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Supplementary Information

Enantiopure ferrocene-1,2-disulfoxides: synthesis and reactivity

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A) Compound Synthesis

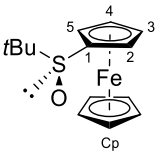
General

All reactions were carried out in Schlenk tubes under a dry argon atmosphere. THF was freshly distilled from sodium-benzophenone. All alkyllithiums were titrated before use.[1] H-TMP was distilled over CaH_2 under vacuum and stored over KOH pellets. rt refers to room temperature (25 °C). Column chromatography separations were achieved on silica gel (40-63 μm). All Thin Layer Chromatographies (TLC) were performed on 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. ^{1}H and ^{13}C{^{1}H} Nuclear Magnetic Resonance (NMR) spectra were recorded either on a Bruker Avance III HD at 500 MHz and 126 MHz respectively, or on a Bruker Avance III spectrometer at 300 MHz and 75.4 MHz respectively. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ^{13}C chemical shifts are relative to the central peak of the solvent signal.[2] Cp refers to the unsubstituted cyclopentadienyl ring of ferrocene. Optical rotations were determined on a Perkin Elmer 341 polarimeter (589 nm; 20 °C); the concentrations (*c*) are given in g/100 mL $CHCl_3$.

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.

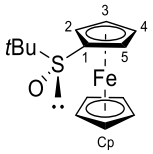
Procedures and analyses of the compounds

(*S*)-*S*-*tert*-Butylferrocenesulfoxide (*S*-FcSO*t*Bu) was prepared as reported previously, by reacting ferrocenyllithium[3] with (*S*,*S*)-2,2-diphenyl-1,2-dihydroxypropyl 2-*O*-*tert*-butylsulfinate.[4] To ferrocene (0.41 g, 2.2 mmol) in THF (3.3 mL) at 0 °C was added dropwise a 1.6 M pentane solution of *t*BuLi (1.1 mL, 1.8 mmol) in order to generate a solution of ferrocenyllithium.[3] After 10 min at 0 °C, this solution was cannulated onto a solution of (*S*,*S*)-2,2-diphenyl-1,2-dihydroxypropyl 2-*O*-*tert*-butylsulfinate[5, 6] (0.28 g, 0.83 mmol) in THF (1 mL) at rt. The reaction was checked by TLC; when conversion was over, the reaction mixture was quenched by addition of 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 80:20; Rf = 0.18) and recrystallization from 1:1 Et_2O-hexane led to ***S*-FcSO*t*Bu** in 70% yield (0.17 g) and >99% ee as a yellow solid: mp 160-162 °C (lit.[4] 156-157 °C); IR (ATR) ν 811, 1009, 1103, 1169, 1183, 1255, 1294, 1360, 1384, 1454, 1597, 1678, 2920, 3074 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 9H, *t*Bu), 4.35 (td, 1H, *J* = 2.5 and 1.3 Hz, H4), 4.37 (s, 5H, Cp), 4.39-4.41 (m, 2H, H3 and H5), 4.69 (dt, 1H, *J* = 2.6 and 1.4 Hz, H2) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.9 ($3CH_3$, C*Me*$_3$), 55.1 (C, *C*Me$_3$), 65.5 (CH, C2), 69.5 (CH, C3), 69.8 (CH, C5), 70.1 (CH, C4), 70.2 (5CH, Cp), 86.6 (C, C1, *C*-SO*t*Bu) ppm; $[\alpha]_D$ +319 (*c* 1) (lit.[4] +339 (*c* 0.8, $CHCl_3$)). Starting from ferrocene (73 g, 391 mmol) and (*S*,*S*)-2,2-diphenyl-1,2-dihydroxypropyl 2-*O*-*tert*-butylsulfinate (49 g, 148 mmol), ***S*-FcSO*t*Bu** was isolated in 79% yield (34 g).

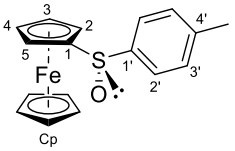


(*R*)-*S*-*tert*-Butylferrocenesulfoxide (*R*-FcSO*t*Bu) was prepared by modifying a reported procedure.[7] A 0.26 M THF solution of *tert*-butylmagnesium bromide (3.8 mL) was added to a solution of (R_C,S_S)-5,5-dimethyl-4-phenyl-*N*-tosyl-1,2,3-oxathiazolidine-2-oxide[7] (0.385 g, 1.0 mmol) in THF (3 mL) at –78 °C. The mixture was stirred for 1 h at this temperature, and then for 1 h at rt in order to allow the sulfinate to be formed. In a second Schlenk containing ferrocene (0.28 g, 1.5 mmol) and potassium *tert*-butoxide (56 mg, 0.50 mmol) in THF (4.5 mL), ferrocenyllithium was prepared[3] by adding dropwise at –78 °C a 1.6 M pentane solution of *t*BuLi (1.25 mL, 2.0 mmol). The resulting mixture was stirred at –78 °C for 15 min, warmed to rt and stirred at rt for 1 h. The formed ferrocenyllithium was

next cannulated onto the sulfinate at –78 °C. After stirring at –78 °C for 15 min and at rt for 1 h, the reaction was quenched by addition of 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 60:40; Rf = 0.35) gave ***R*-FcSO*t*Bu** in 60% yield (0.175 g) and 97% ee as a yellow solid. Its analyses were comparable to the ones of (*S*)-*S*-*tert*-butylferrocenesulfoxide. ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9H, *t*Bu), 4.34 (td, 1H, *J* = 2.5 and 1.3 Hz, H4), 4.36 (s, 5H, Cp), 4.39-4.40 (m, 2H, H3 and H5), 4.68 (dt, 1H, *J* = 2.6 and 1.4 Hz, H2) ppm, similar to that reported previously.[8] $[\alpha]_D$ -320 (*c* 1) (lit.[9] -355 (*c* 0.5, $CHCl_3$)).

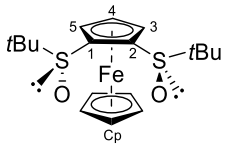


(*S*)-*S*-(4-Tolyl)ferrocenesulfoxide (*S*-FcSO-*p*-Tol) was prepared as follows.[10] To ferrocene (1.5 g, 8.0 mmol) and *t*BuOK (0.11 g, 0.96 mmol) in THF (67 mL) at –50 °C was added dropwise a 1.6 M pentane solution of *t*BuLi (10 mL, 16 mmol). After 1.5 h at this temperature, the reaction mixture was stirred for another 1 h at rt. The red solution was cooled to –55 °C and cannulated dropwise into a solution of (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-4-toluenesulfinate[11] (2.36 g, 8.0 mmol) in THF (40 mL). After 1 h stirring at this temperature, the reaction mixture was warmed to rt. Addition of water (20 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. This was purified by chromatography over silica gel (eluent: petroleum ether-EtOAc 60:40; Rf = 0.40) and next recrystallized from 50:50 heptane-EtOAc to afford ***S*-FcSO-*p*-Tol** in 48% yield (1.25 g) and >99% ee as a yellow solid: mp 148-150 °C (lit.[12] 142-144 °C); IR (ATR) ν 704, 808, 1045, 1082, 1107, 1159, 1402, 1492, 2977 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H, Me), 4.32 (td, 1H, *J* = 2.4 and 1.3 Hz, H4), 4.35-4.38 (m, 2H, H3 and H5), 4.37 (s, 5H, Cp), 4.61 (dt, 1H, *J* = 2.6 and 1.4 Hz, H2), 7.25 (d, 2H, *J* = 8.2 Hz, H3' and H5'), 7.52 (d, 2H, *J* = 8.2 Hz, H2' and H6') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 21.5 (CH_3, Me), 65.4 (CH, C2), 68.0 (CH, C3 or C5), 70.0 (CH, C3, C4 or C5), 70.0 (5CH, Cp), 70.1 (CH, C3, C4 or C5), 94.8 (C, C1, *C*-SOtolyl), 124.5 (2CH, C2' and C6'), 129.8 (2CH, C3' and C5'), 141.1 (C, C4'), 143.1 (C, C1') ppm; $[\alpha]_D$ = +319 (*c* 1) (lit.[13] +305 (c 0.5, $CHCl_3$). The ^{1}H NMR data are similar to those reported previously.[8]

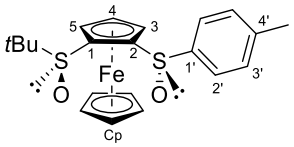


General procedure A: Deprotolithiation of (*R*)- or (*S*)-*S*-*tert*-butylferrocenesulfoxide (*R*-FcSO*t*Bu or *S*-FcSO*t*Bu) using *t*BuLi followed by electrophilic trapping.[14] To a solution of the enantiopure *S*-*tert*-butylferrocenesulfoxide (0.29 g, 1.0 mmol) in THF (12.5 mL) at –80 °C was added dropwise a 1.6 M pentane solution of *t*BuLi (0.94 mL, 1.5 mmol), and the reaction mixture was stirred at this temperature for 1.5 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 30 min before being warmed to rt. Addition of 1 M HCl (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, which was purified by chromatography over silica gel (eluent given in the product description).

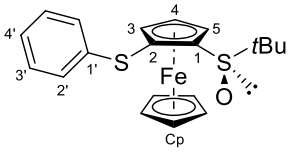
(*R*,*R*)-*S*,*S'*-Di-*tert*-butylferrocene-1,2-disulfoxide (***R*,*R*-1**) was prepared by adapting the general procedure A to (*R*)-*S*-*tert*-butylferrocenesulfoxide (***R*-FcSO*t*Bu**) and using (*R*)-*S*-*tert*-butyl-*tert*-butanethiosulfinate[15] (0.29 g) as the electrophile in THF (1.5 mL). It was isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.11) in 46% yield (0.12 g) as a brownish-yellow solid: mp 156-158 °C; IR (ATR) ν 822, 1044, 1108, 1169, 1361, 1412, 1457, 2964 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 9H, *t*Bu), 1.37 (s, 9H, *t*Bu), 4.53 (s, 5H, Cp), 4.60 (dd, 1H, *J* = 2.6 and 1.4 Hz, H3), 4.64 (t, 1H, *J* = 2.7 Hz, H4), 4.96 (dd, 1H, *J* = 2.6 and 1.4 Hz, H5) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.2 (3CH_3, C*Me*$_3$), 24.3 (3CH_3, C*Me*$_3$), 57.3 (C, *C*Me$_3$), 57.4 (C, *C*Me$_3$), 67.9 (CH, C5), 68.8 (CH, C3), 71.2 (CH, C4), 72.9 (5CH, Cp), 92.2 (C, *C*-SO*t*Bu), 92.5 (C, *C*-SO*t*Bu) ppm; $[\alpha]_D$ -126 (*c* 1). Anal. Calcd for $C_{18}H_{26}FeO_2S_2$ (394.37): C, 54.82; H, 6.65; S, 16.26. Found: C, 54.76; H, 6.90; S, 16.58%.



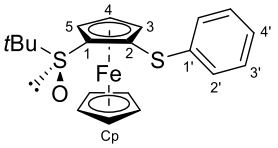
(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-*S'*-tolylferrocene-1,2-disulfoxide (***S*,*S*,*R*$_P$-2**) was prepared by adapting the general procedure A to (*S*)-*S*-*tert*-butylferrocenesulfoxide (***S*-FcSO*t*Bu**) and using (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-4-toluenesulfinate (0.44 g) in THF (1.5 mL). It was isolated (eluent: petroleum ether-EtOAc 40:60; Rf = 0.22) in 88% yield (0.38 g) as a brownish-yellow solid: mp 192-194 °C; IR (ATR) ν 705, 808, 822, 1012, 1043, 1082, 1107, 1152, 1183, 1361, 1410, 1451, 1594, 2983, 3518 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.79 (s, 9H, *t*Bu), 2.33 (s, 3H, Me), 4.46 (dd, 1H, *J* = 2.2 and 1.6 Hz, H5), 4.59 (s, 5H, Cp), 4.59-4.60 (m, 1H, H4), 5.27 (dd, 1H, *J* = 2.3 and 1.5 Hz, H3), 7.17 (d, 2H, *J* = 8.0 Hz, H3' and H5'), 7.66 (d, 2H, *J* = 8.1 Hz, H2' and H6') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 21.5 (CH_3, Me), 22.9 ($3CH_3$, C*Me*$_3$), 56.9 (C, *C*Me$_3$), 67.1 (CH, C3), 69.7 (CH, C5), 71.1 (CH, C4), 72.6 (5CH, Cp), 87.6 (C, C1, *C*-SO*t*Bu), 95.1 (C, C2, *C*-SOtolyl), 127.2 (2CH, C2' and C6'), 129.5 (2CH, C3' and C5'), 141.5 (C, C4', *C*-Me), 145.1 (C, C1') ppm; $[\alpha]_D$ +291 (*c* 1). Anal. Calcd for $C_{21}H_{24}FeO_2S_2$ (428.39): C, 58.88; H, 5.65; S, 14.97. Found: C, 58.43; H, 5.36; S, 14.49%.



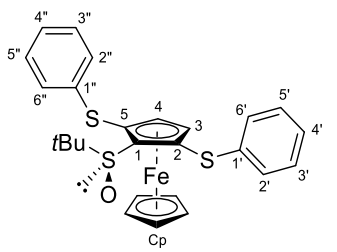
(*R*,*R*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)ferrocenesulfoxide (***R*,*R*$_P$-4**) was prepared by adapting the general procedure A to 1.9 mmol of (*R*)-*S*-*tert*-butylferrocenesulfoxide (***R*-FcSO*t*Bu**; 0.56 g) and using PhSSPh (0.63 g) in THF (4 mL). It was isolated (eluent: petroleum ether-EtOAc 80:20; Rf = 0.14) in 70% yield (0.54 g) as a yellow solid: mp 164-166 °C; IR (ATR) ν 735, 823, 1033, 1106, 1146, 1181, 1362, 1437, 1580, 2959 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9H, *t*Bu), 4.44 (t, 1H, *J* = 2.6 Hz, H4), 4.48 (s, 5H, Cp), 4.49 (dd, 1H, *J* = 2.6 and 1.5 Hz, H5), 4.52 (dd, 1H, *J* = 2.4 and 1.5 Hz, H3), 7.11-7.15 (m, 1H, H4'), 7.21-7.24 (m, 4H, H2', H3', H5' and H6') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 23.9 ($3CH_3$, C*Me*$_3$), 56.5 (C, *C*Me$_3$), 70.6 (CH, C4), 72.2 (CH, C5), 72.3 (5CH, Cp), 77.1 (CH, C3), 80.0 (C, C1 or C2), 84.2 (C, C1 or C2), 125.7 (CH, C4'), 128.1 (2CH, Ph), 128.9 (2CH, Ph), 138.7 (C, C1') ppm; $[\alpha]_D$ -298 (*c* 0.4). Anal. Calcd for $C_{20}H_{22}FeOS_2$ (398.36): C, 60.30; H, 5.57; S, 16.10. Found: C, 60.14; H, 5.62; S, 15.77%.



(*S*,*S*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)ferrocenesulfoxide (***S*,*S*$_P$-4**) was prepared by adapting the general procedure A to 1.8 mmol of (*S*)-*S*-*tert*-butylferrocenesulfoxide (***S*-FcSO*t*Bu**; 0.53 g) and using PhSSPh (0.60 g) in THF (4 mL). It was isolated (eluent: petroleum ether-EtOAc 80:20; Rf = 0.14) in 82% yield (0.60 g) as a yellow solid: mp 164-166 °C; IR (ATR) ν 742, 753, 822, 1044, 1182, 1476, 1579, 2953 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9H, *t*Bu), 4.44 (t, 1H, *J* = 2.6 Hz, H4), 4.48 (s, 5H, Cp), 4.49 (dd, 1H, *J* = 2.6 and 1.5 Hz, H5), 4.52 (dd, 1H, *J* = 2.4 and 1.5 Hz, H3), 7.11-7.15 (m, 1H, H4'), 7.21-7.24 (m, 4H, H2', H3', H5' and H6') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 23.9 ($3CH_3$, C*Me*$_3$), 56.5 (C, *C*Me$_3$), 70.6 (CH, C4), 72.2 (CH, C5), 72.3 (5CH, Cp), 77.1 (CH, C3), 80.0 (C, C1 or C2), 84.2 (C, C1 or C2), 125.7 (CH, C4'), 128.1 (2CH, Ph), 128.9 (2CH, Ph), 138.7 (C, C1') ppm; $[\alpha]_D$ +683 (*c* 1). Anal. Calcd for $C_{20}H_{22}FeOS_2$ (398.36): C, 60.30; H, 5.57; S, 16.10. Found: C, 60.12; H, 5.13; S, 15.68%.

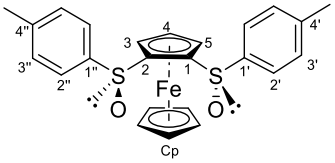


(*S*)-*S*-*tert*-Butyl-2,5-di(phenylthio)ferrocenesulfoxide (***S*-4'**) was similarly isolated (eluent: petroleum ether-EtOAc 80:20; Rf = 0.28) in 9% yield (85 mg) as an orange oil: IR (ATR) ν 736, 826, 892, 958, 1024, 1037, 1081, 1108, 1173, 1215, 1363, 1439, 1477, 1582, 1703, 2962 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 9H, *t*Bu), 4.53 (s, 5H, Cp), 4.62 (d, 1H, *J* = 2.6 Hz, H3 or H4), 4.74 (d, 1H, *J* = 2.6 Hz, H3 or H4), 7.11-7.17 (m, 3H, Ar), 7.19-7.24 (m, 3H, Ar), 7.29-7.30 (m, 4H, Ar) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.4 ($3CH_3$, C*Me*$_3$), 58.1 (C, *C*Me$_3$), 74.5 (5CH, Cp), 76.8 (CH, C3 or C4), 78.4 (CH, C3 or C4), 81.9 (C, C1 or C2 or C5), 83.7 (C, C1 or C2 or C5), 87.3 (C, C1 or C2 or C5), 125.9 (C4' or C4"), 126.4 (C4' or C4"), 126.9, 129.0, 129.1 and 129.2 (4 x 2CH, C2'/C6', C3'/C5', C2"/C6" and C3"/C5"),



137.7 (C, C1' or C1"), 138.4 (C, C1' or C1") ppm; $[\alpha]_D$ +189 (*c* 0.5). Anal. Calcd for $C_{26}H_{26}FeOS_3$ (506.52): C, 61.65; H, 5.17; S, 18.99. Found: C, 61.42; H, 5.11; S, 19.05%.

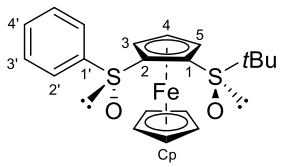
(*S*,*S*)-*S*,*S'*-Di(4-tolyl)ferrocene-1,2-disulfoxide (*S*,*S*-3) was prepared as follows.[16] To a solution of (*S*)-*S*-(4-tolyl)ferrocenesulfoxide (**S-FcSO-*p*-Tol**; 0.27 g , 0.83 mmol) in THF (2 mL) at –80 °C was added dropwise a solution of LiTMP [prepared by adding a 1.4 M hexane solution of *n*BuLi (0.77 mL, 1.1 mmol) to 2,2,6,6-tetramethylpiperidine (0.20 mL, 1.2 mmol) in THF (1 mL) at –15 °C] cooled at –80 °C. The reaction mixture was stirred at this temperature for 30 min before addition of (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-4-toluenesulfinate (0.32 g, 1.1 mmol) in THF (1 mL). The mixture was stirred at –80 °C for 1 h before being warmed to rt. 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, which was purified by chromatography over silica gel (eluent: petroleum ether-EtOAc 40:60; Rf = 0.25). (*S*,*S*)-*S*,*S'*-di(4-tolyl)ferrocene-1,2-disulfoxide (**S,S-3**) was isolated in 65% yield (0.25 g) as a brownish-yellow solid: mp 222-224 °C; IR (ATR) ν 772, 828, 849, 981, 1045, 1067, 1155, 1184, 1323, 1413, 1616, 2975 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H, C_2-SOC_6H_4*Me*), 2.33 (s, 3H, C_1-SOC_6H_4*Me*), 4.21 (dd, 1H, *J* = 2.4 and 1.5 Hz, H5), 4.47 (t, 1H, *J* = 2.7 Hz, H4), 4.55 (s, 5H, Cp), 4.91 (dd, 1H, *J* = 2.4 and 1.4 Hz, H3), 7.10 (d, 2H, *J* = 7.9 Hz, H3" and H5"), 7.22 (d, 2H, *J* = 8.0 Hz, H3' and H5'), 7.46 (d, 2H, *J* = 8.2 Hz, H2" and H6"), 7.47 (d, 2H, *J* = 8.2 Hz, H2' and H6') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 21.5 (CH_3, Me), 21.6 (CH_3, Me), 67.1 (CH, C3), 70.2 (CH, C5), 70.8 (CH, C4), 72.1 (5CH, Cp), 94.9 (C, *C*-SOtolyl), 96.2 (C, *C*-SOtolyl), 125.1 (2CH, C2' and C6', or C2" and C6"), 125.3 (2CH, C2' and C6', or C2" and C6"), 129.6 (2CH, C3' and C5', or C3" and C5"), 129.7 (2CH, C3' and C5', or C3" and C5"), 140.5 (C, C1'), 141.0 (C, C4"), 141.7 (C, C4'), 143.3 (C, C1") ppm; $[\alpha]_D$ +317 (*c* 1). Anal. Calcd for $C_{24}H_{22}FeO_2S_2$ (462.40): C, 62.34; H, 4.80; S, 13.87. Found: C, 62.08; H, 5.26; S, 13.31%.



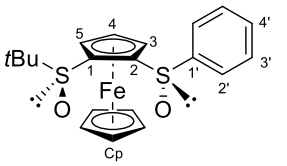
(*S*)-*S*-(4-Tolyl)ferrocenesulfoxide (**S-FcSO-*p*-Tol**) was similarly recovered in 20% yield.

General procedure B: Oxidation of (phenylthio)ferrocenes.[16] To a solution of the (phenylthio)ferrocene (1.0 mmol) in CH_2Cl_2 (6 mL) was added portionwise, at 0 °C, 3-chloroperbenzoic acid (*m*-CPBA; 70%; 0.44 g, 1.8 mmol). The reaction mixture was stirred at 0 °C for 1 h before addition of CH_2Cl_2 (10 mL). The organic phase was washed with a 10% aqueous solution of NaOH (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).

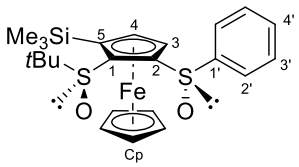
(*R*,*R*,*S*$_P$)-*S*-*tert*-Butyl-*S'*-phenylferrocene-1,2-disulfoxide (**R,R,S$_P$-5**) was prepared by adapting the general procedure B to 1.3 mmol of (*R*,*R*$_P$)-*S*-*tert*-butyl-2-(phenylthio)ferrocenesulfoxide (**R,R$_P$-4**; 0.51 g). It was isolated (eluent: petroleum ether-EtOAc 20:80; Rf = 0.16) in 80% yield (0.42 g) as a brownish-yellow solid: mp 174-176 °C; IR (ATR) ν 761, 822, 859, 1013, 1179, 1231, 1409, 1449, 1649, 2977, 3492 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (s, 9H, *t*Bu), 4.47 (s, 1H, H5), 4.60 (s, 6H, H4 and Cp), 5.27 (s, 1H, H3), 7.36-7.37 (m, 3H), 7.78-7.79 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 22.9 ($3CH_3$, C*Me*$_3$), 56.9 (C, *C*Me$_3$), 67.1 (CH, C3), 69.6 (CH, C5), 71.2 (CH, C4), 72.7 (5CH, Cp), 87.8 (C, C1, *C*-SO*t*Bu), 95.0 (C, C2, *C*-SOPh), 127.2 (2CH, C2' and C6'), 128.9 (2CH, C3' and C5'), 131.1 (CH, C4'), 148.2 (C, C1') ppm; $[\alpha]_D$ -366 (*c* 1). Anal. Calcd for $C_{20}H_{22}FeO_2S_2$ (414.36): C, 57.97; H, 5.35; S, 15.47. Found: C, 58.03; H, 5.66; S, 15.19%.



(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-*S'*-phenylferrocene-1,2-disulfoxide (***S*,*S*,*R*$_P$-5**) was prepared by adapting the general procedure B to 0.30 mmol of (*S*,*S*$_P$)-*S*-*tert*-butyl-2-(phenylthio)ferrocenesulfoxide (***S*,*S*$_P$-4**; 0.12 g). It was isolated (eluent: petroleum ether-EtOAc 20:80; Rf = 0.16) in 85% yield (0.10 g) as a brownish-yellow solid: mp 174-176 °C; IR (ATR) ν 761, 822, 858, 1013, 1082, 1106, 1179, 1310, 1363, 1449, 1471, 1650, 2977, 3439 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 9H, *t*Bu), 4.47 (s, 1H, H5), 4.60 (s, 6H, H4 and Cp), 5.27 (s, 1H, H3), 7.36-7.37 (m, 3H), 7.78-7.79 (m, 2H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.9 ($3CH_3$, C*Me*$_3$), 56.9 (C, *C*Me$_3$), 67.1 (CH, C3), 69.6 (CH, C5), 71.2 (CH, C4), 72.7 (5CH, Cp), 87.8 (C, C1, *C*-SO*t*Bu), 95.0 (C, C2, *C*-SOPh), 127.2 (2CH, C2' and C6'), 128.9 (2CH, C3' and C5'), 131.1 (CH, C4'), 148.2 (C, C1') ppm; $[\alpha]_D$ +94 (*c* 0.6). Anal. Calcd for $C_{20}H_{22}FeO_2S_2$ (414.36): C, 57.97; H, 5.35; S, 15.47. Found: C, 58.45; H, 5.41; S, 15.10%.

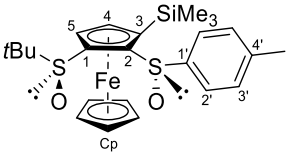


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (***S*,*S*,*R*$_P$-11**) was prepared by adapting the general procedure B to 0.76 mmol of (*S*,*S*$_P$)-*S*-*tert*-butyl-2-(phenylthio)-5-(trimethylsilyl)ferrocenesulfoxide (***S*,*S*$_P$-8b**; 0.35 g). It was isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.25) in 88% yield (0.63 g) as a brownish-yellow solid: mp 160-162 °C; IR (ATR) ν 748, 823, 881, 1037, 1111, 1189, 1249, 1306, 1363, 1412, 1442, 1473, 1580, 1700, 2967, 3386 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H, $SiMe_3$), 0.97 (s, 9H, *t*Bu), 4.49 (d, 1H, *J* = 2.6 Hz, H4), 4.65 (s, 5H, Cp), 5.22 (d, 1H, *J* = 2.7 Hz, H3), 7.40-7.41 (m, 3H), 7.69-7.71 (m, 2H) ppm; ^{13}C{^{1}H NMR ($CDCl_3$) δ 1.7 ($3CH_3$, $SiMe_3$), 24.5 ($3CH_3$, C*Me*$_3$), 57.1 (C, *C*Me$_3$), 72.3 (CH, C3), 73.4 (5CH, Cp), 78.1 (C, C5, *C*-$SiMe_3$), 78.3 (CH, C4), 94.3 (C, C1, *C*-SO*t*Bu), 98.0 (C, C2, *C*-SOPh), 126.9 (2CH, C2' and C6'), 129.0 (2CH, C3' and C5'), 130.9 (CH, C4'), 147.8 (C, C1') ppm; $[\alpha]_D$ +125 (*c* 1). Anal. Calcd for $C_{23}H_{30}FeO_2S_2Si$ (486.54): C, 56.78; H, 6.22; S, 13.18. Found: C, 56.83; H, 6.06; S, 13.39%.



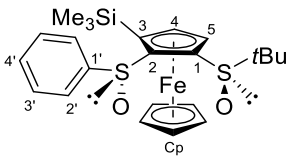
General procedure C: Deprotolithiation using LiTMP (1.3 equiv) at –80 °C followed by electrophilic trapping.[16] To a stirred, cooled (0 °C) solution of H-TMP (0.20 mL, 1.4 mmol) in THF (5 mL) was added dropwise a 1.4 M hexane solution of *n*BuLi (0.93 mL, 1.3 mmol). The mixture was stirred for 5 min at 0 °C and then for 2 min at –80 °C before introduction of the ferrocenesulfoxide (1.0 mmol). After 30 min at this temperature, the electrophile (1.3 mmol; either pure for liquids or in solution for solids, as indicated below) was introduced. The mixture was stirred for 1 h at –80 °C before addition of water and warming to rt. 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).

(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-*S'*-tolyl-3-(trimethylsilyl)ferrocene-1,2-disulfoxide (***S*,*S*,*R*$_P$-6a**) was prepared by adapting the general procedure C to 0.61 mmol of (*S*,*S*,*R*$_P$)-*S*-*tert*-butyl-*S'*-phenylferrocene-1,2-disulfoxide (***S*,*S*,*R*$_P$-2**; 0.26 g) and using $ClSiMe_3$ (0.10 mL). It was isolated (eluent: petroleum ether-EtOAc 20:80; Rf = 0.56) in 28% yield (86 mg) as a brownish-yellow oil: IR (ATR) ν 749, 809, 838, 896, 965, 1038, 1082, 1109, 1191, 1241, 1456, 1493, 1648, 2923, 3413 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 9H, $SiMe_3$), 0.94 (s, 9H, *t*Bu), 2.33 (s, 3H, Me), 4.58 (d, 1H, *J* = 2.6 Hz, H4), 4.61 (s, 5H, Cp), 4.69 (d, 1H, *J* = 2.6 Hz, H5), 7.15 (d, 2H, *J* = 8.0 Hz, H2' and H6'), 7.45 (d, 2H, *J* = 8.1 Hz, H3' and H5') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 2.1 ($3CH_3$, $SiMe_3$), 21.5 (CH_3, Me), 21.5 ($3CH_3$, C*Me*$_3$), 56.8 (C, *C*Me$_3$), 72.9 (5CH, Cp), 72.9 (CH, C5), 74.5 (C, C3, *C*-$SiMe_3$), 79.0 (CH, C4), 90.4 (C, C1, *C*-SO*t*Bu), 98.5 (C, C2, *C*-SOtolyl), 127.9 (2CH, C3' and C5'), 129.3 (2CH, C2' and C6'), 140.8 (C, C4', *C*-Me), 145.0 (C, C1') ppm; $[\alpha]_D$ +34 (*c* 0.4). Anal. Calcd for $C_{24}H_{32}FeO_2S_2Si$ (500.57): C, 57.59; H, 6.44; S, 12.81. Found: C, 58.17; H, 7.12; S, 12.69%.



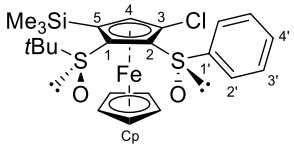
Starting (*S*,*S*,*R*$_P$)-*S*-*tert*-butyl-*S'*-phenylferrocene-1,2-disulfoxide (***S*,*S*,*R*$_P$-2**) was recovered in 50% yield (0.13 g).

(*R*,*R*,*S*P)-*S*-*tert*-Butyl-*S'*-phenyl-3-(trimethylsilyl)ferrocene-1,2-disulfoxide (***R*,*R*,*S*P-7a**) was prepared by adapting the general procedure C to 0.58 mmol of (*R*,*R*,*S*P)-*S*-*tert*-butyl-*S'*-phenylferrocene-1,2-disulfoxide (***R*,*R*,*S*P-5**; 0.30 g) and using $ClSiMe_3$ (0.10 mL). It was isolated (eluent: petroleum ether-EtOAc 60:40; Rf = 0.20) in 10% yield (30 mg) as a brownish-yellow oil: IR (ATR) ν 747, 824, 896, 964, 1037, 1082, 1123, 1191, 1242,1363, 1413, 1443, 1457, 1474, 1711, 2959 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, 9H, $SiMe_3$), 0.95 (s, 9H, *t*Bu), 4.59 (d, 1H, *J* = 2.6 Hz, H4), 4.62 (s, 5H, Cp), 4.71 (d, 1H, *J* = 2.6 Hz, H5), 7.34-7.36 (m, 3H, H3', H4' and H5'), 7.58-7.60 (m, 2H, H2' and H6') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 2.1 ($3CH_3$, $SiMe_3$), 23.5 ($3CH_3$, C*Me*$_3$), 56.8 (C, *C*Me_3), 72.9 (CH, C5), 72.9 (5CH, Cp), 74.6 (C, C3, *C*-$SiMe_3$), 79.1 (CH, C4), 90.7 (C, C1, *C*-SO*t*Bu), 98.6 (C, C2, *C*-SOPh), 127.8 (2CH, C2' and C6'), 128.7 (2CH, C3' and C5'), 130.5 (CH, C4'), 148.0 (C, C1') ppm; $[\alpha]_D$ +27 (*c* 0.4). Anal. Calcd for $C_{23}H_{30}FeO_2S_2Si$ (486.54): C, 56.78; H, 6.22; S, 13.18. Found: C, 56.30; H, 6.13; S, 12.71%.

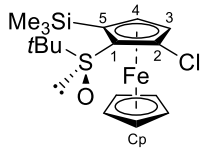


Starting (*R*,*R*,*S*P)-*S*-*tert*-butyl-*S'*-phenylferrocene-1,2-disulfoxide (***R*,*R*,*S*P-5**) was recovered in 38% yield (92 mg).

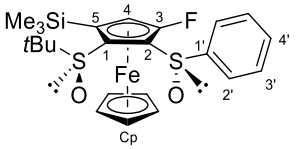
(*S*,*S*,*R*P)-*S*-*tert*-Butyl-3-chloro-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (***S*,*S*,*R*P-12a**) was prepared by adapting the general procedure C to 0.66 mmol of (*S*,*S*,*R*P)-*S*-*tert*-butyl-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (***S*,*S*,*R*P-11**; 0.49 g) and using C_2Cl_6 (0.16 g) in THF (3 mL). It was isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.47) in 37% yield (0.13 g) as a brownish-yellow oil: IR (ATR) ν 747, 830, 929, 1042, 1111, 1250, 1441, 1577, 1700, 2967, 3518 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.39 (s, 9H, $SiMe_3$), 1.24 (s, 9H, *t*Bu), 4.67 (s, 1H, H4), 4.80 (s, 5H, Cp), 7.40-7.44 (m, 3H), 7.50-7.52 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.7 ($3CH_3$, $SiMe_3$), 24.9 ($3CH_3$, C*Me*$_3$), 56.7 (C, *C*Me_3), 75.6 (5CH, Cp), 77.0 (C, C5, *C*-$SiMe_3$), 79.2 (CH, C4), 93.9 (C, C1 or C2), 94.1 (C, C1 or C2), 95.4 (C, C3, C-Cl), 126.2 (2CH, C2' and C6'), 128.8 (2CH, C3' and C5'), 129.8 (CH, C4'), 145.1 (C, C1') ppm; $[\alpha]_D$ +170 (*c* 1). Anal. Calcd for $C_{23}H_{29}ClFeO_2S_2Si$ (520.98): C, 53.03; H, 5.61; S, 12.31. Found: C, 53.62; H, 5.89; S, 12.18%.



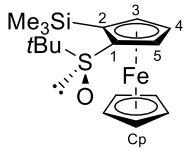
(*S*,*R*P)-*S*-*tert*-Butyl-2-chloro-5-(trimethylsilyl)ferrocenesulfoxide (***S*,*R*P-12a'**) was similarly isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.67) in 4% yield (10 mg) as a yellow oil, and identified by NMR: ^1H NMR ($CDCl_3$) δ 0.31 (s, 9H, $SiMe_3$), 1.29 (s, 9H, *t*Bu), 4.16 (d, 1H, *J* = 2.6 Hz, H4), 4.46 (s, 5H, Cp), 4.79 (d, 1H, *J* = 2.6 Hz, H3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.6 ($3CH_3$, $SiMe_3$), 25.1 ($3CH_3$, C*Me*$_3$), 58.1 (C, *C*Me_3), 73.2 (5CH, Cp), 74.2 (CH, C4), 74.6 (CH, C3), 75.4 (C, C5, *C*-$SiMe_3$), 88.8 (C, C1, *C*-SO*t*Bu), 92.6 (C, C2, C-Cl) ppm; $[\alpha]_D$ +57 (*c* 0.3). Anal. Calcd for $C_{17}H_{25}ClFeOSSi$ (396.83): C, 51.46; H, 6.35; S, 8.08. Found: C, 51.31; H, 6.19; S, 8.16%.



(*S*,*S*,*R*P)-*S*-*tert*-Butyl-3-fluoro-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (***S*,*S*,*R*P-12b**) was prepared by adapting the general procedure C to 0.76 mmol of (*S*,*S*,*R*P)-*S*-*tert*-butyl-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (***S*,*S*,*R*P-11**; 0.37 g) and using NFSI (0.29 g) in THF (3 mL). It was isolated (eluent: petroleum ether-EtOAc 60:40; Rf = 0.22) in 48% yield (0.18 g) as a brownish-yellow oil: IR (ATR) ν 749, 843, 1022, 1112, 1307, 1442, 1575, 2971, 3548 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.36 (s, 9H, $SiMe_3$), 1.24 (s, 9H, *t*Bu), 4.56 (d, 1H, *J* = 2.8 Hz, H4), 4.83 (s, 5H, Cp), 7.42-7.47 (m, 3H), 7.65-7.66 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.7 ($3CH_3$, $SiMe_3$), 24.9 ($3CH_3$, C*Me*$_3$), 56.8 (C, *C*Me_3), 66.2 (d, CH, *J* = 12.3 Hz, C4), 70.9 (C, C5, *C*-$SiMe_3$), 74.6 (5CH, Cp), 87.7 (d, C, *J* = 9.7 Hz, C2, *C*-SOPh), 88.8 (C, C1, *C*-SO*t*Bu), 125.8 (2CH, C2' and C6'), 128.9 (2CH, C3' and C5'), 130.3 (CH, C4'), 135.0 (d, C, *J* = 286.4 Hz, C3), 145.4 (C, C1') ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ -174.7 ppm; $[\alpha]_D$ +85 (*c* 0.3). Anal. Calcd for $C_{23}H_{29}FFeO_2S_2Si$ (504.53): C, 54.75; H, 5.79; S, 12.71. Found: C, 54.67; H, 5.45; S, 12.51%.

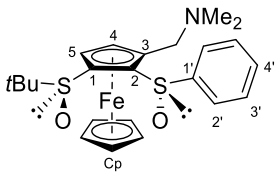


(*S*,*R*P)-*S*-*tert*-Butyl-2-(trimethylsilyl)ferrocenesulfoxide (***S*,*R*P-12b'**) was similarly isolated (eluent: petroleum ether-EtOAc 60:40; Rf = 0.38) in 20% yield (55 mg) as an orange oil: IR (ATR) ν 755, 818, 945, 1027, 1177, 1249, 1362, 1457, 1638, 2958, 3398 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.33 (s, 9H, $SiMe_3$), 1.15 (s, 9H, *t*Bu), 4.24 (dd, 1H, *J* = 2.4 and 1.3 Hz, H3), 4.36 (s, 5H, Cp), 4.60 (t, 1H, *J* = 2.4 Hz, H4), 4.89 (dd, 1H, *J* = 2.5 and 1.3 Hz, H5) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.3 ($3CH_3$, $SiMe_3$), 23.6 ($3CH_3$, C*Me*$_3$), 55.6 (C, *C*Me_3), 68.5 (CH, C5), 70.6 (5CH, Cp), 72.3 (CH, C4), 75.6 (C, C2, *C*-$SiMe_3$), 76.4 (CH, C3), 93.3 (C, C1, *C*-SO*t*Bu) ppm; $[\alpha]_D$ +250 (*c* 1). Anal. Calcd for $C_{17}H_{26}FeOSSi$ (362.38): C, 56.35; H, 7.23; S, 8.85. Found: C, 56.12; H, 7.68; S, 8.96%.

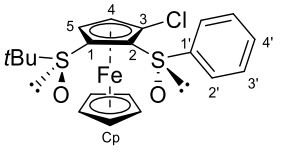


General procedure D: Deprotolithiation using LiTMP (1.5 equiv) at –50 °C followed by electrophilic trapping.[16] To a stirred, cooled (0 °C) solution of H-TMP (0.14 mL, 0.96 mmol) in THF (3 mL) was added dropwise a 1.4 M hexane solution of *n*BuLi (0.64 mL, 0.90 mmol). The mixture was stirred for 5 min at 0 °C and then for 2 min at –50 °C before introduction of (*S*,*S*,*R*P)-*S*-*tert*-butyl-*S'*-phenylferrocene-1,2-disulfoxide (***S*,*S*,*R*P-5**; 0.25 g, 0.60 mmol). After 30 min at this temperature, the electrophile (0.90 mmol; either pure for liquids or in solution for solids, as indicated below) was introduced. The mixture was stirred for 1 h at –50 °C before addition of water and warming to rt. 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).

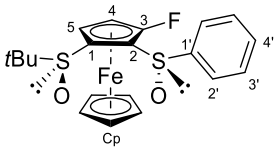
(*S*,*S*,*R*P)-*S*-*tert*-Butyl-3-(dimethylaminomethyl)-*S'*-phenylferrocene-1,2-disulfoxide (***S*,*S*,*R*P-7b**) was prepared by adapting the general procedure D to 0.50 mmol of ***S*,*S*,*R*P-5** (0.21 g) and using *N*,*N*-dimethylmethyleneiminium iodide (0.14 g) as the electrophile in THF (4 mL). It was isolated (eluent: 90:10 EtOAc-NEt_3; Rf = 0.59) in 58% yield (0.14 g) as a brownish-yellow oil: IR (ATR) ν 747, 829, 1033, 1080, 1175, 1239, 1364, 1456, 1667, 2976, 3436 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (s, 9H, *t*Bu), 2.11 (s, 6H, NMe_2), 3.30 (d, 1H, *J* = 14.0 Hz, C*H*HNMe_2), 3.90 (d, 1H, *J* = 13.9 Hz, CH*H*NMe_2), 4.50 (d, 1H, *J* = 2.7 Hz, H5), 4.59 (s, 5H, Cp), 4.69-4.75 (m, 1H, H4), 7.34-7.38 (m, 3H, H3', H4' and H5'), 7.98-8.00 (m, 2H, H2' and H6') ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.5 ($3CH_3$, C*Me*$_3$), 45.5 ($2CH_3$, NMe_2), 56.9 (C, *C*Me_3), 57.0 (CH_2, CH_2NMe_2), 68.6 (CH, C5), 73.5 (5CH, Cp), 73.9 (CH, C4), 88.5 (CH, C3), 89.6 (C, C1 or C2), 91.1 (C, C1 or C2), 127.8 (2CH, C2' and C6'), 128.7 (2CH, C3' and C5'), 130.6 (CH, C4'), 147.4 (C, C1') ppm; $[\alpha]_D$ +122 (*c* 1). Anal. Calcd for $C_{23}H_{29}FeNO_2S_2$ (471.45): C, 58.60; H, 6.20; S, 13.60. Found: C, 59.11; H, 6.77; S, 13.13%.
Starting (*S*,*S*,*R*P)-*S*-*tert*-butyl-*S'*-phenylferrocene-1,2-disulfoxide (***S*,*S*,*R*P-5**) was also recovered in 20% yield.



(*S*,*S*,*R*P)-*S*-*tert*-Butyl-3-chloro-*S'*-phenylferrocene-1,2-disulfoxide (***S*,*S*,*R*P-7c**) was prepared according to the general procedure D and using C_2Cl_6 (0.21 g) in THF (1 mL). It was isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.36) in 66% yield (0.18 g) as a yellow solid: mp 196-198 °C; IR (ATR) ν 751, 832, 1042, 1079, 1173, 1208, 1282, 1308, 1366, 1413, 1477, 1581, 1704, 2978, 3462 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (s, 9H, *t*Bu), 4.54 (d, 1H, *J* = 2.7 Hz, H5), 4.78 (s, 5H, Cp), 4.78 (d, 1H, *J* = 2.7 Hz, H4), 7.37-7.43 (m, 3H), 7.67-7.70 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.7 ($3CH_3$, C*Me*$_3$), 56.7 (C, *C*Me_3), 68.5 (CH, C5), 72.7 (CH, C4), 75.1 (5CH, Cp), 87.9 (C, C1 or C2 or C3), 91.5 (C, C1 or C2 or C3), 93.0 (C, C1 or C2 or C3), 126.4 (2CH, C2' and C6'), 128.8 (2CH, C3' and C5'), 130.3 (CH, C4'), 145.3 (C, C1') ppm; $[\alpha]_D$ +509 (*c* 1). Anal. Calcd for $C_{20}H_{21}ClFeO_2S_2$ (448.80): C, 53.52; H, 4.72; S, 14.29. Found: C, 53.17; H, 5.13; S, 14.18%.

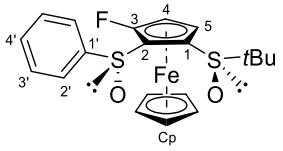


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-3-fluoro-*S'*-phenylferrocene-1,2-disulfoxide (***S*,*S*,*R*$_P$-7d**) was prepared according to the general procedure D and using NFSI (0.28 g) in THF (3 mL). It was isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.28) in 50% yield (0.13 g) as a yellow solid: mp 192-194 °C; IR (ATR) ν 754, 833, 1039, 1083, 1136, 1251, 1304, 1362, 1447, 1582, 1655, 2975, 3462 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9H, *t*Bu), 4.26 (dd, 1H, *J* = 2.8 and 1.5 Hz, H5), 4.69 (t, 1H, *J* = 2.9 Hz, H4), 4.80 (s, 5H, Cp), 7.39-7.44 (m, 3H, H3', H4' and H5'), 7.76-7.79 (m, 2H, H2' and H6') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 23.5 (3CH_3, C*Me*$_3$), 56.6 (C, *C*Me$_3$), 60.3 (d, CH, *J* = 15.4 Hz, C4), 62.7 (d, CH, *J* = 3.6 Hz, C5), 74.1 (5CH, Cp), 82.9 (C, C1, *C*-SO*t*Bu), 84.6 (C, d, *J* = 8.8 Hz, C2, *C*-SOPh), 126.1 (d, 2CH, *J* = 2.2 Hz, C2' and C6'), 128.9 (2CH, C3' and C5'), 130.8 (CH, C4'), 133.2 (d, C, *J* = 285.0 Hz, C3, C-F), 145.9 (C, C1') ppm; ^{19}F{^{1}H} NMR ($CDCl_3$) δ -178.6 ppm; $[\alpha]_D$ +511 (*c* 1). Anal. Calcd for $C_{20}H_{21}FFeO_2S_2$ (432.35): C, 55.56; H, 4.90; S, 14.83. Found: C, 56.11; H, 5.15; S, 15.10%.



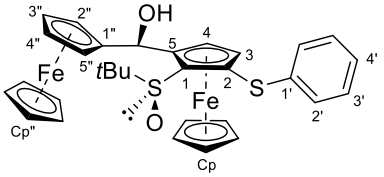
Starting (*S*,*S*,*R*$_P$)-*S*-*tert*-butyl-*S'*-phenylferrocene-1,2-disulfoxide (***S*,*S*,*R*$_P$-5**) was also recovered in 12% yield (28 mg).

Note that (*R*,*R*,*S*$_P$)-*S*-*tert*-butyl-3-fluoro-*S'*-phenylferrocene-1,2-disulfoxide (***R*,*R*,*S*$_P$-7d**) was similarly prepared from (*R*,*R*,*S*$_P$)-*S*-*tert*-butyl-*S'*-phenylferrocene-1,2-disulfoxide (***R*,*R*,*S*$_P$-5**; 0.83 g, 2.0 mmol) and isolated in 60% yield (0.51 g). ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9H, *t*Bu), 4.26 (dd, 1H, *J* = 2.8 and 1.5 Hz, H5), 4.69 (t, 1H, *J* = 2.9 Hz, H4), 4.47 (s, 5H, Cp), 7.39-7.44 (m, 3H, H3', H4' and H5'), 7.76-7.79 (m, 2H, H2' and H6') ppm, and ^{19}F{^{1}H} NMR ($CDCl_3$) δ -178.7 ppm are similar to those reported for its enantiomer.



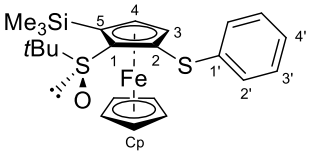
General procedure E: Deprotolithiation using *n*BuLi at rt followed by electrophilic trapping.[4] To a solution of (*S*,*S*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)ferrocenesulfoxide (***S*,*S*$_P$-4**; 0.40 g, 1.0 mmol) in THF (10 mL) at 0 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (0.93 mL, 1.3 mmol) before warming to rt. The reaction was stirred at this temperature for 1 h and cooled to 0 °C before addition of the electrophile (1.3 mmol; either pure for liquids or in solution for solids, as indicated below). The mixture was warmed to rt and stirred for 1 h. Addition of 1 M HCl (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, which was purified by chromatography over silica gel (eluent given in the product description).

(*R*$_C$,*S*$_S$,*S*$_P$)-*S*-*tert*-Butyl-2-(1-(ferrocenyl)hydroxymethyl)-5-(phenylthio)ferrocenesulfoxide (***S*,*S*$_P$-8a**) was prepared by adapting the general procedure E to 0.60 mmol of ***S*,*S*$_P$-4** (0.24 g) and using ferrocenecarboxaldehyde (0.17 g) as the electrophile in THF (3 mL). The main diastereoisomer was isolated (eluent: petroleum ether-EtOAc 60:40; Rf = 0.39) in 56% yield (0.21 g) as a brownish-yellow oil: IR (ATR) ν 739, 819, 928, 1002, 1042, 1106, 1173, 1232, 1364, 1411, 1438, 1477, 1581, 2972 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9H, *t*Bu), 2.90 (br s, 1H, OH), 4.25 (s, 5H, Cp or Cp"), 4.47 (s, 5H, Cp or Cp"), 4.31 (br s, H3" and H4"), 4.46-4.49 (m, 3H, H4, H2" and H5"), 4.61 (d, 1H, *J* = 2.7 Hz, H3), 5.35 (s, 1H, C*H*(OH)), 7.08 (t, 1H, *J* = 7.3 Hz, H4'), 7.14 (d, 2H, *J* = 6.8 Hz, H2' and H6'), 7.20 (t, 2H, *J* = 7.7 Hz, H3' and H5') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.9 (3CH_3, C*Me*$_3$), 57.8 (C, *C*Me$_3$), 65.1 (C2"), 66.1 (CH, CH(OH)), 67.7 (C3" or C4"), 68.6 (C3" or C4"), 68.7 (5CH, Cp or Cp"), 69.4 (C5"), 70.7 (CH, C4), 73.4 (5CH, Cp or Cp"), 77.6 (C, C2), 77.9 (CH, C3), 86.7 (C, C1), 94.4 (C, C1"), 95.6 (C, C5), 125.2 (CH, C4'), 126.5 (2CH, C2' and C6'), 128.9 (2CH, C3' and C5'), 139.7 (C, C1') ppm; $[\alpha]_D$ +163 (*c* 1). Anal. Calcd for $C_{20}H_{21}FFeO_2S_2$ (432.35): C, 55.56; H, 4.90; S, 14.83. Found: C, 55.22; H, 5.19; S, 14.98%.



(*S*,*S*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)-5-(trimethylsilyl)ferrocenesulfoxide (***S*,*S*$_P$-8b**) was prepared by adapting the general procedure E to 0.88 mmol of ***S*,*S*$_P$-4** (0.35 g) and using $ClSiMe_3$ (0.14 mL). It was isolated (eluent: petroleum ether-EtOAc 80:20; Rf = 0.41) in 73% yield. (0.30 g) as an orange oil: IR

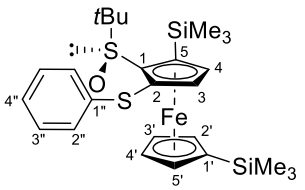
(ATR) ν 749, 819, 877, 896, 965, 1066, 1121, 1172, 1198, 1247, 1362, 1336, 1411, 1456, 1477, 1582, 2958 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H, $SiMe_3$), 1.24 (s, 9H, *t*Bu), 4.35 (d, 1H, *J* = 2.6 Hz, H4), 4.47 (s, 5H, Cp), 4.76 (d, 1H, *J* = 2.5 Hz, H3), 7.11-7.12 (tt, 1H, *J* = 7.0 and 1.5 Hz, H4'), 7.19-7.24 (m, 4H, H2', H3', H5' and H6') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 1.7 ($3CH_3$, $SiMe_3$), 25.1 ($3CH_3$, C*Me*$_3$), 57.3 (C, *C*Me_3), 73.0 (5CH, Cp), 77.5 (CH, C4), 78.1 (C, C5), 80.6 (CH, C3), 81.5 (C, C2), 91.3 (C, C1), 125.4 (CH, C4'), 127.4 (2CH, Ph), 128.9 (2CH, Ph), 139.4 (C, C1') ppm; $[\alpha]_D$ +413 (*c* 1). Anal. Calcd for $C_{23}H_{30}FeOS_2Si$ (470.54): C, 58.71; H, 6.43; S, 13.63. Found: C, 58.97; H, 6.84; S, 13.20%.



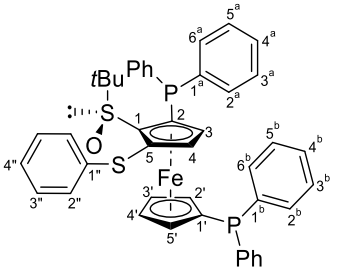
The yield of the reaction could be improved to 85% by increasing the amount of *n*BuLi to 2.5 equivalents.

General procedure F: Double deprotolithiation using *n*BuLi in excess at rt followed by electrophilic trapping.[4] To a solution of (*S*,*S*$_P$)-*S*-*tert*-butyl-2-(phenylthio)ferrocenesulfoxide (***S*,*S*$_P$-4**; 0.40 g, 1.0 mmol) in THF (10 mL) at 0 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (1.8 mL, 2.5 mmol) before warming to rt. The reaction was stirred at this temperature for 1 h and cooled to 0 °C before addition of the electrophile (2.5 mmol; either pure for liquids or in solution for solids, as indicated below). The mixture was warmed to rt and stirred for 1 h. Addition of 1 M HCl (5 mL), or water in the case of Cl_2SiMe_2, 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).

(*S*,*S*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)-5,1'-bis(trimethylsilyl)ferrocenesulfoxide (***S*,*S*$_P$-9a**) was prepared by adapting the general procedure F to 0.70 mmol of ***S*,*S*$_P$-4** (0.28 g) and using $ClSiMe_3$ (0.22 mL). It was isolated (eluent: petroleum ether-EtOAc 70:30; Rf = 0.51) in 85% yield (0.325 g) as an orange solid: mp 168 °C; IR (ATR) ν 702, 741, 826, 893, 966, 1042, 1067, 1164, 1199, 1246, 1362, 1384, 1439, 1455, 1471, 1583, 2956 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H, C1'-$SiMe_3$), 0.35 (s, 9H, C5-$SiMe_3$), 1.24 (s, 9H, *t*Bu), 4.08 (s, 1H, H2'), 4.30 (s, 1H, H5'), 4.32 (d, 1H, *J* = 2.5 Hz, H4), 4.72 (s, 1H, H3'), 4.75 (d, 1H, *J* = 2.4 Hz, H3), 5.13 (s, 1H, H4'), 7.10 (t, 1H, *J* = 7.2 Hz, H4"), 7.16 (dd, 2H, *J* = 8.4 and 1.4 Hz, H2" and H6"), 7.22 (t, 2H, *J* = 7.6 Hz, H3" and H5") ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 0.0 ($3CH_3$, C1'-Si*Me*$_3$), 1.8 ($3CH_3$, C5-Si*Me*$_3$), 25.1 ($3CH_3$, C*Me*$_3$), 57.3 (C, *C*Me_3), 74.6 (CH, C3'), 75.6 (CH, C2'), 76.6 (C, C1', *C*-$SiMe_3$), 77.6 (CH, C4), 77.7 (CH, C4'), 78.2 (C, C5, *C*-$SiMe_3$), 80.5 (CH, C5'), 80.8 (C, C2, *C*-SPh), 81.7 (CH, C3), 91.1 (C, C1, *C*-SO*t*Bu), 125.2 (CH, C4"), 126.8 (2CH, C2" and C6"), 128.9 (2CH, C3" and C5"), 140.0 (C, C1") ppm; $[\alpha]_D$ +456 (*c* 1). Anal. Calcd for $C_{26}H_{38}FeOS_2Si_2$ (542.72): C, 57.54; H, 7.06; S, 11.81. Found: C, 57.62; H, 7.16; S, 11.88%.

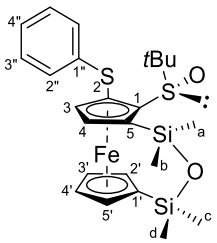


(*S*,*S*$_P$)-*S*-*tert*-Butyl-5,1'-bis(diphenylphosphino)-2-(phenylthio)ferrocenesulfoxide (***S*,*S*$_P$-9b**) was prepared by adapting the general procedure F to 0.60 mmol of ***S*,*S*$_P$-4** (0.24 g) and using $ClPPh_2$ (0.27 mL). It was isolated (eluent: petroleum ether-EtOAc 40:60; Rf = 0.86) in 60% yield (0.28 g) as an orange oil: IR (ATR) ν 739, 832, 893, 1026, 1040, 1066, 1164, 1198, 1306, 1362, 1433, 1477, 1583, 2985 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 9H, *t*Bu), 2.88 (dq, 1H, *J* = 2.9 and 1.5 Hz, H2'), 4.06 (d, 1H, *J* = 2.6 Hz, H3), 4.31 (dp, 1H, *J* = 2.6 and 1.4 Hz, H5'), 4.59 (d, 1H, *J* = 2.6 Hz, H4), 4.79 (td, 1H, *J* = 2.4 and 1.2 Hz, H3'), 5.30 (t, 1H, *J* = 3.3 Hz, H4'), 7.08-7.14 (m, 4H, Ar), 7.18-7.25 (m, 14H, Ar), 7.27-7.35 (m, 5H, Ar), 7.44 (td, 2H, *J* = 8.2 and 1.6 Hz, Ar) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.9 (d, $3CH_3$, *J* = 2.5 Hz, C*Me*$_3$), 58.4 (C, *C*Me_3), 75.2 (CH, C3'), 75.3 (d, CH, *J* = 6.1 Hz, C2'), 75.6 (d, CH, *J* = 4.3 Hz, C3), 79.0 (d, C, *J* = 4.6 Hz), 80.8 (d, CH, *J* = 11.2 Hz, C4'), 81.2 (d, CH, *J* = 4.4 Hz, C4), 82.0 (d, C, *J* = 20.1 Hz), 82.6 (d, CH, *J* = 19.3 Hz, C5'), 85.5 (d, C, *J* = 2.9 Hz), 91.7 (d, C, *J* = 26.8 Hz), 126.3 (CH), 128.2 (CH), 128.3 (CH), 128.3 (2CH), 128.3 (CH), 128.35

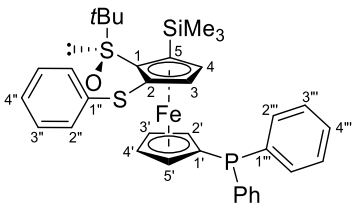


(2CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.8 (CH), 129.1 (2CH), 129.2 (2CH), 129.7 (CH), 133.1 (d, 2CH, J = 19.5 Hz), 132.5 (d, 2CH, J = 19.0 Hz), 133.8 (d, 2CH, J = 20.5 Hz) and 135.2 (d, 2CH, J = 23.3 Hz) (C2^a, C6^a, C2^b and C6^b), 137.2 (d, C, J = 9.5 Hz), 137.9 (C, C1"), 137.9 (d, C, J = 10.5 Hz), 138.8 (d, C, J = 10.5 Hz), 139.2 (d, C, J = 8.8 Hz) ppm; ^{31}P{1H} NMR ($CDCl_3$) δ -26.8, -18.7 ppm; $[\alpha]_D$ +53 (*c* 1). Anal. Calcd for $C_{44}H_{40}FeOP_2S_2$ (766.72): C, 68.93; H, 5.26; S, 8.36. Found: C, 68.37; H, 5.12; S, 8.49%.

(*S*,*S*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)-5,1'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)ferrocenesulfoxide (***S*,*S*$_P$-9c**) was prepared by adapting the general procedure F to 0.40 mmol of ***S*,*S*$_P$-4** (0.16 g) and using Cl_2SiMe_2 (0.12 mL, 1.0 mmol). It was isolated (eluent: petroleum ether-EtOAc 60:40; Rf = 0.82) in 48% yield (0.10 g) as a yellow oil: IR (ATR) ν 737, 789, 820, 871, 903, 968, 1017, 1039, 1123, 1200, 1252, 1385, 1478, 1582, 2959 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 3H, Me^d), 0.32 (s, 3H, Me^b), 0.42 (s, 3H, Me^c), 0.45 (s, 3H, Me^a), 1.22 (s, 9H, *t*Bu), 4.28 (dt, 1H, J = 2.4 and 1.2 Hz, H5'), 4.48 (d, 1H, J = 2.5 Hz, H4), 4.57 (td, 1H, J = 2.4 and 1.1 Hz, H4'), 4.61 (td, 1H, J = 2.4 and 1.1 Hz, H3'), 4.75 (d, 1H, J = 2.5 Hz, H3), 5.17 (dt, 1H, J = 2.4 and 1.2 Hz, H2'), 7.11 (t, 1H, J = 7.2 Hz), 7.18 (dd, 2H, J = 8.5 and 1.4 Hz), 7.23 (t, 2H, J = 7.6 Hz) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 0.1 (CH_3, $SiMe_2$), 0.2 (CH_3, $SiMe_2$), 1.6 (CH_3, $SiMe_2$), 3.8 (CH_3, $SiMe_2$), 25.2 (3CH_3, C*Me*$_3$), 57.8 (C, *C*Me$_3$), 73.7 (C, C1', *C'*-$SiMe_2$), 74.7 (CH, C4'), 75.7 (CH, C5'), 77.7 (C, C5, *C*-$SiMe_2$), 77.9 (CH, C4), 79.1 (CH, C2'), 79.6 (CH, C3'), 80.8 (CH, C3), 80.9 (C, C2, *C*-SPh), 93.1 (C, C1, *C*-SO*t*Bu), 125.5 (CH, C4"), 127.2 (2CH, C2" and C6"), 128.9 (2CH, C3" and C5"), 139.3 (C, C1") ppm; $[\alpha]_D$ +604 (*c* 1). Anal. Calcd for $C_{24}H_{32}FeO_2S_2Si_2$ (528.65): C, 54.53; H, 6.10; S, 12.13. Found: C, 54.97; H, 6.18; S, 12.10%.



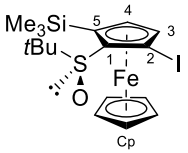
(*S*,*S*$_P$)-*S*-*tert*-Butyl-1'-(diphenylphosphino)-2-(phenylthio)-5-(trimethylsilyl)ferrocenesulfoxide (*S*,*S*$_P$-10) was prepared as follows. To a solution of (*S*,*S*$_P$)-*S*-*tert*-butyl-2-(phenylthio)-5-(trimethylsilyl)ferrocenesulfoxide (***S*,*S*$_P$-8b**; 0.60 g, 1.3 mmol) in THF (13 mL) at 0 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (1.65 mL, 2.3 mmol) before warming to rt. The reaction was stirred at this temperature for 1 h and cooled to 0 °C before addition of $ClPPh_2$ (0.41 mL). The mixture was warmed to rt and stirred for 1 h. Addition of 1 M HCl (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, which was purified by chromatography over silica gel (eluent: petroleum ether-EtOAc 40:60; Rf = 0.81). (*S*,*S*$_P$)-*S*-*tert*-Butyl-1'-(diphenylphosphino)-2-(phenylthio)-5-(trimethylsilyl)ferrocenesulfoxide (***S*,*S*$_P$-10**) was isolated in 67% yield (0.56 g) as an orange solid: mp 80-82 °C; IR (ATR) ν 739, 830, 897, 965, 1025, 1043, 1121, 1164, 1197, 1248, 1434, 1477, 1583, 2958 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9H, $SiMe_3$), 1.22 (s, 9H, *t*Bu), 4.18 (d, 1H, J = 2.5 Hz, H4), 4.20 (br s, 1H, H2'), 4.27 (br s, 1H, H5'), 4.35 (d, 1H, J = 2.5 Hz, H3), 4.92-4.94 (m, 2H, H3' and H4'), 7.13-7.16 (m, 3H, H2", H4" and H6"), 7.21-7.24 (m, 2H, H3" and H5"), 7.24-7.29 (m, 8H, 2H3"', 2H4"', 2H5"' and 2H6"'), 7.32-7.35 (m, 2H, 2H2"') ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 1.7 (3CH_3, $SiMe_3$), 25.2 (3CH_3, C*Me*$_3$), 57.5 (C, *C*Me$_3$), 75.5 (d, CH, J = 4.3 Hz, C3'), 76.2 (d, CH, J = 18.5 Hz, C2'), 78.3 (d, CH, J = 9.1 Hz, C5'), 78.7 (C, C5, *C*-$SiMe_3$), 78.7 (d, CH, J = 6.0 Hz, C4'), 79.4 (d, CH, J = 2.1 Hz, C4), 80.1 (d, C, J = 10.4 Hz, C1', *C*-PPh_2), 81.7 (d, CH, J = 2.3 Hz, C3), 83.3 (C, C2, *C*-SPh), 91.0 (C, C1, *C*-SO*t*Bu), 125.8 (CH, C4"), 128.2 (2CH, Ph), 128.3 (2CH, Ph), 128.4 (2CH, Ph), 128.7 (CH, C4"'), 128.9 (2CH, Ph), 129.1 (CH, C4"'), 133.3 (d, 2CH, J = 19.3 Hz, C2"' or C6"'), 133.9 (d, 2CH, J = 20.4 Hz, C2"' or C6"'), 138.1 (d, C, J = 9.9 Hz, C1"'), 138.6 (C, C1"), 138.9 (d, C, J = 10.2 Hz, C1"') ppm; ^{31}P{1H} NMR ($CDCl_3$) δ -18.9 ppm; $[\alpha]_D$ +429 (*c* 1). Anal. Calcd for $C_{35}H_{39}FeOPS_2Si$ (654.72): C, 64.21; H, 6.00; S, 9.79. Found: C, 64.65; H, 6.18; S, 10.11%.



General procedure G: Sulfoxide/lithium exchange using *t*BuLi.[10] To a stirred, cooled (–90 °C) solution of the ferrocenesulfoxide (1.0 mmol) in THF (10 mL) was added dropwise a 1.6 M pentane

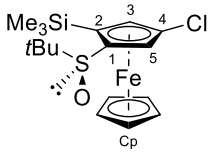
solution of *t*BuLi (0.69 mL, 1.1 mmol), and the reaction was stirred at this temperature (see the reaction time below) before addition of the electrophile (1.1 mmol unless otherwise specified; either pure for liquids or in solution for solids, as indicated below). The mixture was warmed to rt. Addition of 1 M HCl (5 mL), or saturated aqueous $Na_2S_2O_3$ in the case of I_2, 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).

(*S*,*R*P)-*S*-*tert*-Butyl-2-iodo-5-(trimethylsilyl)ferrocenesulfoxide (**S,RP-13a**) was prepared by adapting the general procedure G (30 min) to 0.53 mmol of (*S*,*S*,*R*P)-*S*-*tert*-butyl-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (**S,S,RP-11**; 0.27 g) and using I_2 (0.15 g) as the electrophile in THF (3 mL). It was isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.80) in 35% yield (95 mg) as a yellow solid: mp 184 °C; IR (ATR) ν 759, 819, 838, 871, 944, 1066, 1107, 1174, 1249, 1361, 1383, 1408, 1471, 2957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.31 (s, 9H, $SiMe_3$), 1.30 (s, 9H, *t*Bu), 4.30 (d, 1H, *J* = 2.5 Hz, H4), 4.40 (s, 5H, Cp), 4.85 (d, 1H, *J* = 2.5 Hz, H3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.7 ($3CH_3$, $SiMe_3$), 25.7 ($3CH_3$, C*Me*$_3$), 33.9 (C, C2, C-I), 58.2 (C, *C*Me_3), 74.1 (5CH, Cp), 76.8 (C, C5, *C*-$SiMe_3$), 78.9 (CH, C4), 82.7 (CH, C3), 89.4 (C, C1, *C*-SO*t*Bu) ppm; $[\alpha]_D$ +242 (*c* 1). Anal. Calcd for $C_{17}H_{25}FeIOSSi$ (488.28): C, 41.82; H, 5.16; S, 6.57. Found: C, 42.11; H, 5.29; S, 6.30%.



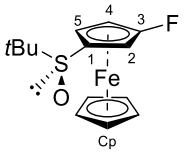
(*S*,*R*P)-*S*-*tert*-Butyl-2-(trimethylsilyl)ferrocenesulfoxide (**S,RP-12b'**) was similarly isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.52) in 40% yield (80 mg) as an orange oil (see above).

(*S*,*R*P)-*S*-*tert*-Butyl-4-chloro-2-(trimethylsilyl)ferrocenesulfoxide (**S,RP-13b**) was prepared by adapting the general procedure G (30 min) to 0.44 mmol of (*S*,*S*,*R*P)-*S*-*tert*-butyl-3-chloro-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (**S,S,RP-12a**; 0.23 g) and using $ClSiMe_3$ (60 µL). It was isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.72) in 29% yield (50 mg) as a yellow oil: IR (ATR) ν 756, 820, 900, 1027, 1105, 1209, 1249, 1361, 1458, 1642, 2958, 3481 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.32 (s, 9H, $SiMe_3$), 1.16 (s, 9H, *t*Bu), 4.42 (s, 5H, Cp), 4.46 (d, 1H, *J* = 1.4 Hz, H3), 5.11 (d, 1H, *J* = 1.4 Hz, H5) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.3 ($3CH_3$, $SiMe_3$), 23.6 ($3CH_3$, C*Me*$_3$), 55.8 (C, *C*Me_3), 68.1 (CH, C5), 72.9 (5CH, Cp), 74.5 (C, C2, *C*-$SiMe_3$), 76.0 (CH, C3), 91.5 (C, C1), 95.0 (C, C4) ppm; $[\alpha]_D$ +336 (*c* 1). Anal. Calcd for $C_{17}H_{25}ClFeOSSi$ (396.83): C, 51.46; H, 6.35; S, 8.08. Found: C, 51.63; H, 6.16; S, 8.03%.

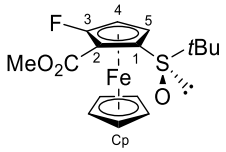


In this reaction, the starting material was also recovered in an estimated 10% yield, as a mixture with (*S*,*R*P)-*S*-*tert*-butyl-2-(trimethylsilyl)ferrocenesulfoxide (**S,RP-12b'**) also formed in about 9% yield.

(*S*,*S*P)-*S*-*tert*-Butyl-3-fluoroferrocenesulfoxide (**S,SP-13c**) was prepared by adapting the general procedure G (10 min) to 0.27 mmol of (*S*,*S*,*R*P)-*S*-*tert*-butyl-3-fluoro-*S'*-phenylferrocene-1,2-disulfoxide (**S,S,RP-7d**; 0.12 g) and using MeOH in excess (2 mL). It was isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.75) in 93% yield (77 mg) as a yellow solid: mp 176-178 °C; IR (ATR) ν 820, 939, 109, 1060, 1108, 1185, 1245, 1358, 1462, 2932 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 9H, *t*Bu), 4.12 (dt, 1H, *J* = 2.7 and 1.4 Hz, H5), 4.48 (s, 5H, Cp), 4.54 (td, 1H, *J* = 2.8 and 1.6 Hz, H4), 4.87 (dt, 1H, *J* = 3.0 and 1.5 Hz, H2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 22.9 ($3CH_3$, C*Me*$_3$), 53.8 (d, CH, *J* = 15.1 Hz, C2), 55.3 (C, *C*Me_3), 58.6 (d, CH, *J* = 16.3 Hz, C4), 63.1 (d, CH, *J* = 3.4 Hz, C5), 71.6 (5CH, Cp), 80.5 (d, C, *J* = 1.6 Hz, C1, *C*-SO*t*Bu), 134.7 (d, C, *J* = 274.3 Hz, C3, C-F) ppm; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ -183.8 ppm; $[\alpha]_D$ +138 (*c* 0.6). Anal. Calcd for $C_{14}H_{17}FFeOS$ (308.19): C, 54.56; H, 5.56; S, 10.40. Found: C, 54.10; H, 6.02; S, 10.13%.

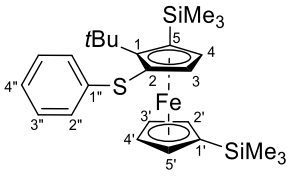


(*R*,*R*$_P$)-*S*-*tert*-Butyl-3-fluoro-2-(methoxycarbonyl)ferrocenesulfoxide (***R*,*R*$_P$-13d**) was prepared by adapting the general procedure G (7 min) to 0.68 mmol of (*R*,*R*,*S*$_P$)-*S*-*tert*-butyl-3-fluoro-*S'*-phenylferrocene-1,2-disulfoxide (***R*,*R*,*S*$_P$-7d**; 0.30 g) and using methyl chloroformiate (0.27 mL, 3.4 mmol; reverse addition). It was isolated (eluent: petroleum ether-EtOAc 30:70; Rf = 0.35) in 46% yield (0.12 g) as a brownish-orange oil: IR (ATR) ν 751, 826, 948, 1047, 1076, 1130, 1175, 1213, 1276, 1335, 1379, 1416, 1452, 1716, 2954, 3089, 3440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9H, *t*Bu), 3.89 (s, 3H, OMe), 4.29 (dd, 1H, *J* = 2.8 and 1.9 Hz, H5), 4.57 (s, 5H, Cp), 4.72 (t, 1H, *J* = 2.9 Hz, H4) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.1 ($3CH_3$, C*Me*$_3$), 52.4 (CH_3, OMe), 56.9 (C, *C*Me$_3$), 59.7 (d, CH, *J* = 15.4 Hz, C4), 63.3 (d, C, *J* = 8.7 Hz, C2, *C*-CO_2Me), 65.8 (d, CH, *J* = 3.7 Hz, C5), 73.6 (5CH, Cp), 81.4 (C, C1, *C*-SO*t*Bu), 134.9 (d, C, *J* = 284.2 Hz, C3, C-F), 167.4 (d, C, *J* = 4.5 Hz, C=O) ppm; ^{19}F{^{1}H} NMR ($CDCl_3$) δ -179.5 ppm; $[\alpha]_D$ -182 (*c* 0.6). Anal. Calcd for $C_{16}H_{19}FFeO_3S$ (366.23): C, 52.47; H, 5.23; S, 8.75. Found: C, 52.11; H, 5.34; S, 8.78%.

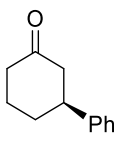


(*R*,*R*$_P$)-*S*-*tert*-Butyl-3-fluoroferrocenesulfoxide (***R*,*R*$_P$-13c**) was also isolated in 9% yield (19 mg) as well as recovered starting material (4% yield).

(*S*$_P$)-1-*tert*-Butyl-2-(phenylthio)-5,1'-bis(trimethylsilyl)ferrocene (*S*$_P$-14) was obtained as follows. To a solution of (*S*,*S*$_P$)-*S*-*tert*-butyl-2-(phenylthio)-5,1'-bis(trimethylsilyl)ferrocenesulfoxide (***S*,*S*$_P$-9a**; 0.55 g, 1.0 mmol) in THF (10 mL) at 0 °C was added dropwise a 1.4 M hexane solution of *n*BuLi (0.86 mL, 1.2 mmol) before warming to rt. The reaction was stirred at this temperature for 1 h and cooled to 0 °C before addition of $ClSiMe_3$ (0.15 mL). The mixture was warmed to rt and stirred for 1 h. Addition of 1 M HCl (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, which was purified by chromatography over silica gel (eluent: petroleum ether-EtOAc 80:20; Rf = 0.84). (*S*$_P$)-1-*tert*-Butyl-2-(phenylthio)-5,1'-bis(trimethylsilyl)ferrocene (***S*$_P$-14**) was isolated in 28% yield (0.135 g) as an orange oil: IR (ATR) ν 736, 752, 823, 870, 900, 967, 1025, 1037, 1065, 1122, 1200, 1246, 1384, 1439, 1456, 1478, 1582, 2955 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9H, C1'-$SiMe_3$), 0.40 (s, 9H, C5-$SiMe_3$), 1.12 (s, 9H, *t*Bu), 4.04 (dt, 1H, *J* = 2.4 and 1.2 Hz, H2'), 4.14 (dt, 1H, *J* = 2.4 and 1.2 Hz, H5'), 4.31 (d, 1H, *J* = 2.6 Hz, H4), 4.35 (td, 1H, *J* = 2.4 and 1.1 Hz, H4'), 4.41 (td, 1H, *J* = 2.3 and 1.1 Hz, H3'), 4.79 (d, 1H, *J* = 2.6 Hz, H3), 7.05 (t, 1H, *J* = 7.2 Hz, H4"), 7.14 (dd, 2H, *J* = 8.5 and 1.4 Hz, H2" and H6"), 7.19 (t, 2H, *J* = 7.6 Hz, H3" and H5") ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 0.0 ($3CH_3$, C1'-Si*Me*$_3$), 1.5 ($3CH_3$, C5-Si*Me*$_3$), 31.9 ($3CH_3$, C*Me*$_3$), 46.8 (C, *C*Me$_3$), 74.5 (CH, C2' or C3'), 74.6 (CH, C2' or C3'), 75.1 (C, C1', *C*-$SiMe_3$), 76.8 (CH, C4), 77.2 (CH, C4'), 78.8 (CH, C5'), 80.1 (C, C5, *C*-$SiMe_3$), 81.0 (CH, C3), 85.3 (C, C1, *C*-*t*Bu), 86.5 (C, C2, *C*-SPh), 124.8 (CH, C4"), 126.1 (2CH, C2" and C6"), 128.7 (2CH, C3" and C5"), 140.7 (C, C1") ppm; $[\alpha]_D$ +305 (*c* 1). Anal. Calcd for $C_{26}H_{38}FeSSi_2$ (494.66): C, 63.13; H, 7.74; S, 6.48. Found: C, 63.17; H, 7.76; S, 6.31%. In this reaction, the starting material was also recovered in a 48% yield (0.26 g).



The evaluation of the ligands in the rhodium-catalysed 1,4-addition of phenylboronic acids to 2-cyclohexenone was performed as follows.[17] A solution of the ligand (***S*,*S*,*R*$_P$-2**; 13 mg, 30 μmol) and $[Rh(C_2H_4)_2Cl]_2$ (6.0 mg, 15 μmol) in degassed toluene was stirred for 30 min at rt. To this solution, was added phenylboronic acid (0.15 g, 1.2 mmol), 2-cyclohexenone (58 mg, 0.60 mmol) and a 2.5 M aqueous solution of NaOH (0.12 mL, 0.30 mmol). Once the starting material was consumed (TLC monitoring using petroleum ether-EtOAc 90:10 as eluent), the crude was purified by chromatography over silica gel (Rf = 0.54) to afford 3-phenylcyclohexanone in 99% yield (0.10 g) as a colourless oil. The product was identified by comparison of its ^{1}H NMR ($CDCl_3$) spectrum with that reported.[17] $[\alpha]_D$ -19 (*c* 1). HPLC: 88% ee in favour of the *S* enantiomer, Chiralpack IA3 column, eluent: *n*-hexane-i-PrOH 97:3, 0.8 mL.min^{-1}, 30 °C, t_R = 8.68 min (major), 9.73 min (minor).



B) X-ray Crystallography

Crystallography. For ***S*-FcSO*t*Bu**, the X-ray diffraction data were collected using D8 VENTURE Bruker AXS diffractometer equipped with a CMOS-PHOTON70 detector. For ***S,S*P-9a** and ***S,R*P-13a**, the X-ray diffraction data were collected using APEXII Kappa-CCD (Bruker-AXS) diffractometer equipped with a CCD plate detector. The structure was solved by dual-space algorithm using the *SHELXT* program,[18] and then refined with full-matrix least-square methods based on F^2 (*SHELXL*).[19] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The molecular diagrams were generated by MERCURY (version 3.9).

Crystal data for *S*-FcSO*t*Bu. $C_{14}H_{18}FeOS$, M = 290.19, T = 150 K; orthorhombic $P\ 2_1\ 2_1\ 2_1$ (I.T.#19), a = 5.9280(4), b = 9.8602(7), c = 22.3535(13) Å, V = 1306.59(15) Å^3. Z = 4, d = 1.475 g.cm^{-3}, μ = 1.294 mm^{-1}. A final refinement on F^2 with 2953 unique intensities and 157 parameters converged at ωR_F^2 = 0.0811 (R_F = 0.0347) for 2849 observed reflections with $I > 2\sigma(I)$. CCDC 2127411.

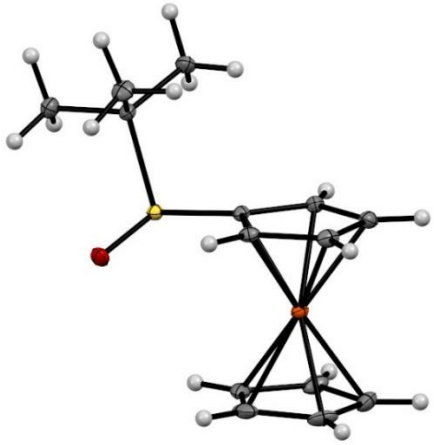


Figure 1. Molecular structure of compound ***S*-FcSO*t*Bu** (thermal ellipsoids shown at the 30% probability level).

Crystal data for *S,S*P-9a. $C_{26}H_{38}FeOS_2Si_2$, M = 542.71, T = 150 K; monoclinic $P\ 2_1$ (I.T.#4), a = 9.3403(6), b = 13.3410(8), c = 12.3446(8) Å, β = 109.899(3) °, V = 1446.40(16) Å^3. Z = 2, d = 1.246 g.cm^{-3}, μ = 0.765 mm^{-1}. A final refinement on F^2 with 4769 unique intensities and 298 parameters converged at ωR_F^2 = 0.0728 (R_F = 0.0339) for 4250 observed reflections with $I > 2\sigma(I)$. CCDC 2127412.

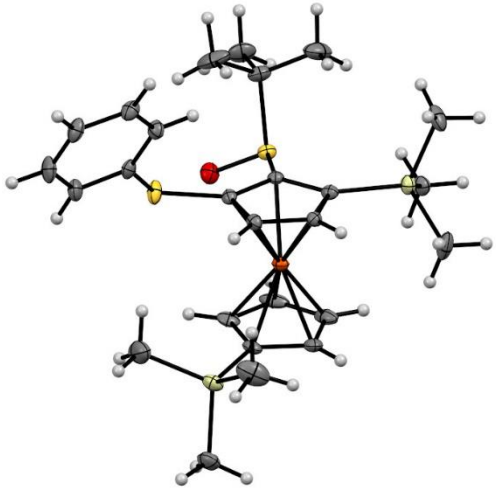


Figure 2. Molecular structure of compound ***S,S*P-9a** (thermal ellipsoids shown at the 30% probability level).

Crystal data for *S,R*$_P$-13a. $C_{17}H_{25}FeIOSSi$, M = 488.27, T = 150 K; orthorhombic $P\ 2_1\ 2_1\ 2_1$ (I.T.#19), a = 10.6604(5), b = 11.6304(6), c = 15.9593(8) Å, V = 1978.71(17) Å^3. Z = 4, d = 1.639 g.cm^{-3}, μ = 2.488 mm^{-1}. A final refinement on F^2 with 4437 unique intensities and 205 parameters converged at ωR_F^2 = 0.0525 (R_F = 0.0247) for 4192 observed reflections with $I > 2\sigma(I)$. CCDC 2127413.

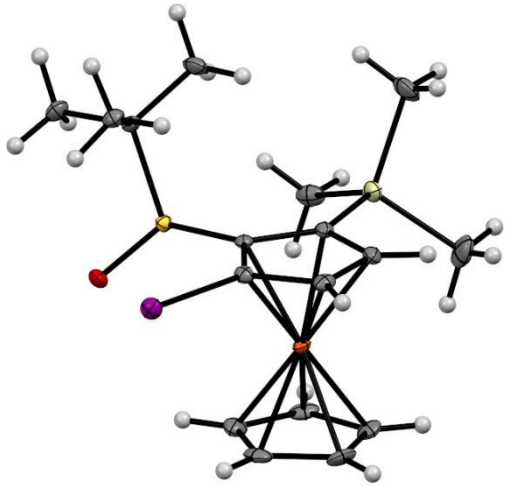


Figure 3. Molecular structure of compound ***S,R*$_P$-13a** (thermal ellipsoids shown at the 30% probability level).

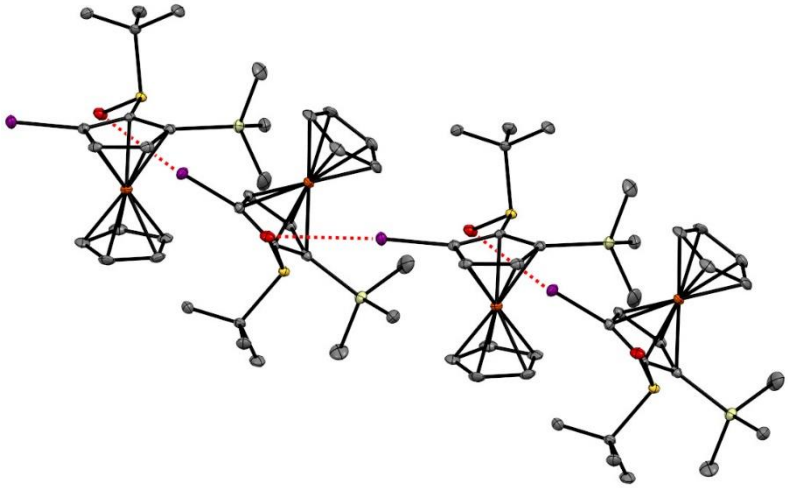
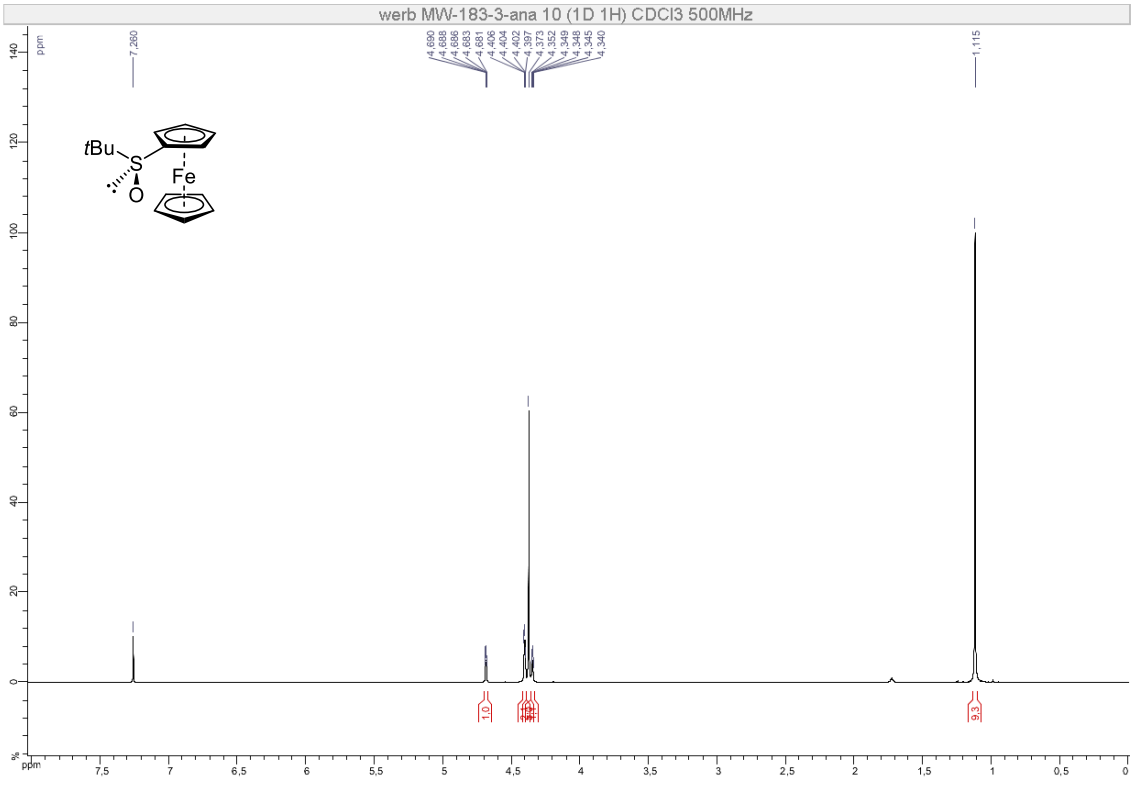


Figure 4. Halogen bond network observed at the solid state for compound ***S,R*$_P$-13a** (thermal ellipsoids shown at the 30% probability level). Hydrogens were omitted for clarity.

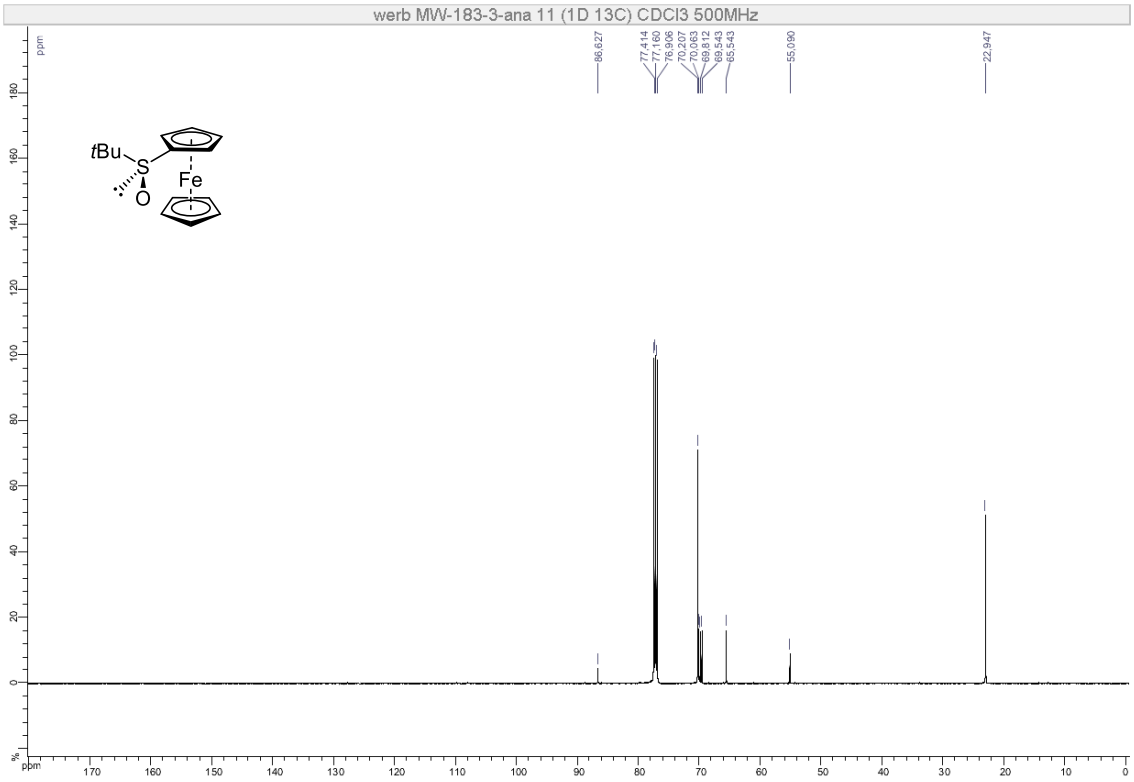
C) NMR Spectra

(*S*)-*S*-*tert*-Butylferrocenesulfoxide (*S*-FcSO*t*Bu)

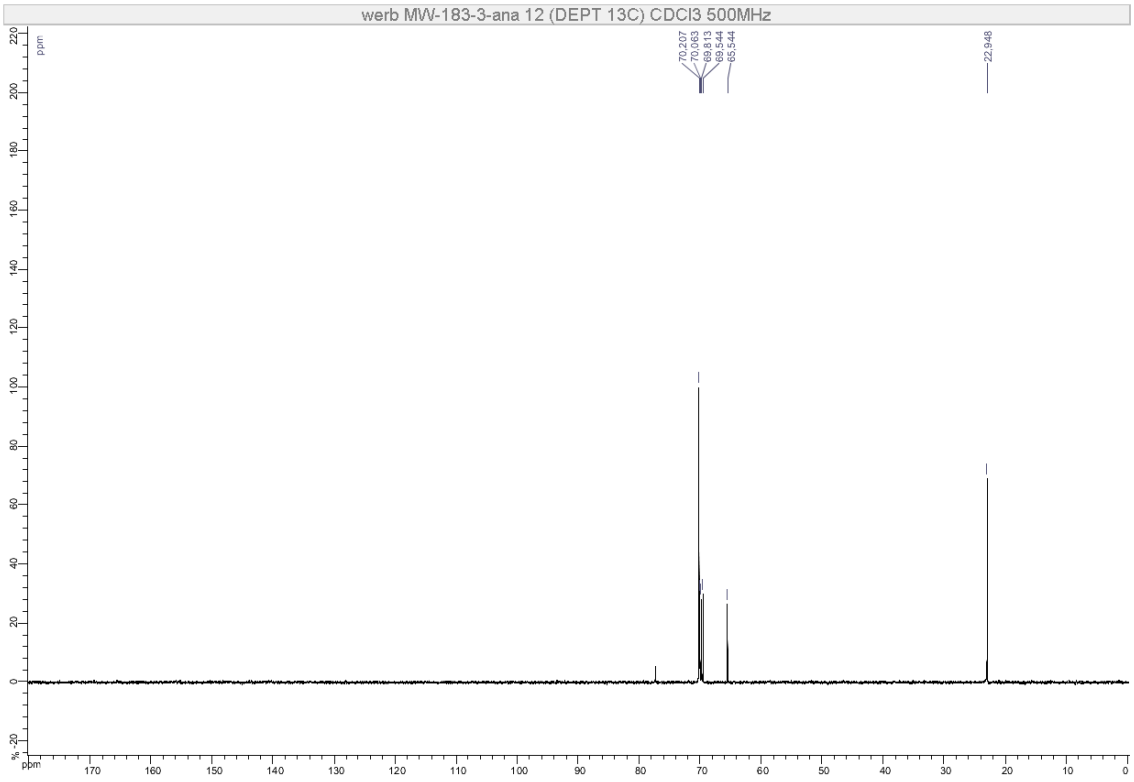
^{1}H NMR (500 MHz, $CDCl_3$)



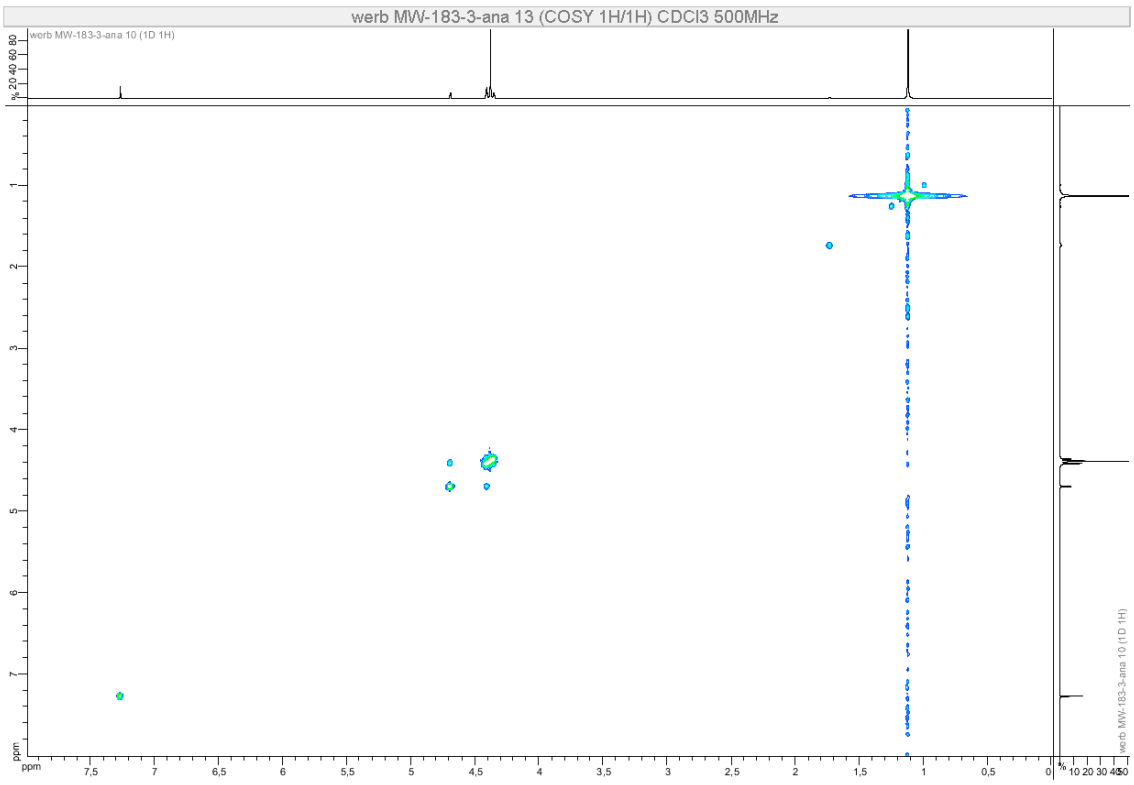
^{13}C NMR (126 MHz, $CDCl_3$)



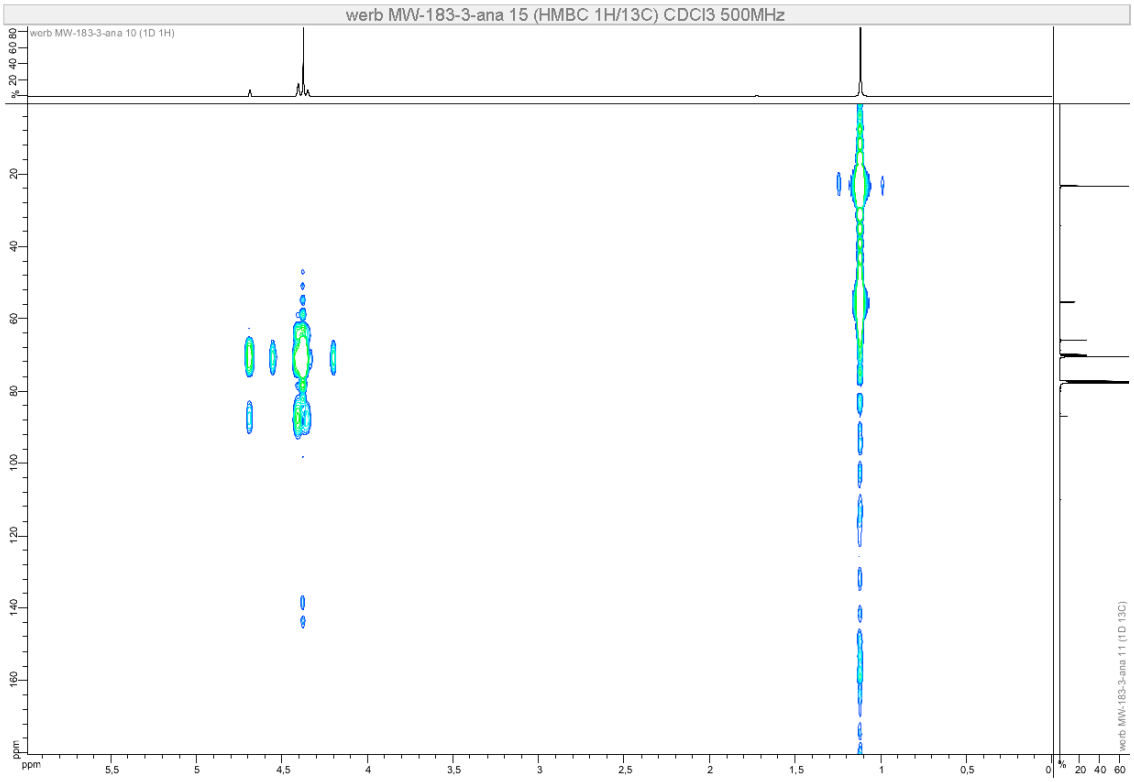
DEPT 135 (126 MHz, $CDCl_3$)



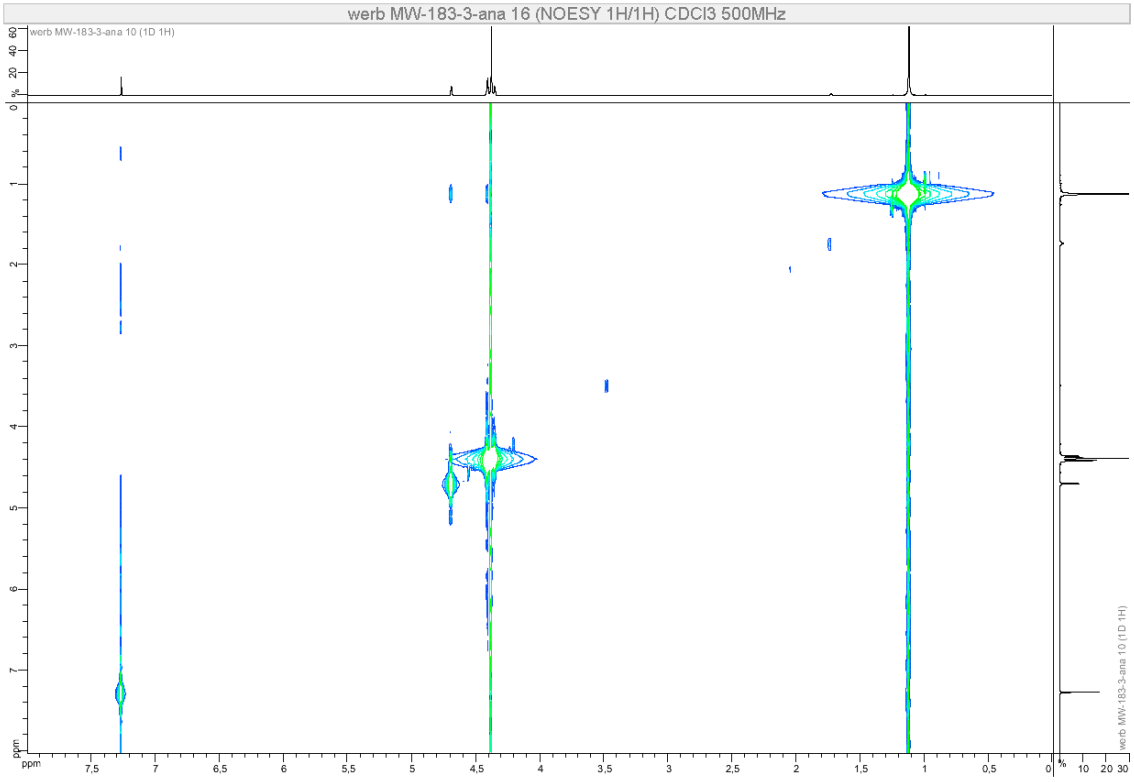
COSY (500 MHz, $CDCl_3$)



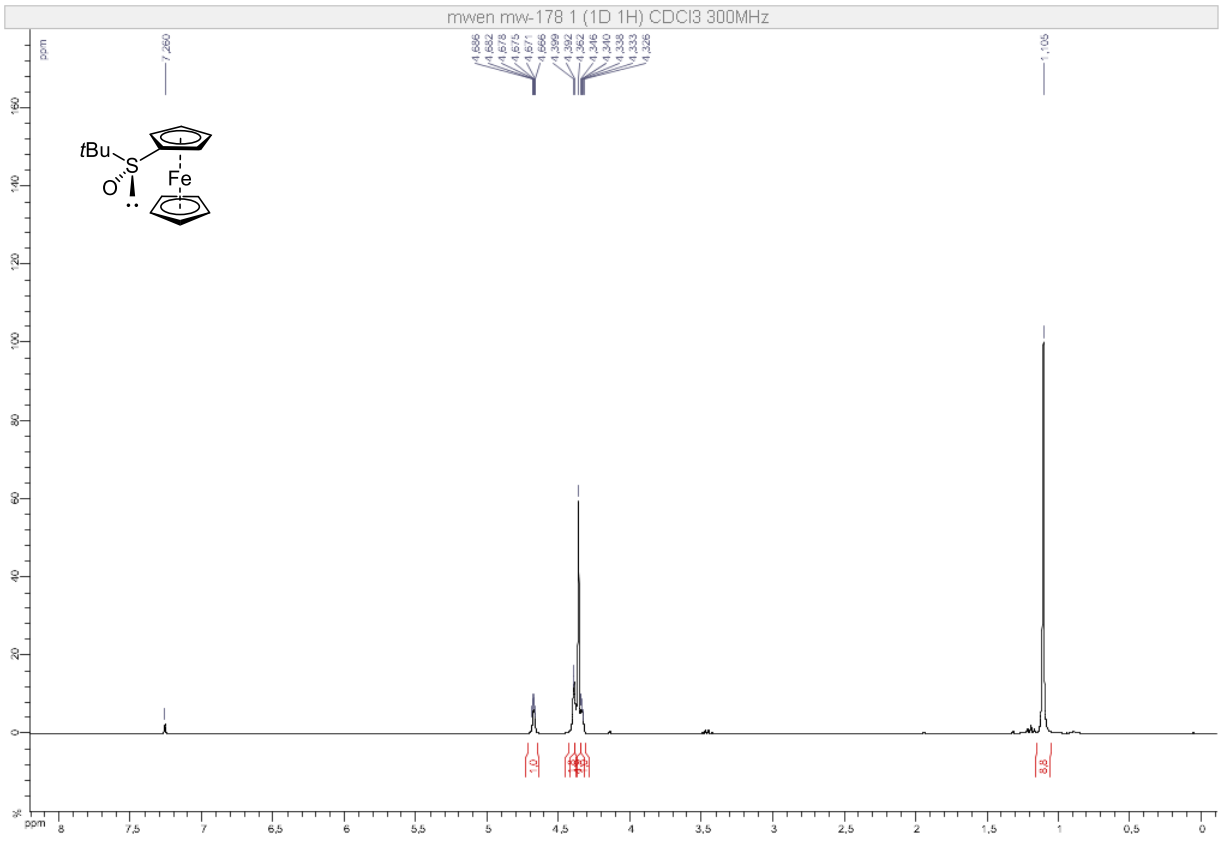
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

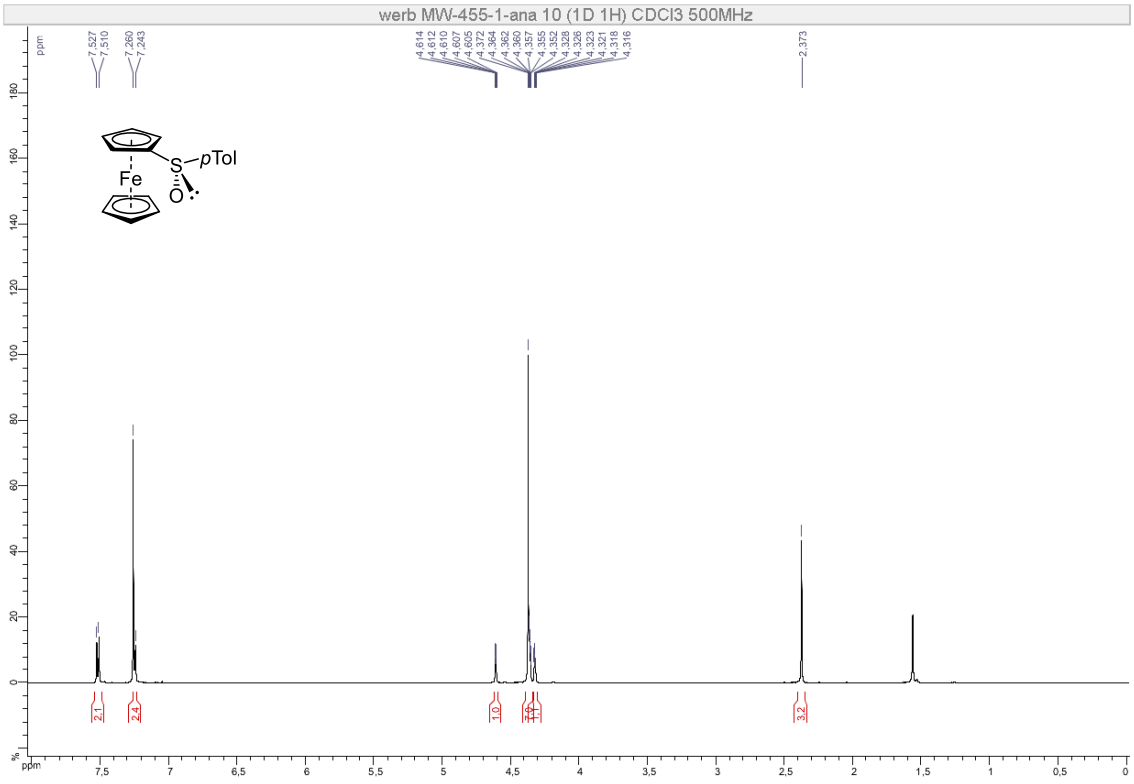


(*R*)-*S*-*tert*-Butylferrocenesulfoxide (*R*-FcSO*t*Bu)

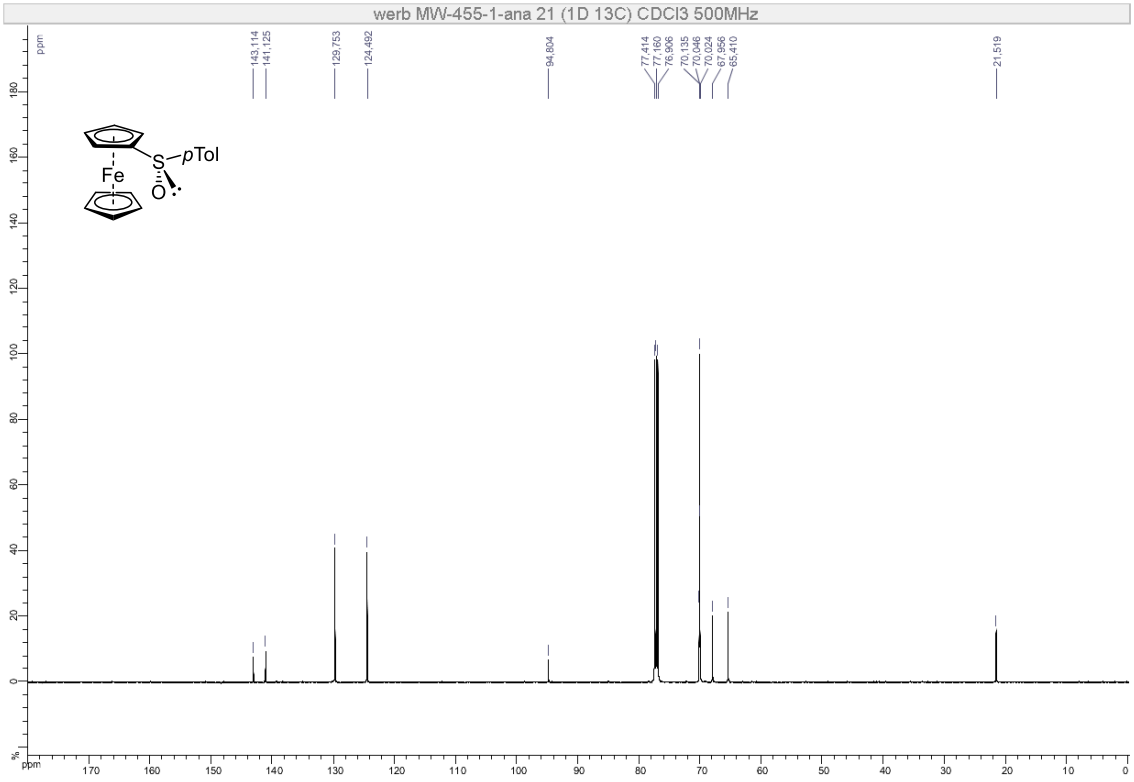


(*S*)-*S*-(4-Tolyl)ferrocenesulfoxide (***S*-FcSO-*p*-Tol**)

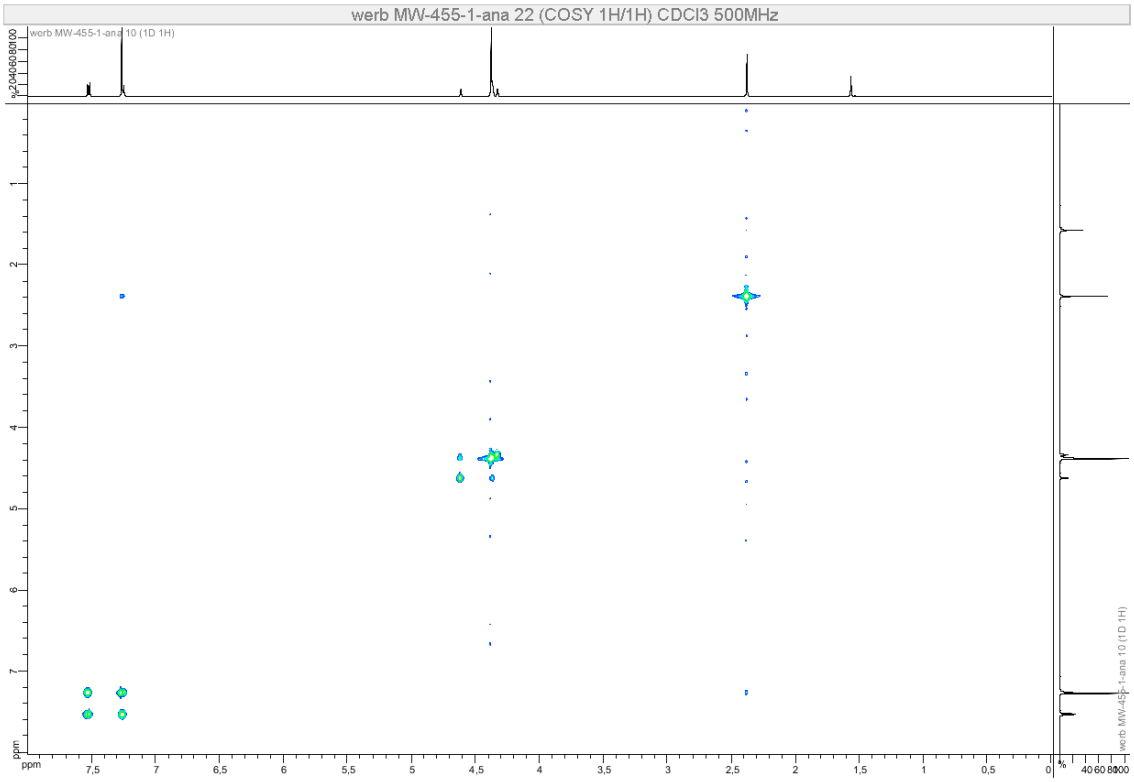
^{1}H NMR (500 MHz, $CDCl_3$)



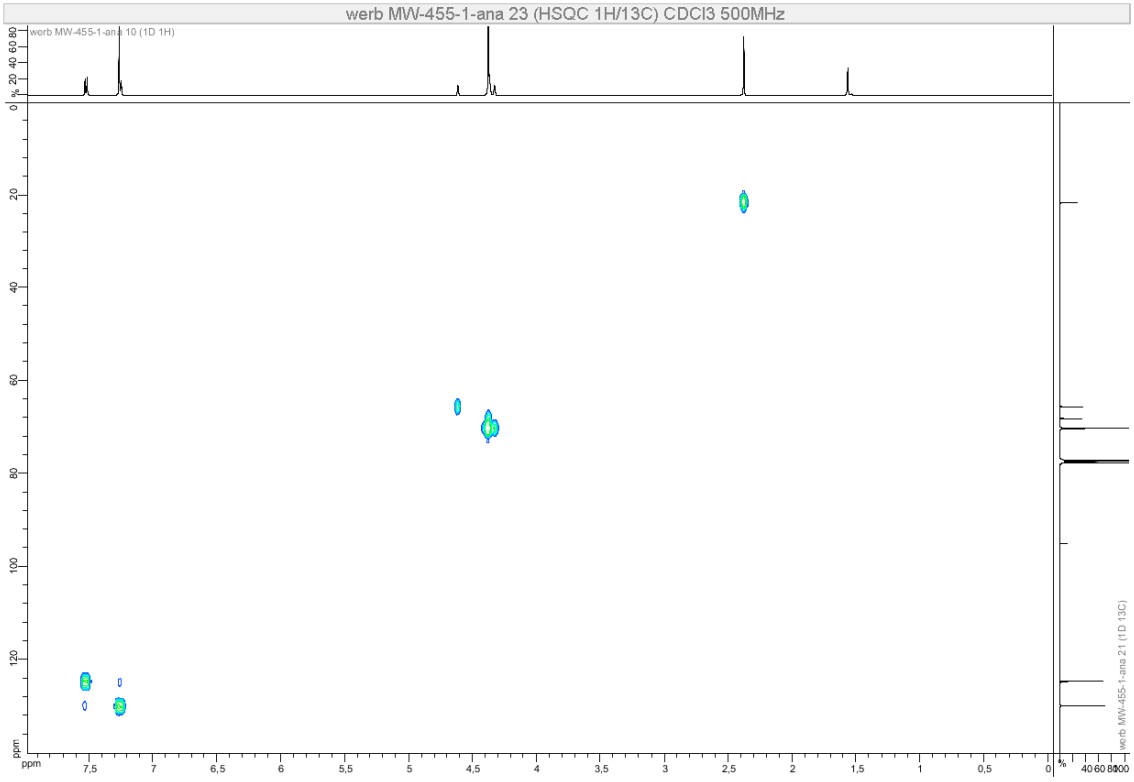
^{13}C NMR (126 MHz, $CDCl_3$)



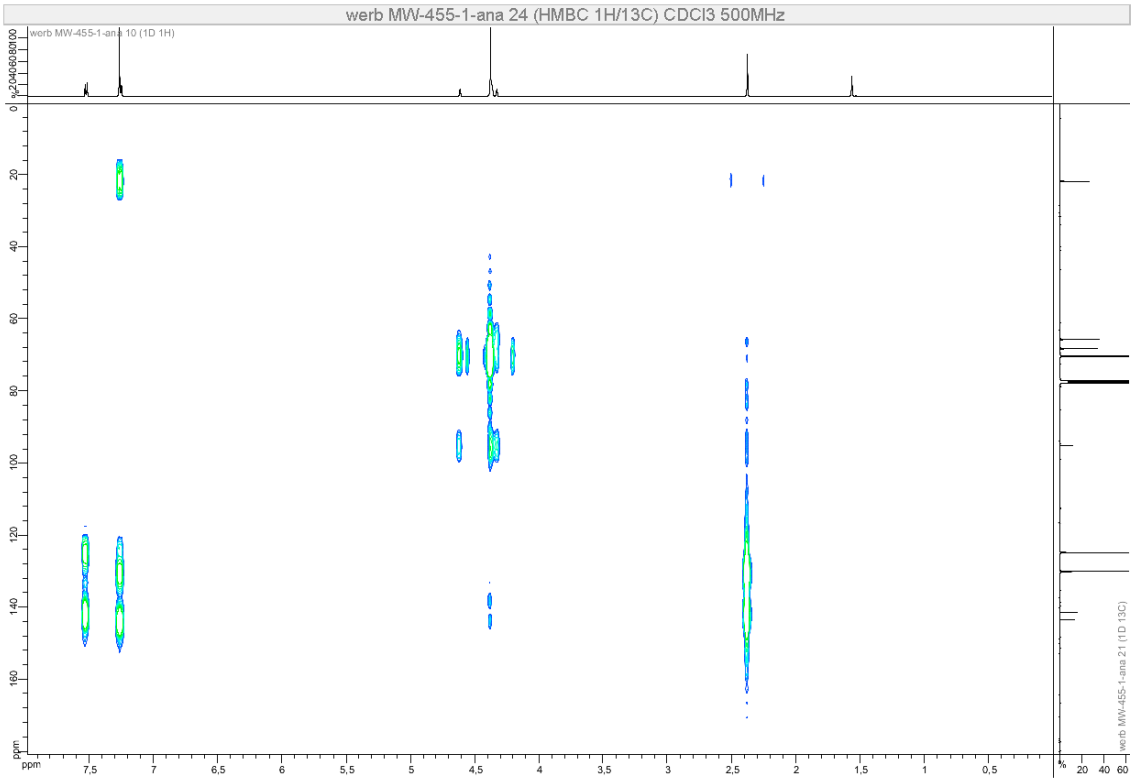
COSY (500 MHz, $CDCl_3$)



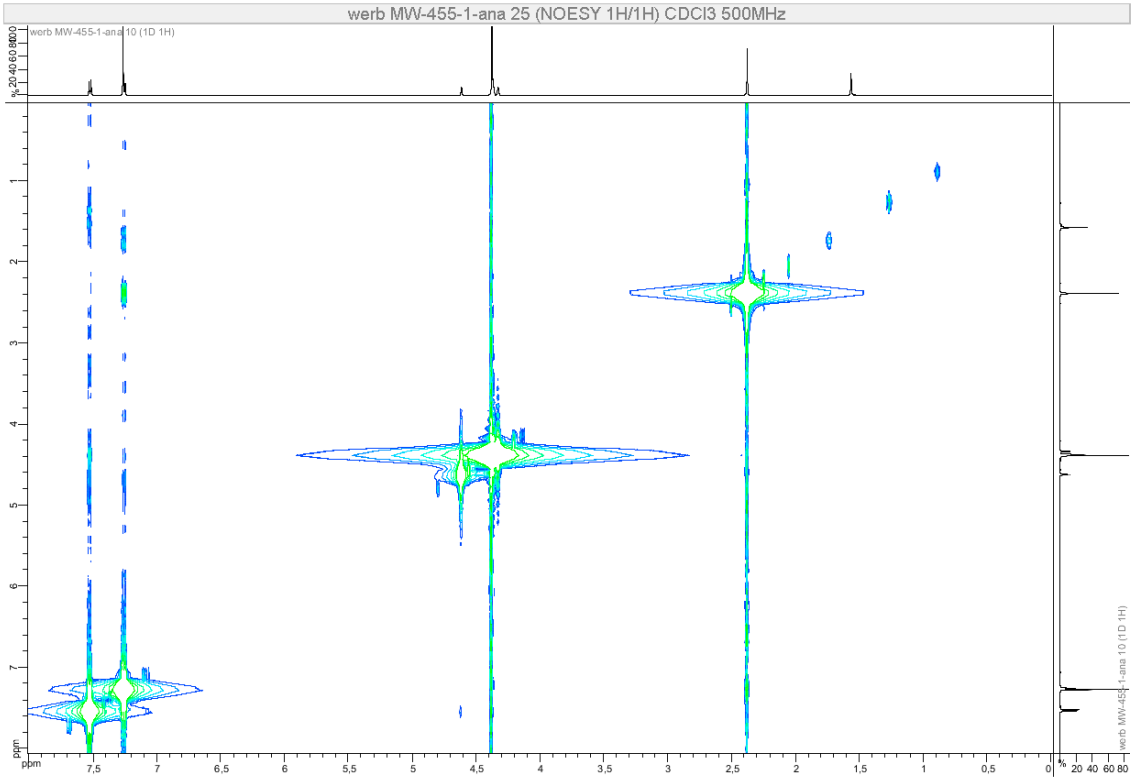
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

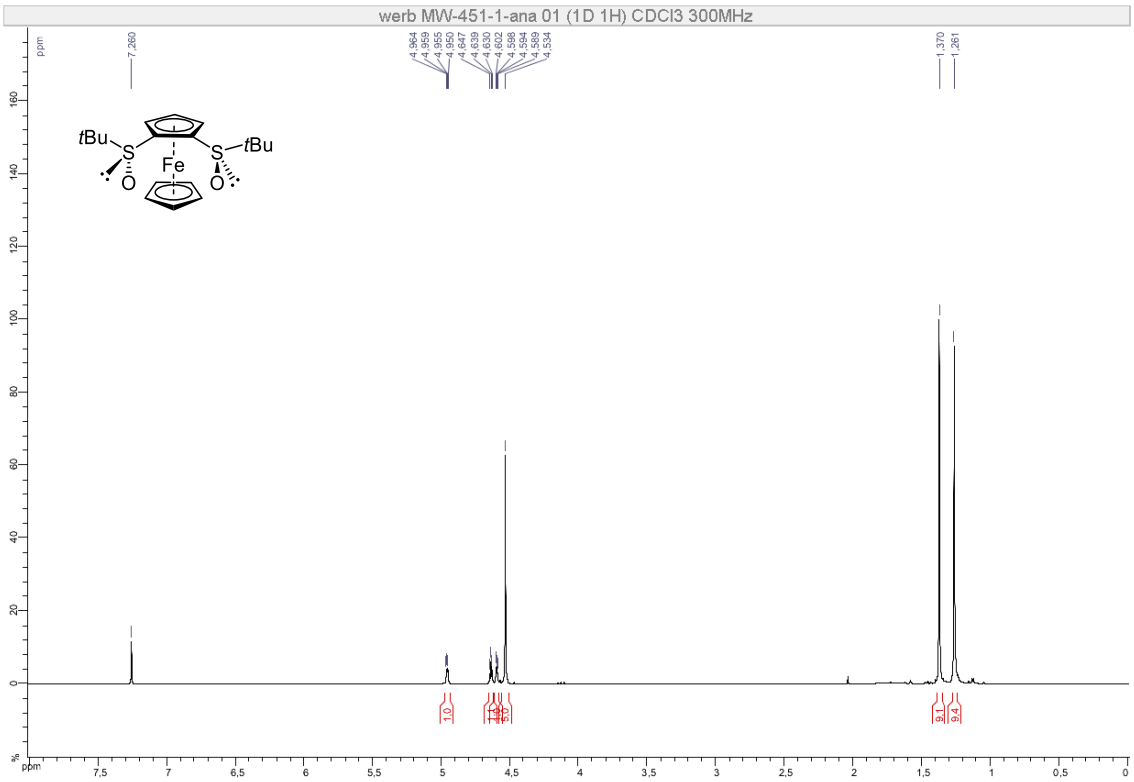


NOESY (500 MHz, $CDCl_3$)

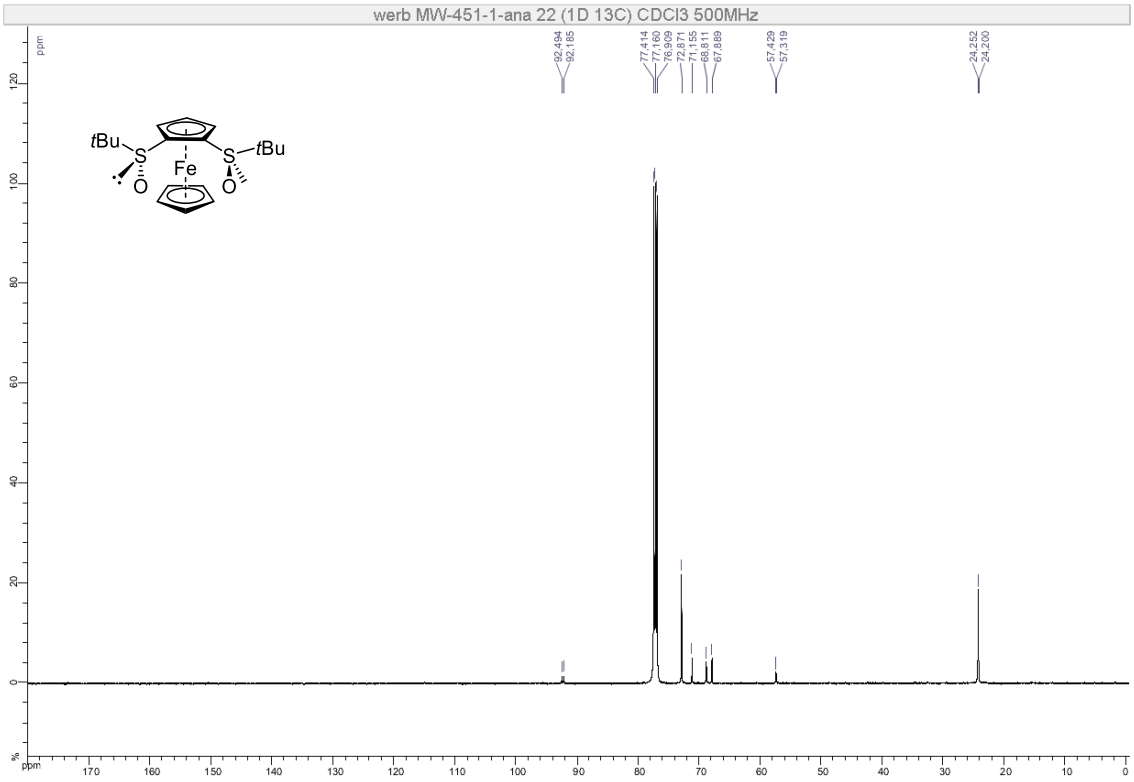


(*R*,*R*)-*S*,*S*'-Di-*tert*-butylferrocene-1,2-disulfoxide (*R*,*R*-1)

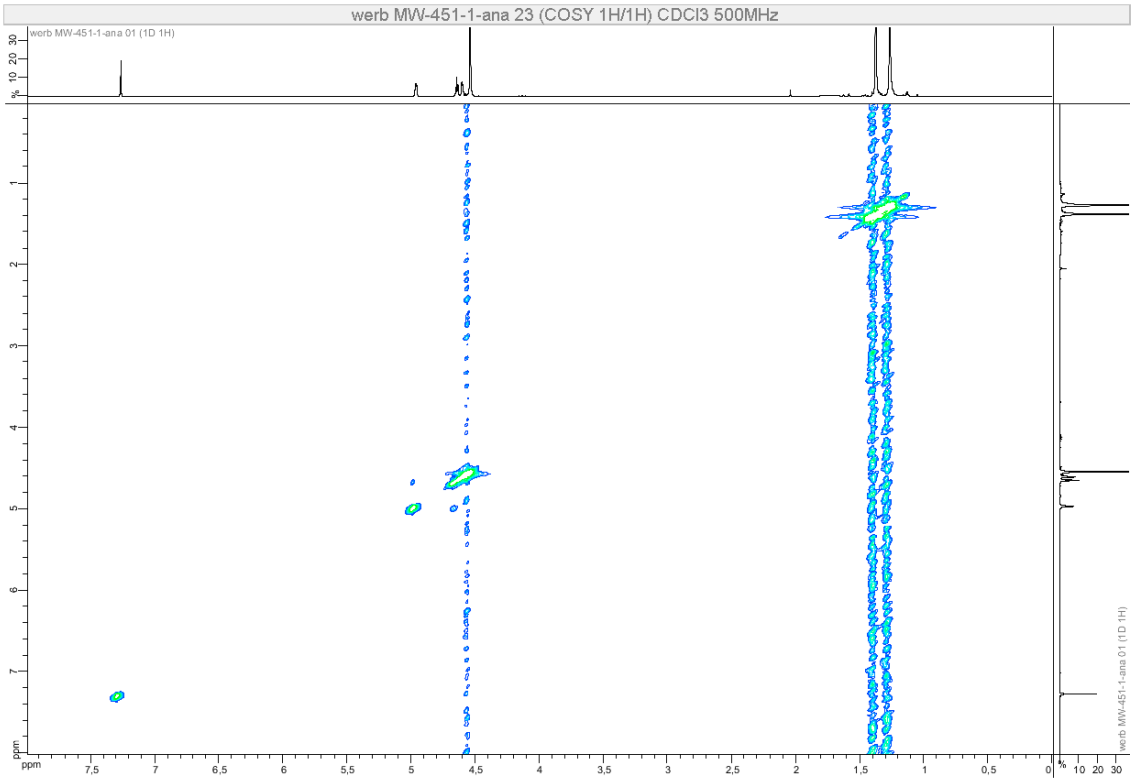
^{1}H NMR (500 MHz, $CDCl_3$)



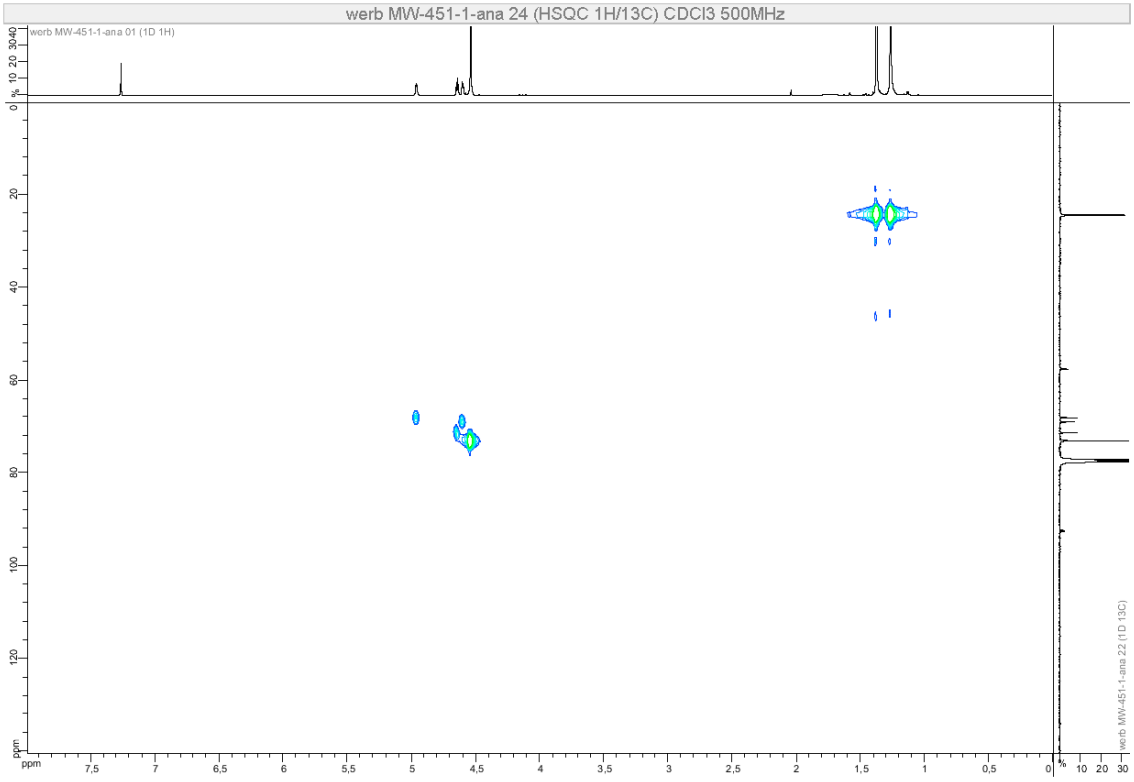
^{13}C NMR (126 MHz, $CDCl_3$)



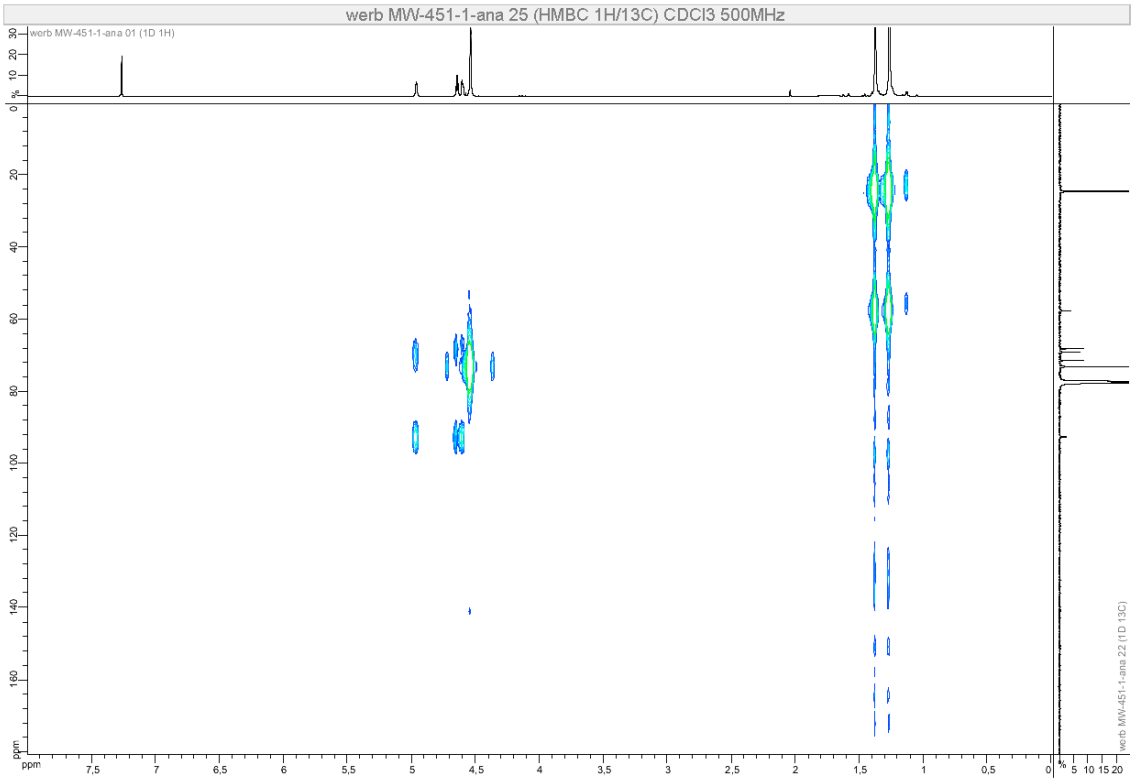
COSY (500 MHz, $CDCl_3$)



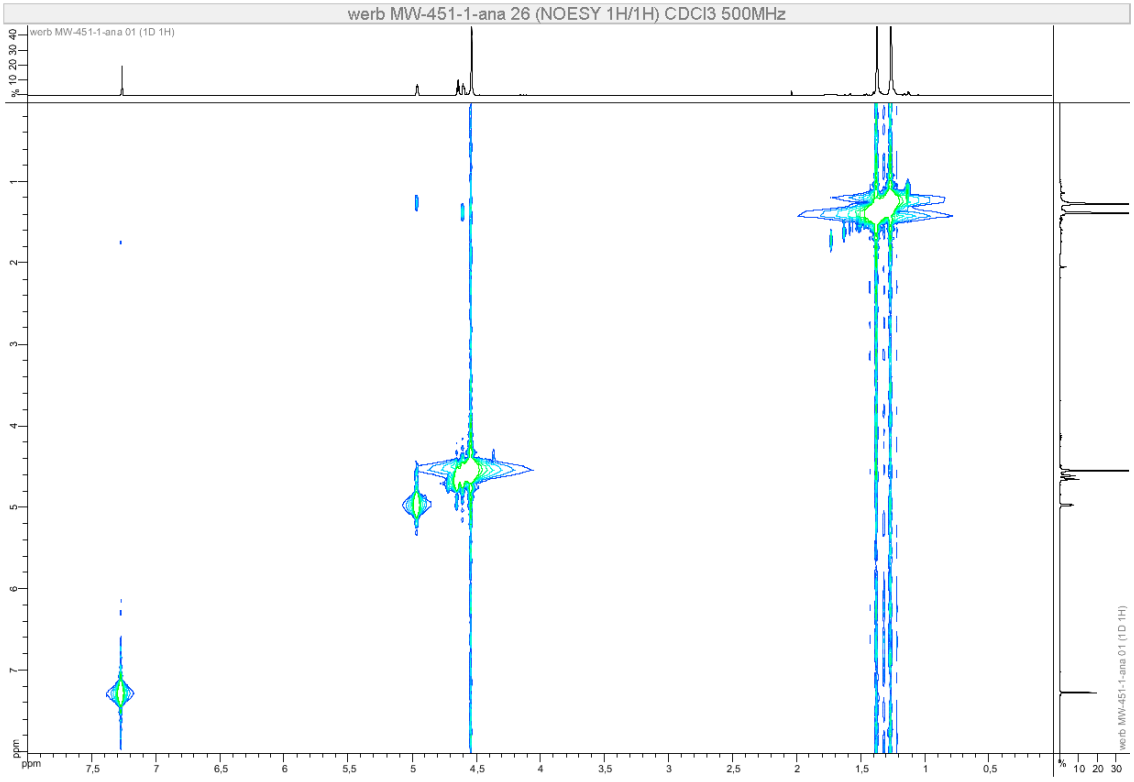
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

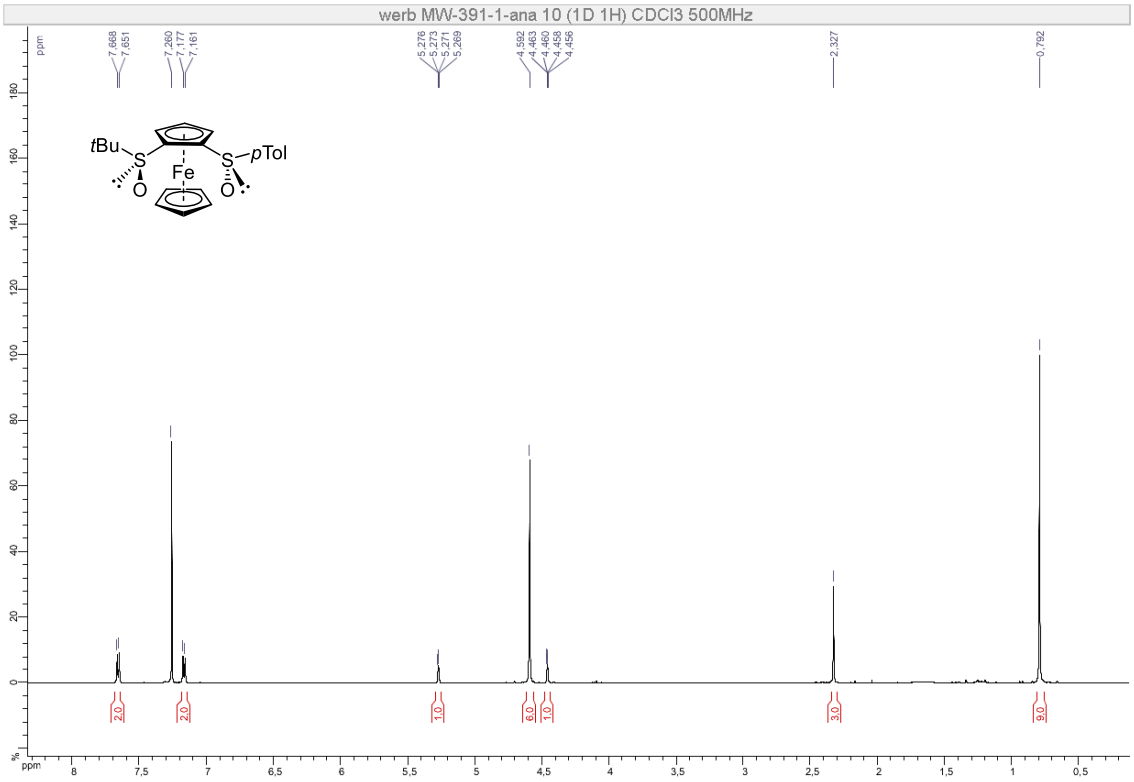


NOESY (500 MHz, $CDCl_3$)

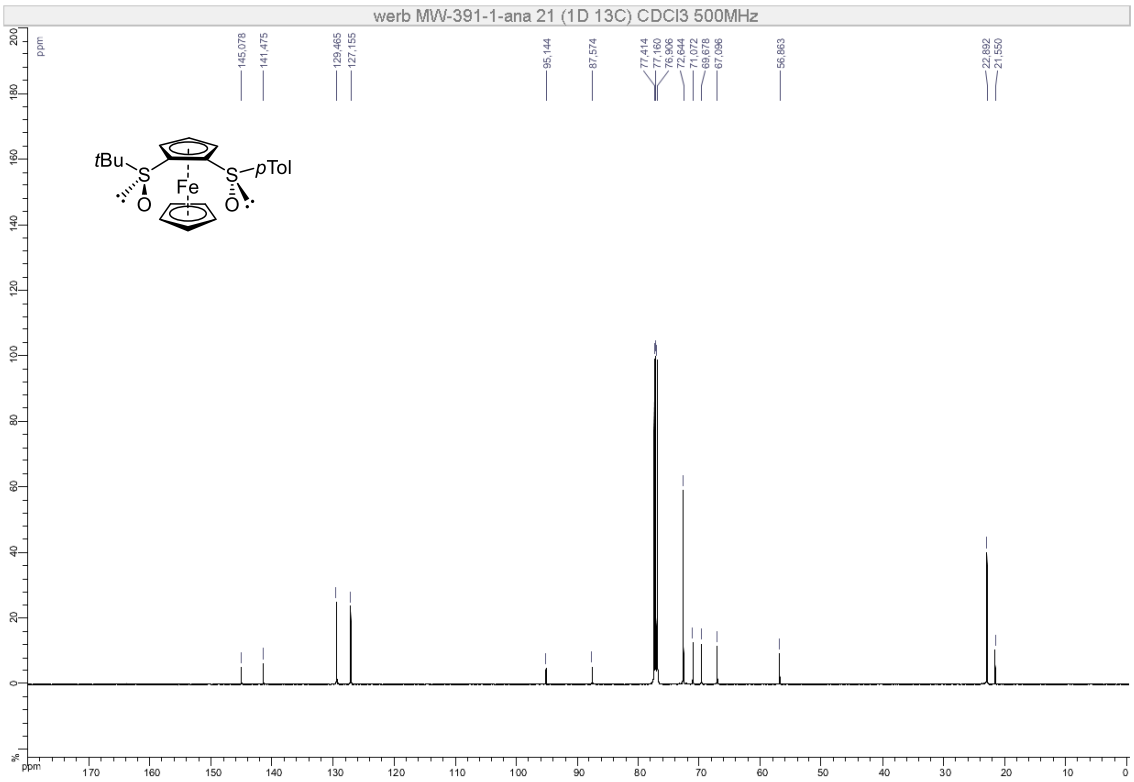


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-*S'*-tolylferrocene-1,2-disulfoxide (*S*,*S*,*R*$_P$-2)

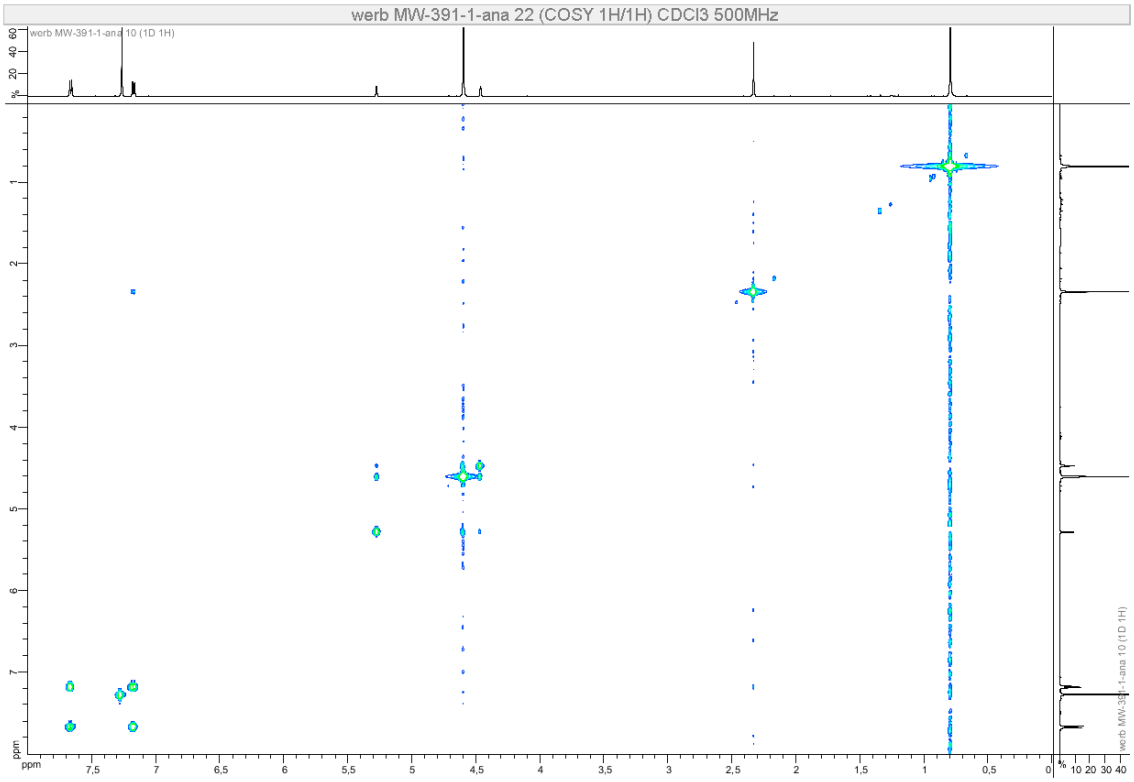
^{1}H NMR (500 MHz, $CDCl_3$)



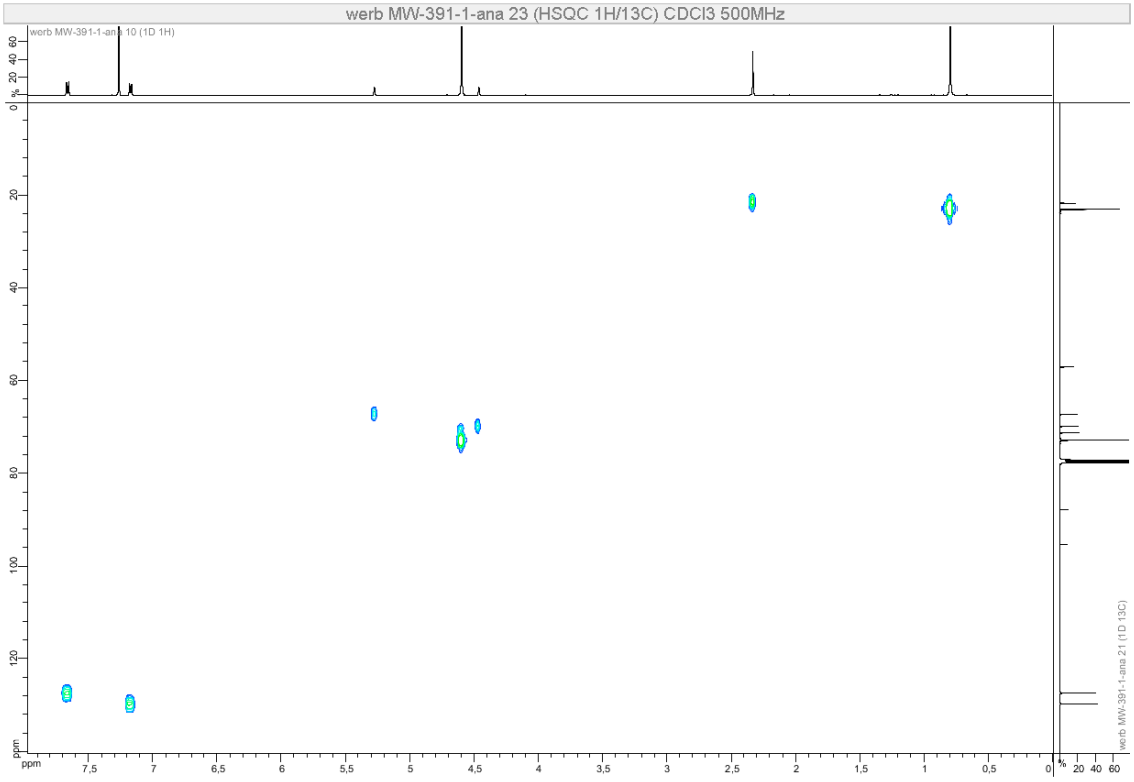
^{13}C NMR (126 MHz, $CDCl_3$)



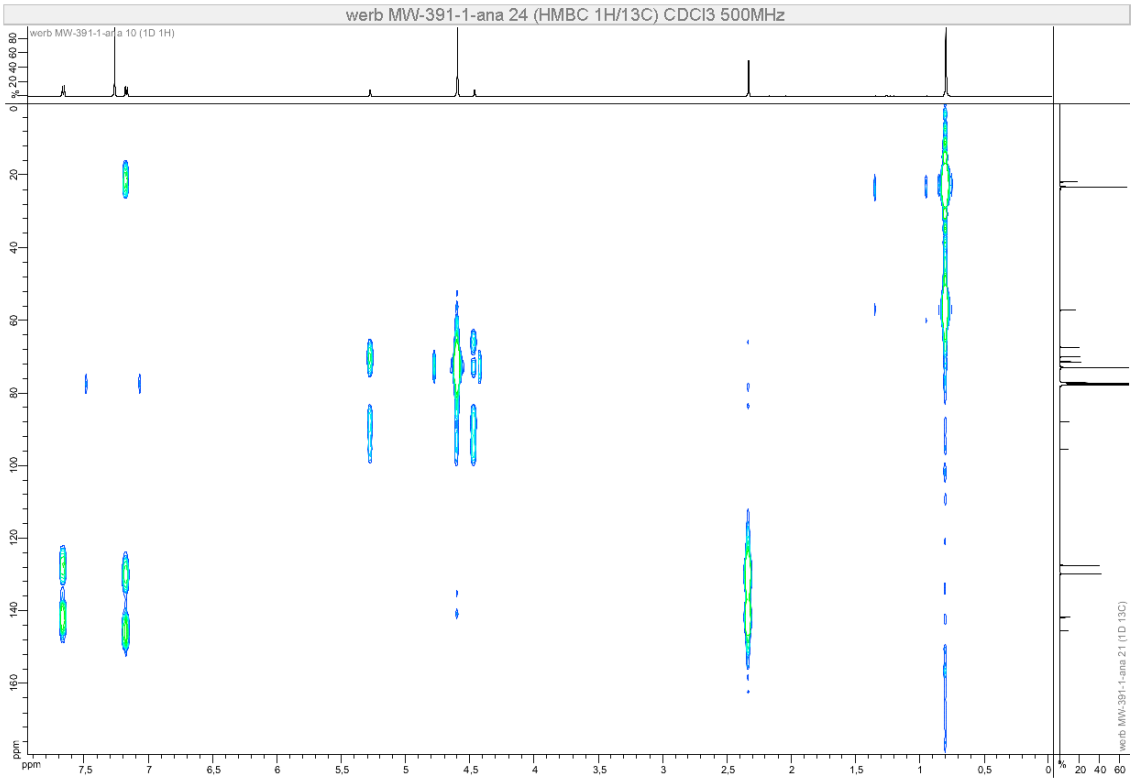
COSY (500 MHz, $CDCl_3$)



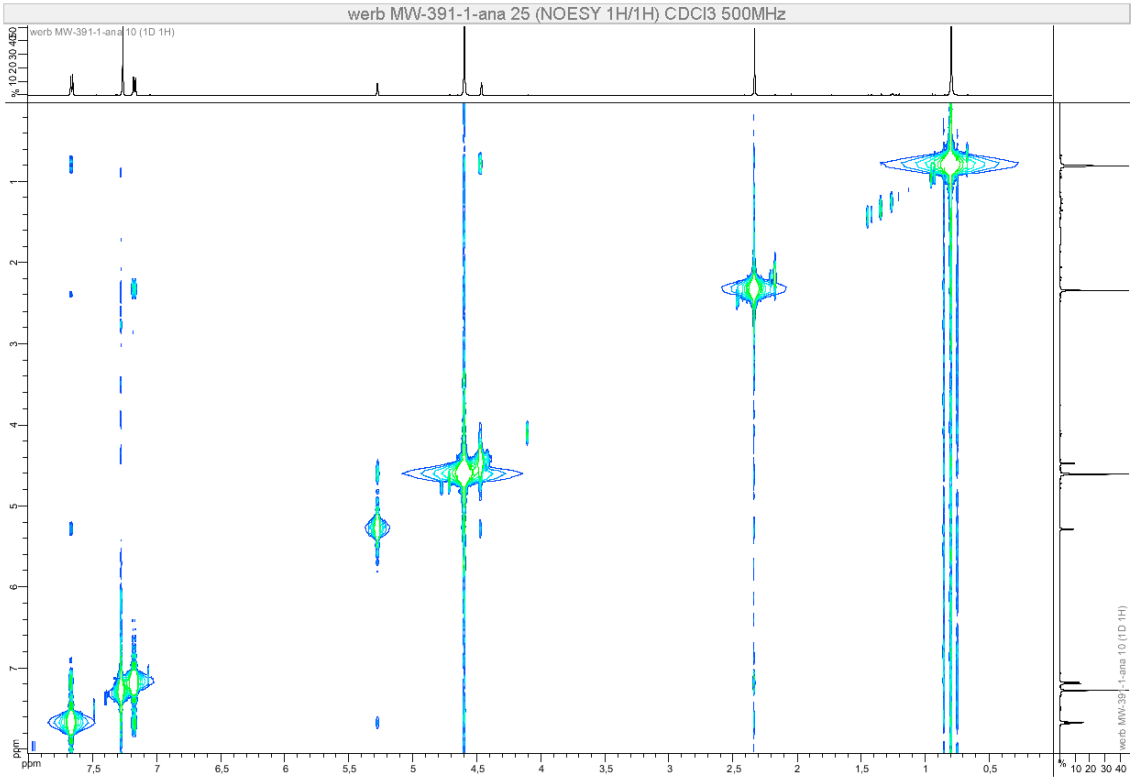
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

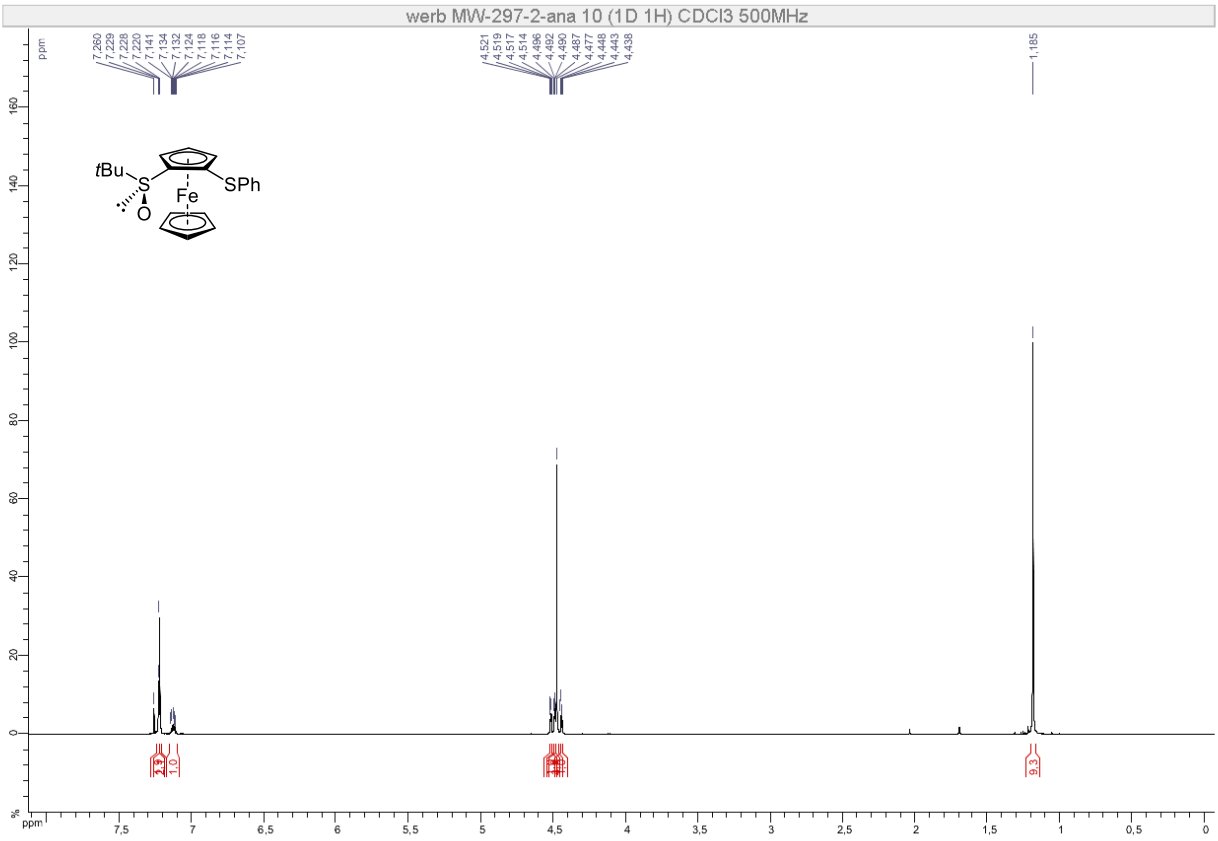


NOESY (500 MHz, $CDCl_3$)

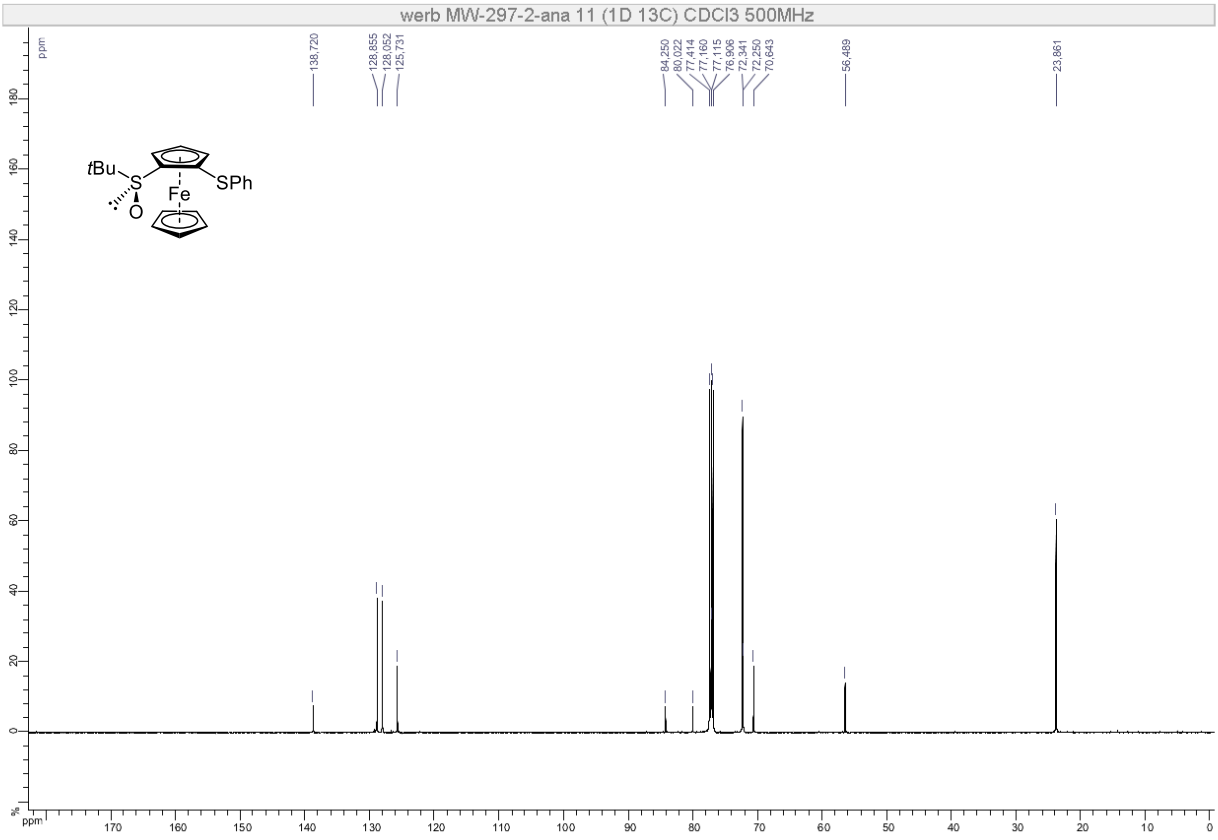


(*S*,*S*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)ferrocenesulfoxide (*S*,*S*$_P$-4)

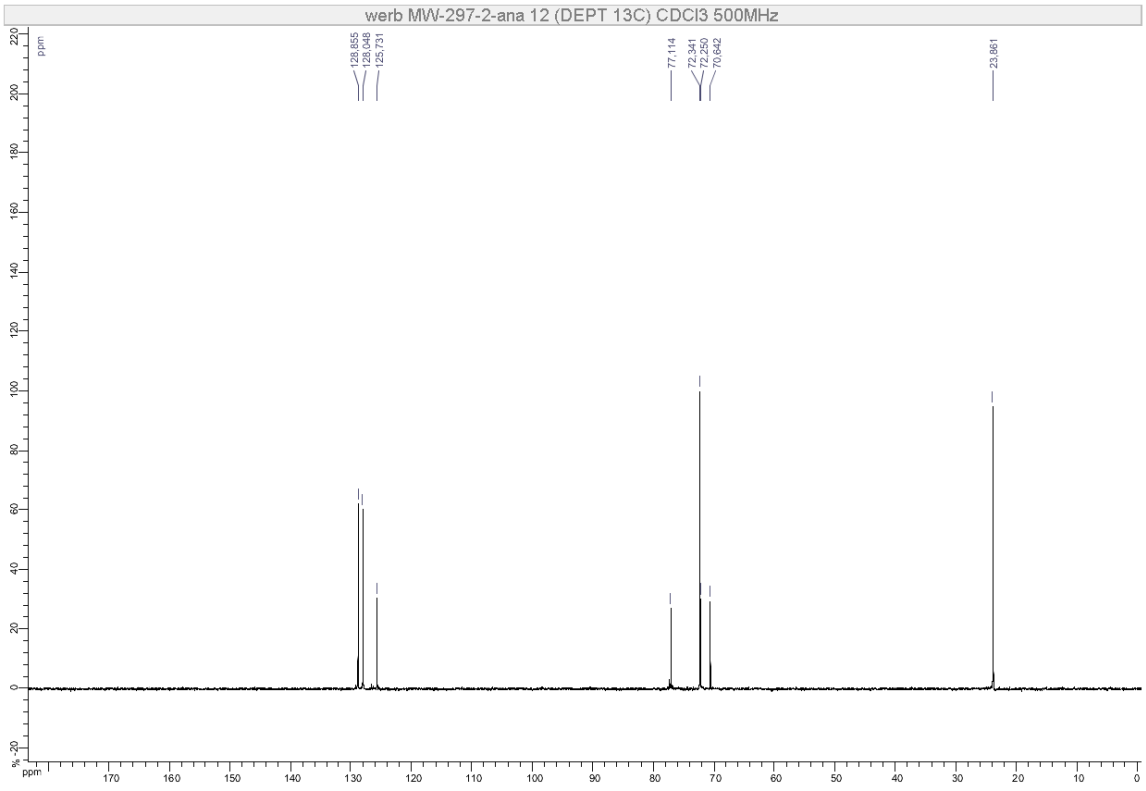
^{1}H NMR (500 MHz, $CDCl_3$)



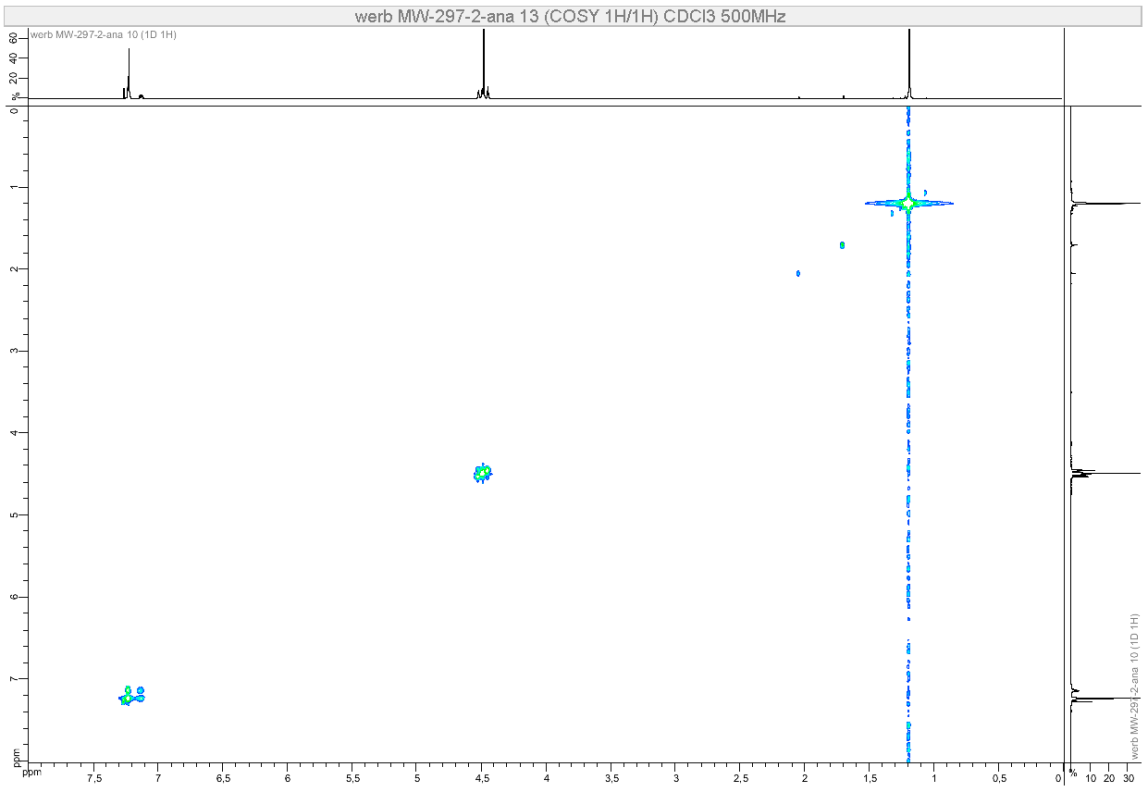
^{13}C NMR (126 MHz, $CDCl_3$)



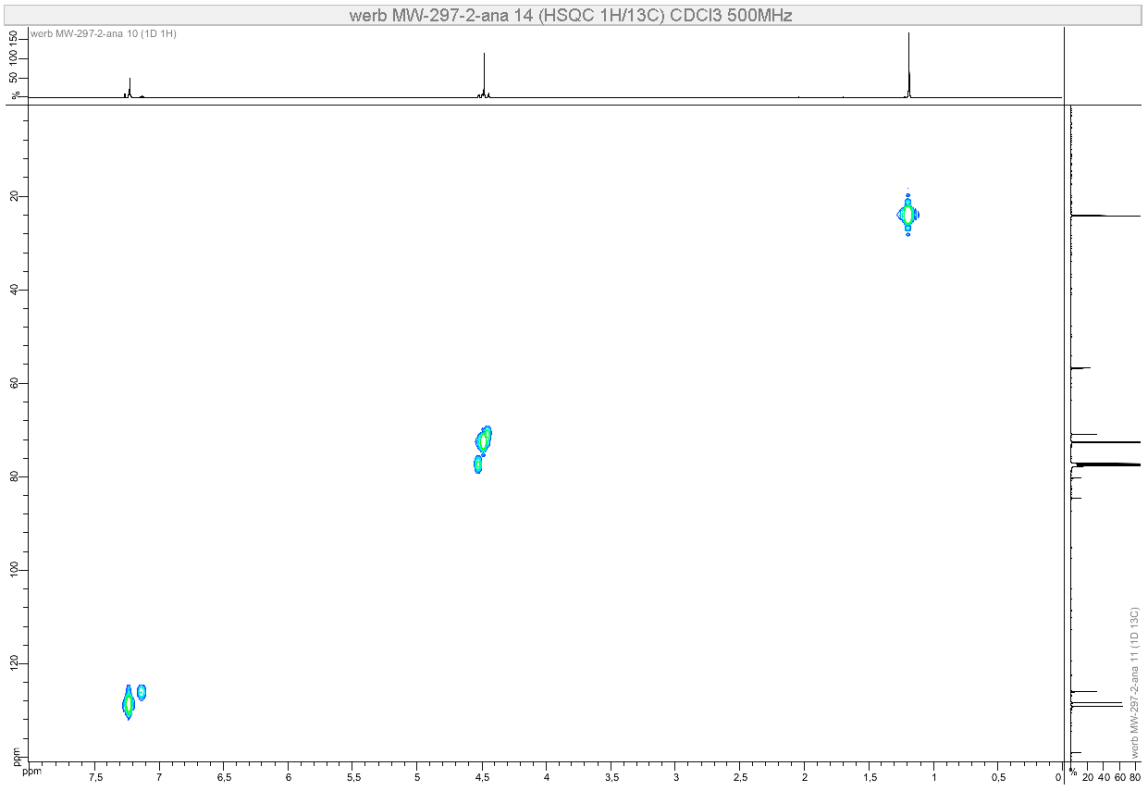
DEPT 135 (126 MHz, $CDCl_3$)



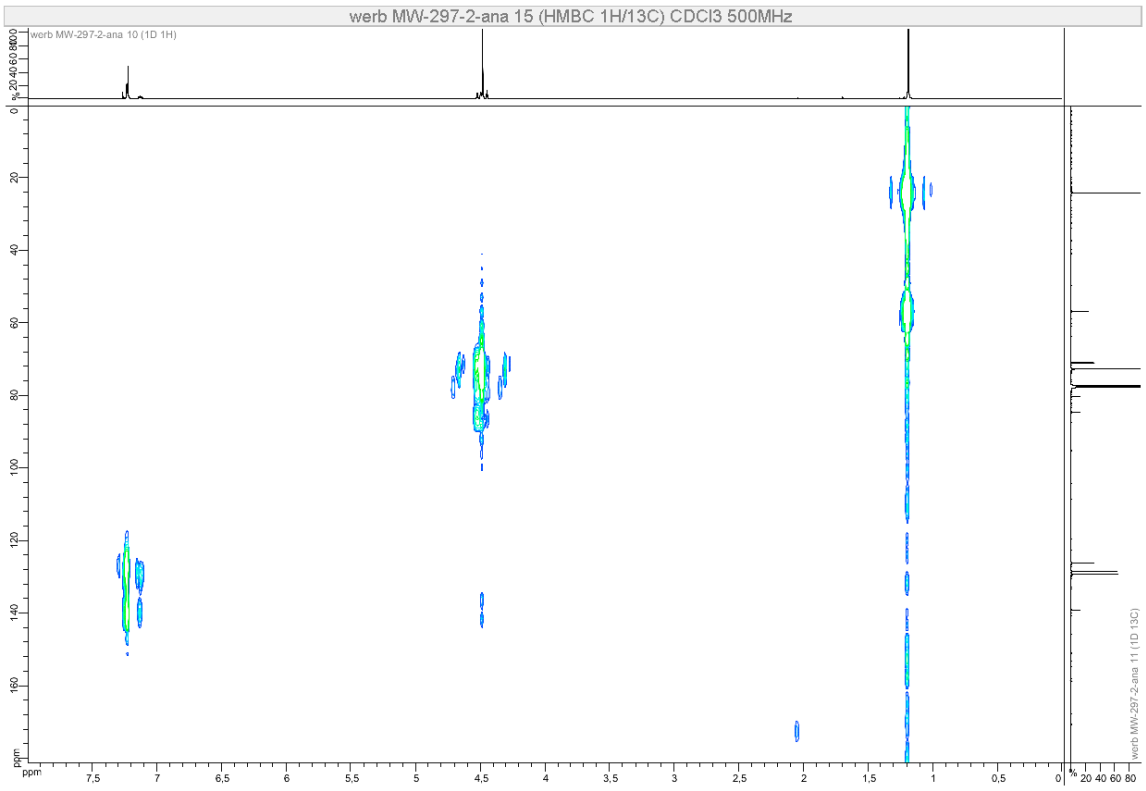
COSY (500 MHz, $CDCl_3$)



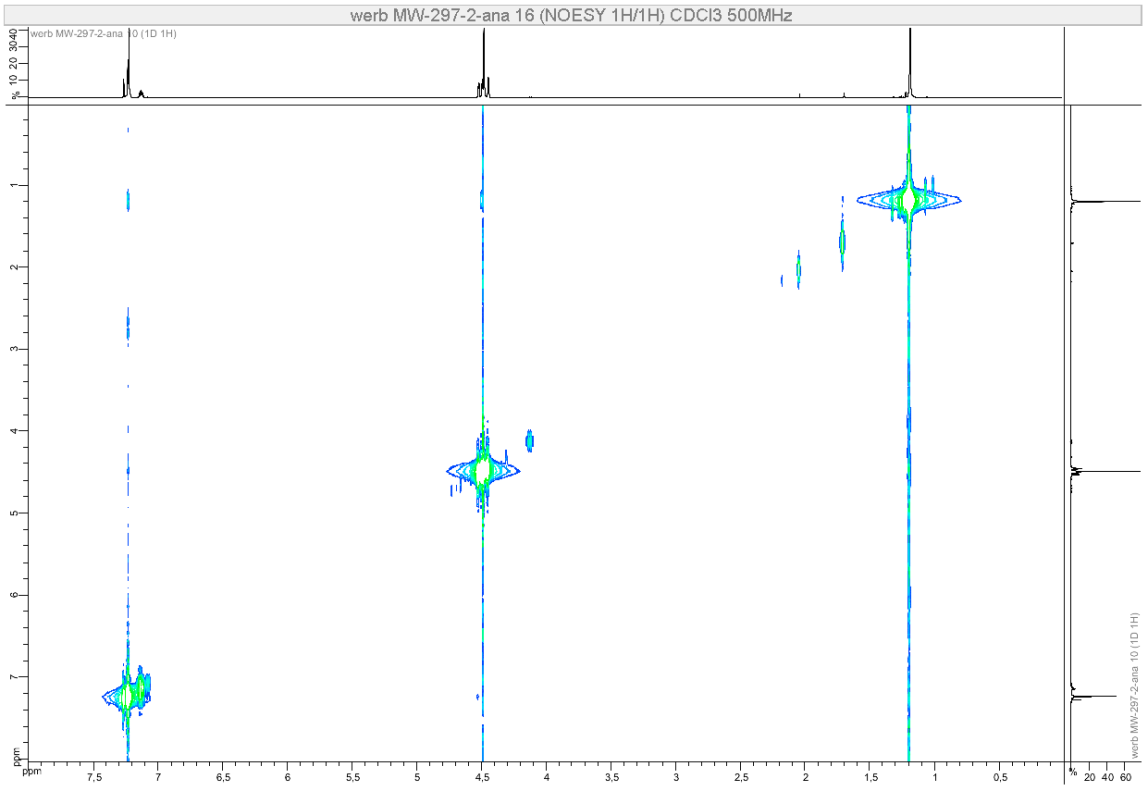
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

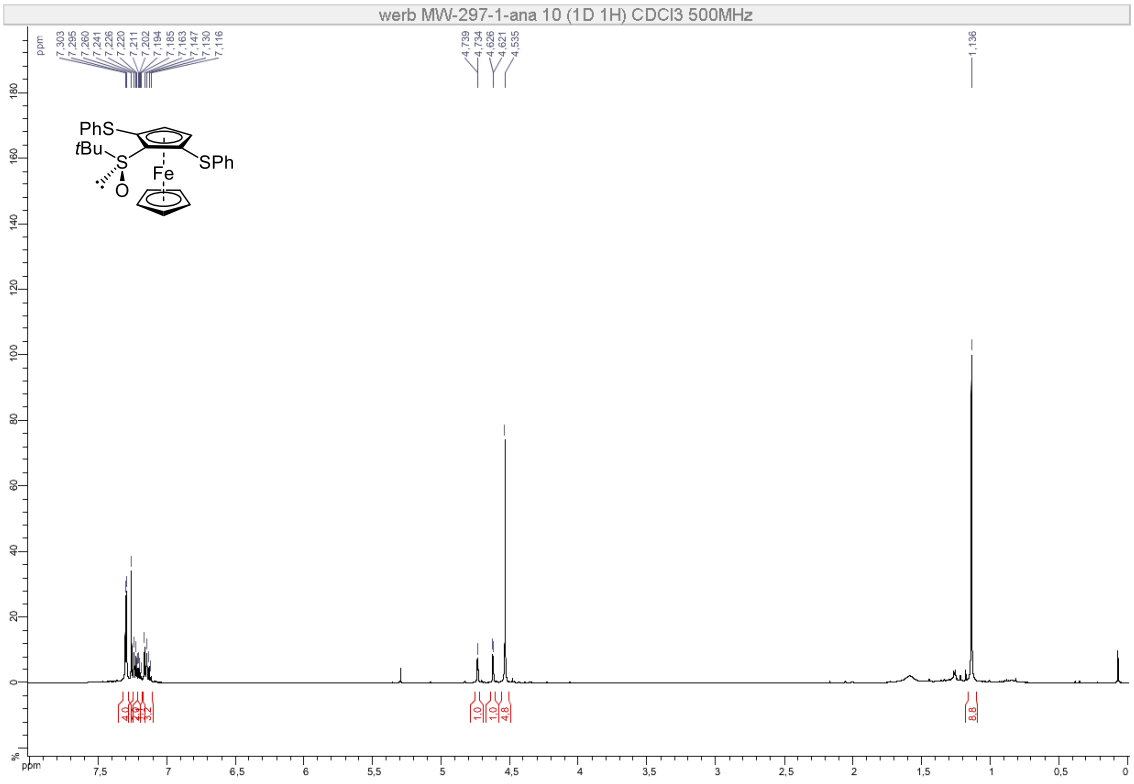


NOESY (500 MHz, $CDCl_3$)

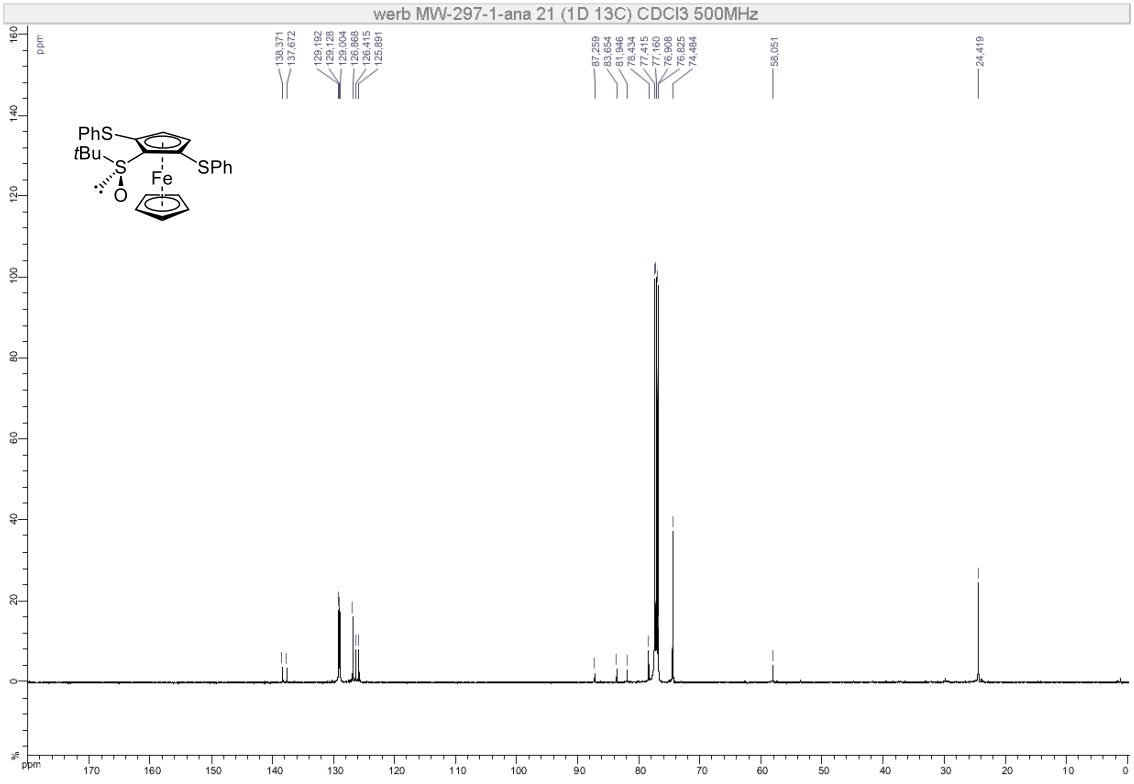


(*S*)-*S*-*tert*-Butyl-2,5-di(phenylthio)ferrocenesulfoxide (*S*-4')

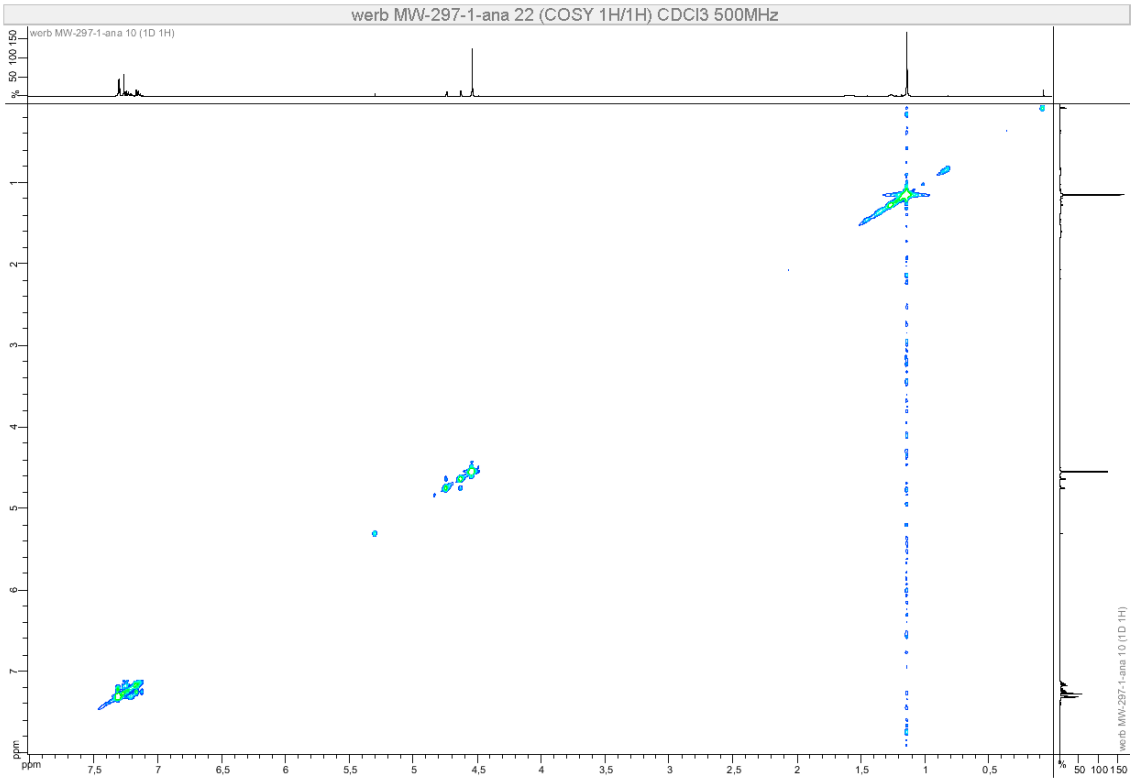
^{1}H NMR (500 MHz, $CDCl_3$)



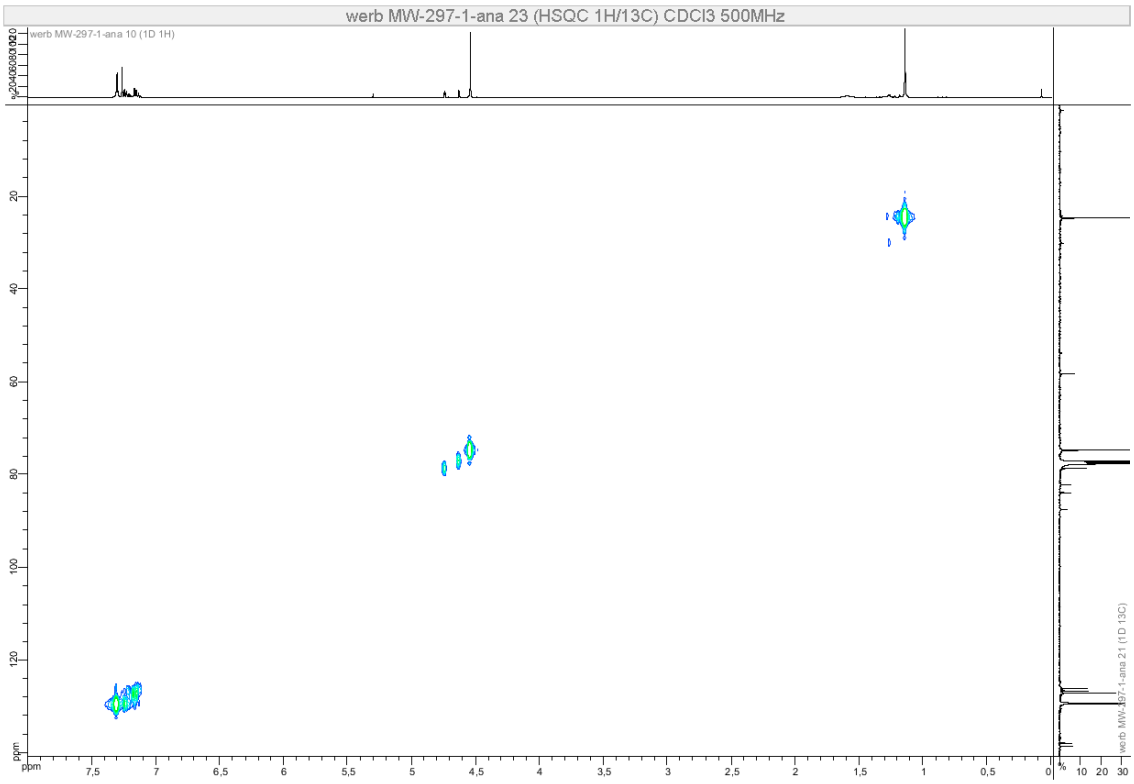
^{13}C NMR (126 MHz, $CDCl_3$)



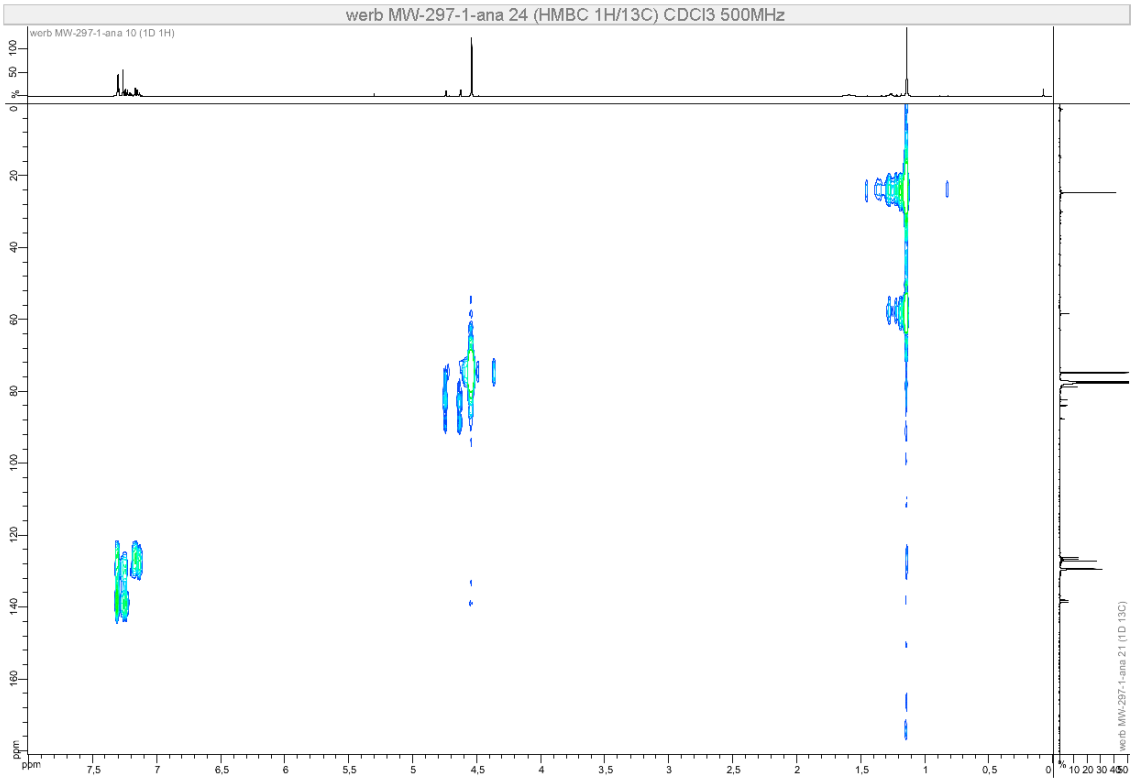
COSY (500 MHz, $CDCl_3$)



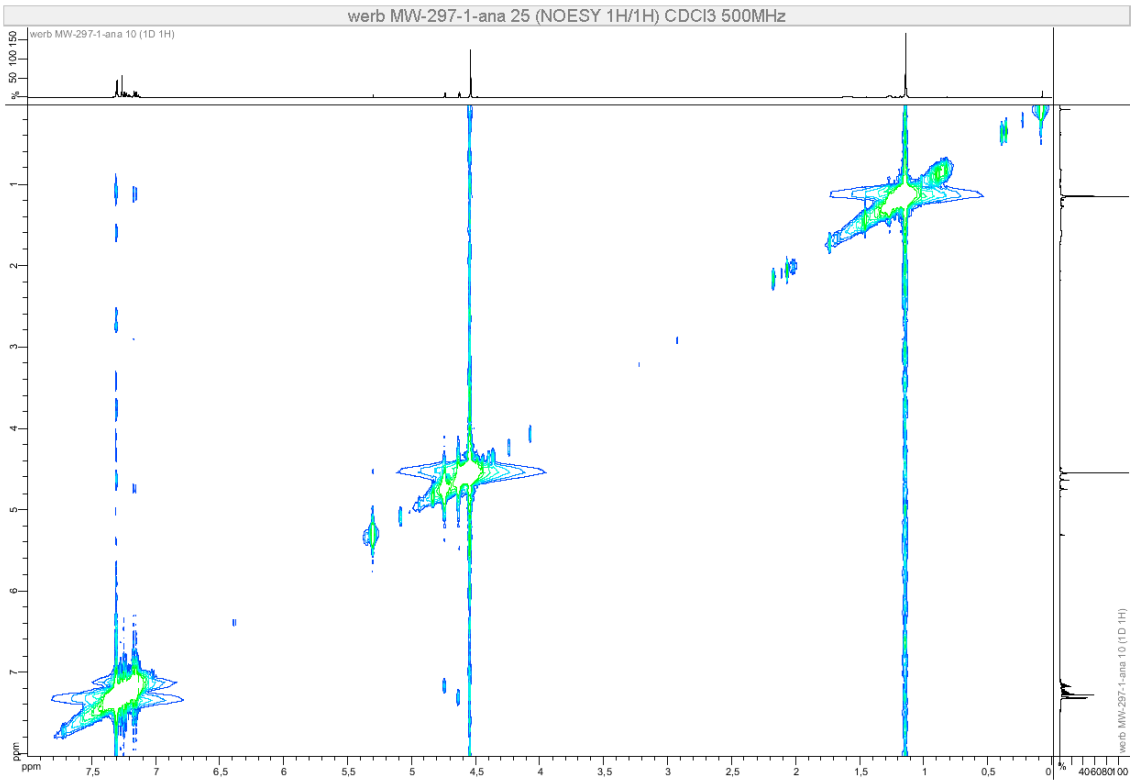
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

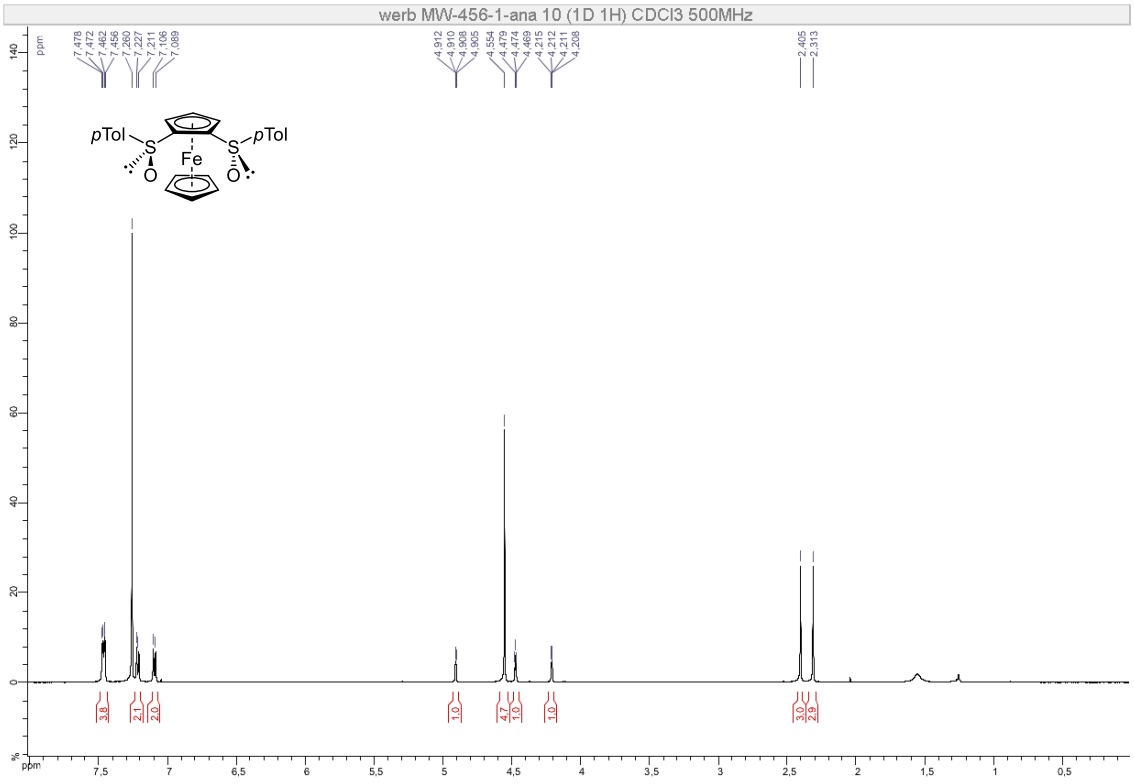


NOESY (500 MHz, $CDCl_3$)

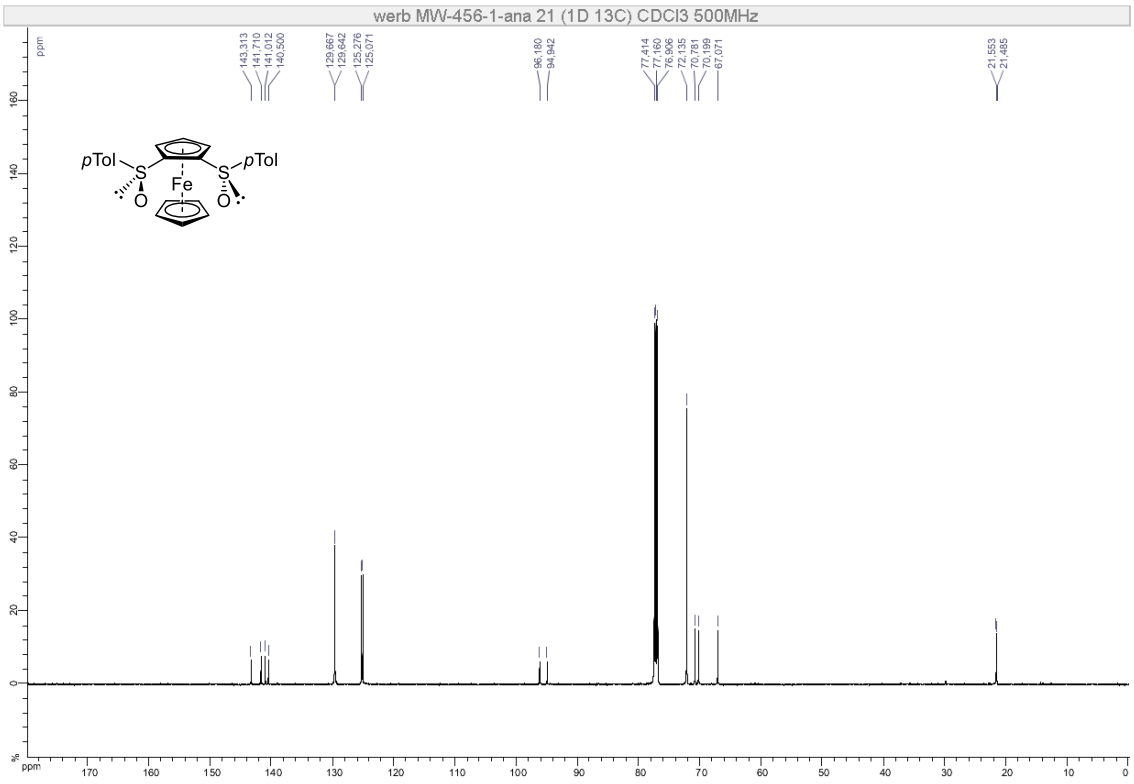


(*S*,*S*)-*S*,*S*'-Di(4-tolyl)ferrocene-1,2-disulfoxide (*S*,*S*-3)

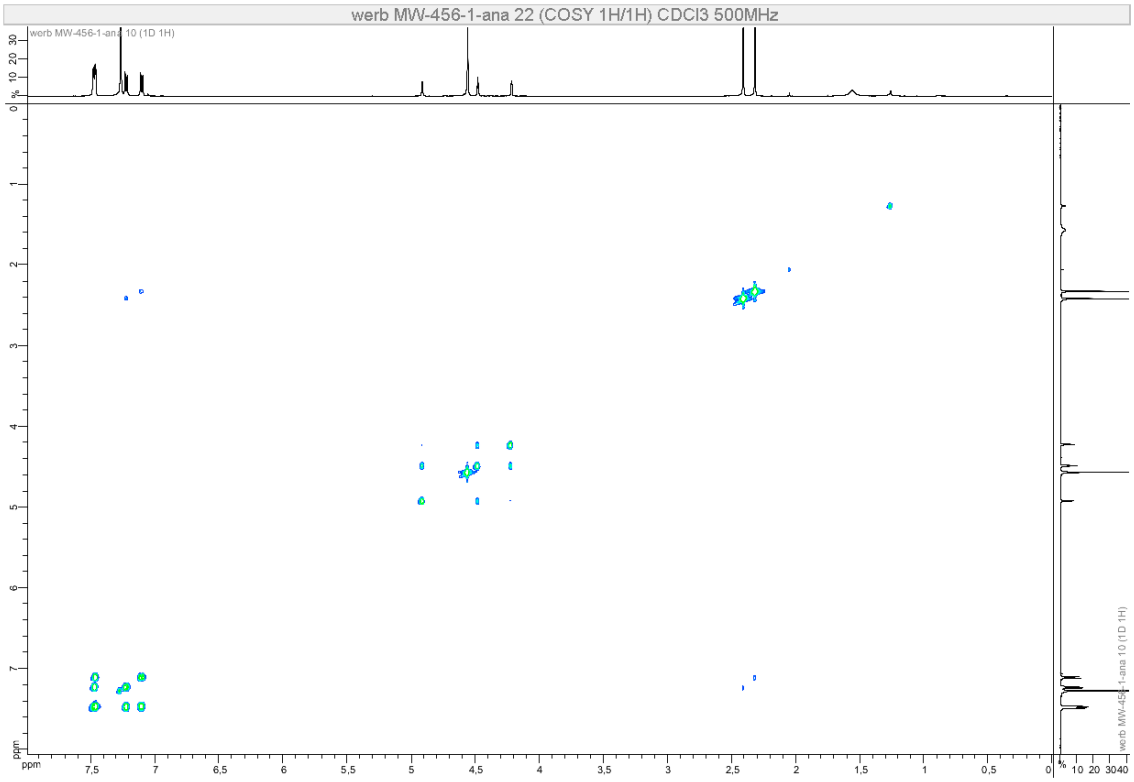
^{1}H NMR (500 MHz, $CDCl_3$)



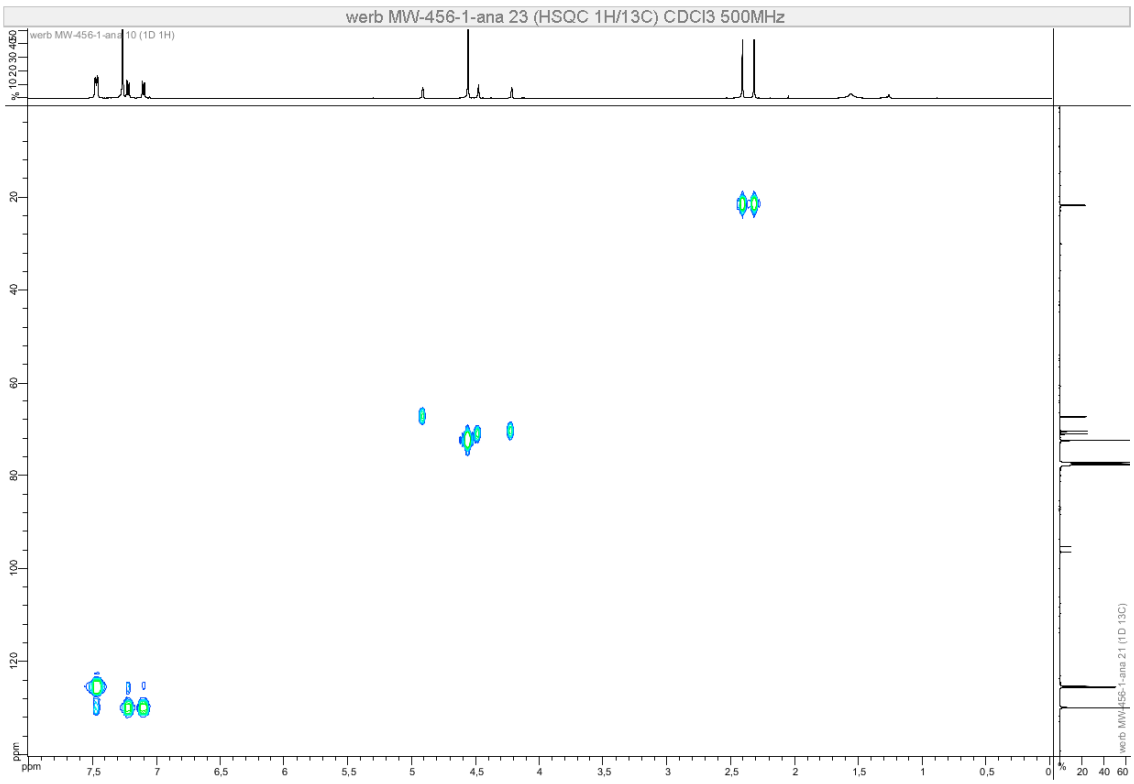
^{13}C NMR (126 MHz, $CDCl_3$)



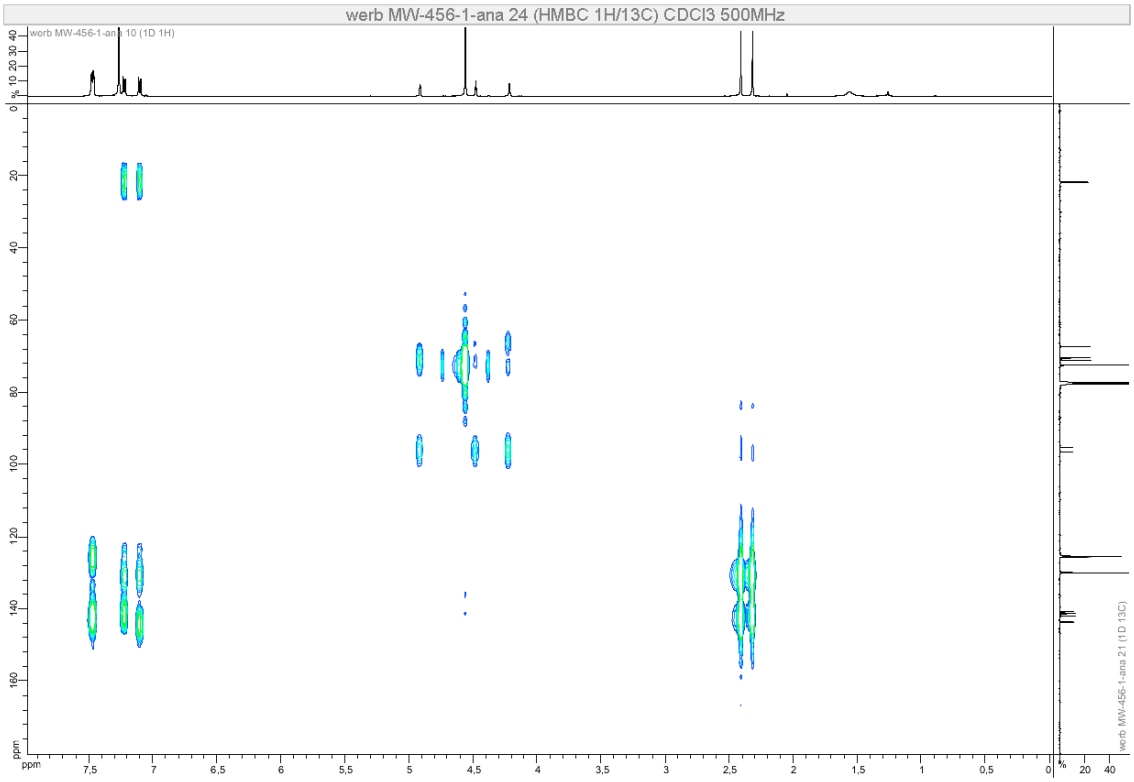
COSY (500 MHz, $CDCl_3$)



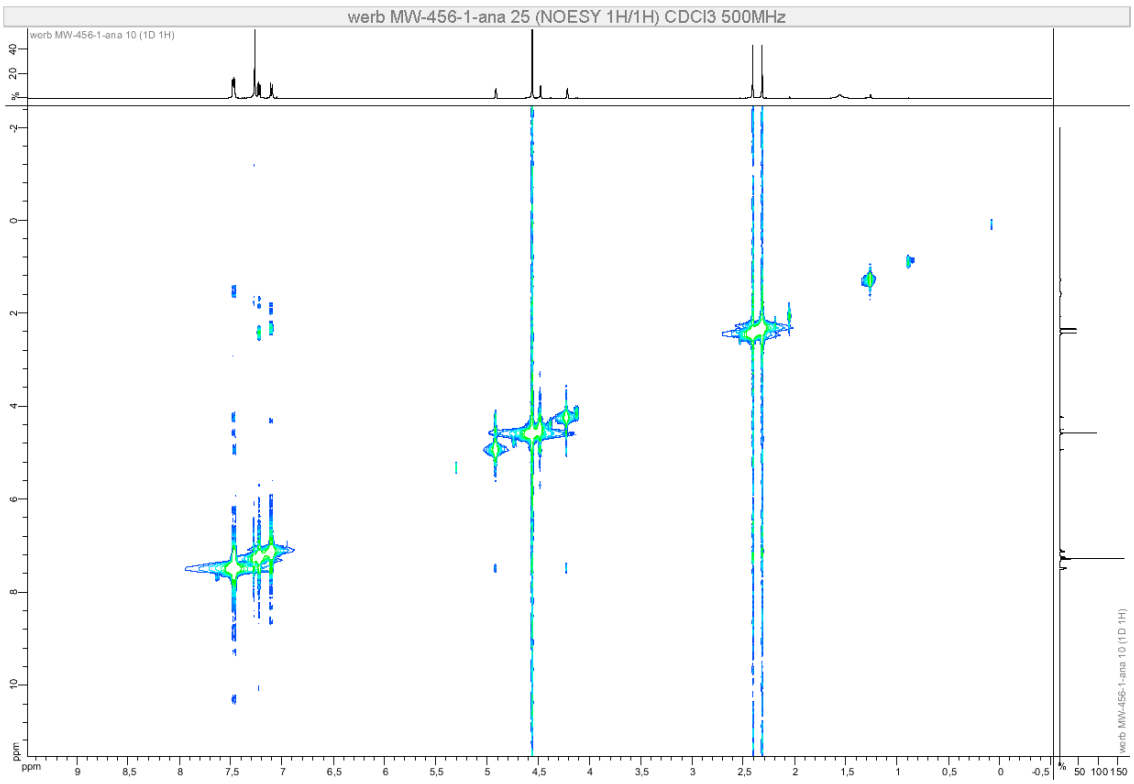
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

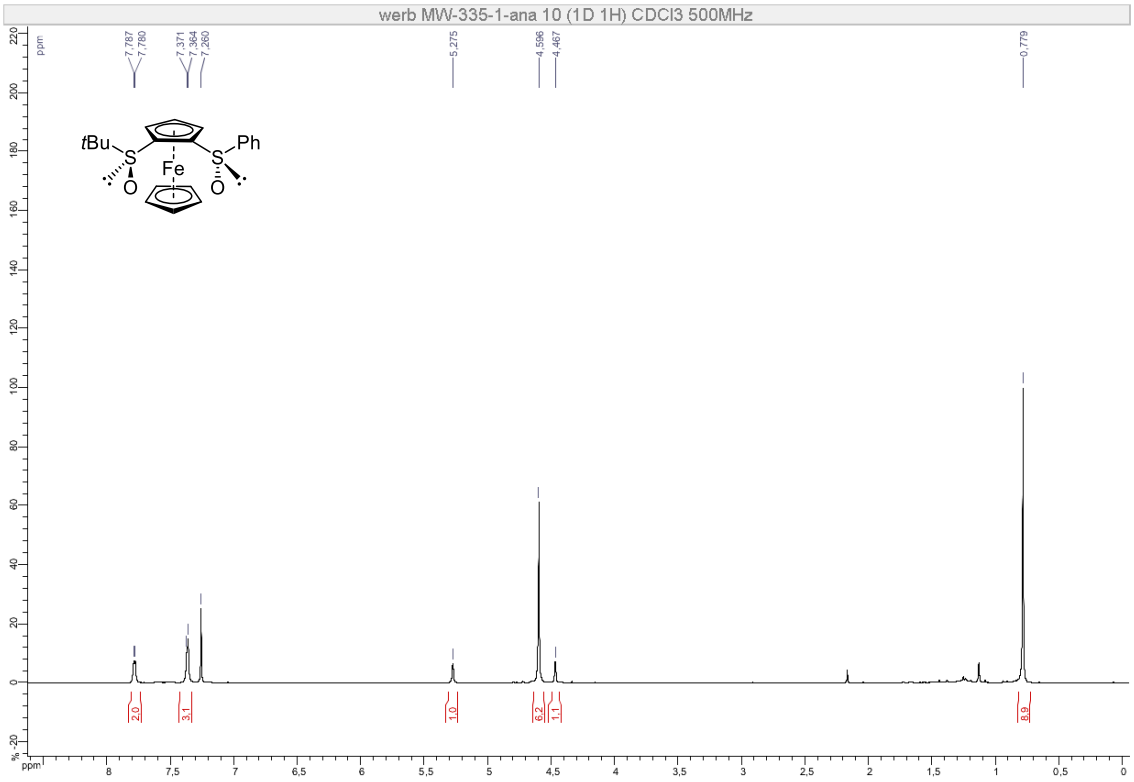


NOESY (500 MHz, $CDCl_3$)

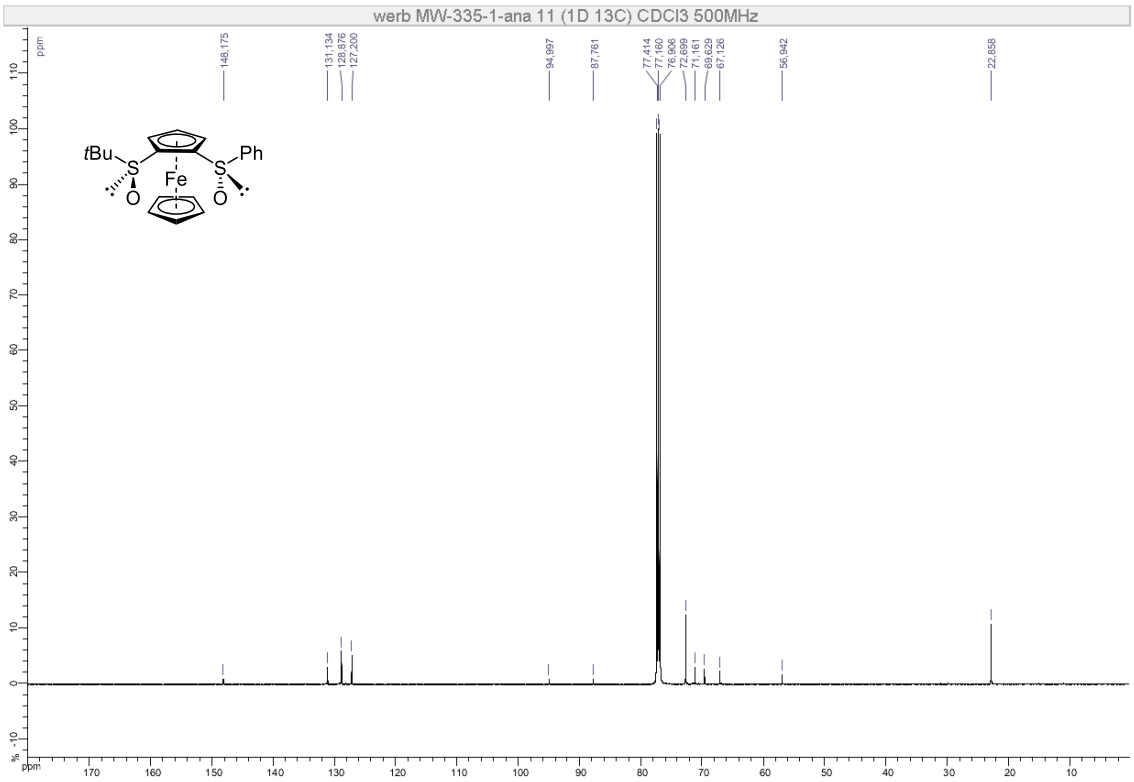


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-*S'*-phenylferrocene-1,2-disulfoxide (*S*,*S*,*R*$_P$-5)

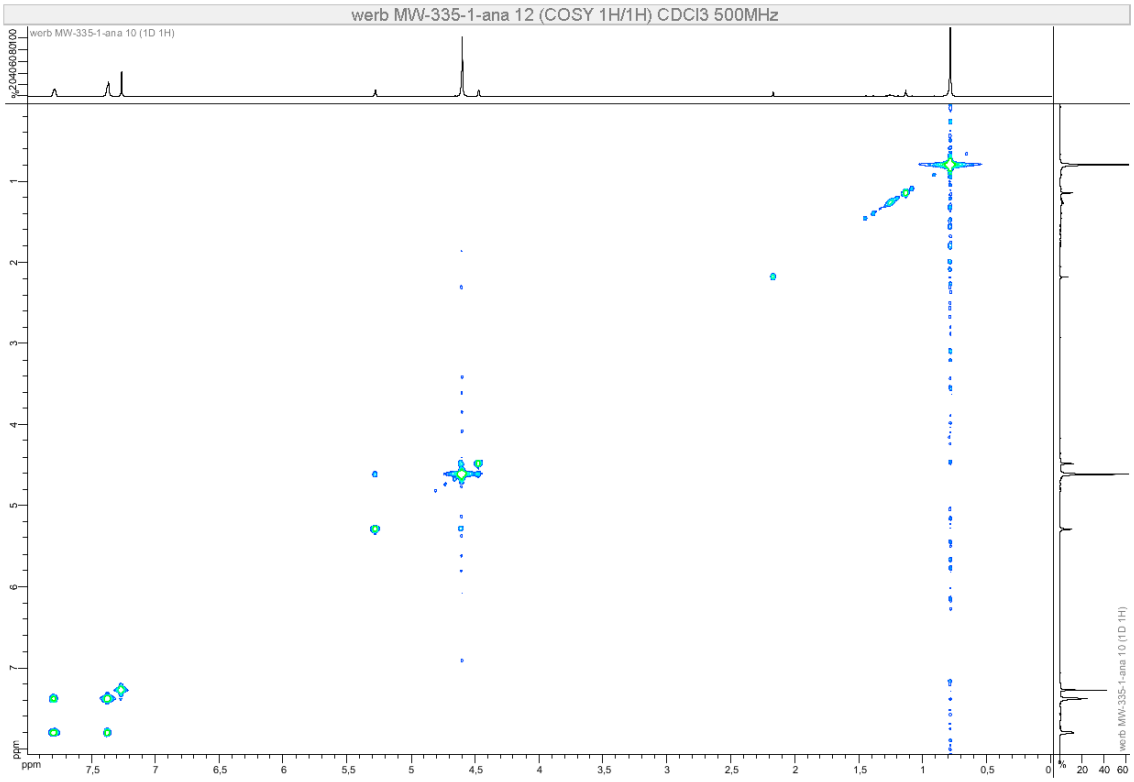
^{1}H NMR (500 MHz, $CDCl_3$)



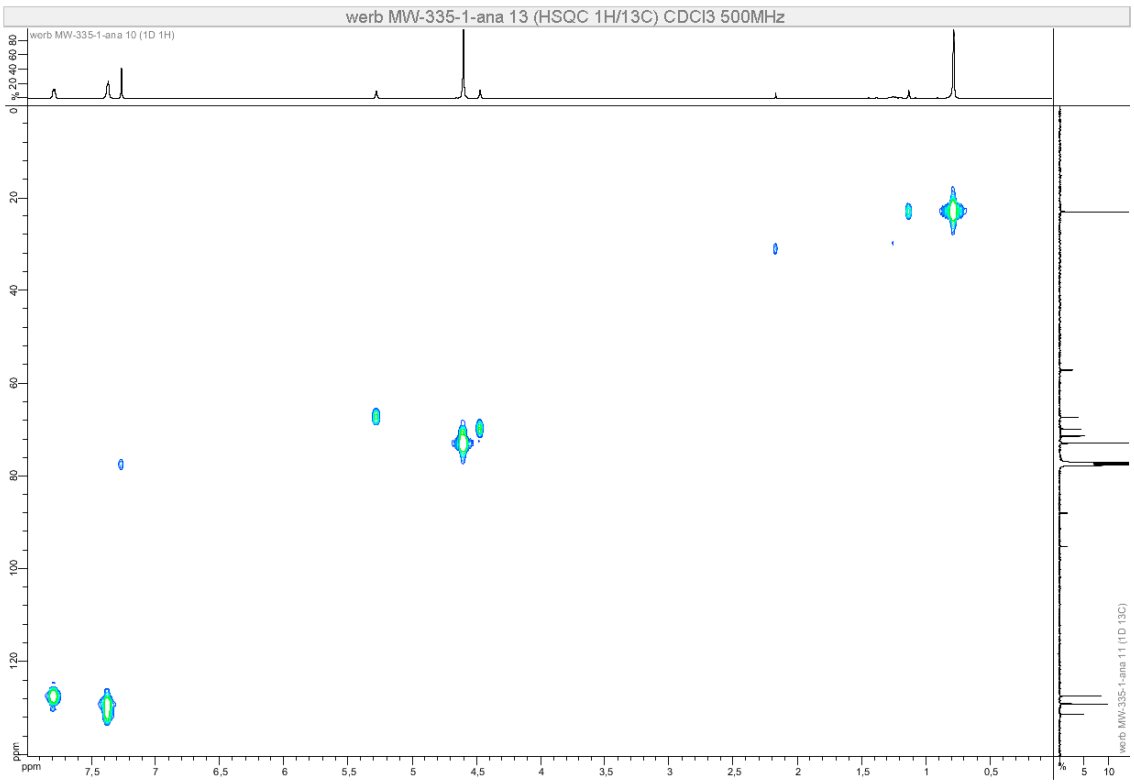
^{13}C NMR (126 MHz, $CDCl_3$)



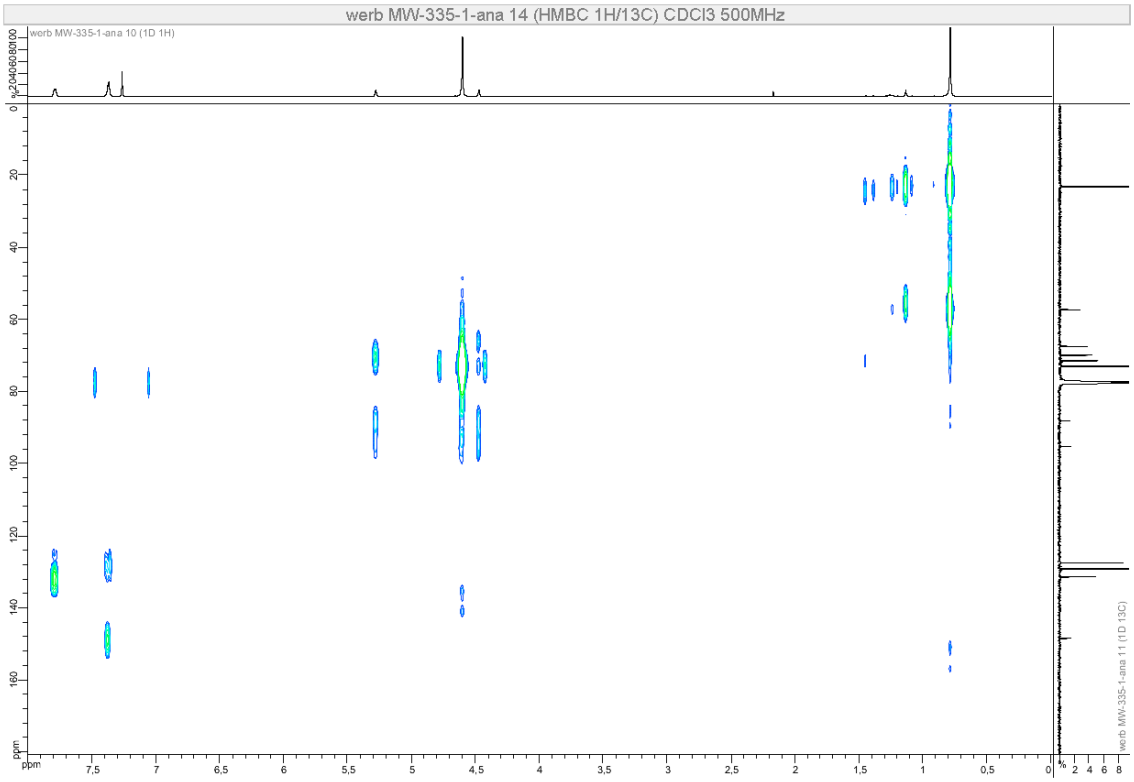
COSY (500 MHz, $CDCl_3$)



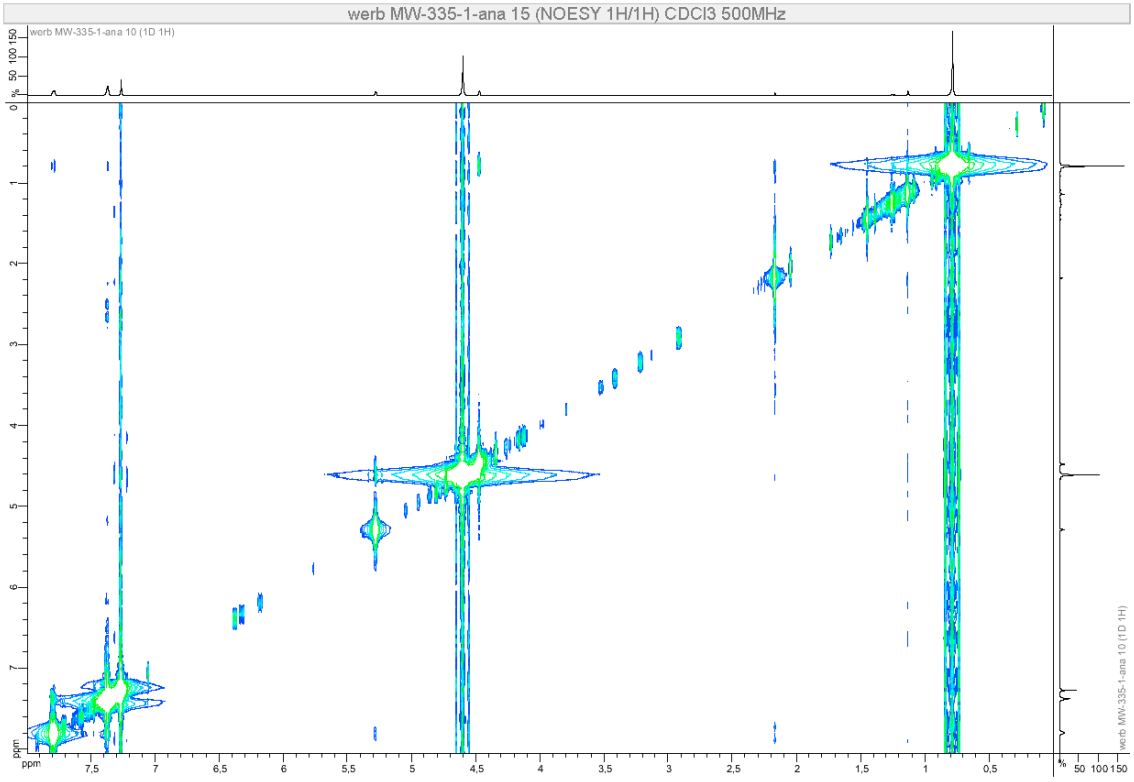
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

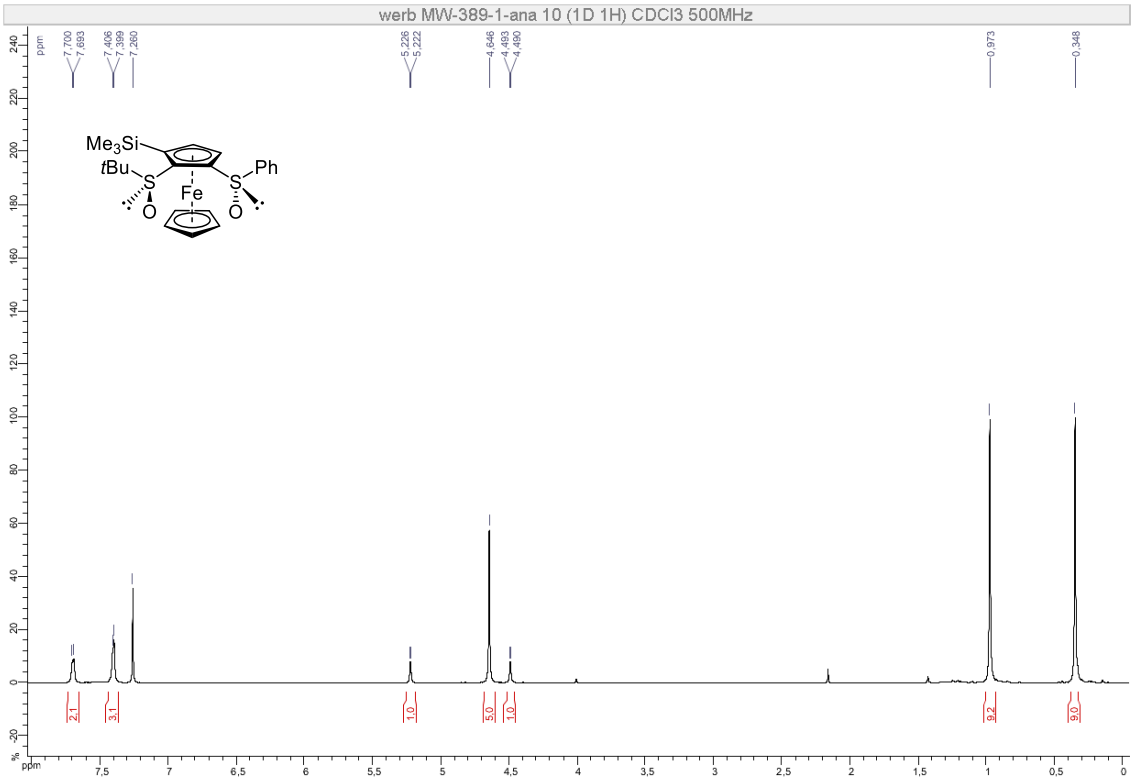


NOESY (500 MHz, $CDCl_3$)

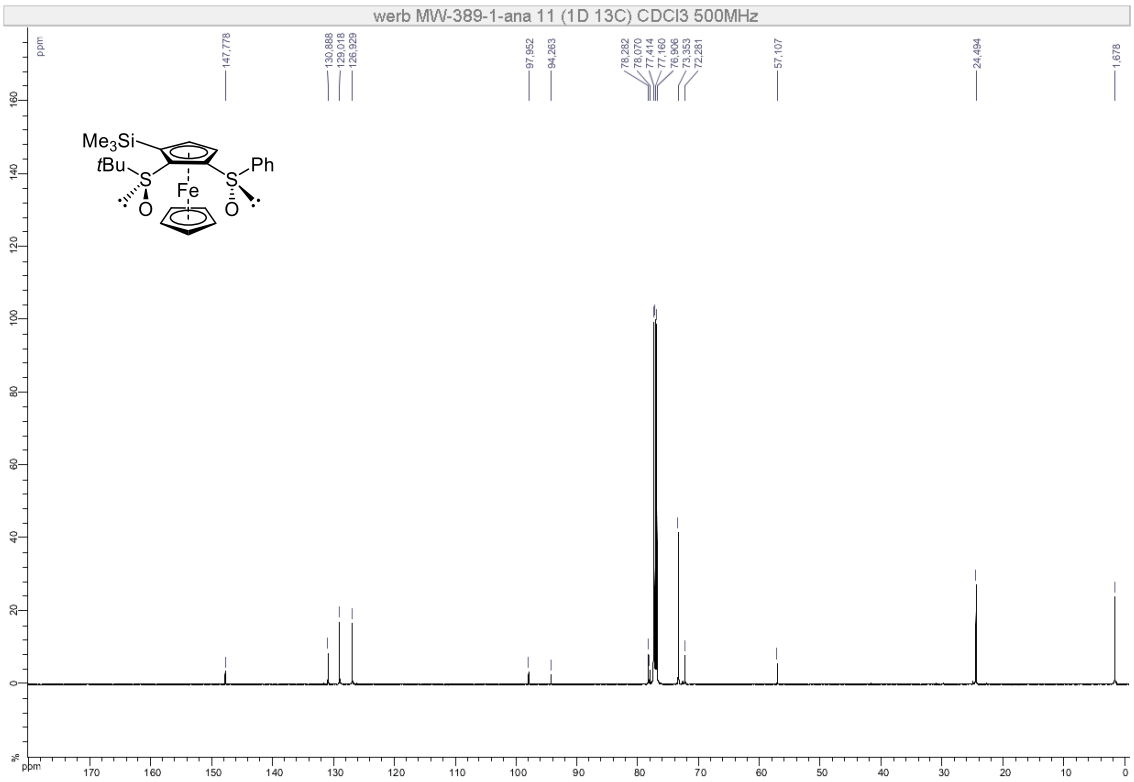


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (*S*,*S*,*R*$_P$-11)

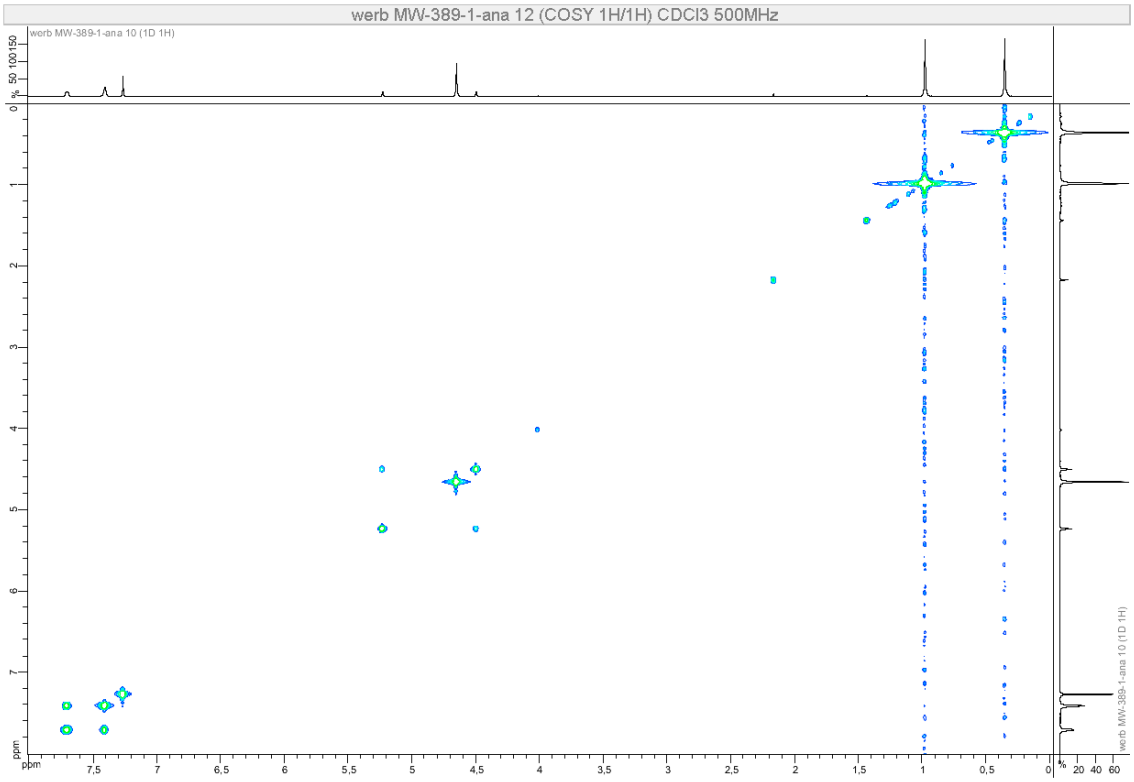
^{1}H NMR (500 MHz, $CDCl_3$)



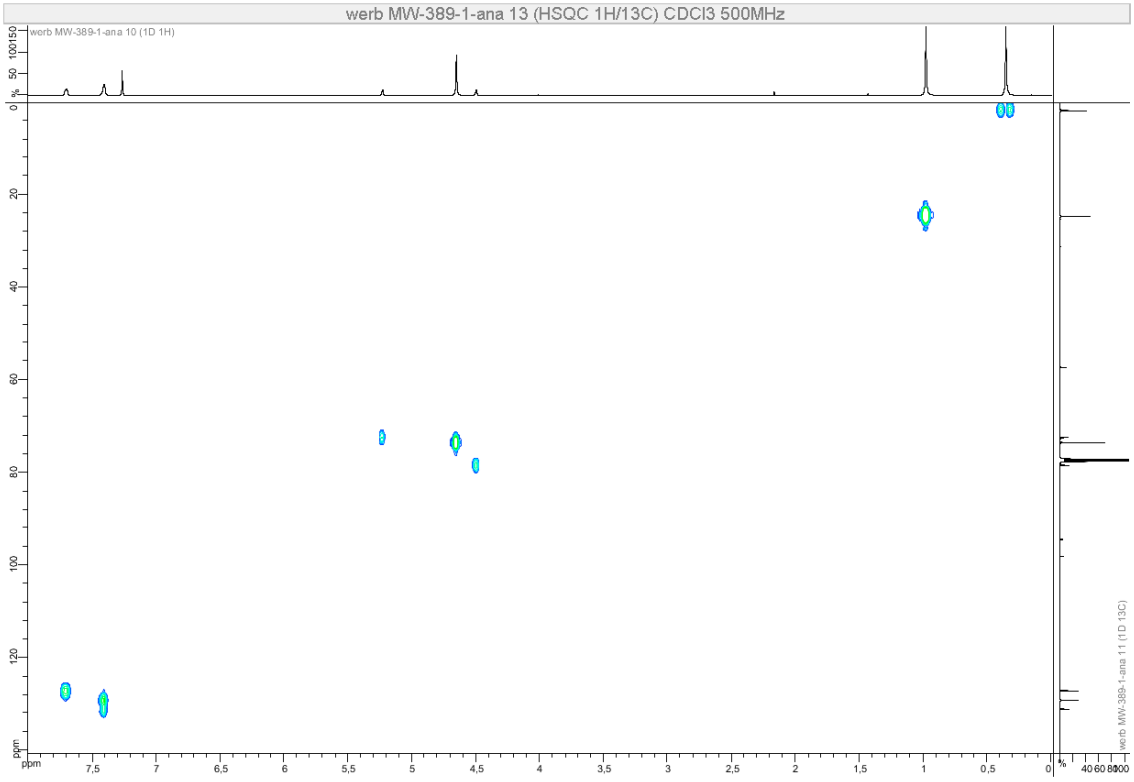
^{13}C NMR (126 MHz, $CDCl_3$)



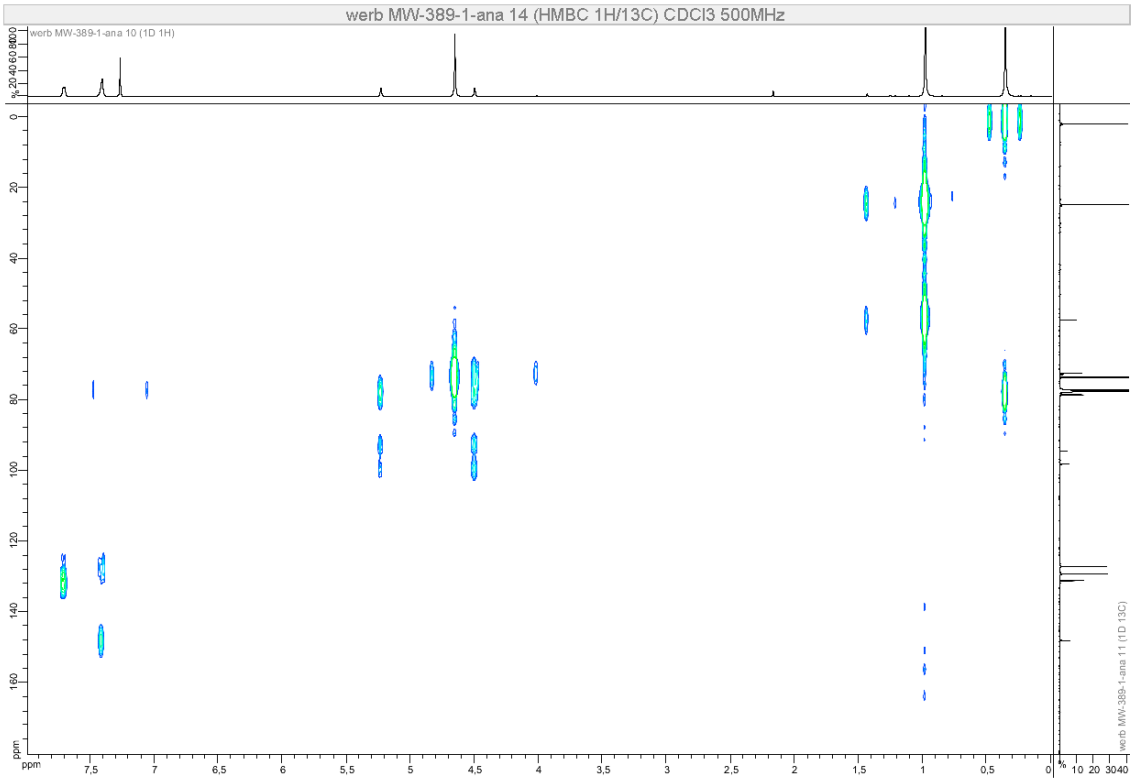
COSY (500 MHz, $CDCl_3$)



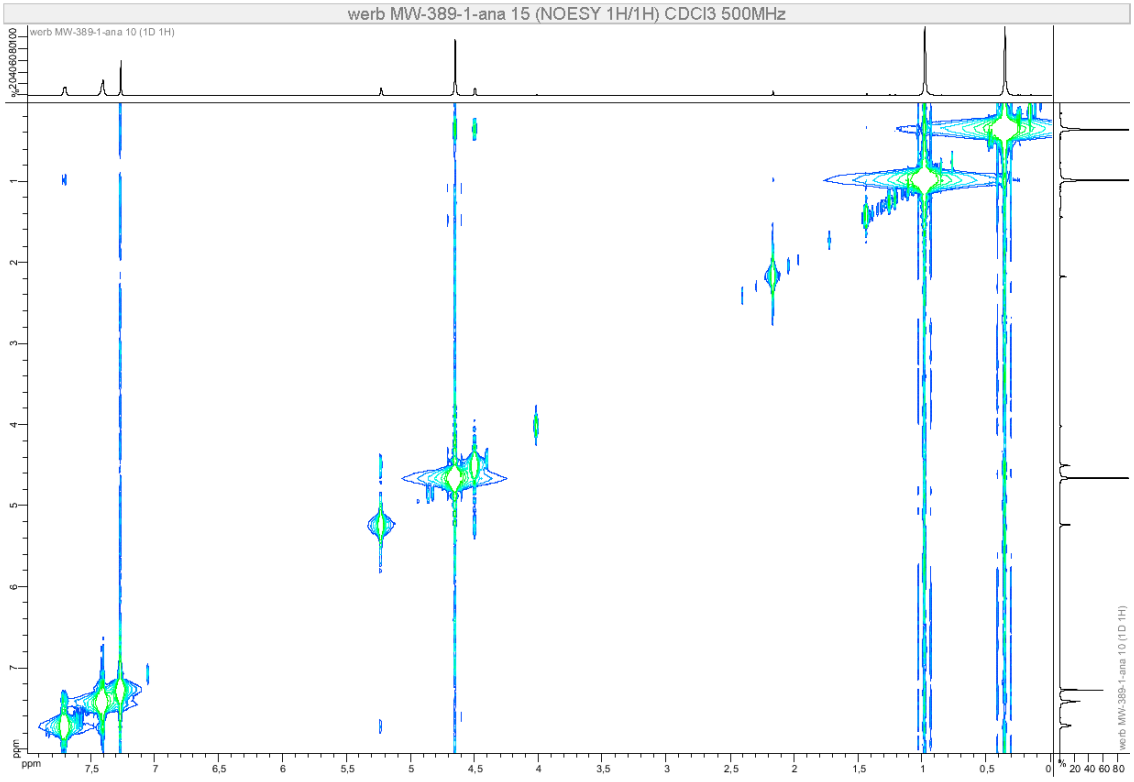
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

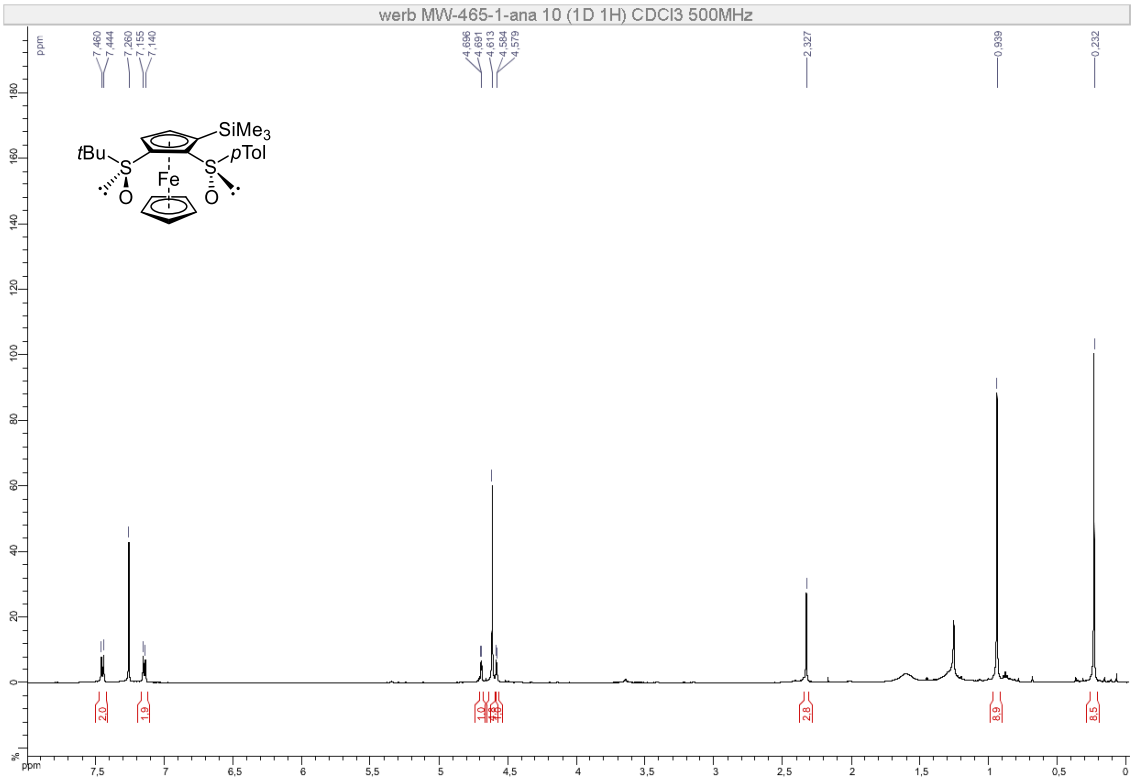


NOESY (500 MHz, $CDCl_3$)

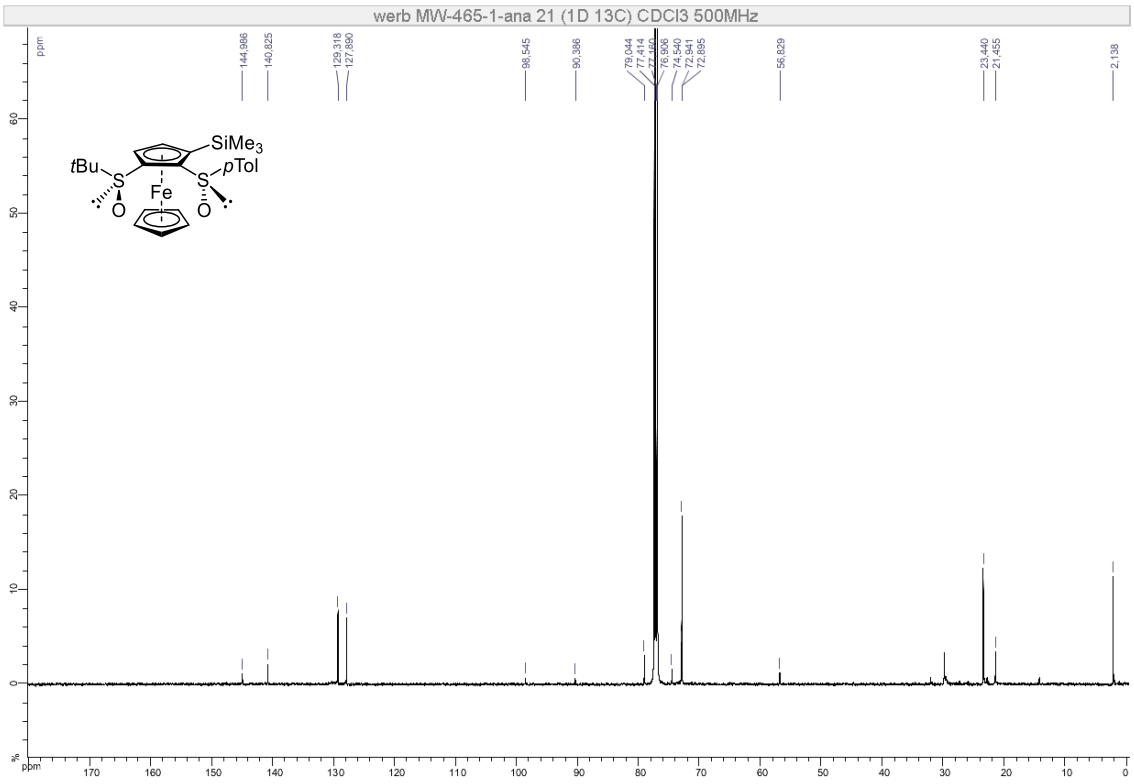


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-*S'*-tolyl-3-(trimethylsilyl)ferrocene-1,2-disulfoxide (*S*,*S*,*R*$_P$-6a)

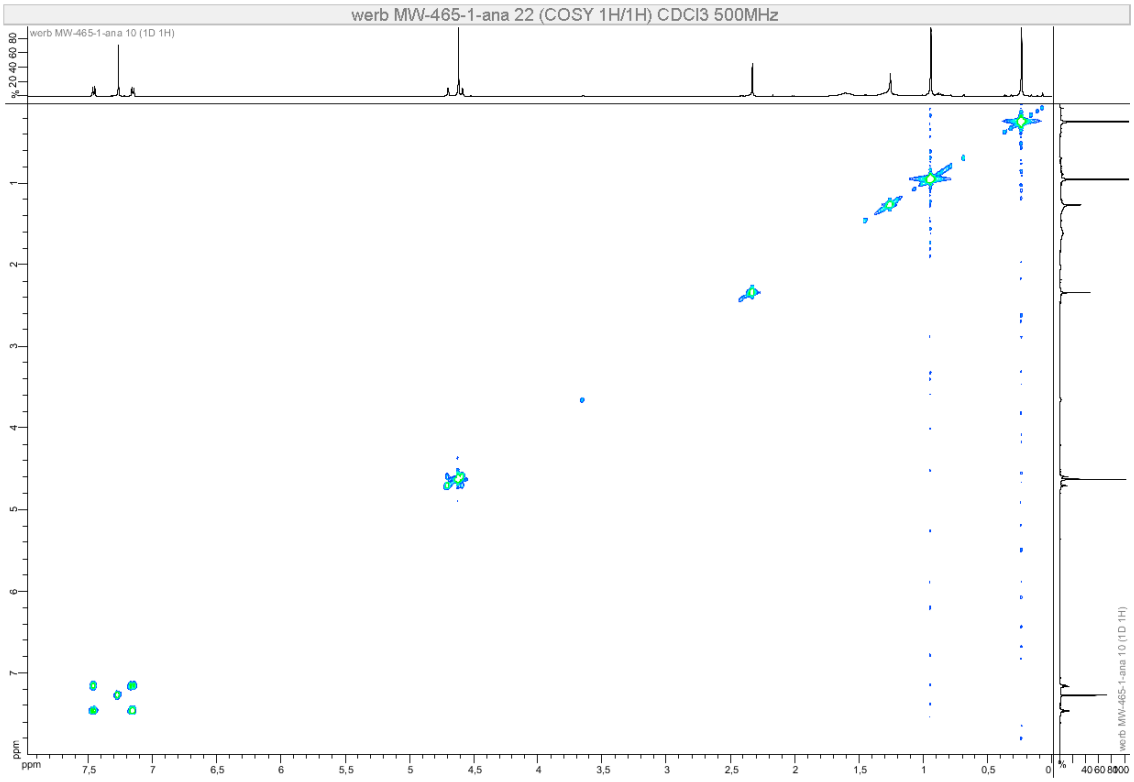
^{1}H NMR (500 MHz, $CDCl_3$)



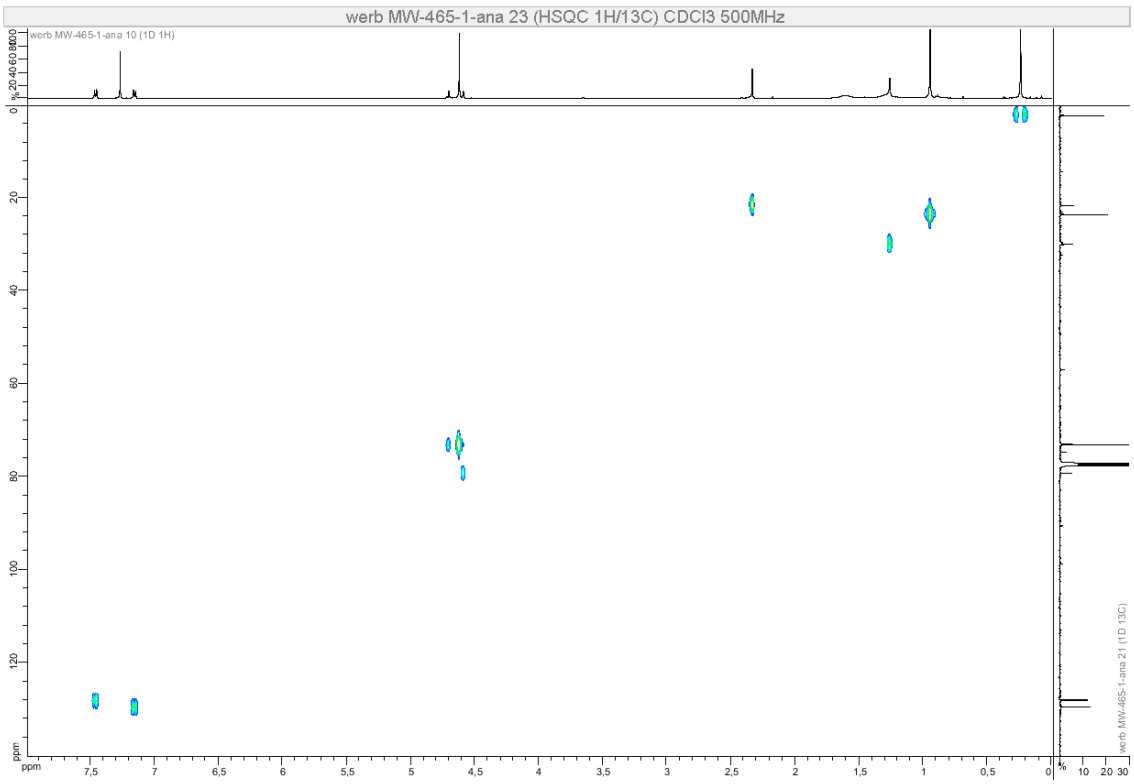
^{13}C NMR (126 MHz, $CDCl_3$)



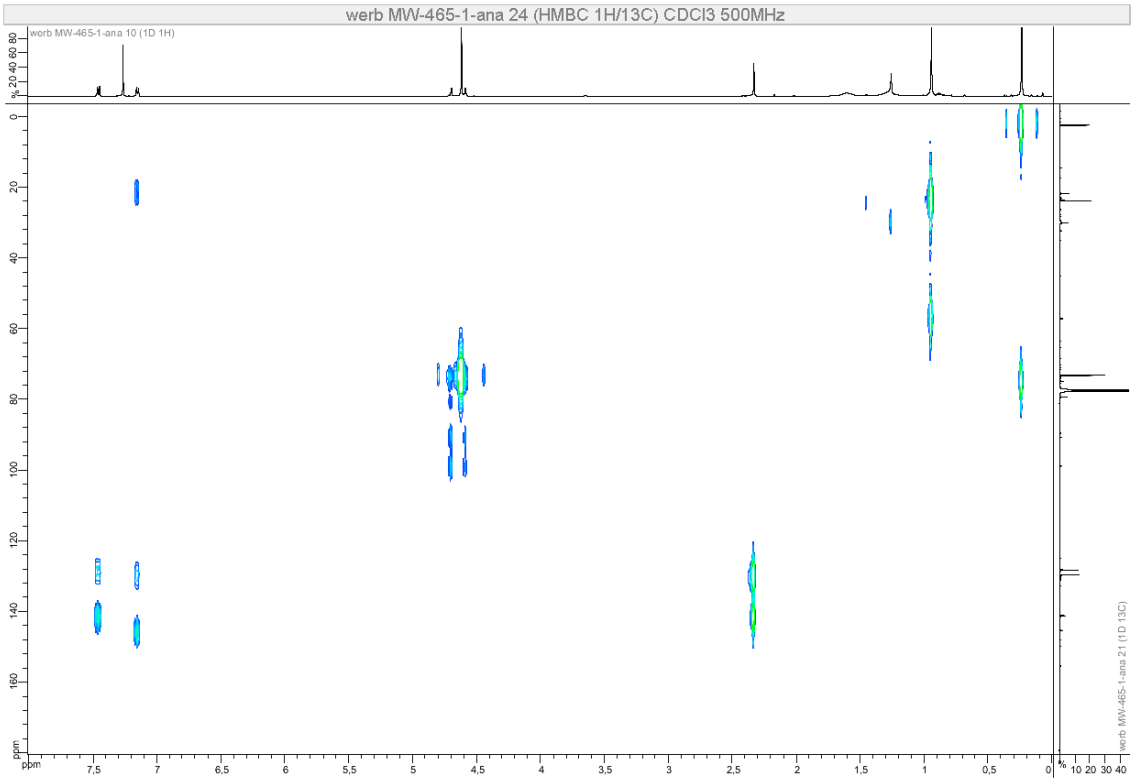
COSY (500 MHz, $CDCl_3$)



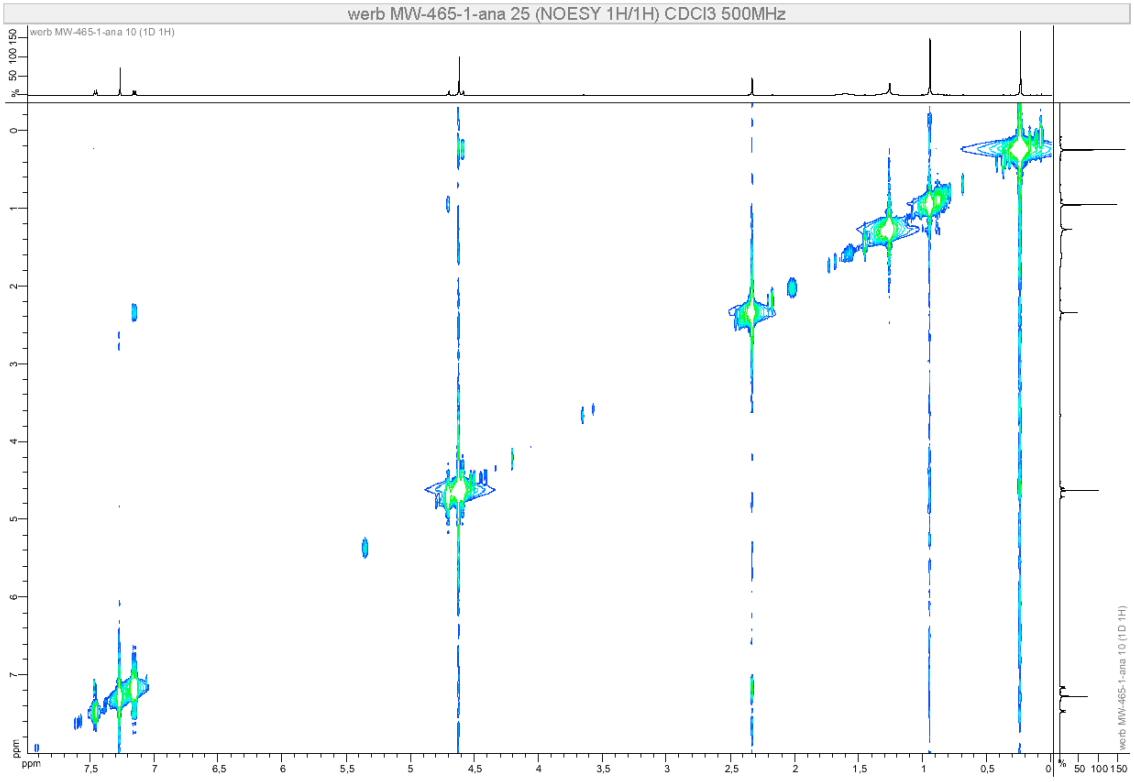
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

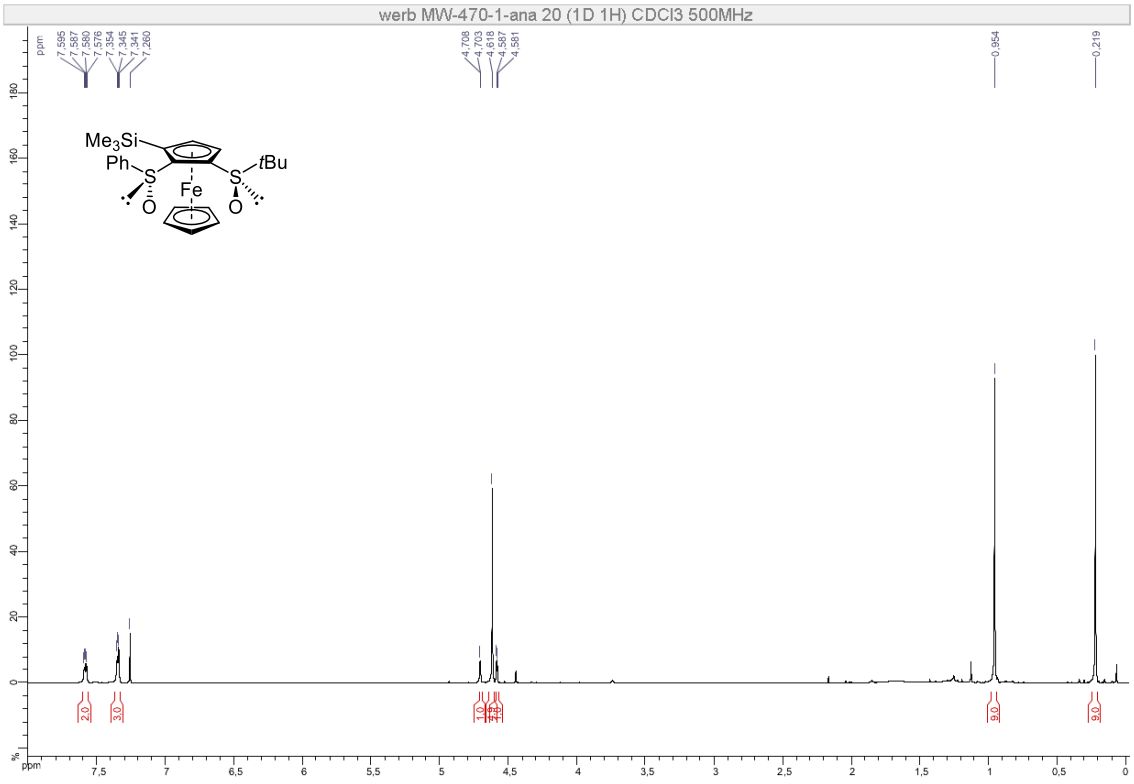


NOESY (500 MHz, $CDCl_3$)

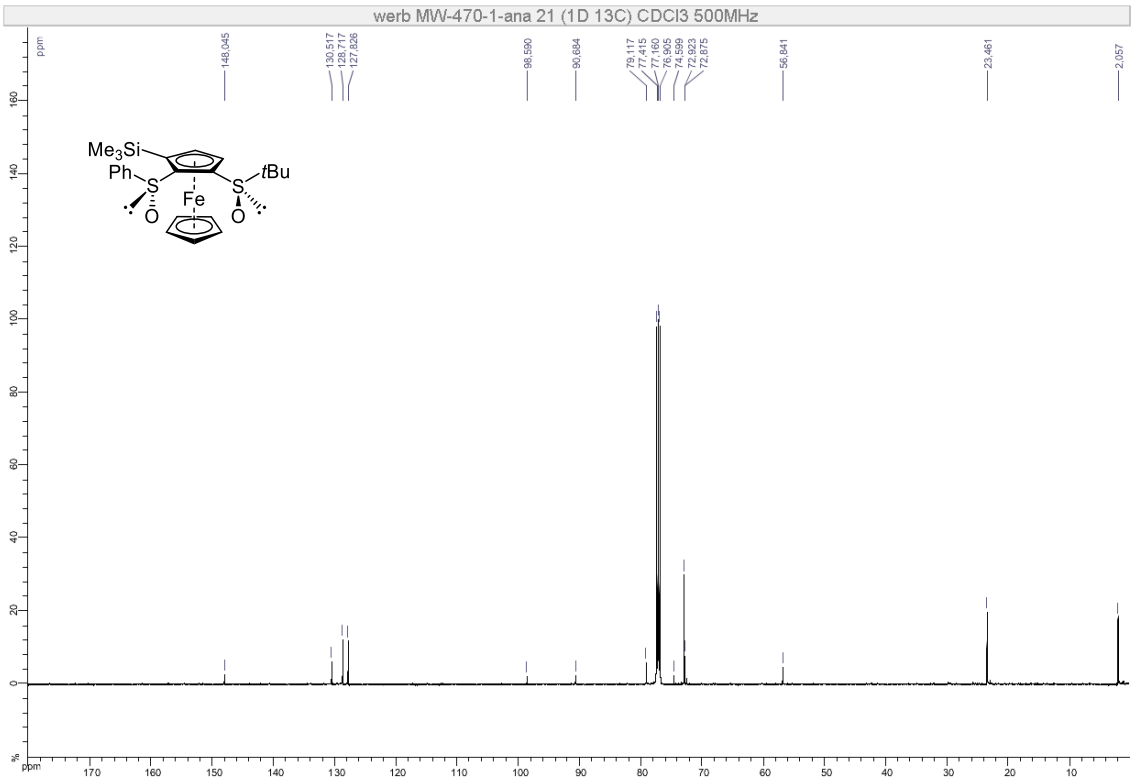


(*R*,*R*,*S*$_P$)-*S*-*tert*-Butyl-*S'*-phenyl-3-(trimethylsilyl)ferrocene-1,2-disulfoxide (*R*,*R*,*S*$_P$-7a)

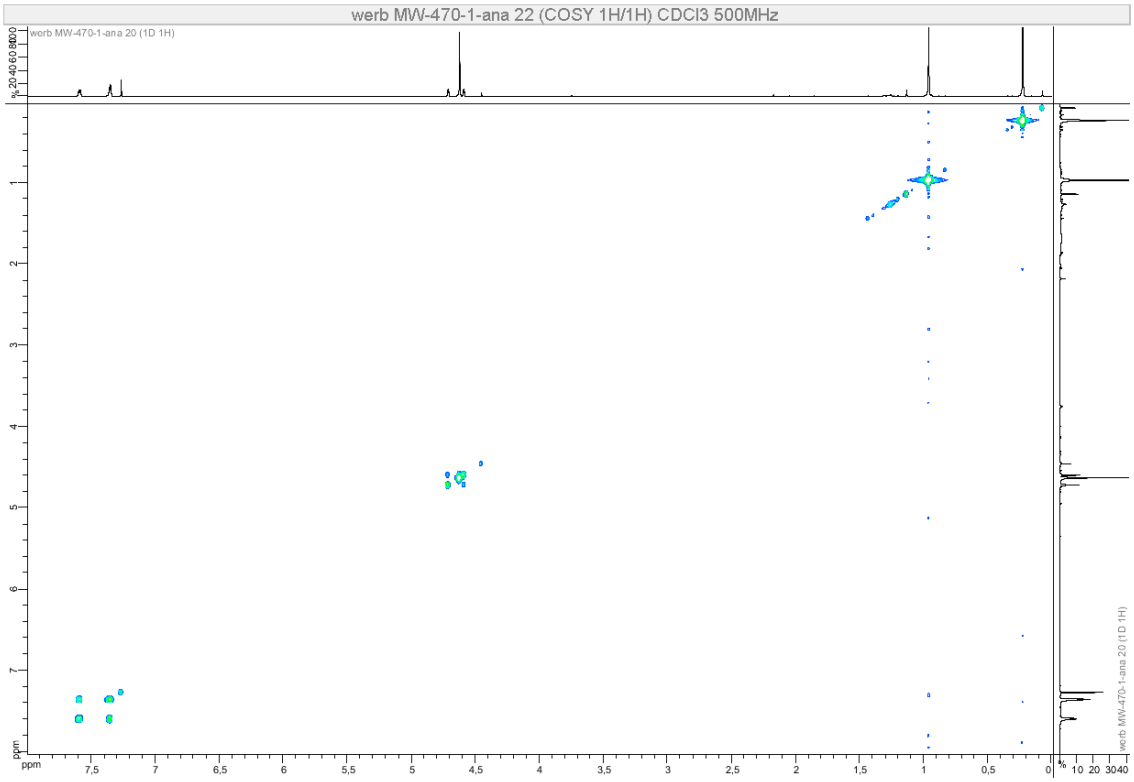
^{1}H NMR (500 MHz, $CDCl_3$)



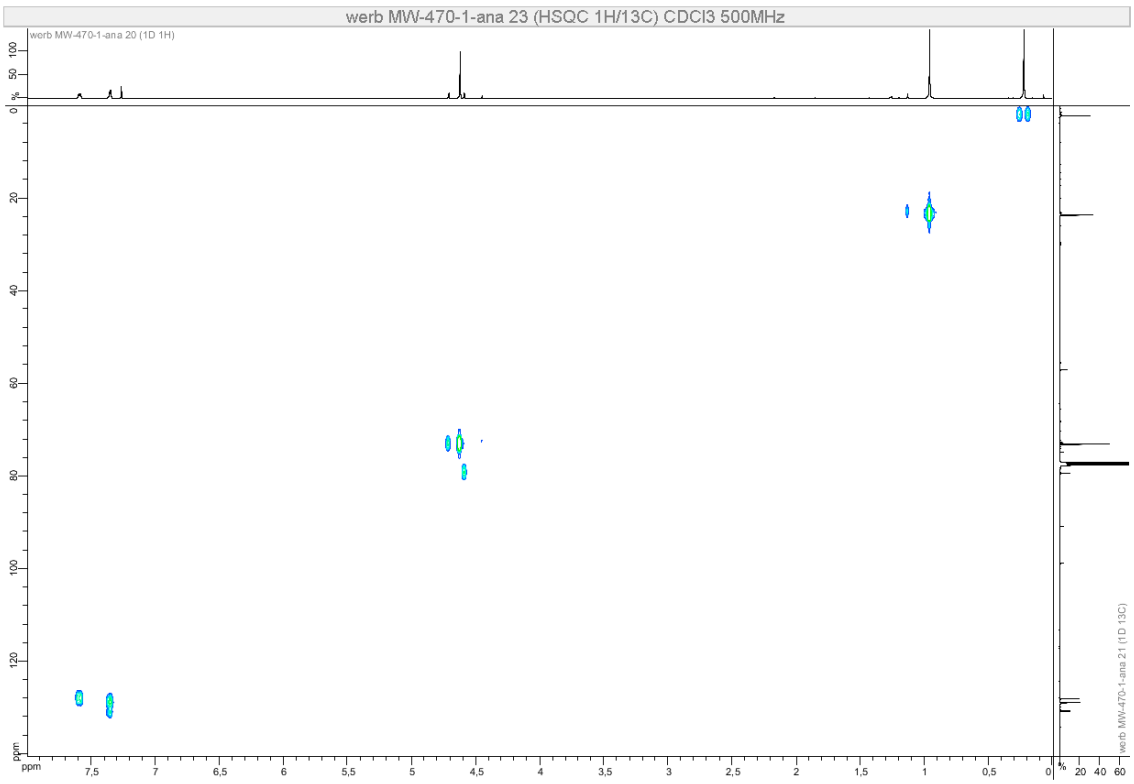
^{13}C NMR (126 MHz, $CDCl_3$)



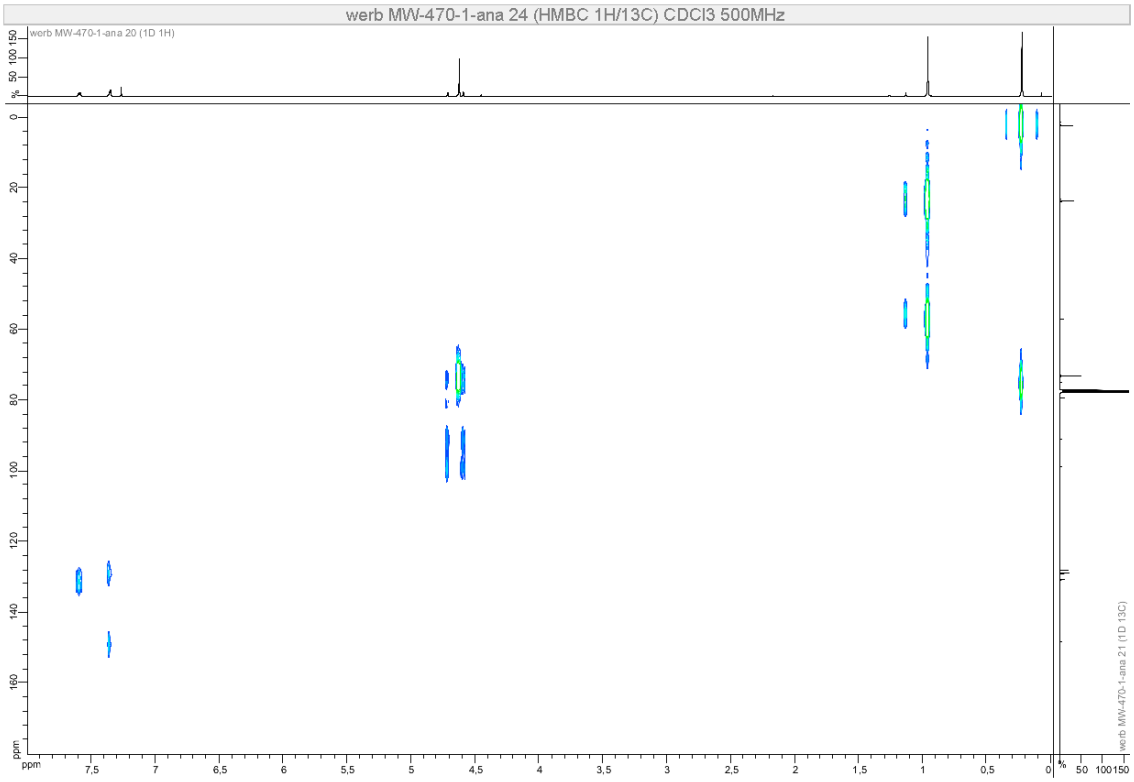
COSY (500 MHz, $CDCl_3$)



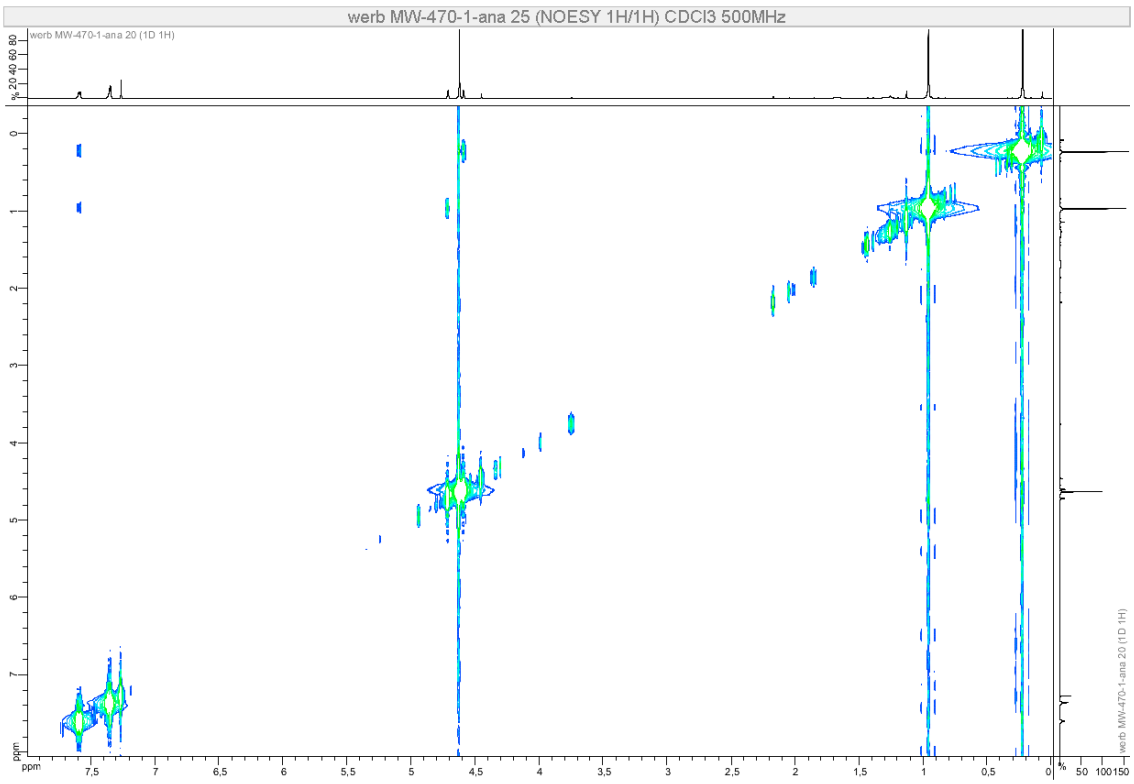
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

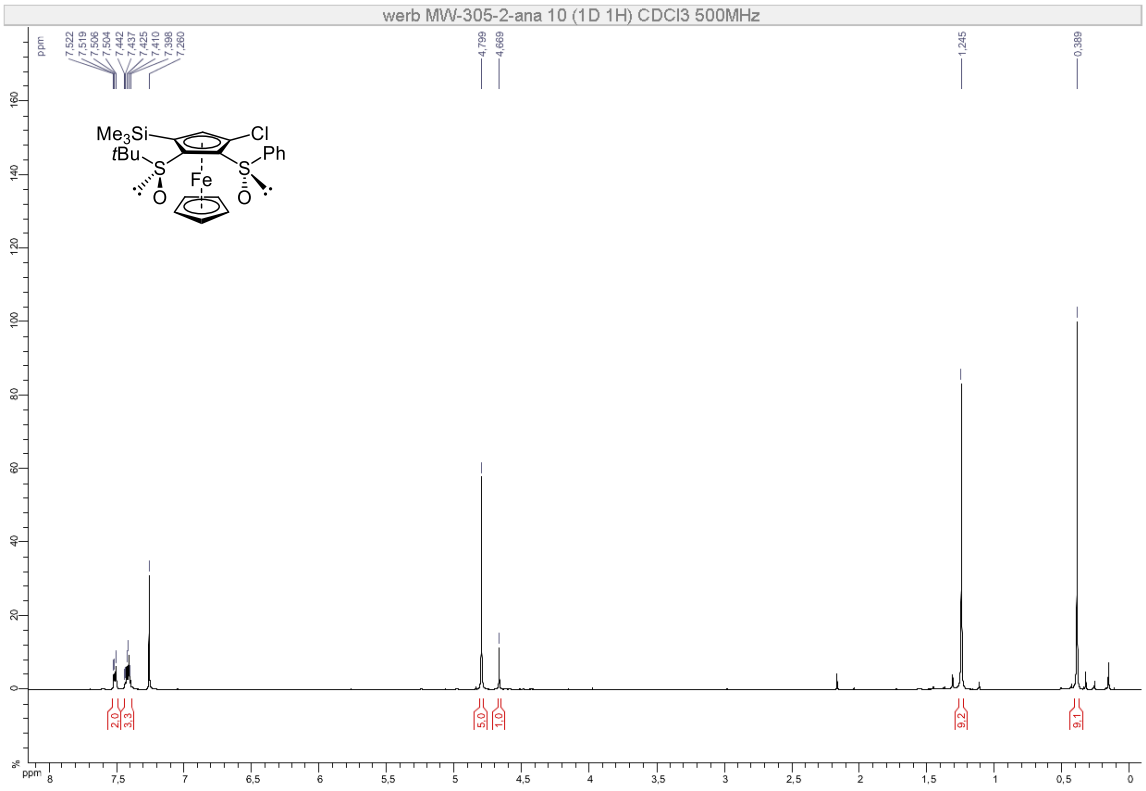


NOESY (500 MHz, $CDCl_3$)

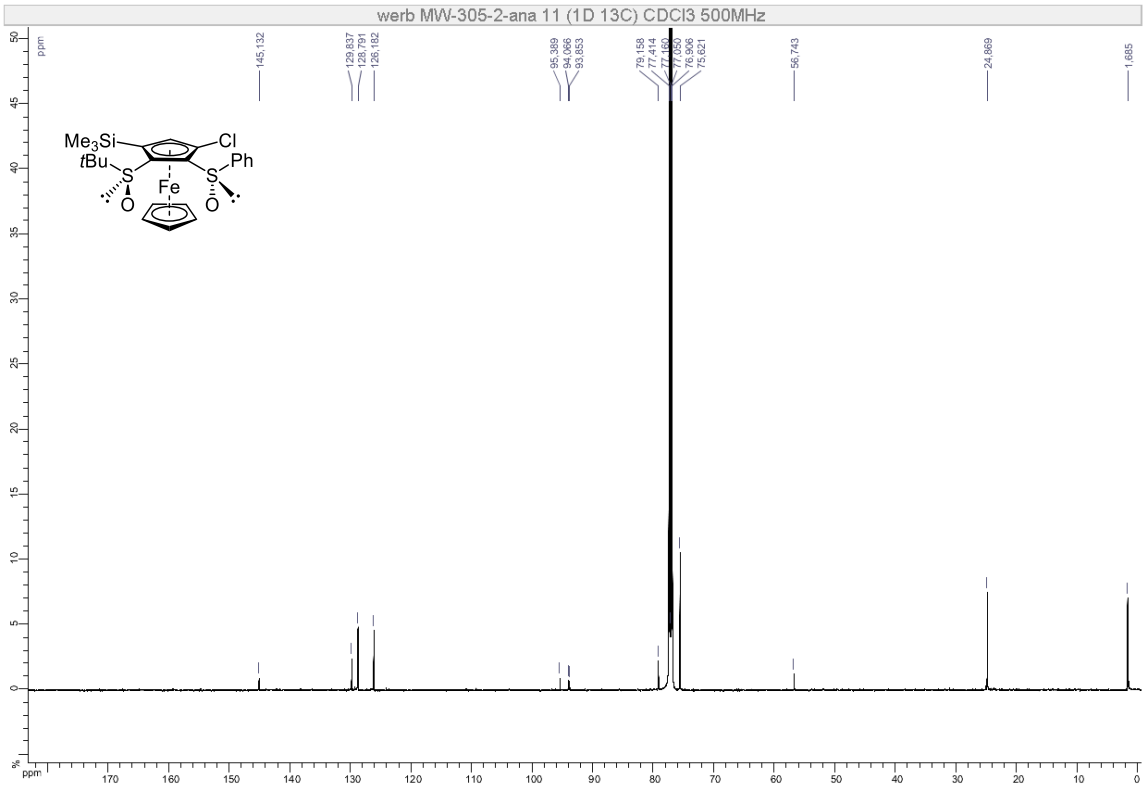


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-3-chloro-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (*S*,*S*,*R*$_P$-12a)

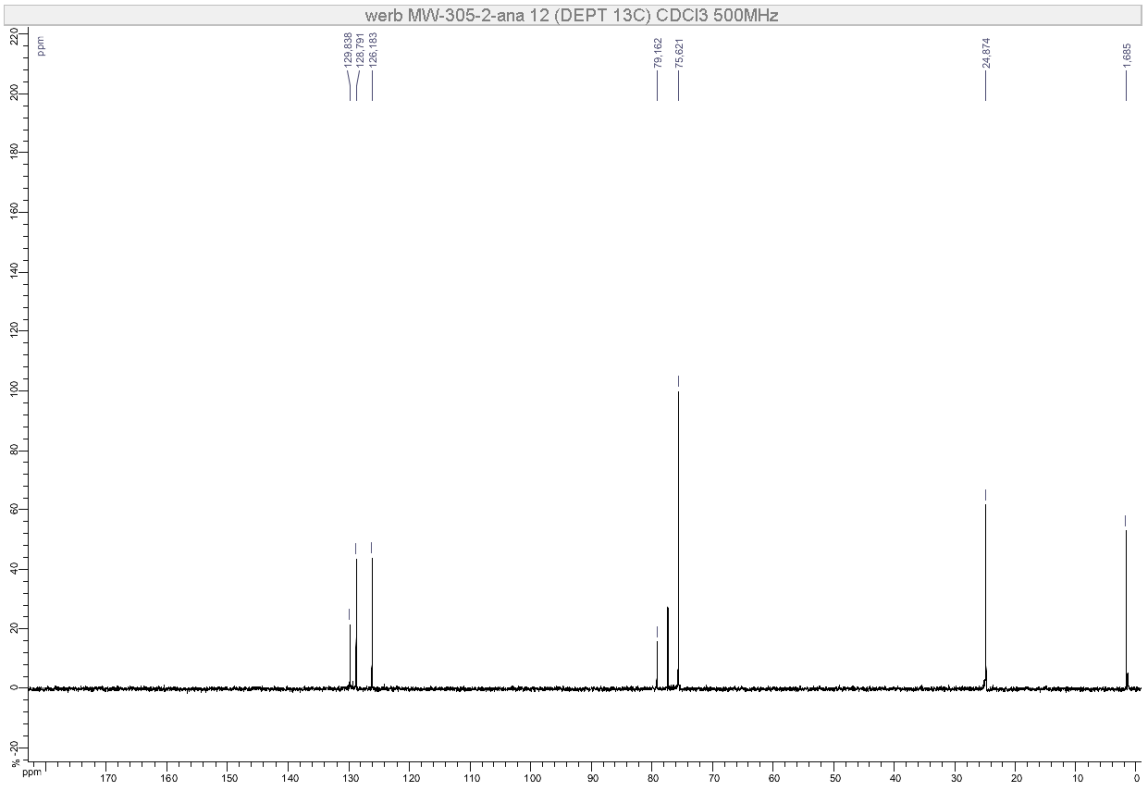
^{1}H NMR (500 MHz, $CDCl_3$)



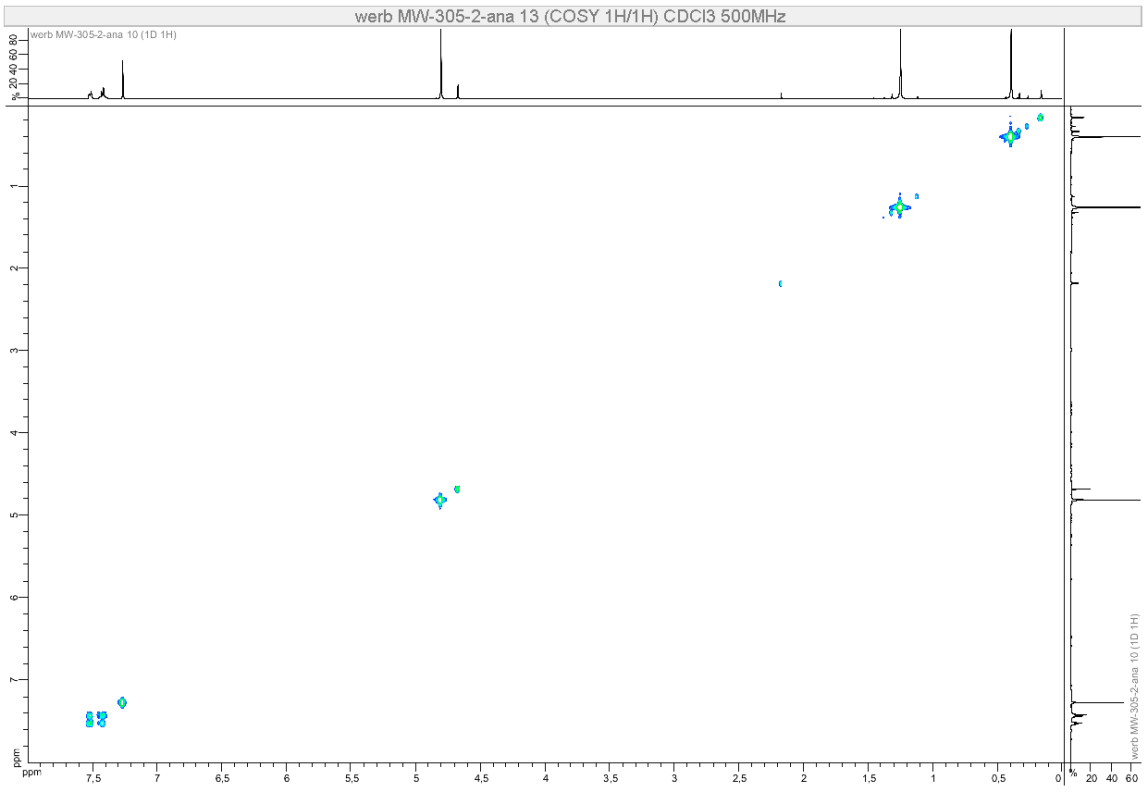
^{13}C NMR (126 MHz, $CDCl_3$)



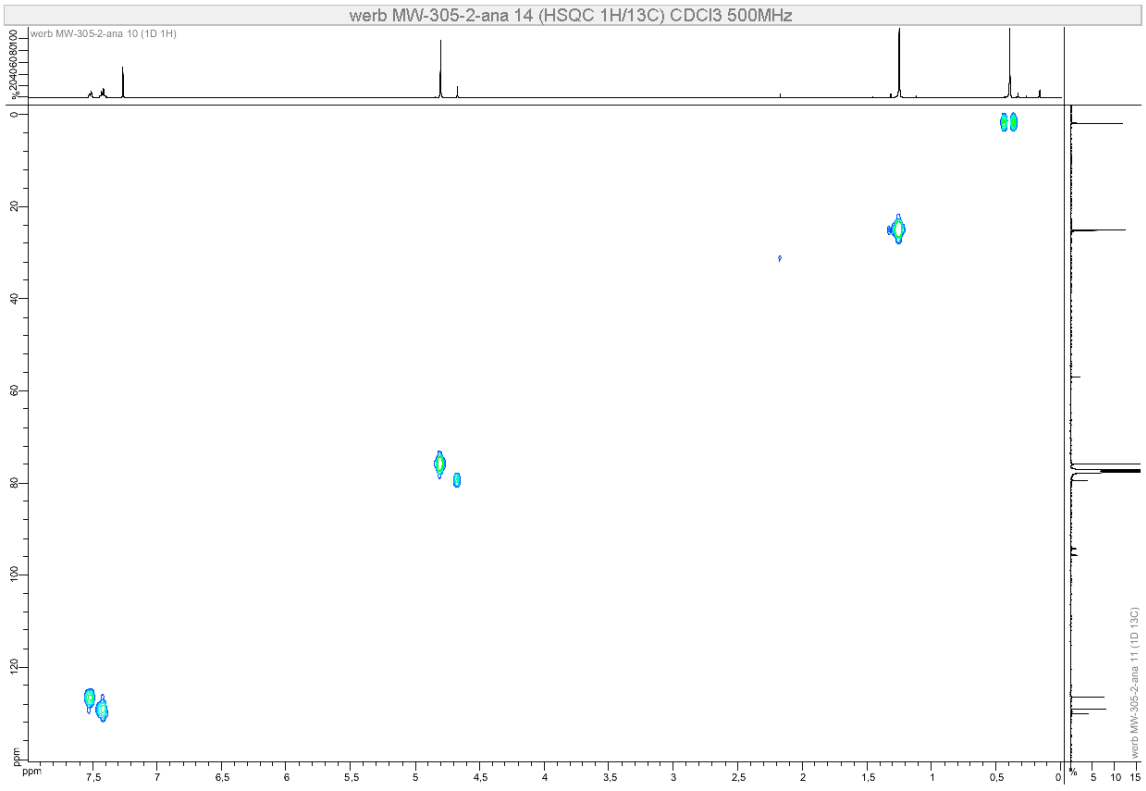
DEPT (126 MHz, $CDCl_3$)



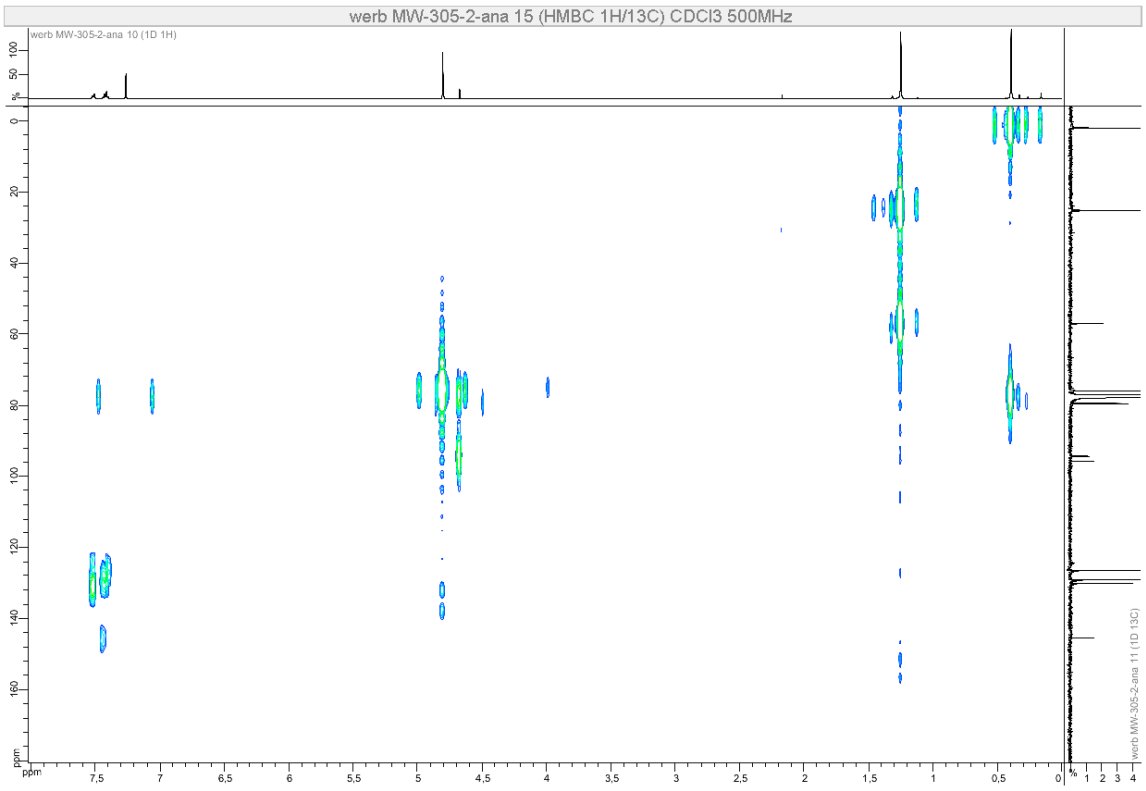
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

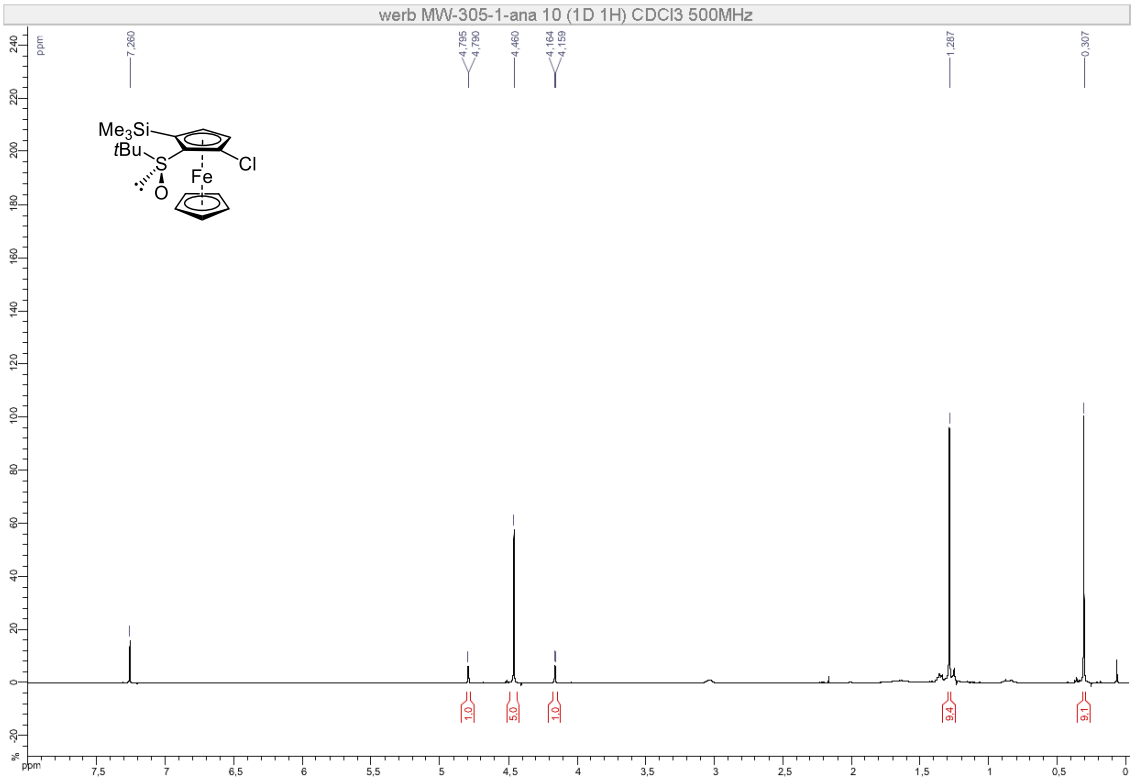


HMBC (500 MHz, $CDCl_3$)

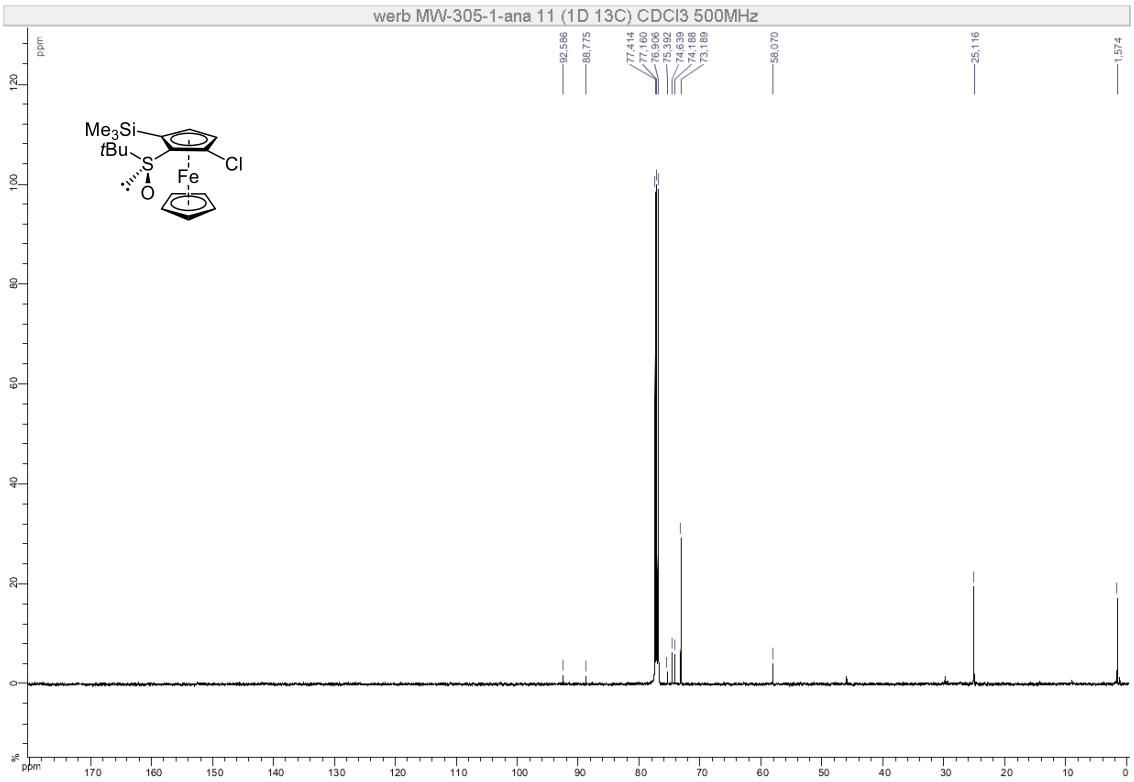


(*S*,*R*$_P$)-*S*-*tert*-Butyl-2-chloro-5-(trimethylsilyl)ferrocenesulfoxide (*S*,*R*$_P$-12a')

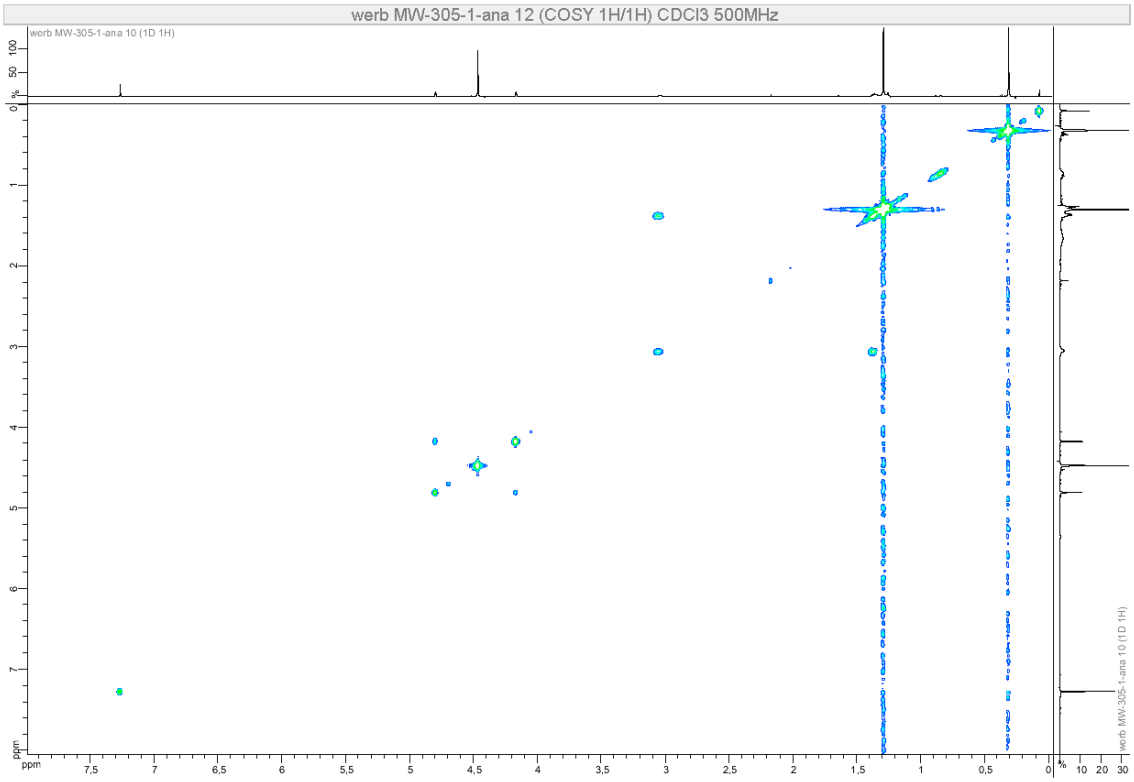
^{1}H NMR (500 MHz, $CDCl_3$)



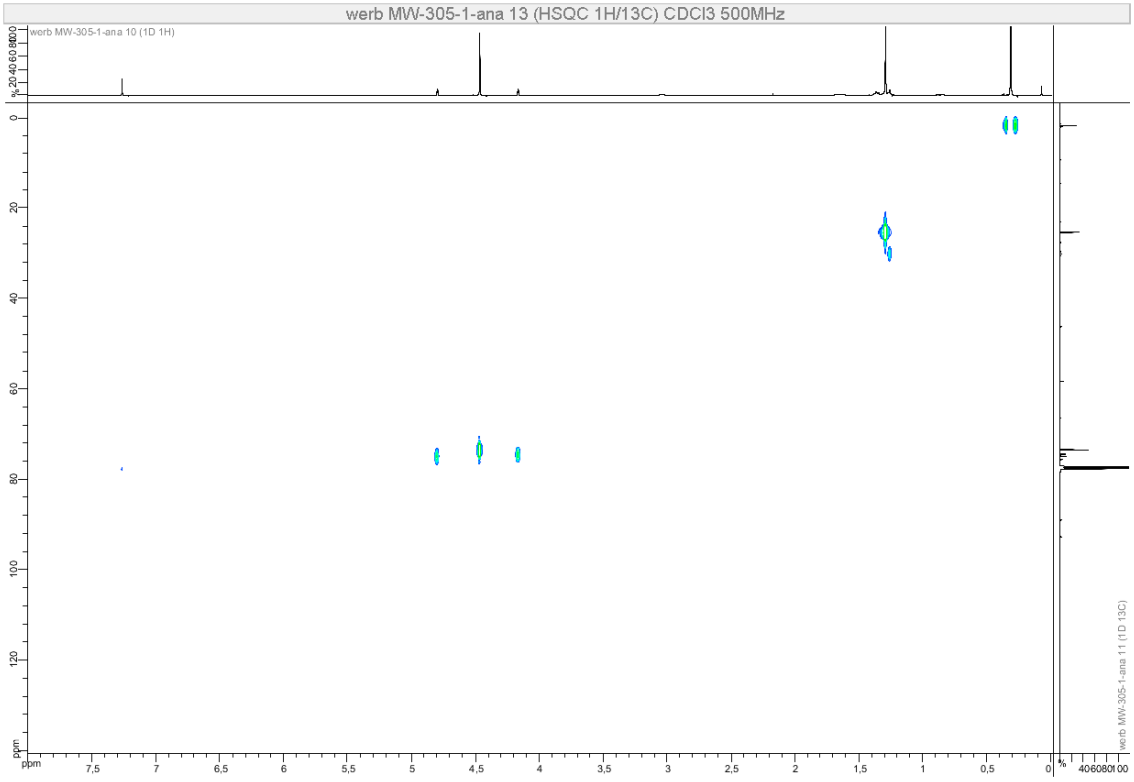
^{13}C NMR (126 MHz, $CDCl_3$)



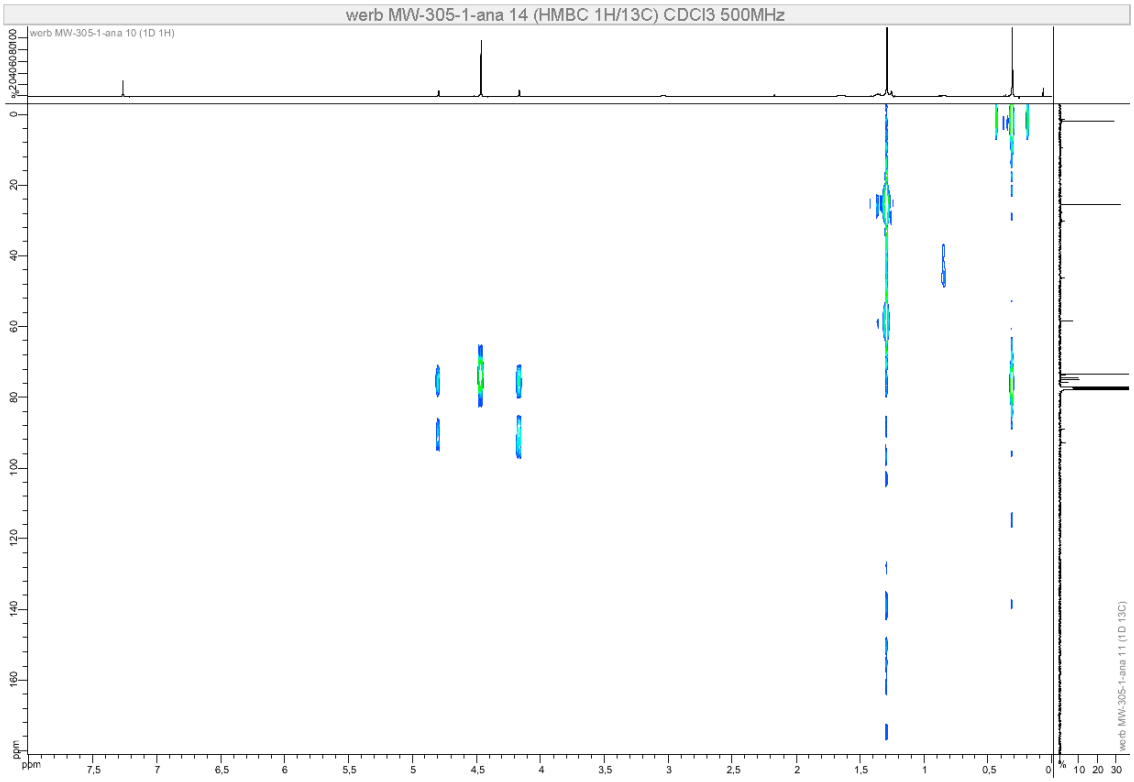
COSY (500 MHz, $CDCl_3$)



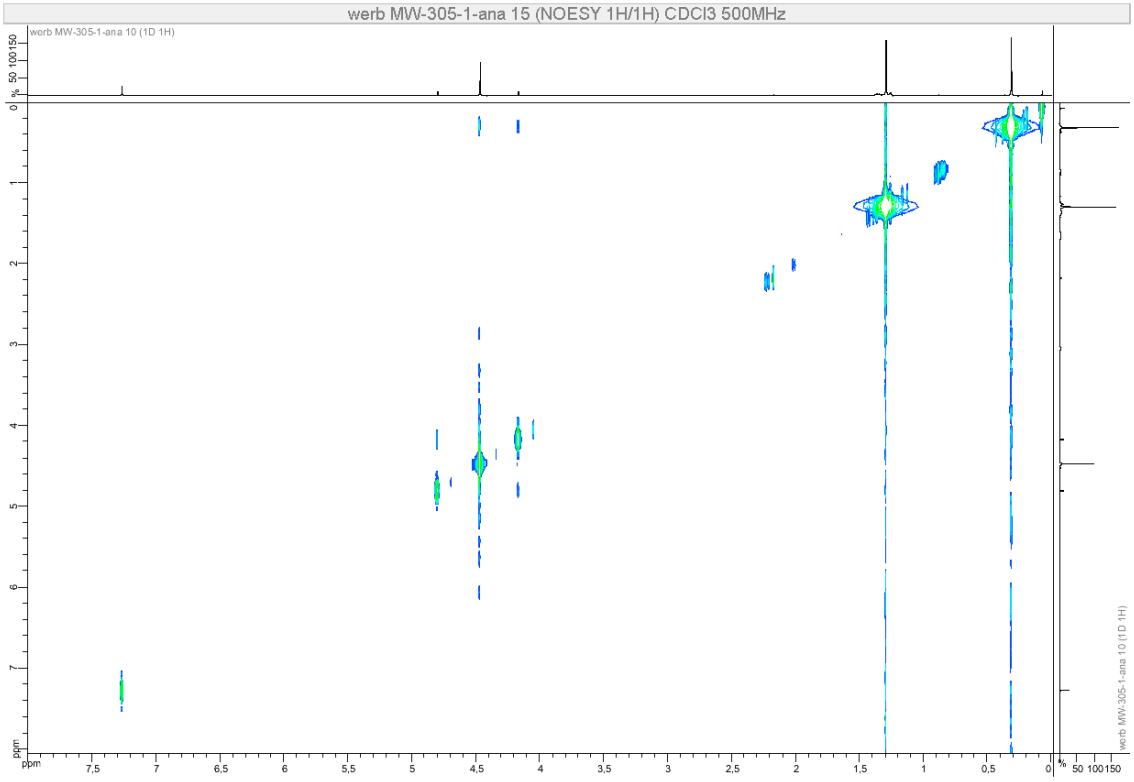
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

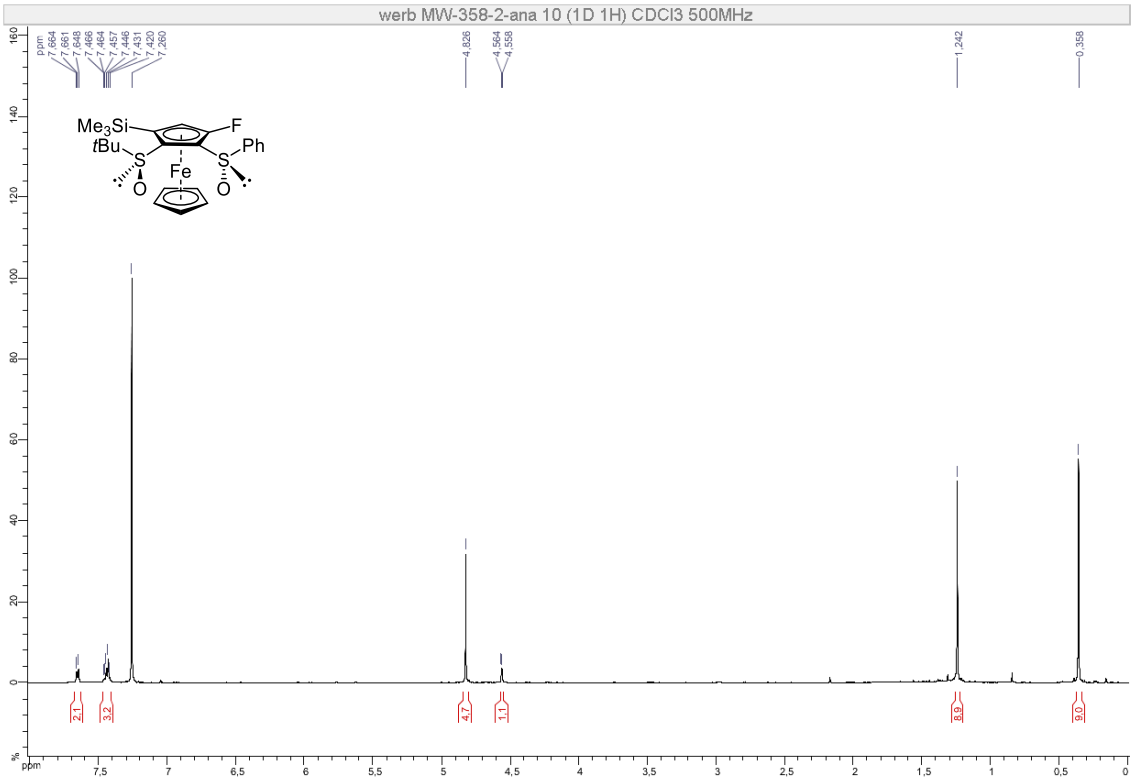


NOESY (500 MHz, $CDCl_3$)

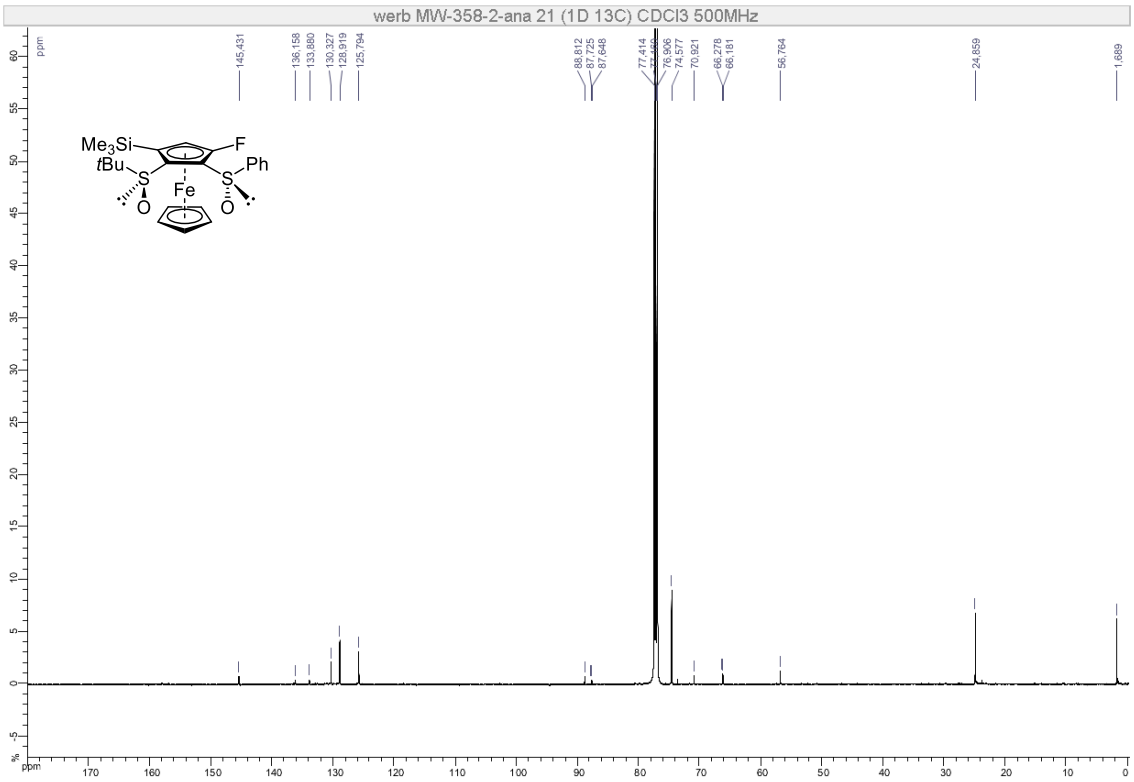


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-3-fluoro-*S'*-phenyl-5-(trimethylsilyl)ferrocene-1,2-disulfoxide (*S*,*S*,*R*$_P$-12b)

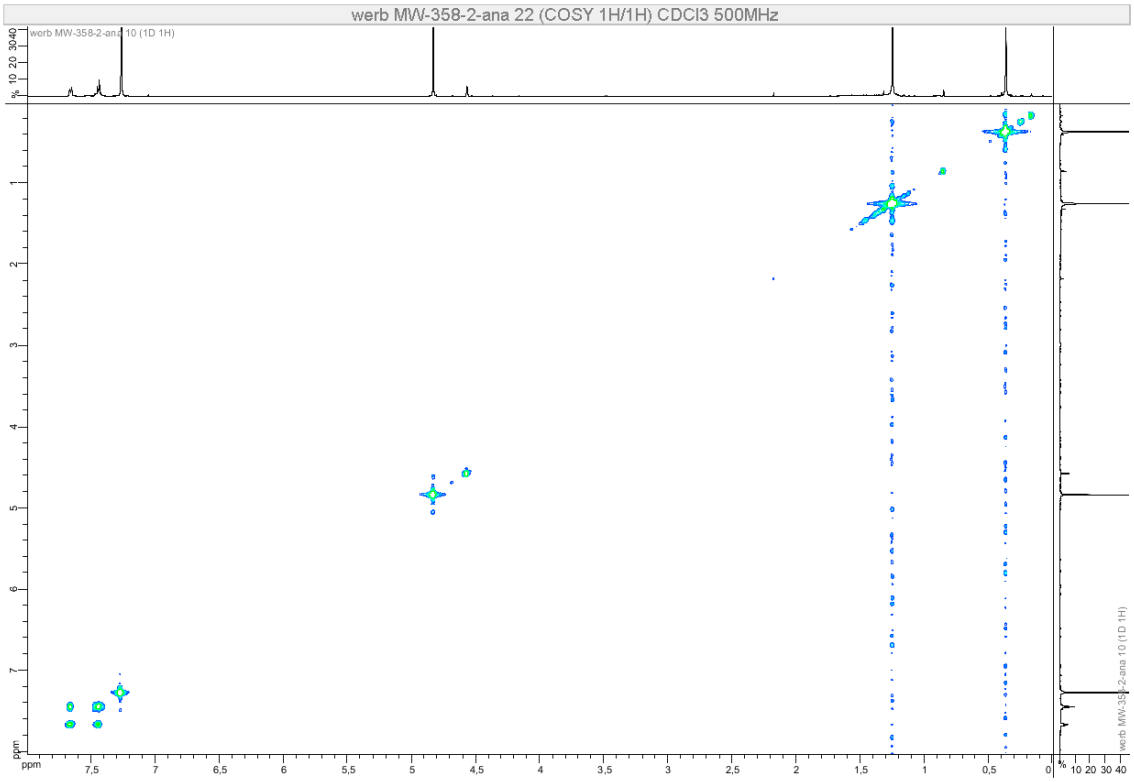
^{1}H NMR (500 MHz, $CDCl_3$)



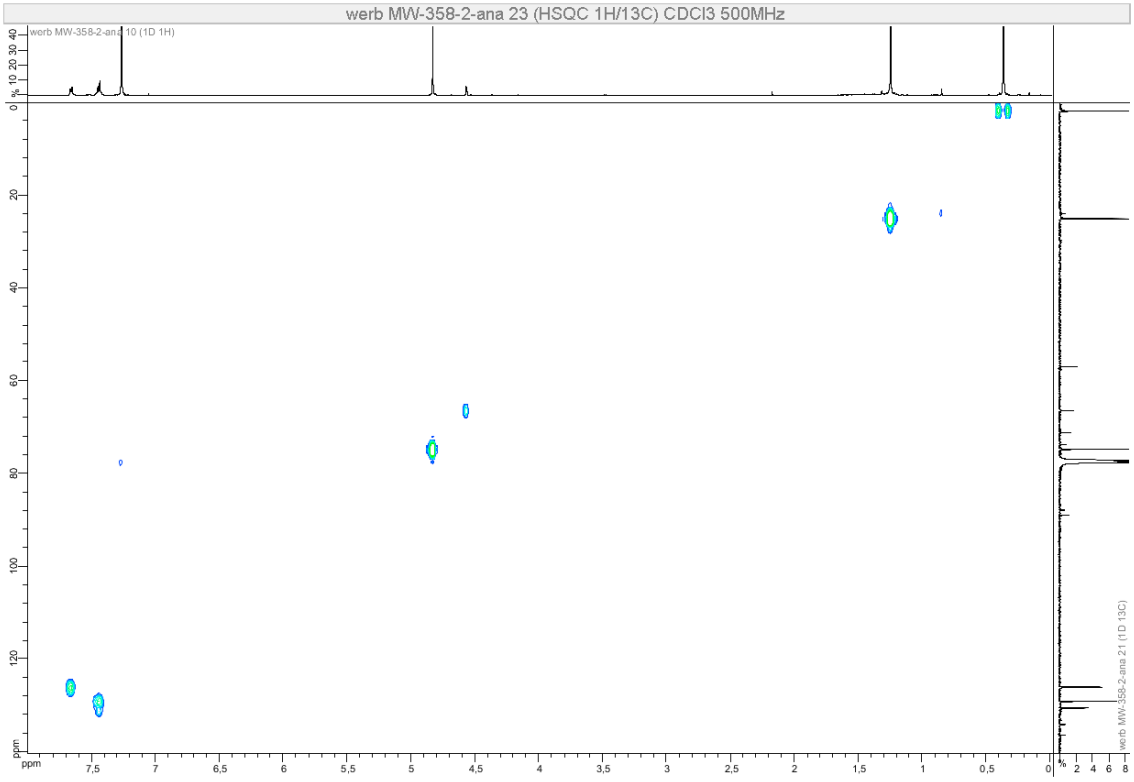
^{13}C NMR (126 MHz, $CDCl_3$)



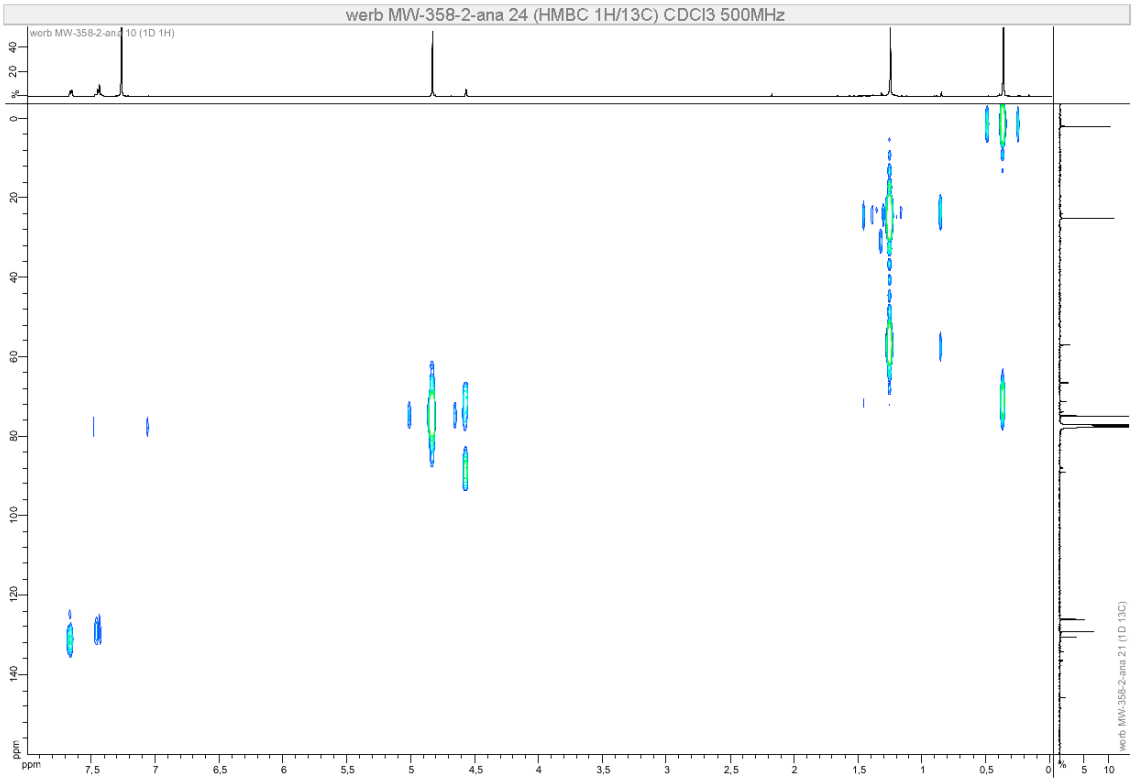
COSY (500 MHz, $CDCl_3$)



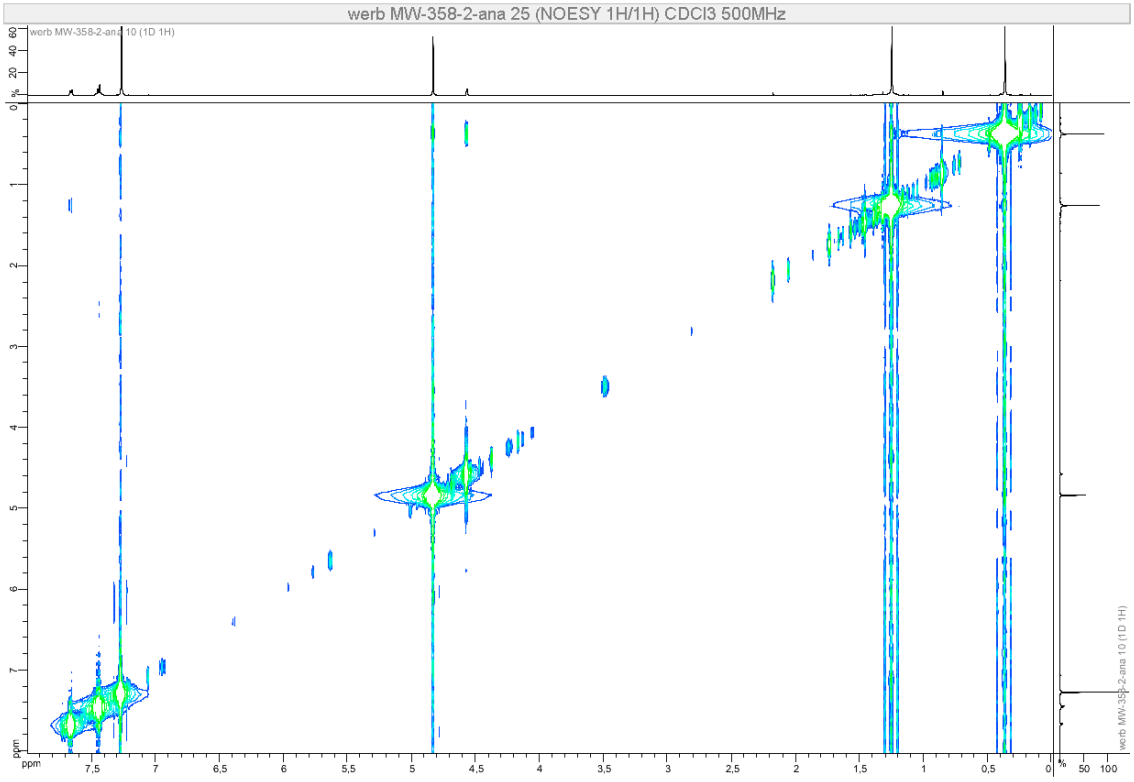
HSQC (500 MHz, $CDCl_3$)



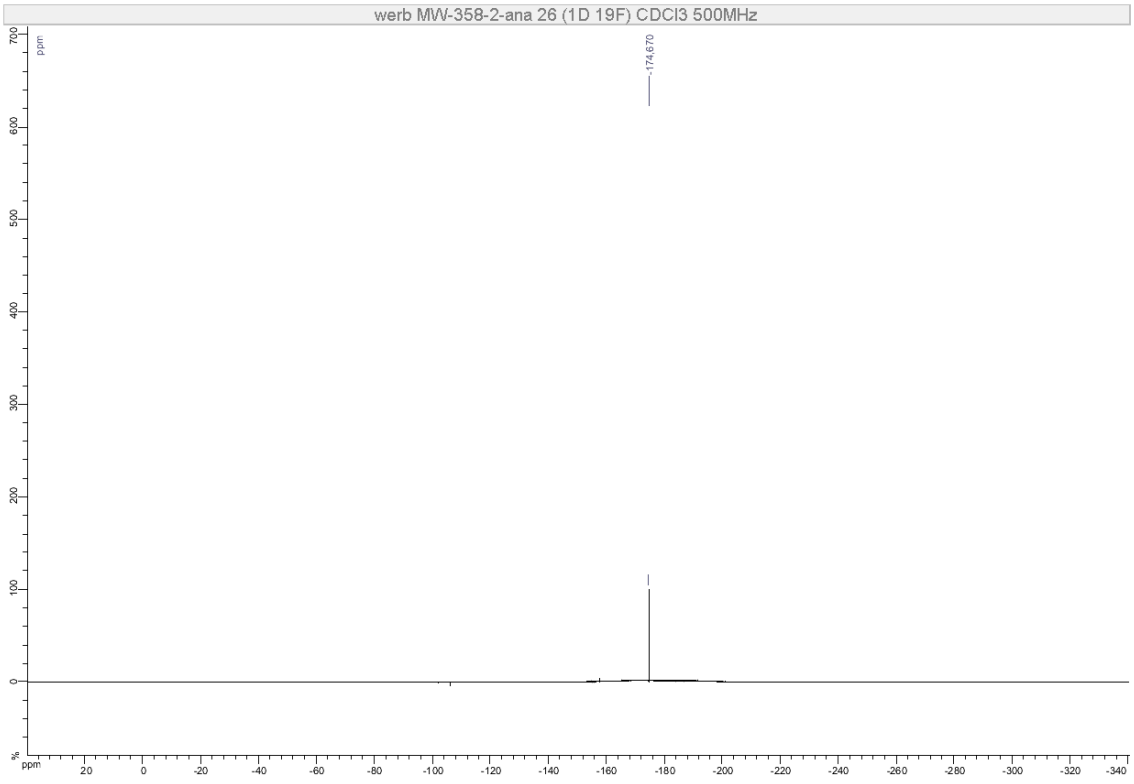
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

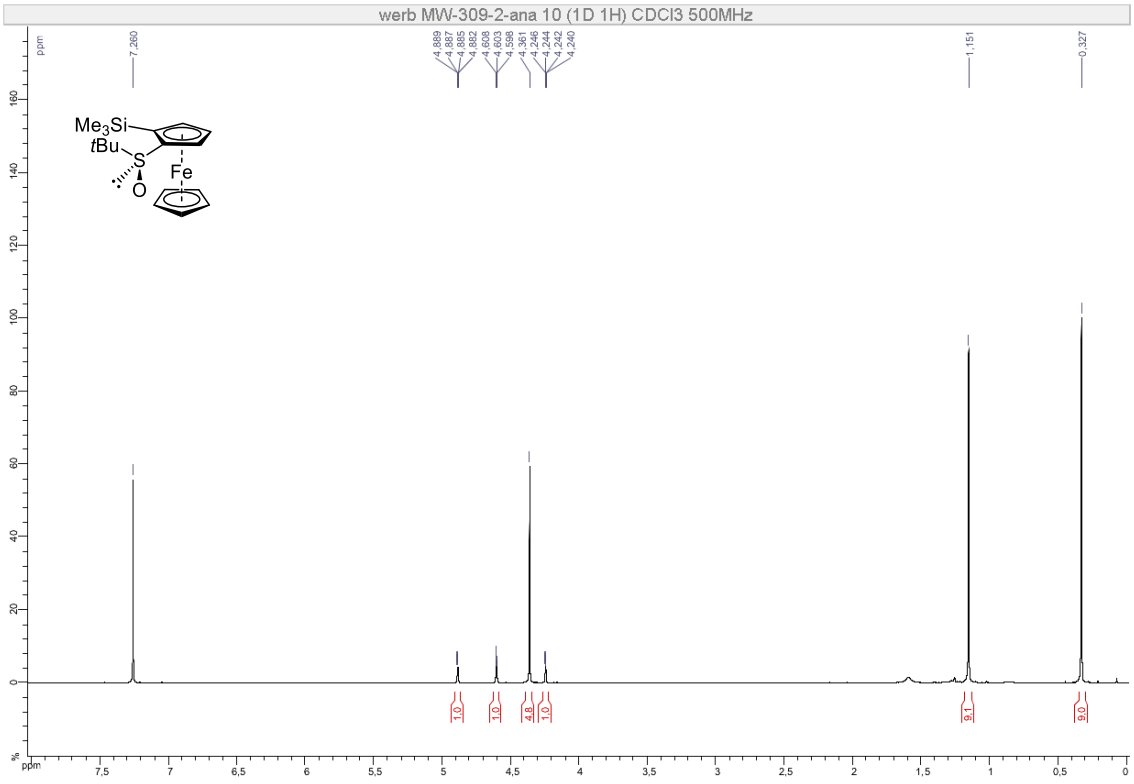


^{19}F NMR (471 MHz, $CDCl_3$)

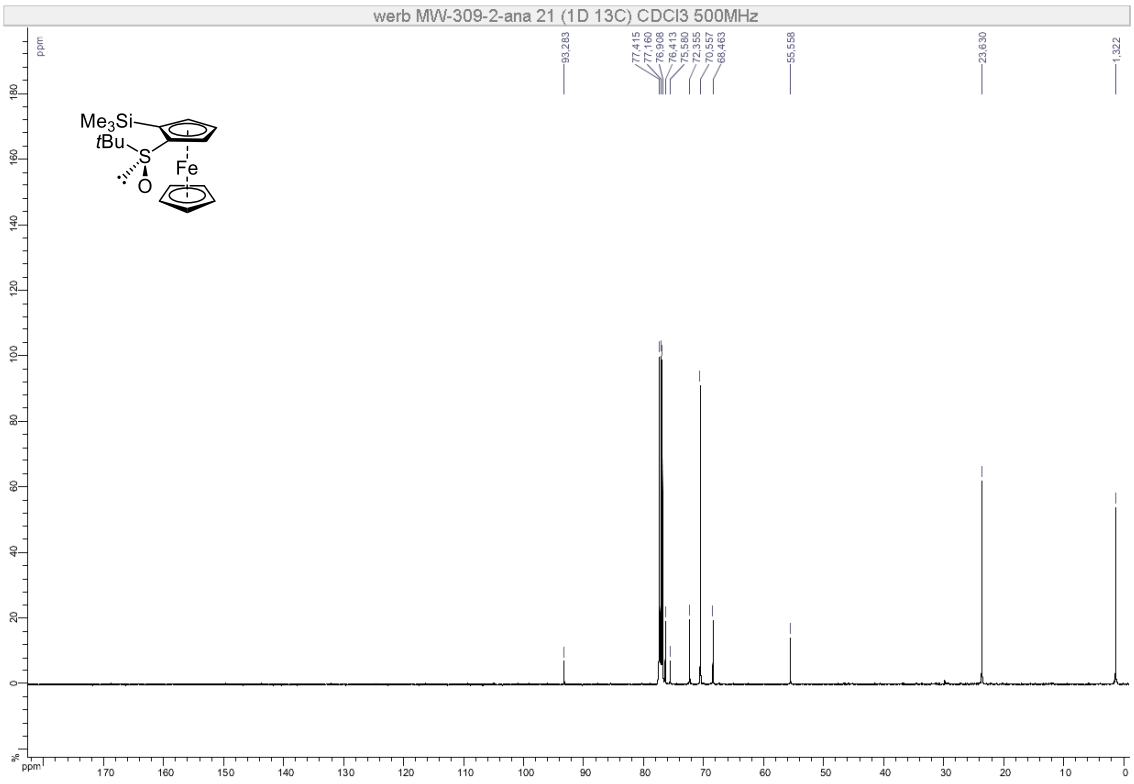


(*S*,*R*$_P$)-*S*-*tert*-Butyl-2-(trimethylsilyl)ferrocenesulfoxide (*S*,*R*$_P$-12b')

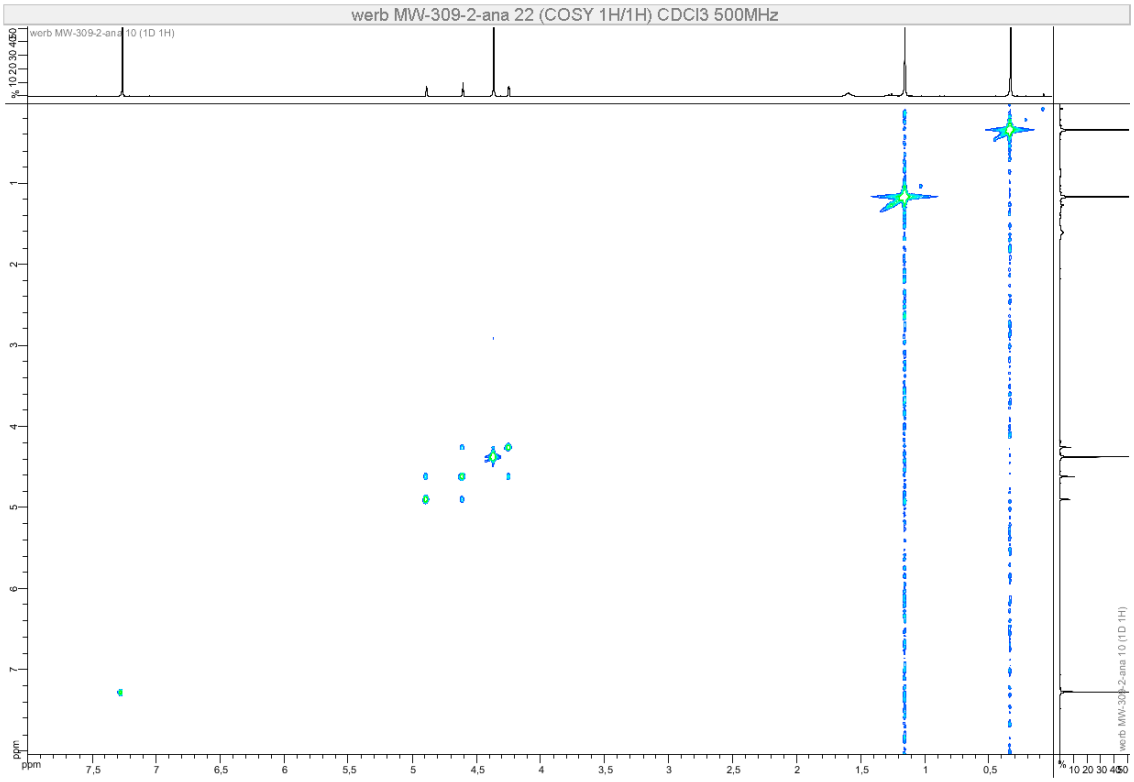
^{1}H NMR (500 MHz, $CDCl_3$)



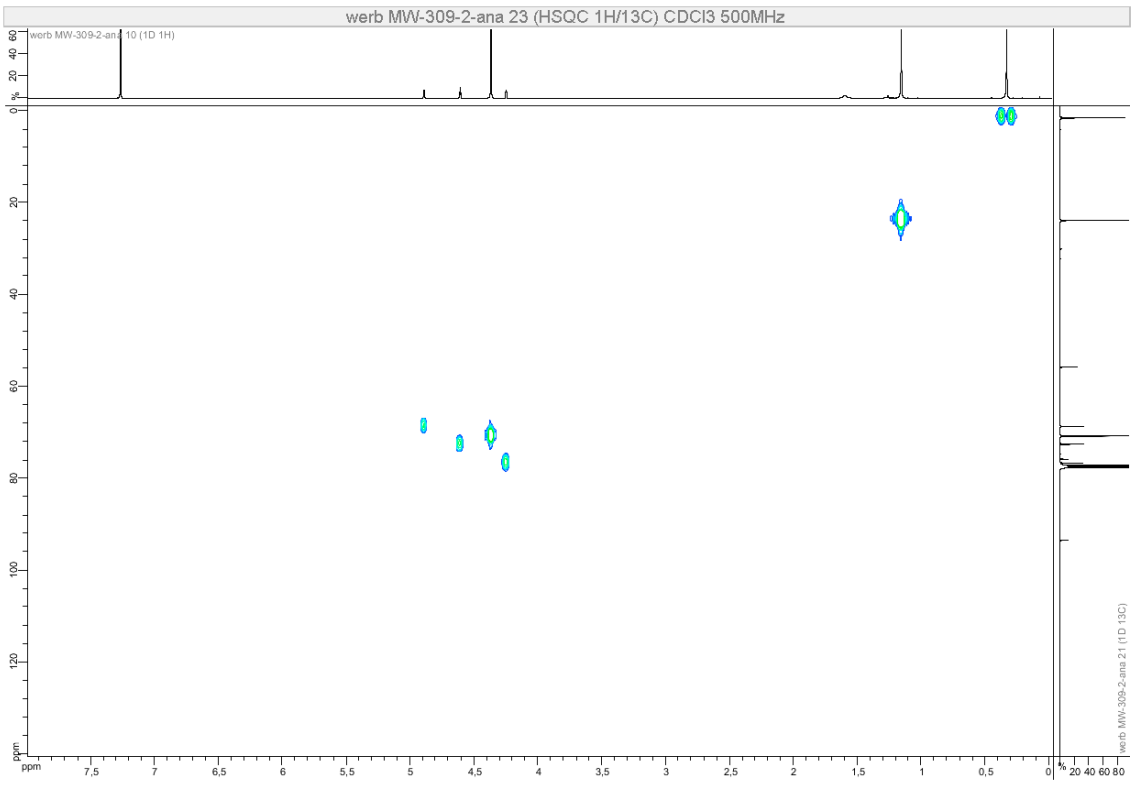
^{13}C NMR (126 MHz, $CDCl_3$)



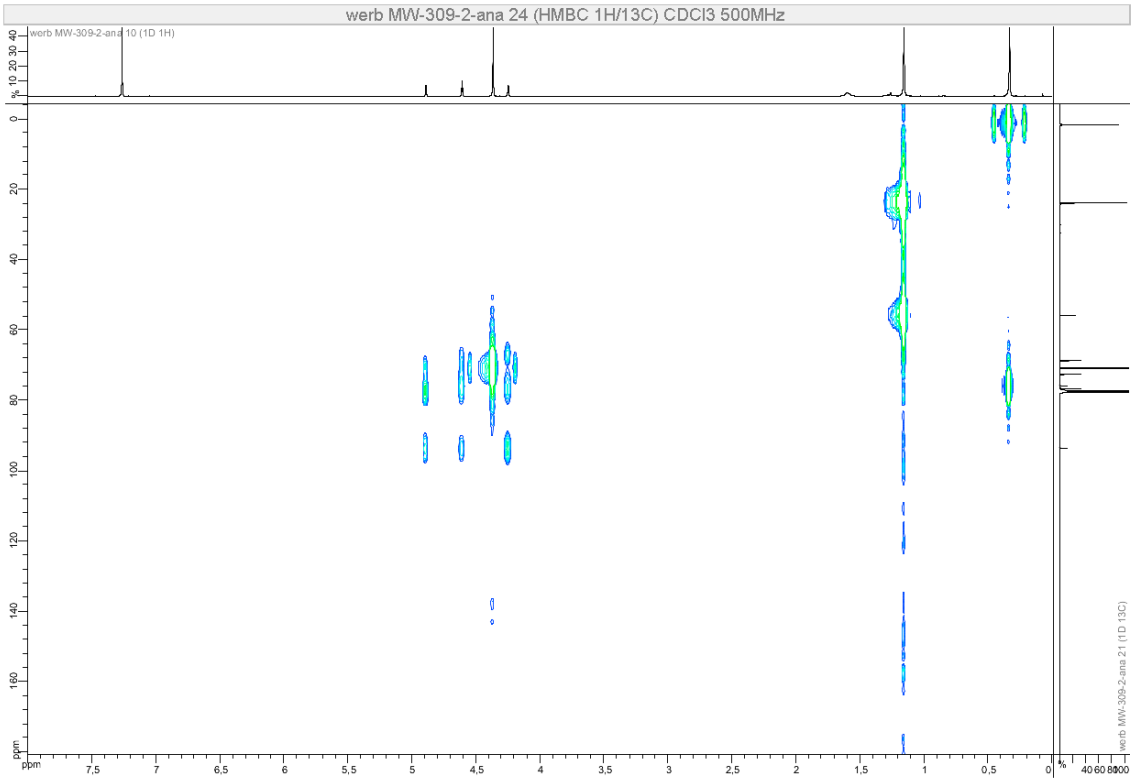
COSY (500 MHz, $CDCl_3$)



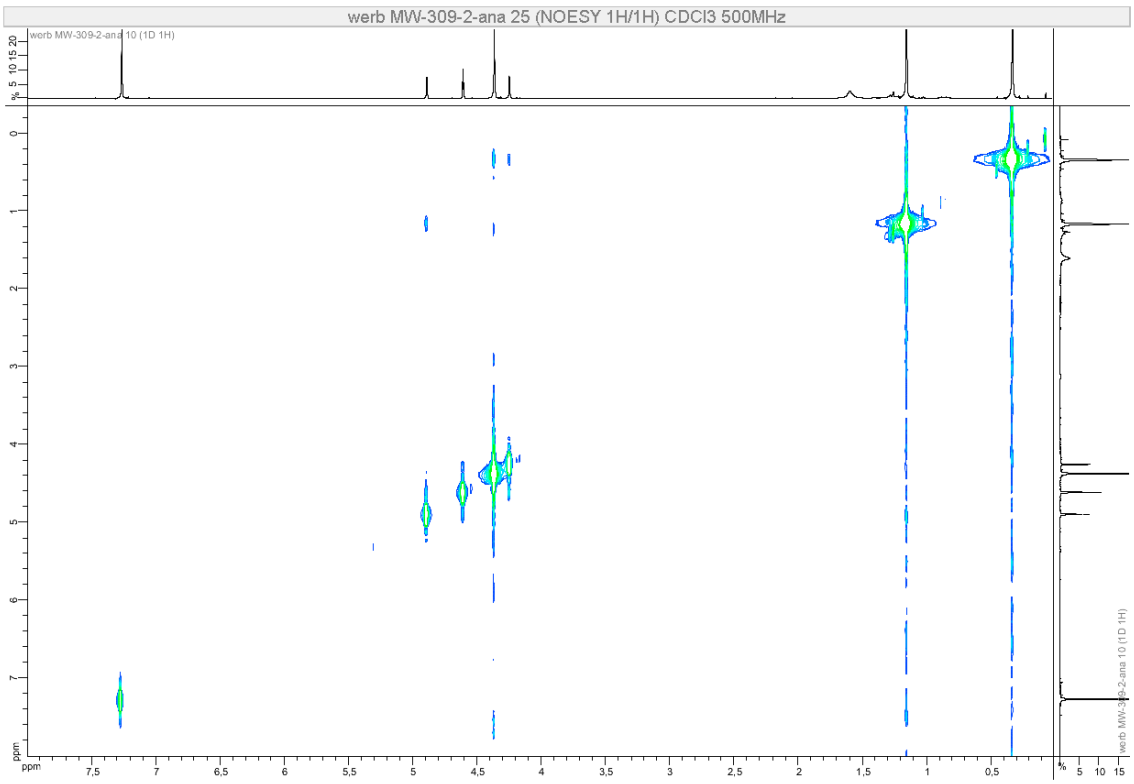
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

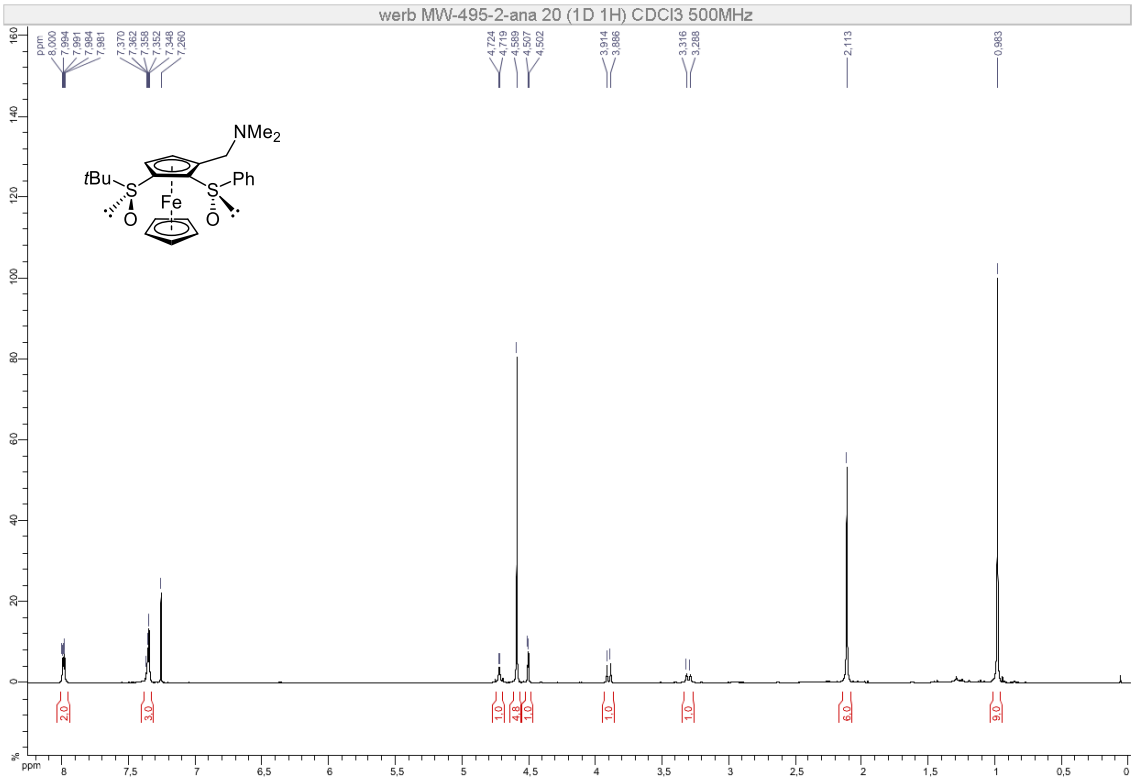


NOESY (500 MHz, $CDCl_3$)

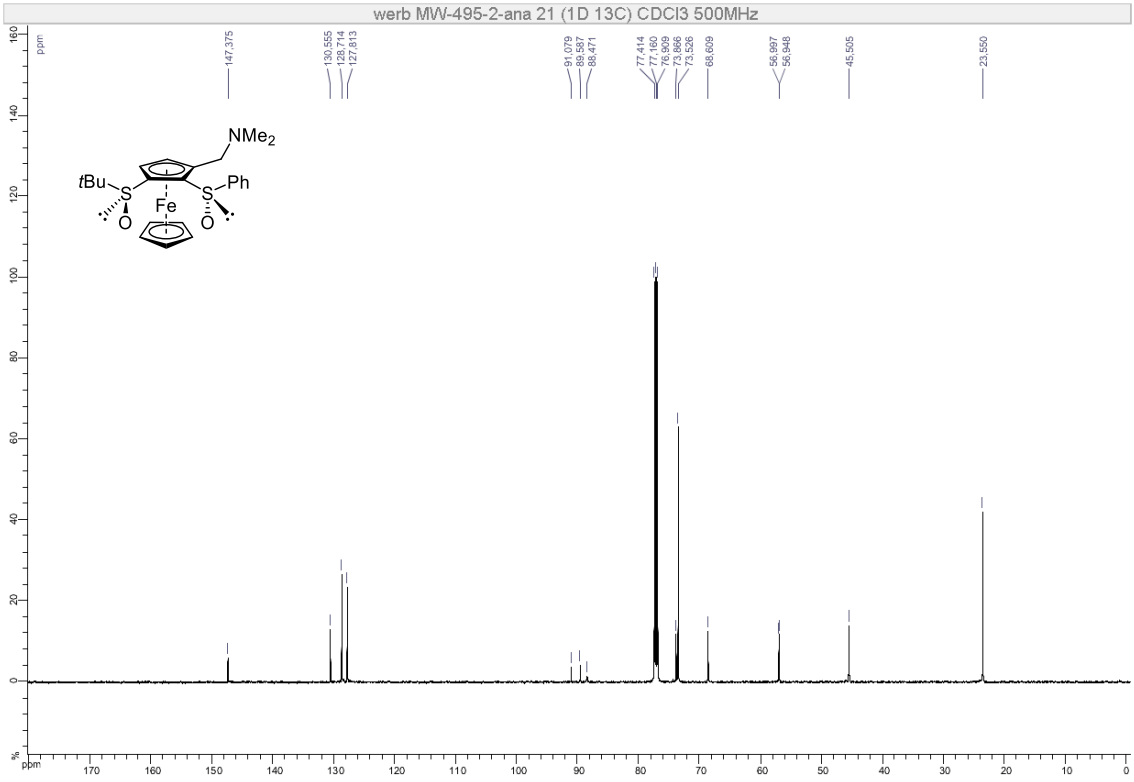


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-3-(dimethylaminomethyl)-*S'*-phenylferrocene-1,2-disulfoxide (*S*,*S*,*R*$_P$-7b)

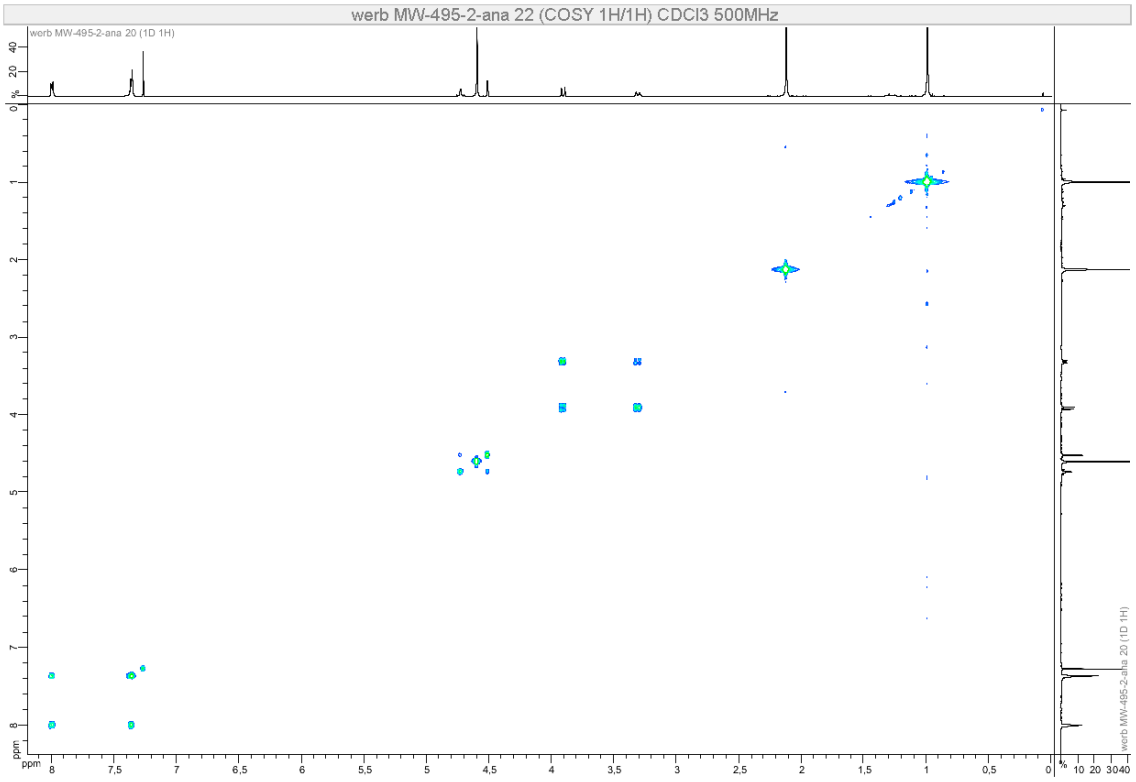
^{1}H NMR (500 MHz, $CDCl_3$)



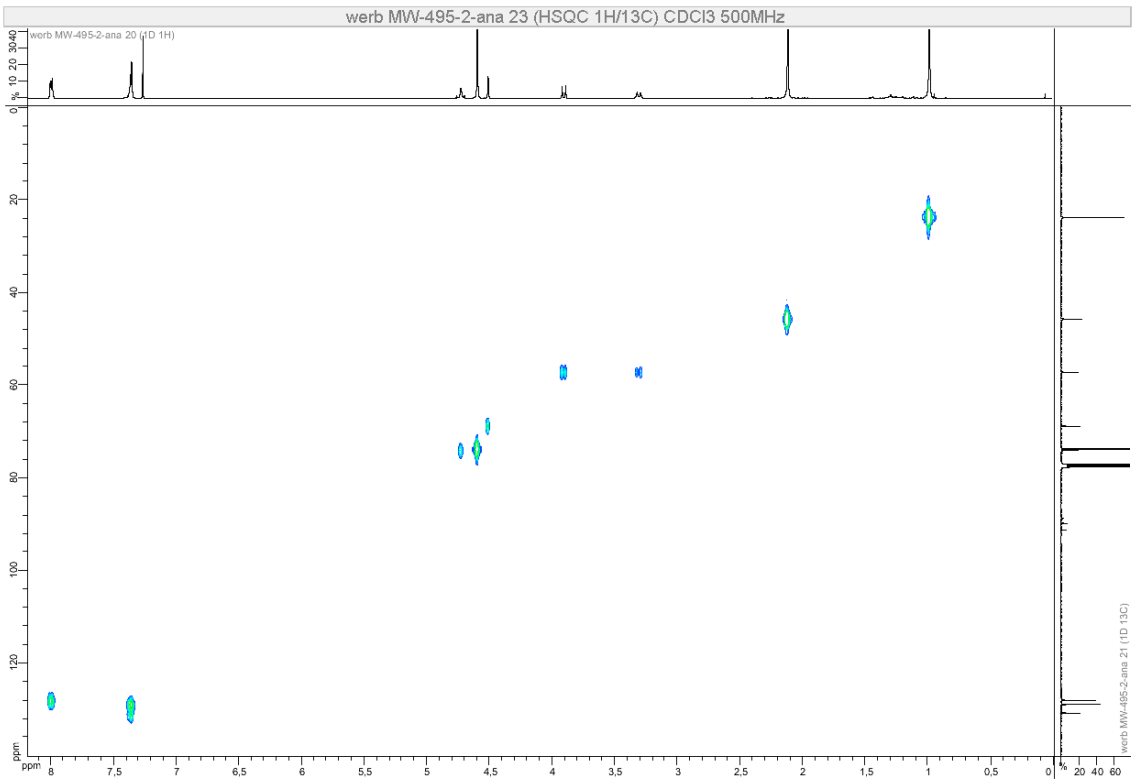
^{13}C NMR (126 MHz, $CDCl_3$)



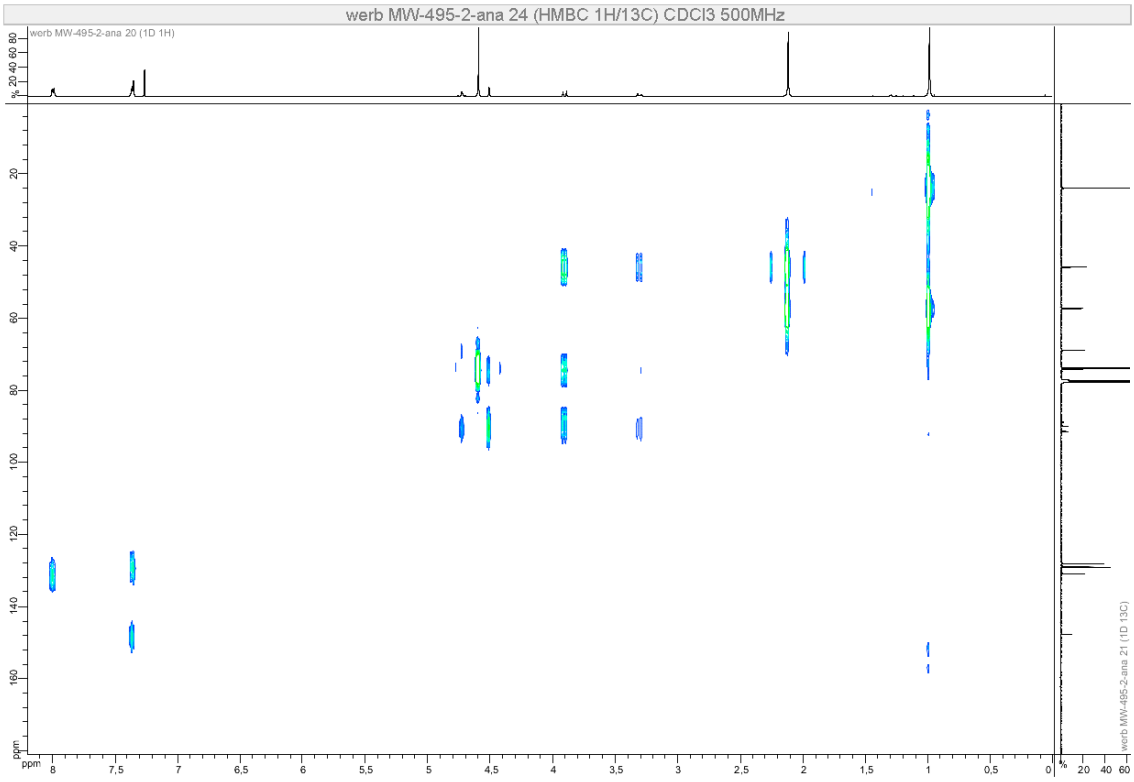
COSY (500 MHz, $CDCl_3$)



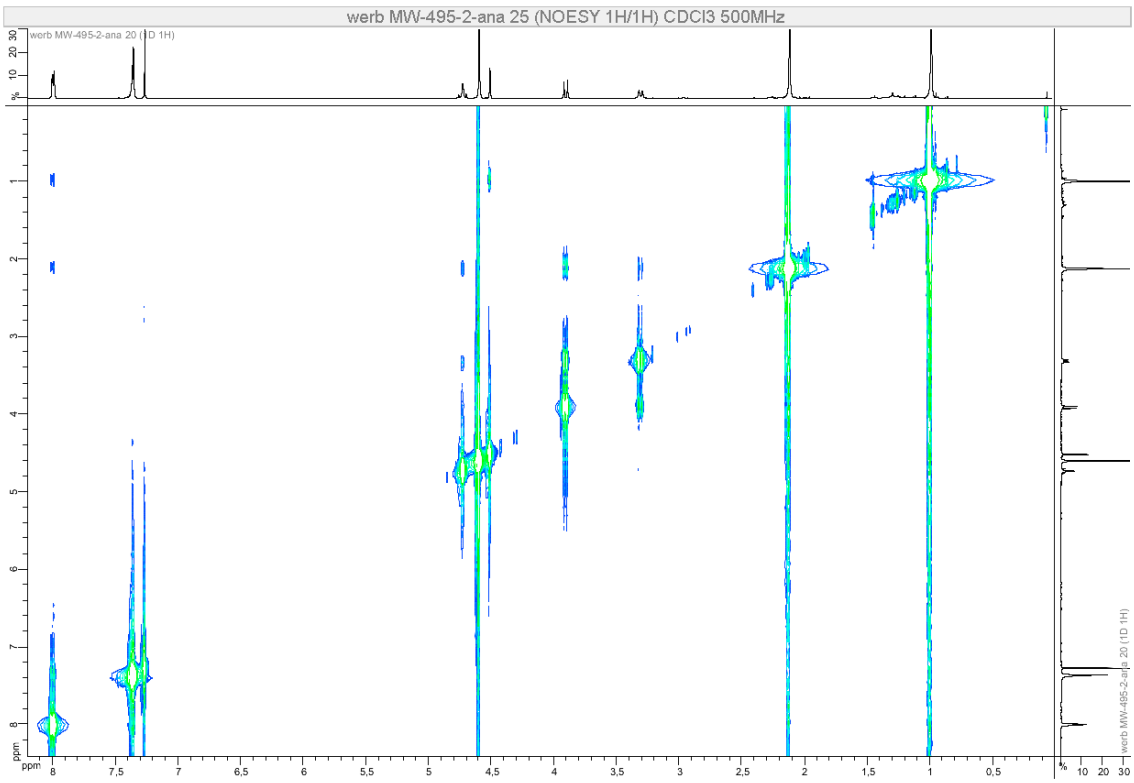
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

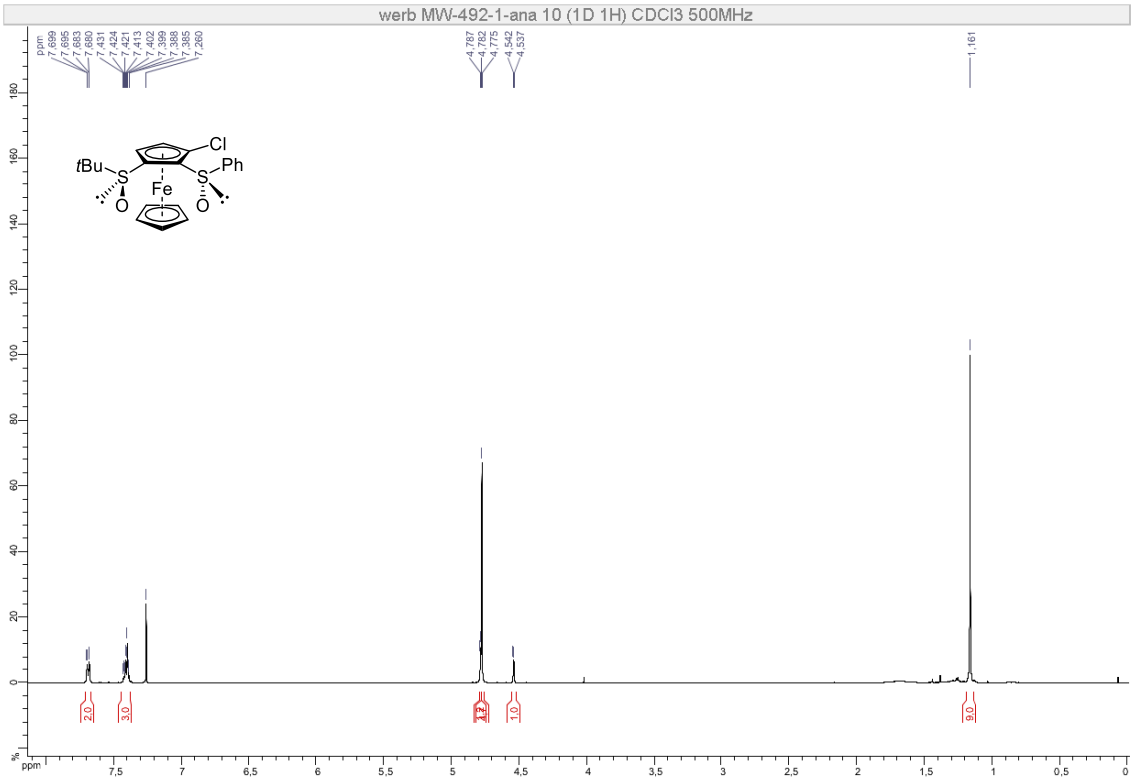


NOESY (500 MHz, $CDCl_3$)

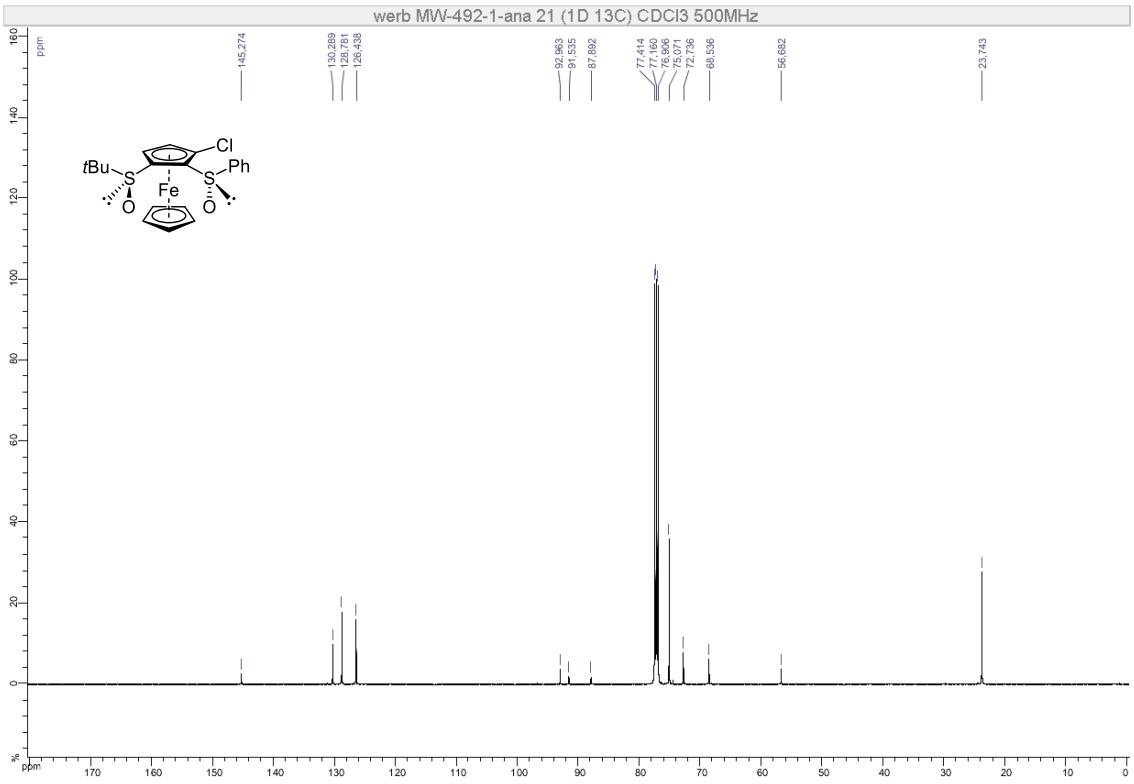


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-3-chloro-*S'*-phenylferrocene-1,2-disulfoxide (*S*,*S*,*R*$_P$-7c)

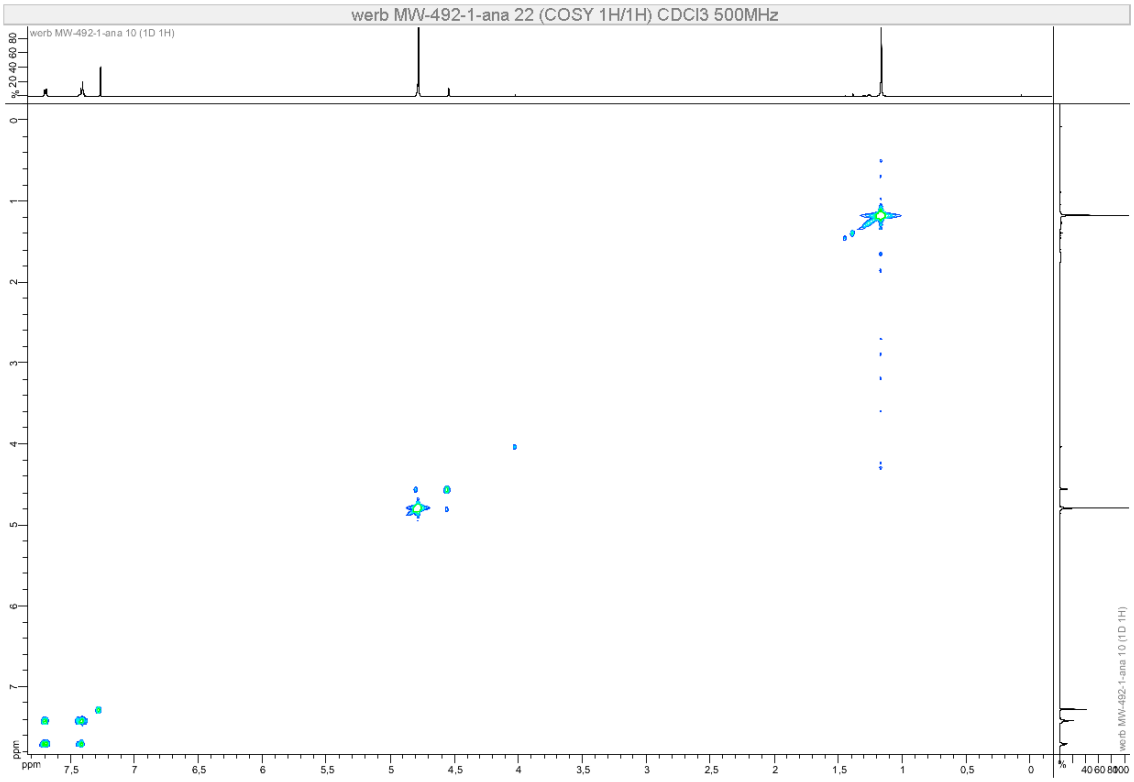
^{1}H NMR (500 MHz, $CDCl_3$)



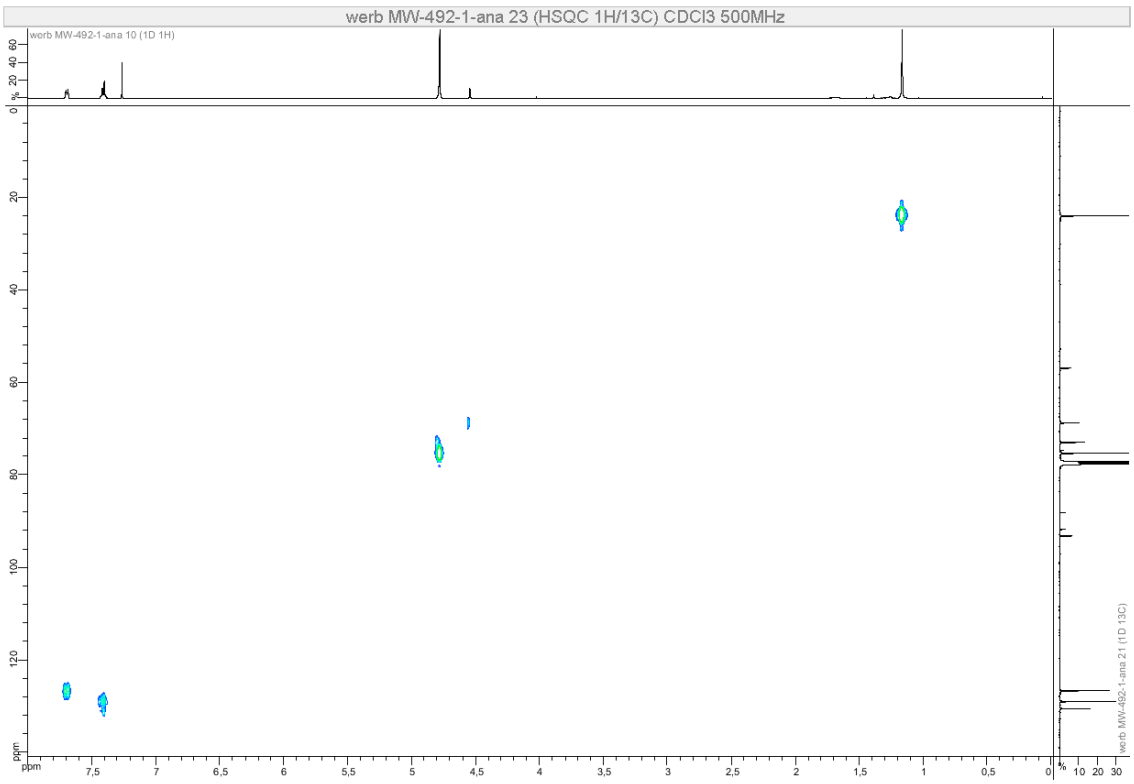
^{13}C NMR (126 MHz, $CDCl_3$)



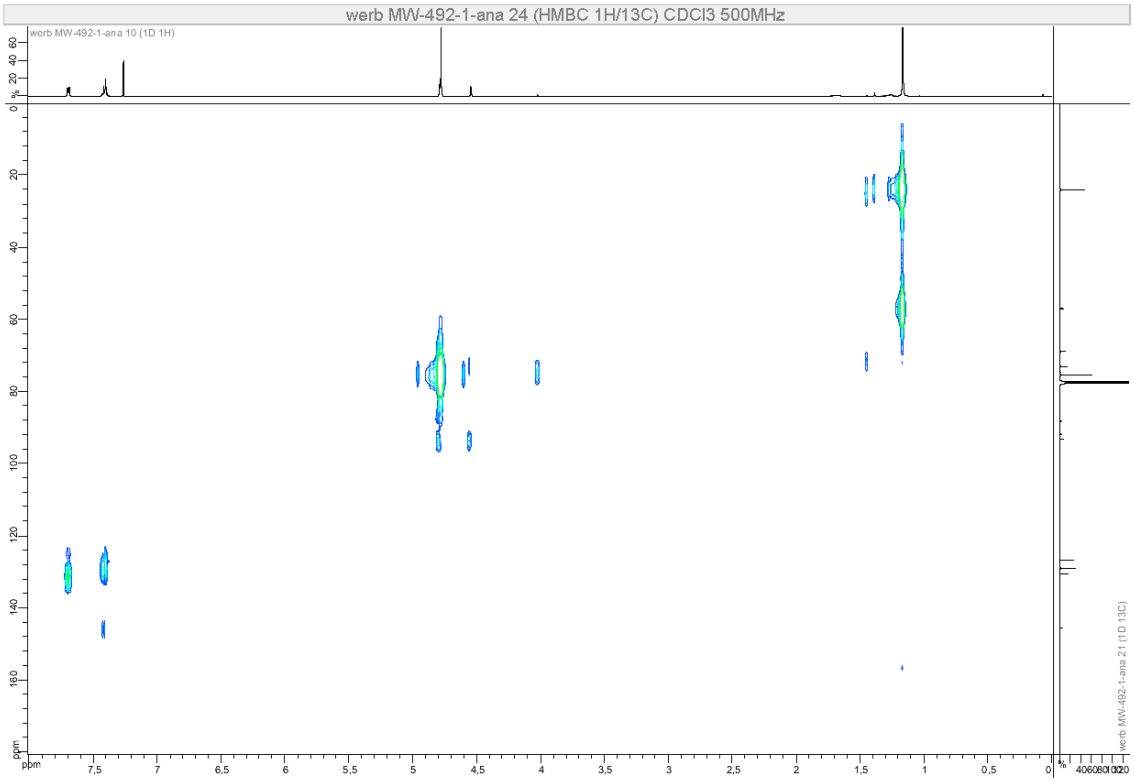
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

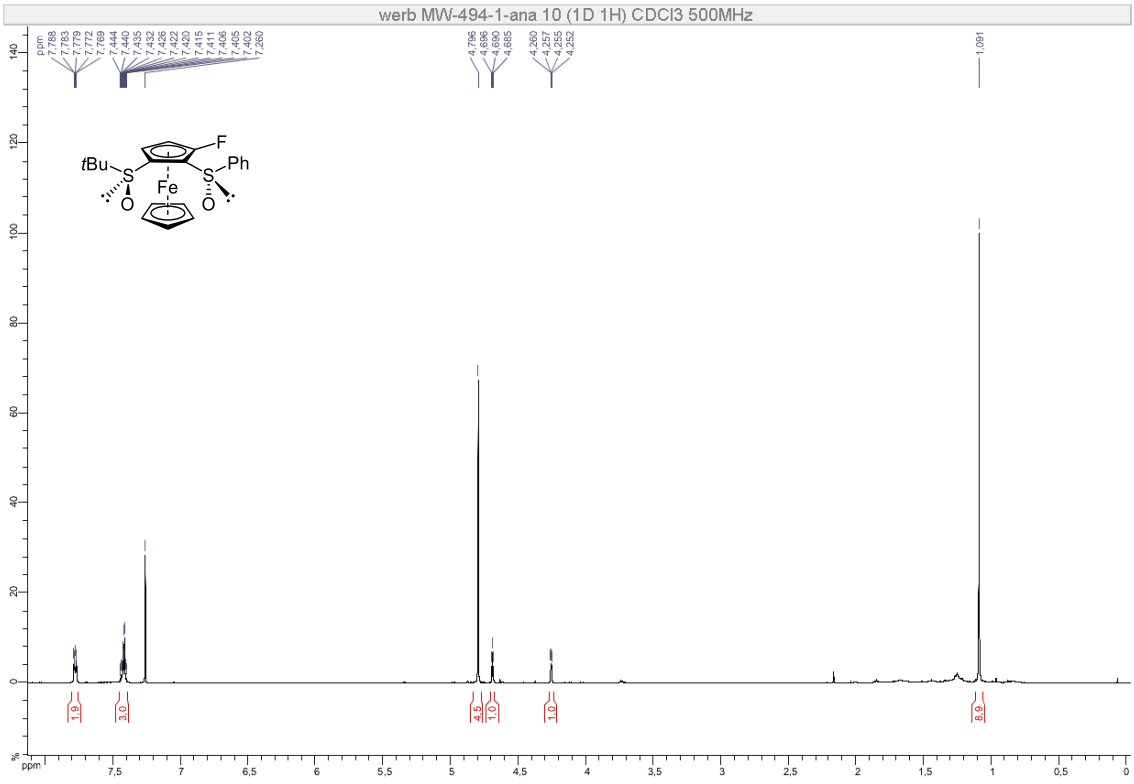


HMBC (500 MHz, $CDCl_3$)

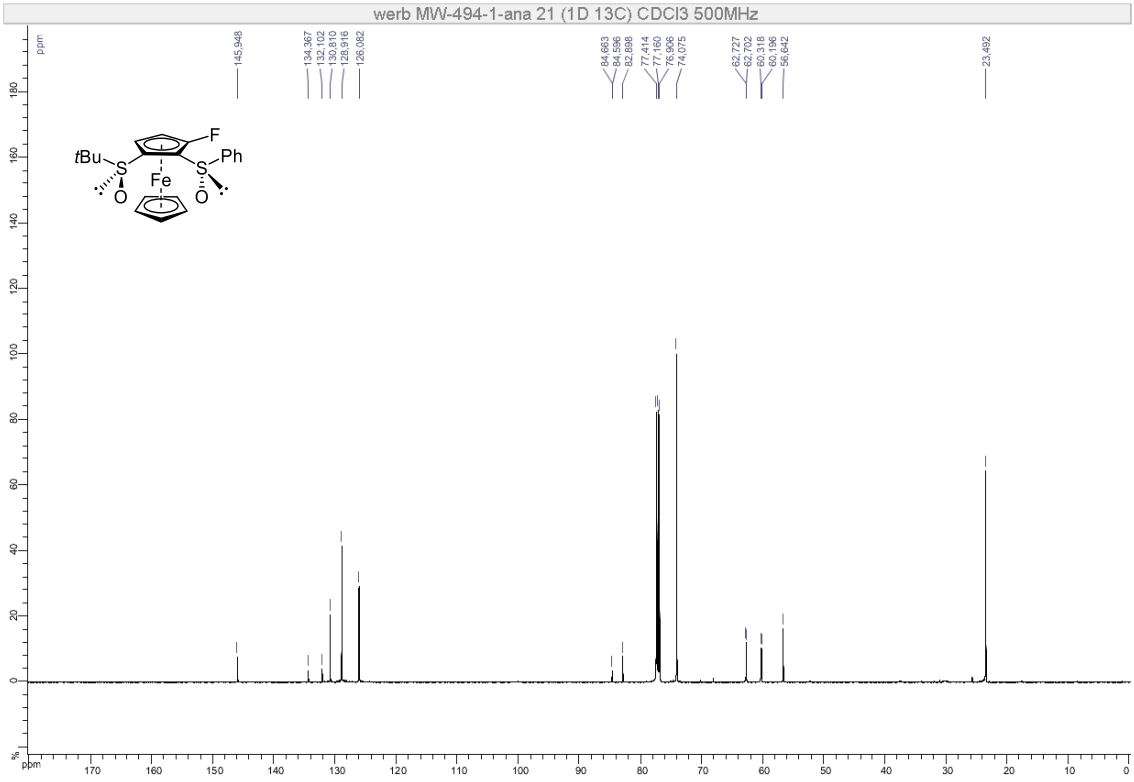


(*S*,*S*,*R*$_P$)-*S*-*tert*-Butyl-3-fluoro-*S'*-phenylferrocene-1,2-disulfoxide (*S*,*S*,*R*$_P$-7d)

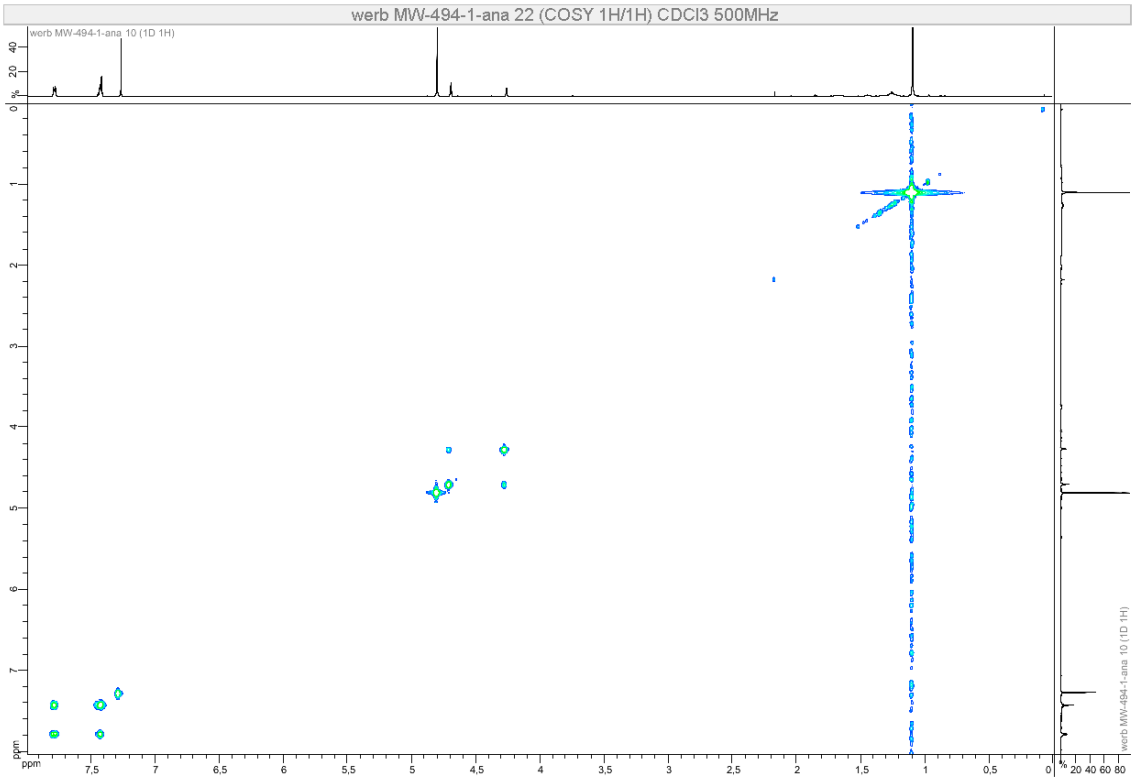
^{1}H NMR (500 MHz, $CDCl_3$)



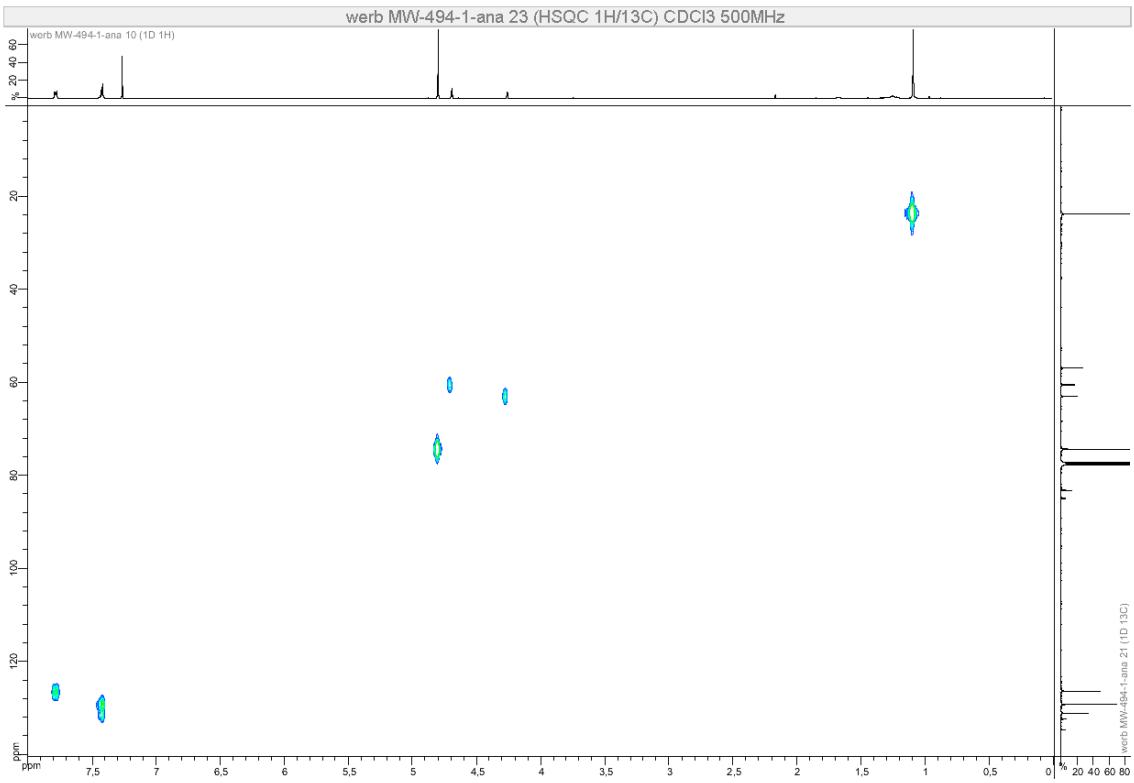
^{13}C NMR (126 MHz, $CDCl_3$)



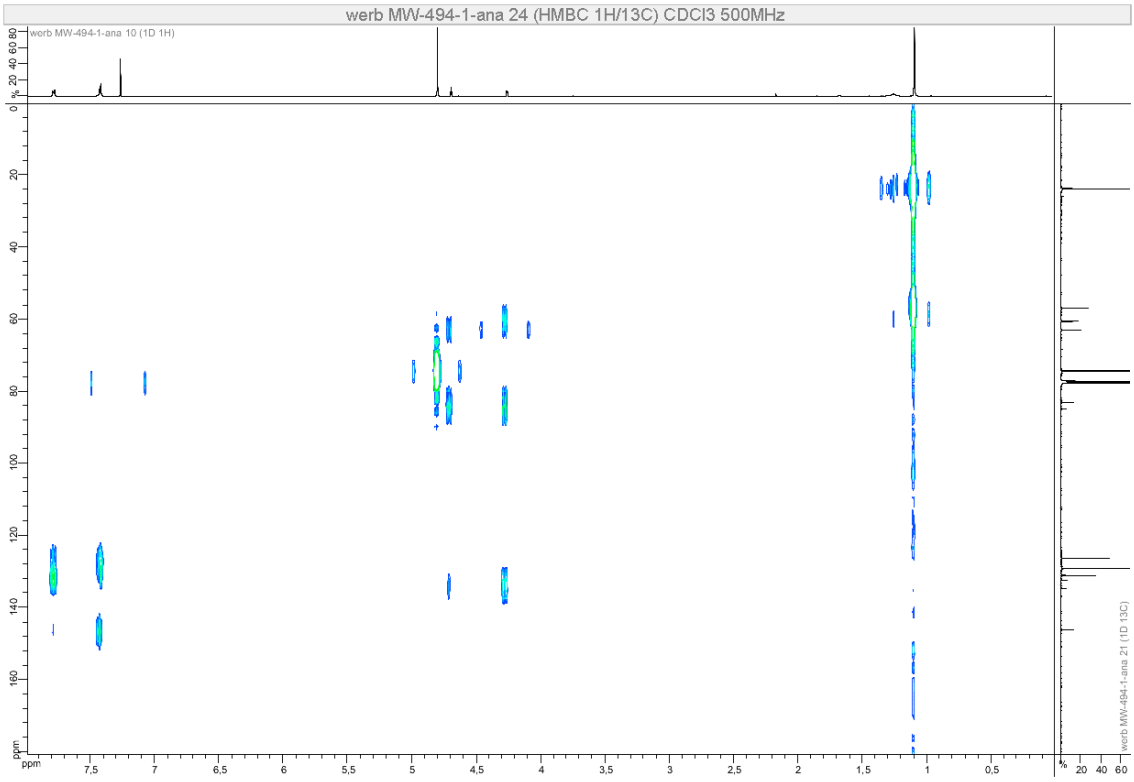
COSY (500 MHz, $CDCl_3$)



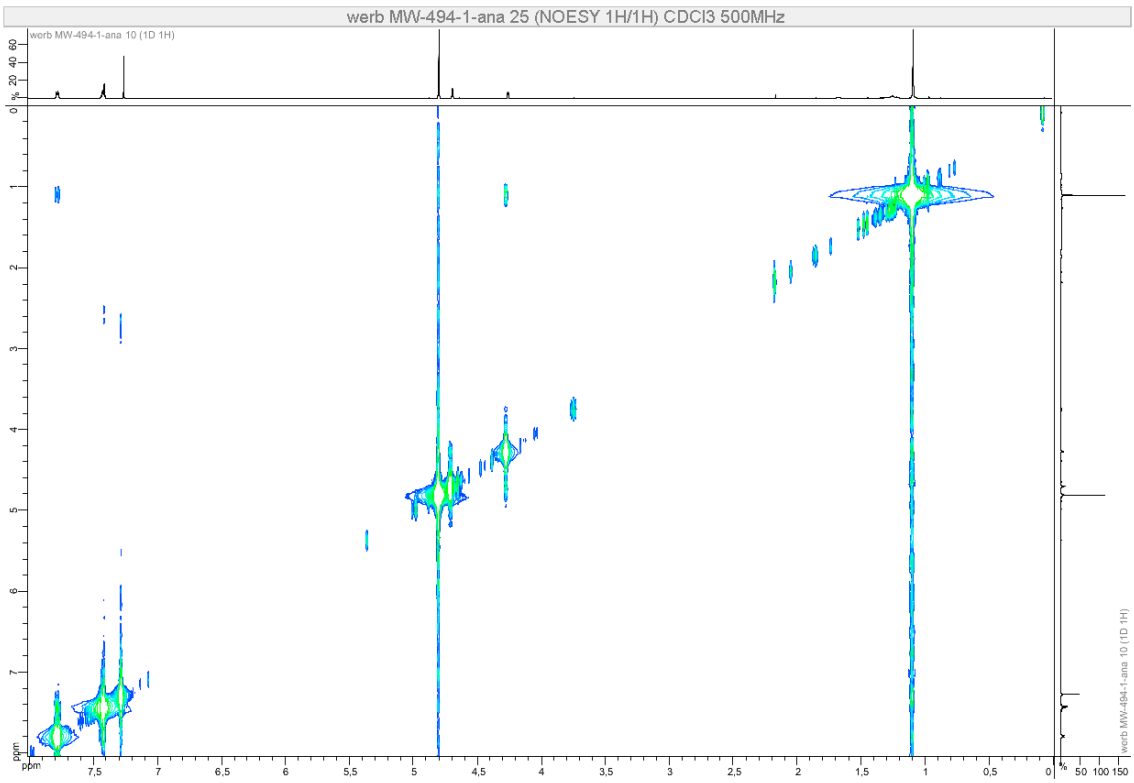
HSQC (500 MHz, $CDCl_3$)



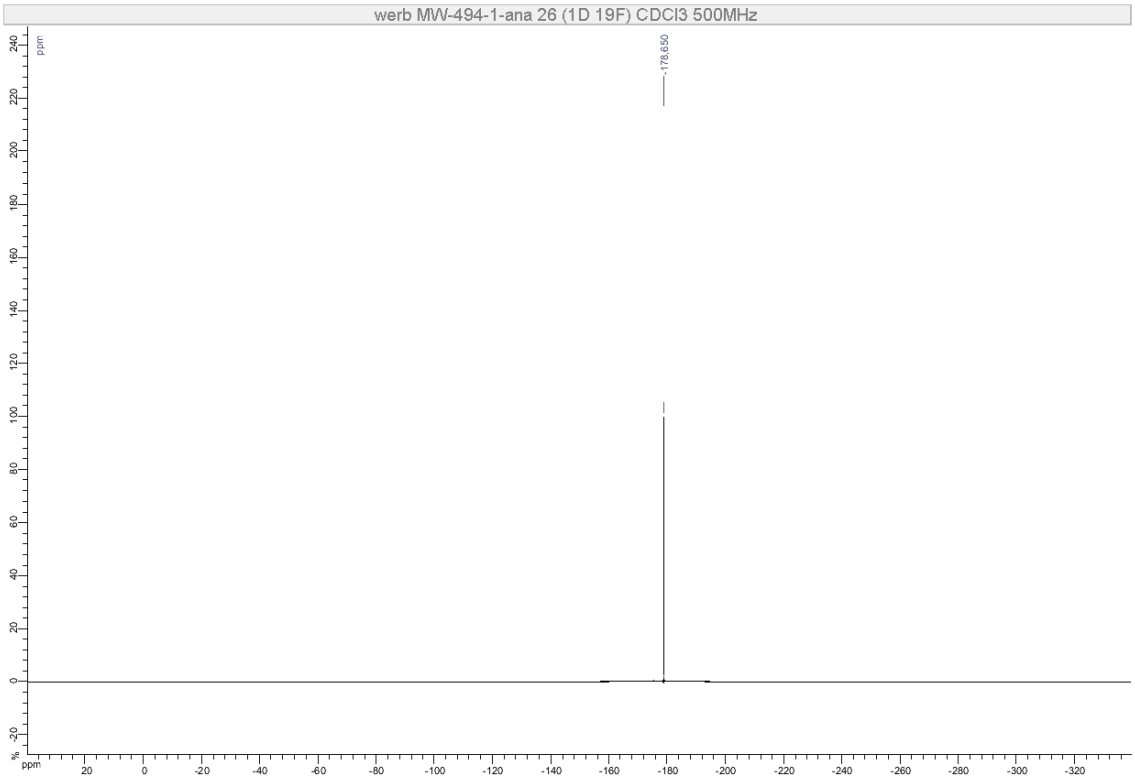
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

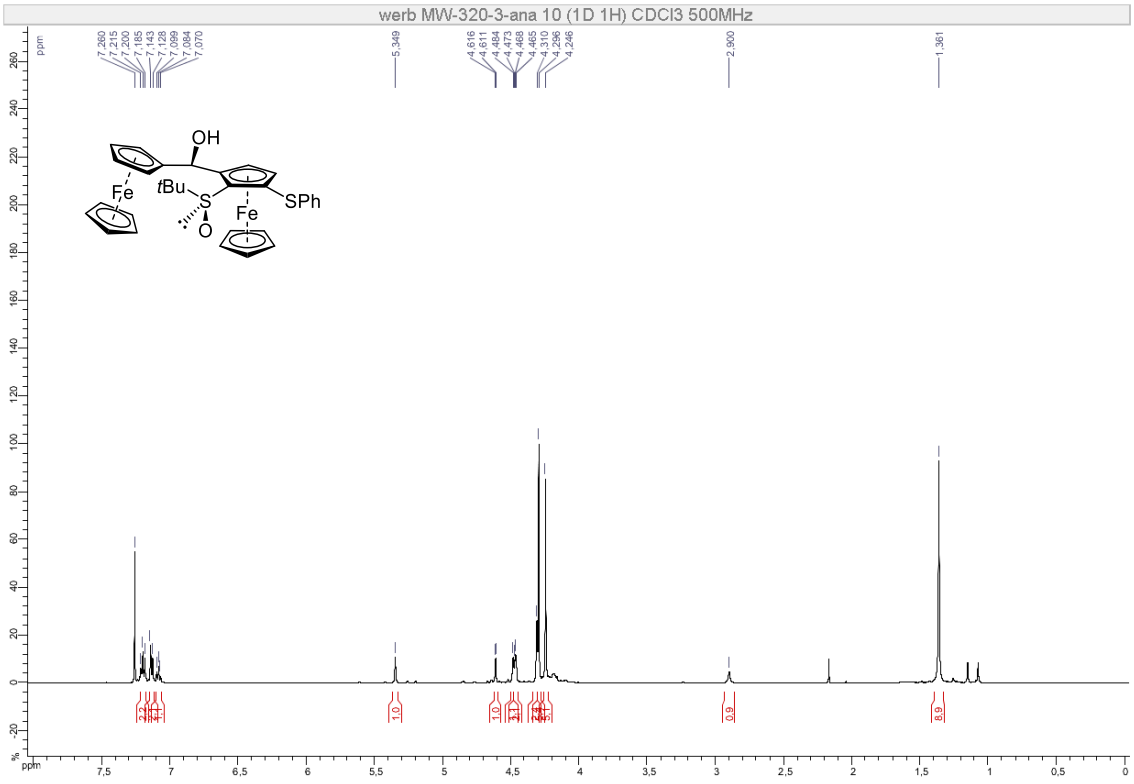


^{19}F NMR (471 MHz, $CDCl_3$)

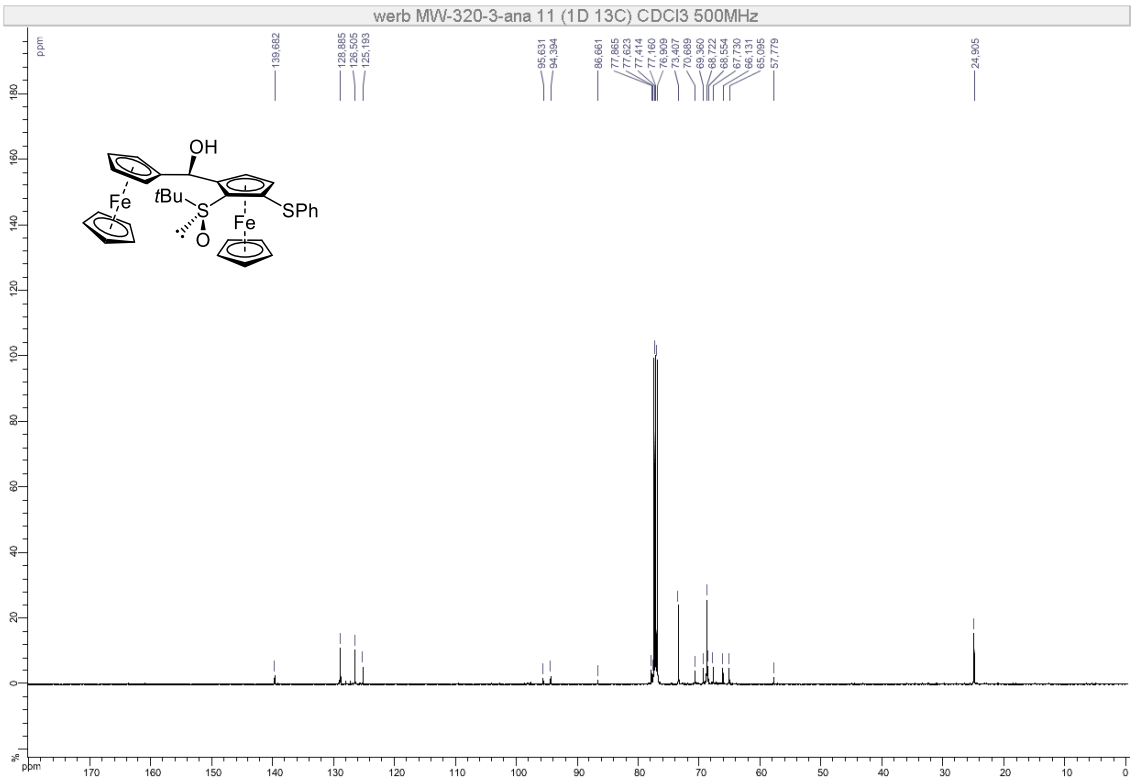


(R_C,S_S,S_P)-*S*-*tert*-Butyl-2-(1-(ferrocenyl)hydroxymethyl)-5-(phenylthio)ferrocenesulfoxide (S,S_P-8a)

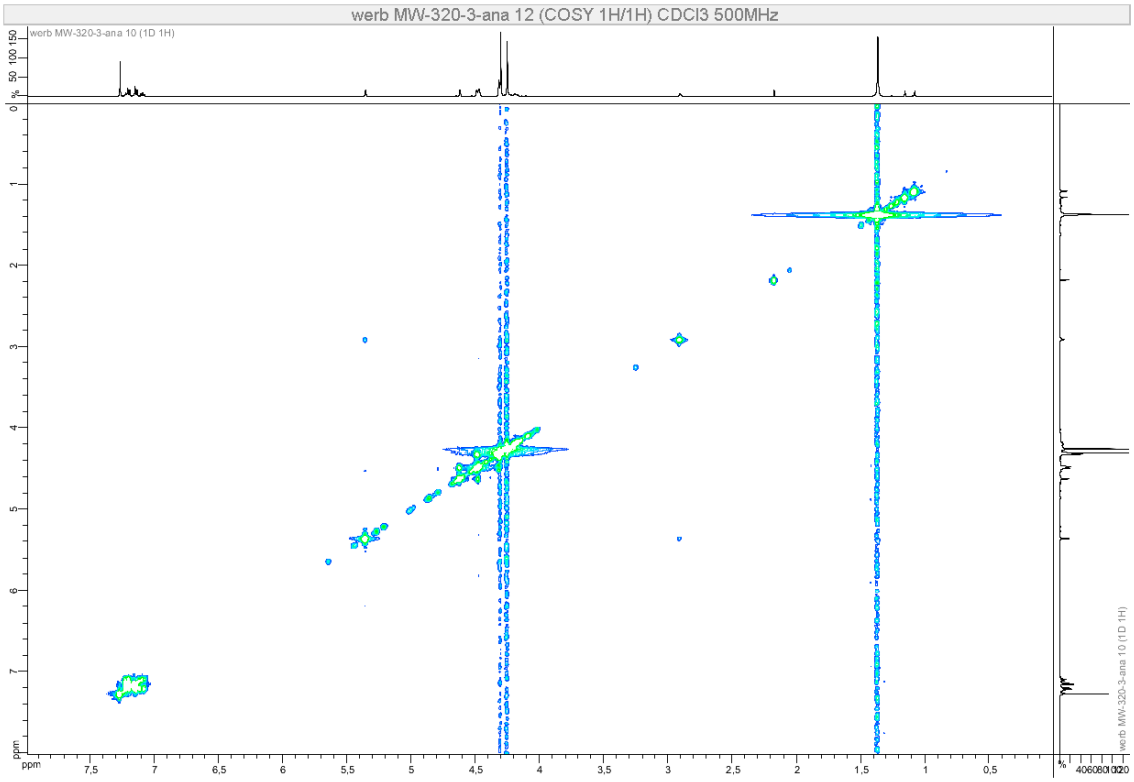
^{1}H NMR (500 MHz, $CDCl_3$)



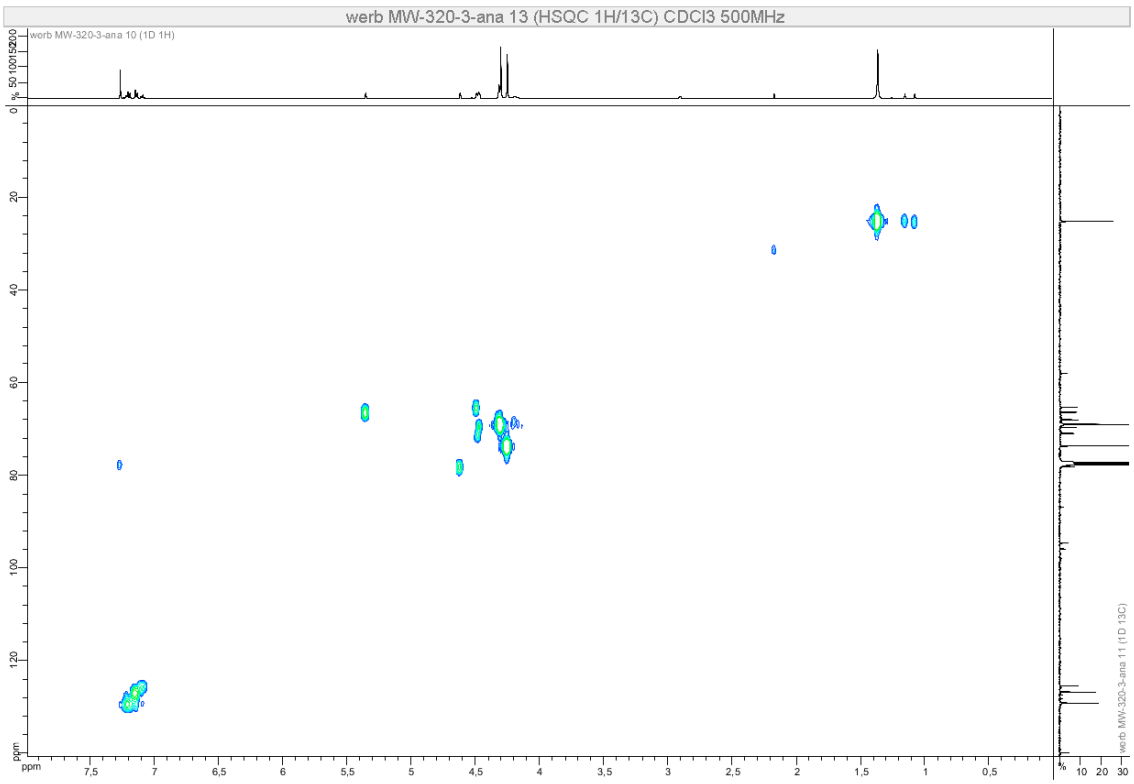
^{13}C NMR (126 MHz, $CDCl_3$)



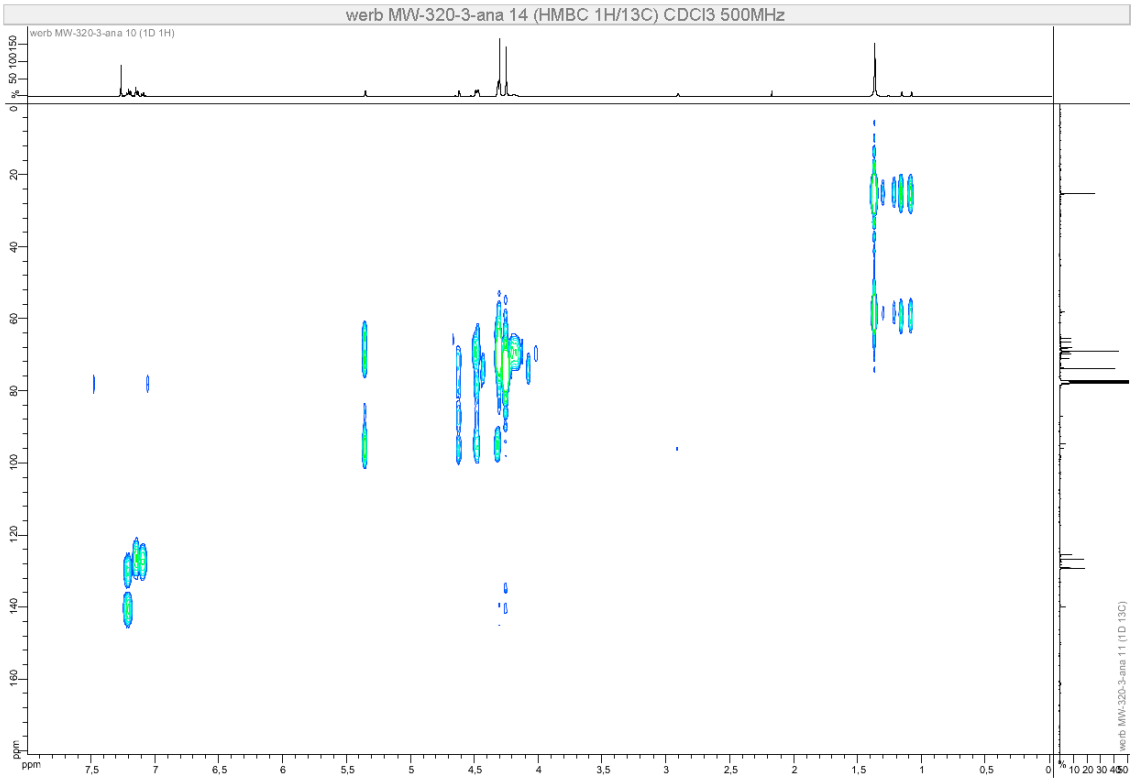
COSY (500 MHz, $CDCl_3$)



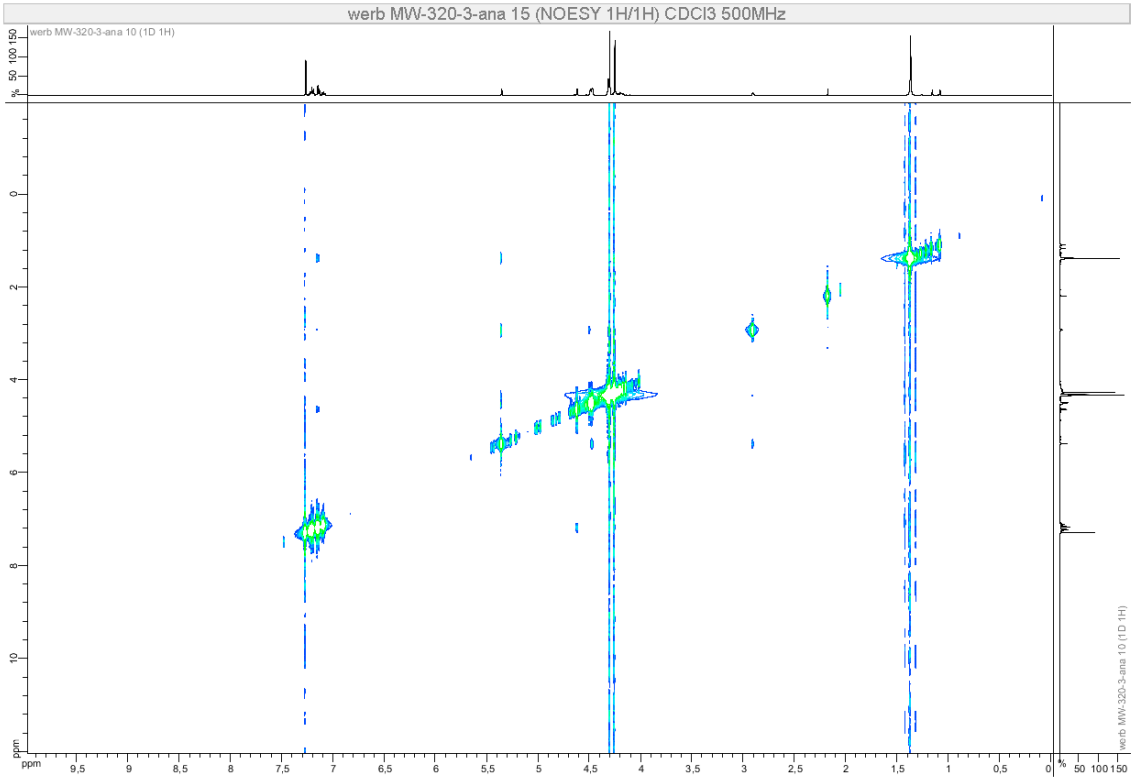
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

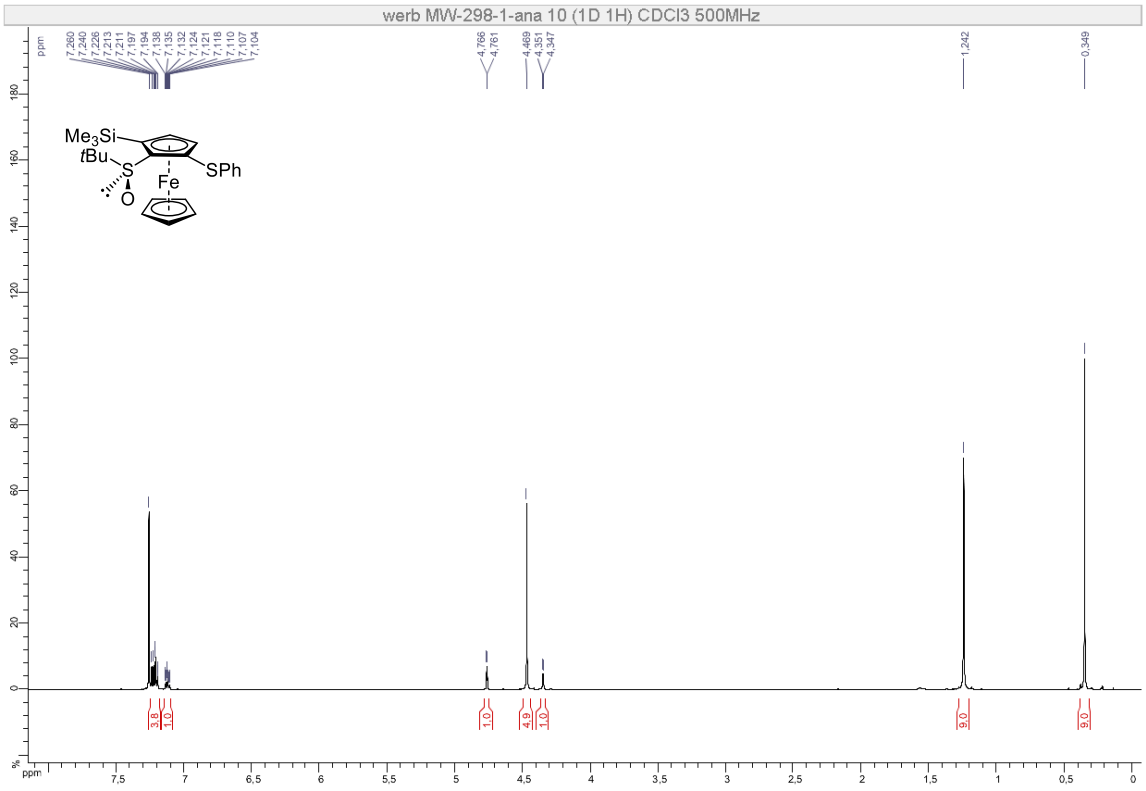


NOESY (500 MHz, $CDCl_3$)

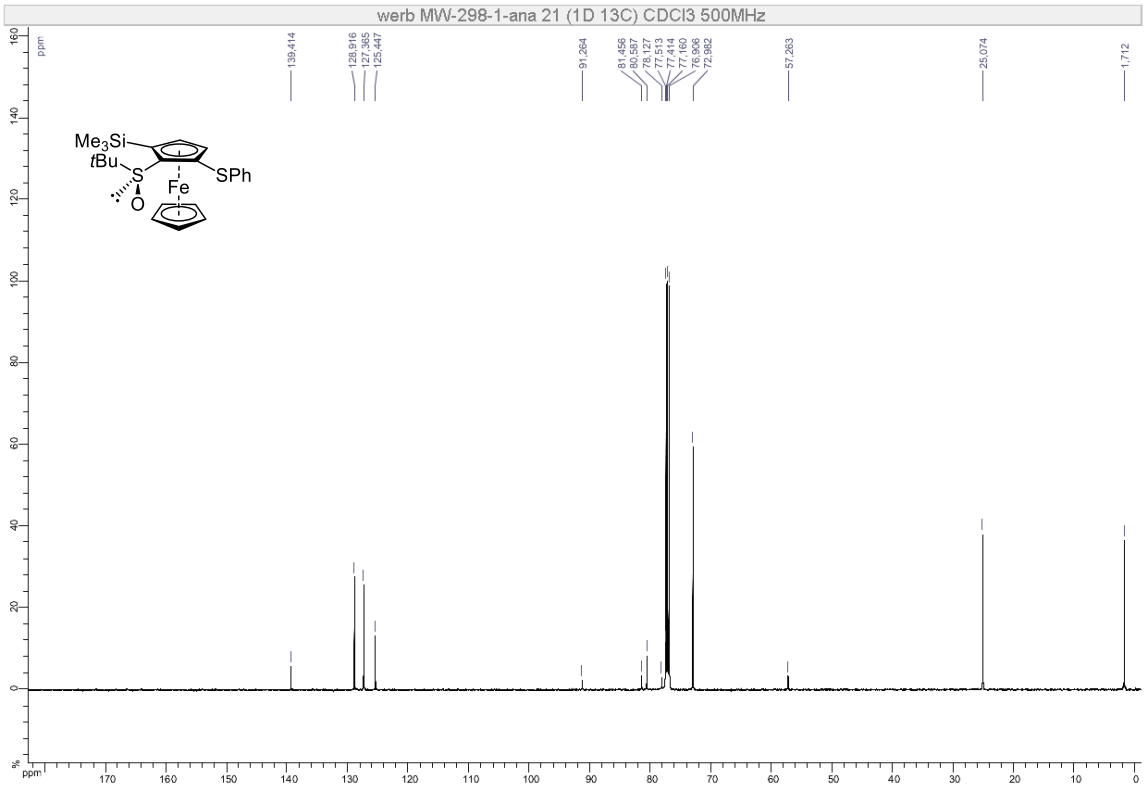


(*S*,*S*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)-5-(trimethylsilyl)ferrocenesulfoxide (*S*,*S*$_P$-8b)

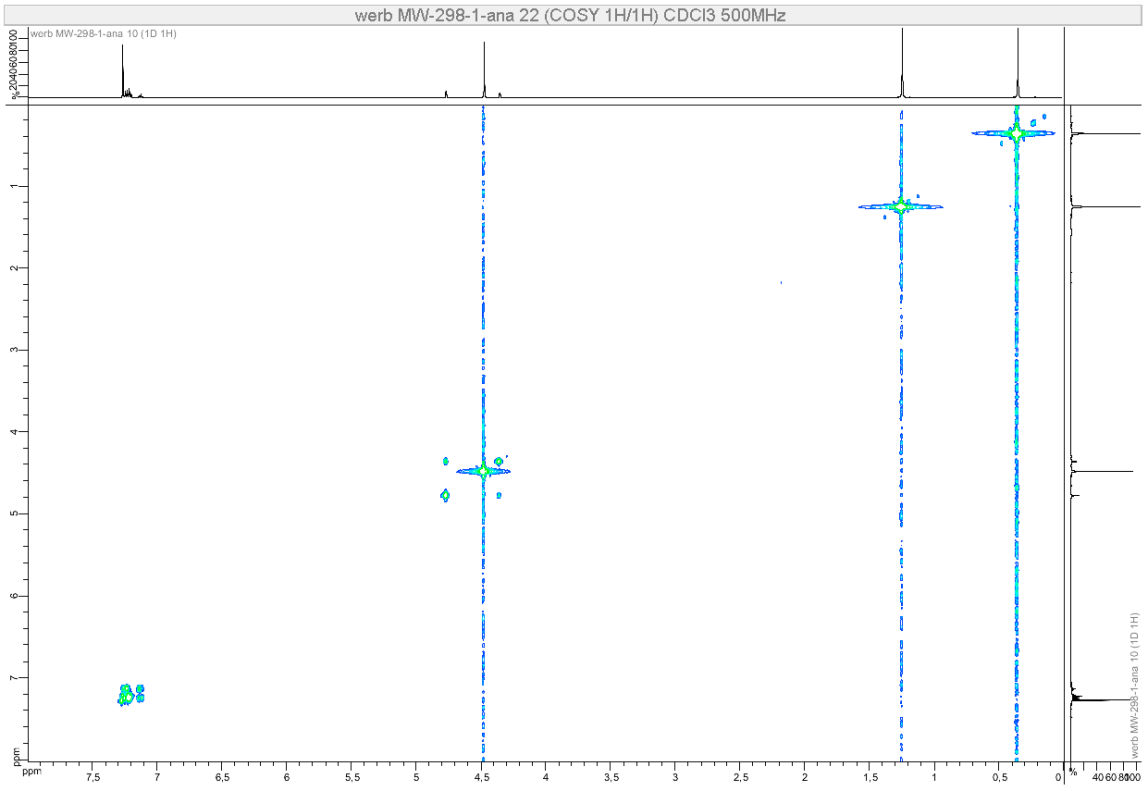
^{1}H NMR (500 MHz, $CDCl_3$)



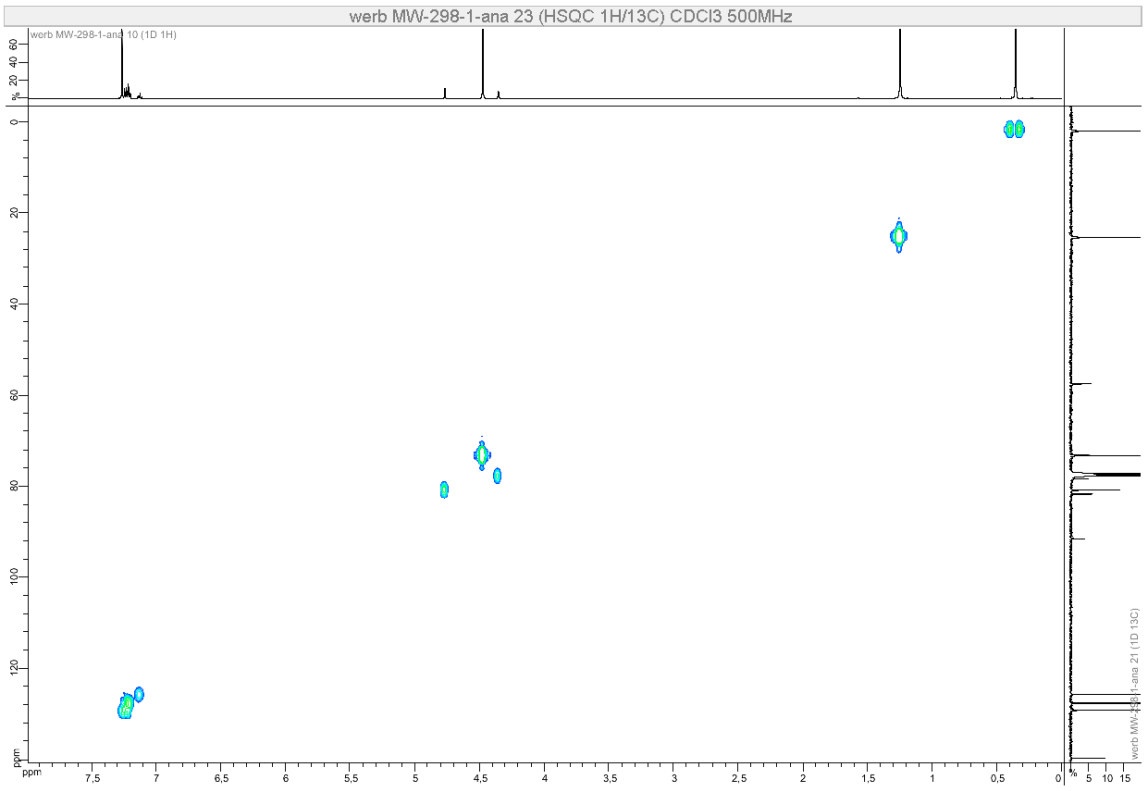
^{13}C NMR (126 MHz, $CDCl_3$)



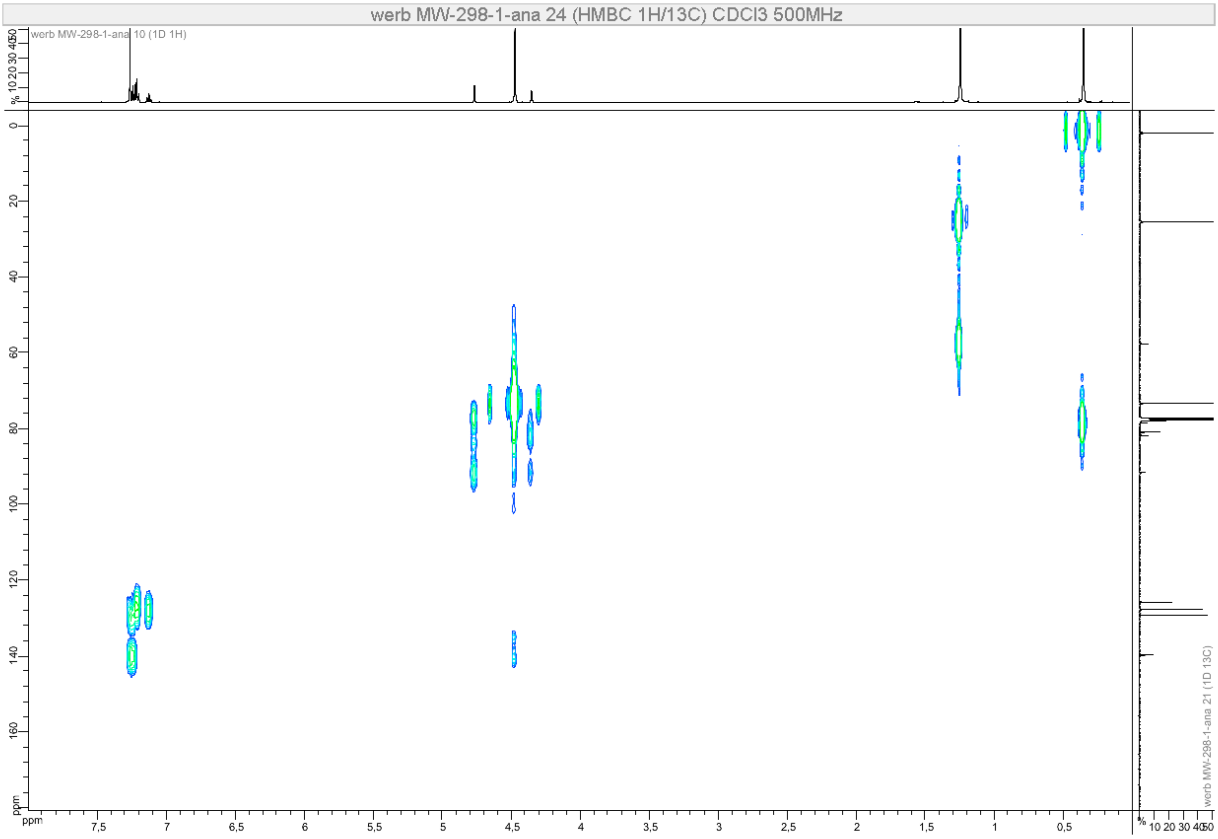
COSY (500 MHz, $CDCl_3$)



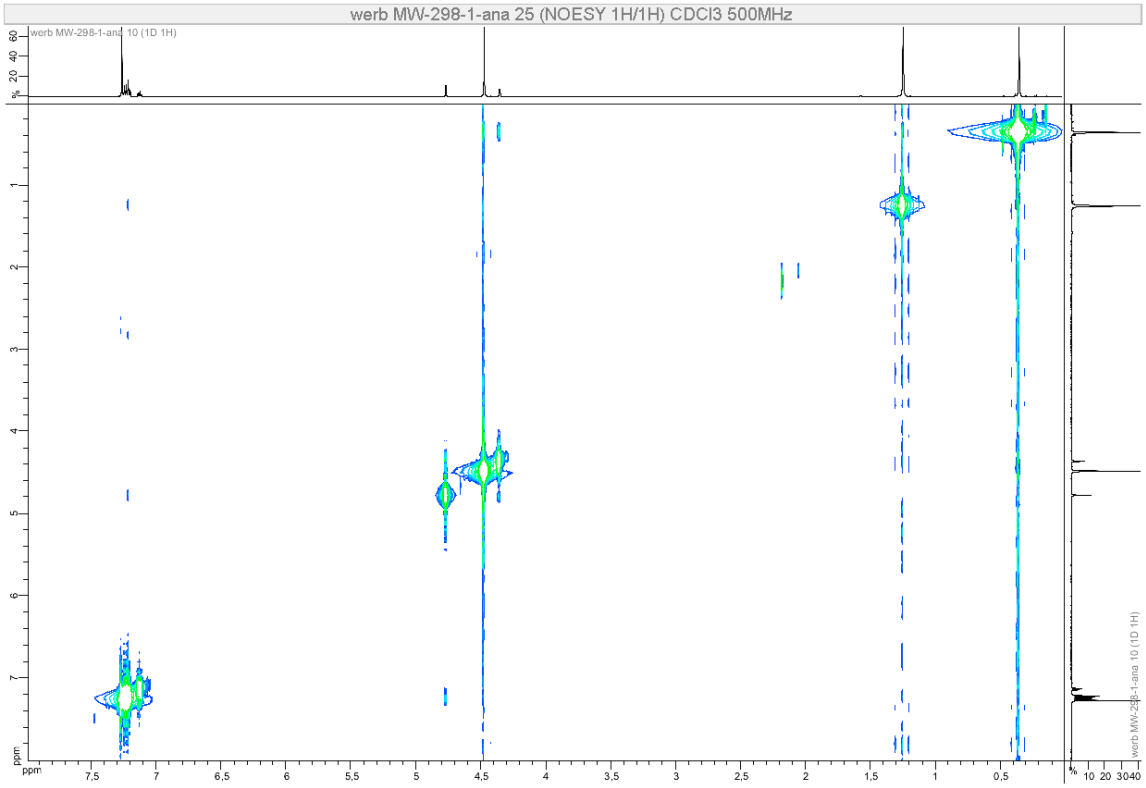
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

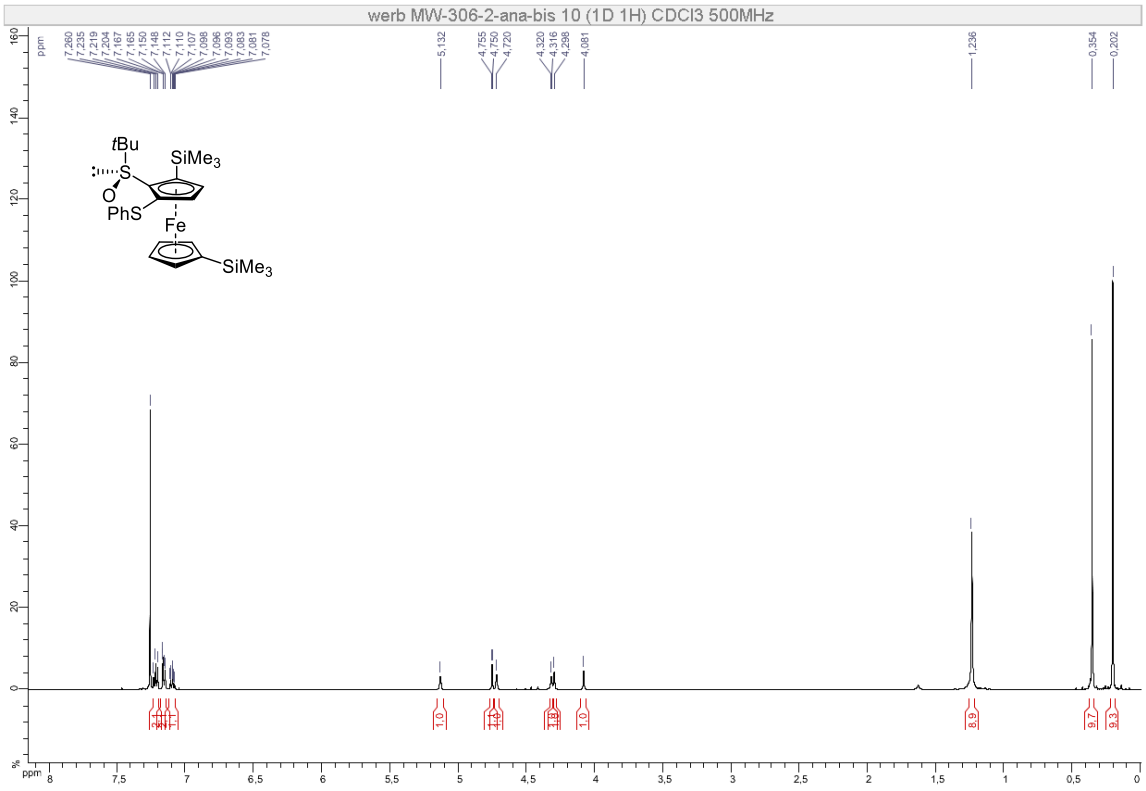


NOESY (500 MHz, $CDCl_3$)

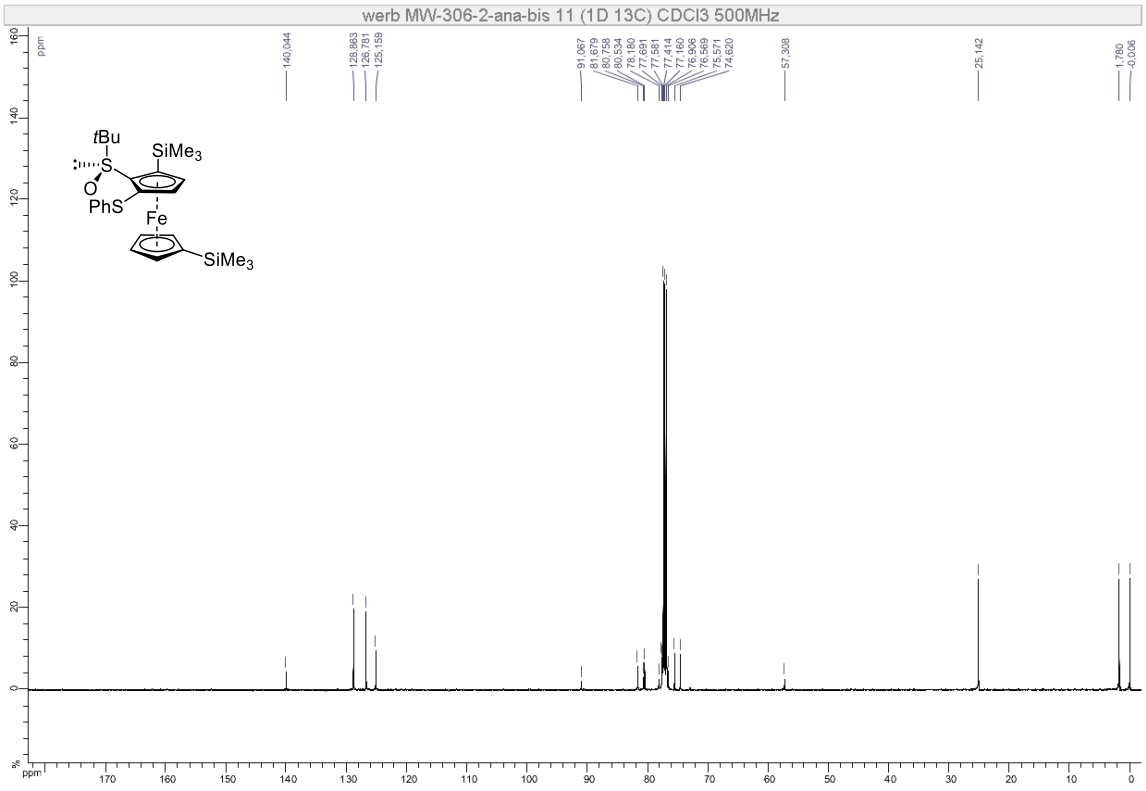


(*S*,*S*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)-5,1'-bis(trimethylsilyl)ferrocenesulfoxide (*S*,*S*$_P$-9a)

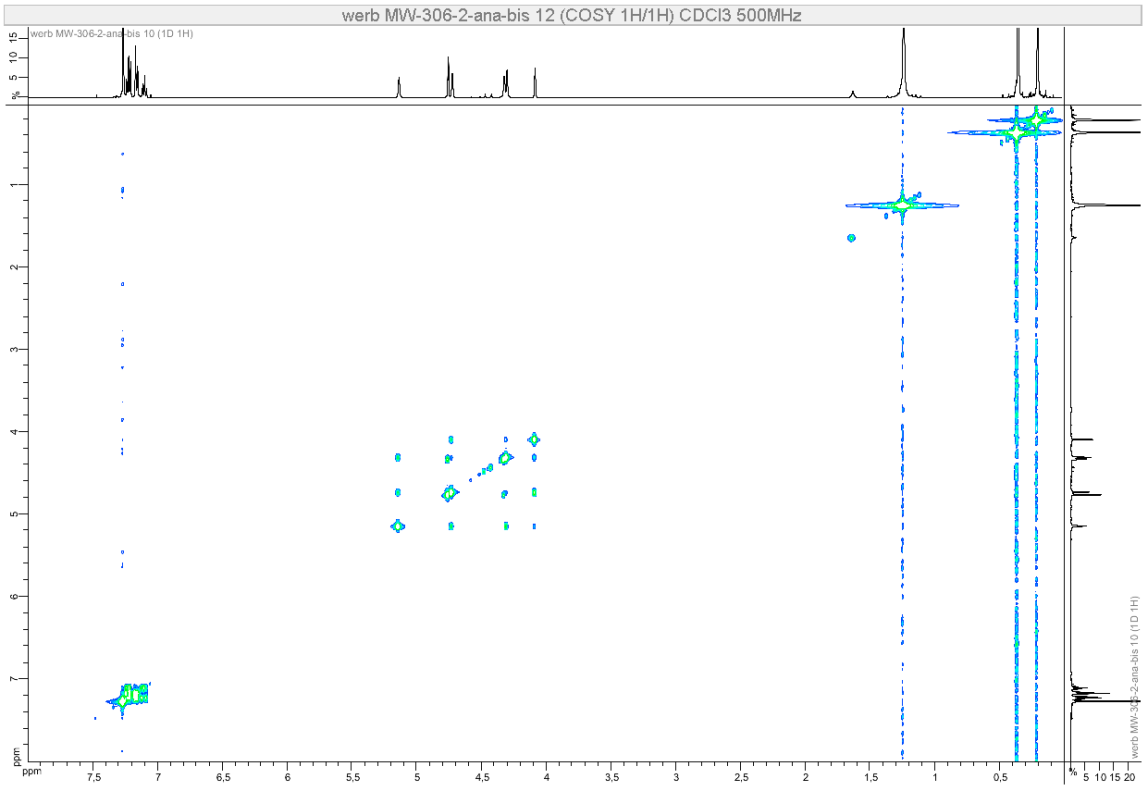
^{1}H NMR (500 MHz, $CDCl_3$)



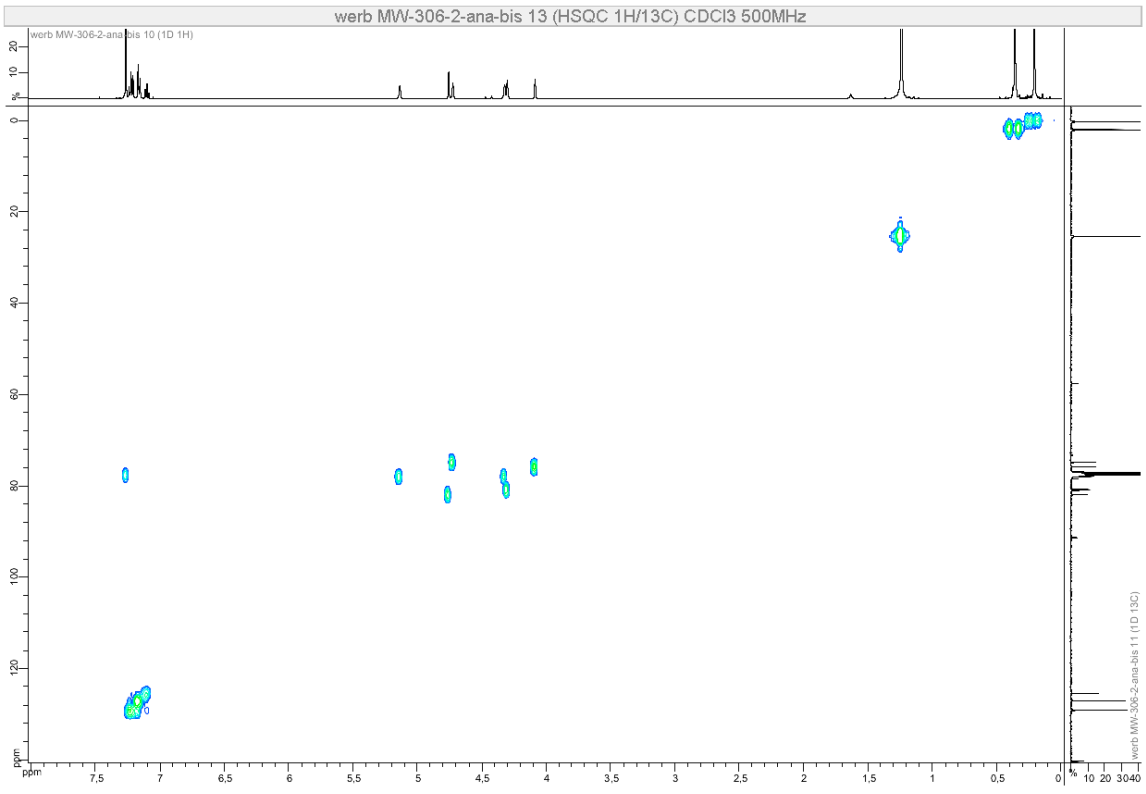
^{13}C NMR (126 MHz, $CDCl_3$)



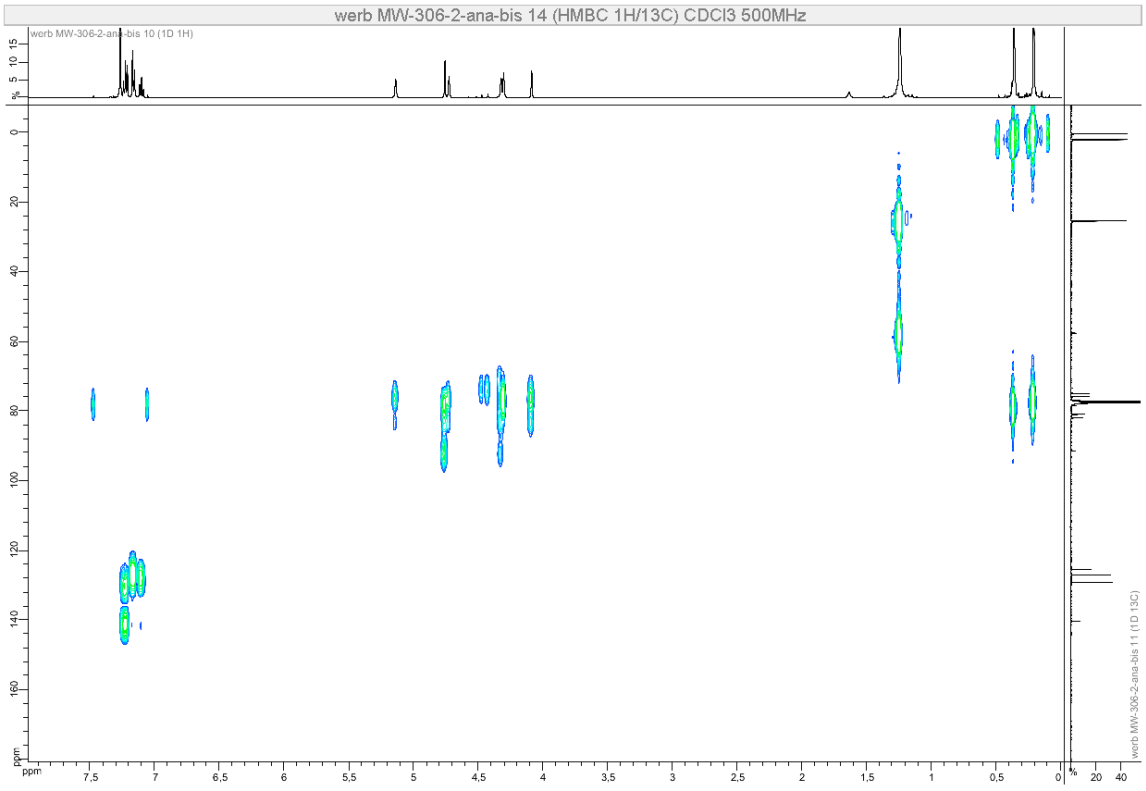
COSY (500 MHz, $CDCl_3$)



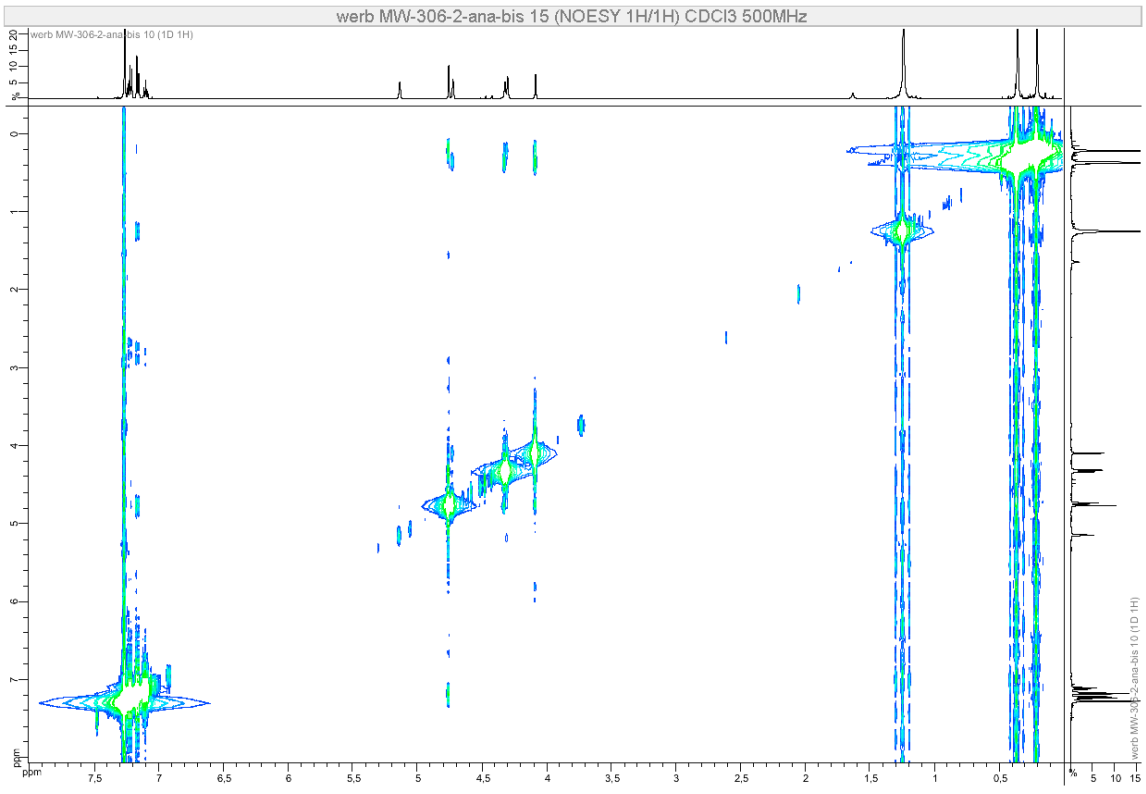
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

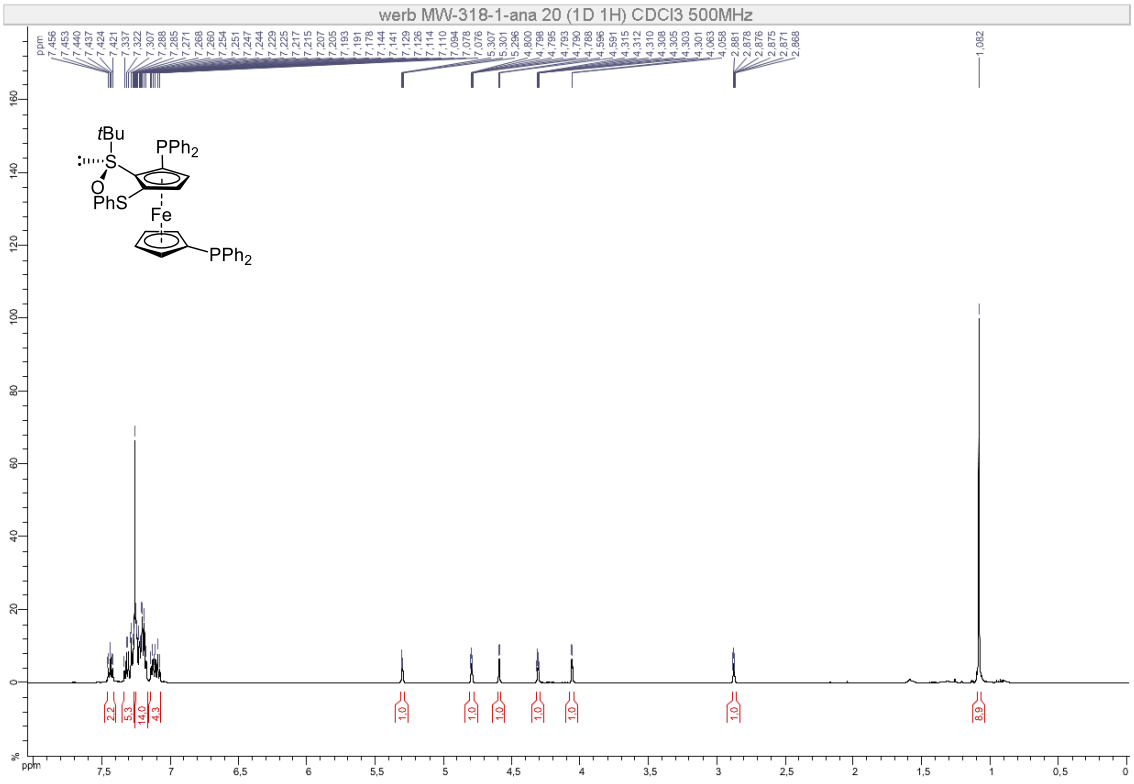


NOESY (500 MHz, $CDCl_3$)

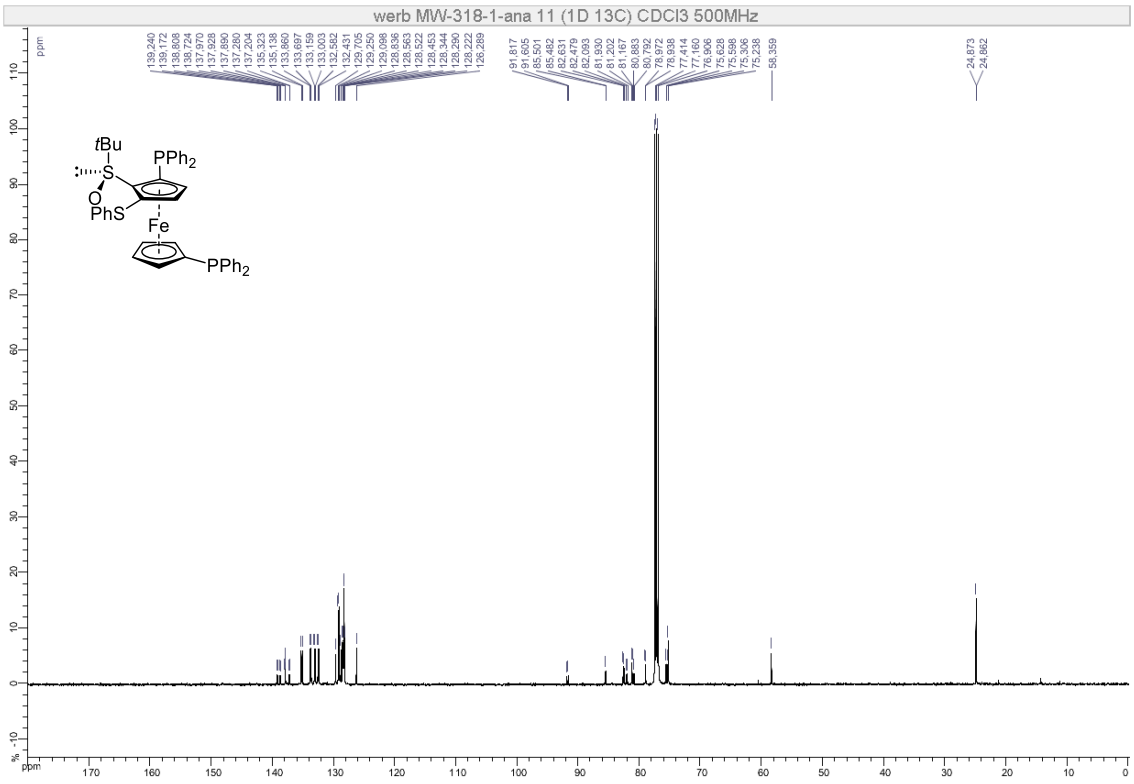


(*S*,*S*$_P$)-*S*-*tert*-Butyl-5,1'-bis(diphenylphosphino)-2-(phenylthio)ferrocenesulfoxide (*S*,*S*-9b)

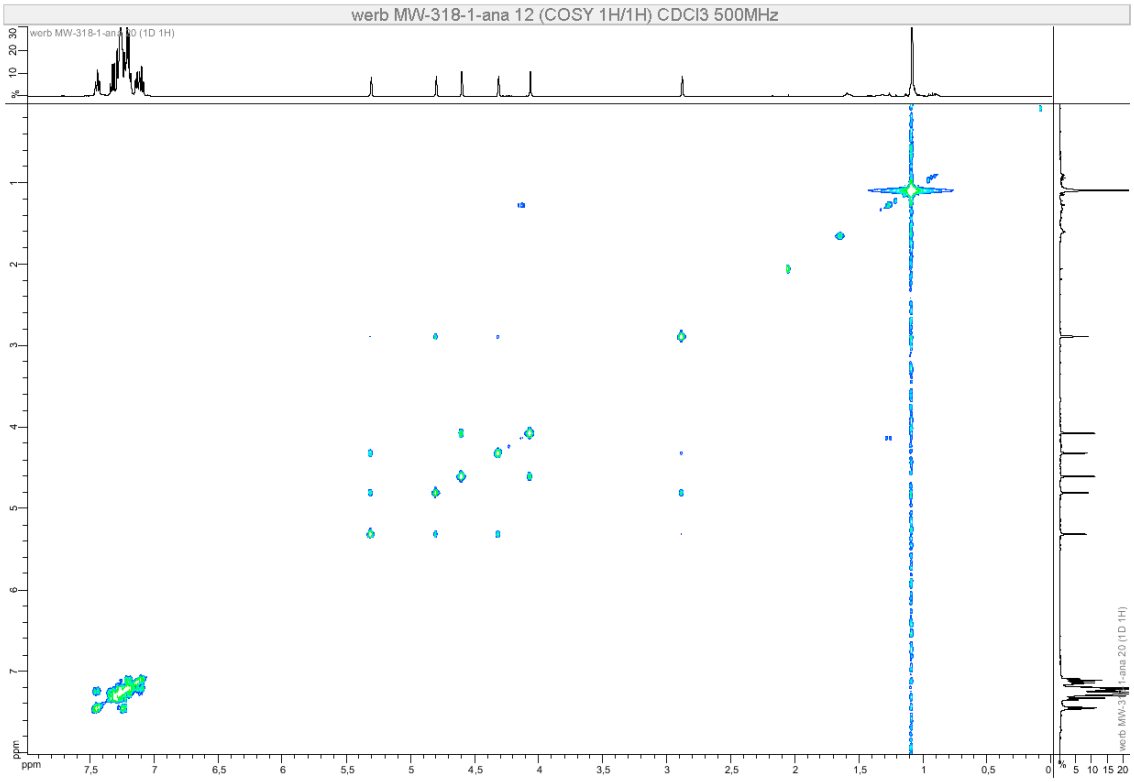
^{1}H NMR (500 MHz, $CDCl_3$)



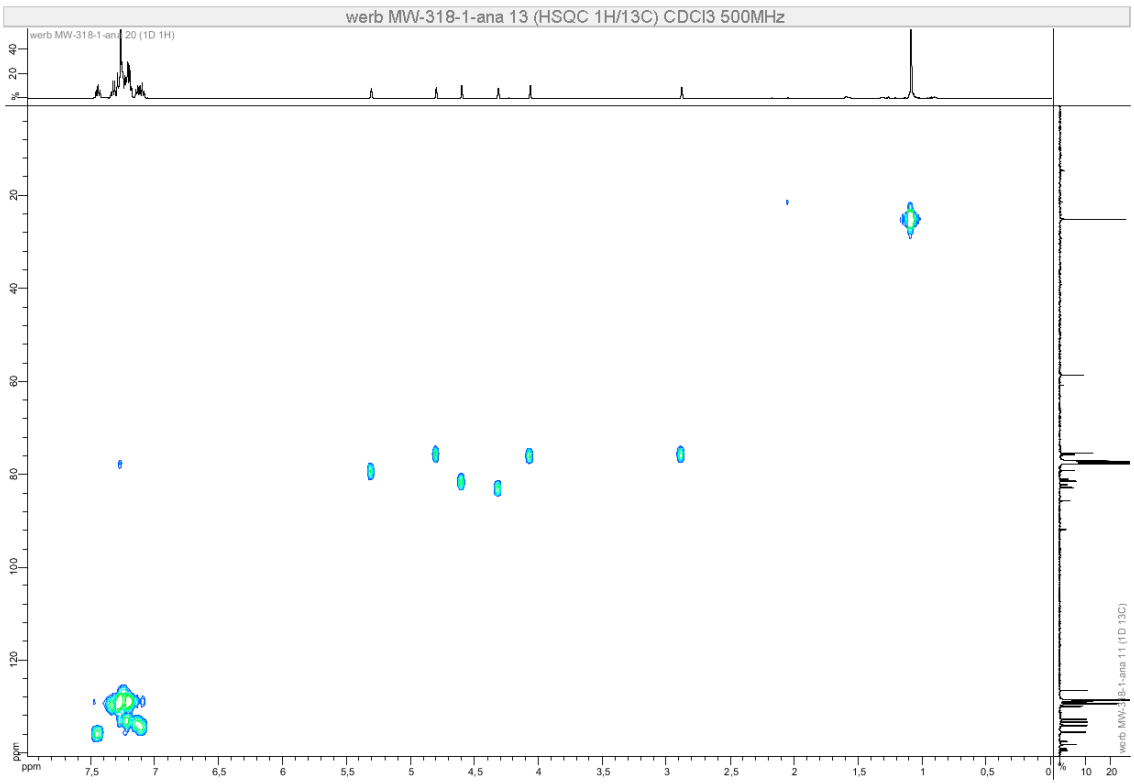
^{13}C NMR (126 MHz, $CDCl_3$)



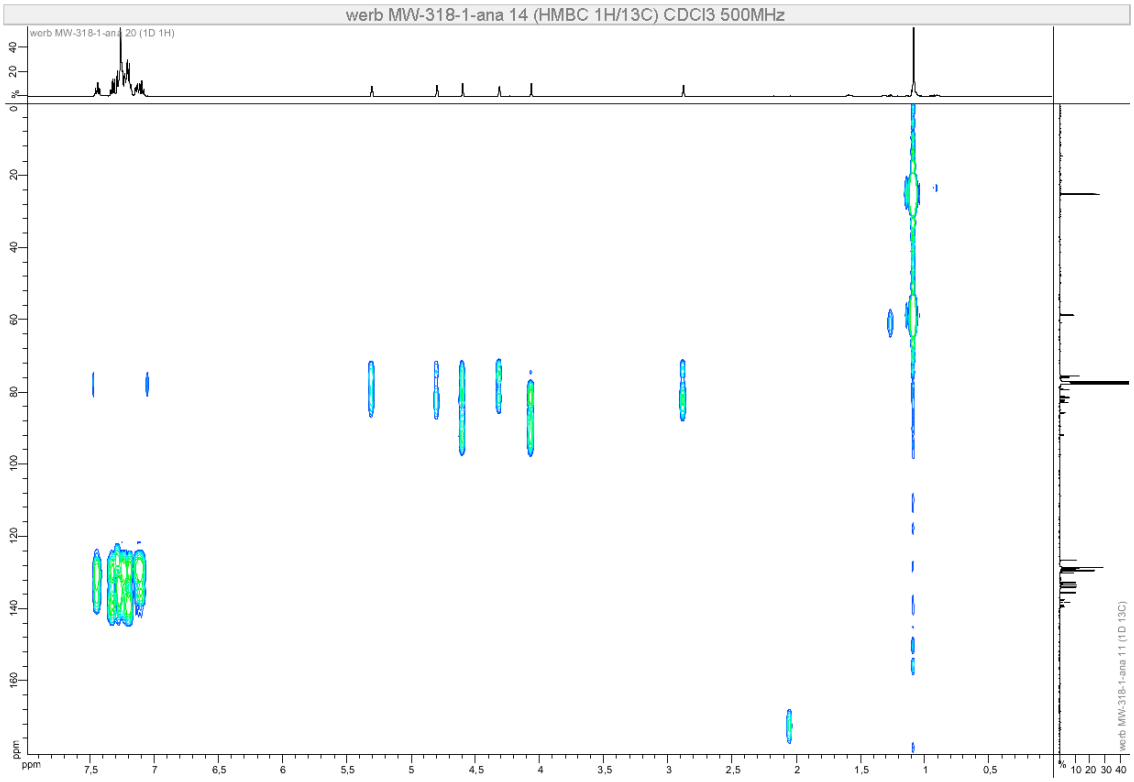
COSY (500 MHz, $CDCl_3$)



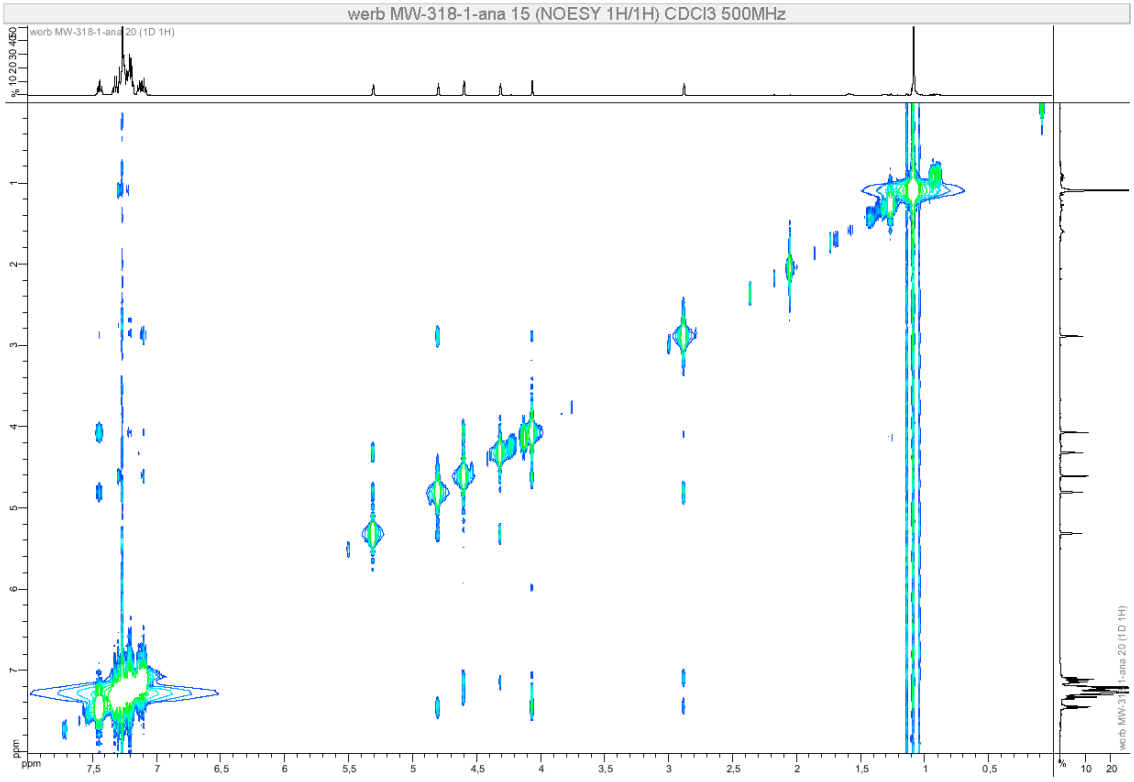
HSQC (500 MHz, $CDCl_3$)



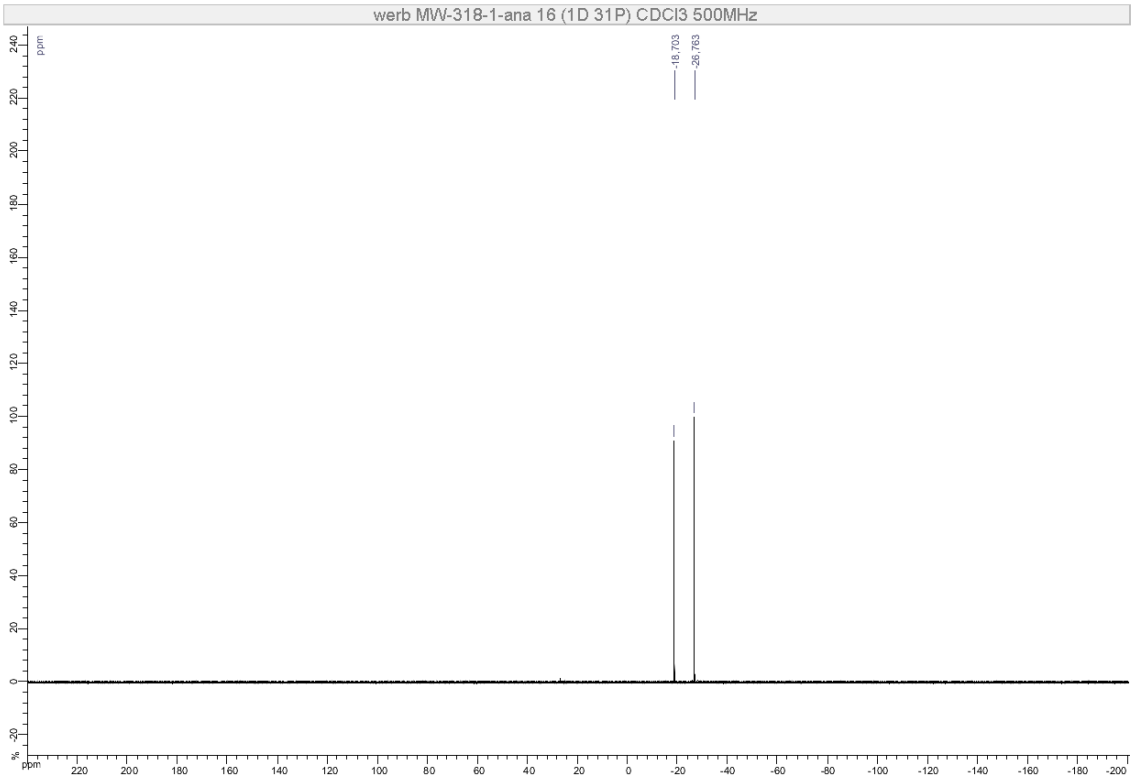
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

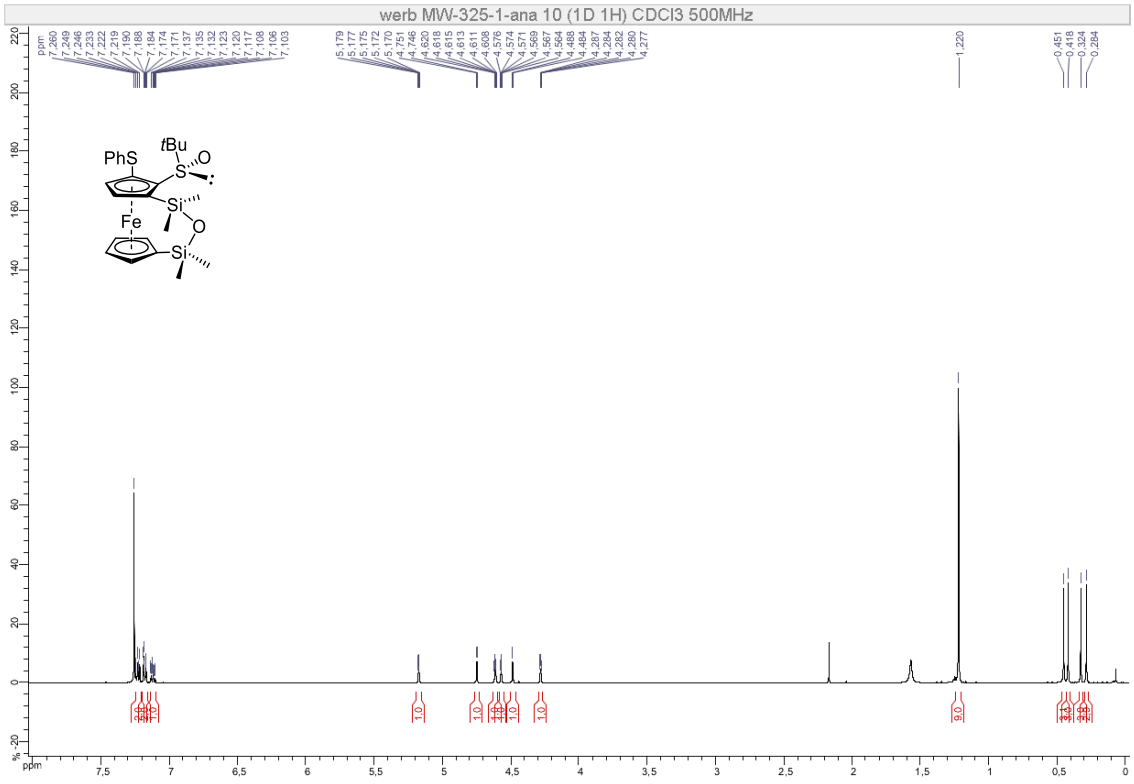


^{31}P NMR (202 MHz, $CDCl_3$)

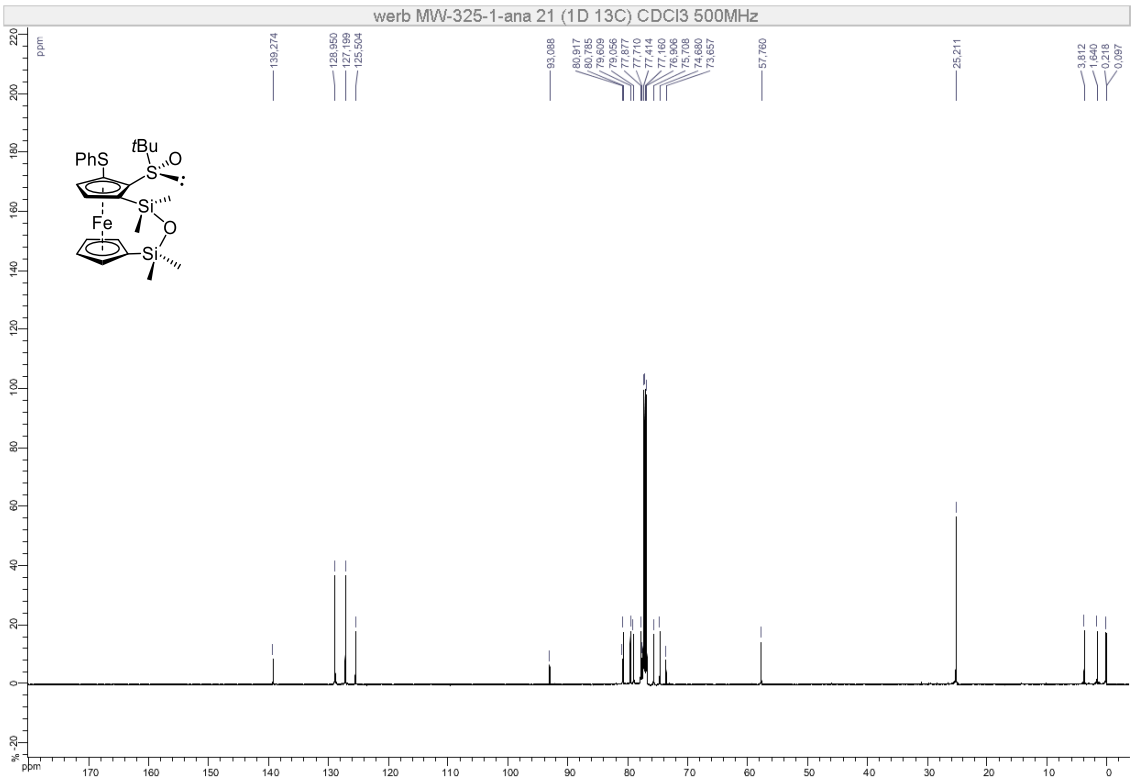


(*S*,*S*$_P$)-*S*-*tert*-Butyl-2-(phenylthio)-5,1'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)ferrocenesulfoxide (*S*,*S*$_P$-9c)

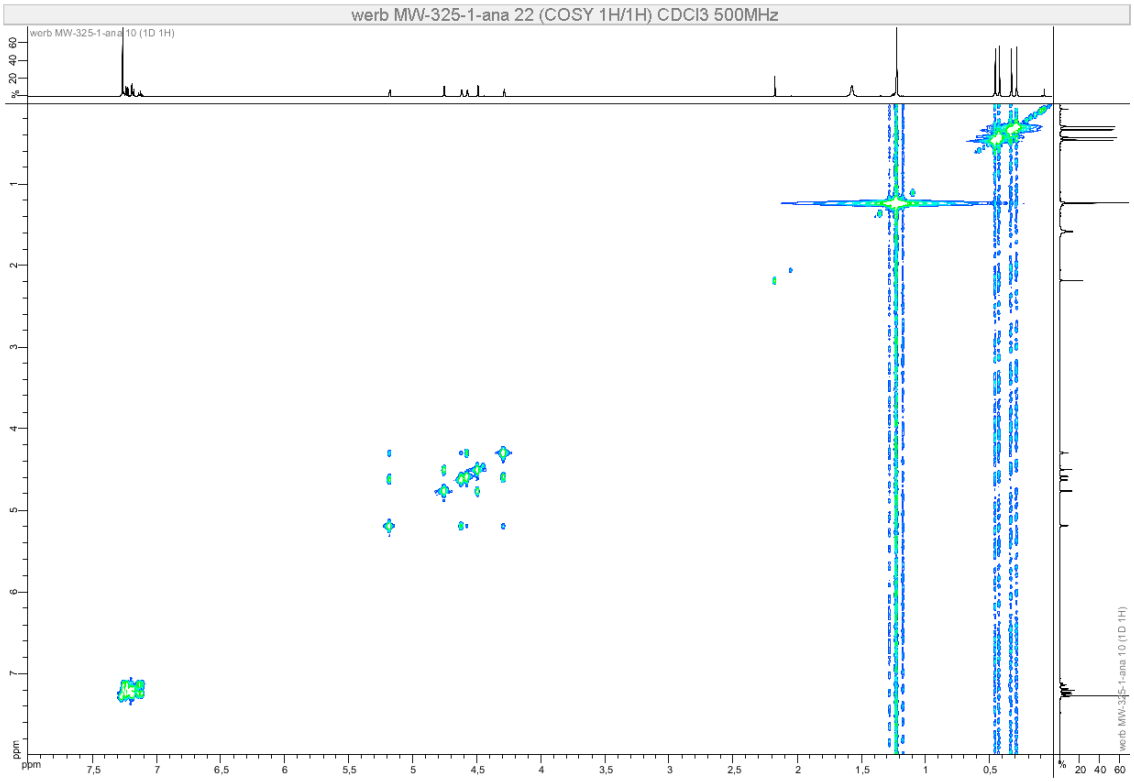
^{1}H NMR (500 MHz, $CDCl_3$)



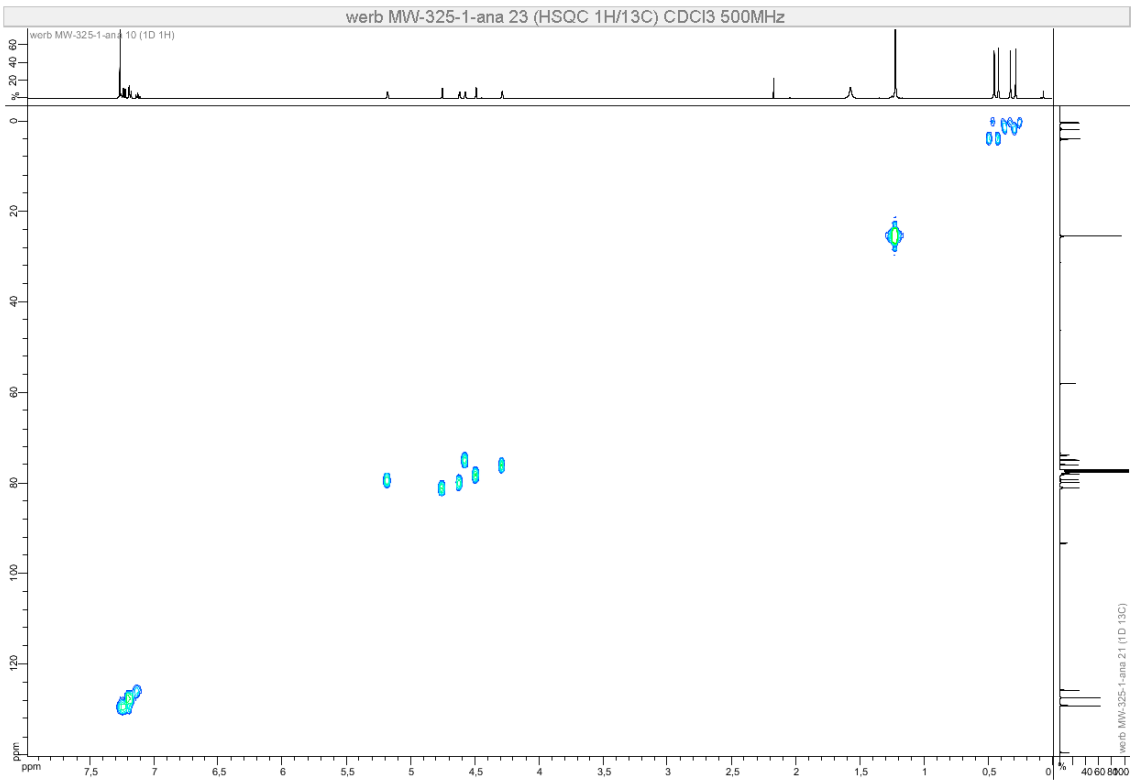
^{13}C NMR (126 MHz, $CDCl_3$)



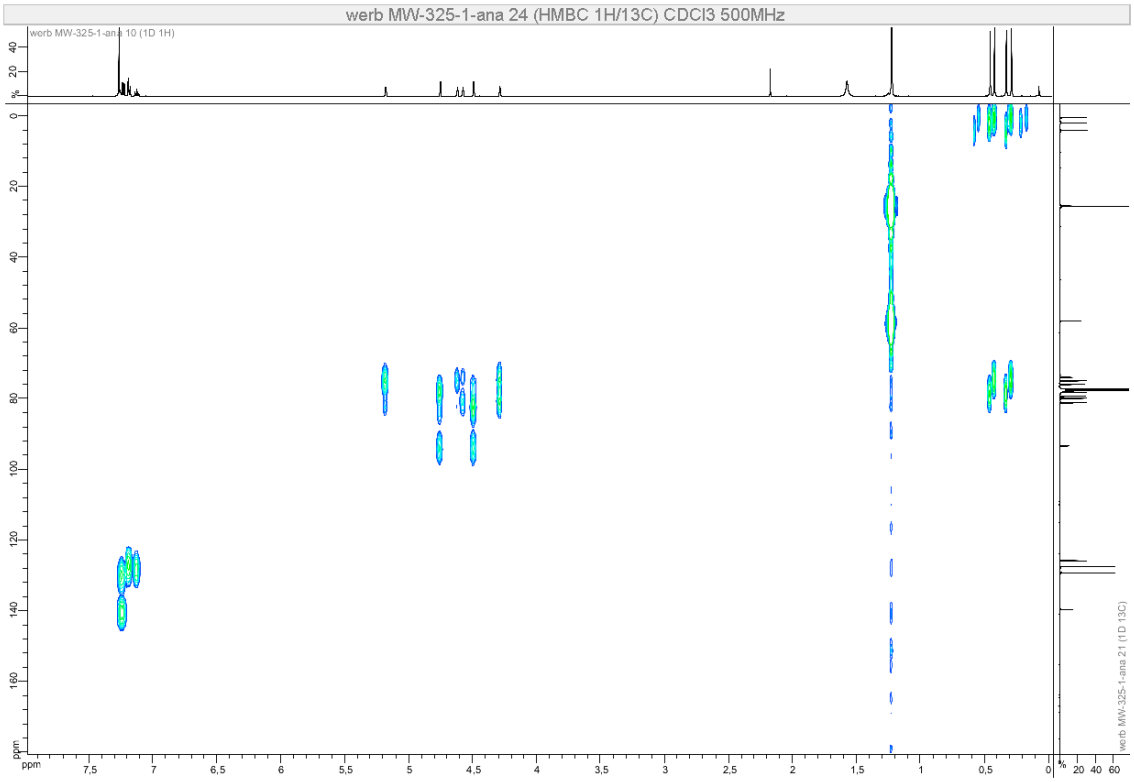
COSY (500 MHz, $CDCl_3$)



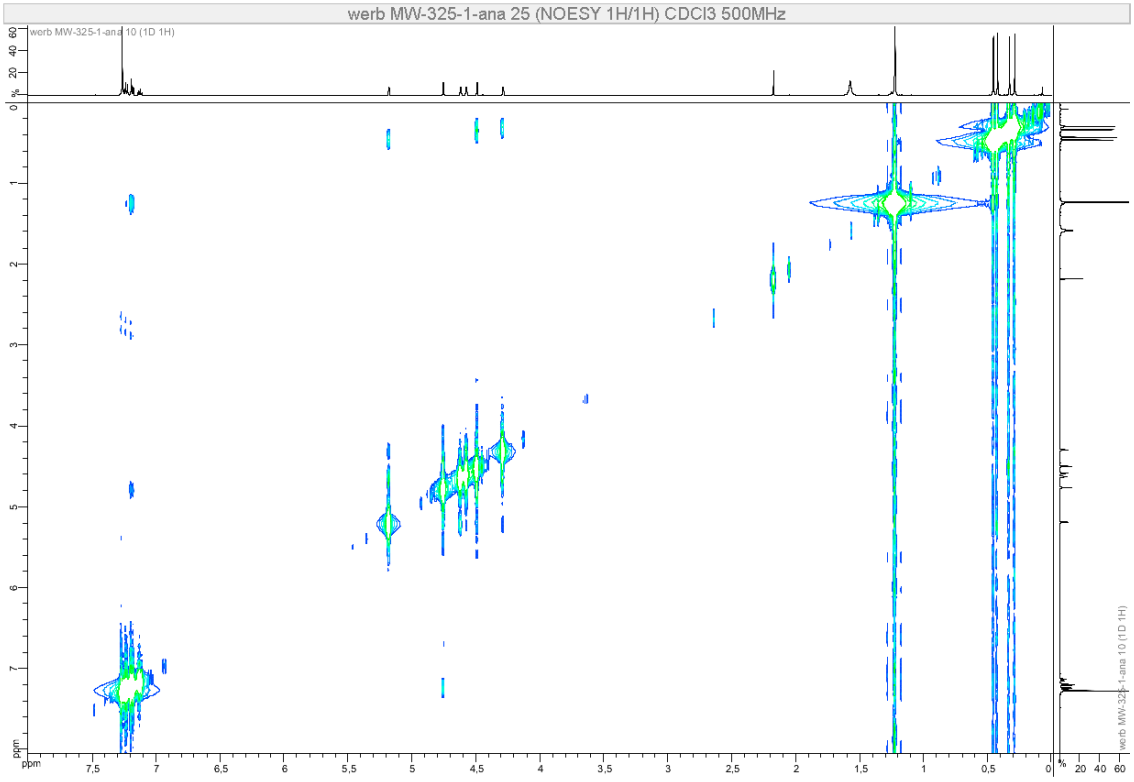
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

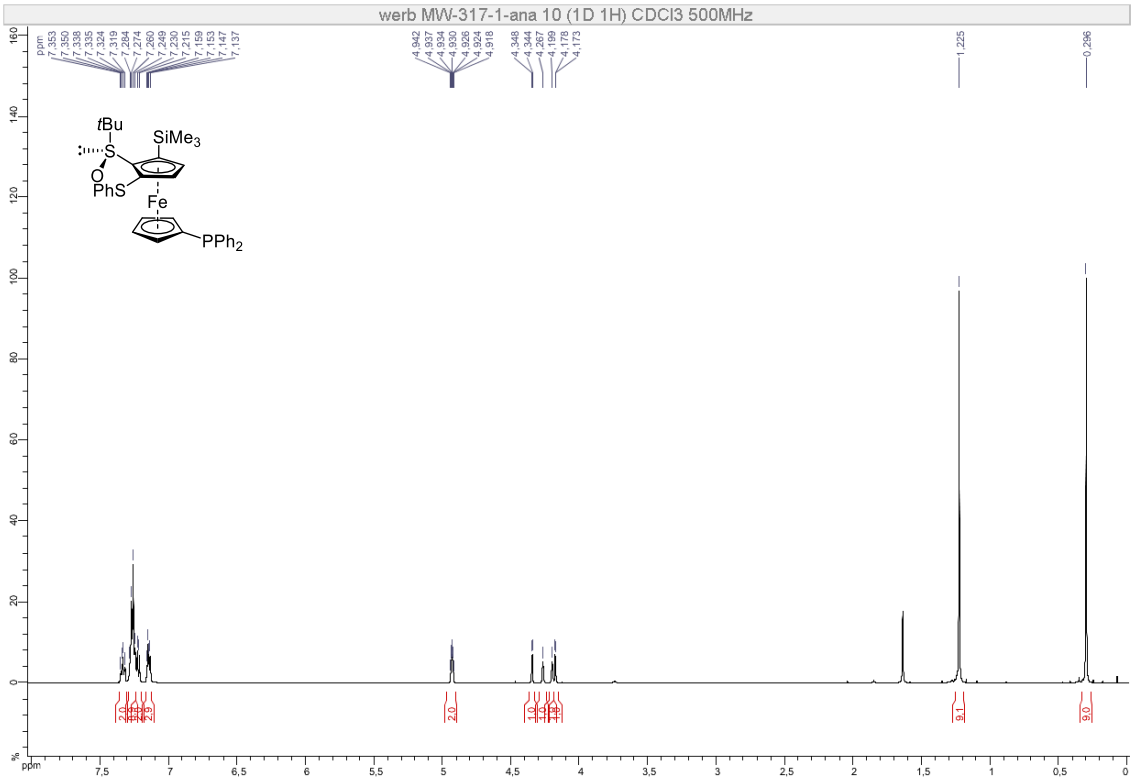


NOESY (500 MHz, $CDCl_3$)

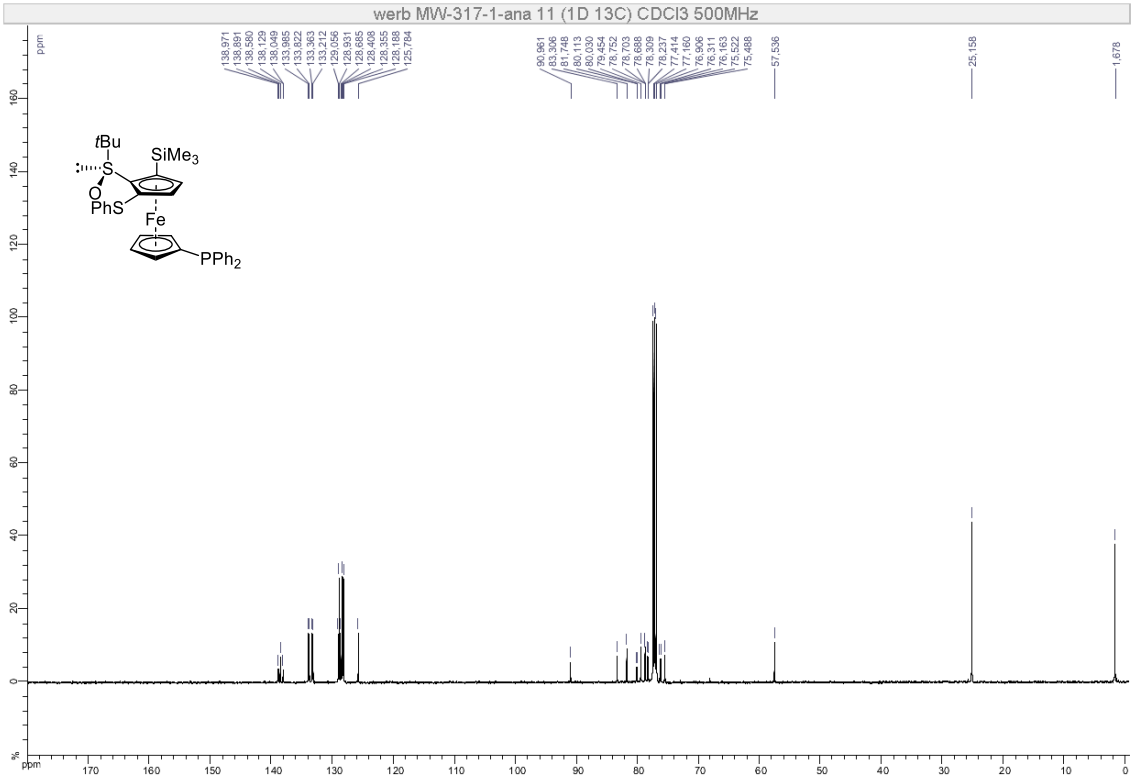


(*S*,*S*$_P$)-*S*-*tert*-Butyl-1'-(diphenylphosphino)-2-(phenylthio)-5-(trimethylsilyl)ferrocenesulfoxide (*S*,*S*$_P$-10)

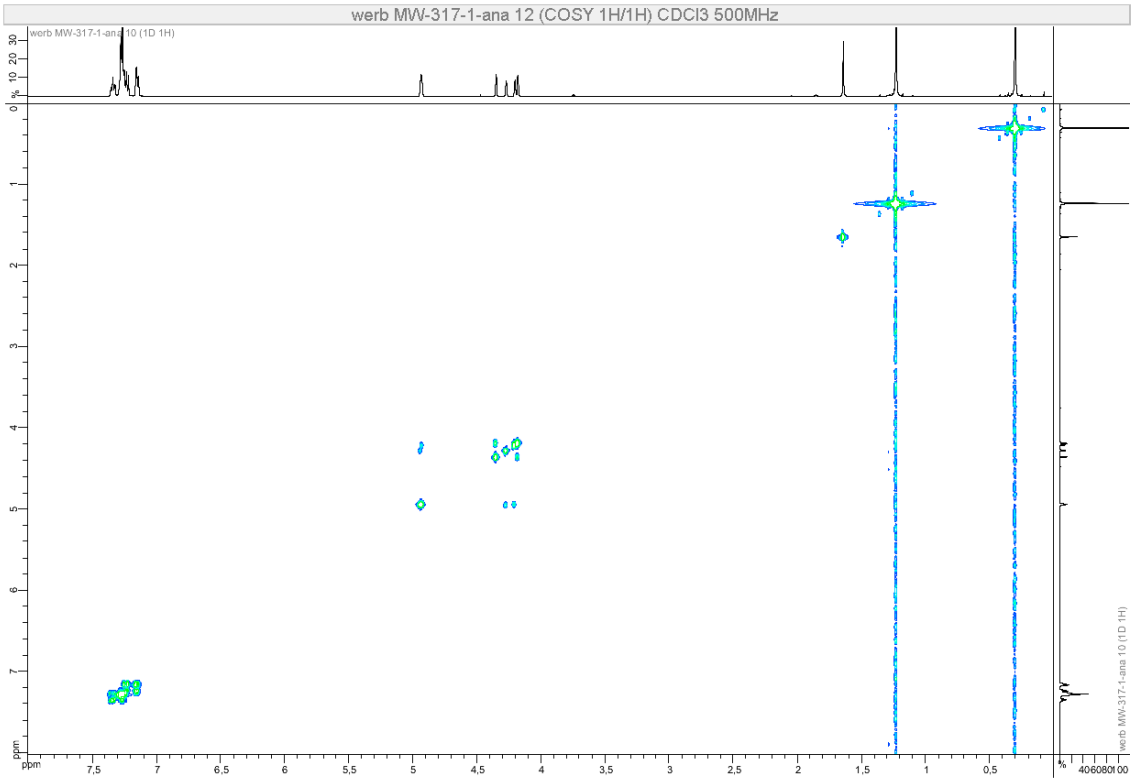
^{1}H NMR (500 MHz, $CDCl_3$)



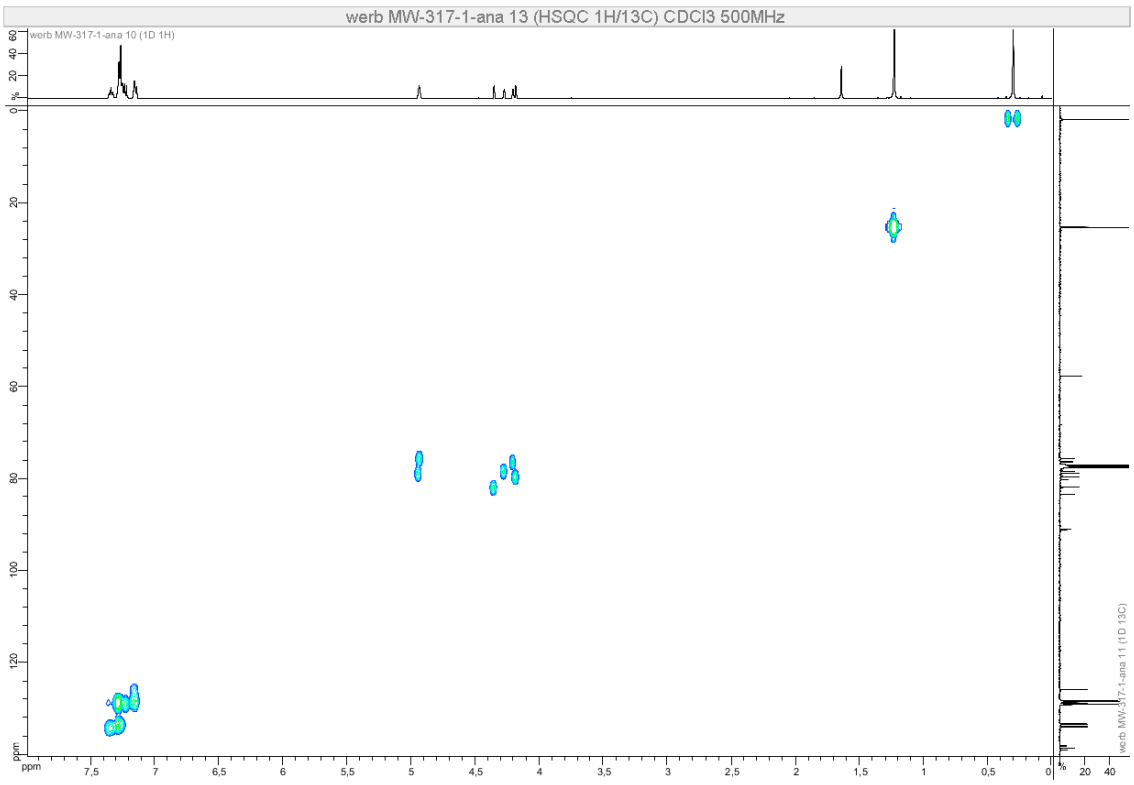
^{13}C NMR (126 MHz, $CDCl_3$)



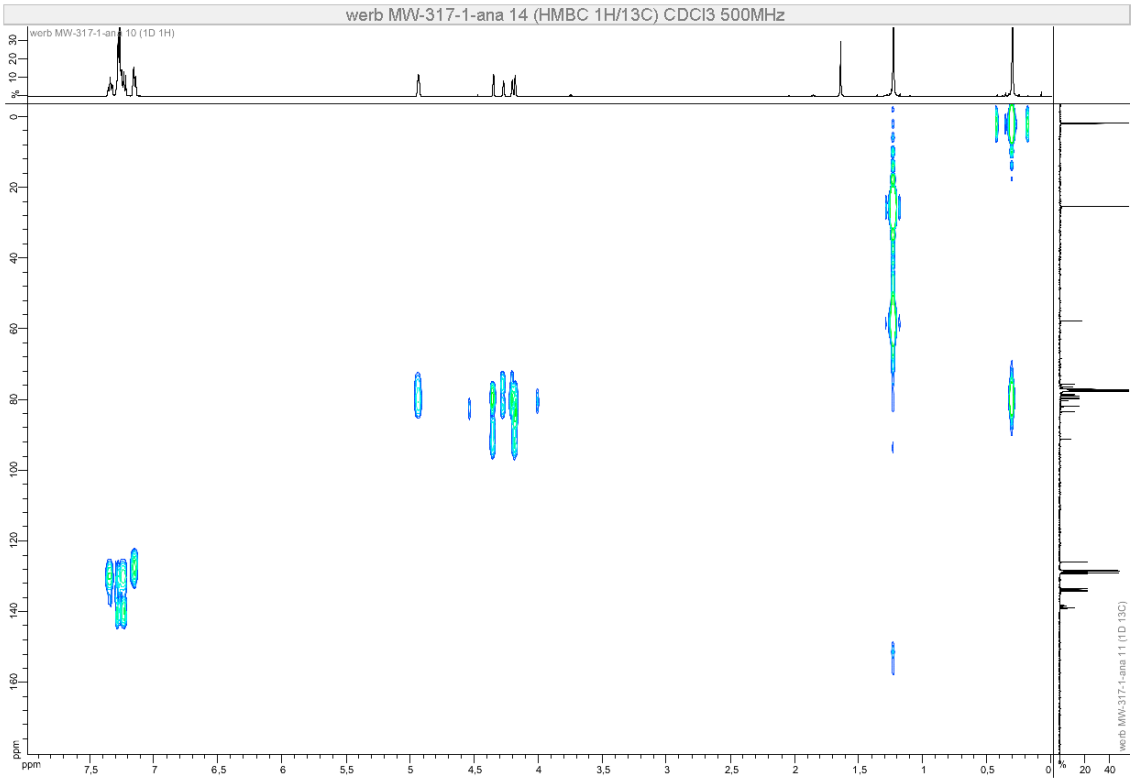
COSY (500 MHz, $CDCl_3$)



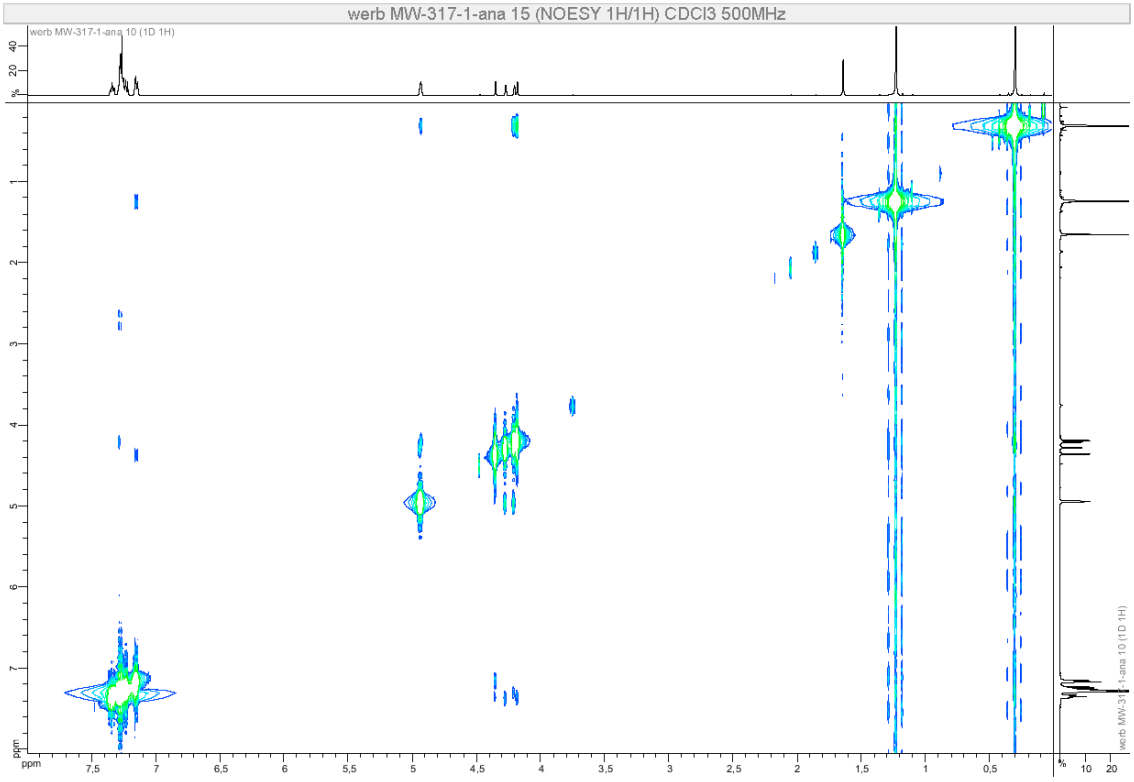
HSQC (500 MHz, $CDCl_3$)



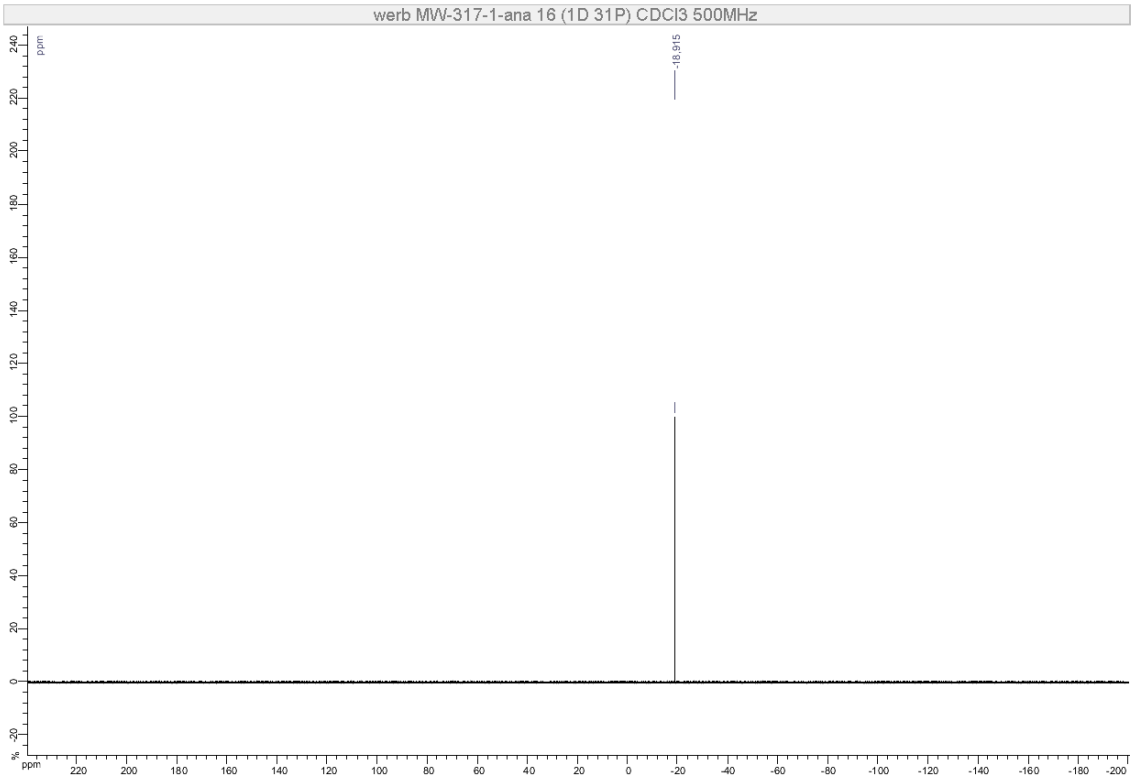
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

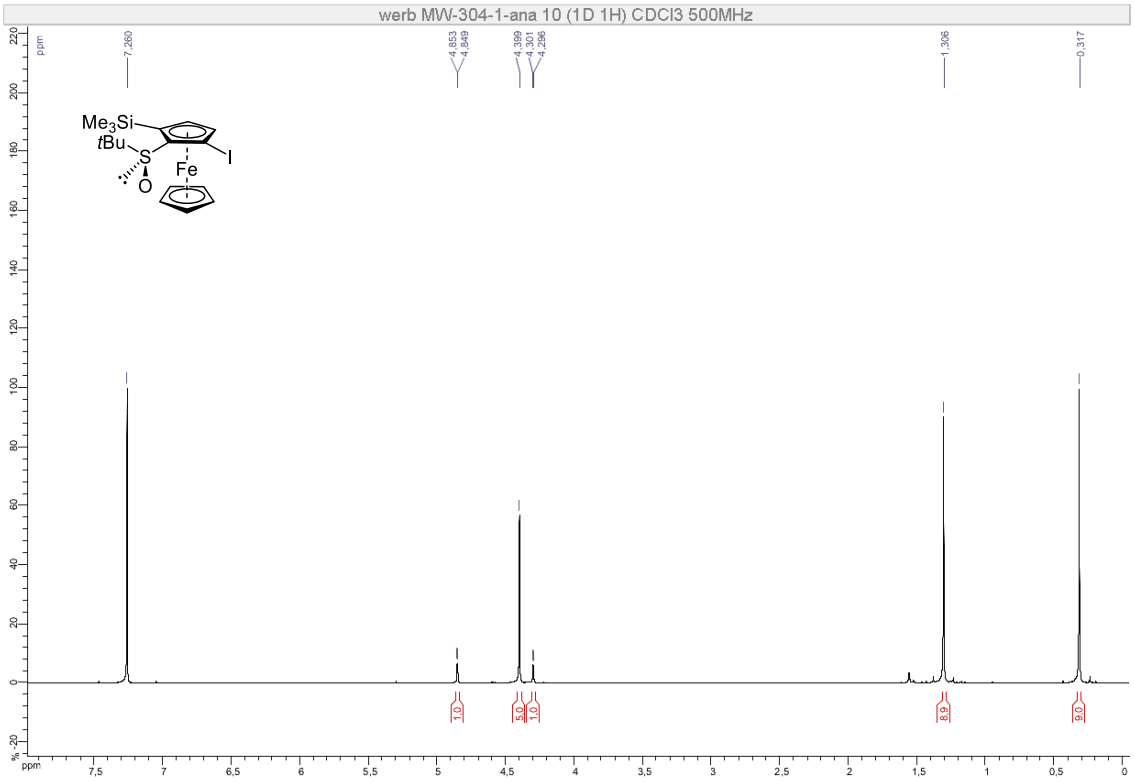


^{31}P NMR (202 MHz, $CDCl_3$)

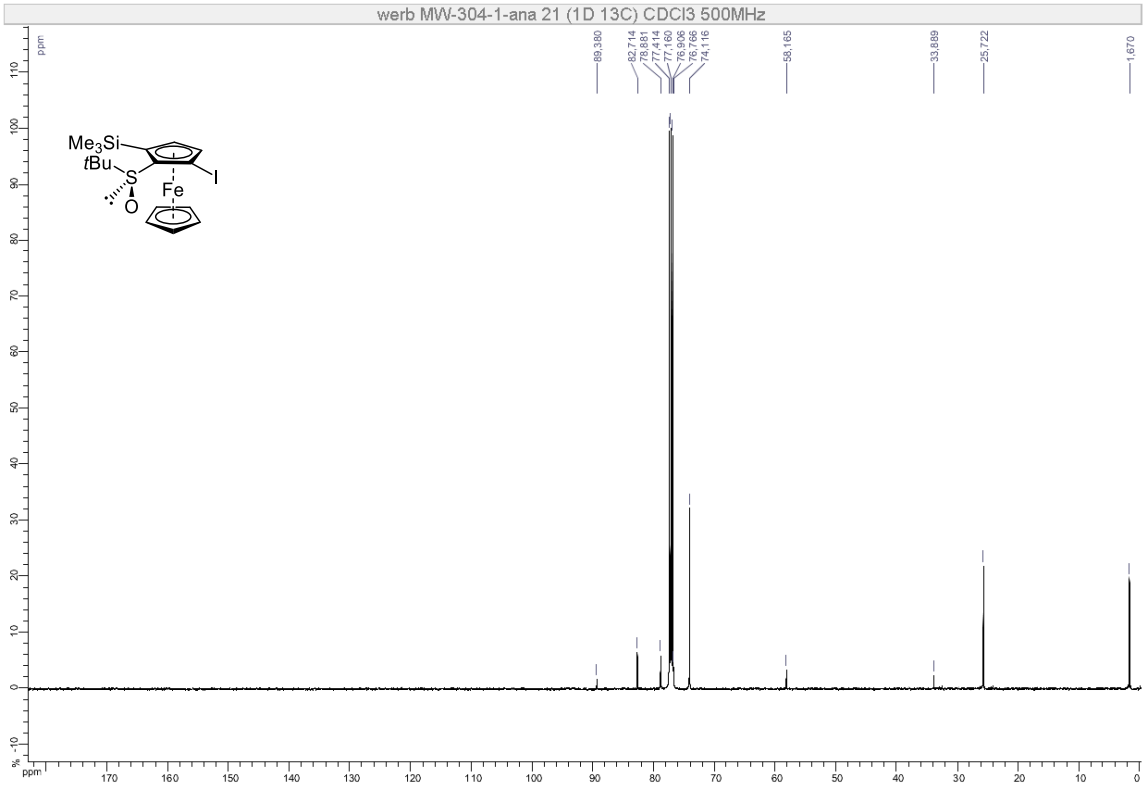


(*S*,*R*$_P$)-*S*-*tert*-Butyl-2-iodo-5-(trimethylsilyl)ferrocenesulfoxide (*S*,*R*$_P$-13a)

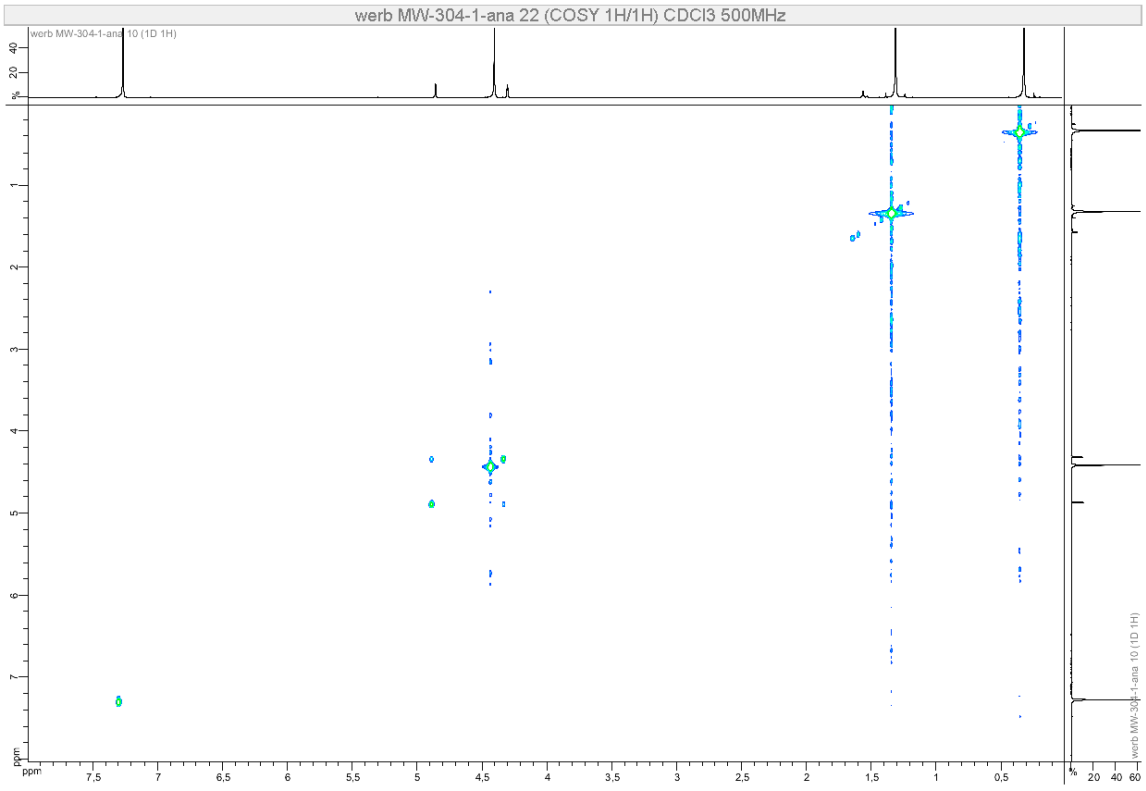
^{1}H NMR (500 MHz, $CDCl_3$)



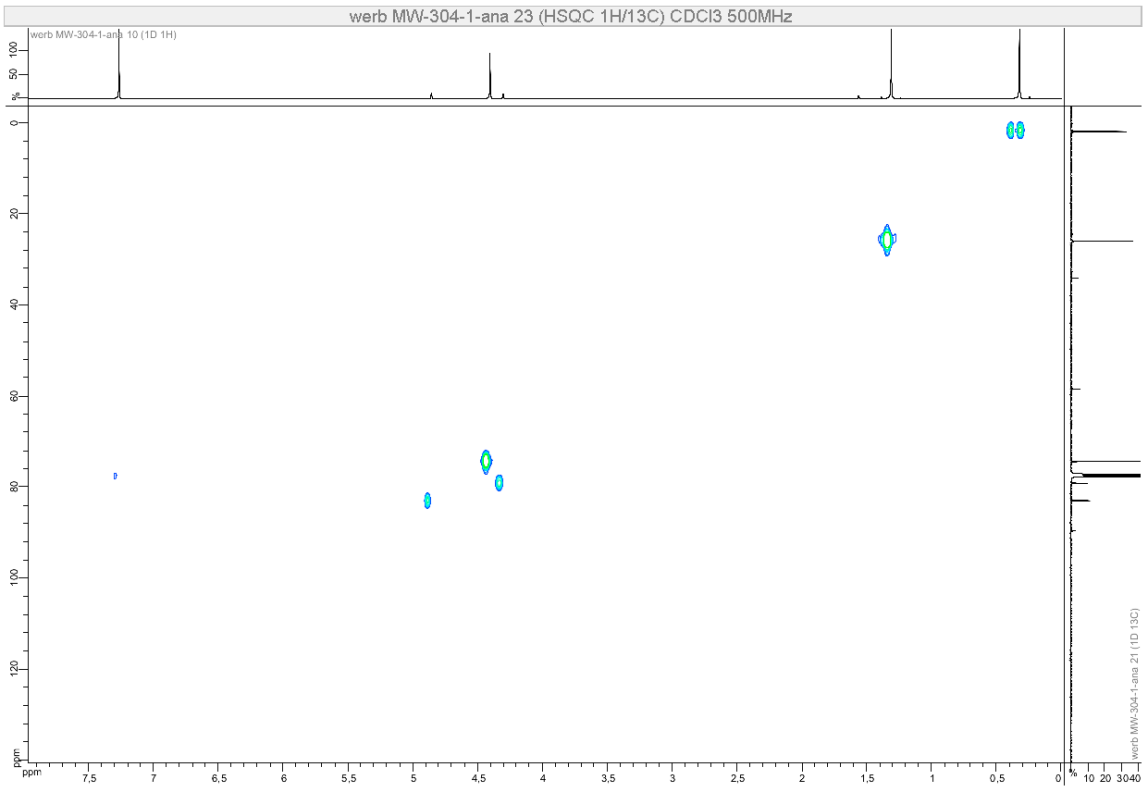
^{13}C NMR (126 MHz, $CDCl_3$)



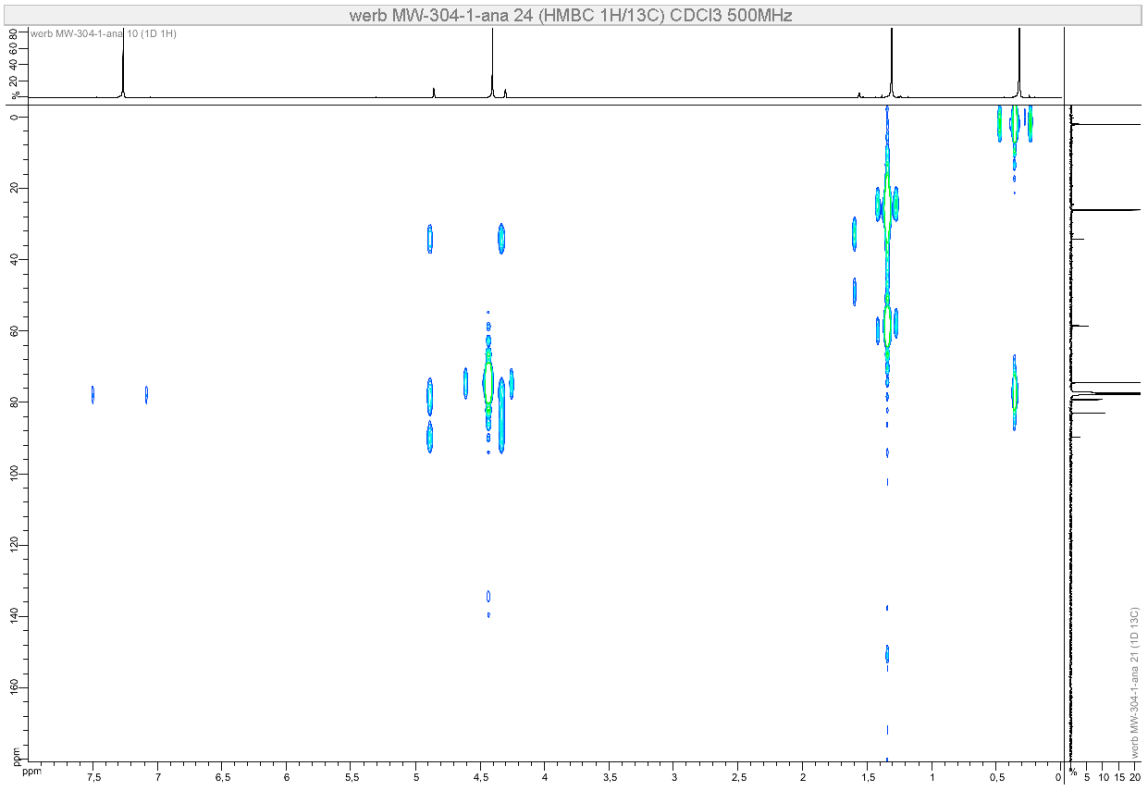
COSY (500 MHz, $CDCl_3$)



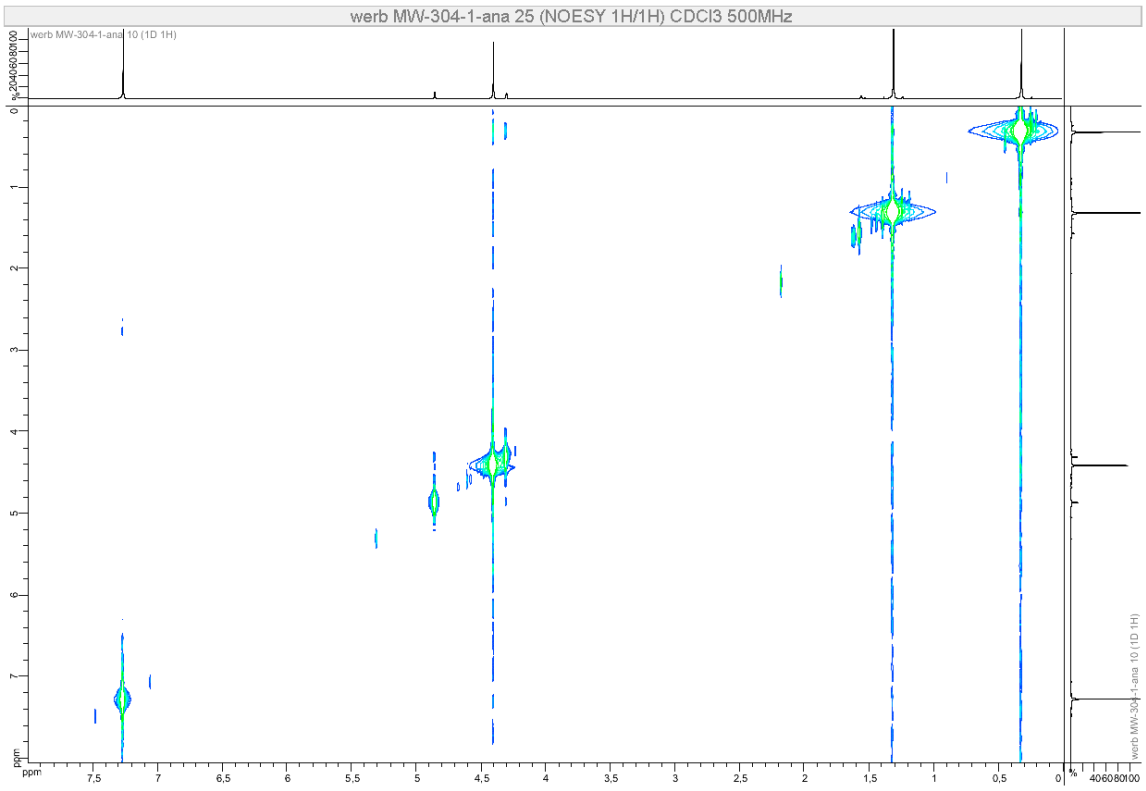
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

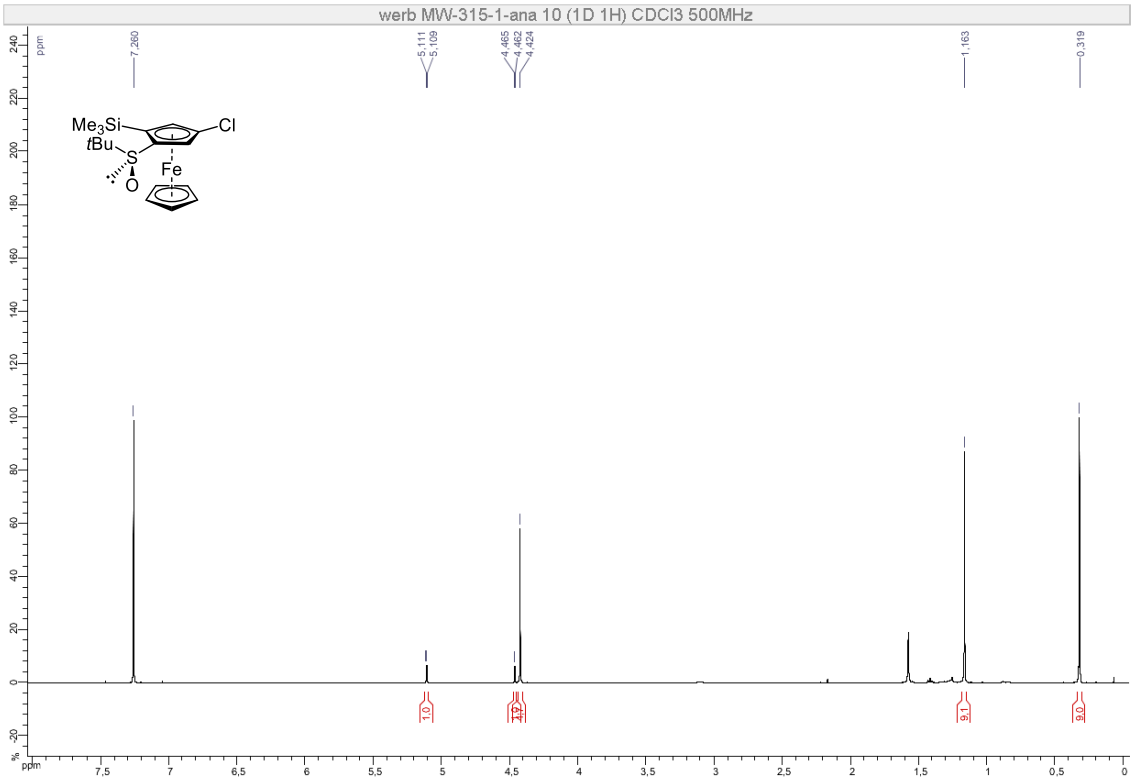


NOESY (500 MHz, $CDCl_3$)

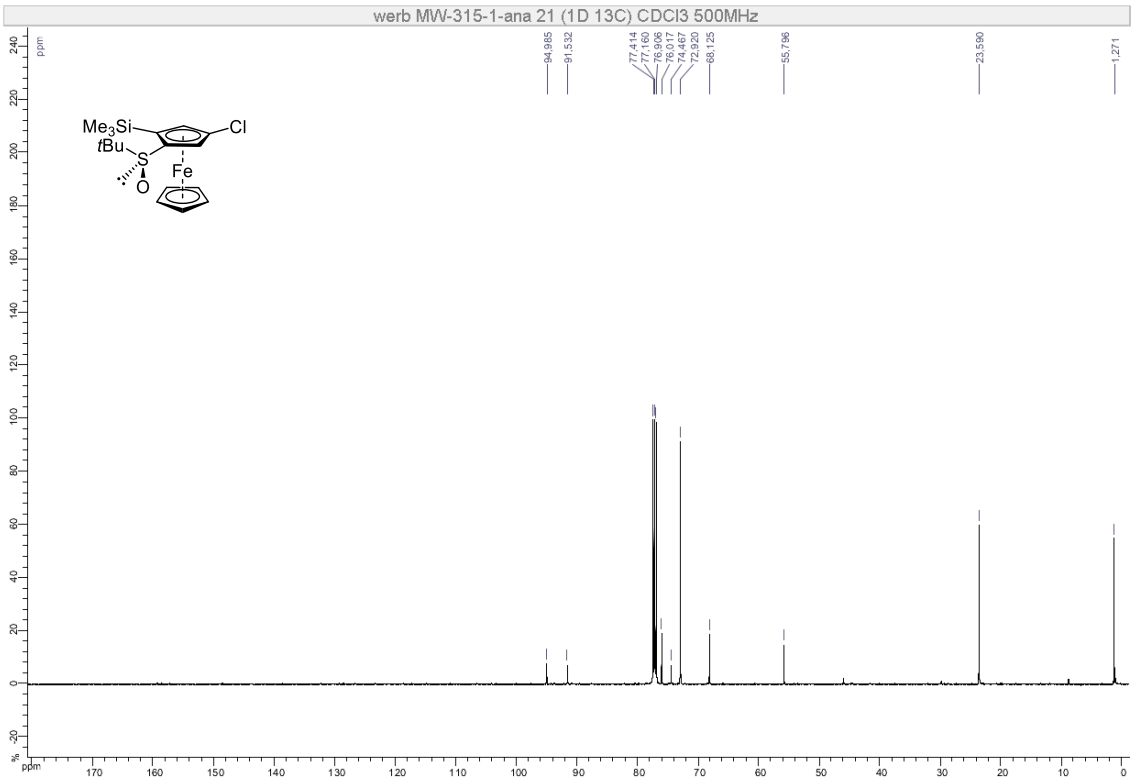


(*S*,*R*$_P$)-*S*-*tert*-Butyl-4-chloro-2-(trimethylsilyl)ferrocenesulfoxide (*S*,*R*$_P$-13b)

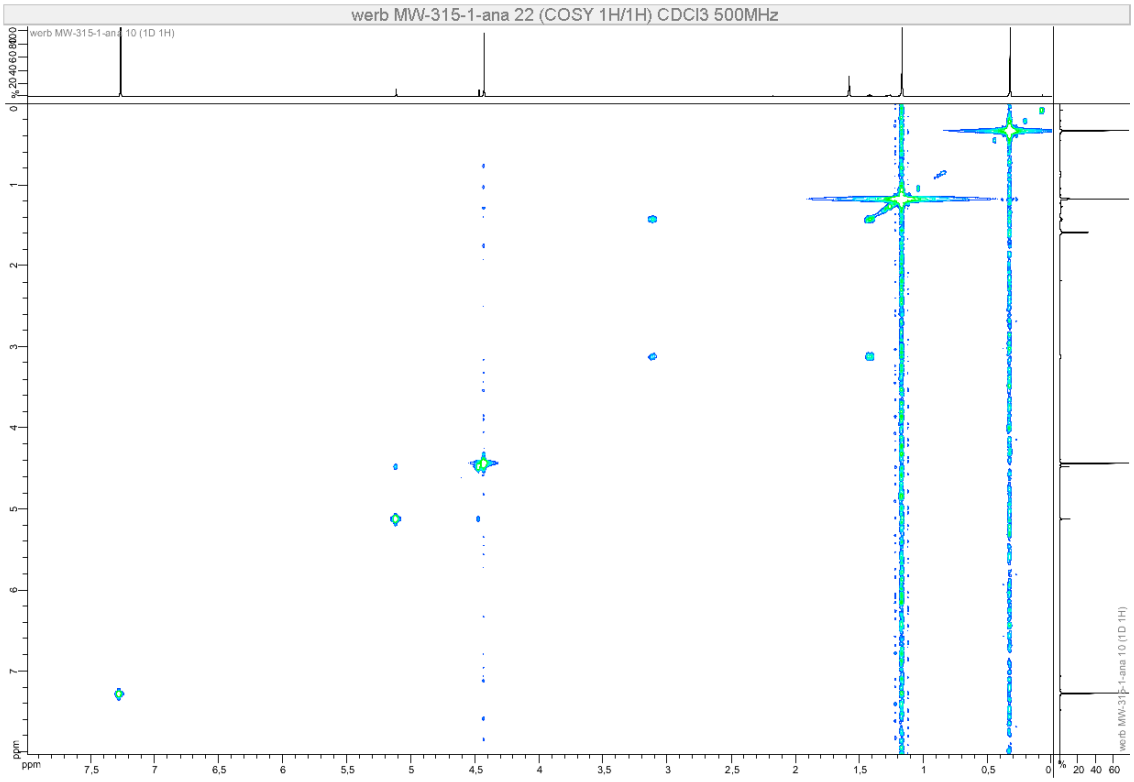
^{1}H NMR (500 MHz, $CDCl_3$)



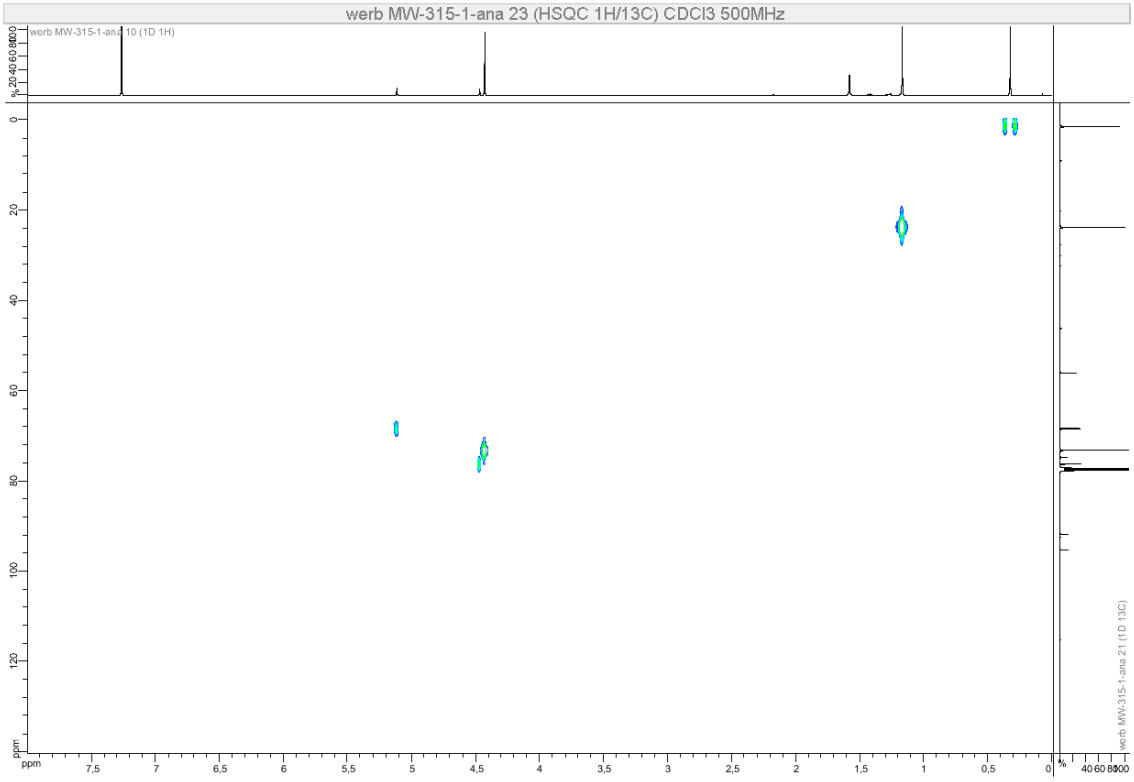
^{13}C NMR (126 MHz, $CDCl_3$)



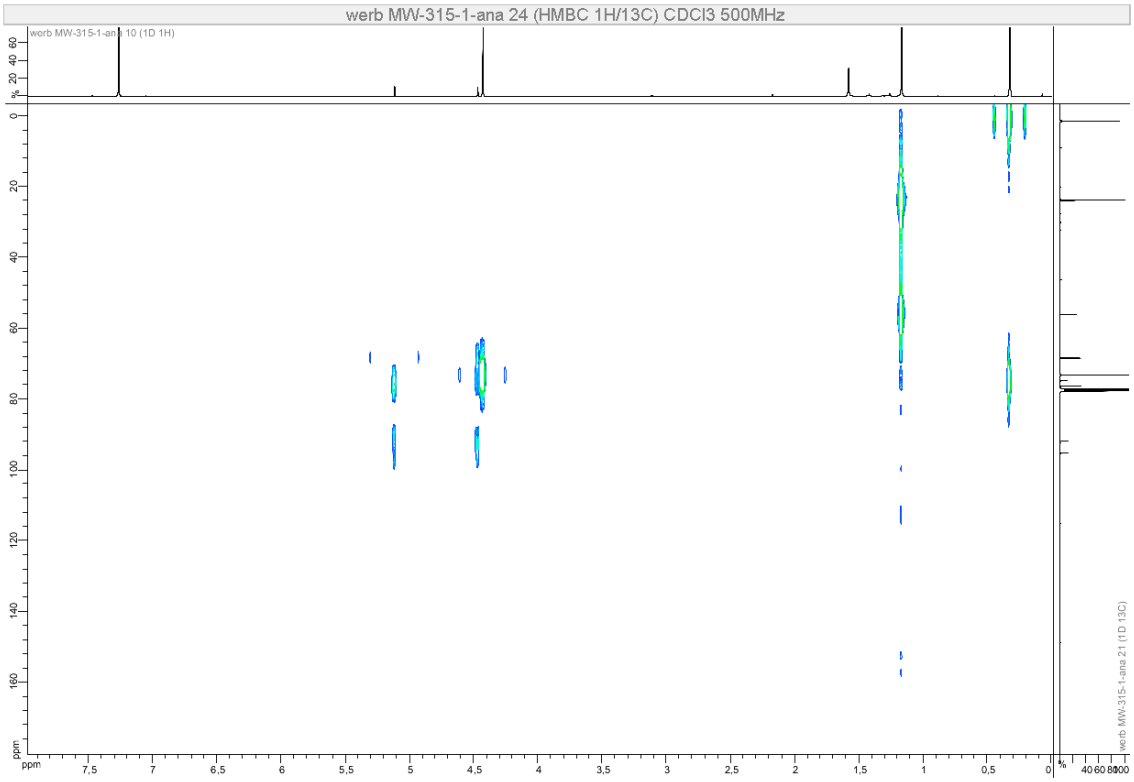
COSY (500 MHz, $CDCl_3$)



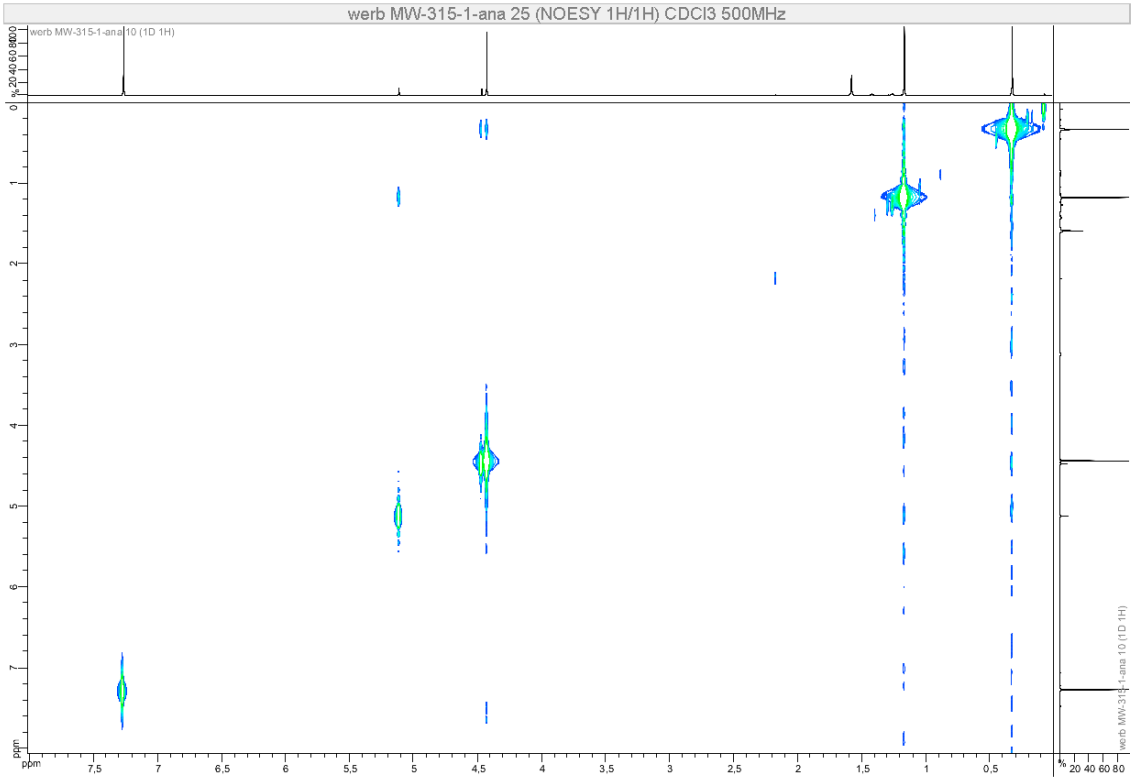
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

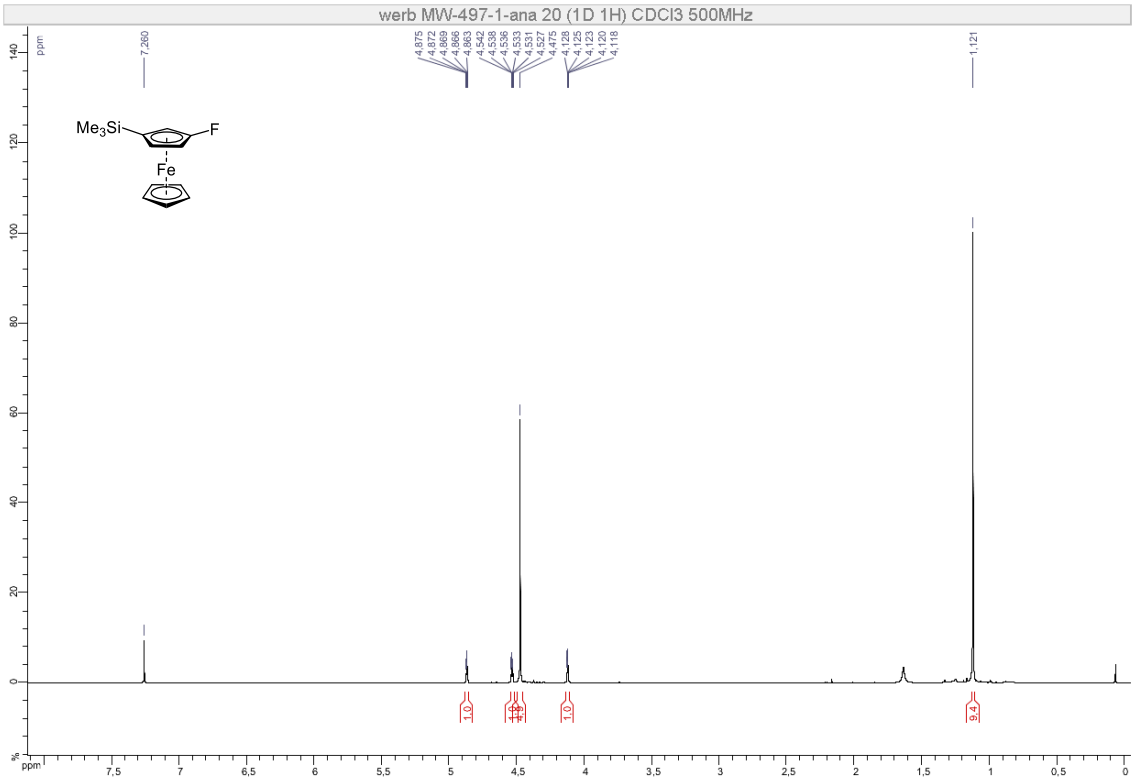


NOESY (500 MHz, $CDCl_3$)

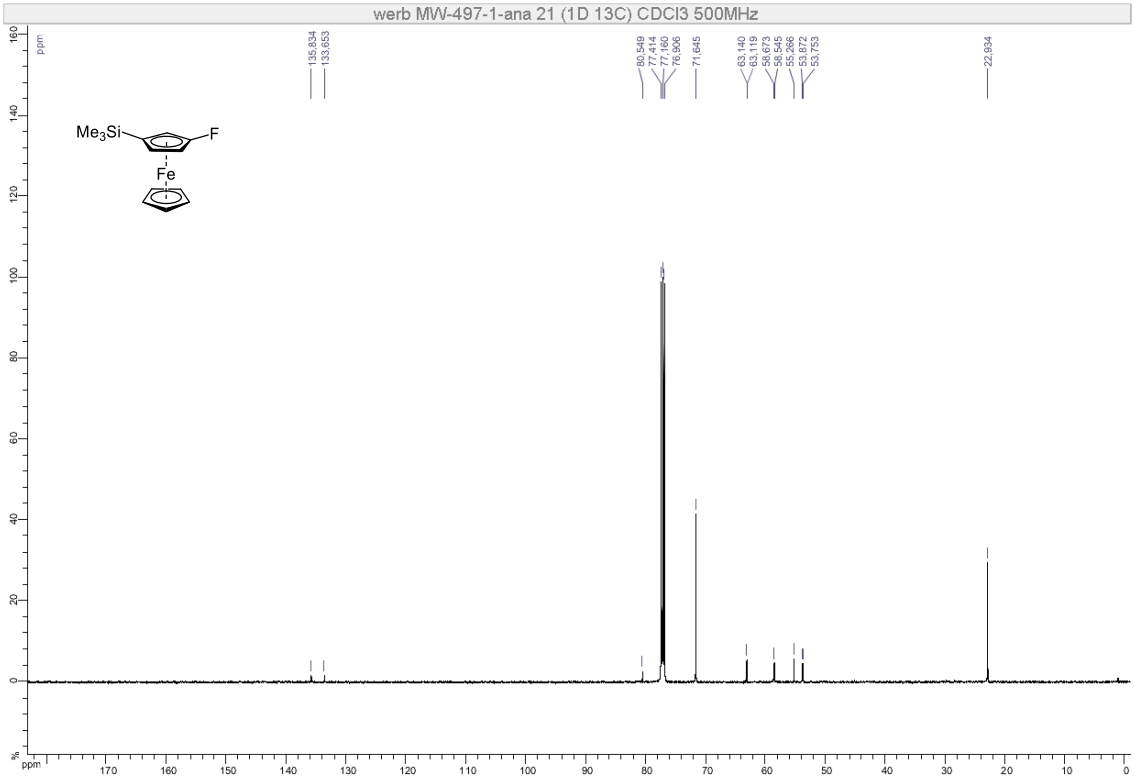


(*S*,*S*$_P$)-*S*-*tert*-Butyl-3-fluoroferrocenesulfoxide (*S*,*S*$_P$-13c)

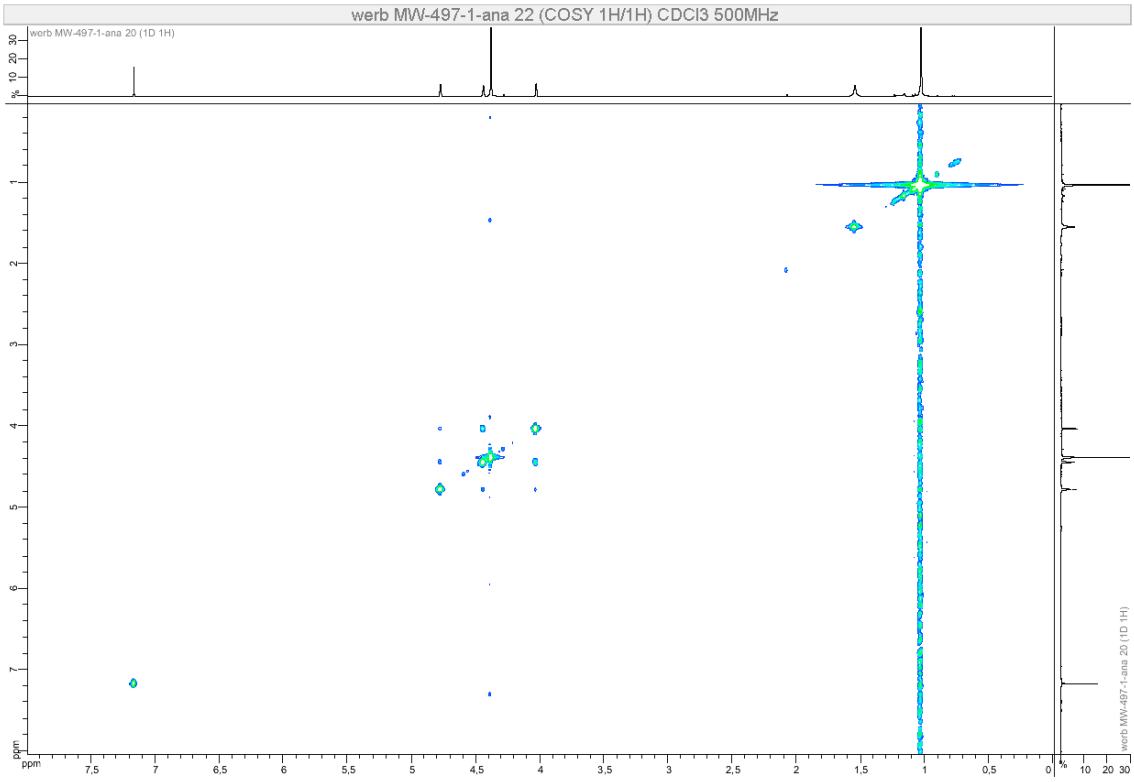
^{1}H NMR (500 MHz, $CDCl_3$)



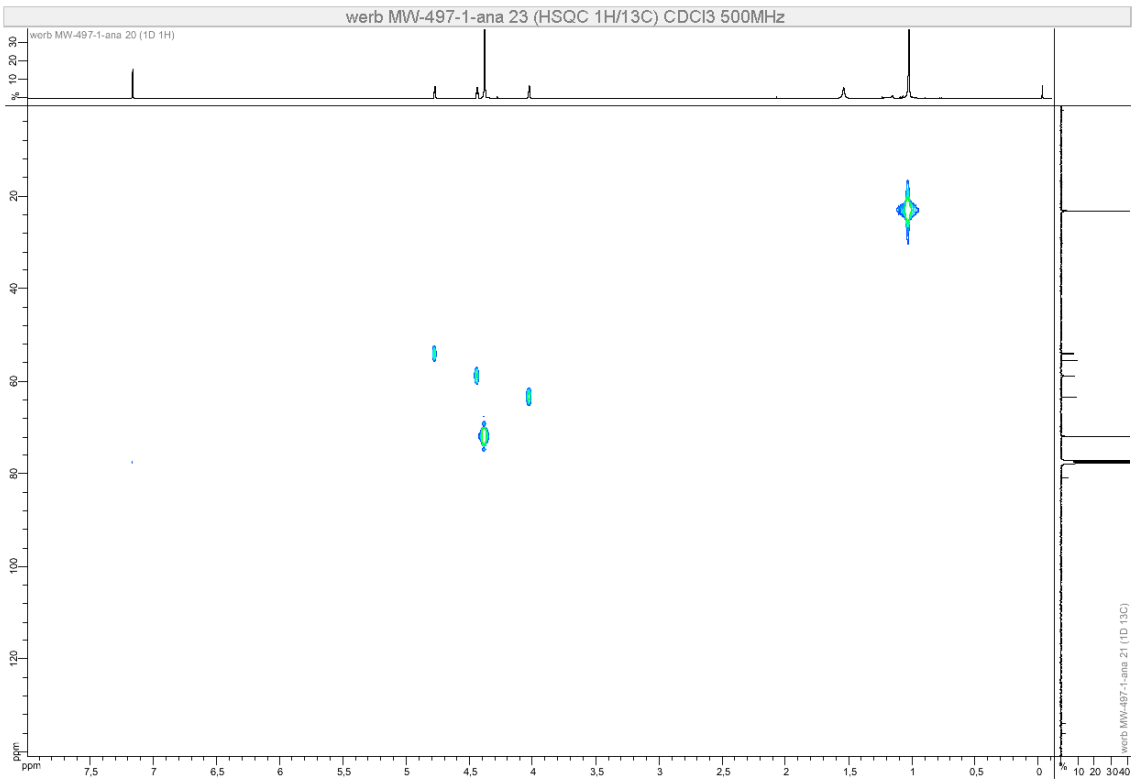
^{13}C NMR (126 MHz, $CDCl_3$)



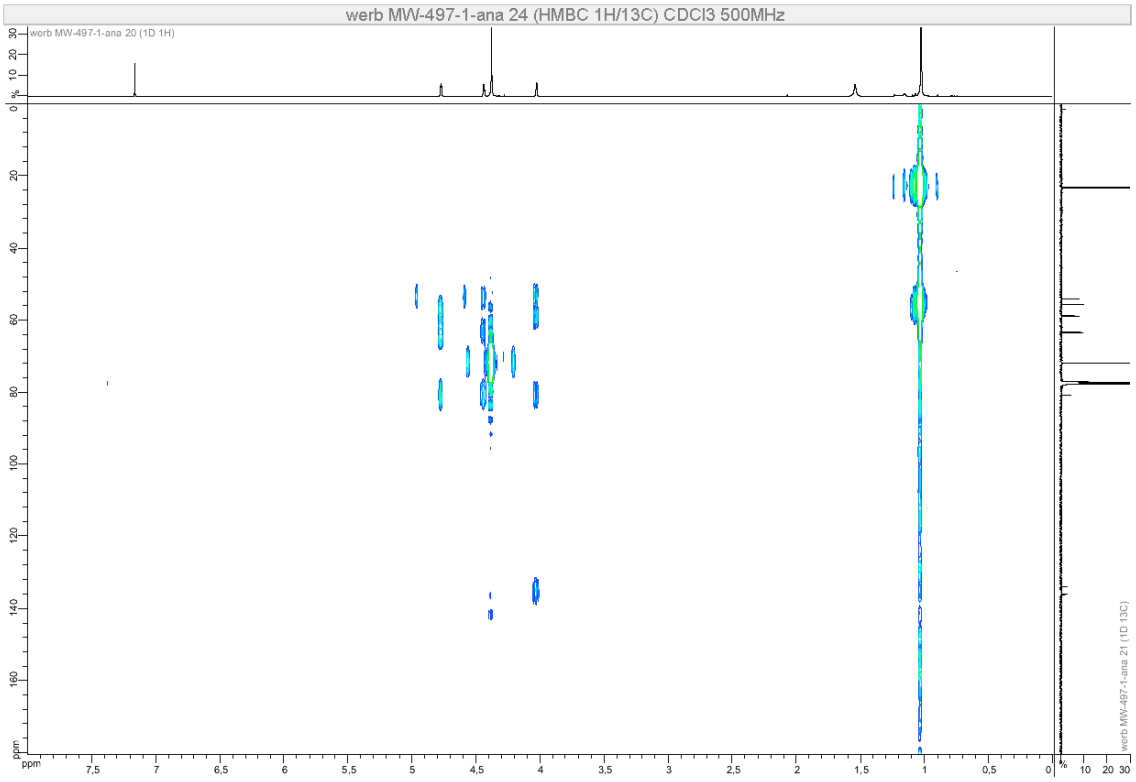
COSY (500 MHz, $CDCl_3$)



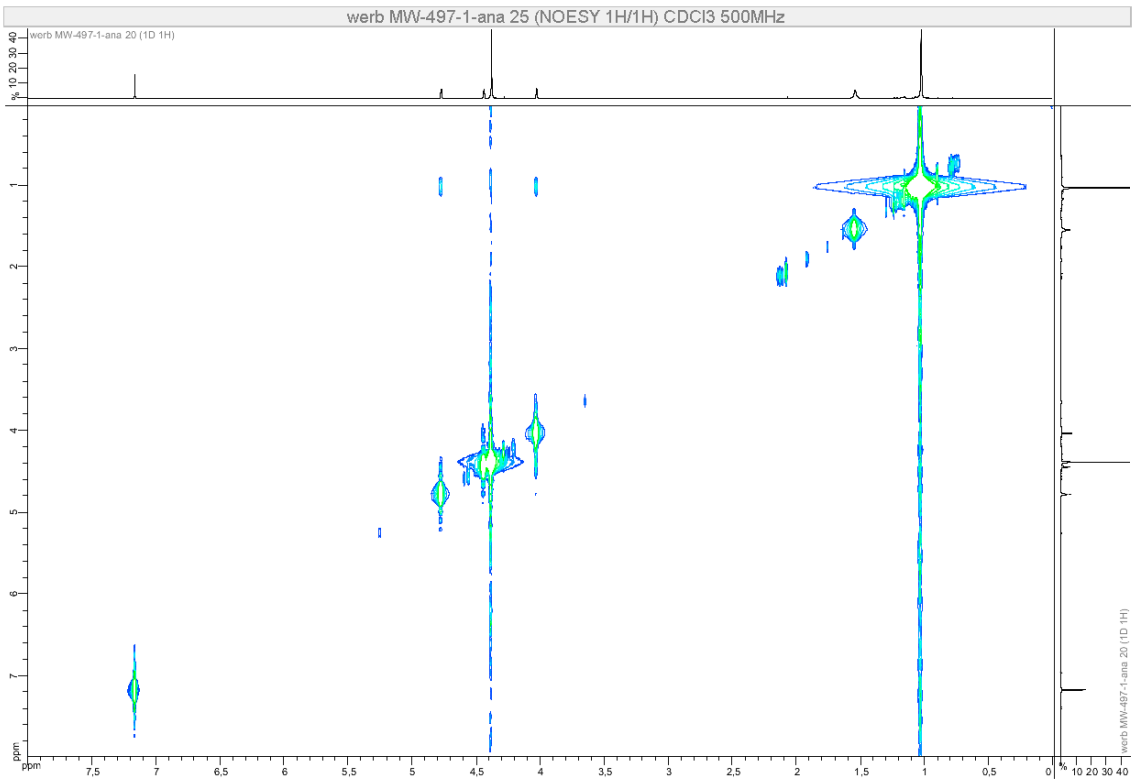
HSQC (500 MHz, $CDCl_3$)



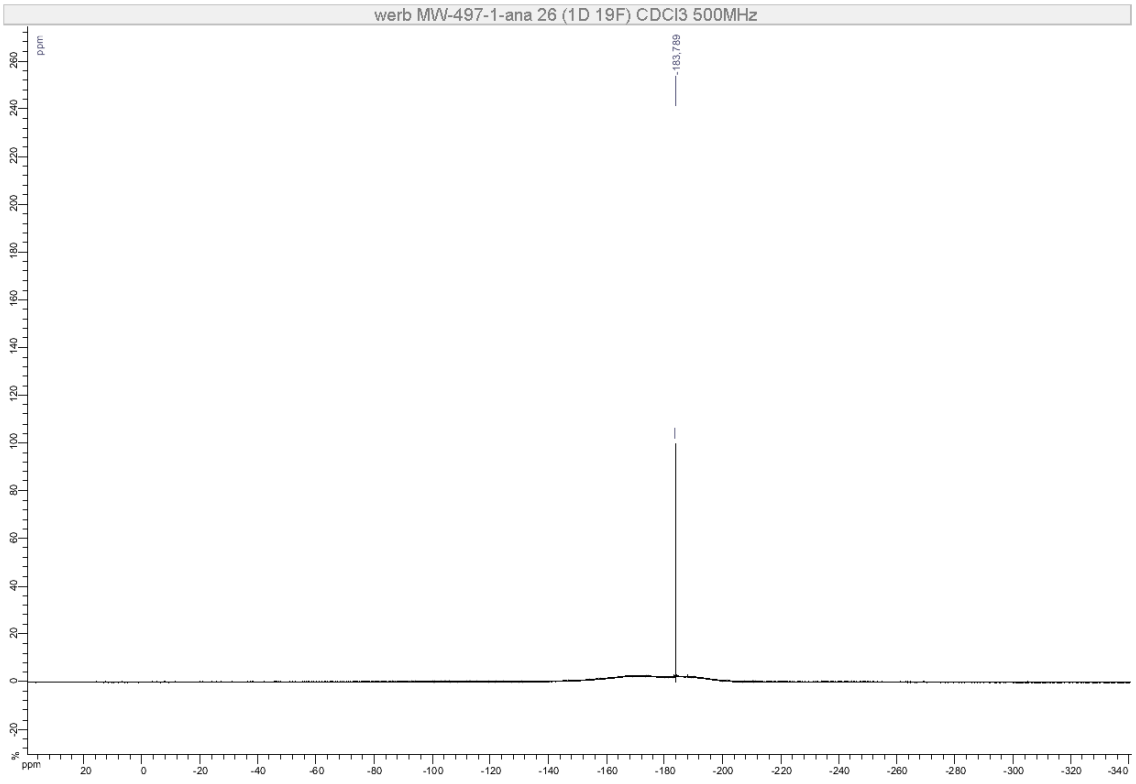
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

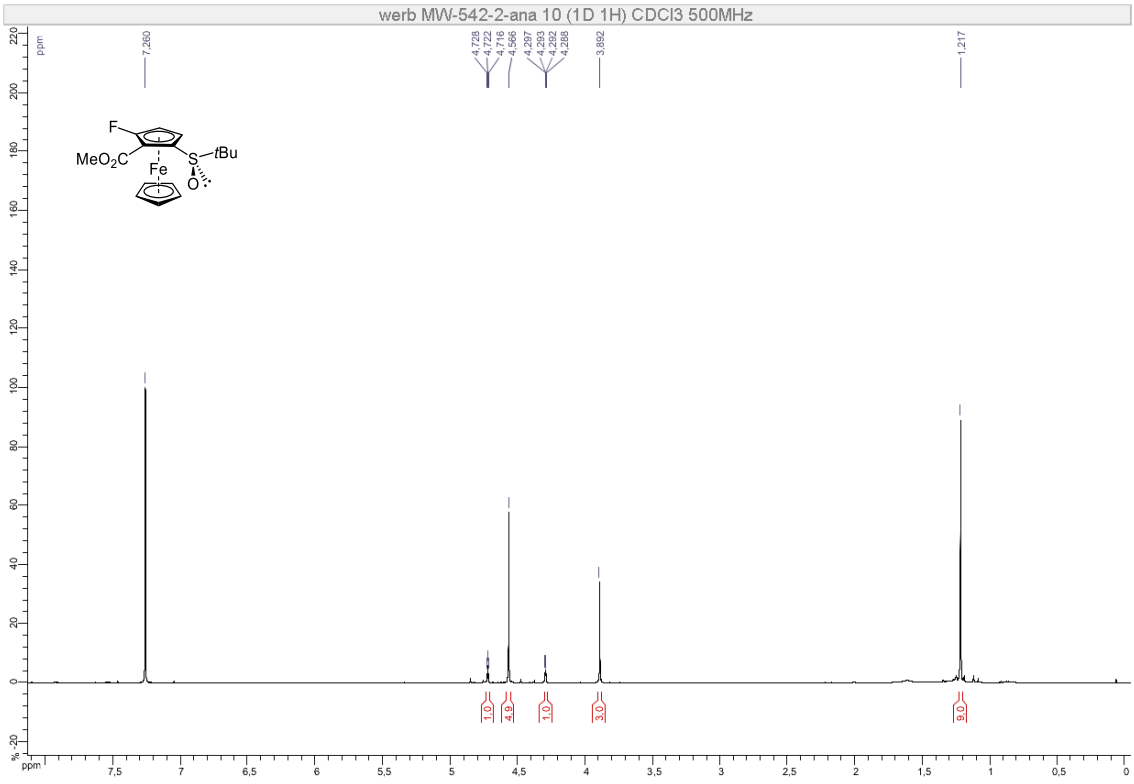


^{19}F NMR (471 MHz, $CDCl_3$)

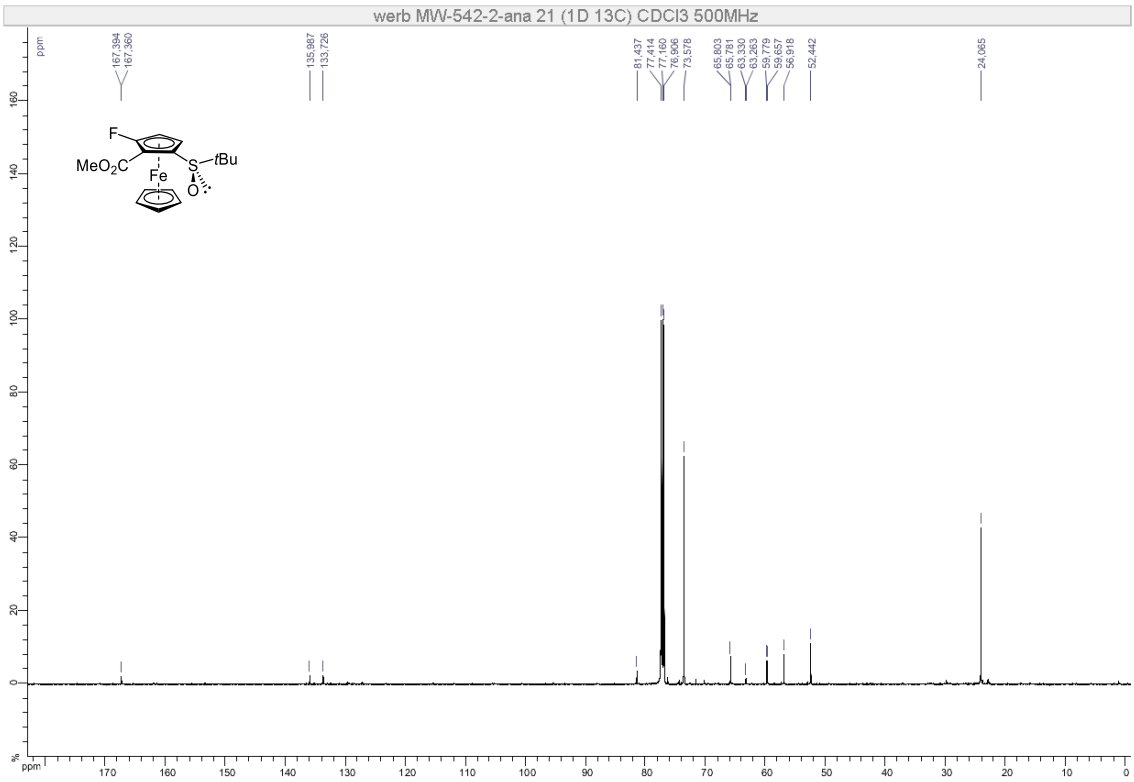


(*R*,*R*$_P$)-*S*-*tert*-Butyl-3-fluoro-2-(methoxycarbonyl)ferrocenesulfoxide (*R*,*R*$_P$-13d)

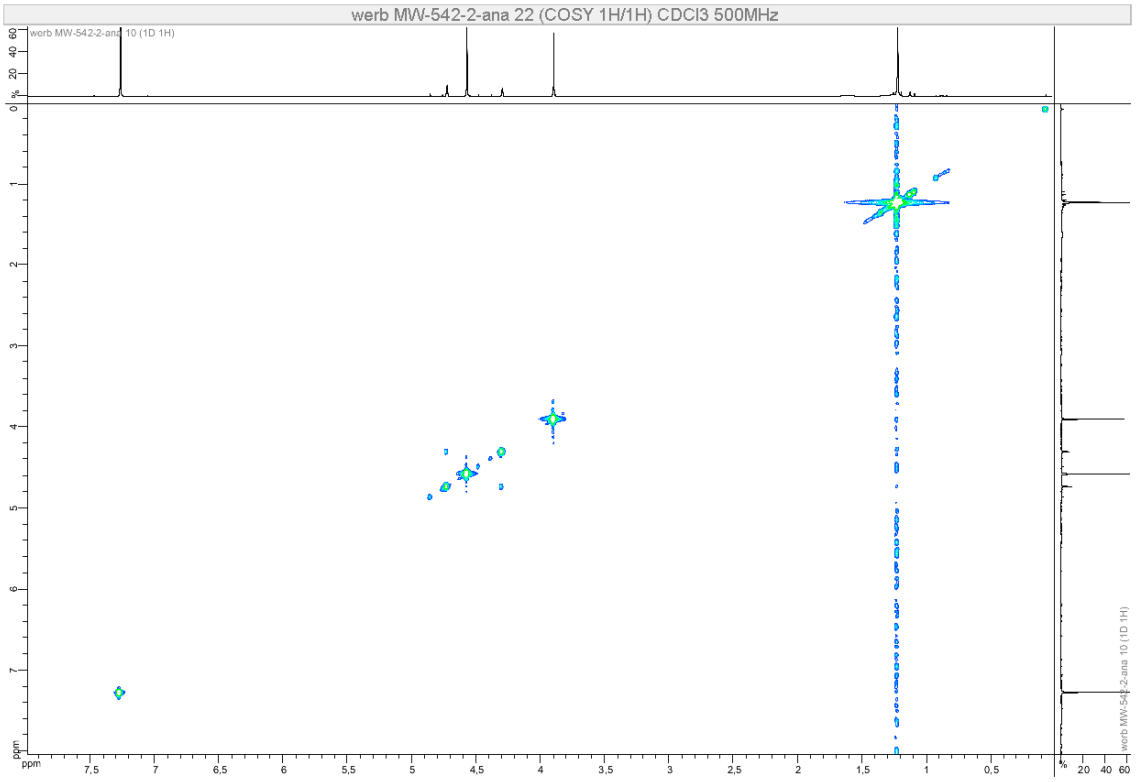
^{1}H NMR (500 MHz, $CDCl_3$)



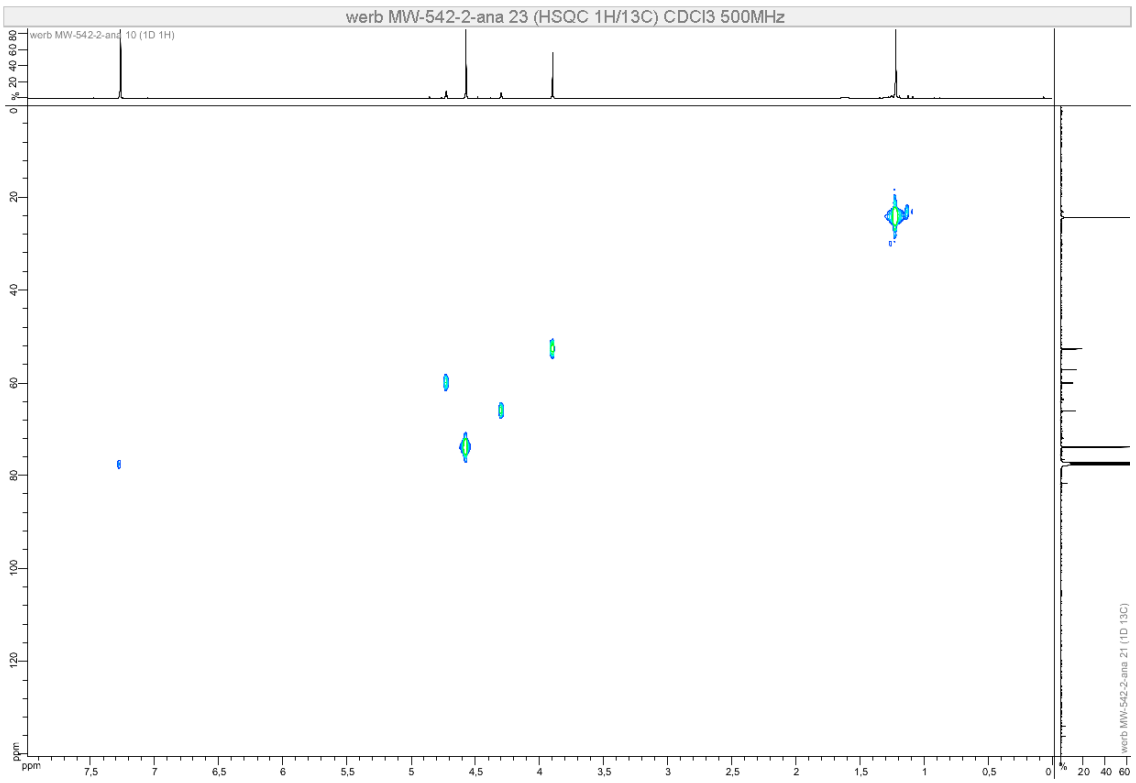
^{13}C NMR (126 MHz, $CDCl_3$)



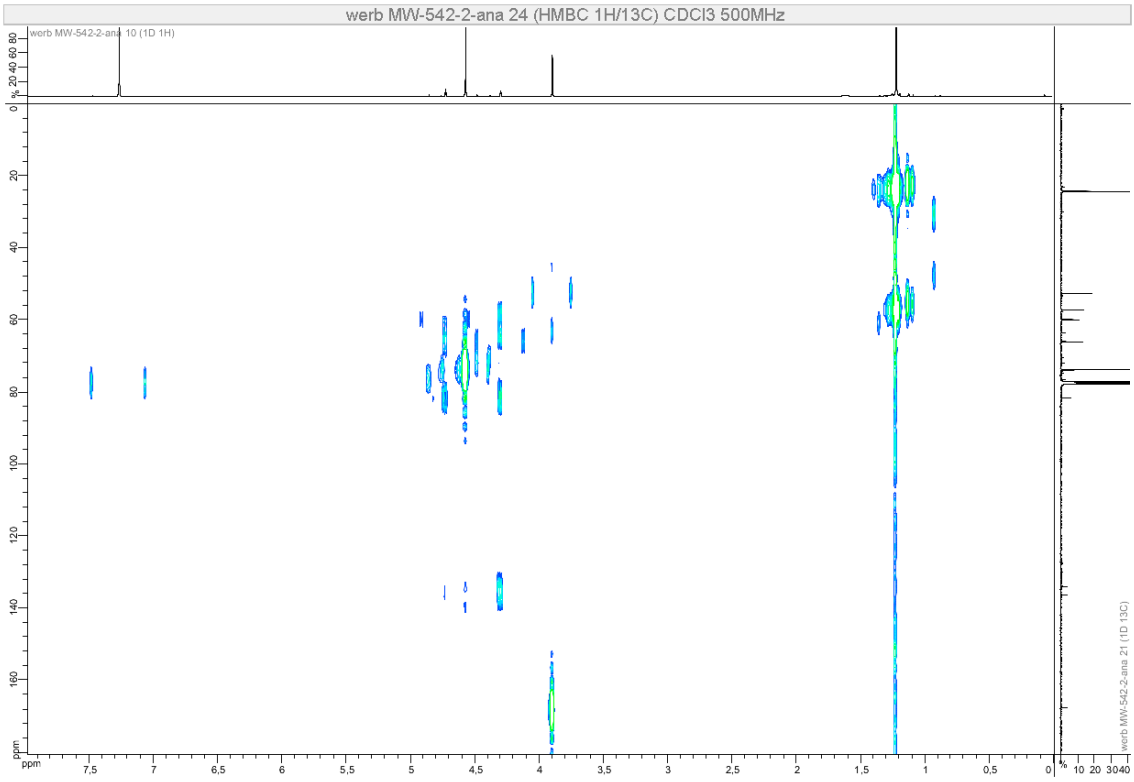
COSY (500 MHz, $CDCl_3$)



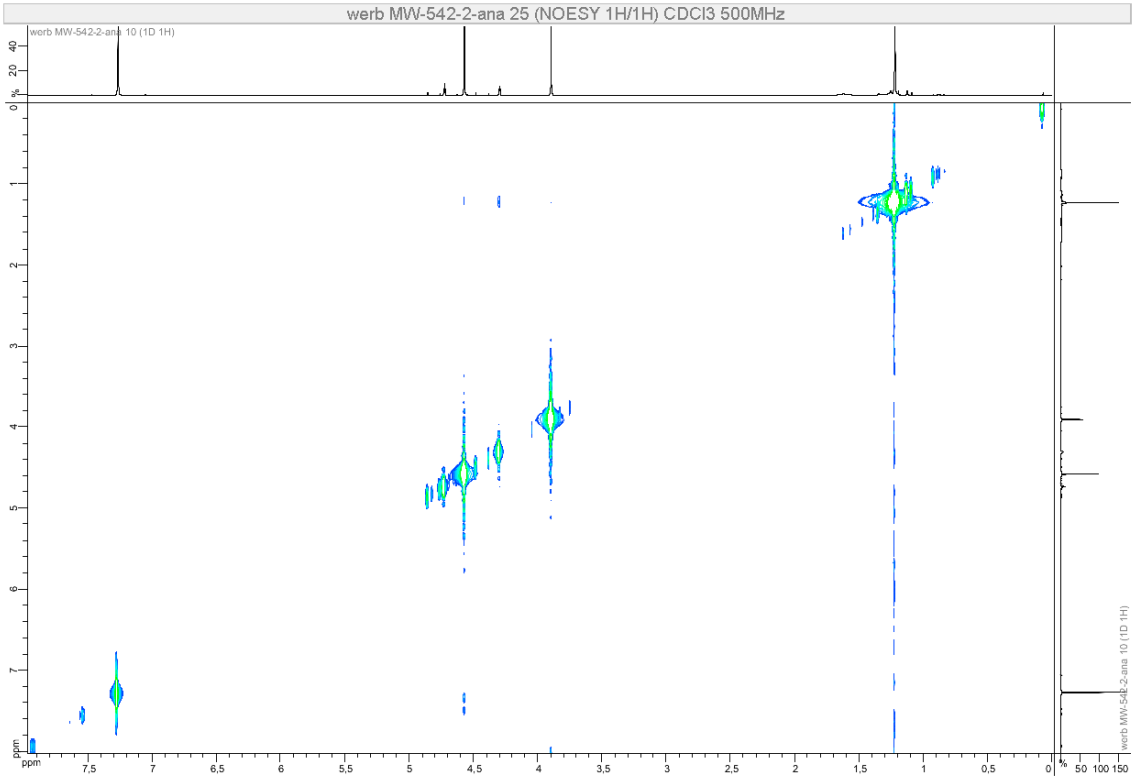
HSQC (500 MHz, $CDCl_3$)



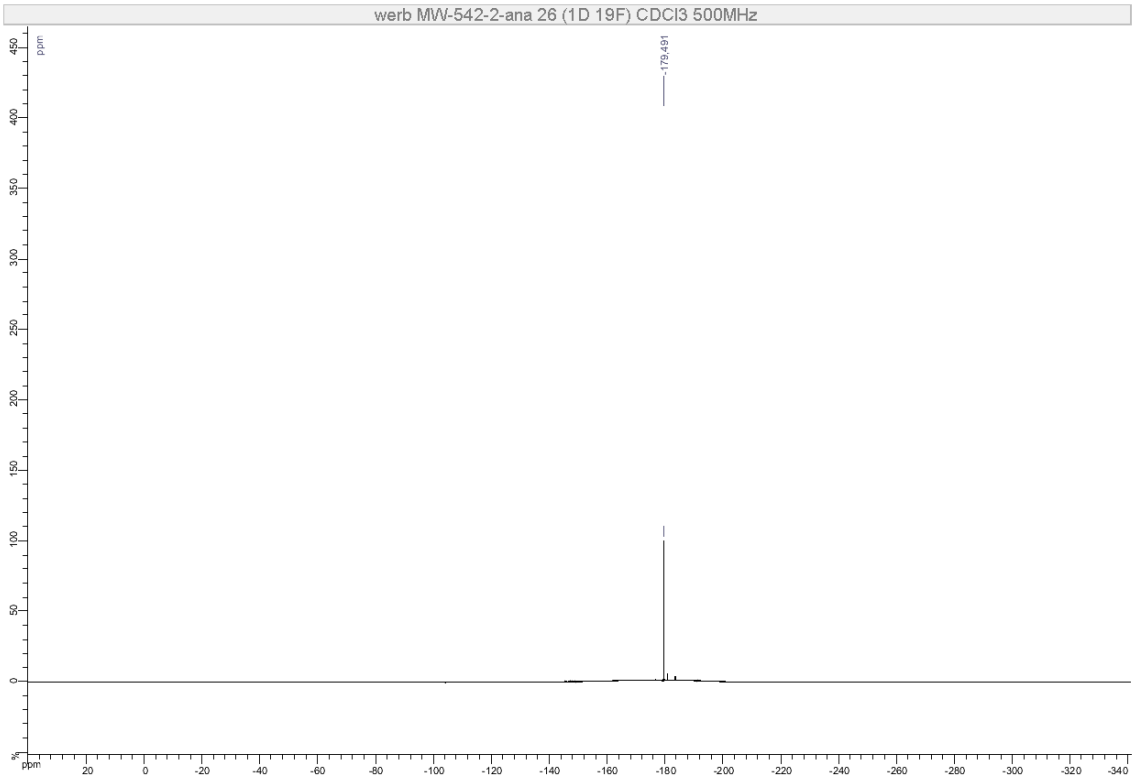
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

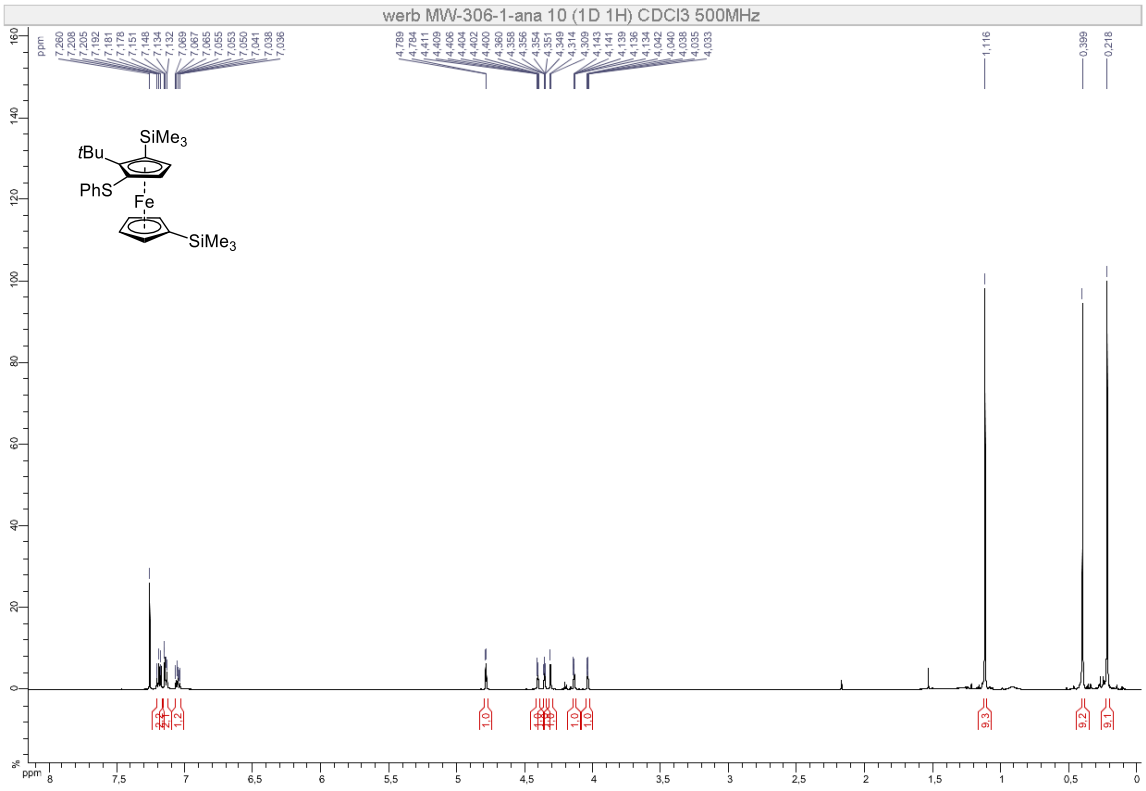


^{19}F NMR (471 MHz, $CDCl_3$)

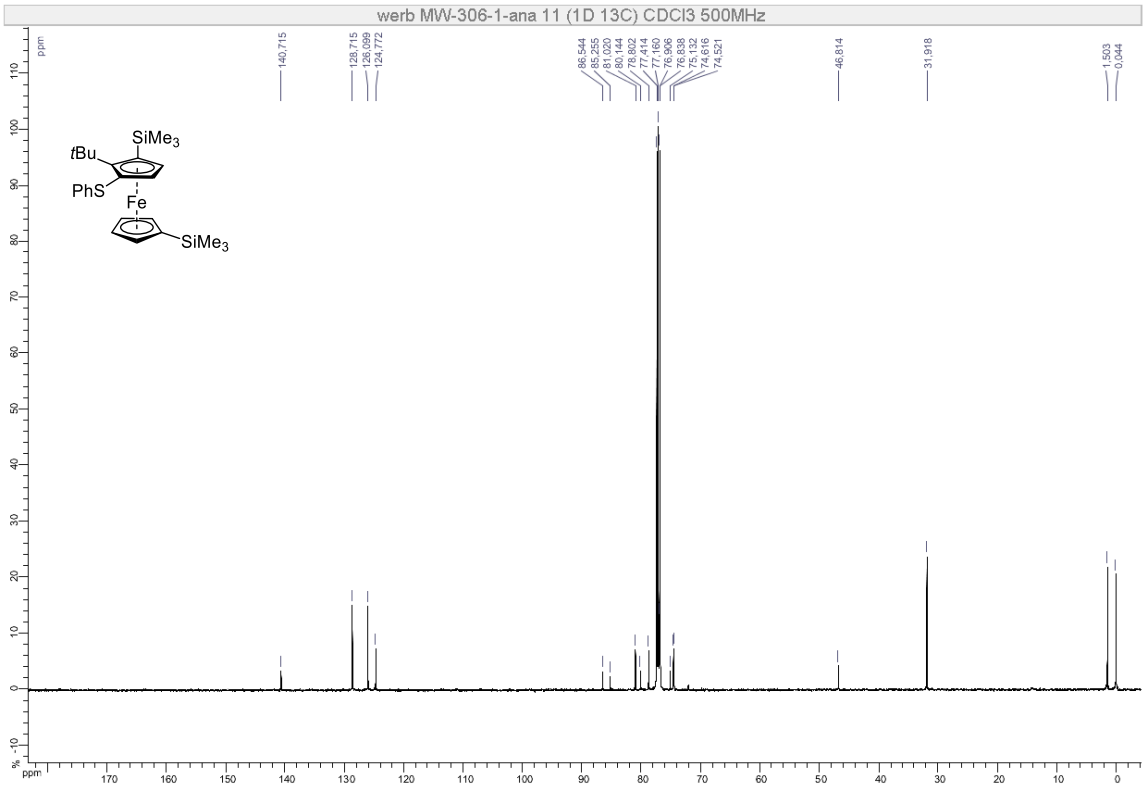


(S_P)-1-*tert*-Butyl-2-(phenylthio)-5,1'-bis(trimethylsilyl)ferrocene (S_P-14)

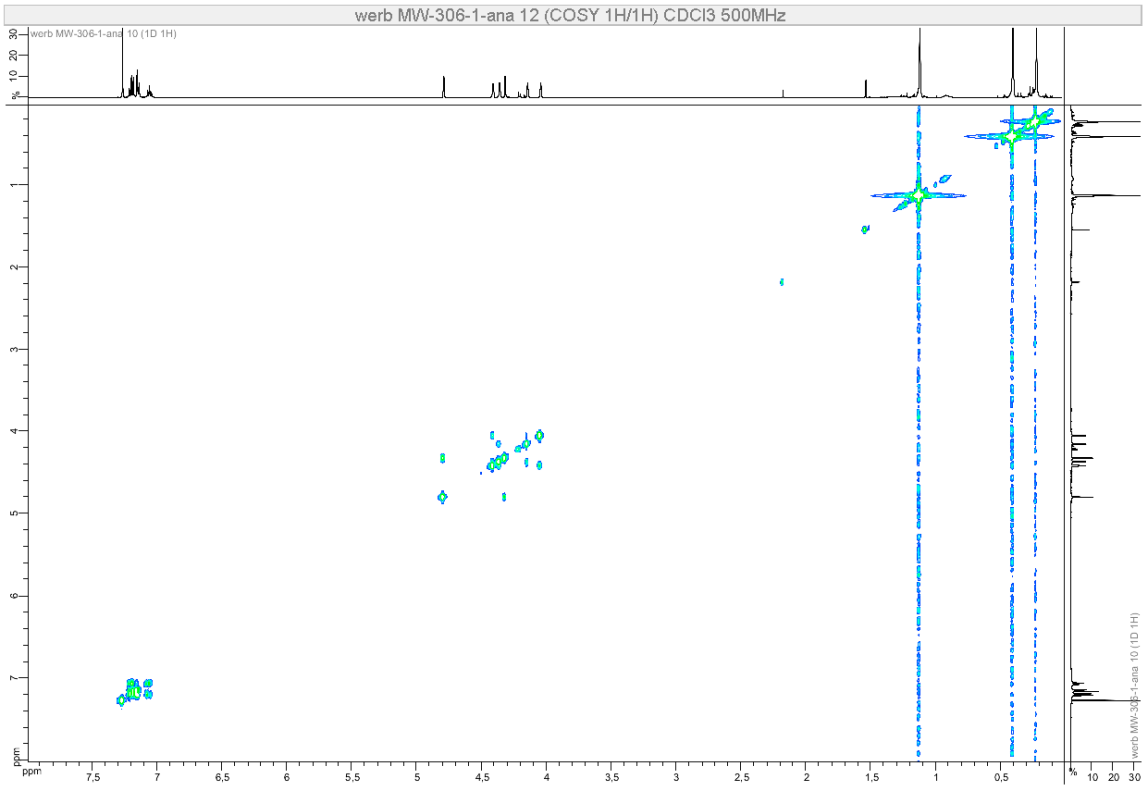
^{1}H NMR (500 MHz, $CDCl_3$)



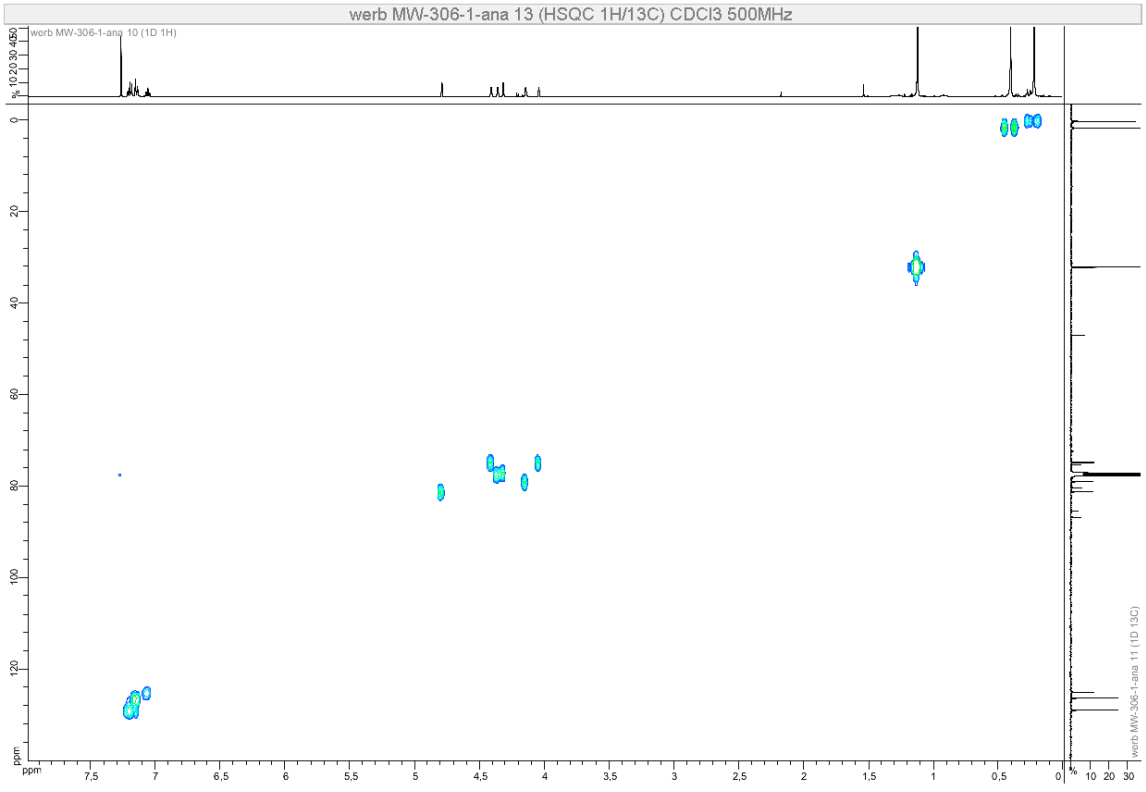
^{13}C NMR (126 MHz, $CDCl_3$)



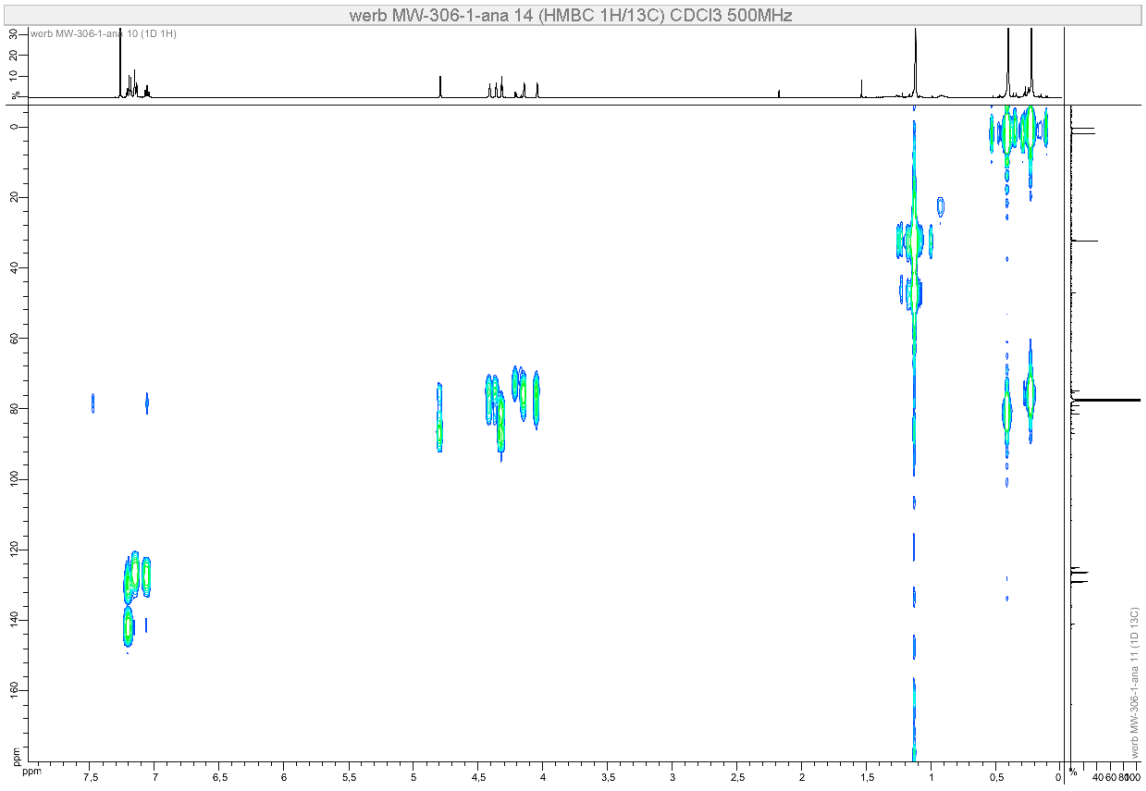
COSY (500 MHz, $CDCl_3$)



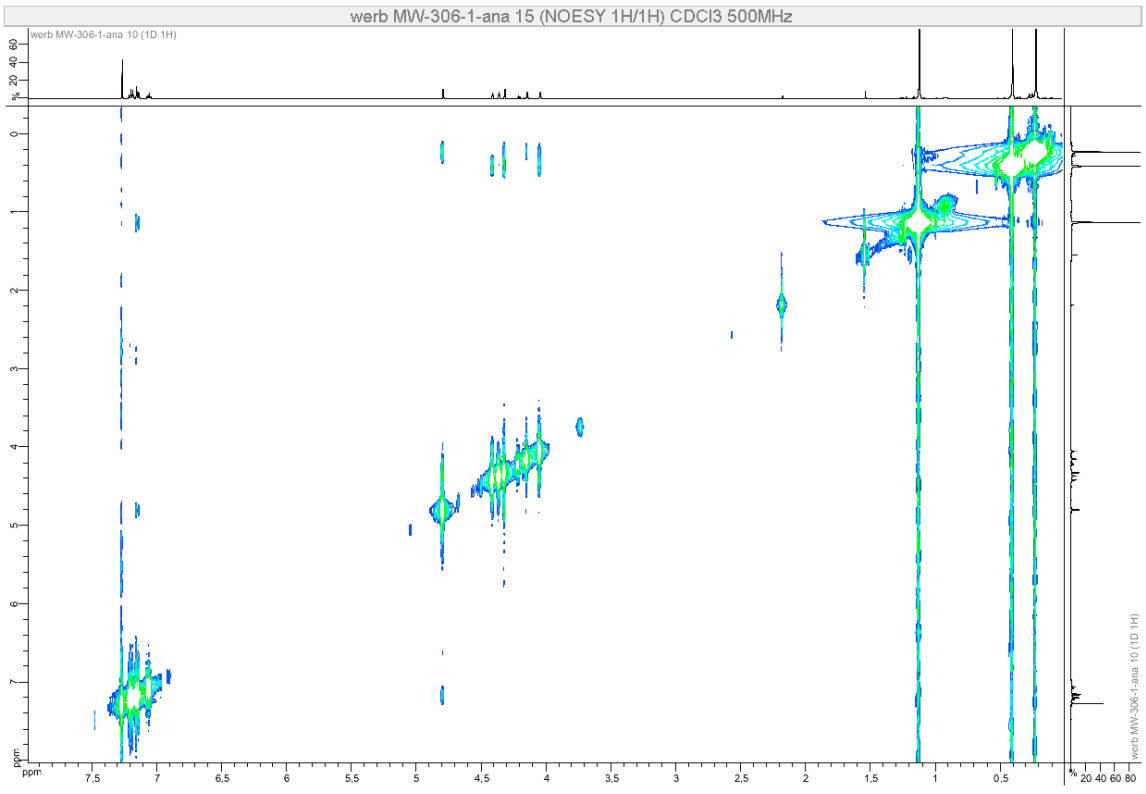
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

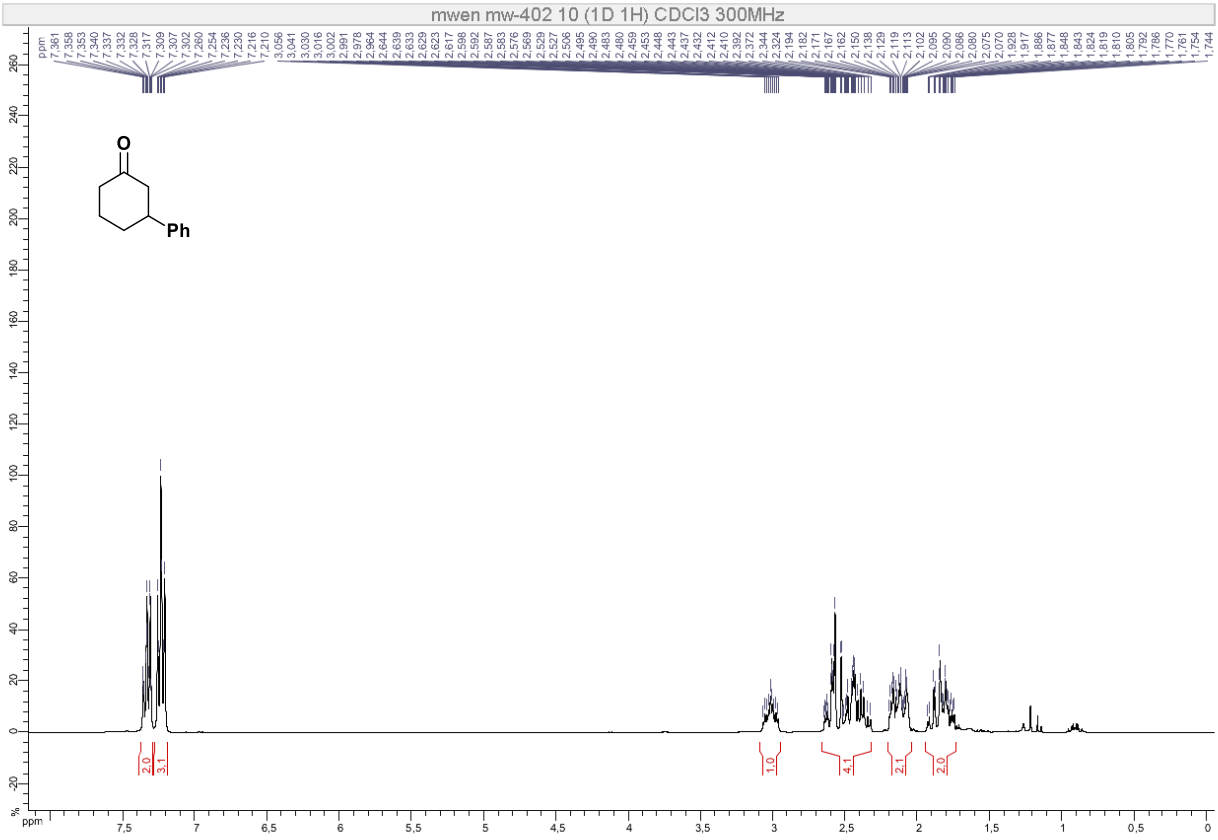


NOESY (500 MHz, $CDCl_3$)

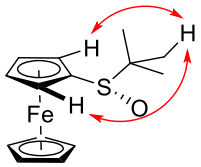


(*R*/*S*)-3-Phenylcyclohexanone

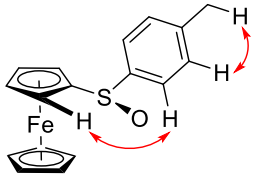
^{1}H NMR (300 MHz, $CDCl_3$)



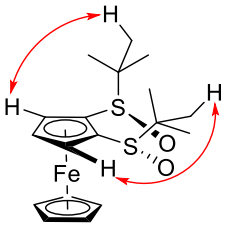
D) Selected NMR NOESY correlations



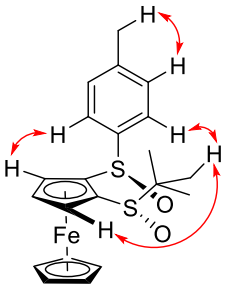
***S*-FcSO*t*Bu**



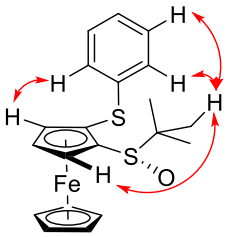
***S*-FcSO-*p*-tol**



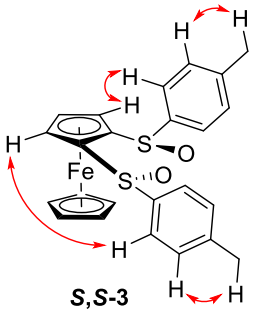
***R*,*R*-1**



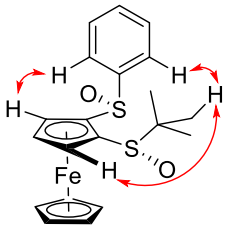
***S*,*S*,*R*$_P$-2**



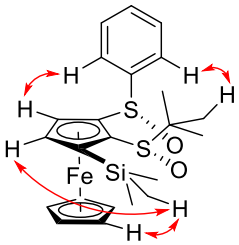
***S*,*S*$_P$-4**



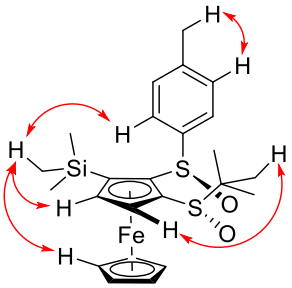
***S*,*S*-3**



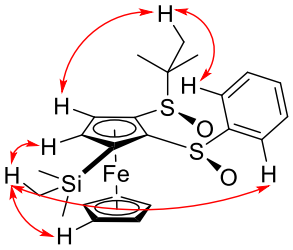
***S*,*S*,*R*$_P$-5**



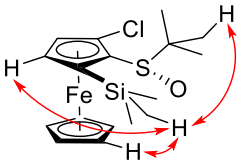
***S*,*S*,*R*$_P$-11**



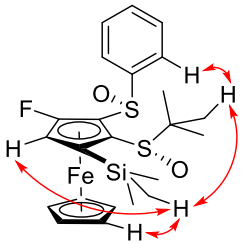
***S*,*S*,*R*$_P$-6a**



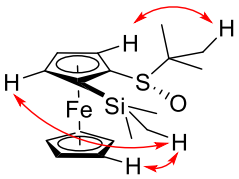
***R*,*R*,*S*$_P$-7a**



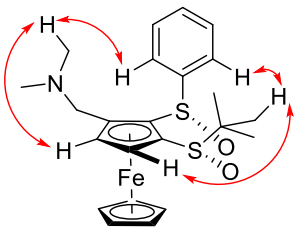
***S*,*R*$_P$-12a'**



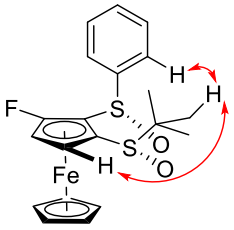
***S*,*S*,*R*$_P$-12b**



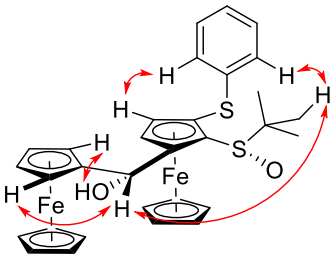
***S*,*R*$_P$-12b'**



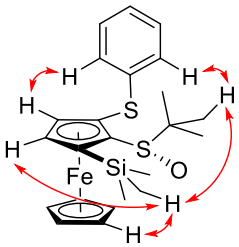
***S*,*S*,*R*$_P$-7b**



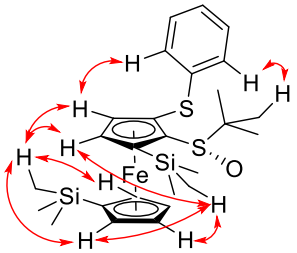
***S*,*S*,*R*$_P$-7d**



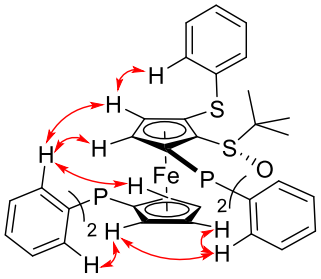
***S*,*S*$_P$-8a**



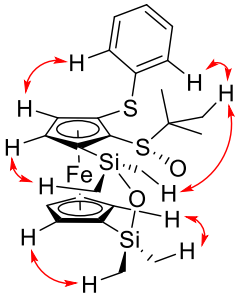
***S*,*S*$_P$-8b**



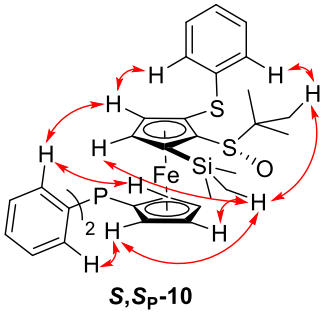
***S*,*S*$_P$-9a**



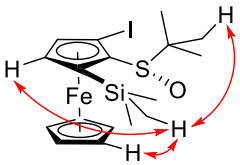
***S*,*S*$_P$-9b**



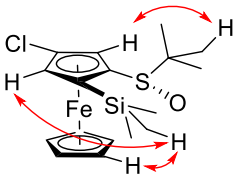
***S*,*S*$_P$-9c**



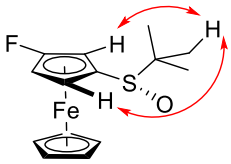
***S*,*S*$_P$-10**



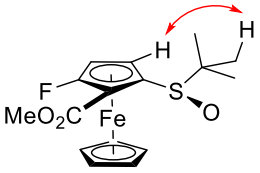
***S*,*R*$_P$-13a**



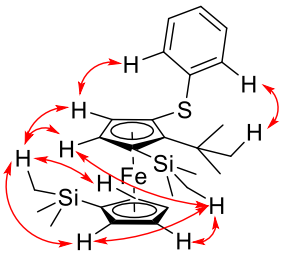
***S*,*R*$_P$-13b**



***S*,*S*$_P$-13c**



***R*,*R*$_P$-13d**



***S*$_P$-14**

E) HPLC Data

(±)-*S*-*tert*-Butylferrocenesulfoxide ((±)-FcSO*t*Bu)

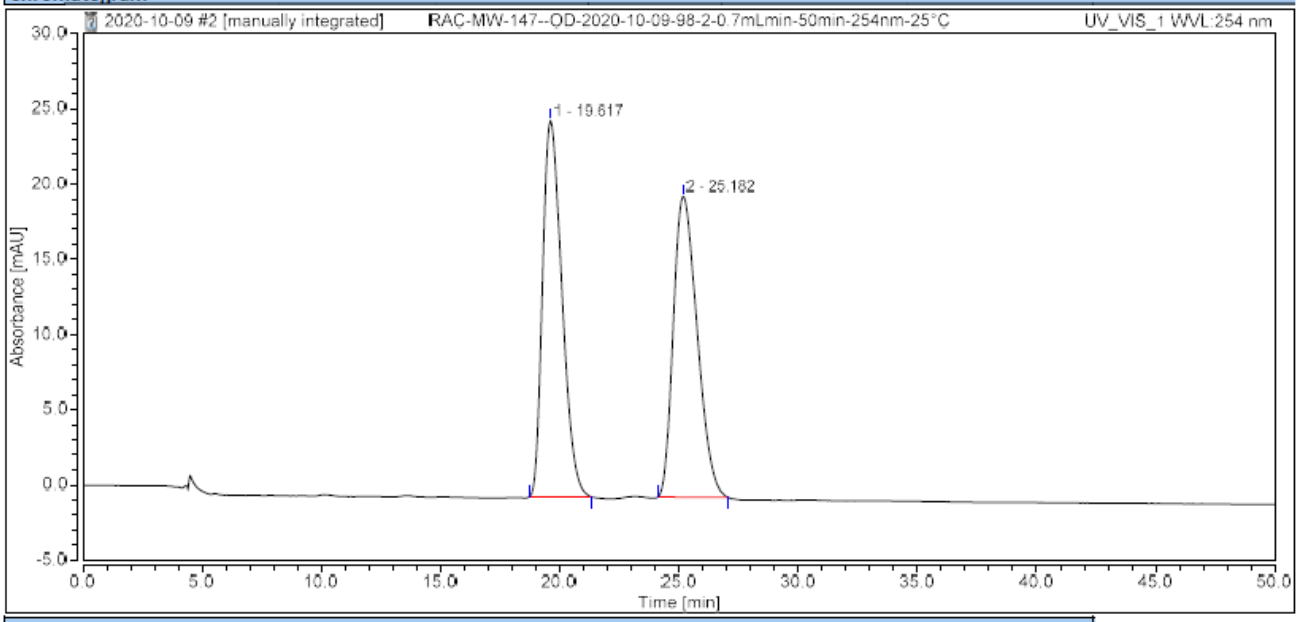
Chromatogram and Results

General informations	
Sequence Name:	2020-10-09
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC-3 DAICEL

Injection Details			
Injection Name:	RAC-MW-147--OD-2020-10-09-98-2-0.7mLmin-50mi	*Run Time:*	50.00 min
Instrument Method:	98-2-0.7mLmin-50min-254nm-25°C	*Injection Volume:*	2.00 µL
Injection Date/Time:	09/oct./20 10:56	*Channel:* UV_VIS_1	
		Wavelength:	254 nm

Instrument Method Details				
Instrument Method:	98-2-0.7mLmin-50min-254nm-25°C			
%A	Isopropanol	2 %		
%B	Hexane	98 %	*Température du four:*	25.0 °C
	Débit:	0.700 mL/min	*Pression:*	18 bars

Chromatogram



Peak Results						
No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		19.617	0.886	3.31	1.35	2717
2		25.182	1.097	n.a.	1.33	2920

Integration Results						
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		19.617	23.570	25.038	50.46	55.59
2		25.182	23.144	20.007	49.54	44.41
Total:			**46.714**	**45.045**	**100.00**	**100.00**

(*R*)-*S*-*tert*-Butylferrocenesulfoxide ((*R*)-FcSO*t*Bu)

Chromatogram and Results

General informations

Sequence Name:	2020-10-09
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC-3 DAICEL

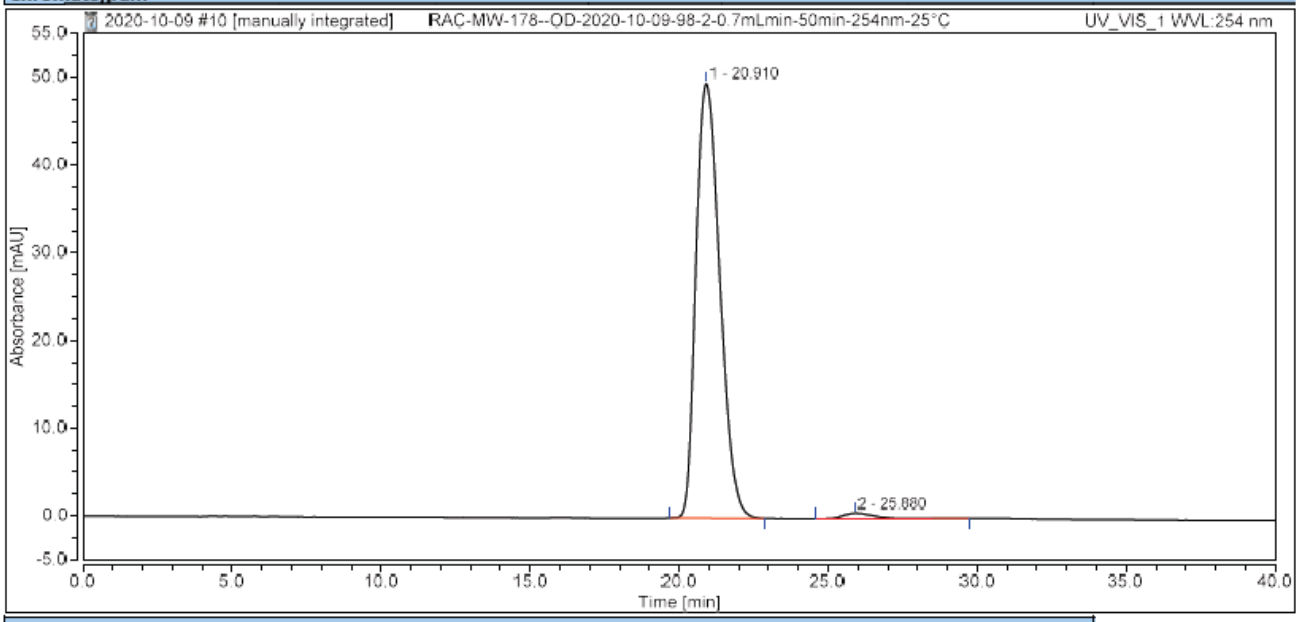
Injection Details

Injection Name:	RAC-MW-178--OD-2020-10-09-98-2-0.7mLmin-50mi	*Run Time:*	40.00 min
Instrument Method:	98-2-0.7mLmin-40min-254nm-25°C	*Injection Volume:*	2.00 µL
Injection Date/Time:	09/oct./20 17:13	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		98-2-0.7mLmin-40min-254nm-25°C			
%A	Isopropanol	2 %			
%B	Hexane	98 %	*Température du four:*	25.0 °C	
	Débit:	0.700 mL/min	*Pression:*	19 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		20.910	0.880	2.97	1.30	3131
2		25.880	1.092	n.a.	1.47	3112

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		20.910	45.851	49.552	98.40	98.80
2		25.880	0.746	0.604	1.60	1.20
Total:			**46.597**	**50.155**	**100.00**	**100.00**

(*S*)-*S*-*tert*-Butylferrocenesulfoxide ((*S*)-FcSO*t*Bu)

Chromatogram and Results

General informations

Sequence Name:	2020-10-15
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC-3 DAICEL

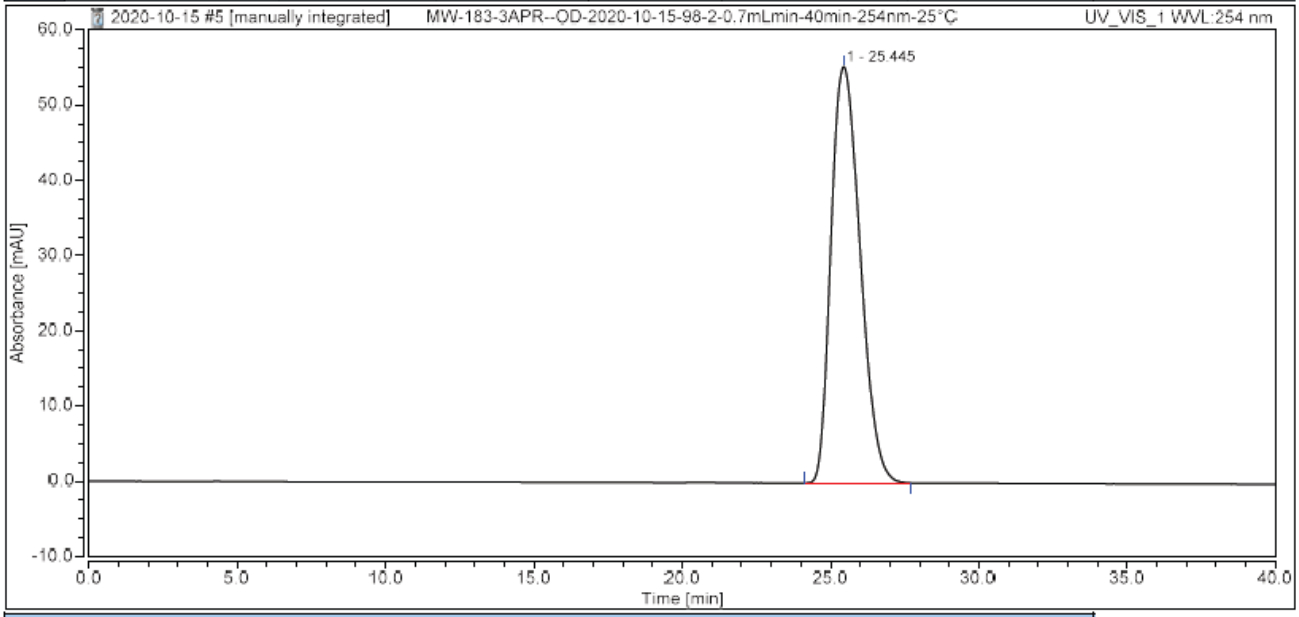
Injection Details

Injection Name:	MW-183-3APR--OD-2020-10-15-98-2-0.7mLmin-40m	*Run Time:*	40.00 min
Instrument Method:	98-2-0.7mLmin-40min-254nm-25°C	*Injection Volume:*	2.00 µL
Injection Date/Time:	15/oct./20 13:33	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	98-2-0.7mLmin-40min-254nm-25°C				
%A	Isopropanol	2 %			
%B	Hexane	98 %	*Température du four:*	25.0 °C	
	Débit:	0.700 mL/min	*Pression:*	18 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		25.445	1.083	n.a.	1.28	3056

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		25.445	63.027	55.389	100.00	100.00
Total:			**63.027**	**55.389**	**100.00**	**100.00**

(±)-*S*-(4-Tolyl)ferrocenesulfoxide ((±)-FcSO-*p*-Tol)

Chromatogram and Results

General informations

Sequence Name:	2021-12-03_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK ASH DAICEL

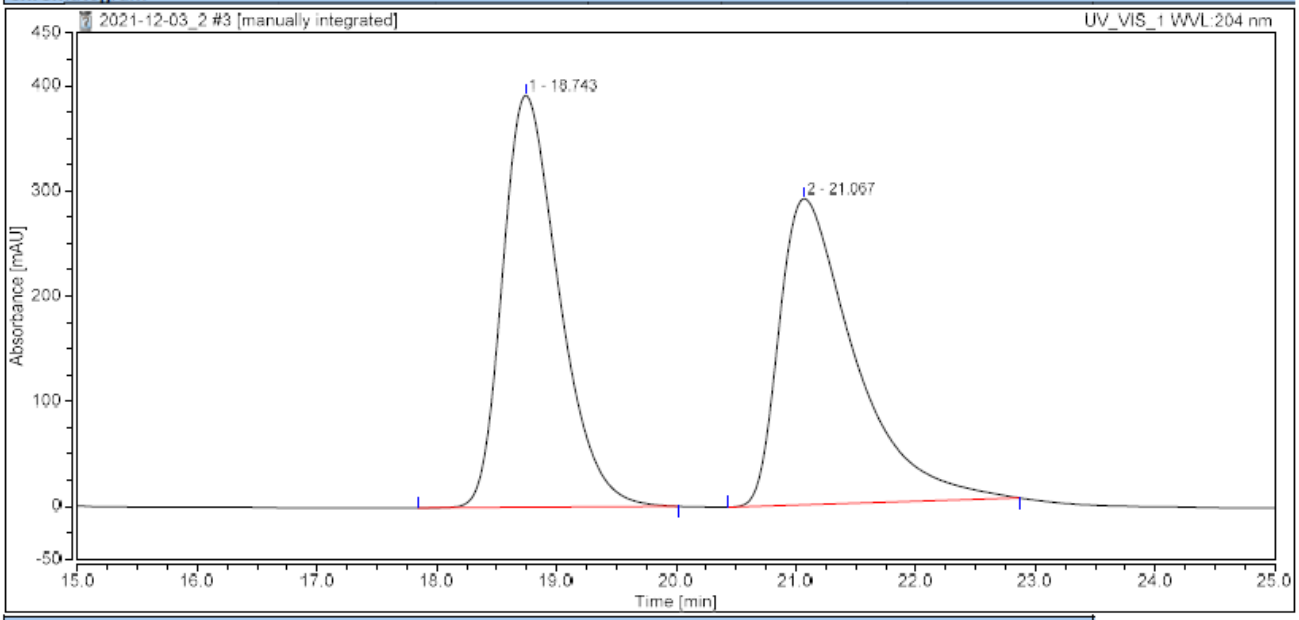
Injection Details

Injection Name:	RAC-MW-199-2-ODH-2021-12-03-90-10-30min-20°C	*Run Time:*	30.00 min
Instrument Method:	90-10-30min-20°C-204nm-0.8mLmin	*Injection Volume:*	1.00 µL
Injection Date/Time:	03/déc./21 17:57	*Channel:*	UV_VIS_1
		Wavelength:	204 nm

Instrument Method Details

Instrument Method:	90-10-30min-20°C-204nm-0.8mLmin		
%A	Isopropanol	10 %	
%B	Hexane	90 %	*Température du four:* 20.0 °C
	Débit:	0.800 mL/min	*Pression:* 34 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		18.743	0.502	2.40	1.37	7717
2		21.067	0.641	n.a.	2.03	5993

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1		18.743	214.105	391.328	50.20
2		21.067	212.386	290.877	49.80
Total:			**426.491**	**682.205**	**100.00**

(*S*)-*S*-(4-Tolyl)ferrocenesulfoxide ((*S*)-FcSO-*p*-Tol)

Chromatogram and Results

General informations

Sequence Name:	2021-12-03_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK ASH DAICEL

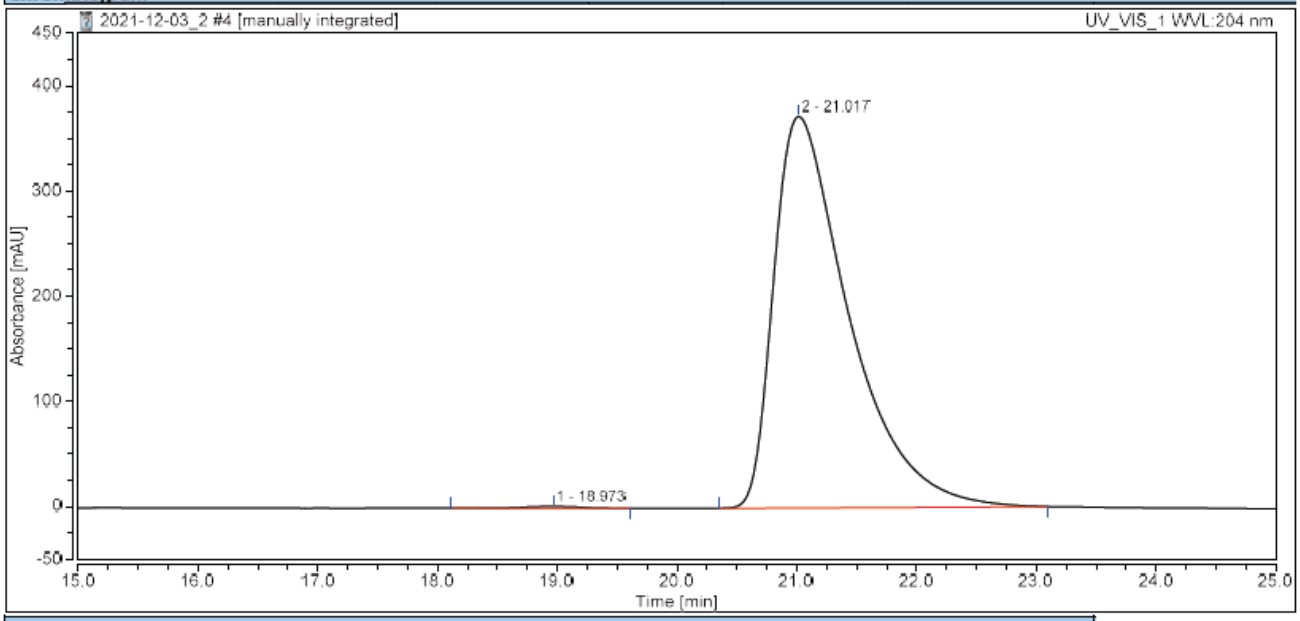
Injection Details

Injection Name:	MW455-recris-ODH-2021-12-03-90-10-30min-20°C-2	*Run Time:*	30.00 min
Instrument Method:	90-10-30min-20°C-204nm-0.8mLmin	*Injection Volume:*	1.00 µL
Injection Date/Time:	03/déc./21 18:28	*Channel:*	UV_VIS_1
		Wavelength:	204 nm

Instrument Method Details

Instrument Method:		90-10-30min-20°C-204nm-0.8mLmin		
%A	Isopropanol	10 %		
%B	Hexane	90 %	*Température du four:*	20.0 °C
	Débit:	0.800 mL/min	*Pression:*	34 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		18.973	0.499	2.11	0.84	8002
2		21.017	0.645	n.a.	1.92	5878

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1		18.973	0.988	1.809	0.36
2		21.017	270.183	371.941	99.64
Total:			**271.171**	**373.750**	**100.00**

(±)-3-Phenylcyclohexanone

Chromatogram and Results

General informations

Sequence Name:	2021-06-08_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC-3 DAICEL

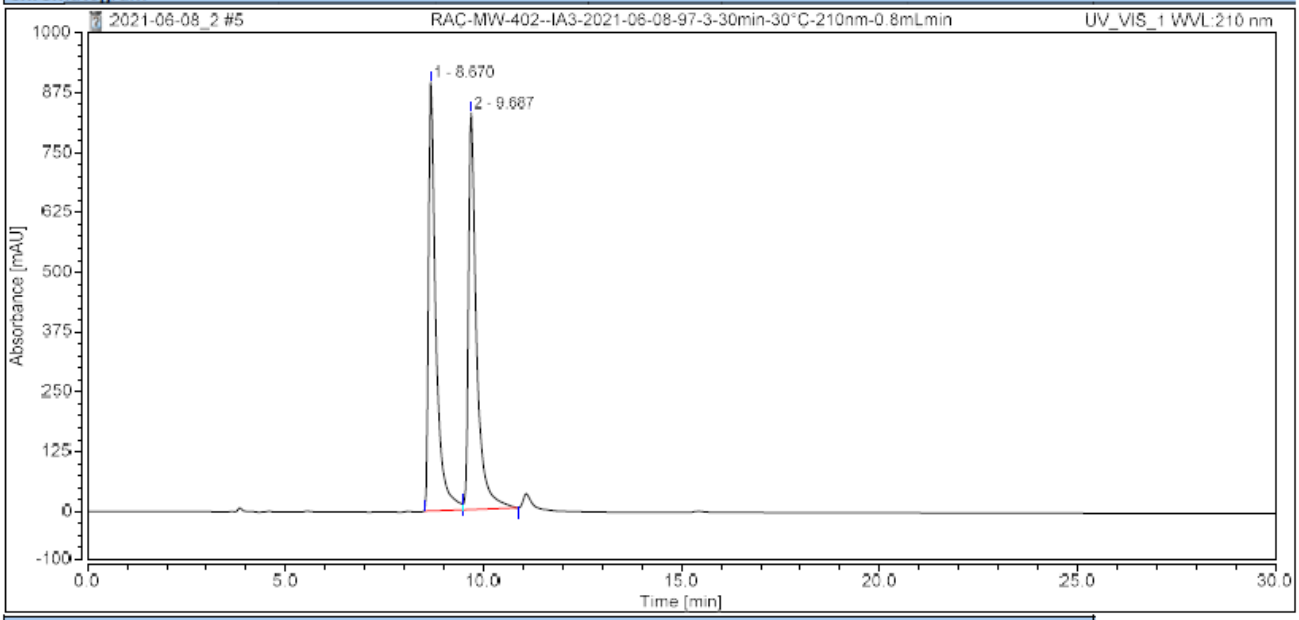
Injection Details

Injection Name:	RAC-MW-402--IA3-2021-06-08-97-3-30min-30°C-210	*Run Time:*	30.00 min
Instrument Method:	97-3-30min-30°C-210nm-0.8mLmin	*Injection Volume:*	5.00 µL
Injection Date/Time:	09/juin/21 00:11	*Channel:*	UV_VIS_1
		Wavelength:	210 nm

Instrument Method Details

Instrument Method:	97-3-30min-30°C-210nm-0.8mLmin		
%A	Isopropanol	3 %	
%B	Hexane	97 %	*Température du four:* 30.0 °C
	Débit:	0.800 mL/min	*Pression:* 61 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		8.670	0.174	3.31	2.22	13796
2		9.687	0.189	n.a.	2.05	14593

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		8.670	193.197	896.289	49.51	51.96
2		9.687	196.987	828.815	50.49	48.04
Total:			**390.184**	**1725.104**	**100.00**	**100.00**

(*S*)-3-Phenylcyclohexanone obtained by using ligand *S*,*S*,*R*p-2

Chromatogram and Results

General informations

Sequence Name:	**2021-06-08_2**
Instrument:	**U3000**
Logiciel used:	**Chromeleon**
Column used:	**CHIRALPAK IC-3 DAICEL**

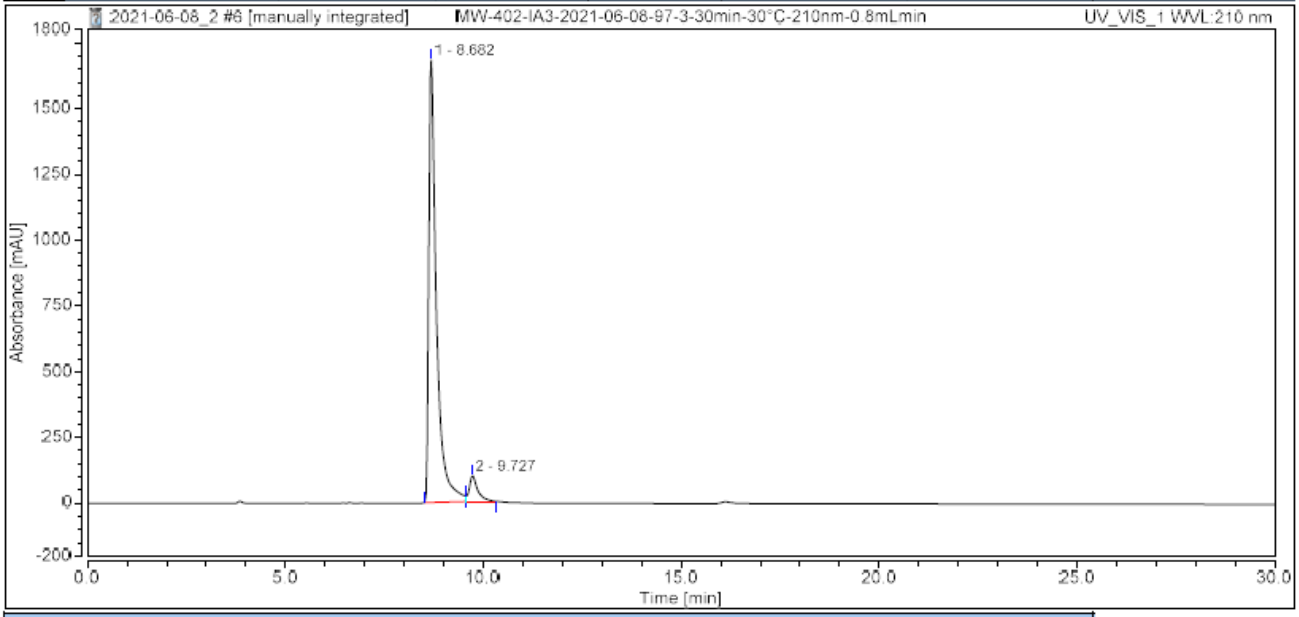
Injection Details

Injection Name:	**MW-402-IA3-2021-06-08-97-3-30min-30°C-210nm-0.**	*Run Time:*	**30.00 min**
Instrument Method:	**97-3-30min-30°C-210nm-0.8mLmin**	*Injection Volume:*	**5.00 µL**
Injection Date/Time:	**09/juin/21 00:41**	*Channel:*	**UV_VIS_1**
		Wavelength:	**210 nm**

Instrument Method Details

Instrument Method:	**97-3-30min-30°C-210nm-0.8mLmin**		
%A **Isopropanol**	**3 %**		
%B **Hexane**	**97 %**	*Température du four:*	**30.0 °C**
Débit:	**0.800 mL/min**	*Pression:*	**60 bars**

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		8.682	0.179	3.26	2.37	12965
2		9.727	0.199	n.a.	n.a.	13280

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		8.682	374.944	1681.907	93.94	94.46
2		9.727	24.193	98.612	6.06	5.54
Total:			**399.138**	**1780.518**	**100.00**	**100.00**

(*S*)-3-Phenylcyclohexanone obtained by using ligand *S,S*-3

Chromatogram and Results

General informations

Sequence Name:	2021-09-02_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA-3 DAICEL

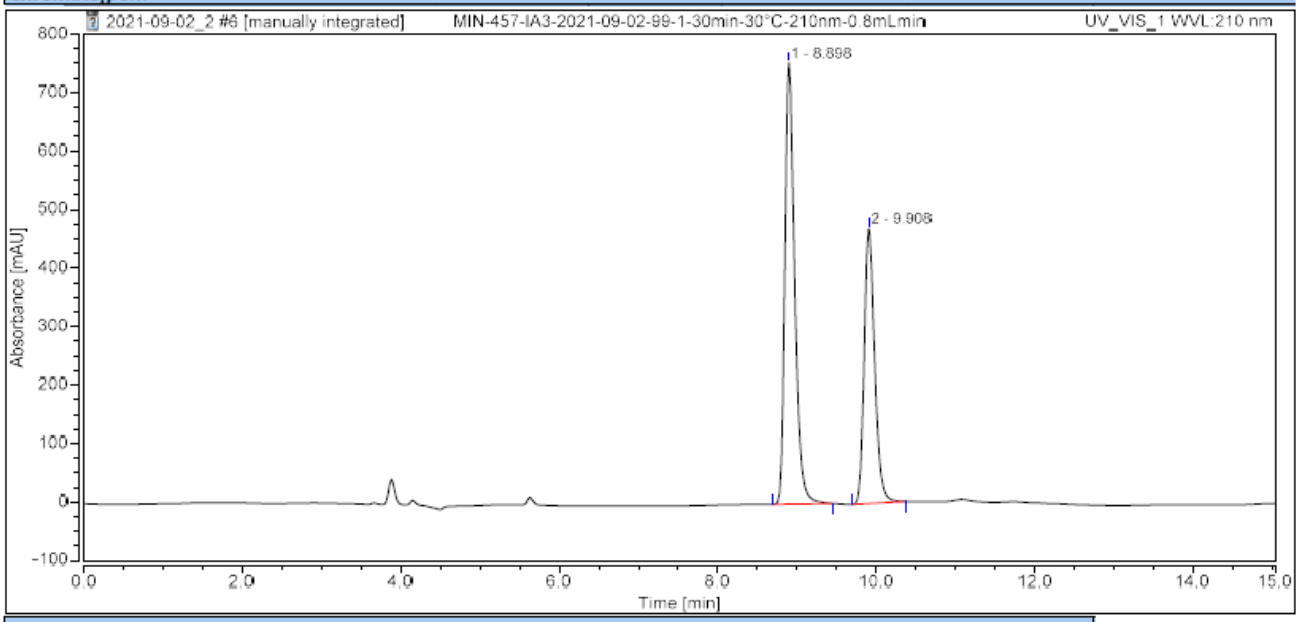
Injection Details

Injection Name:	MIN-457-IA3-2021-09-02-99-1-30min-30°C-210nm-0.	*Run Time:*	15.04 min
Instrument Method:	99-1-30min-30°C-210nm-0.8mLmin	*Injection Volume:*	20.00 µL
Injection Date/Time:	02/sept./21 15:26	*Channel:*	UV_VIS_1
		Wavelength:	210 nm

Instrument Method Details

Instrument Method:	99-1-30min-30°C-210nm-0.8mLmin		
%A	Isopropanol	3 %	
%B	Hexane	97 %	*Température du four:* 30.0 °C
	Débit:	0.800 mL/min	*Pression:* 58 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		8.898	0.129	4.46	1.39	26491
2		9.908	0.138	n.a.	1.24	28458

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		8.898	107.993	754.466	60.06	61.58
2		9.908	71.809	470.650	39.94	38.42
Total:			**179.802**	**1225.116**	**100.00**	**100.00**

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