Electronic Supplementary Information

From ferrocene to decasubstituted enantiopure ferrocene-1,1'-disulfoxide derivatives

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A) Compound Synthesis and Analysis

General

All reactions were carried out in Schlenk tubes under a dry argon atmosphere. THF and Et_2O were freshly distilled from sodium-benzophenone. Dichloromethane and *N*,*N*,*N*',*N*'-tetramethylethylenediamine was distilled over CaH_2 under argon. Toluene and hexane were dried over activated 3Å molecular sieves.[1] All alkyllithiums were titrated before use.[2] 2,2,6,6-Tetramethylpiperidine (H-TMP) was distilled over CaH_2 under vacuum. Room temperature (rt) refers to 25 °C. Column chromatography separations were achieved on silica gel (40-63 μm). All Thin Layer Chromatographies (TLC) were performed on aluminium backed plates pre-coated with silica gel (Merck, Silica Gel 60 F254). They were visualized by exposure to UV light. Melting points were measured on a Kofler apparatus. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer, and the main absorption wavenumbers are given in cm^{-1}. ^1H and $^{13}C\{^1H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded at 300 K either on a Bruker Avance III HD spectrometer fitted with a BBFO probe at 500 MHz and 126 MHz respectively, or on a Bruker Avance III spectrometer fitted with a BBFO probe at 400 MHz and 100 MHz respectively, or on a Bruker Avance III spectrometer fitted with a BBFO probe at 300 MHz and 75.4 MHz respectively. ^1H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ^{13}C chemical shifts are relative to the central peak of the solvent signal.[3] Signal assignment was based on 2D NMR experiments (COSY, HSQC, HMBC, NOESY and HOESY). The designations (H, C) and (H', C') have been used for the two cyclopentadienyl rings of ferrocene while the (H'', C'') and (H''', C''') have been used for the additional aromatic rings. Optical rotations were determined on a Perkin Elmer 341 polarimeter (589 nm; 20 °C); the concentrations (*c*) are given in g/100 mL. (*R*)-*S*-*tert*-Butylferrocenesulfoxide was prepared as reported previously,[4] by modifying a reported procedure.[5] (*E*)-1,3-diphenyl-2-propenyl acetate was prepared as reported previously.[6, 7]

Safety considerations. Due to its high pyrophoric character, *tert*-butyllithium has to be used only by well-trained people under anhydrous conditions and nitrogen or argon atmosphere. Due to the inherent dangers of using cryogenic temperatures, experiments should be performed by well-trained people.

Electrochemical measurements. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) analyses were performed in dry, oxygen-free, dichloromethane, using nBu$_4$PF$_6$ (0.1 M) as the supporting electrolyte. Measurements were done using a glassy carbon disk electrode, an Ag/AgCl reference electrode and a glassy carbon rod as the counter electrode. Ohmic drops were not corrected.

Crystallography. The samples were studied with monochromatized Mo-Kα radiation (λ = 0.71073 Å). The X-ray diffraction data of the compounds **1**, ***R*P,*R*P-2d**, ***R*P,*R*P-2f** and ***R*P,*R*P-8a** were collected at the temperature indicated in the crystal description by using a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 70 detector. The X-ray diffraction data of the compounds ***R*P-2c**, ***R*P,*R*P-3**, ***R*P,*R*P-6'c** and ***R*P,*R*P-6h** were collected at the temperature indicated in the crystal description by using an APEXII Kappa-CCD (Bruker-AXS) diffractometer equipped with a CCD-LDI-APEX2 detector. The crystal structures were solved by dual-space algorithm using *SHELXT* program,[8] and then refined with full-matrix least-square methods based on F^2 (*SHELXL* program).[9] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The molecular diagrams were generated by Mercury 2020.3.0.

Procedures and analyses of the compounds

***S*,*S*'-Di-*tert*-butylferrocene-1,1'-disulfoxide** was prepared as a mixture of stereoisomers by reacting ferrocene-1,1'-dilithium[10] with racemic *S*-*tert*-butyl-*tert*-butanethiosulfinate.[11, 12] To ferrocene (0.39 g, 2.1 mmol) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA; 0.80 mL, 5.25 mmol) in hexane (15 mL) at 0 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (3.8 mL, 5.25 mmol). The

temperature of the reaction mixture was next raised to rt, and stirring was pursued overnight. A solution of racemic *S*-*tert*-butyl-*tert*-butanethiosulfinate (0.815 g, 4.2 mmol) in THF (6 mL) was then added to the mixture cooled at –80 °C. After 15 min at this temperature, the mixture was warmed to rt and stirred for 5 h. The mixture was quenched by addition of 1.0 M HCl (10 mL). Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: EtOAc-MeOH 95:5) led to the title product (mixture of stereoisomers; Rf = 0.29) in 26% yield (0.21 g) as an orange solid which was identified by NMR: ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 9H, *t*Bu), 1.12 (s, 9H, *t*Bu), 4.59 (s, 1H), 4.63 (s, 2H), 4.65 (br s, 2H), 4.72 (s, 1H), 4.79 (s, 1H), 4.85 (s, 1H) ppm. Besides ferrocene and degradation products, *rac*-*S*-*tert*-butylferrocenesulfoxide was also isolated in 17% yield. The use of the sodium salt of (*S*,*S*)-2,2-diphenyl-1,2-dihydroxypropyl 2-*O*-*tert*-butylsulfinate[13] as the electrophile failed (starting material recovered).

***S,S'*-Di-*tert*-butylferrocene-1,1'-disulfoxide** was alternately prepared as a mixture of stereoisomers by reacting ferrocene-1,1'-dilithium[10] with racemic *S*-*tert*-butyl-*tert*-butanethiosulfinate.[11, 12] To ferrocene (2.8 g, 15 mmol) and TMEDA (5.6 mL, 37.5 mmol) in hexane (100 mL) at 0 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (27 mL, 37.5 mmol). The temperature of the reaction mixture was next raised to rt, and stirring was pursued overnight. This time, ferrocene-1,1'-dilithium was filtered and dissolved in cold (–80 °C) THF (80 mL). *S*-*tert*-butyl-*tert*-butanethiosulfinate (6.4 g, 33 mmol) in THF (30 mL) was then added at –80 °C. After 15 min at this temperature, the mixture was warmed to rt and stirred for 5 h. The mixture was quenched by addition of 1.0 M HCl (20 mL). Extraction with EtOAc (3 x 40 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: EtOAc) led to the title product (mixture of stereoisomers; Rf = 0.12) in 15% yield (0.89 g). *rac*-*S*-*tert*-Butylferrocenesulfoxide was also isolated in 26% yield.

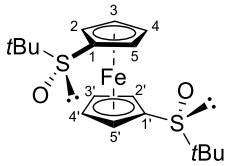
***S,S'*-Di-*tert*-butyl-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (2e)** was prepared as a mixture of stereoisomers as follows. To *S,S'*-di-*tert*-butylferrocene-1,1'-disulfoxide (mixture of stereoisomers; 0.20 g, 0.51 mmol) in THF (5 mL) at –80 °C was added dropwise a 1.6 M pentane solution of *t*BuLi (0.96 mL, 1.5 mmol). After 1 h at this temperature, a solution of PhSSPh (0.33 g, 1.5 mmol) in THF (2 mL) was added and the reaction mixture was stirred at –80 °C for 0.5 h before warming to rt. The mixture was quenched by addition of 1.0 M HCl (5 mL). Extraction with EtOAc (3 x 10 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: EtOAc-petroleum ether 90:10) led to the title product (mixture of stereoisomers; Rf = 0.41) in 45% yield (0.14 g) as an orange solid which was identified by NMR: ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 18H, *t*Bu), 4.61 (s, 2H, H3 and H3'), 4.69 (s, 2H, H4 and H4'), 5.04 (s, 2H, H5 and H5'), 7.19-7.20 (m, 2H, H4" and H4"'), 7.21-7.27 (m, 8H, H2", H2"', H3", H3"', H5", H5"', H6" and H6"') ppm.

***S,S'*-Di-*tert*-butyl-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (2e)** was also prepared as a mixture of stereoisomers on a larger scale as follows. To *S,S'*-di-*tert*-butylferrocene-1,1'-disulfoxide (mixture of stereoisomers; 0.89 g, 2.3 mmol) in THF (23 mL) at –80 °C was added dropwise a 1.6 M pentane solution of *t*BuLi (4.3 mL, 6.8 mmol). After 1 h at this temperature, a solution of PhSSPh (1.5 g, 6.8 mmol) in THF (7 mL) was added and the reaction mixture was stirred at –80 °C for 0.5 h before warming to rt. The mixture was quenched by addition of 1.0 M HCl (20 mL). Extraction with EtOAc (3 x 50 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: EtOAc) led to the title product (mixture of stereoisomers; Rf = 0.50) in 48% yield (0.67 g) as an orange solid which was identified by NMR.

***S,S'*-Di-*tert*-butyl-2,2'-di(phenylthio)-4,4'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (5)** was prepared as a mixture of stereoisomers as follows. To **2e** (mixture of stereoisomers; 0.65 g, 1.1 mmol)

in THF (11 mL) at –80 °C was added dropwise a 1.6 M pentane solution of *t*BuLi (2.0 mL, 3.2 mmol). After 1 h at this temperature, $ClSiMe_3$ (0.40 mL) was added at the same temperature, and the reaction mixture was stirred at –80 °C for 0.5 h before warming to rt. The mixture was quenched by addition of 1.0 M HCl (10 mL). Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: EtOAc) led to the title product (mixture of stereoisomers; Rf = 0.66) in 35% yield (0.29 g) as a red solid which was identified by NMR: ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 18H, $SiMe_3$), 1.26 (s, 18H, *t*Bu), 4.62 (s, 2H, H4 and H4'), 4.76 (s, 2H, H3 and H3'), 7.12 (t, 2H, *J* = 7.4 Hz, H4" and H4"'), 7.22 (t, 4H, *J* = 7.6 Hz, H3", H5", H3"' and H5"'), 7.27 (d, 4H, *J* = 7.5 Hz, H2", H6", H2"' and H6"') ppm.

(*R,R*)-*S,S'*-Di-*tert*-butylferrocene-1,1'-disulfoxide (1) was prepared by reacting ferrocene-1,1'-dilithium[10] with (*R*)-*S*-*tert*-butyl-*tert*-butanethiosulfinate.[14] To ferrocene (6.5 g, 35 mmol) and TMEDA (13 mL, 87.5 mmol) in dry hexane (245 mL) at 0 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (62.5 mL, 87.5 mmol). The temperature of the reaction mixture was next raised to rt and stirring was pursued overnight. After decantation, the upper solvent was removed from the mixture, and ferrocene-1,1'-dilithium was dissolved in cold (–80 °C) THF (180 mL) and TMEDA (26 mL, 0.175 mol). A solution of (*R*)-*S*-*tert*-butyl-*tert*-butanethiosulfinate (15 g, 77 mmol) in THF (50 mL) was then added to the mixture cooled at –80 °C. After 2 h at this temperature, the reaction mixture was warmed to rt and quenched by addition of 1.0 M HCl (50 mL). Extraction with EtOAc (3 x 50 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: EtOAc) and recrystallization from 1:4 CH_2Cl_2-hexane[15] led to **1** (Rf = 0.36) in 41% yield (5.7 g) as an orange solid: mp 184 °C; IR (ATR) ν 744, 823, 1035, 1163, 1249, 1386, 1456, 1471, 1683, 2966, 3077 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 18H, *t*Bu), 4.60 (td, 2H, *J* = 2.5 and 1.3 Hz, H3 and H3'), 4.65 (td, 2H, *J* = 2.5 and 1.4 Hz, H4 and H4'), 4.73 (dt, 2H, *J* = 2.5 and 1.3 Hz, H5 and H5'), 4.79 (dt, 2H, *J* = 2.6 and 1.4 Hz, H2 and H2') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.9 ($6CH_3$, C*Me*$_3$), 55.4 (2C, *C*Me$_3$), 66.8 (2CH, C2 and C2'), 71.4 (2CH, C3 and C3'), 72.5 (2CH, C5 and C5'), 72.7 (2CH, C4 and C4'), 88.7 (2C, C1 and C1', *C*-SO*t*Bu) ppm. The NMR data are similar to those reported.[15] $[\alpha]_D^{20}$ –574 (*c* 1.0, $CHCl_3$) (lit.[15] $[\alpha]_D^{25}$ –566 (*c* 1.0, $CHCl_3$)).

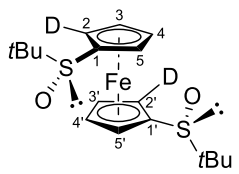


Crystal data for 1. $C_{18}H_{26}FeO_2S_2$, *M* = 394.36, *T* = 250(2) K; monoclinic *C 2* (I.T.#5), *a* = 18.440(3), *b* = 10.1792(16), *c* = 5.9928(9) Å, β = 103.022(5) °, *V* = 1096.0(3) Å^3, *Z* = 2, *d* = 1.195 g.cm^{-3}, μ = 0.884 mm^{-1}. A final refinement on F^2 with 2220 unique intensities and 108 parameters converged at ωR_F^2 = 0.0990 (R_F = 0.0330) for 2213 observed reflections with $I > 2\sigma(I)$. CCDC 2204517.

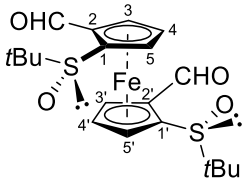
(*R*)-*S*-*tert*-Butylferrocenesulfoxide was similarly isolated in 13% yield by column chromatography (Rf = 0.73) followed by recrystallization from 1:1 diethyl ether-hexane.

General procedure A: Double deprotolithiation using *t*BuLi (3.0 equiv) followed by electrophilic trapping. To a solution of the (*R,R*)-*S,S'*-di-*tert*-butylferrocene-1,1'-disulfoxide (1.0 mmol) in THF (10 mL) at –80 °C was added dropwise a 1.6 M pentane solution of *t*BuLi (1.9 mL, 3.0 mmol), and the reaction mixture was stirred at this temperature for 1 h before addition of the electrophile (3.0 mmol unless otherwise specified; either pure for liquids or in solution for solids, as indicated below). The mixture was stirred at –80 °C for 0.5 h before being warmed to rt; it was next treated as specified in the product description. Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product, which was purified by chromatography over silica gel (eluent given in the product description). Alternatively, the crude reaction mixture was filtered through alumina (eluent given in the product description), the combined filtrates were concentrated under reduced pressure to give the crude product which was purified by chromatography over silica gel (eluent given in the product description).

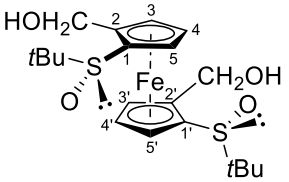
(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-2,2'-dideuterioferrocene-1,1'-disulfoxide (***R*P,*R*P*-**2a)** was prepared by adapting the general procedure A to 0.50 mmol (0.20 g) of **1** and using D_2O (70 μL, 3.75 mmol) as the electrophile before treatment with water (5 mL). This led (no purification was performed in this case) to 0.19 g (98% yield; 90% D) of the title product as a yellow solid: mp 174-176 °C; IR (ATR) ν 744, 790, 831, 1032, 1147, 1178, 1357, 1455, 1666, 2956, 3076 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (s, 18H, *t*Bu), 4.60 (dd, 2H, *J* = 2.6 and 1.3 Hz, H3 and H3'), 4.65 (t, 2H, *J* = 2.5 Hz, H4 and H4'), 4.73 (dd, 2H, *J* = 2.6 and 1.3 Hz, H5 and H5') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 22.9 ($6CH_3$, C*Me*$_3$), 55.3 (2C, *C*Me$_3$), 66.7 (t, 2C, *J* = 28 Hz, C2 and C2'), 71.3 (2CH, C3 and C3'), 72.4 (2CH, C5 and C5'), 72.6 (2CH, C4 and C4'), 88.6 (2C, C1 and C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ –478 (*c* 1.0, $CHCl_3$).



(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-2,2'-diformylferrocene-1,1'-disulfoxide (***R*P,*R*P*-**2b**) was prepared by adapting the general procedure A to 2.8 mmol (1.1 g) of **1** and using dimethylformamide (DMF; 0.66 mL, 8.5 mmol) as the electrophile before treatment with 1.0 M HCl (10 mL). It was isolated (eluent: EtOAc; Rf = 0.32) in 55% yield (0.70 g) as a red solid: mp 214-216 °C; IR (ATR) ν 764, 835, 1044, 1170, 1243, 1307, 1365, 1398, 1423, 1458, 1563, 1673, 2969 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (s, 18H, *t*Bu), 4.93 (t, 2H, *J* = 2.6 Hz, H4 and H4'), 5.27 (dd, 2H, *J* = 2.8 and 1.5 Hz, H3 and H3'), 5.33 (dd, 2H, *J* = 2.7 and 1.5 Hz, H5 and H5'), 10.6 (s, 2H, CHO) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.1 ($6CH_3$, C*Me*$_3$), 56.6 (2C, *C*Me$_3$), 72.3 (2CH, C3 and C3'), 76.9 (2CH, C4 and C4'), 78.2 (2CH, C5 and C5'), 83.7 (2C, C1 and C1', *C*-SO*t*Bu), 92.1 (2C, C2 and C2', *C*-CHO), 192.7 (2C, CHO) ppm; $[\alpha]_D^{20}$ –1408 (*c* 0.8, $CHCl_3$). Anal. Calcd for $C_{20}H_{26}FeO_4S_2$ (450.39): C, 53.34; H, 5.82; S, 14.24. Found: C, 53.17; H, 5.66; S, 14.30%.



Reduction of ***R*P,*R*P*-**2b** was performed as follows. To the dialdehyde ***R*P,*R*P*-**2b** (0.34 g, 0.75 mmol) in MeOH (7.5 mL), was added $NaBH_4$ (0.17 g, 4.5 mmol). The mixture was stirred at 0 °C for 0.5 h. Addition of water (5 mL), extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: EtOAc) led to (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-2,2'-di(hydroxymethyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**3**; Rf = 0.44) in 82% yield (0.28 g) as a yellow solid: mp 220-222 °C; IR (ATR) ν 751, 833, 866, 1003, 1030, 1063, 1082, 1171, 1217, 1361, 1387, 1456, 1671, 2965, 3084, 3295 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (s, 18H, *t*Bu), 4.19 (dd, 2H, *J* = 14.6 and 11.4 Hz, C*H*H-OH), 4.62 (dd, 2H, *J* = 2.6 and 1.5 Hz, H5 and H5'), 4.72 (t, 2H, *J* = 2.6 Hz, H4 and H4'), 4.79 (dd, 2H, *J* = 14.7 and 1.8 Hz, CH*H*-OH), 4.88 (dd, 2H, *J* = 2.6 and 1.6 Hz, H3 and H3'), 5.75 (dd, 2H, *J* = 11.4 and 1.8 Hz, OH) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.2 ($6CH_3$, C*Me*$_3$), 57.5 ($2CH_2$), 57.9 (2C, *C*Me$_3$), 71.2 (2CH, C4 and C4'), 72.5 (2CH, C5 and C5'), 73.5 (2CH, C3 and C3'), 84.0 (2C, C1 and C1', *C*-SO*t*Bu), 93.9 (2C, C2 and C2', *C*-CH_2OH) ppm; $[\alpha]_D^{20}$ –243 (*c* 0.9, $CHCl_3$). Anal. Calcd for $C_{20}H_{30}FeO_4S_2$ (454.42): C, 52.86; H, 6.65; S, 14.11. Found: C, 52.67; H, 6.43; S, 13.95%.

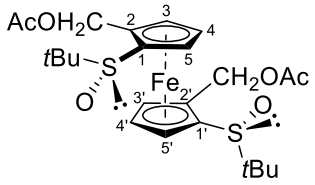


Crystal data for *R*P,*R*P-3. $C_{20}H_{30}FeO_4S_2$, *M* = 454.41, *T* = 150(2) K; tetragonal *P* 4_1 2_1 2 (I.T.#92), *a* = 9.7712(5), *c* = 22.4446(13) Å, *V* = 2142.9(3) $Å^3$, *Z* = 4, *d* = 1.408 $g.cm^{-3}$, μ = 0.921 mm^{-1}. A final refinement on F^2 with 2461 unique intensities and 128 parameters converged at ωR_F^2 = 0.0715 (R_F = 0.0356) for 2170 observed reflections with $I > 2\sigma(I)$. CCDC 2204520.

The attempt to replace the hydroxy groups of ***R*P,*R*P*-**3** by a ferrocenylphosphino bridge failed (treatment by phosphinoferrocene[16] in AcOH at rt;[17] starting material recovered).

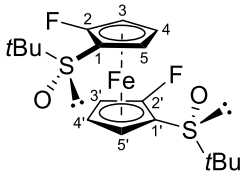
Acetylation of ***R*P,*R*P*-**3** was performed as follows.[6] To a solution of the diol ***R*P,*R*P*-**3** (0.31 g, 0.68 mmol), 4-(dimethylamino)pyridine (DMAP; 0.50 g, 40 μmol) and Et_3N (0.57 mL, 4.1 mmol) in Et_2O (1.5 mL) at 0 °C, was added dropwise Ac_2O (0.38 mL, 4.1 mmol). The mixture was warmed to rt and stirred for 2 h. Addition of a 10% aqueous solution of $NaHCO_3$ (5 mL), extraction with EtOAc (3 x 10 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: EtOAc) led to (*R*,*R*,*R*P,*R*P)-2,2'-

di(acetoxymethyl)-*S*,*S'*-di-*tert*-butylferrocene-1,1'-disulfoxide (***R*P,*R*P-4**) (Rf = 0.50) in 86% yield (0.32 g) as a yellow solid: mp 156-158 °C; IR (ATR) ν 736, 830, 854, 914, 967, 1025, 1041, 1088, 1176, 1229, 1360, 1458, 1728, 2960, 3078 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (s, 18H, *t*Bu), 2.05 (s, 6H, MeC=O), 4.63 (dd, 2H, *J* = 2.7 and 1.5 Hz, H3 and H3'), 4.64 (t, 2H, *J* = 2.7 Hz, H4 and H4'), 4.73 (dd, 2H, *J* = 2.5 and 1.5 Hz, H5 and H5'), 5.27 (d, 2H, *J* = 12.5 Hz, C*H*HOAc), 5.34 (d, 2H, *J* = 12.5 Hz, CH*H*OAc) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 21.0 ($2CH_3$, *Me*C=O), 23.3 ($6CH_3$, C*Me*$_3$), 56.5 (2C, *C*Me_3), 59.6 ($2CH_2$), 73.8 (2CH, C4 and C4', or C5 and C5'), 73.9 (2CH, C4 and C4', or C5 and C5'), 74.6 (2CH, C3 and C3'), 85.1 (2C, C1 and C1', *C*-SO*t*Bu, or C2 and C2', *C*-CH_2OAc), 85.9 (2C, C1 and C1', *C*-SO*t*Bu, or C2 and C2', *C*-CH_2OAc), 170.7 (2C, C=O) ppm; $[\alpha]_D^{20}$ –519 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{24}H_{34}FeO_6S_2$ (538.49): C, 53.53; H, 6.36; S, 11.91. Found: C, 53.56; H, 6.16; S, 12.10%.



All attempts to replace the acetate groups of ***R*P,*R*P-4** failed:
- by a ferrocenylphosphino (treatment by phosphinoferrocene[16] (1.2 equiv) in AcOH at rt[17] for 20 h; starting material recovered),
- by a (ferrocenylmethyl)phosphino bridge (treatment by (phosphinomethyl)ferrocene[18] (1.1 equiv) in degassed AcOH at 60 °C for 16 h;[19] starting material recovered),
- by a (ferrocenylmethyl)phosphino bridge (treatment by (phosphinomethyl)ferrocene[18] (1.2 equiv) in hexafluoroisopropanol at 60 °C for 1 h;[20] starting material recovered),
- by a benzylamino (treatment by 4 equiv of benzylamine in hexafluoroisopropanol at 60 °C for 1 h;[20] starting material recovered),
- or by a *N*,*N*'-dimethylethylene-*N*,*N*'-diamino bridge (treatment by 1.2 equiv of *N*,*N*'-dimethylethylenediamine in hexafluoroisopropanol at 60 °C for 1 h;[20] starting material recovered).

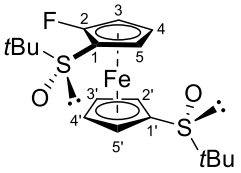
(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-2,2'-difluoroferrocene-1,1'-disulfoxide (***R*P,*R*P-2d**) was prepared by adapting the general procedure A, but at –90 °C instead of –80 °C and at an initial concentration of 0.2 M instead of 0.1 M, to 8.3 mmol (3.3 g) of **1**. After adding *N*-fluorobenzenesulfonimide (NFSI; 7.9 g, 25 mmol) as the electrophile in THF (25 mL), the mixture was warmed to 0 °C before filtration over alumina gel (eluent: CH_2Cl_2-petroleum ether 90:10) and isolation (eluent: EtOAc-petroleum ether 90:10; Rf = 0.35) lead to the title product in 79% yield (2.8 g) as a yellow solid: mp 184-186 °C; IR (ATR) ν 743, 813, 837, 888, 996, 1040, 1082, 1169, 1241, 1408, 1453, 1664, 2960, 3085 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 18H, *t*Bu), 4.46 (td, 2H, *J* = 2.9 and 1.5 Hz, H4 and H4'), 4.69 (t, 2H, *J* = 2.0 Hz, H5 and H5'), 4.85 (q, 2H, *J* = 2.2 Hz, H3 and H3') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.4 ($6CH_3$, C*Me*$_3$), 56.9 (2C, *C*Me_3), 62.1 (d, 2CH, *J* = 13.8 Hz, C3 and C3'), 66.8 (d, 2CH, *J* = 3.6 Hz, C4 and C4'), 68.6 (d, 2CH, *J* = 1.8 Hz, C5 and C5'), 76.7 (d, 2C, *J* = 10.3 Hz, C1 and C1', *C*-SO*t*Bu), 133.9 (d, 2C, *J* = 281 Hz, C2 and C2', C-F) ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –182.7 ppm; $[\alpha]_D^{20}$ –528 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{18}H_{24}F_2FeO_2S_2$ (430.35): C, 50.24; H, 5.62; S, 14.90. Found: C, 50.33; H, 5.70; S, 14.93%; HRMS (ESI), *m/z*: 431.0604 (1 ppm) found (calcd for $C_{18}H_{25}F_2{}^{56}FeO_2S_2$, $[M + H]^+$, requires 431.06079).



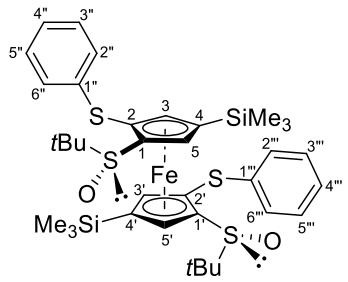
Crystal data for *R*P,*R*P-2d. $C_{18}H_{24}F_2FeO_2S_2$, *M* = 430.34, *T* = 150(2) K; monoclinic *C* 2 (I.T.#5), *a* = 18.4422(19), *b* = 10.1230(10), *c* = 6.0952(7) Å, β = 101.428(4) °, *V* = 1115.4(2) $Å^3$, *Z* = 2, *d* = 1.281 $g.cm^{-3}$, μ = 0.887 mm^{-1}. A final refinement on F^2 with 2355 unique intensities and 117 parameters converged at $\omega R_F{}^2$ = 0.0781 (R_F = 0.0278) for 2321 observed reflections with $I > 2\sigma(I)$. CCDC 2236043.

When the amounts of base and electrophile were reduced to 2.5 equivalents, the reaction under the conditions above applied to 2.0 mmol (0.79 g) of **1**, and using NFSI (1.6 g, 5.0 mmol) as the electrophile in THF (5 mL; –90 °C to –20 °C) before filtration over alumina gel (eluent: CH_2Cl_2-petroleum ether 90:10) and isolation (eluent: EtOAc-petroleum ether 90:10; Rf = 0.35) lead to the title product in 45% yield (0.39 g) while (*R*,*R*,*R*P)-*S*,*S'*-di-*tert*-butyl-2-fluoroferrocene-1,1'-disulfoxide was similarly isolated (Rf = 0.15) in 28% yield (0.235 g), and identified by NMR: ^1H NMR ($CDCl_3$) δ 1.15

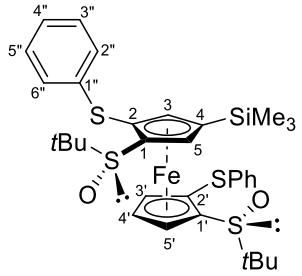
(s, 9H, C1'-SO*t*Bu), 1.23 (s, 9H, C1-SO*t*Bu), 4.32 (td, 1H, *J* = 2.9 and 1.5 Hz, H4), 4.41-4.42 (m, 1H, H5), 4.72 (td, 1H, *J* = 2.6 and 1.6 Hz, H3), 4.74 (td, 1H, *J* = 2.6 and 1.3 Hz, H4'), 4.80 (td, 1H, *J* = 2.5 and 1.3 Hz, H3'), 4.89 (dt, 1H, *J* = 2.7 and 1.4 Hz, H5'), 5.01 (dt, 1H, *J* = 2.6 and 1.3 Hz, H2') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 22.8 ($3CH_3$, C1'-SOC*Me*$_3$), 23.4 ($3CH_3$, C1-SOC*Me*$_3$), 55.5 (C, C1'-SO*C*Me$_3$), 56.8 (C, C1-SO*C*Me$_3$), 60.3 (d, CH, *J* = 13.9 Hz, C3), 64.7 (d, CH, *J* = 3.4 Hz, C4), 67.6 (CH, C5), 67.9 (CH, C5'), 73.0 (CH, C4'), 73.6 (CH, C2'), 74.7 (CH, C3'), 75.8 (d, CH, *J* = 10.6 Hz, C1), 89.8 (C, C1'), 133.7 (d, C, *J* = 281 Hz, C2, C-F) ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –183.6 ppm.



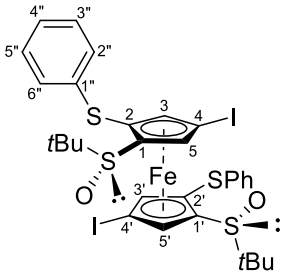
(*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S'*-Di-*tert*-butyl-2,2'-di(phenylthio)-4,4'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*$_P$,*R*$_P$*-**5a**) was prepared by adapting the general procedure A to 0.74 mmol (0.45 g) of (*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S'*-di-*tert*-butyl-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (***R*$_P$,*R*$_P$*-**2e**) and using $ClSiMe_3$ (0.28 mL, 2.2 mmol) as the electrophile before treatment with 1.0 M HCl (5 mL). It was isolated (eluent: EtOAc-petroleum ether 70:30; Rf = 0.54) in 40% yield (0.22 g) as a red solid: mp 208 °C; IR (ATR) ν 724, 744, 829, 920, 1043, 1073, 1173, 1209, 1246, 1472, 1582, 2218, 2961 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.28 (s, 18H, $SiMe_3$), 1.26 (s, 18H, *t*Bu), 4.62 (d, 2H, *J* = 1.6 Hz, H5 and H5'), 4.77 (d, 2H, *J* = 1.6 Hz, H3 and H3'), 7.11 (tt, 2H, *J* = 7.2 and 1.4 Hz, H4" and H4"'), 7.21 (t, 4H, *J* = 7.8 Hz, H3", H5", H3"' and H5"'), 7.26 (dd, 4H, *J* = 8.4 and 1.4 Hz, H2", H6", H2"' and H6"') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 0.3 ($6CH_3$, $SiMe_3$), 24.1 ($6CH_3$, C*Me*$_3$), 57.3 (2C, *C*Me$_3$), 77.2 (2CH, C5 and C5'), 79.5 (2C, C4 and C4', *C*-$SiMe_3$), 83.3 (2CH, C3 and C3'), 86.9 (2C, C1 and C1', *C*-SO*t*Bu, or C2 and C2', *C*-SPh), 88.8 (2C, C1 and C1', *C*-SO*t*Bu, or C2 and C2', *C*-SPh), 126.0 (2CH, C4" and C4"'), 128.8 (4CH, C3", C5", C3"' and C5"'), 129.1 (4CH, C2", C6", C2"' and C6"'), 138.2 (2C, C1" and C1"') ppm; $[\alpha]_D^{20}$ –1007 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{36}H_{50}FeO_2S_4Si_2$ (755.05): C, 57.27; H, 6.68; S, 16.98. Found: C, 57.46; H, 6.85; S, 17.08%; HRMS (ESI), *m/z*: 755.1652 (0 ppm) found (calcd for $C_{36}H_{51}{}^{56}FeO_2S_4Si_2$, $[M + H]^+$, requires 755.16544).



(*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S'*-Di-*tert*-butyl-2,2'-di(phenylthio)-4-(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*$_P$,*R*$_P$*-**5'a)** was similarly isolated (Rf = 0.71) in 11% yield (57 mg), and identified by NMR: ^1H NMR ($CDCl_3$) δ 0.40 (s, 9H, $SiMe_3$), 1.28 (s, 9H, *t*Bu), 1.33 (s, 9H, *t*Bu), 4.44 (s, 1H), 4.73 (s, 1H), 4.95 (m, 2H), 5.08 (t, *J* = 2.6 Hz, 1H), 7.15-7.25 (m, 3H, Ph), 7.27-7.30 (m, 3H, Ph), 7.33-7.36 (m, 2H, Ph), 7.40-7.43 (m, 2H, Ph) ppm.

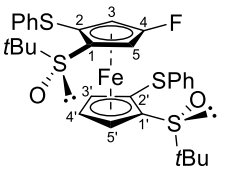


(*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S'*-Di-*tert*-butyl-4,4'-diiodo-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (***R*$_P$,*R*$_P$*-**5b**) was obtained by adapting the general procedure A, but at –50 °C instead of –80 °C, to 0.43 mmol (0.26 g) of ***R*$_P$,*R*$_P$*-**2e** and using I_2 (0.325 g, 1.3 mmol) as the electrophile in THF (2 mL) before treatment with saturated aqueous $Na_2S_2O_3$ (5 mL). It was isolated (eluent: EtOAc-petroleum ether 50:50; Rf = 0.30) in 14% yield (53 mg) as a brownish-orange oil; IR (ATR) ν 703, 751, 862, 879, 1045, 1085, 1172, 1204, 1300, 1363, 1387, 1439, 1472, 1581, 1662, 2964, 3057, 3389 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (s, 18H, *t*Bu), 4.53 (d, 2H, *J* = 1.5 Hz, H3 and H3'), 4.67 (d, 2H, *J* = 1.5 Hz, H5 and H5'), 7.29-7.34 (m, 6H, H3", H4", H5", H3"', H4"' and H5"'), 7.53-7.55 (m, 4H, H2", H6", H2"' and H6"') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 24.0 ($6CH_3$, C*Me*$_3$), 45.1 (2C, C4, C-I), 58.2 (2C, *C*Me$_3$), 82.1 (2CH, C3 and C3'), 82.9 (2CH, C5 and C5'), 84.4 (2C, C1 and C1', *C*-SO*t*Bu, or C2 and C2', *C*-SPh), 92.9 (2C, C1 and C1', *C*-SO*t*Bu, or C2 and C2', *C*-SPh), 128.2 (2CH, C4" and C4"'), 129.5 (4CH, C3", C5", C3"' and C5"'), 133.4 (4CH, C2", C6", C2"' and C6"'), 134.1 (2C, C1" and C1"') ppm; $[\alpha]_D^{20}$ –899 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{30}H_{32}FeI_2O_2S_4$ (862.48): C, 41.78; H, 3.74; S, 14.87. Found: C, 41.82; H, 3.86; S, 14.77%.

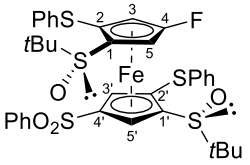


(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-4-fluoro-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**5'c**) and (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4-fluoro-4'-(phenylsulfonyl)-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**5"c**) were obtained by adapting the general procedure A to 0.79 mmol (0.48 g) of ***R*P,*R*P*-**2e** and by using NFSI (0.75 g, 2.4 mmol) as the electrophile in THF (4 mL) before treatment with water (10 mL).

(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-4-fluoro-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**5'c**) was obtained (Rf = 0.45) in 5% yield (27 mg) and identified by NMR: ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 18H, *t*Bu), 4.31 (dd, 1H, *J* = 2.9 and 1.9 Hz, H3' or H4' or H5'), 4.55 (dd, 1H, *J* = 2.7 and 1.5 Hz, H3' or H4' or H5'), 4.85 (dd, 1H, *J* = 2.7 and 1.5 Hz, H3' or H4' or H5'), 4.97 (t, 1H, *J* = 2.7 Hz, H3 or H5), 5.05 (t, 1H, *J* = 2.8 Hz, H3 or H5), 7.27-7.38 (m, 10H, Ph) ppm; ^{19}F{^{1}H} NMR ($CDCl_3$) δ –178.9 ppm.

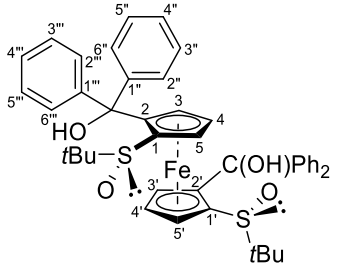


(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-4-fluoro-4'-(phenylsulfonyl)-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**5"c**) was similarly isolated (eluent: EtOAc-petroleum ether 60:40; Rf = 0.58) in 4% yield (25 mg), and was identified by NMR: ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 9H, *t*Bu), 1.38 (s, 9H, *t*Bu), 4.88-4.90 (m, 2H), 4.91 (d, 1H, *J* = 1.6 Hz), 5.09 (dd, 1H, *J* = 2.8 and 1.8 Hz), 7.31-7.36 (m, 5H, Ph), 7.44-7.49 (m, 3H, Ph), 7.54-7.61 (m, 3H, Ph), 7.66-7.69 (m, 2H, Ph), 7.76-7.79 (m, 2H, Ph) ppm; ^{19}F{^{1}H} NMR ($CDCl_3$) δ –182.0 ppm.

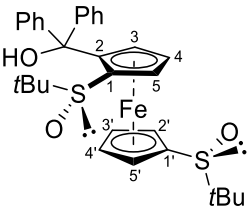


General procedure A': Double deprotolithiation using *t*BuLi (2.6 equiv) followed by electrophilic trapping. To a solution of the (*R*,*R*)-*S*,*S'*-di-*tert*-butylferrocene-1,1'-disulfoxide (1.0 mmol) in THF (10 mL) at –80 °C was added dropwise a 1.6 M pentane solution of *t*BuLi (1.6 mL, 2.6 mmol), and the reaction mixture was stirred at this temperature for 1 h before addition of the electrophile (2.6 mmol unless otherwise specified; either pure for liquids or in solution for solids, as indicated below). The mixture was stirred at –80 °C for 0.5 h before being warmed to rt; it was next treated as specified in the product description. Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product, which was purified by chromatography over silica gel (eluent given in the product description).

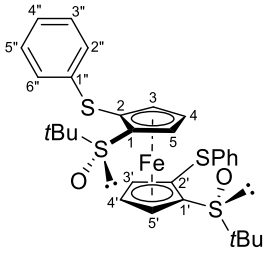
(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-2,2'-di((α,α-diphenyl)hydroxymethyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**2c**) was prepared by adapting the general procedure A' to 1.0 mmol (0.41 g) of **1** and using Ph_2CO (0.47 g, 2.6 mmol) as the electrophile in THF (3 mL) before treatment with water (5 mL). It was isolated (eluent: EtOAc-petroleum ether 70:30; Rf = 0.74) in 78% yield (0.61 g) as a yellow solid: mp 230-232 °C; IR (ATR) ν 749, 827, 902, 1012, 1053, 1169, 1214, 1365, 1447, 1598, 3176 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (s, 18H, *t*Bu), 3.55 (dd, 2H, *J* = 2.7 and 1.6 Hz, H3 and H3'), 4.80 (dd, 2H, *J* = 2.8 and 1.6 Hz, H5 and H5'), 5.41 (t, 2H, *J* = 2.7 Hz, H4 and H4'), 7.03-7.10 (m, 6H, H3"/H5", H4", H3"'/H5"' and H4"'), 7.12 (d, 2H, *J* = 7.3 Hz, H4" or/and H4"'), 7.17 (t, 4H, *J* = 7.5 Hz, H3"/H5", and H3"'/H5"'), 7.23 (d, 4H, *J* = 7.1 Hz, H2"/H6", and H2"'/H6"'), 7.31 (dd, 4H, *J* = 8.1 and 1.7 Hz, H2"/H6", and H2"'/H6"'), 7.41 (s, 2H, OH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 23.5 ($6CH_3$, C*Me*$_3$), 58.0 (2C, *C*Me$_3$), 74.0 (2CH, C4 and C4'), 76.5 (2C, C2 and C2', *C*-C(OH)Ph_2), 77.7 (2CH, C5 or C5'), 78.1 (2CH, C3 and C3'), 83.1 (C, C1 and C1', *C*-SO*t*Bu), 101.8 (2C, C(OH)), 127.0 (2CH, C4" or/and C4"'), 127.1 (2CH, C4" or/and C4"'), 127.2, 127.2, 127.3 and 127.7 (4CH each, C2", C3", C5", C6", C2"', C3"', C5"' and C6"'), 145.2 (2C, C1" or/and C1"'), 149.3 (2C, C1" or/and C1"') ppm; $[\alpha]_D^{20}$ –342 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{44}H_{46}FeO_4S_2$ (758.81): C, 69.65; H, 6.11; S, 8.45. Found: C, 69.65; H, 6.18; S, 8.31%.



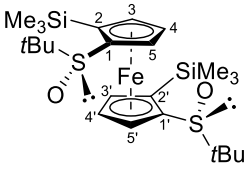
(*R*,*R*,*R*$_P$)-*S*,*S'*-Di-*tert*-butyl-2-((α,α-diphenyl)hydroxymethyl)ferrocene-1,1'-disulfoxide was similarly isolated (Rf = 0.21) in 15% yield (67 mg), and identified by NMR: ^{1}H NMR ($CDCl_3$) δ0.79 (s, 9H, *t*Bu), 1.11 (s, 9H, *t*Bu), 4.19 (t, 1H, *J* = 1.9 Hz), 4.29 (br s, 1H), 4.47 (t, 1H, *J* = 1.0 Hz), 4.73 (t, 1H, *J* = 2.6 Hz), 4.79 (t, 1H, *J* = 1.0 Hz), 4.81 (t, 1H, *J* = 1.9 Hz), 5.10 (br s, 1H), 7.10-7.24 (m, 4H), 7.30-7.35 (m, 4H), 7.51 (s, 1H, OH), 7.63 (d, 2H, *J* = 7.5 Hz) ppm.



(*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S'*-Di-*tert*-butyl-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (***R*$_P$,*R*$_P$*-**2e**) was prepared by adapting the general procedure A' to 2.5 mmol (0.99 g) of **1**, and using PhSSPh (1.6 g, 7.5 mmol) as the electrophile in THF (7 mL) before treatment with 1.0 M HCl (10 mL). It was isolated (eluent: EtOAc-petroleum ether 90:10; Rf = 0.41) in 78% yield (1.2 g) as an orange solid: mp 208-210 °C; IR (ATR) ν 744, 826, 950, 1038, 1063, 1180, 1229, 1363, 1445, 1470, 1581, 1666, 2980, 3057 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ1.24 (s, 18H, *t*Bu), 4.61 (dd, 2H, *J* = 2.6 and 1.5 Hz, H3 and H3'), 4.70 (t, 2H, *J* = 2.7 Hz, H4 and H4'), 5.04 (dd, 2H, *J* = 2.8 and 1.5 Hz, H5 and H5'), 7.18-7.22 (m, 2H, H4" and H4"'), 7.24-7.29 (m, 8H, H2", H3", H5", H6", H2"', H3"', H5"', H6"') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 23.9 ($6CH_3$, C*Me*$_3$), 57.3 (2C, *C*Me$_3$), 75.7 (2CH, C5 and C5'), 77.7 (2CH, C4 and C4'), 79.4 (2CH, C3 and C3'), 85.2 (2C, C1 and C1', *C*-SO*t*Bu, or C2 and C2', *C*-SPh), 85.5 (2C, C1 and C1', *C*-SO*t*Bu, or C2 and C2', *C*-SPh), 126.9 (2CH, C4" and C4"'), 129.2 and 130.0 (8CH, C2", C3", C5", C6", C2"', C3"', C5"' and C6"'), 136.6 (2C, C1" and C1"') ppm; $[\alpha]_D^{20}$ –3029 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{30}H_{34}FeO_2S_4$ (610.68): C, 59.00; H, 5.61; S, 21.00. Found: C, 58.93; H, 5.56; S, 21.14%.

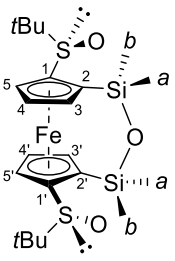


(*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S'*-Di-*tert*-butyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*$_P$,*R*$_P$*-**2f**) was prepared by adapting the general procedure A' to 2.0 mmol (0.79 g) of **1**, and using $ClSiMe_3$ (0.66 mL, 5.2 mmol) as the electrophile before treatment with 1.0 M HCl (10 mL). It was isolated (eluent: EtOAc-petroleum ether 70:30; Rf = 0.68) in 92% yield (0.99 g) as an orange solid: mp 174-176 °C; IR (ATR) ν 725, 752, 826, 921, 948, 1048, 1134, 1171, 1244, 1361, 1459, 2229, 2958 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 18H, $SiMe_3$), 1.15 (s, 18H, *t*Bu), 4.39 (dd, 2H, *J* = 2.6 and 1.2 Hz, H3 and H3'), 4.71 (dd, 2H, *J* = 2.6 and 1.3 Hz, H5 and H5'), 4.74 (t, 2H, *J* = 2.5 Hz, H4 and H4') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ2.3 ($6CH_3$, $SiMe_3$), 23.7 ($6CH_3$, C*Me*$_3$), 56.6 (2C, *C*Me$_3$), 72.7 (2C, C2 and C2', *C*-$SiMe_3$), 73.7 (2CH, C5 and C5'), 75.4 (2CH, C4 and C4'), 78.6 (2CH, C3 and C3'), 93.4 (2C, C1 and C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ –188 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{24}H_{42}FeO_2S_2Si_2$ (538.73): C, 53.51; H, 7.86; S, 11.90. Found: C, 53.62; H, 8.15; S, 11.88%.



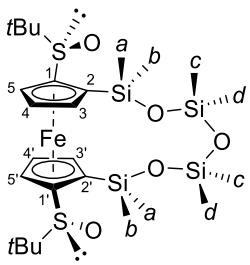
Crystal data for *R*$_P$,*R*$_P$-2f. $C_{24}H_{42}FeO_2S_2Si_2$, *M* = 538.72, *T* = 200(2) K; orthorhombic *P* 2_1 2_1 2_1 (I.T.#19), *a* = 12.5430(3), *b* = 12.7335(3), *c* = 18.3899(5) Å, *V* = 2937.17(13) Å^3, *Z* = 4, *d* = 1.218 g.cm^{-3}, μ = 0.755 mm^{-1}. A final refinement on F^2 with 6636 unique intensities and 296 parameters converged at $\omega R(F^2)$ = 0.0898 (R_F = 0.0368) for 6089 observed reflections with $I > 2\sigma(I)$. CCDC 2204519.

(*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S'*-Di-*tert*-butyl-2,2'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)ferrocene-1,1'-disulfoxide (***R*$_P$,*R*$_P$*-**2g1**) was prepared by adapting the general procedure A' to 0.95 mmol (0.37 g) of **1**, and using Cl_2SiMe_2 (0.30 mL, 2.5 mmol) as the electrophile before treatment with water (5 mL). It was isolated (eluent: EtOAc-petroleum ether 30:70; Rf = 0.57) in 17% yield (86 mg) as a yellow solid: mp 190-192 °C; IR (ATR) ν 701, 781, 824, 956, 1045, 1135, 1172, 1249, 1364, 1457, 1658, 2958 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.47 (s, 6H, SiMe-*a*), 0.55 (s, 6H, SiMe-*b*), 1.14 (s, 18H, *t*Bu), 4.56 (dd, 2H, *J* = 2.4 and 1.6 Hz, H5 and H5'), 4.69-4.71 (m, 4H, H3, H3', H4, H4') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ2.4 ($2CH_3$, SiMe-*a*), 3.9 ($2CH_3$, SiMe-*b*), 23.9 ($6CH_3$, C*Me*$_3$), 56.4 (2C, *C*Me$_3$), 72.5 (2CH, C5 and C5'), 73.3 (2CH, C4 and C4'), 74.9 (2C, C2 and C2', *C*-$SiMe_3$), 81.8 (2CH, C3 and C3'), 92.7 (2C, C1

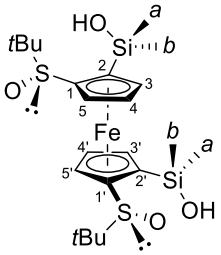


and C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ +20 (*c* 0.6, $CHCl_3$); HRMS (ESI), *m/z*: 547.0885 (0 ppm) found (calcd for $C_{22}H_{36}{}^{56}FeNaO_3S_2Si_2$, $[M + Na]^+$, requires 547.0886).

(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-2,2'-(1,1,3,3,5,5,7,7-octamethyl-1,7-tetrasiloxanediyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**2g2**) was similarly isolated (Rf = 0.46) in 12% yield (79 mg) as an orange oil: IR (ATR) ν 796, 948, 1042, 1072, 1142, 1177, 1257, 1363, 1394, 1474, 2902, 2959 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (s, 6H, SiMe-*c*), 0.15 (s, 6H, SiMe-*d*), 0.29 (s, 6H, SiMe-*b*), 0.71 (s, 6H, SiMe-*a*), 1.13 (s, 18H, *t*Bu), 4.64 (dd, 2H, *J* = 2.4 and 1.4 Hz, H5 and H5'), 4.82 (t, 2H, *J* = 2.4 Hz, H4 and H4'), 4.89 (dd, 2H, *J* = 2.3 and 1.4 Hz, H3 and H3') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.3 and 1.5 ($4CH_3$, SiMe-*c* and SiMe-*d*), 4.4 ($2CH_3$, SiMe-*a*), 4.8 ($2CH_3$, SiMe-*b*), 23.5 ($6CH_3$, C*Me*$_3$), 56.6 (2C, *C*Me$_3$), 72.5 (2CH, C5 and C5'), 72.7 (2C, C2 and C2'), 75.5 (2CH, C4 and C4'), 80.6 (2CH, C3 and C3'), 93.2 (2C, C1 and C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ –48 (*c* 1.0, $CHCl_3$); HRMS (ESI), *m/z*: 695.1272 (2 ppm) found (calcd for $C_{26}H_{48}{}^{56}FeNaO_5S_2Si_4$, $[M + Na]^+$, requires 695.1262).

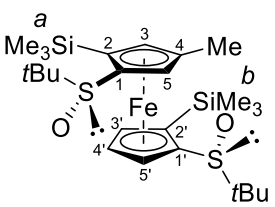


A third product was similarly obtained (Rf = 0.24) as an orange oil. It was identified as being (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-2,2'-bis(hydroxydimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**2g3**; 33% yield, 171 mg): IR (ATR) ν 700, 735, 773, 816, 909, 956, 1007, 1043, 1137, 1173, 1250, 1364, 1393, 1458, 1474, 1658, 2902, 2959, 3184 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 6H, SiMe-*a*), 0.42 (s, 6H, SiMe-*b*), 1.22 (s, 18H, *t*Bu), 4.35 (dd, 2H, *J* = 2.5 and 1.2 Hz, H3 and H3'), 4.92 (dd, 2H, *J* = 2.6 and 1.3 Hz, H5 and H5'), 5.04 (t, 2H, *J* = 2.5 Hz, H4 and H4'), 6.32 (br s, 2H, OH) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.5 ($2CH_3$, SiMe-*b*), 3.8 ($2CH_3$, SiMe-*a*), 23.5 ($6CH_3$, C*Me*$_3$), 56.8 (2C, *C*Me$_3$), 74.4 (2C, C2 and C2', C-Si(OH)Me$_2$), 77.0 (2CH, C4 and C4'), 77.2 (2CH, C5 and C5'), 78.4 (2CH, C3 and C3'), 91.1 (2C, C1 and C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ –378 (*c* 0.5, $CHCl_3$); HRMS (ESI), *m/z*: 565.1004 (2 ppm) found (calcd for $C_{22}H_{38}{}^{56}FeNaO_4S_2Si_2$, $[M + Na]^+$, requires 565.0992).



General procedure B: Deprotolithiation using *s*BuLi·TMEDA (1.5 equiv) followed by electrophilic trapping. To a solution of (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**2f**; 0.54 g, 1.0 mmol) and TMEDA (0.23 mL, 1.5 mmol) in THF (10 mL) at –80 °C was added dropwise a 1.3 M cyclohexane solution of *s*BuLi (1.2 mL, 1.5 mmol), and the reaction mixture was stirred at this temperature for 1 h before addition of the electrophile (1.5 mmol unless otherwise specified; either pure for liquids or in solution for solids, as indicated below). The mixture was stirred at –80 °C for 0.5 h before being warmed to rt; it was next treated as specified in the product description. Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product, which was purified by chromatography over silica gel (eluent given in the product description).

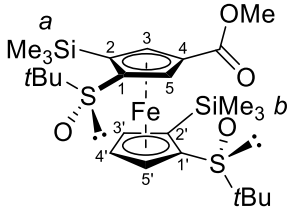
(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-4-methyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**6a**) was prepared by adapting the general procedure B to 0.83 mmol (0.45 g) of ***R*P,*R*P*-**2f** and using MeI (80 µL, 1.25 mmol) as the electrophile before treatment with water (5 mL). It was isolated (eluent: EtOAc-petroleum ether 50:50; Rf = 0.61) in 90% yield (0.41 g) as an orange oil: IR (ATR) ν 748, 829, 946, 974, 1042, 1094, 1135, 1173, 1240, 1362, 1389, 1458, 1474, 2900, 2956 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.36 (s, 9H, $SiMe_3$-*a*), 0.38 (s, 9H, $SiMe_3$-*b*), 1.13 (s, 9H, *t*Bu), 1.14 (s, 9H, *t*Bu), 2.10 (s, 3H, Me), 4.28 (d, 1H, *J* = 1.6 Hz, H3), 4.37 (dd, 1H, *J* = 2.5 and 1.3 Hz, H3'), 4.53 (d, 1H, *J* = 1.5 Hz, H5), 4.65 (dd, 1H, *J* = 2.5 and 1.3 Hz, H5'), 4.71 (t, 1H, *J* = 2.5 Hz, H4') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 2.5 ($3CH_3$, $SiMe_3$), 2.8 ($3CH_3$, $SiMe_3$), 13.7 (CH_3), 23.7 ($3CH_3$, C*Me*$_3$), 23.8 ($3CH_3$, C*Me*$_3$), 56.6 (C, *C*Me$_3$), 56.9 (C, *C*Me$_3$), 71.7 (CH, C5'), 71.7 (C, C2, *C*-$SiMe_3$), 72.5 (CH, C5), 74.3 (C, C2', *C*-$SiMe_3$), 74.4 (CH, C4'), 79.1 (CH, C3), 80.3 (CH, C3'), 91.0 (C,



C4, *C*-Me), 91.9 (C, C1, *C*-SO*t*Bu), 93.6 (C, C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ –36 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{25}H_{44}FeO_2S_2Si_2$ (552.76): C, 54.32; H, 8.02; S, 11.60. Found: C, 54.51; H, 8.13; S, 11.63%.

Attempts to deprotometallate ***R*P,*R*P-6a** by using *s*BuLi·TMEDA (1.5 equiv) in THF at –80 °C for 1 h before interception with different electrophiles ($ClPPh_2$, $ClSiMe_3$, $CH_2{=}NMe_2I$) all failed (starting material recovered).

(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-4-(methoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P-6b**) was prepared by adapting the general procedure B to 0.65 mmol (0.35 g) of ***R*P,*R*P-2f**, and using $ClCO_2Me$ (80 µg, 0.98 mmol) as the electrophile before treatment with water (5 mL). It was isolated (eluent: EtOAc-petroleum ether 40:60; Rf = 0.43) in 81% yield (0.31 g) as a reddish orange solid: mp 190-192 °C; IR (ATR) ν 750, 831, 945, 1044, 1167, 1241, 1298, 1362, 1457, 1719, 2957, 3017 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 (s, 9H, $SiMe_3$-*b*), 0.40 (s, 9H, $SiMe_3$-*a*), 1.11 (s, 9H, *t*Bu-*b*), 1.15 (s, 9H, *t*Bu-*a*), 3.84 (s, 3H, OMe), 4.31 (dd, 1H, *J* = 2.4 and 1.3 Hz, H3'), 4.70-4.73 (m, 2H, H4' and H5'), 5.01 (d, 1H, *J* = 1.3 Hz, H3), 5.22 (d, 1H, *J* = 1.3 Hz, H5) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 2.4 ($3CH_3$, $SiMe_3$), 2.6 ($3CH_3$, $SiMe_3$), 23.7 ($3CH_3$, C*Me*$_3$), 23.8 ($3CH_3$, C*Me*$_3$), 52.1 (CH_3, OMe), 57.3 (C, *C*Me$_3$), 57.4 (C, *C*Me$_3$), 71.5 (CH, C4' or C5'), 71.8 (CH, C5), 74.0 (CH, C4' or C5'), 75.5 (C, C2', *C*-$SiMe_3$), 76.6 (C, C2, *C*-$SiMe_3$), 76.9 (C, C4, *C*-CO_2Me), 79.5 (CH, C3), 80.6 (CH, C3'), 95.7 (C, C1', *C*-SO*t*Bu), 96.7 (C, C1, *C*-SO*t*Bu), 169.6 (C, C=O) ppm (one signal (C4) is missing); $[\alpha]_D^{20}$ –18 (*c* 0.6, $CHCl_3$). Anal. Calcd for $C_{26}H_{44}FeO_4S_2Si_2$ (596.77): C, 52.33; H, 7.43; S, 10.74. Found: C, 52.22; H, 7.39; S, 10.88%.



By increasing the amount of *s*BuLi and TMEDA to 3 equiv, inseparable mixtures of (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4,4'-di(methoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P-6'b**) and (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4-(methoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P-6b)** were obtained in ~3:7 ratios.

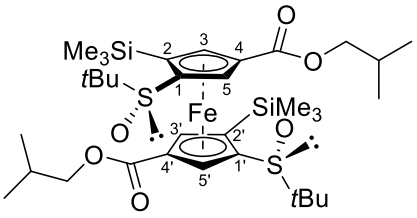
Note that general procedure B using $ClCO_2iBu$ as the electrophile led to an inseparable mixture of the 4-substituted derivative (59% estimated yield) and the 4,4'-disubstituted derivative (21% estimated yield). An attempt to treat again the inseparable mixture according to general procedure B failed in changing the ratio in favour of the 4,4'-disubstituted derivative.

Note that general procedure B with subsequent deuteration using concentrated DCl led to 70% deuteration at C4 and 20% deuteration at C5 (orange solid: mp 180-182 °C; $[\alpha]_D^{20}$ –214 (*c* 1.1, $CHCl_3$)).

Note that general procedure B performed on ***R*P,*R*P-6b** led to a mixture containing 50% of recovered ***R*P,*R*P-6b** and 17% of the corresponding 4,4'-disubstituted derivative ***R*P,*R*P-6'b**.

General procedure B': Deprotolithiation using *s*BuLi·TMEDA (3.0 equiv) followed by electrophilic trapping. To a solution of (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P-2f**; 0.54 g, 1.0 mmol) and TMEDA (0.46 mL, 3.0 mmol) in THF (10 mL) at –80 °C was added dropwise a 1.3 M cyclohexane solution of *s*BuLi (2.4 mL, 3.0 mmol), and the reaction mixture was stirred at this temperature for 1 h before addition of the electrophile (3.0 mmol unless otherwise specified; either pure for liquids or in solution for solids, as indicated below). The mixture was stirred at –80 °C for 0.5 h before being warmed to rt; it was next treated as specified in the product description. Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product, which was purified by chromatography over silica gel (eluent given in the product description).

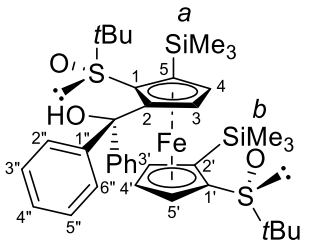
(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-4,4'-di(isobutoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**6'c**) was prepared by adapting the general procedure B' to 0.54 mmol (0.29 g) of ***R*P,*R*P*-**2f**, and using $ClCO_2$*i*Bu (0.27 mL, 1.6 mmol) as the electrophile in THF (2 mL) before treatment with 1.0 M HCl (5 mL). It was isolated (eluent: EtOAc-petroleum ether 60:40; Rf = 0.55) in 32% yield (0.13 g) as a reddish orange solid: mp 154-156 °C; IR (ATR) ν 751, 825, 986, 1008, 1052, 1166, 1242, 1242, 1294, 1362, 1457, 1713, 2958 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.44 (s, 18H, $SiMe_3$), 1.00 (d, 6H, *J* = 6.8 Hz, CH*Me*$_2$), 1.01 (d, 6H, *J* = 6.8 Hz, CH*Me*$_2$), 1.14 (s, 18H, *t*Bu), 2.07 (hept, 2H, *J* = 6.8 Hz, C*H*Me$_2$), 4.08 (d, 4H, *J* = 6.9 Hz, CH_2), 4.78 (d, 1H, *J* = 1.3 Hz, H3 and H3'), 5.27 (d, 2H, *J* = 1.3 Hz, H5 and H5') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 2.6 (6CH_3, $SiMe_3$), 19.4 (2CH_3, CH*Me*$_2$), 19.4 (2CH_3, CH*Me*$_2$), 23.7 (6CH_3, C*Me*$_3$), 28.0 (2CH, *C*HMe$_2$), 58.0 (2C, *C*Me$_3$), 71.3 (2CH_2), 71.9 (2CH, C5 and C5'), 77.9 (2C, C4 and C4'), 78.8 (2C, C2 and C2', *C*-$SiMe_3$), 81.7 (2CH, C3 and C3'), 98.0 (2C, C1 and C1', *C*-SO*t*Bu), 168.6 (2C, C=O) ppm; $[\alpha]_D^{20}$ –76 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{34}H_{58}FeO_6S_2Si_2$ (738.97): C, 55.26; H, 7.91; S, 8.68. Found: C, 55.11; H, 7.95; S, 8.70%.



Crystal data for *R*P,*R*P-6'c. $C_{34}H_{58}FeO_6S_2Si_2 \cdot CHCl_3$, *M* = 858.32, *T* = 150(2) K; monoclinic *P* 2_1 (I.T.#4), *a* = 10.7592(16), *b* = 20.291(3), *c* = 10.9077(15) Å, β = 111.313(4) °, *V* = 2218.4(6) $Å^3$, *Z* = 2, *d* = 1.285 $g.cm^{-3}$, μ = 0.707 mm^{-1}. A final refinement on F^2 with 8989 unique intensities and 458 parameters converged at ωR_F^2 = 0.1222 (R_F = 0.0554) for 7236 observed reflections with $I > 2\sigma(I)$. CCDC 2204521.

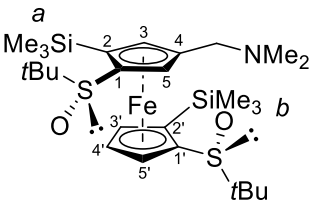
A mixture of ***R*P,*R*P-6'c** (estimated yield: 25%), (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4-(isobutoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P-6c**; estimated yield: 7%; Rf = 0.53) and starting material (***R*P,*R*P-2f**; 2%) was similarly obtained.

(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-2-((α,α-diphenyl)hydroxymethyl)-5,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P-6"d**) was prepared by adapting the general procedure B' to 0.33 mmol (0.18 g) of ***R*P,*R*P-2f**, and using Ph_2CO (0.18 g, 0.99 mmol) as the electrophile in THF (1 mL) before treatment with water (5 mL). It was isolated (eluent: EtOAc-petroleum ether 60:40; Rf = 0.79) in 25% yield (59 mg) as an orange oil: IR (ATR) ν 749, 828, 911, 1011, 1052, 1171, 1215, 1241, 1362, 1448, 2963 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.32 (s, 9H, $SiMe_3$-*b*), 0.45 (s, 9H, $SiMe_3$-*a*), 0.91 (s, 9H, *t*Bu-*b*), 0.98 (br s, 9H, *t*Bu-*a*), 4.70 (s, 1H, H3'), 4.72 (s, 1H, H4'), 4.89 (d, 1H, *J* = 2.7 Hz, H4), 4.92 (s, 1H, H5'), 5.10 (d, 1H, *J* = 2.8 Hz, H3), 7.07-7.11 (m, 3H, H2", H4" and H6"), 7.13-7.16 (m, 2H, H3" and H5"), 7.24 (t, 1H, *J* = 7.3 Hz, H4"'), 7.39 (t, 2H, *J* = 7.9 Hz, H3"' and H5"'), 7.60 (d, 2H, *J* = 7.3 Hz, H2"' and H6"') ppm (OH not seen); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 3.1 (3CH_3, $SiMe_3$-*b*), 4.0 (3CH_3, $SiMe_3$-*a*), 23.8 (3CH_3, C*Me*$_3$-*b*), 26.4 (3CH_3, C*Me*$_3$-*a*), 56.9 (C, *C*Me$_3$-*b*), 59.8 (C, *C*Me$_3$-*a*), 70.9 (CH, C5'), 73.9 (C, C2', *C*-$SiMe_3$), 75.4 (C, C5, *C*-$SiMe_3$), 75.4 (CH, C3), 77.4 (CH, C4'), 78.9 (C, C-OH), 79.9 (CH, C3'), 80.0 (CH, C4), 93.8 (C, C1, *C*-SO*t*Bu), 95.8 (C, C1', *C*-SO*t*Bu), 100.4 (C, C2), 126.6 (2CH, C2"' and C6"'), 126.9 (2CH, C2" and C6"), 127.2 (CH, C4" or C4"'), 127.3 (CH, C4" or C4"'), 128.0 (2CH, C3" and C5"), 128.9 (2CH, C3"' and C5"'), 146.8 (C, C1"'), 148.5 (C, C1") ppm; $[\alpha]_D^{20}$ –49 (*c* 0.6, $CHCl_3$). Anal. Calcd for $C_{37}H_{52}FeO_3S_2Si_2$ (720.95): C, 61.64; H, 7.27; S, 8.89. Found: C, 61.77; H, 7.33; S, 8.98%.



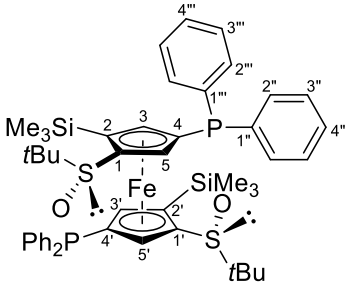
Chromatography (Rf = 0.40) also afforded a mixture of (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4-((α,α-diphenyl)hydroxymethyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P-6d**; estimated yield: 47%) and (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4,4'-bis((α,α-diphenyl)hydroxymethyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P-6'd**; estimated yield: 24%).

(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-4-(dimethylaminomethyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**6e**) was prepared by adapting the general procedure B' to 0.70 mmol (0.37 g) of ***R*P,*R*P*-**2f**, and using *N*,*N*-dimethylmethyleneiminium iodide (0.39 g, 2.1 mmol) as the electrophile in THF (2 mL) before treatment with water (5 mL). It was isolated (eluent: EtOAc-petroleum ether 70:30 with 10% of NEt_3; Rf = 0.68) in 64% yield (0.27 g) as a reddish orange solid: mp 68-70 °C; IR (ATR) ν 727, 749, 825, 902, 926, 1002, 1052, 1107, 1172, 1214, 1241, 1209, 1364, 1456, 3964, 3077 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 ($3CH_3$, $SiMe_3$-*a*), 0.38 ($3CH_3$, $SiMe_3$-*b*), 1.14 (s, 9H, *t*Bu-*b*), 1.14 (s, 9H, *t*Bu-*a*), 2.18 (s, 6H, NMe_2), 3.39 (d, 1H, *J* = 13.1 Hz, C*H*H), 3.45 (d, 1H, *J* = 13.1 Hz, CH*H*), 4.38 (dd, 1H, *J* = 2.5 and 1.4 Hz, H3'), 4.41 (d, 1H, *J* = 1.4 Hz, H3), 4.66 (d, 1H, *J* = 1.4 Hz, H5), 4.67 (dd, 1H, *J* = 2.6 and 1.4 Hz, H5'), 4.71 (t, 1H, *J* = 2.5 Hz, H4') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 2.5 ($3CH_3$, $SiMe_3$), 2.8 ($3CH_3$, $SiMe_3$), 23.8 ($3CH_3$, C*Me*$_3$), 23.8 ($3CH_3$, C*Me*$_3$), 45.1 ($2CH_3$, NMe_2), 56.8 (C, *C*Me_3), 57.1 (C, *C*Me_3), 57.8 (CH_2), 71.7 (CH, C5'), 72.9 (C, C2, *C*-$SiMe_3$), 73.1 (CH, C5), 74.2 (C, C2', *C*-$SiMe_3$), 74.3 (CH, C4'), 79.5 (CH, C3), 80.0 (CH, C3'), 90.3 (C, C4), 92.9 (C, C1, *C*-SO*t*Bu), 94.2 (C, C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ –56 (*c* 1.8, $CHCl_3$). Anal. Calcd for $C_{27}H_{49}FeNO_2S_2Si_2$ (595.83): C, 54.43; H, 8.29; N, 2.35; S, 10.76. Found: C, 54.60; H, 8.20; N, 2.37; S, 10.61%.

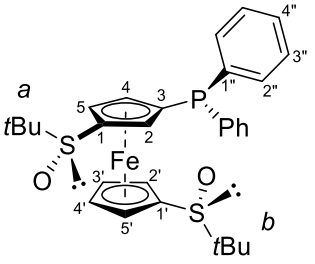


Starting material (***R*P,*R*P*-**2f**; similarly isolated in 18% yield) and (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4,4'-bis(dimethylaminomethyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**6'e**; estimated 15% yield) were also obtained after chromatography.

(*R*,*R*,*S*P,*S*P)-*S*,*S'*-Di-*tert*-butyl-4,4'-bis(diphenylphosphino)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*P,*S*P*-**6'f**) was prepared by adapting the general procedure B' to 3.1 mmol (1.7 g) of ***R*P,*R*P*-**2f**, and using $ClPPh_2$ (1.6 mL, 9.2 mmol) as the electrophile. After 1 h stirring at rt, MeOH (1 mL) was added before removal of the solvent under reduced pressure. It was isolated (eluent: EtOAc-petroleum ether 50:50; Rf = 0.41) in 38% yield (1.1 g) as an orange oil: IR (ATR) ν 739, 749, 832, 909, 964, 1050, 1071, 1137, 1169, 1202, 1240, 1434, 1476, 1585, 1730, 2228, 2951 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.27 (s, 18H, $SiMe_3$), 1.12 (s, 18H, *t*Bu), 4.36 (2H, H3 and H3'), 4.58 (s, 2H, H5 and H5'), 7.23-7.35 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 3.0 ($6CH_3$, $SiMe_3$), 23.8 ($6CH_3$, C*Me*$_3$), 57.6 (2C, *C*Me_3), 73.3 (d, 2CH, *J* = 12.1 Hz, C5 and C5'), 76.5 (2C, C2 and C2', *C*-$SiMe_3$), 84.1 (t, CH, *J* = 7.3 Hz, C3 or C3'), 84.2 (t, CH, *J* = 7.2 Hz, C3 or C3'), 84.9 (d, 2C, *J* = 15.5 Hz, C4 and C4'), 96.6 (2C, C1 and C1', *C*-SO*t*Bu), 128.6 (m, 8CH, C3", C5", C3"' and C5"'), 129.0 and 129.3 (4CH, C4"' and C4"'), 133.8 (d, 4CH, *J* = 21.8 Hz, C2"/C6", C2"'/C6"'), 134.2 (d, 4CH, *J* = 22.2 Hz, C2"/C6", C2"'/C6"'), 138.5 (d, 2C, *J* = 13.4 Hz, C1"/C1"'), 139.0 (d, 2C, *J* = 13.5 Hz, C1"/C1"') ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ –20.6 ppm; $[\alpha]_D^{20}$ –35 (*c* 0.5, $CHCl_3$). Anal. Calcd for $C_{48}H_{60}FeO_2P_2S_2Si_2$ (907.09): C, 63.56; H, 6.67; S, 7.07. Found: C, 63.62; H, 6.68; S, 6.96%.

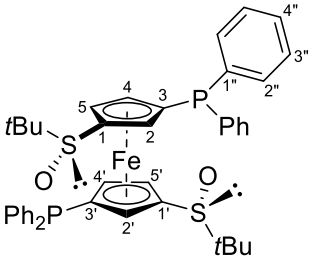


(*R*,*R*,*S*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-4-(diphenylphosphino)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*P,*R*P*-**6f**) was similarly obtained (Rf = 0.36) in 35% yield (0.795 g, 1.1 mmol) as a yellow solid, and directly converted to (*R*,*R*,*S*P)-*S*,*S'*-di-*tert*-butyl-3-(diphenylphosphino)ferrocene-1,1'-disulfoxide (***S*P*-**7'**) by treatment in THF (1.1 mL) with a 1.0 M solution of *n*Bu_4NF in THF (4.4 mL, 4.4 mmol). After 1 h stirring at rt, MeOH (1 mL) was added before removal of the solvent under reduced pressure. Purification by chromatography over silica gel (eluent: EtOAc) led to ***S*P*-**7'** (Rf = 0.25) in a quantitative yield (0.64 g) as a yellow solid: mp 124-126 °C; IR (ATR) ν 742, 836, 1034, 1172, 1361, 1041, 1432, 1474, 2974 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (s, 9H, *t*Bu-*b*), 1.16 (s, 9H, *t*Bu-*a*), 4.36 (td, 1H, *J* = 2.5 and 1.3 Hz, H3'), 4.39 (td, 1H, *J* = 2.6 and 1.4 Hz, H4'), 4.47 (dt, 1H, *J* = 2.8 and 1.4 Hz, H4), 4.55 (dt, 1H, *J* = 2.6 and 1.3 Hz, H5'), 4.65 (q, 1H, *J* = 1.5 Hz, H2), 4.88 (dt, 1H,

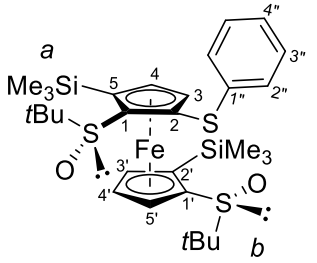


J = 2.7 and 1.3 Hz, H2'), 5.06 (dd, 1H, *J* = 2.6 and 1.3 Hz, H5), 7.28-7.33 (m, 5H, Ph), 7.34-7.36 (m, 3H, Ph), 7.38-7.42 (m, 2H, Ph) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 22.9 ($3CH_3$, C*Me*$_3$-*b*), 23.0 ($3CH_3$, C*Me*$_3$-*a*), 55.3 (C, *C*Me$_3$-*b*), 55.5 (C, *C*Me$_3$-*a*), 69.0 (d, CH, *J* = 1.8 Hz, C2'), 69.5 (d, CH, *J* = 2.5 Hz, C5), 72.3 (CH, C3'), 72.3 (CH, C4'), 73.3 (d, CH, *J* = 2.1 Hz, C5'), 75.6 (d, CH, *J* = 9.8 Hz, C4), 76.4 (d, CH, *J* = 18.7 Hz, C2), 81.9 (d, C, *J* = 14.6 Hz, C3, *C*-PPh_2), 90.0 (C, C1', *C*-SO*t*Bu), 91.4 (d, C, *J* = 3.5 Hz, C1, *C*-SO*t*Bu), 128.5 (d, 2CH, *J* = 6.7 Hz, C3"/C3"' and C5"/C5"'), 128.6 (d, 2CH, *J* = 7.3 Hz, C3"/C3"' and C5"/C5"'), 128.9 (CH, C4"/C4"'), 129.2 (CH, C4"/C4"'), 133.1 (d, 2CH, *J* = 19.4 Hz, C2"/C6"' and C2"'/C6"'), 134.0 (d, 2CH, *J* = 20.5 Hz, C2"/C6"' and C2"'/C6"'), 137.7 (d, C, *J* = 10.5 Hz, C1"/C1"'), 138.6 (d, C, *J* = 10.6 Hz, C1"/C1"') ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ –18.9 ppm; $[\alpha]_D^{20}$ –171 (*c* 0.5, $CHCl_3$). Anal. Calcd for $C_{30}H_{35}FeO_2PS_2$ (578.55): C, 62.28; H, 6.10; S, 11.08. Found: C, 62.31; H, 6.29; S, 11.16%.

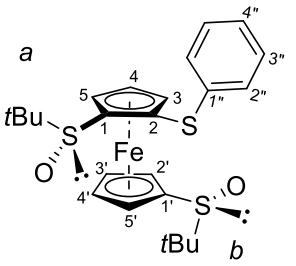
Similarly,(*R*,*R*,*S*$_P$,*S*$_P$)-*S*,*S'*-di-*tert*-butyl-3,3'-bis(diphenylphosphino)ferrocene-1,1'-disulfoxide (***S*$_P$,*S*$_P$-7**) was obtained by treating ***S*$_P$,*S*$_P$-6'f** (0.38 g, 0.41 mmol) in THF (0.3 mL) with a 1.0 M solution of *n*Bu_4NF in THF (1.7 mL, 1.7 mmol). After 1 h stirring at rt, MeOH (1 mL) was added before removal of the solvent under reduced pressure. Purification by chromatography over silica gel (eluent: EtOAc) led to ***S*$_P$,*S*$_P$-7** (Rf = 0.28) in 90% yield (0.28 g) as an orange oil: IR (ATR) ν 740, 789, 851, 908, 1027, 1057, 1094, 1176, 1216, 1362, 1390, 1434, 1476, 1585, 2971, 3052 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (s, 18H, *t*Bu), 4.21 (s, 2H, H4 and H4'), 4.62 (s, 2H, H2 and H2'), 5.00 (s, 2H, H5 and H5'), 7.17-7.21 (m, 4H, H2"' and H6"'), 7.28-7.29 (m, 10H, Ph), 7.32 (d, 2H, *J* = 7.1 Hz, Ph), 7.35 (t, 4H, *J* = 7.9 Hz, H2" and H6") ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.0 ($6CH_3$, C*Me*$_3$), 55.3 (2C, *C*Me$_3$), 70.7 (2CH, C5 and C5'), 75.5 (2CH, C4 and C4'), 78.6 (d, 2CH, *J* = 26.3 Hz, C2 and C2'), 82.7 (d, 2C, *J* = 16.0 Hz, C3 and C3'), 92.2-92.3 (m, 2C, C1 and C1', *C*-SO*t*Bu), 128.5, 128.5, 128.5, 128.6, 128.6 and 128.7 (10CH, Ph), 129.5 (2CH, C4"/C4"'), 132.7 (d, 4CH, *J* = 19.5 Hz, C2"'/C6"'), 134.5 (d, 4CH, *J* = 21.9 Hz, C2"/C6"), 137.2 (d, 2C, *J* = 10.6 Hz, C1"/C1"'), 139.1 (d, 2C, *J* = 10.9 Hz, C1"/C1"') ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ –19.2 ppm; $[\alpha]_D^{20}$ –71 (*c* 2.3, $CHCl_3$). Anal. Calcd for $C_{42}H_{44}FeO_2P_2S_2$ (762.72): C, 66.14; H, 5.81; S, 8.41. Found: C, 66.32; H, 5.99; S, 8.18%.



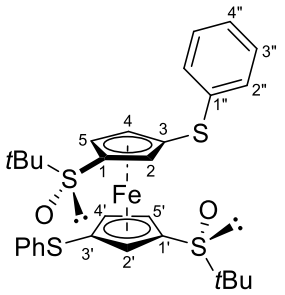
(*R*,*R*,*S*$_P$,*R*$_P$)-*S*,*S'*-Di-*tert*-butyl-2-(phenylthio)-5,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*$_P$,*R*$_P$-6"g)** was prepared by adapting the general procedure B' to 0.91 mmol (0.49 g) of ***R*$_P$,*R*$_P$-2f**, and using PhSSPh (0.59 g, 2.7 mmol) as the electrophile in THF (3 mL) before treatment with a 10% aqueous solution of NaOH (10 mL). It was isolated (eluent: EtOAc-petroleum ether 70:30; Rf = 0.90) in 16% yield (95 mg) as an orange oil: IR (ATR) ν 749, 828, 899, 914, 965, 1044, 1123, 1173, 1215, 1241, 1363, 1457, 1582, 2958 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 (s, 9H, $SiMe_3$-*b*), 0.42 (s, 9H, $SiMe_3$-*a*), 1.13 (s, 9H, *t*Bu-*a*), 1.17 (s, 9H, *t*Bu-*b*), 4.50 (dd, 1H, *J* = 2.5 and 1.3 Hz, H3'), 4.65 (d, 1H, *J* = 2.5 Hz, H4), 4.79 (dd, 1H, *J* = 2.6 and 1.3 Hz, H5'), 4.97 (t, 1H, *J* = 2.4 Hz, H4'), 5.06 (d, 1H, *J* = 2.5 Hz, H3), 7.08-7.11 (m, 1H, H4"), 7.11-7.13 (m, 2H, H2" and H6"), 7.19-7.22 (m, 2H, H3" and H5") ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 2.6 ($3CH_3$, $SiMe_3$), 2.8 ($3CH_3$, $SiMe_3$), 23.9 ($3CH_3$, C*Me*$_3$-*b*), 25.0 ($3CH_3$, C*Me*$_3$-*a*), 56.8 (C, *C*Me$_3$-*b*), 58.2 (C, *C*Me$_3$-*a*), 74.2 (CH, C5'), 74.6 (C, C5, *C*-$SiMe_3$), 74.8 (C, C2', *C*-$SiMe_3$), 77.4 (CH, C4'), 80.0 (CH, C3'), 80.6 (CH, C4), 83.3 (C, C2, *C*-SPh), 83.5 (CH, C3), 94.9 (C, C1, *C*-SO*t*Bu), 96.1 (C, C1', *C*-SO*t*Bu), 125.6 (CH, C4"), 126.6 (2CH, C2" and C6"), 129.0 (2CH, C3" and C5"), 138.5 (C, C1") ppm; $[\alpha]_D^{20}$ +11 (*c* 0.5, $CHCl_3$). Anal. Calcd for $C_{30}H_{46}FeO_2S_3Si_2$ (646.89): C, 55.70; H, 7.17; S, 14.87. Found: C, 55.78; H, 7.22; S, 15.08%.



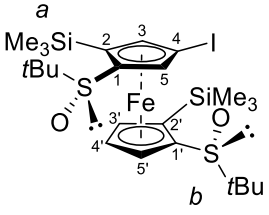
The structure of ***S*P,*R*P-6"g** was confirmed by desilylation of 0.15 mmol (treatment with a 1.0 M THF solution of *n*Bu$_4$NF (0.62 mL, 062 mmol) at rt for 0.5 h) towards (*R,R,S*P)-*S,S'*-di-*tert*-butyl-2-(phenylthio)ferrocene-1,1'-disulfoxide (***S*P,*R*P-6"g-desi**), isolated (eluent: EtOAc; Rf = 0.20) as a yellow oil in a quantitative yield (79 mg): IR (ATR) ν 738, 789, 831, 942, 1039, 1173, 1362, 1389, 1456, 1473, 1582, 296, 3074 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 9H, *t*Bu-*a*), 1.13 (s, 9H, *t*Bu-*b*), 4.58 (dt, 1H, *J* = 2.7 and 1.3 Hz, H5'), 4.81 (td, 1H, *J* = 2.6 and 1.4 Hz, H4'), 4.83 (h, 1H, *J* = 1.3 Hz, H3'), 4.87 (dt, 1H, *J* = 2.7 and 1.3 Hz, H2'), 4.92 (t, 1H, *J* = 2.7 Hz, H4), 4.97 (dd, 1H, *J* = 2.8 and 1.4 Hz, H5), 5.04 (dd, 1H, *J* = 2.6 and 1.5 Hz, H3), 7.11 (tt, 1H, *J* = 6.5 and 1.4 Hz, H4"), 7.15 (dd, 2H, *J* = 8.5 and 1.4 Hz, H2" and H6"), 7.21 (t, 2H, *J* = 7.4 Hz, H3" and H5") ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.9 ($3CH_3$, C*Me*$_3$-*b*), 23.1 ($3CH_3$, C*Me*$_3$-*a*), 55.4 (C, *C*Me$_3$-*b*), 56.3 (C, *C*Me$_3$-*a*), 67.9 (CH, C2'), 69.1 (CH, C5), 73.5 (CH, C4), 73.5 (CH, C3'), 74.4 (CH, C5'), 75.4 (CH, C4'), 80.9 (CH, C3), 82.1 (C, C2, *C*-SPh), 90.1 (C, C1', *C*-SO*t*Bu), 92.2 (C, C1, *C*-SO*t*Bu), 126.0 (CH, C4"), 127.2 (2CH, C2" and C6"), 129.0 (2CH, C3" and C5"), 137.9 (C, C1") ppm; $[\alpha]_D^{20}$ –65 (*c* 0.6, $CHCl_3$). Anal. Calcd for $C_{24}H_{30}FeO_2S_3$ (502.53): C, 57.36; H, 6.02; S, 19.14. Found: C, 57.27; H, 6.12; S, 18.89%.



Another fraction, similarly obtained (Rf = 0.61), corresponds to an inseparable mixture of starting material (***R*P,*R*P-2f**) and (*R,R,S*P,*S*P)-*S,S'*-di-*tert*-butyl-4,4'-di(phenylthio)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*P,*S*P-6'g**). Indeed, by subsequent treatment with a 1.0 M THF solution of *n*Bu$_4$NF (2.5 mL, 2.5 mmol) at rt for 0.5 h, in addition to the starting bis-sulfoxide **1** isolated in 59% yield (0.16 g) by chromatography over silica gel (eluent: EtOAc-petroleum ether 70:30), (*R,R,S*P,*S*P)-*S,S'*-di-*tert*-butyl-3,3'-di(phenylthio)ferrocene-1,1'-disulfoxide (***S*P,*S*P-6'g-desi**) was obtained (Rf = 0.24) in overall 10% yield (43 mg) as a yellow oil: IR (ATR) ν 737, 847, 910, 1024, 1046, 1173, 1301, 1363, 1439, 1476, 1582, 1498, 2964 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 18H, *t*Bu), 4.79 (s, 2H, H2 and H2"), 4.88 (s, 2H, H4 and H4'), 5.03 (s, 2H, H5 and H5'), 7.12-7.15 (m, 6H, Ph, H2", H4", H6", H2"', H4"' and H6"'), 7.22 (t, 4H, *J* = 7.6 Hz, H3", H5", H3"' and H5"') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.9 ($6CH_3$, C*Me*$_3$), 55.7 (2C, *C*Me$_3$), 70.3 (2CH, C5 and C5'), 78.4 (2CH, C4 and C4'), 78.7 (2CH, C2 and C2'), 83.8 (2C, C3 and C3', *C*-SPh), 91.6 (2C, C1 and C1', *C*-SO*t*Bu), 126.2 (2CH, C4" and C4"'), 127.7 (4CH, C2", C6", C2"' and C6"'), 129.1 (4CH, C3", C5", C3"' and C5"'), 138.2 (2C, C1" and C1"') ppm; $[\alpha]_D^{20}$ +593 (*c* 0.5, $CHCl_3$). Anal. Calcd for $C_{30}H_{34}FeO_2S_4$ (610.68): C, 59.00; H, 5.61; S, 21.00. Found: C, 58.88; H, 5.52; S, 20.89%.



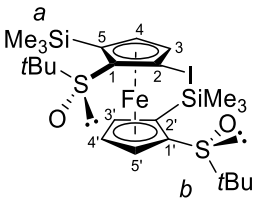
(*R,R,R*P,*R*P)-*S,S'*-Di-*tert*-butyl-4-iodo-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P-6h**) was prepared by adapting the general procedure B' to 0.58 mmol (0.31 g) of ***R*P,*R*P-2f**, and using I_2 (0.44 g, 1.7 mmol) as the electrophile in THF (2 mL) before treatment with saturated aqueous $Na_2S_2O_3$ (5 mL). It was isolated (eluent: EtOAc-petroleum ether 70:30; Rf = 0.60) in 77% yield (0.30 g) as an orange solid: mp 154 °C; IR (ATR) ν 725, 752, 850, 877, 945, 1041, 1174, 1242, 1361, 1458, 2235, 2960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 9H, SiMe$_3$-*a*), 0.46 (s, 9H, SiMe$_3$-*b*), 1.12 (s, 9H, *t*Bu-*b*), 1.13 (s, 9H, *t*Bu-*a*), 4.08 (dd, 1H, *J* = 2.5 and 1.3 Hz, H3'), 4.58 (d, 1H, *J* = 1.3 Hz, H3), 4.70 (dd, 1H, *J* = 2.5 and 1.3 Hz, H5'), 4.77 (t, 1H, *J* = 2.5 Hz, H4'), 4.87 (d, 1H, *J* = 1.3 Hz, H5) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 2.7 ($3CH_3$, SiMe$_3$-*a*), 3.2 ($3CH_3$, SiMe$_3$-*b*), 23.6 ($3CH_3$, C*Me*$_3$), 23.7 ($3CH_3$, C*Me*$_3$), 42.9 (C, C4, C-I), 57.3 (2C, *C*Me$_3$), 70.8 (CH, C5'), 73.9 (CH, C4'), 74.0 (C, C2, *C*-SiMe$_3$), 76.0 (C, C2', *C*-SiMe$_3$), 76.2 (CH, C5), 83.1 (CH, C3), 87.0 (CH, C3'), 94.6 (C, C1, *C*-SO*t*Bu), 95.5 (C, C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ –20 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{24}H_{41}FeIO_2S_2Si_2$ (664.63): C, 43.37; H, 6.22; S, 9.65. Found: C, 43.47; H, 6.35; S, 9.47%.



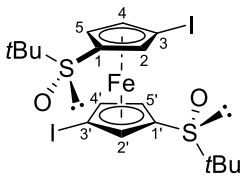
Crystal data for *R*P,*R*P-6h. $C_{24}H_{41}FeIO_2S_2Si_2$, *M* = 664.62, *T* = 296(2) K; monoclinic *P* 2$_1$ (I.T.#4), *a* = 11.8827(7), *b* = 11.1068(5), *c* = 13.1403(7) Å, β = 94.755(2) °, *V* = 1728.27(16) Å^3, *Z* = 2, *d* = 1.277

g.cm^{-3}, μ = 1.536 mm^{-1}. A final refinement on F^2 with 6772 unique intensities and 302 parameters converged at ωR_F^2 = 0.0949 (R_F = 0.0398) for 4723 observed reflections with $I > 2\sigma(I)$. CCDC 2204522.

(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-2-iodo-5,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (**RP,RP-6"h)** was similarly isolated (Rf = 0.86) as an orange oil in 15% yield (57 mg) as an orange oil: IR (ATR) ν 752, 827, 943, 1037, 1047, 1177, 1242, 1253, 1363, 1457, 1473, 2959 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9H, $SiMe_3$-*b*), 0.40 (s, 9H, $SiMe_3$-*a*), 1.16 (s, 9H, *t*Bu-*b*), 1.30 (s, 9H, *t*Bu-*a*), 4.42 (dd, 1H, *J* = 2.4 and 1.3 Hz, H3'), 4.52 (d, 1H, *J* = 2.5 Hz, H4), 4.60 (dd, 1H, *J* = 2.6 and 1.3 Hz, H5'), 4.95 (d, 1H, *J* = 2.5 Hz, H3), 5.04 (t, 1H, *J* = 2.5 Hz, H4'), ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 2.5 ($3CH_3$, $SiMe_3$-*b*), 2.7 ($3CH_3$, $SiMe_3$-*a*), 24.0 ($3CH_3$, C*Me*$_3$-*b*), 25.7 ($3CH_3$, C*Me*$_3$-*a*), 48.6 (C, C2, C-I), 56.2 (C, *C*Me_3-b), 59.1 (C, *C*Me_3-a), 72.2 (C, C5, *C*-$SiMe_3$), 74.8 (C, C2', *C*-$SiMe_3$), 76.9 (CH, C5'), 77.4 (CH, C4'), 79.7 (CH, C3'), 80.5 (CH, C4), 82.7 (CH, C3), 94.2 (C, C1, *C*-SO*t*Bu), 95.5 (C, C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ –292 (*c* 1.2, $CHCl_3$); HRMS (ESI), *m/z*: 687.0376 (0 ppm) found (calcd for $C_{24}H_{41}{}^{56}FeINaO_2S_2Si_2$, $[M + Na]^+$, requires 687.0373).



In a reaction performed on a larger amount (2 mmol), a mixture containing (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4,4'-diiodo-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (**RP,RP-6'h**) was isolated by chromatography; its treatment with *n*Bu_4NF (2-3 equiv) in THF at rt for 0.5 h allows, after purification by chromatography over silica gel (eluent: EtOAc), (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-3,3'-diiodoferrocene-1,1'-disulfoxide (**RP,RP-6'h-desi**) to be isolated (Rf = 0.15) as a yellow solid: mp 196-198 °C; IR (ATR) ν 750, 831, 874, 1017, 1029, 1042, 1173, 1214, 1362, 1387, 1455, 2976, 3106 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 18H, *t*Bu), 4.67 (t, 2H, *J* = 1.3 Hz, H2 and H2'), 4.74 (dd, 2H, *J* = 2.6 and 1.3 Hz, H5 and H5'), 4.87 (dd, 2H, *J* = 2.6 and 1.3 Hz, H4 and H4') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.9 ($6CH_3$, C*Me*$_3$), 40.5 (2C, C3 and C3', C-I), 55.7 (2C, *C*Me_3), 71.7 (2CH, C5 and C5'), 80.0 (2CH, C4 and C4'), 81.6 (2CH, C2 and C2'), 91.5 (2C, C1 and C1', *C*-SO*t*Bu) ppm; $[\alpha]_D^{20}$ –287 (*c* 1.0, $CHCl_3$).



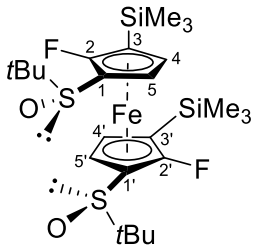
An attempt to deprotonate **RP,RP-2f** by using *t*BuLi (2.6 equiv) in THF at –80 °C for 1 h followed by interception with iodine (from –80 °C to rt) only led to ~5% of the 4-iodinated derivative **RP,RP-6h** while 95% of the starting material was recovered. Similarly, using *t*BuLi (3.0 equiv) in THF at –50 °C for 1 h followed by interception with iodine (from –50 °C to rt) furnished a mixture of polyiodinated derivatives (degradation also noticed) while using *n*BuLi (3.0 equiv) in THF at 0 °C for 1 h followed by interception with iodine (from 0 °C to rt) gave a mixture of polyiodinated derivatives, starting material and the 4-iodinated derivative **RP,RP-6h**.

The attempts to deprotonate **RP,RP-2f** in the presence of $ZnCl_2$·TMEDA (2 or 4 equiv) as an *in situ* trap by using LiTMP (6 or 12 equiv) in THF at –50 °C for 1 h before warming to –10 °C, and then iodine as the electrophile only afforded inseparable mixtures of the 4-iodo derivative and starting material (estimated yields of the 4-iodo derivative: 36% and ~30%; starting material or starting material/degradation observed, respectively). The 4-iodinated derivative was also formed when LiTMP (6 equiv) was transferred to a mixture of starting material and $ZnCl_2$·TMEDA (2 equiv) at rt.

(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-4,4'-diformyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide was prepared by adapting the general procedure B' to 0.53 mmol (0.29 g) of **RP,RP-2f**, and using DMF (0.13 mL, 1.6 mmol) as the electrophile before treatment with 1.0 M HCl (5 mL). However, TLC (eluent: EtOAc-petroleum ether 60:40) showed only one spot corresponding, on the basis of the NMR spectra, to a mixture of (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4,4'-diformyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (^{1}H NMR ($CDCl_3$) δ 0.43 (s, 18H, $SiMe_3$), 1.16 (s, 18H, *t*Bu), 4.96 (d, 2H, *J* = 1.3 Hz), 5.26 (d, 2H, *J* = 1.3 Hz), 10.02 (s, 2H, CHO) ppm) starting material (**RP,RP-2f**) and (*R*,*R*,*R*P,*R*P)-*S*,*S'*-di-*tert*-butyl-4-formyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide in a 64:27:9 NMR ratio.

General procedure C: Deprotolithiation using *s*BuLi (3.0 equiv) followed by electrophilic trapping. To a solution of the starting 2,2'-difluoroferrocene-1,1'-disulfoxide (1.0 mmol) in THF (10 mL) at –90 °C was added dropwise a 1.3 M cyclohexane solution of *s*BuLi (2.4 mL, 3.0 mmol), and the mixture was stirred at this temperature for 1 h. The electrophile (3.0 mmol unless otherwise specified; either pure for liquids or in solution for solids, as indicated below) was then added, and the mixture was stirred and treated under the conditions specified in the product description. Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product, which was purified by chromatography over silica gel (eluent given in the product description).

(*R*,*R*,*R*P,*R*P)-*S*,*S'*-Di-*tert*-butyl-2,2'-difluoro-3,3'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***R*P,*R*P*-**8a**) was prepared by adapting the general procedure C (but in the presence of TMEDA, as in the general procedure B') to 0.79 mmol (0.34 g) of ***R*P,*R*P*-**2d**, and using $ClSiMe_3$ (0.30 mL, 2.4 mmol) as the electrophile. The mixture was stirred at –90 °C for 0.5 h before being warmed to rt and treated with 1M HCl (5 mL). It was isolated (eluent: EtOAc-petroleum ether 90:10; Rf = 0.75) in 44% yield (0.20 g) as an orange solid: mp 178 °C; IR (ATR) ν 757, 837, 889, 1042, 1059, 1095, 1138, 1174, 1245, 1321, 1363, 1403, 1456, 1647, 2959, 3084 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.34 (s, 18H, $SiMe_3$), 1.20 (s, 18H, *t*Bu), 4.39 (d, 2H, *J* = 2.8 Hz, H4 and H4'), 4.48 (t, 2H, *J* = 2.2 Hz, H5 and H5') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ –0.4 ($6CH_3$, $SiMe_3$), 23.4 ($6CH_3$, C*Me*$_3$), 57.1 (2C, *C*Me_3), 66.5 (2CH, C4 and C4'), 68.8 (d, 2C, *J* = 20.3 Hz, C3 and C3', *C*-$SiMe_3$), 70.3 (d, 2CH, *J* = 6.9 Hz, C5 and C5'), 77.3 (d, 2C, *J* = 6.3 Hz, C1 and C1', *C*-SO*t*Bu), 137.7 (d, 2C, *J* = 279 Hz, C2 and C2') ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –172.5 ppm; $[\alpha]_D^{20}$ –297 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{24}H_{40}F_2FeO_2S_2Si_2$ (574.71): C, 50.16; H, 7.02; S, 11.16. Found: C, 50.27; H, 7.15; S, 11.07%.

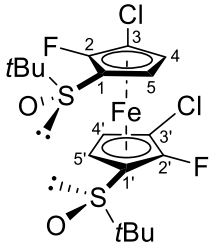


Crystal data for *R*P,*R*P-8a. $C_{24}H_{40}F_2FeO_2S_2Si_2$, *M* = 574.71, *T* = 150(2) K; tetragonal *P* 4_3 (I.T.#78), *a* = 12.9086(13), *c* = 17.950(2) Å, *V* = 2991.0(7) $Å^3$, *Z* = 4, *d* = 1.276 $g.cm^{-3}$, μ = 0.755 mm^{-1}. A final refinement on F^2 with 6869 unique intensities and 310 parameters converged at $\omega R(F)^2$ = 0.0612 (R_F = 0.0278) for 6469 observed reflections with $I > 2\sigma$. CCDC 2204523.

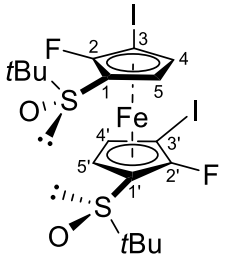
When *s*BuLi (2.5 equiv) was instead employed without TMEDA in THF at –80 °C for 1 h, the title product was isolated in 38% yield due to competitive degradation at this temperature.

By using LiTMP (2.5 equiv) in the presence of TMEDA (1.4 equiv) in hexane at rt for 20 min,[21] only recovered starting material and degradation products were noticed.

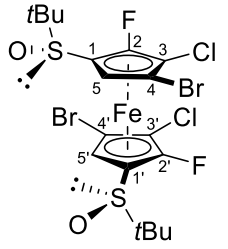
(*R*,*R*,*S*P,*S*P)-*S*,*S'*-Di-*tert*-butyl-3,3'-dichloro-2,2'-difluoroferrocene-1,1'-disulfoxide (***S*P,*S*P*-**8b**) was prepared by adapting the general procedure C, but at an initial 0.2 M concentration instead of 0.1 M, to 5.8 mmol (2.5 g) of ***R*P,*R*P*-**2d** and using C_2Cl_6 (4.1 g, 17.3 mmol) as the electrophile in THF (3 mL). The mixture was stirred at –90 °C during the addition of the electrophile and then warmed to –10 °C before addition of methanol (1 mL) and removal of the solvent under reduced pressure. The title product was isolated (eluent: petroleum ether-EtOAc-Et_3N 70:29:1; Rf = 0.43) in 61% yield (1.8 g) as a yellow solid: Rf (EtOAc-petroleum ether 90:10) = 0.41; mp 192-194 °C; IR (ATR) ν 674, 745, 824, 869, 1011, 1044, 1112, 1173, 1241, 1368, 1455, 1644, 2962, 3078 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 18H, *t*Bu), 4.68 (dd, 2H, *J* = 3.1 and 0.9 Hz, H4 and H4'), 4.85 (dd, 2H, *J* = 3.1 and 1.1 Hz, H5 and H5') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.4 ($6CH_3$, C*Me*$_3$), 57.4 (2C, *C*Me_3), 66.6 (d, 2CH, *J* = 1.7 Hz, C5 and C5'), 68.6 (2CH, C4 and C4'), 76.5 (d, 2C, *J* = 9.4 Hz, C1 and C1', *C*-SO*t*Bu), 84.9 (d, 2C, *J* = 13.8 Hz, C3 and C3'), 129.5 (d, 2C, *J* = 286 Hz, C2 and C2') ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –187.1 ppm; $[\alpha]_D^{20}$ –470 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{18}H_{22}Cl_2F_2FeO_2S_2$ (499.23): C, 43.31; H, 4.44; S, 12.84. Found: C, 43.34; H, 4.50; S, 12.87%; HRMS (ESI), *m/z*: 520.9649 (0 ppm) found (calcd for $C_{18}H_{22}{}^{56}Fe^{35}Cl_2F_2NaO_2S_2$, $[M + Na]^+$, requires 520.96479).



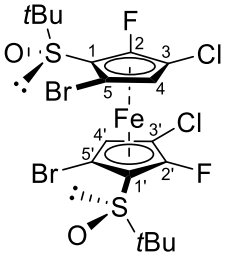
(*R*,*R*,*S*P,*S*P)-*S*,*S'*-Di-*tert*-butyl-2,2'-difluoro-3,3'-diiodoferrocene-1,1'-disulfoxide (***S*P,*S*P-8c**) was prepared by adapting the general procedure C, but using 2.6 equivalents of *s*BuLi, to 0.77 mmol (0.34 g) of ***R*P,*R*P-2d**. After addition of I_2 (0.51 g, 2.0 mmol) used as the electrophile in THF (2 mL), the mixture was stirred at –90 °C for 0.5 h before being warmed to rt and treated with saturated aqueous $Na_2S_2O_3$ (10 mL). The title product was isolated (eluent: EtOAc-petroleum ether 90:10; Rf = 0.37) in 48% yield (0.25 g) as a yellow solid: mp 246 °C; IR (ATR) ν 753, 827, 887, 1012, 1057, 1175, 1226, 1368, 1436, 1473, 2955, 3087 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 18H, *t*Bu), 4.62 (dd, 2H, *J* = 3.0 and 1.1 Hz, H4 and H4'), 4.89 (dd, 2H, *J* = 3.0 and 1.0 Hz, H5 and H5') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.4 ($6CH_3$, C*Me*$_3$), 36.9 (d, 2C, *J* = 19.4 Hz, C3 and C3', C-I), 57.5 (2C, *C*Me$_3$), 69.9 (2CH, C5 and C5'), 74.3 (2CH, C4 and C4'), 76.8 (d, 2C, *J* = 10.1 Hz, C1 and C1', *C*-SO*t*Bu), 132.9 (d, 2C, *J* = 283 Hz, C2 and C2') ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –180.0 ppm; $[\alpha]_D^{20}$ –160 (*c* 0.6, $CHCl_3$). Anal. Calcd for $C_{18}H_{22}F_2FeI_2O_2S_2$ (682.14): C, 31.69; H, 3.25; S, 9.40. Found: C, 31.65; H, 3.17; S, 9.29%.



(*R*,*R*,*S*P,*S*P)-4,4'-Dibromo-*S*,*S'*-di-*tert*-butyl-3,3'-dichloro-2,2'-difluoroferrocene-1,1'-disulfoxide (***S*P,*S*P-9a**) was prepared by adapting the general procedure C, but at an initial 0.2 M concentration instead of 0.1 M, to 0.9 mmol (0.45 g) of ***S*P,*S*P-8b** and using $CF_3CFBrCF_2Br$ (0.39 mL, 2.7 mmol) as the electrophile. The mixture was stirred at –90 °C during the addition of the electrophile and then warmed to –10 °C before addition of methanol (1 mL) and removal of the solvent under reduced pressure. The title product was isolated (eluent: EtOAc-petroleum ether 90:10; Rf = 0.58) in 35% yield (0.21 g) as an orange oil: IR (ATR) ν 746, 842, 880, 936, 1050, 1174, 1365, 1458, 1625, 2049, 2969, 3380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 18H, *t*Bu), 5.21 (s, 2H, H5 and H5') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.4 ($6CH_3$, C*Me*$_3$), 58.0 (2C, *C*Me$_3$), 69.2 (2CH, C5 and C5'), 75.8 (2C, C4 and C4', C-Br), 76.5 (d, 2C, *J* = 9.4 Hz, C1 and C1', *C*-SO*t*Bu), 86.5 (d, 2C, *J* = 12.8 Hz, C3 and C3', C-Cl), 126.2 (d, 2C, *J* = 292 Hz, C2 and C2', C-F) ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –186.9 ppm; $[\alpha]_D^{20}$ –302 (*c* 0.50, $CHCl_3$). Anal. Calcd for $C_{18}H_{20}Br_2Cl_2F_2FeO_2S_2$ (657.03): C, 32.91; H, 3.07; S, 9.76. Found: C, 32.90; H, 3.07; S, 9.80%; HRMS (ESI), *m/z*: 654.8039 (0 ppm) found (calcd for $C_{18}H_{21}{}^{79}Br_2{}^{35}Cl_2F_2{}^{56}FeO_2S_2$, $[M + H]^+$, requires 654.80387).

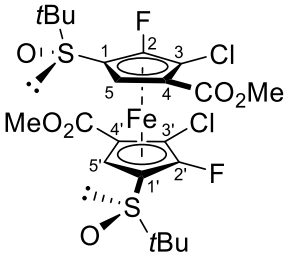


In this reaction, (*R*,*R*,*S*P,*S*P)-5,5'-dibromo-*S*,*S'*-di-*tert*-butyl-3,3'-dichloro-2,2'-difluoroferrocene-1,1'-disulfoxide (***S*P,*S*P-9'a**) was also isolated (Rf = 0.86) in 9% yield (51 mg) as a yellow oil: IR (ATR) ν 734, 750, 832, 909, 1055, 1118, 1171, 1213, 1267, 1313, 1362, 1455, 1731, 2967 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 18H, *t*Bu), 5.46 (s, 2H, H4 and H4') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.8 ($6CH_3$, C*Me*$_3$), 59.3 (2C, *C*Me$_3$), 71.5 (2CH, C4 and C4'), 75.8 (2C, C5 and C5', C-Br), 79.4 (d, 2C, *J* = 6.3 Hz, C1 and C1', *C*-SO*t*Bu), 84.9 (d, 2C, *J* = 14.5 Hz, C3 and C3', C-Cl), 125.8 (d, 2C, *J* = 292 Hz, C2 and C2', C-F) ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –187.9 ppm; $[\alpha]_D^{20}$ –176 (*c* 1.0, $CHCl_3$); HRMS (ESI), *m/z*: 654.8036 (0 ppm) found (calcd for $C_{18}H_{21}{}^{79}Br_2{}^{35}Cl_2F_2{}^{56}FeO_2S_2$, $[M + H]^+$, requires 654.80387).

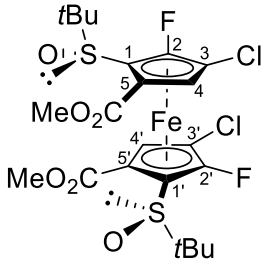


Adapting the general procedure C, but using 2.6 equivalents of *s*BuLi, to 0.74 mmol (0.37 g) of ***S*P,*S*P-8b** and using $CF_3CFBrCF_2Br$ (0.27 mL, 1.9 mmol) as the electrophile (stirring for 30 min at –90 °C and warming to –10 °C before addition of 5 mL of water) led to ***S*P,*S*P-9a** and ***S*P,*S*P-9'a** in 32% and 10% yield, respectively.

(*R*,*R*,*S*P,*S*P)-*S*,*S'*-Di-*tert*-butyl-3,3'-dichloro-2,2'-difluoro-4,4'-di(methoxycarbonyl)ferrocene-1,1'-disulfoxide (***S*P,*S*P-9b**) was prepared by adapting the general procedure C, but at an initial 0.2 M concentration instead of 0.1 M, to 1.0 mmol (0.50 g) of ***S*P,*S*P-8b** and using $ClCO_2Me$ (0.70 mL, 9.0 mmol) as the electrophile. The mixture was stirred at –90 °C during the addition of the electrophile and then warmed to rt before addition of methanol (1 mL) and removal of the solvent under reduced pressure. The title product was isolated (eluent: EtOAc; Rf = 0.10) in 16% yield (0.10 g) as a yellow solid: mp 196-198 °C; IR (ATR) ν 723, 770, 815, 848, 938, 1006, 1207, 1298, 1366, 1447, 1727, 2952 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 (s, 18H, *t*Bu), 3.90 (s, 6H, OMe), 5.44 (d, 2H, *J* = 1.0 Hz, H5 and H5') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.4 ($6CH_3$, C*Me*$_3$), 52.9 ($2CH_3$, OMe), 58.0 (2C, *C*Me$_3$), 68.2 (2CH, C5 and C5'), 69.9 (2C, C4 and C4', *C*-CO_2Me), 79.8 (d, 2C, *J* = 8.8 Hz, C1 and C1', *C*-SO*t*Bu), 85.2 (d, 2C, *J* = 13.4 Hz, C3 and C3', C-Cl), 129.5 (d, 2C, *J* = 290 Hz, C2 and C2', C-F), 164.6 (2C, C=O) ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –181.5 ppm; $[\alpha]_D^{20}$ –245 (*c* 1.0, $CHCl_3$); HRMS (ESI), *m/z*: 636.9762 (1 ppm) found (calcd for $C_{22}H_{26}{}^{35}Cl_2F_2{}^{56}FeNaO_6S_2$, $[M + Na]^+$, requires 636.97575).

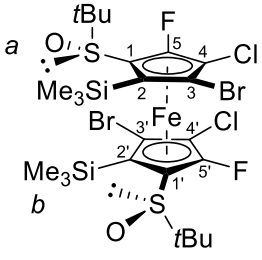


In this reaction, (*R*,*R*,*S*P,*S*P)-*S*,*S'*-di-*tert*-butyl-3,3'-dichloro-2,2'-difluoroferrocene-5,5'-di(methoxycarbonyl)-1,1'-disulfoxide (***S*P,*S*P-9'b**) was also similarly isolated (Rf = 0.34) in 15% yield (91 mg) as a yellow solid: mp 210-212 °C; IR (ATR) ν 728, 766, 789, 810, 855, 921, 995, 1052, 1118, 1172, 1210, 1307, 1339, 1369, 1469, 1731, 2927, 2962, 3125 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (s, 18H, *t*Bu), 3.85 (s, 6H, OMe), 5.90 (d, 2H, *J* = 1.4 Hz, H4 and H4') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.7 ($6CH_3$, C*Me*$_3$), 52.8 ($2CH_3$, OMe), 59.3 (2C, *C*Me$_3$), 69.9 (2C, C5 and C5', *C*-CO_2Me), 72.3 (2CH, C4 and C4'), 80.1 (d, 2C, *J* = 7.1 Hz, C1 and C1', *C*-SO*t*Bu), 86.1 (d, 2C, *J* = 15.5 Hz, C3 and C3', C-Cl), 128.9 (d, 2C, *J* = 293 Hz, C2 and C2', C-F) ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –182.4 ppm; $[\alpha]_D^{20}$ –636 (*c* 1.0, $CHCl_3$); HRMS (ESI), *m/z*: 636.9762 (1 ppm) found (calcd for $C_{22}H_{26}{}^{35}Cl_2F_2{}^{56}FeNaO_6S_2$, $[M + Na]^+$, requires 636.97575).



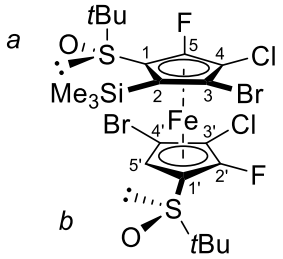
General procedure D: Deprotolithiation using LiTMP (3.0 equiv) at –90 °C followed by electrophilic trapping. To a solution of the *S*,*S'*-di-*tert*-butyl-3,3'-dichloro-2,2'-difluoroferrocene-1,1'-disulfoxide (0.50 mmol) in THF (5 mL) at –90 °C was added dropwise a –90 °C LiTMP solution [prepared by adding *n*BuLi (1.1 mL, 1.5 mmol) to 2,2,6,6-tetramethylpiperidine (H-TMP; 0.27 mL, 1.6 mmol) in THF (1 mL) at -10 °C and stirring at this temperature for 5 min before cooling to –90 °C], and the mixture was stirred at this temperature for 1 h. The electrophile (1.5 mmol unless otherwise stated; either pure for liquids or in solution for solids, as indicated below) was then added, and the mixture was stirred and treated under the conditions specified in the product description before addition of water (5 mL). Extraction with EtOAc (3 x 10 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product, which was purified by chromatography over silica gel (eluent given in the product description). Alternatively, the crude reaction mixture was filtered through alumina (eluent given in the product description), the combined filtrates were concentrated under reduced pressure to give the crude product which was purified by chromatography over silica gel (eluent given in the product description).

(*R*,*R*,*S*P,*S*P)-3,3'-Dibromo-*S*,*S'*-di-*tert*-butyl-4,4'-dichloro-5,5'-difluoro-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*P,*S*P-10a**) was prepared by adapting the general procedure D to 0.56 mmol (0.37 g) of ***S*P,*S*P-9a**. After addition of $ClSiMe_3$ (0.22 mL, 1.7 mmol) as the electrophile, the mixture was stirred at –90 °C for 0.5 h and then warmed to rt before treatment with water (5 mL). The title product was isolated (eluent: EtOAc-petroleum ether 60:40; Rf = 0.52) in 52% yield (0.23 g) as a brownish-yellow oil: IR (ATR) ν 706, 841, 956, 1050, 1168, 1216, 1252, 1350, 1364, 1390, 1443, 1456, 1737, 2990, 2960

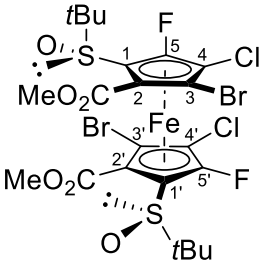


cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.45 (s, 18H, $SiMe_3$), 1.26 (s, 18H, *t*Bu) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 1.5 (d, $6CH_3$, J = 3.0 Hz, $SiMe_3$), 24.7 (d, $6CH_3$, J = 2.2 Hz, C*Me*$_3$), 59.0 (2C, *C*Me$_3$), 70.9 (d, 2C, J = 2.9 Hz, C2 and C2', *C*-$SiMe_3$), 84.8 (2C, C3 and C3', C-Br), 86.6 (d, 2C, J = 5.2 Hz, C1 and C1', *C*-SO*t*Bu), 87.2 (d, 2C, J = 13.0 Hz, C4 and C4', C-Cl), 129.0 (d, 2C, J = 292 Hz, C5 and C5', C-F) ppm; $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) δ –173.4 ppm; $[\alpha]_D^{20}$ –149 (*c* 1.3, $CHCl_3$). Anal. Calcd for $C_{24}H_{36}Br_2Cl_2F_2FeO_2S_2Si_2$ (801.39): C, 35.97; H, 4.53; S, 8.00. Found: C, 36.00; H, 4.57; S, 8.10%; HRMS (ESI), *m/z*: 798.8824 (1 ppm) found (calcd for $C_{24}H_{37}{}^{79}Br_2{}^{35}Cl_2F_2{}^{56}FeO_2S_2Si_2$, $[M + H]^+$, requires 798.88293).

(*R*,*R*,*S*$_P$,*S*$_P$)-3,4'-Dibromo-*S*,*S'*-di-*tert*-butyl-4,3'-dichloro-5,2'-difluoro-2-(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*$_P$,*S*$_P$*-10'''a**) was similarly isolated (Rf = 0.69) as a brownish-yellow solid in 13% yield (55 mg): mp 184-186 °C; IR (ATR) ν 714, 751, 842, 924, 959, 1039, 1066, 1169, 1248, 1335, 1362, 1454, 1518, 1584, 1670, 2962 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.51 (s, 9H, $SiMe_3$), 1.23 (s, 9H, *t*Bu-*b*), 1.32 (s, 9H, *t*Bu-*a*), 4.87 (s, 1H, H5') ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 1.6 ($3CH_3$, $SiMe_3$), 23.3 ($3CH_3$, C*Me*$_3$-*b*), 24.6 ($3CH_3$, C*Me*$_3$-*a*), 58.5 (C, *C*Me$_3$-*b*), 59.3 (C, *C*Me$_3$-*a*), 66.9 (CH, C5'), 73.7 (d, C, J = 2.5 Hz, C2, *C*-$SiMe_3$), 77.2 (C, C1', *C*-SO*t*Bu), 77.2 (C, C4', C-Br), 83.0 (d, C, J = 5.0 Hz, C1, *C*-SO*t*Bu), 83.1 (C, C3, C-Br), 84.9 (d, C, J = 13.5 Hz, C3', C-Cl), 88.8 (d, C, J = 14.0 Hz, C4, C-Cl), 127.8 (d, C, J = 293 Hz, C5 or C2', C-F), 127.9 (d, C, J = 293 Hz, C5 or C2', C-F) ppm; $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) δ –182.1, –179.2 ppm; $[\alpha]_D^{20}$ –187 (*c* 0.7, $CHCl_3$). Anal. Calcd for $C_{21}H_{28}Br_2Cl_2F_2FeO_2S_2Si$ (729.21): C, 34.59; H, 3.87; S, 8.79. Found: C, 34.68; H, 4.15; S, 8.67%; HRMS (ESI), *m/z*: 726.8431 (0 ppm) found (calcd for $C_{21}H_{29}{}^{79}Br_2{}^{35}Cl_2F_2{}^{56}FeO_2S_2Si$, $[M + H]^+$, requires 726.8434).



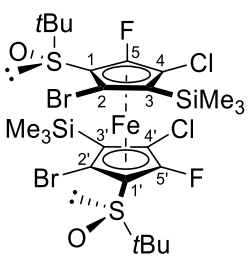
(*R*,*R*,*S*$_P$,*S*$_P$)-3,3'-Dibromo-*S*,*S'*-di-*tert*-butyl-4,4'-dichloro-5,5'-difluoro-2,2'-di(methoxycarbonyl)ferrocene-1,1'-disulfoxide (***S*$_P$,*S*$_P$*-10b**) was prepared by adapting the general procedure D to 0.86 mmol (0.57 g) of ***S*$_P$,*S*$_P$*-9a**, but at an initial 0.2 M concentration instead of 0.1 M. The mixture was transferred to a solution of $ClCO_2Me$ (0.94 mL, 12 mmol) as the electrophile in THF (1 mL) at –90 °C. After 0.5 h at this temperature, the mixture was warmed to –15 °C before filtration over alumina gel (eluent: CH_2Cl_2). The title product was isolated (eluent: EtOAc-petroleum ether 70:30; Rf = 0.63) in 10% yield (80 mg) as an orange oil: IR (ATR) ν 746, 940, 1019, 1060, 1169, 1217, 1325, 1401, 1365, 1440, 1730, 2961 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 18H, *t*Bu), 3.97 (s, 6H, OMe) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 24.0 ($6CH_3$, C*Me*$_3$), 53.2 ($2CH_3$, OMe), 60.1 (2C, *C*Me$_3$), 71.1 (2C, C2 and C2', *C*-CO_2Me), 76.1 (2C, C3 and C3', C-Br), 82.1 (d, 2C, J = 9.0 Hz, C1 and C1', *C*-SO*t*Bu), 84.4 (d, 2C, J = 13.9 Hz, C4 and C4', C-Cl), 125.9 (d, 2C, J = 295 Hz, C5 and C5', C-F), 163.9 (2C, C=O) ppm; $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) δ –181.0 ppm; $[\alpha]_D^{20}$ –265 (*c* 1.0, $CHCl_3$); HRMS (ESI), *m/z*: 792.7966 (0 ppm) found (calcd for $C_{22}H_{24}{}^{79}Br_2{}^{35}Cl_2F_2{}^{56}FeNaO_6S_2$, $[M + Na]^+$, requires 792.79678).



This compound showed a low stability.

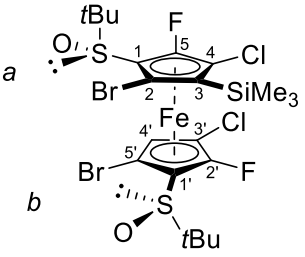
(*R*,*R*,*S*$_P$,*S*$_P$)-2,3'-dibromo-*S*,*S'*-di-*tert*-butyl-4,4'-dichloro-5,5'-difluoro-3,2'-di(methoxycarbonyl)ferrocene-1,1'-disulfoxide (***S*$_P$,*S*$_P$*-10'b**) was also detected, but could not be isolated as a pure product.

(*R*,*R*,*S*$_P$,*S*$_P$)-2,2'-Dibromo-*S*,*S'*-di-*tert*-butyl-4,4'-dichloro-5,5'-difluoro-3,3'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*$_P$,*S*$_P$*-10'a**) was formed by adapting the general procedure D to 0.56 mmol (0.37 g) of ***S*$_P$,*S*$_P$*-9'a**, but at an initial 0.2 M concentration instead of 0.1 M. After addition of $ClSiMe_3$ (0.22 mL, 1.7 mmol) as the electrophile, the mixture was stirred at –90 °C for 0.5 h and then warmed to rt before filtration over alumina gel (eluent: CH_2Cl_2). The title product was obtained (eluent: petroleum ether-EtOAc 70:30; Rf = 0.70) in an estimated 38% yield (59 mg), as a mixture (orange oil) with (*R*,*R*,*S*$_P$,*S*$_P$)-2,5'-

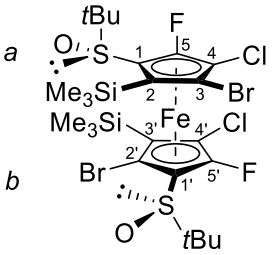


dibromo-*S,S'*-di-*tert*-butyl-4,3'-dichloro-5,2'-difluoro-3-(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*P,*S*P-10””a**), and identified by NMR: ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 18H, $SiMe_3$), 1.32 (s, 18H, *t*Bu) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 0.7 ($6CH_3$, $SiMe_3$), 24.1 ($6CH_3$, C*Me*$_3$), 61.3 (2C, *C*Me$_3$), 73.3 (d, 2C, *J* = 3.3 Hz, C3 and C3', *C*-$SiMe_3$), 79.5 (d, 2C, *J* = 3.0 Hz, C2 and C2', C-Br), 80.8 (d, 2C, *J* = 8.8 Hz, C1 and C1', *C*-SO*t*Bu), 88.1 (d, 2C, *J* = 11.5 Hz, C4 and C4', C-Cl), 128.7 (d, 2C, *J* = 292 Hz, C5 and C5', C-F) ppm; $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) δ –180.0 ppm; HRMS (ESI), *m/z*: 820.8642 (1 ppm) found (calcd for $C_{24}H_{36}{}^{79}Br_2{}^{35}Cl_2F_2{}^{56}FeNaO_2S_2Si_2$, $[M + Na]^+$, requires 820.86487).

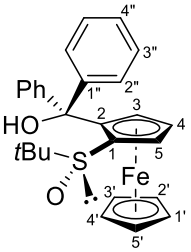
(*R,R,S*P,*S*P)-2,5'-Dibromo-*S,S'*-di-*tert*-butyl-4,3'-dichloro-5,2'-difluoro-3-(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*P,*S*P-10””a**; Rf = 0.70), obtained in an estimated 14% yield (22 mg) as a mixture (orange oil) with ***S*P,*S*P-10'a**), was similarly identified by NMR: ^{1}H NMR ($CDCl_3$) δ 0.53 (s, 9H, $SiMe_3$), 1.31 (s, 9H, *t*Bu), 1.35 (s, 9H, *t*Bu), 5.35 (d, 1H, *J* = 1.0 Hz, H4') ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 0.7 ($3CH_3$, $SiMe_3$), 24.0 ($6CH_3$, C*Me*$_3$), 59.6 (C, *C*Me$_3$), 60.2 (C, *C*Me$_3$), 69.7 (CH, C4'), 74.4 (d, C, *J* = 1.6 Hz, C5', C-Br), 74.9 (d, C, *J* = 4.0 Hz, C3, *C*-$SiMe_3$), 79.1 (d, C, *J* = 2.4 Hz, C2, C-Br), 80.0 (d, C, *J* = 9.4 Hz, C1, *C*-SO*t*Bu), 80.5 (d, C, *J* = 9.3 Hz, C1', *C*-SO*t*Bu), 84.8 (d, C, *J* = 14.7 Hz, C3', C-Cl), 88.9 (d, C, *J* = 11.5 Hz, C4, C-Cl), 126.4 (d, C, *J* = 291 Hz, C5 or C2', C-F), 127.1 (d, C, *J* = 294 Hz, C5 or C2', C-F) ppm; $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) δ –184.2, –184.1 ppm; HRMS (ESI), *m/z*: 748.8251 (0 ppm) found (calcd for $C_{21}H_{28}{}^{79}Br_2{}^{35}Cl_2F_2{}^{56}FeNaO_2S_2Si$, $[M + Na]^+$, requires 748.82535).



(*R,R,S*P,*S*P)-3,2'-Dibromo-*S,S'*-di-*tert*-butyl-4,4'-dichloro-5,5'-difluoro-2,3'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*P,*S*P-10”a**) was similarly isolated (Rf = 0.53) as an orange solid in 16% yield (73 mg): mp 158-160 °C; IR (ATR) ν 751, 842, 955, 1056, 1169, 1253, 1362, 1362, 1455, 2971 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.46 (s, 9H, $SiMe_3$-*a*), 0.47 (s, 9H, $SiMe_3$-*b*), 1.28 (s, 9H, *t*Bu-*b*), 1.29 (d, 9H, *J* = 1.1 Hz, *t*Bu-*a*) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 1.3 ($3CH_3$, $SiMe_3$), 1.4 (d, $3CH_3$, *J* = 3.0 Hz, $SiMe_3$), 24.2 ($3CH_3$, C*Me*$_3$-*b*), 24.6 ($3CH_3$, C*Me*$_3$-*a*), 59.4 (C, *C*Me$_3$-*a*), 60.7 (C, *C*Me$_3$-*b*), 71.8 (d, C, *J* = 3.4 Hz, C2, *C*-$SiMe_3$), 73.4 (d, C, *J* = 3.7 Hz, C3', *C*-$SiMe_3$), 78.1 (t, C, *J* = 2.8 Hz, C3 or C2', C-Br), 83.3 (C, C3 or C2', C-Br), 83.4 (d, C, *J* = 10.4 Hz, C1 or C1', *C*-SO*t*Bu), 86.1 (d, C, *J* = 4.9 Hz, C1 or C1', *C*-SO*t*Bu), 86.9 (d, C, *J* = 11.6 Hz, C4 or C4', C-Cl), 88.8 (d, C, *J* = 13.7 Hz, C4 or C4', C-Cl), 125.1 (d, C, *J* = 293 Hz, C5 or C5', C-F), 129.1 (d, C, *J* = 292 Hz, C5 or C5', C-F) ppm; $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) δ –181.1, –176.9 ppm; $[\alpha]_D^{20}$ –187 (*c* 1.0, $CHCl_3$); HRMS (ESI), *m/z*: 820.8656 (1 ppm) found (calcd for $C_{24}H_{36}{}^{79}Br_2{}^{35}Cl_2F_2{}^{56}FeNaO_2S_2Si_2$, $[M + H]^+$, requires 820.86487).



(*R,R*P)-*S*-*tert*-Butyl-2-[(α,α-diphenyl)hydroxymethyl]ferrocenesulfoxide (*R*P-2c) was prepared as follows. To (*R*)-*S*-*tert*-butylferrocenesulfoxide (1.0 g, 3.45 mmol) in THF (35 mL) at –80 °C was added dropwise a 1.6 M pentane solution of *t*BuLi (2.8 mL, 4.5 mmol). After 1 h at this temperature, a solution of Ph_2CO (0.82 g, 4.5 mmol) in THF (6 mL) was added and the reaction mixture was stirred at –80 °C for 0.5 h before warming to rt. The mixture was quenched by addition water (10 mL). Extraction with EtOAc (3 x 20 mL), drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: petroleum ether-EtOAc 70:30) led to the title product (Rf = 0.63) in 82% yield (1.3 g) as an orange solid: mp 224-226 °C; IR (ATR) ν 750, 824, 902, 1007, 1053, 1107, 1171, 1213, 1365, 1446, 1490, 3078 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 9H, *t*Bu), 3.99 (dd, 1H, *J* = 2.7 and 1.6 Hz, H3), 4.37 (s, 5H, H1', H2', H3', H4' and H5'), 4.40 (t, 1H, *J* = 2.6 Hz, H4), 4.48 (dd, 1H, *J* = 2.7 and 1.6 Hz, H5), 7.12 (tt, 1H, *J* = 7.2 and 1.4 Hz, H4”'), 7.19 (t, 2H, *J* = 7.5 Hz, H3” and H5”), 7.23 (tt, 1H, *J* = 7.3 and 1.4 Hz, H4”), 7.31-7.34 (m, 4H, H2”, H6”, H3”' and H5”'), 7.55 (s, 1H, OH), 7.65 (dd, 2H, *J* = 8.4 and 1.4 Hz, H2”' and H6”') ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 23.5 ($3CH_3$, C*Me*$_3$), 57.4 (C, *C*Me$_3$), 69.4 (CH, C4), 71.8 (5CH, C1', C2', C3', C4' and C5'), 71.9 (CH, C5), 74.6 (CH, C3), 77.4 (*C*-OH), 80.3 (C, C1, *C*-SO*t*Bu), 100.5 (C, C2), 126.8 (CH, C4” or C4”'), 126.8 (CH,



C4" or C4"'), 127.2 (2CH, Ph), 127.5 (2CH, Ph), 127.6 (2CH, Ph), 128.2 (2CH, C2"' and C6"'), 146.5 (C1"), 150.0 (C1"') ppm; $[\alpha]_D^{20}$ –183 (*c* 1.0, $CHCl_3$). The NMR data are similar to those reported for the (*S*,S_P)-enantiomer.[22]

Crystal data for R_P-2c. $C_{27}H_{28}FeO_2S$, M = 472.40, T = 150(2) K; tetragonal $P\,4_3$ (I.T.#78), a = 9.1285(3), c = 27.3023(11) Å, V = 2275.09(18) Å^3, Z = 4, d = 1.379 g.cm^{-3}, μ = 0.776 mm^{-1}. A final refinement on F^2 with 5190 unique intensities and 286 parameters converged at ωR_F^2 = 0.0660 (R_F = 0.0334) for 4871 observed reflections with $I > 2\sigma(I)$. CCDC 2204518.

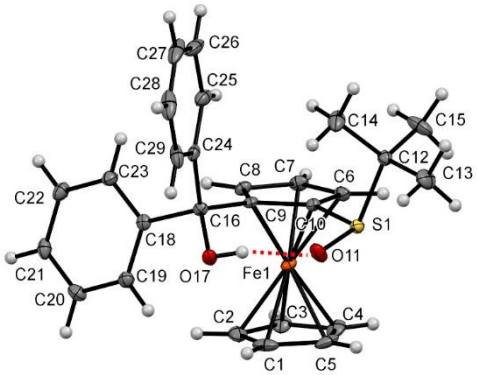


Figure 1. Molecular structure of compound R_P-**2c** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C10-S1 1.779(3), C9-C16 1.537(4), C5-Cg1···Cg2-C10 -18.63(0.27) (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C9-C10-S1-O11 7.1(3), C9-C10-S1-C12 -105.4(3), H17···O11 1.8221(0.0252), O17-H17···O11 169.48(3.99), H17···O11-S1 111.73(1.24).

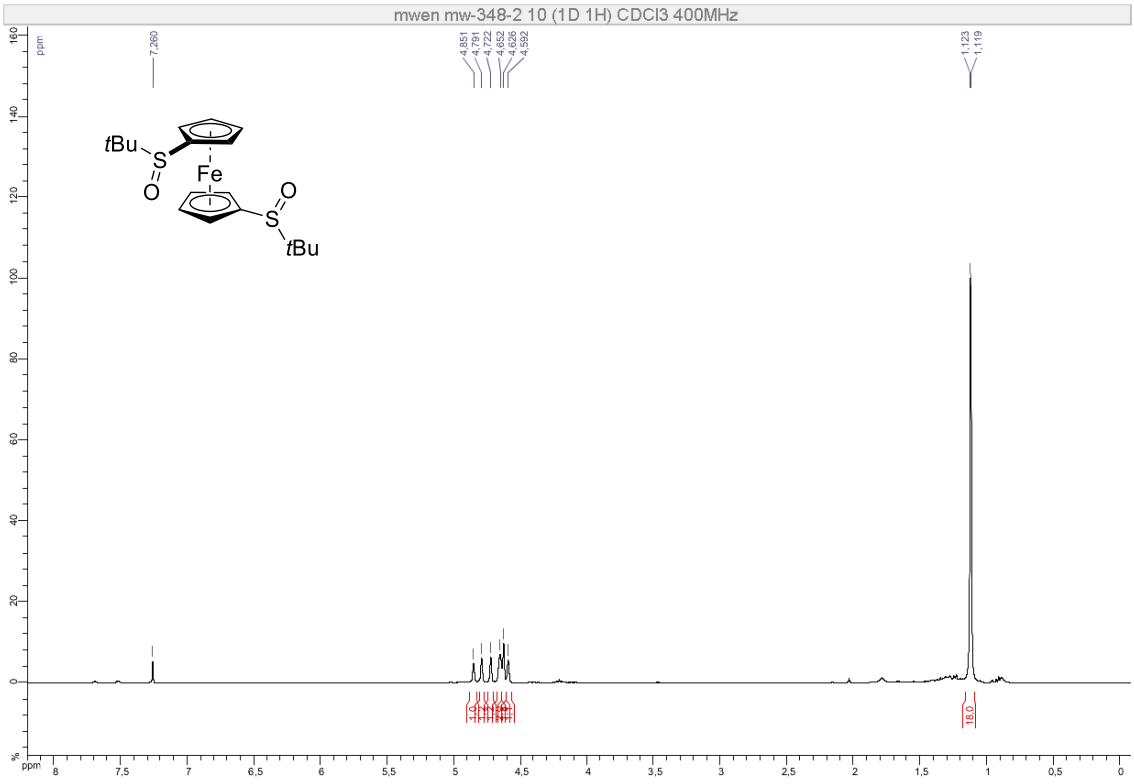
Typical procedure used for the asymmetric addition of diethylzinc to benzaldehyde.[23] To a solution of (*R*,*R*,R_P,R_P)-*S*,*S'*-di-*tert*-butyl-2,2'-di((α,α-diphenyl)hydroxymethyl)ferrocene-1,1'-disulfoxide (***R*$_P$,*R*$_P$-2c**; 76 mg, 0.10 mmol) in hexane under argon, was added dropwise at rt a 1.0 M solution of Et_2Zn in hexane (2.0 mL, 2.0 mmol). The resulting solution was stirred for 0.5 h, and cooled to 0 °C before addition of PhCHO (0.11 mL, 1.0 mmol). After stirring for 18 h at rt, a 5% aqueous HCl solution (5 mL) was added. Extraction with Et_2O, drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: petroleum ether-EtOAc 90:10) led to 1-phenyl-1-propanol (Rf = 0.26) in 92% yield (0.125 g) as a colourless oil. The product was identified by comparison of its ^{1}H NMR ($CDCl_3$) spectrum with that reported.[23] $[\alpha]_D^{20}$ +5 (*c* 1.0, $CHCl_3$) (in accordance with what has been published previously).[24] HPLC:[23] 24% ee in favour of the *R* enantiomer, Chiralcel OD column, eluent: *n*-hexane-isopropanol 99:1, 0.8 mL.min^{-1}, 25 °C, t_R = 30.7 min (major), 35.5 min (minor).

Typical procedure used for the asymmetric allylic alkylation.[25] To a degassed solution of (*E*)-1,3-diphenyl-2-propenyl acetate (0.17 g, 0.69 mmol), (*R*,*R*,S_P,S_P)-*S*,*S'*-di-*tert*-butyl-4,4'-bis(diphenylphosphino)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (***S*$_P$,*S*$_P$-6'f**; 63 mg, 69 μmol) and allylpalladium(II) chloride dimer (6.3 mg, 17 μmol) in CH_2Cl_2 (2.5 mL), was added at –15 °C another solution of *N*,*O*-bis-(trimethylsilyl)acetamide (BSA; 0.42 g, 2.1 mmol), dimethyl malonate (0.27 g, 2.1 mmol) and KOAc (2.7 mg, 28 μmol) in CH_2Cl_2 (2.5 mL). The mixture was stirred overnight at this temperature before addition of water (5 mL) and extraction with CH_2Cl_2 (3 x 10 mL). Drying over $MgSO_4$ and removal of the solvents under reduced pressure led to the crude product. Purification by chromatography over silica gel (eluent: petroleum ether-EtOAc 90:10) led to dimethyl (*E*)-2-(1,3-diphenylprop-2-enyl)malonate (Rf = 0.38) in 45% yield (0.10 g) as a white solid.
The product was identified by comparison of its ^{1}H NMR ($CDCl_3$) spectrum with that reported.[26] $[\alpha]_D^{20}$ –11 (*c* 1.0, $CHCl_3$) (in accordance with what has been published previously).[27, 28]
HPLC: 50% ee in favour of the *S* enantiomer, Chiralpack IA3 column, eluent: *n*-hexane-isopropanol 90:10, 1.0 mL.min^{-1}, 25 °C, t_R = 9.38 min (major), 7.58 min (minor).

B) NMR Spectra

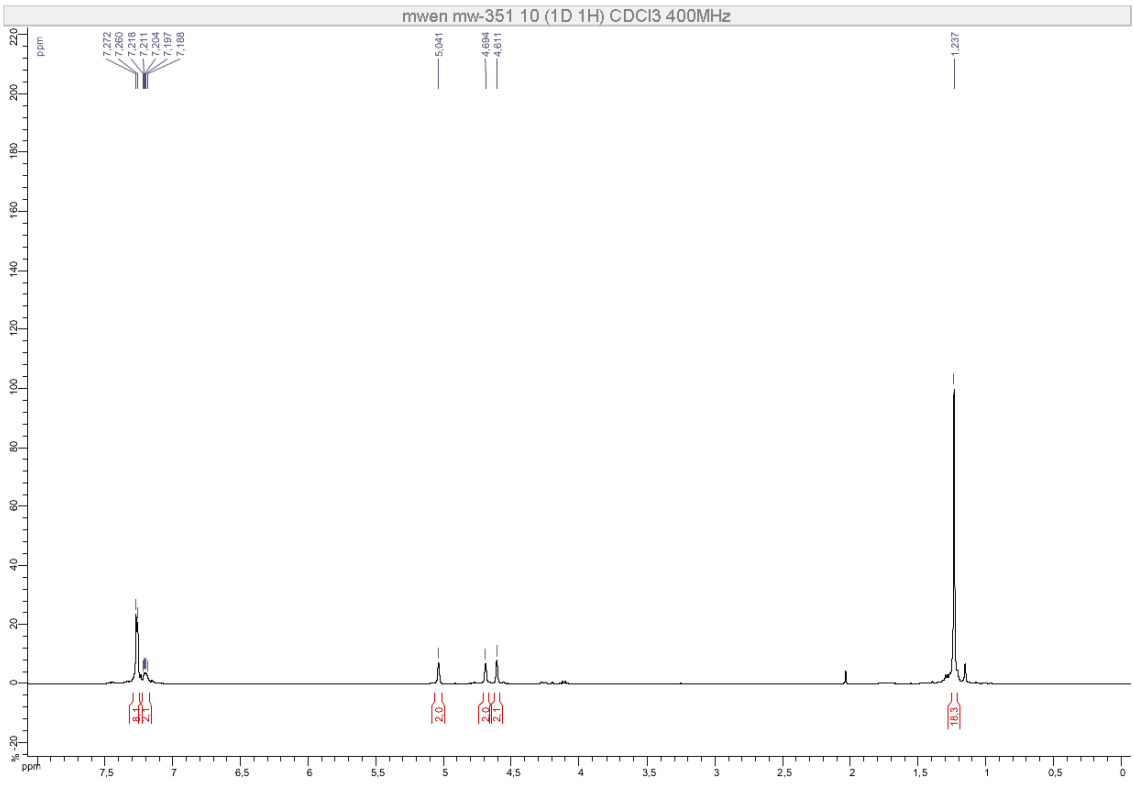
S,S'-Di-*tert*-butylferrocene-1,1'-disulfoxide (mixture of stereoisomers)

^{1}H NMR (400 MHz, $CDCl_3$)



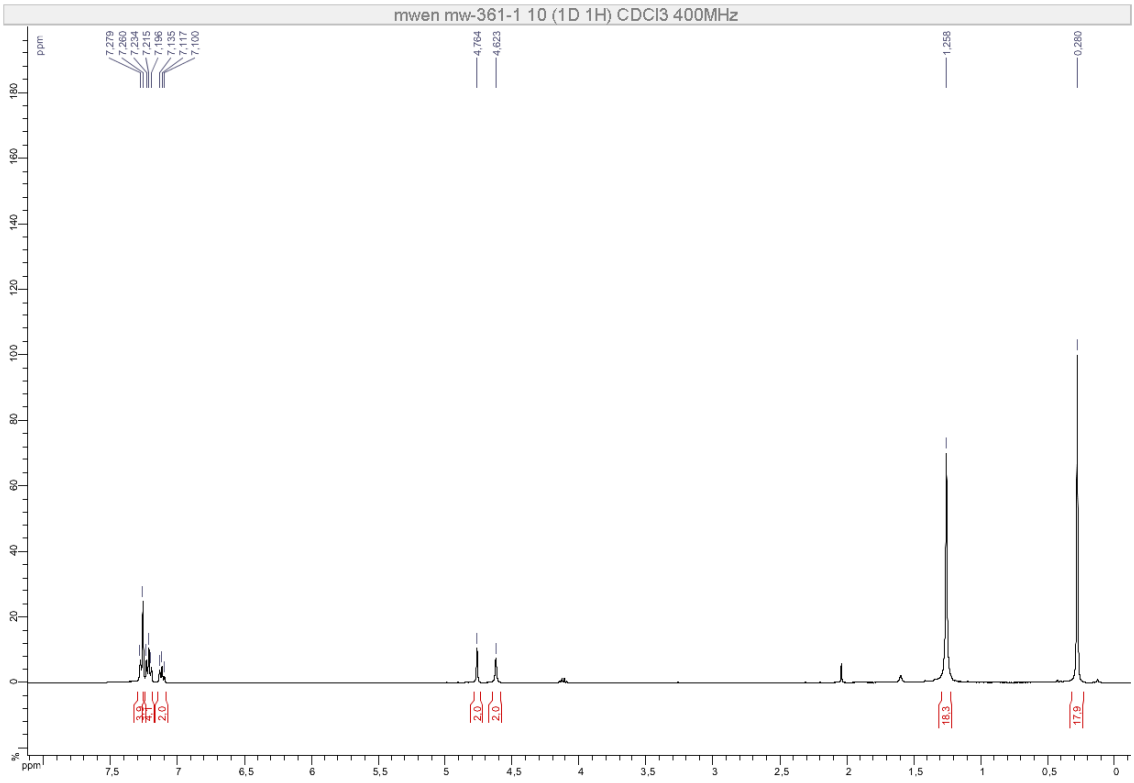
_S,S'_-Di-_tert_-butyl-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (2e; mixture of stereoisomers)

^{1}H NMR (400 MHz, $CDCl_3$)



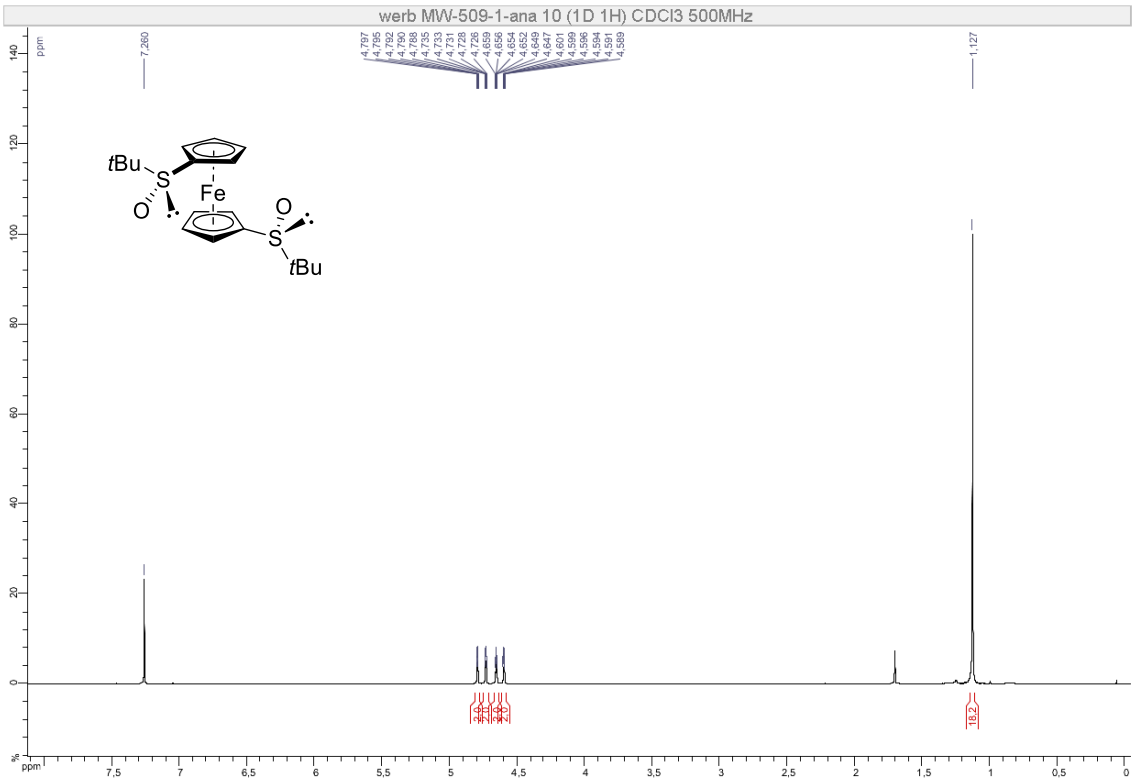
_S,S'_-Di-_tert_-butyl-2,2'-di(phenylthio)-4,4'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (5; mixture of stereoisomers)

^{1}H NMR (400 MHz, $CDCl_3$)

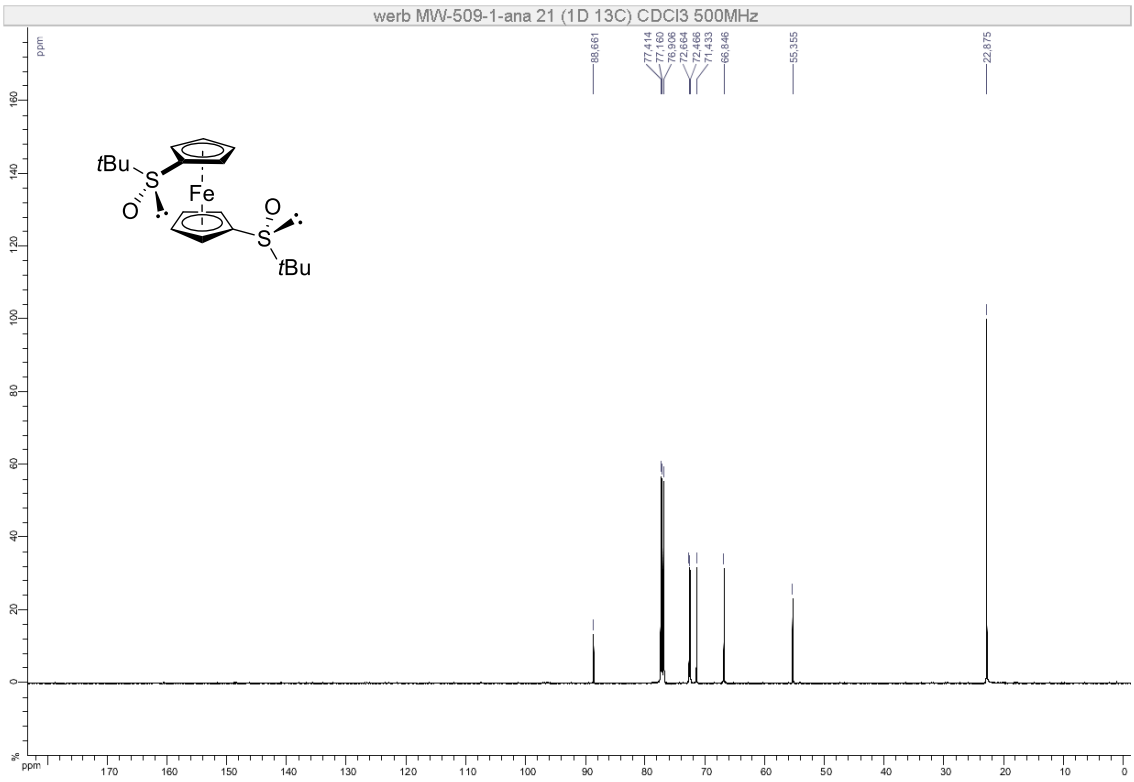


(*R*,*R*)-*S*,*S*'-Di-*tert*-butylferrocene-1,1'-disulfoxide (1)

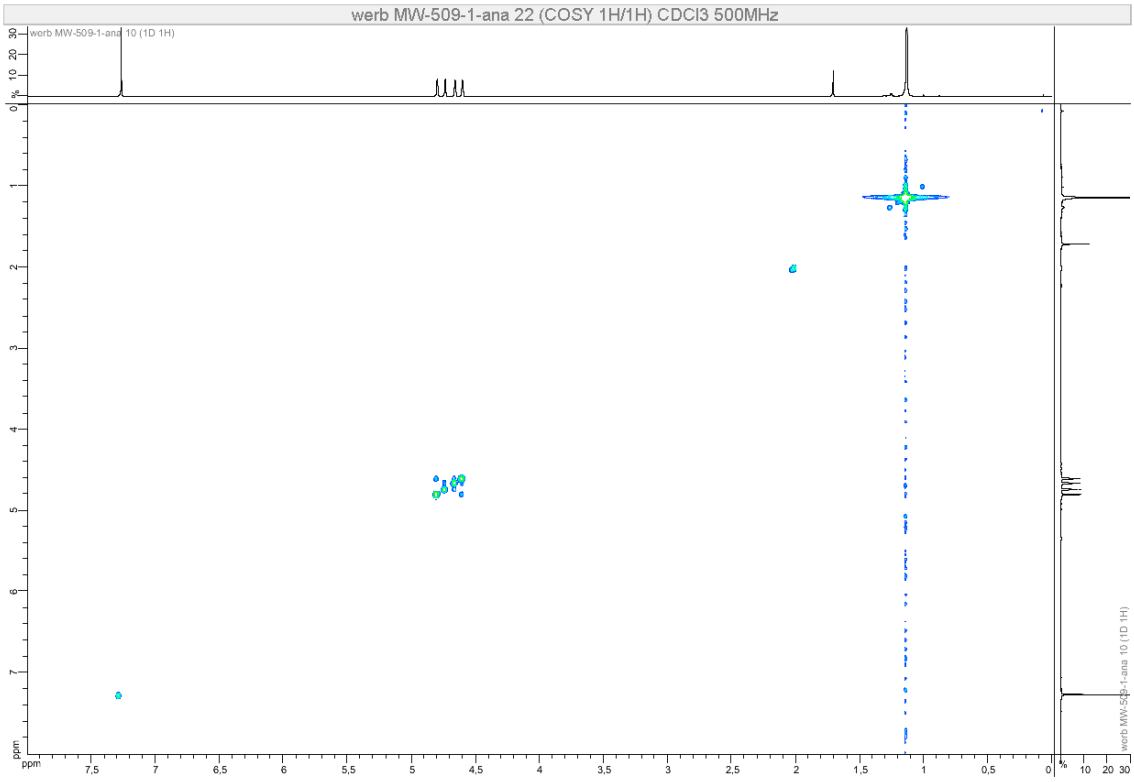
^{1}H NMR (500 MHz, $CDCl_3$)



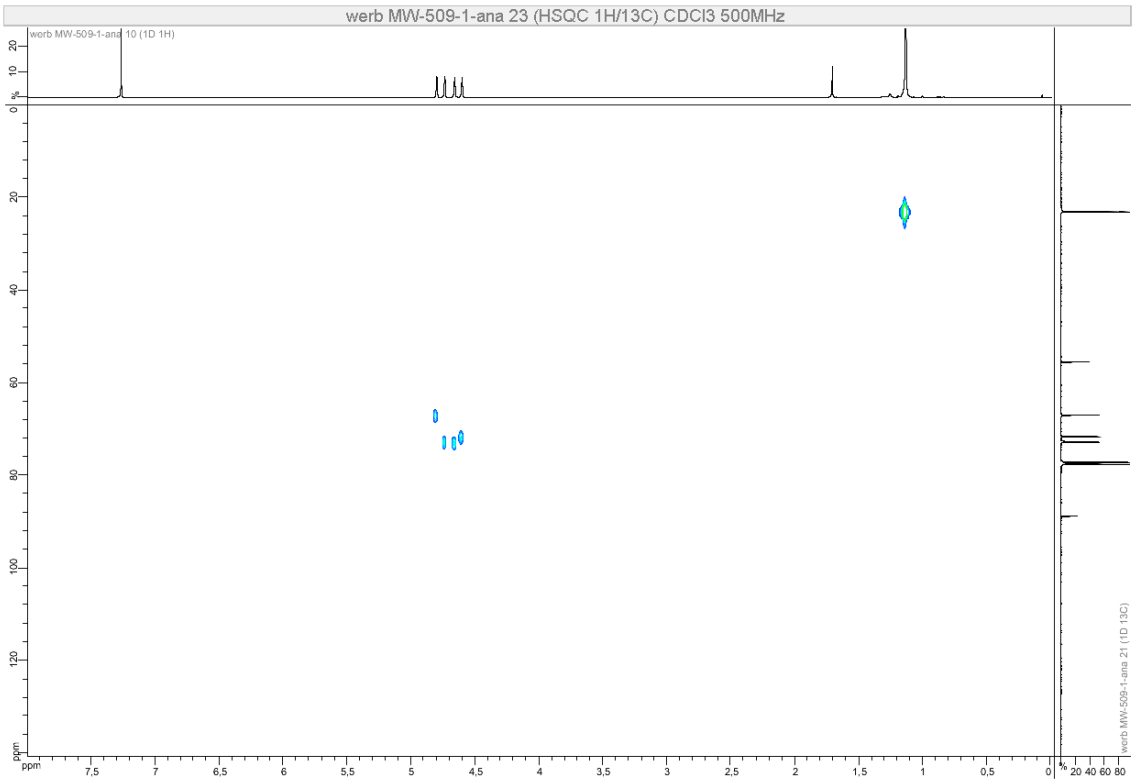
^{13}C NMR (126 MHz, $CDCl_3$)



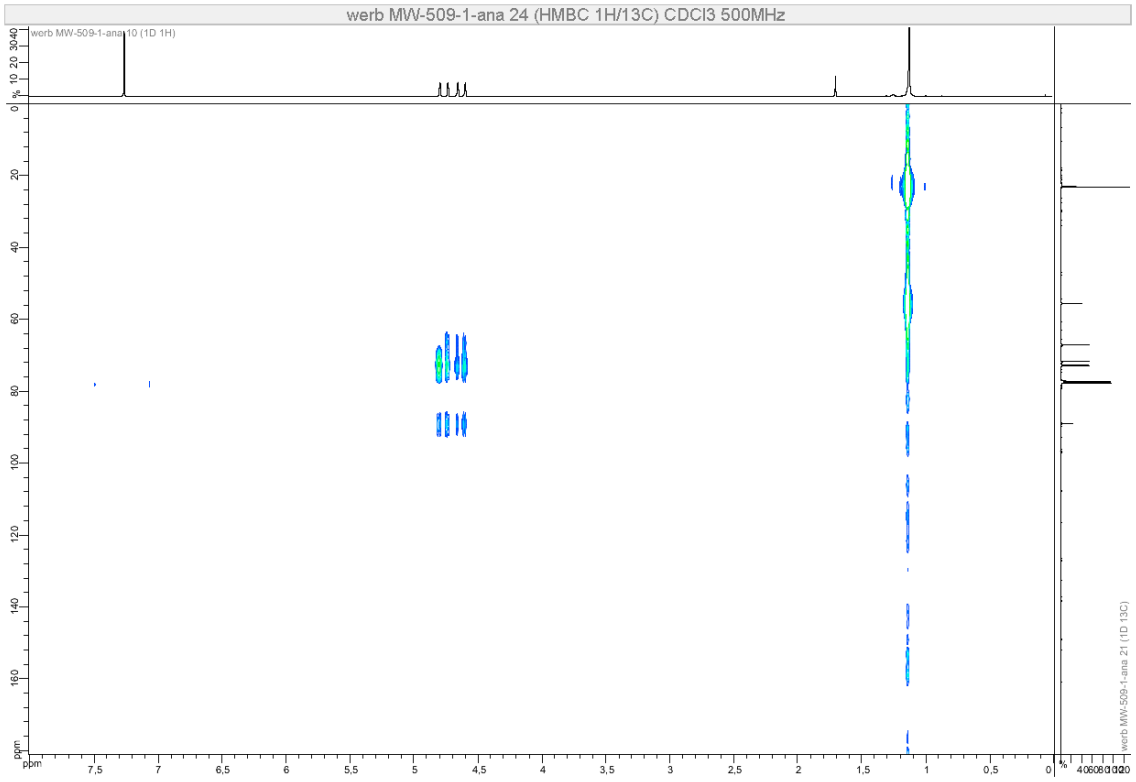
COSY (500 MHz, $CDCl_3$)



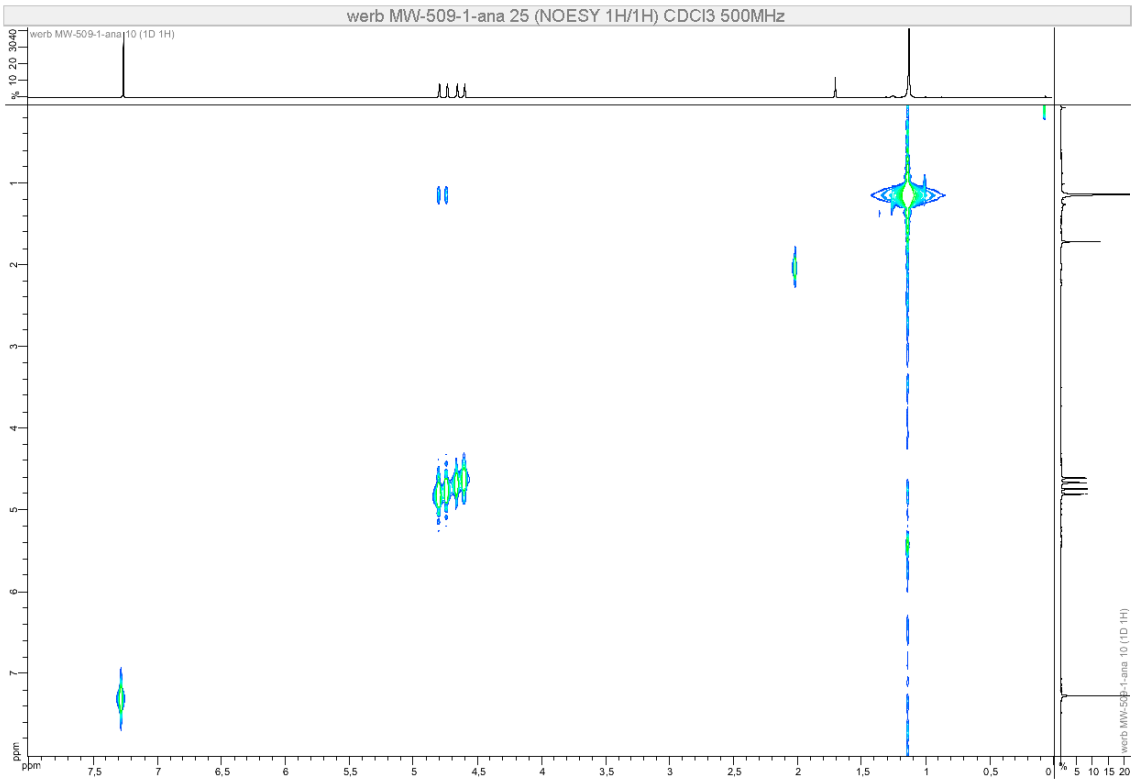
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

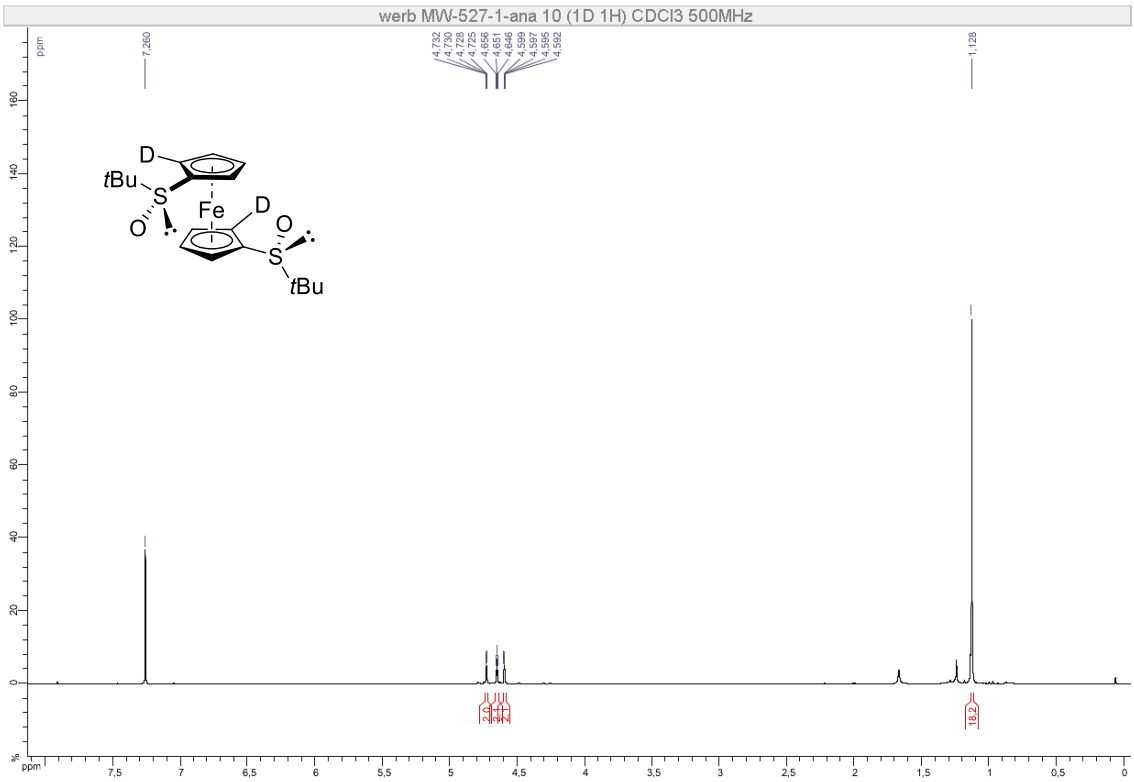


NOESY (500 MHz, $CDCl_3$)

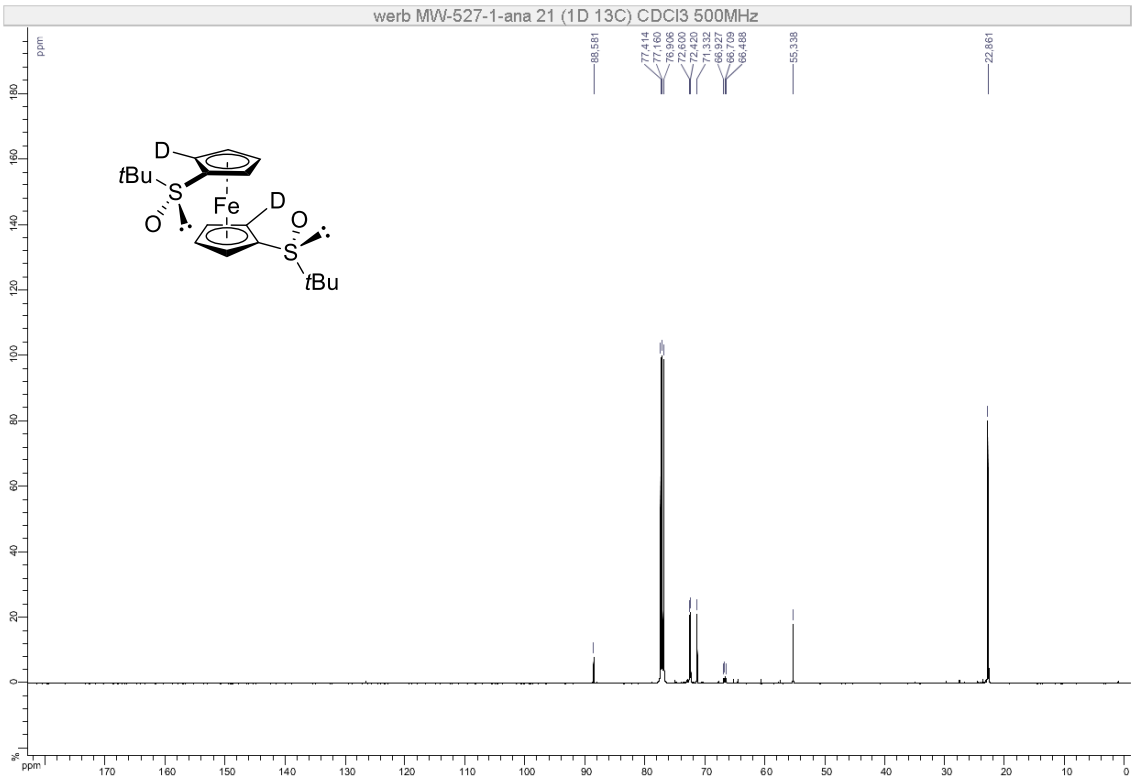


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-dideuterioferrocene-1,1'-disulfoxide (*R*P,*R*P-2a)

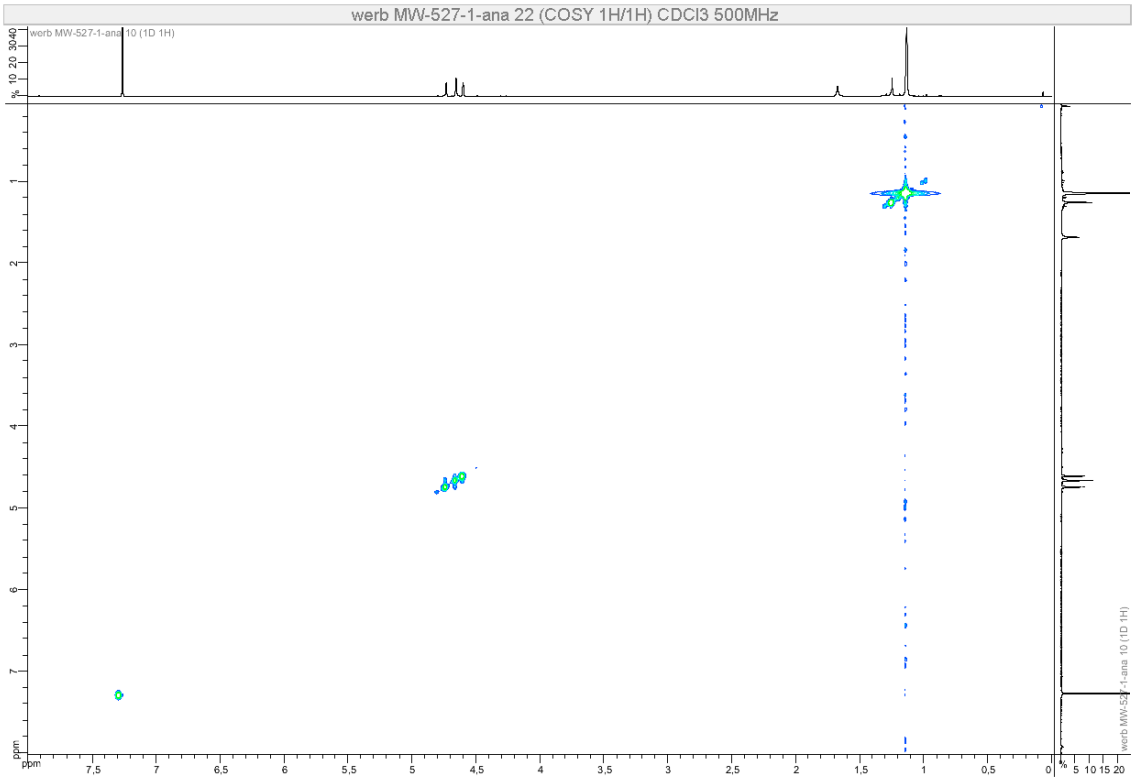
^{1}H NMR (500 MHz, $CDCl_3$)



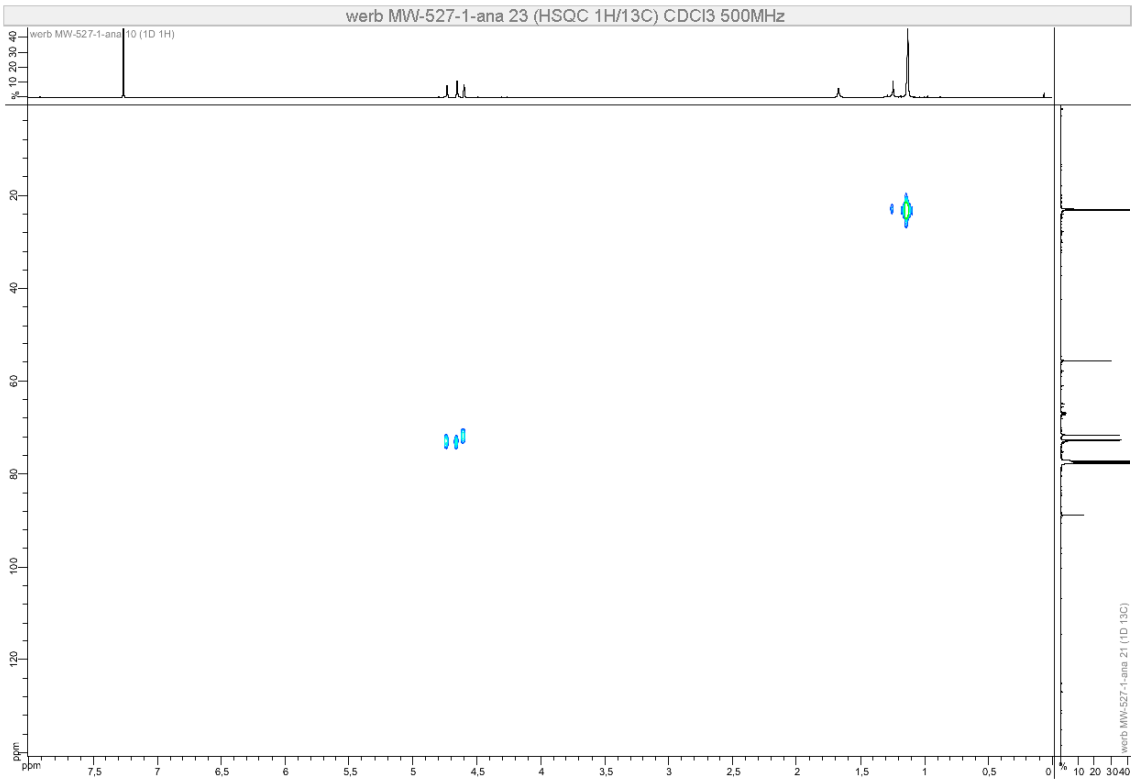
^{13}C NMR (126 MHz, $CDCl_3$)



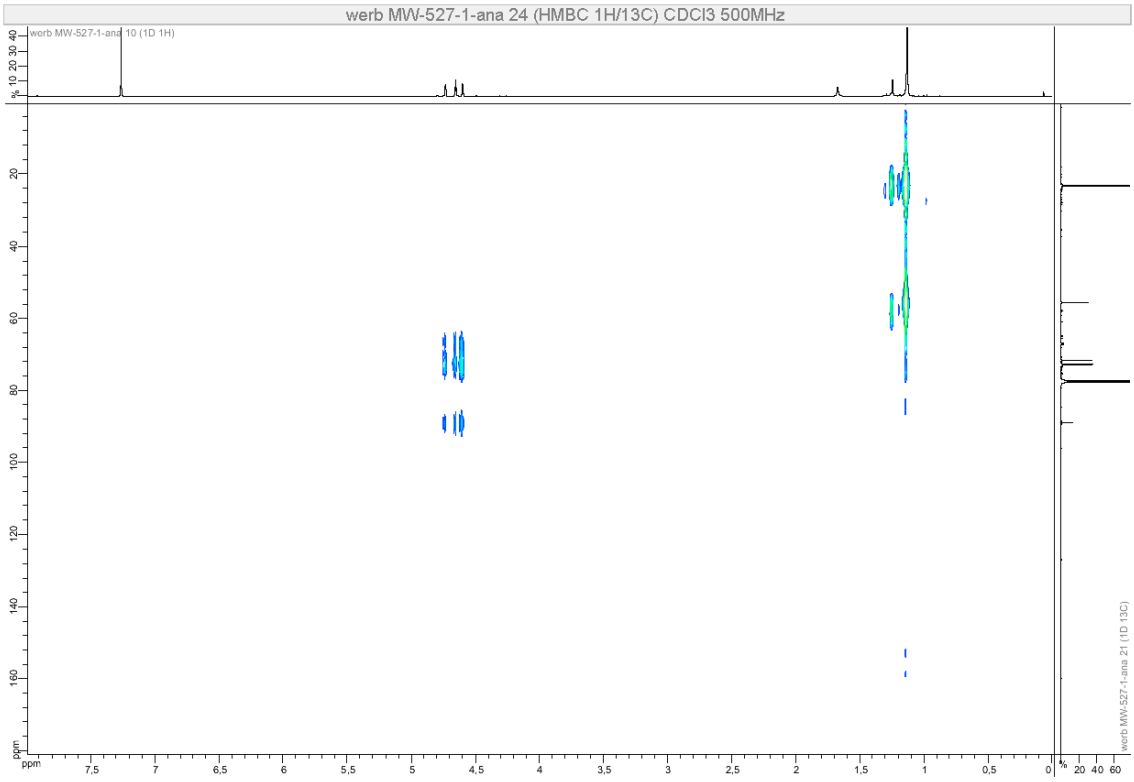
COSY (500 MHz, $CDCl_3$)



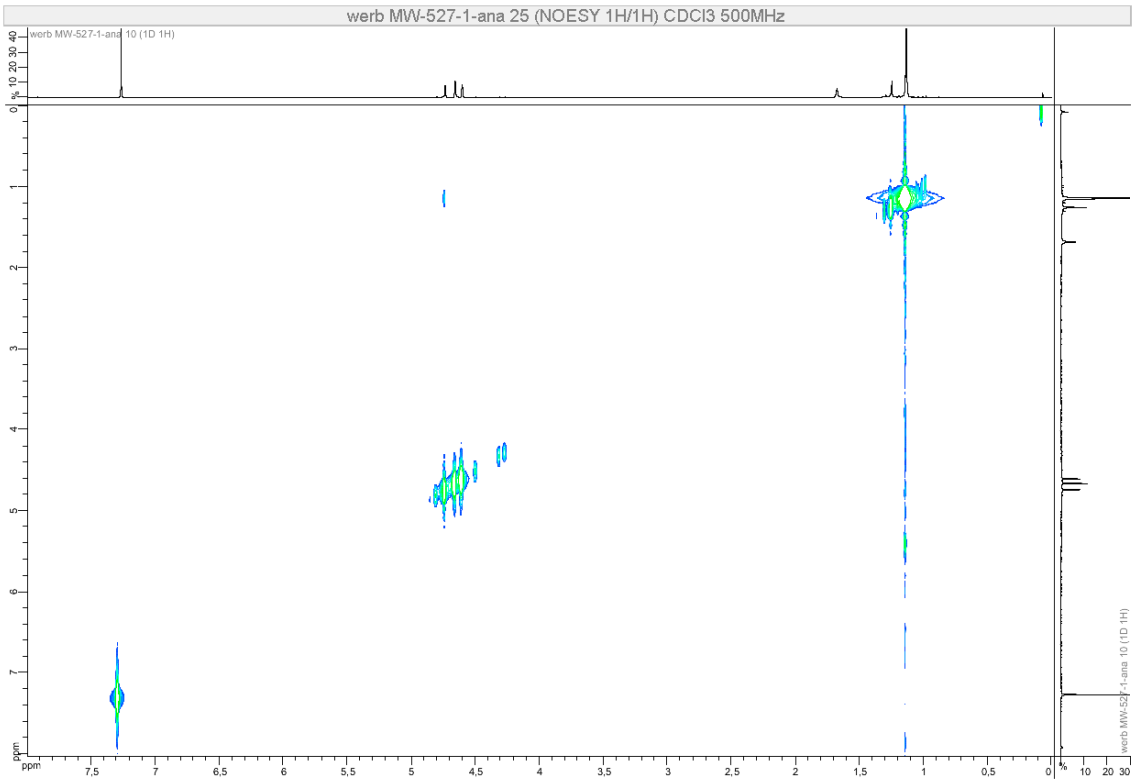
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

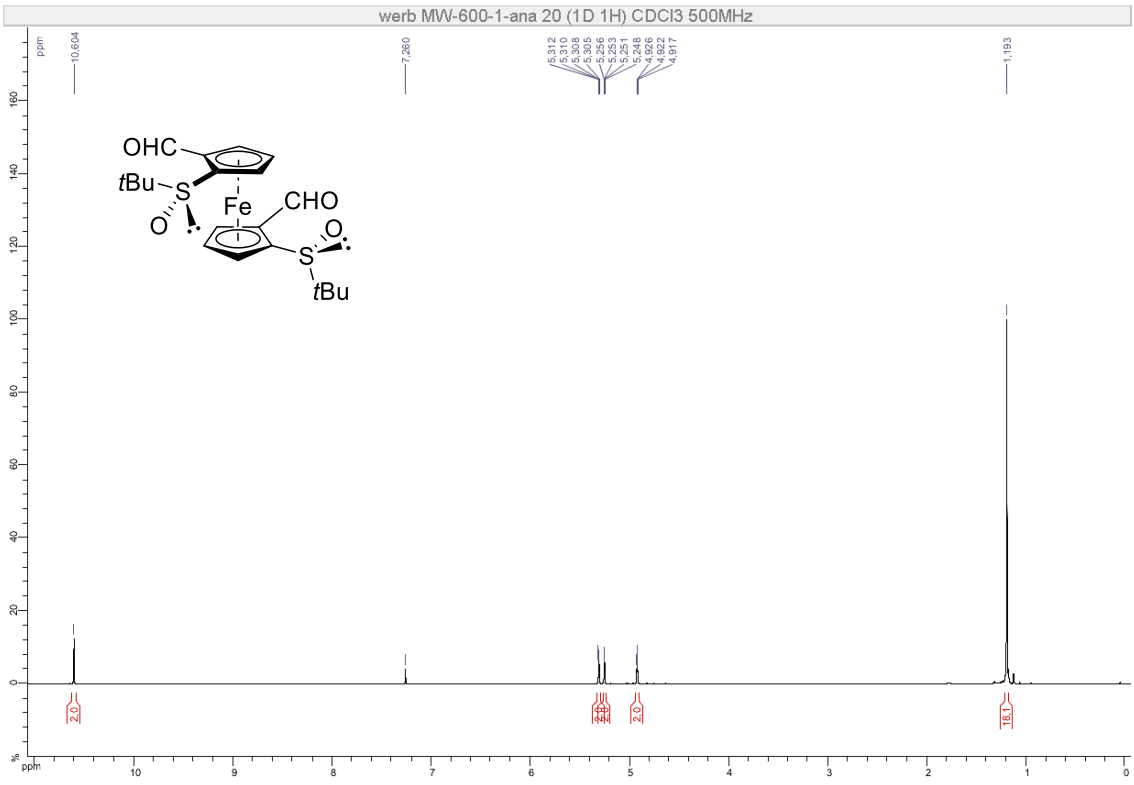


NOESY (500 MHz, $CDCl_3$)

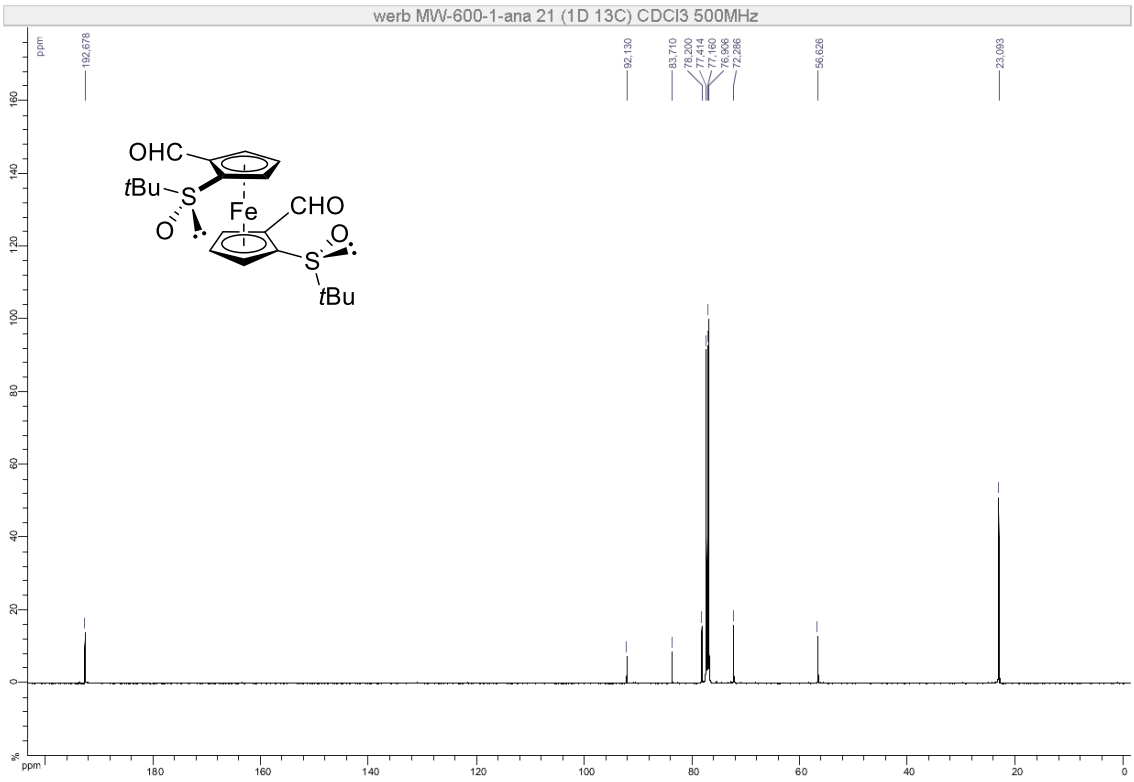


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-diformylferrocene-1,1'-disulfoxide (*R*P,*R*P-2b)

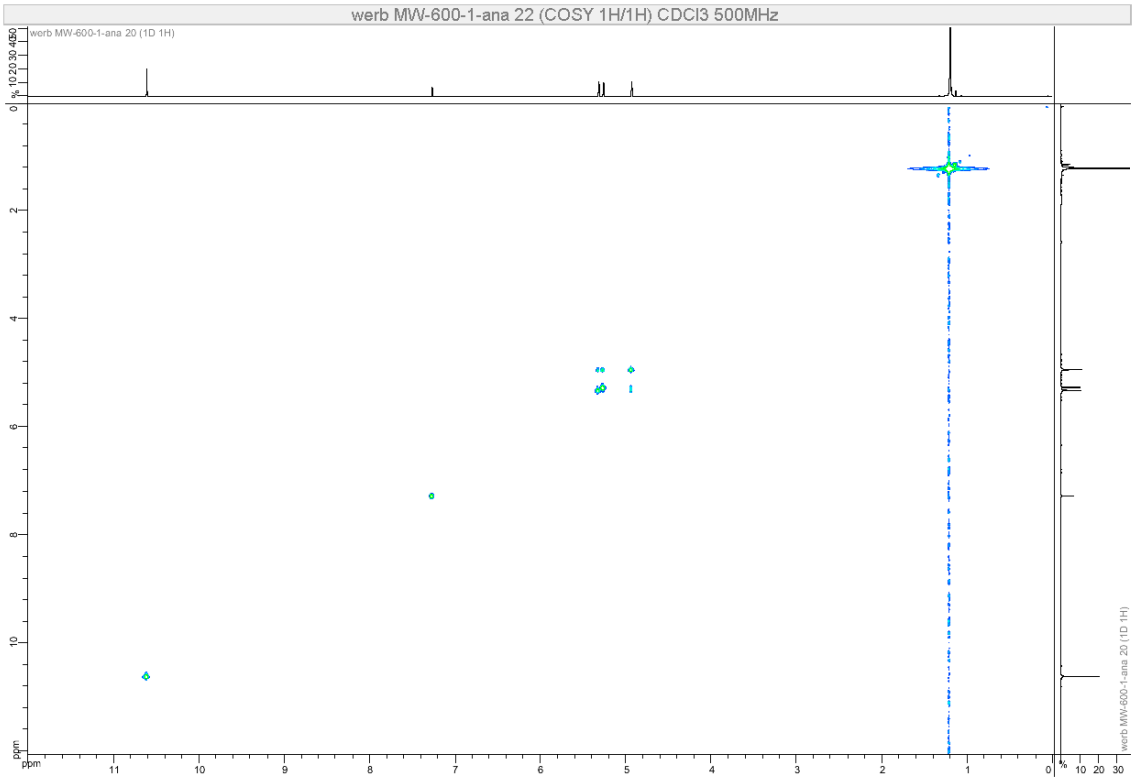
^{1}H NMR (500 MHz, $CDCl_3$)



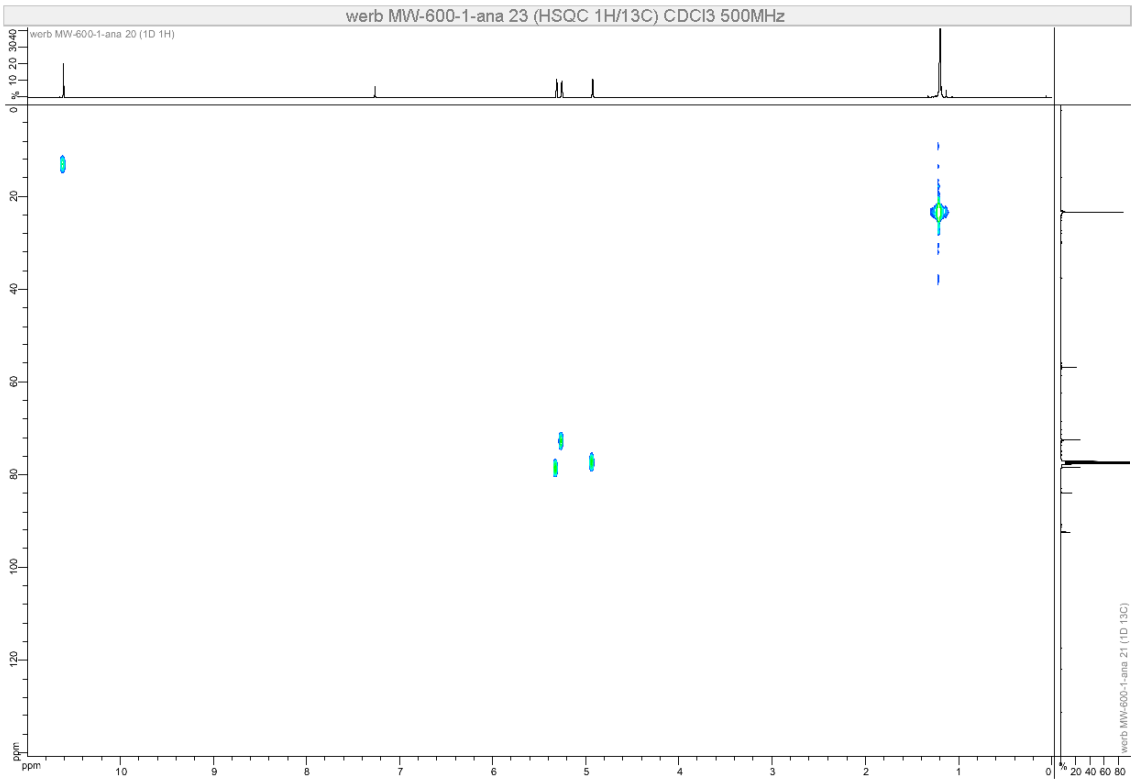
^{13}C NMR (126 MHz, $CDCl_3$)



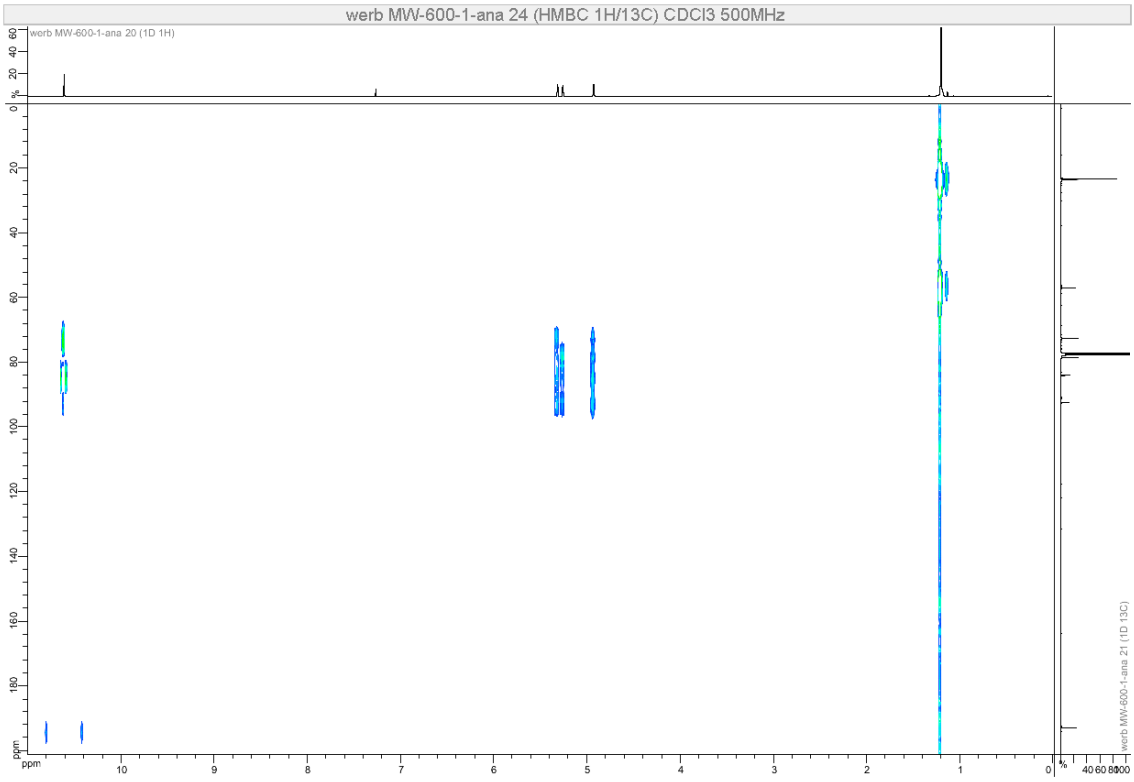
COSY (500 MHz, $CDCl_3$)



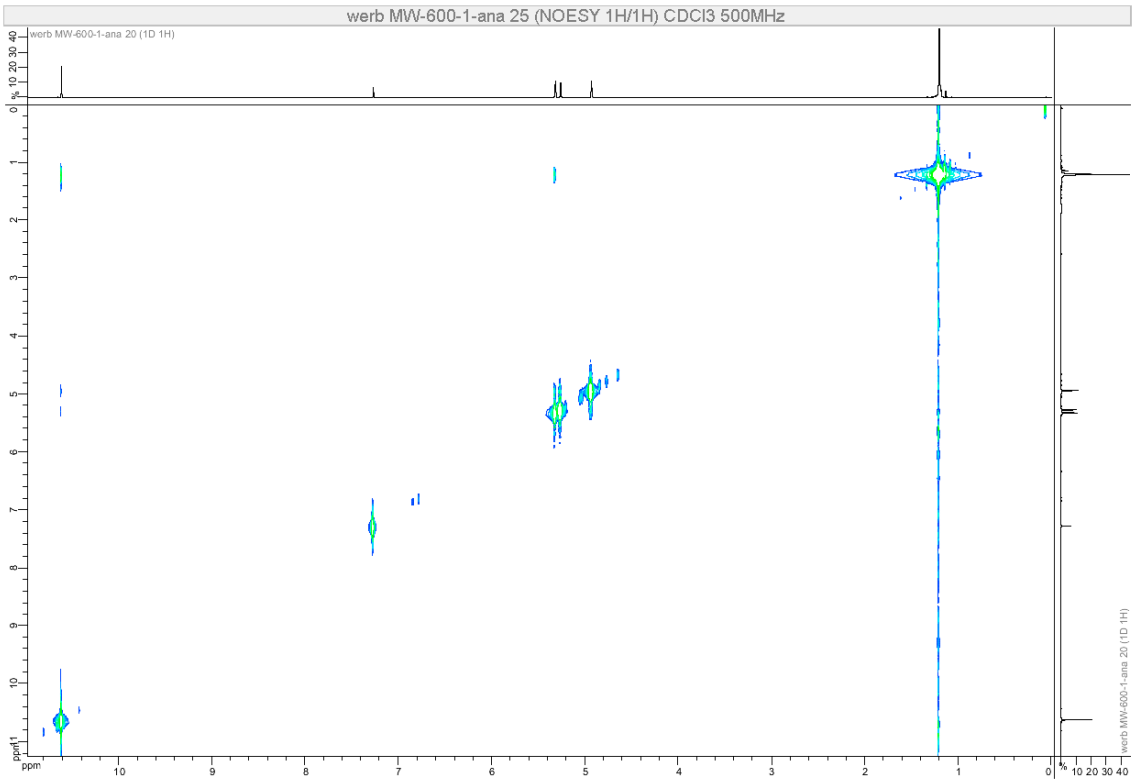
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

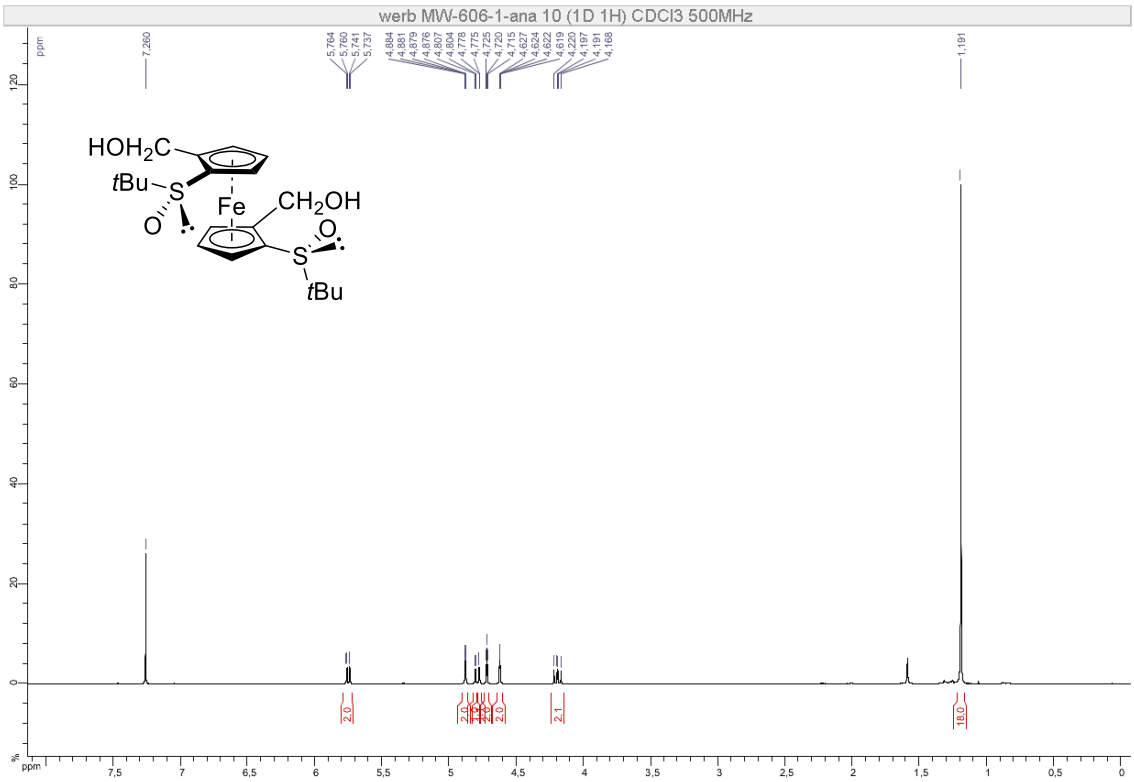


NOESY (500 MHz, $CDCl_3$)

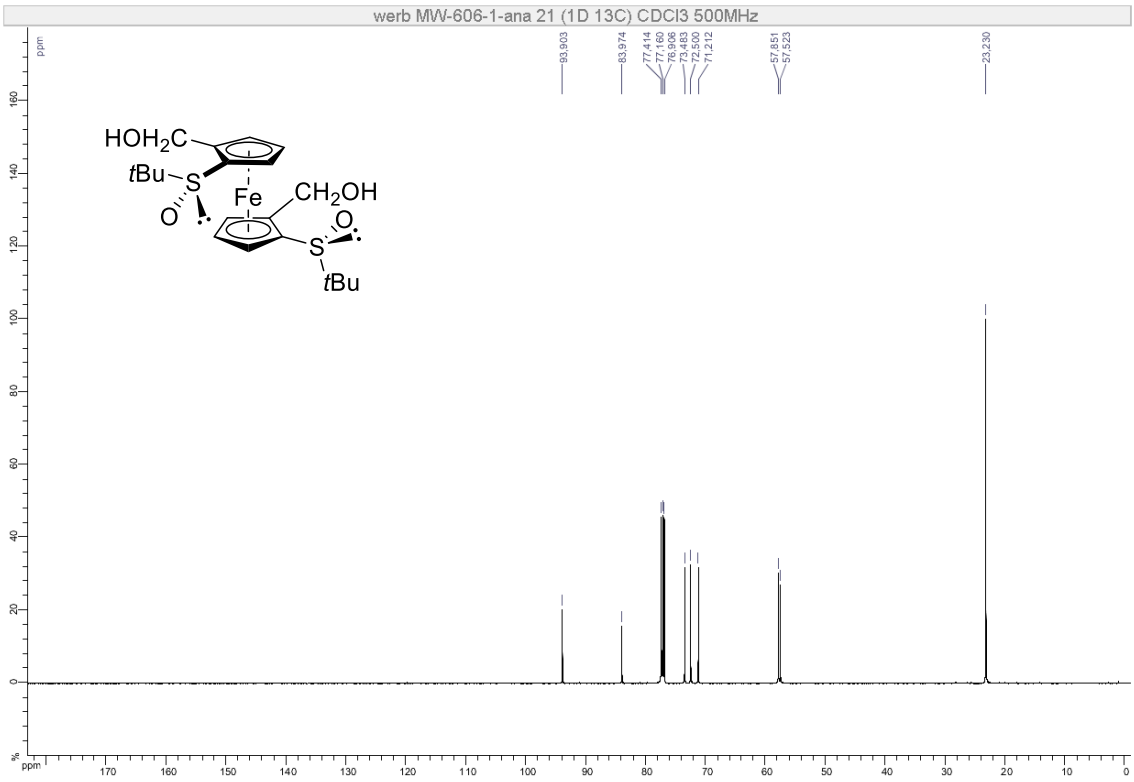


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-di(hydroxymethyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-3)

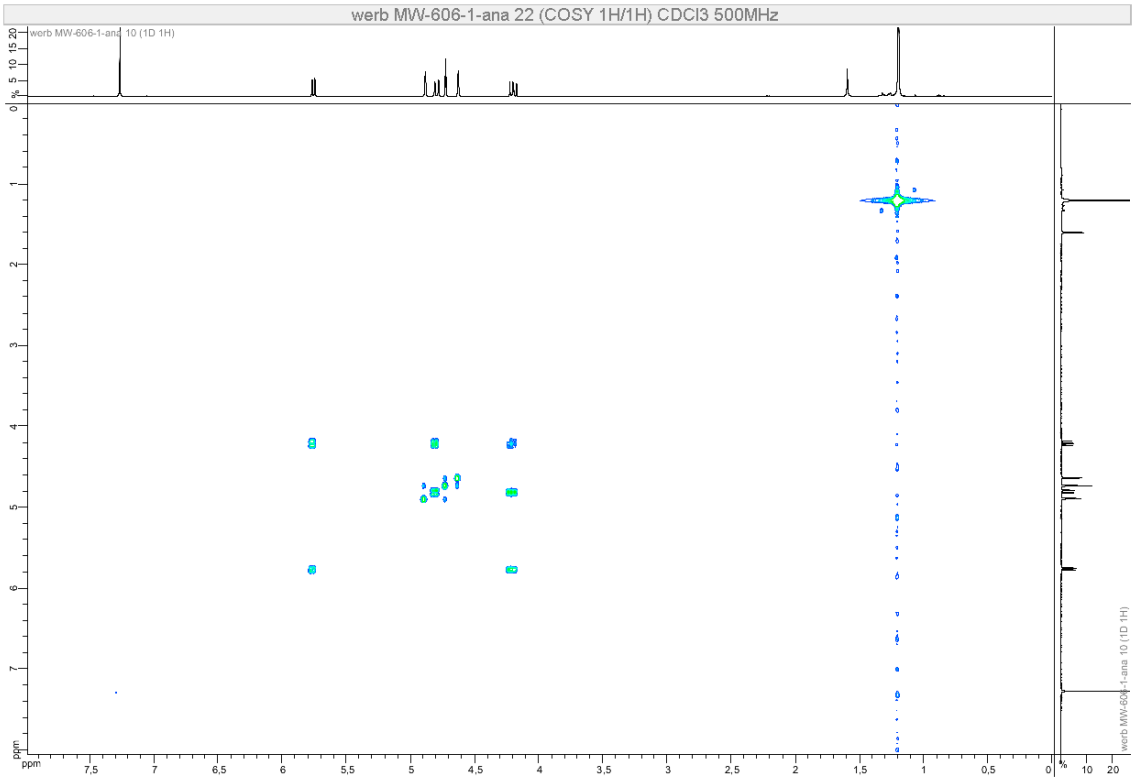
^{1}H NMR (500 MHz, $CDCl_3$)



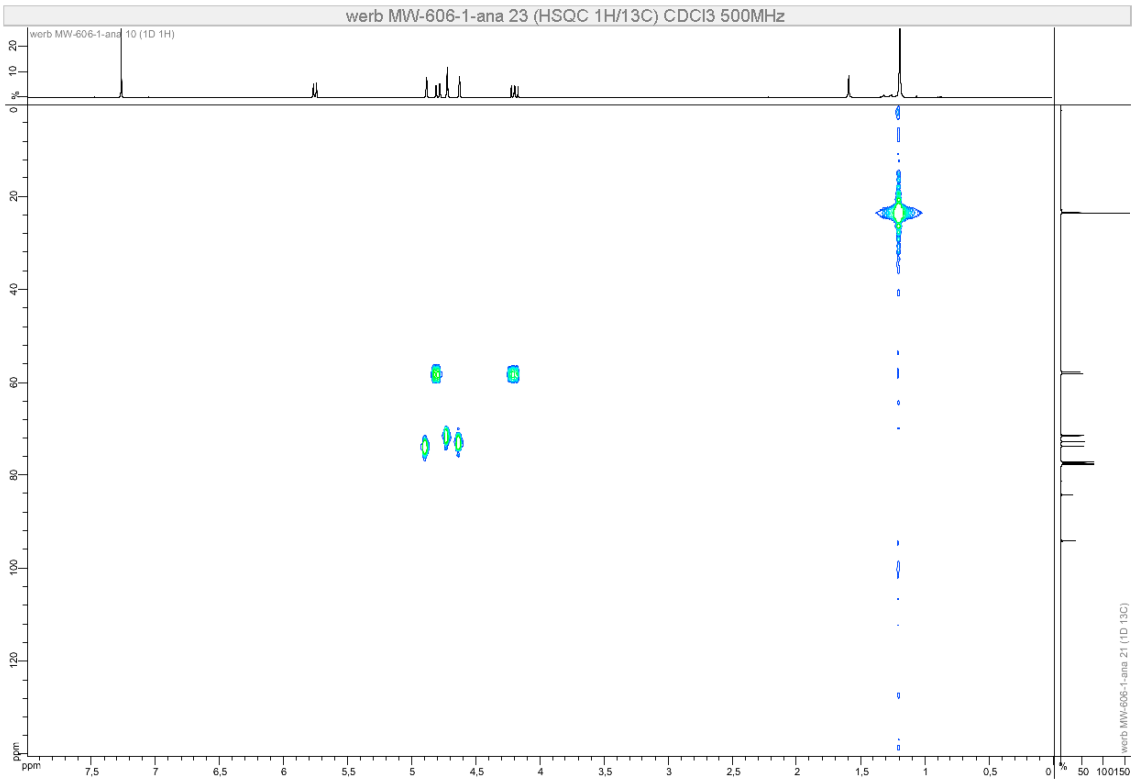
^{13}C NMR (126 MHz, $CDCl_3$)



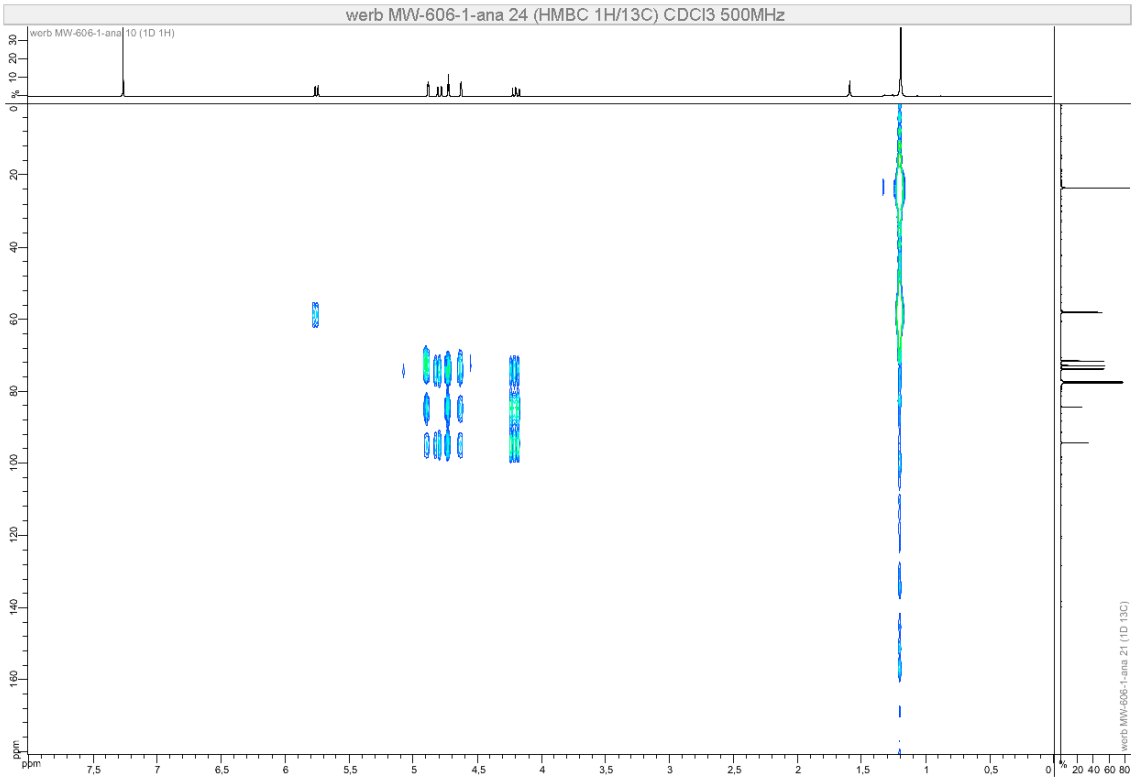
COSY (500 MHz, $CDCl_3$)



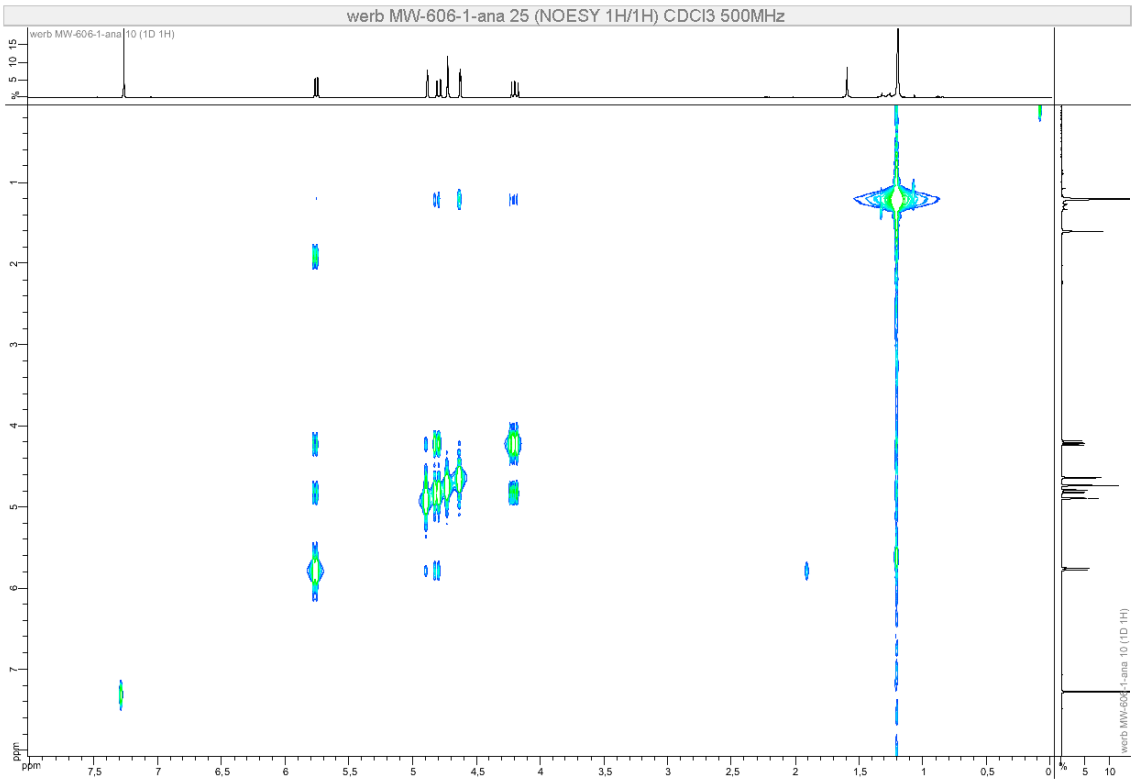
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

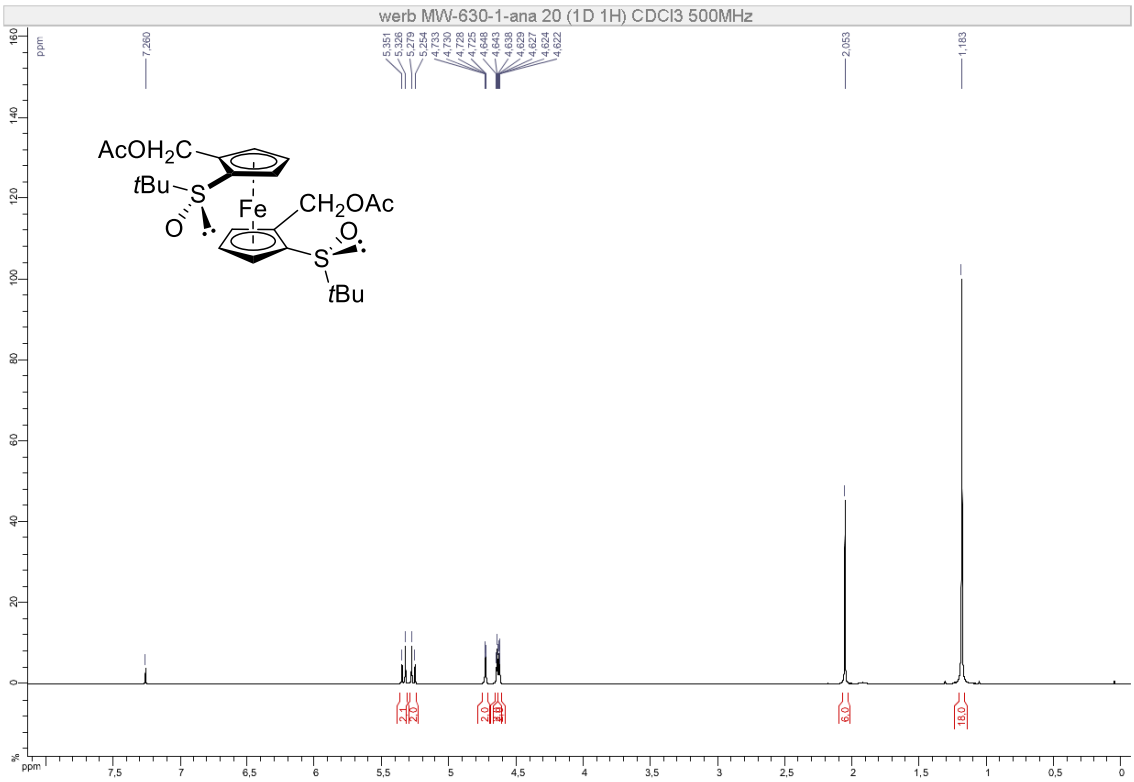


NOESY (500 MHz, $CDCl_3$)

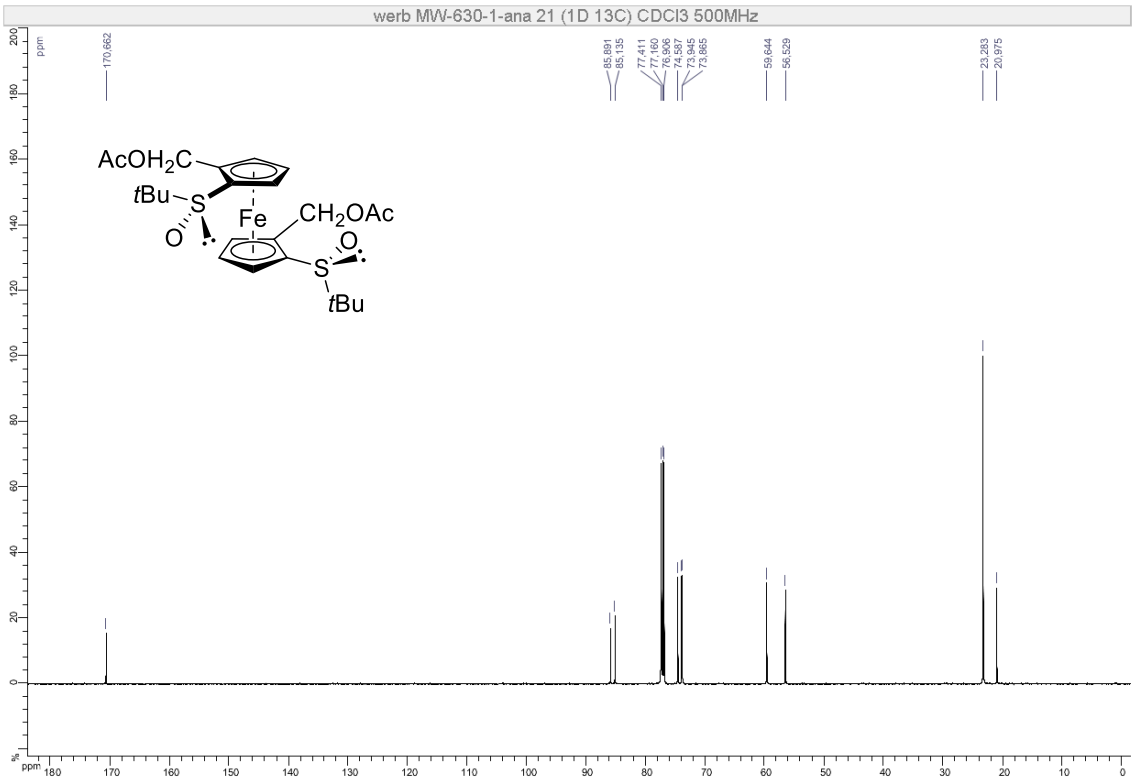


(*R*,*R*,*R*P,*R*P)-2,2'-Di(acetyloxymethyl)-*S*,*S*'-di-*tert*-butylferrocene-1,1'-disulfoxide (*R*P,*R*P-4)

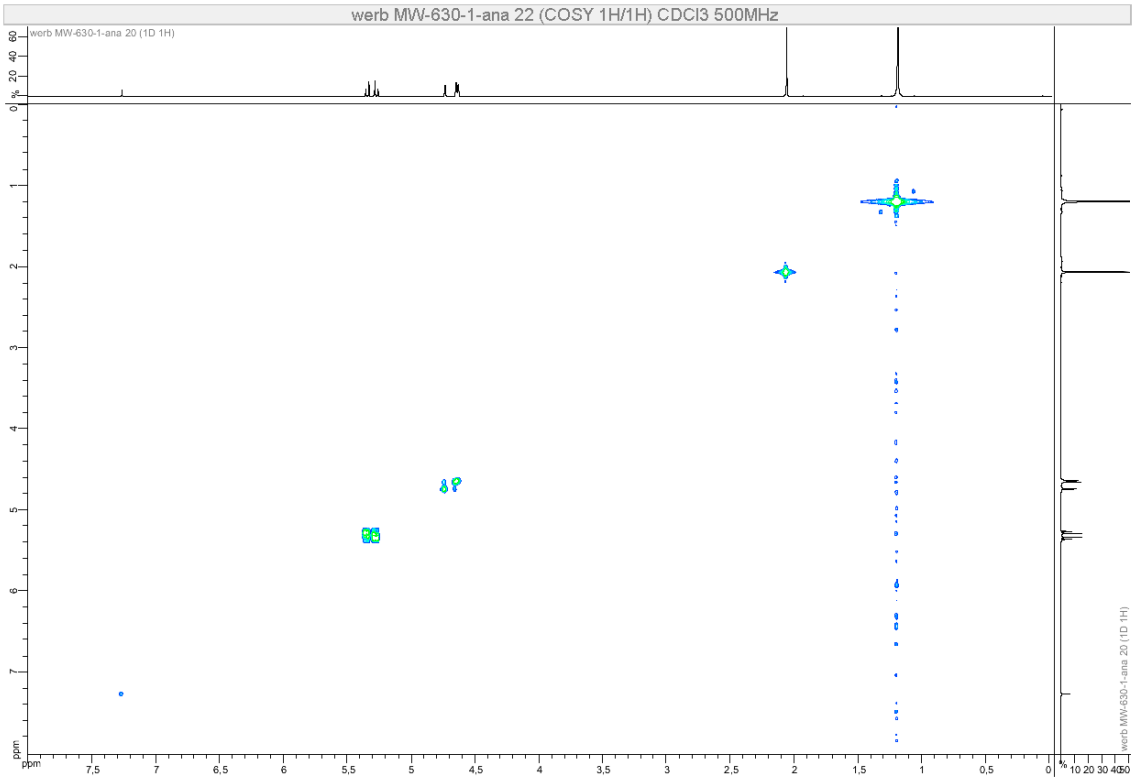
^{1}H NMR (500 MHz, $CDCl_3$)



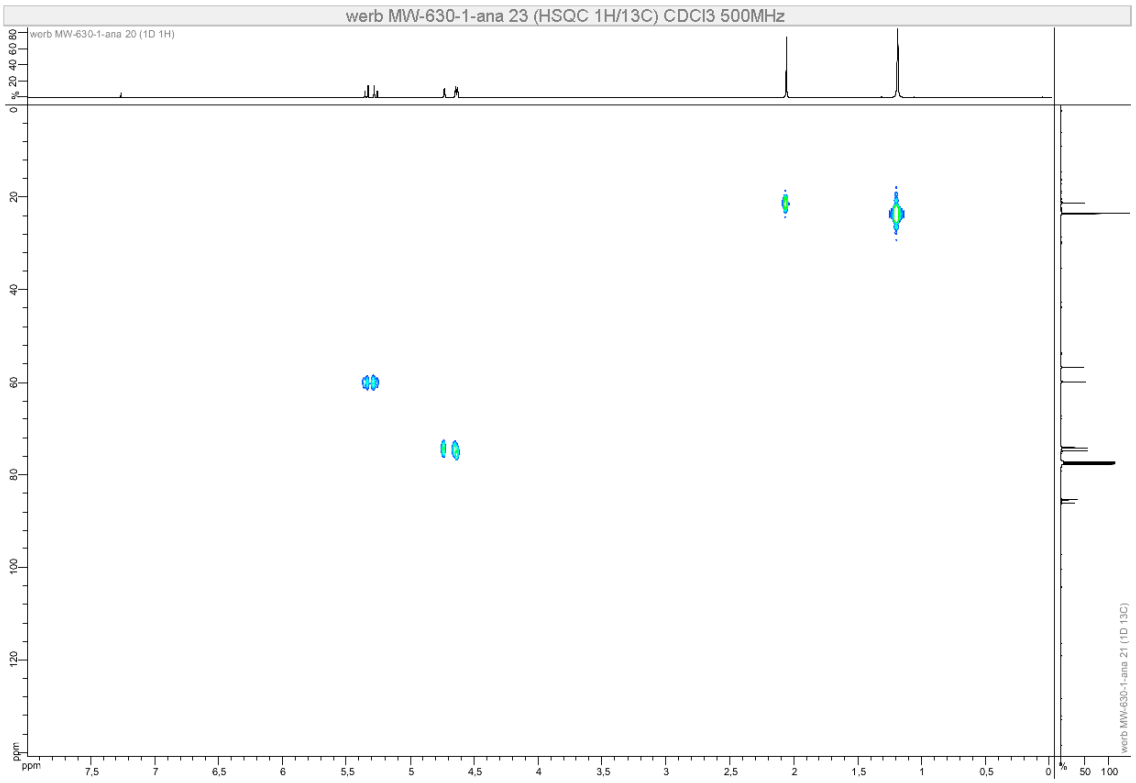
^{13}C NMR (126 MHz, $CDCl_3$)



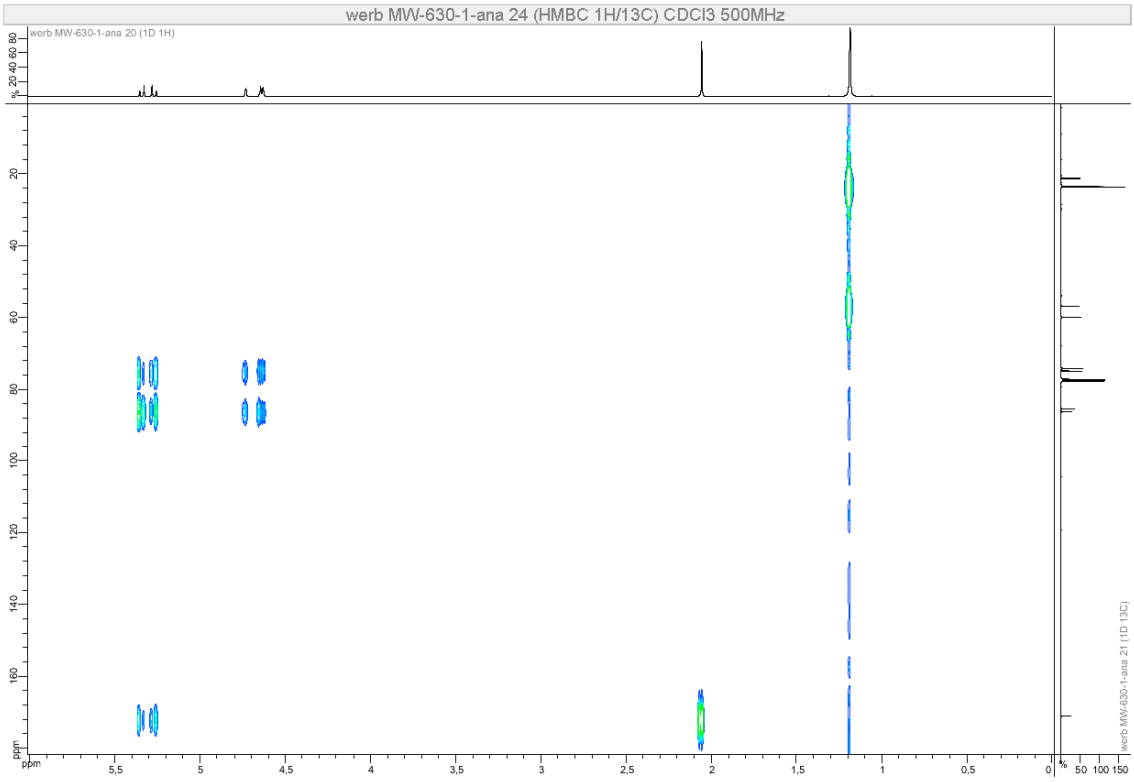
COSY (500 MHz, $CDCl_3$)



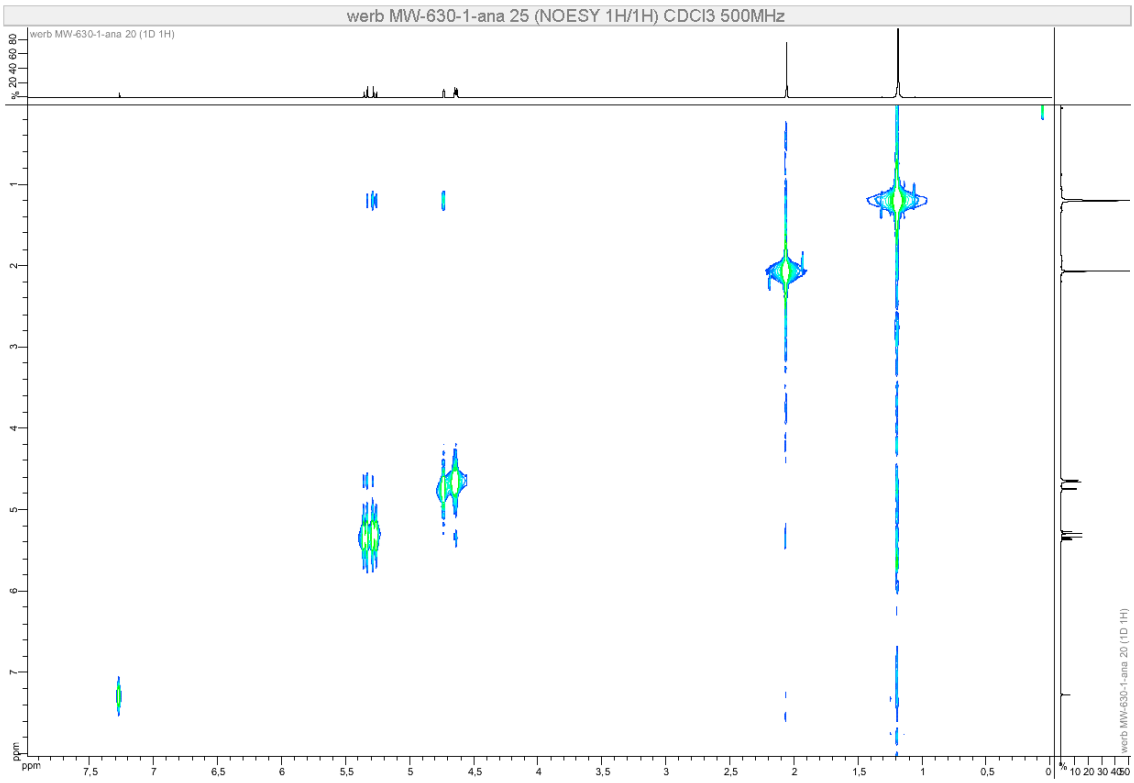
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

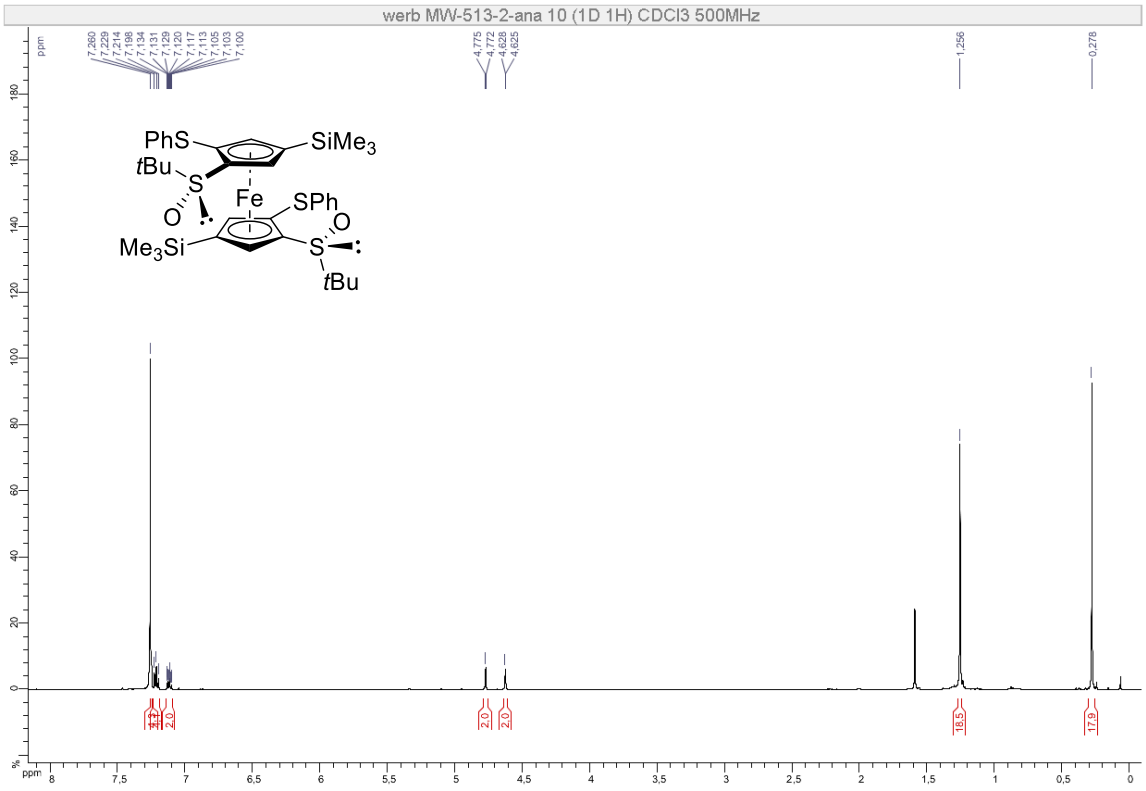


NOESY (500 MHz, $CDCl_3$)

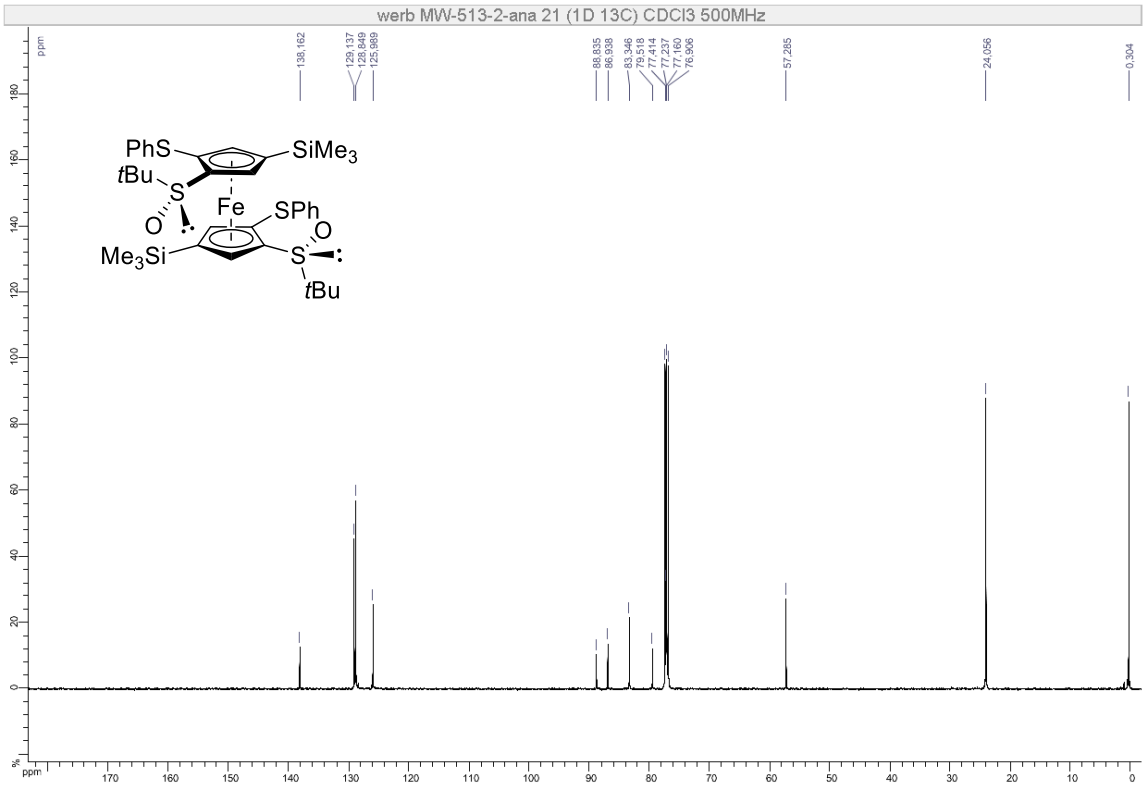


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-di(phenylthio)-4,4'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-5a)

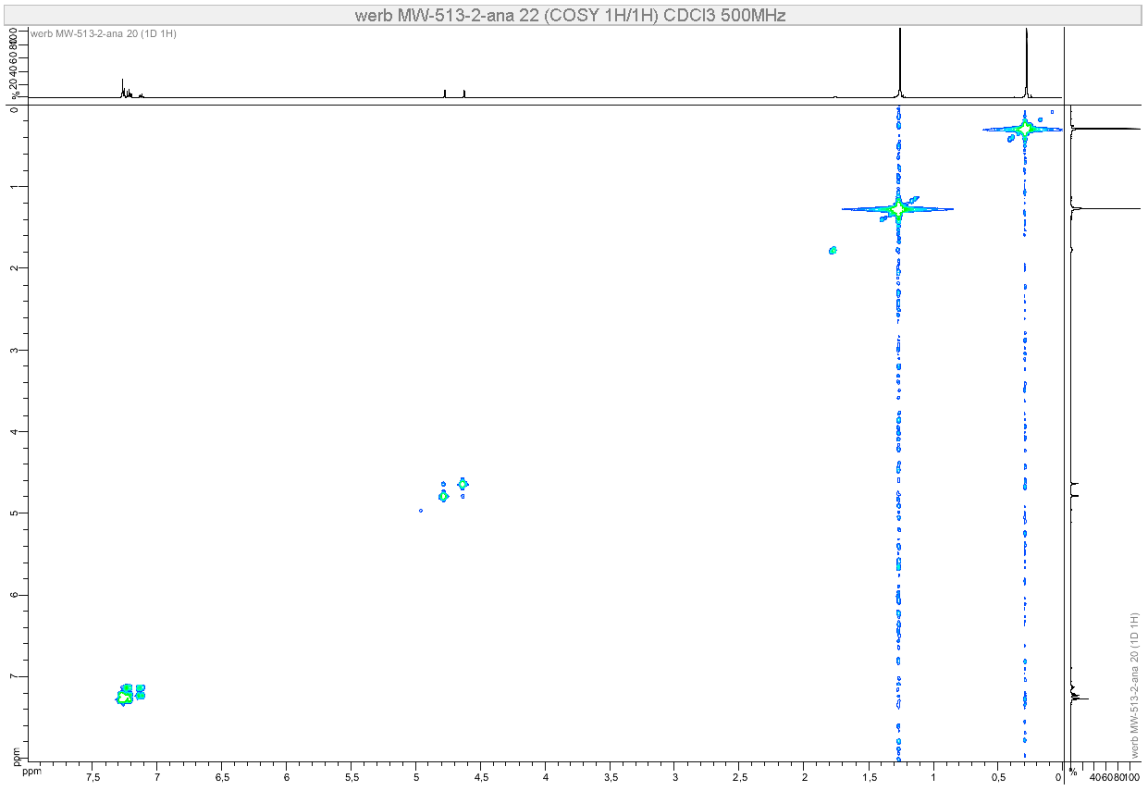
^{1}H NMR (500 MHz, $CDCl_3$)



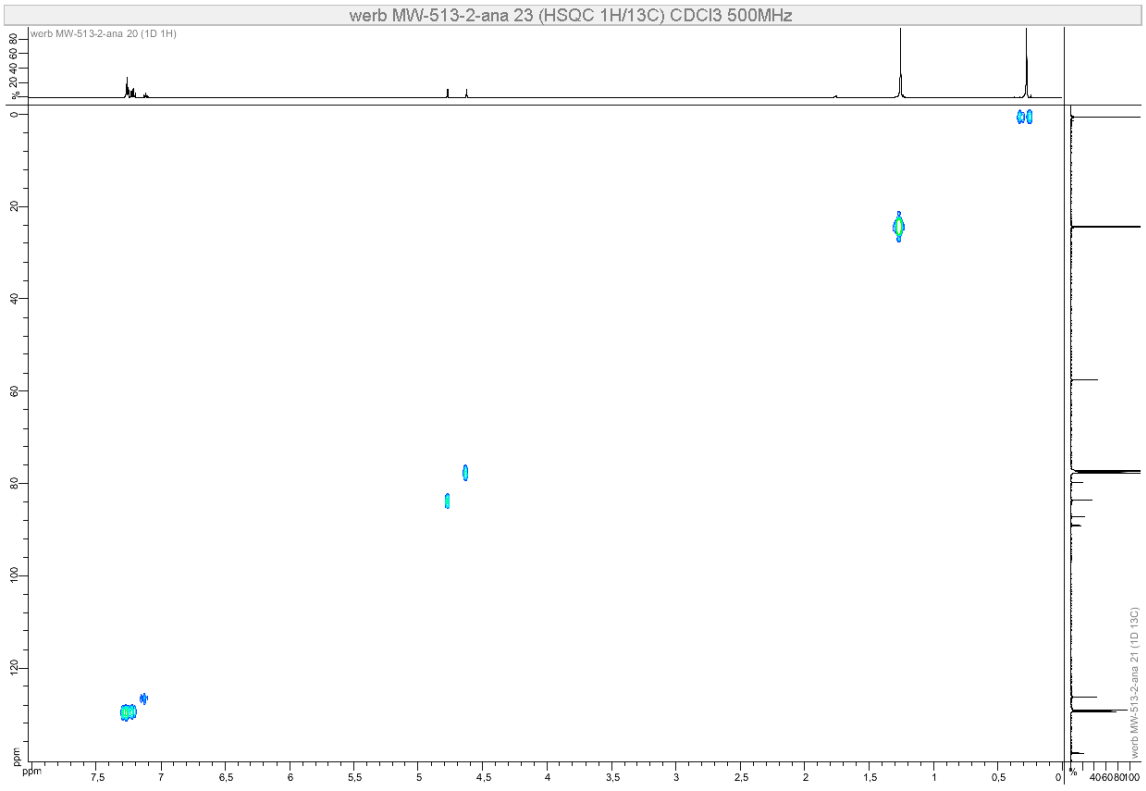
^{13}C NMR (126 MHz, $CDCl_3$)



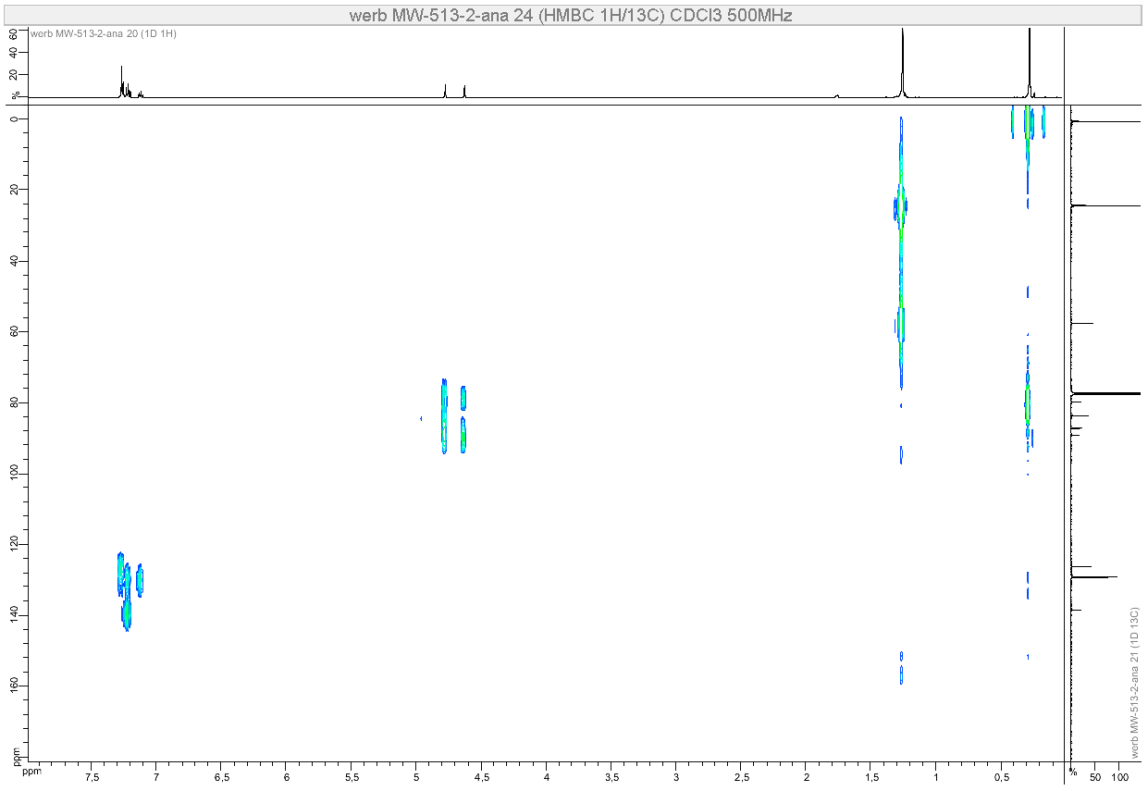
COSY (500 MHz, $CDCl_3$)



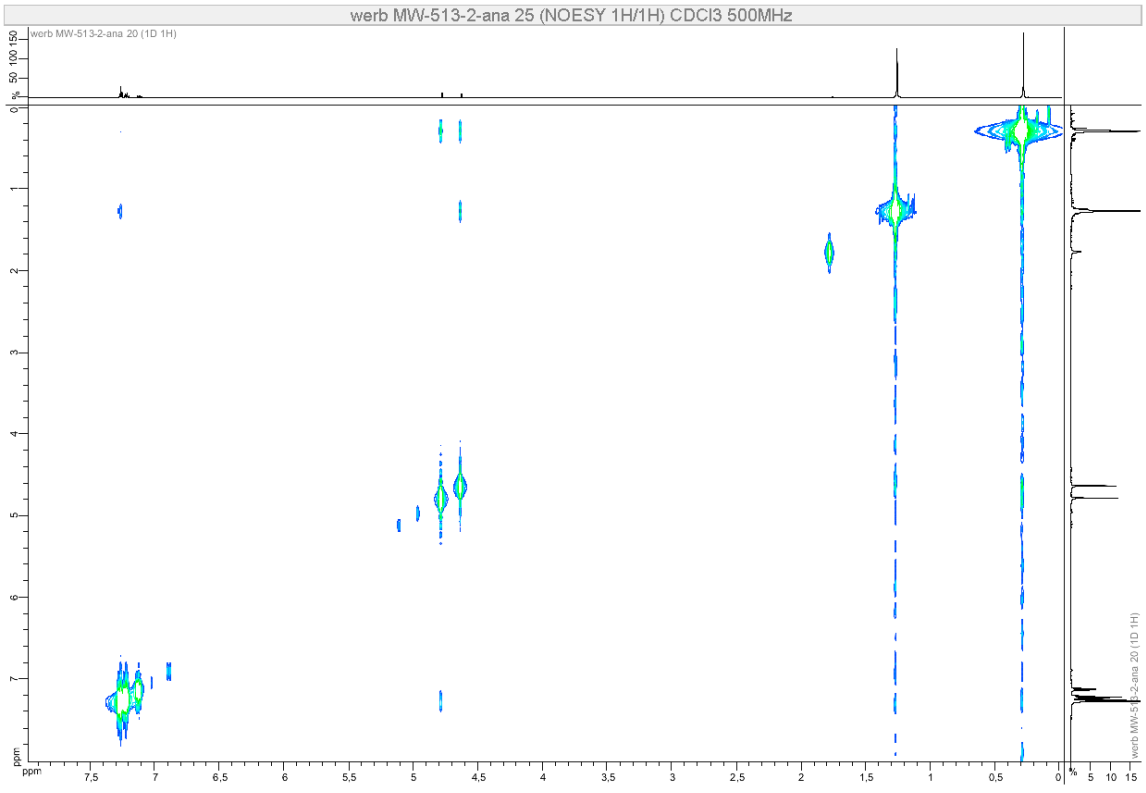
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

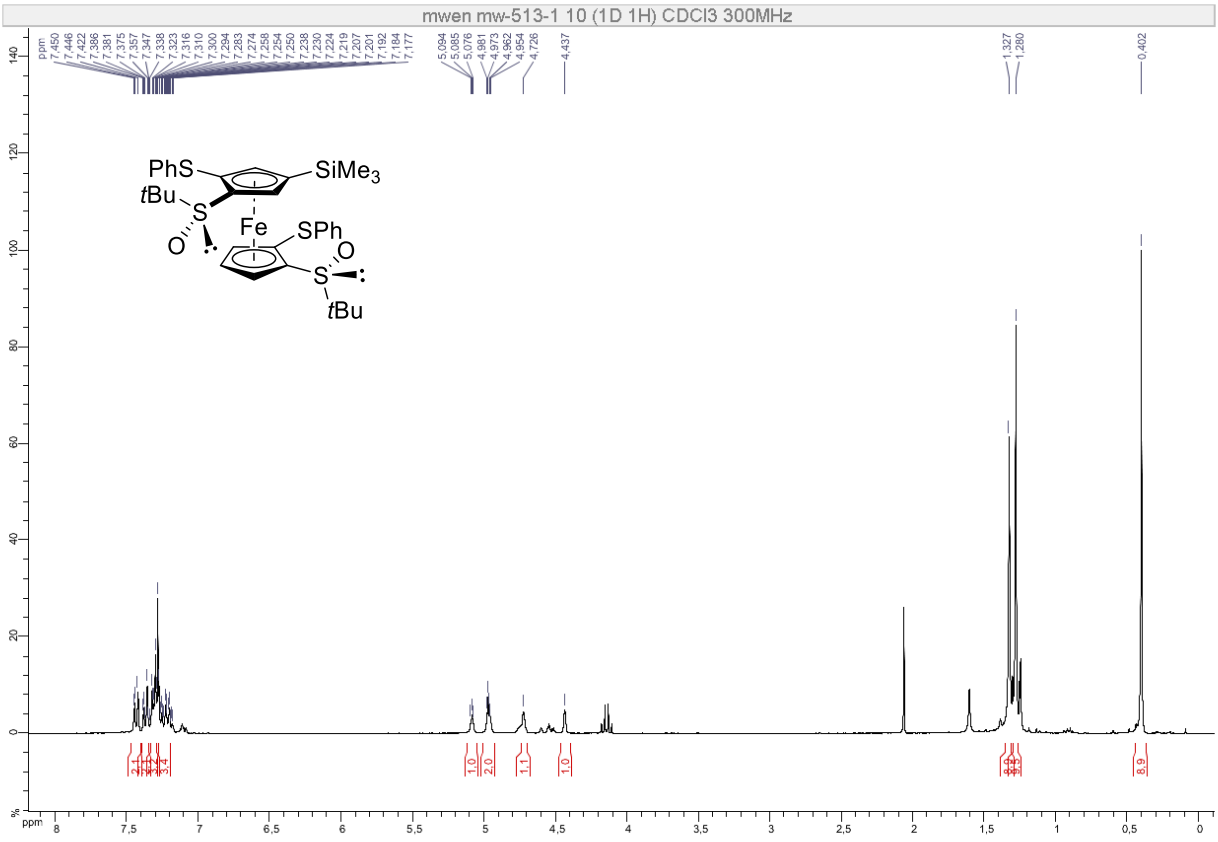


NOESY (500 MHz, $CDCl_3$)



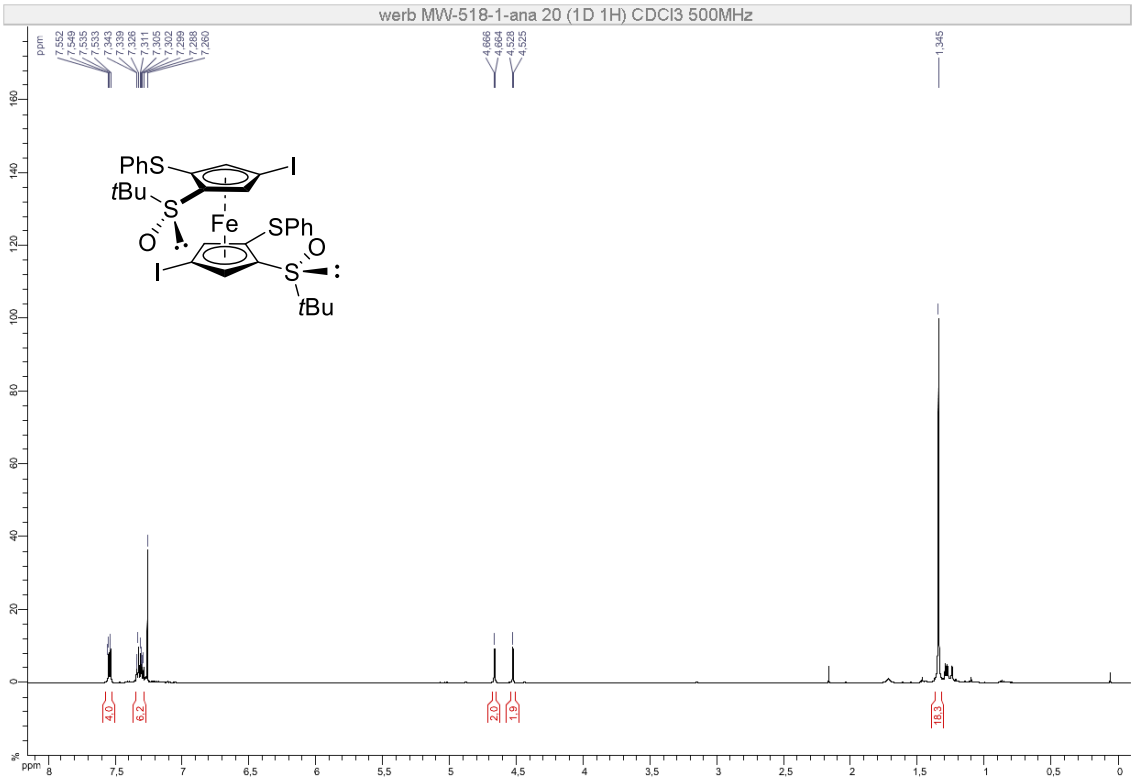
(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-di(phenylthio)-4-(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-5'a)

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

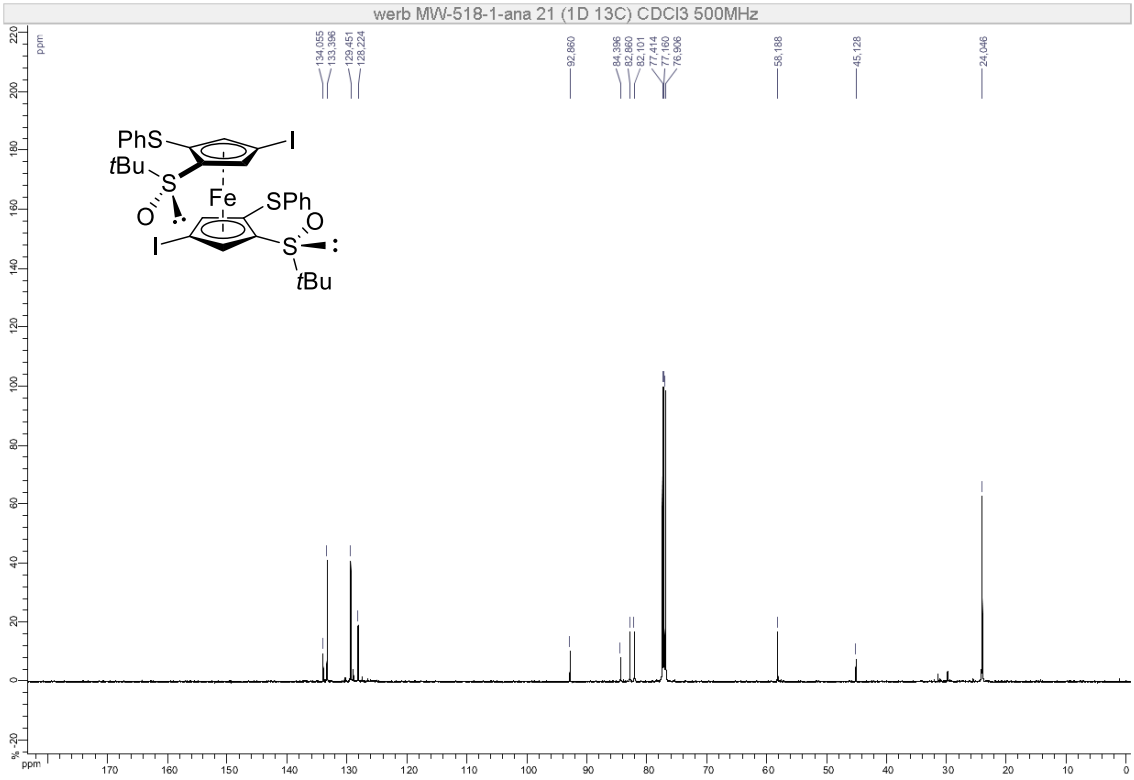


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4,4'-diiodo-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (*R*P,*R*P-5b)

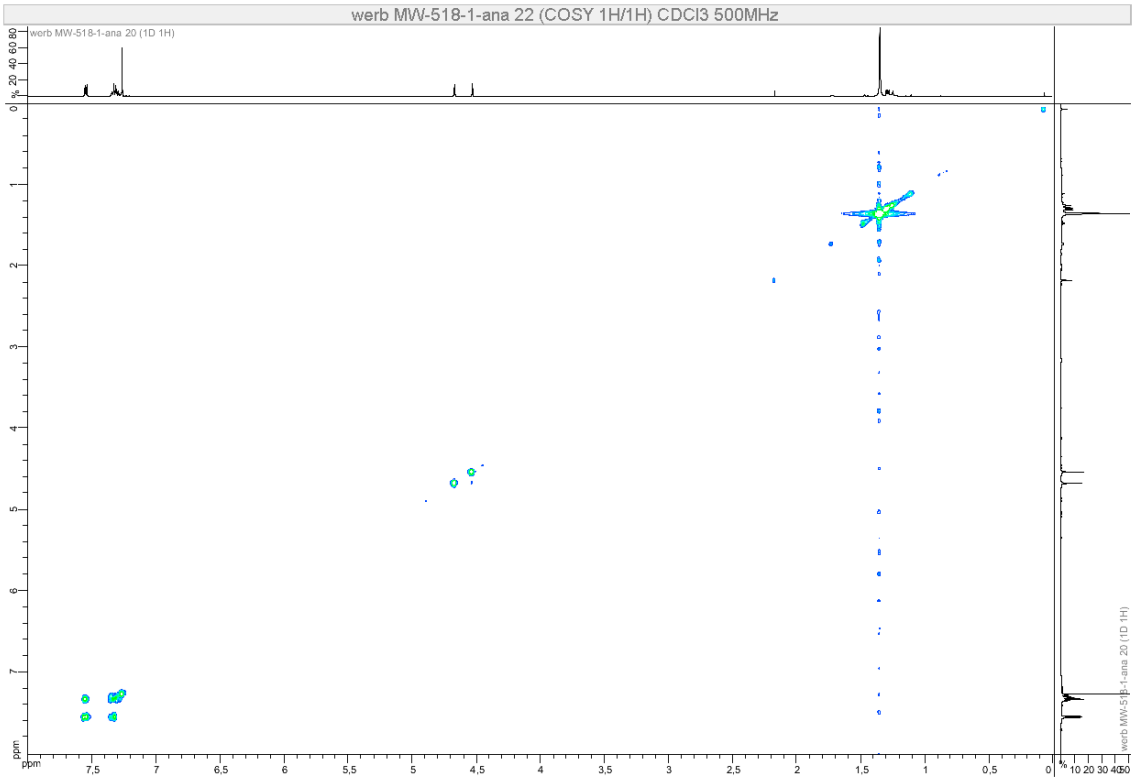
^{1}H NMR (500 MHz, $CDCl_3$)



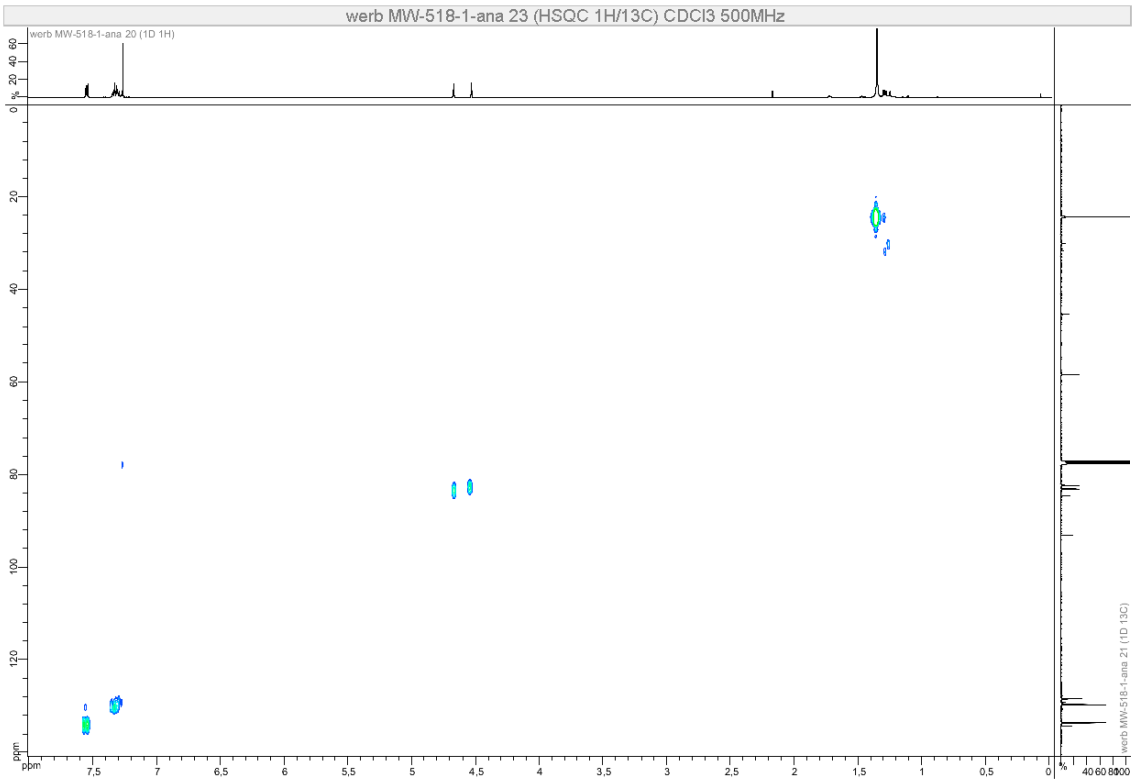
^{13}C NMR (126 MHz, $CDCl_3$)



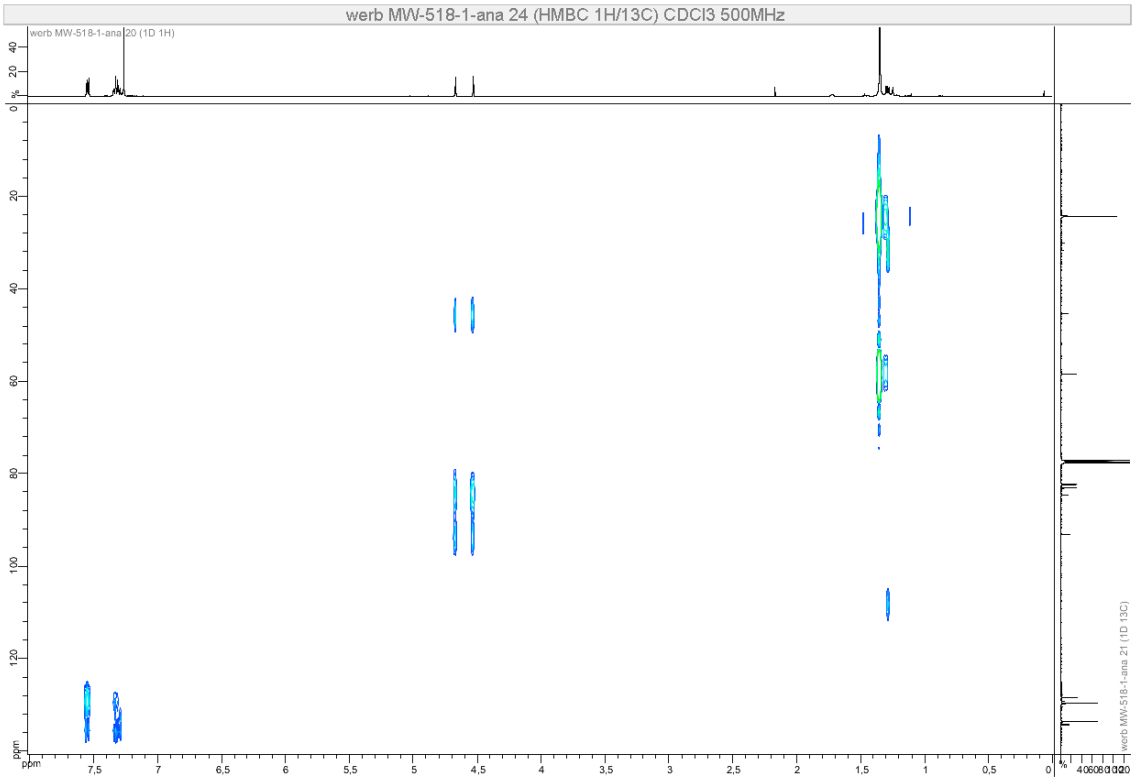
COSY (500 MHz, $CDCl_3$)



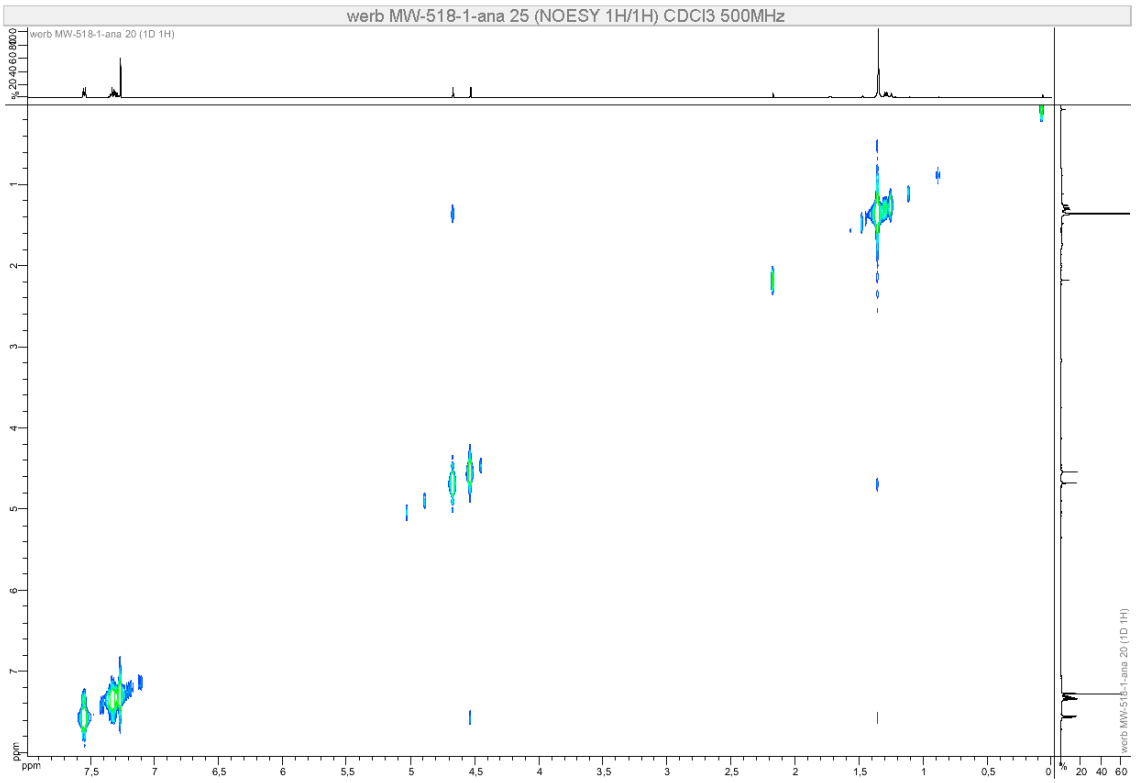
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

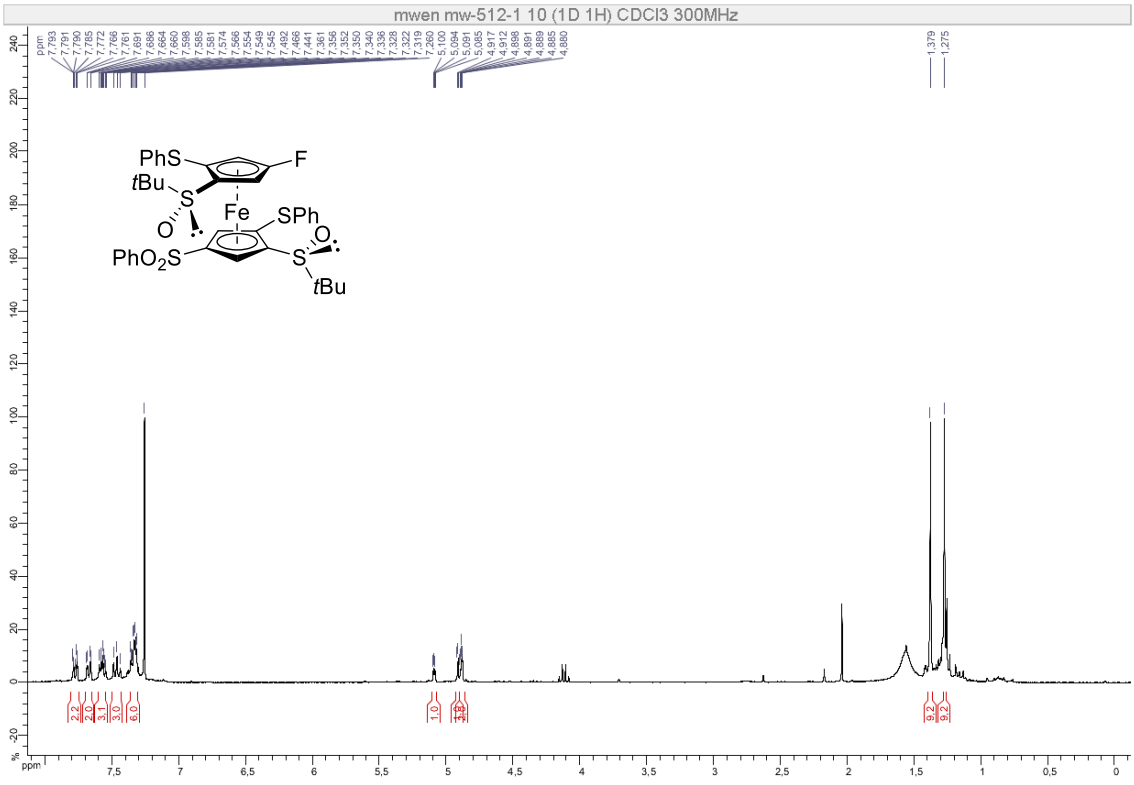


NOESY (500 MHz, $CDCl_3$)

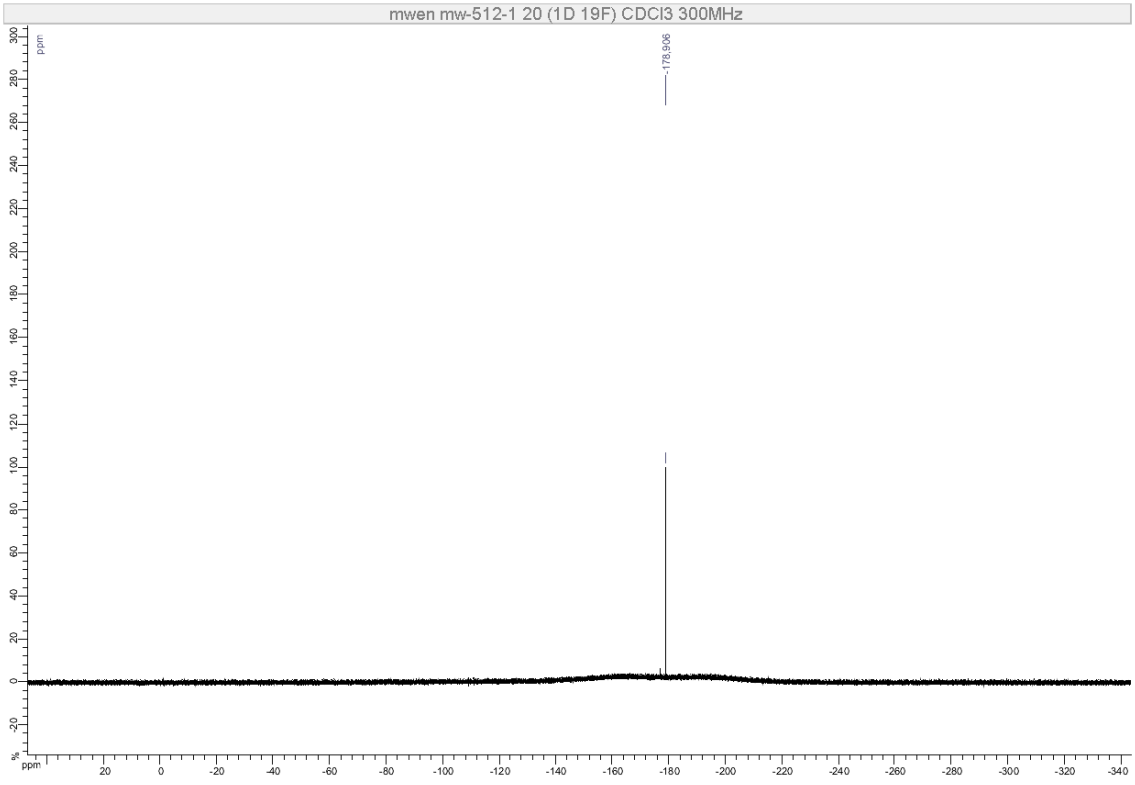


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4-fluoro-4'-(phenylsulfonyl)-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (*R*P,*R*P-5"c)

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

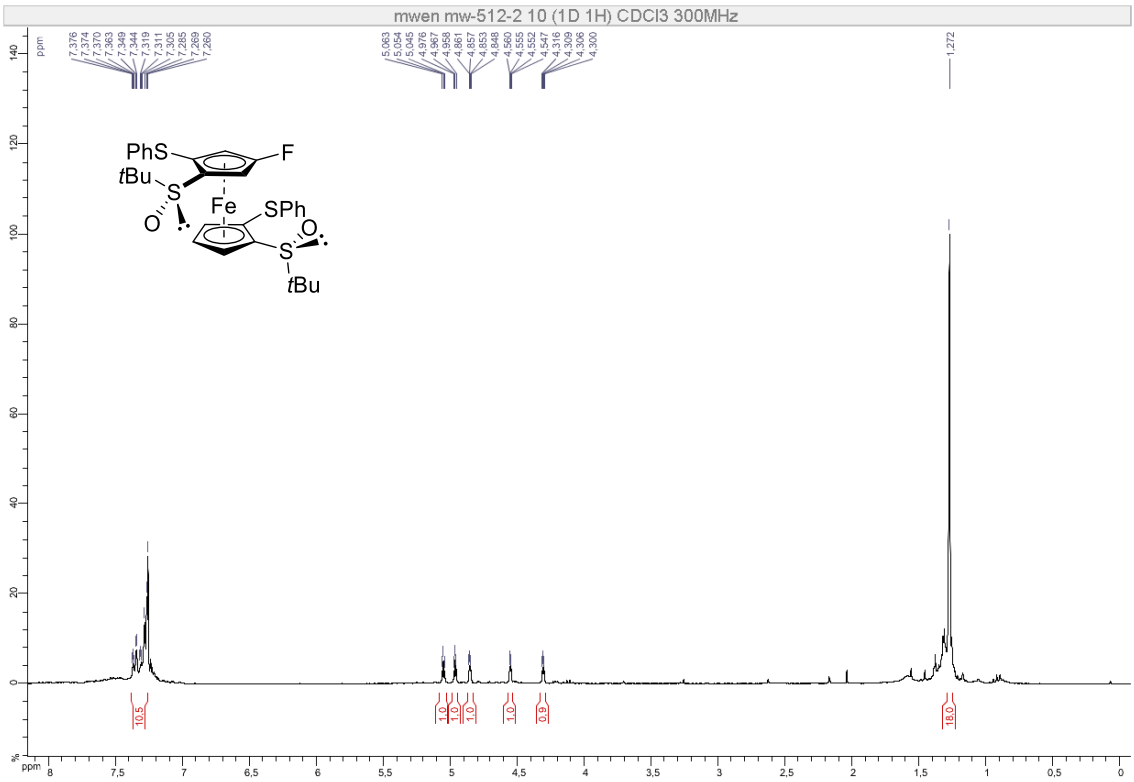


^{19}F NMR (282 MHz, $CDCl_3$)

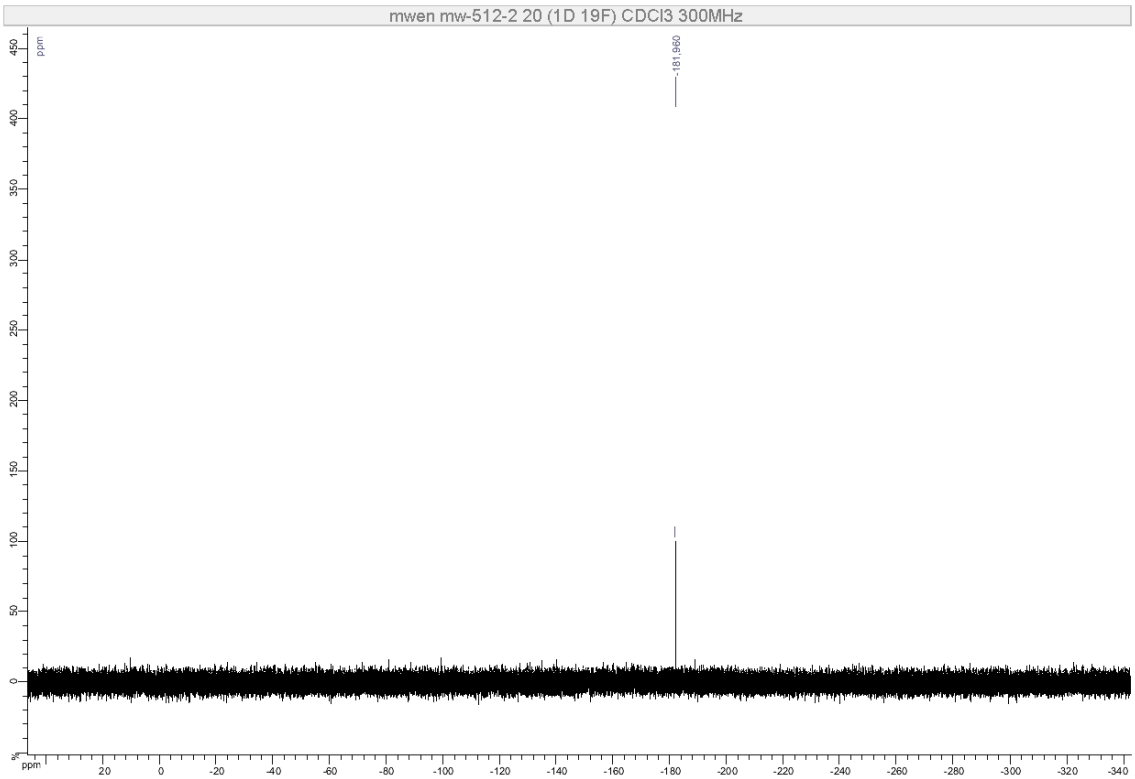


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4-fluoro-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (*R*P,*R*P-5'c)

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

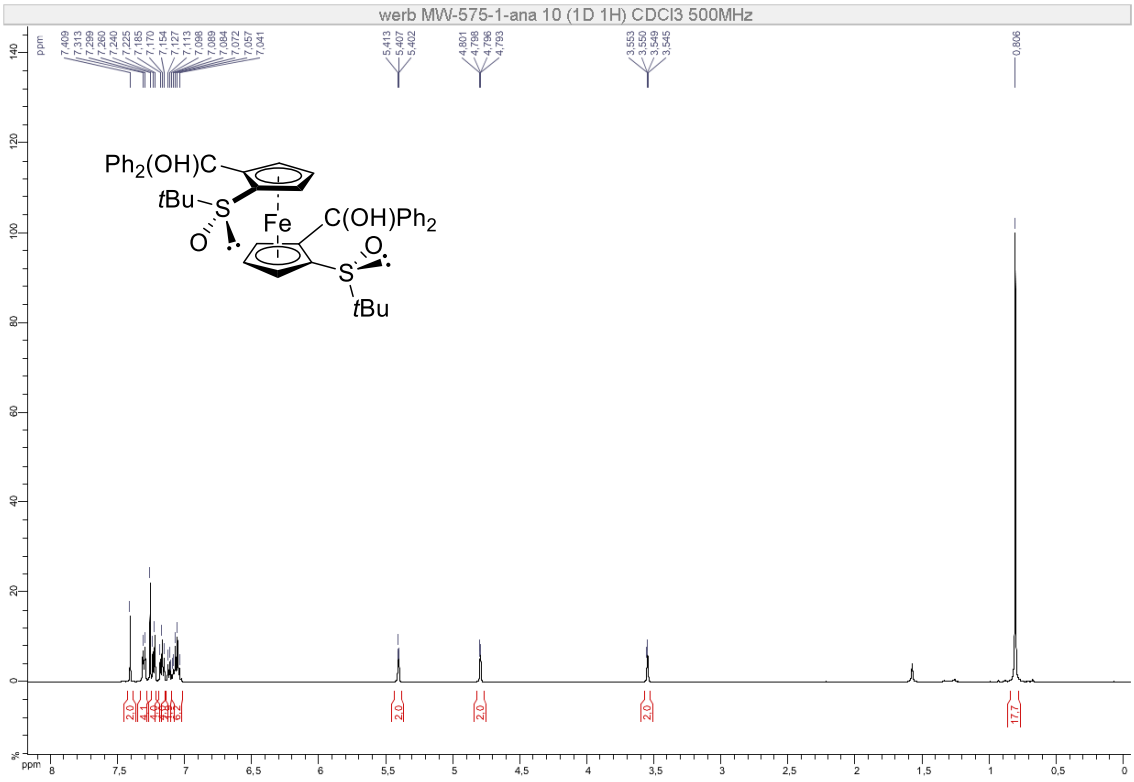


^{19}F NMR (282 MHz, $CDCl_3$)

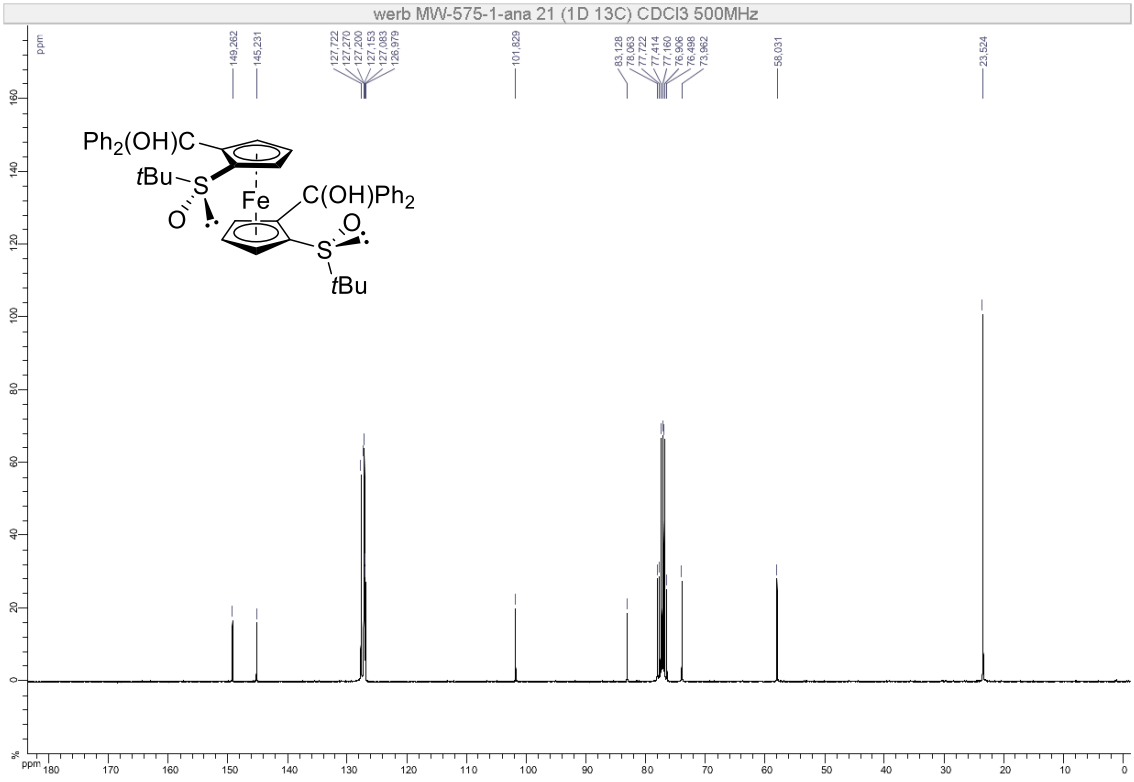


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-di((α,α-diphenyl)hydroxymethyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-2c)

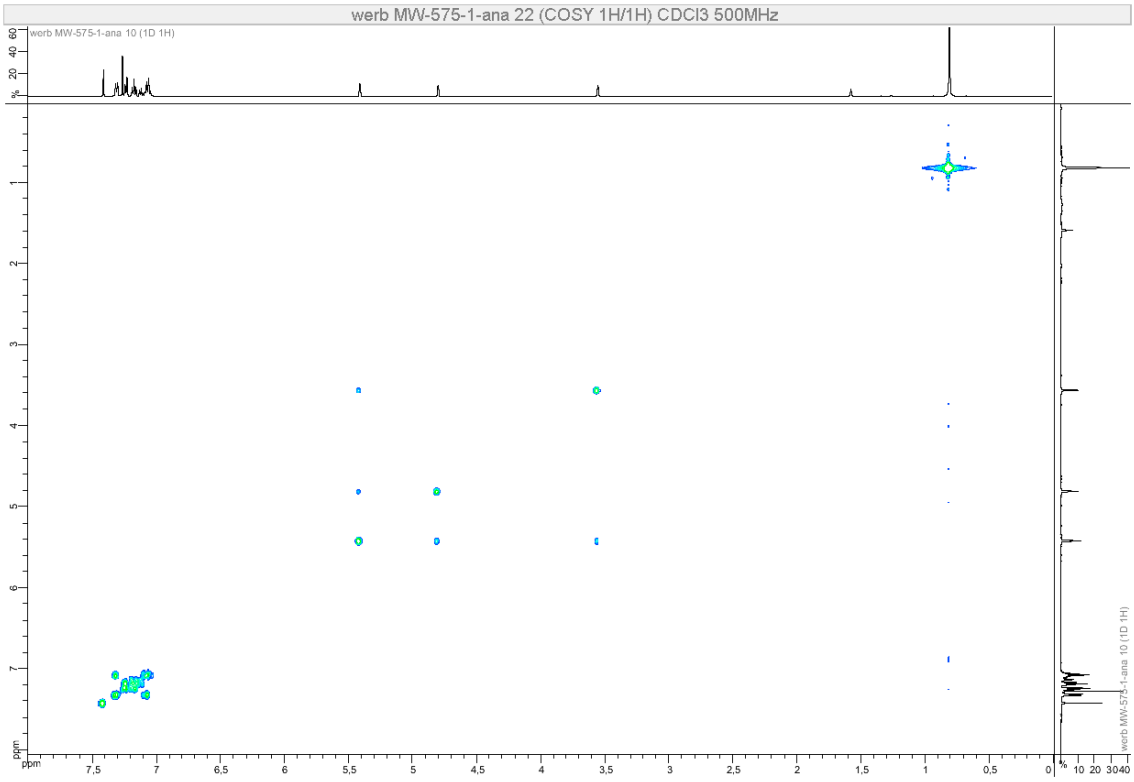
^{1}H NMR (500 MHz, $CDCl_3$)



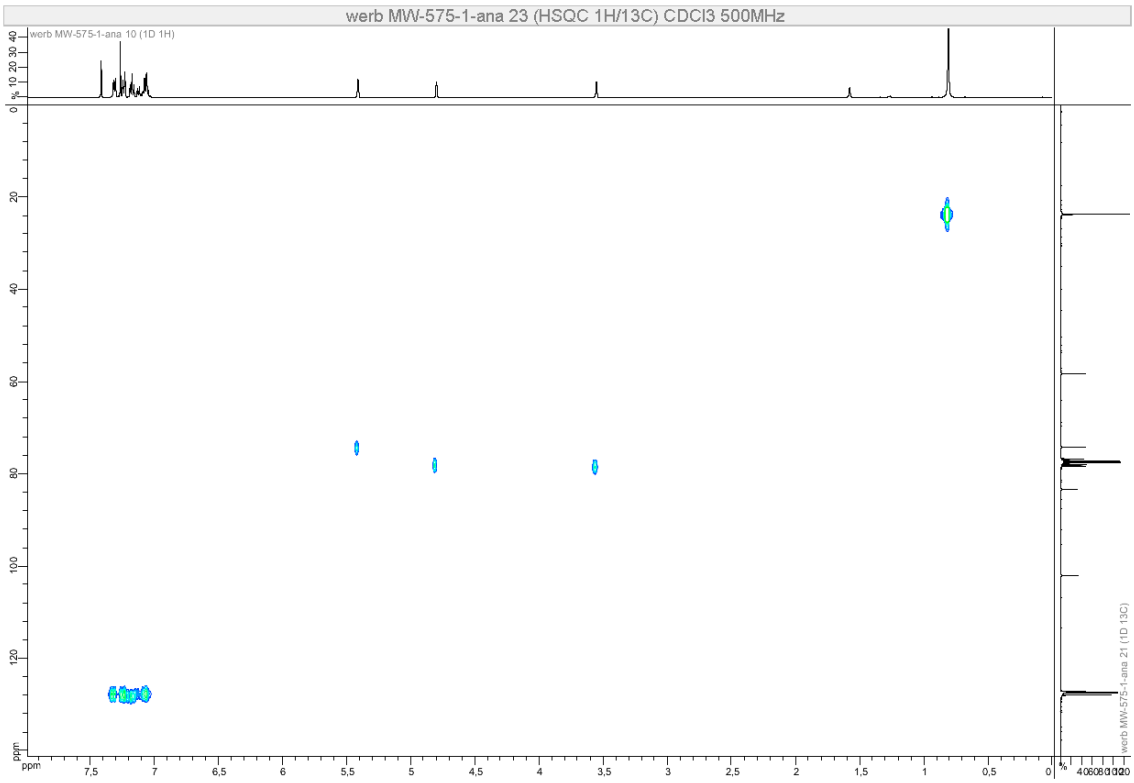
^{13}C NMR (126 MHz, $CDCl_3$)



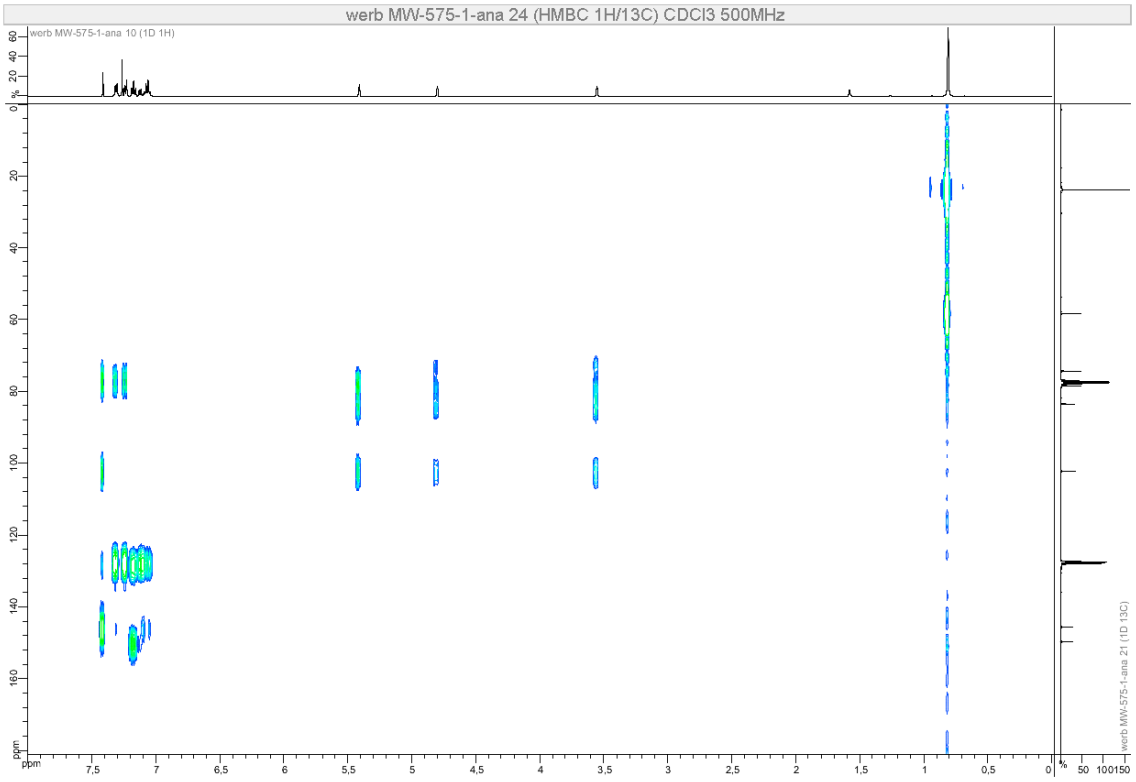
COSY (500 MHz, $CDCl_3$)



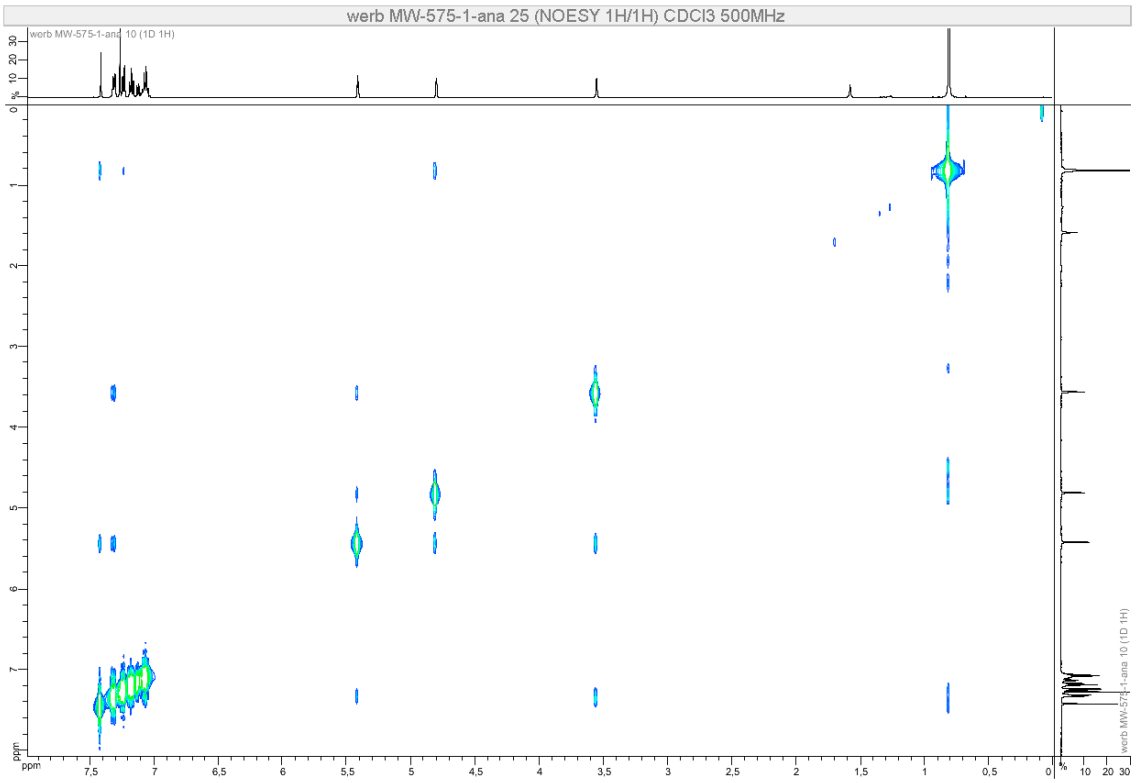
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

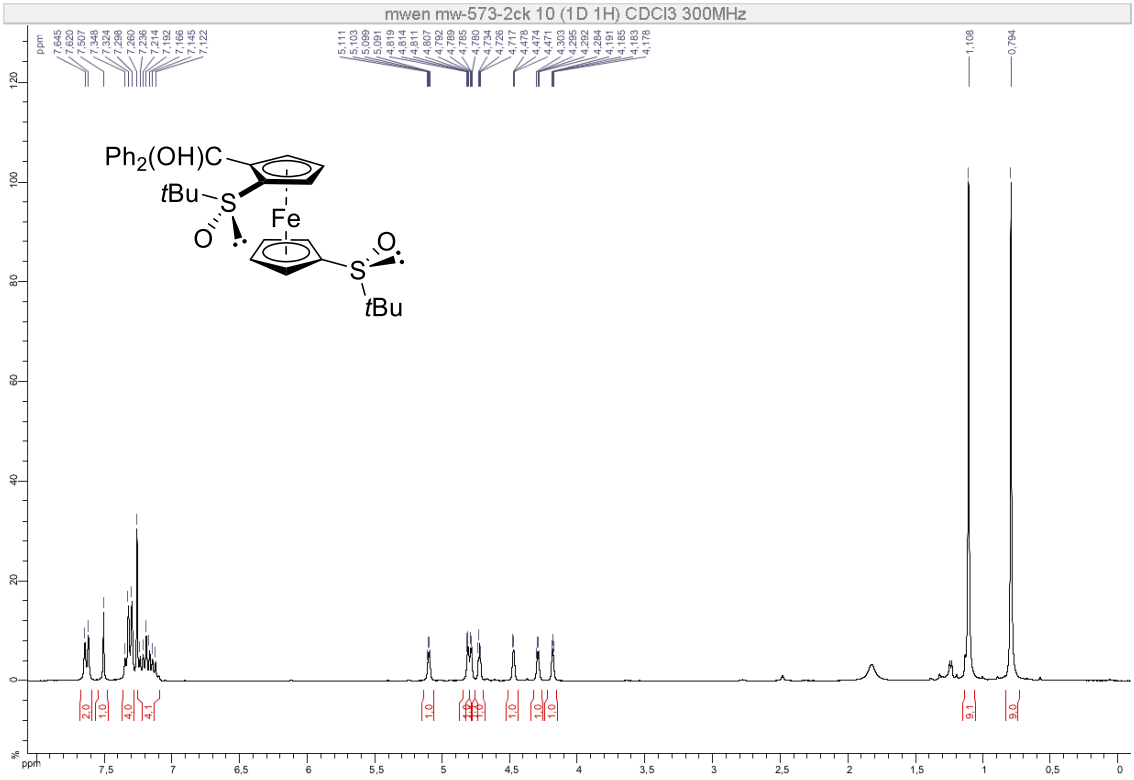


NOESY (500 MHz, $CDCl_3$)



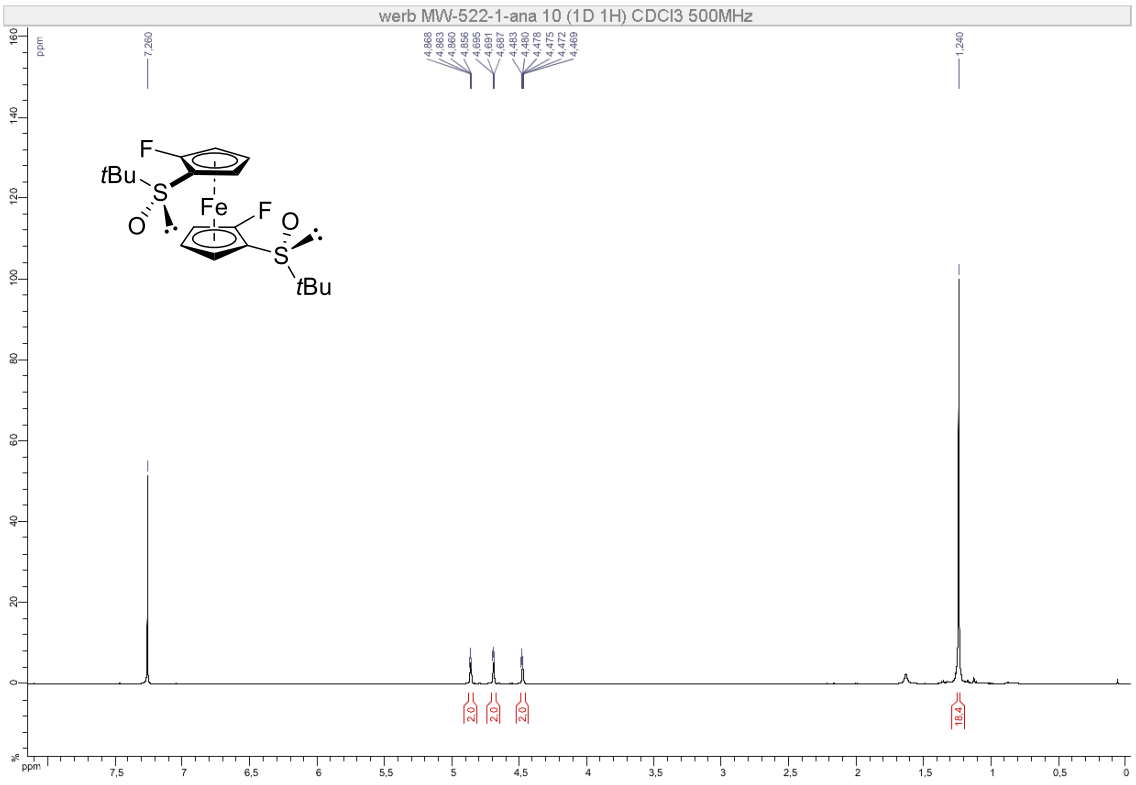
(*R*,*R*,*R*$_P$)-*S*,*S*'-Di-*tert*-butyl-2-((α,α-diphenyl)hydroxymethyl)ferrocene-1,1'-disulfoxide

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

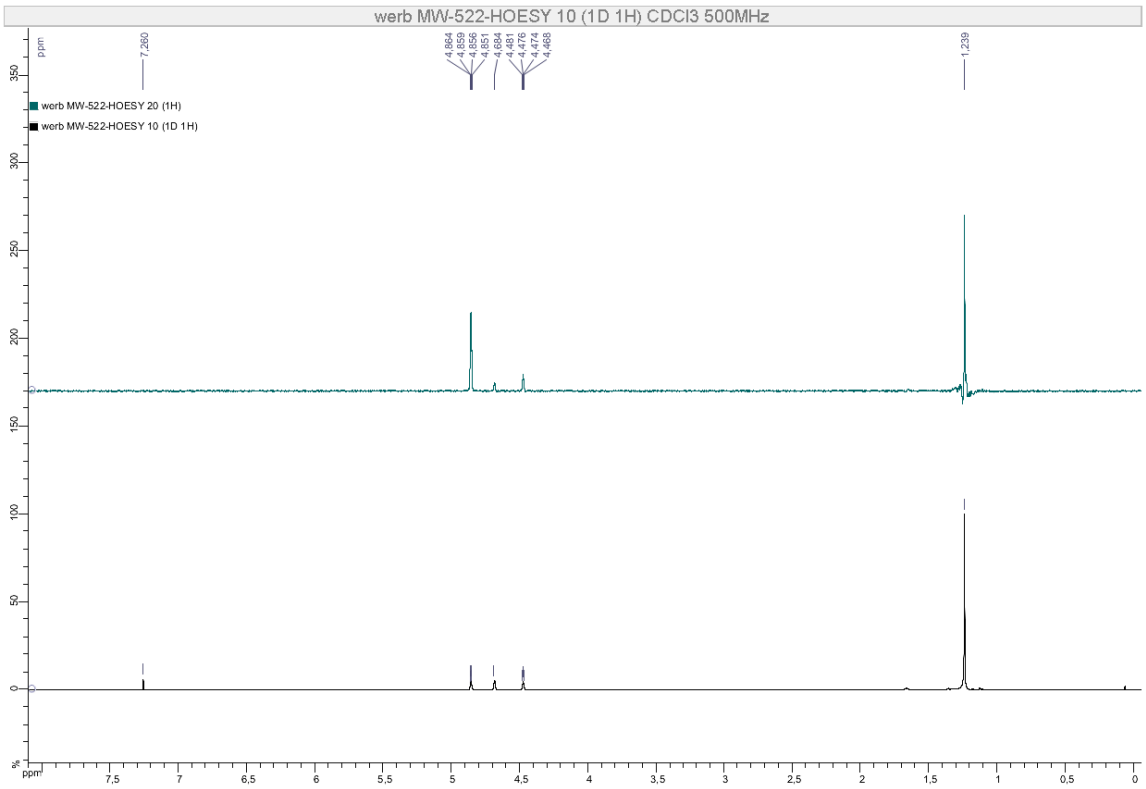


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-difluoroferrocene-1,1'-disulfoxide (*R*P,*R*P-2d)

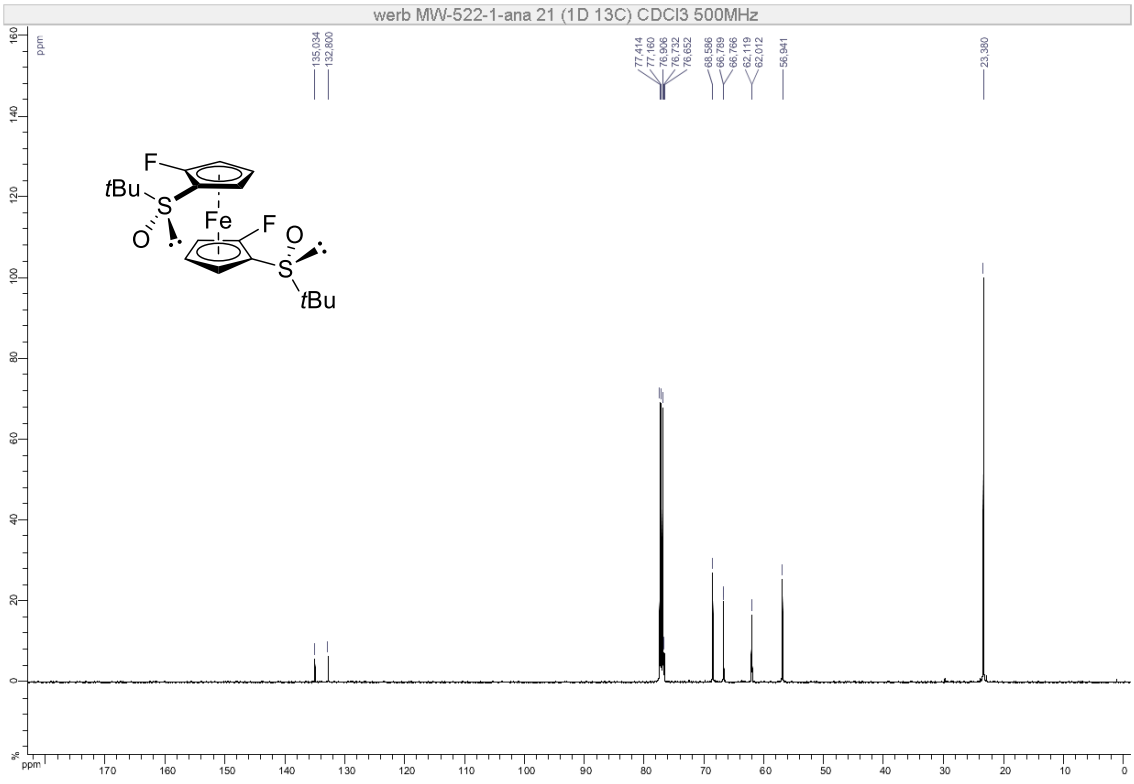
^{1}H NMR (500 MHz, $CDCl_3$)



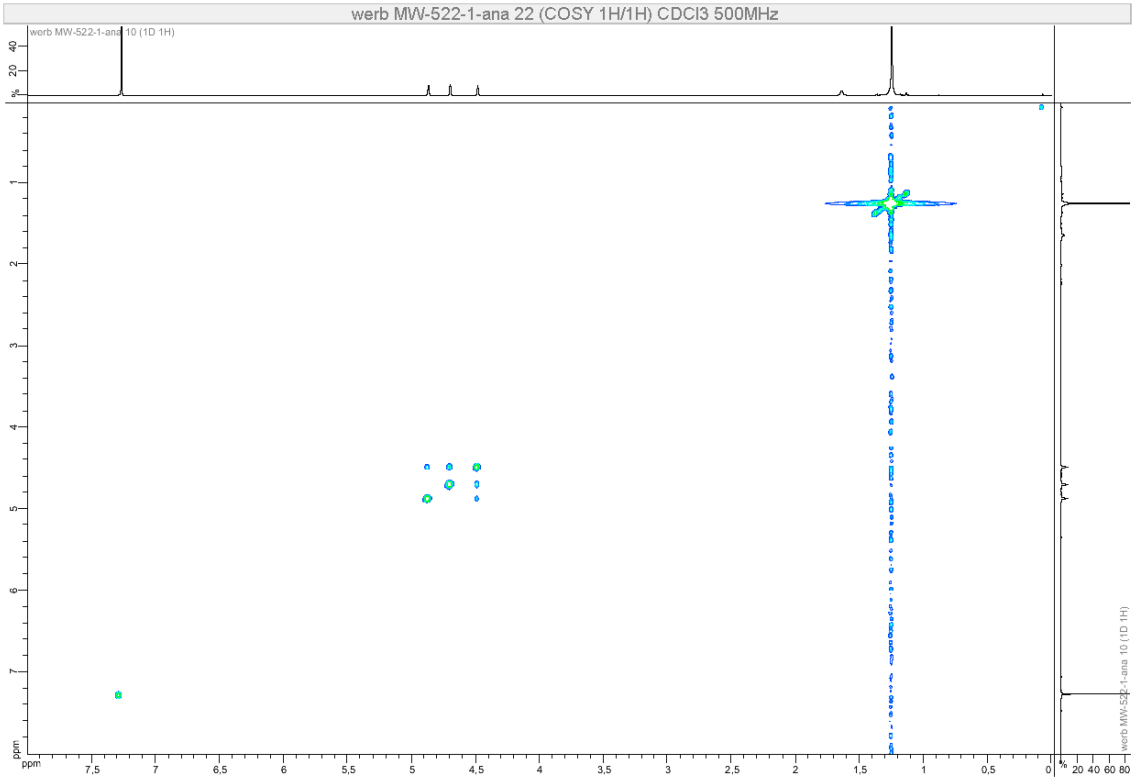
HOESY (500 MHz, $CDCl_3$) Irradiation at -182.6 ppm – Superposition of ^{1}H (bottom) and HOESY (top) spectra.



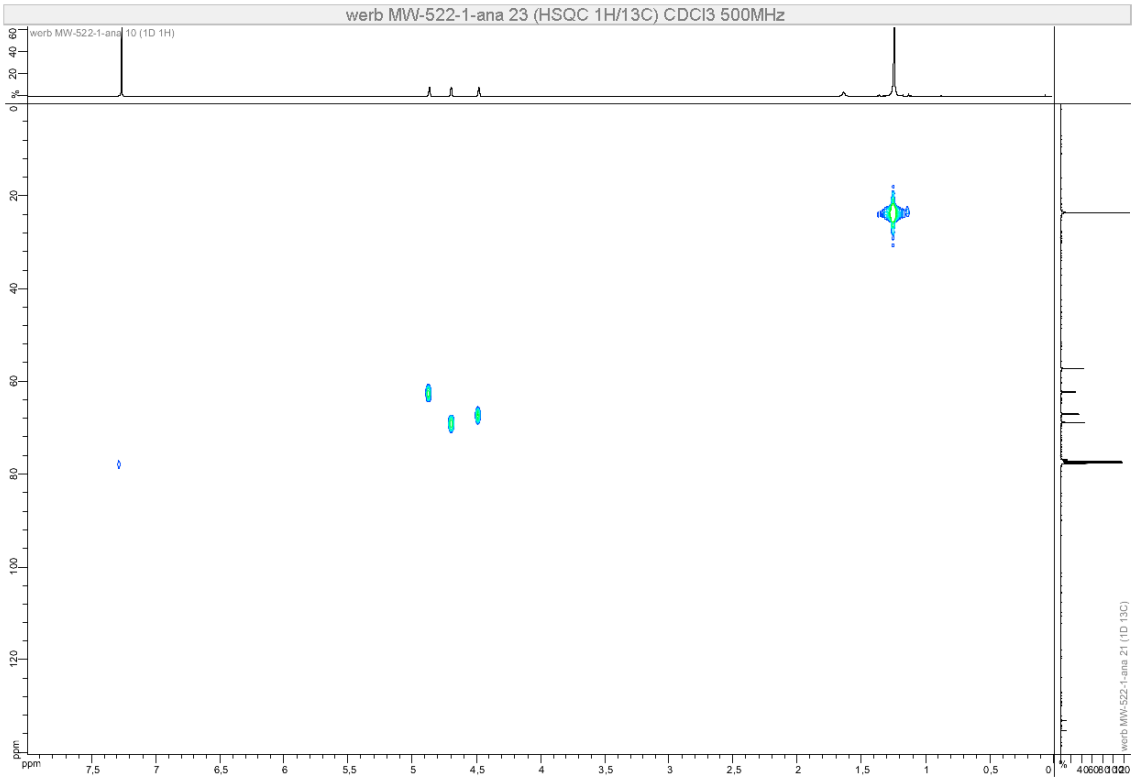
^{13}C NMR (126 MHz, $CDCl_3$)



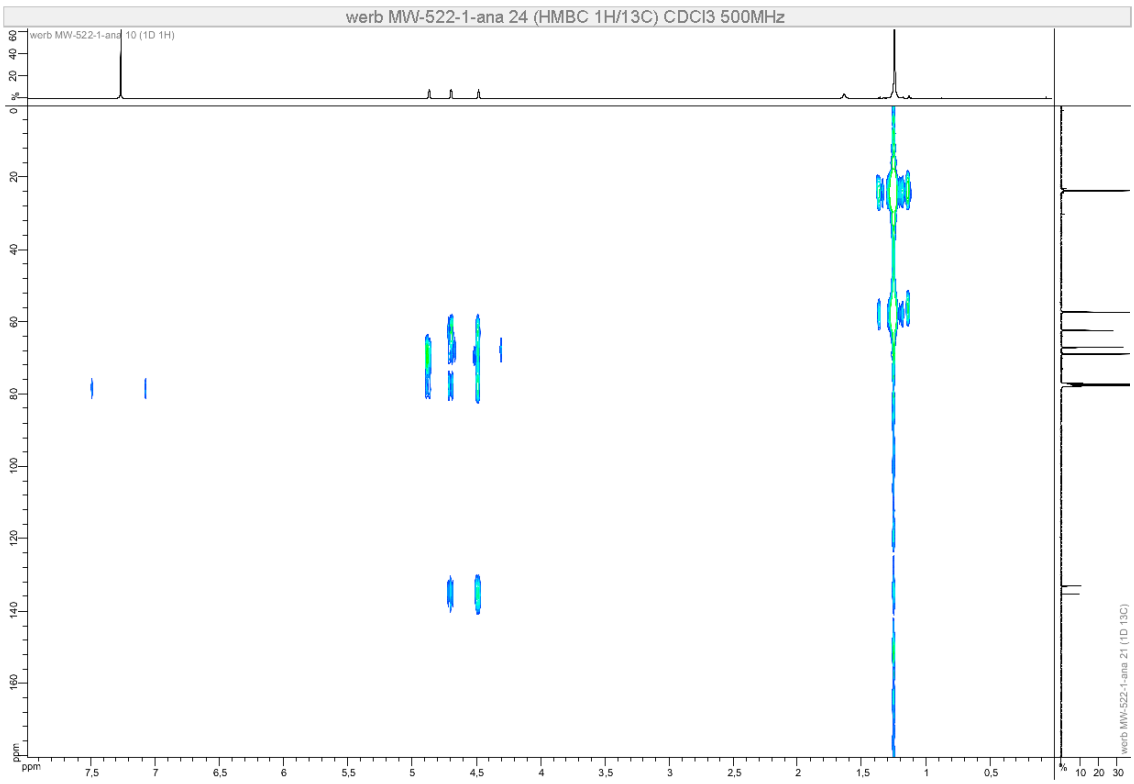
COSY (500 MHz, $CDCl_3$)



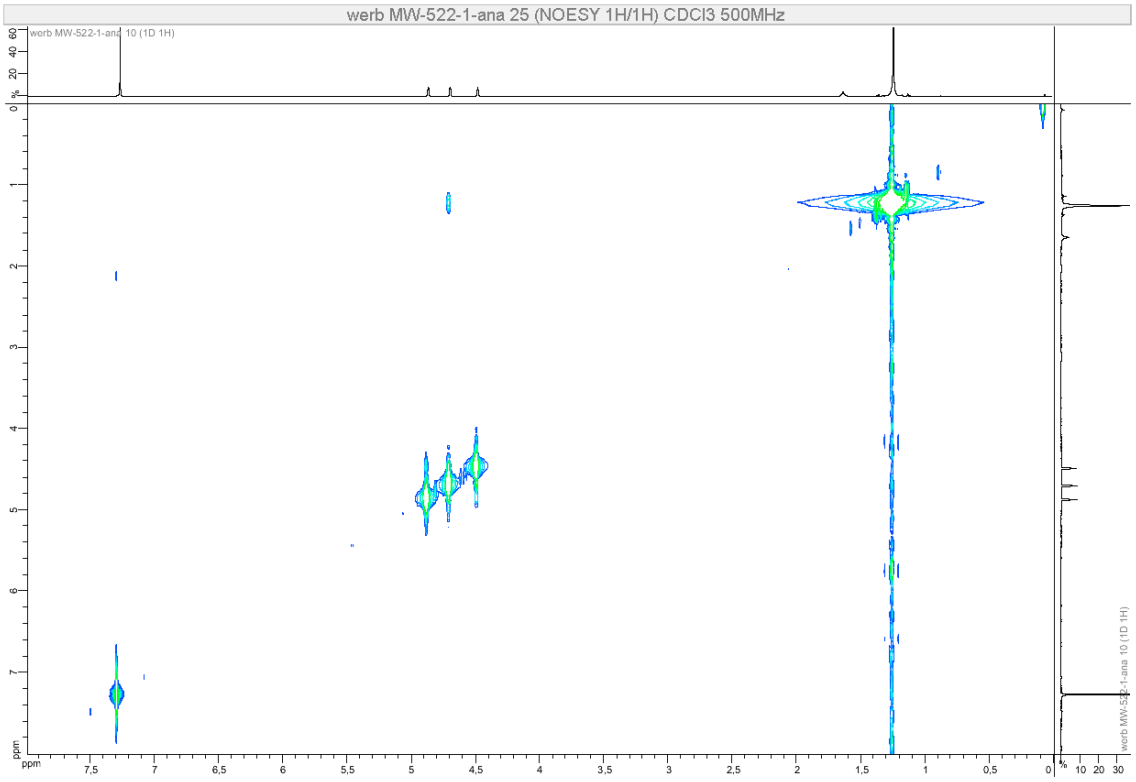
HSQC (500 MHz, $CDCl_3$)



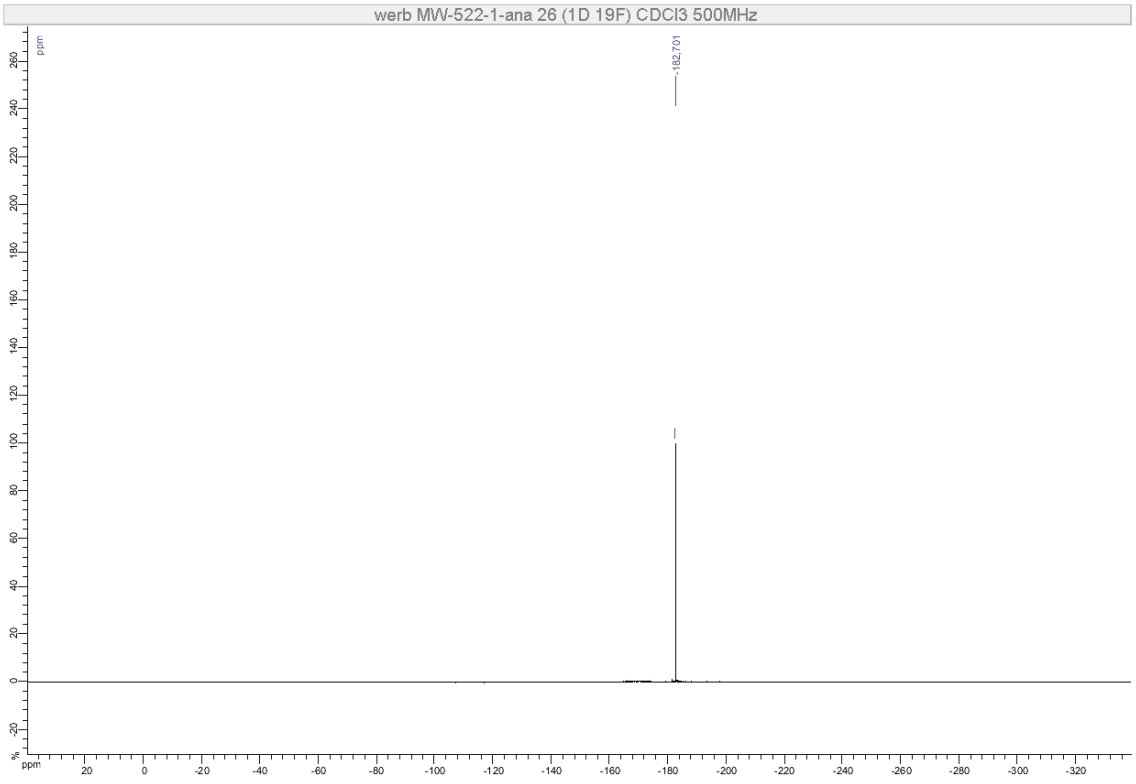
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

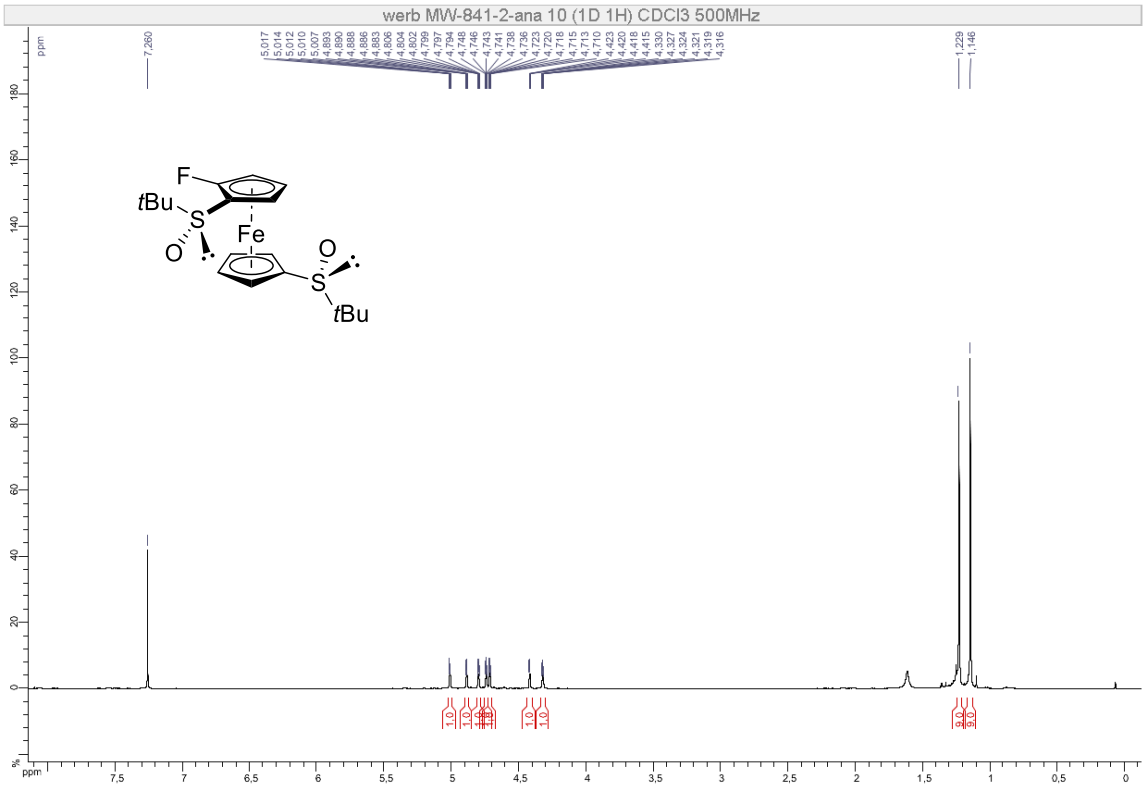


^{19}F NMR (470 MHz, $CDCl_3$)

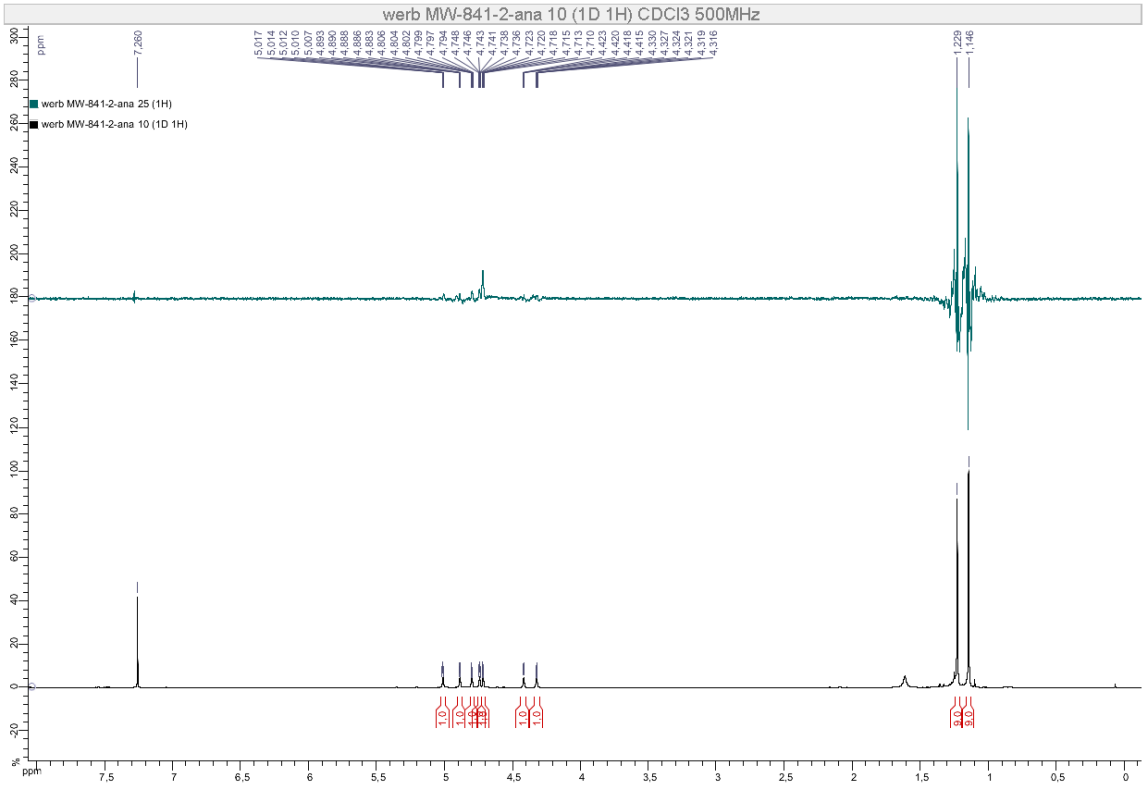


(*R*,*R*,*R*P)-*S*,*S*'-Di-*tert*-butyl-2-fluoroferrocene-1,1'-disulfoxide

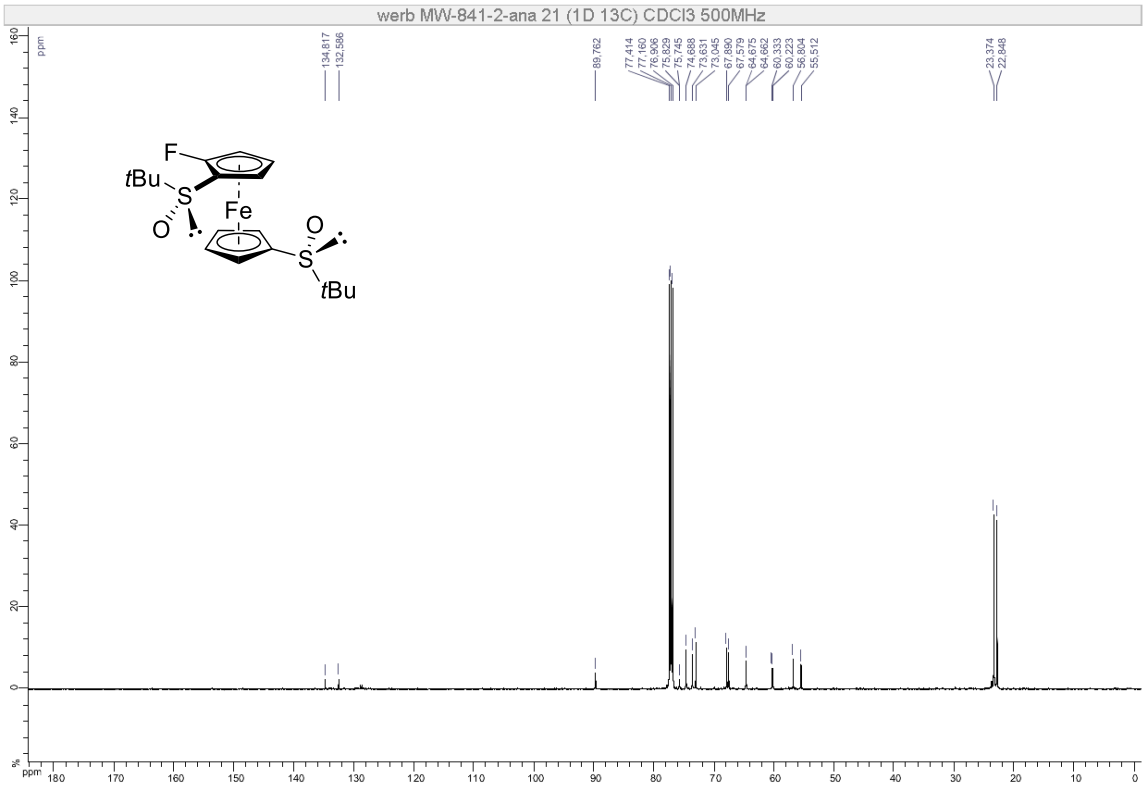
^{1}H NMR (500 MHz, $CDCl_3$)



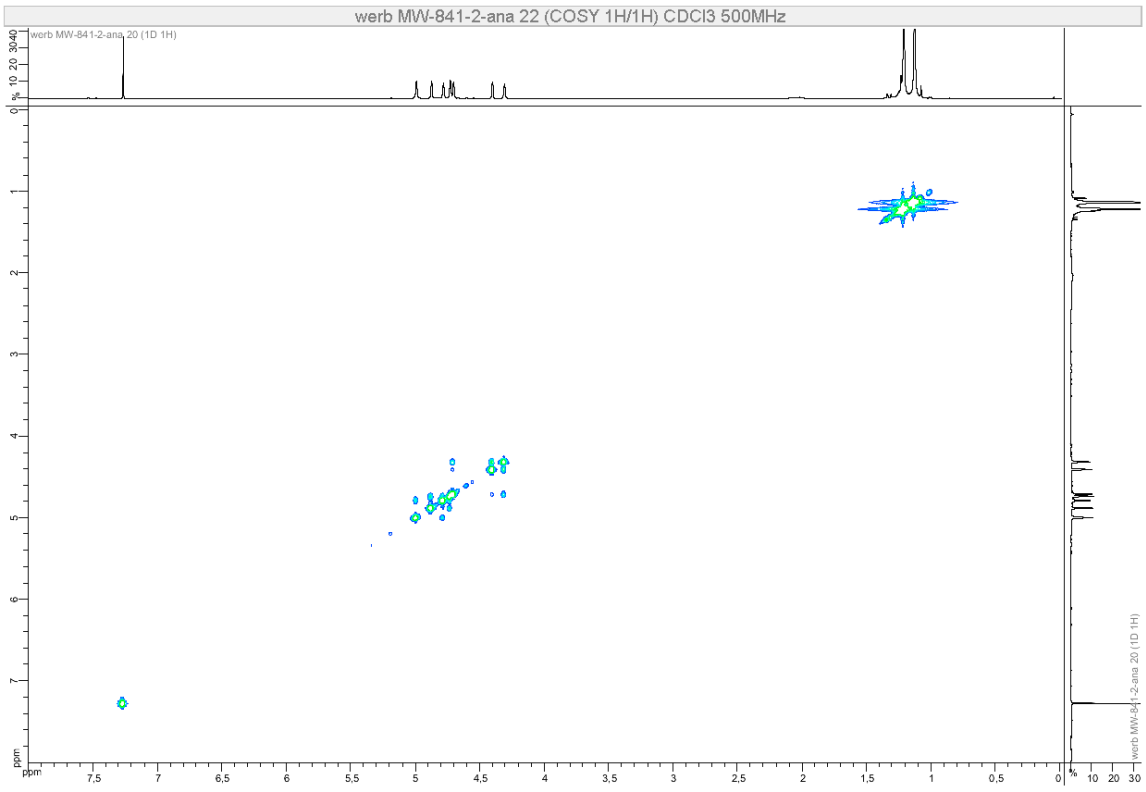
HOESY (500 MHz, $CDCl_3$) Irradiation at -183.6 ppm – Superposition of ^{1}H (bottom) and HOESY (top) spectra.



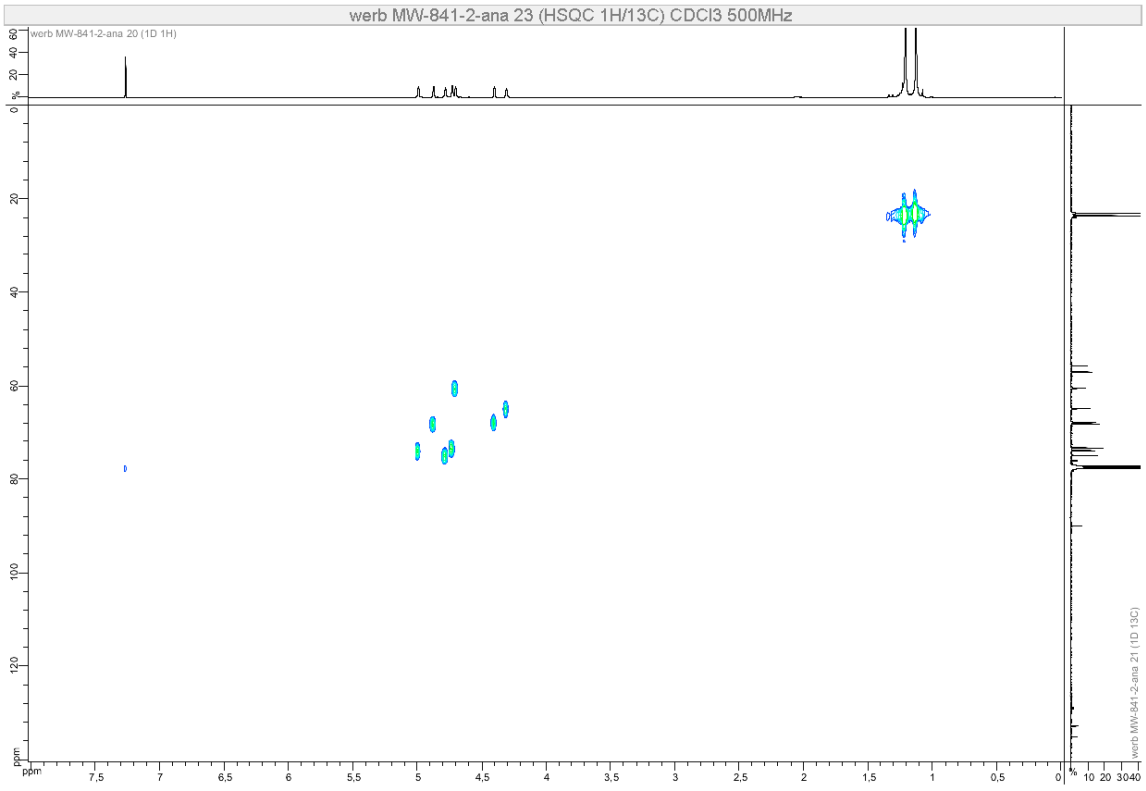
^{13}C NMR (126 MHz, $CDCl_3$)



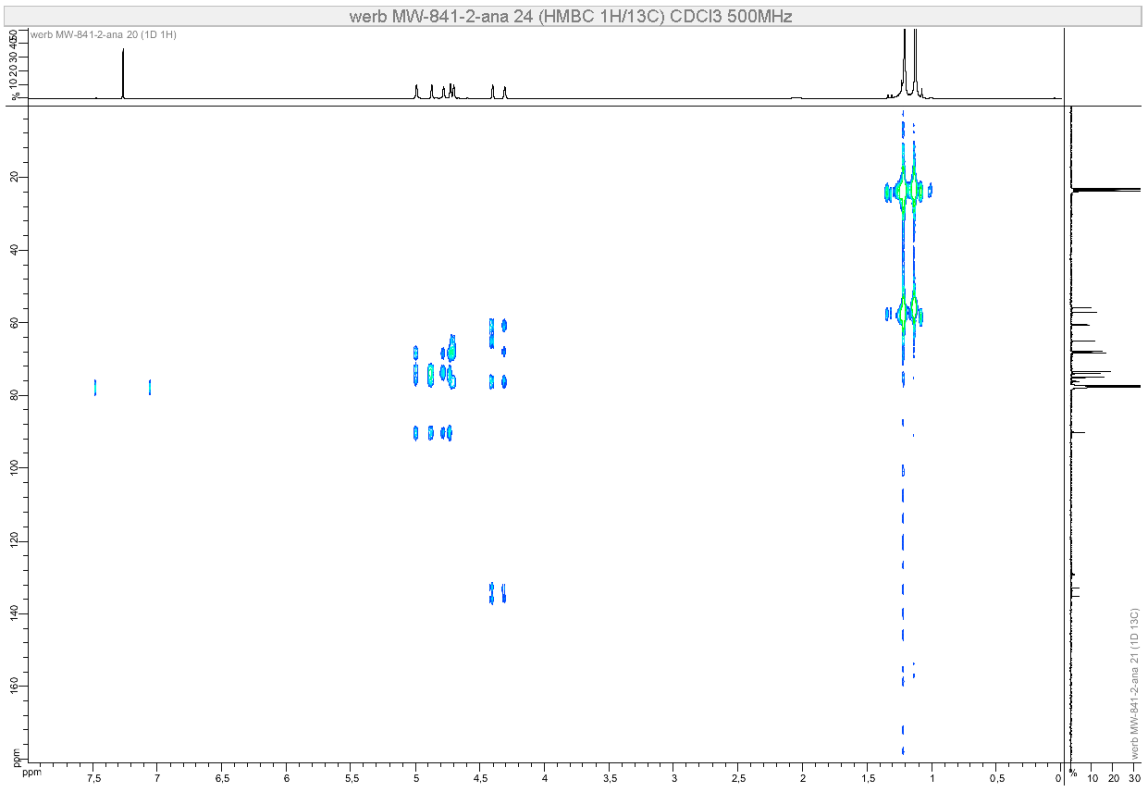
COSY (500 MHz, $CDCl_3$)



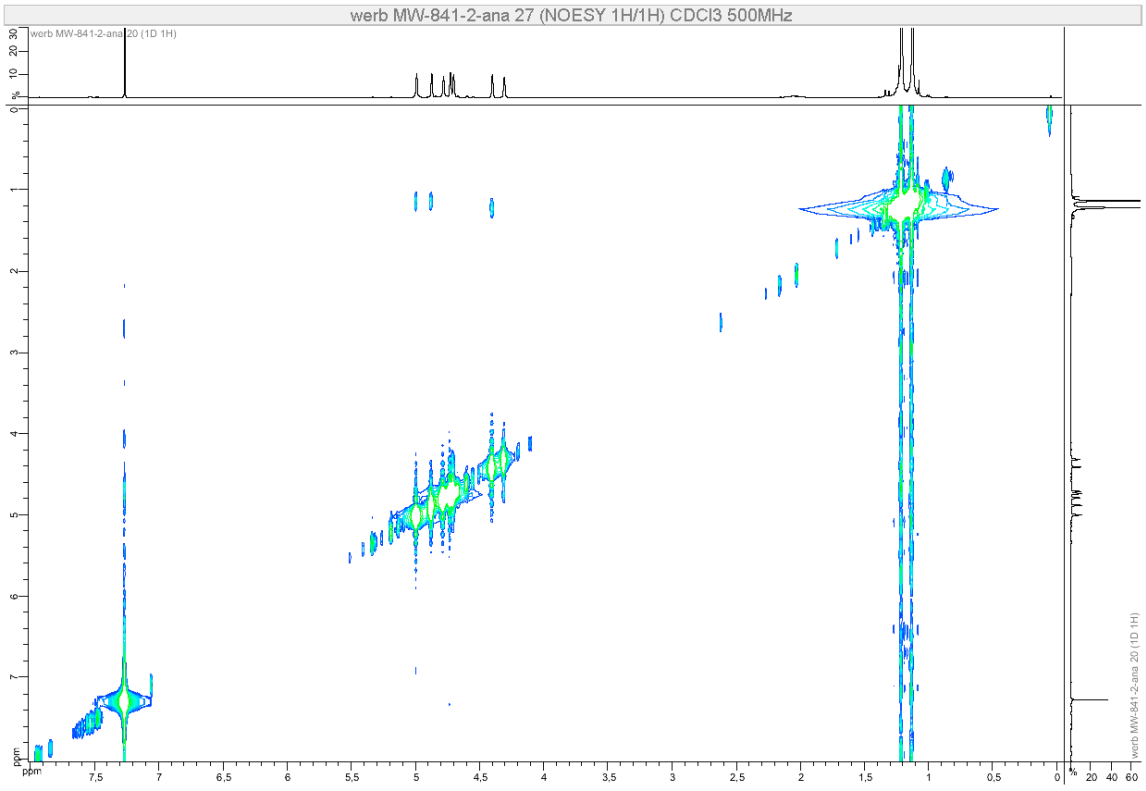
HSQC (500 MHz, $CDCl_3$)



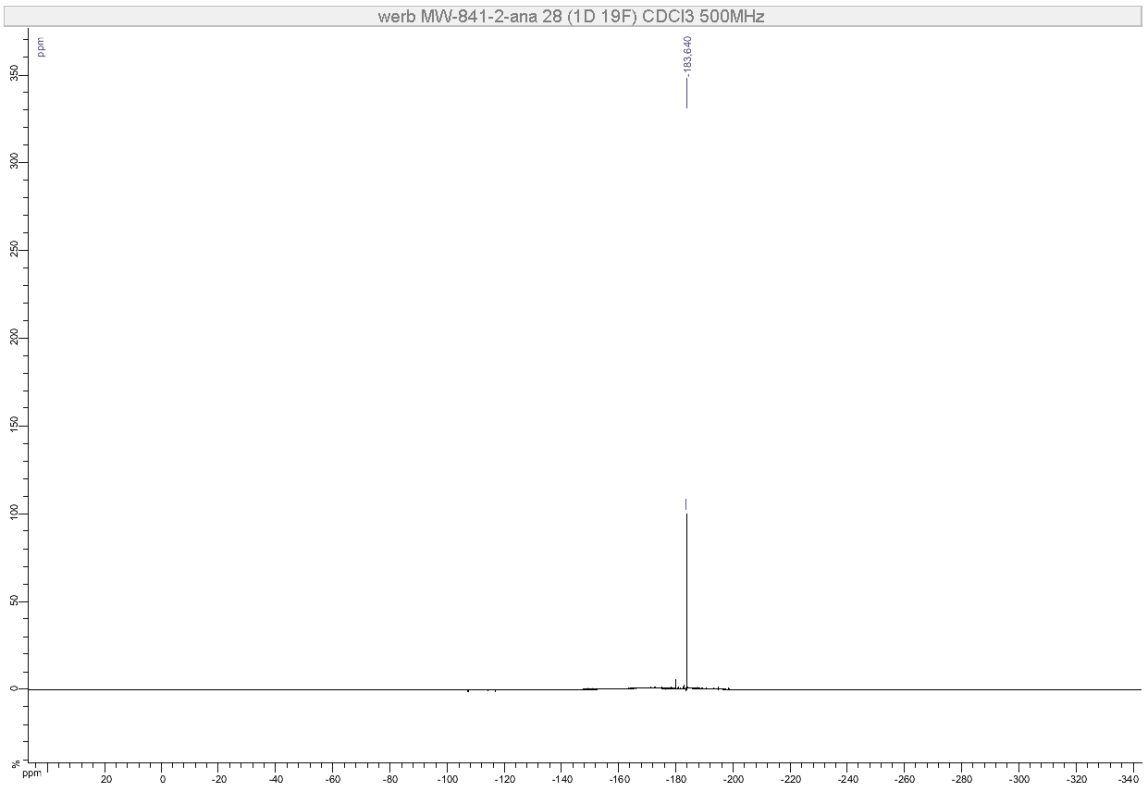
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

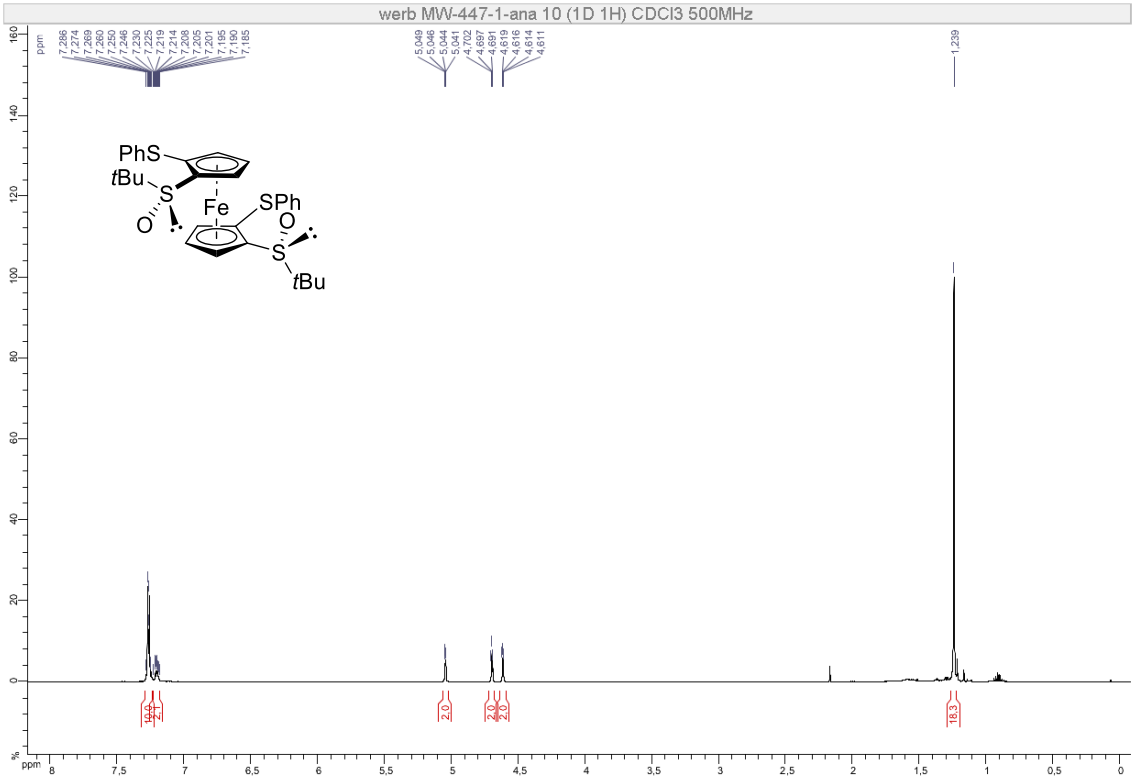


^{19}F NMR (470 MHz, $CDCl_3$)

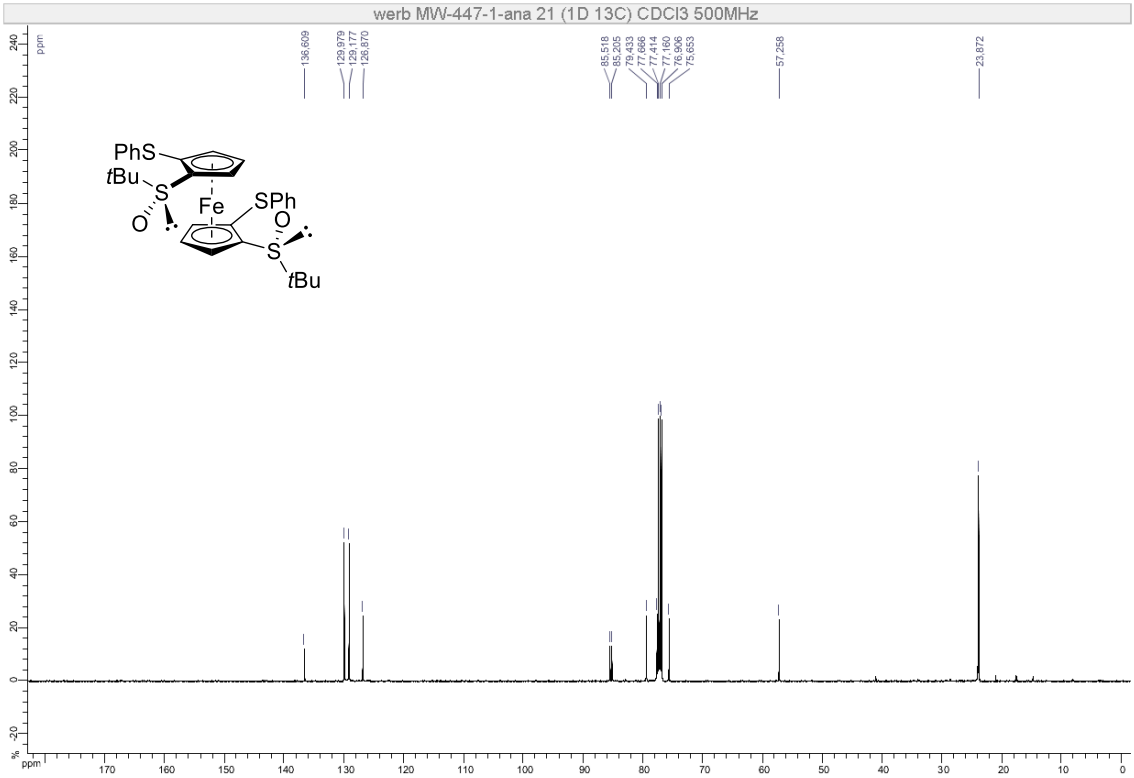


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (*R*P,*R*P-2e)

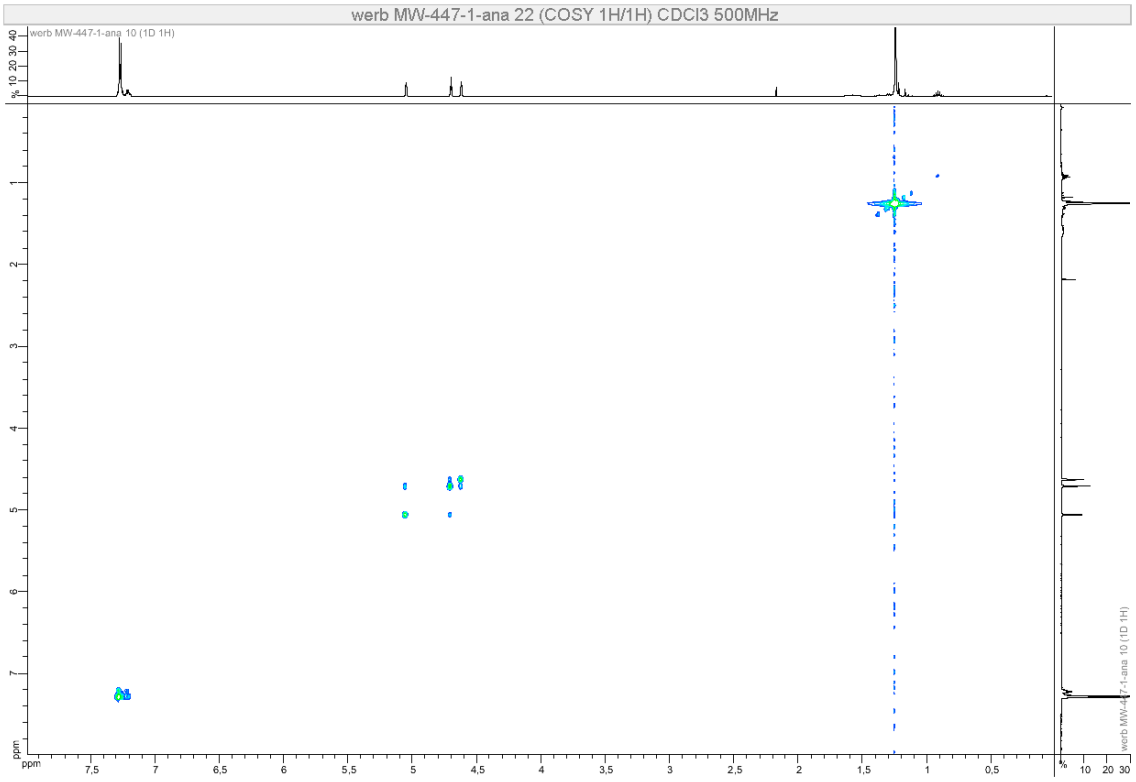
^{1}H NMR (500 MHz, $CDCl_3$)



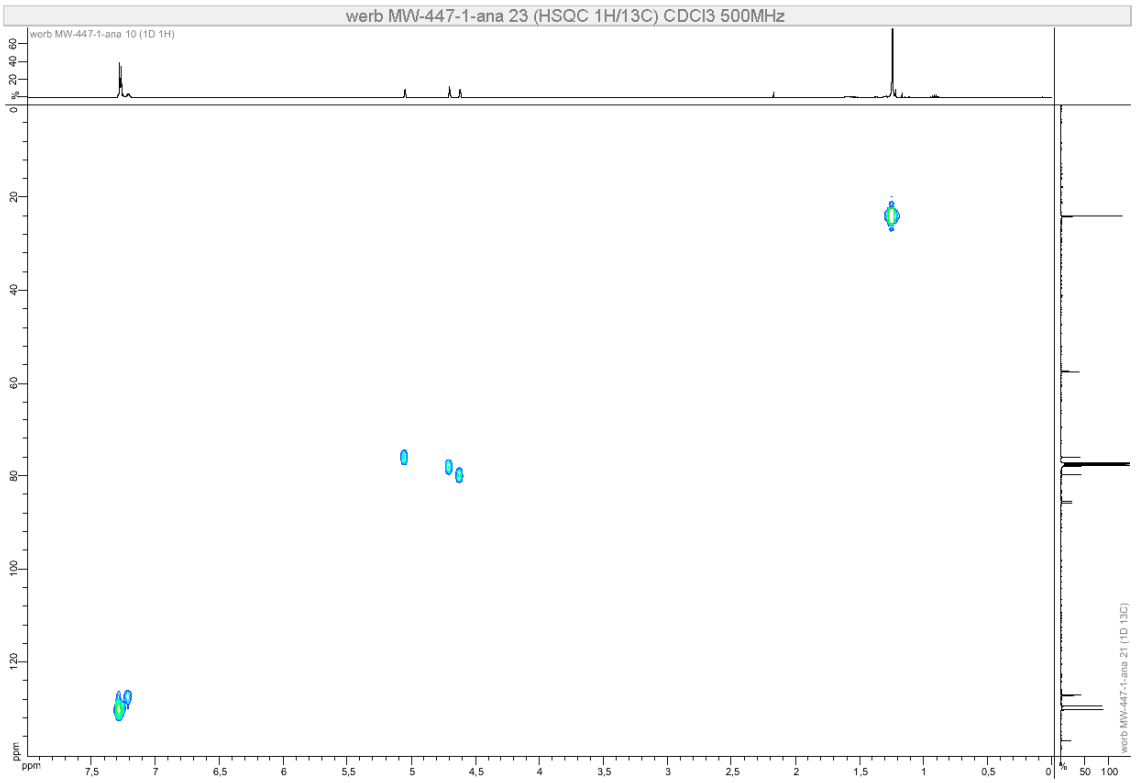
^{13}C NMR (126 MHz, $CDCl_3$)



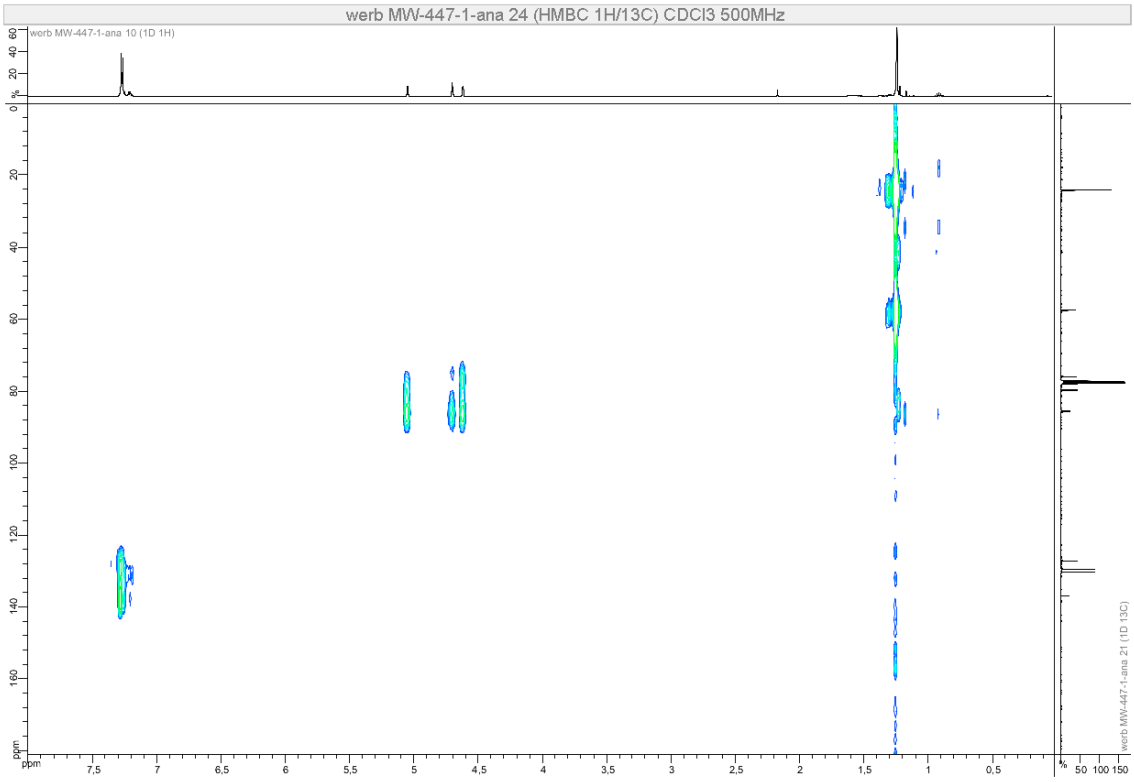
COSY (500 MHz, $CDCl_3$)



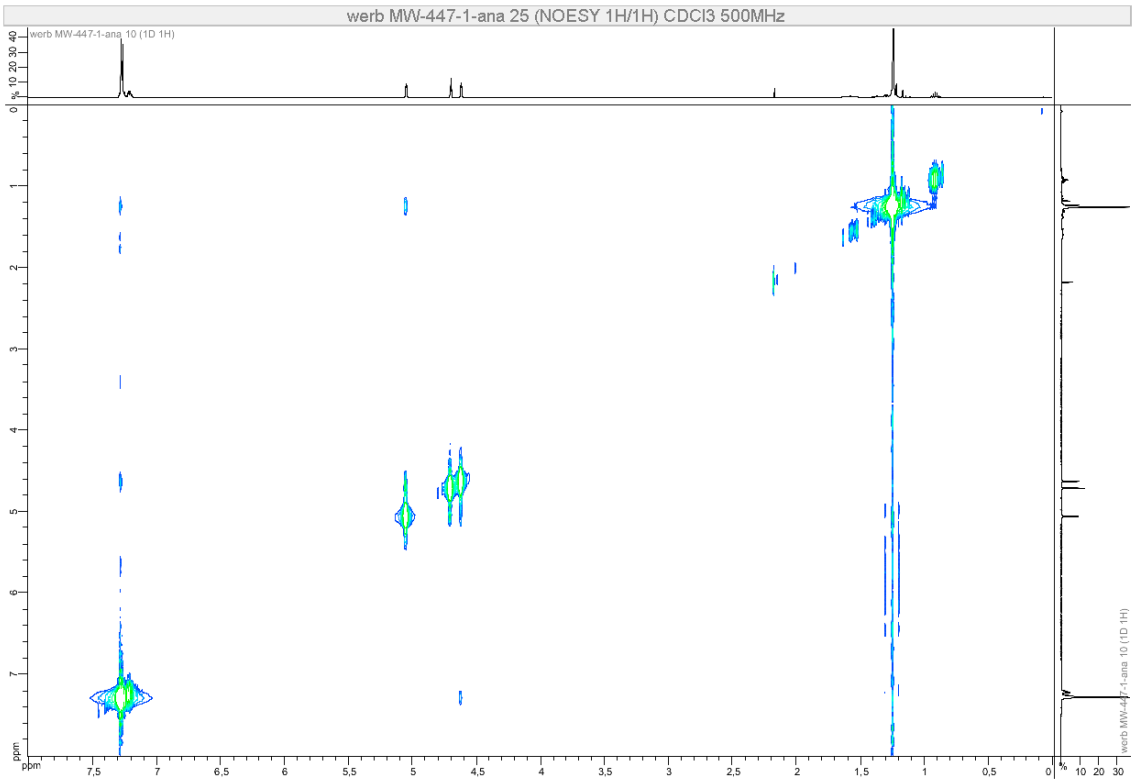
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

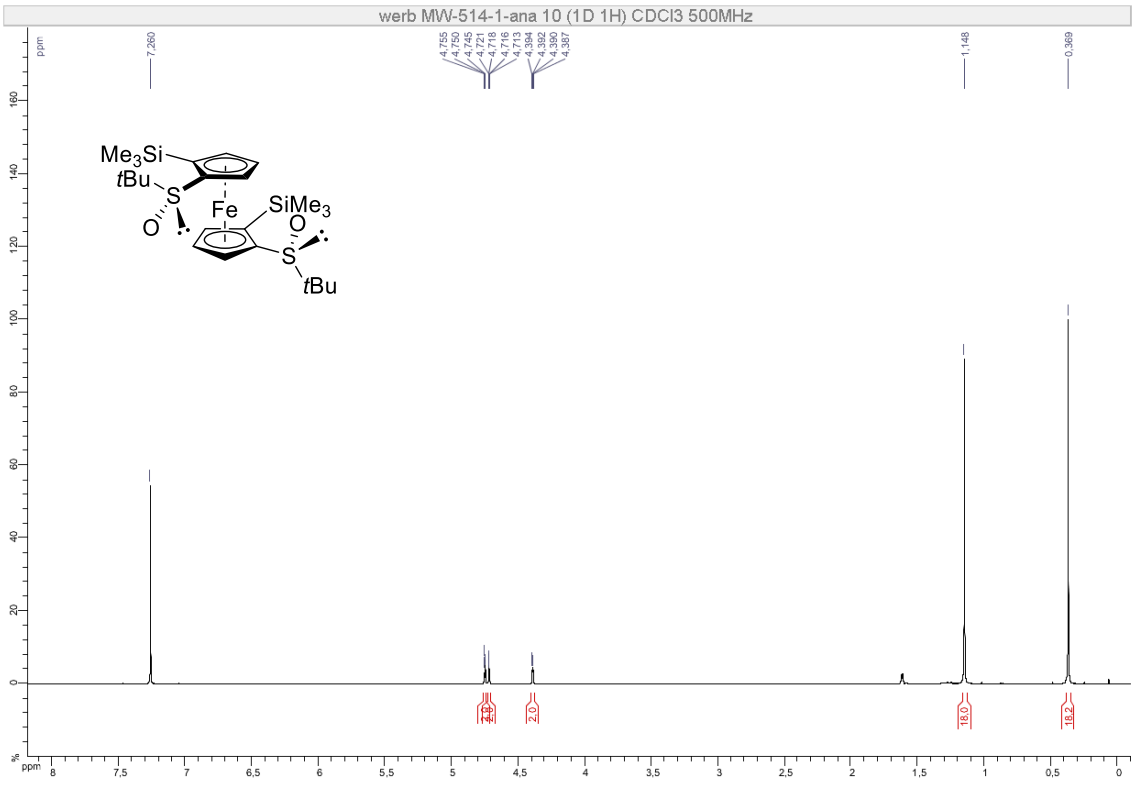


NOESY (500 MHz, $CDCl_3$)

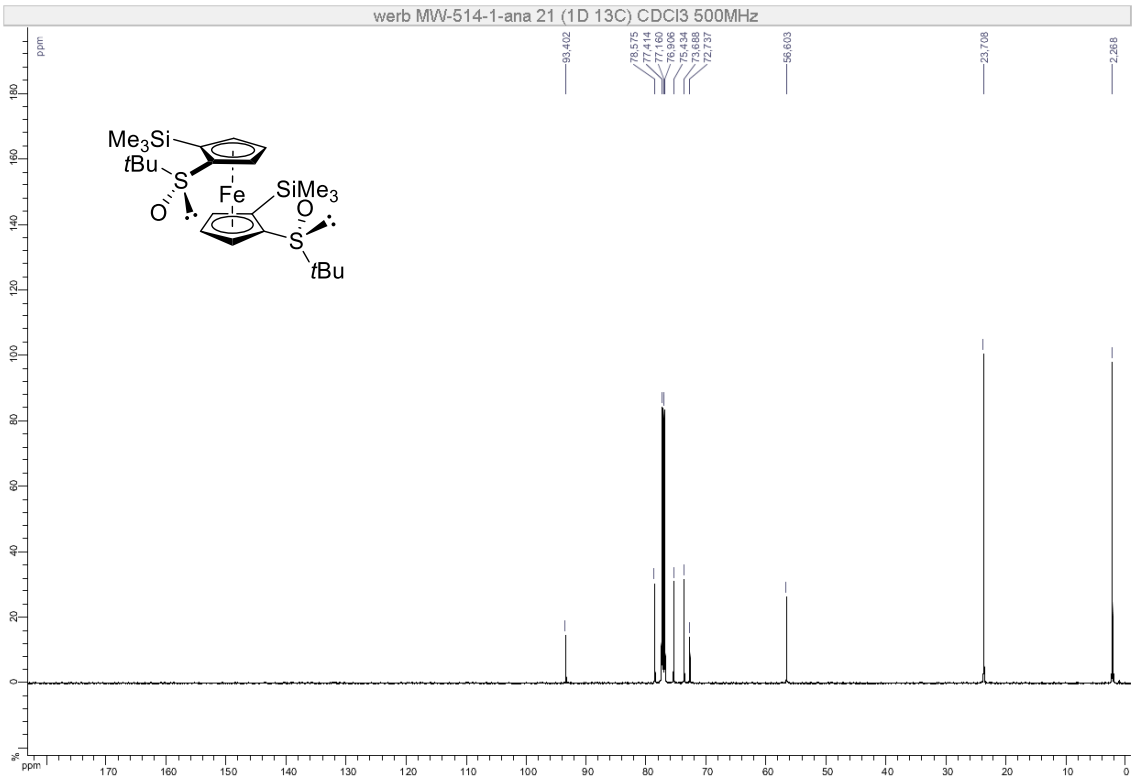


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-2f)

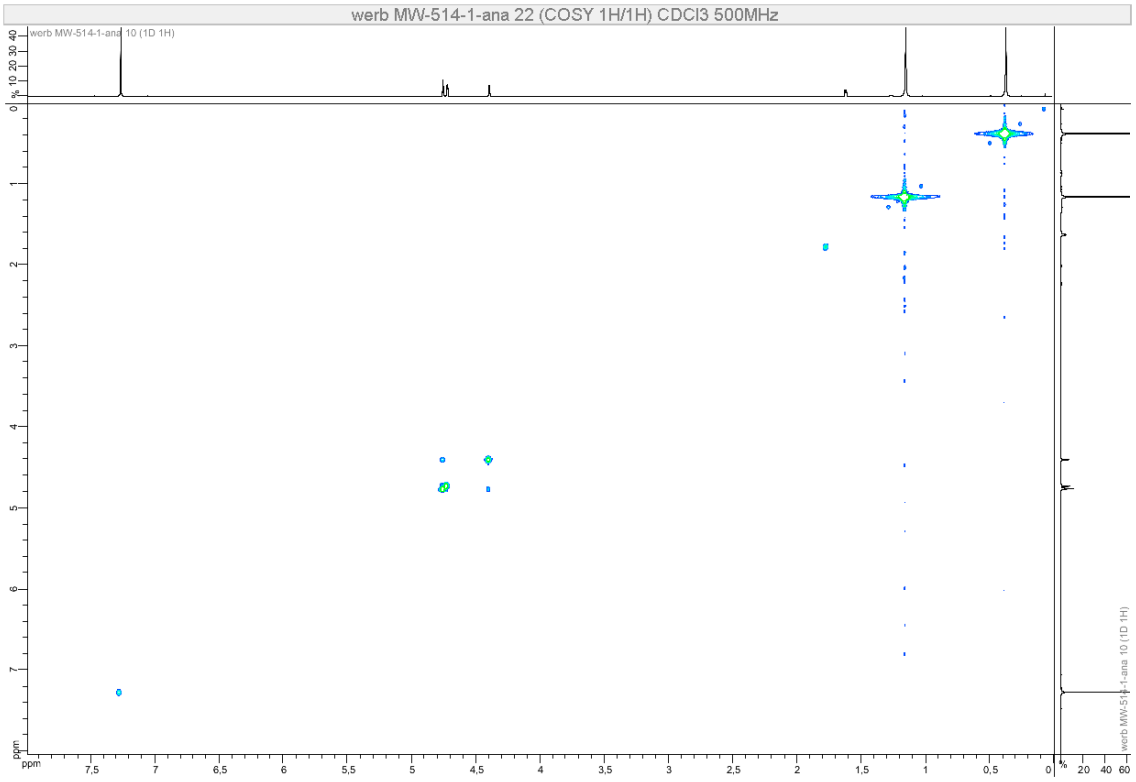
^{1}H NMR (500 MHz, $CDCl_3$)



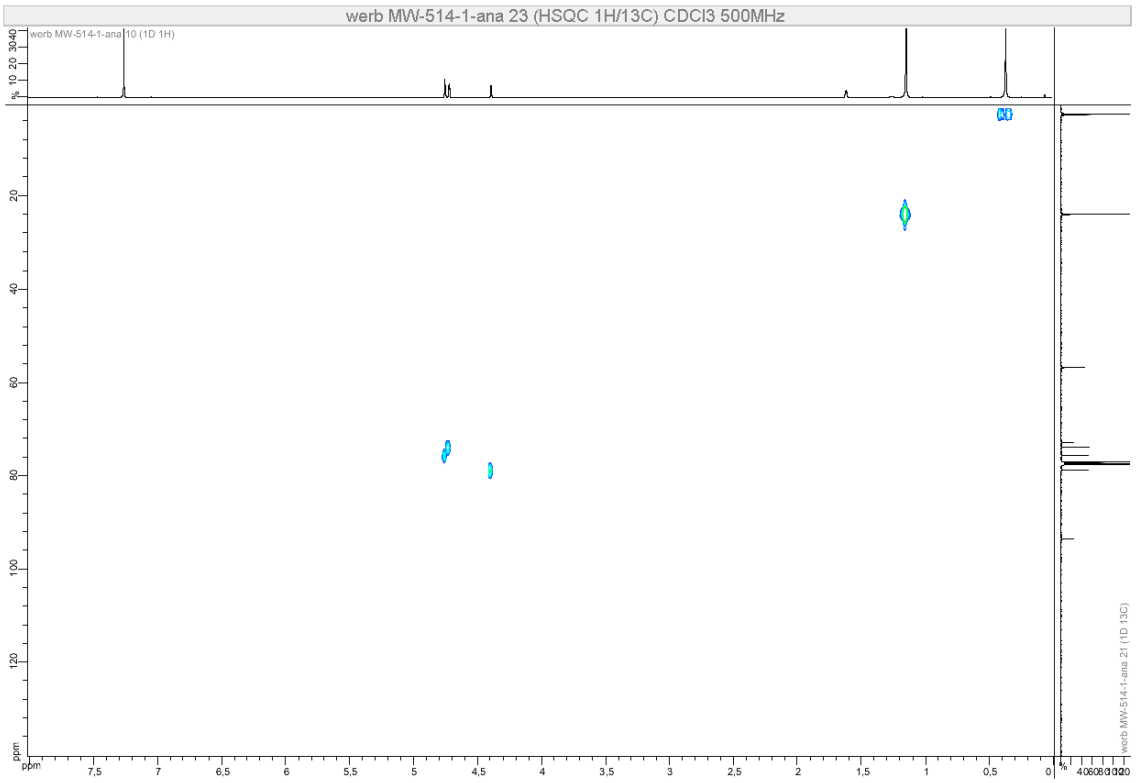
^{13}C NMR (126 MHz, $CDCl_3$)



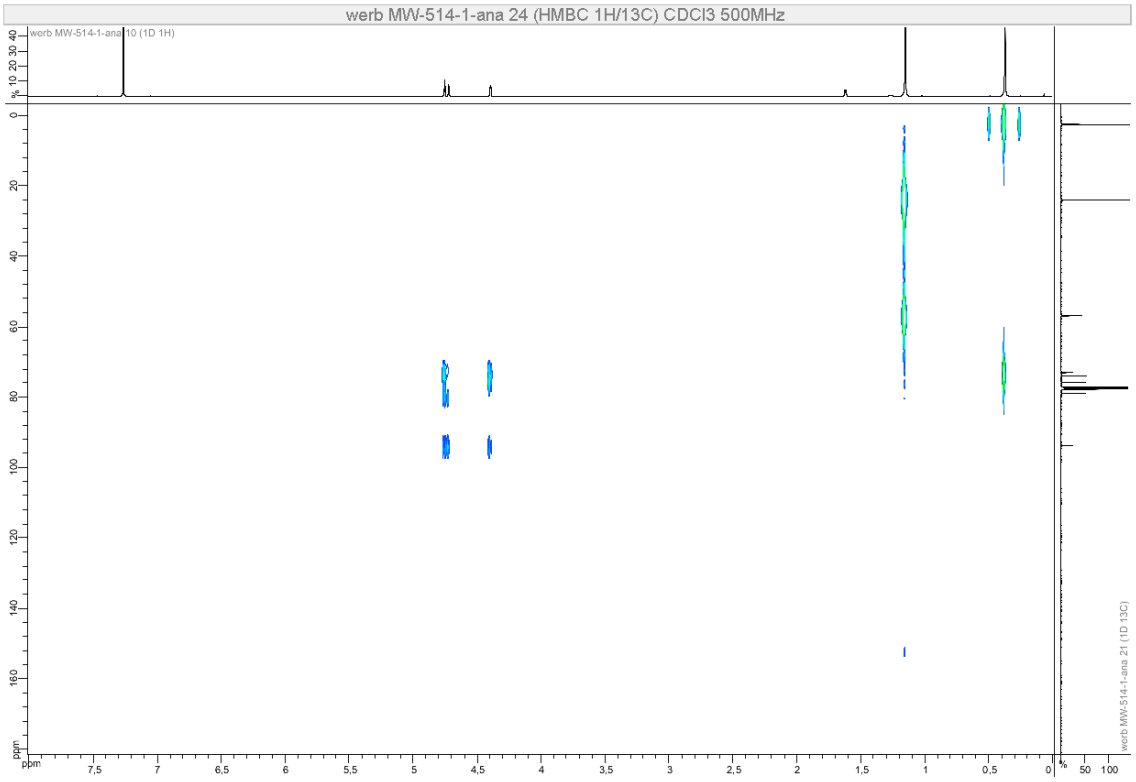
COSY (500 MHz, $CDCl_3$)



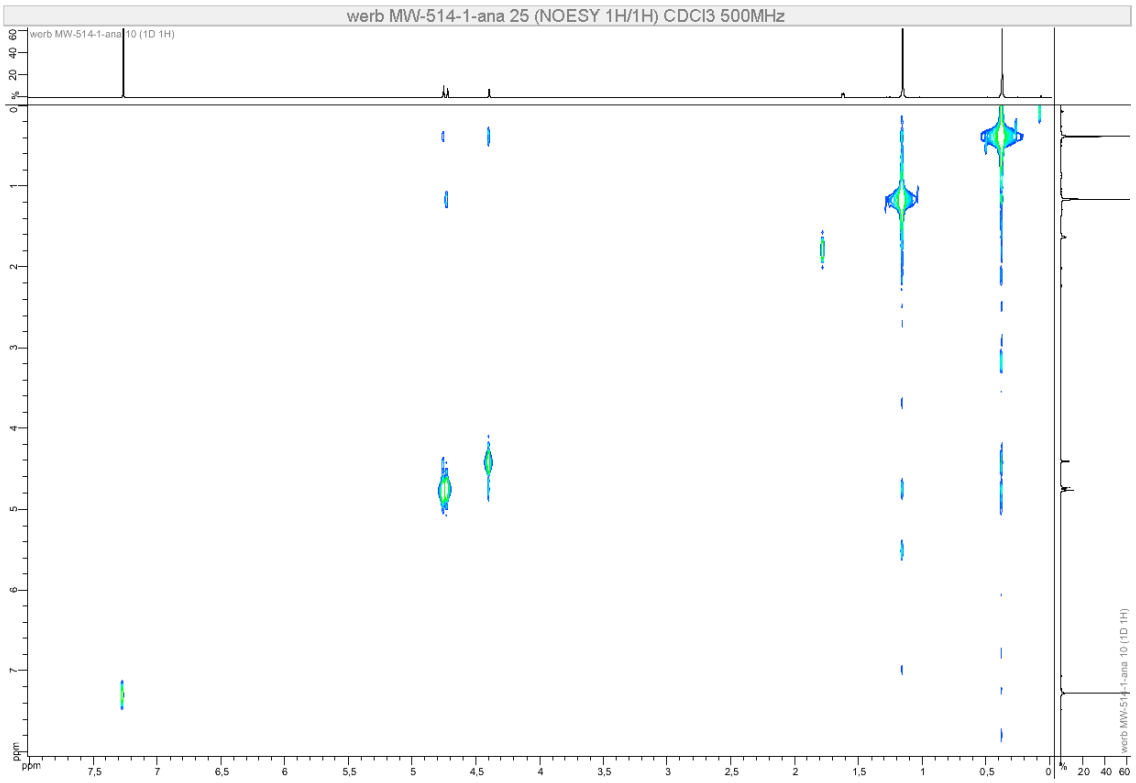
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

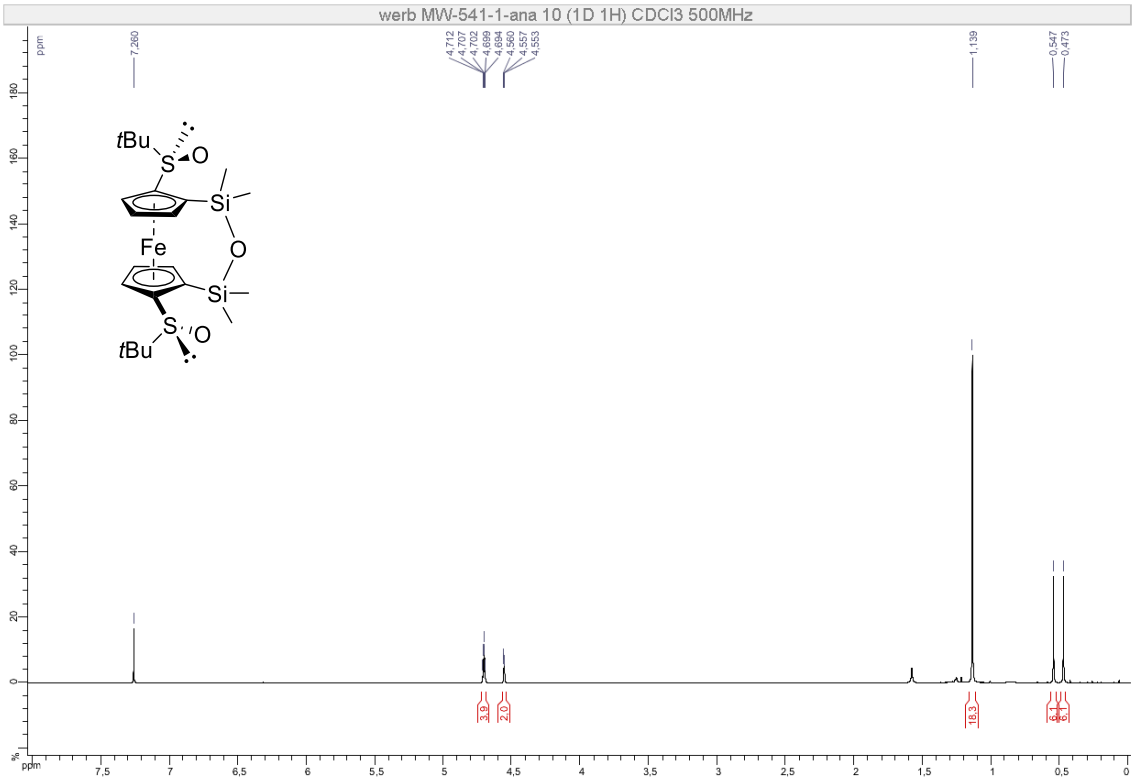


NOESY (500 MHz, $CDCl_3$)

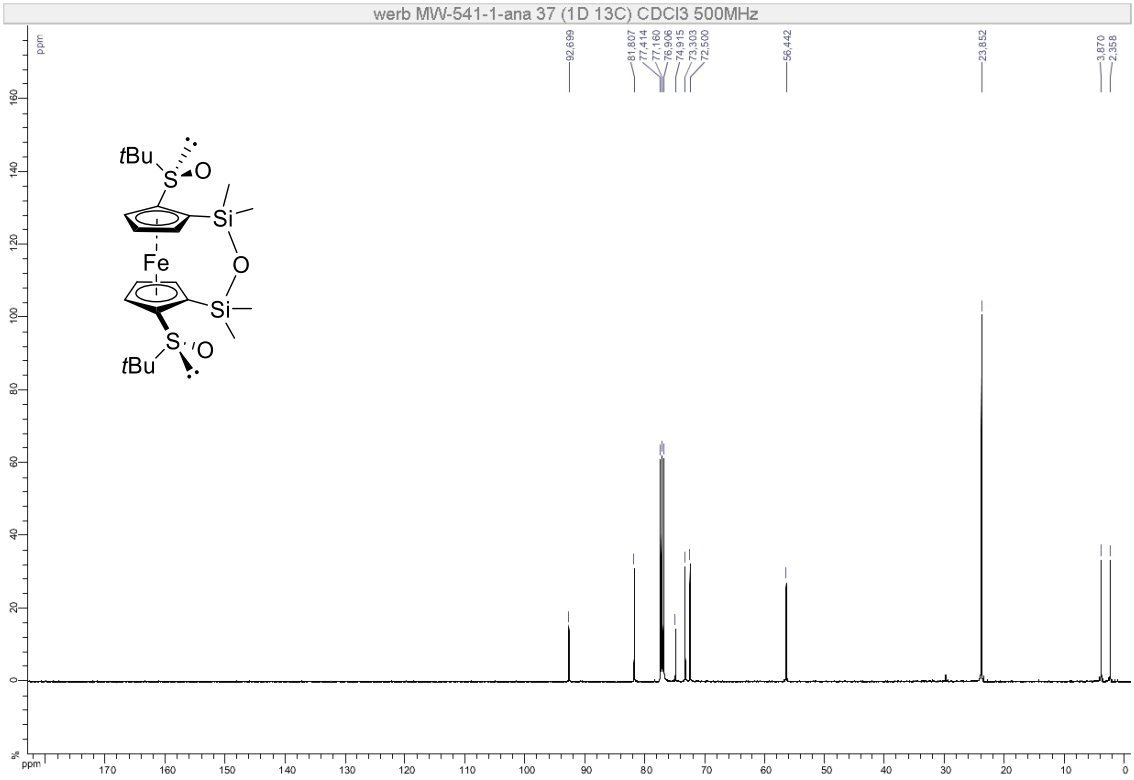


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-2g1)

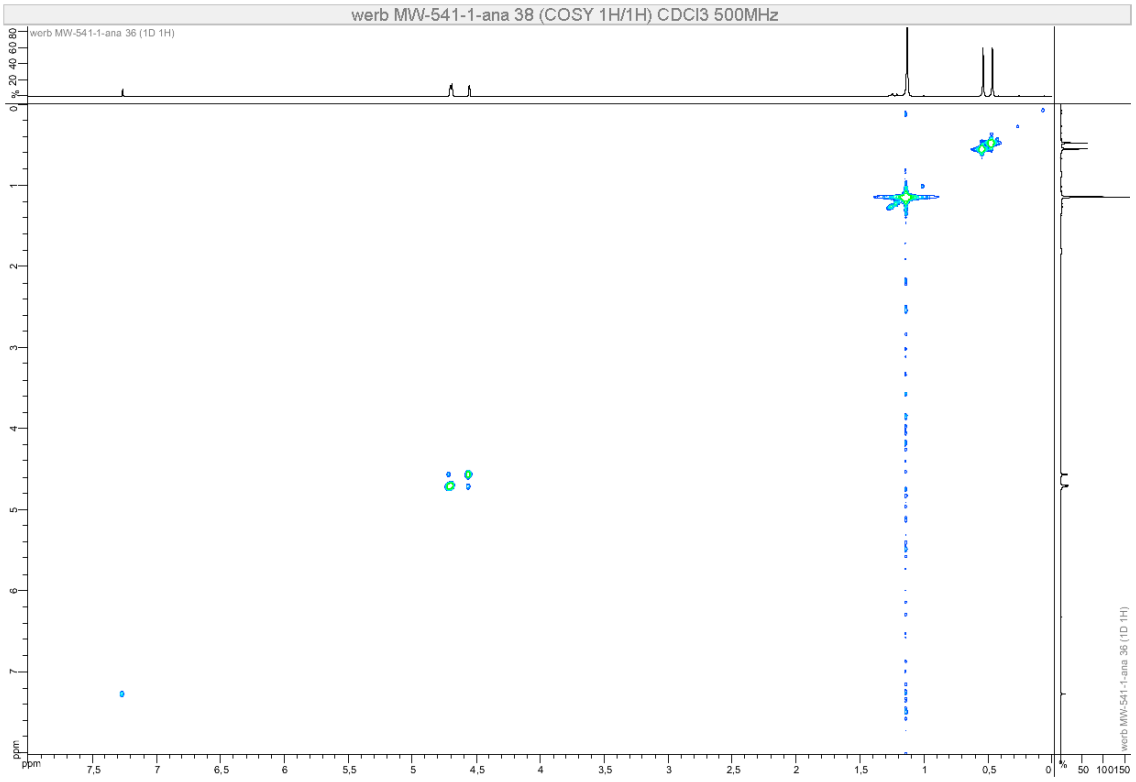
^{1}H NMR (500 MHz, $CDCl_3$)



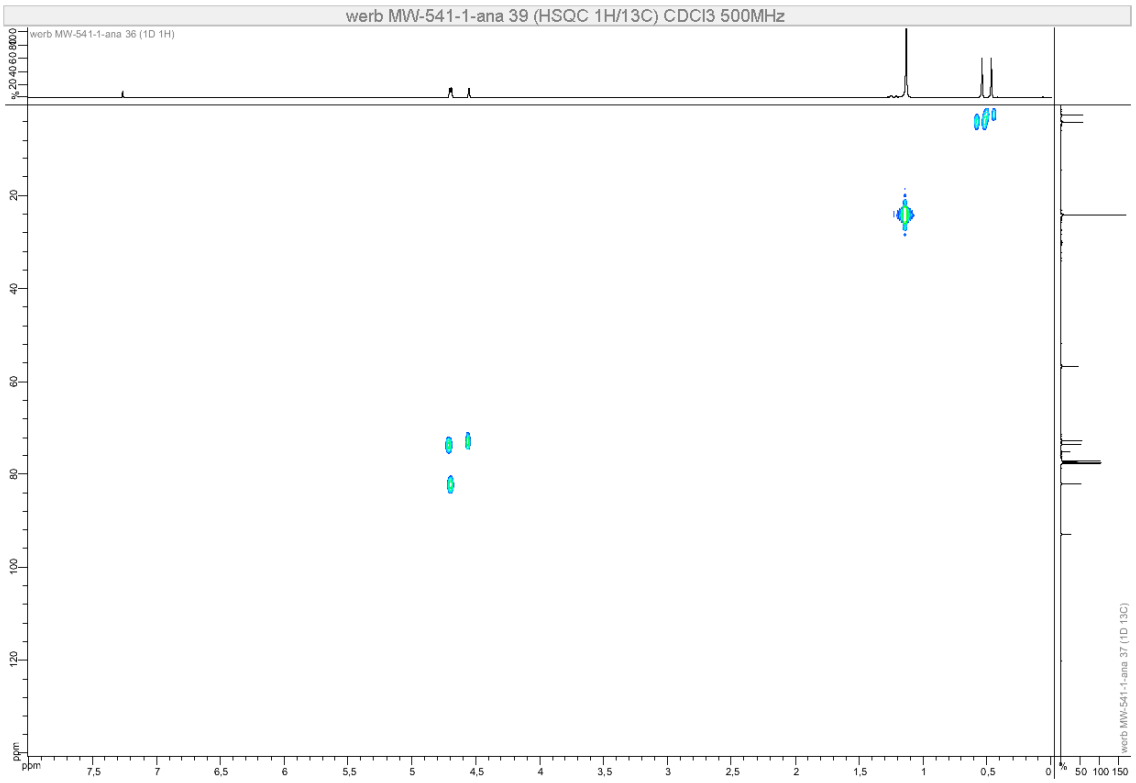
^{13}C NMR (126 MHz, $CDCl_3$)



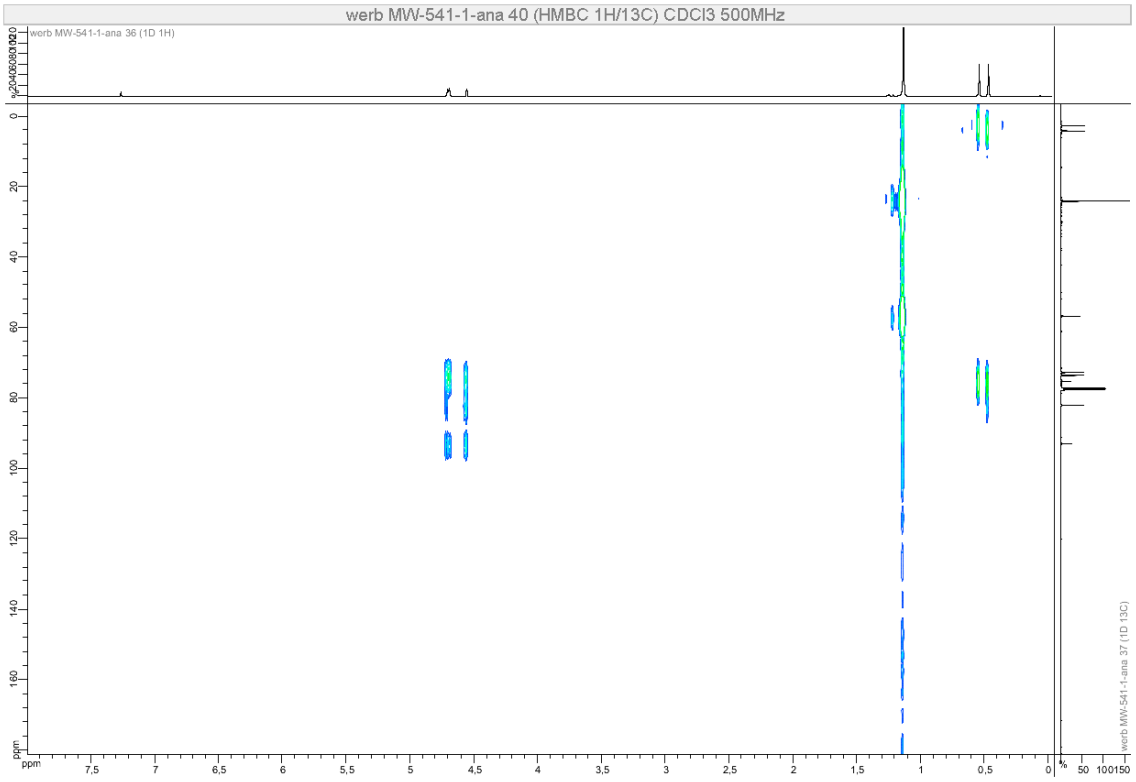
COSY (500 MHz, $CDCl_3$)



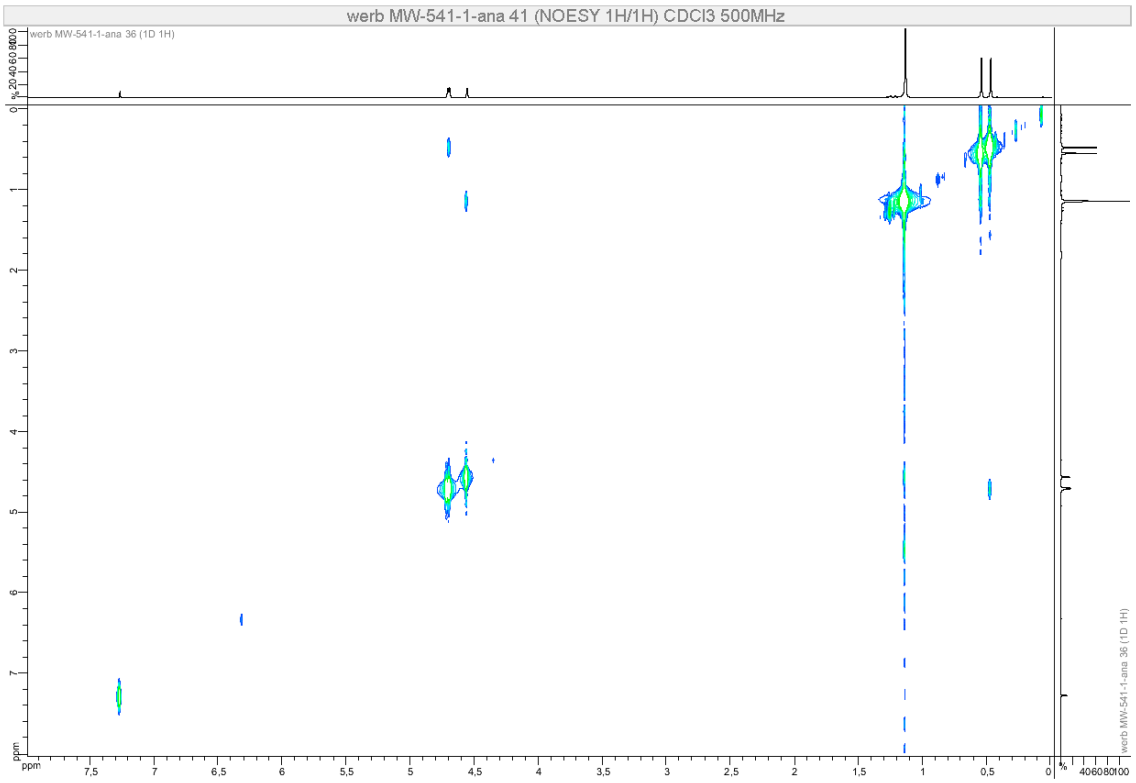
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

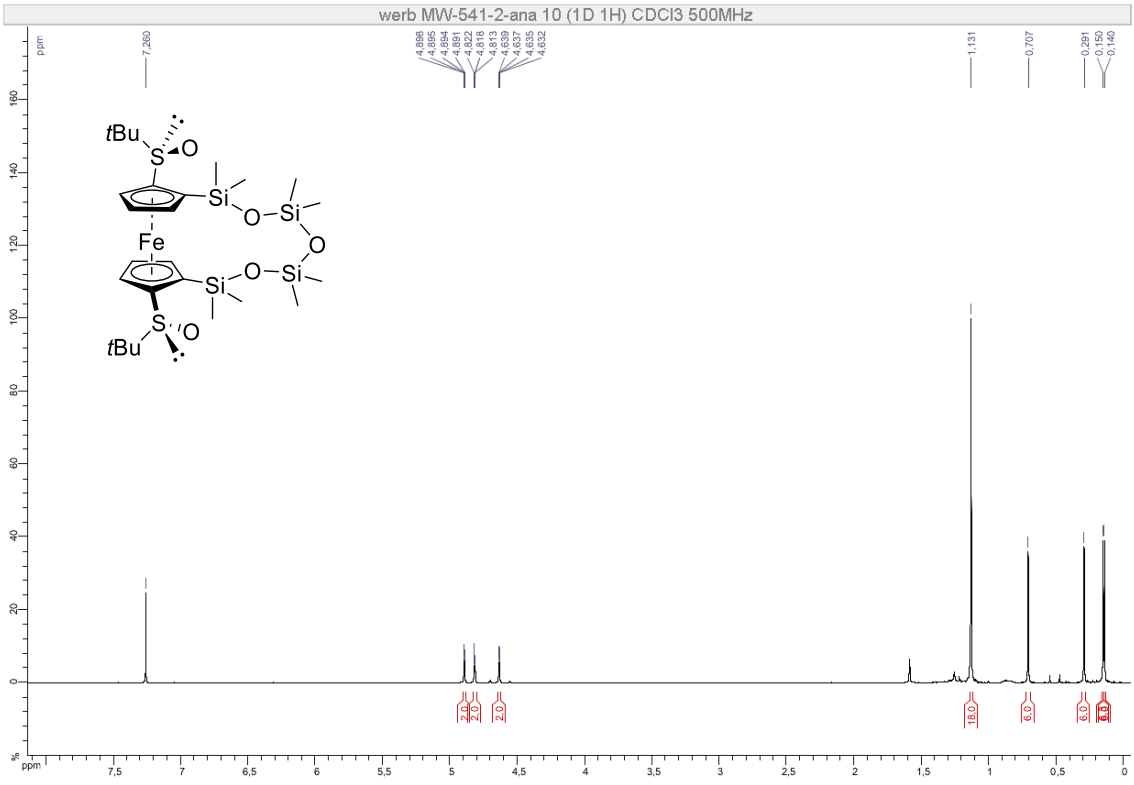


NOESY (500 MHz, $CDCl_3$)

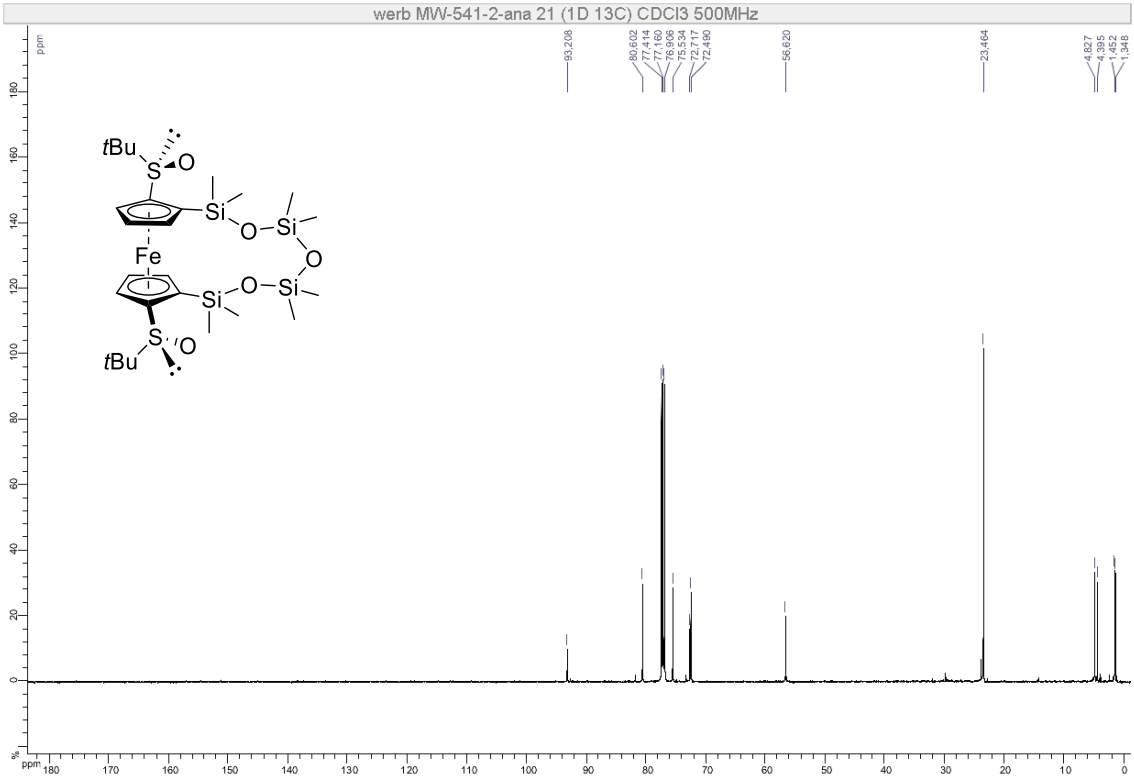


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-(1,1,3,3,5,5,7,7-octamethyl-1,7-tetrasiloxanediyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-2g2)

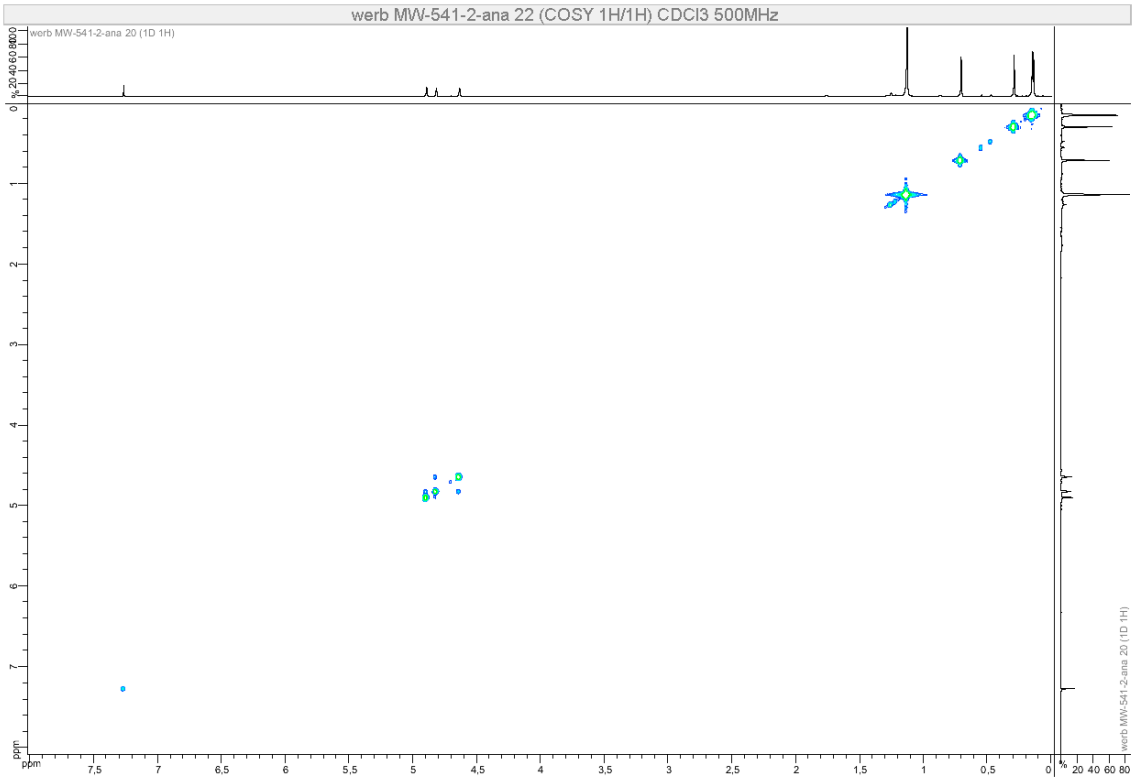
^{1}H NMR (500 MHz, $CDCl_3$)



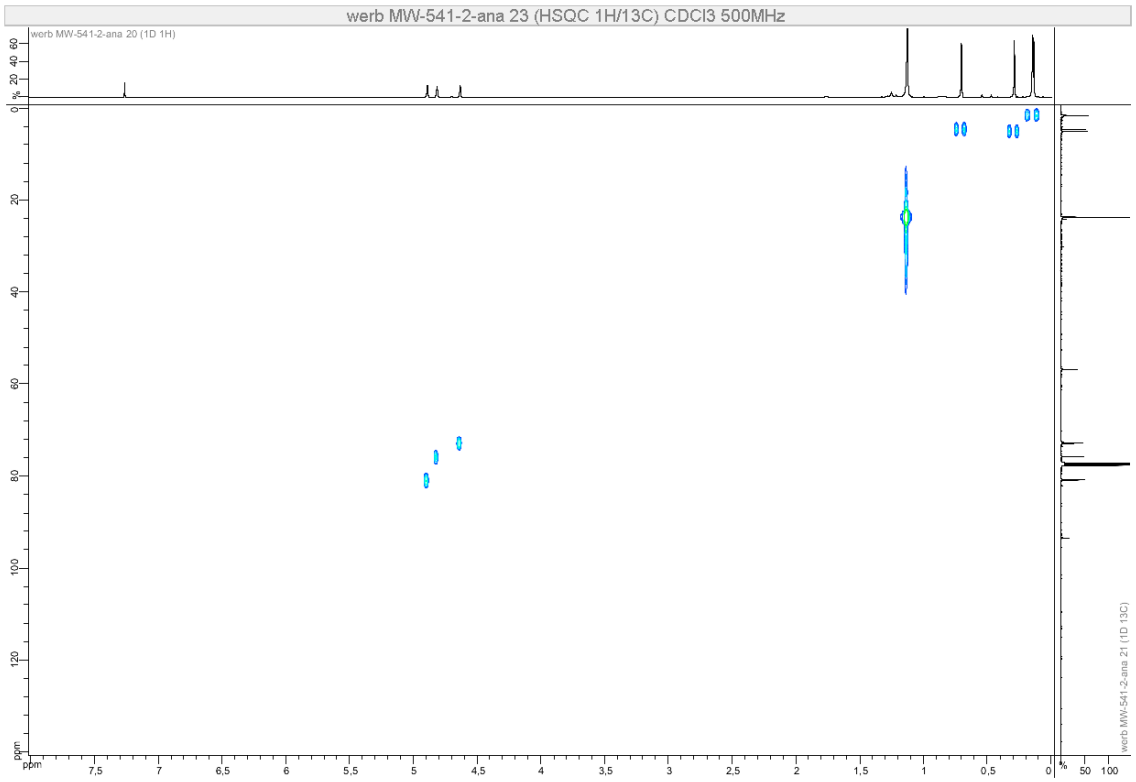
^{13}C NMR (126 MHz, $CDCl_3$)



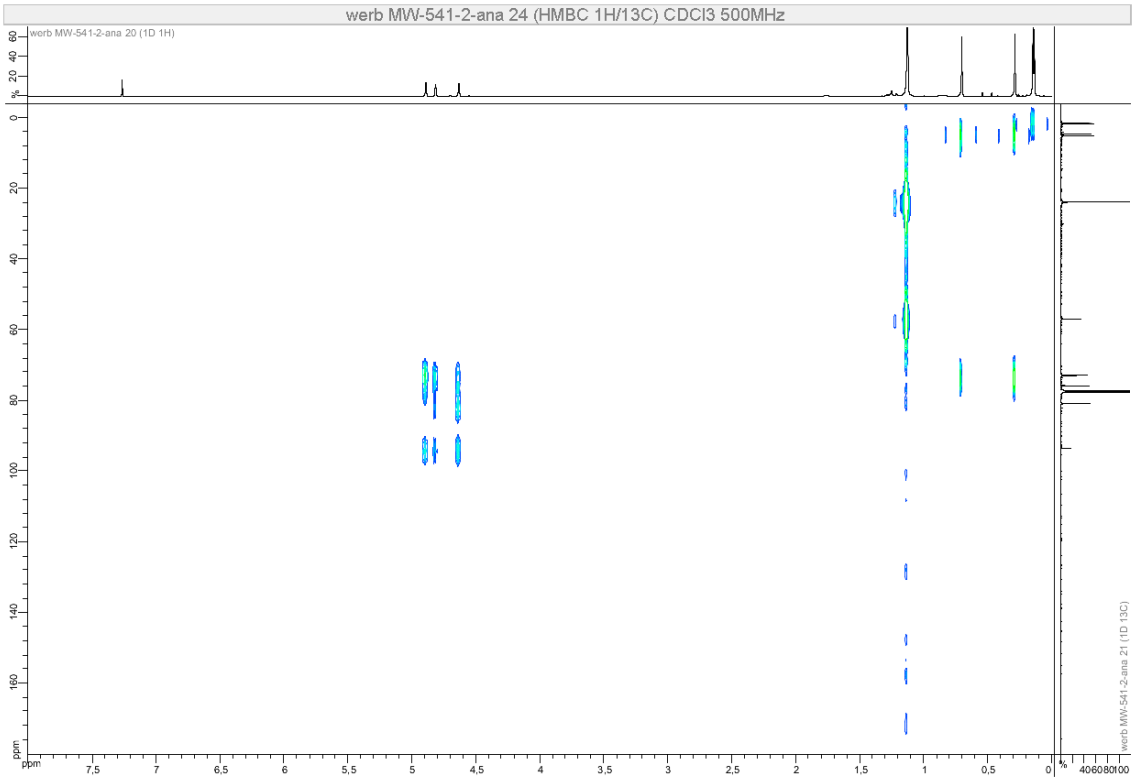
COSY (500 MHz, $CDCl_3$)



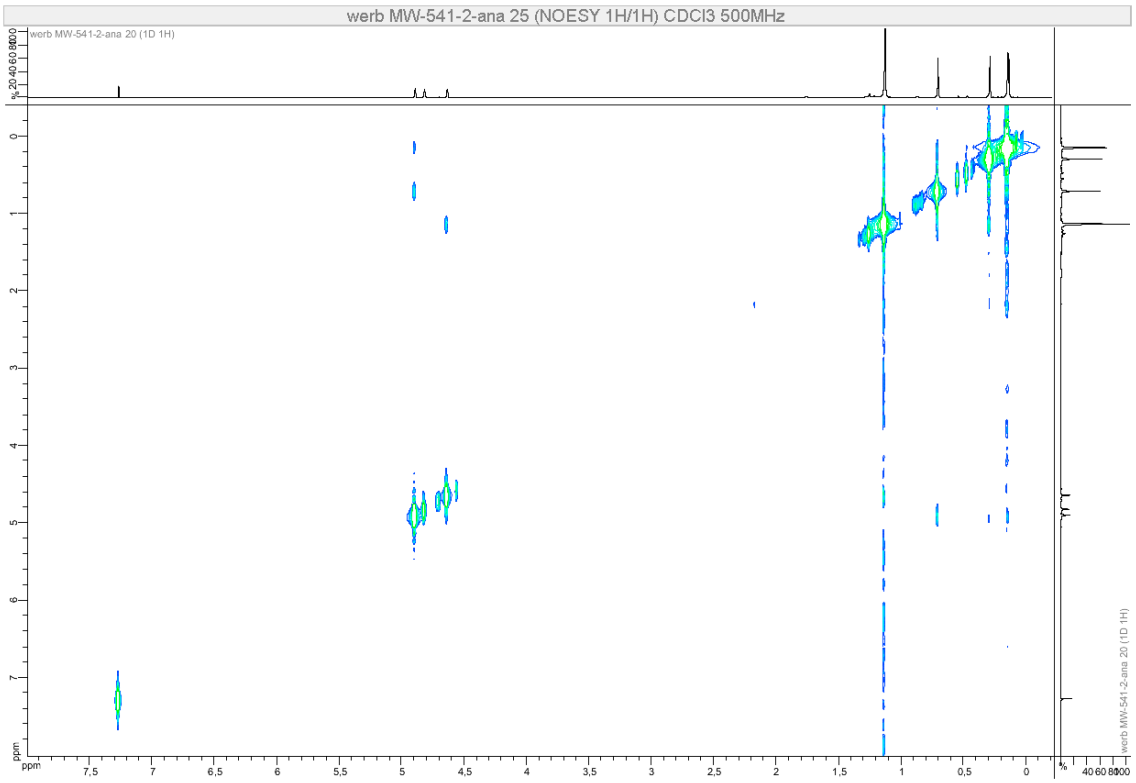
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

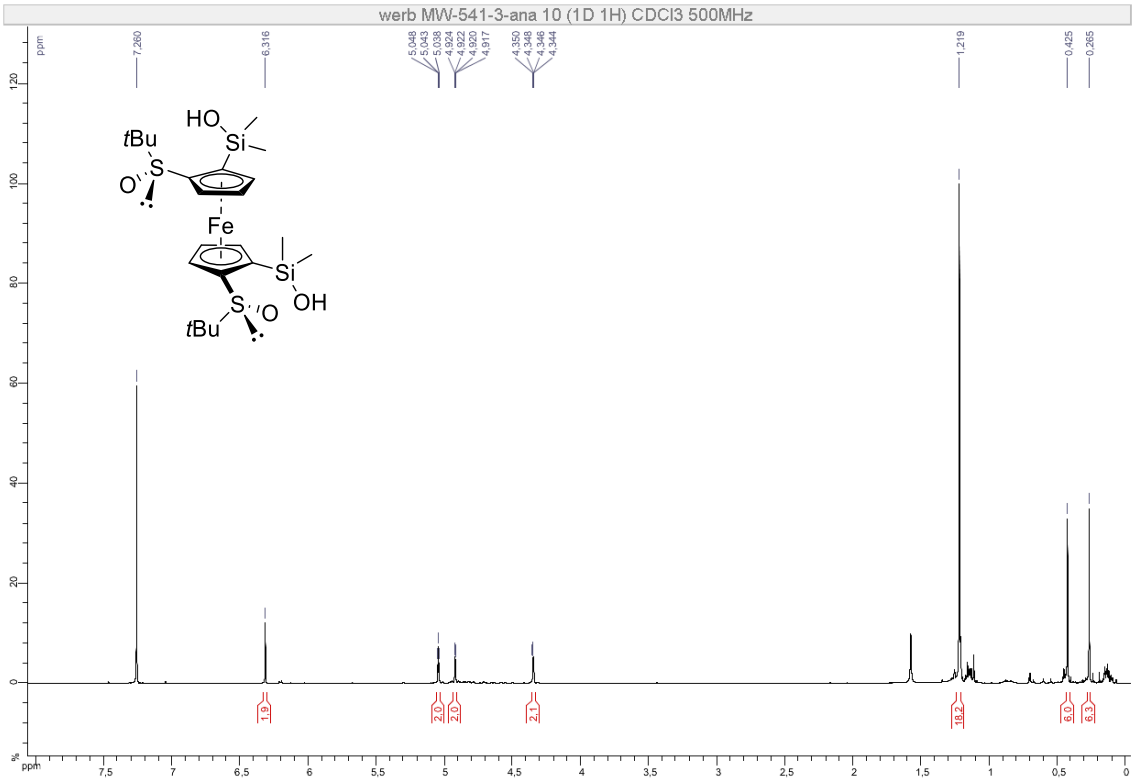


NOESY (500 MHz, $CDCl_3$)

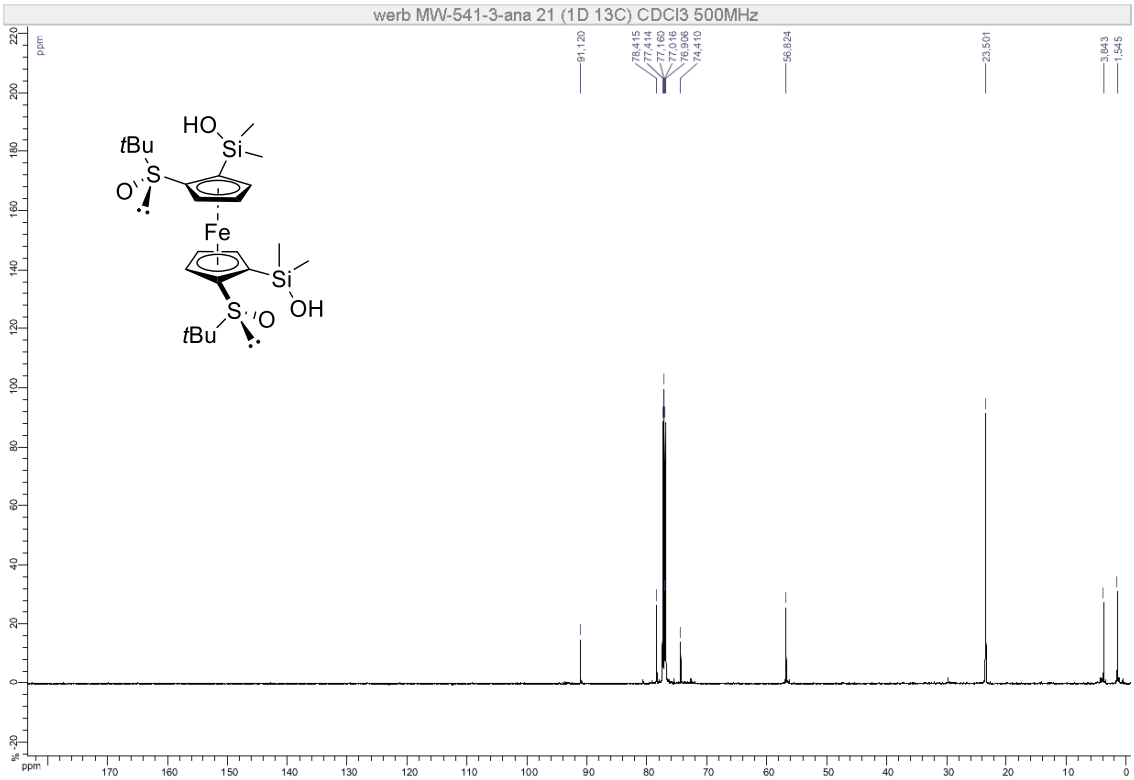


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-bis(hydroxydimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-2g3)

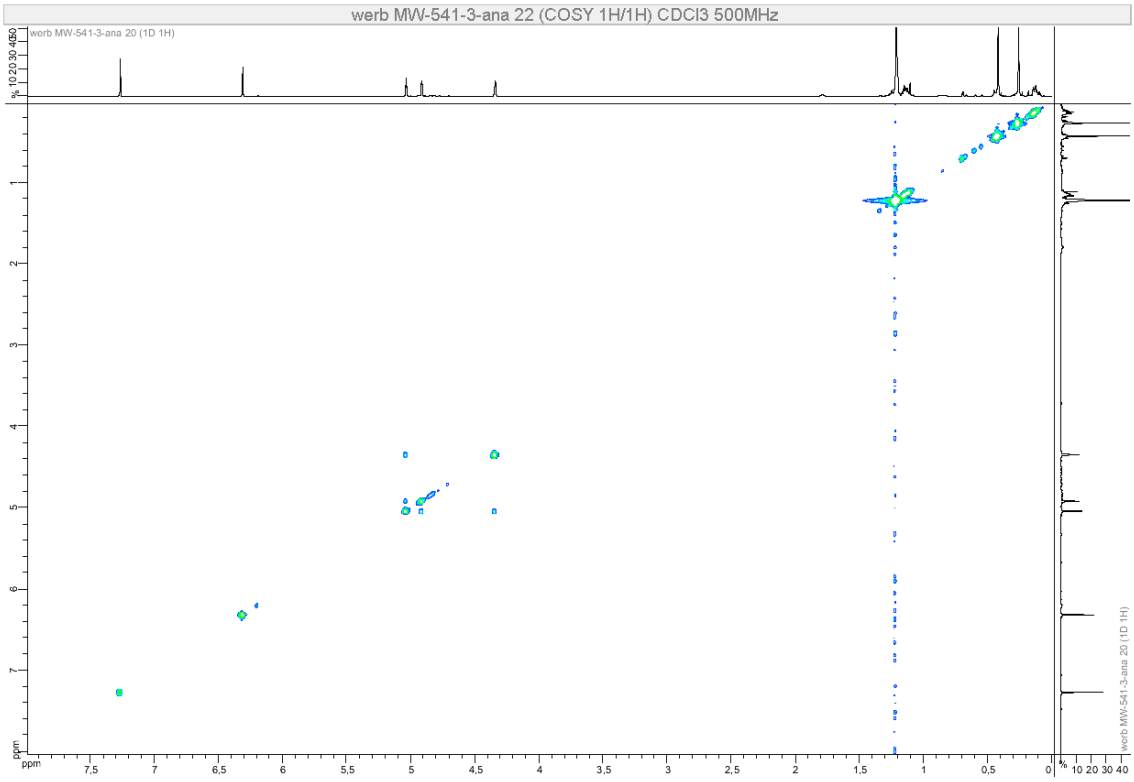
^{1}H NMR (500 MHz, $CDCl_3$)



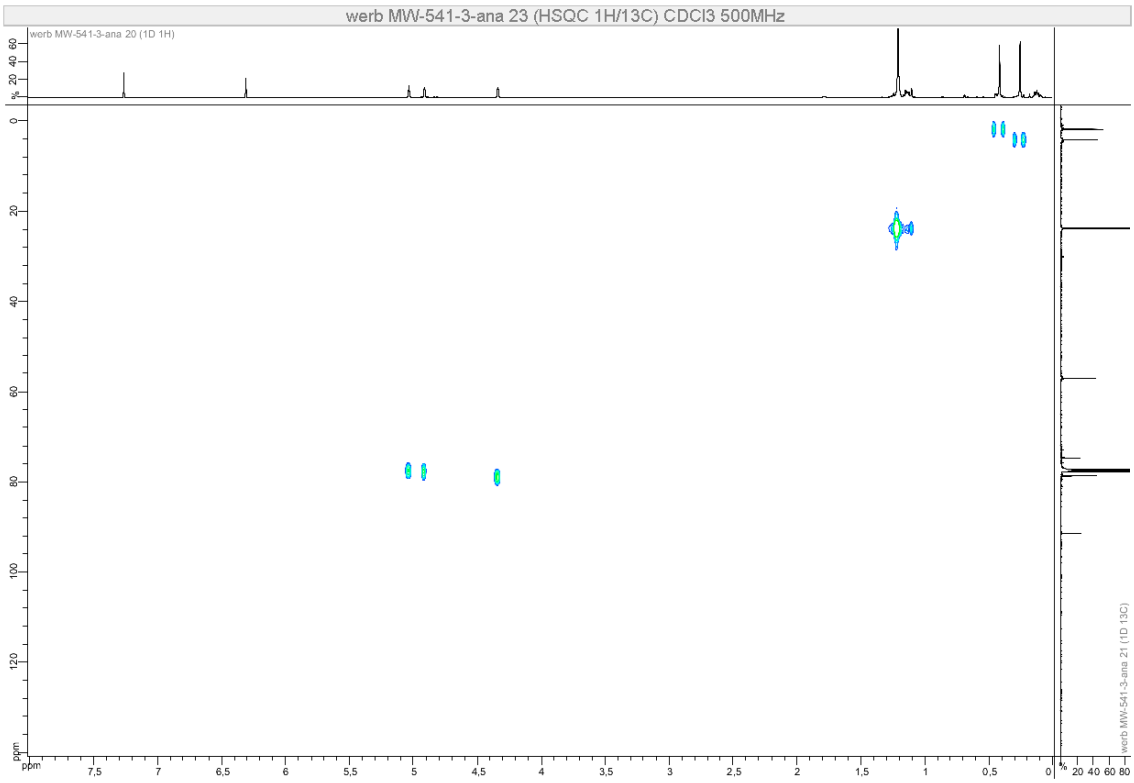
^{13}C NMR (126 MHz, $CDCl_3$)



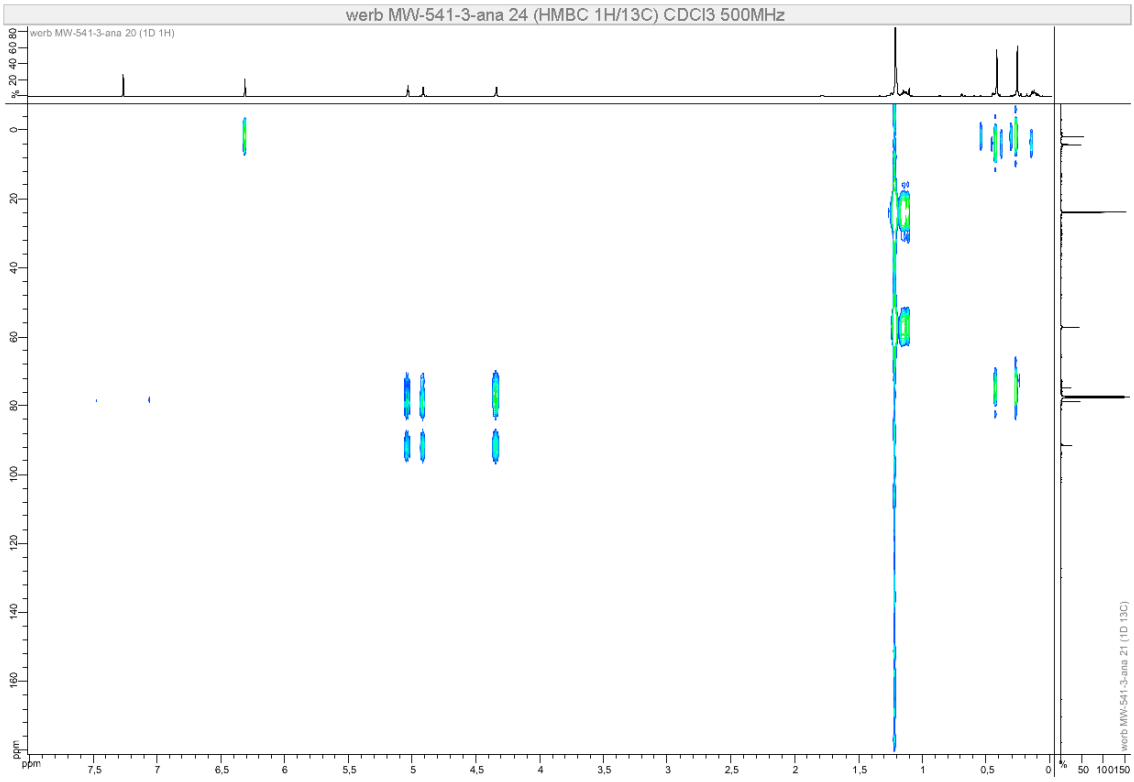
COSY (500 MHz, $CDCl_3$)



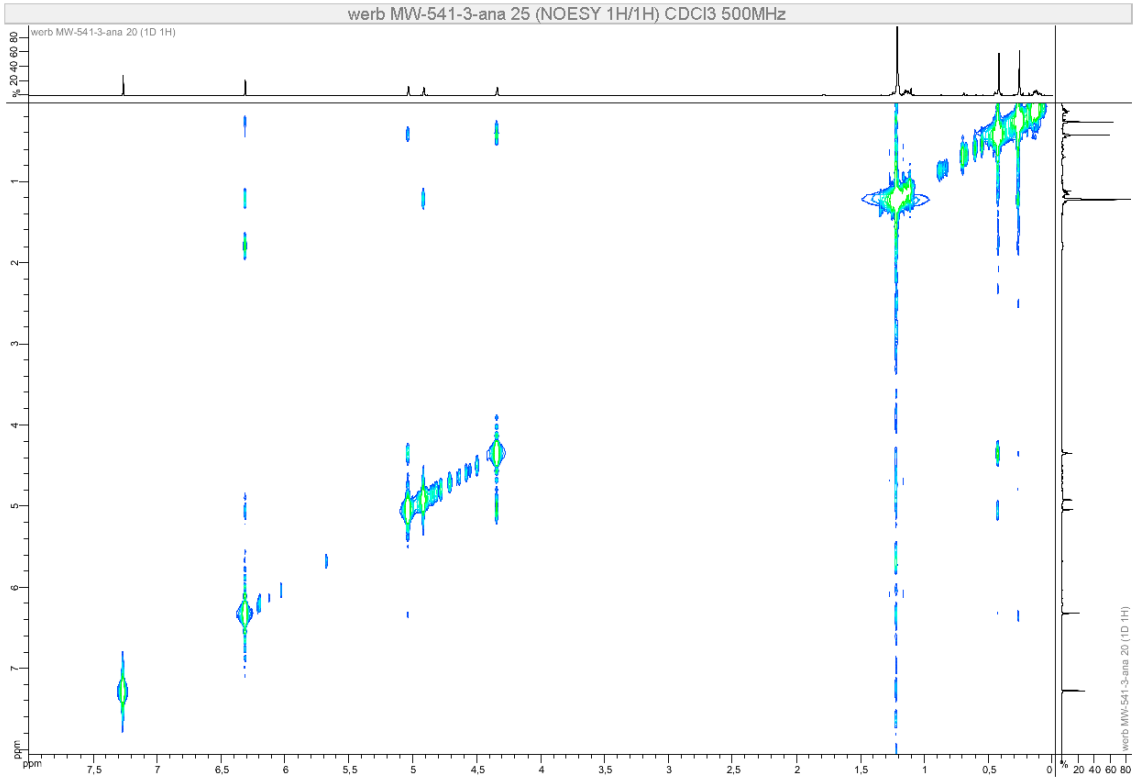
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

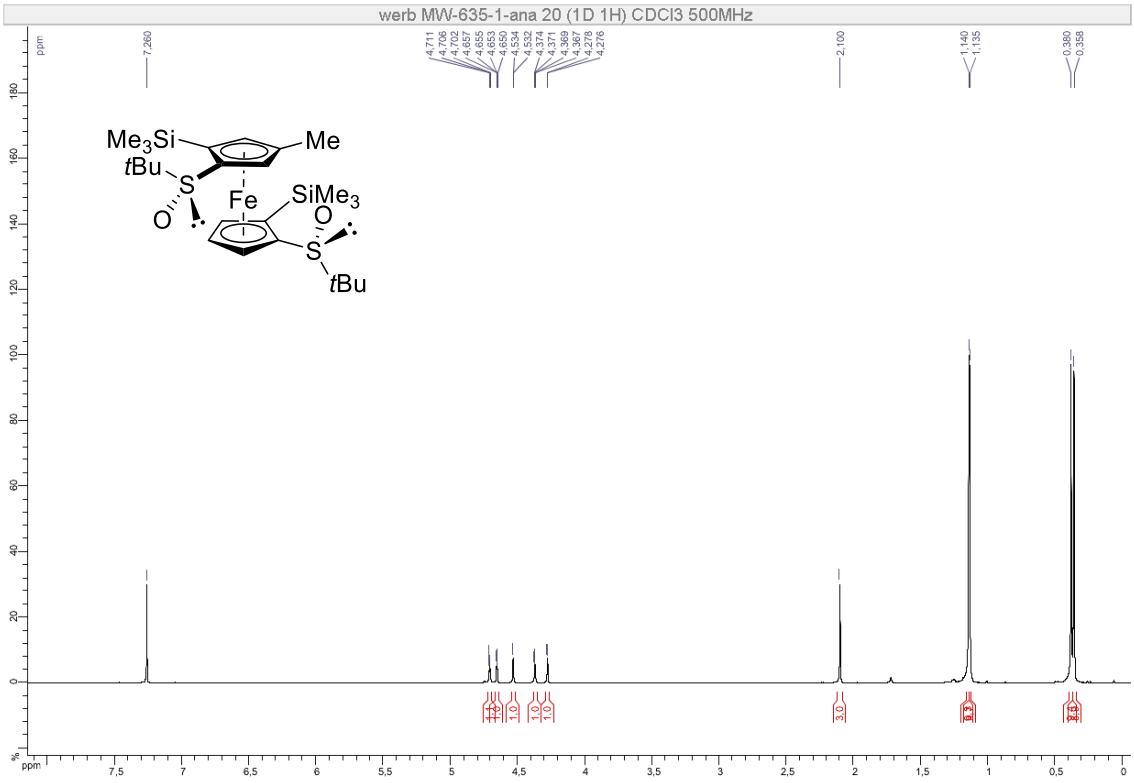


NOESY (500 MHz, $CDCl_3$)

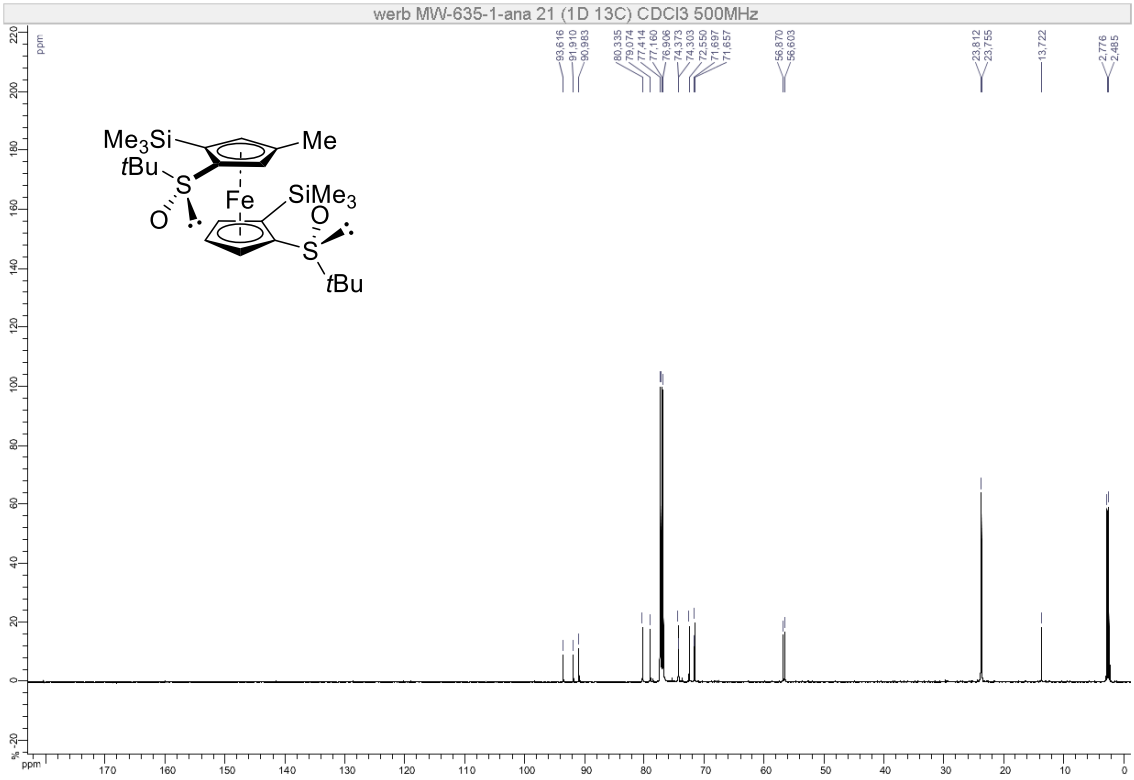


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4-methyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6a)

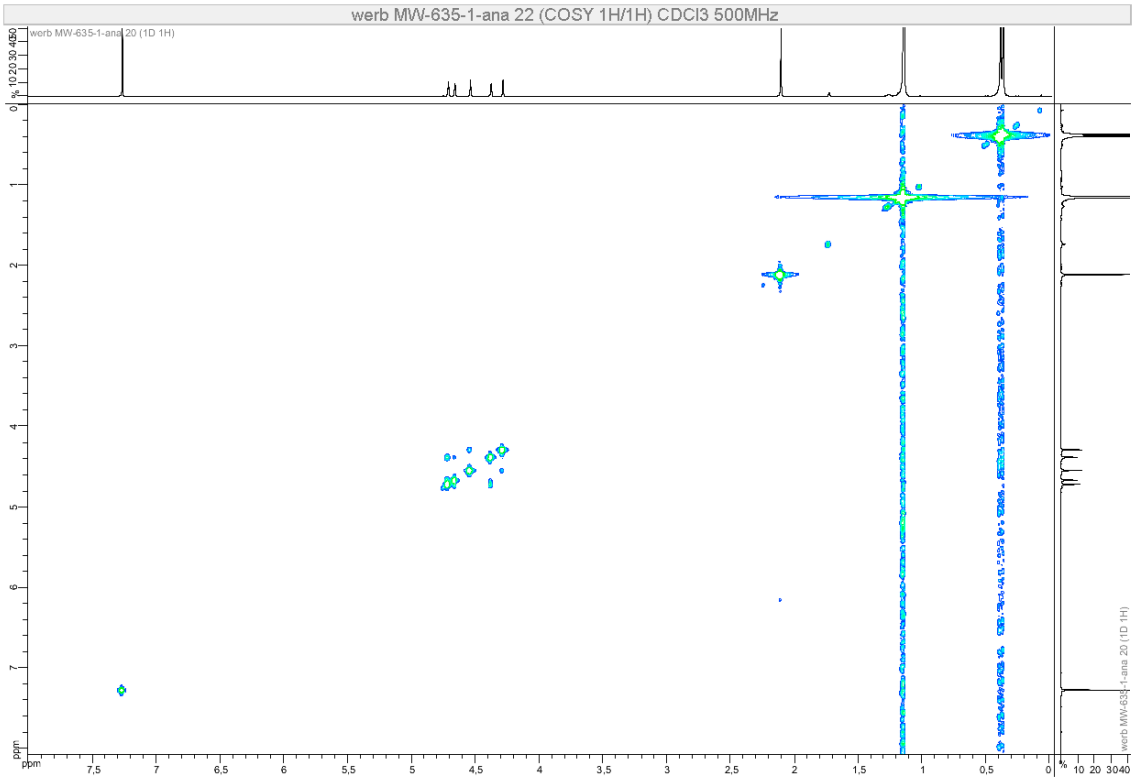
^{1}H NMR (500 MHz, $CDCl_3$)



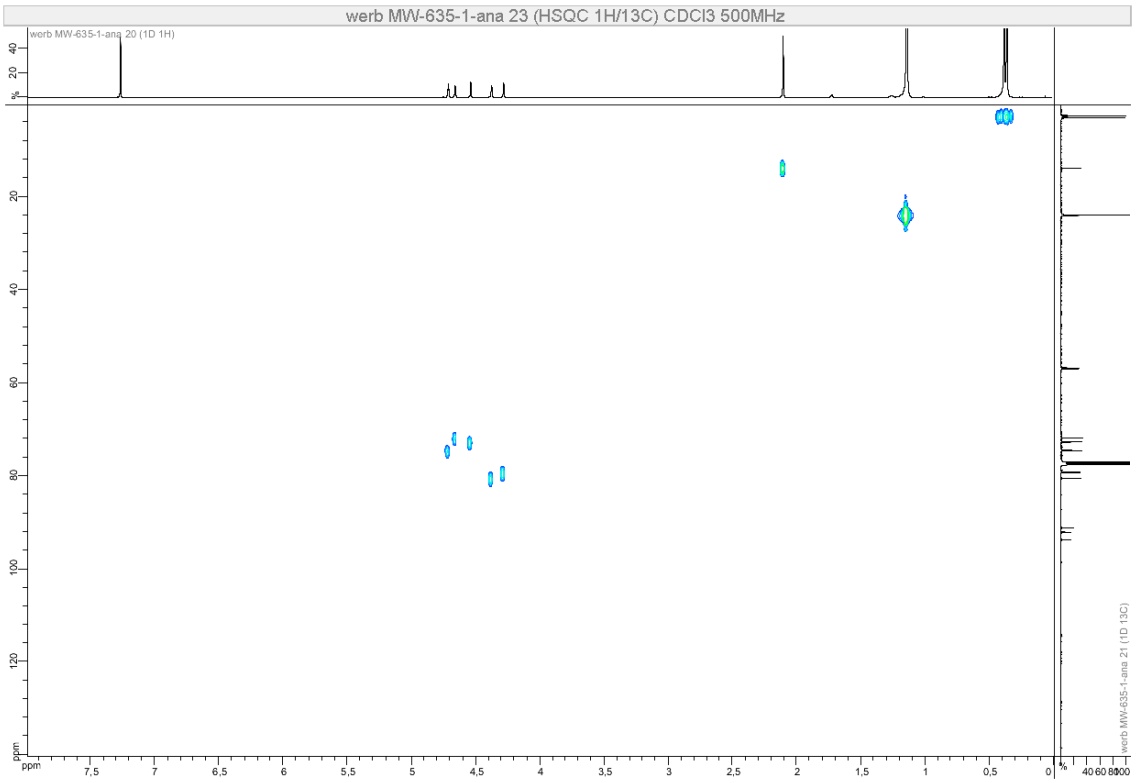
^{13}C NMR (126 MHz, $CDCl_3$)



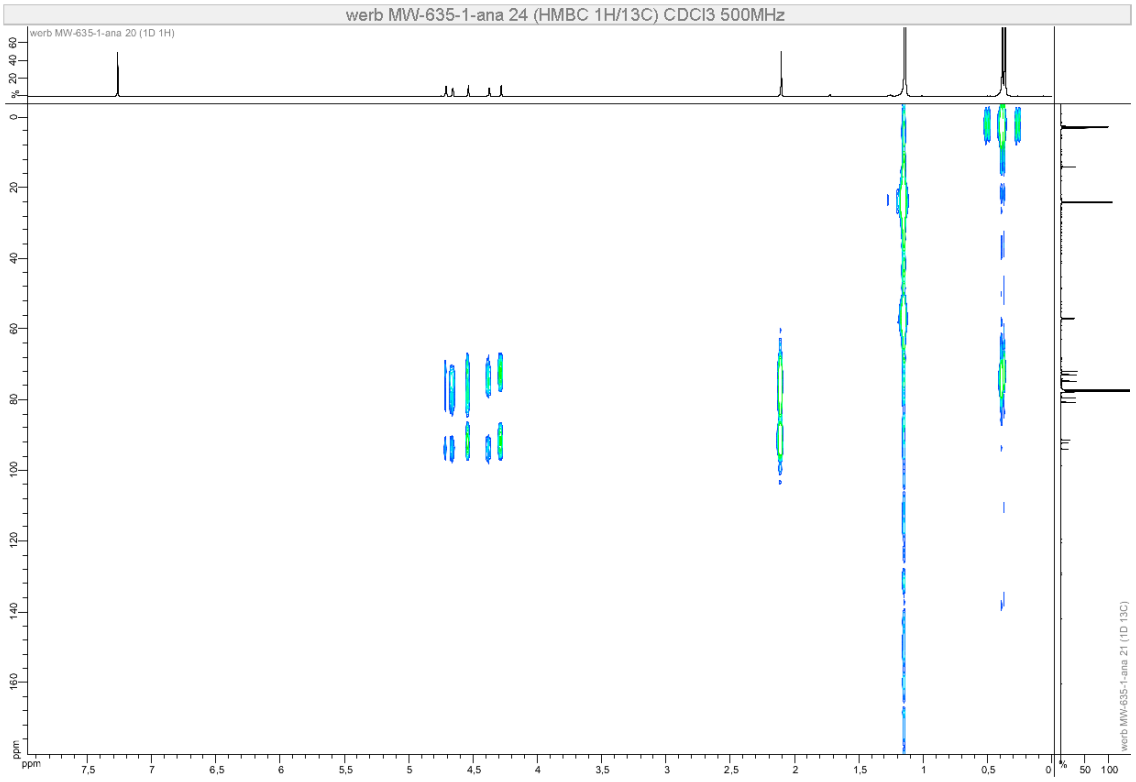
COSY (500 MHz, $CDCl_3$)



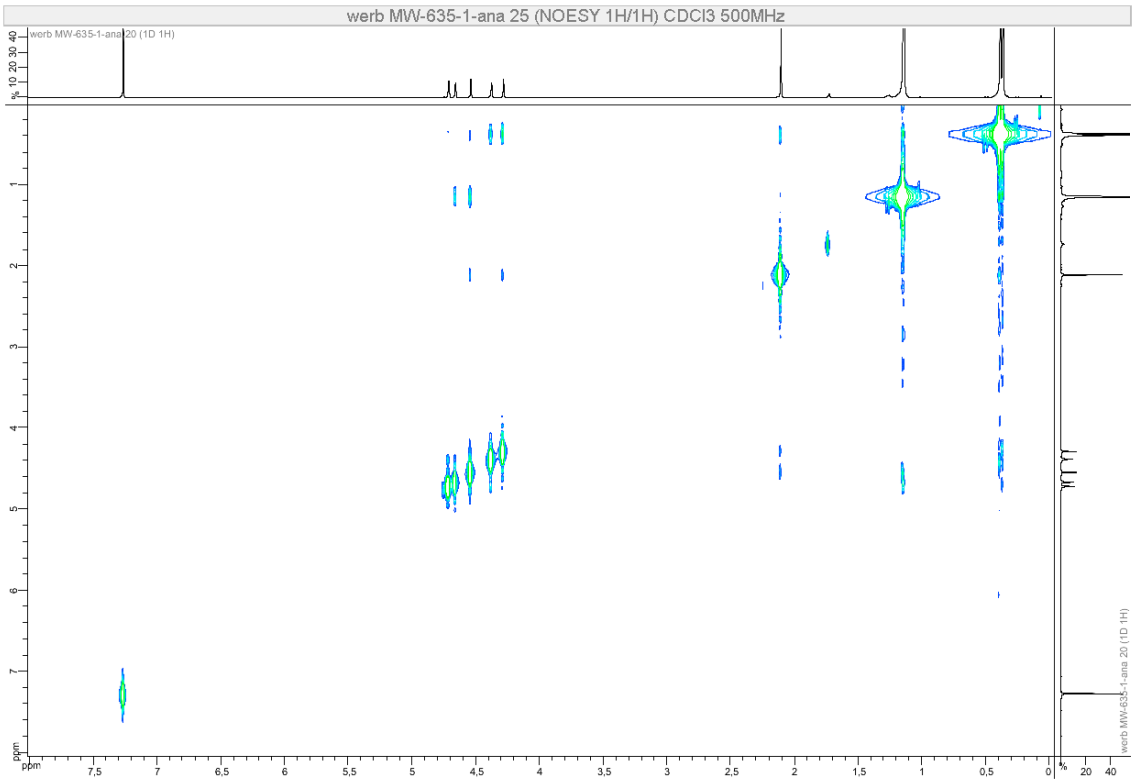
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

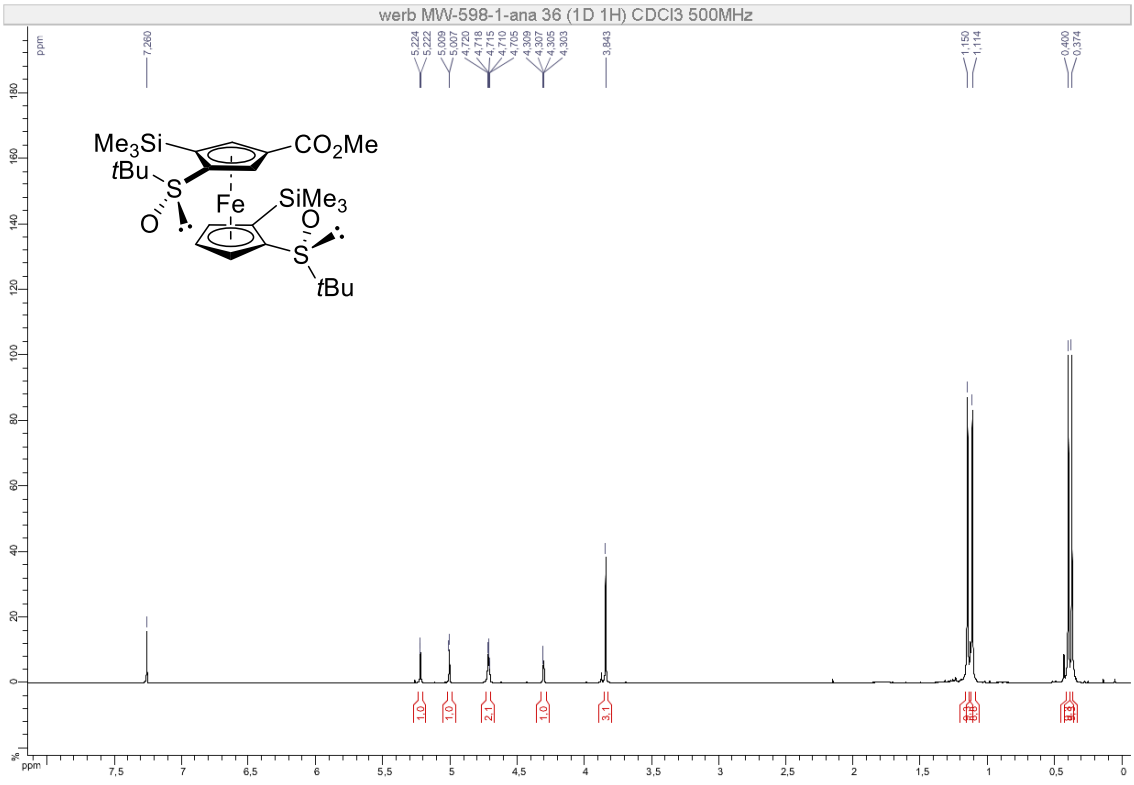


NOESY (500 MHz, $CDCl_3$)

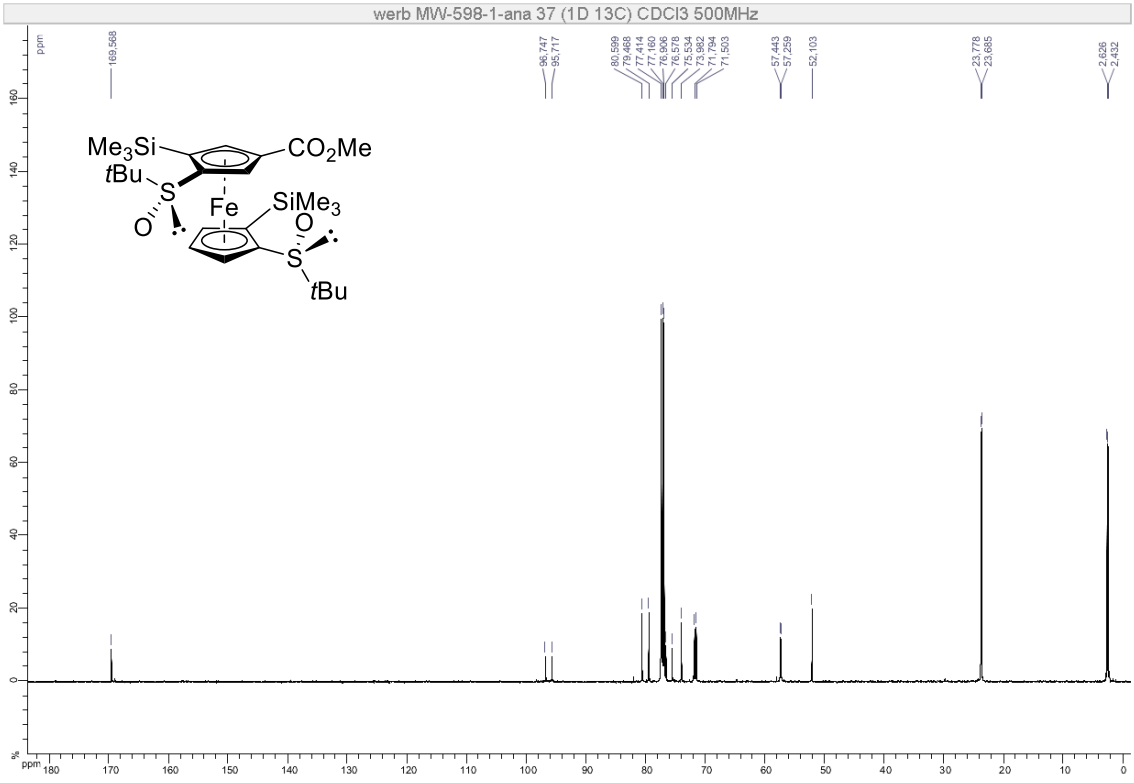


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4-(methoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6b)

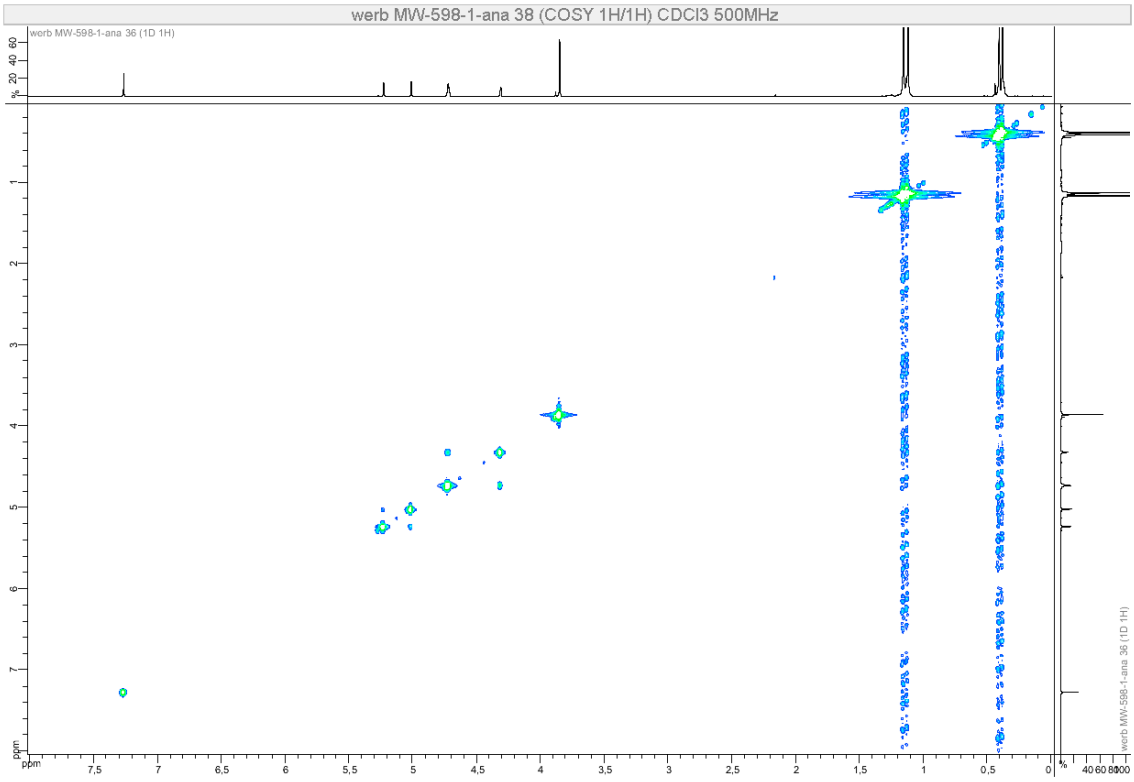
^{1}H NMR (500 MHz, $CDCl_3$)



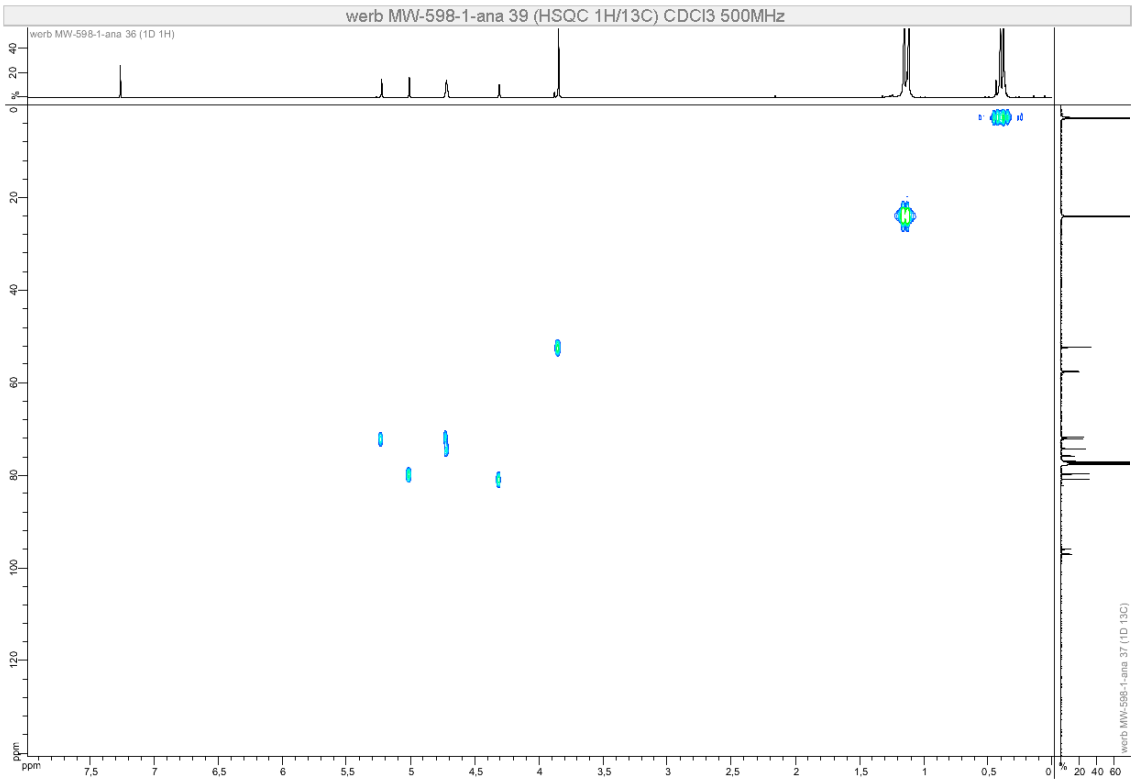
^{13}C NMR (126 MHz, $CDCl_3$)



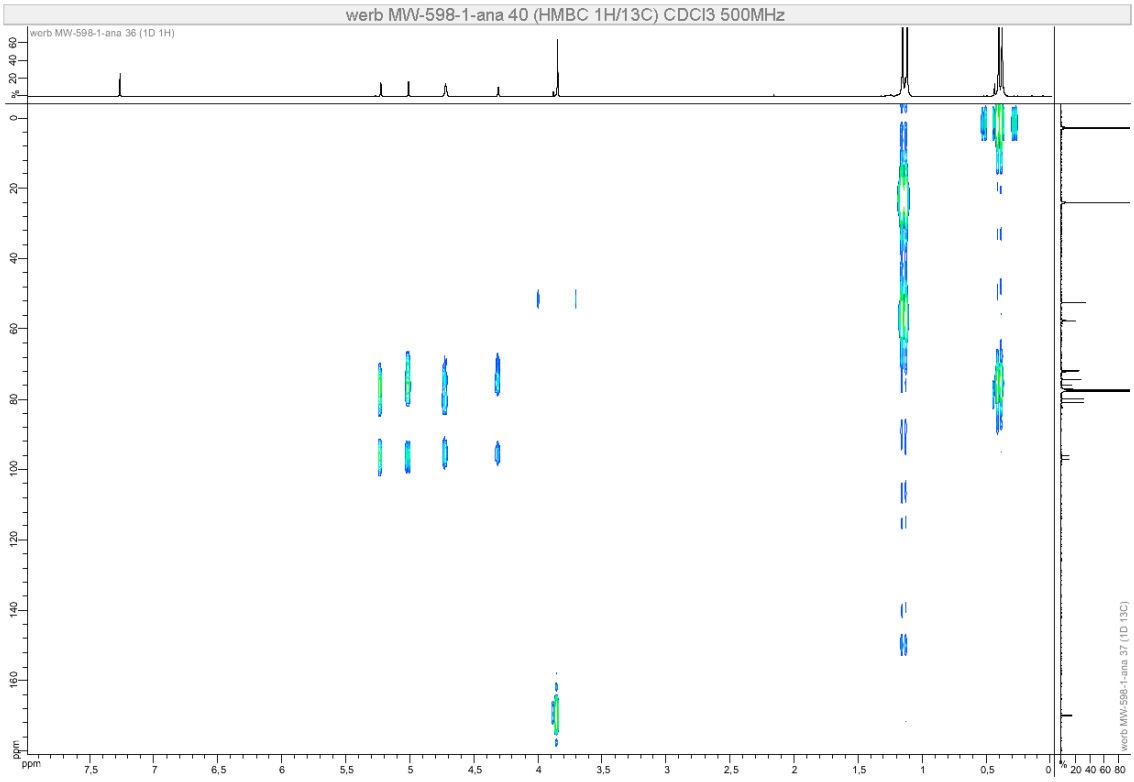
COSY (500 MHz, $CDCl_3$)



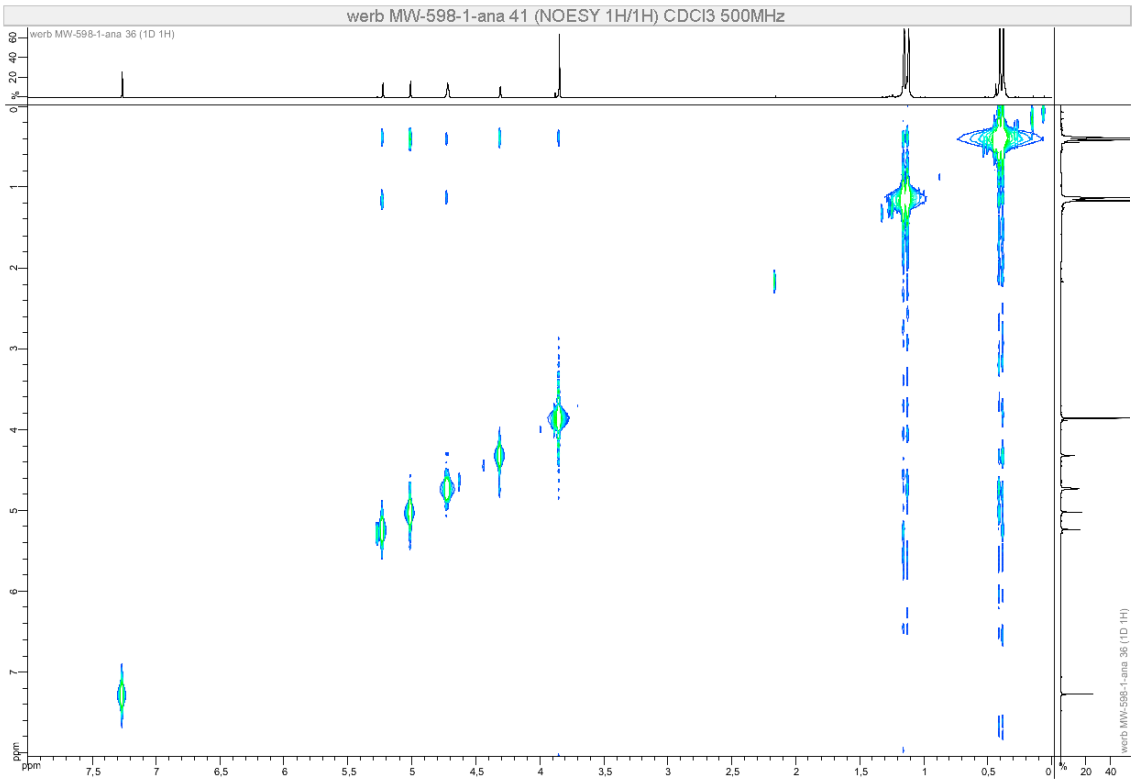
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

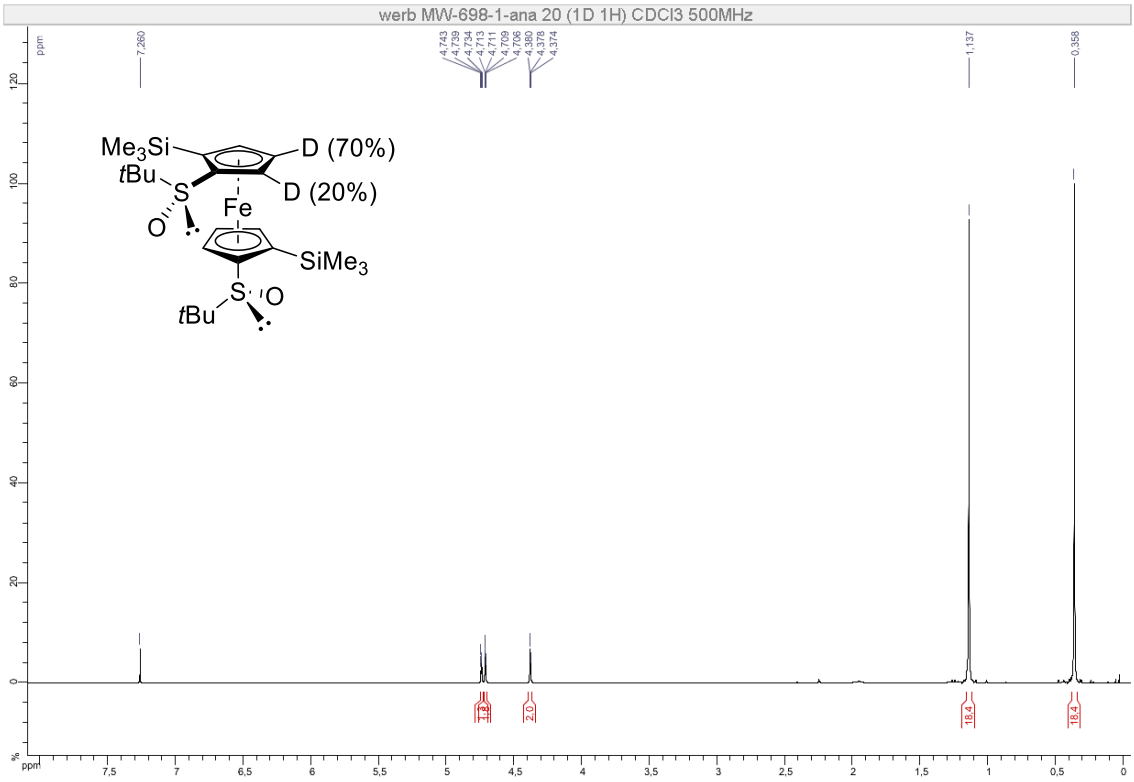


NOESY (500 MHz, $CDCl_3$)

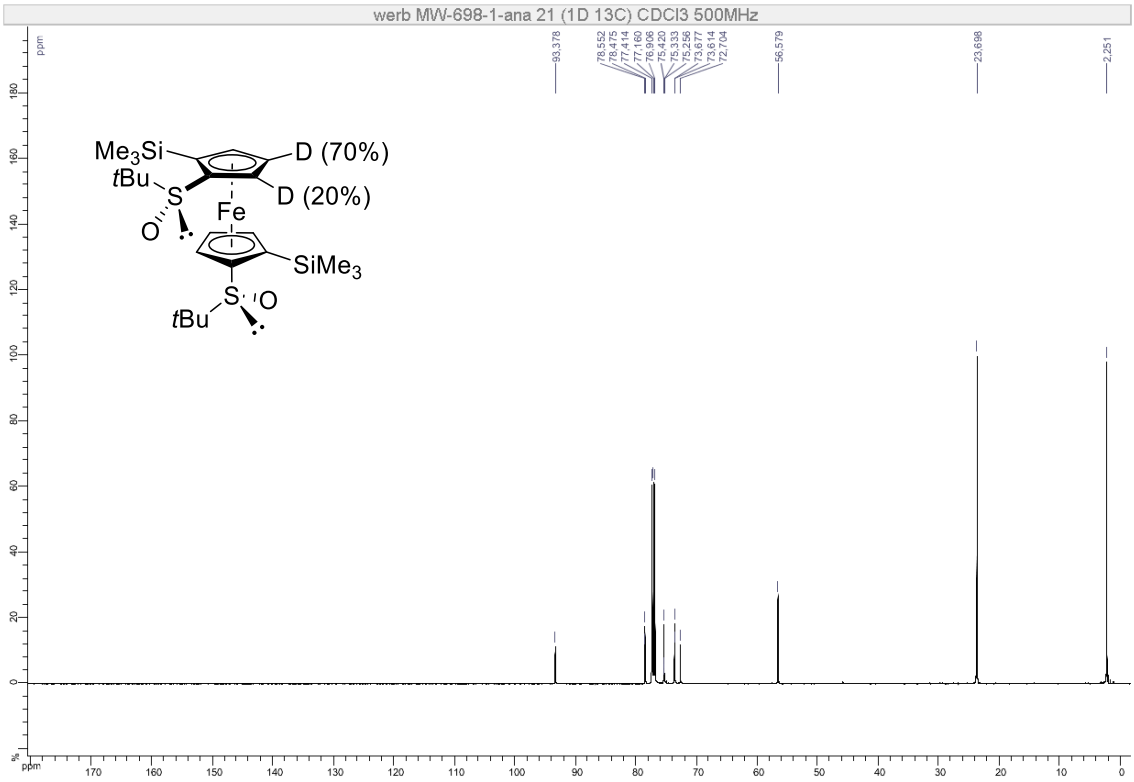


Deuteration of (*R*,*R*,*R*P,*R*P)-*S*,*S*'-di-*tert*-butyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-2f)

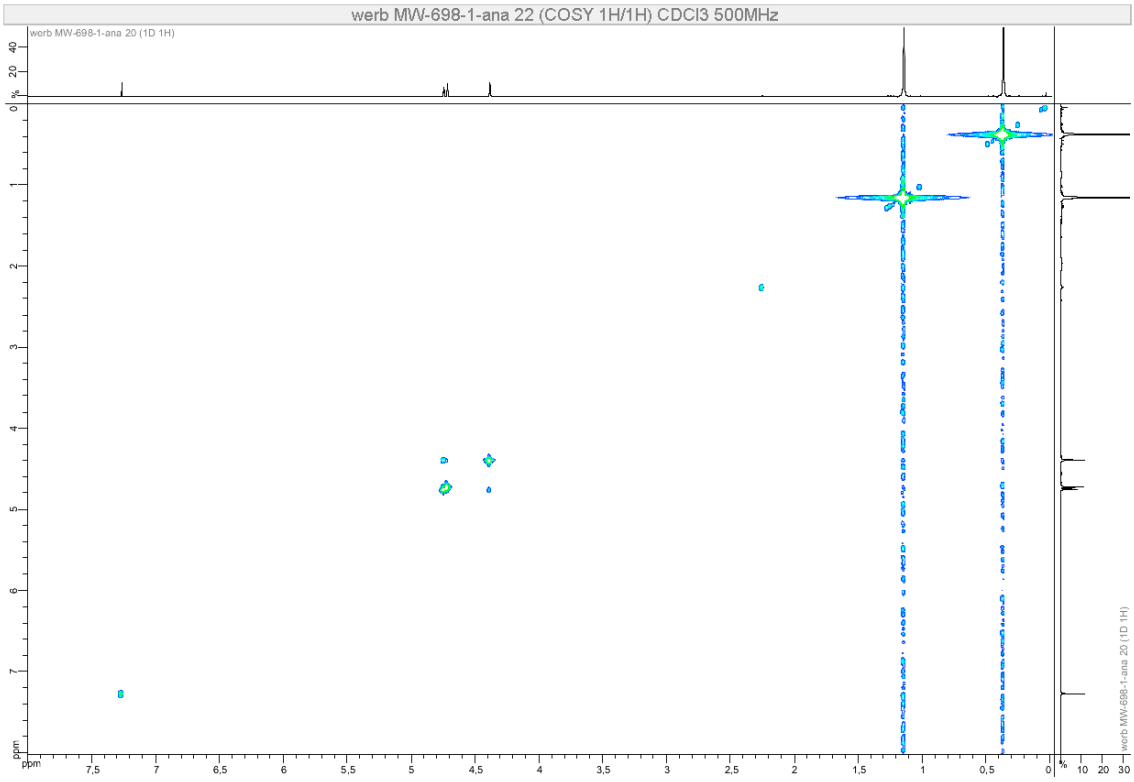
^{1}H NMR (500 MHz, $CDCl_3$)



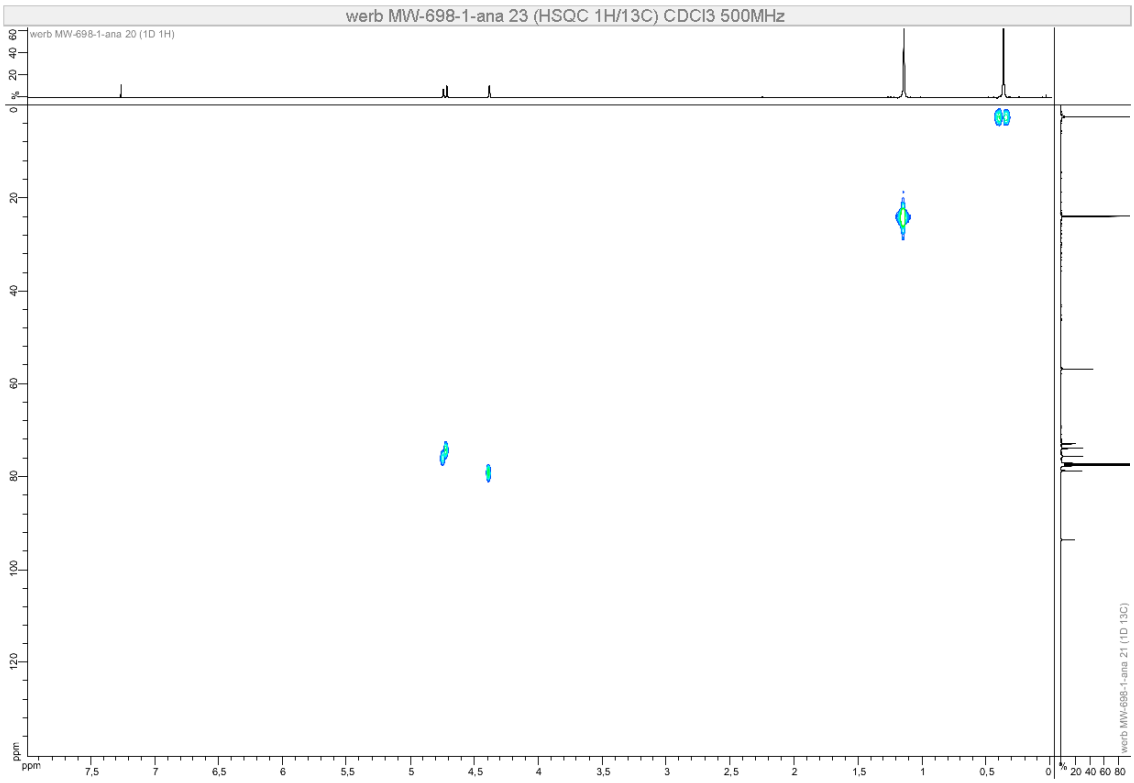
^{13}C NMR (126 MHz, $CDCl_3$)



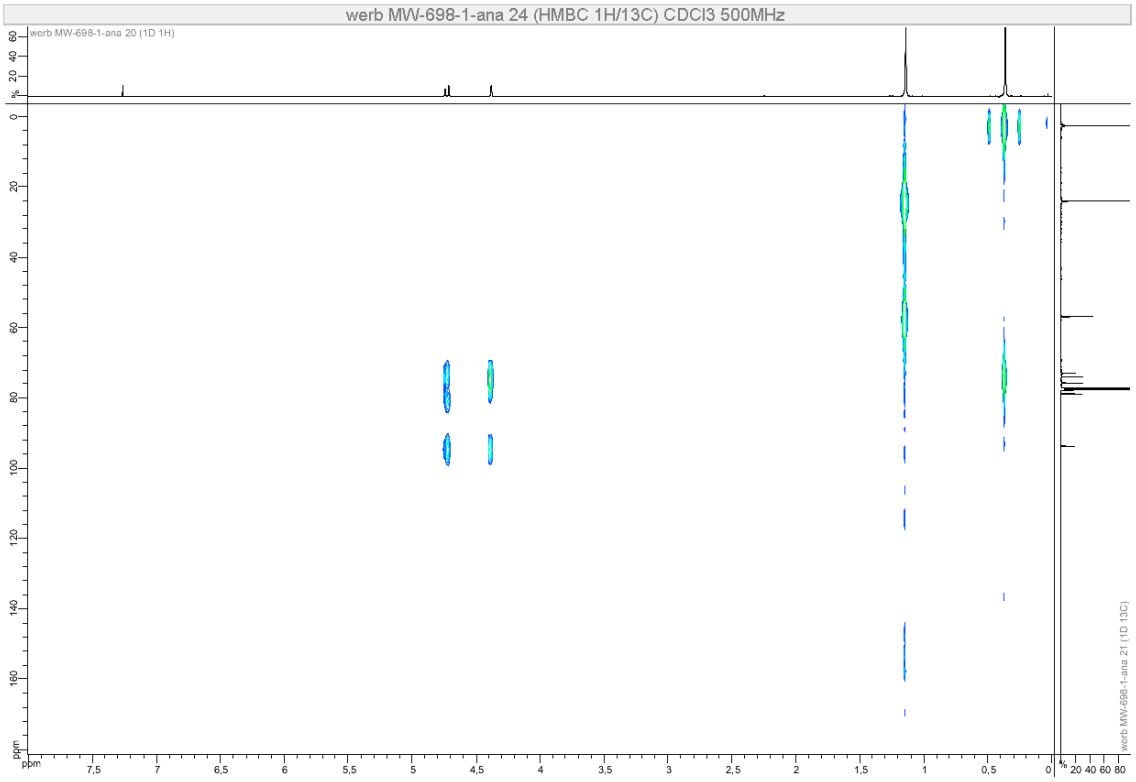
COSY (500 MHz, $CDCl_3$)



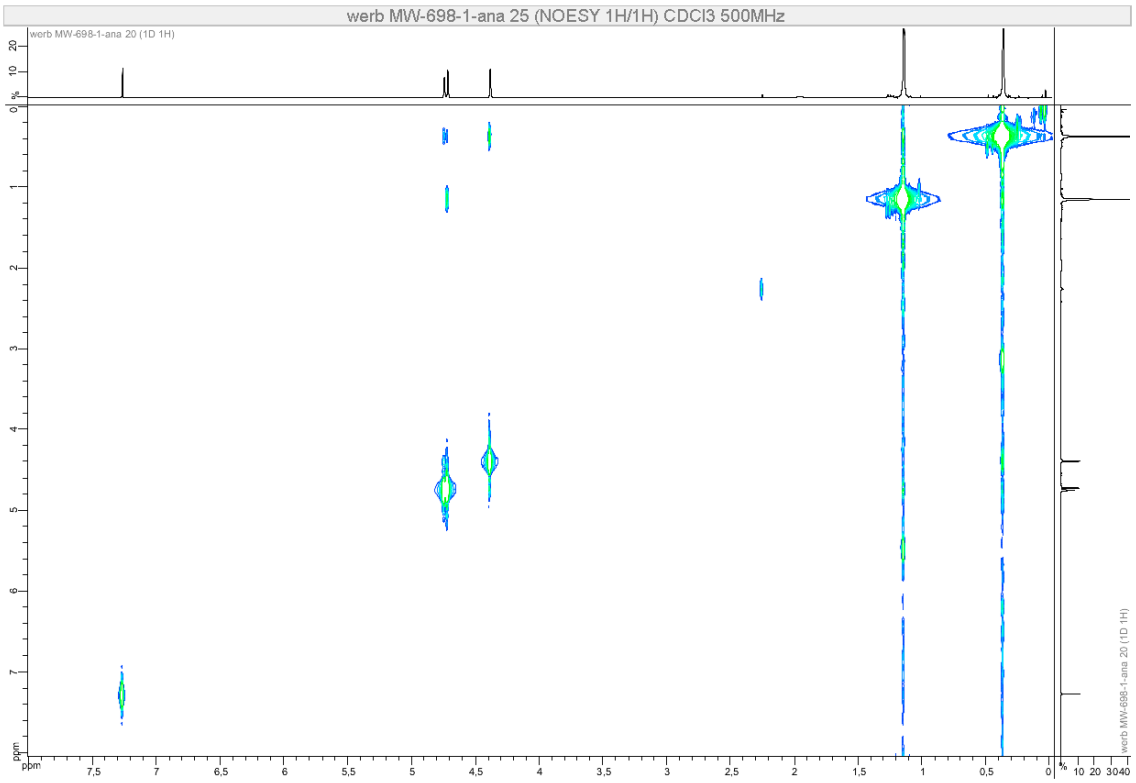
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

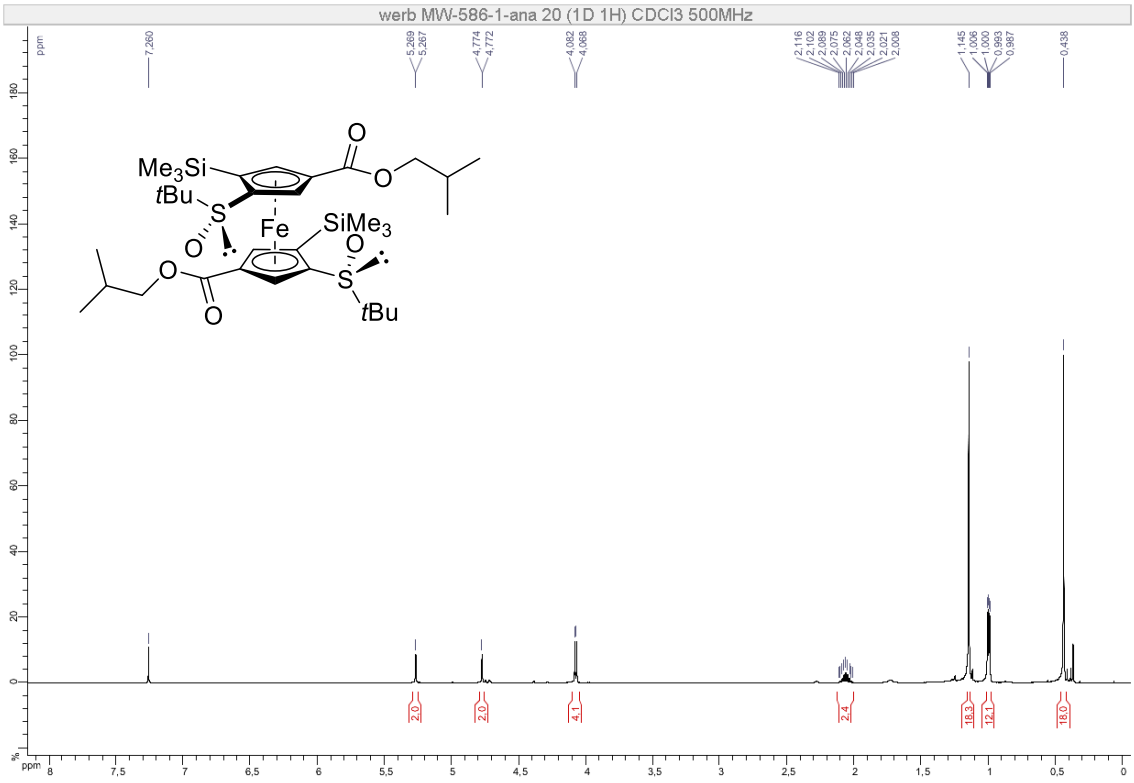


NOESY (500 MHz, $CDCl_3$)

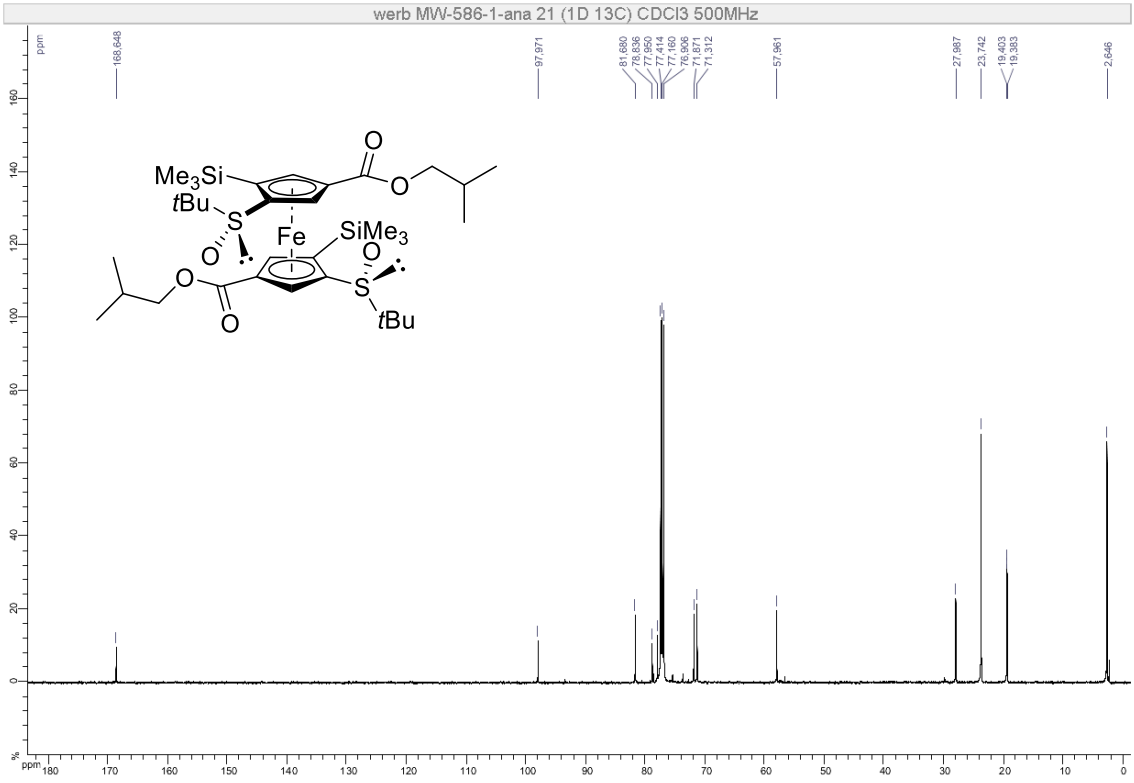


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4,4'-di(isobutoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6'c)

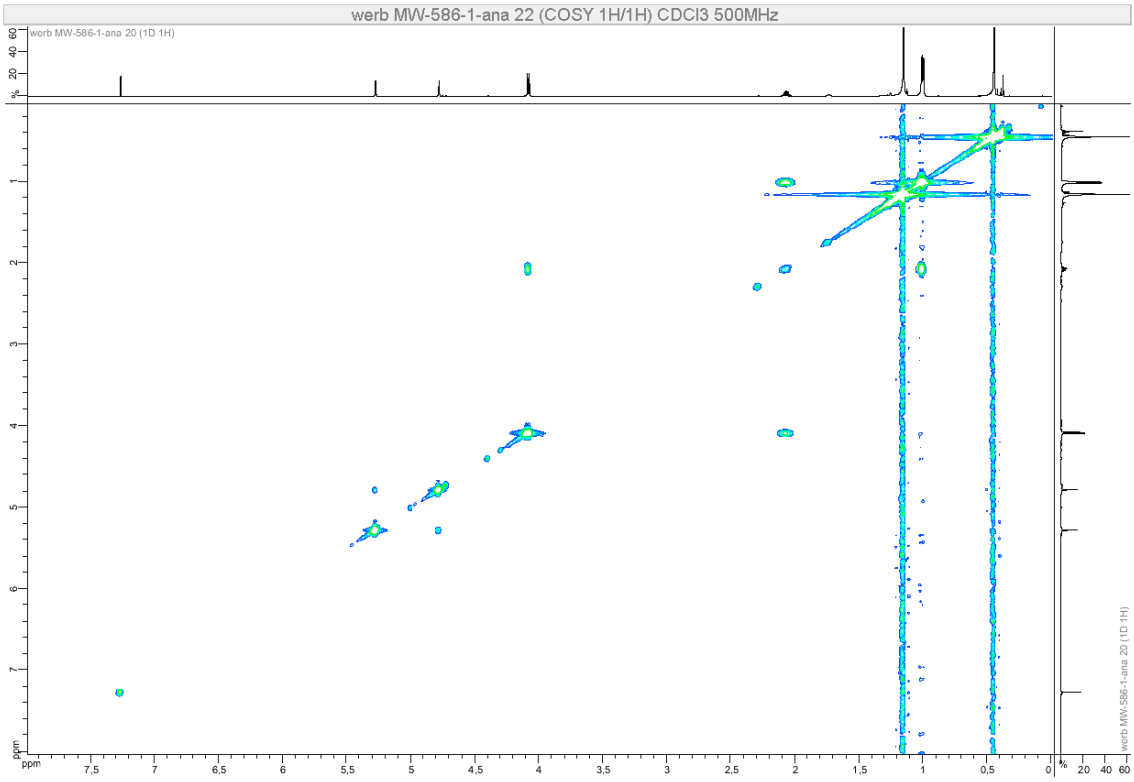
^{1}H NMR (500 MHz, $CDCl_3$)



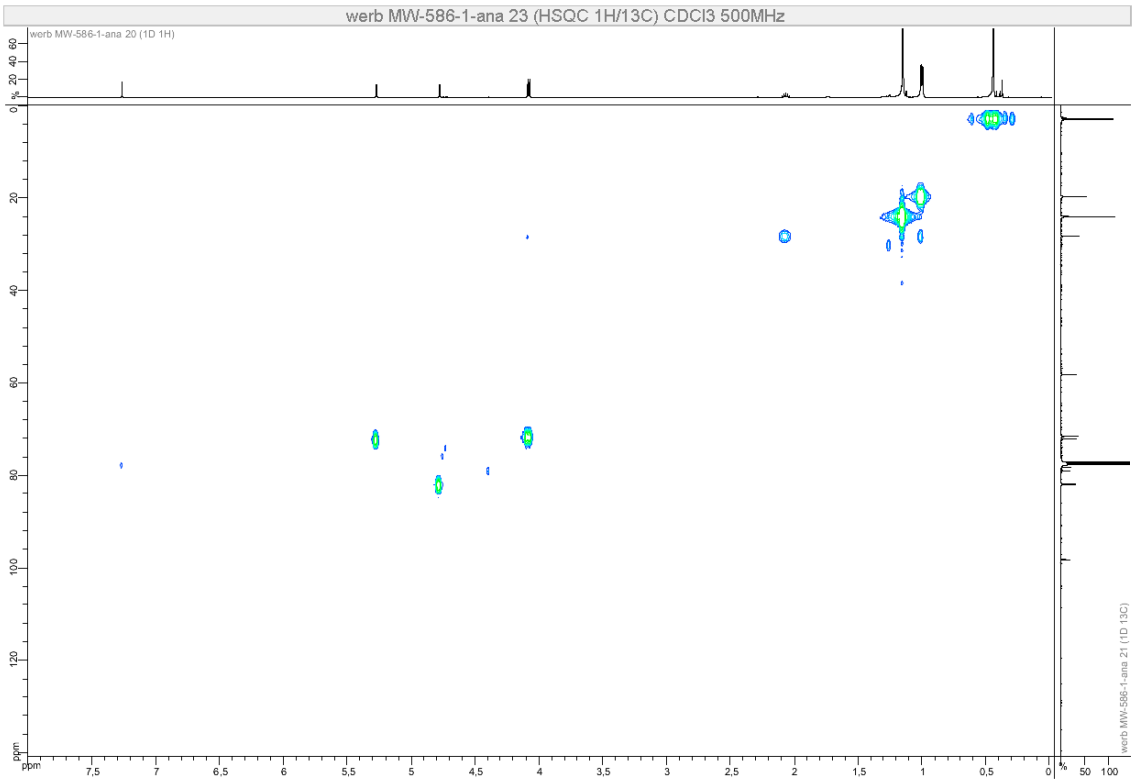
^{13}C NMR (126 MHz, $CDCl_3$)



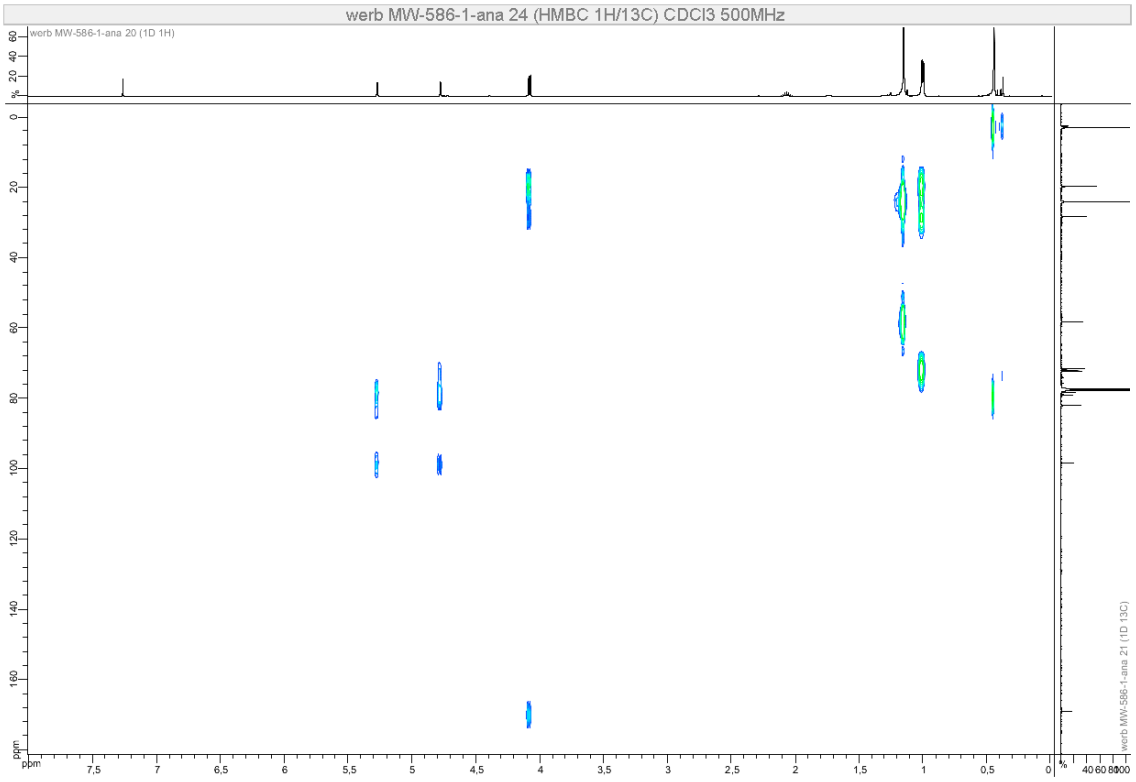
COSY (500 MHz, $CDCl_3$)



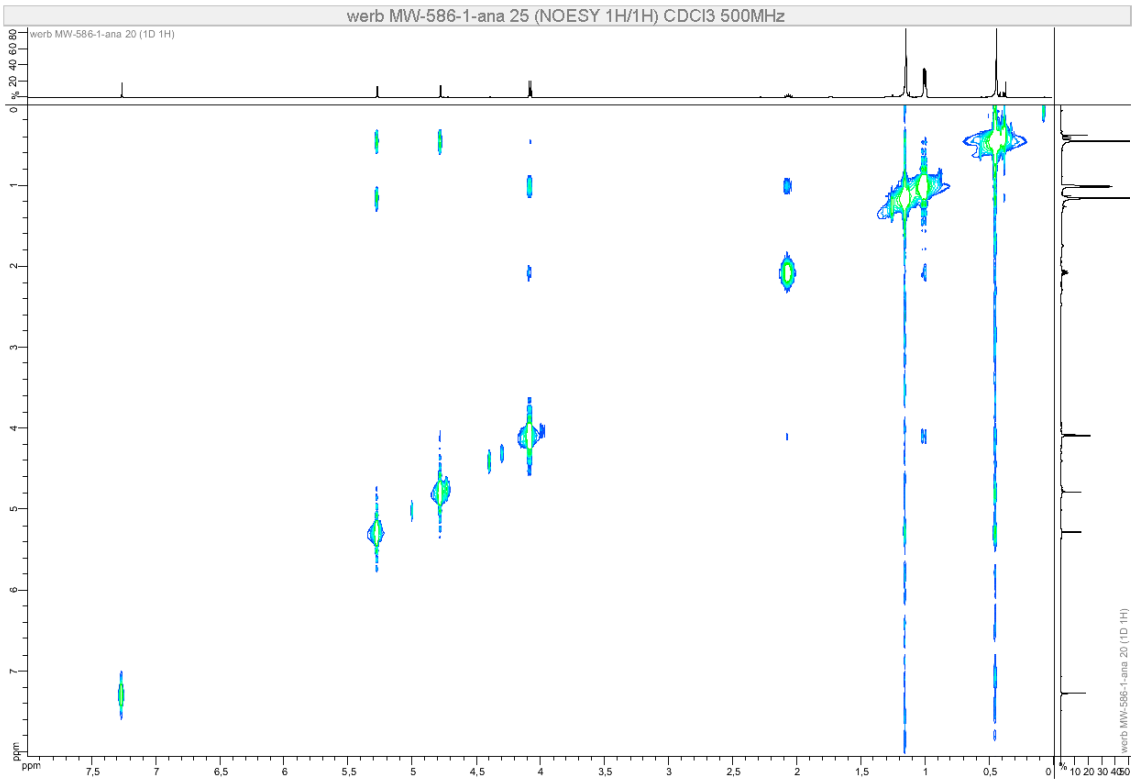
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

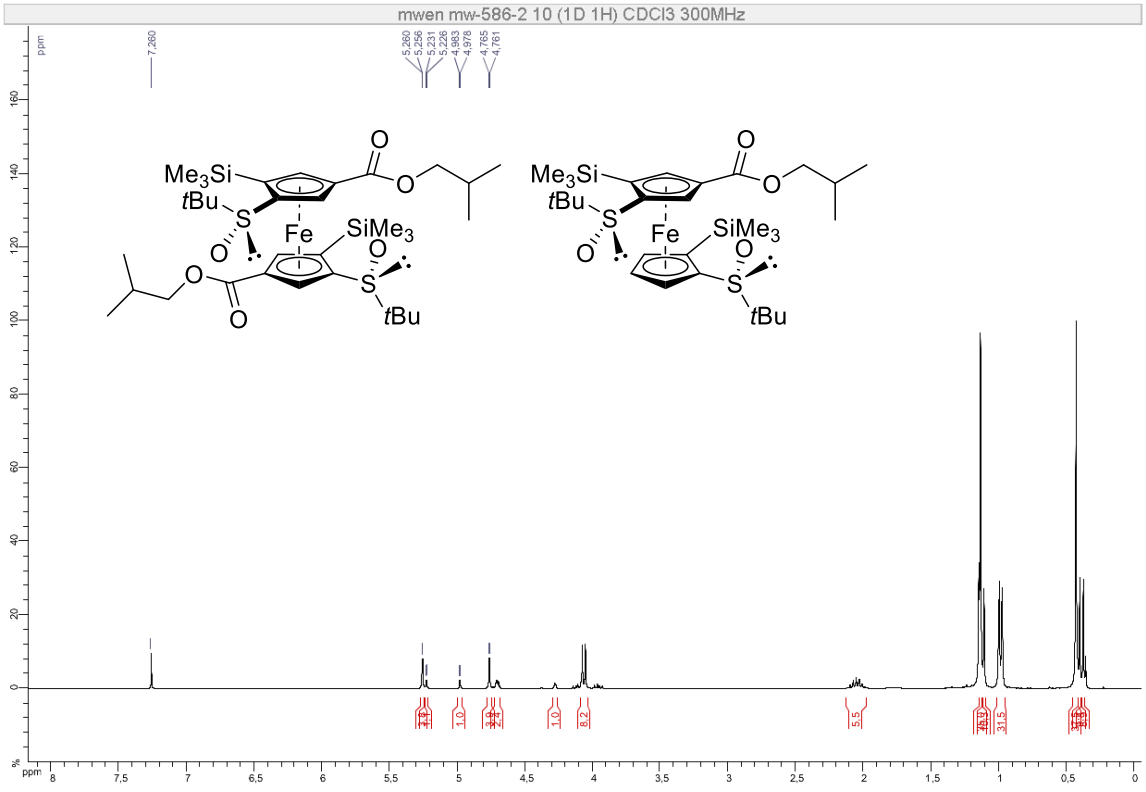


NOESY (500 MHz, $CDCl_3$)



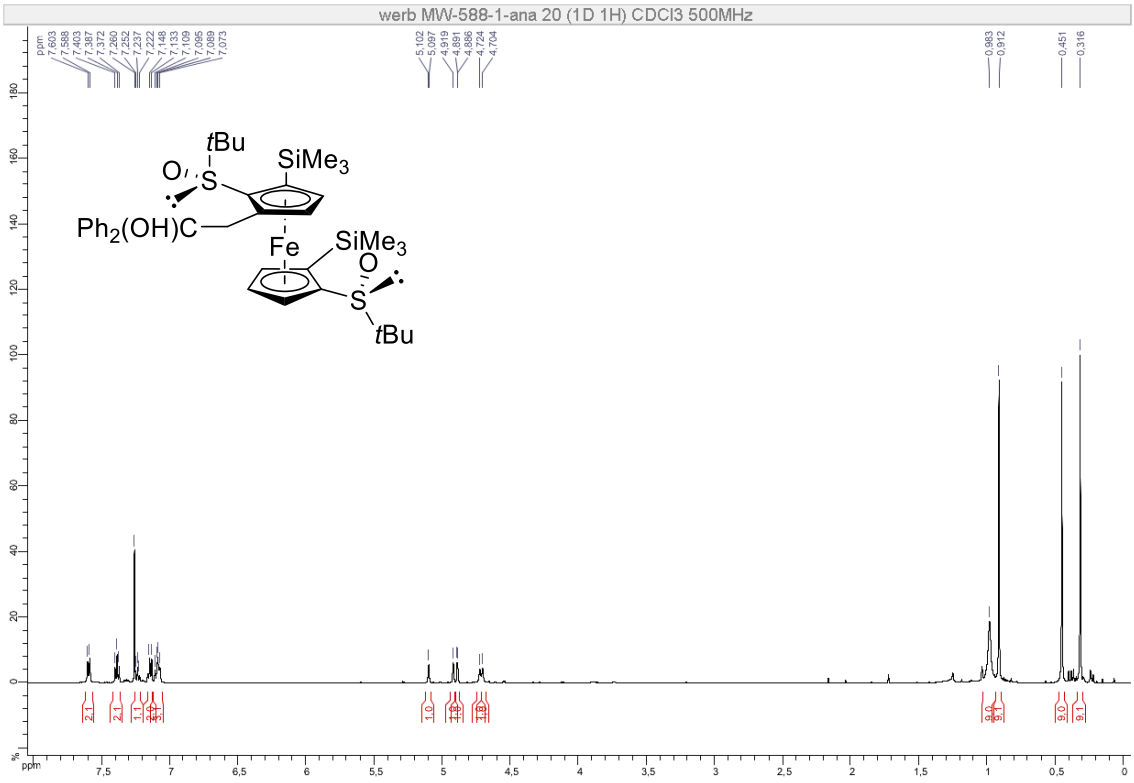
Mixture of (*R*,*R*,*R*P,*R*P)-*S*,*S*'-di-*tert*-butyl-4,4'-di(isobutoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6'c) and (*R*,*R*,*R*P,*R*P)-*S*,*S*'-di-*tert*-butyl-4-(isobutoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6c)

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

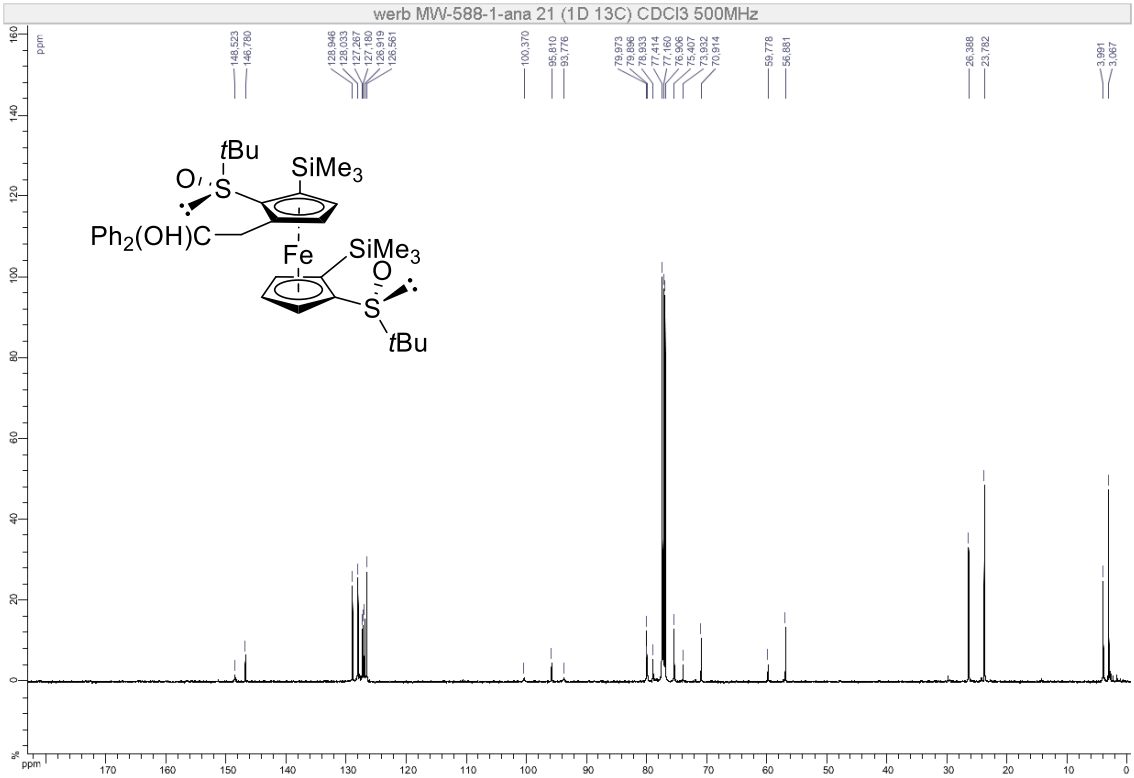


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2-((α,α-diphenyl)hydroxymethyl)-5,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6"d)

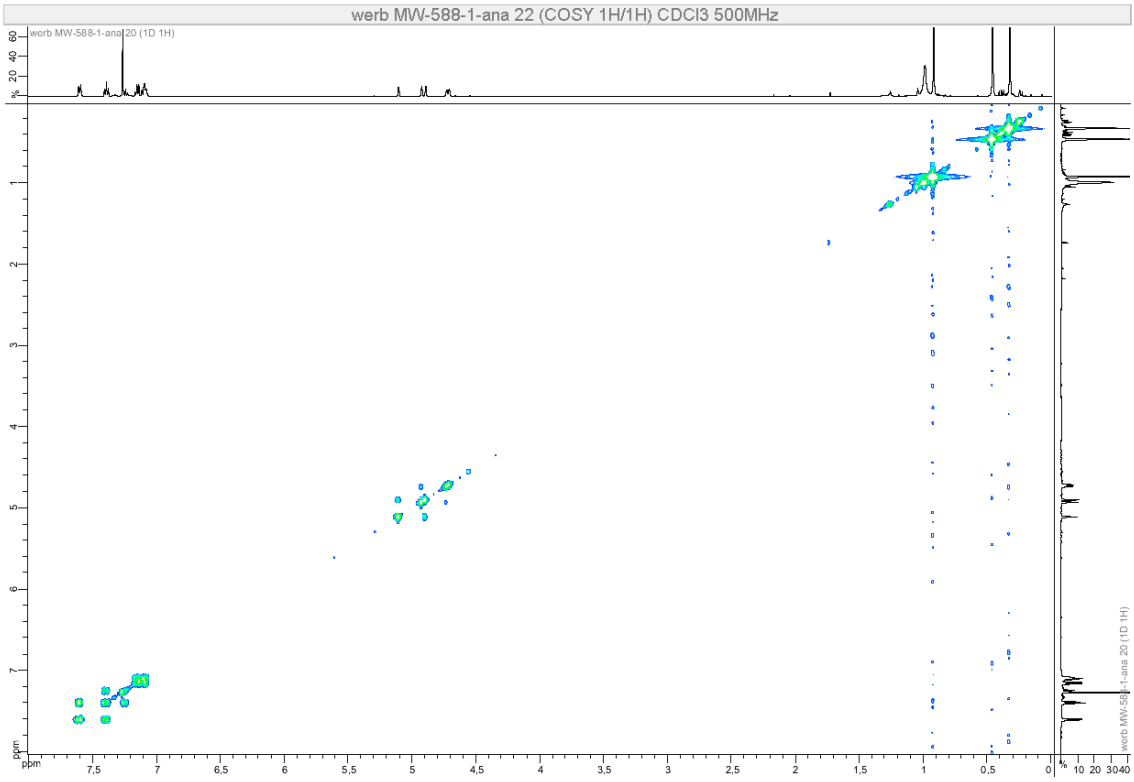
^{1}H NMR (500 MHz, $CDCl_3$)



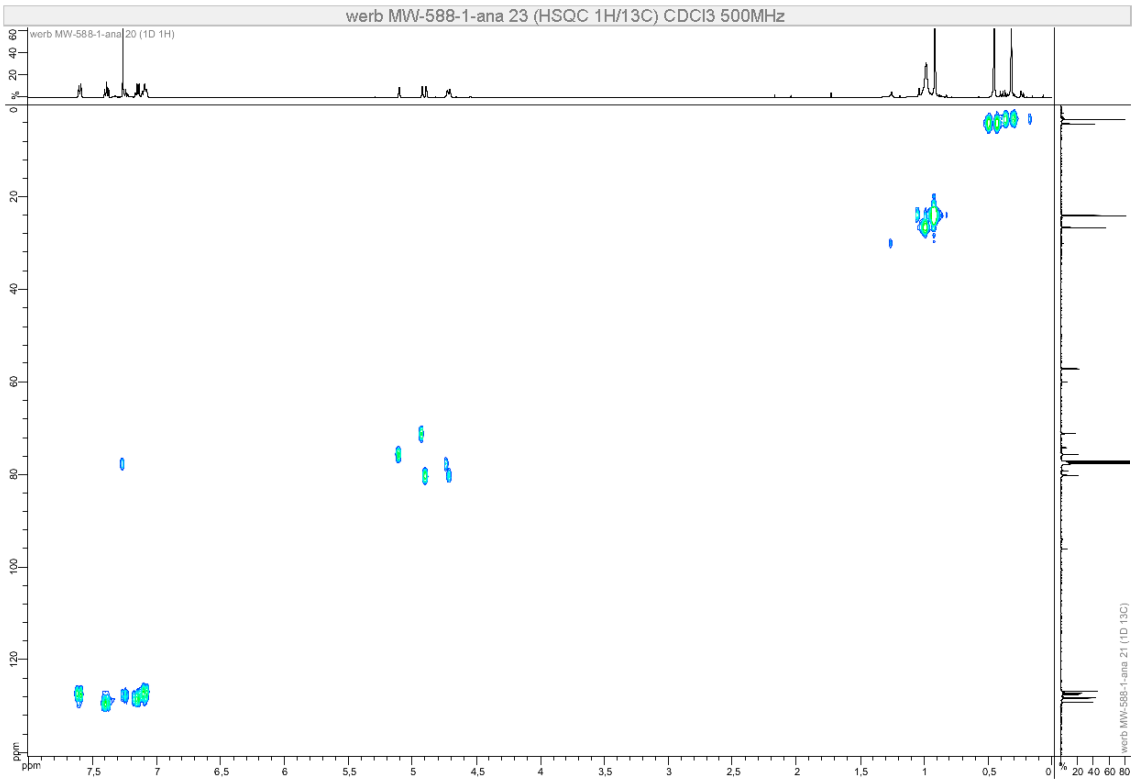
^{13}C NMR (126 MHz, $CDCl_3$)



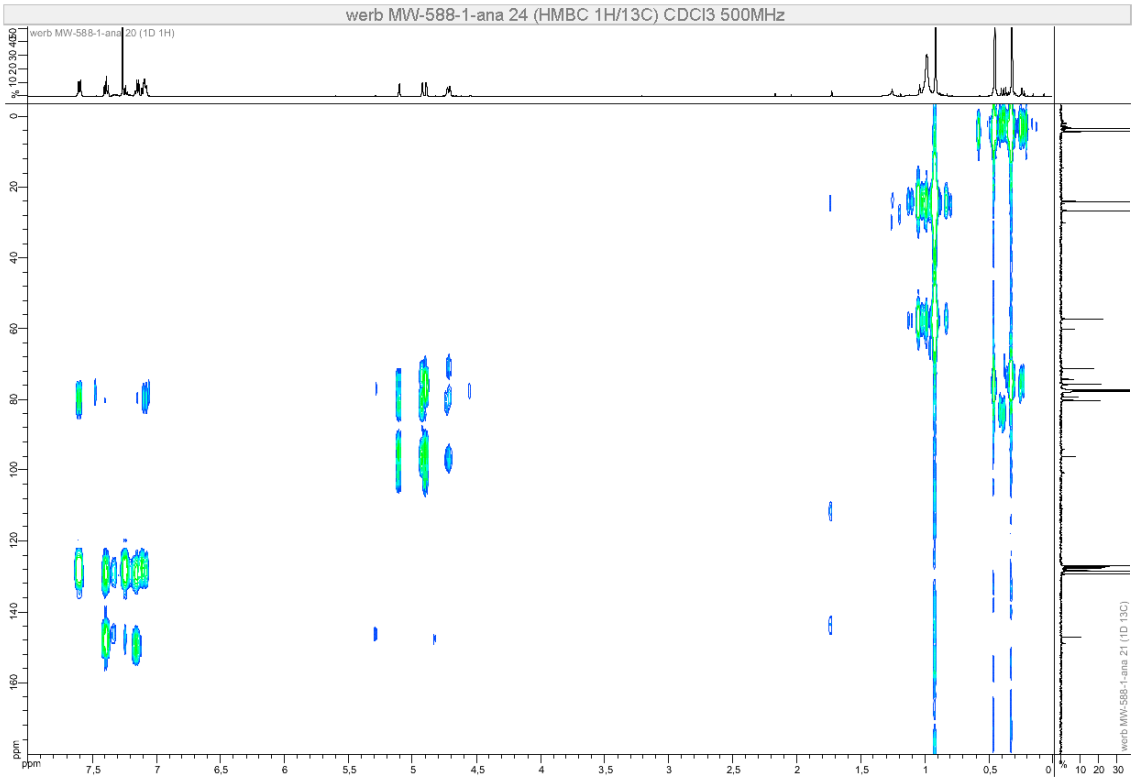
COSY (500 MHz, $CDCl_3$)



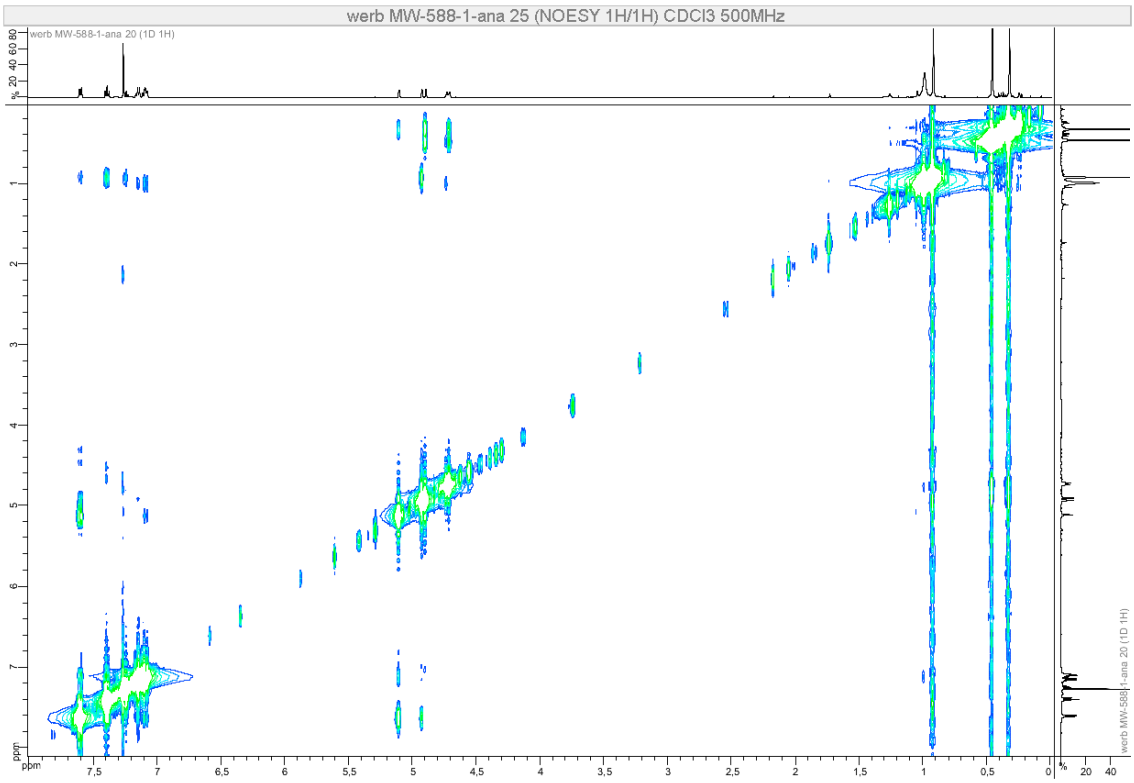
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

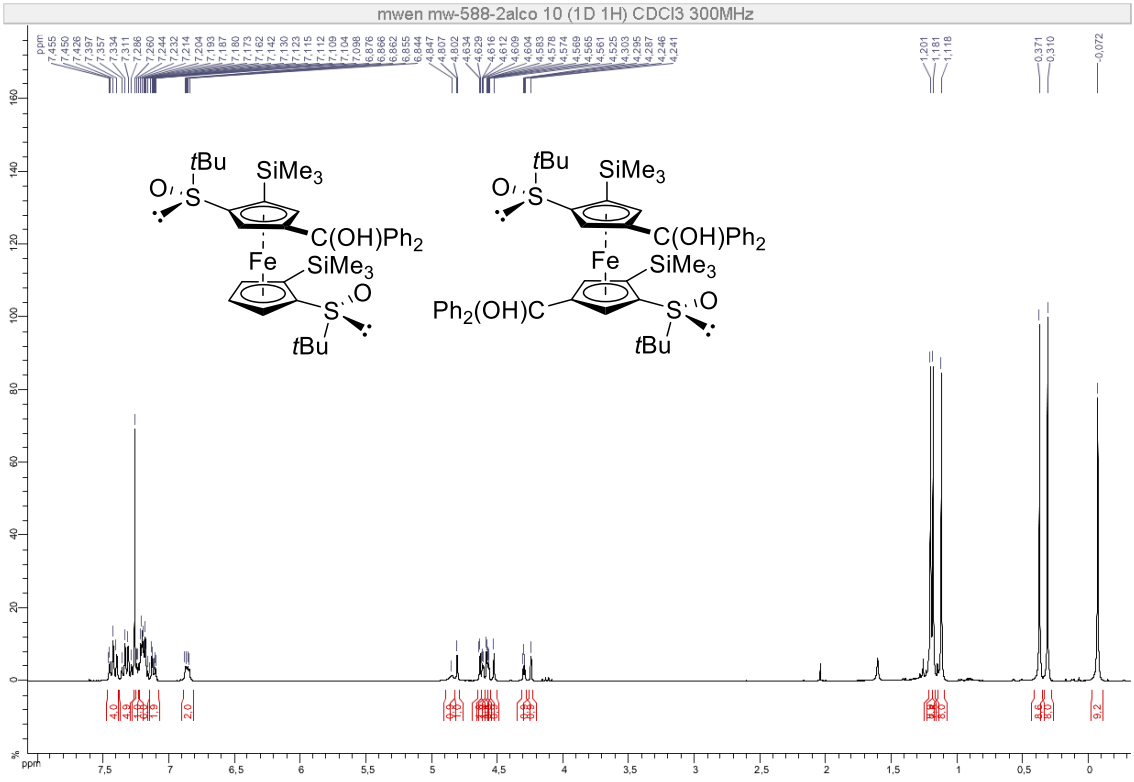


NOESY (500 MHz, $CDCl_3$)



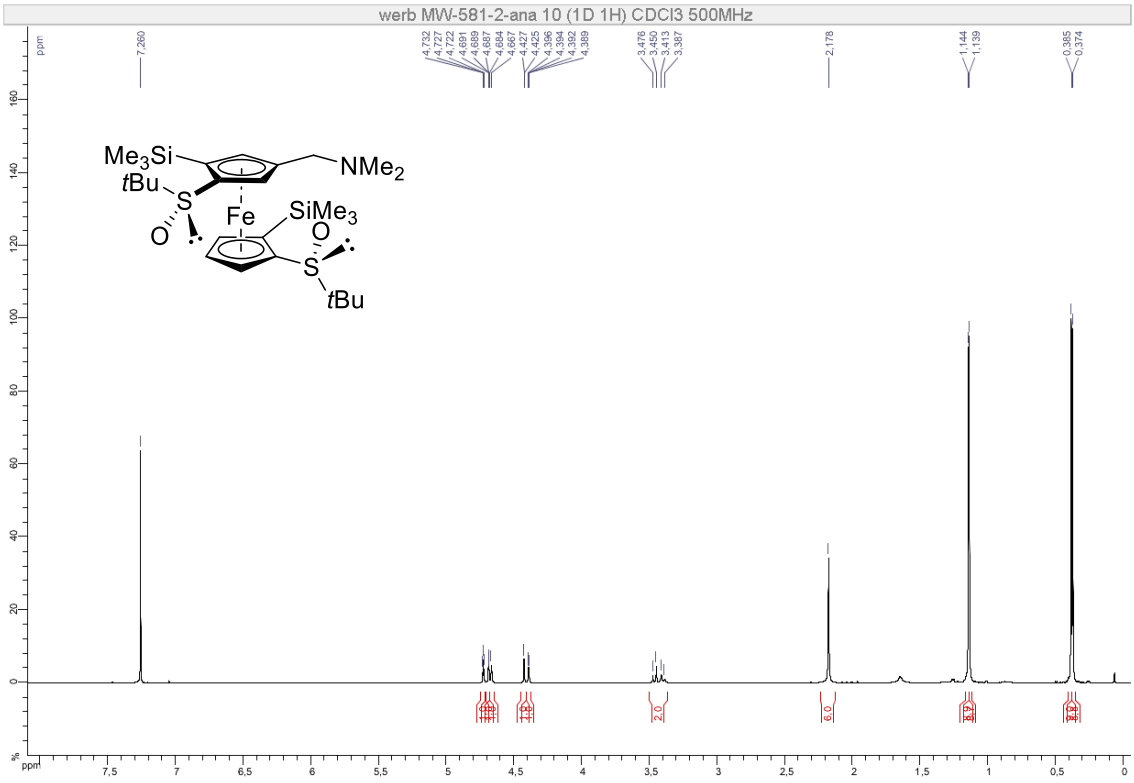
(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4-((α,α-diphenyl)hydroxymethyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6d) and (*R*,*R*,*R*P,*R*P)-*S*,*S*'-di-*tert*-butyl-4,4'-bis-((α,α-diphenyl)hydroxymethyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6'd)

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

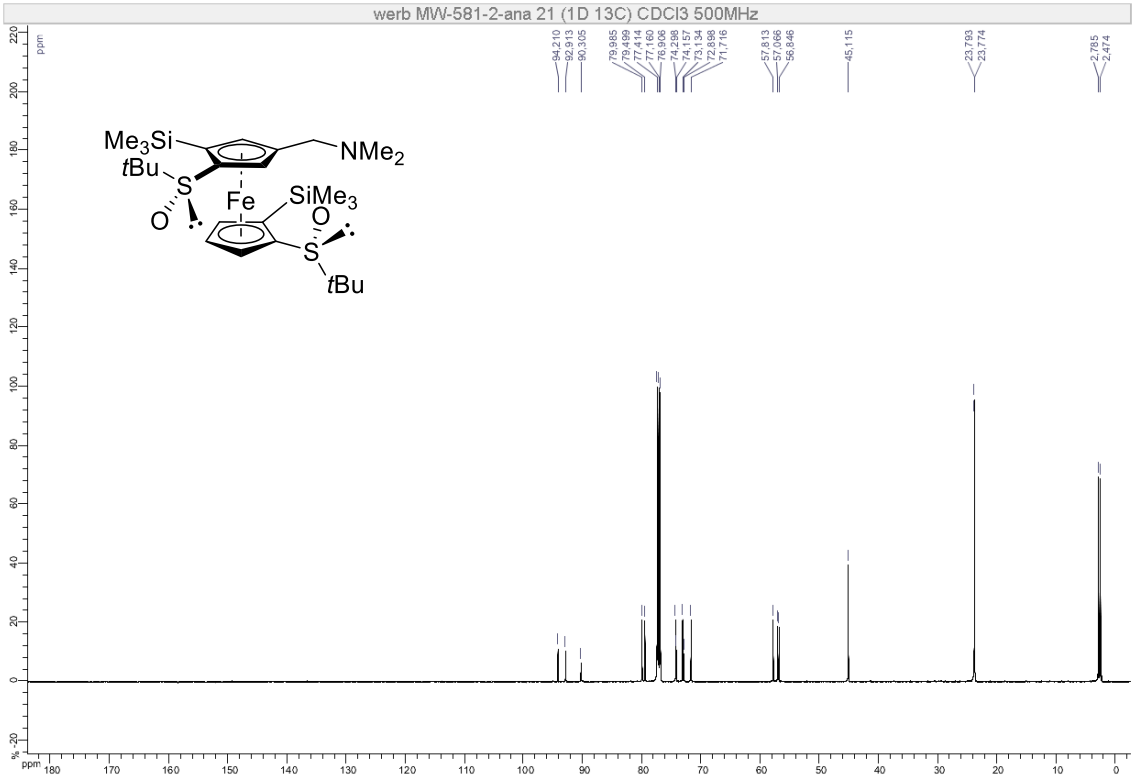


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4-(dimethylaminomethyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6e)

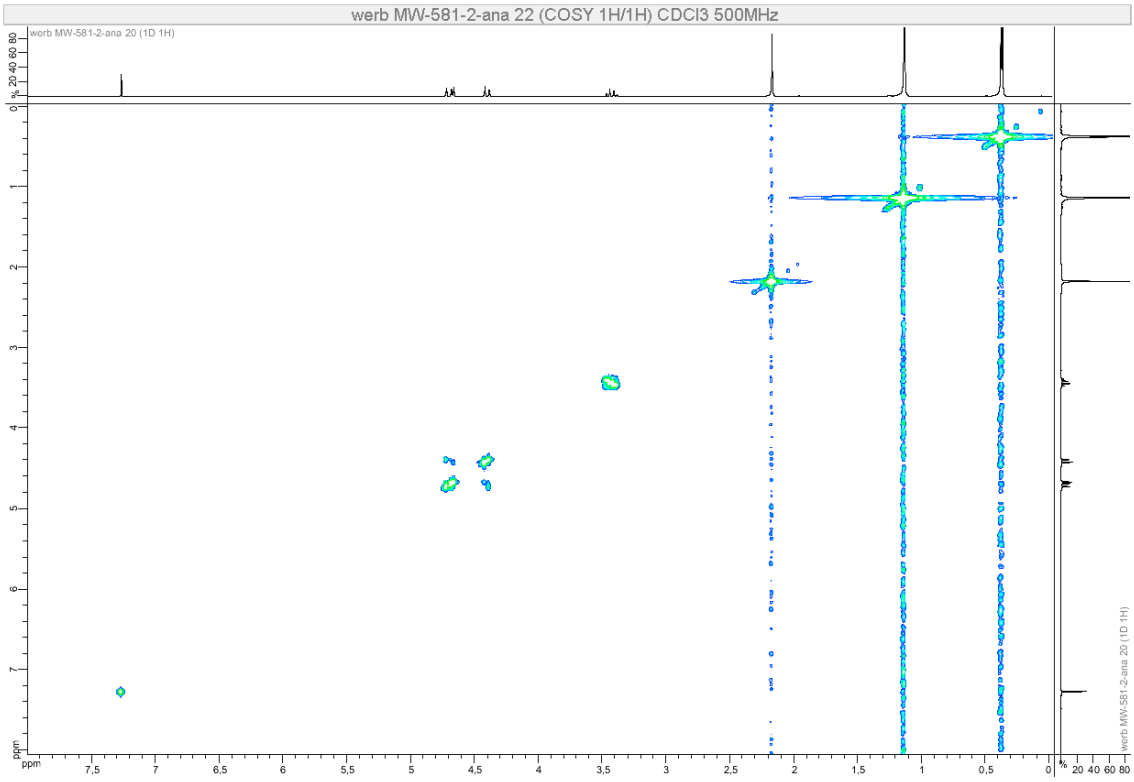
^{1}H NMR (500 MHz, $CDCl_3$)



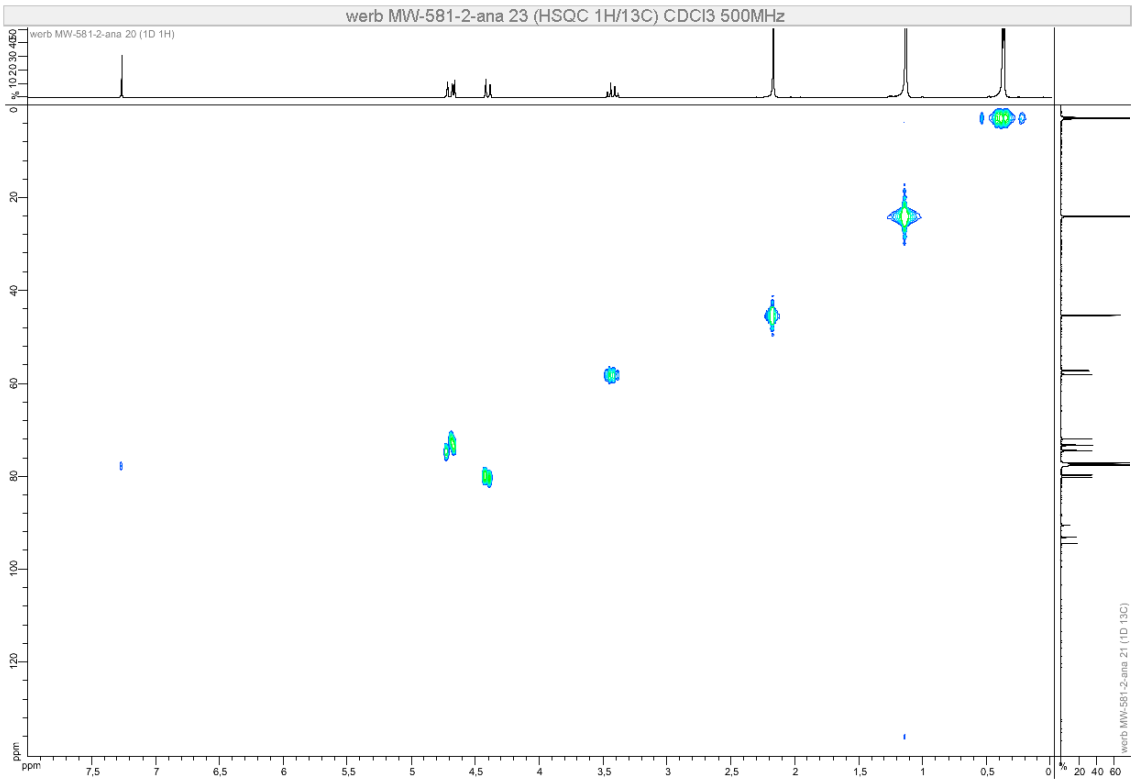
^{13}C NMR (126 MHz, $CDCl_3$)



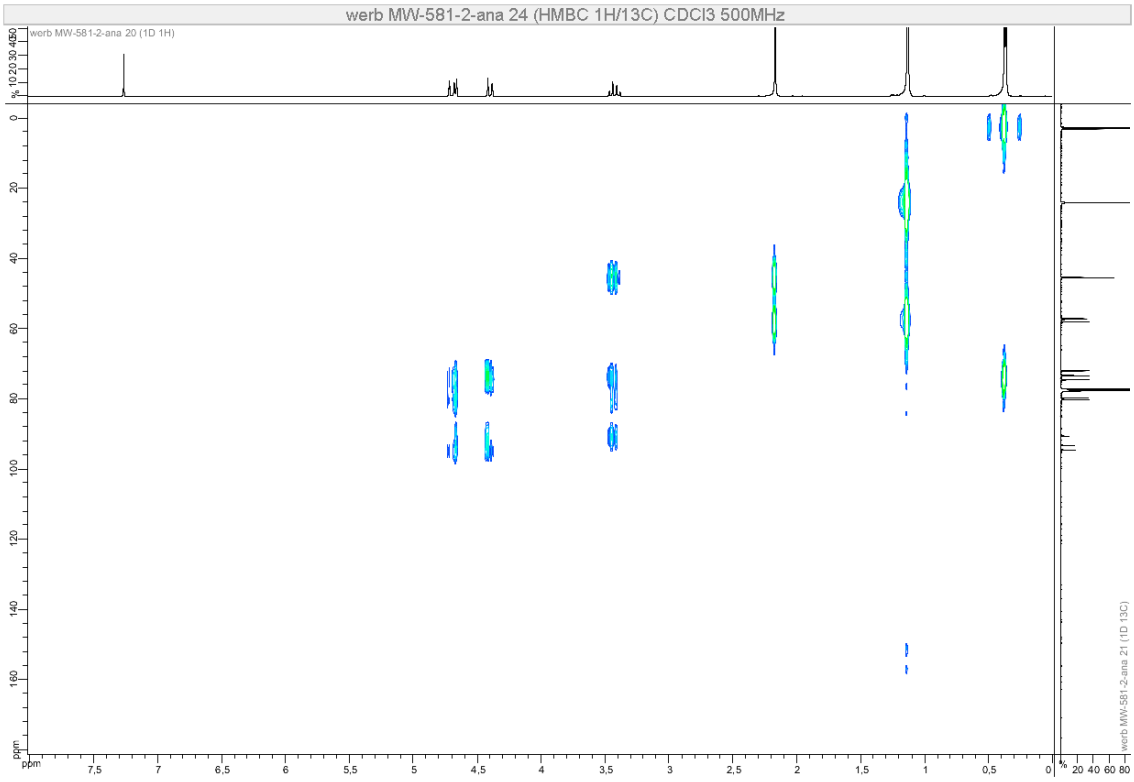
COSY (500 MHz, $CDCl_3$)



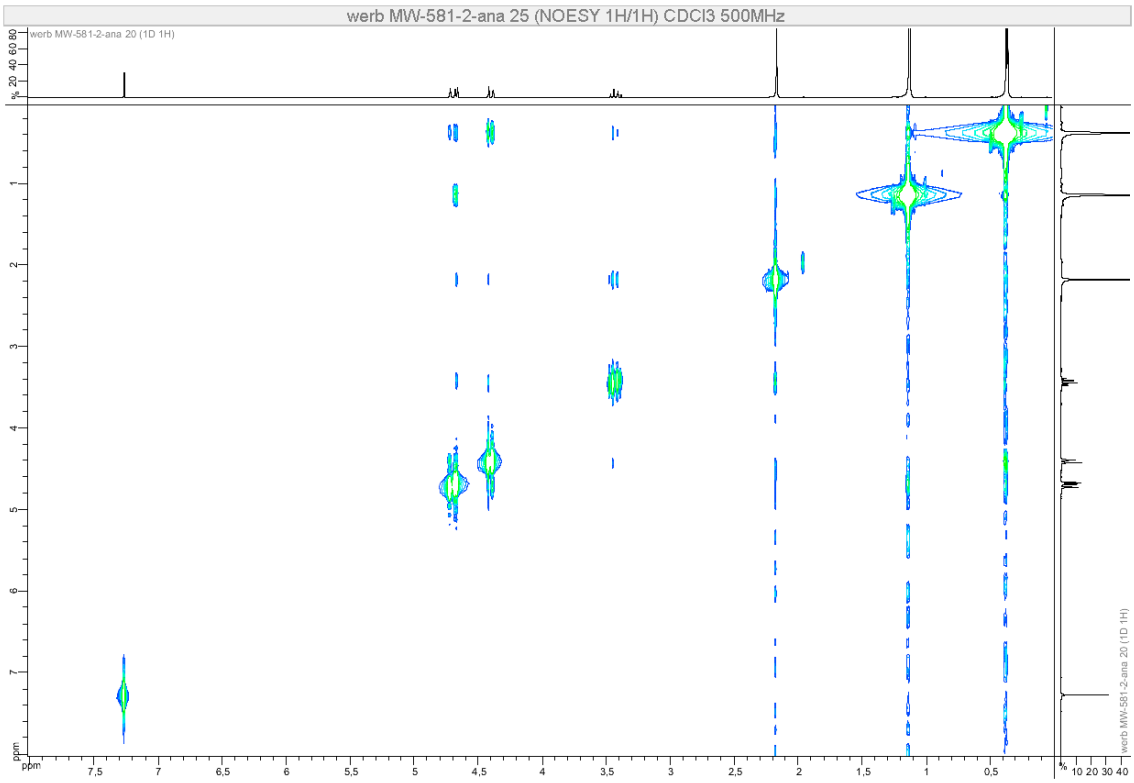
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

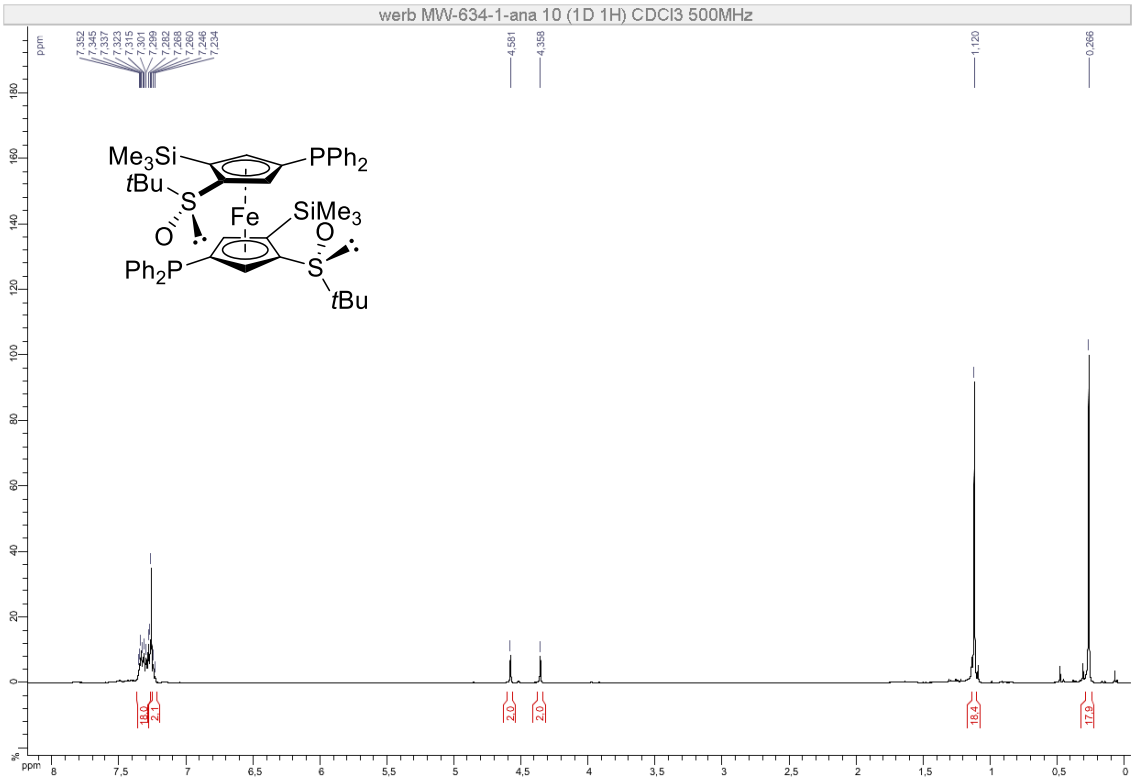


NOESY (500 MHz, $CDCl_3$)

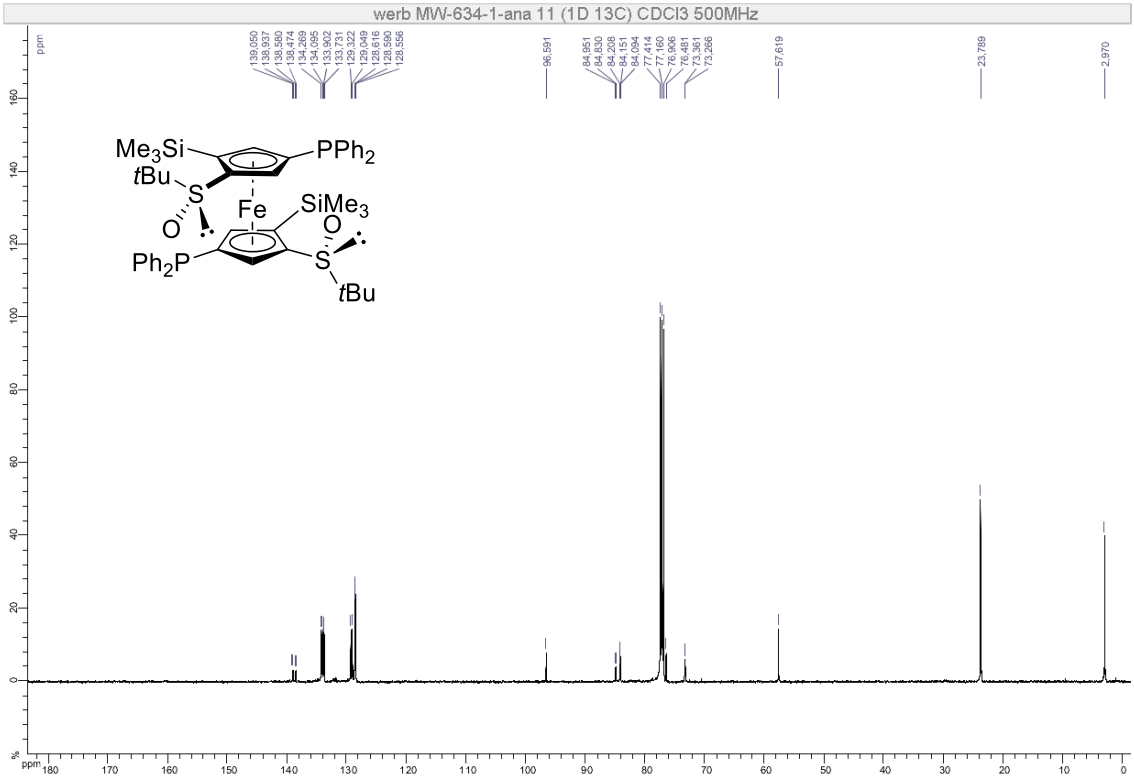


(*R*,*R*,*S*P,*S*P)-*S*,*S*'-Di-*tert*-butyl-4,4'-bis(diphenylphosphino)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*S*P,*S*P-6'f)

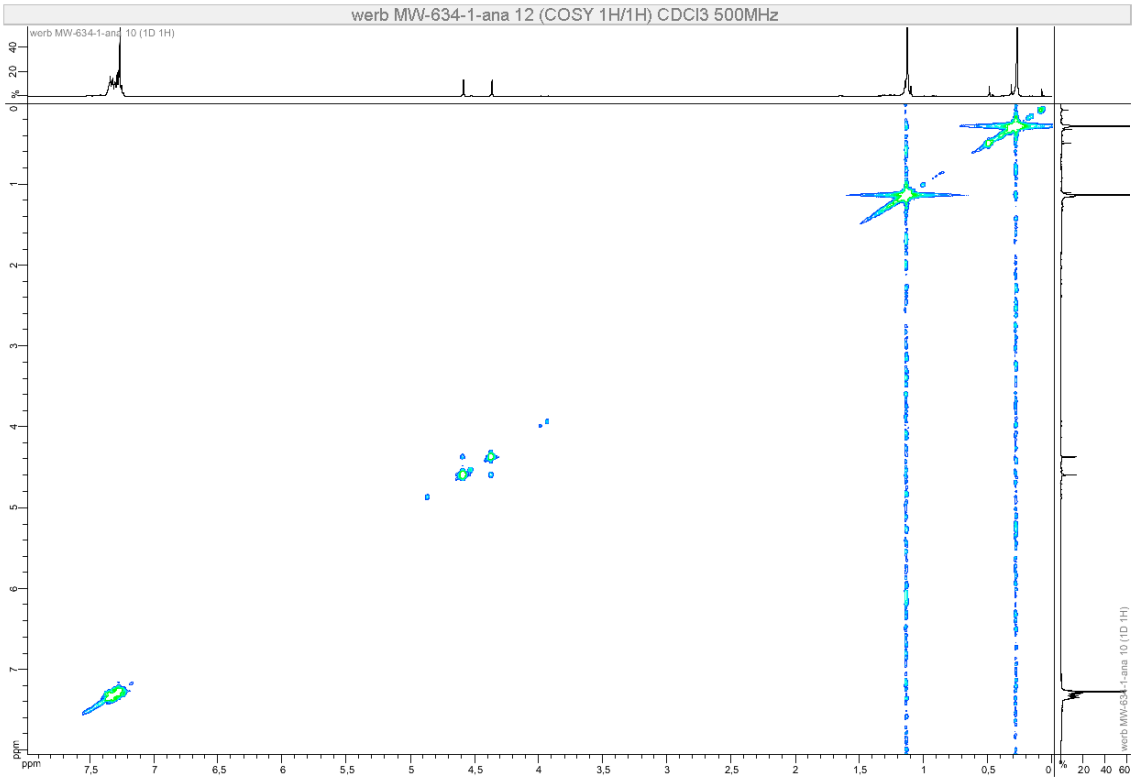
^{1}H NMR (500 MHz, $CDCl_3$)



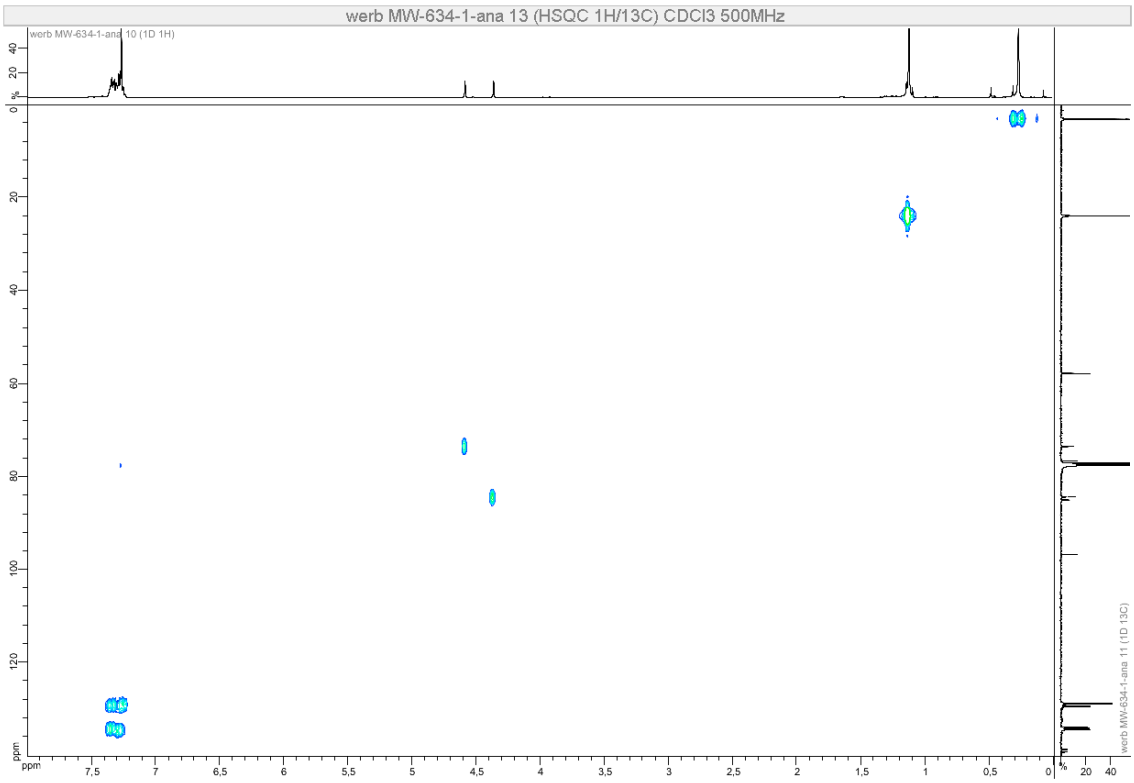
^{13}C NMR (126 MHz, $CDCl_3$)



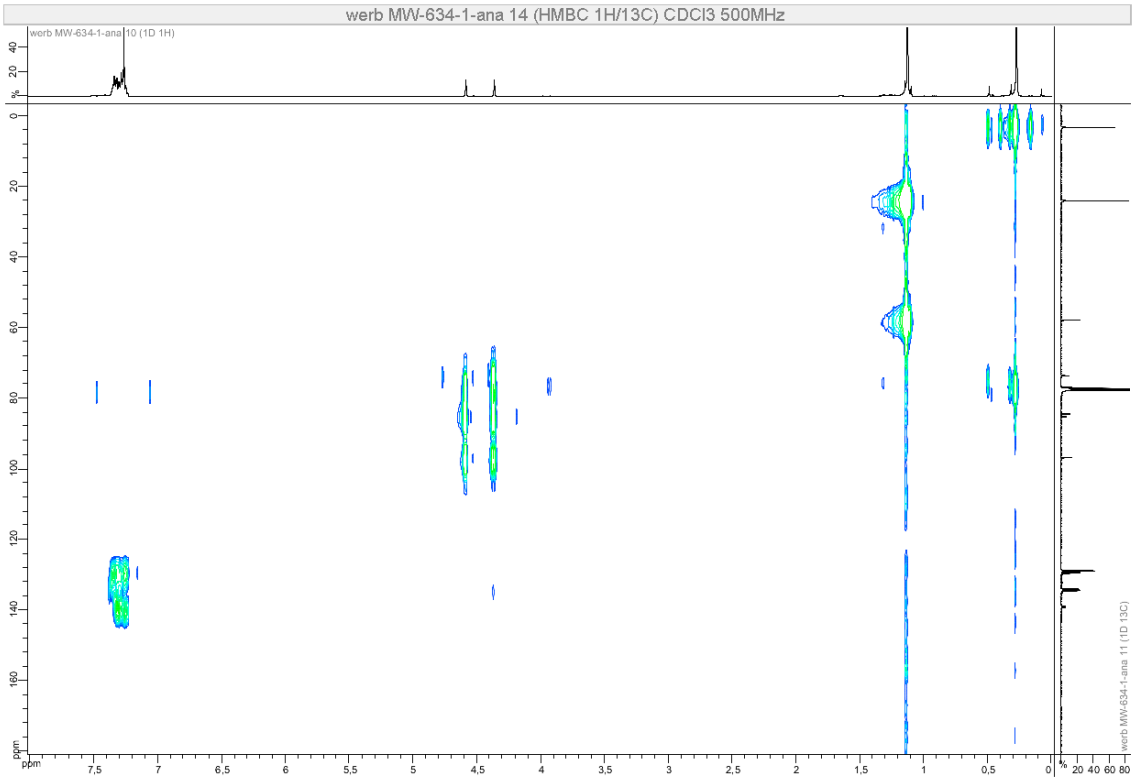
COSY (500 MHz, $CDCl_3$)



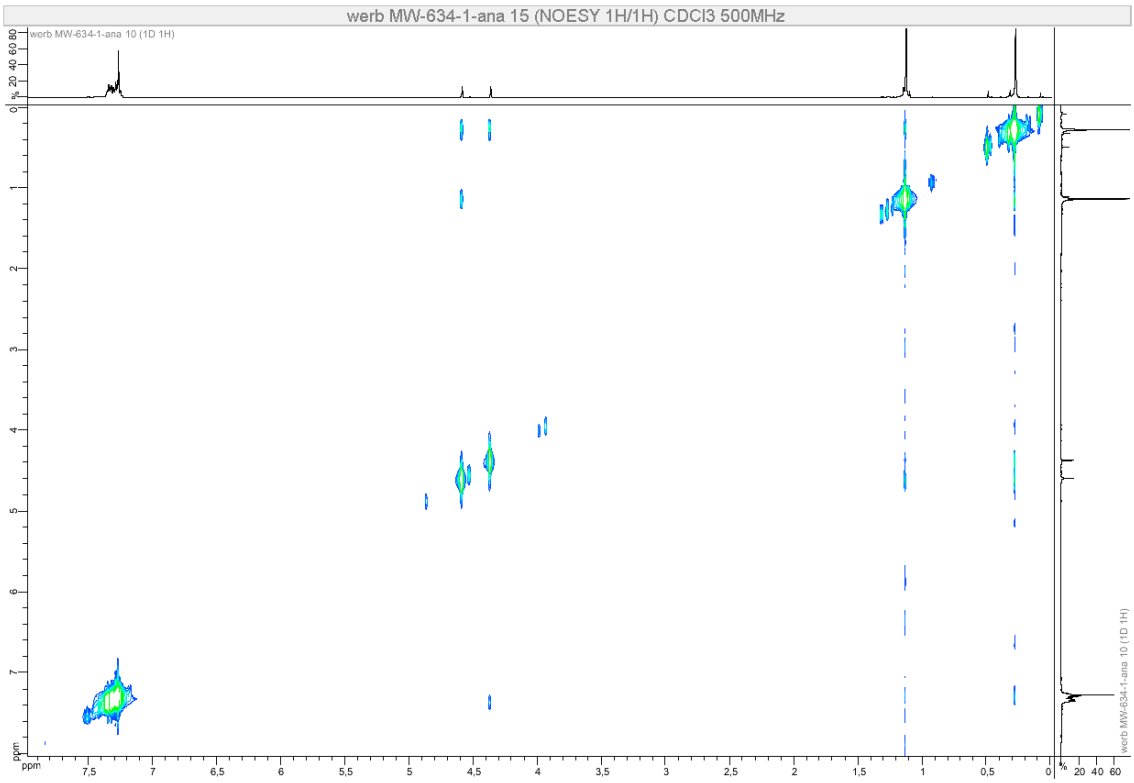
HSQC (500 MHz, $CDCl_3$)



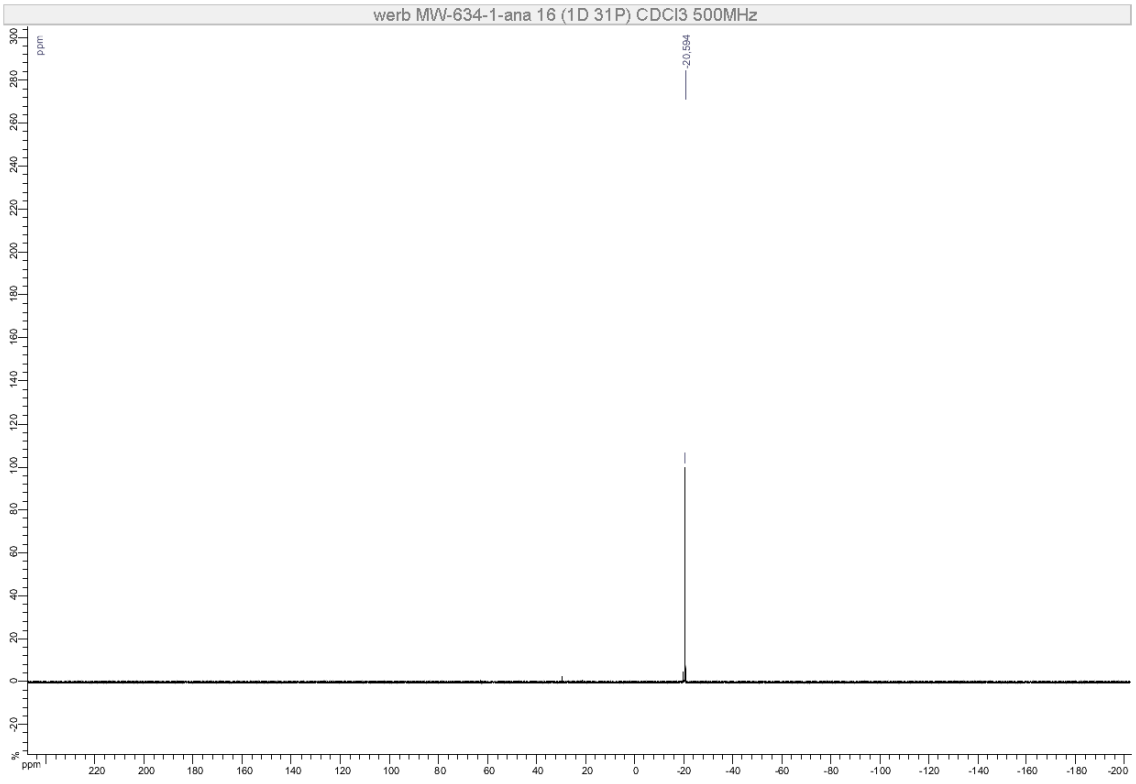
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

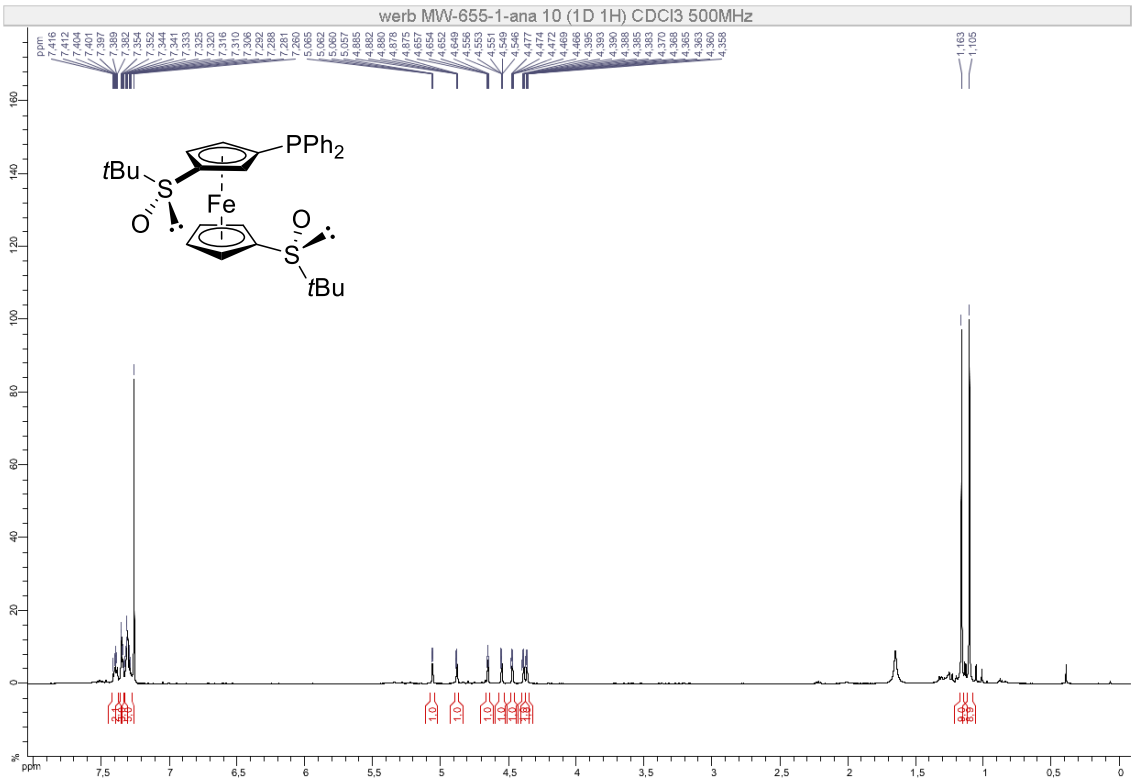


^{31}P NMR (202 MHz, $CDCl_3$)

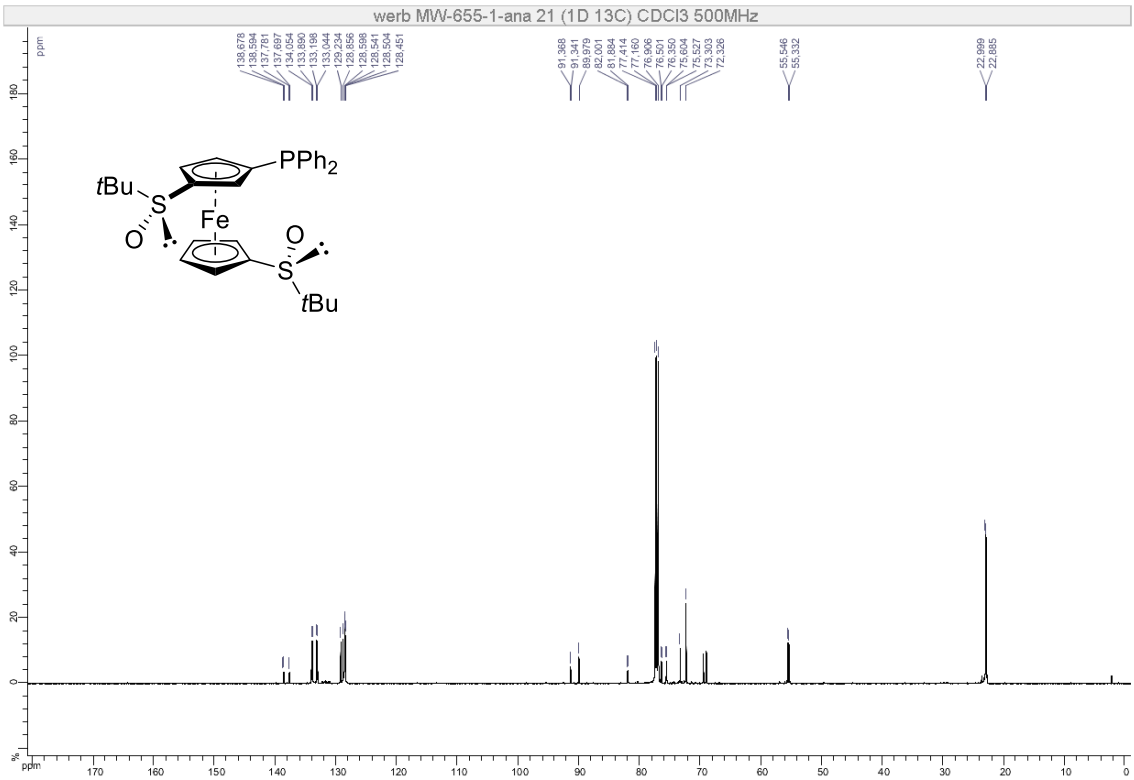


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-3-(diphenylphosphino)ferrocene-1,1'-disulfoxide (*S*P-7')

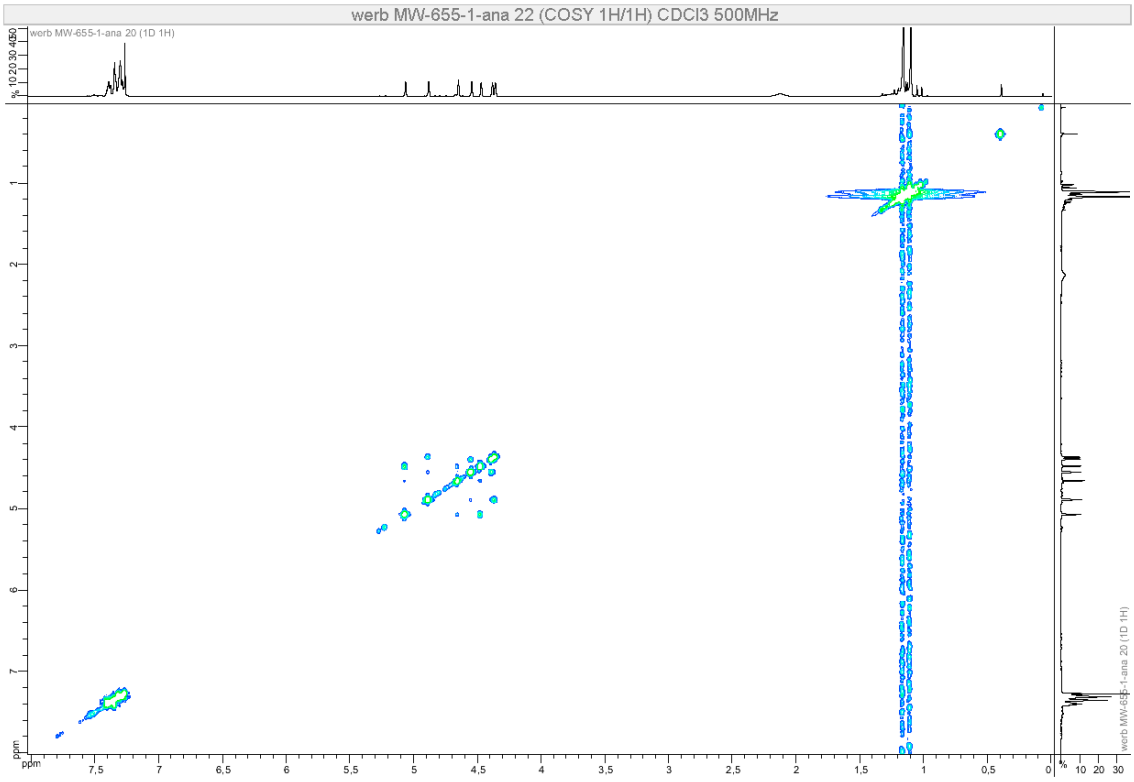
^{1}H NMR (500 MHz, $CDCl_3$)



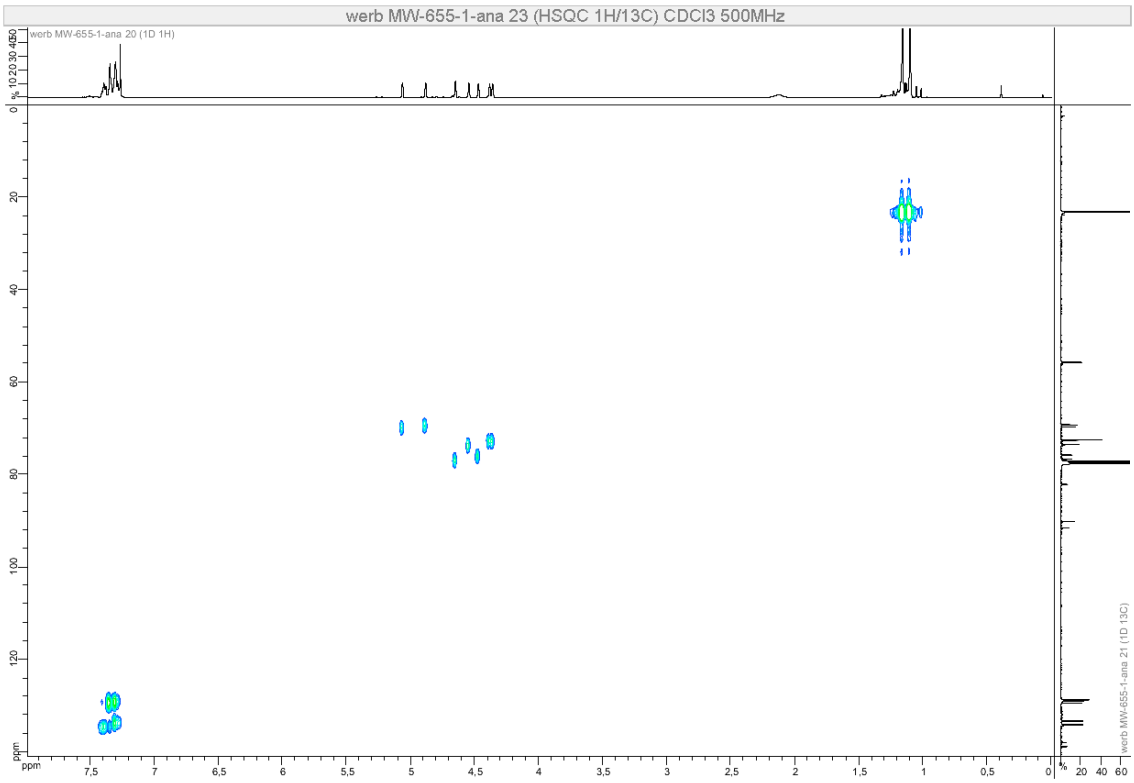
^{13}C NMR (126 MHz, $CDCl_3$)



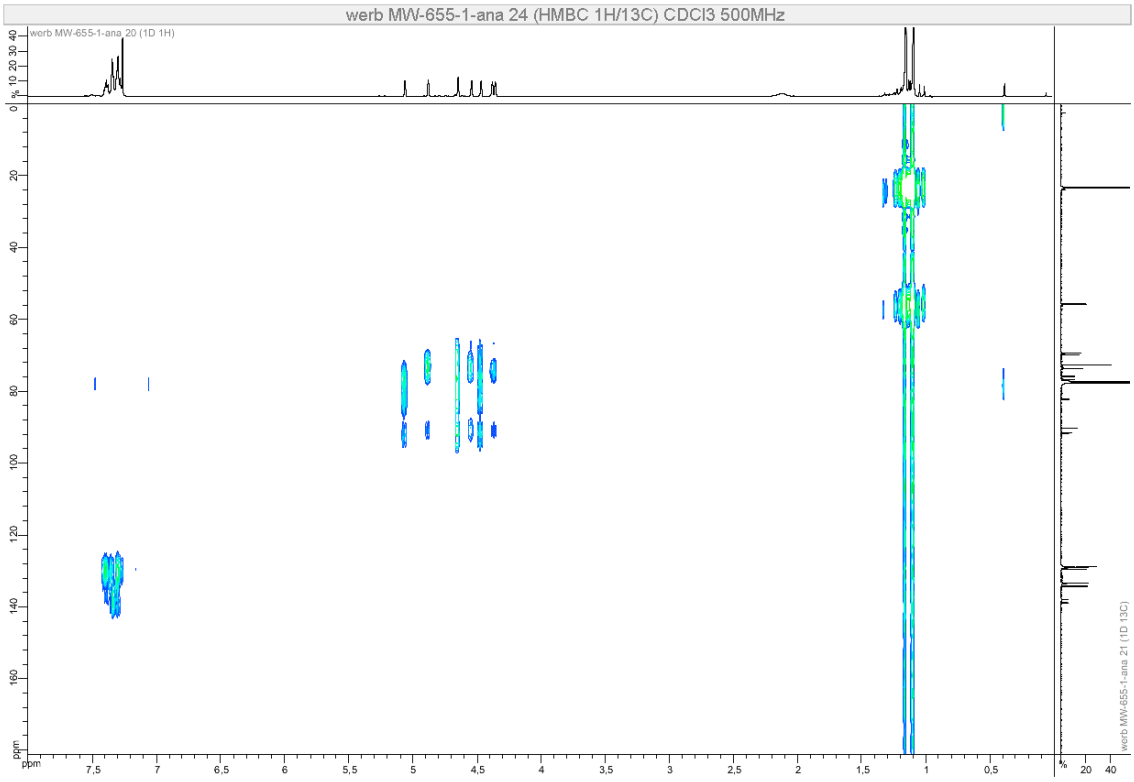
COSY (500 MHz, $CDCl_3$)



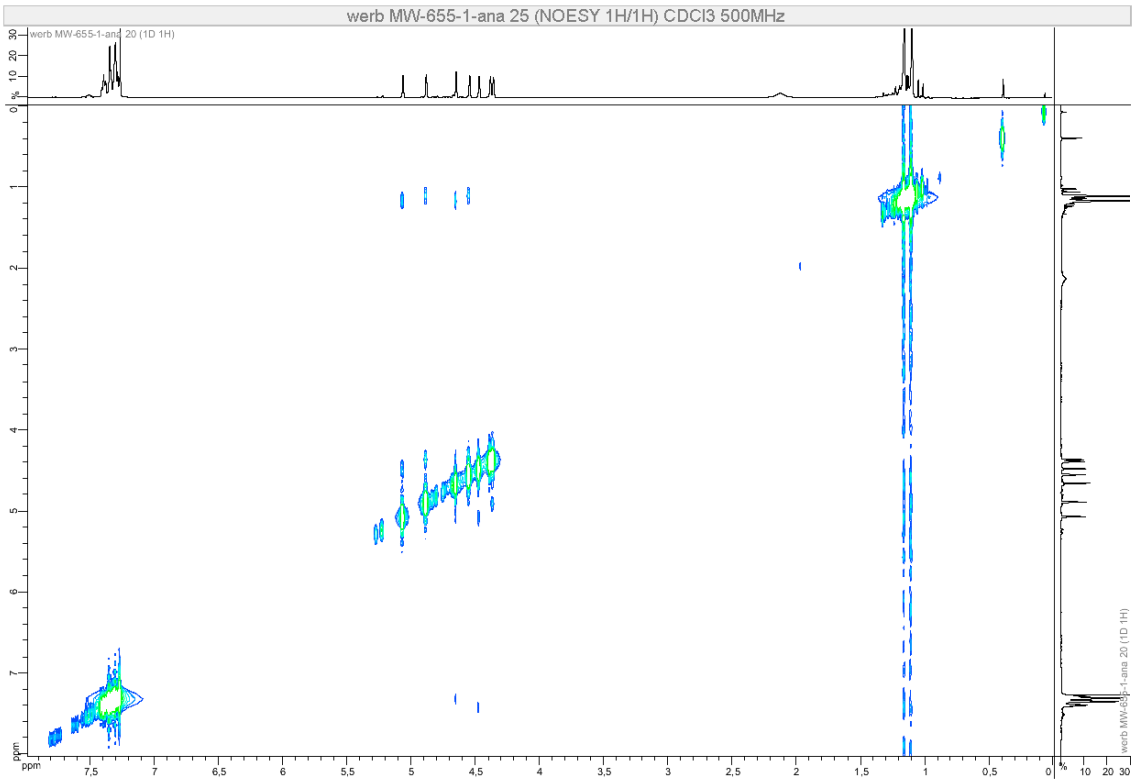
HSQC (500 MHz, $CDCl_3$)



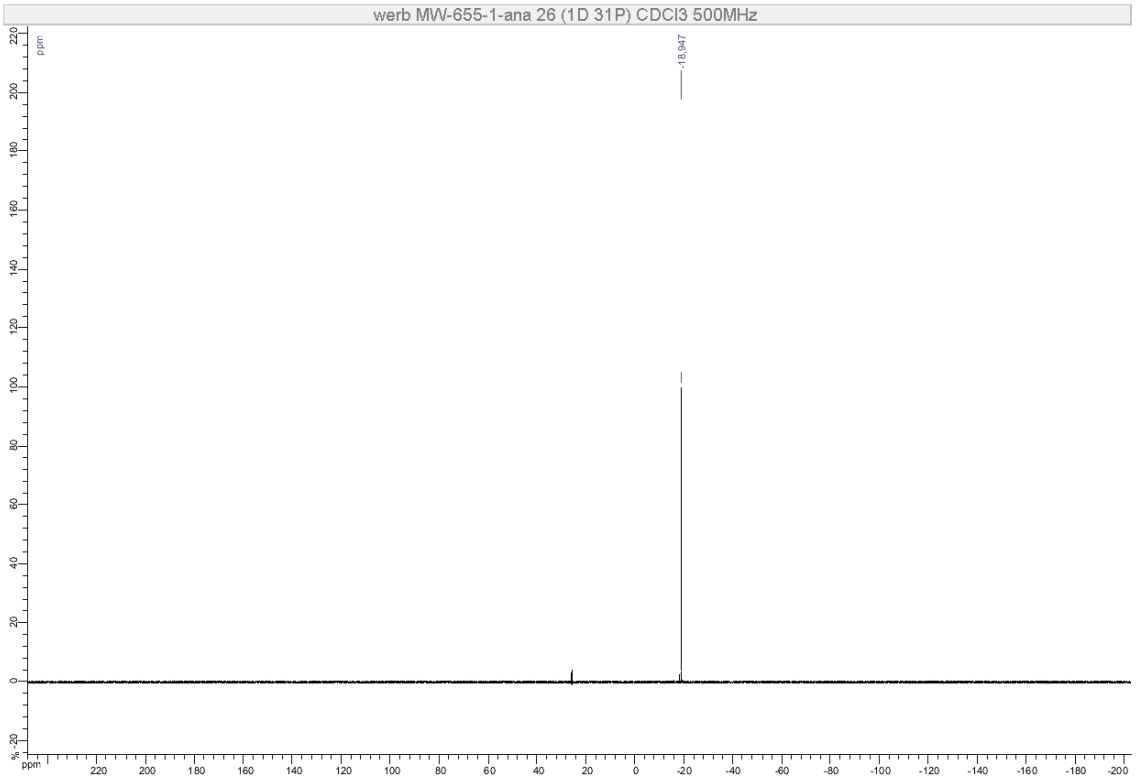
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

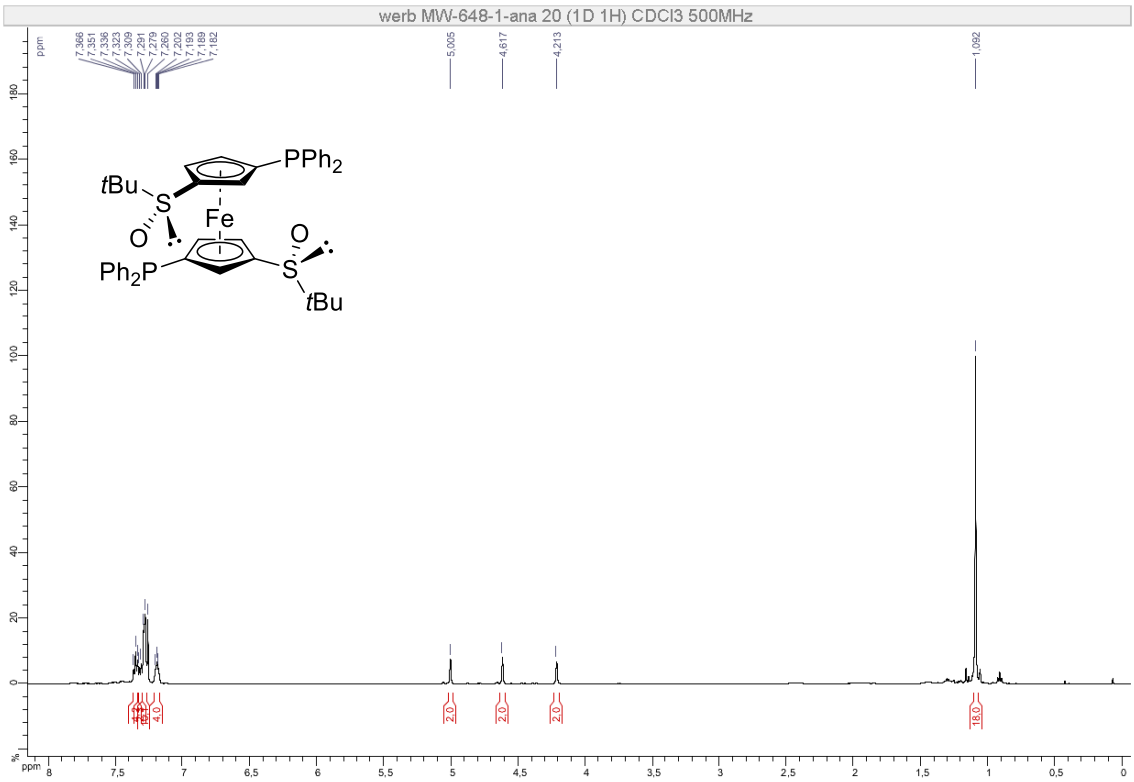


^{31}P NMR (202 MHz, $CDCl_3$)

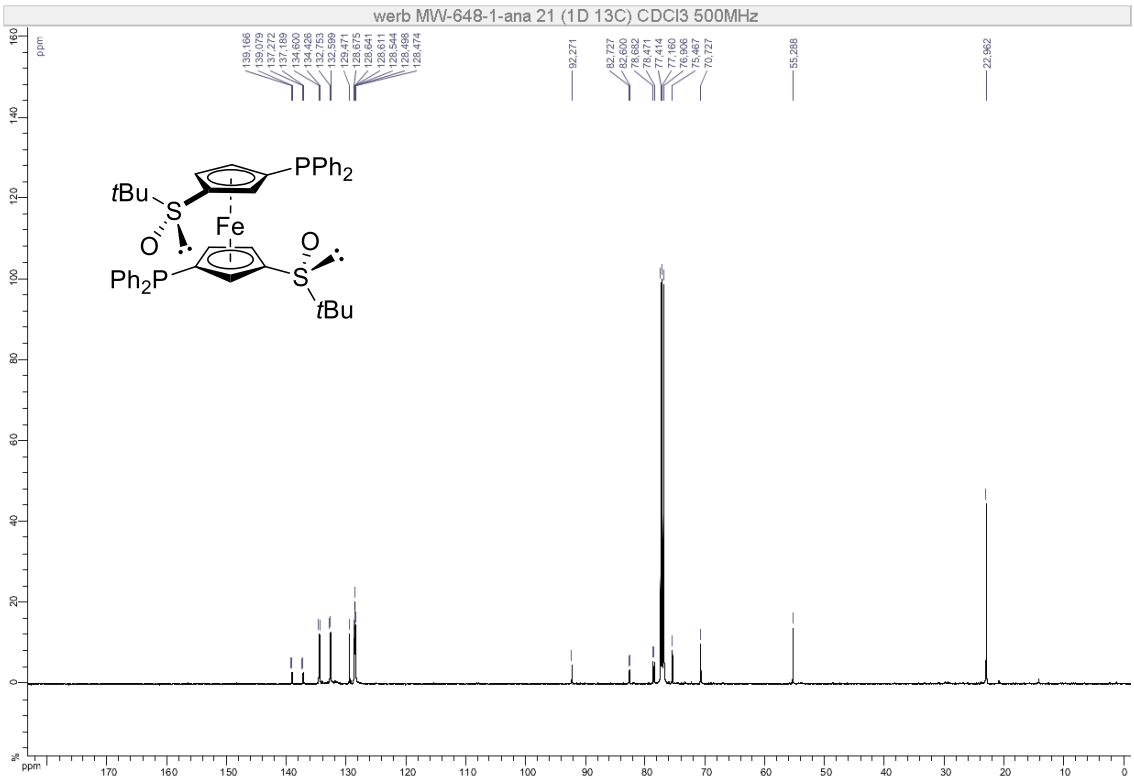


(*R*,*R*,*S*P,*S*P)-*S*,*S*'-Di-*tert*-butyl-3,3'-bis(diphenylphosphino)ferrocene-1,1'-disulfoxide (*S*P,*S*P-7)

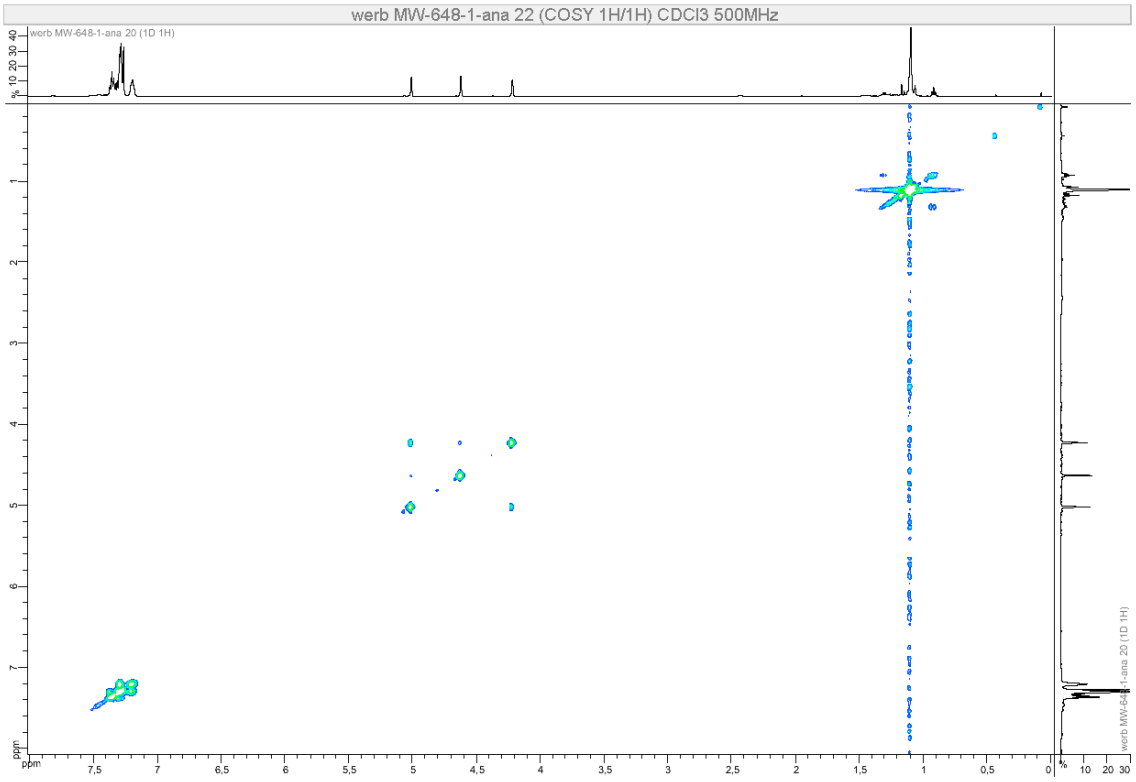
^{1}H NMR (500 MHz, $CDCl_3$)



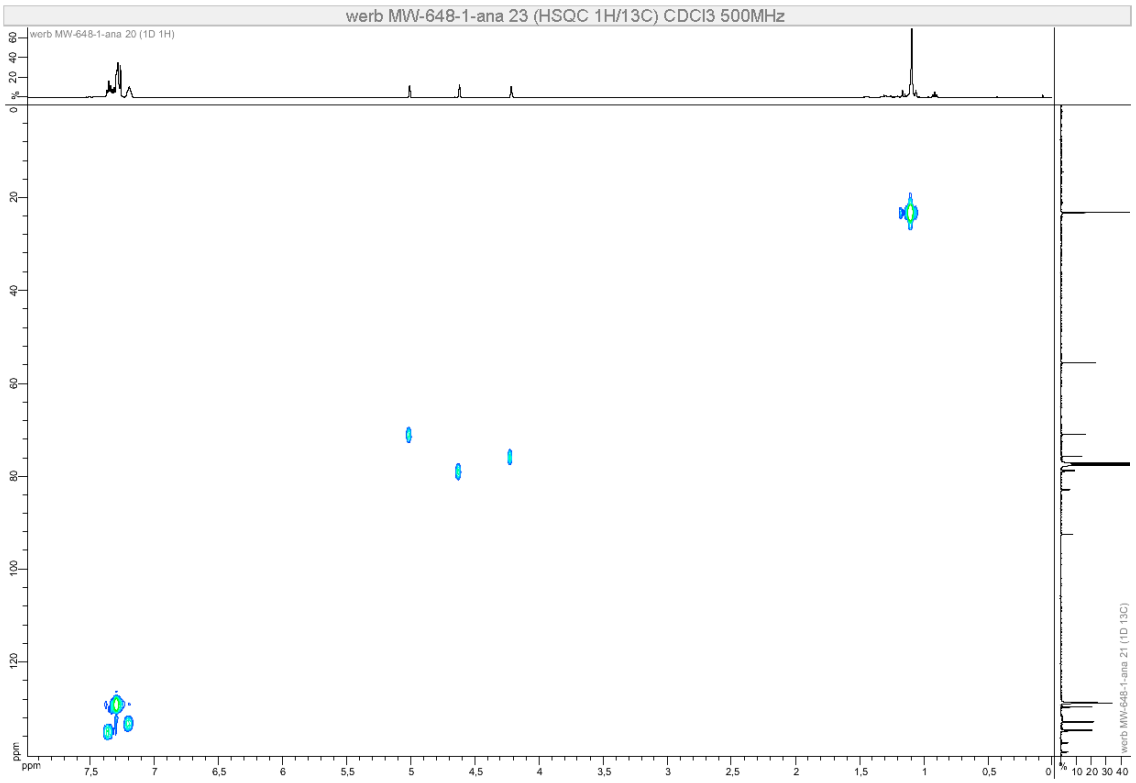
^{13}C NMR (126 MHz, $CDCl_3$)



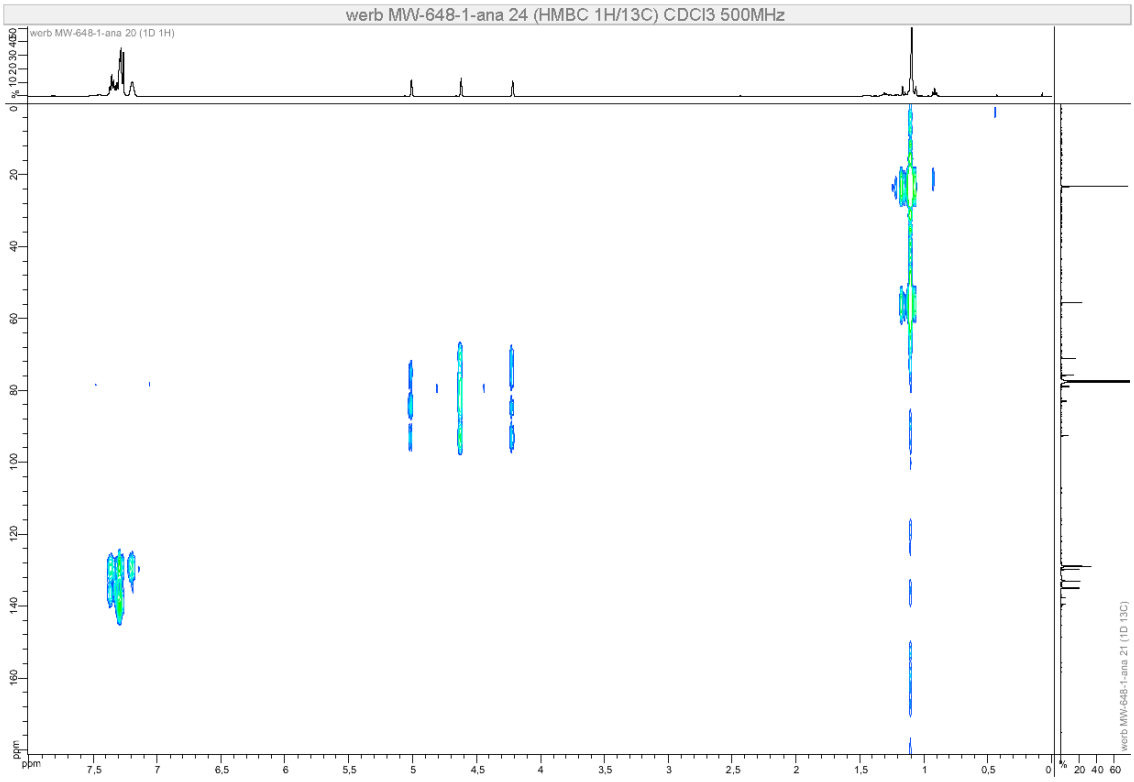
COSY (500 MHz, $CDCl_3$)



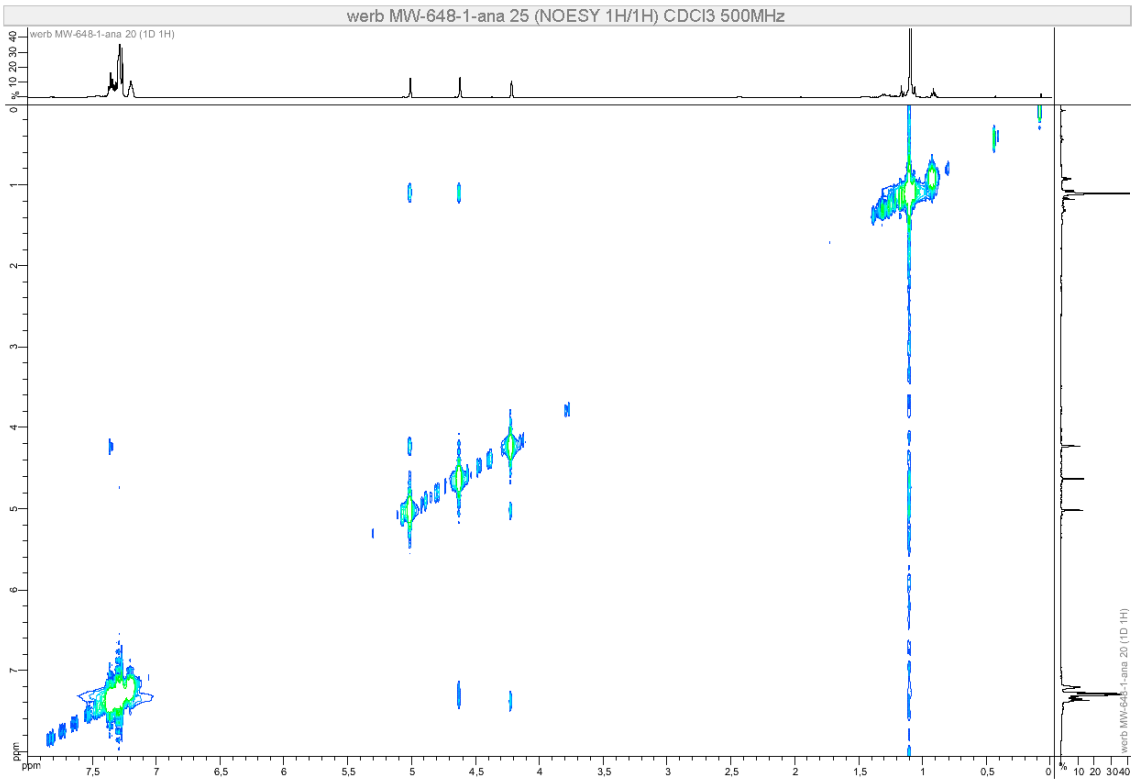
HSQC (500 MHz, $CDCl_3$)



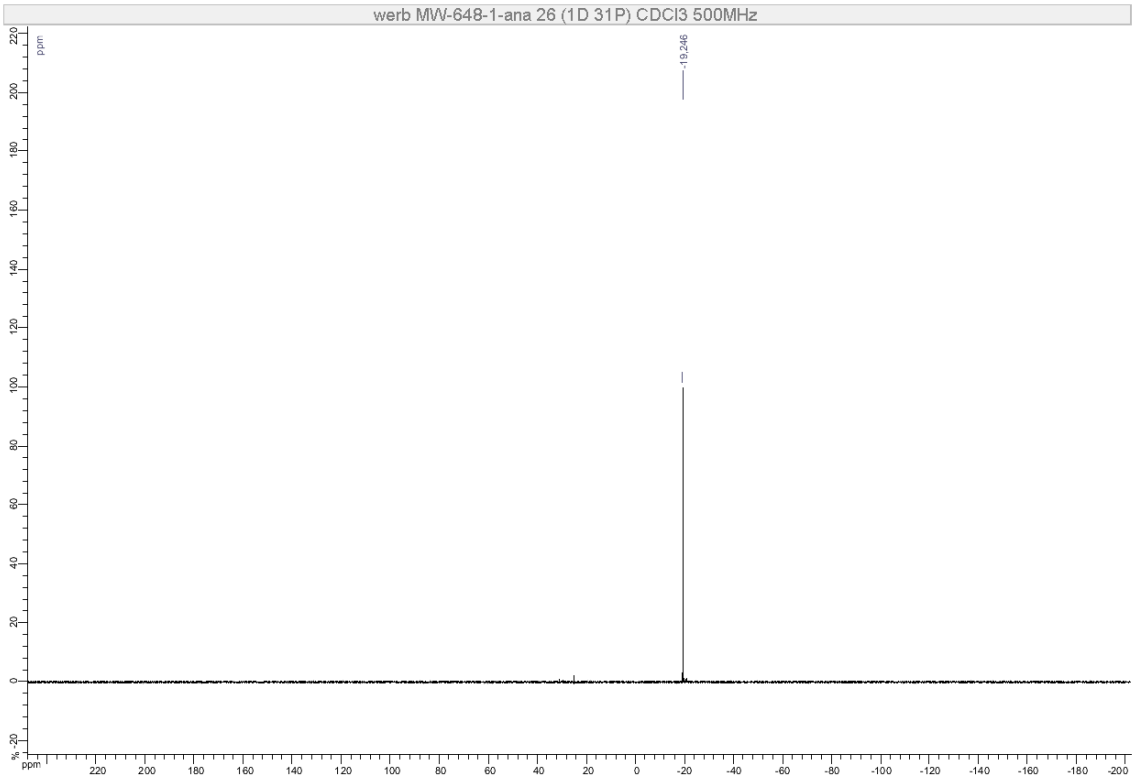
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

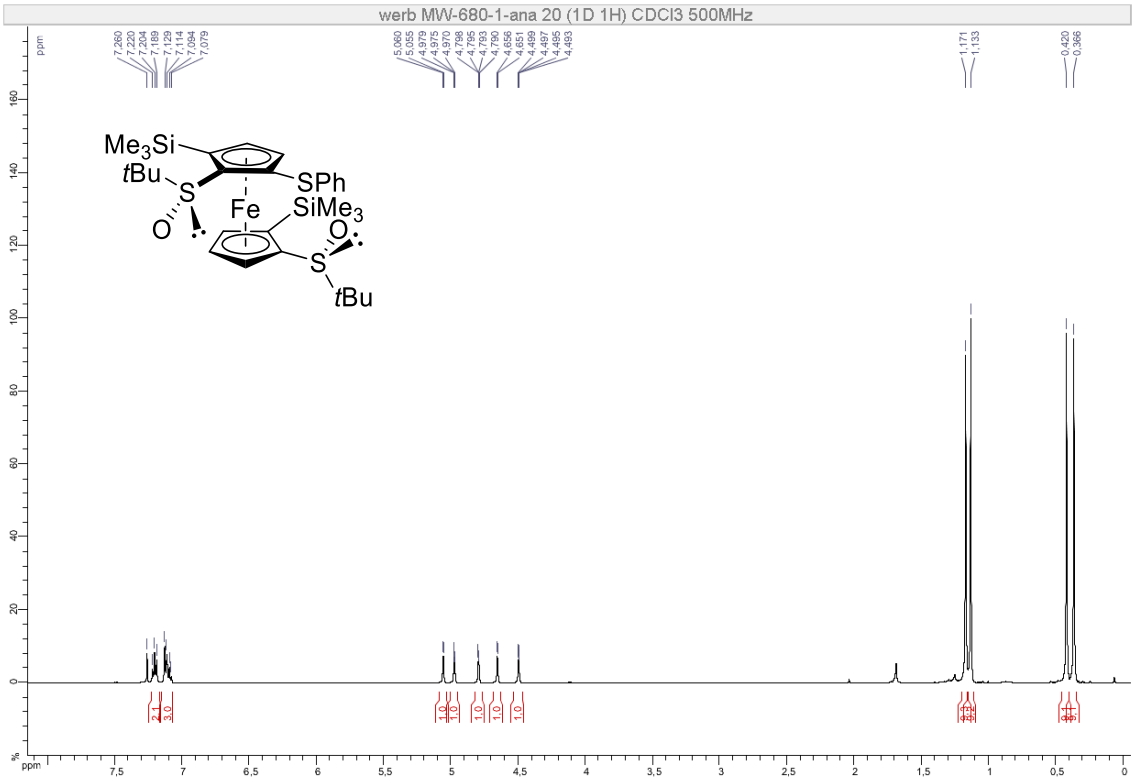


^{31}P NMR (202 MHz, $CDCl_3$)

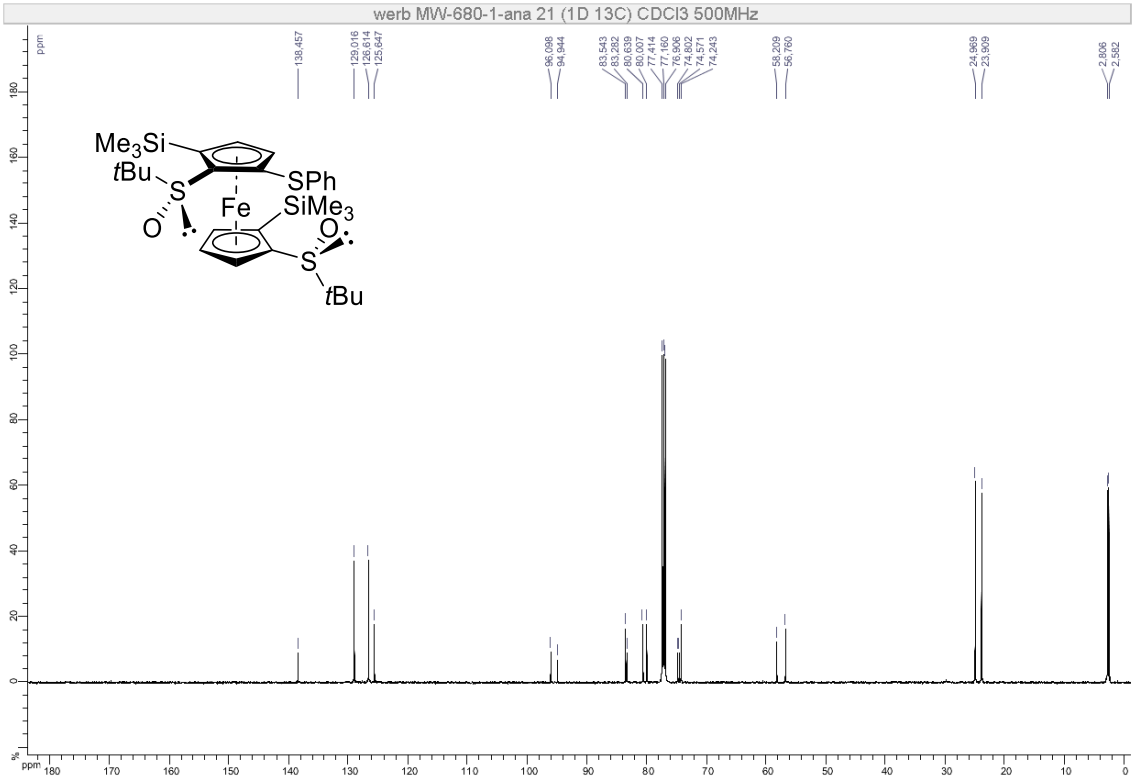


(*R*,*R*,*S*$_P$,*R*$_P$)-*S*,*S*'-Di-*tert*-butyl-2-(phenylthio)-5,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*S*$_P$,*R*$_P$-6"g)

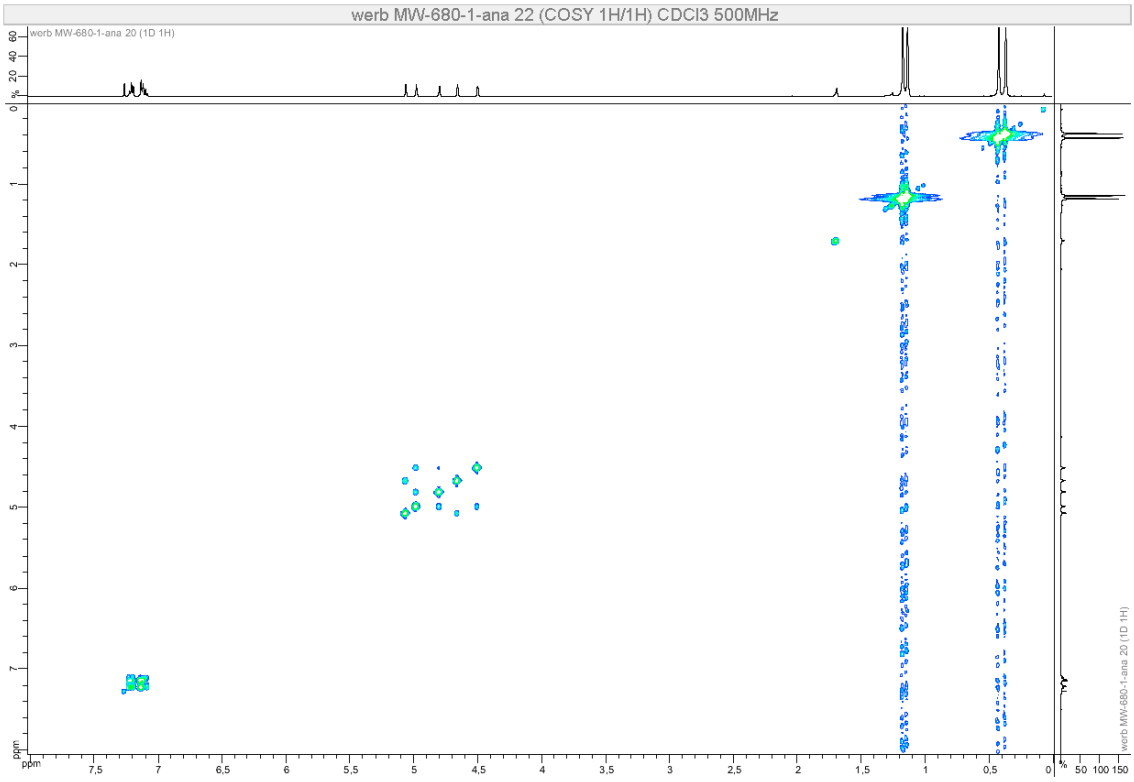
^{1}H NMR (500 MHz, $CDCl_3$)



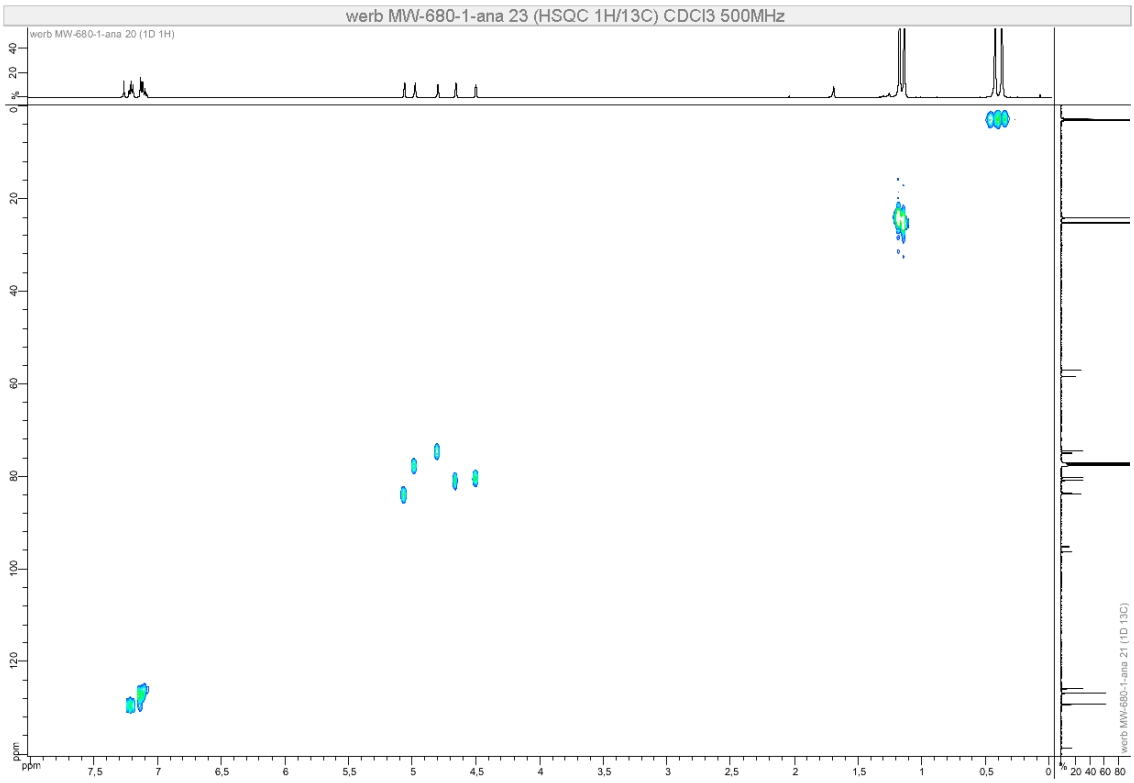
^{13}C NMR (126 MHz, $CDCl_3$)



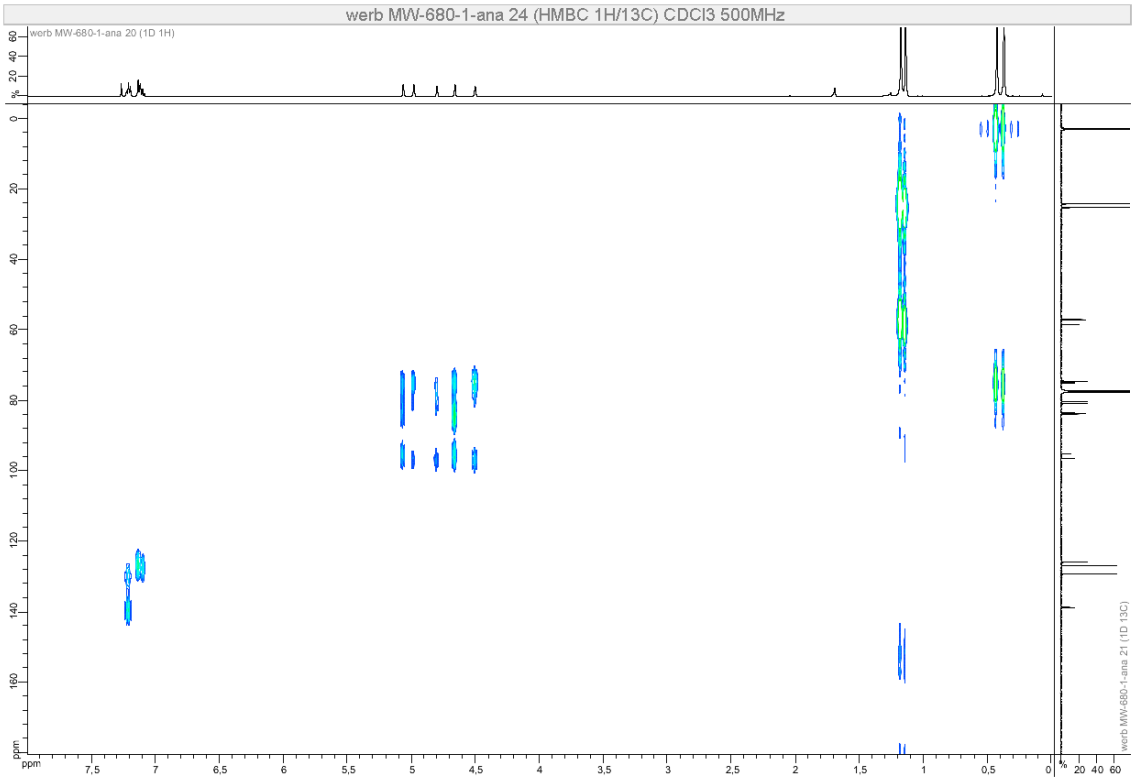
COSY (500 MHz, $CDCl_3$)



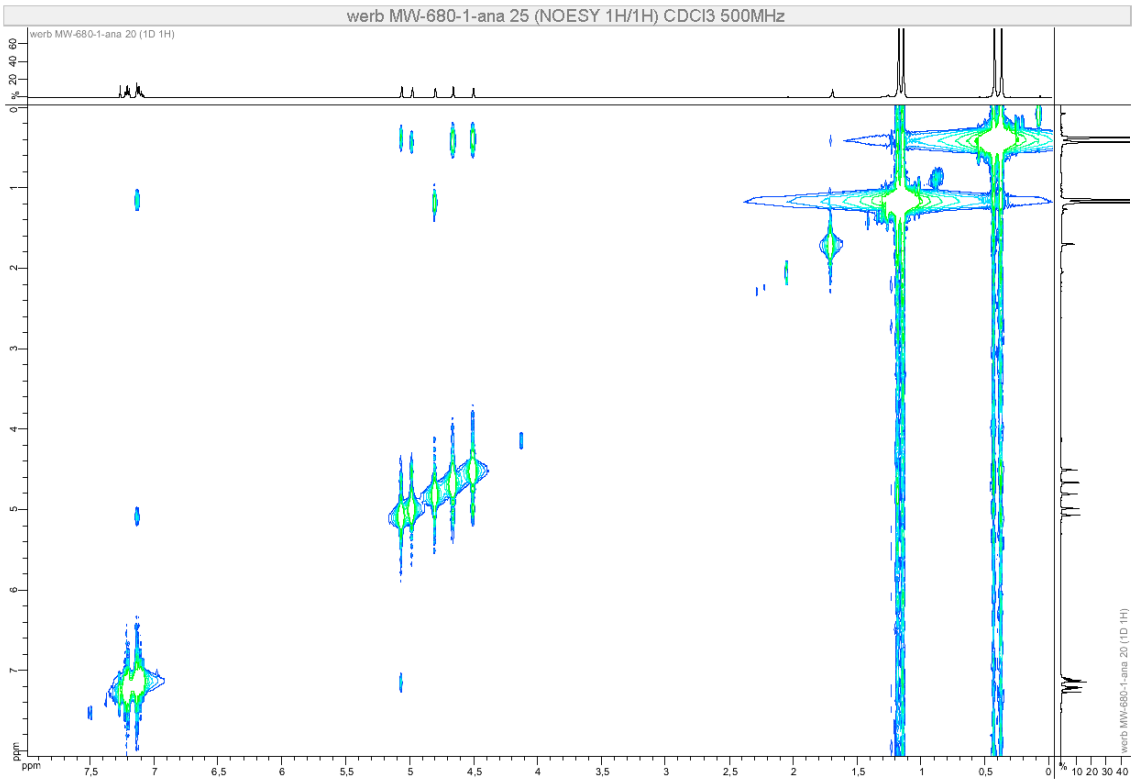
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

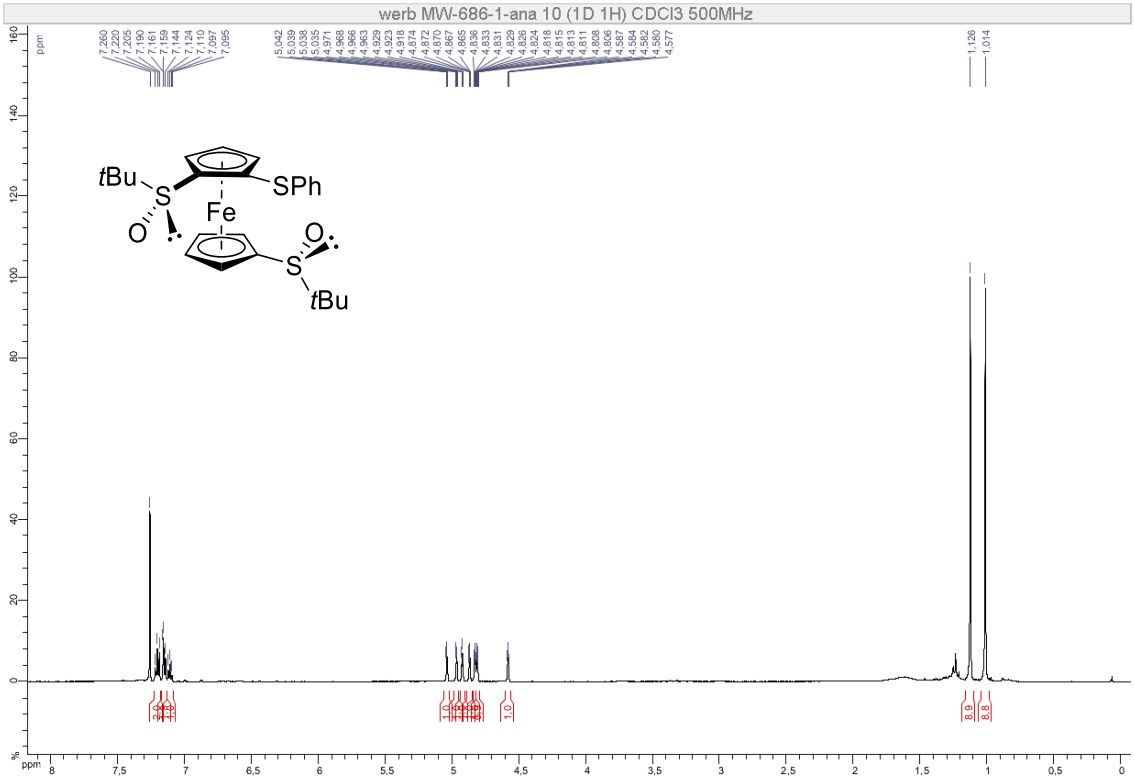


NOESY (500 MHz, $CDCl_3$)

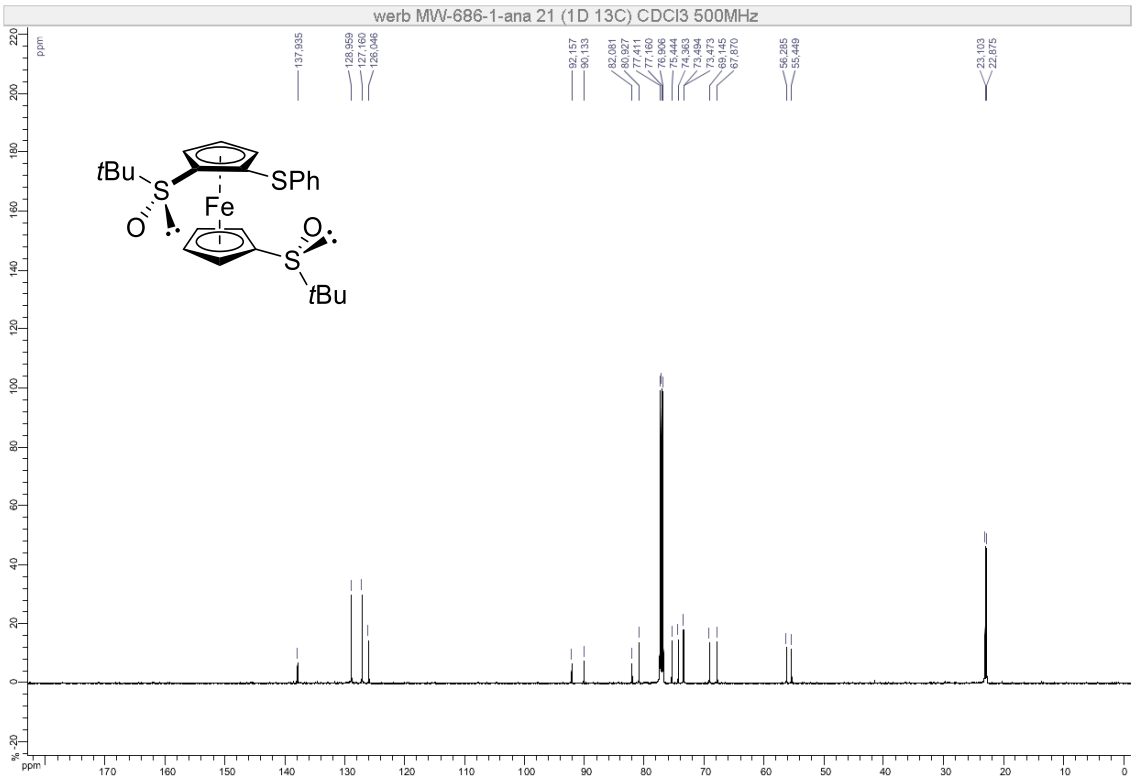


(*R*,*R*,*S*P)-*S*,*S*'-Di-*tert*-butyl-2-(phenylthio)ferrocene-1,1'-disulfoxide (*S*P,*R*P-6"g-desi)

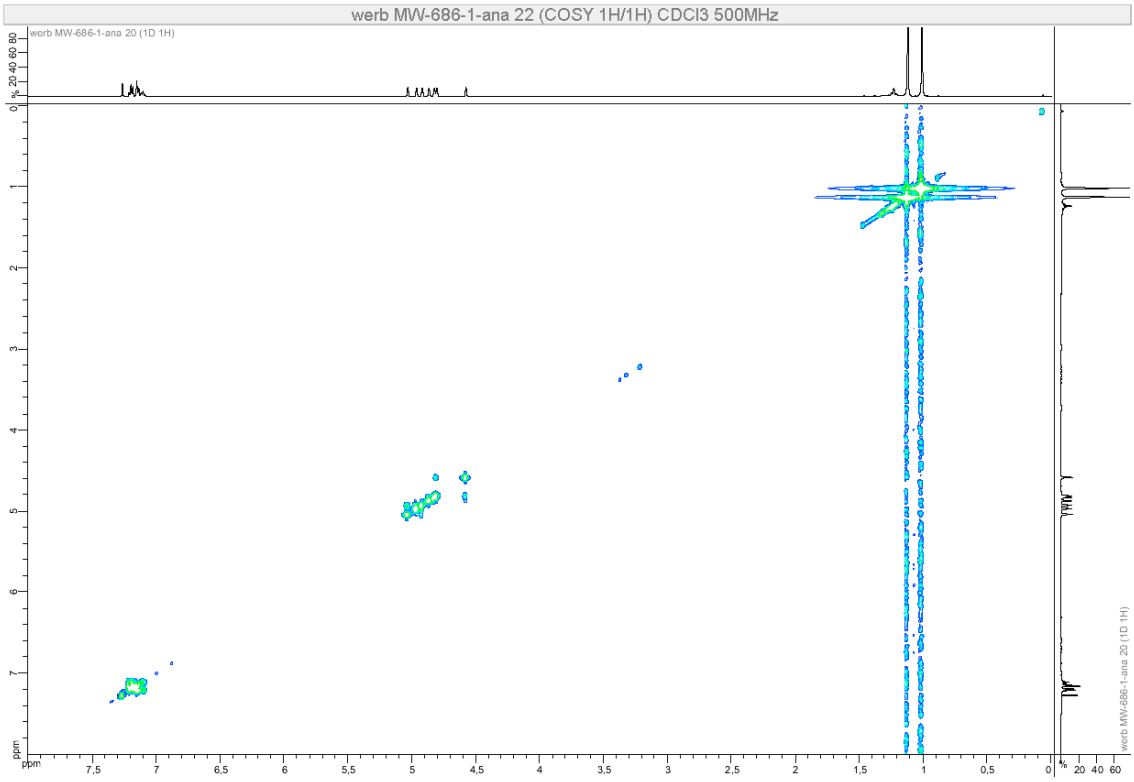
^{1}H NMR (500 MHz, $CDCl_3$)



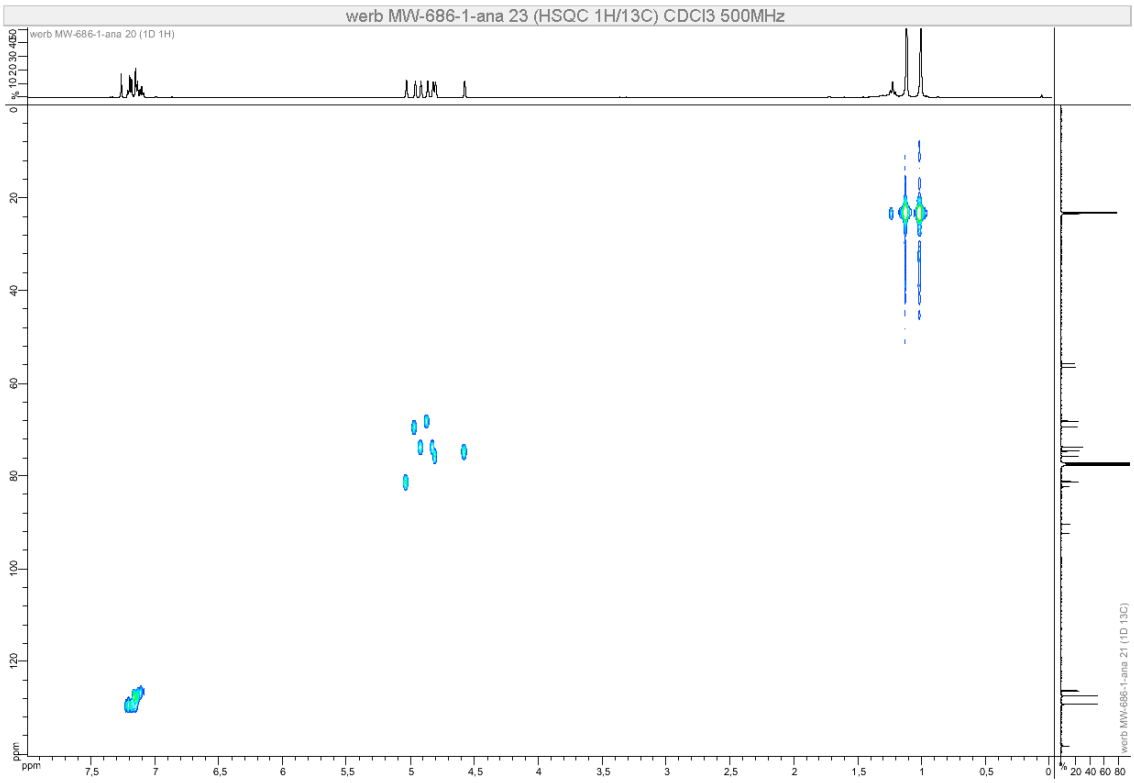
^{13}C NMR (126 MHz, $CDCl_3$)



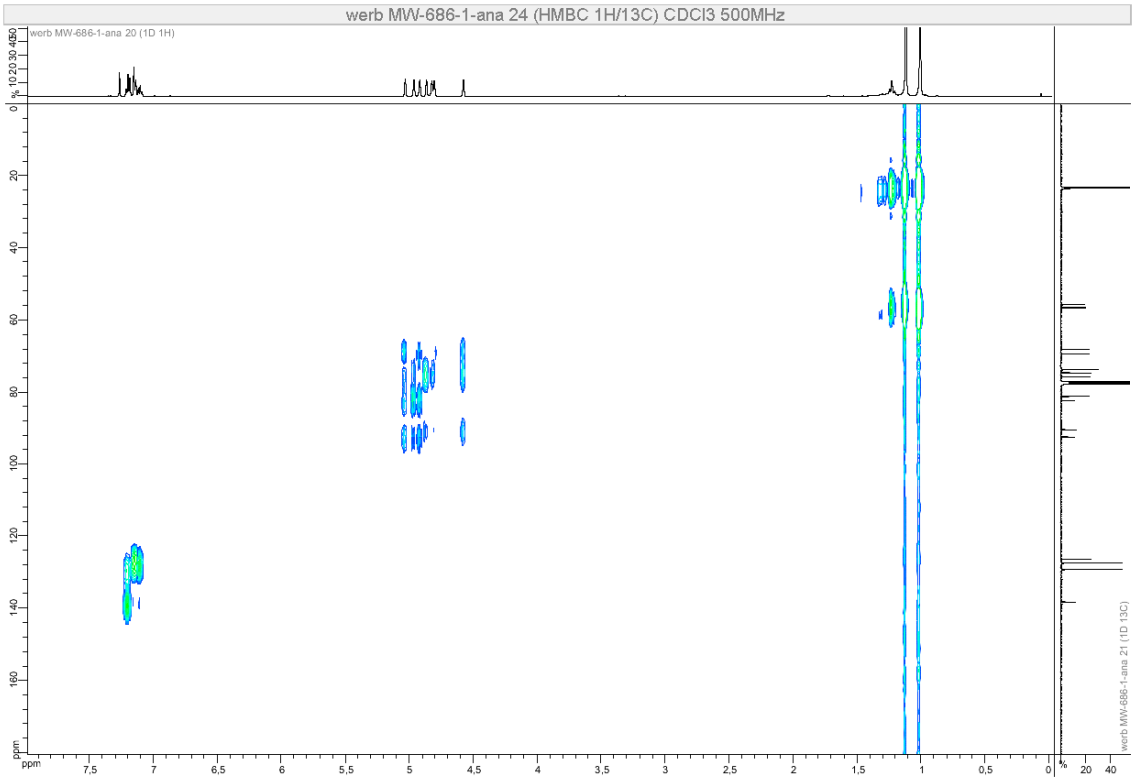
COSY (500 MHz, $CDCl_3$)



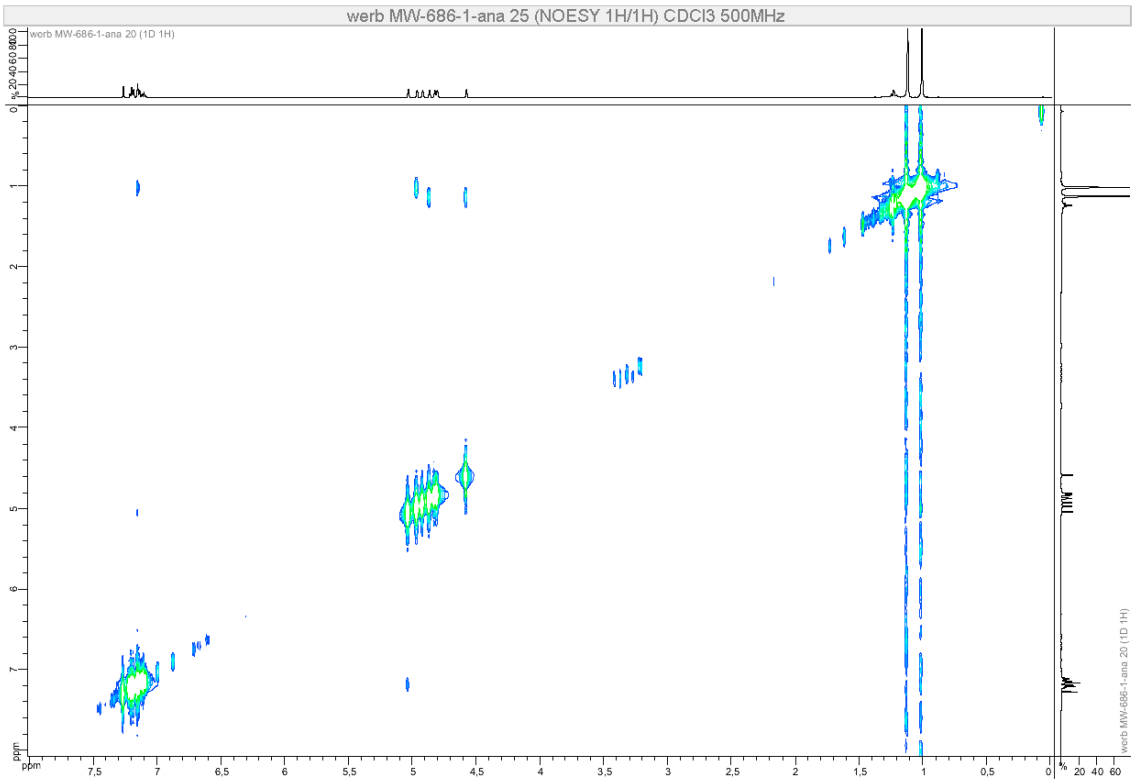
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

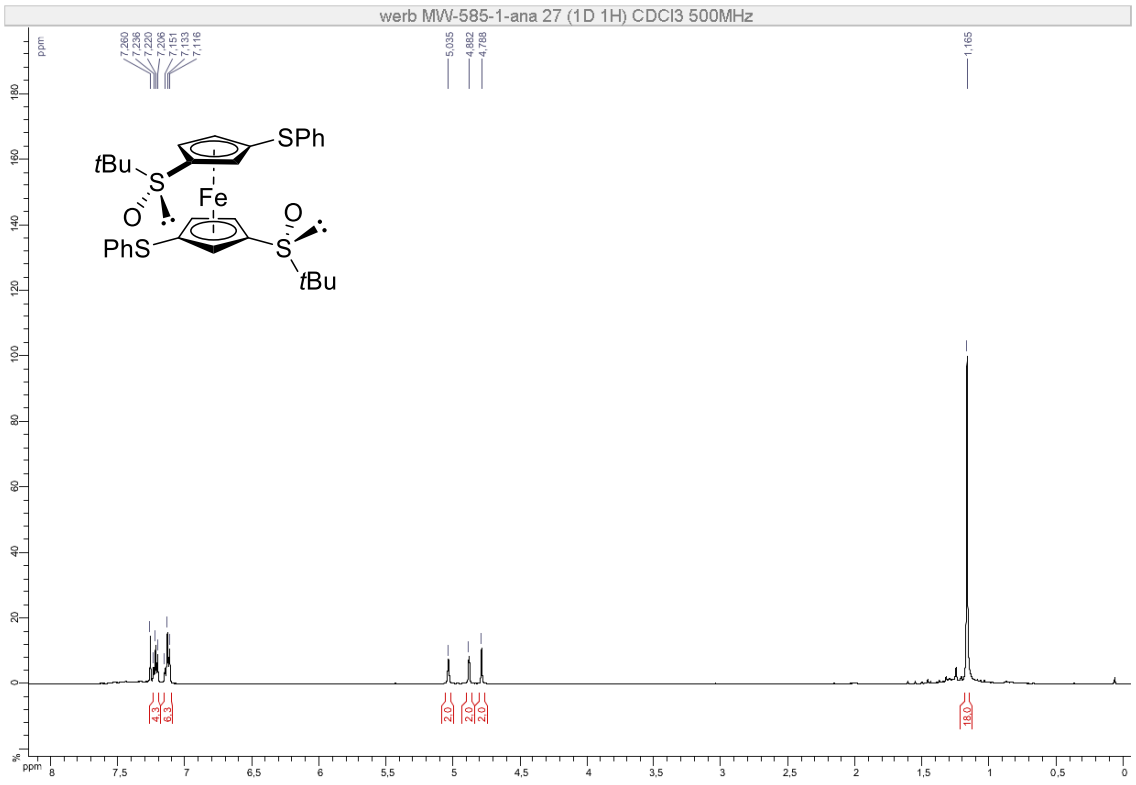


NOESY (500 MHz, $CDCl_3$)

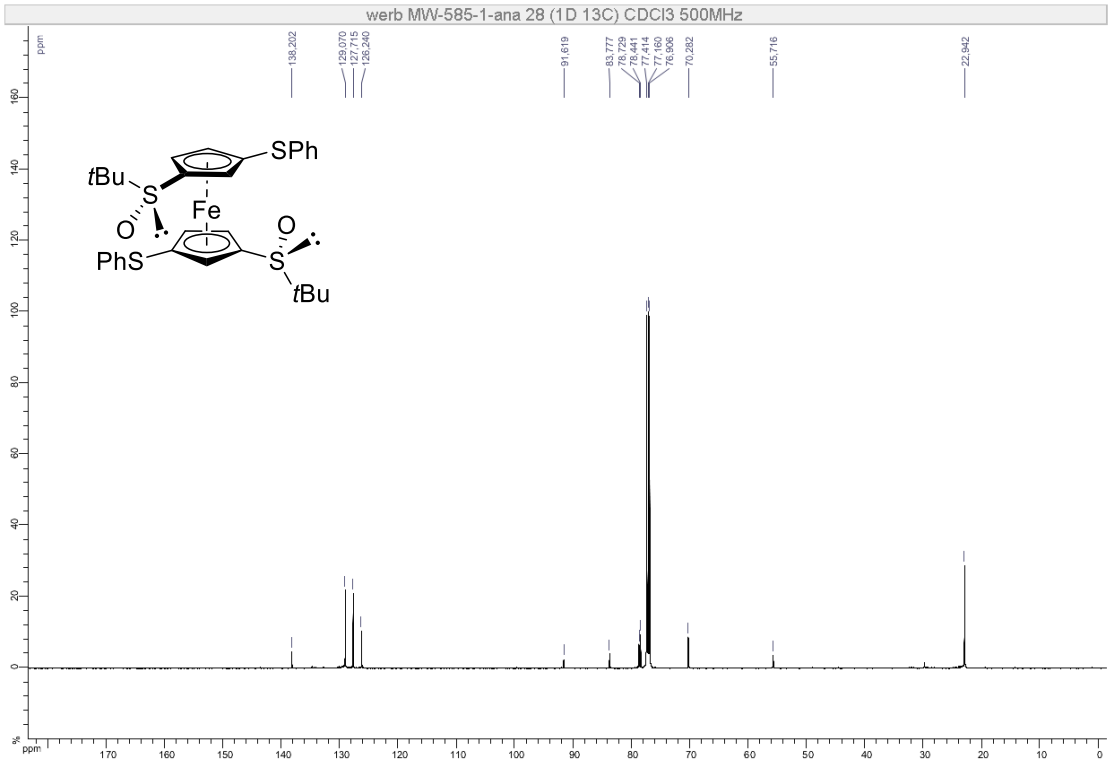


(*R*,*R*,*S*P,*S*P)-*S*,*S*'-Di-*tert*-butyl-3,3'-di(phenylthio)ferrocene-1,1'-disulfoxide (*S*P,*S*P-6'g-desi)

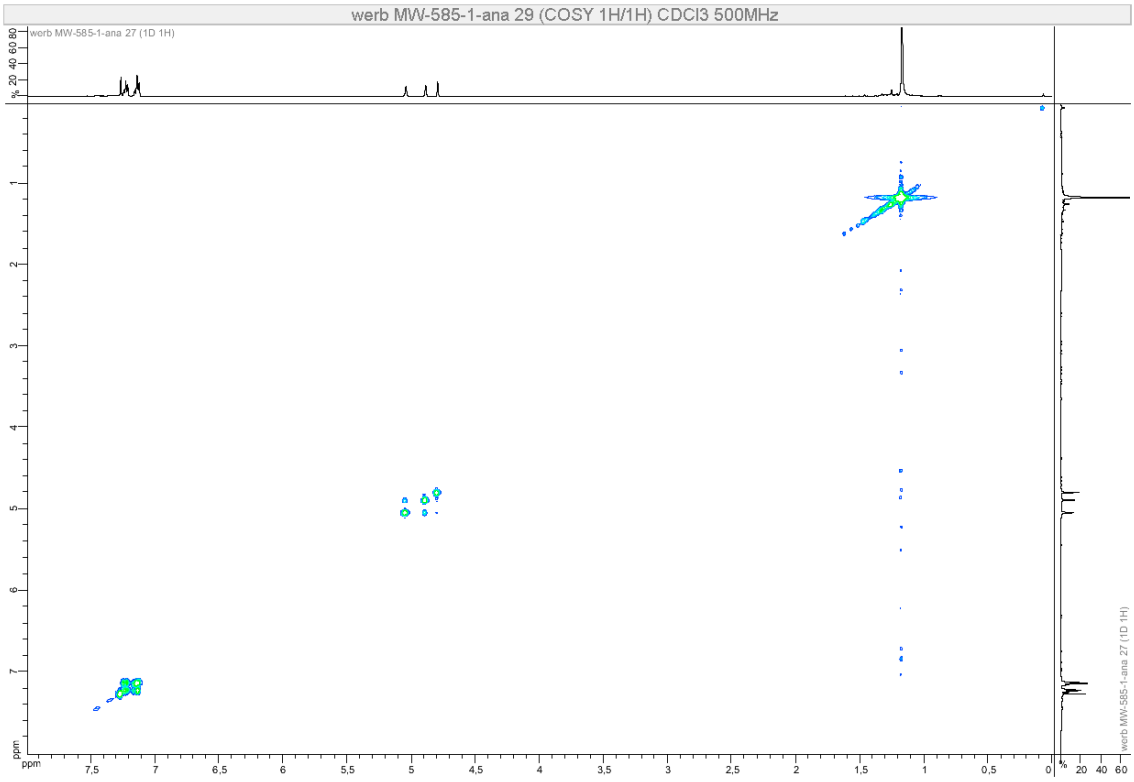
^{1}H NMR (500 MHz, $CDCl_3$)



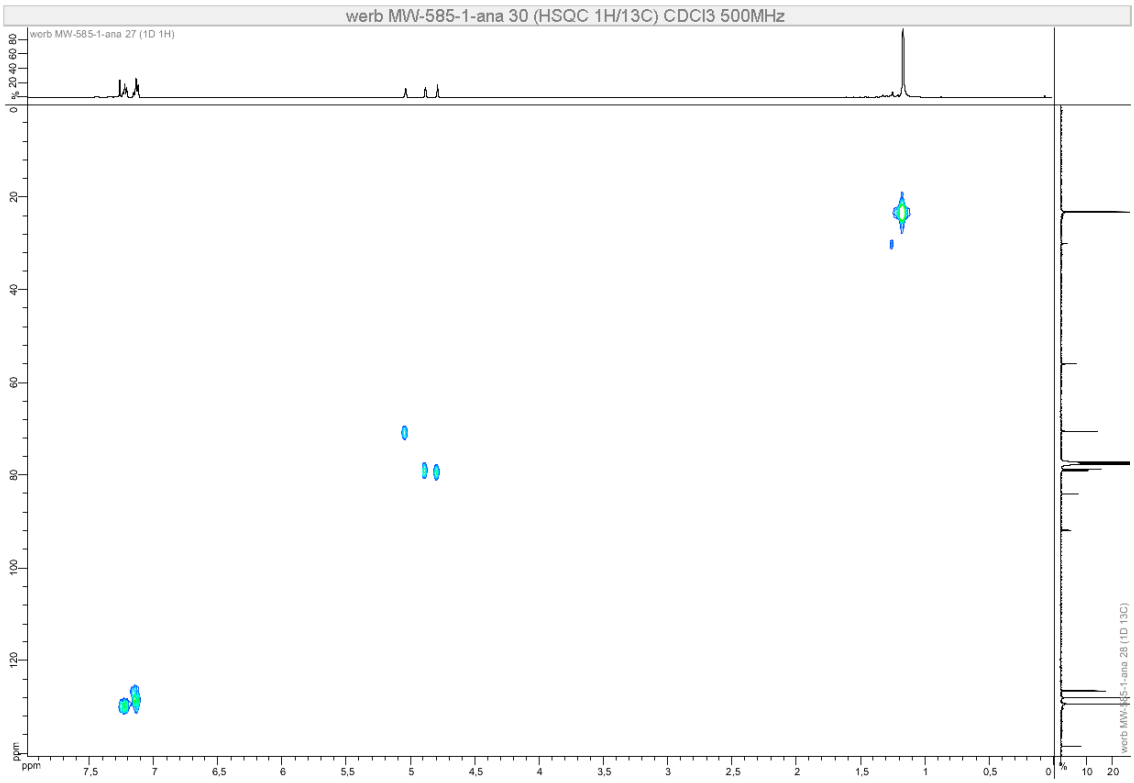
^{13}C NMR (126 MHz, $CDCl_3$)



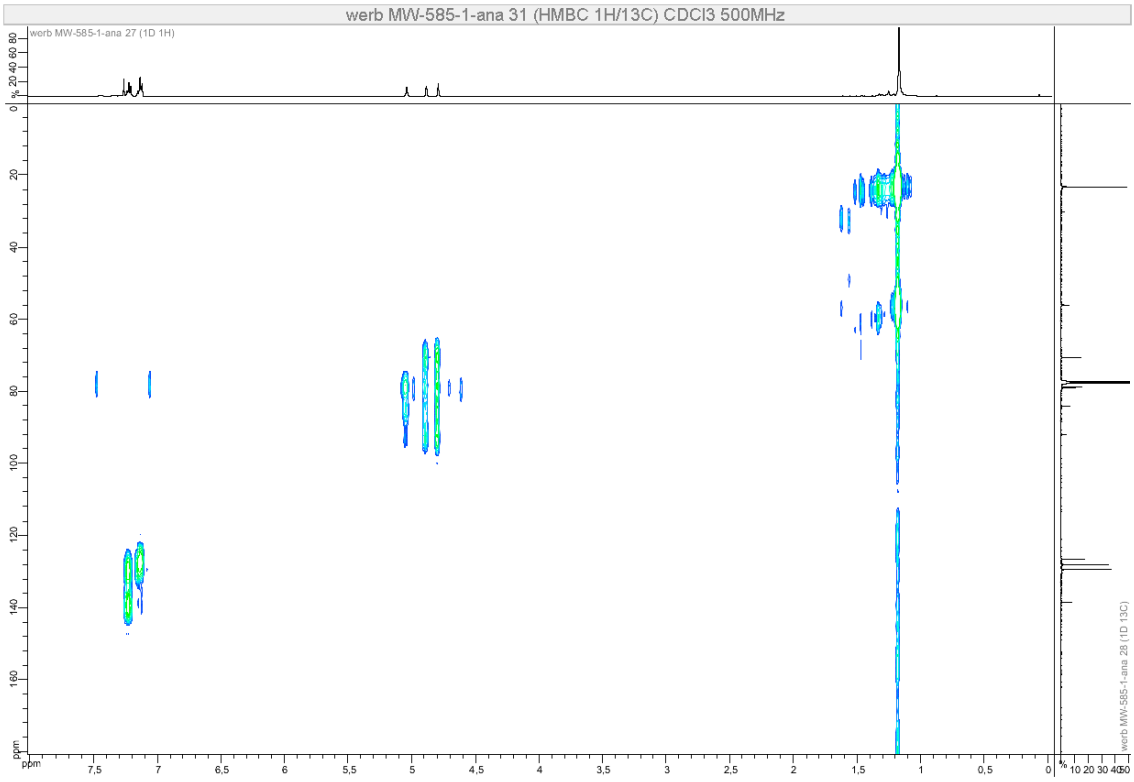
COSY (500 MHz, $CDCl_3$)



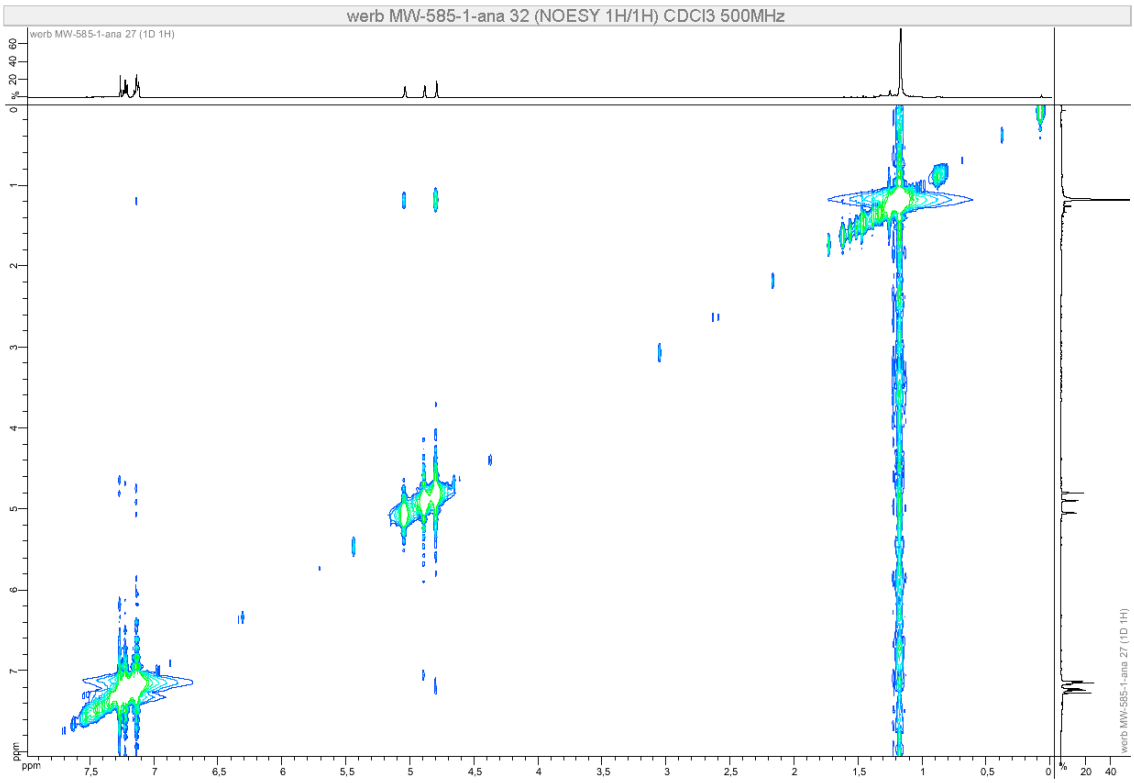
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

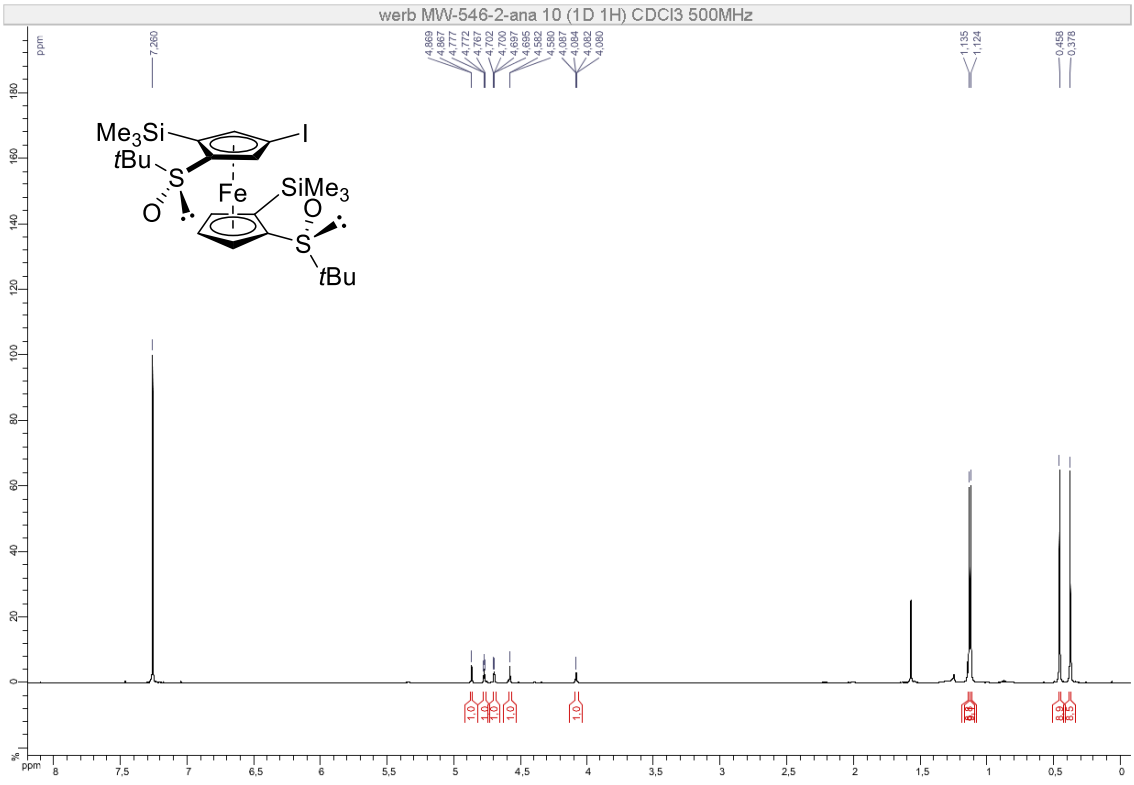


NOESY (500 MHz, $CDCl_3$)

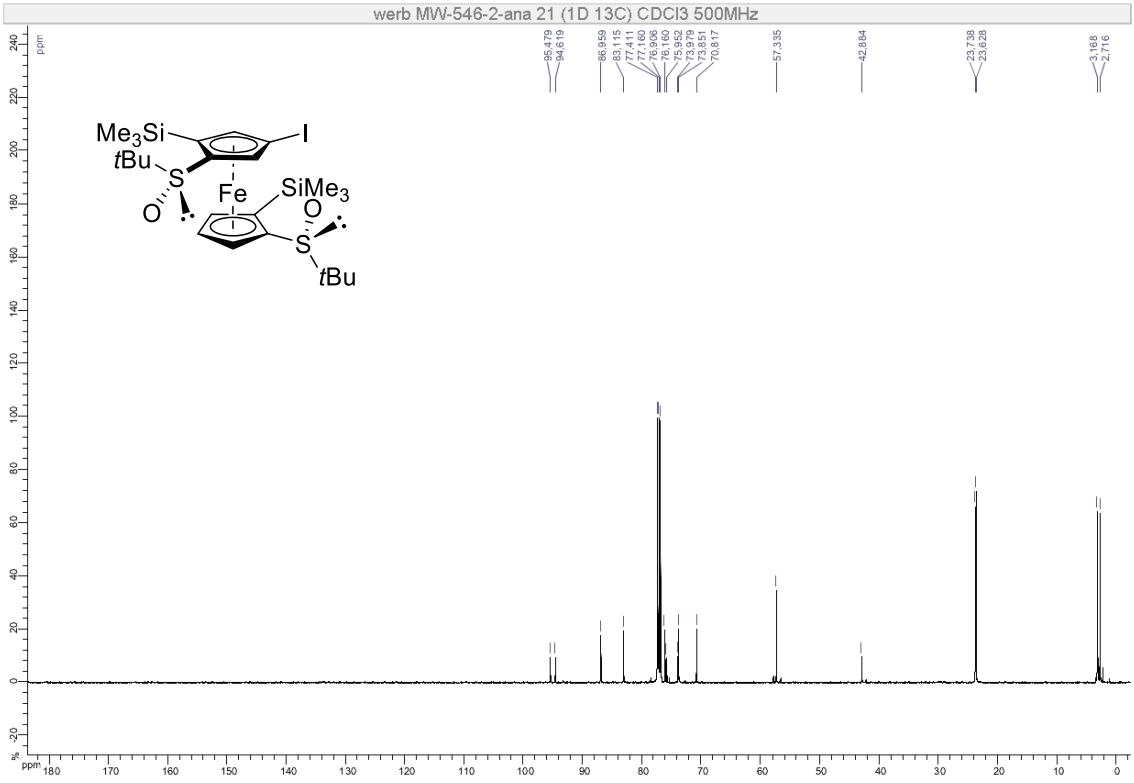


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4-iodo-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6h)

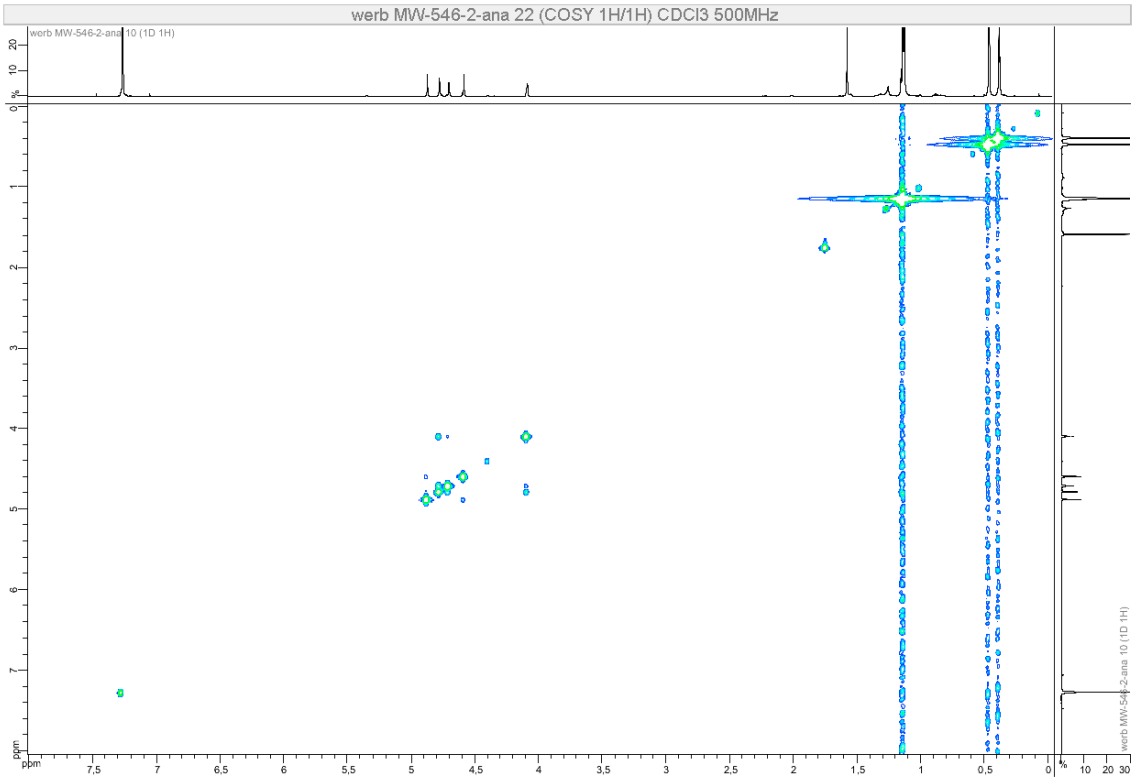
^{1}H NMR (500 MHz, $CDCl_3$)



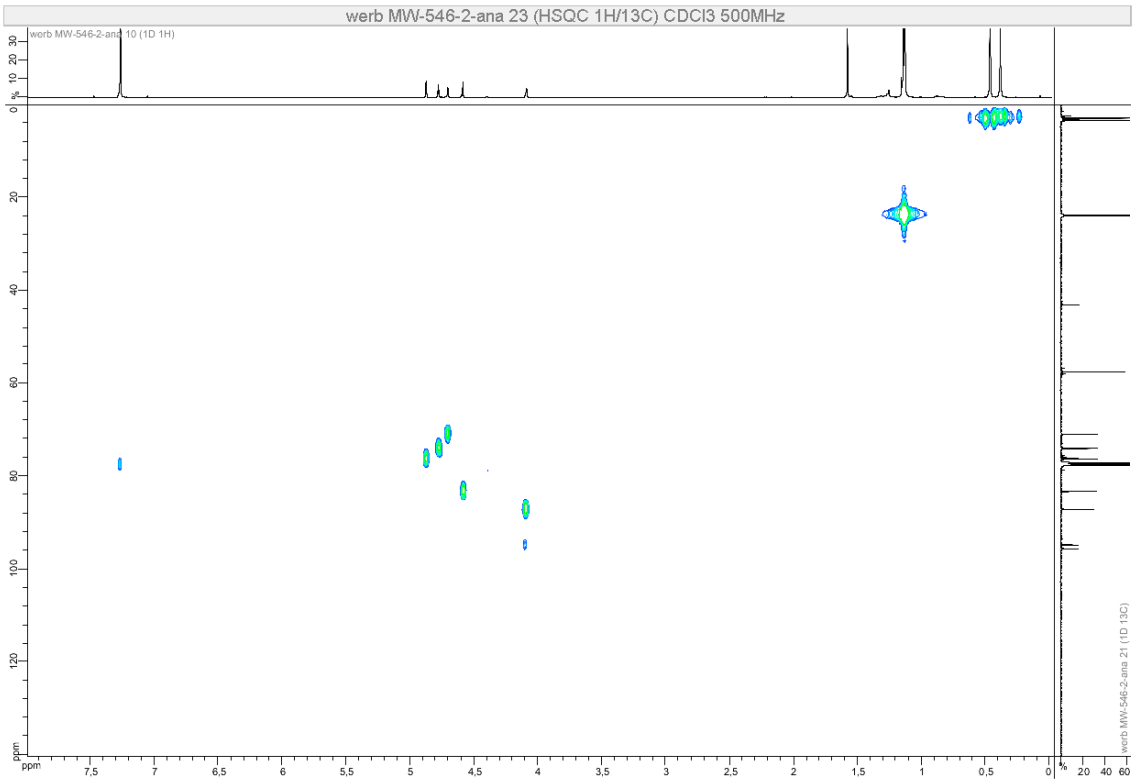
^{13}C NMR (126 MHz, $CDCl_3$)



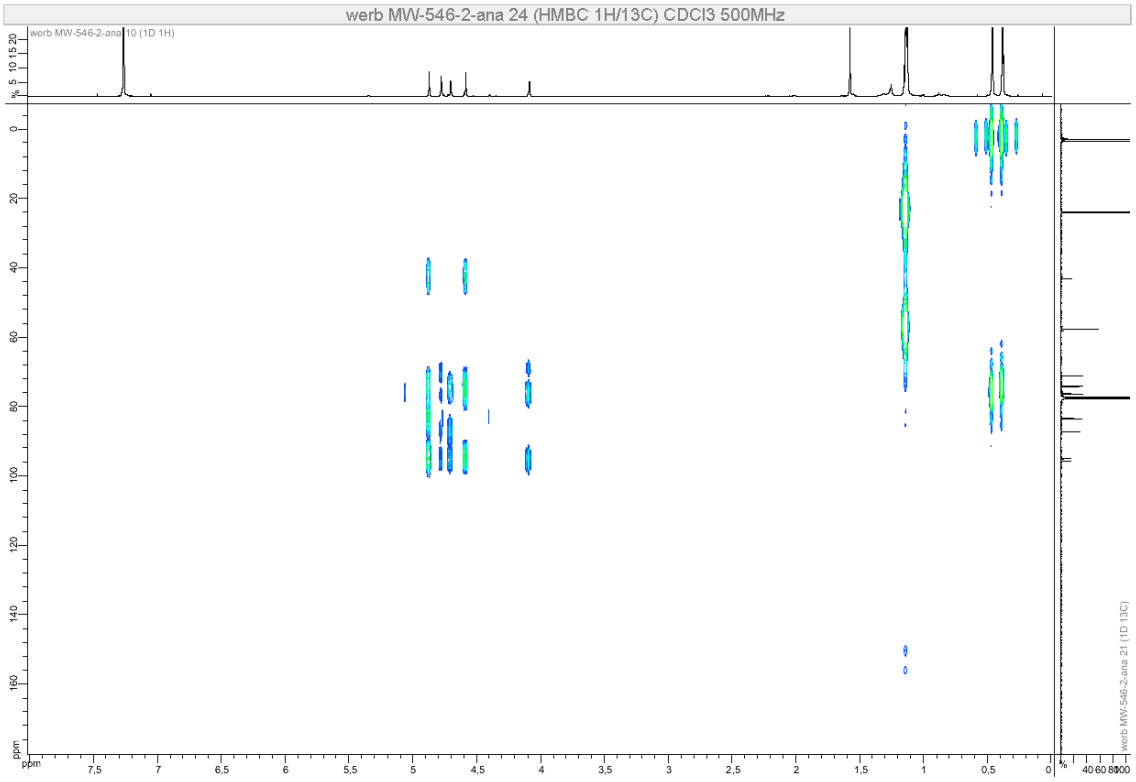
COSY (500 MHz, $CDCl_3$)



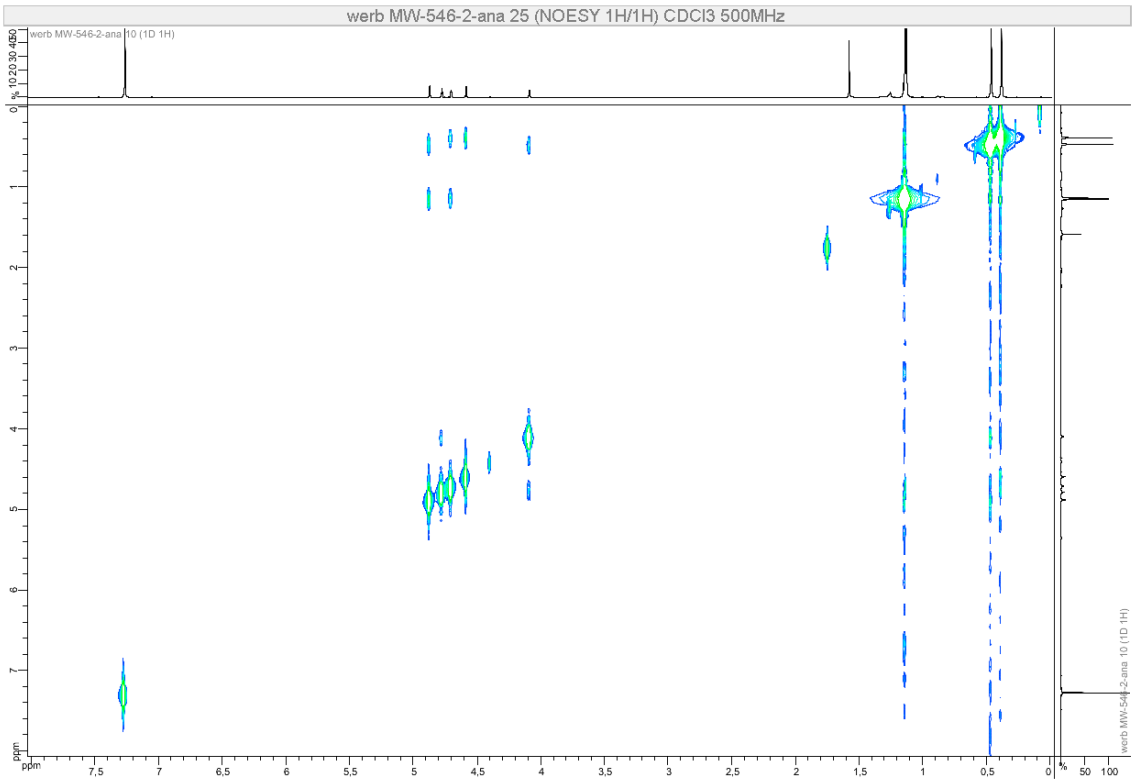
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

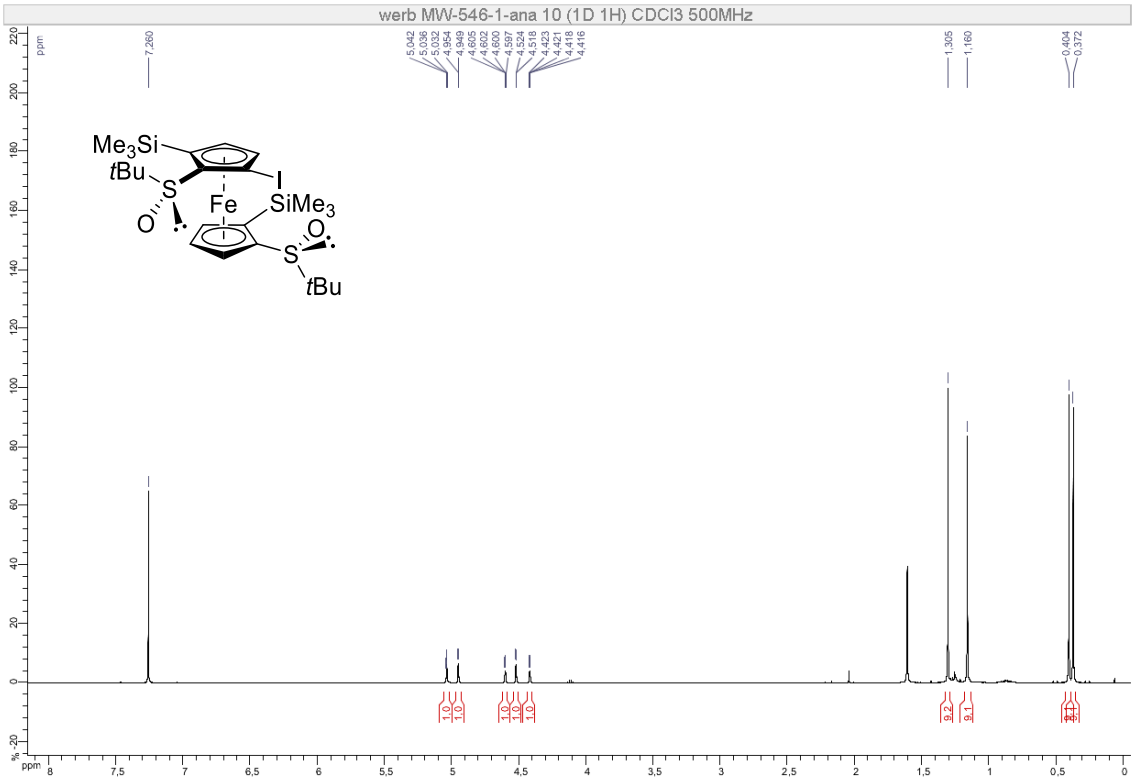


NOESY (500 MHz, $CDCl_3$)

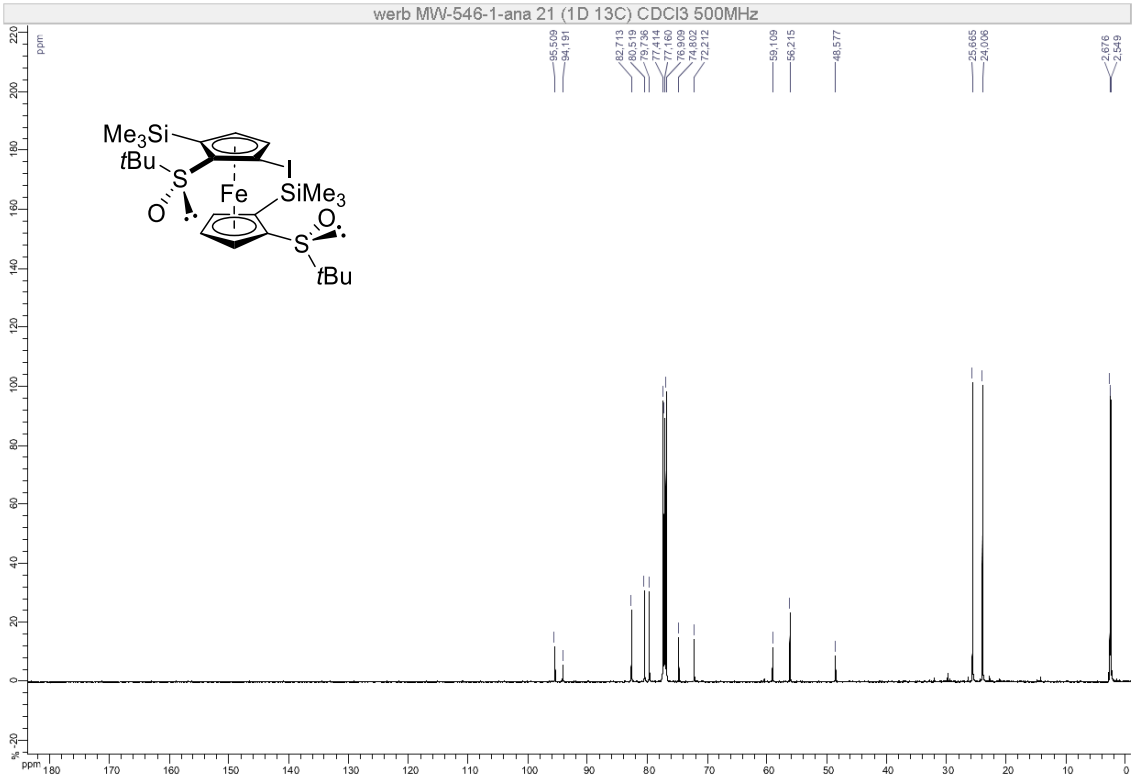


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2-iodo-5,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6"h)

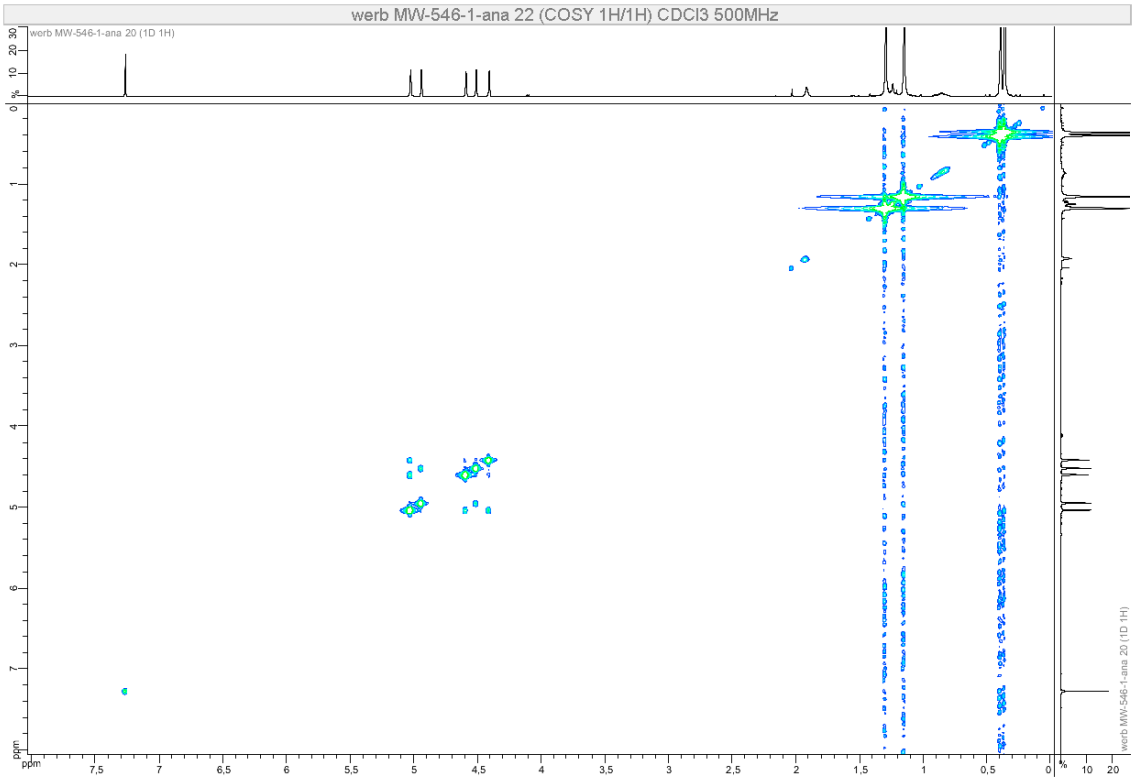
^{1}H NMR (500 MHz, $CDCl_3$)



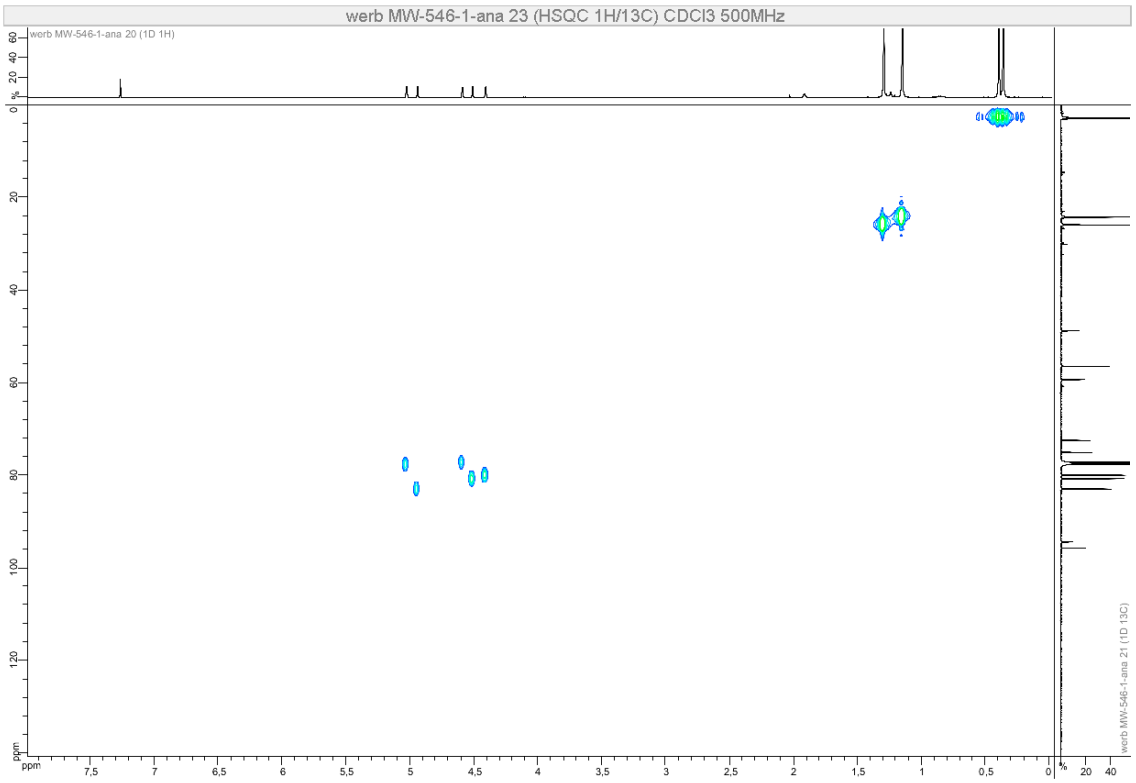
^{13}C NMR (126 MHz, $CDCl_3$)



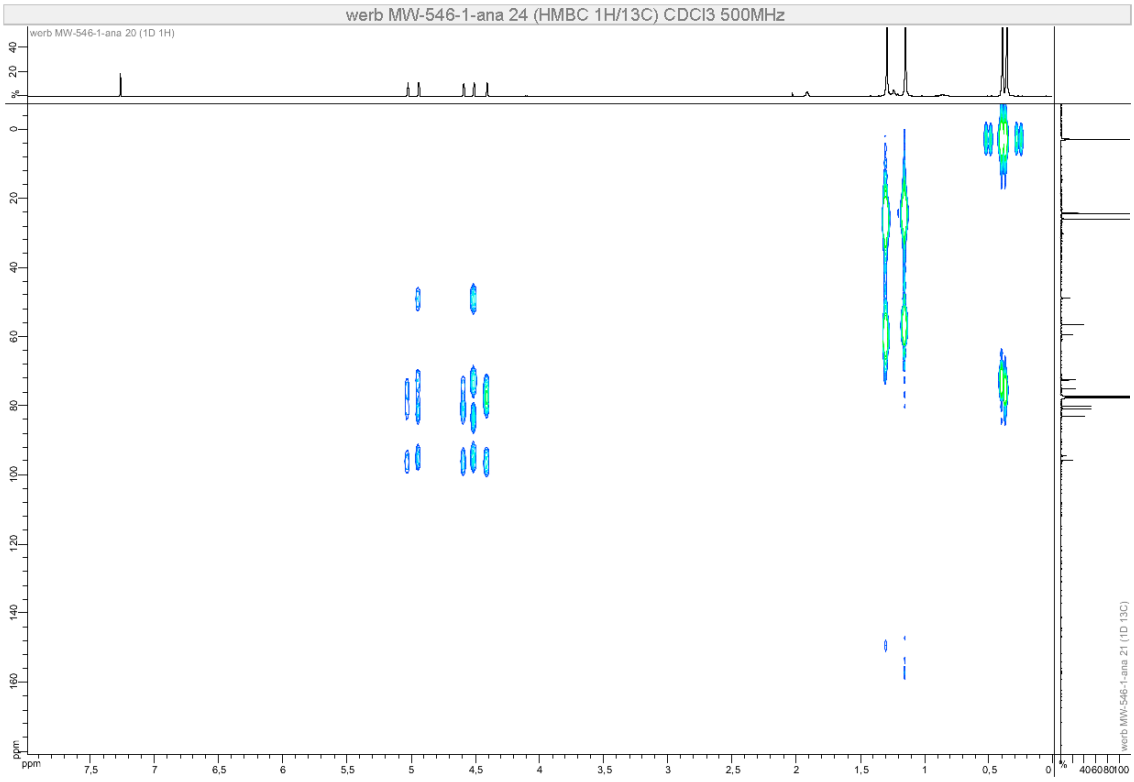
COSY (500 MHz, $CDCl_3$)



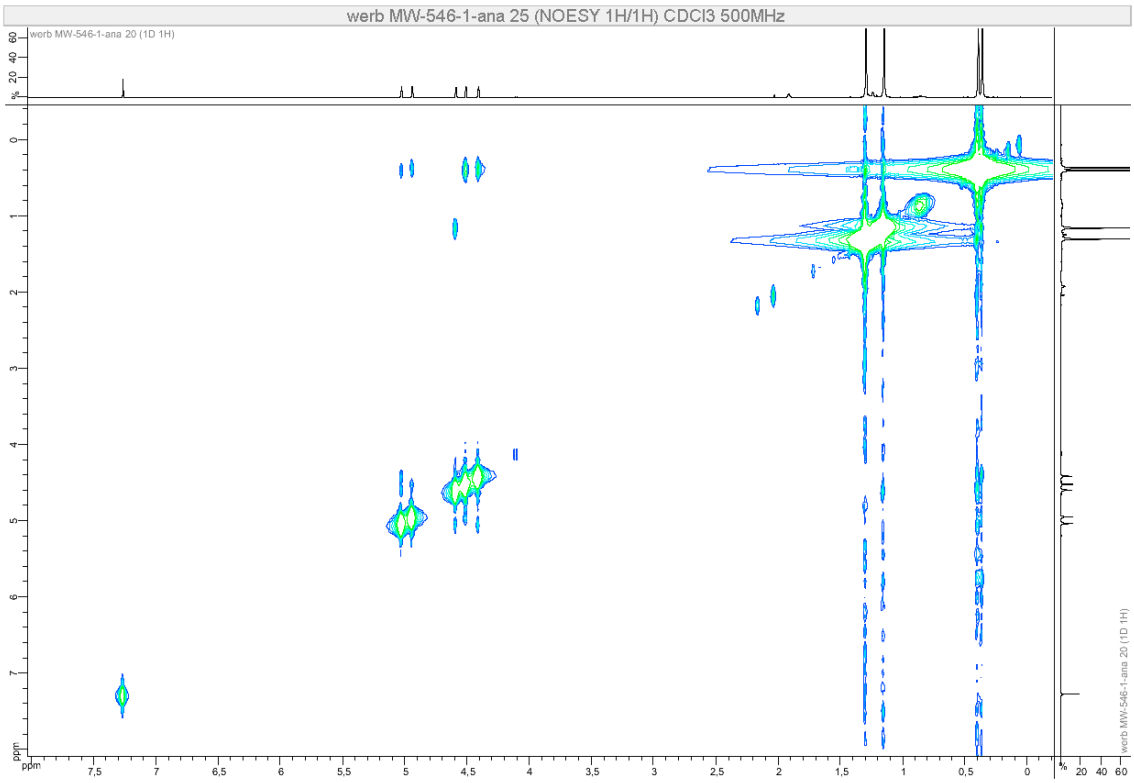
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

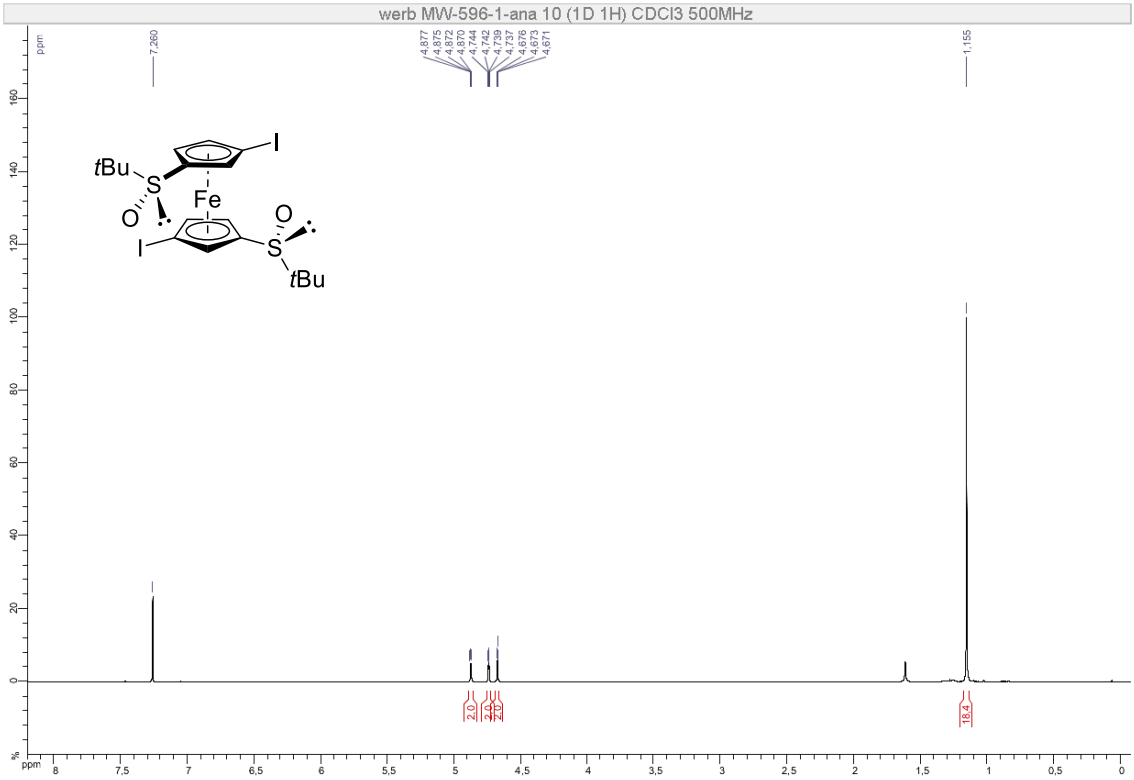


NOESY (500 MHz, $CDCl_3$)

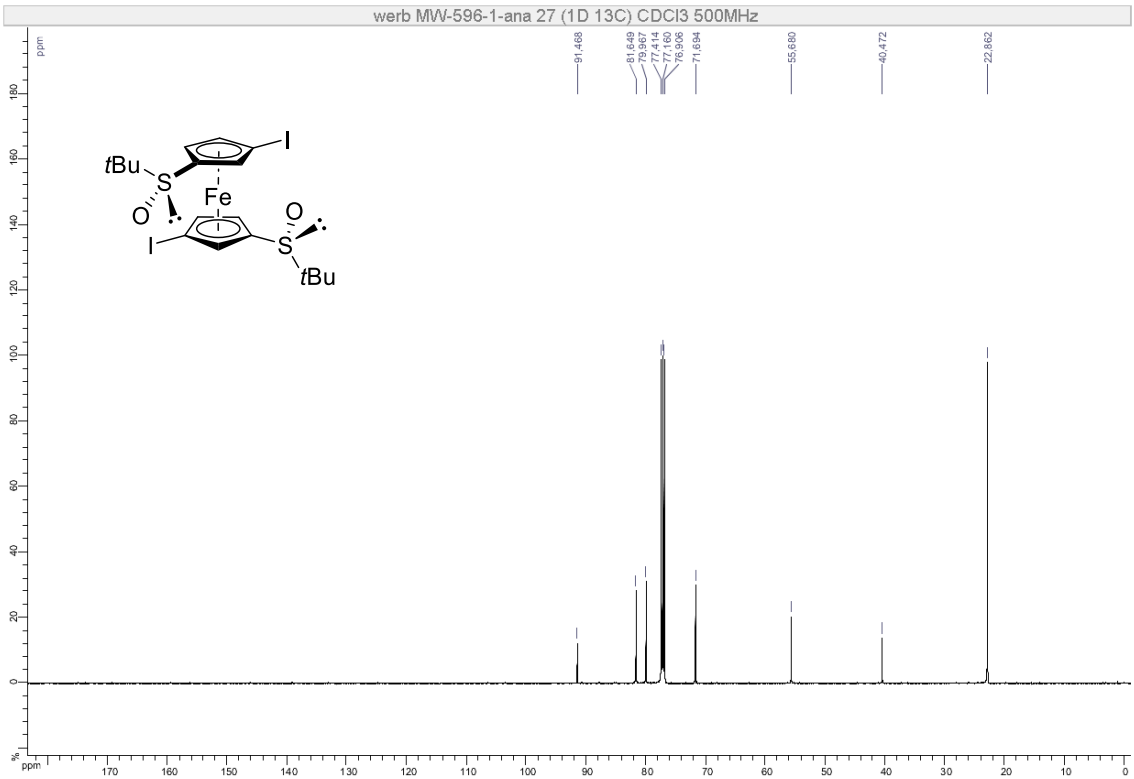


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-3,3'-diiodoferrocene-1,1'-disulfoxide (*R*P,*R*P-6'h-desi)

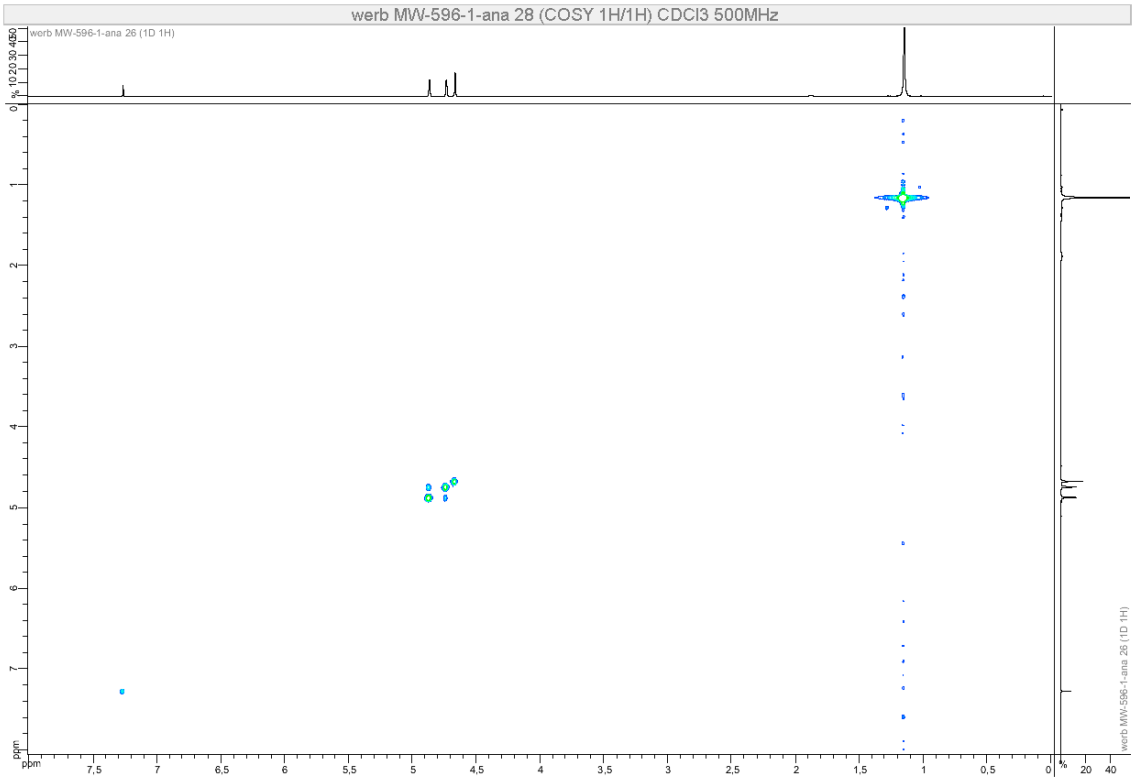
^{1}H NMR (500 MHz, $CDCl_3$)



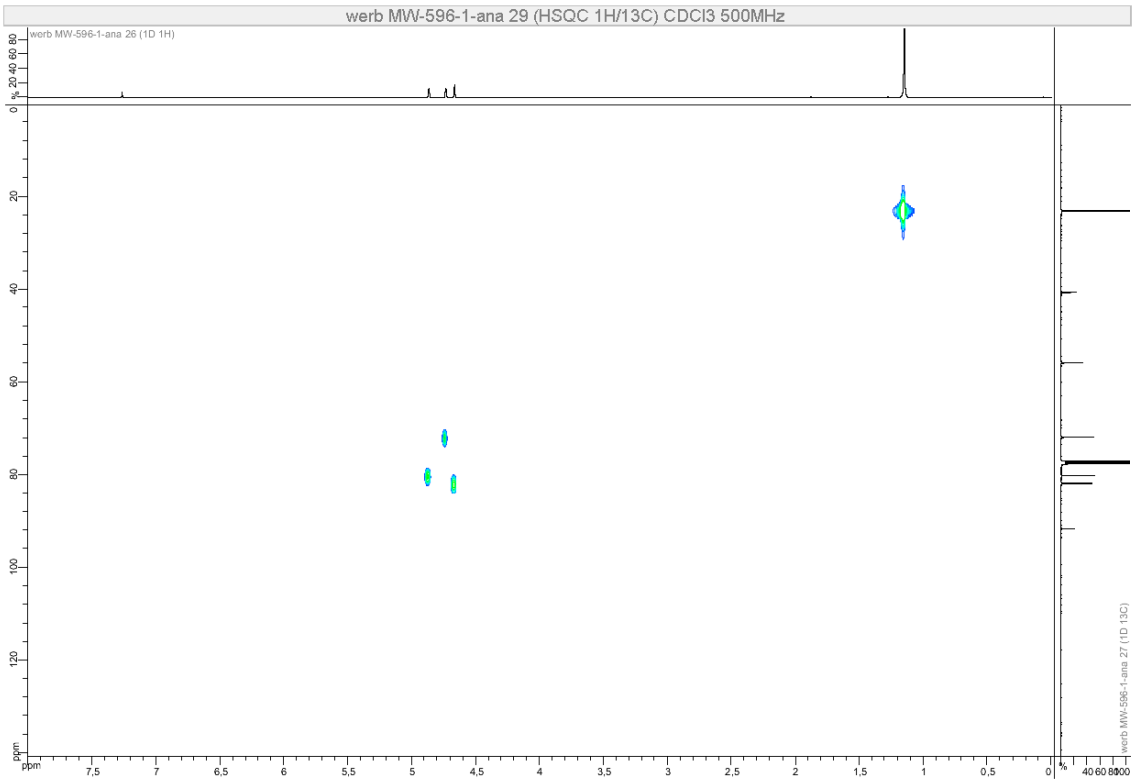
^{13}C NMR (126 MHz, $CDCl_3$)



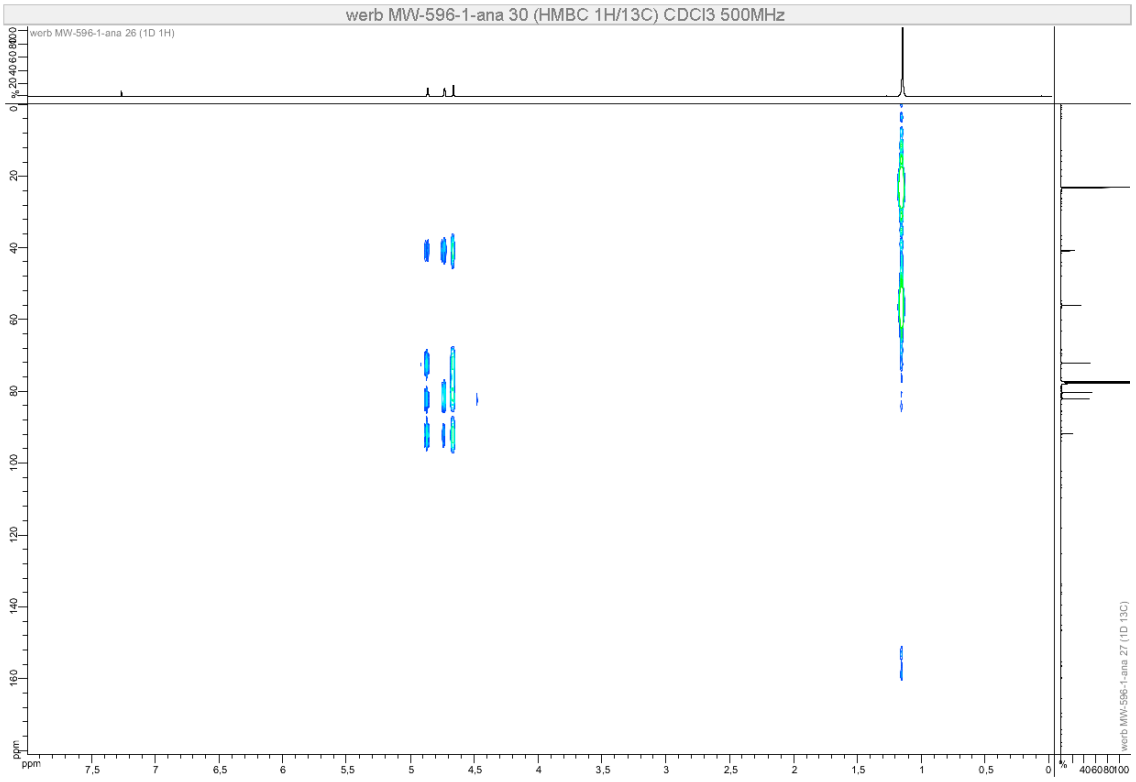
COSY (500 MHz, $CDCl_3$)



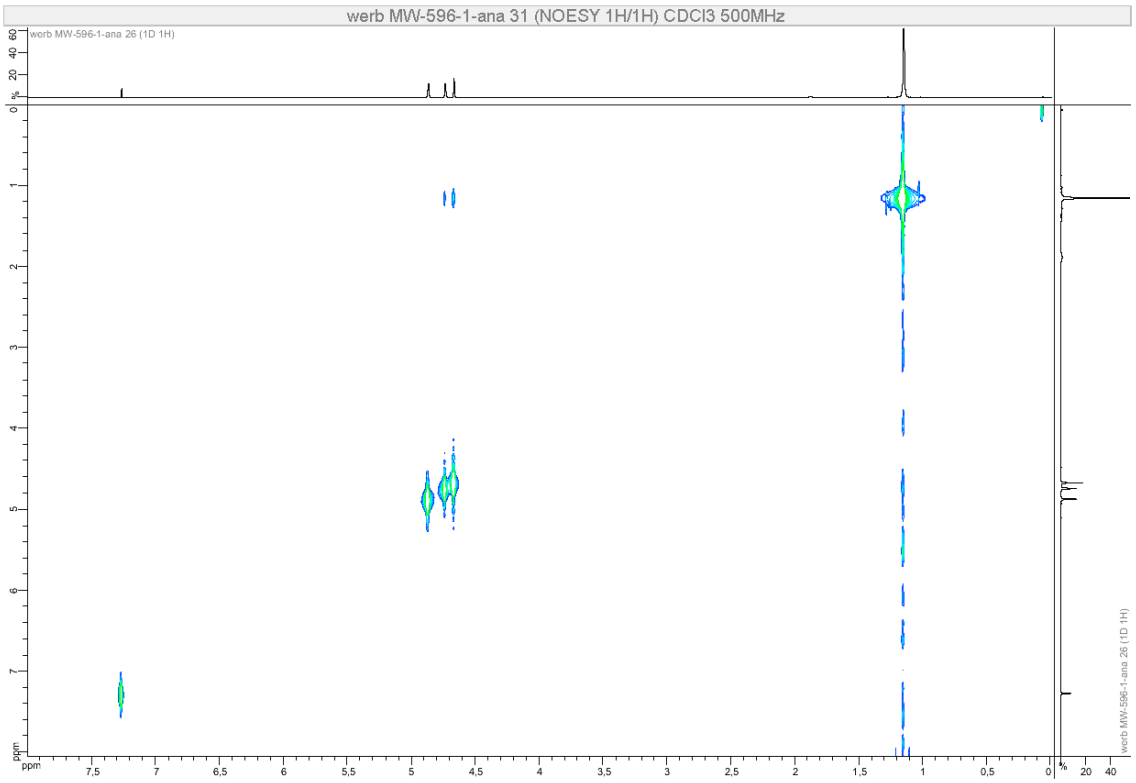
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

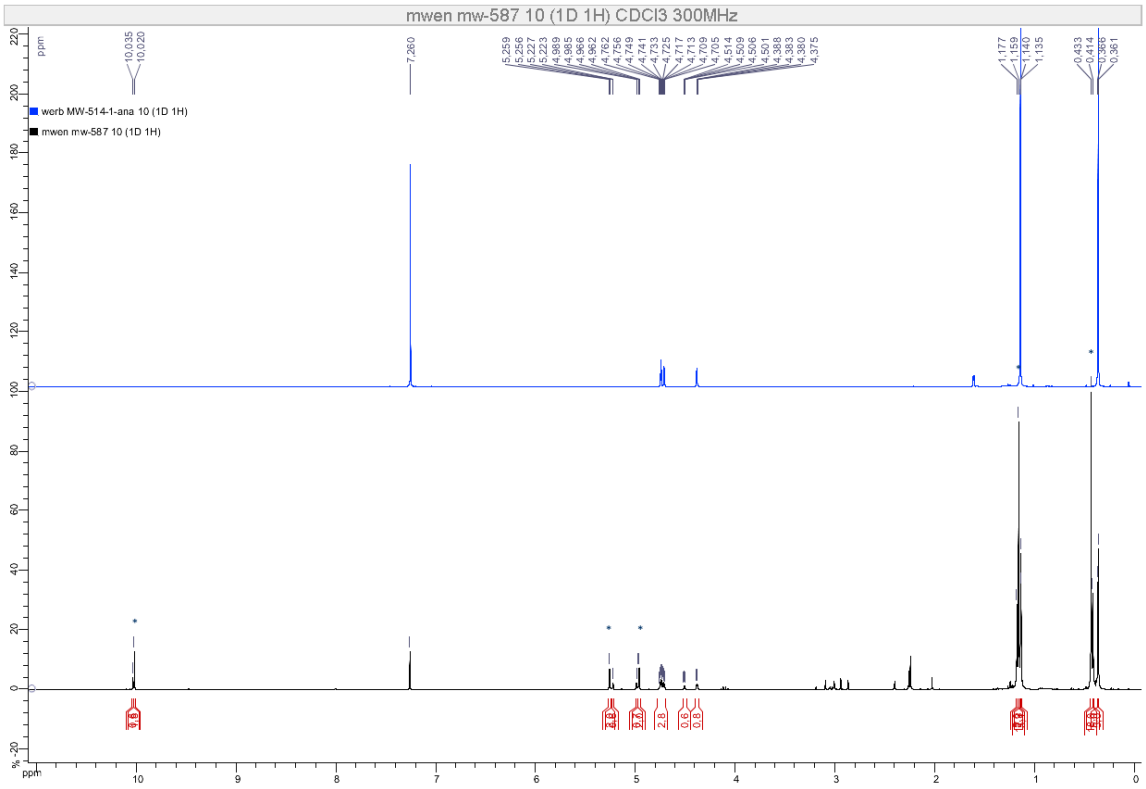


NOESY (500 MHz, $CDCl_3$)



(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4,4'-diformyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide and (*R*,*R*,*R*P,*R*P)-*S*,*S*'-di-*tert*-butyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-2f)

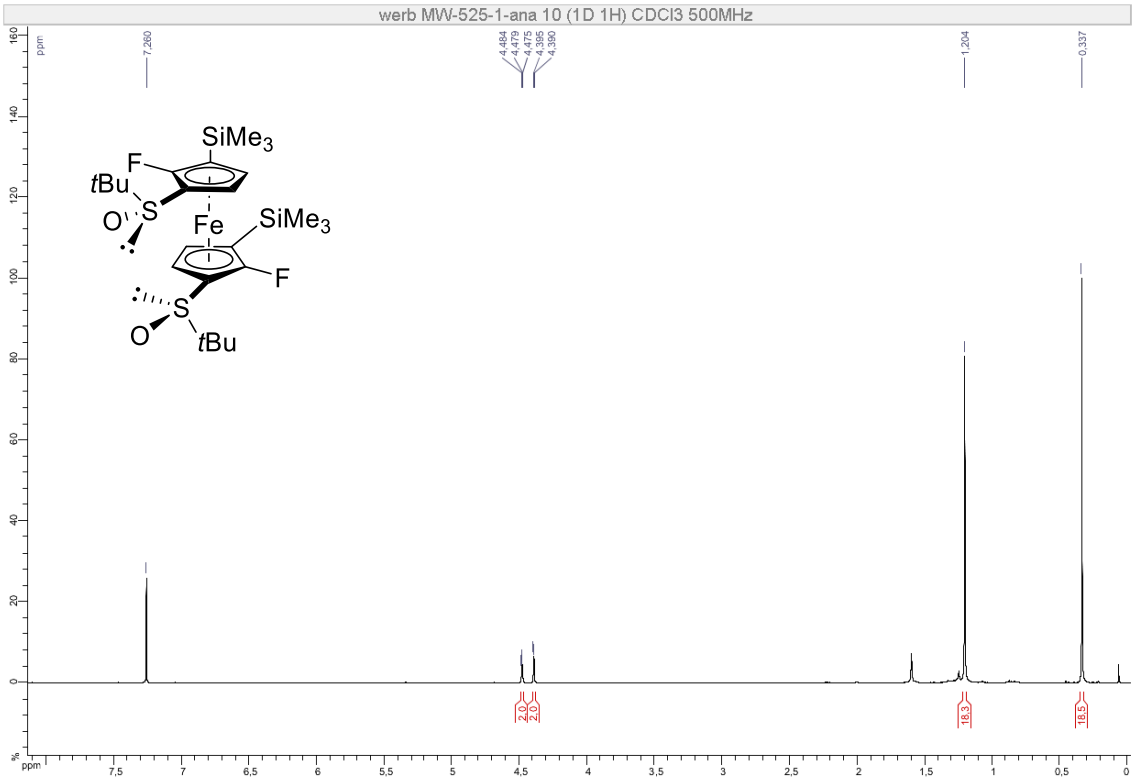
^{1}H NMR (500 MHz, $CDCl_3$)



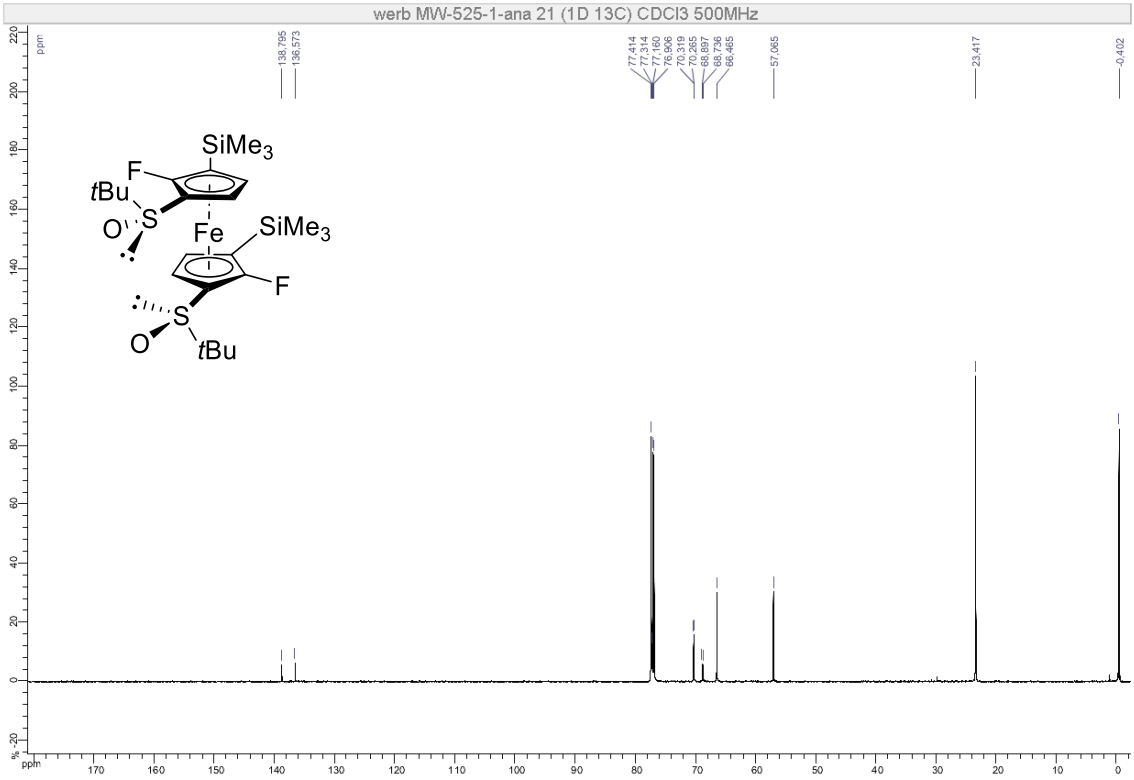
In black: mixture of (*R*,*R*,*R*P,*R*P)-*S*,*S*'-di-*tert*-butyl-4,4'-diformyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide, indicated with *, ***R*P,*R*P-2f** and (*R*,*R*,*R*P,*R*P)-*S*,*S*'-di-*tert*-butyl-4-formyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide in a 64:27:9 NMR ratio.
In blue: pure ***R*P,*R*P-2f**.

(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-difluoro-3,3'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-8a)

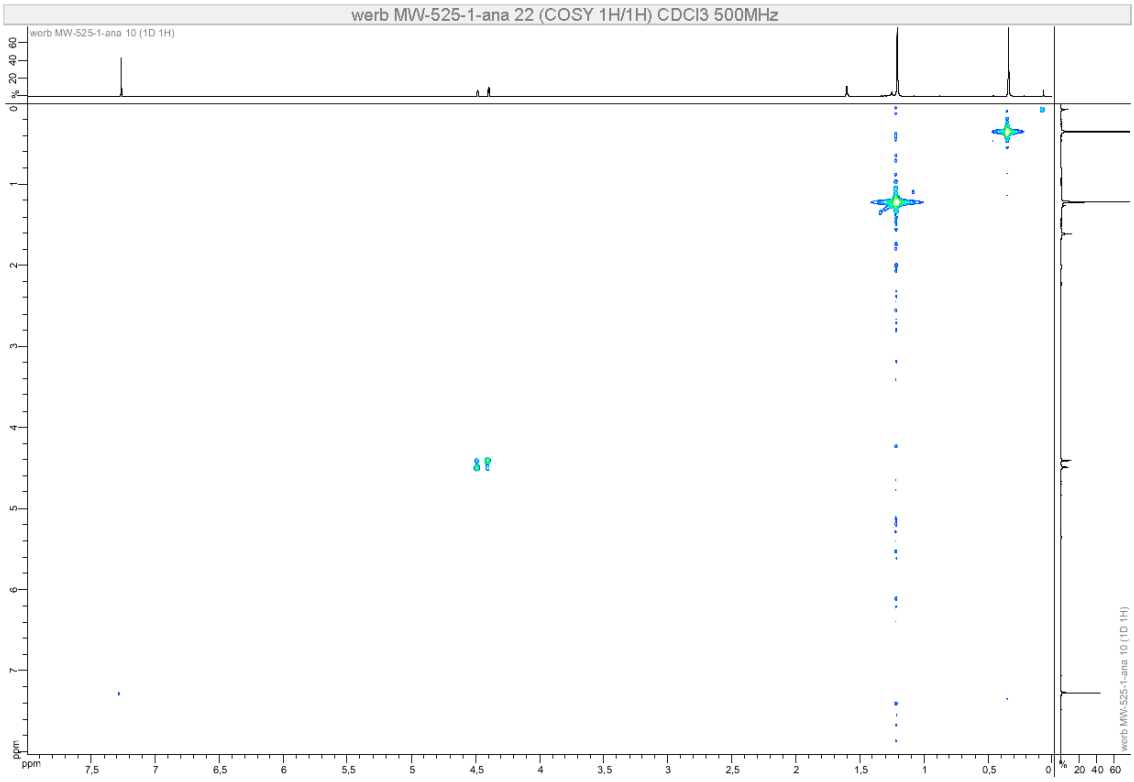
^{1}H NMR (500 MHz, $CDCl_3$)



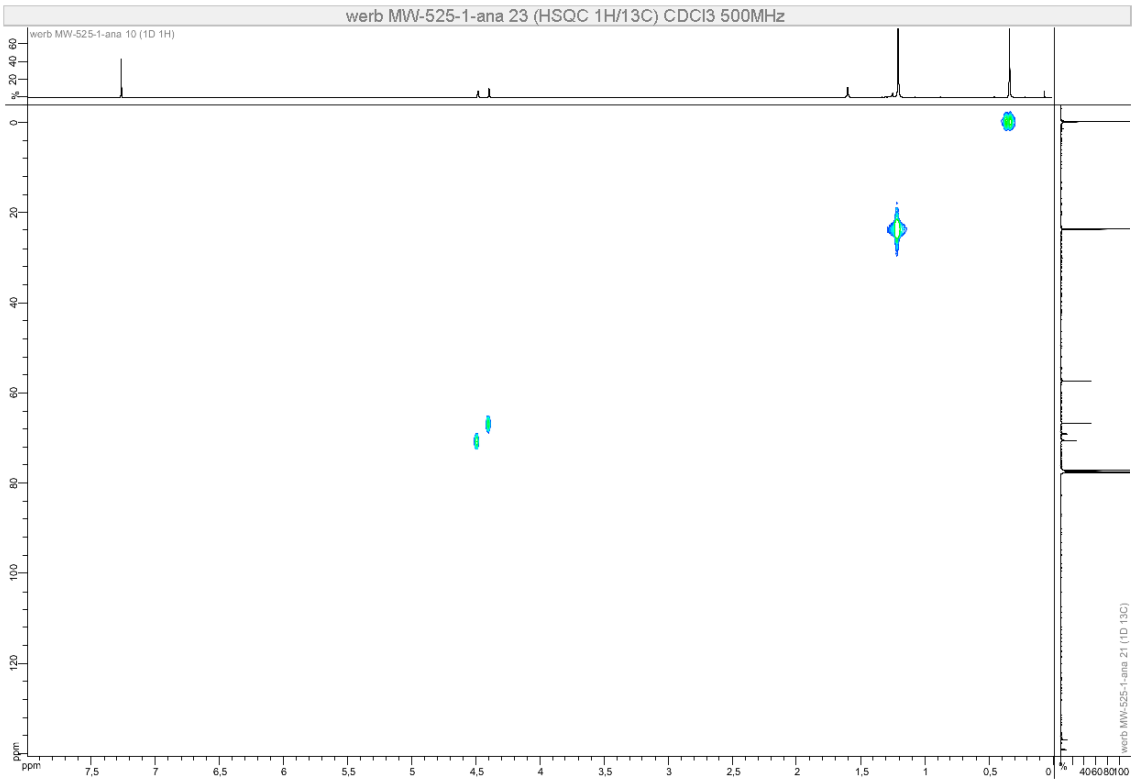
^{13}C NMR (126 MHz, $CDCl_3$)



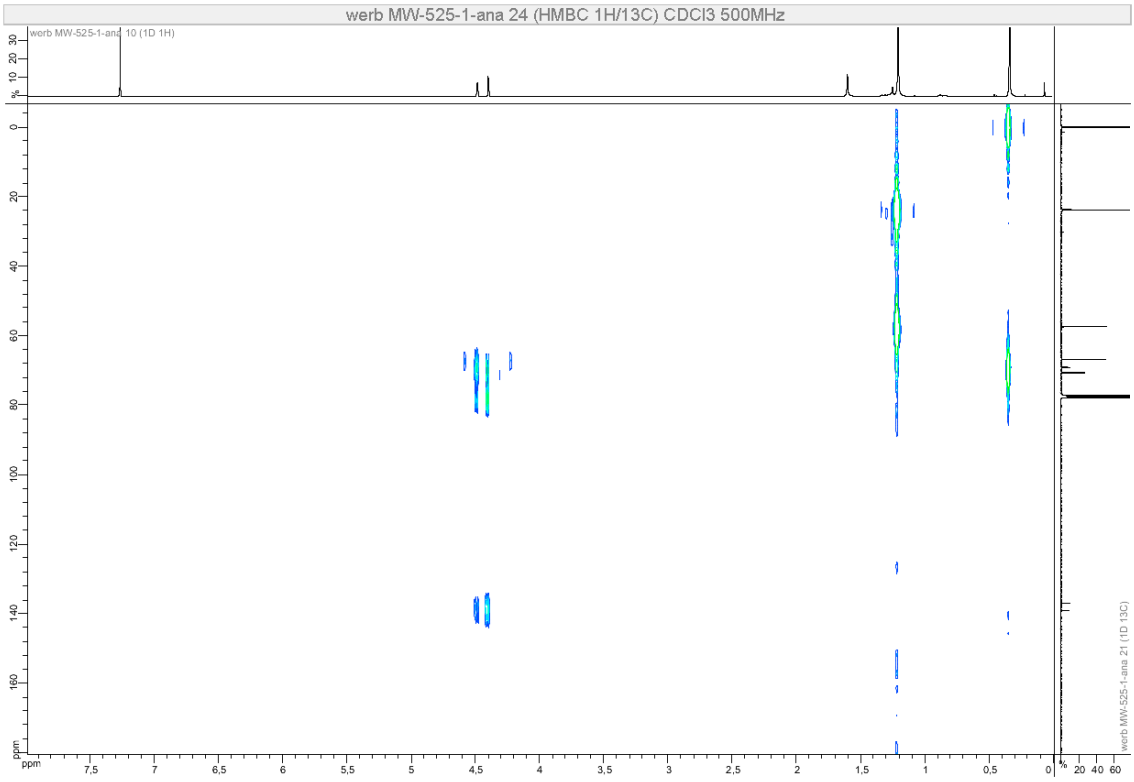
COSY (500 MHz, $CDCl_3$)



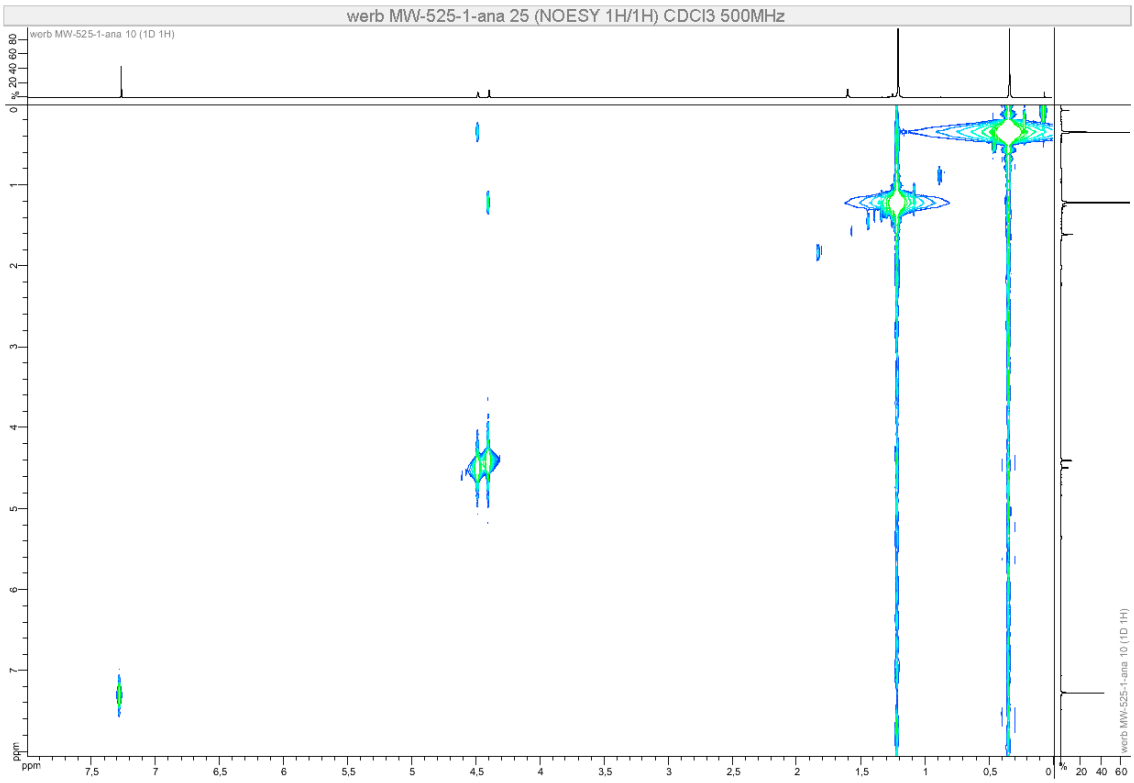
HSQC (500 MHz, $CDCl_3$)



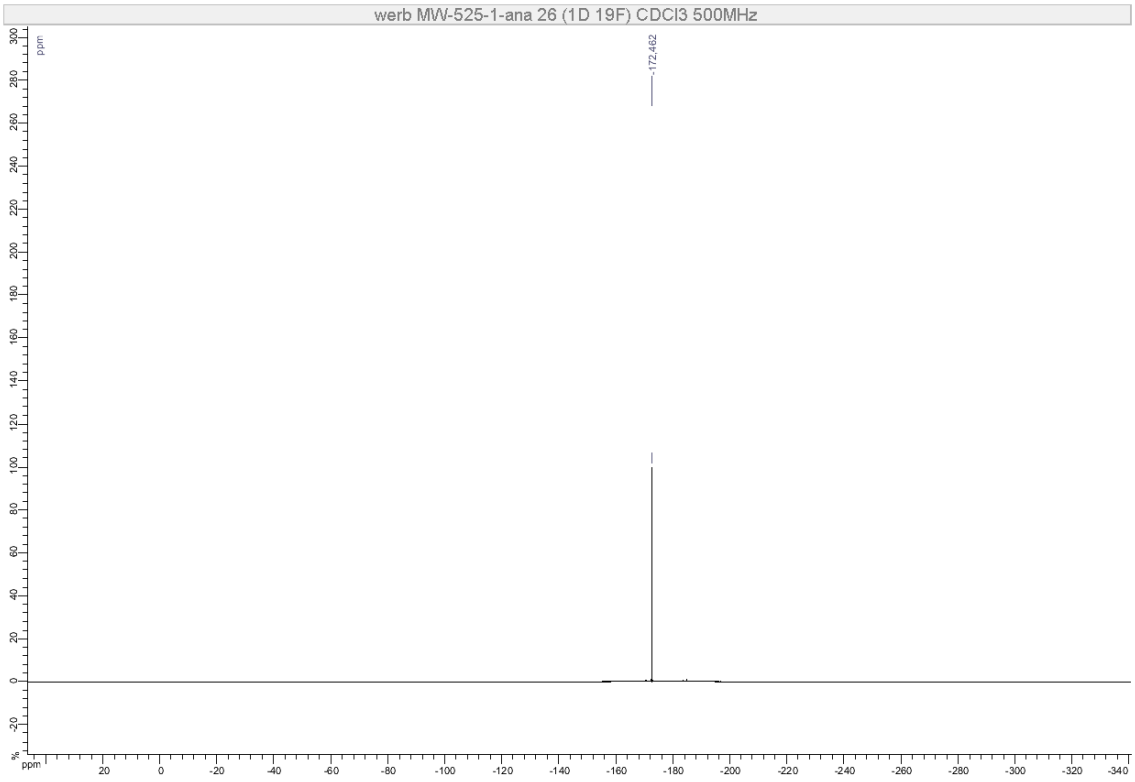
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

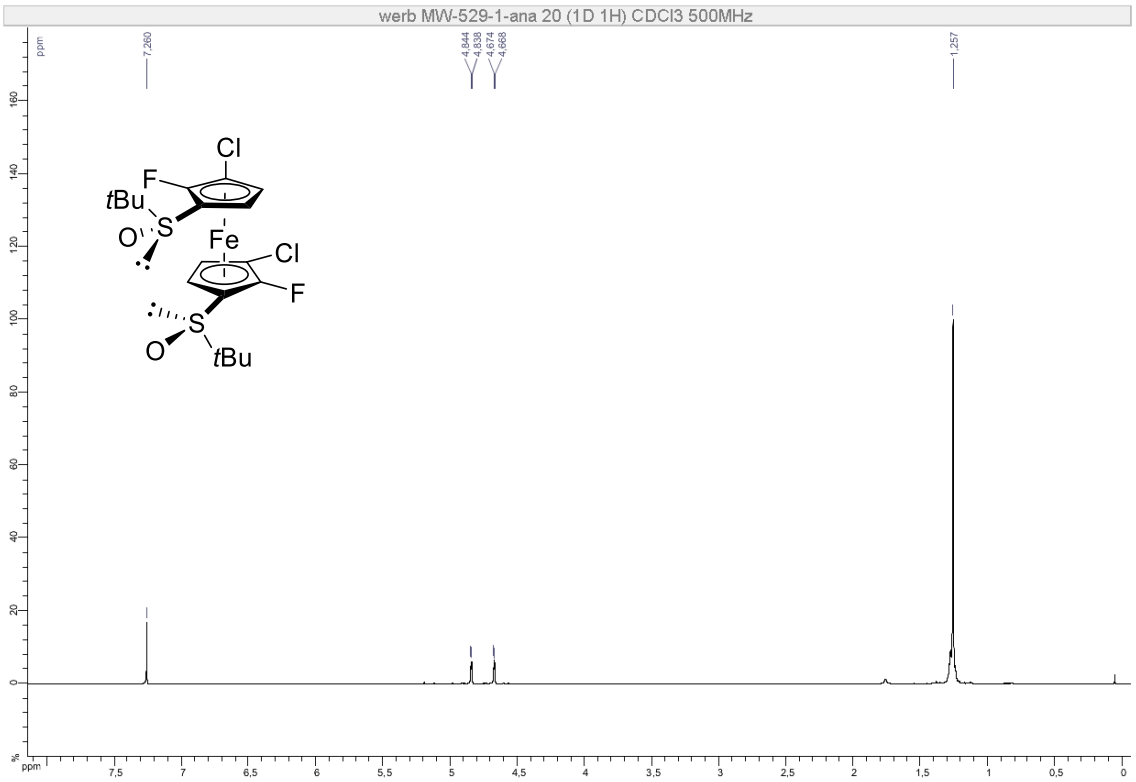


^{19}F NMR (470 MHz, $CDCl_3$)

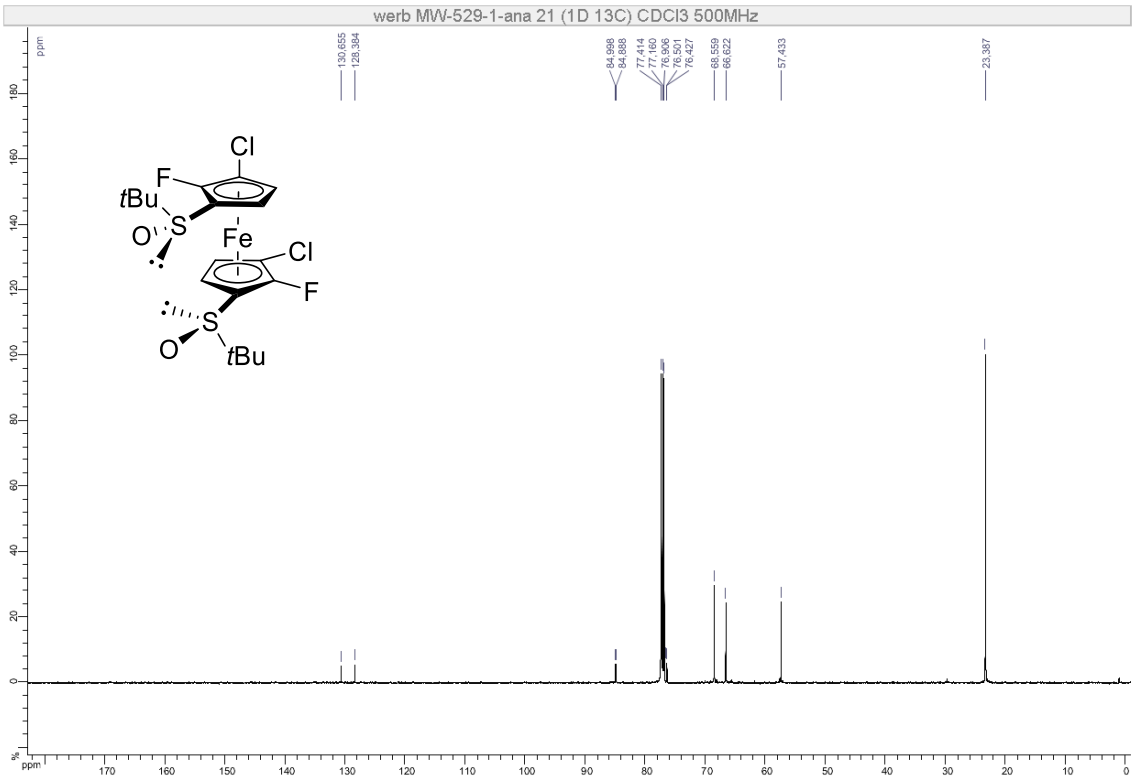


(*R*,*R*,*S*P,*S*P)-*S*,*S*'-Di-*tert*-butyl-3,3'-dichloro-2,2'-difluoroferrocene-1,1'-disulfoxide (*S*P,*S*P-8b)

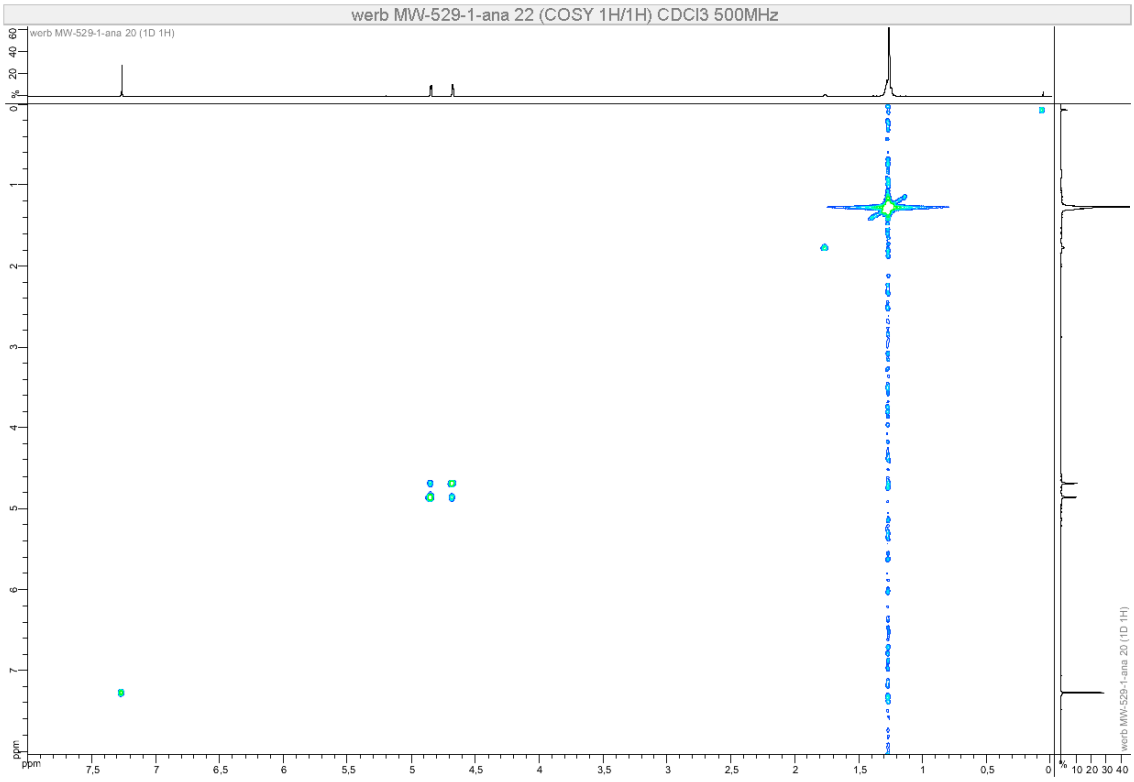
^{1}H NMR (500 MHz, $CDCl_3$)



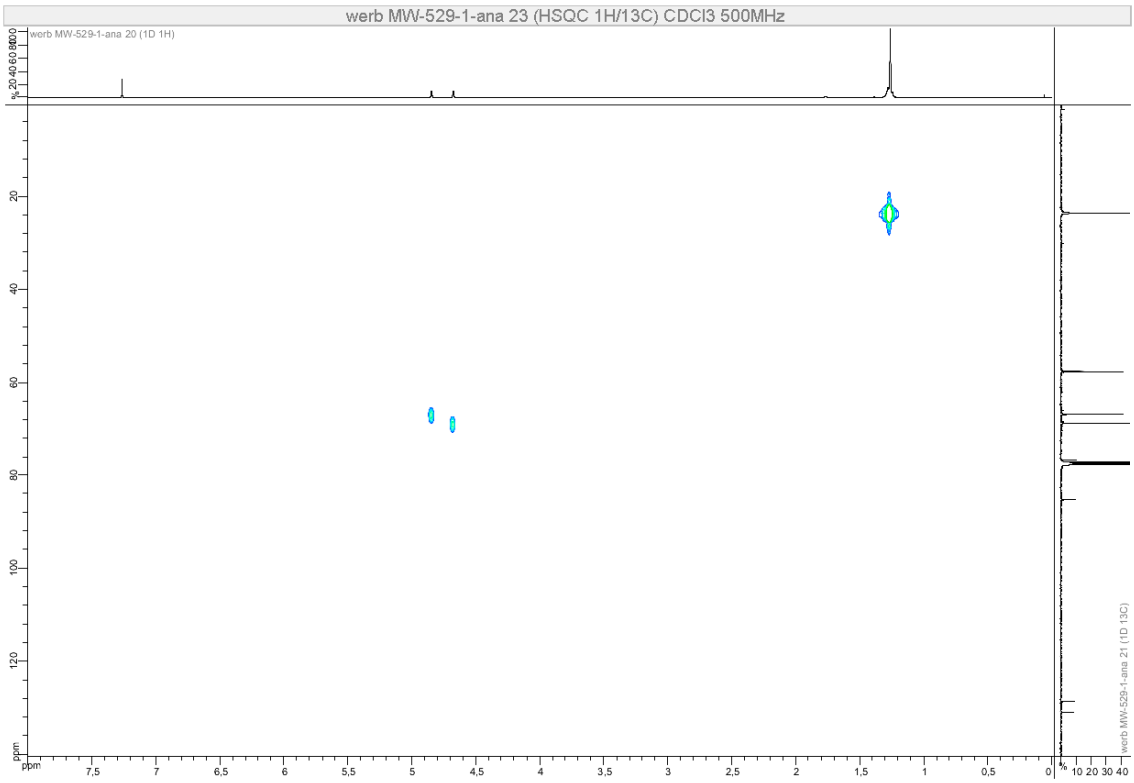
^{13}C NMR (126 MHz, $CDCl_3$)



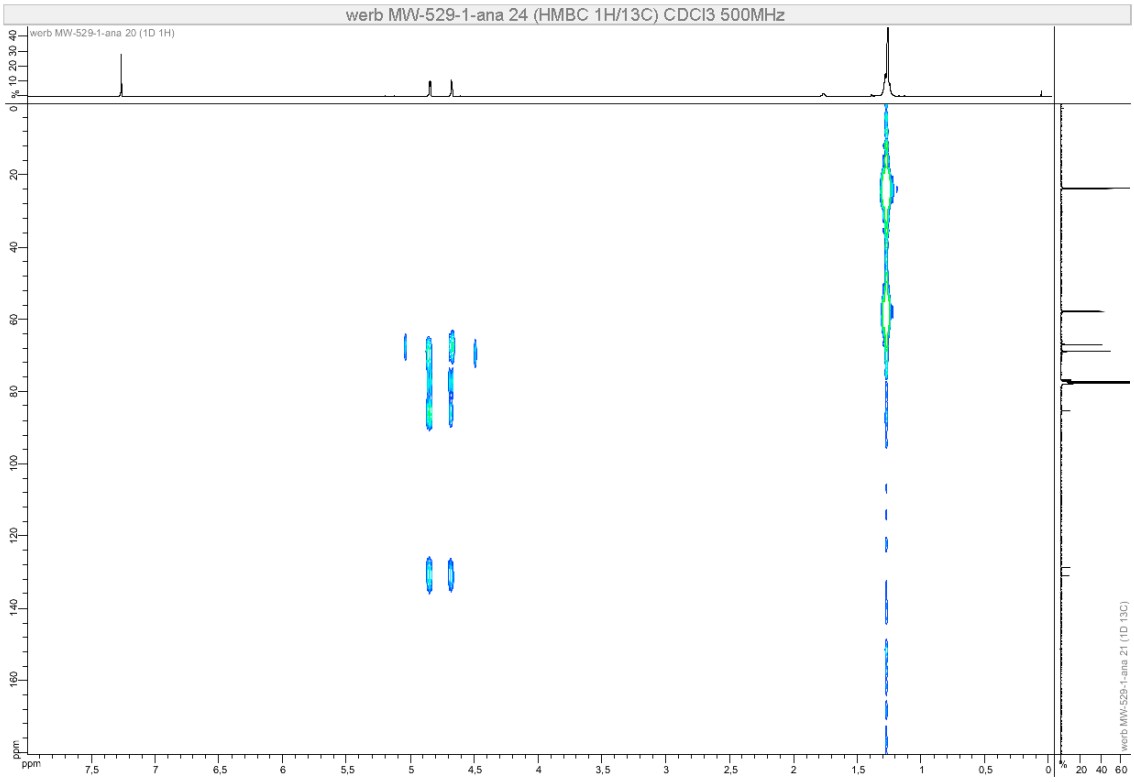
COSY (500 MHz, $CDCl_3$)



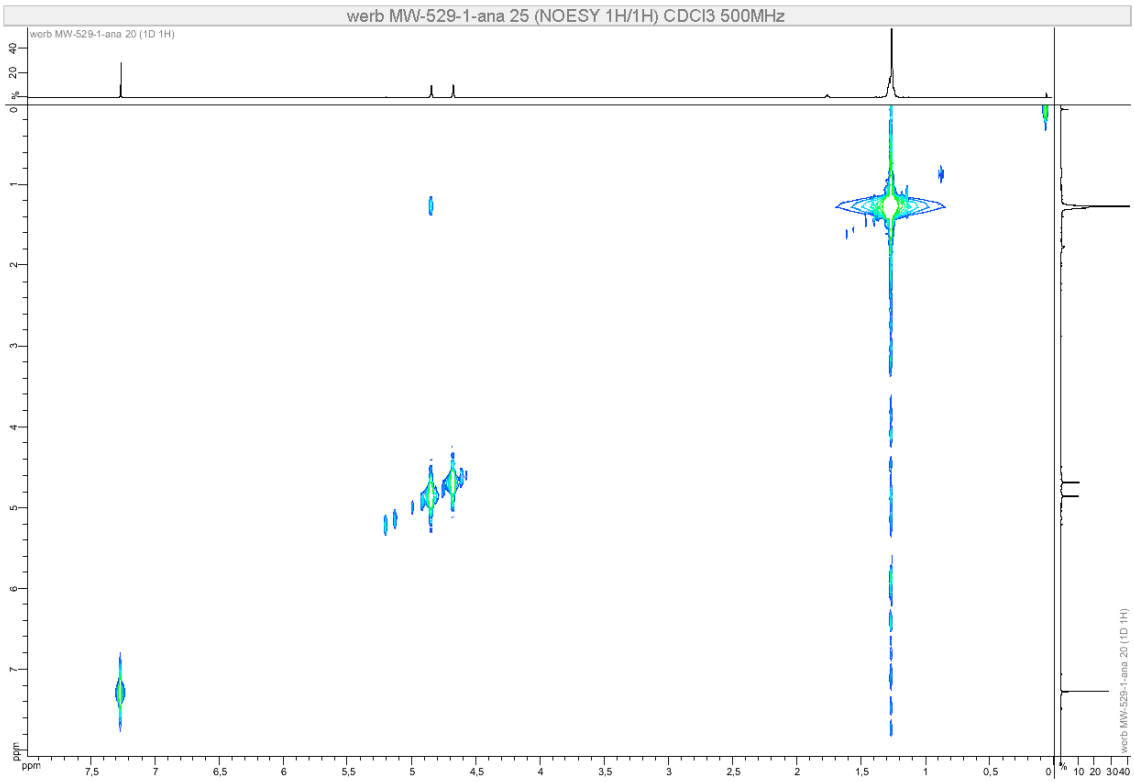
HSQC (500 MHz, $CDCl_3$)



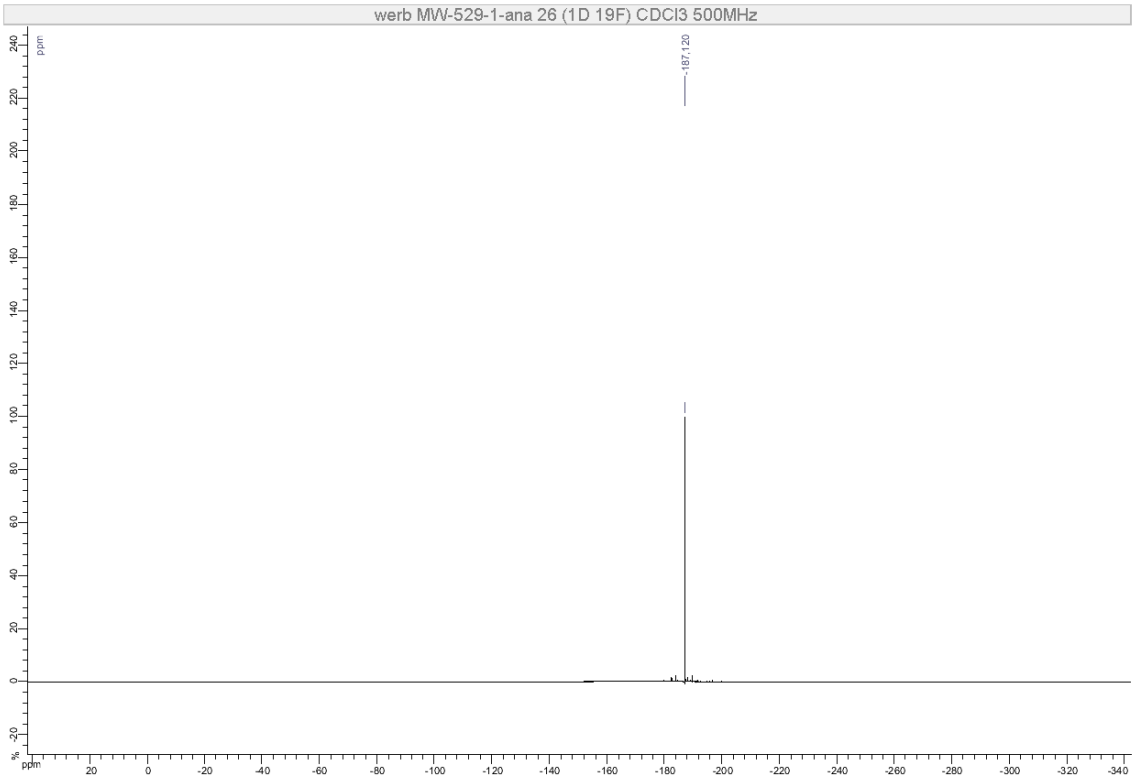
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

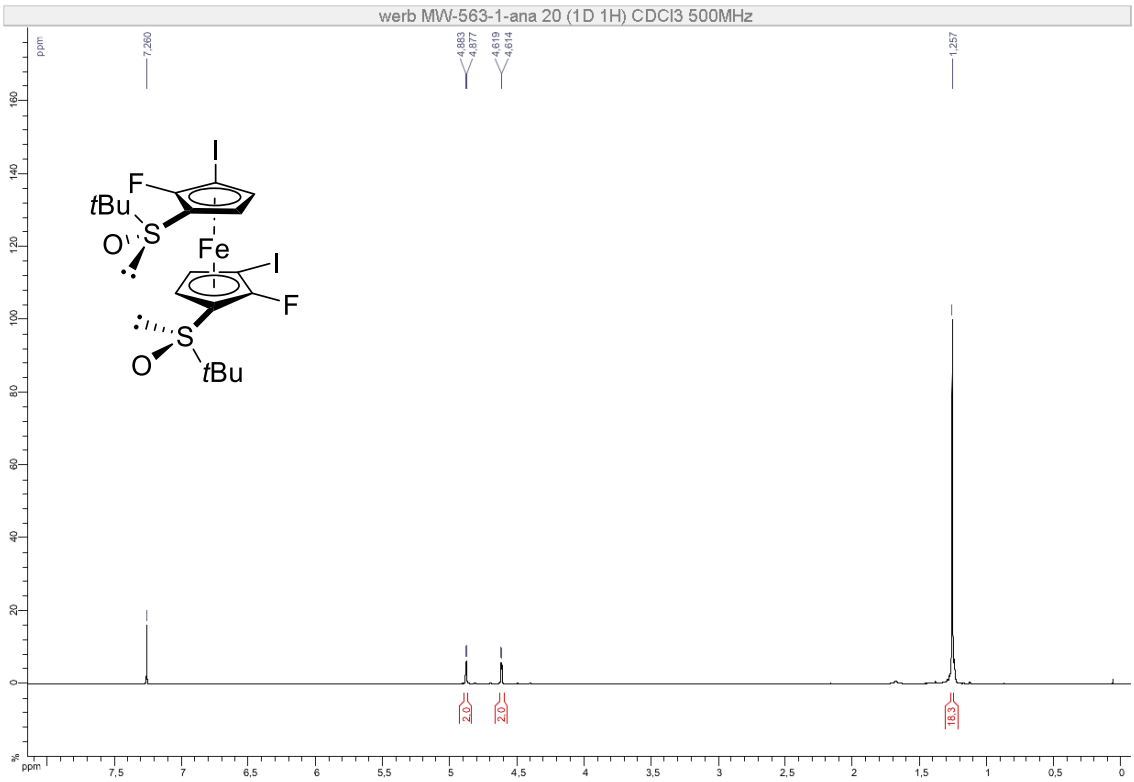


^{19}F NMR (470 MHz, $CDCl_3$)

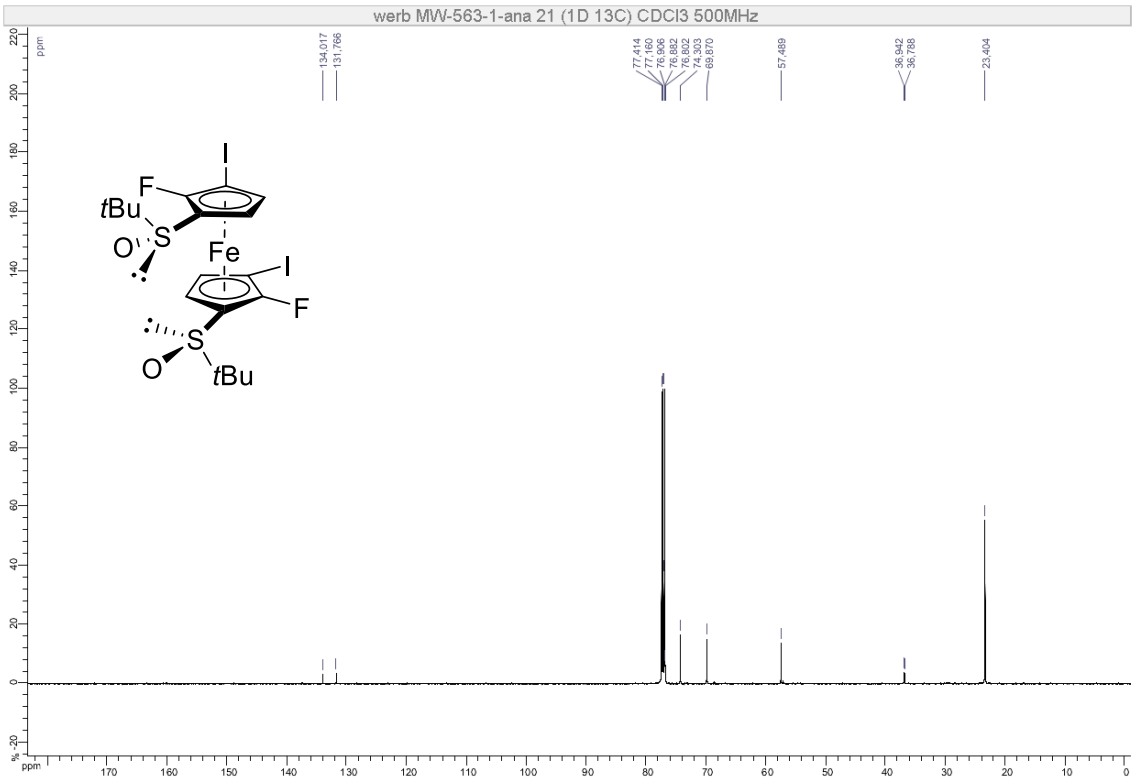


(*R*,*R*,*S*P,*S*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-difluoro-3,3'-diiodoferrocene-1,1'-disulfoxide (*S*P,*S*P-8c)

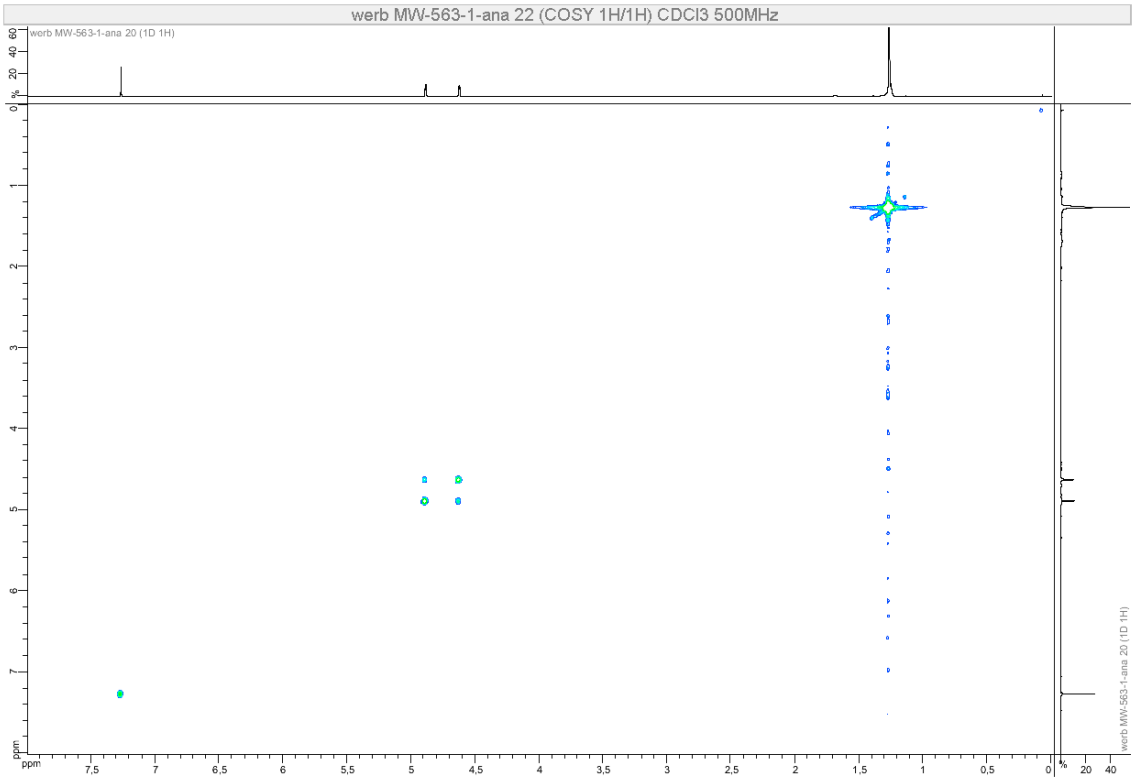
^{1}H NMR (500 MHz, $CDCl_3$)



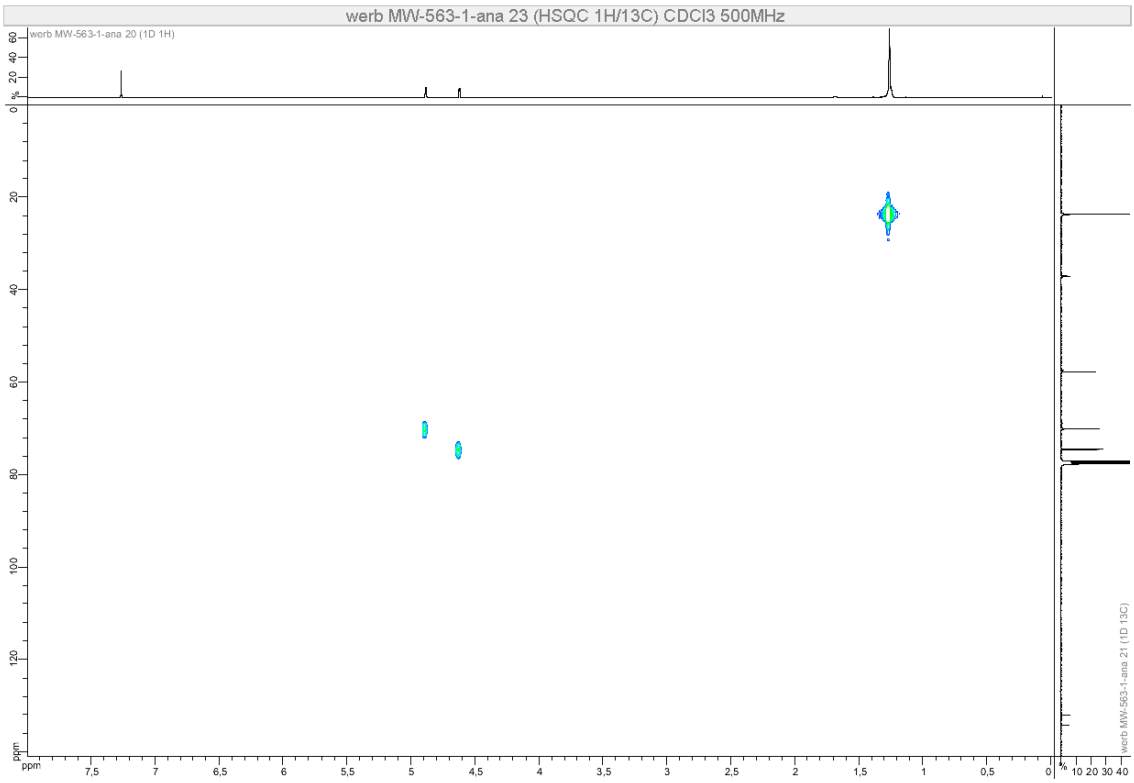
^{13}C NMR (126 MHz, $CDCl_3$)



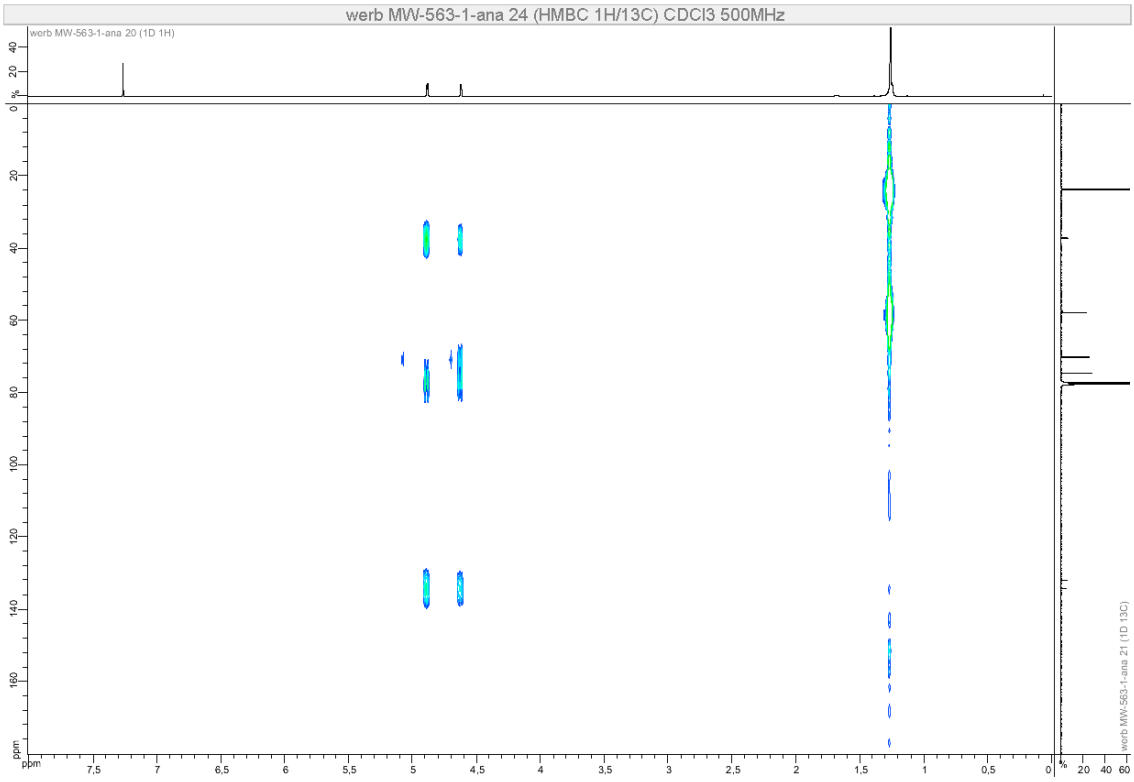
COSY (500 MHz, $CDCl_3$)



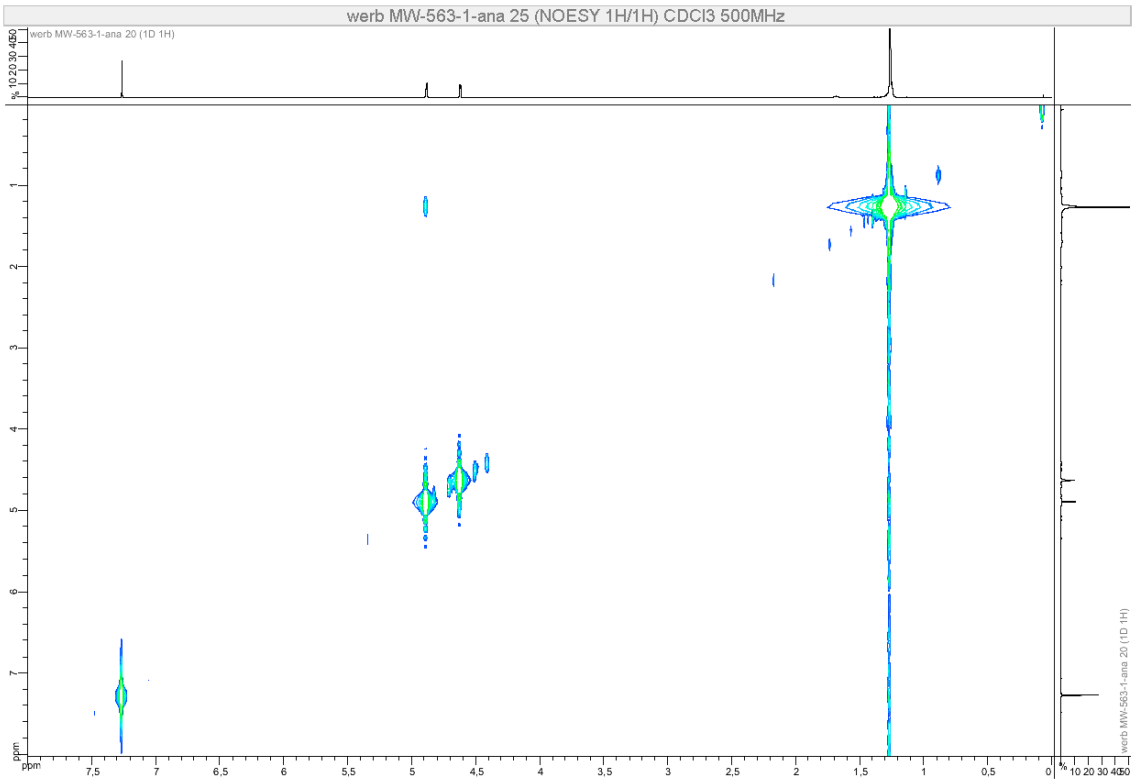
HSQC (500 MHz, $CDCl_3$)



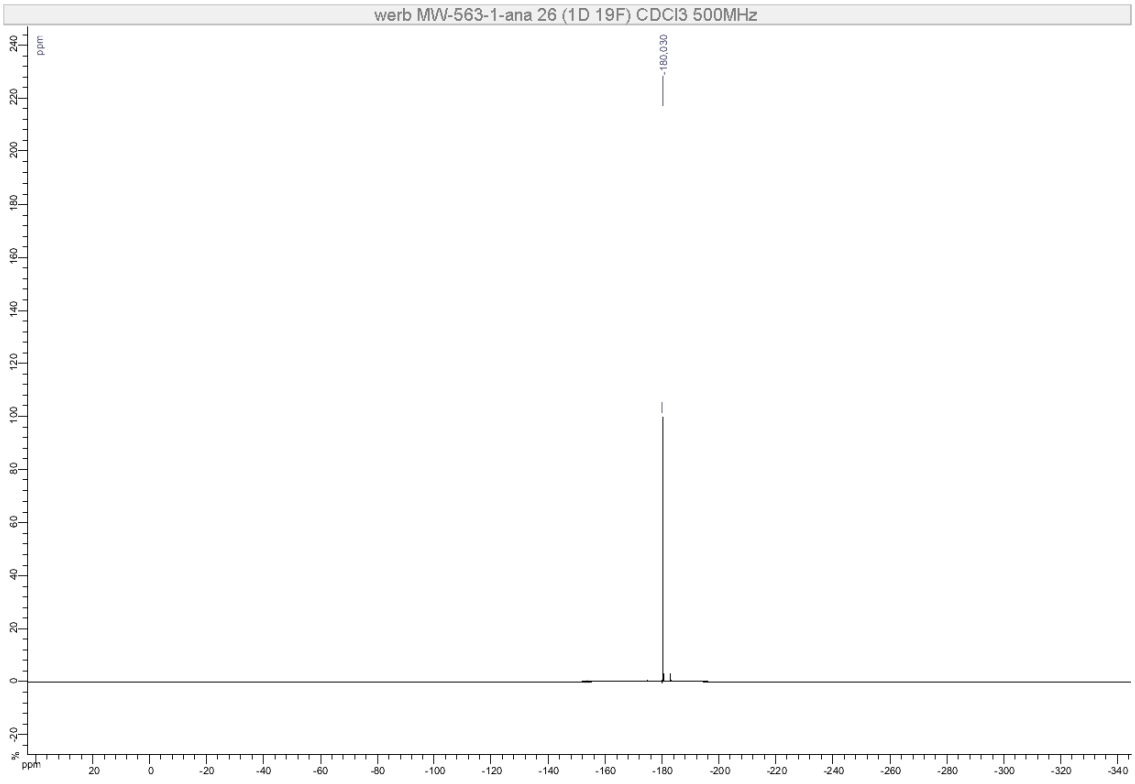
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

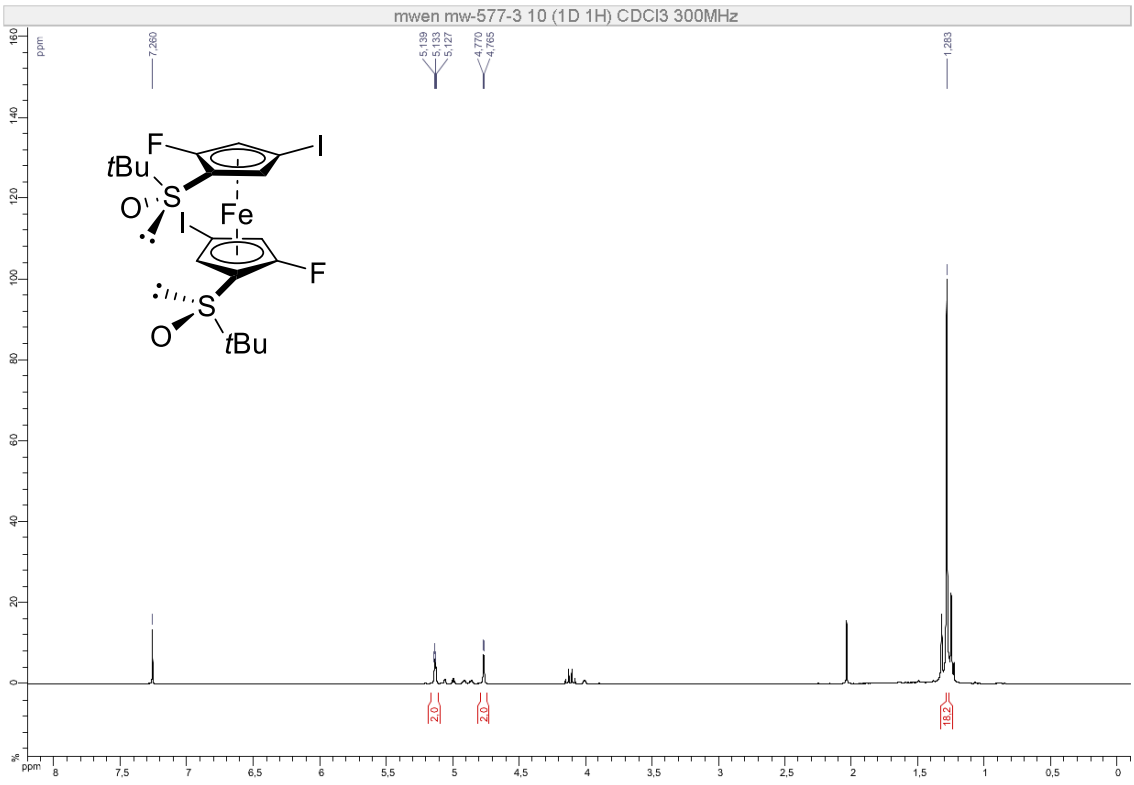


^{19}F NMR (470 MHz, $CDCl_3$)



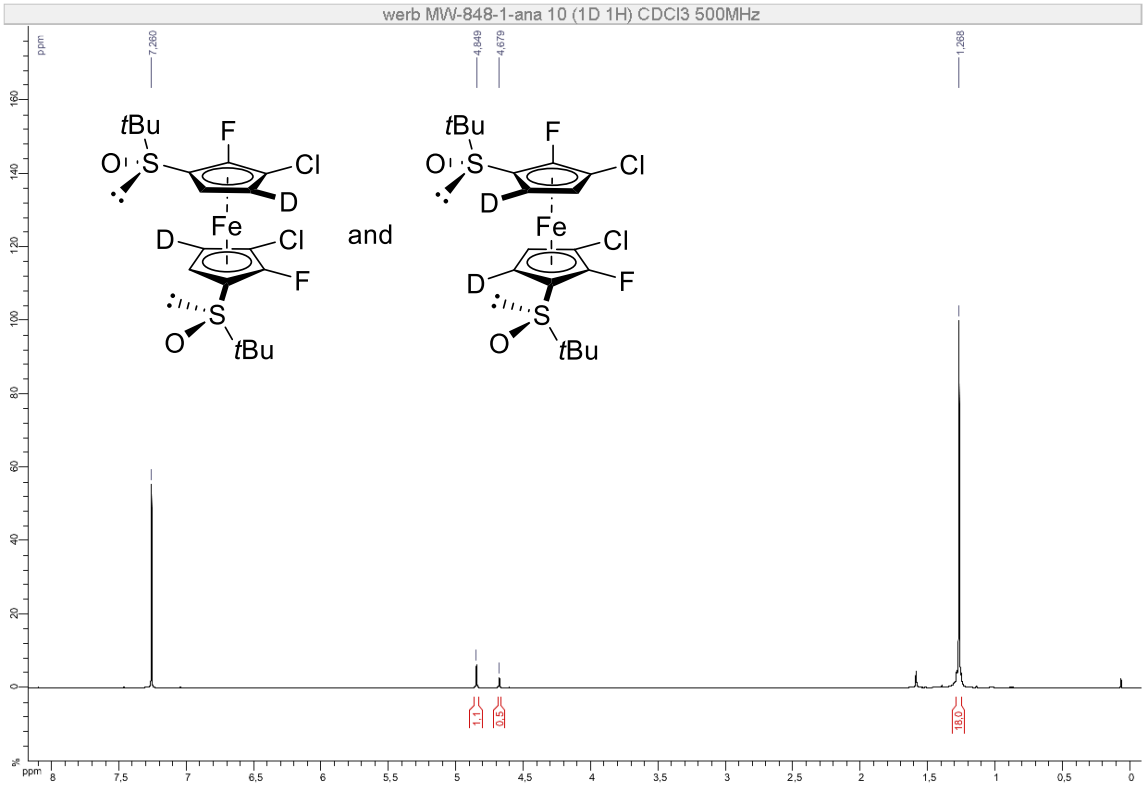
(*R*,*R*,*S*P,*S*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-difluoro-4,4'-diiodoferrocene-1,1'-disulfoxide

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

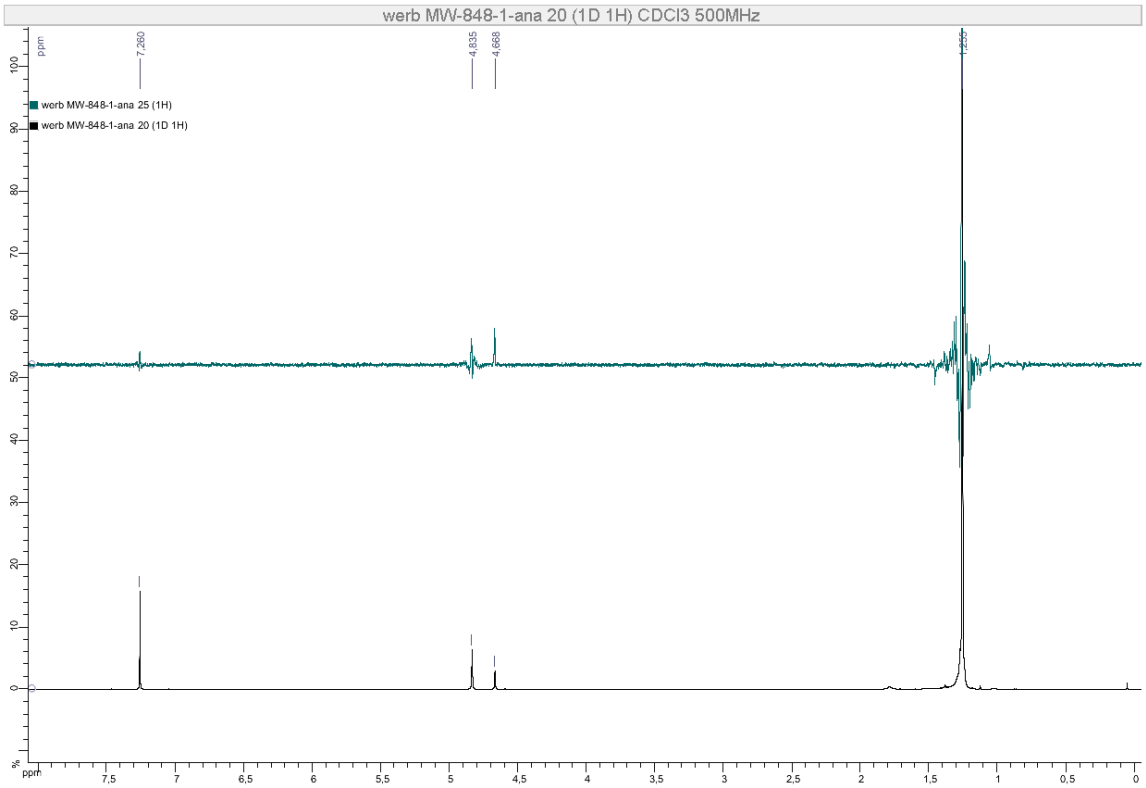


(*R*,*R*,*S*P,*S*P)-*S*,*S*'-Di-*tert*-butyl-3,3'-dichloro-4,4'-dideutero-2,2'-difluoroferrocene-1,1'-disulfoxide and (*R*,*R*,*S*P,*S*P)-*S*,*S*'-di-*tert*-butyl-3,3'-dichloro-5,5'-dideutero-2,2'-difluoroferrocene-1,1'-disulfoxide

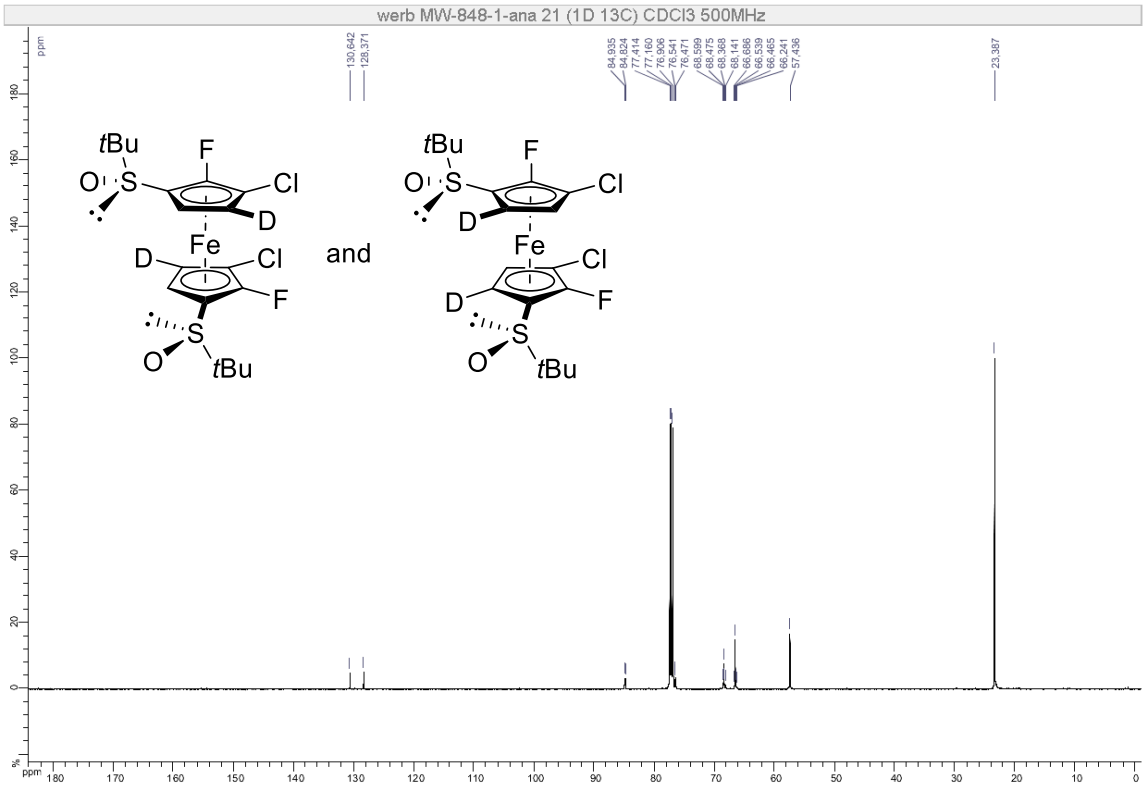
^{1}H NMR (500 MHz, $CDCl_3$)



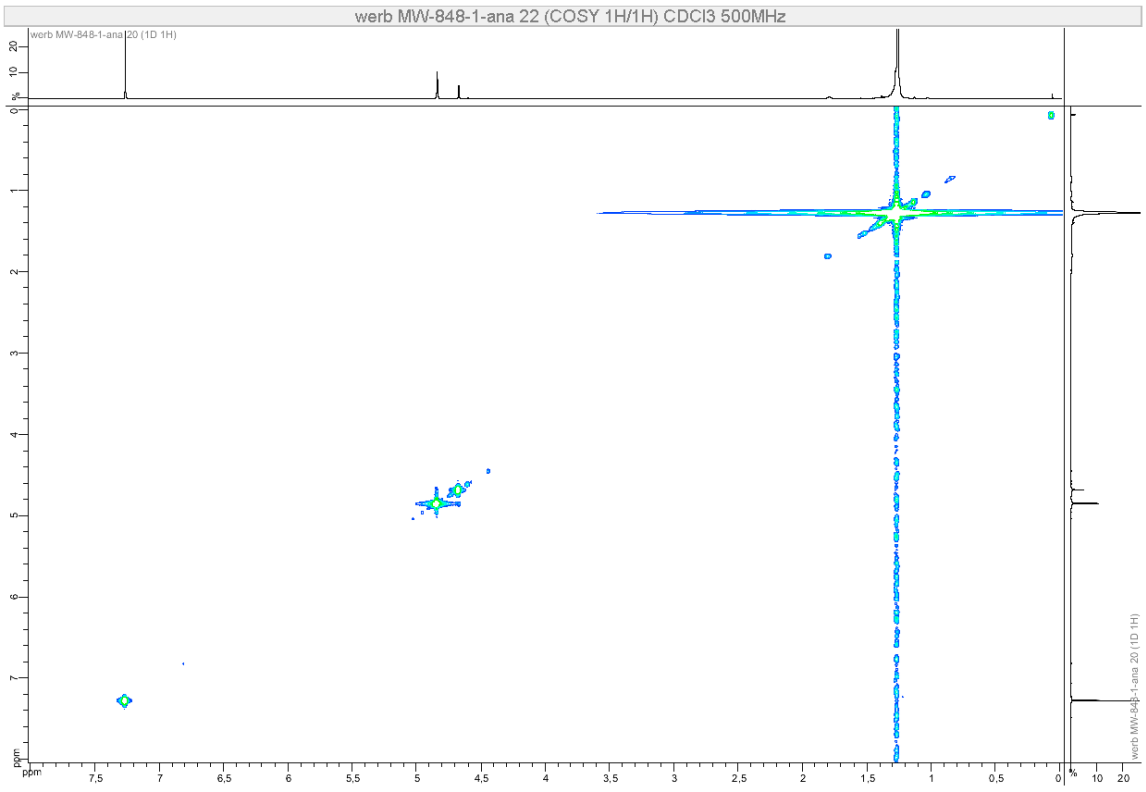
HOESY (500 MHz, $CDCl_3$) Irradiation at -187.2 ppm – Superposition of ^{1}H (bottom) and HOESY (top) spectra.



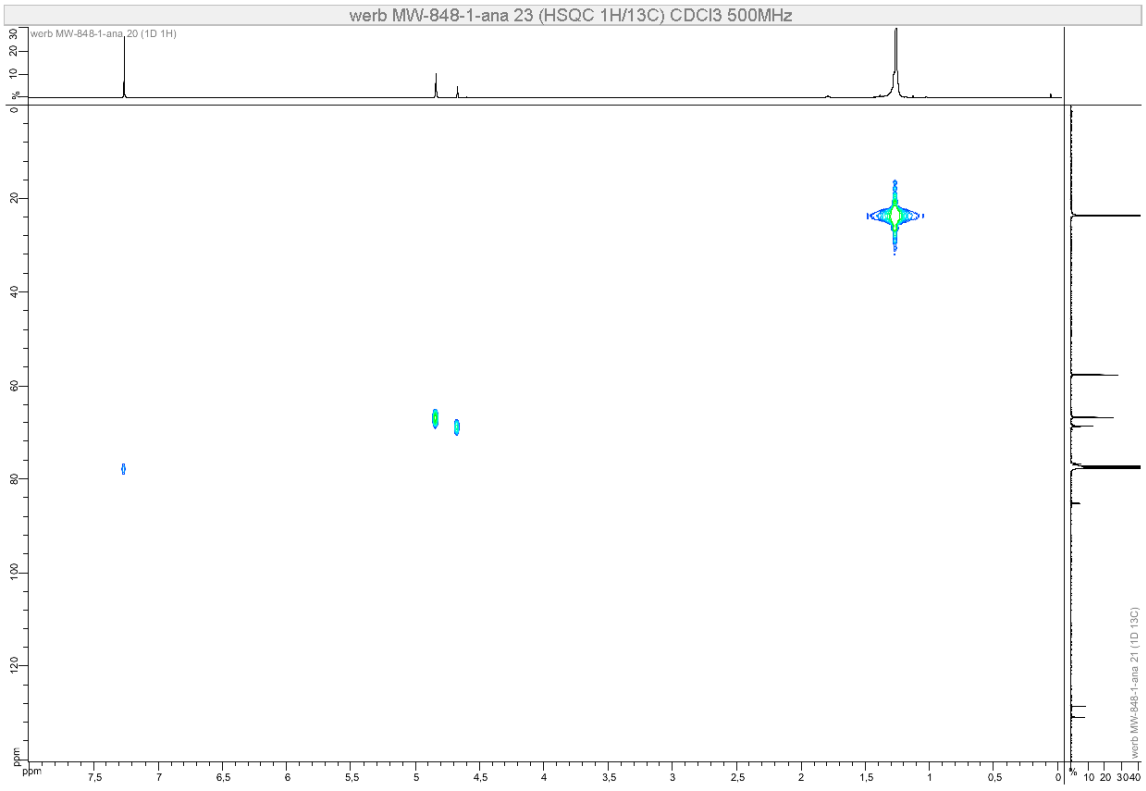
^{13}C NMR (126 MHz, $CDCl_3$)



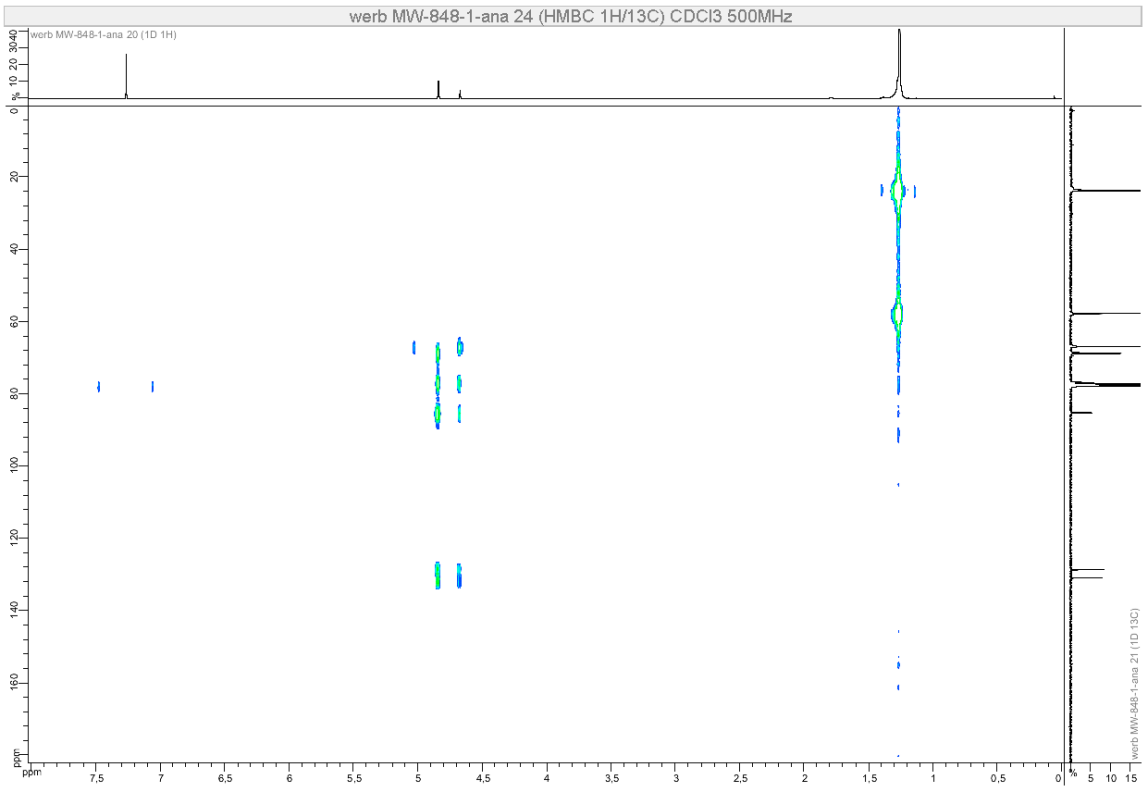
COSY (500 MHz, $CDCl_3$)



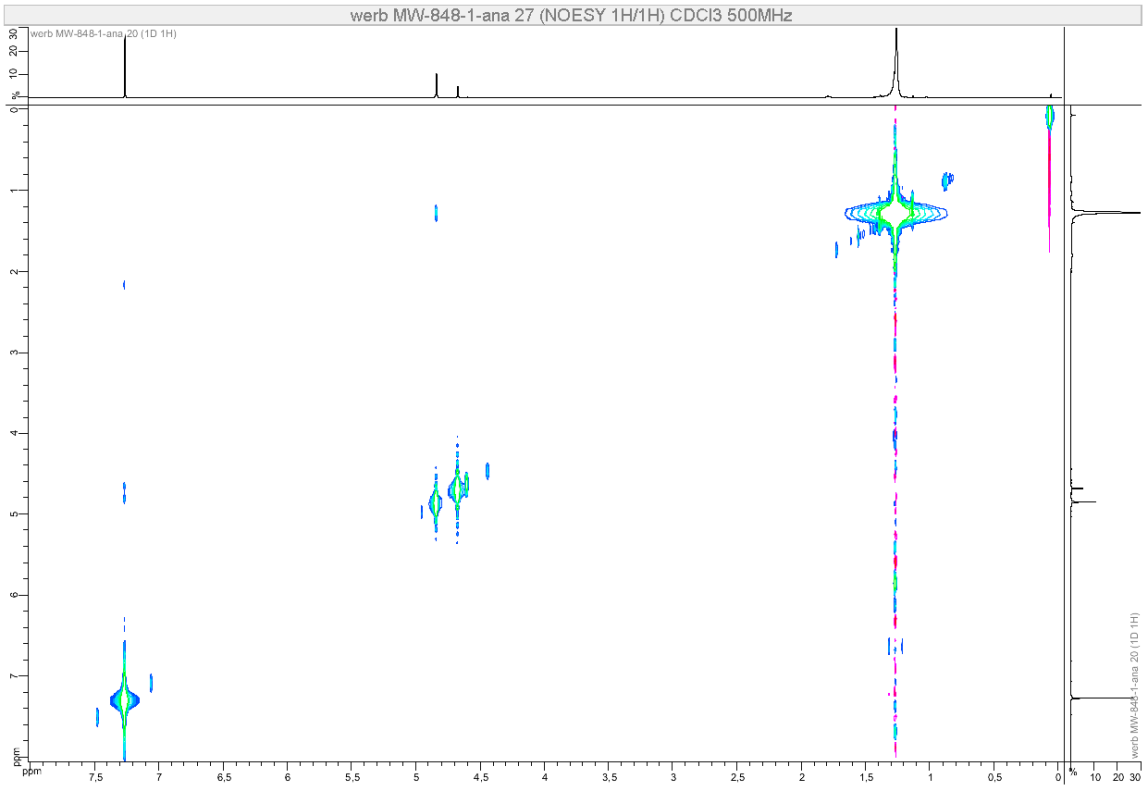
HSQC (500 MHz, $CDCl_3$)



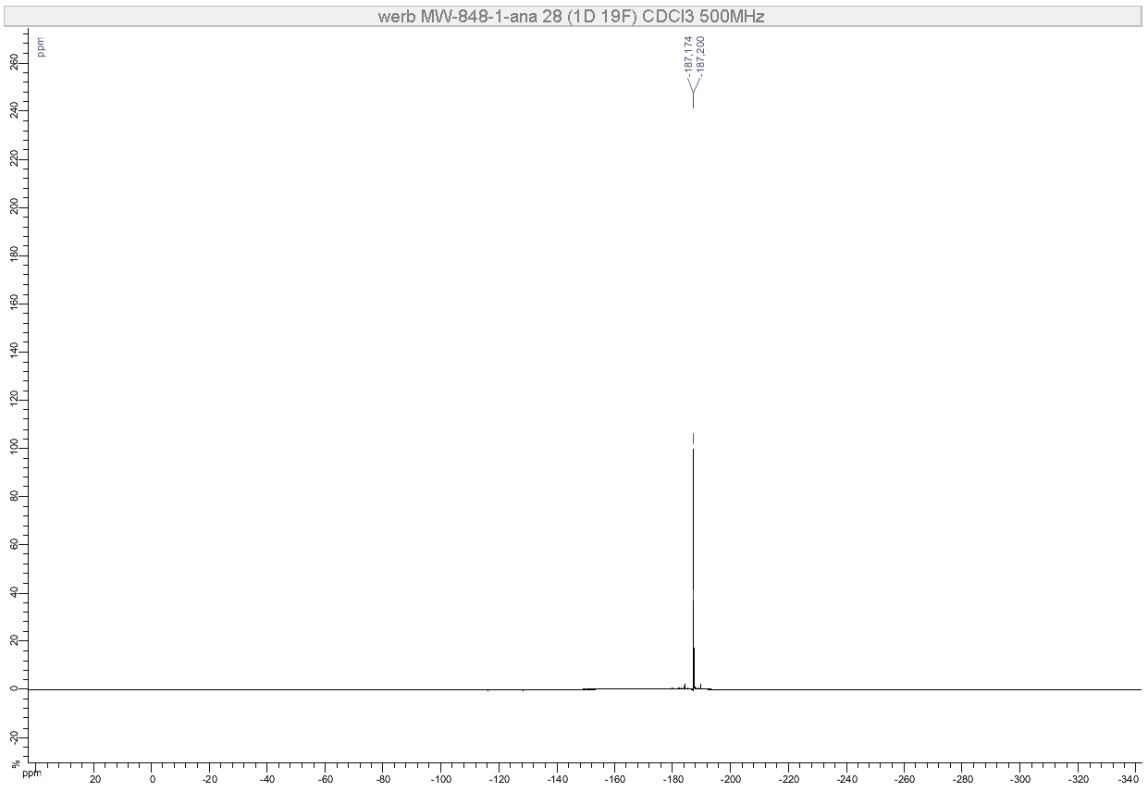
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

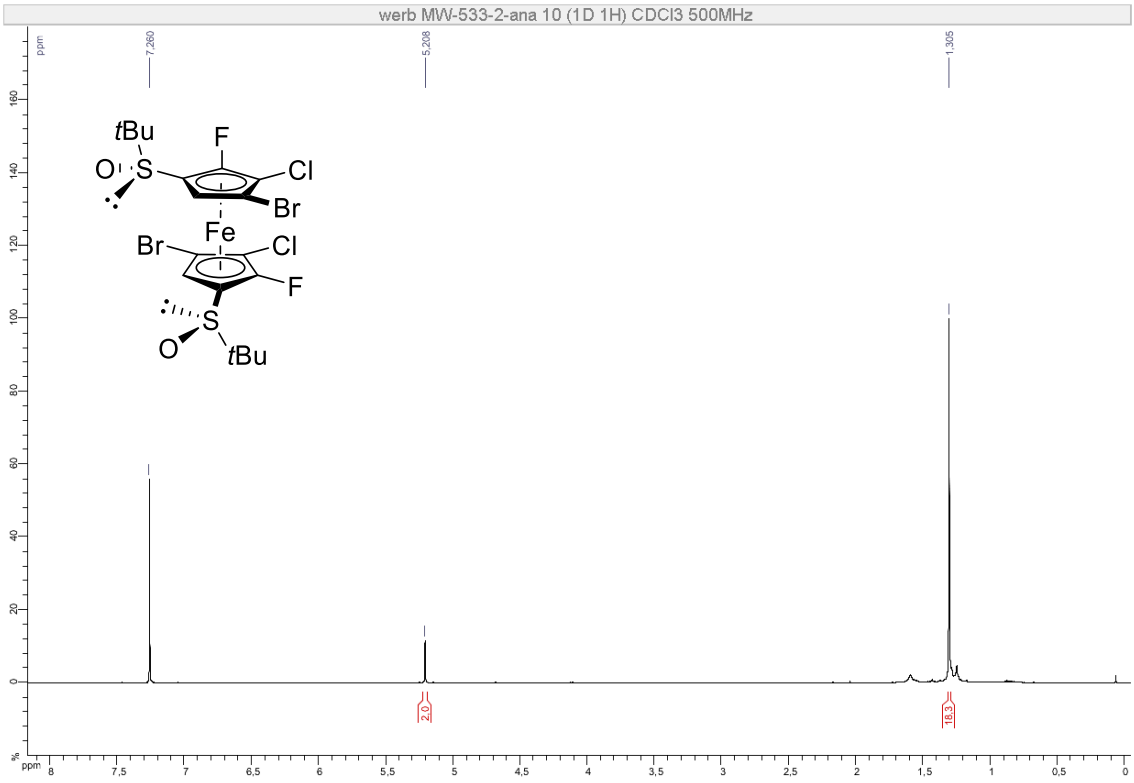


^{19}F NMR (470 MHz, $CDCl_3$)

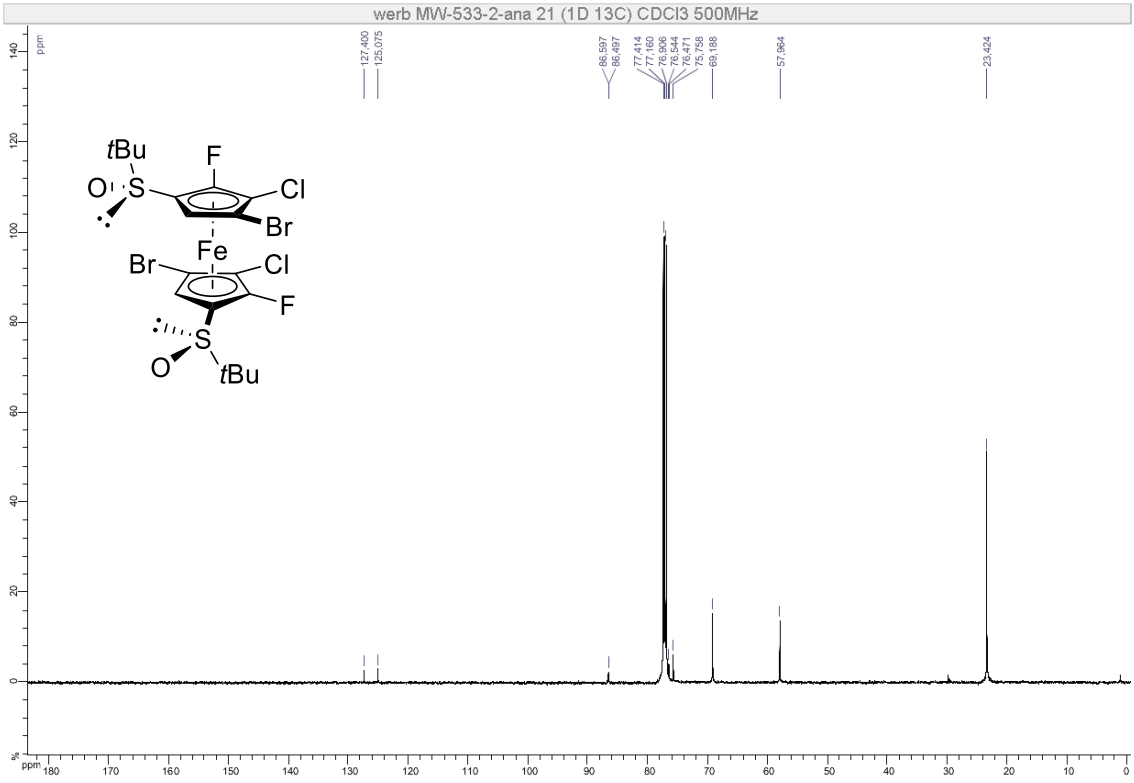


(*R*,*R*,*S*P,*S*P)-4,4'-Dibromo-*S*,*S*'-di-*tert*-butyl-3,3'-dichloro-2,2'-difluoroferrocene-1,1'-disulfoxide (*S*P,*S*P-9a)

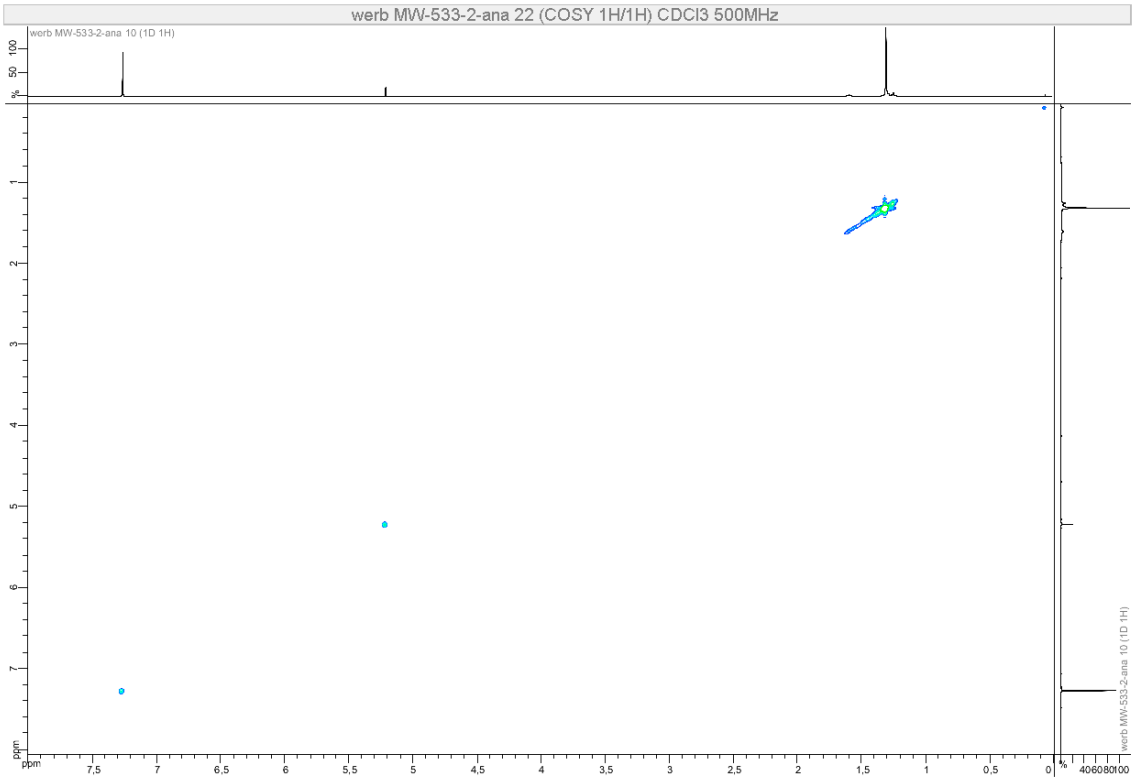
^{1}H NMR (500 MHz, $CDCl_3$)



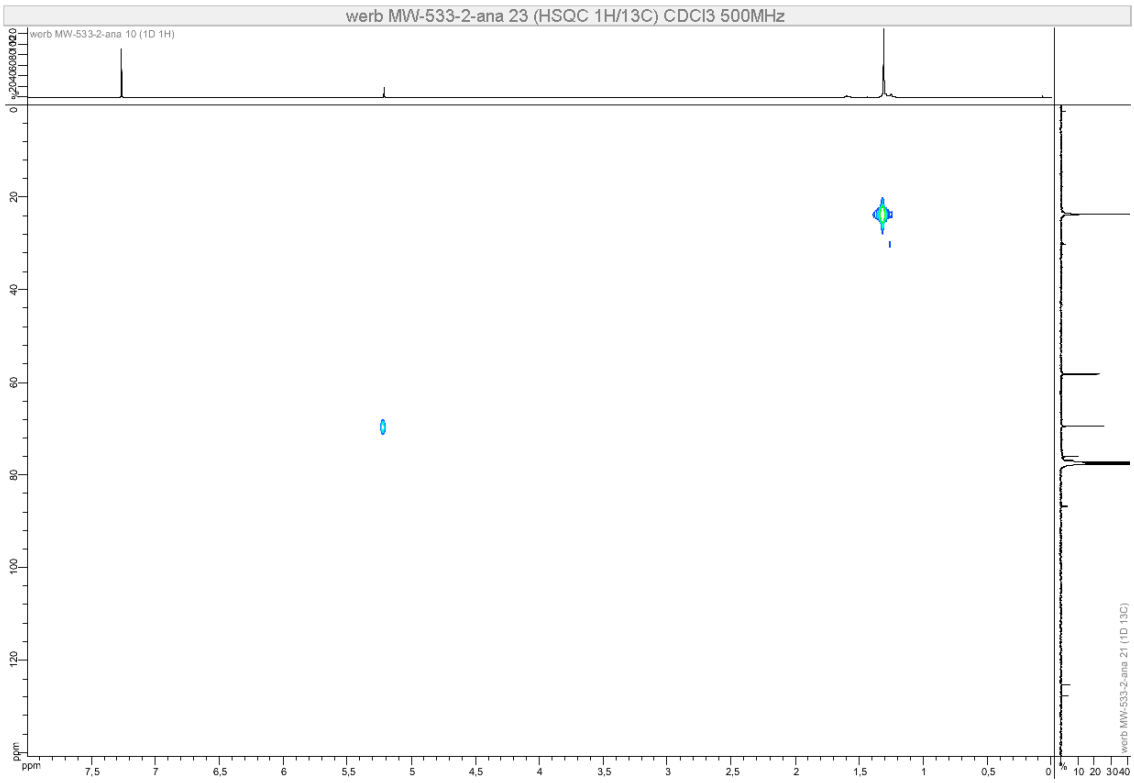
^{13}C NMR (126 MHz, $CDCl_3$)



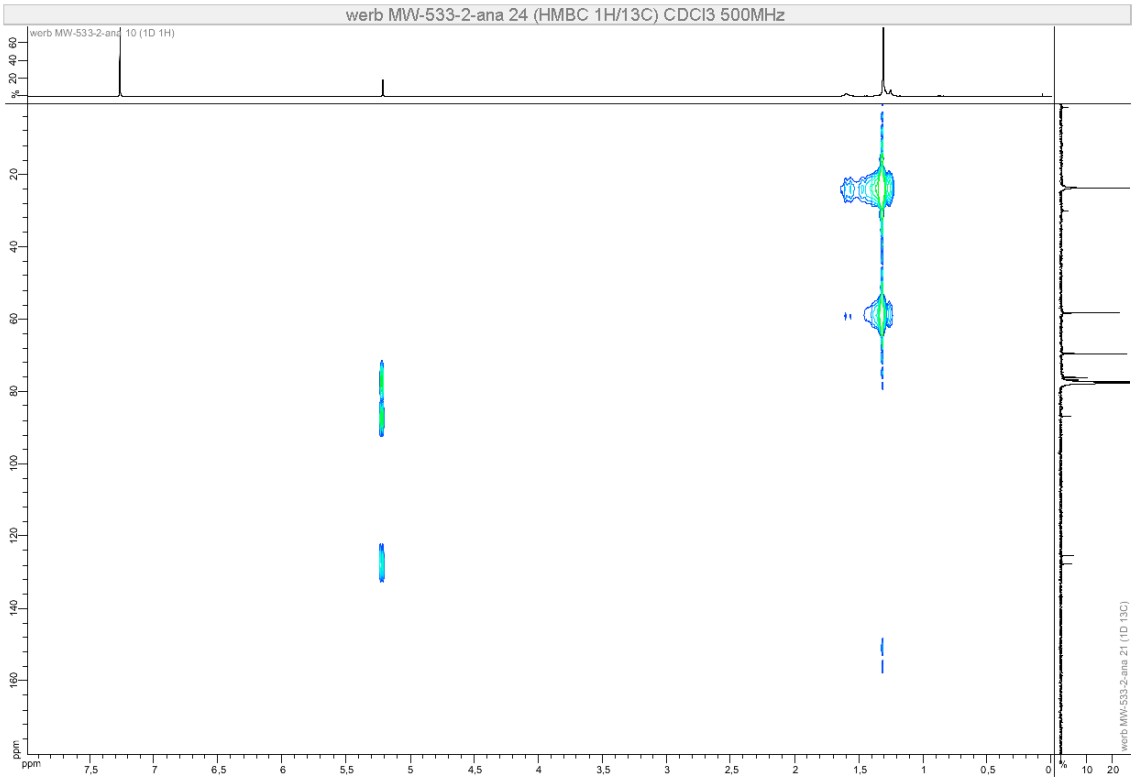
COSY (500 MHz, $CDCl_3$)



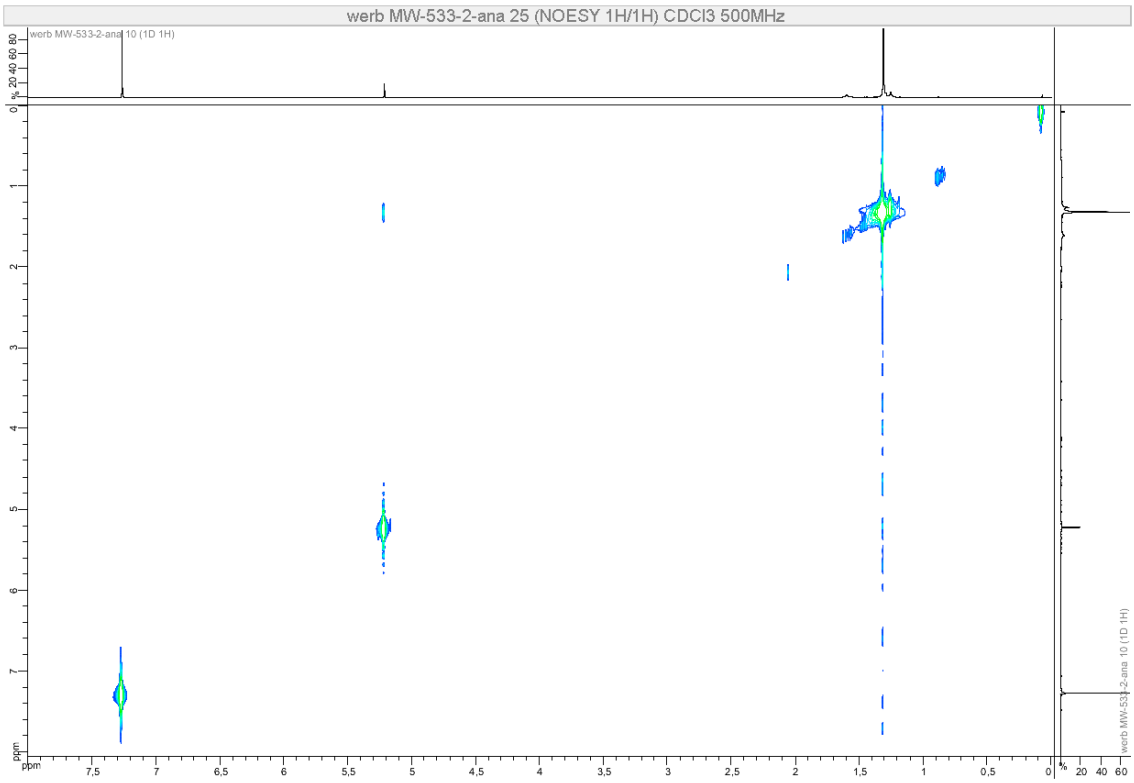
HSQC (500 MHz, $CDCl_3$)



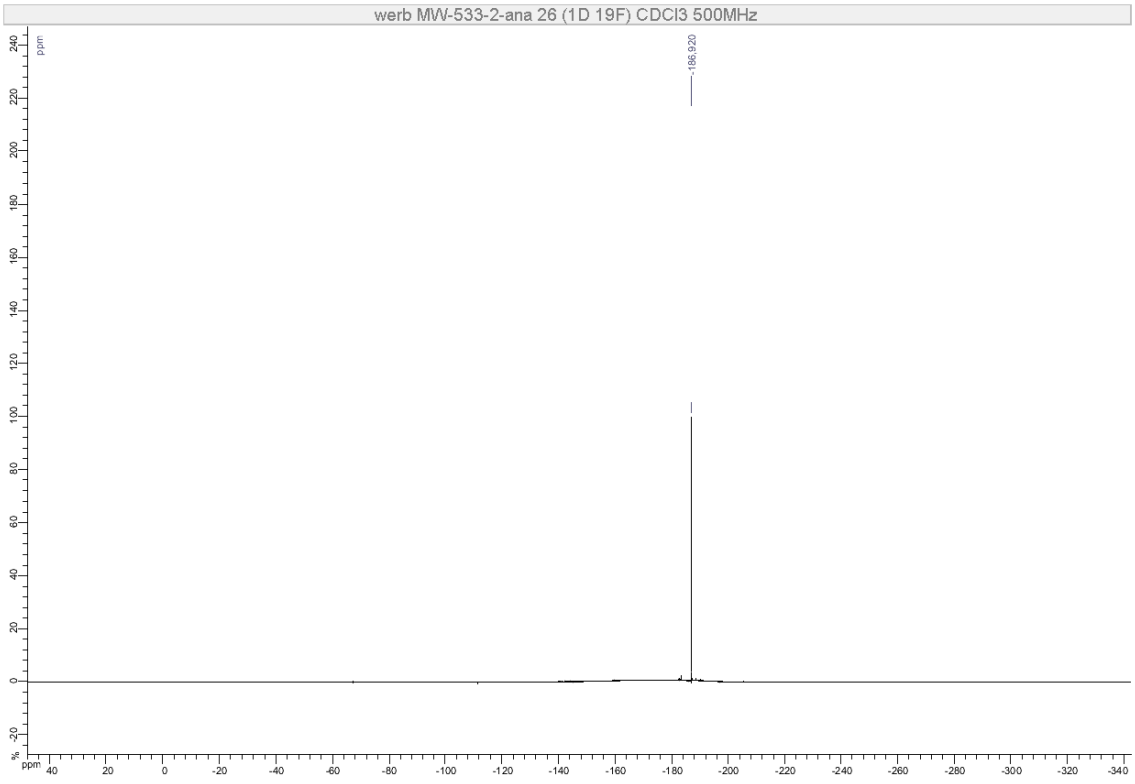
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

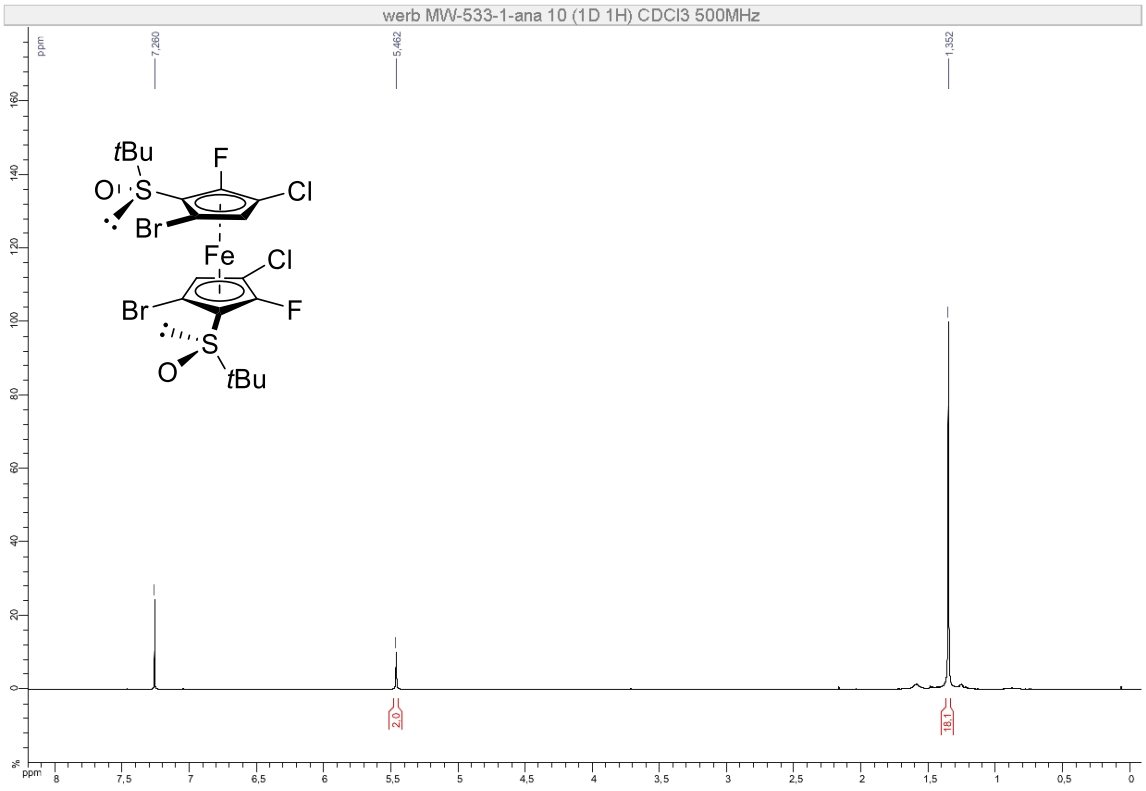


^{19}F NMR (470 MHz, $CDCl_3$)

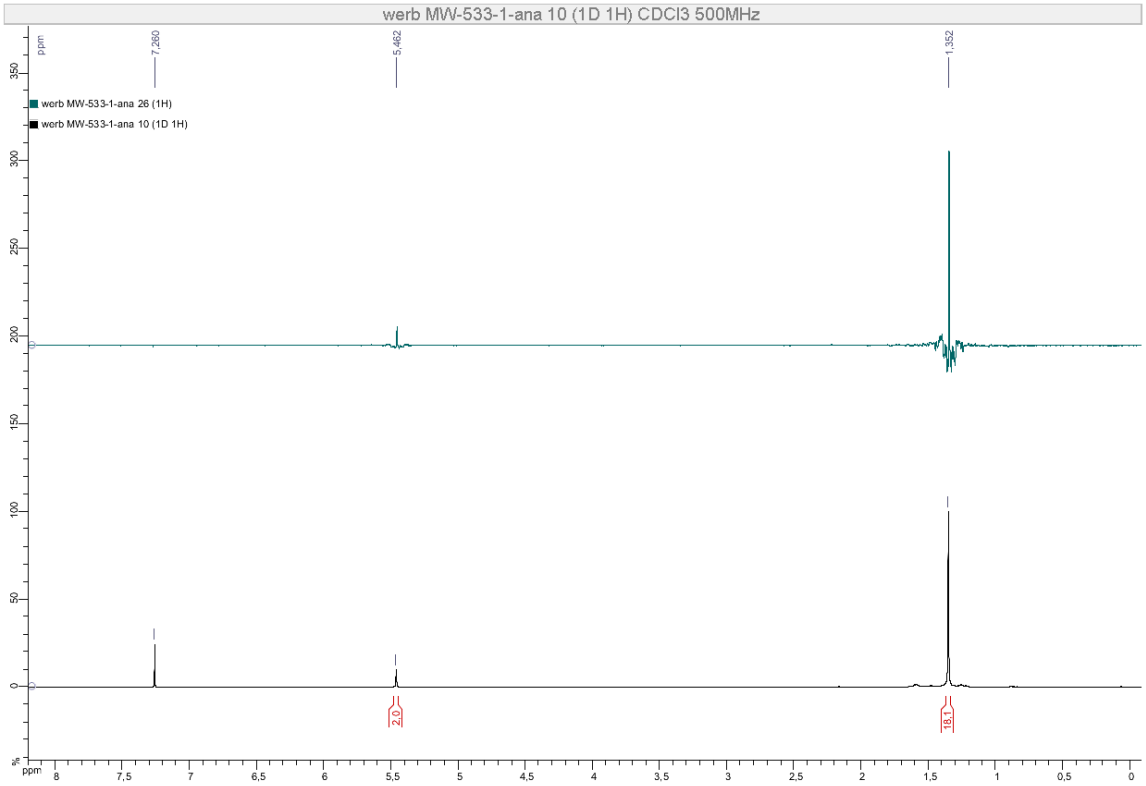


(*R*,*R*,*S*P,*S*P)-5,5'-Dibromo-*S*,*S*'-di-*tert*-butyl-3,3'-dichloro-2,2'-difluoroferrocene-1,1'-disulfoxide (*S*P,*S*P-9'a)

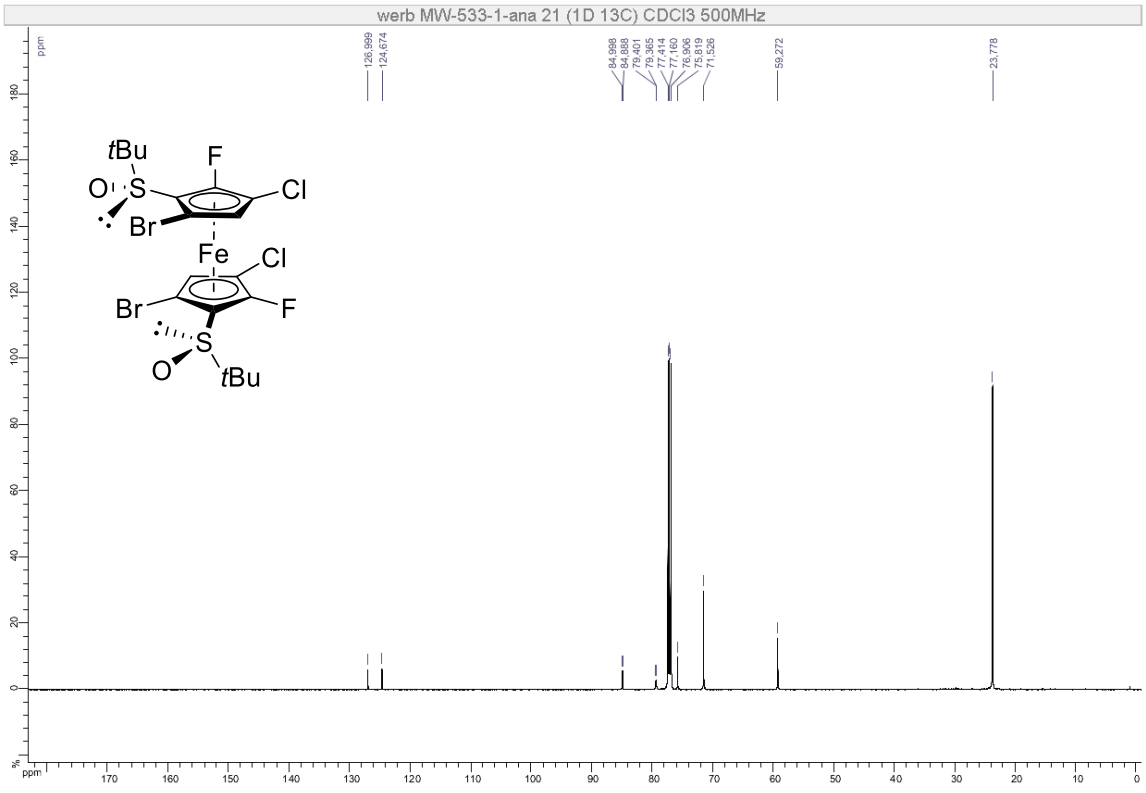
^{1}H NMR (500 MHz, $CDCl_3$)



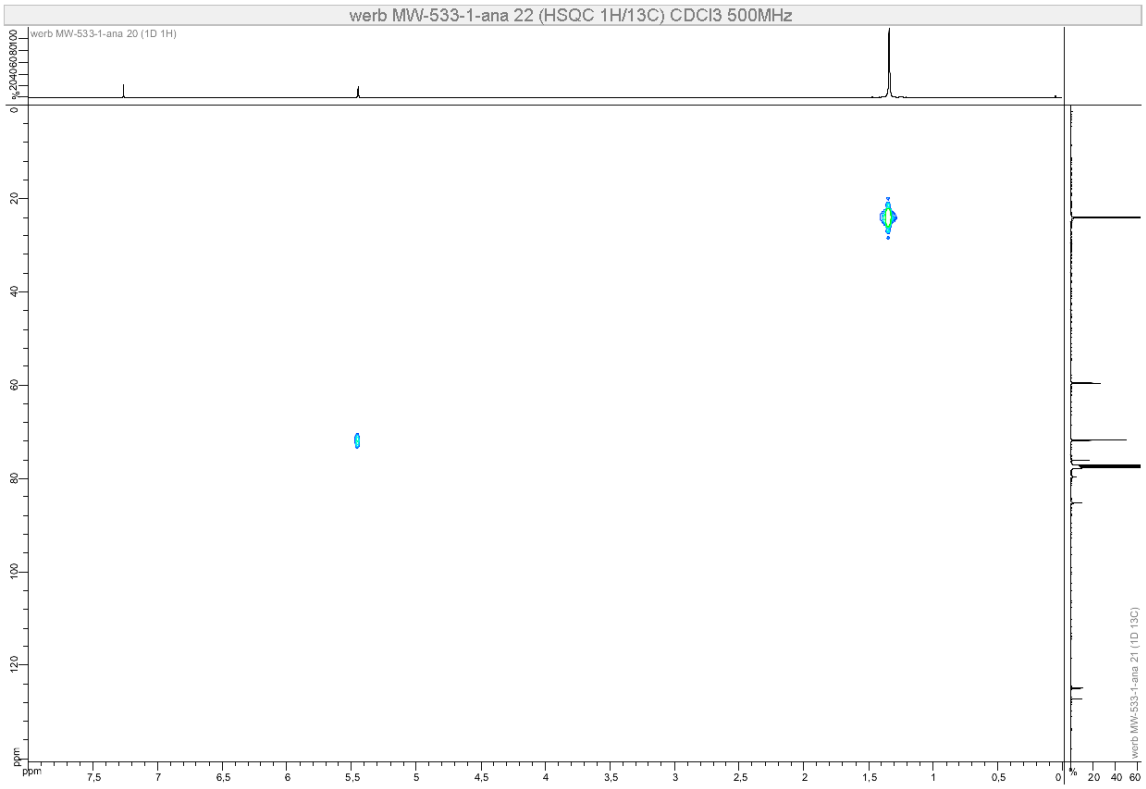
HOESY (500 MHz, $CDCl_3$) Irradiation at -187.9 ppm – Superposition of ^{1}H (bottom) and HOESY (top) spectra.



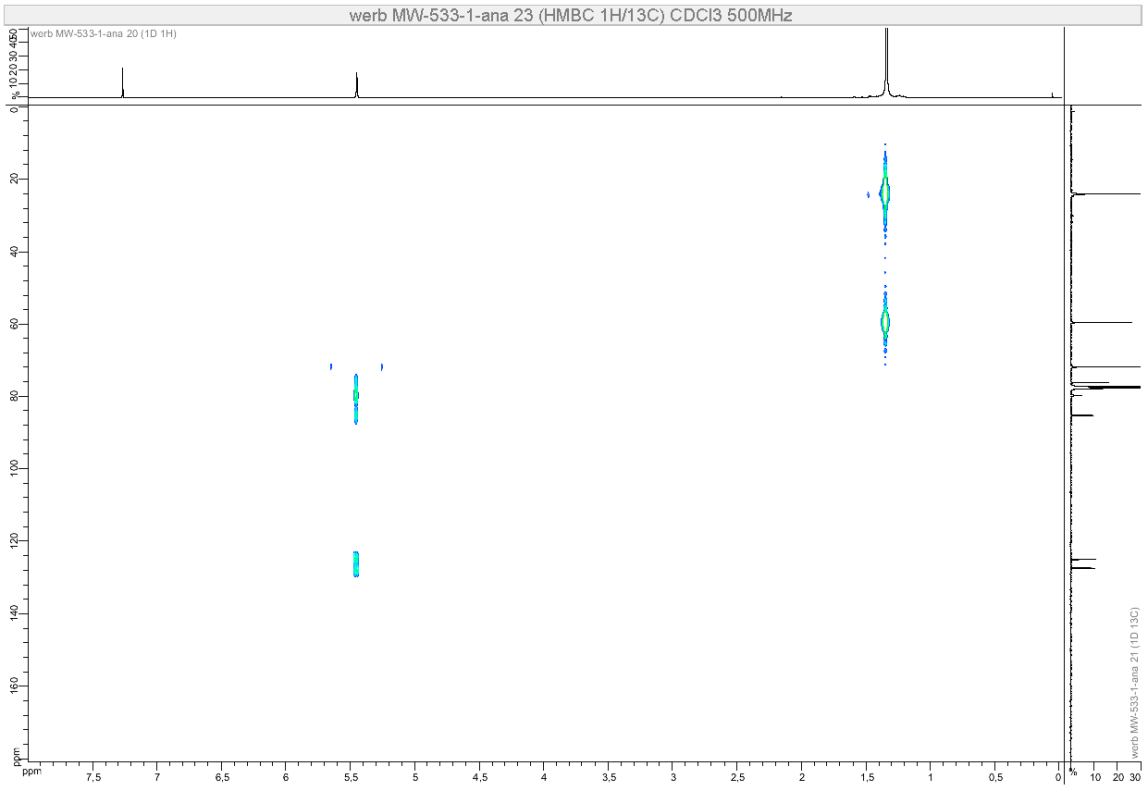
^{13}C NMR (126 MHz, $CDCl_3$)



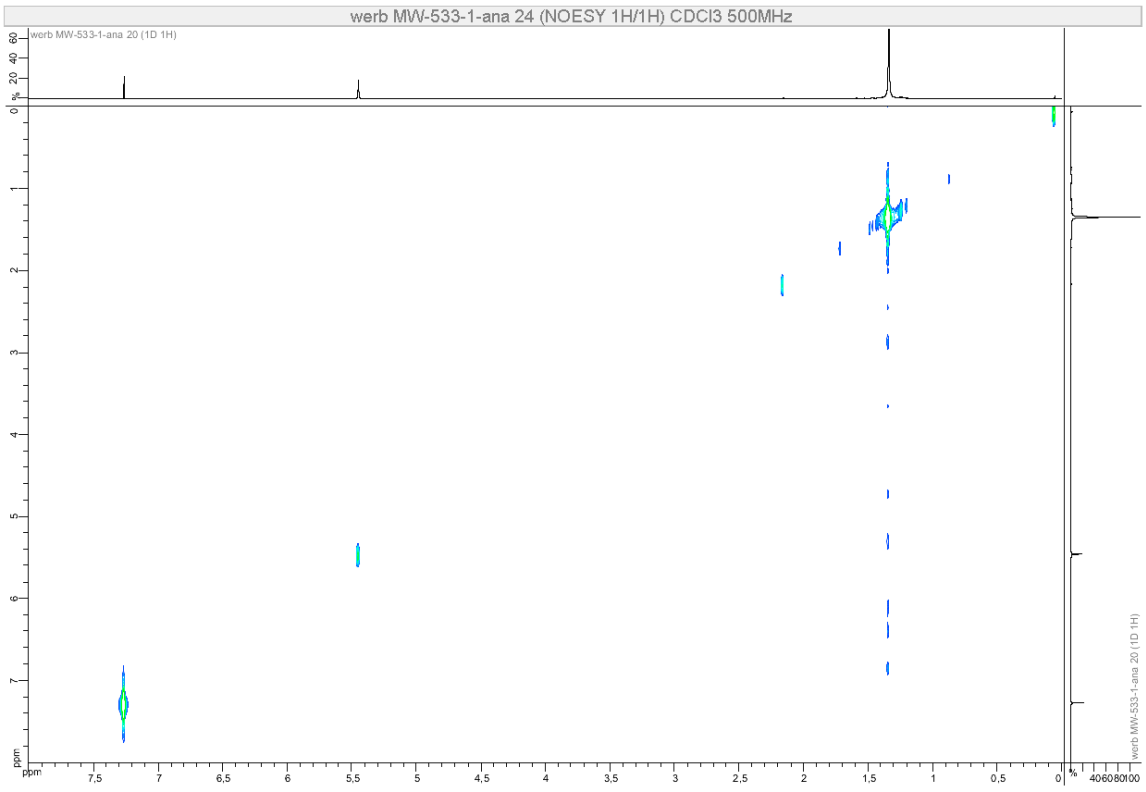
HSQC (500 MHz, $CDCl_3$)



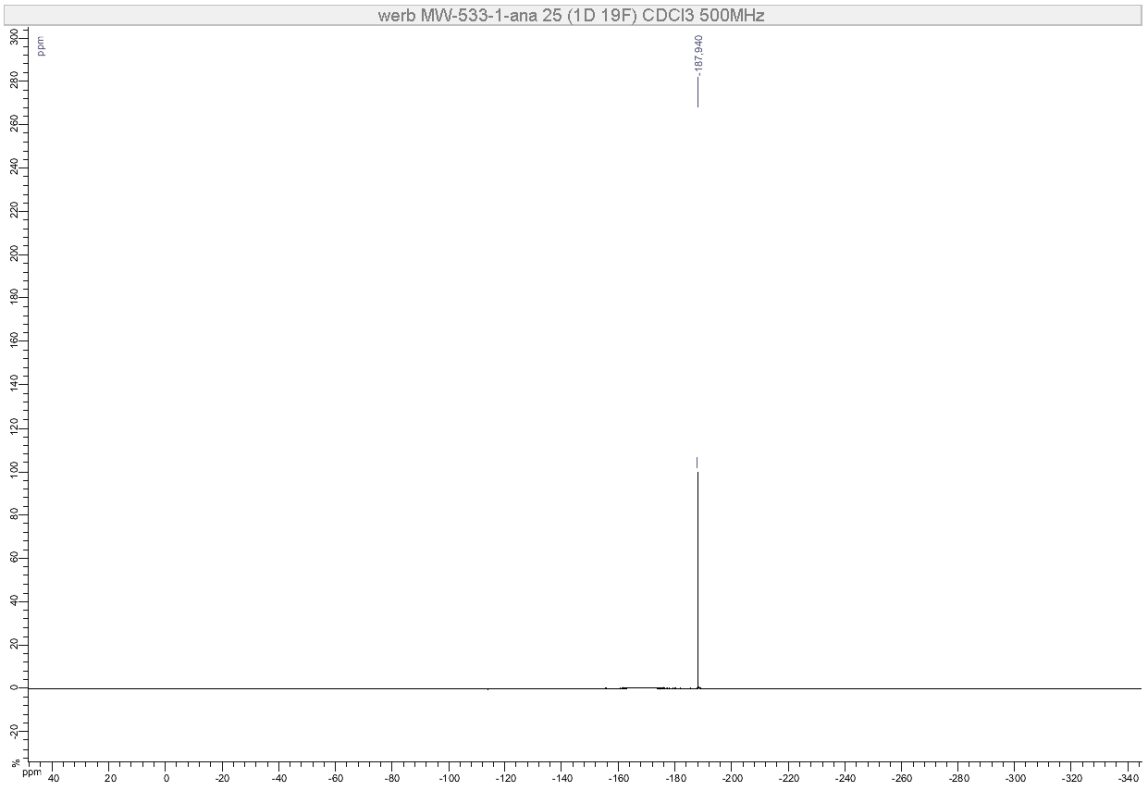
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

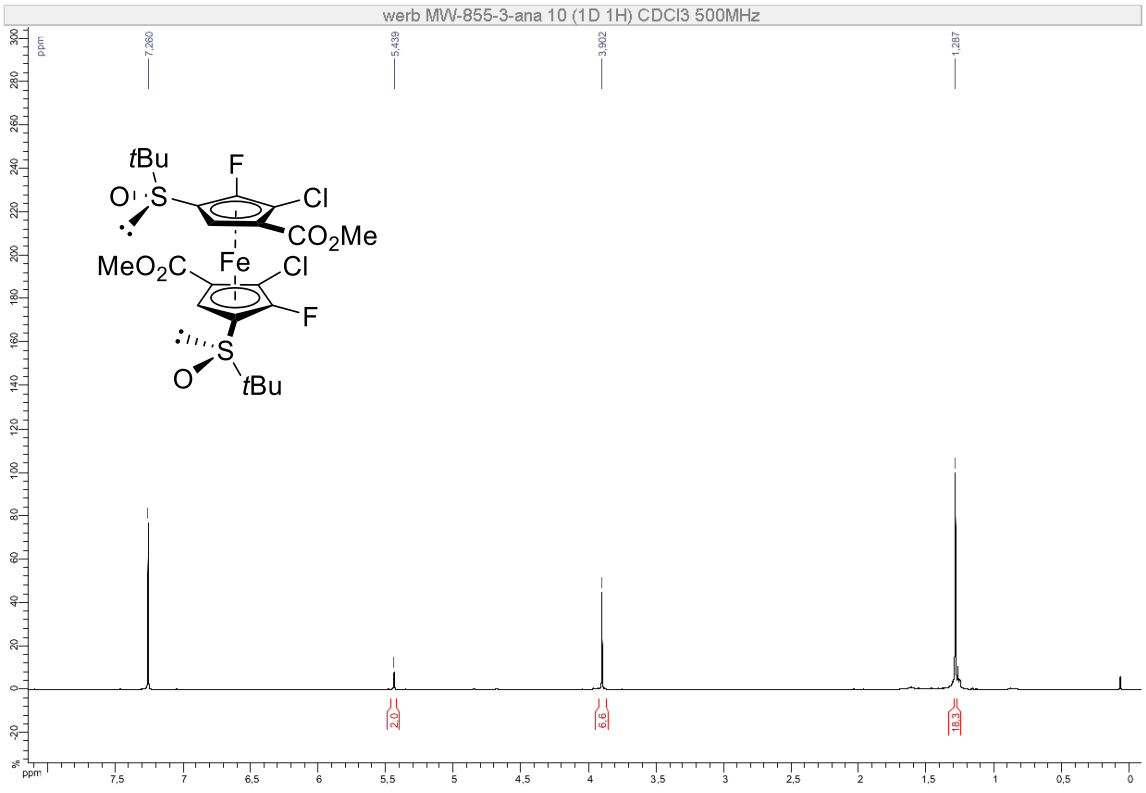


^{19}F NMR (470 MHz, $CDCl_3$)

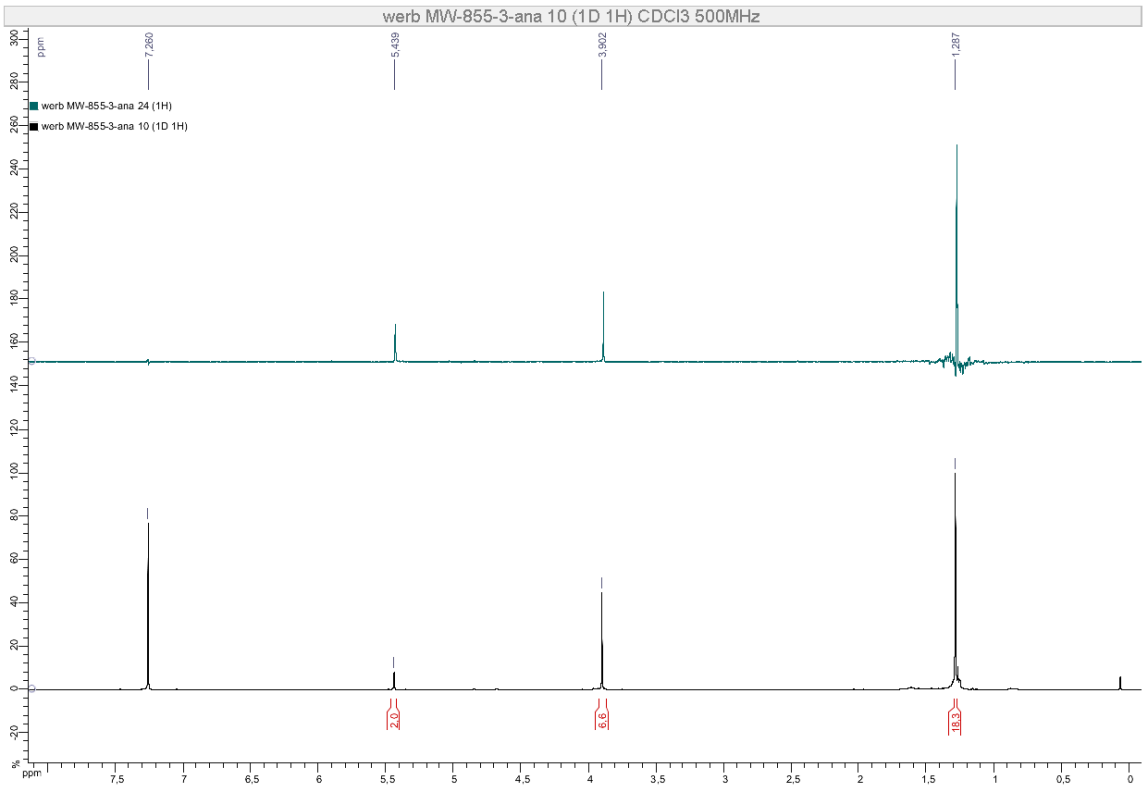


(*R*,*R*,*S*P,*S*P)-*S*,*S*'-Di-*tert*-butyl-3,3'-dichloro-2,2'-difluoro-4,4'-di(methoxycarbonyl)ferrocene-1,1'-disulfoxide (*S*P,*S*P-9b)

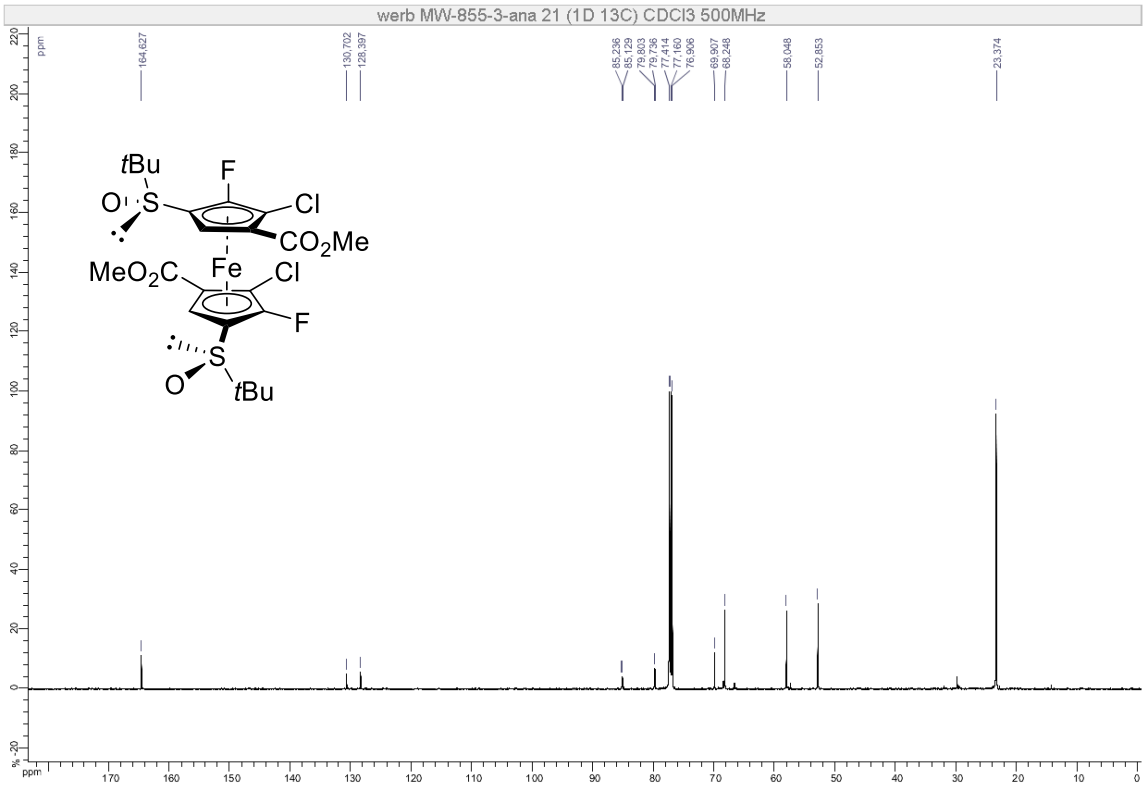
^{1}H NMR (500 MHz, $CDCl_3$)



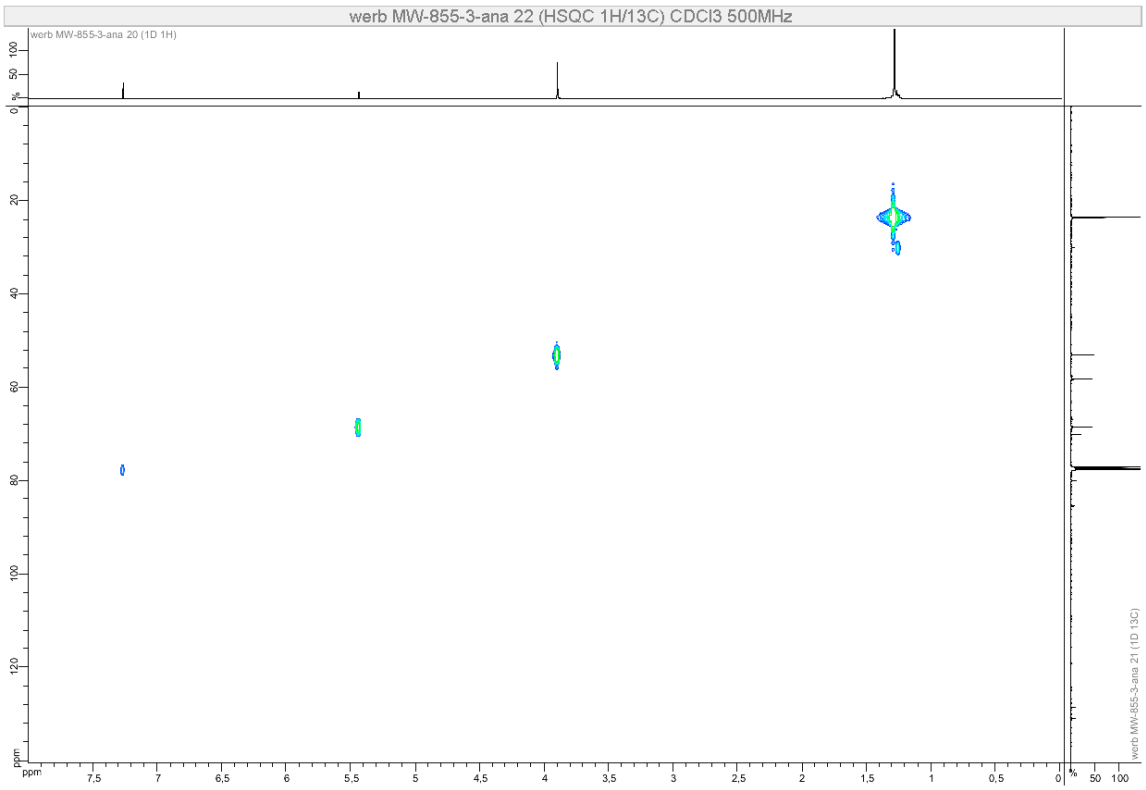
HOESY (500 MHz, $CDCl_3$) Irradiation at -181.5 ppm – Superposition of ^{1}H (bottom) and HOESY (top) spectra.



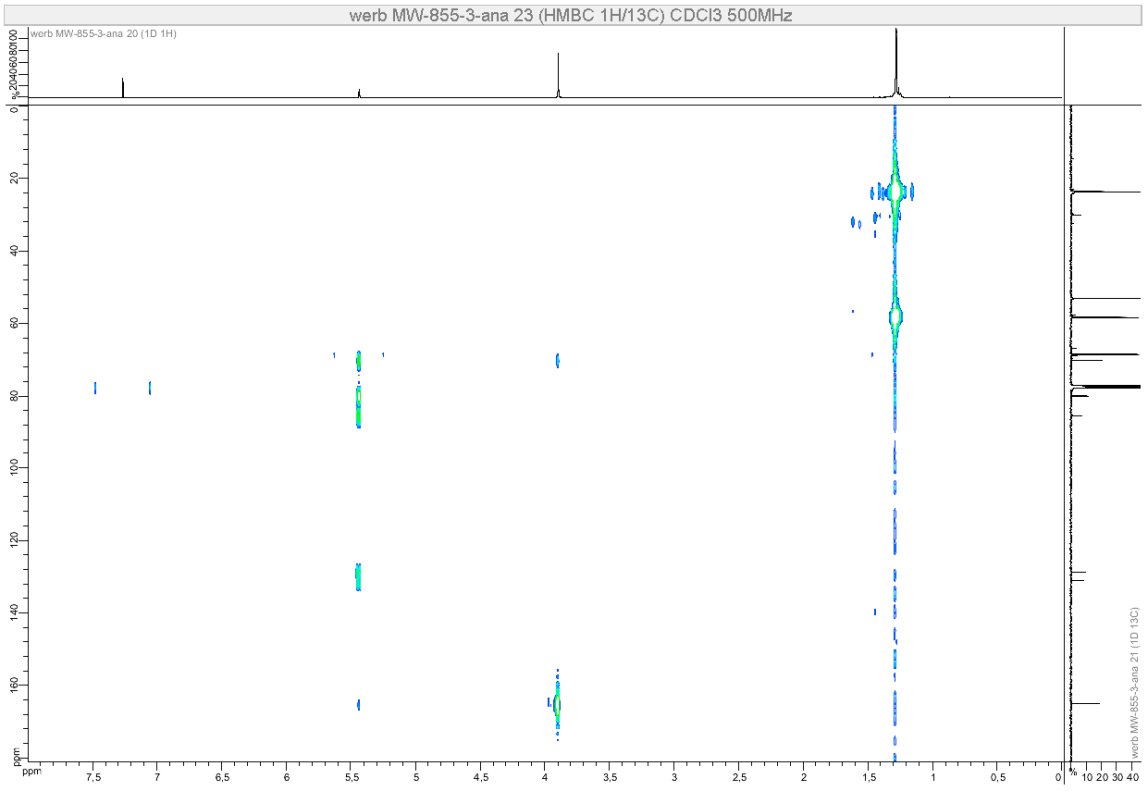
^{13}C NMR (126 MHz, $CDCl_3$)



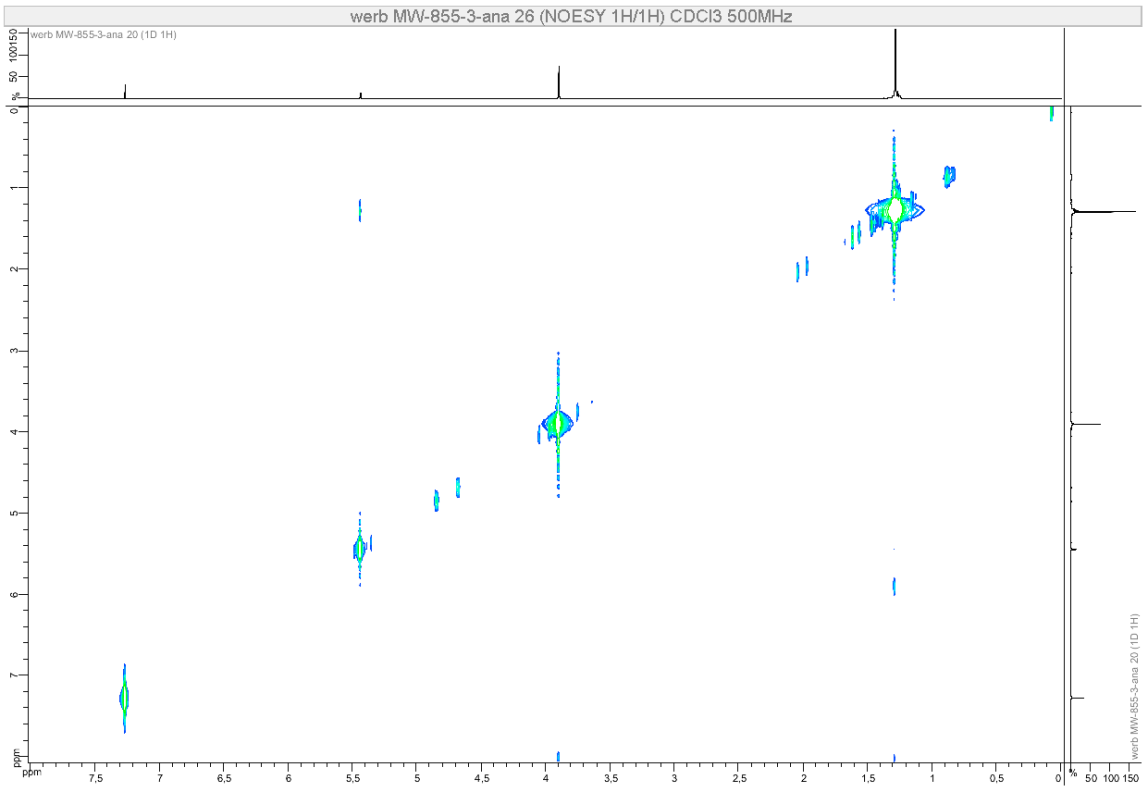
HSQC (500 MHz, $CDCl_3$)



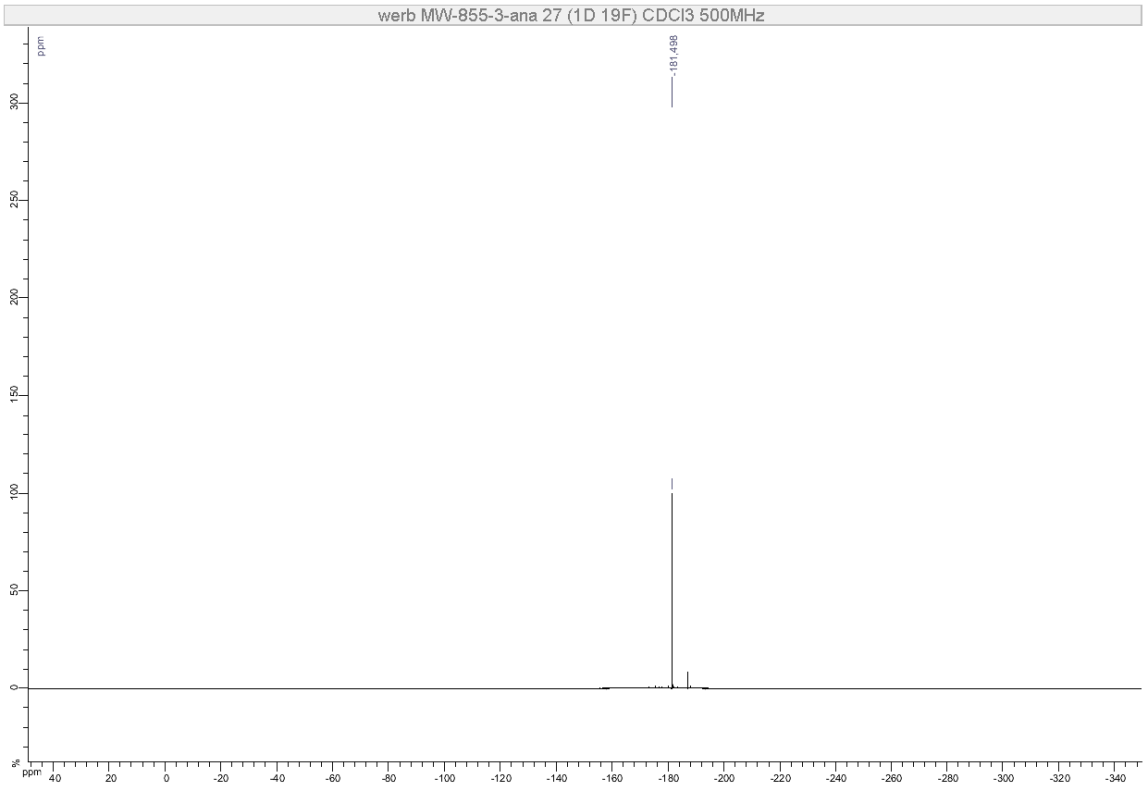
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

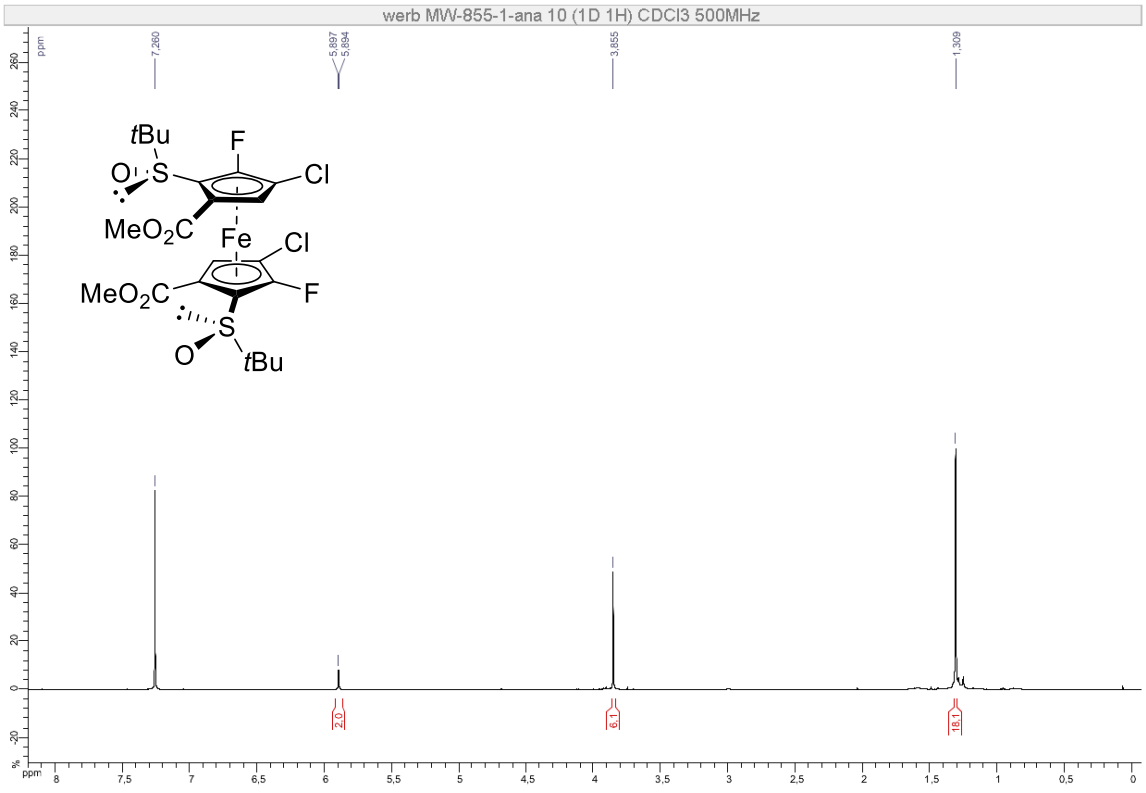


^{19}F NMR (470 MHz, $CDCl_3$)

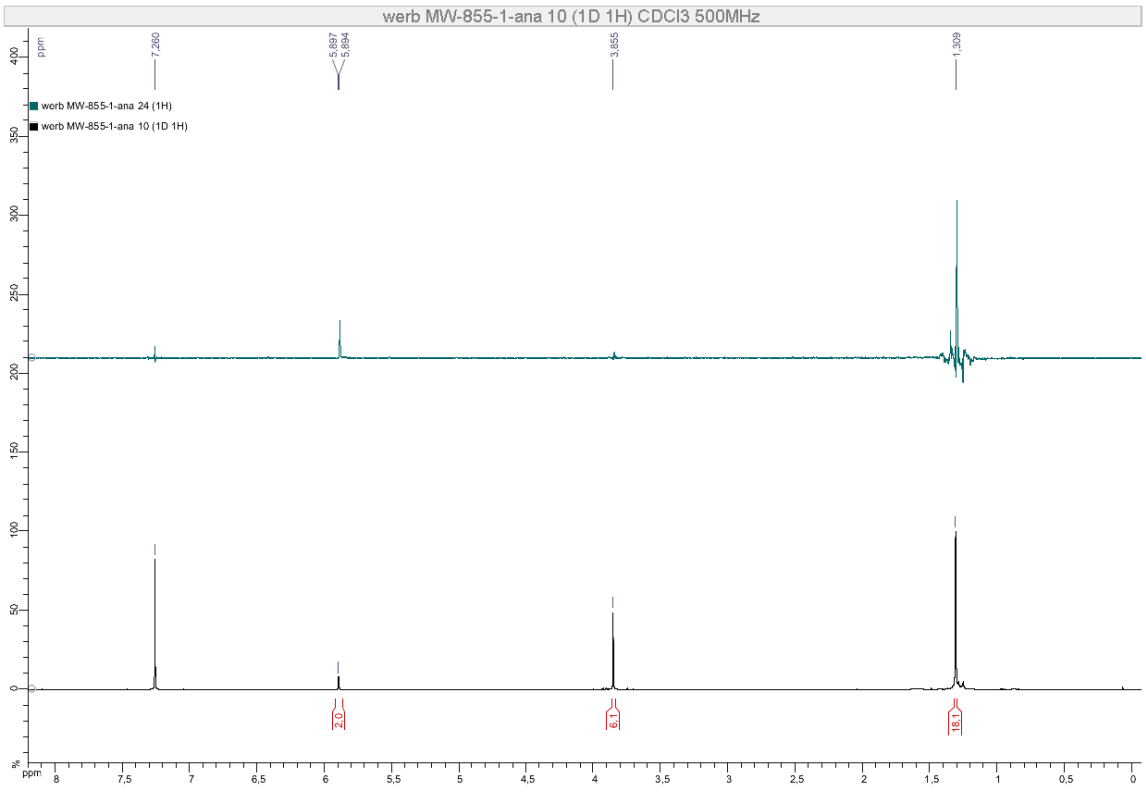


(*R*,*R*,*S*P,*S*P)-*S*,*S*'-Di-*tert*-butyl-3,3'-dichloro-2,2'-difluoroferrocene-5,5'-di(methoxycarbonyl)-1,1'-disulfoxide (*S*P,*S*P-9'b)

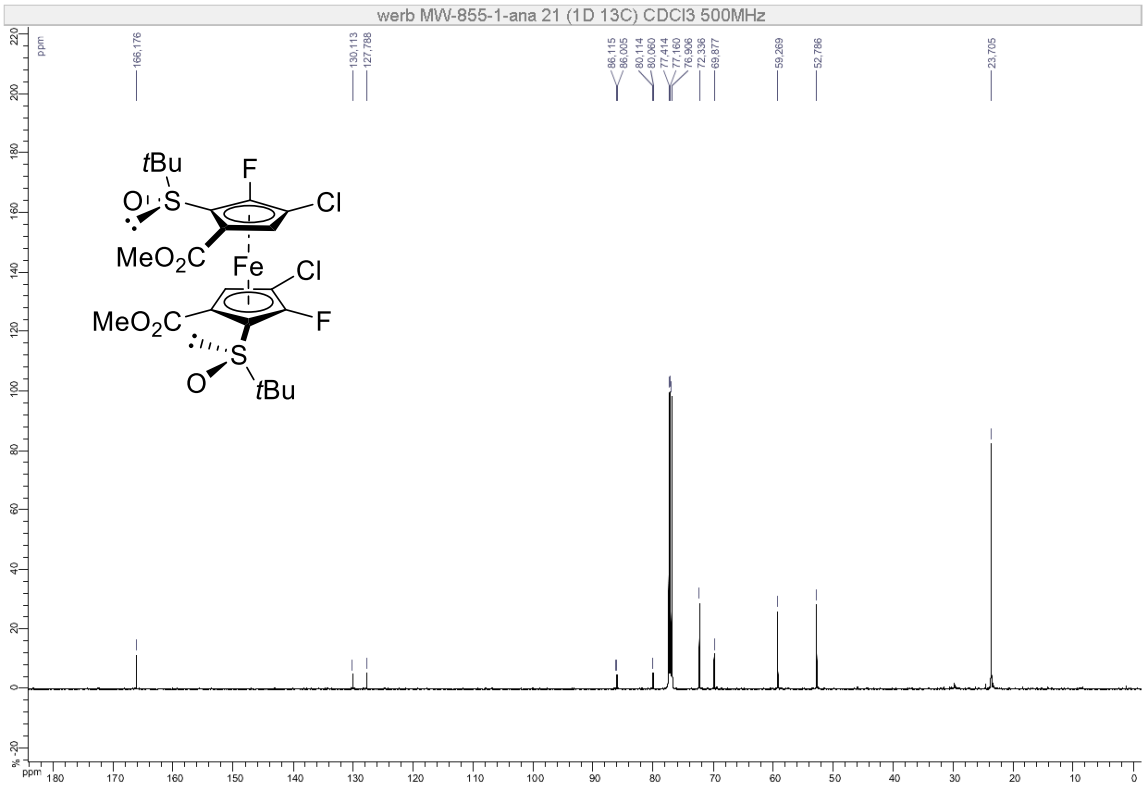
^{1}H NMR (500 MHz, $CDCl_3$)



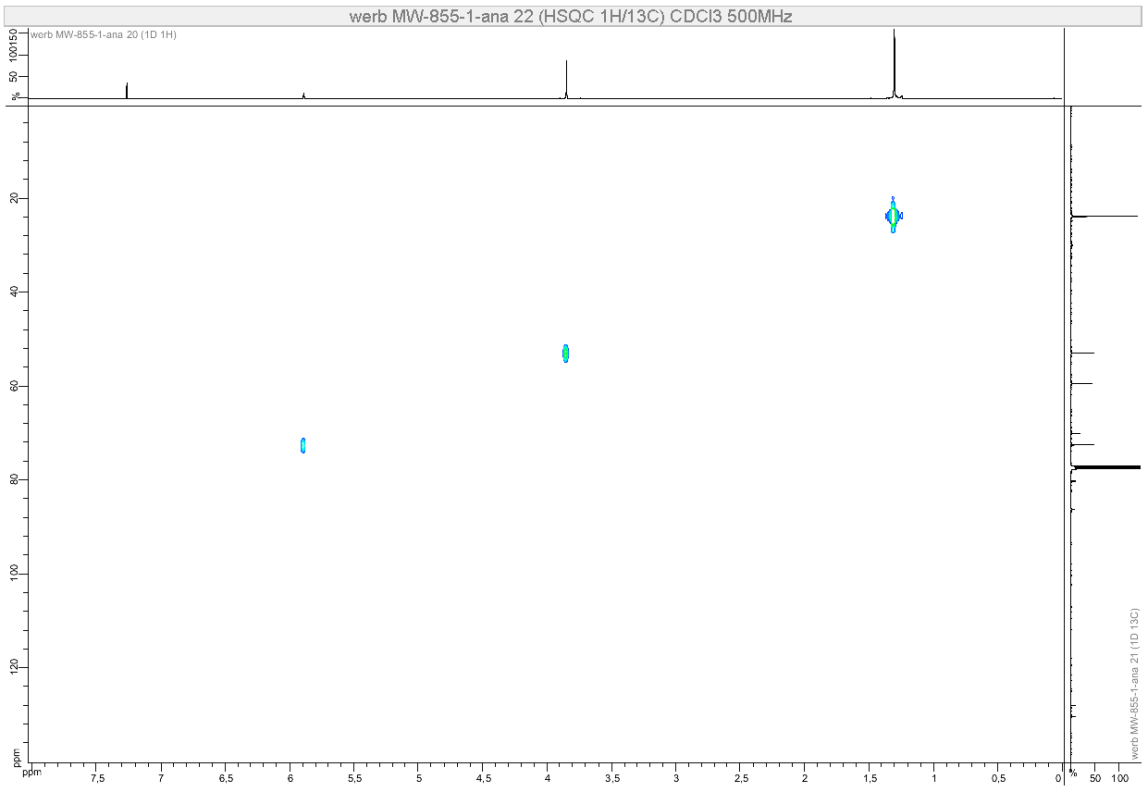
HOESY (500 MHz, $CDCl_3$) Irradiation at -182.4 ppm – Superposition of ^{1}H (bottom) and HOESY (top) spectra.



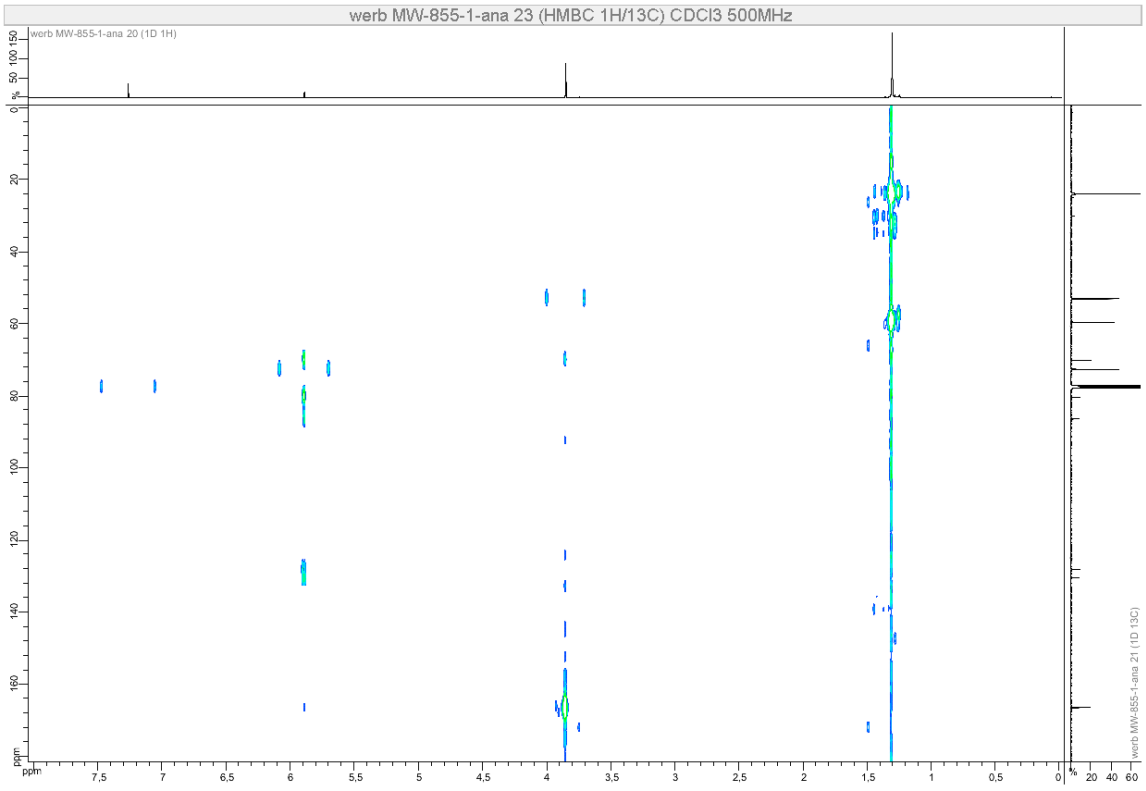
^{13}C NMR (126 MHz, $CDCl_3$)



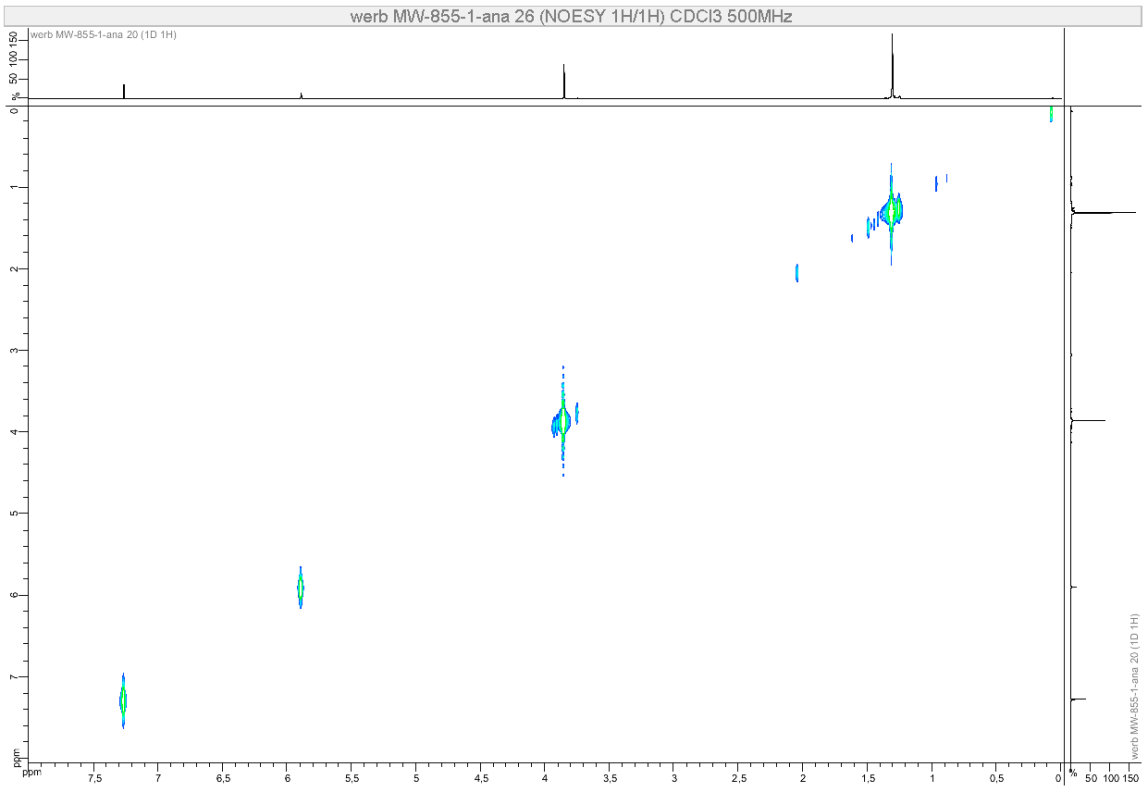
HSQC (500 MHz, $CDCl_3$)



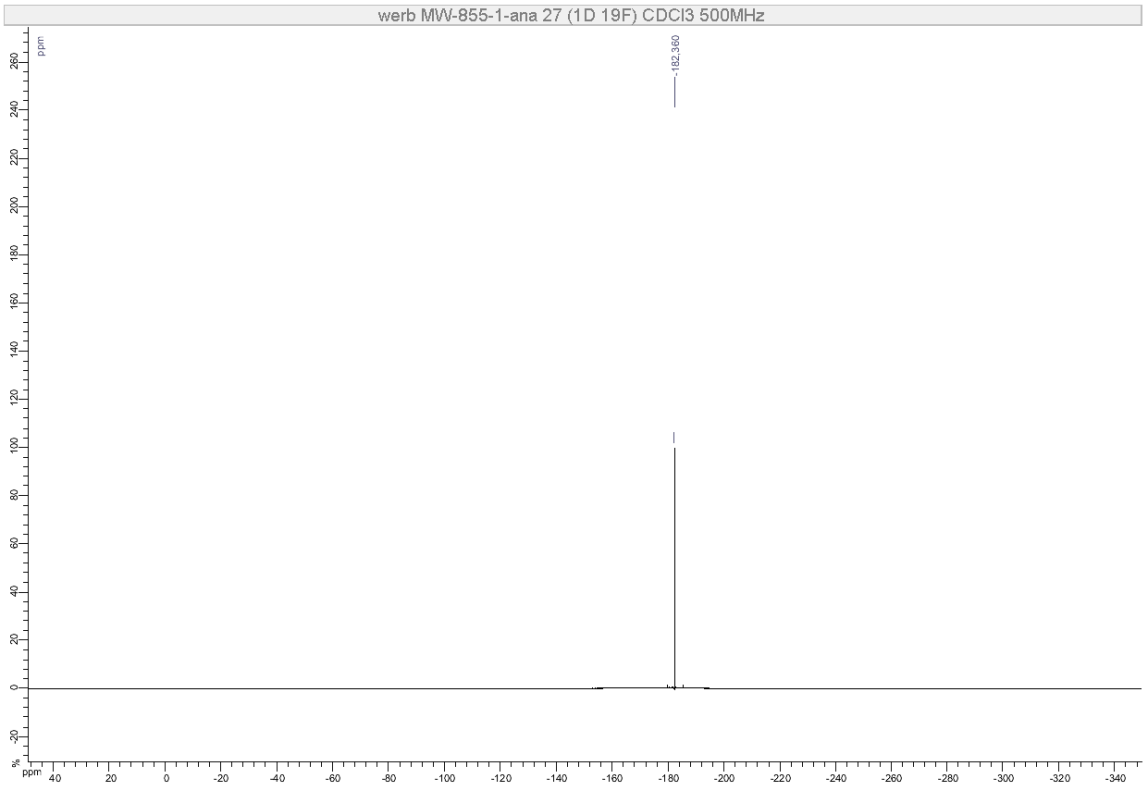
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

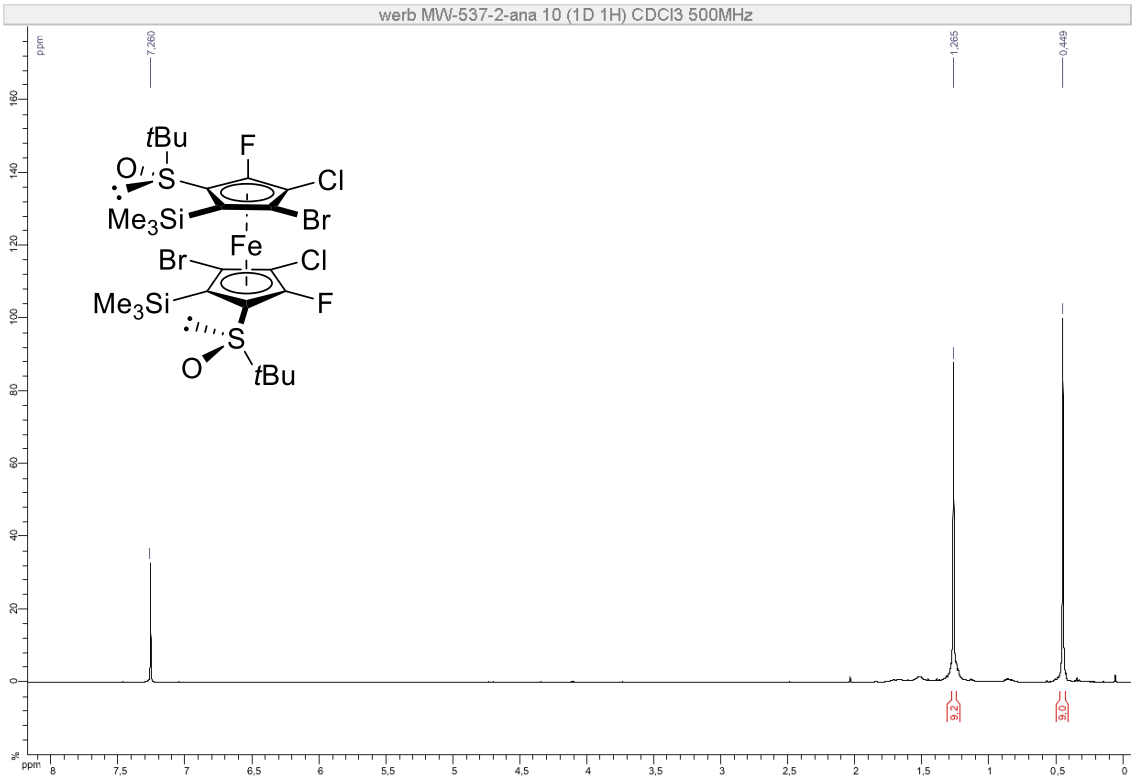


^{19}F NMR (470 MHz, $CDCl_3$)

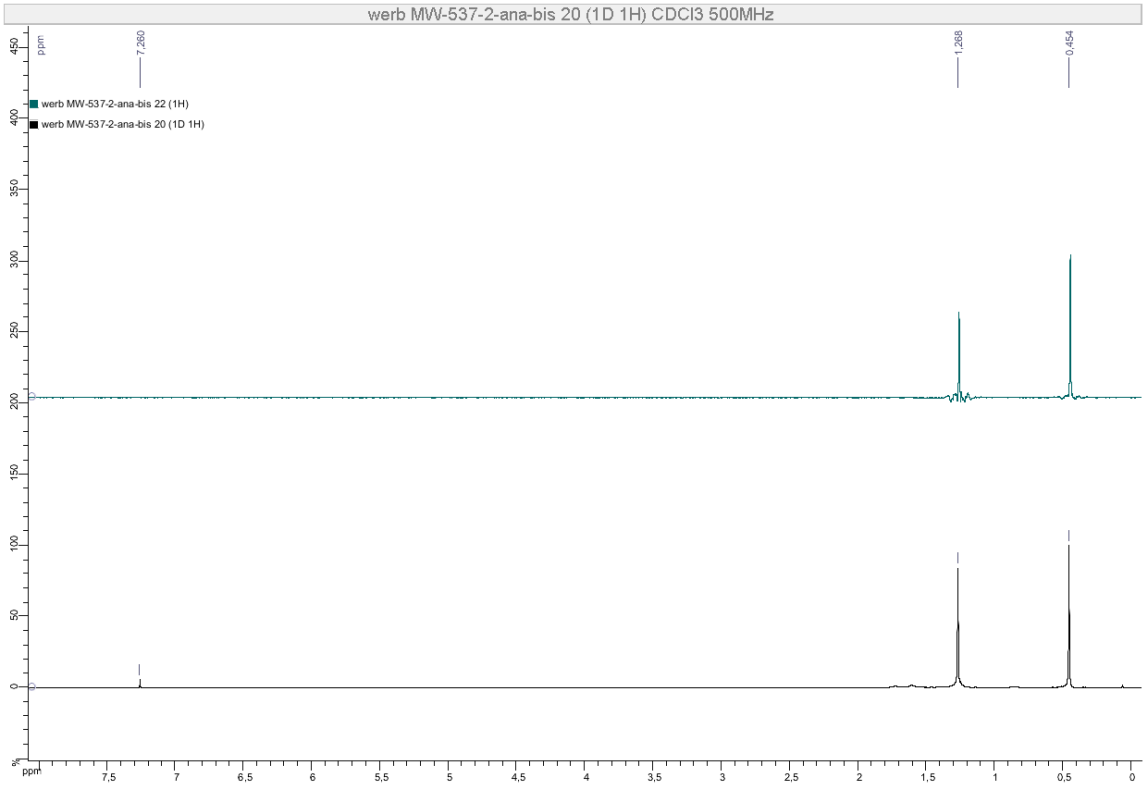


(*R*,*R*,*S*P,*S*P)-3,3'-Dibromo-*S*,*S*'-di-*tert*-butyl-4,4'-dichloro-5,5'-difluoro-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*S*P,*S*P-10a)

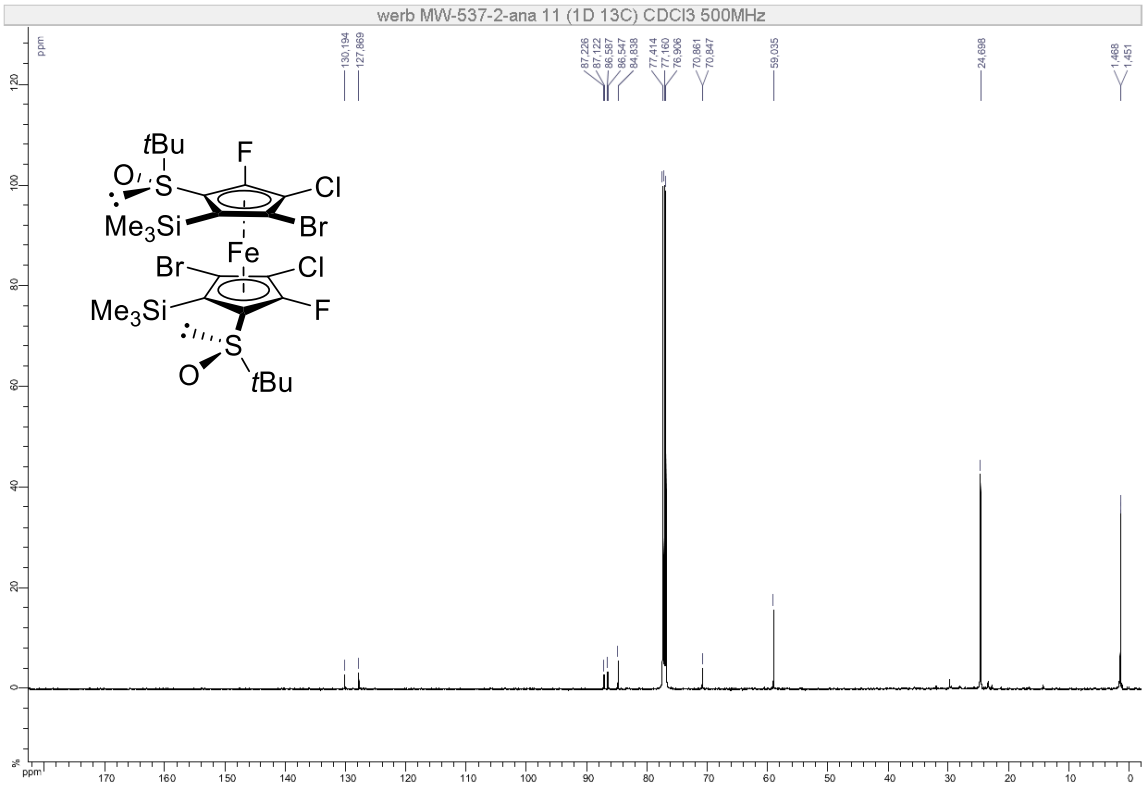
^{1}H NMR (500 MHz, $CDCl_3$)



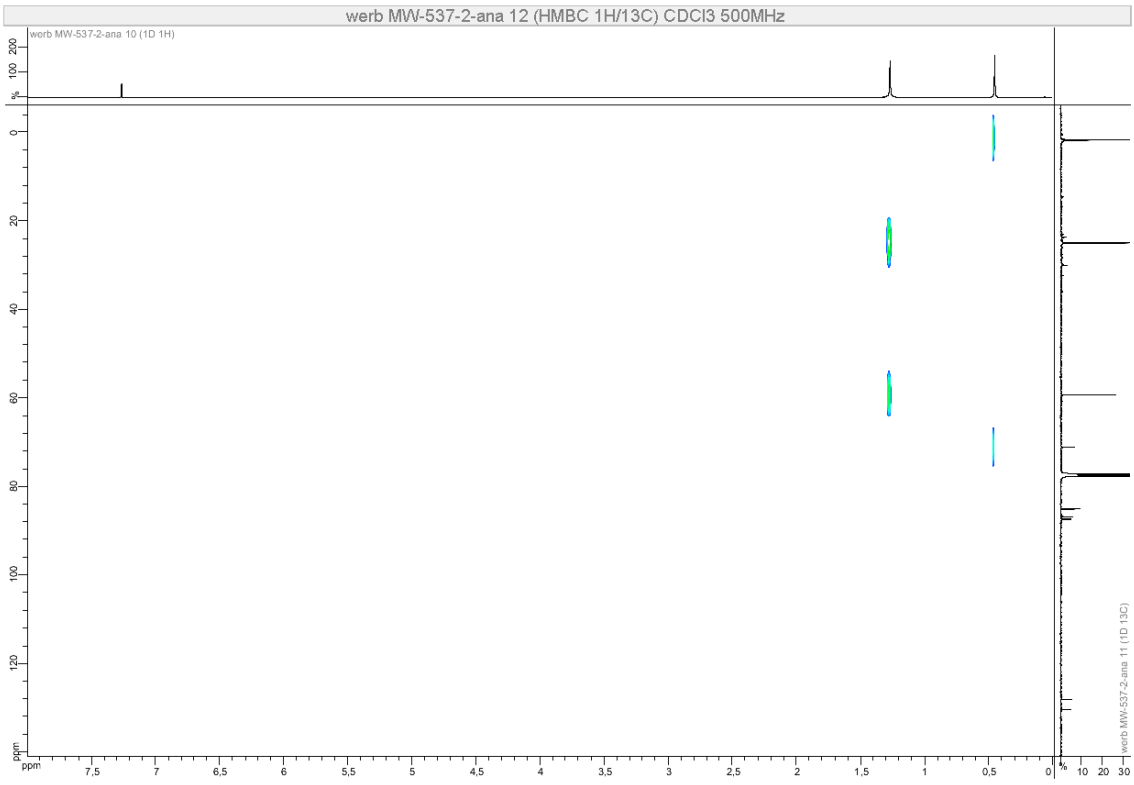
HOESY (500 MHz, $CDCl_3$) Irradiation at -173.4 ppm – Superposition of ^{1}H (bottom) and HOESY (top) spectra.



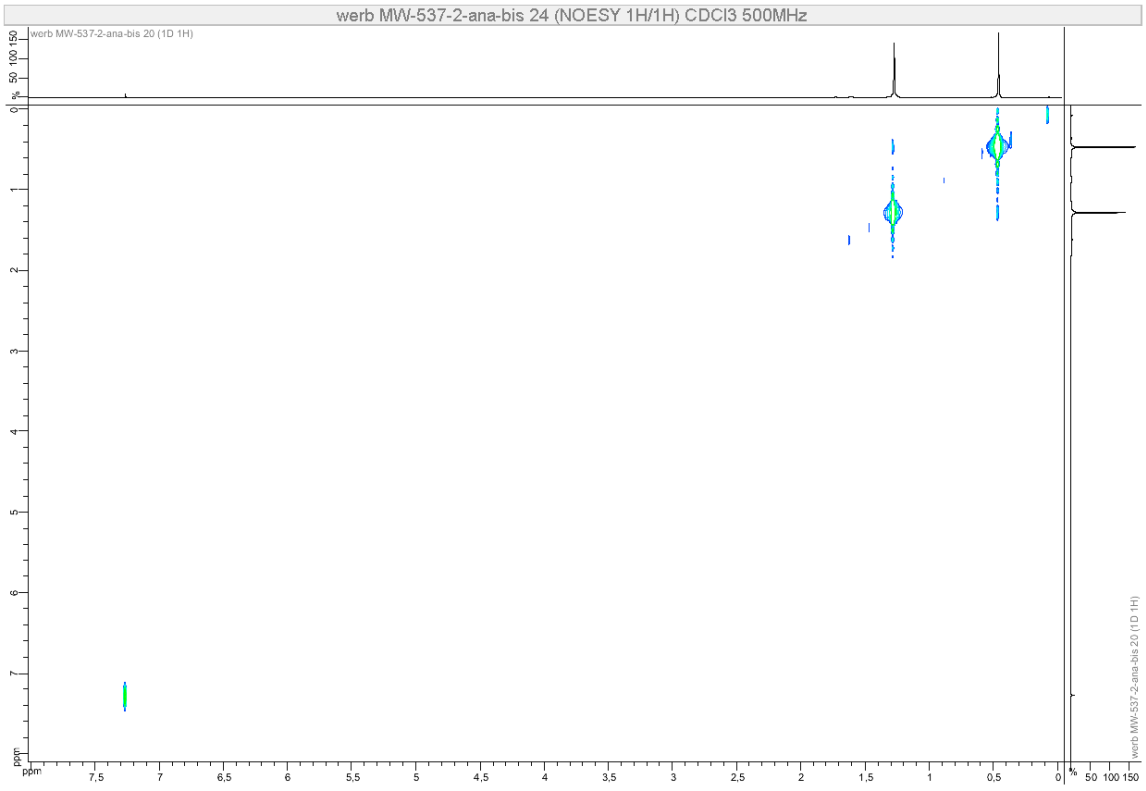
^{13}C NMR (126 MHz, $CDCl_3$)



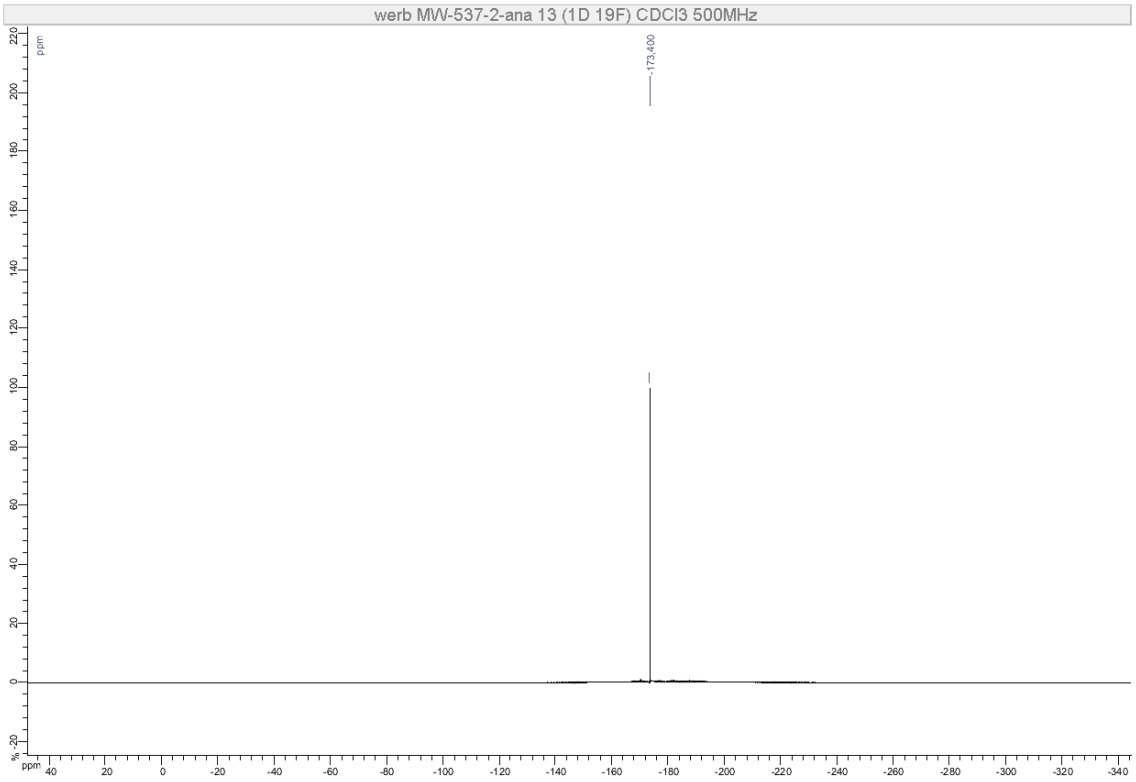
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

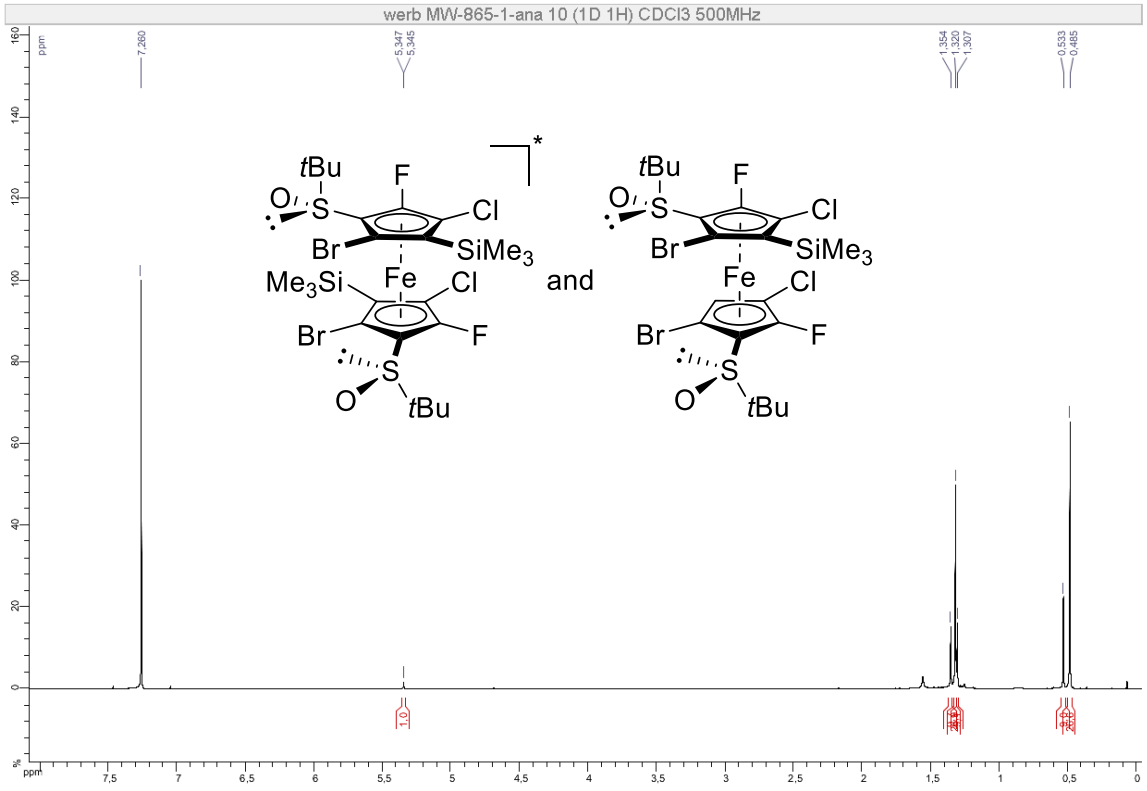


^{19}F NMR (470 MHz, $CDCl_3$)

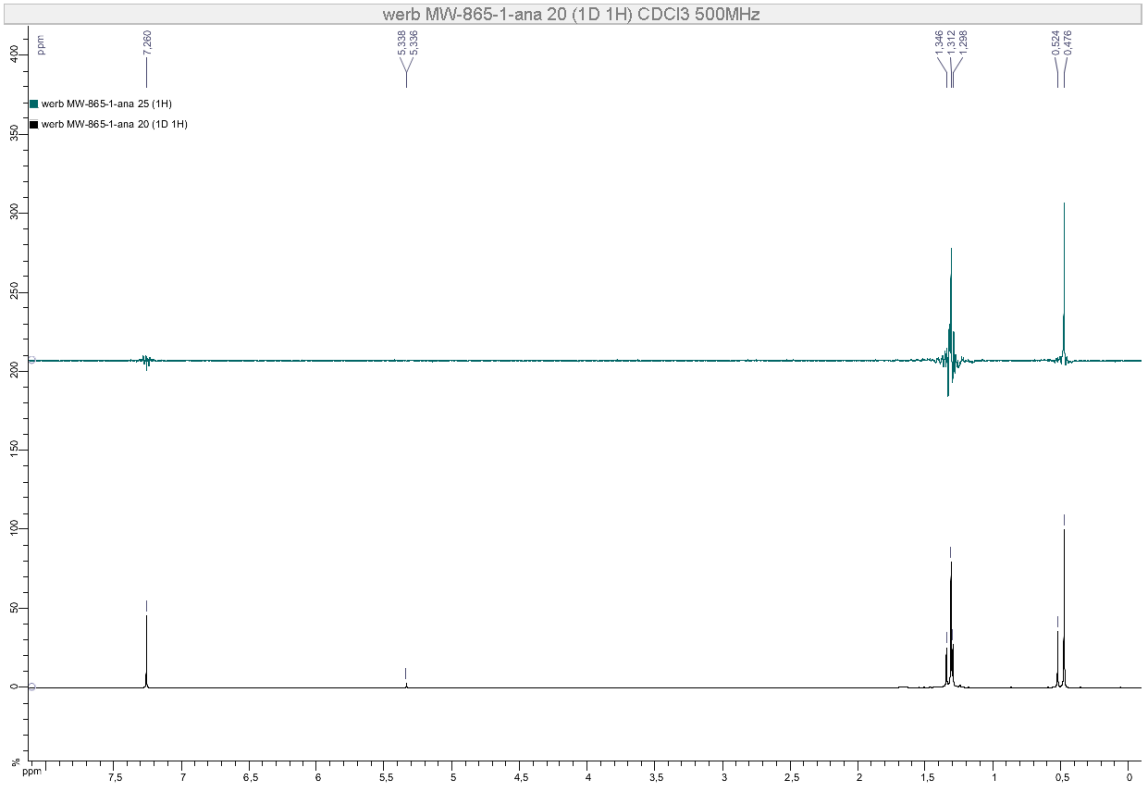


Mixture of (*R*,*R*,*S*P,*S*P)-2,2'-dibromo-*S*,*S*'-di-*tert*-butyl-4,4'-dichloro-5,5'-difluoro-3,3'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*S*P,*S*P-10'a), signals indicated by *, and (*R*,*R*,*S*P,*S*P)-2,5'-dibromo-*S*,*S*'-di-*tert*-butyl-4,3'-dichloro-5,2'-difluoro-3-(trimethylsilyl)ferrocene-1,1'-disulfoxide (*S*P,*S*P-10""a)

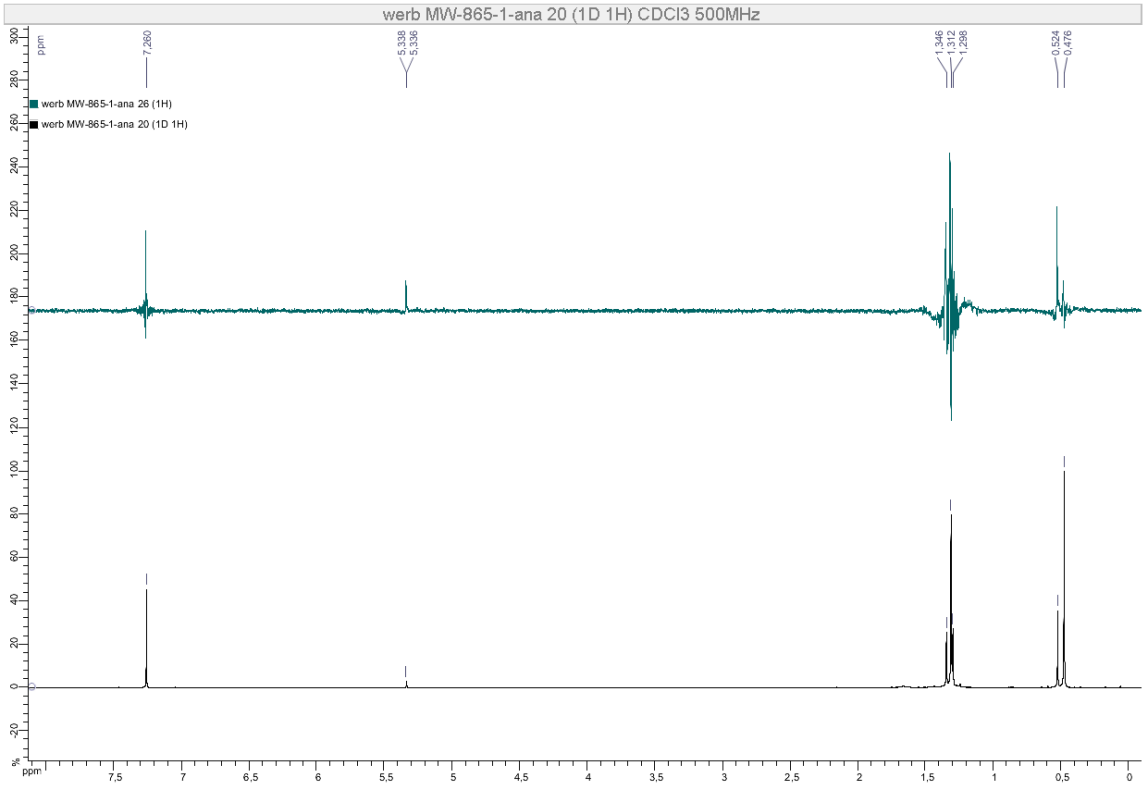
^{1}H NMR (500 MHz, $CDCl_3$)



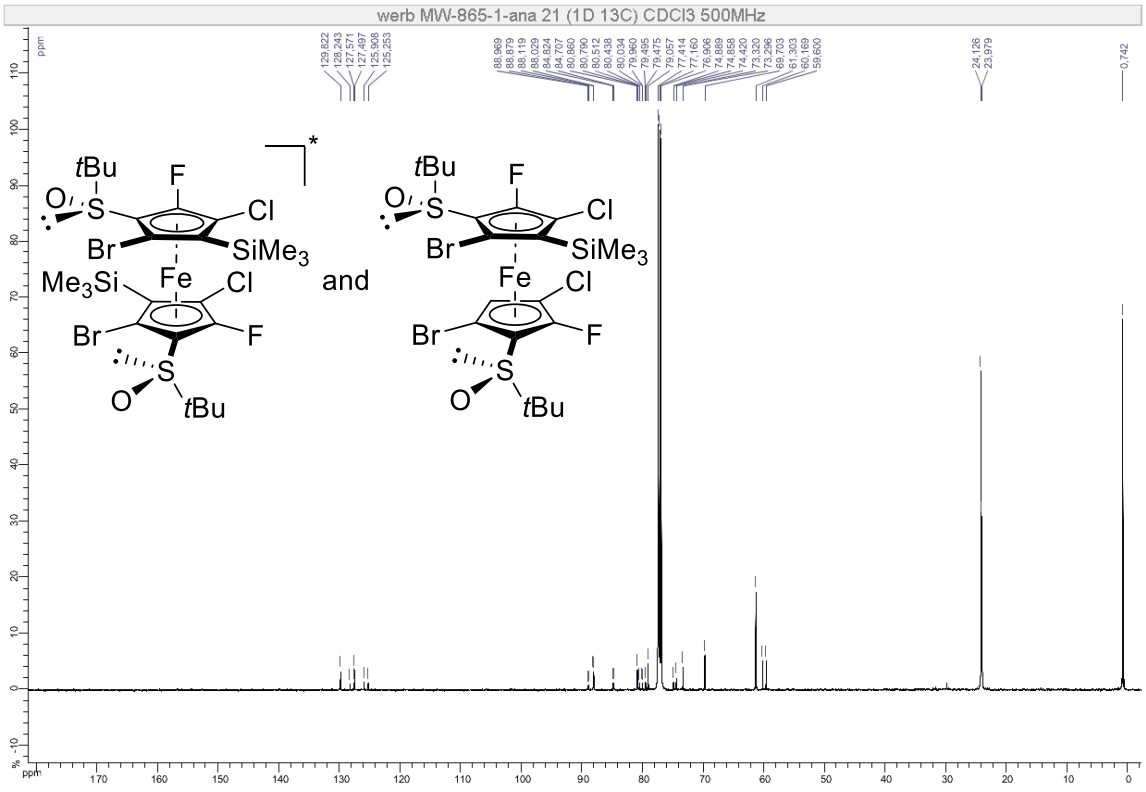
HOESY (500 MHz, $CDCl_3$) Irradiation at -180.0 ppm – Superposition of ^{1}H (bottom) and HOESY (top) spectra.



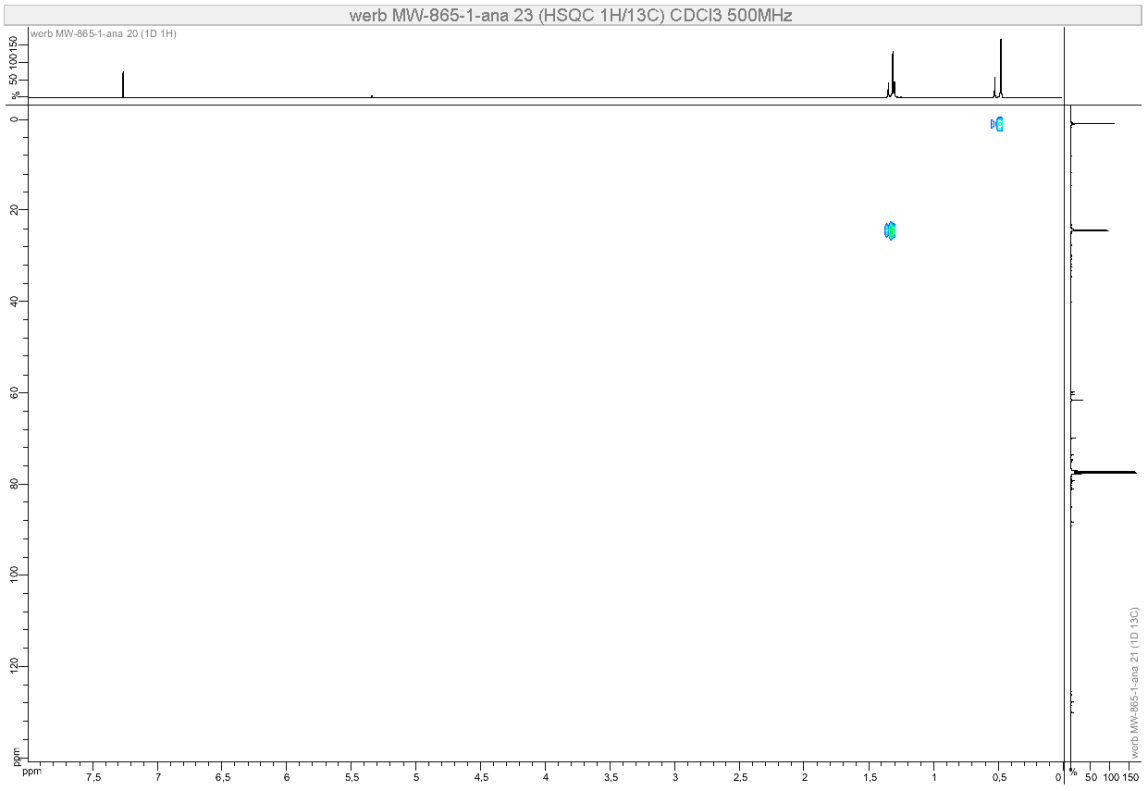
HOESY (500 MHz, $CDCl_3$) Irradiation at -184.2 ppm – Superposition of ^1H (bottom) and HOESY (top) spectra.



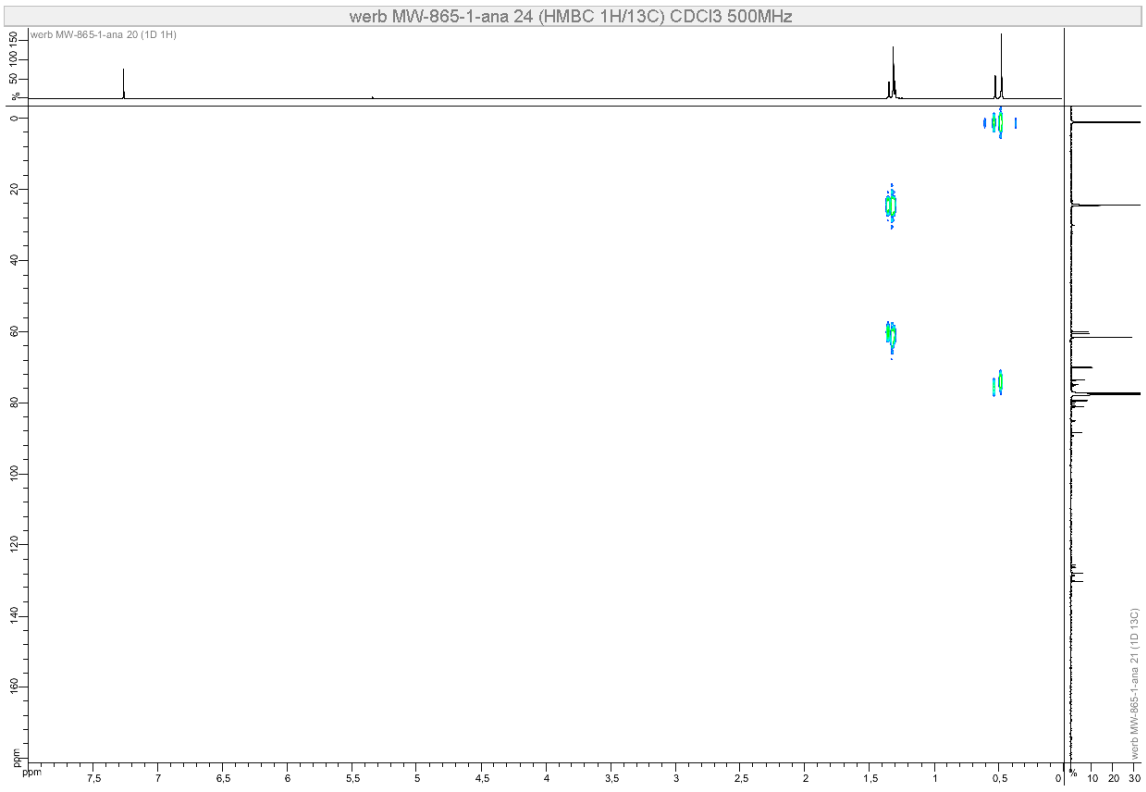
^{13}C NMR (126 MHz, $CDCl_3$)



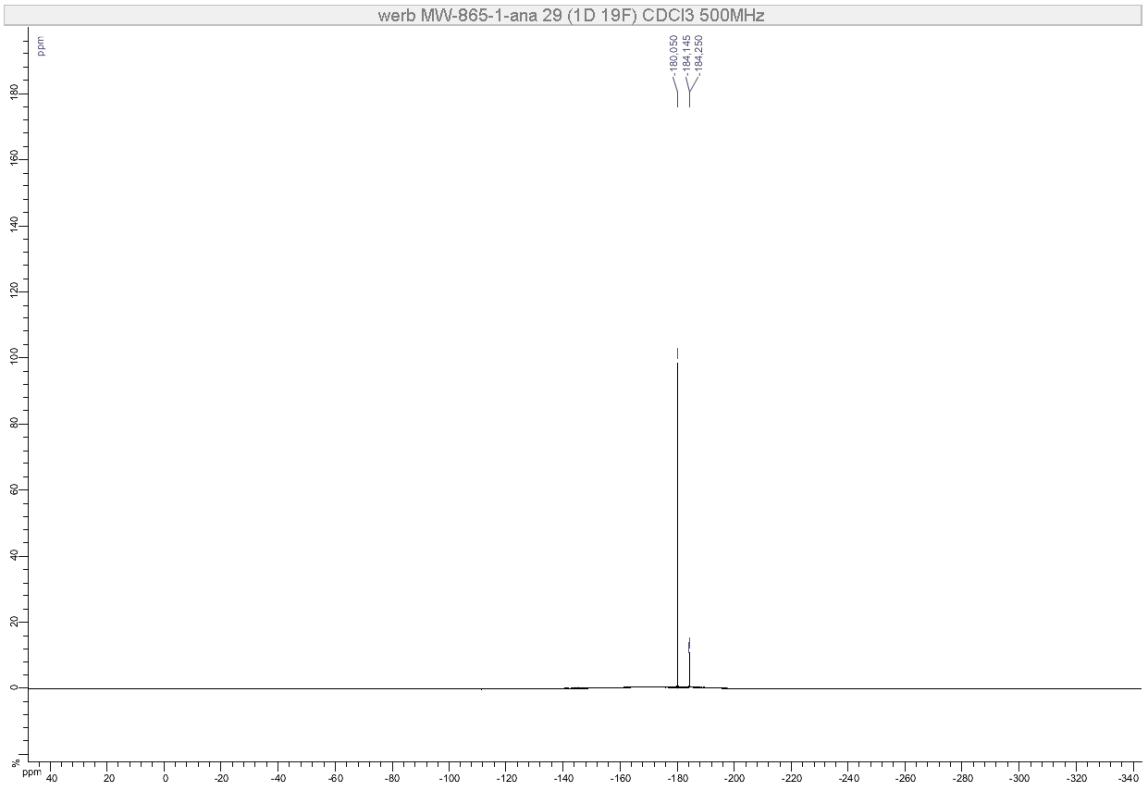
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

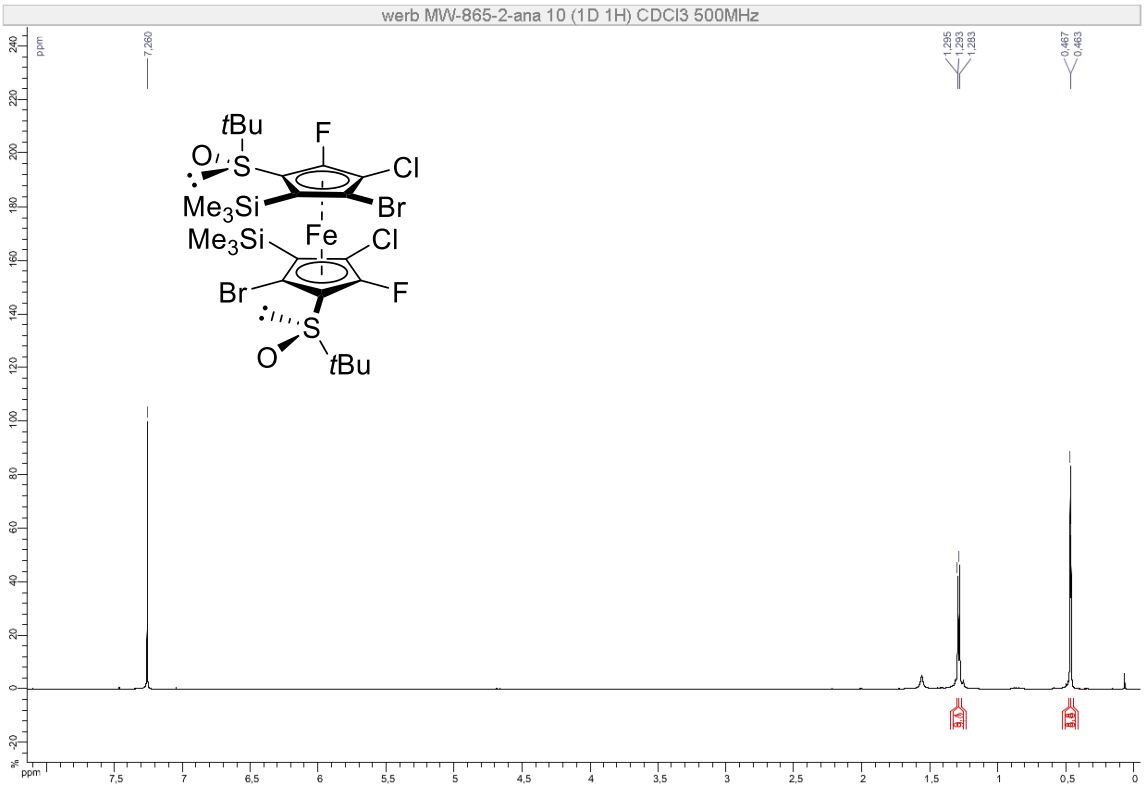


^{19}F NMR (470 MHz, $CDCl_3$)

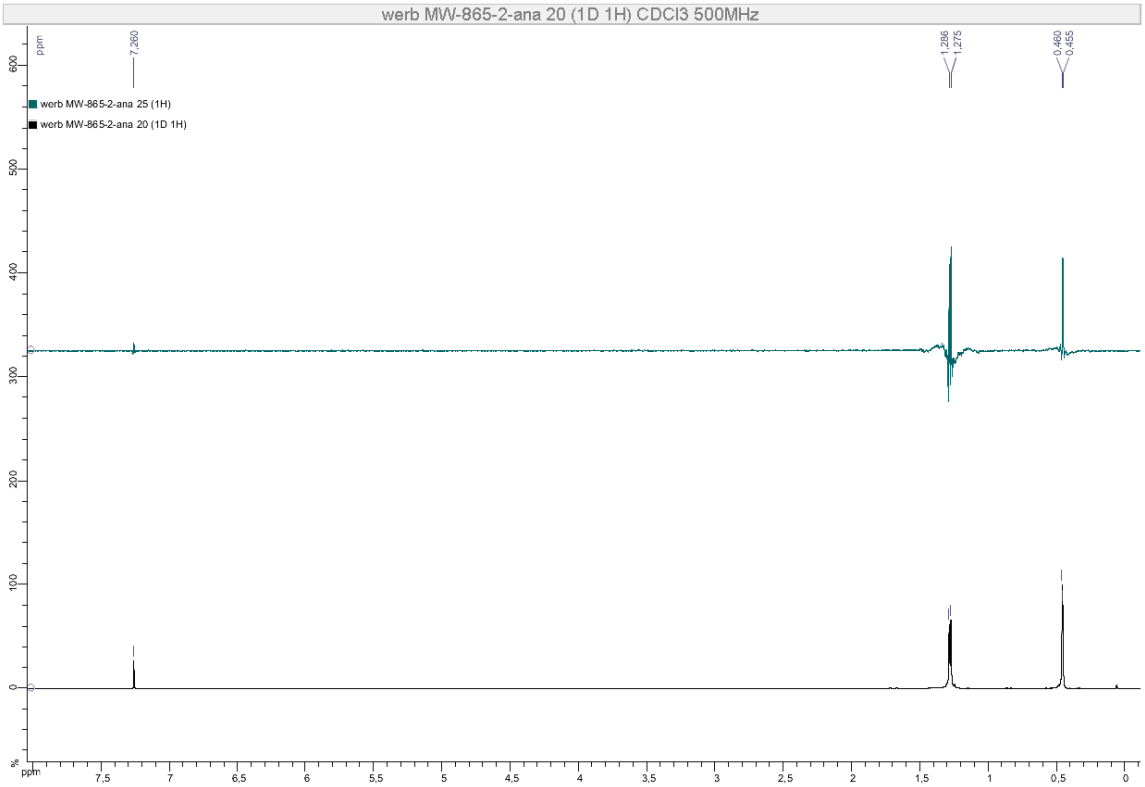


(*R*,*R*,*S*P,*S*P)-3,2'-Dibromo-*S*,*S*'-di-*tert*-butyl-4,4'-dichloro-5,5'-difluoro-2,3'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*S*P,*S*P-10"a)

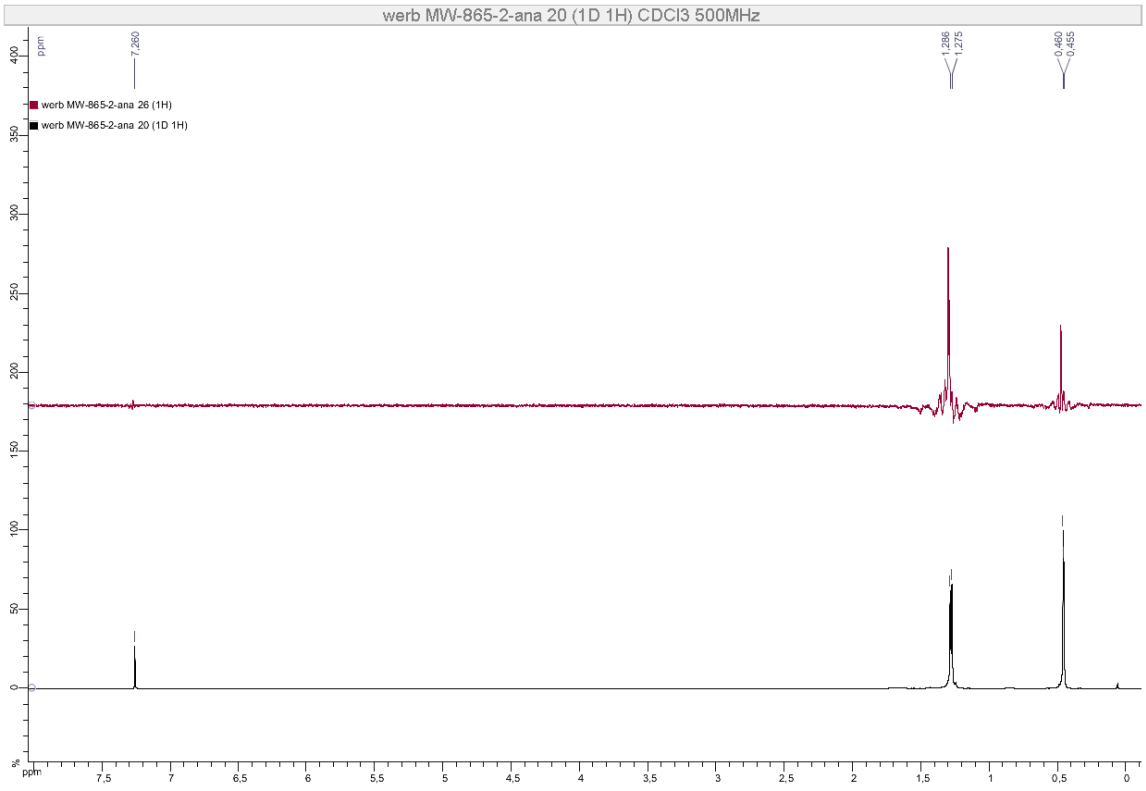
^{1}H NMR (500 MHz, $CDCl_3$)



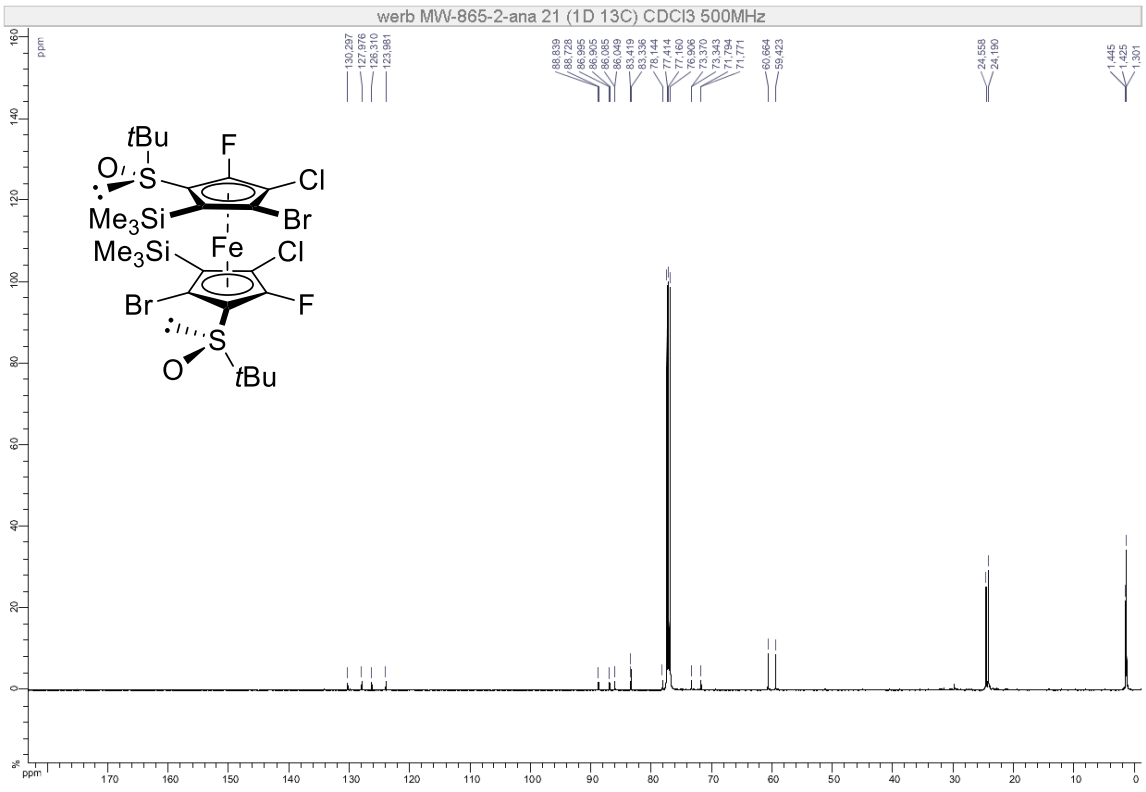
HOESY (500 MHz, $CDCl_3$) Irradiation at -176.8 ppm – Superposition of ^{1}H (bottom) and HOESY (top) spectra.



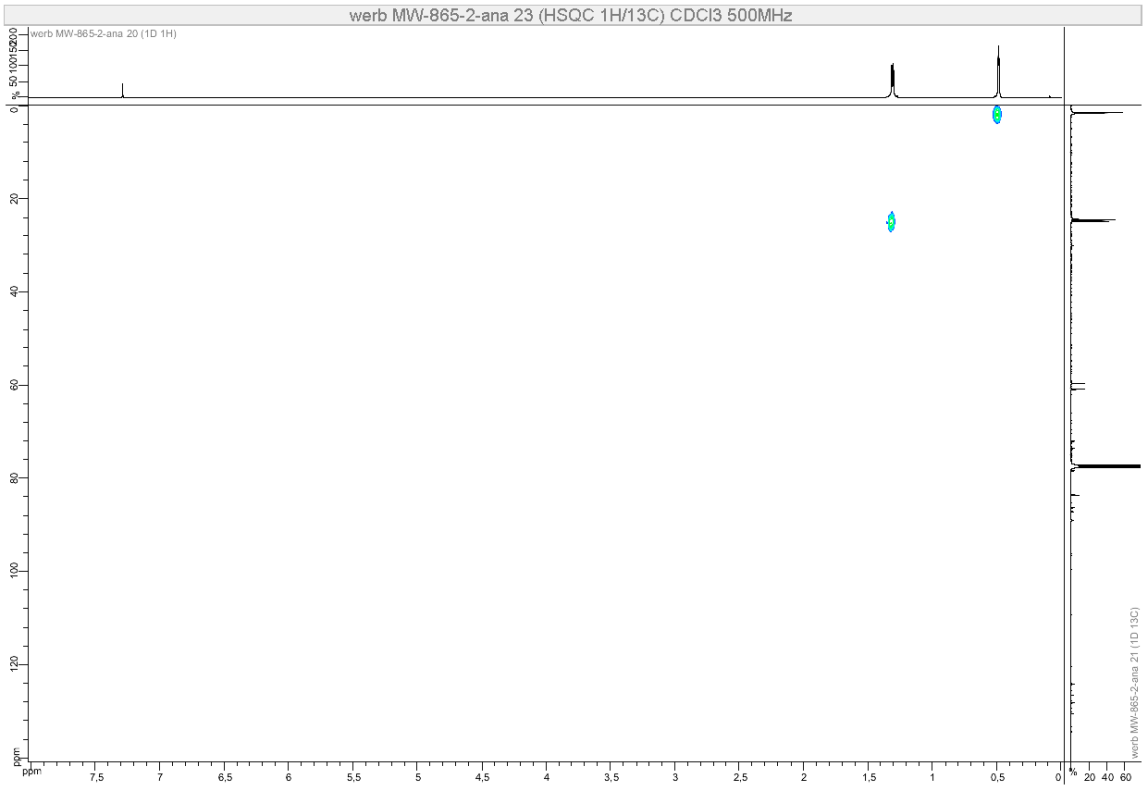
HOESY (500 MHz, $CDCl_3$) Irradiation at -181.1 ppm – Superposition of ^1H (bottom) and HOESY (top) spectra.



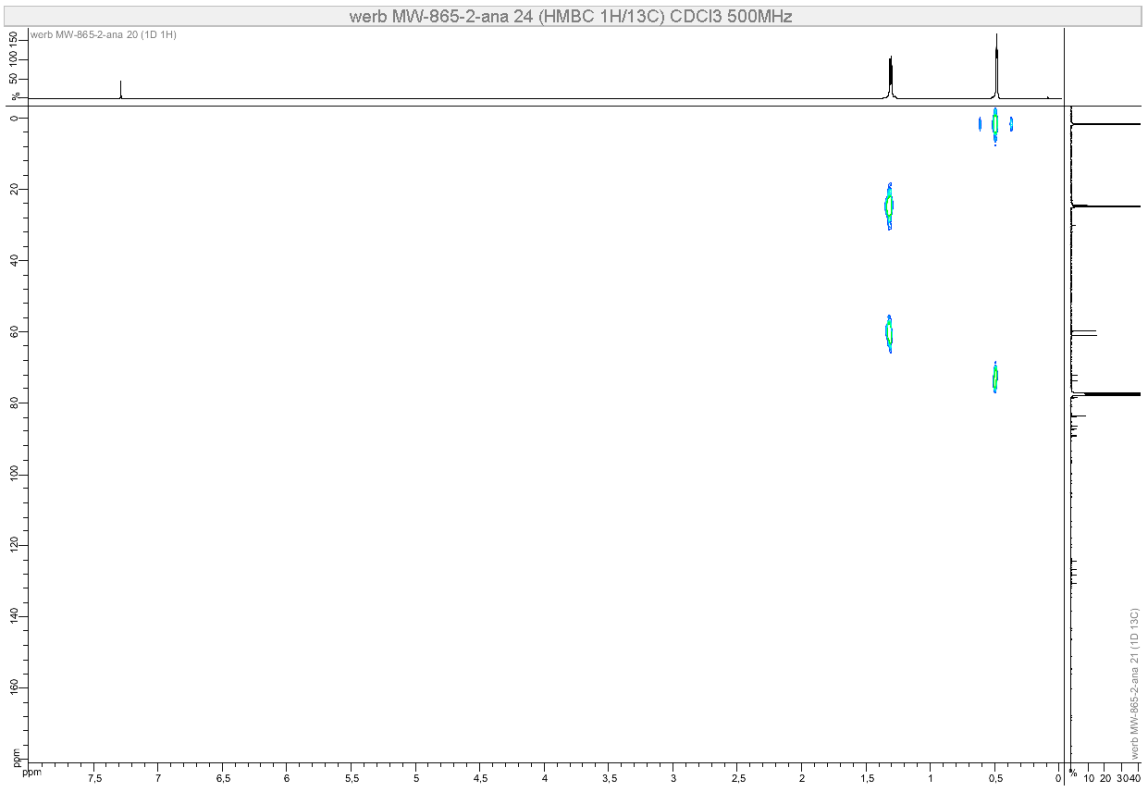
^{13}C NMR (126 MHz, $CDCl_3$)



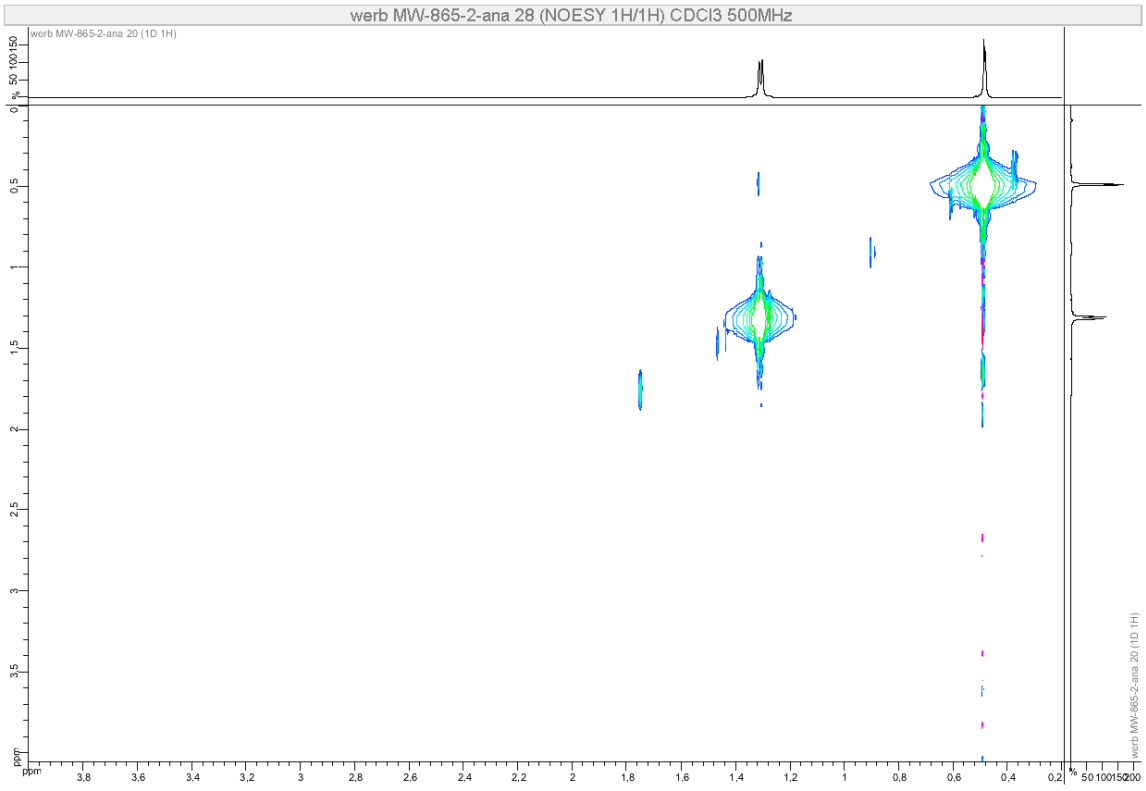
HSQC (500 MHz, $CDCl_3$)



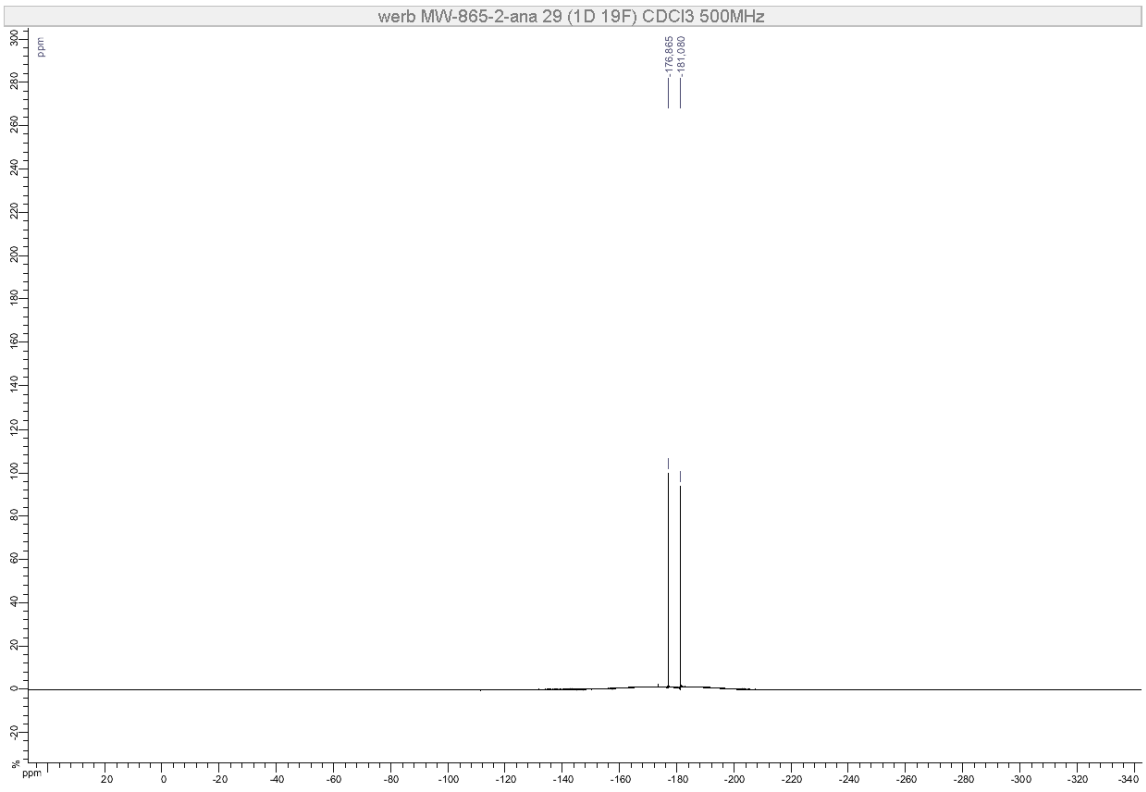
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

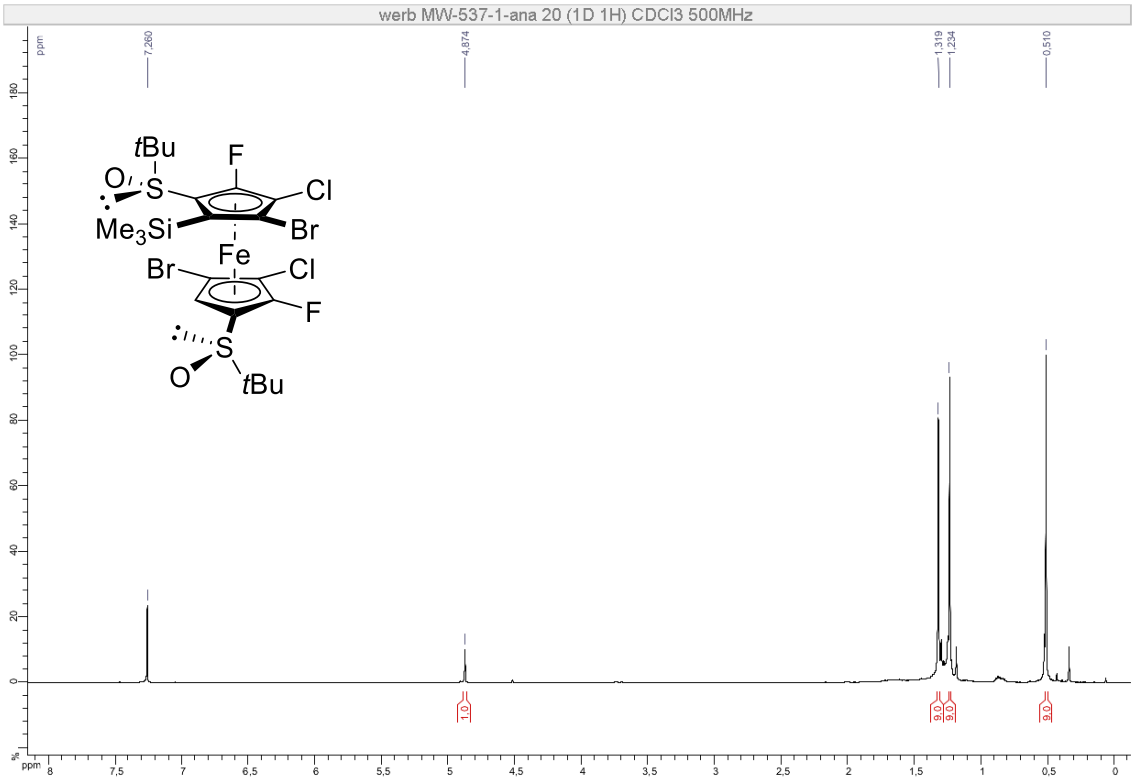


^{19}F NMR (470 MHz, $CDCl_3$)

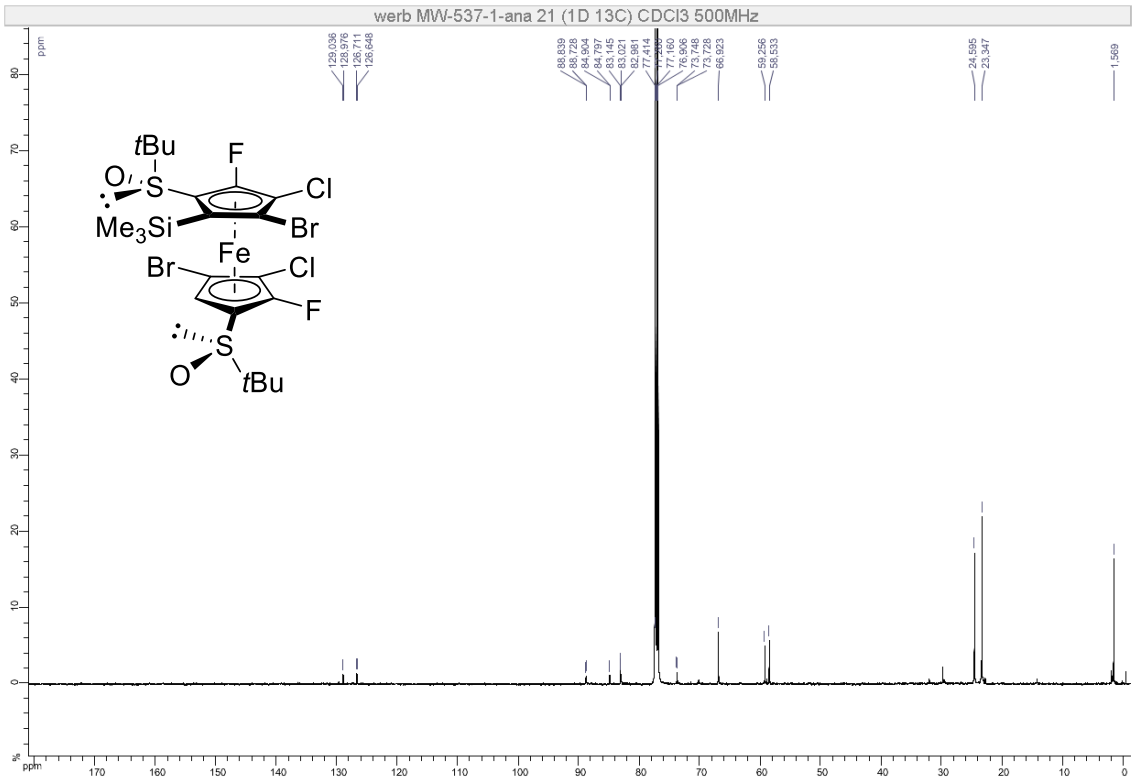


(*R*,*R*,*S*P,*S*P)-3,4'-Dibromo-*S*,*S*'-di-*tert*-butyl-4,3'-dichloro-5,2'-difluoro-2-(trimethylsilyl)ferrocene-1,1'-disulfoxide (*S*P,*S*P-10"'a)

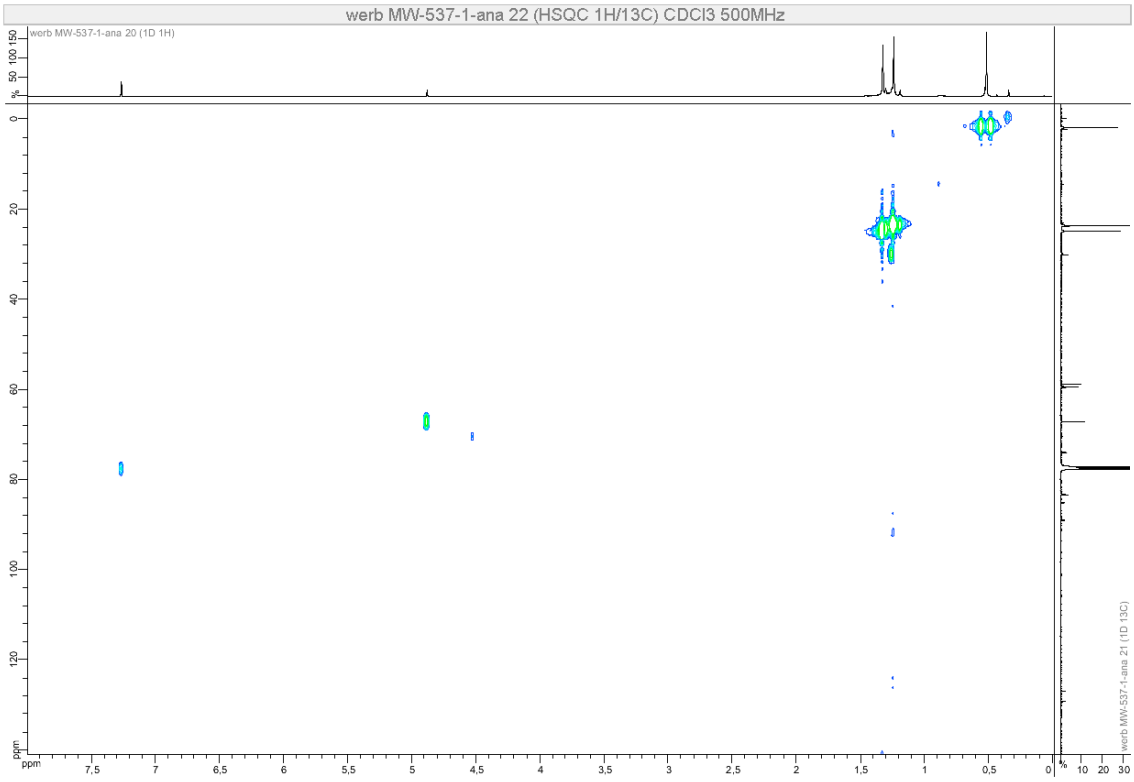
^{1}H NMR (500 MHz, $CDCl_3$)



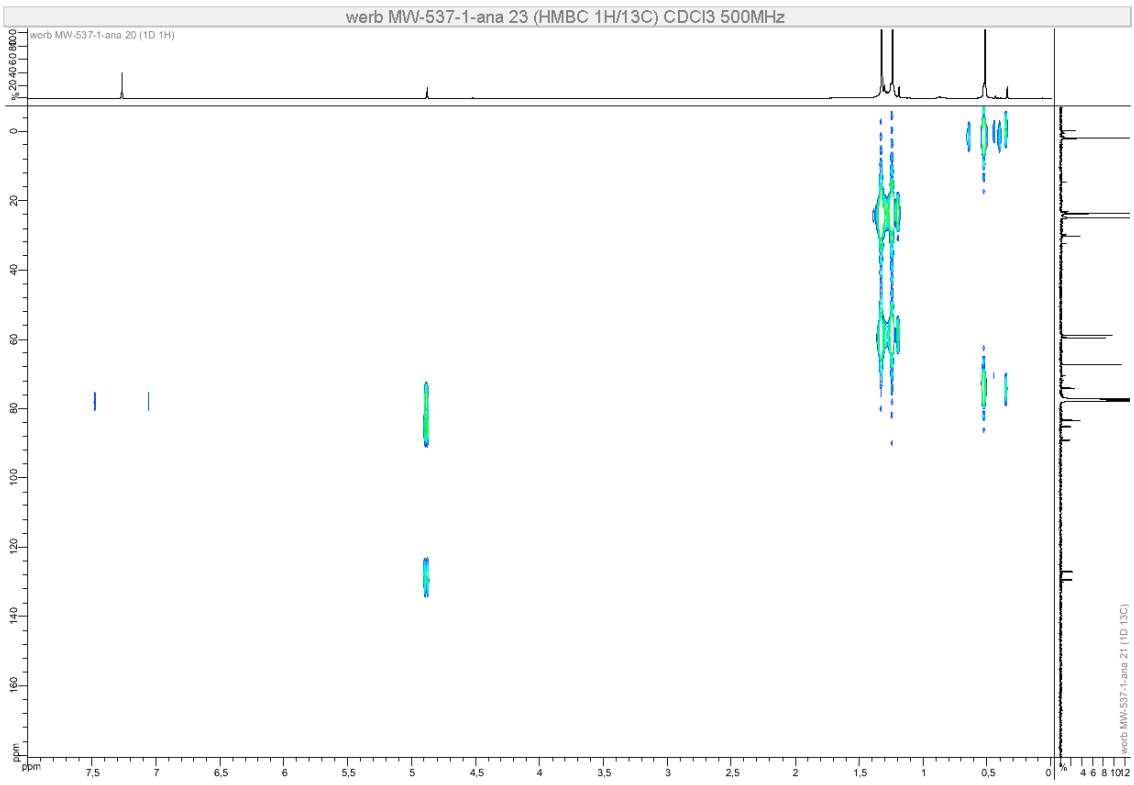
^{13}C NMR (126 MHz, $CDCl_3$)



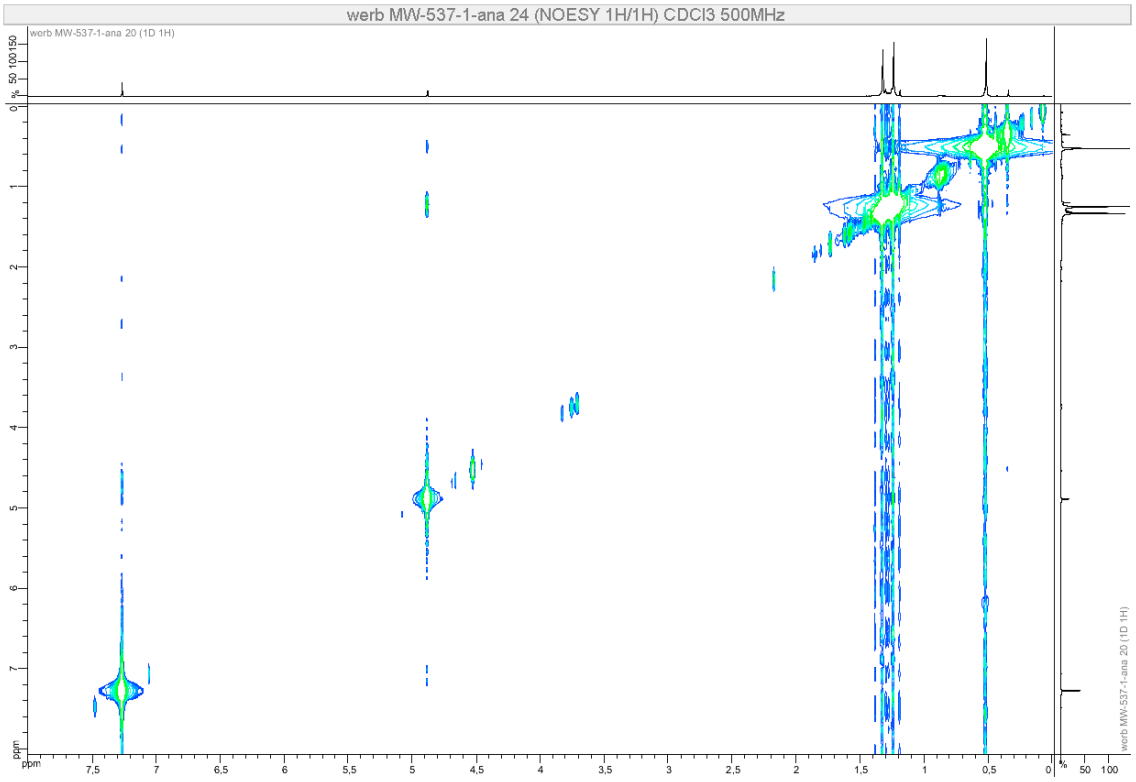
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

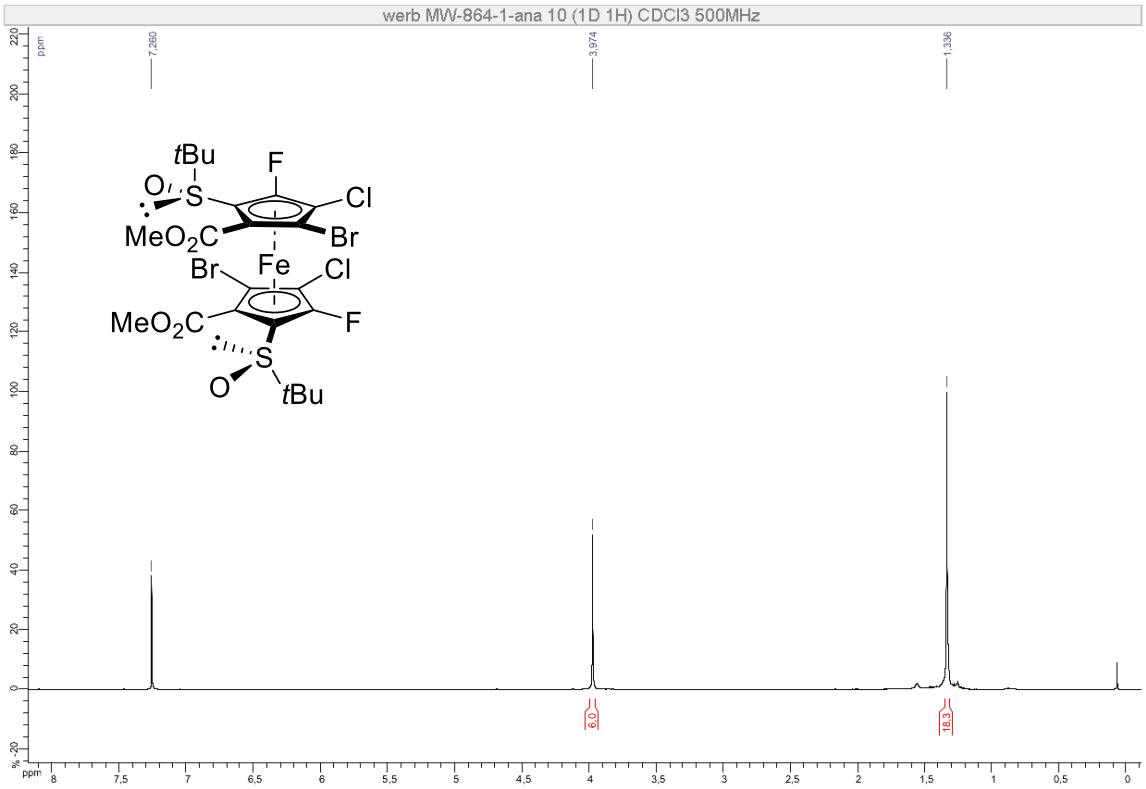


NOESY (500 MHz, $CDCl_3$)

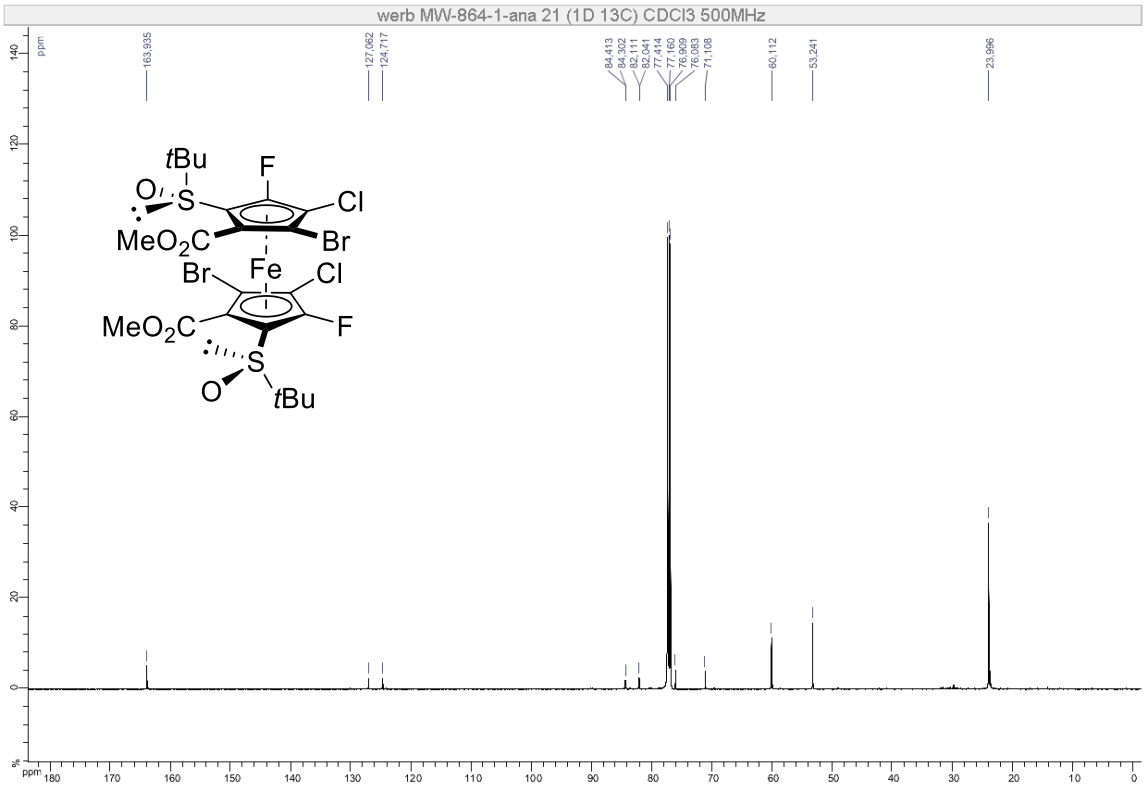


(*R*,*R*,*S*P,*S*P)-3,3'-Dibromo-*S*,*S*'-di-*tert*-butyl-4,4'-dichloro-5,5'-difluoro-2,2'-di(methoxycarbonyl)ferrocene-1,1'-disulfoxide (*S*P,*S*P-10b)

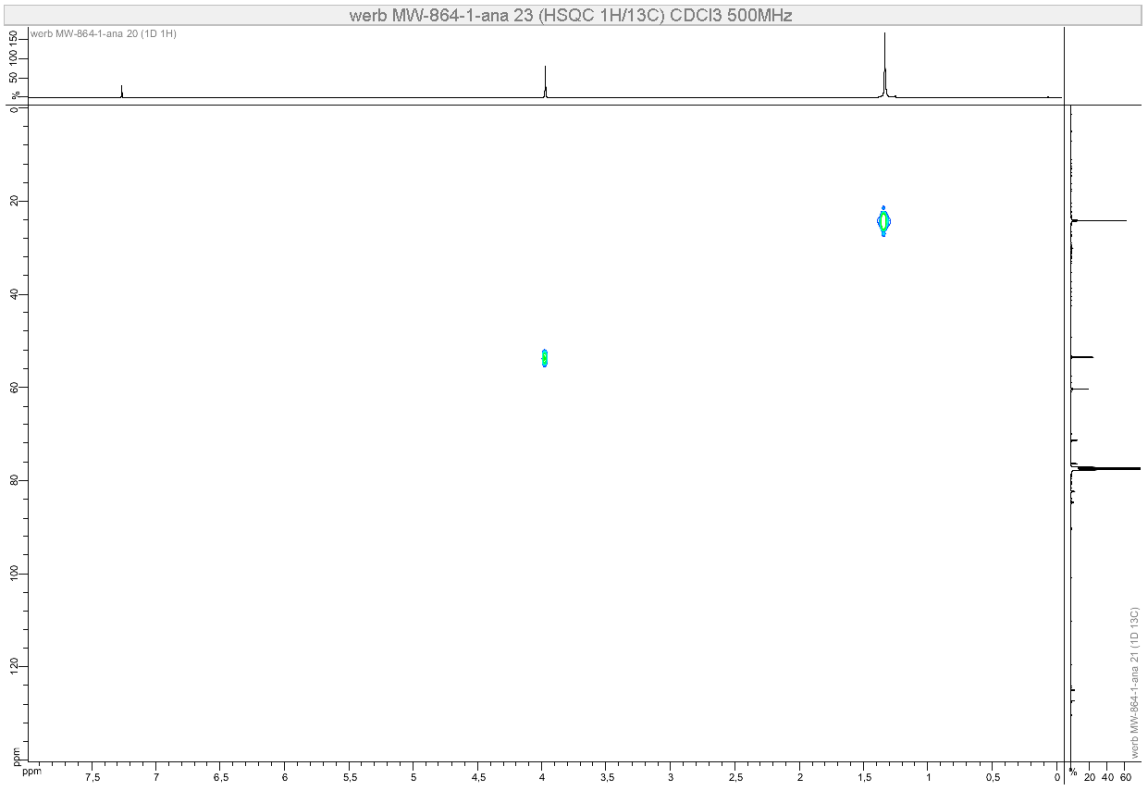
^{1}H NMR (500 MHz, $CDCl_3$)



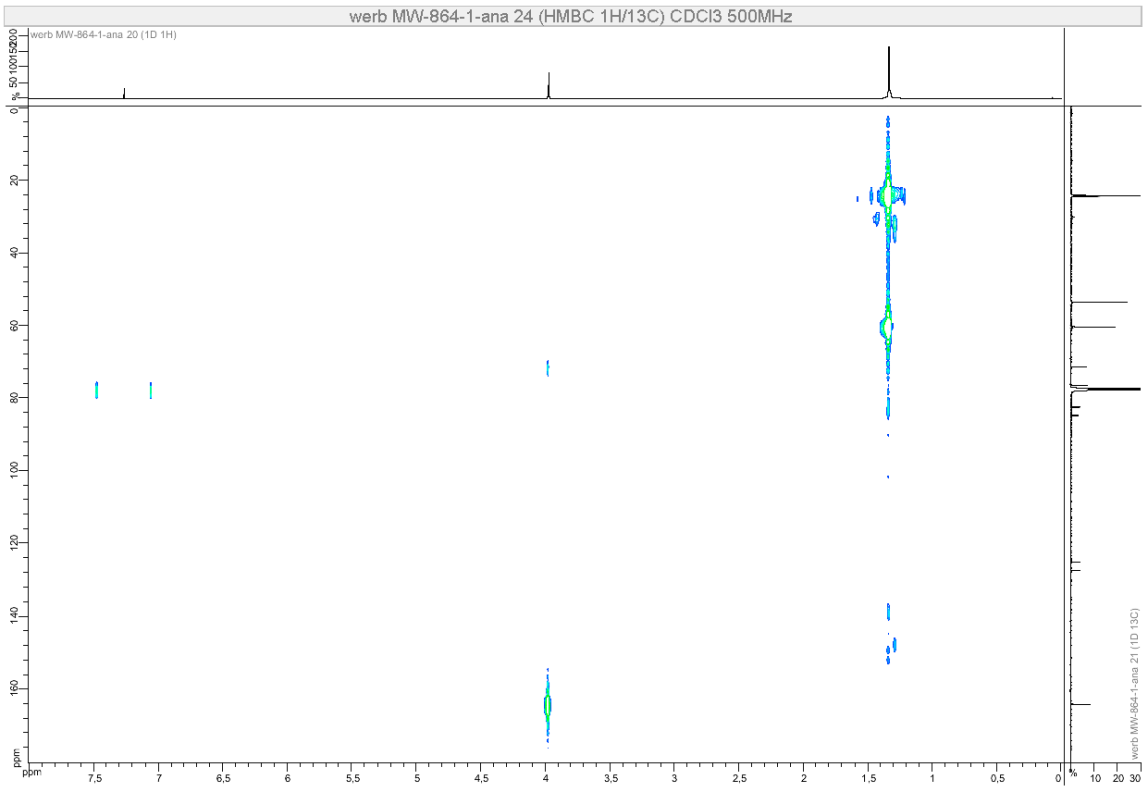
^{13}C NMR (126 MHz, $CDCl_3$)



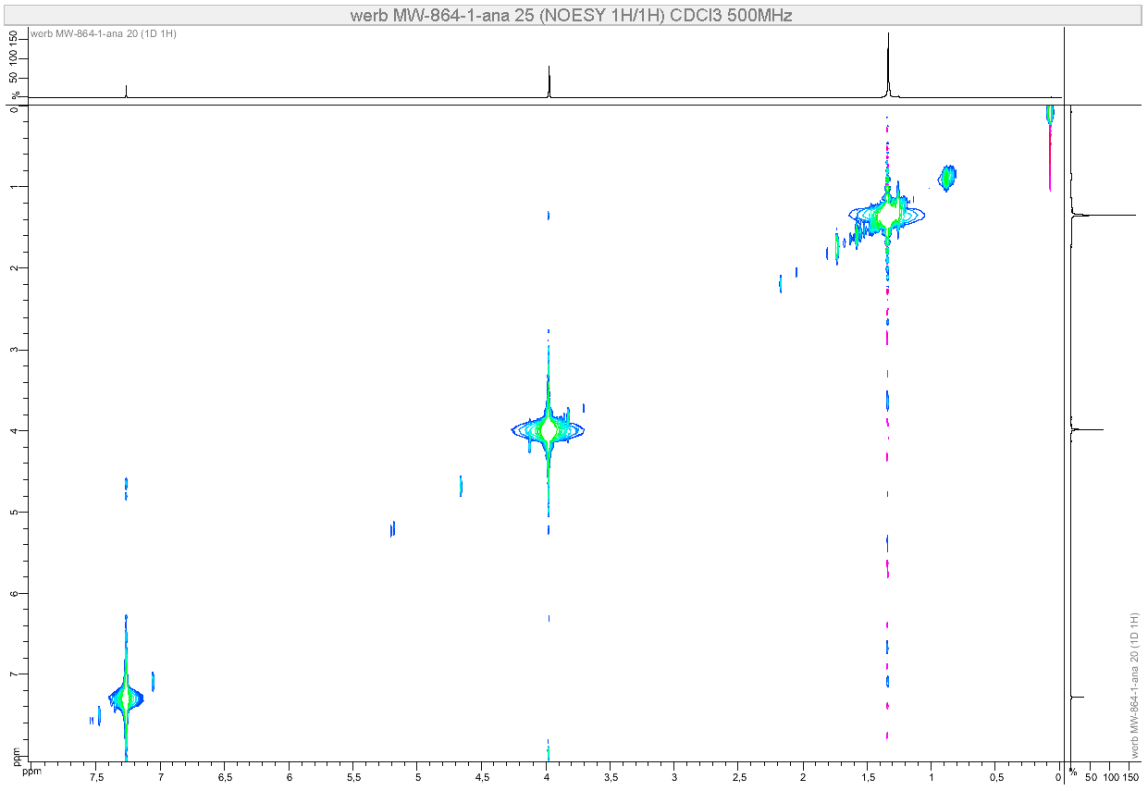
HSQC (500 MHz, $CDCl_3$)



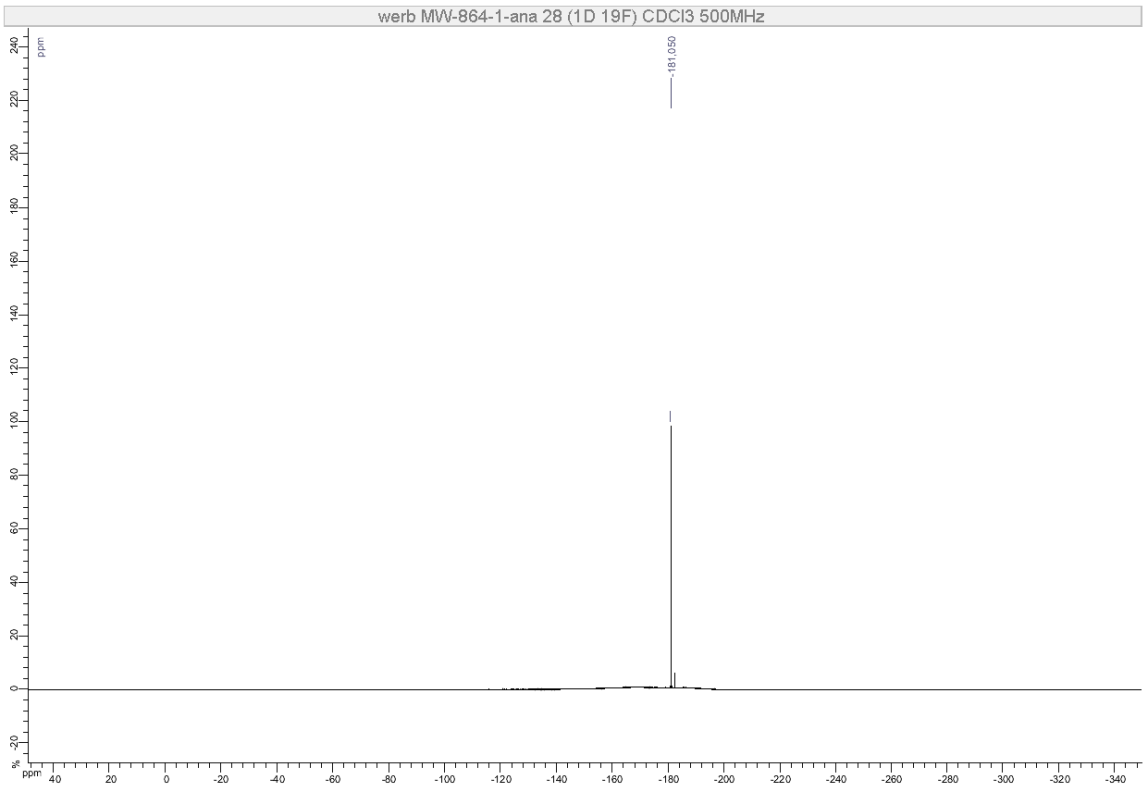
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

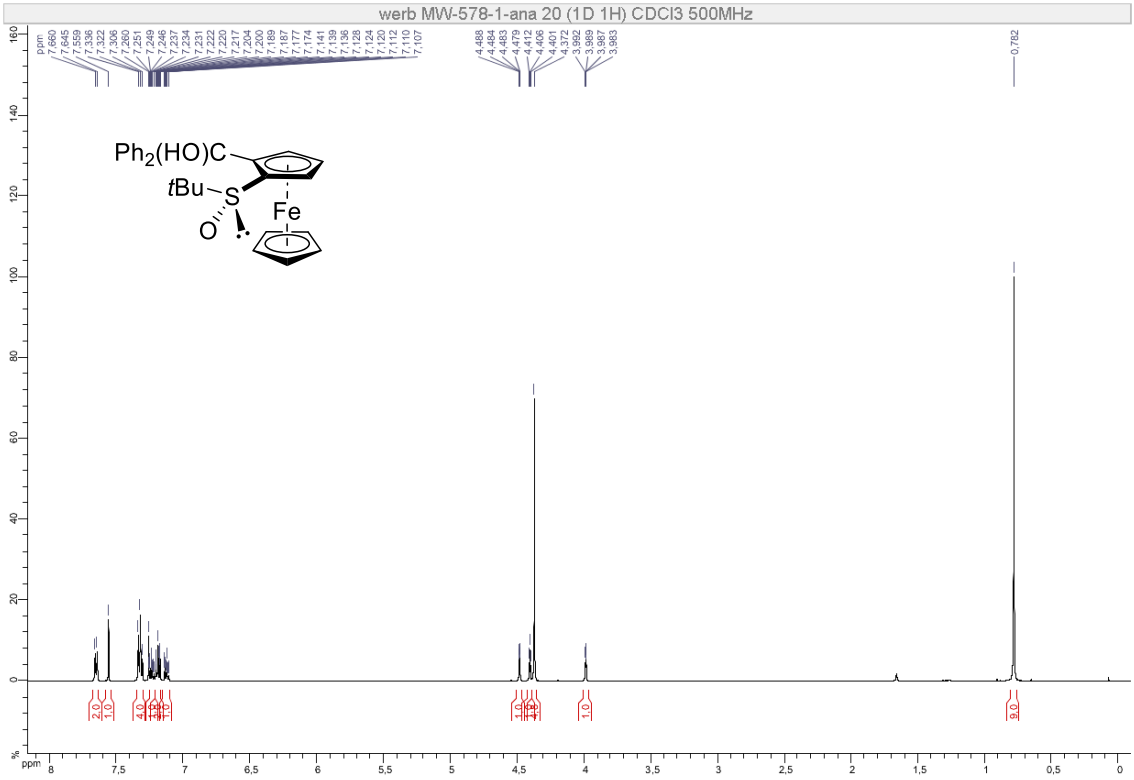


^{19}F NMR (470 MHz, $CDCl_3$)

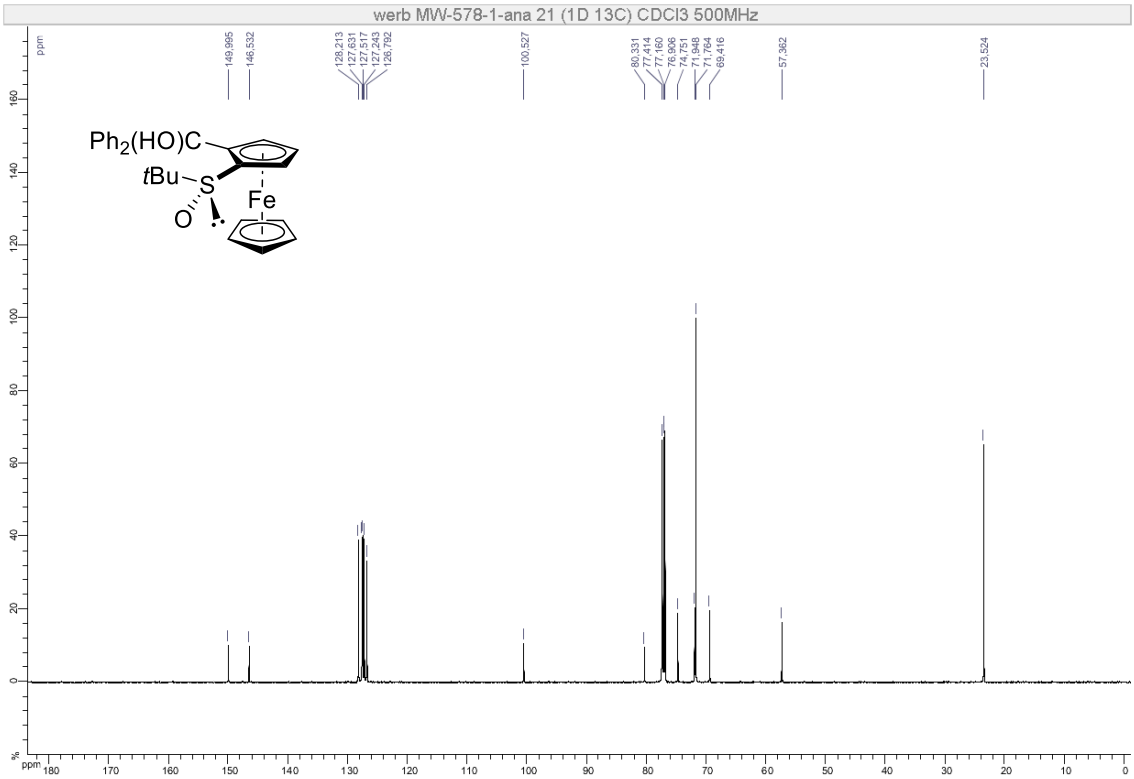


(*R*,*R*P)-*S*-*tert*-Butyl-2-[(α,α-diphenyl)hydroxymethyl]ferrocenesulfoxide (*R*P-2c)

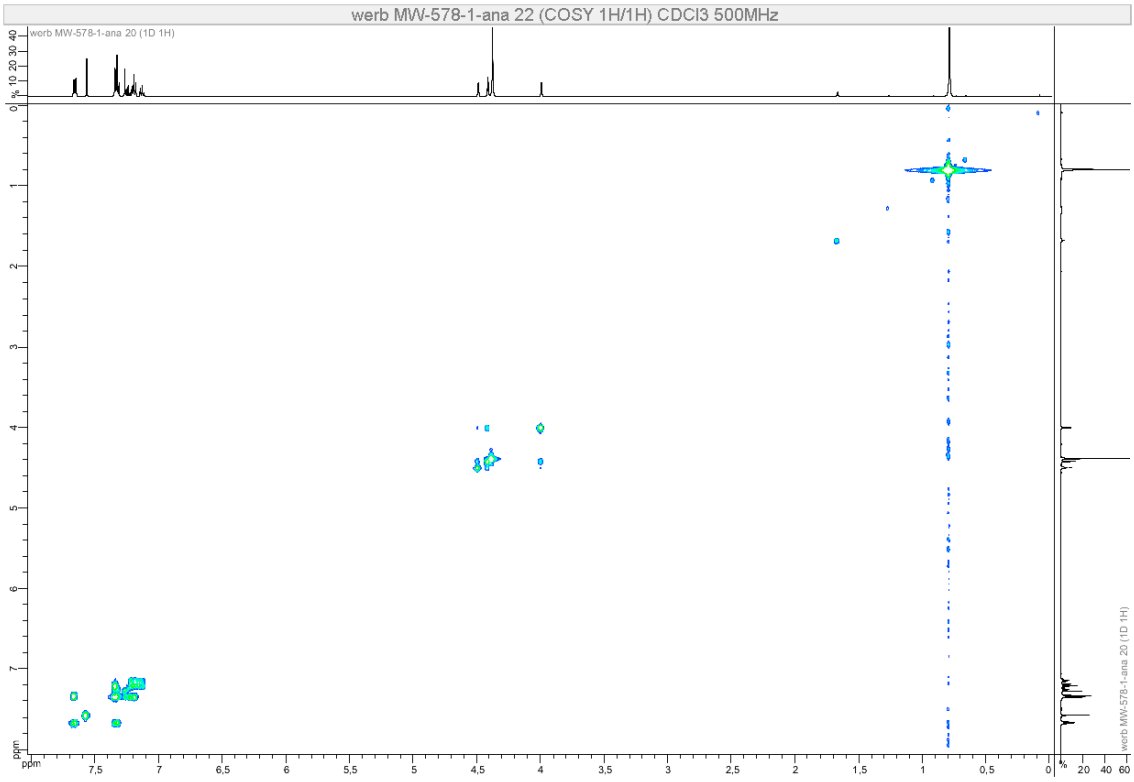
^{1}H NMR (500 MHz, $CDCl_3$)



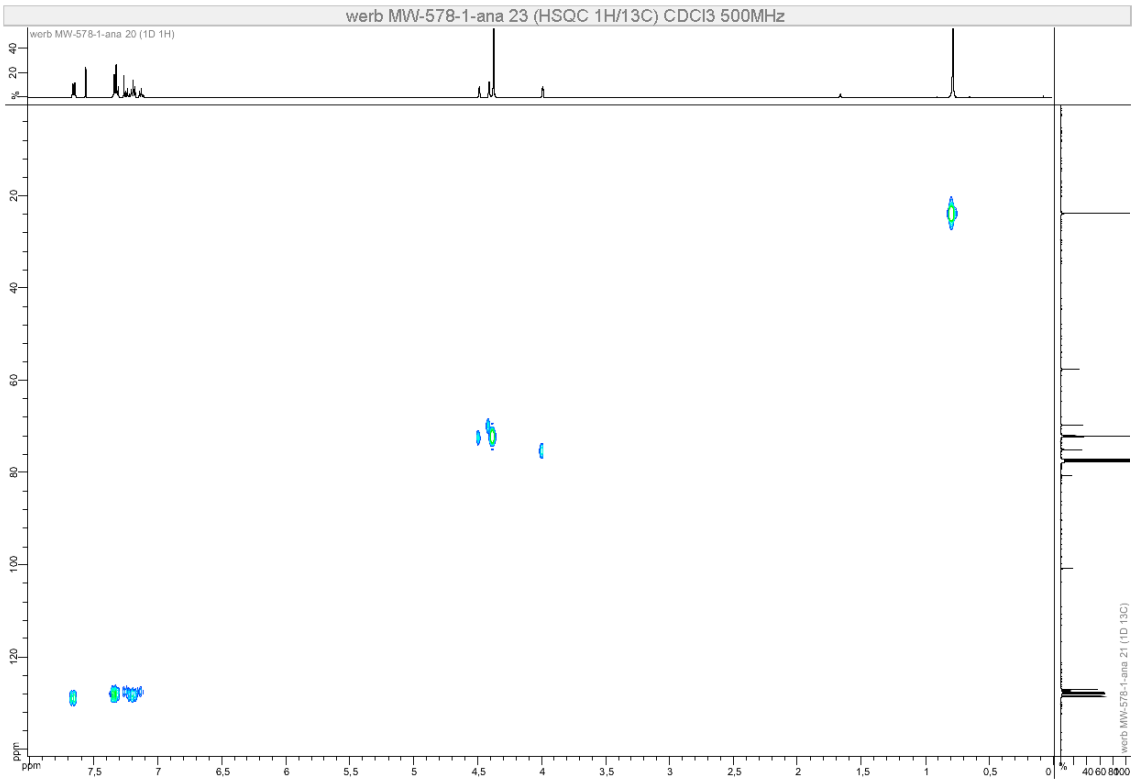
^{13}C NMR (126 MHz, $CDCl_3$)



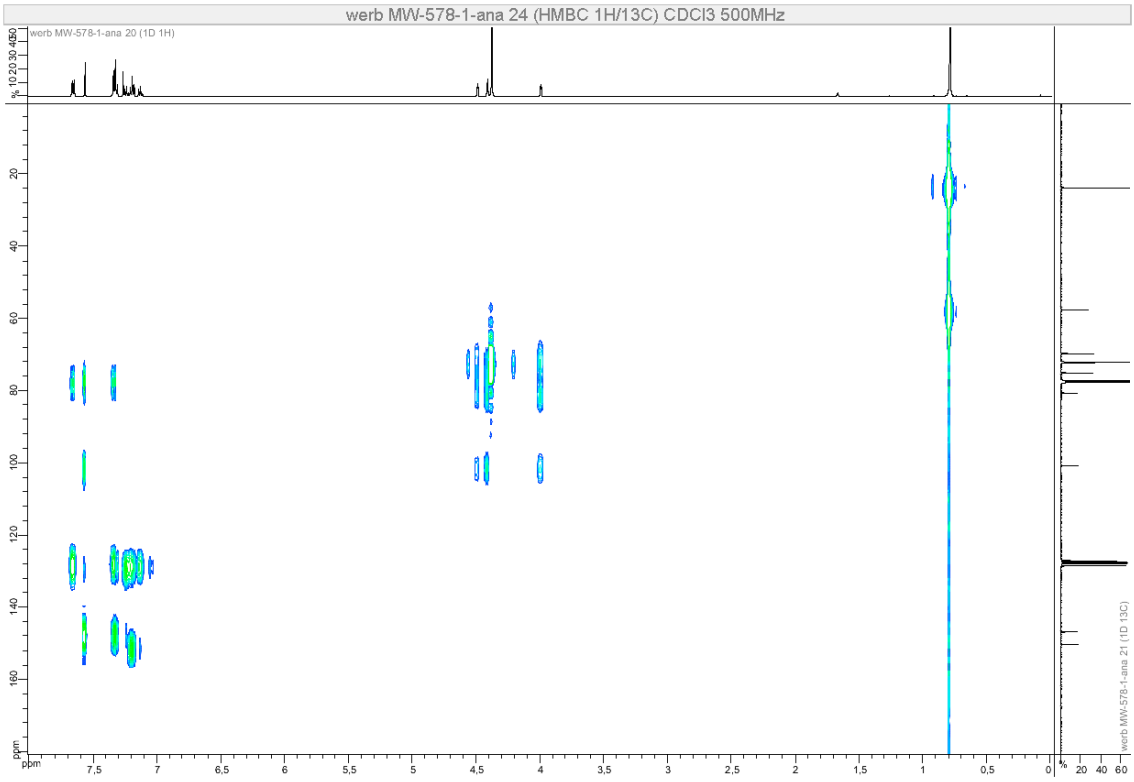
COSY (500 MHz, $CDCl_3$)



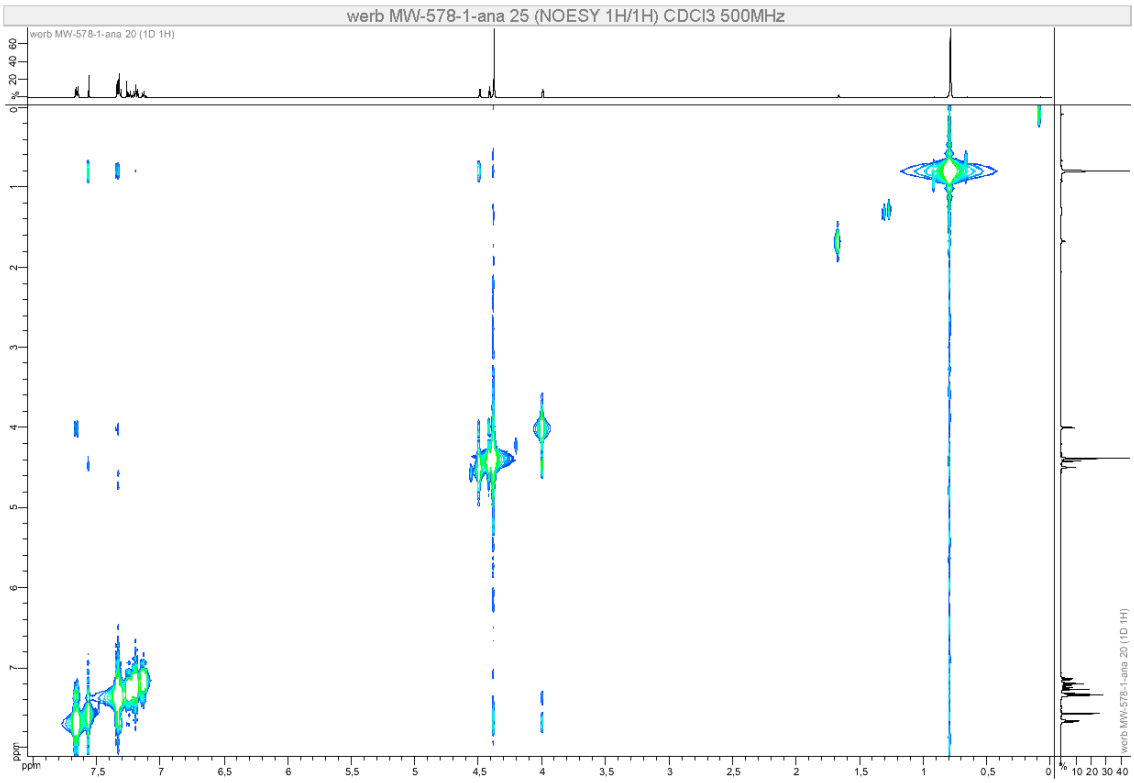
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

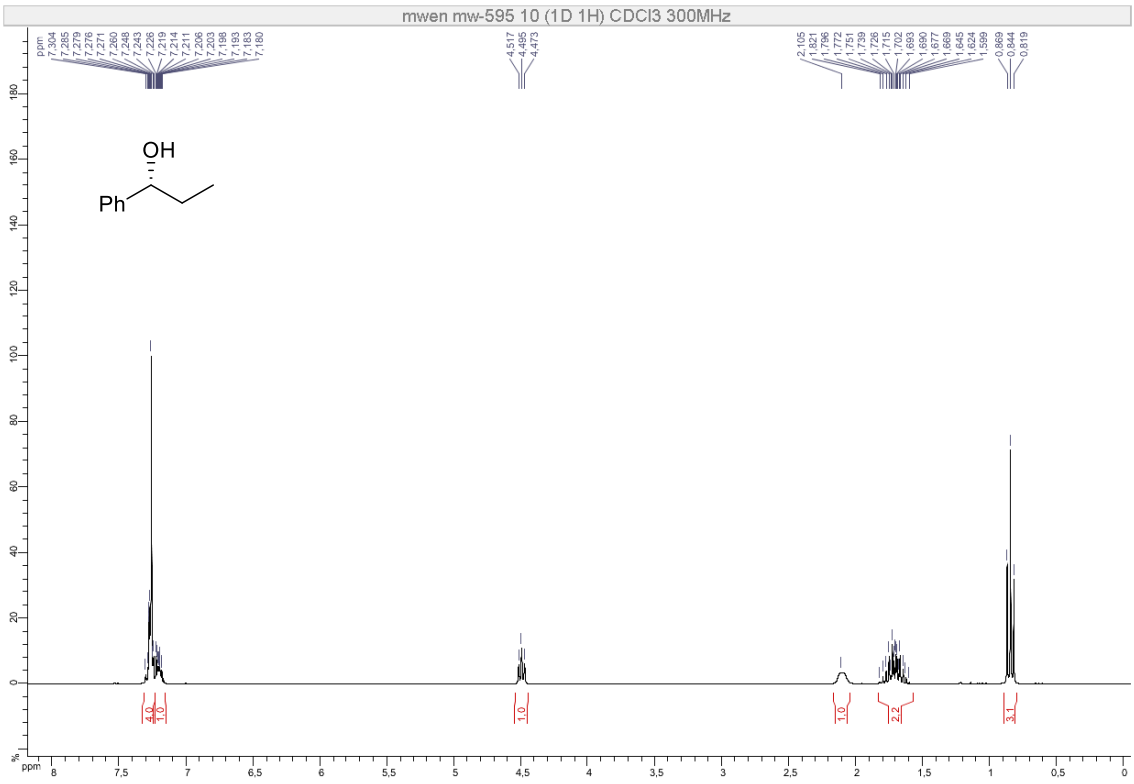


NOESY (500 MHz, $CDCl_3$)



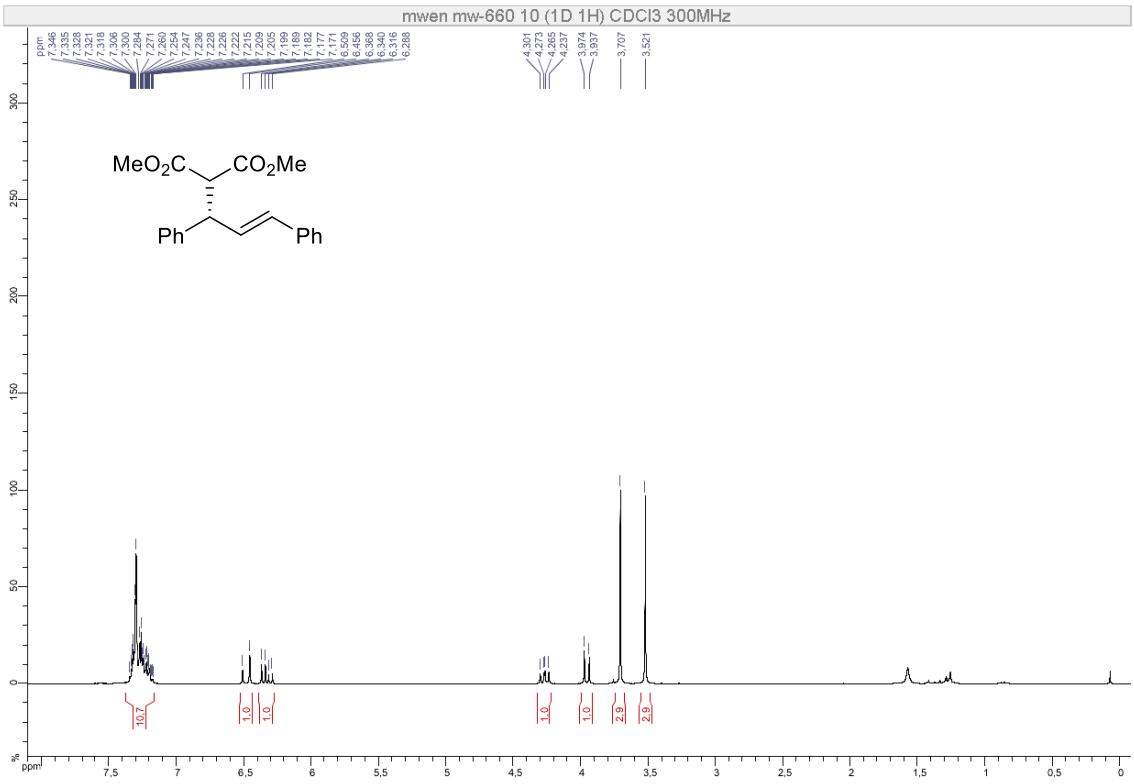
(*R*)-1-Phenylpropan-1-ol

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

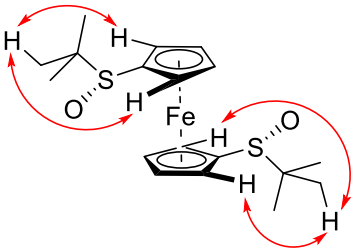
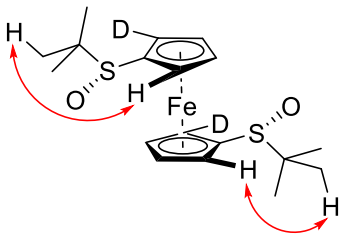
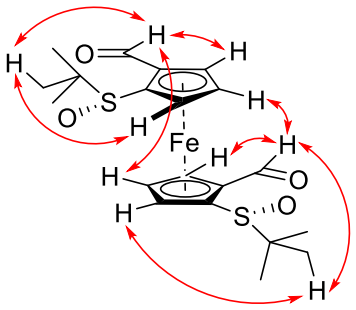
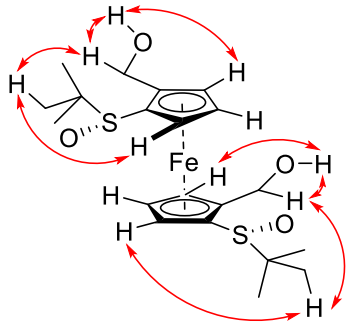
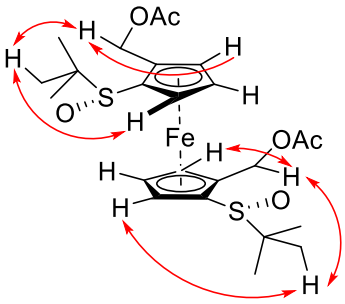
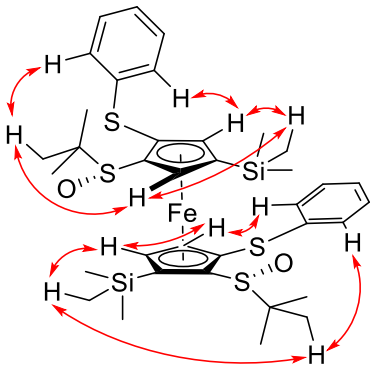
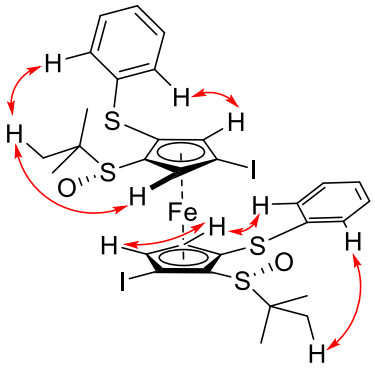
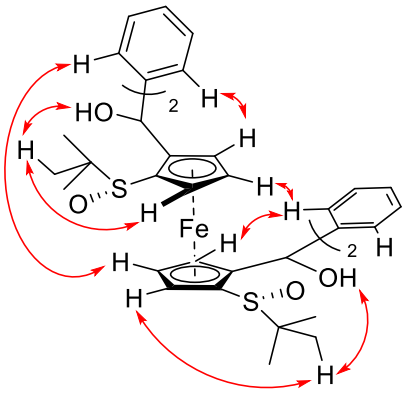
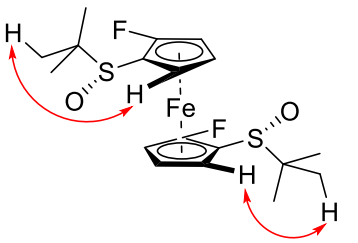
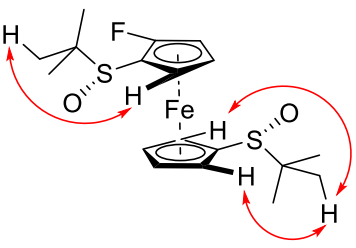
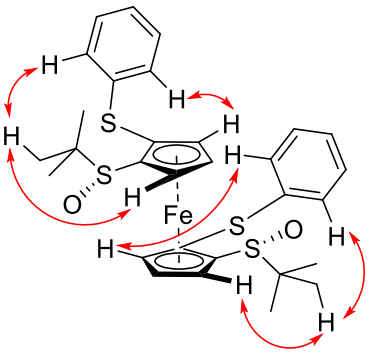
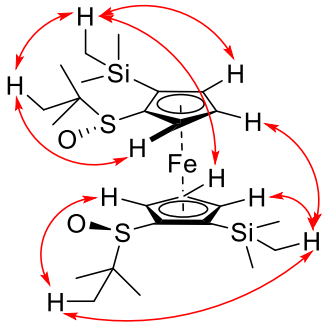


Dimethyl (*E*)-2-(1,3-diphenylprop-2-enyl)malonate

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

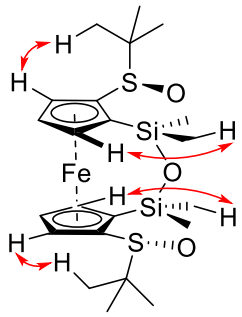
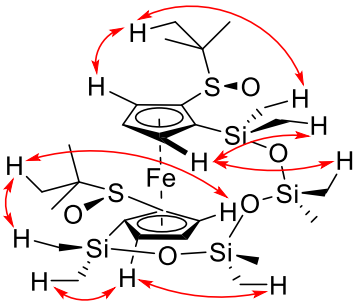
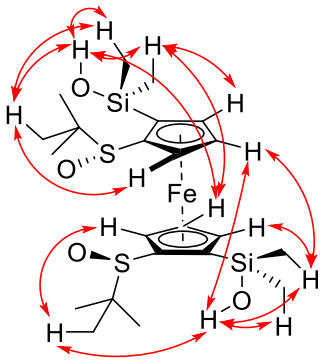
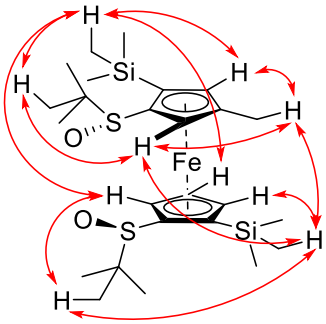
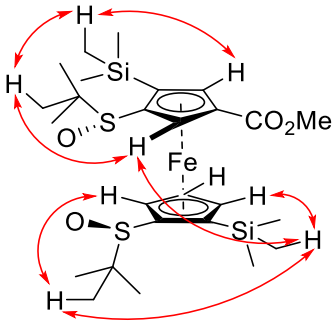
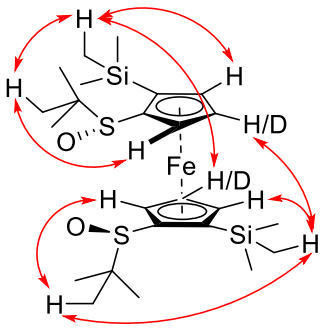
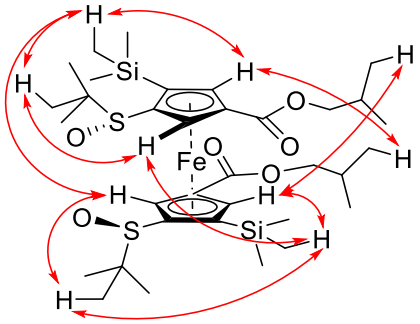
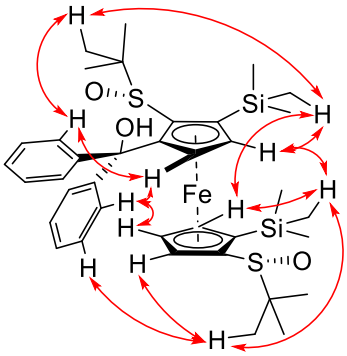
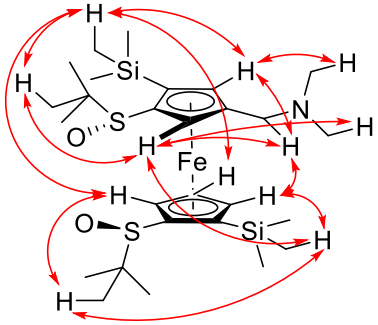
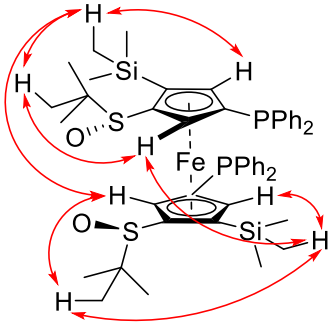
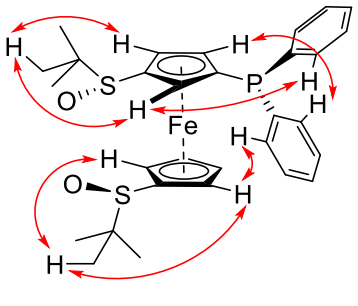
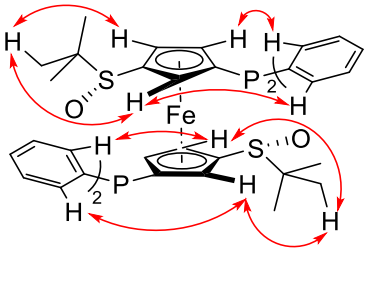


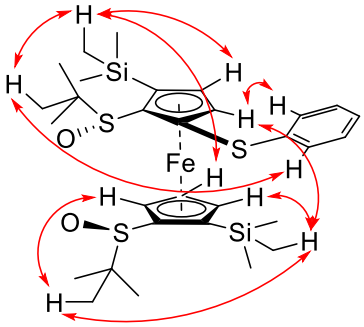
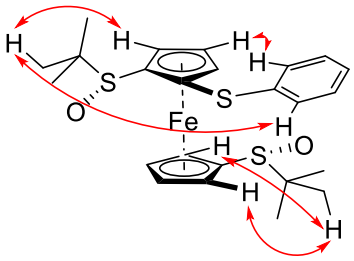
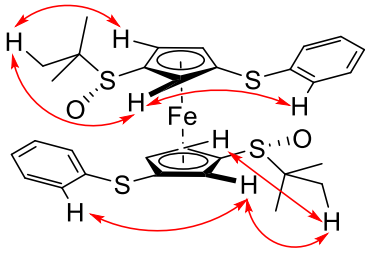
C) Selected NMR NOESY correlations

		
1	***R*P,*R*P-2a**	***R*P,*R*P-2b**
		
***R*P,*R*P-3**	***R*P,*R*P-4**	***R*P,*R*P-5a**
		
***R*P,*R*P-5b**	***R*P,*R*P-2c**	***R*P,*R*P-2d**
		
†	***R*P,*R*P-2e**	***R*P,*R*P-2f ***

* Proposed conformation based on observed NOESY correlations.

† Proposed conformation based on observed HOESY correlations.

		
***R*P,*R*P-2g1**	***R*P,*R*P-2g2 ***	***R*P,*R*P-2g3 ***
		
***R*P,*R*P-6a ***	***R*P,*R*P-6b ***	***R*P,*R*P-2f ***
		
***R*P,*R*P-6'c ***	***R*P,*R*P-6"d ***	***R*P,*R*P-6e ***
		
***S*P,*S*P-6'f ***	***S*P-7' ***	***S*P,*S*P-7**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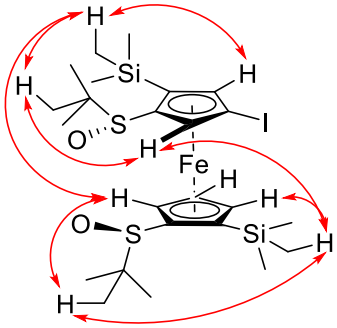
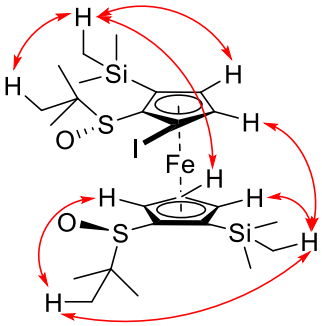
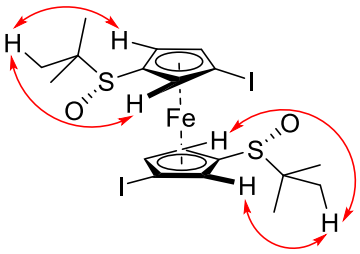
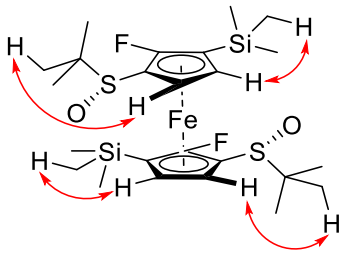
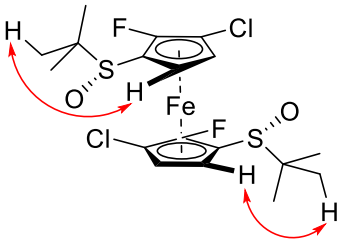
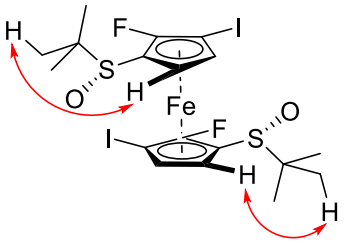
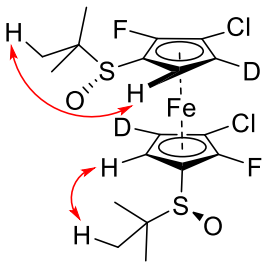
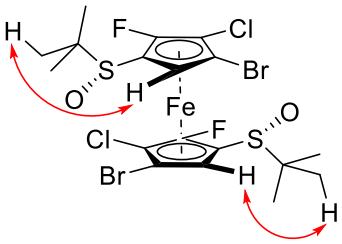
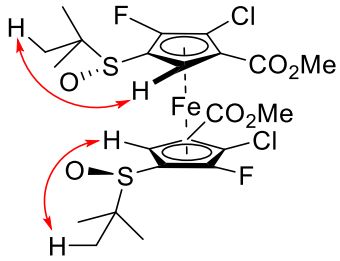
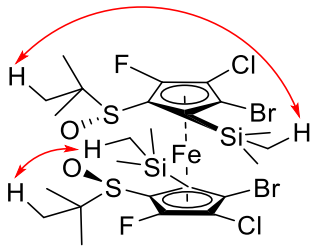
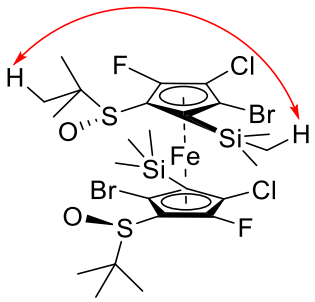
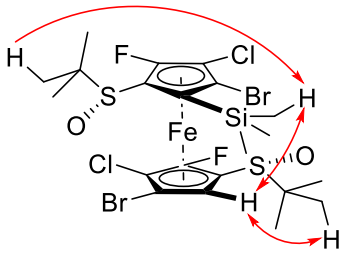
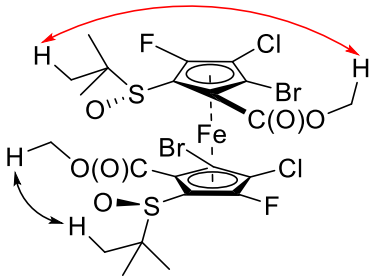
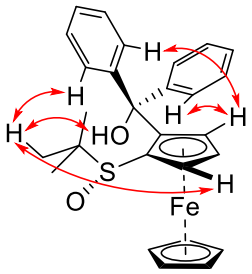
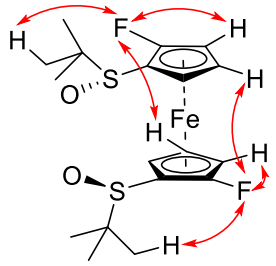
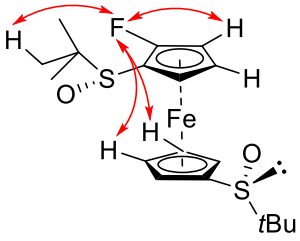
		
***R*P,*R*P-6h ***	***R*P,*R*P-6”h ***	***R*P,*R*P-6’h-desi**
		
***R*P,*R*P-8a**	***S*P,*S*P-8b**	***S*P,*S*P-8c**
		
†	***S*P,*S*P-9a**	***S*P,*S*P-9b**†

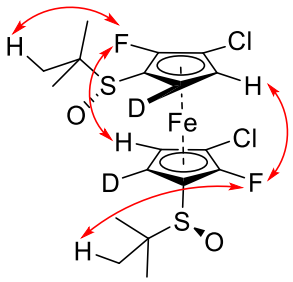
		
***S*P,*S*P-10a**†	***S*P,*S*P-10”a**†	***S*P,*S*P-10”’a**
		
***S*P,*S*P-10b**	***R*P-2c**	

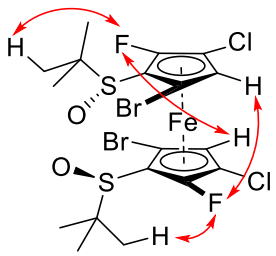
D) Selected NMR HOESY correlations



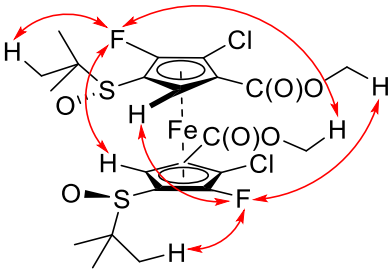
***R*P,*R*P-2d**



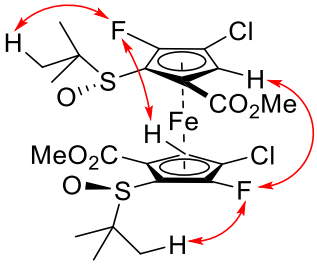




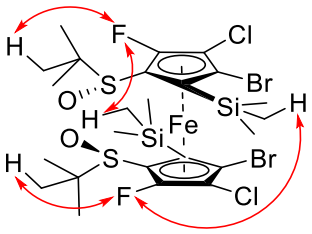
***S*P,*S*P-9'a**



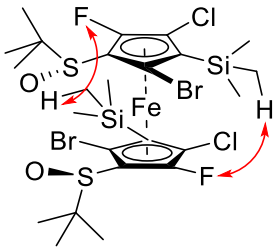
***S*P,*S*P-9b**



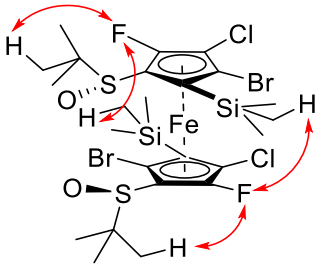
***S*P,*S*P-9'b**



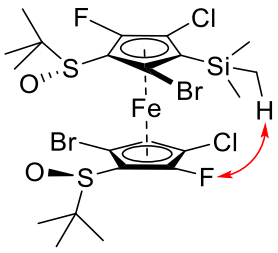
***S*P,*S*P-10a**



***S*P,*S*P-10'a**



***S*P,*S*P-10"a**



***S*P,*S*P-10""a**

E) HPLC Data

Enantioenriched 1-phenyl-1-propanol

Chromatogram and Results

General informations

Sequence Name:	2022-02-18
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALCEL OD DAICEL

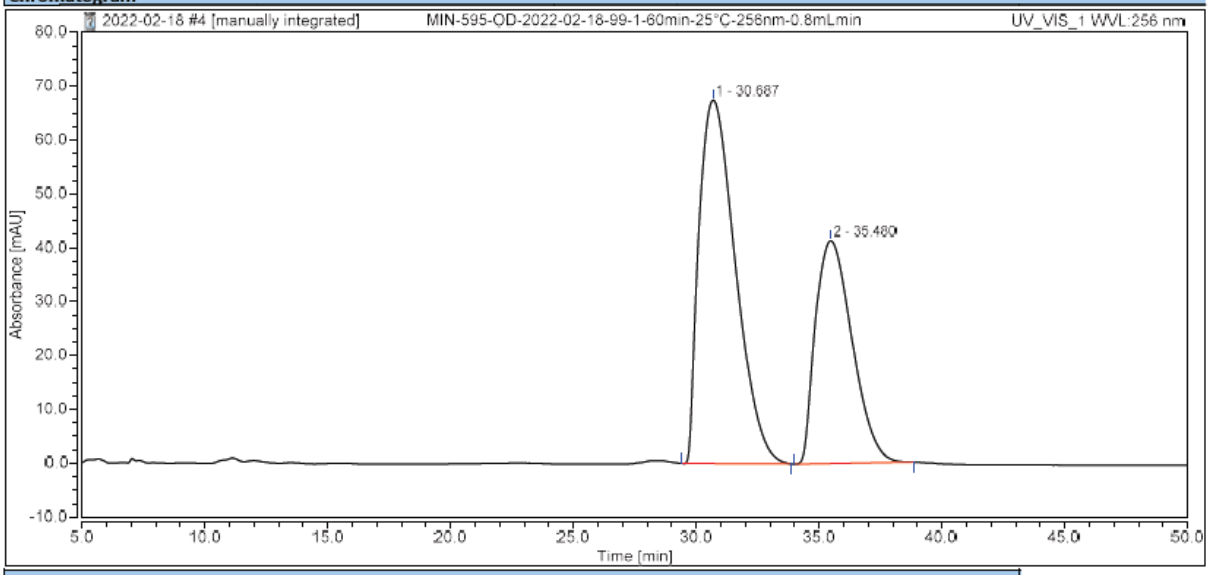
Injection Details

Injection Name:	MIN-595-OD-2022-02-18-99-1-60min-25°C-256nm-0.8	*Run Time:*	50.00 min
Instrument Method:	99-1-50min-25°C-256nm-0.8mLmin	*Injection Volume:*	100.00 µL
Injection Date/Time:	18/févr./22 12:31	*Channel:*	UV_VIS_1
		Wavelength:	256 nm

Instrument Method Details

Instrument Method:		99-1-50min-25°C-256nm-0.8mLmin			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	25.0 °C	
	Débit:	0.800 mL/min	*Pression:*	17 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		30.687	1.667	1.69	1.64	1878
2		35.480	1.677	n.a.	1.44	2479

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		30.687	115.967	67.465	61.87	62.00
2		35.480	71.467	41.344	38.13	38.00
Total:			**187.434**	**108.809**	**100.00**	**100.00**

(±)-Dimethyl (*E*)-2-(1,3-diphenylprop-2-enyl)malonate

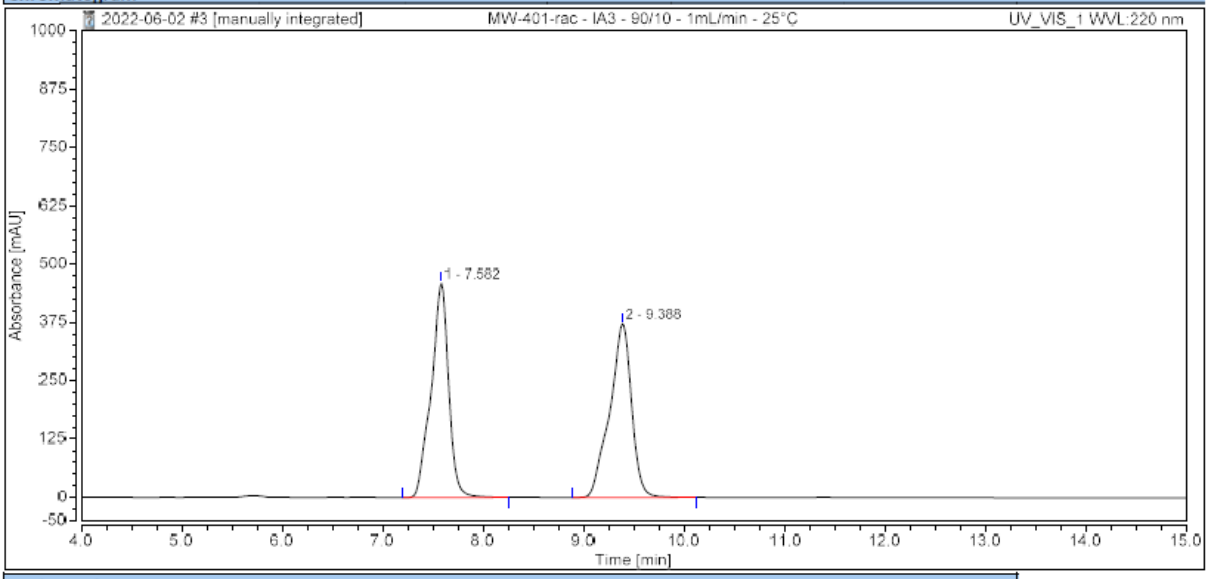
Chromatogram and Results

General informations	
Sequence Name:	2022-06-02
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA3 DAICEL

Injection Details			
Injection Name:	MW-401-rac - IA3 - 90/10 - 1mL/min - 25°C	*Run Time:*	15.00 min
Instrument Method:	Enantio Fc Will	*Injection Volume:*	5.00 µL
Injection Date/Time:	02/juin/22 09:31	*Channel:*	UV_VIS_1
		Wavelength:	220 nm

Instrument Method Details				
Instrument Method:	Enantio Fc Will			
%A	iPrOH 10	10 %		
%B	Hexane 90	90 %	*Température du four:*	25.0 °C
	Débit:	1.000 mL/min	*Pression:*	87 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		7.582	0.175	5.41	0.89	10398
2		9.388	0.219	n.a.	0.86	10158

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		7.582	92.711	459.605	49.72	55.21
2		9.388	93.771	372.900	50.28	44.79
Total:			**186.483**	**832.505**	**100.00**	**100.00**

Enantioenriched dimethyl (*E*)-2-(1,3-diphenylprop-2-enyl)malonate

Chromatogram and Results

General informations

Sequence Name:	2022-06-02
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA3 DAICEL

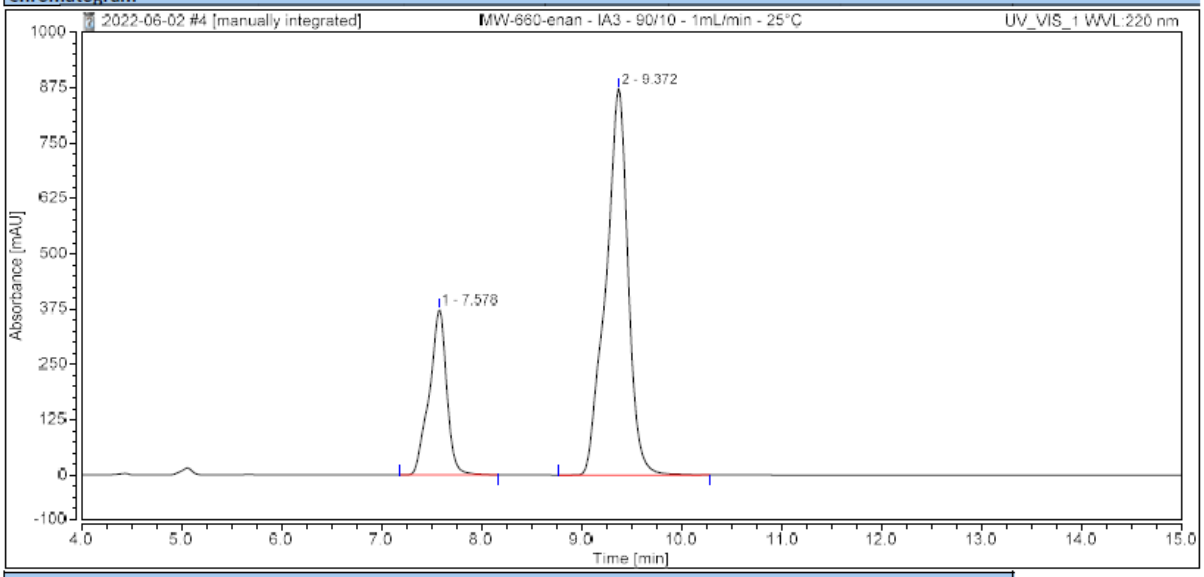
Injection Details

Injection Name:	MW-660-enan - IA3 - 90/10 - 1mL/min - 25°C	*Run Time:*	15.00 min
Instrument Method:	Enantio Fc Will	*Injection Volume:*	1.00 µL
Injection Date/Time:	02/juin/22 09:47	*Channel:*	UV_VIS_1
		Wavelength:	220 nm

Instrument Method Details

Instrument Method:	Enantio Fc Will				
%A	iPrOH 10	10 %			
%B	Hexane 90	90 %	*Température du four:*	25.0 °C	
	Débit:	1.000 mL/min	*Pression:*	87 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		7.578	0.174	5.32	0.89	10502
2		9.372	0.224	n.a.	0.90	9711

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		7.578	75.197	374.036	25.01	29.98
2		9.372	225.442	873.496	74.99	70.02
Total:			**300.639**	**1247.533**	**100.00**	**100.00**

F) Computational Details

In order to calculate the pK_a values of species as C–H acids, we used the approach developed earlier and applied successfully, including ferrocenesulfoxides.[29]
In brief, all electronic structure calculations were carried out using standard DFT methods implemented in Gaussian 16 package.[30] We employed the CAM-B3LYP hybrid functional.[31] Vibrational frequencies were calculated to prove the nature of the stationary points (no imaginary values). The LANL2DZ basis set[32] with the effective core potential was used to describe both Fe and I, while the 6-31G(d) basis set[33] was used for the rest of the atoms during optimizations. The single point energies in turn were calculated at the CAM-B3LYP/LANL2DZ + 6-311+G(d,p) level.
The discussed pK_a values were obtained from the Gibbs free energy of the isodesmic reaction between the studied (R–H) and a probe compound (Het–H):

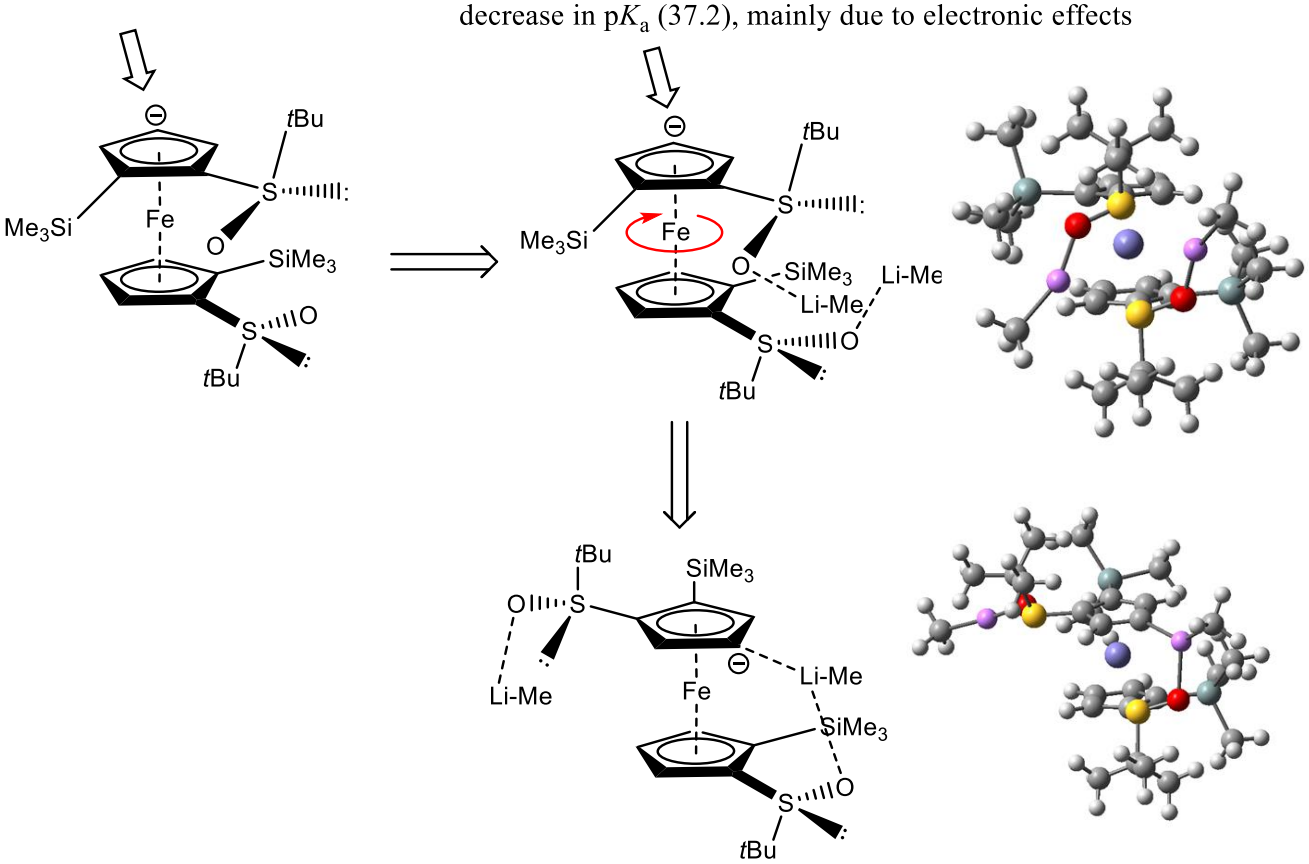
$$\text{R–H(solv)} + \text{Het}^{-}\text{(solv)} \rightarrow \text{R}^{-}\text{(solv)} + \text{Het–H(solv)}$$

here furan with pK_a(THF) of 35.6[34] was used as the probe compound. The solvent influence during calculations was accounted for by using polarizable continuum model (IEF-PCM)[35] with the default parameters for THF in order to mimic experimental conditions.

G) Illustration of Possible Lithium Stabilization Effect

Structure not coordinated by MeLi, pK_a 40.0

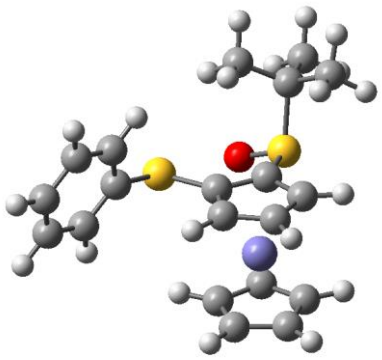
Coordination of MeLi leads to a local minimum on the PES of the anion, the formation of which corresponds to a slight decrease in pK_a (37.2), mainly due to electronic effects



The low rotation barrier allows the anion to adopt a more stable structure by the formation of a briged complex with the participation of lithium ion, leading to a decrease in pK_a (25.2)

H) Cartesian coordinates of DFT optimized structures

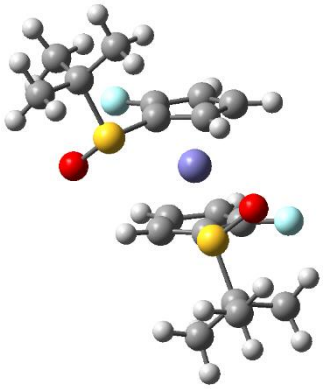
***R*$_P$-2e**



atom	X	Y	Z
Fe	-0.32789	1.78547	0.35739
S	-2.48414	-0.56154	-0.51887
C	0.36438	2.66046	-1.37152
C	-1.05433	2.60292	-1.38727
C	-1.53484	3.33621	-0.26660
C	-0.41083	3.84578	0.44071
C	0.76374	3.42806	-0.24326
C	-1.33348	0.67818	1.74800
C	-0.05469	1.01593	2.25306
C	0.92551	0.49320	1.36522
C	0.26664	-0.19997	0.30933
C	-1.14201	-0.08295	0.55189
O	-1.89523	-0.75765	-1.89828
C	-2.90005	-2.26293	0.12528
C	-1.70277	-3.19319	-0.01157
C	-4.04324	-2.72185	-0.78394
C	-3.37113	-2.12869	1.57003
H	1.02013	2.14745	-2.06097
H	-1.64892	2.03081	-2.08624
H	-2.57117	3.45346	0.01883
H	-0.44226	4.41768	1.35790
H	1.78134	3.62472	0.06493
H	-2.28919	0.96206	2.16594
H	1.99489	0.61182	1.45645
H	-2.00760	-4.21958	0.22187
H	-0.89549	-2.91403	0.67066
H	-1.31459	-3.16775	-1.03221
H	-4.35736	-3.73028	-0.49558
H	-3.72143	-2.74354	-1.82810
H	-4.91247	-2.06044	-0.70248
H	-4.18995	-1.40661	1.66381
H	-2.55961	-1.82334	2.23573
H	-3.74393	-3.09767	1.91867
H	0.14479	1.60869	3.13479
S	1.03142	-1.03678	-1.06125
C	2.71181	-1.16249	-0.46117
C	3.70831	-0.38238	-1.04597
C	3.05292	-2.08155	0.53339
C	5.03216	-0.51522	-0.63696
H	3.44197	0.32636	-1.82320
C	4.37257	-2.20246	0.94941
H	2.27904	-2.70009	0.97627
C	5.36485	-1.42077	0.36343
H	5.80259	0.09367	-1.09986

H	4.62971	-2.91678	1.72552
H	6.39695	-1.52235	0.68430

R_P,R_P-2d



atom	X	Y	Z
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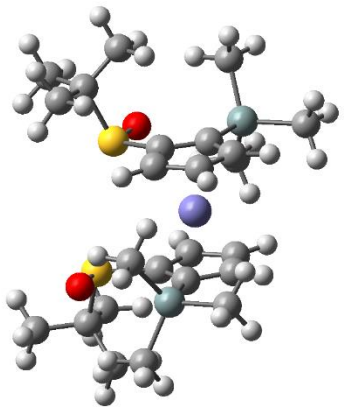
F	1.71837	2.43358	1.93861
C	-0.47525	1.60447	2.58781
H	-0.35164	1.62977	3.66103
C	-1.62117	1.17125	1.85815
H	-2.53631	0.78792	2.28671
C	-1.33507	1.25906	0.47330
H	-1.97184	0.90853	-0.32796
C	0.00000	1.75716	0.32536
S	0.84074	1.85688	-1.24801
O	2.28399	1.45512	-1.04933
C	0.84705	3.69933	-1.53145
C	1.71569	4.38688	-0.48565
H	2.68263	3.88324	-0.40899
H	1.24715	4.38470	0.50078
H	1.88446	5.42848	-0.77955
C	-0.59553	4.19457	-1.52198
H	-0.61643	5.24747	-1.82234
H	-1.04566	4.12012	-0.52857
H	-1.22015	3.63610	-2.22777
C	1.46930	3.84712	-2.92313
H	0.86502	3.34884	-3.68841
H	2.47610	3.42207	-2.94480
H	1.53602	4.90863	-3.18215
C	-0.50804	-1.96469	1.64007
F	-1.71837	-2.43358	1.93861
C	0.47525	-1.60447	2.58781
H	0.35164	-1.62977	3.66103
C	1.62117	-1.17125	1.85815
H	2.53631	-0.78792	2.28671
C	1.33507	-1.25906	0.47330
H	1.97184	-0.90853	-0.32796
C	0.00000	-1.75716	0.32536
S	-0.84074	-1.85688	-1.24801
O	-2.28399	-1.45512	-1.04933
C	-0.84705	-3.69933	-1.53145
C	-1.71569	-4.38688	-0.48565
H	-2.68263	-3.88324	-0.40899
H	-1.24715	-4.38470	0.50078
H	-1.88446	-5.42848	-0.77955
C	0.59553	-4.19457	-1.52198
H	0.61643	-5.24747	-1.82234
H	1.04566	-4.12012	-0.52857
H	1.22015	-3.63610	-2.22777
C	-1.46930	-3.84712	-2.92313

H	-0.86502	-3.34884	-3.68841
H	-2.47610	-3.42207	-2.94480
H	-1.53602	-4.90863	-3.18215

***R*$_P$,*R*$_P$-2f**



atom	X	Y	Z
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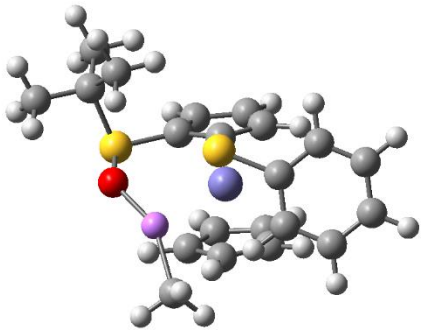
C	-1.37411	1.38092	1.81446
C	-0.07897	1.70322	2.29050
C	0.81194	1.92813	1.19078
Si	2.64392	2.35623	1.46121
C	2.86329	2.34656	3.34195
C	3.05787	4.08706	0.85276
C	3.87307	1.12596	0.74654
S	0.57796	1.82510	-1.66770
O	2.06323	2.11836	-1.57345
C	-0.22417	3.40684	-2.26290
C	-1.72722	3.17717	-2.39755
C	0.09657	4.56646	-1.33070
C	0.41279	3.62596	-3.63785
C	0.00000	-1.74156	0.01941
C	1.32821	-1.38287	0.39785
C	1.37411	-1.38092	1.81446
C	0.07897	-1.70322	2.29050
C	-0.81194	-1.92813	1.19078
Si	-2.64392	-2.35623	1.46121
C	-3.87307	-1.12596	0.74654
C	-2.86329	-2.34656	3.34195
C	-3.05787	-4.08706	0.85276
S	-0.57796	-1.82510	-1.66770
O	-2.06323	-2.11836	-1.57345
C	0.22417	-3.40684	-2.26290
C	-0.09657	-4.56646	-1.33070
C	-0.41279	-3.62596	-3.63785
C	1.72722	-3.17717	-2.39755
H	-2.13522	1.11293	-0.26769
H	-2.22966	1.12264	2.42248
H	0.20824	1.72764	3.33228
H	3.90697	2.57179	3.58832
H	2.62878	1.37233	3.78514
H	2.24287	3.10007	3.83906
H	2.31021	4.82555	1.16003
H	3.12547	4.09070	-0.23721
H	4.02447	4.40475	1.26017
H	4.89052	1.49896	0.91358
H	3.71811	1.02081	-0.32874
H	3.80609	0.14201	1.22027
H	-1.95207	2.26617	-2.96280
H	-2.22075	3.11741	-1.42517
H	-2.16834	4.02059	-2.93923

H	-0.35110	4.42702	-0.34267
H	1.17567	4.67947	-1.21155
H	-0.30029	5.49549	-1.75492
H	0.18094	2.80350	-4.32302
H	0.02139	4.55015	-4.07514
H	1.49859	3.71070	-3.55366
H	2.13522	-1.11293	-0.26769
H	2.22966	-1.12264	2.42248
H	-0.20824	-1.72764	3.33228
H	-4.89052	-1.49896	0.91358
H	-3.71811	-1.02081	-0.32874
H	-3.80609	-0.14201	1.22027
H	-2.62878	-1.37233	3.78514
H	-2.24287	-3.10007	3.83906
H	-3.90697	-2.57179	3.58832
H	-2.31021	-4.82555	1.16003
H	-3.12547	-4.09070	-0.23721
H	-4.02447	-4.40475	1.26017
H	-1.17567	-4.67947	-1.21155
H	0.35110	-4.42702	-0.34267
H	0.30029	-5.49549	-1.75492
H	-0.18094	-2.80350	-4.32302
H	-1.49859	-3.71070	-3.55366
H	-0.02139	-4.55015	-4.07514
H	2.16834	-4.02059	-2.93923
H	2.22075	-3.11741	-1.42517
H	1.95207	-2.26617	-2.96280

R_P-2e·LiMe



atom	X	Y	Z
Fe	-0.09497	1.68543	-0.32283
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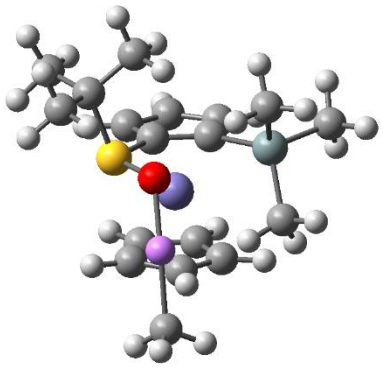
C	-1.01956	1.83118	1.53521
C	0.17889	2.59506	1.51534
C	0.06919	3.57168	0.48860
C	-1.20051	3.41028	-0.13213
C	-1.86876	2.33366	0.51324
C	1.51499	1.40013	-1.54399
C	0.34123	1.48720	-2.32920
C	-0.54459	0.45192	-1.92776
C	0.07238	-0.30758	-0.89702
C	1.35918	0.28669	-0.65537
O	1.88822	-0.83472	1.71662
C	3.66530	-1.33384	-0.24268
C	2.86652	-2.57027	-0.63095
C	4.71157	-1.67298	0.82274
C	4.31208	-0.66135	-1.45108
H	-1.22435	0.99866	2.20184
H	1.03440	2.43798	2.15843
H	0.82886	4.28736	0.20520
H	-1.57325	3.97915	-0.97293
H	-2.83743	1.93401	0.24693
H	2.36661	2.06506	-1.57751
H	-1.54143	0.28304	-2.30705
H	3.55192	-3.33803	-1.00546
H	2.13977	-2.35575	-1.41868
H	2.33739	-2.98002	0.23264
H	5.41199	-2.40907	0.41602
H	4.24194	-2.09852	1.71271
H	5.28564	-0.78946	1.12057
H	4.83369	0.26081	-1.17280
H	3.58060	-0.42908	-2.22922
H	5.05318	-1.34298	-1.88039
H	0.13086	2.24475	-3.07106
S	-0.54441	-1.79081	-0.13562
C	-2.31509	-1.61545	-0.31598
C	-3.07724	-1.23107	0.78641
C	-2.92898	-1.93458	-1.52781
C	-4.46020	-1.13828	0.65631
H	-2.58561	-1.03164	1.73673
C	-4.30946	-1.82799	-1.64947
H	-2.32677	-2.27101	-2.36594
C	-5.07444	-1.42609	-0.55806
H	-5.05731	-0.84522	1.51408
H	-4.78864	-2.07159	-2.59260
H	-6.15351	-1.35132	-0.65197

Li	0.15774	-1.10082	2.36022
C	-1.25368	-1.00493	3.80545
H	-2.09533	-0.28909	3.80551
H	-1.72341	-1.99345	3.95911
H	-0.71712	-0.79465	4.74815

R_P-2f·LiMe



atom	X	Y	Z
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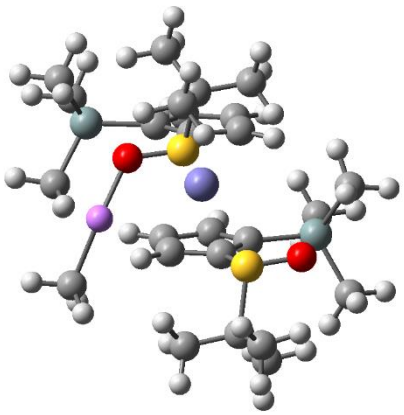
Si	0.19355	2.47502	-0.40222
C	2.24523	-0.69193	1.47016
C	2.01982	-2.05179	1.12655
C	2.82656	-2.36723	0.00010
C	3.55480	-1.19921	-0.35614
C	3.19273	-0.16712	0.55079
C	-0.04742	-1.60412	-1.53794
C	0.89767	-1.06328	-2.44076
C	1.04888	0.31236	-2.13609
C	0.19964	0.68493	-1.04455
C	-0.48618	-0.53420	-0.69584
C	1.01826	2.71945	1.26823
C	1.21211	3.45063	-1.66033
C	-1.52916	3.22873	-0.36908
O	-1.67874	0.45130	1.45752
C	-3.28994	-0.89764	-0.24213
C	-3.52946	0.35375	-1.07329
C	-4.29785	-0.99760	0.90603
C	-3.32291	-2.16230	-1.09886
H	1.76414	-0.16434	2.28567
H	1.32989	-2.71921	1.62471
H	2.85347	-3.31541	-0.51942
H	4.23223	-1.10283	-1.19352
H	3.55702	0.84997	0.52562
H	-0.35403	-2.63830	-1.47066
H	1.73933	0.98015	-2.63108
H	0.88628	3.76321	1.57737
H	2.09466	2.53355	1.21020
H	0.62498	2.08932	2.06951
H	0.79598	3.39132	-2.67154
H	2.25455	3.11748	-1.70337
H	1.22449	4.50785	-1.37292
H	-2.13364	2.78396	0.42452
H	-2.05686	3.10750	-1.32029
H	-1.44691	4.30375	-0.17251
H	-4.52093	0.29112	-1.53476
H	-2.78966	0.45602	-1.87191
H	-3.49926	1.24942	-0.45191
H	-5.30735	-1.06619	0.48880
H	-4.25101	-0.11679	1.55013
H	-4.12610	-1.88851	1.51922
H	-3.05693	-3.05471	-0.52228
H	-2.65806	-2.08773	-1.96218
H	-4.34116	-2.30343	-1.47489

H	1.44621	-1.61577	-3.19104
Li	-0.85686	0.50536	3.10653
C	0.48492	0.26083	4.56528
H	0.87678	-0.76636	4.65498
H	1.37227	0.91180	4.48864
H	0.04567	0.48942	5.55081

***R*P,*R*P-2f·LiMe**



atom	X	Y	Z
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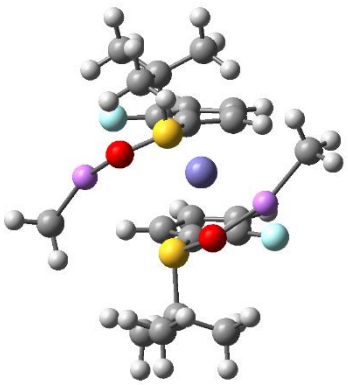
C	0.49193	-1.20421	1.61971
C	0.46371	-2.52672	1.11851
C	1.37556	-2.60012	0.03704
C	2.01662	-1.33597	-0.16944
Si	3.30558	-1.12981	-1.55582
C	3.59031	-2.87733	-2.21712
C	4.95452	-0.49622	-0.91190
C	2.75470	-0.08556	-3.01704
S	1.75713	1.23285	1.16831
O	2.66839	1.72173	0.02581
C	2.85612	1.21063	2.67554
C	2.01019	0.74140	3.85856
C	4.07635	0.32708	2.46469
C	3.26142	2.67676	2.85217
C	-1.59921	0.17664	-0.72189
C	-0.68167	0.15453	-1.81452
C	-0.68441	-1.16422	-2.33083
C	-1.56963	-1.94109	-1.54308
C	-2.15680	-1.13222	-0.51529
Si	-3.37892	-1.86338	0.74587
C	-2.83460	-1.78679	2.54440
C	-3.51585	-3.69140	0.27187
C	-5.09474	-1.11160	0.59466
S	-1.88023	1.61446	0.29897
O	-2.74363	1.13580	1.45274
C	-2.97798	2.66488	-0.78839
C	-4.27584	1.93634	-1.10245
C	-3.24666	3.89666	0.08159
C	-2.21427	3.04976	-2.05137
H	-0.13337	-0.79898	2.40176
H	-0.18270	-3.32214	1.46111
H	1.53458	-3.47567	-0.57605
H	4.35134	-2.84471	-3.00464
H	2.68720	-3.30971	-2.66129
H	3.94951	-3.56448	-1.44378
H	5.31991	-1.07667	-0.05891
H	4.87973	0.55197	-0.61418
H	5.70421	-0.57192	-1.70763
H	3.60117	0.01629	-3.70686
H	2.41822	0.92485	-2.77011
H	1.94733	-0.57137	-3.57296
H	1.07643	1.30679	3.94575
H	1.77310	-0.32273	3.79495
H	2.58076	0.89955	4.77921

H	3.79616	-0.71702	2.30070
H	4.66736	0.66886	1.61414
H	4.70708	0.37217	3.35908
H	2.38882	3.32372	2.99054
H	3.89032	2.76613	3.74335
H	3.83092	3.03641	1.99232
H	-0.09107	0.98924	-2.17296
H	-0.08153	-1.52587	-3.15157
H	-1.74032	-3.00126	-1.66746
H	-3.65055	-2.15697	3.17632
H	-2.62422	-0.75367	2.82759
H	-1.95827	-2.40867	2.75076
H	-2.55431	-4.21408	0.32644
H	-3.91718	-3.83119	-0.73766
H	-4.19841	-4.19586	0.96489
H	-5.42093	-1.00922	-0.44501
H	-5.11232	-0.12532	1.06267
H	-5.82183	-1.74979	1.10975
H	-4.80100	1.66257	-0.18625
H	-4.09780	1.03032	-1.68895
H	-4.92555	2.59543	-1.68867
H	-2.32346	4.44703	0.29069
H	-3.70946	3.61359	1.03064
H	-3.92690	4.57056	-0.44883
H	-2.75661	3.85601	-2.55662
H	-2.14021	2.21530	-2.75232
H	-1.20167	3.41115	-1.84566
Li	2.09001	2.80954	-1.33231
C	1.24805	3.53165	-2.99506
H	0.70044	4.48046	-2.87481
H	2.06911	3.75889	-3.69783
H	0.56991	2.86735	-3.55612

R_P,R_P-2d·2LiMe



atom	X	Y	Z
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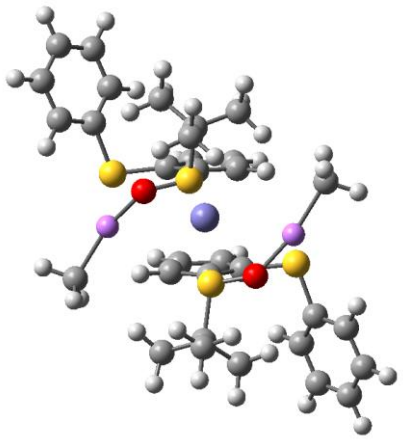
C	-1.59130	2.72519	0.80195
C	-1.66113	2.75264	-0.62169
C	-1.74431	1.41037	-1.04776
S	-1.79319	-1.22448	0.07702
O	-1.29375	-1.64551	-1.30935
C	-3.63121	-1.52655	0.04943
C	-4.20705	-0.95625	1.34368
C	-4.26351	-0.91625	-1.19424
C	-3.73955	-3.05440	0.02451
C	1.72348	0.55002	-0.08511
C	1.61665	1.37684	-1.24624
C	1.59112	2.72477	-0.80376
C	1.66098	2.75309	0.61986
C	1.74420	1.41110	1.04673
S	1.79308	-1.22452	-0.07613
O	1.29365	-1.64435	1.31058
C	3.63111	-1.52655	-0.04848
C	4.26355	-0.91541	1.19471
C	3.73947	-3.05439	-0.02251
C	4.20686	-0.95714	-1.34317
H	-1.51620	1.00637	2.26206
H	-1.48328	3.59083	1.44021
H	-1.62540	3.61753	-1.26820
H	-3.66149	-1.30743	2.22539
H	-4.19756	0.13667	1.34782
H	-5.24770	-1.28232	1.43876
H	-4.23438	0.17632	-1.17407
H	-3.76500	-1.26705	-2.10108
H	-5.31418	-1.22023	-1.24361
H	-3.27950	-3.50365	0.91022
H	-4.79691	-3.33620	0.01329
H	-3.26360	-3.47051	-0.86711
H	1.51626	1.00497	-2.26278
H	1.48327	3.58999	-1.44262
H	1.62543	3.61838	1.26586
H	3.76530	-1.26576	2.10186
H	4.23424	0.17714	1.17391
H	5.31429	-1.21918	1.24401
H	3.27947	-3.50424	-0.90794
H	3.26347	-3.46989	0.86937
H	4.79682	-3.33619	-0.01101
H	5.24745	-1.28343	-1.43817
H	4.19752	0.13578	-1.34797

H	3.66112	-1.30880	-2.22457
Li	-0.47003	-0.79920	-2.74711
C	0.97458	-0.37882	-4.09314
H	2.00993	-0.68479	-3.85762
H	0.72366	-0.95094	-5.00401
H	1.05031	0.66768	-4.44058
Li	0.47109	-0.79544	2.74776
C	-0.97359	-0.37554	4.09384
H	-2.00839	-0.68335	3.85827
H	-0.72208	-0.94634	5.00535
H	-1.05100	0.67121	4.44015
F	-1.85354	1.00201	-2.32163
F	1.85343	1.00361	2.32094

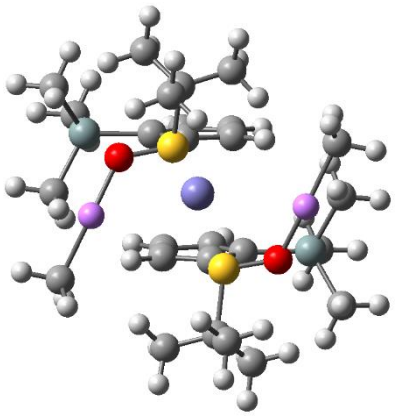
R_P,R_P-2e·2LiMe



atom	X	Y	Z
Fe	0.00000	0.00000	1.38188
C	-1.14258	1.29512	0.24819
C	-1.98527	0.32609	0.86997
C	-1.82132	0.44912	2.27288
C	-0.87286	1.46965	2.52620
C	-0.42944	2.00584	1.27897
S	-1.02876	1.38644	-1.53187
O	0.17939	2.25922	-1.87681
C	-2.50606	2.41997	-2.00515
C	-3.76707	1.70180	-1.53256
C	-2.38042	3.82269	-1.43066
C	-2.43223	2.44112	-3.53574
C	1.14258	-1.29512	0.24819
C	1.98527	-0.32609	0.86997
C	1.82132	-0.44912	2.27288
C	0.87286	-1.46965	2.52620
C	0.42944	-2.00584	1.27897
S	1.02876	-1.38644	-1.53187
O	-0.17939	-2.25922	-1.87681
C	2.50606	-2.41997	-2.00515
C	2.38042	-3.82269	-1.43066
C	2.43223	-2.44112	-3.53574
C	3.76707	-1.70180	-1.53256
H	-2.61554	-0.39137	0.34622
H	-2.30106	-0.17467	3.01438
H	-0.48393	1.76874	3.48990
H	-3.77304	0.64076	-1.80150
H	-3.89816	1.78267	-0.45070
H	-4.63218	2.17651	-2.00688
H	-2.45851	3.82380	-0.34088
H	-1.43123	4.28432	-1.71083
H	-3.19396	4.44034	-1.82573
H	-2.52446	1.43443	-3.95528
H	-3.26156	3.04329	-3.91925
H	-1.49603	2.88521	-3.88340
H	2.61554	0.39137	0.34622
H	2.30106	0.17467	3.01438
H	0.48393	-1.76874	3.48990
H	1.43123	-4.28432	-1.71083
H	2.45851	-3.82380	-0.34088
H	3.19396	-4.44034	-1.82573
H	2.52446	-1.43443	-3.95528
H	1.49603	-2.88521	-3.88340
H	3.26156	-3.04329	-3.91925
H	4.63218	-2.17651	-2.00688
H	3.89816	-1.78267	-0.45070

H	3.77304	-0.64076	-1.80150
Li	1.91880	2.31396	-1.26425
C	3.90163	1.94644	-1.20277
H	4.31140	1.57418	-2.15824
H	4.33861	2.95692	-1.09086
H	4.40251	1.35040	-0.42029
Li	-1.91880	-2.31396	-1.26425
C	-3.90163	-1.94644	-1.20277
H	-4.31140	-1.57418	-2.15824
H	-4.33861	-2.95692	-1.09086
H	-4.40251	-1.35040	-0.42029
S	-0.89526	-3.17594	1.15572
C	-0.05449	-4.75059	1.03345
C	-0.57664	-5.69685	0.15381
C	1.04117	-5.07232	1.83265
C	0.00000	-6.96012	0.07304
H	-1.42924	-5.44482	-0.46936
C	1.62562	-6.32905	1.73030
H	1.44019	-4.34179	2.52882
C	1.10568	-7.27675	0.85383
H	-0.41192	-7.69335	-0.61313
H	2.48501	-6.57179	2.34763
H	1.56046	-8.25949	0.78212
S	0.89526	3.17594	1.15572
C	0.05449	4.75059	1.03345
C	0.57664	5.69685	0.15381
C	-1.04117	5.07232	1.83265
C	0.00000	6.96012	0.07304
H	1.42924	5.44482	-0.46936
C	-1.62562	6.32905	1.73030
H	-1.44019	4.34179	2.52882
C	-1.10568	7.27675	0.85383
H	0.41192	7.69335	-0.61313
H	-2.48501	6.57179	2.34763
H	-1.56046	8.25949	0.78212

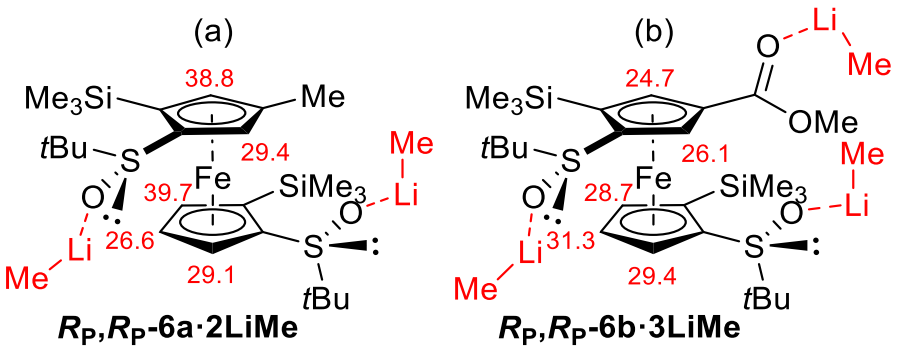
***R*P,*R*P-2f·2LiMe**



atom	X	Y	Z
Fe	0.00000	0.00000	1.31350
C	-1.70407	-0.43413	0.22952
C	-1.08349	-1.63991	0.68039
C	-1.07700	-1.59461	2.09320
C	-1.66088	-0.36810	2.49422
C	-2.06579	0.39517	1.35096
Si	-2.89488	2.09595	1.59210
C	-3.22277	2.21148	3.44996
C	-4.55067	2.23487	0.71610
C	-1.83951	3.58263	1.13938
S	-1.86055	-0.12676	-1.51068
O	-2.28442	1.34992	-1.64568
C	-3.36436	-1.10539	-2.02075
C	-3.09010	-2.58037	-1.74127
C	-4.60738	-0.60843	-1.30043
C	-3.45977	-0.84791	-3.52788
C	1.70407	0.43413	0.22952
C	1.08349	1.63991	0.68039
C	1.07700	1.59461	2.09320
C	1.66088	0.36810	2.49422
C	2.06579	-0.39517	1.35096
Si	2.89488	-2.09595	1.59210
C	1.83951	-3.58263	1.13938
C	3.22277	-2.21148	3.44996
C	4.55067	-2.23487	0.71610
S	1.86055	0.12676	-1.51068
O	2.28442	-1.34992	-1.64568
C	3.36436	1.10539	-2.02075
C	4.60738	0.60843	-1.30043
C	3.45977	0.84791	-3.52788
C	3.09010	2.58037	-1.74127
H	-0.69237	-2.42931	0.04972
H	-0.65518	-2.34121	2.75079
H	-1.74966	-0.03368	3.51801
H	-3.74234	3.15188	3.66447
H	-2.30045	2.21279	4.04107
H	-3.85725	1.39694	3.81477
H	-5.22023	1.39833	0.93698
H	-4.41592	2.29550	-0.36580
H	-5.04865	3.15296	1.04814
H	-2.43927	4.48595	1.30409
H	-1.49755	3.61128	0.10120
H	-0.95654	3.66647	1.77971
H	-2.12119	-2.91278	-2.12613
H	-3.13399	-2.80499	-0.67288
H	-3.86683	-3.17255	-2.23596

H	-4.52352	-0.73745	-0.21800
H	-4.79910	0.44321	-1.51594
H	-5.46804	-1.19232	-1.64356
H	-2.57349	-1.21551	-4.05462
H	-4.32913	-1.38278	-3.92220
H	-3.58748	0.21584	-3.74541
H	0.69237	2.42931	0.04972
H	0.65518	2.34121	2.75079
H	1.74966	0.03368	3.51801
H	2.43927	-4.48595	1.30409
H	1.49755	-3.61128	0.10120
H	0.95654	-3.66647	1.77971
H	2.30045	-2.21279	4.04107
H	3.85725	-1.39694	3.81477
H	3.74234	-3.15188	3.66447
H	5.22023	-1.39833	0.93698
H	4.41592	-2.29550	-0.36580
H	5.04865	-3.15296	1.04814
H	4.79910	-0.44321	-1.51594
H	4.52352	0.73745	-0.21800
H	5.46804	1.19232	-1.64356
H	2.57349	1.21551	-4.05462
H	3.58748	-0.21584	-3.74541
H	4.32913	1.38278	-3.92220
H	3.86683	3.17255	-2.23596
H	3.13399	2.80499	-0.67288
H	2.12119	2.91278	-2.12613
Li	-1.22613	2.74676	-2.14979
C	0.00000	4.32925	-2.15781
H	0.65632	4.43626	-3.03692
H	-0.67825	5.20036	-2.20312
H	0.64065	4.52048	-1.28094
Li	1.22613	-2.74676	-2.14979
C	0.00000	-4.32925	-2.15781
H	-0.65632	-4.43626	-3.03692
H	0.67825	-5.20036	-2.20312
H	-0.64065	-4.52048	-1.28094

I) Selected pK_a Values of R_P,R_P-6a and R_P,R_P-6b (as complexes with two and three LiMe, respectively)

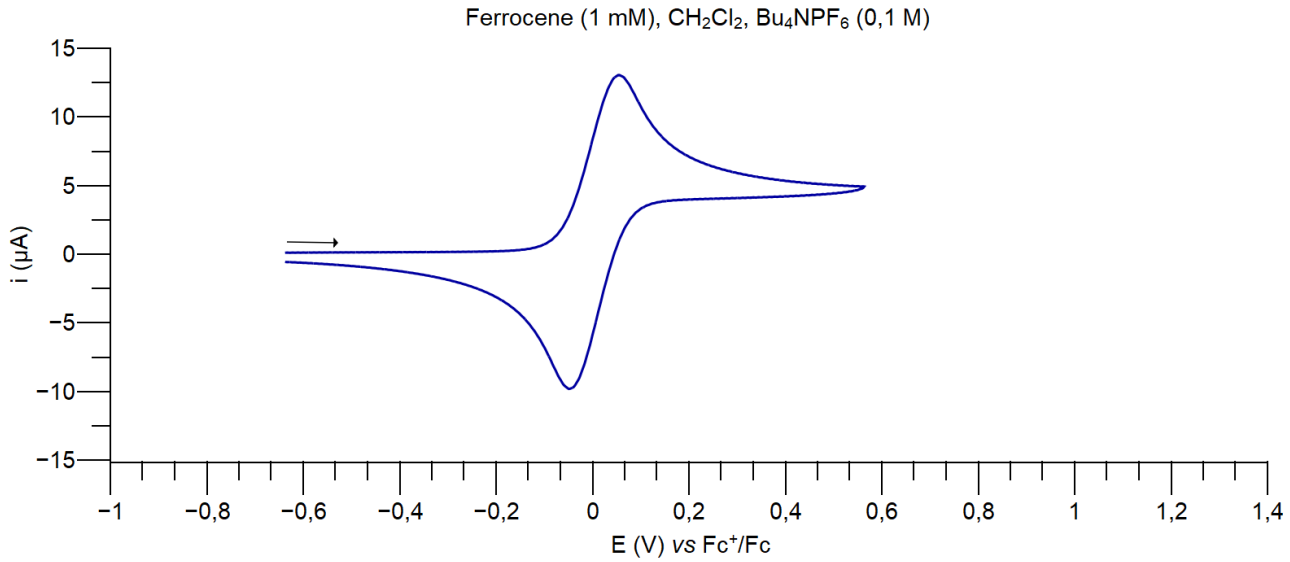


R_P,R_P-6a·2LiMe R_P,R_P-6b·3LiMe

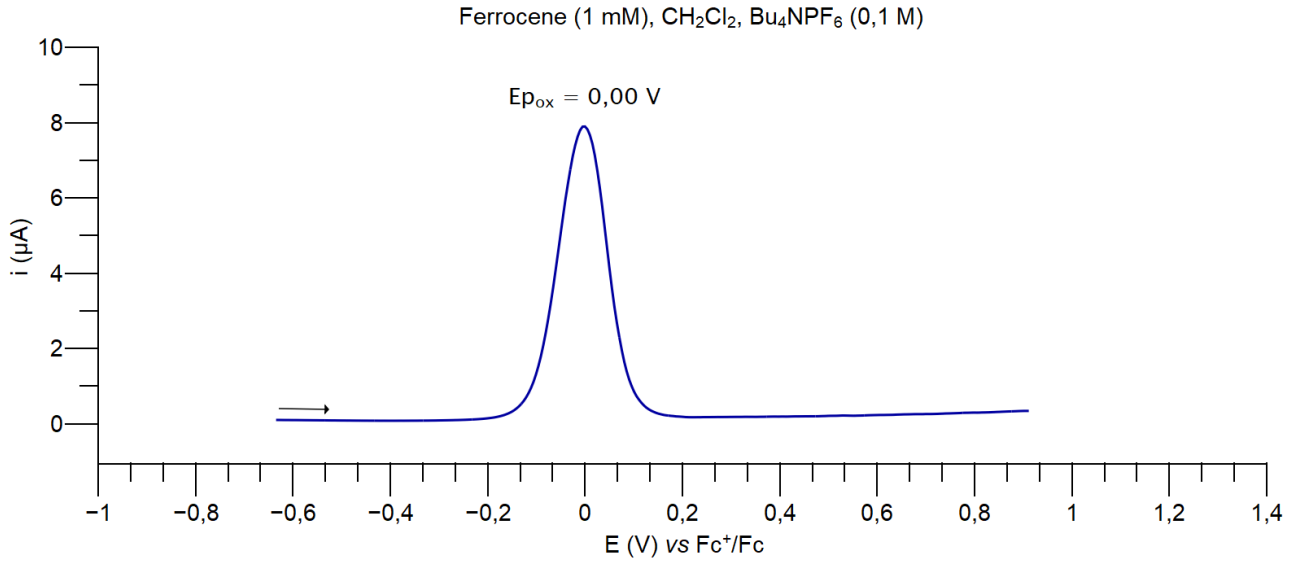
J) Voltammograms

Ferrocene

Cyclic voltammetry

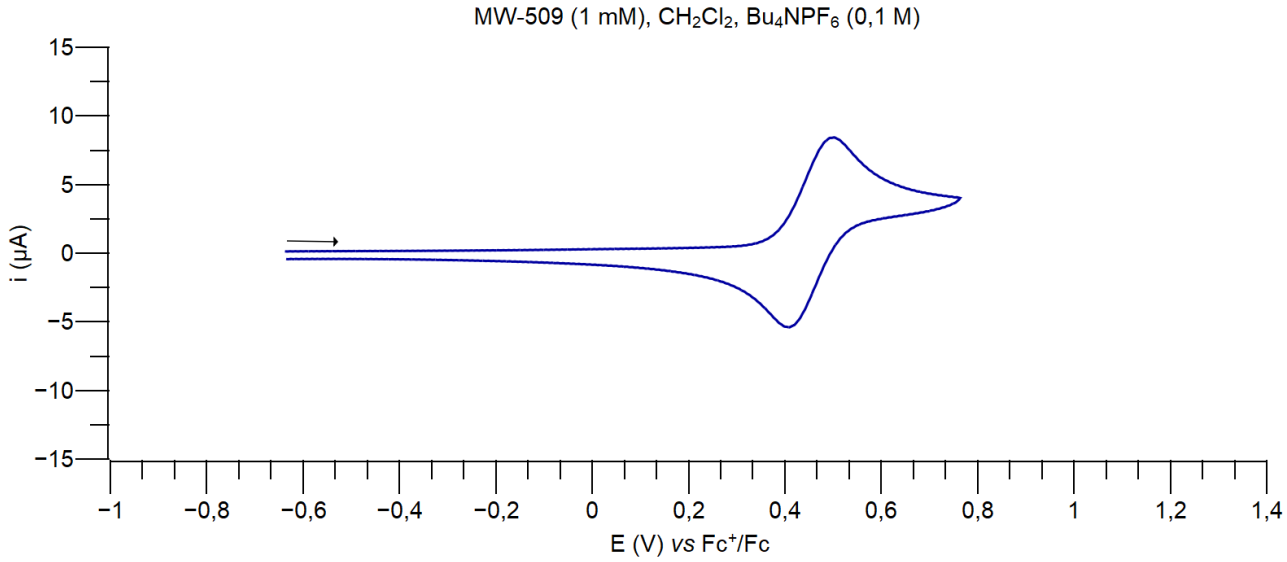


Differential pulse voltammetry

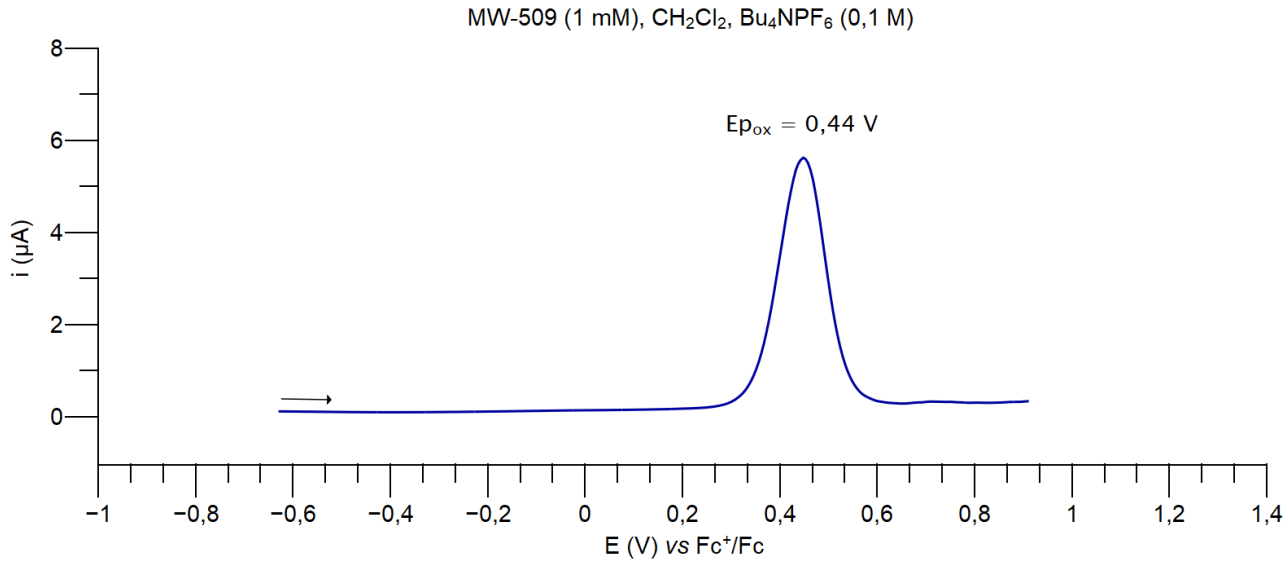


(*R*,*R*)-*S*,*S*'-Di-*tert*-butylferrocene-1,1'-disulfoxide (1)

Cyclic voltammetry

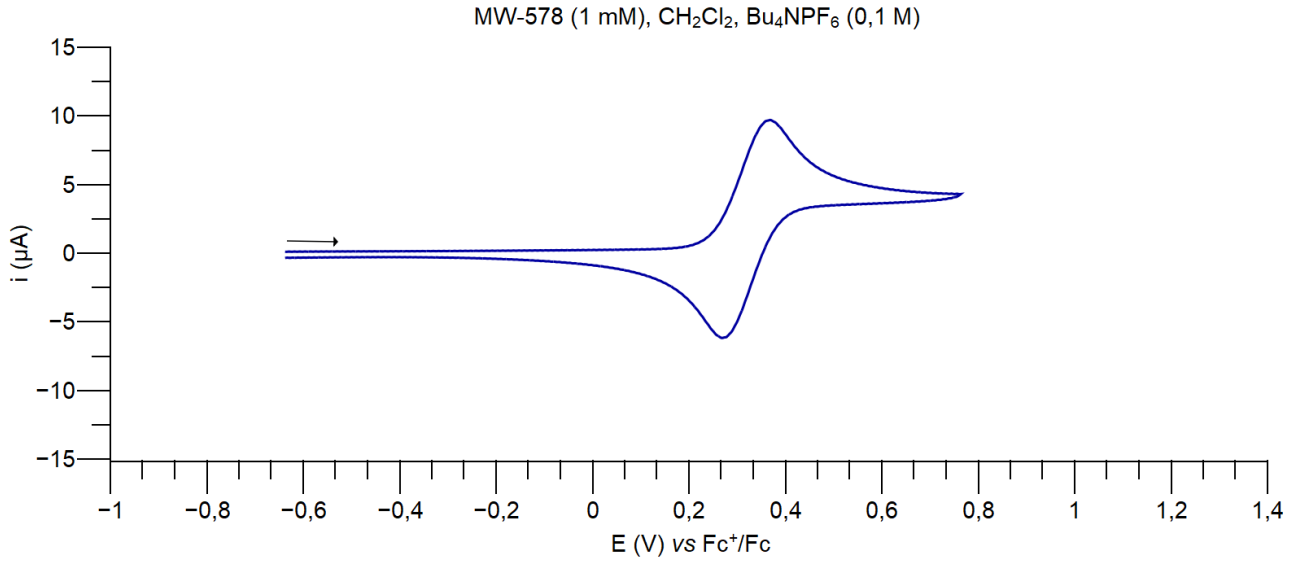


Differential pulse voltammetry

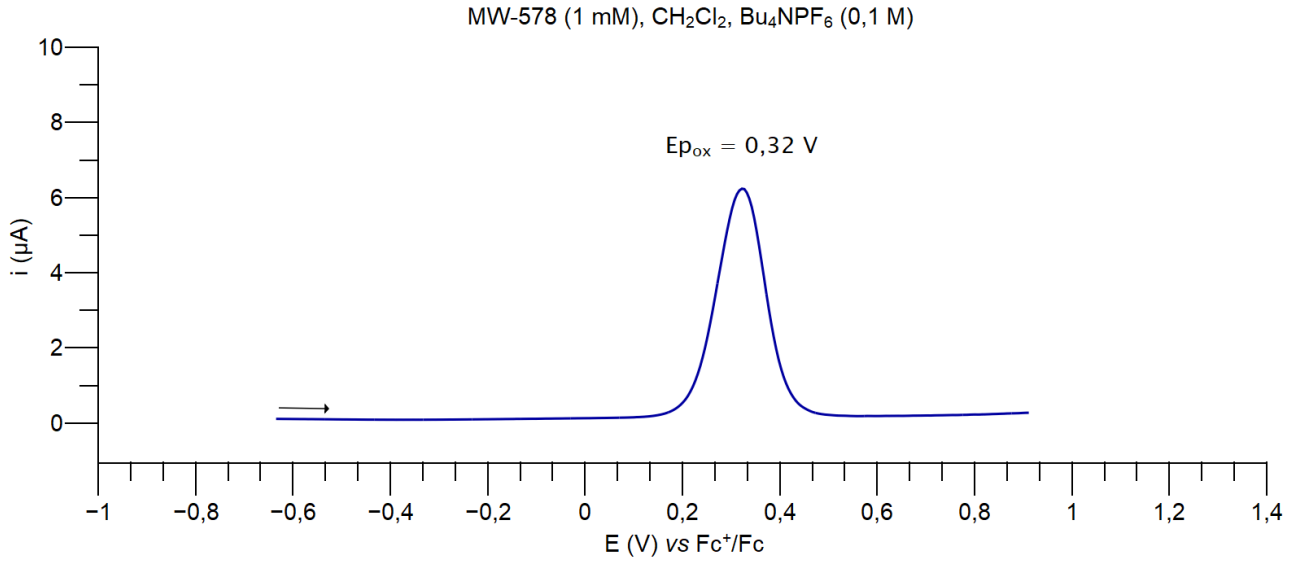


(*R*,*R*$_P$)-*S*-*tert*-Butyl-2-[(α,α-diphenyl)hydroxymethyl]ferrocenesulfoxide (*R*$_P$-2c)

Cyclic voltammetry

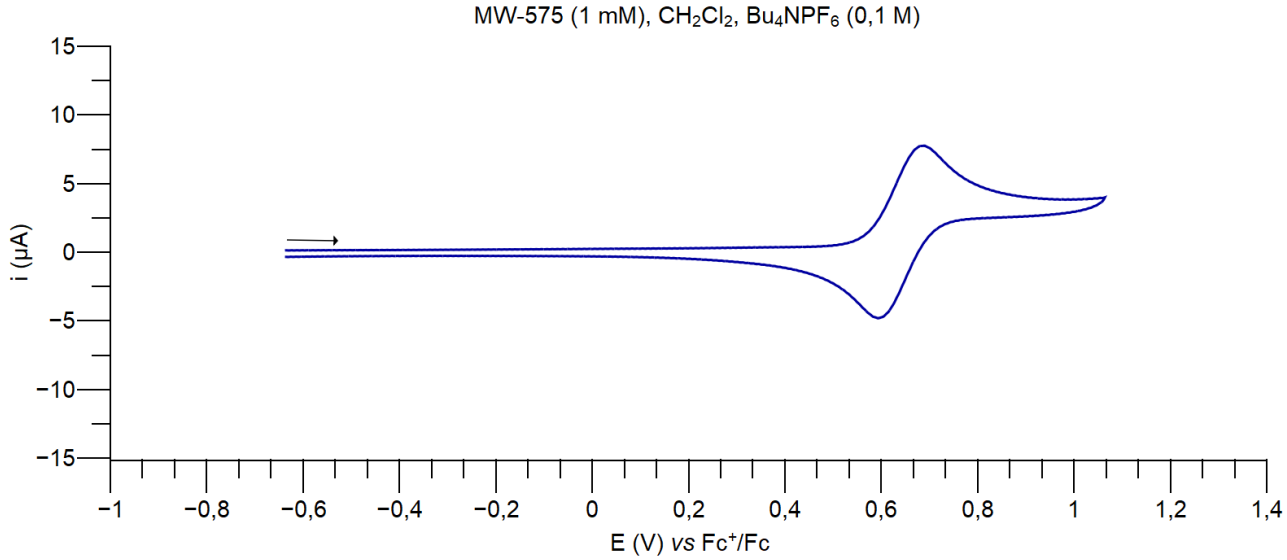


Differential pulse voltammetry

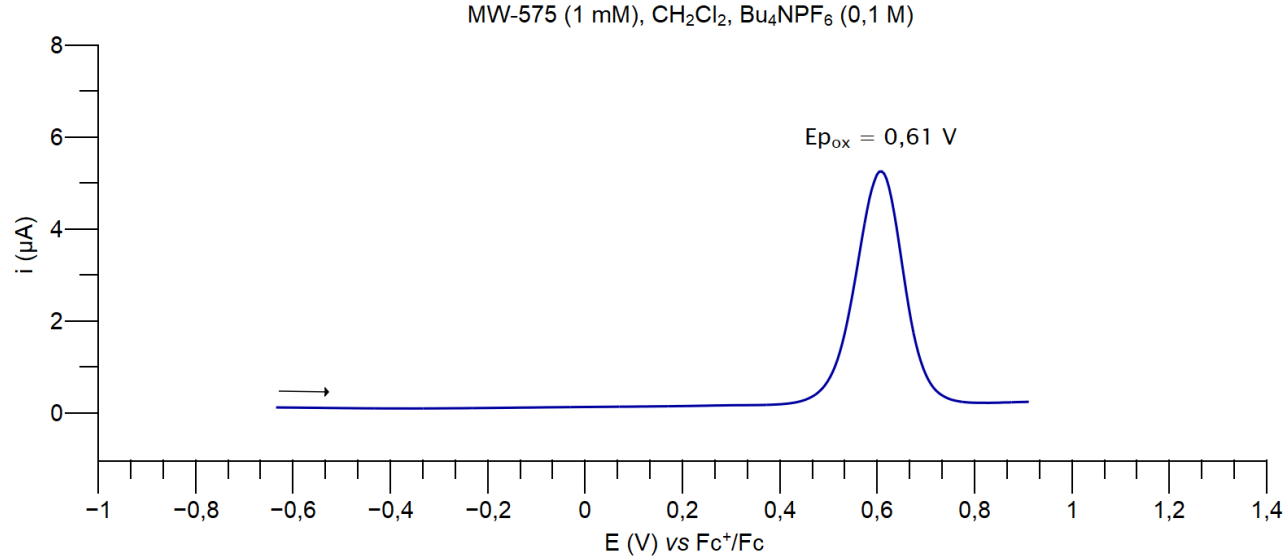


(*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S*'-Di-*tert*-butyl-2,2'-di((α,α-diphenyl)hydroxymethyl)ferrocene-1,1'-disulfoxide (*R*$_P$,*R*$_P$-2c)

Cyclic voltammetry

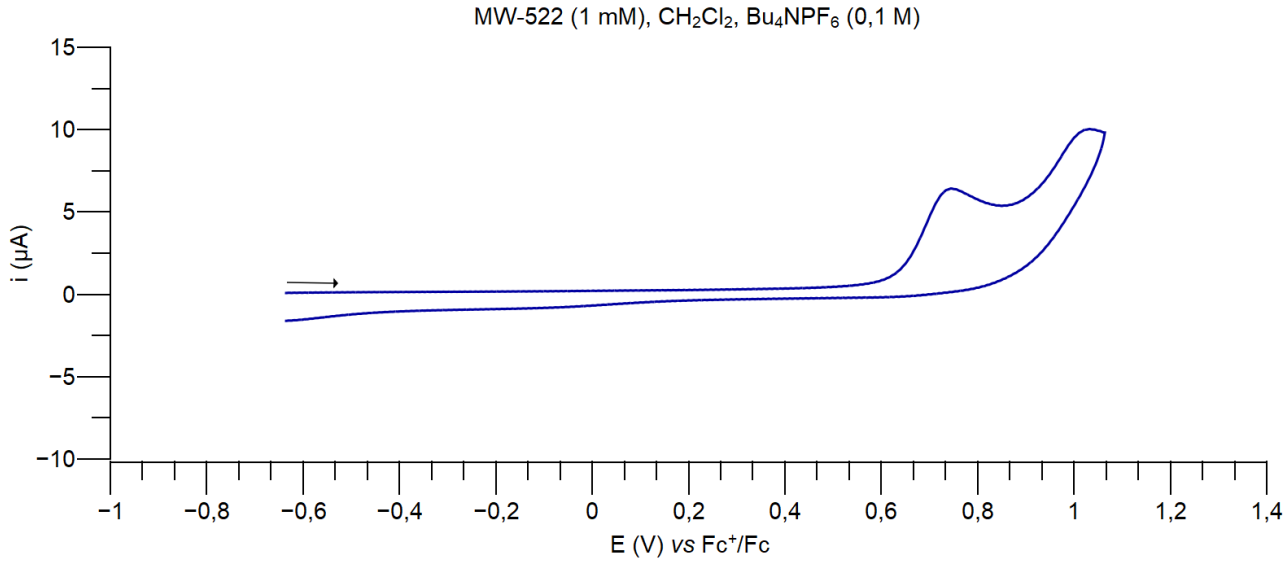


Differential pulse voltammetry

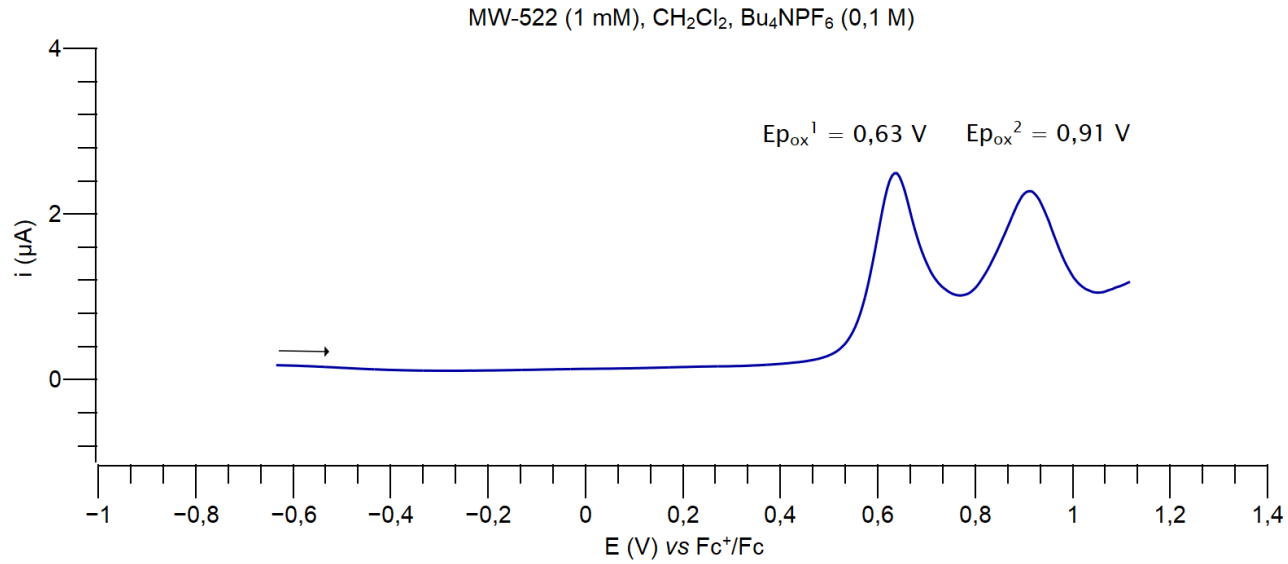


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-difluoroferrocene-1,1'-disulfoxide (*R*P,*R*P-2d)

Cyclic voltammetry

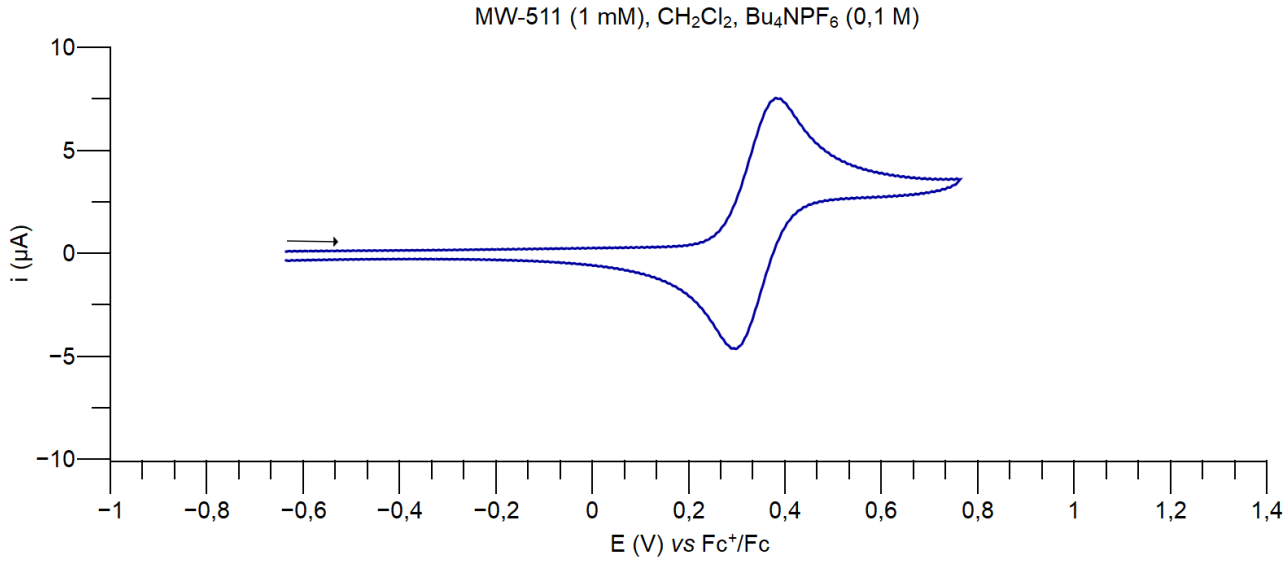


Differential pulse voltammetry

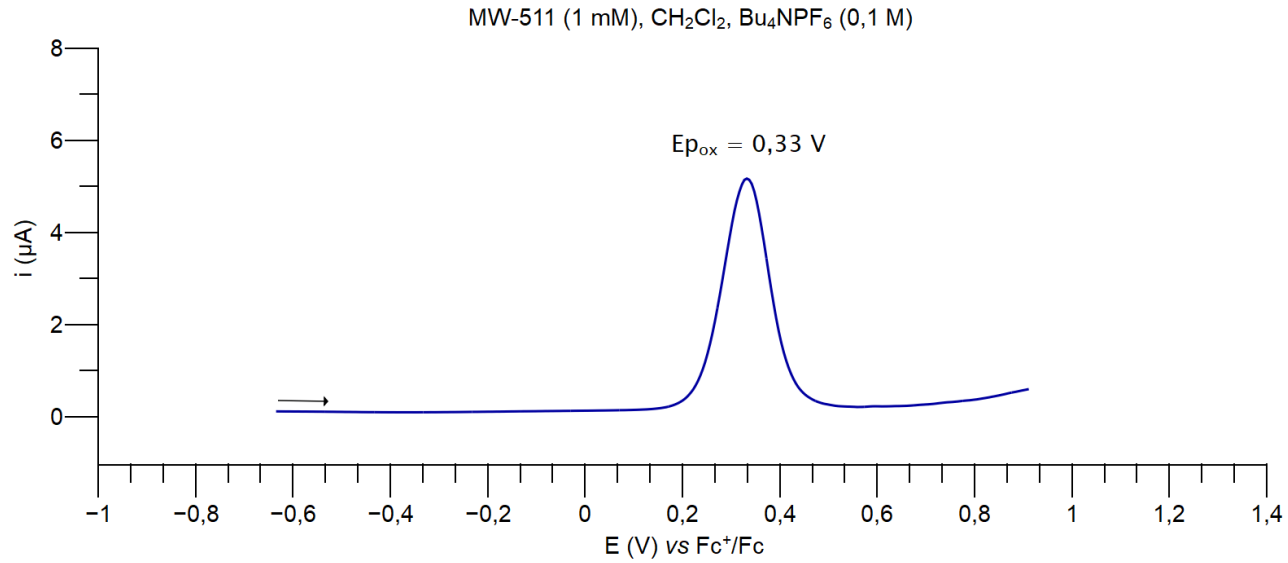


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-2,2'-di(phenylthio)ferrocene-1,1'-disulfoxide (*R*P,*R*P-2e)

Cyclic voltammetry

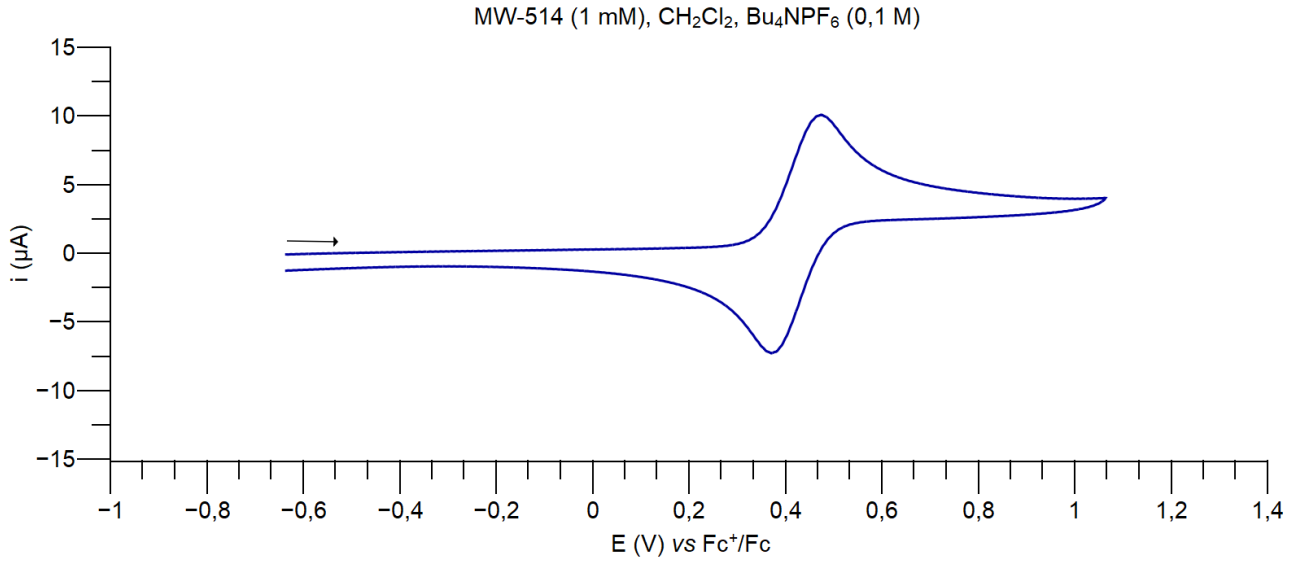


Differential pulse voltammetry

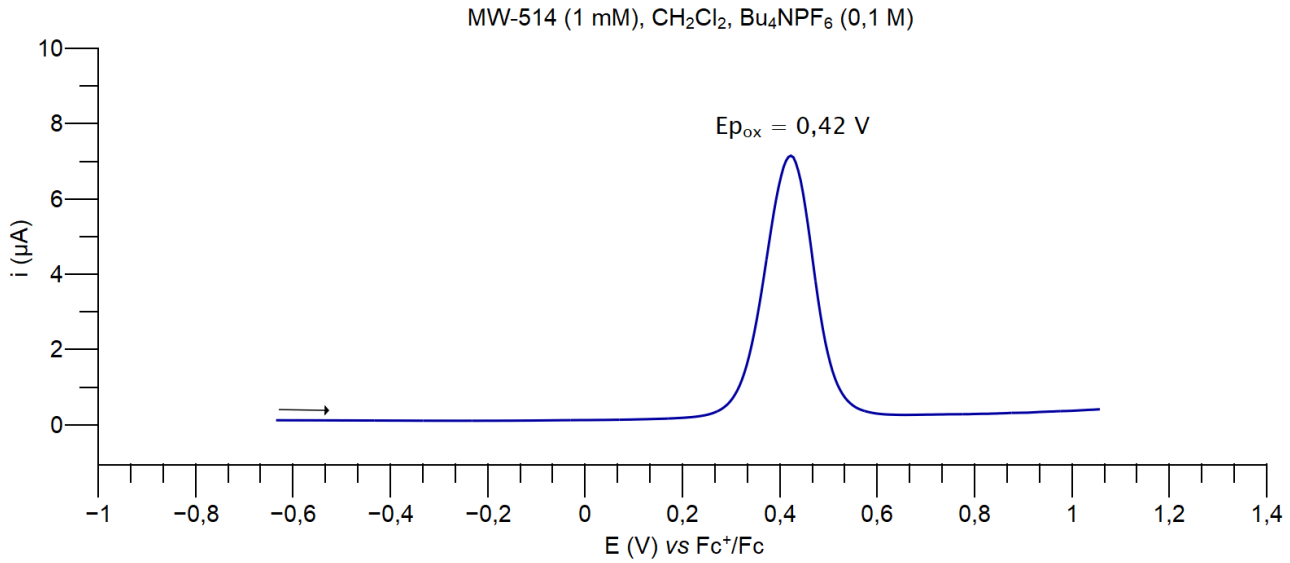


(*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S*'-Di-*tert*-butyl-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*$_P$,*R*$_P$-2f)

Cyclic voltammetry

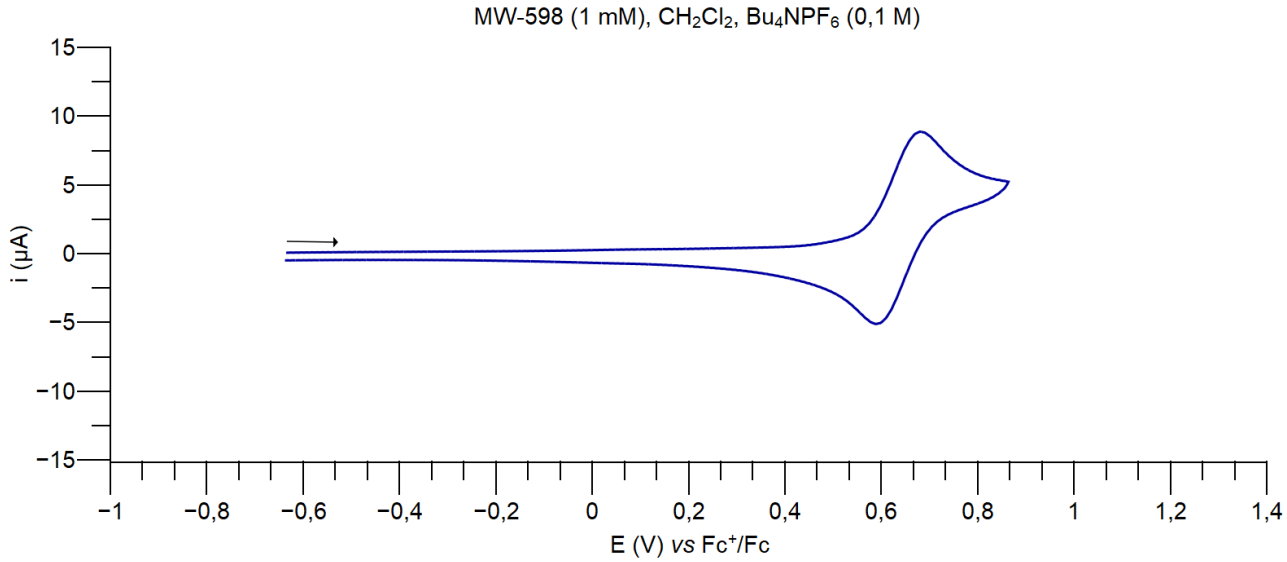


Differential pulse voltammetry

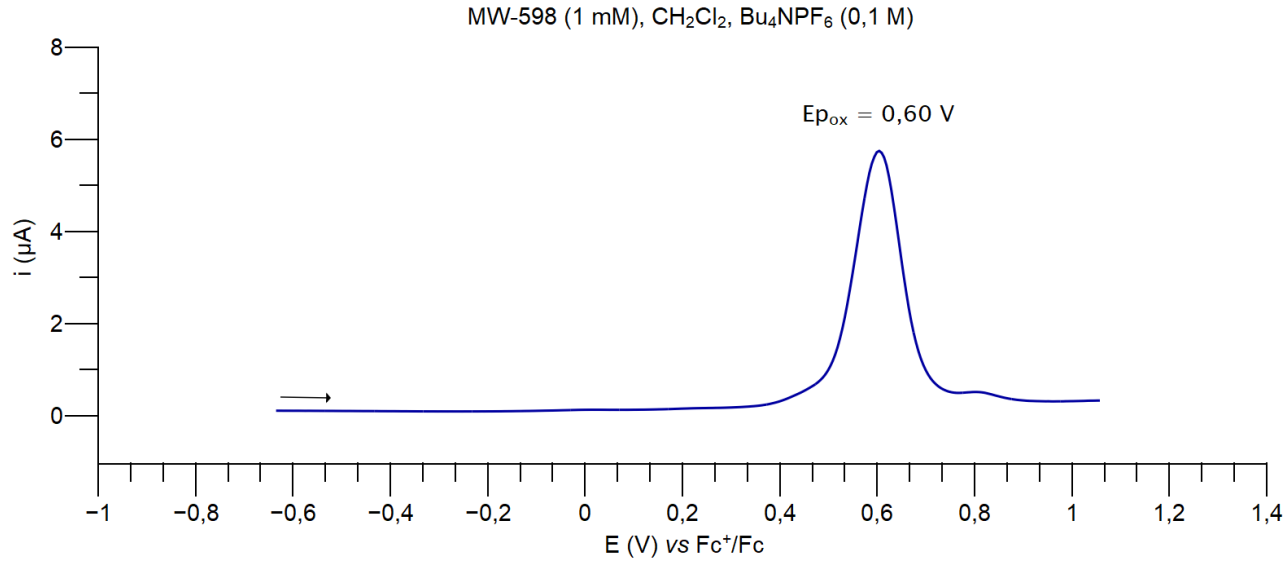


(*R*,*R*,*R*P,*R*P)-*S*,*S*'-Di-*tert*-butyl-4-(methoxycarbonyl)-2,2'-bis(trimethylsilyl)ferrocene-1,1'-disulfoxide (*R*P,*R*P-6b)

Cyclic voltammetry

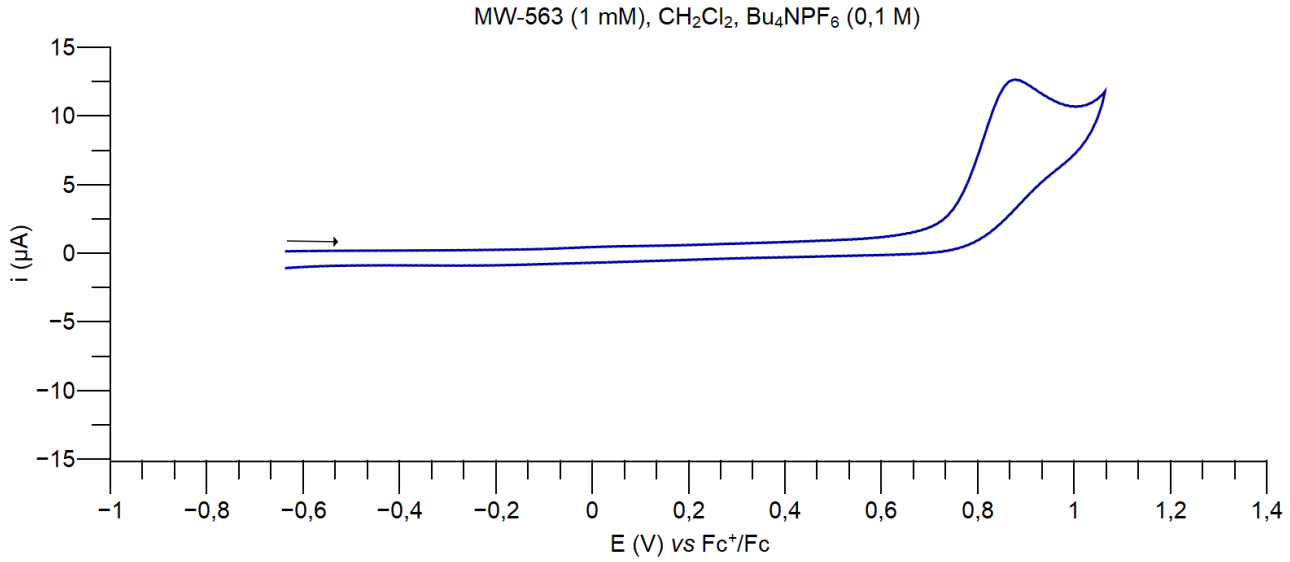


Differential pulse voltammetry

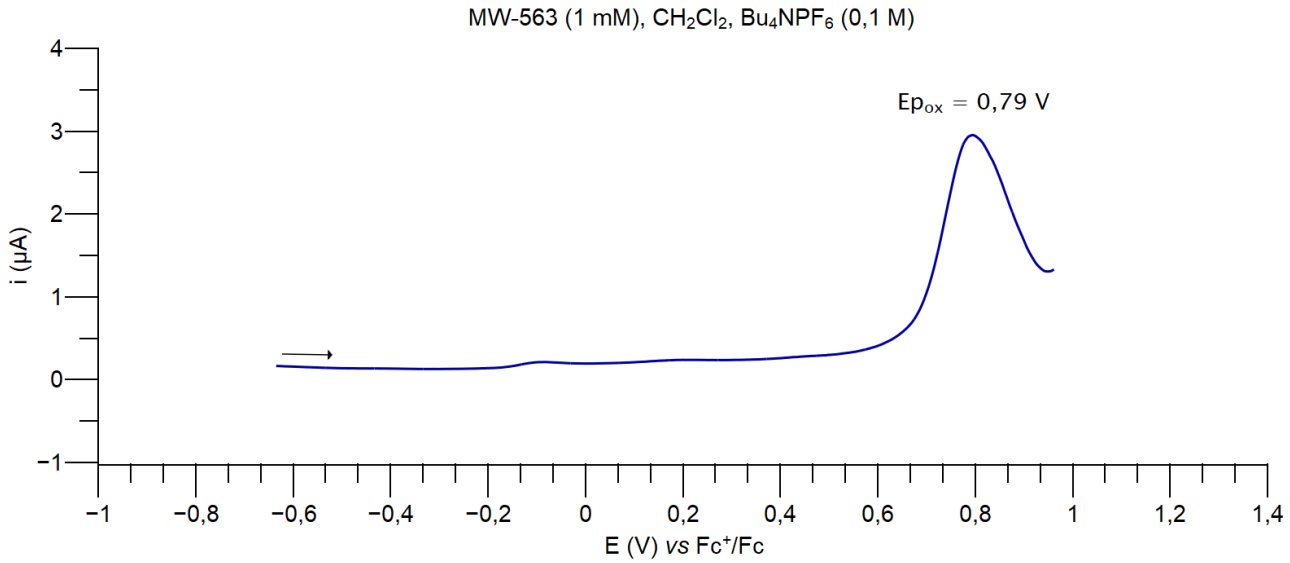


(*R*,*R*,S_P,S_P)-*S*,*S*'-Di-*tert*-butyl-2,2'-difluoro-3,3'-diiodoferrocene-1,1'-disulfoxide (S_P,S_P-8c)

Cyclic voltammetry

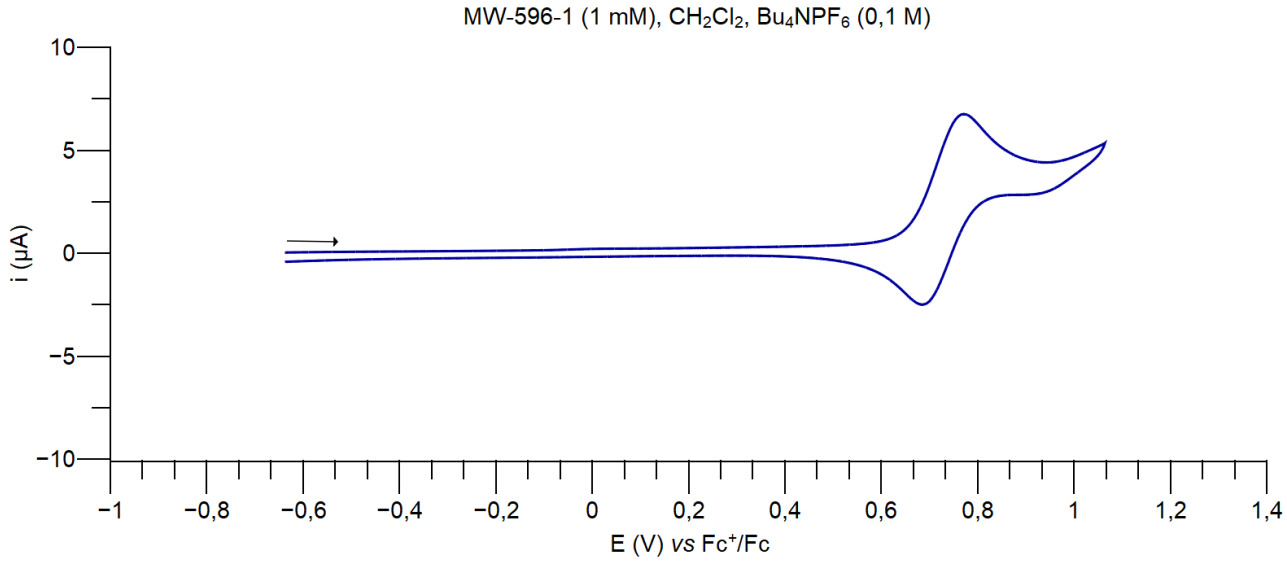


Differential pulse voltammetry

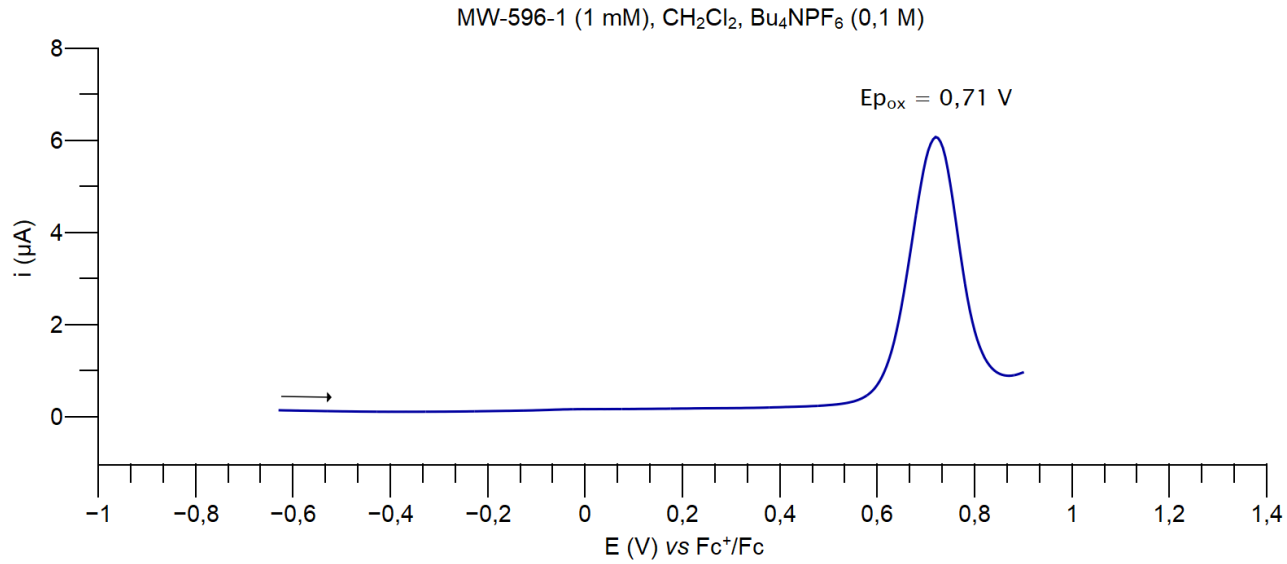


(*R*,*R*,*R*$_P$,*R*$_P$)-*S*,*S*'-Di-*tert*-butyl-3,3'-diiodoferrocene-1,1'-disulfoxide (*R*$_P$,*R*$_P$-6'h-desi)

Cyclic voltammetry

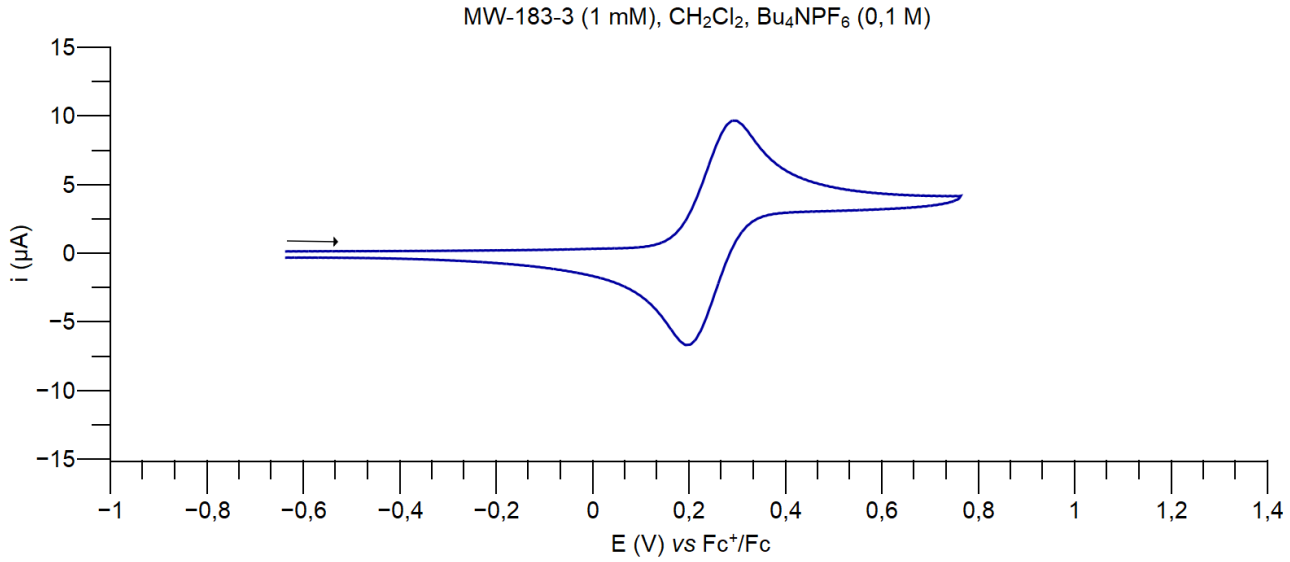


Differential pulse voltammetry

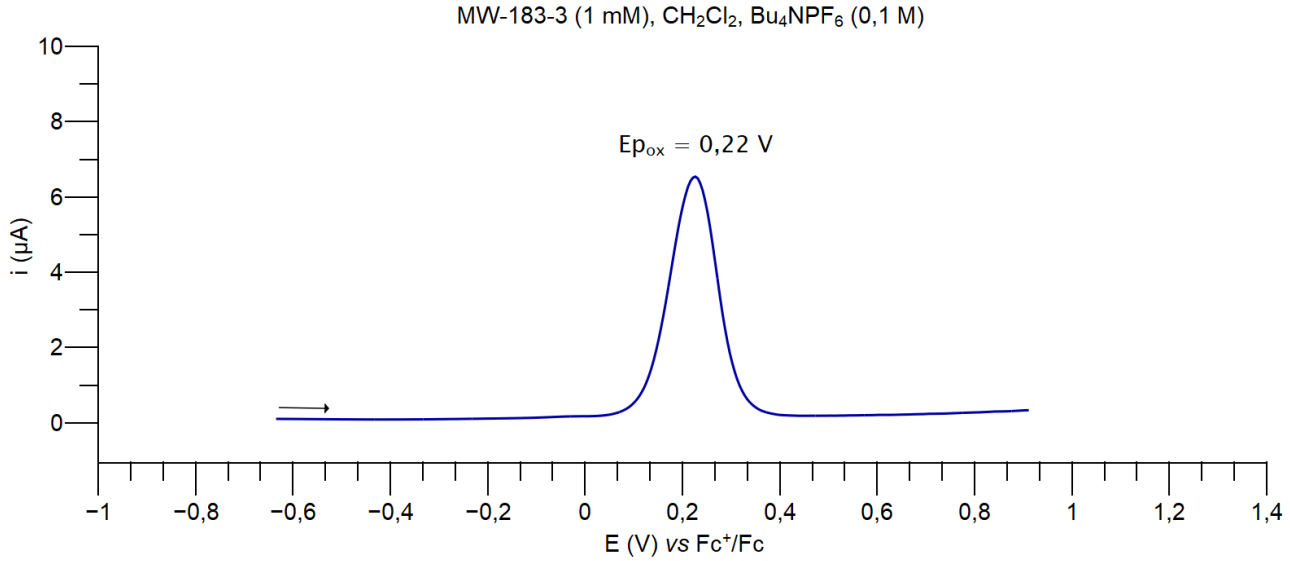


(*S*)-*S*-*tert*-Butylferrocenesulfoxide (11)

Cyclic voltammetry

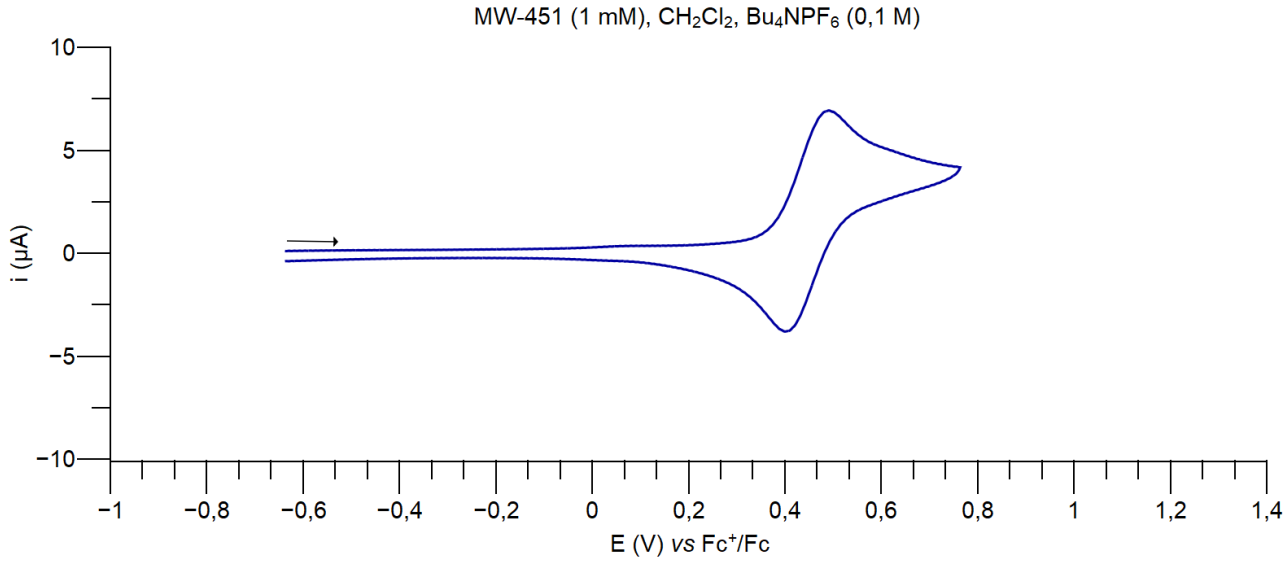


Differential pulse voltammetry

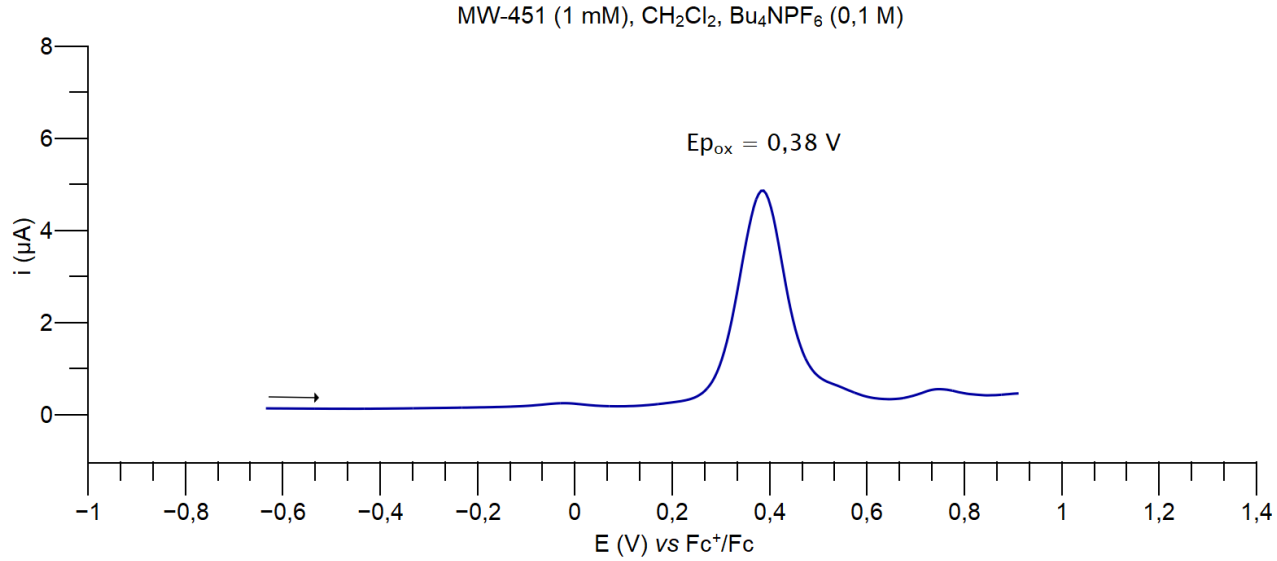


(*R*,*R*)-*S*,*S*'-Di-*tert*-butylferrocene-1,2-disulfoxide (*R*,*R*-1)

Cyclic voltammetry

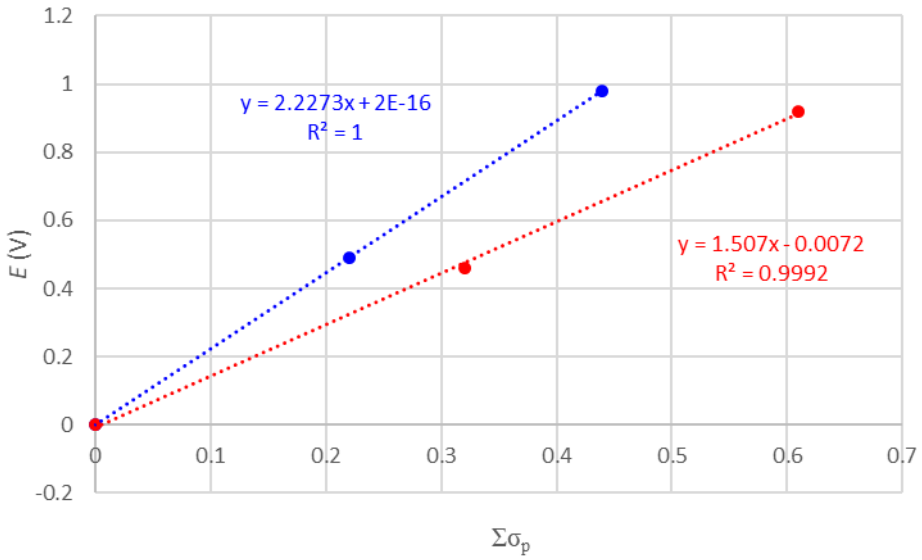


Differential pulse voltammetry

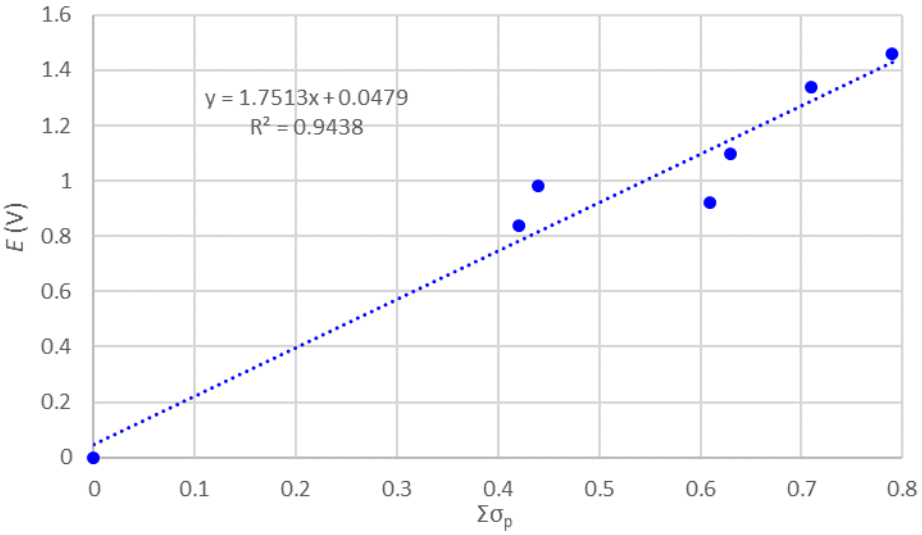


K) Additional Plots

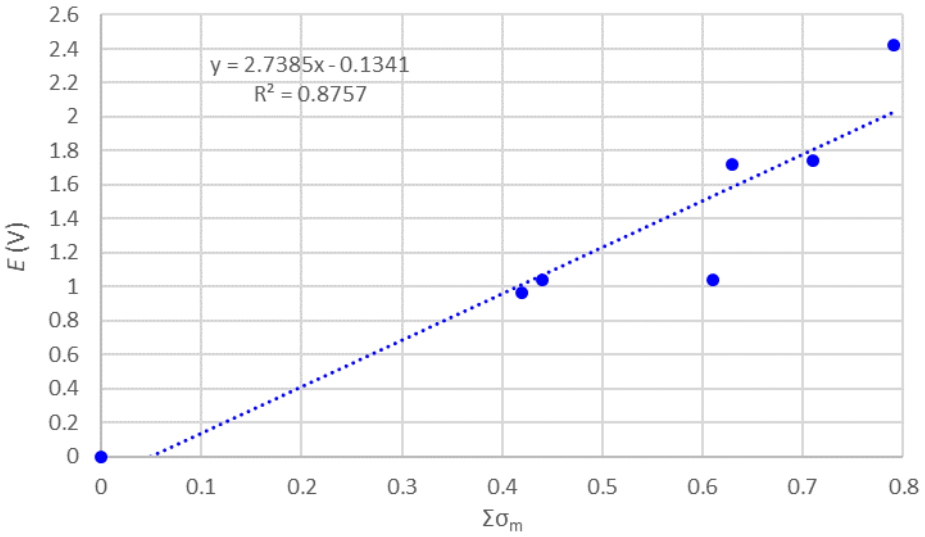
Plot SI1: *E* (V) *vs*. $\Sigma\sigma_p$ for ferrocene, compounds **11** and **12** (red) and for ferrocene, **11** and **1** (blue).



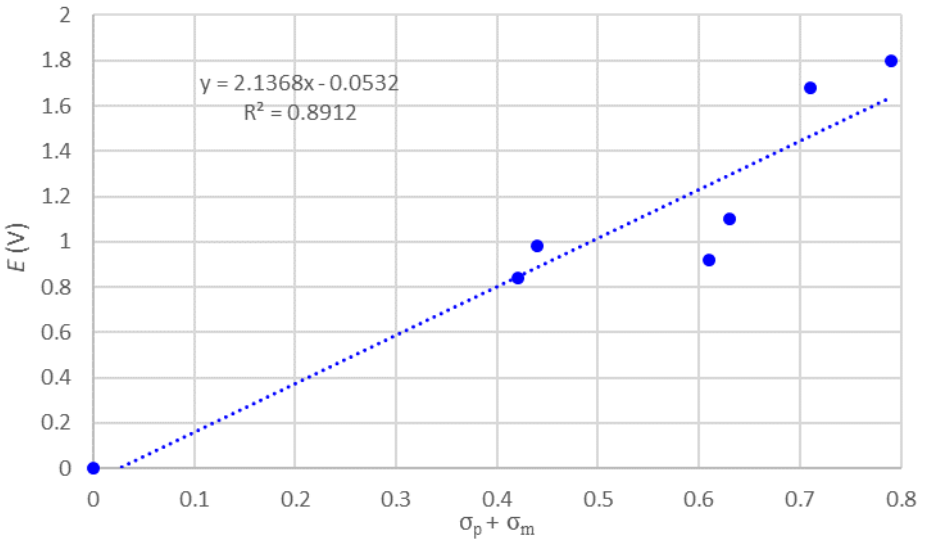
Plot SI2: *E* (V) *vs*. $\Sigma\sigma_p$ for ferrocene and compounds **1**, **2c**, **2d**, **2f**, **8c** and ***R*P,*R*P-6'h-desi**.



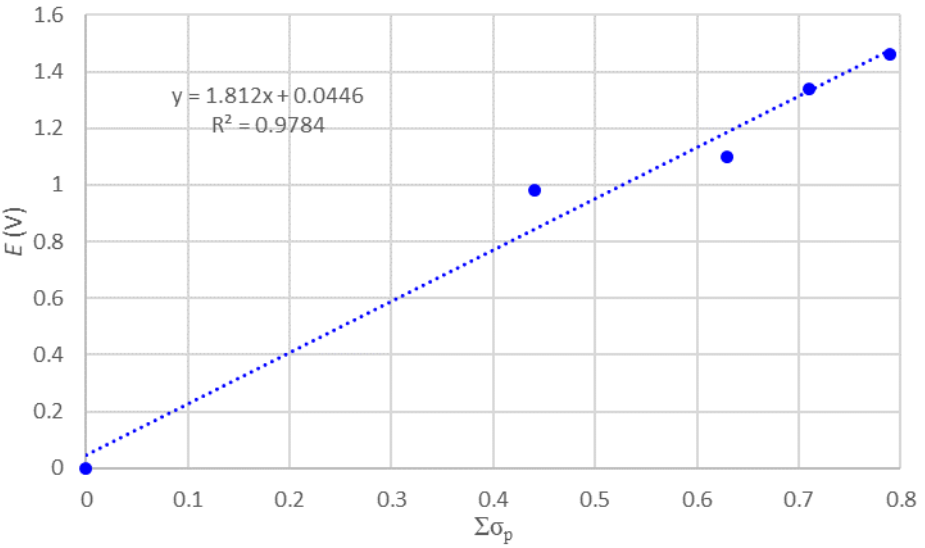
Plot SI3: *E* (V) *vs*. $\Sigma\sigma_m$ for ferrocene and compounds **1**, **2c**, **2d**, **2f**, **8c** and ***R*P,*R*P-6'h-desi**.



Plot SI4: *E* (V) *vs*. $\sigma_p + \sigma m$ for ferrocene and compounds **1**, **2c**, **2d**, **2f**, **8c** and ***R*P,*R*P-6'h-desi**.



Plot SI5: *E* (V) *vs*. $\Sigma\sigma_p$ for ferrocene and compounds **1**, **2d**, **8c** and ***R*P,*R*P-6'h-desi**.



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