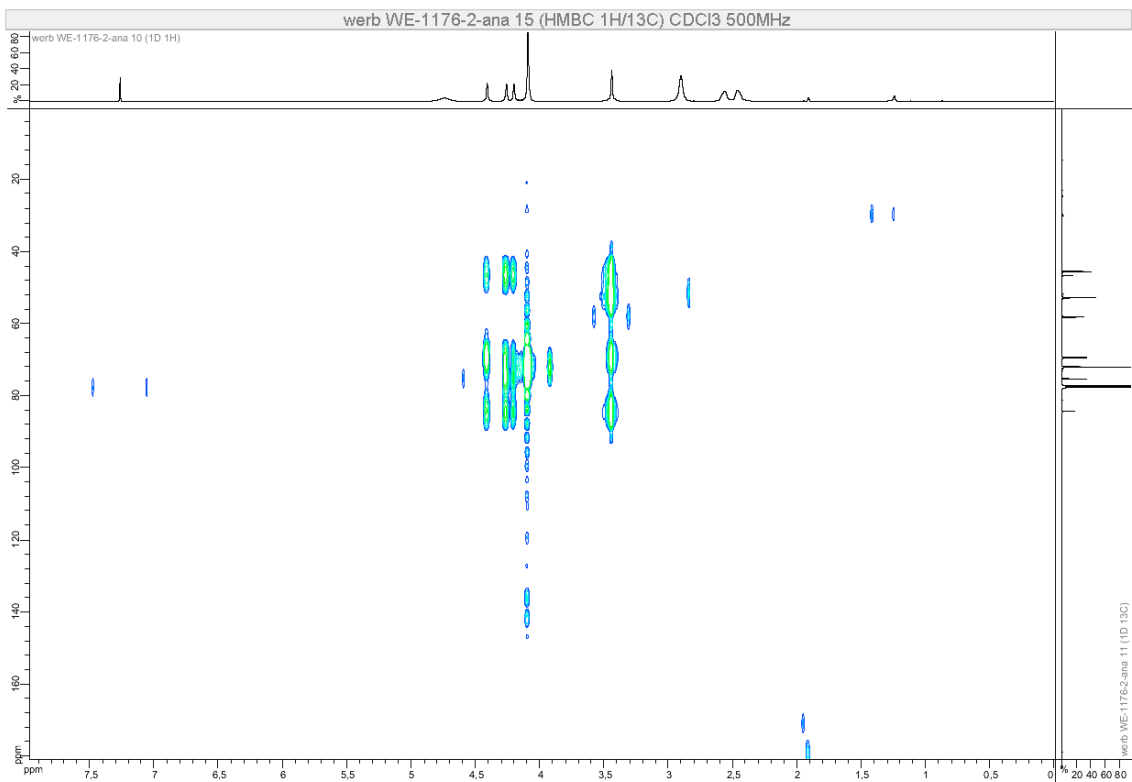
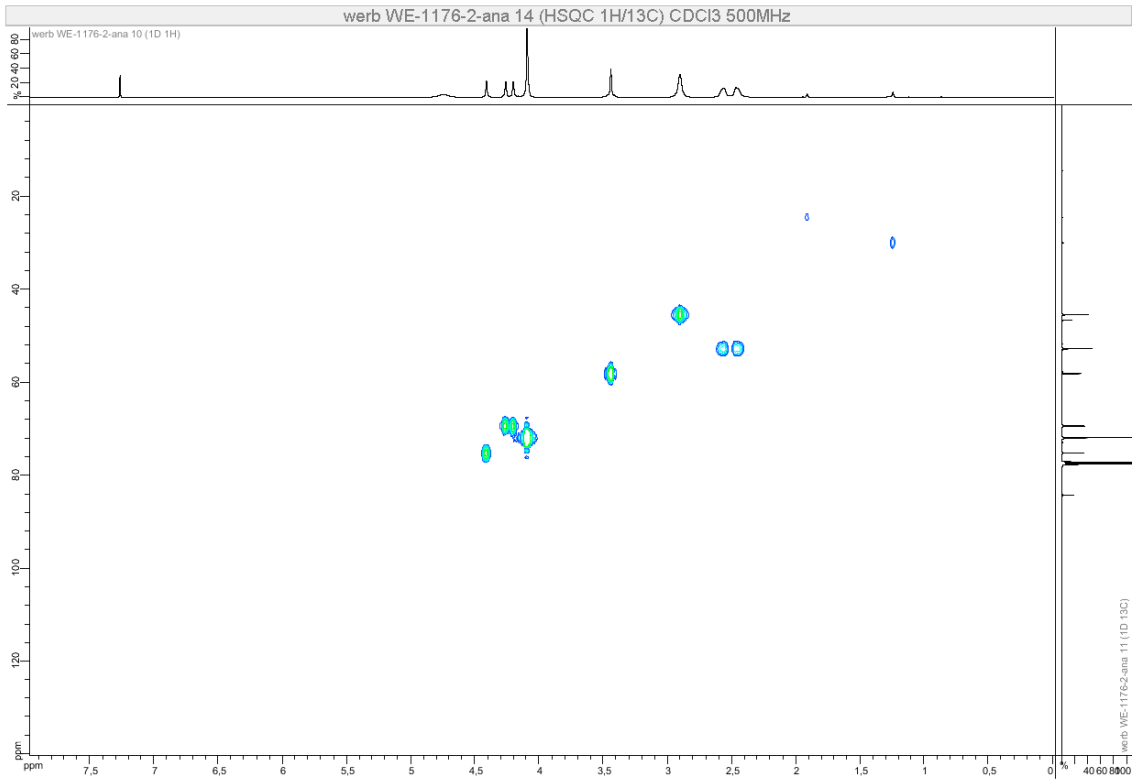




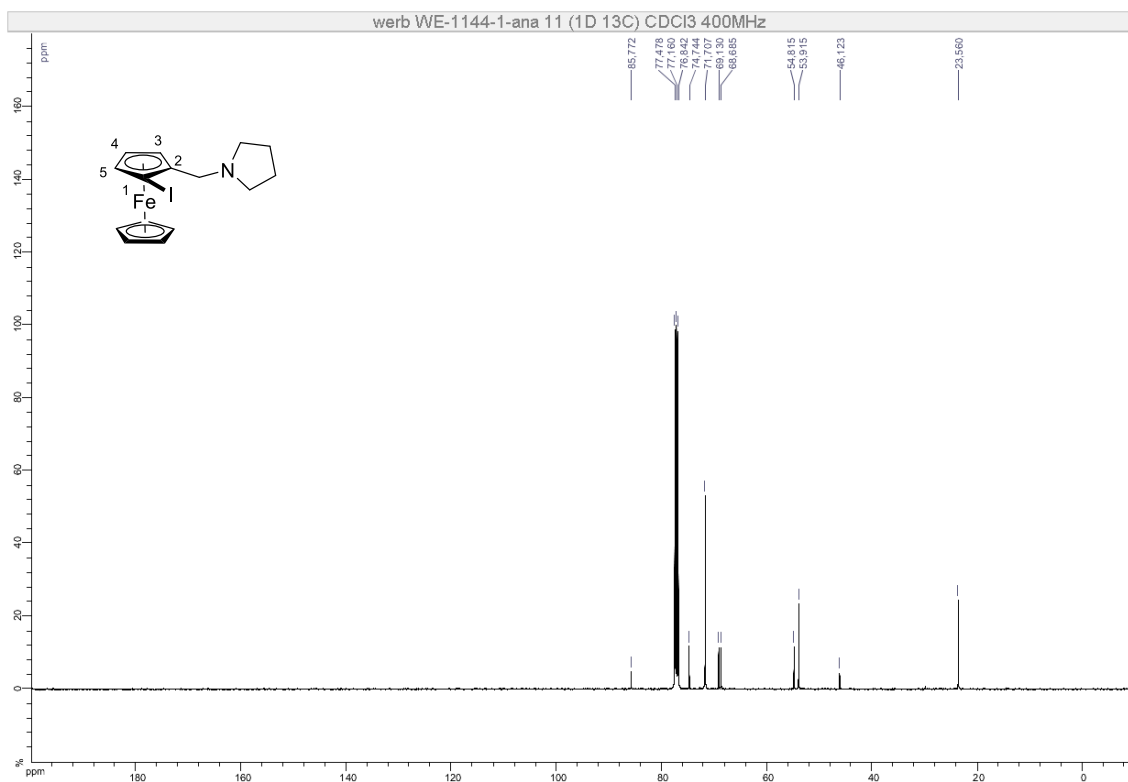
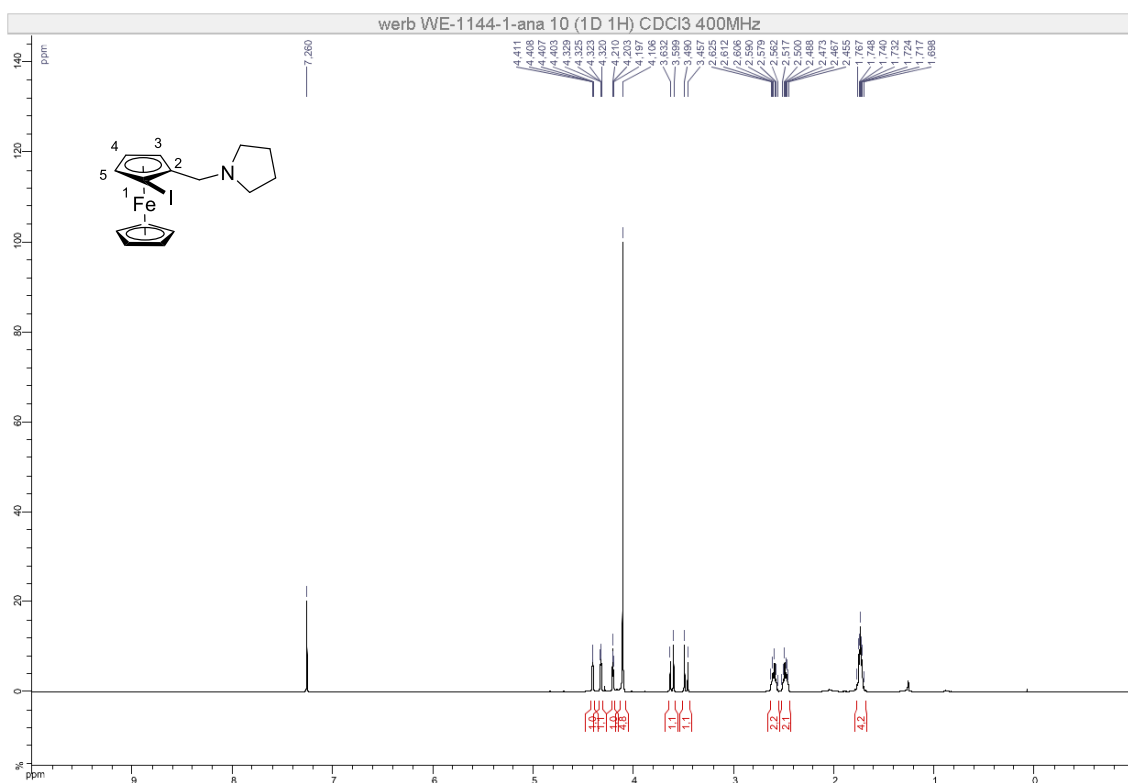
Compound (\pm)-4c

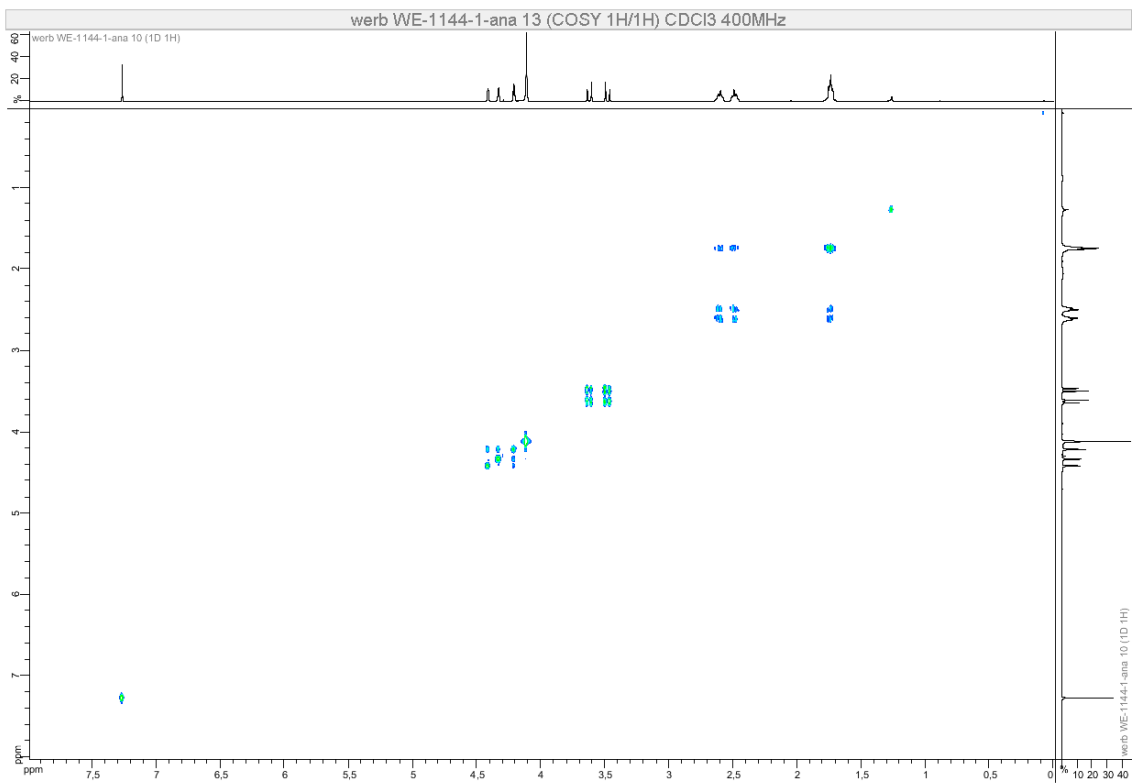
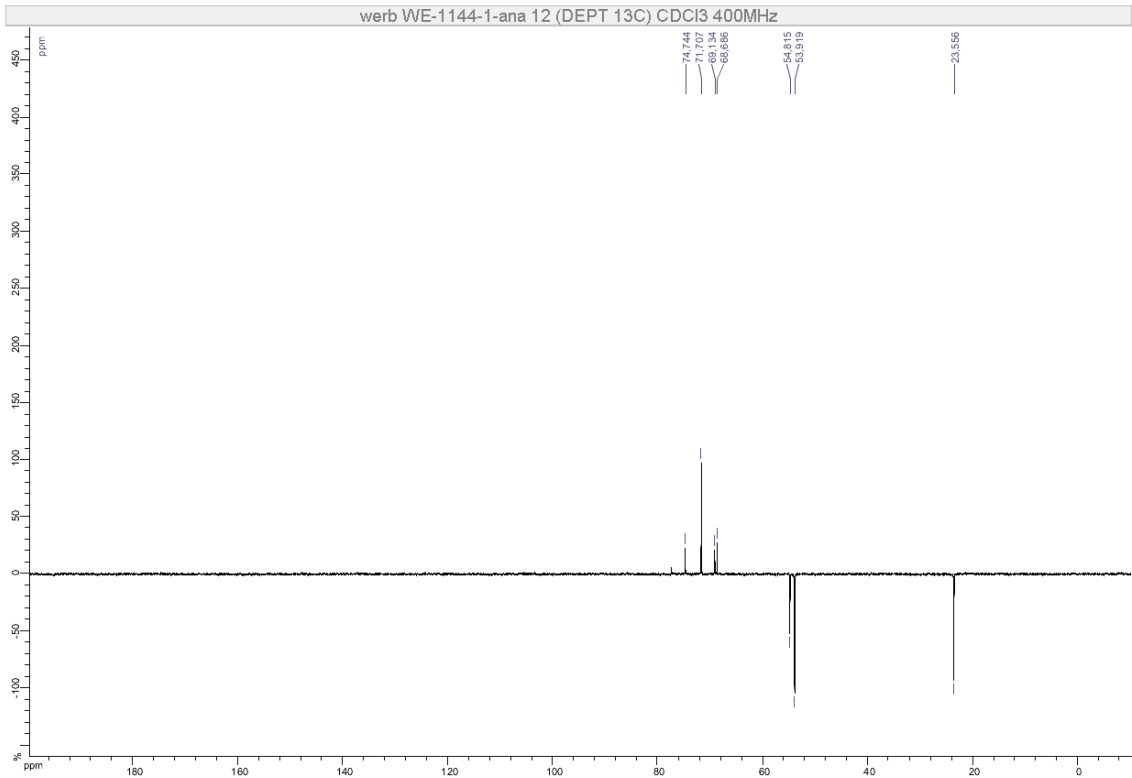


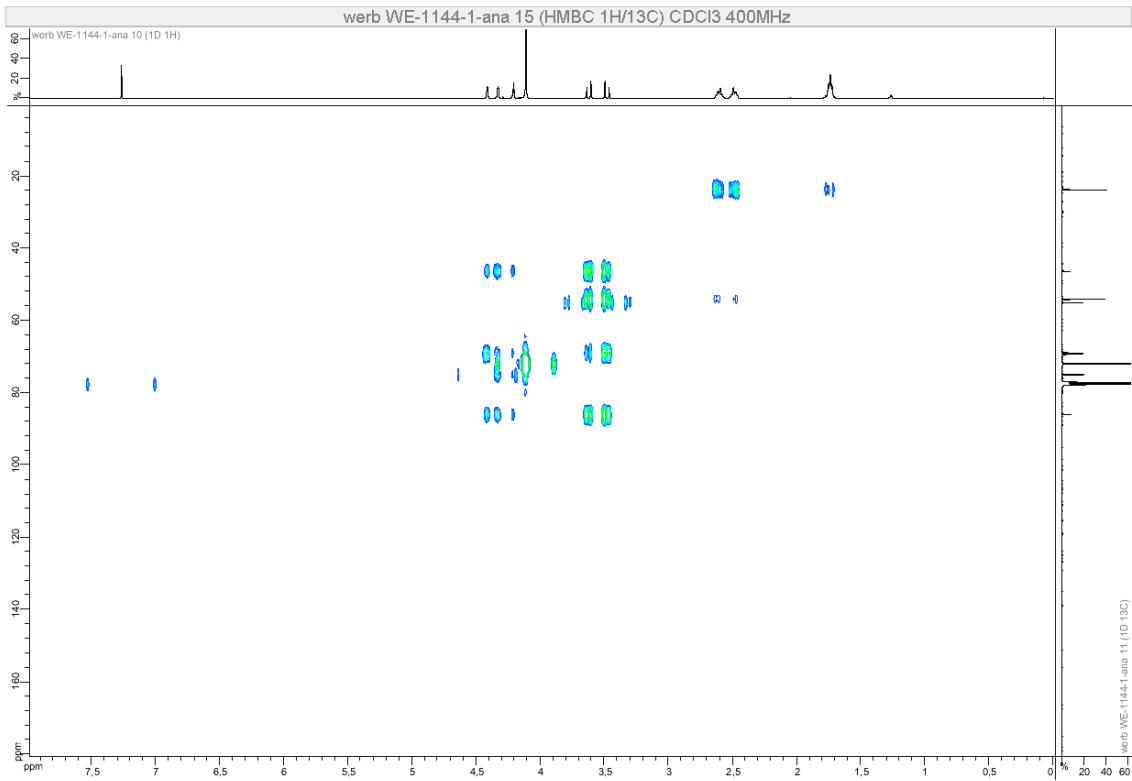
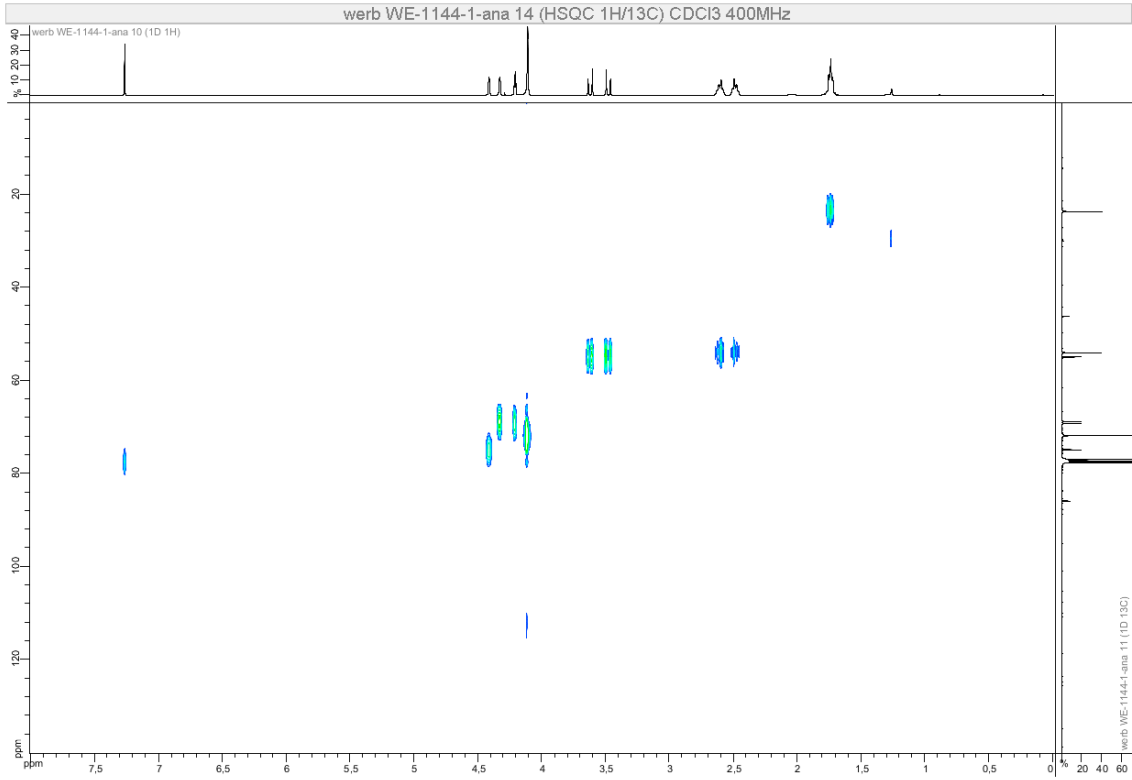




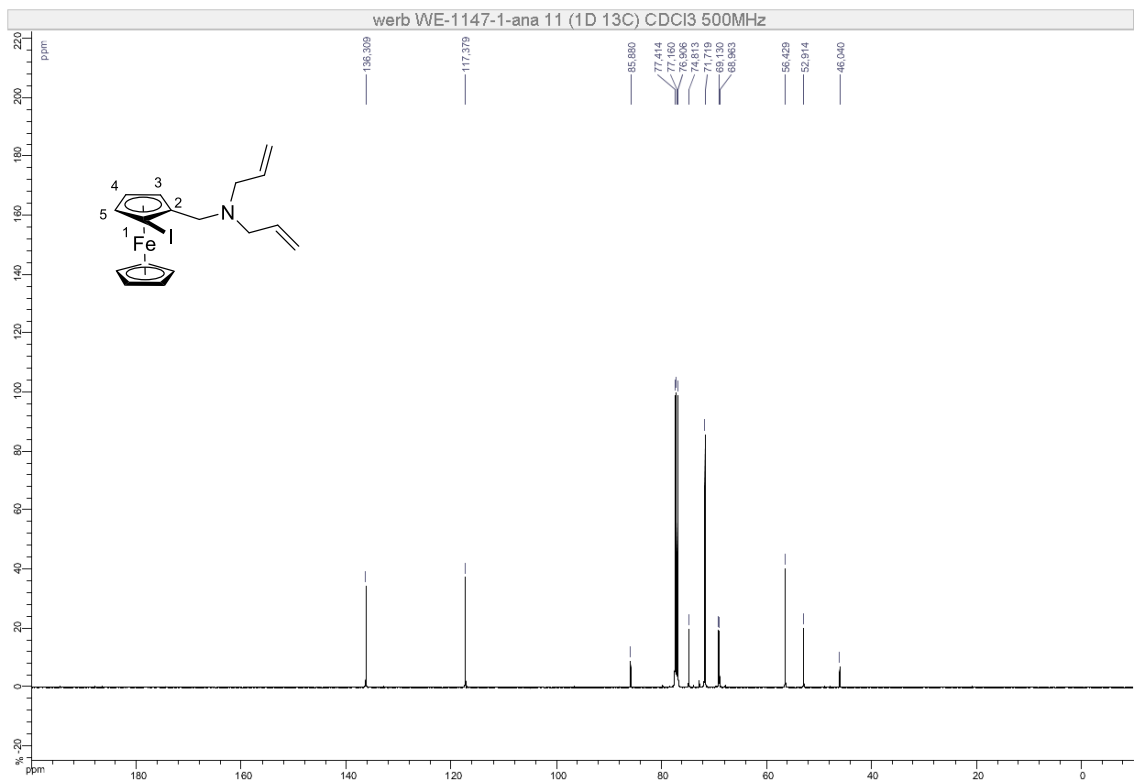
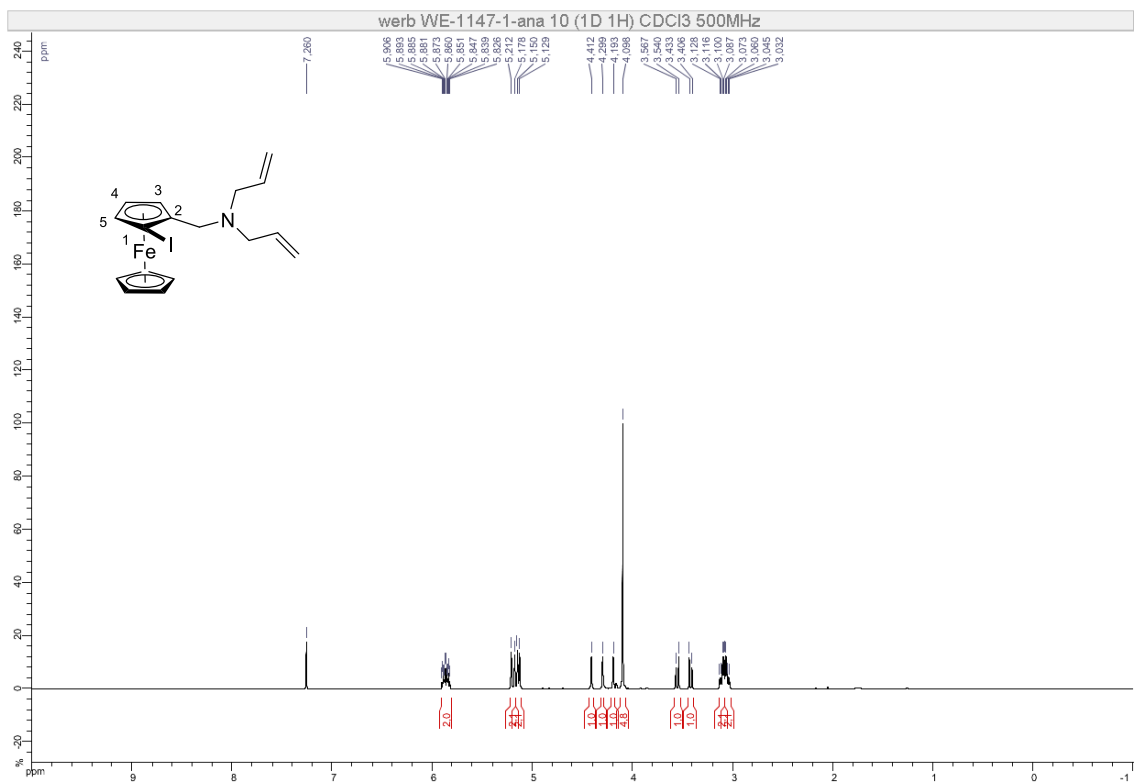
Compound (\pm)-4d

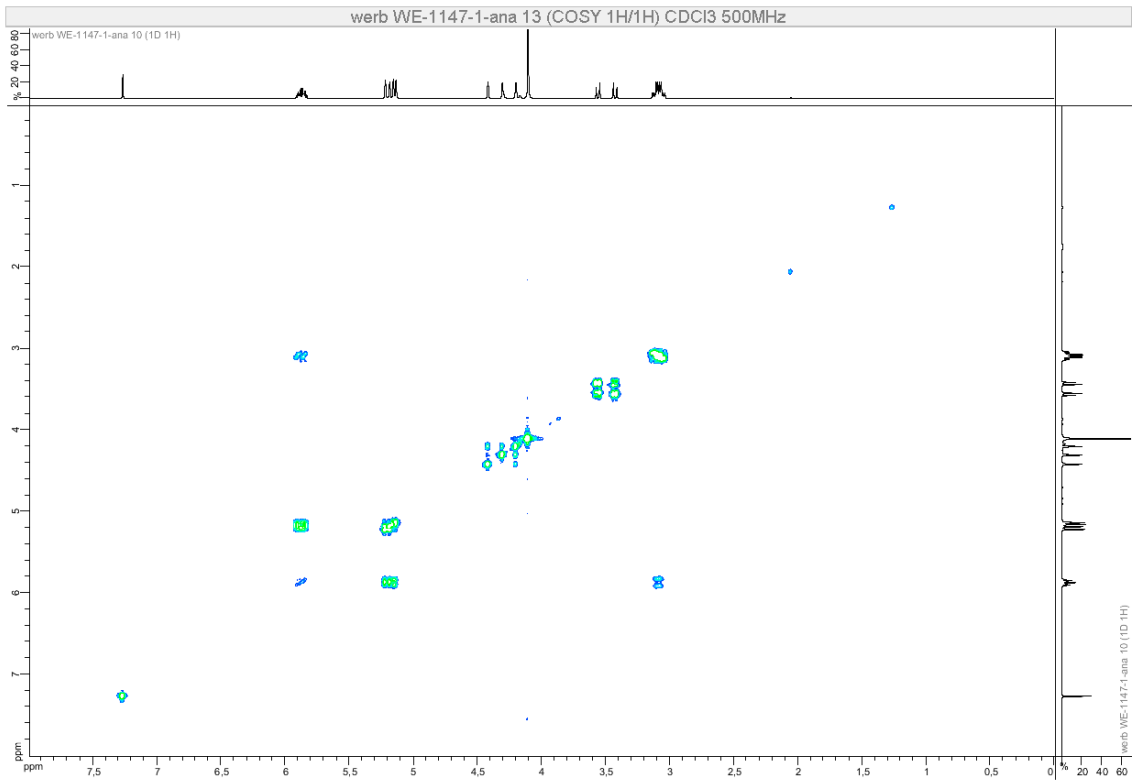
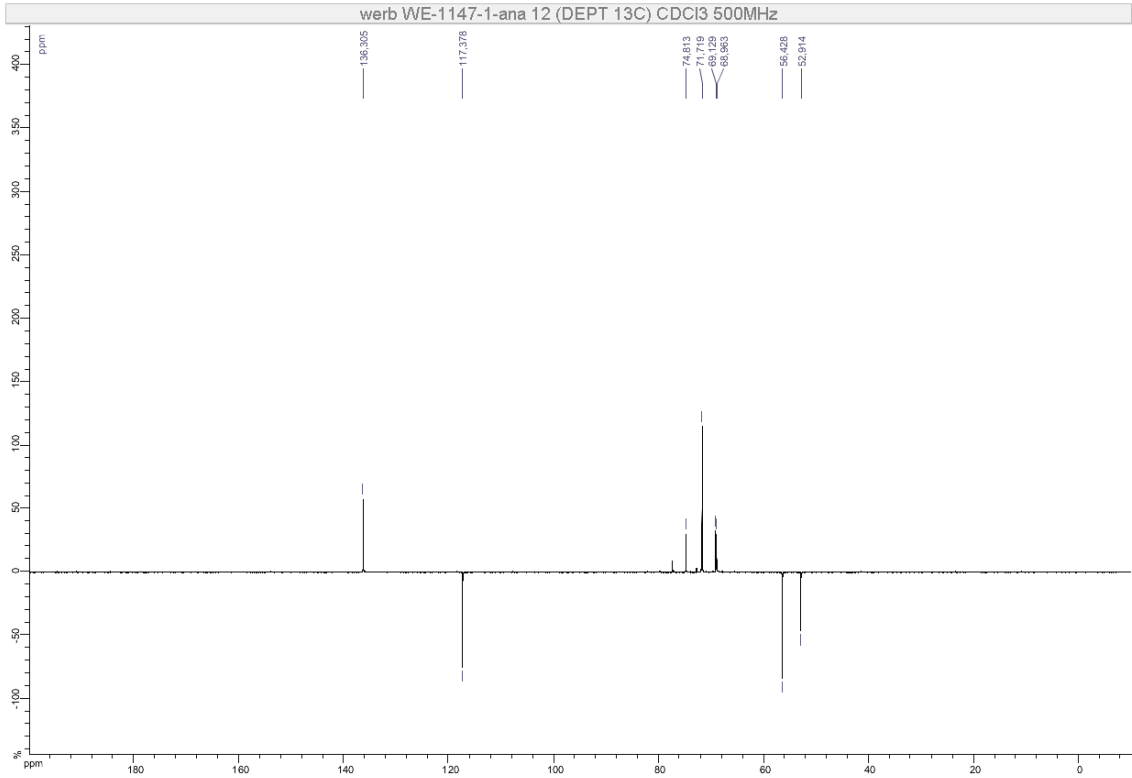


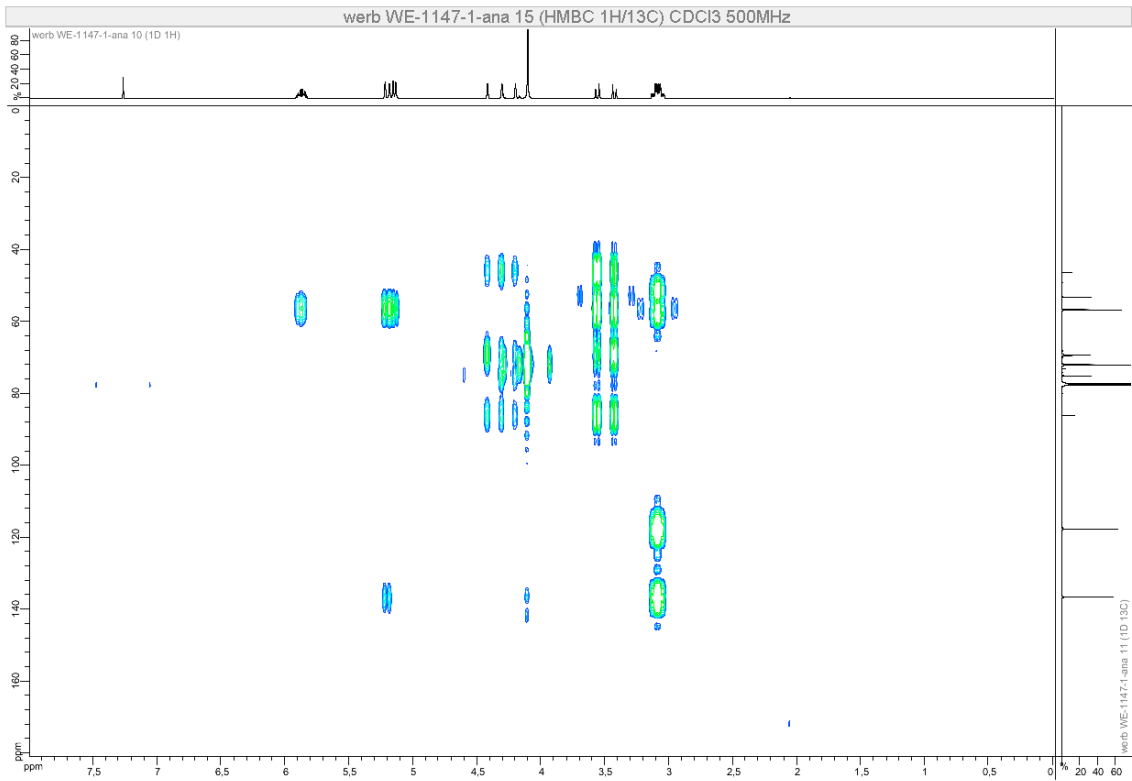
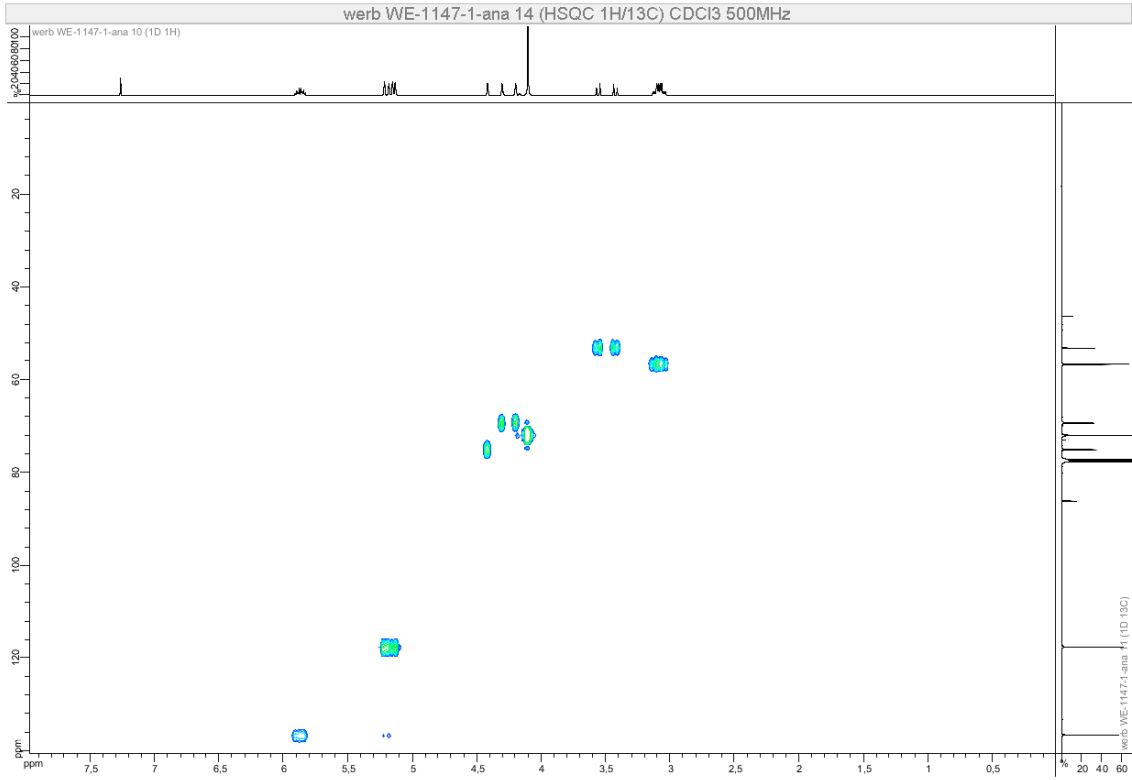


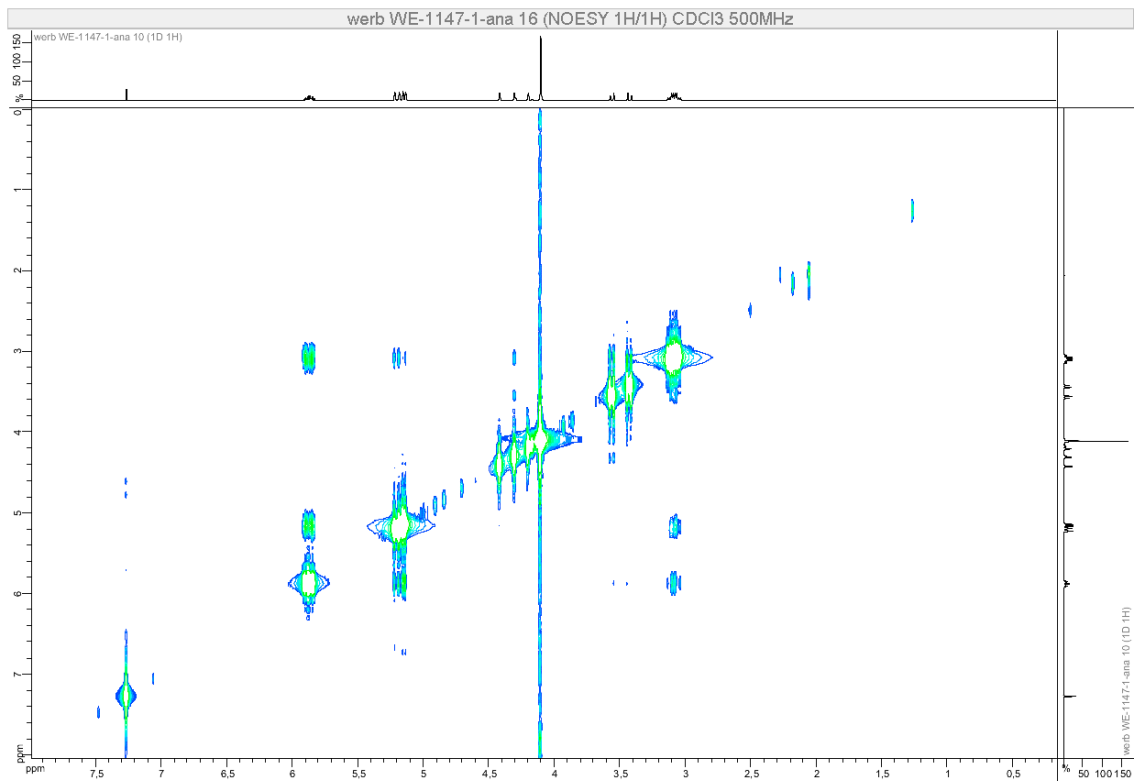


Compound (\pm)-4e

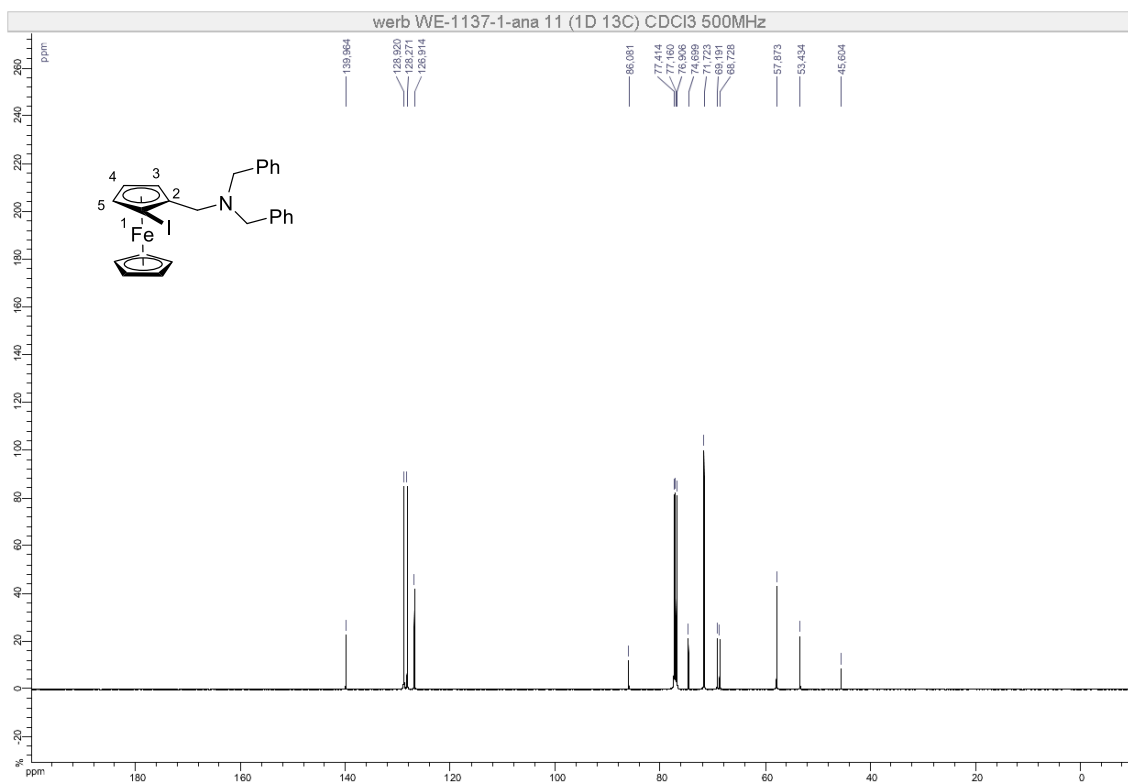
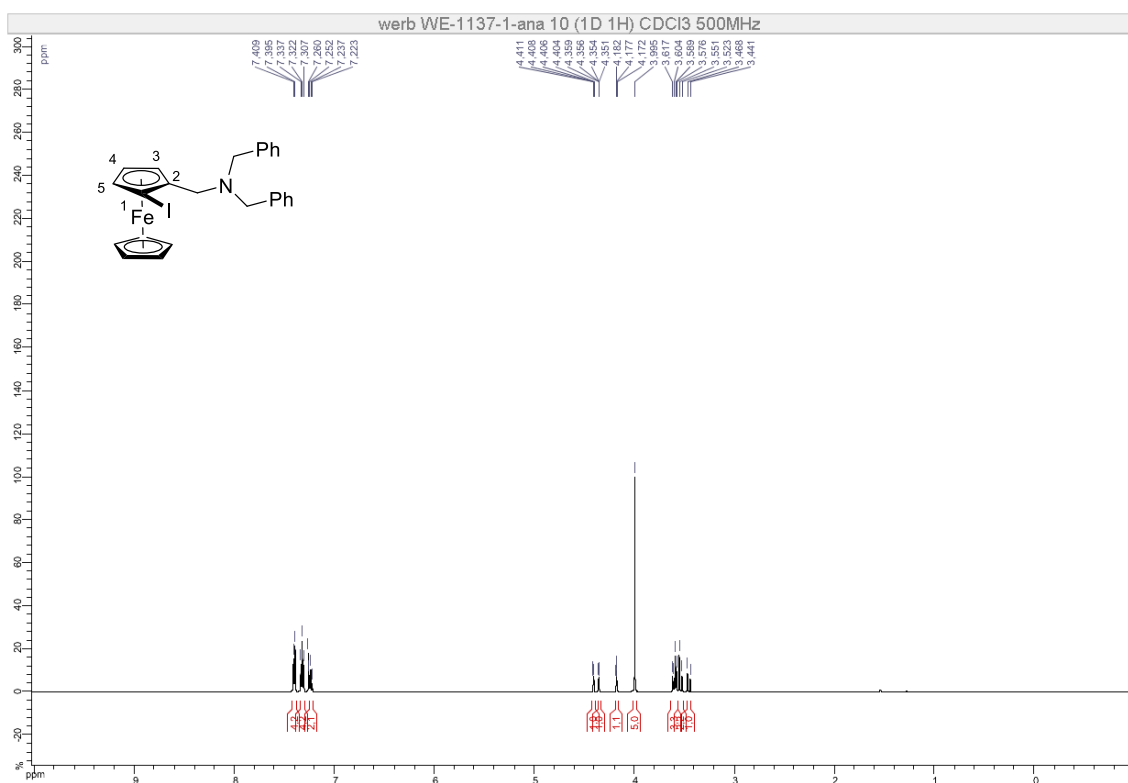


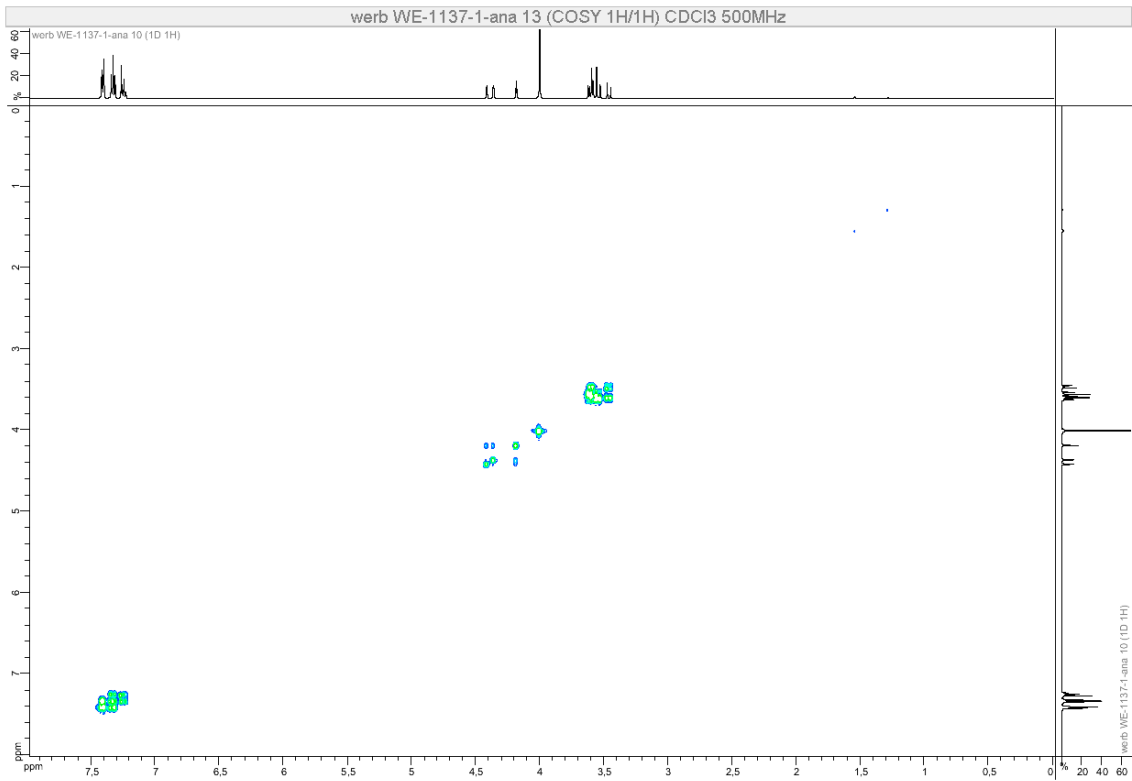
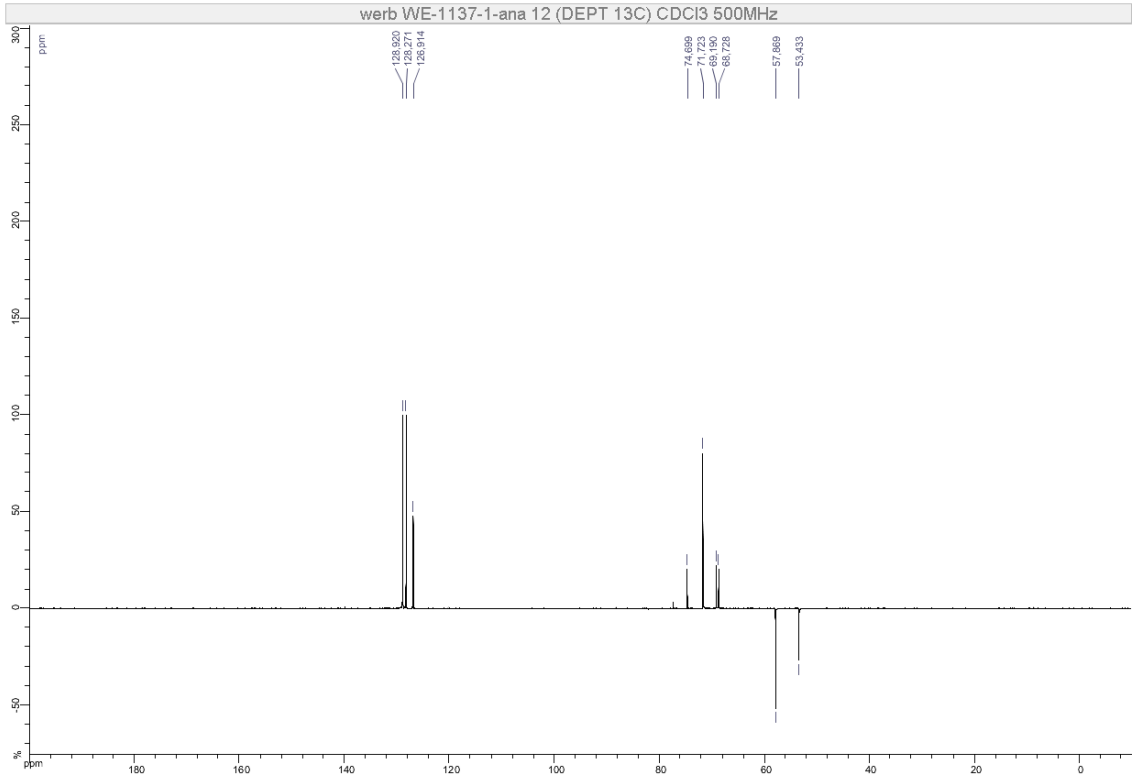


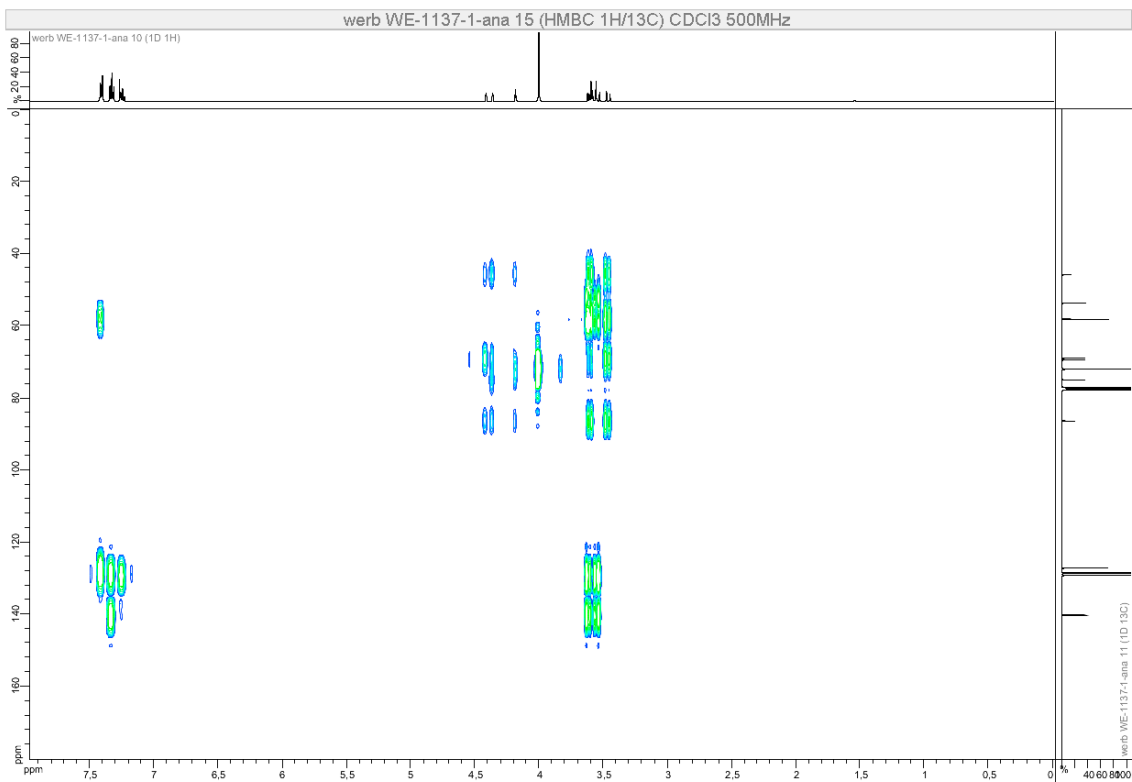
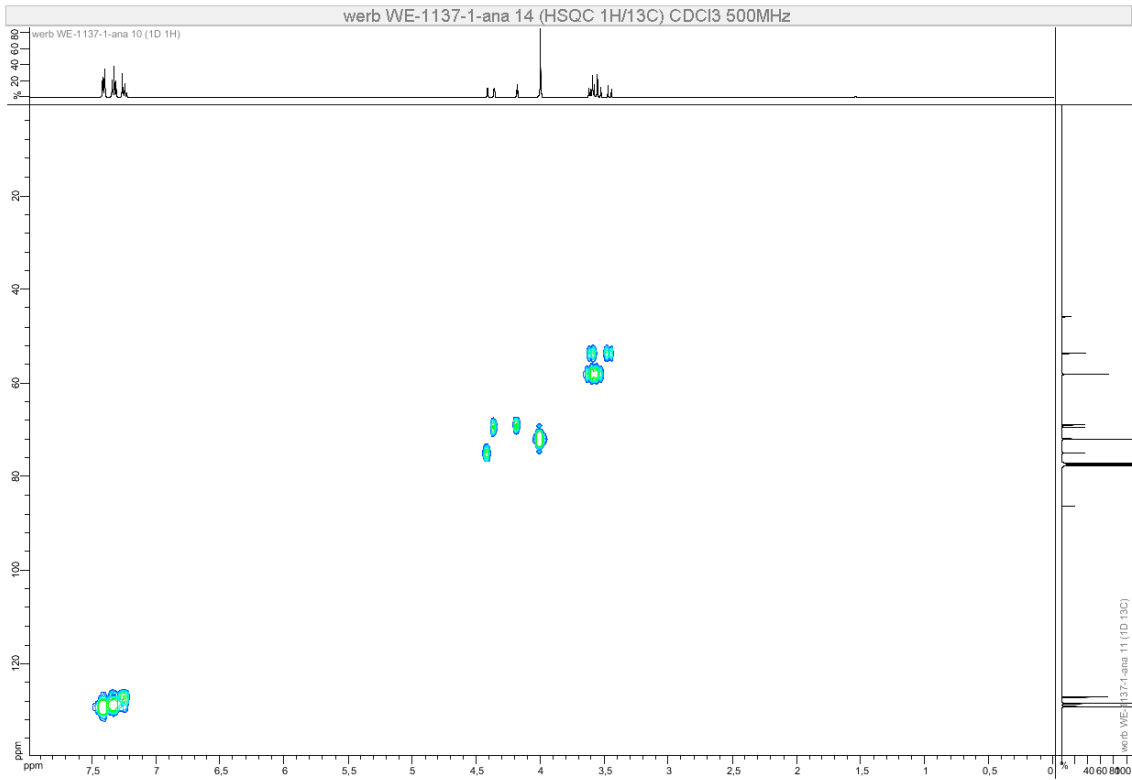


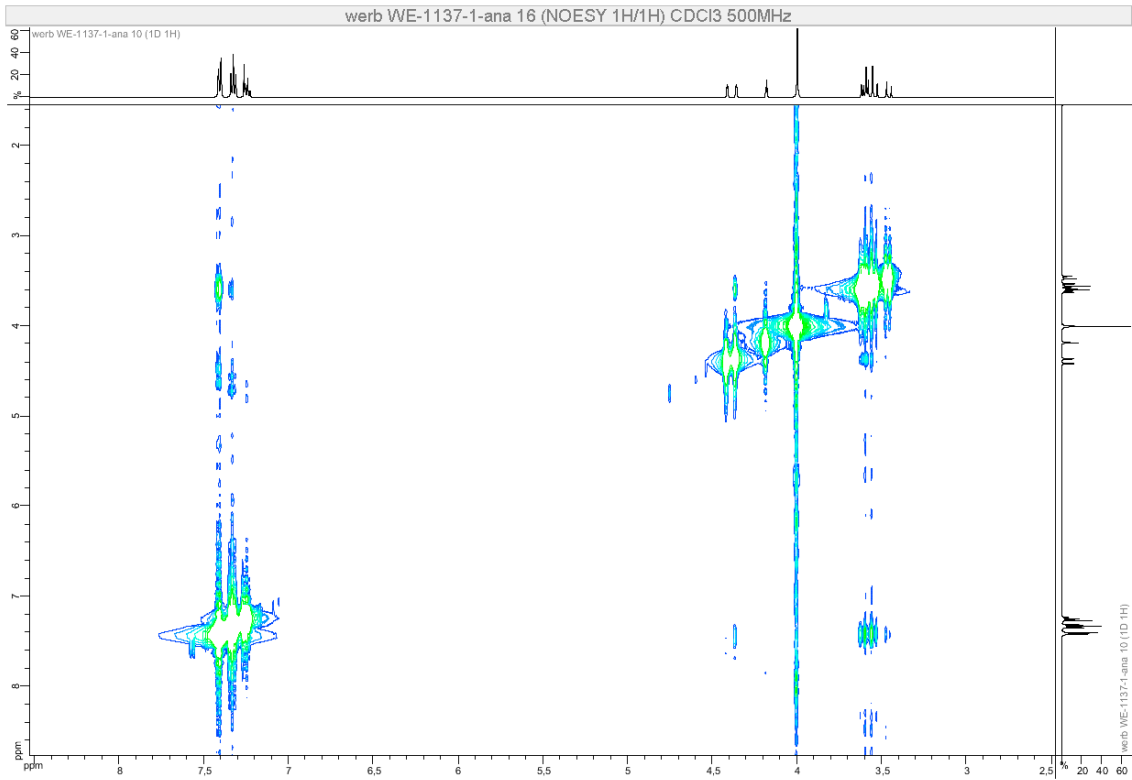


Compound (\pm)-4f

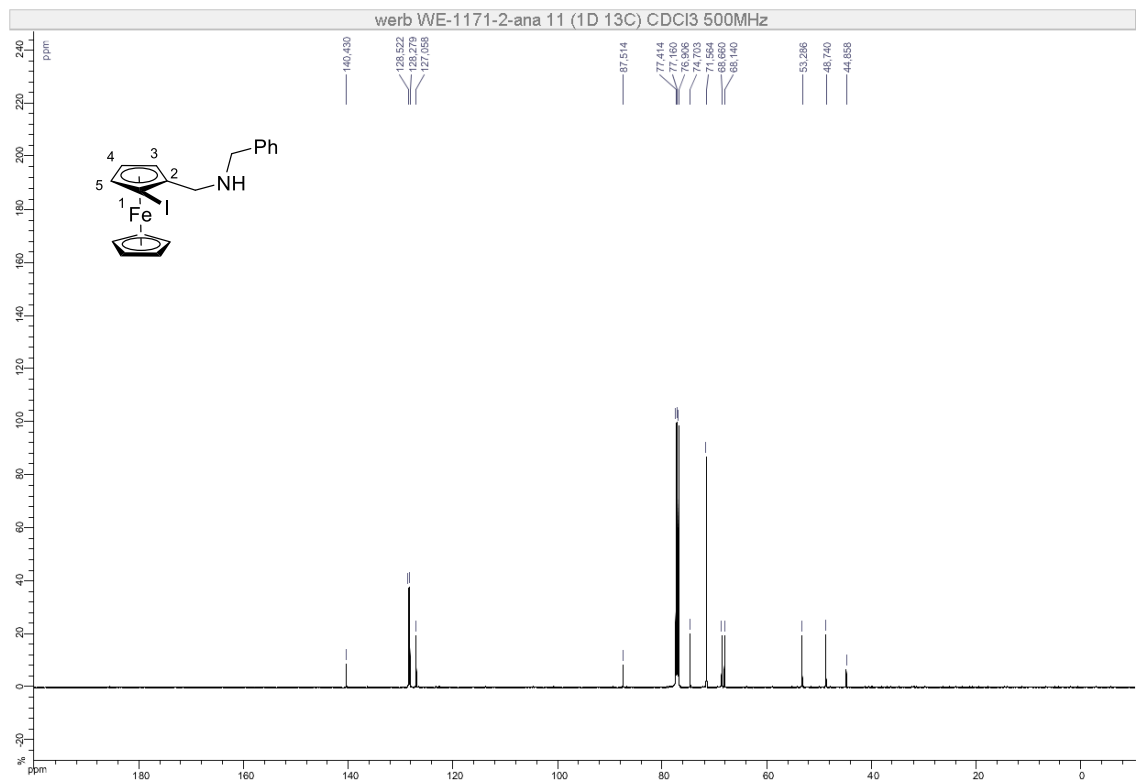
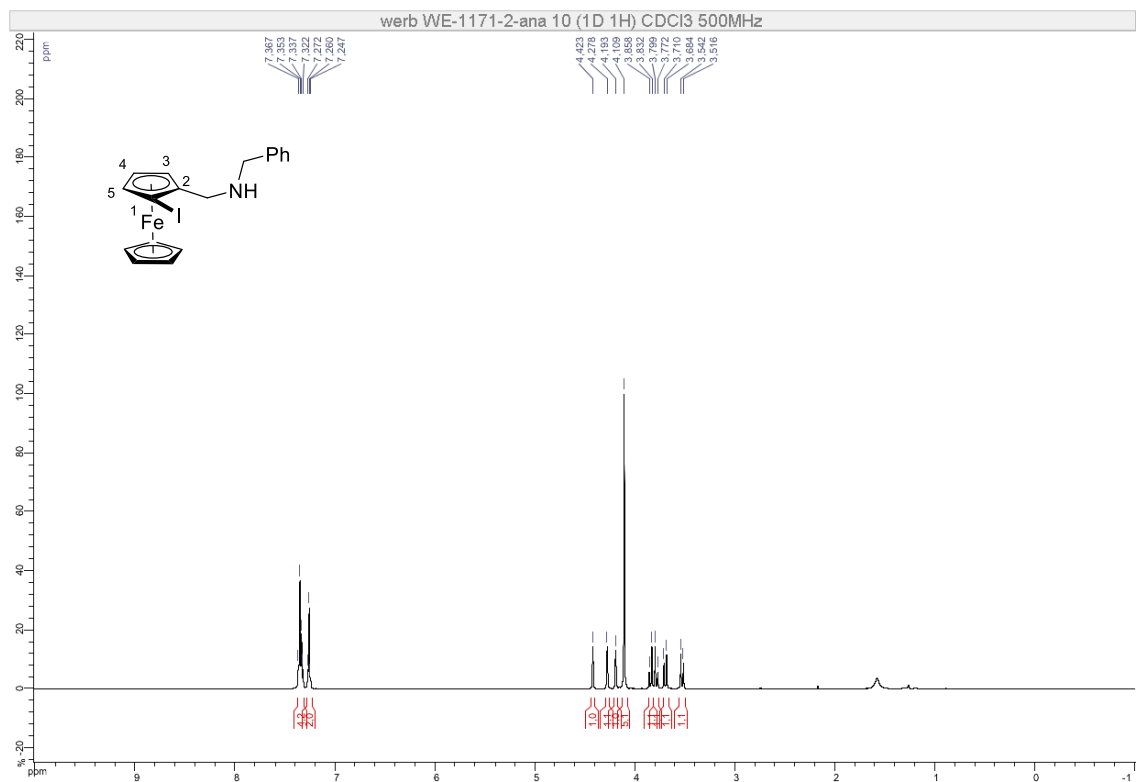


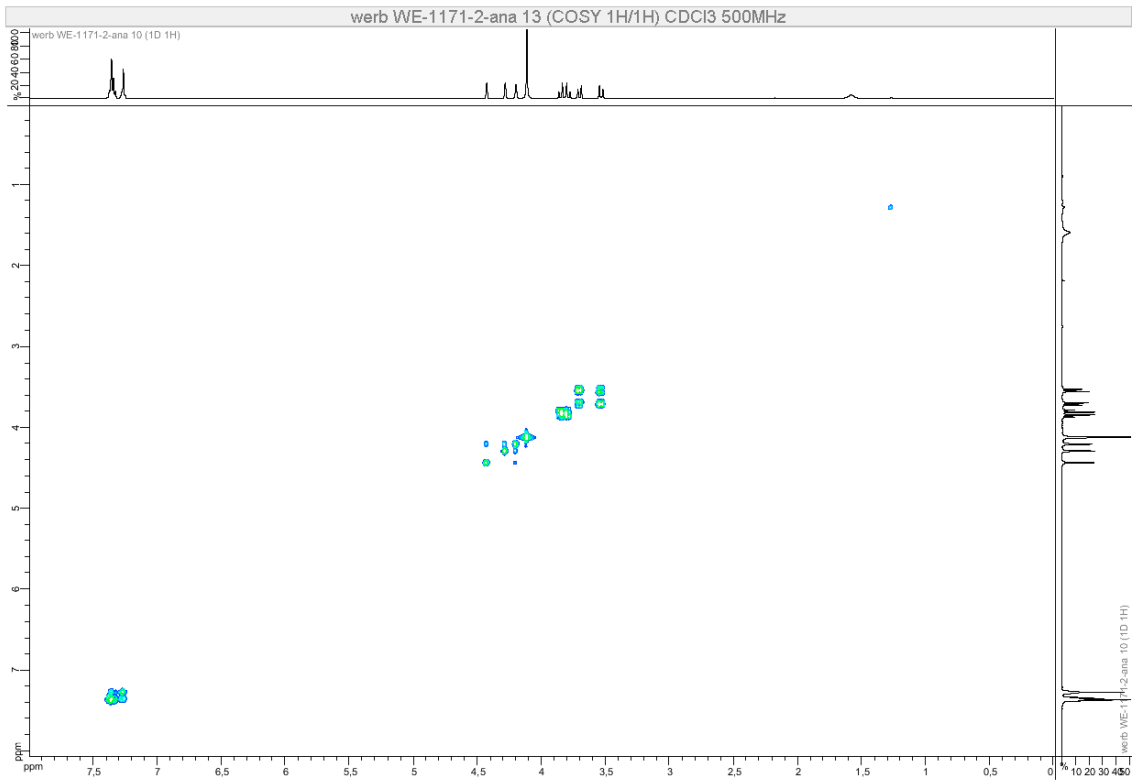
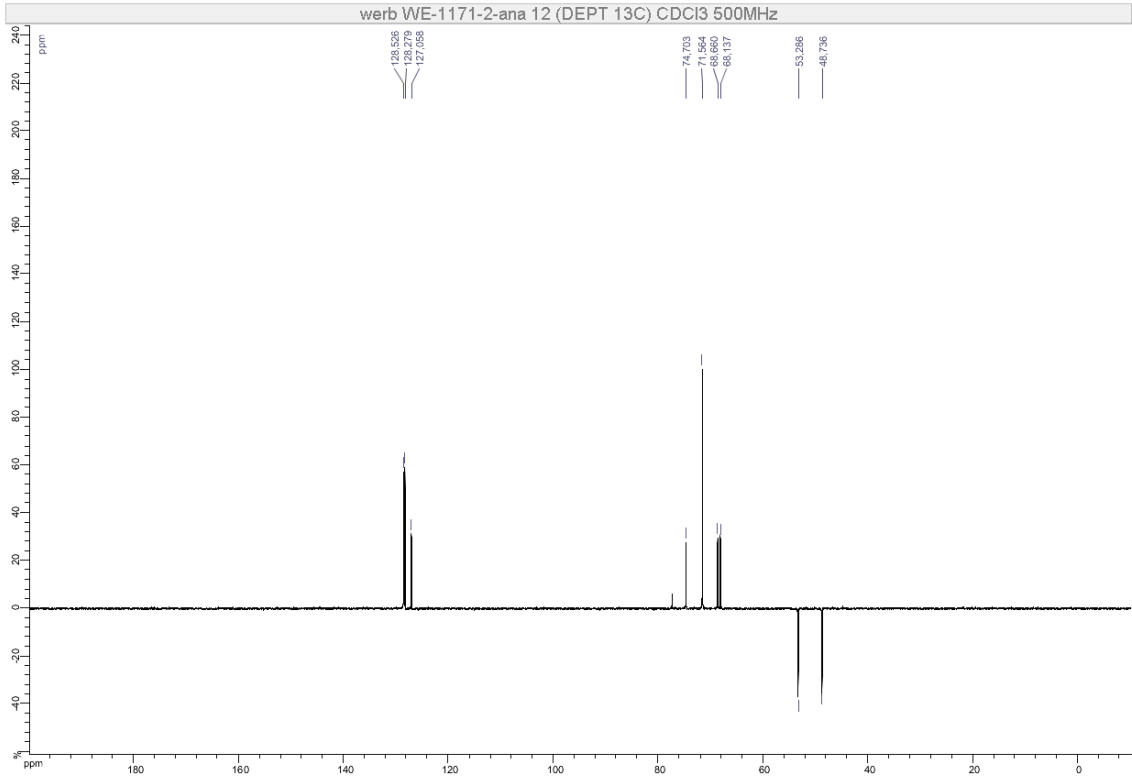


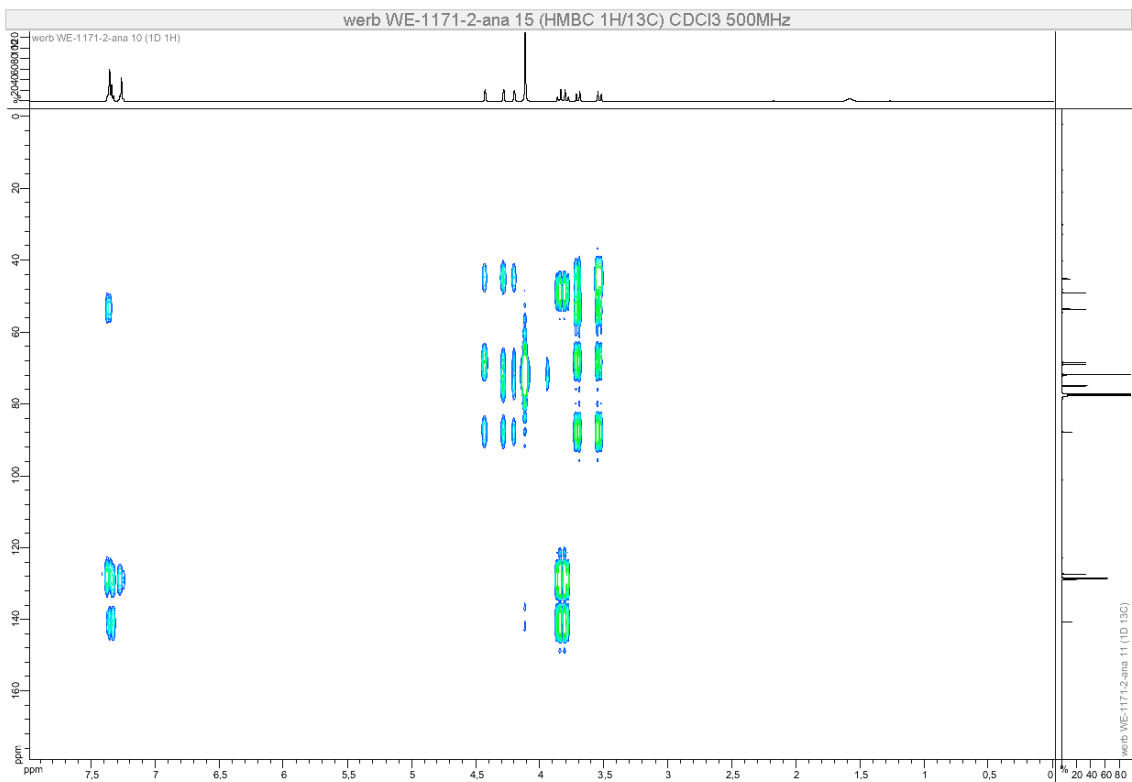
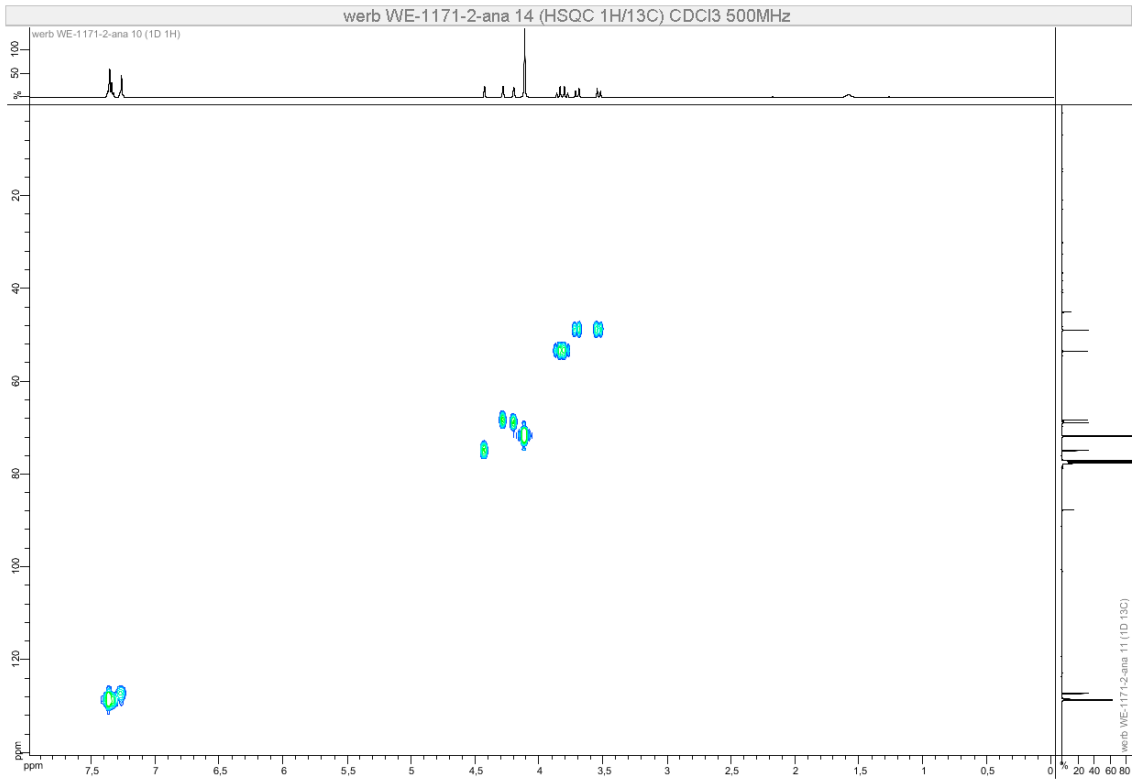




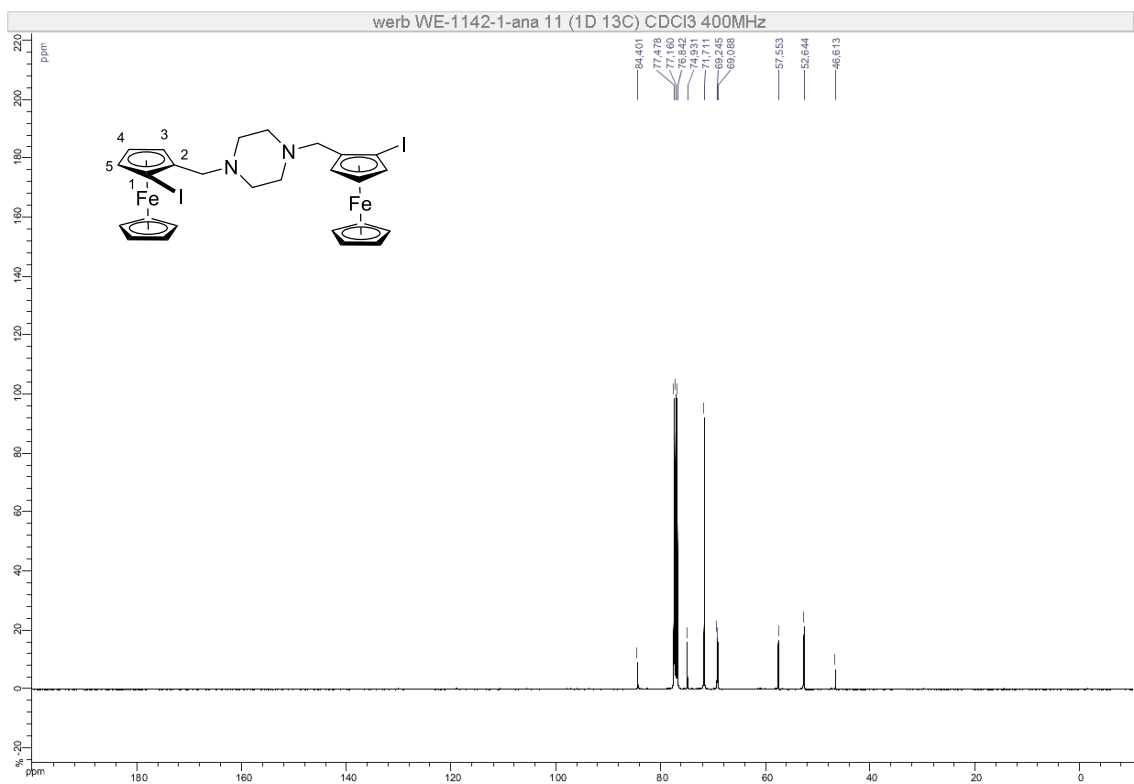
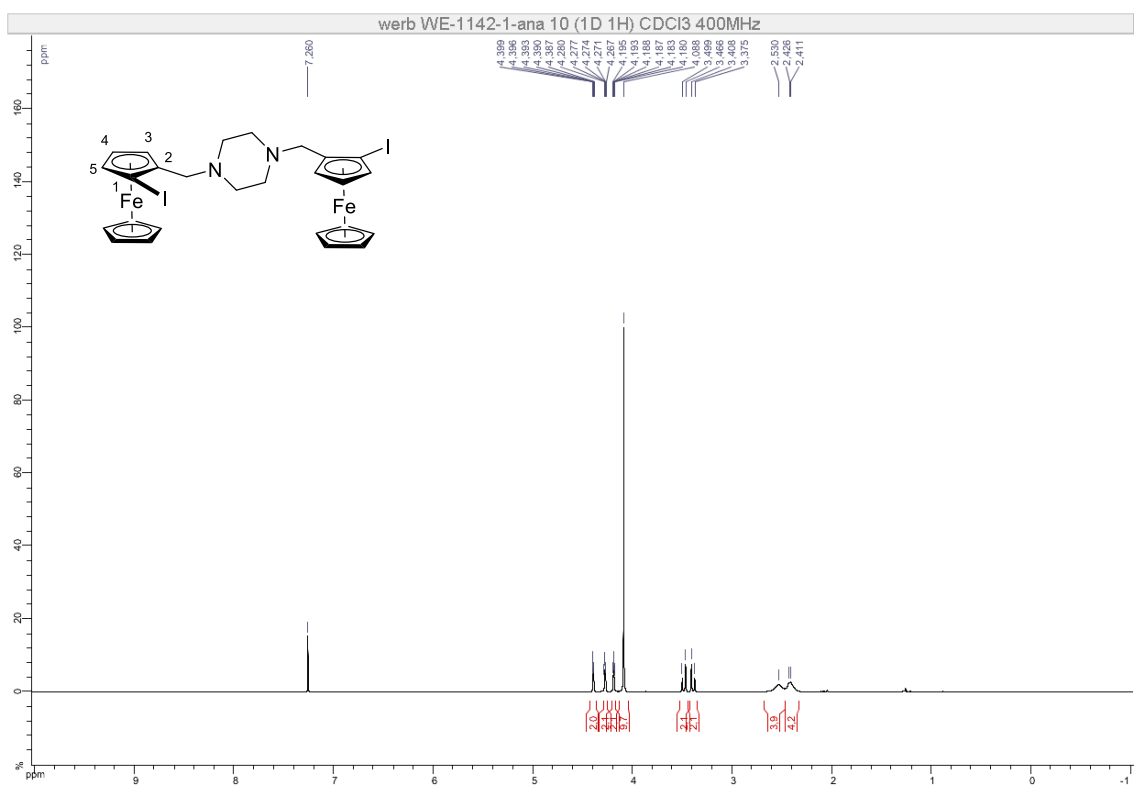
Compound (\pm)-4g

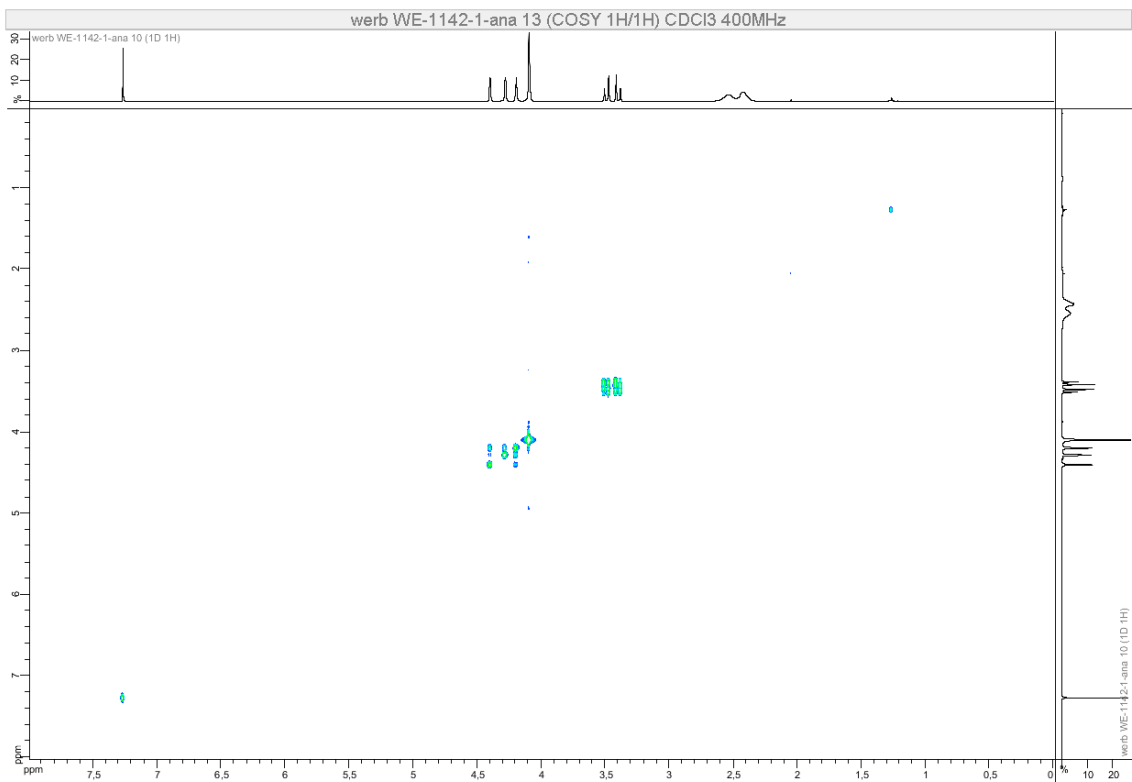
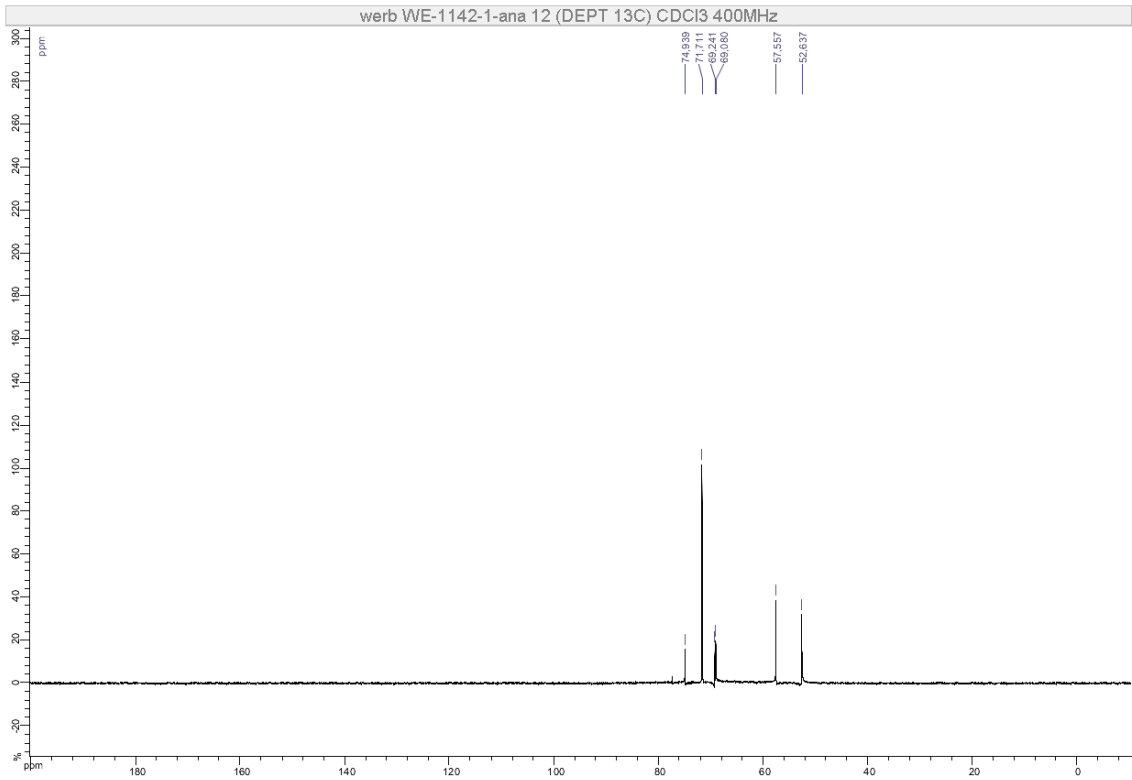


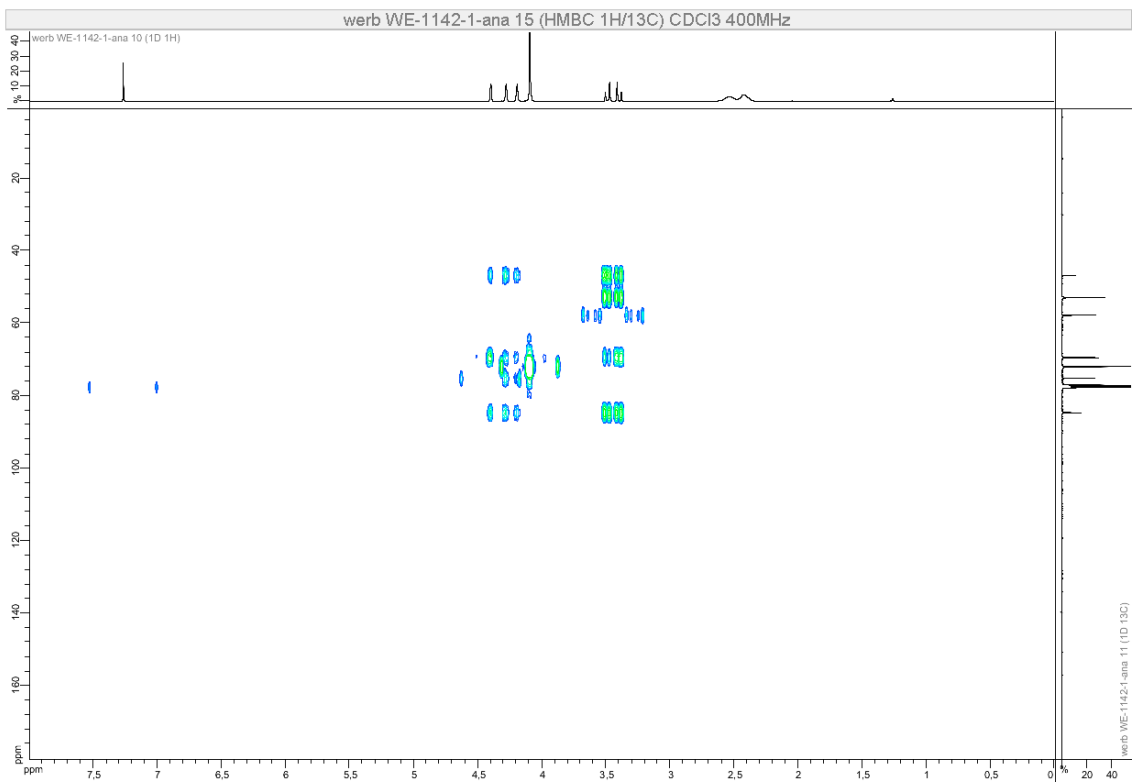
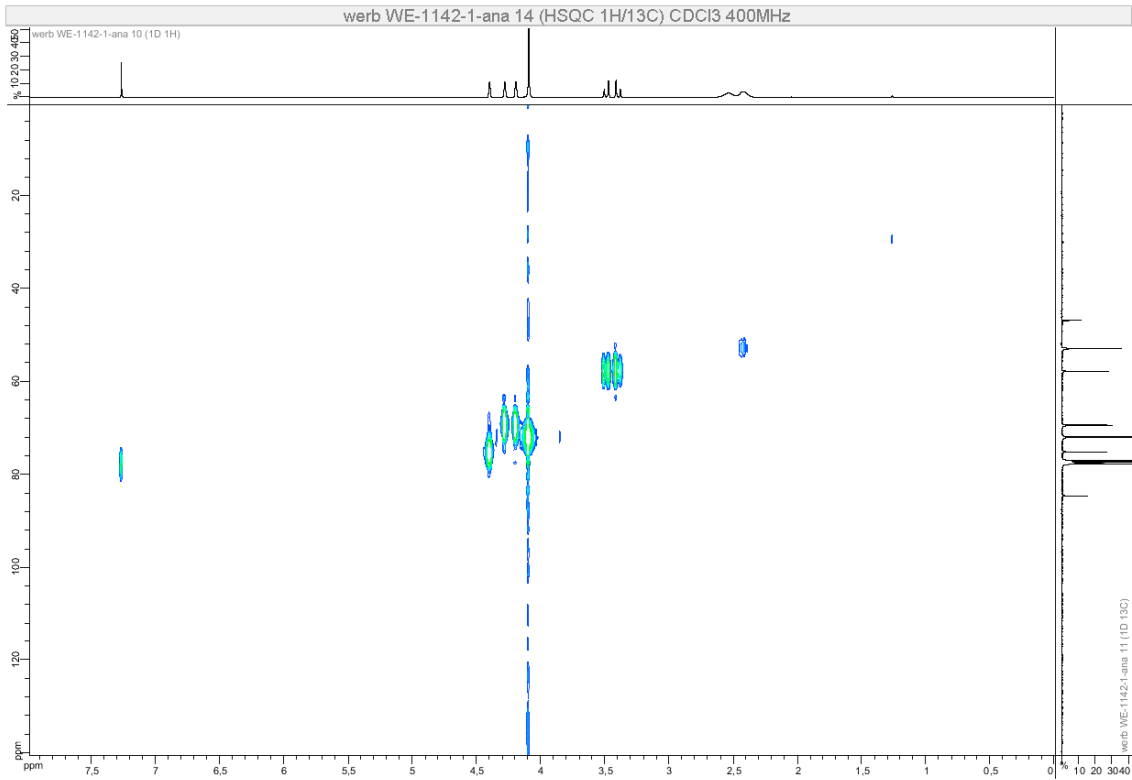




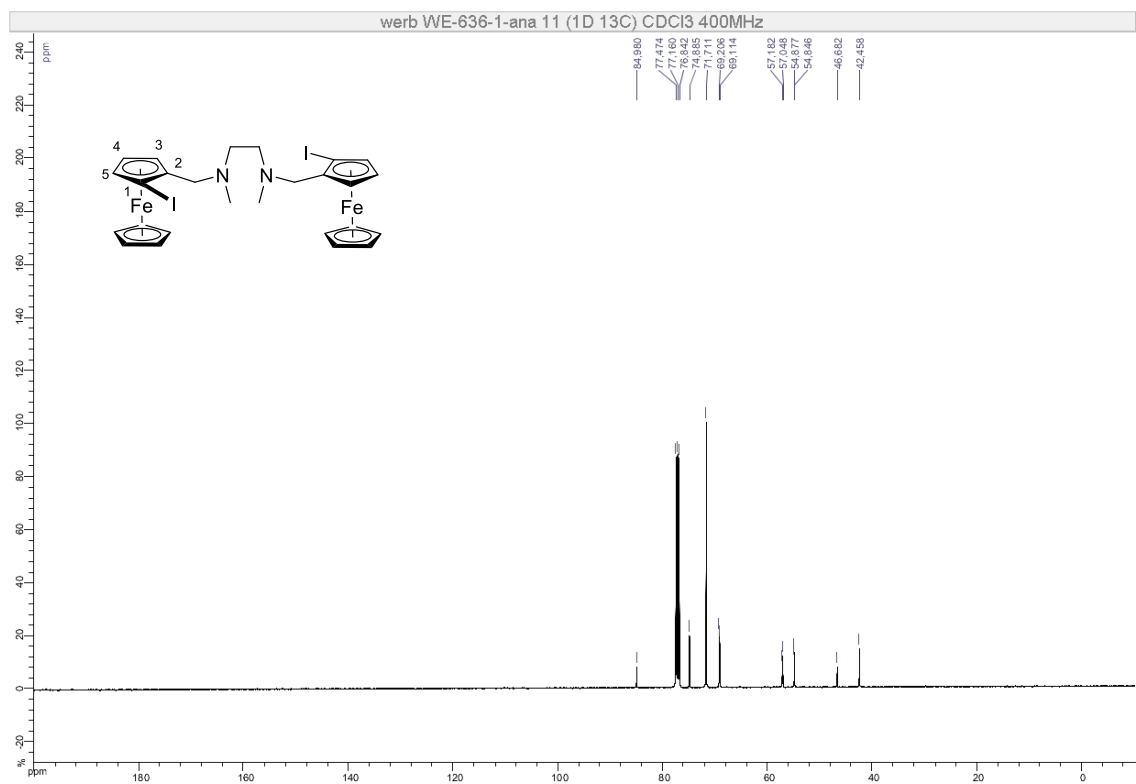
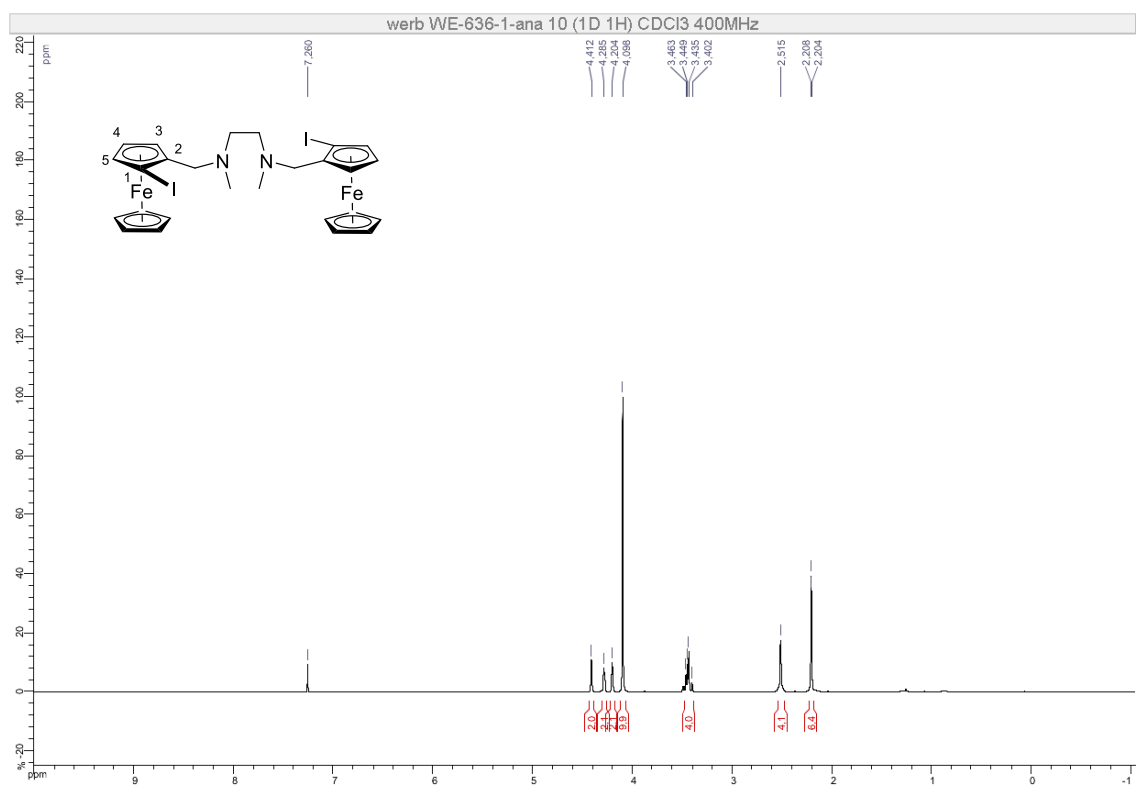
Compound 4h

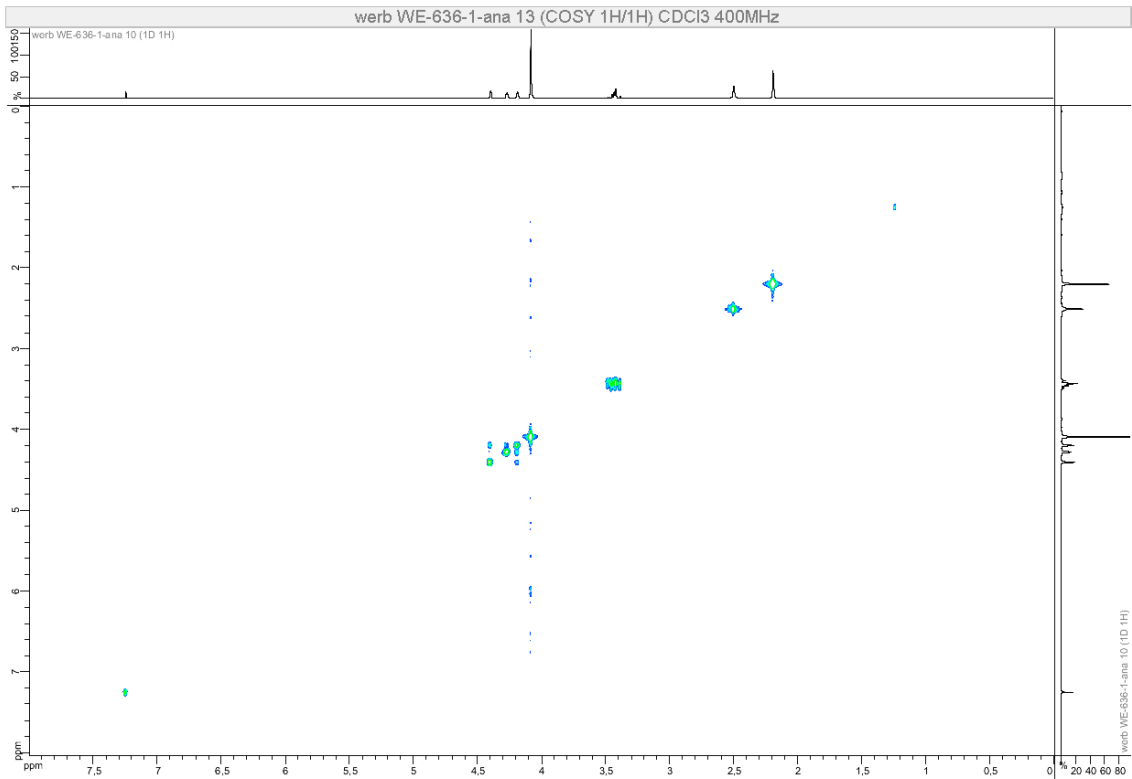
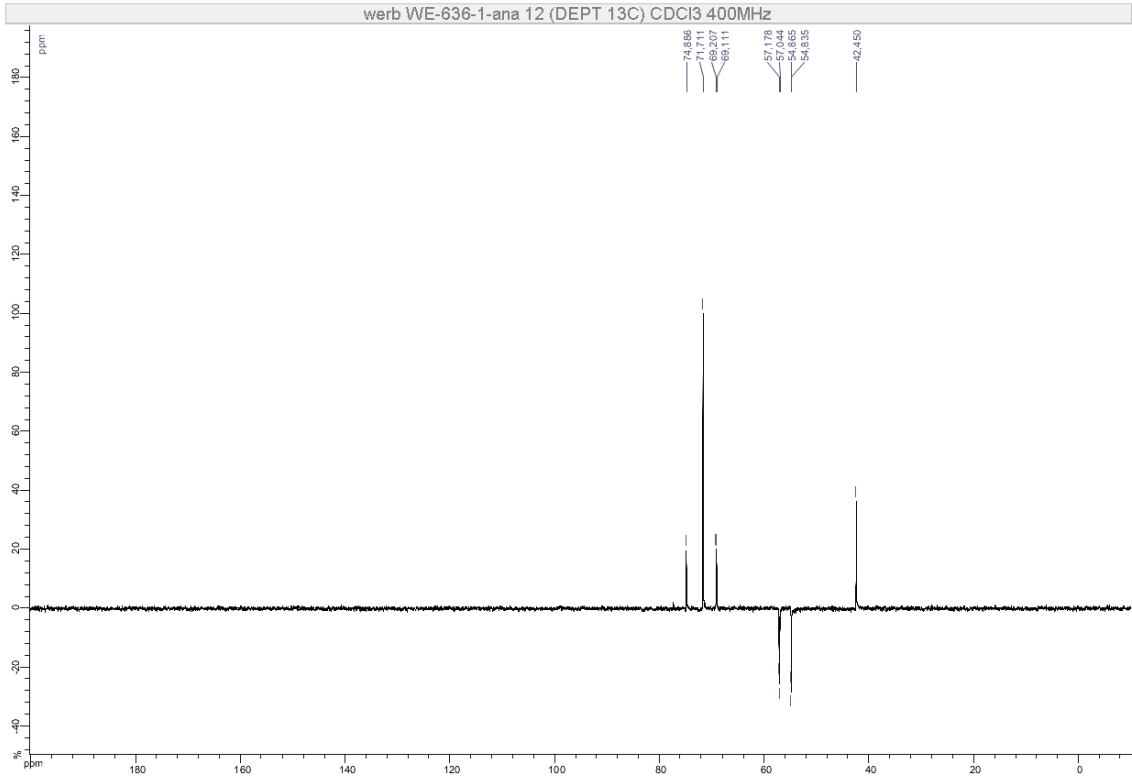


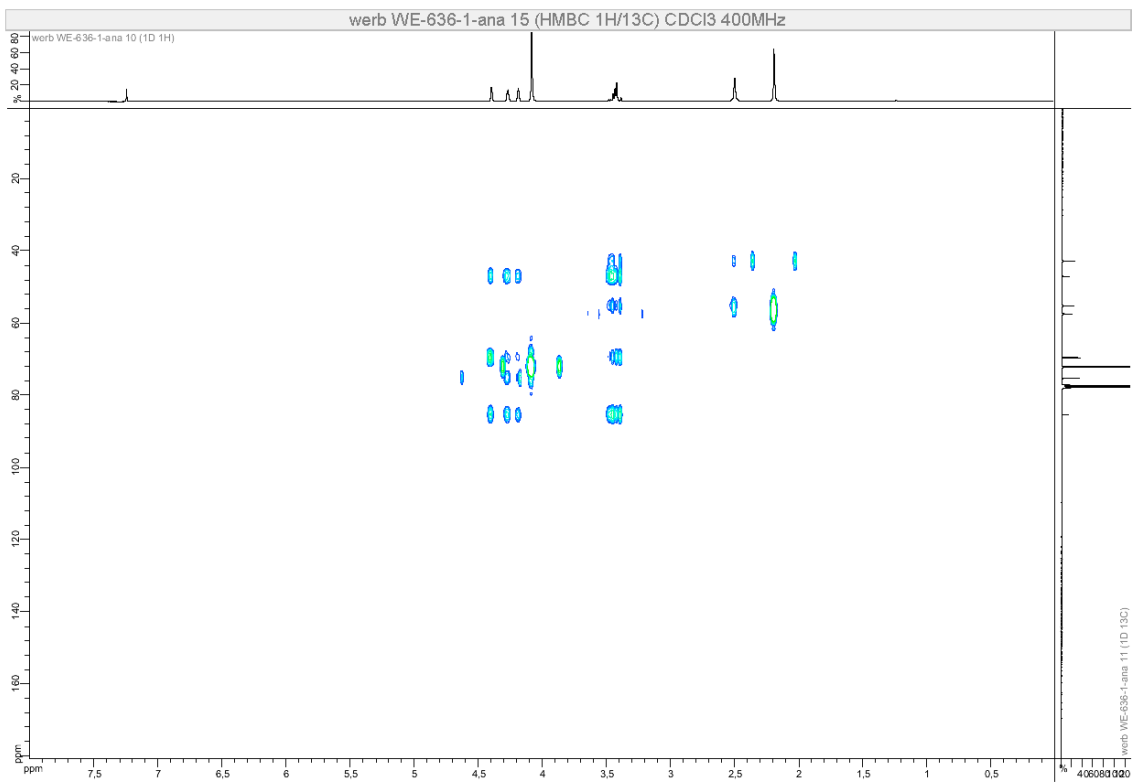
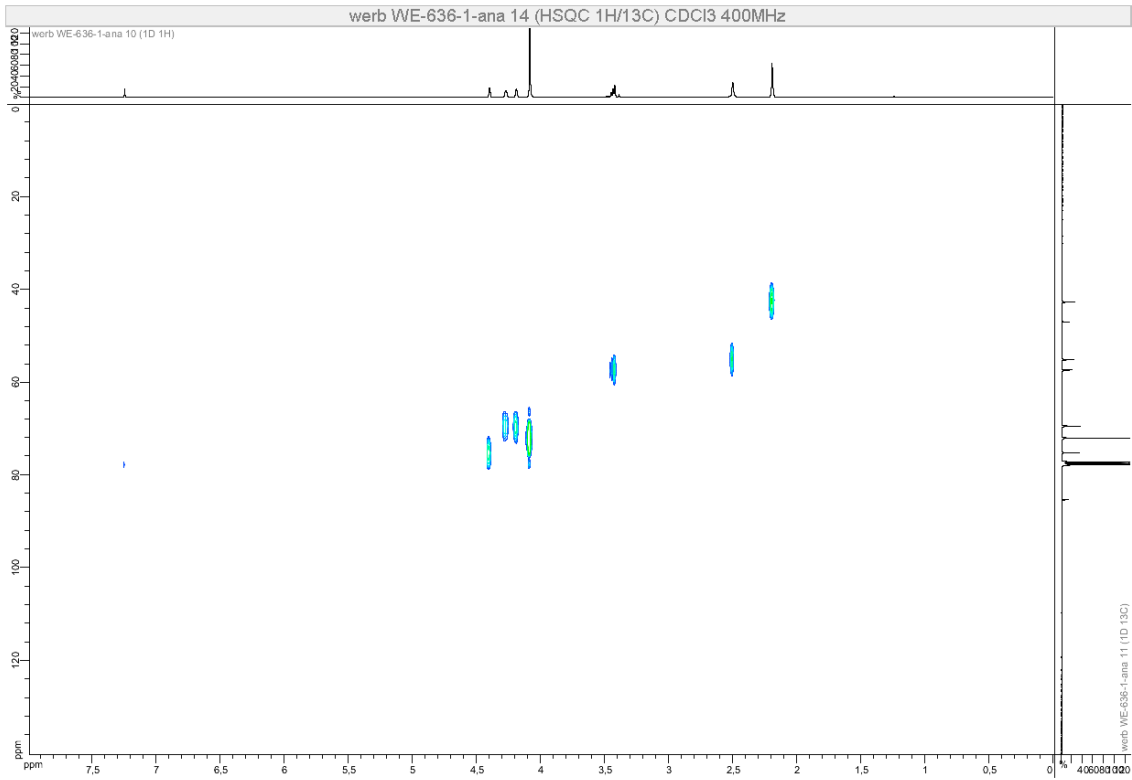




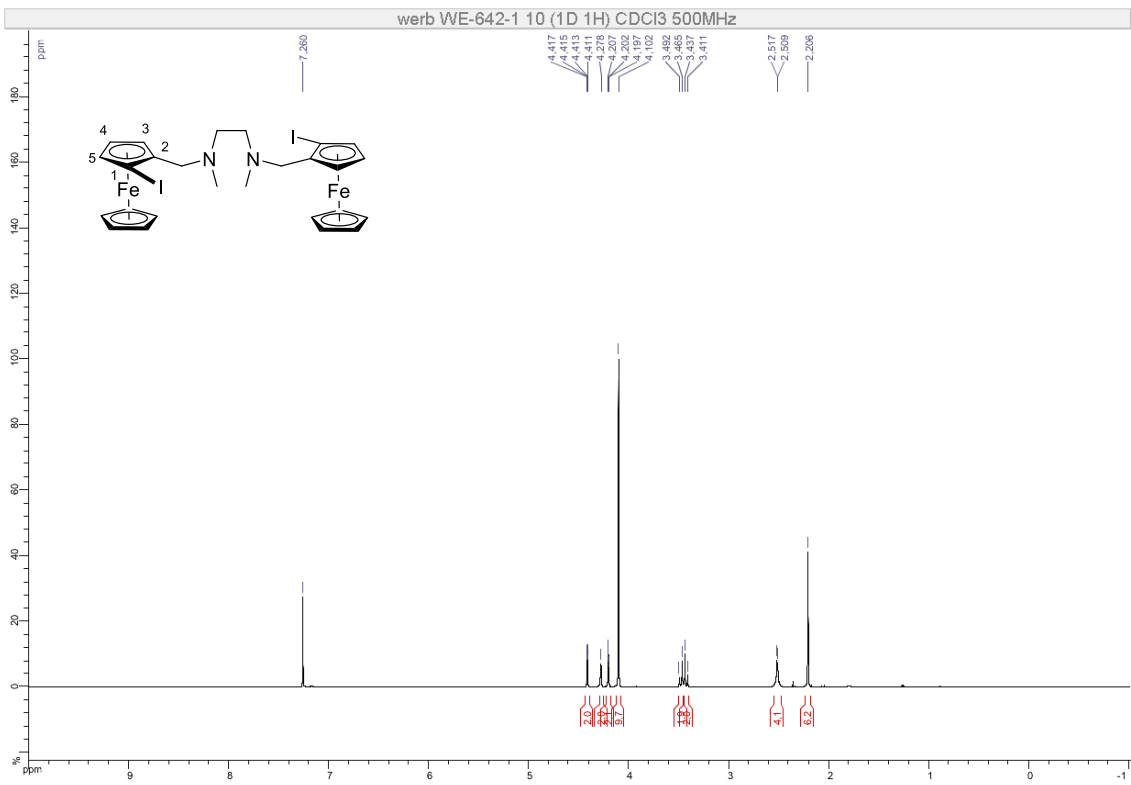
Compound 4i



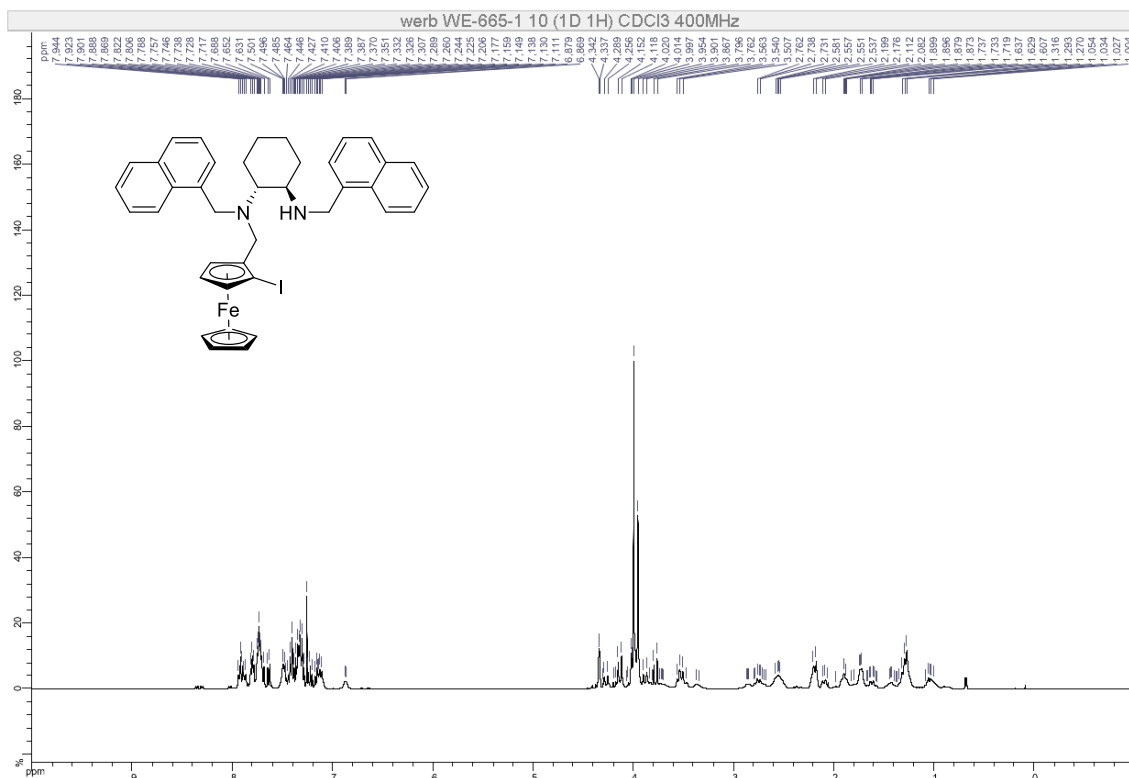




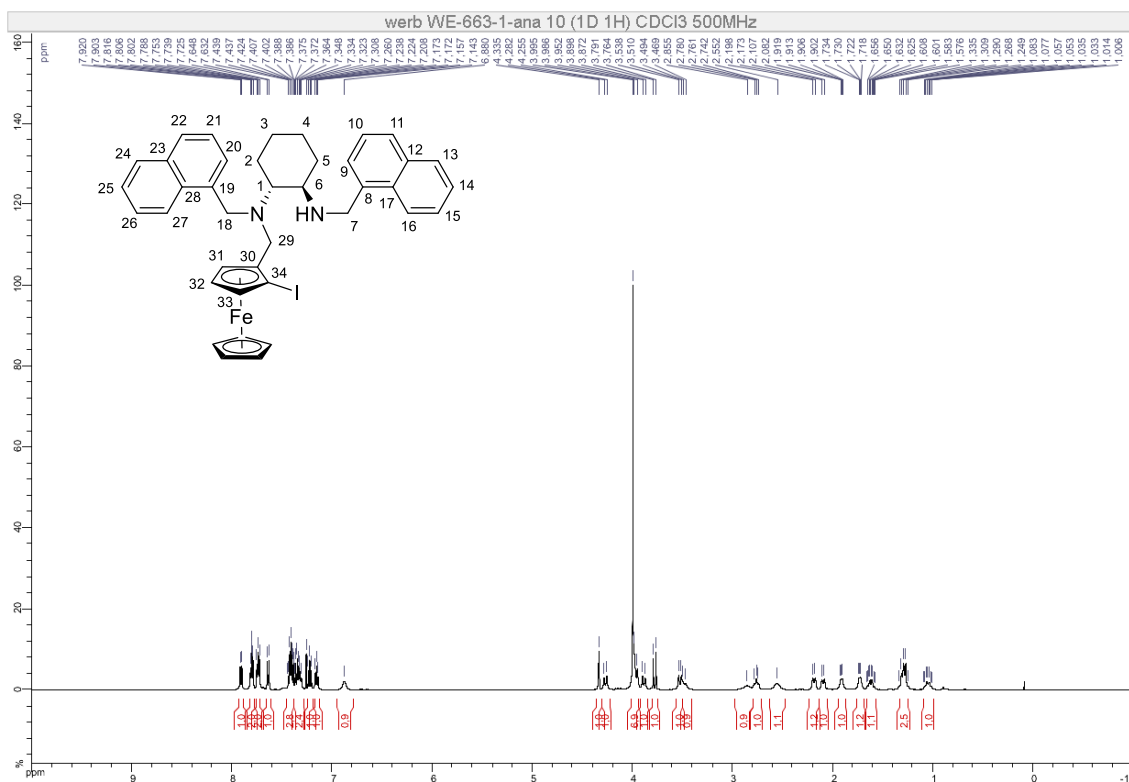
Compound (*S_p*,*S_p*)-4i

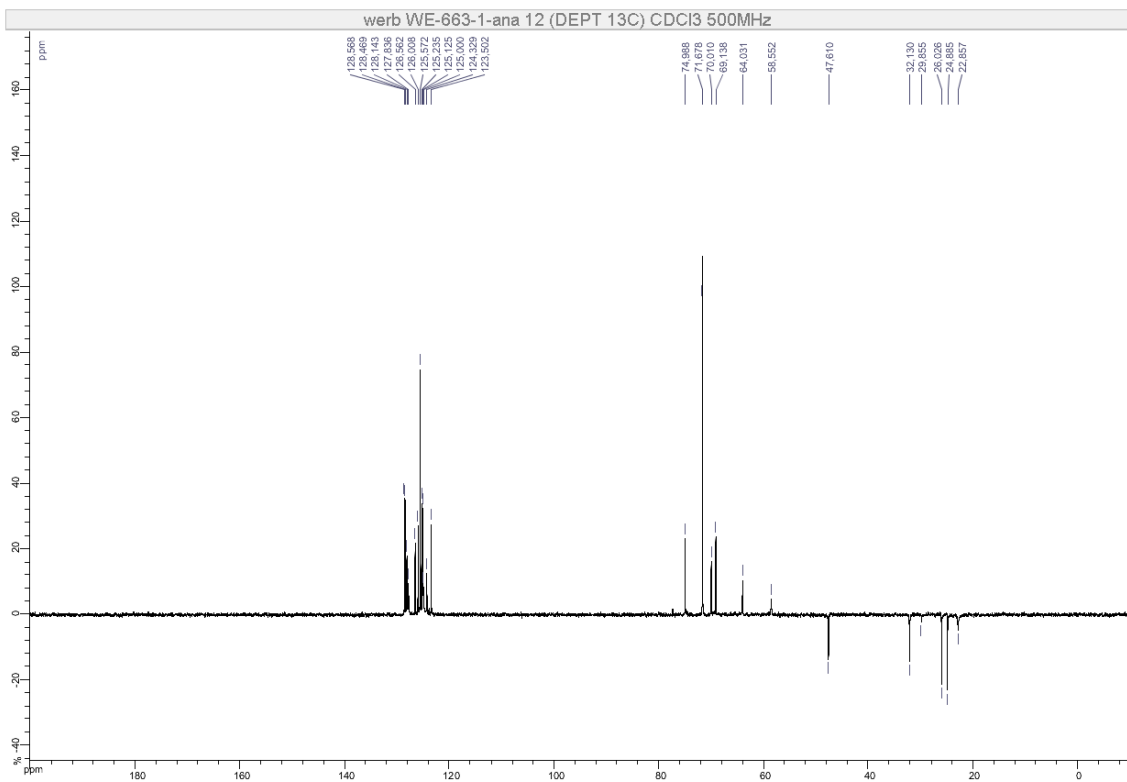
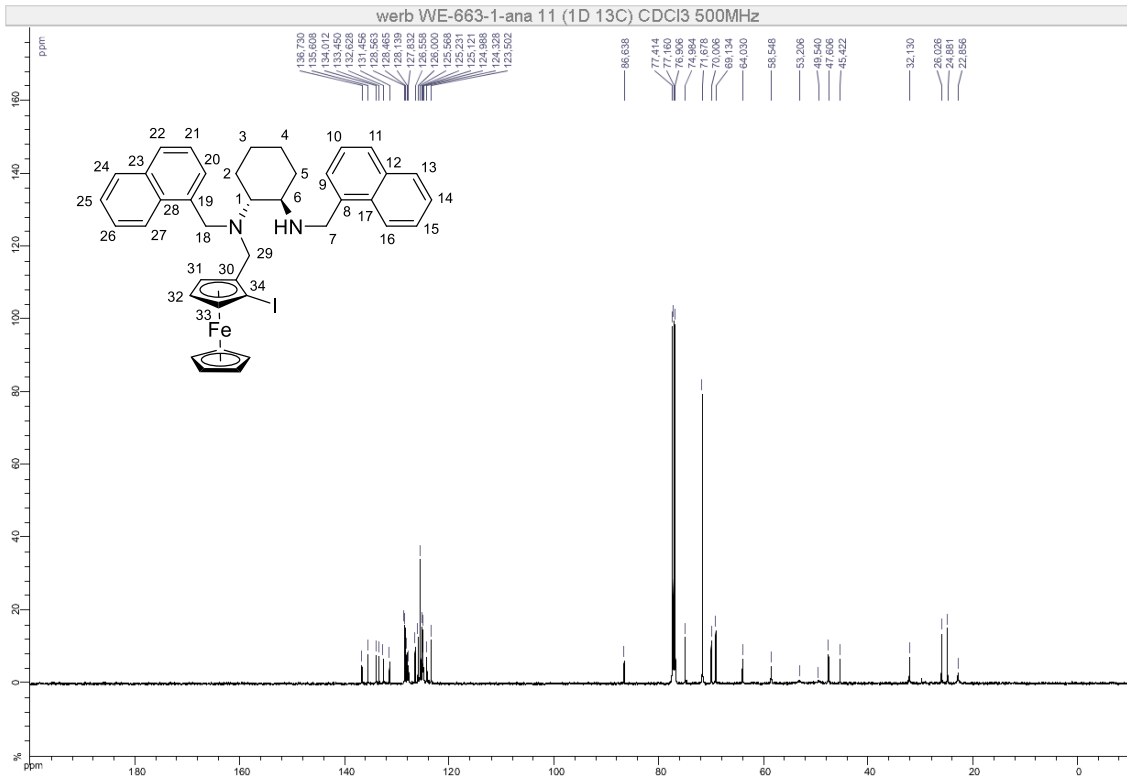


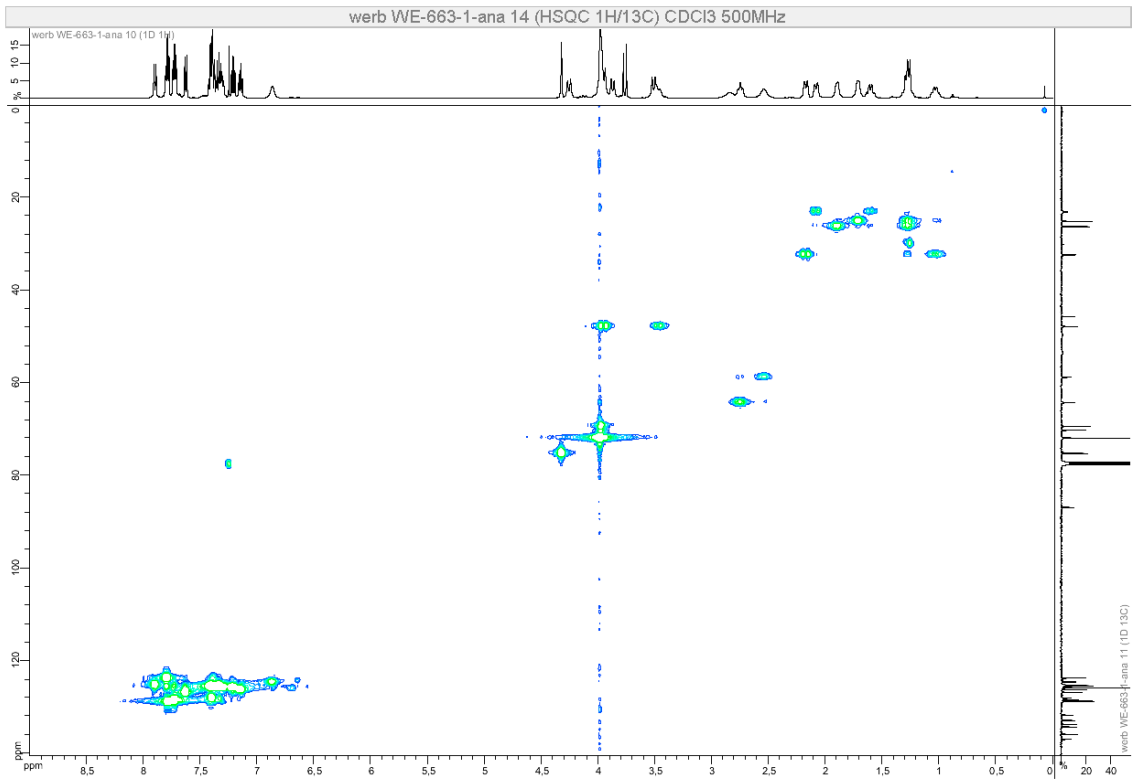
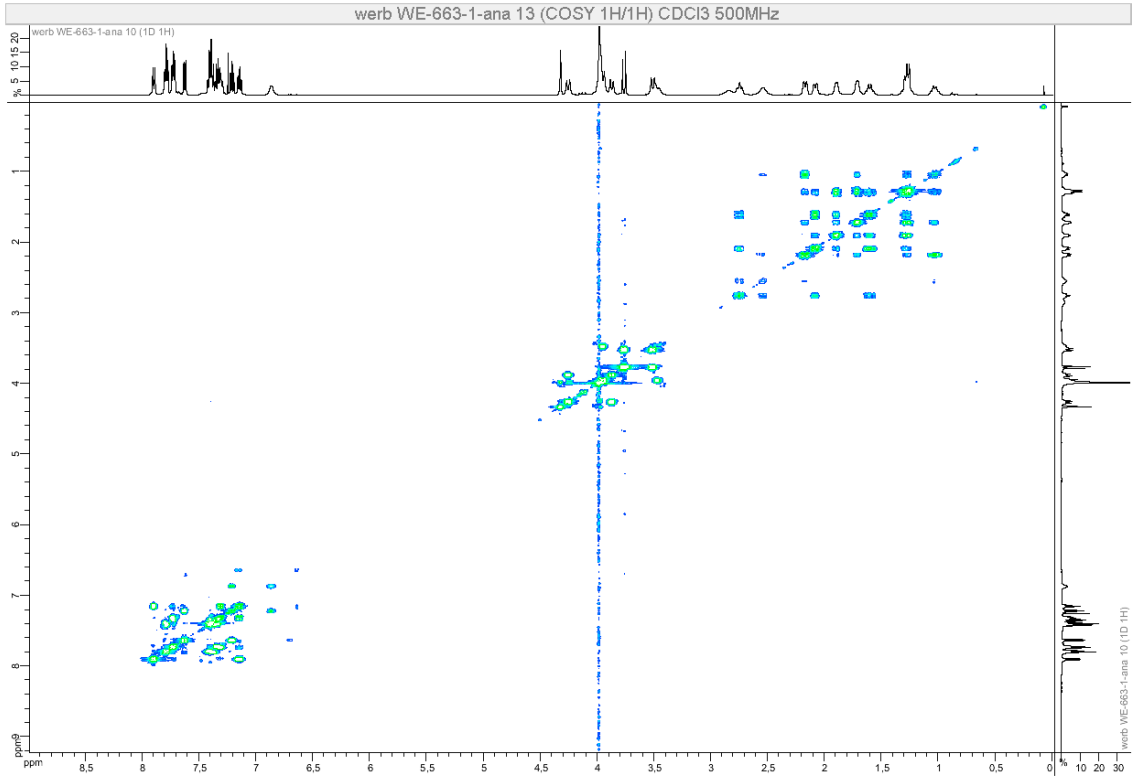
Compound 4j

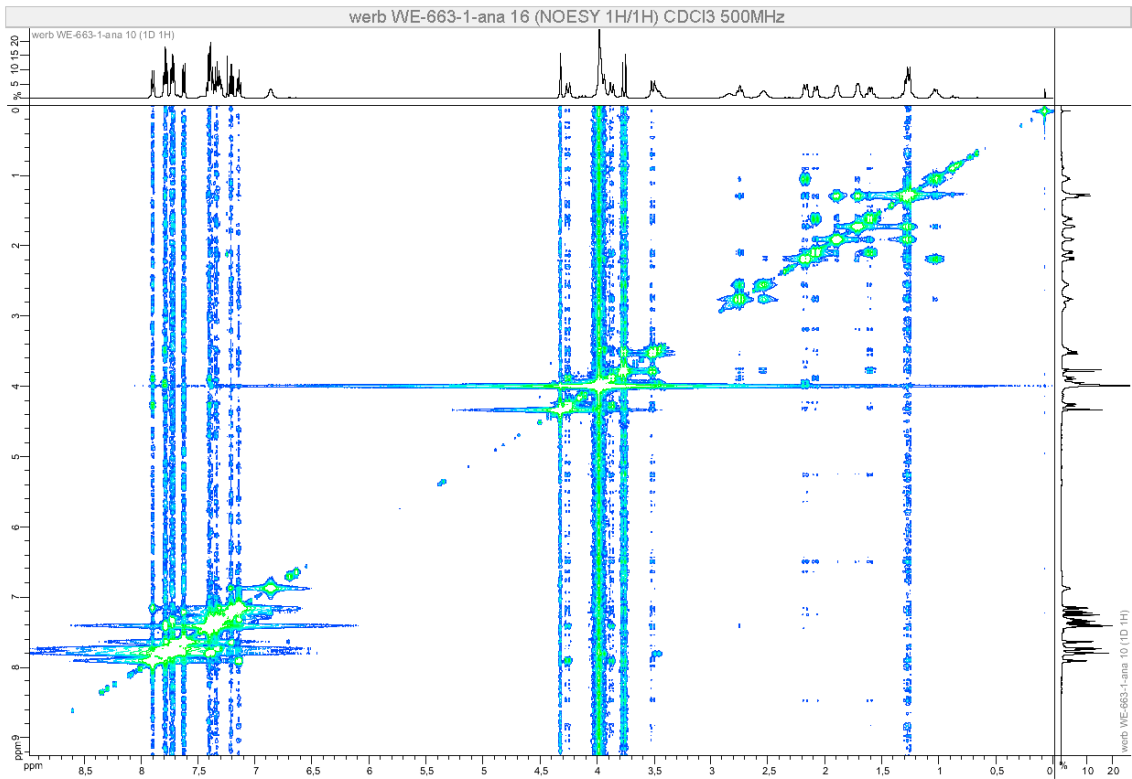
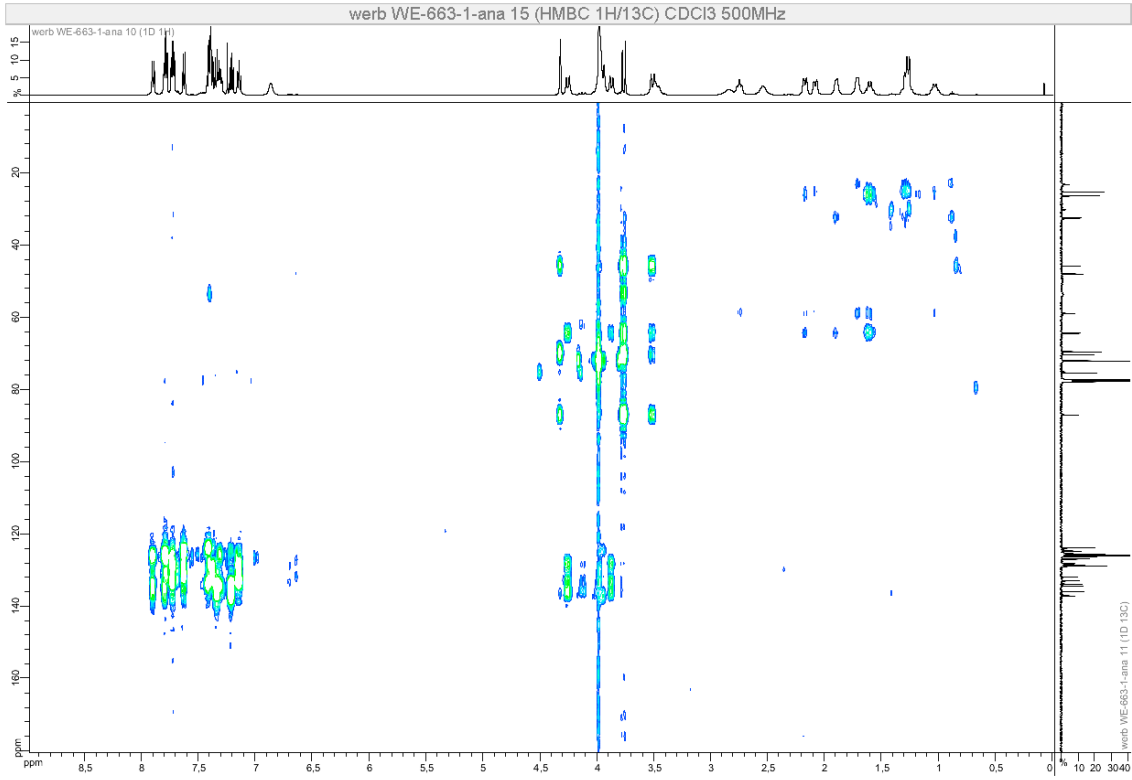


Compound (R,R,S_D)-4j

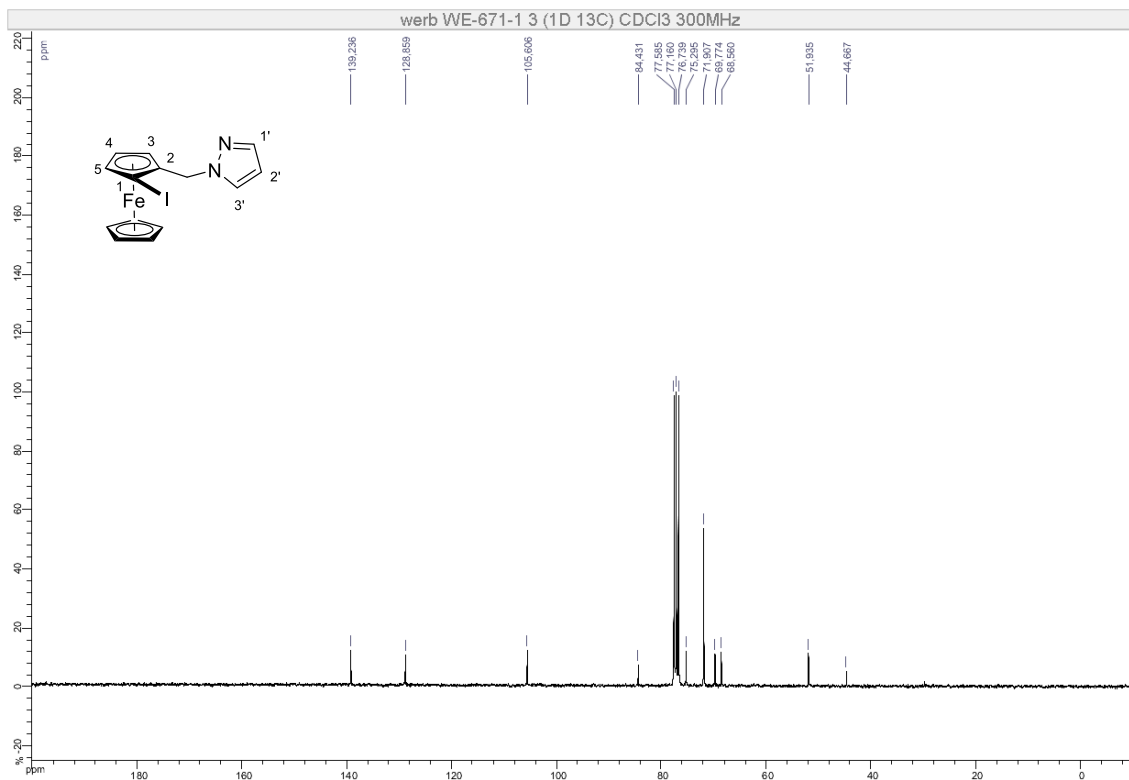
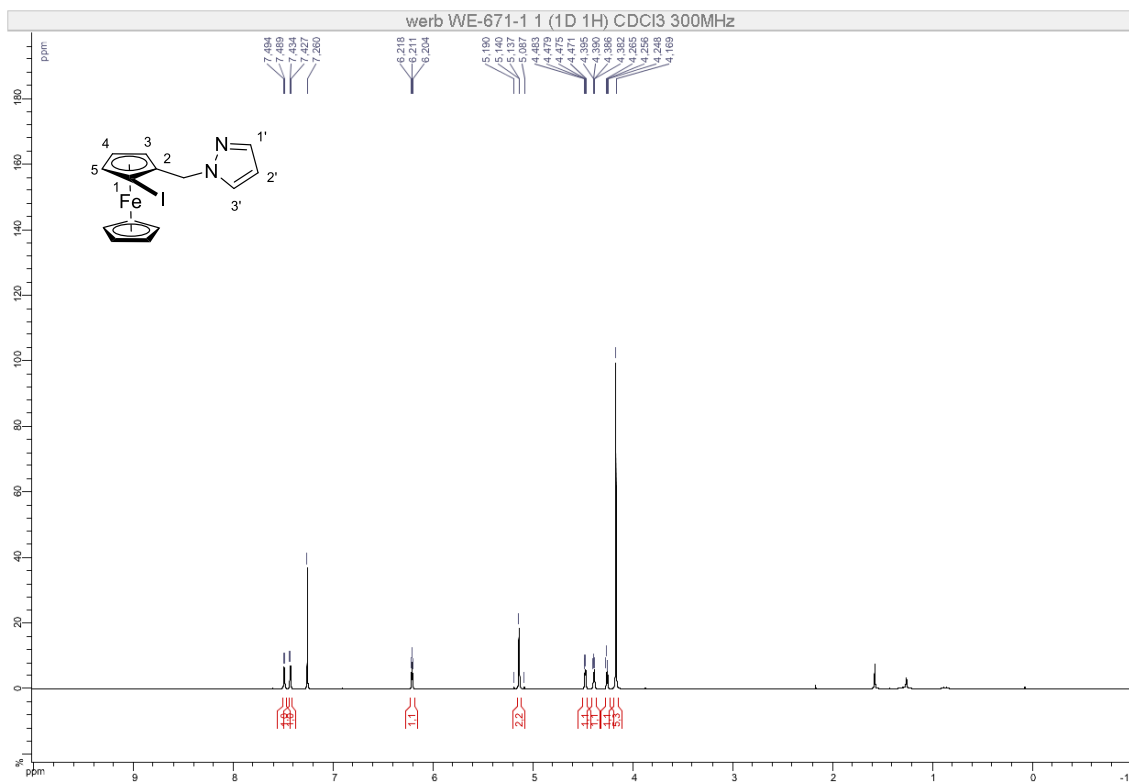


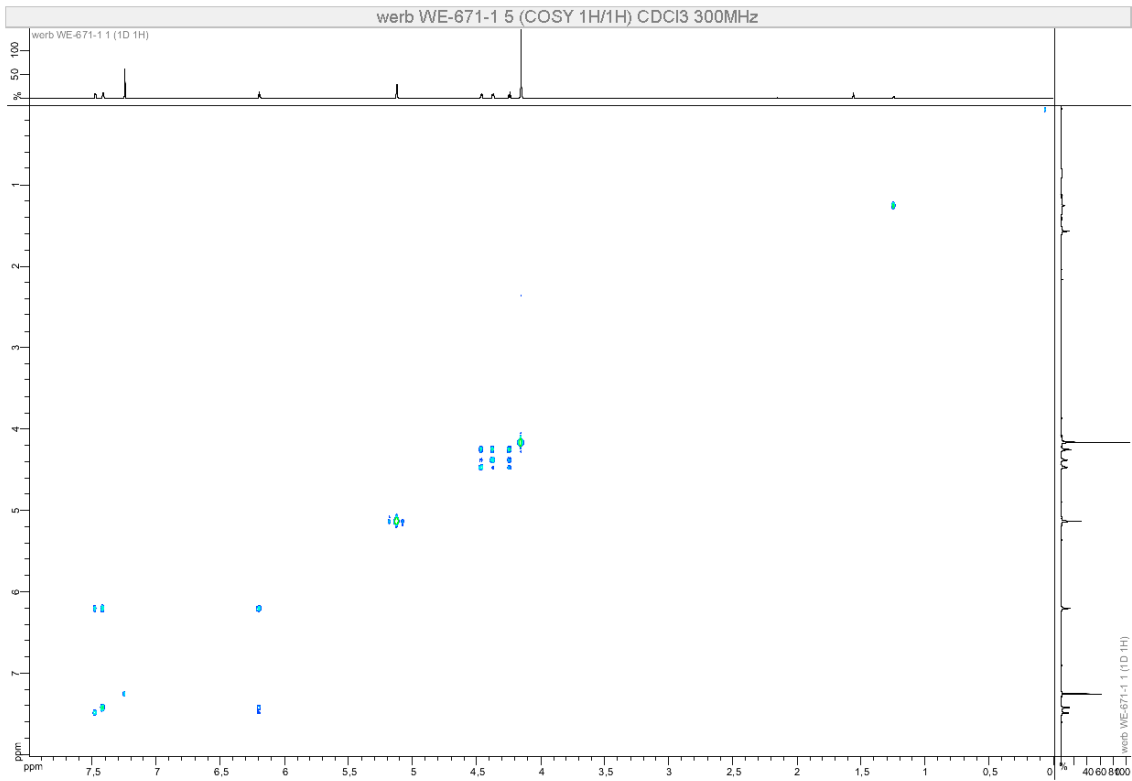
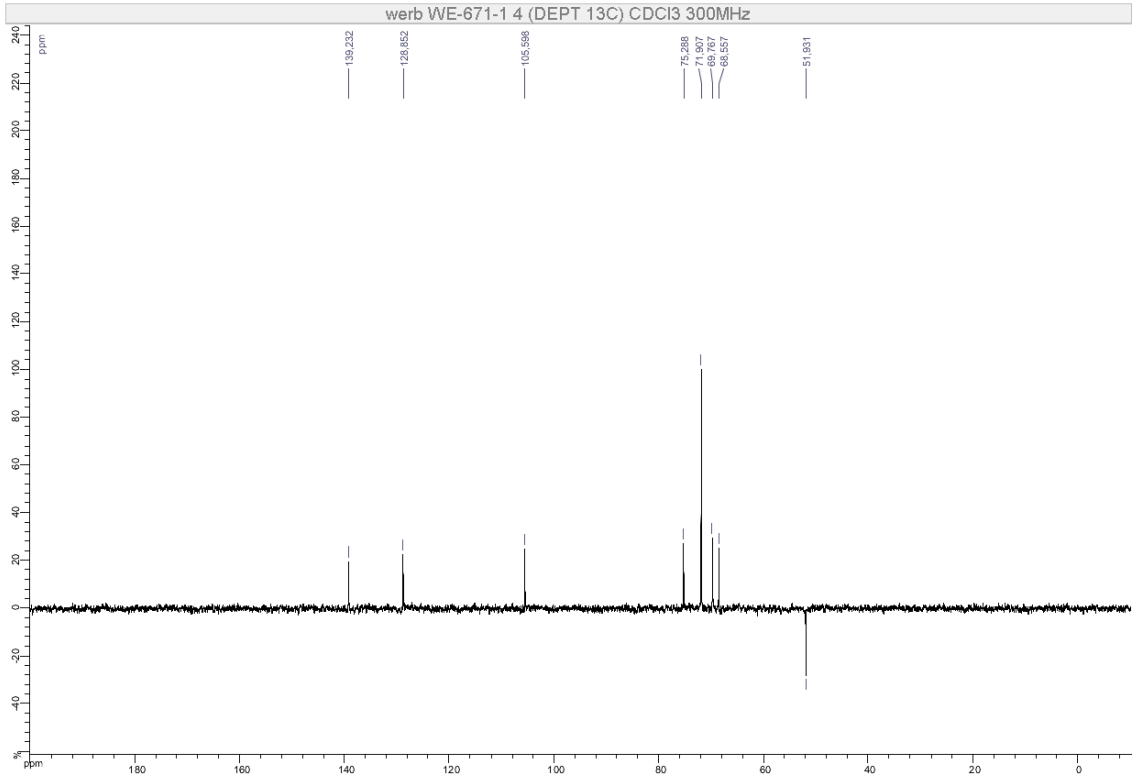


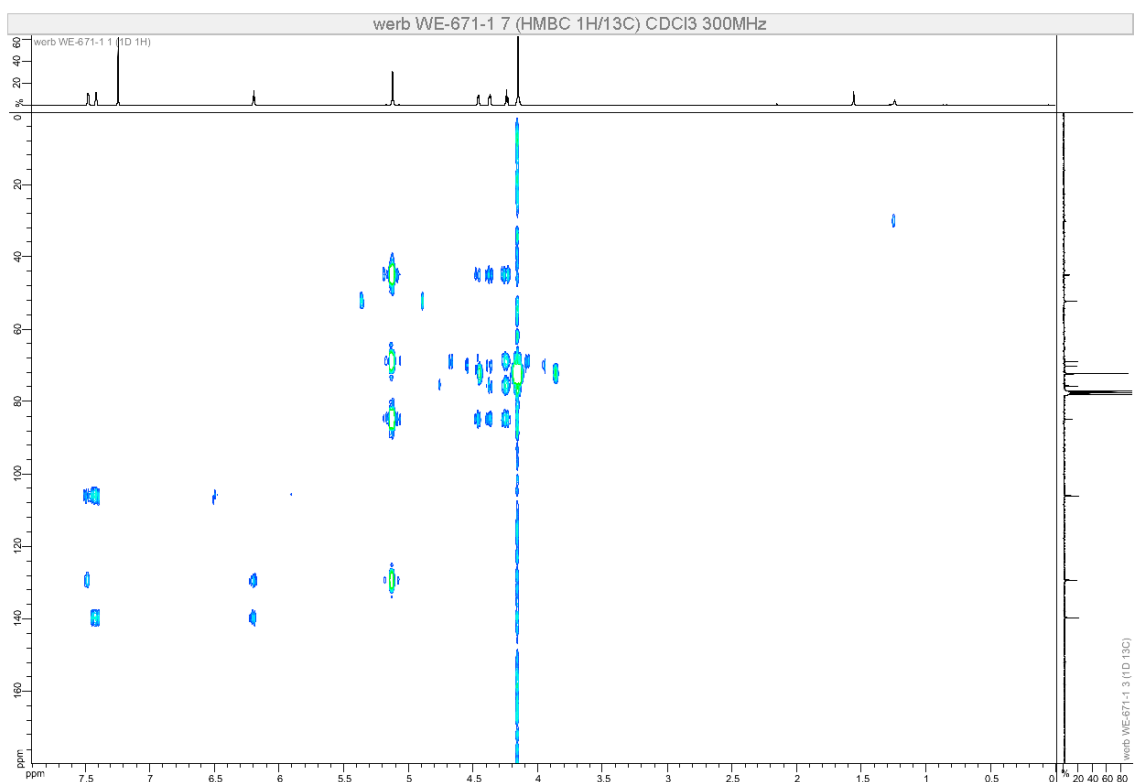
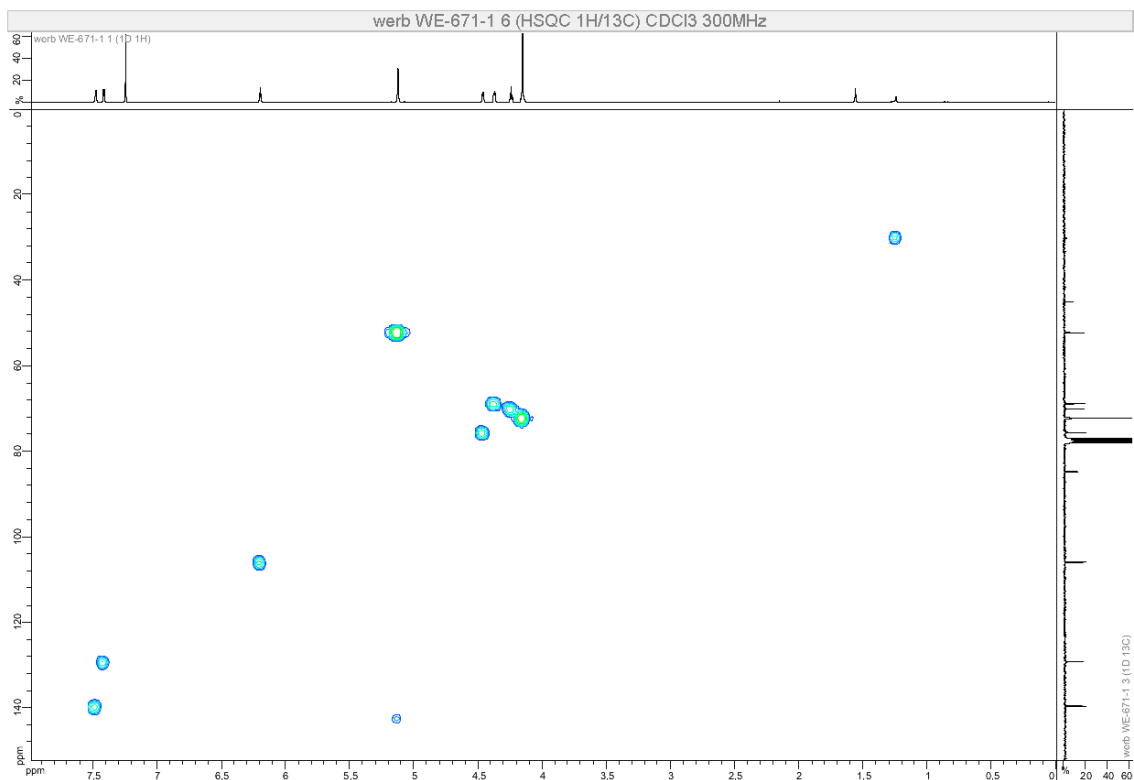


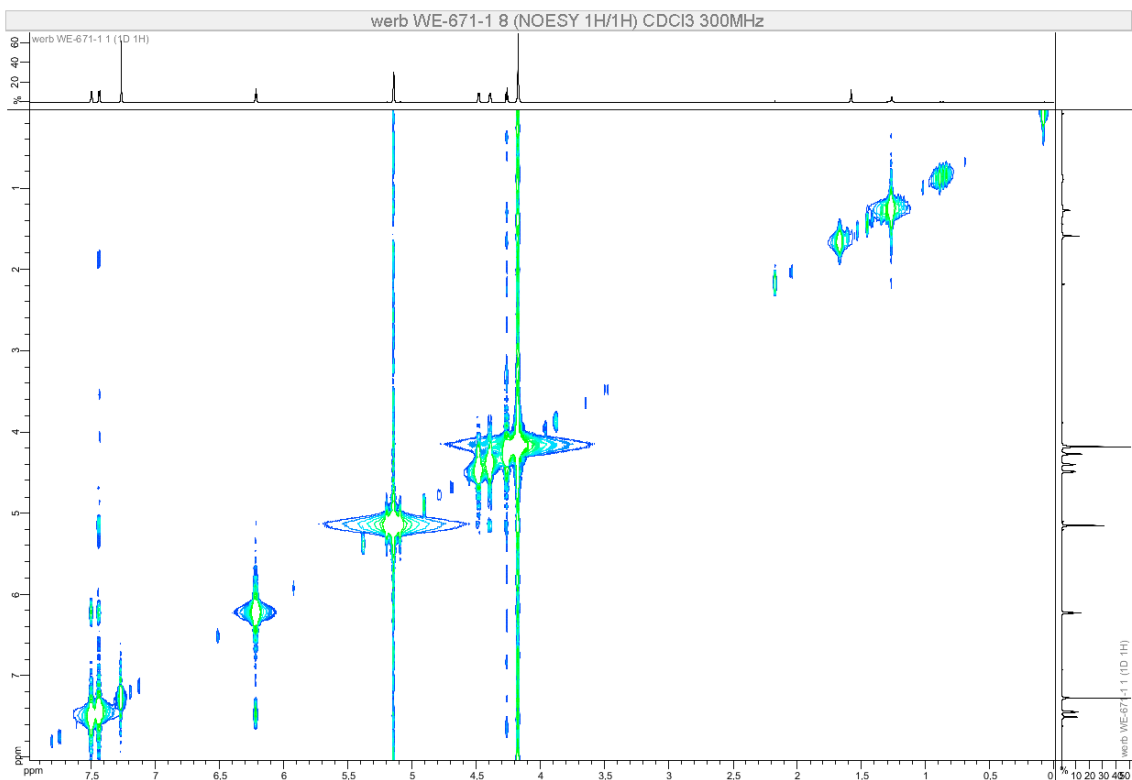


Compound (\pm)-4k

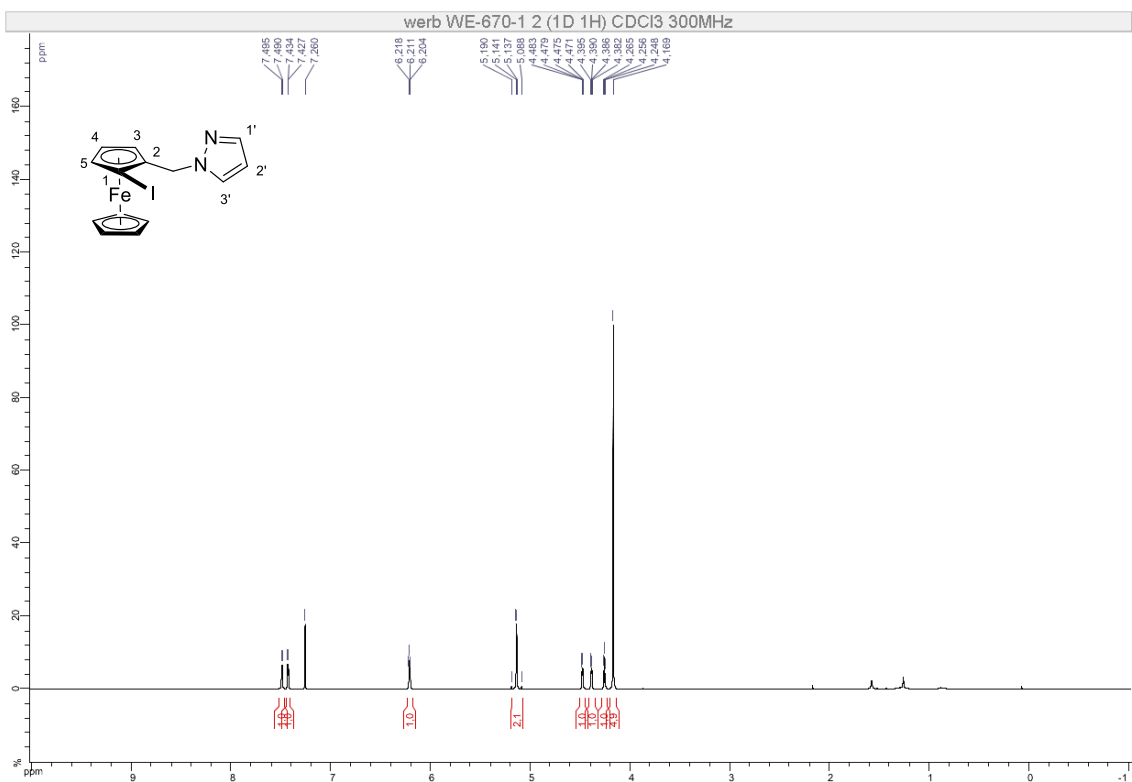




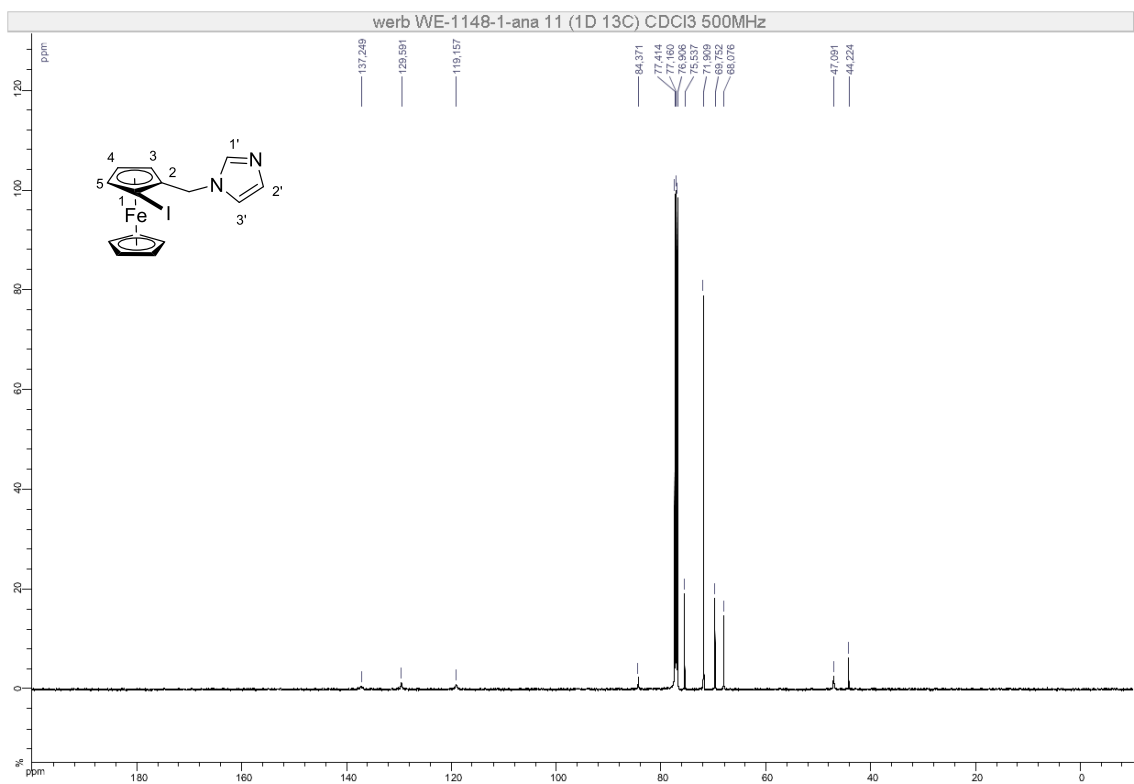
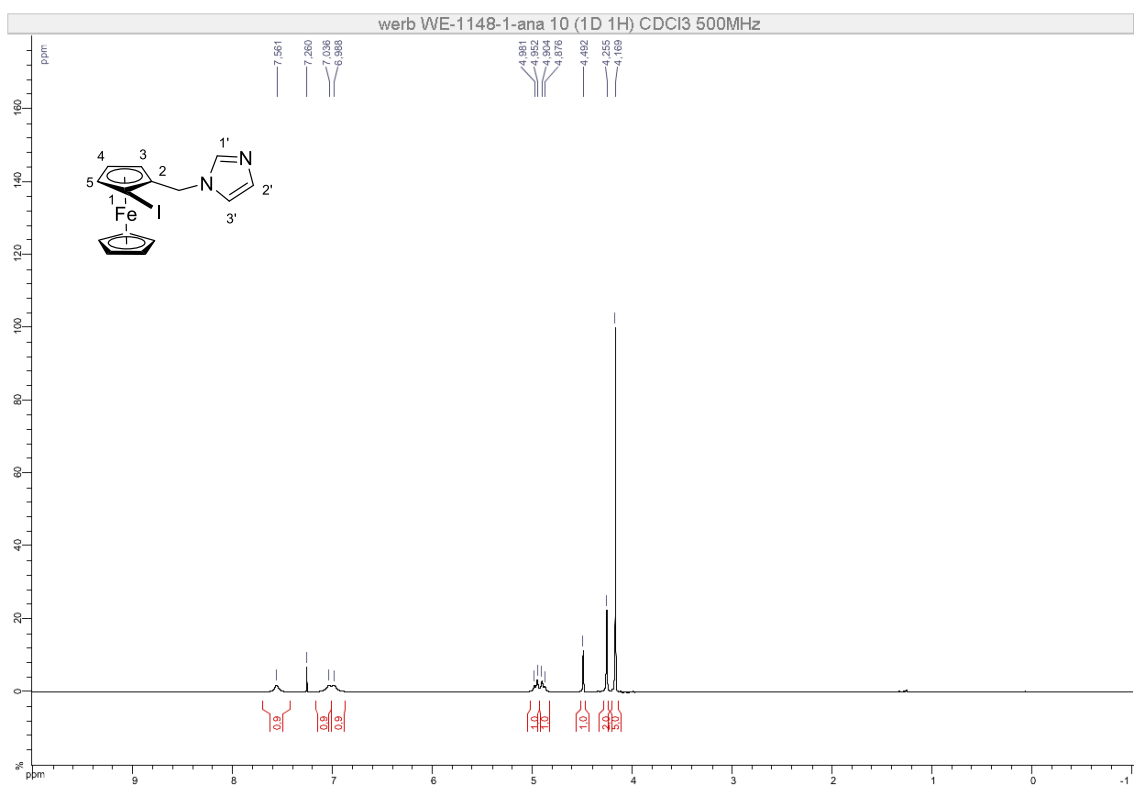


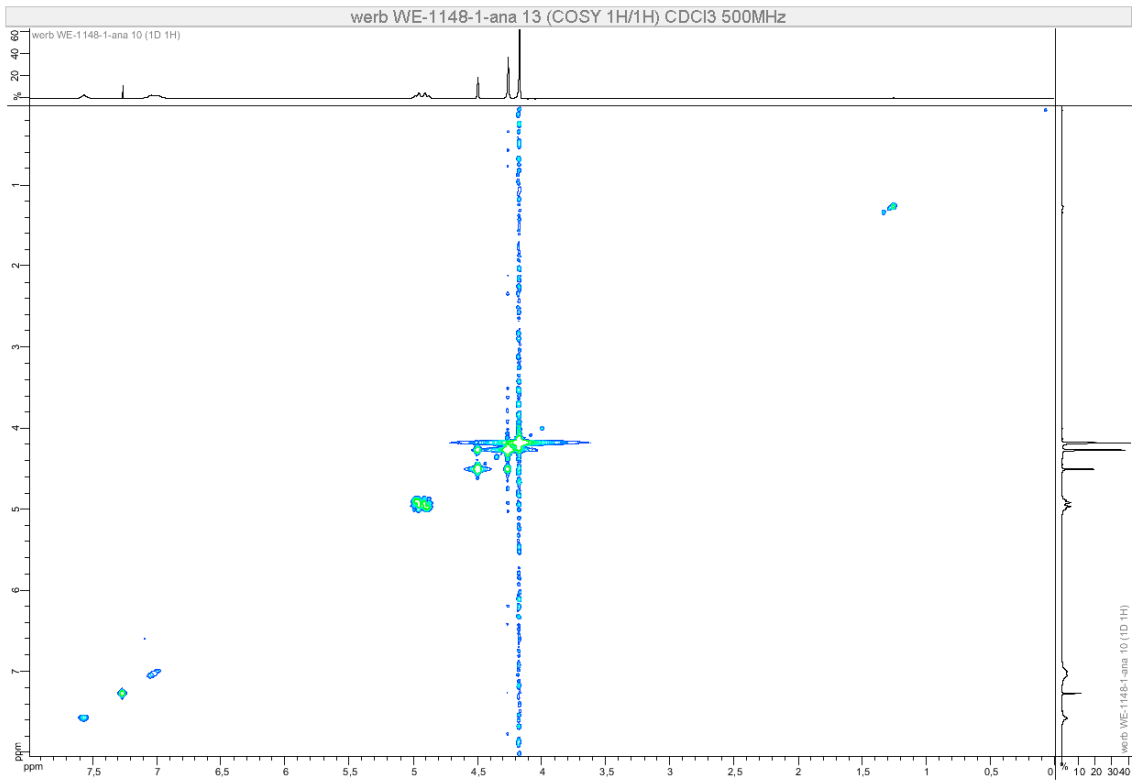
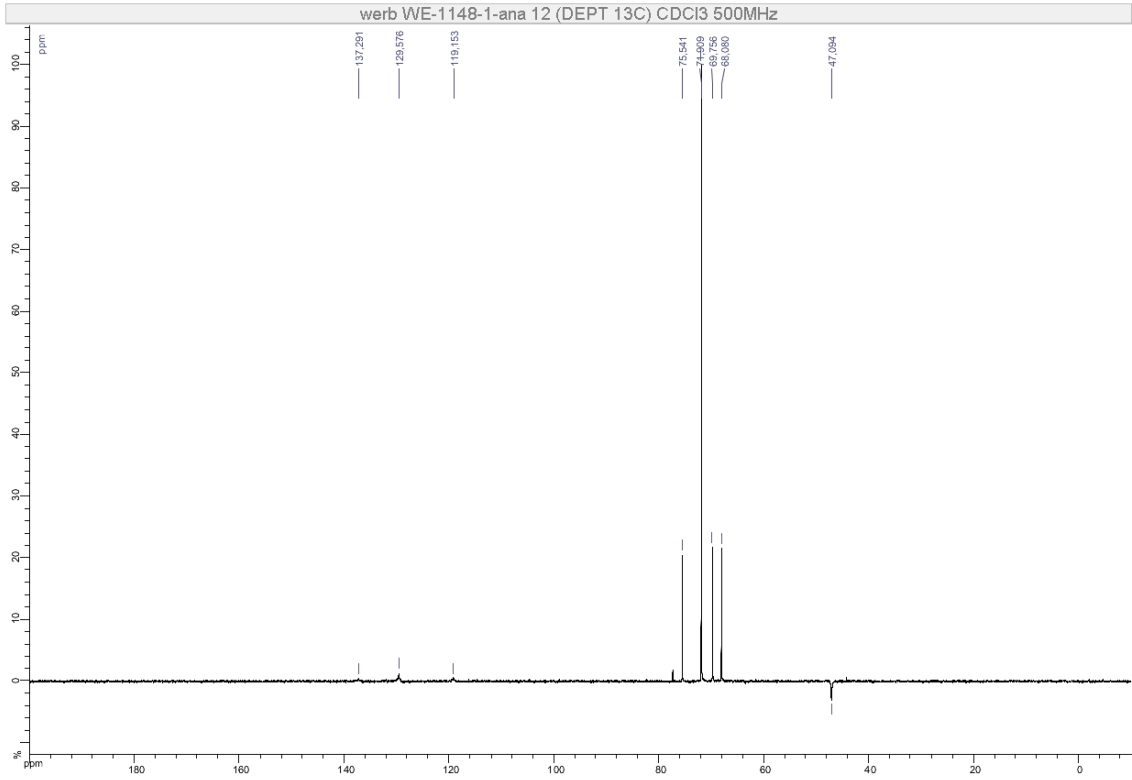


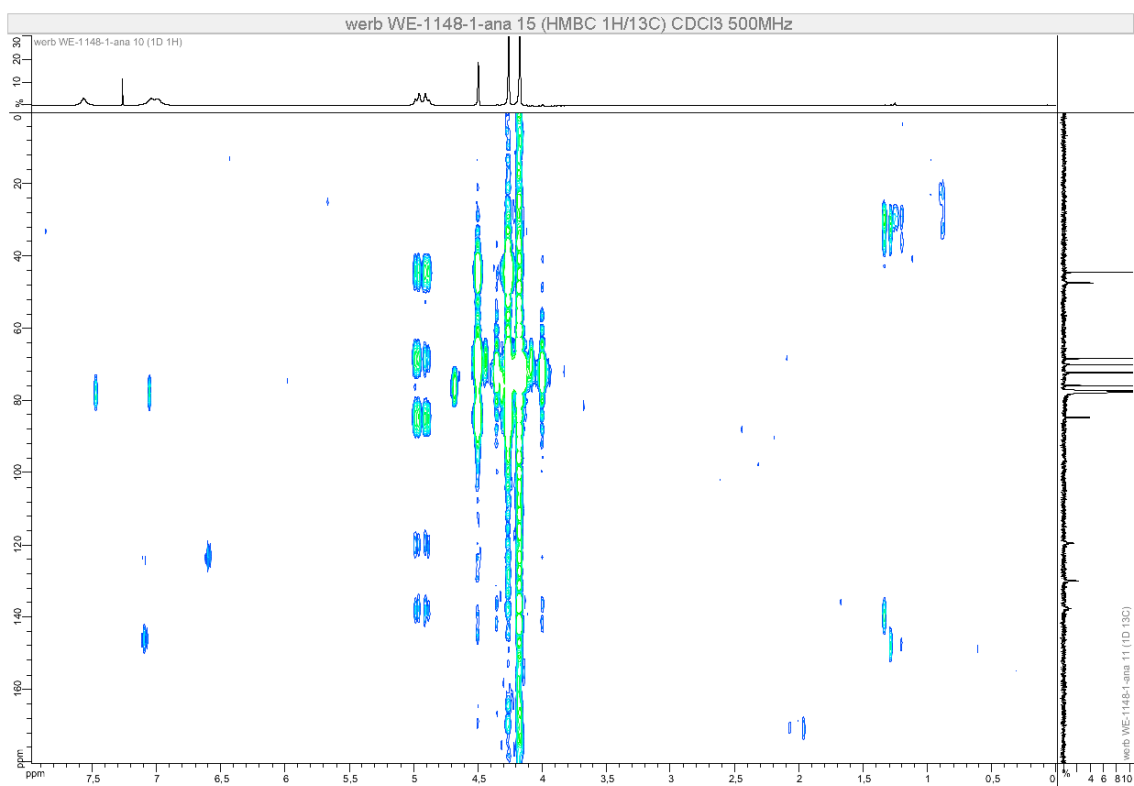
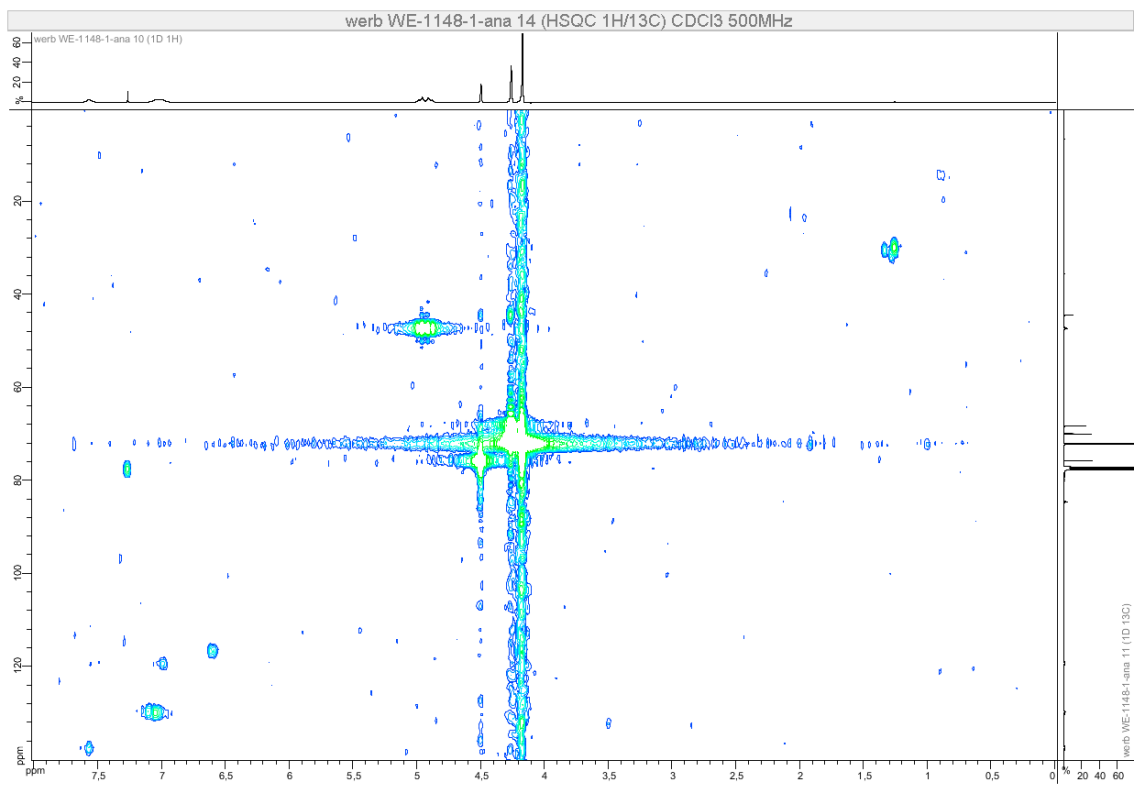
Compound (*S_p*)-4k



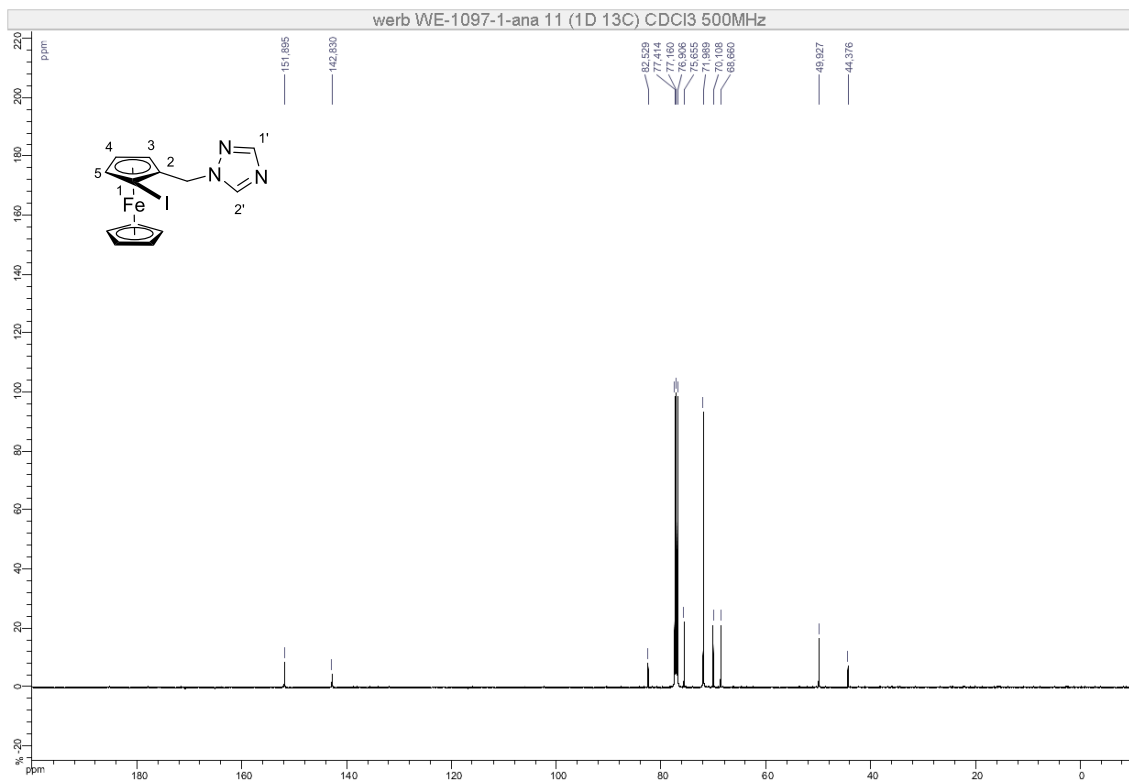
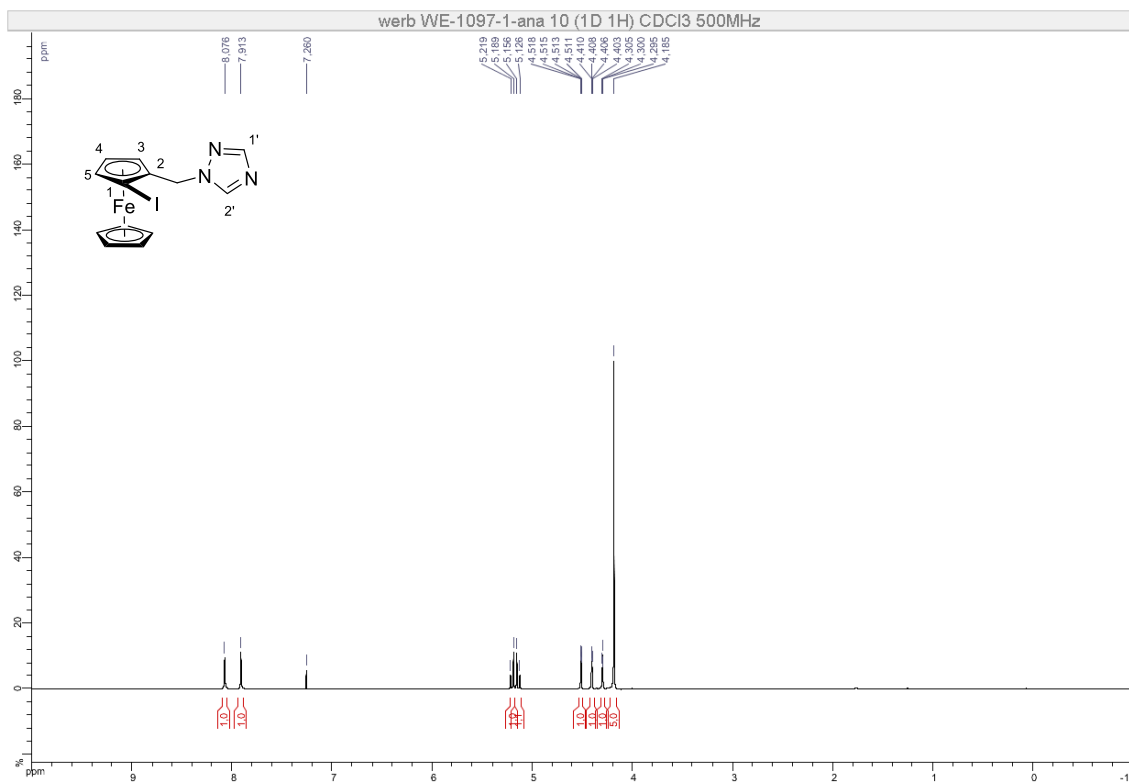
Compound (\pm)-4I

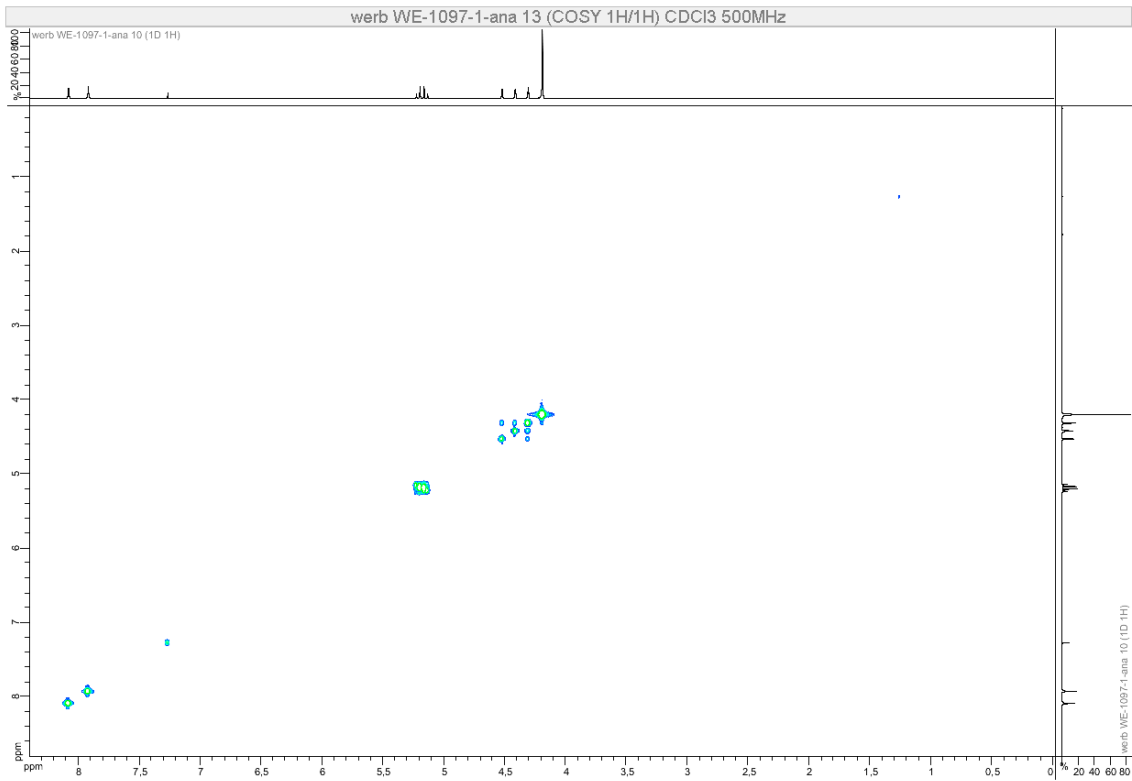
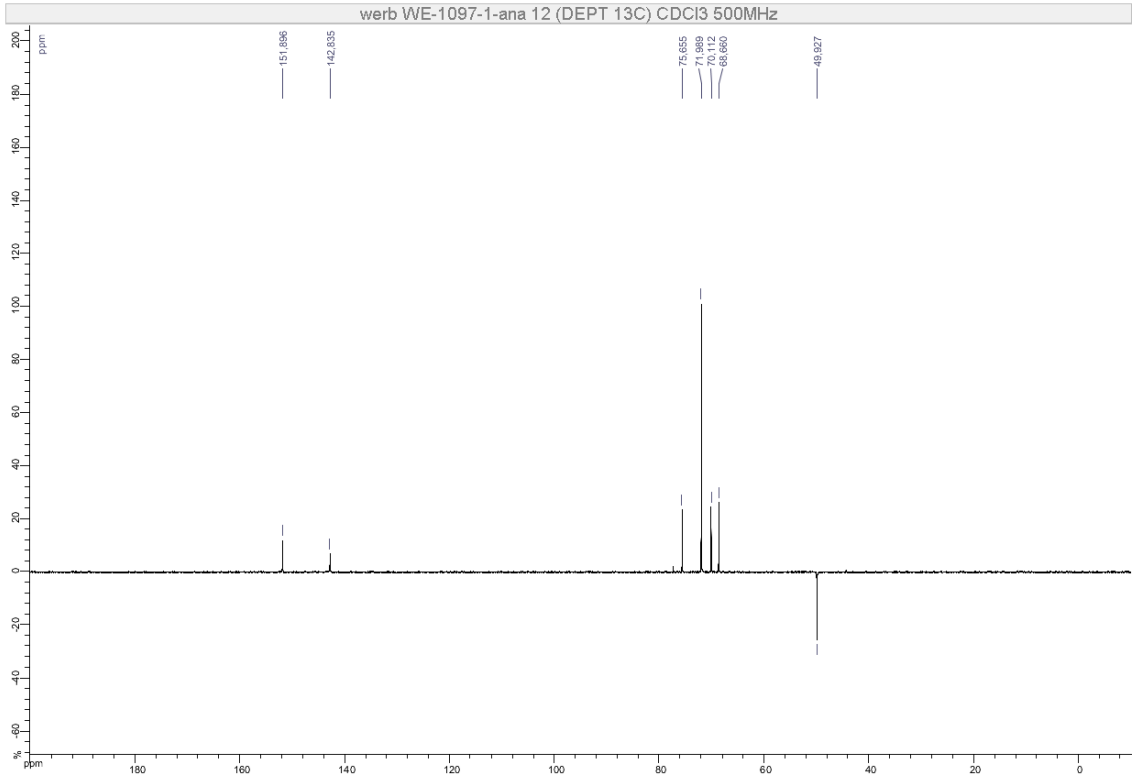


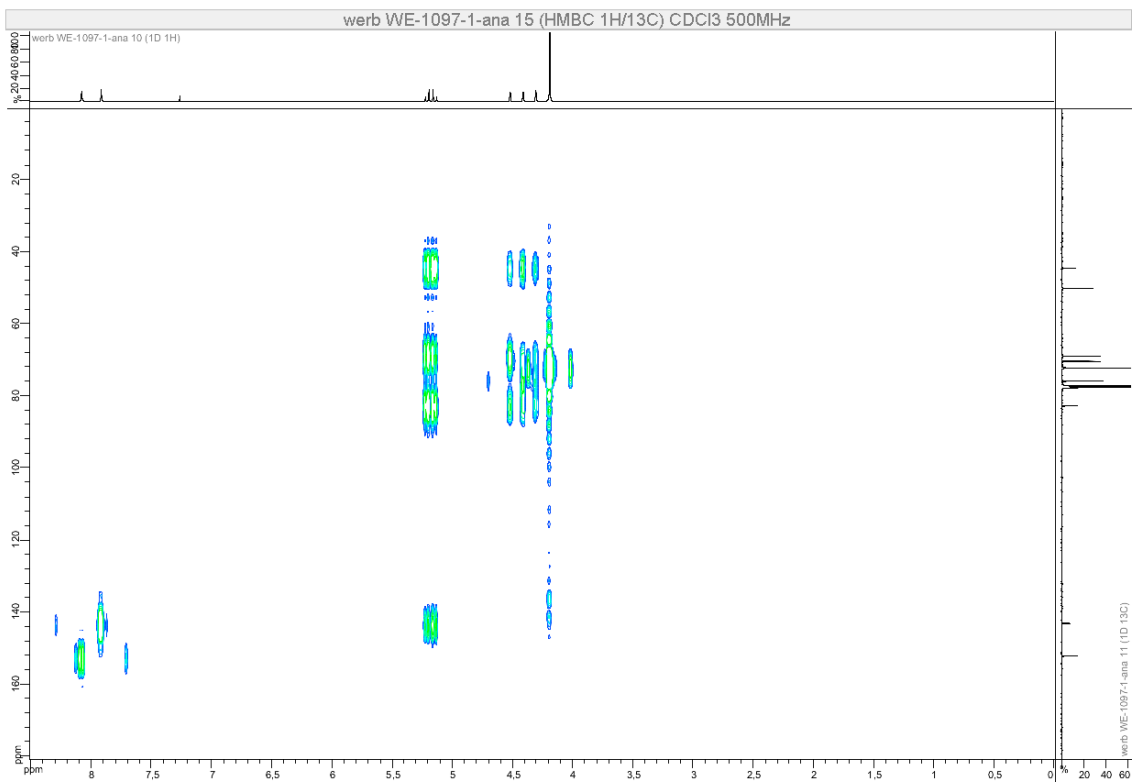
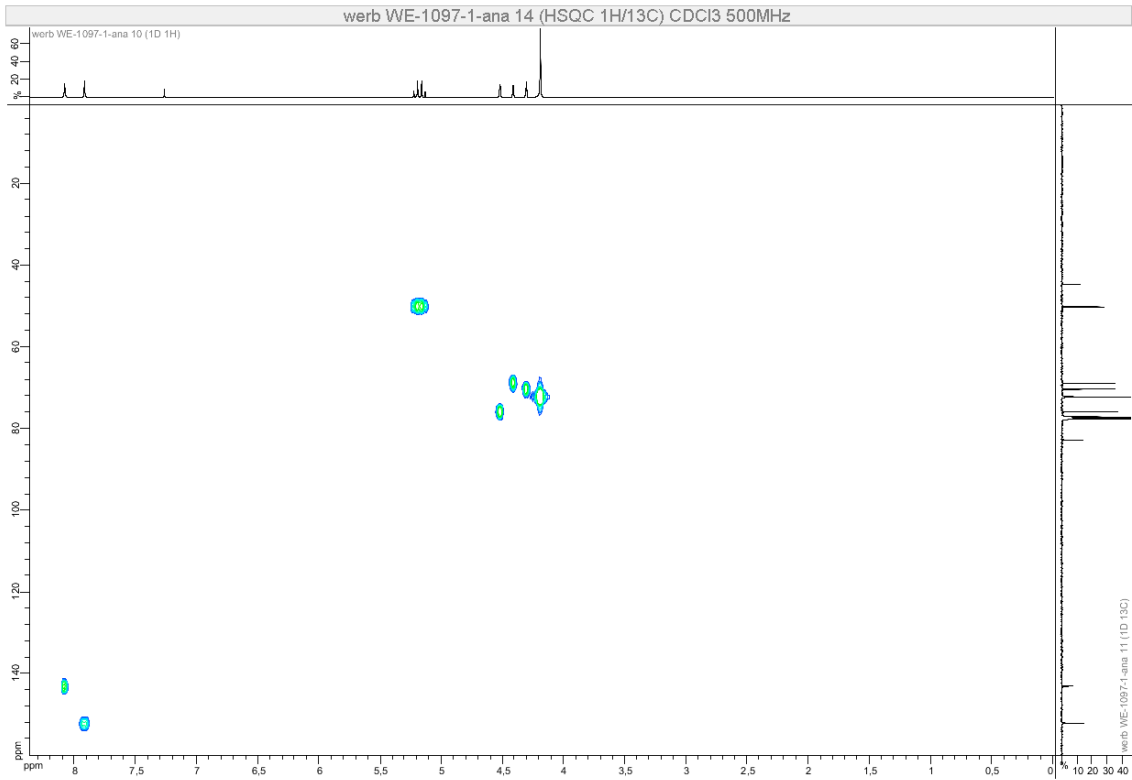




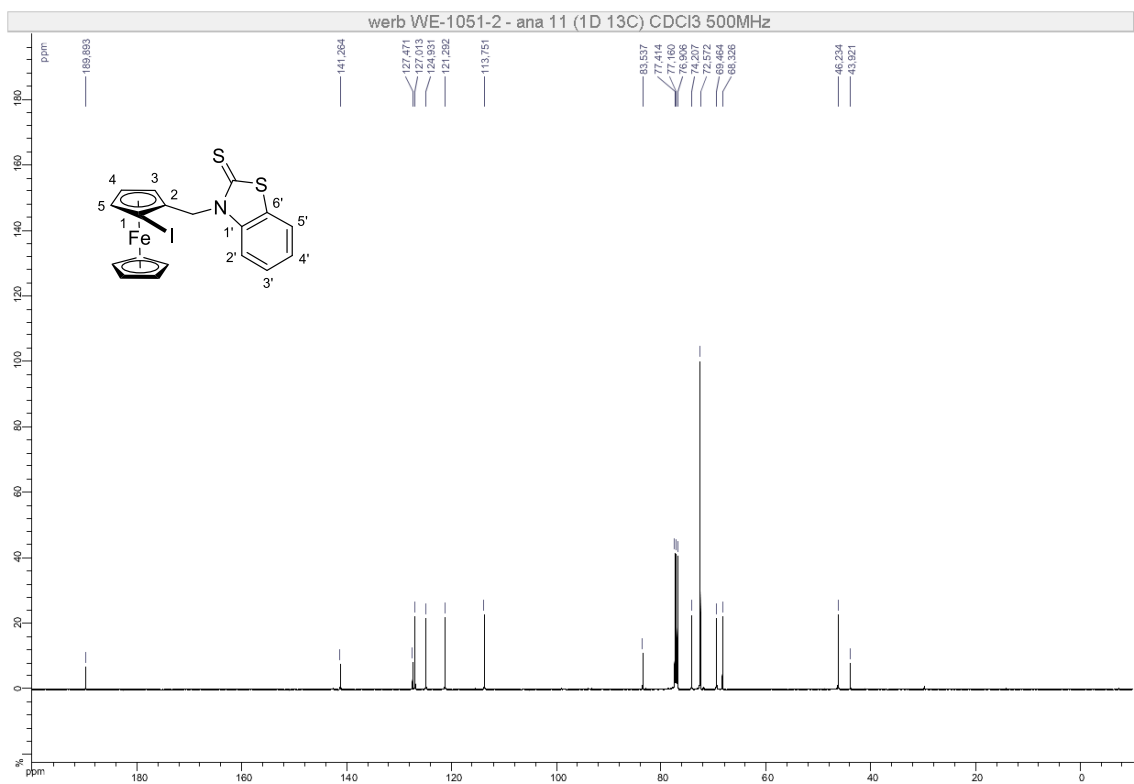
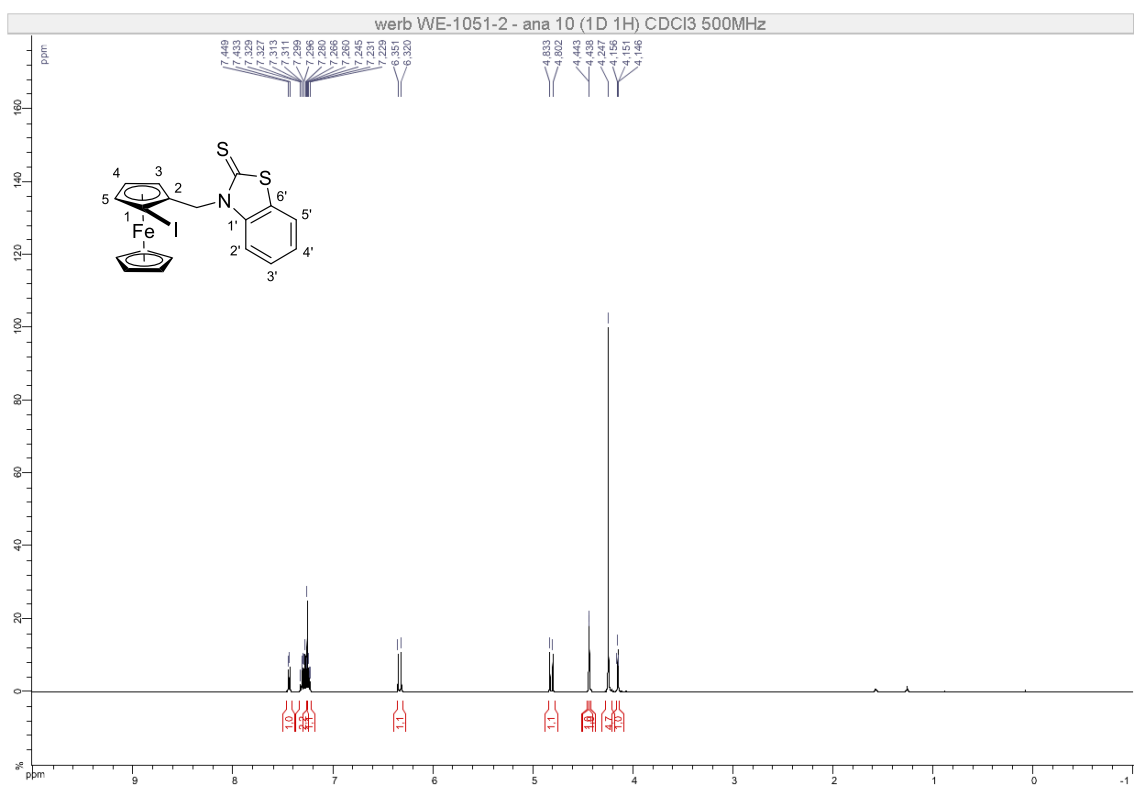
Compound (\pm)-4m

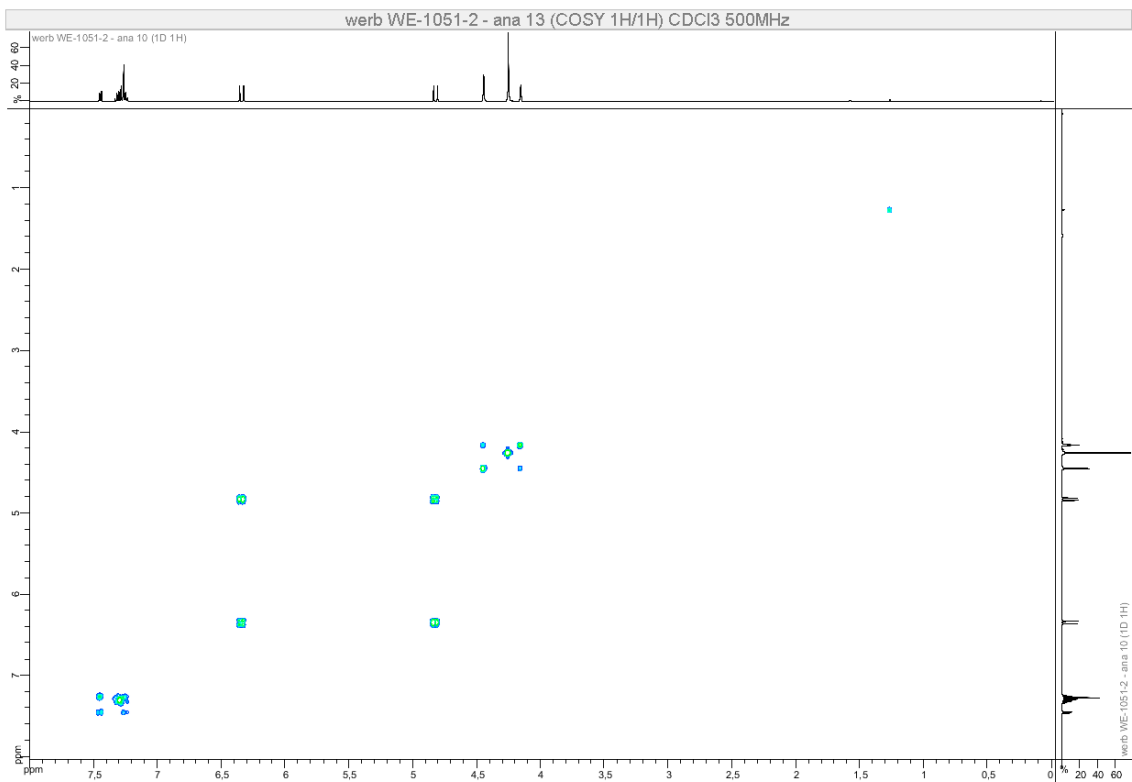
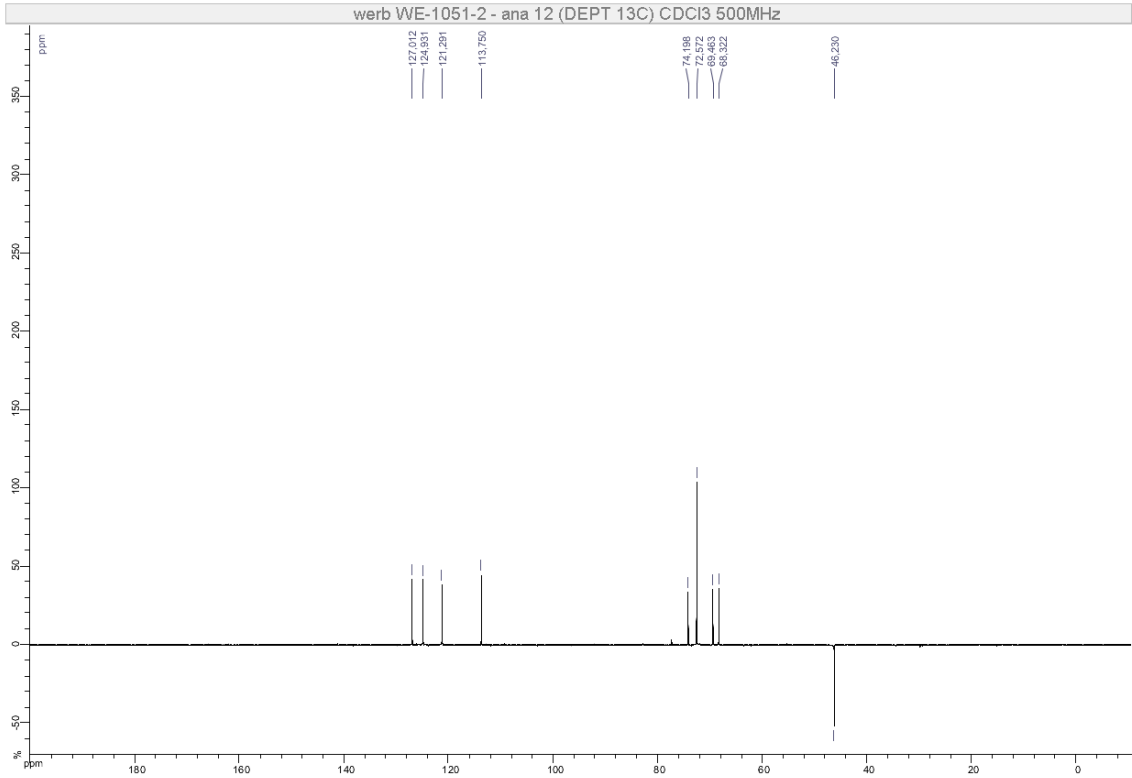


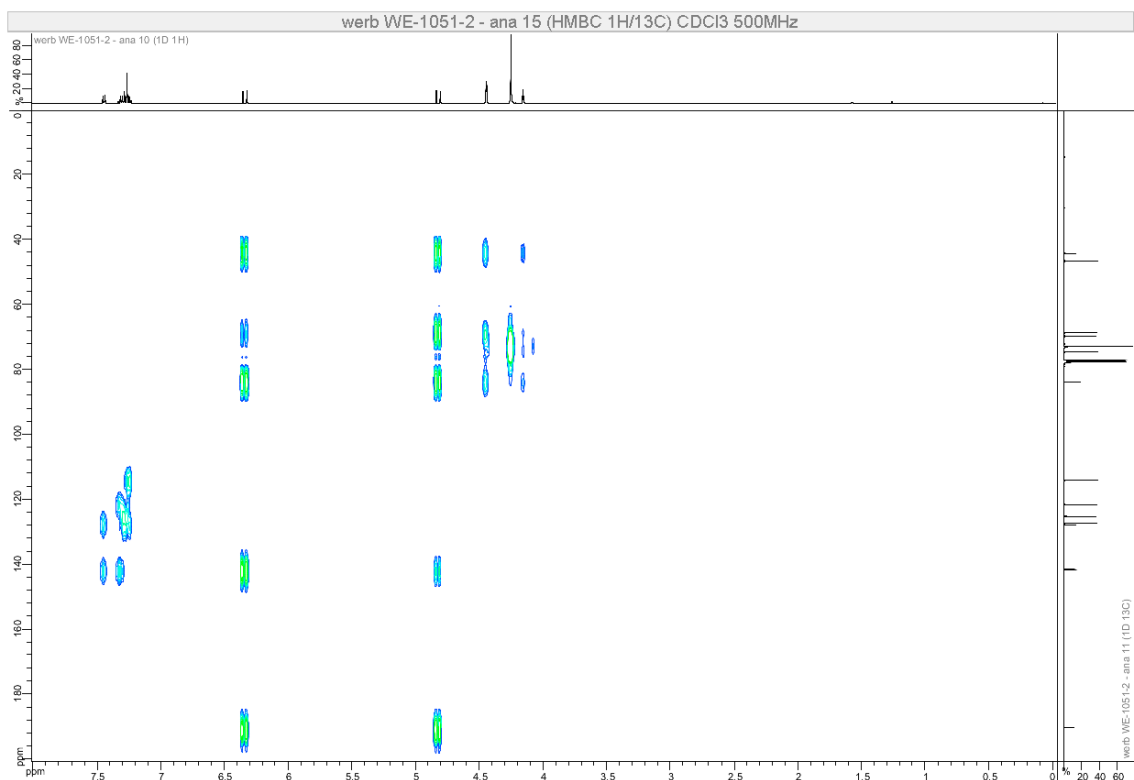
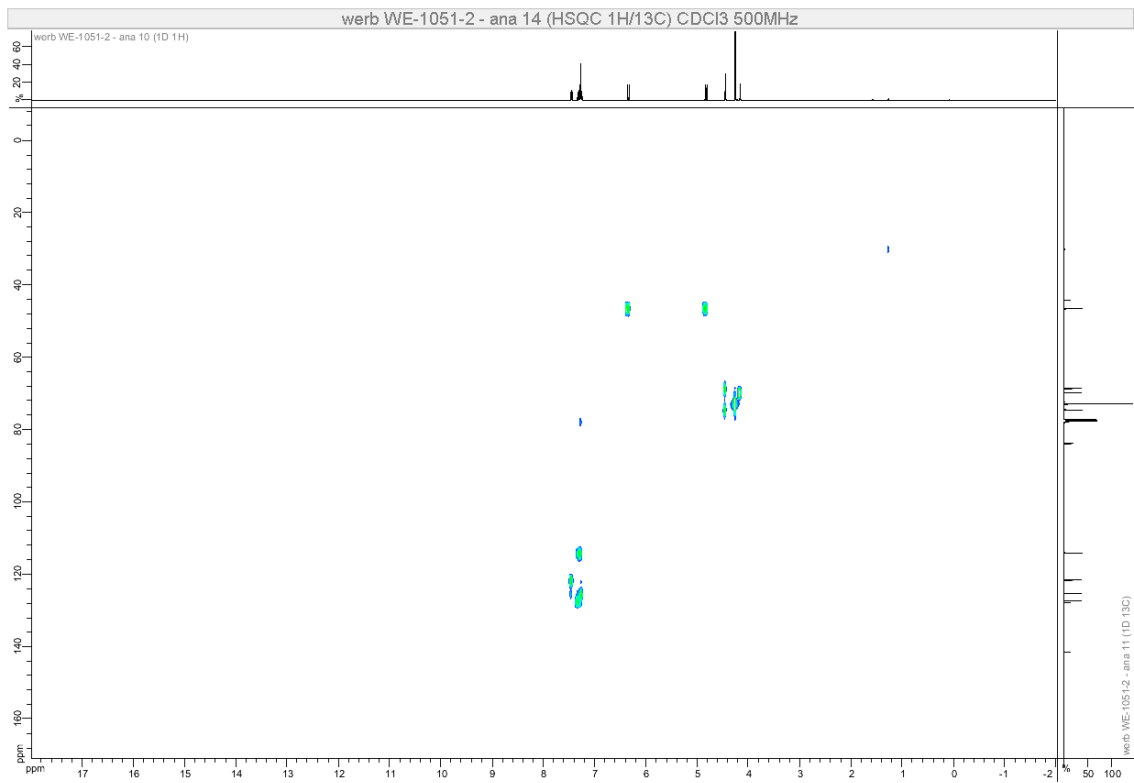


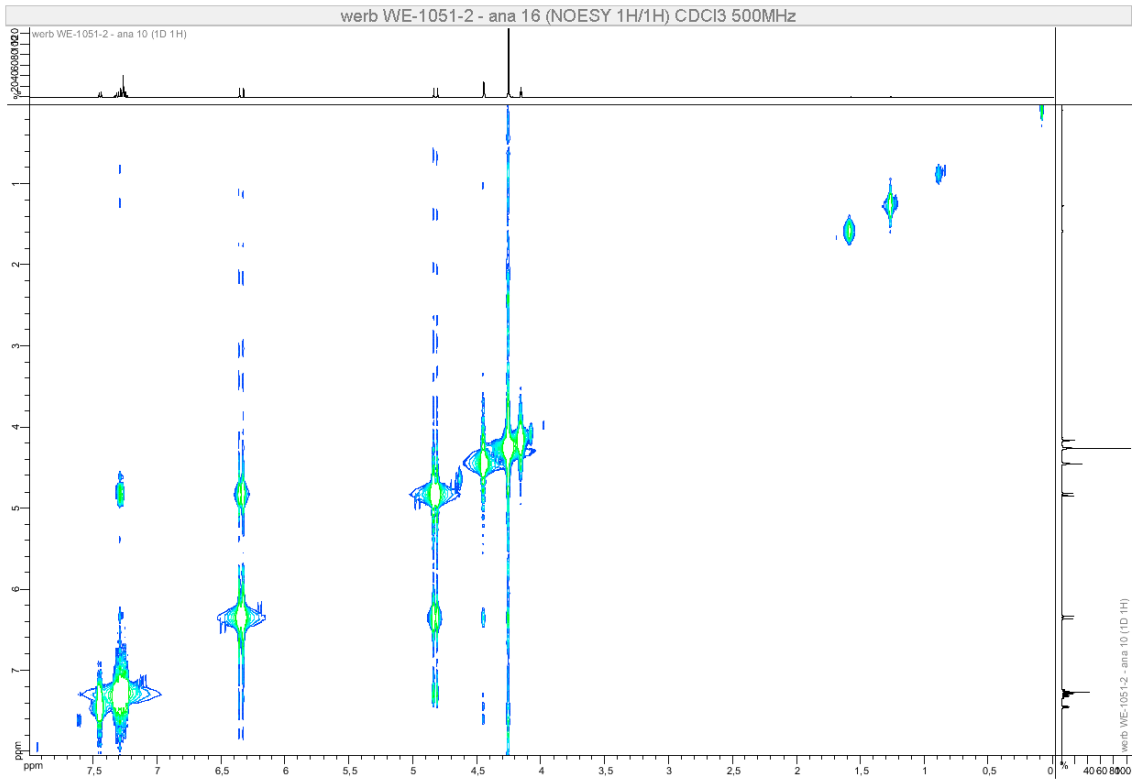


Compound (\pm)-4n

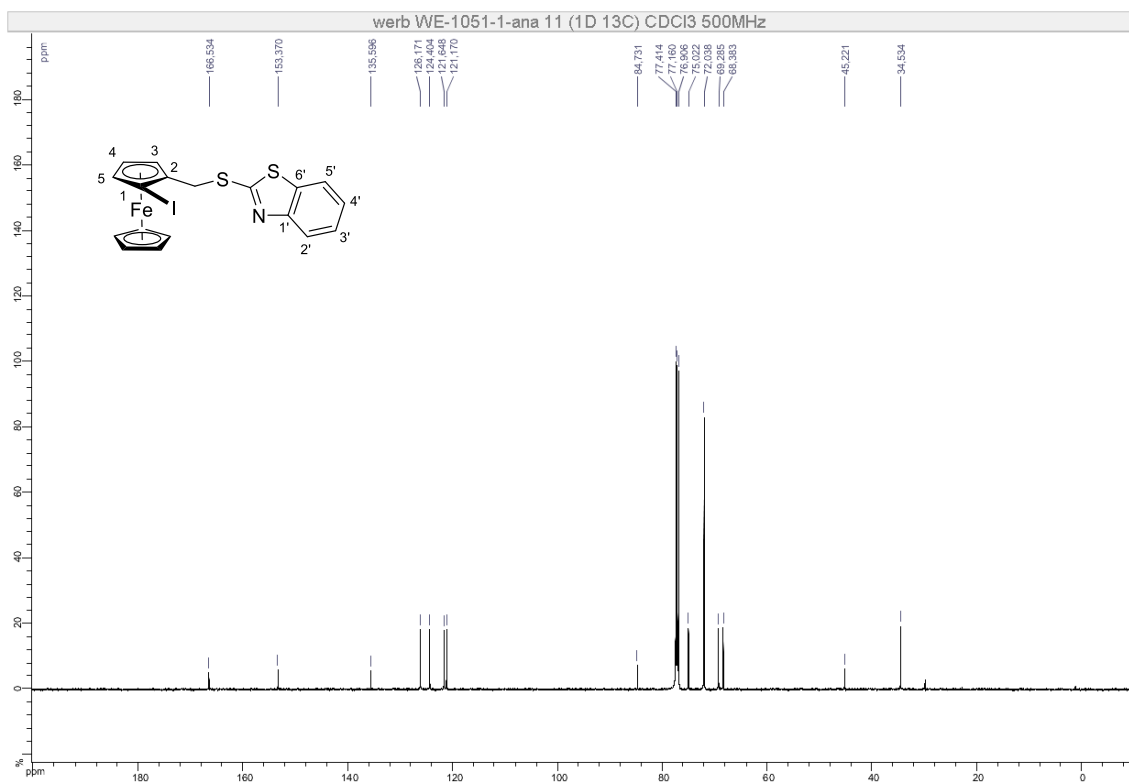
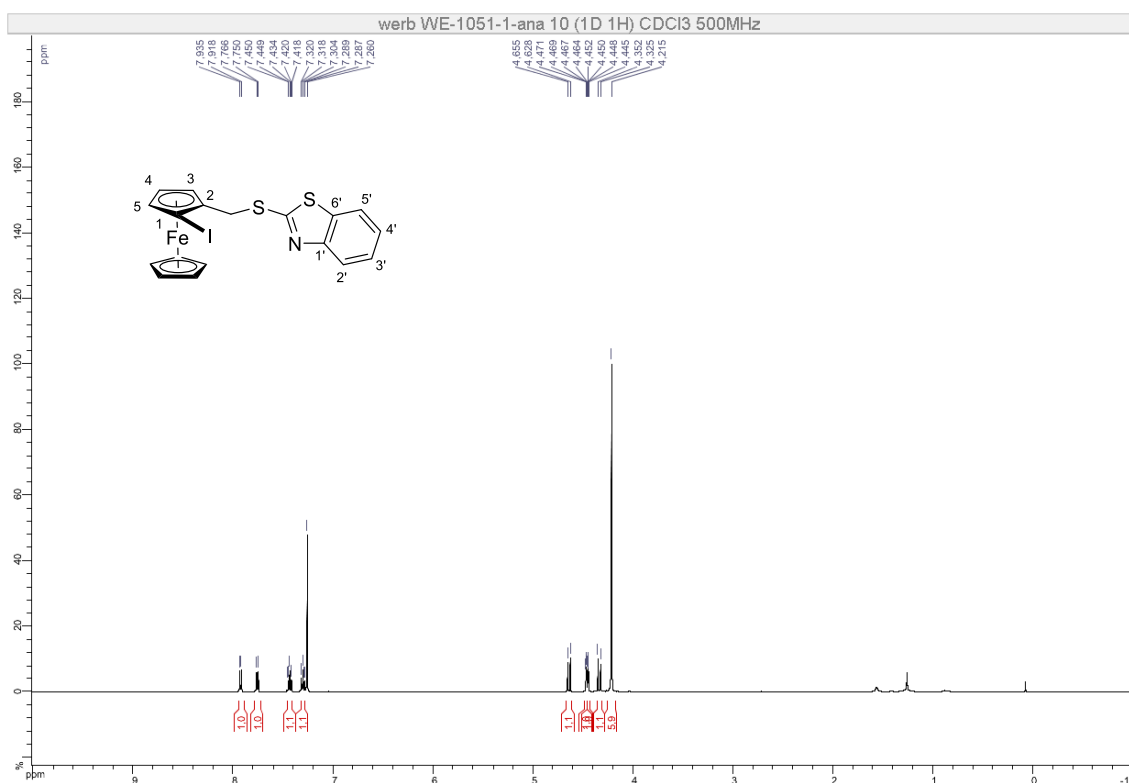


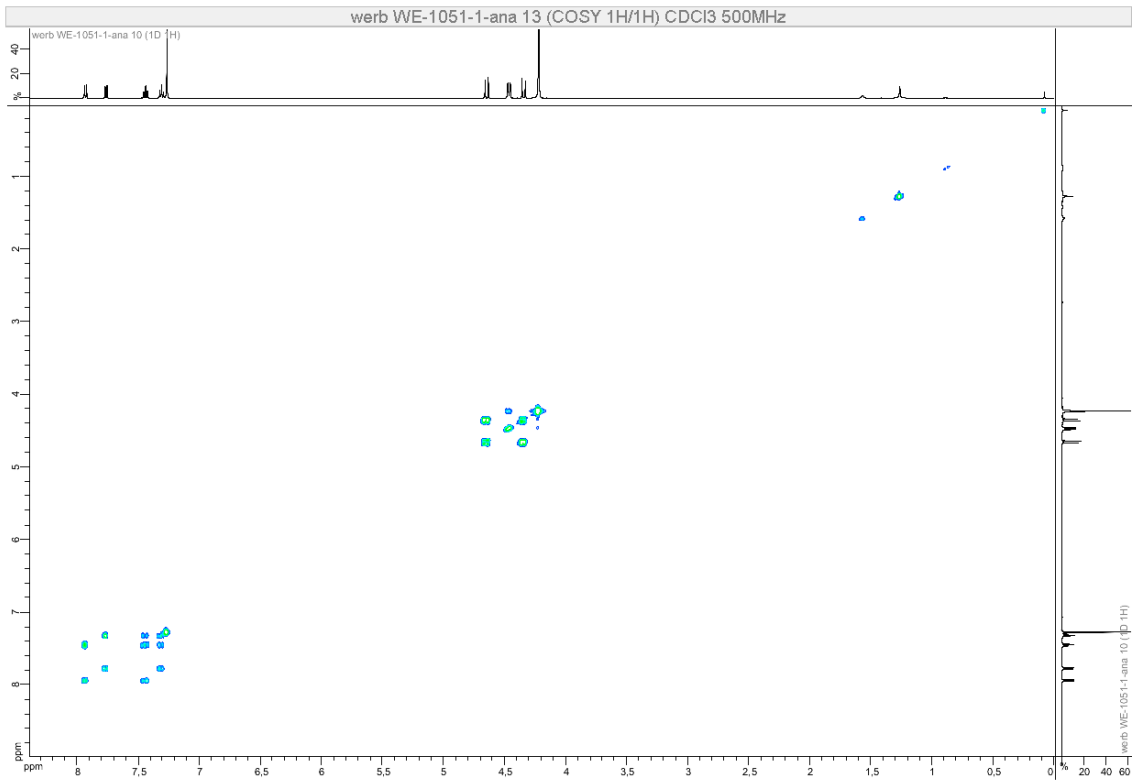
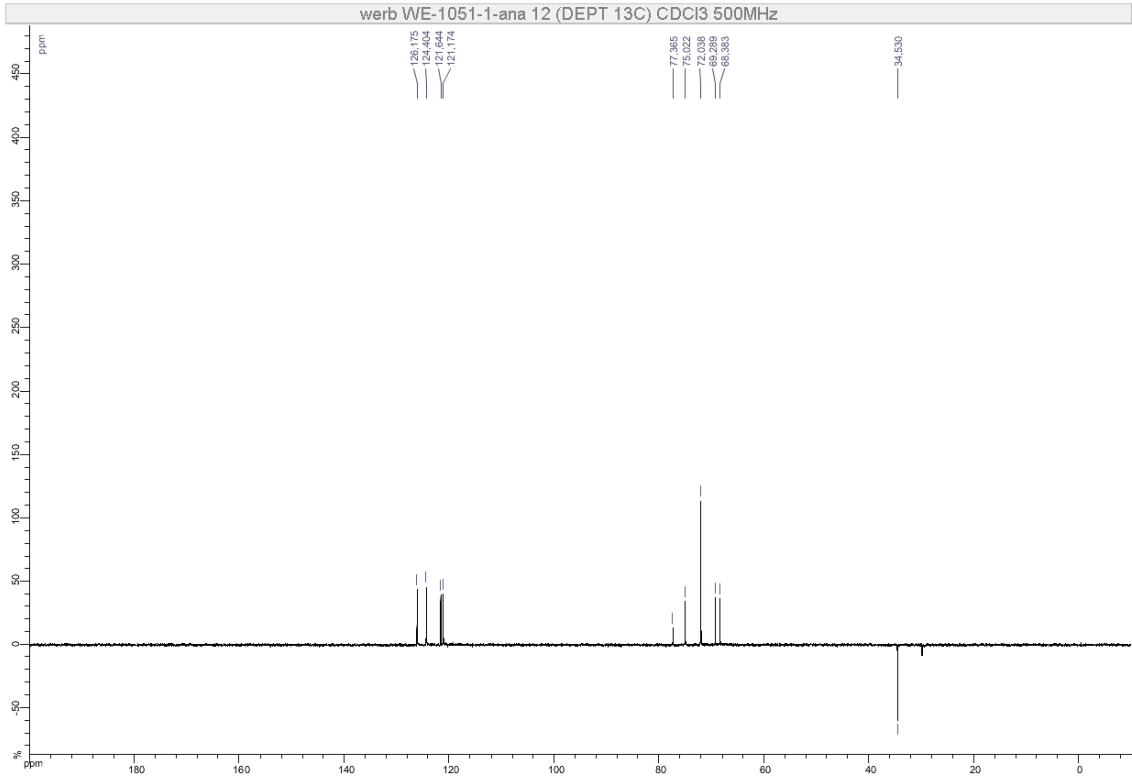


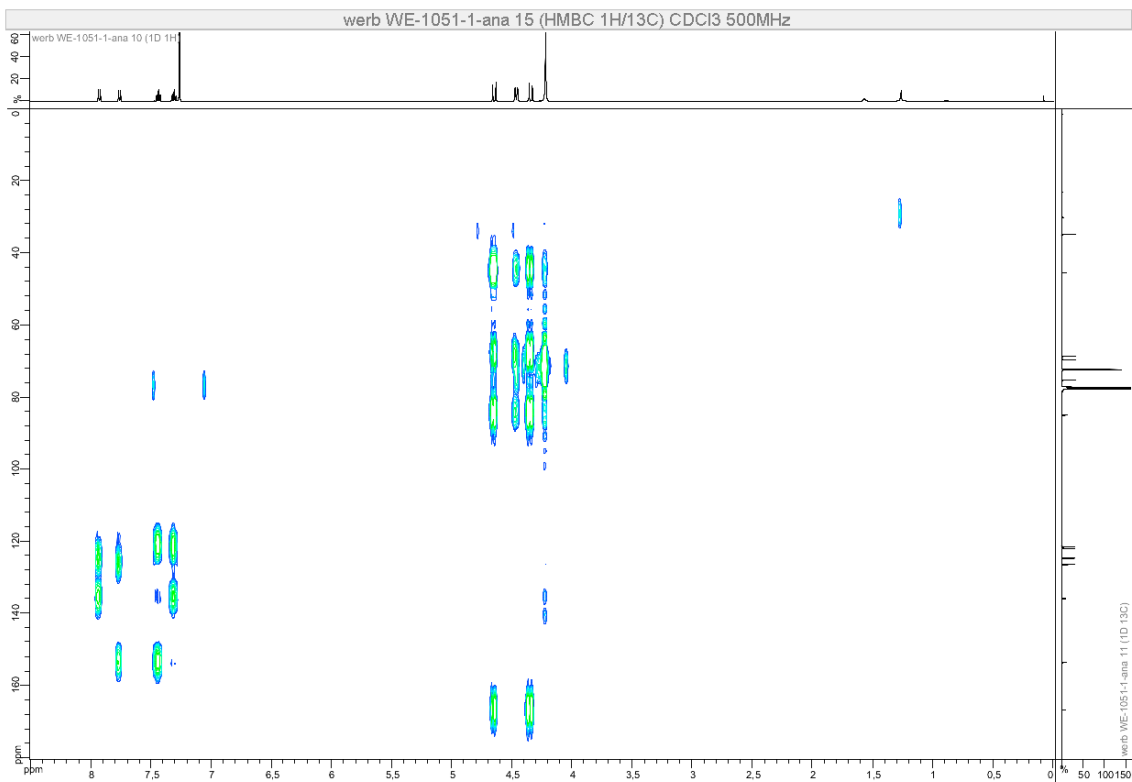
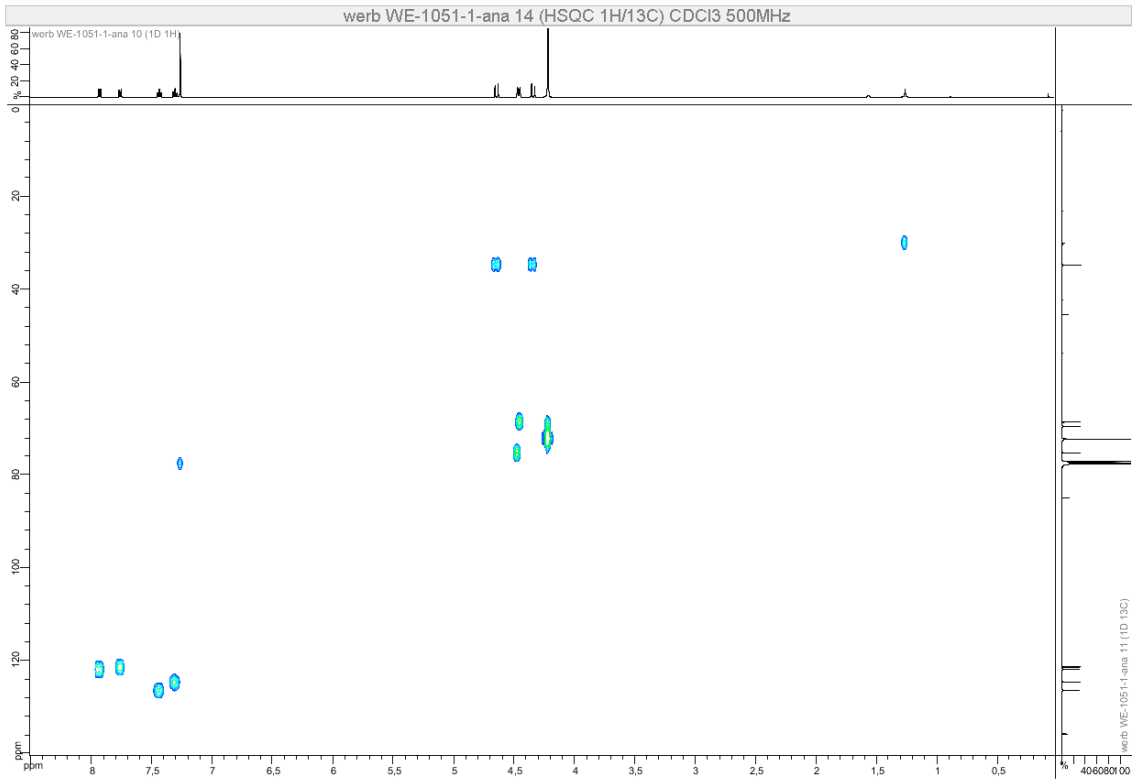




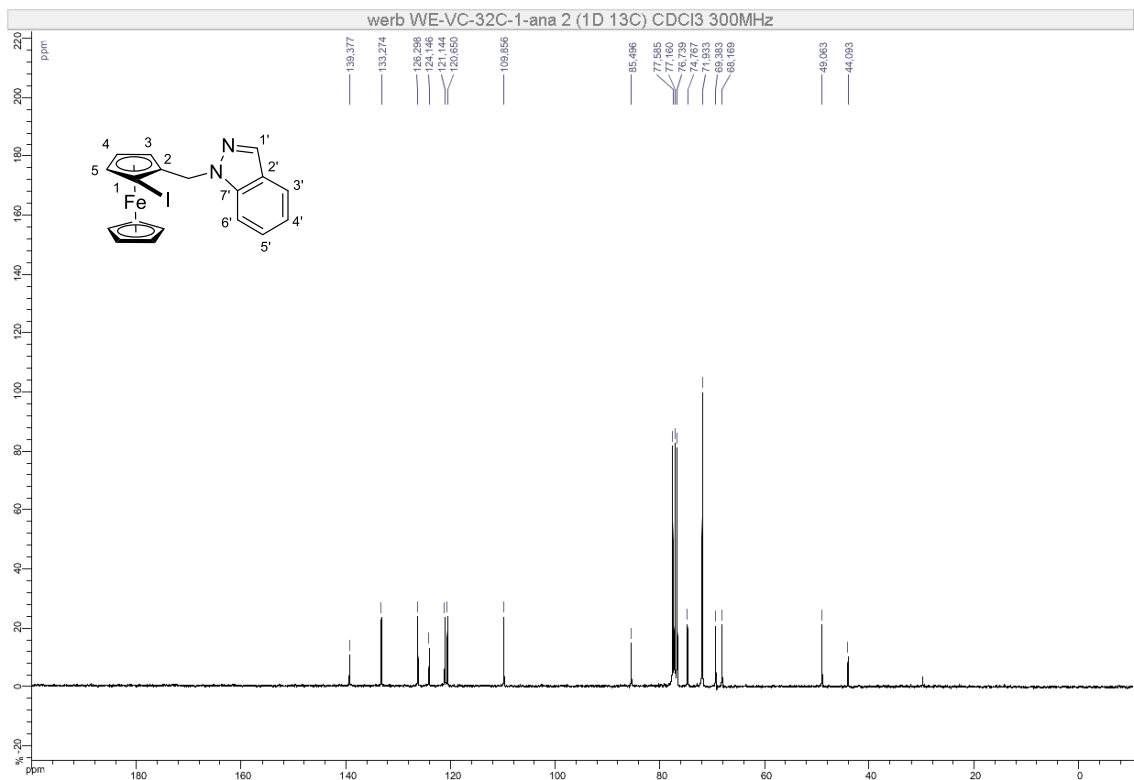
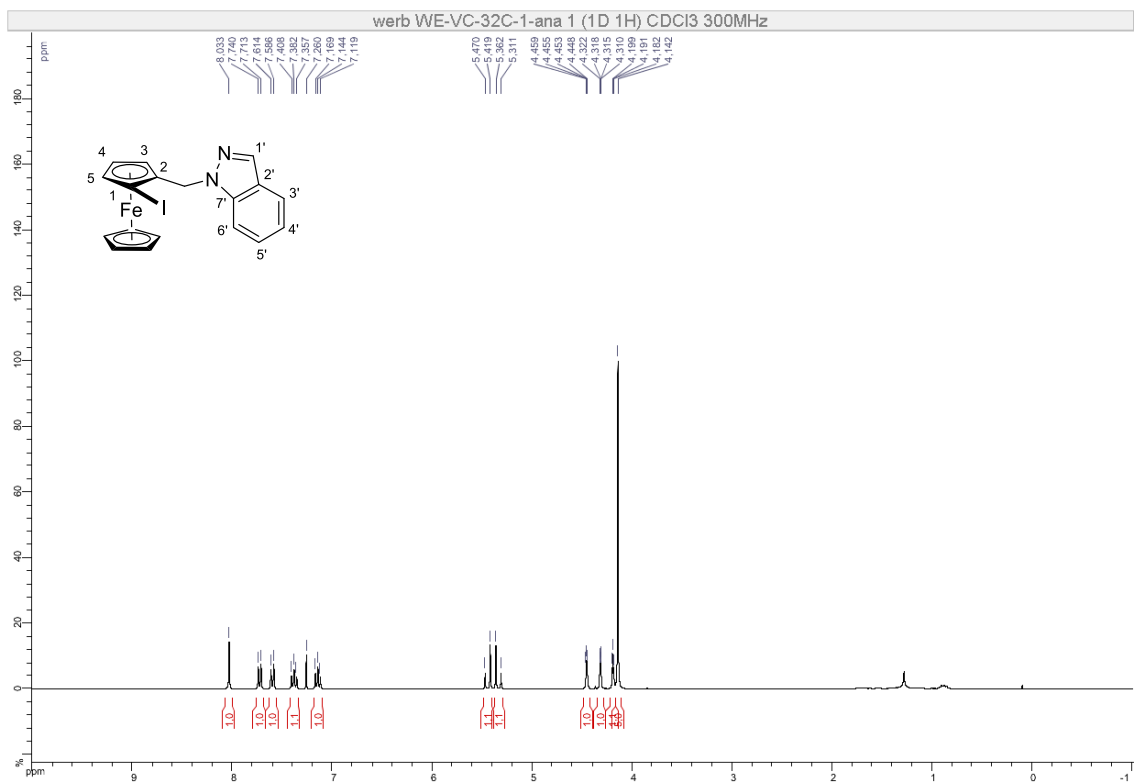
Compound (\pm)-4n'

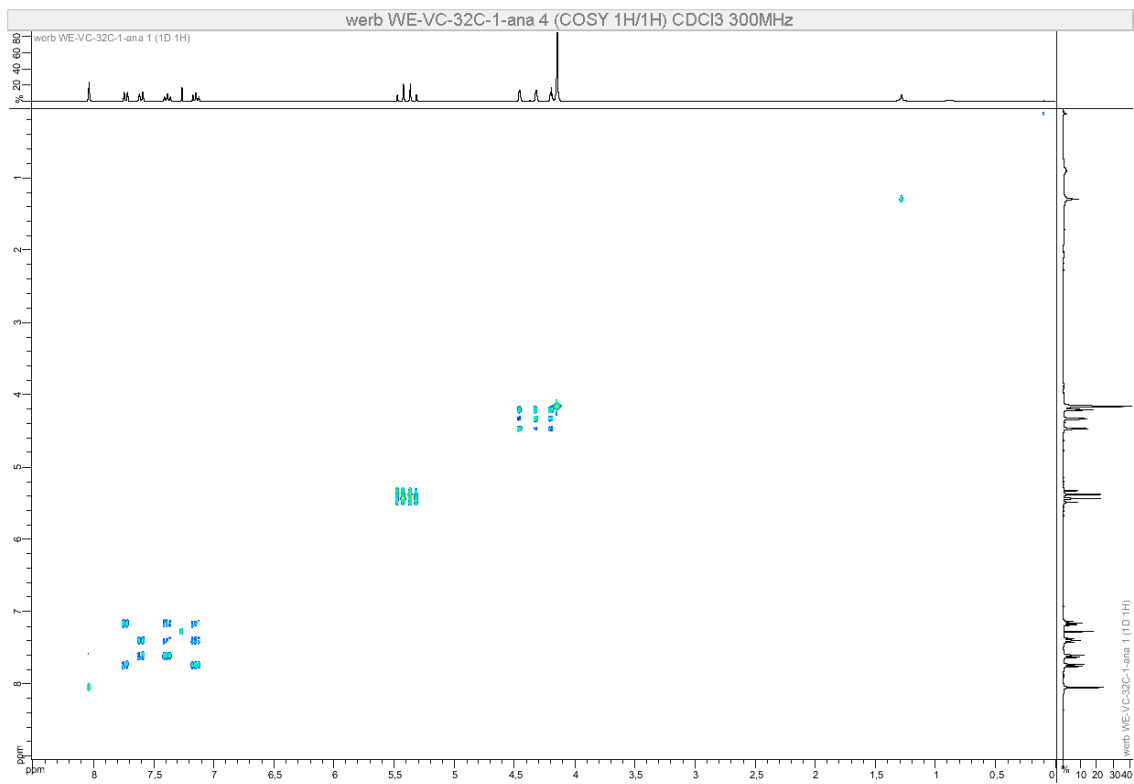
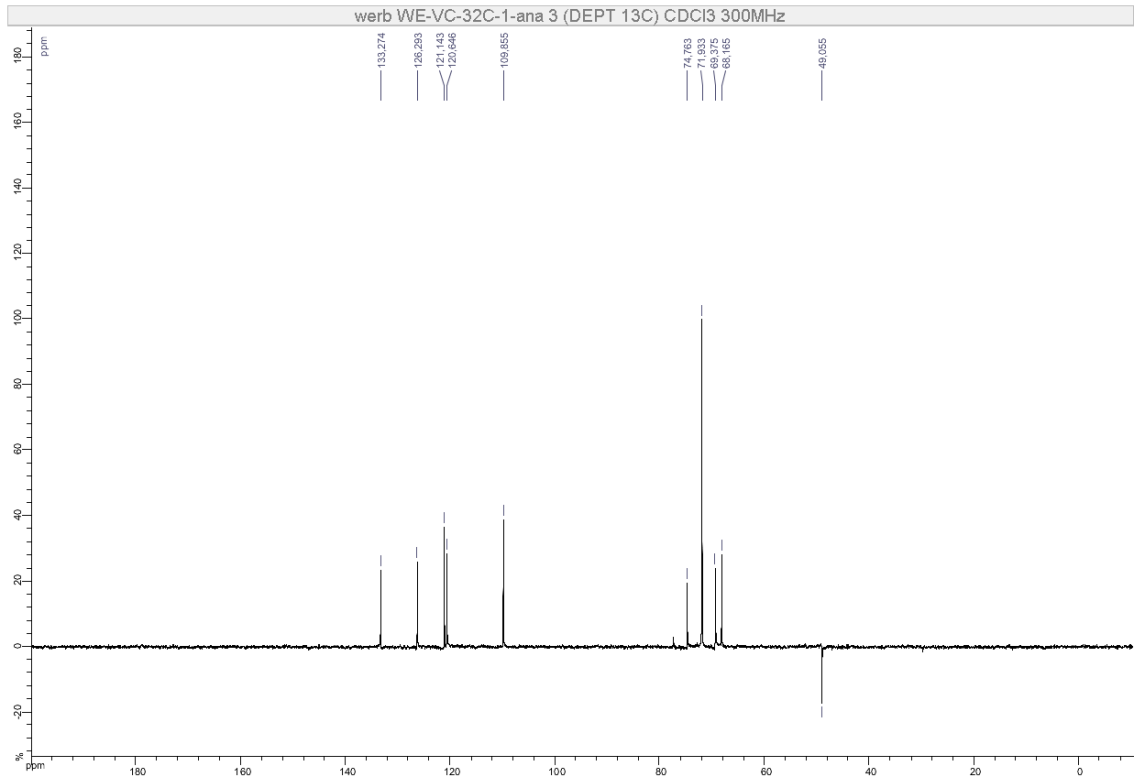


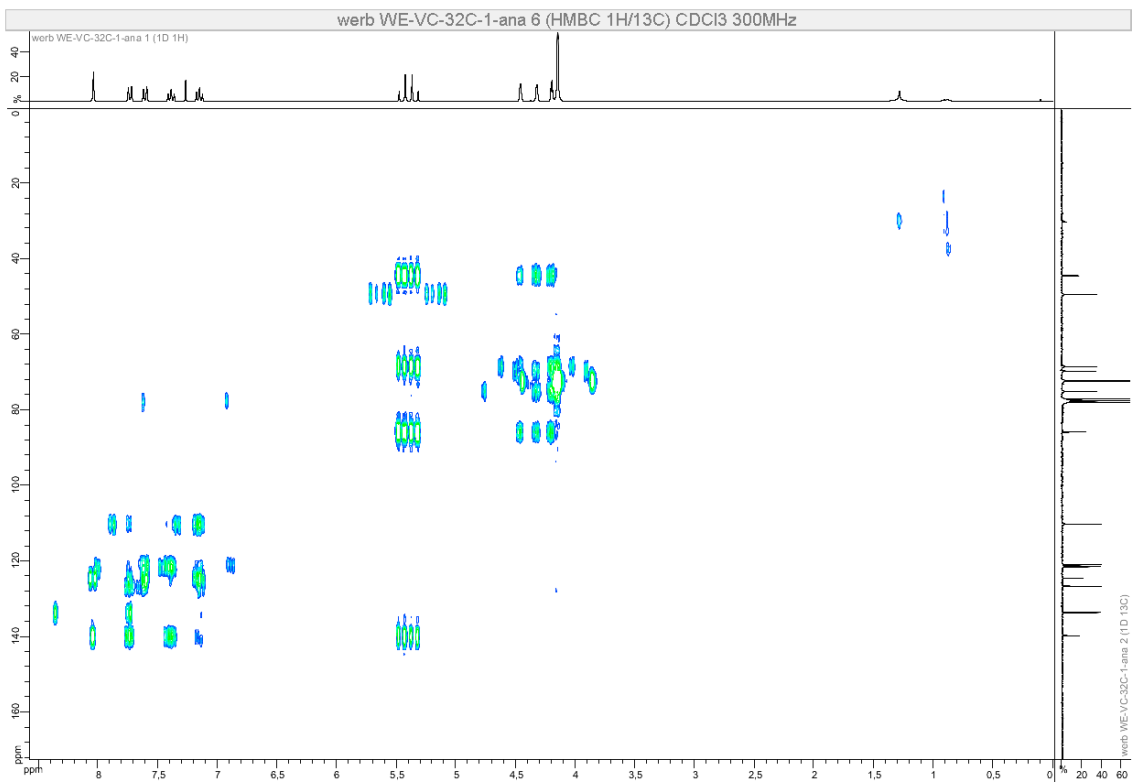
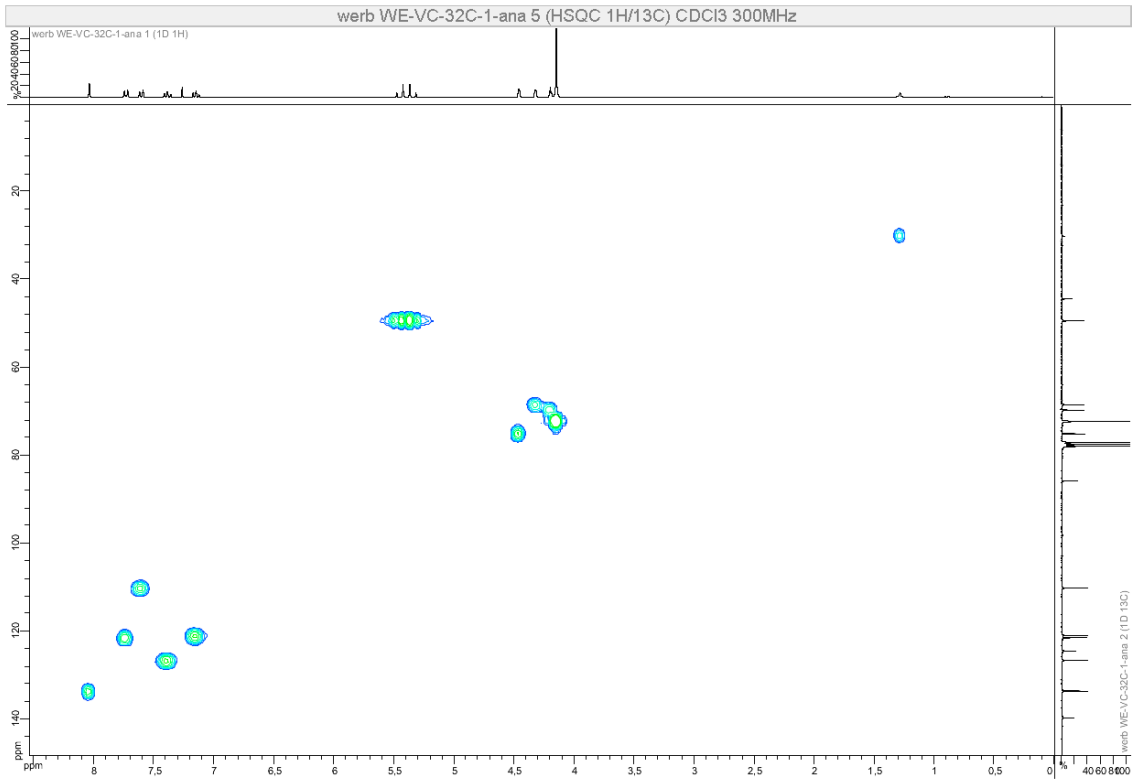


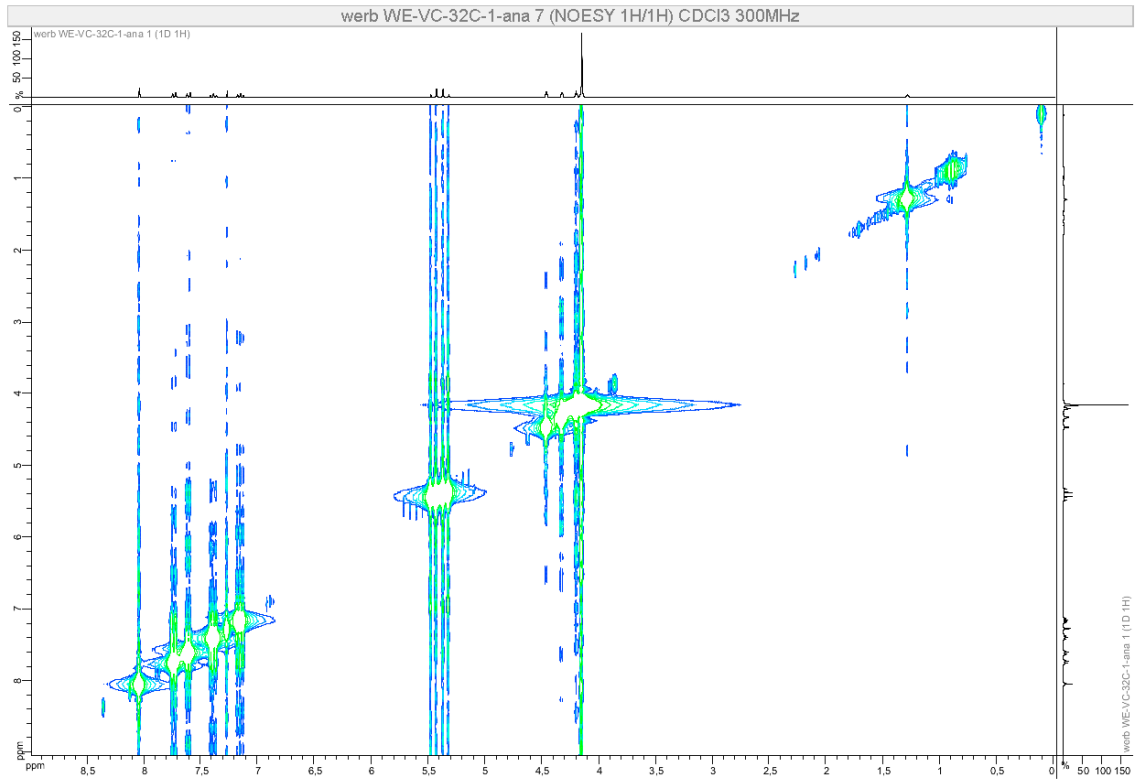


Compound (\pm)-4o

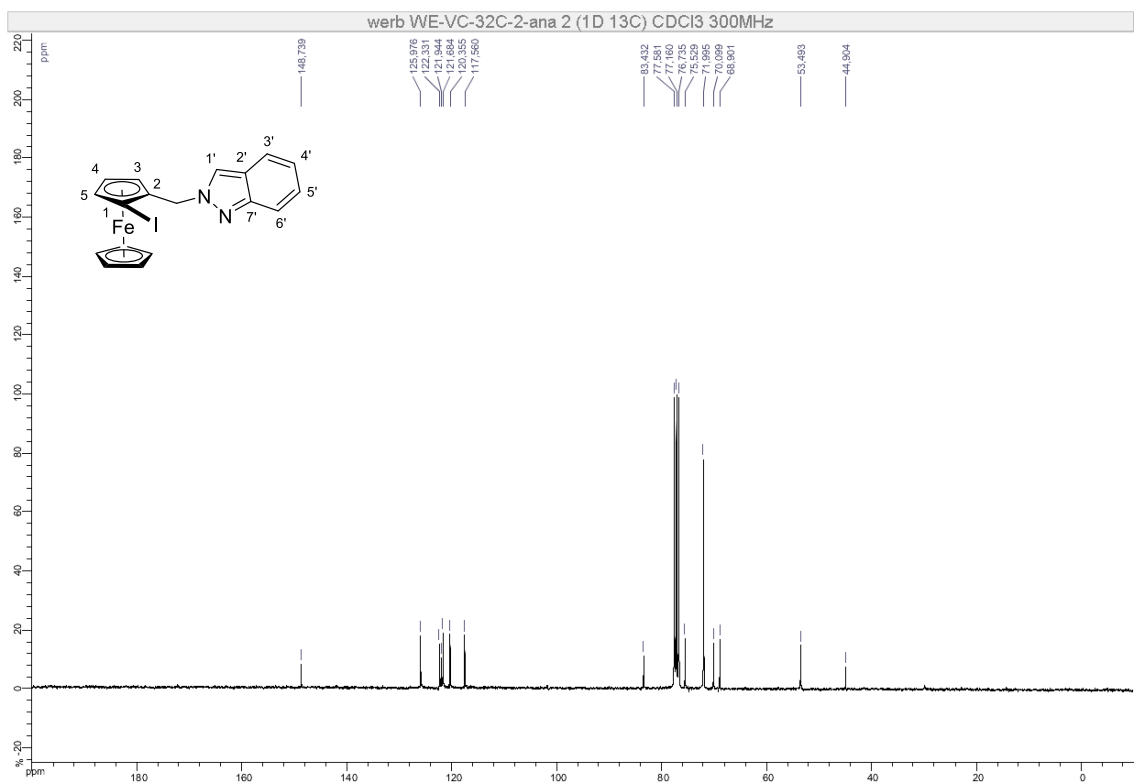
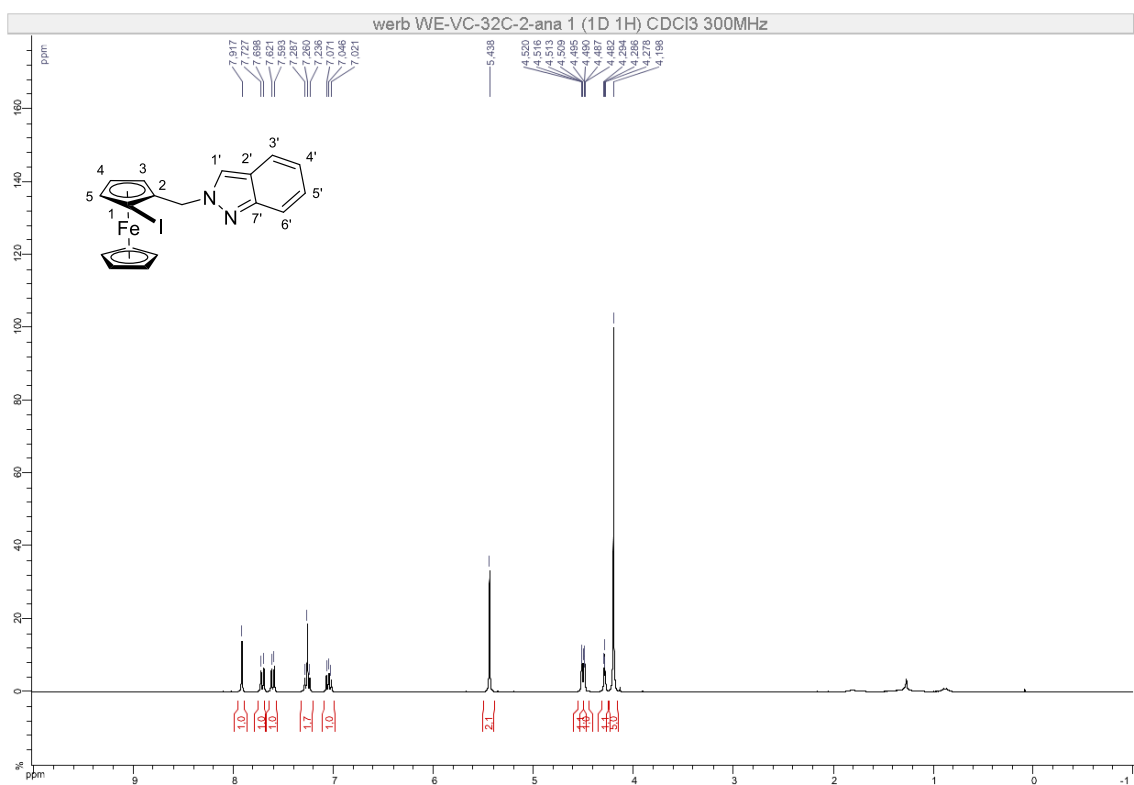


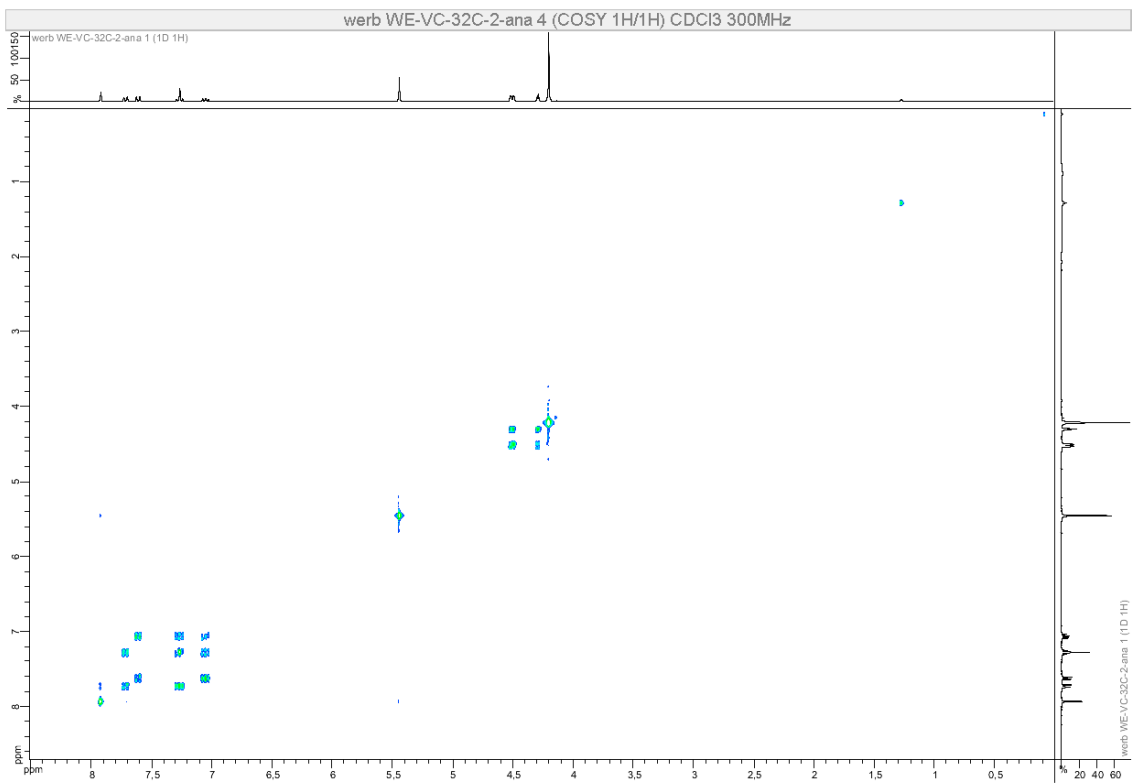
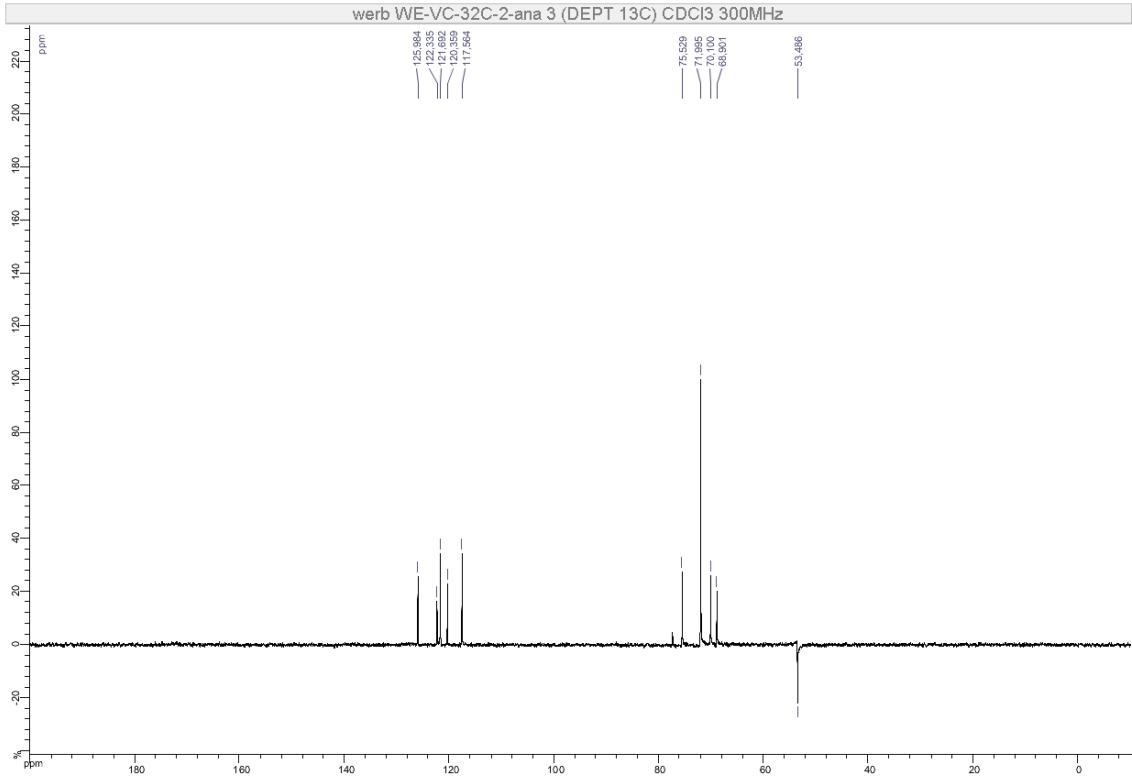


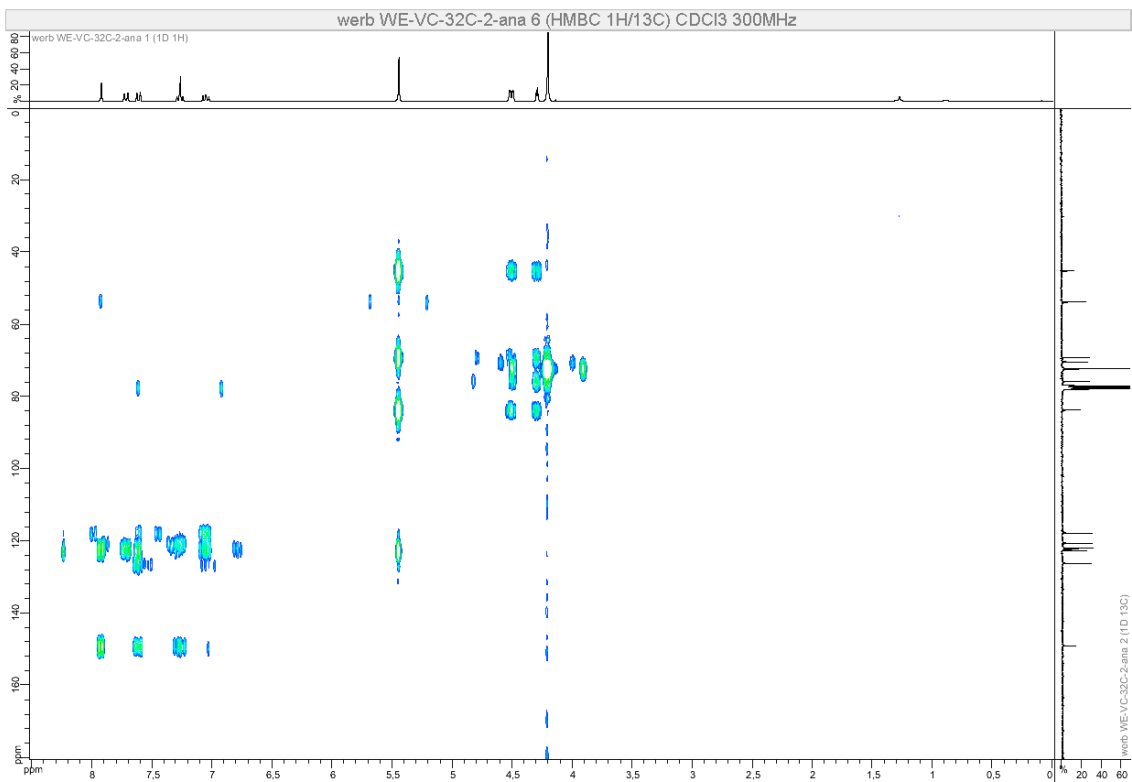
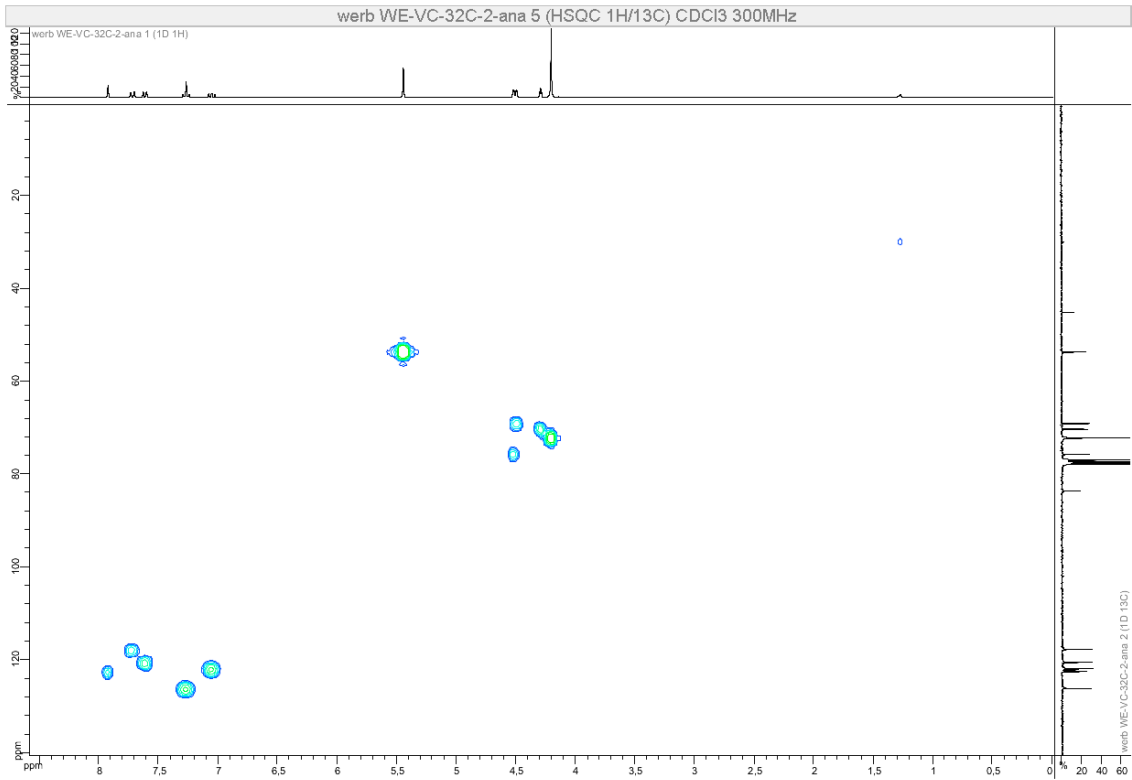


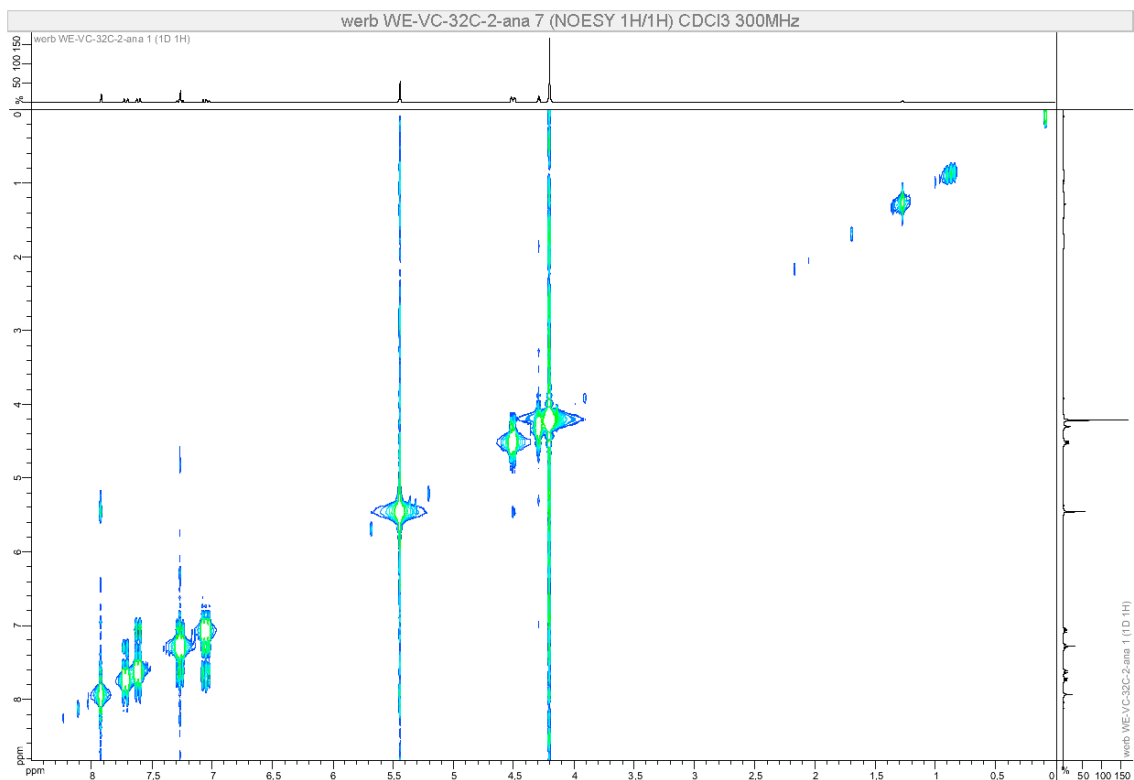


Compound (\pm)-4o'

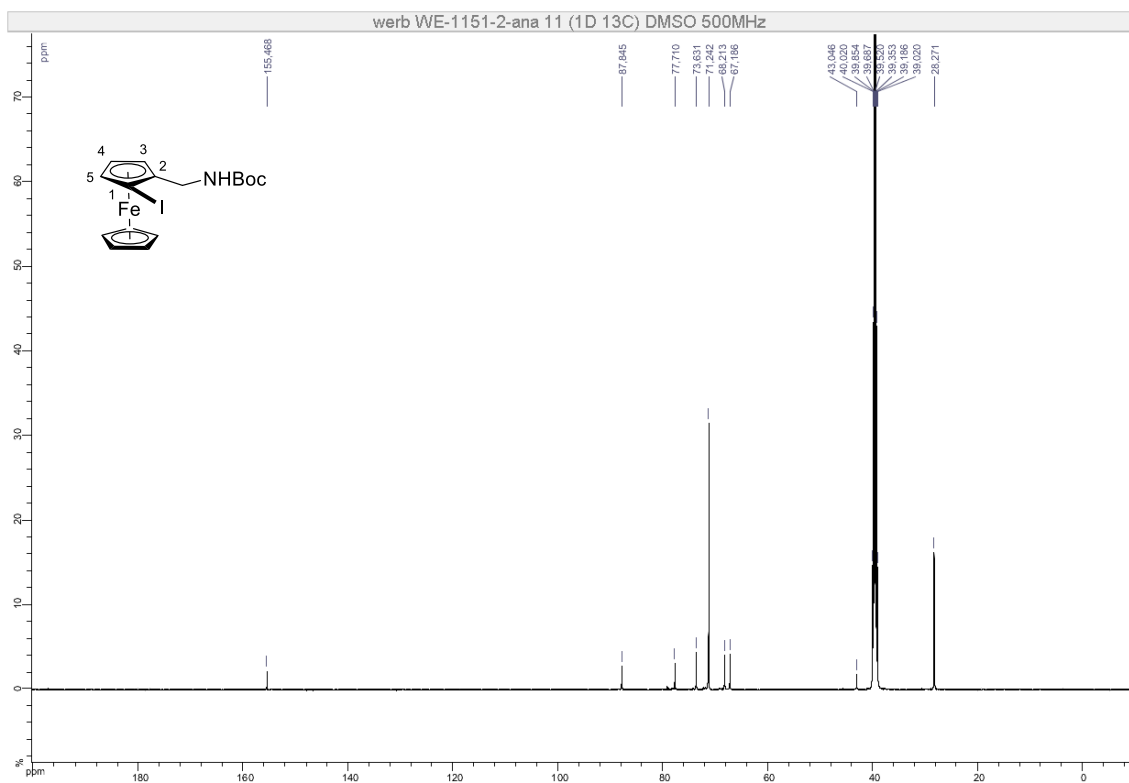
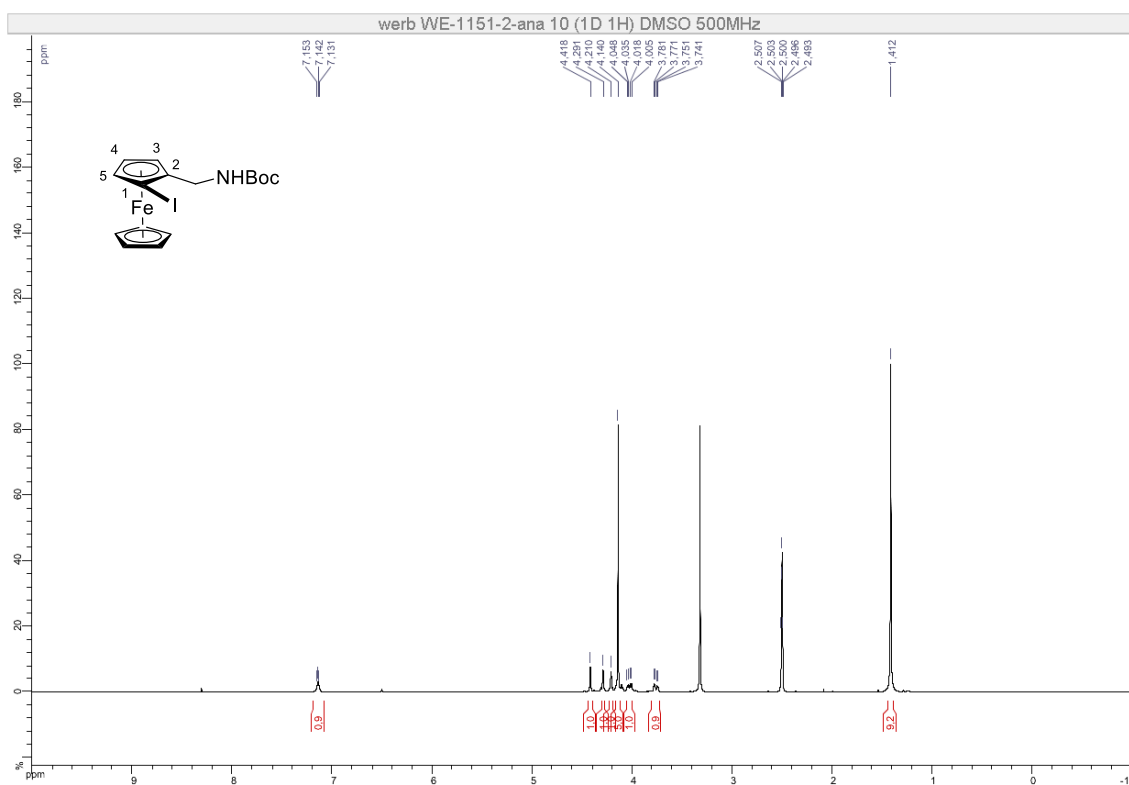


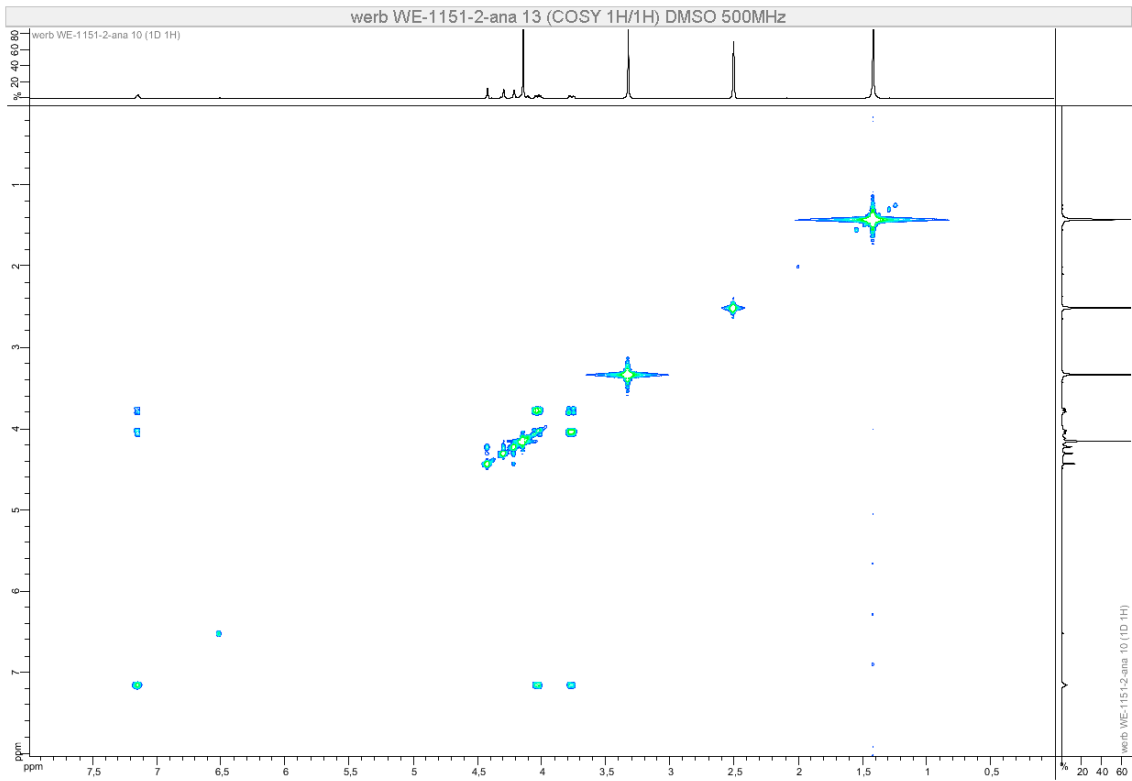
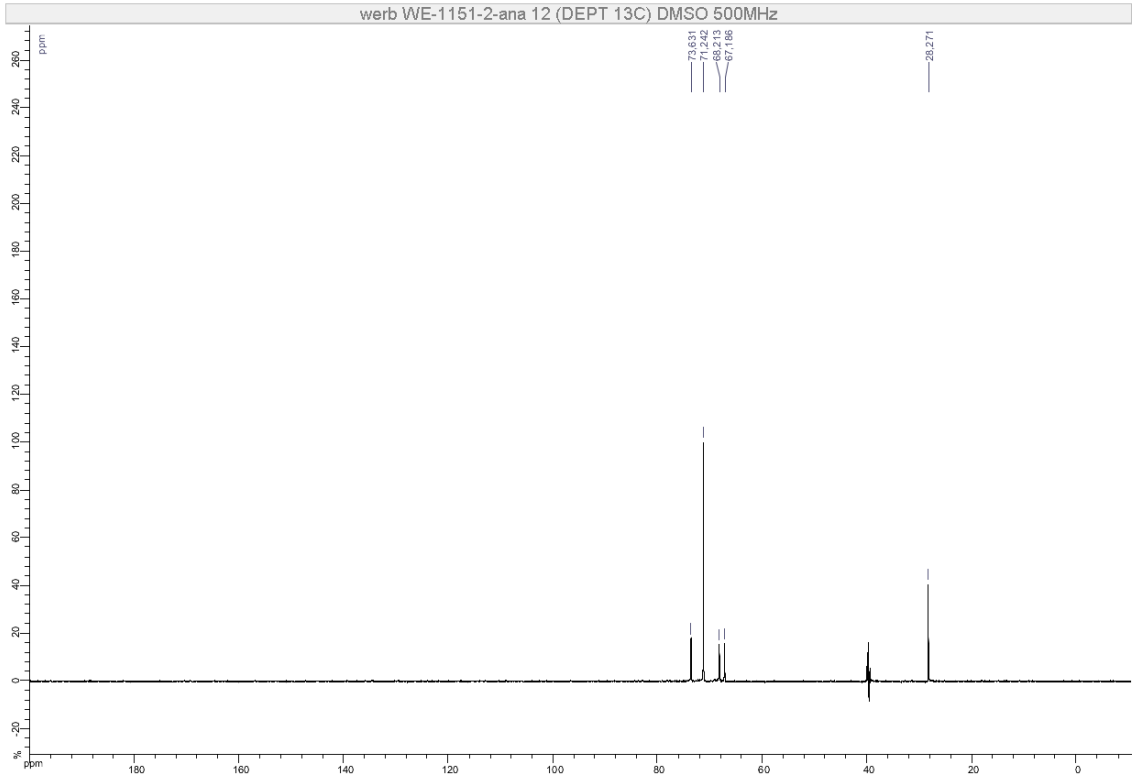


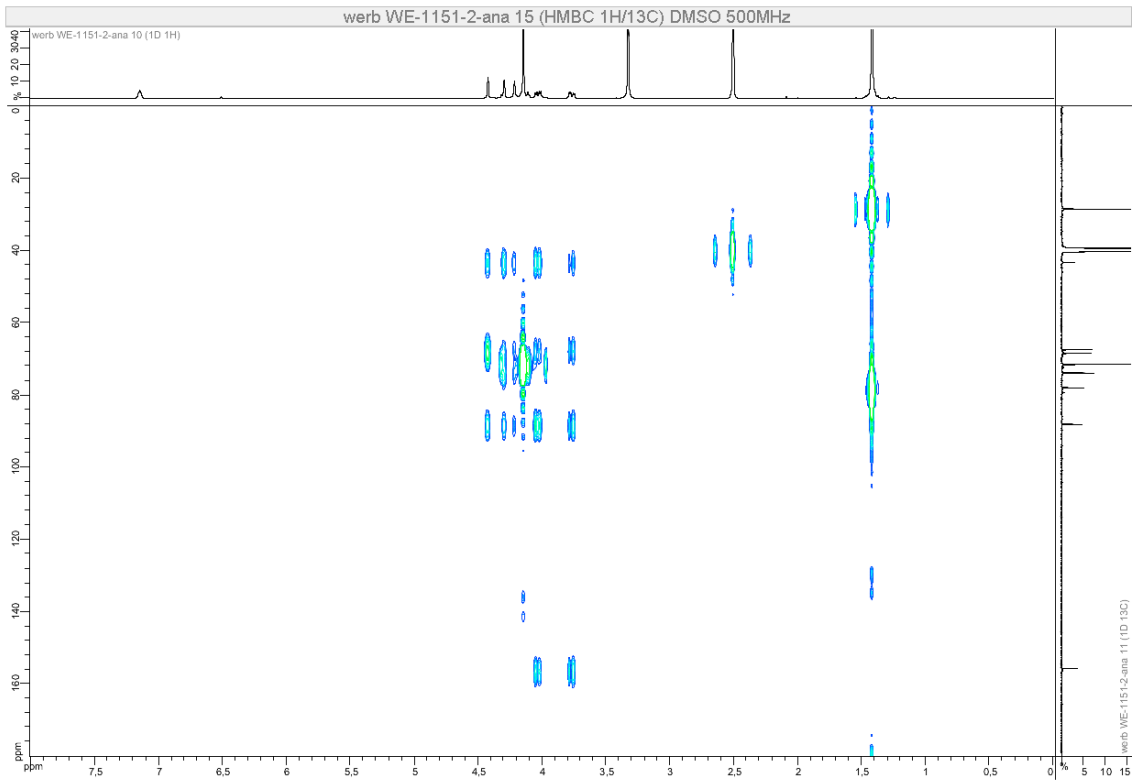
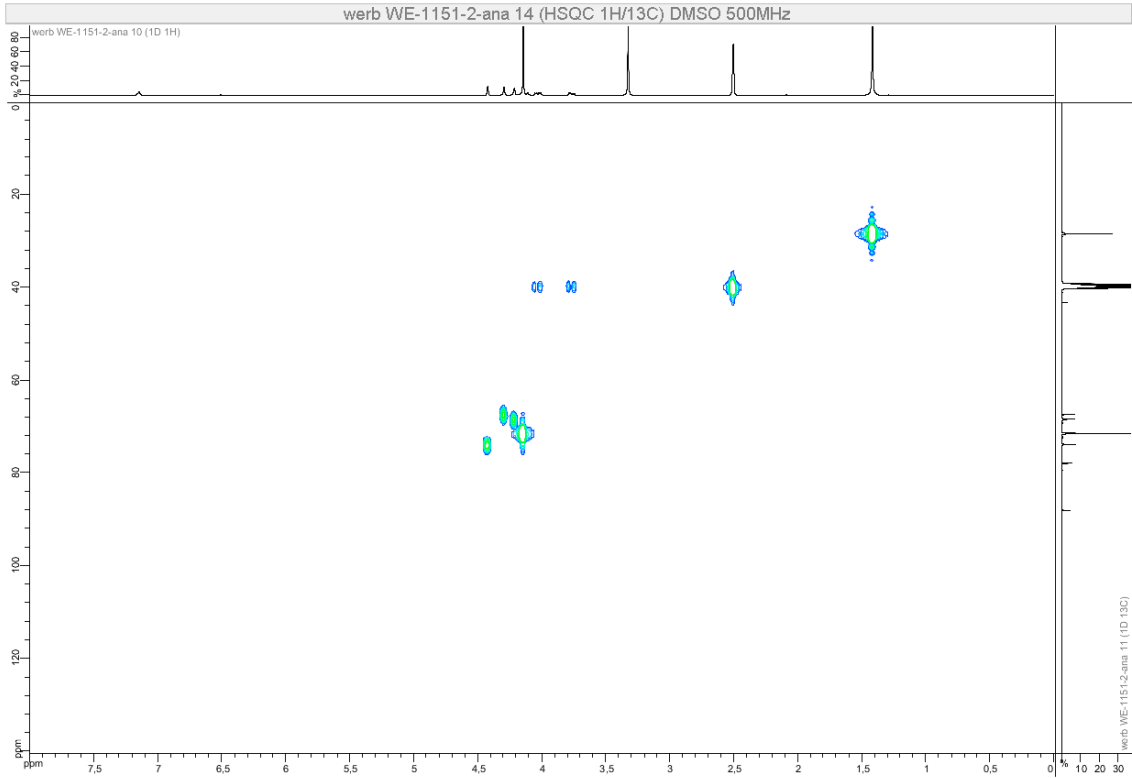


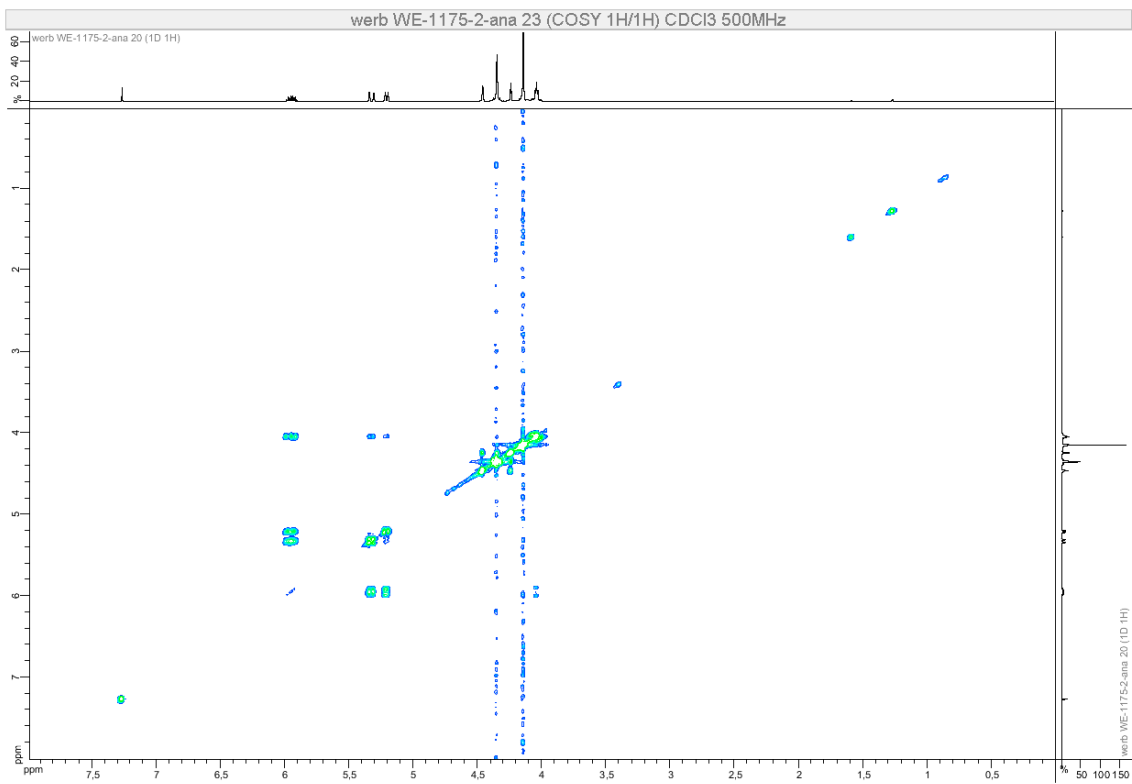
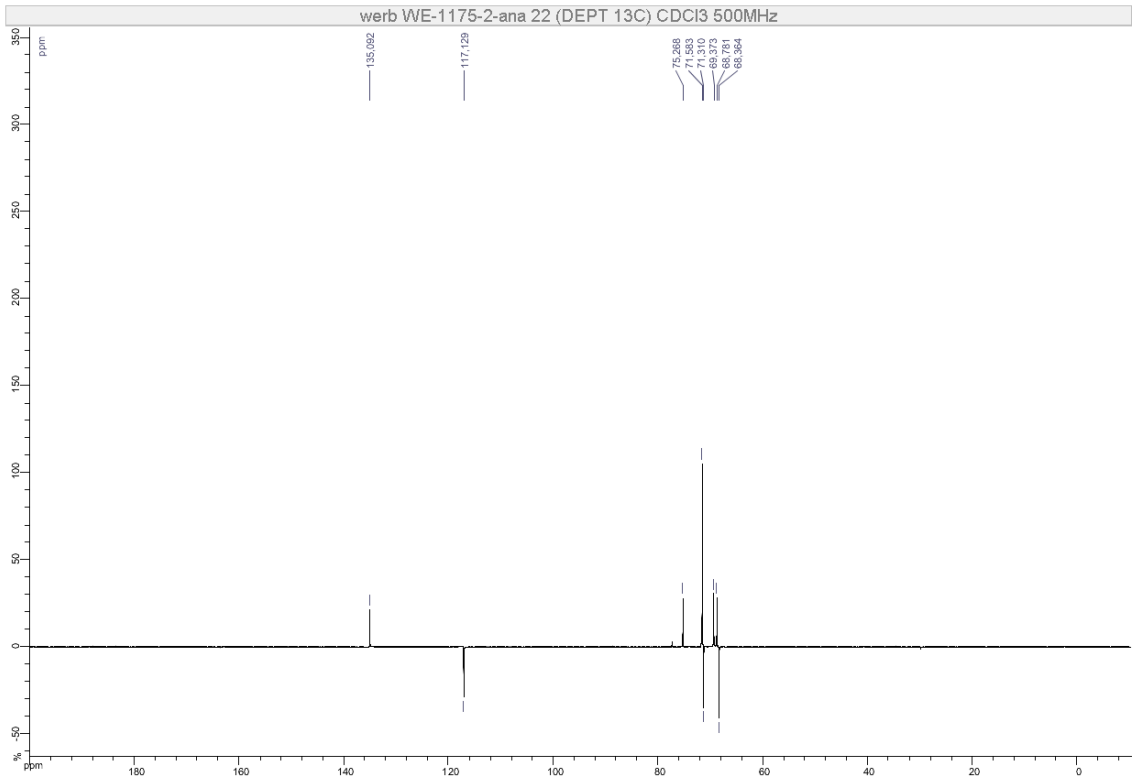


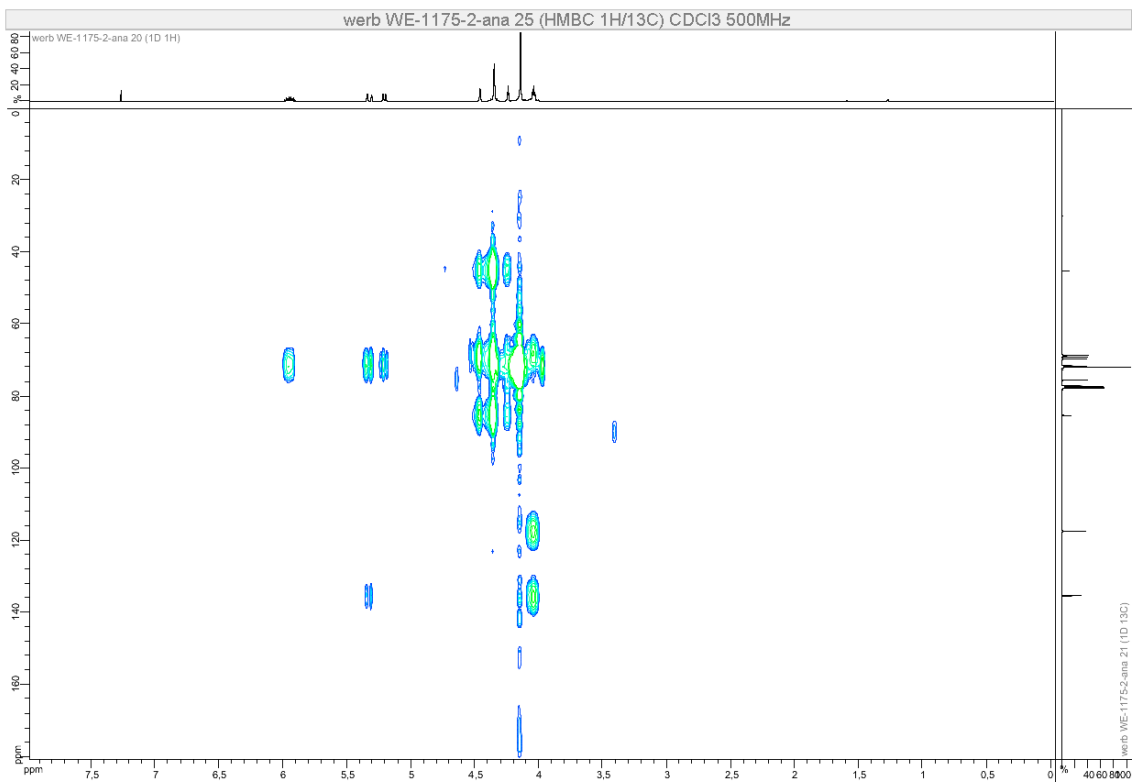
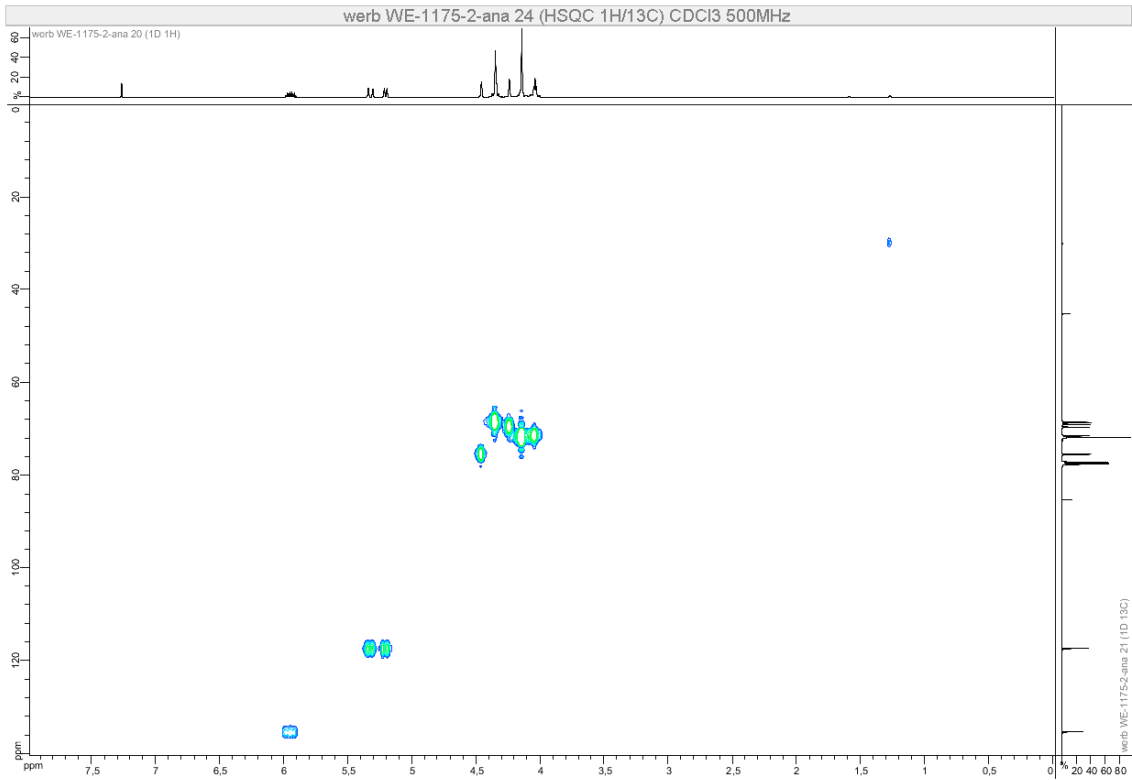
Compound (\pm)-4p

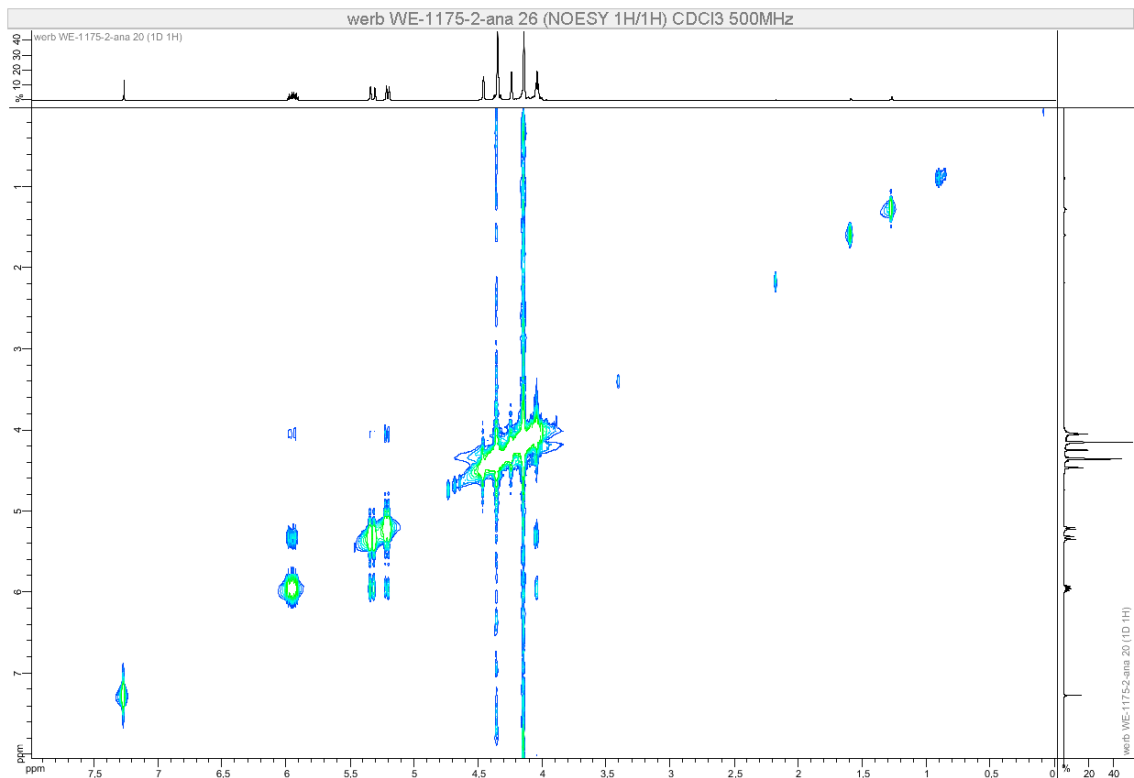




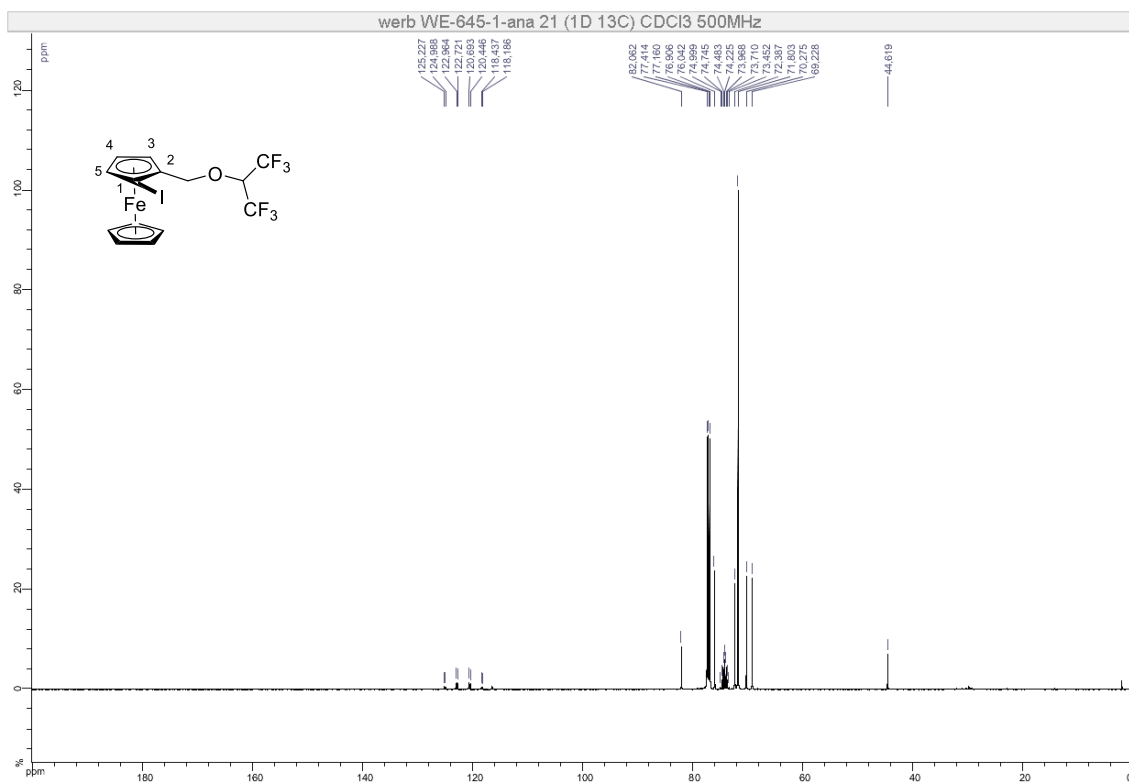
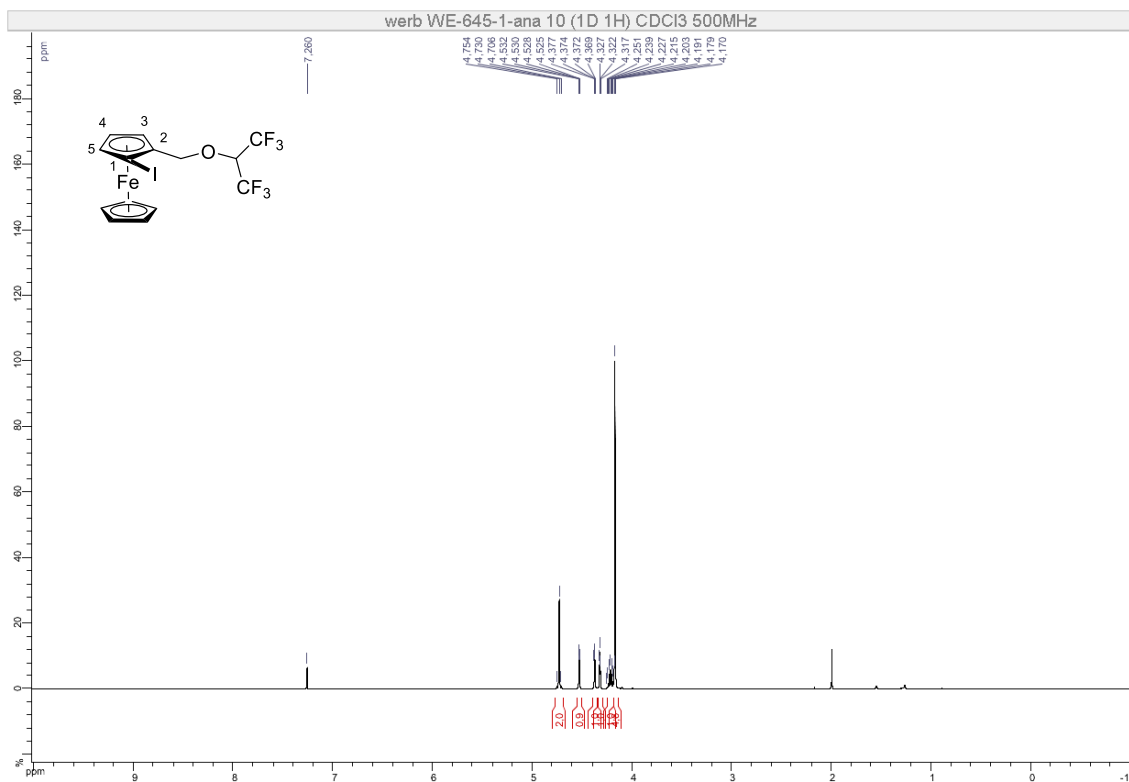


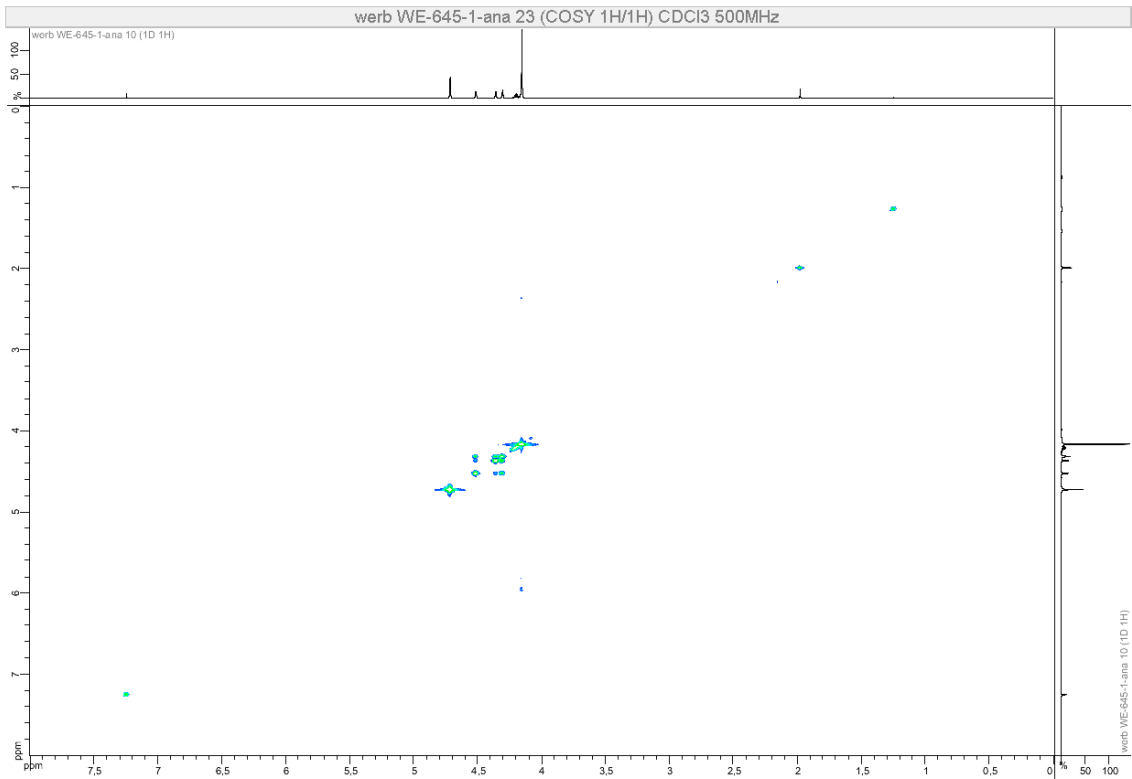
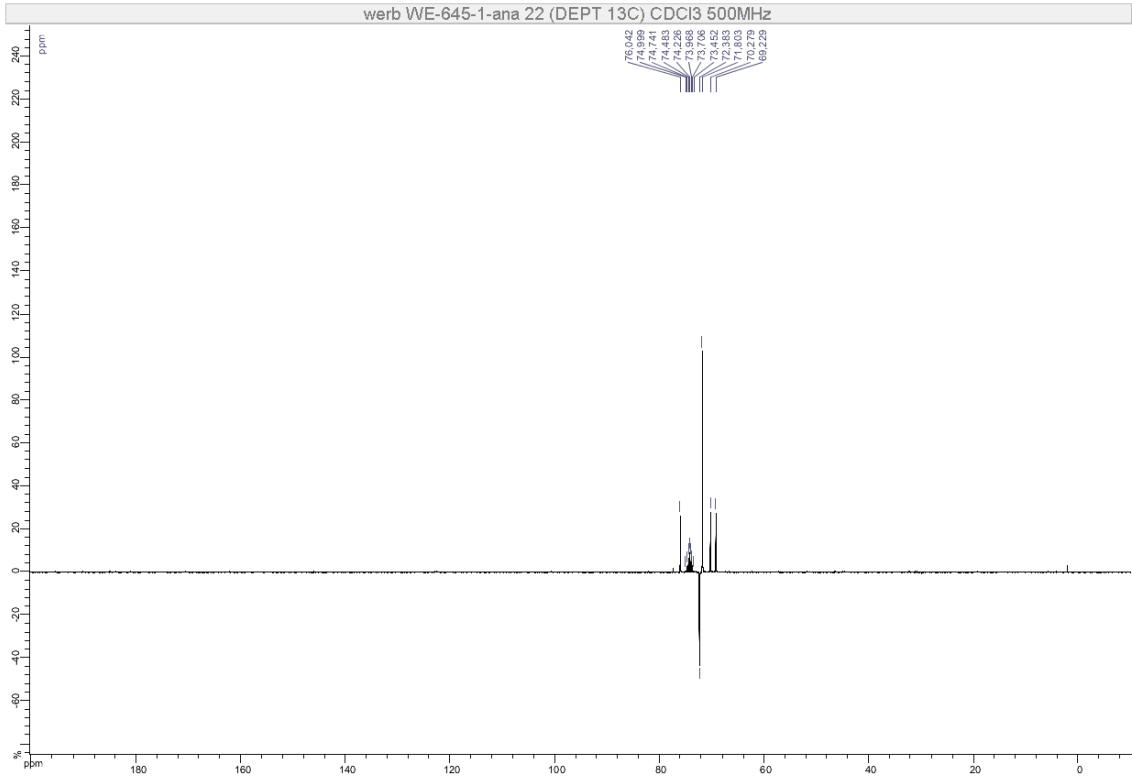


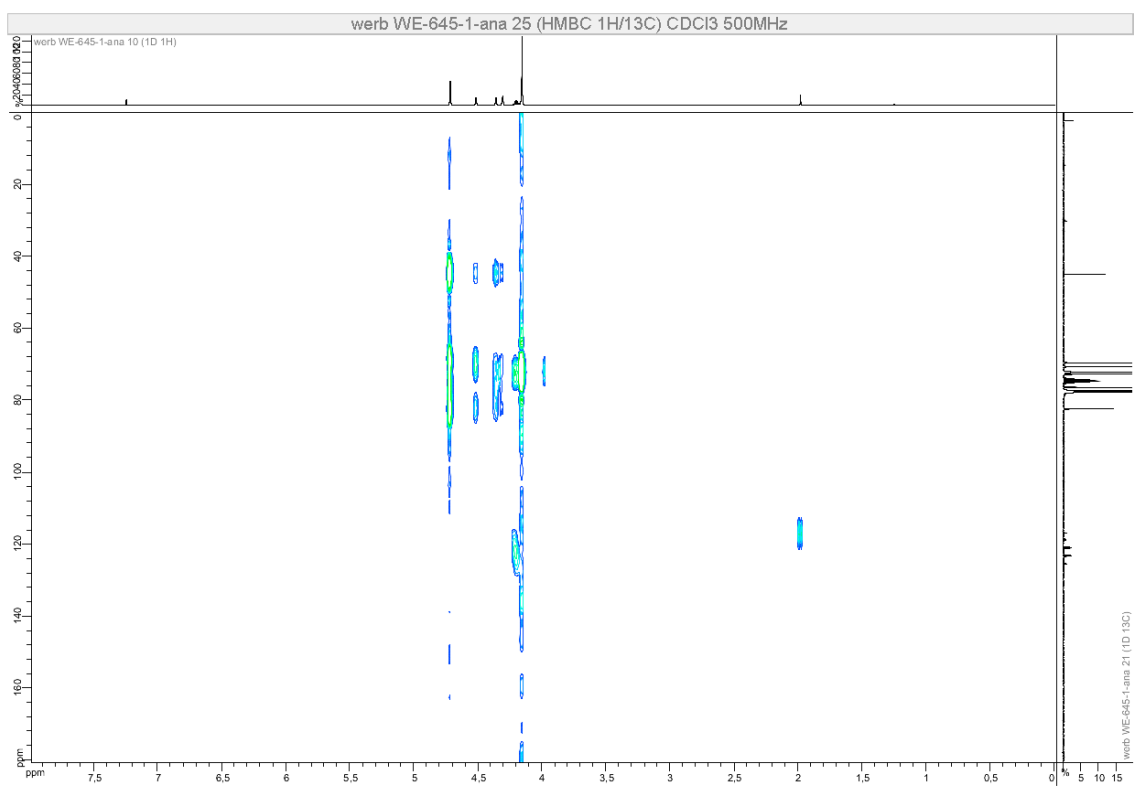
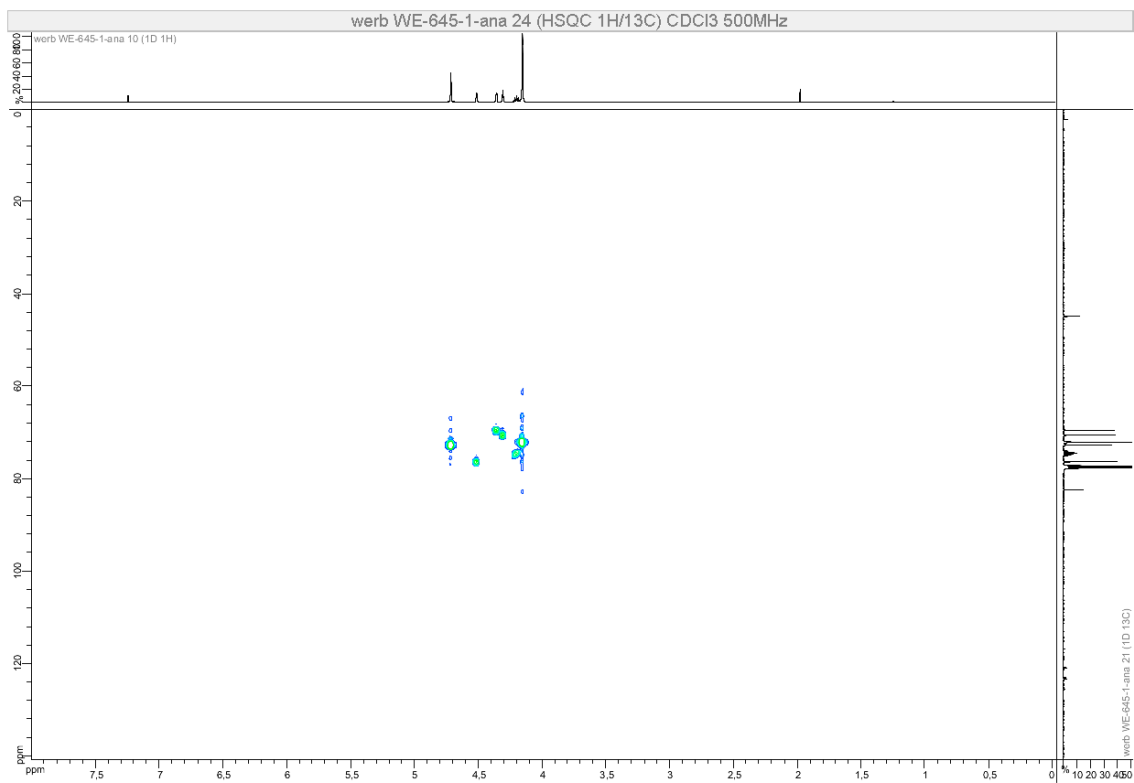


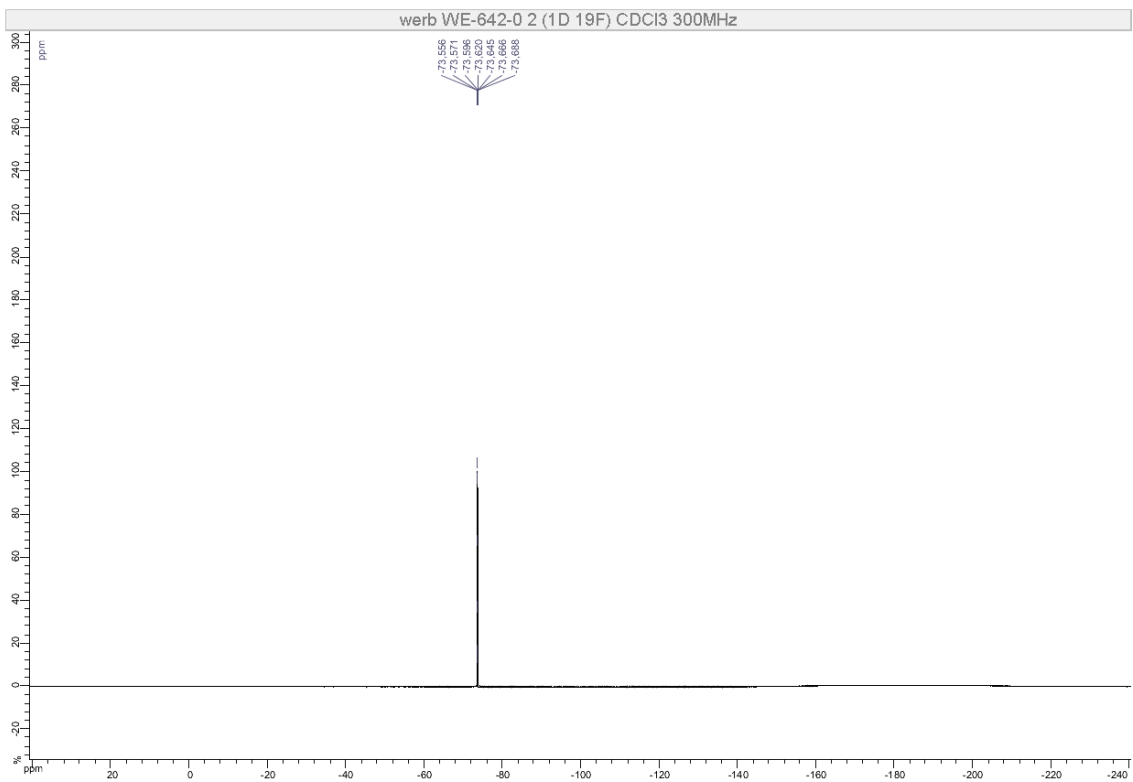
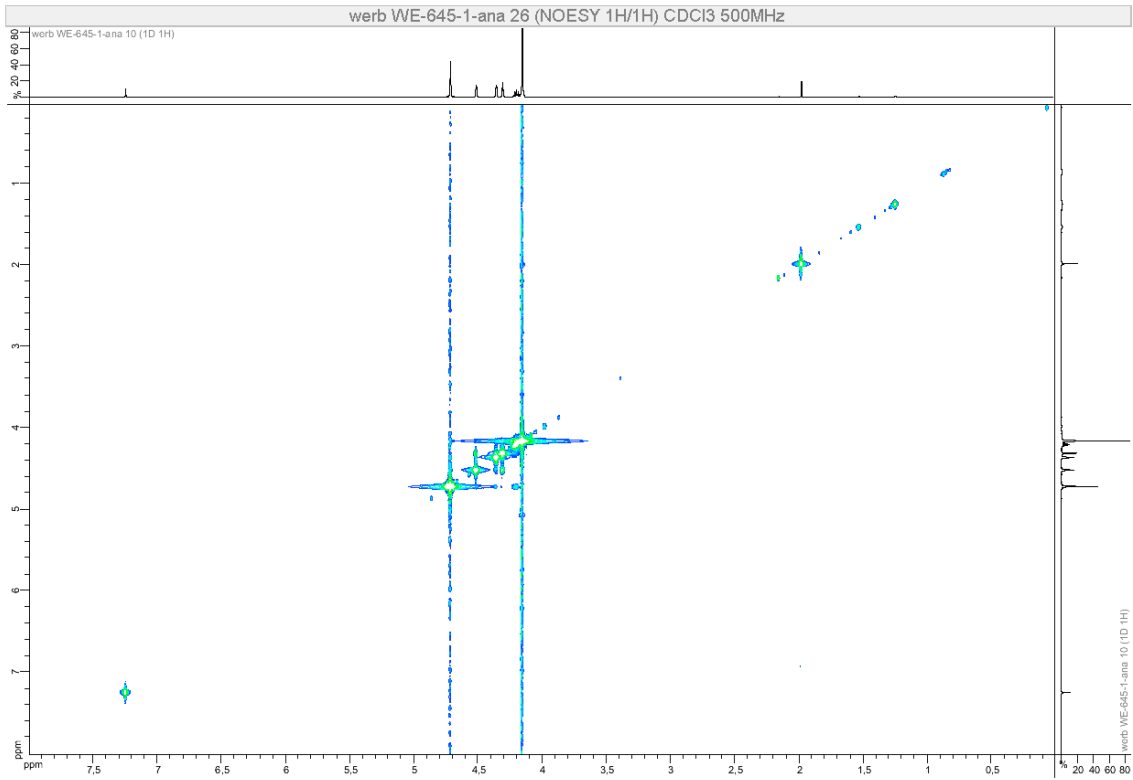


Compound (\pm)-4r

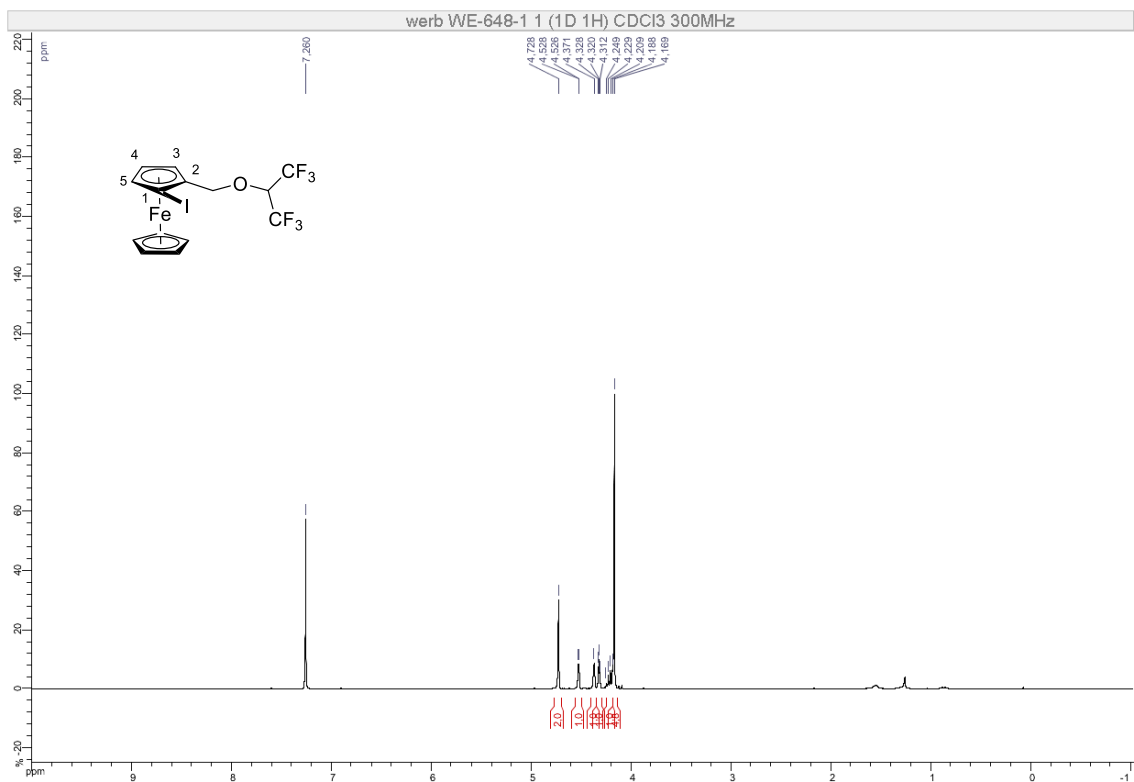




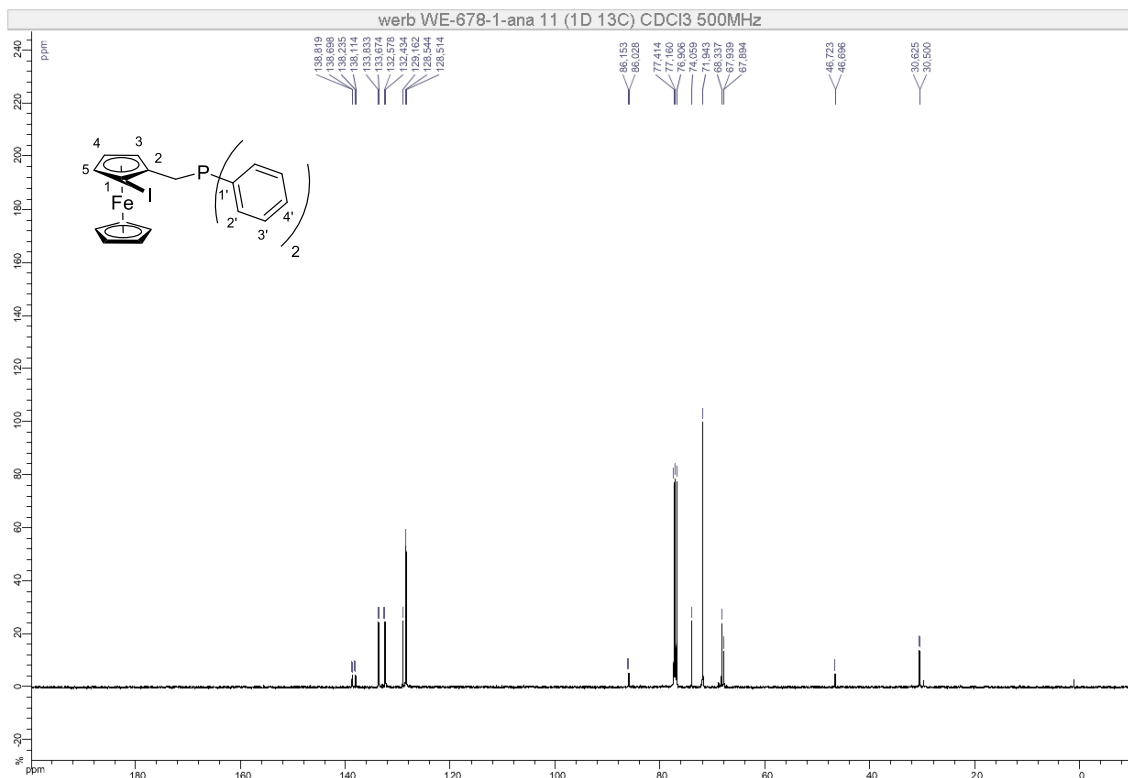
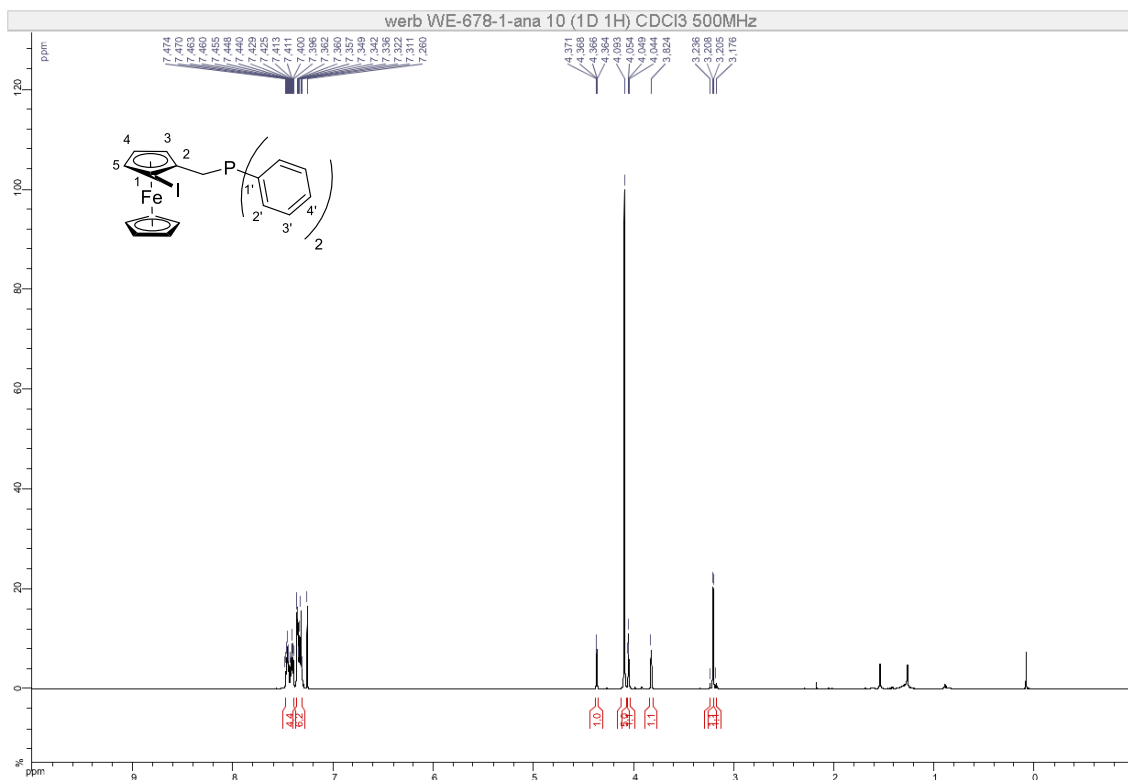


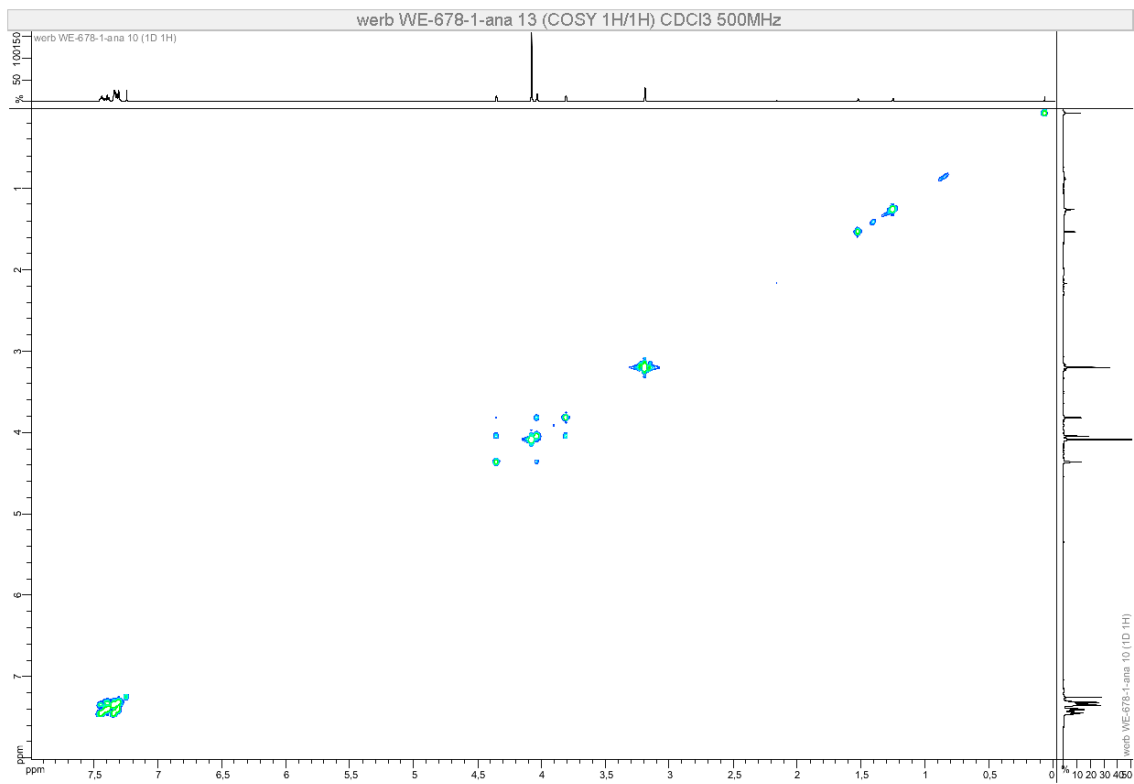
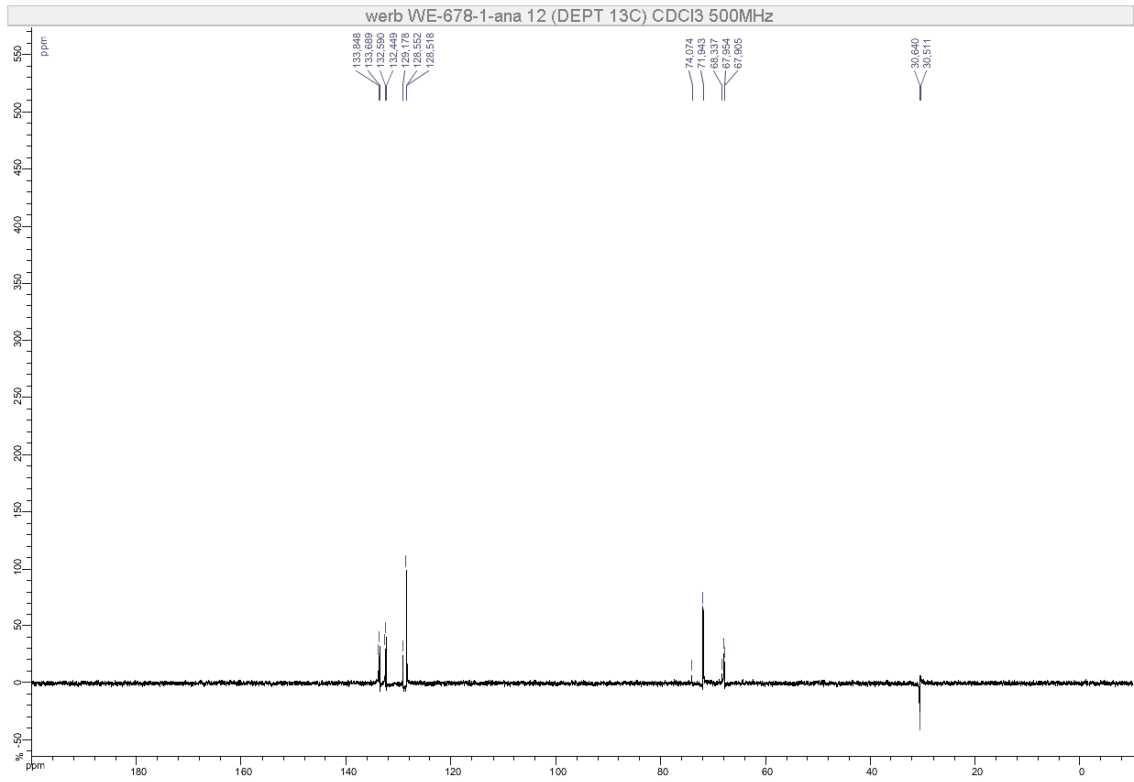


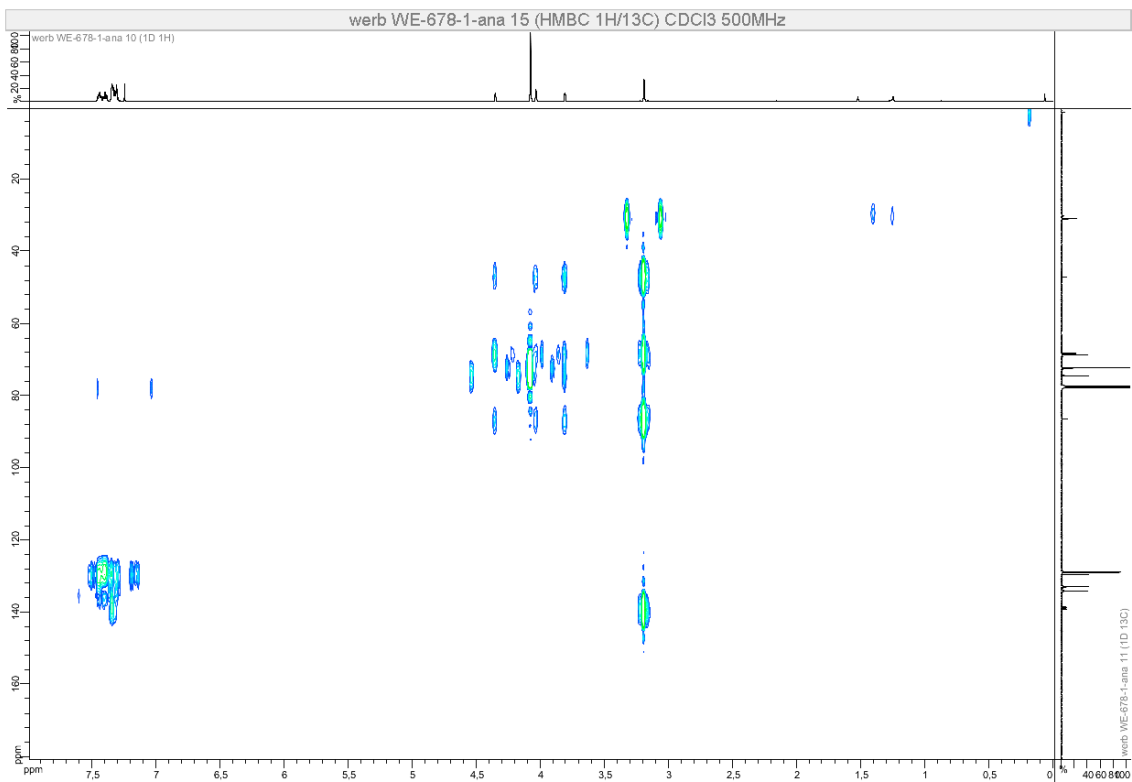
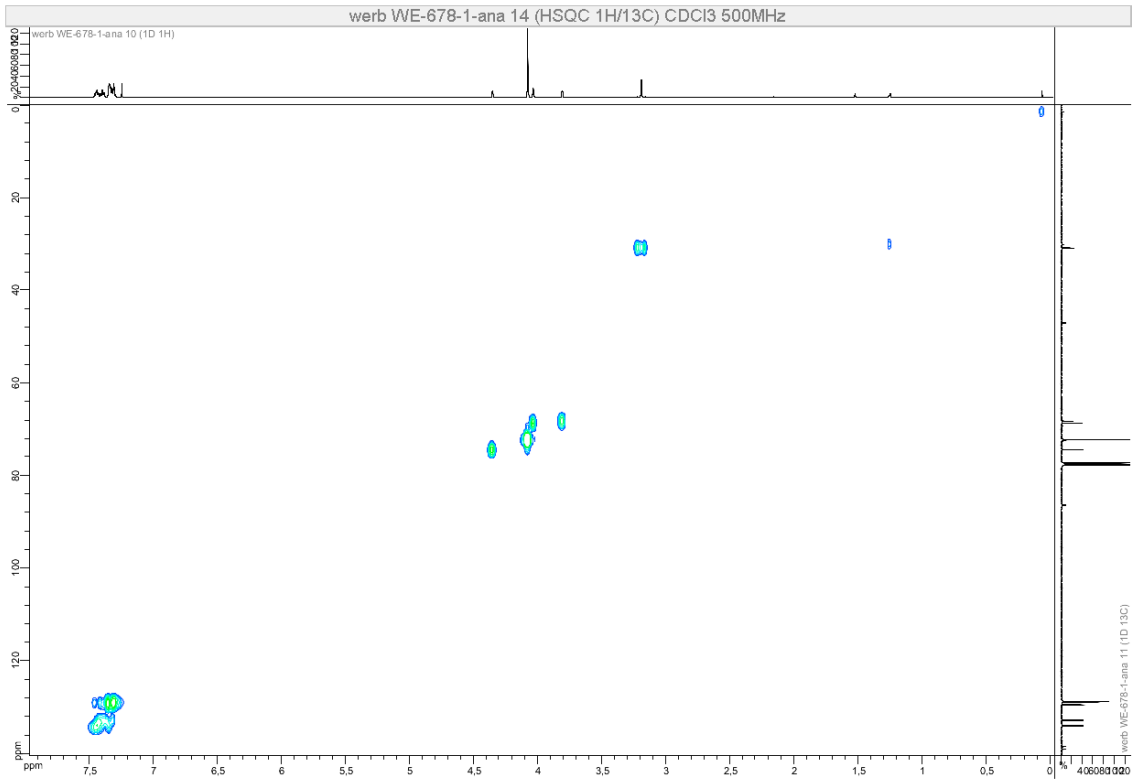
Compound (*S_p*)-4r

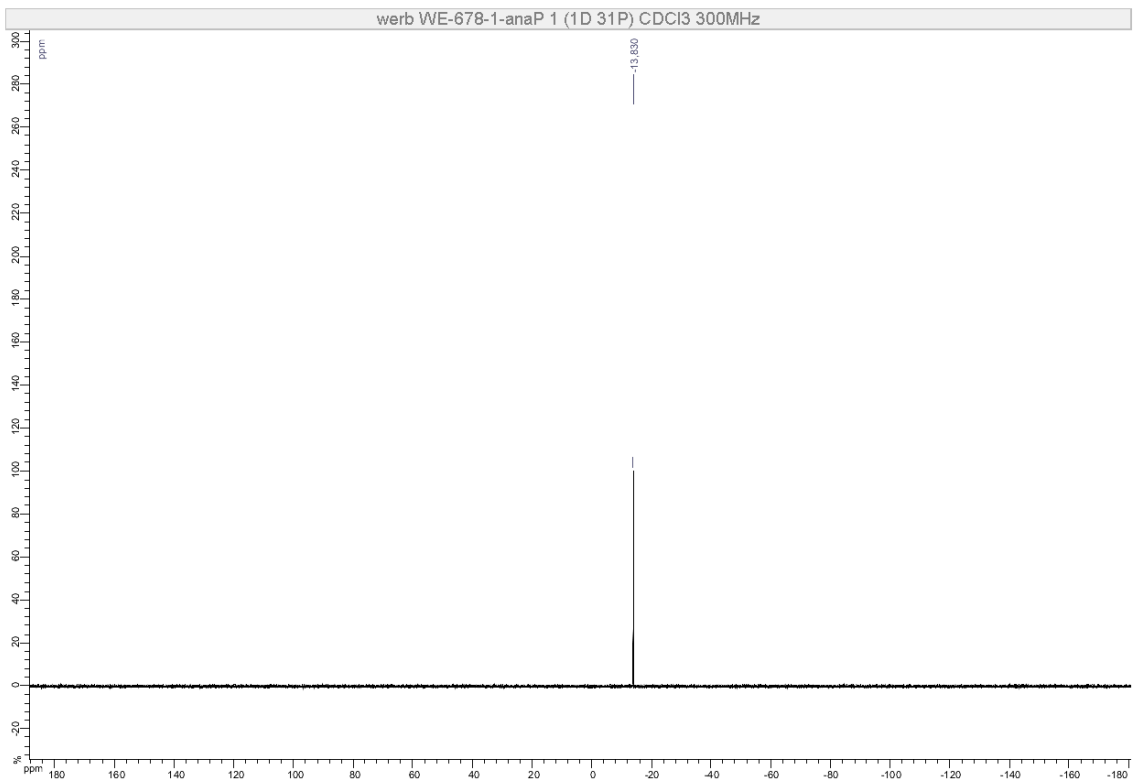
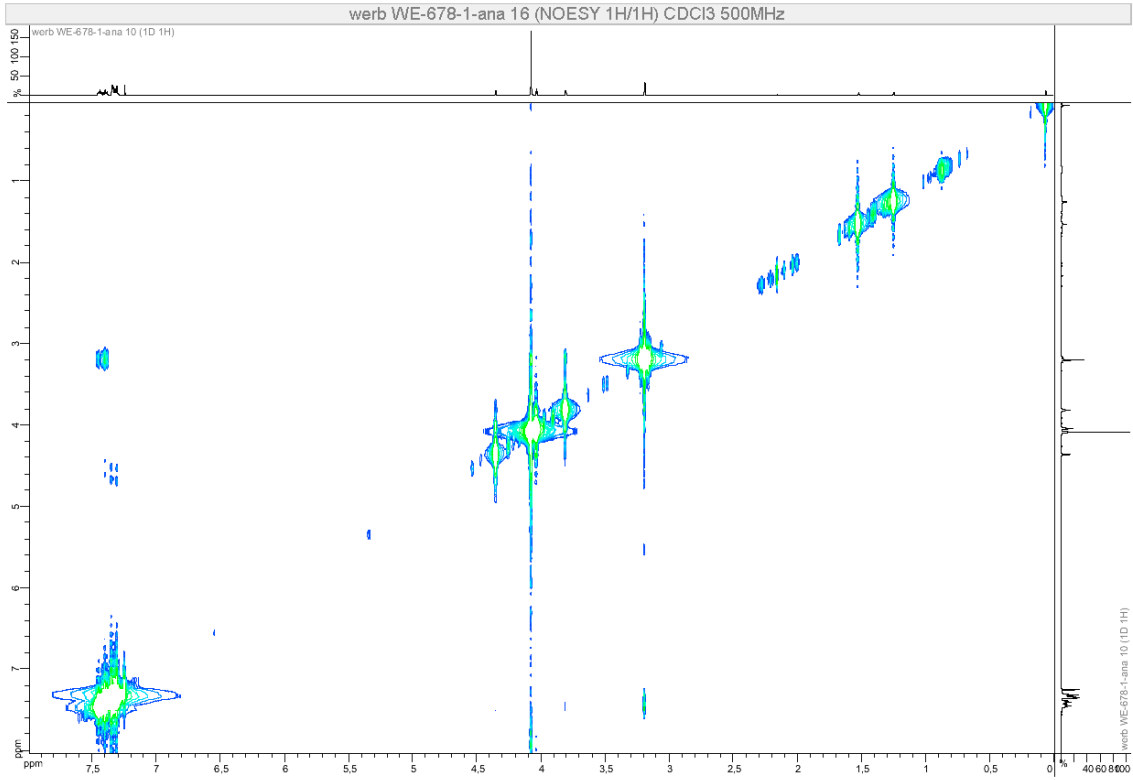


Compound (\pm)-4s

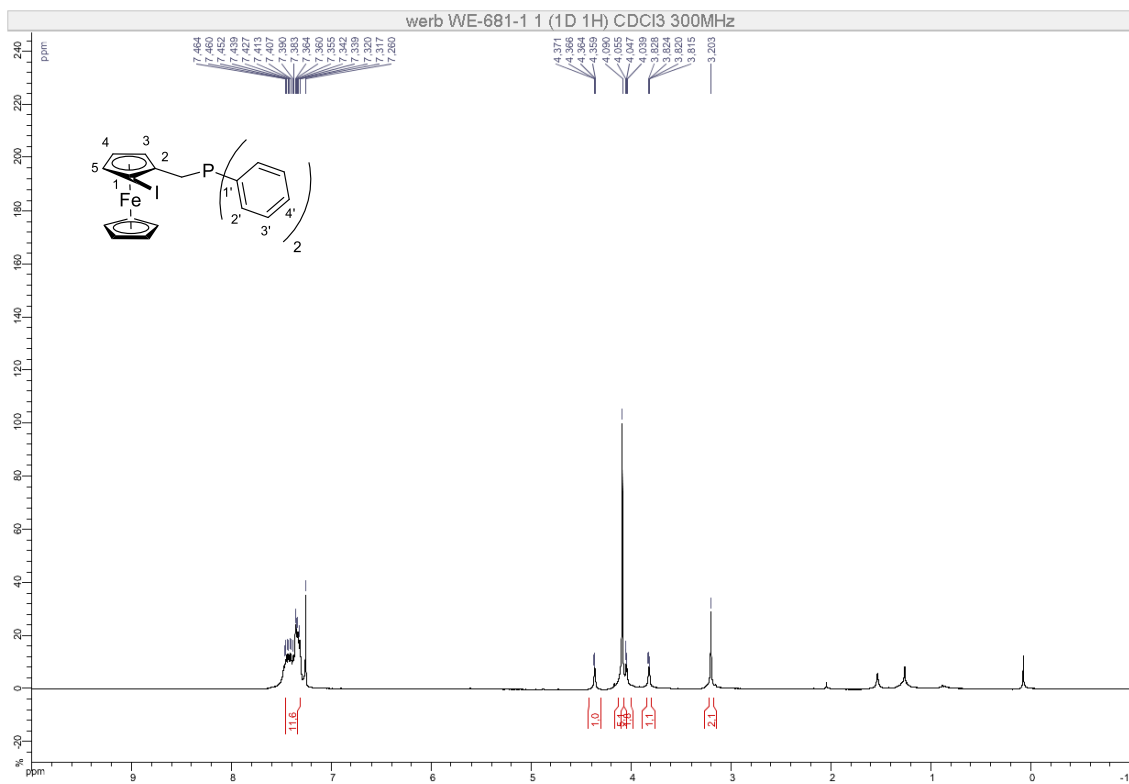




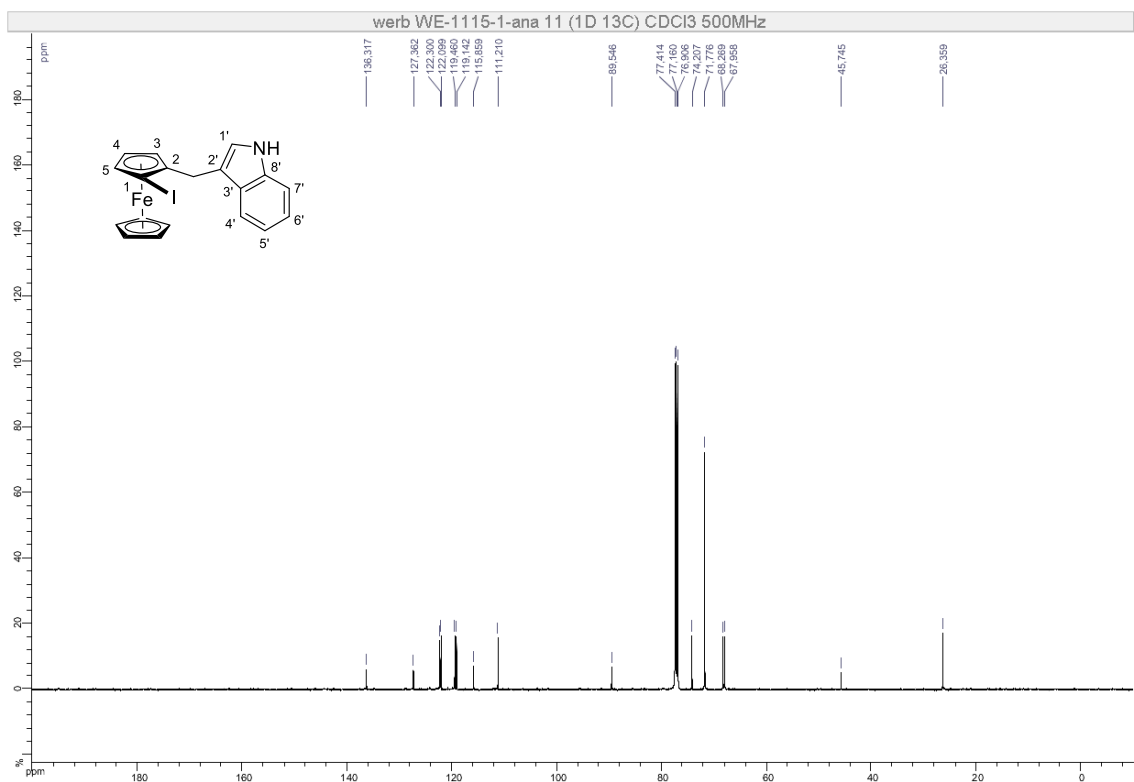
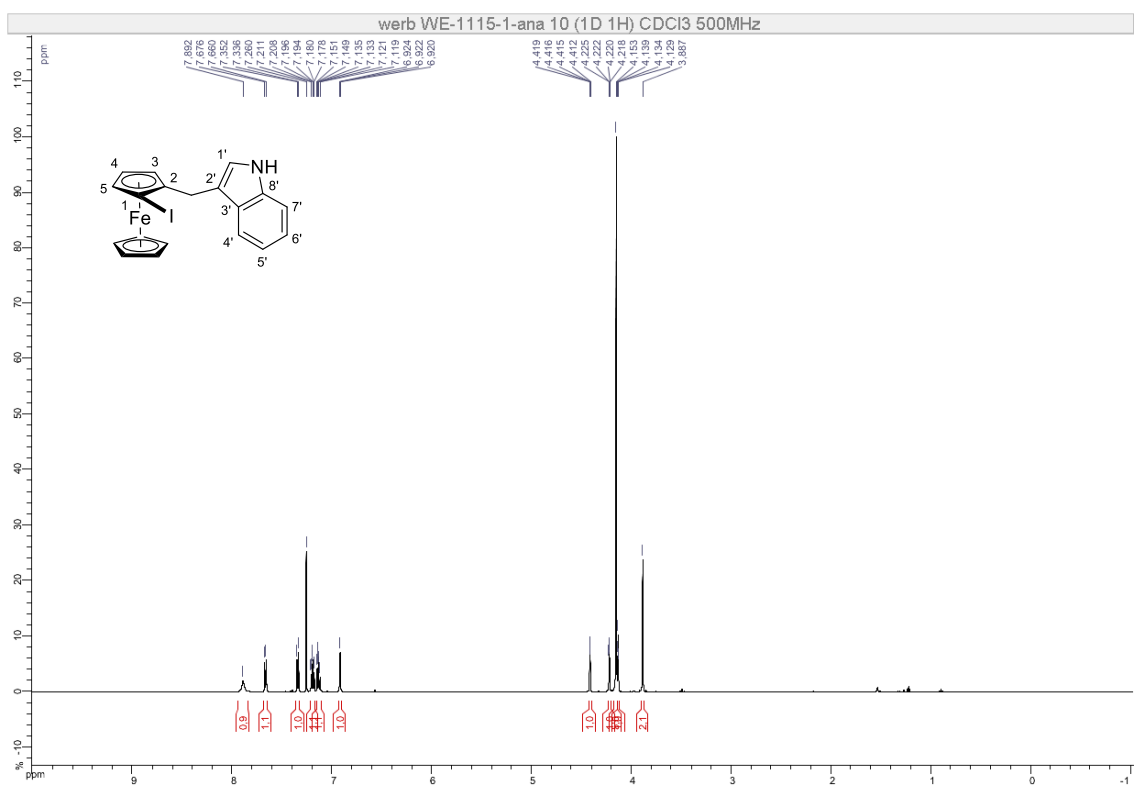


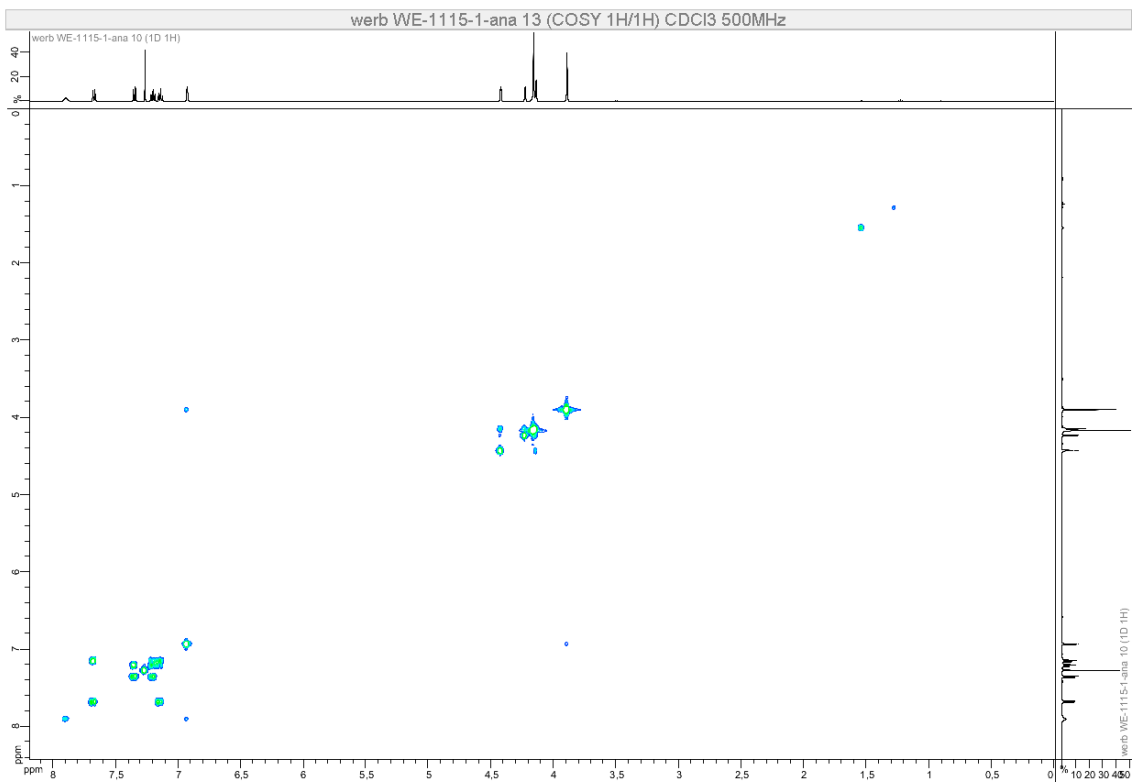
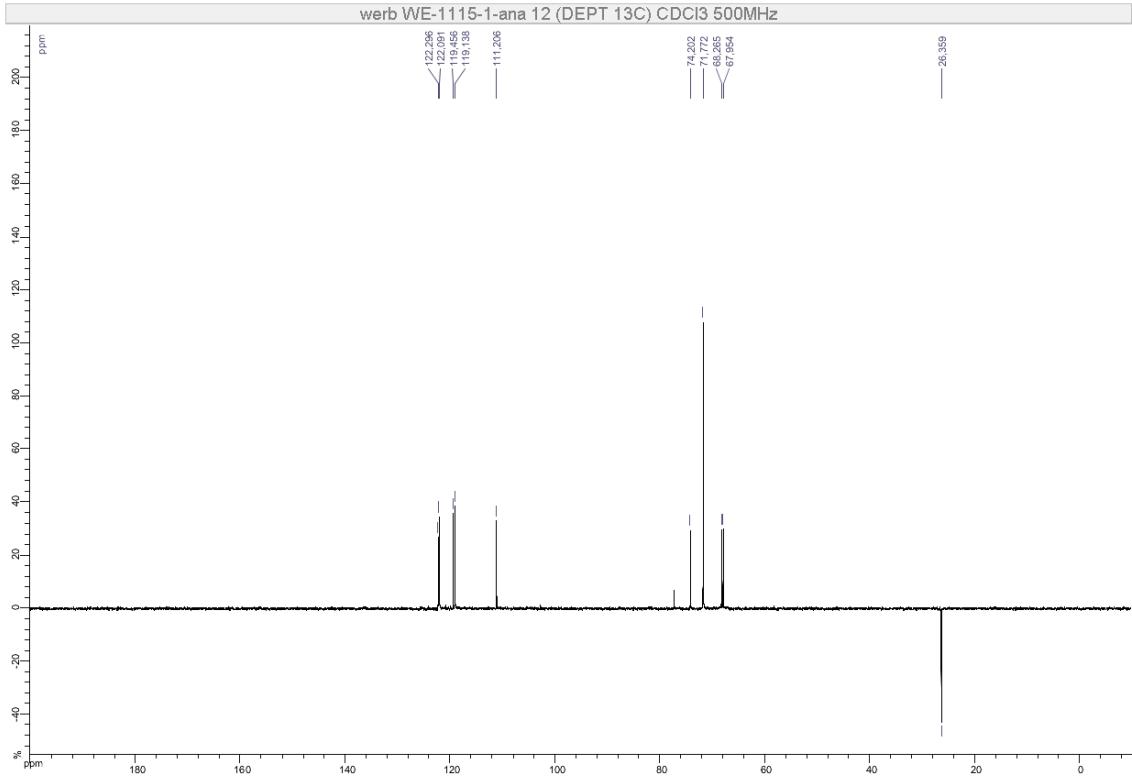


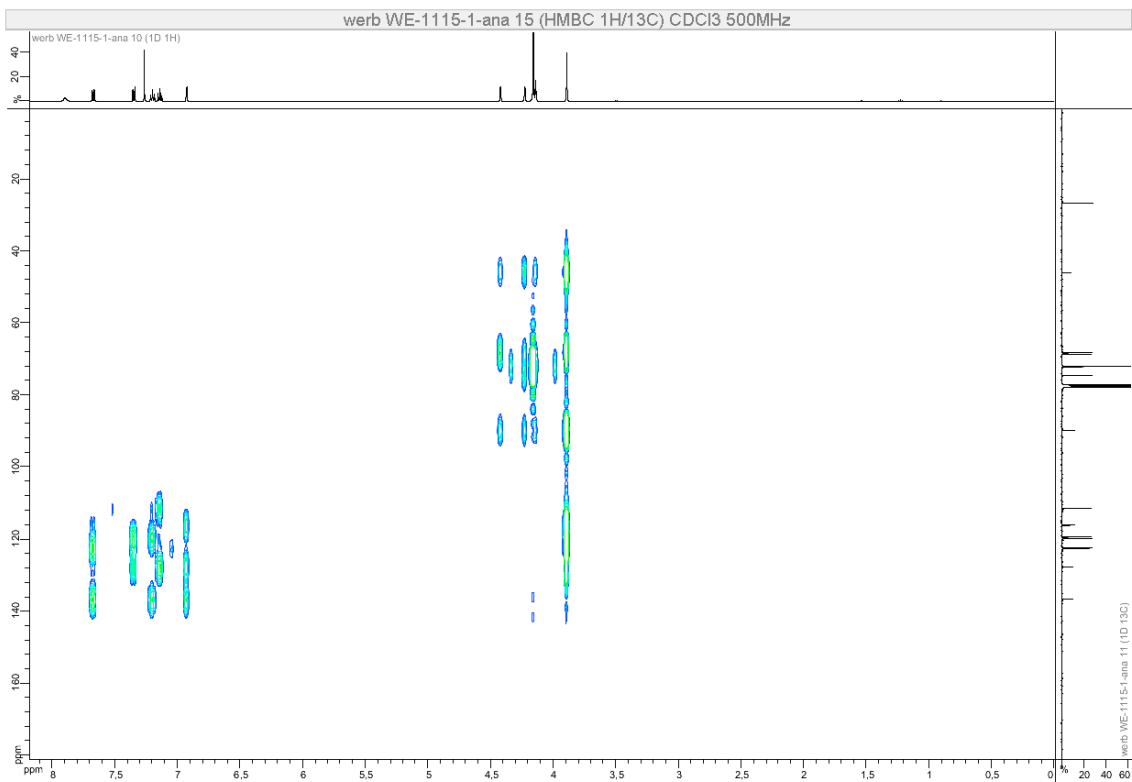
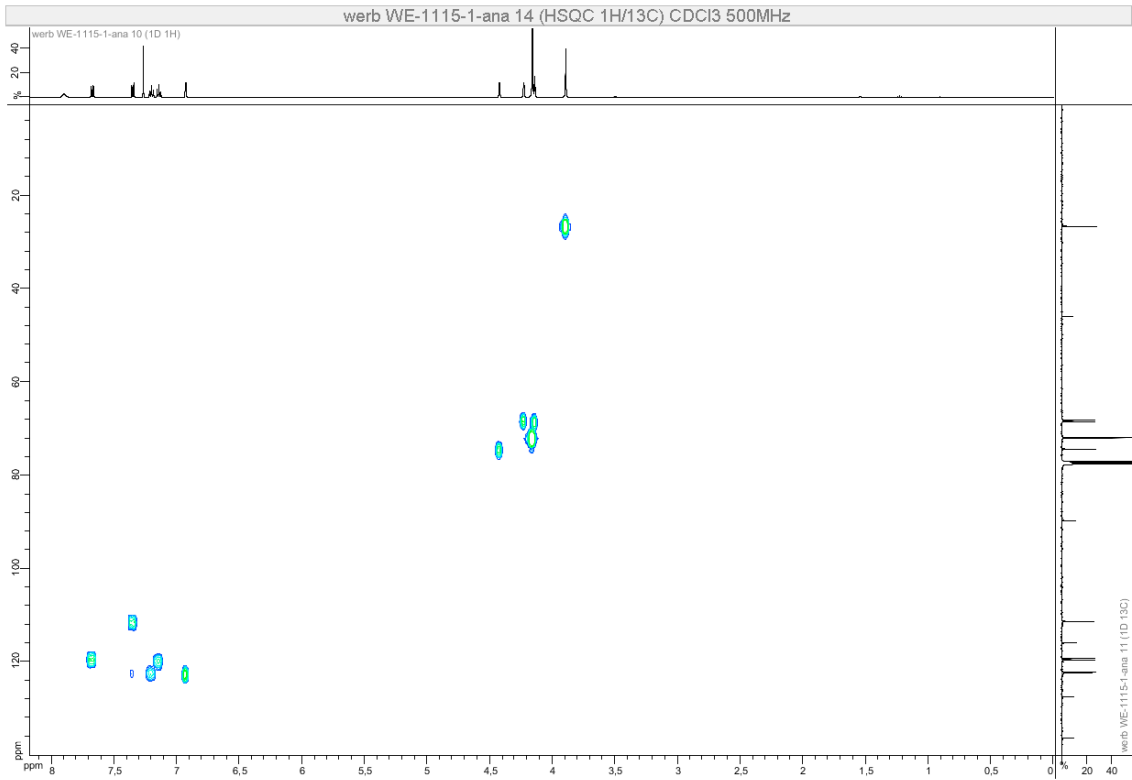
Compound (*S_p*)-4s

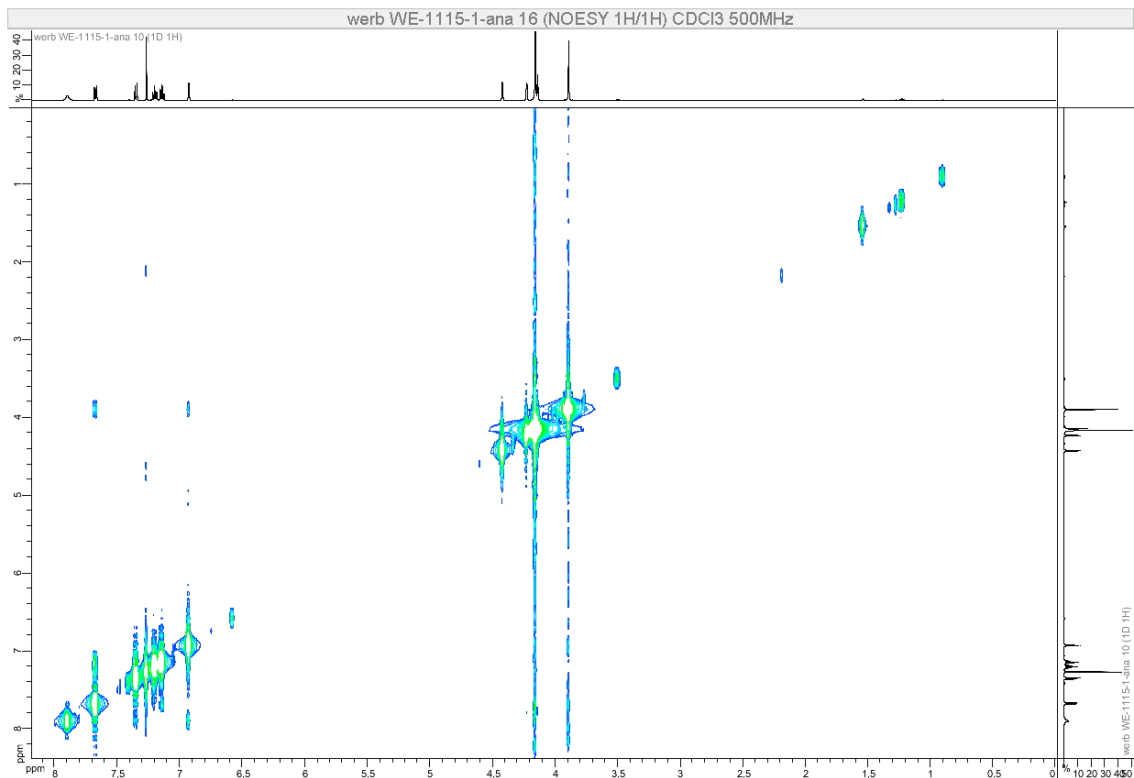


Compound (\pm)-4t

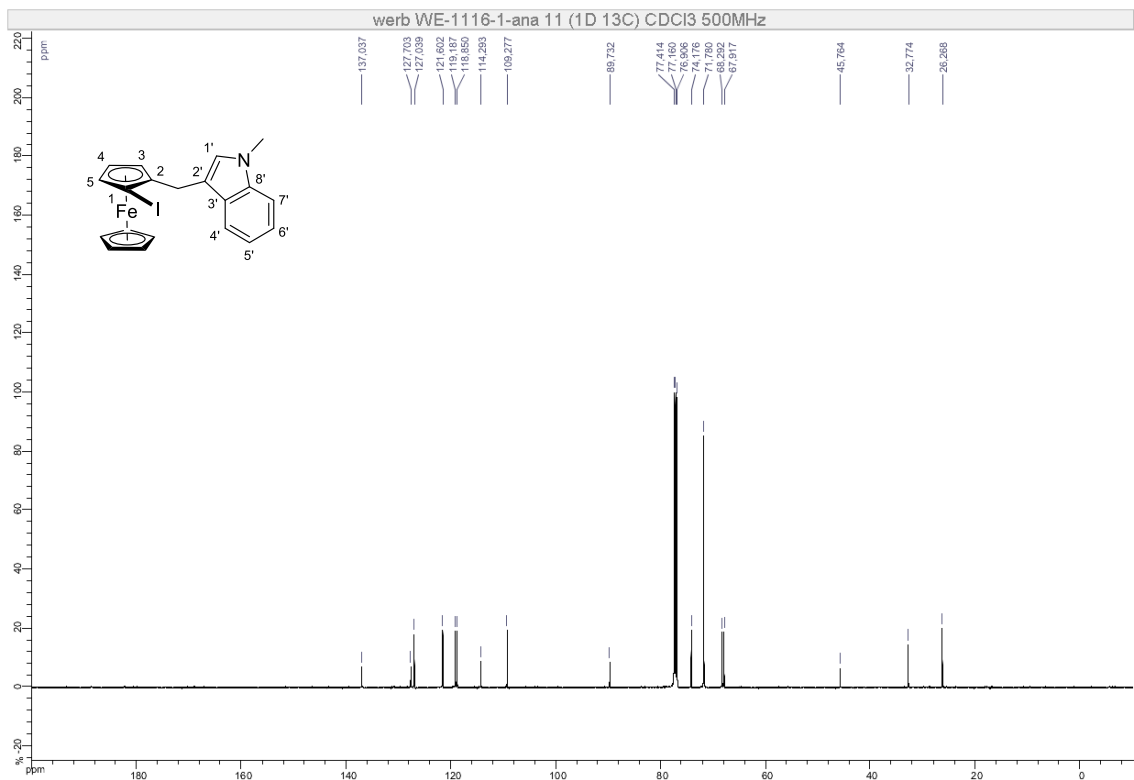
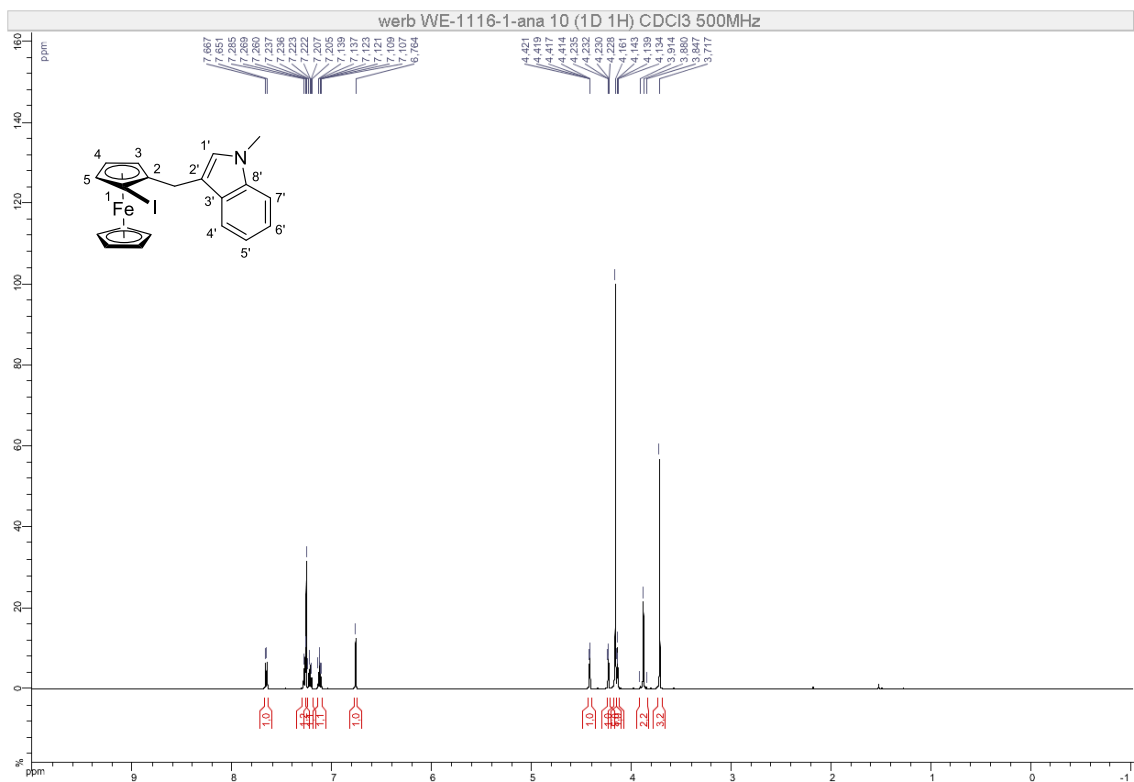


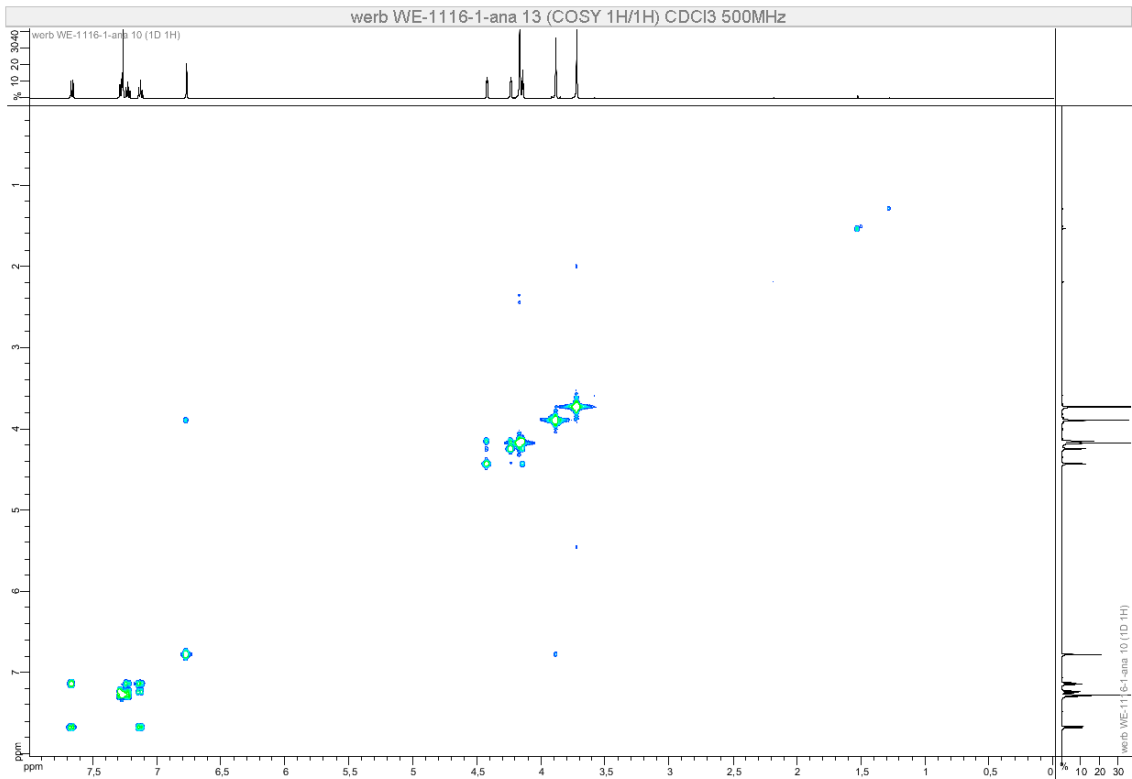
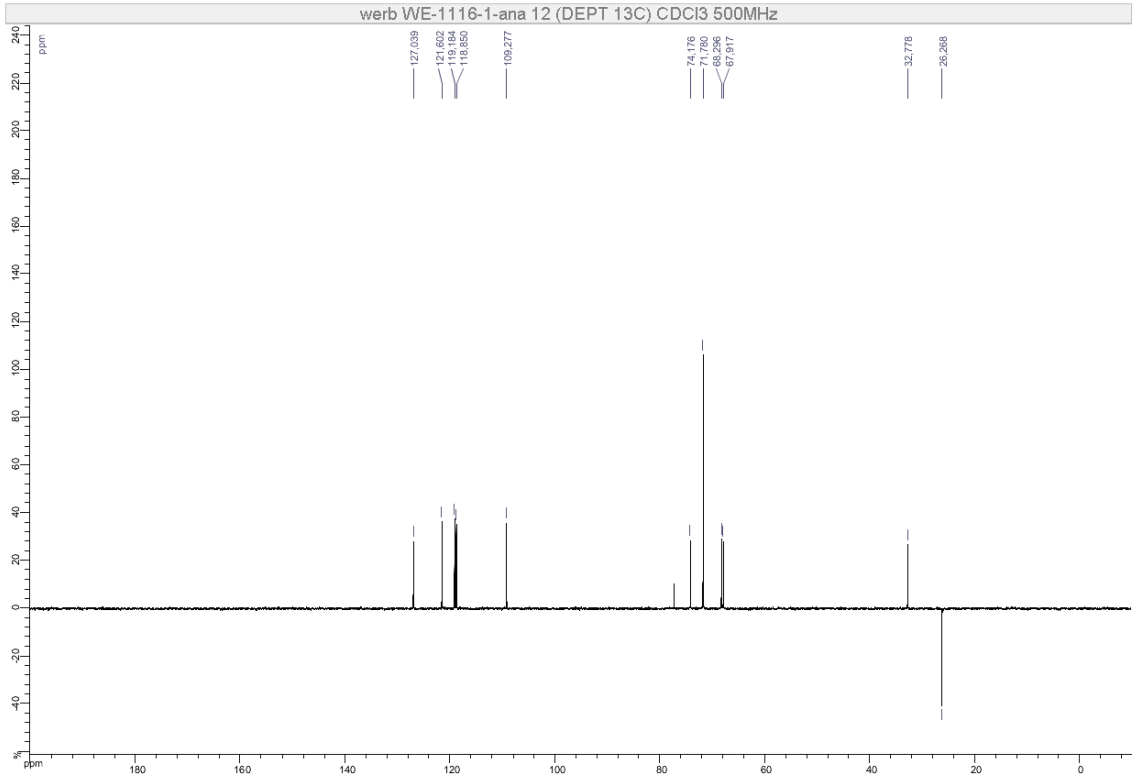


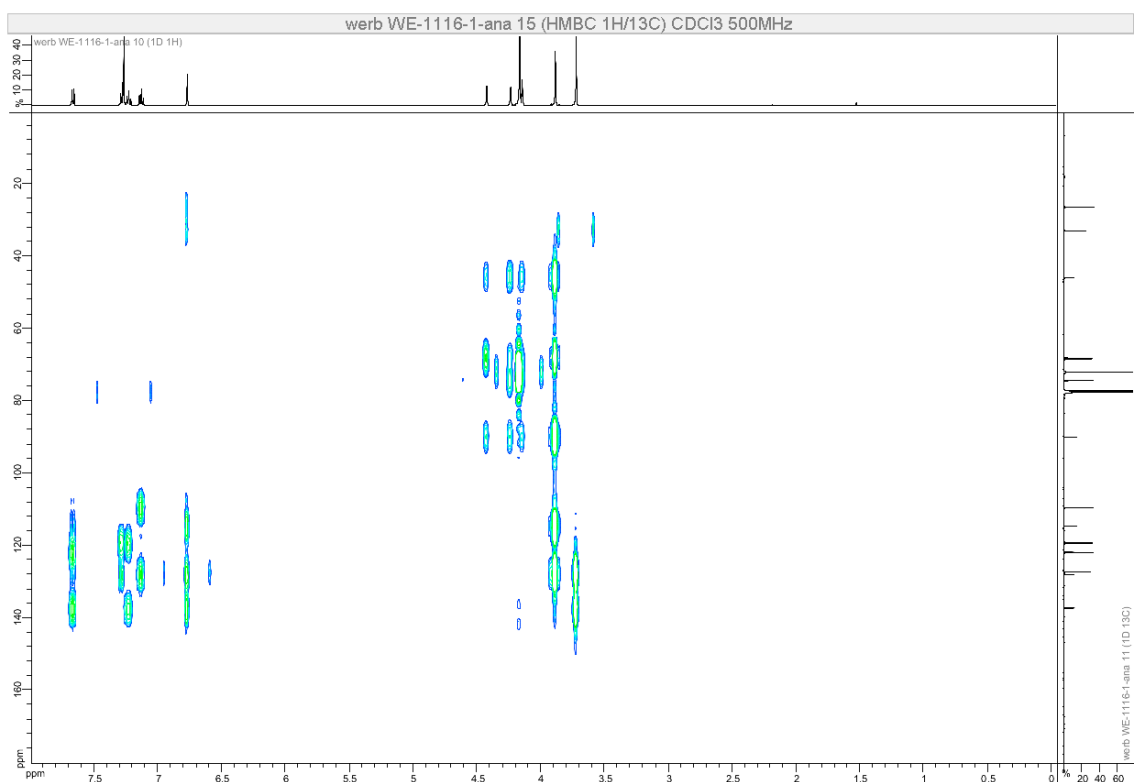
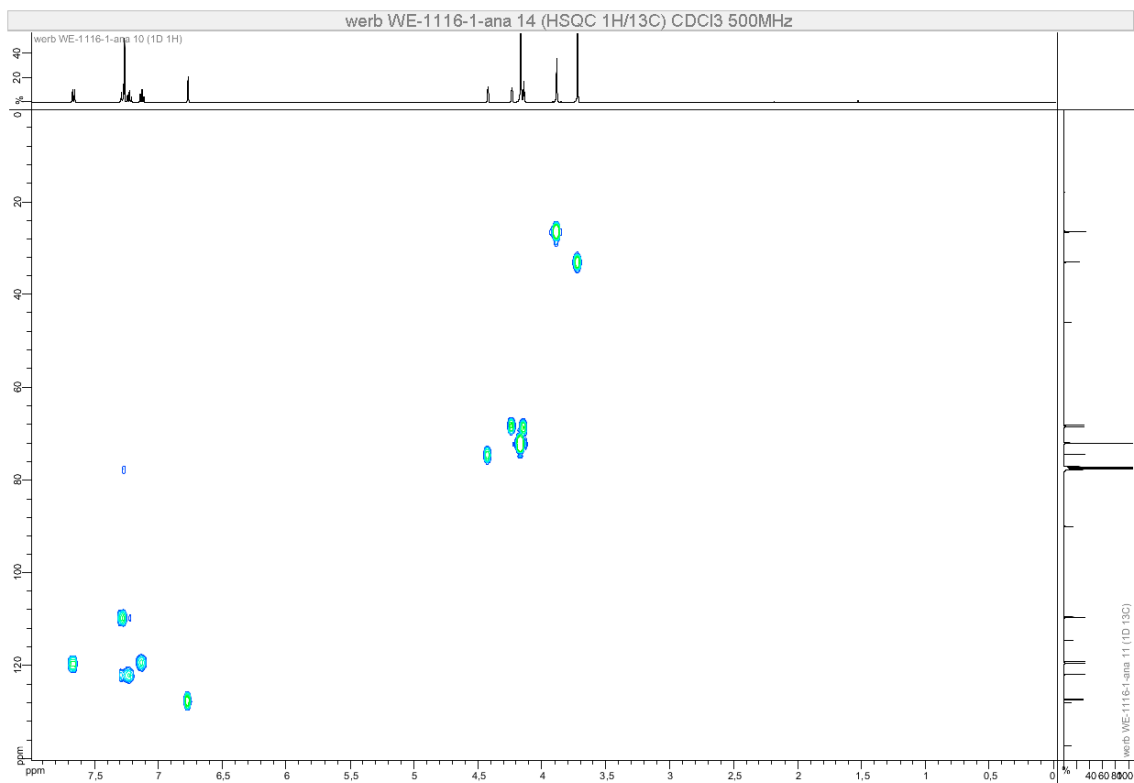




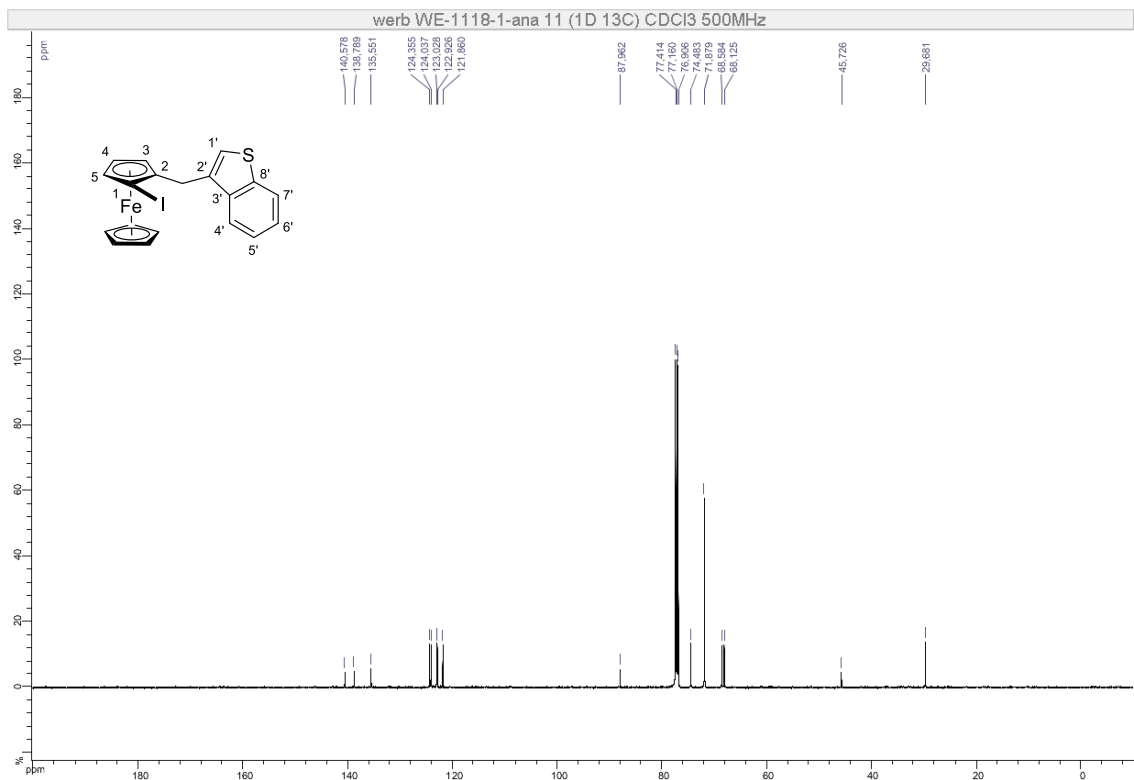
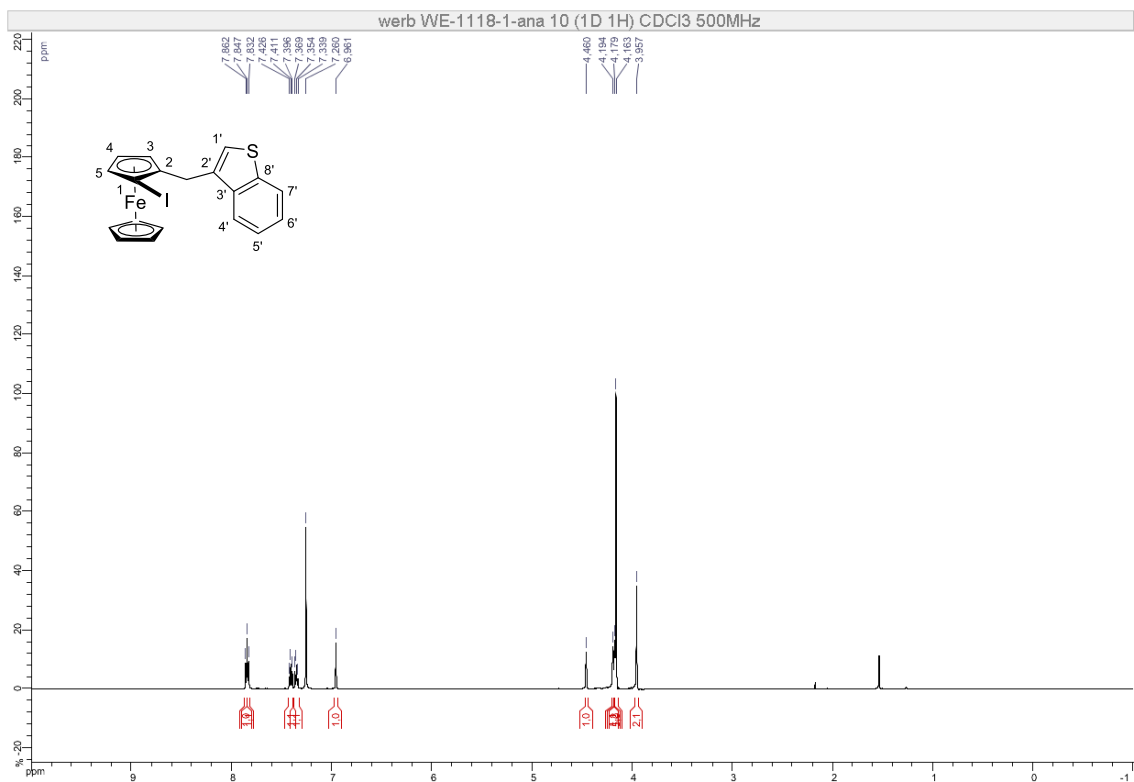
Compound (\pm)-4u

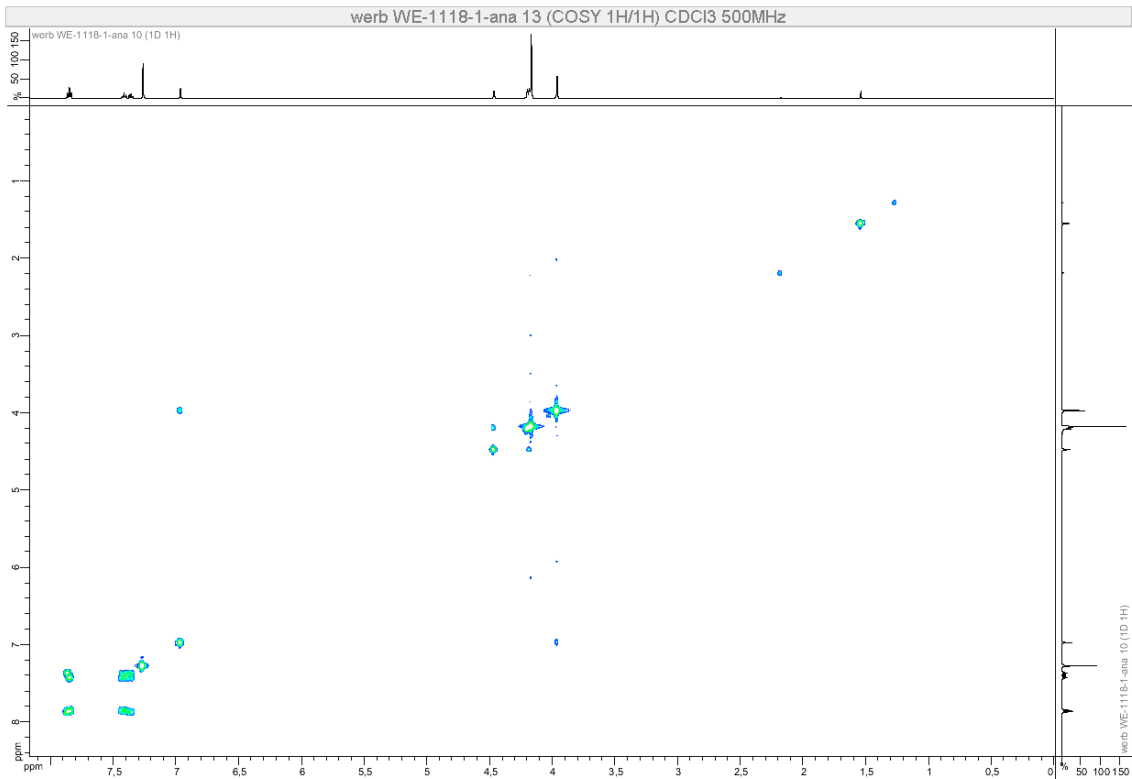
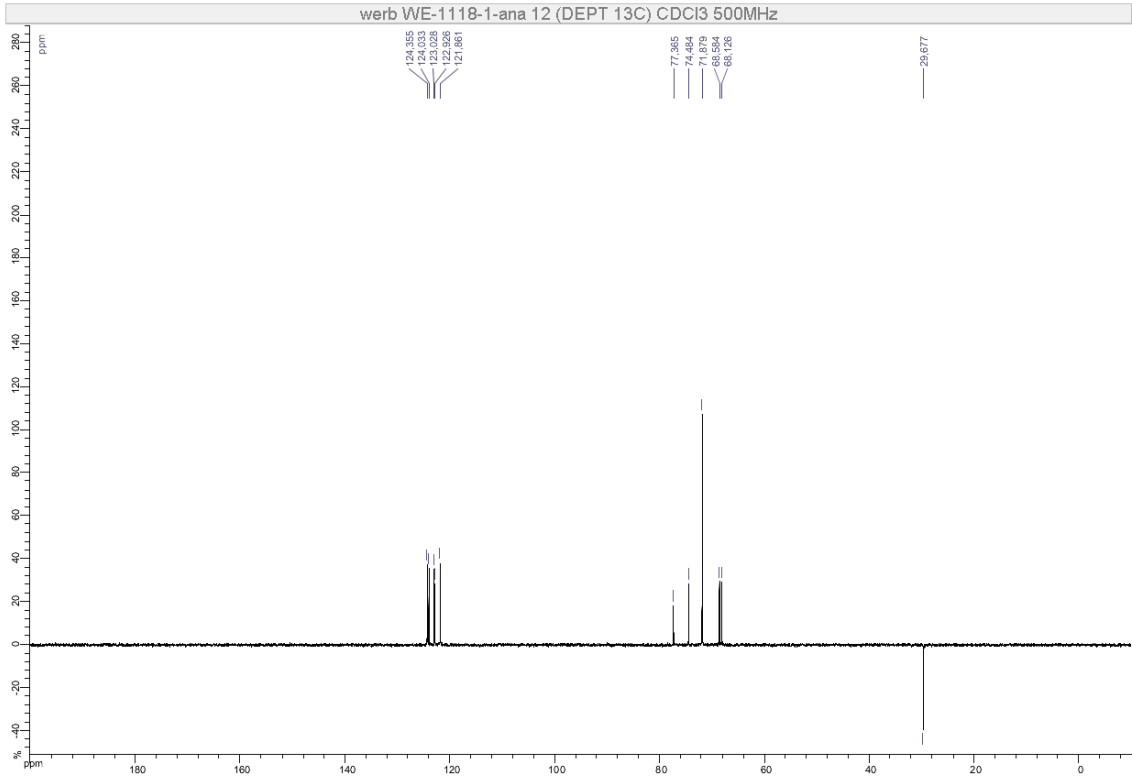


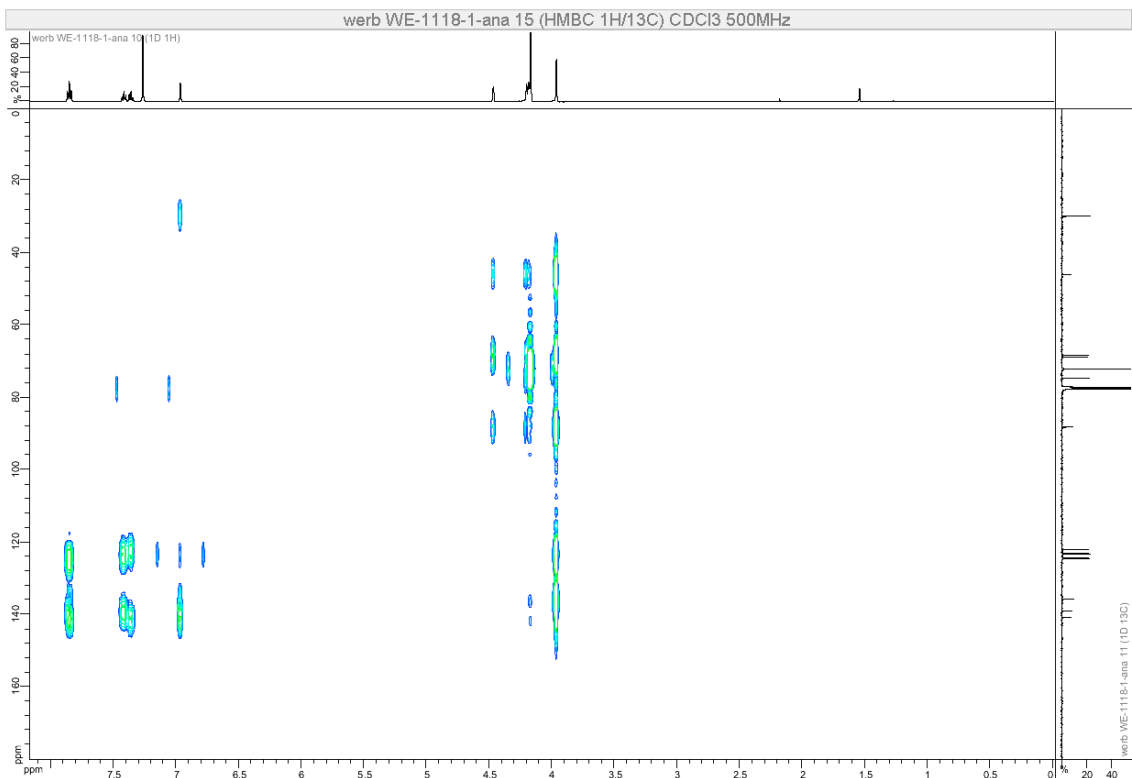
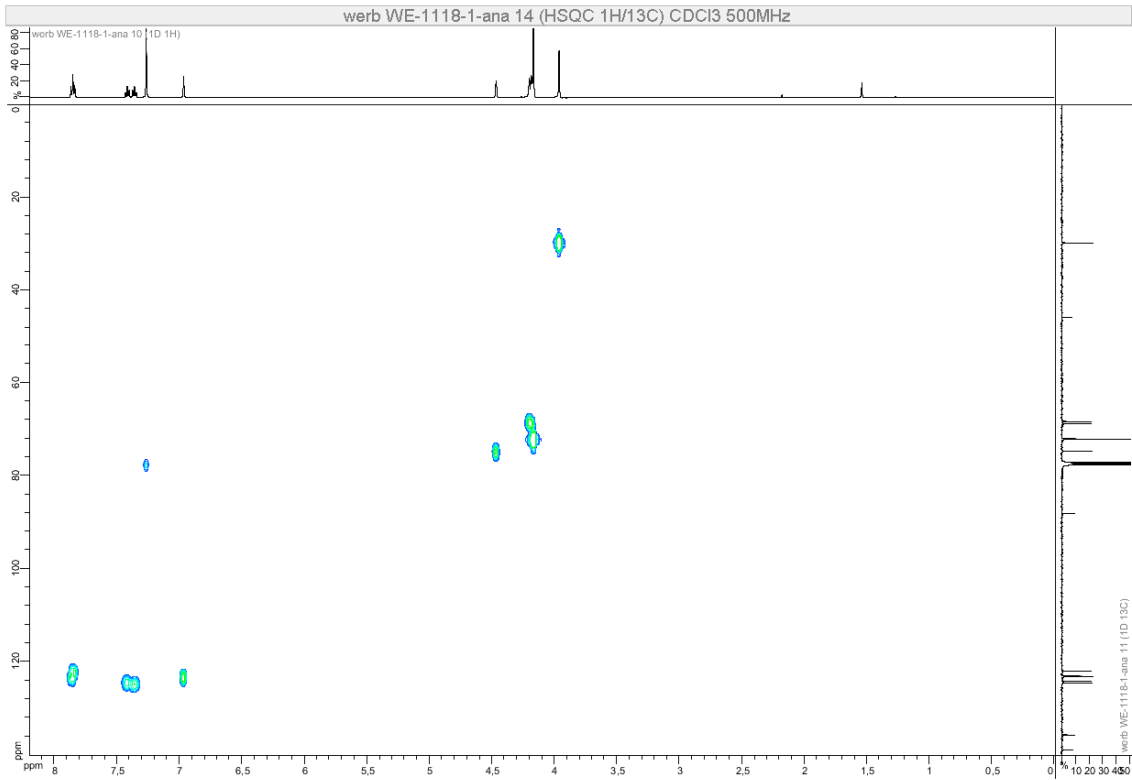


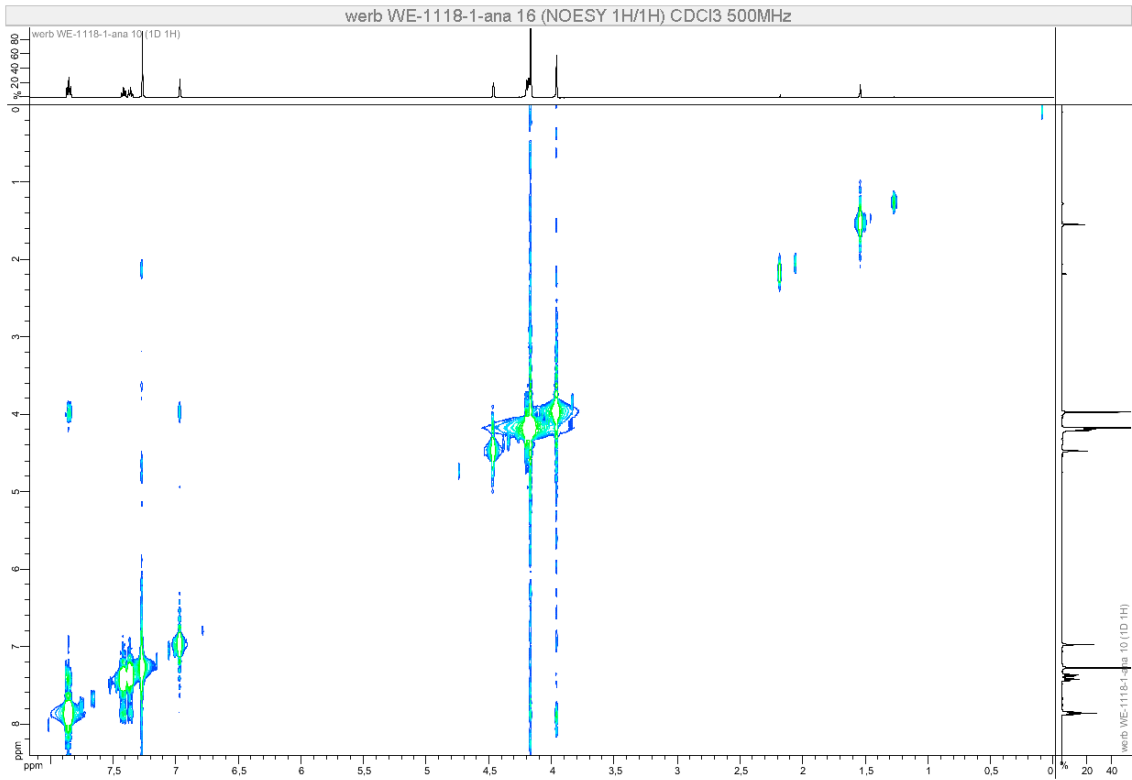


Compound (\pm)-4v

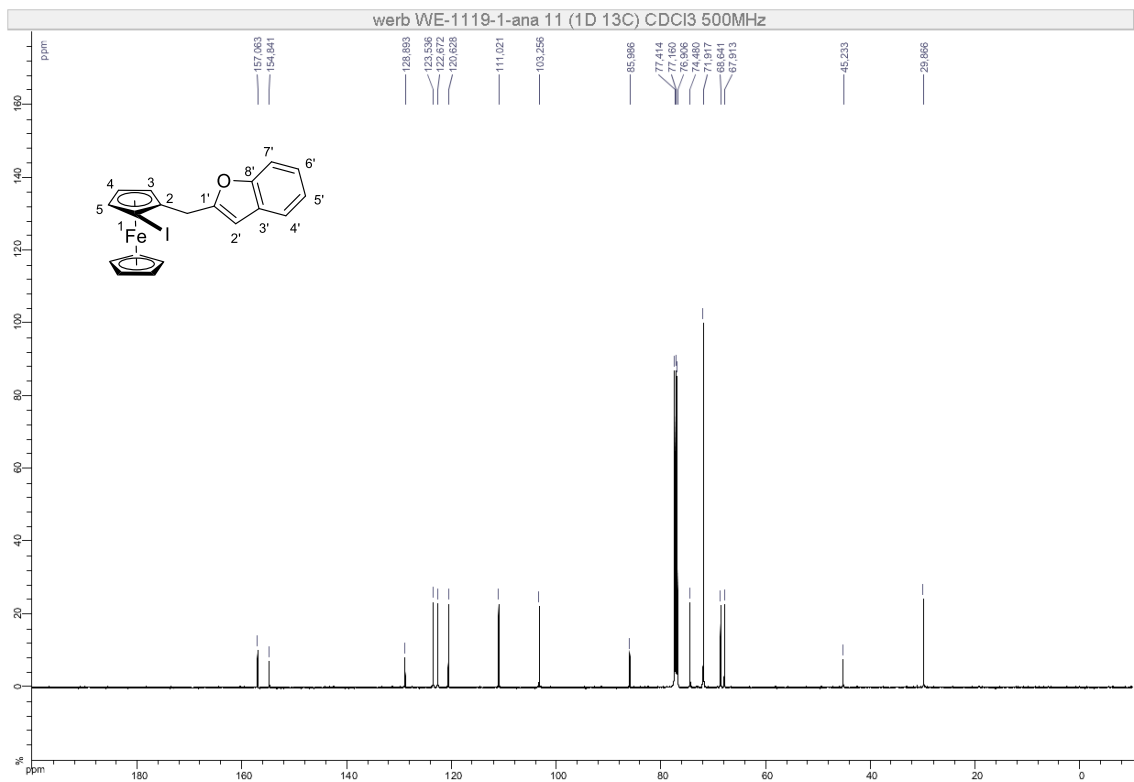
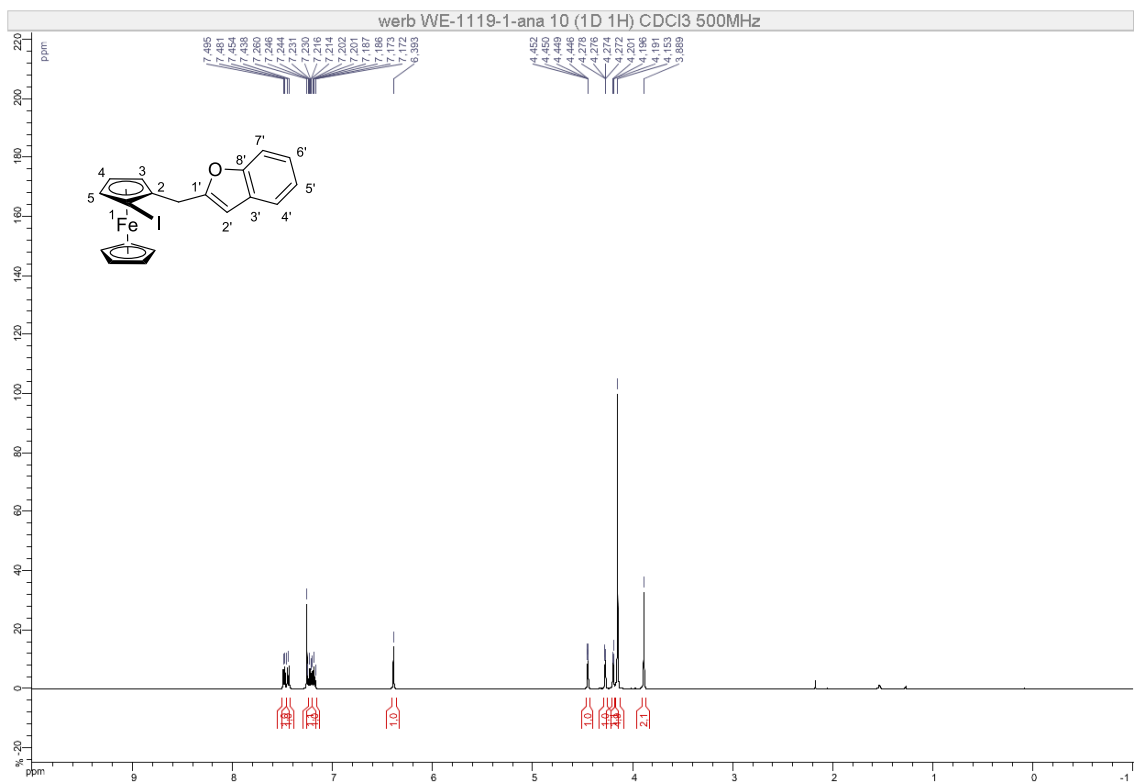


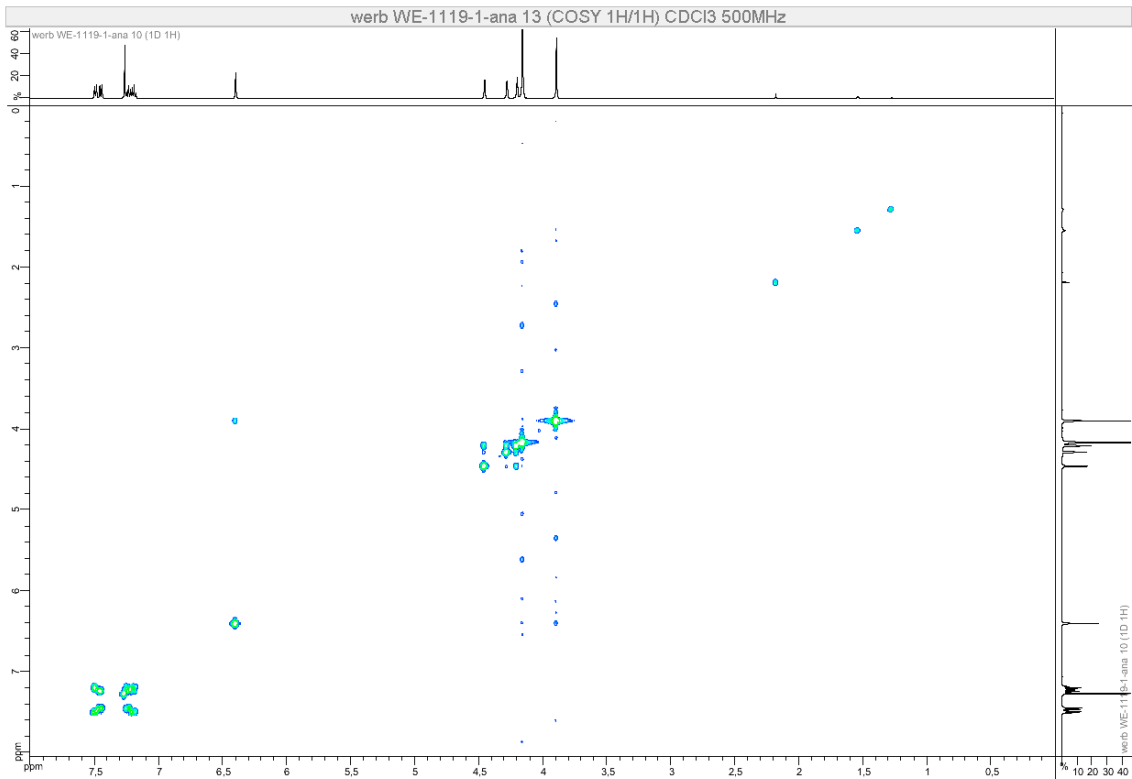
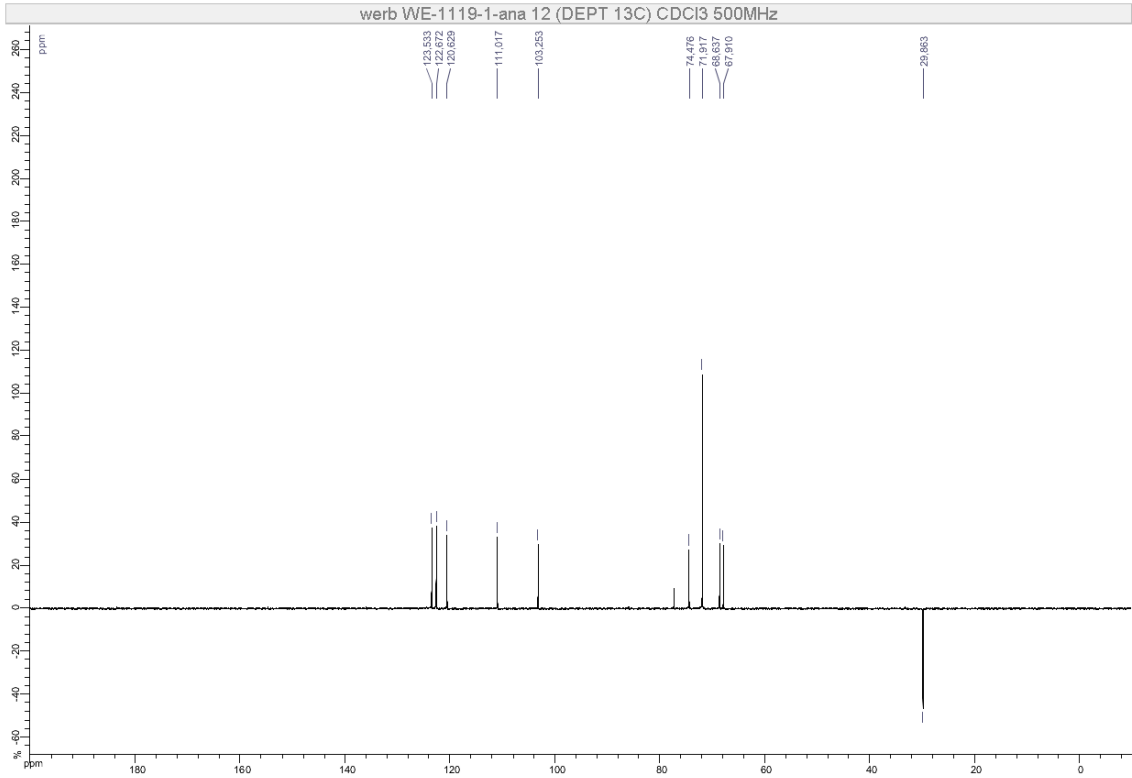


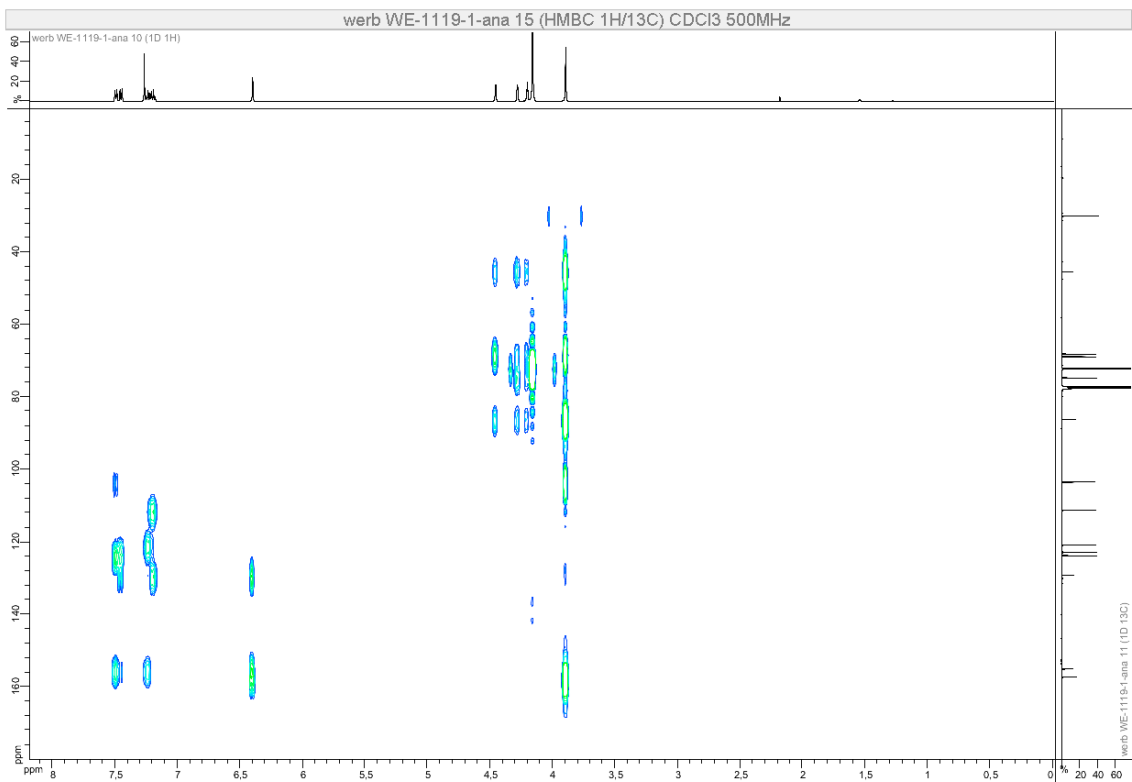
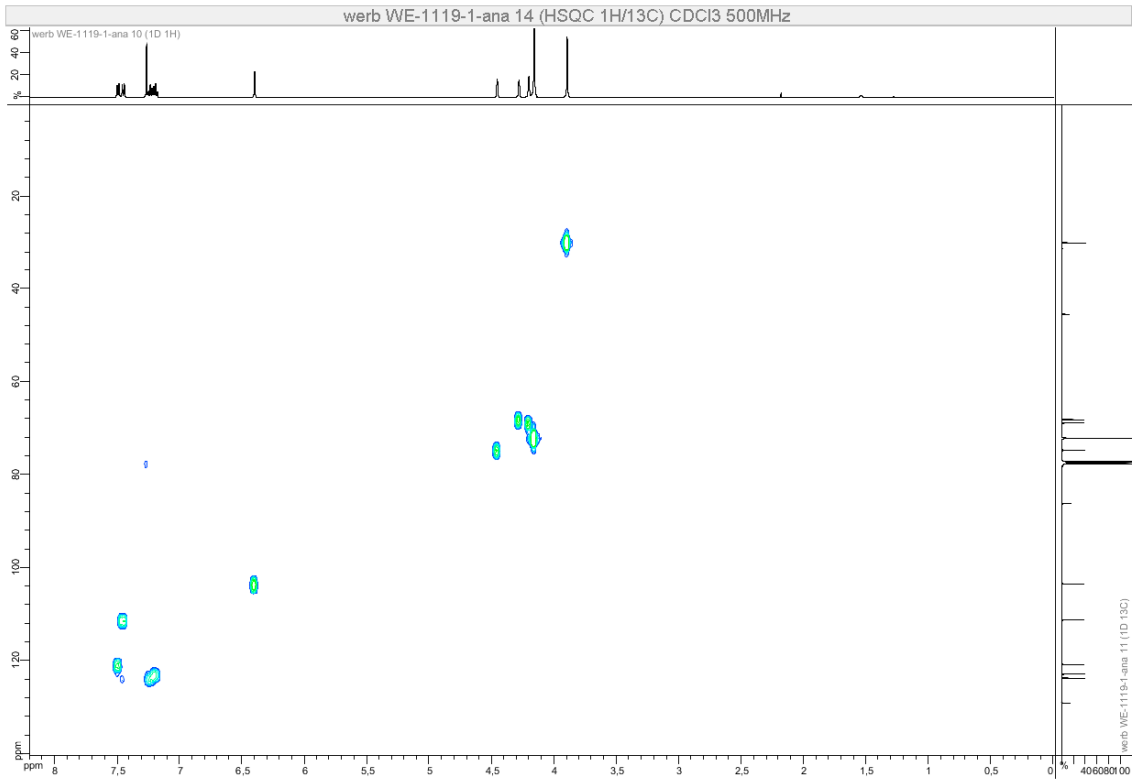


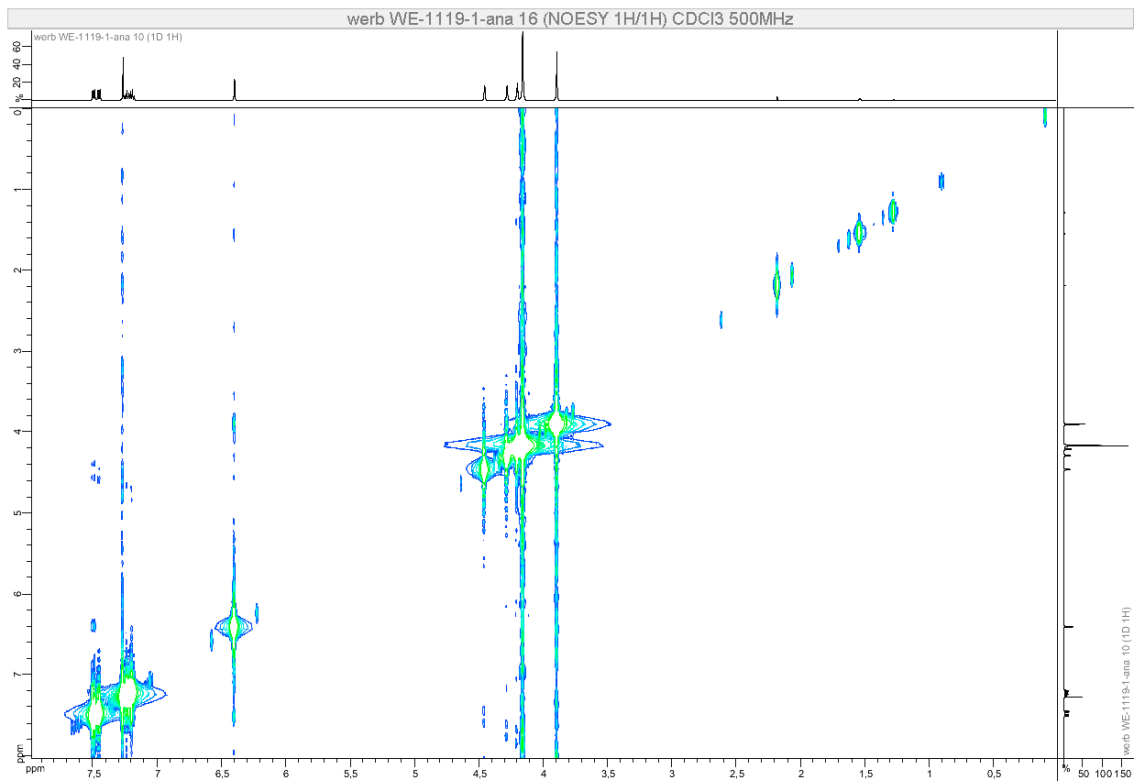


Compound (\pm)-4v

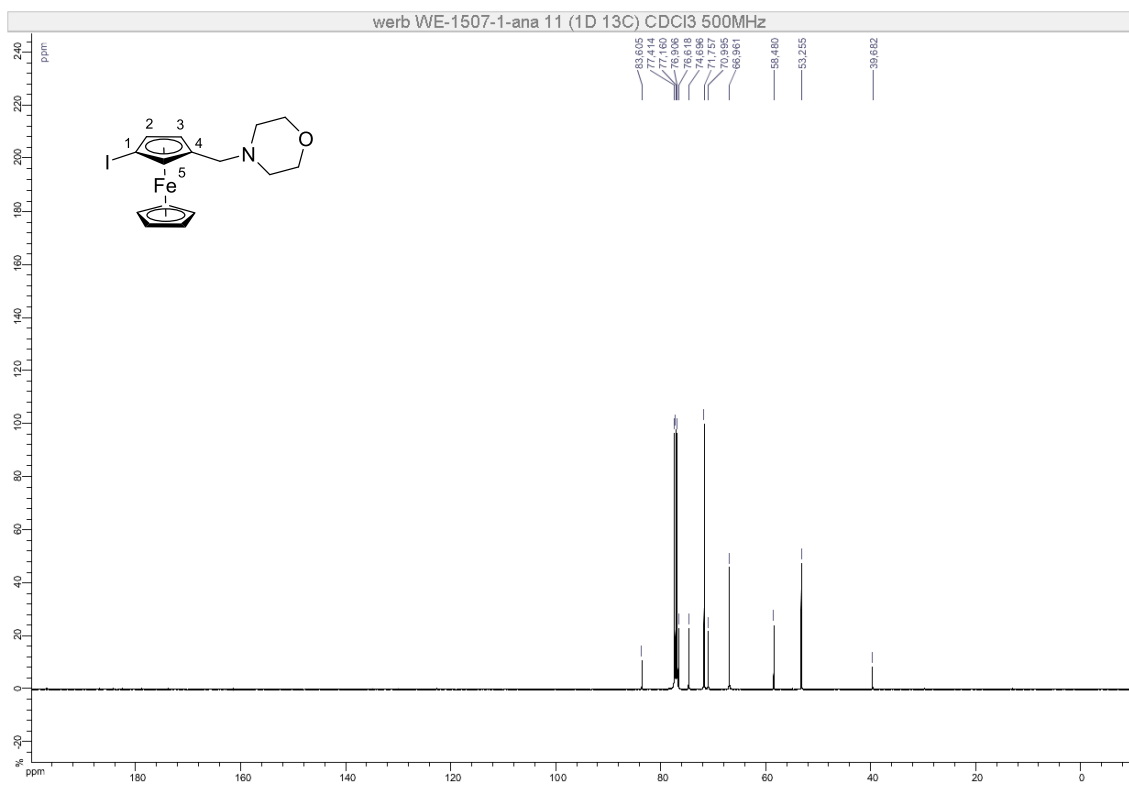
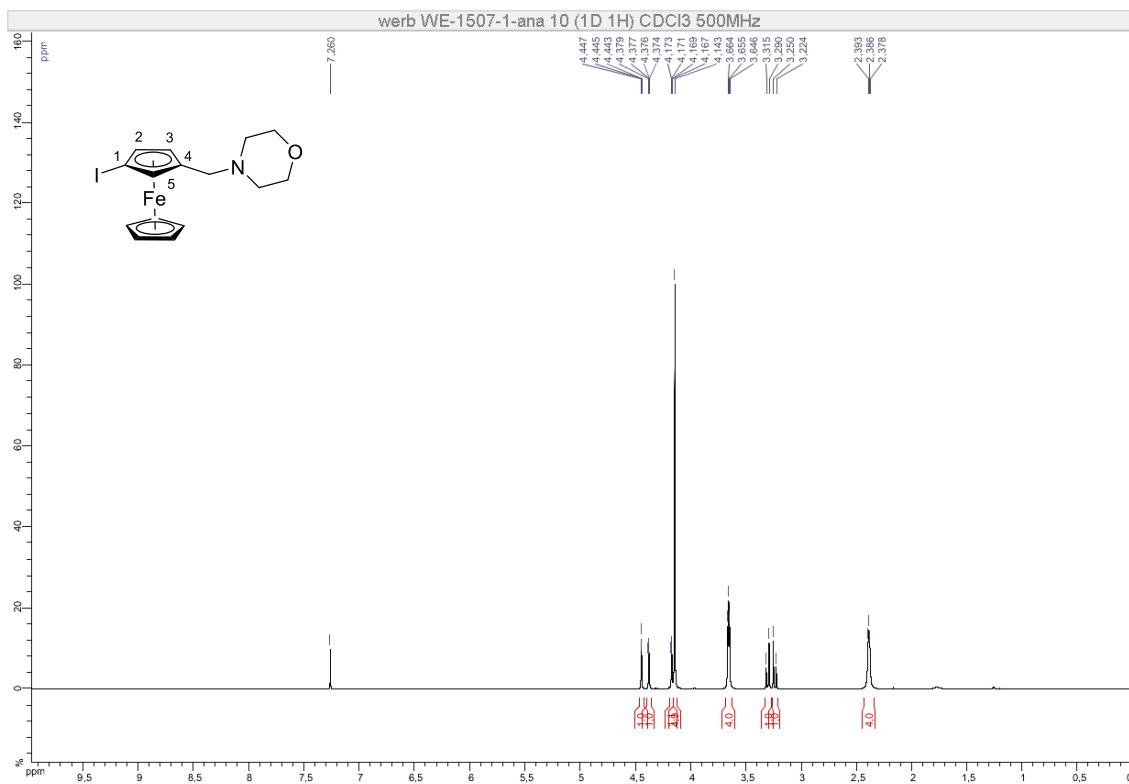


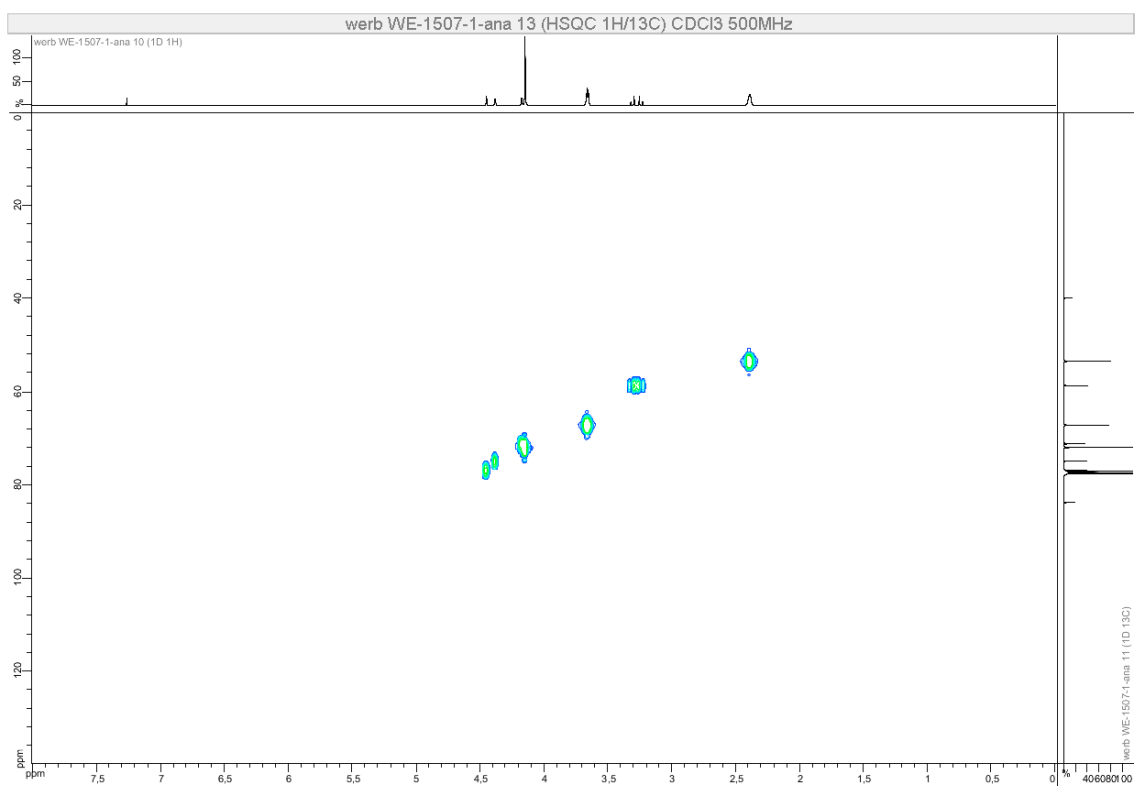
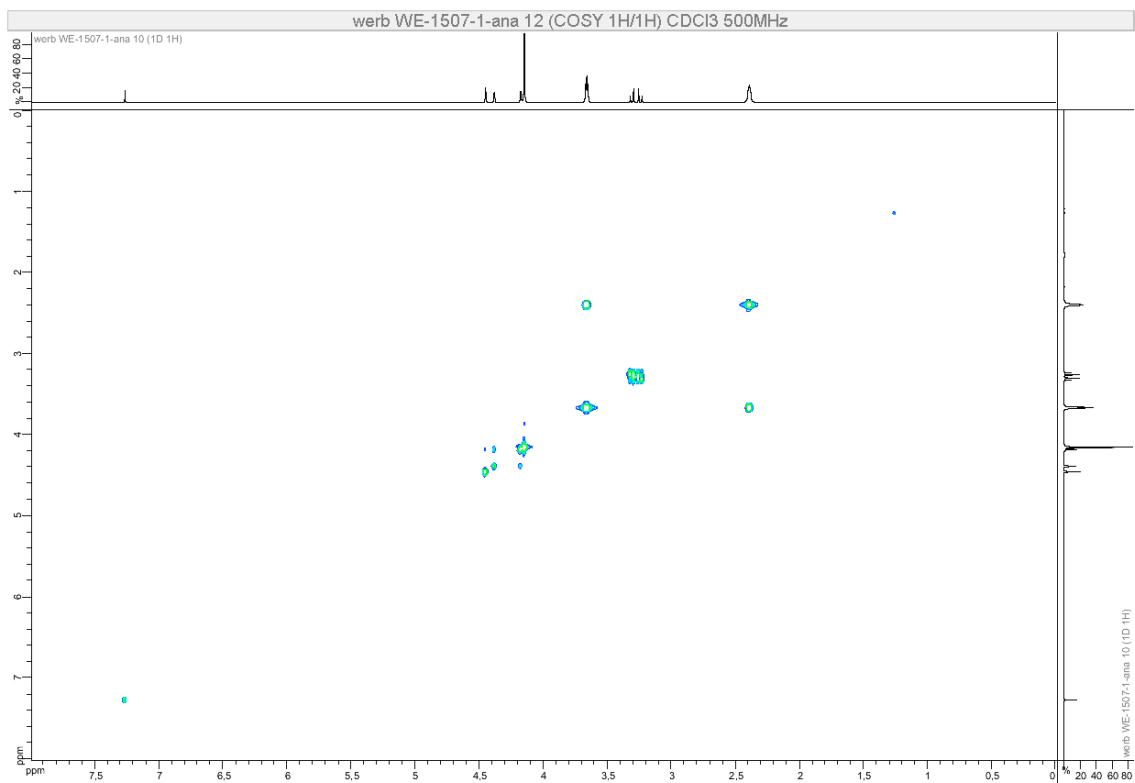


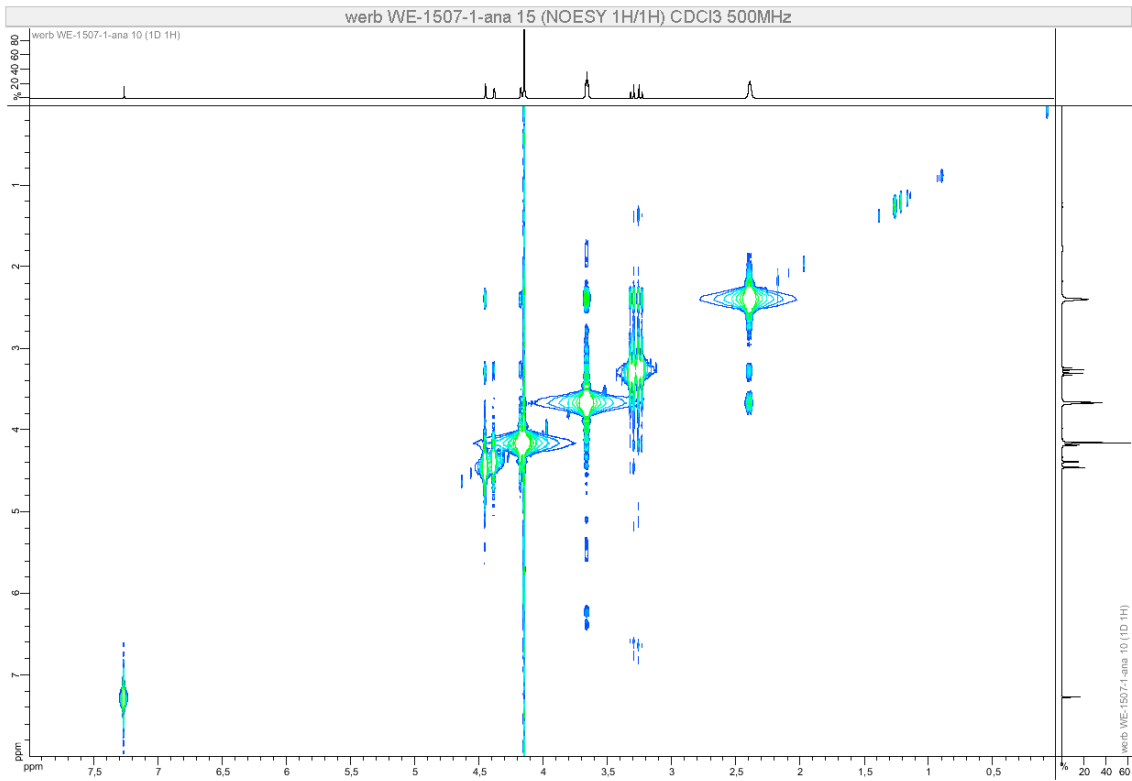
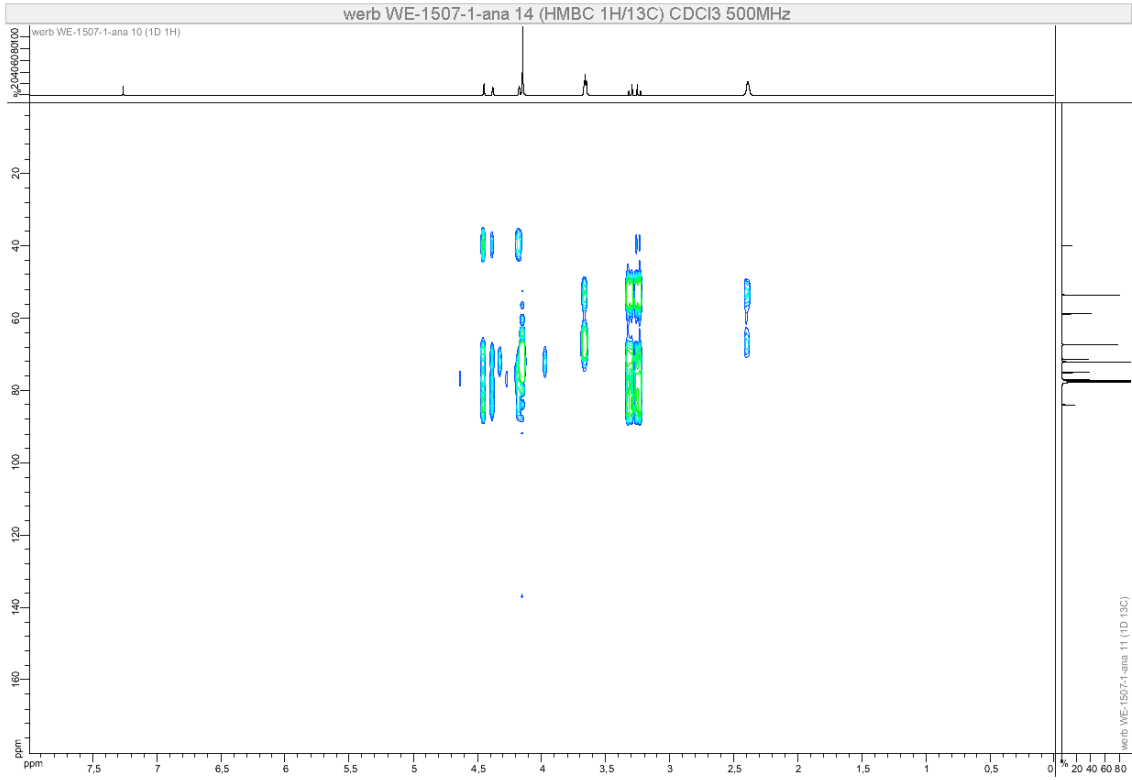




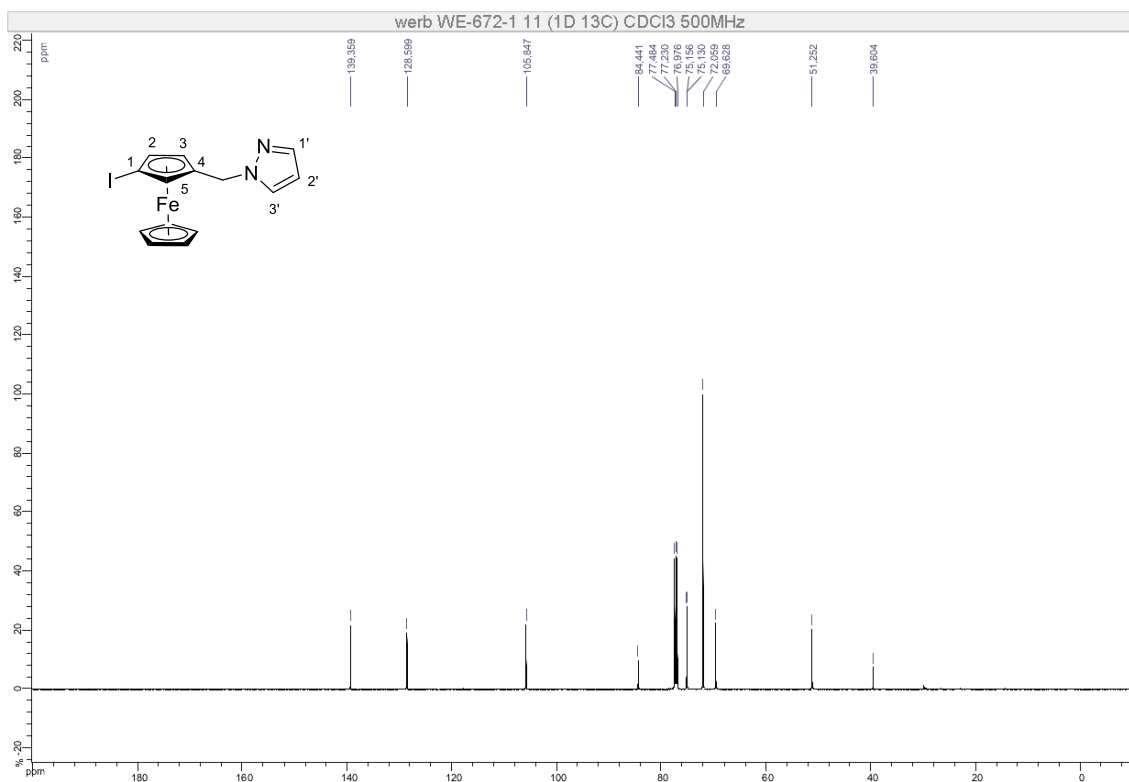
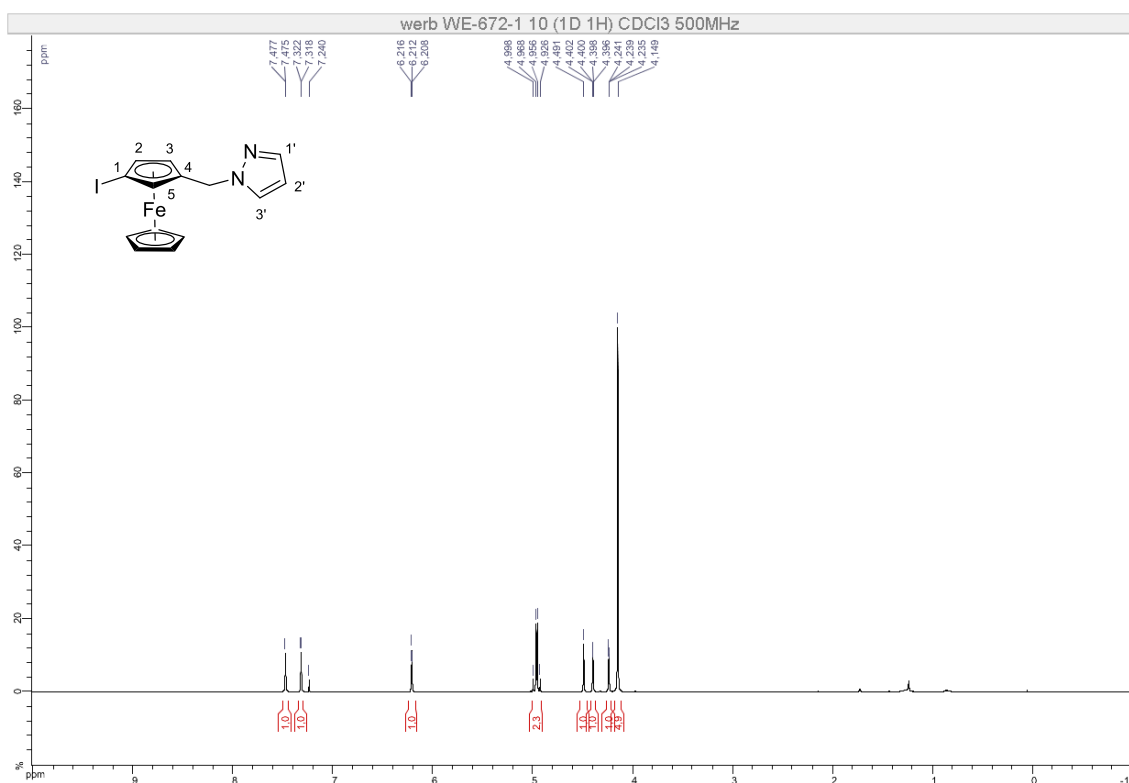
Compound (\pm)-7a

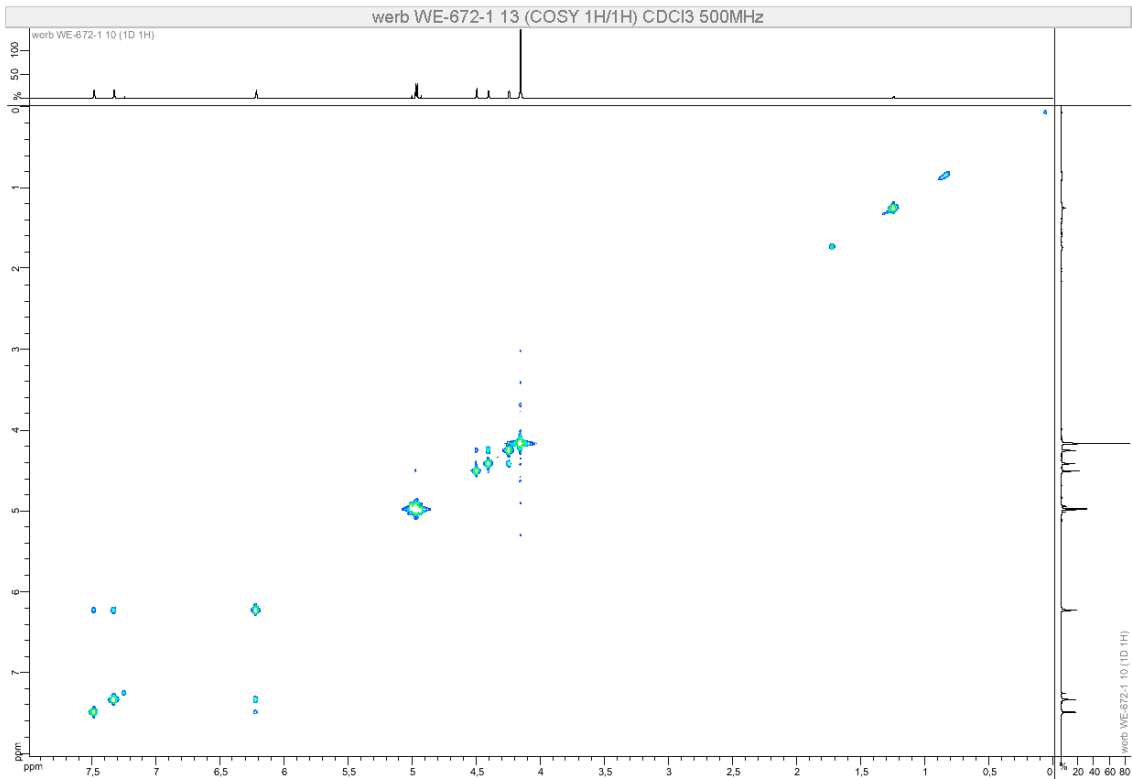
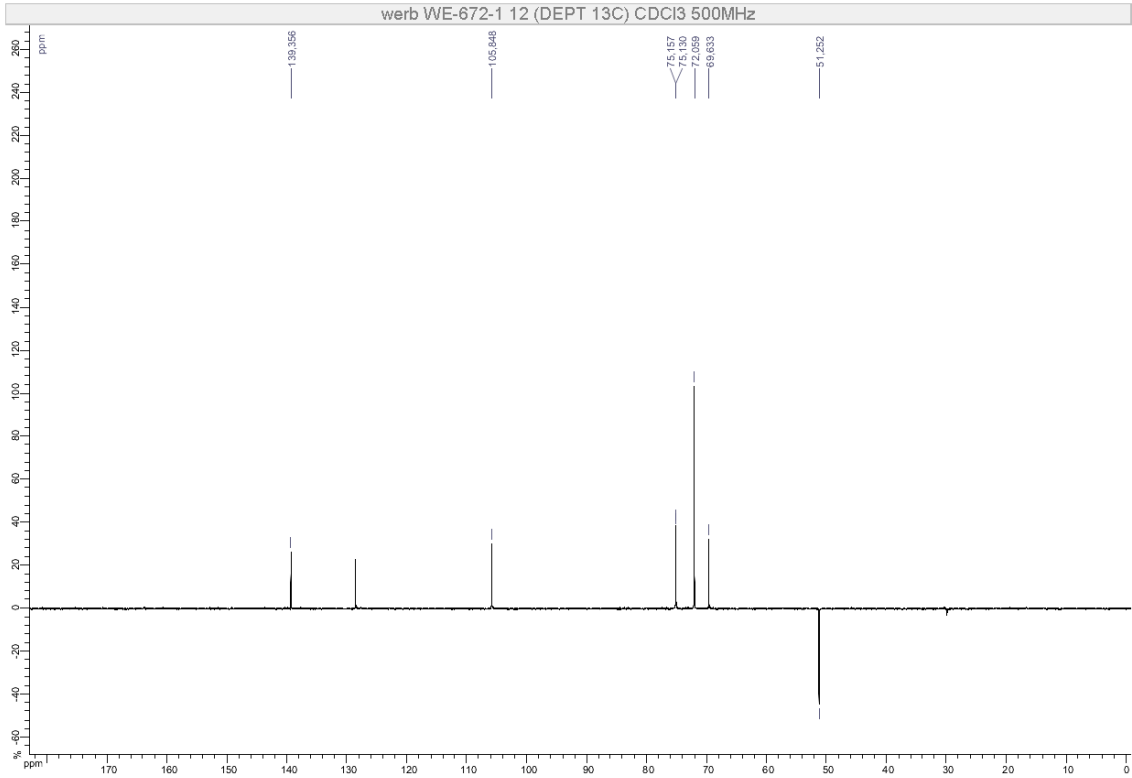


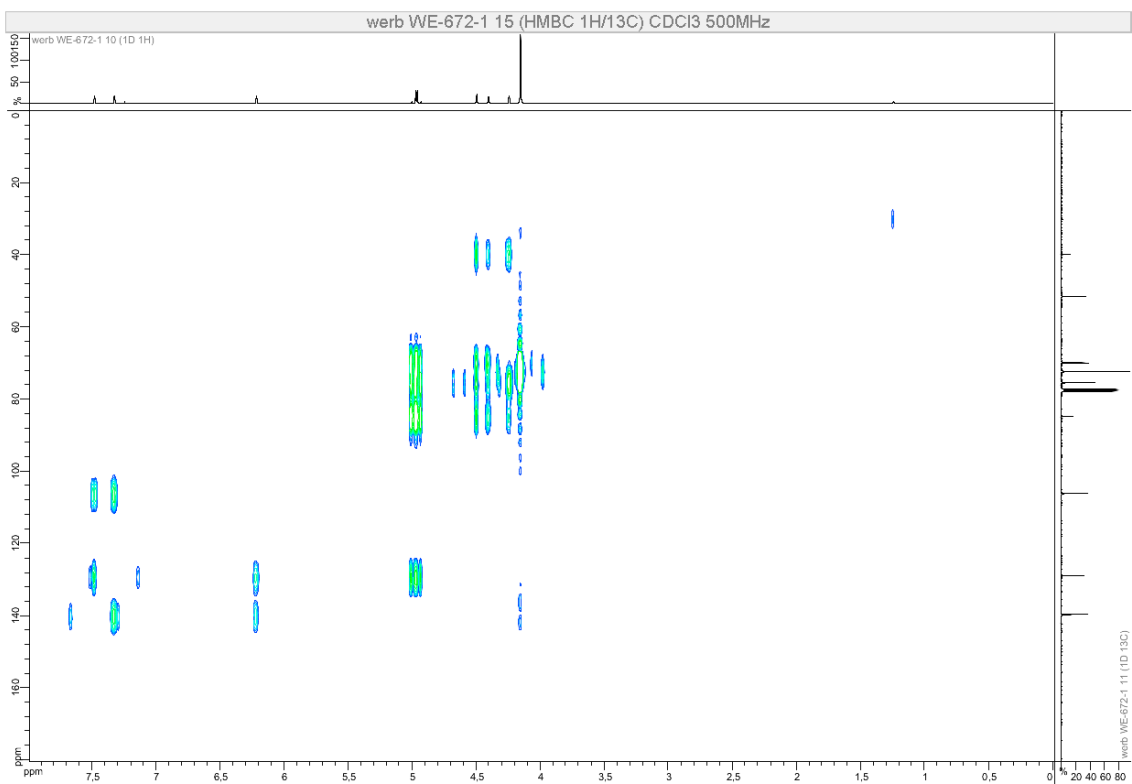
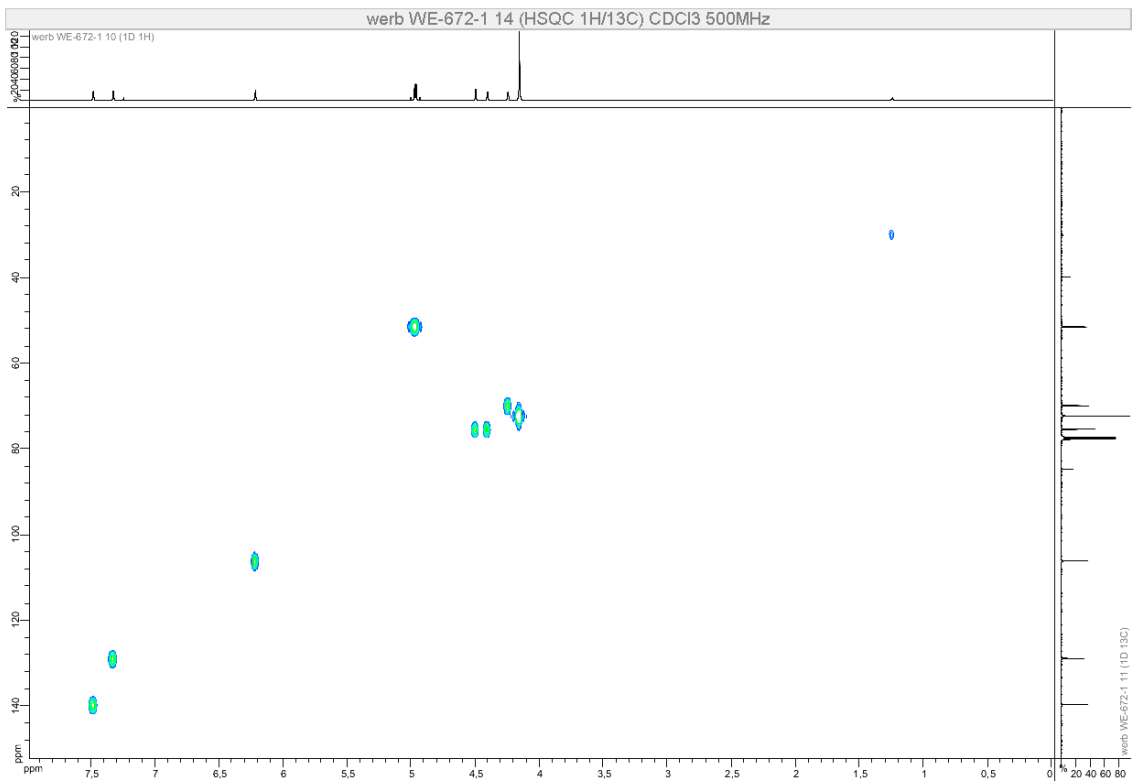


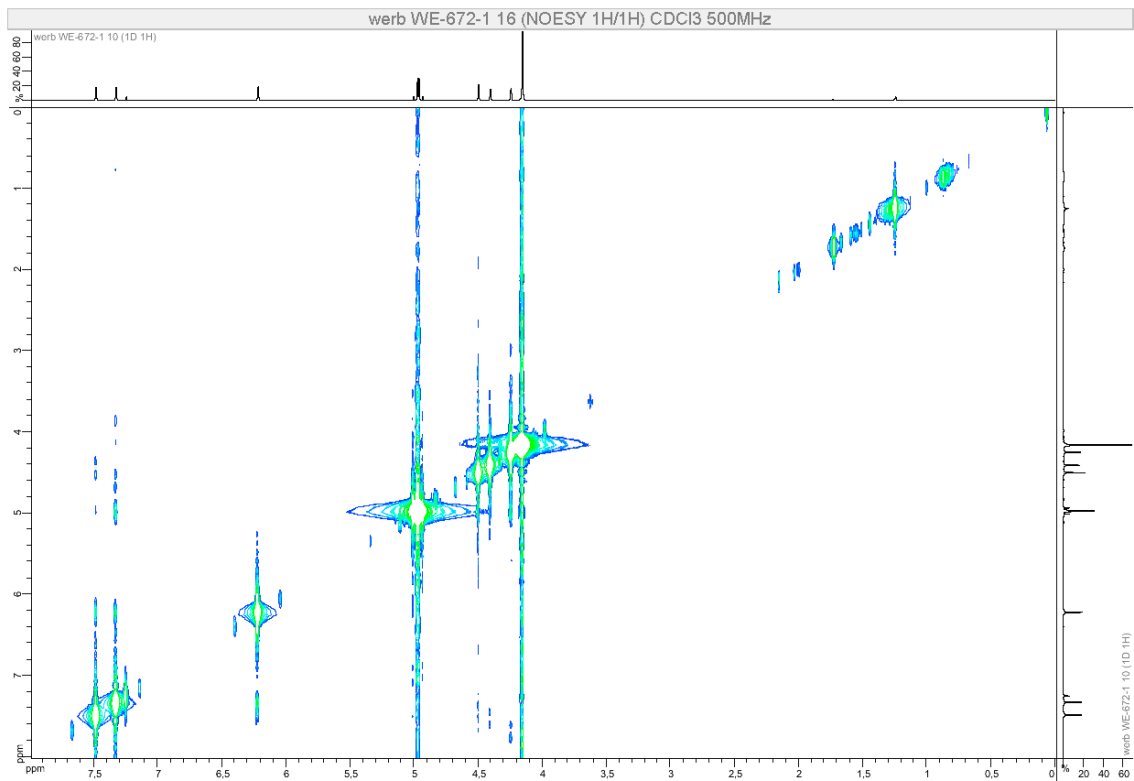


Compound (\pm)-7b

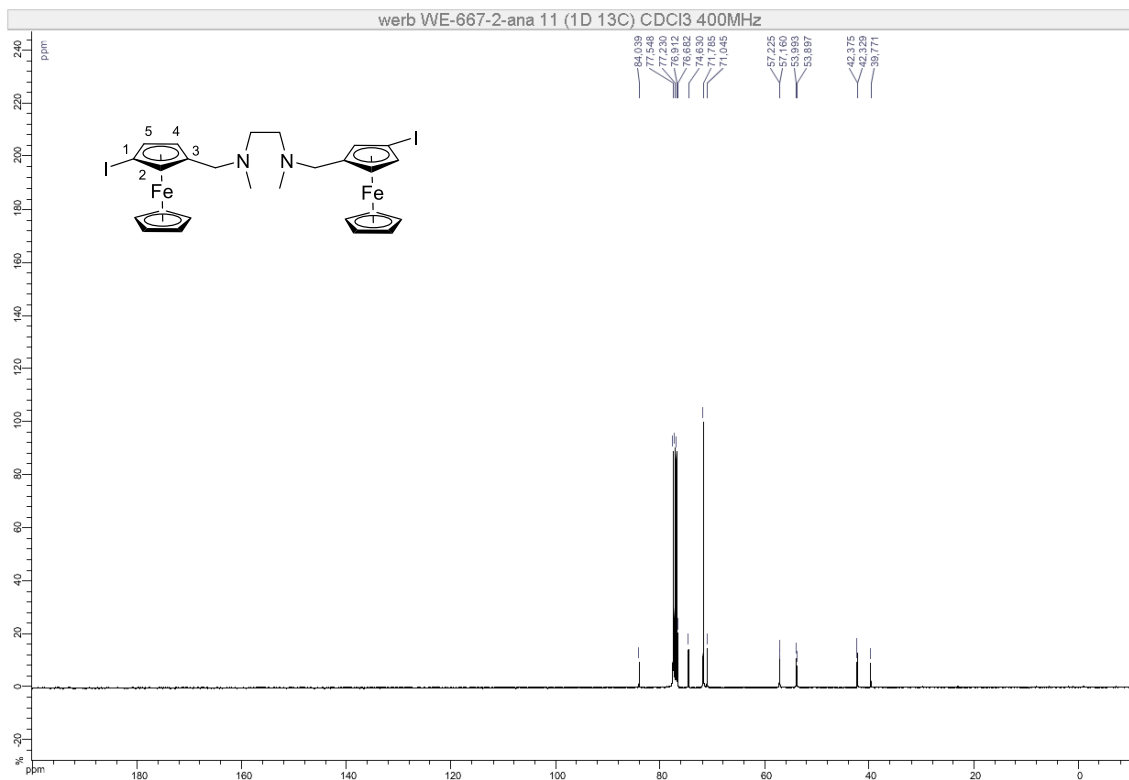
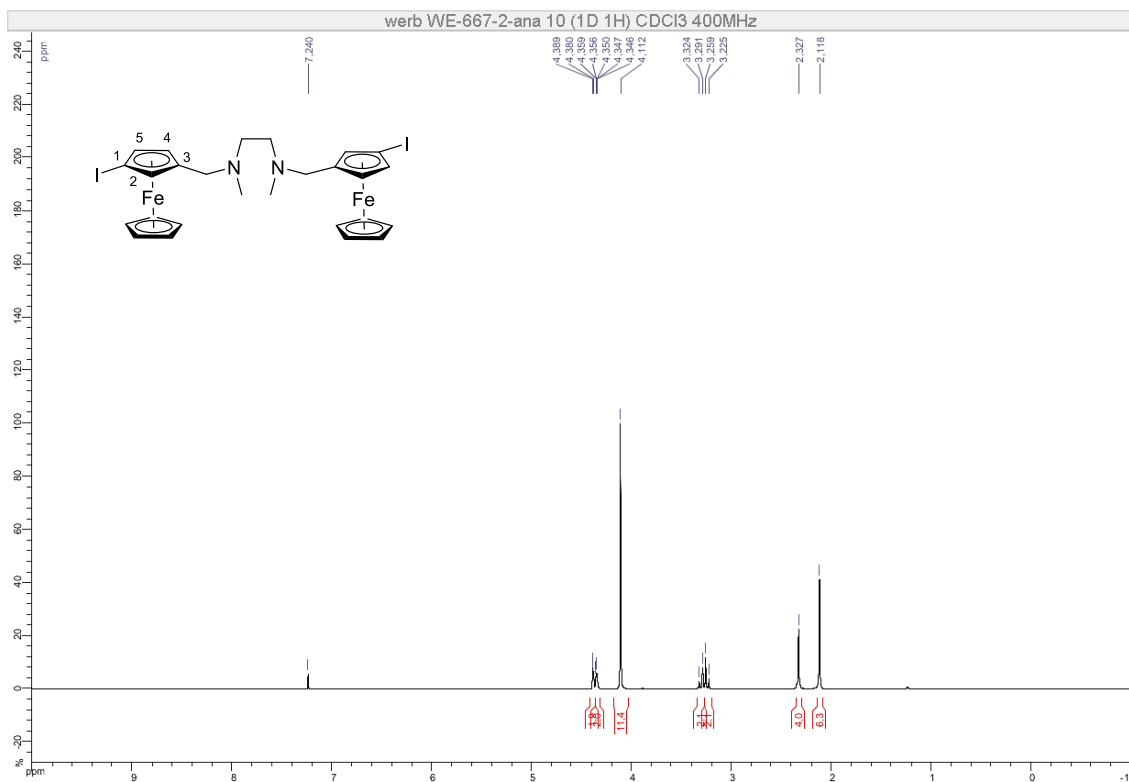


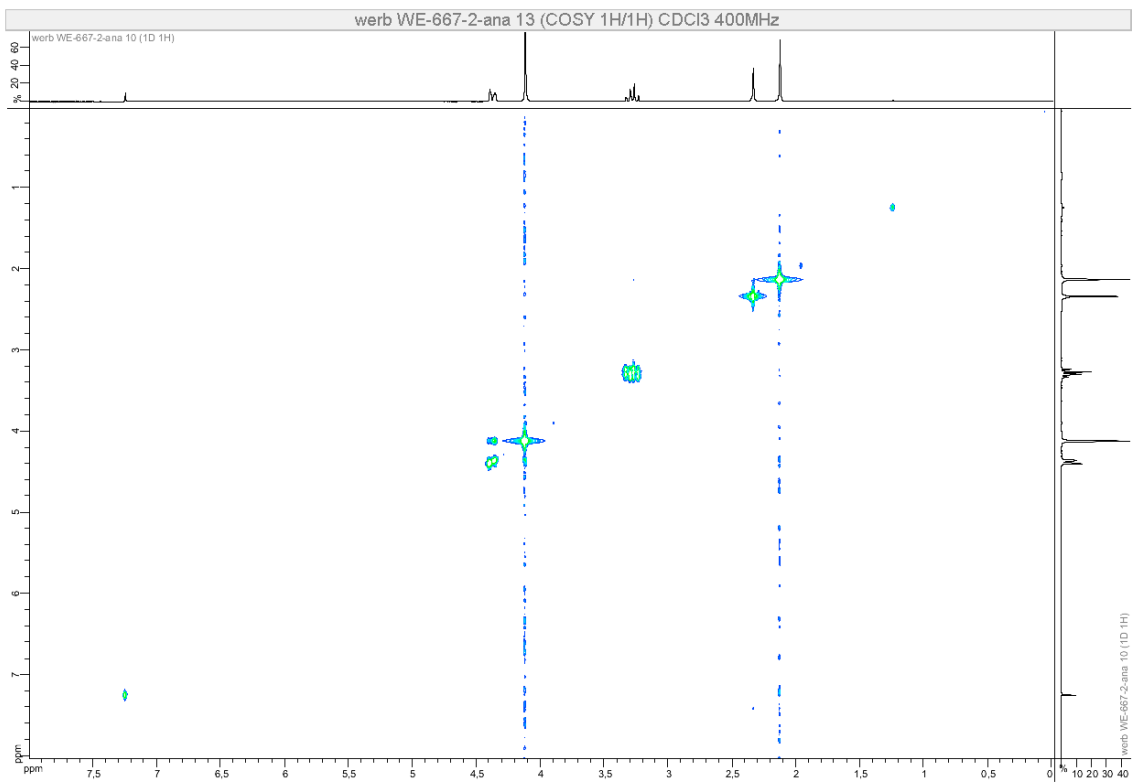
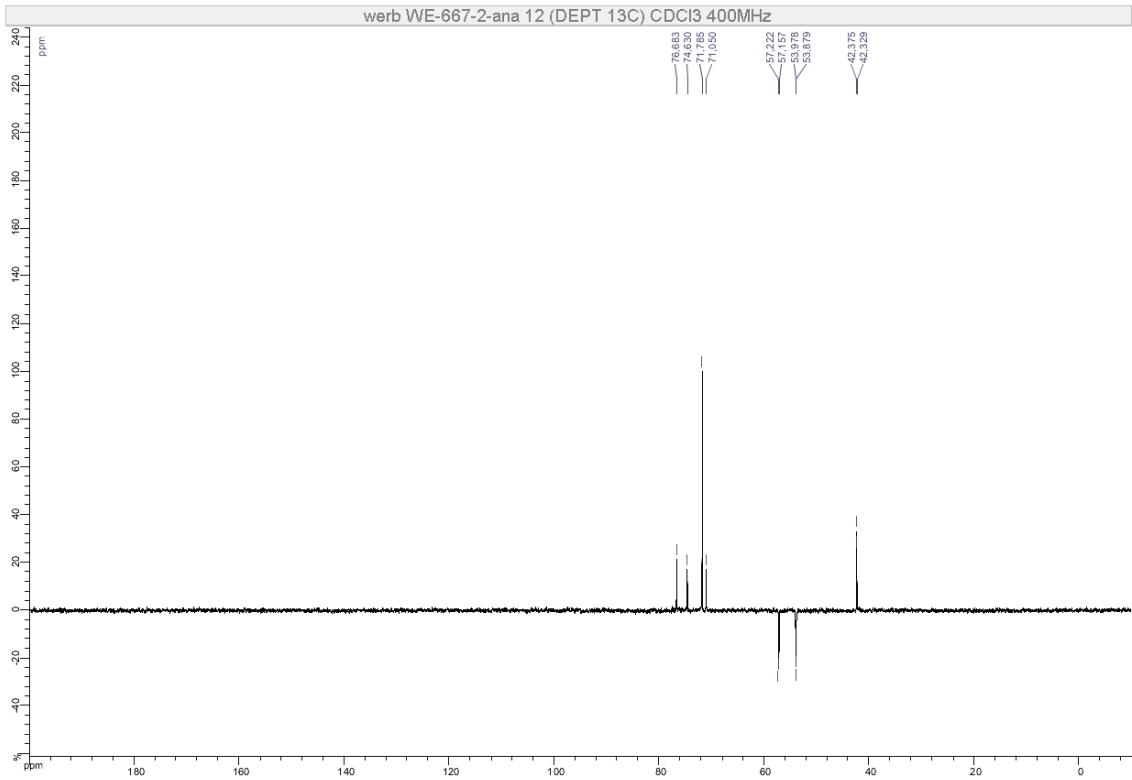


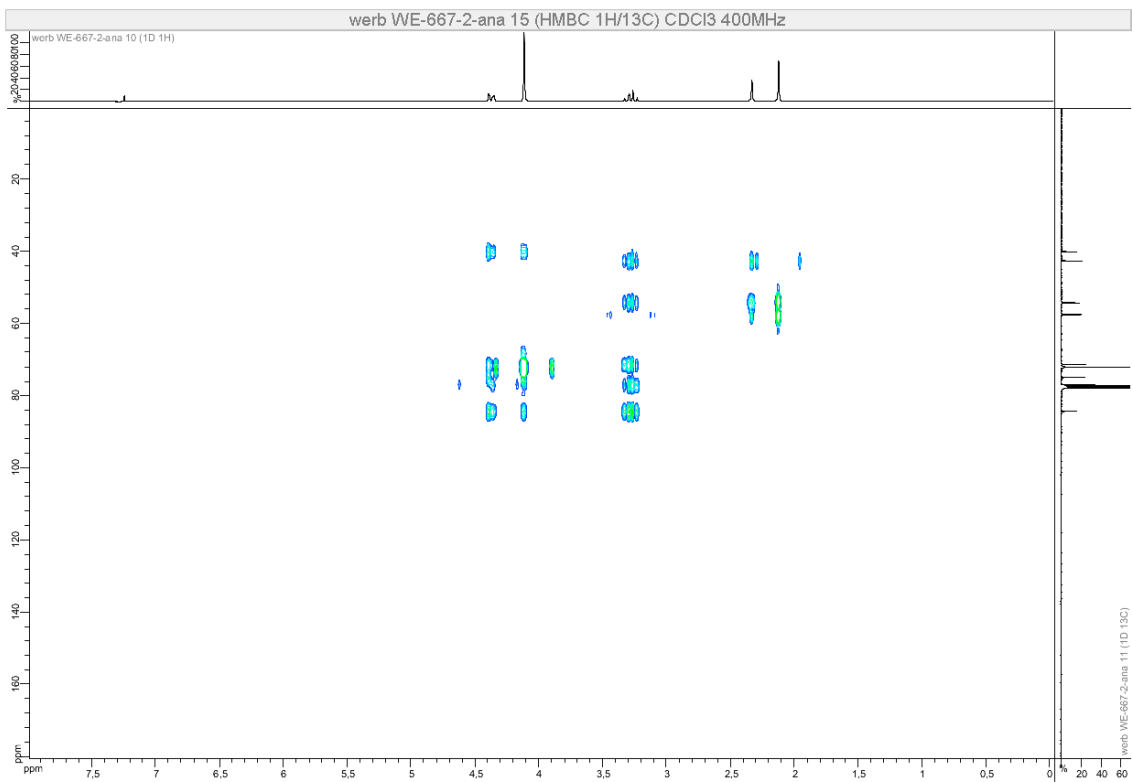
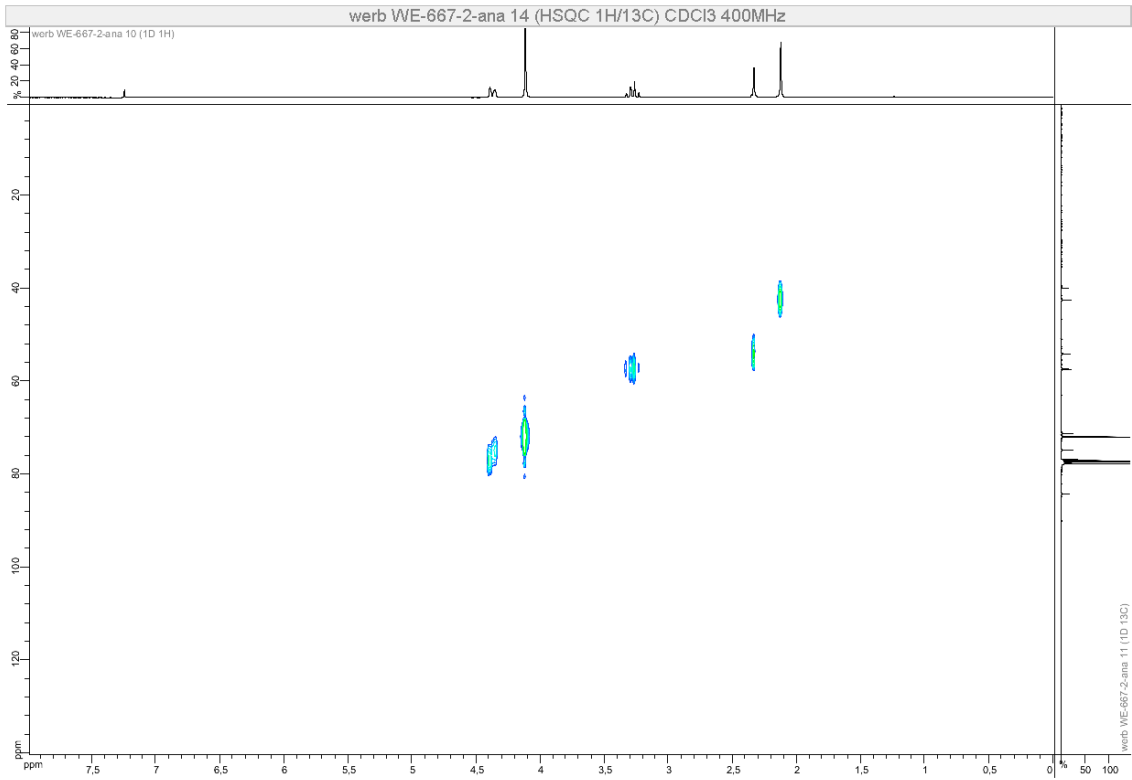


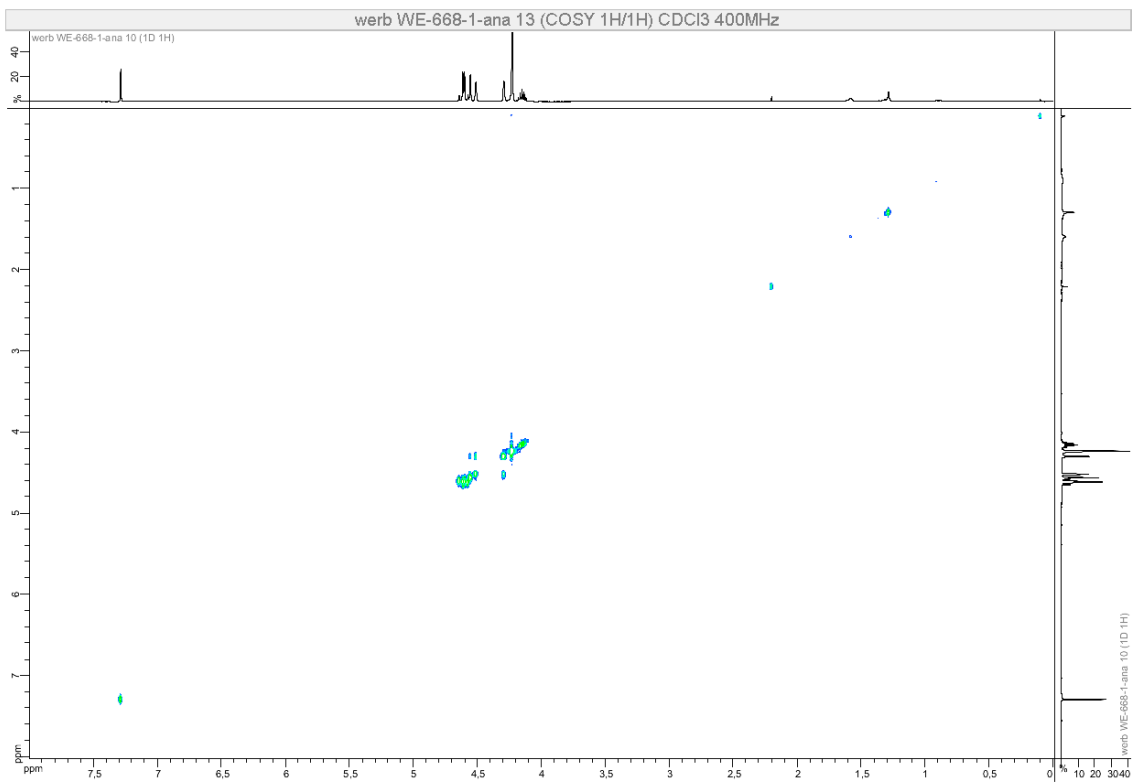
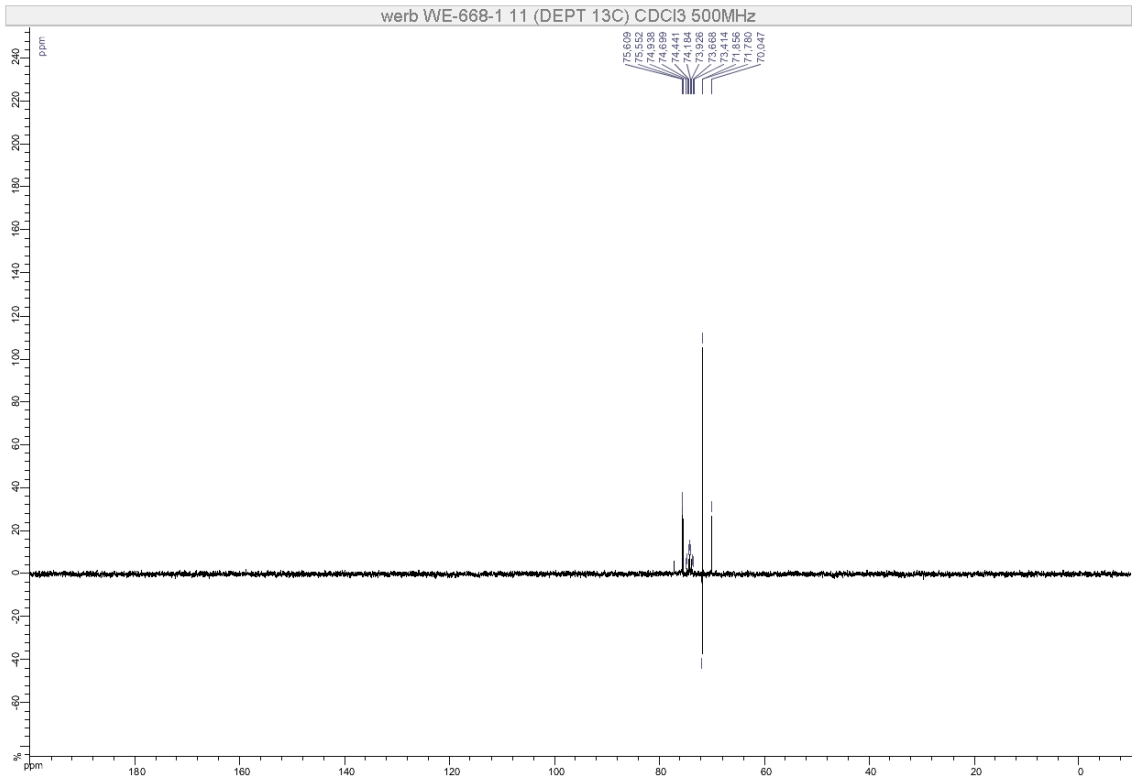


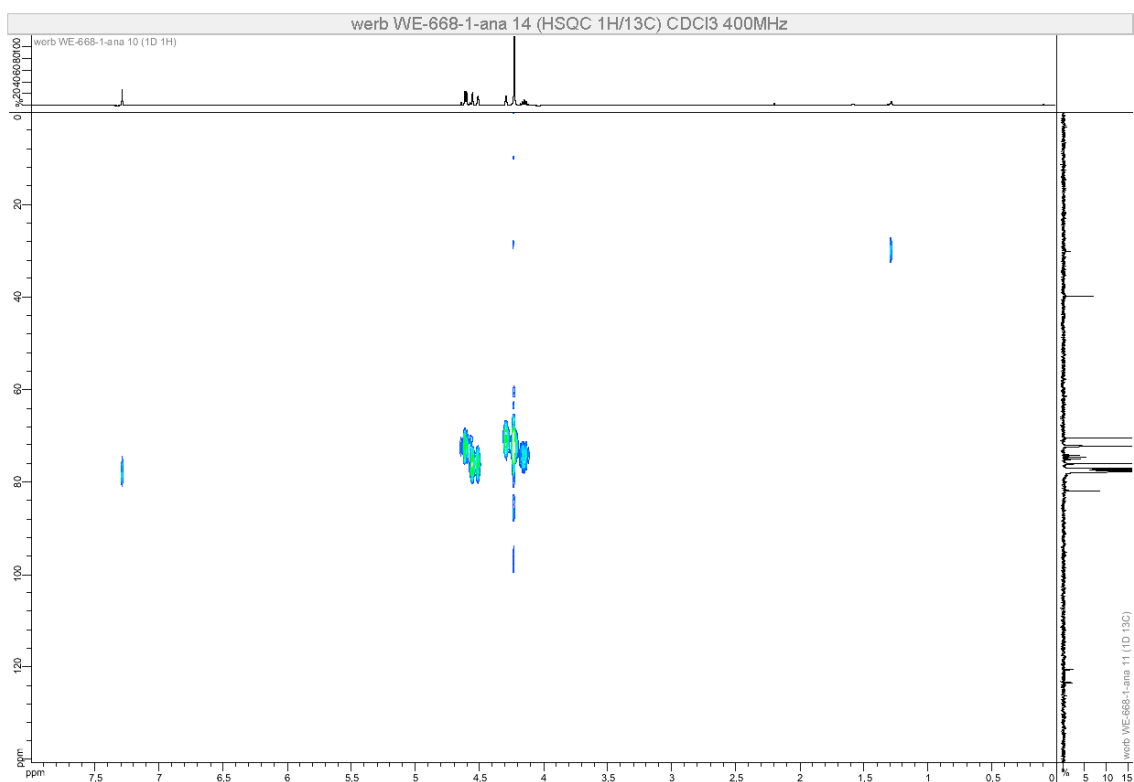
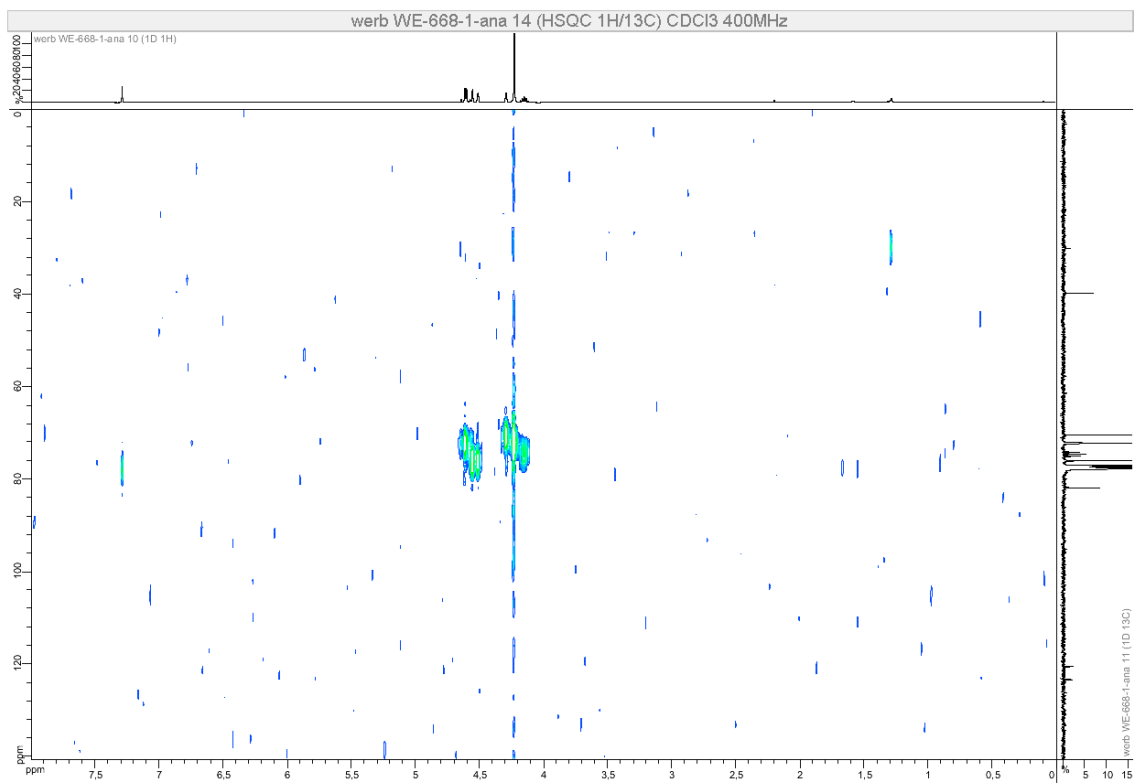
Compound 7c

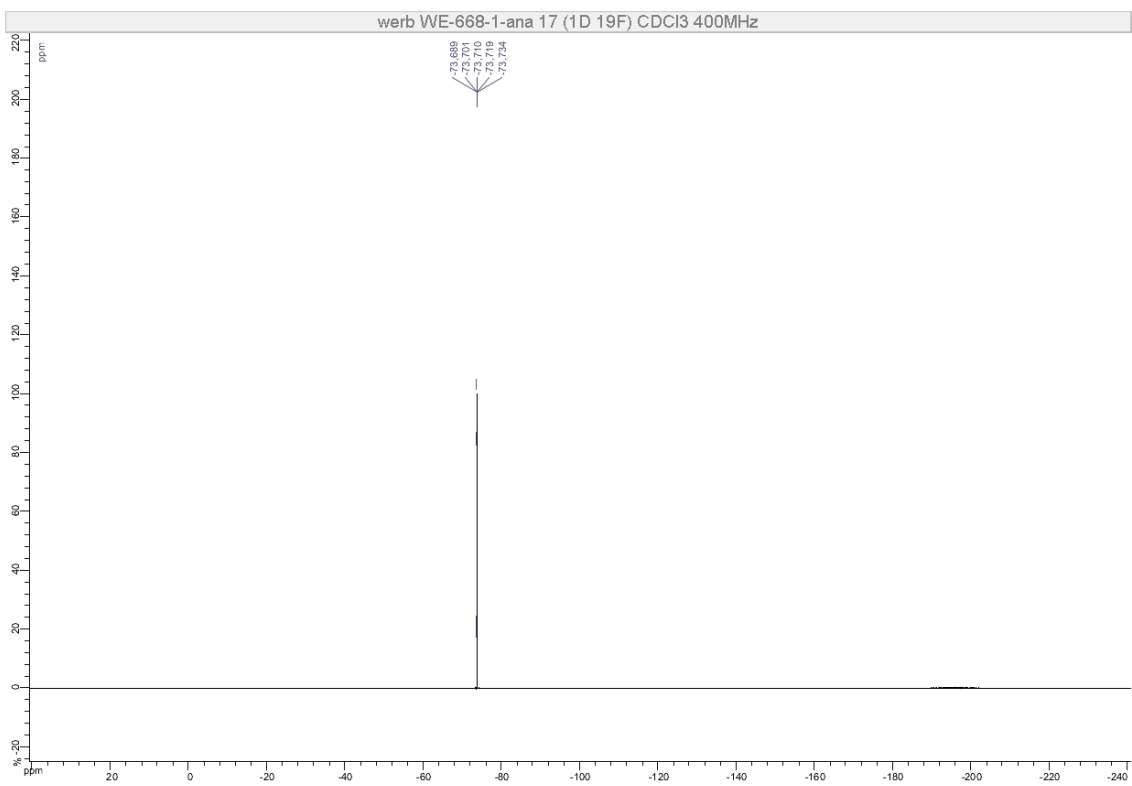
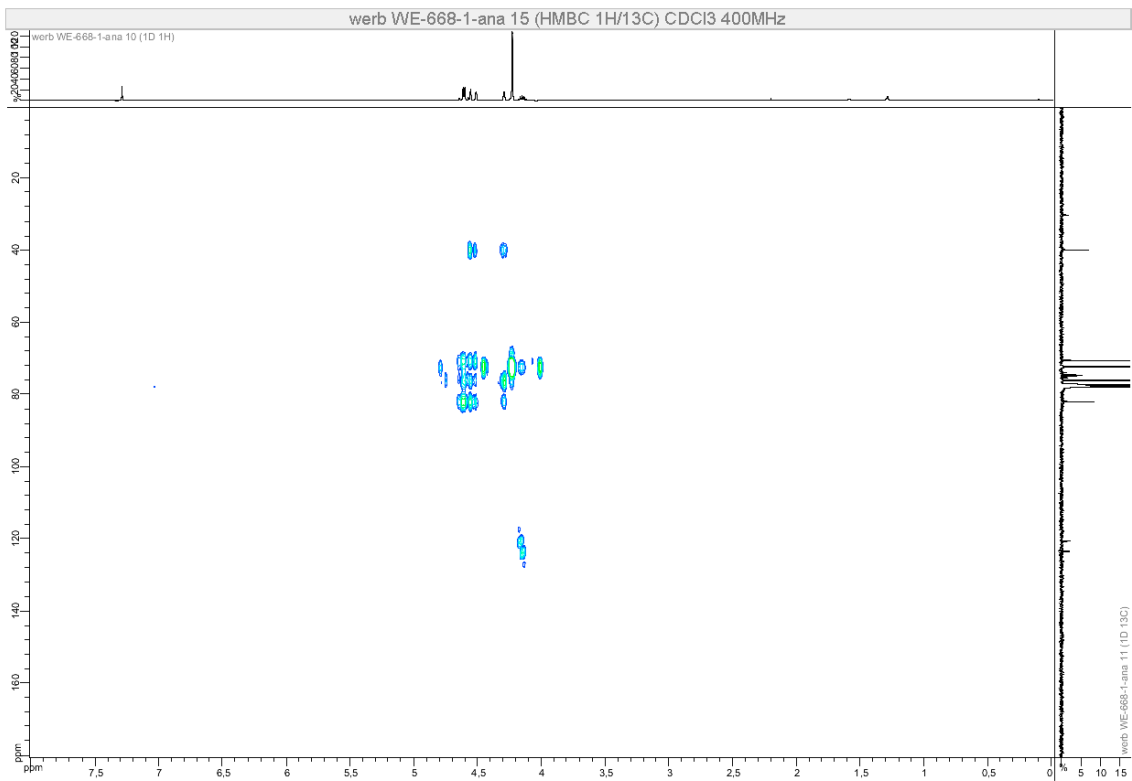




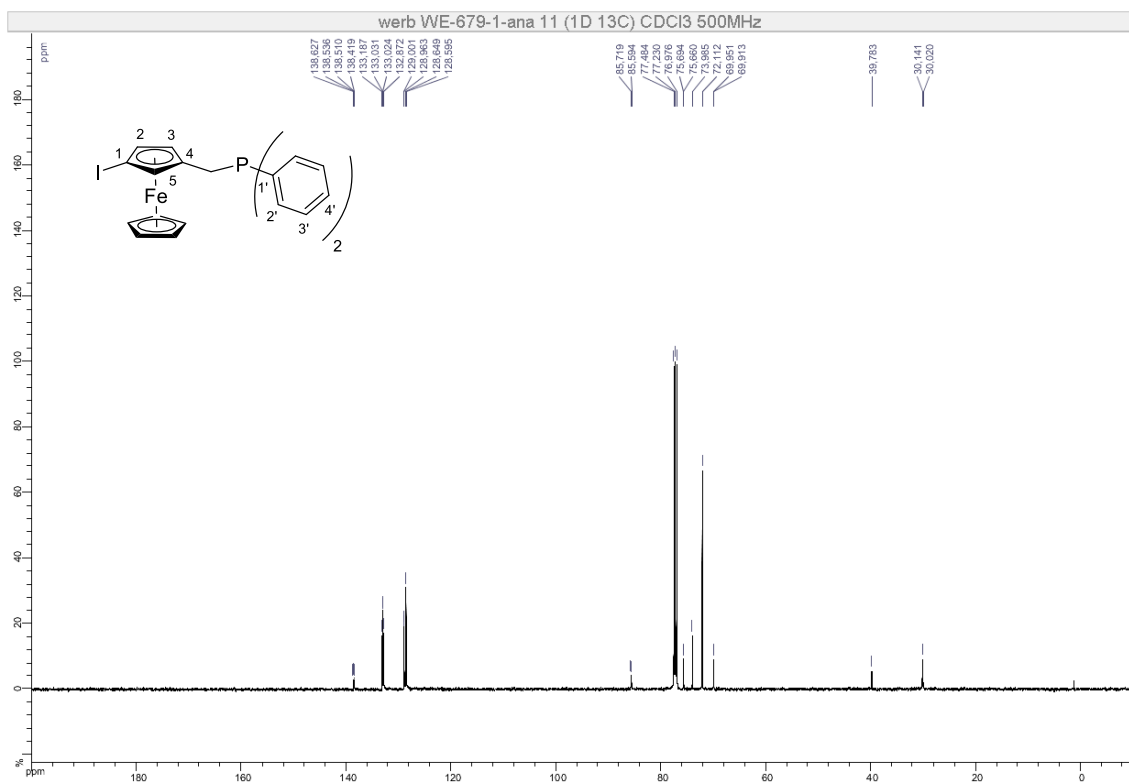
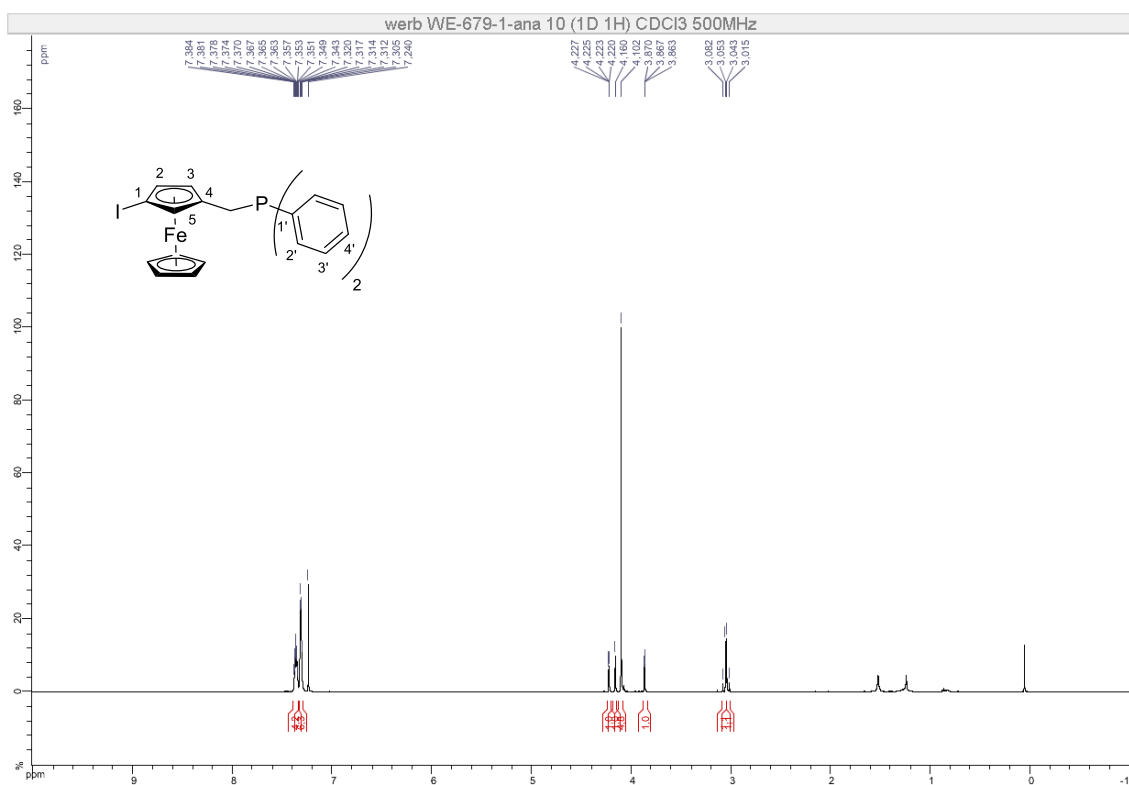


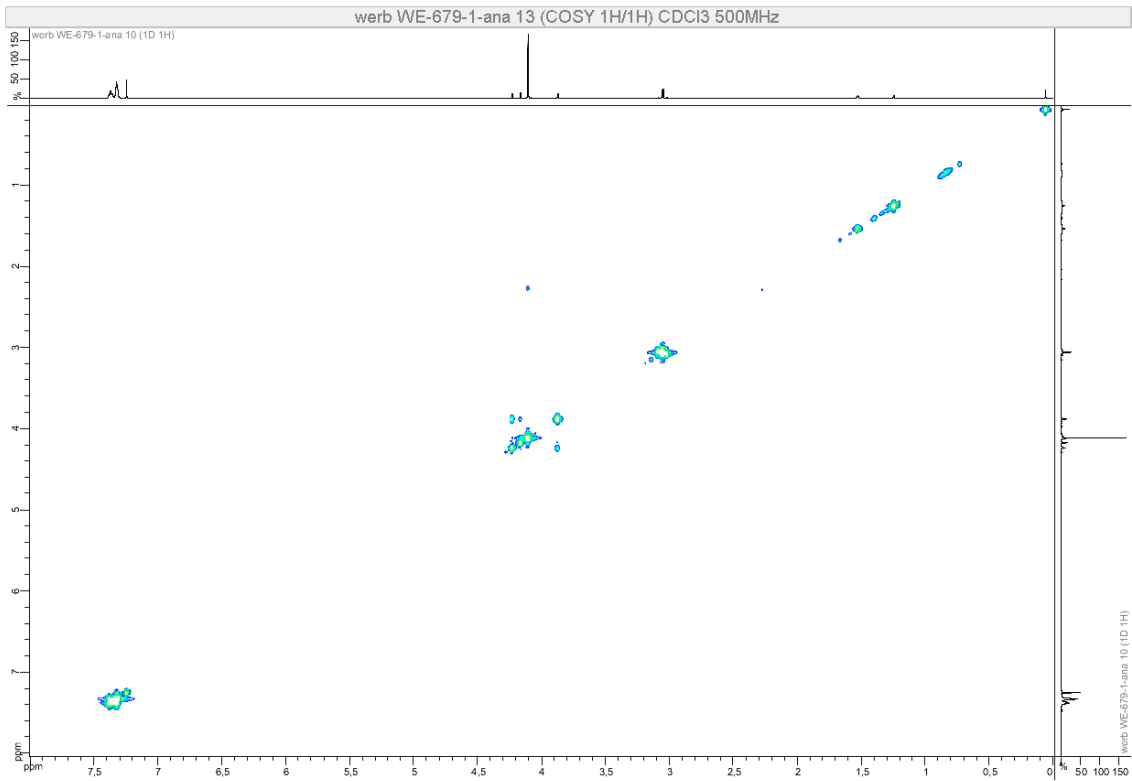
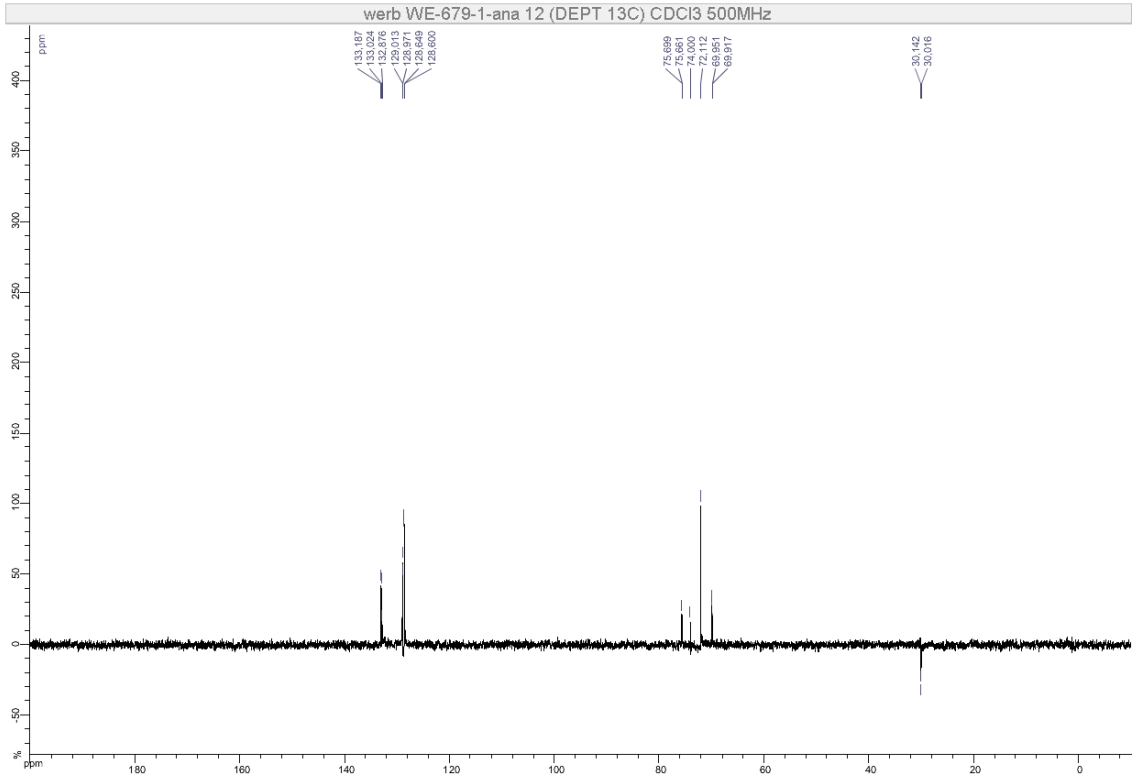


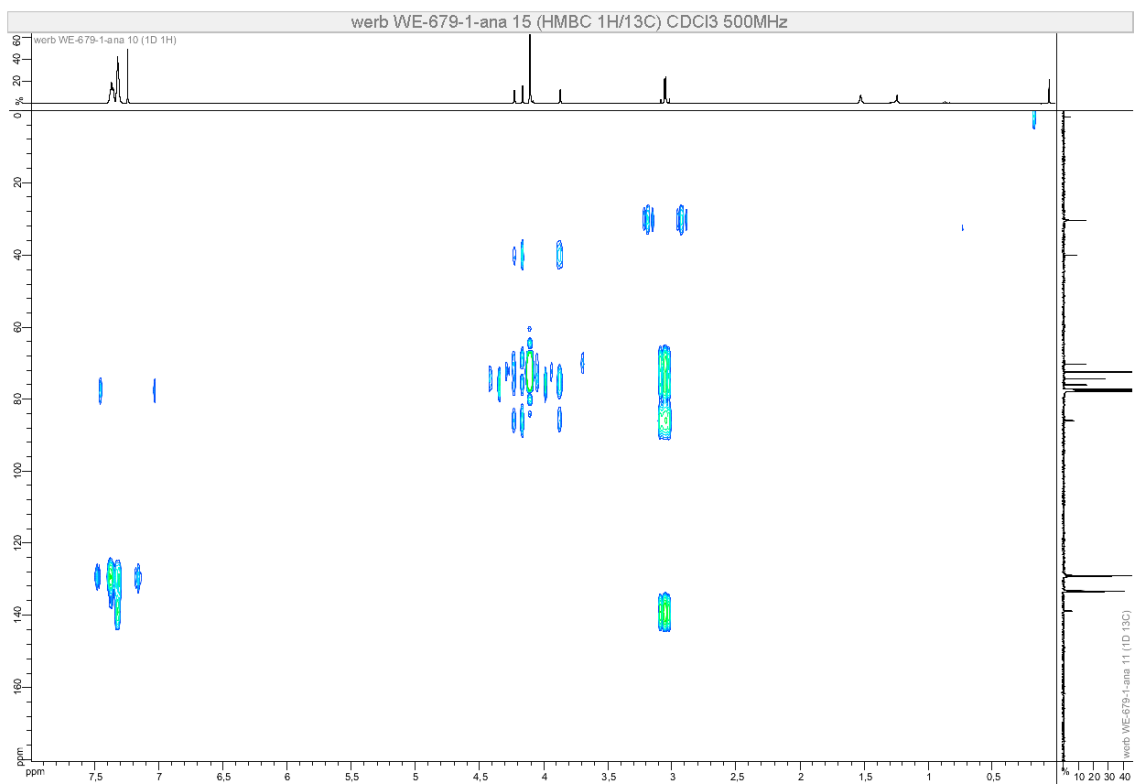
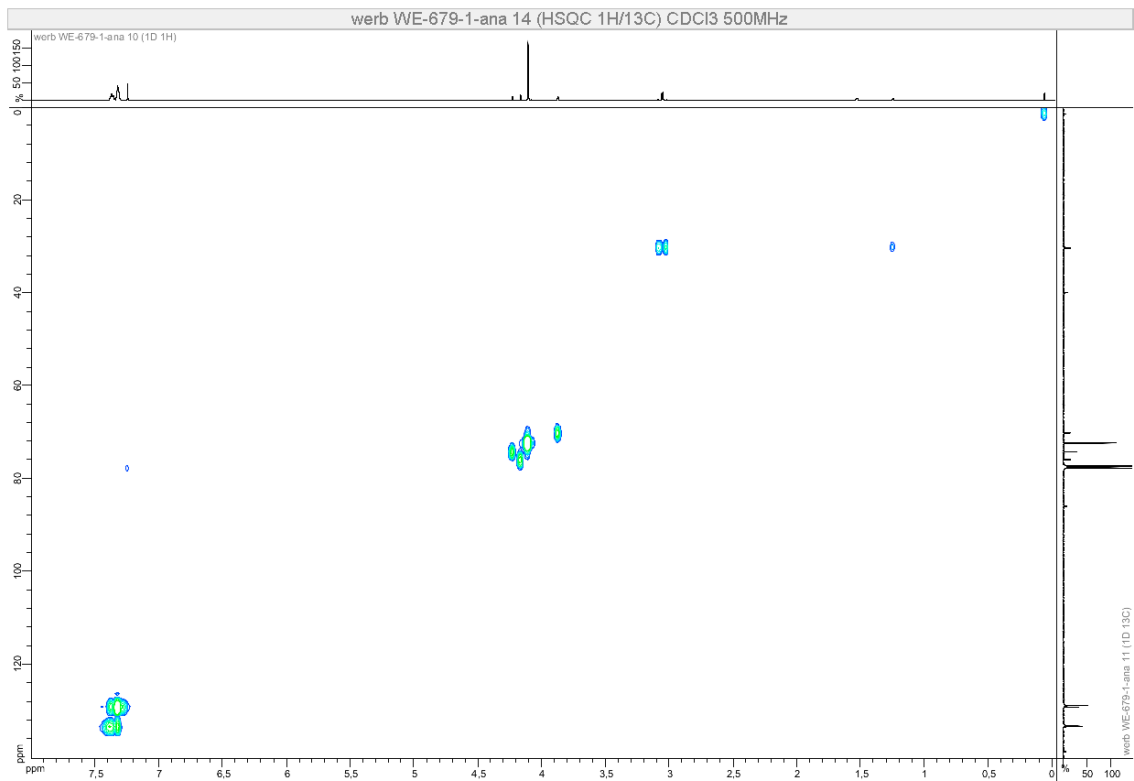


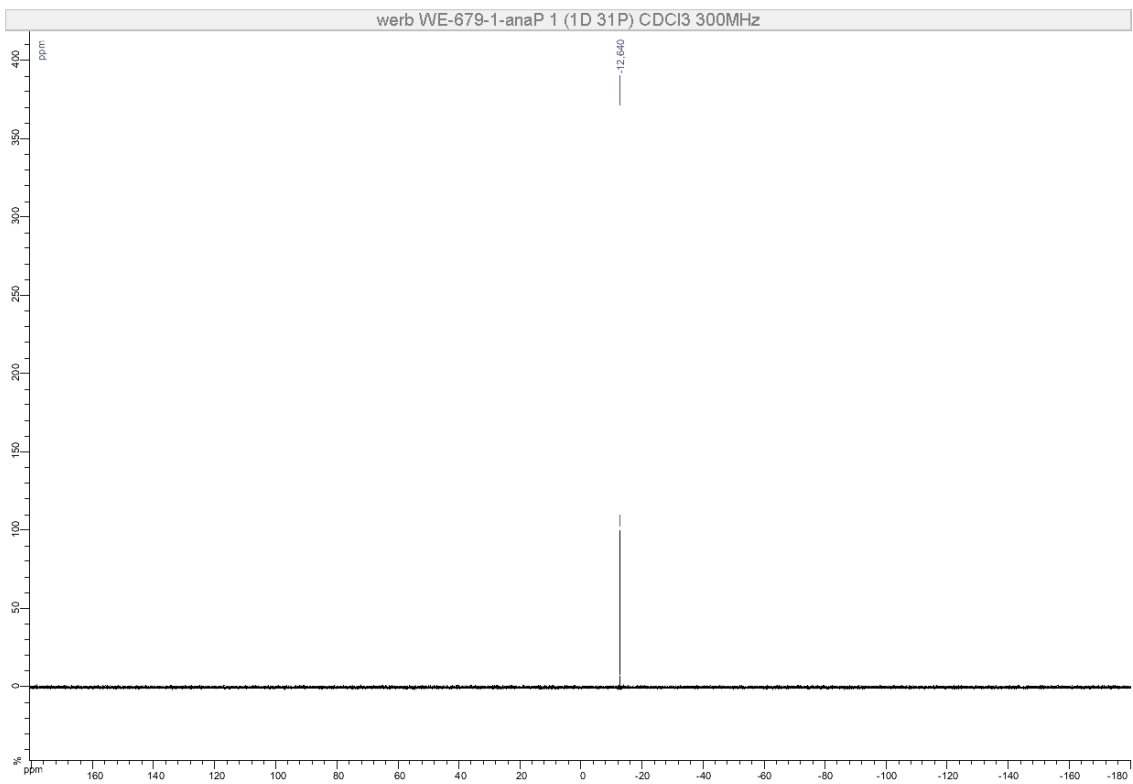
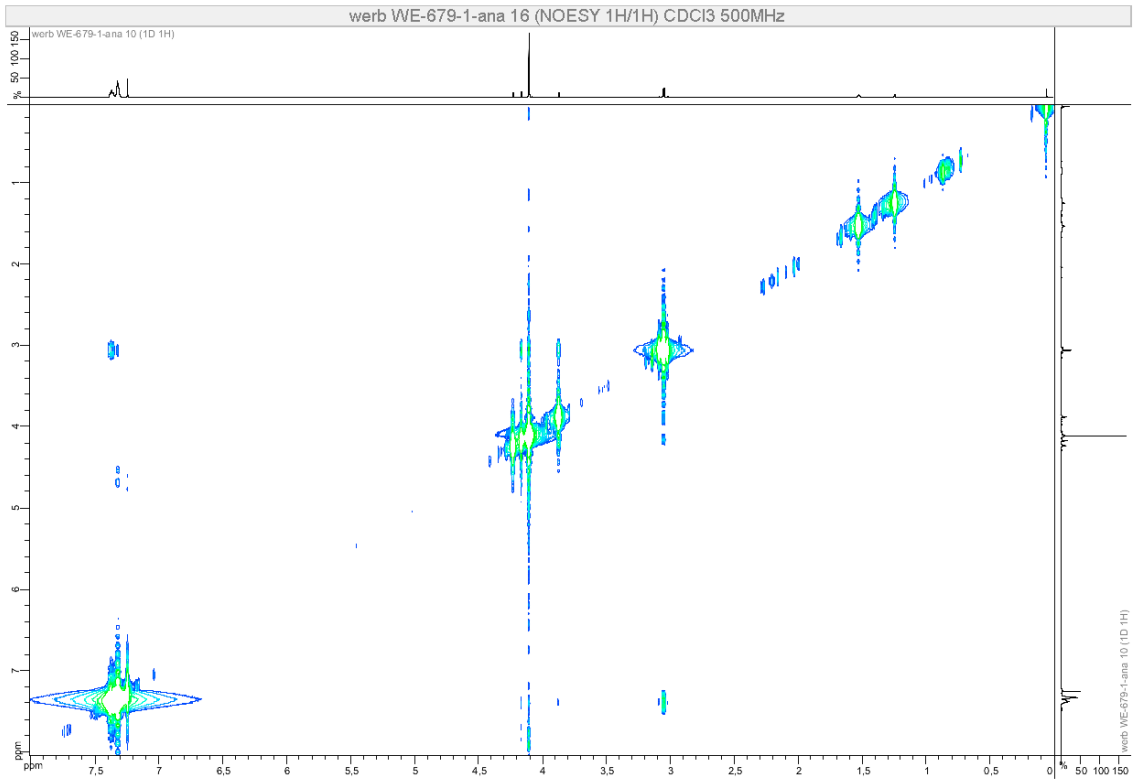


Compound (\pm)-7e

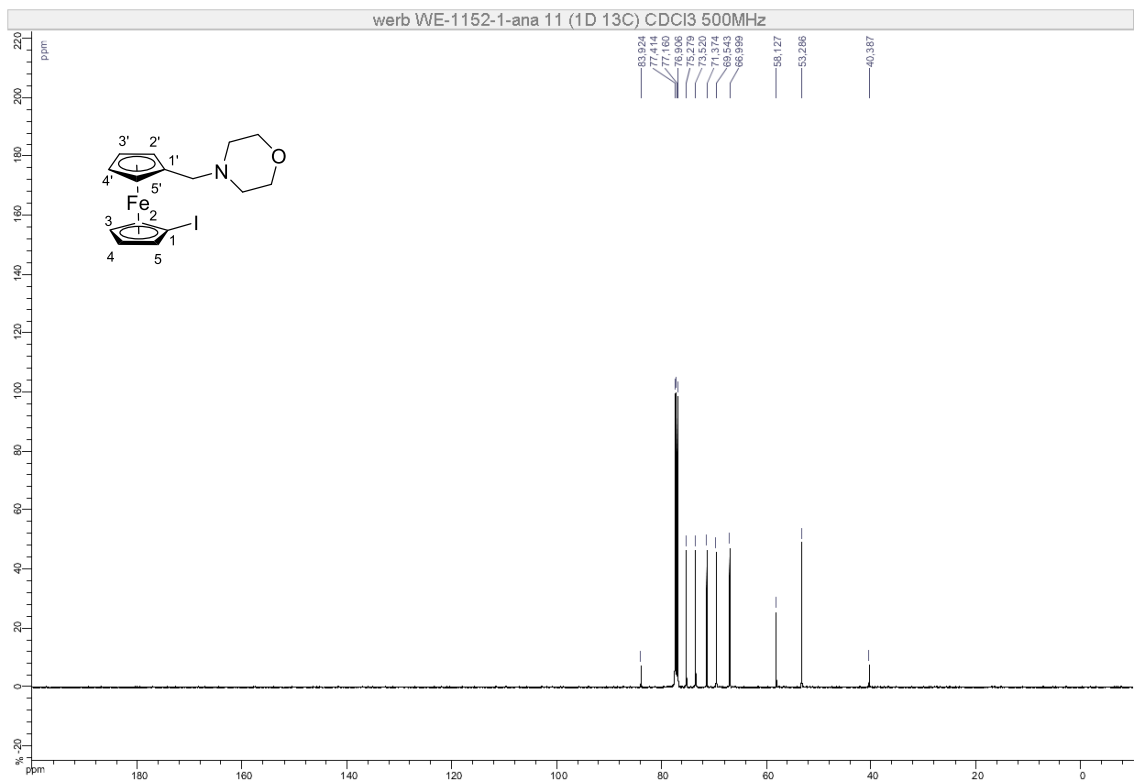
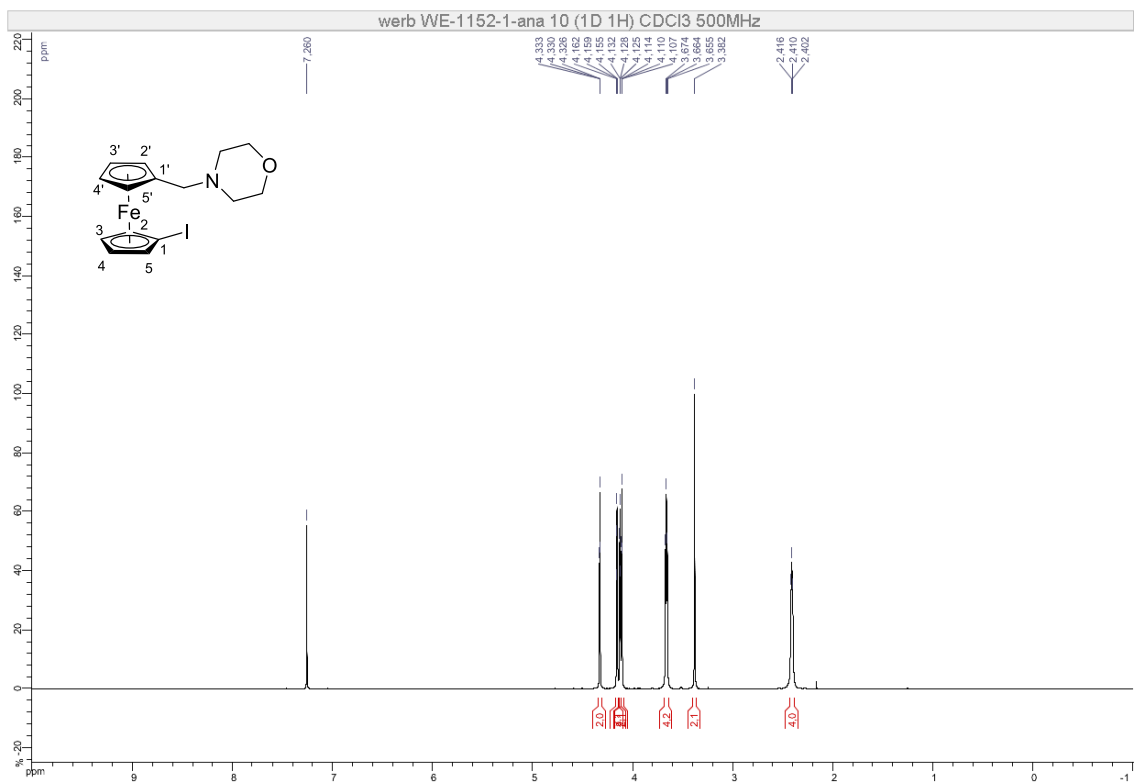


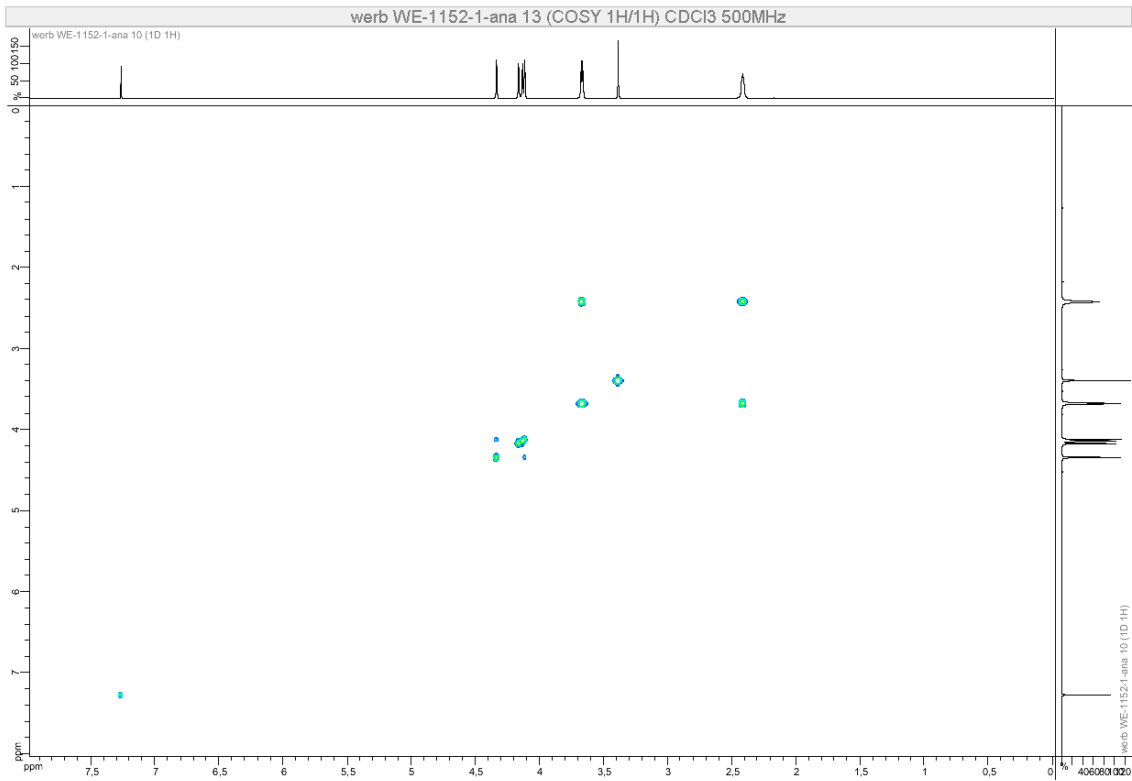
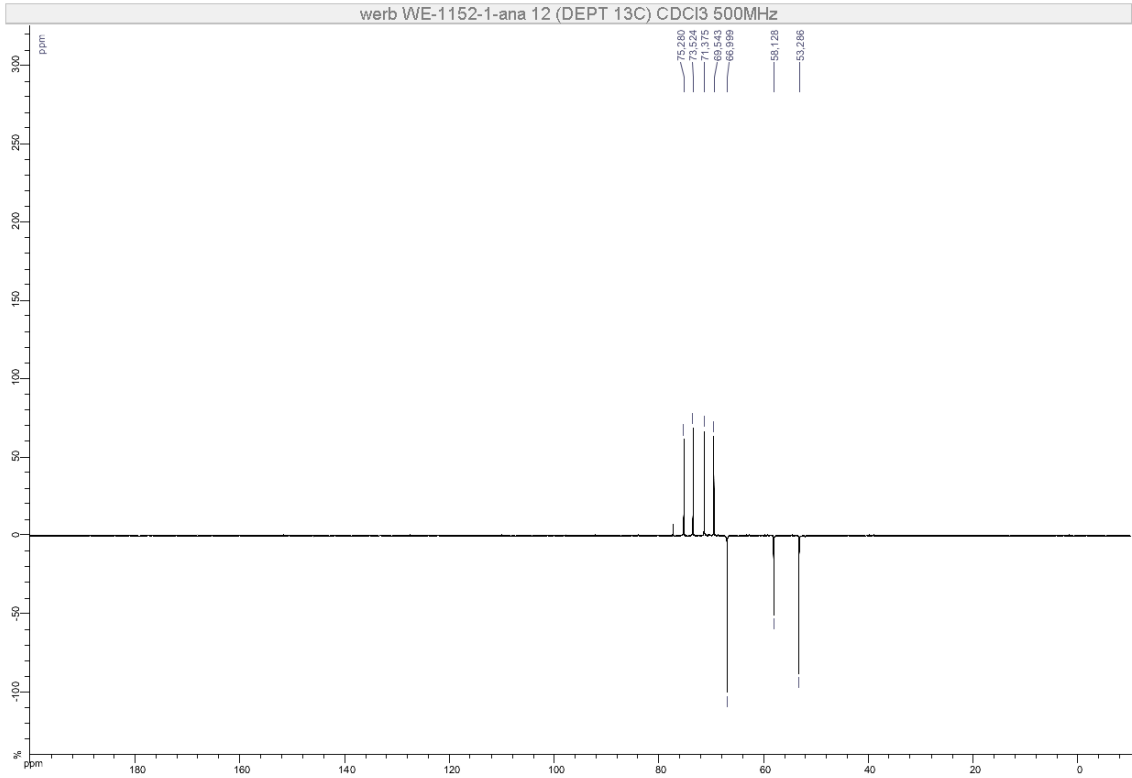


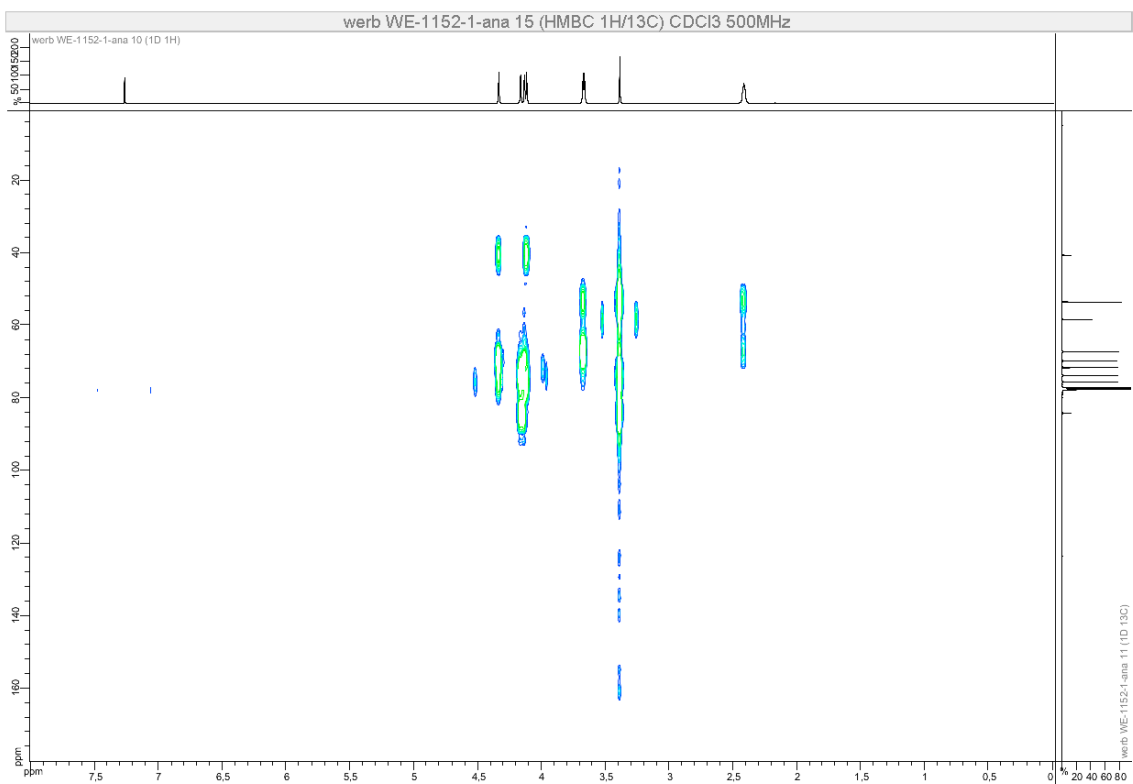
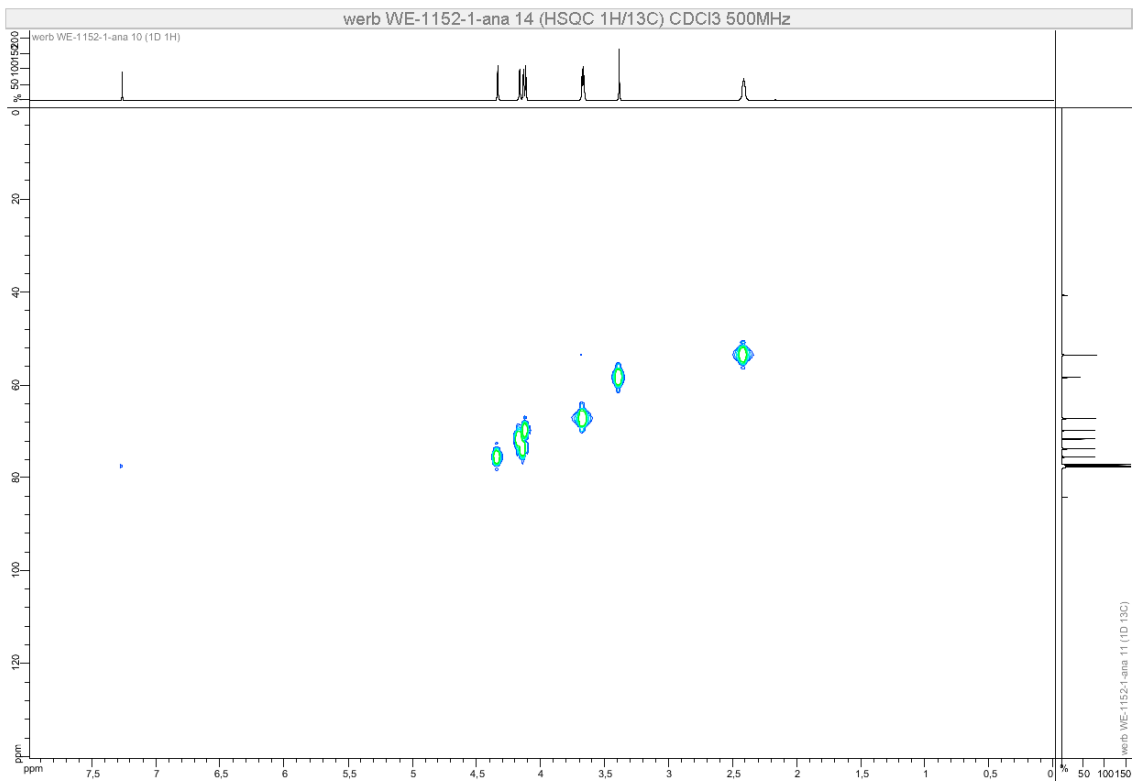


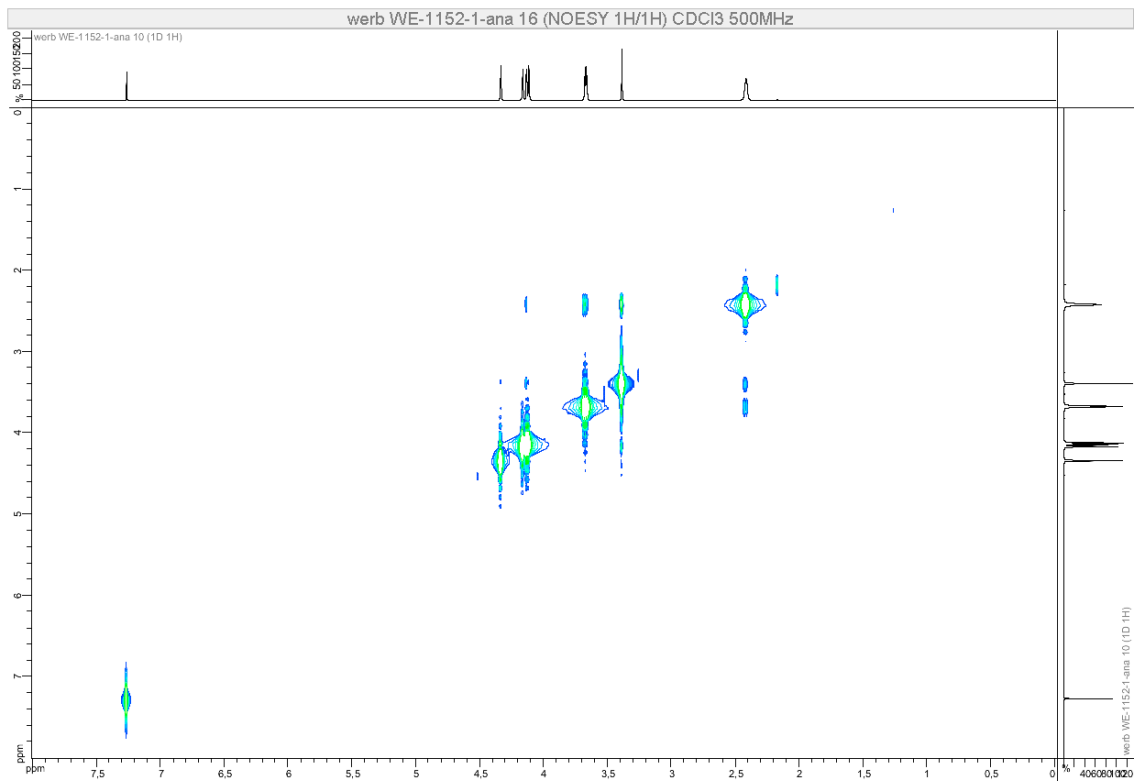


Compound 8a

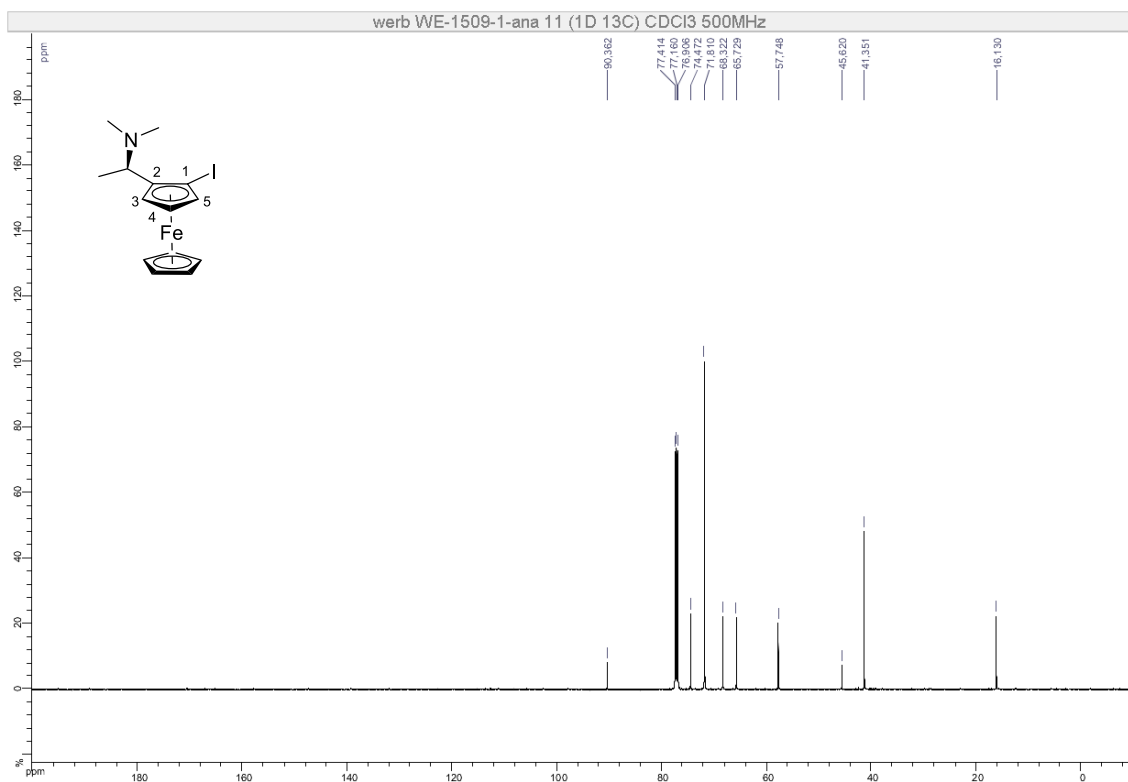
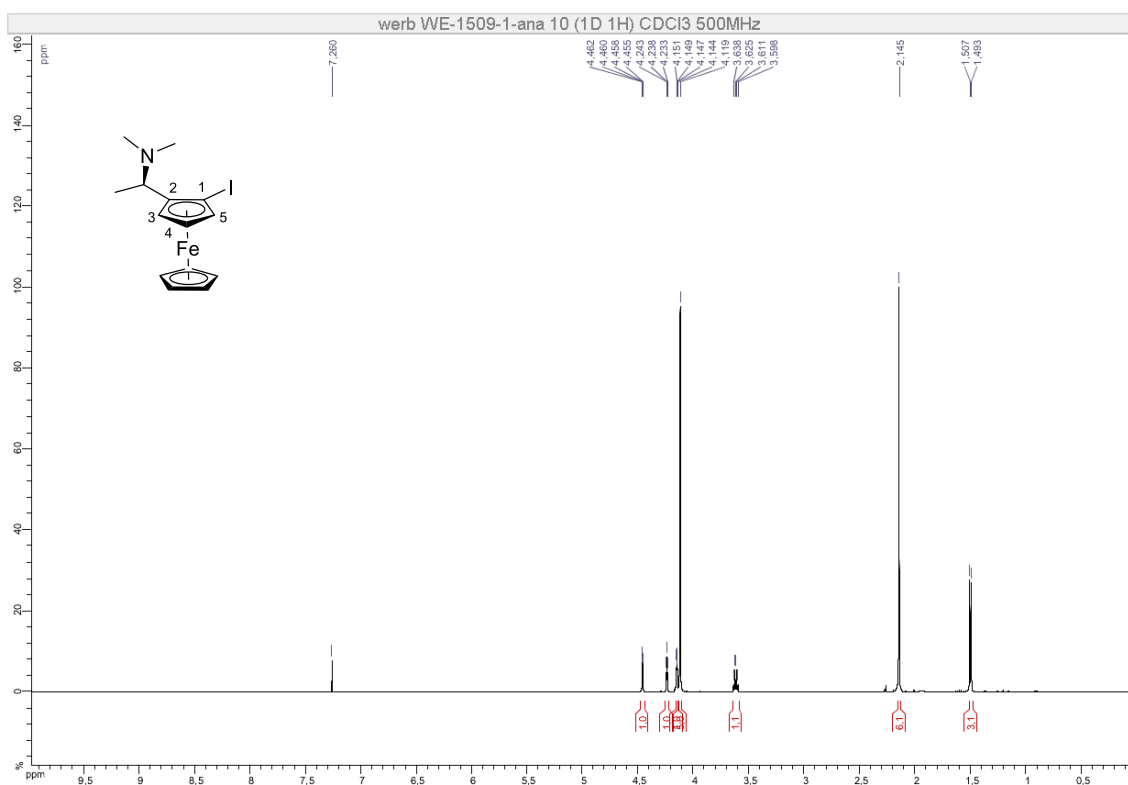


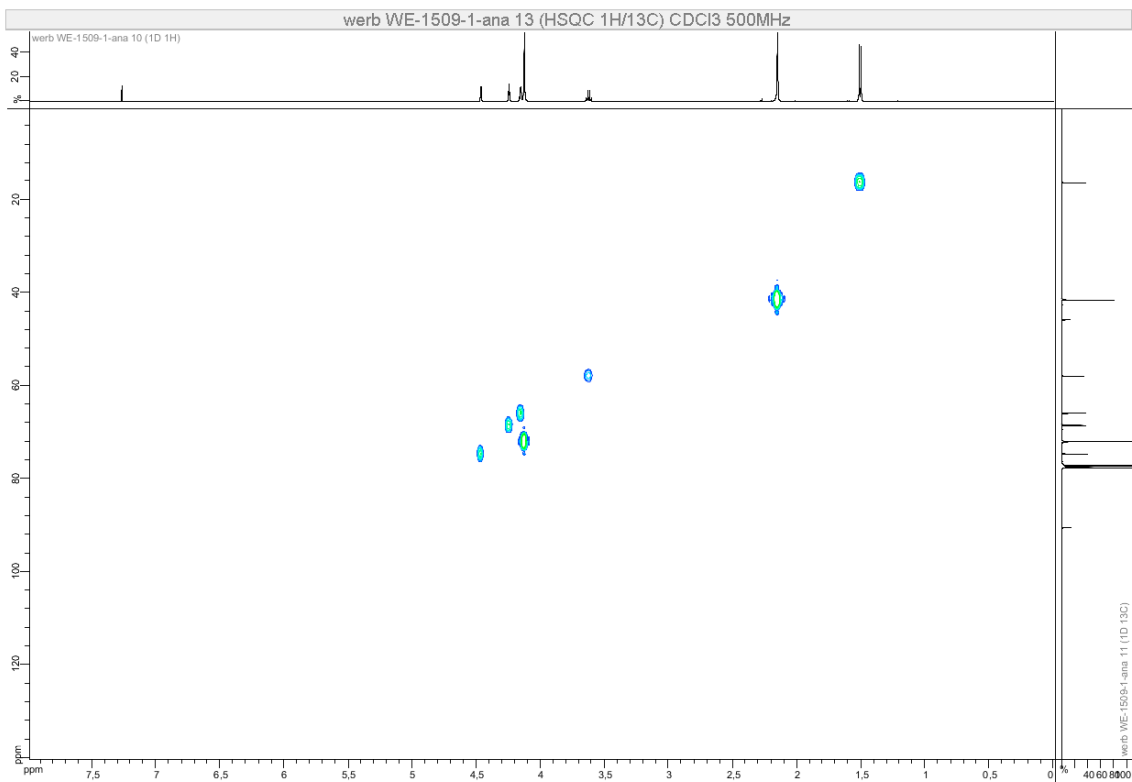
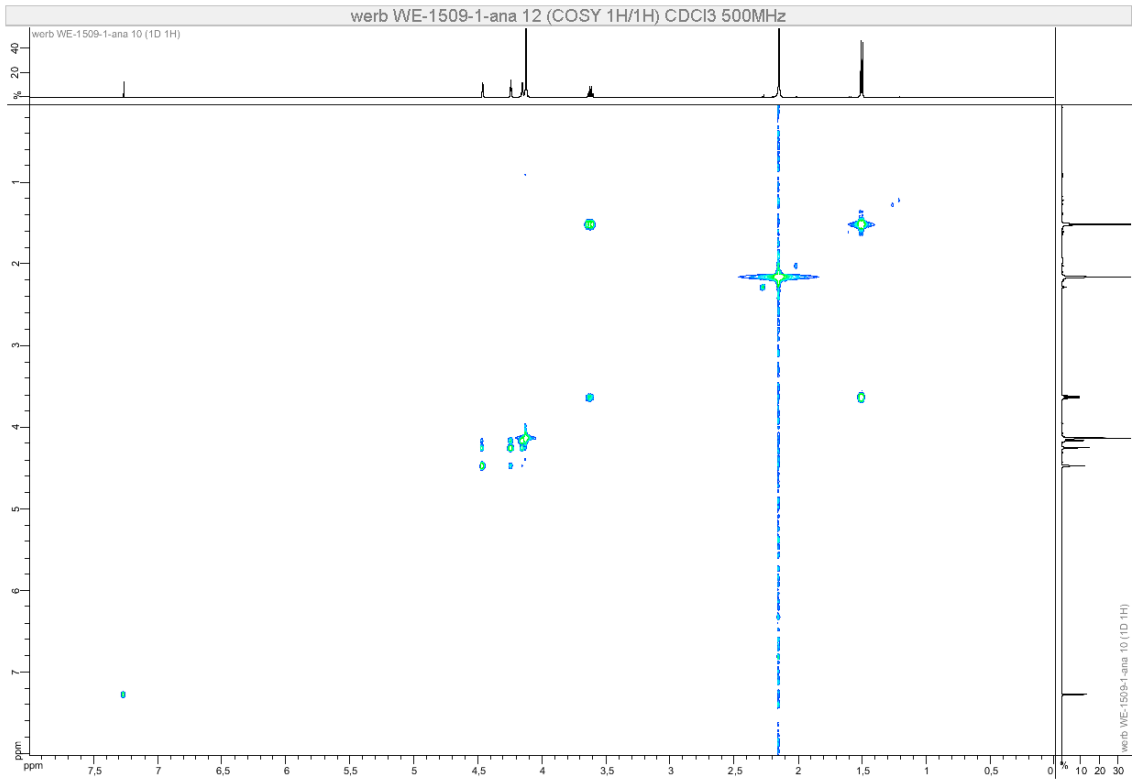


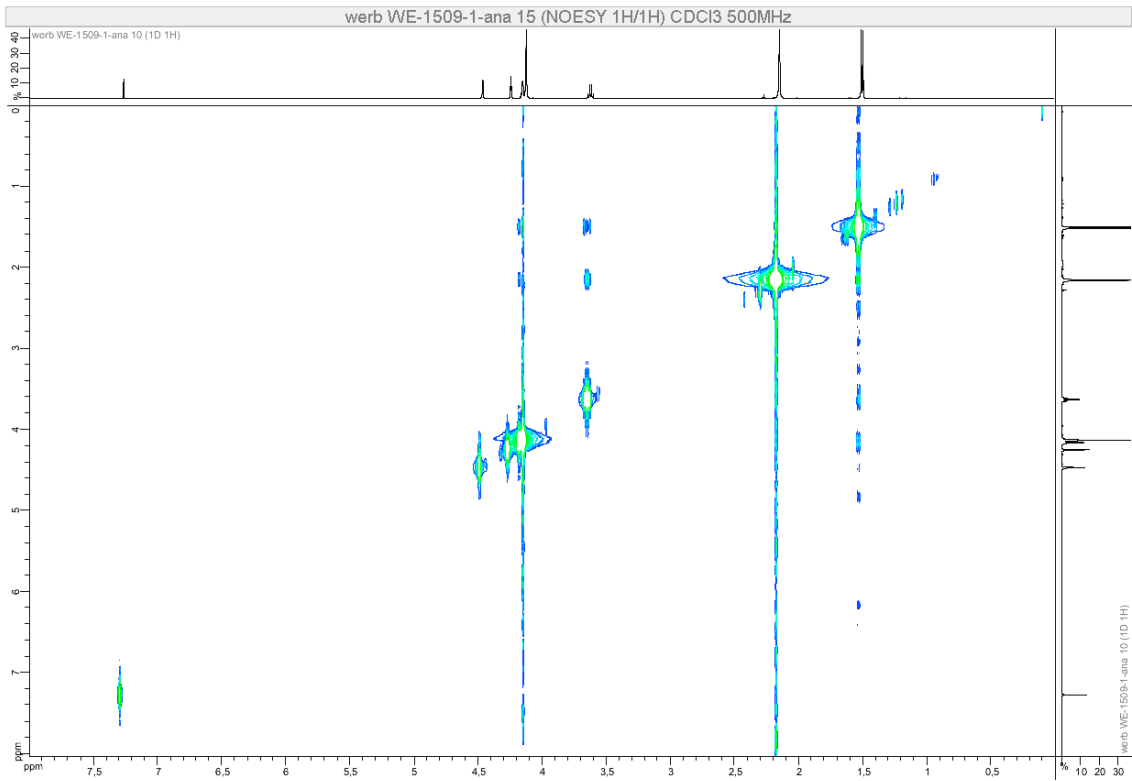
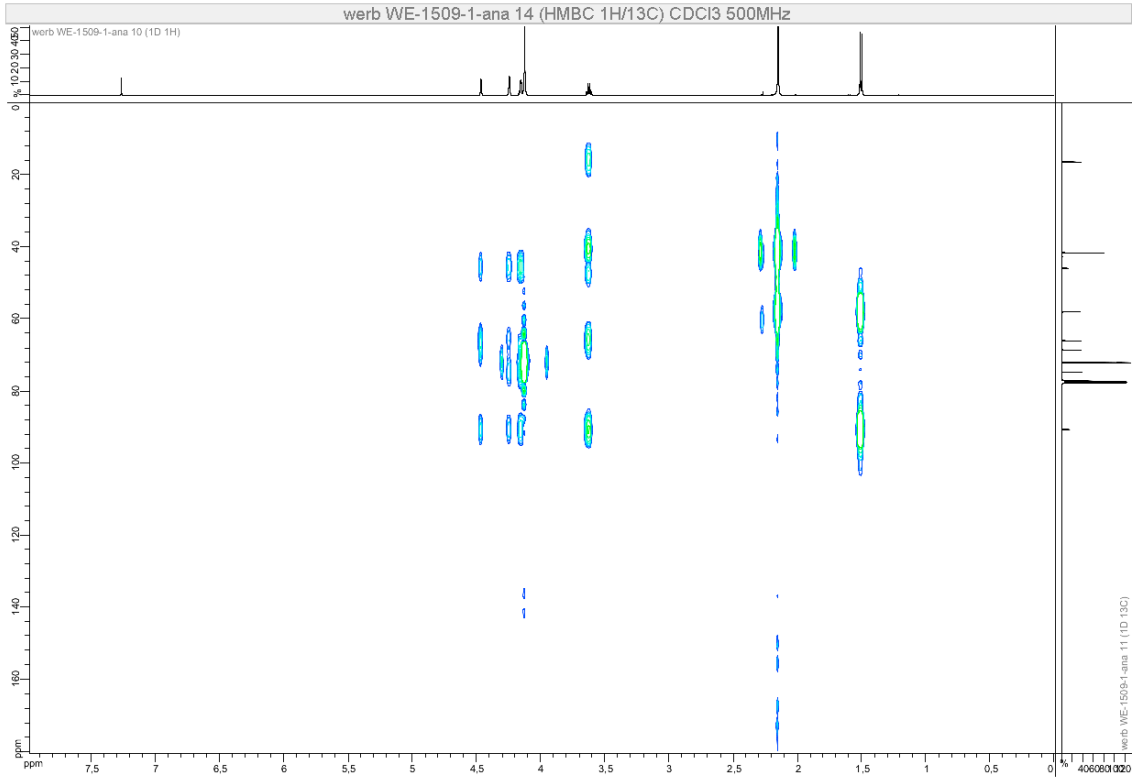




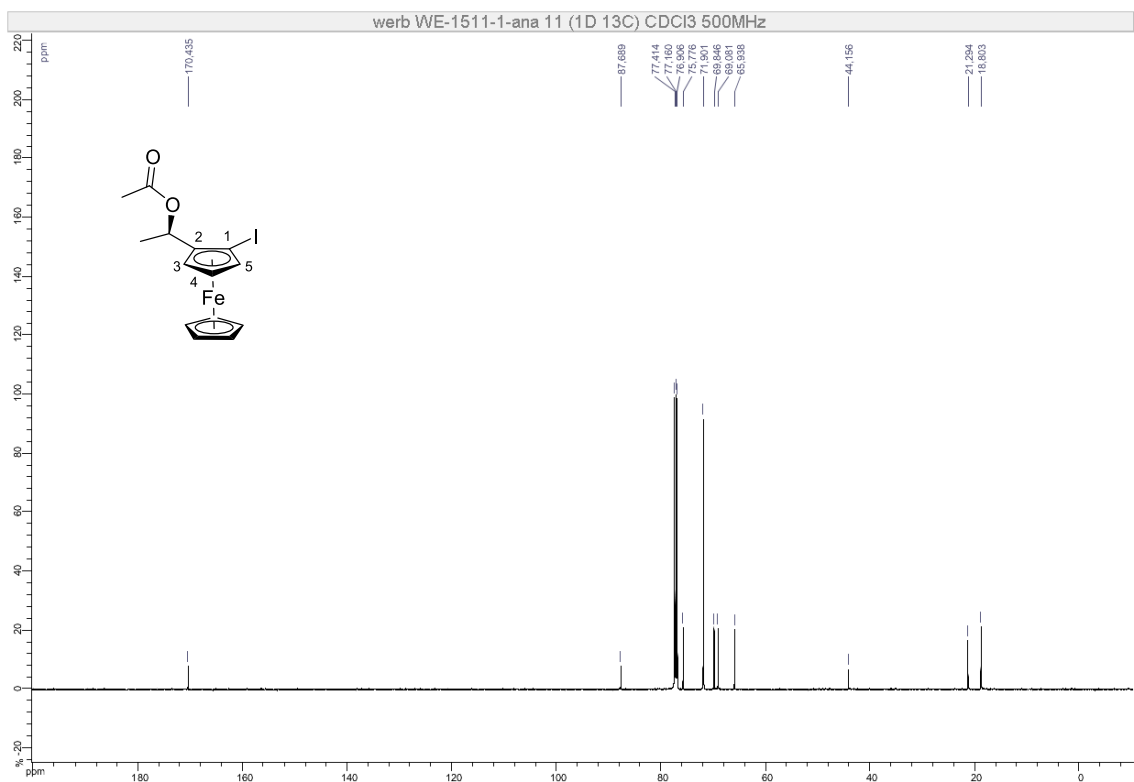
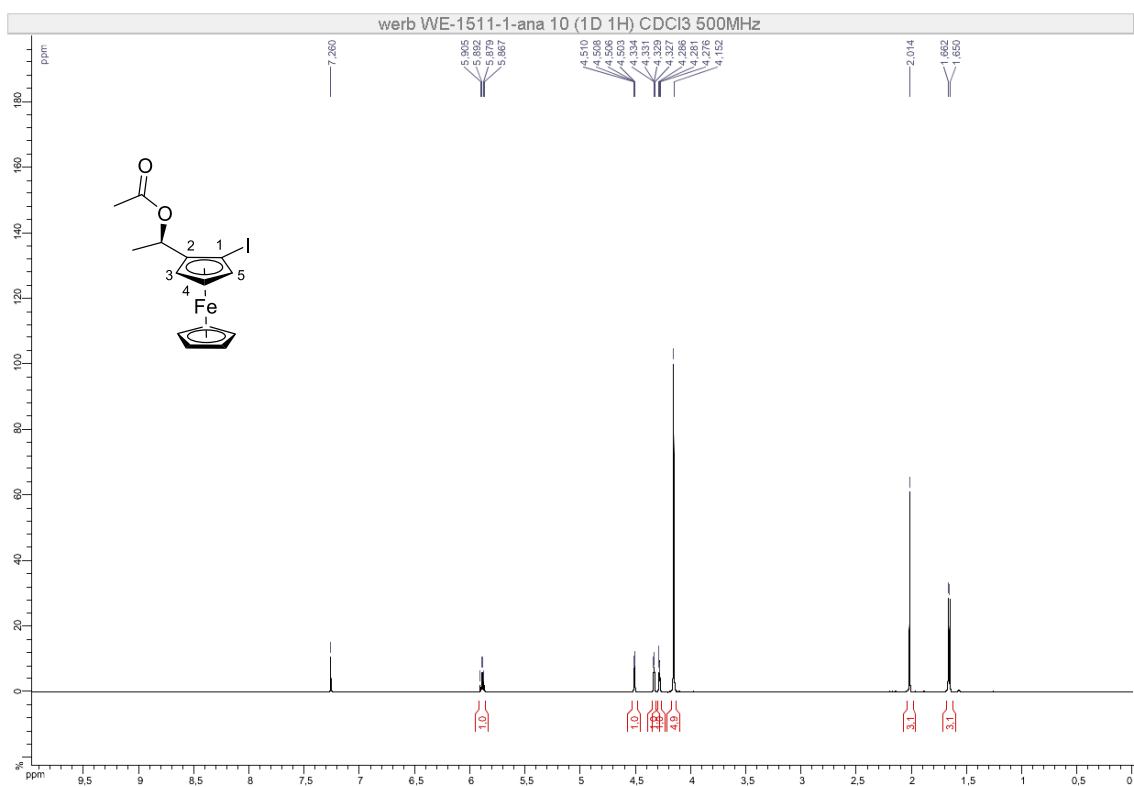
Compound (*R,S*)-9a

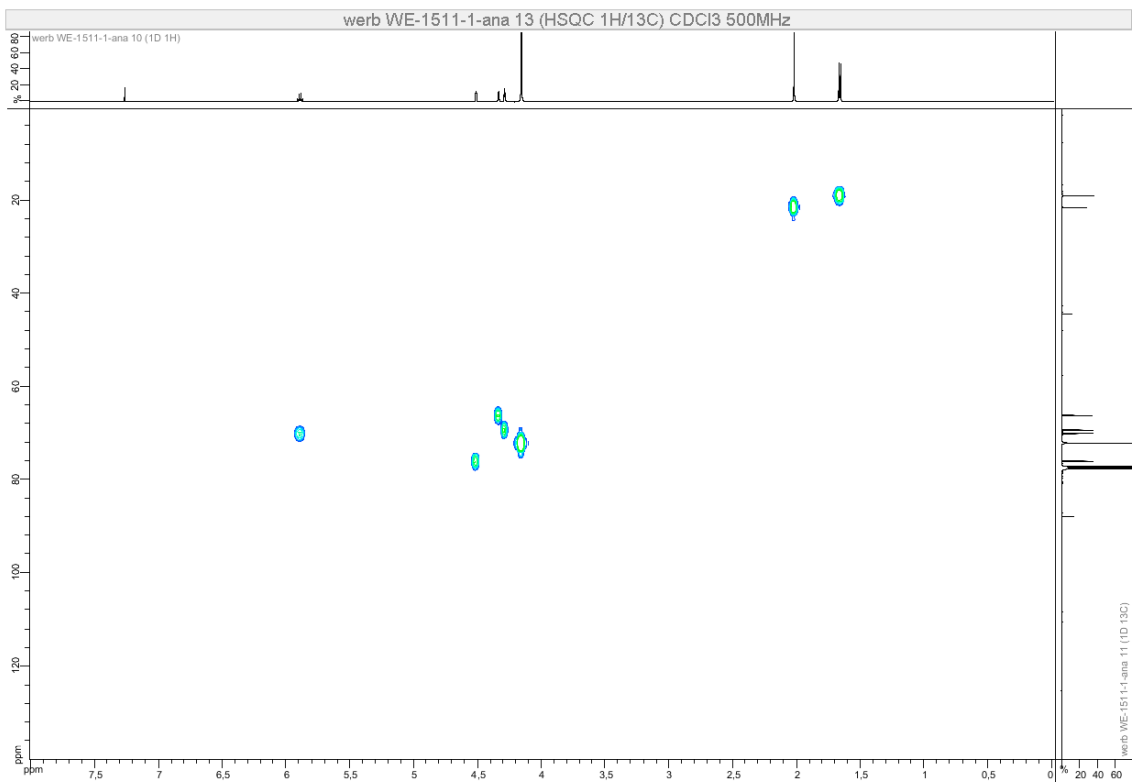
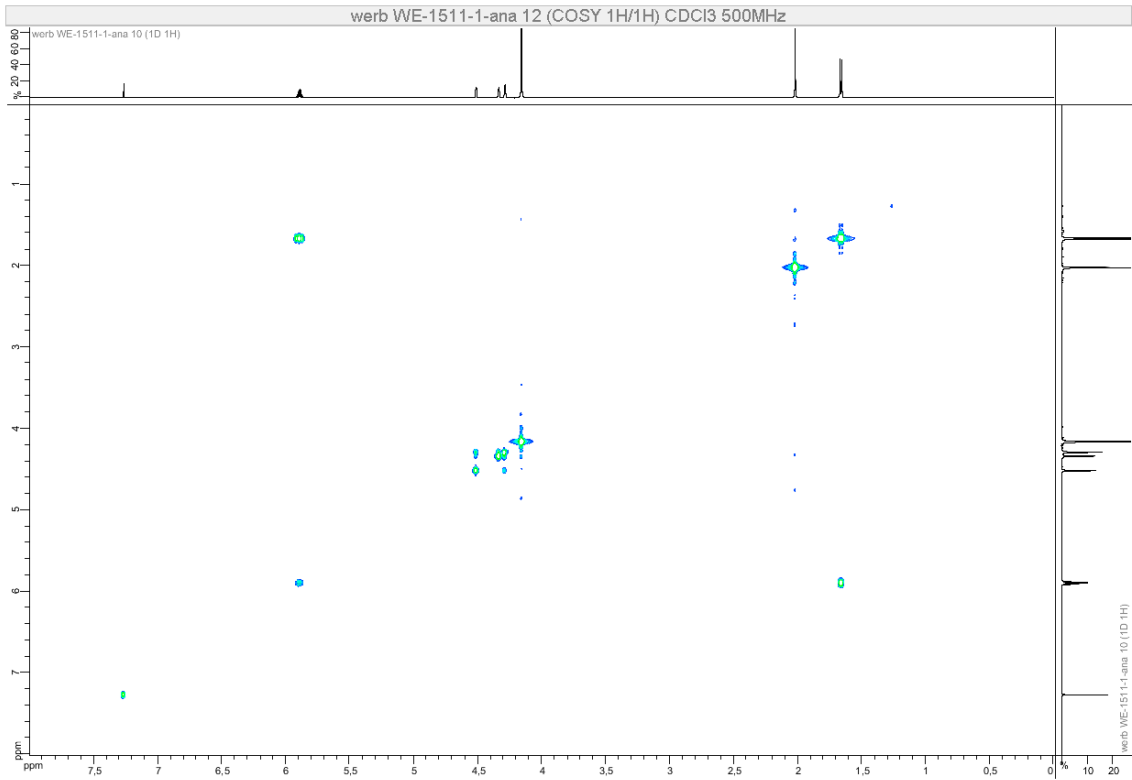


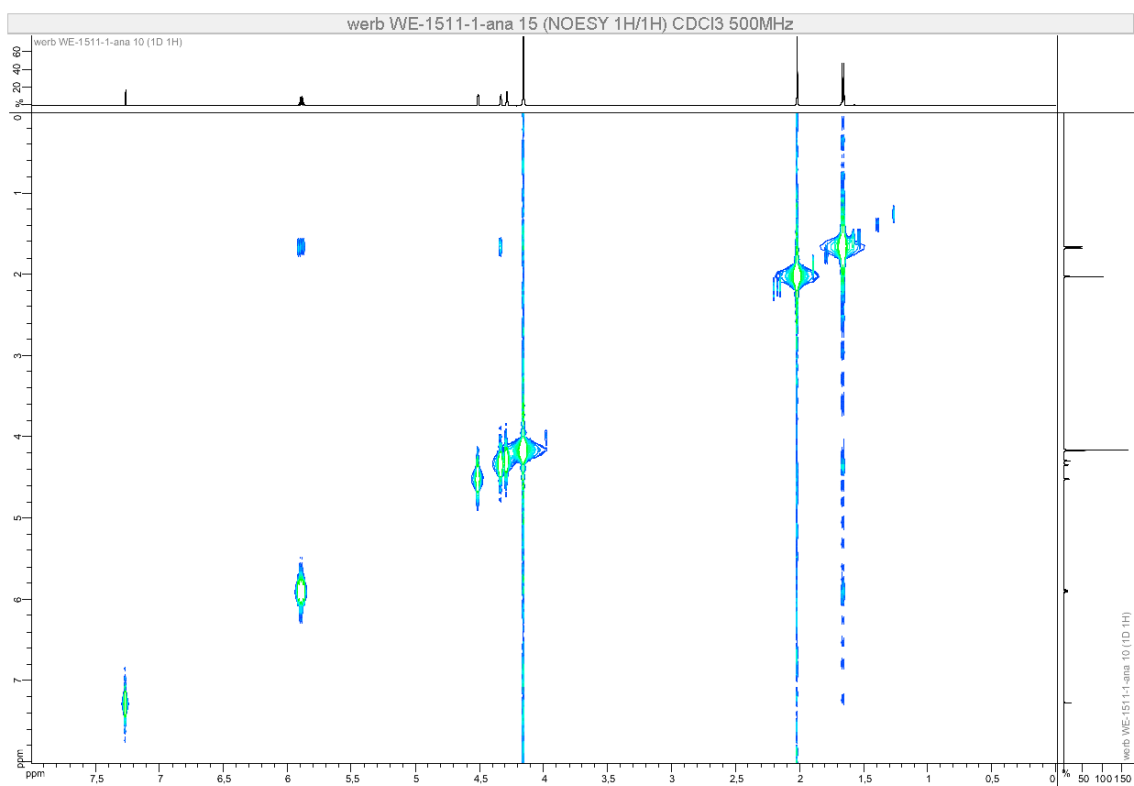
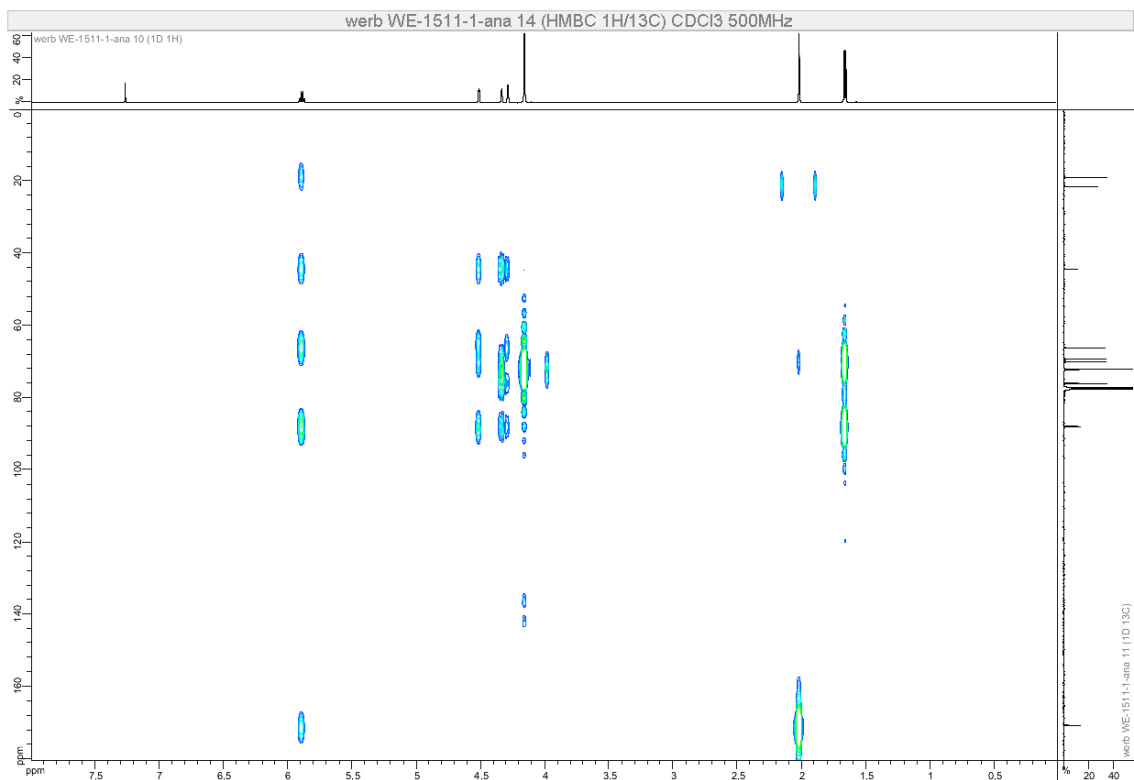




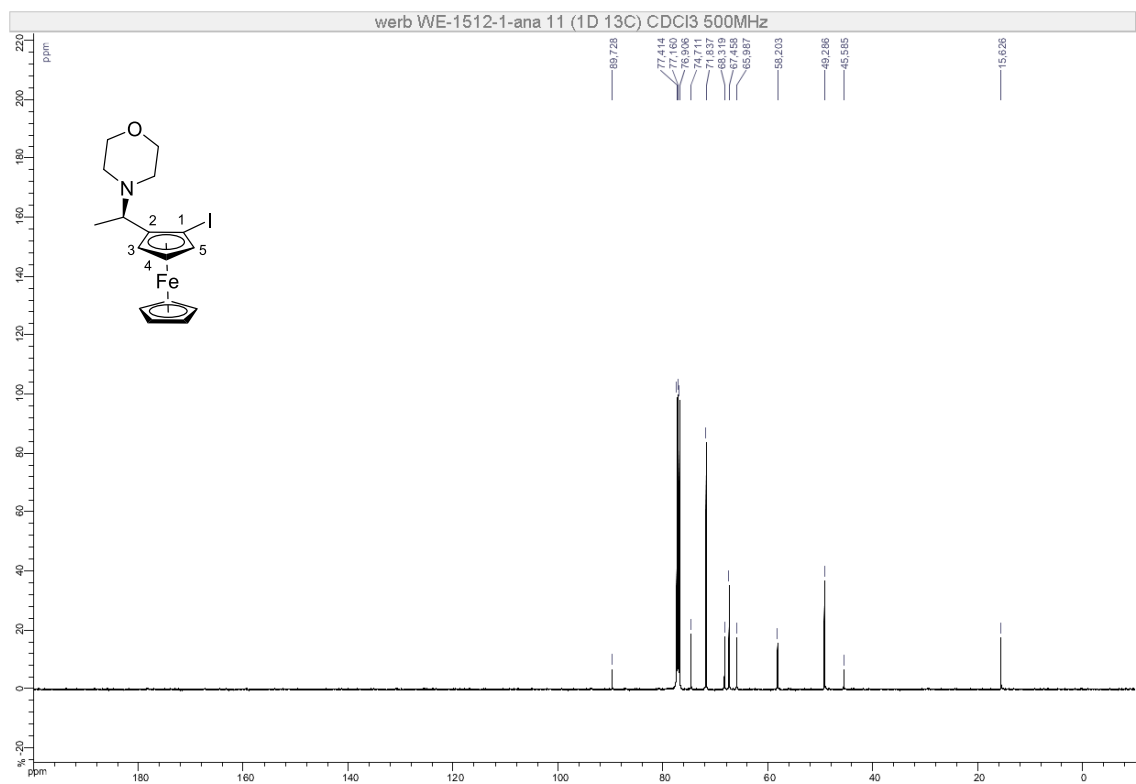
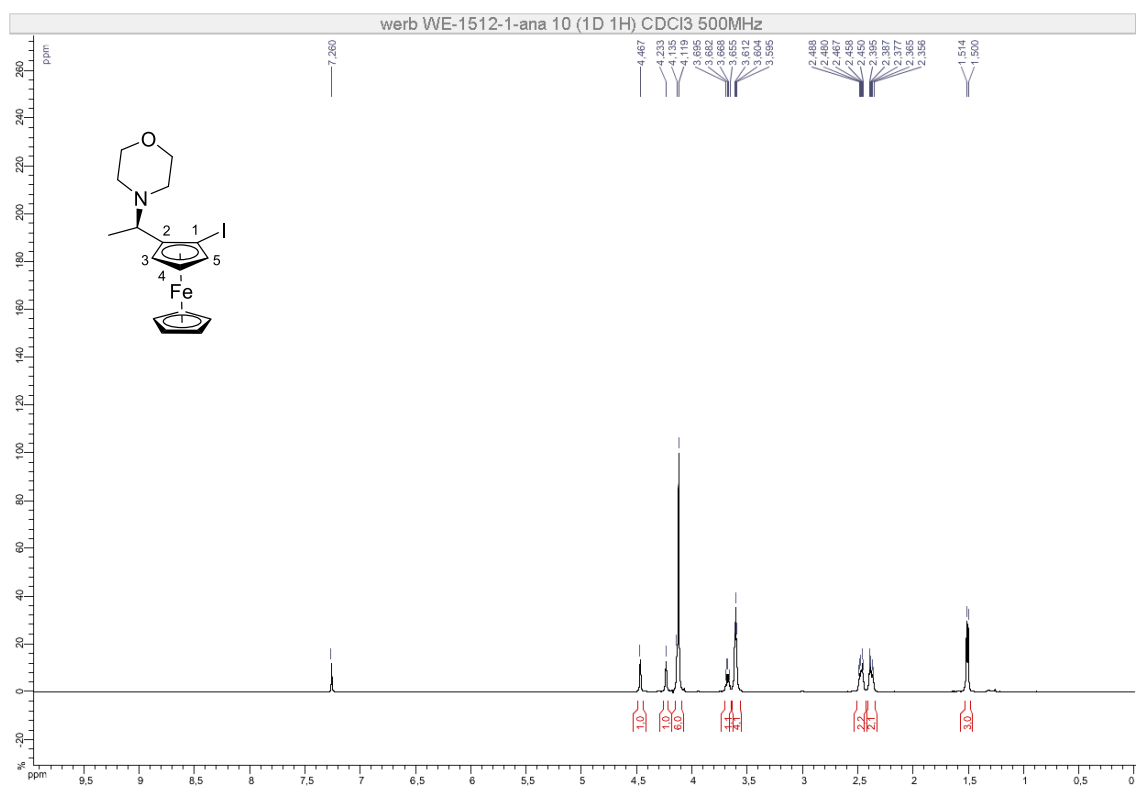
Compound (*R,S*)-9b

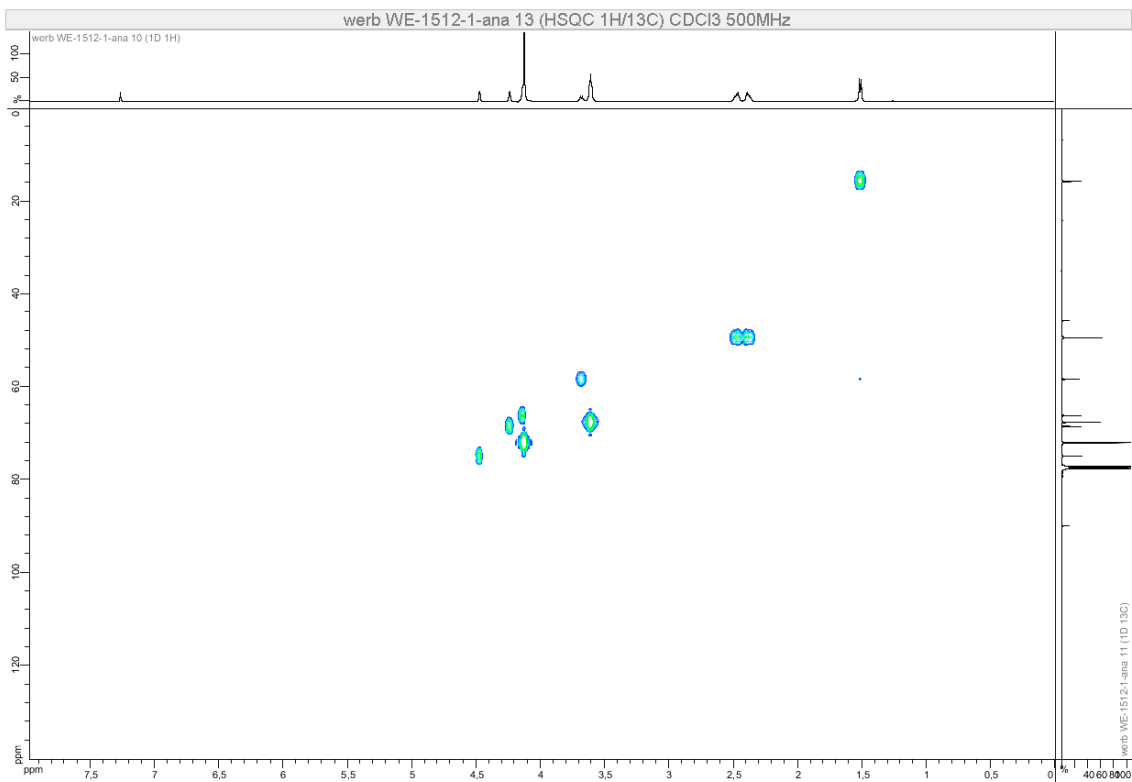
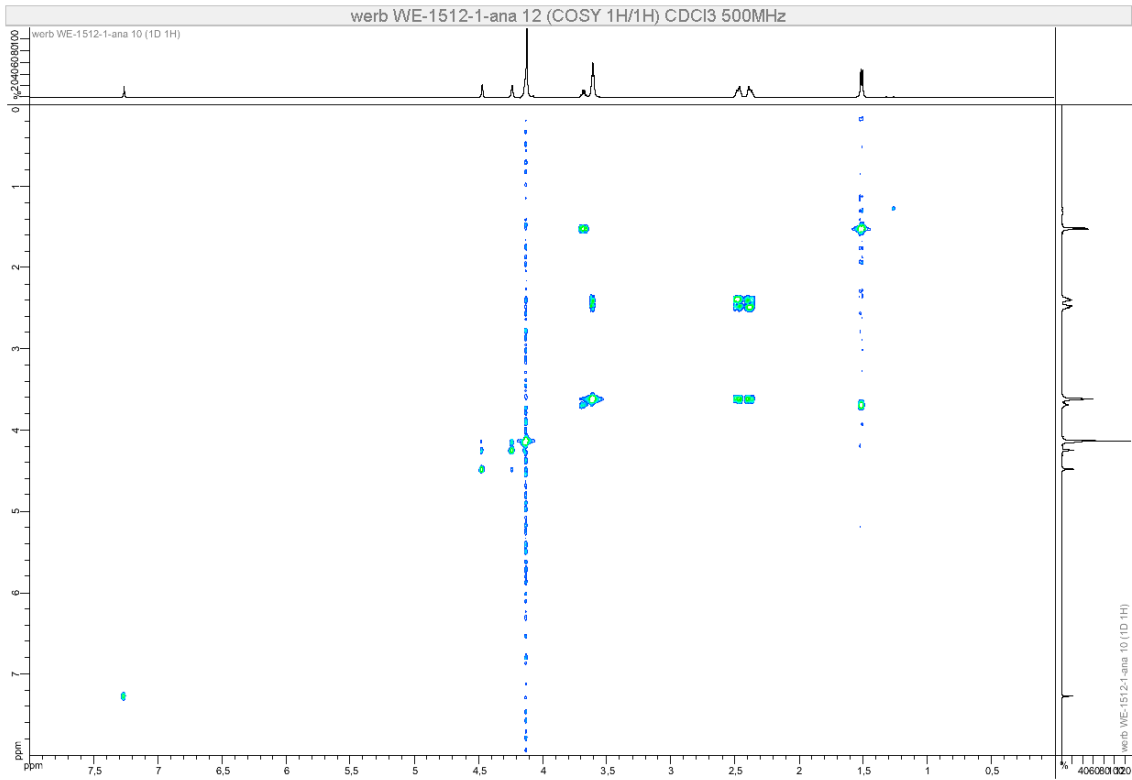


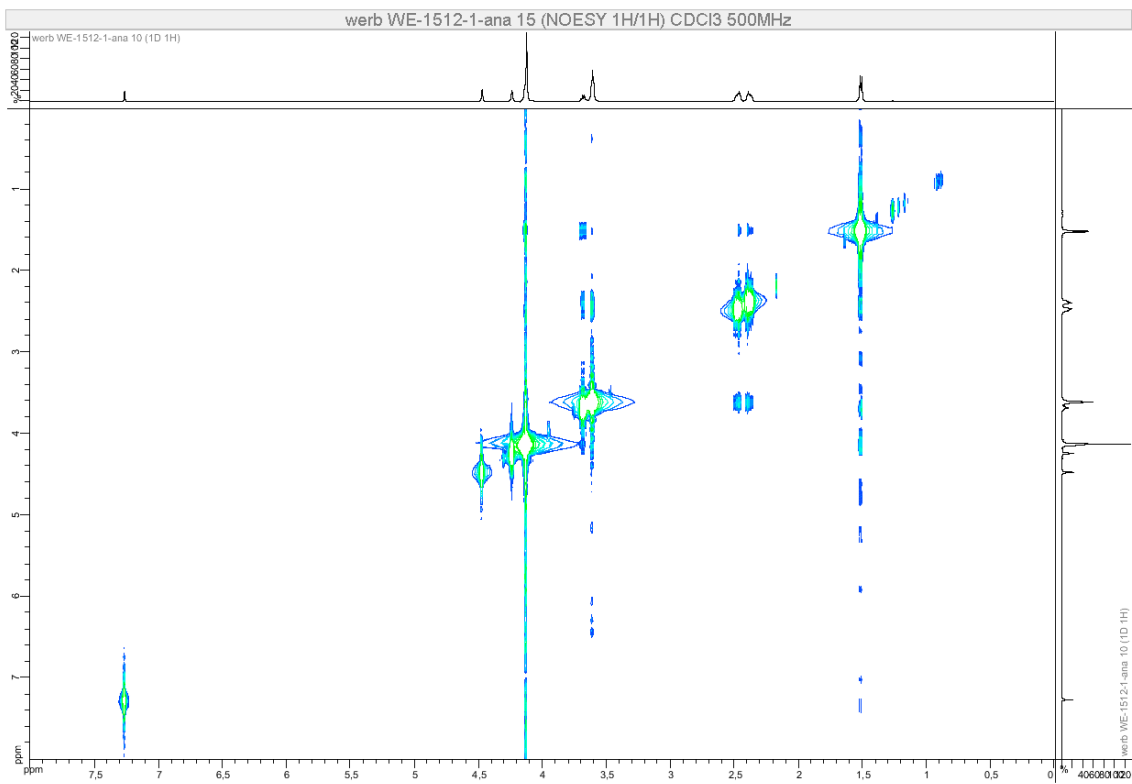
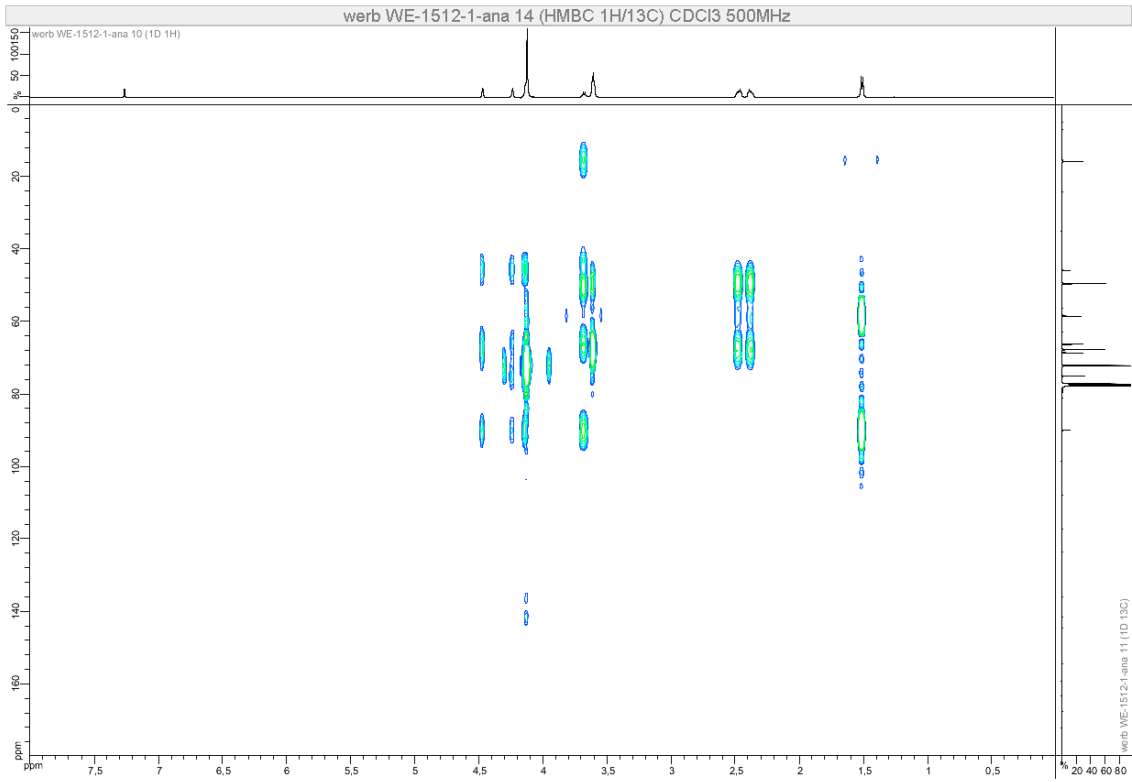




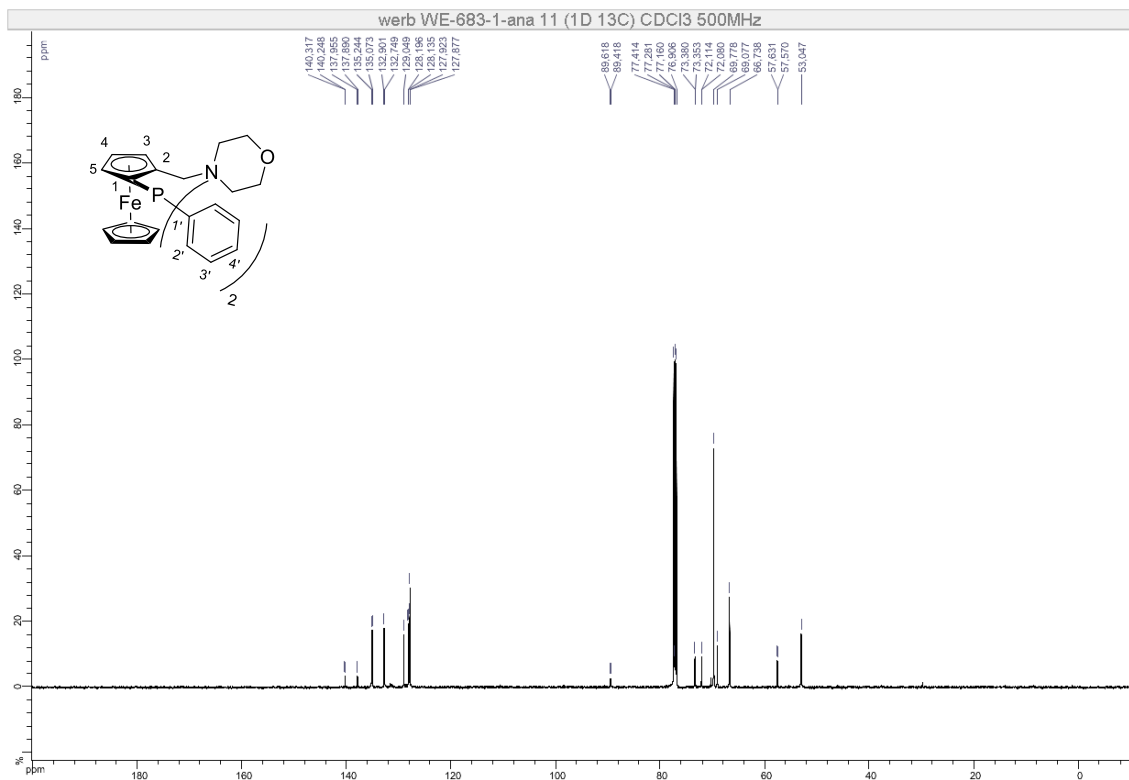
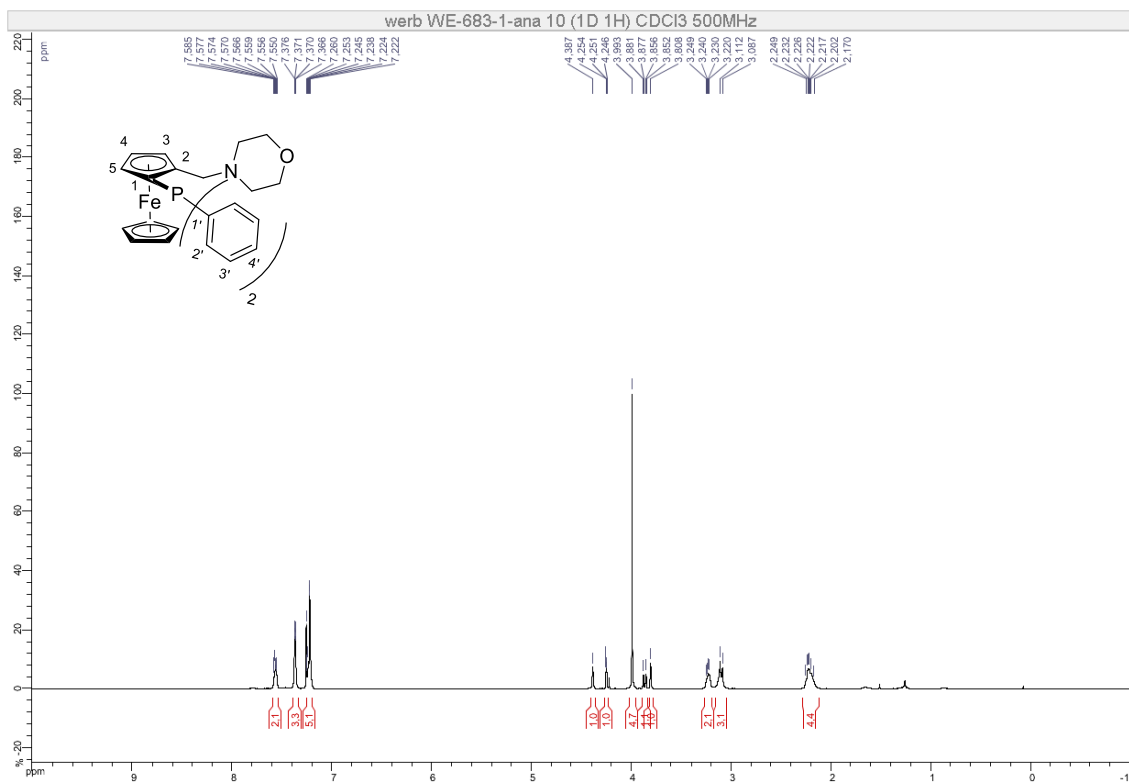
Compound (*R,S*)-10

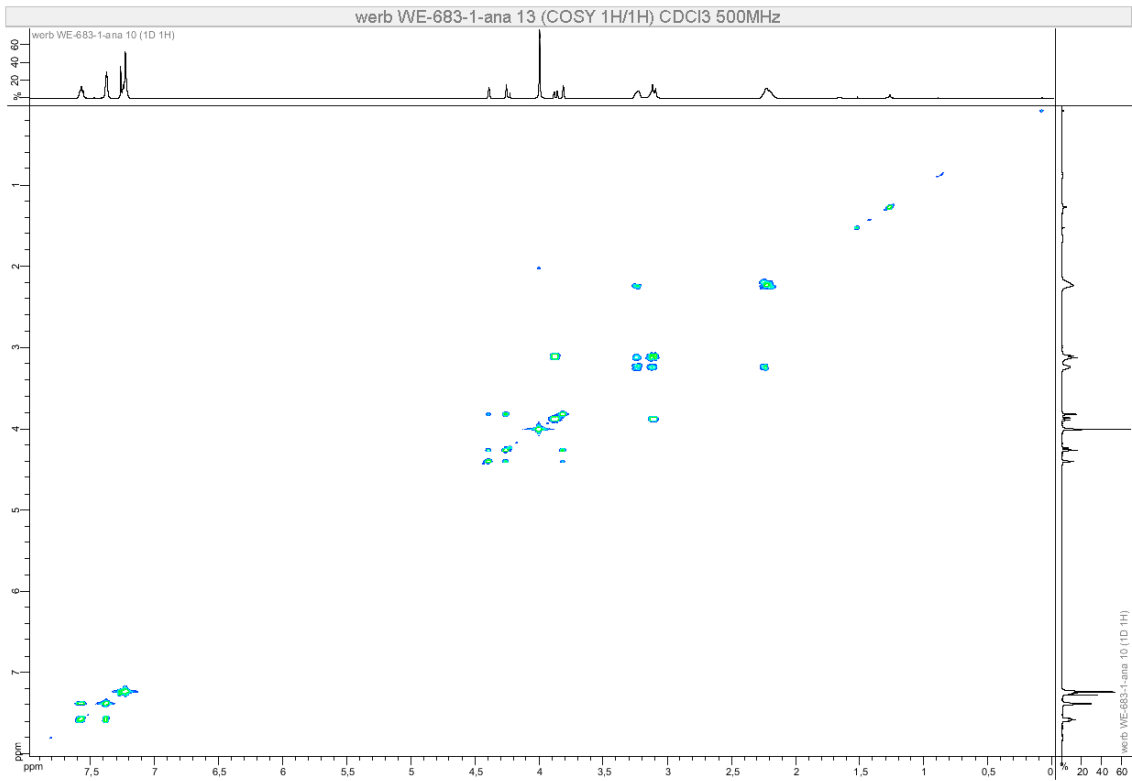
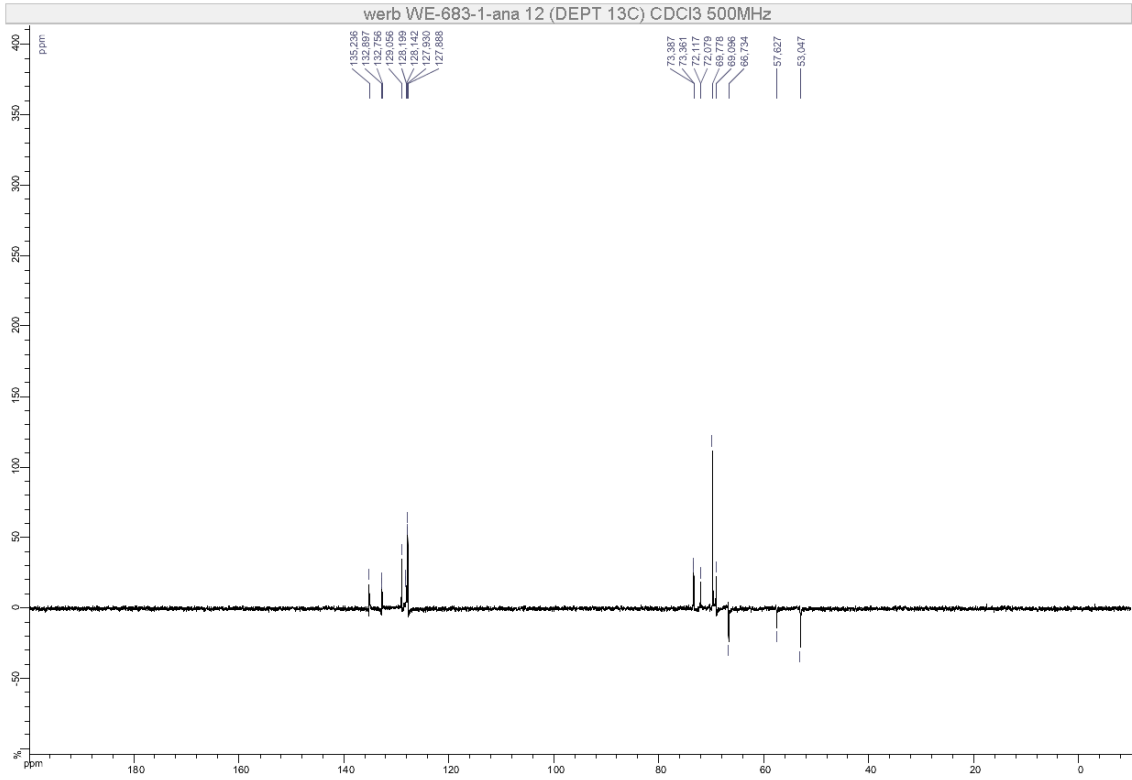


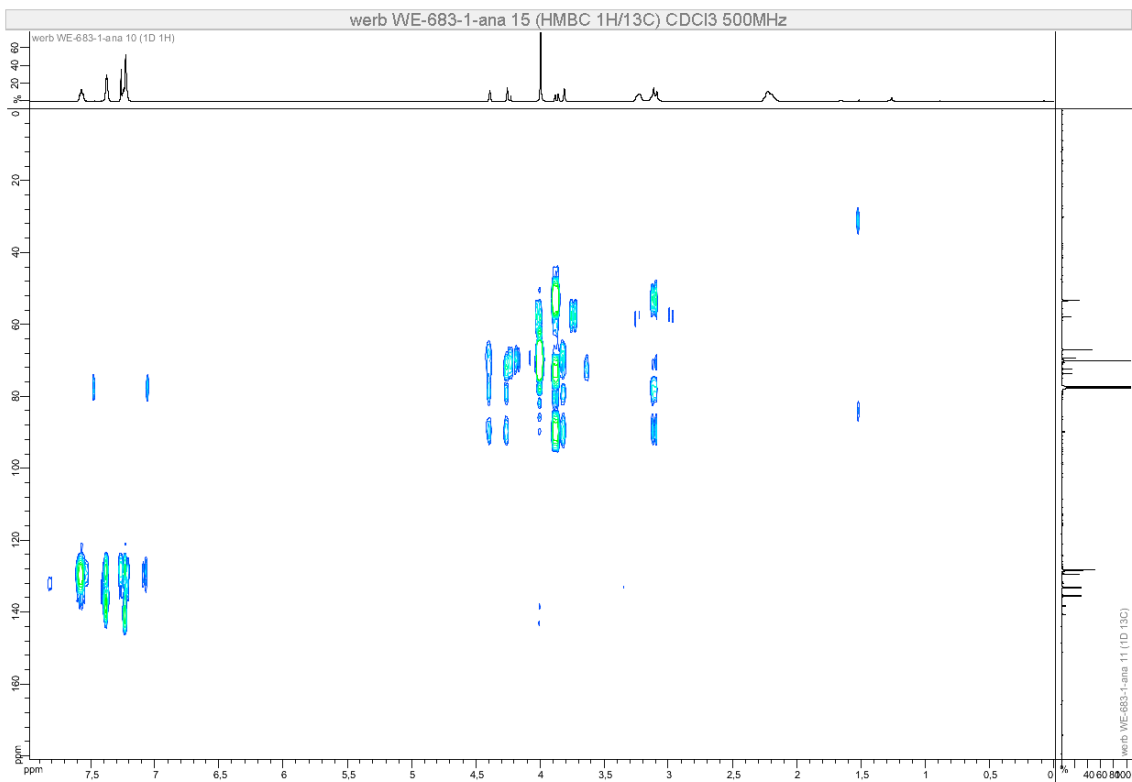
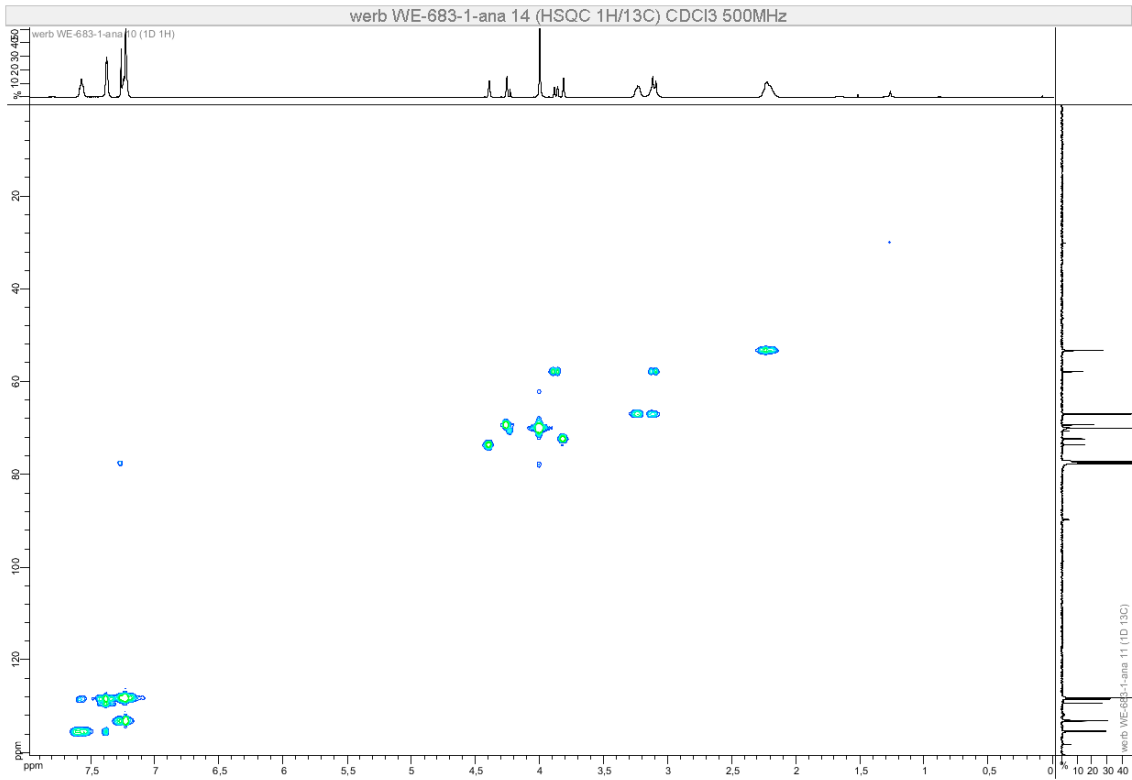


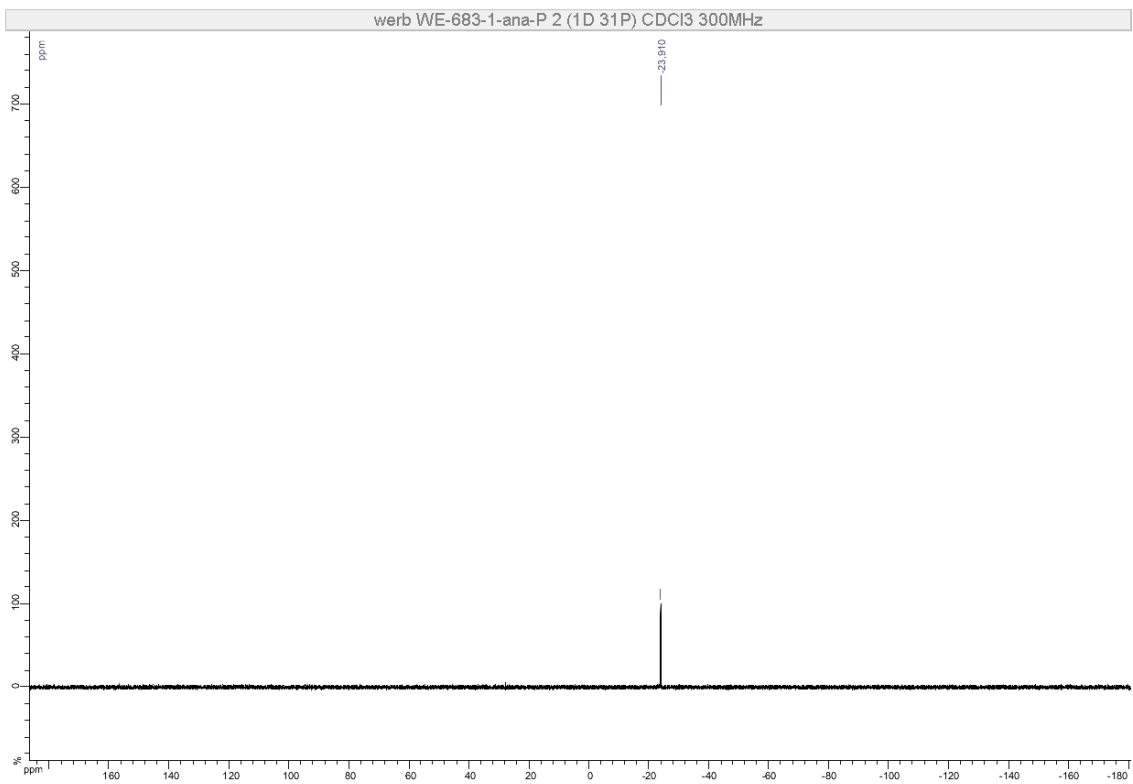
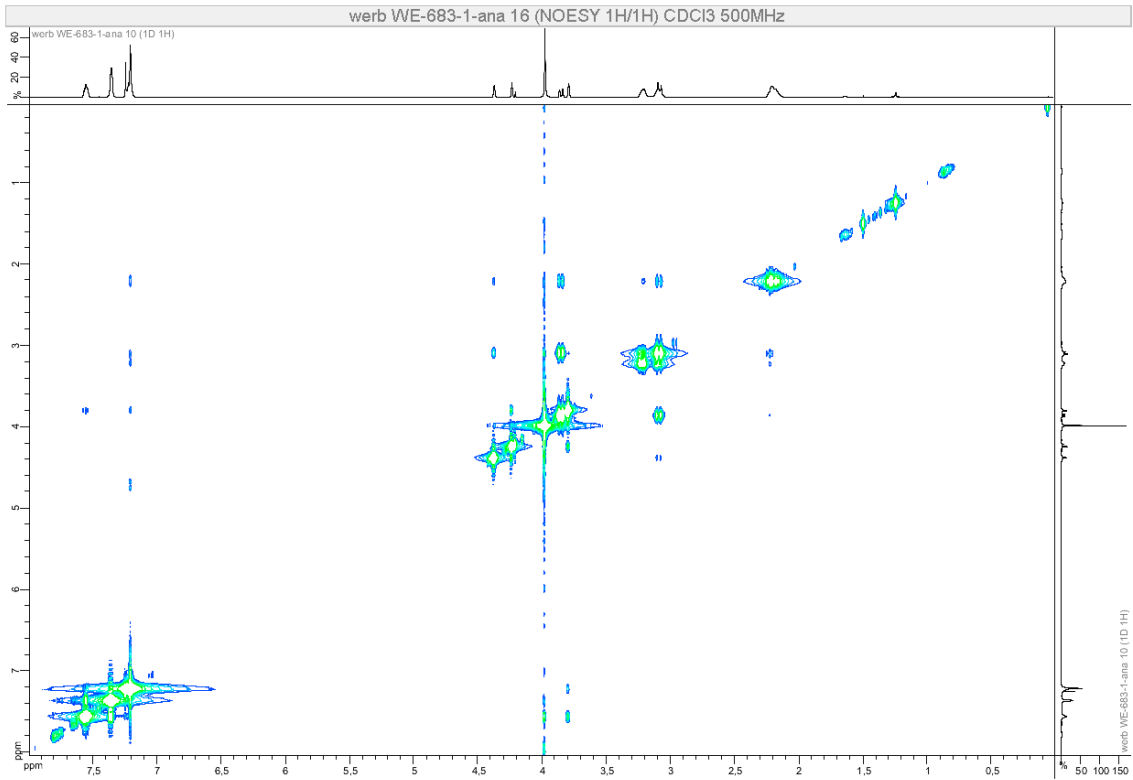


Compound (\pm)-11a

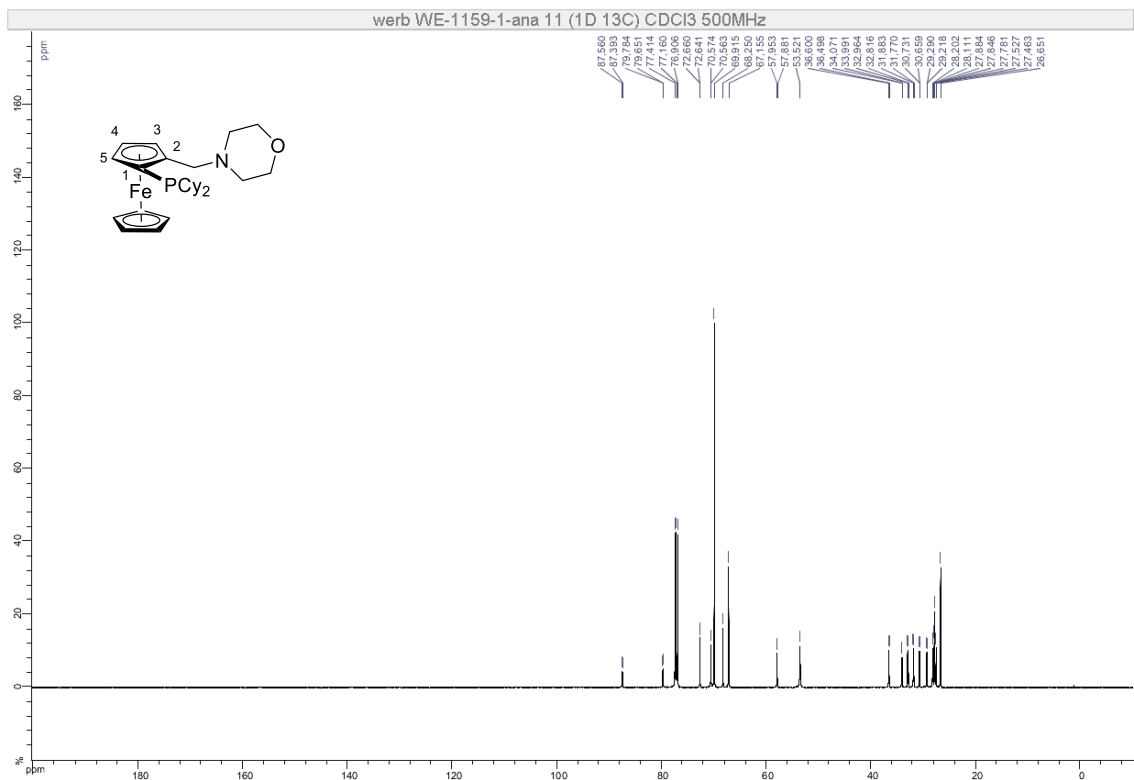
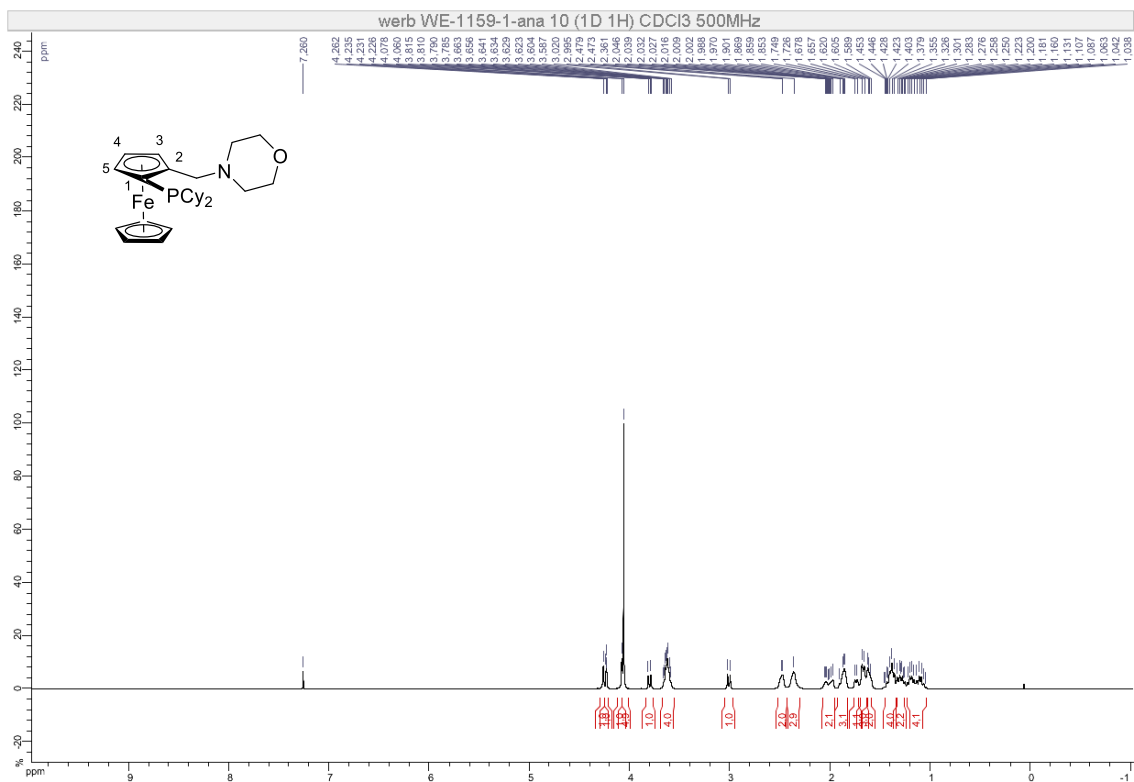


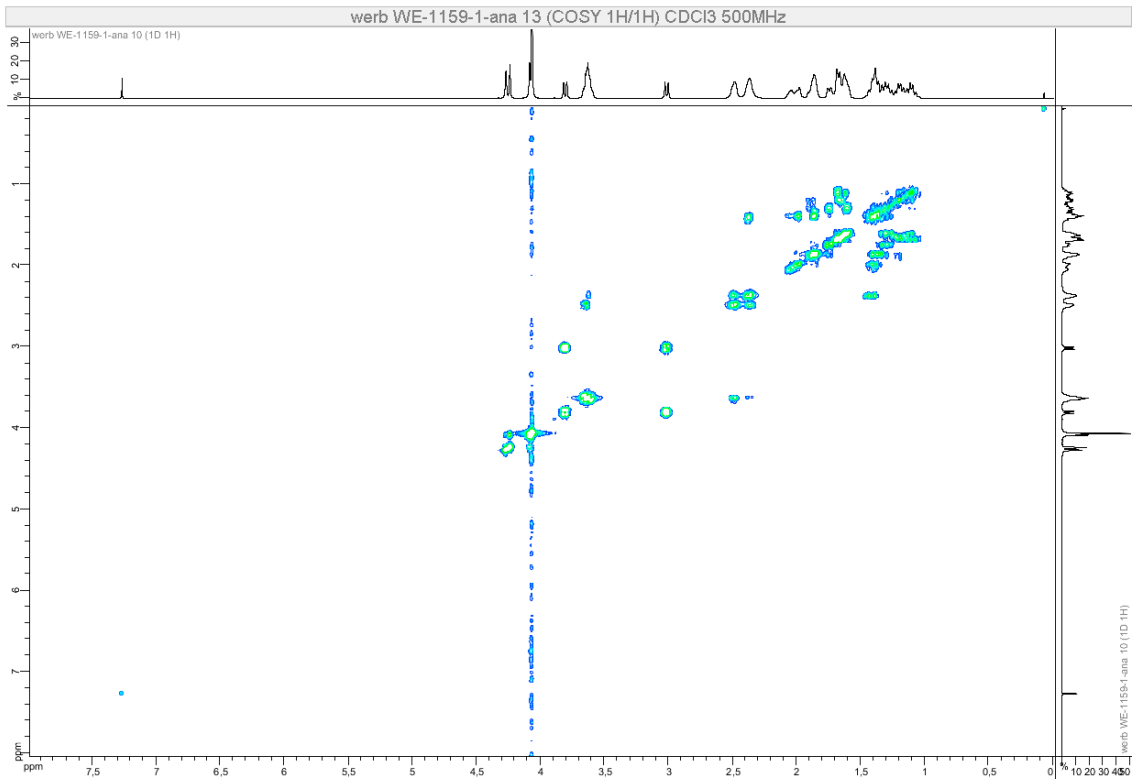
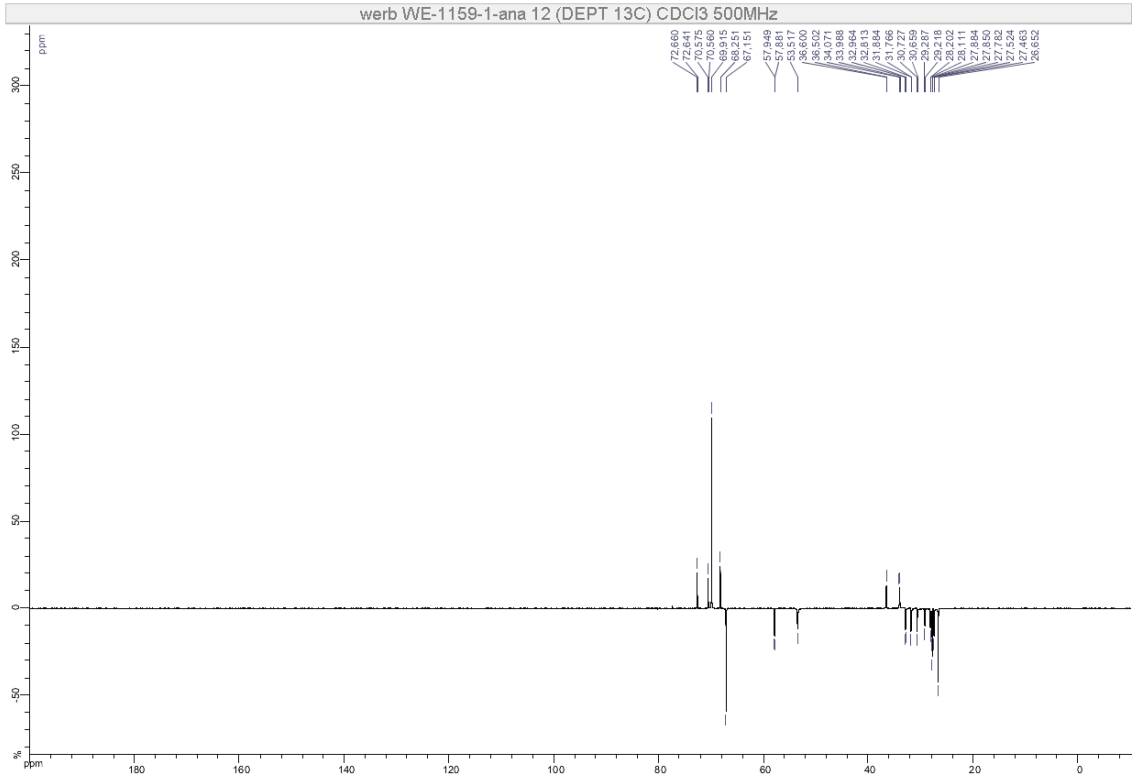


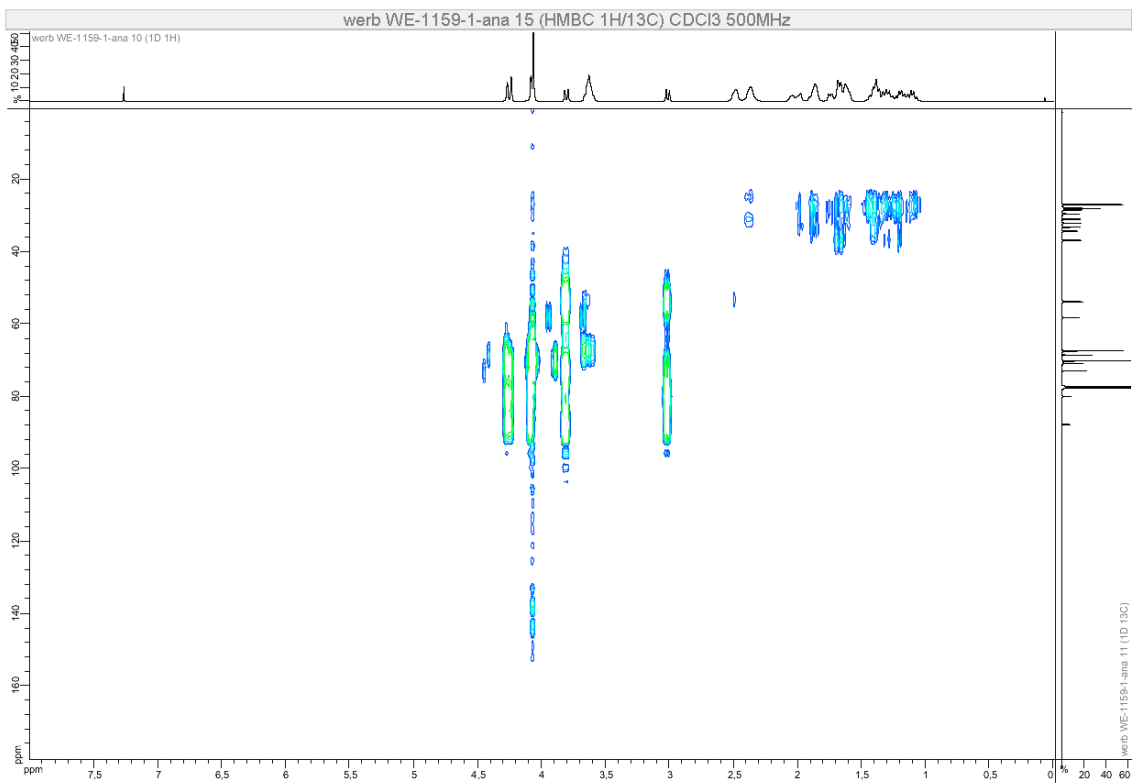
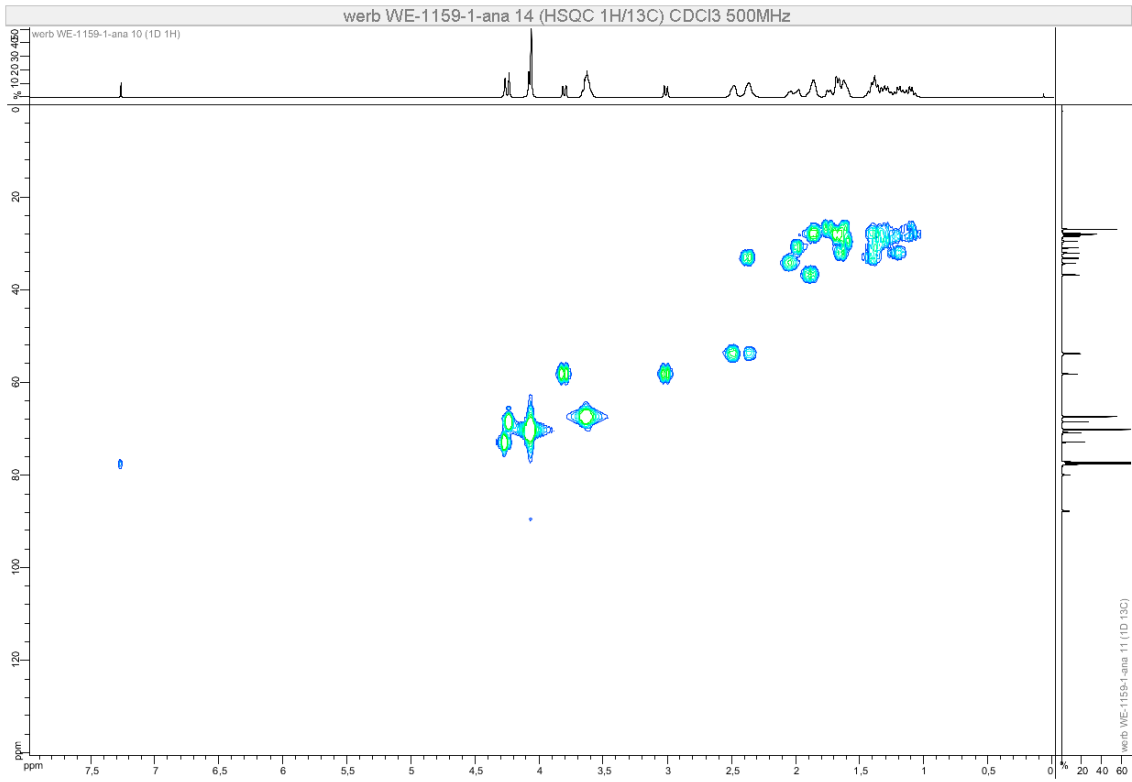




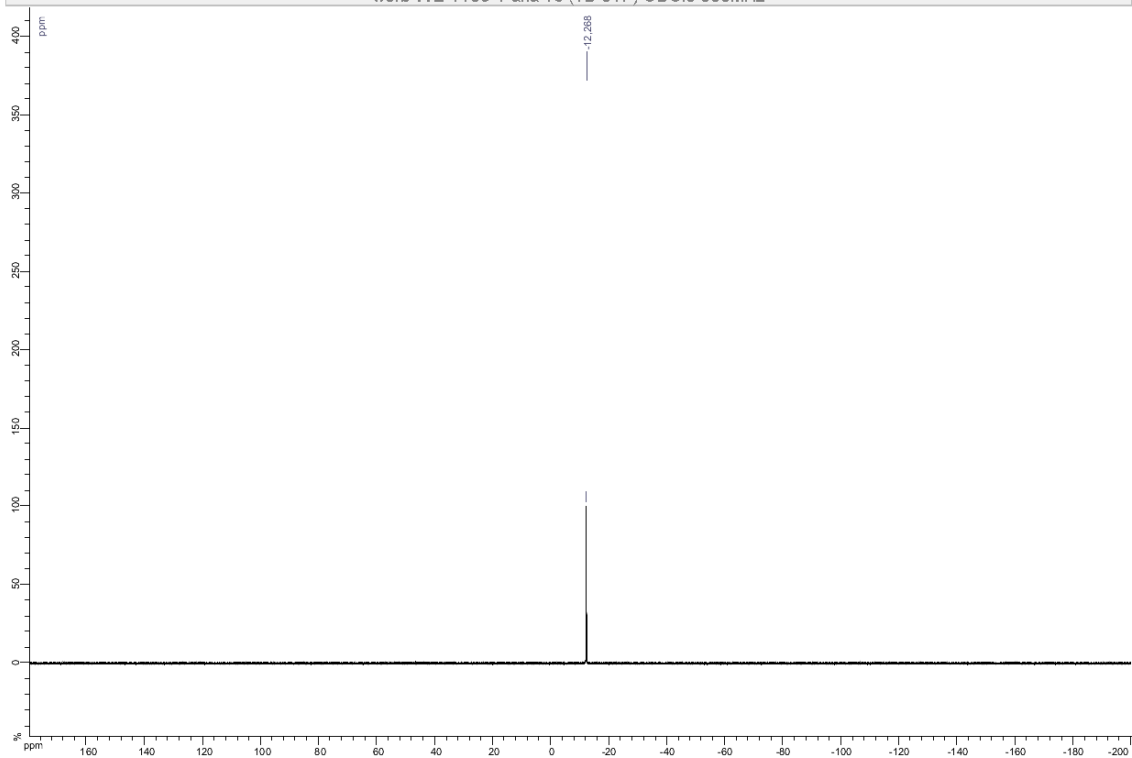
Compound (+)-11b



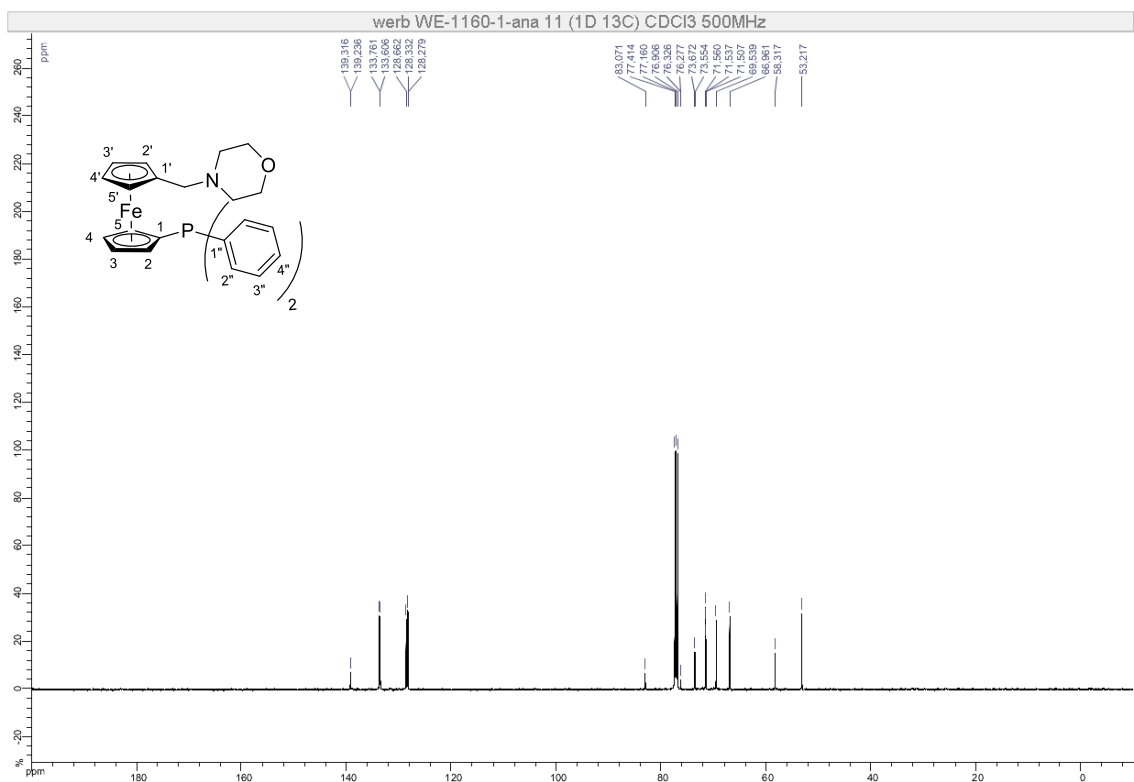
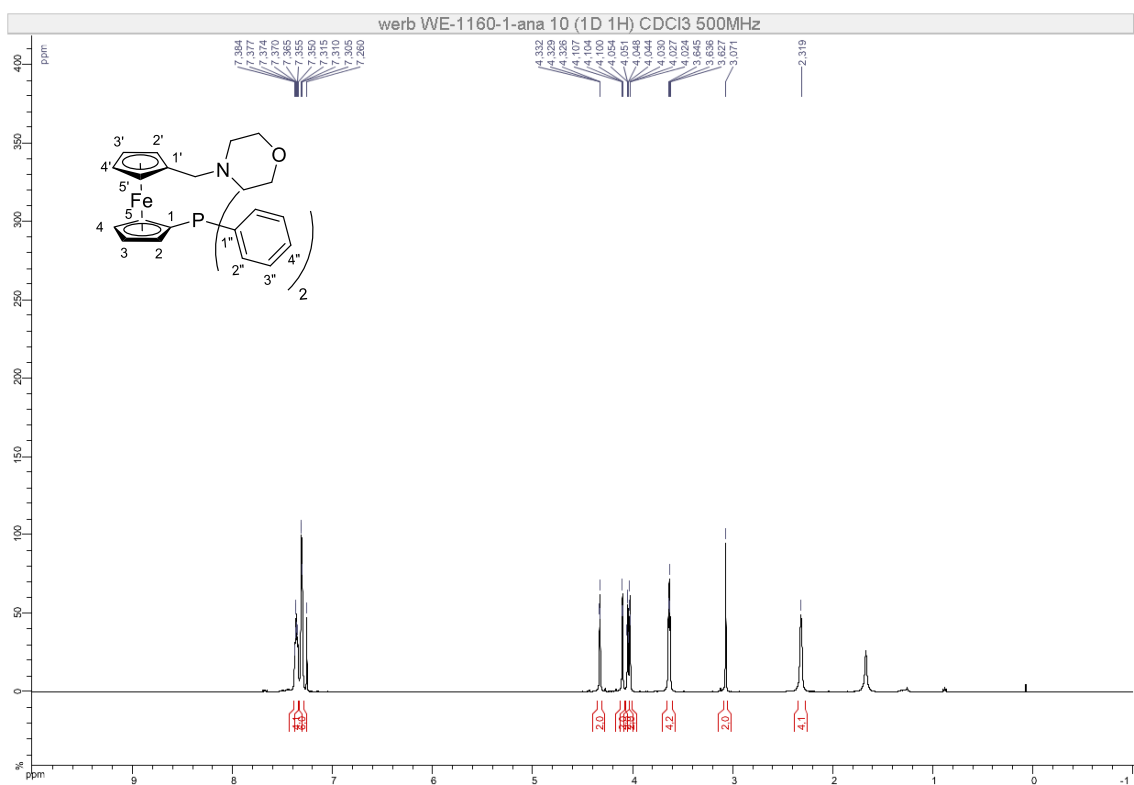


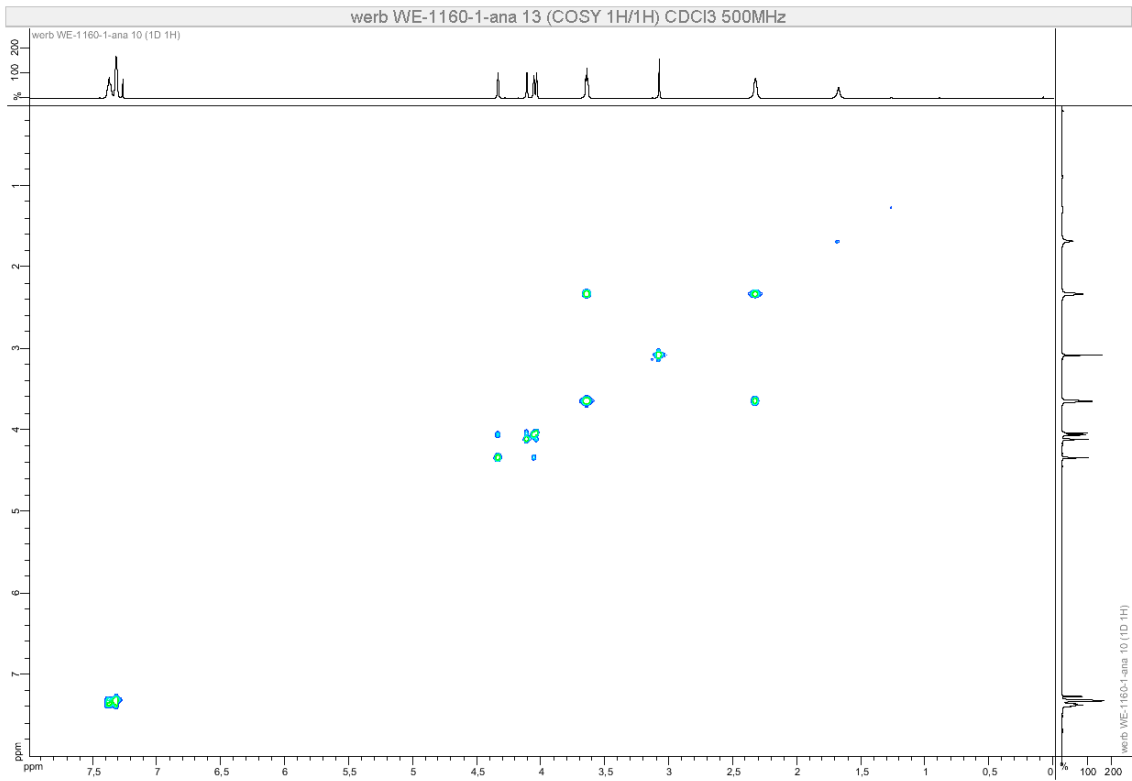
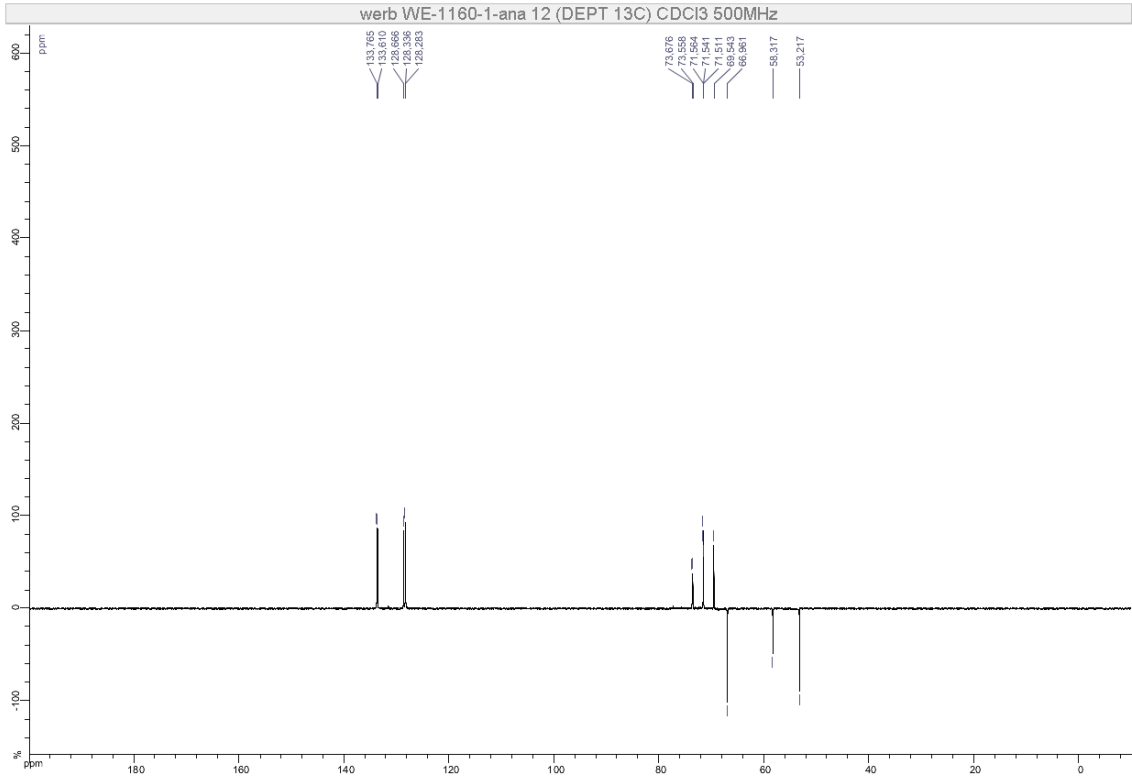


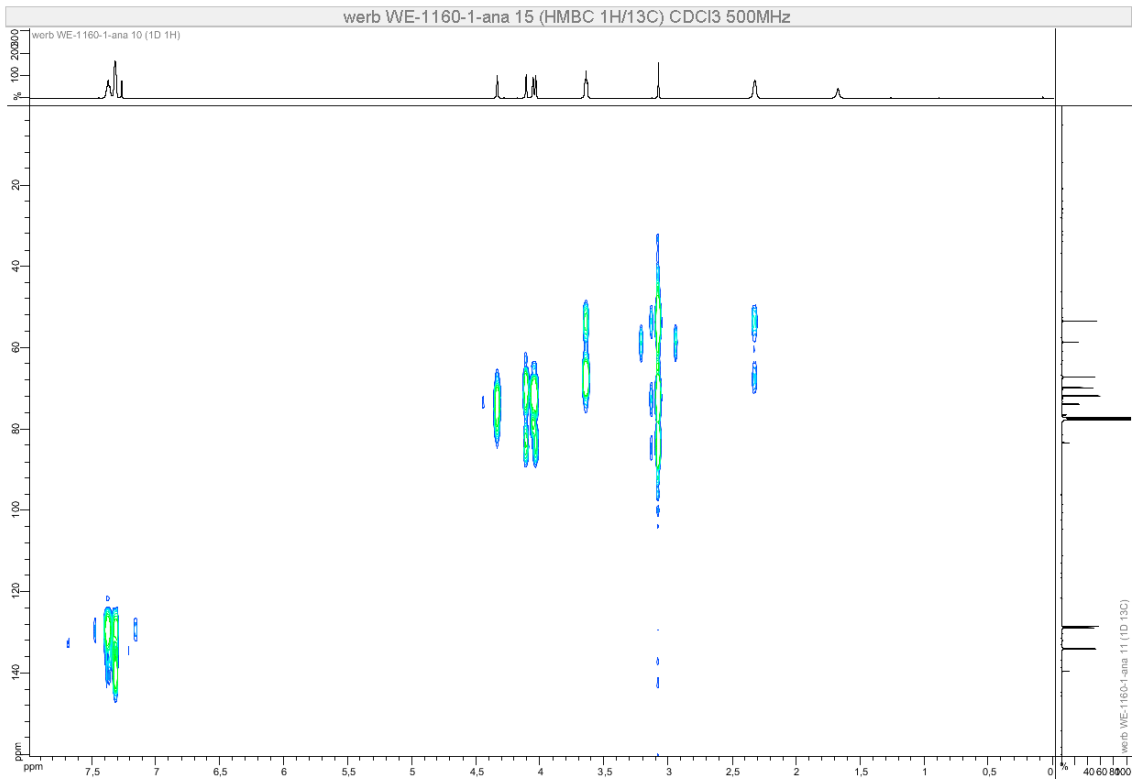
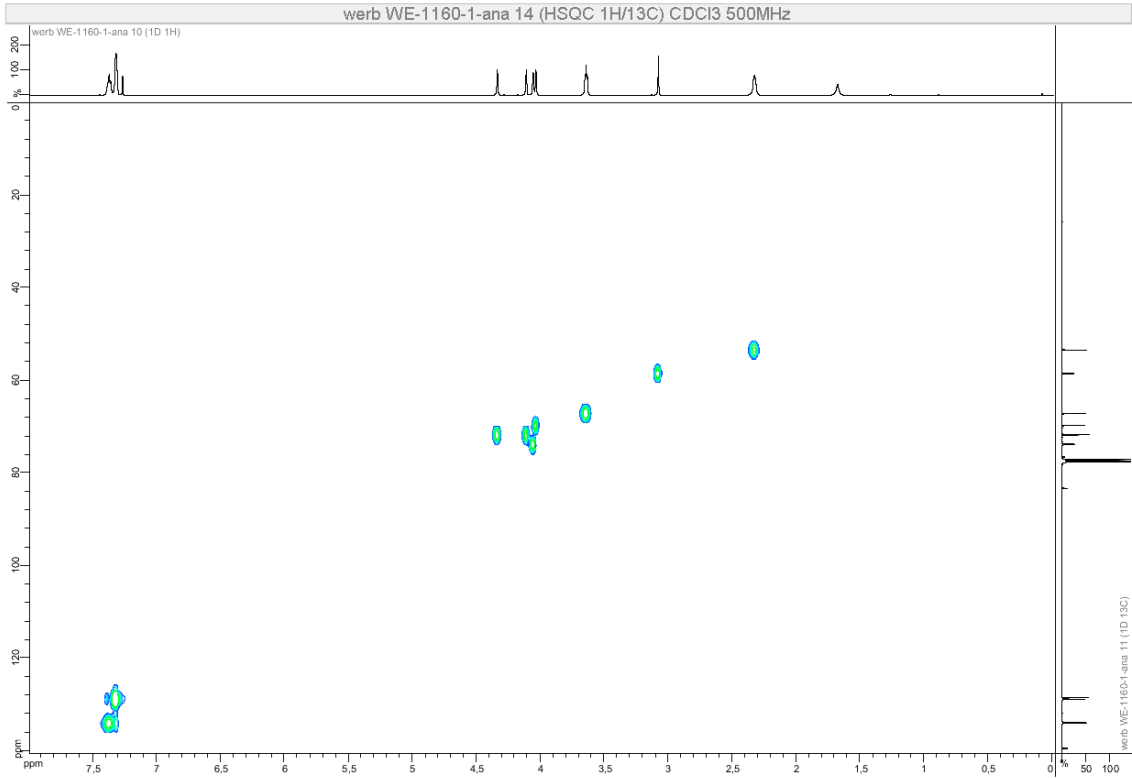
werb WE-1159-1-ana 16 (1D 31P) CDCl3 500MHz

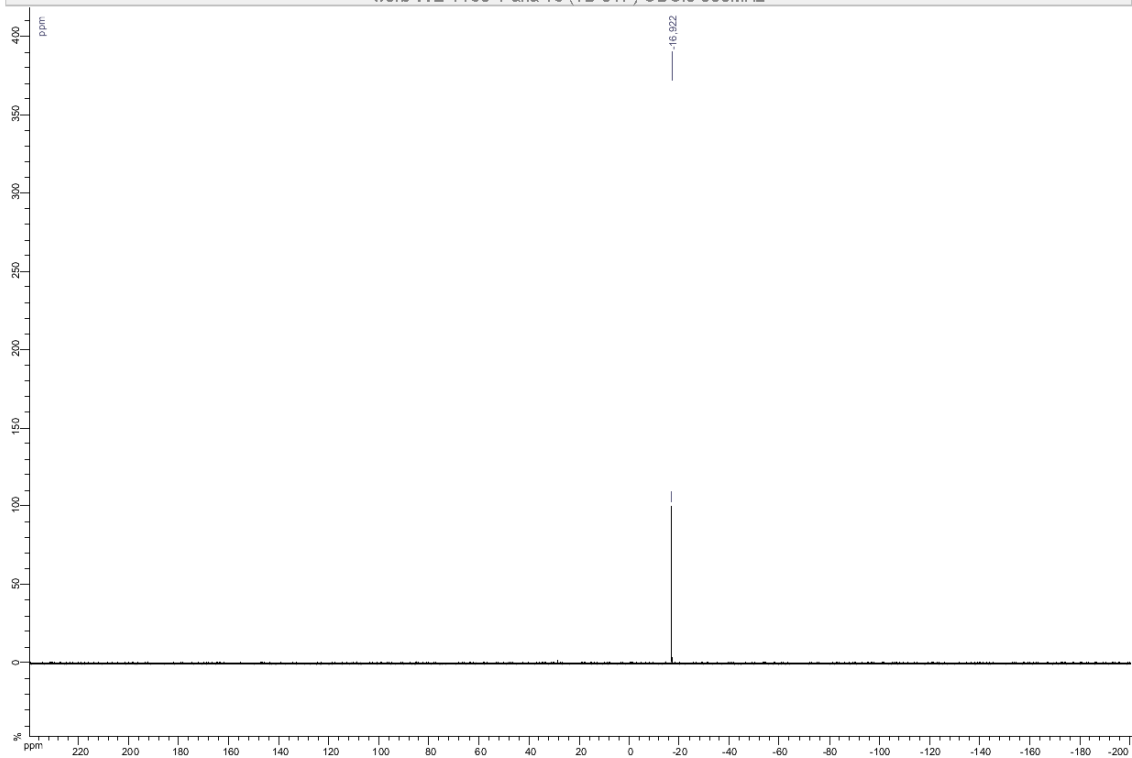


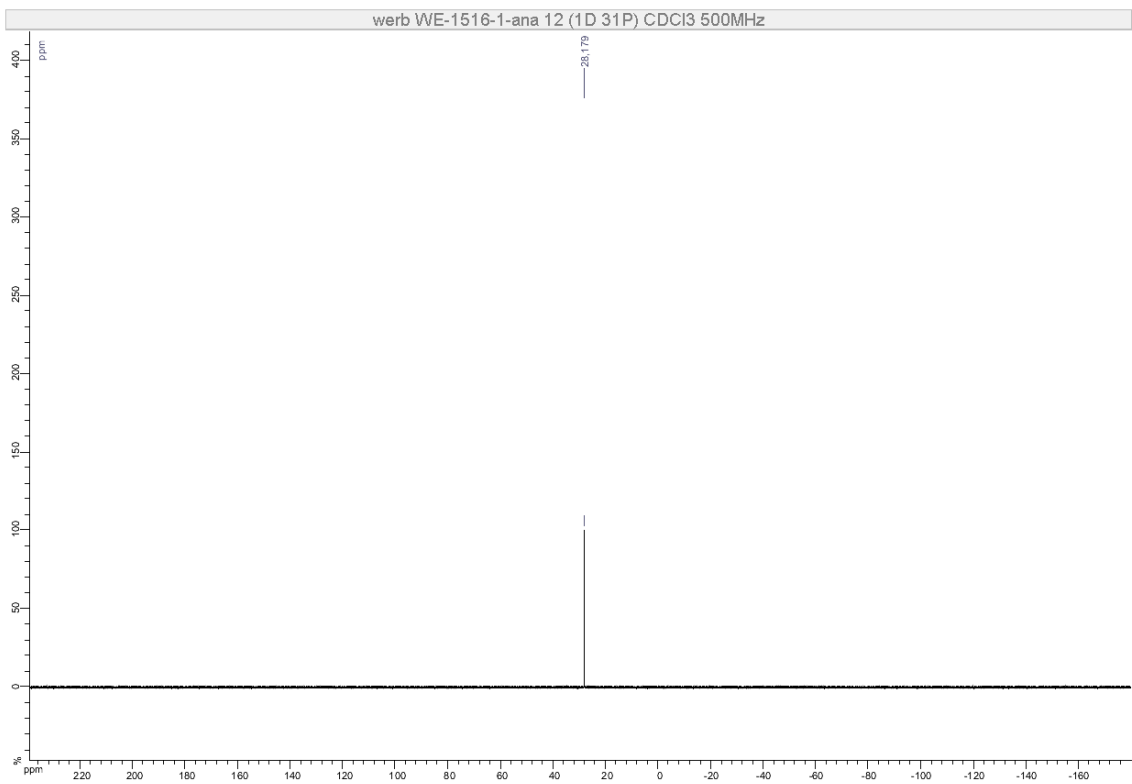
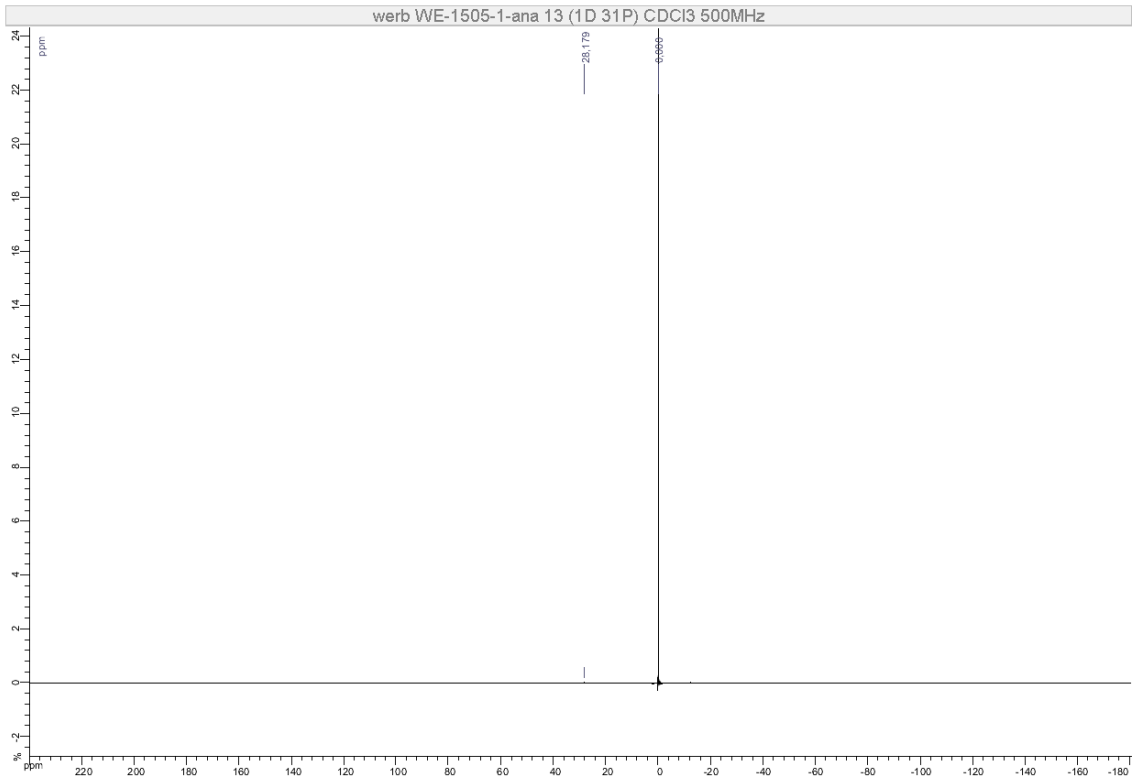
Compound 11c



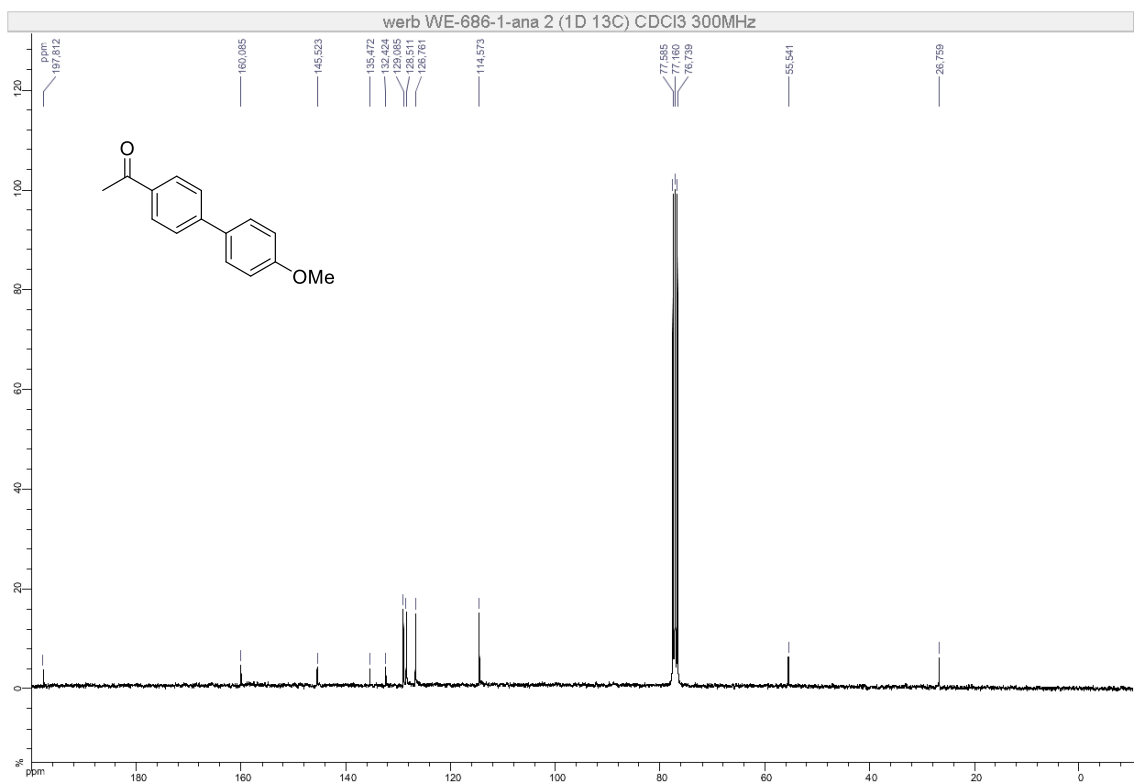
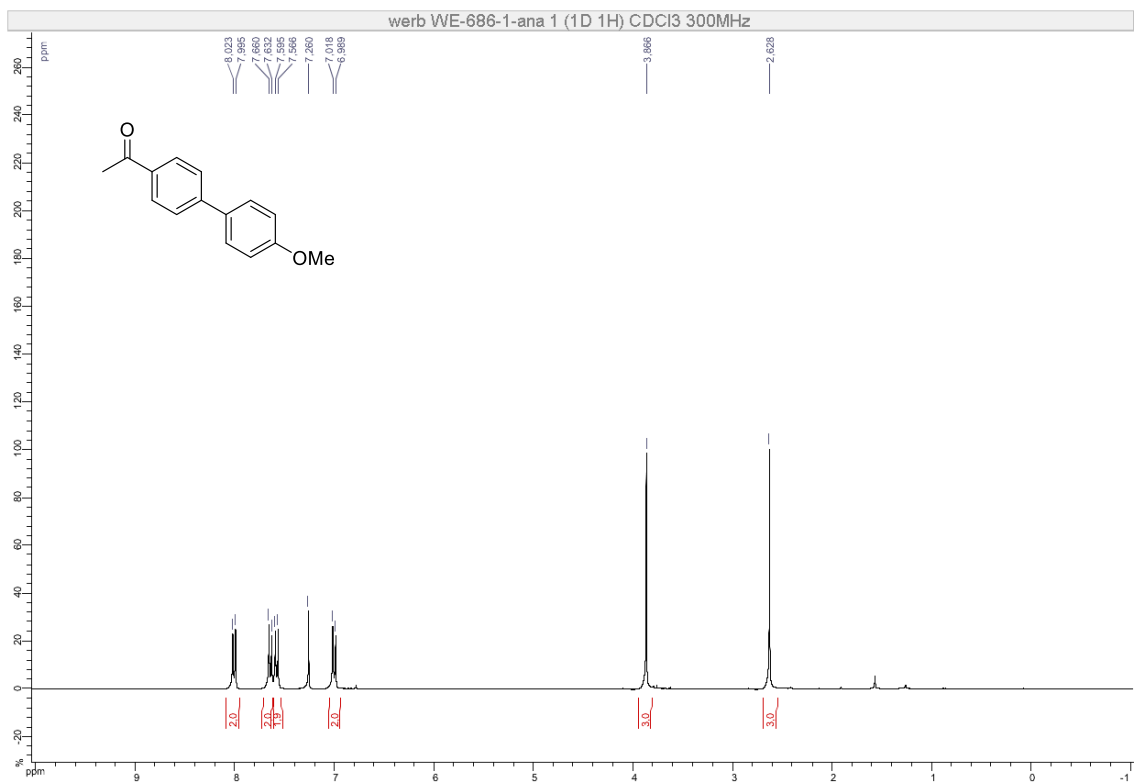


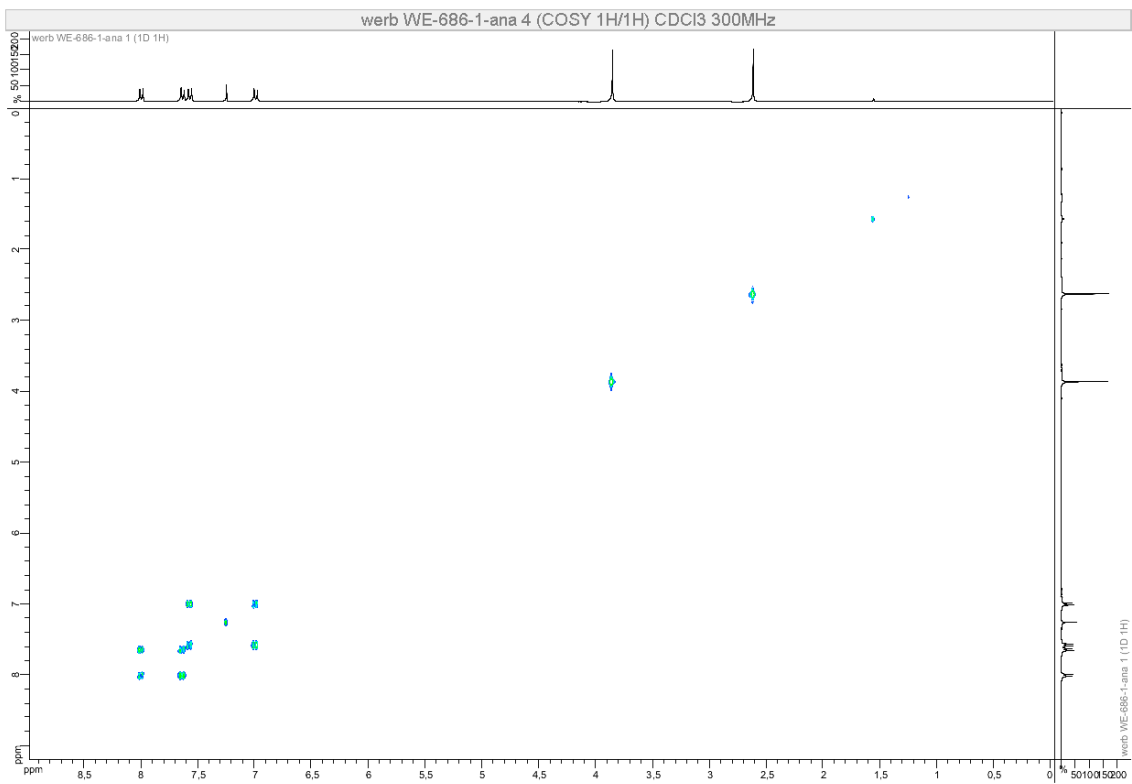
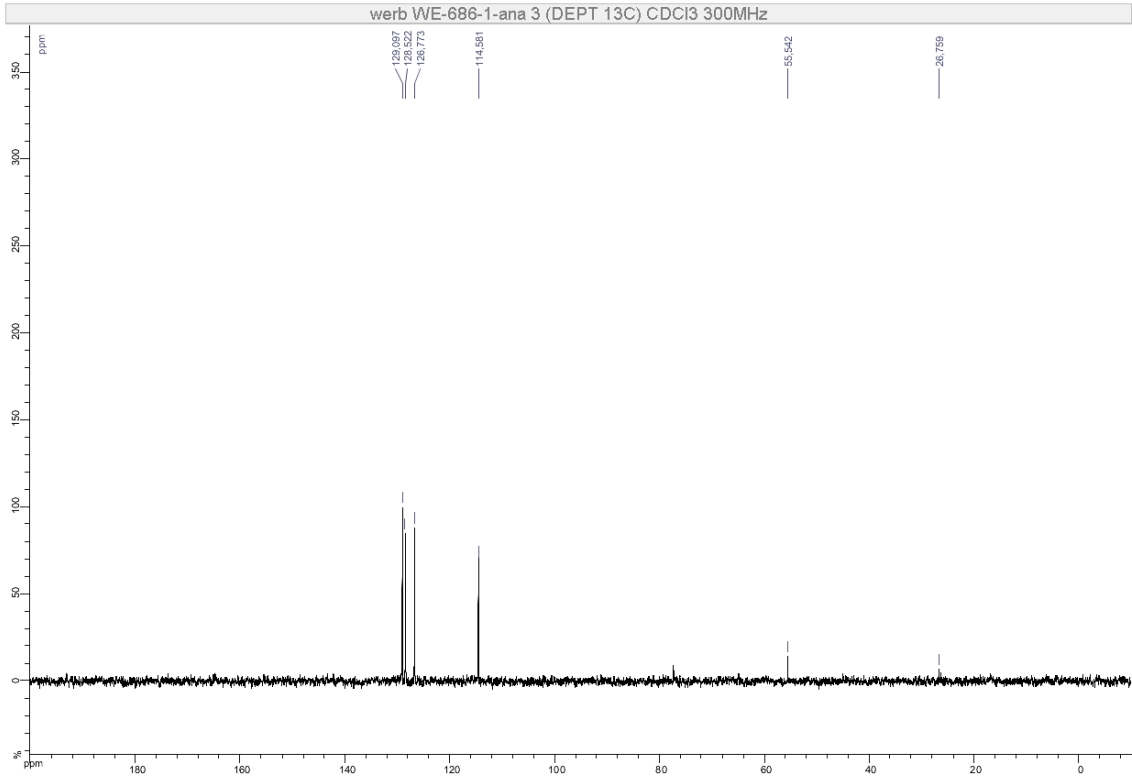


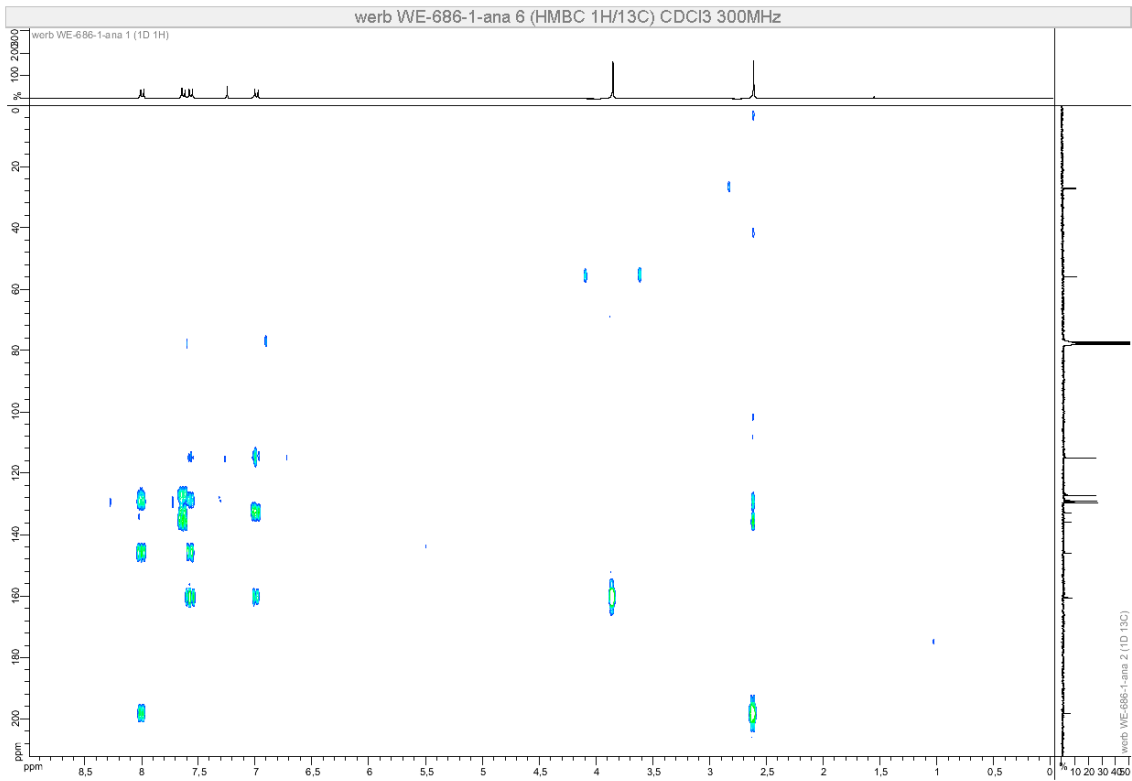
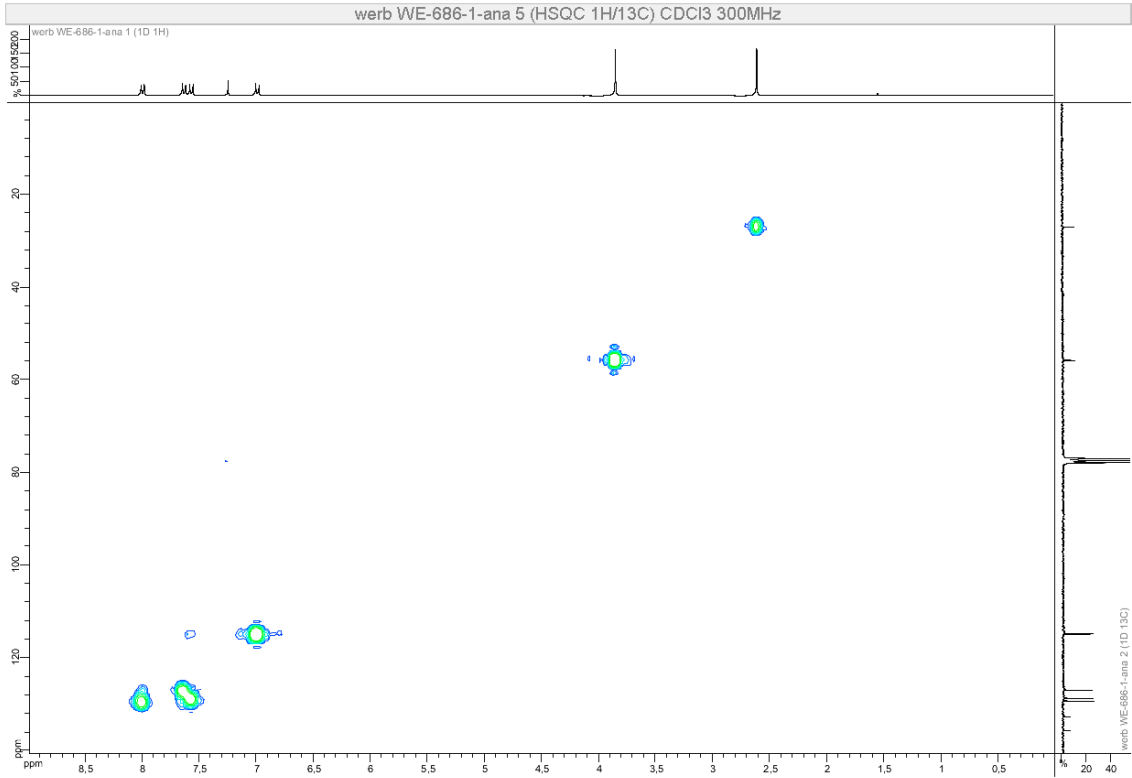




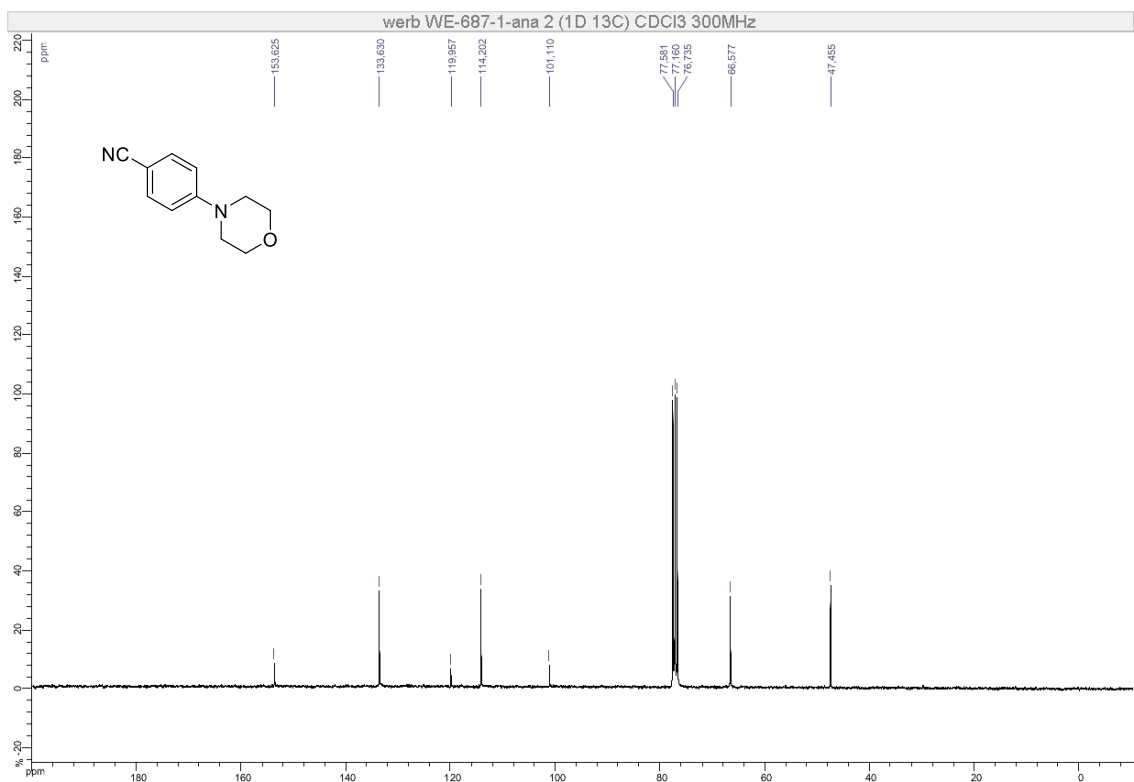
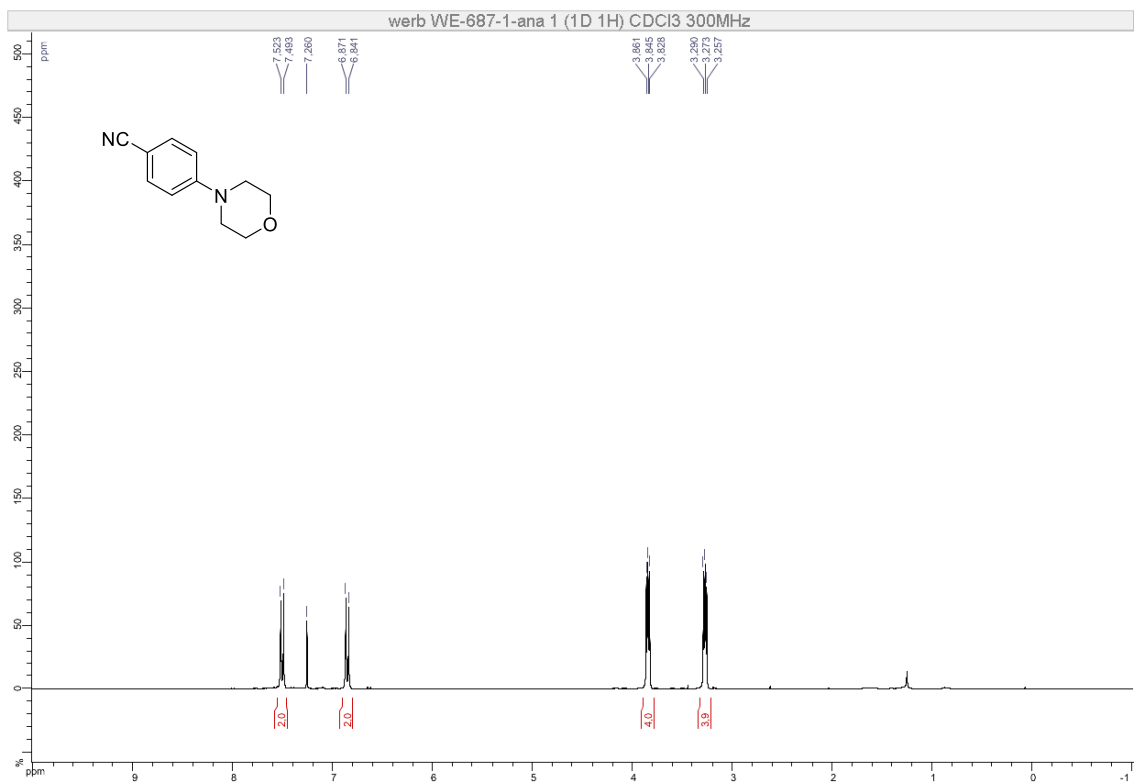
Compound 15

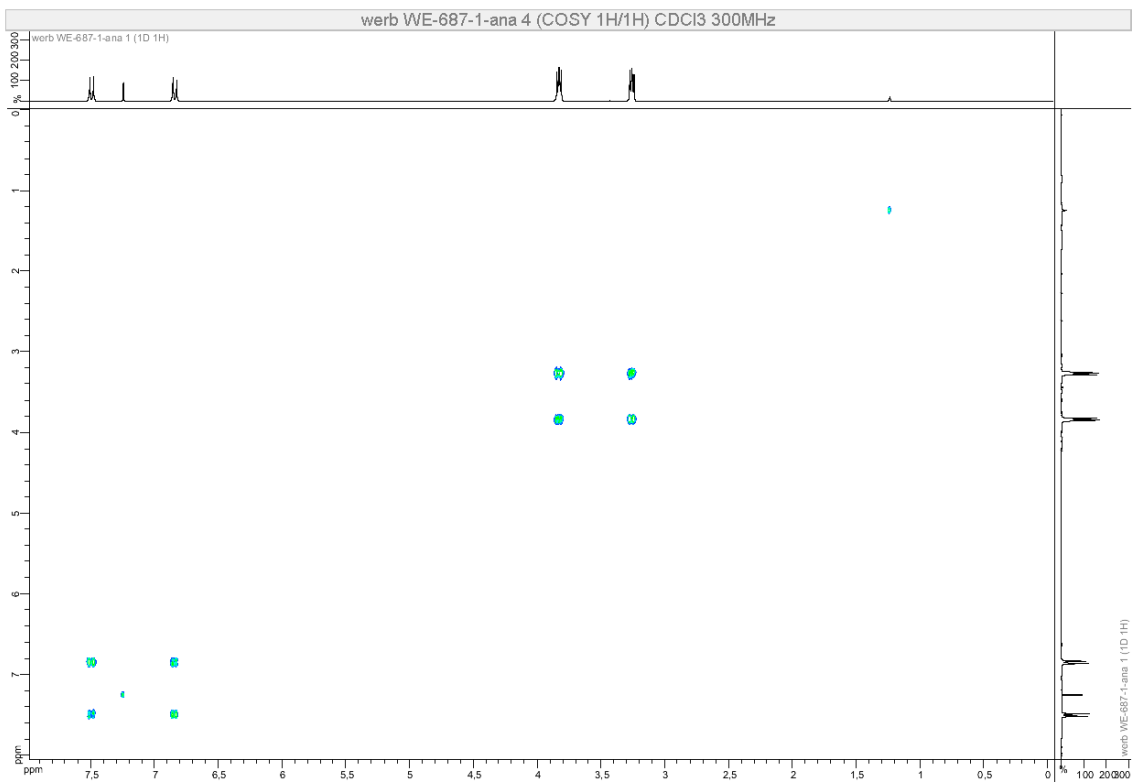
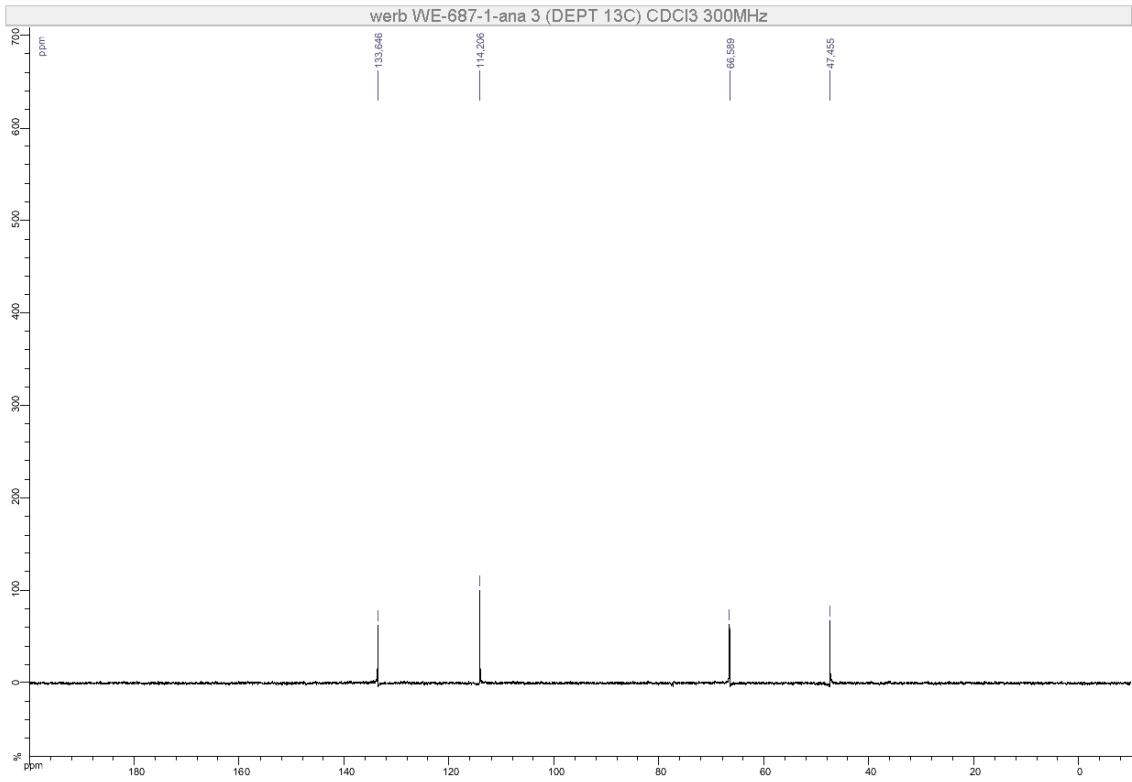


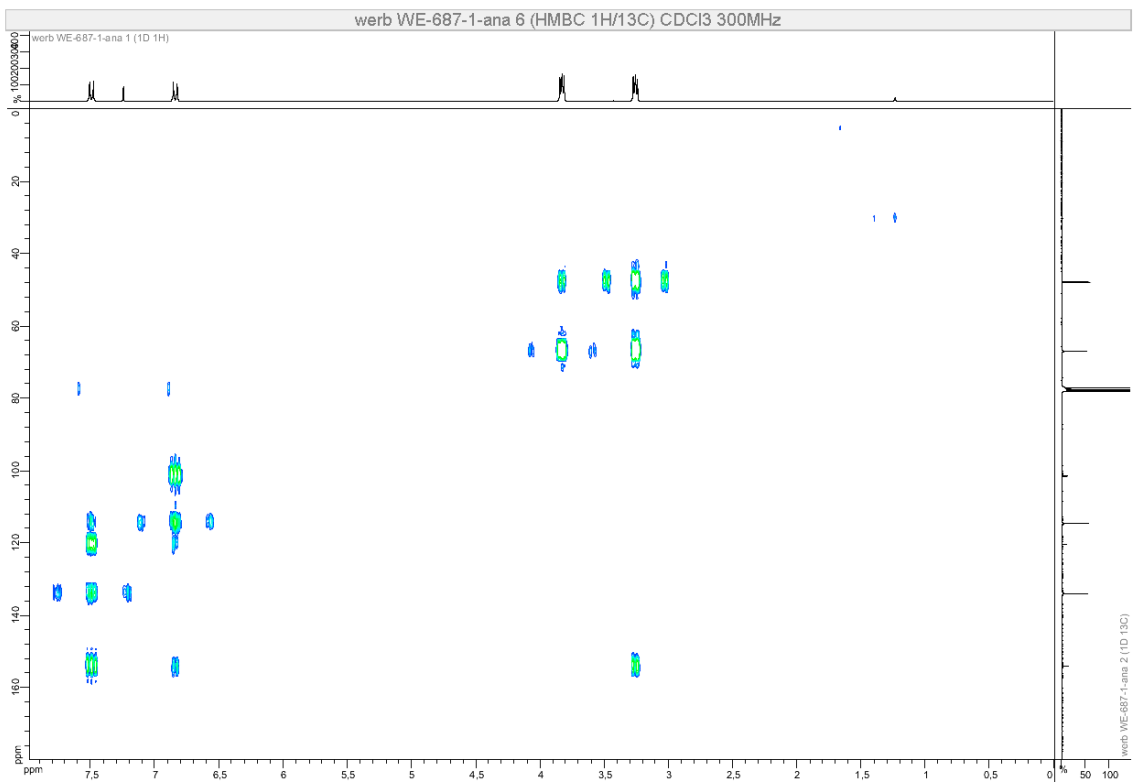
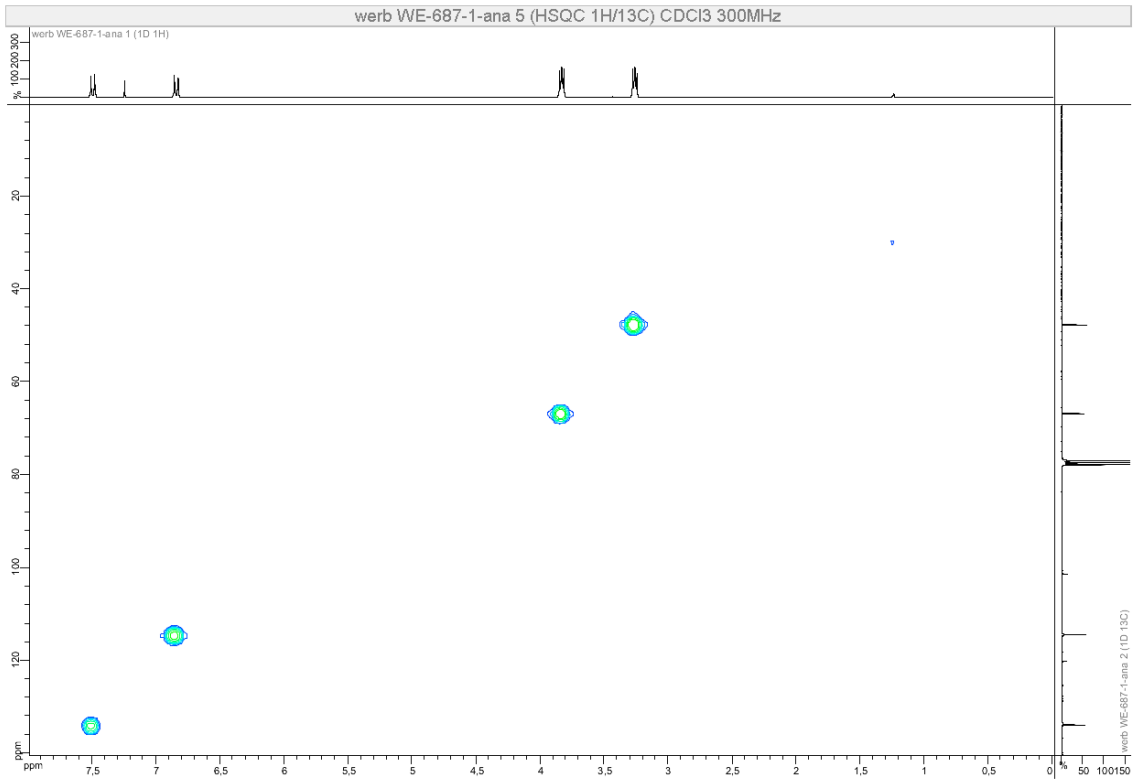




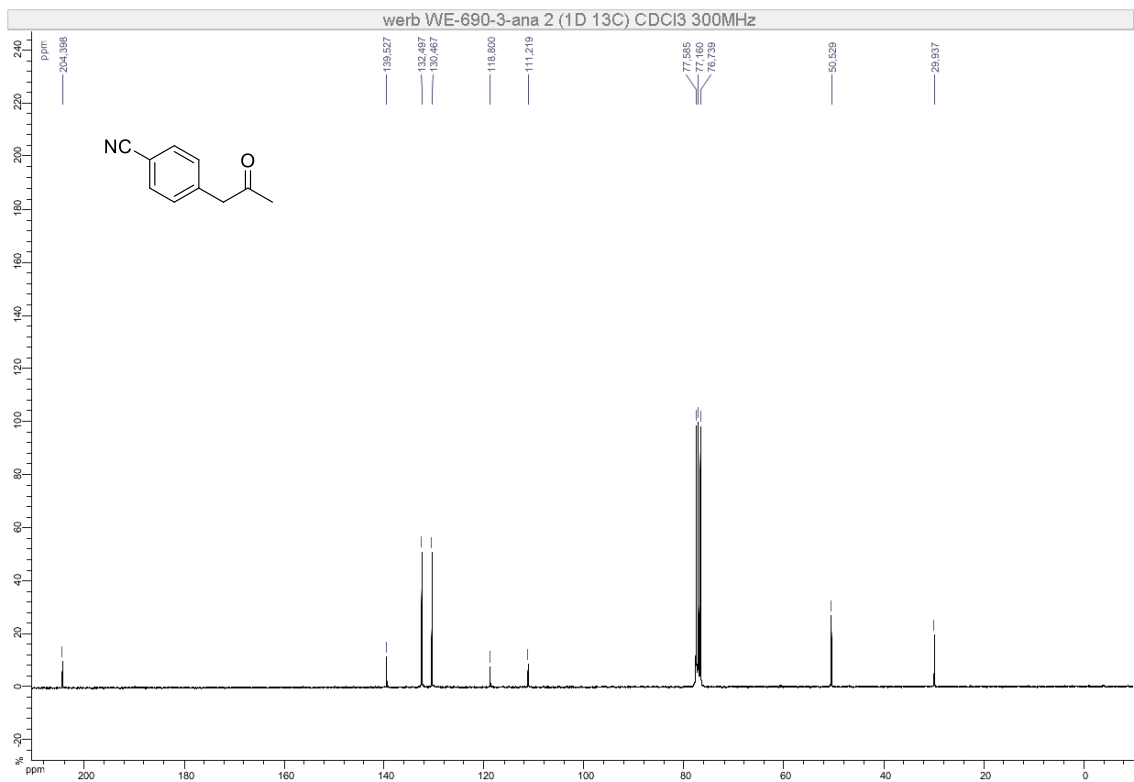
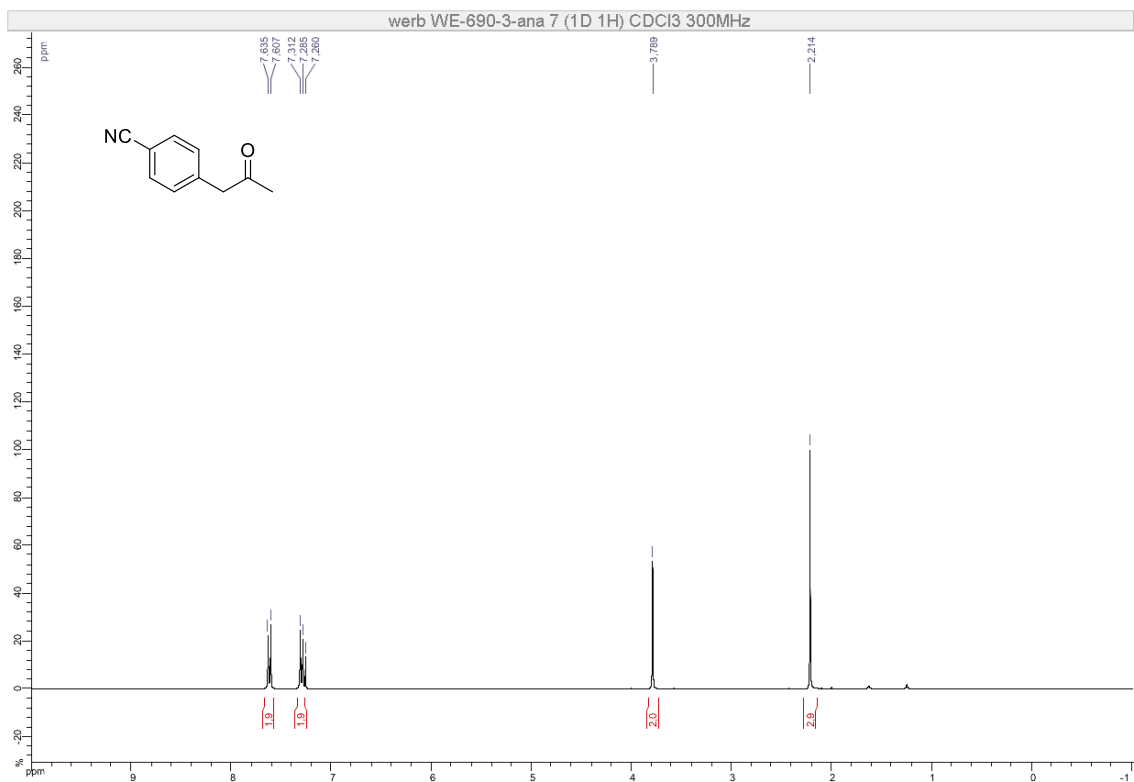
Compound 17

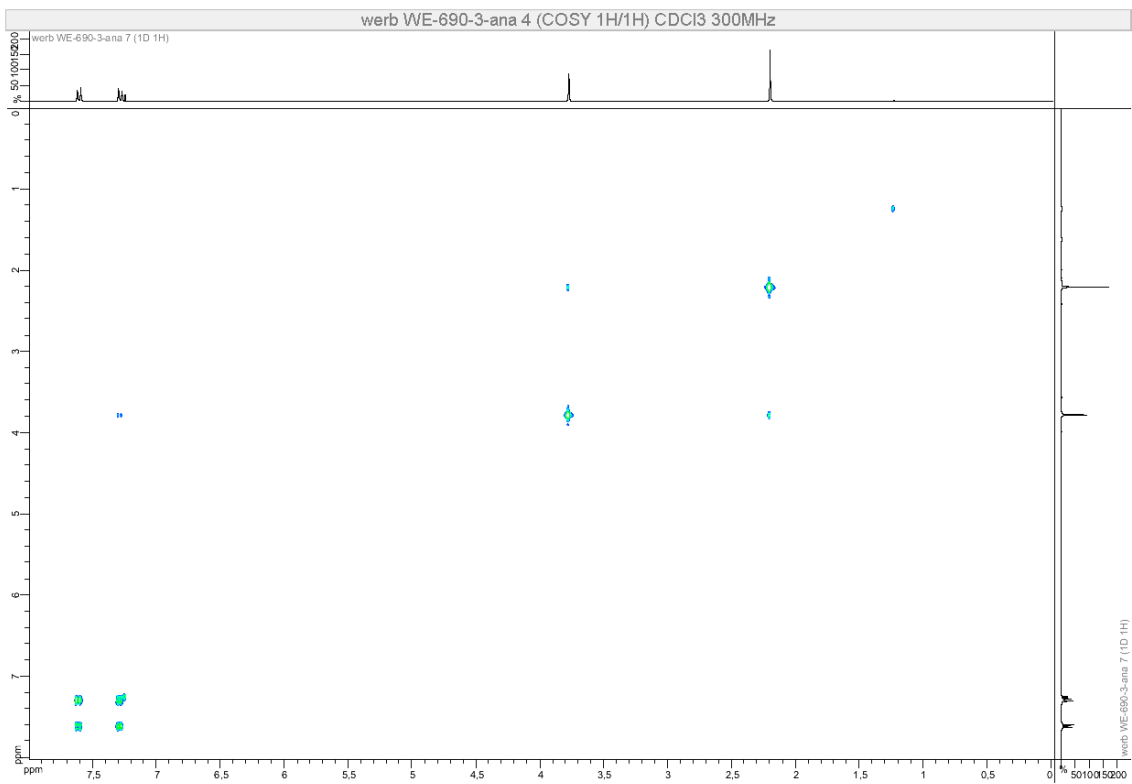
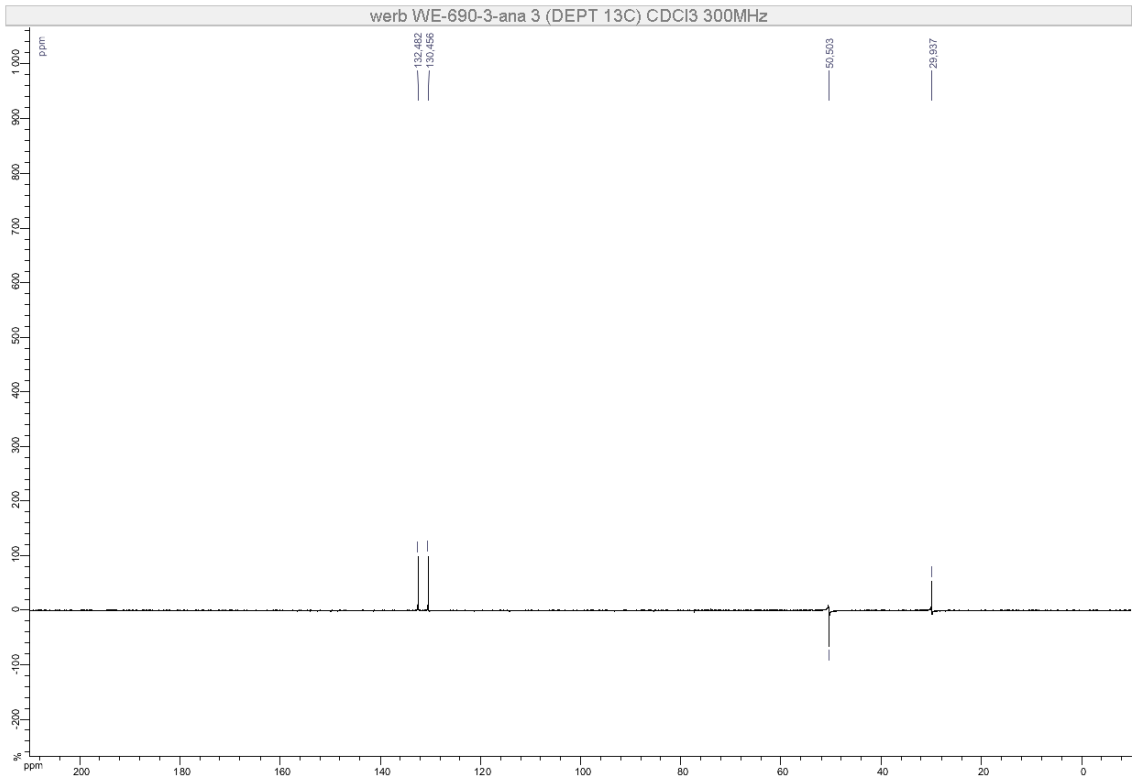


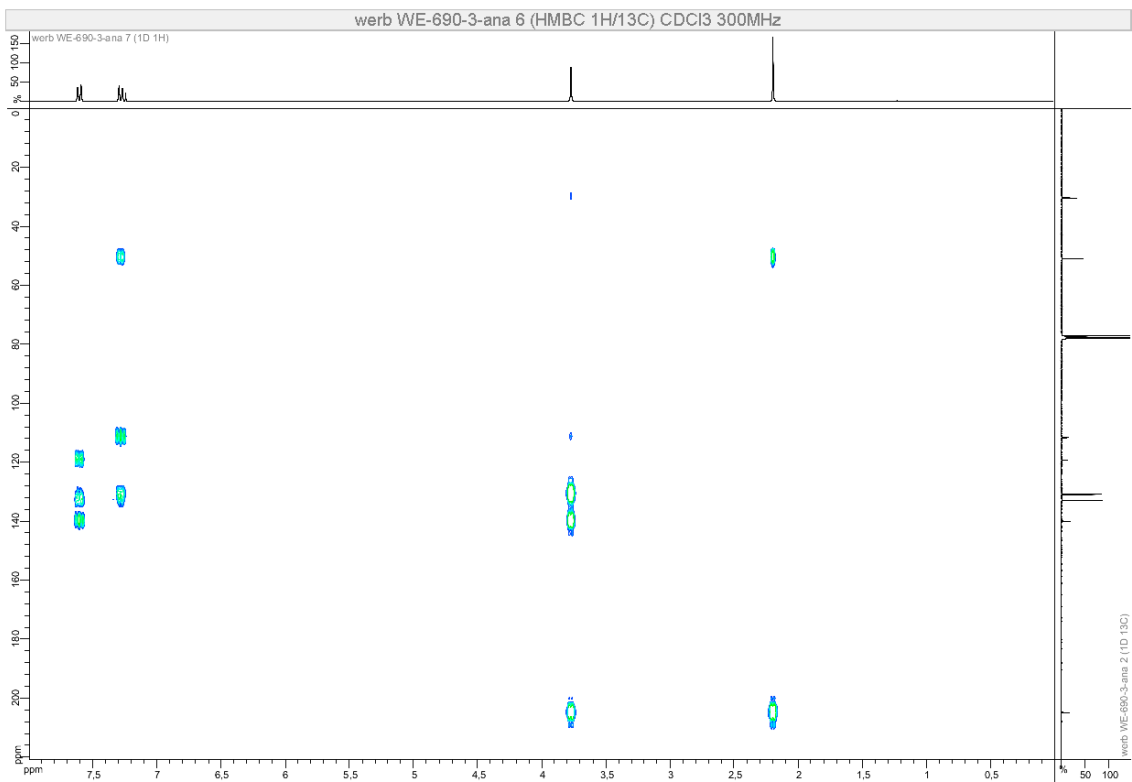
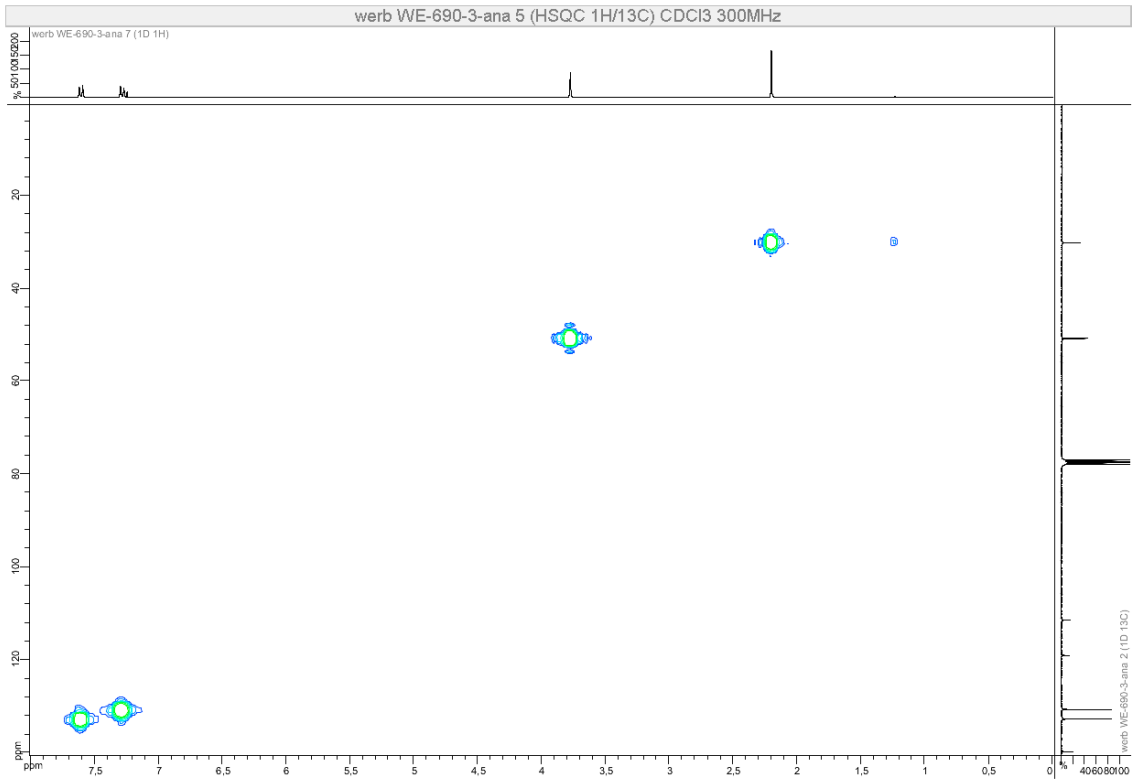




Compound 19

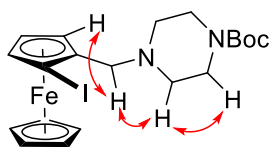




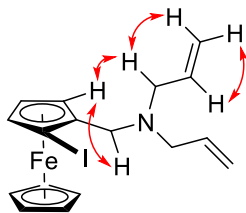


Selected NMR NOESY correlations

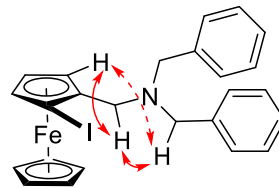
Compound (\pm)-4b



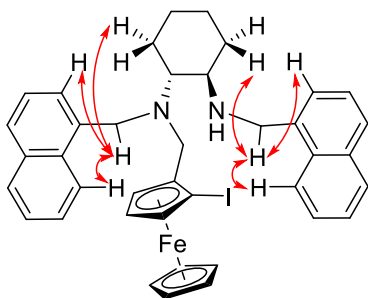
Compound (\pm)-4e



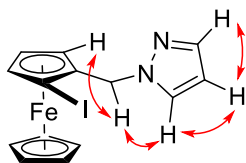
Compound (\pm)-4f



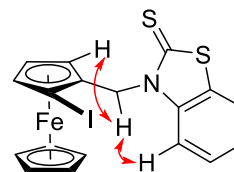
Compound (*R,R,S_D*)-4j



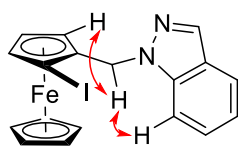
Compound (\pm)-4k



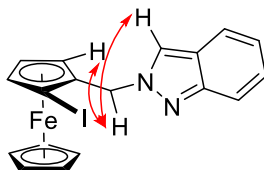
Compound (\pm)-4n



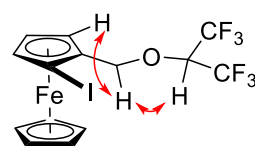
Compound (\pm)-4o



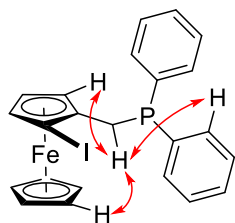
Compound (\pm)-4o'



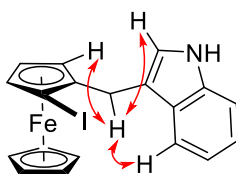
Compound (\pm)-4r



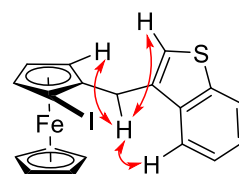
Compound (\pm)-4s



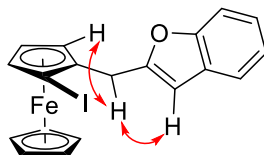
Compound (\pm)-4t



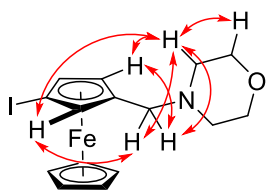
Compound (\pm)-4v



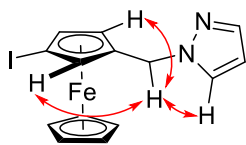
Compound (\pm)-4w



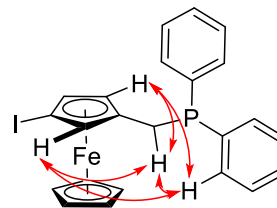
Compound (\pm)-7a



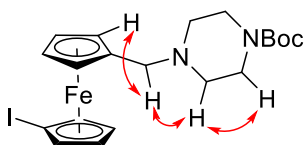
Compound (\pm)-7b



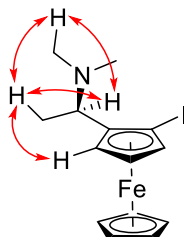
Compound (\pm)-7e



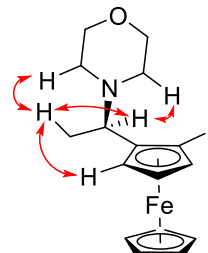
Compound 8a



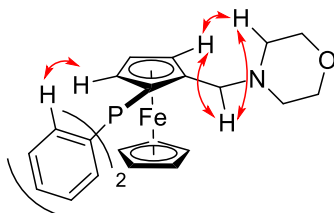
Compound (R,S_p)-9a



Compound (R,S_p)-10

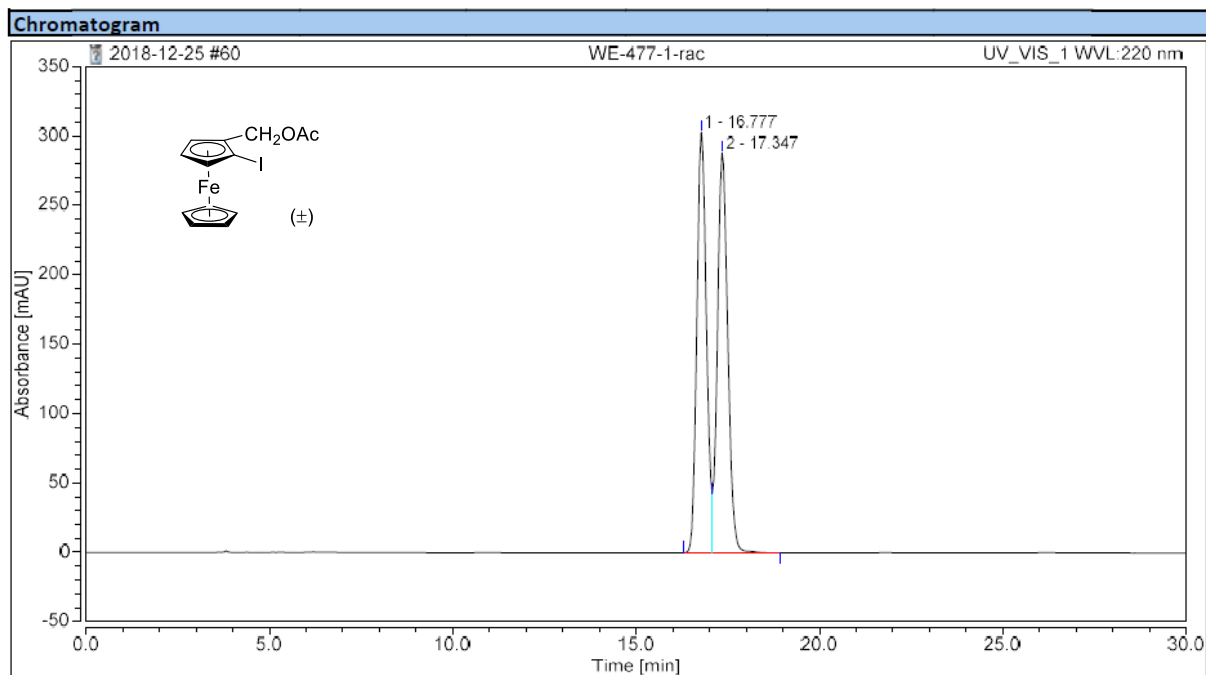


Compound (\pm)-11a



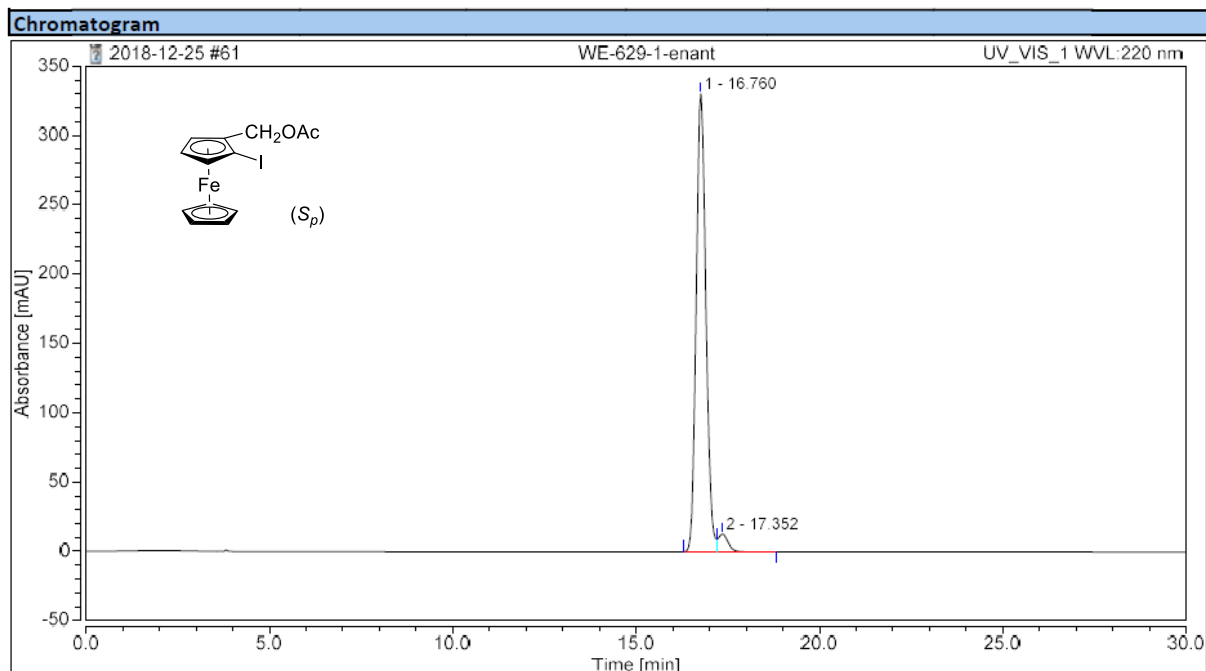
HPLC Chromatograms

Compounds (\pm)- and (S_p)-2



Integration Results

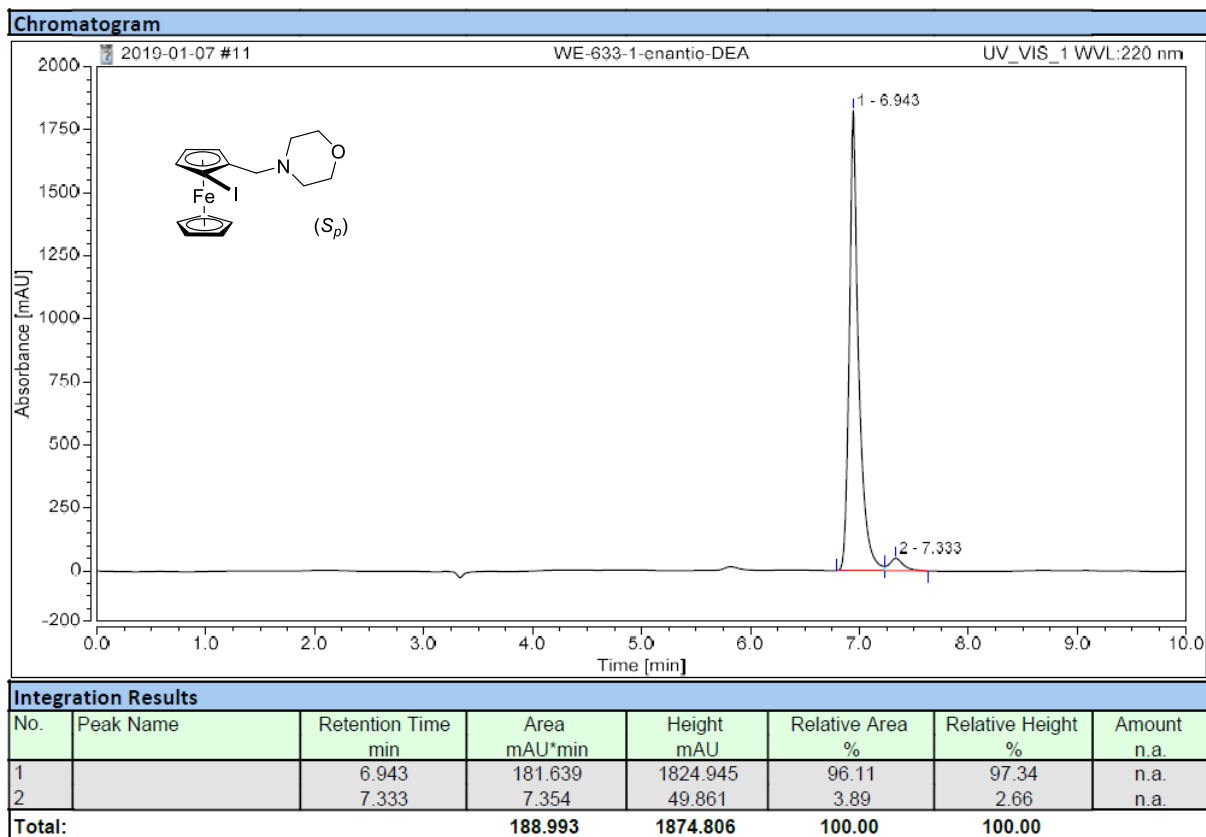
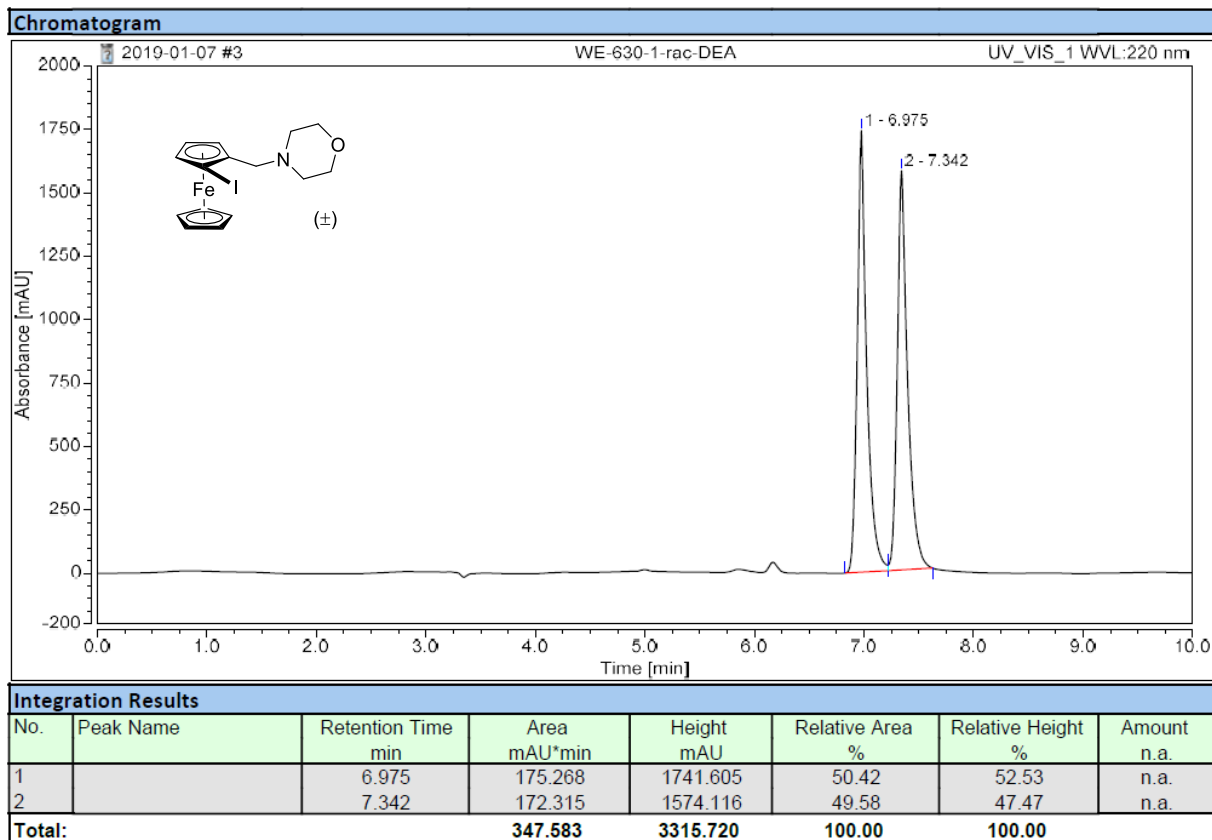
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.777	91.387	303.153	49.24	51.27	n.a.
2		17.347	94.217	288.182	50.76	48.73	n.a.
Total:			185.605	591.335	100.00	100.00	



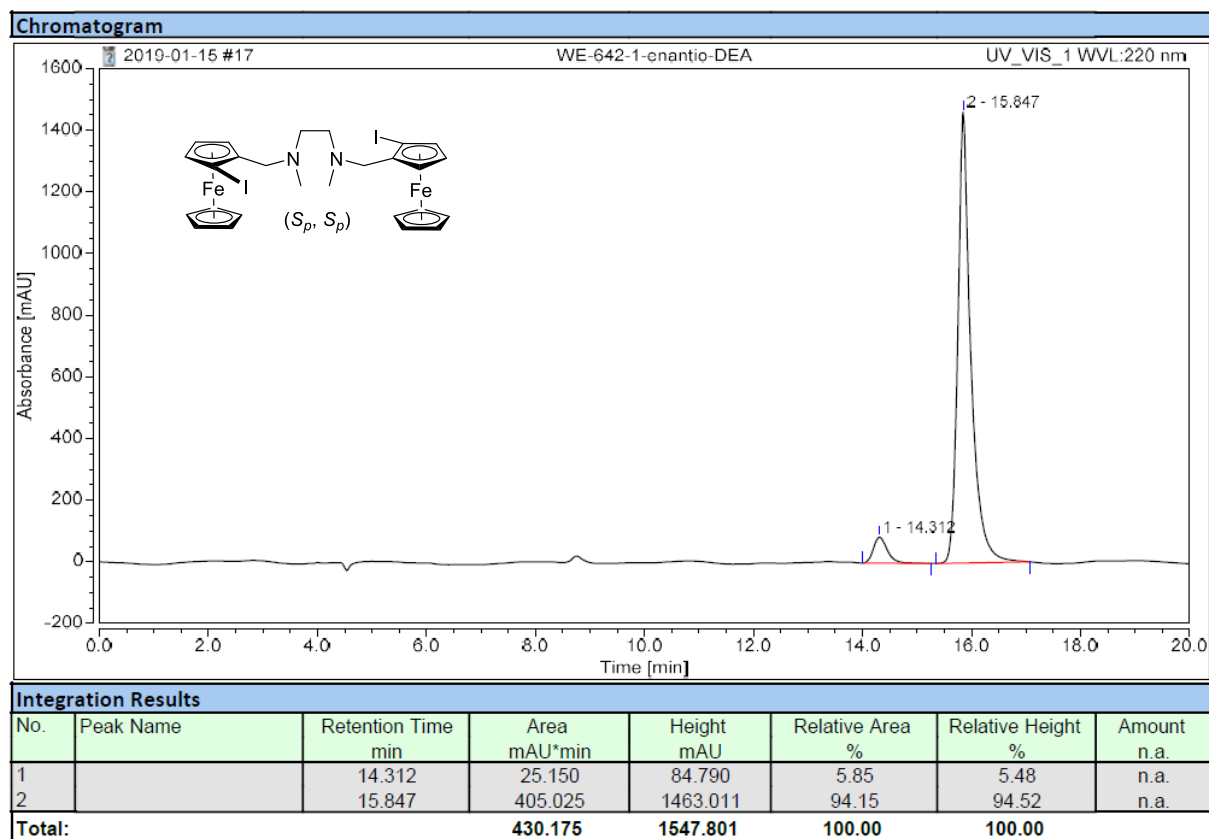
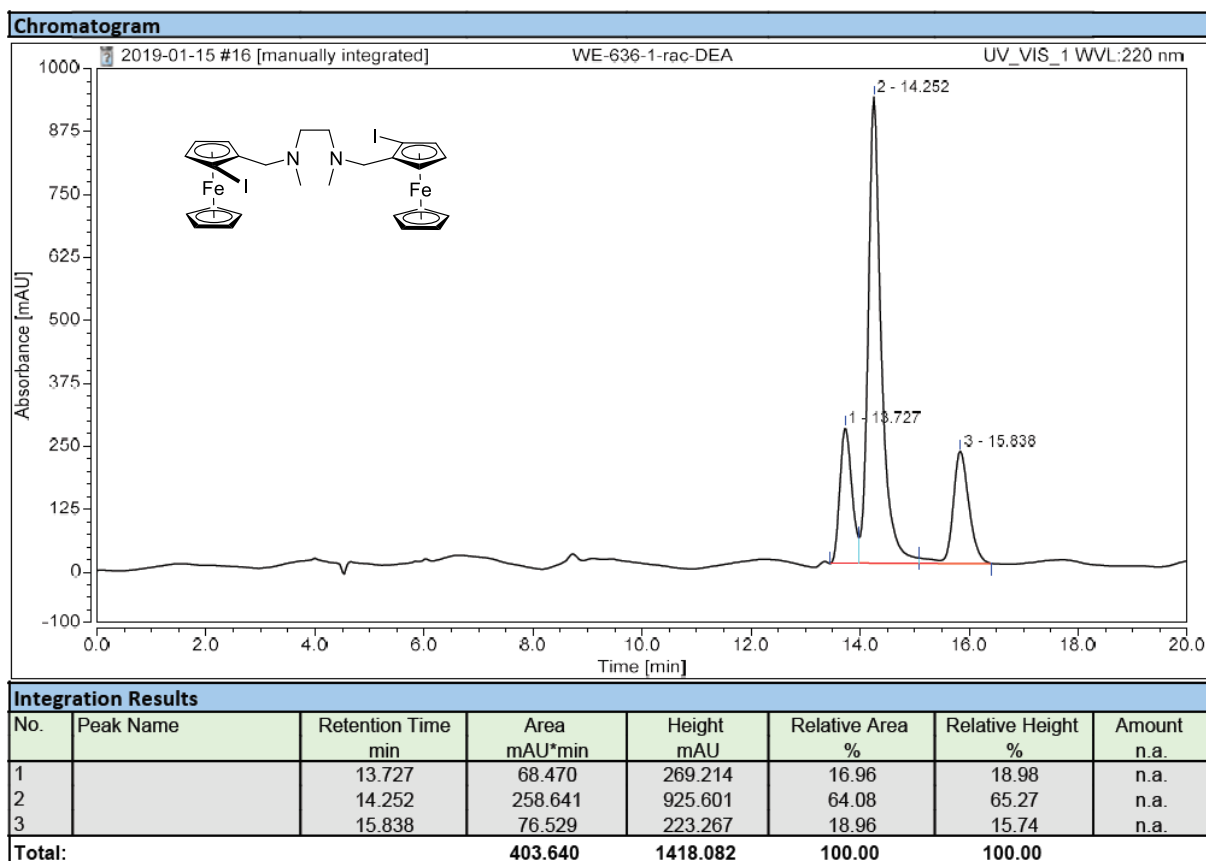
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.760	101.350	330.660	96.13	96.25	n.a.
2		17.352	4.085	12.889	3.87	3.75	n.a.
Total:			105.435	343.549	100.00	100.00	

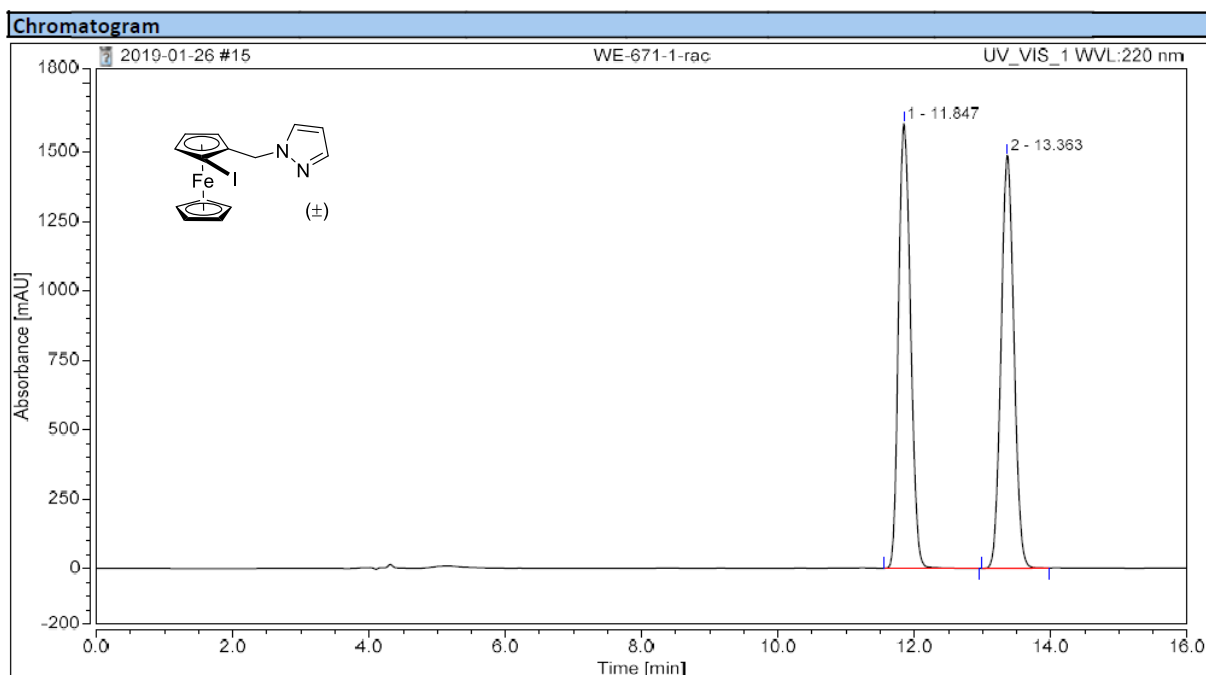
Compounds (\pm)- and (S_p)-4a



Compounds 4i (mixture of stereoisomers and (*S_p*,*S_p*))

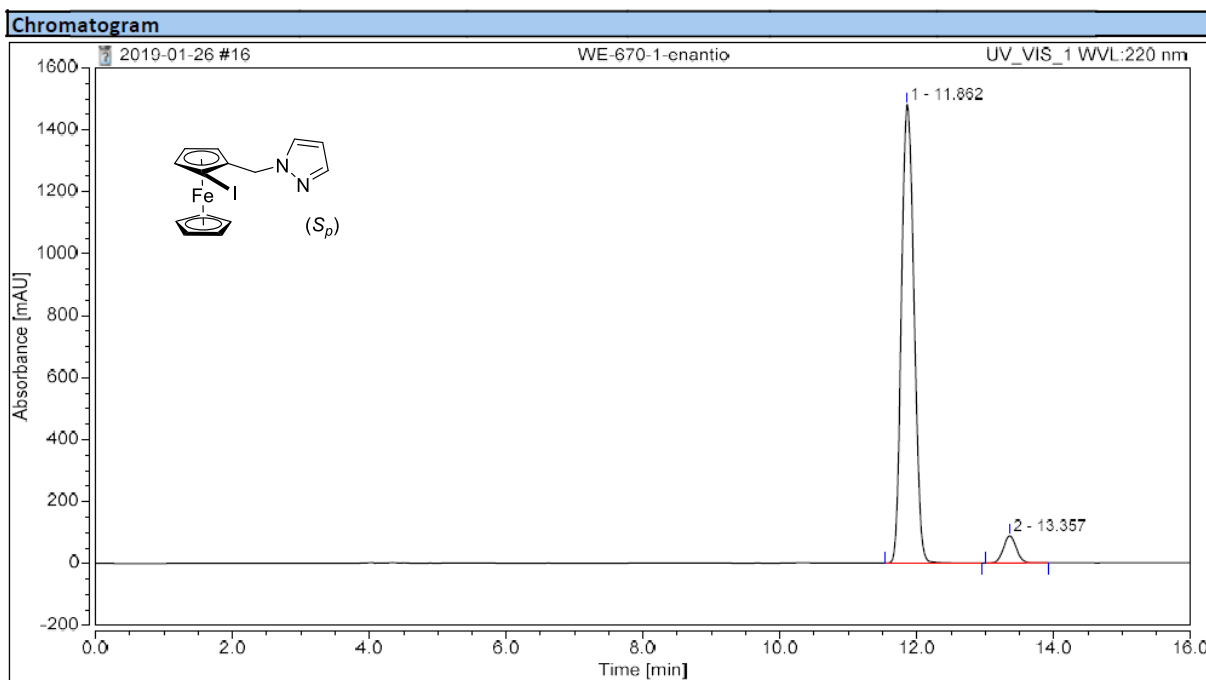


Compounds (\pm)- and (S_p)-4k



Integration Results

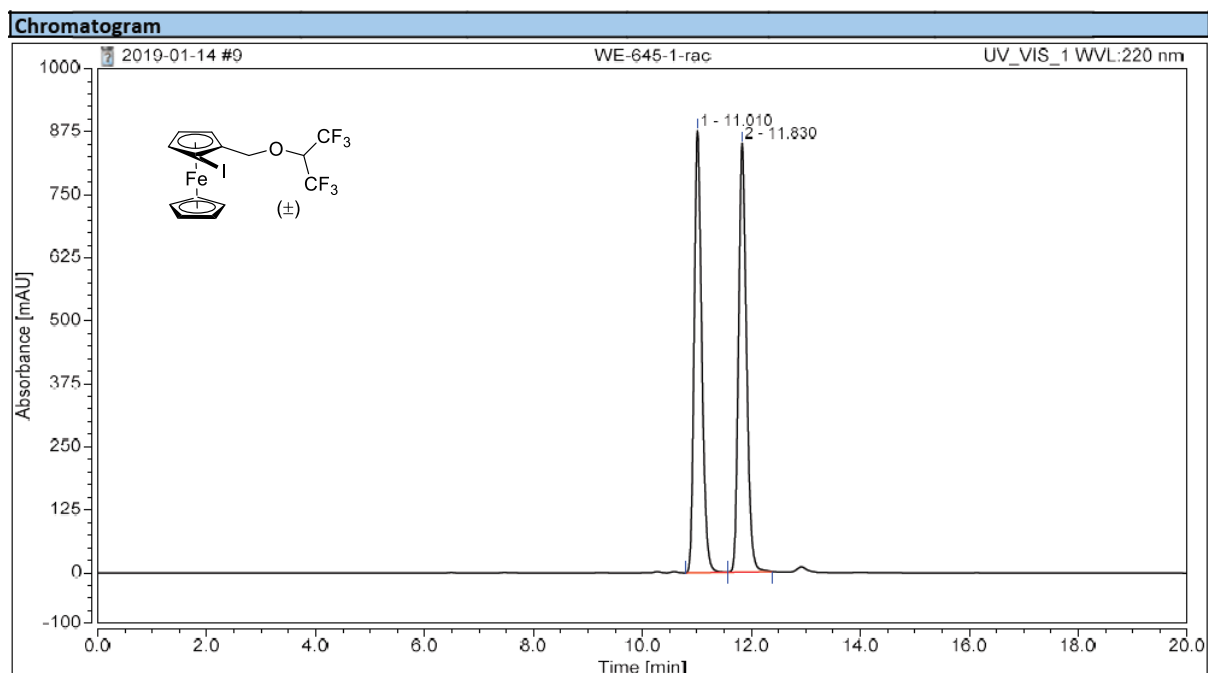
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.847	327.447	1601.665	50.09	51.85	n.a.
2		13.363	326.222	1487.443	49.91	48.15	n.a.
Total:			653.668	3089.108	100.00	100.00	



Integration Results

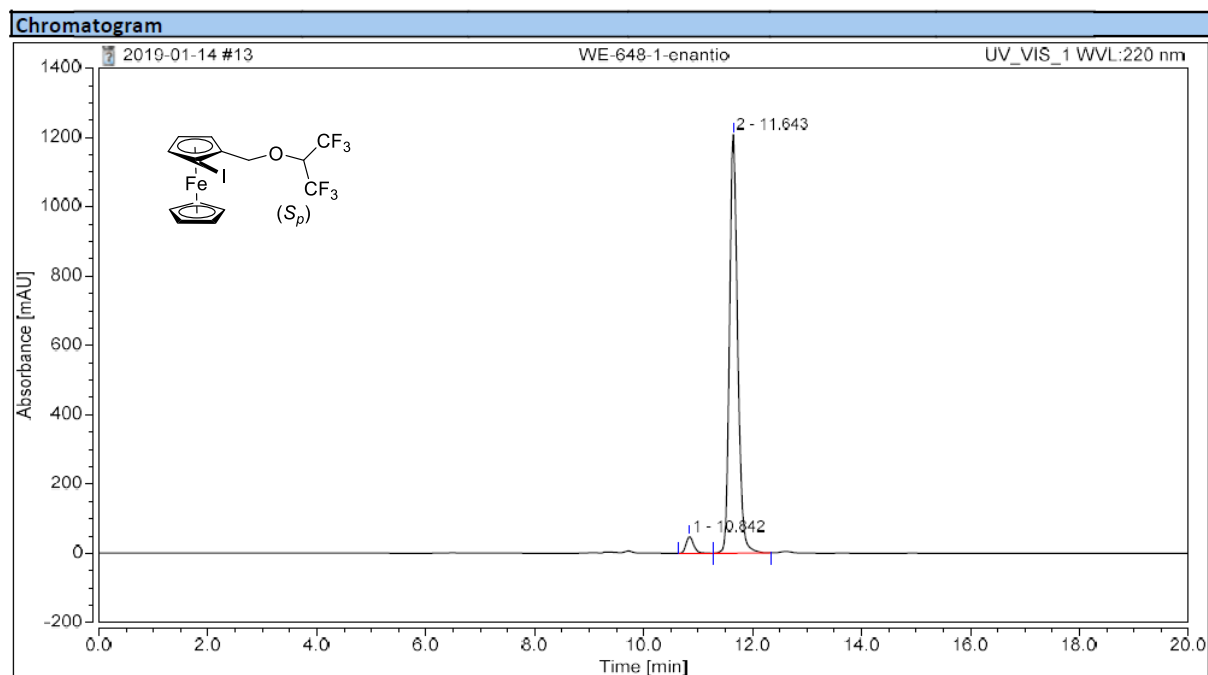
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.862	314.578	1481.057	94.31	94.39	n.a.
2		13.357	18.986	87.958	5.69	5.61	n.a.
Total:			333.564	1569.014	100.00	100.00	

Compounds (±)- and (*S_p*)-4r



Integration Results

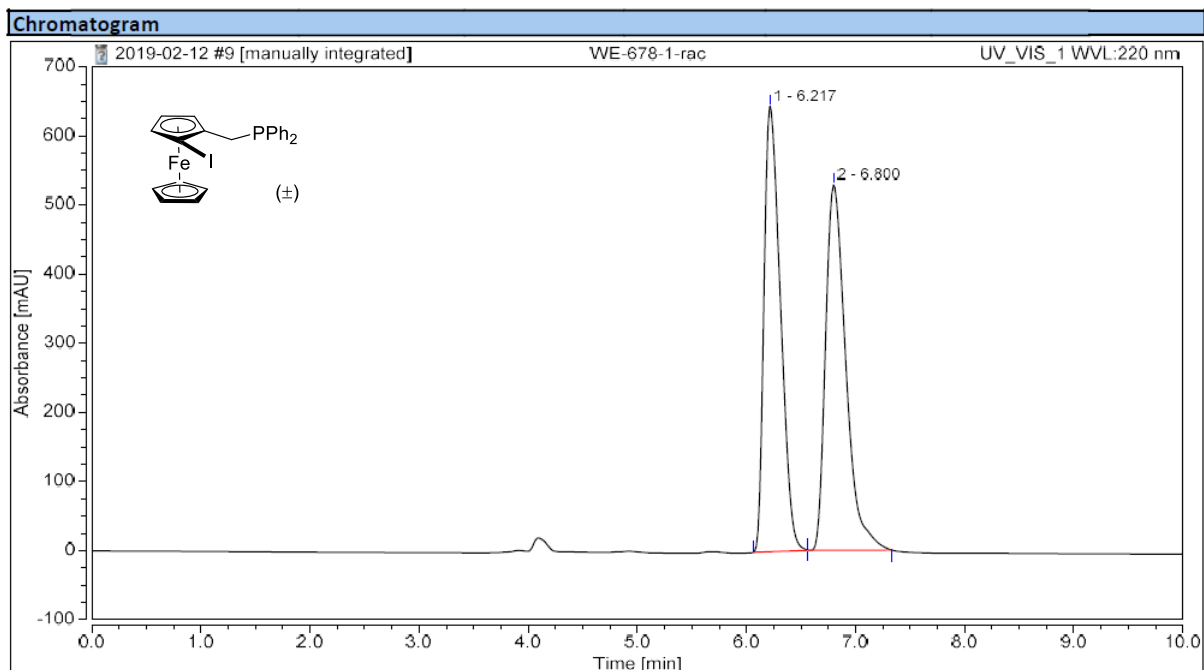
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.010	142.731	876.686	49.83	50.75	n.a.
2		11.830	143.689	850.766	50.17	49.25	n.a.
Total:			286.420	1727.452	100.00	100.00	



Integration Results

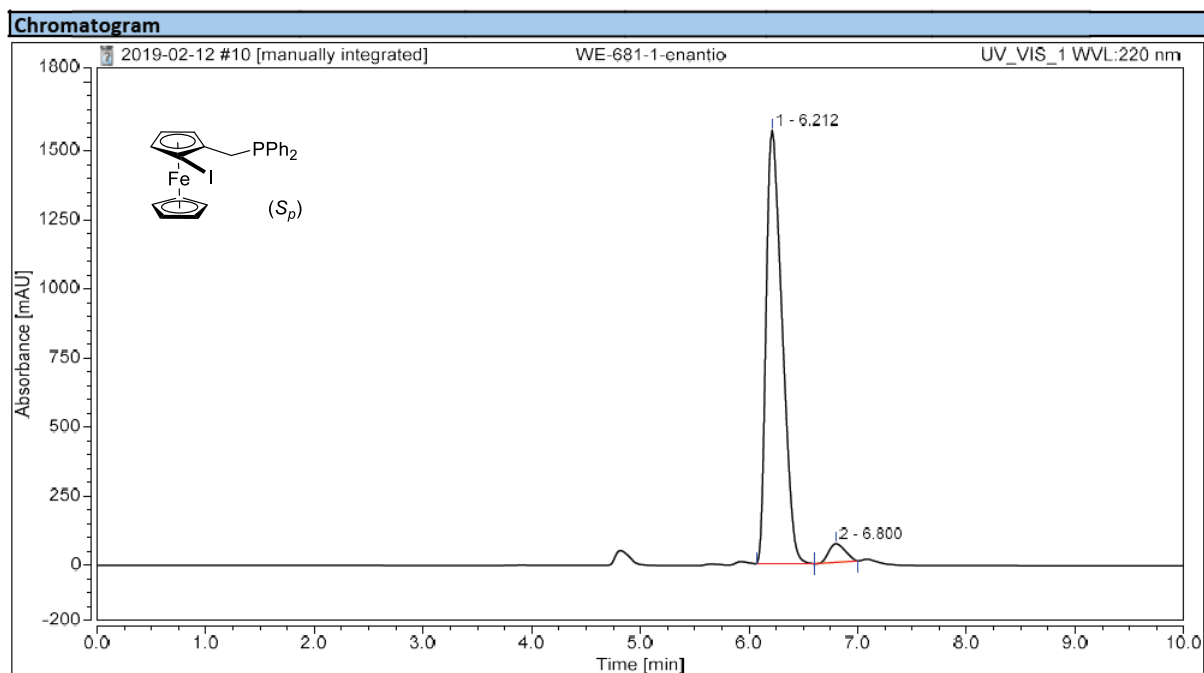
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.842	7.834	48.914	3.58	3.89	n.a.
2		11.643	210.798	1208.319	96.42	96.11	n.a.
Total:			218.632	1257.233	100.00	100.00	

Compounds (\pm)- and (S_p)-4s



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.217	112.311	644.894	49.66	54.91	n.a.
2		6.800	113.869	529.484	50.34	45.09	n.a.
Total:			226.180	1174.378	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.212	267.650	1569.599	95.78	95.88	n.a.
2		6.800	11.788	67.461	4.22	4.12	n.a.
Total:			279.438	1637.059	100.00	100.00	

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