

Supporting Information

Enantioselective Synthesis of Planar Chiral Ferrocene Triflones

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A) General and safety considerations, crystallography and electrochemical measurements

General. All reactions were carried out in Schlenk tubes under a dry argon atmosphere. Tetrahydrofuran (THF), Et₂O and toluene were freshly distilled from sodium-benzophenone under argon. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was distilled over CaH₂ under argon. (*R,R*)-bis(α -phenylethyl)amine [(*R*)-PEAH], (*S,S*)-bis(α -phenylethyl)amine [(*S*)-PEAH] and (+)-sparteine were purified by Kugelrohr distillation under vacuum and stored under argon. All alkyllithiums were titrated before use.^[1] 2,2,6,6-Tetramethylpiperidine (TMPH) was distilled over CaH₂ under vacuum and stored under argon. Room temperature (rt) refers to 25 °C. Column chromatography separations were achieved on silica gel (40-63 μ m). All Thin Layer Chromatographies (TLC) were performed on aluminium backed plates pre-coated with silica gel (Merck, Silica gGel 60 F254). They were visualised by exposure to UV light. Melting points were measured on a Kofler apparatus. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer, and the main absorption wavenumbers are given in cm⁻¹. ¹H and ¹³C{¹H} Nuclear Magnetic Resonance (NMR) spectra were recorded at 300 K either on a Bruker Avance III HD spectrometer fitted with a BBFO probe at 500 MHz and 126 MHz respectively, or on a Bruker Avance III spectrometer fitted with a BBFO probe at 400 MHz and 100 MHz respectively, or on a Bruker Avance III spectrometer fitted with a BBFO probe at 300 MHz and 75.4 MHz respectively. ¹H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ¹³C chemical shifts are relative to the central peak of the solvent signal.^[2] Signal assignment was based on 2D NMR experiments (COSY, HSQC, HMBC, NOESY and HOESY). Cp refers to the unsubstituted cyclopentadienyl ring of ferrocene. Specific rotations were determined from the observed rotation α measured on a Perkin Elmer 341 polarimeter (589 nm; 20 °C) using the equation $[\alpha] = (100 \cdot \alpha) / (l \cdot c)$ with the path length (*l*) given in dm and the concentrations (*c*) given in g/100 mL. Ferrocenesulfonyl fluoride^[3] and ZnCl₂·TMEDA^[4] were prepared as reported previously. (*R,R*)-*N,N,N',N'*-tetramethylcyclohexane-1,2-diamine [(*R*)-TMCDA] was prepared according to Jacobsen^[5] and Alexakis.^[6]

Throughout this supporting information, racemic mixtures are denoted **rac-X**, enantiopure compounds **R_P-X** or **S_P-X**, and enantioenriched compounds simply **X**.

Racemic ferrocene derivatives **rac-2a**, **rac-2b**, **rac-2c**, **rac-2d**, **rac-2e**, **rac-2f**, **rac-2h**, **rac-3af**, **rac-4af**, **rac-5f** and **rac-10** were prepared in unoptimised deprotolithiation-electrophilic trapping sequences using achiral bases for HPLC analysis purpose only.

Safety considerations. Due to its high pyrophoric character, *t*BuLi 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.

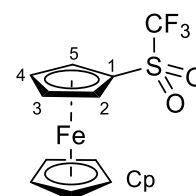
Crystallography. The samples were studied with monochromatised Mo-K α radiation ($\lambda = 0.71073$ Å). The X-ray diffraction data of the compounds **2aa**, **SP-2e**, **RP-2a**, **RP-3af**, **RP-4af**, **RP-5f**, **SP-9**, **SP-5I** and **SP-10** were collected at the temperature indicated in the crystal description by using a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 70 detector. The crystal structures were solved by dual-space algorithm using *SHELXT* program,^[7] and then refined with full-matrix least-square methods based on F^2 (*SHELXL* program).^[8] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The molecular diagrams were generated by Mercury 2020.3.0.

Electrochemical measurements. Measurements were performed in dry, oxygen-free CH₂Cl₂ at a concentration of 1 mM, with Bu₄NPF₆ (0.1 M) as the supporting electrolyte. For all the experiments, the working electrode was a glassy carbon disk (diameter 1.5 mm) which was polished (5 μ m grain size) with a slurry of alumina and ethanol and rinsed with CH₂Cl₂ before to use. The reference electrode was Ag/AgCl separated from the solution by a glass frit, while the counter electrode was a glassy carbon rod.

B) Compound synthesis, analyses, and X-ray crystallographic details

Ferrocenetriflone (**1**).

To ferrocenesulfonyl fluoride (14 g, 52 mmol) and 3 Å activated molecular sieves (11 g) in THF (52 mL) at rt was added Bu₄NF (1.0 M solution in THF; 52 mL, 52 mmol) and, dropwise over 2 h, Me₃SiCF₃ (Ruppert-Prakash's reagent; 31 mL, 0.21 mol). After addition of water (30 mL), the product was extracted using EtOAc (3 x 30 mL). Drying the organic phase over MgSO₄, removal of the solvent under reduced pressure and filtration over silica gel (eluent: petroleum ether-EtOAc 80:20) led to the mixture of **1** and starting ferrocenesulfonyl fluoride. This was dissolved in dioxane (250 mL) and treated with NaOH (4.2 g, 0.10 mol) in water (250 mL) at 85 °C for 16 h. After extraction using CH₂Cl₂ (3 x 50 mL), drying over MgSO₄ and removal of the solvent under reduced pressure, a filtration through silica (eluent: petroleum ether-EtOAc 80:20) led to the title product in 65% yield (11 g, 34 mmol) as an orange solid: R_f (eluent: petroleum ether-EtOAc 90:10) 0.67; mp 70-72 °C; IR (ATR) ν 759, 825, 898, 1018, 1034, 1104, 1176, 1192, 1211, 1351, 1413, 1740, 2921, 3120 cm⁻¹; ¹H NMR (CDCl₃) δ 4.51 (s, 5H, Cp), 4.66 (t, 1H, *J* = 2.0 Hz, H3 and H4), 4.80 (t, 2H, *J* = 2.0 Hz, H2 and H5) ppm; ¹³C{¹H} NMR (CDCl₃) δ 71.4 (5CH, Cp), 71.7 (2CH, C2 and C5), 73.7 (2CH, C3 and C4), 76.6 (q, C, *J* = 2.3 Hz, C1, C-SO₂CF₃), 119.4 (q, *J* = 325 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -79.5 ppm. The NMR data are similar to those reported.^[9]



General procedure 1 for the asymmetric deprotonation using stoichiometric chiral diamine.

The protocol was adapted from previously reported procedures.^[10] A solution of the desired butyllithium (1.2 mmol) was added dropwise to a solution of the desired diamine (1.2 mmol) in a solvent (3.5 mL) at -80 °C. After 0.5 h of stirring, a solution of ferrocenetriflone (**1**; 0.38 g, 1.2 mmol) in a solvent (2 mL) was added over 10 min using a syringe pump. After addition, the reaction mixture was stirred for 1 h at a given temperature. Me₃SiCl (0.15 mL, 0.13 g, 1.2 mmol) was added and the reaction mixture was stirred at -80 °C for 0.5 h. The reaction mixture was warmed to rt out of the cooling bath and stirred for 0.5 h. Aqueous HCl (1 M) was added, and the reaction mixture was extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, filtered over cotton wool, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5). The *ee* values were determined by HPLC analysis on a Chiralpak-IB column using hexane-*i*PrOH (99:1) as the eluent at 0.5 mL.min⁻¹ and 10 °C, λ = 254 nm, *t* (minor, **R_P-2a**) = 10.80 min, *t* (major, **S_P-2a**) = 11.66 min.

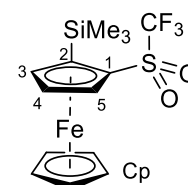
General procedure 2 for the asymmetric deprotonation using catalytic chiral diamine.

The protocol was adapted from previously reported procedures.^[10] *s*BuLi (1.0 M solution in cyclohexane; 1.2 mL, 1.2 mmol) was added dropwise to a solution of (+)-sparteine (0.11 mL, 0.11 g, 0.48 mmol) in *t*BuOMe (TBME; 3.5 mL) at -80 °C. After 0.5 h of stirring, the reaction mixture was

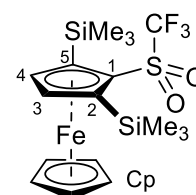
cooled to $-100\text{ }^{\circ}\text{C}$ and a solution of ferrocenetriflone (**1**; 0.38 g, 1.2 mmol) in *t*BuOMe (TBME; 2 mL) was added over 10 min using a syringe pump. After addition, the reaction mixture was stirred for 1 h at $-100\text{ }^{\circ}\text{C}$. The desired electrophile was then added (see details in the product description) and the reaction mixture was stirred at $-100\text{ }^{\circ}\text{C}$ for 0.5 h. The reaction mixture was warmed to rt out of the cooling bath and stirred for 0.5 h. Aqueous HCl (1 M) was added, and the reaction mixture was extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, filtrated over cotton wool, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography over silica gel (eluent given in the product description). The *ee* values were determined as above.

2-(Trimethylsilyl)ferrocenetriflone (**2a**).

Following the general procedure 1 using (+)-sparteine (275 μL , 0.28 g) and BuLi (1.15 M solution in hexane; 1.0 mL) in Et₂O at $-80\text{ }^{\circ}\text{C}$, the title product was obtained as an orange solid in 84% yield (0.39 g) and 26% *ee* in favour of the *S_P* enantiomer: R_f (eluent: petroleum ether) 0.54; mp 90-92 $^{\circ}\text{C}$; IR (ATR) ν 760, 832, 858, 957, 1004, 1042, 1067, 1111, 1144, 1185, 1209, 1247, 1274, 1356, 1414, 1711, 2902, 2957 cm^{-1} ; ¹H NMR (CDCl₃) δ 0.34 (s, 9H, SiMe₃), 4.49 (s, 5H, Cp), 4.58 (dd, 1H, *J* = 2.6 and 1.4 Hz, H3), 4.78 (t, 1H, *J* = 2.6 Hz, H4), 4.95-4.96 (m, 1H, H5) ppm; ¹³C{¹H} NMR (CDCl₃) δ 0.73 (3CH₃), 71.4 (5CH, Cp), 75.4 (CH, C4), 76.1 (CH, C5), 77.2 (C, C2, C-SiMe₃), 80.8 (CH, C3), 81.0 (q, C, *J* = 2.2 Hz, C1, C-SO₂CF₃), 119.5 (q, C, *J* = 326 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -78.6 ppm. Anal. Calcd for C₁₄H₁₇F₃FeO₂SSi (390.27): C, 43.09; H, 4.39; S, 8.21. Found: C, 43.05; H, 4.57; S, 8.15%.



2,5-Bis(trimethylsilyl)ferrocenetriflone (**2aa**) was also obtained in 2% yield (11 mg) as an orange solid: R_f (petroleum ether-EtOAc 95:5) 0.78; mp 159-160 $^{\circ}\text{C}$; IR (ATR) ν 691, 762, 825, 889, 904, 1004, 1084, 1122, 1188, 1210, 1226, 1251, 1353, 1412, 2959 cm^{-1} ; ¹H NMR (CDCl₃) δ 0.35 (s, 18H, 2SiMe₃), 4.47 (s, 5H, Cp), 4.72 (s, 2H, H3 and H4) ppm; ¹³C{¹H} NMR (CDCl₃) δ 1.3 (6CH₃), 71.6 (5CH, Cp), 81.2 (2C, C2 and C5, C-SiMe₃), 83.5 (2CH, C3 and C4), 85.1 (q, C, *J* = 2.3 Hz, C1, C-SO₂CF₃), 119.6 (q, C, *J* = 328 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -75.7 ppm.



2% of starting **1** were recovered.

Compound **2aa** was obtained in 66% yield (0.36 g) when 2 equivalents of chelate were employed.

Following the general procedure 1 using (+)-sparteine (275 μL , 0.28 g) and *s*BuLi (1.0 M solution in cyclohexane; 1.2 mL) in Et₂O at $-80\text{ }^{\circ}\text{C}$, **2a** was obtained in 78% yield (365 mg) and 59% *ee* in favour of the *S_P* enantiomer. Compound **2aa** was also isolated in 14% yield (76 mg).

Following the general procedure 1 using (+)-sparteine (275 μL , 0.28 g) and *s*BuLi (1.0 M solution in cyclohexane; 1.2 mL) in *t*BuOMe (TBME) at $-80\text{ }^{\circ}\text{C}$, **2a** was obtained in 86% yield (405 mg) and 67% *ee* in favour of the *S_P* enantiomer. Compound **2aa** (1% yield, 51 mg) and **1** (2% yield, 7 mg) were also isolated.

Following the general procedure 1 using (+)-sparteine (275 μ L, 0.28 g) and *s*BuLi (1.0 M solution in cyclohexane; 1.2 mL) in *t*BuOMe (TBME) at -100 $^{\circ}$ C, **2a** was obtained in 85% yield (0.40 g) and 84% *ee* in favour of the *S_P* enantiomer. Compound **2aa** (2% yield, 11 mg) and **1** (4% yield, 15 mg) were also isolated.

Following the general procedure 1 using (*R*)-TMCDA (0.23 mL, 0.20 g) and BuLi (1.4 M solution in hexane; 0.86 mL) in Et₂O at -80 $^{\circ}$ C, **2a** was obtained in 23% yield (0.11 g) and 4% *ee* in favour of the *S_P* enantiomer. 36% of starting **1** were recovered.

Following the general procedure 1 using (*R*)-TMCDA (0.23 mL, 0.20 g) and *s*BuLi (1.0 M solution in cyclohexane; 1.2 mL) in Et₂O at -80 $^{\circ}$ C, *rac*-**2a** was obtained in 42% yield (0.20 g). Compound **2aa** was also isolated in 1% yield (7 mg) while 41% of starting **1** were recovered.

Following the general procedure 2 using Me₃SiCl (0.15 mL, 0.13 g, 1.2 mmol), the title product was obtained (eluent: petroleum ether-EtOAc 95:5) in 51% yield (0.24 g) and 80% *ee* in favour of the *S_P* enantiomer. 39% of starting **1** were also recovered.

Crystal data for 2aa. C₁₇H₂₅F₃FeO₂SSi₂, *M* = 462.46, *T* = 150(2) K; monoclinic *P* 2₁/*n* (I.T.#14), *a* = 11.568(2), *b* = 12.885(2), *c* = 13.879(2) \AA , β = 90.807(7) $^{\circ}$, *V* = 2068.5(6) \AA^3 . *Z* = 4, *d* = 1.485 g.cm⁻³, μ = 0.981 mm⁻¹. A final refinement on *F*² with 4714 unique intensities and 152 parameters converged at $\omega R(F)^2$ = 0.2382 (*R_F* = 0.1037) for 4522 observed reflections with *I* > 2 σ . CCDC 2364199.

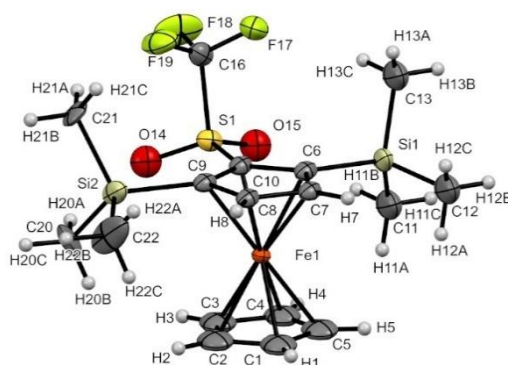
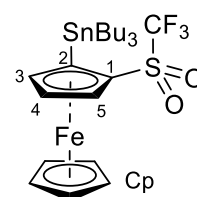


Figure S1. Molecular structure of compound **2aa** (thermal ellipsoids shown at the 30% probability level). Selected lengths [\AA] and angles ($^{\circ}$): C9-Si2 1.951(6), C10-S1 1.698(5), C6-Si1 1.924(6), C10-Cg2...Cg1-C4 41.63 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C9-C10-S1-O14 -24.5(6), C6-C10-S1-O15 20.4(6), C16-S1-C10-C9 86.9(6).

2-(Tributylstannyl)ferrocenetriflone (**2b**).

Following the general procedure 2 using Bu₃SnCl (325 μ L, 0.39 g, 1.2 mmol), the title product was obtained (eluent: petroleum ether-EtOAc 95:5; *R_f* 0.76) in 67% yield (0.49 g), and 82% *ee* in favour of the *R_P* enantiomer as an orange oil: IR (ATR) ν 760, 826, 861, 931, 960, 1003, 1073, 1110, 1185, 1213, 1275, 1357, 1415, 1464, 2854, 2921, 2956 cm⁻¹; ¹H NMR (CDCl₃) δ 0.92 (t, 9H, *J* = 7.3 Hz, 3Me), 1.08-1.19 (m, 6H, 3CH₂Pr), 1.37 (h, 6H, *J* = 7.2 Hz, 3CH₂Me), 1.52-1.58 (m, 6H, 3CH₂CH₂Et), 4.43



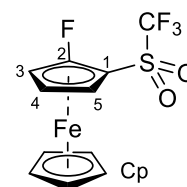
(s, 5H, Cp), 4.48 (dd, 1H, $J = 2.5$ and 1.3 Hz, H3), 4.80 (t, 1H, $J = 2.4$ Hz, H4), 4.94 (d, 1H, $J = 4.0$ Hz, H5) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 11.4 (3CH₂, CH₂Pr), 13.8 (3CH₃), 27.5 (3CH₂, CH₂Me), 29.2 (3CH₂, CH₂CH₂Et), 71.1 (5CH, Cp), 74.4 (CH, C5), 76.1 (C, C2, C-Sn), 76.4 (CH, C4), 80.5 (CH, C3), 81.6 (q, C, $J = 2.1$ Hz, C1, C-SO₂CF₃), 119.5 (q, C, $J = 326$ Hz, CF₃) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -78.9 ppm; $[\alpha]_D^{20}$ -11.6 (c 1.0, CHCl₃). Anal. Calcd for C₂₃H₃₅F₃FeO₂SSn (607.14): C, 45.50; H, 5.81; S, 5.28. Found: C, 45.59; H, 5.98; S, 5.19%.

The *ee* value was determined by HPLC analysis on a Chiralpak-ODH column using hexane-*i*PrOH (99:1) as the eluent at 0.4 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (major, **SP-2b**) = 8.94 min, t (minor, **RP-2b**) = 9.56 min.

27% of starting **1** were also recovered.

2-Fluoroferoconetriflone (2c).

Following the general procedure 2 using a solution of *N*-fluorobenzenesulfonimide (NFSI; 0.38 g, 1.2 mmol) in THF (3 mL), the title product was obtained (eluent: petroleum ether-EtOAc 94:6; R_f 0.32) in 32% yield (0.13 g) and 79% *ee* in favour of the *S_P* enantiomer as an orange solid: mp 65-66 °C; IR (ATR) ν 457, 487, 515, 545, 563, 617, 665, 761, 805, 827, 1003, 1077, 1120, 1178, 1216, 1366, 1403, 1467 cm⁻¹; ^1H NMR (CDCl_3) δ 4.35 (td, 1H, $J = 2.9$ and 1.6 Hz, H4), 4.47 (dd, 1H, $J = 3.0$ and 1.6 Hz, H5), 4.62 (s, 5H, Cp), 4.80 (td, 1H, $J = 2.9$ and 1.6 Hz, H3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 61.3 (d, CH, $J = 13.1$ Hz, C3), 65.2 (d, CH, $J = 3.0$ Hz, C4), 65.7 (ddd, C, $J = 12.0$ and 2.0 Hz, C1, C-SO₂CF₃), 65.8 (CH, C5), 72.8 (5CH, Cp), 119.4 (q, C, $J = 325$ Hz, CF₃), 134.5 (d, C, $J = 285$ Hz, C2, C-F) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -185.9 (q, 3F, $J = 1.7$ Hz, CF₃), -79.5 (d, 1F, $J = 1.6$ Hz, C2-F) ppm; $[\alpha]_D^{20}$ -3.6 (c 0.5, CHCl₃). Anal. Calcd for C₁₁H₈F₄FeO₂S (336.08): C, 39.31; H, 2.40; S, 9.54. Found: C, 39.54; H, 2.78; S, 9.29%.

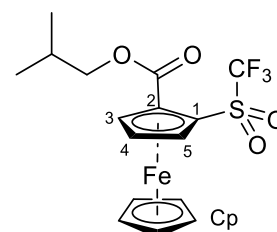


The *ee* value was determined by HPLC analysis on a Chiralpak-IC column using hexane-*i*PrOH (99:1) as the eluent at 0.5 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (minor, **RP-2c**) = 19.43 min, t (major, **SP-2c**) = 17.39 min.

63% of starting **1** were recovered.

2-(Isobutoxycarbonyl)ferroconetriflone (2d).

Following the general procedure 2 using ClCO₂iBu (155 μL , 0.16 g, 1.2 mmol), the title product was obtained (eluent: petroleum ether-EtOAc 90:10; R_f 0.39) in 77% yield (0.39 g) and 84% *ee* in favour of the *S_P* enantiomer as a red solid: mp 64-66 °C; IR (ATR) ν 769, 792, 816, 837, 869, 908, 947, 972, 991, 1035, 1072, 1117, 1155, 1188, 1210, 1273, 1328, 1358, 1440, 1705, 2972 cm⁻¹; ^1H NMR (CDCl_3) δ 1.00 (t, 6H, $J = 6.7$ Hz, CHMe₂), 2.04 (non, 1H, $J = 6.7$ Hz, CHMe₂), 4.01 (dd, 1H, $J = 10.6$ and 6.6 Hz, CHHiPr), 4.07 (dd, 1H, $J = 10.6$ and 6.6 Hz, CHHiPr), 4.58 (s, 5H, Cp), 4.82 (t, 1H, $J = 2.8$ Hz, H4), 5.00 (dd, 1H, $J = 2.8$ and 1.7 Hz, H5), 5.29 (dd, 1H, $J = 2.8$ and



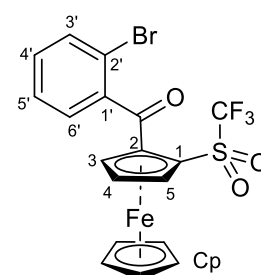
1.7 Hz, H3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 19.2 (CH_3), 19.3 (CH_3), 27.9 (CH , CHMe_2), 71.9 (CH_2 , CH_2iPr), 73.4 (5CH, Cp), 73.6 (CH , C4), 76.3 (q, C, $J = 2.4$ Hz, C1, C-SO₂CF₃), 76.6 (C, C2, C-CO₂iBu), 77.5 (CH , C5), 78.9 (CH , C3), 119.6 (q, C, $J = 326$ Hz, CF₃), 167.6 (C, CO₂iBu) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -76.9 ppm; $[\alpha]_D^{20} +15.2$ (c 1.0, CHCl_3). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{FeO}_4\text{S}$ (418.21): C, 45.95; H, 4.10; S, 7.67. Found: C, 45.86; H, 4.33; S, 7.78%.

The *ee* value was determined by HPLC analysis on a Chiralpak-IB column using hexane-isopropanol (99:1) as the eluent at 0.5 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (minor, **RP-2d**) = 22.35 min, t (major, **SP-2d**) = 23.22 min.

14% of starting **1** were recovered.

2-(2-Bromobenzoyl)ferrocenetriflone (**2e**).

Following the general procedure 2 using ferrocenetriflone (1.6 g, 5.0 mmol), *s*BuLi (4.55 mL, 5.0 mmol), (+)-sparteine (0.46 mL, 0.47 g, 2.0 mmol) and 2-BrC₆H₄C(O)Cl (0.65 mL, 1.1 g, 5.0 mmol), and warming the reaction mixture to -60 °C instead of rt after addition of the electrophile, the title product was obtained (eluent: petroleum ether-EtOAc-NEt₃ 78:20:2 to 69:29:2) in 77% yield (1.9 g) and 83% *ee* in favour of the *S_P* enantiomer as a red solid: R_f (eluent: petroleum ether-EtOAc 70:30) 0.46; mp 211-212 °C (dec.); IR (ATR) ν 454, 497, 517, 556, 596, 633, 649, 688, 735, 756, 777, 836, 871, 887, 1012, 1028, 1044, 1062, 1088, 1122, 1172, 1189, 1198, 1210, 1242, 1270, 1336, 1352, 1428, 1589, 1670, 3122 cm⁻¹; ^1H NMR (CDCl_3) δ 4.64 (s, 5H, Cp), 4.83 (dd, 1H, $J = 2.8$ and 1.6 Hz, H3), 4.88 (t, 1H, $J = 2.8$ Hz, H4), 5.24 (dd, 1H, $J = 2.7$ and 1.6 Hz, H5), 7.33 (ddd, 1H, $J = 8.0$, 6.7 and 2.5 Hz, H4'), 7.39-7.44 (m, 2H, H5' and H6'), 7.62 (d, 1H, $J = 8.3$ Hz, H3') ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 73.7 (5CH, Cp), 74.3 (CH, C4), 78.6 (q, C, $J = 2.3$ Hz, C1, C-SO₂CF₃), 78.9 (CH, C5), 80.3 (CH, C3), 81.8 (C, C2, C-CO), 119.5 (C, C2', C-Br), 119.6 (q, C, $J = 327$ Hz, CF₃), 127.2 (CH, C5' or C6'), 128.6 (CH, C5' or C6'), 131.5 (CH, C4'), 133.6 (CH, C3'), 141.2 (C, C1', C-CO), 195.3 (C, C=O) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -76.4 ppm; $[\alpha]_D^{20} +109.7$ (c 1.0, CHCl_3). Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{BrF}_3\text{FeO}_3\text{S}$ (501.10): C, 43.15; H, 2.41; S, 6.40. Found: C, 43.14; H, 2.43; S, 6.19%.



The *ee* value was determined by HPLC analysis on a Chiralpak-IB column using hexane-isopropanol (80:20) as the eluent at 1.0 mL.min⁻¹ and 25 °C, $\lambda = 254$ nm, t (minor, **RP-2e**) = 16.68 min, t (major, **SP-2e**) = 9.98 min.

A solution of the title product in CHCl_3 (40 mL) in a Schlenk tube was layered with petroleum ether (200 mL) and was let aside for 3 days, shielded from light using aluminum foil. The resulting crystals were filtrated and washed with the minimal amount of cold petroleum ether to give the title product in 53% yield (1.3 g) and > 99.5% *ee*.

Crystal data for SP-2e. $\text{C}_{18}\text{H}_{12}\text{BrF}_3\text{FeO}_3\text{S}$, $M = 501.10$, $T = 150(2)$ K; orthorhombic $P 2_1 2_1 2_1$ (I.T.#19), $a = 7.5739(6)$, $b = 11.7599(12)$, $c = 20.1567(13)$ Å, $V = 1795.3(3)$ Å³. $Z = 4$, $d = 1.854$ g.cm⁻³

³, $\mu = 3.228 \text{ mm}^{-1}$. A final refinement on F^2 with 4097 unique intensities and 192 parameters converged at $\omega R(F^2) = 0.0759$ ($R_F = 0.0301$) for 3869 observed reflections with $I > 2\sigma$. CCDC 2364200.

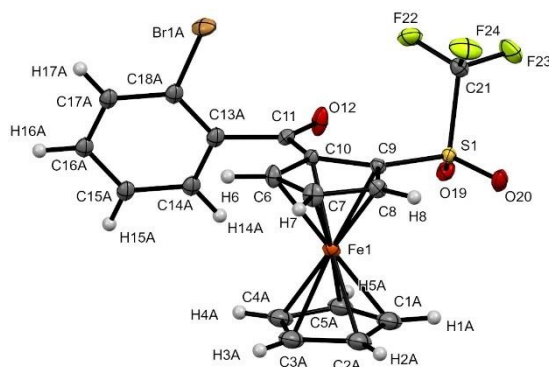
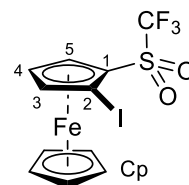


Figure S2. Molecular structure of compound **Sp-2e** (thermal ellipsoids shown at the 30% probability level). Selected lengths [\AA] and angles ($^\circ$): C10-C11 1.469(5), C9-S1 1.723(4), C9-Cg2...Cg1-C1 26.17 (Cg1 being the centroid of the C1A-C2A-C3A-C4A-C5A ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C8-C9-S1-O20 7.9(4), C10-C9-S1-O19 -34.1(4), C21-S1-C9-C8 -102.3(3).

Deprotolithiation using (*R*)-PEALi in the presence of [(*R*)-PEA]₂Zn as an *in situ* trap.

The protocol was adapted from a previously reported procedure.^[11] To a solution of [(*R*)-PEA]₂Zn [prepared by adding BuLi (1.3 M solution in hexane; 1.2 mL, 1.6 mmol) and, 5 min later, ZnCl₂·TMEDA (0.20 g, 0.80 mmol) to (*R*)-PEAH (0.37 mL, 1.6 mmol) in THF (5 mL) at -15°C and stirring at this temperature for 15 min], was added ferrocenetriflone (**1**; 0.25 g, 0.80 mmol). The mixture was stirred for 15 min at -15°C and cooled to -80°C before dropwise addition of a (*R*)-PEALi solution [prepared by adding BuLi (1.3 M solution in hexane; 0.62 mL, 0.80 mmol) to (*R*)-PEAH (0.18 mL, 0.80 mmol) in THF (5 mL) at -15°C and stirring at this temperature for 5 min before cooling to -80°C]. The temperature was raised to -10°C over 3 h before addition of a solution of I₂ (0.61 g, 2.4 mmol) in THF (3 mL) and, 1 h later, treatment with saturated aqueous Na₂S₂O₃ (10 mL). Extraction with EtOAc (3 x 10 mL), drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5) to afford 2-iodoferrocenetriflone (**2f**) in 10% yield (36 mg) and 51% *ee* in favour of the *R_P* enantiomer as an orange solid: R_f (eluent: petroleum ether-EtOAc 90:10) 0.60; mp 112-114 $^\circ\text{C}$; IR (ATR) ν 759, 823, 924, 1033, 1108, 1188, 1215, 1293, 1359, 2969, 3117 cm^{-1} ; ¹H NMR (CDCl₃) δ 4.53 (s, 5H, Cp), 4.70 (t, 1H, $J = 2.7$ Hz, H4), 4.88 (dd, 1H, $J = 2.9$ and 1.5 Hz, H5), 4.93 (dd, 1H, $J = 2.6$ and 1.5 Hz, H3) ppm; ¹³C{¹H} NMR (CDCl₃) δ 38.1 (C, C2, C-I), 73.0 (CH, C5), 74.5 (5CH, Cp), 74.7 (CH, C4), 77.9 (q, C, $J = 2.3$ Hz, C1, C-SO₂CF₃), 82.4 (CH, C3), 119.4 (q, C, $J = 326$ Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -78.2 ppm. Anal. Calcd for C₁₁H₈F₃FeIO₂S (443.99): C, 29.76; H, 1.82; S, 7.22. Found: C, 29.85; H, 2.01; S, 7.32%.



79% of starting **1** were recovered.

When (*R*)-PEAH was replaced by (*S*)-PEAH, **2f** was obtained in an estimated 22% yield (79 mg) and 61% *ee* in favour of the *S_P* enantiomer while 55% of starting **1** were recovered.

The *ee* values were determined by HPLC analysis on a Chiralpak-OD column using hexane-*i*PrOH (99:1) as the eluent at 0.4 mL.min⁻¹ and 10 °C, λ = 254 nm, *t* (minor, **Sp-2f**) = 28.40 min, *t* (major, **Rp-2f**) = 32.19 min.

Deprotolithiation using (*S*)-PEALi in the presence of ZnCl₂·TMEDA as an *in situ* trap.

The protocol was adapted from a previously reported procedure.^[11] A solution of (*S*)-PEALi [prepared by adding BuLi (1.3 M solution in hexane; 2.6 mL, 3.3 mmol) to a solution of (*S*)-PEAH (755 μ L, 3.3 mmol) in THF (7 mL) at -15 °C and stirring at this temperature for 5 min before cooling to -90 °C] was added to a solution of ferrocenetriflone (**1**; 0.35 g, 1.1 mmol) and ZnCl₂·TMEDA (0.28 g, 1.1 mmol) in THF (7 mL) at -90 °C. After addition, the reaction mixture was stirred for 0.5 h at -90 °C, and a solution of I₂ (0.84 g, 3.3 mmol) in THF (2 mL) was added. The reaction mixture was warmed to rt and saturated aqueous Na₂S₂O₃ was added (10 mL). The reaction mixture was extracted with Et₂O (3 x 20 mL). The combined organic layers were washed with water (5 mL), 1 M aqueous HCl (5 mL), water (5 mL), dried over MgSO₄, and the solvent was removed under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5) afforded 2-iodoferrocenetriflone (**2f**) in 29% yield (0.14 g) and 93% *ee* in favour of the *S*_P enantiomer.

The *ee* value was determined as above.

45% of starting **1** were recovered.

Deprotolithiation using (*R*)-PEALi in the presence of Me₃SiCl as an *in situ* trap.

The protocol was adapted from a previously reported procedure.^[11] To a solution of ferrocenetriflone (**1**; 0.29 g, 0.92 mmol) and Me₃SiCl (0.14 mL, 1.1 mmol) in THF (5.5 mL) at -80 °C was added dropwise a (*R*)-PEALi solution [prepared by adding BuLi (1.1 M solution in hexane; 1.0 mL, 1.1 mmol) to (*R*)-PEAH (0.25 mL, 1.1 mmol) in THF (5.5 mL) at -15 °C and stirring at this temperature for 5 min before cooling to -80 °C]. After 0.5 h at this temperature, saturated aqueous NH₄Cl (5 mL) was added. Extraction with EtOAc (3 x 10 mL), drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 90:10; R_f 0.68) to afford 2-(trimethylsilyl)ferrocenetriflone (**2a**) in 40% yield (0.145 g) and 79% *ee* in favour of the *S*_P enantiomer. The *ee* value was determined as above.

Deprotolithiation using (*S*)-PEALi in the presence of Me₃SiCl as an *in situ* trap.

The protocol was adapted from a previously reported procedure.^[11] To a solution of ferrocenetriflone (**1**; 0.34 g, 1.1 mmol) and Me₃SiCl (0.16 mL, 1.3 mmol) in THF (6.5 mL) at -80 °C was added dropwise a (*S*)-PEALi solution [prepared by adding BuLi (1.3 M solution in hexane; 1.0 mL, 1.3 mmol) to (*S*)-PEAH (0.30 mL, 1.3 mmol) in THF (6.5 mL) at -15 °C and stirring at this temperature for 5 min before cooling to -80 °C]. After 0.5 h at this temperature, saturated aqueous

NH₄Cl (6 mL) was added. Extraction with EtOAc (3 x 10 mL), drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5; R_f 0.62) to afford **2a** in 48% yield (0.205 g) and 79% *ee* in favour of the *R_P* enantiomer. The *ee* value was determined as above.

35% of starting **1** were recovered.

When the reaction from **1** (16 mmol) was carried out using 2 equivalents of base at -90 °C, **2a** was obtained in 55% yield (0.23 g) and 89% *ee*. Compound **2aa** was also formed in 8% yield (35 mg) while 24% of starting **1** were recovered.

The *ee* values were determined as above.

Slow crystallisation of **2a** (5.9 g, 15 mmol, 89% *ee*) from hexane was achieved as indicated in part C, allowing the isolation of enantiopure *R_P*-**2a** in 65% yield (3.8 g).

Crystal data for R_P-2a. C₁₄H₁₇F₃FeO₂SSi, *M* = 390.27, *T* = 150(2) K; orthorhombic *P* 2₁ 2₁ 2₁ (I.T.#19), *a* = 9.9977(9), *b* = 11.2232(10), *c* = 14.5845(14) Å, *V* = 1636.5(3) Å³. *Z* = 4, *d* = 1.584 g.cm⁻³, *μ* = 1.154 mm⁻¹. A final refinement on *F*² with 3736 unique intensities and 202 parameters converged at *ωR*(*F*²) = 0.0565 (*R_F* = 0.0229) for 3627 observed reflections with *I* > 2σ. CCDC 2364201.

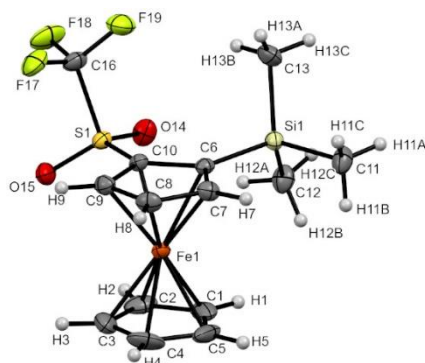


Figure S3. Molecular structure of compound *R_P*-**2a** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C6-Si1 1.884(2), C10-S1 1.716(2), C10-Cg2...Cg1-C2 2.80 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C9-C10-S1-O15 -29.3(2), C6-C10-S1-O14 8.1(2), C16-S1-C10-C6 -104.0(2).

Large-scale deprotolithiation using (*S*)-PEALi in the presence of Me₃SiCl as an *in situ* trap, and recovery of the chiral amine.

To a solution of ferrocenetriflone (**1**; 7.6 g, 24 mmol) and Me₃SiCl (6.1 mL, 48 mmol) in THF (96 mL) at -90 °C was added dropwise a solution of (*S*)-PEALi [prepared by adding BuLi (1.4 M solution in hexane; 34 mL, 48 mmol) to (*S*)-PEAH (11 mL, 48 mmol) in THF (96 mL) at -15 °C and stirring at this temperature for 5 min before cooling to -90 °C]. After 0.5 h at this temperature, 5% aqueous H₃PO₄ (100 mL) was added, and the reaction mixture was warmed to rt and stirred for 0.5 h. Extraction with Et₂O (2 x 100 mL), washing the combined organic layers with 5% aqueous H₃PO₄ (2 x 50 mL), drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude. This was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5) to

afford **2a** in 43% yield (4.0 g) and 90% *ee* (orange solid, as above; $[\alpha]_D^{20} +111$ (*c* 1.0, CHCl₃)), as well as **2aa** in 3% yield (0.32 g).

48% of starting **1** were recovered.

The *ee* value was determined as above.

To recover the chiral amine, the combined aqueous acidic phases were basified until pH 11 with 20% aqueous NaOH and were extracted with Et₂O (3 x 50 mL). The combined organic layers were dried over K₂CO₃, and the solvent was removed under reduced pressure to give the crude amine. This was purified by Kugelrohr distillation (200 °C, 5.5 mbar) to give pure (*S*)-PEAH in 83% recovery (9.0 g) as a colourless oil: ¹H NMR (CDCl₃) δ 1.29 (d, 6H, *J* = 6.7 Hz, Me), 3.52 (q, 2H, *J* = 6.7 Hz, CHMe), 7.22-7.29 (m, 6H, Ph), 7.31-7.37 (m, 4H, Ph); $[\alpha]_D^{20} -157$ (*c* 0.024, EtOH).

Large-scale deprotolithiation using (*S*)-PEALi in the presence of Bu₃SnCl as an *in situ* trap, and recovery of the chiral amine.

To a solution of ferrocenetriflone (**1**; 5.7 g, 18 mmol) and Bu₃SnCl (9.8 mL, 36 mmol) in THF (72 mL) at -90 °C was added dropwise a solution of (*S*)-PEALi [prepared by adding BuLi (1.25 M solution in hexane; 28 mL, 36 mmol) to (*S*)-PEAH (8.2 mL, 36 mmol) in THF (72 mL) at -15 °C and stirring at this temperature for 5 min before cooling to -90 °C]. After 0.5 h at this temperature, 5% aqueous H₃PO₄ (100 mL) was added, and the reaction mixture was warmed to rt and stirred for 0.5 h. Extraction with Et₂O (2 x 100 mL), washing the combined organic layers with 5% aqueous H₃PO₄ (2 x 50 mL) and then 20% aqueous NaOH^[12] (3 x 50 mL), drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude. This was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5) to afford 2-(tributylstannyl)ferrocenetriflone (**2b**) in 51% yield (5.6 g) and 93% *ee*.

The *ee* value was determined as above.

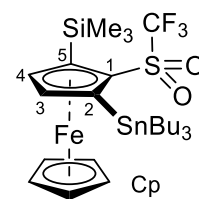
To recover the chiral amine, the combined aqueous acidic phases were basified until pH 11 with 20% aqueous NaOH and were extracted with Et₂O (3 x 50 mL). The combined organic layers were dried over K₂CO₃, and the solvent was removed under reduced pressure to give the crude amine. This was purified by Kugelrohr distillation (200 °C, 5.5 mbar) to give pure (*S*)-PEAH in 83% recovery (6.8 g) as a colourless oil: $[\alpha]_D^{20} -157$ (*c* 0.024, EtOH).

Iododestannylation of **2b** was attempted as follows. I₂ (0.38 g, 1.5 mmol) was added in one portion to a solution of the above **2b** (455 mg, 0.75 mmol) in CH₂Cl₂ (45 mL) at rt, and the reaction mixture was stirred for 14 h. Saturated aqueous Na₂S₂O₃ (10 mL) was added and the reaction mixture was extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried over MgSO₄, and the solvent was removed under reduced pressure to give the crude. Purification by column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5) afforded 2-iodoferrocenetriflone (**2f**) in 1.5% yield (5 mg) and 93% *ee* in favour of the *S*_P enantiomer.

Stannyl/lithium exchange of **2b** was attempted as follows. To a solution of the above **2e** (0.67 g, 1.1 mmol) in THF (5 mL) at -80 °C, was added dropwise BuLi (1.3 M solution in hexane; 0.94 mL,

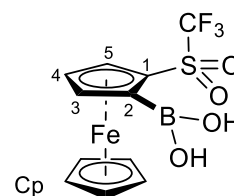
1.2 mmol). After 5 min at $-80\text{ }^{\circ}\text{C}$, Me_3SiCl (0.15 mL, 1.2 mmol) was added, and the reaction mixture was warmed to rt. 1 M aqueous HCl (5 mL) was added, and the reaction mixture was extracted with Et_2O (3 x 10 mL). Drying over MgSO_4 and removal of the solvent under reduced pressure led the crude product. Purification by column chromatography over silica gel (petroleum ether-EtOAc 95:5) afforded enantioenriched (94% *ee* in favour of the R_P enantiomer) 2-(trimethylsilyl)ferrocenetriflone (**2a**) in 36% yield (0.16 g) in addition to 20% of recovered **2b**.

In addition, enantioenriched (in favour of the S_P enantiomer) 2-(tributylstannyl)-5-(trimethylsilyl)ferrocenetriflone (**3ba**) was similarly isolated in 9% yield (67 mg) as an orange oil: IR (ATR) ν 668, 692, 734, 761, 824, 840, 880, 909, 973, 1004, 1072, 1116, 1187, 1209, 1249, 1354, 1377, 1414, 1464, 2855, 2922, 2956 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.34 (s, 9H, SiMe_3), 0.93 (t, 9H, $J = 7.3$ Hz, $3(\text{CH}_2)_3\text{Me}$), 1.07-1.20 (m, 6H, $3\text{CH}_2\text{Pr}$), 1.37 (h, 6H, $J = 7.2$ Hz, $3\text{CH}_2\text{Me}$), 1.49-1.61 (m, 6H, $3\text{CH}_2\text{CH}_2\text{Et}$), 4.42 (s, 5H, Cp), 4.62 (d, 1H, $J = 2.4$ Hz, H3), 4.73 (d, 1H, $J = 2.4$ Hz, H4) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 1.2 (3CH_3 , SiMe_3), 11.8 (3CH_2 , CH_2Pr), 13.8 (3CH_3 , $(\text{CH}_2)_3\text{Me}$), 27.6 (3CH_2 , CH_2Me), 29.2 (3CH_2 , $\text{CH}_2\text{CH}_2\text{Et}$), 71.2 (5CH, Cp), 79.3 (CH, C5), 81.2 (C, C2, C-Sn), 83.0 (CH, C3), 83.4 (CH, C4), 85.5 (q, C, $J = 2.3$ Hz, C1, C-SO₂CF₃), 119.5 (q, C, $J = 327$ Hz, CF₃) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -76.7 ppm; $[\alpha]_D^{20}$ -55.9 (c 1.0, CHCl_3) Anal. Calcd for $\text{C}_{26}\text{H}_{43}\text{F}_3\text{FeO}_2\text{SSiSn}$ (679.32): C, 45.97; H, 6.38; S, 4.72. Found: C, 46.15; H, 6.17; S, 4.69%.



Large-scale deprotolithiation using (*S*)-PEALi in the presence of $\text{B}(\text{OiPr})_3$ as an *in situ* trap, and recovery of the chiral amine.

To a solution of ferrocenetriflone (**1**; 4.8 g, 15 mmol) and $\text{B}(\text{OiPr})_3$ (6.9 mL, 30 mmol) in THF (60 mL) at $-90\text{ }^{\circ}\text{C}$ was added dropwise a solution of (*S*)-PEALi [prepared by adding BuLi (1.25 M solution in hexane; 24 mL, 30 mmol) to (*S*)-PEAH (6.9 mL, 30 mmol) in THF (60 mL) at $-15\text{ }^{\circ}\text{C}$ and stirring at this temperature for 5 min before cooling to $-90\text{ }^{\circ}\text{C}$]. After 0.5 h at this temperature, MeOH (10 mL) was added and the reaction mixture was warmed to rt. 5% aqueous H_3PO_4 (100 mL) was added, and the reaction mixture was stirred for 15 min. Extraction with Et_2O (2 x 100 mL), washing the combined organic layers with 5% aqueous H_3PO_4 (2 x 50 mL), drying over MgSO_4 and removal of the solvents under reduced pressure led to the crude. This was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 70:30 to 60:40) and isolated after subsequent treatment as follows. It was dissolved in Et_2O (100 mL) and extracted with a basic sorbitol solution (5 x 25 mL).^[13] The combined aqueous layers were washed with Et_2O (20 mL) before acidification with 6 M aqueous HCl until pH 1. The aqueous layers were extracted with Et_2O . Drying over MgSO_4 and removal of the solvent under reduced pressure finally gave enantioenriched 2-(dihydroxyboryl)ferrocenetriflone (**2g**) in 17% yield (0.95 g) as an orange solid: IR (ATR) ν 671, 690, 725, 761, 822, 873, 954, 1005, 1036, 1077, 1105, 1159, 1186, 1276, 1317, 1338, 1377, 1418, 1438, 2929, 3386 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.52 (s, 5H, Cp), 4.91 (t, 1H, $J = 2.7$ Hz, H4), 5.03 (dd, 1H, $J = 2.7$ and 1.6 Hz,



H5), 5.09 (dd, 1H, $J = 2.7$ and 1.6 Hz, H3), 6.29 (s, 2H, OH) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 66.0 (C, C2, C-B), 72.2 (5CH, Cp), 76.7 (CH, C4), 77.7 (CH, C5), 79.5 (q, C, $J = 2.1$ Hz, C1, C-SO₂CF₃), 82.3 (CH, C3), 119.3 (q, C, $J = 325$ Hz, CF₃) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -79.2 ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3) δ 29.8 ppm.

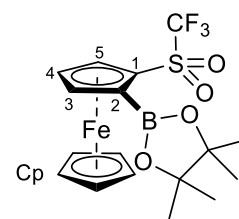
To recover the chiral amine, the combined aqueous acidic phases were basified until pH 11 with 20% aqueous NaOH and were extracted with Et₂O (3 x 50 mL). The combined organic layers were dried over K₂CO₃, and the solvent was removed under reduced pressure to give the crude amine. This was purified by Kugelrohr distillation (200 °C, 5.5 mbar) to give pure (*S*)-PEAH in 73% recovery (4.9 g) as a colourless oil: $[\alpha]_D^{20} -156$ (c 0.024, EtOH).

In order to determine the *ee* value of the obtained 2-(dihydroxyboryl)ferrocenetriflone (**2g**), it was converted to the pinacol ester as follows. Pinacol (71 mg, 0.60 mmol) was added to a solution of the obtained **2g** (0.11 g, 0.30 mmol) in THF (2 mL) at rt and the reaction mixture was stirred for 1 h. The volatiles were removed under reduced pressure, THF (2 mL) was added to the residue and the reaction mixture was stirred for 1 h at rt. The volatiles were removed under reduced pressure. Water (5 mL) was added, and the reaction mixture was extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄, and the solvent was removed under reduced pressure to give the crude product. This was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 80:20) to afford 2-(4,4,5,5-tetramethyl-1,3-dioxo-2-borolyl)ferrocenetriflone (**2h**) in 91% yield (0.12 g) and 98% *ee*. The *ee* value was determined by HPLC analysis on a Chiralpak-ODH column using hexane-*i*PrOH (99:1) as the eluent at 0.4 mL·min⁻¹ and 5 °C, $\lambda = 254$ nm, t (major, **Rp-2h**) = 13.71 min, t (minor, **Sp-2h**) = 15.63 min.

Large-scale deprotolithiation using (*S*)-PEALi in the presence of B(OiPr)₃ as an *in situ* trap, followed by conversion to the pinacol ester and recovery of the chiral amine.

To a solution of ferrocenetriflone (**1**; 4.8 g, 15 mmol) and B(OiPr)₃ (6.9 mL, 30 mmol) in THF (60 mL) at -90 °C was added dropwise a solution of (*S*)-PEALi [prepared by adding BuLi (1.2 M solution in hexane; 25 mL, 30 mmol) to (*S*)-PEAH (6.9 mL, 30 mmol) in THF (60 mL) at -15 °C and stirring at this temperature for 5 min before cooling to -90 °C]. After 0.5 h at this temperature, MeOH (35 mL) was added, the reaction mixture was warmed to rt and stirred for 1 h before volatiles were removed under reduced pressure. A solution of pinacol (3.5 g, 30 mmol) in THF (35 mL) was added to the reaction mixture which was stirred at rt for 4 h.^[14] The reaction mixture was diluted with Et₂O (100 mL), and 5% aqueous H₃PO₄ (50 mL) was added. Layers were separated and the organic layer was washed with 5% aqueous H₃PO₄ (2 x 50 mL). Drying over MgSO₄ and removal of the solvents under reduced pressure gave the crude. Purification by column chromatography over silica gel (eluent: petroleum ether-EtOAc 98:2 to 97:3) afforded 2-(4,4,5,5-tetramethyl-1,3-dioxo-2-borolyl)ferrocenetriflone (**2h**) in 45% yield (3.0 g) and 91% *ee* (determined as above) as an orange solid: R_f (eluent: petroleum ether-EtOAc 80:20) 0.76; mp 88-90 °C; IR (ATR) ν 705, 760, 783, 826,

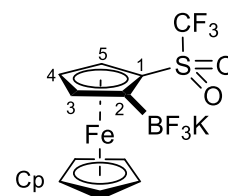
853, 951, 973, 1004, 1035, 1064, 1110, 1139, 1189, 1261, 1319, 1330, 1356, 1383, 1457, 1483, 1686, 2979 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.33 (s, 6H, 2CMe₂), 1.33 (s, 6H, 2CMe₂), 4.50 (s, 5H, Cp), 4.75 (t, 1H, $J = 2.6$ Hz, H4), 4.86 (dd, 1H, $J = 2.6$ and 1.5 Hz, H3), 4.95 (dd, 1H, $J = 2.6$ and 1.5 Hz, H5) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 24.8 (2CH₃), 24.9 (2CH₃), 67.1 (C, C2, C-B), 72.1 (5CH, Cp), 75.3 (CH, C4), 76.5 (CH, C5), 79.7 (q, C, $J = 2.2$ Hz, C1, C-SO₂CF₃), 81.1 (CH, C3), 84.2 (2C, CMe₂), 119.5 (q, C, $J = 326$ Hz, CF₃) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -78.4 ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3) δ 31.8 ppm; $[\alpha]_D^{20}$ -27 (c 1.0, CHCl_3). Anal. Calcd for C₁₇H₂₀BF₃FeO₄S (444.05): C, 45.98; H, 4.54; S, 7.22. Found: C, 45.89; H, 4.38; S, 7.13%.



To recover the chiral amine, the combined aqueous acidic phases were washed with Et₂O (2 x 50 mL), basified until pH 11 with 20% aqueous NaOH and extracted with Et₂O (3 x 50 mL). The combined organic layers were dried over K₂CO₃, and the solvent was removed under reduced pressure to give the crude amine. This was purified by Kugelrohr distillation (200 °C, 5.5 mbar) to give pure (*S*)-PEAH in 85% recovery (5.7 g) as a colourless oil: $[\alpha]_D^{20}$ -156 (c 0.024, EtOH).

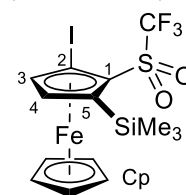
Potassium 2-(trifluoroboryl)ferrocenetriflone (2i).

It was prepared by fluorination of the boronic acid **2g** as follows.^[15] Water (0.4 mL) was added to a solution of the obtained 2-(dihydroxyboryl)ferrocenetriflone (**2g**; 0.11 g, 0.30 mmol) in MeCN (3 mL) at rt, and the reaction mixture was stirred for 15 min. A solution of KF (70 mg, 1.2 mmol) in water (0.2 mL) was added, and the reaction mixture was stirred at rt for 0.5 h. A solution of tartaric acid (95 mg, 0.63 mmol) in THF (0.6 mL) was added dropwise to the reaction mixture which was stirred for 0.5 h at rt. The resulting solids were filtrated using a sintered glass funnel and washed with MeCN. The combined filtrates were concentrated under reduced pressure to give the crude product. This was dissolved in Et₂O, filtrated using a sintered glass funnel, and petroleum ether was added to the filtrate. The solids were filtrated and dried under vacuum to give the title product in 48% yield (62 mg) as a light-yellow solid: R_f (petroleum ether-EtOAc 50:50) 0.24; mp 125-128 °C (dec.); IR (ATR) ν 666, 761, 827, 897, 1003, 1088, 1117, 1204, 1294, 1347, 1385, 1422, 1630, 3632 cm^{-1} ; ^1H NMR ((CD₃)₂SO) δ 4.33 (s, 5H, Cp), 4.54 (t, 1H, $J = 2.5$ Hz, H4), 4.56-4.57 (m, 2H, H3 and H5) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR ((CD₃)₂SO) δ 70.3 (5CH, Cp), 72.4 (CH, C4), 73.2 (CH, C5), 76.8 (C, C1, C-SO₂CF₃), 79.3 (CH, C3), 90.4 (C, C2, C-B), 119.1 (q, C, $J = 328$ Hz, CF₃) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -78.4 (q, $J = 3.6$ Hz, CF₃), -132.5 (d, $J = 75.5$ Hz, BF₃K) ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3) δ 2.6 ppm; $[\alpha]_D^{20}$ +18.5 (c 0.25, CHCl_3). Anal. Calcd for C₁₁H₈BF₆FeKO₂S (423.99): C, 31.16; H, 1.90; S, 7.59. Found: C, 31.29; H, 1.87; S, 7.40%.



(*R_P*)-2-Iodo-5-(trimethylsilyl)ferrocenetriflone (*R_P*-3af).

To a solution of (*R_p*)-2-(trimethylsilyl)ferrocenetriflone (**R_p**-2a; 3.5 g, 9.0 mmol) in THF (60 mL) at -80 °C was added dropwise *s*BuLi (1.1 M solution in cyclohexane; 12.3 mL, 13.5 mmol), and the reaction mixture was stirred at this temperature for 1 h before addition of a solution of I₂ (3.4 g, 13.5 mmol) in THF (15 mL). The mixture was then warmed to rt before treatment with saturated aqueous Na₂S₂O₃ (50 mL). Extraction with EtOAc (3 x 100 mL), drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5). The title product was isolated in 92% yield (4.3 g) and > 99.5% *ee* as an orange solid: R_f (eluent: petroleum ether-EtOAc 90:10) 0.68; mp 136-138 °C; IR (ATR) ν 760, 829, 840, 874, 958, 1005, 1066, 1115, 1184, 1210, 1240, 1360, 1415, 2968 cm⁻¹; ¹H NMR (CDCl₃) δ 0.32 (s, 9H, SiMe₃), 4.50 (s, 5H, Cp), 4.65 (d, 1H, *J* = 2.6 Hz, H4), 5.05 (d, 1H, *J* = 2.6 Hz, H3) ppm; ¹³C{¹H} NMR (CDCl₃) δ 0.92 (3CH₃), 42.0 (C, C2, C-I), 74.6 (5CH, Cp), 78.9 (C, C5, C-SiMe₃), 82.2 (CH, C4), 82.5 (q, C, *J* = 2.4 Hz, C1, C-SO₂CF₃), 85.0 (CH, C3), 119.5 (q, C, *J* = 327 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -75.9 ppm; [α]_D²⁰ +137.5 (*c* 1.0, CHCl₃). Anal. Calcd for C₁₄H₁₆F₃FeIO₂SSi (516.17): C, 32.58; H, 3.12; S, 6.21. Found: C, 32.54; H, 3.02; S, 6.27%.



The *ee* value was determined by HPLC analysis on a Chiralpak-ODH column using hexane-*i*PrOH (99:1) as the eluent at 0.4 mL·min⁻¹ and 5 °C, λ = 254 nm, *t* (major, **R_p**-3af) = 14.47 min, *t* (minor, **S_p**-3af) = 15.14 min.

Crystal data for R_p-3af. C₁₄H₁₆F₃FeIO₂SSi, *M* = 516.17, *T* = 150(2) K; orthorhombic *P* 2₁ 2₁ 2₁ (I.T.#19), *a* = 6.7983(4), *b* = 15.9729(10), *c* = 16.5422(10) Å, *V* = 1796.29(19) Å³. *Z* = 4, *d* = 1.909 g·cm⁻³, μ = 2.773 mm⁻¹. A final refinement on *F*² with 4095 unique intensities and 211 parameters converged at ω R(*F*²) = 0.0540 (*R_F* = 0.0204) for 4033 observed reflections with *I* > 2 σ . CCDC 2364202.

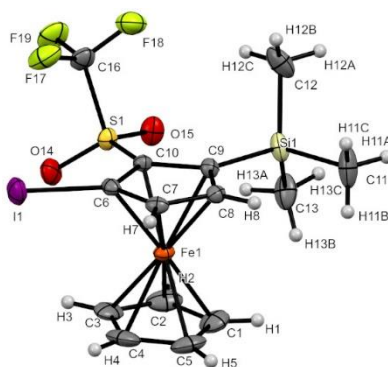
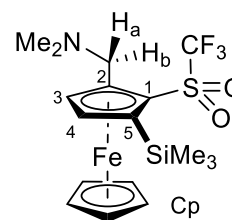


Figure S4. Molecular structure of compound **R_p**-3af (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C9-Si1 1.890(3), C10-Si1 1.724(3), C6-I1 2.073(3), C10-Cg2...Cg1-C2 30.68 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C9-C10-S1-O15 6.4(3), C6-C10-S1-O14 -30.2(3), C16-S1-C10-C9 -103.9(3).

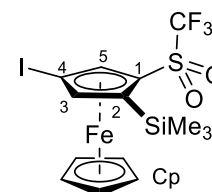
(*R_p*)-2-(Dimethylaminomethyl)-5-(trimethylsilyl)ferrocenetriflone (R_p**-3aj).**

To a solution of (*R_p*)-2-(trimethylsilyl)ferrocenetriflone (**R_p-2a**; 4.0 g, 10.3 mmol) in THF (70 mL) at $-80\text{ }^{\circ}\text{C}$ was added dropwise *s*BuLi (1.0 M solution in cyclohexane; 15.5 mL, 15.5 mmol), and the reaction mixture was stirred at this temperature for 1 h before addition of $\text{CH}_2=\text{NMe}_2\text{I}$ (2.9 g, 15.5 mmol). The mixture was then warmed to rt before addition of water (50 mL). Extraction with EtOAc (3 x 100 mL), drying over MgSO_4 and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc-Et₃N 70:29:1; R_f 0.50). The title product was isolated in 59% yield (2.7 g) and $> 99\%$ *ee* as an orange oil: IR (ATR) ν 759, 825, 837, 920, 962, 1004, 1037, 1068, 1139, 1185, 1209, 1243, 1353, 1413, 1458, 1679, 2771, 2819, 2947 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.32 (s, 9H, SiMe₃), 2.23 (s, 6H, NMe₂), 3.46 (d, 1H, $J = 14.5$ Hz, CH_aH_bNMe₂), 3.51 (d, 1H, $J = 14.6$ Hz, CH_aH_bNMe₂), 4.42 (s, 5H, Cp), 4.55 (d, 1H, $J = 2.6$ Hz, CH, C4), 4.96 (d, 1H, $J = 2.7$ Hz, CH, C3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 1.1 (3CH₃, SiMe₃), 45.9 (2CH₃, NMe₂), 57.0 (CH₂), 72.3 (5CH, Cp), 77.9 (CH, C3), 78.2 (C, C5, C-SiMe₃), 79.3 (CH, C4), 79.5 (q, C, $J = 2.3$ Hz, C1, C-SO₂CF₃), 79.3 (CH, C4), 93.5 (C, C2, C-CH₂NMe₂), 119.7 (q, C, $J = 328$ Hz, CF₃) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -75.9 ppm; $[\alpha]_D^{20} +90$ (*c* 1.0, CHCl_3). Anal. Calcd for C₁₇H₂₄F₃FeNO₂SSi (447.37): C, 45.64; H, 5.41; N, 3.13; S, 7.17. Found: C, 45.70; H, 5.45; N, 3.02; S, 7.03%. 13% of starting **R_p-2a** were also recovered.



(*R_p*)-4-Iodo-2-(trimethylsilyl)ferrocenetriflone (**R_p-4af**).

The protocol was adapted from a previously reported procedure.^[16] To a TMPLi solution [prepared by adding BuLi (1.3 M solution in hexane; 4.1 mL, 5.3 mmol) to TMPH (0.91 mL, 5.3 mmol) in THF (7 mL) at $-10\text{ }^{\circ}\text{C}$ and stirring at this temperature for 5 min before cooling to $-50\text{ }^{\circ}\text{C}$] was added in one portion (*R_p*)-2-iodo-5-(trimethylsilyl)ferrocenetriflone (**R_p-3af**; 2.5 g, 4.8 mmol) at $-50\text{ }^{\circ}\text{C}$. After 15 min at this temperature, excess MeOH (2 mL) was introduced before warming to rt and addition of 1 M aqueous HCl (5 mL). Extraction with EtOAc (3 x 10 mL), drying over MgSO_4 and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5; R_f 0.62). The title product was isolated in 62% yield (1.5 g) and $> 99.5\%$ *ee* as an orange solid: mp $58\text{--}60\text{ }^{\circ}\text{C}$; IR (ATR) ν 758, 827, 876, 975, 1006, 1057, 1115, 1184, 1249, 1299, 1357, 1414, 2954, 3122 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.33 (s, 9H, SiMe₃), 4.50 (s, 5H, Cp), 4.77 (d, 1H, $J = 1.4$ Hz, H3), 5.17 (d, 1H, $J = 1.3$ Hz, H5) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 0.61 (3CH₃), 41.8 (C, C4, C-I), 74.3 (5CH, Cp), 79.1 (C, C2, C-SiMe₃), 81.3 (CH, C5), 82.0 (q, C, $J = 2.2$ Hz, C1, C-SO₂CF₃), 87.2 (CH, C3), 119.4 (q, C, $J = 326$ Hz, CF₃) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -78.3 ppm; $[\alpha]_D^{20} +39.1$ (*c* 1.0, CHCl_3). Anal. Calcd for C₁₄H₁₆F₃FeIO₂SSi (516.17): C, 32.58; H, 3.12; S, 6.21. Found: C, 32.29; H, 3.03; S, 5.90%.



The *ee* value was determined by HPLC analysis on a Chiralpak-IB column using hexane-*i*PrOH (99:1) as the eluent at $0.5\text{ mL}\cdot\text{min}^{-1}$ and $5\text{ }^{\circ}\text{C}$, $\lambda = 254\text{ nm}$, t (major, **R_p-4af**) = 8.92 min, t (minor, **S_p-4af**) = 9.70 min.

Crystal data for **R_p-4af**. C₁₄H₁₆F₃FeIO₂SSi, *M* = 516.17, *T* = 150(2) K; orthorhombic *P* 2₁ 2₁ 2₁ (I.T.#19), *a* = 13.8854(4), *b* = 15.0813(7), *c* = 17.2896(8) Å, *V* = 3620.6(3) Å³. *Z* = 8, *d* = 1.894 g.cm⁻³, *μ* = 2.751 mm⁻¹. A final refinement on *F*² with 8261 unique intensities and 421 parameters converged at *ωR*(*F*²) = 0.0476 (*R_F* = 0.0207) for 7877 observed reflections with *I* > 2σ. CCDC 2364203.

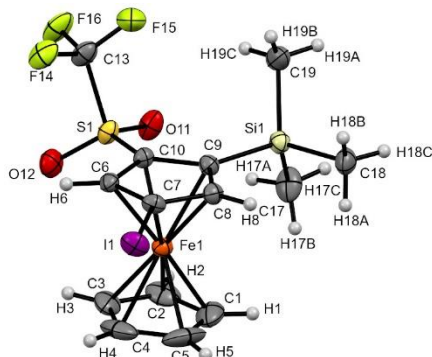
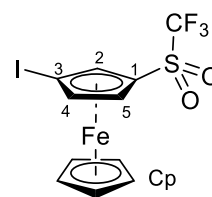


Figure S5. Molecular structure of compound **R_p-4af** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C7-I1 2.071(3), C10-S1 1.721(3), C9-Si1 1.889(4), C10-Cg2...Cg1-C2 30.74 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C6-C10-S1-O12 -27.3(3), C9-C10-S1-O11 7.1(4), C13-S1-C10-C9 -105.0(3).

(**R_p**)-3-Iodoferrocenetriflone (**R_p-5f**).

The protocol was adapted from a previously reported procedure.^[17] To a solution of (**R_p**)-4-iodo-2-(trimethylsilyl)ferrocenetriflone (**R_p-4af**; 0.10 g, 0.20 mmol) in THF (1 mL) was added Bu₄NF (1.0 M solution in THF; 0.4 mL, 0.4 mmol). After stirring for 5 min, water (2 mL) was added before extraction using EtOAc (3 x 5 mL), removal of the solvent under reduced pressure, and column chromatography over silica gel (eluent: petroleum ether-EtOAc 95:5; *R_f* 0.43). The title product was isolated in 61% yield (54 mg) and 99% *ee* as an orange solid: mp 76-78 °C; IR (ATR) *ν* 760, 802, 829, 868, 899, 1003, 1032, 1049, 1111, 1187, 1214, 1356, 1415, 1672, 2919, 3114 cm⁻¹; ¹H NMR (CDCl₃) δ 4.53 (s, 5H, Cp), 4.80 (dd, 1H, *J* = 2.7 and 1.2 Hz, H5), 4.89 (dd, 1H, *J* = 2.6 and 1.3 Hz, H4), 5.05 (t, 1H, *J* = 1.3 Hz, H2) ppm; ¹³C{¹H} NMR (CDCl₃) δ 39.9 (C, C3, C-I), 72.7 (CH, C5), 74.3 (5CH, Cp), 77.2 (CH, C2), 77.7 (q, C, *J* = 2.2 Hz, C1, C-SO₂CF₃), 80.3 (CH, C4), 119.3 (q, C, *J* = 325 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -79.2 ppm; [*α*]_D²⁰ -45.7 (*c* 1.0, CHCl₃). Anal. Calcd for C₁₁H₈F₃FeIO₂S (443.99): C, 29.76; H, 1.82; S, 7.22. Found: C, 29.65; H, 1.43; S, 7.27%.



The *ee* value was determined by HPLC analysis on a Chiralpak-IB column using hexane-*i*PrOH (99:1) as the eluent at 0.5 mL.min⁻¹ and 5 °C, λ = 254 nm, *t* (major, **R_p-5f**) = 18.33 min, *t* (minor, **S_p-5f**) = 17.17 min.

Crystal data for **R_p-5f**. C₁₁H₈F₃FeIO₂S, *M* = 443.98, *T* = 150(2) K; monoclinic *C* 2 (I.T.#5), *a* = 18.791(2), *b* = 6.8854(8), *c* = 21.142(3) Å, β = 101.402(4) °, *V* = 2681.4(5) Å³. *Z* = 8, *d* = 2.200 g.cm⁻³, *μ* = 3.611 mm⁻¹. A final refinement on *F*² with 5557 unique intensities and 310 parameters

converged at $\omega R(F)^2 = 0.1099$ ($R_F = 0.0443$) for 5394 observed reflections with $I > 2\sigma$. CCDC 2364204.

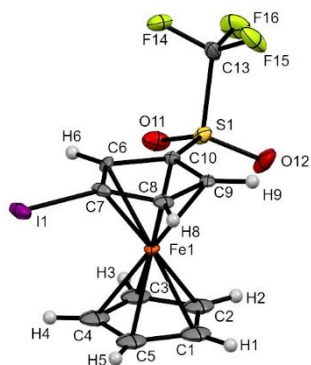


Figure S6. Molecular structure of compound **R_p-5f** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C10-S1 1.725(8), C7-I1 2.066(10), C10-Cg2...Cg1-C2 34.00 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C6-C10-S1-O11 -16.9(10), C9-C10-C1-O12 19.1(10), C13-S1-C10-C9 - 93.7(8).

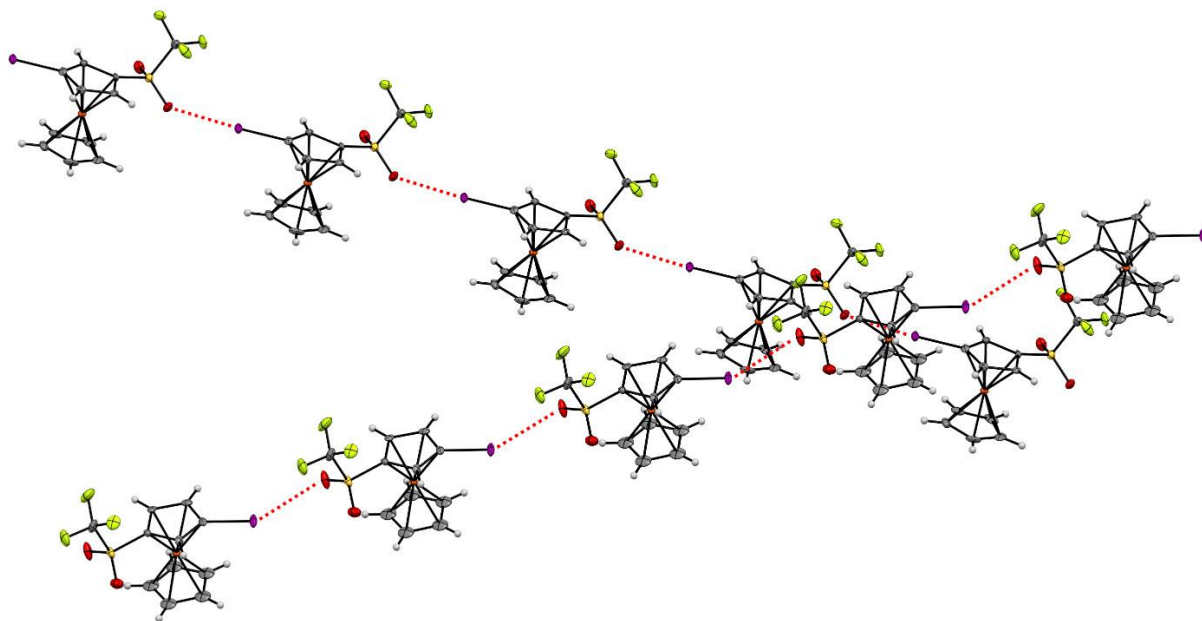


Figure S7. Hydrogen bonding network (I1-O12 3.340 Å) observed at the solid state for compound **R_p-5f**.

When the reaction was repeated from 1.0 mmol of **R_p-4af**, **5f** was obtained in 89% yield (0.40 g) and 90% *ee*.

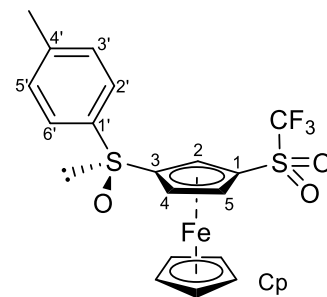
When the reaction was repeated from 3.0 mmol of **R_p-4af**, **5f** was obtained in 87% yield (1.2 g) and 76% *ee*.

(S,_SP)-3-(4-Tolylsulfinyl)ferrocenetriflone (S_P-5k).

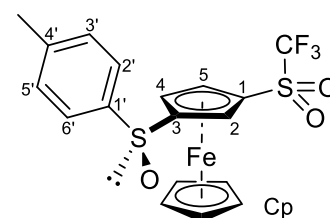
It was prepared by iodine/lithium exchange^[18] followed by electrophilic trapping using (1*R*,2*S*,5*R*)-(-)-menthyl (*S*)-4-toluenesulfinate (Andersen method).^[19] To a solution of enantioenriched 3-iodoferrocenetriflone (**5f**; 355 mg, 0.80 mmol, 76% *ee* in favour of the *R_p* enantiomer) in THF (3

mL) at $-90\text{ }^{\circ}\text{C}$ was added dropwise *t*BuLi (1.6 M solution in pentane; 1.0 mL, 1.6 mmol), and the reaction mixture was stirred at this temperature for 5 min. A solution of (1*R*,2*S*,5*R*)-(-)-menthyl (*S*)-4-toluenesulfinate (0.47 g, 1.6 mmol) in THF (4 mL) was then added at $-90\text{ }^{\circ}\text{C}$, and the reaction mixture was warmed to rt. Water (5 mL) was added and the reaction mixture was extracted with EtOAc (3 x 10 mL). Drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 80:20 to 70:30), shielded from light using aluminium foil. The title product was isolated in

42% yield (0.15 g) as a brown oil: R_f (petroleum ether-EtOAc 80:20) 0.32; IR (ATR) ν 704, 731, 762, 809, 831, 906, 1015, 1050, 1084, 1117, 1191, 1220, 1364, 1400, 1417, 1493, 1596, 3104 cm⁻¹; ¹H NMR (CDCl₃) δ 2.41 (s, 3H, Me), 4.72 (s, 5H, Cp), 4.93 (dd, 1H, *J* = 2.6 and 1.5 Hz, H5), 5.02-5.03 (m, 2H, H2 and H4), 7.32 (d, 2H, *J* = 8.0 Hz, H3' and H5'), 7.52 (d, 2H, *J* = 8.3 Hz, H2' and H6') ppm; ¹³C{¹H} NMR (CDCl₃) δ 21.6 (CH₃), 70.2 (CH, C2 or C4), 70.5 (CH, C2 or C4), 73.0 (CH, C5), 73.4 (5CH, Cp), 78.3 (q, C, *J* = 2.3 Hz, C1, C-SO₂CF₃), 100.3 (C, C3, C-SO-4-tolyl), 119.3 (q, C, *J* = 325 Hz, CF₃), 124.3 (2CH, C2' and C6'), 130.3 (2CH, C3' and C5'), 141.6 (C, C1'), 142.3 (C, C4', C-Me) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -79.0 ppm; $[\alpha]_D^{20}$ +108.5 (*c* 0.18, CHCl₃). Anal. Calcd for C₁₈H₁₅F₃FeO₃S₂ (456.28): C, 47.38; H, 3.31; S, 14.05. Found: C, 47.50; H, 3.56; S, 13.97%.



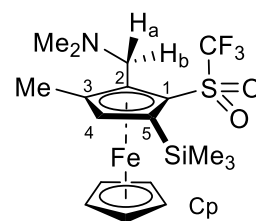
(*S*,*R_P*)-3-(4-Tolylsulfinyl)ferrocenetriflone (**R_P-5k**) was similarly isolated (R_f 0.37) in 9% yield (34 mg) as a brown solid: mp 171-173 $^{\circ}\text{C}$; IR (ATR) ν 705, 733, 762, 810, 833, 905, 1016, 1051, 1085, 1118, 1194, 1220, 1365, 1400, 1417, 1493, 1596, 3111 cm⁻¹; ¹H NMR (CDCl₃) δ 2.42 (s, 3H, Me), 4.70 (s, 5H, Cp), 4.83 (dd, 1H, *J* = 2.8 and 1.4 Hz, H4), 4.91 (dd, 1H, *J* = 2.7 and 1.3 Hz, H5), 5.13 (t, 1H, *J* = 1.4 Hz, H2), 7.33 (d, 2H, *J* = 7.6 Hz, H3' and H5'), 7.54 (d, 2H, *J* = 8.3 Hz, H2' and H6') ppm; ¹³C{¹H} NMR (CDCl₃) δ 21.6 (CH₃), 68.7 (CH, C2), 72.2 (CH, C4), 73.1 (CH, C5), 73.4 (5CH, Cp), 78.0 (q, C, *J* = 2.2 Hz, C1, C-SO₂CF₃), 100.9 (C, C3, C-SO-4-tolyl), 119.3 (q, C, *J* = 325 Hz, CF₃), 124.5 (2CH, C2' and C6'), 130.3 (2CH, C3' and C5'), 141.3 (C, C1'), 142.5 (C, C4', C-Me) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -79.0 ppm; $[\alpha]_D^{20}$ +101 (*c* 0.25, CHCl₃). Anal. Calcd for C₁₈H₁₅F₃FeO₃S₂ (456.28): C, 47.38; H, 3.31; S, 14.05. Found: C, 47.41; H, 3.34; S, 13.92%.



(*R_P*)-2-(Dimethylaminomethyl)-3-methyl-5-(trimethylsilyl)ferrocenetriflone (**R_P-6**).

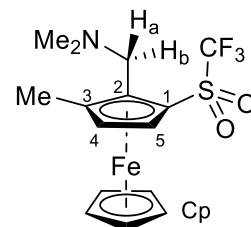
To a solution of (*R_P*)-2-(dimethylaminomethyl)-5-(trimethylsilyl)ferrocenetriflone (**R_P-3aj**; 2.6 g, 5.7 mmol) in THF (40 mL) at $-80\text{ }^{\circ}\text{C}$ was added dropwise *s*BuLi (0.95 M solution in cyclohexane; 9.0 mL, 8.6 mmol), and the reaction mixture was stirred at this temperature for 1 h before addition of MeI (0.53 mL, 8.6 mmol). The mixture was then warmed to rt before addition of water (20 mL). Extraction with EtOAc (3 x 100 mL), drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent:

petroleum ether-EtOAc-Et₃N 89:10:1; Rf 0.89). The title product was isolated in 47% yield (1.2 g) as an orange oil: IR (ATR) ν 760, 824, 829, 941, 1026, 1110, 1121, 1140, 1181, 1245, 1290, 1352, 1381, 1412, 1459, 2766, 2816, 2949 cm⁻¹; ¹H NMR (CDCl₃) δ 0.31 (s, 9H, SiMe₃), 2.07 (s, 3H, C-Me), 2.11 (s, 6H, NMe₂), 3.12 (d, 1H, *J* = 13.0 Hz, CH_aH_bNMe₂), 3.87 (d, 1H, *J* = 13.0 Hz, CH_aH_bNMe₂), 4.32 (s, 5H, Cp), 4.48 (s, 1H, H4) ppm; ¹³C{¹H} NMR (CDCl₃) δ 1.1 (3CH₃, SiMe₃), 14.2 (CH₃, C-Me), 44.9 (2CH₃, NMe₂), 54.2 (CH₂), 72.7 (5CH, Cp), 76.5 (C, C5, C-SiMe₃), 81.1 (q, C, *J* = 2.8 Hz, C1, C-SO₂CF₃), 81.2 (CH, C4), 90.5 (C, C3, C-Me), 92.3 (C, C2, C-CH₂NMe₂), 119.7 (q, C, *J* = 329 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -72.8 ppm; [α]_D²⁰ +25 (*c* 1.0, CHCl₃). Anal. Calcd for C₁₈H₂₆F₃FeNO₂SSi (461.40): C, 46.86; H, 5.68; N, 3.04; S, 6.95. Found: C, 46.91; H, 3.09; N, 3.05; S, 6.99%.



(Sp)-2-(Dimethylaminomethyl)-3-methylferrocenetriflone (Sp-7).

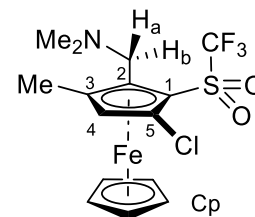
It was prepared by adapting conditions reported.^[17] To a solution of (*R_P*)-2-(dimethylaminomethyl)-3-methyl-5-(trimethylsilyl)ferrocenetriflone (**R_P-6**; 1.1 g, 2.4 mmol) in THF (7 mL) was added Bu₄NF (1.0 M solution in THF; 4.8 mL, 4.8 mmol). After stirring for 0.5 h, water (10 mL) was added before extraction using EtOAc (3 x 25 mL), removal of the solvent under reduced pressure, and column chromatography over silica gel (eluent: petroleum ether-EtOAc-Et₃N 89:10:1 Rf 0.85). The title product was isolated in 92% yield (0.86 g) as an orange solid: mp 86-88 °C; IR (ATR) ν 764, 835, 894, 1000, 1043, 1150, 1194, 1278, 1349, 2972 cm⁻¹; ¹H NMR (CDCl₃) δ 2.09 (s, 3H, C-Me), 2.13 (s, 6H, NMe₂), 3.21 (d, 1H, *J* = 13.0 Hz, CH_aH_bNMe₂), 3.76 (d, 1H, *J* = 13.0 Hz, CH_aH_bNMe₂), 4.34 (s, 5H, Cp), 4.57 (d, 1H, *J* = 2.8 Hz, H4), 4.66 (d, 1H, *J* = 2.7 Hz, H5) ppm; ¹³C{¹H} NMR (CDCl₃) δ 14.1 (CH₃, C-Me), 45.0 (2CH₃, NMe₂), 54.1 (CH₂), 71.6 (CH, C5), 72.6 (5CH, Cp), 73.8 (CH, C4), 75.7 (q, C, *J* = 2.4 Hz, C1, C-SO₂CF₃), 87.4 (C, C2, C-CH₂NMe₂), 90.7 (C, C3, C-Me), 119.6 (q, C, *J* = 327 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -77.3 ppm; [α]_D²⁰ -39 (*c* 1.0, CHCl₃). Anal. Calcd for C₁₅H₁₈F₃FeNO₂S (389.21): C, 46.29; H, 4.66; N, 3.60; S, 8.24. Found: C, 46.31; H, 4.53; N, 3.72; S, 8.27%.



(Sp)-5-Chloro-2-(dimethylaminomethyl)-3-methylferrocenetriflone (Sp-8).

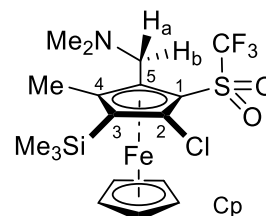
To a solution of (*S_P*)-2-(dimethylaminomethyl)-3-methylferrocenetriflone (**S_P-7**; 0.76 g, 1.95 mmol) in THF (15 mL) at -80 °C was added dropwise *s*BuLi (0.95 M solution in cyclohexane; 3.1 mL, 2.9 mmol), and the reaction mixture was stirred at this temperature for 1 h before addition of C₂Cl₆ (0.69 g, 2.9 mmol) in THF (3 mL). The mixture was then warmed to rt and water (15 mL) was added. Extraction with EtOAc (3 x 40 mL), drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc-Et₃N 94:5:1; Rf 0.68). The title product was isolated in 69% yield (0.57 g) as an orange solid: mp 114-116 °C; IR (ATR) ν 723, 761, 828, 841, 874, 933, 958, 1010, 1099, 1115,

1142, 1183, 1240, 1301, 1360, 1414, 1642, 1687, 2764, 2817, 2970 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.05 (s, 3H, C-Me), 2.12 (s, 6H, NMe_2), 3.08 (d, 1H, $J = 13.1$ Hz, $\text{CH}_a\text{H}_b\text{NMe}_2$), 3.78 (d, 1H, $J = 13.1$ Hz, $\text{CH}_a\text{H}_b\text{NMe}_2$), 4.42 (s, 5H, Cp), 4.83 (s, 1H, H4) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 13.7 (CH_3 , C-Me), 45.0 (2CH_3 , NMe_2), 53.9 (CH_2), 73.4 (q, C, $J = 2.7$ Hz, C1, C-SO₂CF₃), 74.9 (5CH, Cp), 75.0 (CH, C4), 86.5 (C, C2, C-CH₂NMe₂), 87.4 (C, C3, C-Me), 94.5 (C, C5, C-Cl), 119.7 (q, C, $J = 327$ Hz, CF₃) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -76.4 ppm; $[\alpha]_D^{20}$ -39 (c 1.0, CHCl_3). Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{ClF}_3\text{FeNO}_2\text{S}$ (423.66): C, 42.53; H, 4.04; N, 3.31; S, 7.57. Found: C, 42.41; H, 4.05; N, 3.39; S, 7.52%.



(Sp)-2-Chloro-5-(dimethylaminomethyl)-4-methyl-3-(trimethylsilyl)ferrocenetriflone (Sp-9).

To a solution of (*Sp*)-5-chloro-2-(dimethylaminomethyl)-3-methylferrocenetriflone (**Sp-8**; 0.41 g, 0.97 mmol) in THF (2 mL) at -80 °C was added dropwise a TMPLi solution [prepared by adding BuLi (1.4 M solution in hexane; 1.4 mL, 1.9 mmol) to TMPH (0.33 mL, 1.9 mmol) in THF (3 mL) at -10 °C and stirring at this temperature for 5 min before cooling to -80 °C]. After 1 h at this temperature, Me₃SiCl (0.19 mL, 1.5 mmol) was added. The mixture was then warmed to rt before addition of water (5 mL). Extraction with EtOAc (3 x 10 mL), drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc-Et₃N 94:5:1; R_f 0.75). The title product was isolated in 90% yield (0.43 g) as an orange solid: mp 112-114 °C; IR (ATR) ν 718, 764, 827, 946, 1008, 1024, 1099, 1128, 1186, 1251, 1315, 1330, 1361, 1466, 2765, 2817, 2946 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.45 (s, 9H, SiMe₃), 2.07 (s, 3H, C-Me), 2.13 (s, 6H, NMe_2), 3.13 (d, 1H, $J = 13.2$ Hz, $\text{CH}_a\text{H}_b\text{NMe}_2$), 3.81 (d, 1H, $J = 13.2$ Hz, $\text{CH}_a\text{H}_b\text{NMe}_2$), 4.39 (s, 5H, Cp) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 1.6 (3CH_3 , SiMe₃), 14.5 (CH_3 , C-Me), 45.0 (2CH_3 , NMe_2), 53.7 (CH_2), 74.9 (5CH, Cp), 75.1 (q, C, $J = 2.7$ Hz, C1, C-SO₂CF₃), 76.3 (C, C3, C-SiMe₃), 88.8 (C, C5, C-CH₂NMe₂), 92.0 (C, C4, C-Me), 100.6



(C, C2, C-Cl), 119.7 (q, C, $J = 328$ Hz, CF₃) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -75.9 ppm; $[\alpha]_D^{20}$ -3.7 (c 1.0, CHCl_3). Anal. Calcd for $\text{C}_{18}\text{H}_{25}\text{ClF}_3\text{FeNO}_2\text{SSi}$ (495.84): C, 43.60; H, 5.08; N, 2.82; S, 6.47. Found: C, 43.48; H, 4.98; N, 2.63; S, 6.58%.

Crystal data for Sp-9. $\text{C}_{18}\text{H}_{25}\text{ClF}_3\text{FeNO}_2\text{SSi}$, $M = 495.84$, $T = 150(2)$ K; monoclinic $P 2_1$ (I.T.#4), $a = 8.1853(8)$, $b = 15.9523(15)$, $c = 8.9733(8)$ Å, $\beta = 106.870(3)$ °, $V = 1121.26(18)$ Å³. $Z = 2$, $d = 1.469$ g.cm⁻³, $\mu = 0.976$ mm⁻¹. A final refinement on F^2 with 5100 unique intensities and 259 parameters converged at $\omega R(F)^2 = 0.0538$ ($R_F = 0.0219$) for 4948 observed reflections with $I > 2\sigma$. CCDC 2364205.

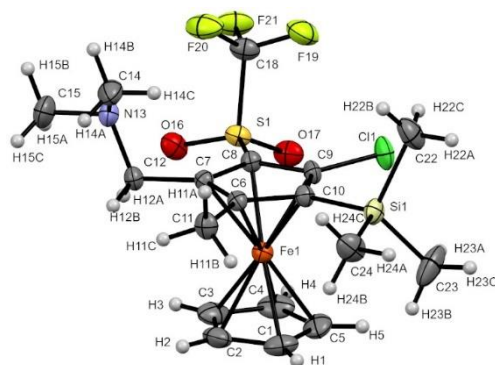
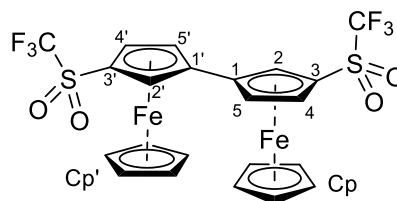


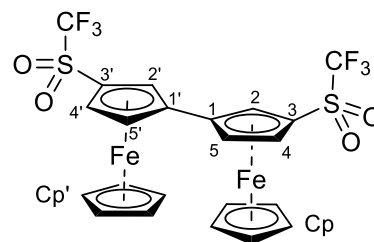
Figure S8. Molecular structure of compound **Sp-9** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C8-S1 1.726(2), C7-C12 1.502(3), C6-C11 1.501(3), C10-Si1 1.894(2), C9-C11 1.703(3), C8-Cg2...Cg1-C4 25.91 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C9-C8-S1-O17 27.4(3), C7-C8-S1-O16 -11.5(3), C18-S1-C8-C7 99.9(2).

(*Sp,Sp*)-1,1'-Biferrocene-3,3'-bis(triflate) (*Sp,Sp*-5l).

It was prepared by adapting conditions reported.^[20] Enantioenriched 3-iodoferrocenetriflate (**5f**; 0.27 g, 0.60 mmol, 90% *ee* in favour of the *R_p* enantiomer), sodium hydride (60% in oil, 0.19 g, 4.8 mmol), bis(triphenylphosphine)nickel(II) dichloride (0.39 g, 0.60 mmol), triphenylphosphine (315 mg, 1.2 mmol) and zinc dust (0.16 g, 2.4 mmol) were placed in a Schlenk tube subjected to three cycles of vacuum/argon. Under argon, degassed toluene (4.5 mL) was added, and the reaction mixture was heated at 75 °C for 14 h in a pre-heated oil bath. The reaction mixture was cooled to rt, water (5 mL) was added, and the reaction mixture was extracted with EtOAc (3 x 10 mL). Drying over MgSO₄ and removal of the solvents under reduced pressure led to the crude, which was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 90:10 to 80:20). The title product was isolated as an orange solid in 61% yield (0.12 g) as an orange solid: R_f (petroleum ether-EtOAc 90:10) 0.17; mp 220-221 °C; IR (ATR) ν 761, 827, 905, 1004, 1021, 1051, 1109, 1140, 1184, 1212, 1293, 1359, 1416, 3118 cm⁻¹; ¹H NMR (CDCl₃) δ 4.39 (s, 10H, Cp and Cp'), 4.84 (dd, 2H, *J* = 2.7 and 1.5 Hz, H5 and H5'), 4.90 (dd, 2H, *J* = 2.7 and 1.3 Hz, H4 and H4'), 5.04 (t, 2H, *J* = 1.4 Hz, H2 and H2') ppm; ¹³C{¹H} NMR (CDCl₃) δ 69.1 (2CH, C2 and C2'), 71.6 (2CH, C5 and C5'), 72.0 (2CH, C4 and C4'), 73.0 (10CH, Cp and Cp'), 77.3 (q, 2C, *J* = 2.1 Hz, C3 and C3', C-SO₂CF₃), 86.5 (2C, C1 and C1'), 119.5 (q, 2C, *J* = 325 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -79.2 ppm; [α]_D²⁰ -394 (*c* 1.0, CHCl₃). Anal. Calcd for C₂₂H₁₆F₆Fe₂O₄S₂ (634.17): C, 41.67; H, 2.54; S, 10.11. Found: C, 41.52; H, 2.50; S, 10.13%.



(*S_P,R_P*)-1,1'-Biferrocene-3,3'-bis(triflone) (*meso*-**5l**) was similarly isolated in 4% yield (7 mg) as an orange solid: R_f (petroleum ether-EtOAc 90:10) 0.37; mp > 260 °C; IR (ATR) ν 761, 835, 908, 1020, 1044, 1112, 1183, 1195, 1215, 1364 cm⁻¹; ¹H NMR (CDCl₃) δ 4.38 (s, 10H, Cp and Cp'), 4.89 (dd, 2H, *J* = 2.7 and 1.5 Hz, H5 and H5'), 4.92 (dd, 2H, *J* = 2.7 and 1.3 Hz, H4 and H4'), 4.98 (t, 2H, *J* = 1.4 Hz, H2 and H2') ppm; ¹³C{¹H} NMR (CDCl₃) δ 68.9 (2CH, C2 and C2'), 71.7 (2CH, C5 and C5'), 72.1 (2CH, C4 and C4'), 73.0 (10CH, Cp and Cp'), 86.5 (2C, C1 and C1'), 119.5 (q, 2C, *J* = 325 Hz, CF₃) ppm (1 signal not seen (2C, C3 and C3', C-SO₂CF₃), behind the CDCl₃ peak); ¹⁹F{¹H} NMR (CDCl₃) δ -79.2 ppm; [α]_D²⁰ 0.0 (*c* 1.0, CHCl₃). Anal. Calcd for C₂₂H₁₆F₆Fe₂O₄S₂ (634.17): C, 41.67; H, 2.54; S, 10.11. Found: C, 41.69; H, 2.54; S, 10.17%.



Crystal data for S_P,S_P-5l. C₂₂H₁₆F₆Fe₂O₄S₂, *M* = 634.17, *T* = 150(2) K; orthorhombic *P* 2₁ 2₁ 2 (I.T.#18), *a* = 18.752(2), *b* = 16.0012(16), *c* = 16.4774(16) Å, *V* = 4944.2(9) Å³. *Z* = 8, *d* = 1.704 g·cm⁻³, μ = 1.415 mm⁻¹. A final refinement on *F*² with 11336 unique intensities and 649 parameters converged at $\omega R(F^2)$ = 0.0582 (*R_F* = 0.0287) for 10438 observed reflections with *I* > 2 σ . CCDC 2364206.

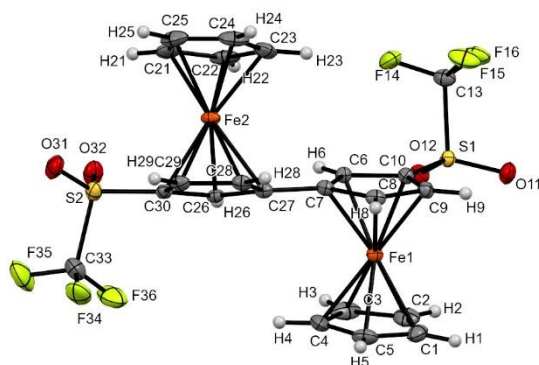
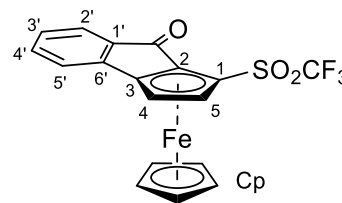


Figure S9. Molecular structure of compound *S_P,S_P-5l* (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C10-S1 1.722(3), C30-S2 1.723(3), C7-C27 1.470(5), C10-Cg2...Cg1-C2 7.17 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C30-Cg4...Cg3-C21 -10.49 (Cg3 being the centroid of the C21-C22-C23-C24-C25 ring and Cg4 being the centroid of the C26-C27-C28-C29-C30 ring), plane C6-C7-C8-C9-C10...C26-C27-C28-C29-C30 21.172(0.160), C6-C10-S1-O12 -31.7(3), C9-C10-S1-O11 13.7(4), C26-C30-S2-O32 -22.4(3), C29-C30-S2-O31 14.6(4), C13-S1-C10-C9 -97.6(3), C33-S2-C30-C29 -96.6(3).

The ferrocenic analogue of fluorenone *S_P-10*.

(*S_P*)-2-(2-Bromobenzoyl)ferrocenetriflone (**2e**; 1.15 g, 2.3 mmol), Pd(OAc)₂ (13 mg, 57.5 mmol), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl ((±)-BINAP; 72 mg, 0.11 mmol), Cs₂CO₃ (1.1 g, 3.45 mmol) and *t*BuCO₂H (70.5 mg, 0.69 mmol) were placed in a Schlenk tube and subjected to three cycles vacuum/argon. Degassed toluene (13 mL) was added and the reaction mixture was stirred at 90 °C in a pre-heated oil bath, shielded from light for 16 h. The reaction mixture was cooled to rt and was directly purified by column chromatography over silica gel (eluent: petroleum ether-

EtOAc 70:30 to 60:40) to give the title product in 74% yield (0.71 g) and > 99.5% *ee* as a dark red solid: *R_f* (petroleum ether-EtOAc 70:30) 0.40; mp 264-265 °C (dec.); IR (ATR) ν 505, 523, 551, 596, 636, 662, 692, 710, 754, 830, 869, 1007, 1078, 1102, 1124, 1169, 1195, 1215, 1372, 1401, 1438, 1606, 1692, 3120 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.48 (s, 5H, Cp), 5.26 (d, 1H, *J* = 2.6 Hz, H4), 5.36 (d, 1H, *J* = 2.6 Hz, H5), 7.23-7.28 (m, 2H, H3' and H5'), 7.41 (td, 1H, *J* = 7.5 and 1.2 Hz, H4'), 7.60 (dt, 1H, *J* = 7.4 and 1.0 Hz, H2') ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 69.2 (CH, C4), 75.3 (q, C, *J* = 2.2 Hz, C1, C-SO₂CF₃), 75.9 (5CH, Cp), 78.4 (C, C2), 79.5 (CH, C5), 97.4 (C, C3), 119.5 (q, C, *J* = 326 Hz, CF₃), 121.0 (CH, C3' or C5'), 124.2 (CH, C2'), 128.5 (CH, C3' or C5'), 134.1 (CH, C4'), 139.6 (C, C1'), 140.1 (C, C6'), 189.8 (C, C=O) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3) δ -78.7 ppm; $[\alpha]_D^{20}$ +524.2 (*c* 0.062, CHCl_3). Anal. Calcd for C₁₈H₁₁F₃FeO₃S (420.18): C, 51.45; H, 2.64; S, 7.63. Found: C, 51.51; H, 2.62; S, 7.64%.



The *ee* value was determined by HPLC analysis on a Chiralpak-IB column using hexane-isopropanol (90:10) as the eluent at 1.0 mL.min⁻¹ and 25 °C, λ = 254 nm, *t* (minor, **R_P-10**) = 11.84 min, *t* (major, **S_P-10**) = 15.17 min.

Crystal data for S_P-10. C₁₈H₁₁F₃FeO₃S, *M* = 420.18, *T* = 150(2) K; monoclinic *P* 2₁ (I.T.#4), *a* = 7.2261(3), *b* = 6.6984(2), *c* = 16.4777(5) Å, β = 98.6940(10) °, *V* = 788.41(5) Å³. *Z* = 2, *d* = 1.770 g.cm⁻³, μ = 1.138 mm⁻¹. A final refinement on *F*² with 3510 unique intensities and 236 parameters converged at $\omega R(F)^2$ = 0.0507 (*R_F* = 0.0181) for 3485 observed reflections with *I* > 2 σ . CCDC 2364207.

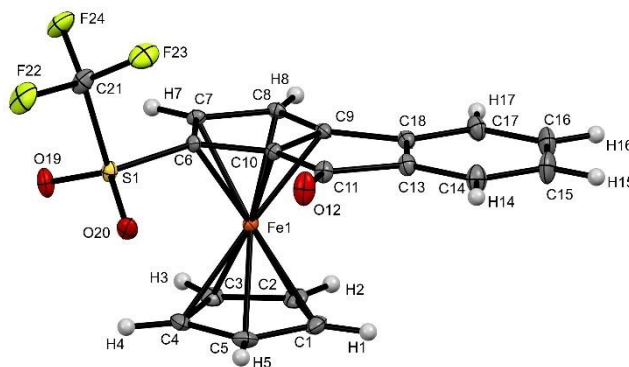


Figure S10. Molecular structure of compound **S_P-10** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C9-C18 1.469(3), C10-C11 1.484(3), C6-S1 1.720(2), C9-Cg2...Cg1-C1 20.86 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C7-C6-S1-O19 12.9(2), C10-C6-S1-O20 -20.3(2), C21-S1-C6-C7 -98.24(19), C6-C10-C11-O12 -2.9(5).

C) Crystallisation details for compound **2a**

Initial crystallisation attempts of 2-(trimethylsilyl)ferrocenetriflone (**2a**; 89% *ee*) were made by dissolving 15-20 mg of product in either hexane and *tert*-butylmethylether at 40 °C and allowing the solvent to slowly evaporates. Crystals at the bottom of the tube were recovered and analysed by HPLC. While *tert*-butylmethylether afforded the title product in 92% *ee*, hexane delivered the product in an excellent > 99.5% *ee* (see HPLC data).

A first large-scale crystallisation of compound **2a** (5.85 g, 15 mmol, 89% *ee*) was then attempted using hexane as solvent in a beaker. The solvent was allowed to slowly evaporates over one week, given crystal both on the inner walls and at the bottom of the beaker (Figure S11). Crystals at the top and at the bottom of the beaker were visually different and HPLC analysis was performed on some portions of the crystals (recovered approximately at 5.5, 3 and 1 cm). We found that the *ee* increases from the top (61% *ee*) to the bottom (85% *ee*) while crystallisation occurred.

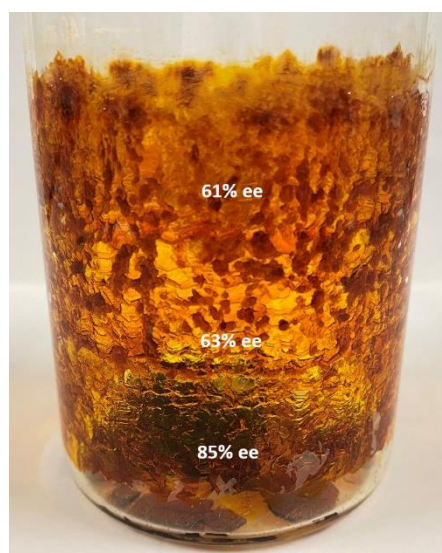


Figure S11. Evolution of the *ee* of the crystals on the inner wall of the beaker.

Concerning the crystals at the bottom of the beaker, we also observed some modification of their aspect during the last day of crystallisation. Indeed, before complete evaporation of hexane, large crystals of rectangular shape were predominant (Figure S12a) while after evaporation of the remain solvent, smaller crystals of diamond-like shape appeared (Figure S12b).

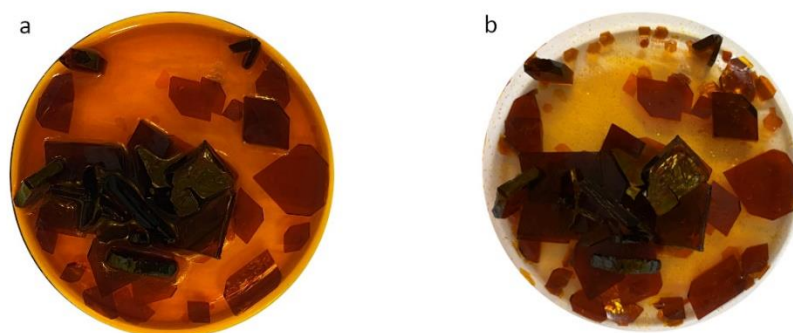


Figure S12. a) Crystals before and b) after complete evaporation of hexane.

We separated the two types of crystals which were analysed by X-ray diffraction. We soon realised that the product was able to crystallise in either the orthorhombic and the monoclinic systems for the big and the small crystals, respectively. Furthermore, we only found the R_P enantiomer of **2a** in the orthorhombic crystals while the racemate crystallised in the monoclinic system (Figure S13a and S13b). However, the solid-state structure of the R_P enantiomer found in the two crystal systems were almost identical (RMS 0.202) (Figure S13c).

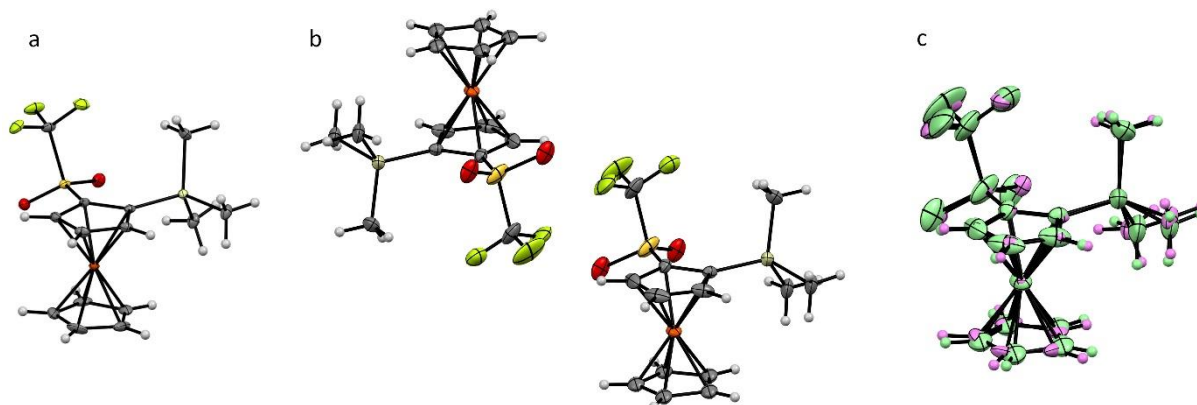


Figure S13. a) Enantiomer R_P -**2a** found in the orthorhombic crystal. b) rac -**2a** found in the monoclinic crystal. c) Superposition of the R_P -**2a** enantiomers; in purple from orthorhombic crystal, in green from monoclinic crystal.

The composition of the two types of crystals was further confirmed by HPLC analysis, as only the R_P enantiomer was identified in the orthorhombic crystals (> 99% ee , Figure S14a) while the racemate was observed in the monoclinic crystals (Figure S14b). Gathering the orthorhombic crystals afforded the enantiopure R_P -**2a** in 65% yield (3.8 g).

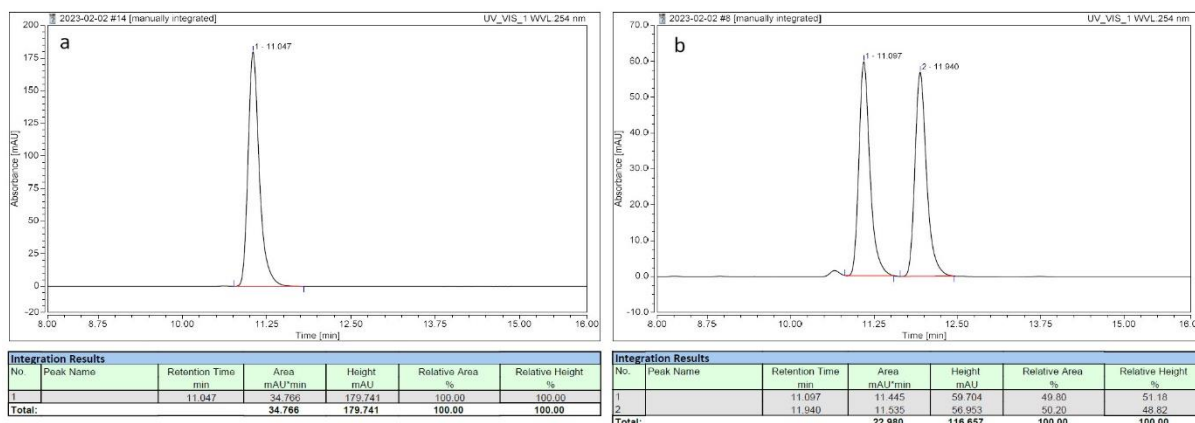


Figure S14. a) HPLC analysis of the orthorhombic crystals. b) HPLC analysis of the monoclinic crystals.

To evaluate the repeatability of these results, we performed the crystallisation a second time. In a round-bottom flask, compound **2a** (6.8 g, 17 mmol, 90% *ee*) was dissolved in hexane, preheated at 40 °C. The resulting solution was transferred to a 150 mL beaker and the flask was washed with hexane (2 x 5 mL). The beaker was covered by aluminium foil, pierced was many small holes and the solvent was allowed to evaporate over 5 days, until approximately 10 mL of solution remained to avoid the formation of monoclinic racemate crystals (Figure S15 and S16).

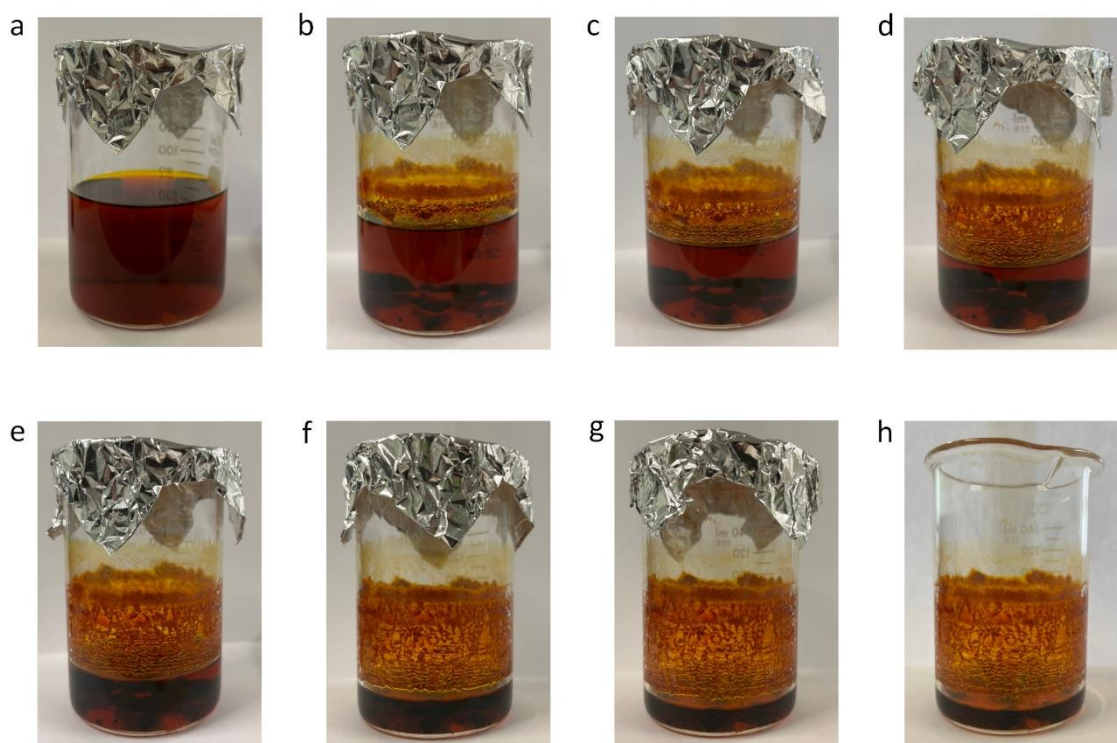


Figure S15. Front view during the crystallisation of compound **2a** at: a) 0 h; b) 15 h; c) 27 h; d) 42 h; e) 53 h; f) 74 h; g) 96 h and h) 112 h.

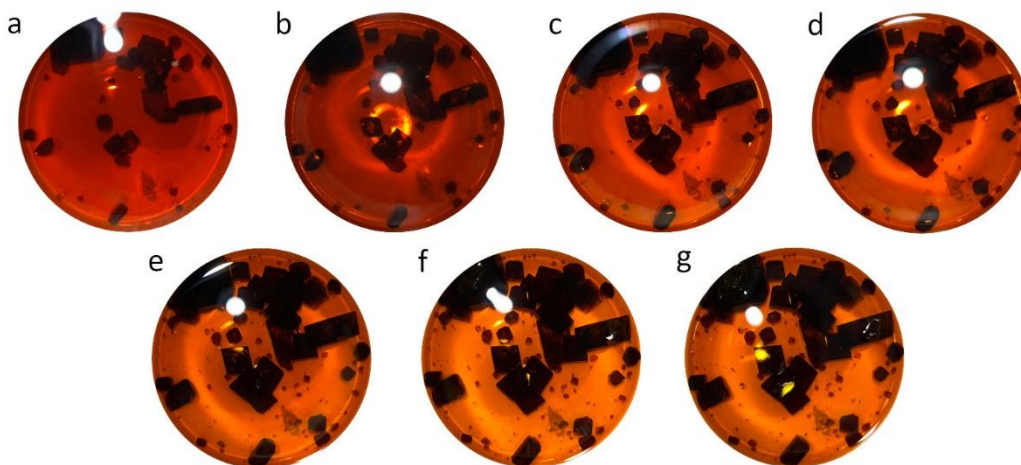


Figure S16. Top view during the crystallisation of compound **2a** at: a) 15 h; b) 27 h; c) 42 h; d) 53 h; e) 74 h; f) 96 h and h) 112 h.

Large crystals of similar shape were collected and washed with a few drops of petroleum ether on a filter paper before being allowed to dry at air (Figure S17). Four crystals were randomly selected (C1-C4) and analysed by HPLC giving *ee* values > 99% in all cases (Figure S18). Gathering all collected crystals gave 4.1 g of the enantiopure product **Rp-2a** (61% recovery). All remaining solids were collected and stored as a mixture of enantiomers.



Figure S17. Collected crystals of compounds **2a**.

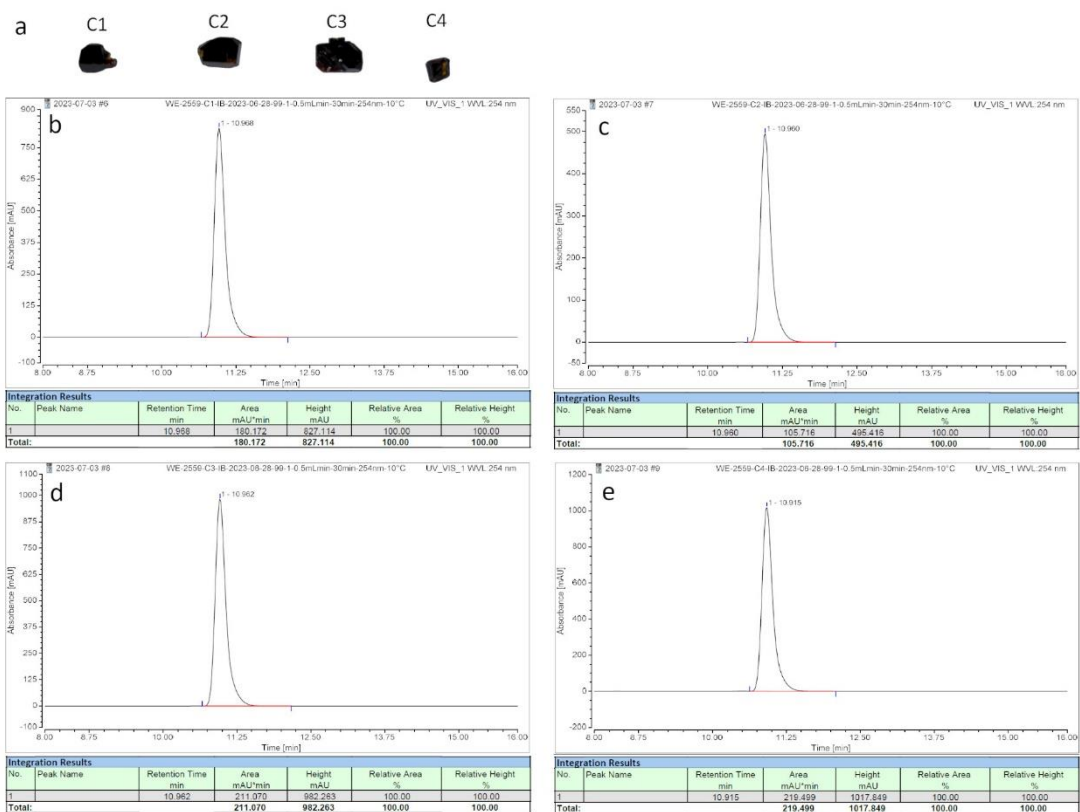
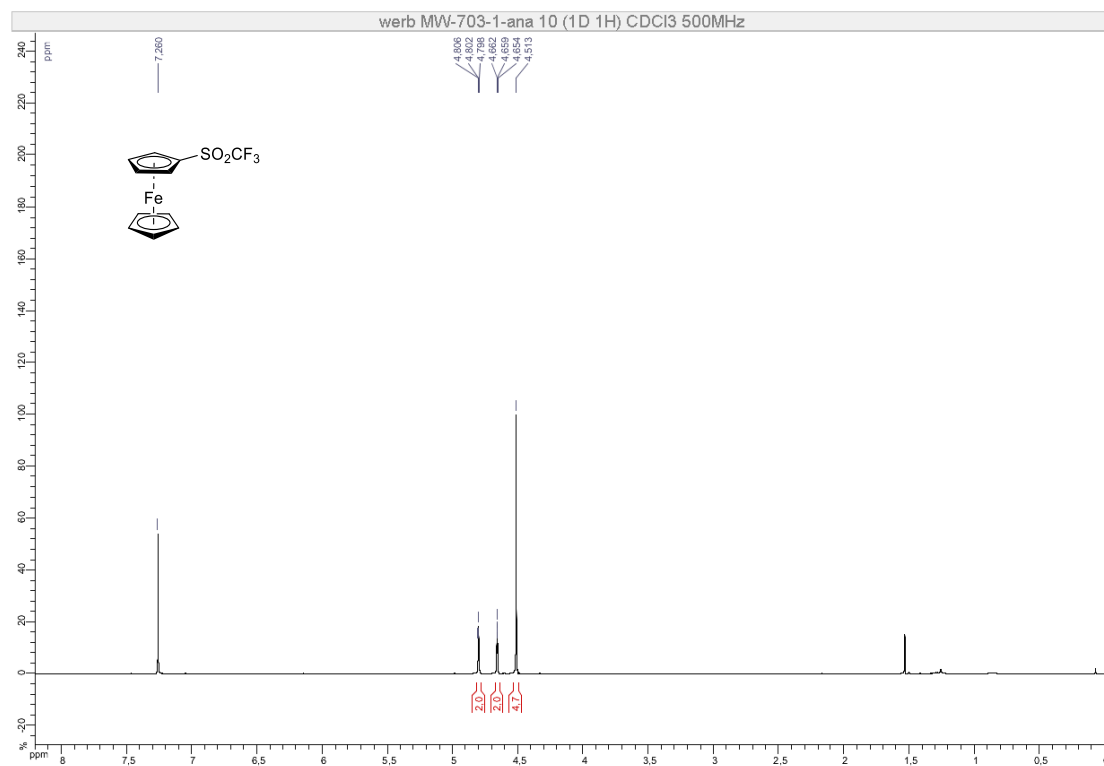


Figure S18. a) Crystals C1-4 of compound **2a** selected for HPLC analysis. b) HPLC data of crystal C1. c) HPLC data of crystal C2. d) HPLC data of crystal C3. e) HPLC data of crystal C4.

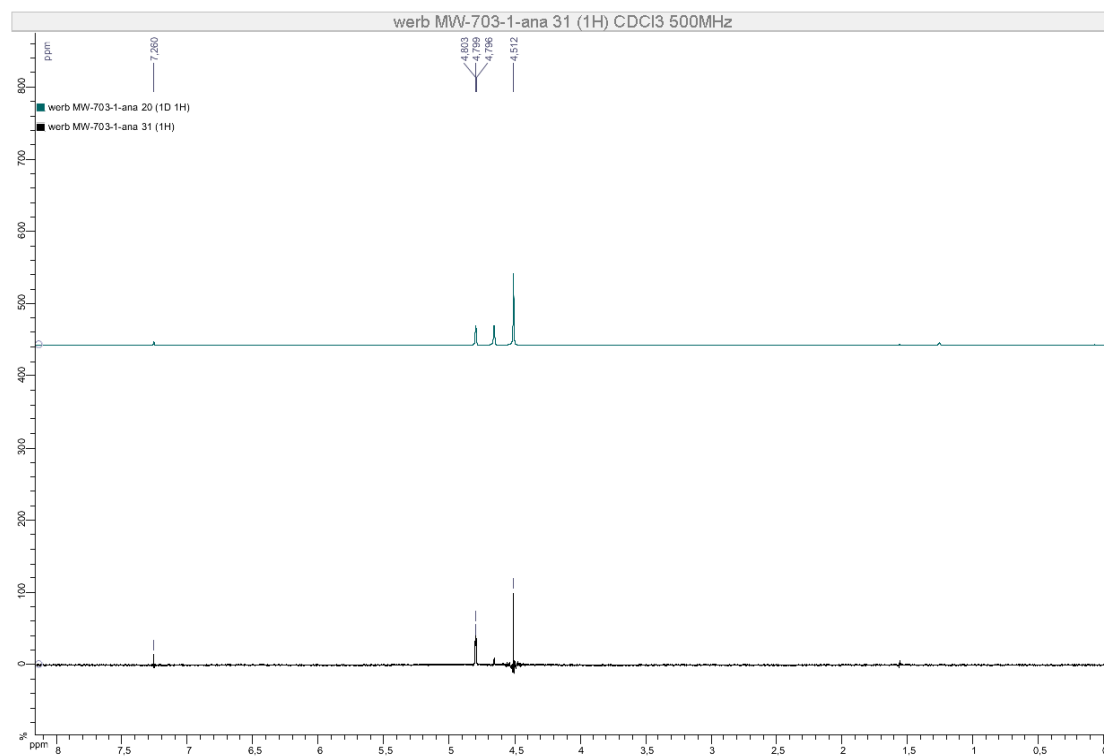
D) NMR Spectra

Ferrocenetriflone (1)

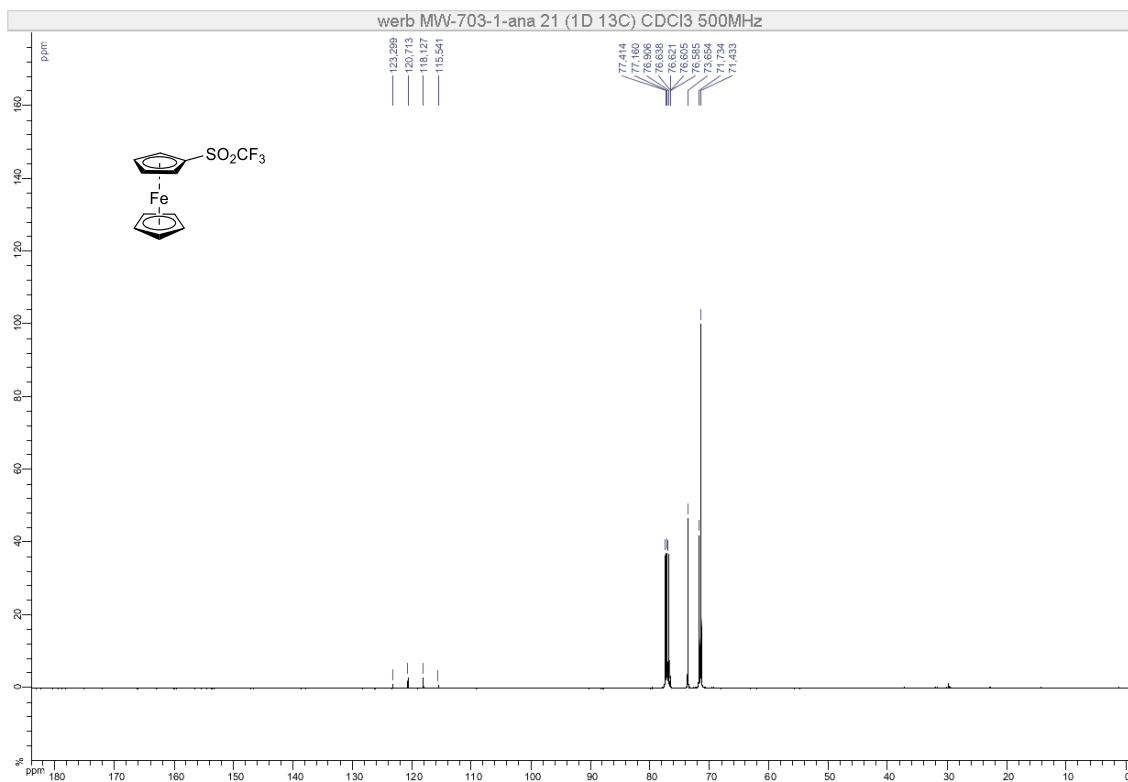
^1H NMR (500 MHz, CDCl_3)



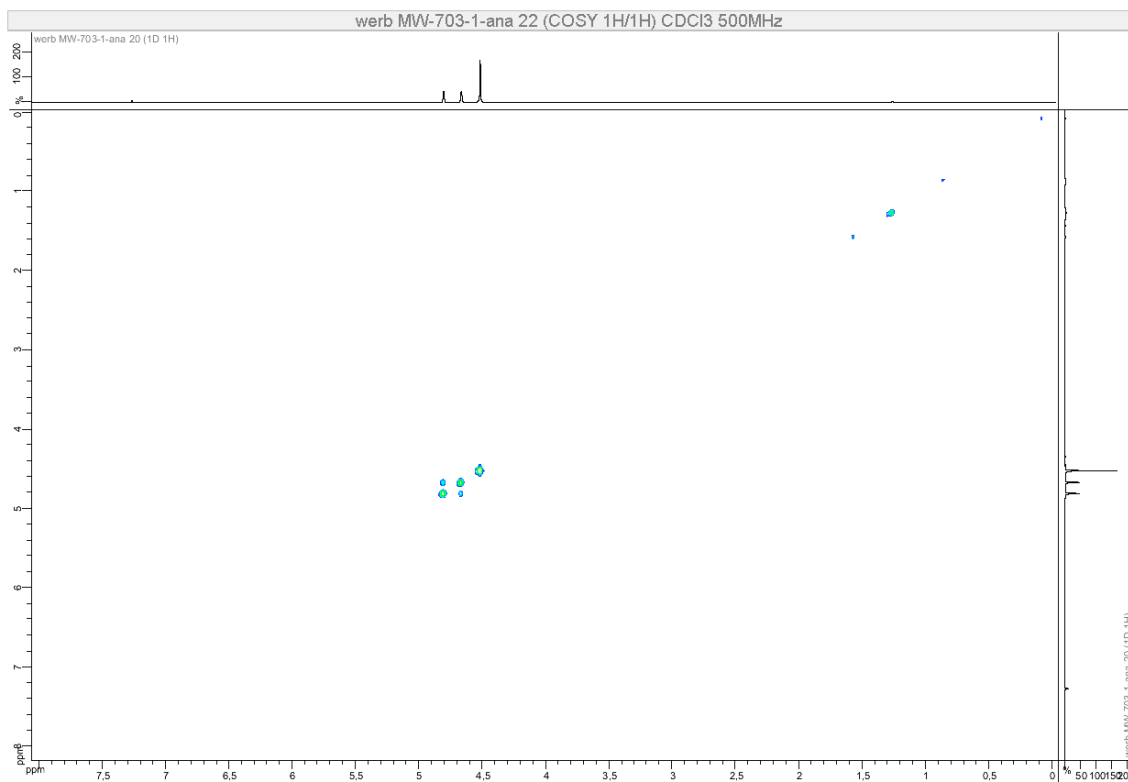
HOESY (500 MHz, CDCl_3) Irradiation at -74.5 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



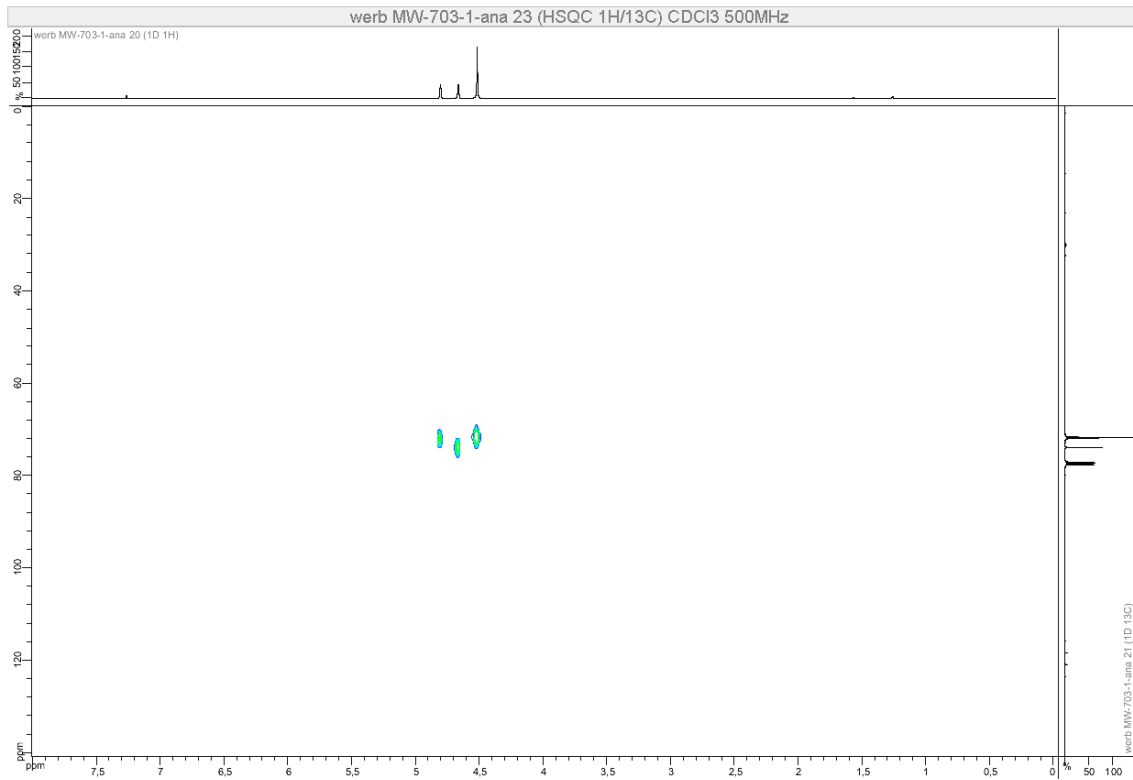
^{13}C NMR (126 MHz, CDCl_3)



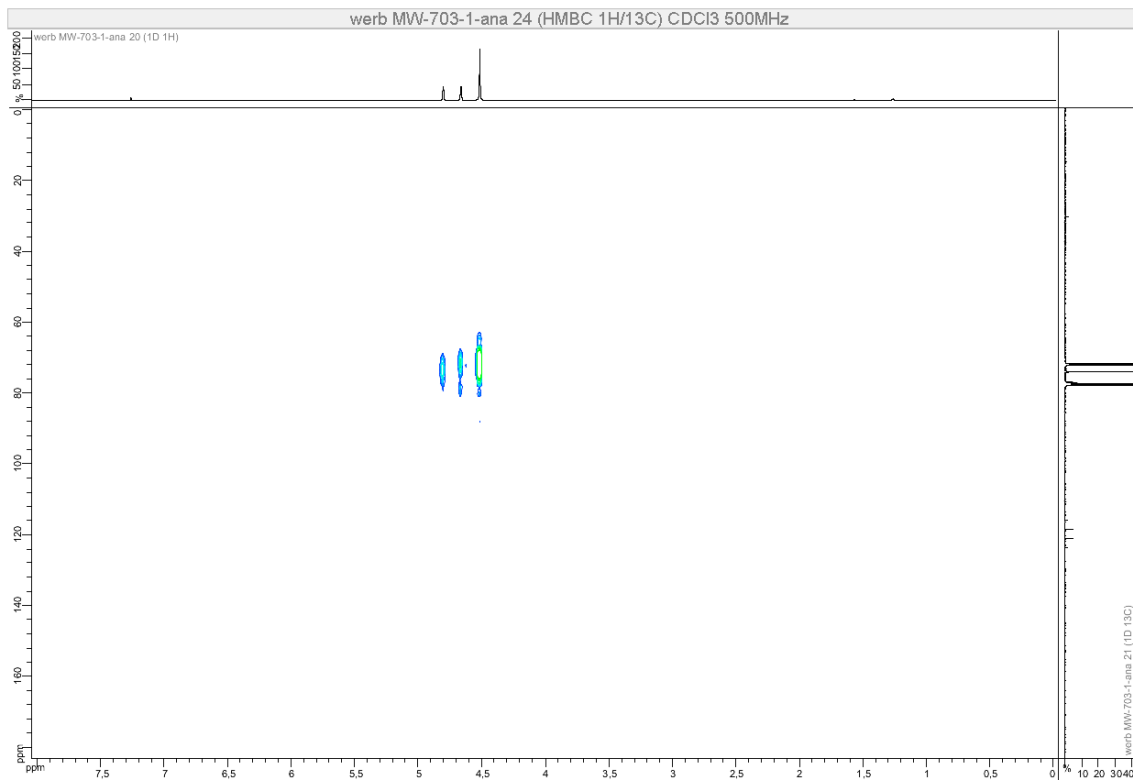
COSY (500 MHz, CDCl_3)



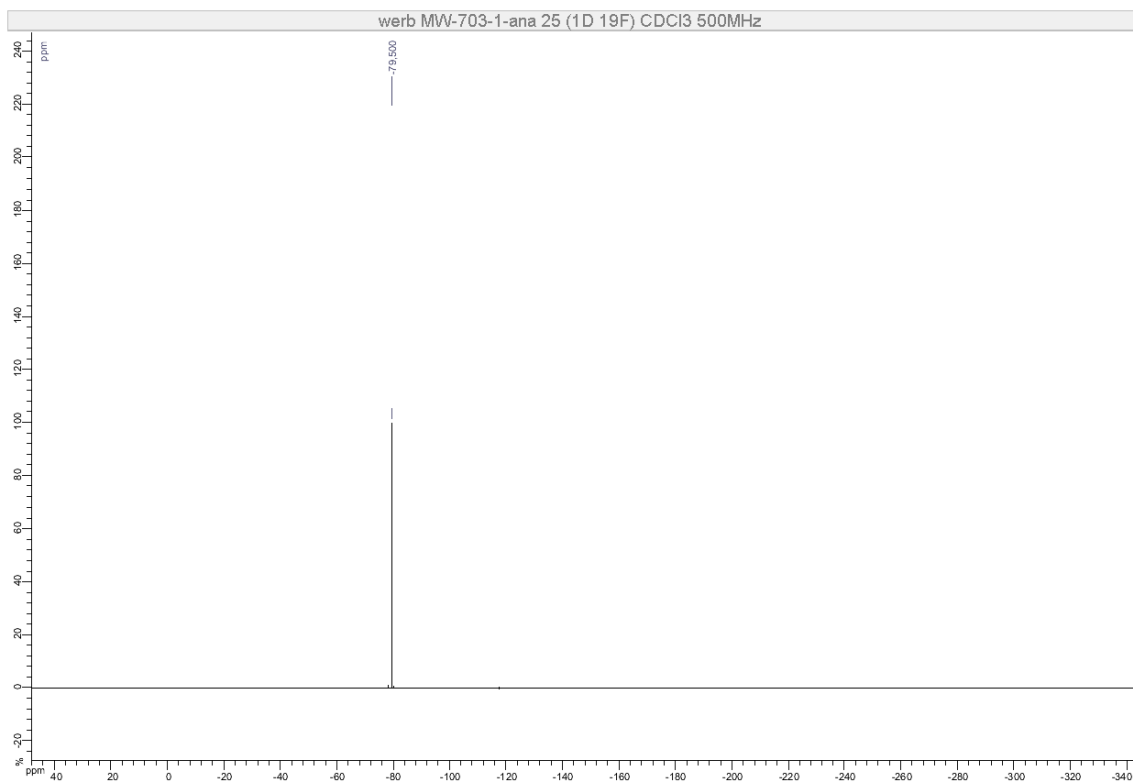
HSQC (500 MHz, CDCl₃)



HMBC (500 MHz, CDCl₃)

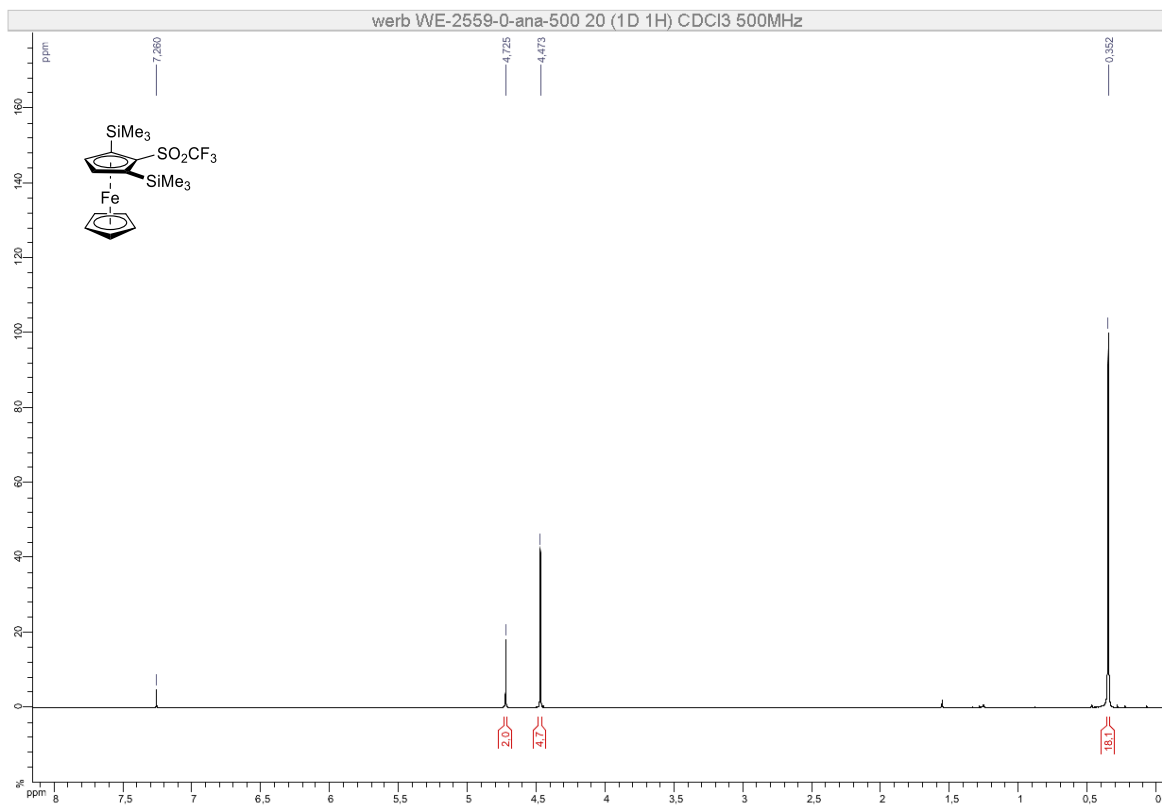


^{19}F NMR (470 MHz, CDCl_3)

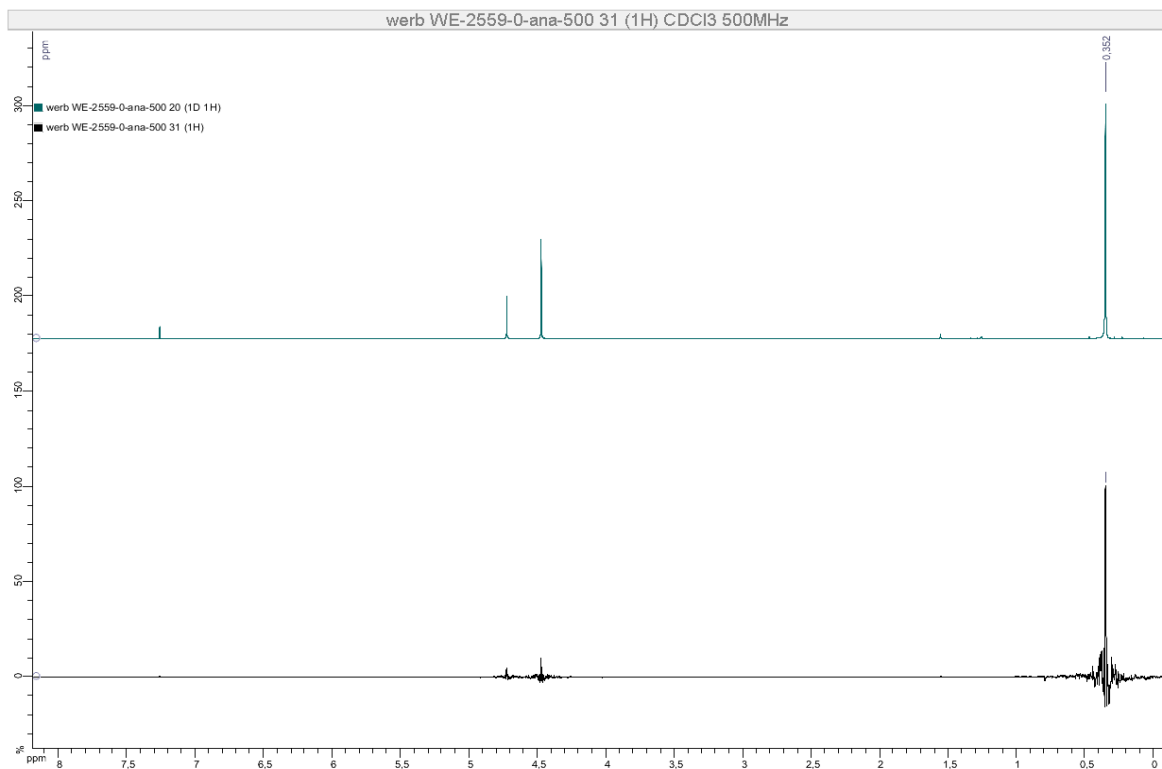


2,5-Bis(trimethylsilyl)ferrocenetriflone (2aa)

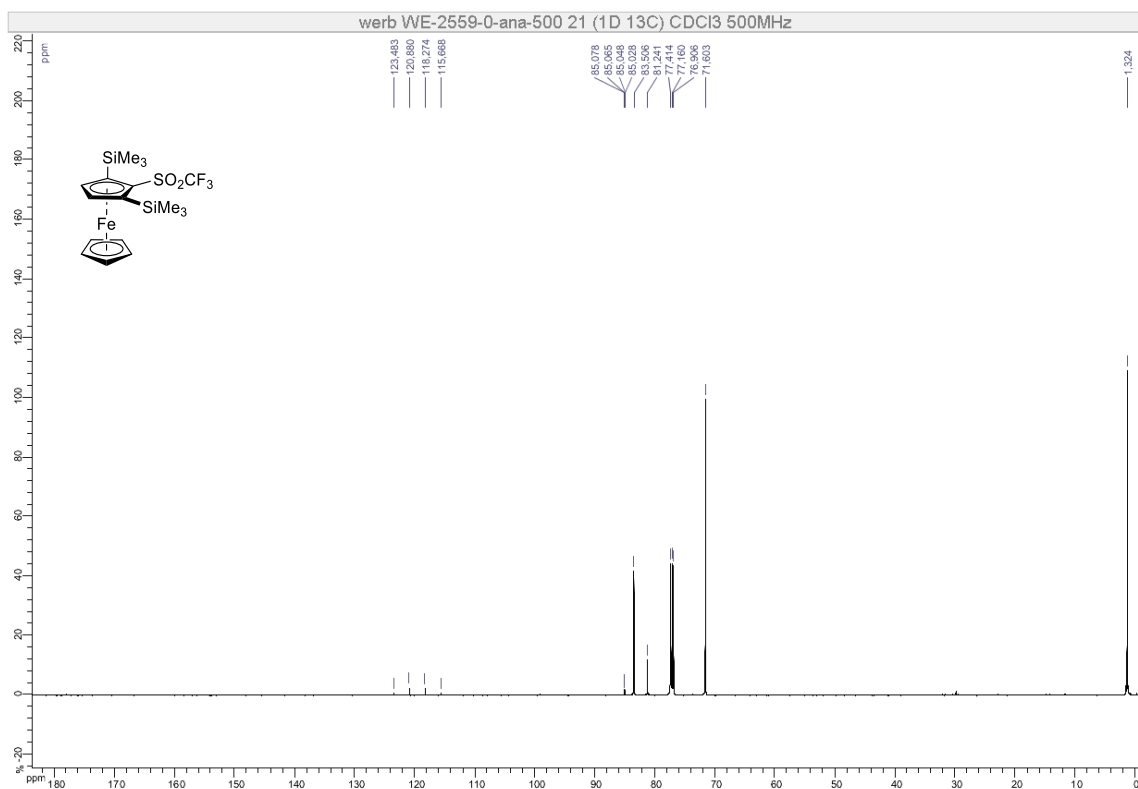
^1H NMR (500 MHz, CDCl_3)



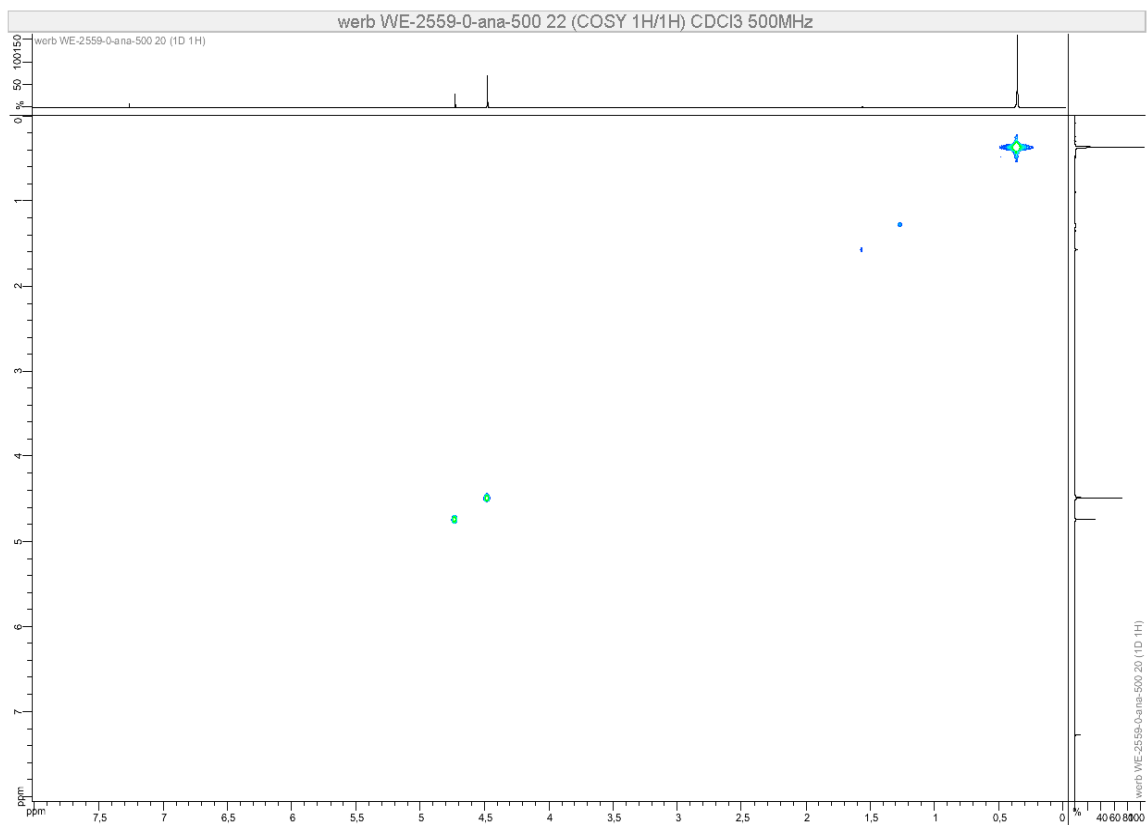
HOESY (500 MHz, CDCl_3) Irradiation at -75.7 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



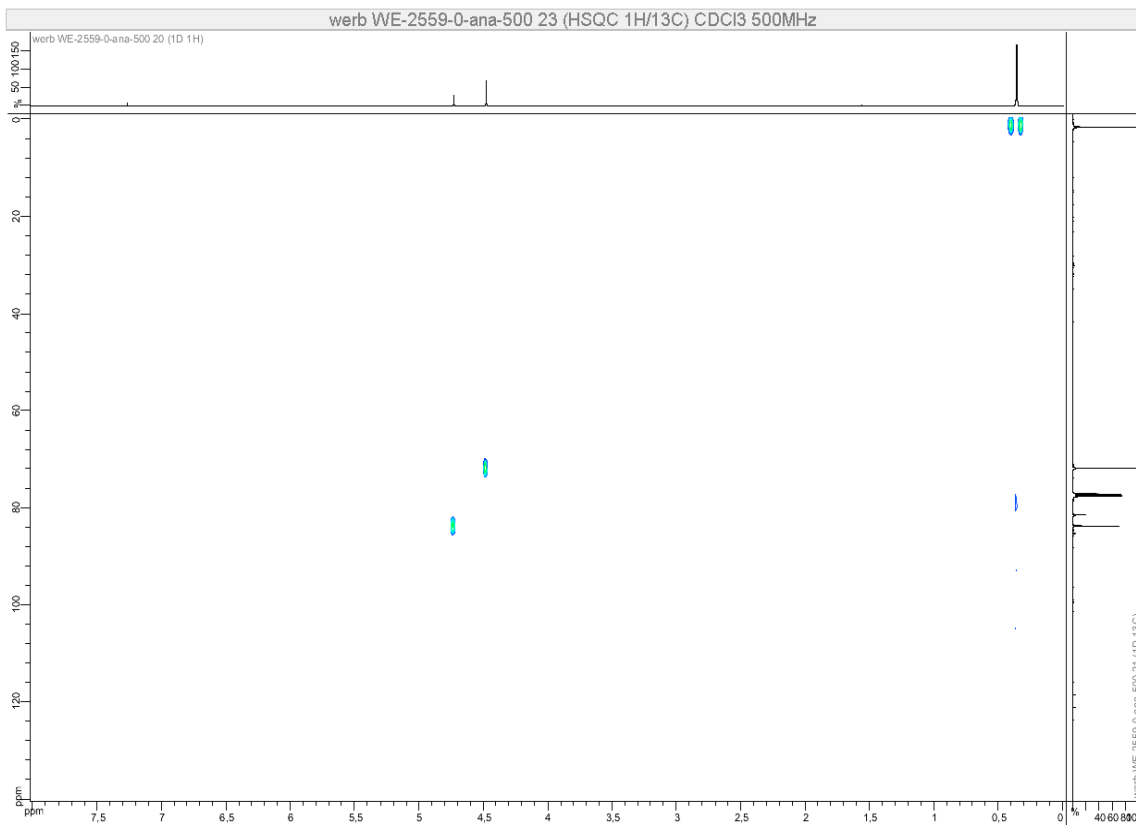
^{13}C NMR (126 MHz, CDCl_3)



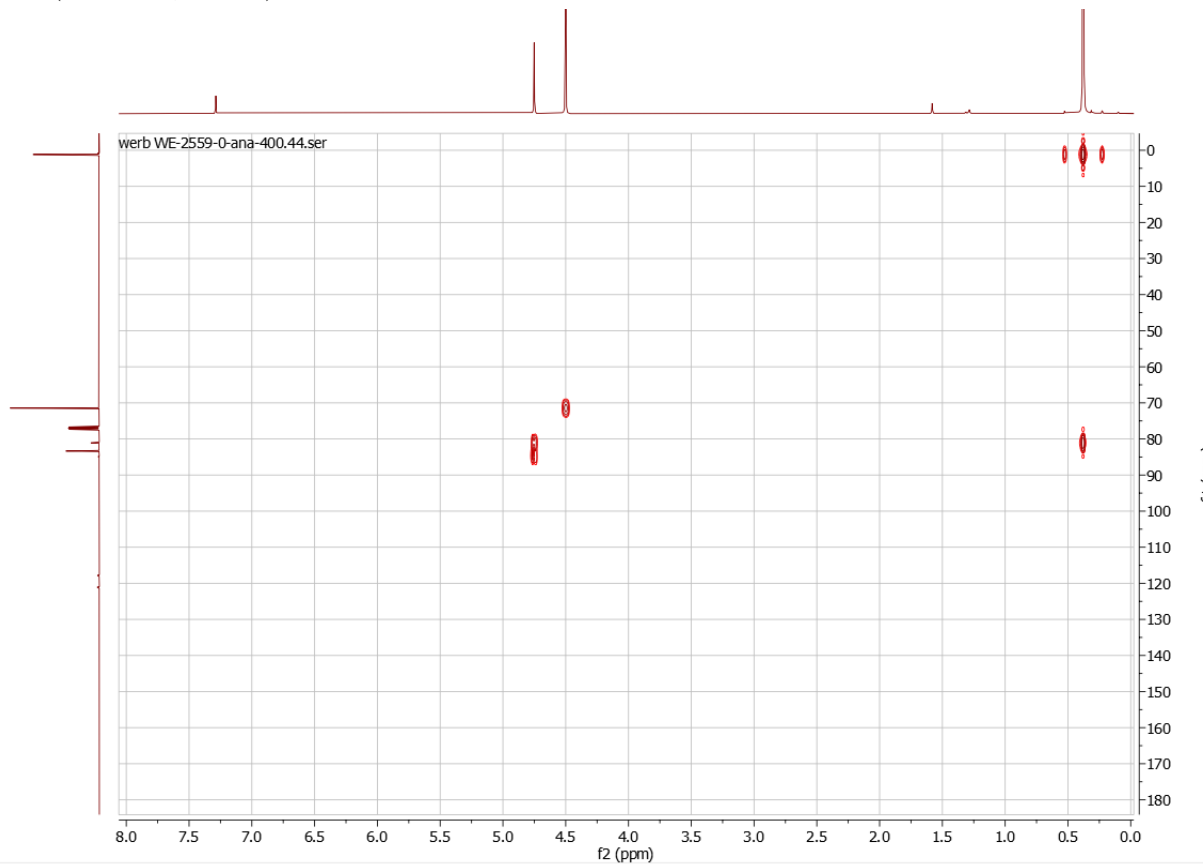
COSY (500 MHz, CDCl_3)



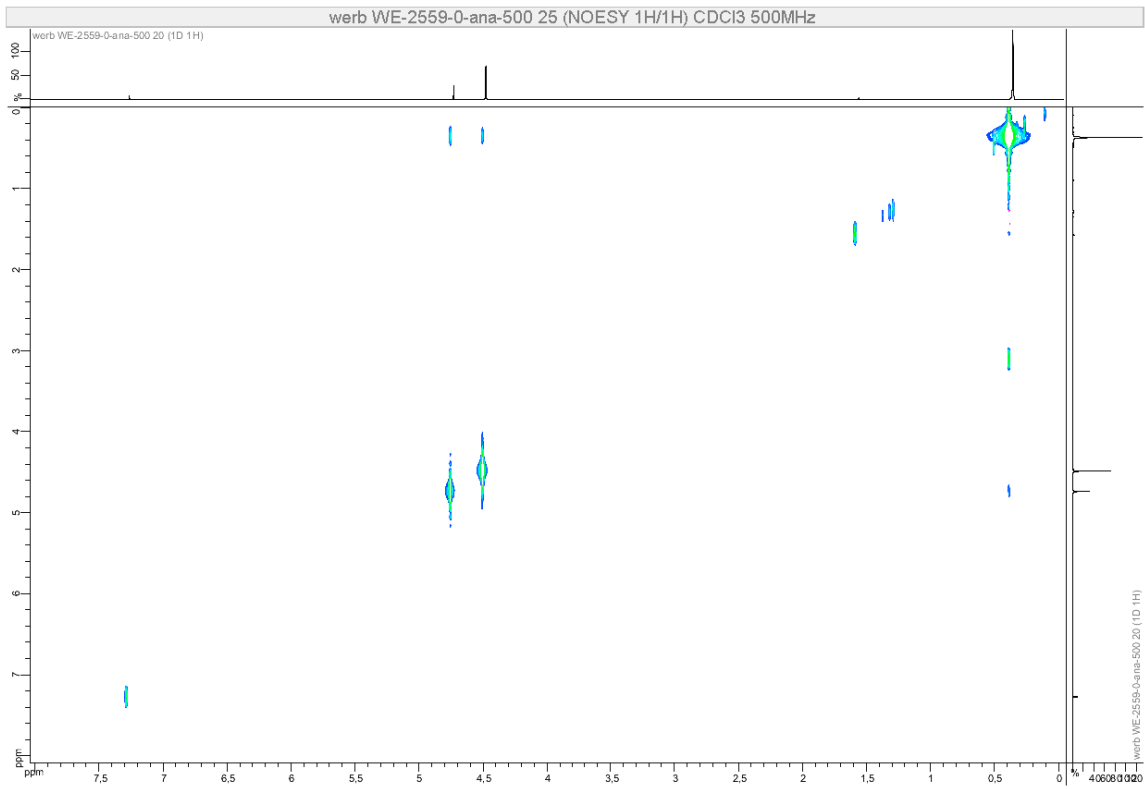
HSQC (500 MHz, CDCl₃)



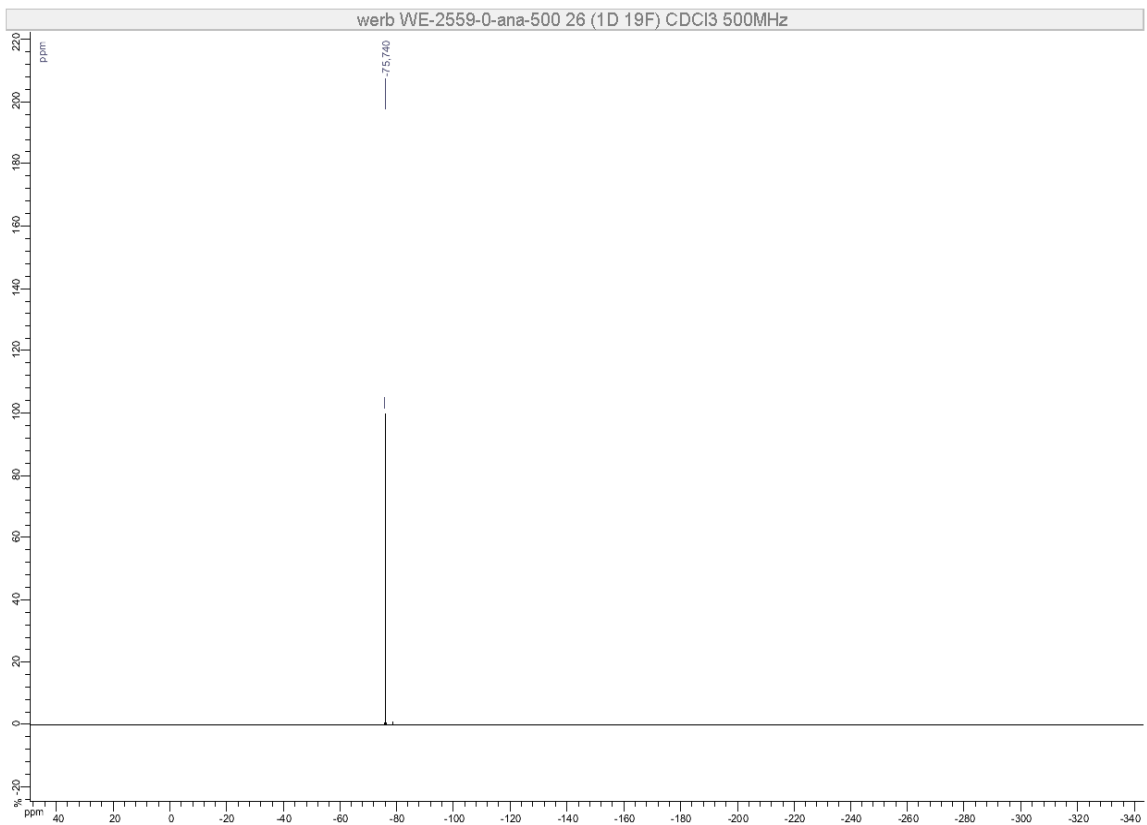
HMBC (500 MHz, CDCl₃)



NOESY (400 MHz, CDCl₃)

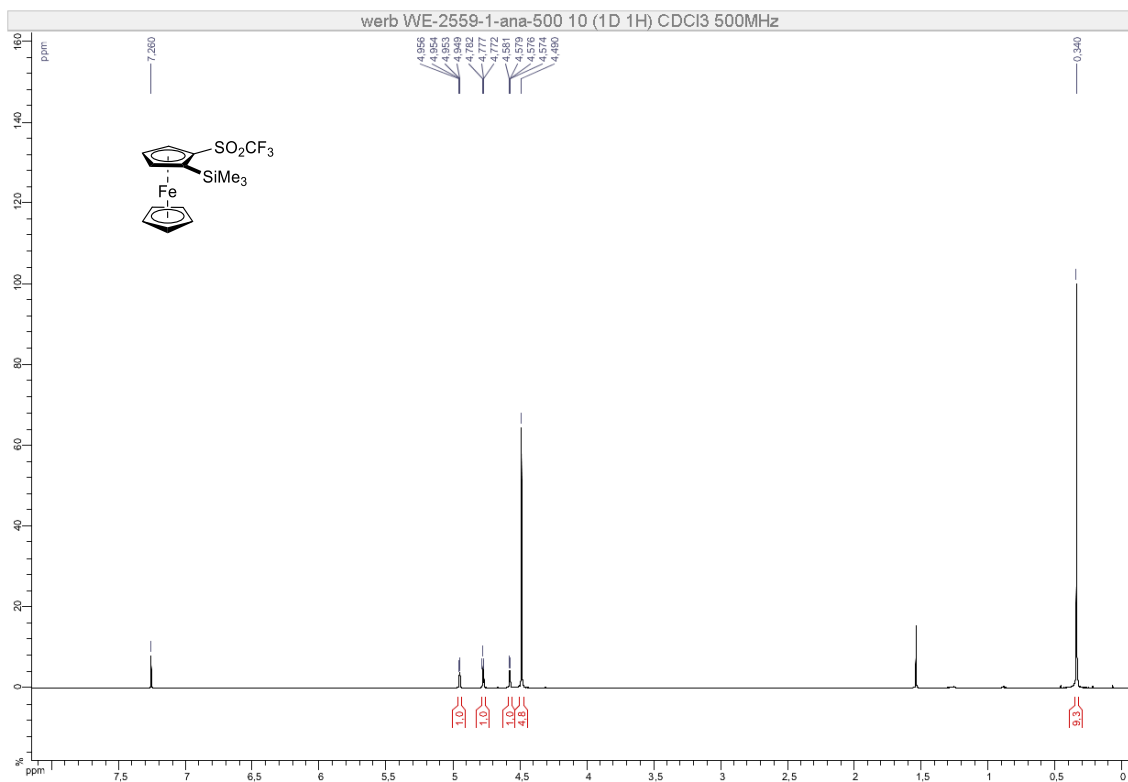


¹⁹F NMR (470 MHz, CDCl₃)

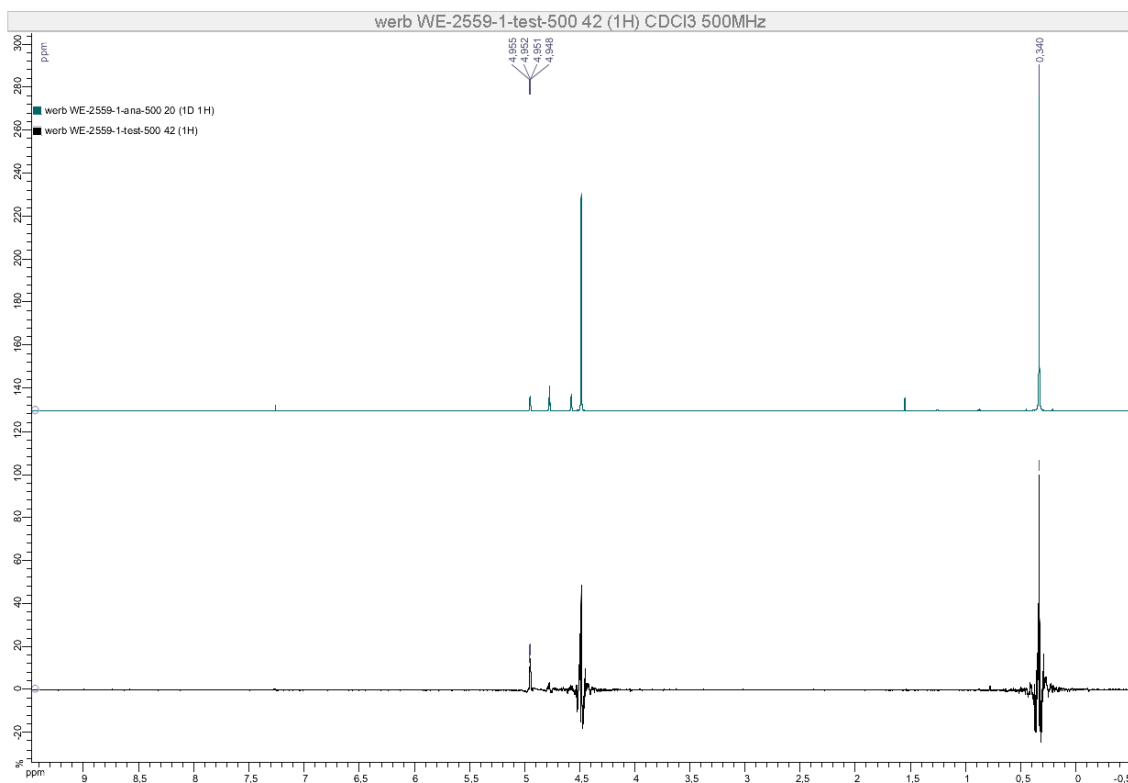


(*R_p*)-2-(Trimethylsilyl)ferrocenetriflone (*R_p*-2a)

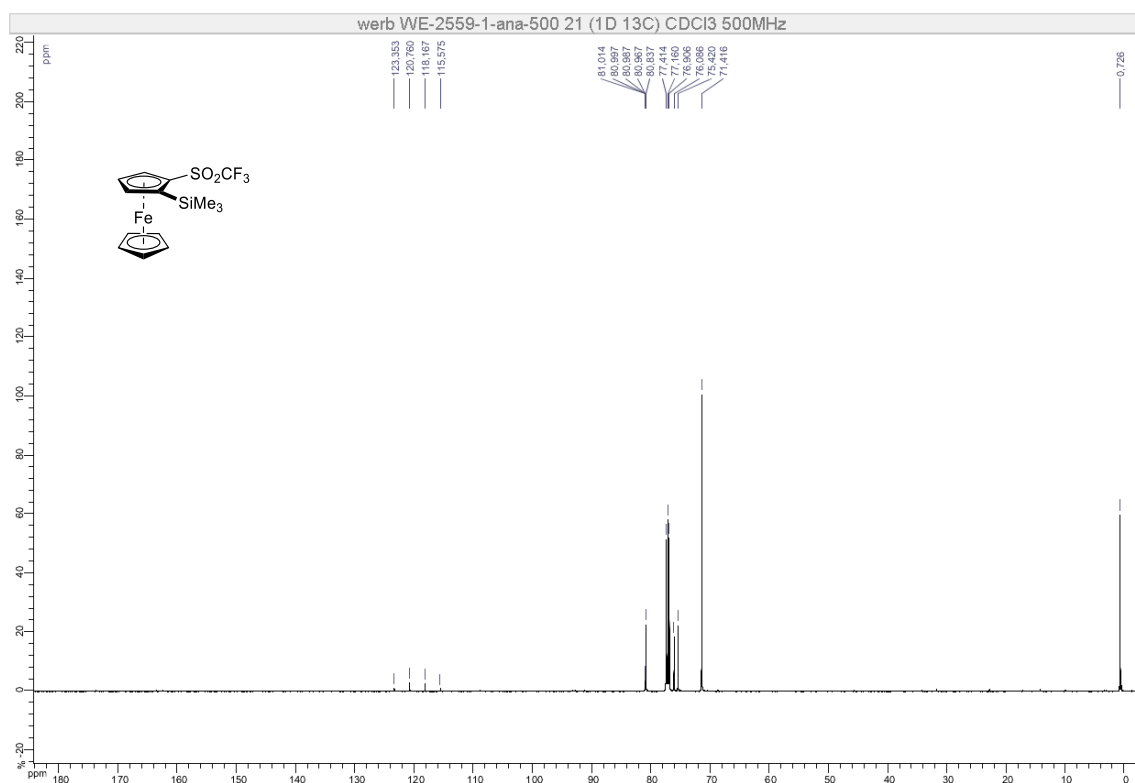
¹H NMR (500 MHz, CDCl₃)



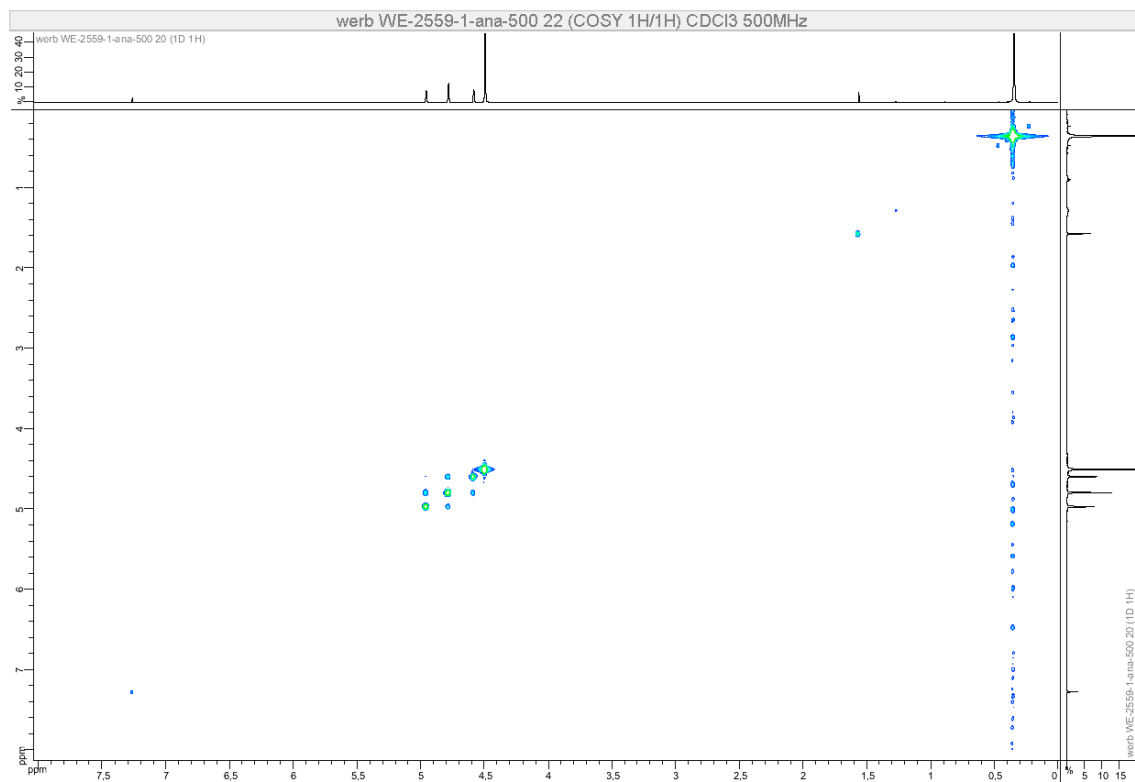
HOESY (500 MHz, CDCl₃) Irradiation at -78.6 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



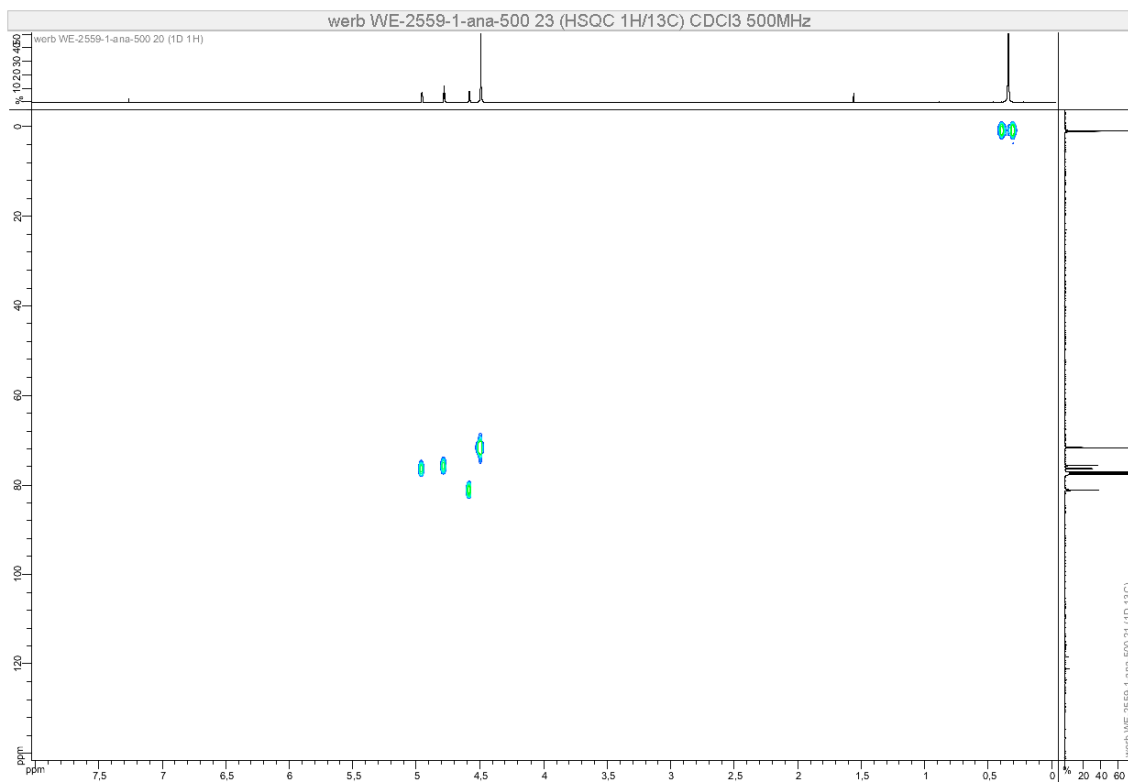
^{13}C NMR (126 MHz, CDCl_3)



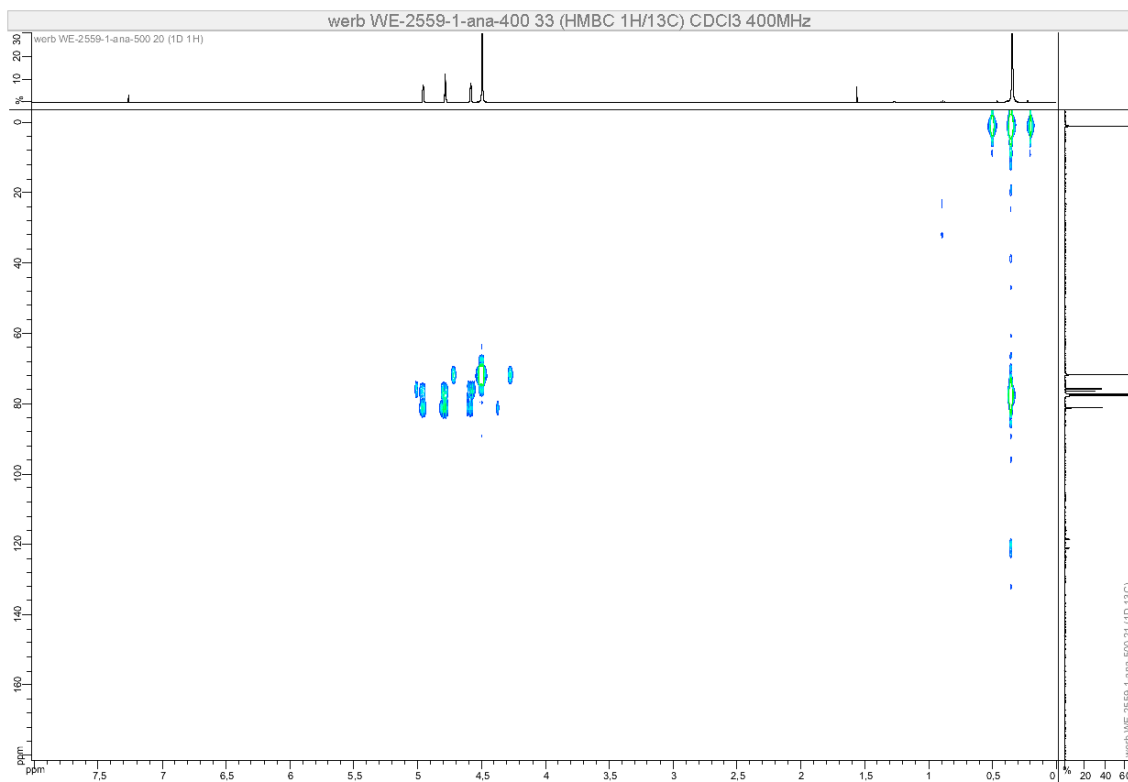
COSY (500 MHz, CDCl_3)



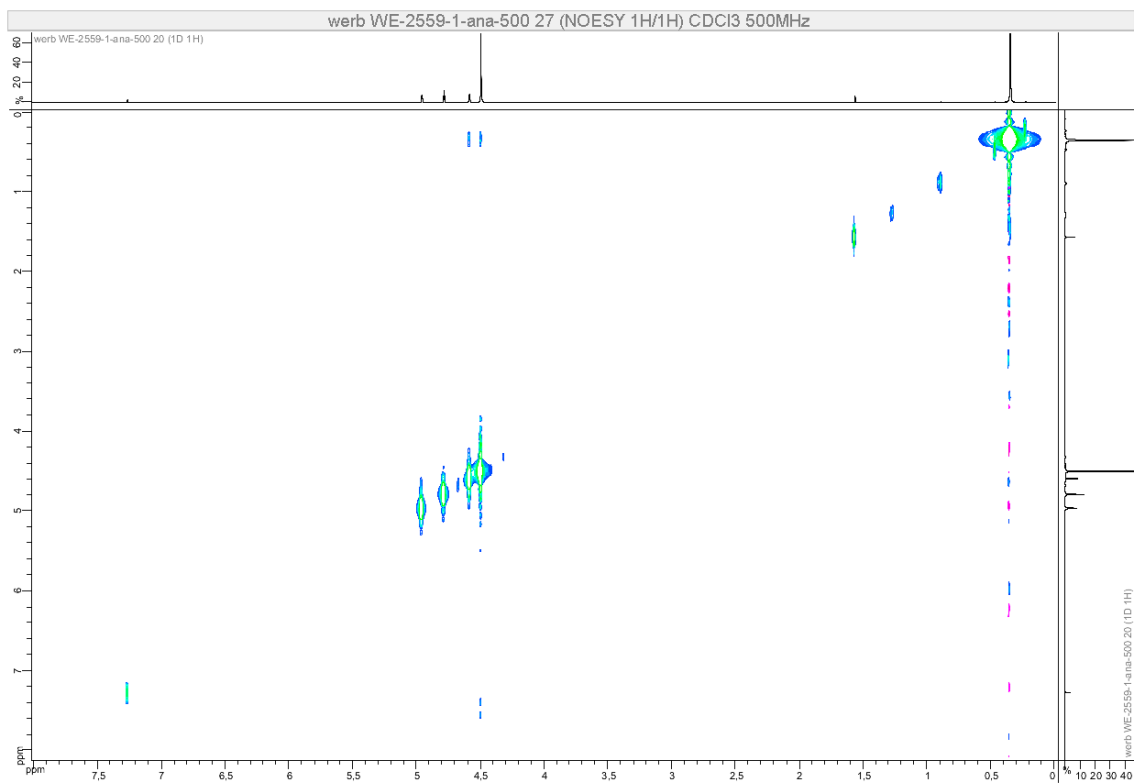
HSQC (500 MHz, CDCl₃)



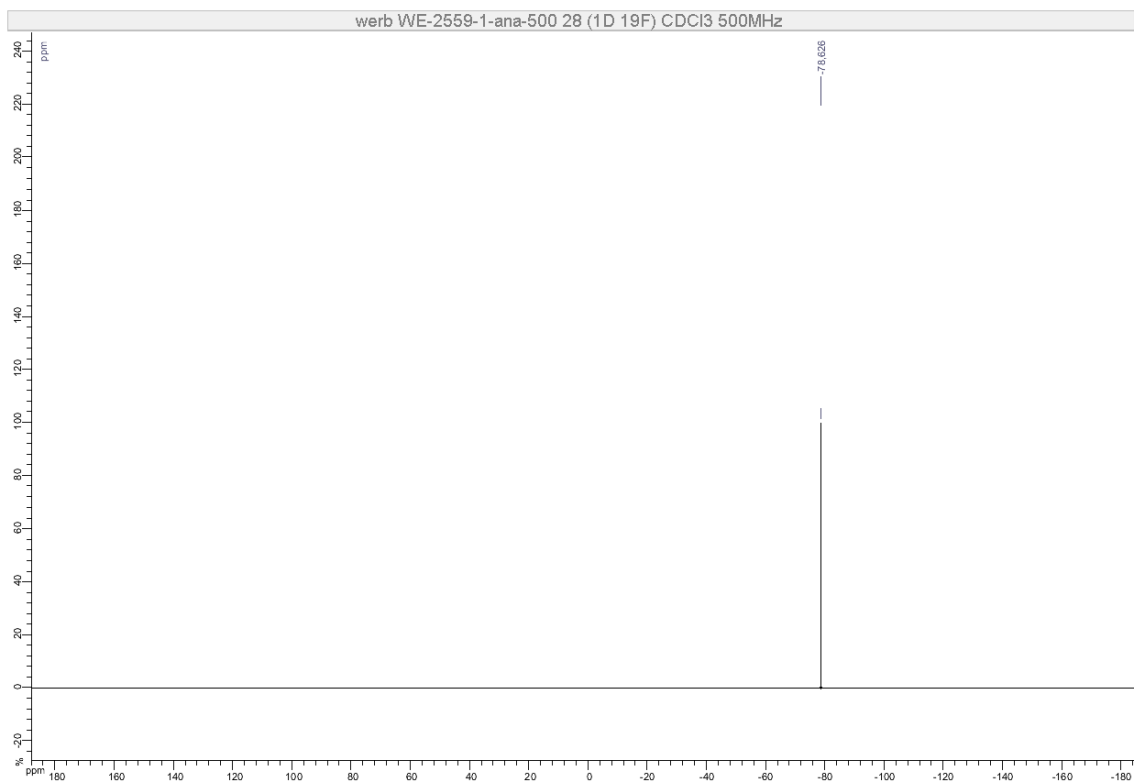
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

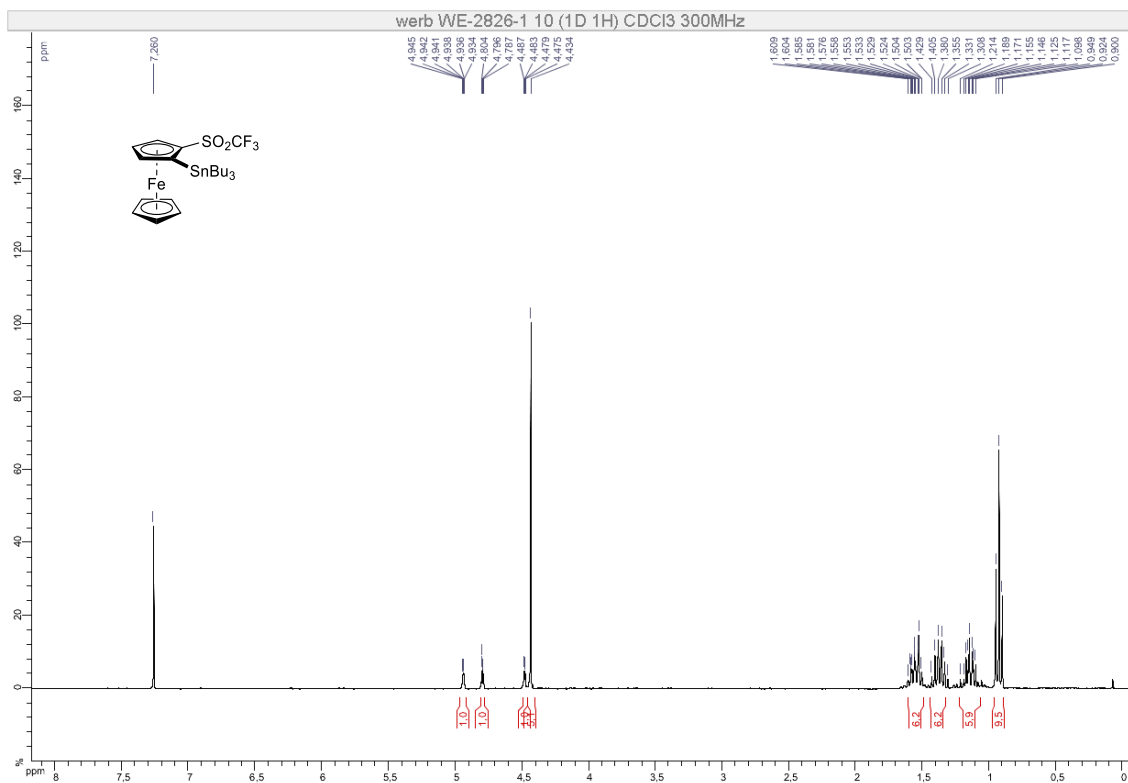


¹⁹F NMR (470 MHz, CDCl₃)

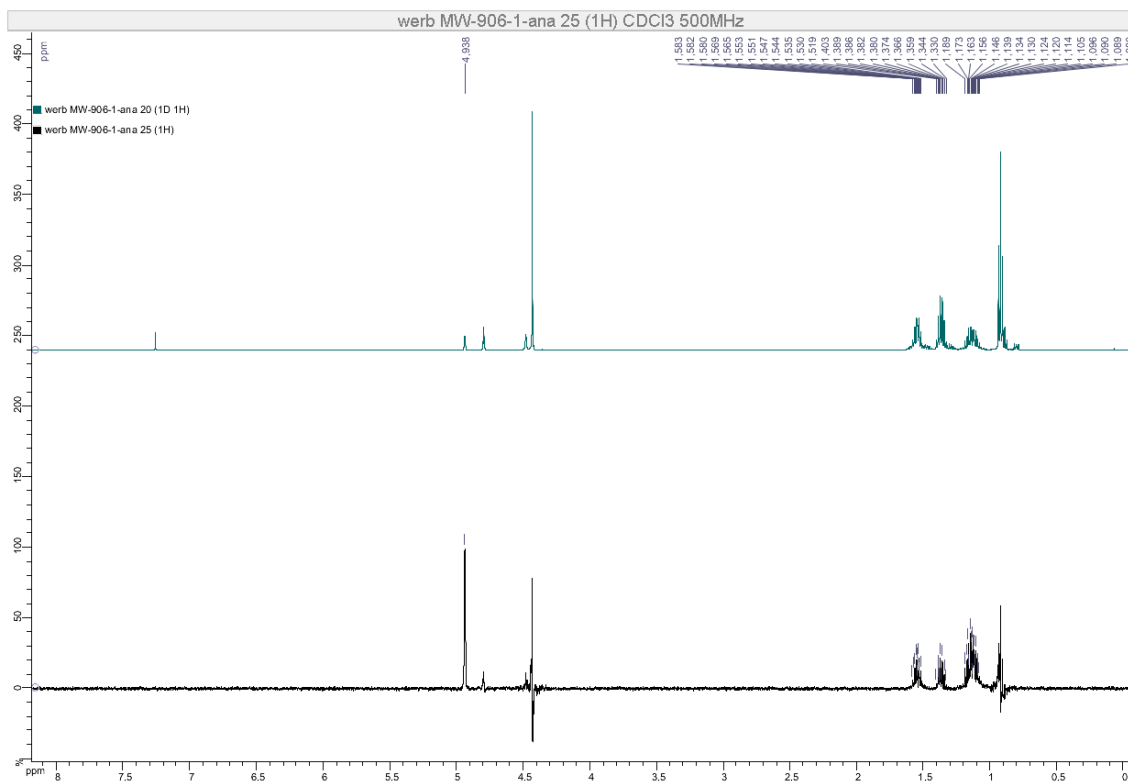


2-(Tributylstannyl)ferrocenetriflone (2b)

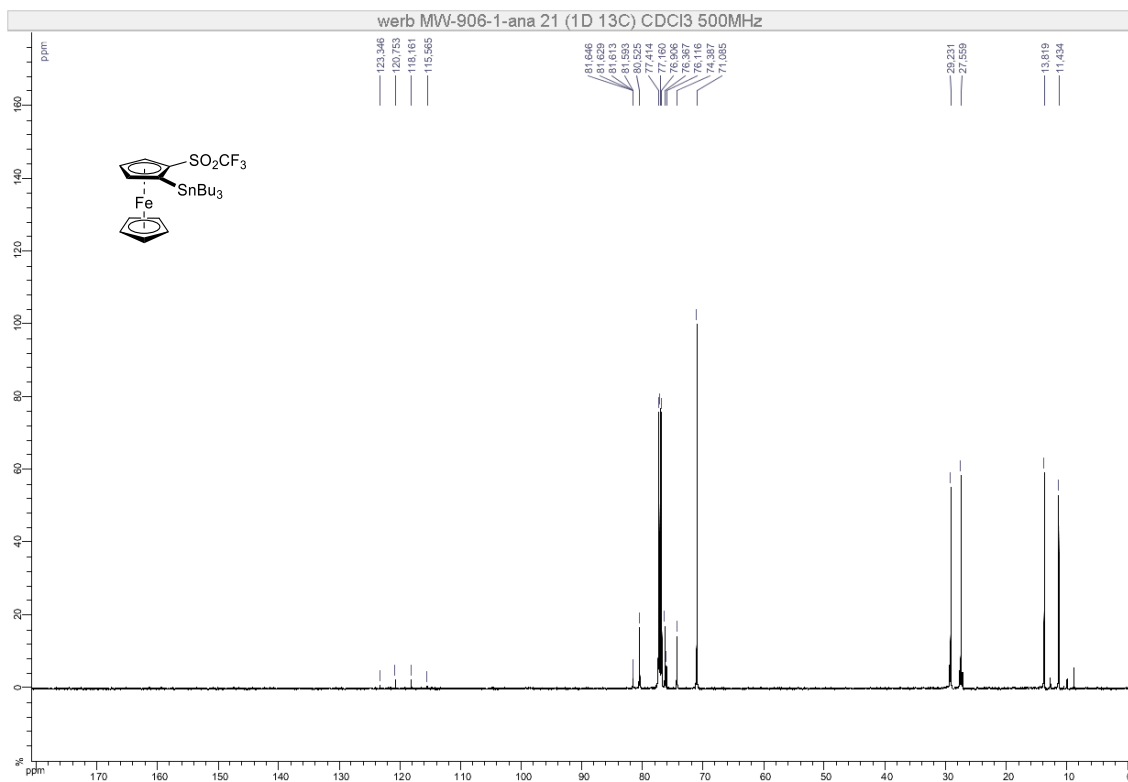
^1H NMR (300 MHz, CDCl_3)



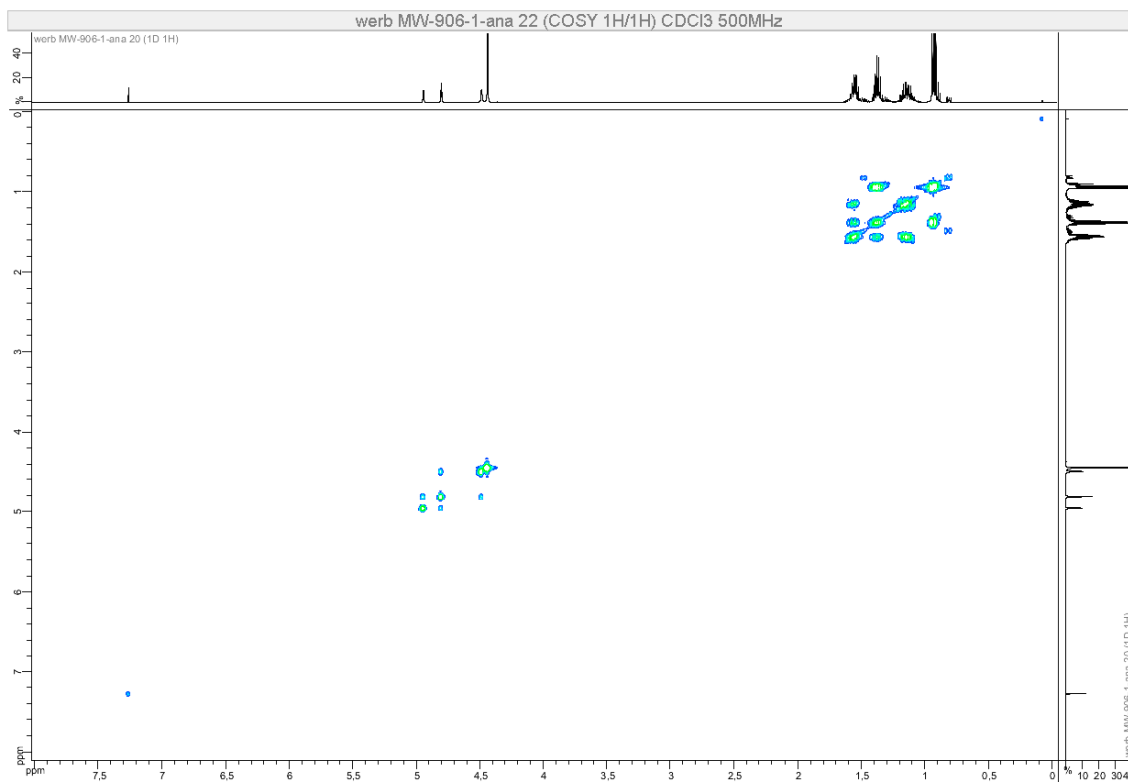
HOESY (500 MHz, CDCl_3) Irradiation at -78.8 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



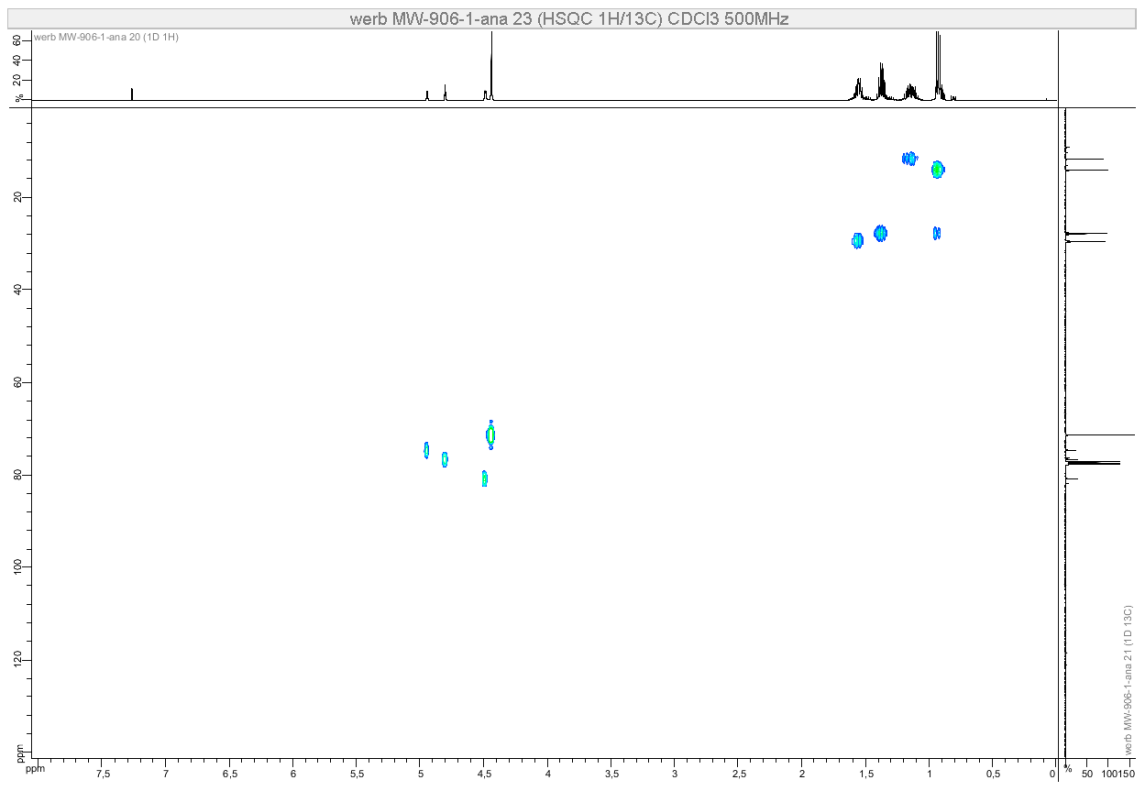
^{13}C NMR (126 MHz, CDCl_3)



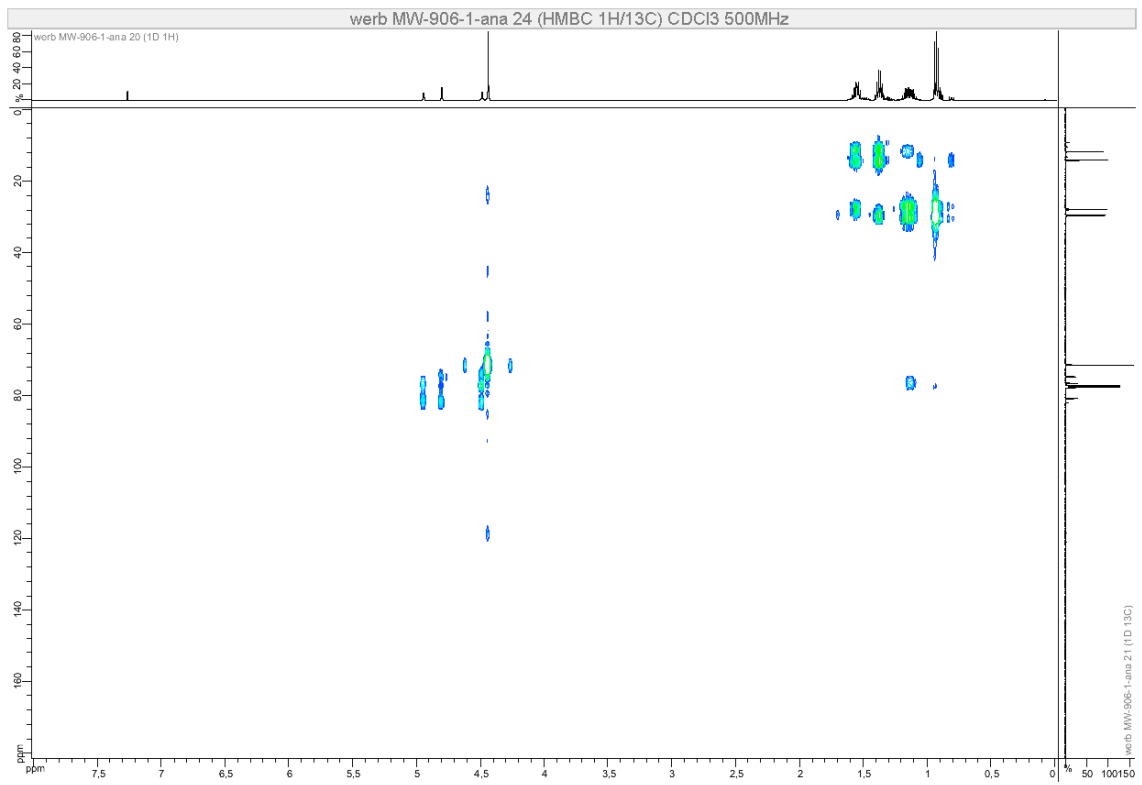
COSY (500 MHz, CDCl_3)



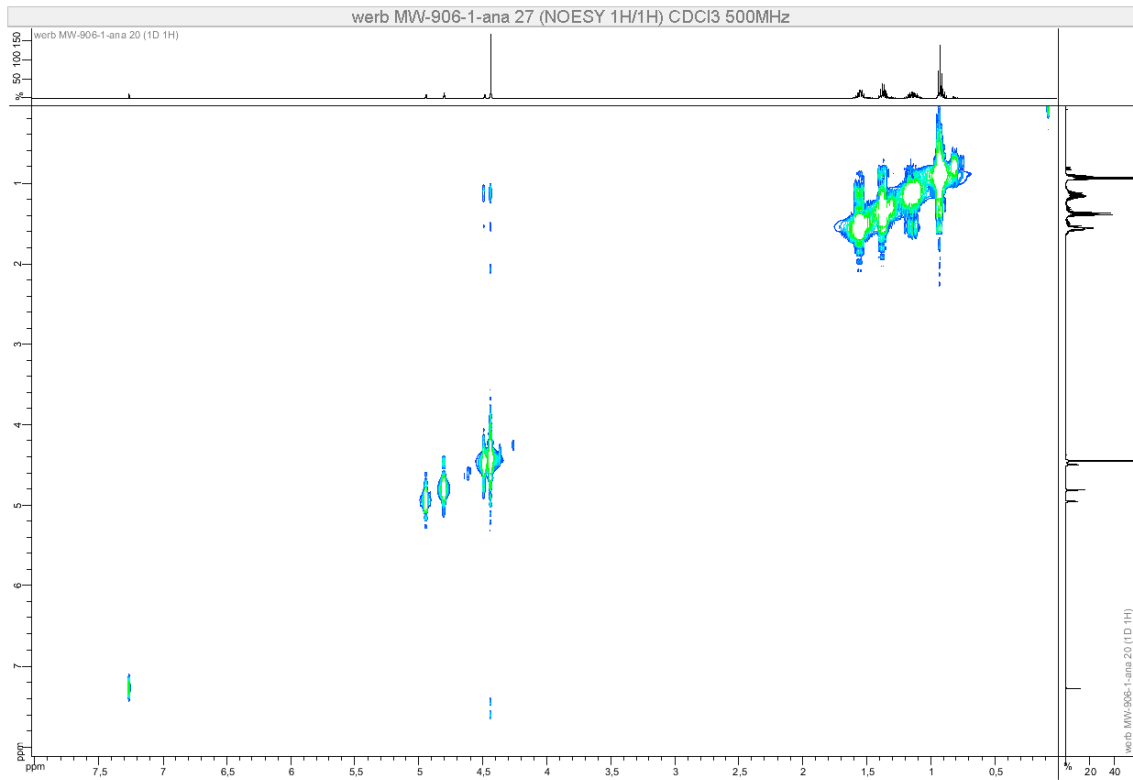
HSQC (500 MHz, CDCl₃)



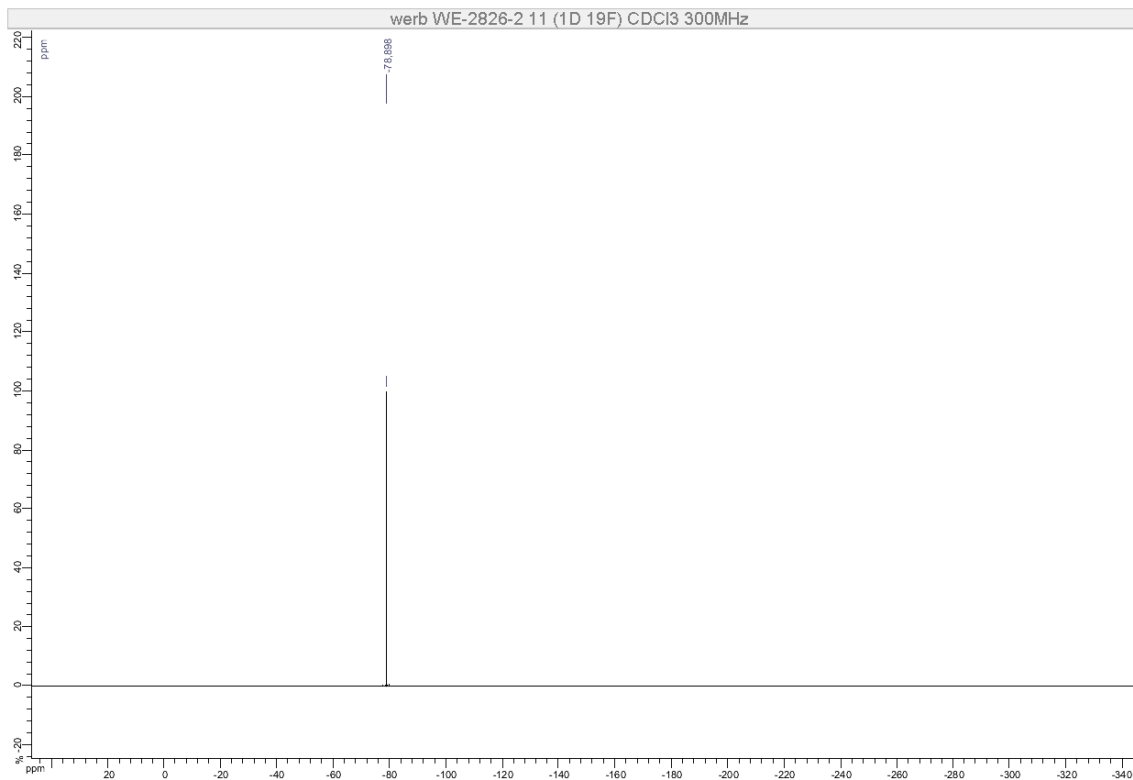
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NOESY (500 MHz, CDCl₃)

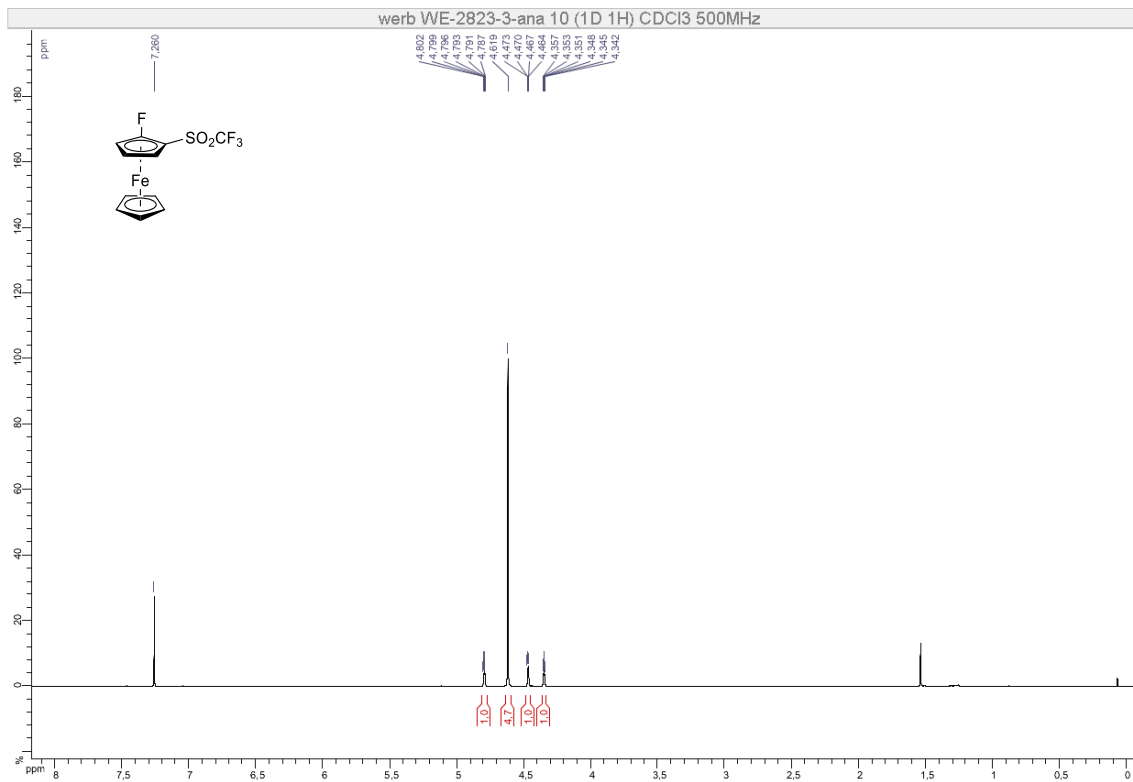


¹⁹F NMR (470 MHz, CDCl₃)

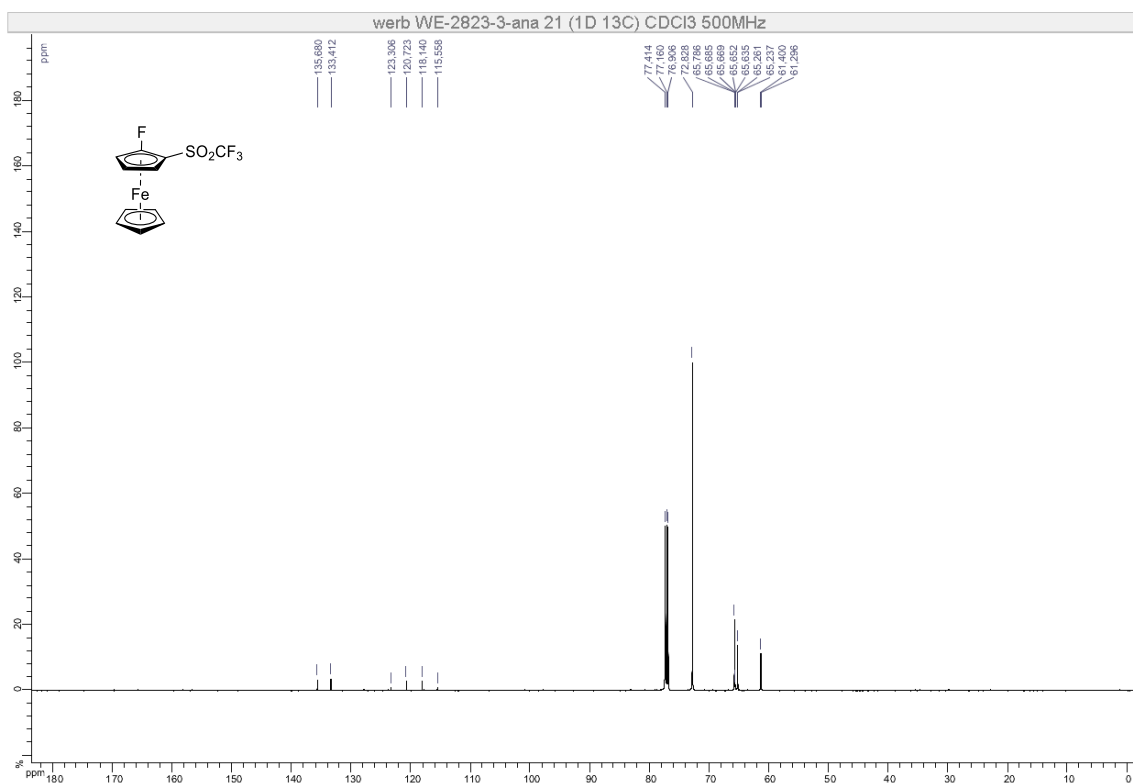


2-Fluoroferrocenetriplone (2c)

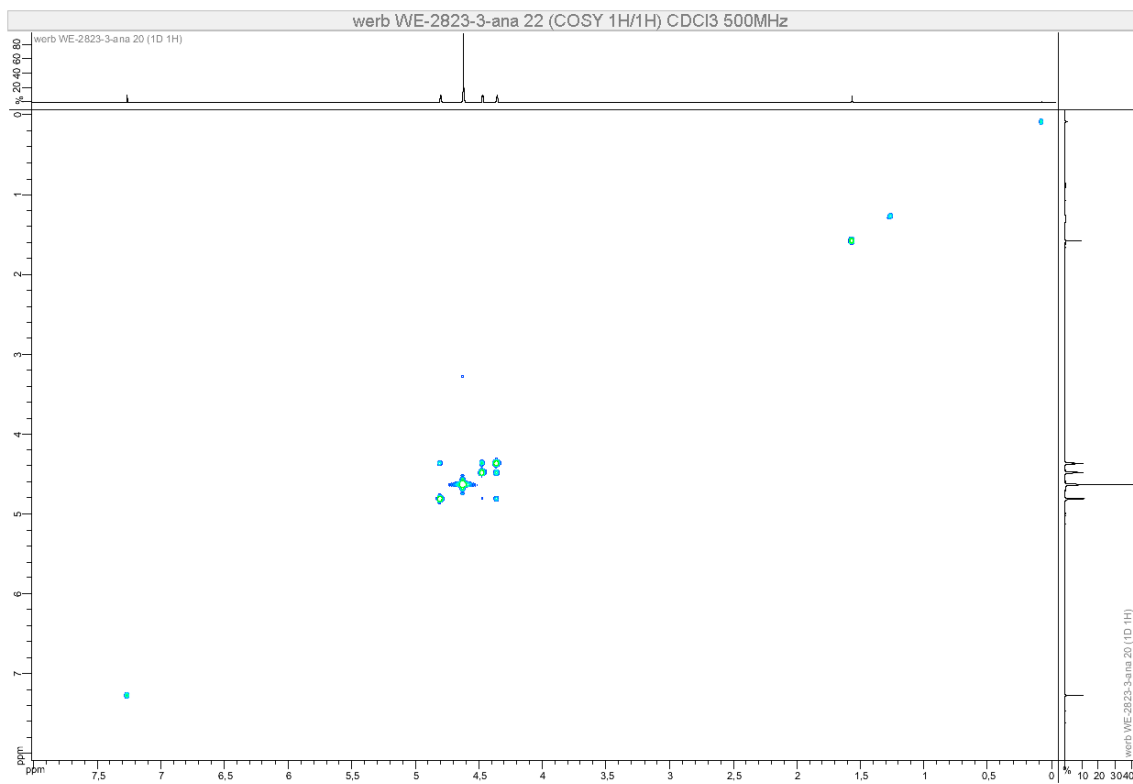
^1H NMR (500 MHz, CDCl_3)



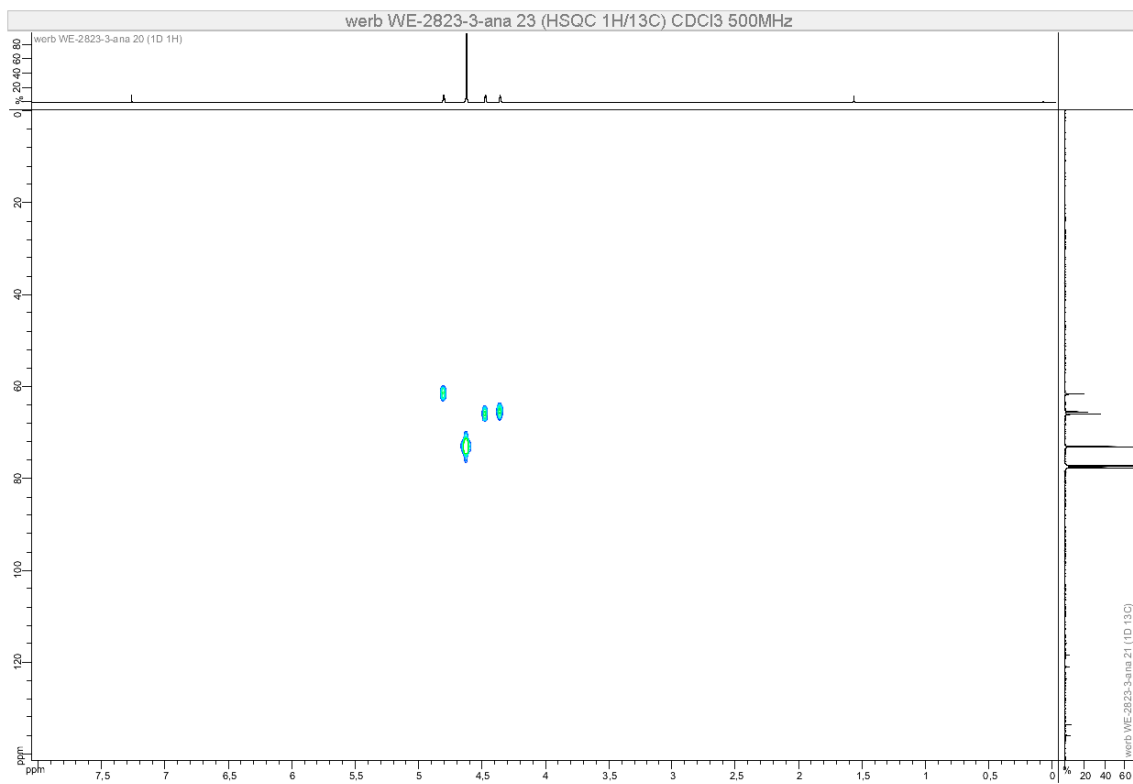
^{13}C NMR (126 MHz, CDCl_3)



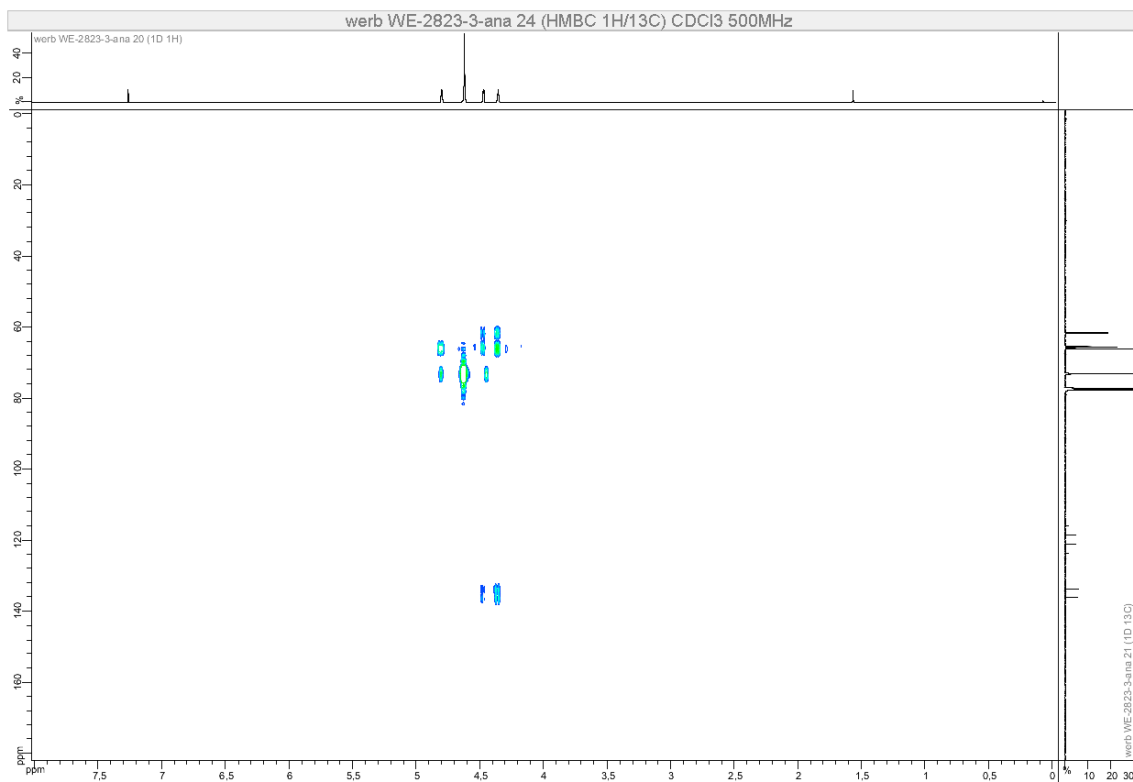
COSY (500 MHz, CDCl₃)



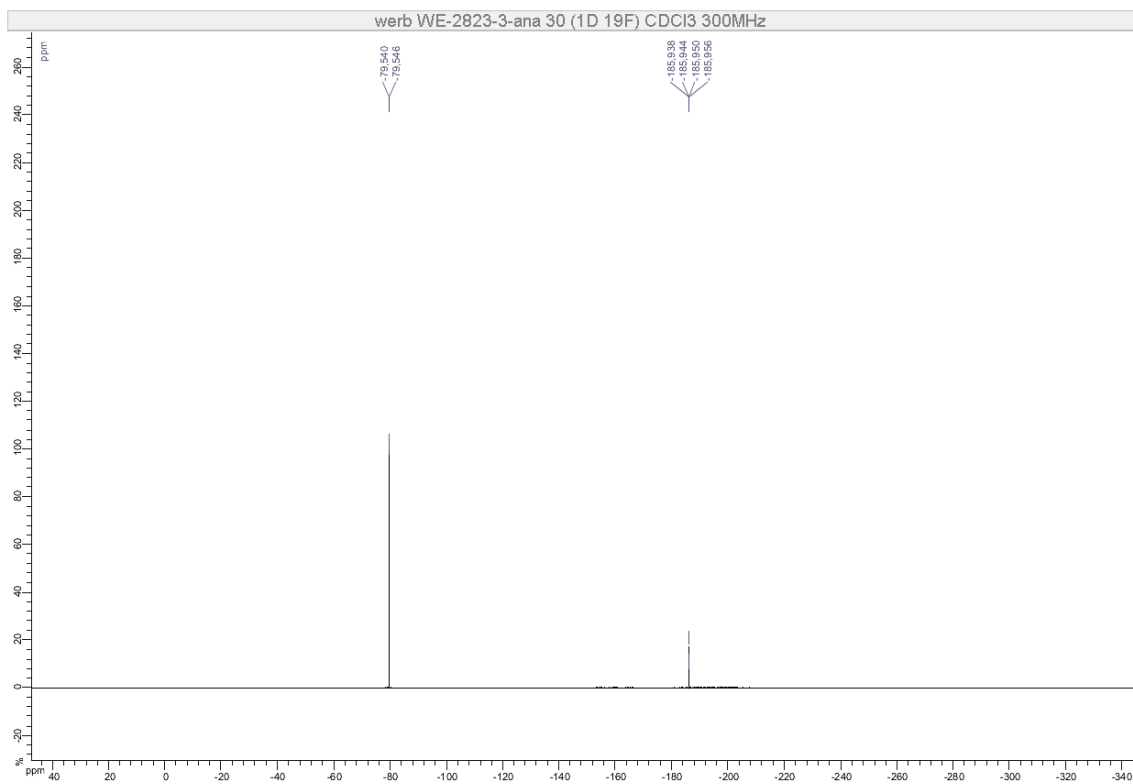
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HMBC (500 MHz, CDCl₃)

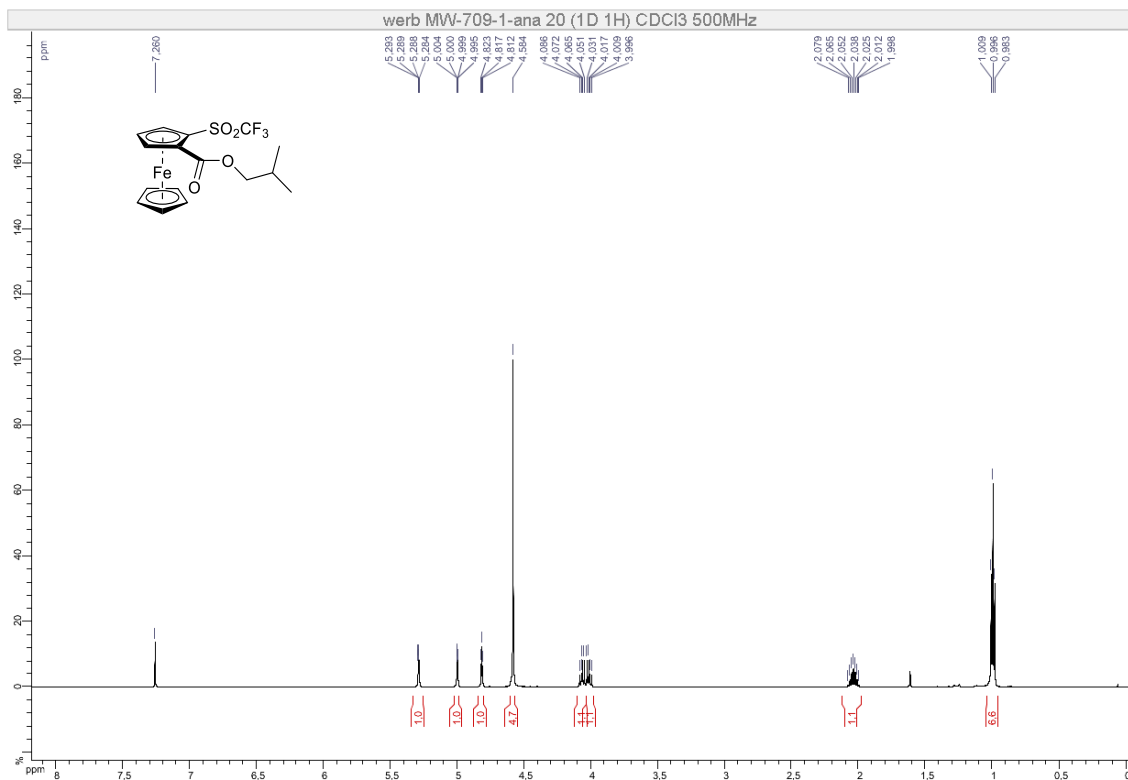


¹⁹F NMR (470 MHz, CDCl₃)

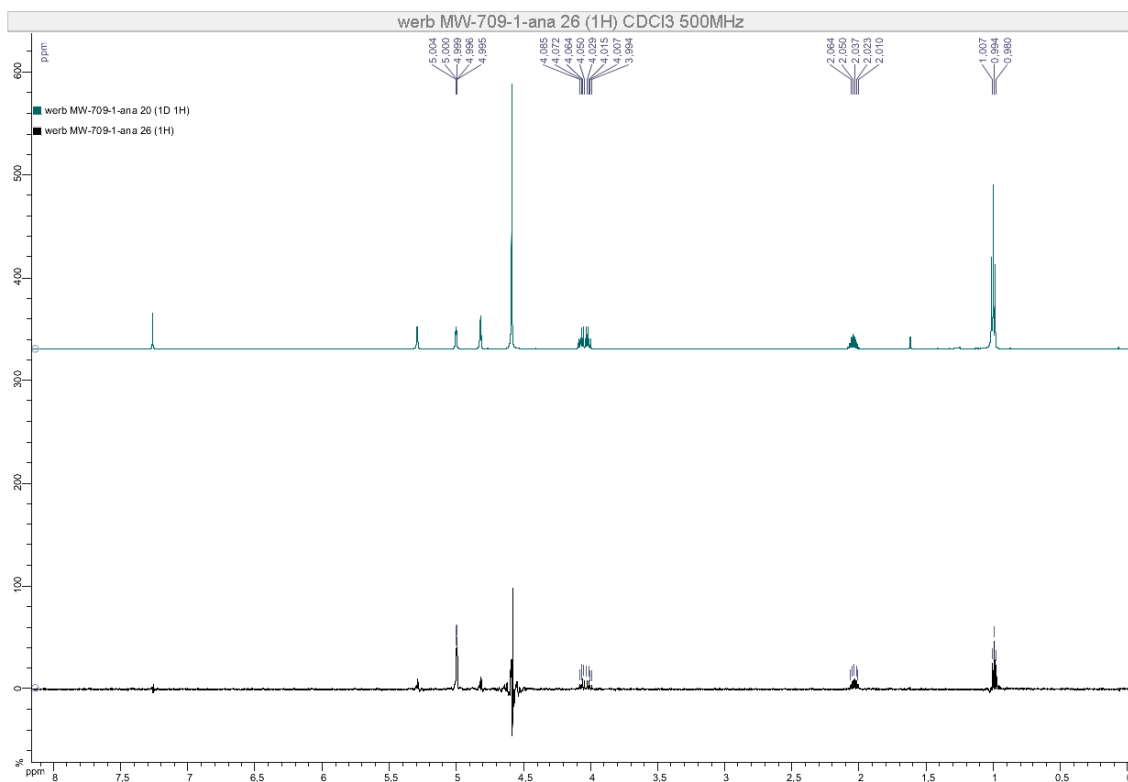


2-(Isobutoxycarbonyl)ferrocenetriflone (2d)

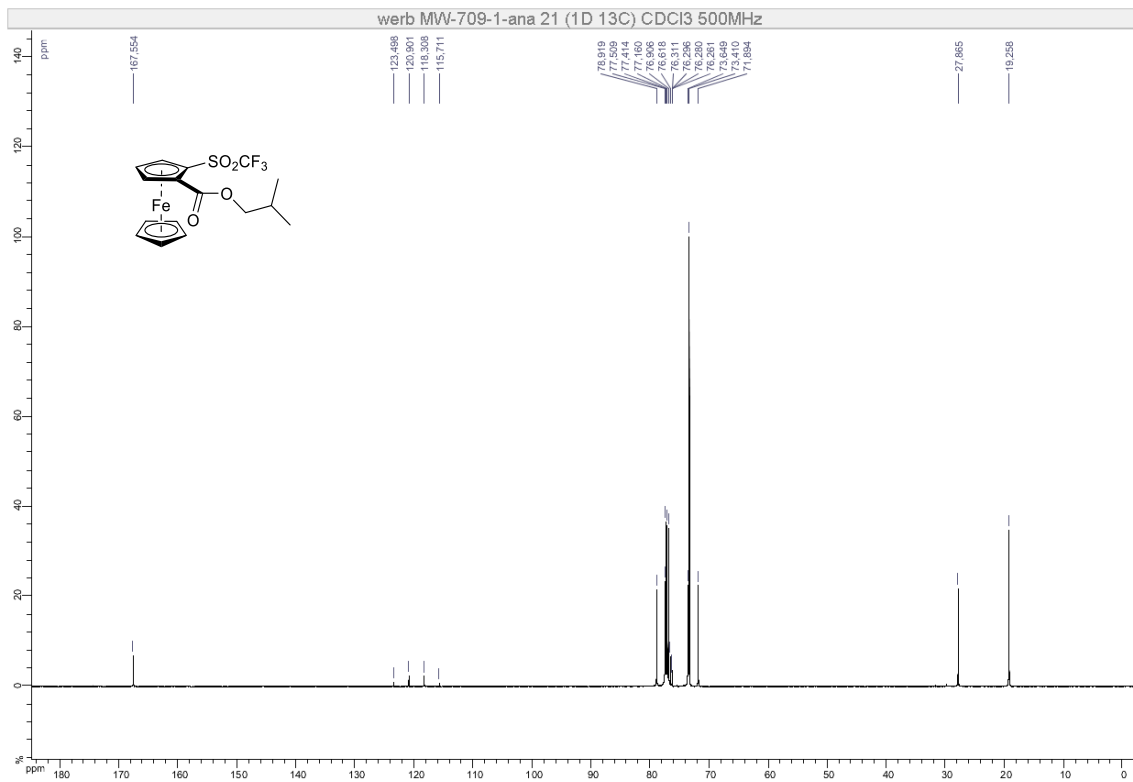
^1H NMR (500 MHz, CDCl_3)



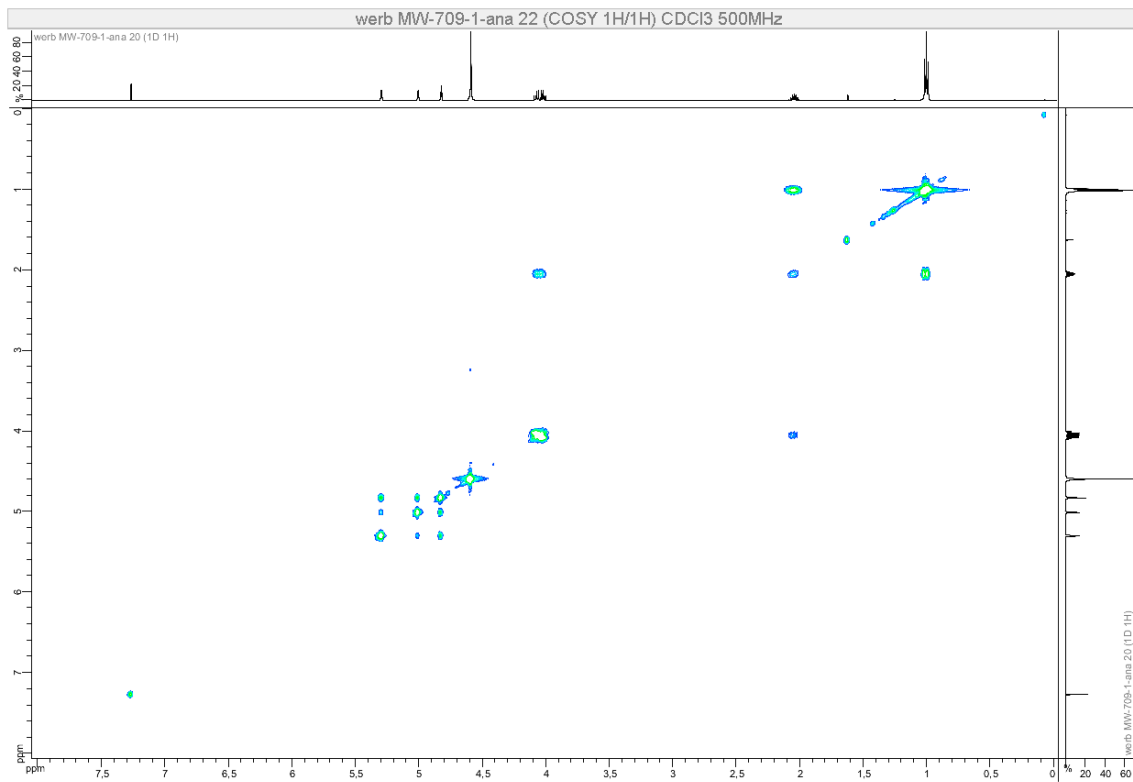
HOESY (500 MHz, CDCl_3) Irradiation at -76.8 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



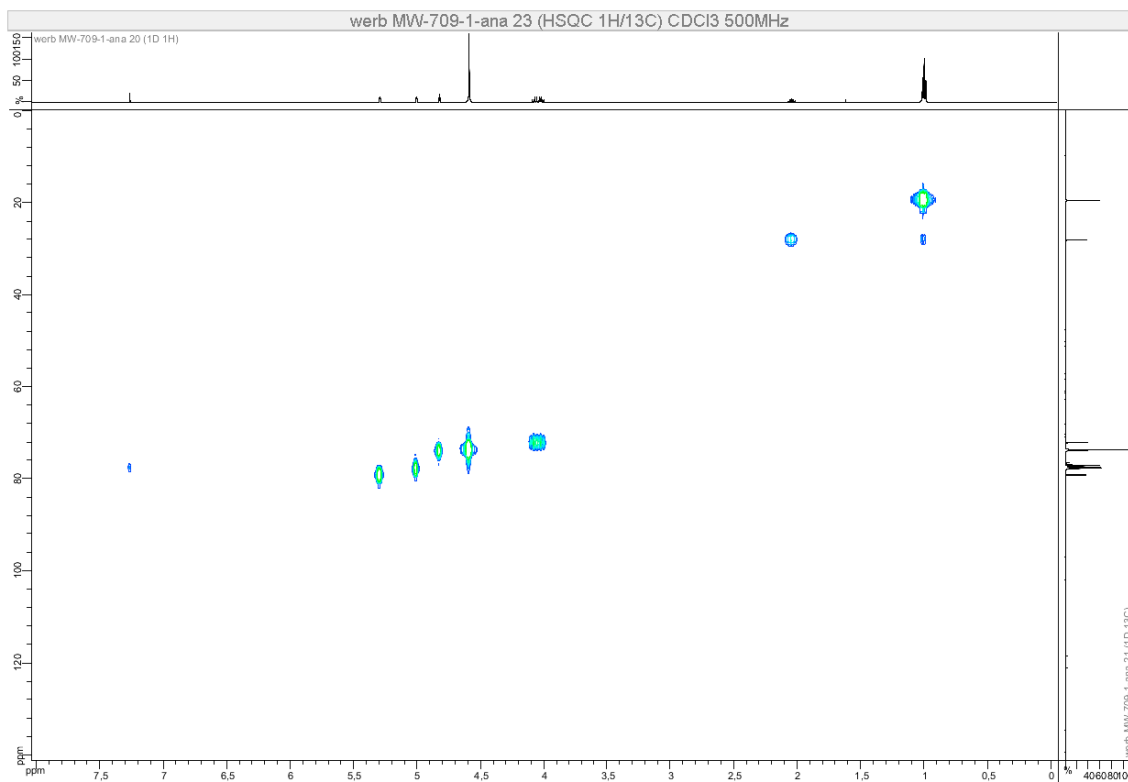
^{13}C NMR (126 MHz, CDCl_3)



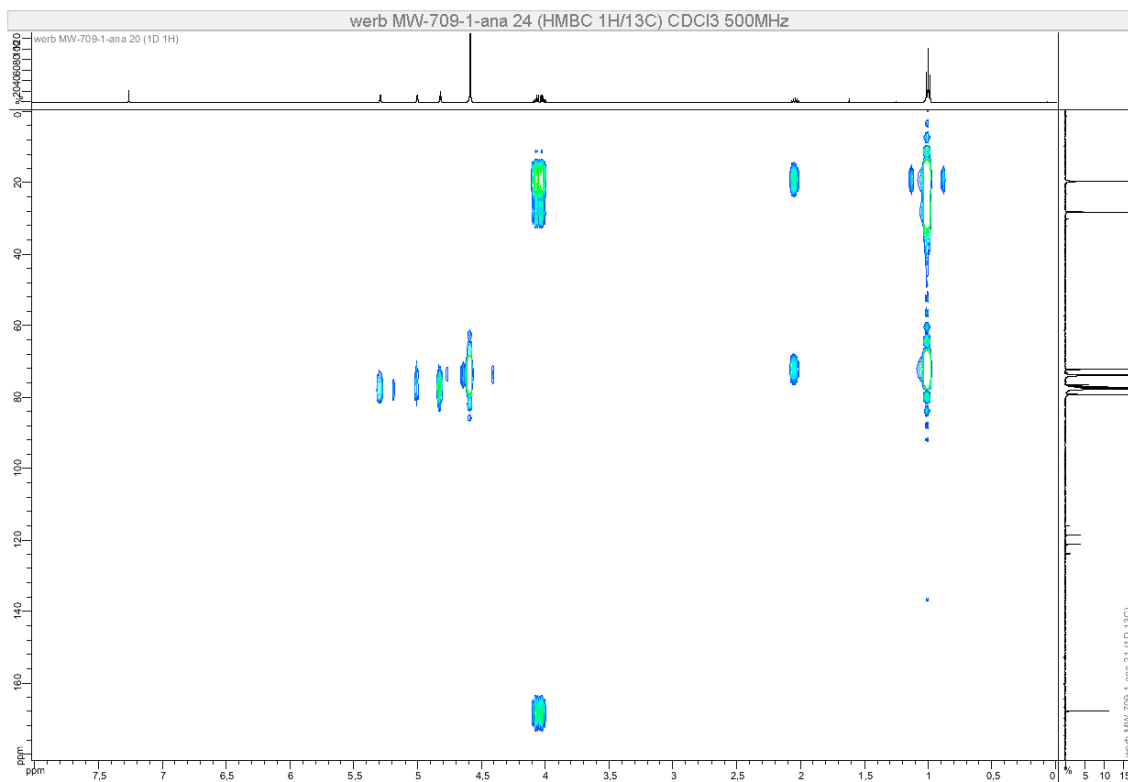
COSY (500 MHz, CDCl_3)



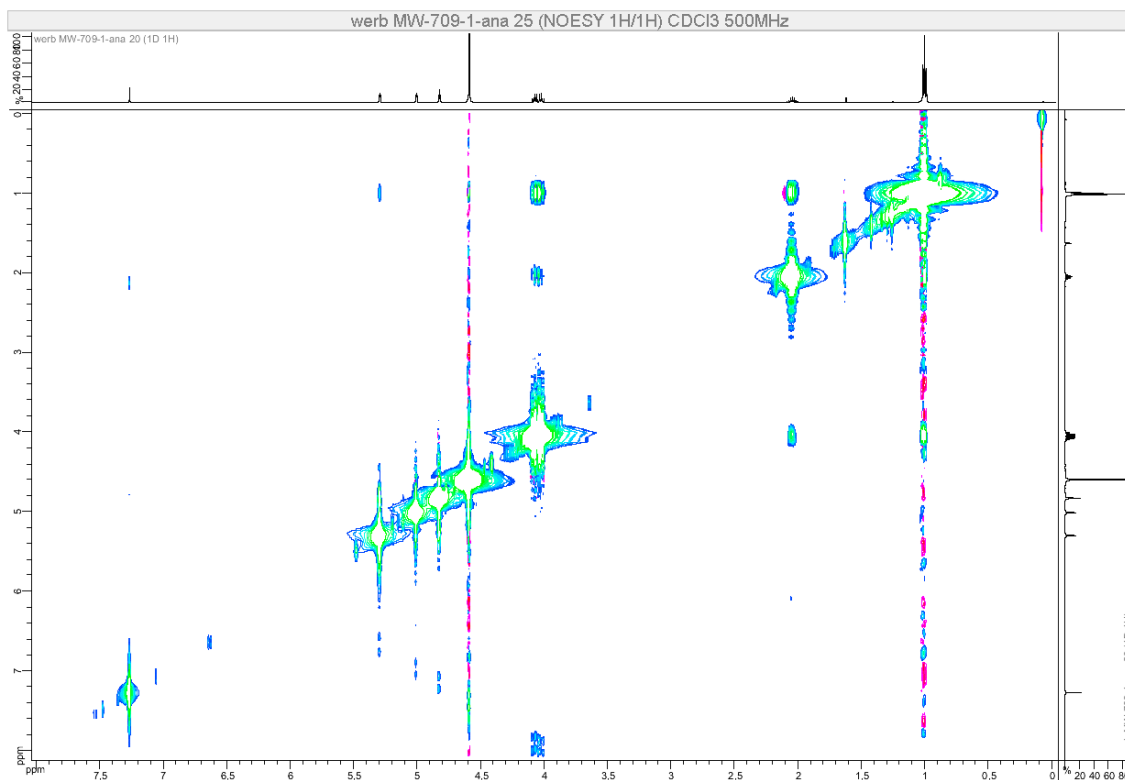
HSQC (500 MHz, CDCl₃)



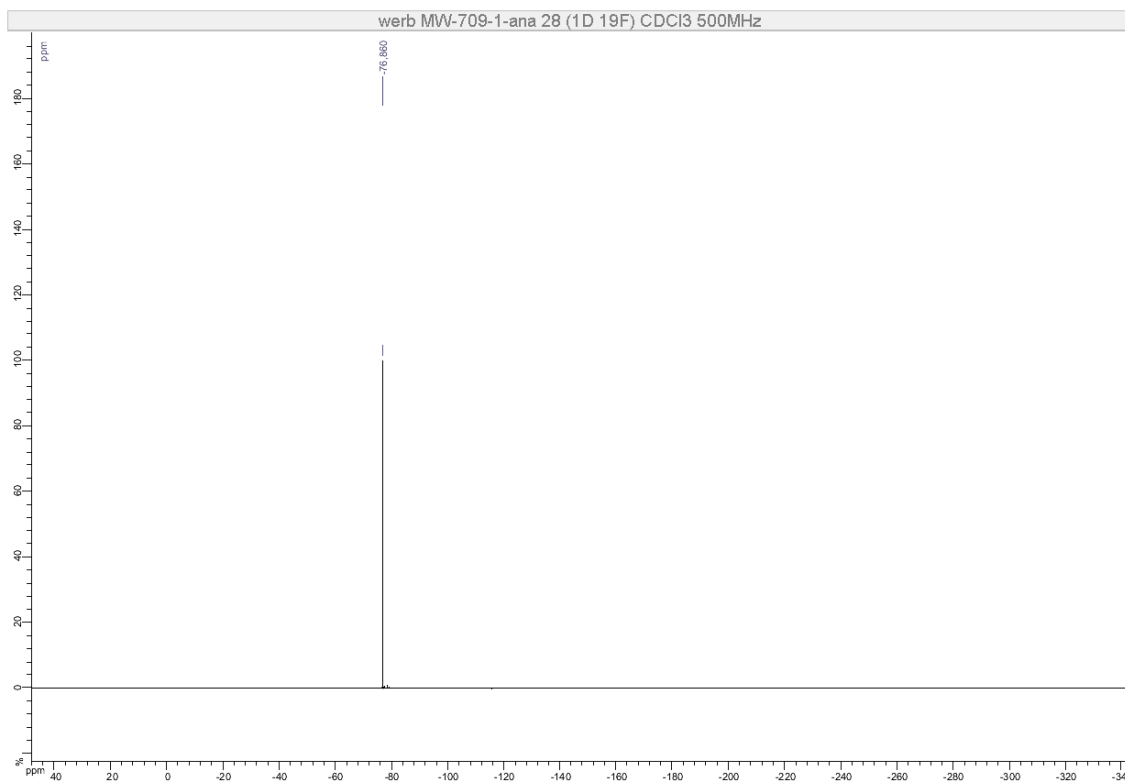
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

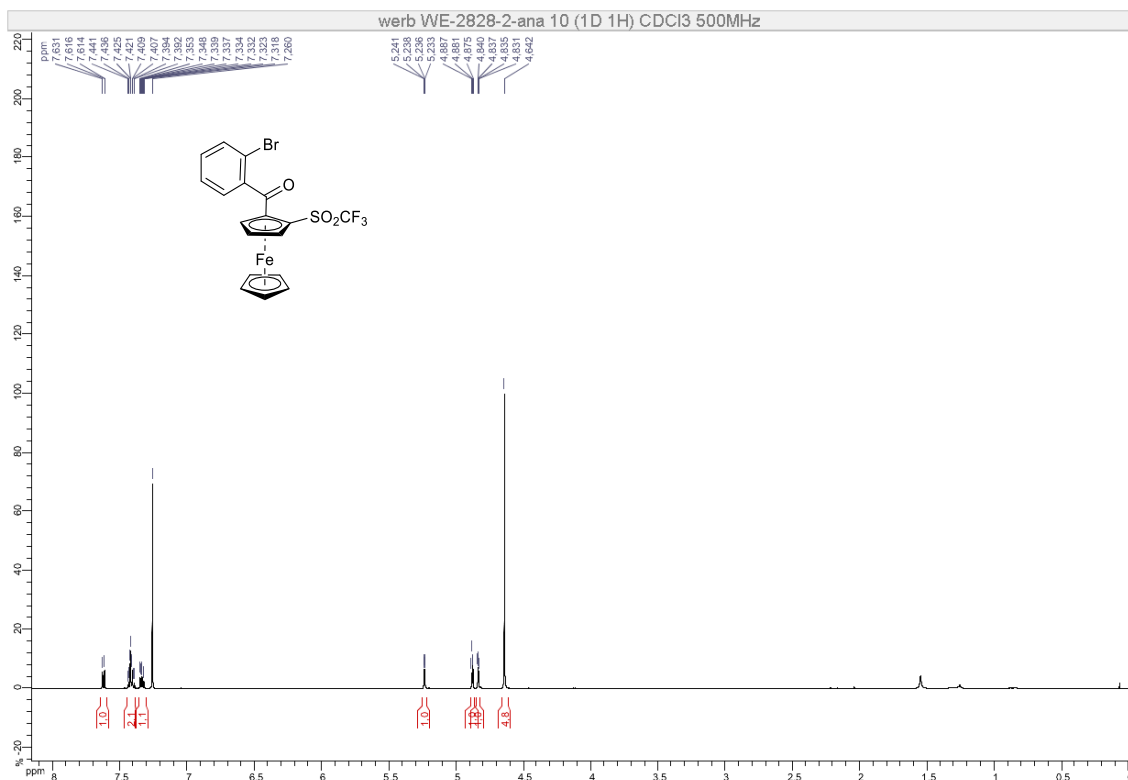


¹⁹F NMR (470 MHz, CDCl₃)

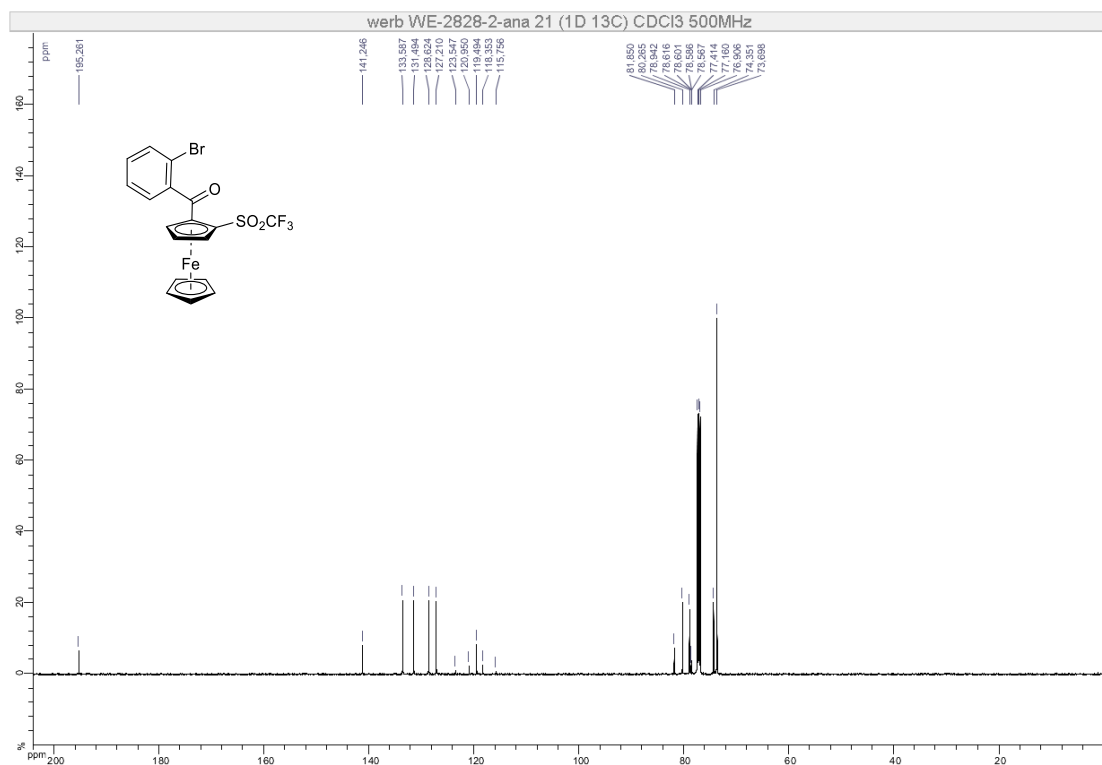


(*Sp*)-2-(2-Bromobenzoyl)ferrocenetriflone (*Sp*-2e)

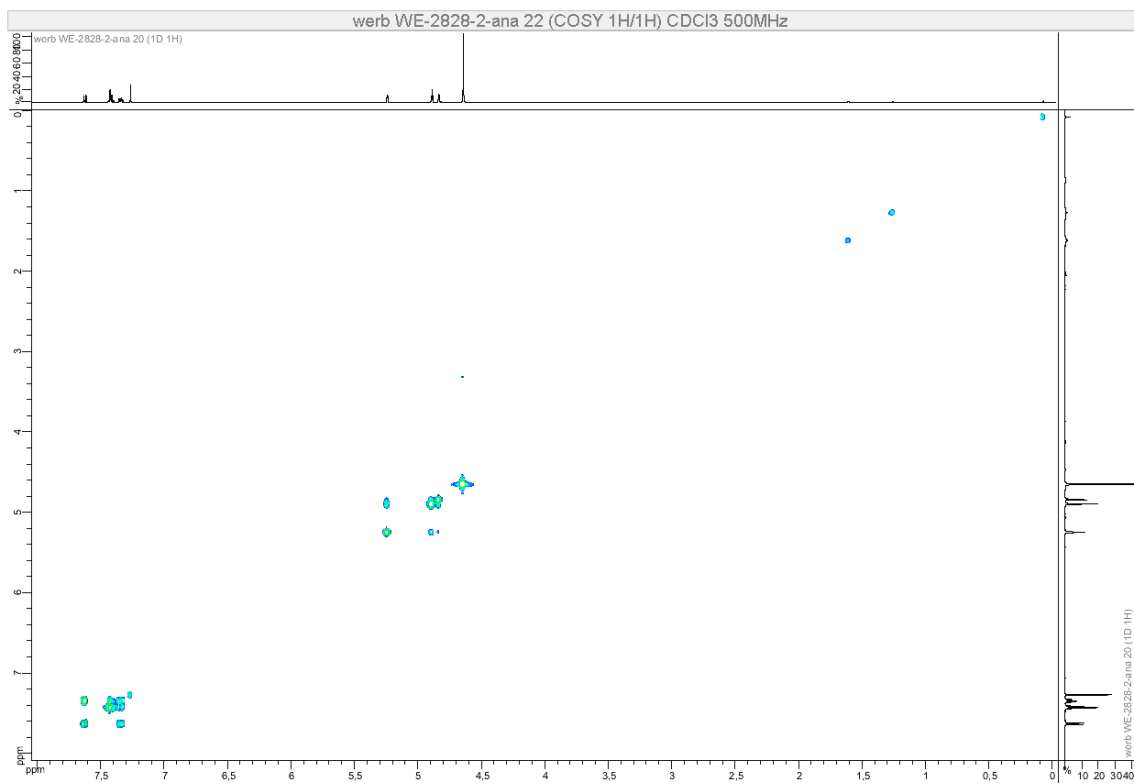
¹H NMR (500 MHz, CDCl₃)



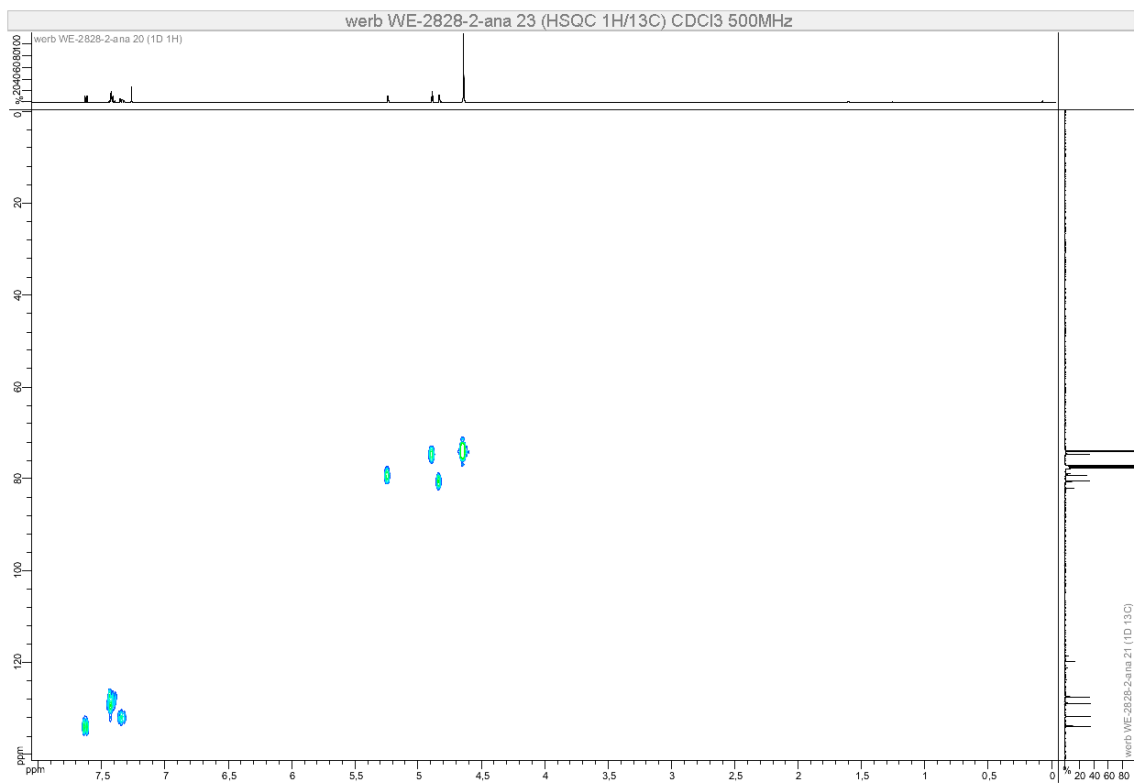
¹³C NMR (126 MHz, CDCl₃)



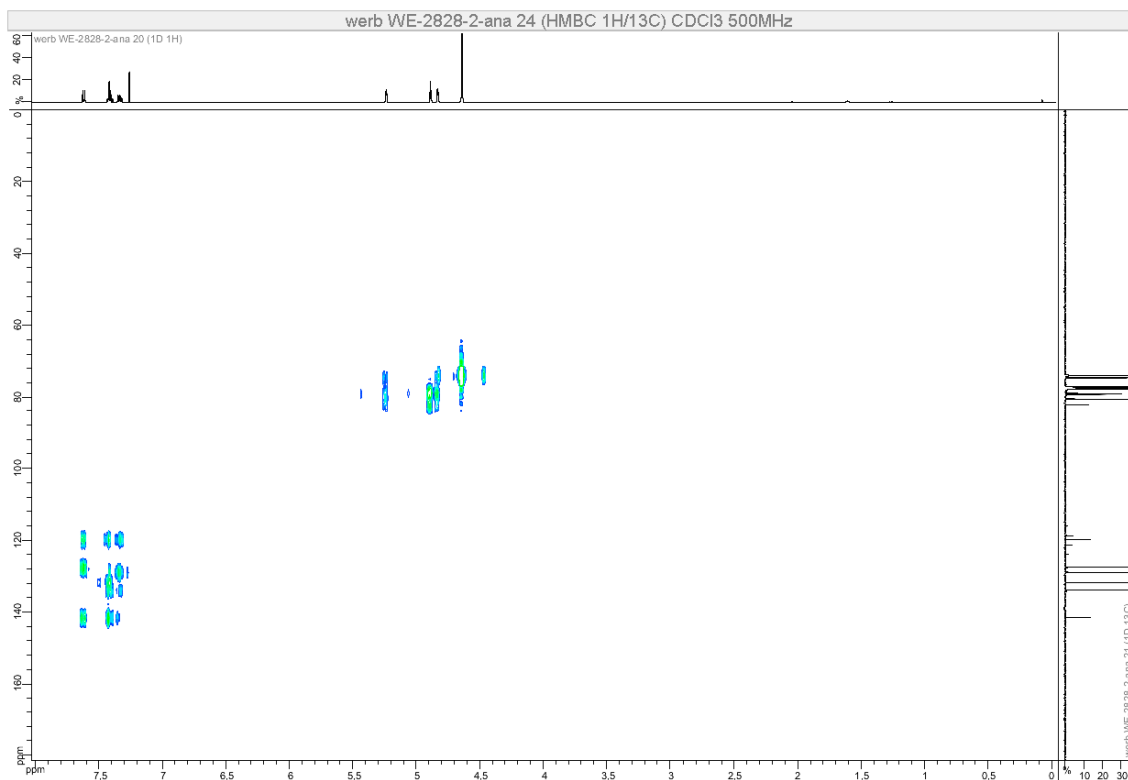
COSY (500 MHz, CDCl₃)



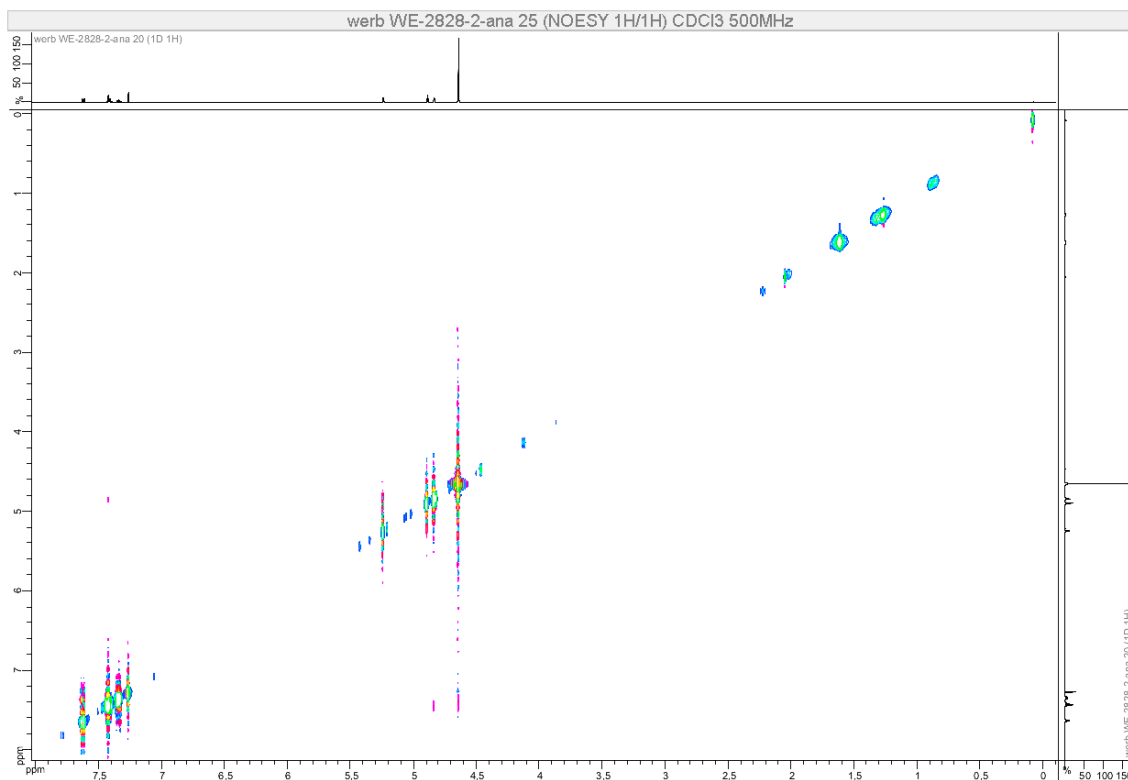
HSQC (500 MHz, CDCl₃)



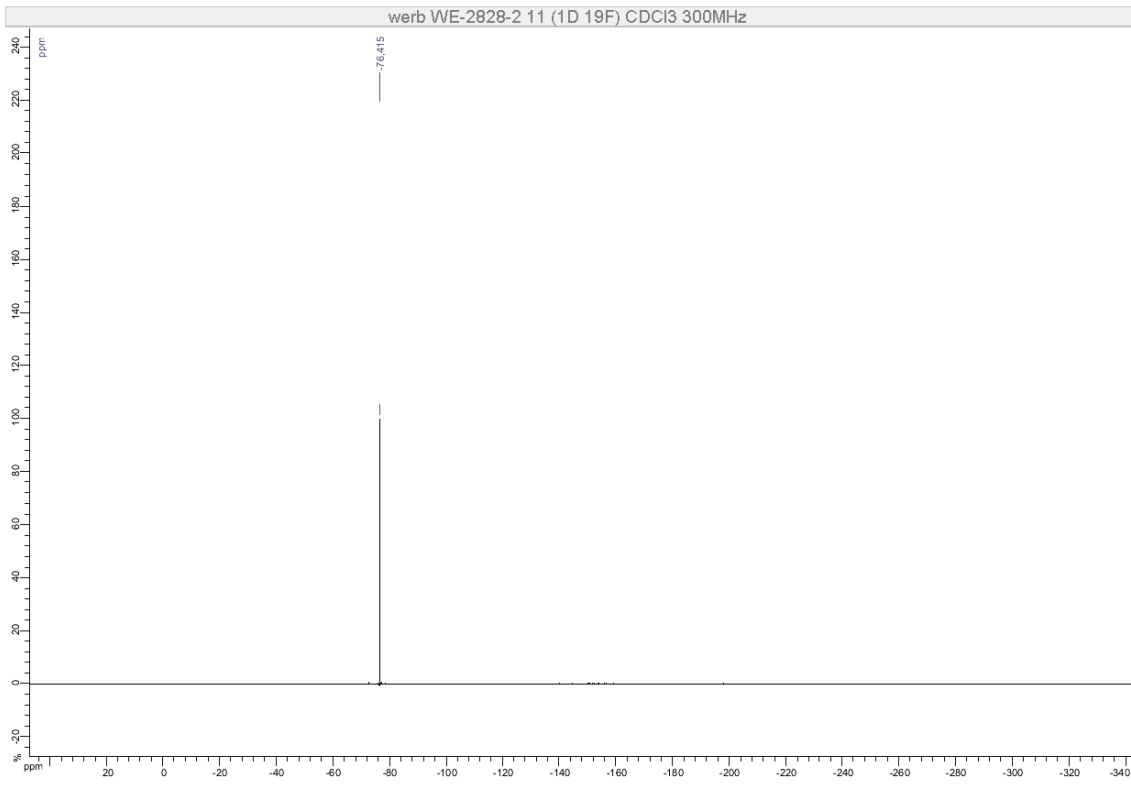
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

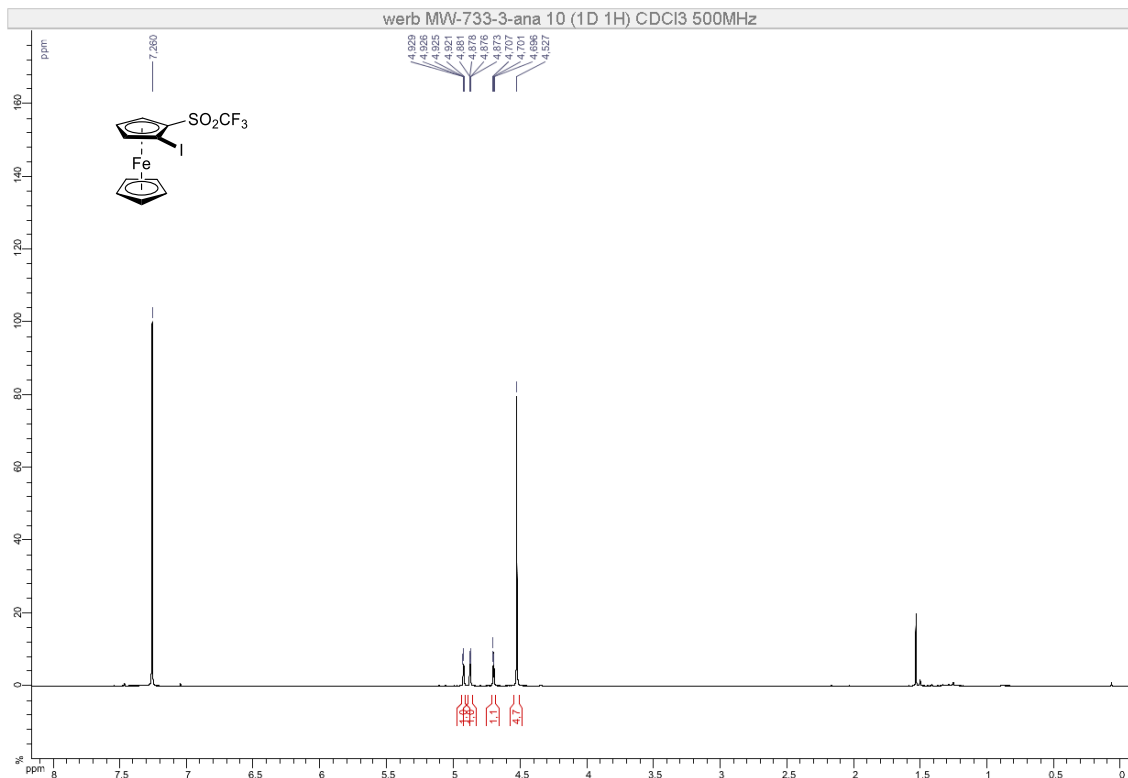


^{19}F NMR (282 MHz, CDCl_3)

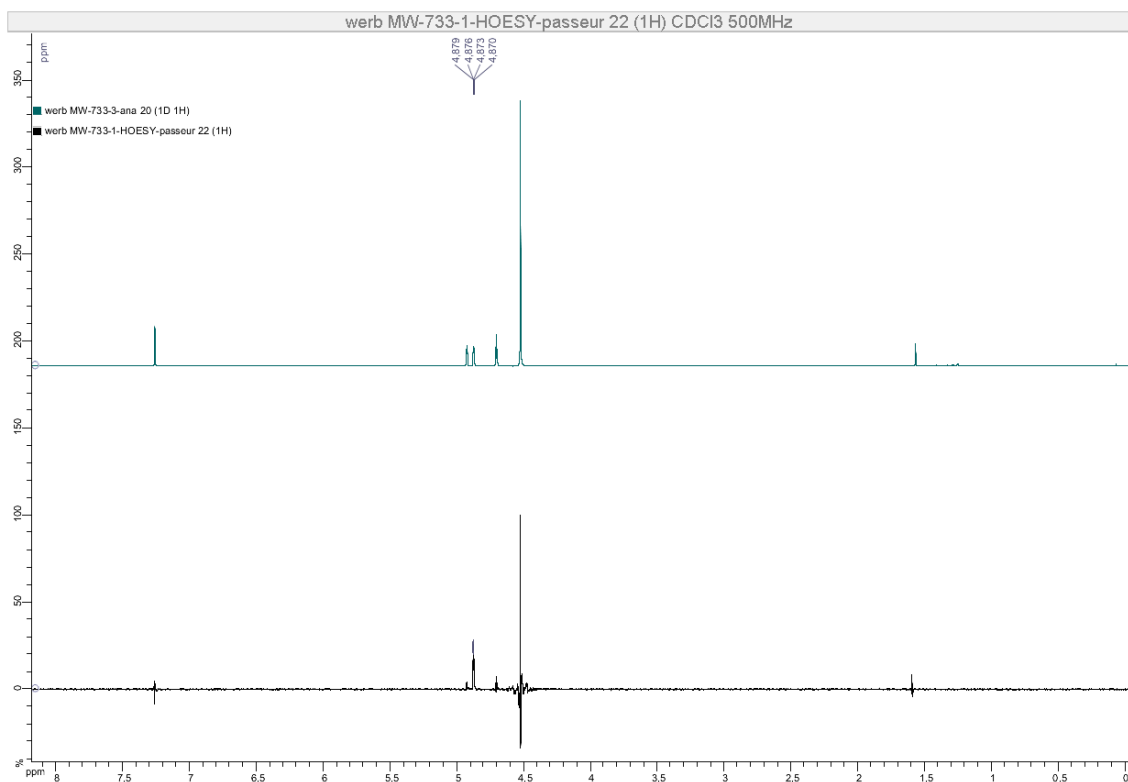


2-Iodoferrocenetriflone (2f)

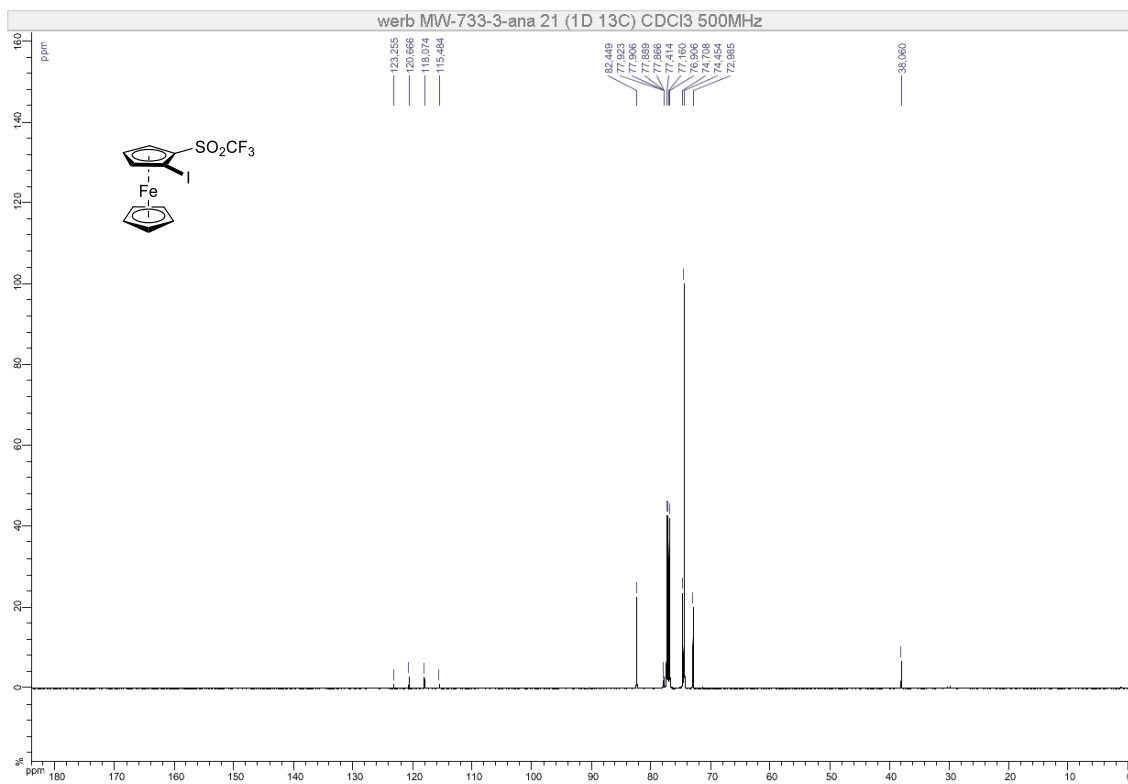
^1H NMR (500 MHz, CDCl_3)



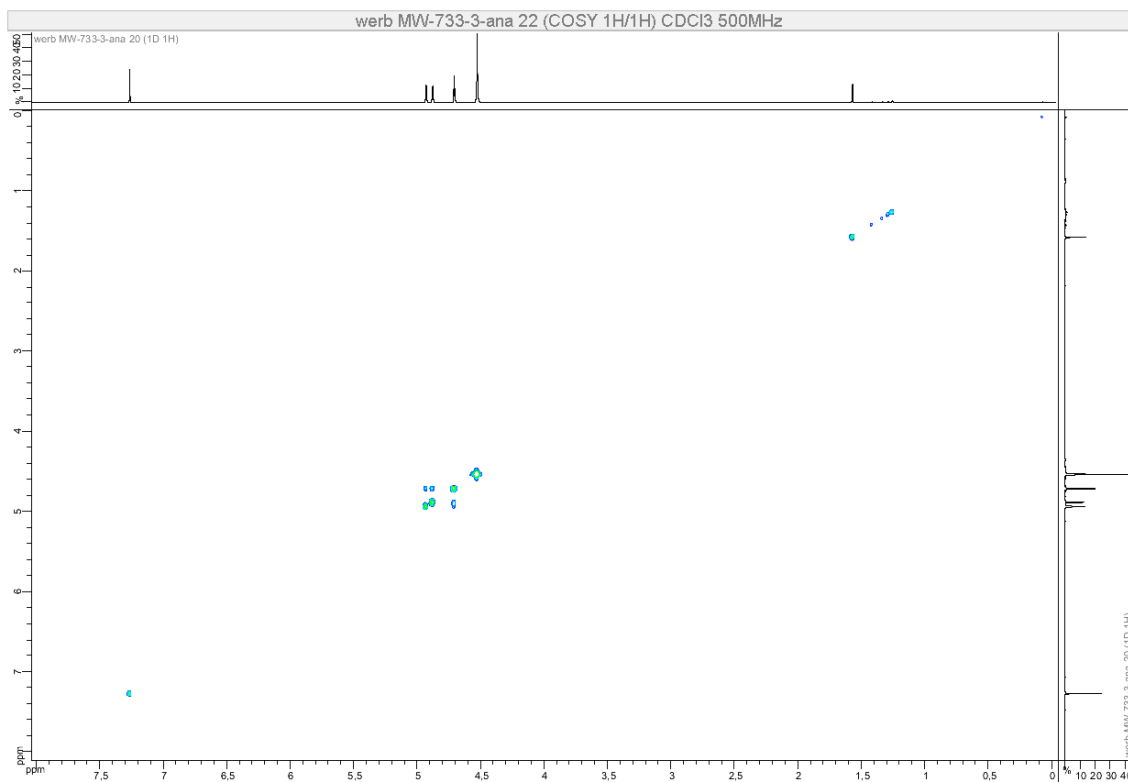
HOESY (500 MHz, CDCl_3) Irradiation at -78.2 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



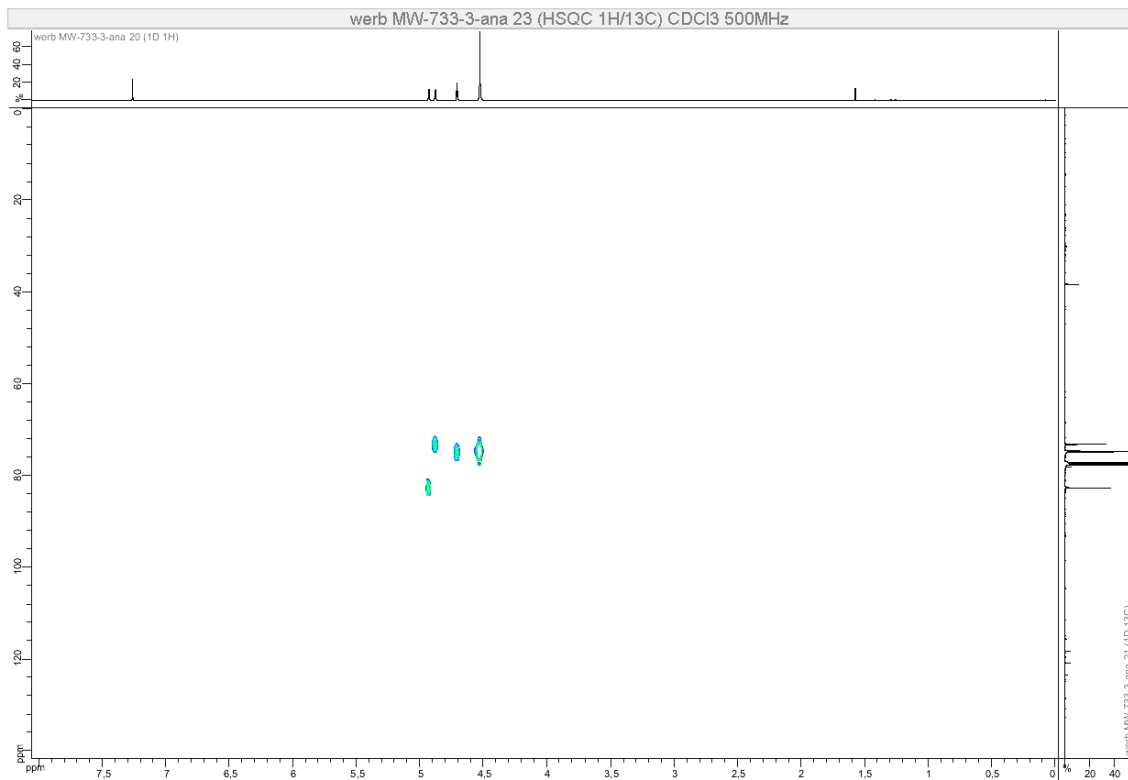
^{13}C NMR (126 MHz, CDCl_3)



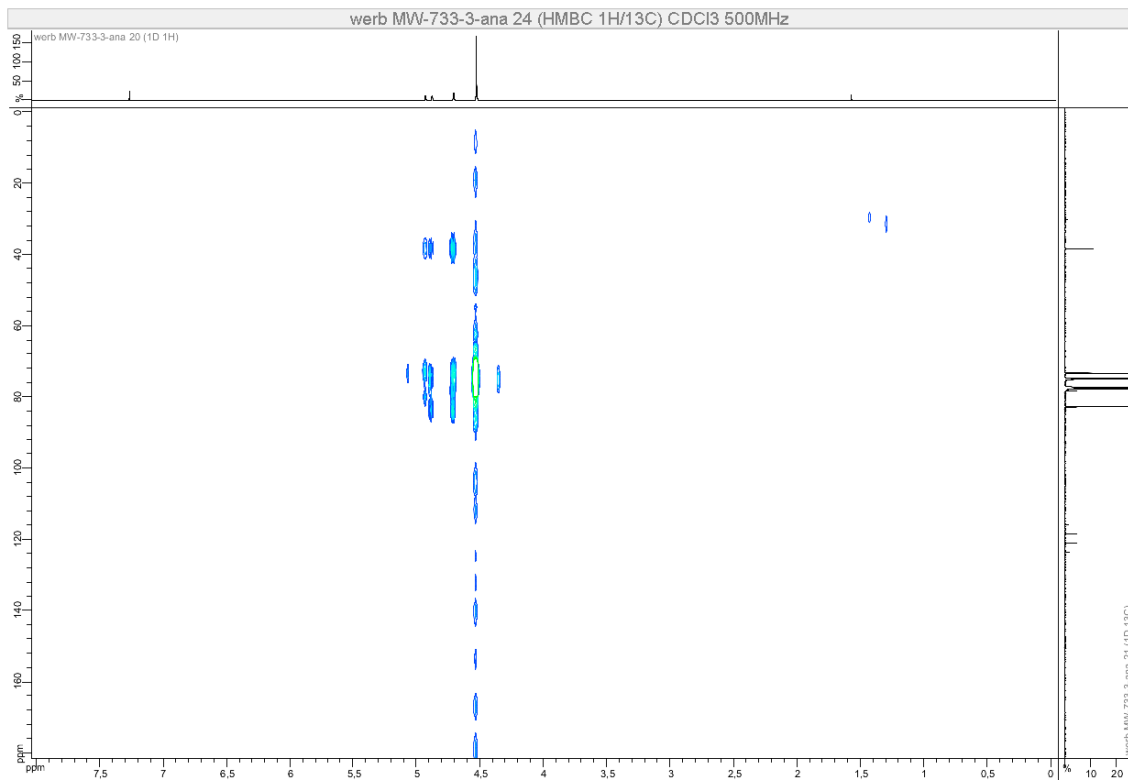
COSY (500 MHz, CDCl_3)



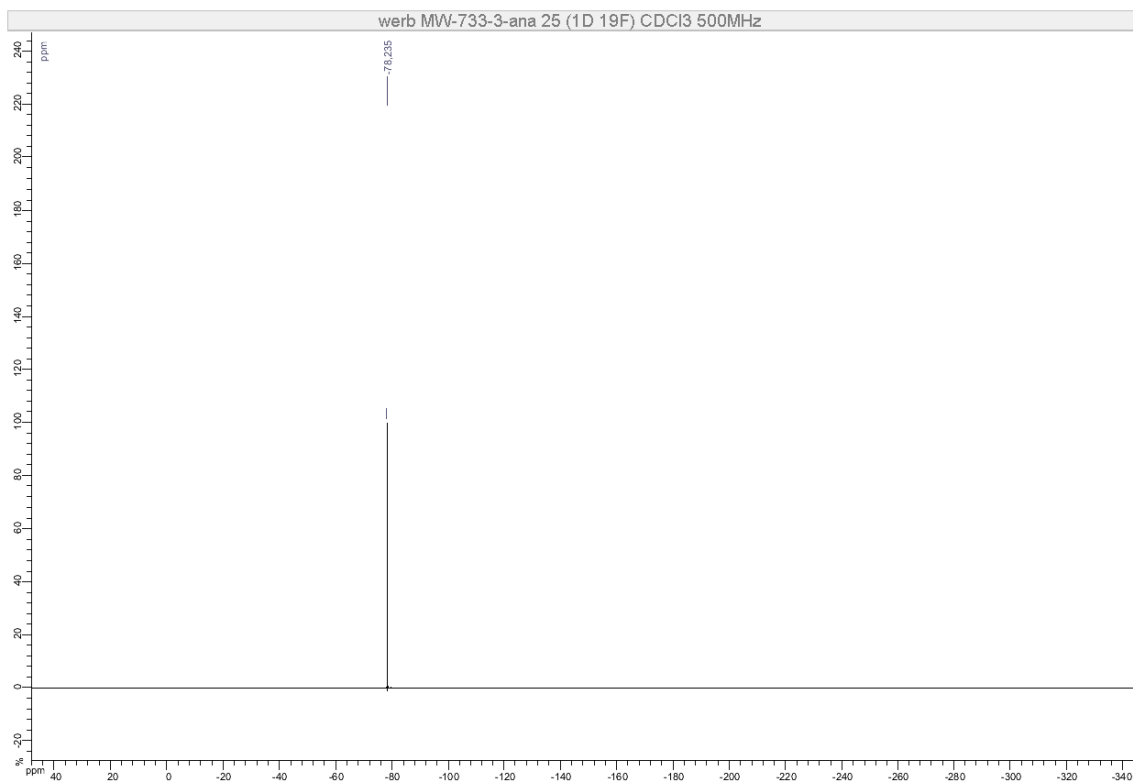
HSQC (500 MHz, CDCl₃)



HMBC (500 MHz, CDCl₃)

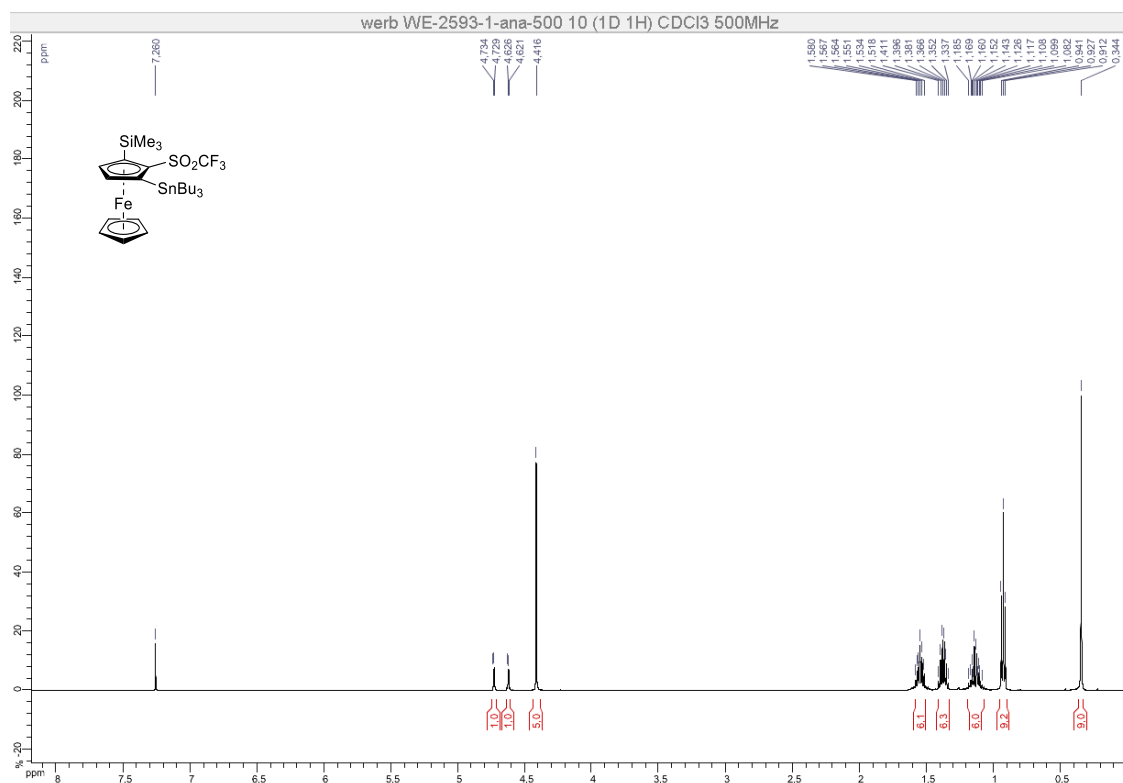


^{19}F NMR (470 MHz, CDCl_3)

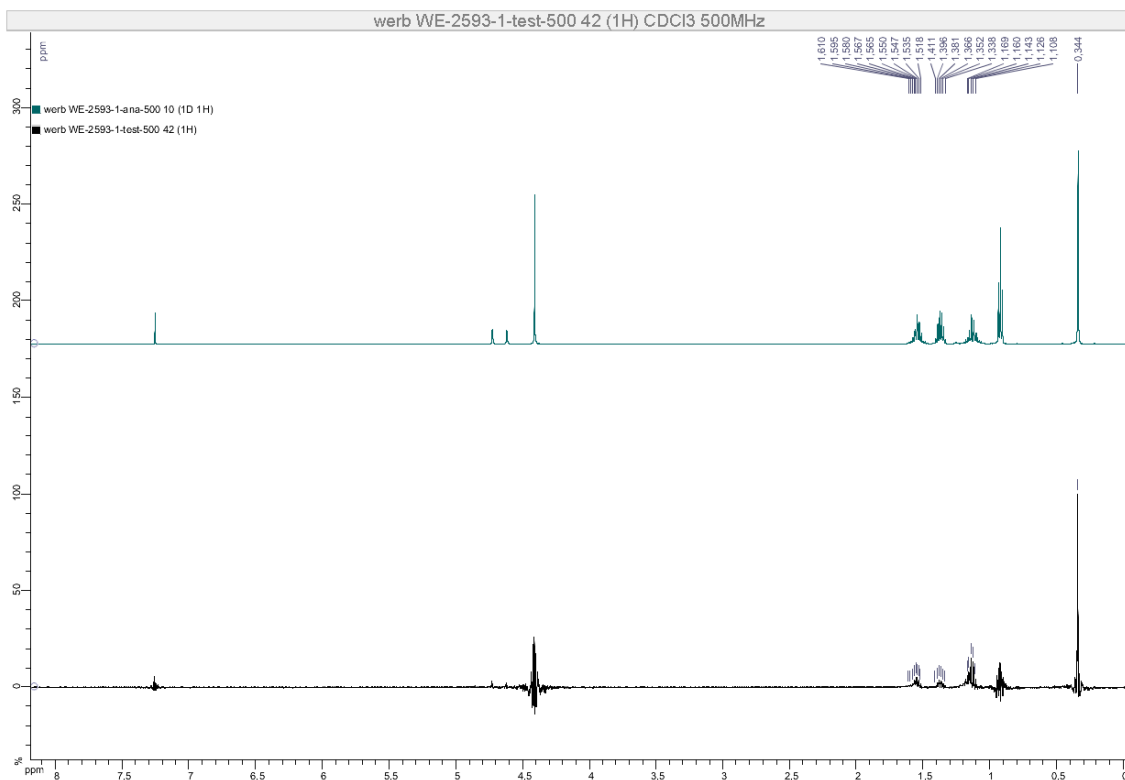


2-(Tributylstannyl)-5-(trimethylsilyl)ferrocenetriflone (3ba)

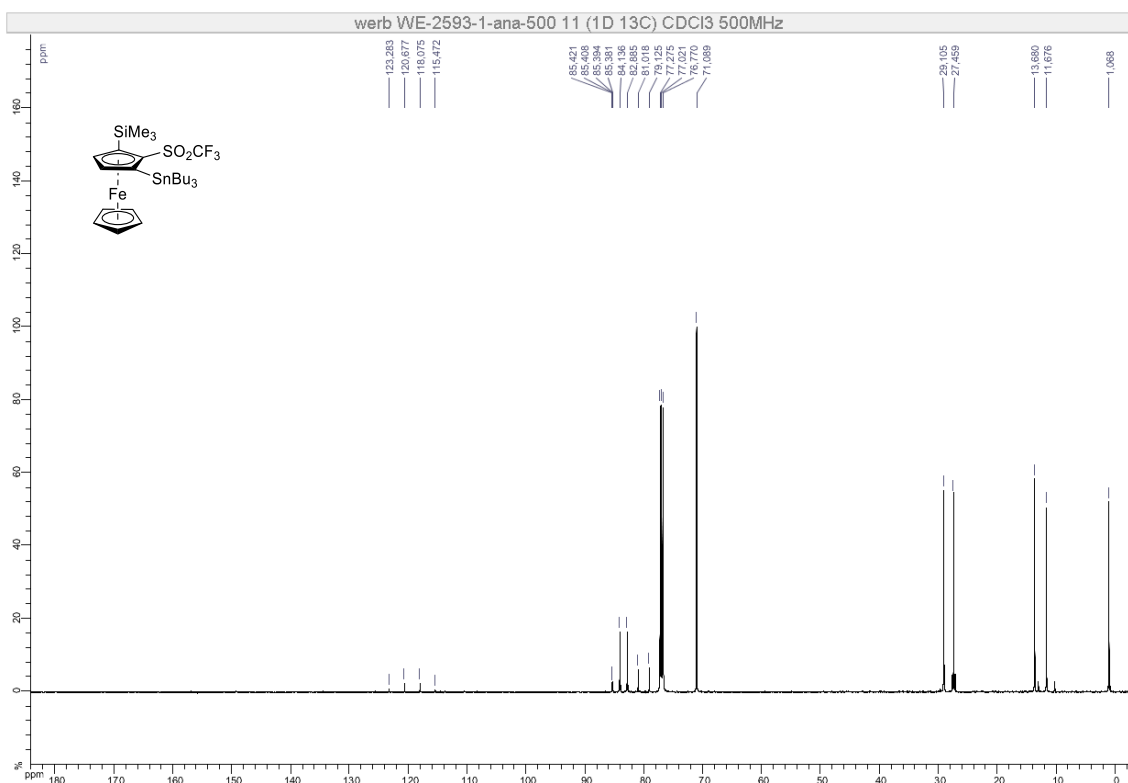
^1H NMR (500 MHz, CDCl_3)



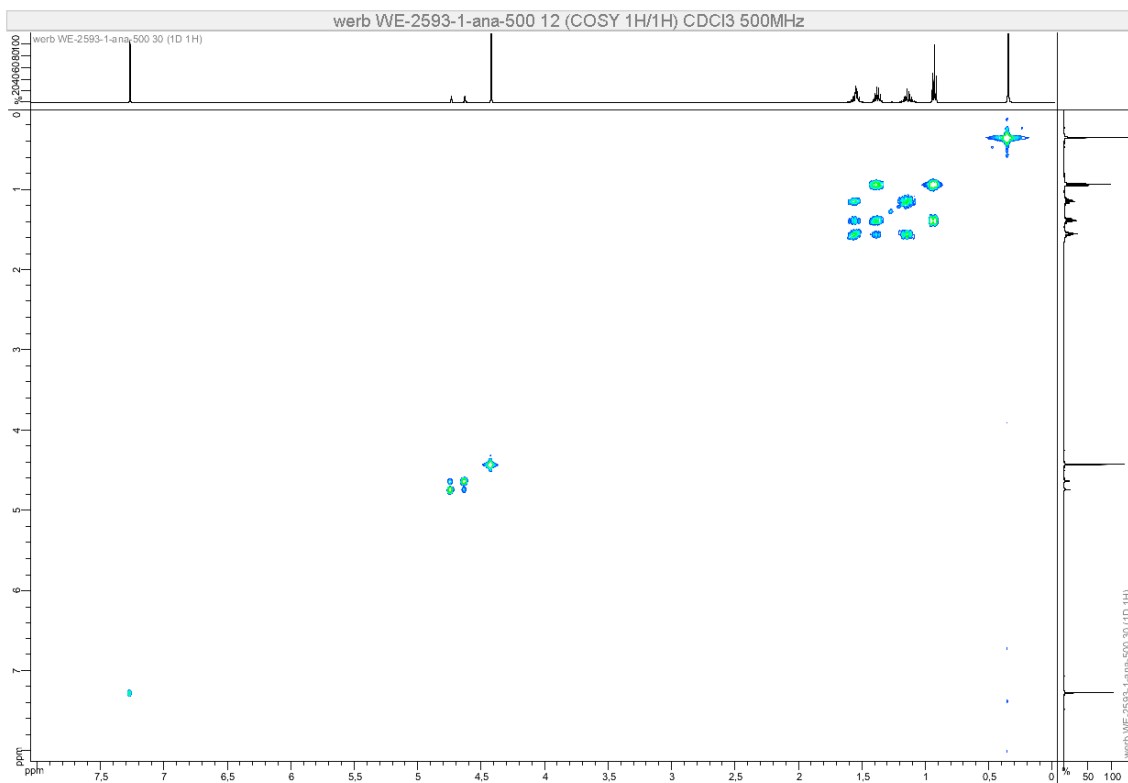
HOESY (500 MHz, CDCl_3) Irradiation at -76.7 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



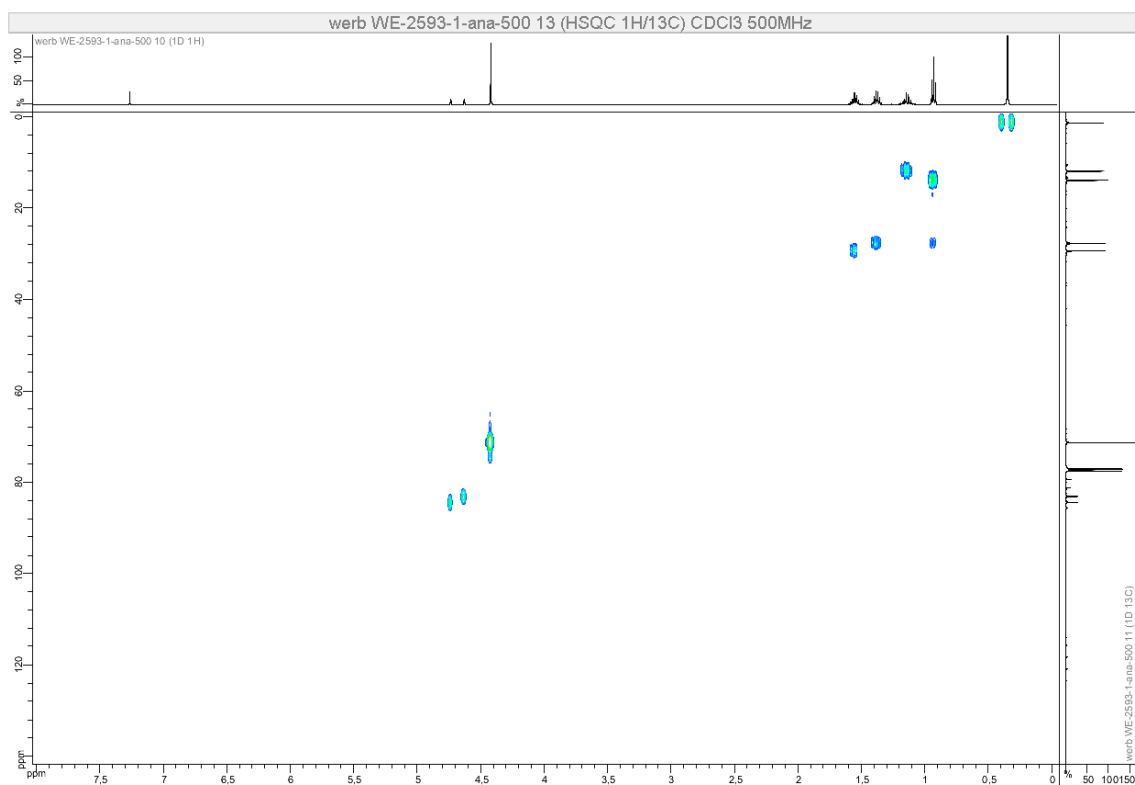
^{13}C NMR (126 MHz, CDCl_3)



COSY (500 MHz, CDCl_3)



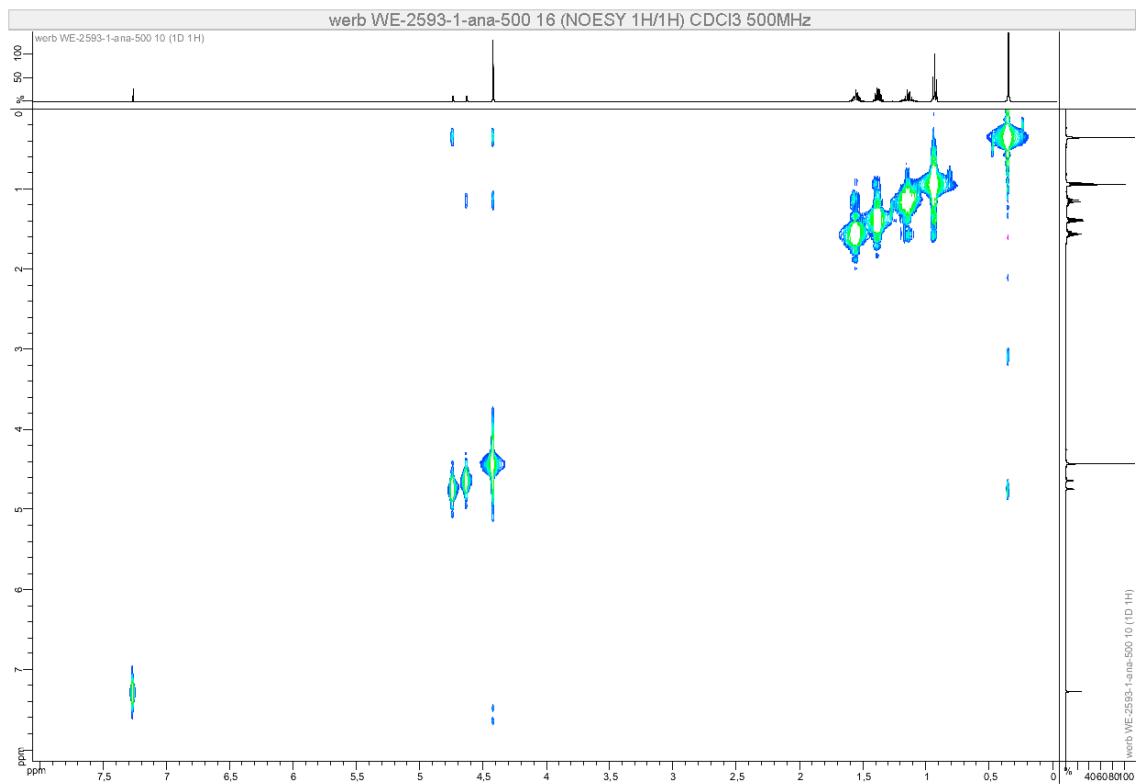
HSQC (500 MHz, CDCl₃)



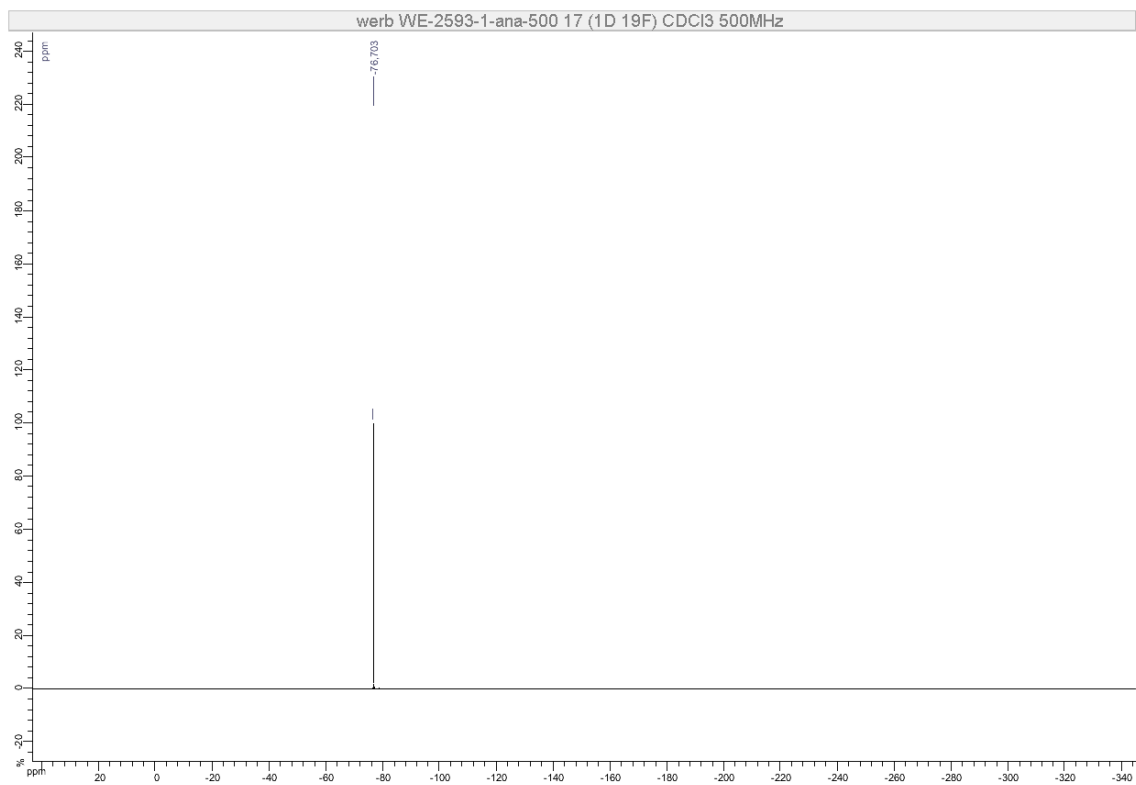
HMBC (400 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

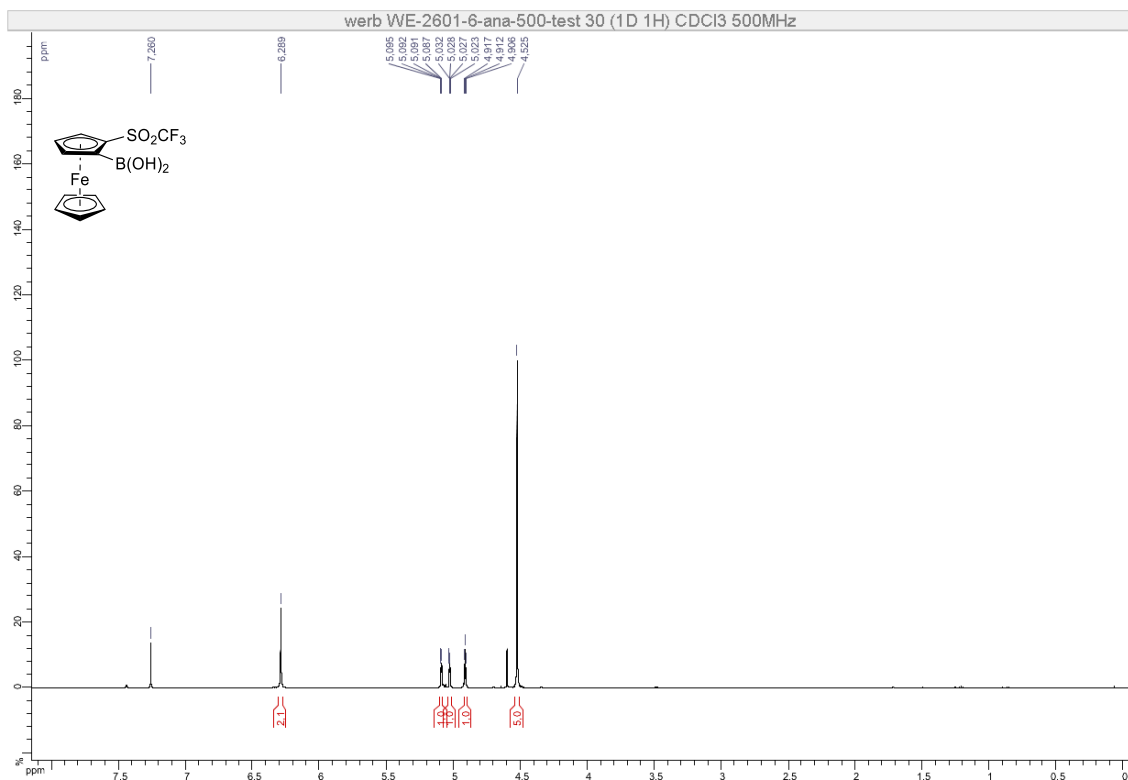


¹⁹F NMR (470 MHz, CDCl₃)

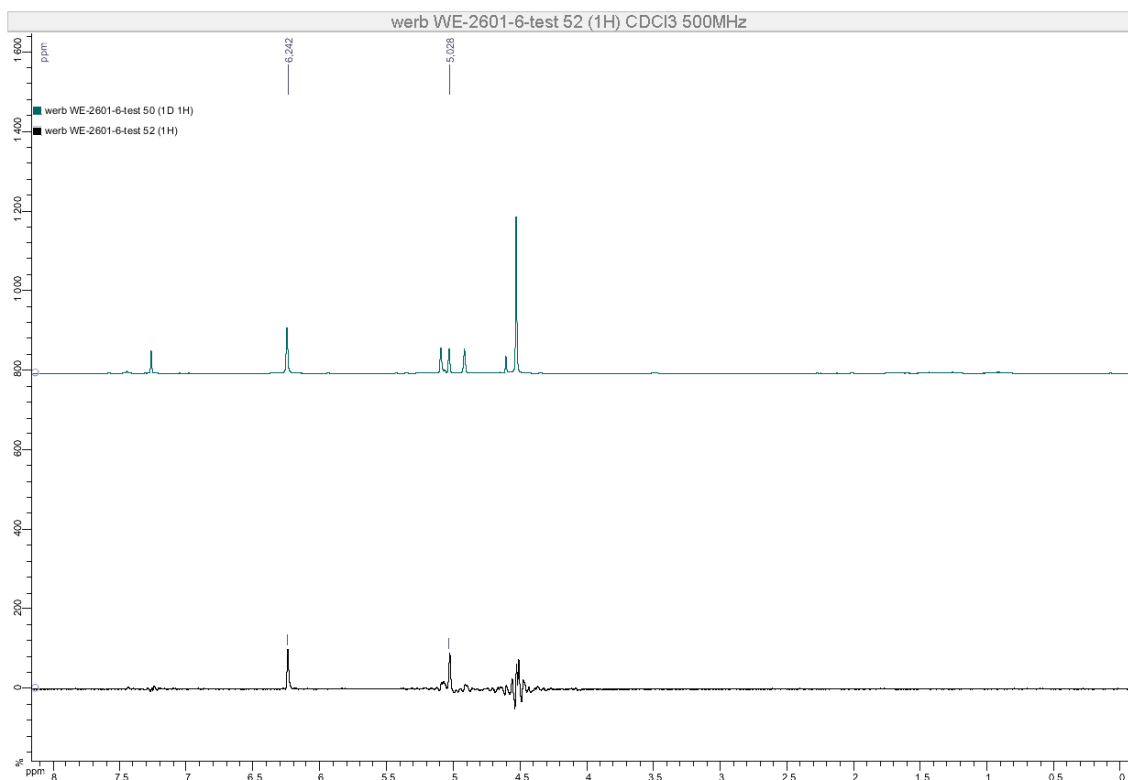


2-(Dihydroxyboryl)ferrocenetriflone (2g)

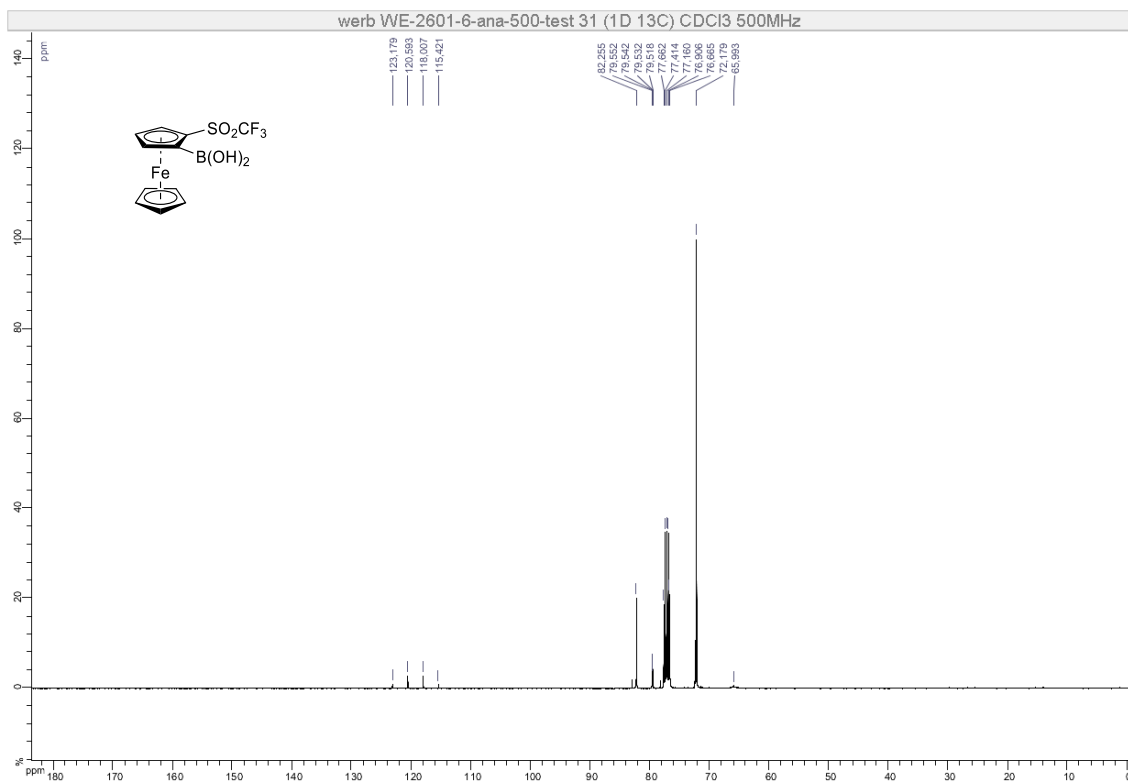
^1H NMR (500 MHz, CDCl_3)



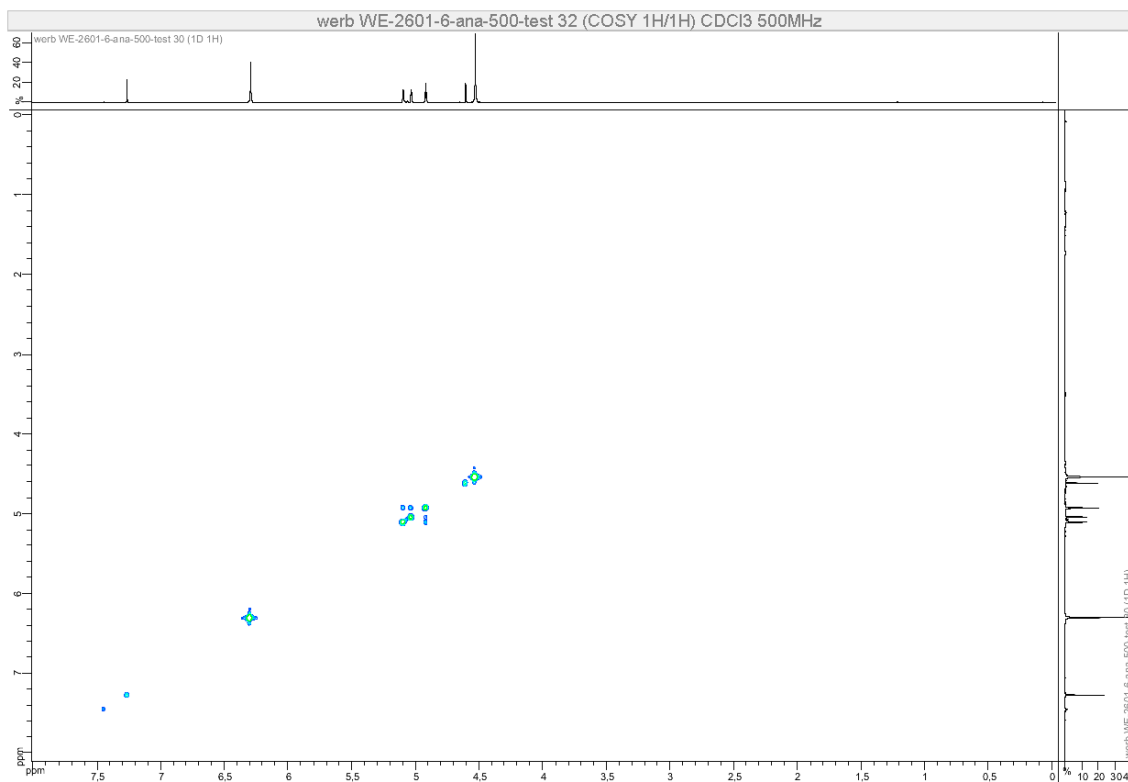
HOESY (500 MHz, CDCl_3) Irradiation at -79.2 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



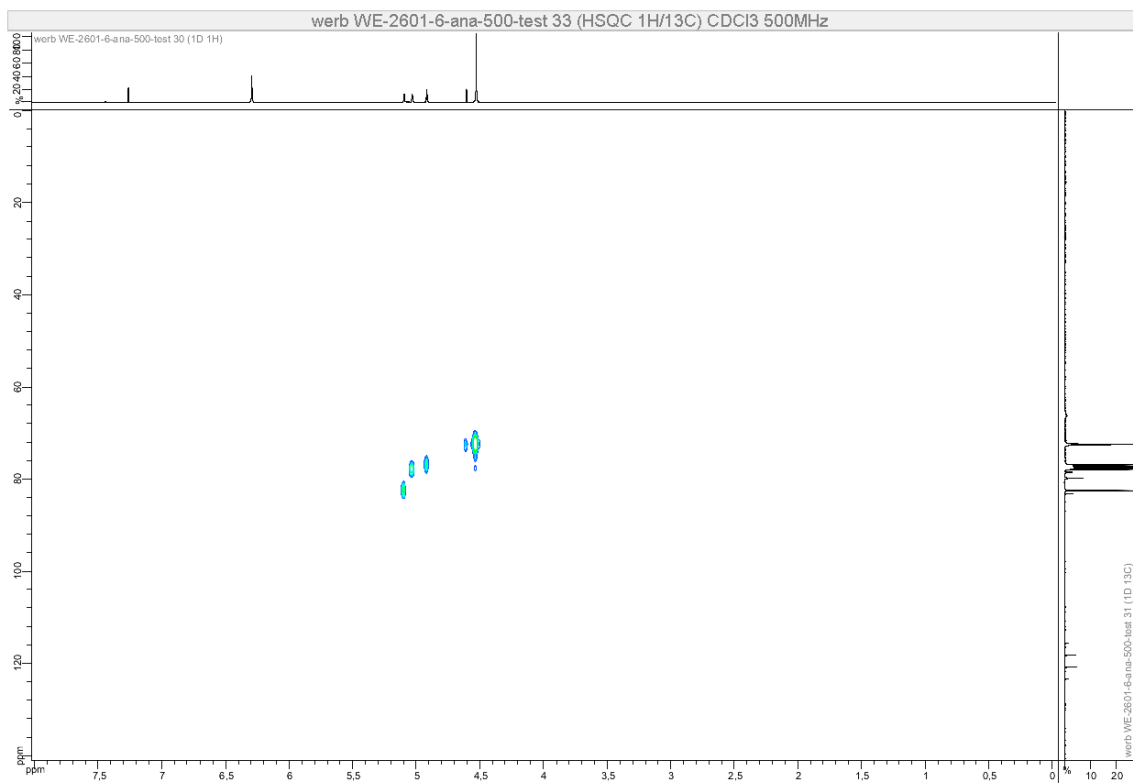
^{13}C NMR (126 MHz, CDCl_3)



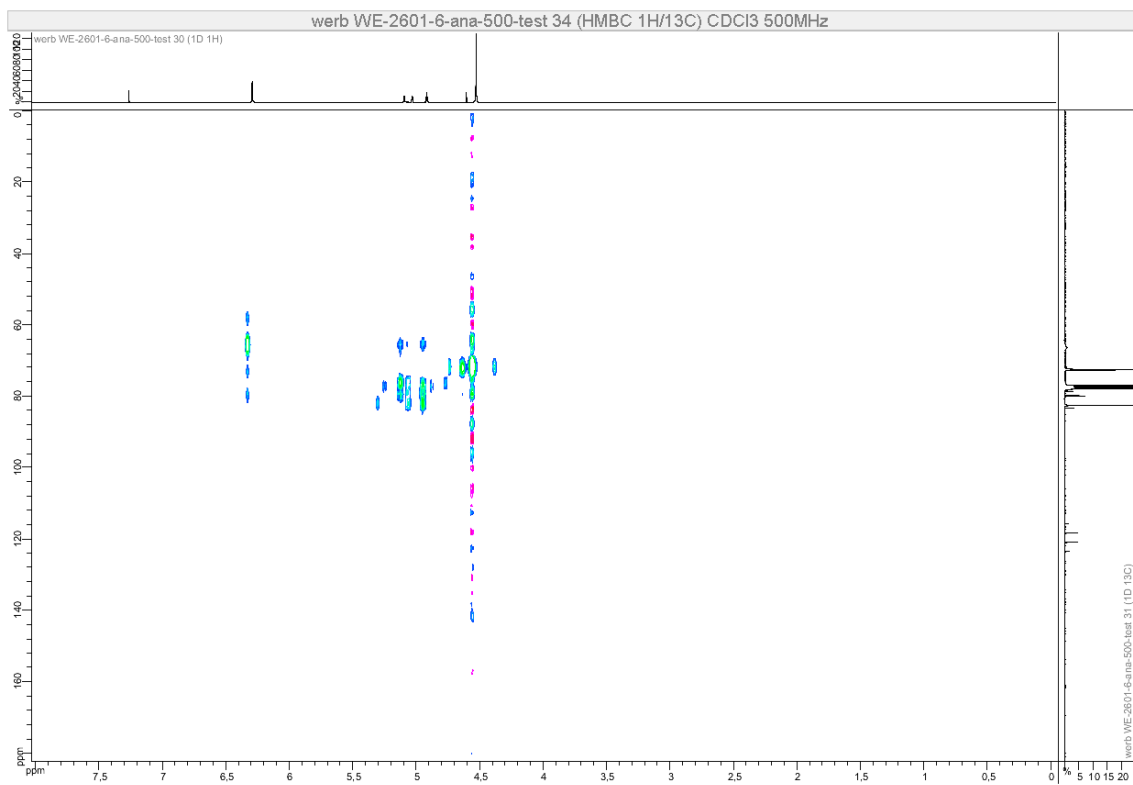
COSY (500 MHz, CDCl_3)



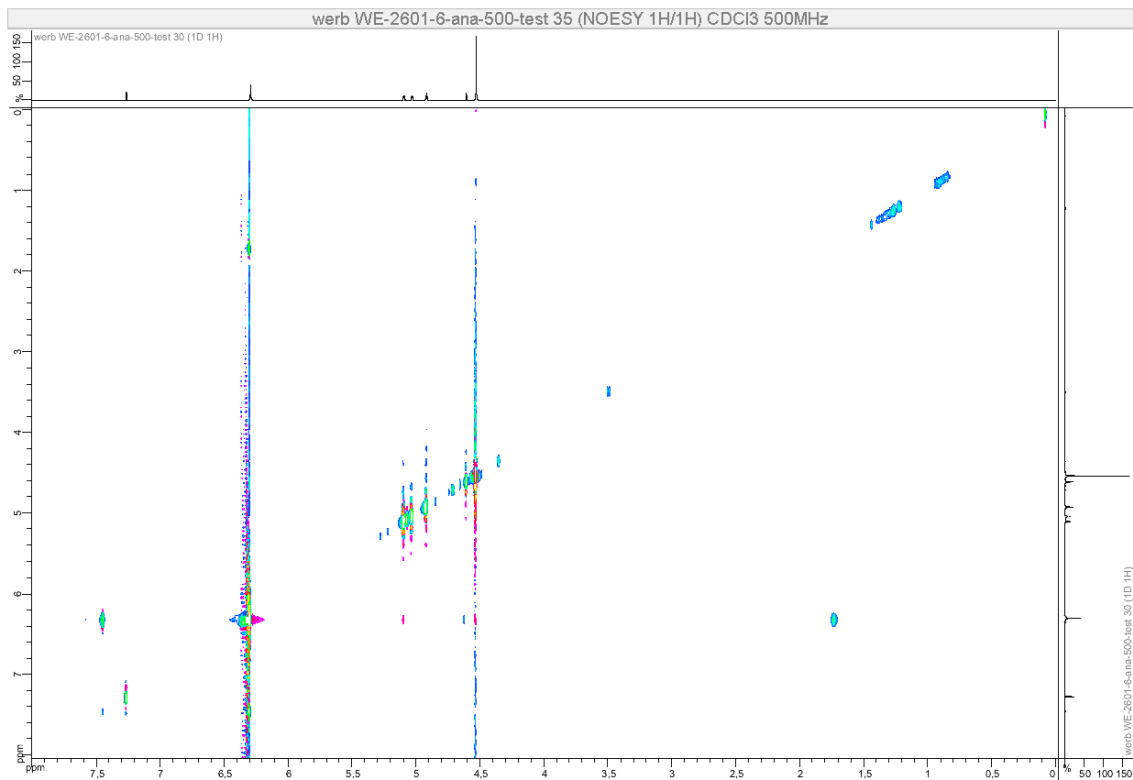
HSQC (500 MHz, CDCl₃)



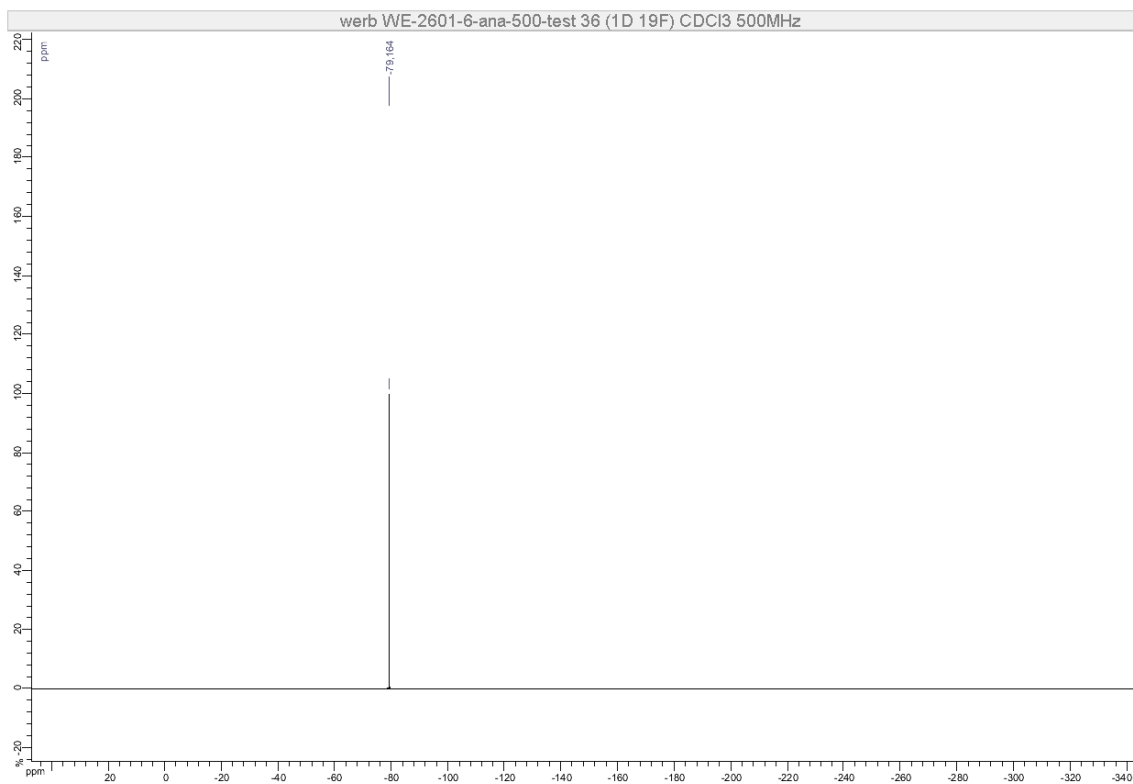
HMBC (500 MHz, CDCl₃)



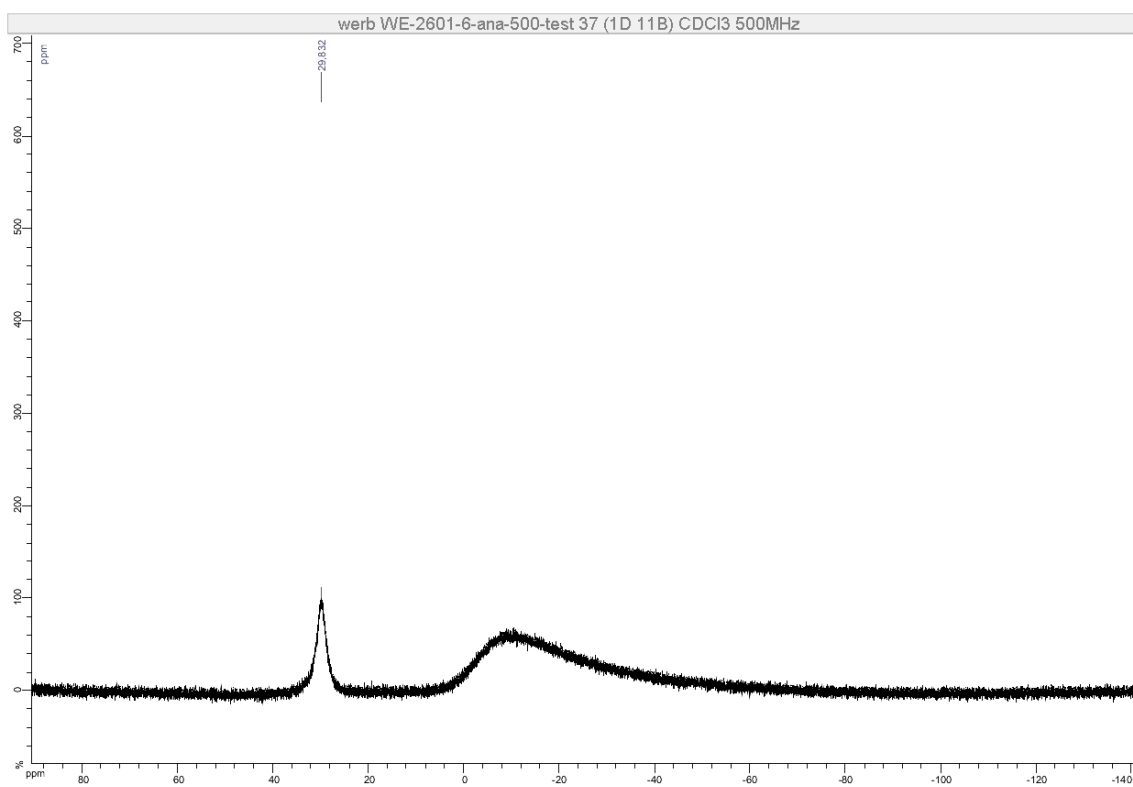
NOESY (500 MHz, CDCl₃)



¹⁹F NMR (470 MHz, CDCl₃)

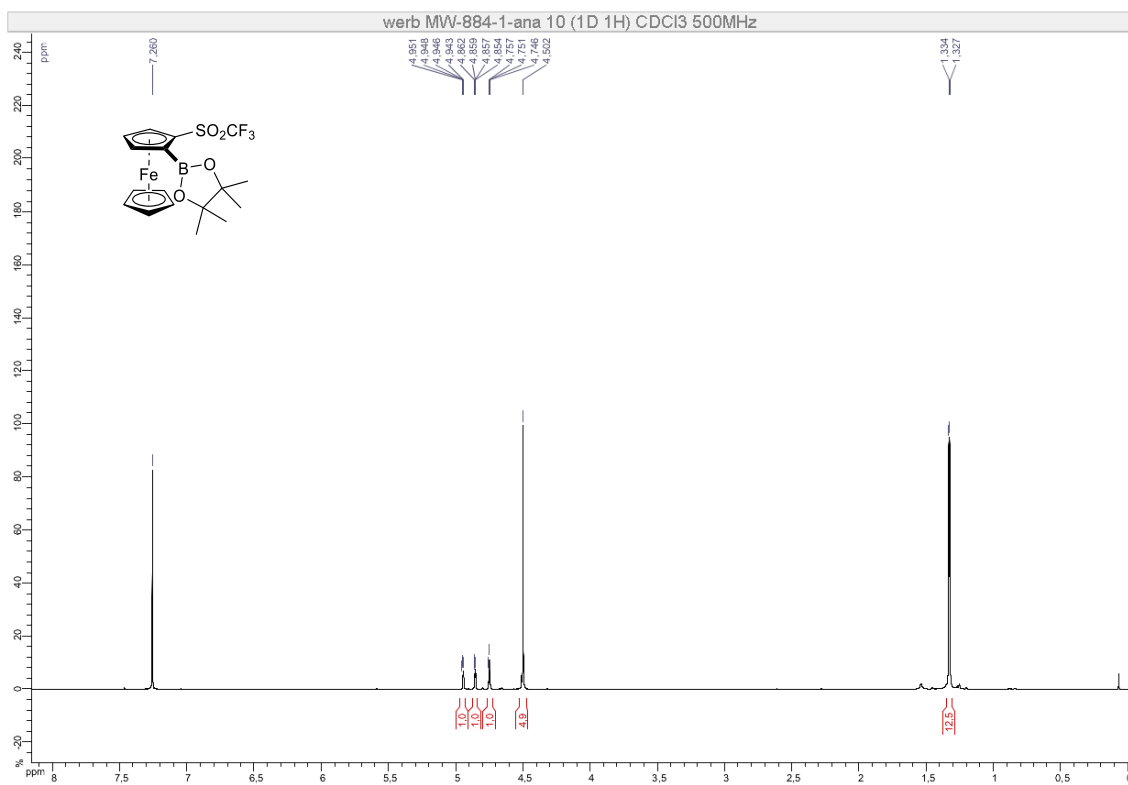


^{11}B NMR (160 MHz, CDCl_3)

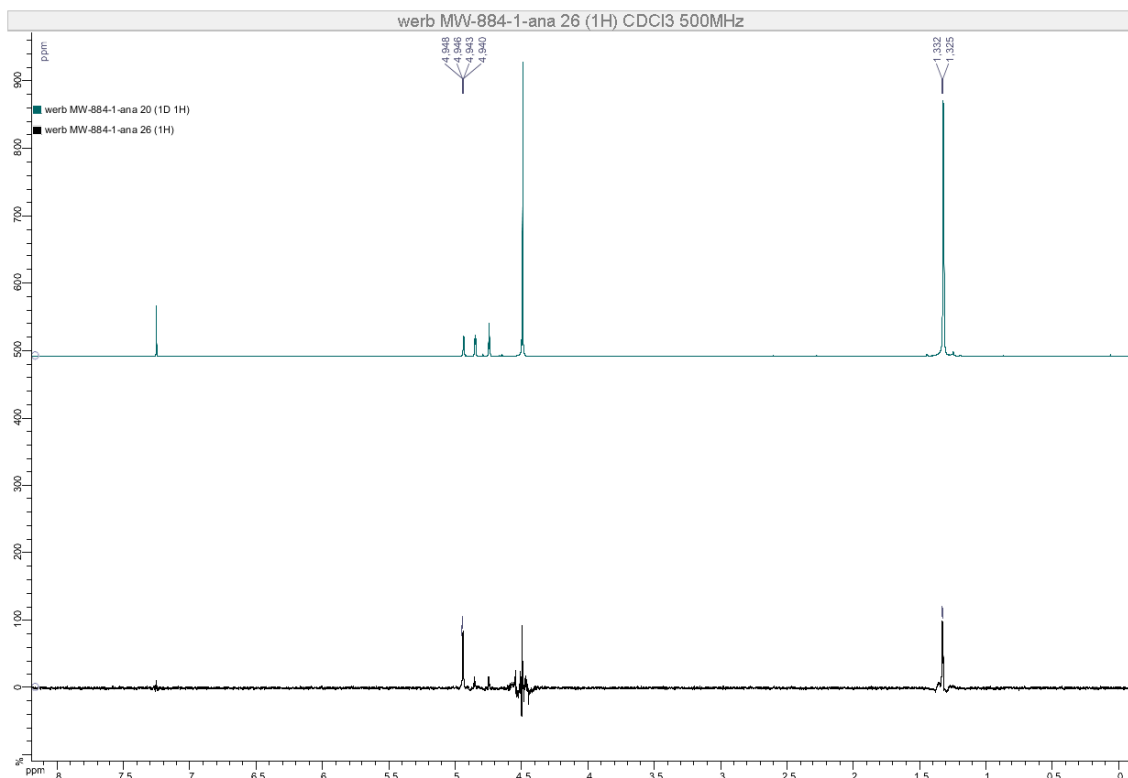


2-(4,4,5,5-Tetramethyl-1,3-dioxa-2-boroly)ferrocenetriflone (2h)

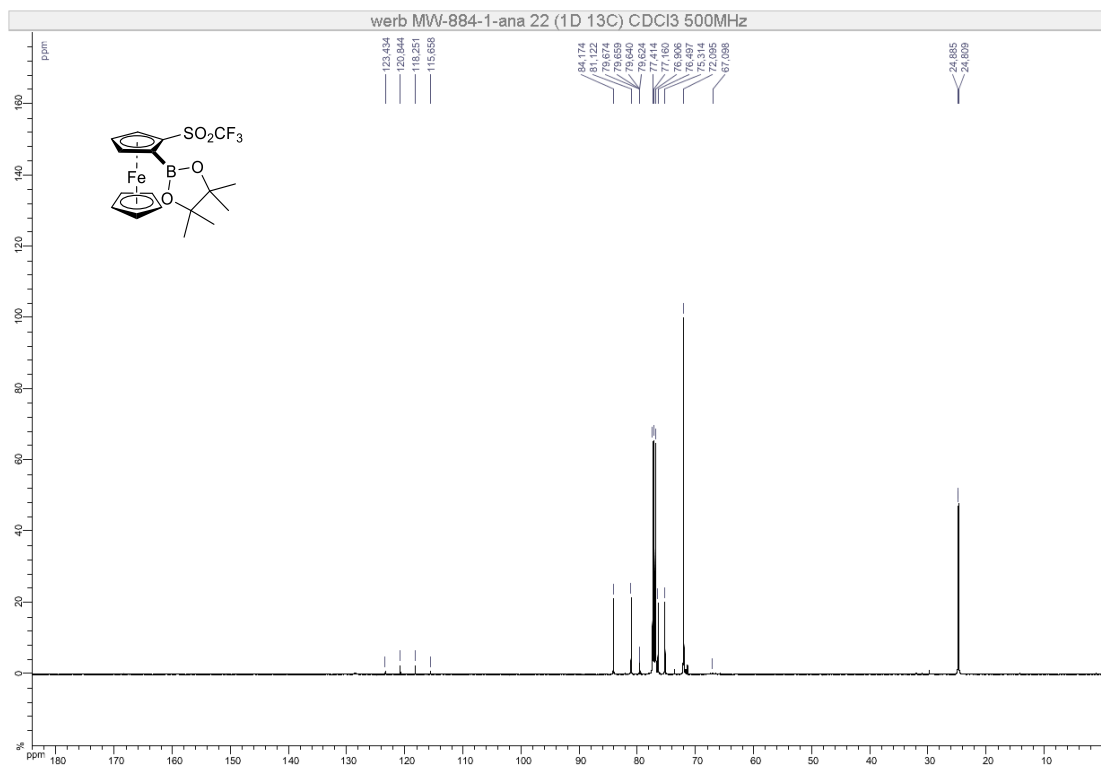
^1H NMR (500 MHz, CDCl_3)



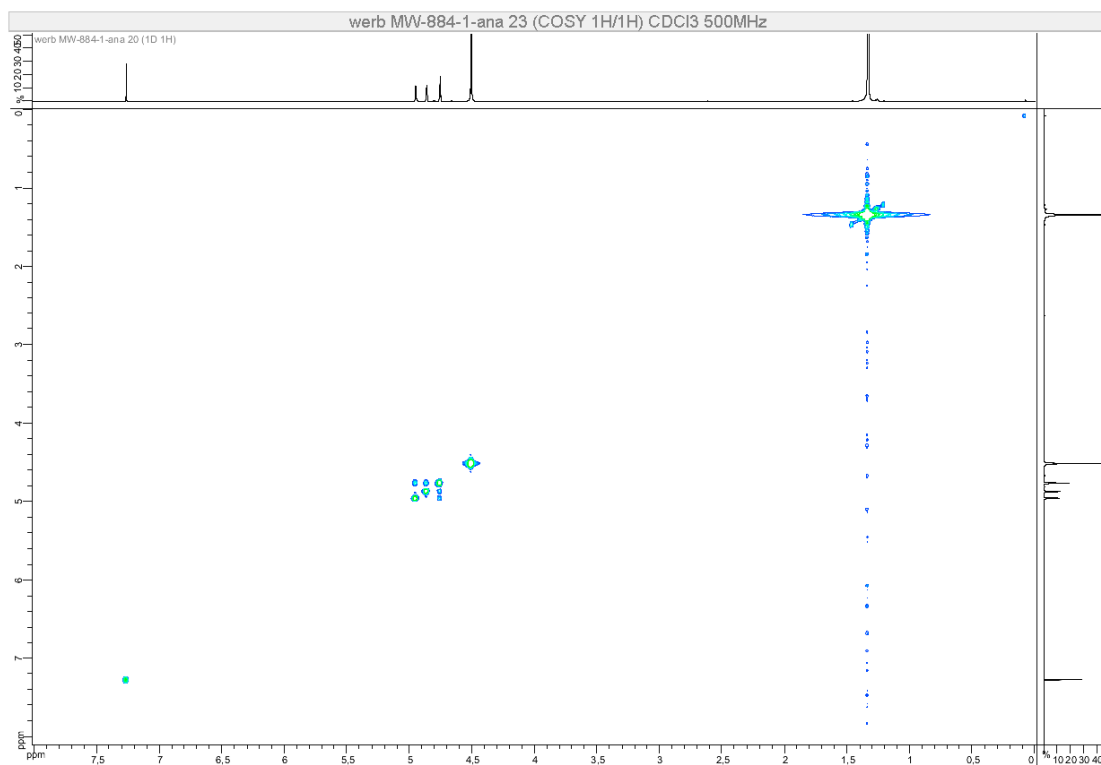
HOESY (500 MHz, CDCl_3) Irradiation at -78.4 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



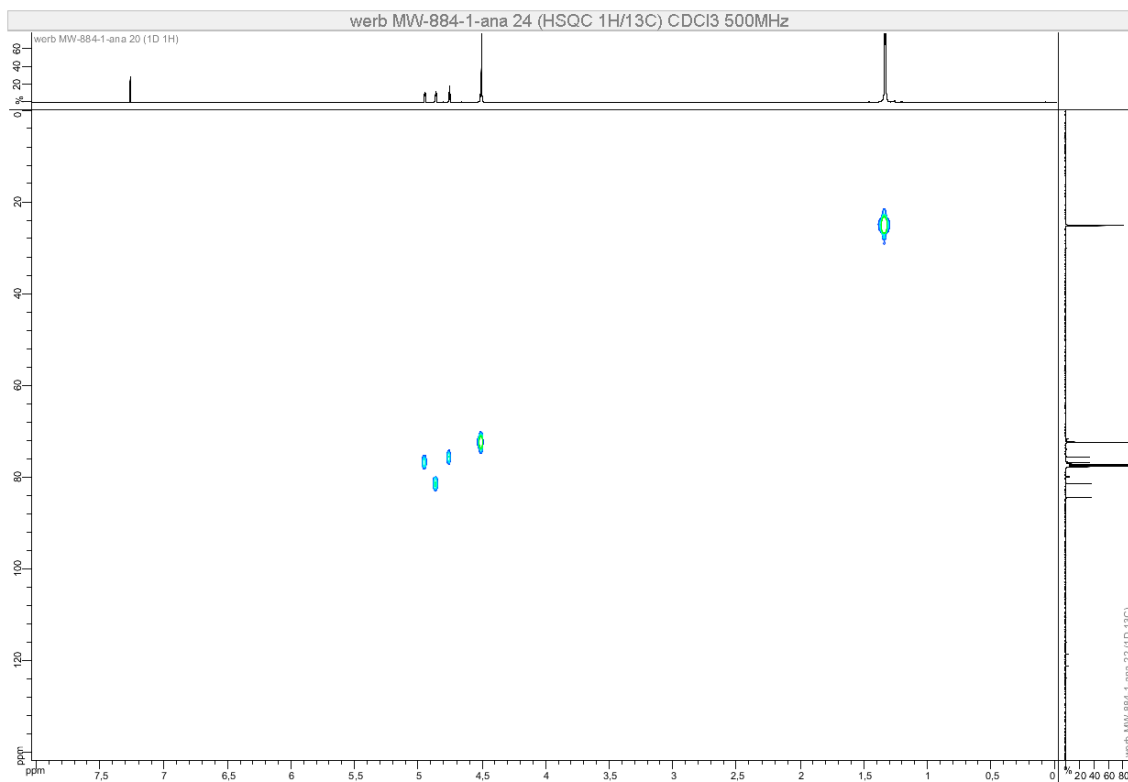
^{13}C NMR (126 MHz, CDCl_3)



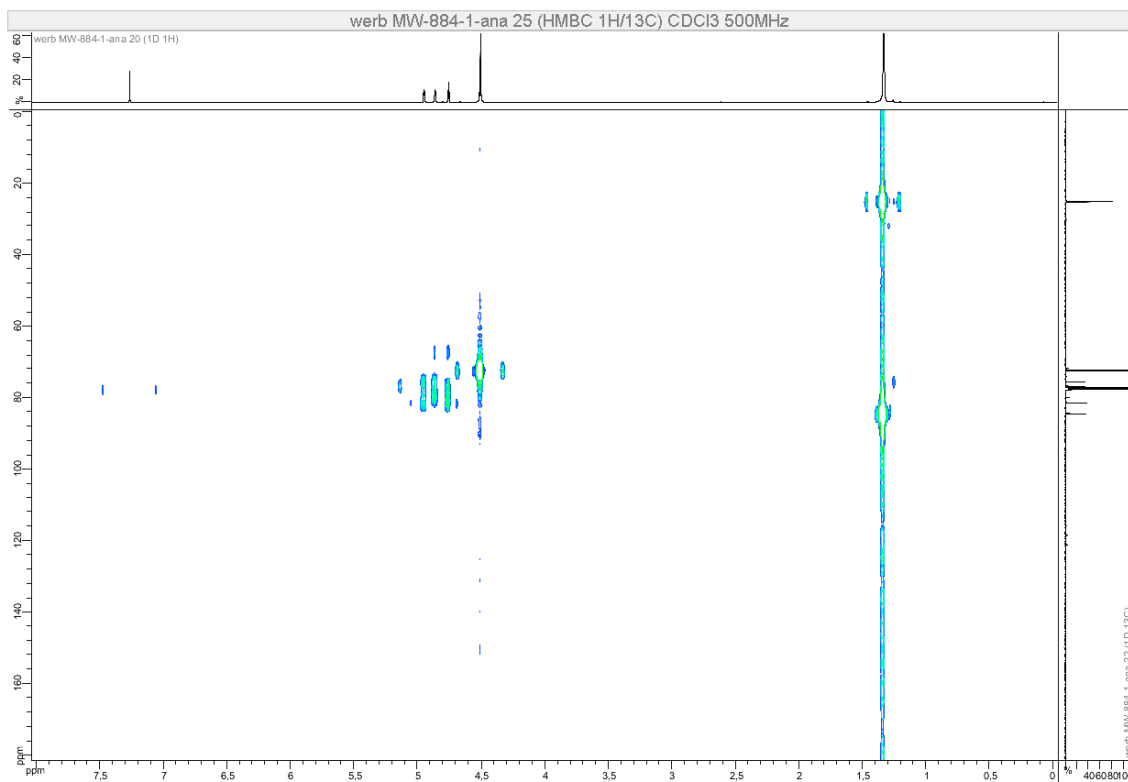
COSY (500 MHz, CDCl_3)



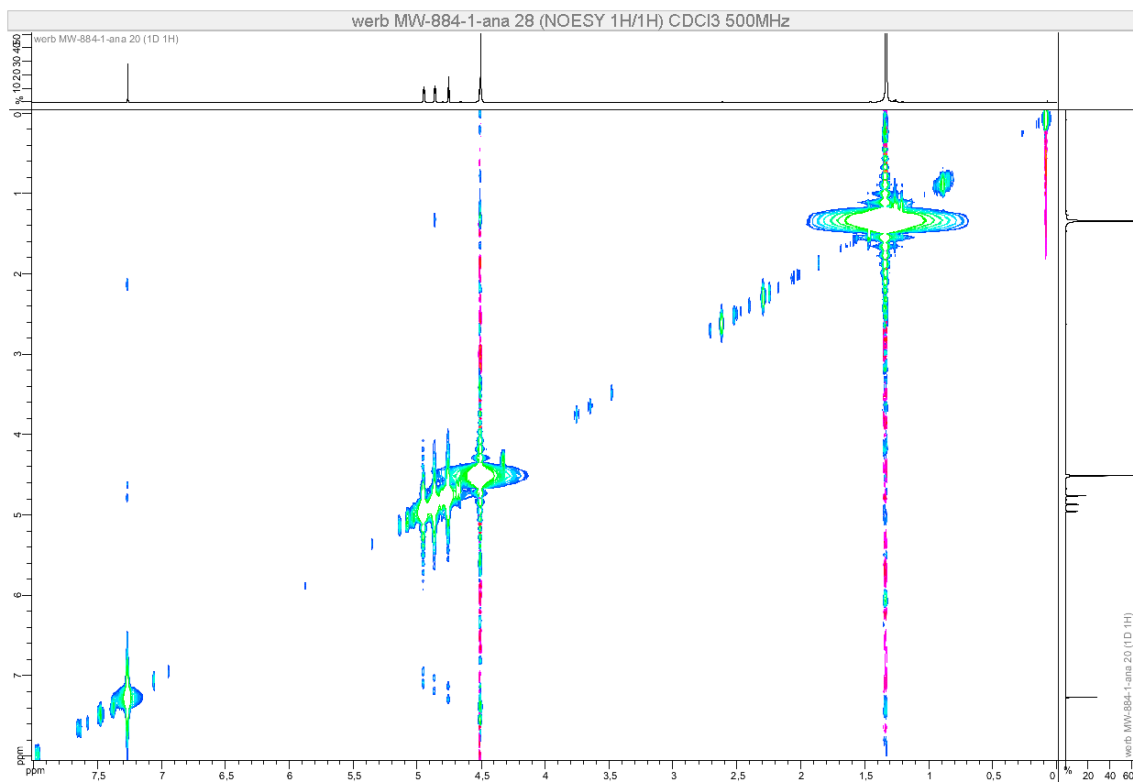
HSQC (500 MHz, CDCl₃)



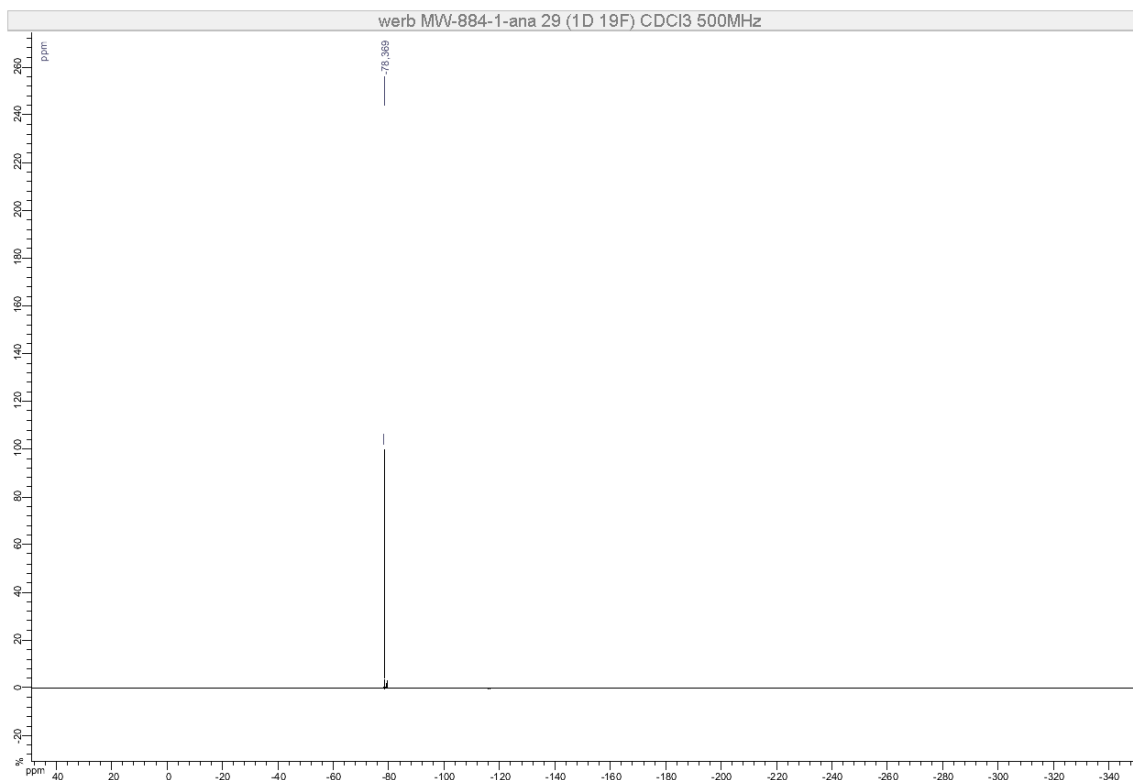
HMBC (500 MHz, CDCl₃)



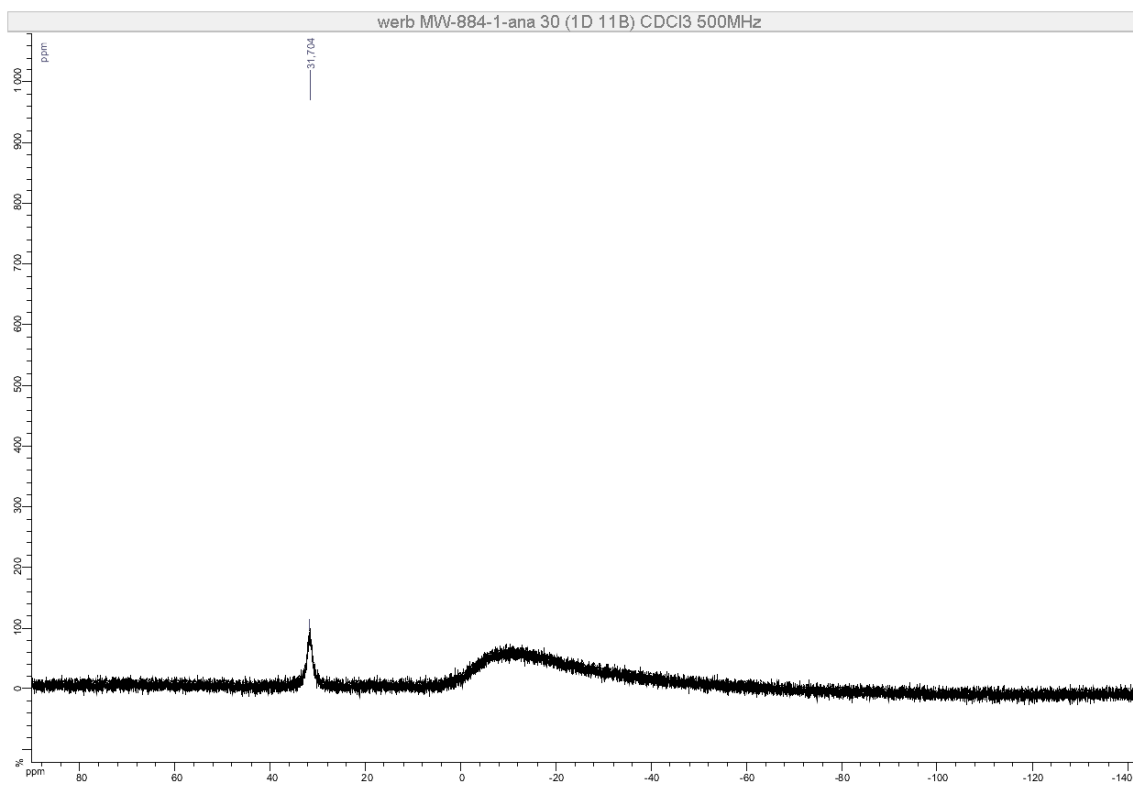
NOESY (500 MHz, CDCl₃)



¹⁹F NMR (470 MHz, CDCl₃)

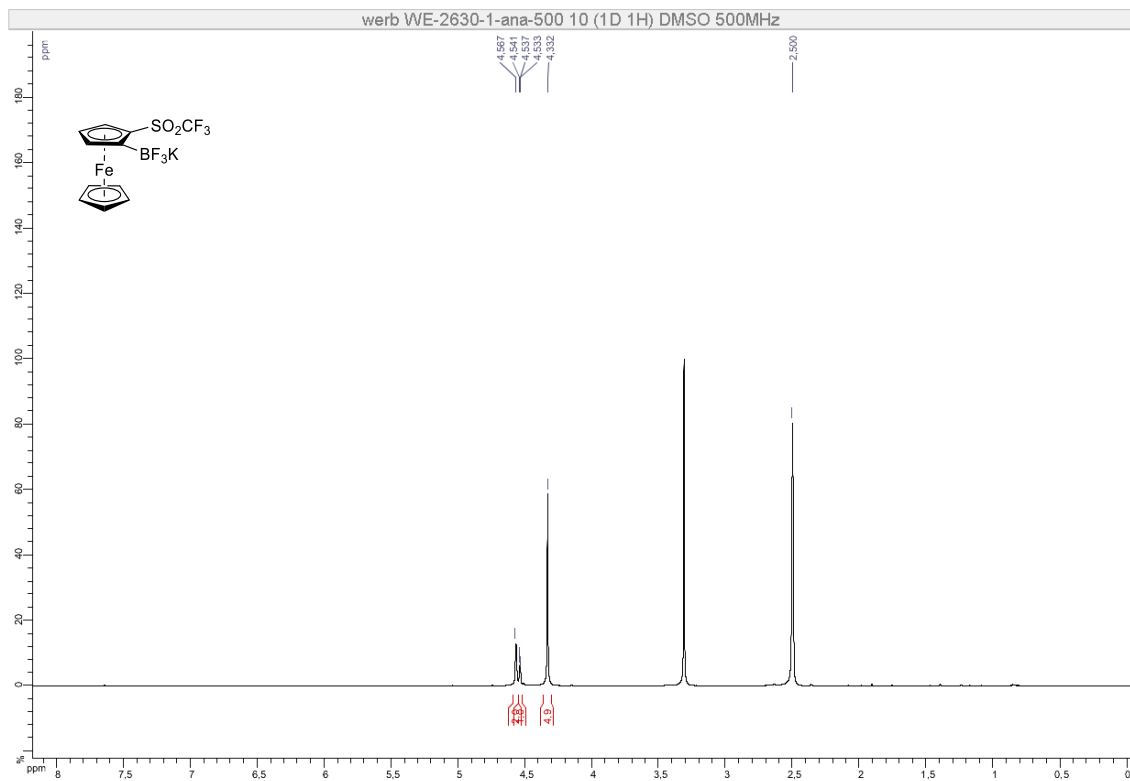


^{11}B NMR (160 MHz, CDCl_3)

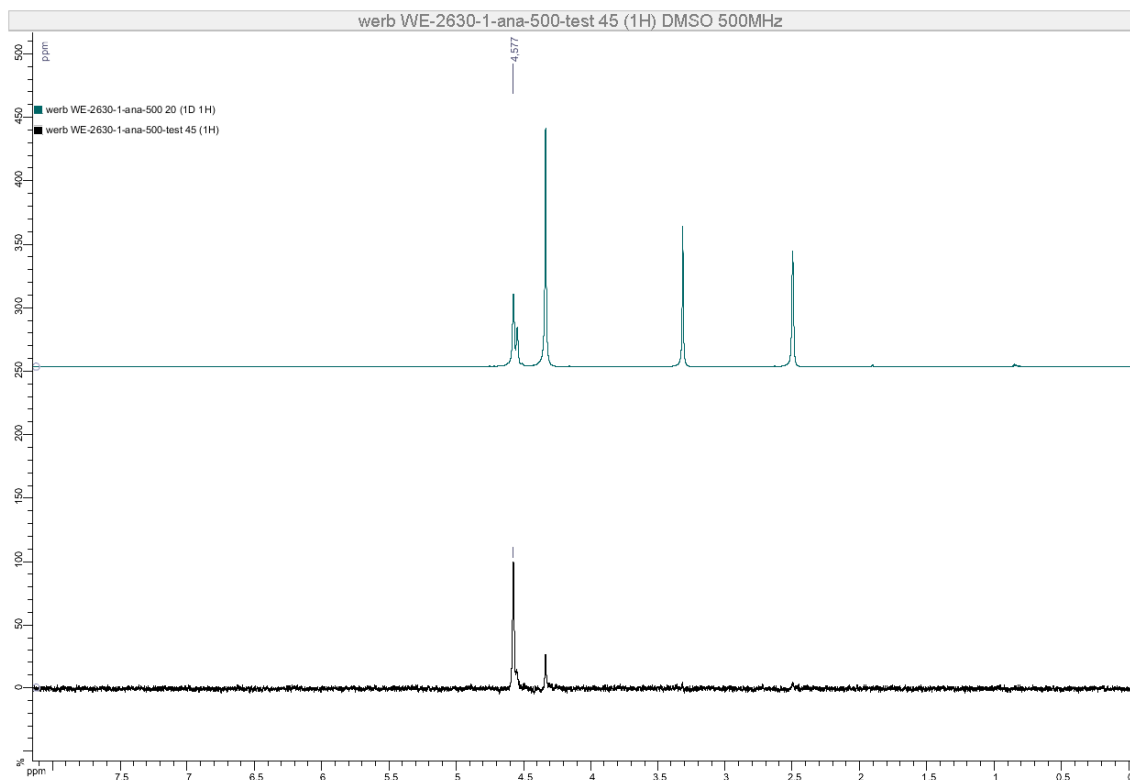


Potassium 2-(trifluoroboryl)ferrocenetriflone (2i)

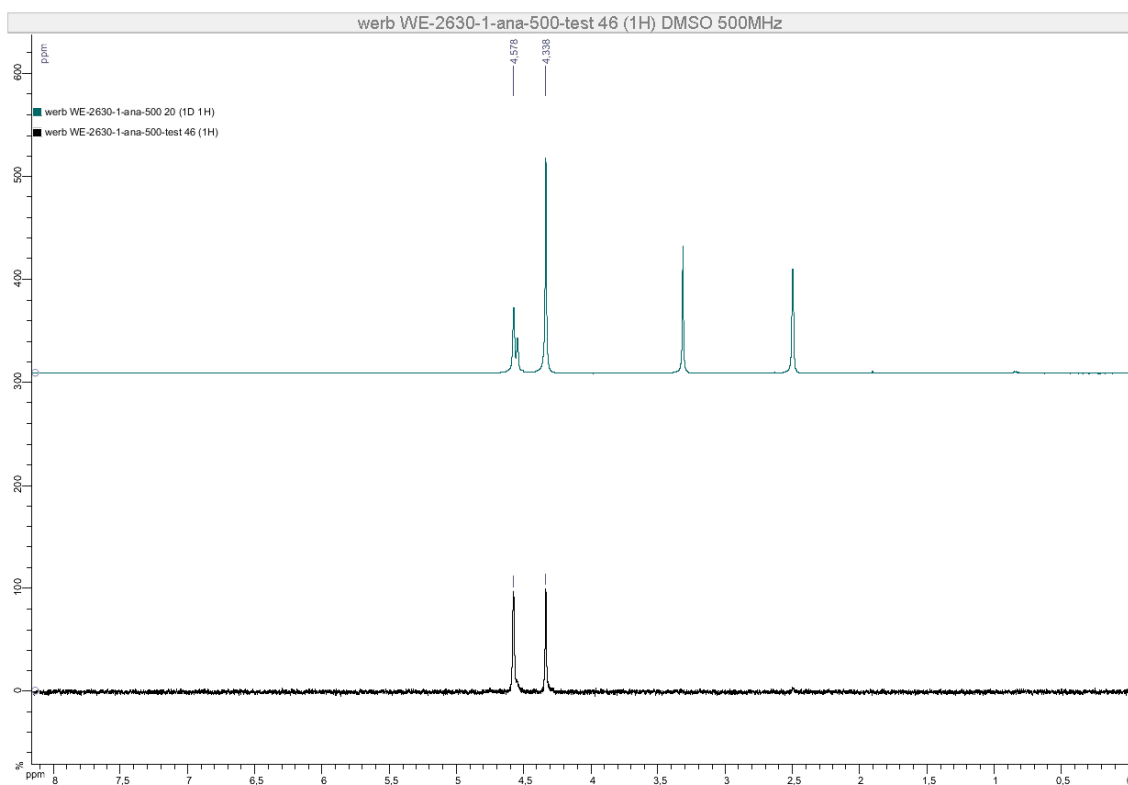
^1H NMR (500 MHz, CDCl_3)



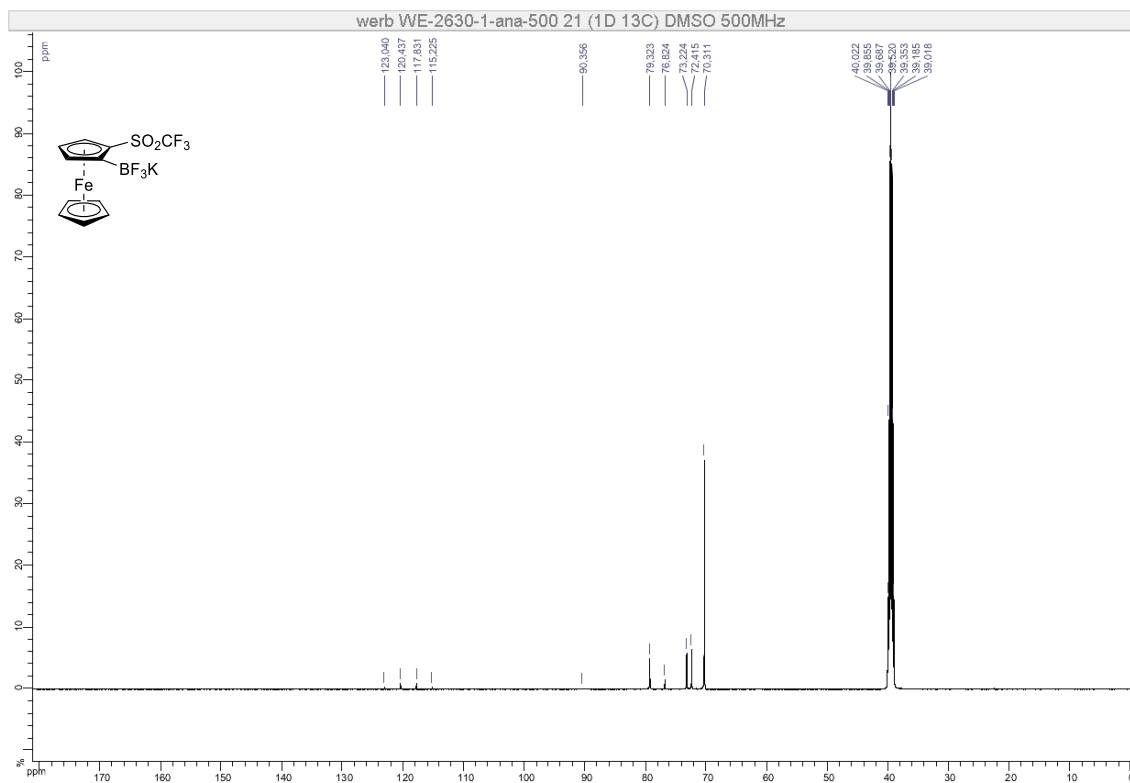
HOESY (500 MHz, CDCl_3) Irradiation at -78.4 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



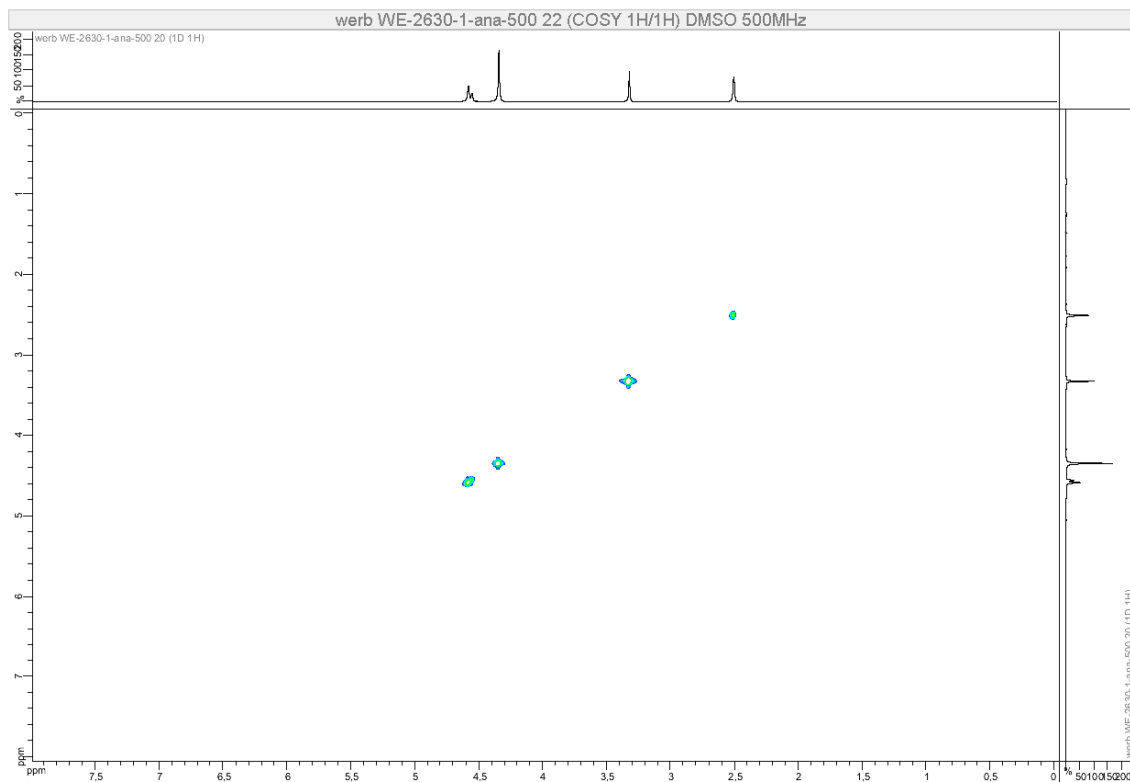
HOESY (500 MHz, CDCl₃) Irradiation at -132.5 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



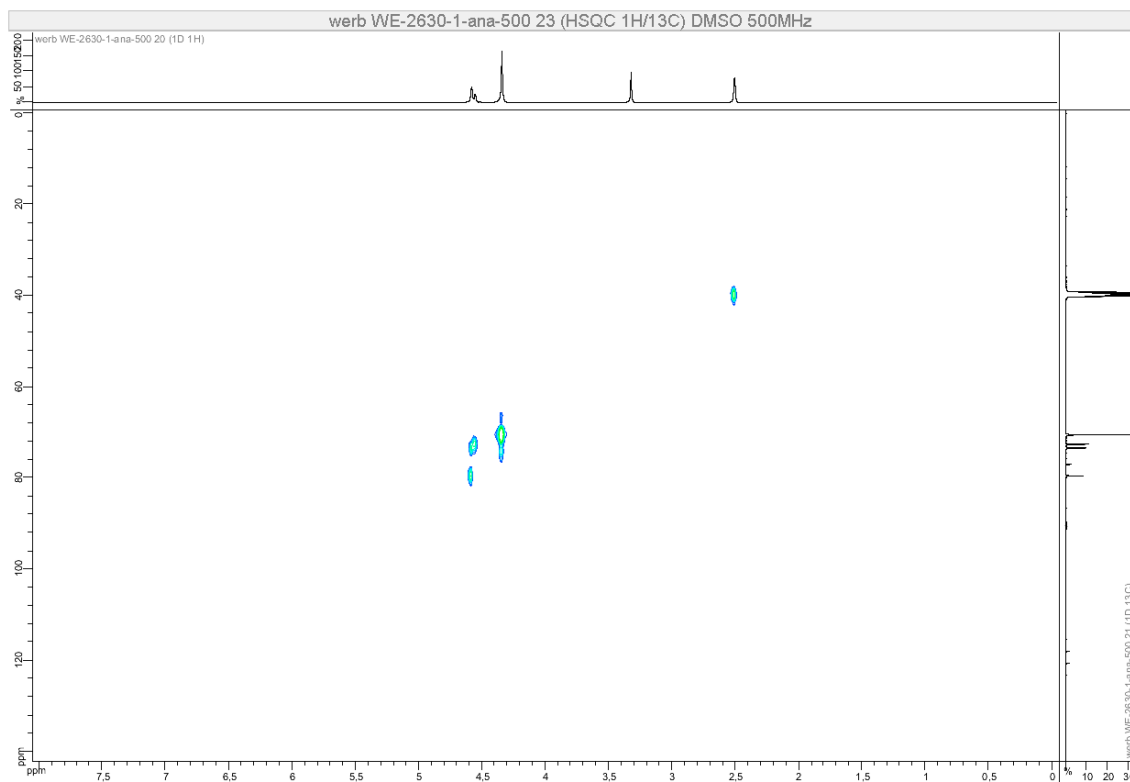
¹³C NMR (126 MHz, CDCl₃)



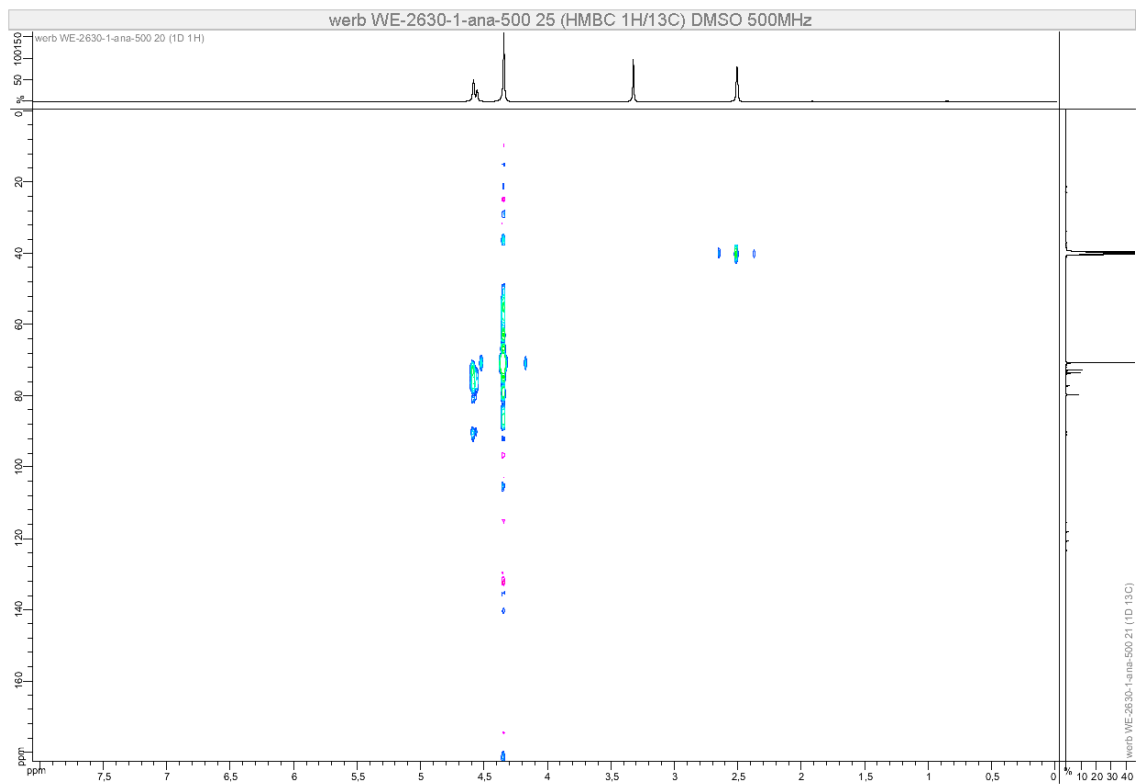
COSY (500 MHz, CDCl₃)



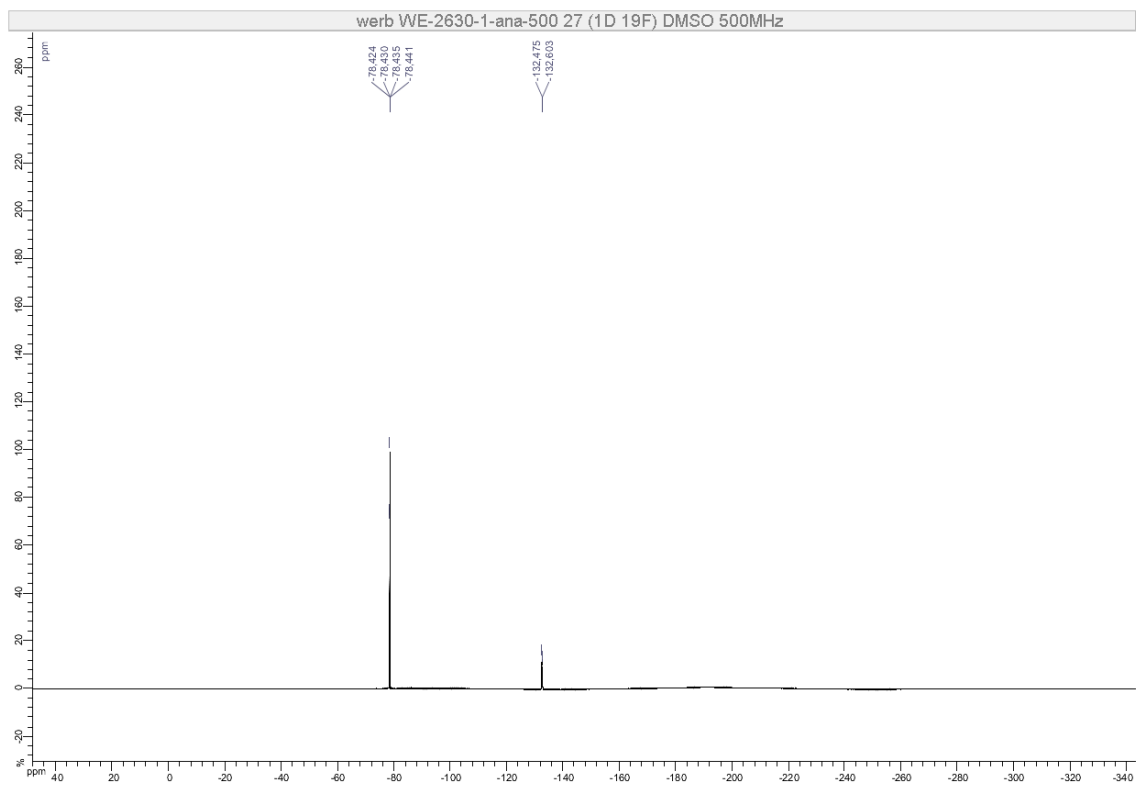
HSQC (500 MHz, CDCl₃)



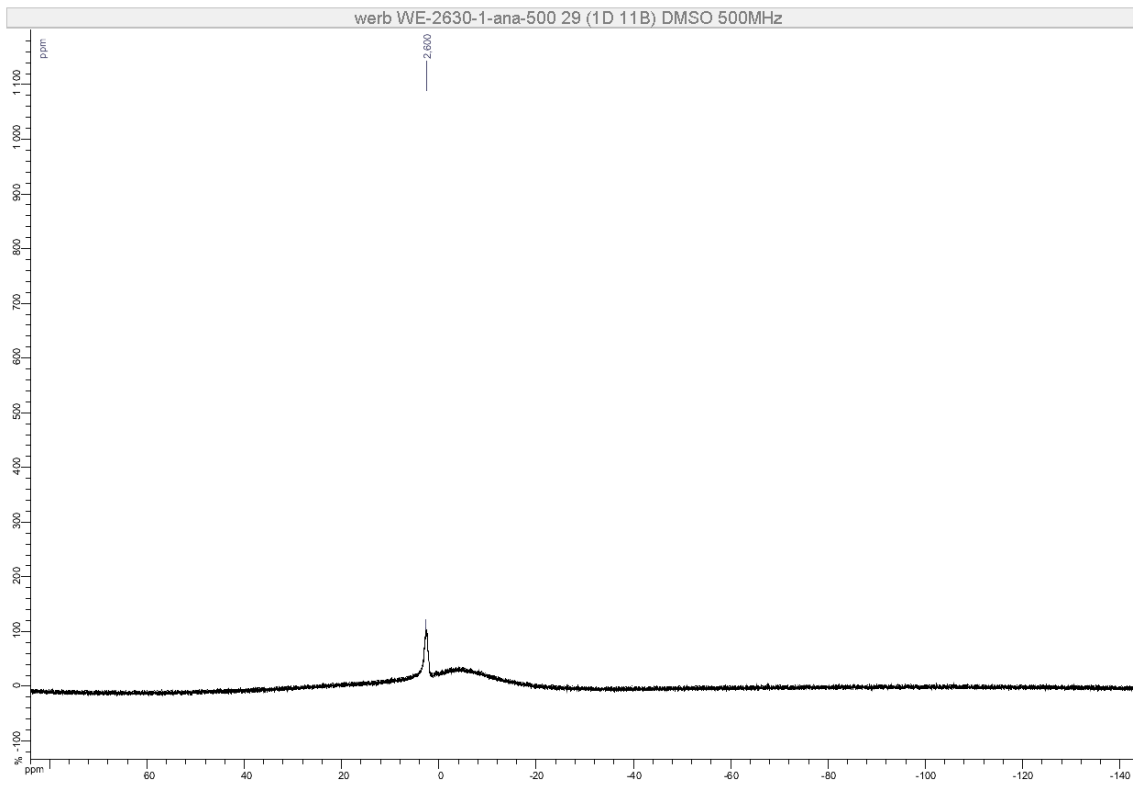
HMBC (500 MHz, CDCl₃)



¹⁹F NMR (470 MHz, CDCl₃)

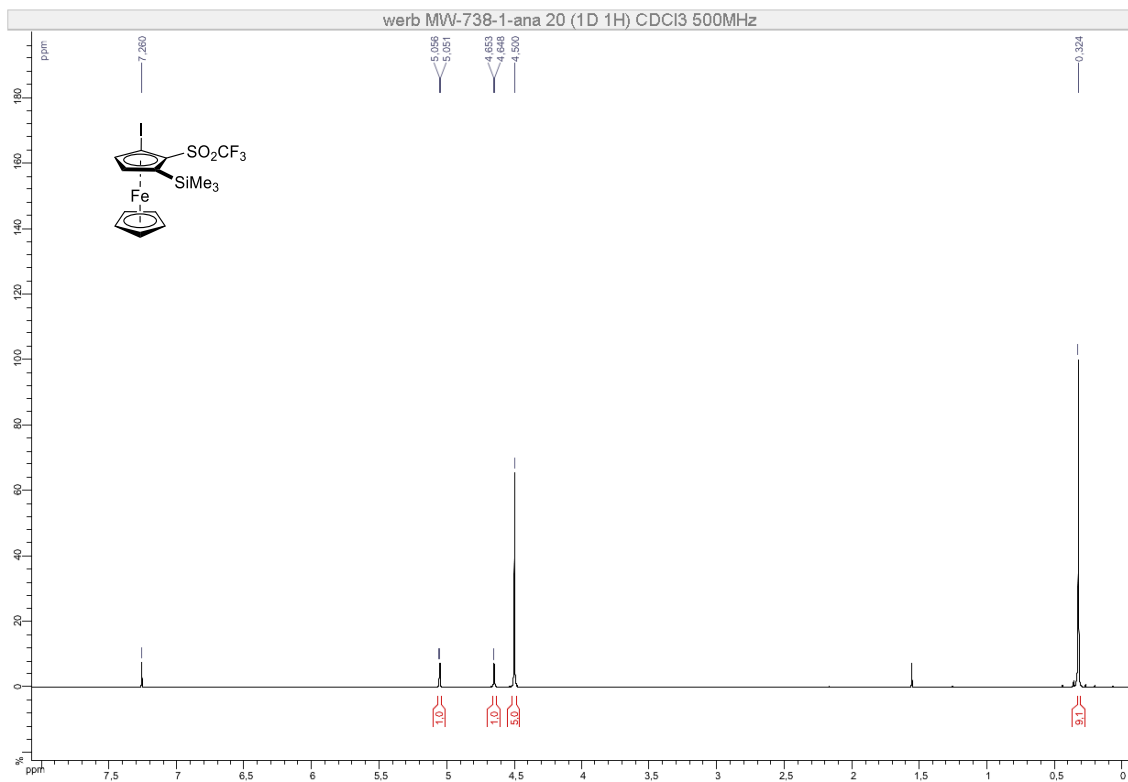


^{11}B NMR (160 MHz, CDCl_3)

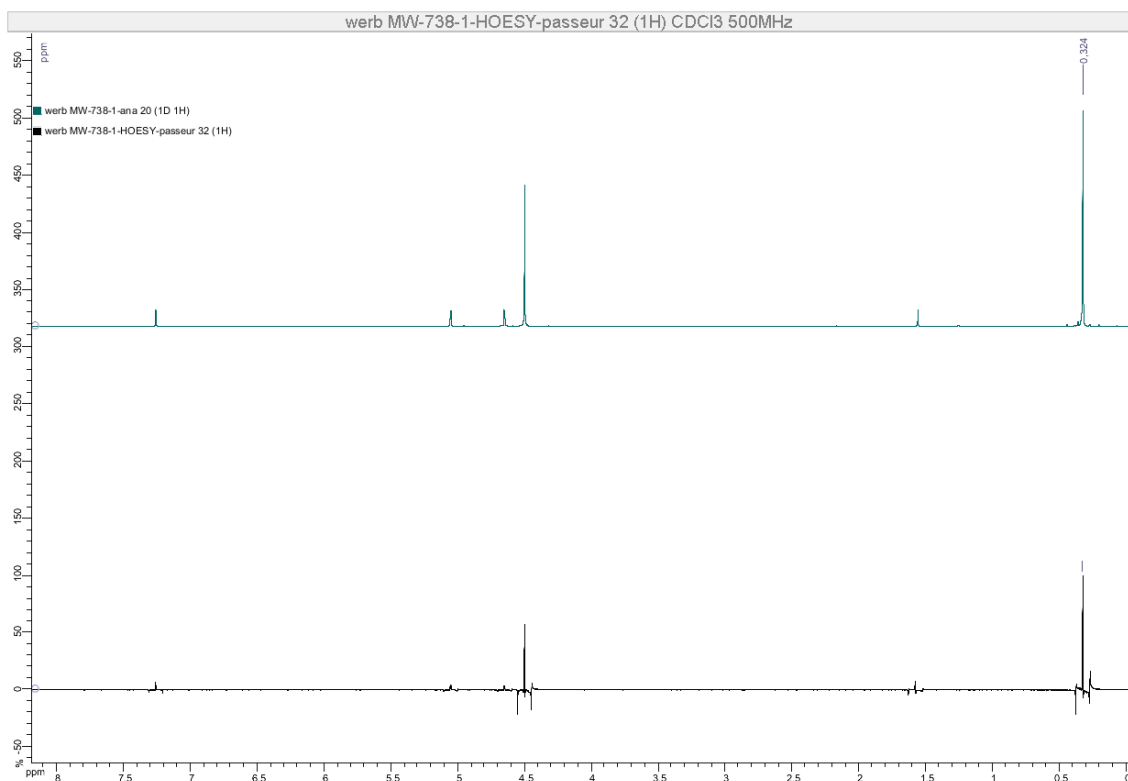


(*R_P*)-2-Iodo-5-(trimethylsilyl)ferrocenetriflone (*R_P*-3af)

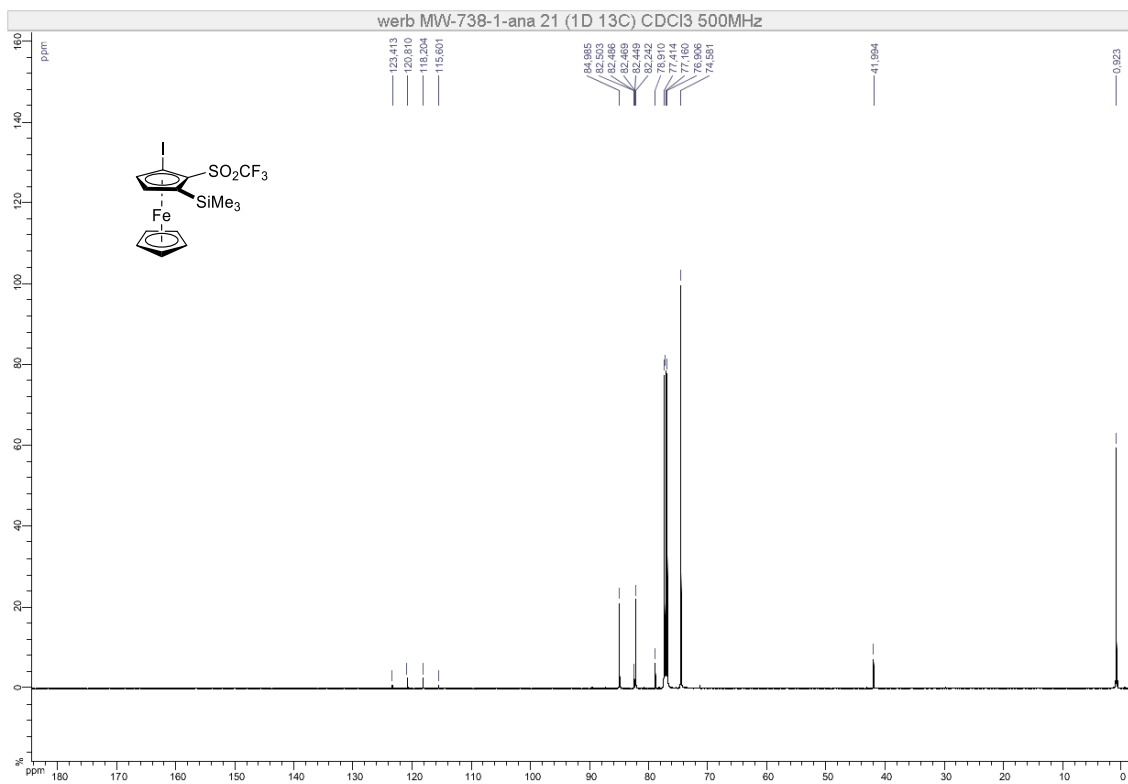
¹H NMR (500 MHz, CDCl₃)



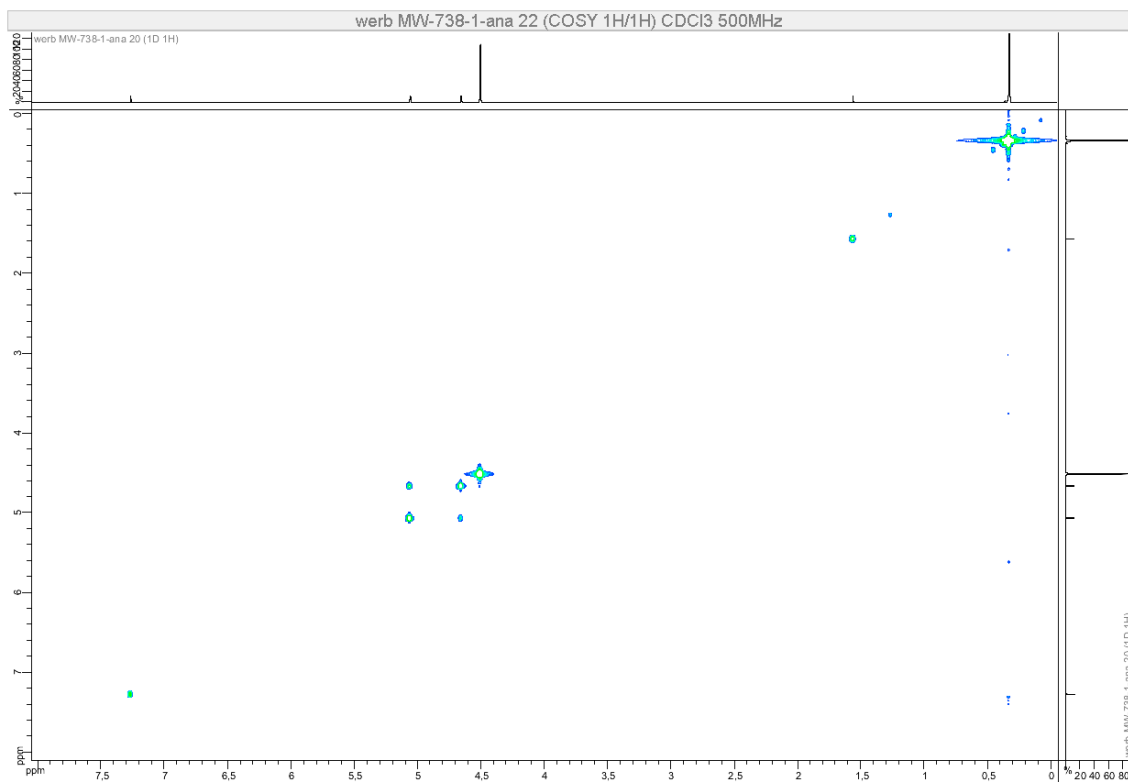
HOESY (500 MHz, CDCl₃) Irradiation at -75.8 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



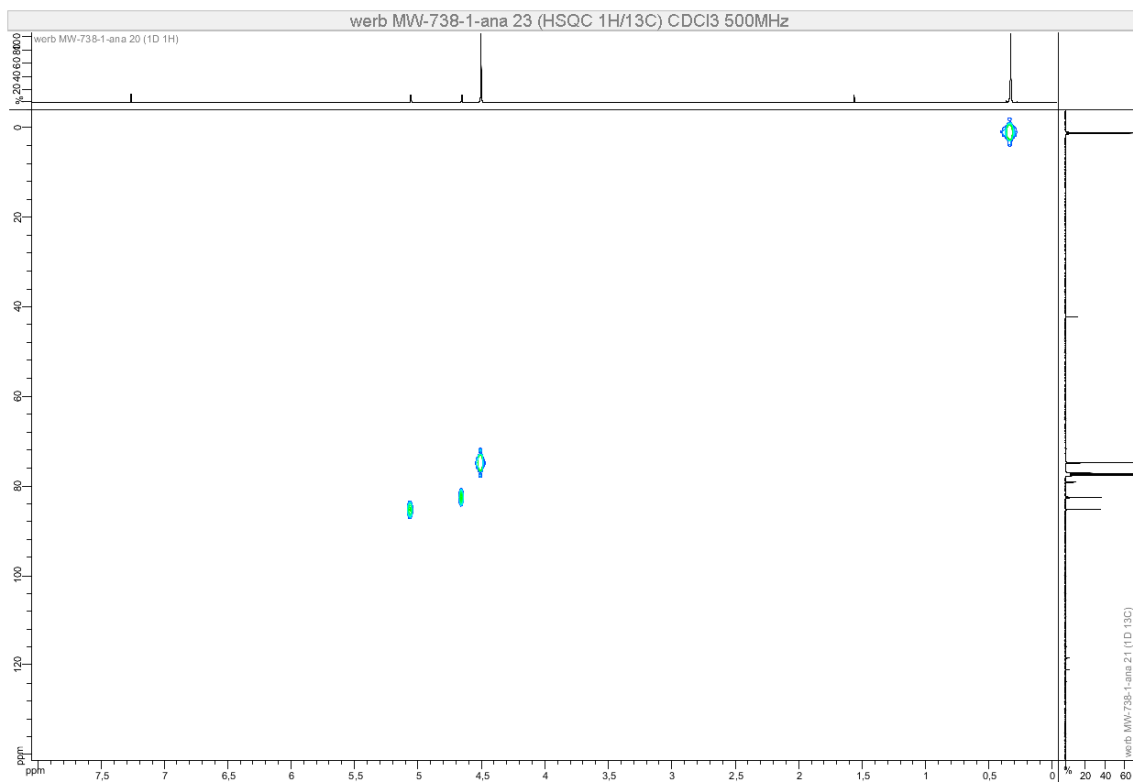
^{13}C NMR (126 MHz, CDCl_3)



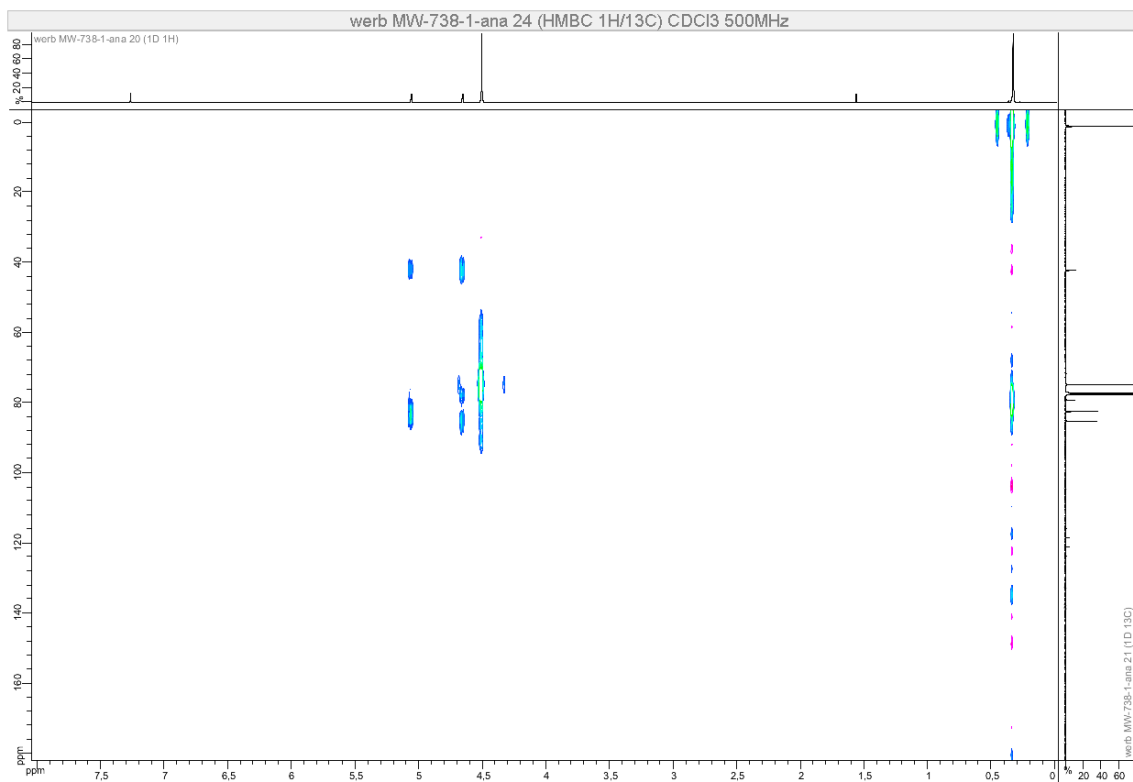
COSY (500 MHz, CDCl_3)



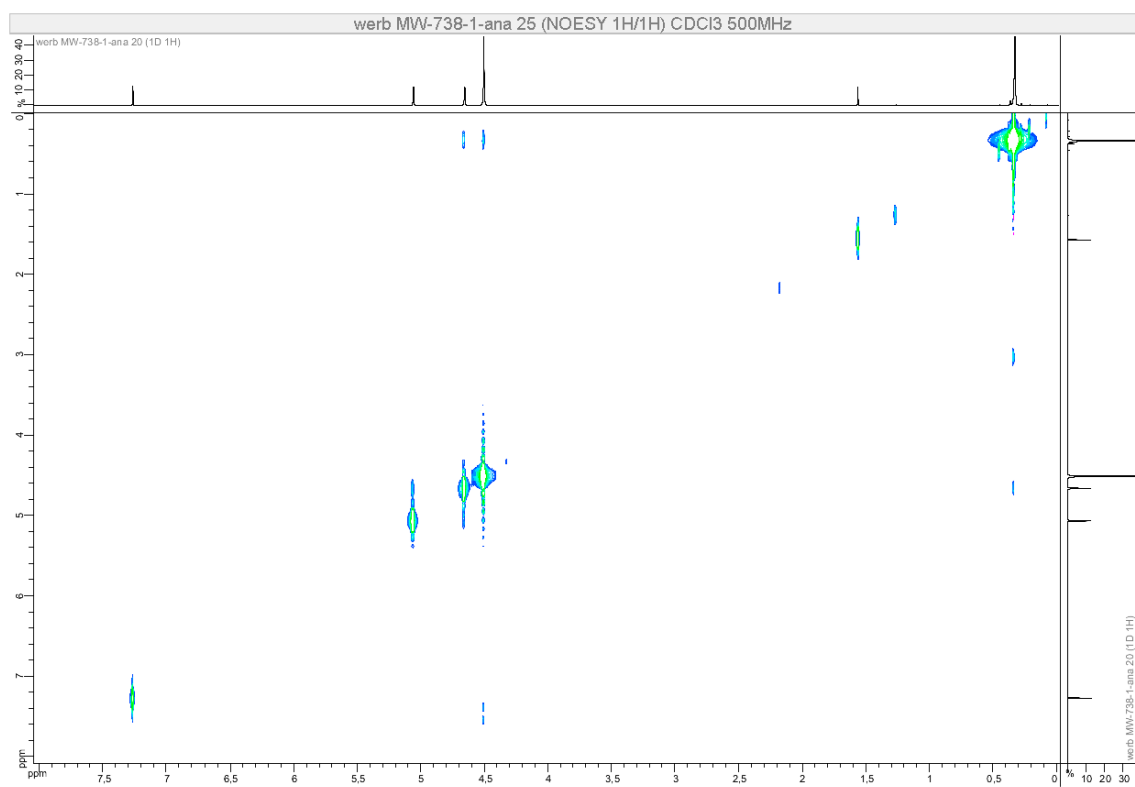
HSQC (500 MHz, CDCl₃)



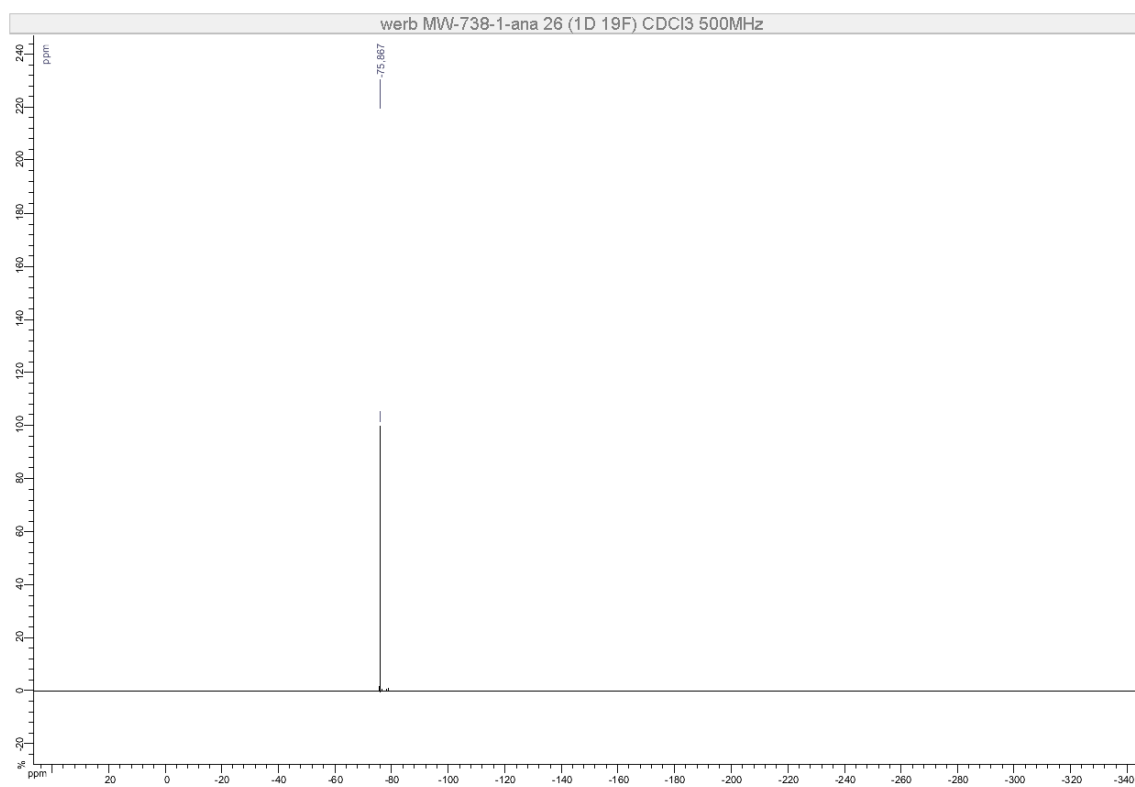
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

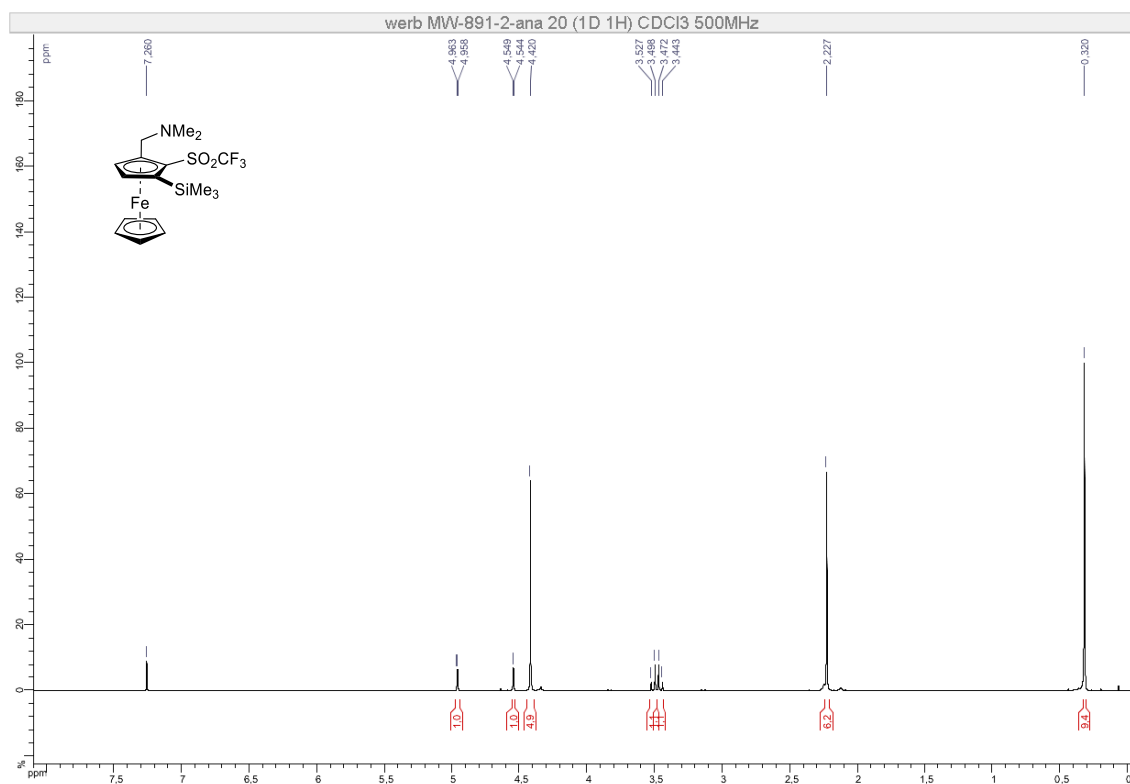


¹⁹F NMR (470 MHz, CDCl₃)

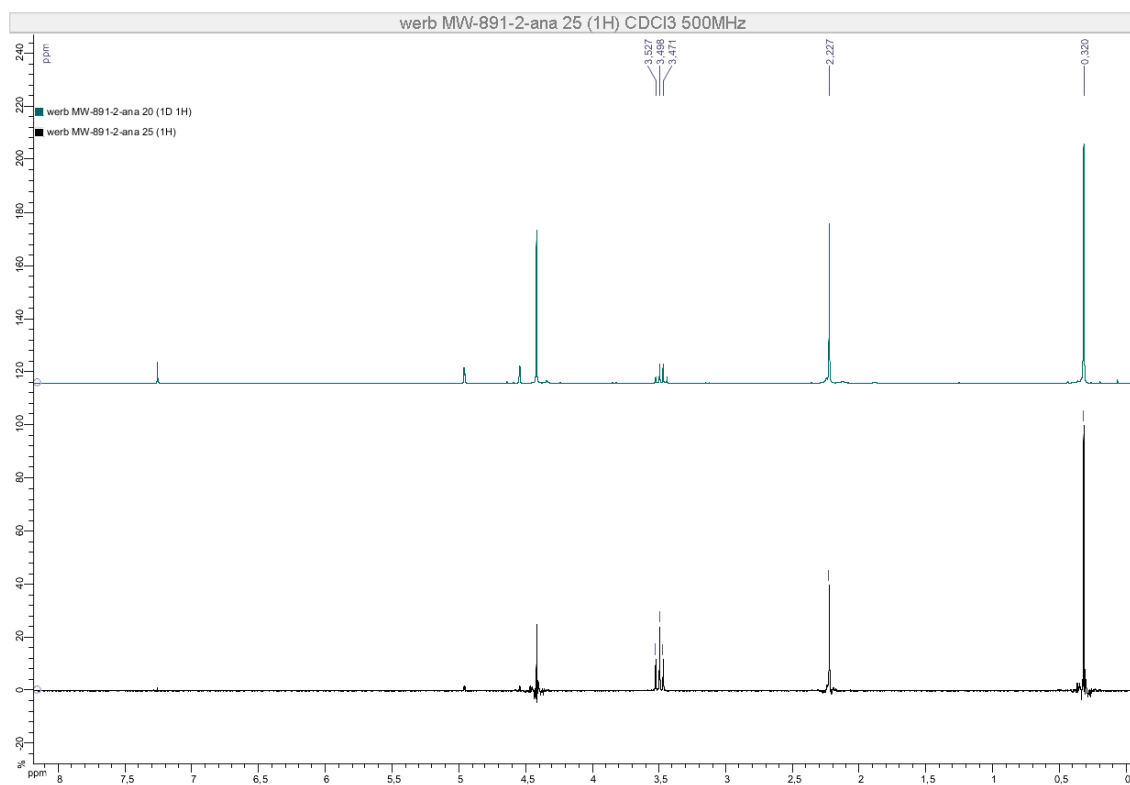


(*R_p*)-2-(Dimethylaminomethyl)-5-(trimethylsilyl)ferrocenetriflone (*R_p*-3aj)

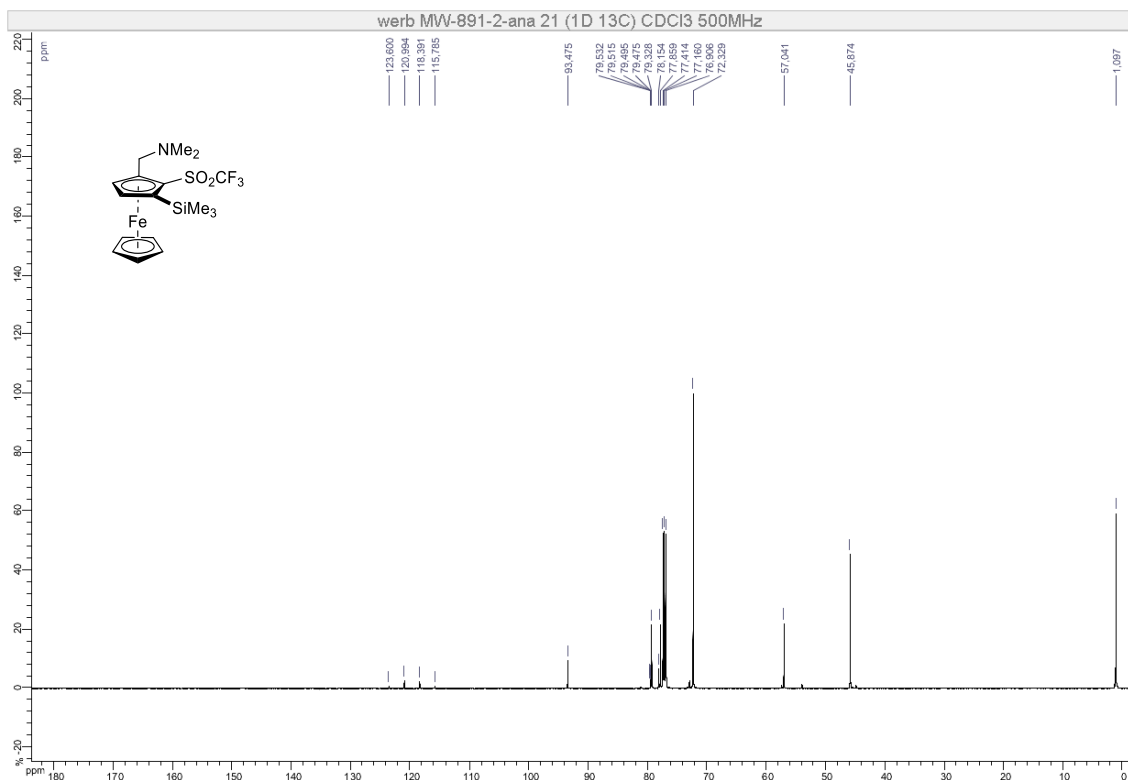
¹H NMR (500 MHz, CDCl₃)



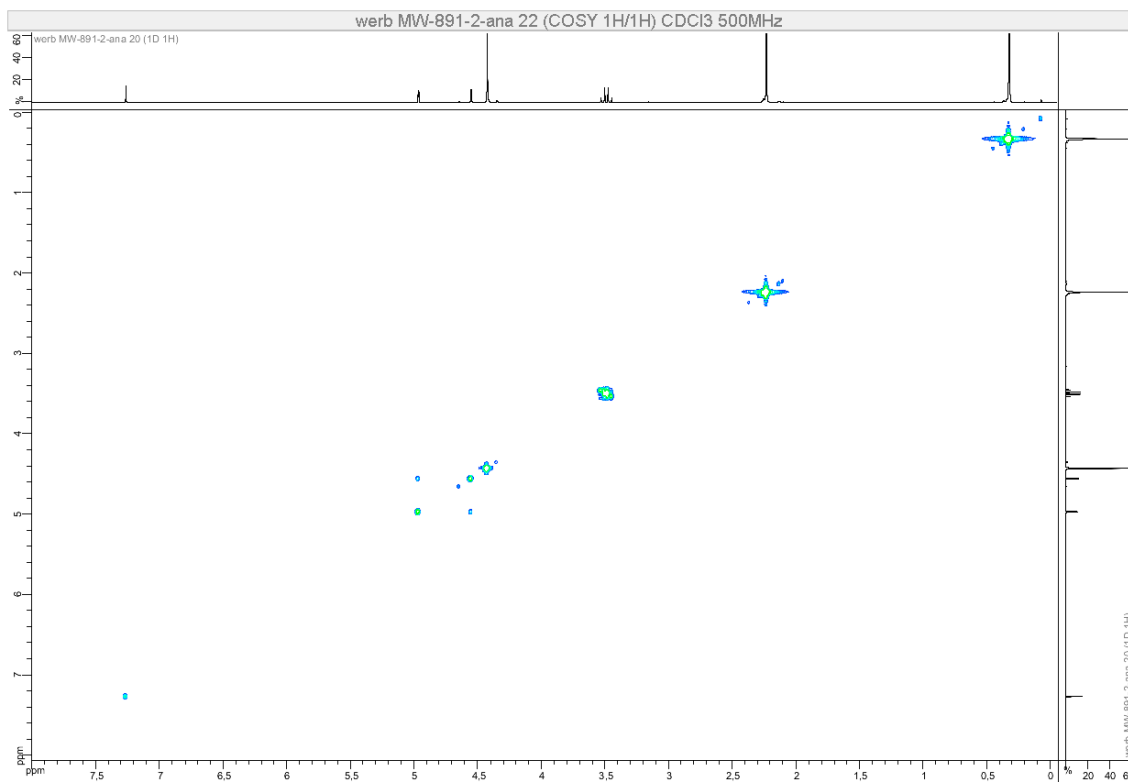
HOESY (500 MHz, CDCl₃) Irradiation at -75.9 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



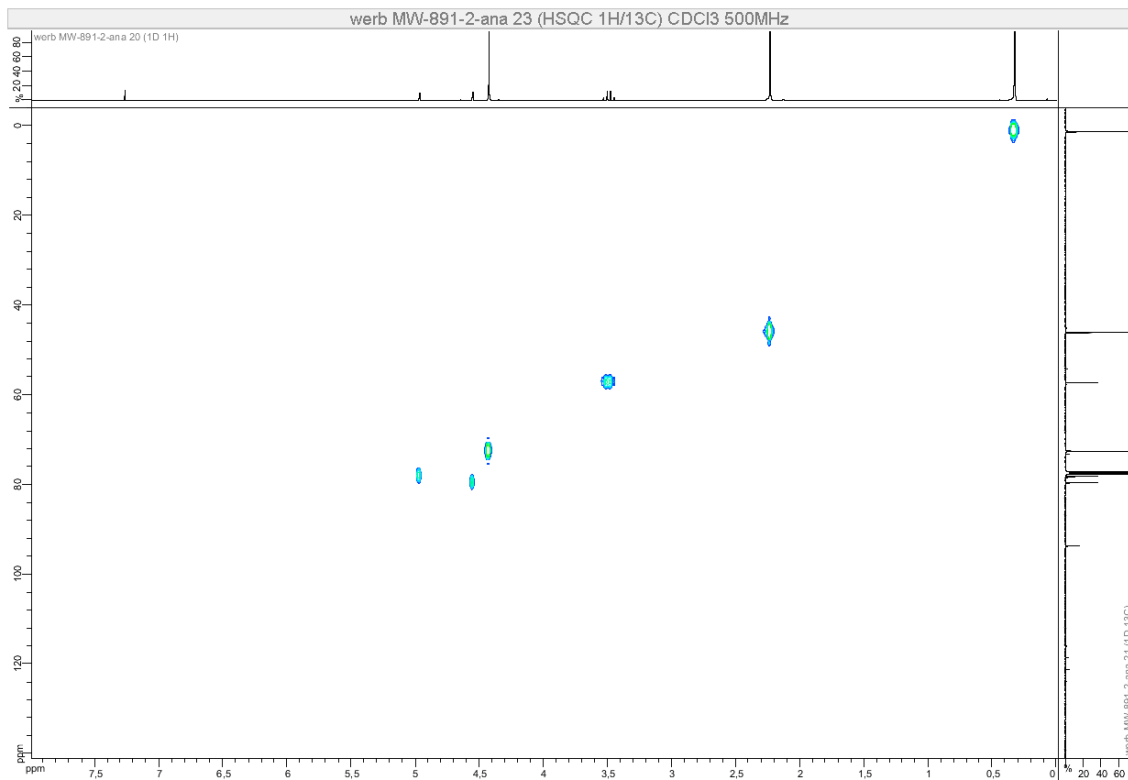
^{13}C NMR (126 MHz, CDCl_3)



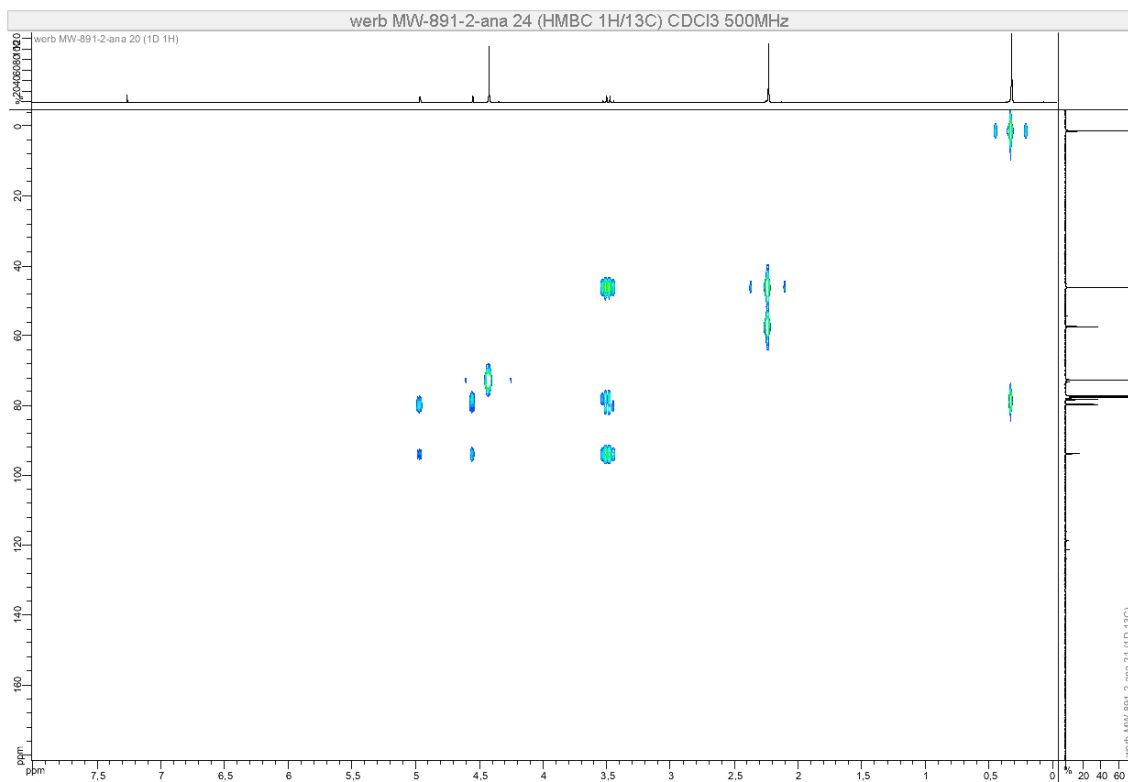
COSY (500 MHz, CDCl_3)



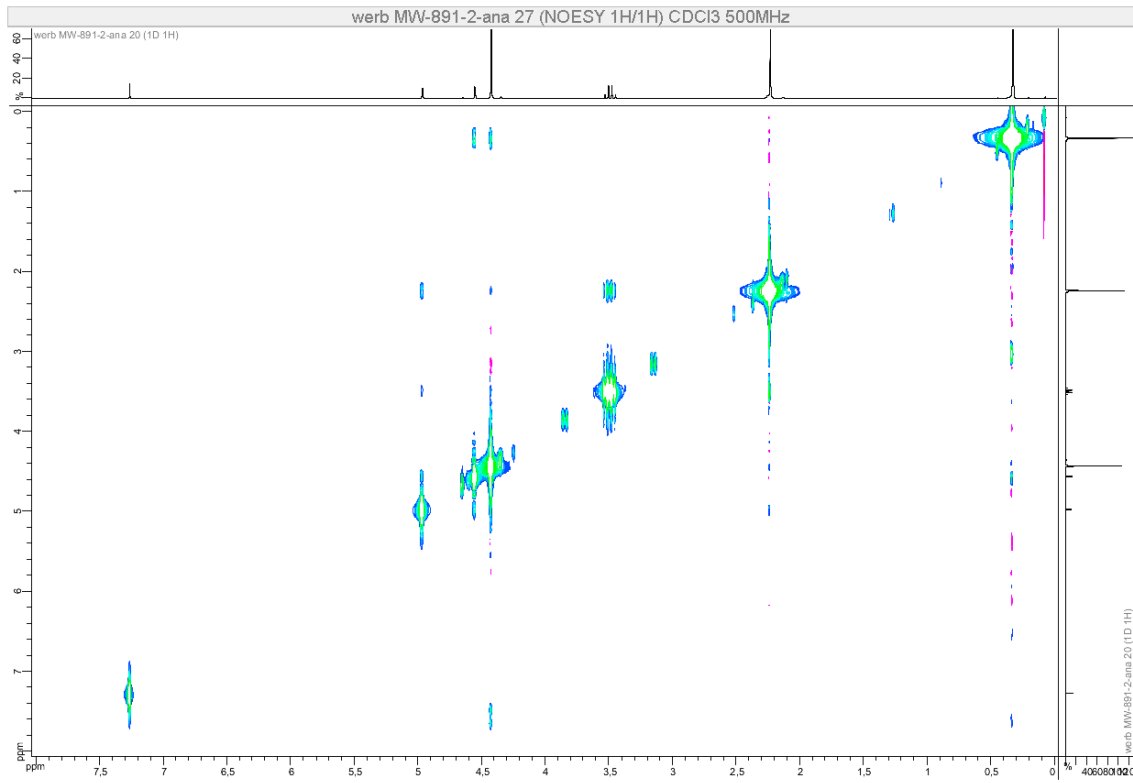
HSQC (500 MHz, CDCl₃)



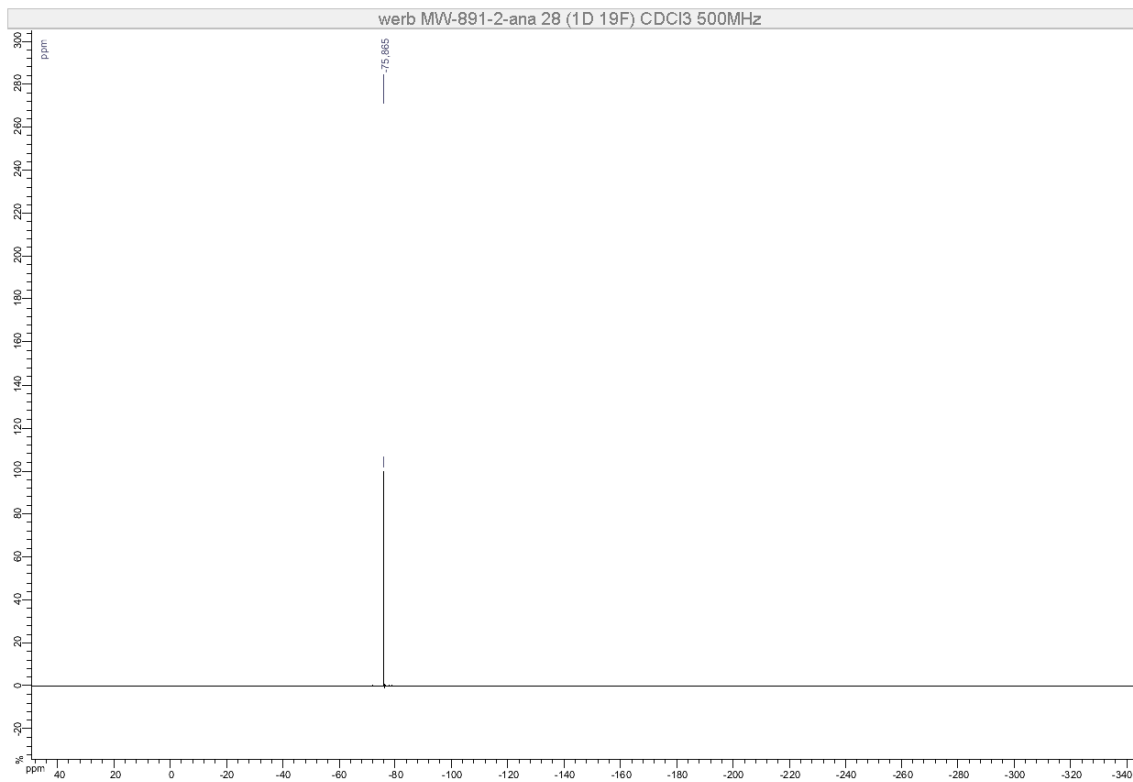
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

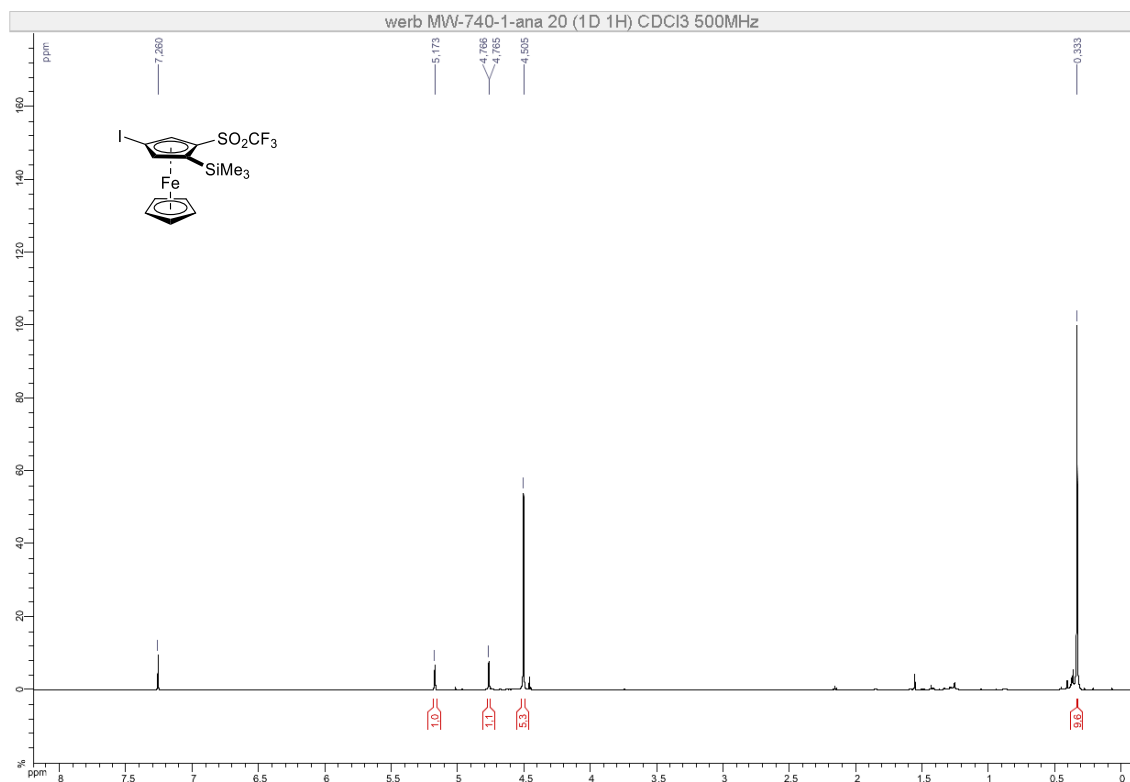


¹⁹F NMR (470 MHz, CDCl₃)

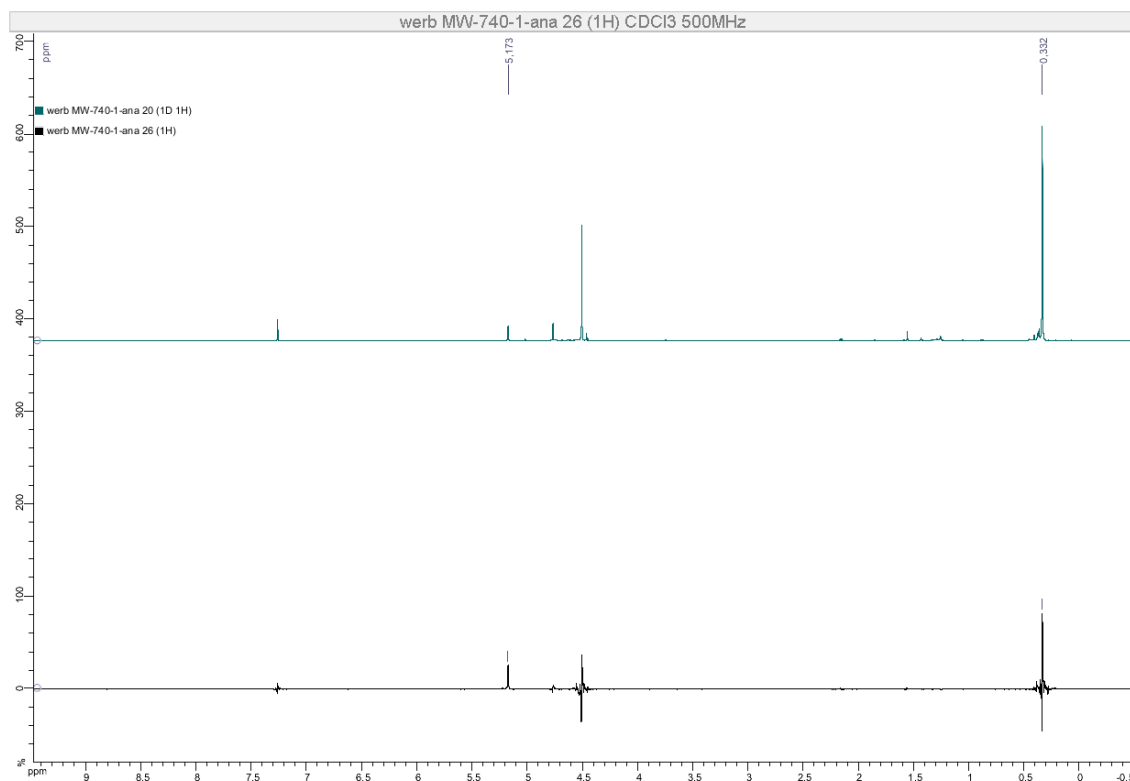


(*R_P*)-4-Iodo-2-(trimethylsilyl)ferrocenetriflone (*R_P*-4af)

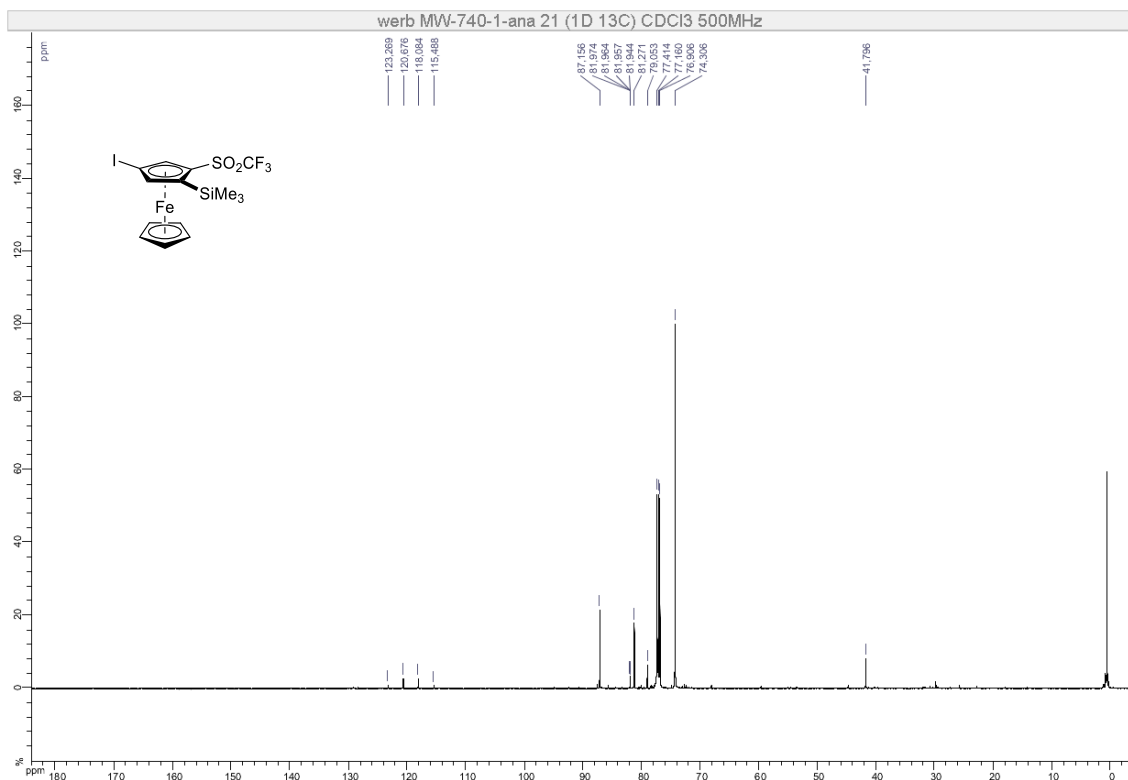
¹H NMR (500 MHz, CDCl₃)



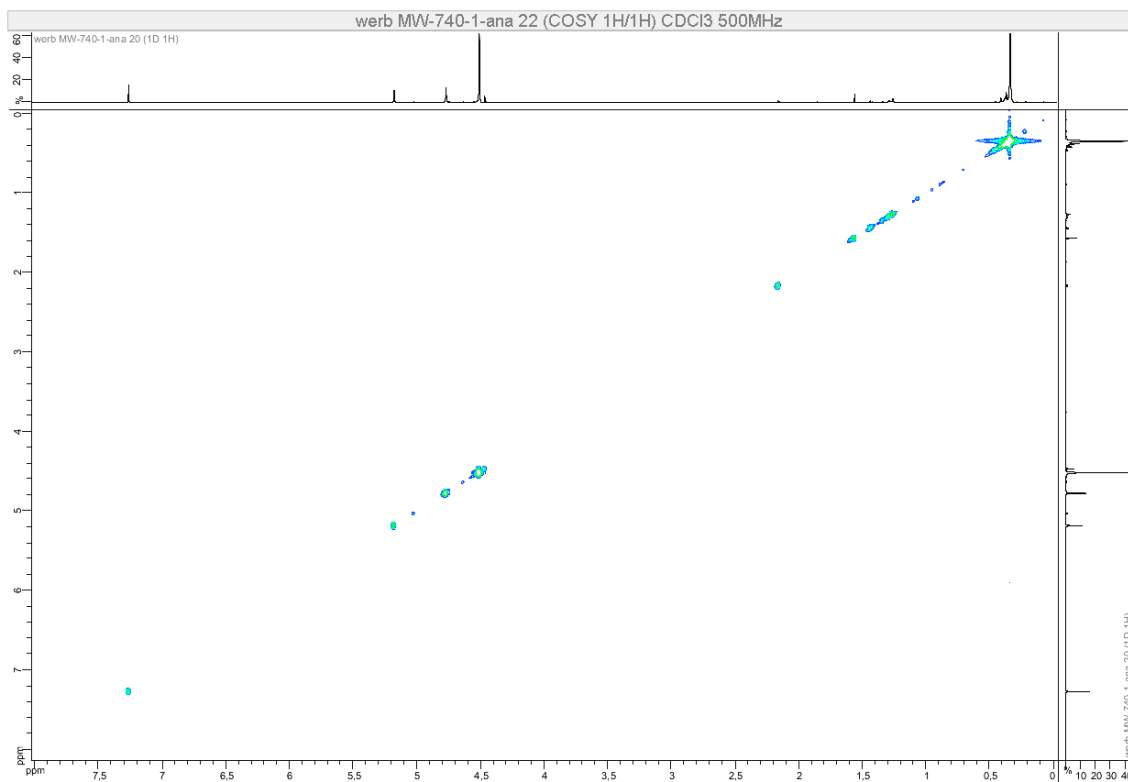
HOESY (500 MHz, CDCl₃) Irradiation at -78.3 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



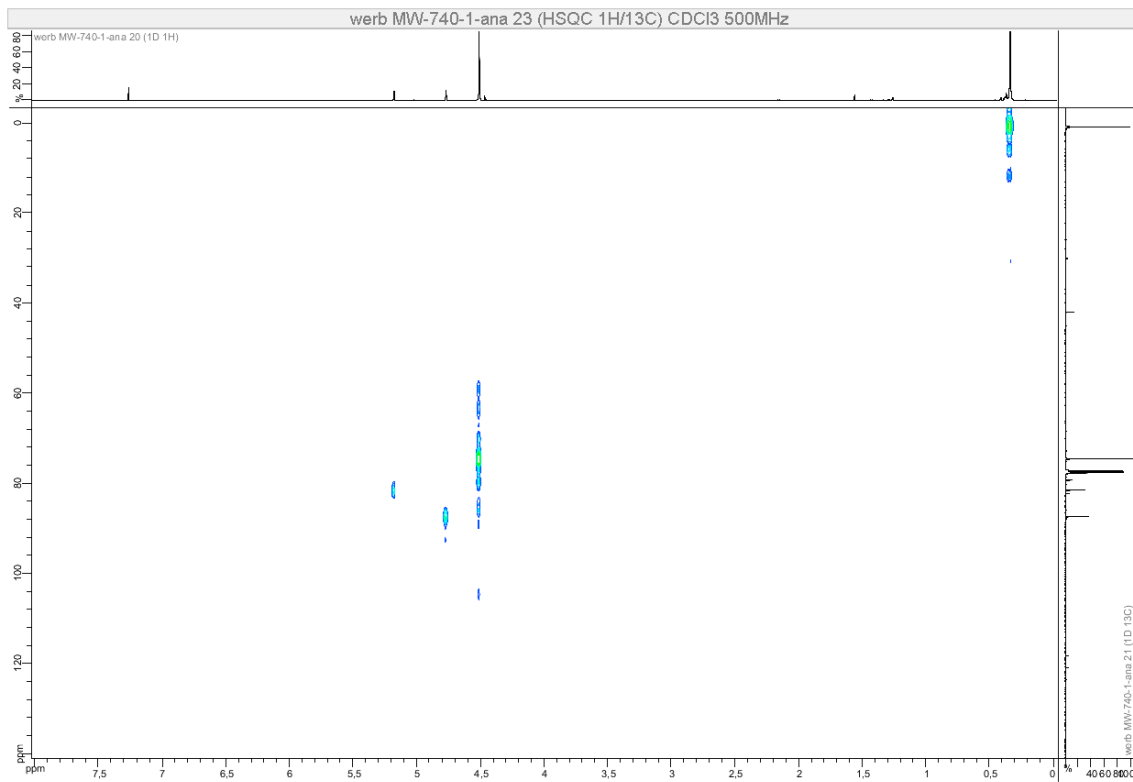
^{13}C NMR (126 MHz, CDCl_3)



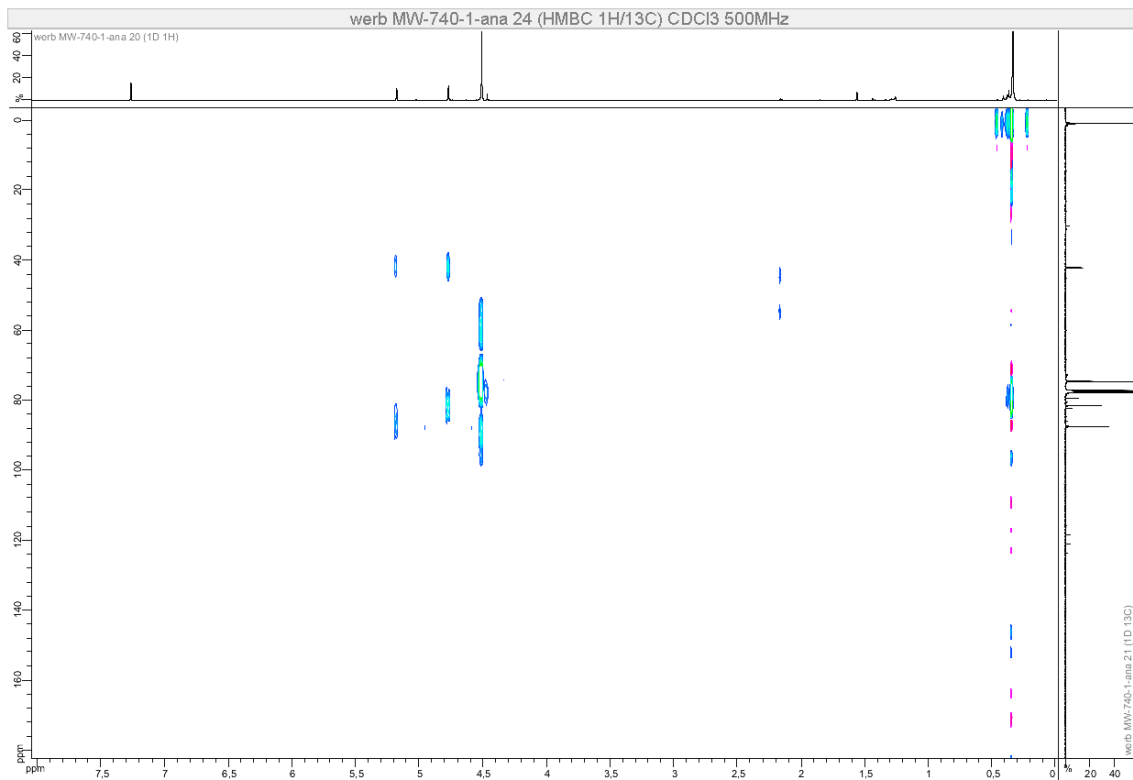
COSY (500 MHz, CDCl_3)



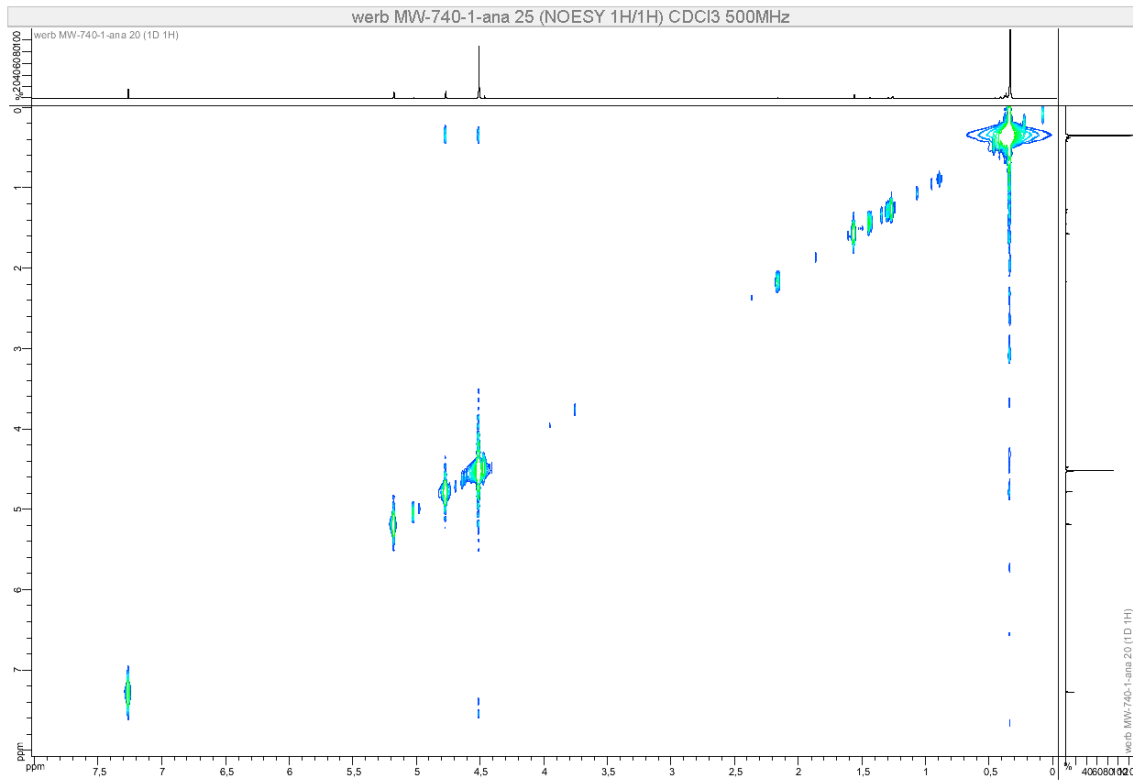
HSQC (500 MHz, CDCl₃)



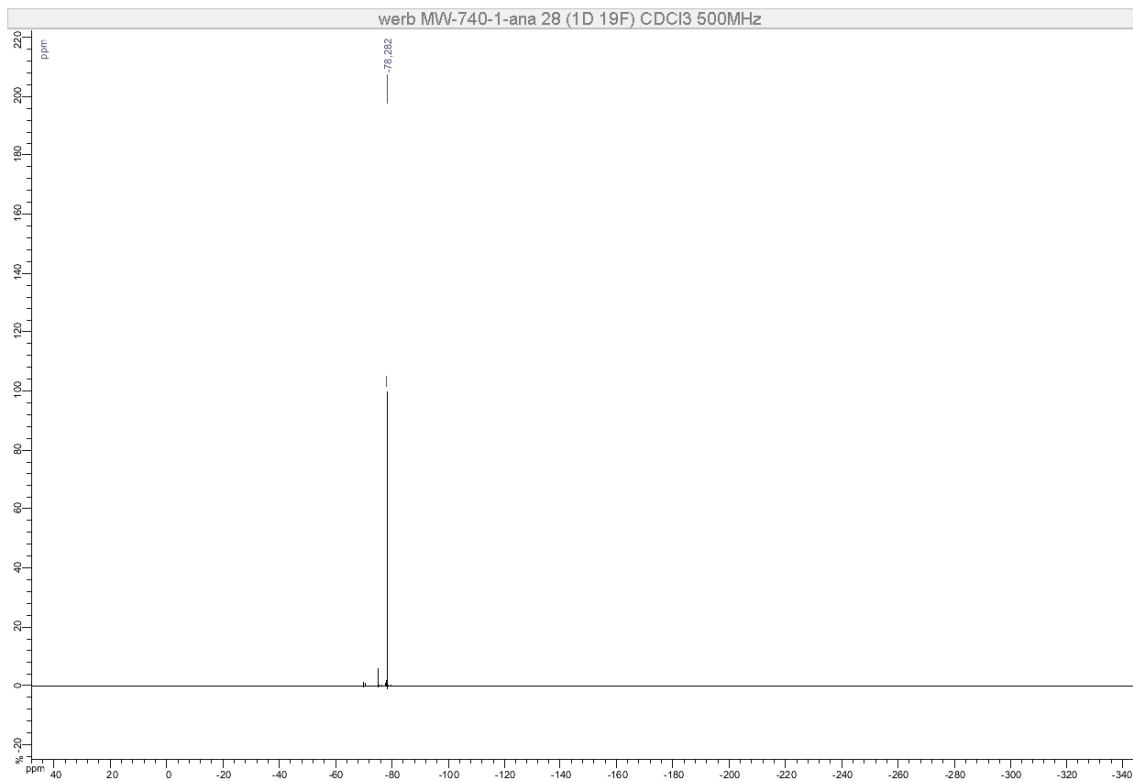
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

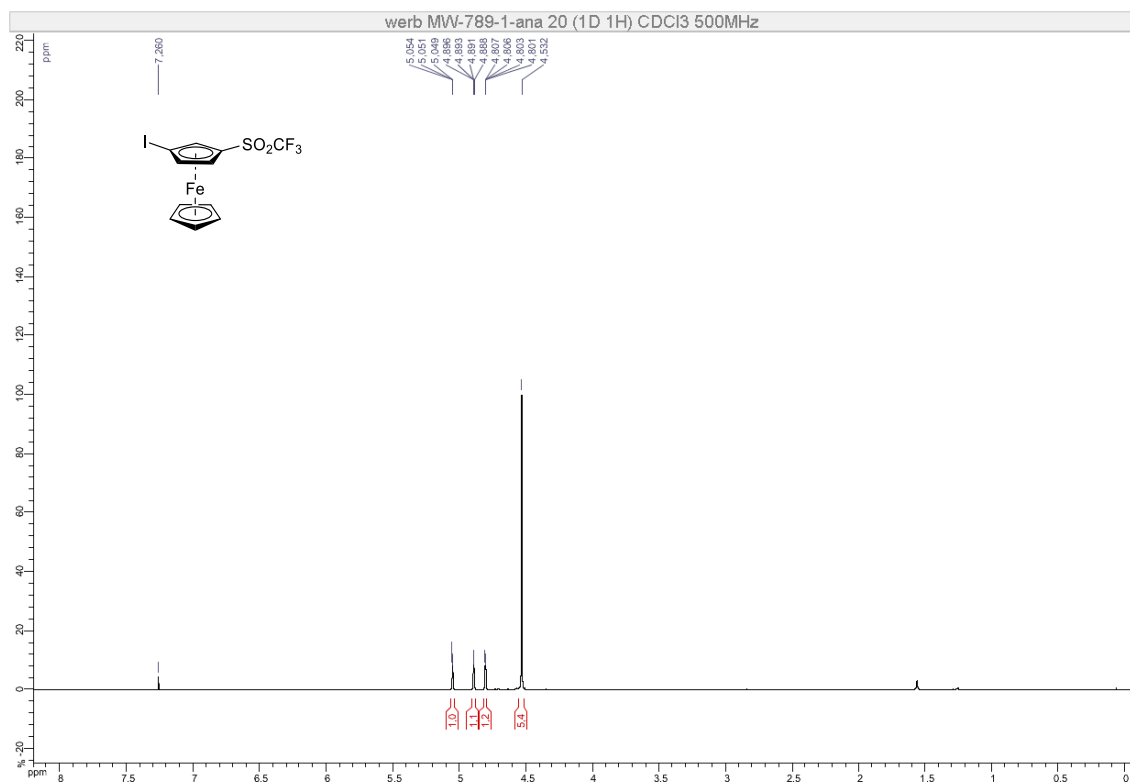


¹⁹F NMR (470 MHz, CDCl₃)

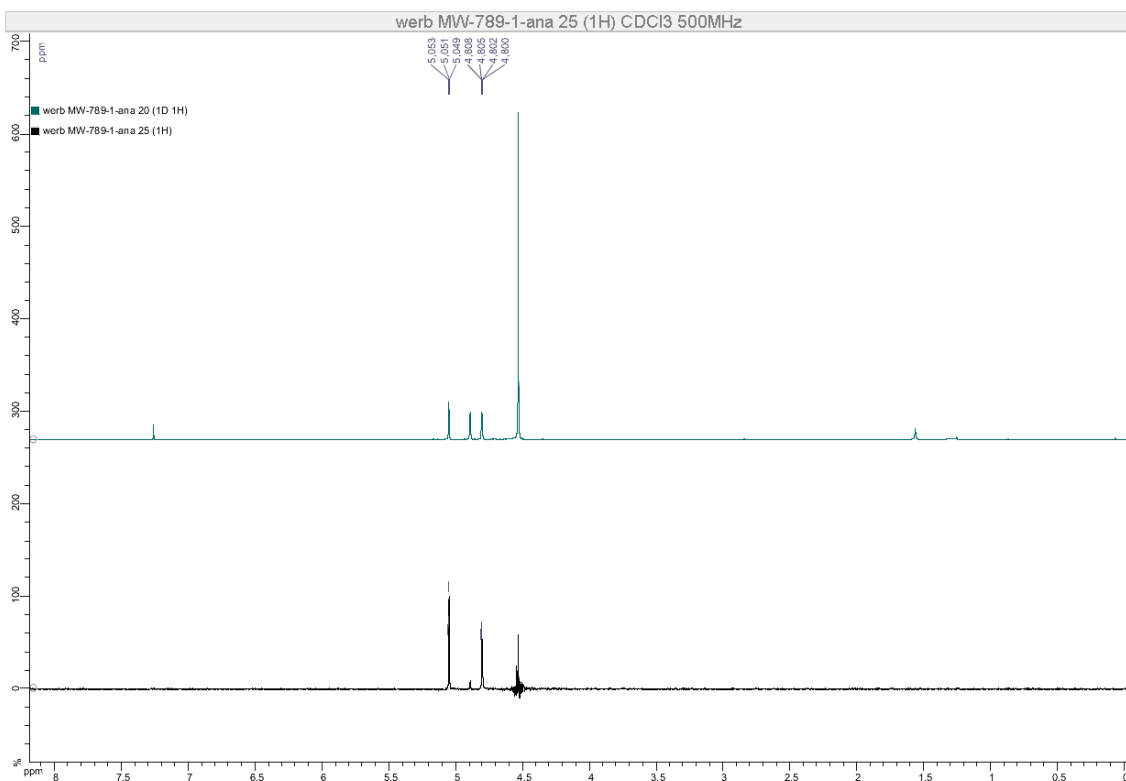


(*R_P*)-3-Iodoferrocenetriflone (*R_P*-5f)

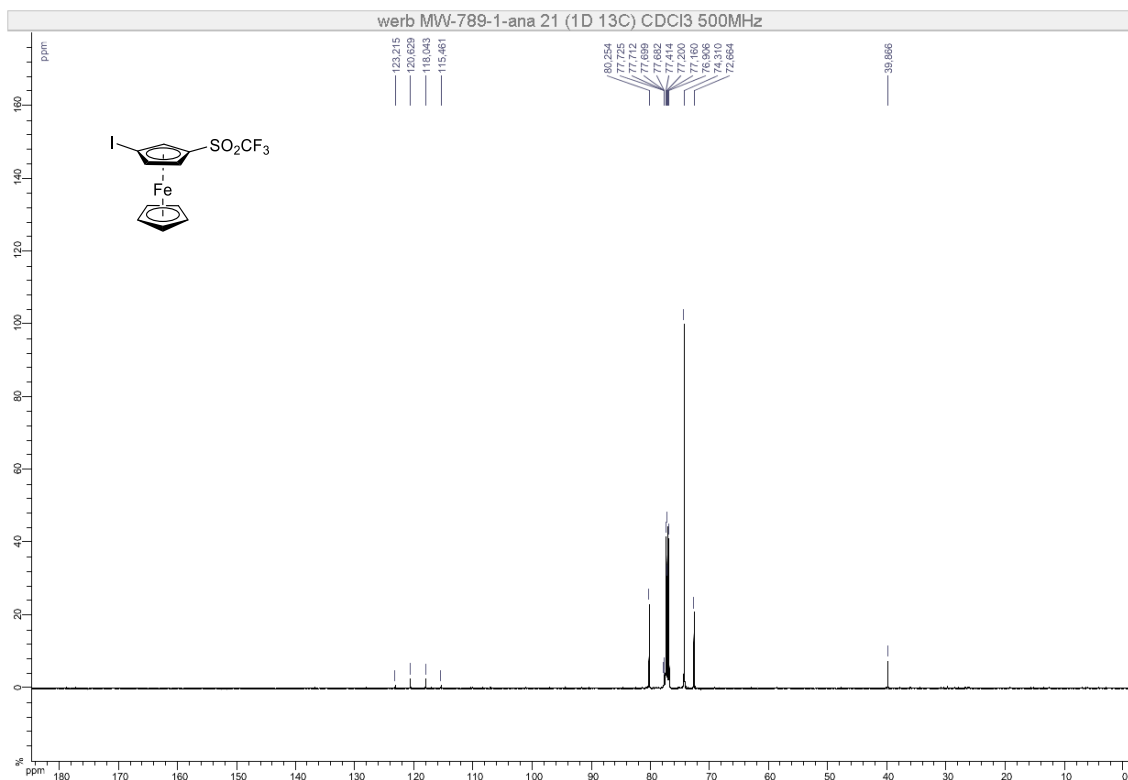
¹H NMR (500 MHz, CDCl₃)



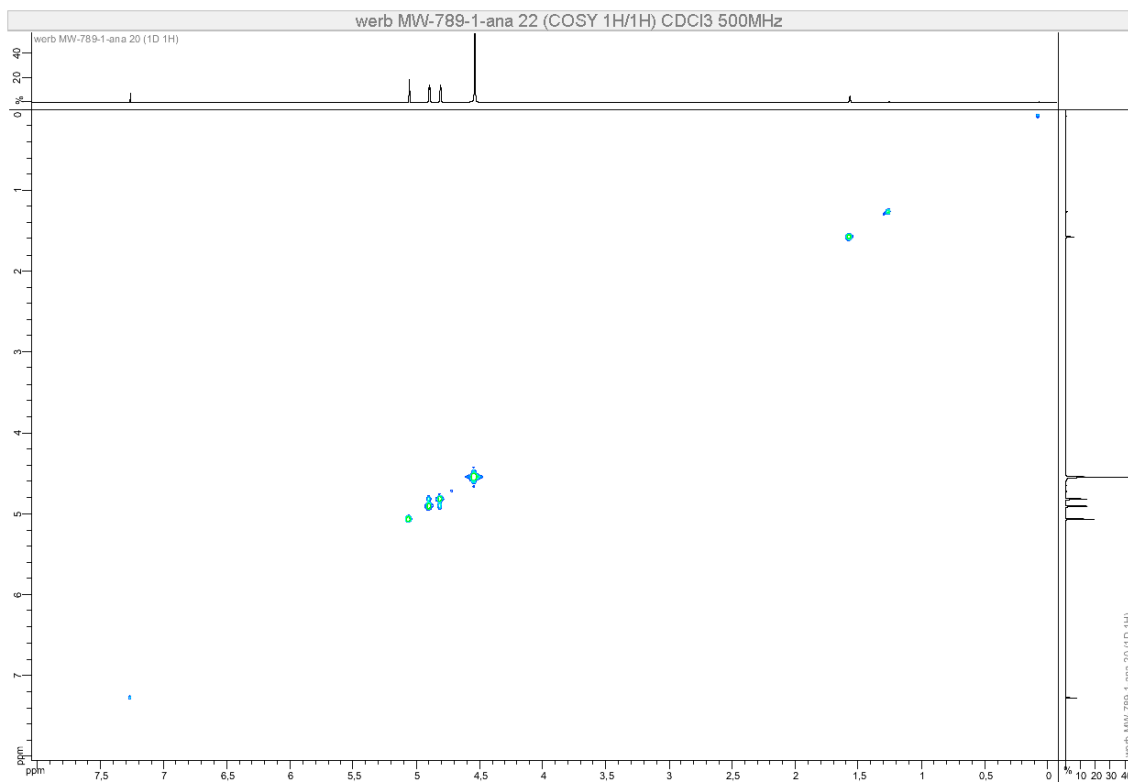
HOESY (500 MHz, CDCl₃) Irradiation at -79.1 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



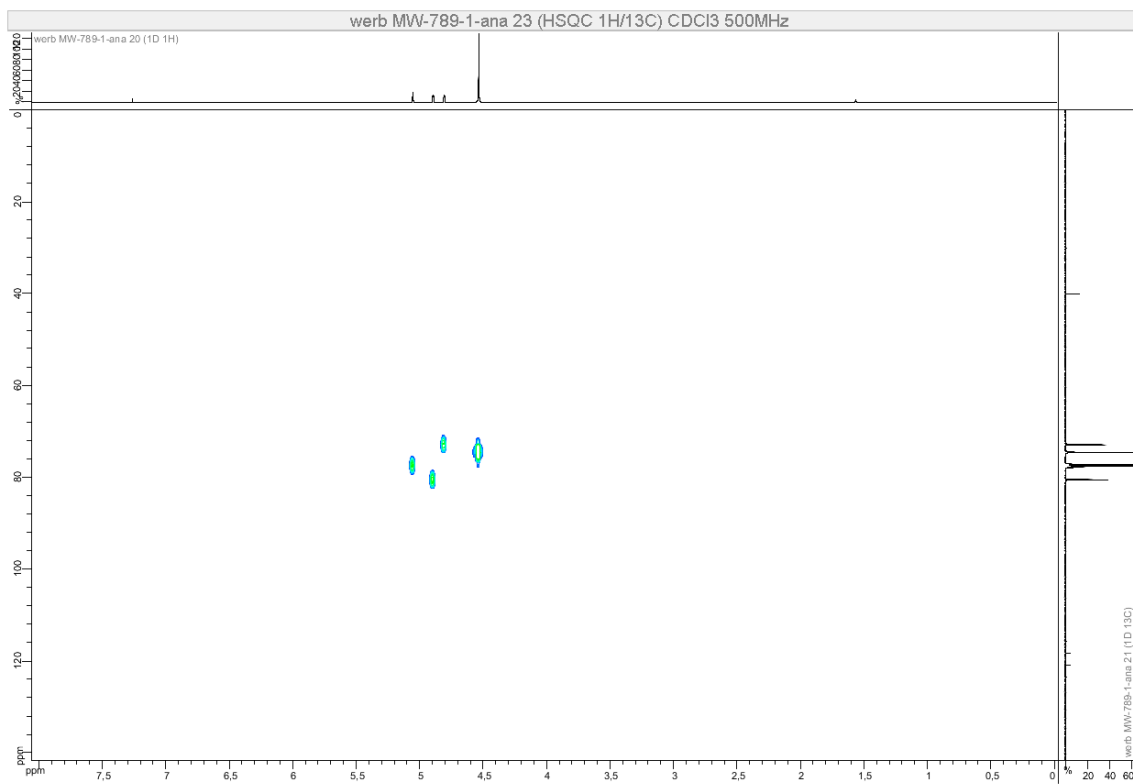
^{13}C NMR (126 MHz, CDCl_3)



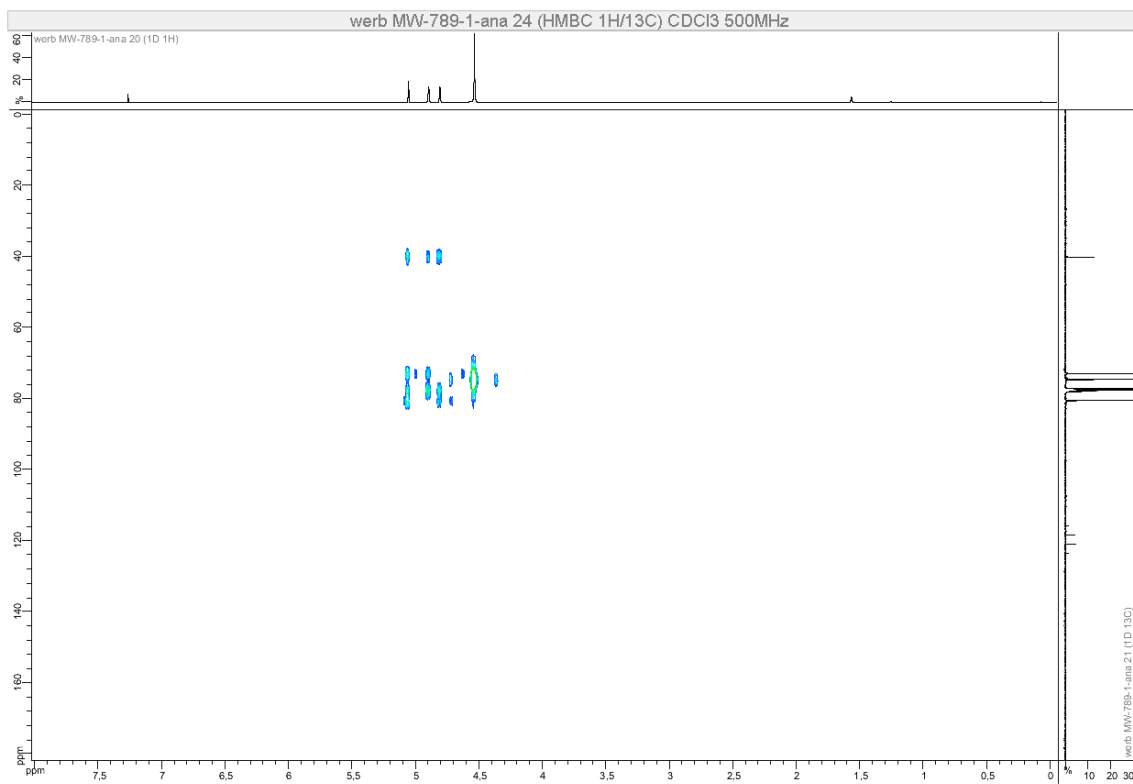
COSY (500 MHz, CDCl_3)



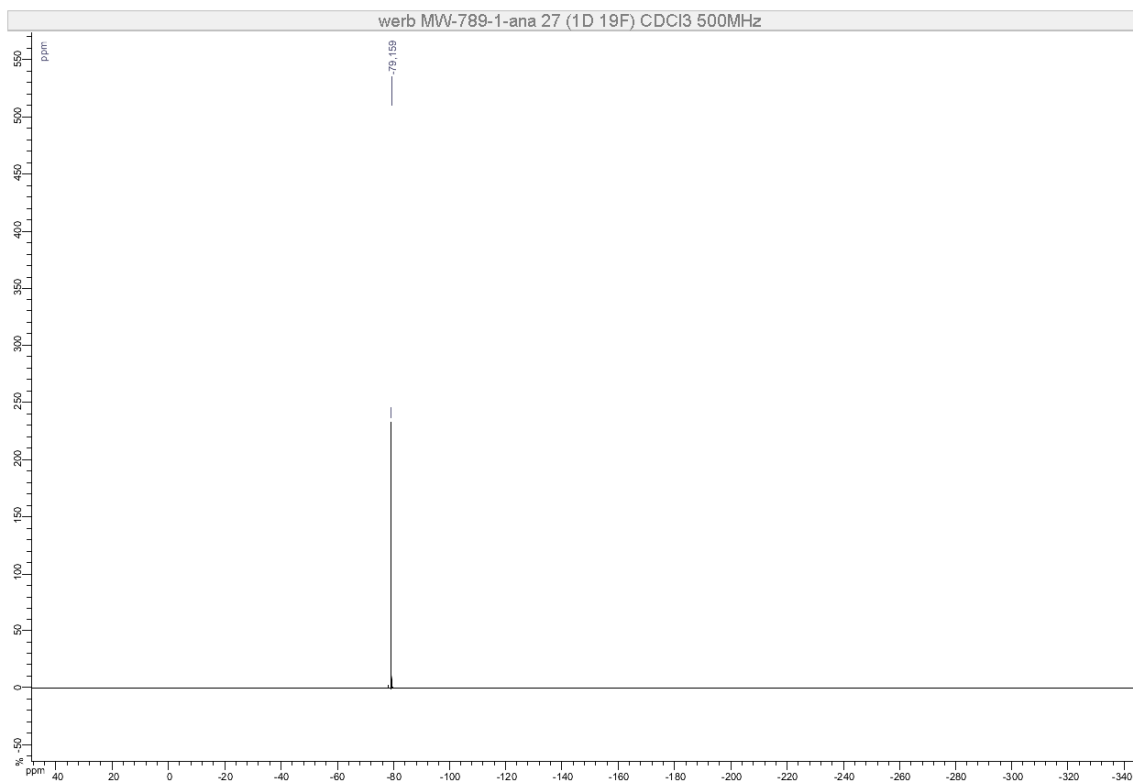
HSQC (500 MHz, CDCl₃)



HMBC (500 MHz, CDCl₃)

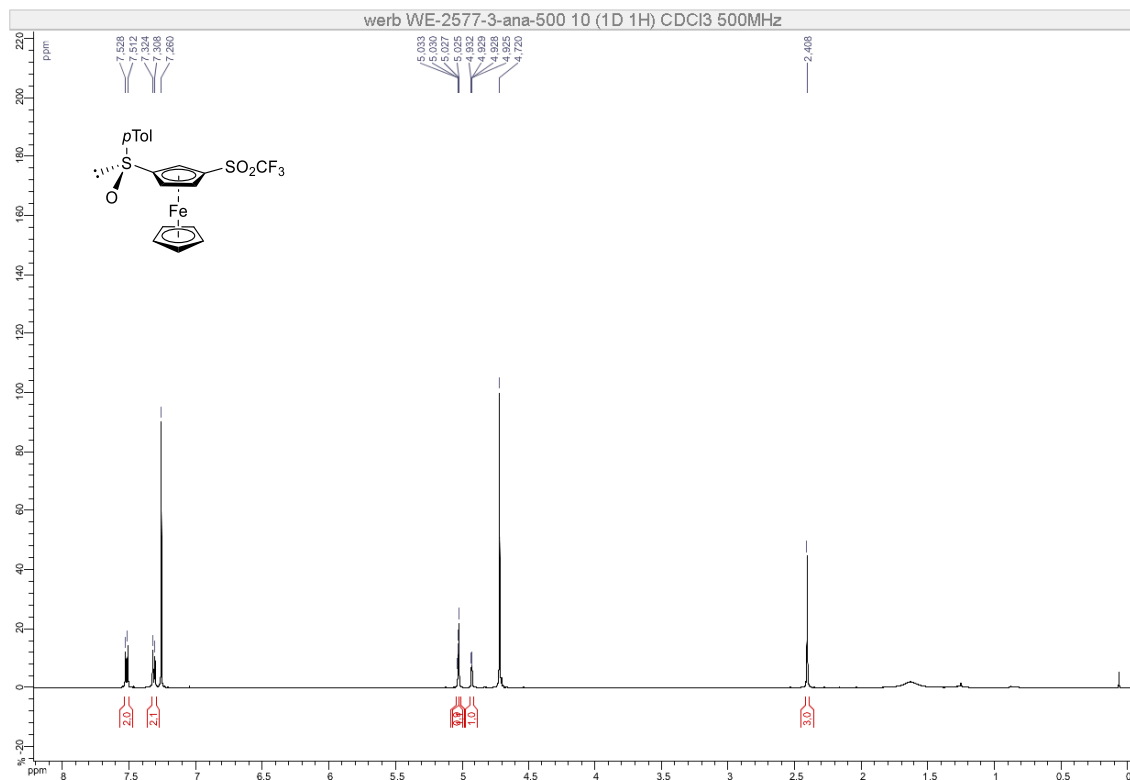


^{19}F NMR (470 MHz, CDCl_3)

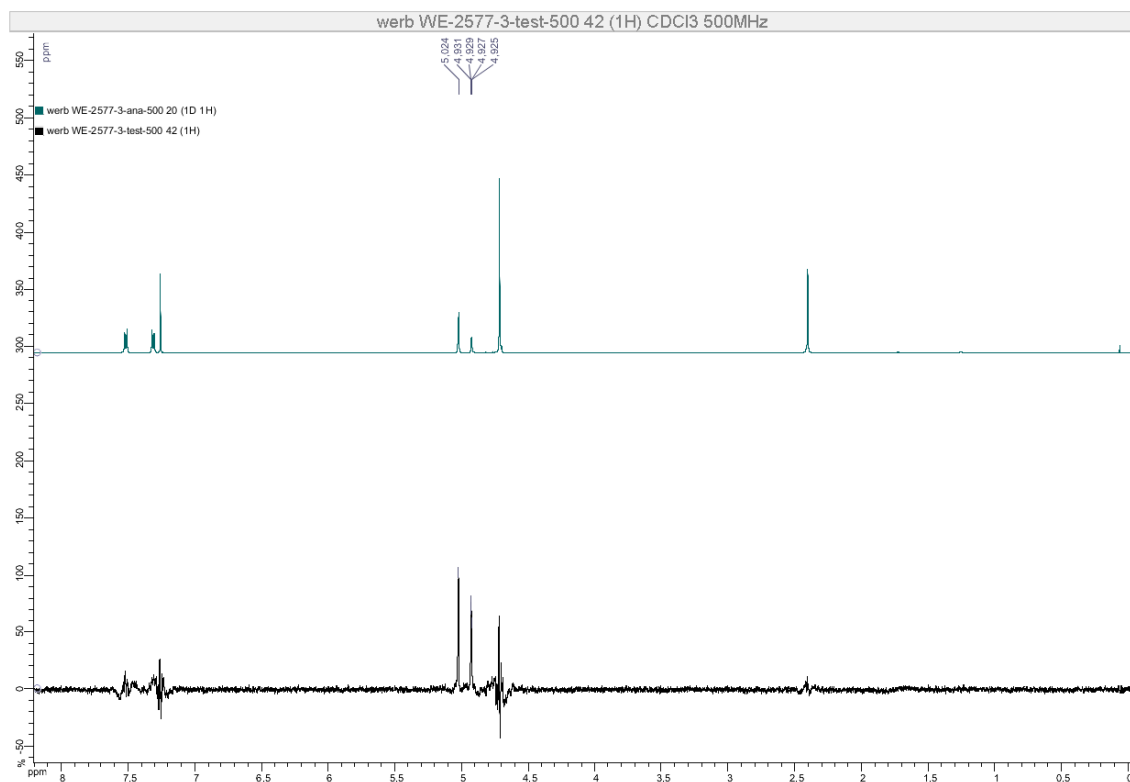


(*S,S*)-3-(4-Tolylsulfinyl)ferrocenetriflone (*S*_P-5k)

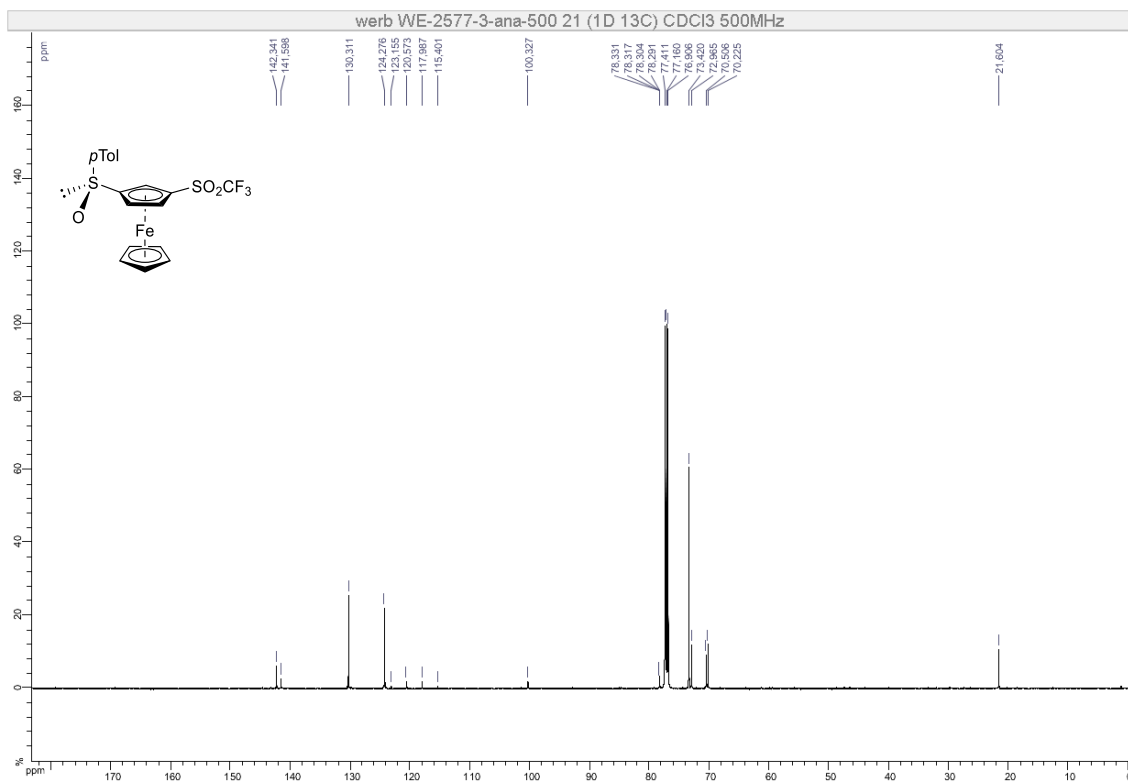
¹H NMR (500 MHz, CDCl₃)



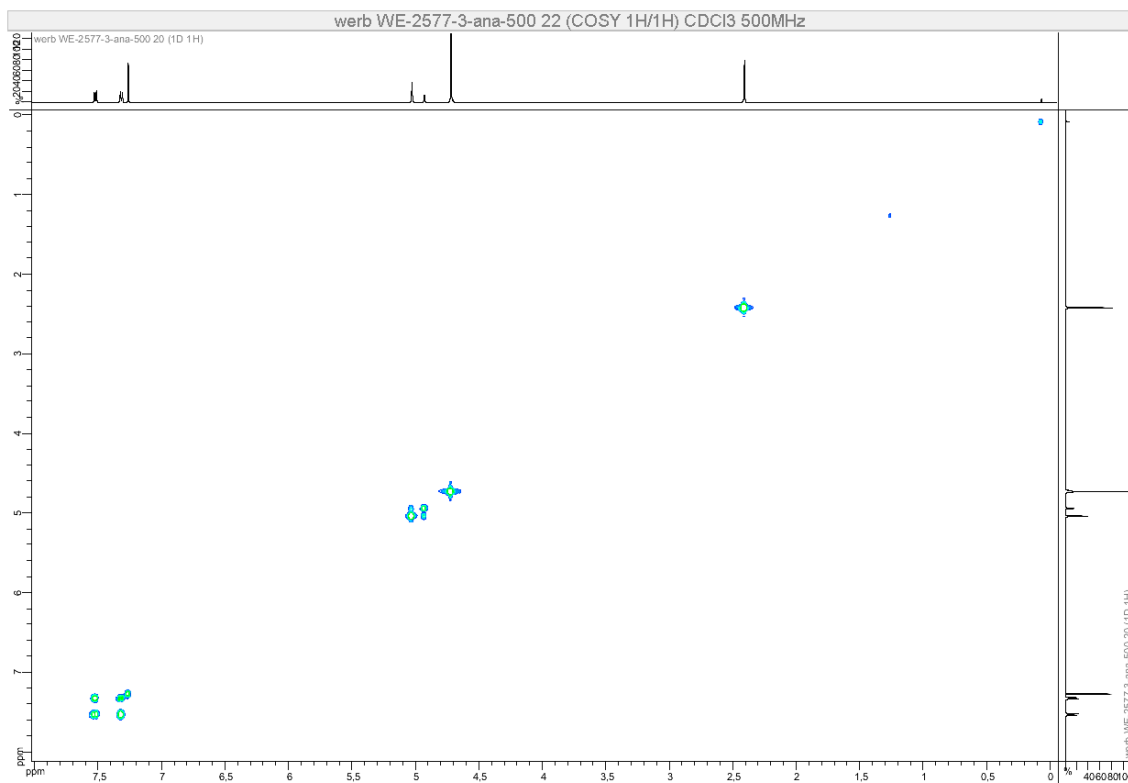
HOESY (500 MHz, CDCl₃) Irradiation at -78.9 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



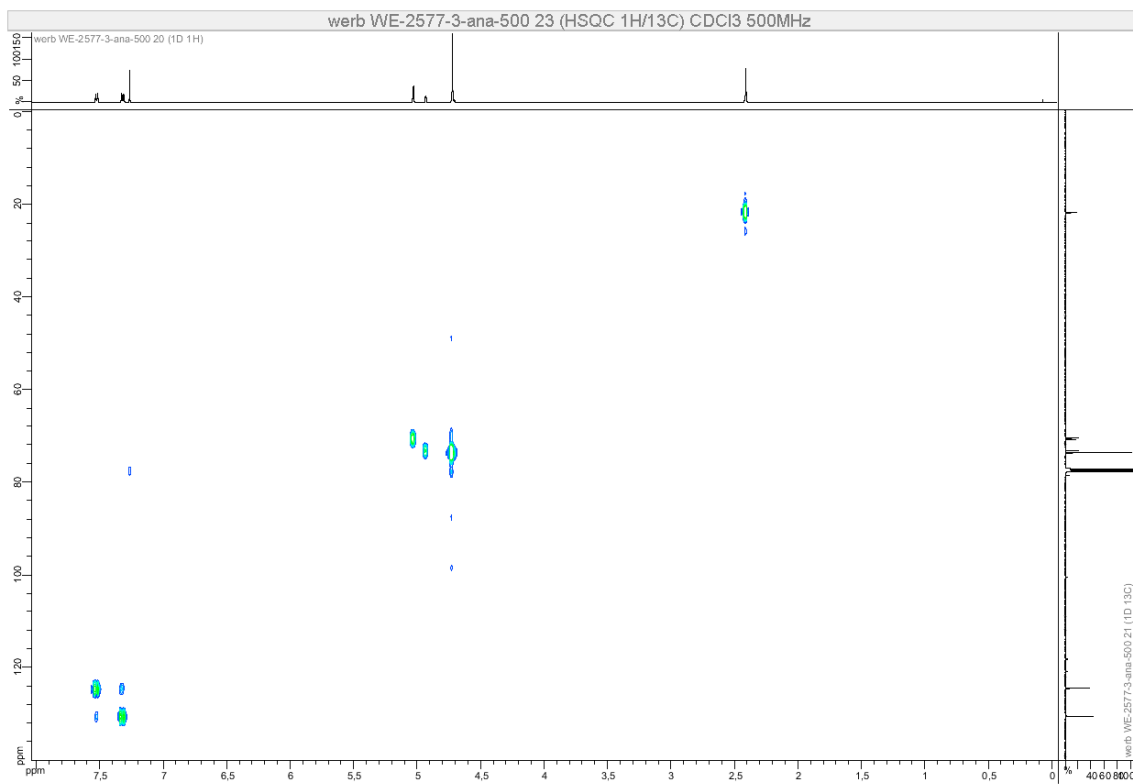
^{13}C NMR (126 MHz, CDCl_3)



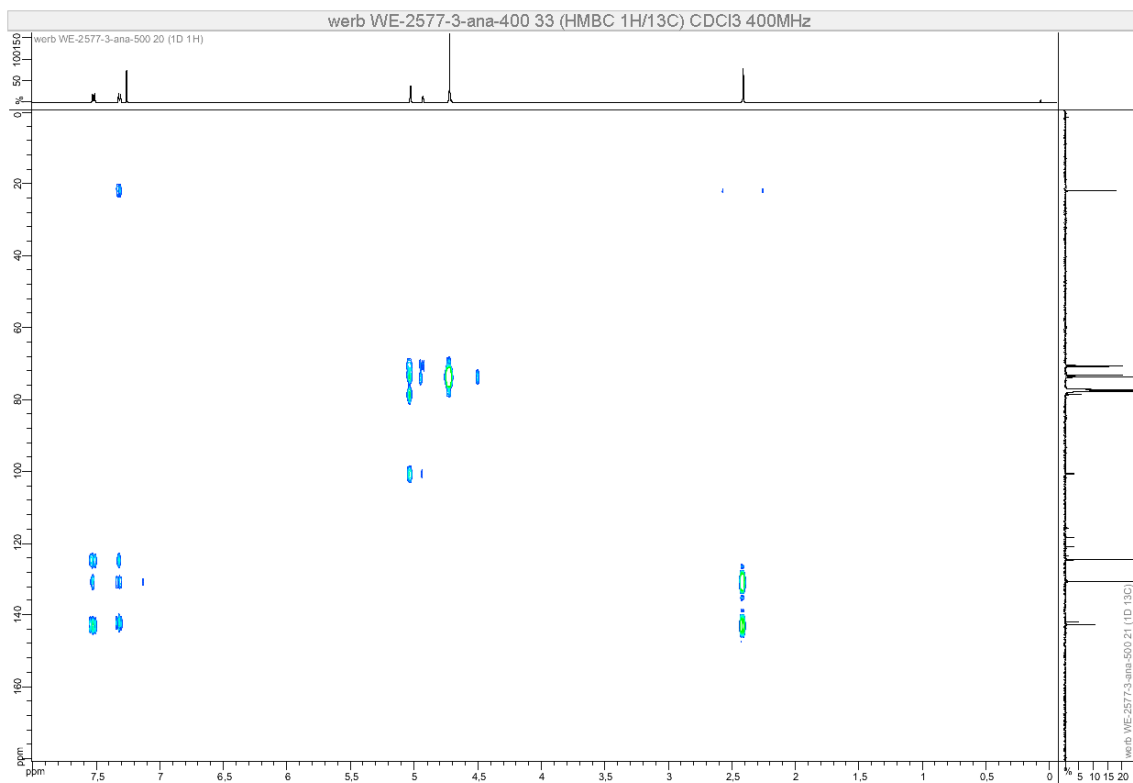
COSY (500 MHz, CDCl_3)



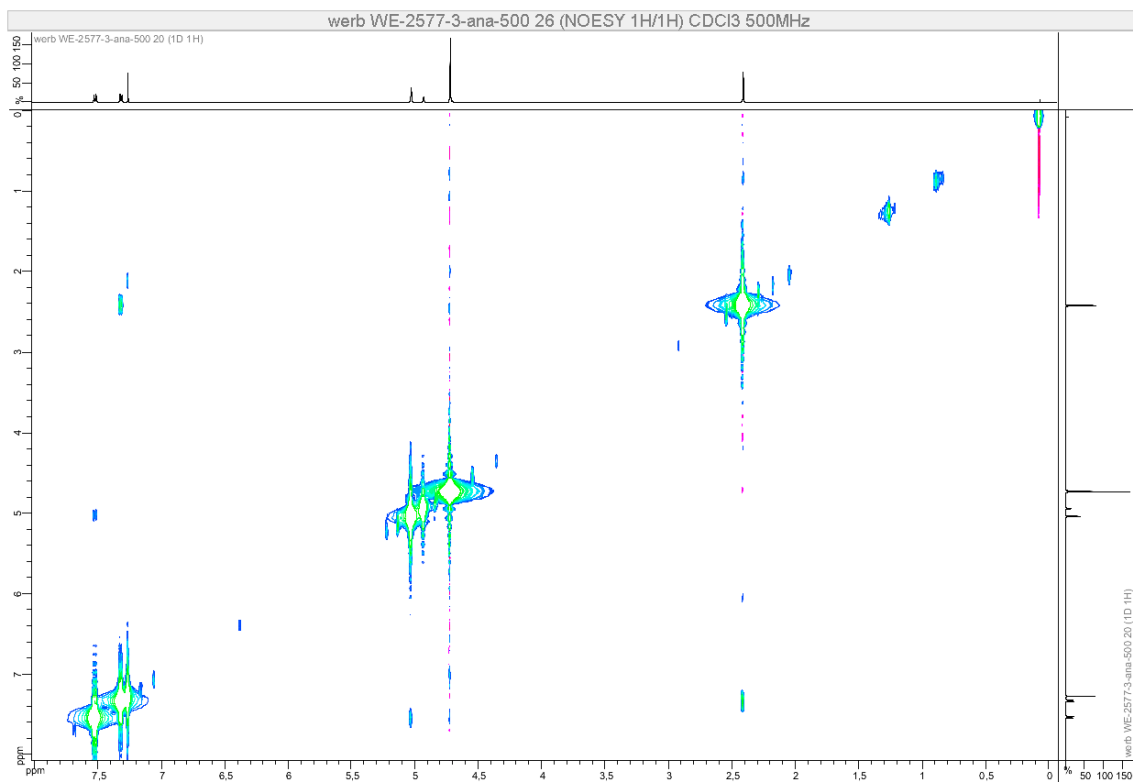
HSQC (500 MHz, CDCl₃)



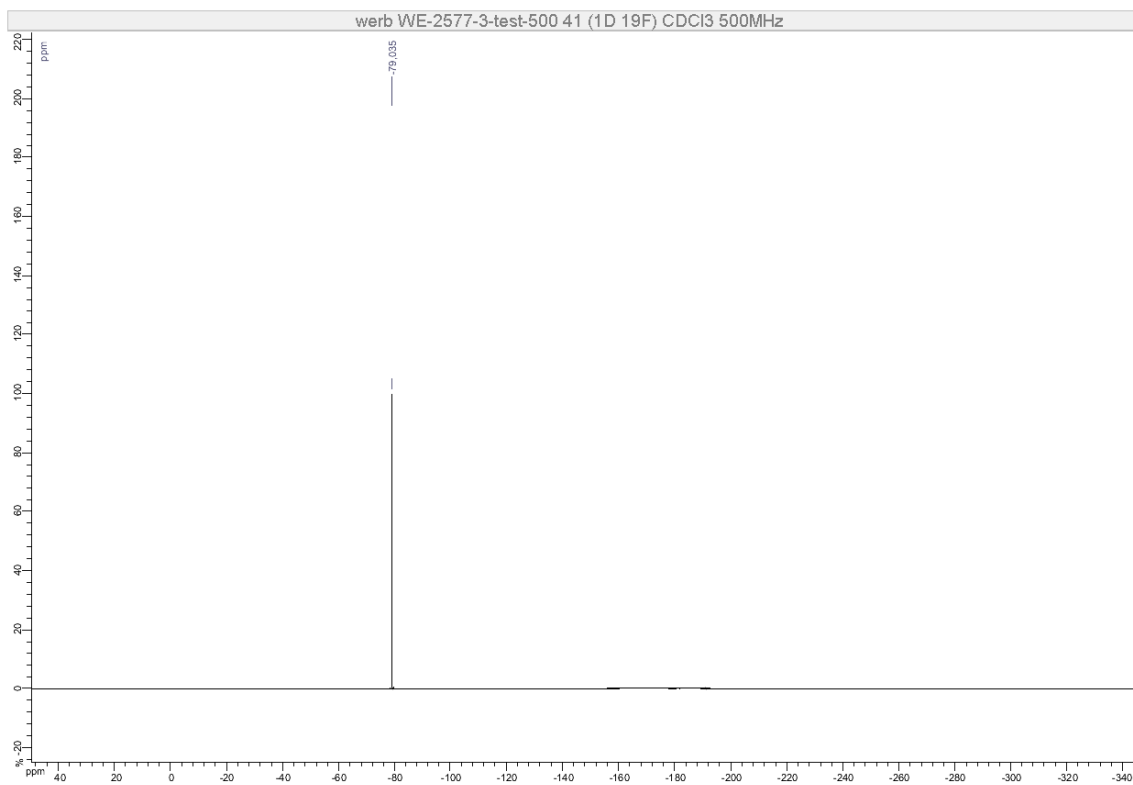
HMBC (400 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

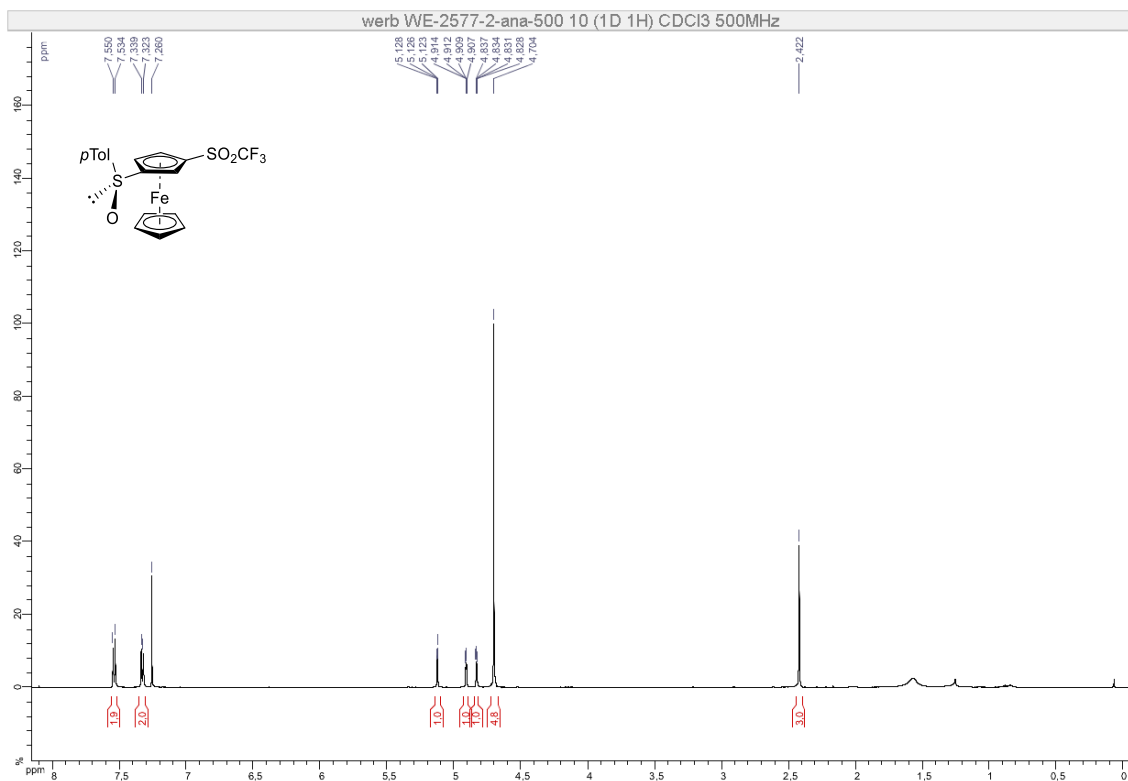


¹⁹F NMR (470 MHz, CDCl₃)

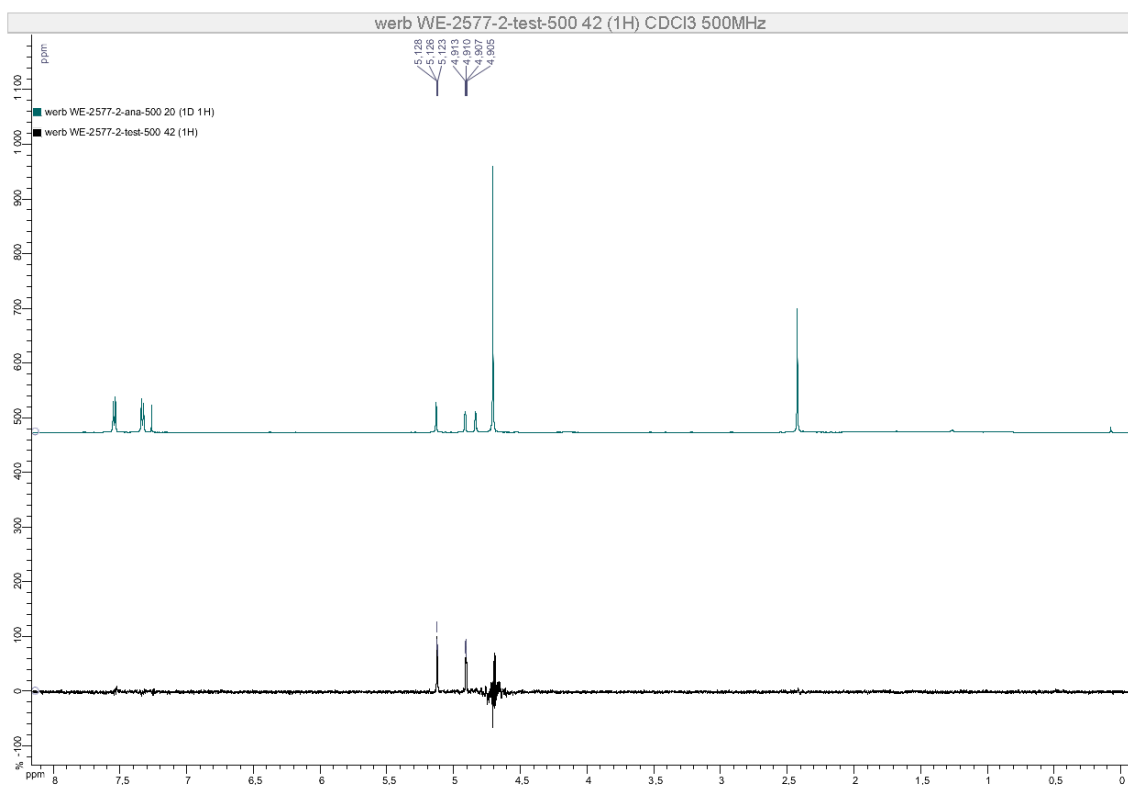


(*S,R*)-3-(4-Tolylsulfinyl)ferrocenetriflone (*R*_P-5k)

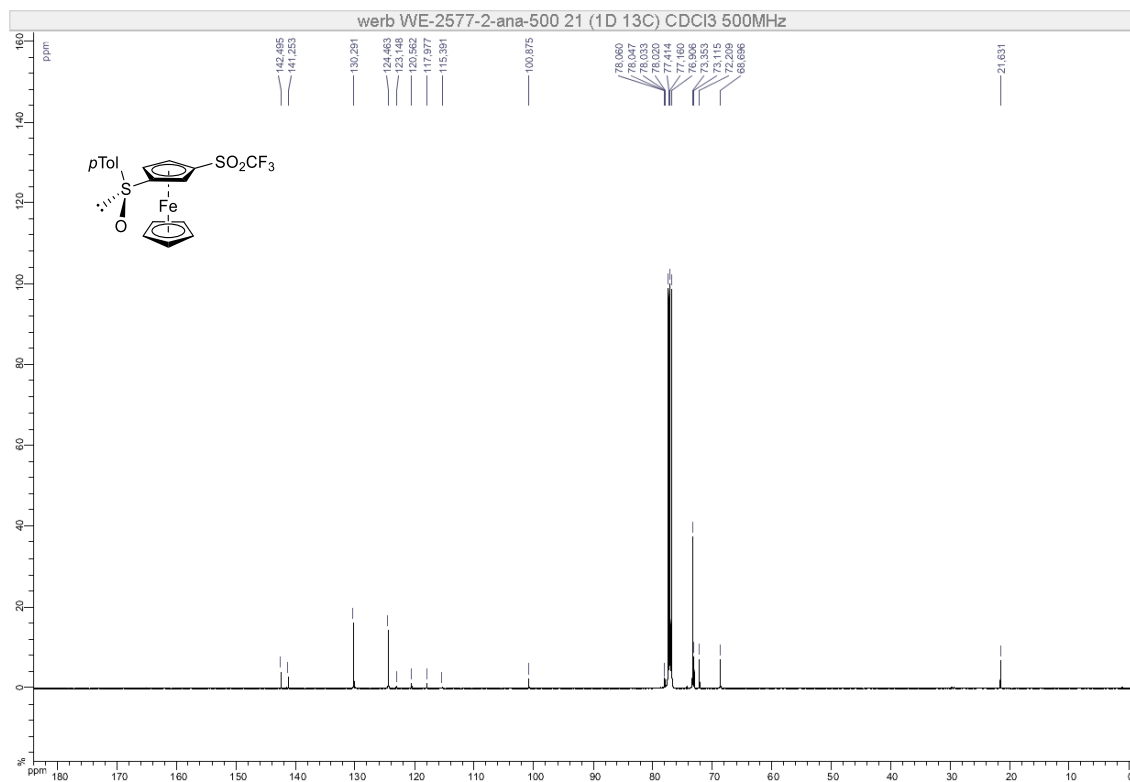
¹H NMR (500 MHz, CDCl₃)



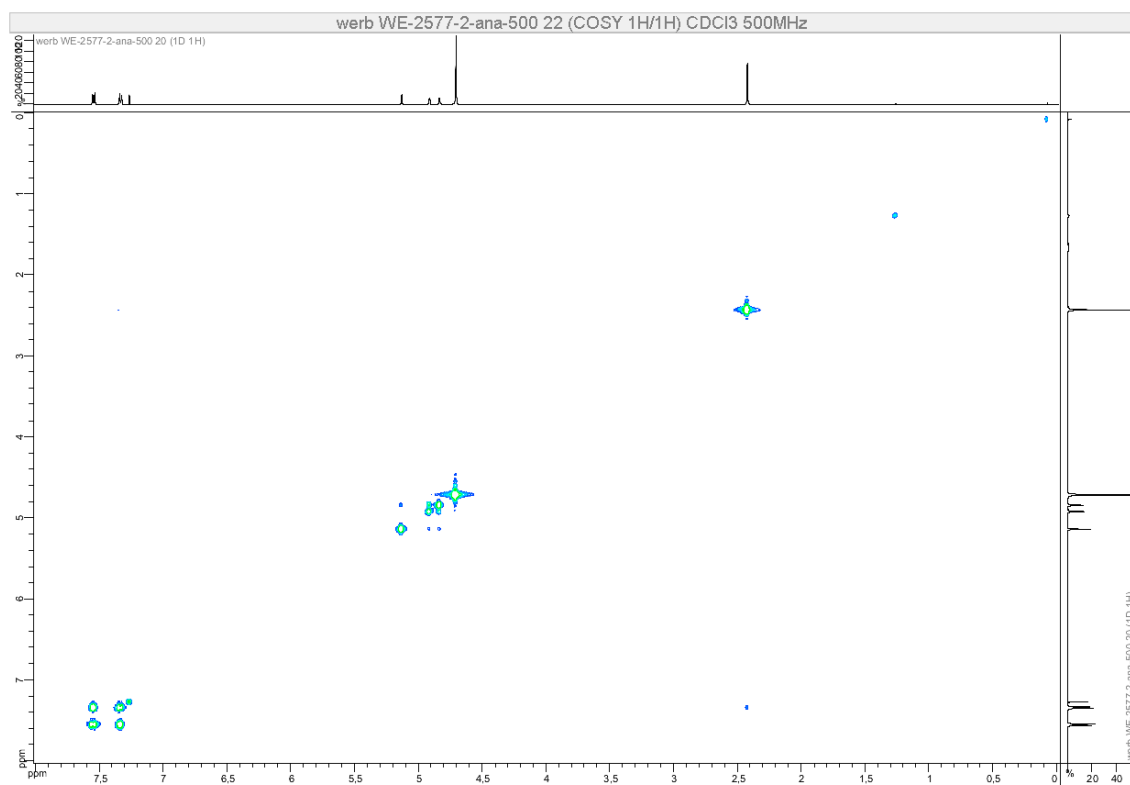
HOESY (500 MHz, CDCl₃) Irradiation at -78.9 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



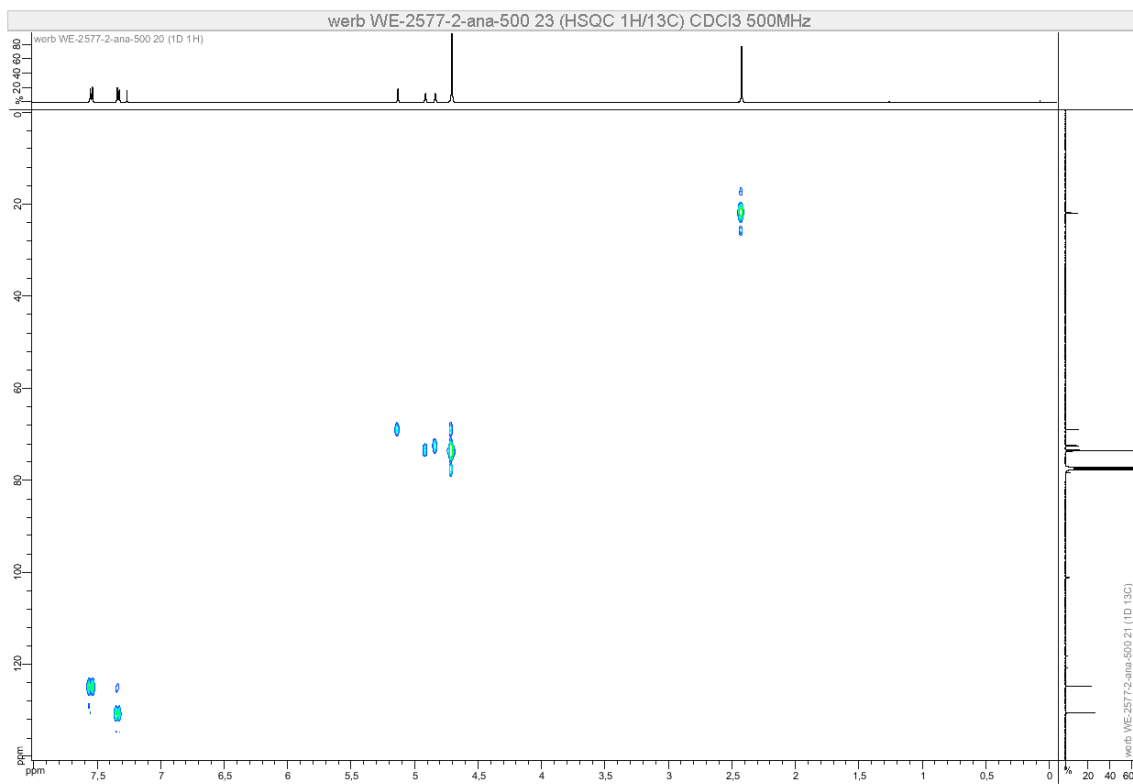
^{13}C NMR (126 MHz, CDCl_3)



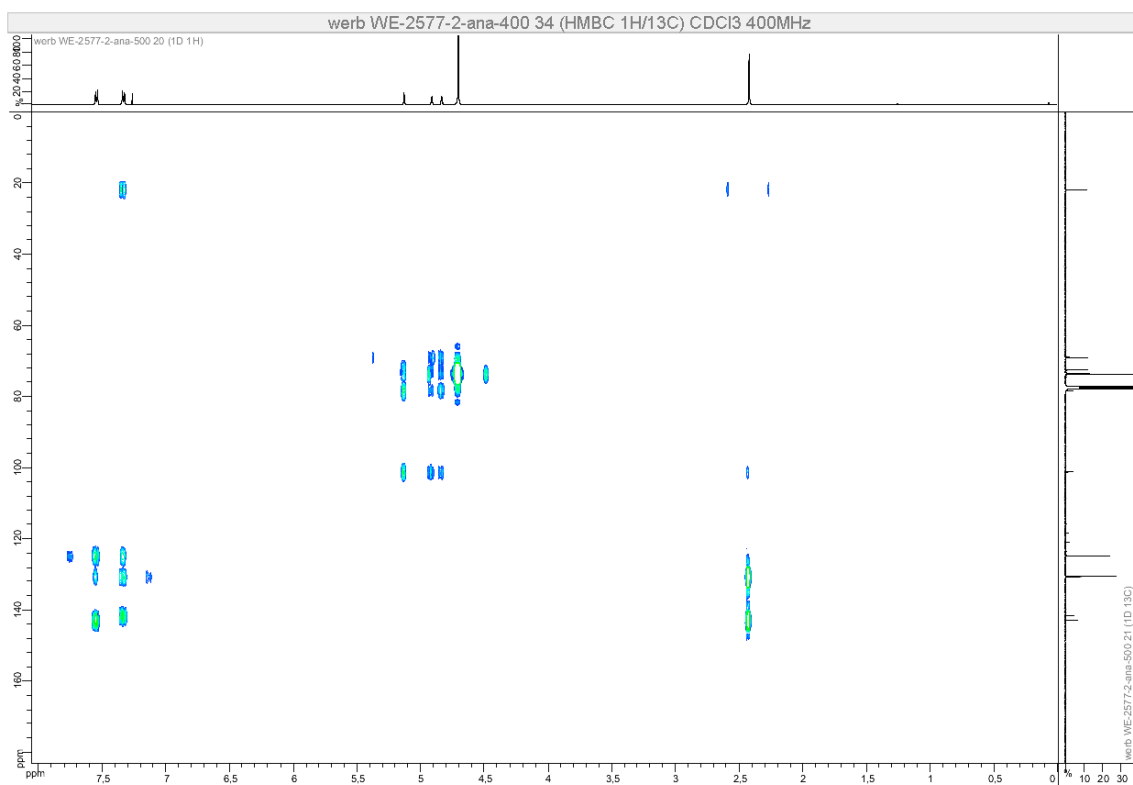
COSY (500 MHz, CDCl_3)



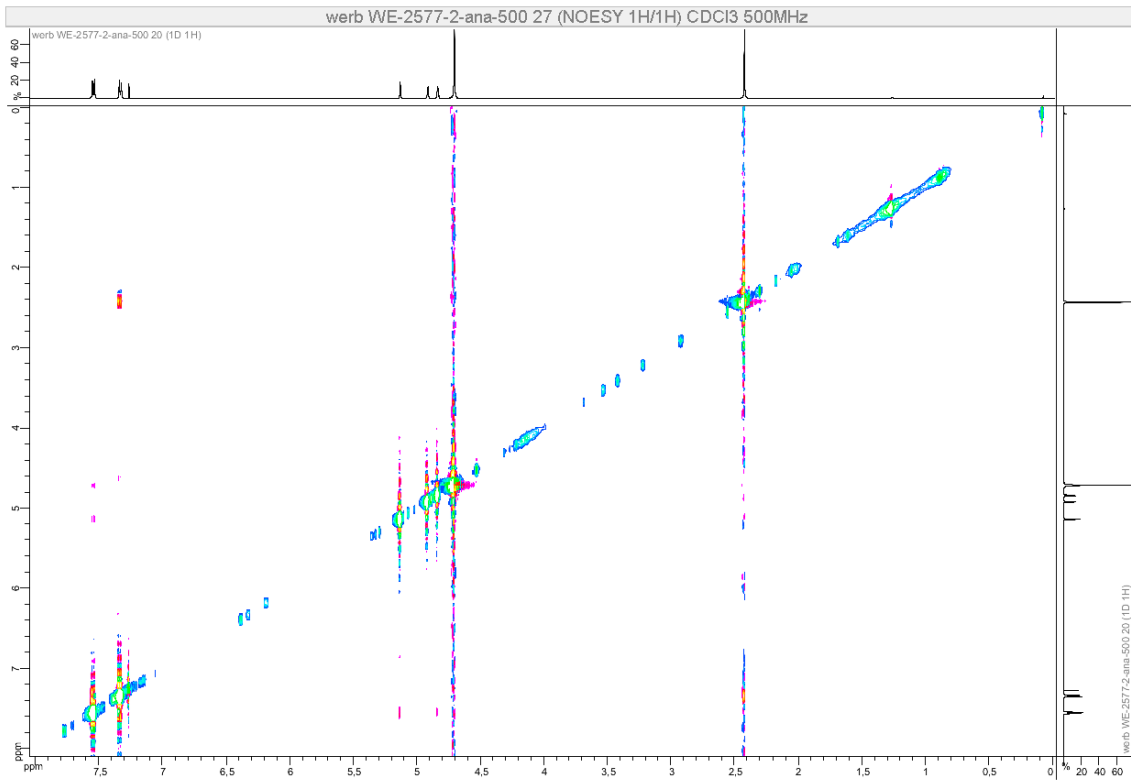
HSQC (500 MHz, CDCl₃)



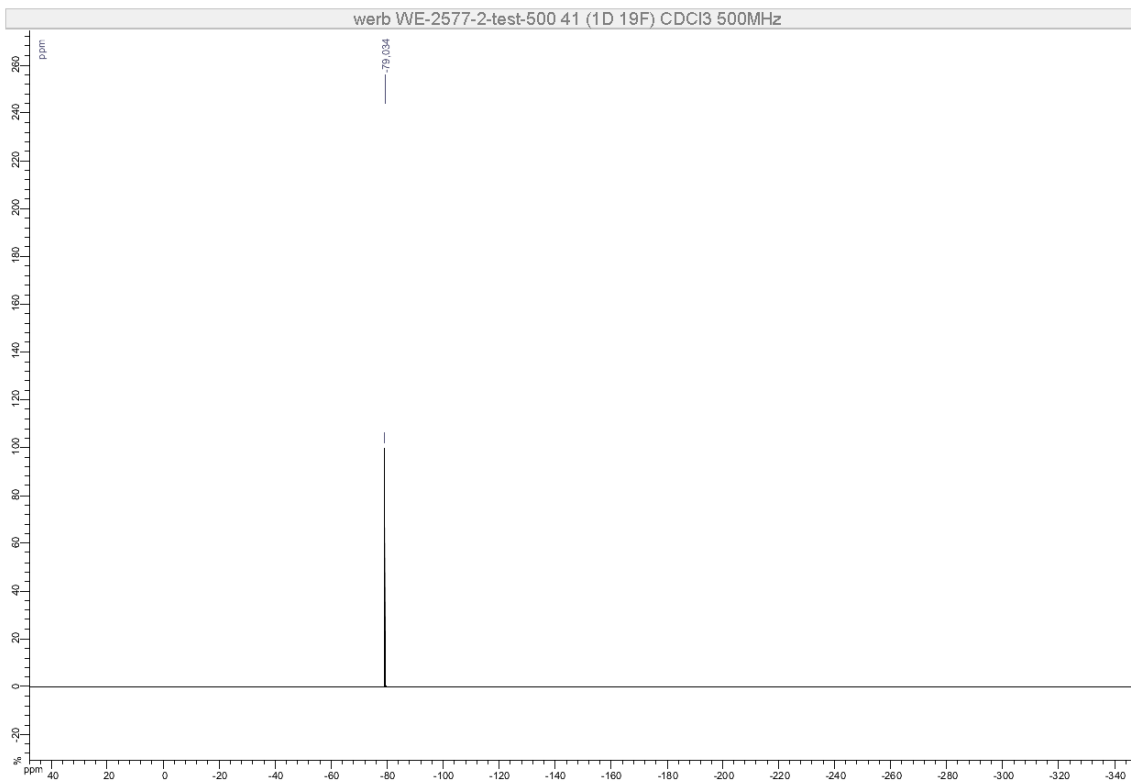
HMBC (400 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

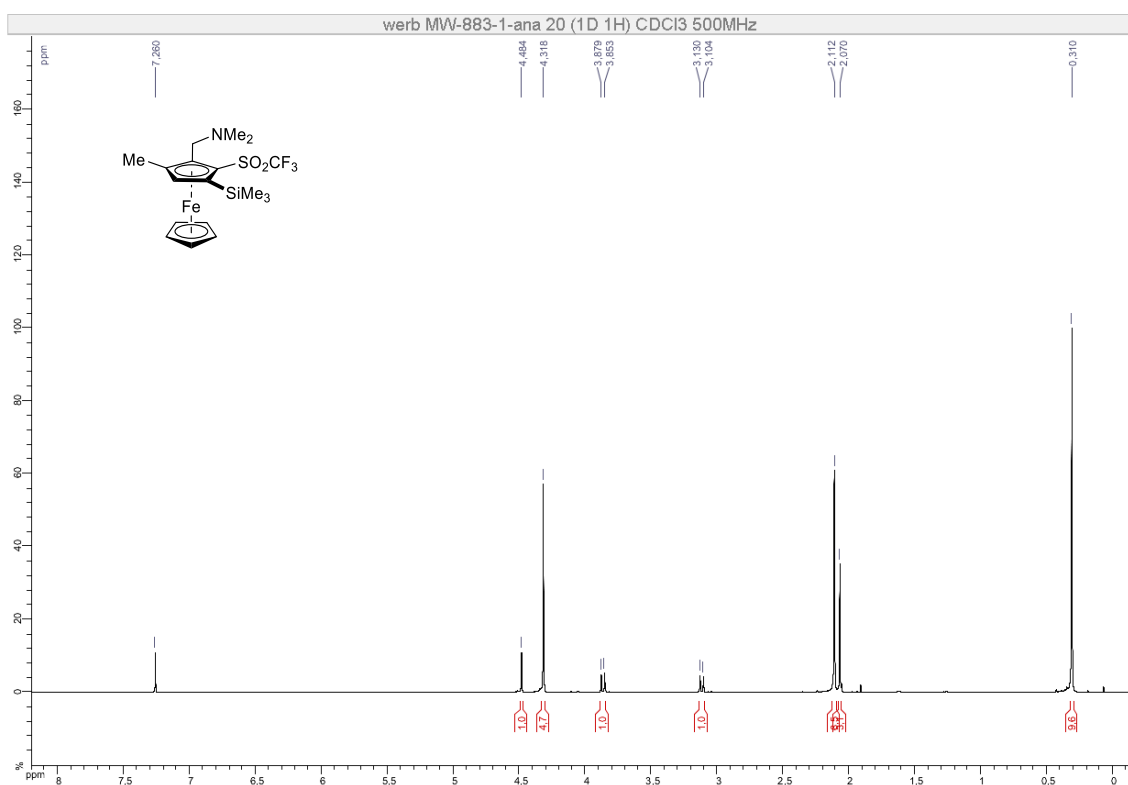


¹⁹F NMR (470 MHz, CDCl₃)

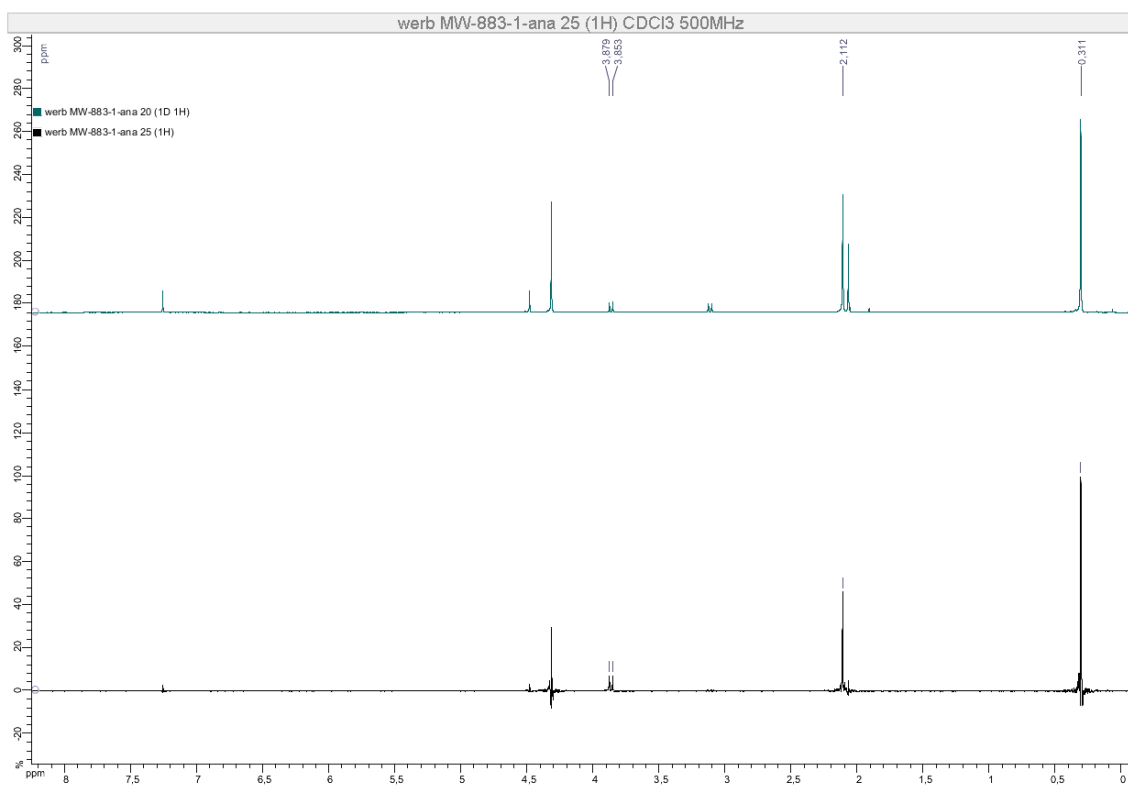


(*R_P*)-2-(Dimethylaminomethyl)-3-methyl-5-(trimethylsilyl)ferrocenetriflone (*R_P*-6)

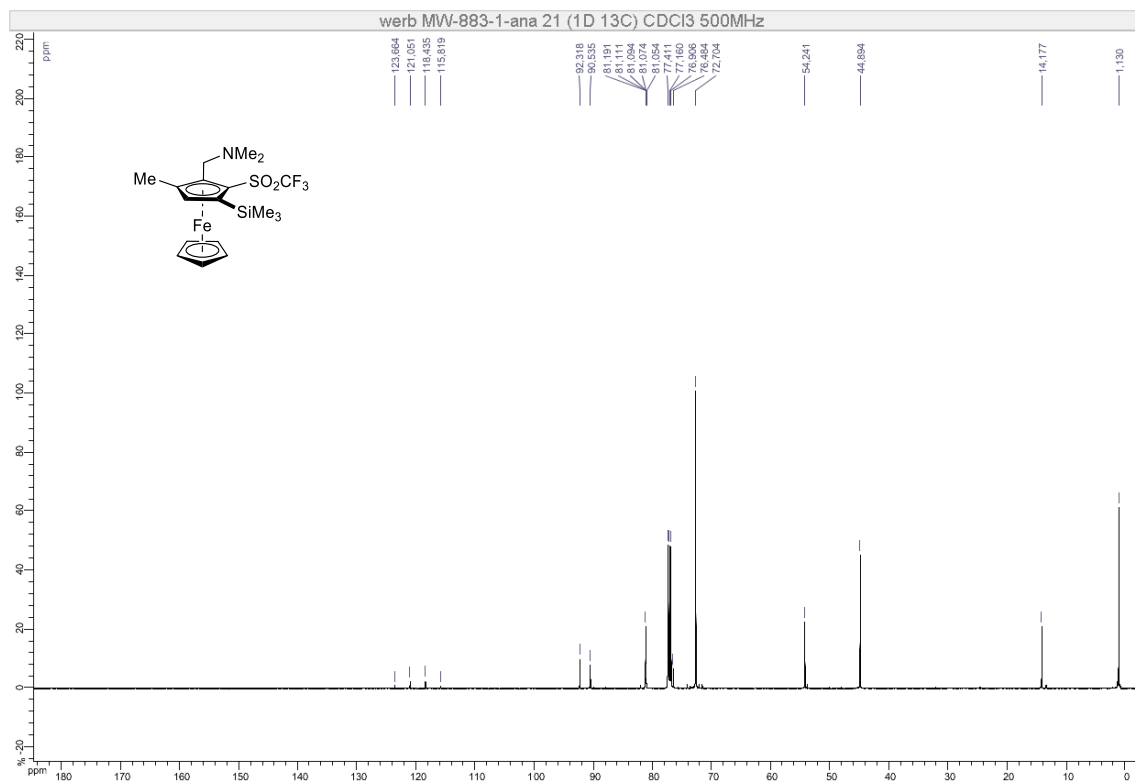
¹H NMR (500 MHz, CDCl₃)



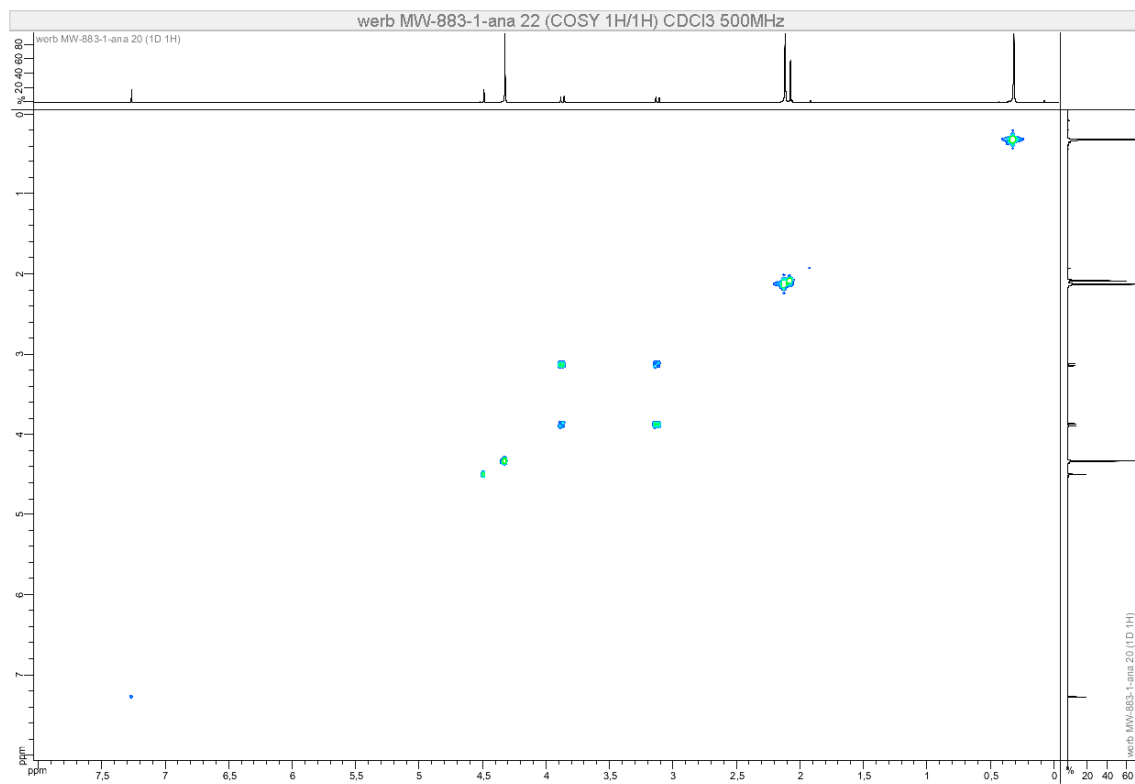
HOESY (500 MHz, CDCl₃) Irradiation at -72.8 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



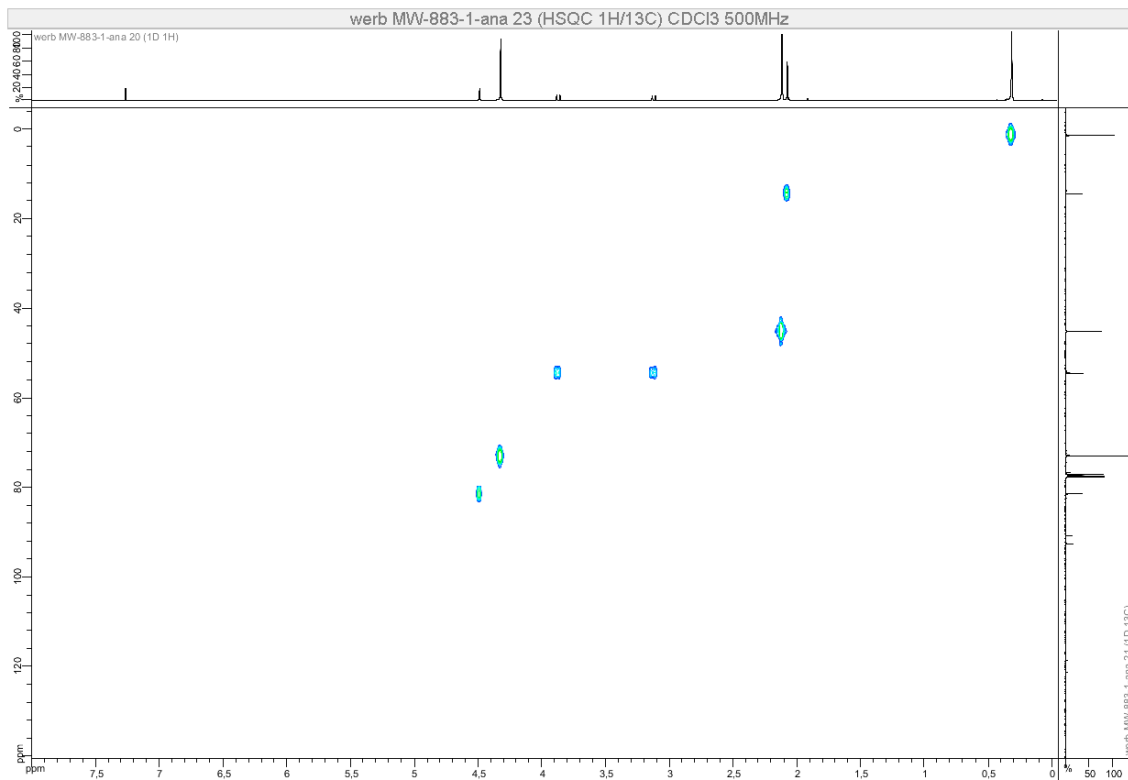
^{13}C NMR (126 MHz, CDCl_3)



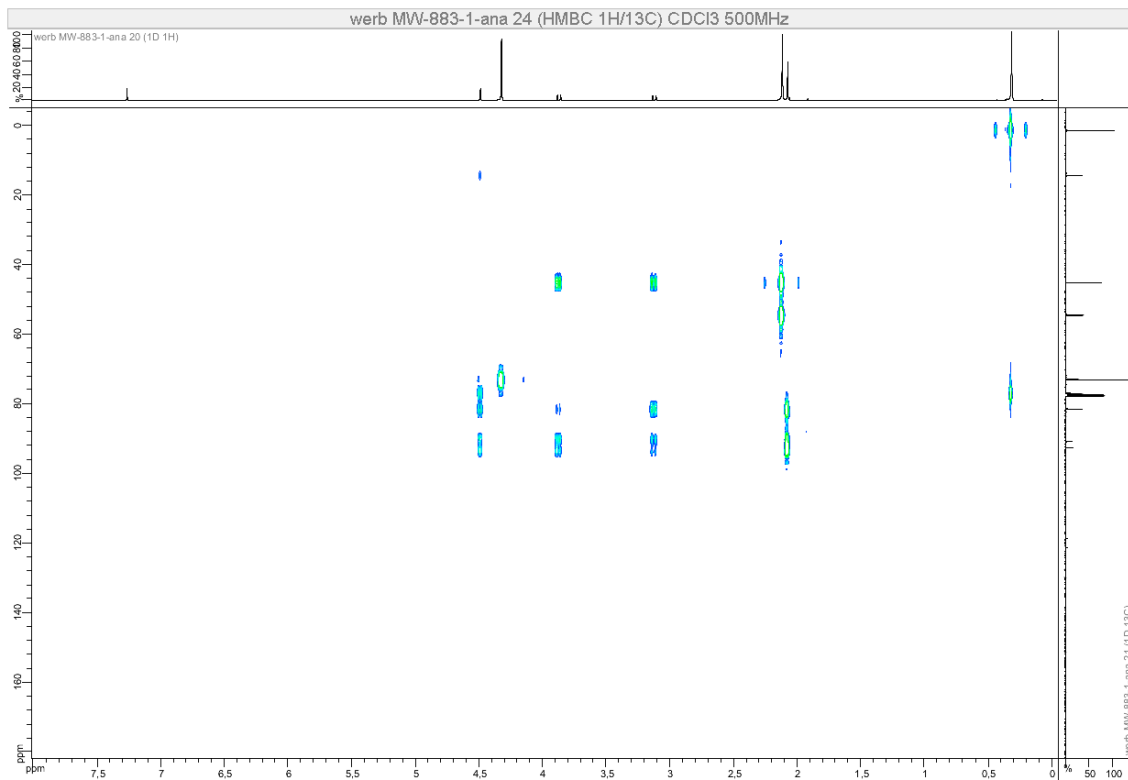
COSY (500 MHz, CDCl_3)



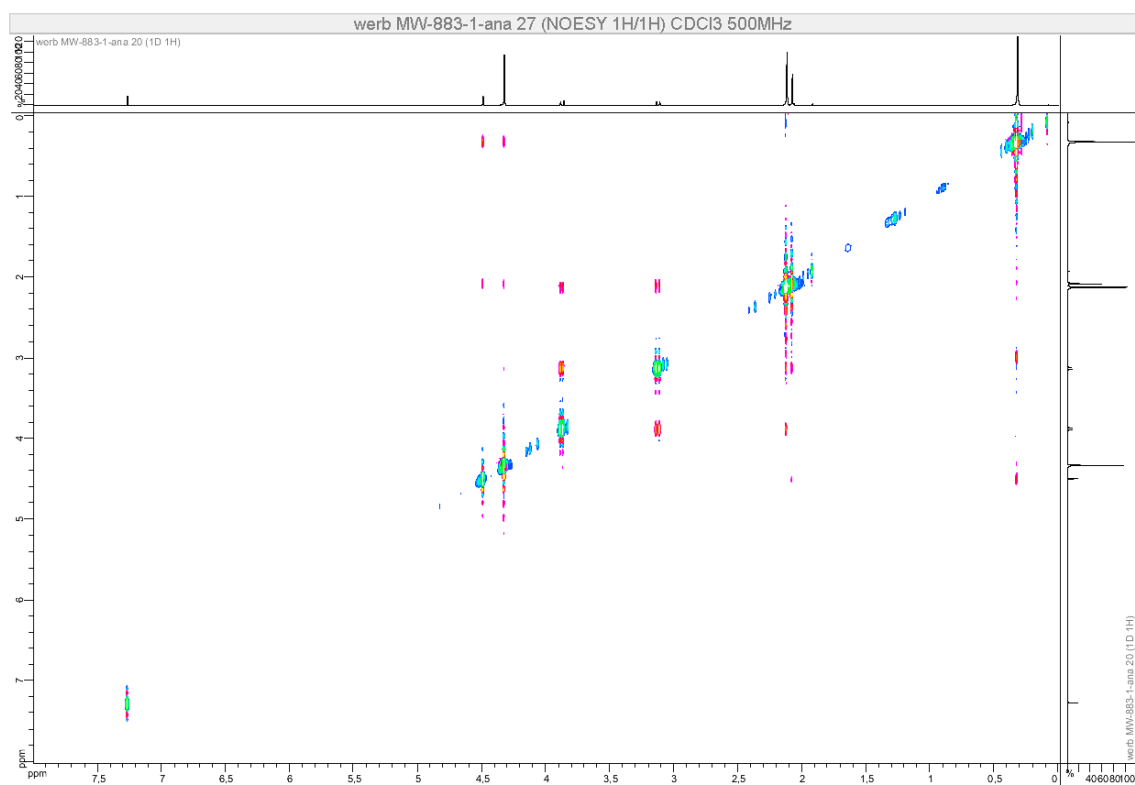
HSQC (500 MHz, CDCl₃)



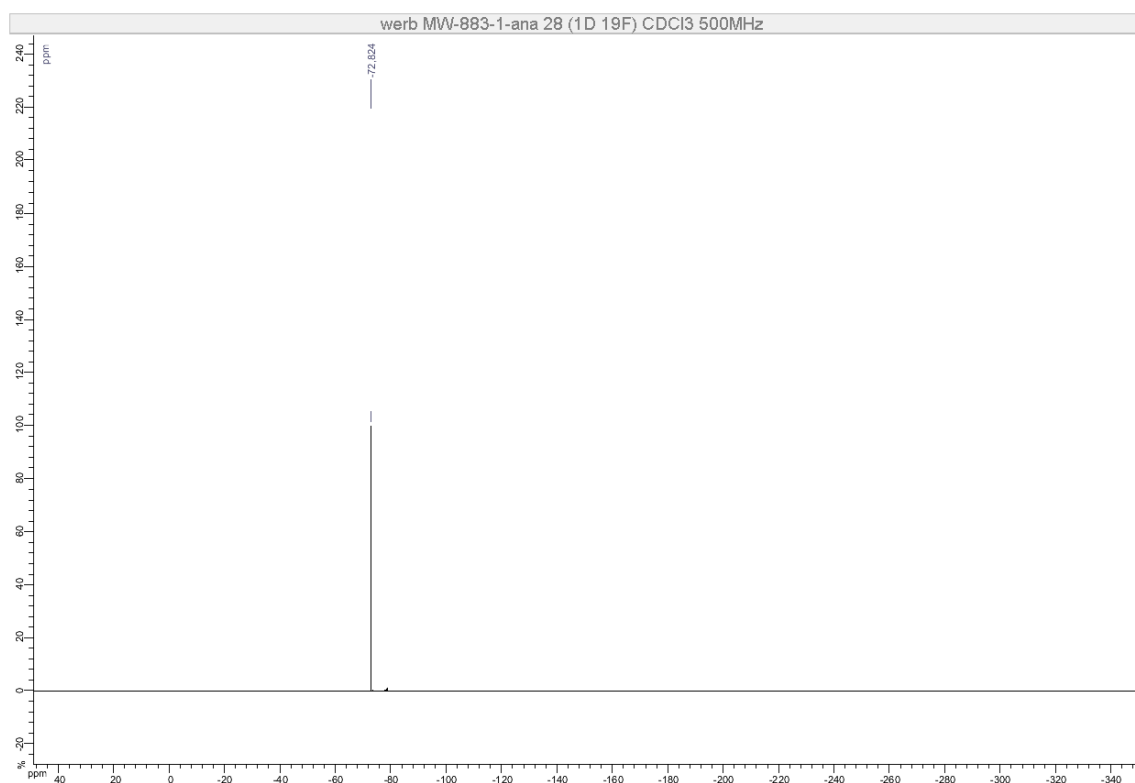
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

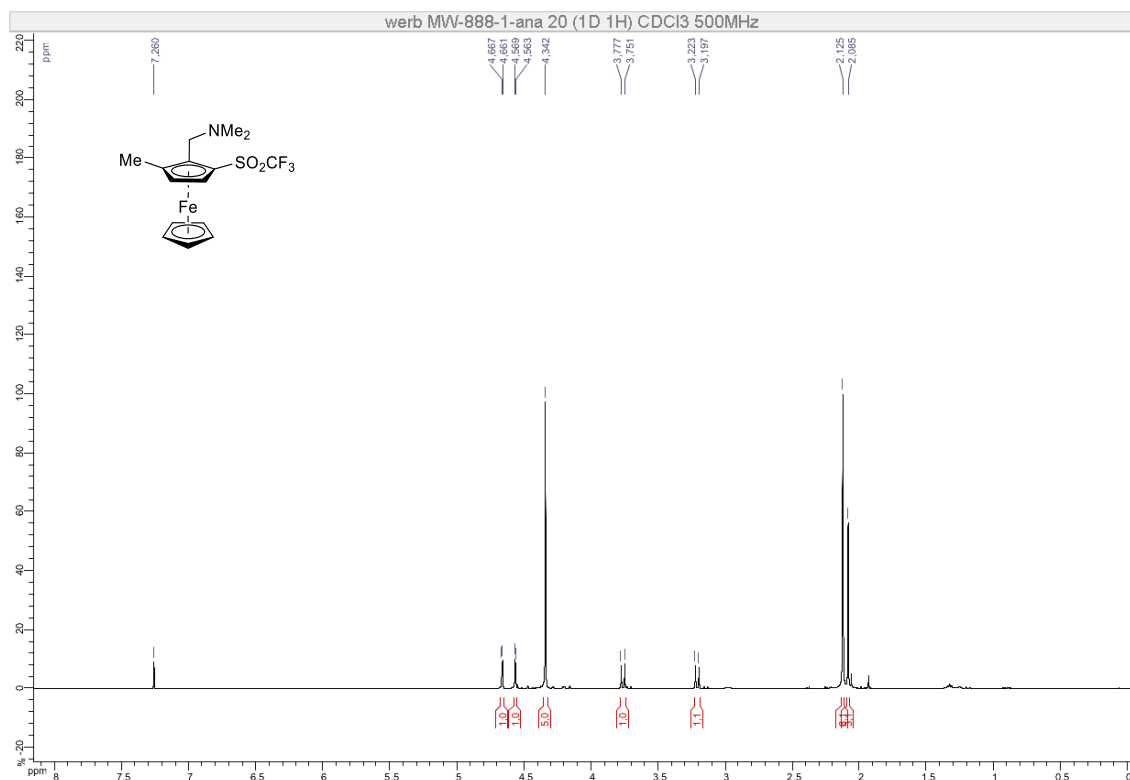


¹⁹F NMR (470 MHz, CDCl₃)

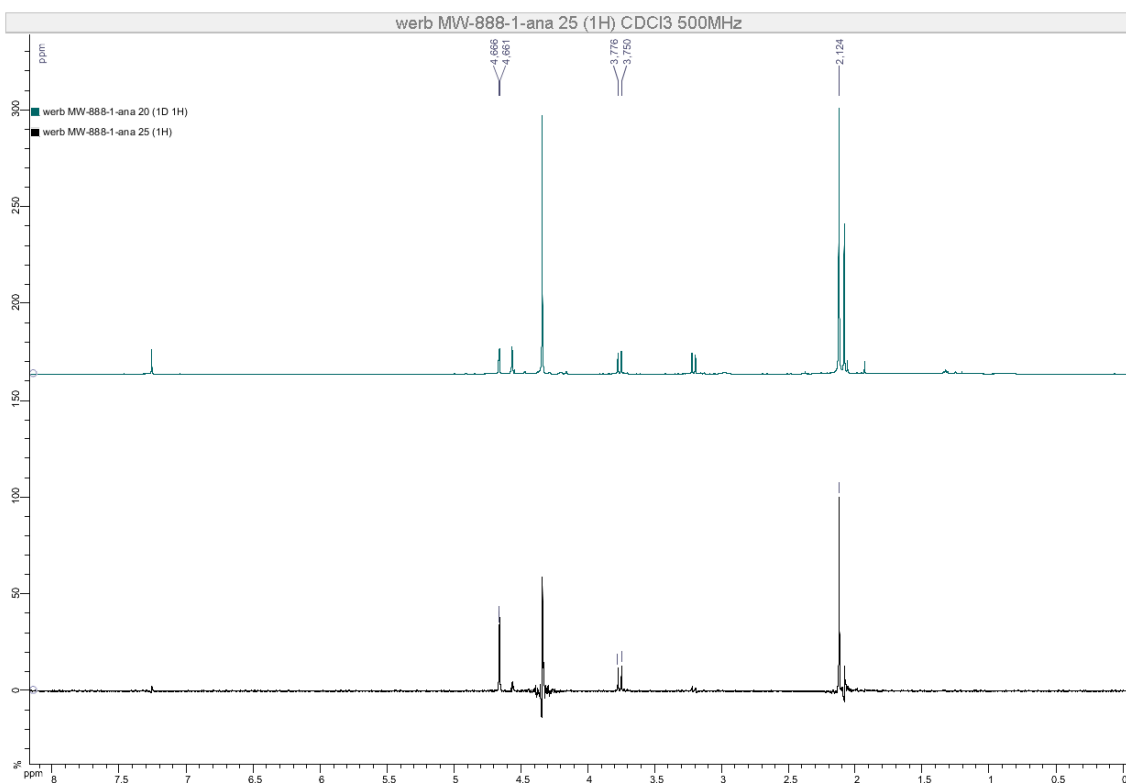


(*S_P*)-2-(Dimethylaminomethyl)-3-methylferrocenetriflone (*S_P*-7)

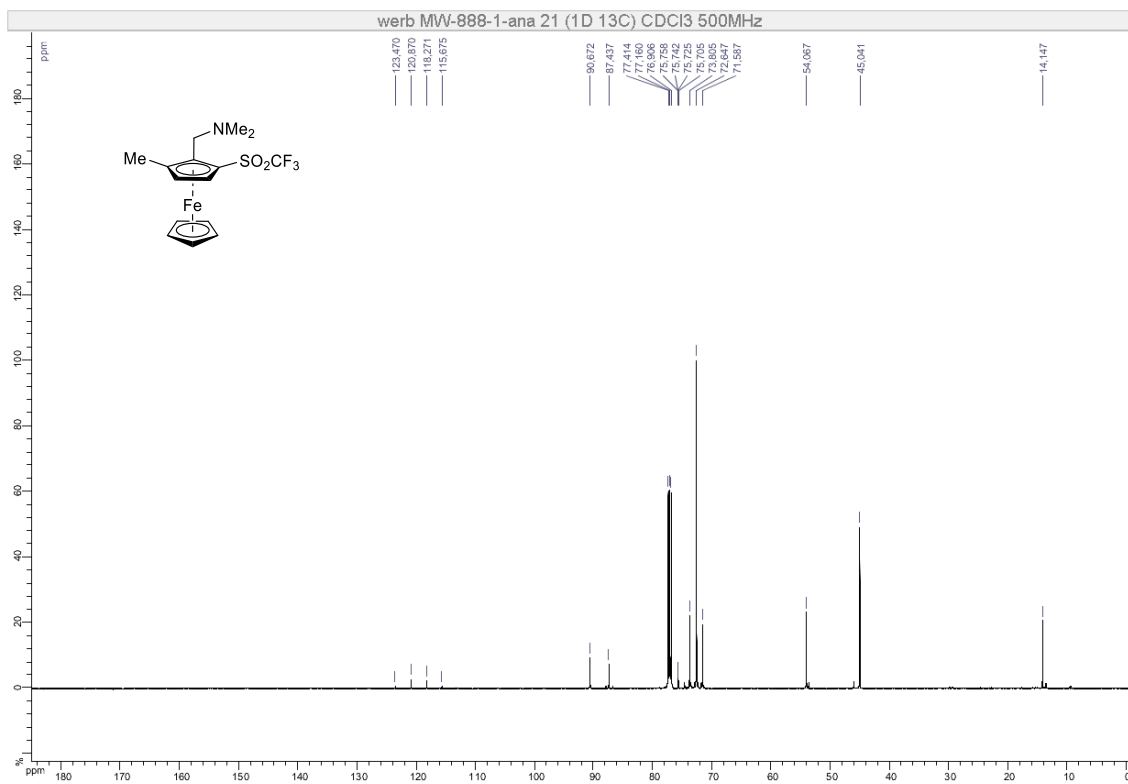
¹H NMR (500 MHz, CDCl₃)



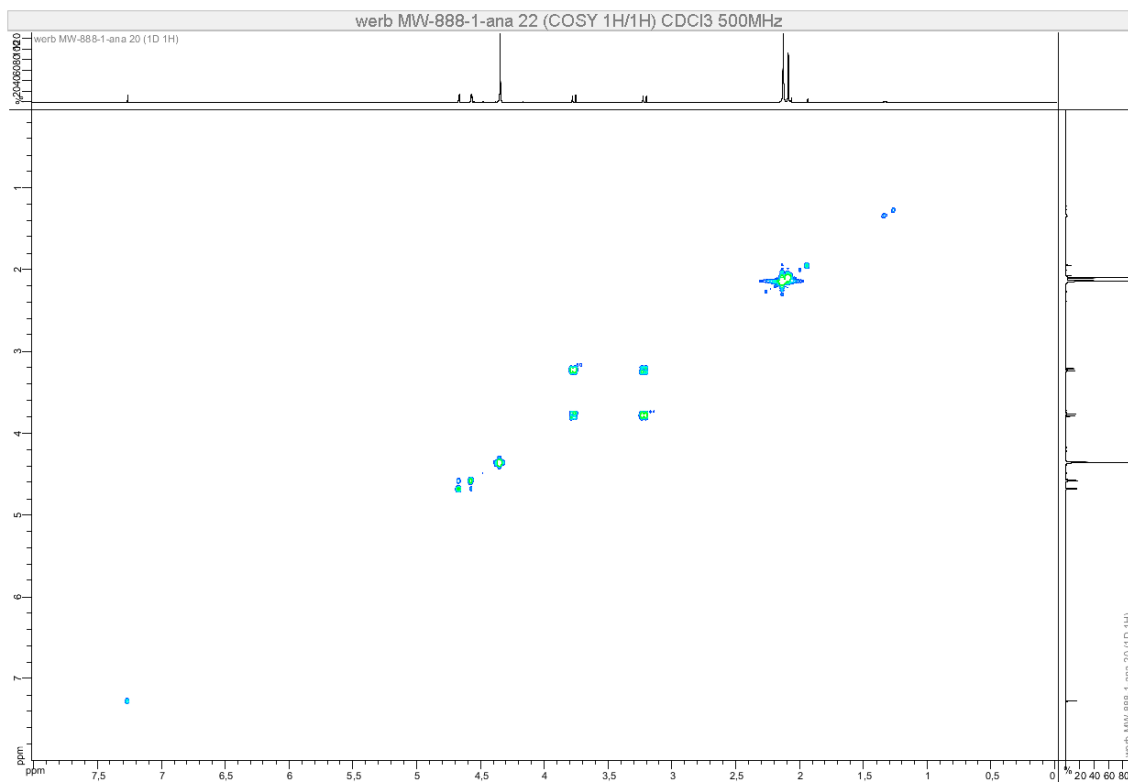
HOESY (500 MHz, CDCl₃) Irradiation at -77.2 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



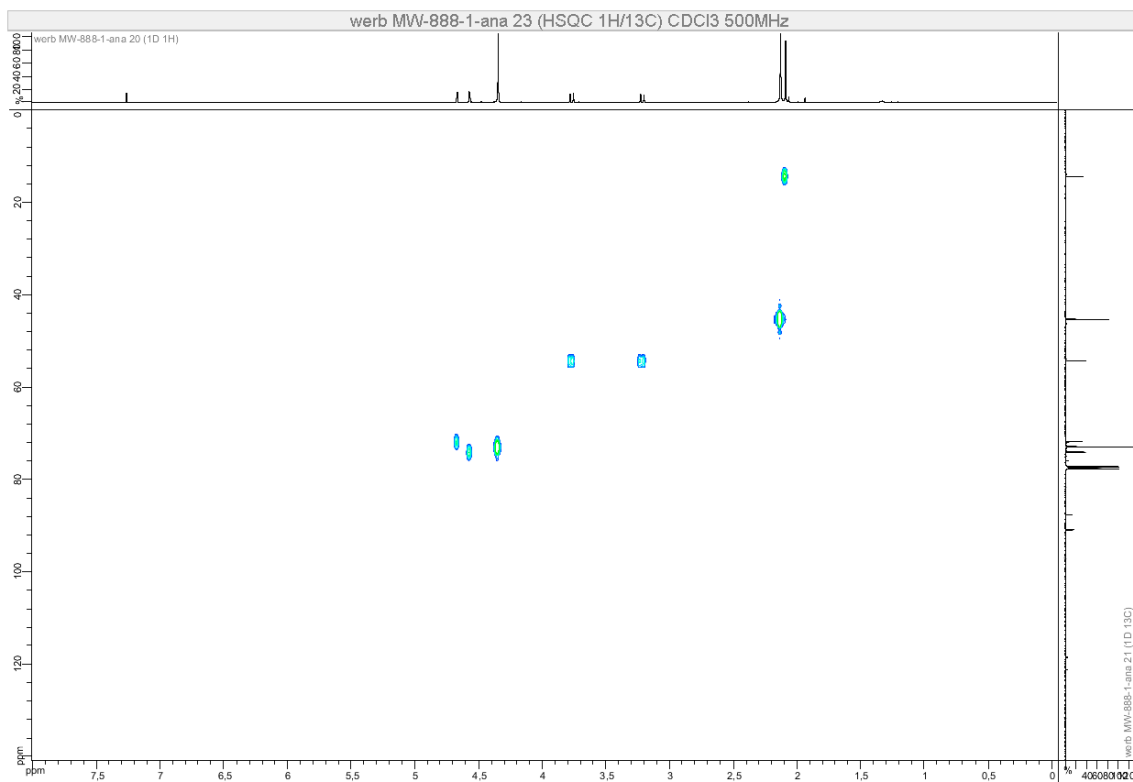
^{13}C NMR (126 MHz, CDCl_3)



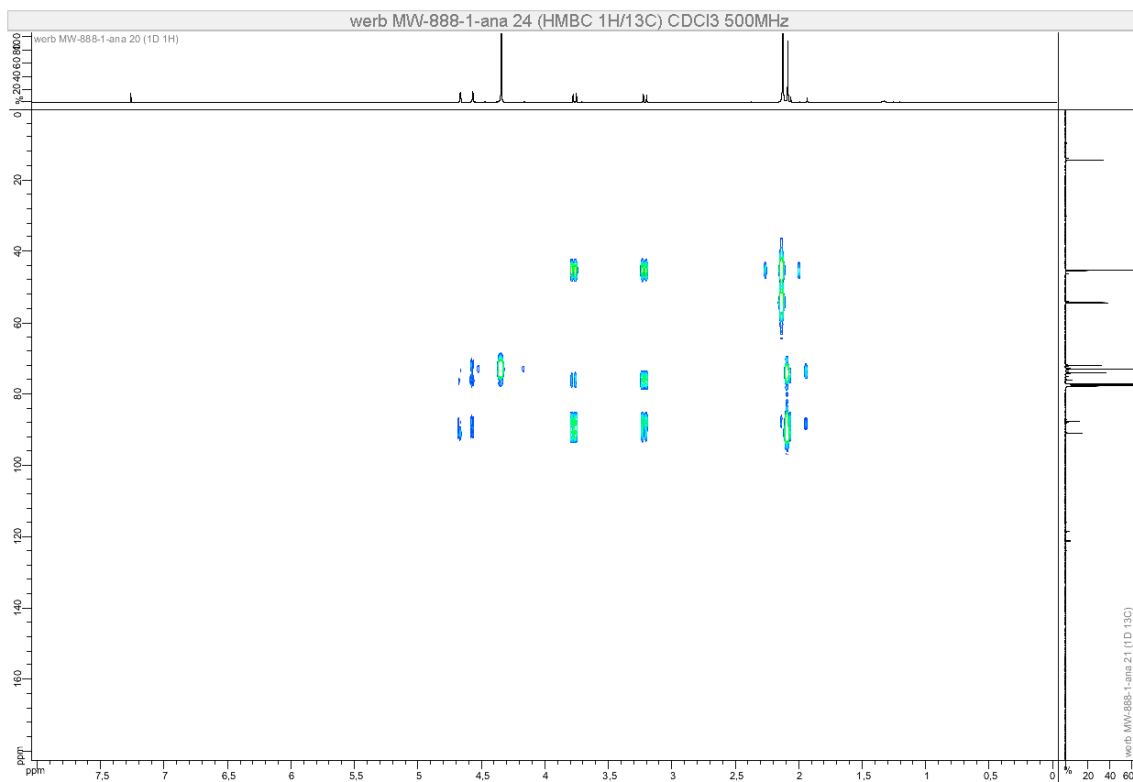
COSY (500 MHz, CDCl_3)



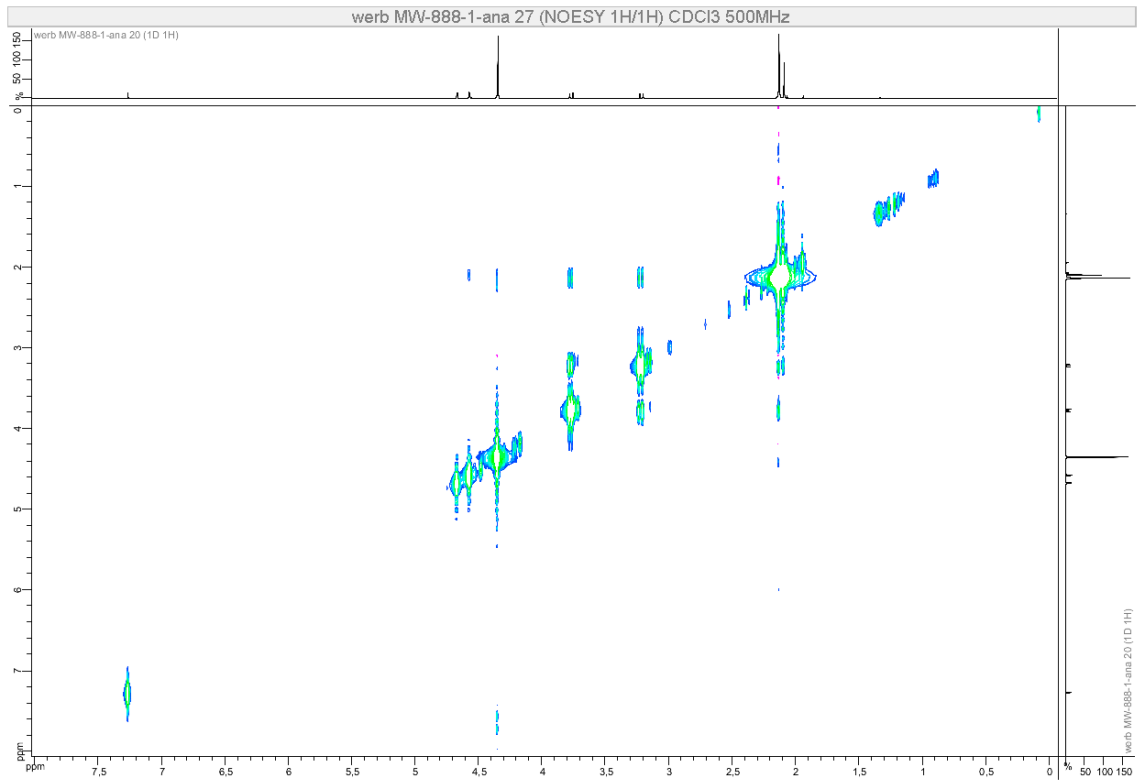
HSQC (500 MHz, CDCl₃)



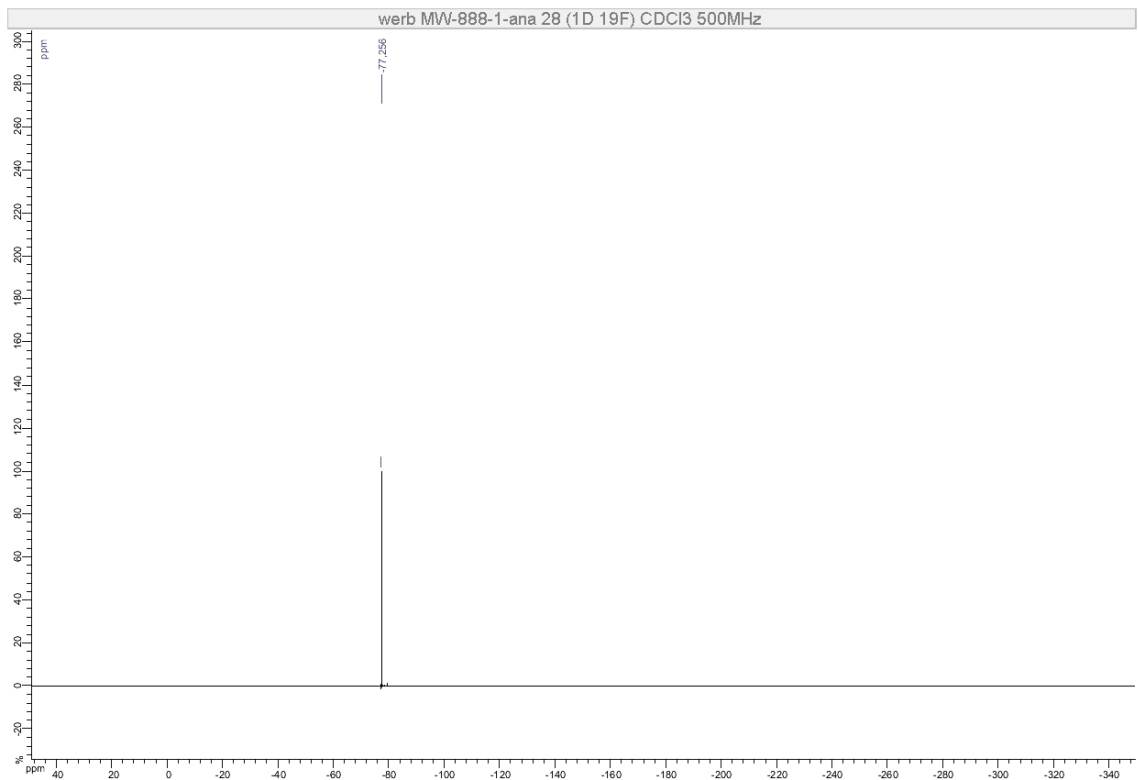
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

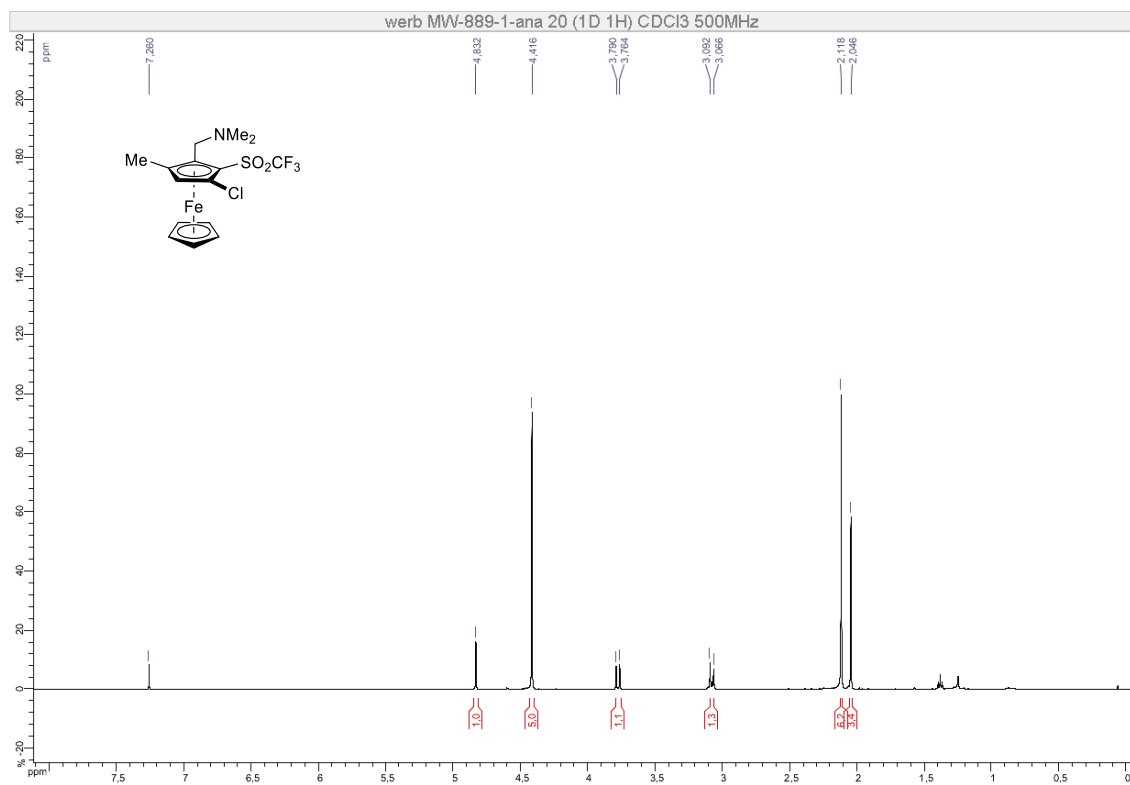


¹⁹F NMR (470 MHz, CDCl₃)

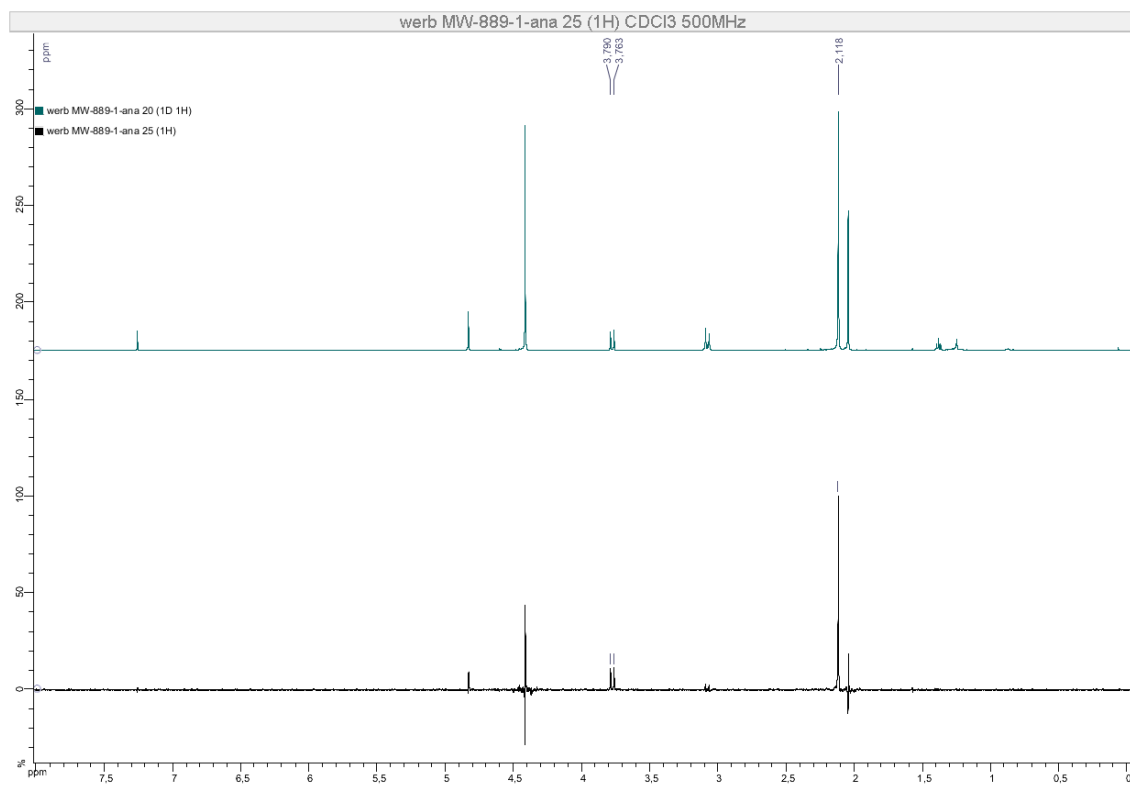


(*S_P*)-5-Chloro-2-(dimethylaminomethyl)-3-methylferrocenetriflone (*S_P*-8)

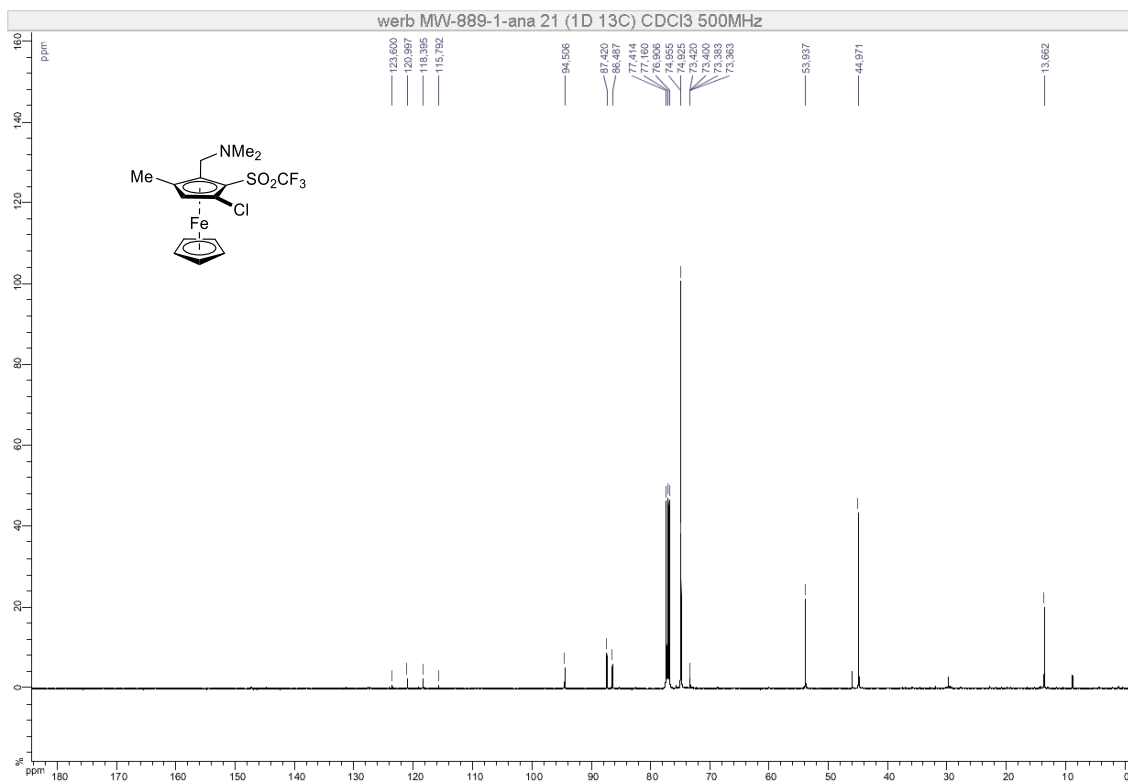
¹H NMR (500 MHz, CDCl₃)



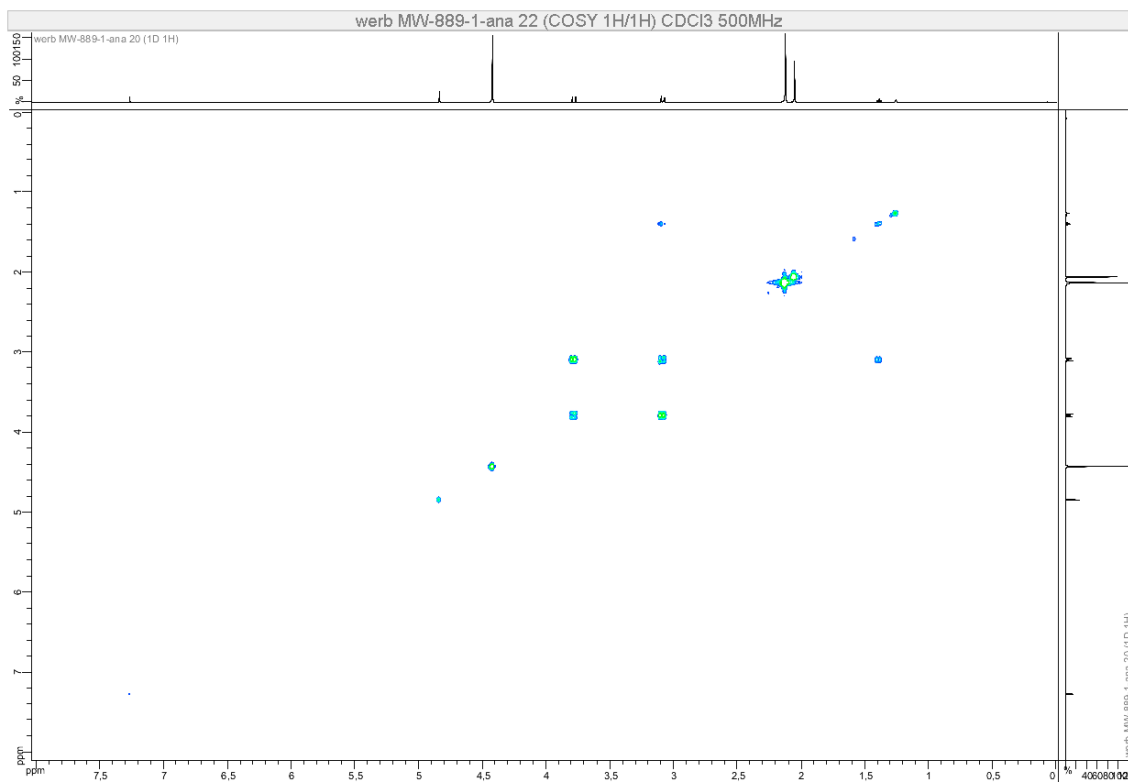
HOESY (500 MHz, CDCl₃) Irradiation at -76.4 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



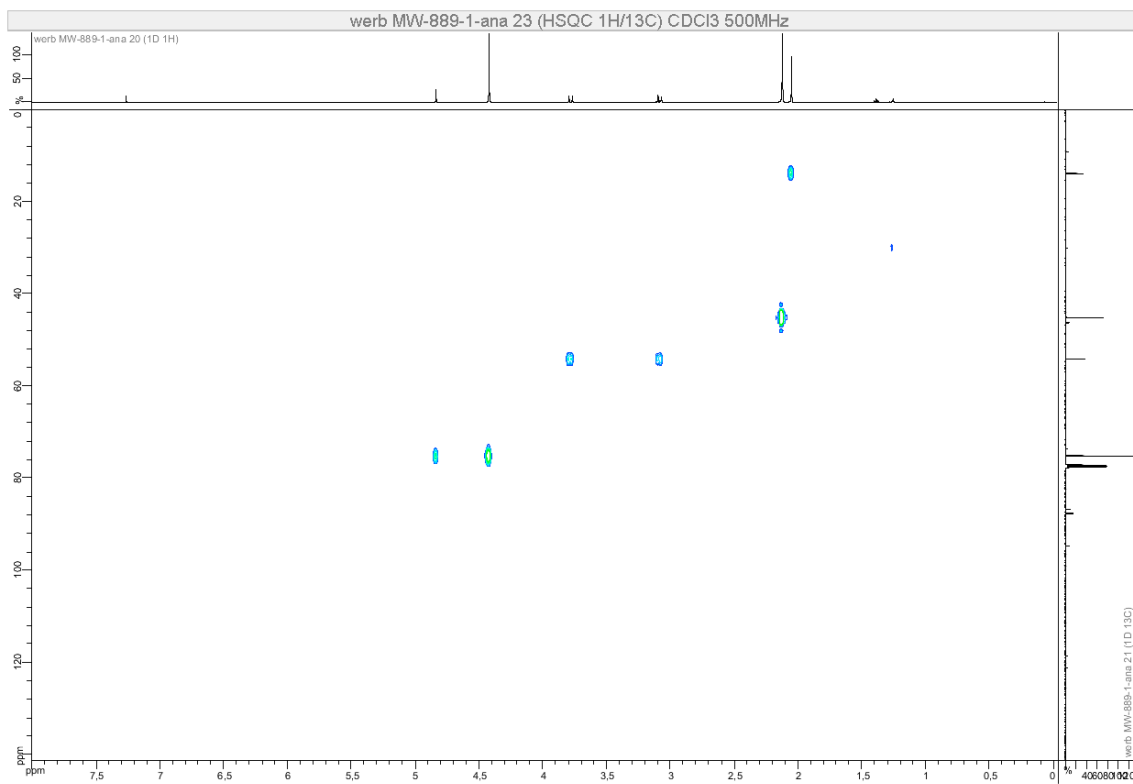
^{13}C NMR (126 MHz, CDCl_3)



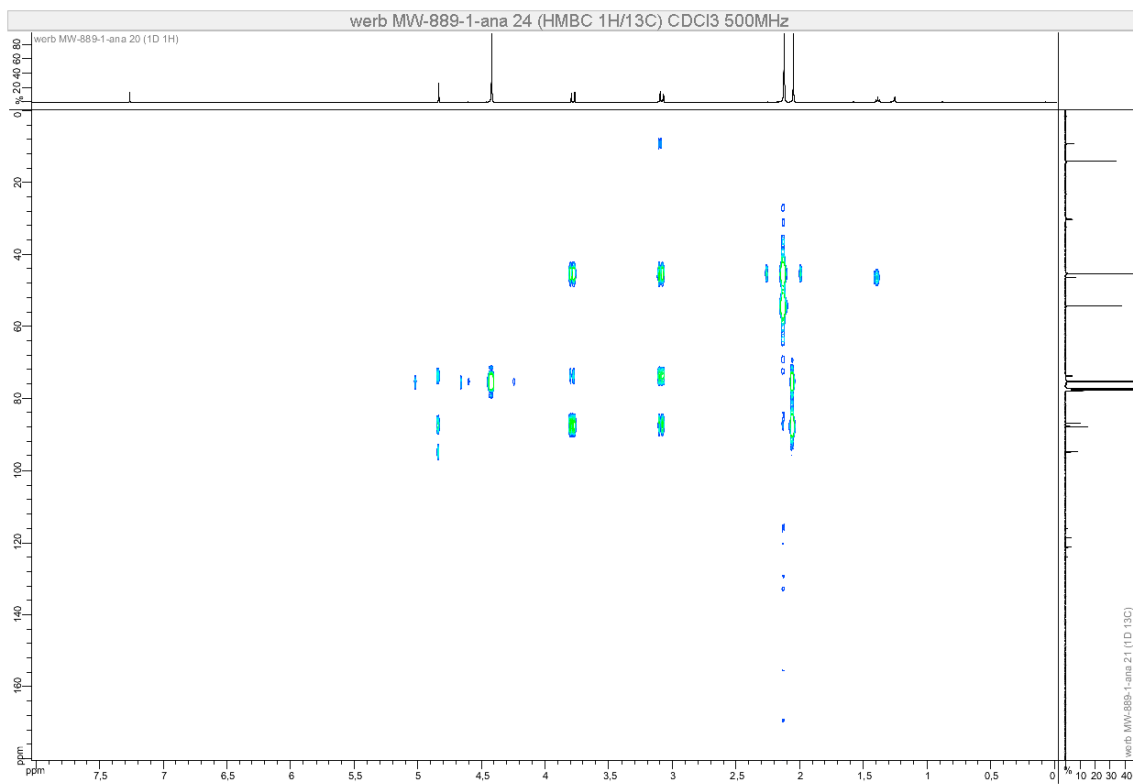
COSY (500 MHz, CDCl_3)



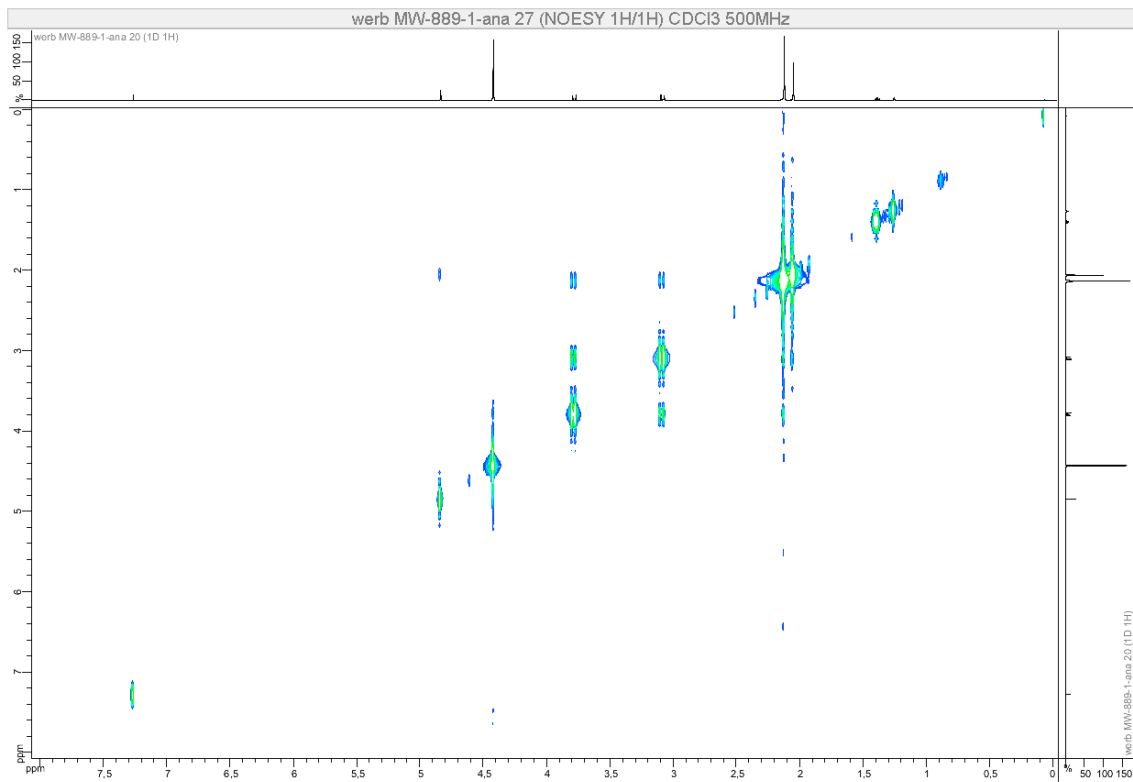
HSQC (500 MHz, CDCl₃)



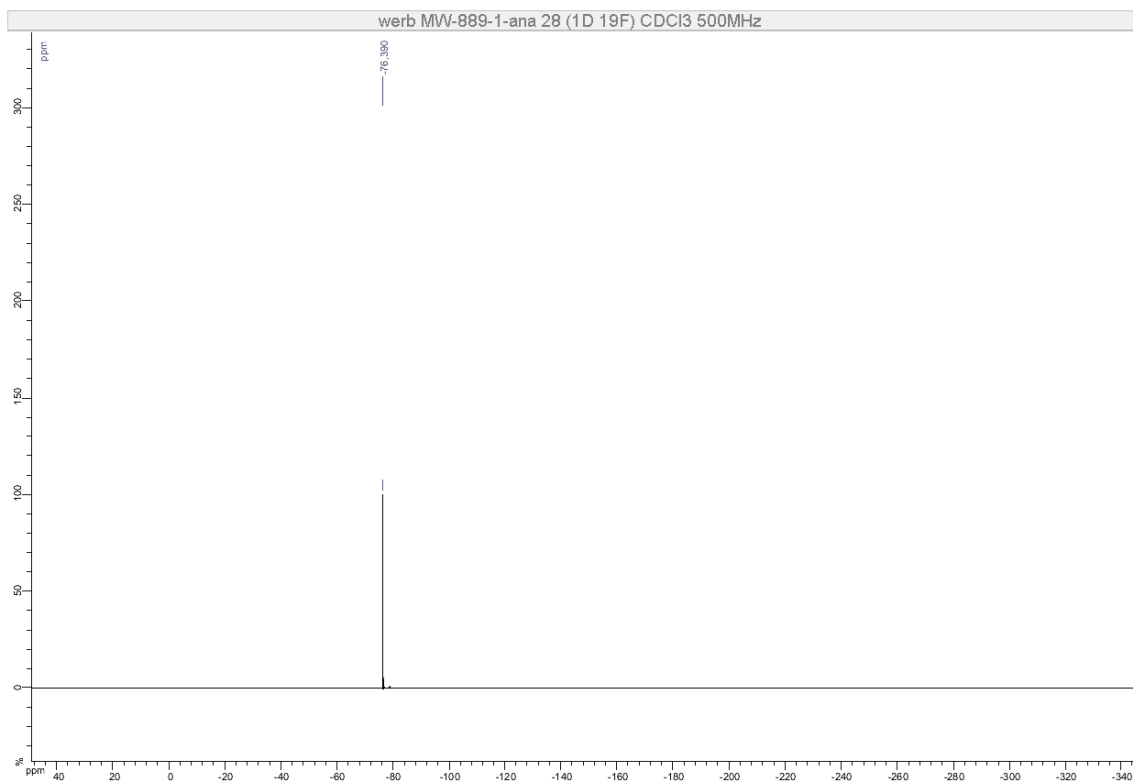
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

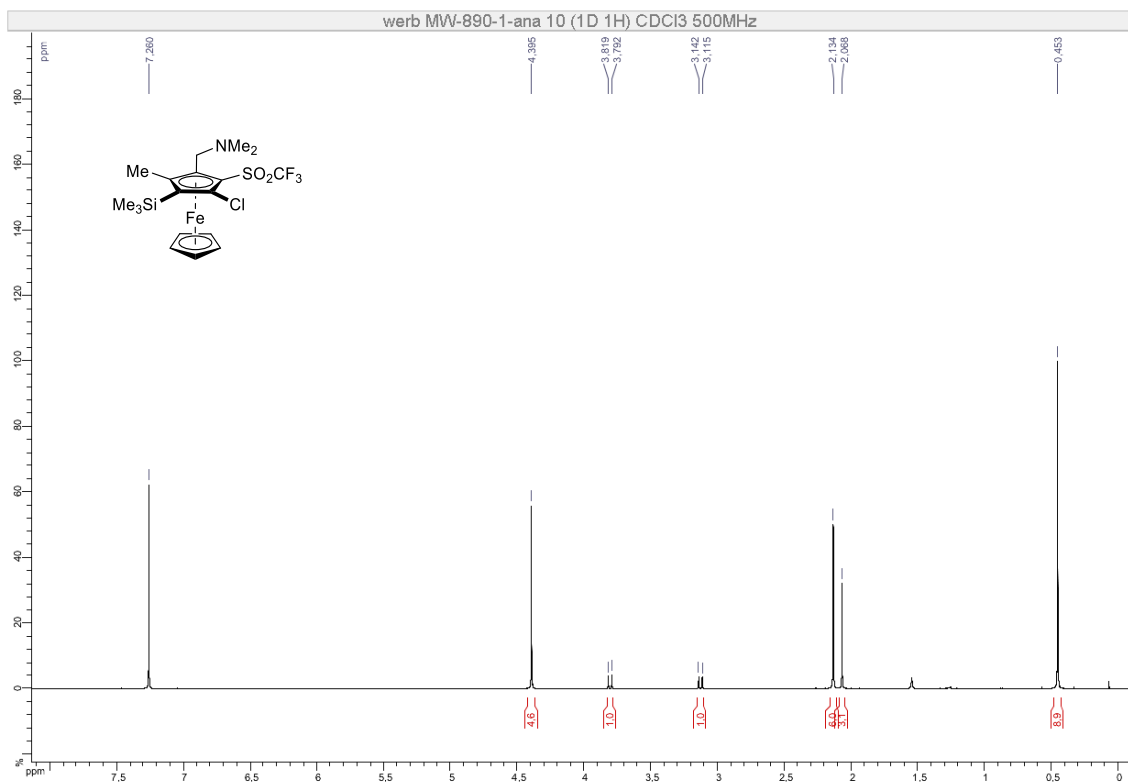


¹⁹F NMR (470 MHz, CDCl₃)

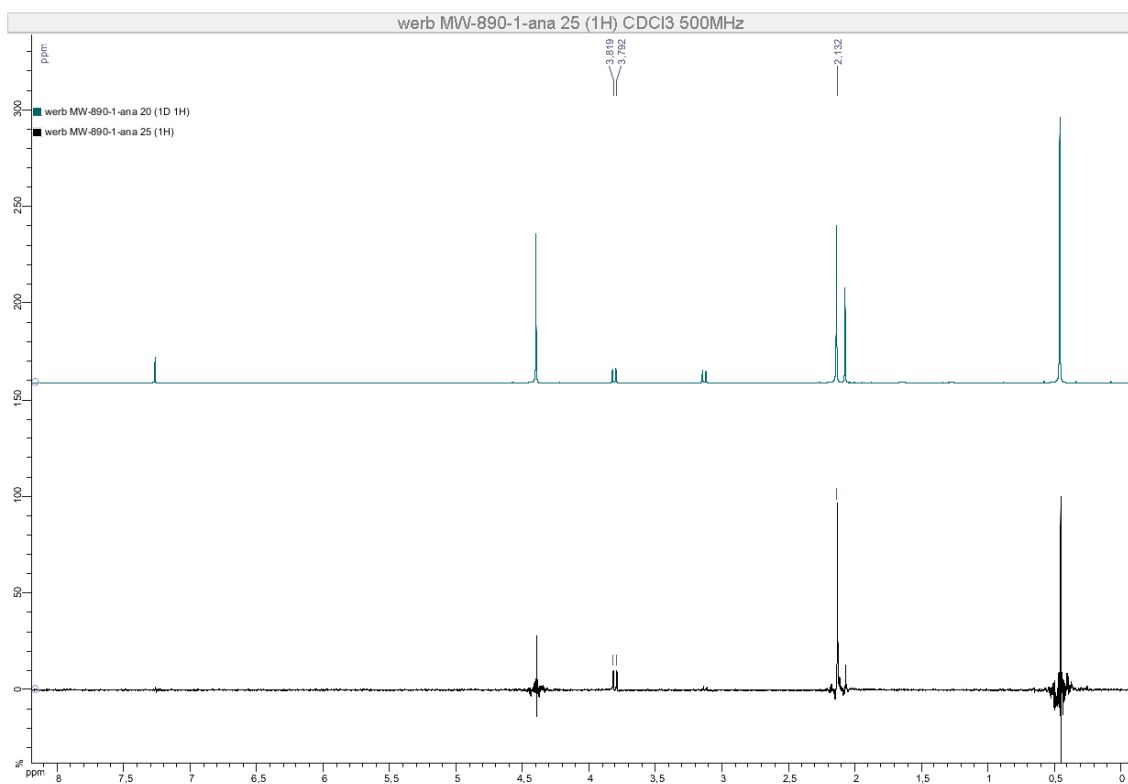


(*Sp*)-2-Chloro-5-(dimethylaminomethyl)-4-methyl-3-(trimethylsilyl)ferrocenetriflone (*Sp*-9)

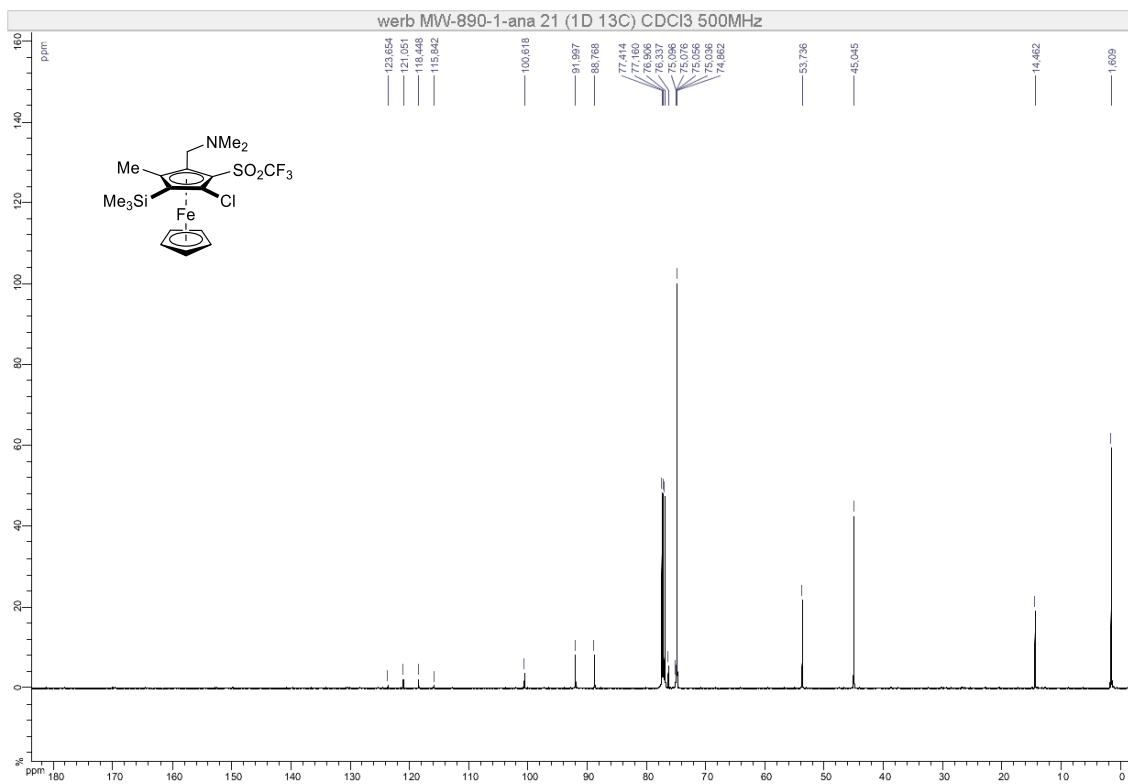
¹H NMR (500 MHz, CDCl₃)



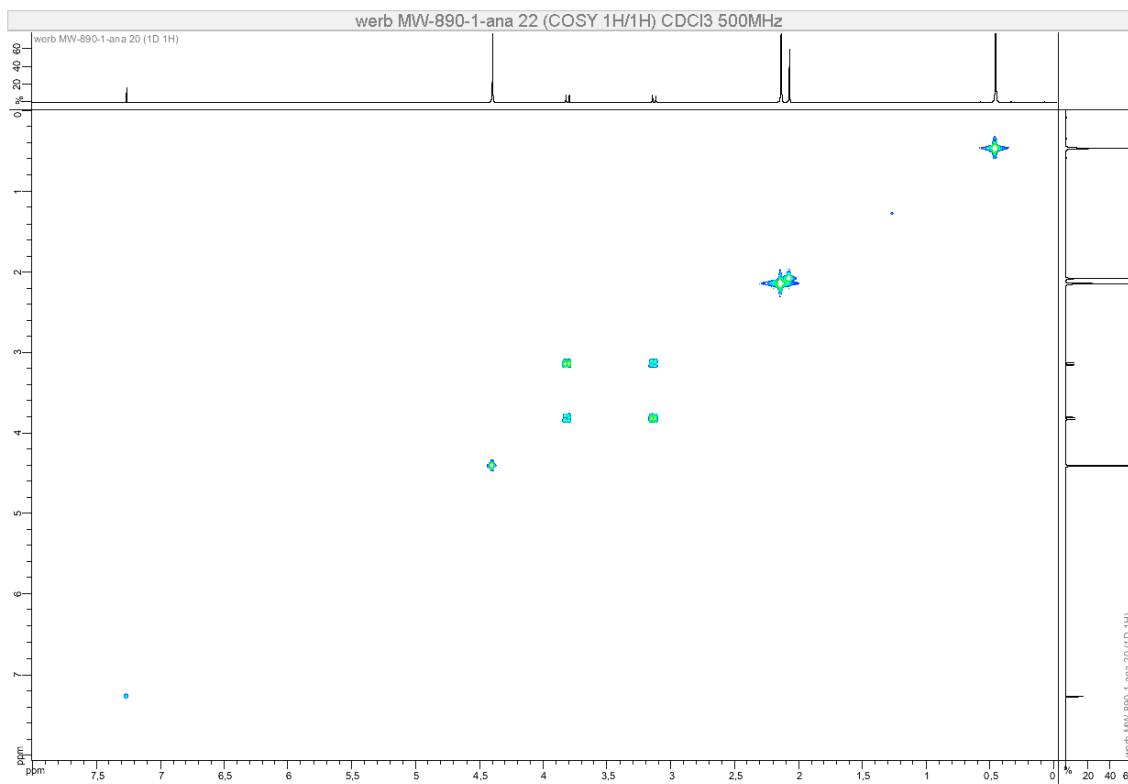
HOESY (500 MHz, CDCl₃) Irradiation at -182.6 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



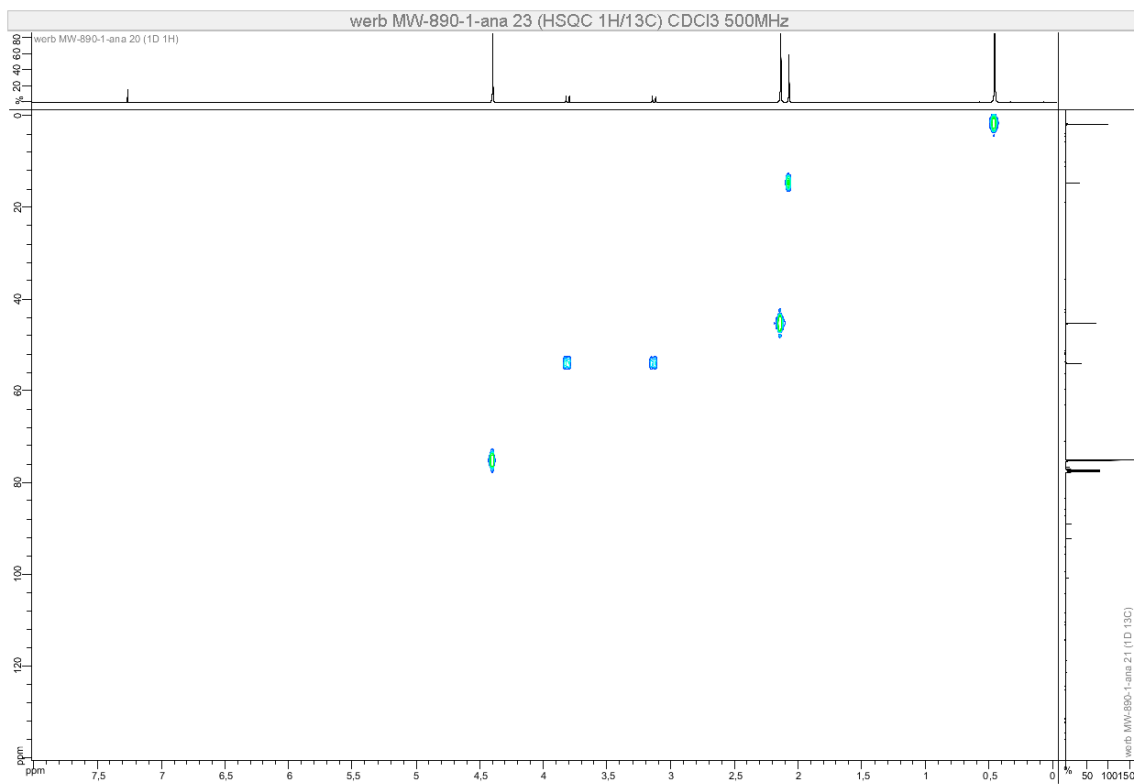
^{13}C NMR (126 MHz, CDCl_3)



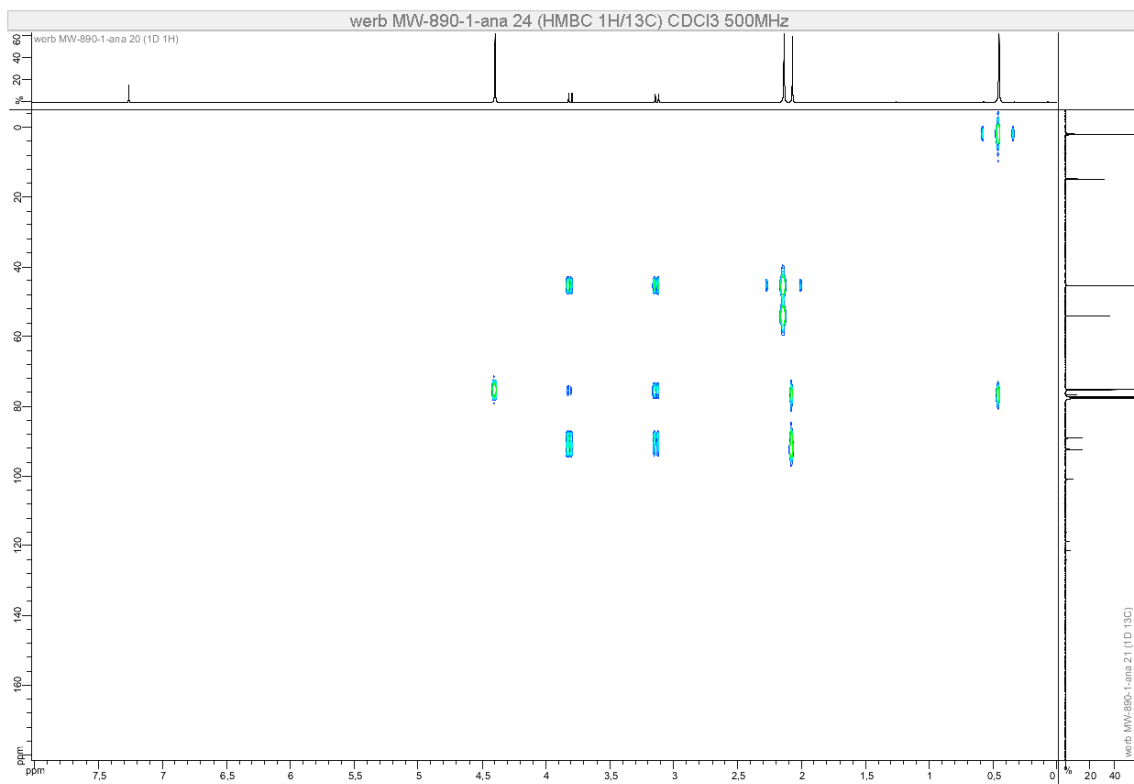
COSY (500 MHz, CDCl_3)



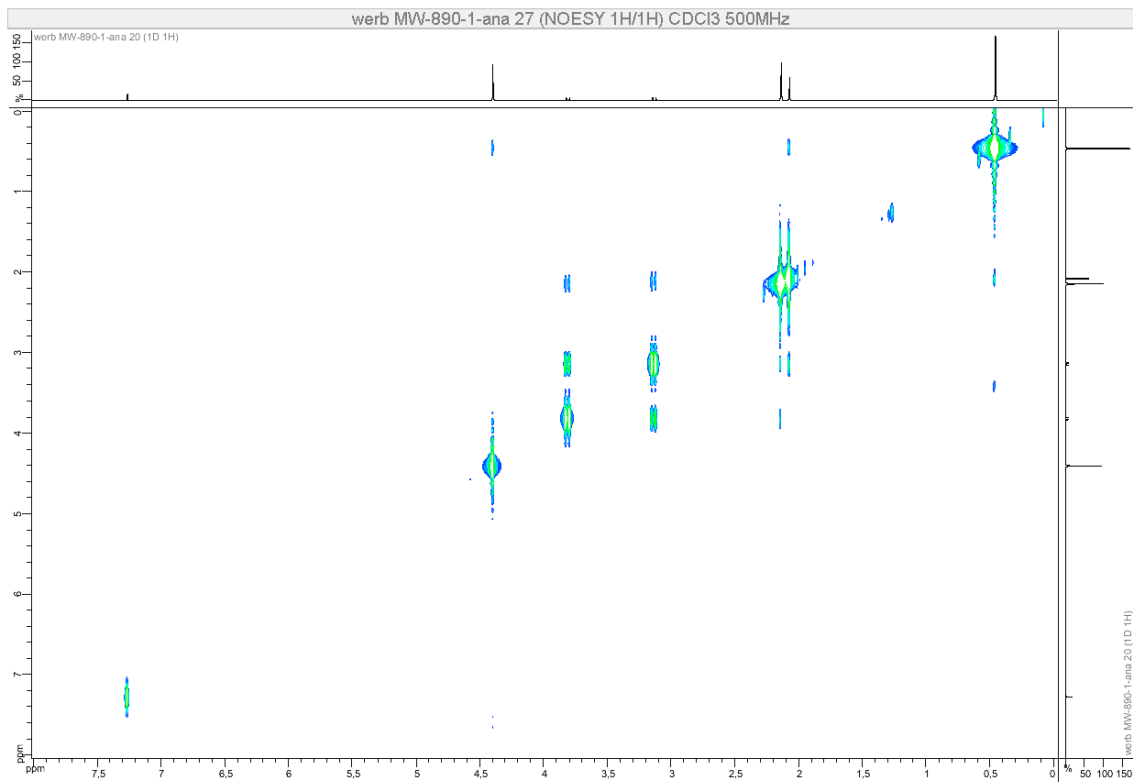
HSQC (500 MHz, CDCl₃)



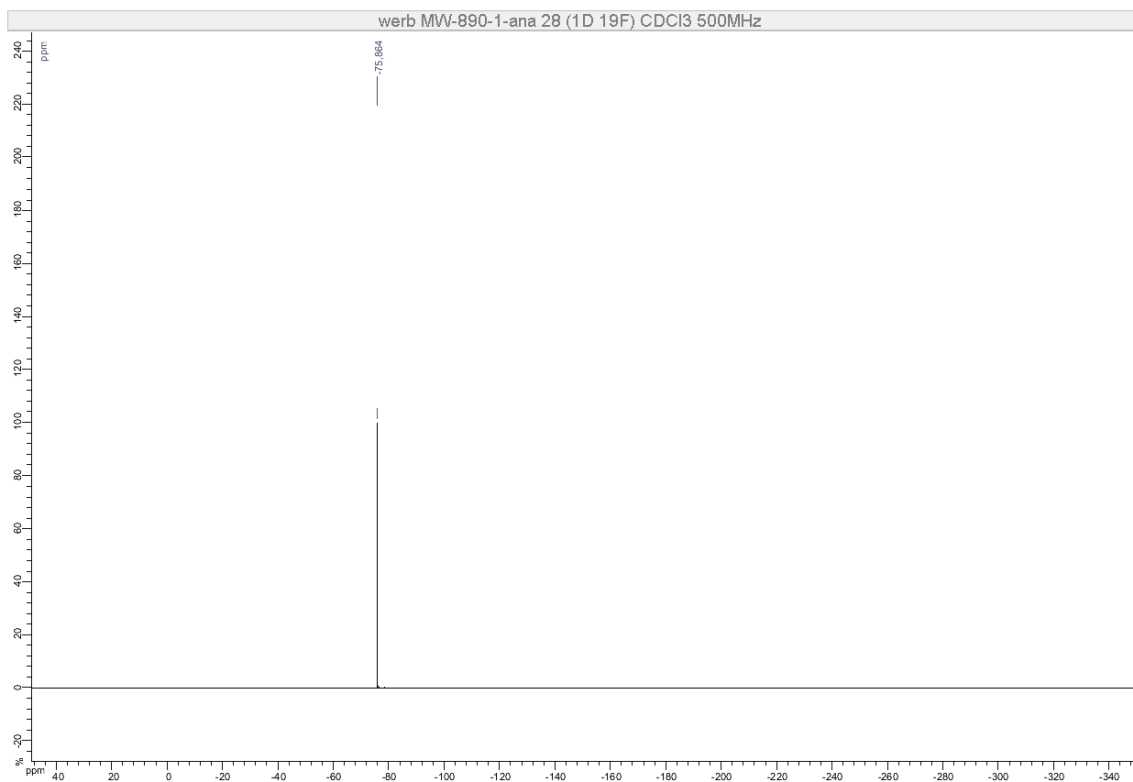
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

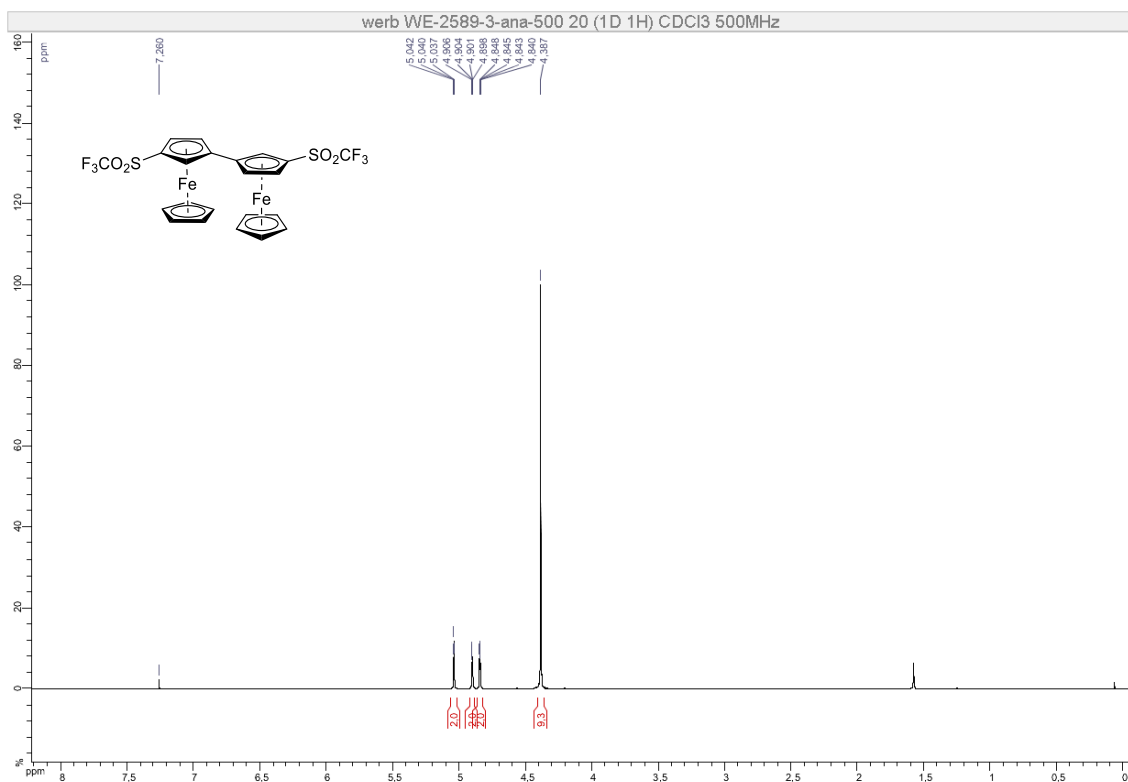


¹⁹F NMR (470 MHz, CDCl₃)

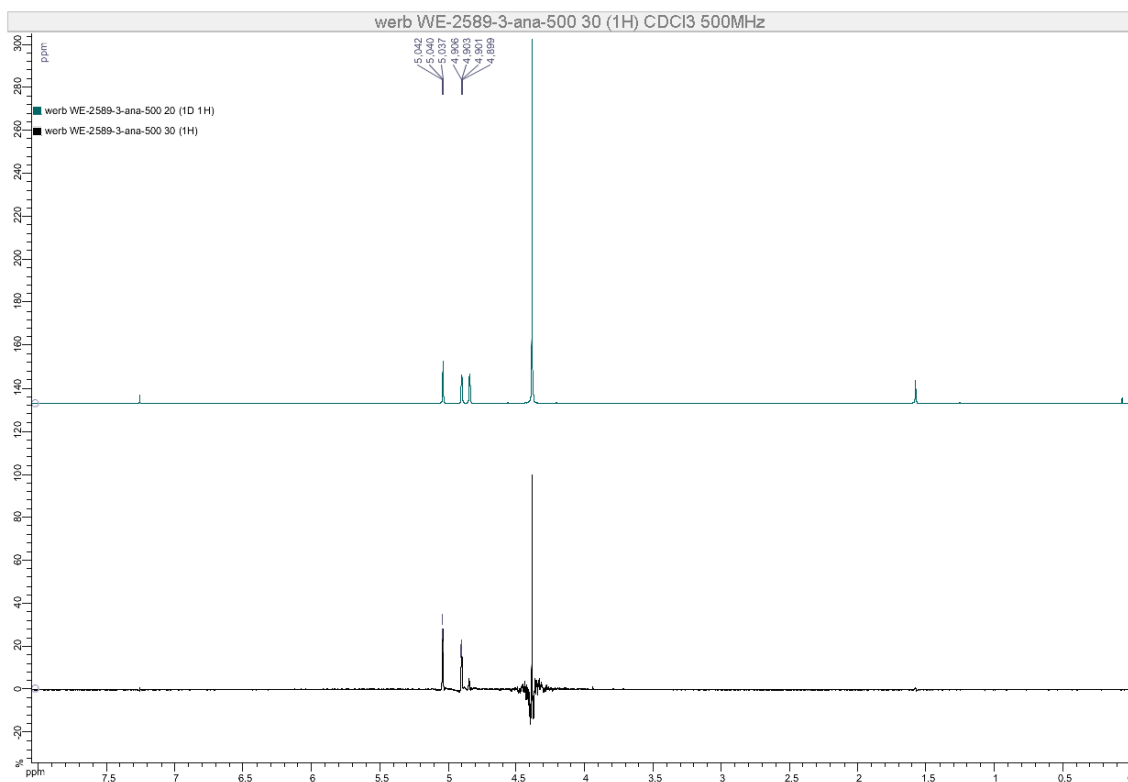


(*S_P*,*S_P*)-1,1'-Biferrocene-3,3'-bis(triflone) (*S_P*,*S_P*-5I)

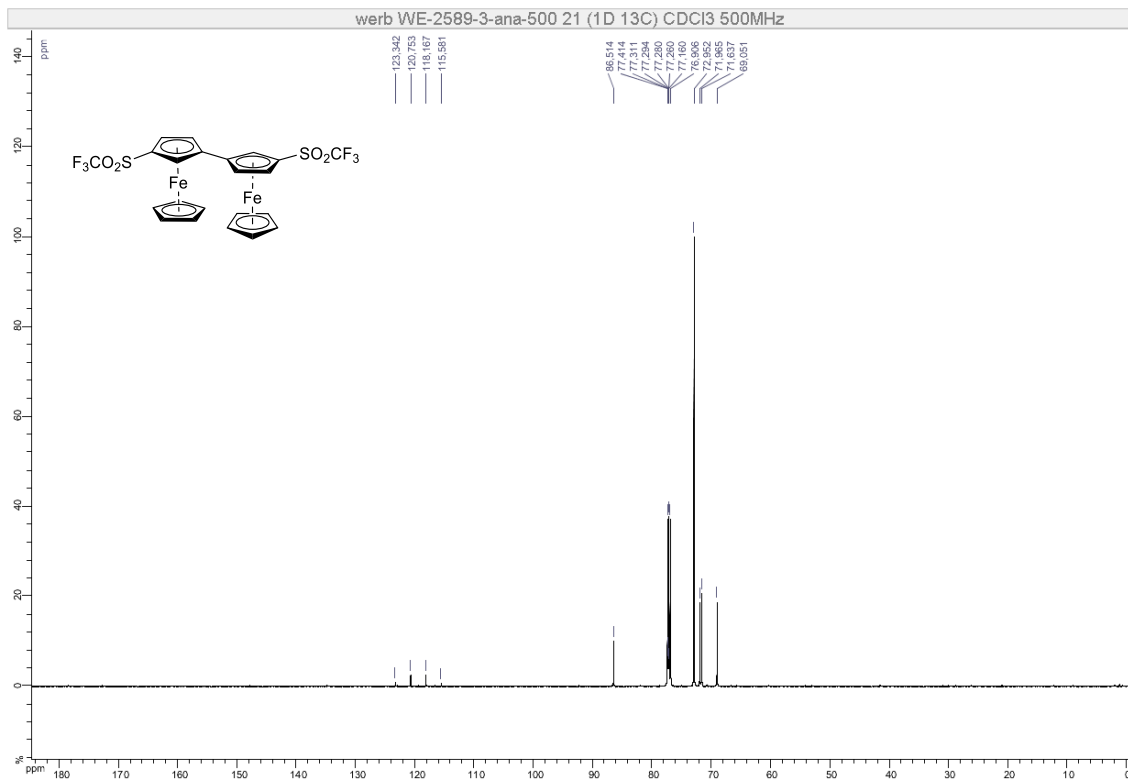
¹H NMR (500 MHz, CDCl₃)



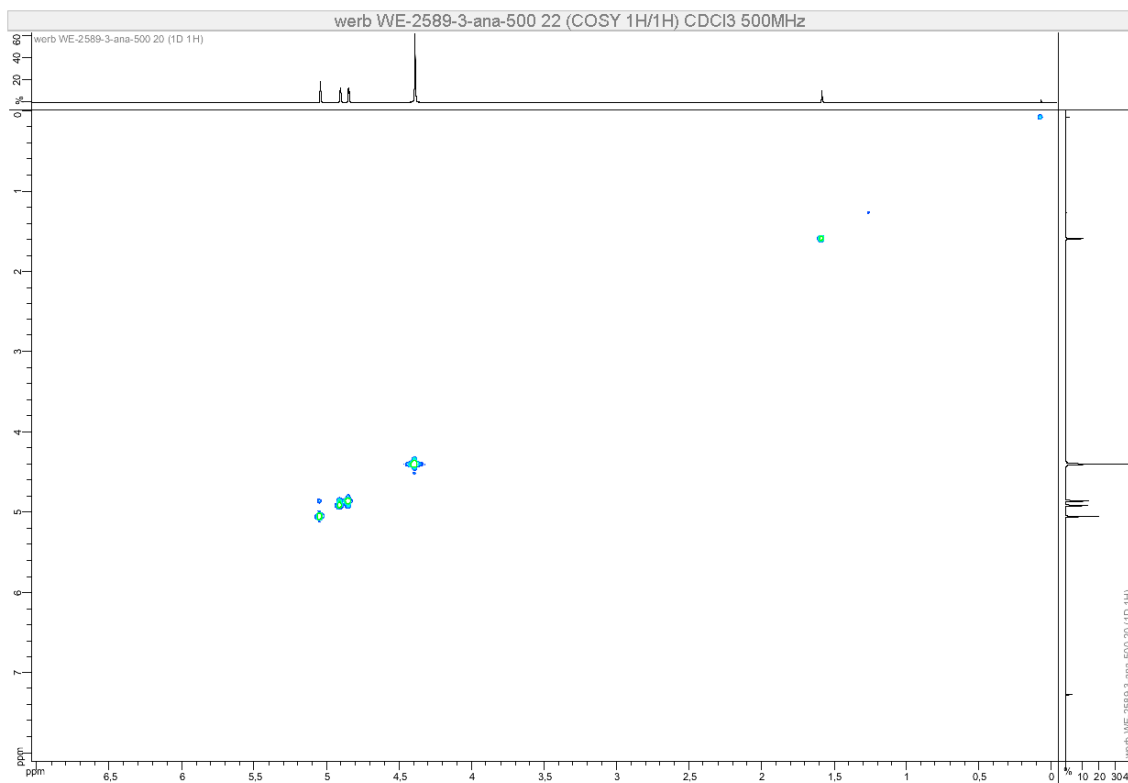
HOESY (500 MHz, CDCl₃) Irradiation at -79.2 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



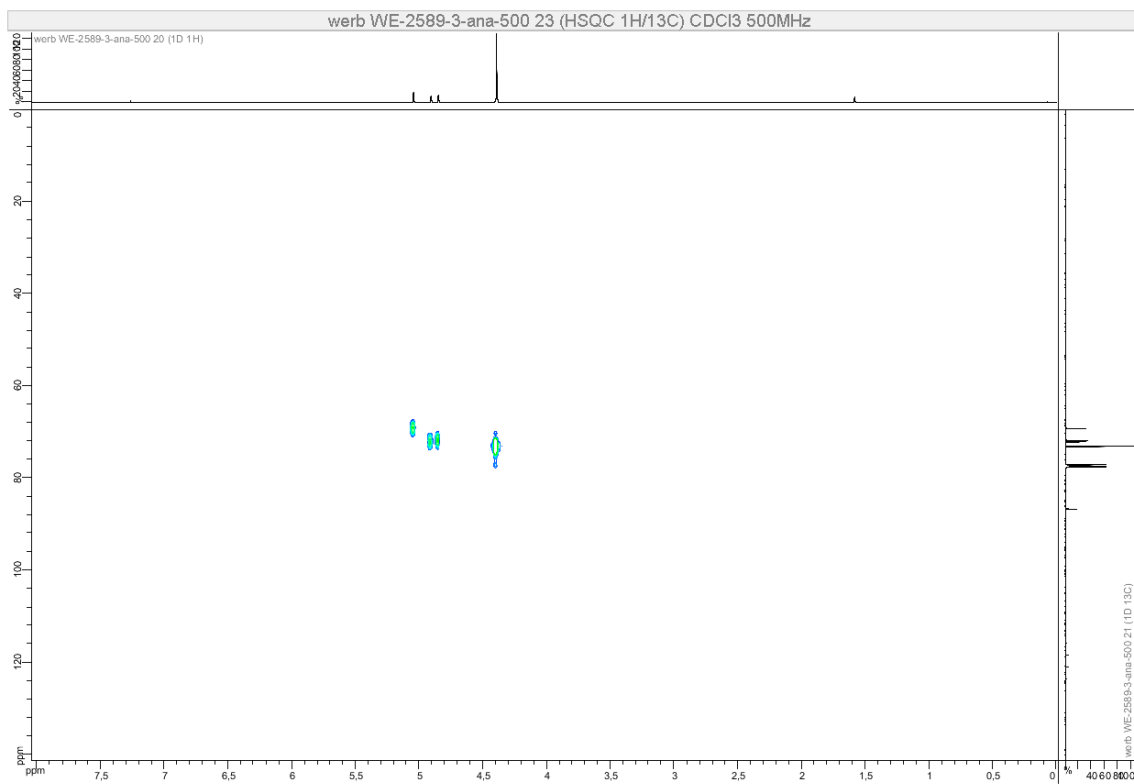
^{13}C NMR (126 MHz, CDCl_3)



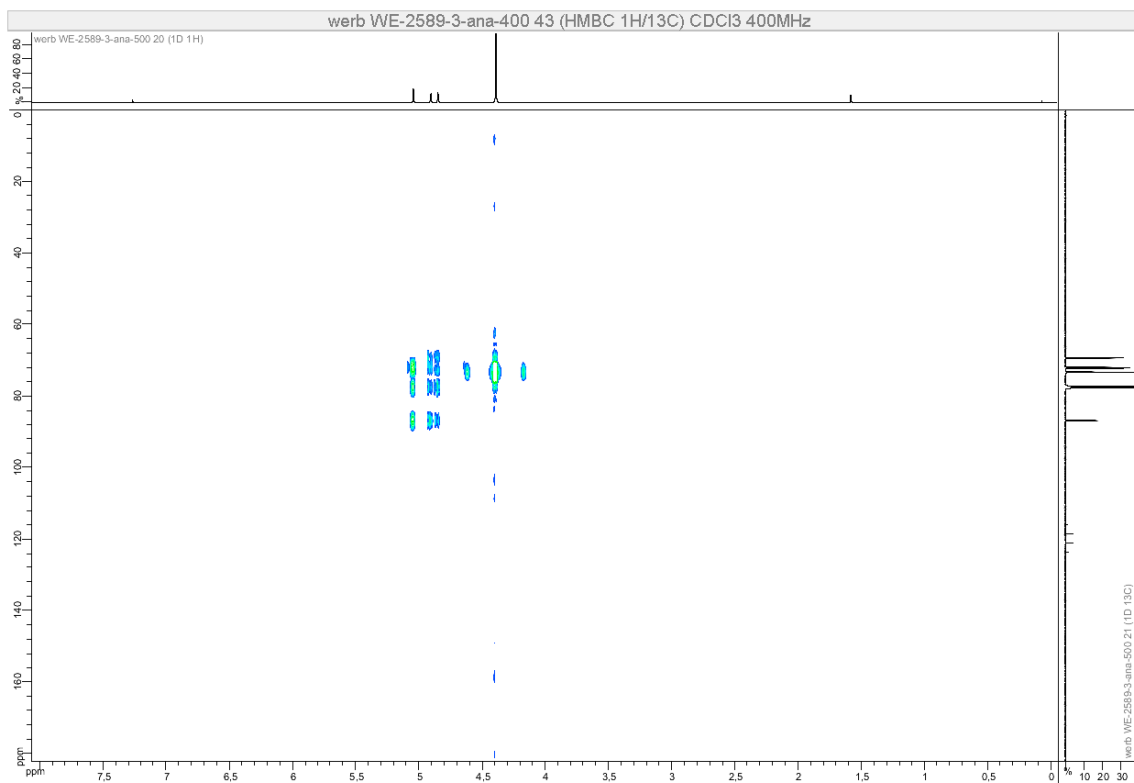
COSY (500 MHz, CDCl_3)



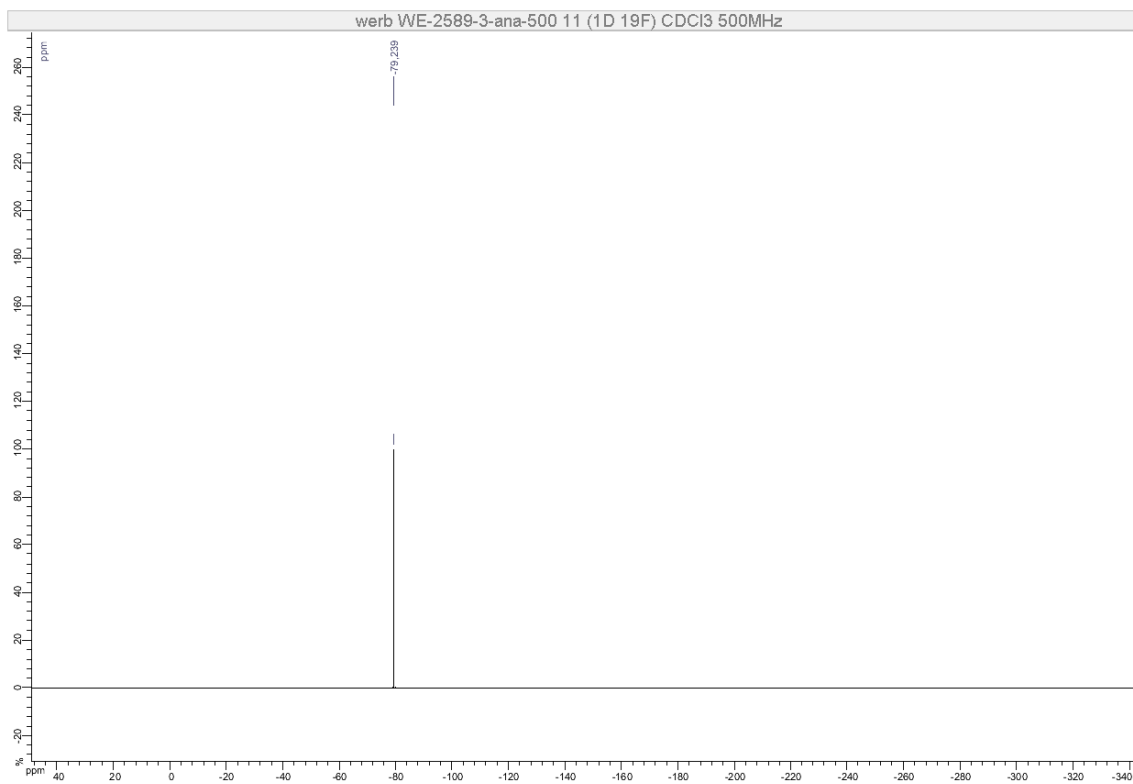
HSQC (500 MHz, CDCl₃)



HMBC (400 MHz, CDCl₃)

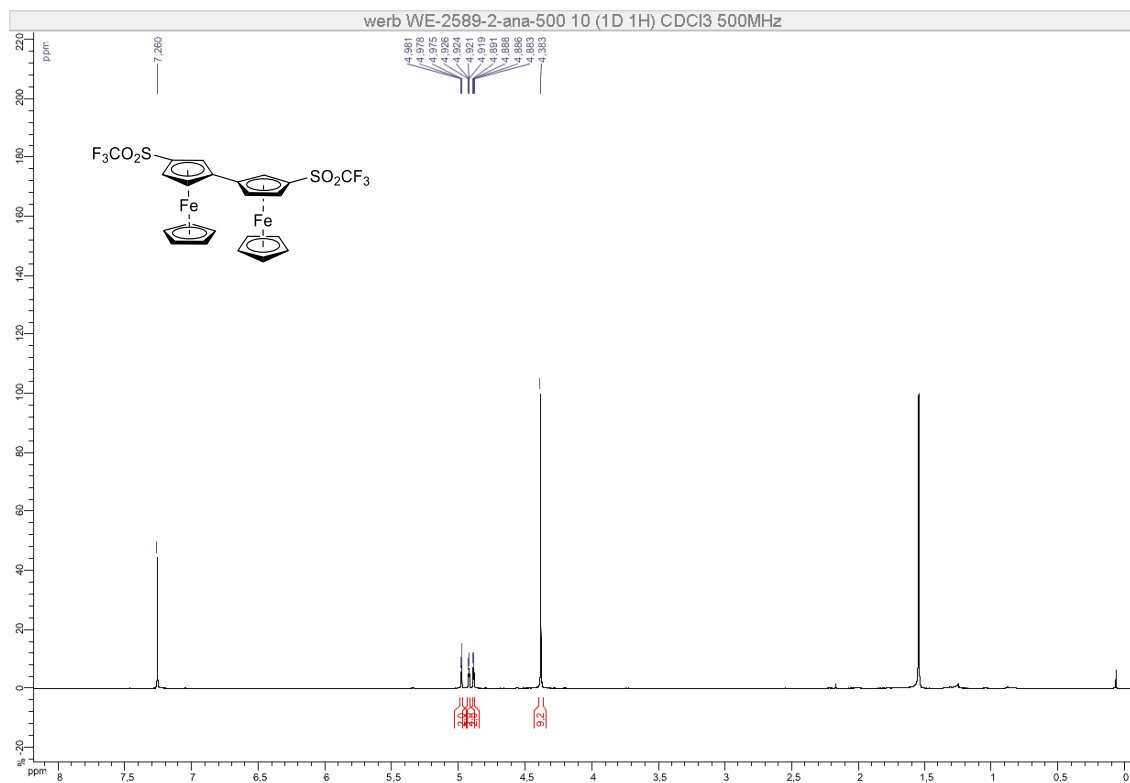


^{19}F NMR (470 MHz, CDCl_3)

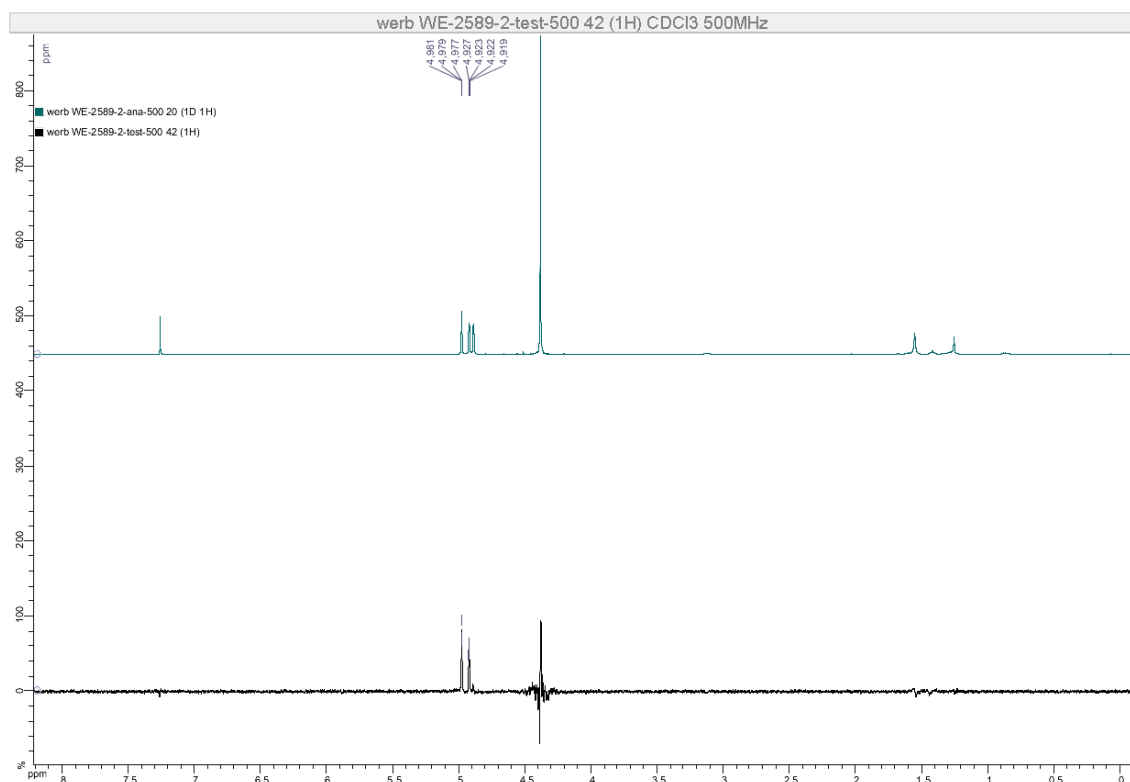


(*R_P*,*S_P*)-1,1'-Biferrocene-3,3'-bis(triflone) (*meso*-5I)

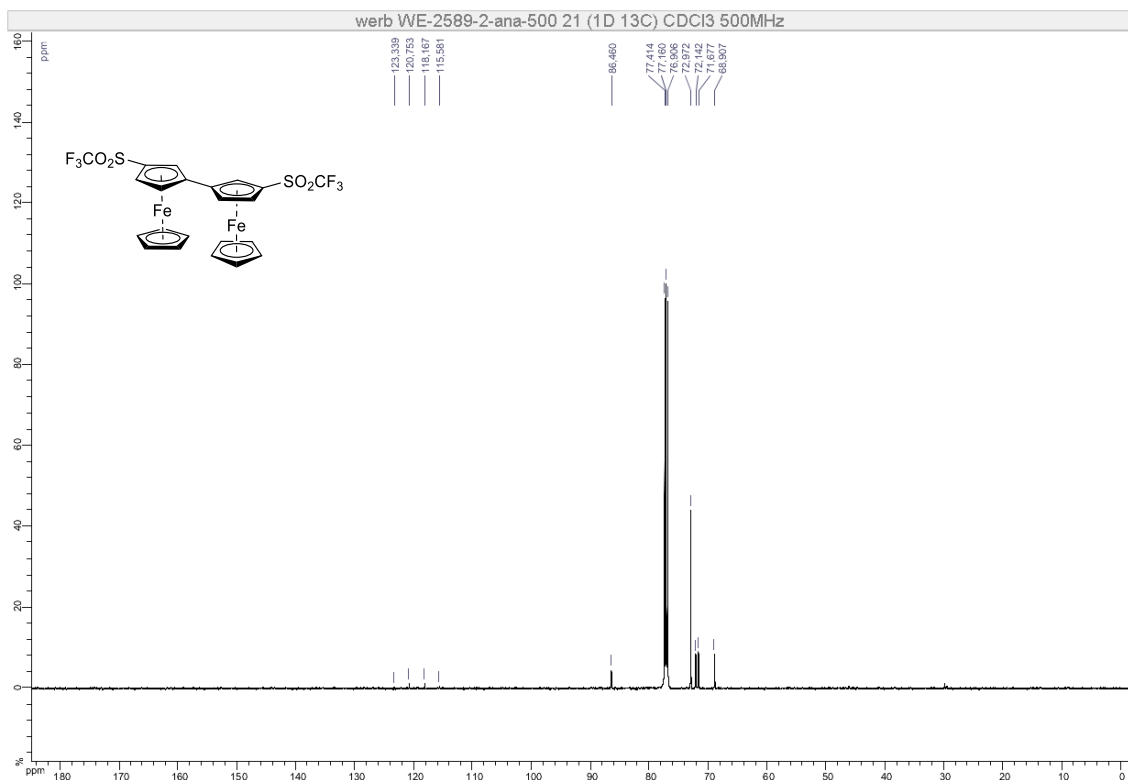
¹H NMR (500 MHz, CDCl₃)



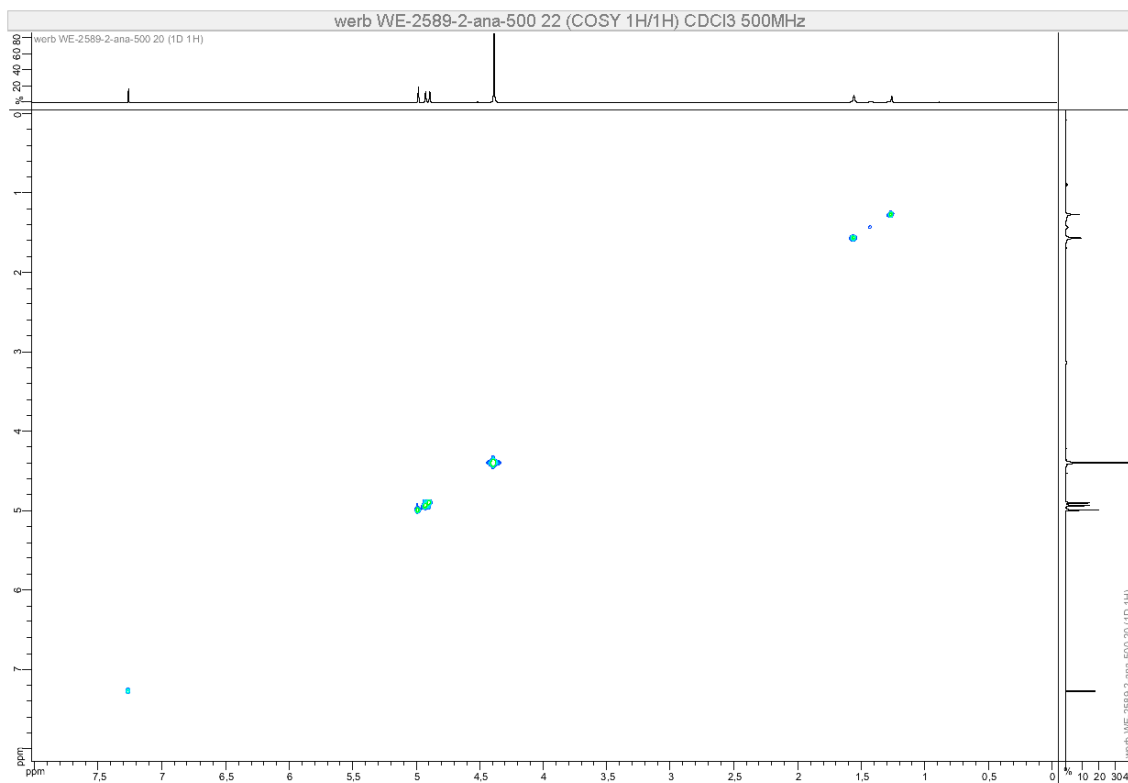
HOESY (500 MHz, CDCl₃) Irradiation at -79.1 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



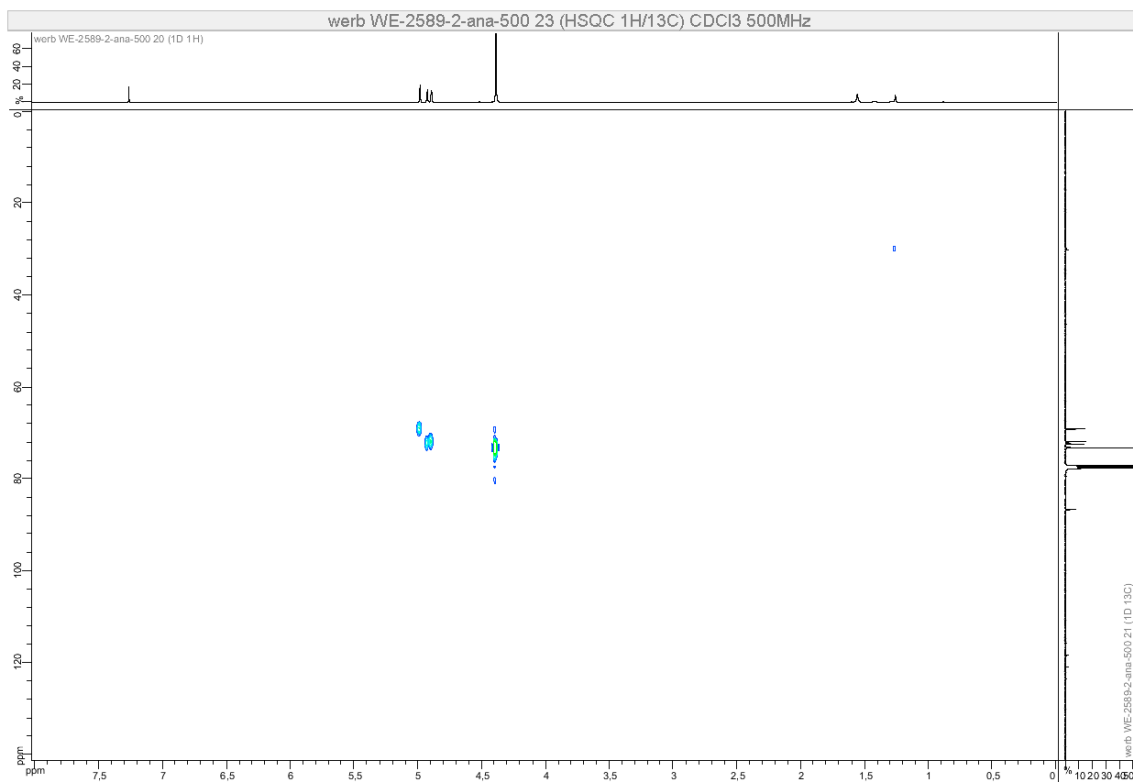
^{13}C NMR (126 MHz, CDCl_3)



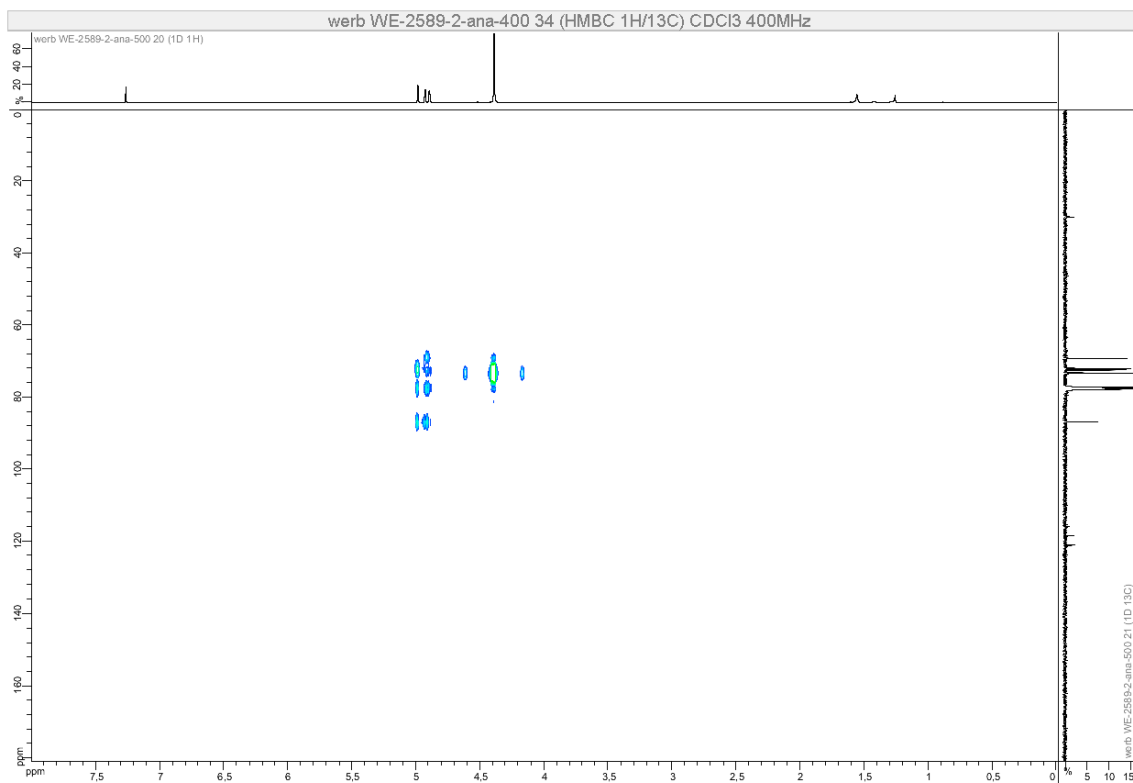
COSY (500 MHz, CDCl_3)



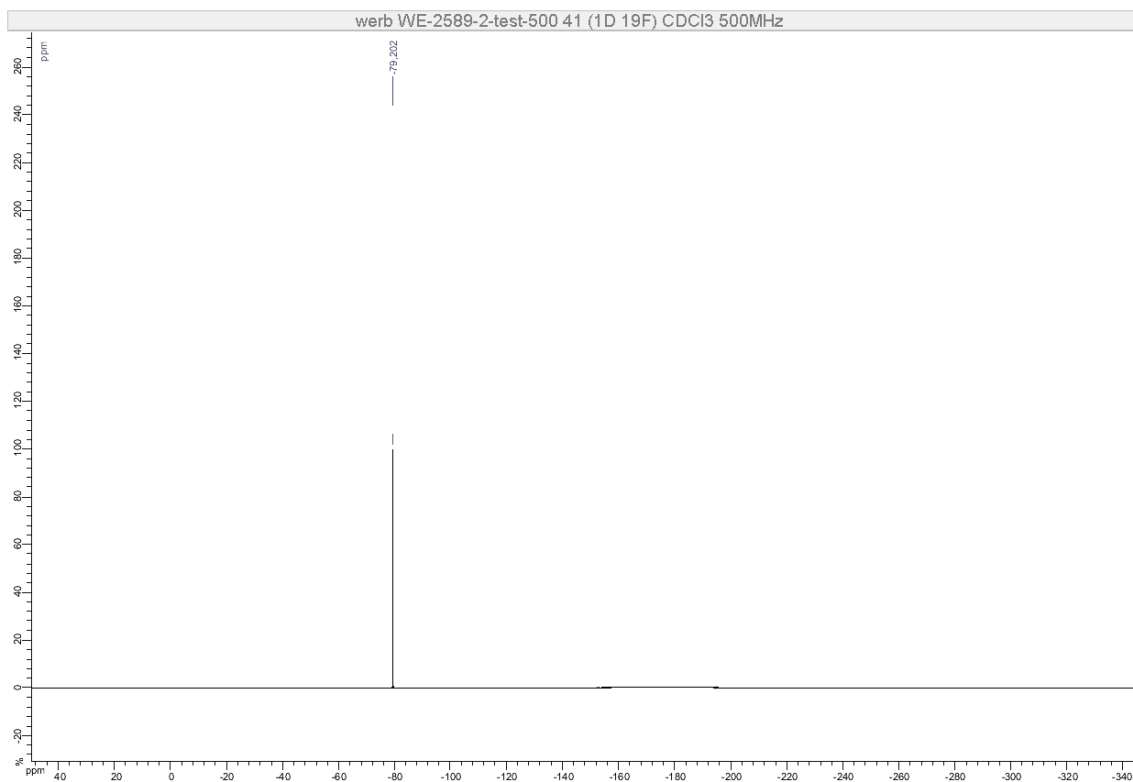
HSQC (500 MHz, CDCl₃)



HMBC (400 MHz, CDCl₃)

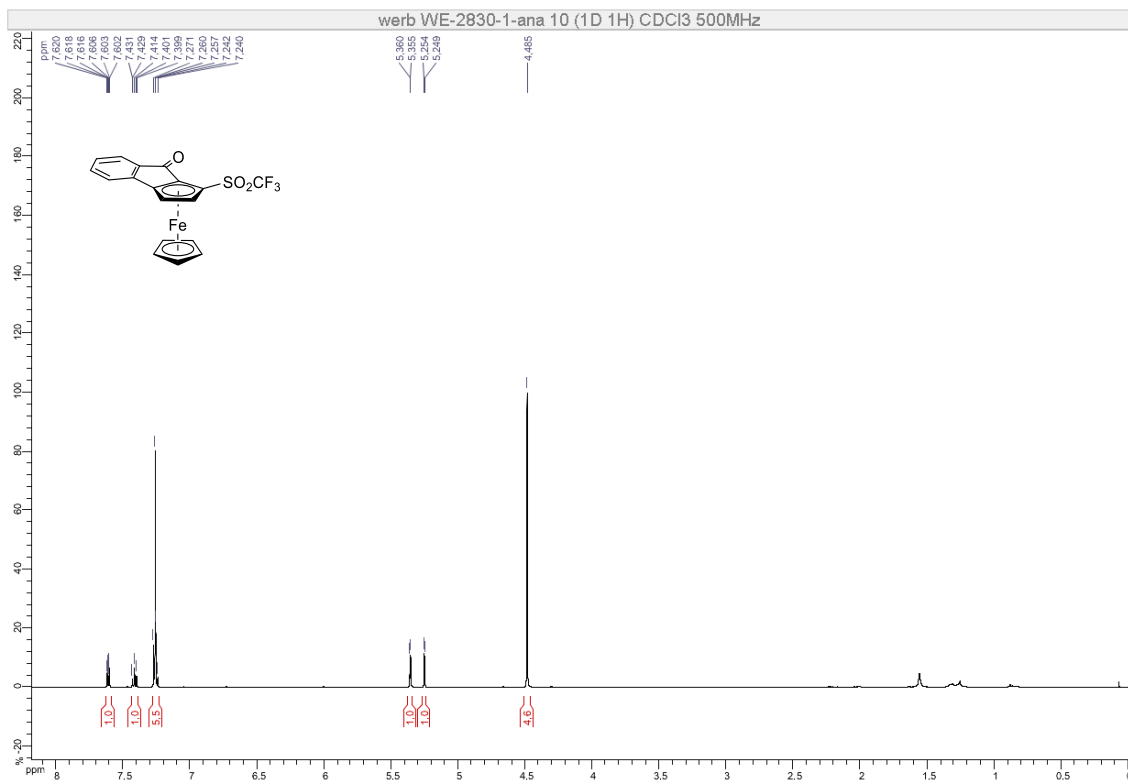


^{19}F NMR (470 MHz, CDCl_3)

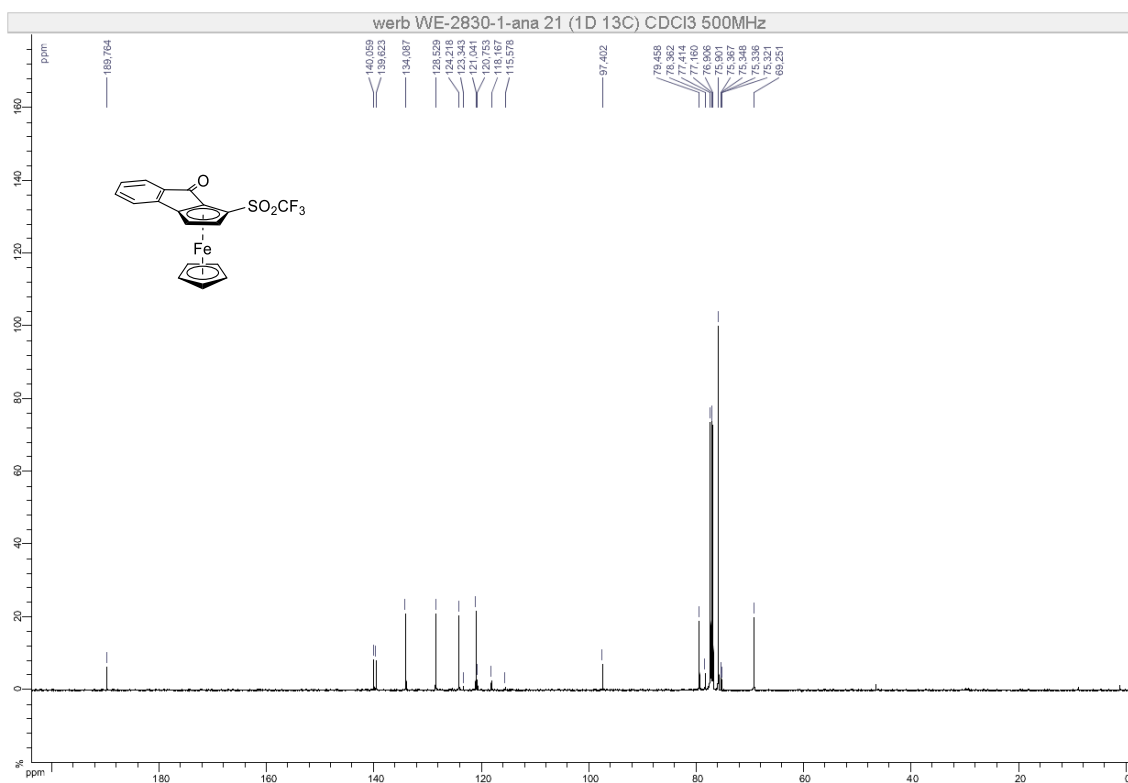


The ferrocenic analogue of fluorenone *Sp*-10

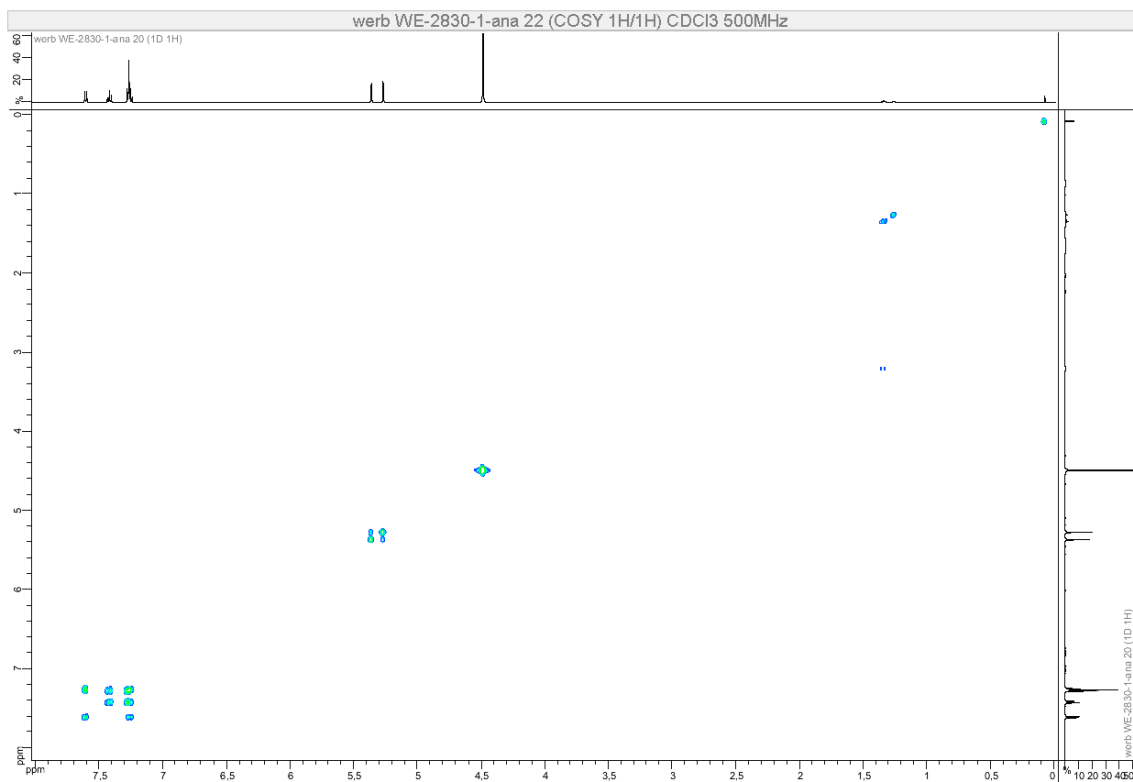
^1H NMR (500 MHz, CDCl_3)



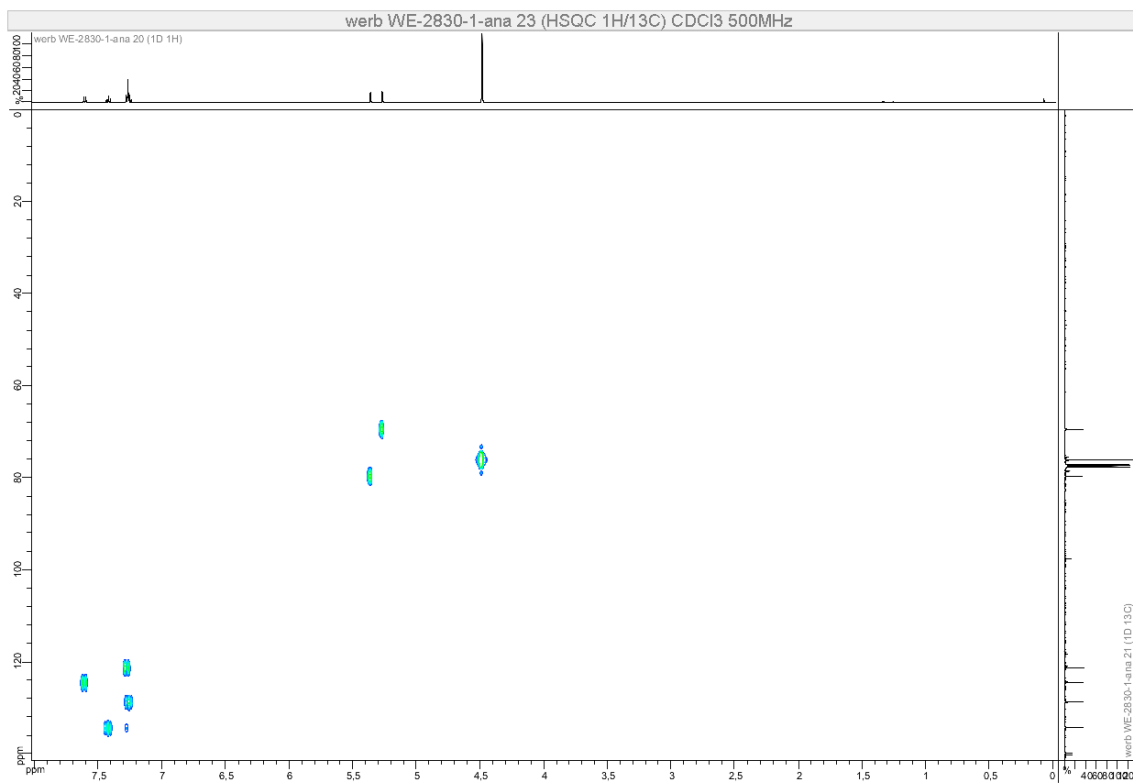
^{13}C NMR (126 MHz, CDCl_3)



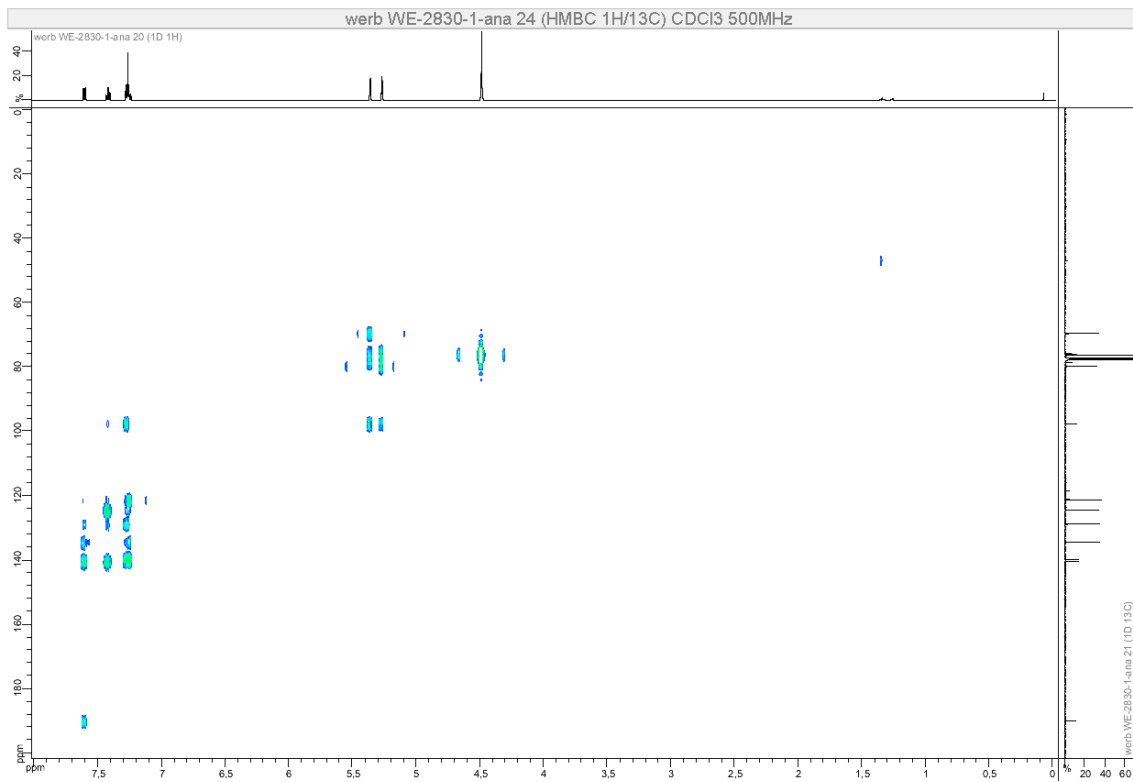
COSY (500 MHz, CDCl₃)



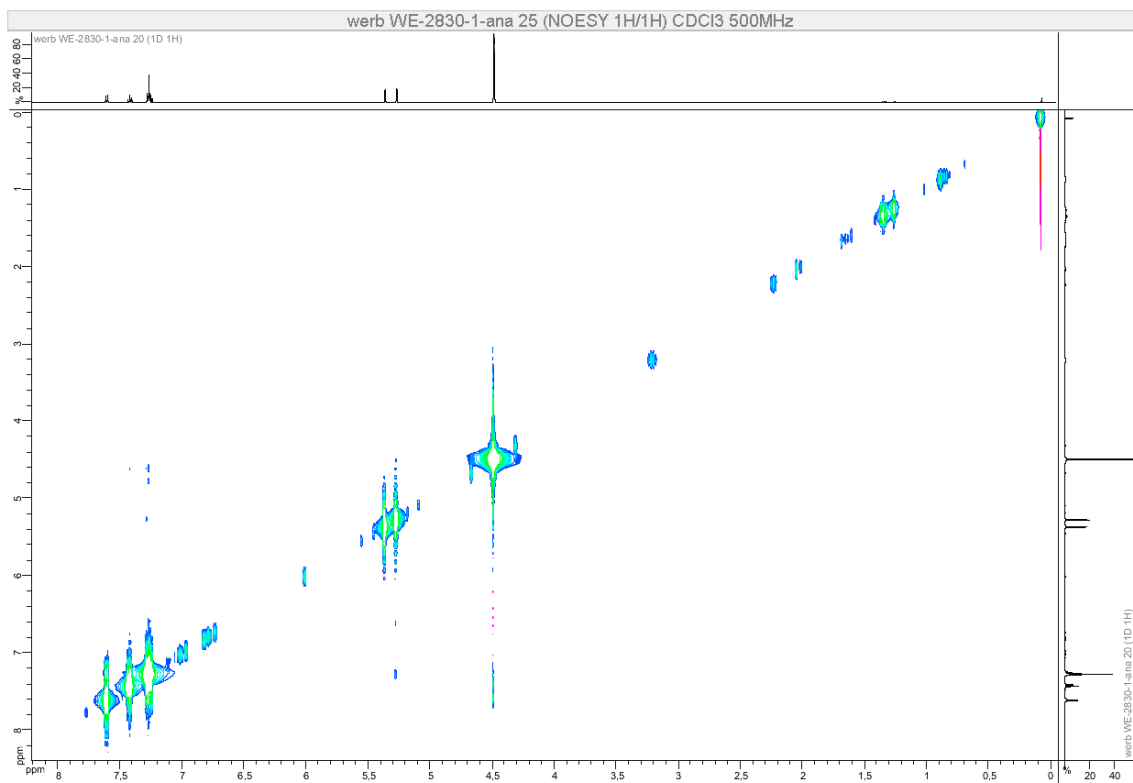
HSQC (500 MHz, CDCl₃)



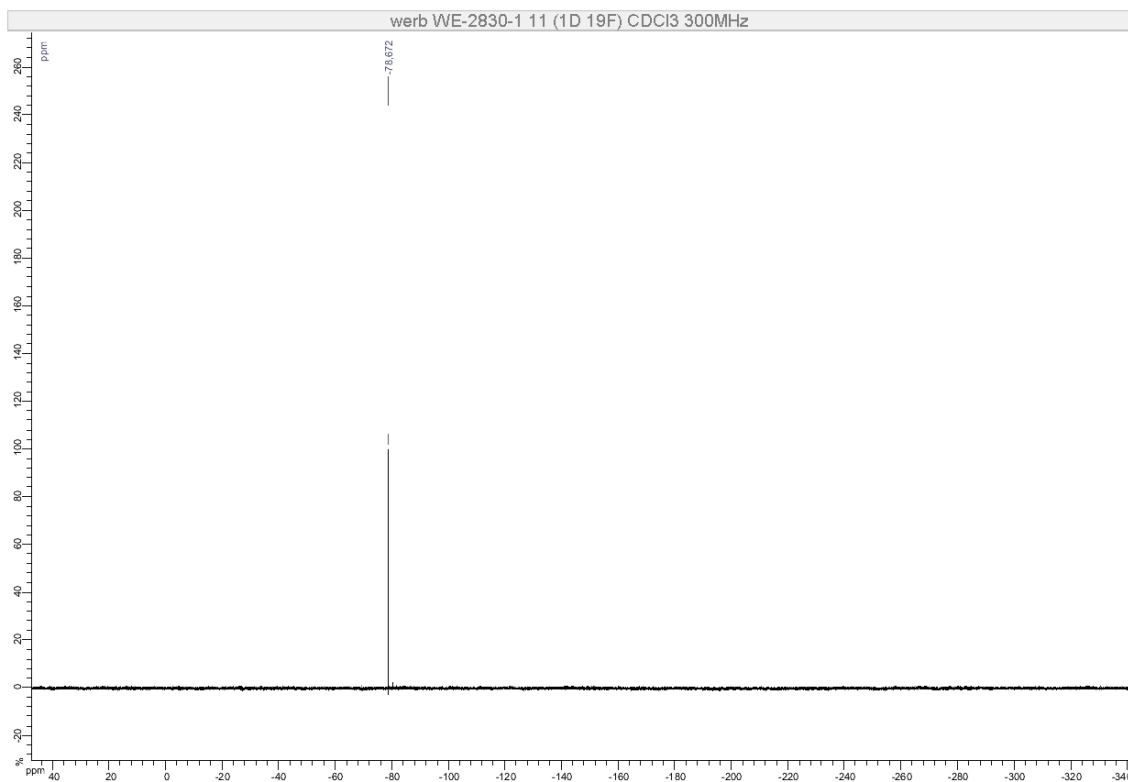
HMBC (500 MHz, CDCl₃)



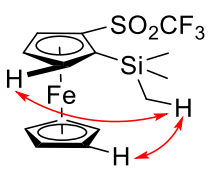
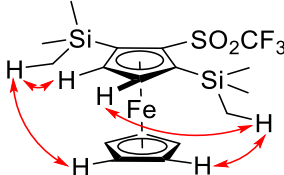
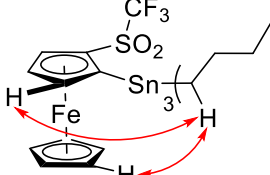
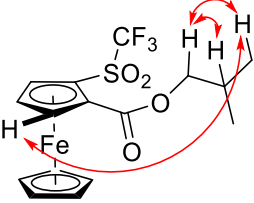
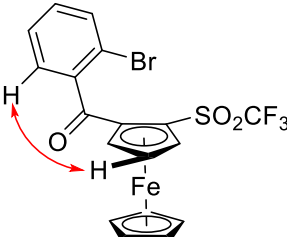
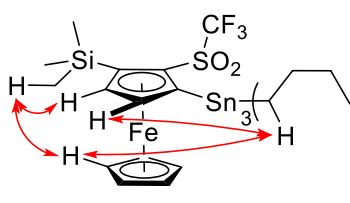
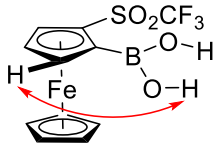
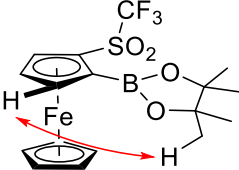
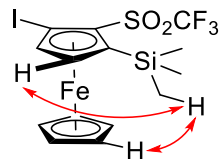
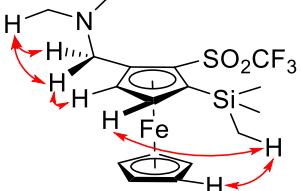
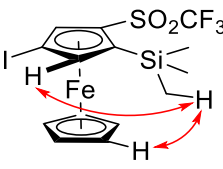
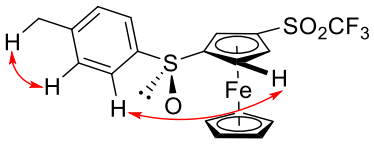
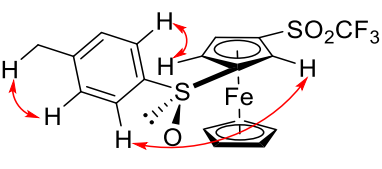
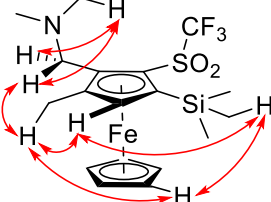
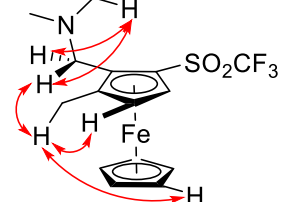
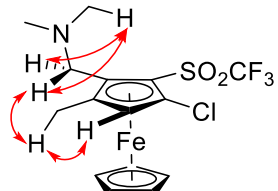
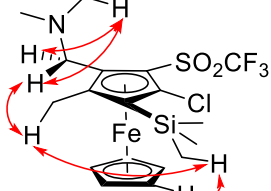
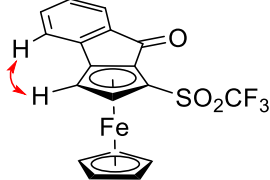
NOESY (500 MHz, CDCl₃)



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

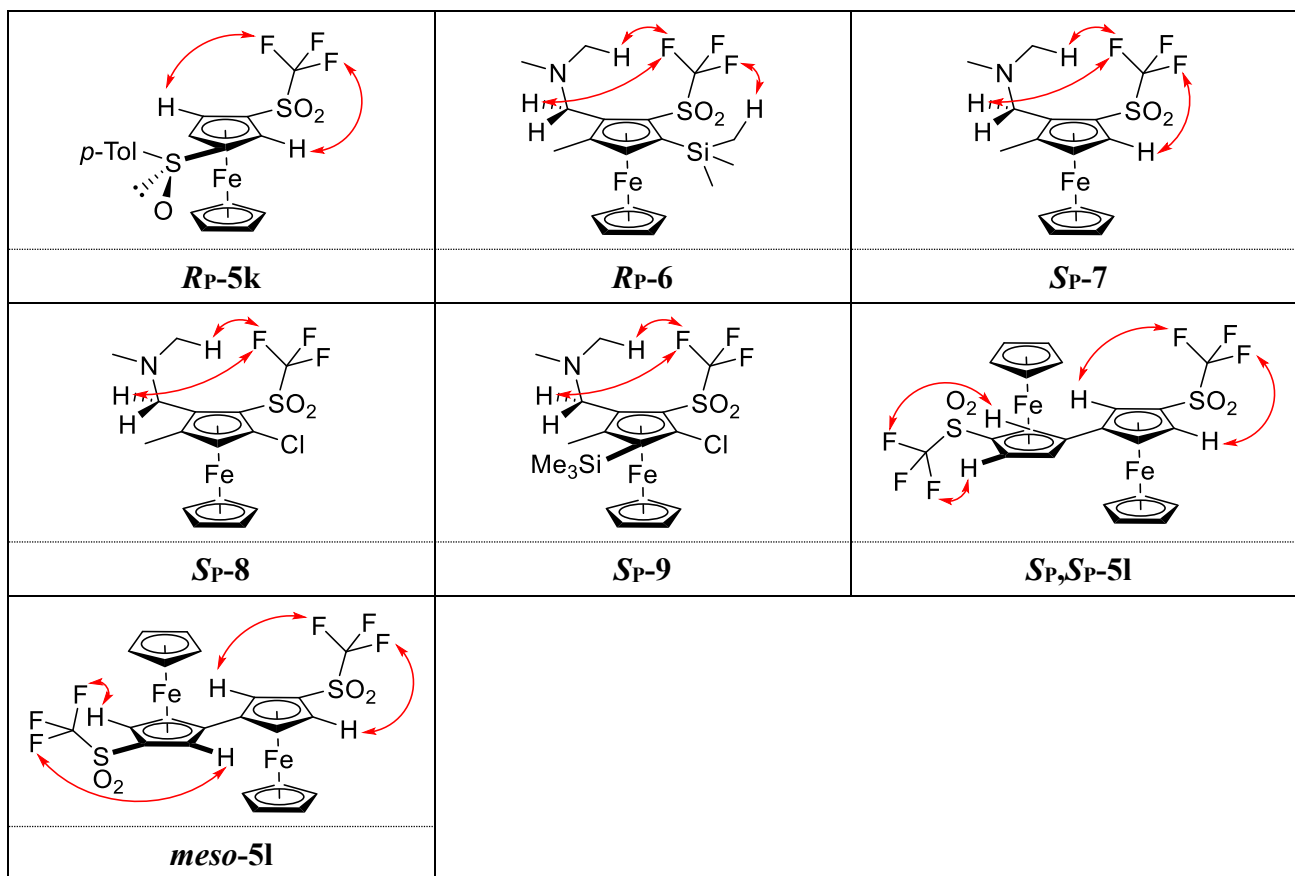


E) Selected NMR NOESY correlations

| | | |
|---|---|---|
|  |  |  |
| Rp-2a | 2aa | 2b |
|  |  |  |
| 2d | Sp-2e | 3ba |
|  |  |  |
| 2g | 2h | Rp-3af |
|  |  |  |
| Rp-3aj | Rp-4af | Sp-5k |
|  |  |  |
| Rp-5k | Rp-6 | Sp-7 |
|  |  |  |
| Sp-8 | Sp-9 | Sp-10 |

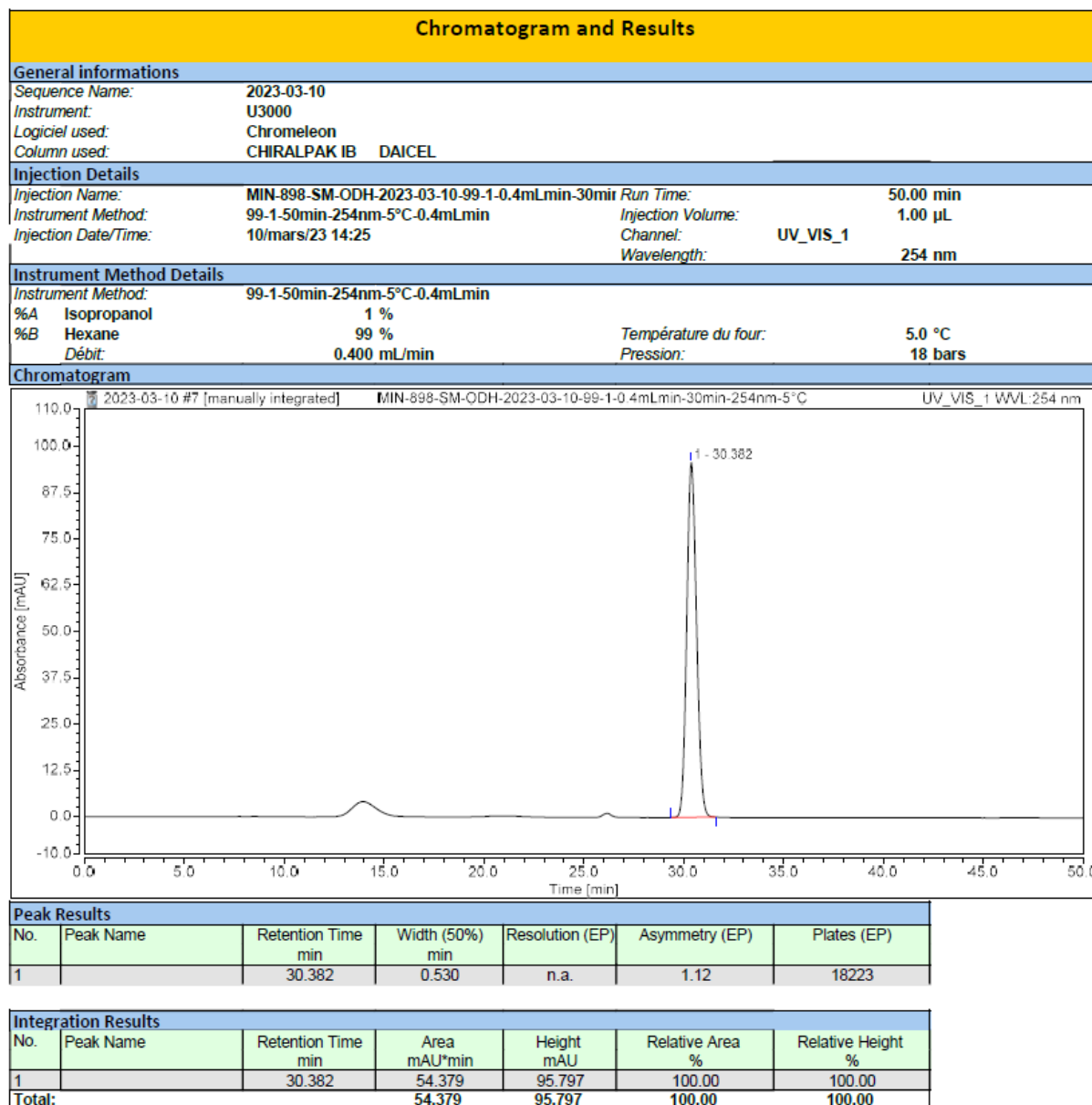
F) Selected NMR HOESY correlations

| | | |
|---------------|---------------|---------------|
| | | |
| 1 | 2aa | Rp-2a |
| | | |
| 2b | 2d | 2f |
| | | |
| 3ba | 2g | 2h |
| | | |
| 2i | Rp-3af | Rp-3aj |
| | | |
| Rp-4af | Rp-5f | Sp-5k |

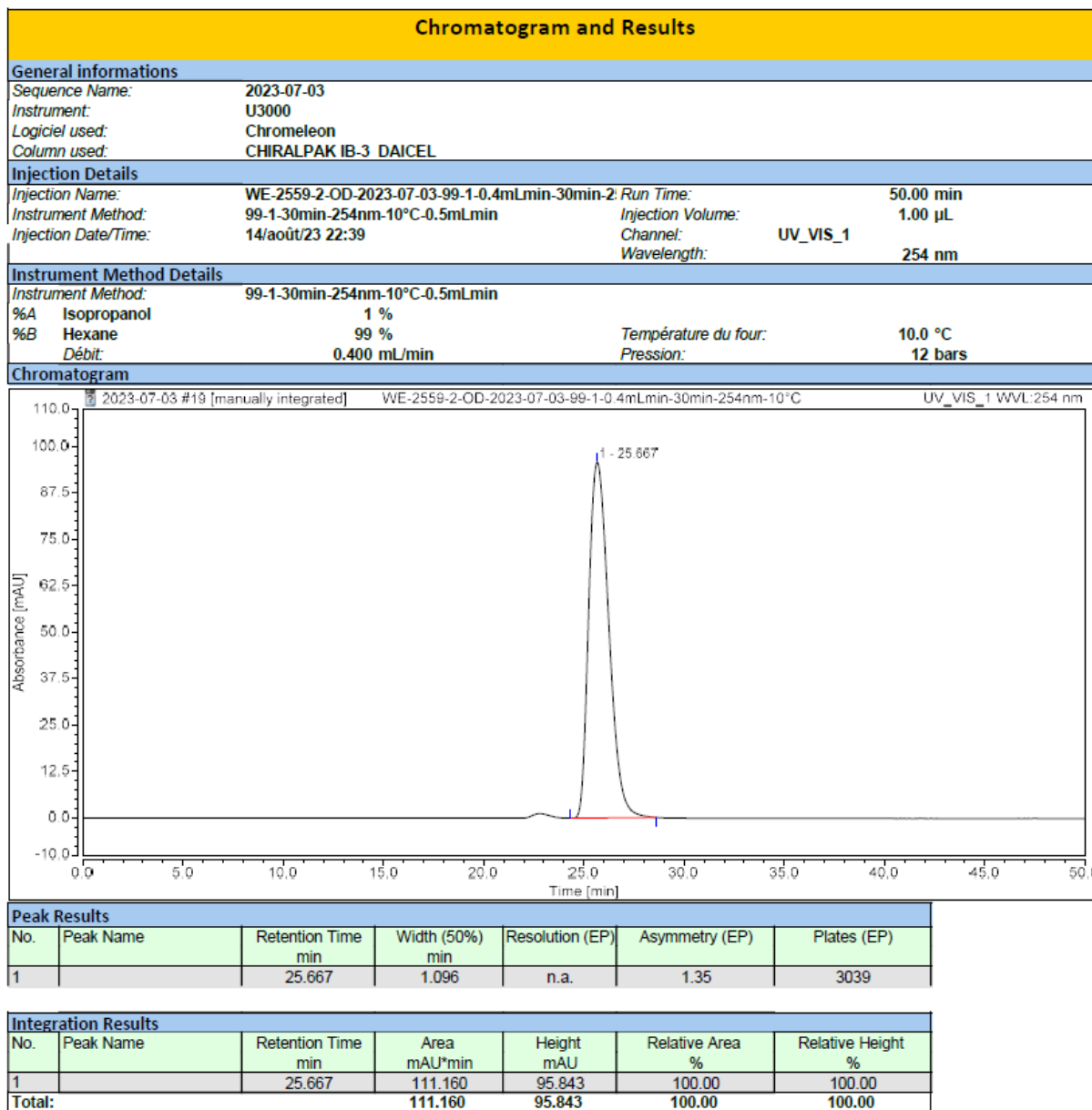


G) HPLC Data

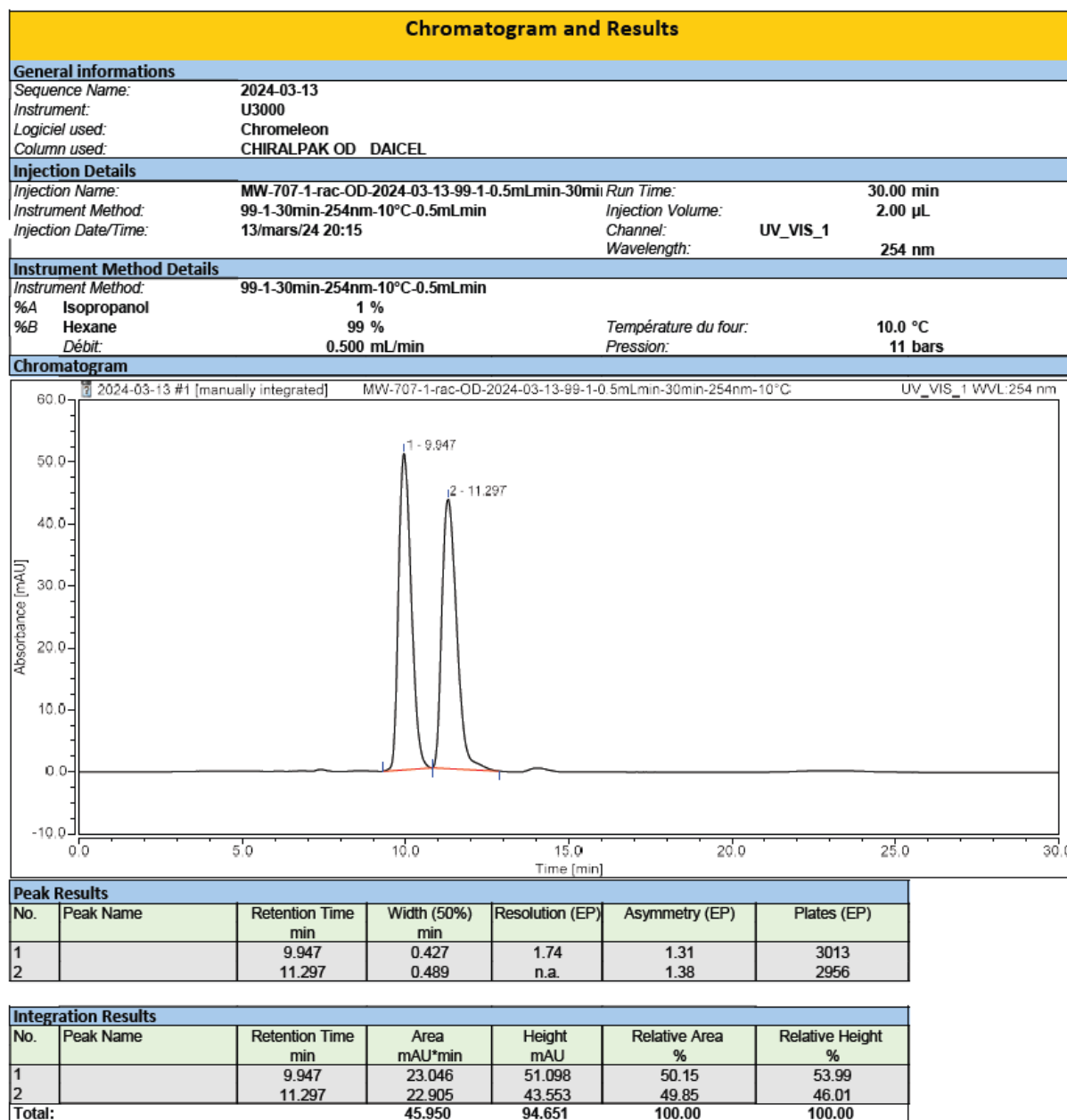
Ferrocenetriflone (1)



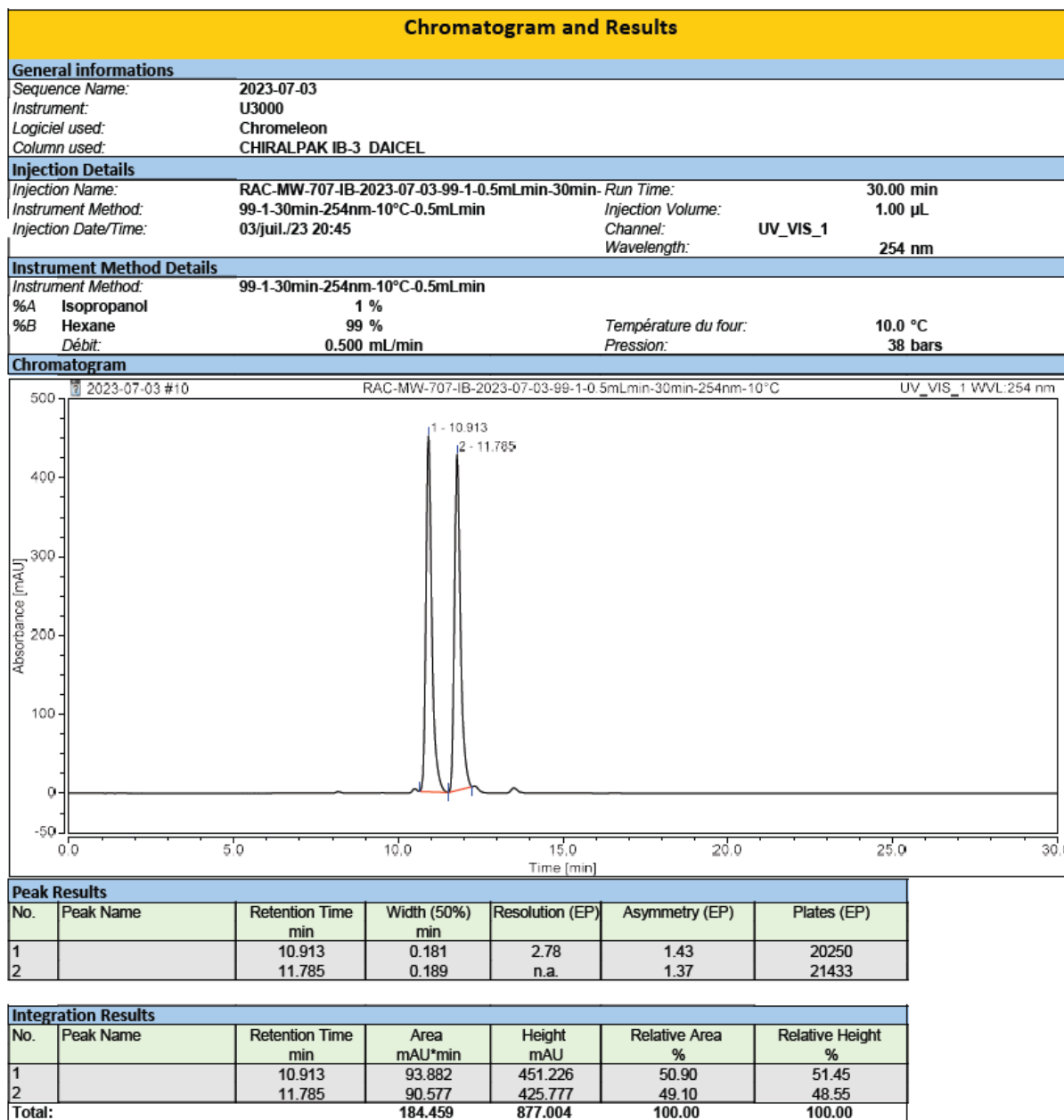
Ferrocenetriflone (1)



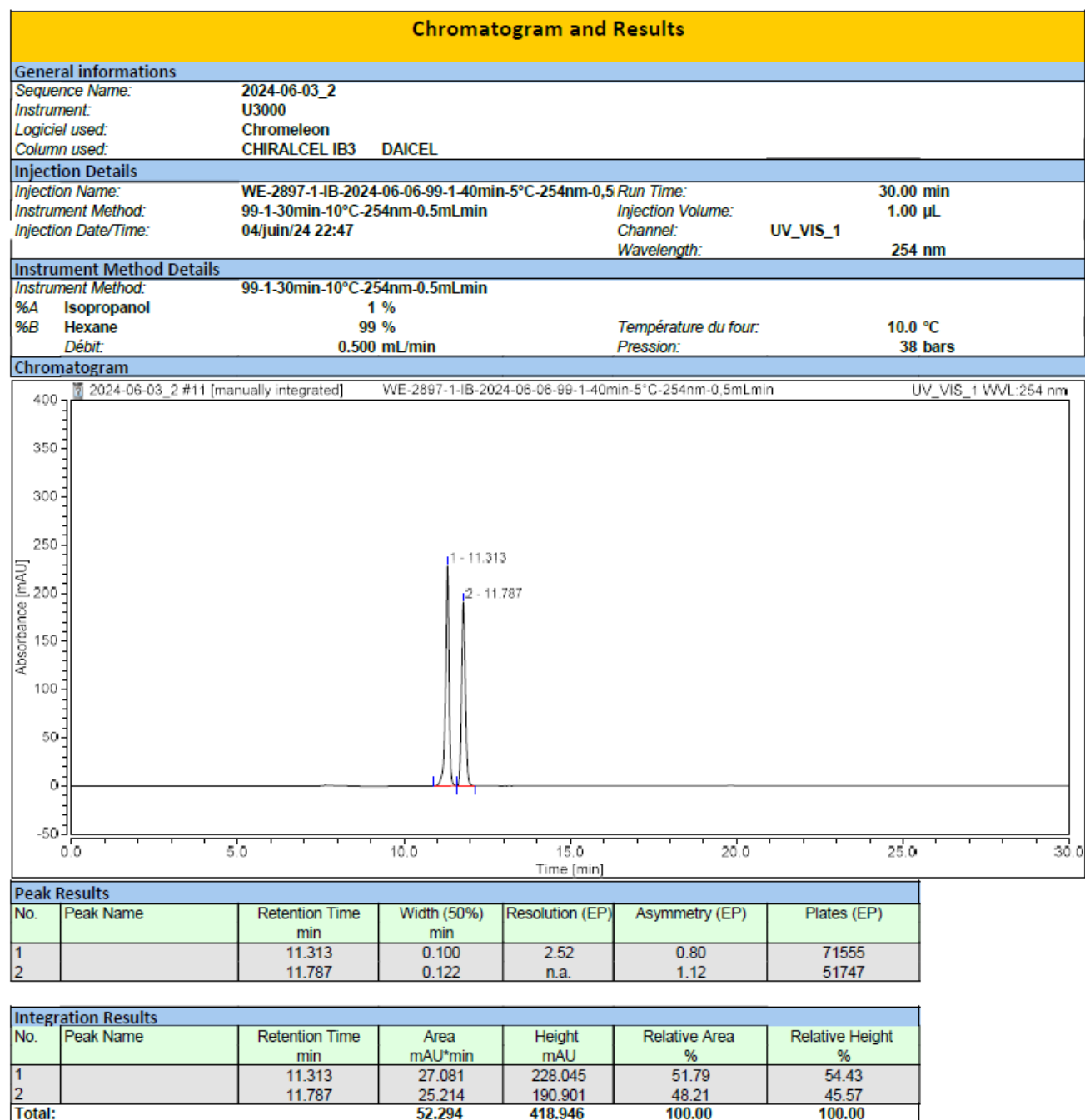
(±)-2-(Trimethylsilyl)ferrocenetriflone (*rac*-2a)



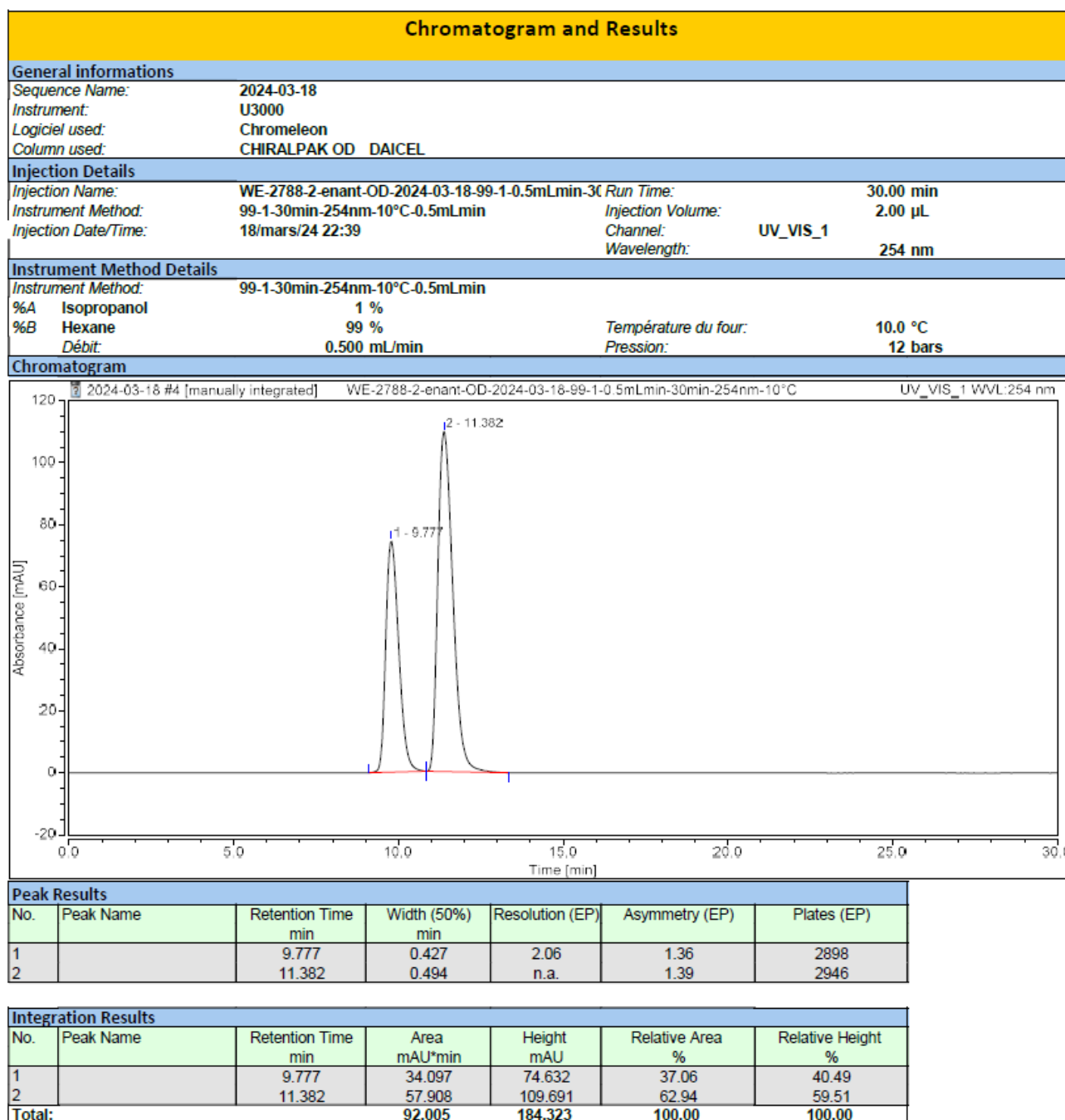
(±)-2-(Trimethylsilyl)ferrocenetriflone (*rac*-2a)



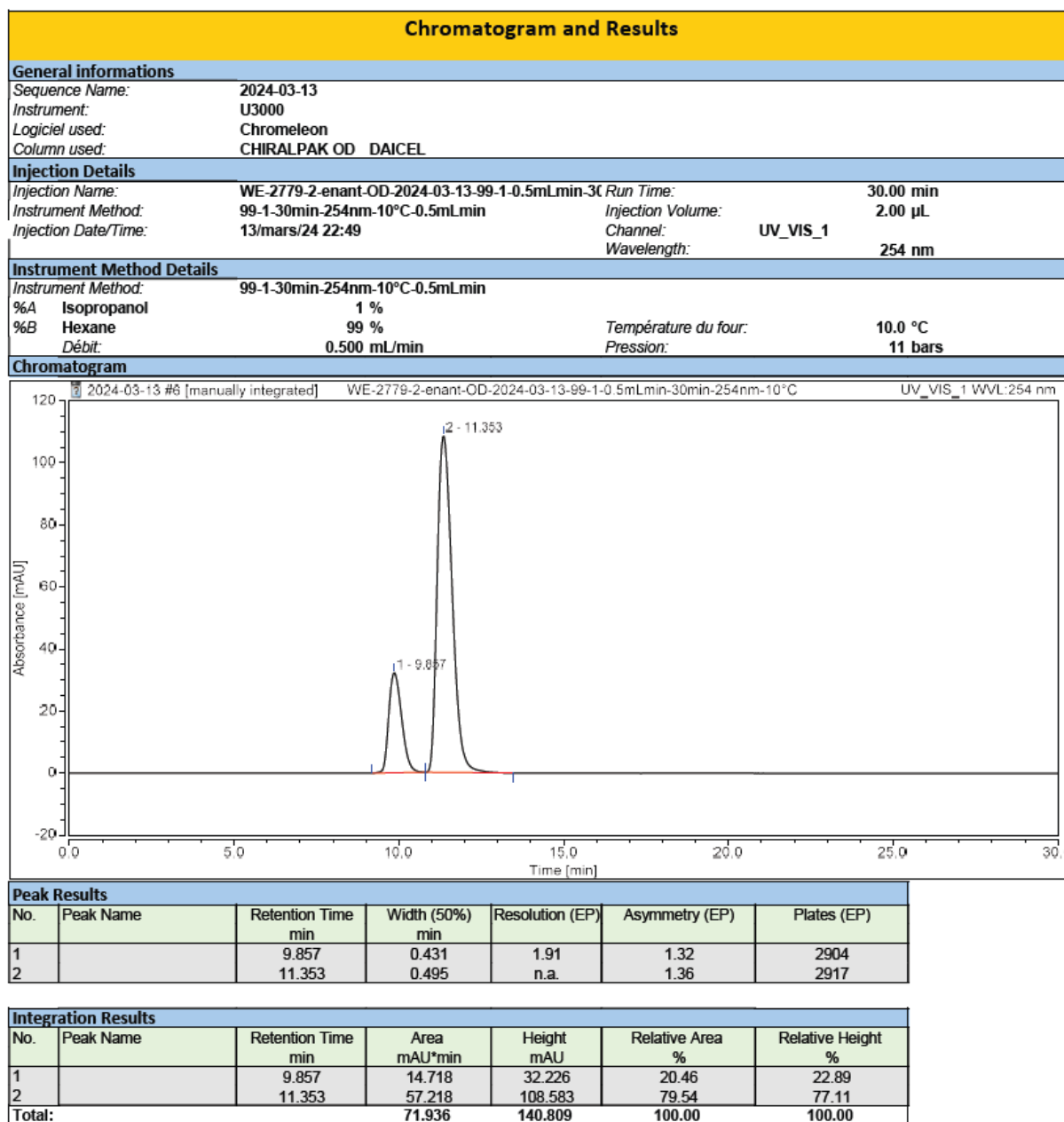
Deprotonation of 1 using BuLi(*R*)-TMCDA (1:1) using Me₃SiCl as the electrophile



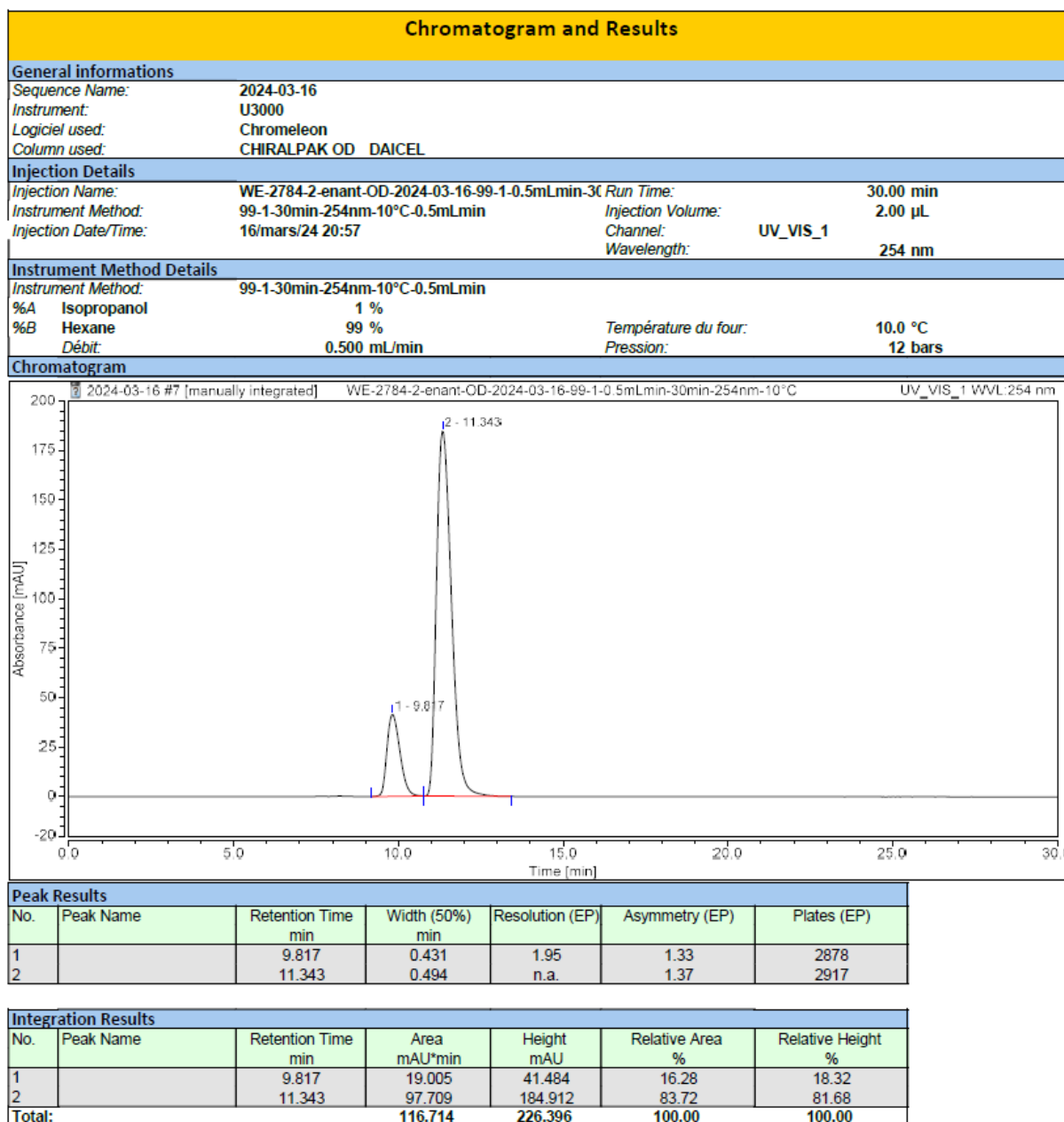
Deprotonation of 1 using BuLi(+)-sparteine (1:1) in Et₂O at -80 °C and Me₃SiCl as the electrophile



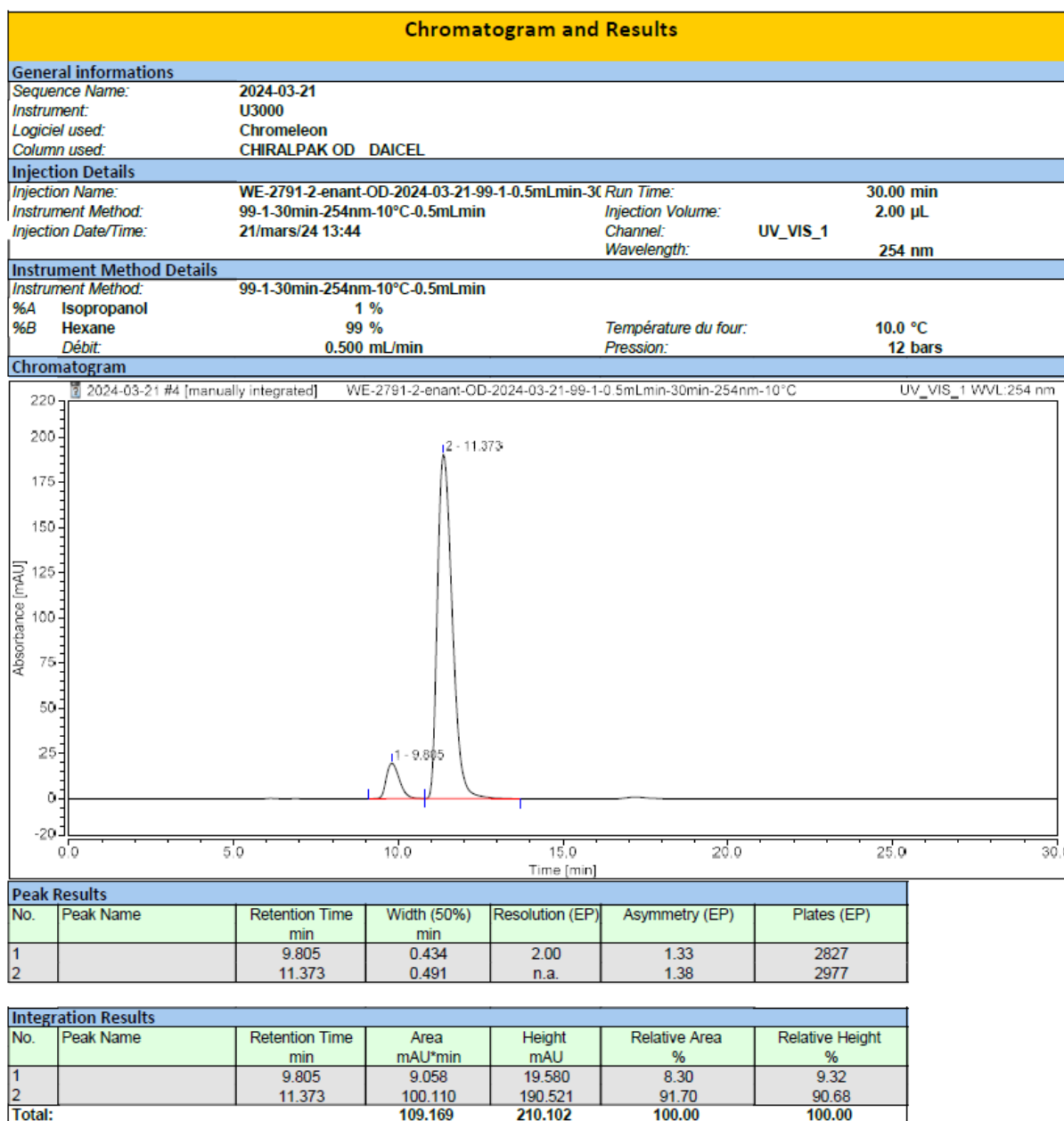
Deprotonation of 1 using *s*BuLi(+)-sparteine (1:1) in Et₂O at –80 °C and Me₃SiCl as the electrophile



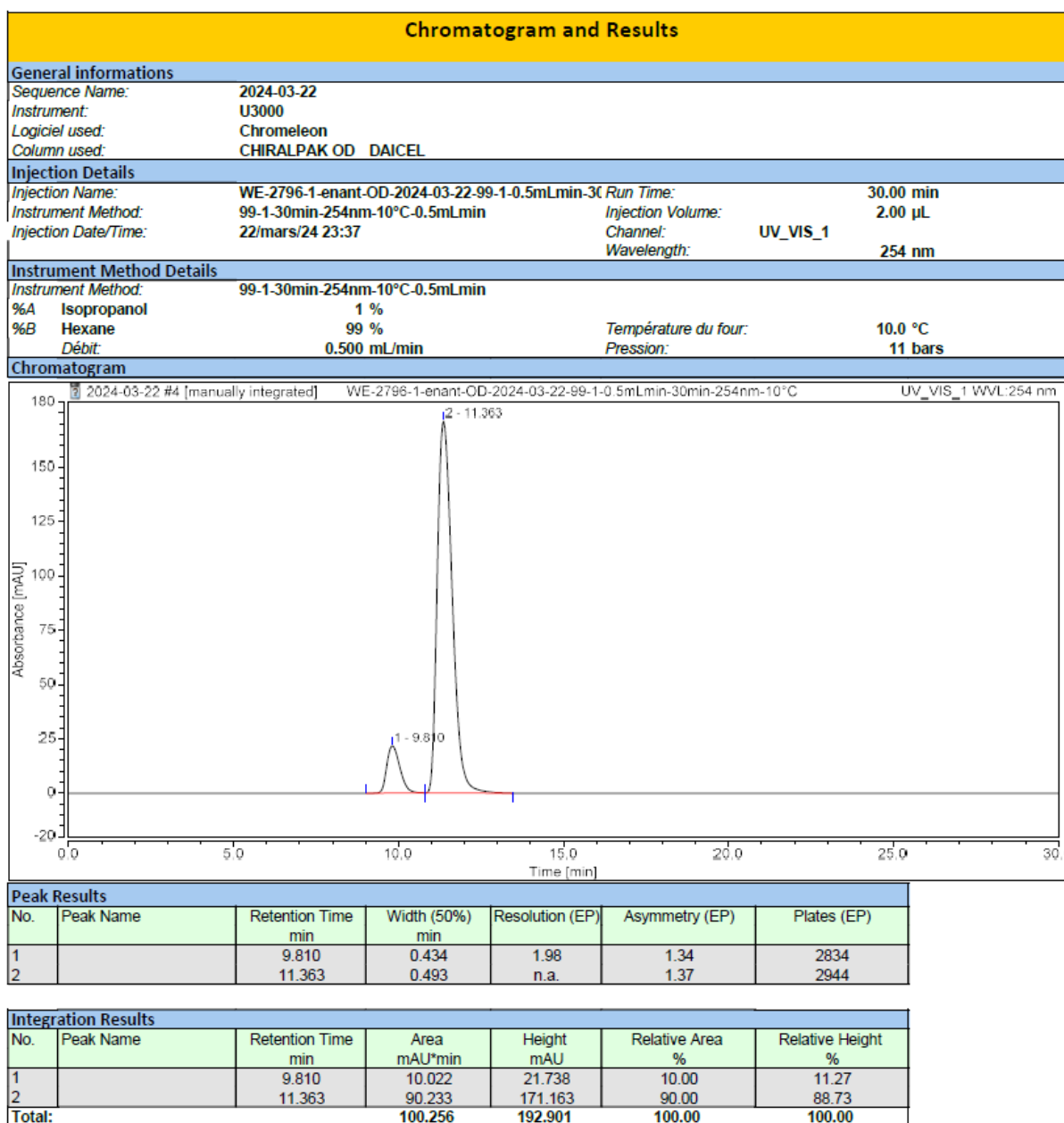
Deprotonation of 1 using *s*BuLi(+)-sparteine (1:1) in TBME at $-80\text{ }^{\circ}\text{C}$ and Me_3SiCl as the electrophile



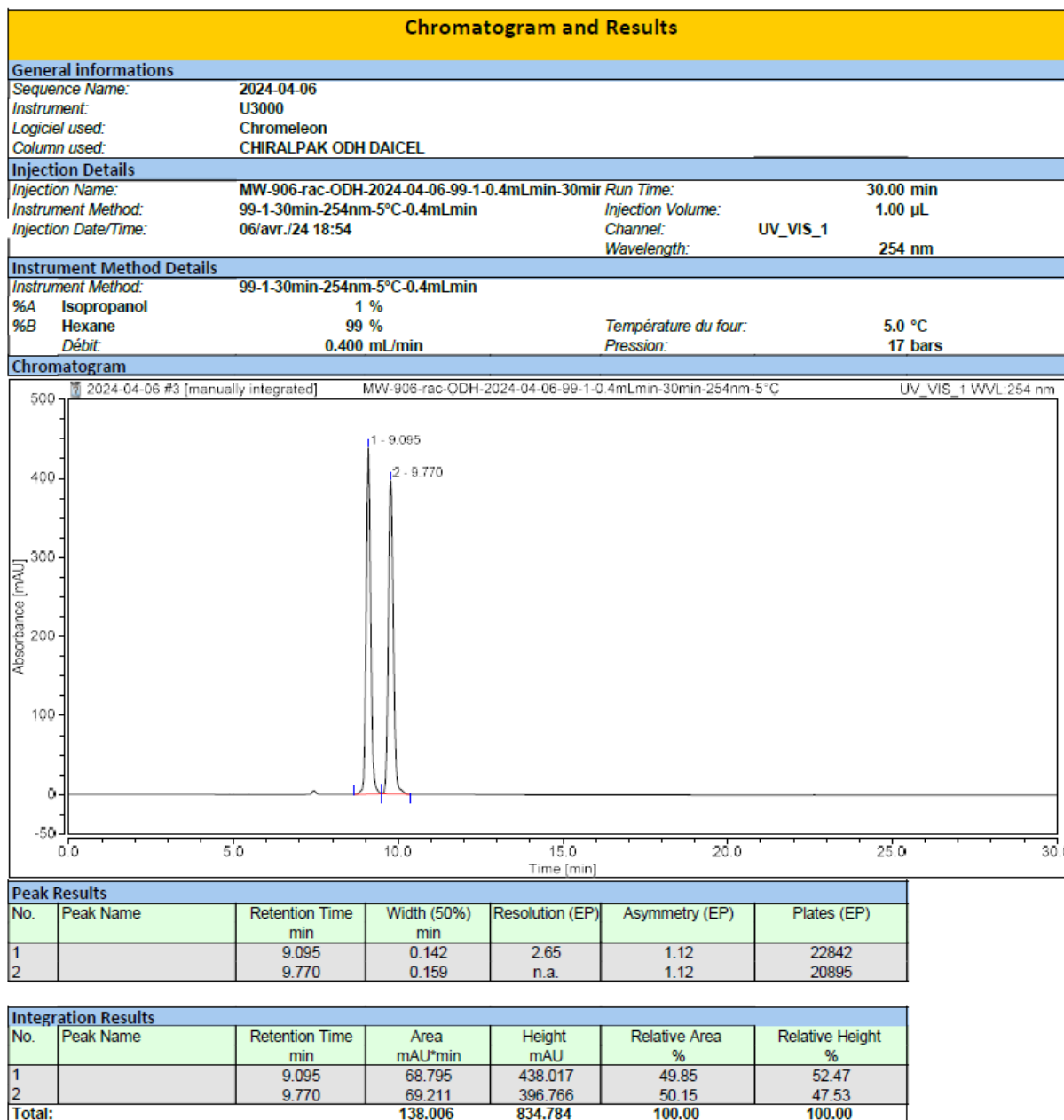
Deprotonation of 1 using *s*BuLi(+)-sparteine (1:1) in TBME at $-100\text{ }^{\circ}\text{C}$ and Me_3SiCl as the electrophile



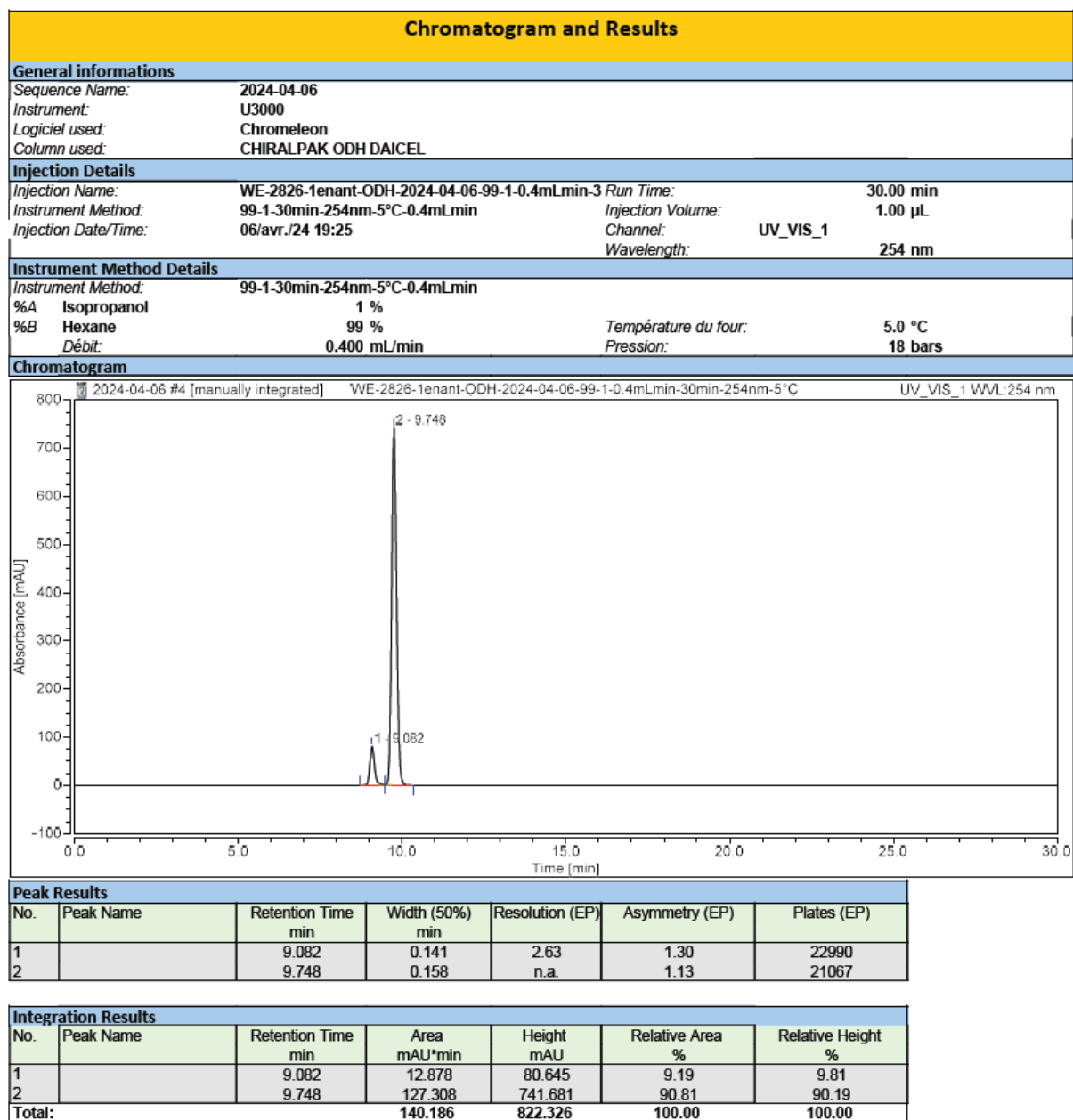
Deprotonation of 1 using *s*BuLi(+)-sparteine (1:0.4) in TBME at $-100\text{ }^{\circ}\text{C}$ and Me_3SiCl as the electrophile



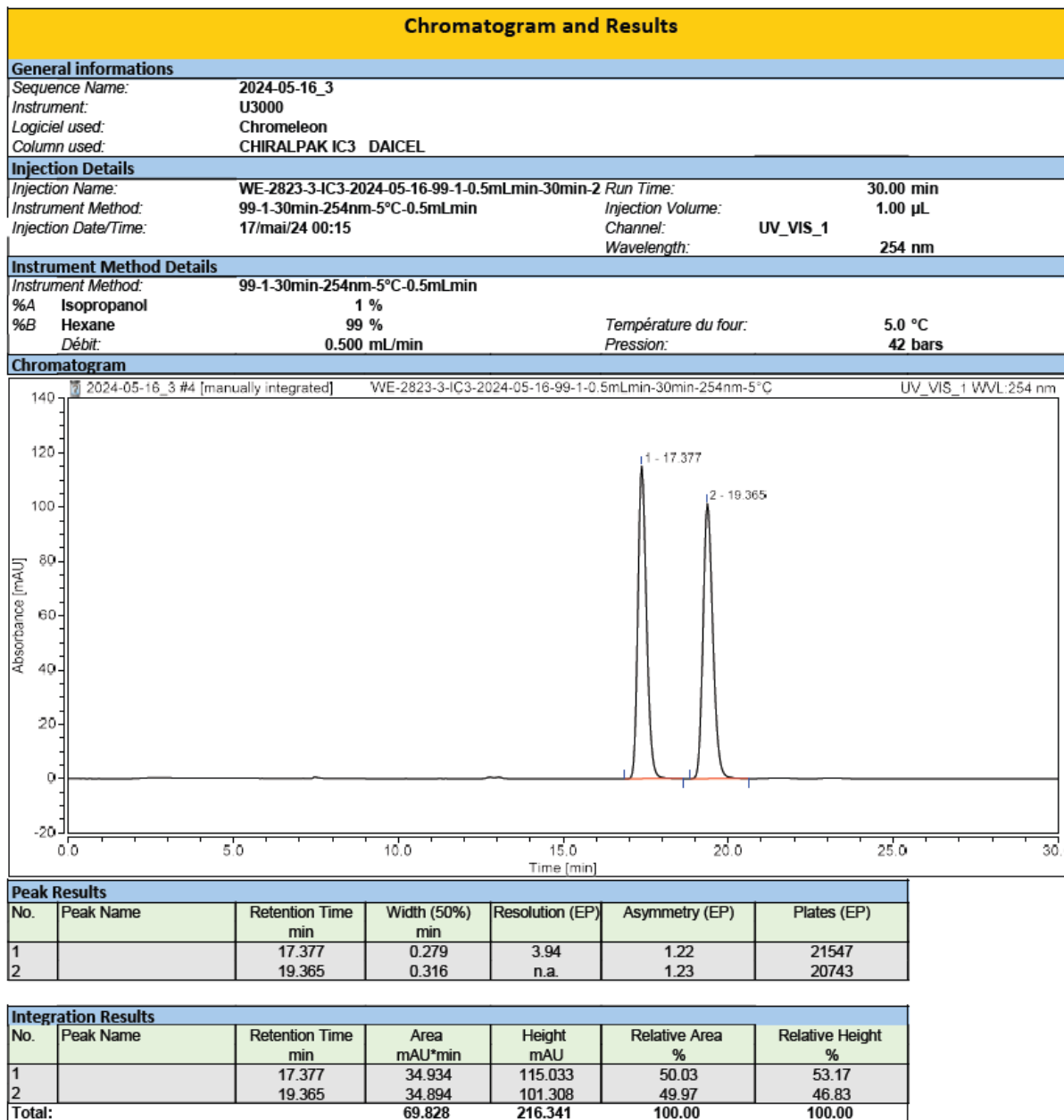
(±)-2-(Tributylstannyl)ferrocenetriflone (*rac*-2b)



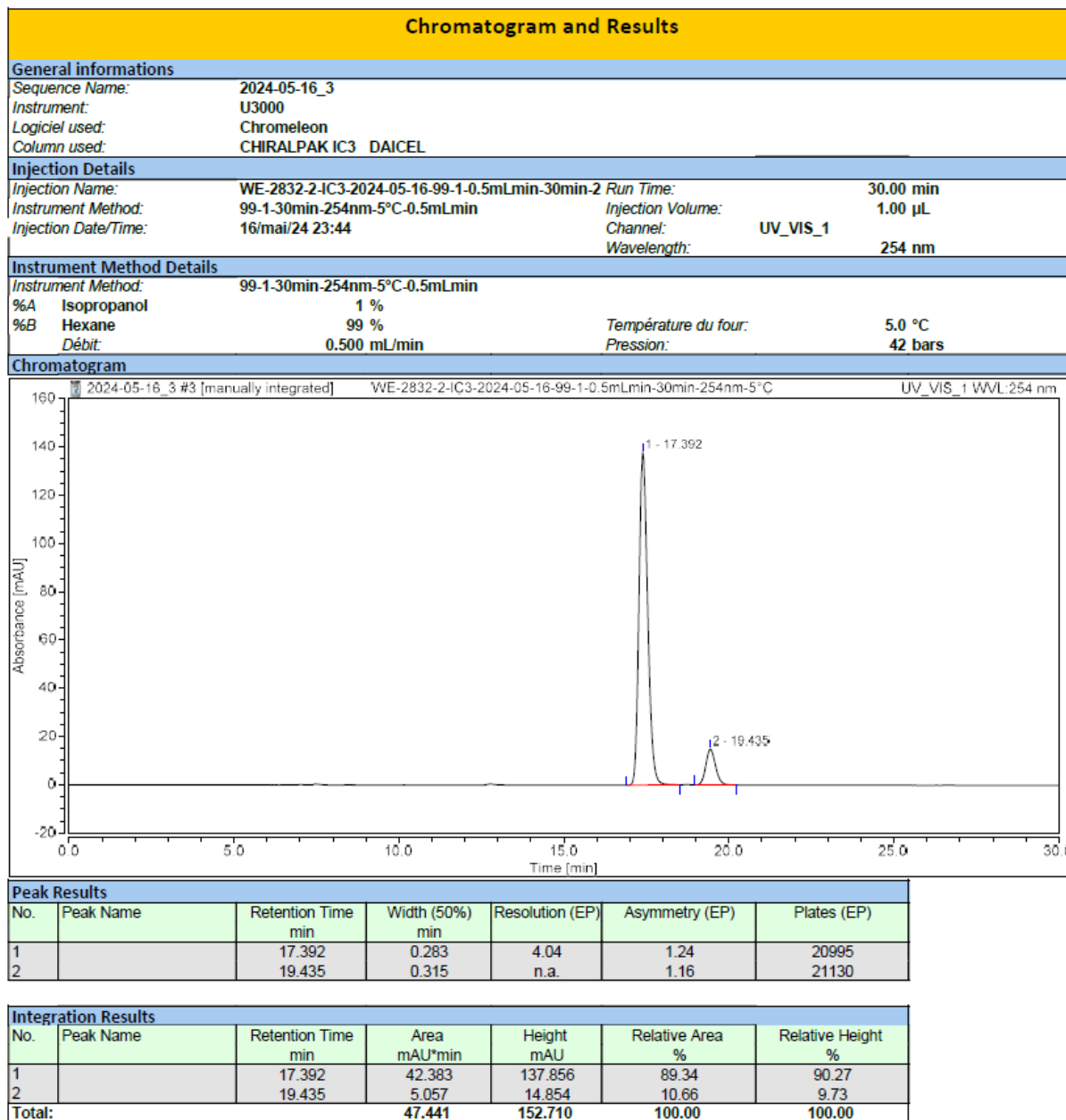
Deprotonation of 1 with *s*BuLi(+)-sparteine using Bu₃SnCl as the electrophile



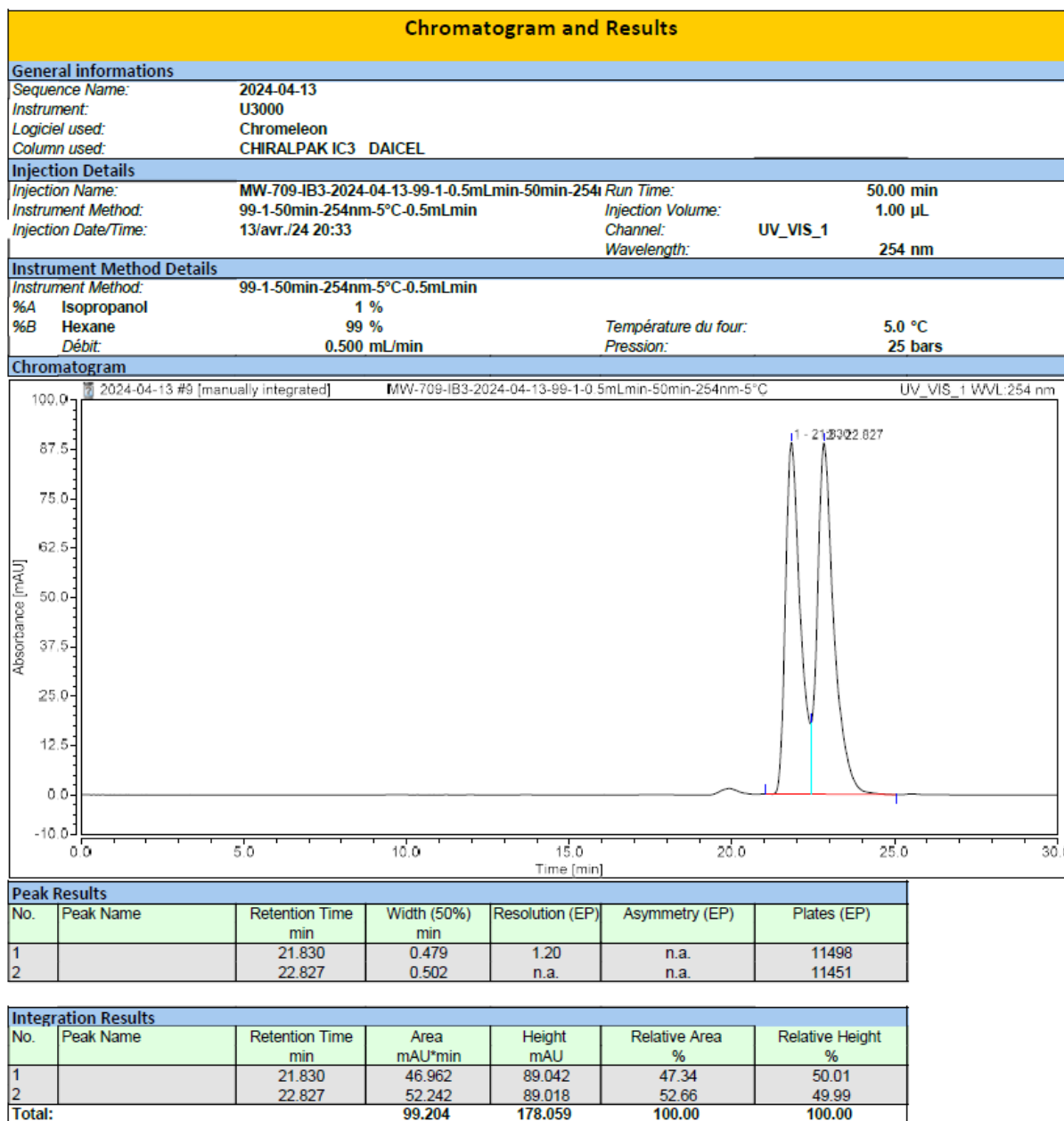
(±)-2-Fluoroferrocenetriflone (*rac*-2c)



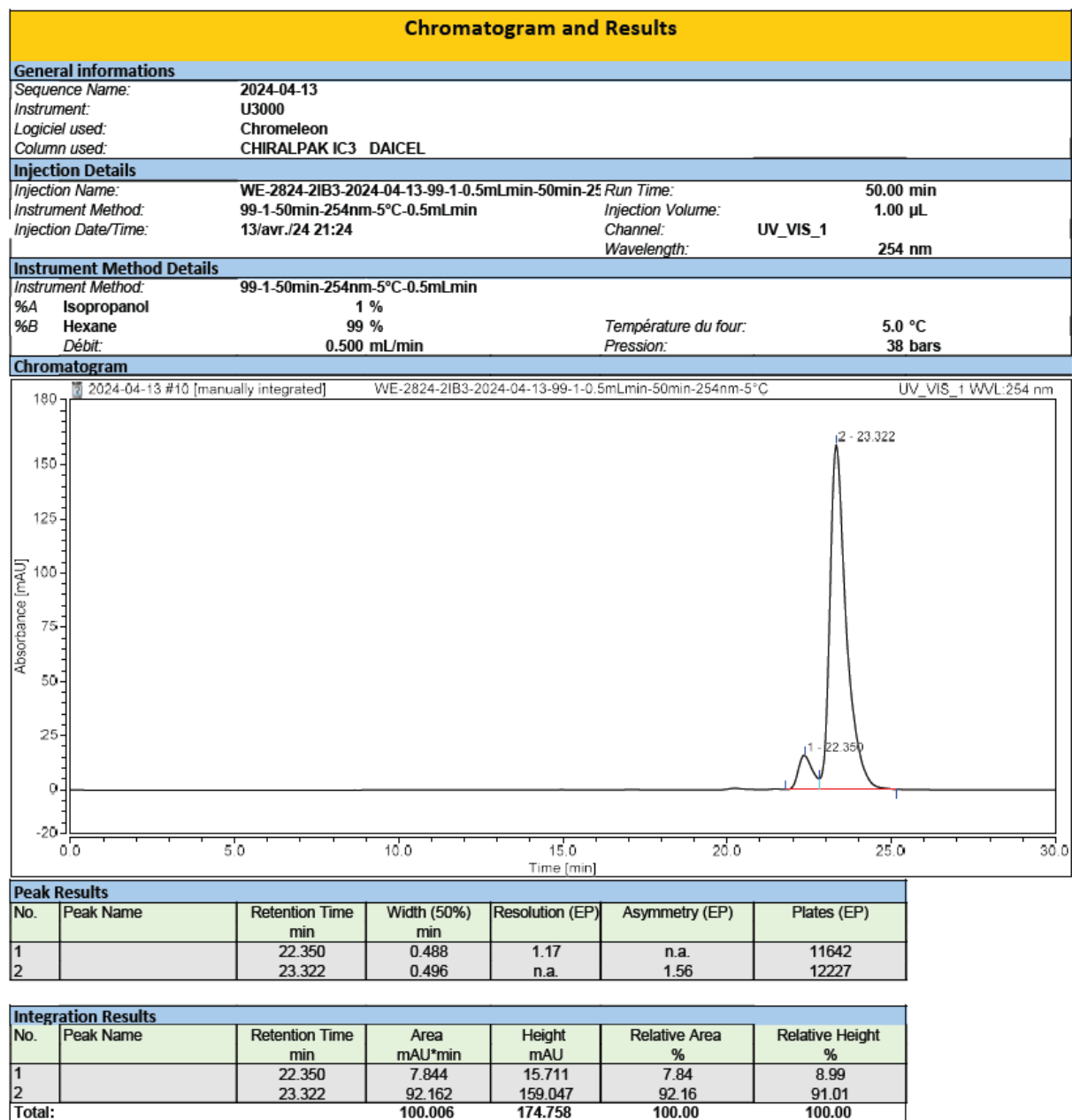
Deprotonation of 1 with *s*BuLi(+)-sparteine using NFSI as the electrophile



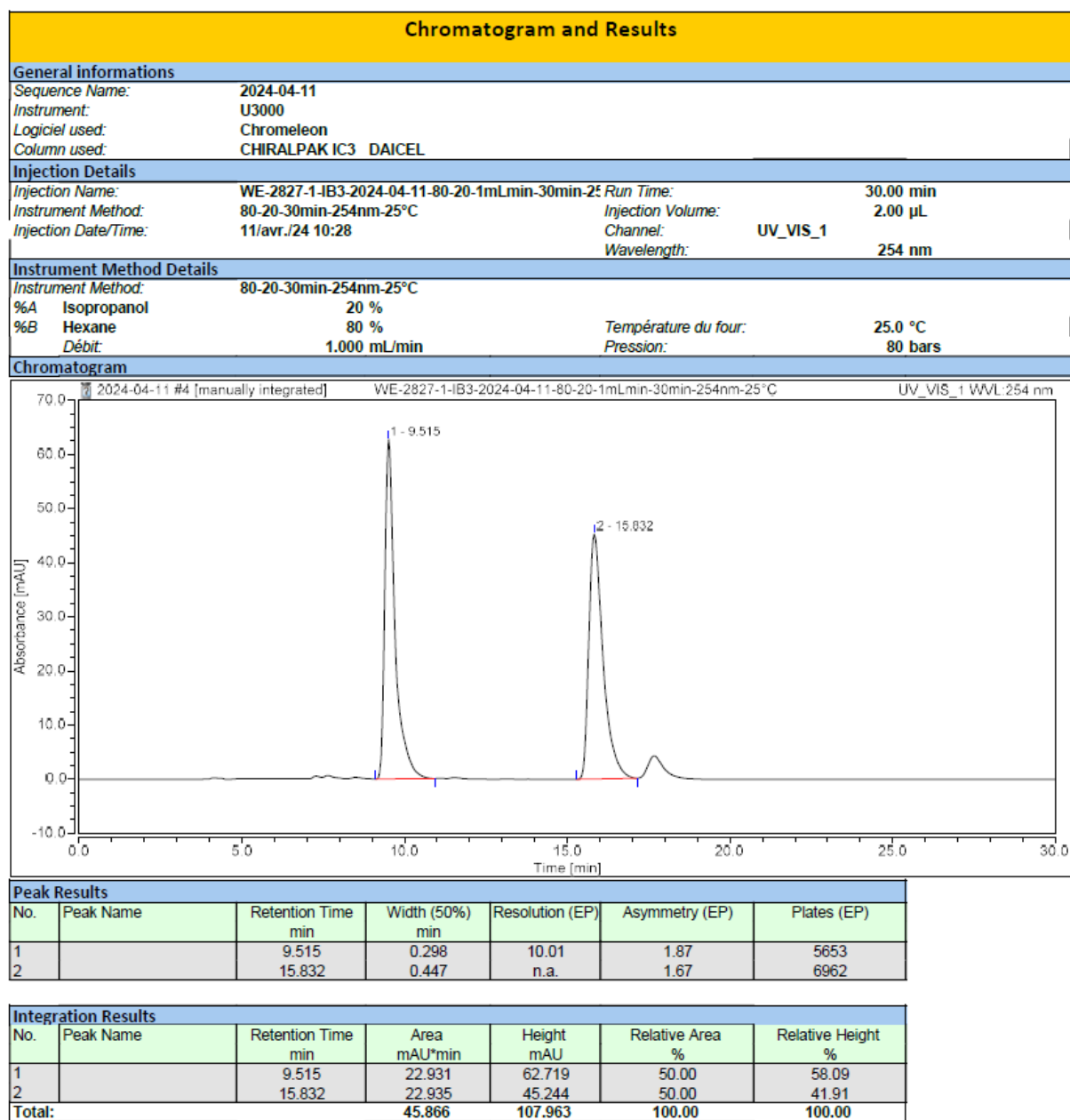
(±)-2-(Isobutoxycarbonyl)ferrocenetriflone (*rac*-2d)



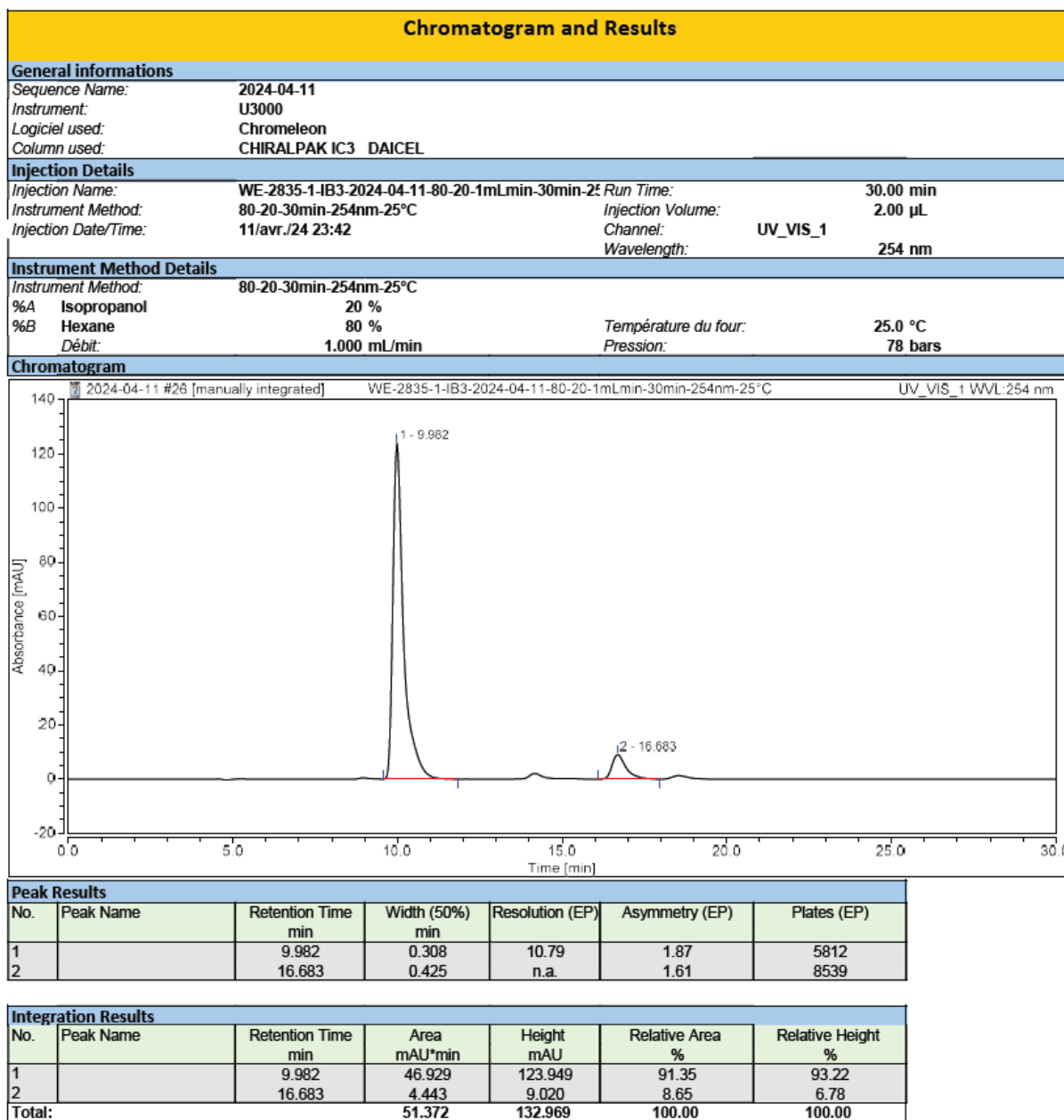
Deprotonation of 1 with *s*BuLi(+)-sparteine using ClCO₂iBu as the electrophile



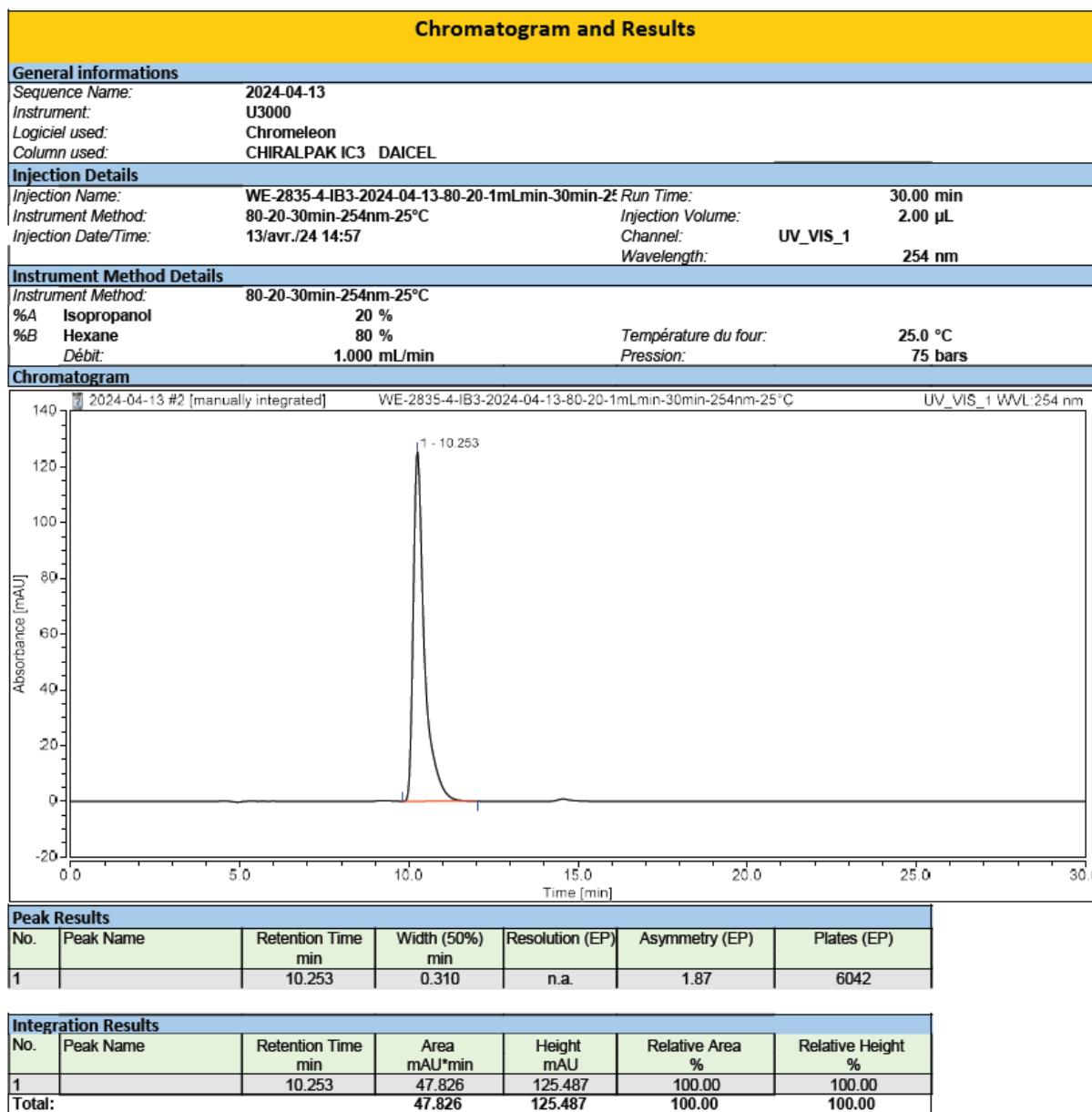
(±)-2-(2-Bromobenzoyl)ferrocenetriflone (*rac*-2e)



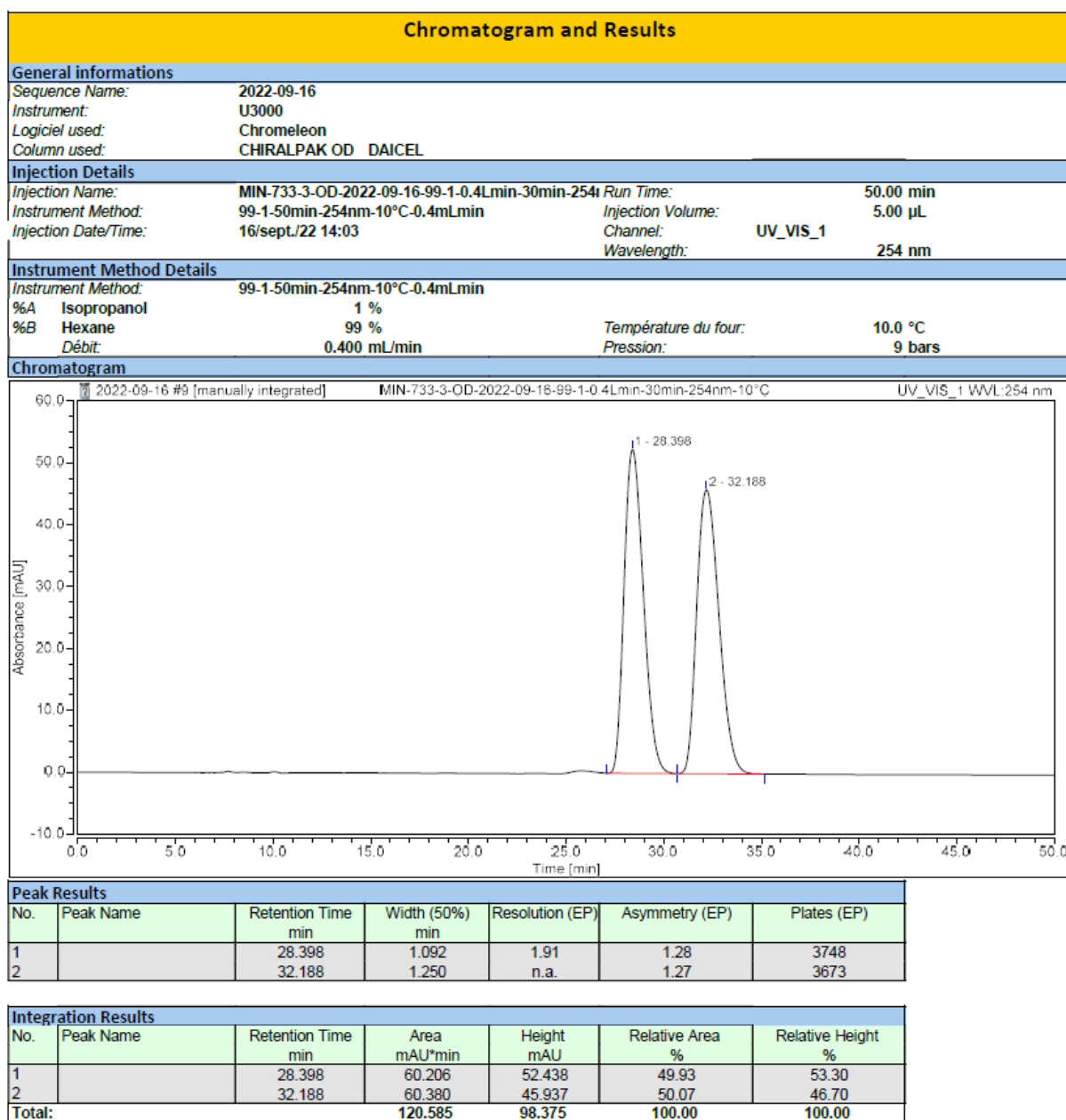
Deprotonation of 1 with *s*BuLi(+)-sparteine using 2-BrC₆H₄C(O)Cl as the electrophile



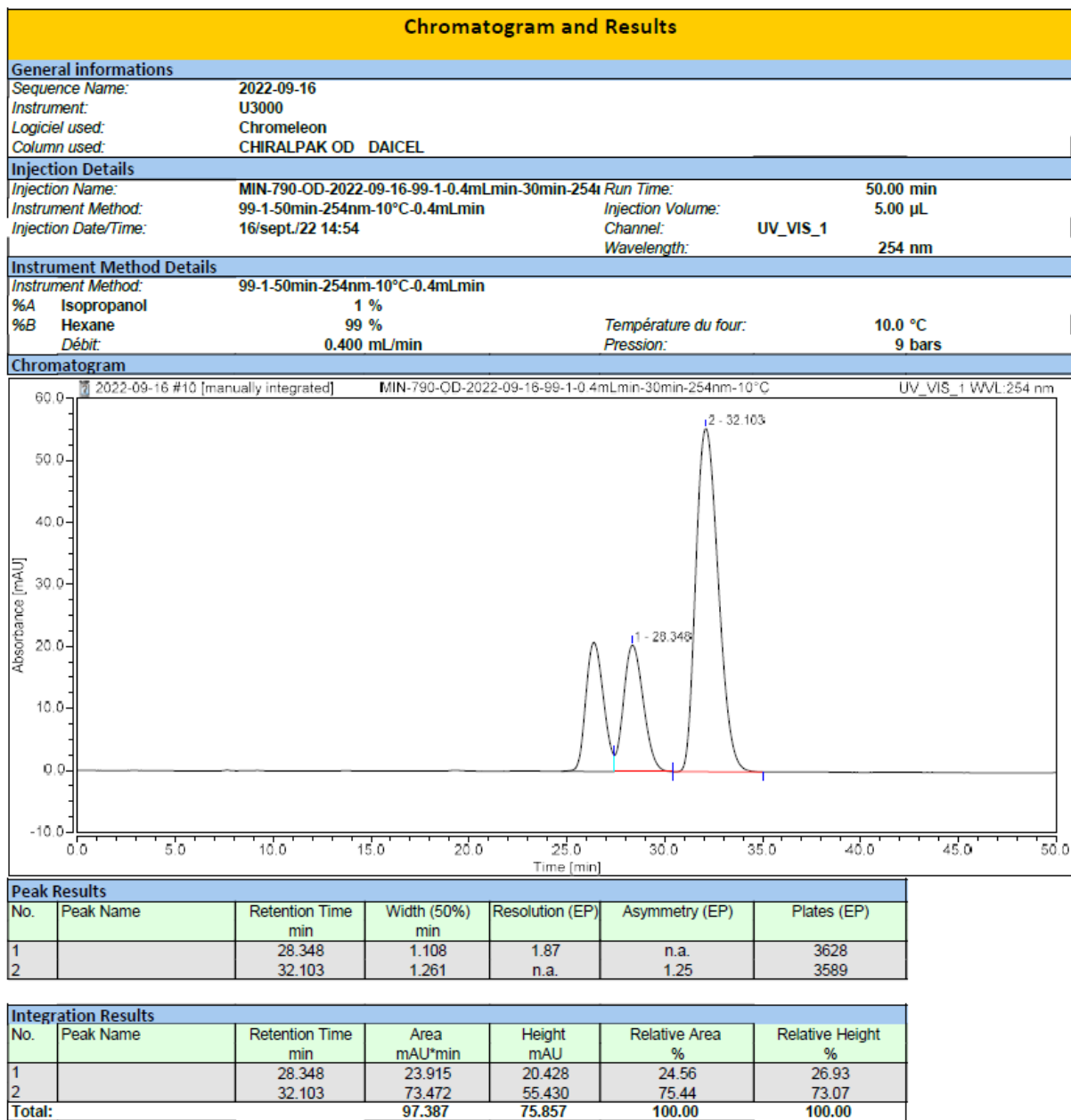
(S_P)-2-(2-Bromobenzoyl)ferrocenetriflone (S_P-2e), obtained by recrystallisation



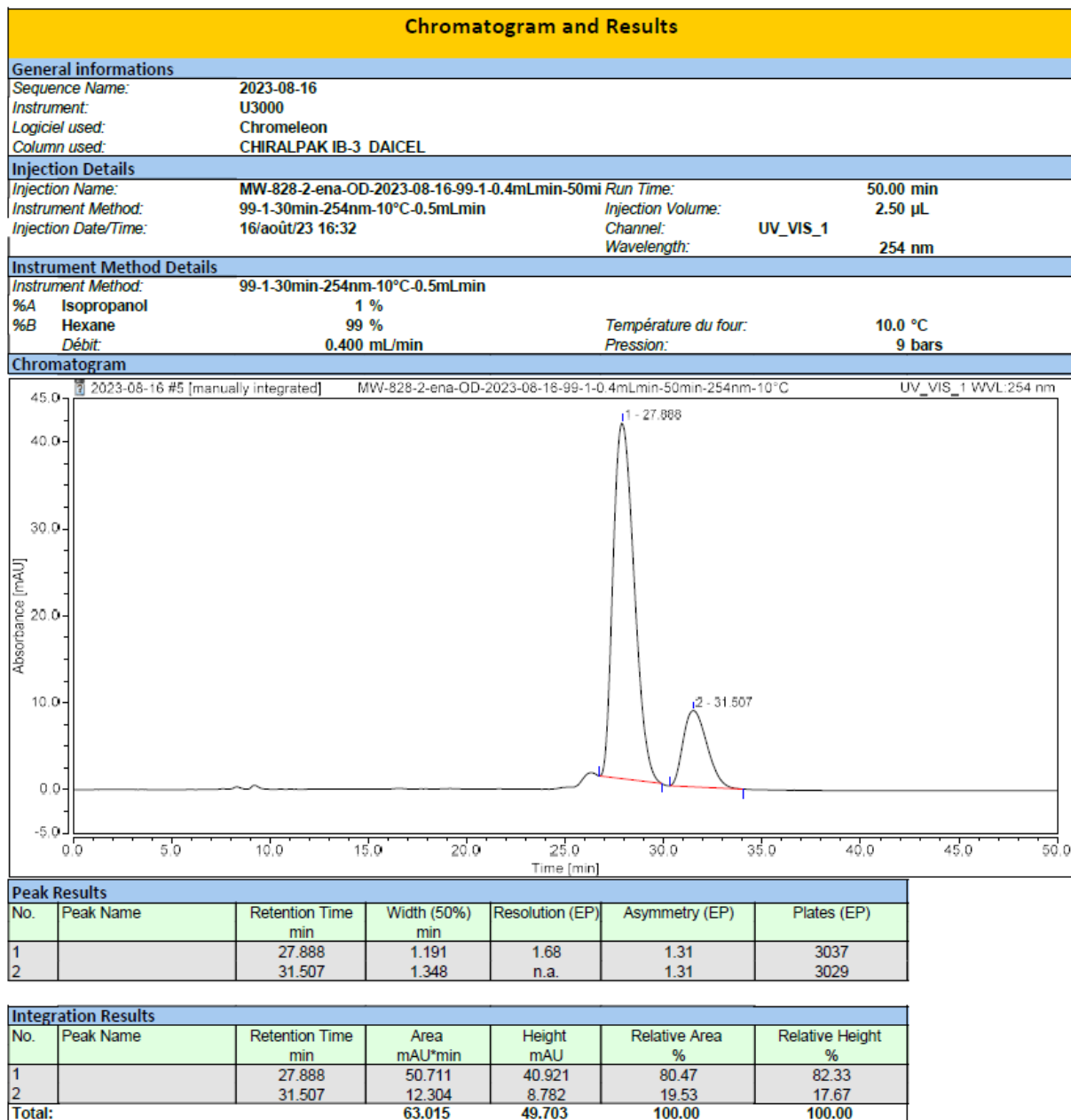
(±)-2-Iodoferrocenetriflone (*rac*-2f)



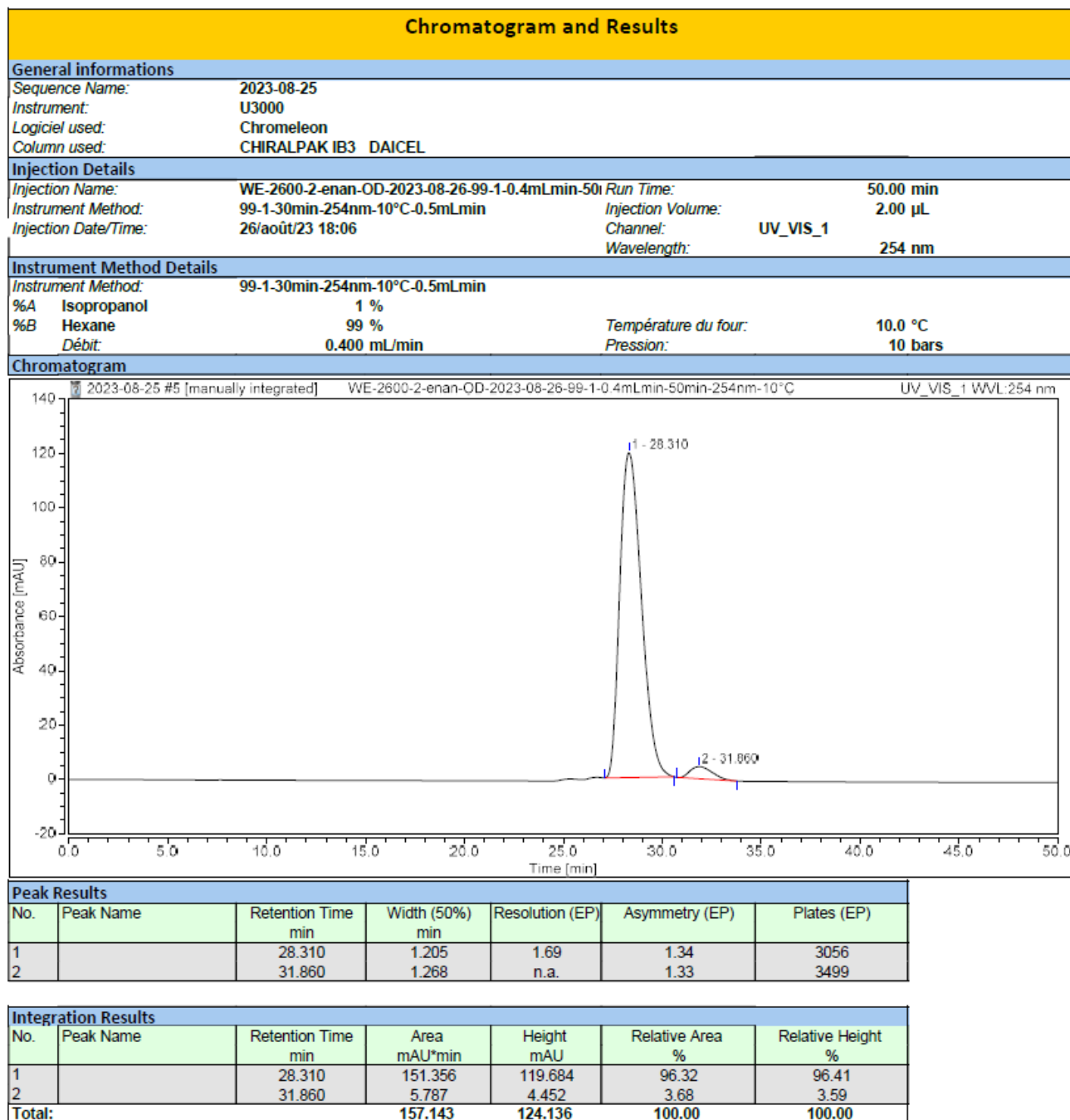
Deprotonation of 1 with (R)-PEALi using [(R)-PEA]₂Zn as the *in situ* trap



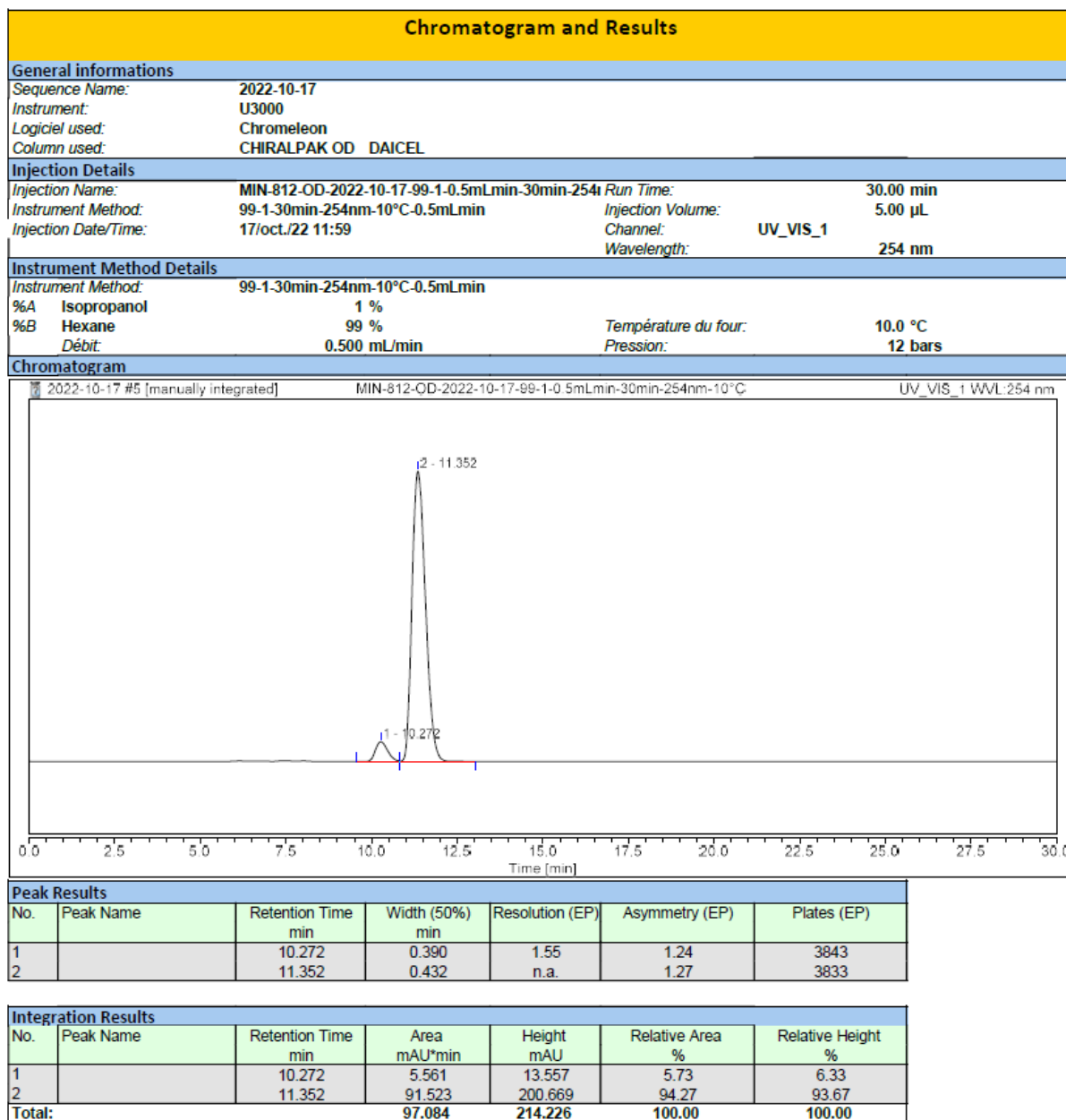
Deprotonation of 1 with (S)-PEALi using [(S)-PEA]₂Zn as the *in situ* trap



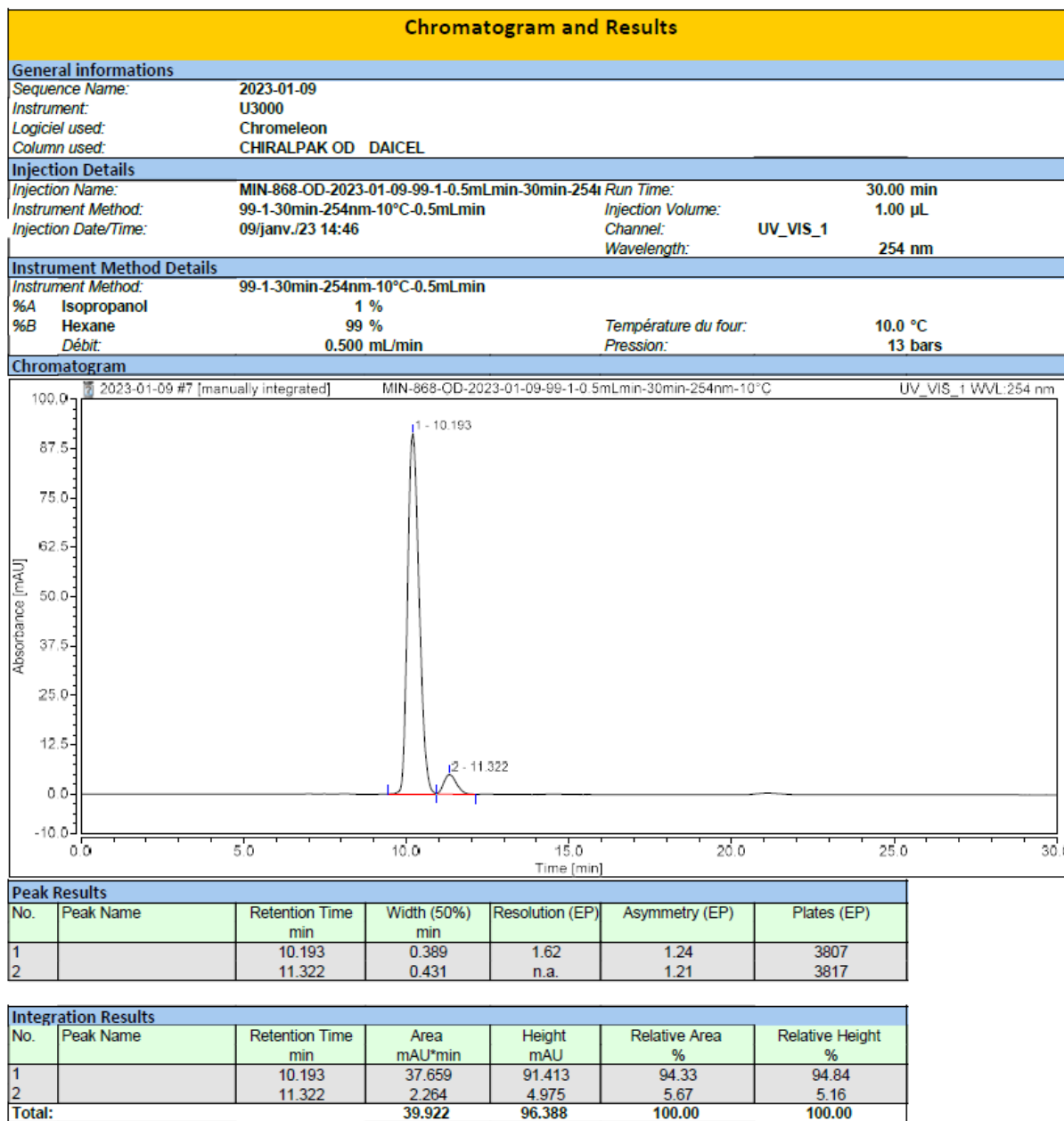
Deprotonation of 1 with (S)-PEALi using ZnCl₂·TMEDA as the *in situ* trap



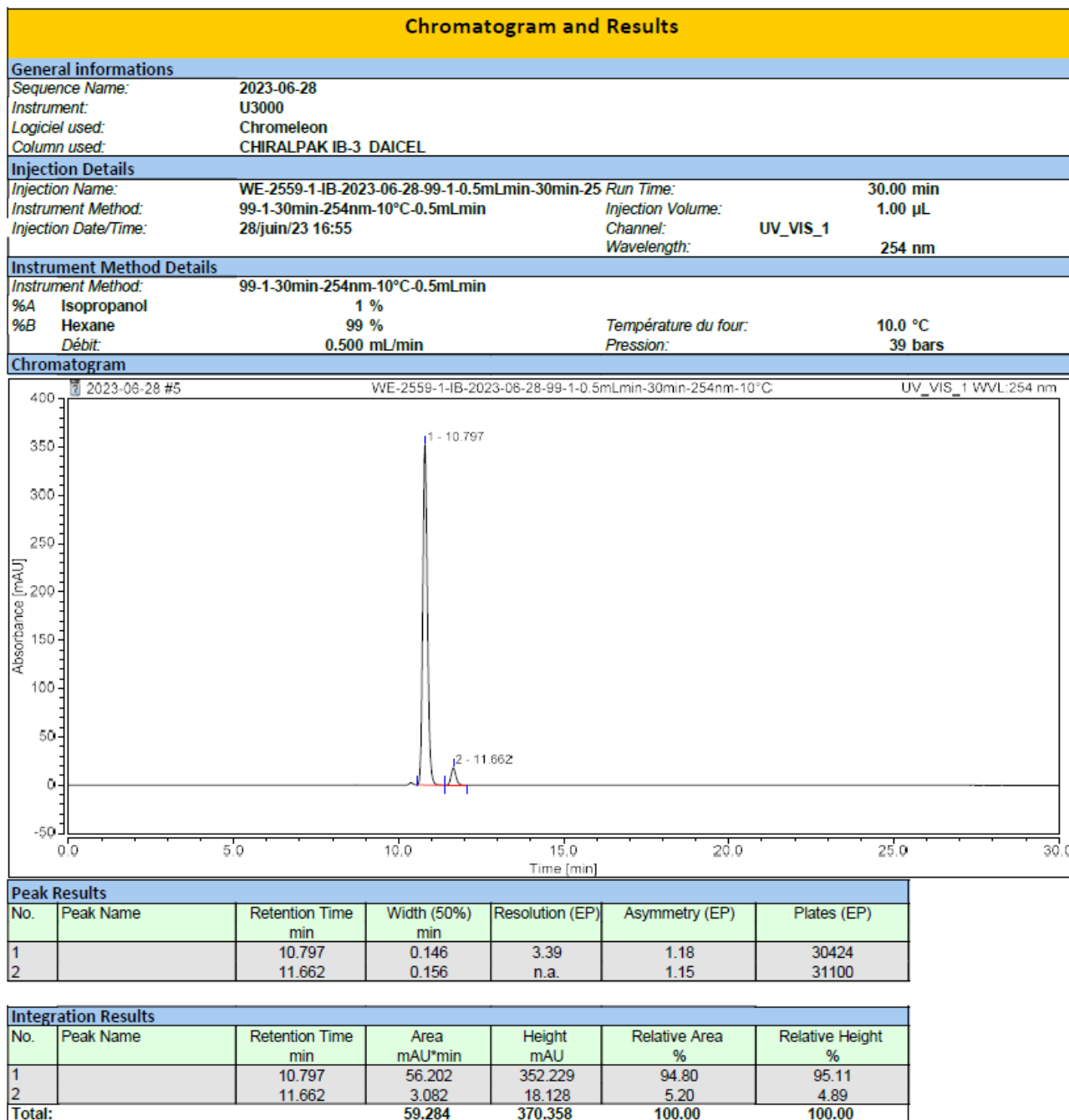
Deprotonation of 1 with (R)-PEALi using Me₃SiCl as the electrophile



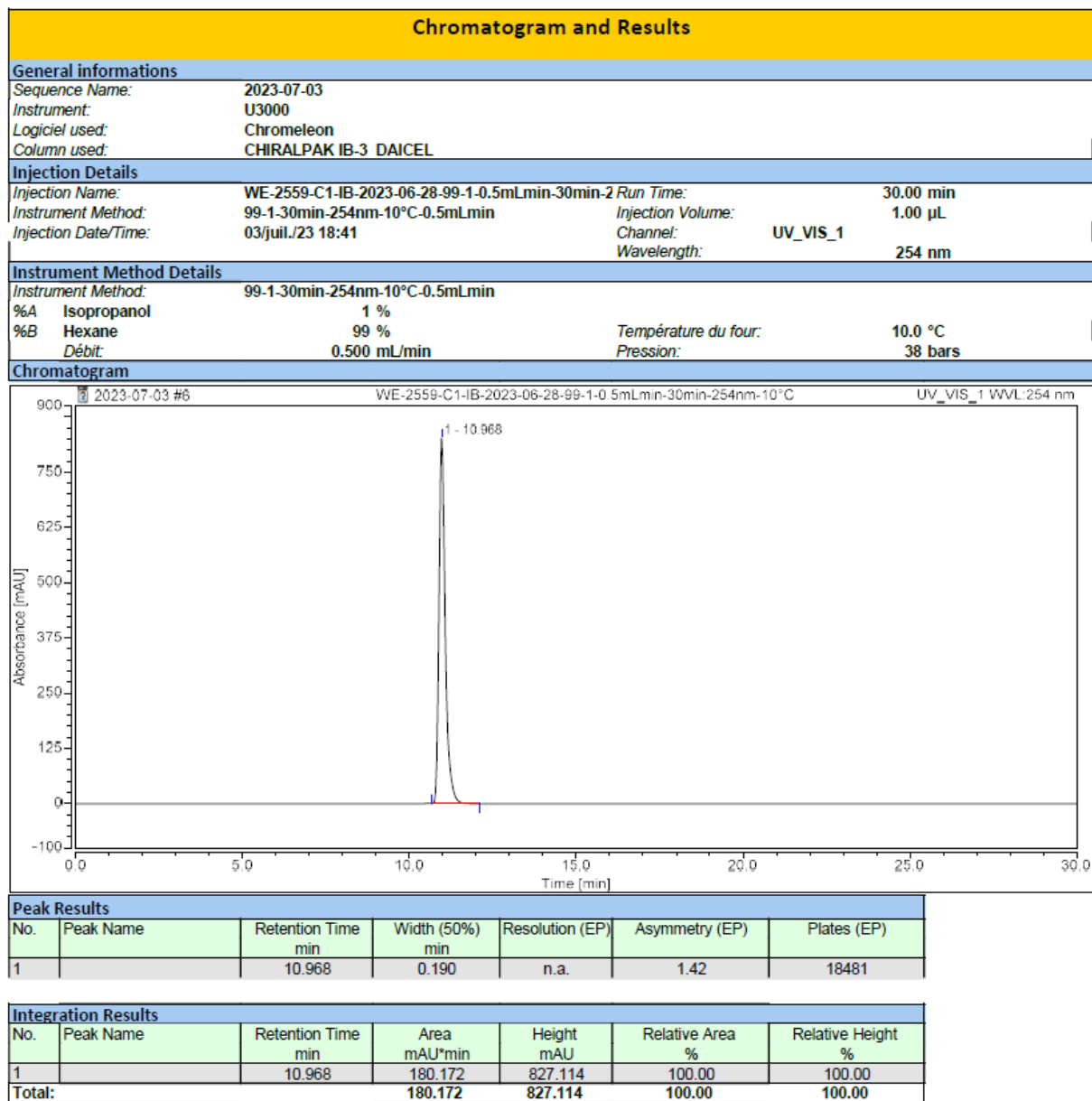
Deprotonation of 1 with (S)-PEALi using Me₃SiCl as the electrophile



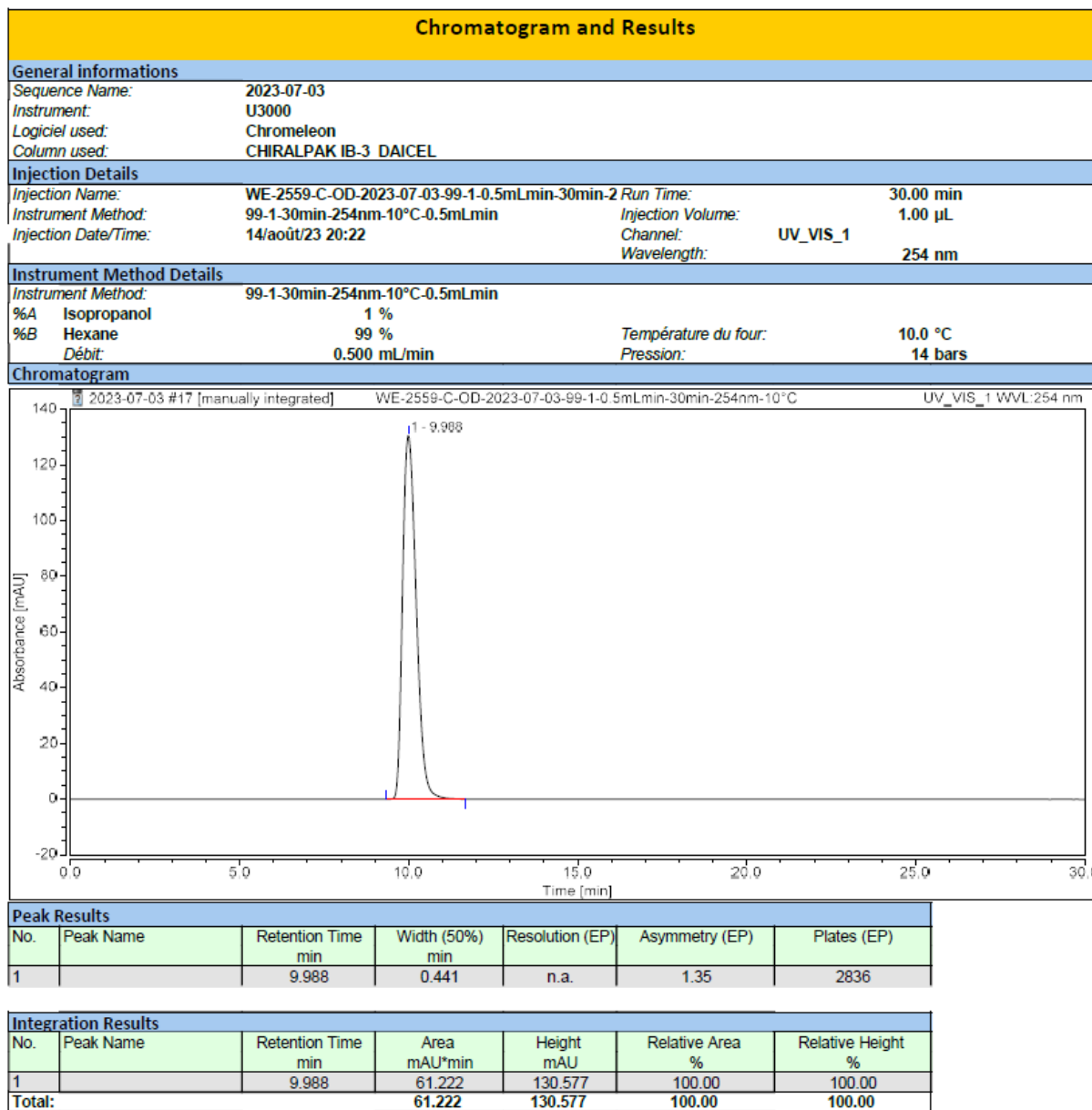
Large-scale deprotonation of 1 with (S)-PEALi using Me₃SiCl as the electrophile



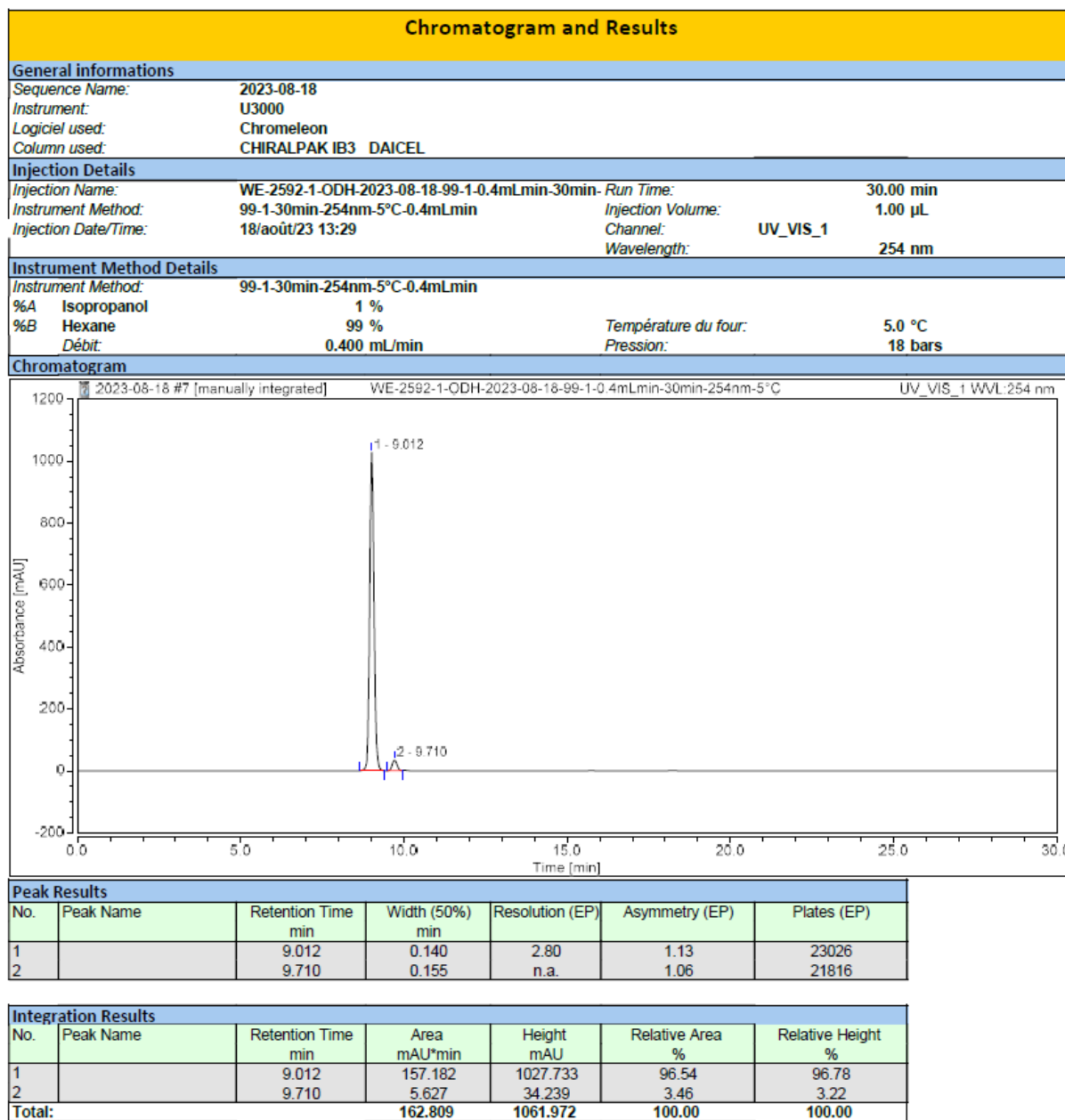
Large-scale crystallisation of (R_P)-2-(trimethylsilyl)ferrocenetriflone (R_P-2a) in hexane (IB)



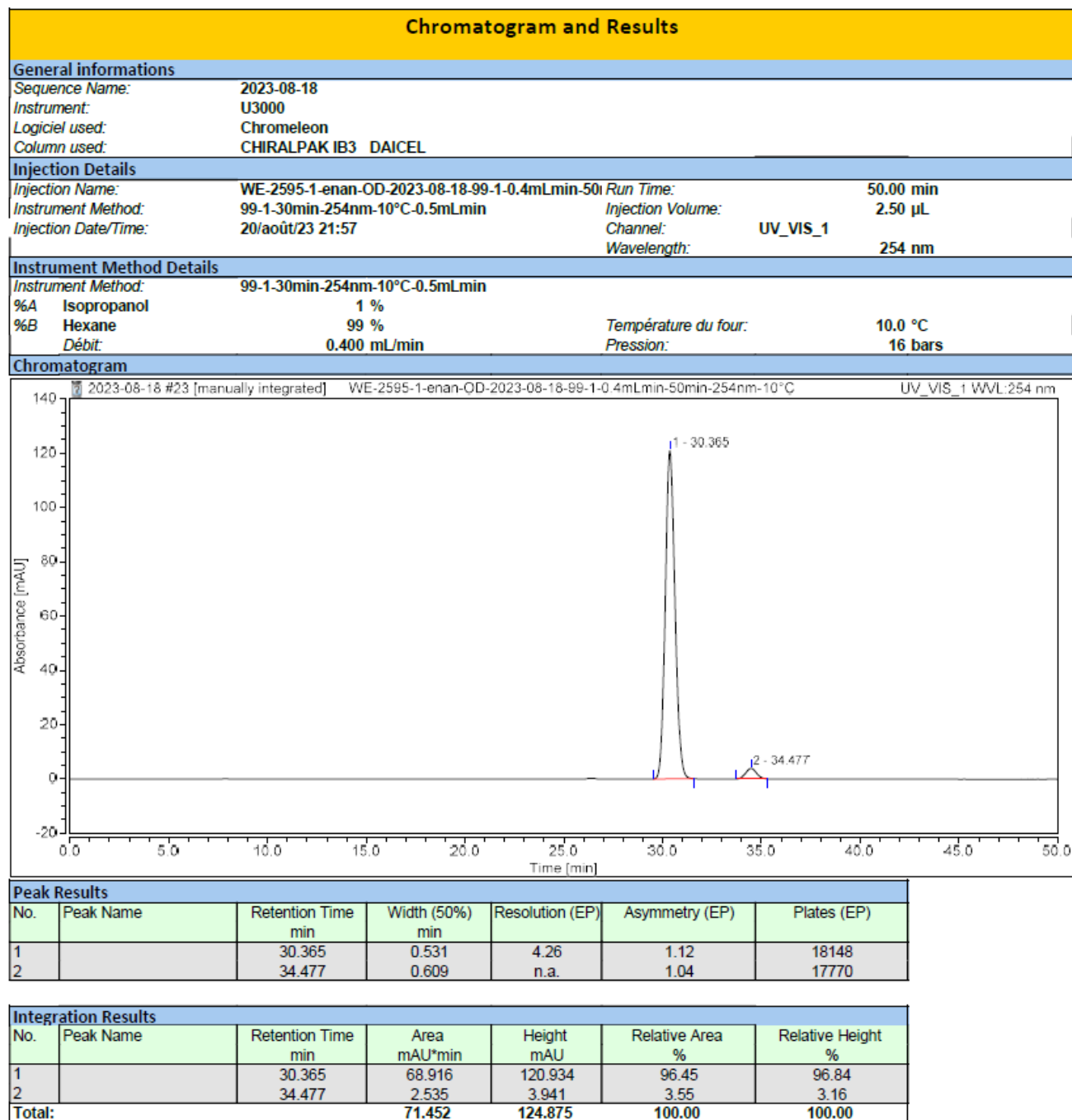
Large-scale crystallisation of (R_P)-2-(trimethylsilyl)ferrocenetriflone (R_P-2a) in hexane (OD)



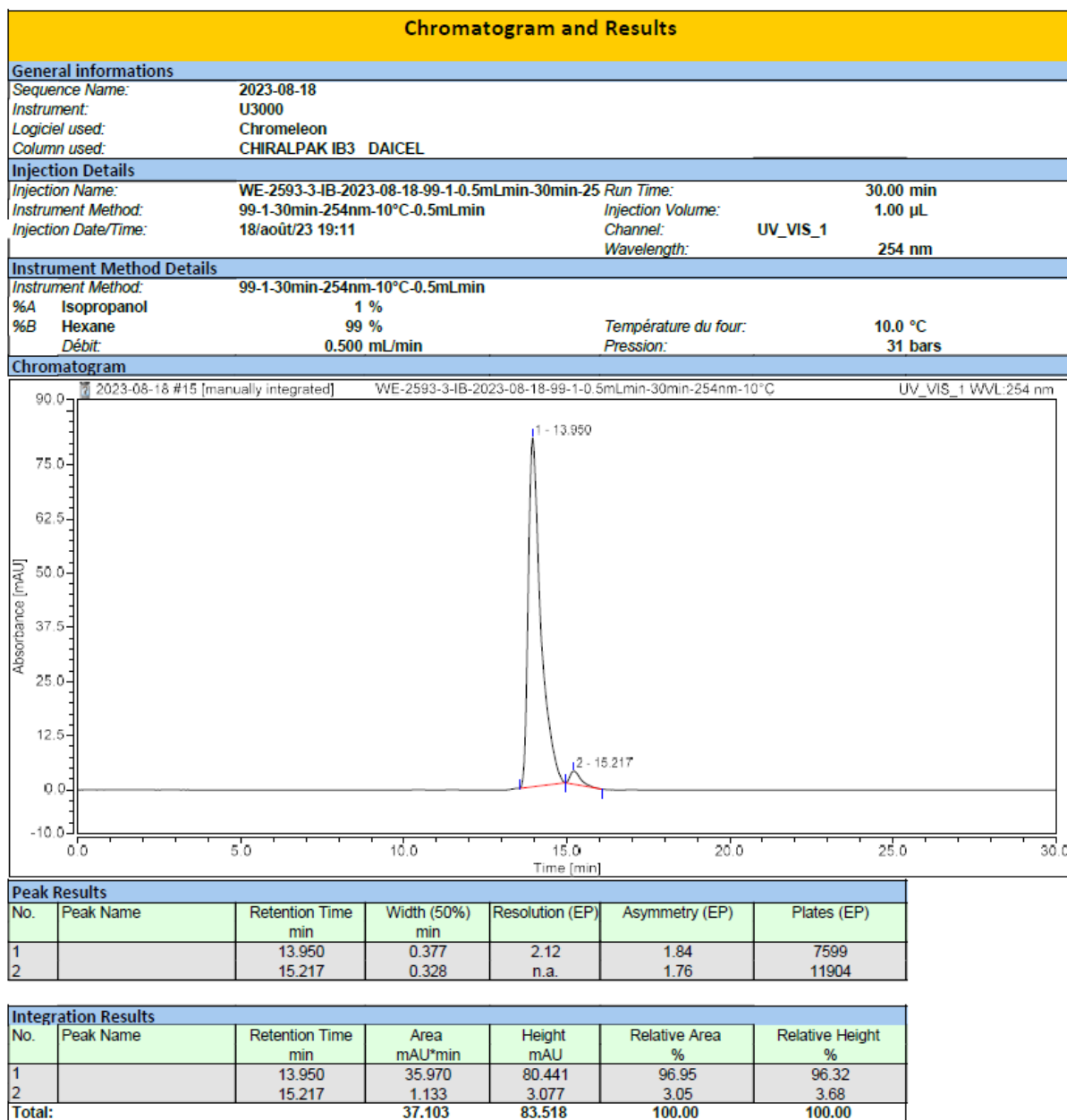
Large-scale deprotonation of 1 with (S)-PEALi using Bu₃SnCl as the electrophile



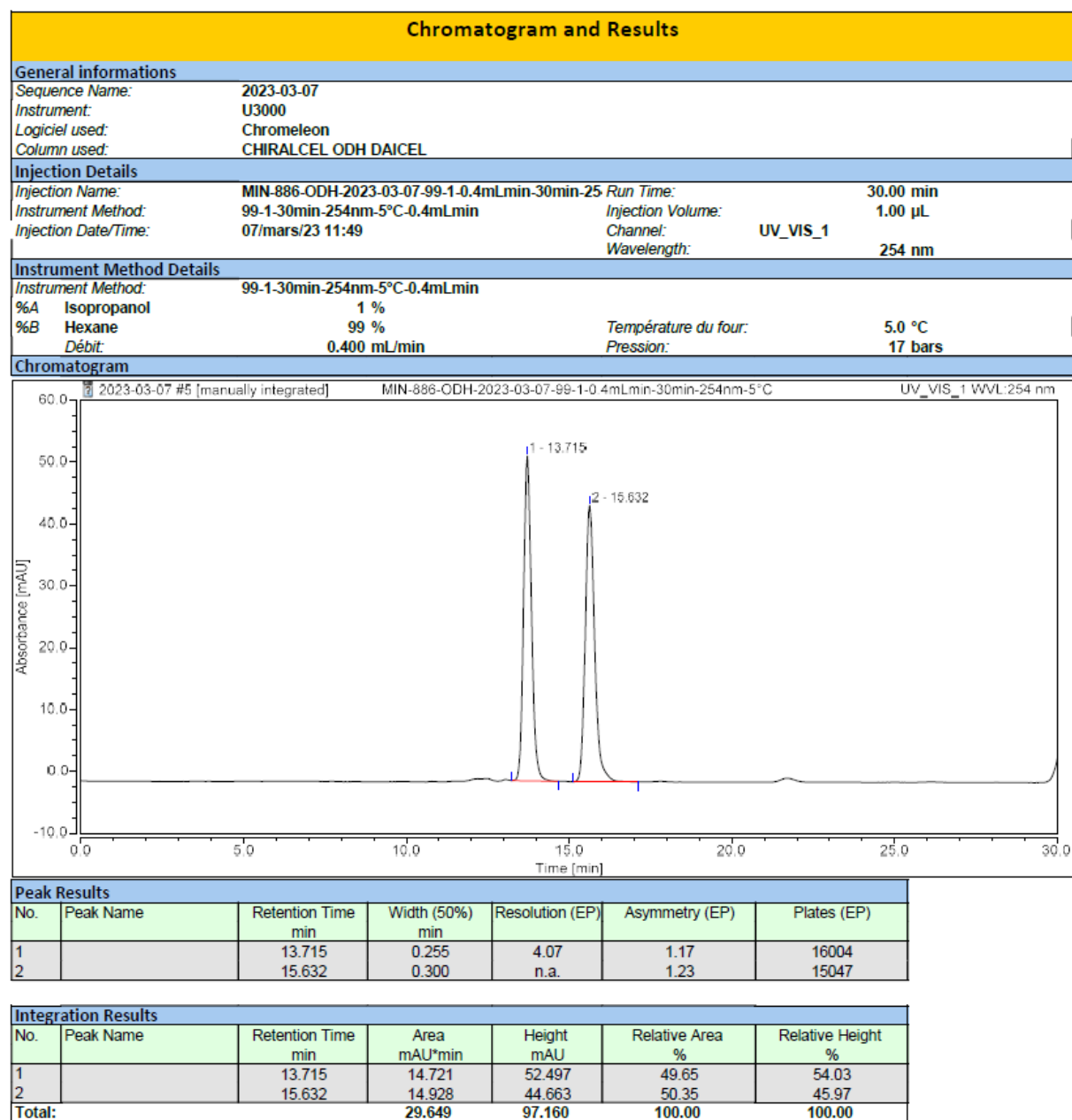
Iododestannylation from 2-(tributylstannyl)ferrocenetriflone (2b)



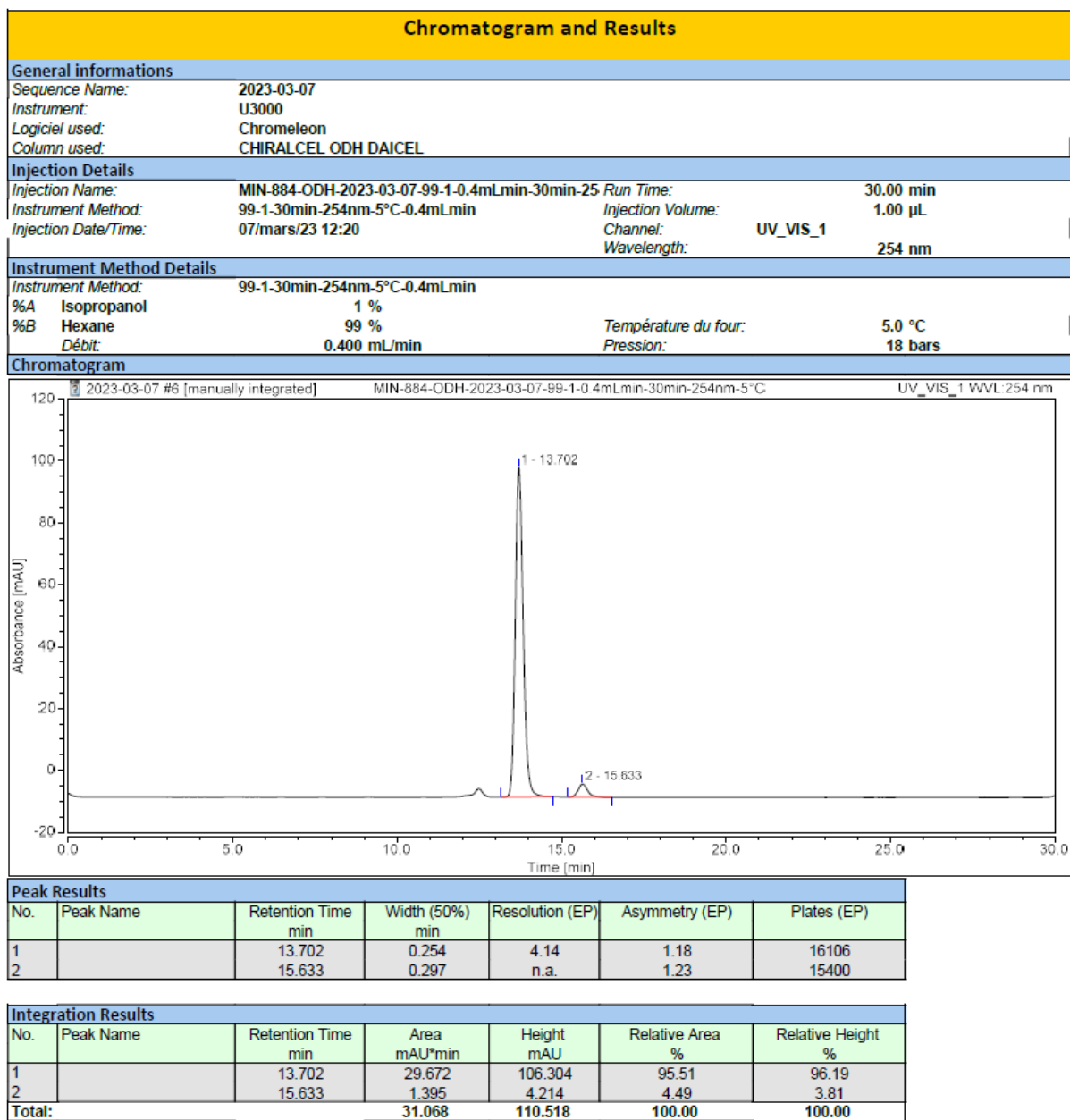
Sn/Li exchange from 2-(tributylstannyl)ferrocenetriflone (2b) using Me₃SiCl as the electrophile



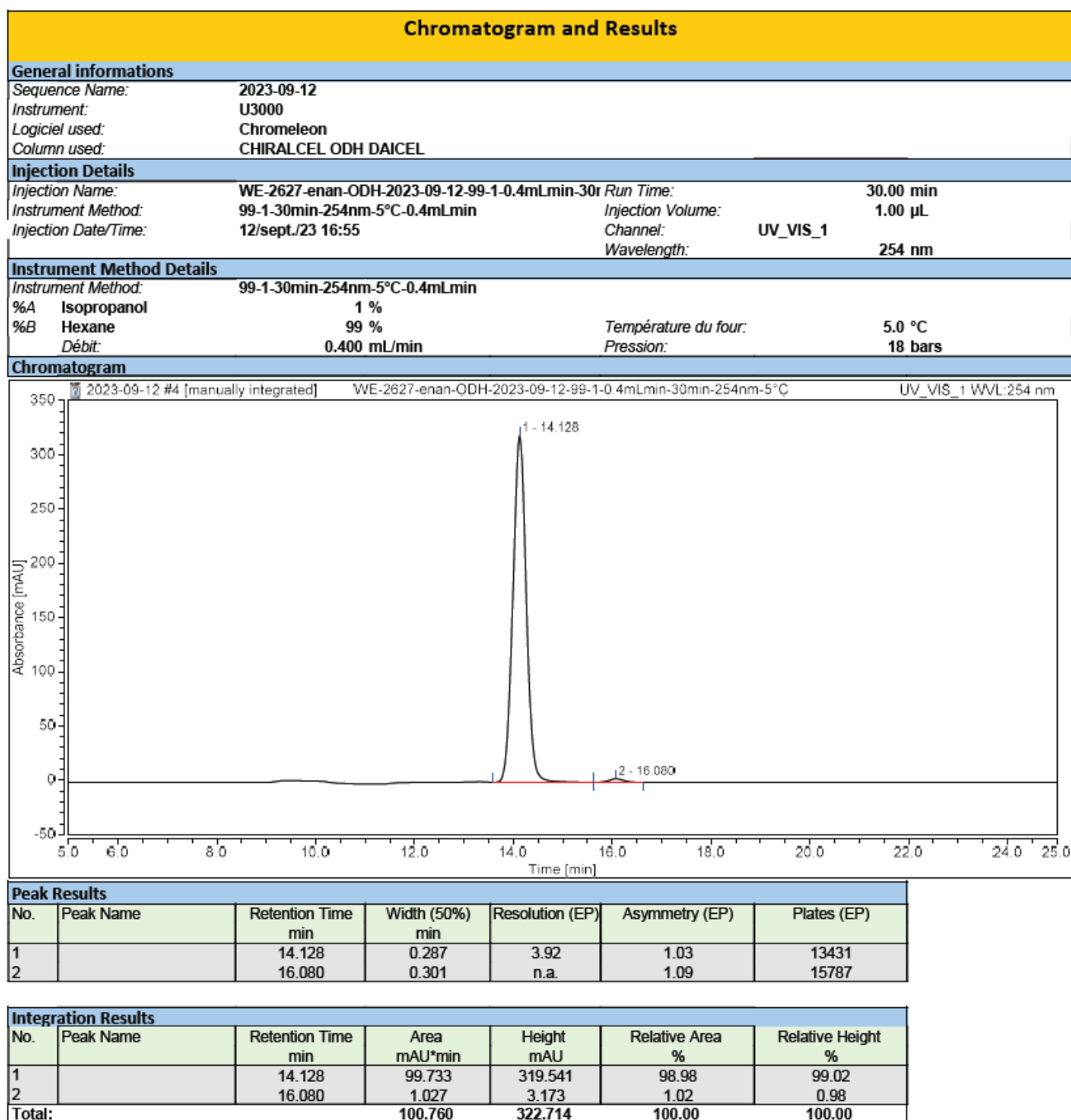
(±)-2-(4,4,5,5-Tetramethyl-1,3-dioxa-2-borolyl)ferrocenetriflone (*rac*-2h)



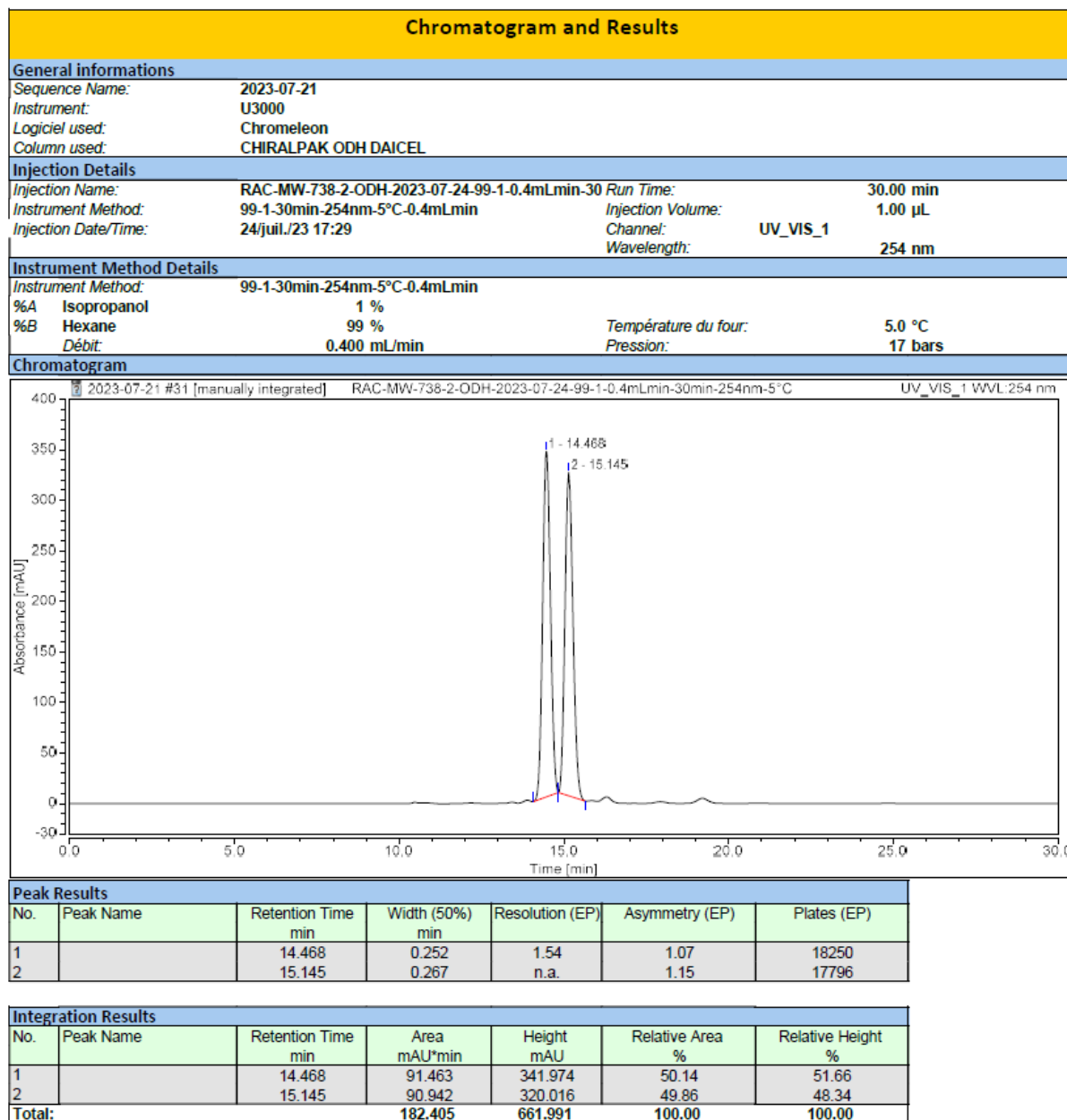
Deprotonation of 1 with (S)-PEALi using B(OiPr)₃ as the electrophile followed by transesterification using pinacol



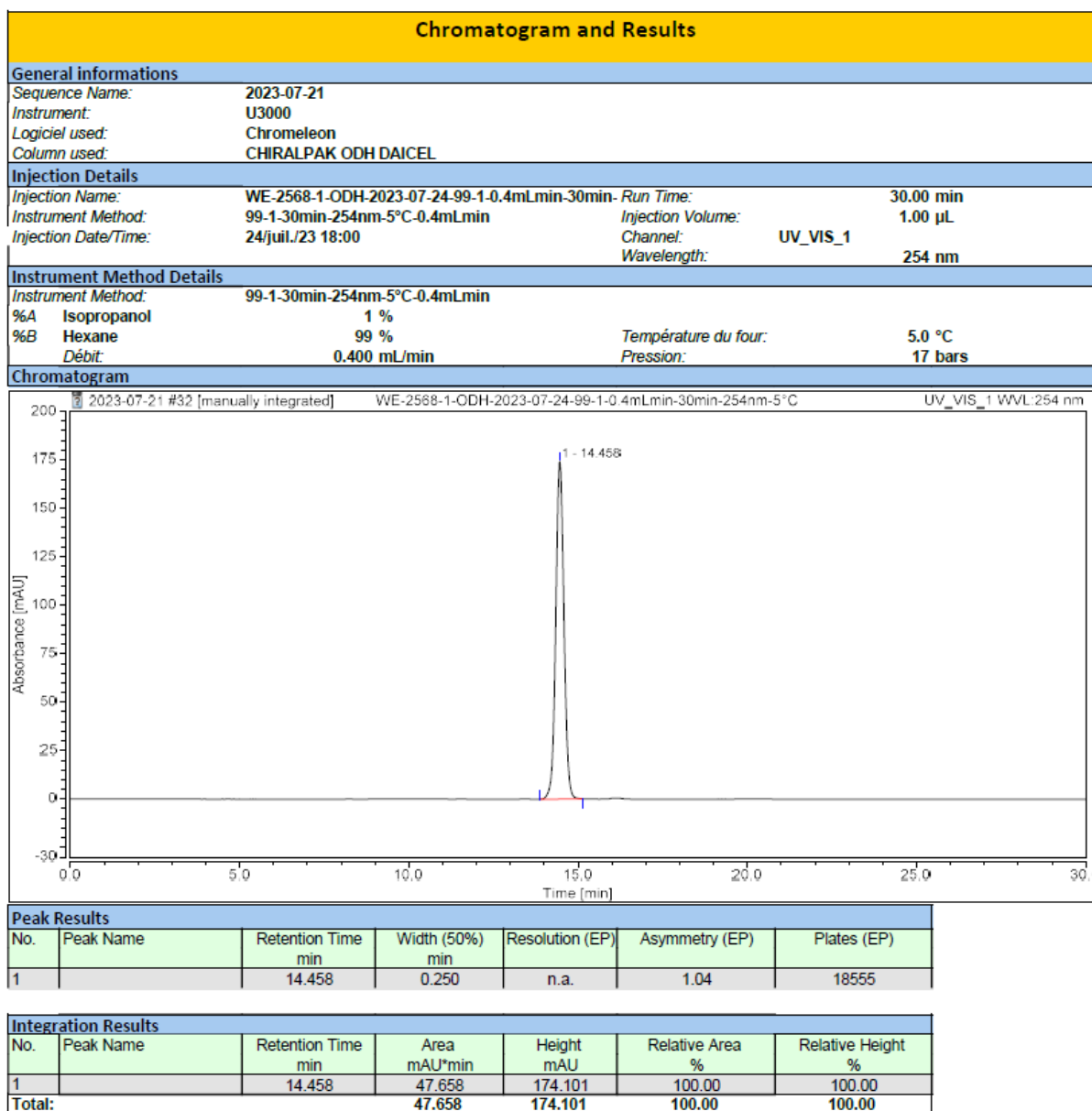
2-(4,4,5,5-Tetramethyl-1,3-dioxo-2-borolyl)ferrocenetriflone (2h) obtained by esterification of the boronic acid 2g



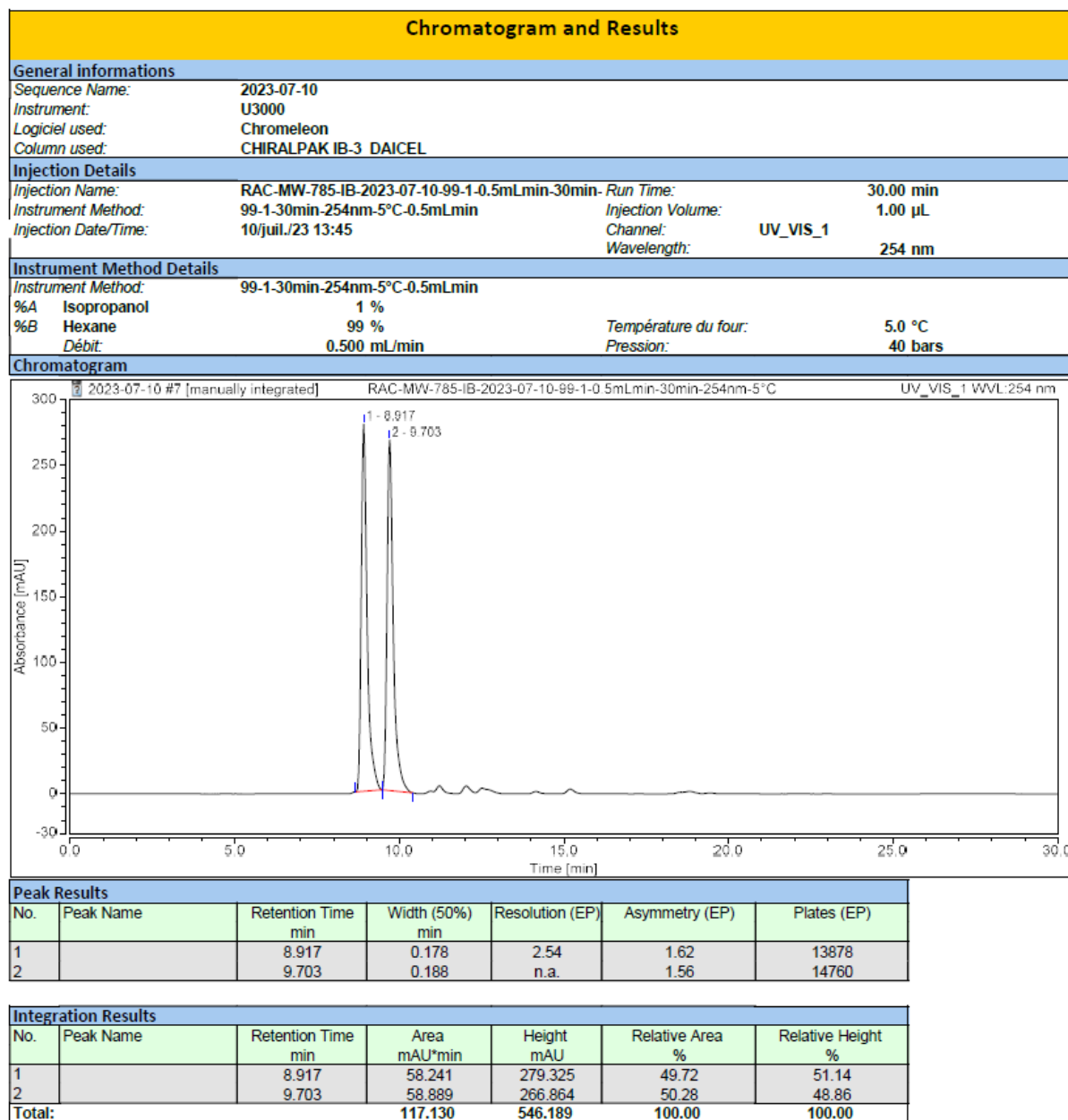
(±)-2-Iodo-5-(trimethylsilyl)ferrocenetriflone (*rac*-3af)



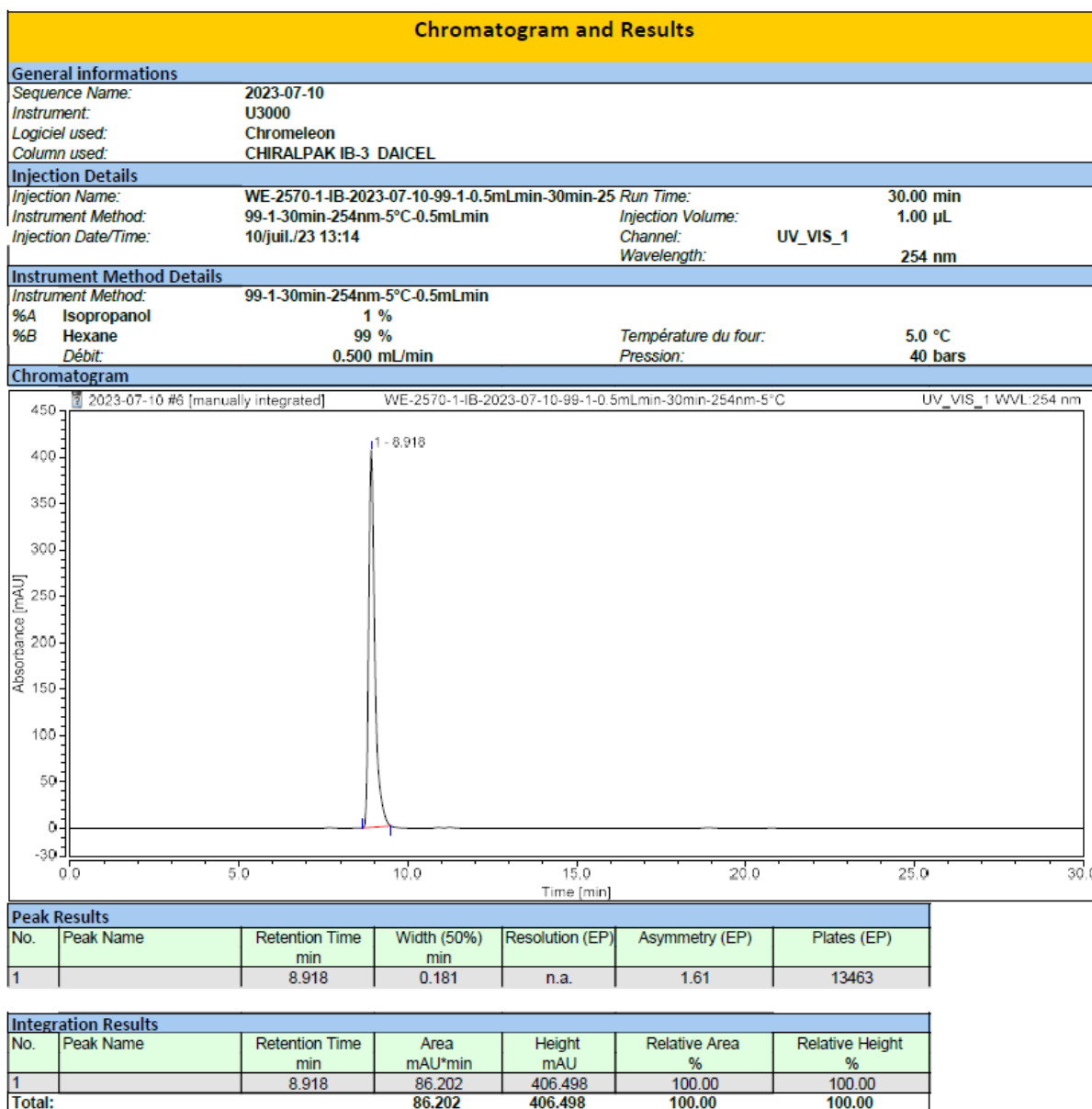
(R_P)-2-Iodo-5-(trimethylsilyl)ferrocenetriflone (R_P-3af)



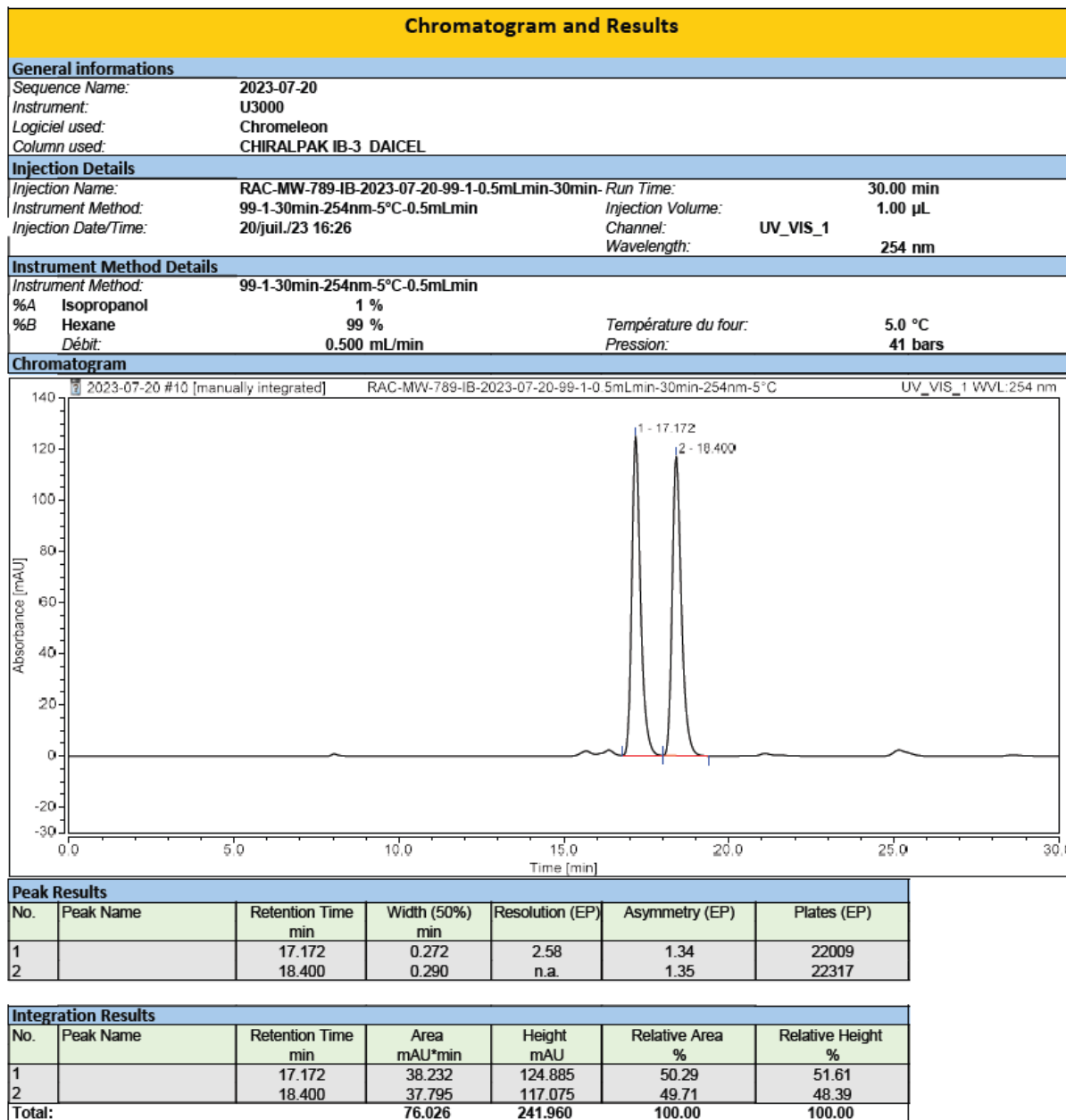
(±)-4-Iodo-2-(trimethylsilyl)ferrocenetriflone (*rac*-4af)



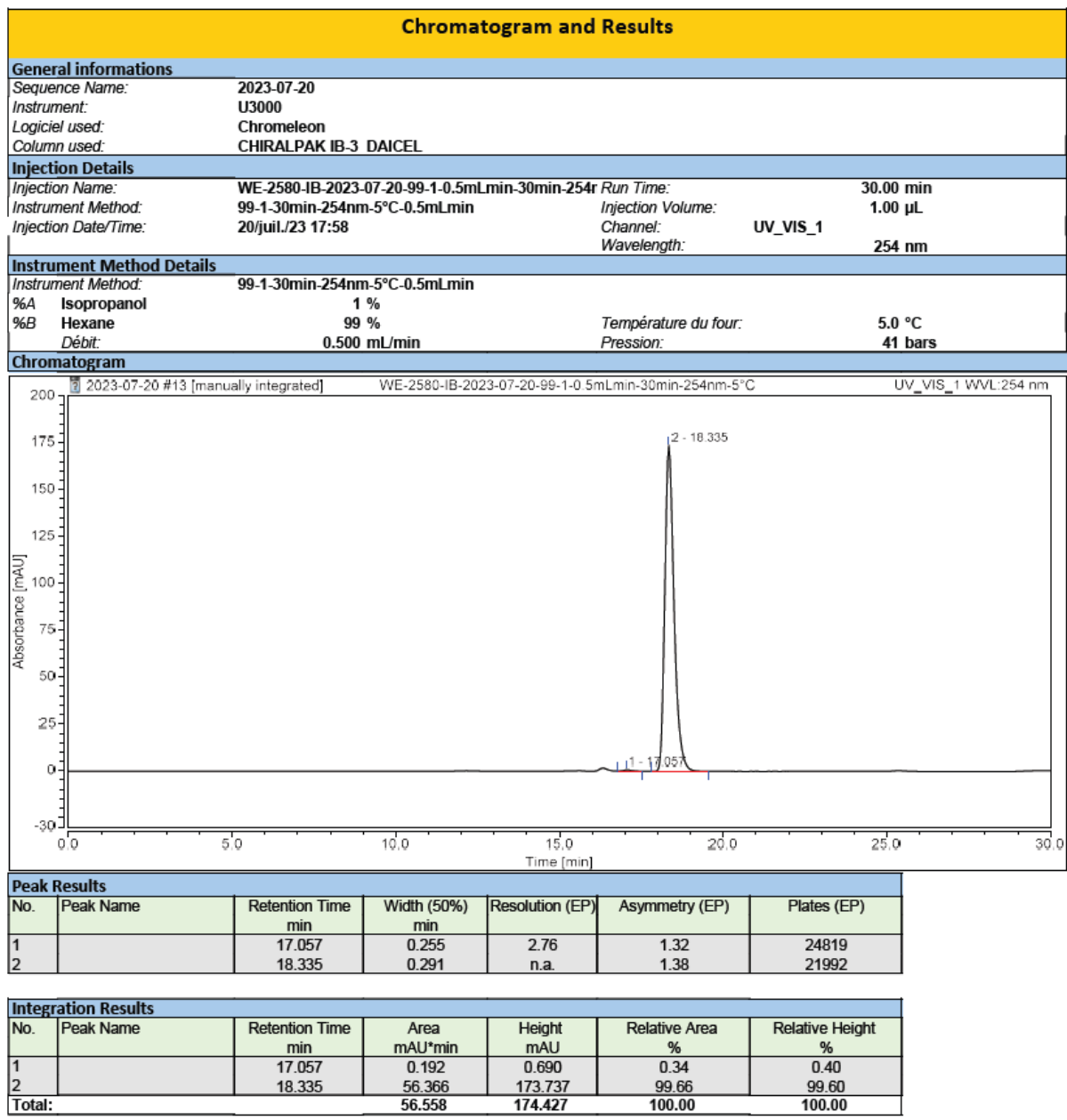
(R_P)-4-Iodo-2-(trimethylsilyl)ferrocenetriflone (R_P-4af)



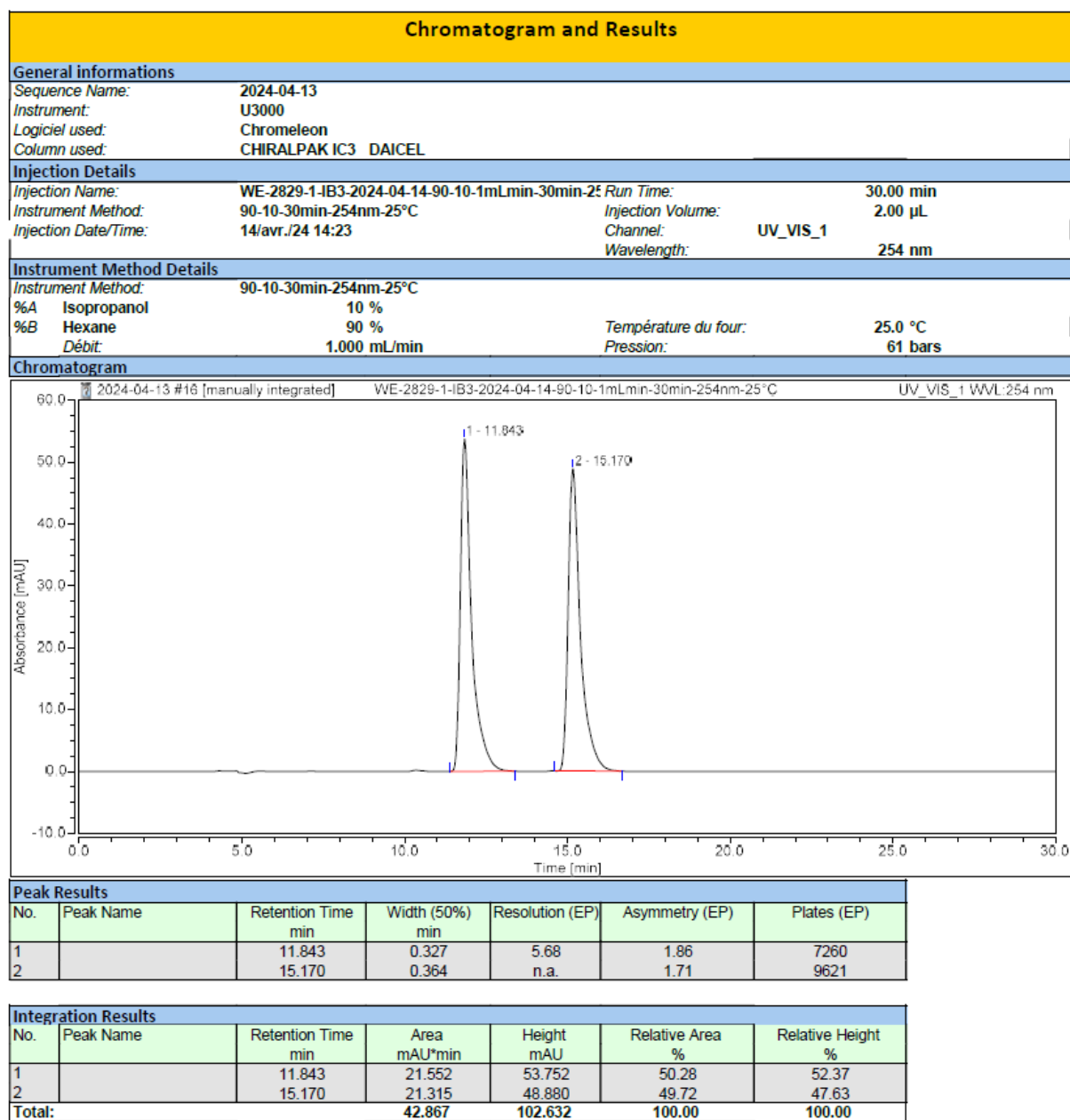
(±)-3-Iodoferrocenetriflone (*rac*-5f)



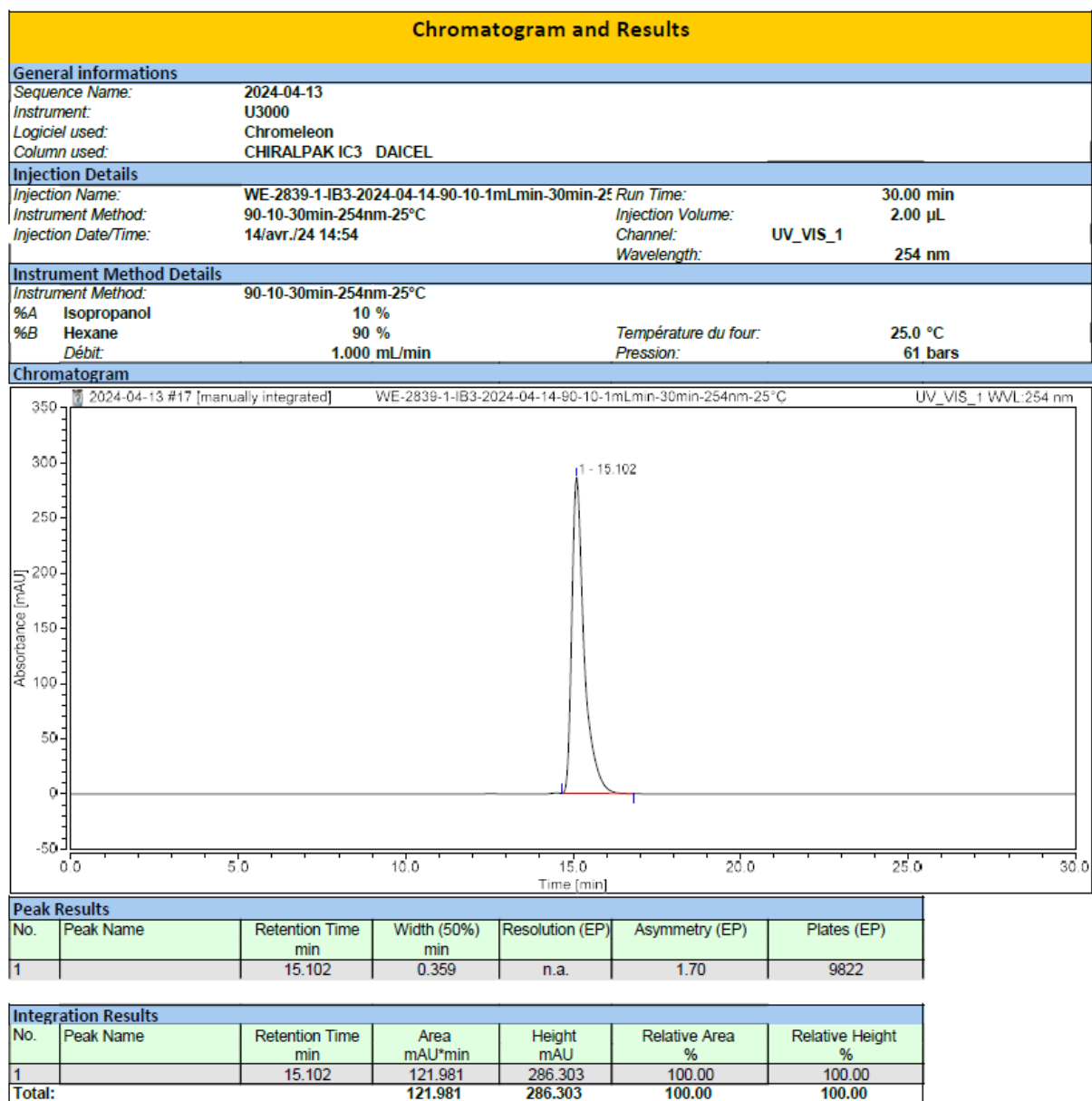
(Rp)-3-Iodoferrocenetriflone (Rp-5f)



The ferrocenic analogue of fluorenone *rac*-10



The ferrocenic analogue of fluorenone Sp-10



H) Determination of the enantiomeric excess of *R**P*-**3aj**, *R**P*-**6**, *S**P*-**7**, *S**P*-**8** and *S**P*-**9**

To confirm the enantiomeric excess of *R**P*-**3aj**, we recorded the NMR spectra of both *rac*-**3aj** and the **3aj** sample for which we want to determine the *ee* in the presence of (*R*)-(+)-*tert*-butylphenylphosphinothioic acid as a chiral resolving agent.^[21]

Thus, *rac*-**3aj** (40 mg, 90 μmol) and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid (19 mg, 90 μmol) were first dissolved in CDCl_3 (0.5 mL). The resulting solution was stirred for 1 min at rt before being filtrated over a 0.22 μm nylon syringe filter directly into an NMR tube.

In the ^1H NMR spectrum, apart from the expected doublet of the *t*Bu protons of the chiral resolving agent at 1.17 ppm ($^3J_{\text{HP}} = 16.2$ Hz), we observed two sets of resonances in a 1:1 ratio for all the signals of ferrocene **3aj** (Figure S19). A similar observation was also done in the ^{19}F NMR spectrum, with two signals at -76.4 and -76.8 ppm, also in a 1:1 ratio (Figure S20). In the ^{13}C NMR spectrum, although not all signals were observed, most of the peaks of ferrocene **3aj** were obtained as sets of two signals (Figure S21). Exceptions concern the quaternary carbon of the trifluorosulfonyl group, giving only one quartet at 119.6 ppm ($^1J_{\text{CF}} = 327$ Hz), and the quaternary carbon of the ferrocene bearing the trifluorosulfonyl group, not observed under these conditions. Furthermore, the signals of the dimethylammonium group were barely observed in the ^{13}C NMR spectra, probably due to unfavourable relaxation as broad singlets were also observed for this group in the ^1H spectrum. Finally, only one signal of the phosphinothioic acid was observed in the ^{31}P NMR spectrum (Figure S22).

Taken together, all these experiments confirm the use of (*R*)-(+)-*tert*-butylphenylphosphinothioic acid as a chiral resolving agent for compound **3aj**.

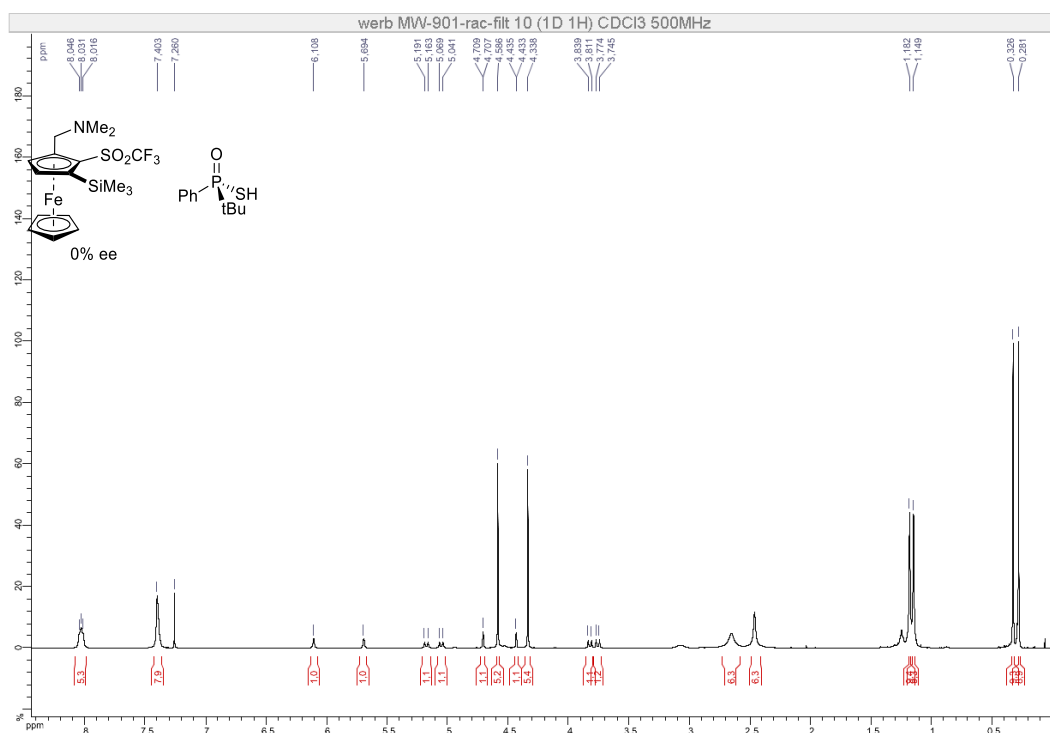


Figure S19. ^1H spectrum of *rac*-**3aj** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

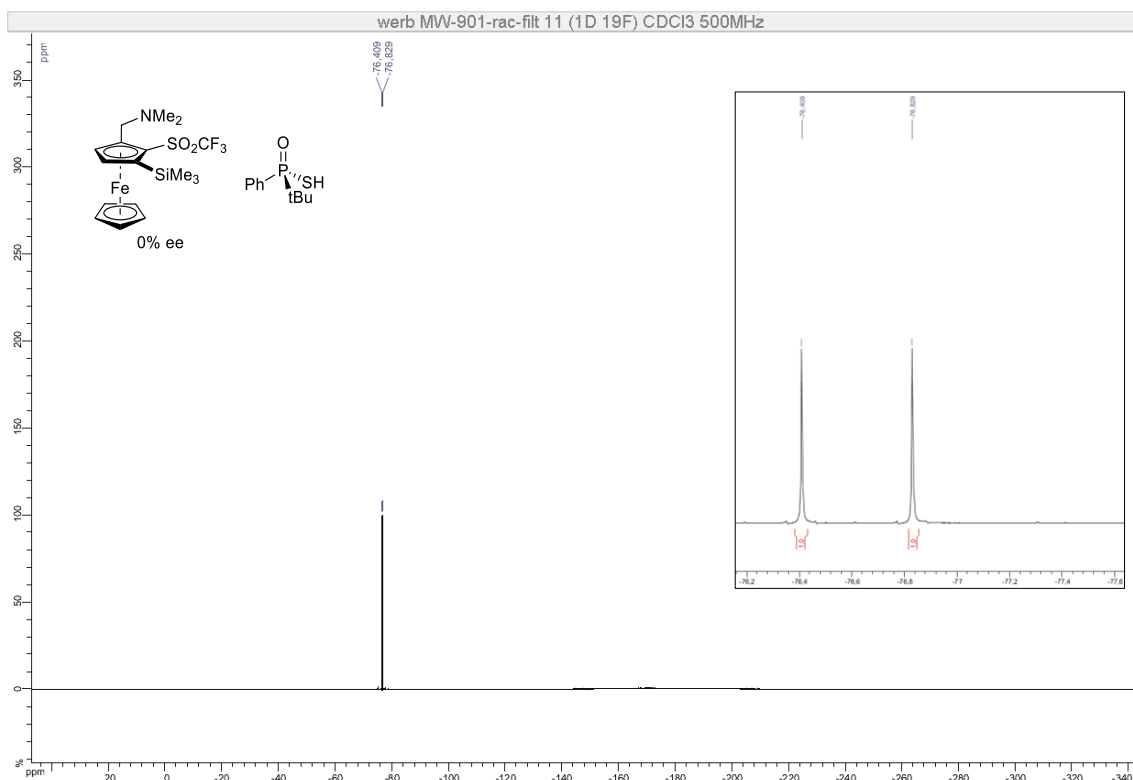


Figure S20. ¹⁹F spectrum of *rac*-**3aj** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 470 MHz.

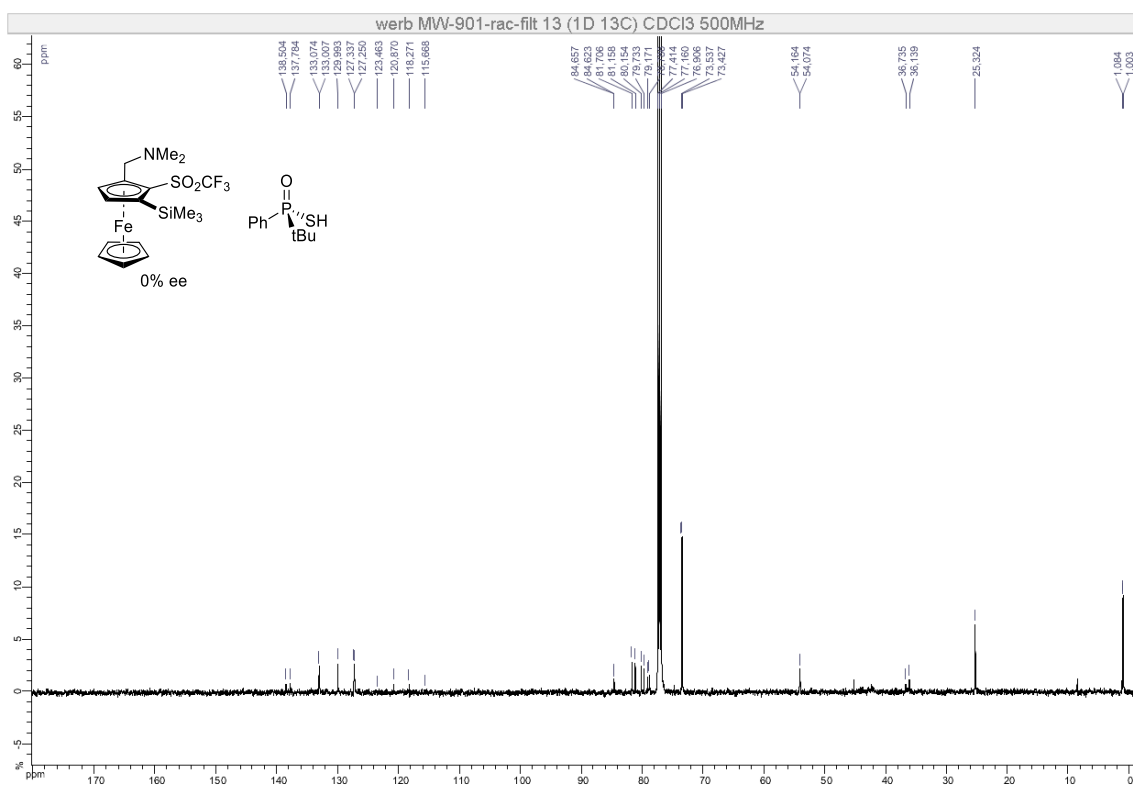


Figure S21. ¹³C spectrum of *rac*-**3aj** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

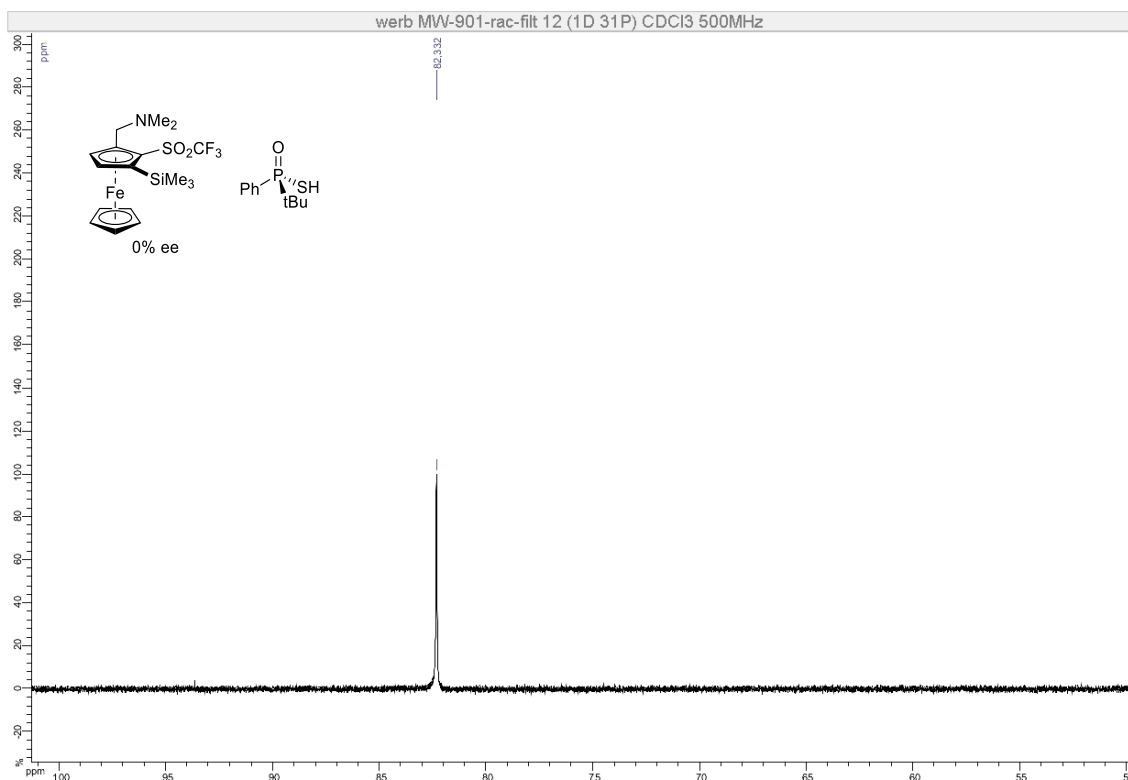


Figure S22. ³¹P spectrum of *rac*-**3aj** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 202 MHz.

We then performed the same experiments starting from an expected enantiopure **Rp-3aj**, coming from **Rp-2a** with an *ee* > 99%.

In the ¹H NMR spectrum, the minor diastereoisomer was barely detectable (Figure S23), the most valuable signals being those of the Cp ring (with a 5.1:0.032 integration ratio) and the trimethylsilyl group (with a 9.3:0.087 integration ratio). Being at the limit of the detection, we estimated the ratio to be close to 99:1.

In the ¹⁹F NMR spectrum, the minor diastereoisomer was again barely observed, the integration of the two peaks giving a 1:0.006 ratio (Figure S24). We therefore estimated a ratio > 99:1.

Finally, in the ¹³C NMR spectrum, the main diastereoisomer was the only product identified (Figure S25). Furthermore, the previously missing signals (dimethylamino group and ferrocene quaternary carbon bearing the trifluorosulfonyl group) were observed at 42.3 and 79.1 ppm, respectively, although not well resolved.

Taken together these results, and considering the limit of detection, we estimated the *ee* of **Rp-3aj** being > 99%, in good agreement with the HPLC results.

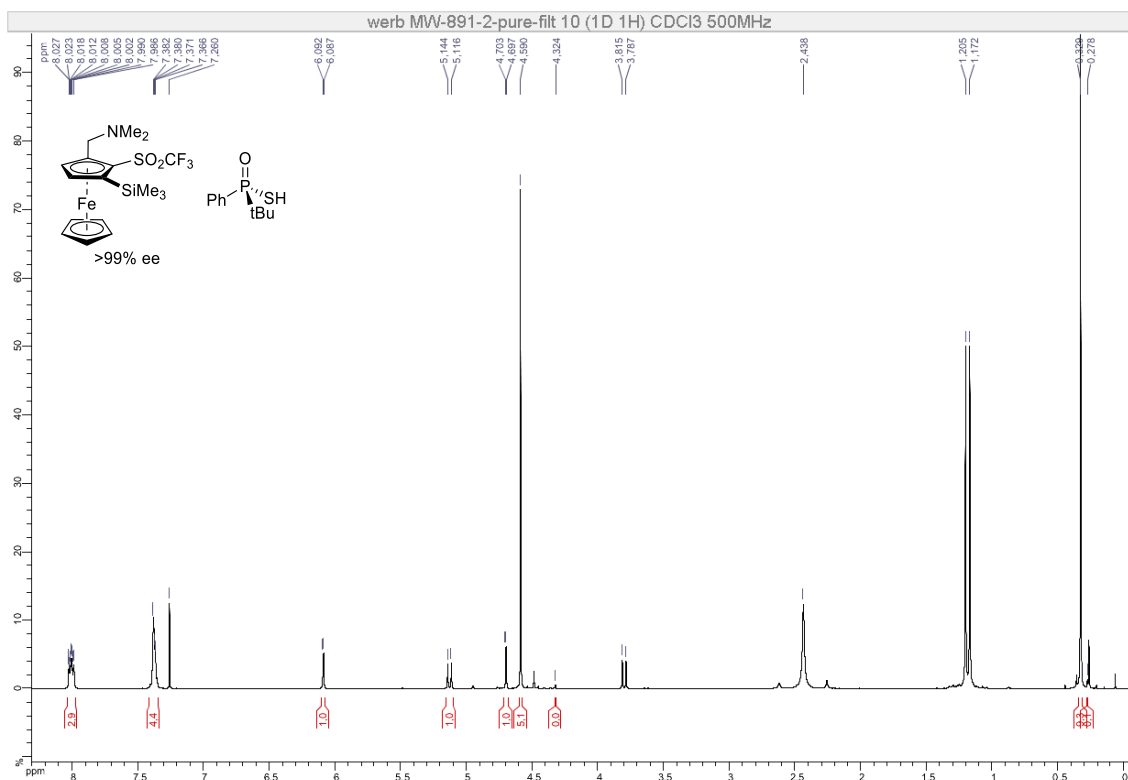


Figure S23. ^1H NMR spectrum of enantiopure **R_p-3aj** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

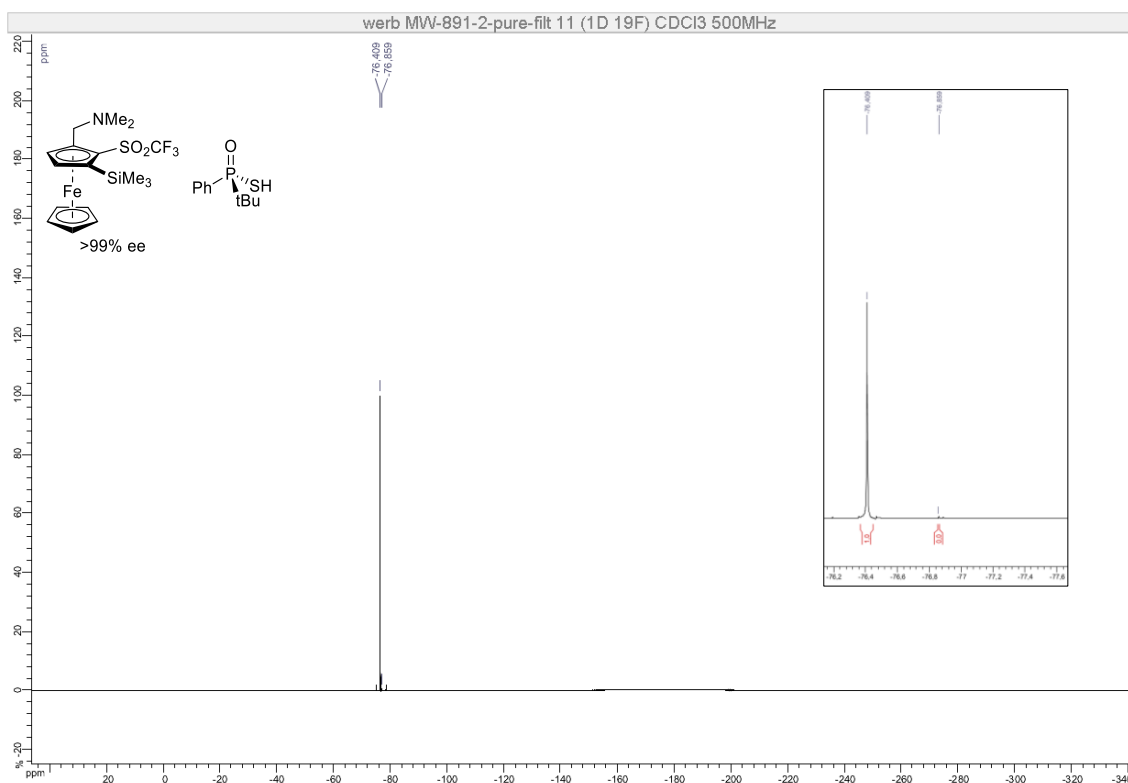


Figure S24. ^{19}F NMR spectrum of enantiopure **R_p-3aj** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 470 MHz.

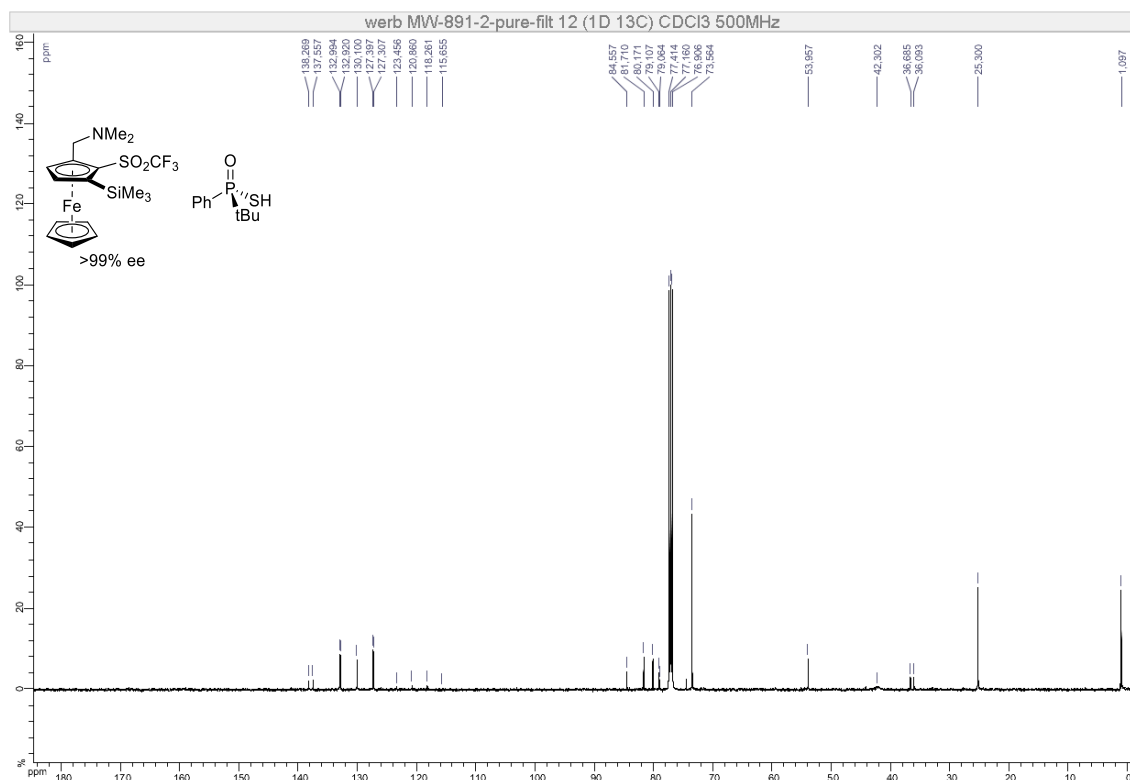


Figure S25. ^{13}C NMR spectrum of enantiopure **R_P-3aj** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

As (*R*)-(+)-*tert*-butylphenylphosphinothioic acid was a suitable chiral resolving agent to determine the enantiomeric purity of **R_P-3aj**, we further used it for compounds **R_P-6**, **S_P-7**, **S_P-8** and **S_P-9**. Although racemic products were not available, we were looking for any duplication of signals which might indicate partial racemisation, based on the chemical shifts observed upon mixing **R_P-3aj** with (*R*)-(+)-*tert*-butylphenylphosphinothioic acid.

Thus, **R_P-6** (24 mg, 50 μmol) and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid (11 mg, 50 μmol) were dissolved in CDCl_3 (0.5 mL). The solution was stirred at rt for 1 min before being filtrated over a 0.22 μm nylon syringe filter directly into an NMR tube.

In the ^1H NMR spectrum, although a few minor additional peaks were observed (Figure S26), none of them was attributed to a minor diastereoisomer according to the chemical shifts previously recorded in **R_P-3aj**. They were therefore considered as decomposition impurities. As no duplication of the main signals (Cp ring, trimethylsilyl group) was observed, we estimated a ratio > 99:1.

In the ^{19}F NMR spectrum, the minor diastereoisomer was barely observed, the integration of the two peaks giving a 1:0.006 ratio (Figure S27). We therefore estimated a ratio > 99:1.

A similar result was recorded in the ^{13}C NMR spectrum (Figure S28), as only one diastereoisomer was observed.

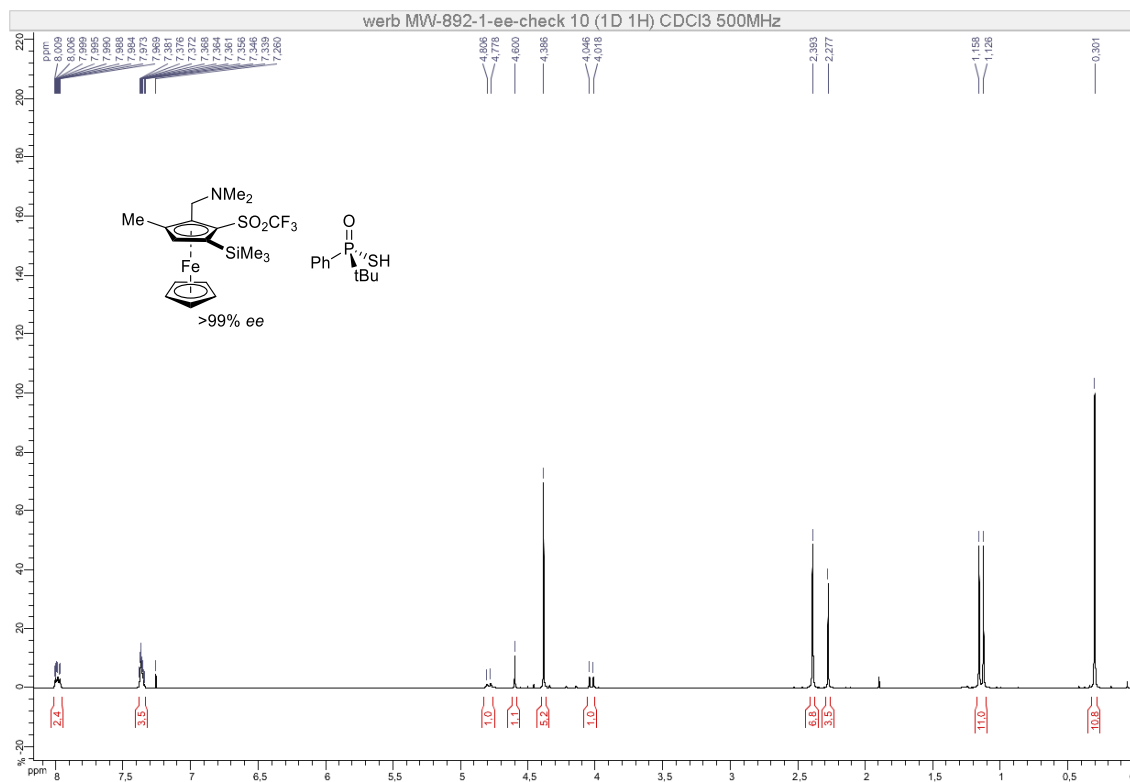


Figure S26. ^1H NMR spectrum of enantiopure **Rr-6** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

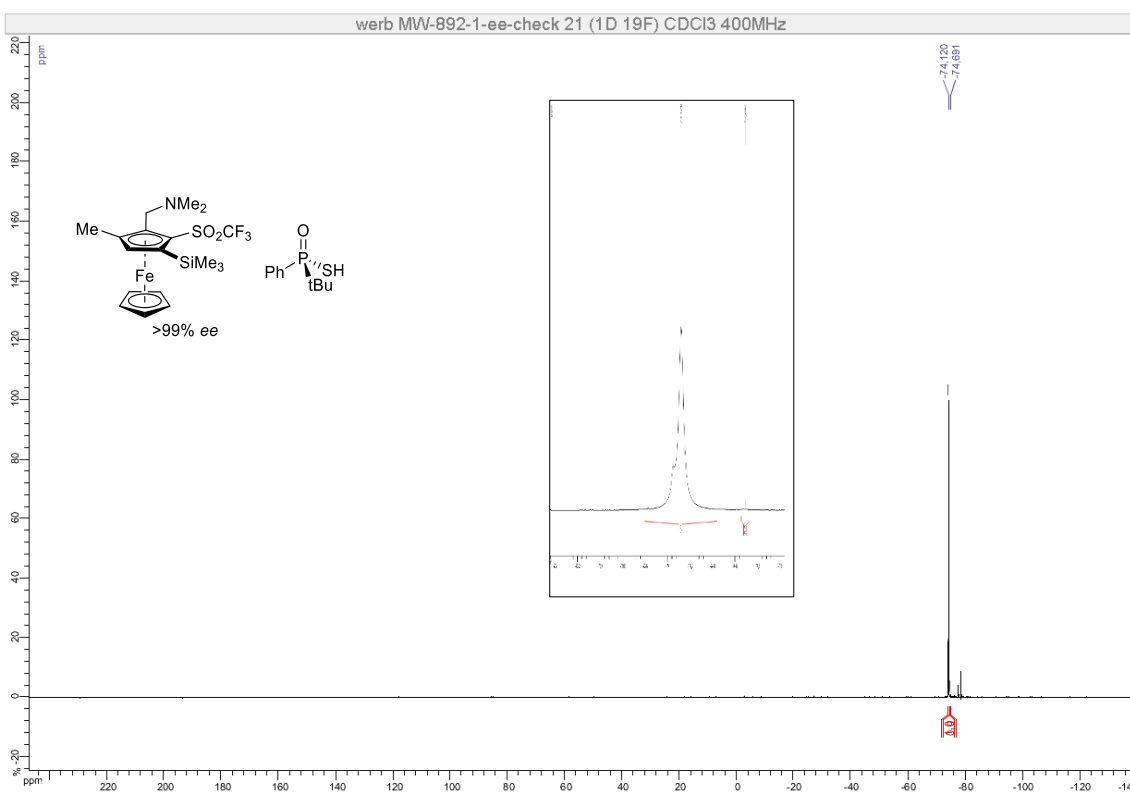


Figure S27. ^{19}F NMR spectrum of enantiopure **Rr-6** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 376 MHz.

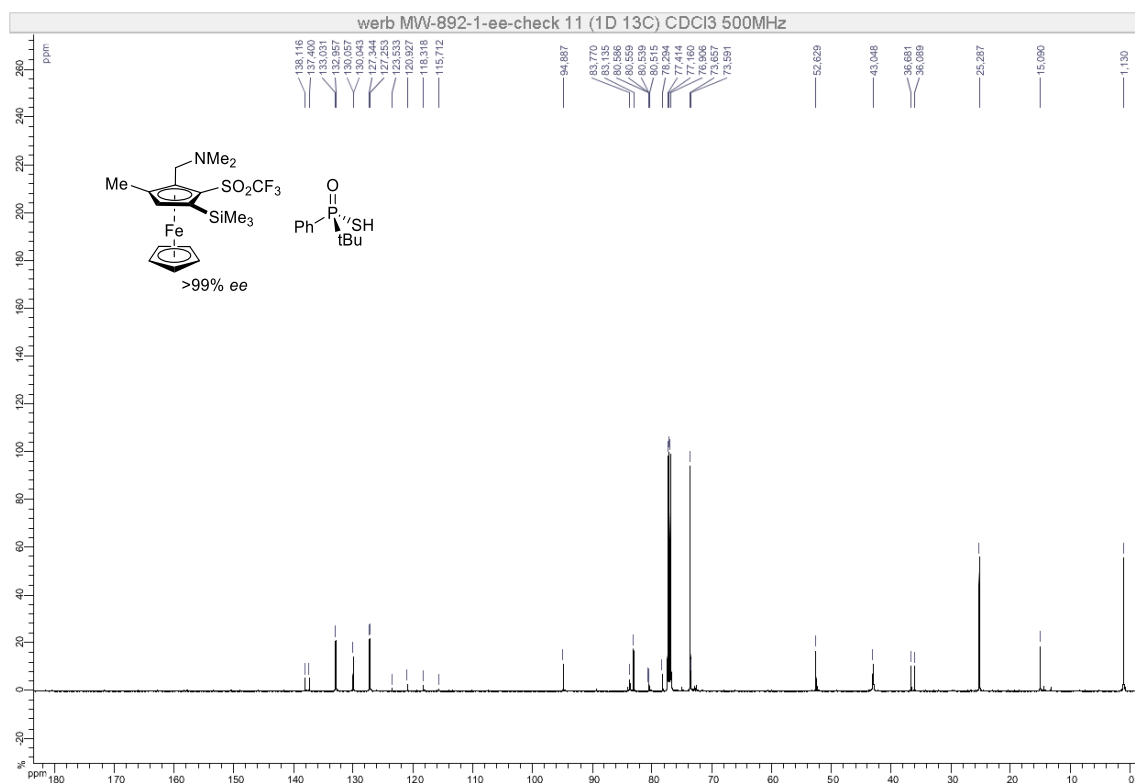


Figure S28. ¹³C NMR spectrum of enantiopure **Rp-6** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

We conducted the same experiments from **Sp-7**, concerned about a possible racemisation during the Bu₄NF induced desilylation, as previously observed. Thus, **Sp-7** (15.5 mg, 40 μmol) and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid (8.4 mg, 40 μmol) were dissolved in CDCl₃ (0.5 mL). The solution was stirred at rt for 1 min before being filtrated over a 0.22 μm nylon syringe filter directly into an NMR tube.

In the ¹H NMR spectrum, a few weak additional signals were observed in addition to those of the main product (Figure S29). However, as their chemical shifts did not correspond to those expected for a diastereoisomer, they were considered as impurities. Furthermore, no duplication of the methyl and Cp signals, expected for a diastereoisomer, was noticed. Therefore, we estimated a ratio > 99:1.

In the ¹⁹F NMR spectrum, the minor diastereoisomer was barely observed, the integration of the two peaks giving a 1:0.005 ratio (Figure S30). We therefore estimated a ratio > 99:1.

Similar observation was made in the ¹³C NMR spectrum with no duplication of the main signals (Figure S31).

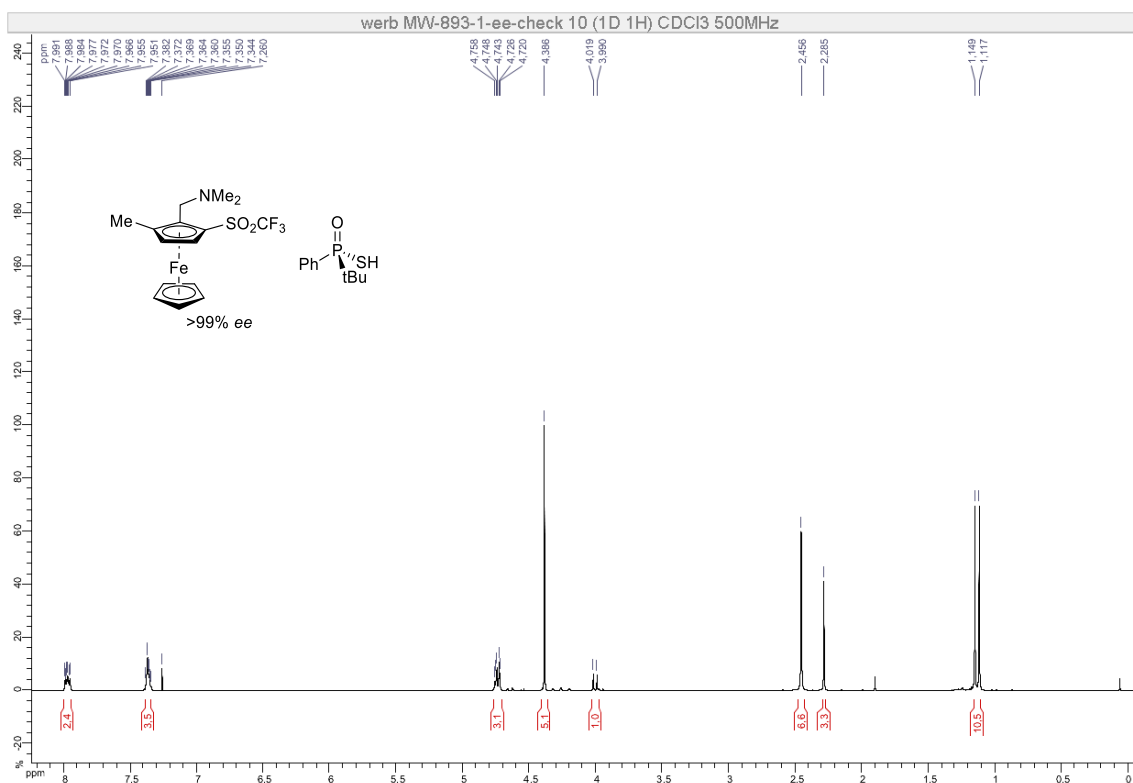


Figure S29. ^1H NMR spectrum of enantiopure **Sp-7** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

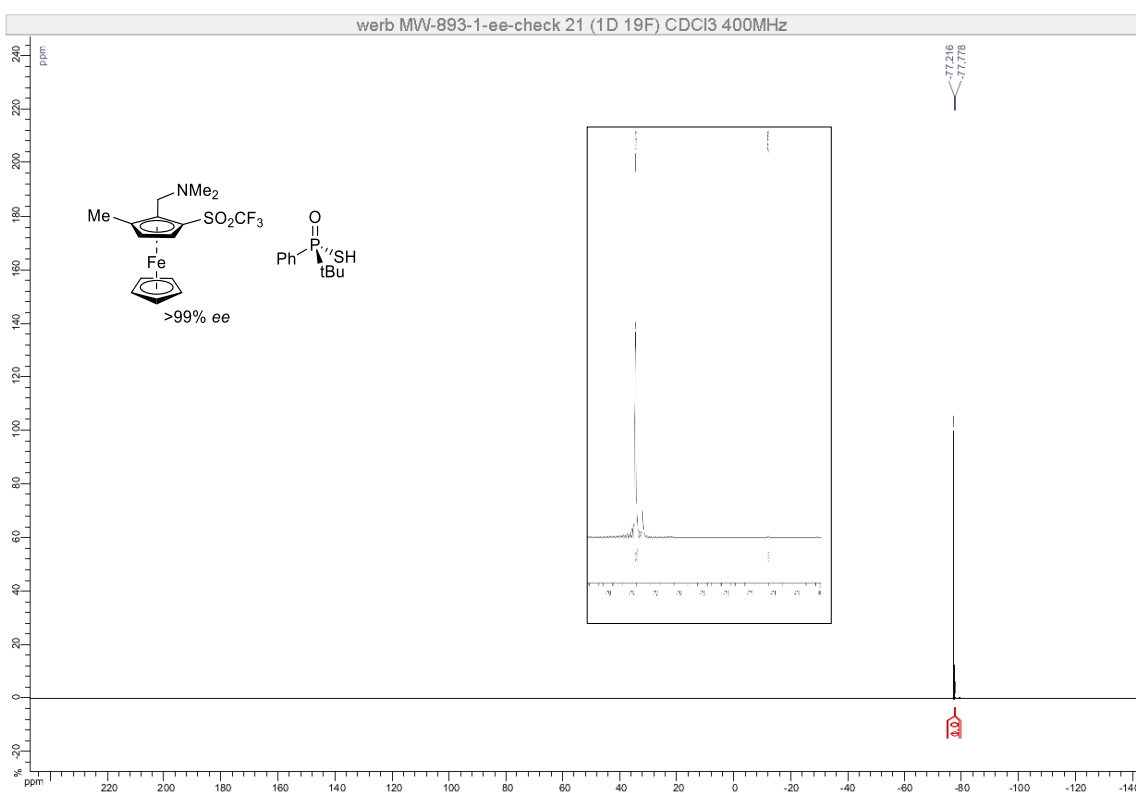


Figure S30. ^{19}F NMR spectrum of enantiopure **Sp-7** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 376 MHz.

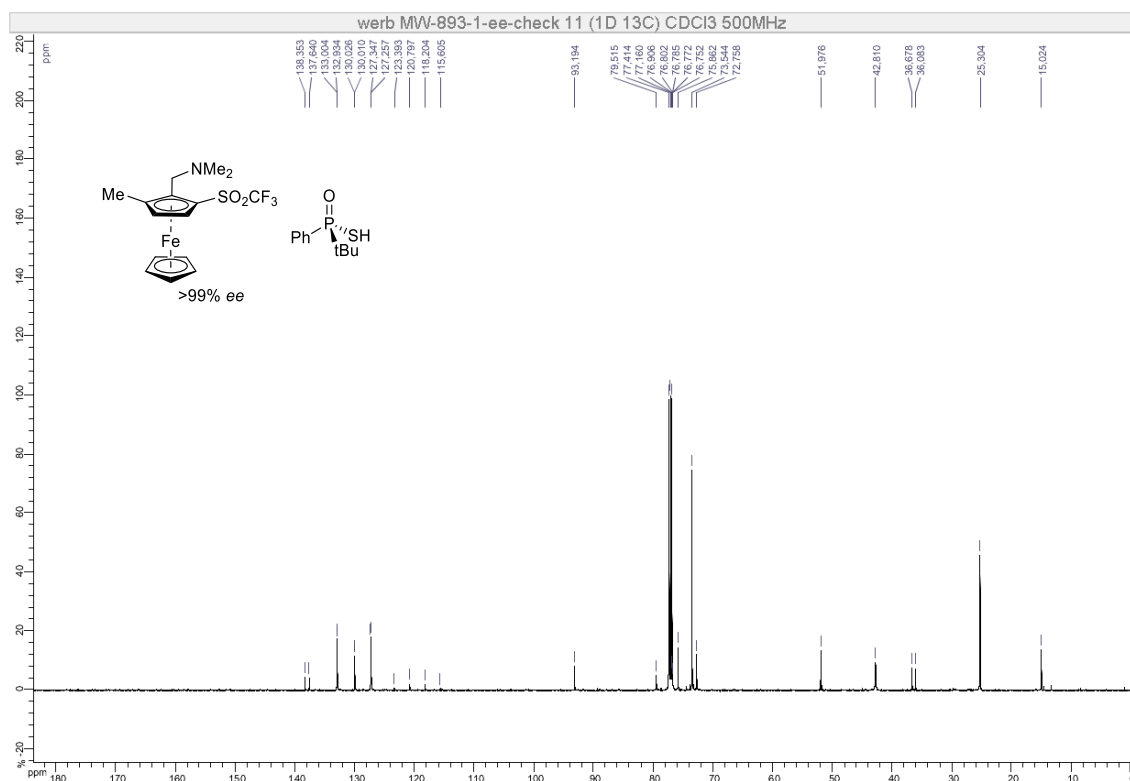


Figure S31. ^{13}C NMR spectrum of enantiopure **Sp-7** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

Next, **Sp-8** (38 mg, 90 μmol) and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid (19 mg, 90 μmol) were dissolved in CDCl_3 (0.5 mL). The solution was stirred at rt for 1 min before being filtrated over a 0.22 μm nylon syringe filter directly into a NMR tube.

While no duplication of signals was noticed in the ^1H (Figure S32) and ^{13}C (Figure S34) spectra, we observed a peak in the ^{19}F spectrum which might correspond to a putative diastereoisomer of **Sp-8**. The integration of the two peaks giving a 1:0.005 ratio (Figure S33), we estimated a ratio > 99:1.

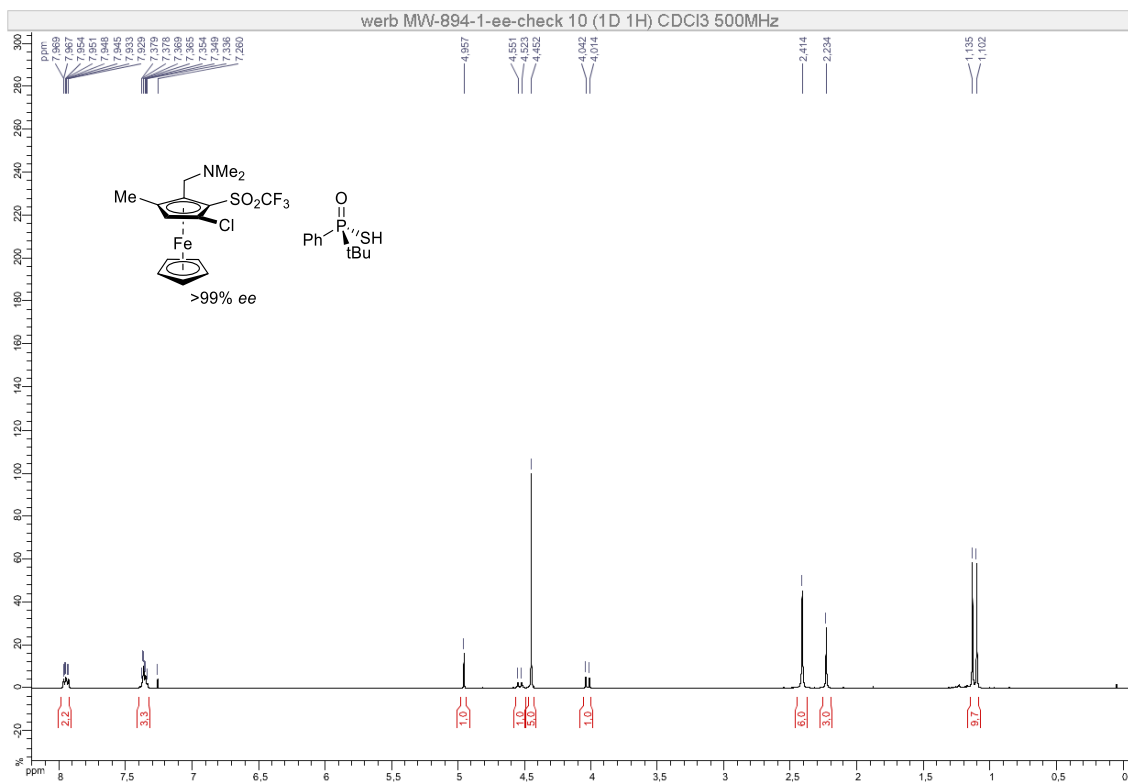


Figure S32. ^1H NMR spectrum of enantiopure **Sp-8** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

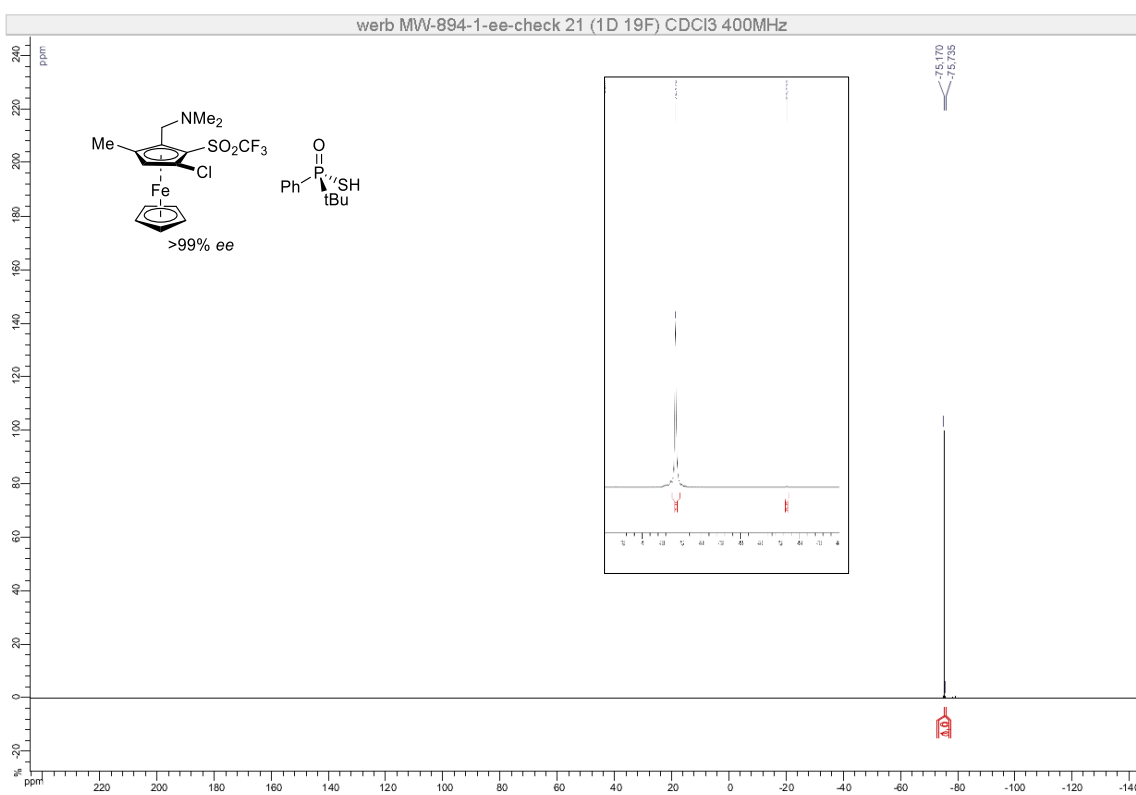


Figure S33. ^{19}F NMR spectrum of enantiopure **Sp-8** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 376 MHz.

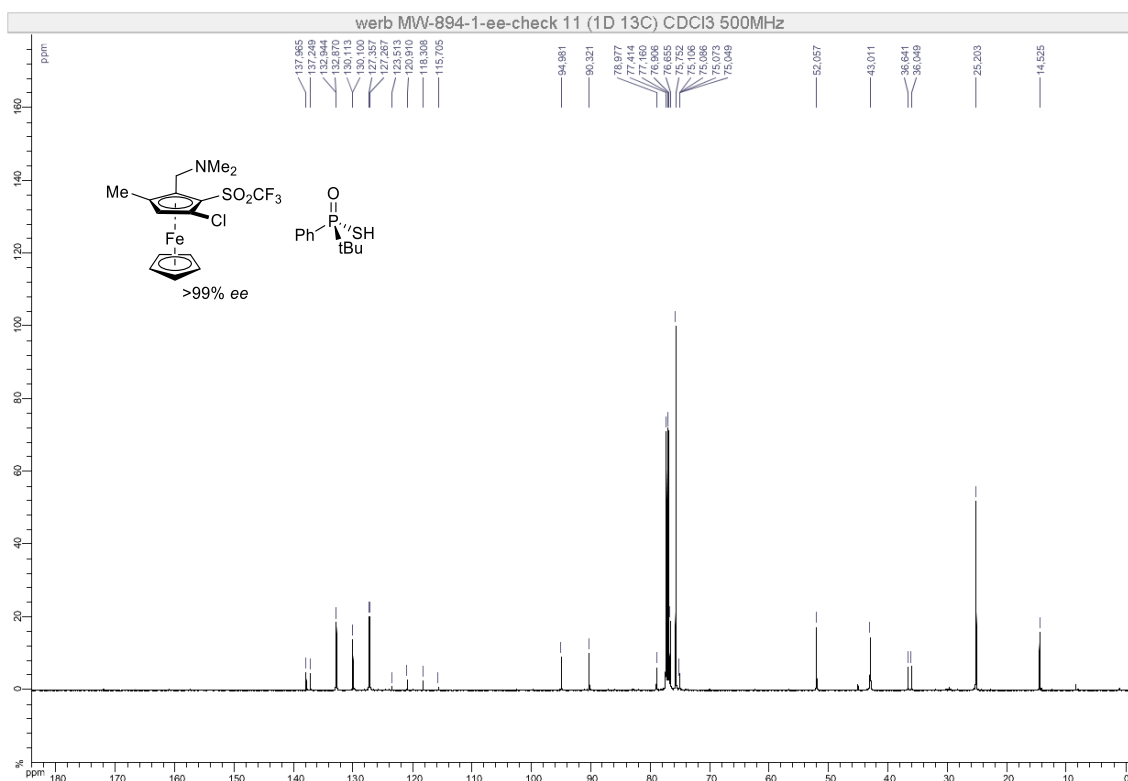


Figure S34. ^{13}C NMR spectrum of enantiopure **Sp-8** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

Finally, **Sp-9** (45 mg, 90 μmol) and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid (19 mg, 90 μmol) were dissolved in CDCl_3 (0.5 mL). The solution was stirred at rt for 1 min before being filtrated over a 0.22 μm nylon syringe filter directly into an NMR tube.

No duplication of signals was noticed in the ^1H (Figure S35) and ^{13}C (Figure S37) NMR spectra. In the ^{19}F NMR spectrum (Figure S36), a peak was tentatively assigned to the minor diastereoisomer with a 1:0.004 ratio, giving a diastereoisomeric ratio $> 99:1$.

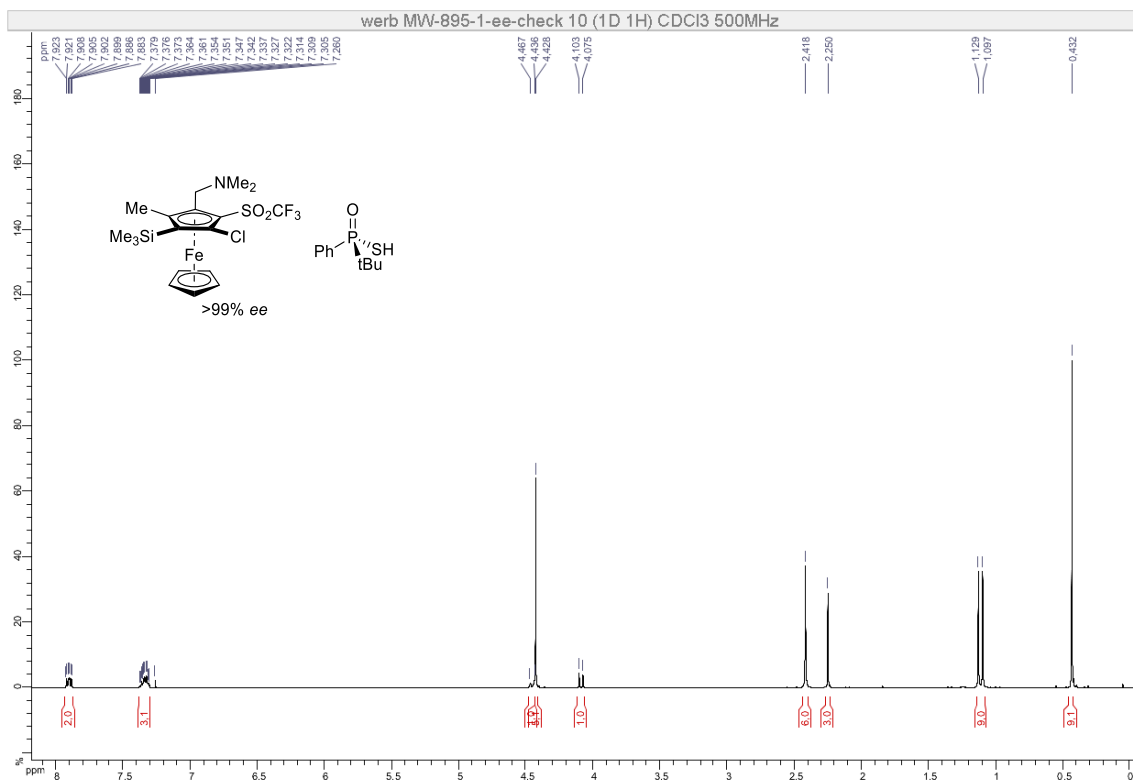


Figure S35. ^1H NMR spectrum of enantiopure **Sp-9** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

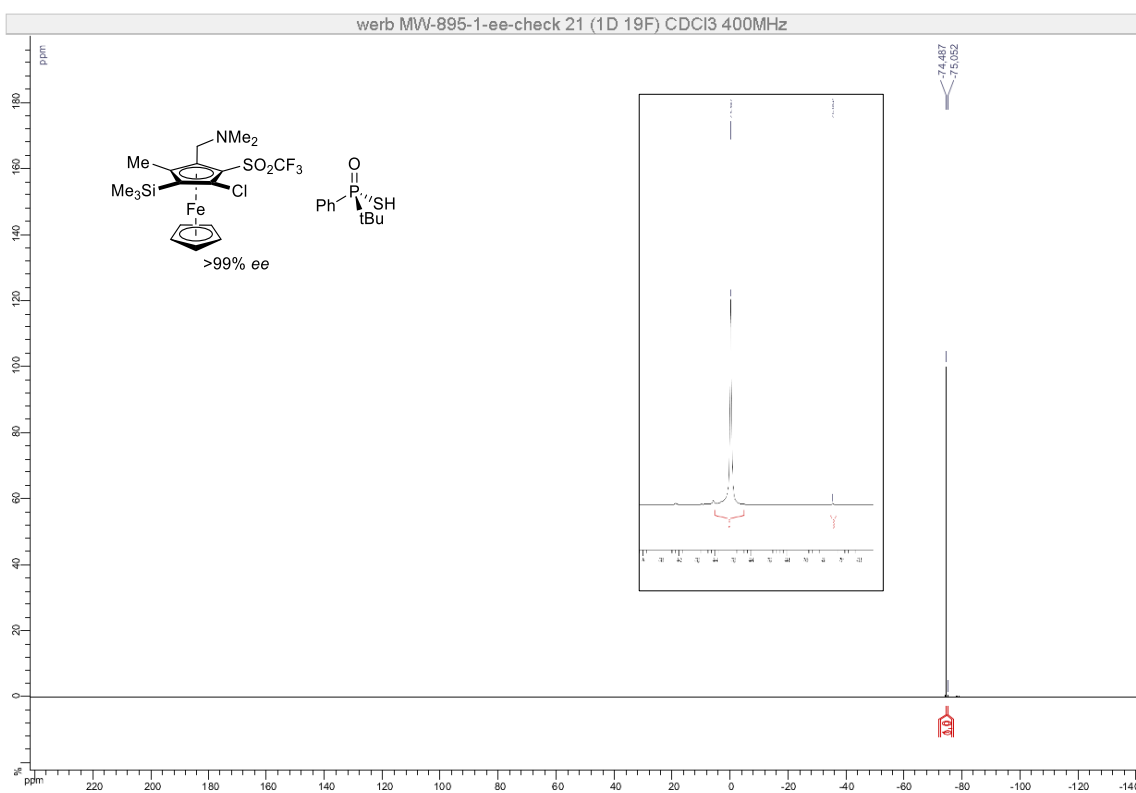


Figure S36. ^{19}F NMR spectrum of enantiopure **Sp-9** and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 376 MHz.

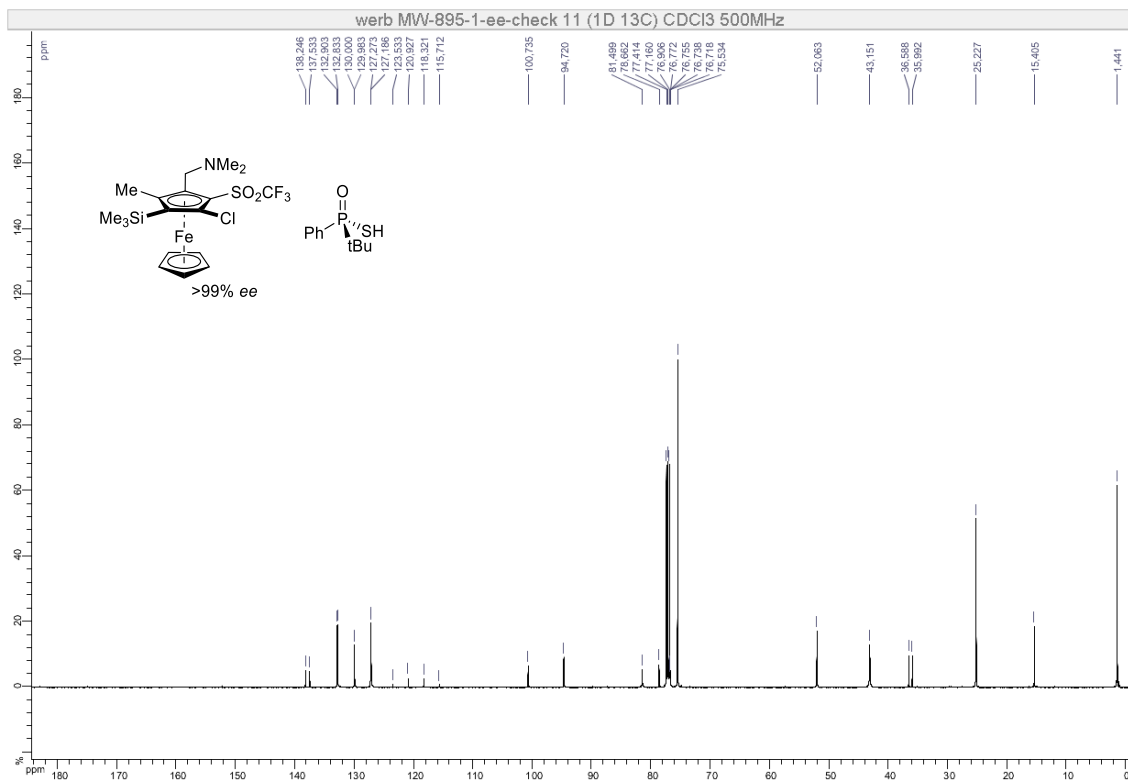


Figure S37. ¹³C NMR spectrum of enantiopure **Sp-9** and *(R)*-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

I) Computational details for p*K*_a calculations

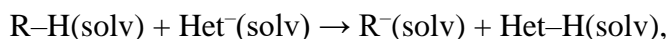
In order to study the C–H acidity of the considered ferrocenes and to compare it with related systems, we used the approach developed earlier and applied successfully, including ferrocenesulfoxides,^[22] ferrocenesulfonamides,^[23] ferrocenesulfonates,^[10b] ferrocenesulfonyl fluorides,^[14] and other ferrocene halides.^[24]

Thus, all electronic structure calculations were carried out using standard DFT methods implemented in Gaussian 16 package.^[25] We used the CAM-B3LYP hybrid functional.^[26] The structures of stable conformers for each substance were obtained by full geometry optimisation without any symmetry constraints from different initial guesses (including XRD structures where available). Further, all data correspond to the most stable conformer. The LANL2DZ basis set^[27] with the effective core potential was used to describe both Fe and I, while the 6-31G(d) basis set^[28] was used for the rest of the atoms during optimisations. Vibrational frequencies were calculated in order to characterise stationary points and calculate zero-point vibrational energies (ZPVE) and thermal corrections. The single point energies in turn were calculated at the CAM-B3LYP/LANL2DZ + 6-311+G(d,p) level.

Further, the gas-phase Gibbs energies were derived and the gas-phase acidity ΔG_{acid} was defined as the Gibbs energy of deprotonation of the corresponding substrate R–H ($\text{R–H(g)} \rightarrow \text{R}^{\text{--}}(\text{g}) + \text{H}^+(\text{g})$):

$$\Delta G_{\text{acid}} = G^0_{298}(\text{R}^{\text{--}}) + G^0_{298}(\text{H}^+) - G^0_{298}(\text{R–H}).$$

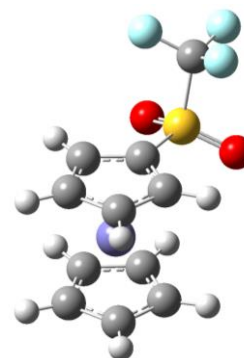
The discussed p*K*_a values were obtained from the Gibbs free energy of the isodesmic reaction between the studied (R–H) and a probe compound (Het–H):



here furan with p*K*_a(THF) of 35.6^[29] was used as the probe compound. The solvent influence during calculations was accounted for by using polarisable continuum model (IEF-PCM)^[30] with the default parameters for THF in order to mimic experimental conditions.

J) Cartesian coordinates of the DFT optimised structure for compound 1

| atom | X | Y | Z |
|------|----------|----------|----------|
| Fe | 1.64129 | 0.24585 | 0.00008 |
| C | -0.34858 | 0.57680 | 0.00014 |
| C | 0.22401 | 1.17406 | 1.16540 |
| C | 1.15361 | 2.13901 | 0.71252 |
| C | 1.15358 | 2.13896 | -0.71241 |
| C | 0.22397 | 1.17396 | -1.16518 |
| C | 1.96244 | -1.78877 | -0.00024 |
| C | 2.55248 | -1.19833 | 1.14992 |
| C | 3.51036 | -0.24315 | 0.71063 |
| C | 3.51025 | -0.24292 | -0.71087 |
| C | 2.55227 | -1.19794 | -1.15032 |
| H | 0.00218 | 0.90006 | 2.18618 |
| H | 1.78820 | 2.74524 | 1.34354 |
| H | 1.78819 | 2.74510 | -1.34350 |
| H | 0.00204 | 0.89992 | -2.18593 |
| H | 1.16689 | -2.52064 | -0.00030 |
| H | 2.28800 | -1.41174 | 2.17603 |
| H | 4.10552 | 0.39873 | 1.34530 |
| H | 4.10528 | 0.39920 | -1.34542 |
| H | 2.28759 | -1.41100 | -2.17645 |
| S | -1.48280 | -0.74580 | 0.00022 |
| O | -1.41693 | -1.44707 | -1.27395 |
| O | -1.41731 | -1.44663 | 1.27465 |
| C | -3.10097 | 0.14855 | -0.00018 |
| F | -4.08853 | -0.73378 | -0.00038 |
| F | -3.18714 | 0.91486 | -1.08381 |
| F | -3.18759 | 0.91490 | 1.08340 |



K) Computational details to rationalise the enantioselectivity observed using (*R*)-PEALi

All calculations were carried with the Gaussian 16 (revision A.03) program package.^[25] The molecular structures and harmonic vibrational frequencies were obtained using the hybrid density functional method based on the unrestricted B3LYP^[31] method. We used LANL2DZ basis set^[27, 32] for a Fe atom and 6-31+G** basis set for all other atoms. Geometry optimisation and vibrational analysis were performed at the same level. All stationary points were optimised without any symmetry assumptions, and characterised by normal coordinate analysis at the same level of theory (number of imaginary frequencies, NIMAG, 0 for minima and 1 for TSs). The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.^[33]

| | | | | | | |
|---------------------------------|----------------------|-------------|---------------|---------------|-------------|-------------|
| | | | C -3.76347600 | 0.46906200 | -1.26631500 | |
| • INT1 (<i>S_p</i>) | | | H -4.76003900 | 0.93318100 | -1.11517400 | |
| Energy (RB3LYP): | -2079.037906 hartree | | C -2.58010300 | 2.54394300 | -0.69385200 | |
| Gibbs Free Energy: | -2078.628512 hartree | | H -2.27558700 | 2.76421800 | -1.73839400 | |
| | | | C -3.90092800 | -0.95575000 | -0.72237000 | |
| Fe | 2.52096300 | -0.39288500 | -1.32346700 | C -3.21468000 | -2.05612300 | -1.25979900 |
| C | 1.09397900 | -1.50040900 | -0.31205100 | C -4.68005200 | -1.16814900 | 0.43060500 |
| C | 1.97834300 | -2.38881200 | -1.02357900 | C -3.31126100 | -3.32568300 | -0.67462300 |
| C | 1.85908300 | -2.06361900 | -2.40031000 | H -2.60529500 | -1.92830200 | -2.14872600 |
| C | 0.92279200 | -0.98925100 | -2.53772500 | C -4.77983800 | -2.43262100 | 1.01990800 |
| H | 0.64803100 | -0.50464800 | -3.46461500 | H -5.22147200 | -0.32605900 | 0.85618600 |
| C | 0.44373700 | -0.62194100 | -1.25303800 | C -4.09205300 | -3.51856500 | 0.46708900 |
| C | 3.97525900 | 0.50419500 | -0.11060700 | H -2.77310400 | -4.16242500 | -1.11225900 |
| H | 4.13338300 | 0.28628600 | 0.93457100 | H -5.39642700 | -2.57062700 | 1.90420700 |
| C | 4.59672300 | -0.16934800 | -1.20304600 | H -4.16489300 | -4.50257600 | 0.92147300 |
| H | 5.29279600 | -0.99378300 | -1.12913400 | C -1.45694200 | 3.08558100 | 0.18562600 |
| C | 4.09953500 | 0.40640000 | -2.41331600 | C -1.48729200 | 2.92145600 | 1.58103500 |
| H | 4.35176700 | 0.09316500 | -3.41732700 | C -0.38231000 | 3.79802400 | -0.36515600 |
| C | 3.17386500 | 1.43794300 | -2.06309500 | C -0.47707100 | 3.44091400 | 2.39454100 |
| H | 2.59702600 | 2.03534800 | -2.75591200 | H -2.32564200 | 2.39502400 | 2.03083000 |
| C | 3.09071000 | 1.49662000 | -0.63952600 | C 0.62949200 | 4.32994100 | 0.44313900 |
| H | 2.44847200 | 2.15258600 | -0.06792800 | H -0.34393700 | 3.94517500 | -1.44261600 |
| H | 2.41575500 | -2.52720600 | -3.20320900 | C 0.58837600 | 4.15006400 | 1.82850700 |
| N | -2.73212400 | 1.11707700 | -0.45866000 | H -0.52590500 | 3.30284900 | 3.47182100 |

| | | | | | | | |
|----|-------------|-------------|-------------|---|-------------|-------------|-------------|
| H | 1.44531800 | 4.88887500 | -0.00924900 | C | 3.17386500 | 1.43794300 | -2.06309500 |
| H | 1.37022500 | 4.56306700 | 2.46023900 | H | 2.59702600 | 2.03534800 | -2.75591200 |
| C | -3.51885600 | 0.50512400 | -2.79286100 | C | 3.09071000 | 1.49662000 | -0.63952600 |
| H | -4.28732000 | -0.05660400 | -3.33870400 | H | 2.44847200 | 2.15258600 | -0.06792800 |
| H | -3.54497400 | 1.53811700 | -3.15470200 | H | 2.41575500 | -2.52720600 | -3.20320900 |
| H | -2.53462100 | 0.09571600 | -3.04950900 | N | -2.73212400 | 1.11707700 | -0.45866000 |
| C | -3.86508200 | 3.38546300 | -0.45063500 | C | -3.76347600 | 0.46906200 | -1.26631500 |
| H | -3.66552500 | 4.45488500 | -0.58930900 | H | -4.76003900 | 0.93318100 | -1.11517400 |
| H | -4.66163200 | 3.10402400 | -1.14762800 | C | -2.58010300 | 2.54394300 | -0.69385200 |
| H | -4.23787500 | 3.23137700 | 0.56879400 | H | -2.27558700 | 2.76421800 | -1.73839400 |
| H | -0.30398700 | 0.13499500 | -1.03251100 | C | -3.90092800 | -0.95575000 | -0.72237000 |
| H | 2.58662200 | -3.16469800 | -0.58199600 | C | -3.21468000 | -2.05612300 | -1.25979900 |
| Li | -2.11212200 | -0.05631500 | 0.79126900 | C | -4.68005200 | -1.16814900 | 0.43060500 |
| S | 0.59193200 | -1.73534200 | 1.35534300 | C | -3.31126100 | -3.32568300 | -0.67462300 |
| O | 0.69176300 | -3.15014100 | 1.71047500 | H | -2.60529500 | -1.92830200 | -2.14872600 |
| O | -0.66423300 | -0.98637100 | 1.58619500 | C | -4.77983800 | -2.43262100 | 1.01990800 |
| C | 1.79811300 | -0.86892800 | 2.53254200 | H | -5.22147200 | -0.32605900 | 0.85618600 |
| F | 1.35605500 | -1.06902400 | 3.77665000 | C | -4.09205300 | -3.51856500 | 0.46708900 |
| F | 1.85750500 | 0.44273700 | 2.29232000 | H | -2.77310400 | -4.16242500 | -1.11225900 |
| F | 3.02238500 | -1.40184500 | 2.41240300 | H | -5.39642700 | -2.57062700 | 1.90420700 |

• TS (S_p)

Energy (RB3LYP): -2079.015068 hartree

Gibbs Free Energy: -2078.609389 hartree

| | | | | | | | |
|----|------------|-------------|-------------|---|-------------|-------------|-------------|
| Fe | 2.52096300 | -0.39288500 | -1.32346700 | H | -4.16489300 | -4.50257600 | 0.92147300 |
| C | 1.09397900 | -1.50040900 | -0.31205100 | C | -1.45694200 | 3.08558100 | 0.18562600 |
| C | 1.97834300 | -2.38881200 | -1.02357900 | C | -1.48729200 | 2.92145600 | 1.58103500 |
| C | 1.85908300 | -2.06361900 | -2.40031000 | C | -0.38231000 | 3.79802400 | -0.36515600 |
| C | 0.92279200 | -0.98925100 | -2.53772500 | C | -0.47707100 | 3.44091400 | 2.39454100 |
| H | 0.64803100 | -0.50464800 | -3.46461500 | H | -2.32564200 | 2.39502400 | 2.03083000 |
| C | 0.44373700 | -0.62194100 | -1.25303800 | C | 0.62949200 | 4.32994100 | 0.44313900 |
| C | 3.97525900 | 0.50419500 | -0.11060700 | H | -0.34393700 | 3.94517500 | -1.44261600 |
| H | 4.13338300 | 0.28628600 | 0.93457100 | C | 0.58837600 | 4.15006400 | 1.82850700 |
| C | 4.59672300 | -0.16934800 | -1.20304600 | H | -0.52590500 | 3.30284900 | 3.47182100 |
| H | 5.29279600 | -0.99378300 | -1.12913400 | H | 1.44531800 | 4.88887500 | -0.00924900 |
| C | 4.09953500 | 0.40640000 | -2.41331600 | H | 1.37022500 | 4.56306700 | 2.46023900 |
| H | 4.35176700 | 0.09316500 | -3.41732700 | C | -3.51885600 | 0.50512400 | -2.79286100 |
| | | | | H | -4.28732000 | -0.05660400 | -3.33870400 |
| | | | | H | -3.54497400 | 1.53811700 | -3.15470200 |
| | | | | H | -2.53462100 | 0.09571600 | -3.04950900 |
| | | | | C | -3.86508200 | 3.38546300 | -0.45063500 |
| | | | | H | -3.66552500 | 4.45488500 | -0.58930900 |

| | | | | | | | |
|----|-------------|-------------|-------------|---|-------------|-------------|-------------|
| H | -4.66163200 | 3.10402400 | -1.14762800 | C | -3.33768800 | 1.54685100 | 1.07433600 |
| H | -4.23787500 | 3.23137700 | 0.56879400 | H | -4.41890100 | 1.74487500 | 1.06960400 |
| H | -0.30398700 | 0.13499500 | -1.03251100 | C | -3.34411400 | -1.99435400 | -0.41385900 |
| H | 2.58662200 | -3.16469800 | -0.58199600 | C | -3.78621600 | -1.97903600 | -1.74686400 |
| Li | -2.11212200 | -0.05631500 | 0.79126900 | C | -2.49044900 | -3.02797400 | -0.00313400 |
| S | 0.59193200 | -1.73534200 | 1.35534300 | C | -3.38122700 | -2.96860800 | -2.64497900 |
| O | 0.69176300 | -3.15014100 | 1.71047500 | H | -4.45708800 | -1.19608100 | -2.09293800 |
| O | -0.66423300 | -0.98637100 | 1.58619500 | C | -2.08480100 | -4.02133300 | -0.89942700 |
| C | 1.79811300 | -0.86892800 | 2.53254200 | H | -2.13094600 | -3.05363500 | 1.02232300 |
| F | 1.35605500 | -1.06902400 | 3.77665000 | C | -2.52907100 | -3.99374000 | -2.22268700 |
| F | 1.85750500 | 0.44273700 | 2.29232000 | H | -3.73122600 | -2.93952400 | -3.67307700 |
| F | 3.02238500 | -1.40184500 | 2.41240300 | H | -1.41484400 | -4.80649300 | -0.56192500 |

• INT2 (S_p)

Energy (RB3LYP): -2079.048312 hartree

Gibbs Free Energy: -2078.634367 hartree

| | | | | | | | |
|----|-------------|-------------|-------------|----|-------------|-------------|-------------|
| Fe | 2.58749200 | 0.19545500 | -1.25176500 | C | -2.67108200 | 2.76605200 | 0.45050600 |
| C | 1.57521000 | -1.27209000 | -0.23442400 | C | -1.28812000 | 2.98599200 | 0.54871000 |
| C | 2.72957000 | -1.84239100 | -0.88923400 | C | -3.44664800 | 3.69423600 | -0.25898500 |
| C | 2.50384700 | -1.61497300 | -2.27299800 | C | -0.70001200 | 4.10439100 | -0.04684700 |
| C | 1.24919600 | -0.92314100 | -2.41270700 | H | -0.66256300 | 2.29213100 | 1.10398500 |
| H | 0.85863700 | -0.58620900 | -3.36659600 | C | -2.86191100 | 4.81449600 | -0.85744500 |
| C | 0.60694900 | -0.69542600 | -1.15271400 | H | -4.52127100 | 3.54319900 | -0.33719900 |
| C | 4.01580900 | 1.33867600 | -0.23592700 | C | -1.48485300 | 5.02249700 | -0.75139800 |
| H | 4.53231900 | 1.02877000 | 0.66158700 | H | 0.37087600 | 4.26163500 | 0.04244200 |
| C | 4.43933100 | 1.09212400 | -1.57677000 | H | -3.48175800 | 5.52334700 | -1.39924000 |
| H | 5.32363000 | 0.54375000 | -1.87252800 | H | -1.02567300 | 5.89298400 | -1.21096500 |
| C | 3.46225300 | 1.64591800 | -2.46074100 | C | -5.29203000 | -0.76435500 | 0.66618900 |
| H | 3.47694000 | 1.58884700 | -3.54067800 | H | -5.74393500 | -1.73900000 | 0.87428200 |
| C | 2.43372800 | 2.24027400 | -1.66456300 | H | -5.58727500 | -0.08307800 | 1.46981300 |
| H | 1.52851700 | 2.69984300 | -2.03640400 | H | -5.72126900 | -0.39016400 | -0.27016500 |
| C | 2.77488200 | 2.04997900 | -0.29398300 | C | -2.91276600 | 1.30118700 | 2.52848700 |
| H | 2.18491400 | 2.35825500 | 0.55710800 | H | -3.04043800 | 2.22028900 | 3.10776000 |
| H | 3.19121600 | -1.87357200 | -3.06939000 | H | -3.52671400 | 0.52641600 | 2.99766300 |
| N | -3.04116500 | 0.35623300 | 0.21424000 | H | -1.86840100 | 0.98546400 | 2.60059700 |
| C | -3.76223000 | -0.90995500 | 0.57209000 | H | -3.31974600 | 0.60498400 | -0.73674700 |
| H | -3.38520800 | -1.20565100 | 1.55565500 | H | 3.57480300 | -2.33753500 | -0.43157300 |
| | | | | Li | -1.02829600 | -0.14590400 | -0.04106000 |
| | | | | S | 1.09447200 | -1.50205700 | 1.42877500 |
| | | | | O | 1.15460500 | -2.91013900 | 1.84195700 |
| | | | | O | -0.17023700 | -0.73768900 | 1.64983500 |

| | | | | | | | |
|--------------------------|----------------------|-------------|-------------|----|-------------|-------------|-------------|
| C | 2.31703400 | -0.65454700 | 2.60547500 | C | 5.00282100 | -3.15776100 | 0.50024600 |
| F | 2.00541200 | -1.00311300 | 3.85976200 | H | 5.88468700 | -1.22110100 | 0.85274200 |
| F | 2.25887400 | 0.68097000 | 2.50911600 | C | 4.06735100 | -3.89031000 | -0.23816200 |
| F | 3.57023500 | -1.05664500 | 2.34186700 | H | 2.57192000 | -3.80174900 | -1.78983600 |
| | | | | H | 5.60526600 | -3.65201900 | 1.25796800 |
| | | | | H | 3.93911200 | -4.95427500 | -0.05967200 |
| | | | | C | 2.05036800 | 2.93166800 | 0.35142300 |
| • INT1 (R _p) | | | | C | 1.64085900 | 2.58115200 | 1.64966000 |
| Energy (RB3LYP): | -2079.038384 hartree | | | C | 1.20293100 | 3.75784900 | -0.40134100 |
| Gibbs Free Energy: | -2078.629206 hartree | | | C | 0.42864000 | 3.03831500 | 2.17518500 |
| | | | | H | 2.28875900 | 1.95283600 | 2.25515600 |
| Fe | -3.17553000 | -0.02725400 | -1.07615000 | C | -0.00943800 | 4.22557300 | 0.11930600 |
| C | -1.32380700 | -0.74419800 | -0.55224300 | H | 1.50251400 | 4.04145800 | -1.40783500 |
| C | -1.76274100 | -1.37695600 | -1.77223400 | C | -0.40350700 | 3.86614500 | 1.41207300 |
| C | -1.92405900 | -0.33936800 | -2.72837800 | H | 0.13892800 | 2.76018200 | 3.18551300 |
| C | -1.59789600 | 0.90961400 | -2.11126800 | H | -0.64129200 | 4.87542800 | -0.48169600 |
| H | -1.66099900 | 1.88321600 | -2.57697100 | H | -1.33897500 | 4.23473900 | 1.82492800 |
| C | -1.21687400 | 0.67434100 | -0.76517000 | C | 4.72808600 | 0.75971000 | -2.39133900 |
| C | -4.77851800 | -0.83909200 | -0.01023800 | H | 5.57046200 | 0.21063900 | -2.83059300 |
| H | -4.72260700 | -1.74512800 | 0.57598300 | H | 4.93722300 | 1.82920600 | -2.49980400 |
| C | -5.10345600 | -0.75957100 | -1.39608800 | H | 3.82459600 | 0.54102000 | -2.97225500 |
| H | -5.32909900 | -1.59544600 | -2.04421200 | C | 4.55185700 | 3.05803900 | 0.60905700 |
| C | -5.02432700 | 0.61217500 | -1.79084900 | H | 4.48239100 | 4.15257000 | 0.64253100 |
| H | -5.18014500 | 0.99646000 | -2.78967600 | H | 5.51748000 | 2.79993700 | 0.16129300 |
| C | -4.65392700 | 1.38001400 | -0.64456000 | H | 4.54630900 | 2.67586100 | 1.63639600 |
| H | -4.47606200 | 2.44658300 | -0.62511800 | H | -0.90844700 | 1.41748400 | -0.04285600 |
| C | -4.49826300 | 0.48514500 | 0.45543200 | H | -1.91814100 | -2.43688400 | -1.90966500 |
| H | -4.19981200 | 0.75911200 | 1.45731100 | Li | 2.23524400 | -0.27618500 | 0.38140400 |
| H | -2.27491400 | -0.47233800 | -3.74252600 | S | -0.66881000 | -1.66112600 | 0.79282700 |
| N | 3.37082700 | 0.99261000 | -0.25616300 | C | -1.61484600 | -1.19616700 | 2.37005400 |
| C | 4.53555300 | 0.39151500 | -0.89744700 | O | -0.89951200 | -3.09021000 | 0.58760700 |
| H | 5.48448400 | 0.67219500 | -0.39625000 | O | 0.68937600 | -1.15493100 | 1.09534700 |
| C | 3.38173700 | 2.44386400 | -0.21035800 | F | -0.94825900 | -1.70480800 | 3.40719000 |
| H | 3.45983100 | 2.89172600 | -1.22200600 | F | -2.84904900 | -1.70970100 | 2.34881700 |
| C | 4.40413300 | -1.11889200 | -0.70470500 | F | -1.69126100 | 0.13405100 | 2.50077100 |
| C | 3.46688200 | -1.86925300 | -1.43789300 | | | | |
| C | 5.16191700 | -1.78773100 | 0.27033500 | | | | |
| C | 3.29872100 | -3.24100800 | -1.20758700 | | | | |
| H | 2.87676400 | -1.37842000 | -2.20735800 | | | | |

• TS (R_p)
Energy (RB3LYP): -2079.015068 hartree
Gibbs Free Energy: -2078.606258 hartree

| | | | |
|----|-------------|-------------|-------------|
| Fe | -2.15739000 | -0.47491200 | -1.40295600 |
| C | -0.65997200 | -1.49758800 | -0.40538700 |
| C | -1.41468200 | -2.40498900 | -1.24447300 |
| C | -1.23643700 | -1.92970600 | -2.56786700 |
| C | -0.40774800 | -0.75717200 | -2.50767500 |
| H | -0.14533900 | -0.15981800 | -3.37337500 |
| C | -0.00976100 | -0.44969200 | -1.16789000 |
| C | -4.23008200 | -0.49507600 | -1.65203300 |
| H | -4.79417000 | -1.38428700 | -1.89936700 |
| C | -3.62600900 | 0.40262900 | -2.58638700 |
| H | -3.65366500 | 0.31333800 | -3.66391900 |
| C | -2.93768200 | 1.41133200 | -1.84319500 |
| H | -2.34450500 | 2.21188500 | -2.26268700 |
| C | -3.10857100 | 1.13510100 | -0.45551000 |
| H | -2.67568000 | 1.69766700 | 0.35867300 |
| C | -3.91051600 | -0.04444300 | -0.33760800 |
| H | -4.21051900 | -0.52191900 | 0.58343400 |
| H | -1.69126700 | -2.35358400 | -3.45430000 |
| N | 2.07937700 | 1.26016400 | -0.59321100 |
| C | 3.25455400 | 0.78692100 | -1.35710500 |
| H | 4.08957800 | 1.48418800 | -1.19873800 |
| C | 1.69100100 | 2.66618300 | -0.79537800 |
| H | 1.11073600 | 2.78259400 | -1.73015000 |
| C | 3.70379000 | -0.52910700 | -0.71243800 |
| C | 3.30712700 | -1.79308400 | -1.17426800 |
| C | 4.49942700 | -0.47198500 | 0.44826700 |
| C | 3.69133400 | -2.95797300 | -0.50056200 |
| H | 2.68598900 | -1.87562100 | -2.05965000 |
| C | 4.88467700 | -1.63334300 | 1.12538800 |
| H | 4.83889700 | 0.49831900 | 0.80778300 |
| C | 4.47799700 | -2.88423000 | 0.65109300 |
| H | 3.36467600 | -3.92463800 | -0.87332300 |
| H | 5.50630900 | -1.56123600 | 2.01375100 |
| H | 4.76914700 | -3.79010000 | 1.17448200 |

| | | | |
|----|-------------|-------------|-------------|
| C | 0.77372900 | 3.11176300 | 0.34340600 |
| C | 1.16317000 | 2.96787400 | 1.68535700 |
| C | -0.45017400 | 3.74004800 | 0.08041500 |
| C | 0.35149300 | 3.41899400 | 2.72906800 |
| H | 2.13164400 | 2.52686500 | 1.91586600 |
| C | -1.26634700 | 4.20122500 | 1.11863400 |
| H | -0.76848800 | 3.86868400 | -0.95130500 |
| C | -0.87144700 | 4.03697700 | 2.44876400 |
| H | 0.67547200 | 3.29508600 | 3.75898000 |
| H | -2.21261700 | 4.68309300 | 0.88719800 |
| H | -1.50617600 | 4.38794200 | 3.25736700 |
| C | 3.04628000 | 0.69100200 | -2.88119800 |
| H | 3.96079300 | 0.35251400 | -3.38233100 |
| H | 2.78716300 | 1.67437600 | -3.28761100 |
| H | 2.23680300 | 0.00499400 | -3.14282300 |
| C | 2.87145500 | 3.66047300 | -0.89048300 |
| H | 2.48735100 | 4.68456400 | -0.93936100 |
| H | 3.48074200 | 3.49351200 | -1.78407200 |
| H | 3.52178800 | 3.58682000 | -0.01112300 |
| H | 1.03435400 | 0.50124600 | -0.87287100 |
| H | -1.97140400 | -3.27430400 | -0.92380500 |
| Li | 1.91957100 | 0.21830900 | 0.99803500 |
| S | -0.32281100 | -1.86182000 | 1.27557000 |
| C | -1.77234100 | -1.37783200 | 2.39804900 |
| O | -0.19720500 | -3.30702300 | 1.48153600 |
| O | 0.75010400 | -0.95976300 | 1.78455500 |
| F | -1.43153200 | -1.68057300 | 3.65633500 |
| F | -2.86882800 | -2.07519400 | 2.06777900 |
| F | -2.04115600 | -0.07012000 | 2.32663700 |

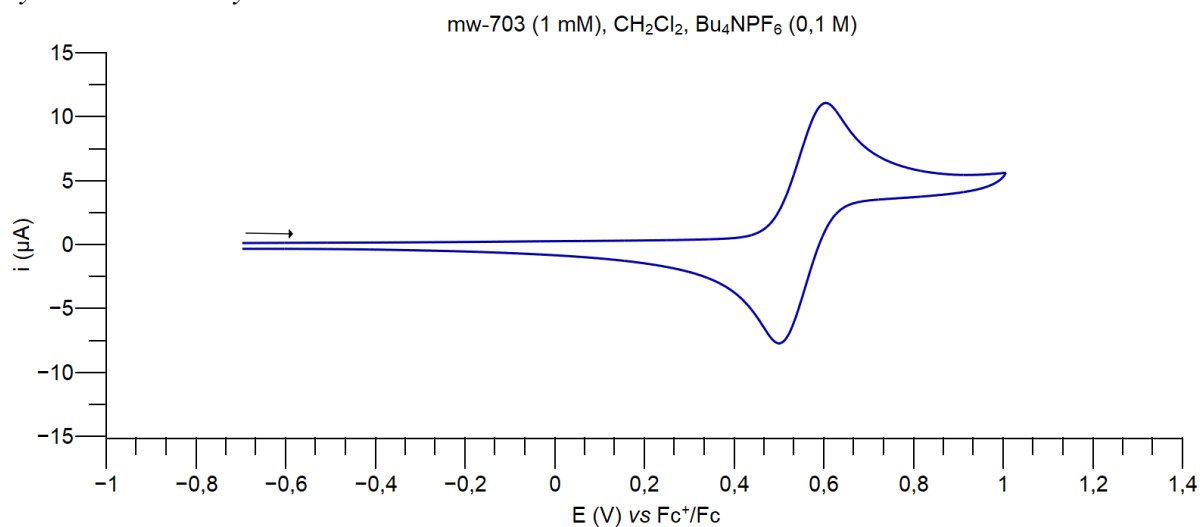
• INT2 (R_p)
Energy (RB3LYP): -2079.048312 hartree
Gibbs Free Energy: -2078.634361 hartree

| | | | |
|----|-------------|-------------|-------------|
| Fe | -2.58754500 | 0.19355600 | -1.25184500 |
| C | -1.57468000 | -1.27283500 | -0.23344900 |
| C | -2.72891200 | -1.84405800 | -0.88773700 |

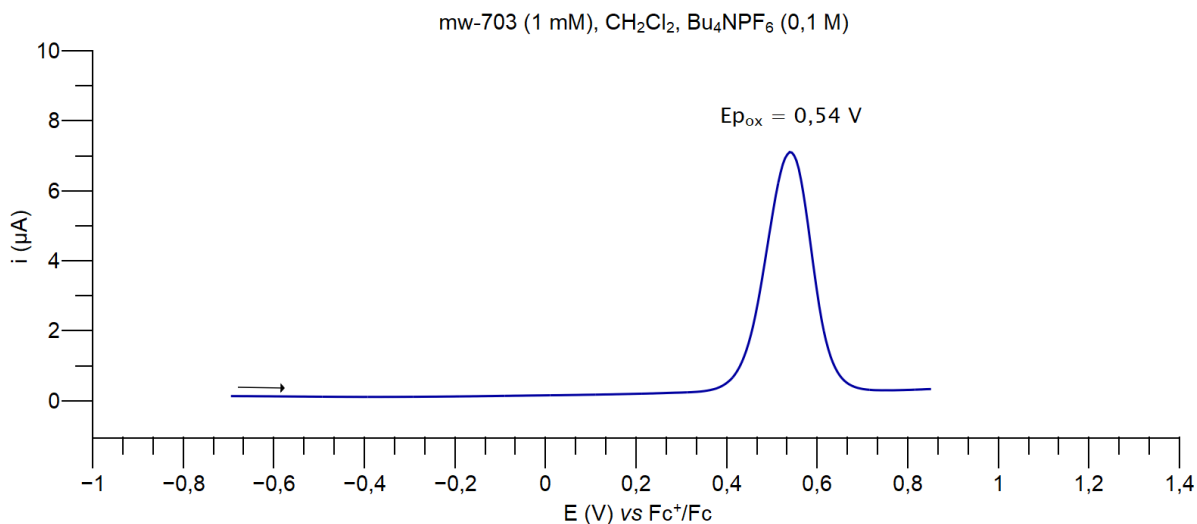
| | | | | | | | |
|---|-------------|-------------|-------------|----|-------------|-------------|-------------|
| C | -2.50335600 | -1.61763000 | -2.27169200 | C | 1.48217400 | 5.02228700 | -0.75272800 |
| C | -1.24896900 | -0.92543700 | -2.41201500 | H | -0.37298300 | 4.26062700 | 0.04167900 |
| H | -0.85857800 | -0.58905500 | -3.36616700 | H | 3.47867000 | 5.52405900 | -1.40112100 |
| C | -0.60669700 | -0.69648000 | -1.15224300 | H | 1.02242100 | 5.89241000 | -1.21241900 |
| C | -4.43913400 | 1.09009700 | -1.57895500 | C | 5.29247200 | -0.76259900 | 0.66621500 |
| H | -5.32316600 | 0.54147700 | -1.87506800 | H | 5.74473700 | -1.73700100 | 0.87467400 |
| C | -3.46127800 | 1.64318600 | -2.46251700 | H | 5.58748600 | -0.08090200 | 1.46956800 |
| H | -3.47500100 | 1.58523800 | -3.54242100 | H | 5.72157600 | -0.38861100 | -0.27028900 |
| C | -2.43336700 | 2.23805000 | -1.66590600 | C | 2.91276800 | 1.30263000 | 2.52782700 |
| H | -1.52771000 | 2.69708800 | -2.03731200 | H | 3.03989400 | 2.22201900 | 3.10677000 |
| C | -2.77563400 | 2.04869300 | -0.29546600 | H | 3.52733000 | 0.52845300 | 2.99718300 |
| H | -2.18648500 | 2.35778000 | 0.55589900 | H | 1.86862700 | 0.98622000 | 2.60020300 |
| C | -4.01668900 | 1.33754900 | -0.23793200 | H | 3.32007900 | 0.60561200 | -0.73723300 |
| H | -4.53395200 | 1.02831300 | 0.65938500 | H | -3.57385100 | -2.33924700 | -0.42958100 |
| H | -3.19070100 | -1.87707600 | -3.06783400 | Li | 1.02829000 | -0.14531000 | -0.04091000 |
| N | 3.04124500 | 0.35707600 | 0.21375700 | S | -1.09401300 | -1.50107000 | 1.42998800 |
| C | 3.76273600 | -0.90877200 | 0.57218000 | C | -2.31691600 | -0.65275800 | 2.60579300 |
| H | 3.38576500 | -1.20414000 | 1.55586400 | O | -1.15373800 | -2.90874900 | 1.84458100 |
| C | 3.33729300 | 1.54811200 | 1.07351400 | O | 0.17048300 | -0.73611700 | 1.65036000 |
| H | 4.41839800 | 1.74672000 | 1.06848600 | F | -2.00542000 | -1.00026700 | 3.86041900 |
| C | 3.34492500 | -1.99370800 | -0.41329600 | F | -3.57001000 | -1.05526500 | 2.34232500 |
| C | 3.78733300 | -1.97908900 | -1.74620400 | F | -2.25894800 | 0.68269000 | 2.50838800 |
| C | 2.49121900 | -3.02715600 | -0.00220500 | | | | |
| C | 3.38259700 | -2.96916700 | -2.64388700 | | | | |
| H | 4.45826500 | -1.19630200 | -2.09254500 | | | | |
| C | 2.08582800 | -4.02101200 | -0.89805500 | | | | |
| H | 2.13149800 | -3.05228800 | 1.02319300 | | | | |
| C | 2.53039500 | -3.99411000 | -2.22123500 | | | | |
| H | 3.73284000 | -2.94062300 | -3.67192000 | | | | |
| H | 1.41584000 | -4.80603700 | -0.56028900 | | | | |
| H | 2.21259700 | -4.76224200 | -2.92028100 | | | | |
| C | 2.66988900 | 2.76678200 | 0.44949400 | | | | |
| C | 1.28681700 | 2.98601400 | 0.54796400 | | | | |
| C | 3.44479000 | 3.69519600 | -0.26040900 | | | | |
| C | 0.69797700 | 4.10393400 | -0.04776300 | | | | |
| H | 0.66176100 | 2.29201800 | 1.10364500 | | | | |
| C | 2.85931900 | 4.81500600 | -0.85901700 | | | | |
| H | 4.51947800 | 3.54471100 | -0.33883500 | | | | |

L) Voltammograms for compound 1

Cyclic voltammetry



Differential pulse voltammetry



The measurements were done in dry, oxygen-free, CH₂Cl₂, using Bu₄PF₆ (0.1 M) as the supporting electrolyte, using a glassy carbon disk working electrode, an Ag/AgCl reference electrode and a glassy carbon rod counter electrode.

| Compound | $E_{\text{pa}}^{[a]}$ | $E_{\text{pc}}^{[a]}$ | $i_{\text{pa}}/i_{\text{pc}}^{[a]}$ | $E_{1/2}^{[b]}$ |
|----------|-----------------------|-----------------------|-------------------------------------|-----------------|
| 1 | 0.60 | 0.50 | 0.94 | 0.54 |

Table S1. Electrochemical data (in V) for ferrocenetriflone (**1**). Potentials values given relative to FcH/FcH⁺, scan rate = 100 mV·s⁻¹. [a] For the ferrocene core, from CV experiments. [b] From DPV experiments.

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