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 µm). 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 $[\alpha] = (100 \cdot \alpha)/(1 \cdot c)$ with the path length (1) 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**, *S***P**-**2e**, *R***P**-**2a**, *R***P**-**3af**, *R***P**-**4af**, *R***P**-**5f**, *S***P**-**9**, *S***P**, *S***P**-**5l** and *S***P**-**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 CH_2Cl_2 at a concentration of 1 mM, with Bu_4NPF_6 (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 µm grain size) with a slurry of alumina and ethanol and rinsed with CH_2Cl_2 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: Rf (eluent: petroleum ether-EtOAc 90:10) 0.67; mp 70-72 °C; IR (ATR) v 759, 825, 898, 1018, 1034, 1104, 1176, 1192, 1211, 1351, 1413, 1740, 2921, 3120 CF_3 cm^{-1} ; ¹H NMR (CDCl₃) δ 4.51 (s, 5H, Cp), 4.66 (t, 1H, J = 2.0 Hz, H3 and H4), 4.80 20 (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 deprotolithiation 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, filtrated 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-iPrOH (99:1) as the eluent at 0.5 mL.min⁻¹ and 10 °C, $\lambda = 254$ nm, t (minor, **R**_P-**2a**) = 10.80 min, t (major, **S**_P-**2a**) = 11.66 min.

General procedure 2 for the asymmetric deprotolithiation 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 °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 °C. The desired electrophile was then added (see details in the product description) and the reaction mixture was stirred at -100 °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 °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: Rf (eluent: petroleum ether) 0.54; mp 90-92 °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, Fe 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: Rf (petroleum ether-EtOAc 95:5) 0.78; mp 159-160 °C; IR (ATR) *v* 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 μ L, 0.28 g) and *s*BuLi (1.0 M solution in cyclohexane; 1.2 mL) in Et₂O at -80 °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 μ L, 0.28 g) and *s*BuLi (1.0 M solution in cyclohexane; 1.2 mL) in *t*BuOMe (TBME) at -80 °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 °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 °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 °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 $P 2_1/n$ (I.T.#14), a = 11.568(2), b = 12.885(2), c = 13.879(2) Å, $\beta = 90.807(7)$ °, V = 2068.5(6) Å³. Z = 4, d = 1.485 g.cm⁻³, $\mu = 0.981$ mm⁻¹. A final refinement on F² 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.

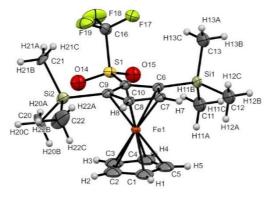


Figure S1. Molecular structure of compound **2aa** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C9-Si2 1.951(6), C10-S1 1.698(5), C6-Si1 1.924(6), C10-Cg2…Cg1-C4 41.63 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the 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 µL, 0.39 g, 1.2 mmol), the title product was obtained (eluent: petroleum ether-EtOAc 95:5; Rf 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, F_{e} $rac{2}{1}$ $rac{3}{5}$ $rac{2}{1}$ $rac{5}{5}$ $rac{5}{0}$ $rac{2}{1}$ $rac{1}{5}$ $rac{5}{0}$ $rac{2}{1}$ $rac{5}{5}$ $rac{5}{0}$ $rac{5}{5}$ $rac{5}{1}$ $rac{5}{1}$ $rac{5}{5}$ $rac{5}{1}$ $rac{5}{1}$ $rac{5}{5}$ $rac{5}{1}$ $rac{5}{5}$ $rac{5}{1}$ $rac{5}{1}$ $rac{5}{5}$ $rac{5}{1}$ $rac{5}{1}$ $rac{5}{5}$ $rac{5}{1}$ $rac{5}$

(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; ¹³C{¹H} NMR (CDCl₃) 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; ¹⁹F{¹H} NMR (CDCl₃) 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%.

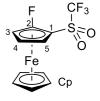
The *ee* value was determined by HPLC analysis on a Chiralpak-ODH column using hexane-iPrOH (99:1) as the eluent at 0.4 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (major, **Sp-2b**) = 8.94 min, t (minor, **Rp-2b**) = 9.56 min.

27% of starting 1 were also recovered.

2-Fluoroferrocenetriflone (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; Rf

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) *v* 457, 487, 515, 545, 563, 617, 665, 761, 805, 827, 1003, 1077, 1120, 1178, 1216, 1366, 1403, 1467 cm⁻¹; ¹H NMR (CDCl₃) 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; ¹³C{¹H} NMR (CDCl₃) 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; ¹⁹F{¹H} NMR (CDCl₃) 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%.

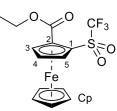
The *ee* value was determined by HPLC analysis on a Chiralpak-IC column using hexane-iPrOH (99:1) as the eluent at 0.5 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (minor, *R***P**-**2c**) = 19.43 min, t (major, *S***P**-**2c**) = 17.39 min.

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

2-(Isobutoxycarbonyl)ferrocenetriflone (2d).

Following the general procedure 2 using ClCO₂iBu (155 μ L, 0.16 g, 1.2 mmol), the title product was obtained (eluent: petroleum ether-EtOAc 90:10; Rf 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) *v* 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 (CDCl₃) δ 1.00 (t, 6H, J = 6.7 Hz, CH Me_2), 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; ¹³C{¹H} NMR (CDCl₃) δ 19.2 (CH₃), 19.3 (CH₃), 27.9 (CH, *C*HMe₂), 71.9 (CH₂, CH₂iPr), 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, *C*O₂iBu) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ –76.9 ppm; $[\alpha]_D^{20}$ +15.2 (*c* 1.0, CHCl₃). Anal. Calcd for C₁₆H₁₇F₃FeO₄S (418.21): C, 45.95; H, 4.10; S, 7.67. Found: C, 45.86; H, 4.33; S, 7.78%.

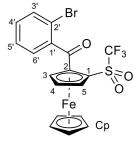
The *ee* value was determined by HPLC analysis on a Chiralpak-IB column using hexane-isopropanol (99:1) as the eluent at 0.5 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (minor, *R*P-2d) = 22.35 min, t (major, *S*P-2d) = 23.22 min.

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: Rf (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 (CDCl₃) 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; ¹³C{¹H} NMR (CDCl₃) 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; ¹⁹F{¹H} NMR (CDCl₃) δ -76.4 ppm;



 $[\alpha]_D^{20}$ +109.7 (*c* 1.0, CHCl₃). Anal. Calcd for C₁₈H₁₂BrF₃FeO₃S (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, *R*_P-2e) = 16.68 min, t (major, *S*_P-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 S_{P} -2*e*. C₁₈H₁₂BrF₃FeO₃S, 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, $\mu = 3.228$ mm⁻¹. A final refinement on F² 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.

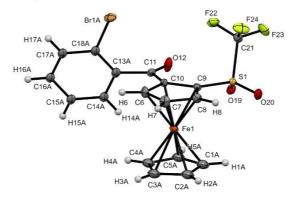


Figure S2. Molecular structure of compound *S***P**-2**e** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C10-C11 1.469(5), C9-S1 1.723(4), C9-Cg2···Cg1-C1 26.17 (Cg1 being the centroid of the C1A-C2A-C3A-C4A-C5A ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 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: Rf (eluent: petroleum ether-EtOAc 90:10) 0.60; mp 112-114 °C; IR (ATR) v 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 CF_3 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-iPrOH (99:1) as the eluent at 0.4 mL.min⁻¹ and 10 °C, $\lambda = 254$ 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 silica (eluent: petroleum ether-EtOAc 90:10; Rf 0.68) afford over gel to 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 $-80 \text{ }^{\circ}\text{C}$ 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 $-15 \text{ }^{\circ}\text{C}$ and stirring at this temperature for 5 min before cooling to $-80 \text{ }^{\circ}\text{C}$]. 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; Rf 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*}-2*a*. 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 F² with 3736 unique intensities and 202 parameters converged at ω R(F²) = 0.0565 (R_F = 0.0229) for 3627 observed reflections with *I* > 2 σ . CCDC 2364201.

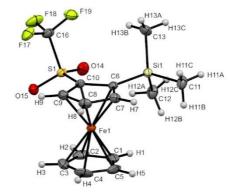


Figure S3. Molecular structure of compound R_P -2a (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C6-Si1 1.884(2), C10-S1 1.716(2), C10-Cg2····Cg1-C2 2.80 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C9-C10-S1-015 -29.3(2), C6-C10-S1-014 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, C*H*Me), 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).

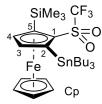
Iododestannylation of **2b** was attempted as follows. I₂ (0.38 g, 1.5 mmol) was added in one portion to a solution of the above **2b** (455 mg, 0.75 mmol) in CH₂Cl₂ (45 mL) at rt, and the reaction mixture was stirred for 14 h. Saturated aqueous Na₂S₂O₃ (10 mL) was added and the reaction mixture was 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 °C, Me₃SiCl (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 Et₂O (3 x 10 mL). Drying over MgSO₄ 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 (CDCl₃) δ 0.34 (s, 9H, SiMe₃), 0.93 (t, 9H, J = 7.3 Hz,

 $3(CH_2)_3Me$), 1.07-1.20 (m, 6H, $3CH_2Pr$), 1.37 (h, 6H, J = 7.2 Hz, $3CH_2Me$), 1.49-1.61 (m, 6H, $3CH_2CH_2Et$), 4.42 (s, 5H, Cp), 4.62 (d, 1H, J = 2.4 Hz, H3), 4.73 (d, 1H, J = 2.4 Hz, H4) ppm; ¹³C{¹H} NMR (CDCl₃) δ 1.2 (3CH₃, SiMe₃), 11.8 (3CH₂, CH₂Pr), 13.8 (3CH₃, (CH₂)₃Me), 27.6 (3CH₂, CH₂Me), 29.2 (3CH₂, CH₂CH₂Et), 71.2 (5CH, Cp), 79.3 (CH, C5), 81.2 (C, C2, C-Sn), 83.0 (CH, C3), 83.4 (CH, C4),

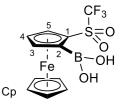


85.5 (q, C, J = 2.3 Hz, C1, C-SO₂CF₃), 119.5 (q, C, J = 327 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -76.7 ppm; $[\alpha]_D^{20}$ -55.9 (*c* 1.0, CHCl₃) Anal. Calcd for C₂₆H₄₃F₃FeO₂SSiSn (679.32): C, 45.97; H, 6.38; S, 4.72. Found: C, 46.15; H, 6.17; S, 4.69%.

Large-scale deprotolithiation using (*S*)-PEALi in the presence of B(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 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 (1.25 M solution in hexane; 24 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 (10 mL) was added and the reaction mixture was warmed to rt. 5% aqueous H₃PO₄ (100 mL) was added, and the reaction mixture was stirred for 15 min. 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 70:30 to 60:40) and isolated after subsequent treatment as follows. It was dissolved in Et₂O (100 mL) and extracted with a basic sorbitol solution (5 x 25 mL).^[13] The combined aqueous layers were washed with Et₂O (20 mL) before acidification with 6 M aqueous HCl until pH 1. The aqueous layers were extracted with Et₂O. Drying over MgSO₄ 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) *v* 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 (CDCl₃) 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; ¹³C{¹H} NMR (CDCl₃) 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; ¹⁹F{¹H} NMR (CDCl₃) δ –79.2 ppm; ¹¹B{¹H} NMR (CDCl₃) δ 29.8 ppm.

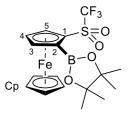
To recover the chiral amine, the combined aqueous acidic phases were basified until pH 11 with 20% aqueous NaOH and were extracted with Et₂O (3 x 50 mL). The combined organic layers were dried over K₂CO₃, and the solvent was removed under reduced pressure to give the crude amine. This was purified by 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-dioxa-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-iPrOH (99:1) as the eluent at 0.4 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (major, **R**_P-**2h**) = 13.71 min, t (minor, **S**_P-**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: ether-EtOAc 98:2 97:3) afforded 2-(4,4,5,5-tetramethyl-1,3-dioxa-2petroleum to borolyl)ferrocenetriflone (2h) in 45% yield (3.0 g) and 91% ee (determined as above) as an orange solid: Rf (eluent: petroleum ether-EtOAc 80:20) 0.76; mp 88-90 °C; IR (ATR) v 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 (CDCl₃) 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; ¹³C{¹H} NMR (CDCl₃) 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; ¹⁹F{¹H} NMR (CDCl₃) δ -78.4 ppm; ¹¹B{¹H} NMR (CDCl₃) δ 31.8 ppm; $[\alpha]_D^{20}$ -27 (c 1.0, CHCl₃). 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: Rf (petroleum ether-EtOAc 50:50) 0.24; mp 125-128 °C (dec.); IR (ATR) *v* 666, 761, 827, 897, 1003, 1088, 1117, 1204, 1294, 1347, 1385, 1422, 1630, 3632 cm⁻¹; ¹H NMR $((CD_3)_2SO) \delta 4.33$ (s, 5H, Cp), 4.54 (t, 1H, J = 2.5 Hz, H4), 4.56-4.57 (m, 2H, H3 and H5) ppm; ¹³C{¹H} NMR ((CD₃)₂SO) δ70.3 (5CH, Cp), 72.4 (CH, C4), 73.2 (CH, C5), 76.8 CF_3 (C, C1, C-SO₂CF₃), 79.3 (CH, C3), 90.4 (C, C2, C-B), 119.1 (q, C, J = 328 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -78.4 (q, J = 3.6 Hz, CF₃), -132.5 (d, J = 75.5 Hz, BF₃K) ppm; ¹¹B{¹H} NMR (CDCl₃) δ 2.6 ppm; $[\alpha]_D^{20}$ +18.5 (c 0.25, CHCl₃). 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 sBuLi (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: Rf (eluent: petroleum ether-EtOAc 90:10) 0.68; mp 136-138 °C; IR (ATR) v 760, 829, 840, 874, 958, 1005, 1066, 1115, 1184, 1210, 1240, 1360, 1415, 2968 cm⁻¹; ¹H CF₃ NMR (CDCl₃) $\delta 0.32$ (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, (F0 SiMe₃ 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} Ср NMR (CDCl₃) δ -75.9 ppm; $[\alpha]_D^{20}$ +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-iPrOH (99:1) as the eluent at 0.4 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (major, *R***P**-**3af**) = 14.47 min, t (minor, *S***P**-**3**

3af = 15.14 min.

*Crystal data for R*_{*P*}**-3af**. C₁₄H₁₆F₃FeIO₂SSi, M = 516.17, T = 150(2) K; orthorhombic $P \ 2_1 \ 2_1 \ 2_1$ (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, $\mu = 2.773$ mm⁻¹. A final refinement on F² with 4095 unique intensities and 211 parameters converged at $\omega R(F^2) = 0.0540$ ($R_F = 0.0204$) for 4033 observed reflections with $I > 2\sigma$. CCDC 2364202.

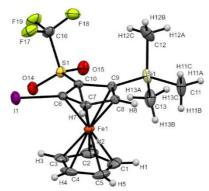


Figure S4. Molecular structure of compound *R*_P-3af (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C9-Si1 1.890(3), C10-S1 1.724(3), C6-I1 2.073(3), C10-Cg2···Cg1-C2 30.68 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of 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 °C was added dropwise sBuLi (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 CH₂=NMe₂I (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 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 70:29:1; Rf 0.50). The title product was isolated in 59% yield (2.7 g) and > 99% ee as an orange oil: IR (ATR) v 759, 825, 837, 920, 962, 1004, 1037, 1068, 1139, 1185, 1209, 1243, 1353, 1413, 1458, 1679, 2771, 2819, 2947 cm⁻¹; ¹H NMR (CDCl₃) δ 0.32 (s, 9H, SiMe₃), 2.23 (s, 6H, NMe₂), 3.46 (d, 1H, J = 14.5 Hz, $CH_aH_bNMe_2$), 3.51 (d, 1H, J = 14.6 Hz, $CH_aH_bNMe_2$), 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; ¹³C{¹H} NMR H_a K₁, H_b CF₃ Me₂N (CDCl₃) 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, Fe SiMe₃ *C*-SO₂CF₃), 79.3 (CH, C4), 93.5 (C, C2, *C*-CH₂NMe₂), 119.7 (q, C, *J* = 328 Hz, Ср CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -75.9 ppm; $[\alpha]_D^{20}$ +90 (*c* 1.0, CHCl₃). 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 °C and stirring at this temperature for 5 min before cooling to -50 °C] was added in one portion (R_p)-2-iodo-5-(trimethylsilyl)ferrocenetriflone (R_{P} -3af; 2.5 g, 4.8 mmol) at -50 °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 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; Rf 0.62). The title product was isolated in 62% yield (1.5 g) and > 99.5% *ee* as an orange solid: mp 58-60 °C; IR (ATR) ν 758, 827, 876, 975, 1006, 1057, 1115, 1184, 1249, 1299, 1357, 1414, 2954, 3122 cm⁻¹; ¹H CF₃

NMR (CDCl₃) $\delta 0.33$ (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; ¹³C{¹H} NMR (CDCl₃) $\delta 0.61$ (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; ¹⁹F{¹H}



NMR (CDCl₃) δ -78.3 ppm; [α]_D²⁰ +39.1 (*c* 1.0, CHCl₃). 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-iPrOH (99:1) as the eluent at 0.5 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (major, *R*_P-4af) = 8.92 min, t (minor, *S*_P-4af) = 9.70 min.

*Crystal data for R*_{*P*}-4*af*. 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, $\mu = 2.751$ mm⁻¹. A final refinement on F² with 8261 unique intensities and 421 parameters converged at ω R(F²) = 0.0476 (R_F = 0.0207) for 7877 observed reflections with $I > 2\sigma$. CCDC 2364203.

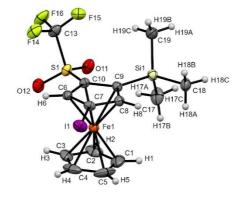
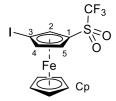


Figure S5. Molecular structure of compound *R*_P-4af (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C7-II 2.071(3), C10-S1 1.721(3), C9-Si1 1.889(4), C10-Cg2····Cg1-C2 30.74 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10 ring), C6-C10-S1-012 -27.3(3), C9-C10-S1-011 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)-4iodo-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; Rf 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) v760, 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; $[\alpha]_D^{20}$ -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-iPrOH (99:1) as the eluent at 0.5 mL.min⁻¹ and 5 °C, $\lambda = 254$ nm, t (major, *R*_P-**5f**) = 18.33 min, t (minor, *S*_P-**5f**) = 17.17 min.

*Crystal data for R*_{*P*}-5*f*. 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 F² 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.

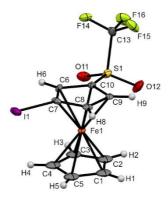


Figure S6. Molecular structure of compound *R***P-5f** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C10-S1 1.725(8), C7-II 2.066(10), C10-Cg2···Cg1-C2 34.00 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid of the C6-C7-C8-C9-C10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

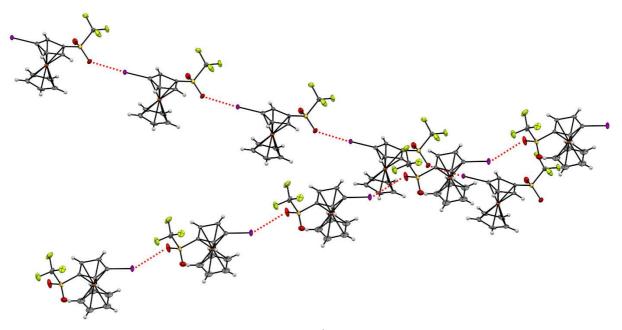


Figure S7. Hydrogen bonding network (I1-O12 3.340 Å) observed at the solid state for compound RP-5f.

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

It was prepared by iodine/lithium exchange^[18] followed by electrophilic trapping using (1R,2S,5R)-(–)-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 °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 (1R,2S,5R)-(–)-menthyl (*S*)-4-toluenesulfinate (0.47 g, 1.6 mmol) in THF (4 mL) was then added at -90 °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: Rf (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%.

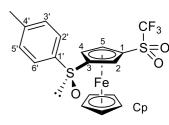
 $(S,R_{\rm P})$ -3-(4-Tolylsulfinyl)ferrocenetriflone (*R*P-**5k**) was similarly isolated (Rf 0.37) in 9% yield (34 mg) as a brown solid: mp 171-173 °C; IR (ATR) v 705, 733, 762, 810, 833, 905, 1016, 1051, 1085, 1118, 1194, 1220, 1365, 1400, 1417, 1493, 1596, 3111 cm⁻¹; ¹H NMR

(CDCl₃) $\delta 2.42$ (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) $\delta 21.6$ (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%.

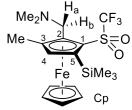
(*R*_P)-2-(Dimethylaminomethyl)-3-methyl-5-(trimethylsilyl)ferrocenetriflone (*R*_P-6).

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 °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

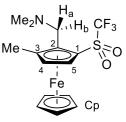


(CH₃, C-*Me*), 44.9 (2CH₃, NMe₂), 54.2 (CH₂), 72.7 (5CH, Cp), 76.5 (C, C5, *C*-SiMe₃), 81.1 (q, C, J = 2.8 Hz, C1, *C*-SO₂CF₃), 81.2 (CH, C4), 90.5 (C, C3, *C*-Me), 92.3 (C, C2, *C*-CH₂NMe₂), 119.7 (q, C, J = 329 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -72.8 ppm; $[\alpha]_D^{20} + 25$ (*c* 1.0, CHCl₃). 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%.

(S_P)-2-(Dimethylaminomethyl)-3-methylferrocenetriflone (S_P-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) v 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_a H_bNMe₂), 3.76 (d, 1H, J = 1.4 Ha

= 13.0 Hz, CH_a H_b NMe₂), 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;

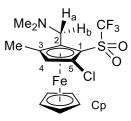


 $[\alpha]_D^{20}$ –39 (*c* 1.0, CHCl₃). Anal. Calcd for C₁₅H₁₈F₃FeNO₂S (389.21): C, 46.29; H, 4.66; N, 3.60; S, 8.24. Found: C, 46.31; H, 4.53; N, 3.72; S, 8.27%.

(S_P)-5-Chloro-2-(dimethylaminomethyl)-3-methylferrocenetriflone (S_P-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 (CDCl₃) δ 2.05 (s, 3H, C-*Me*), 2.12 (s, 6H, NMe₂), 3.08 (d, 1H, *J* = 13.1 Hz, CH_aH_bNMe₂), 3.78 (d, 1H, *J* = 13.1 Hz, CH_aH_bNMe₂), 4.42 (s, 5H, Cp), 4.83 (s, 1H, H4) ppm; ¹³C{¹H} NMR (CDCl₃) δ 13.7 (CH₃, C-*Me*), 45.0 (2CH₃, NMe₂), 53.9 (CH₂), 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-

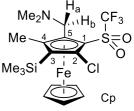


Cl), 119.7 (q, C, J = 327 Hz, CF₃) ppm; ¹⁹F{¹H} NMR (CDCl₃) δ -76.4 ppm; $[\alpha]_D^{20}$ -39 (*c* 1.0, CHCl₃). Anal. Calcd for C₁₅H₁₇ClF₃FeNO₂S (423.66): C, 42.53; H, 4.04; N, 3.31; S, 7.57. Found: C, 42.41; H, 4.05; N, 3.39; S, 7.52%.

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

To a solution of (*S*_P)-5-chloro-2-(dimethylaminomethyl)-3-methylferrocenetriflone (*S*_P-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; Rf 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 (CDCl₃) δ 0.45 (s, 9H, SiMe₃), 2.07 (s, 3H, C-*Me*), 2.13 (s, 6H, NMe₂), 3.13 (d, 1H, J = 13.2 Hz, $Me_2N \bigvee_{L_1H_2}^{H_a}$ CF₃

C $H_{a}H_{b}NMe_{2}$), 3.81 (d, 1H, J = 13.2 Hz, C $H_{a}H_{b}NMe_{2}$), 4.39 (s, 5H, Cp) ppm; ¹³C{¹H} NMR (CDCl₃) δ 1.6 (3CH₃, SiMe₃), 14.5 (CH₃, C-*Me*), 45.0 (2CH₃, NMe₂), 53.7 (CH₂), 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; ¹⁹F{¹H} NMR (CDCl₃) δ -75.9 ppm; $[\alpha]_D^{20}$ -3.7 (*c* 1.0, CHCl₃). Anal. Calcd for C₁₈H₂₅ClF₃FeNO₂SSi (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 S_P-9. C₁₈H₂₅ClF₃FeNO₂SSi, 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 F² 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 σ . CCDC 2364205.

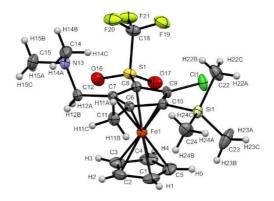
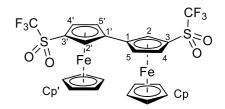


Figure S8. Molecular structure of compound *S***P-9** (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C8-S1 1.726(2), C7-C12 1.502(3), C6-C11 1.501(3), C10-Si1 1.894(2), C9-Cl1 1.703(3), C8-Cg2···Cg1-C4 25.91 (Cg1 being the centroid of the C1-C2-C3-C4-C5 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).

(S_P,S_P)-1,1'-Biferrocene-3,3'-bis(triflone) (S_P,S_P-5l).

It was prepared by adapting conditions reported.^[20] Enantioenriched 3-iodoferrocenetriflone (**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: Rf (petroleum ether-EtOAc 90:10) 0.17; mp 220-221 °C; IR (ATR) v 761, 827, 905, 1004, 1021, 1051, 1109, 1140, 1184, 1212, 1293,

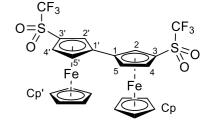
1359, 1416, 3118 cm⁻¹; ¹H NMR (CDCl₃) δ 4.39 (s, 10H, Cp and Cp'), 4.84 (dd, 2H, J = 2.7 and 1.5 Hz, H5 and H5'), 4.90 (dd, 2H, J = 2.7 and 1.3 Hz, H4 and H4'), 5.04 (t, 2H, J = 1.4 Hz, H2 and H2') ppm; ¹³C{¹H} NMR (CDCl₃) δ 69.1 (2CH, C2 and C2'), 71.6 (2CH, C5 and C5'), 72.0 (2CH, C4 and C4'), 73.0 (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; $[\alpha]_D^{20}$ –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-5*l) was similarly isolated in 4% yield (7 mg) as an orange solid: Rf (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]²⁰_D 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 -5*l*. C₂₂H₁₆F₆Fe₂O₄S₂, M = 634.17, T = 150(2) K; orthorhombic $P \ 2_1 \$

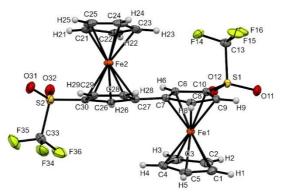


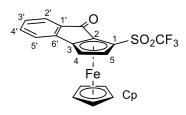
Figure S9. Molecular structure of compound *S*_P,*S*_P-**5**I (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C10-S1 1.722(3), C30-S2 1.723(3), C7-C27 1.470(5), C10-Cg2···Cg1-C2 7.17 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid 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: Rf (petroleum ether-EtOAc 70:30) 0.40; mp 264-265 °C (dec.); IR (ATR) v 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 (CDCl₃) 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; ¹³C{¹H} NMR (CDCl₃) 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; ${}^{19}F{}^{1}H{}$ NMR (CDCl₃) δ –78.7 ppm; $[\alpha]_D^{20}$ +524.2 (*c* 0.062, CHCl₃). 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, $\lambda = 254$ 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 $P \ 2_1$ (I.T.#4), a = 7.2261(3), b = 6.6984(2), c = 16.4777(5) Å, $\beta = 98.6940(10)$ °, V = 788.41(5) Å³. Z = 2, d = 1.770 g.cm⁻³, $\mu = 1.138$ mm⁻¹. A final refinement on F² 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.

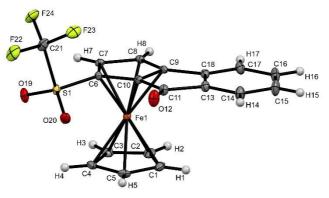


Figure S10. Molecular structure of compound *S***P**-10 (thermal ellipsoids shown at the 30% probability level). Selected lengths [Å] and angles (°): C9-C18 1.469(3), C10-C11 1.484(3), C6-S1 1.720(2), C9-Cg2···Cg1-C1 20.86 (Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 being the centroid 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).

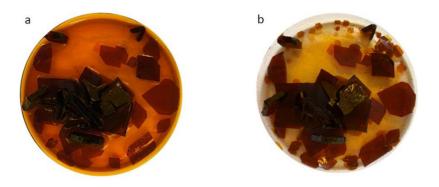


Figure S12. a) Crystals before and b) after complete evaporation of hexane.

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).

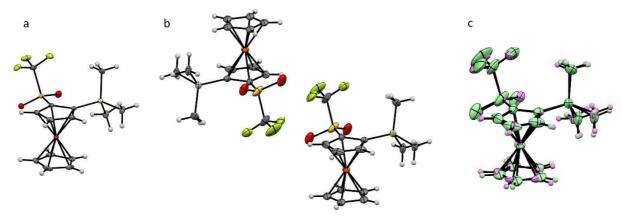


Figure S13. a) Enantiomer *R*_P-2a found in the orthorhombic crystal. b) *rac*-2a found in the monoclinic crystal. c) Superposition of the *R*_P-2a enantiomers; in purple from orthorhombic crystal, in green from monoclinic crystal.

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).

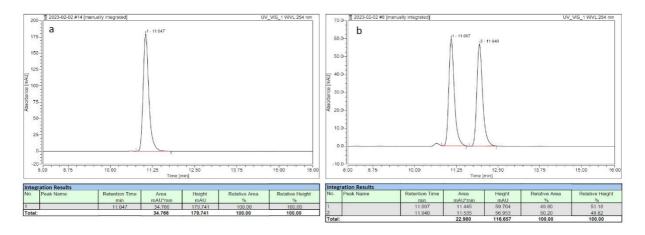


Figure S14. a) HPLC analysis of the orthorhombic crystals. b) HPLC analysis of the monoclinic crystals.

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).

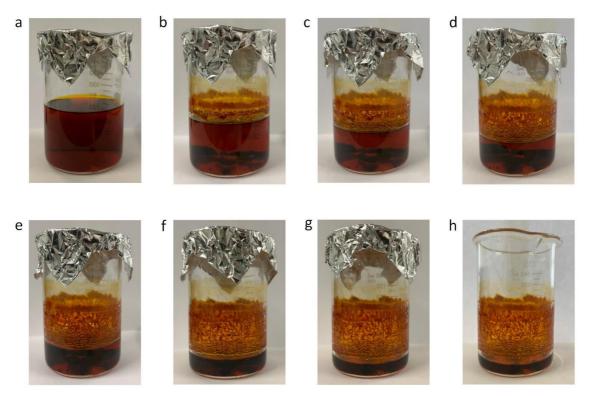


Figure S15. Front view during the crystallisation of compound **2a** at: a) 0 h; b) 15 h; c) 27 h; d) 42 h; e) 53 h; f) 74 h; g) 96 h and h) 112 h.

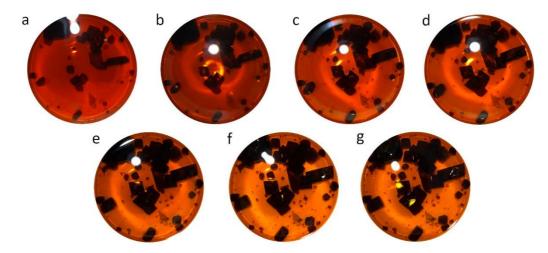


Figure S16. Top view during the crystallisation of compound 2a at: a) 15 h; b) 27 h; c) 42 h; d) 53 h; e) 74 h; f) 96 h and h) 112 h.

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 *R***P**-**2a** (61% recovery). All remaining solids were collected and stored as a mixture of enantiomers.

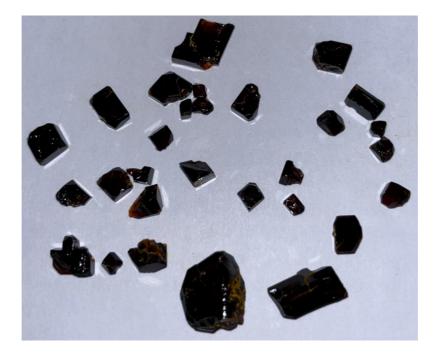


Figure S17. Collected crystals of compounds 2a.

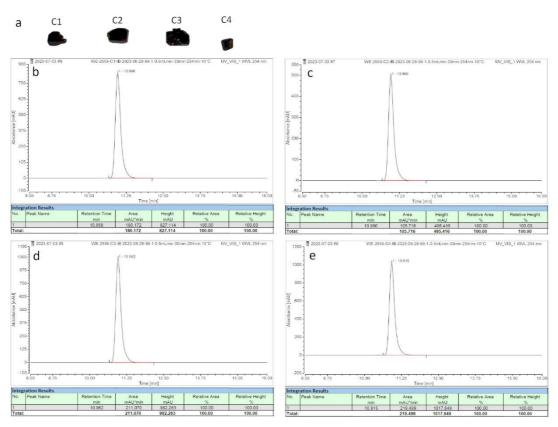
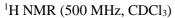
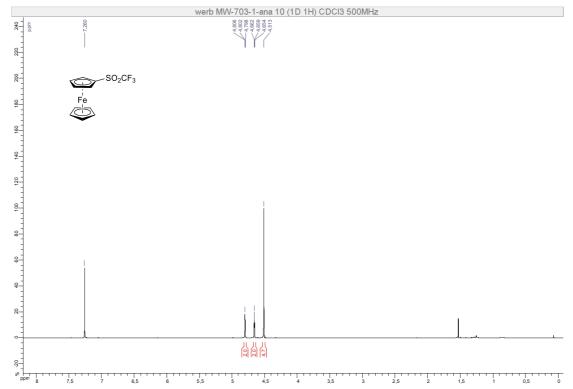


Figure S18. a) Crystals C1-4 of compound 2a selected for HPLC analysis. b) HPLC data of crystal C1. c) HPLC data of crystal C2. d) HPLC data of crystal C3. e) HPLC data of crystal C4.

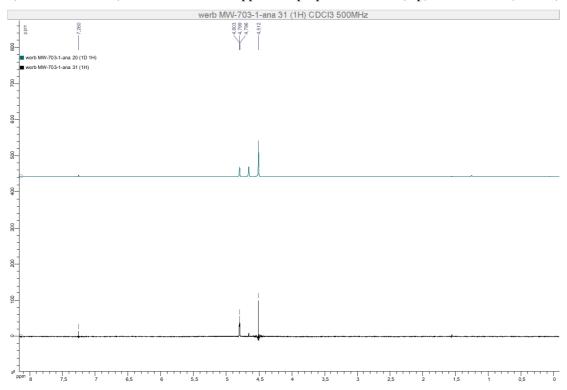
D) NMR Spectra

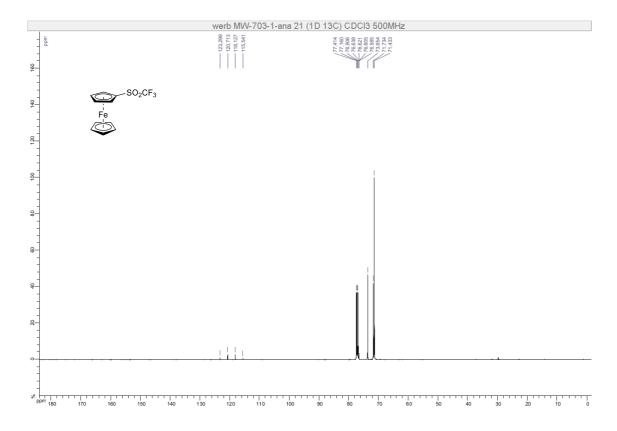
Ferrocenetriflone (1)



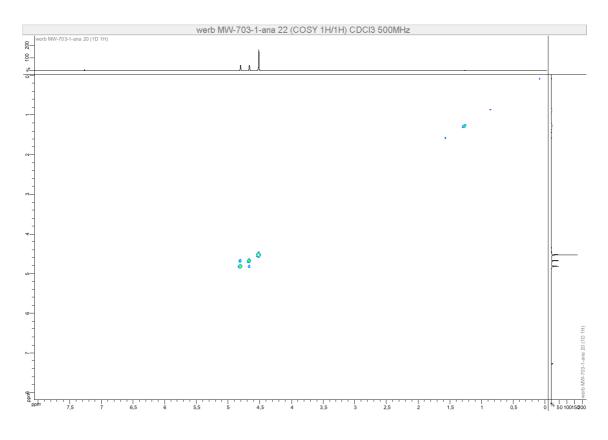


HOESY (500 MHz, CDCl₃) Irradiation at -74.5 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

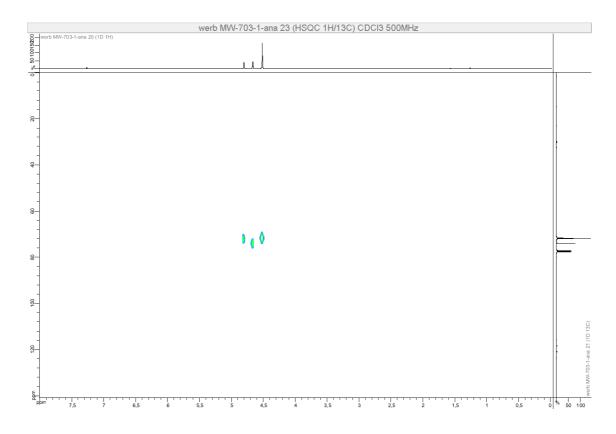




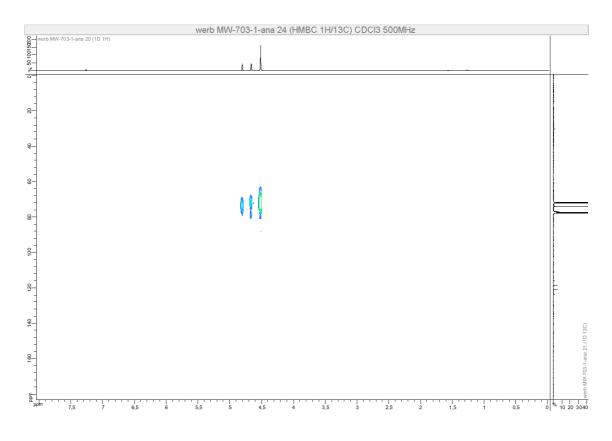
COSY (500 MHz, CDCl₃)



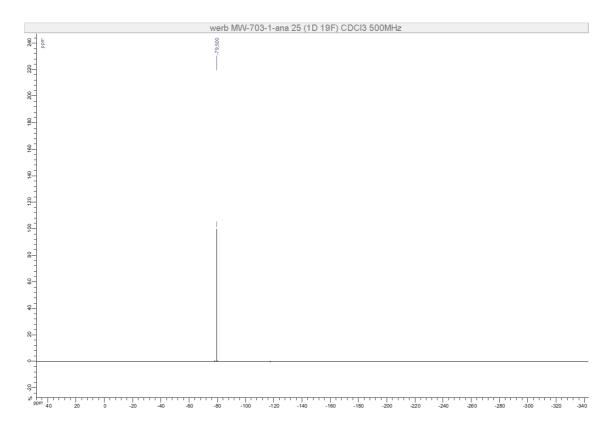
HSQC (500 MHz, CDCl₃)



HMBC (500 MHz, CDCl₃)

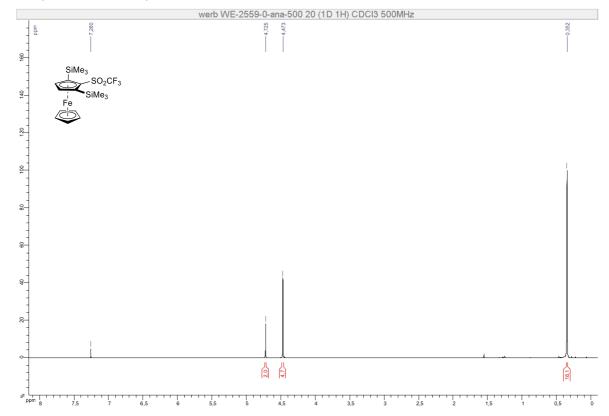


¹⁹F NMR (470 MHz, CDCl₃)

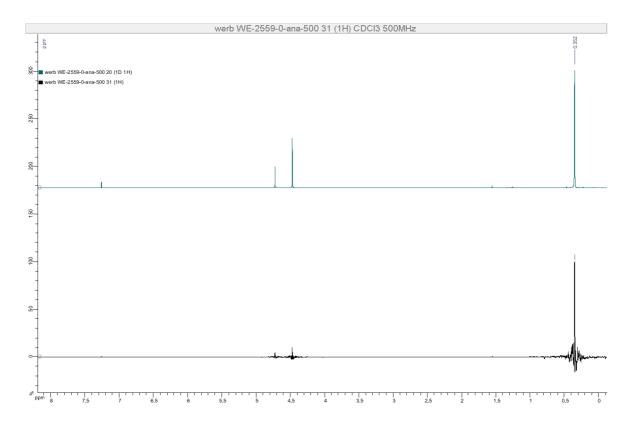


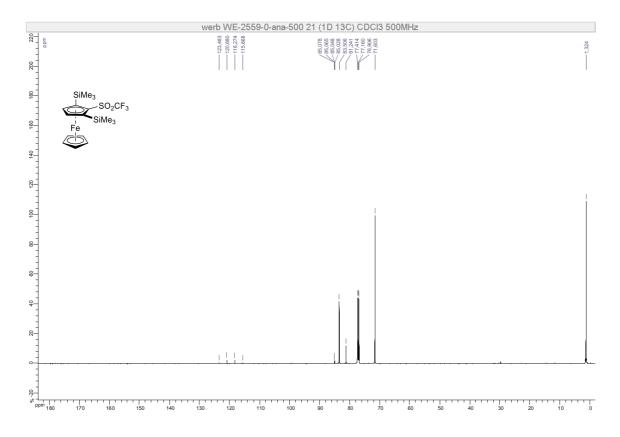
2,5-Bis(trimethylsilyl)ferrocenetriflone (2aa)

¹H NMR (500 MHz, CDCl₃)

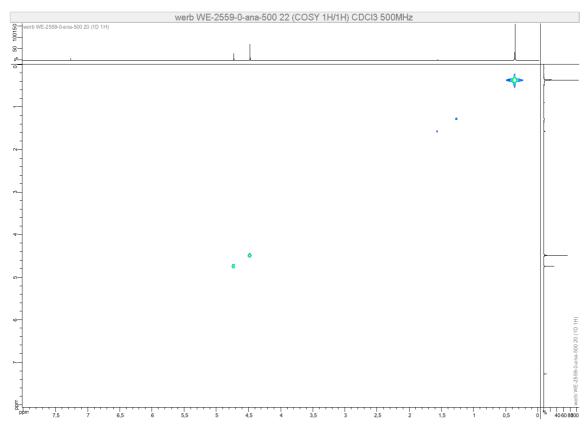


HOESY (500 MHz, CDCl₃) Irradiation at -75.7 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

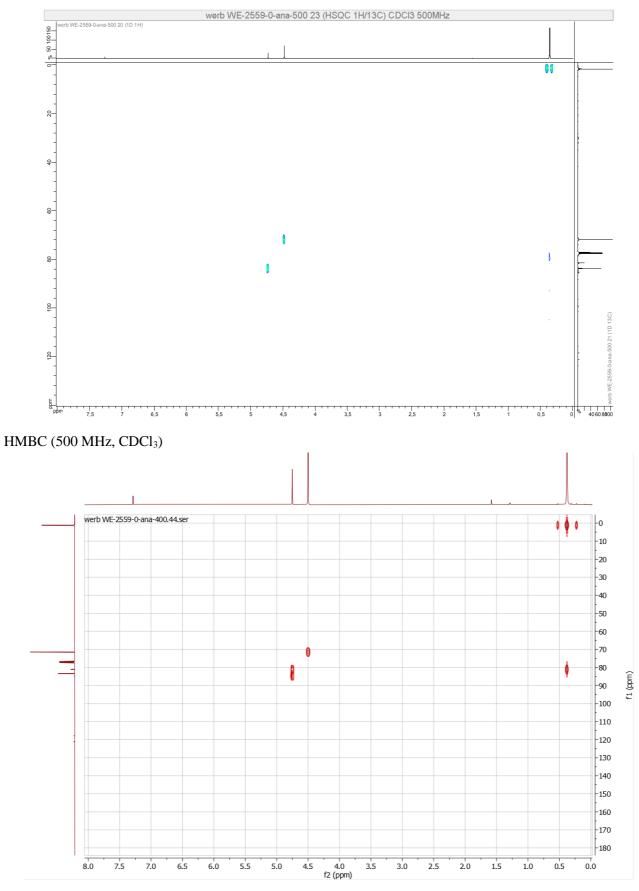




COSY (500 MHz, CDCl₃)

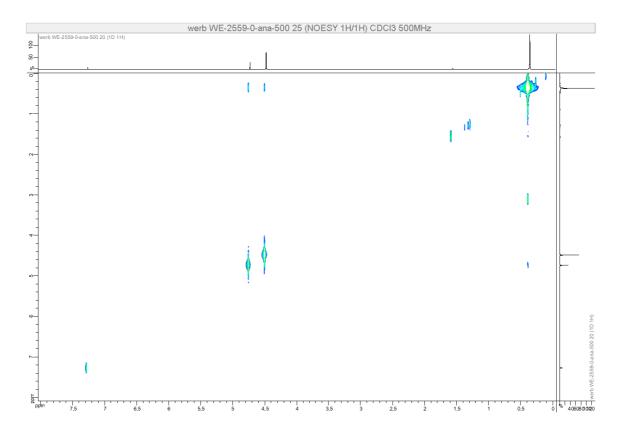


S36

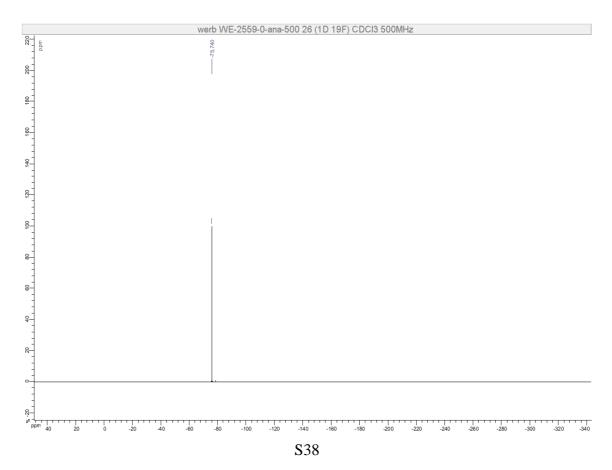




NOESY (400 MHz, CDCl₃)

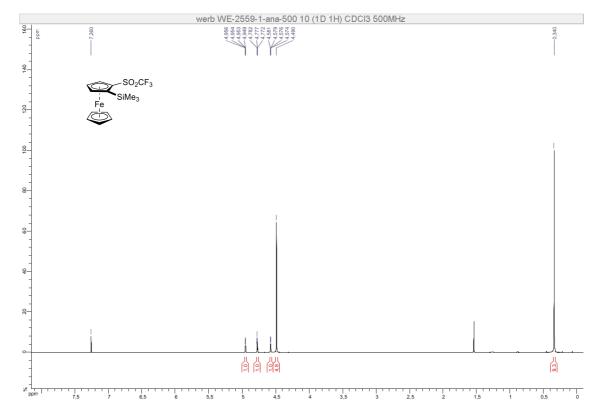


¹⁹F NMR (470 MHz, CDCl₃)

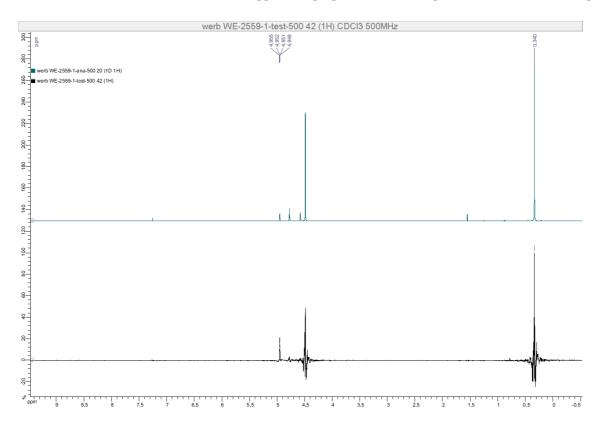


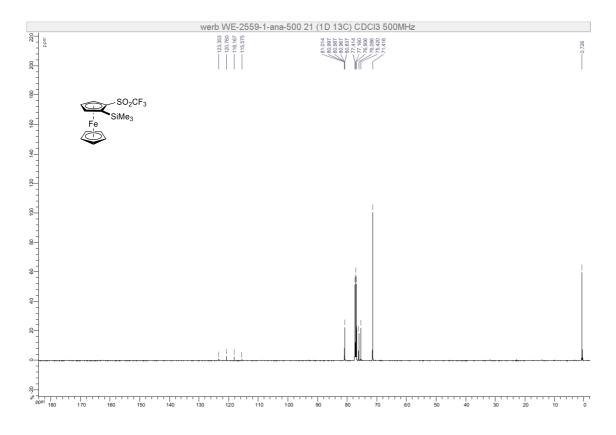
(*R*_P)-2-(Trimethylsilyl)ferrocenetriflone (*R*_P-2a)

¹H NMR (500 MHz, CDCl₃)

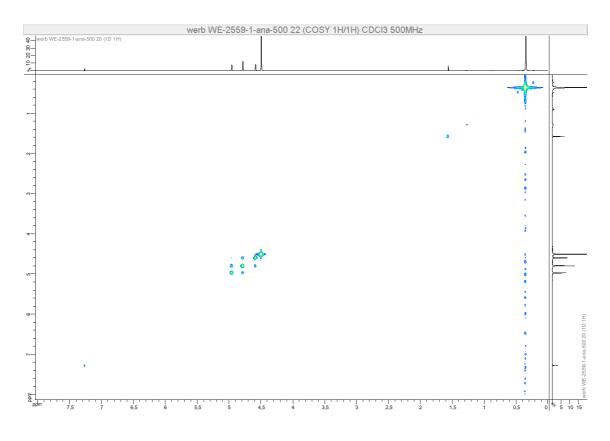


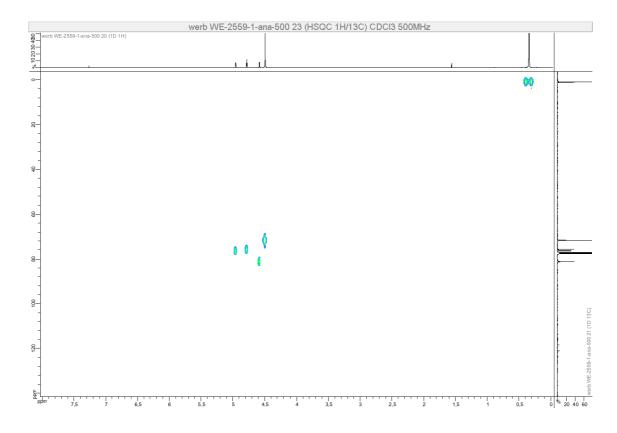
HOESY (500 MHz, CDCl₃) Irradiation at -78.6 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



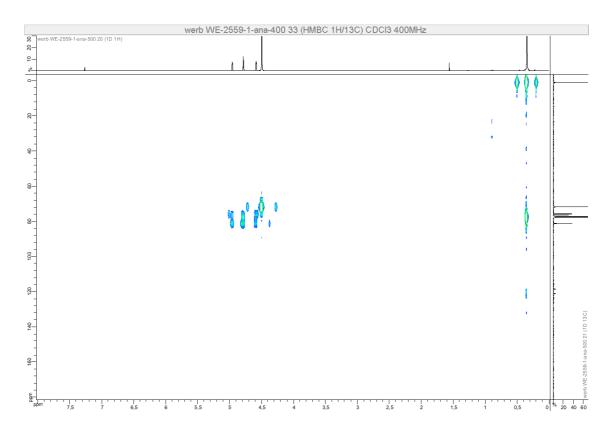


COSY (500 MHz, CDCl₃)

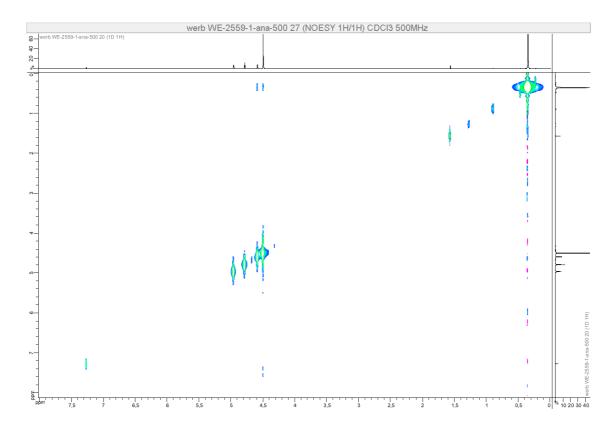




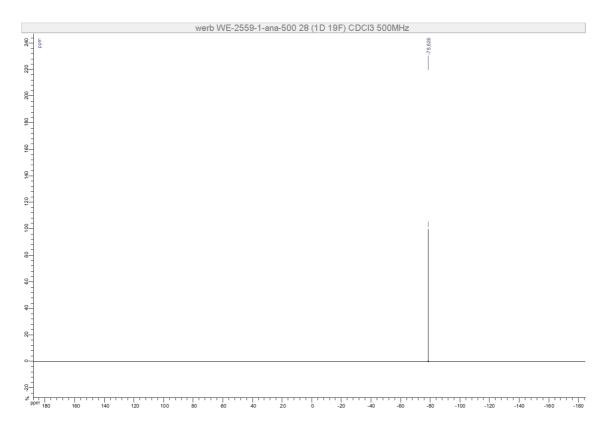
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

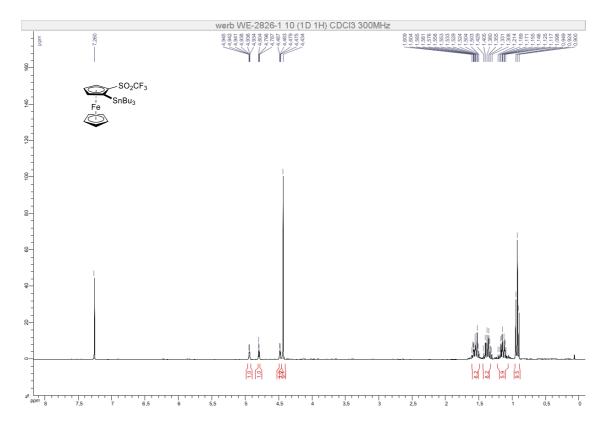


¹⁹F NMR (470 MHz, CDCl₃)

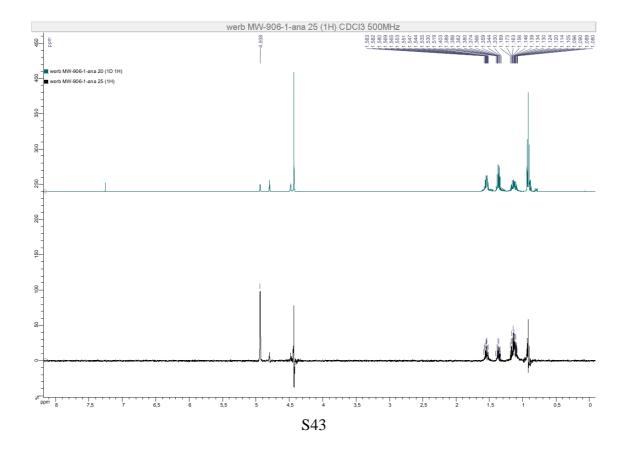


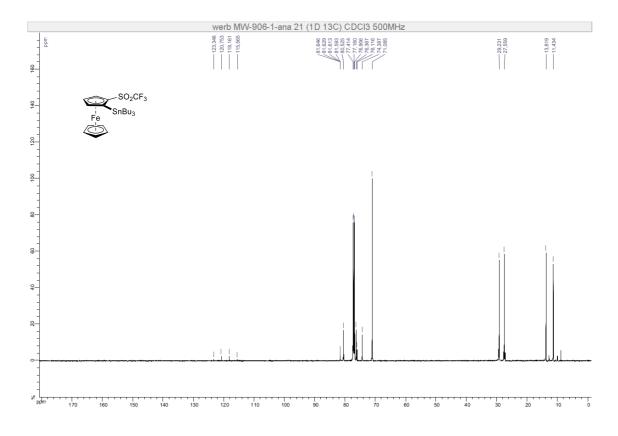
2-(Tributylstannyl)ferrocenetriflone (2b)

¹H NMR (300 MHz, CDCl₃)

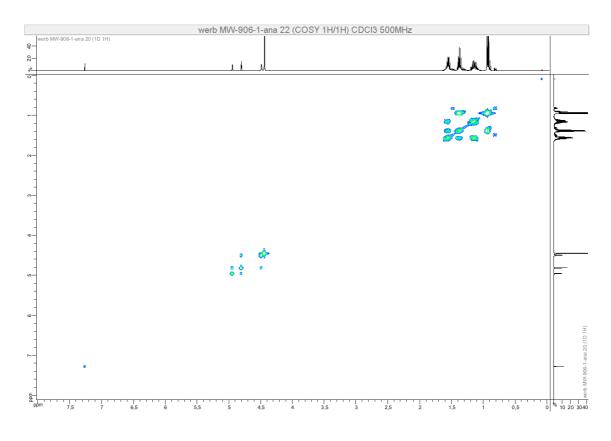


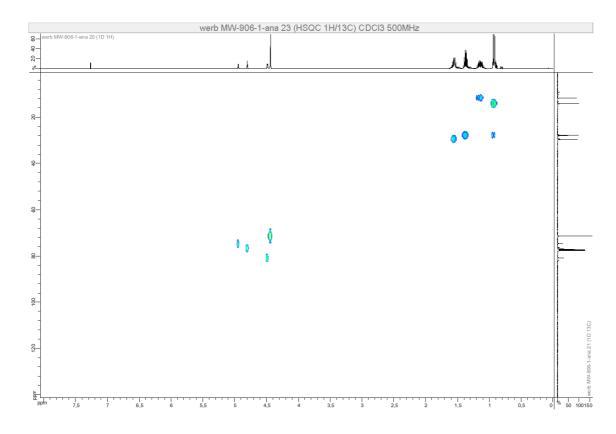
HOESY (500 MHz, CDCl₃) Irradiation at -78.8 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



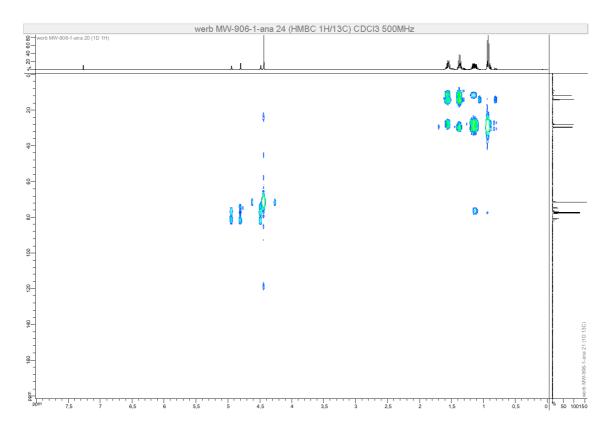


COSY (500 MHz, CDCl₃)

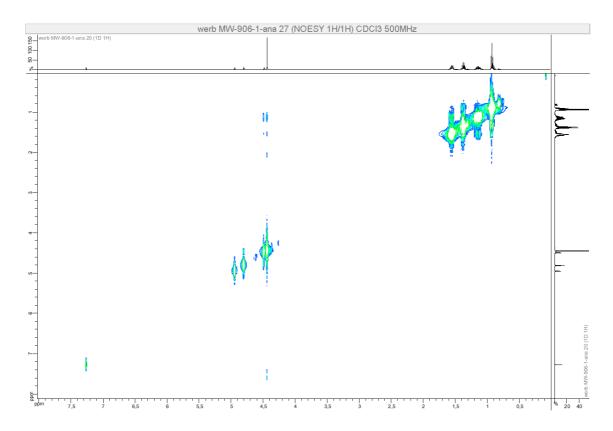




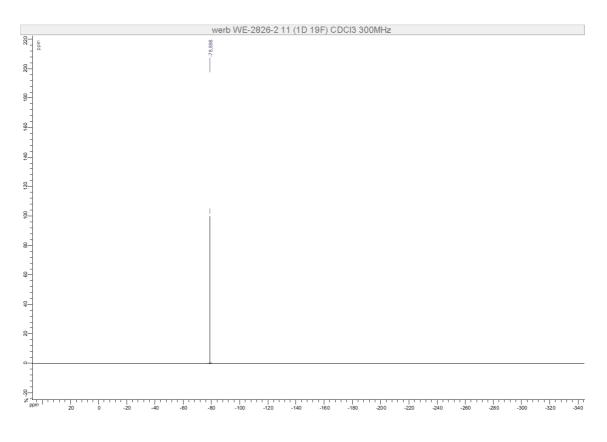
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

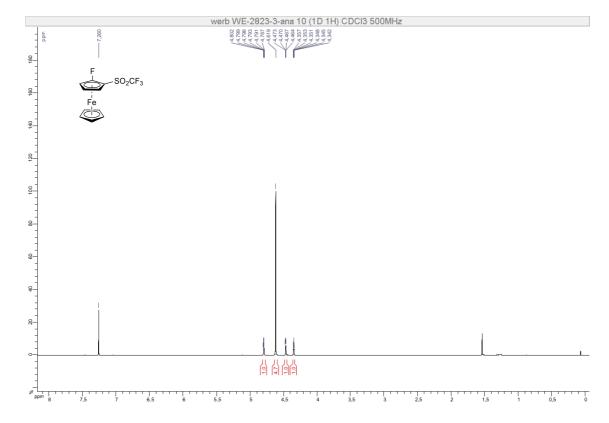


¹⁹F NMR (470 MHz, CDCl₃)

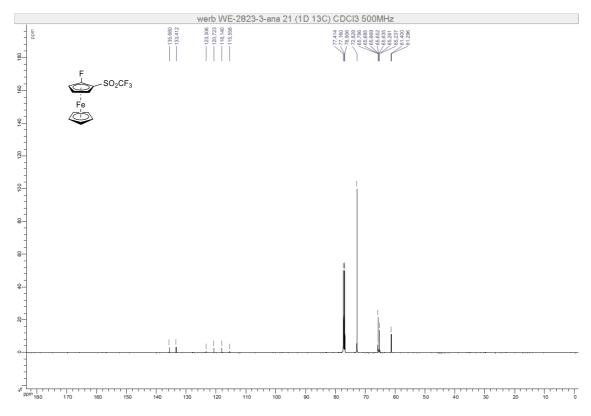


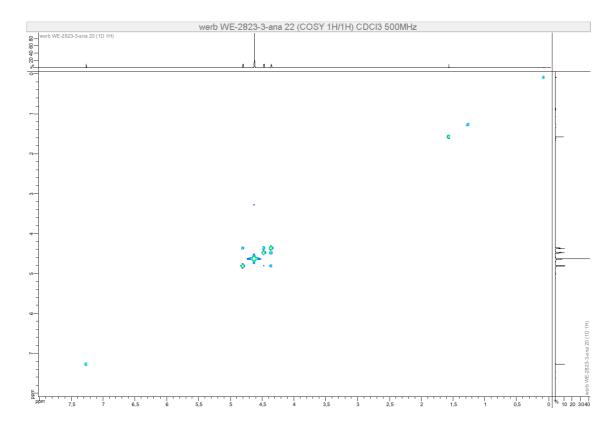
2-Fluoroferrocenetriflone (2c)

¹H NMR (500 MHz, CDCl₃)

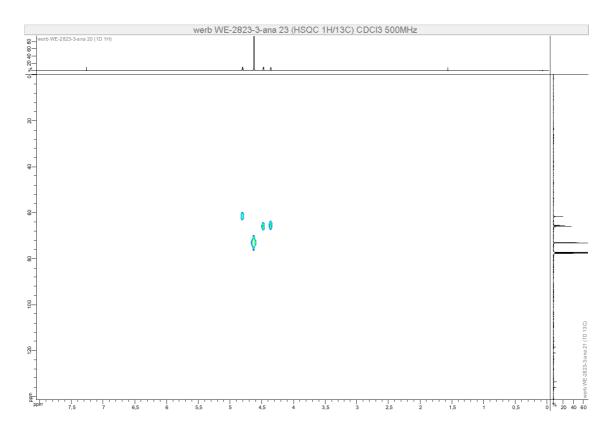


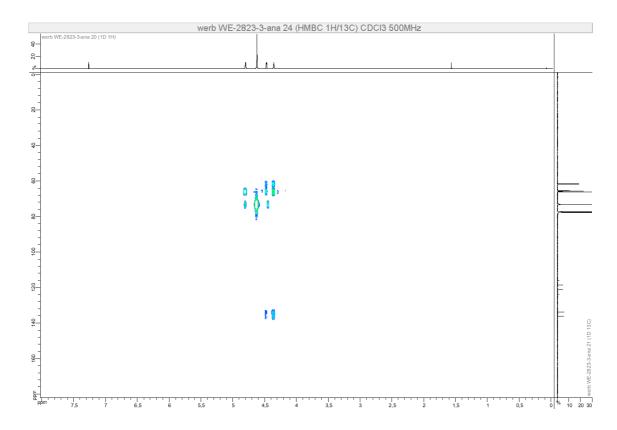
¹³C NMR (126 MHz, CDCl₃)



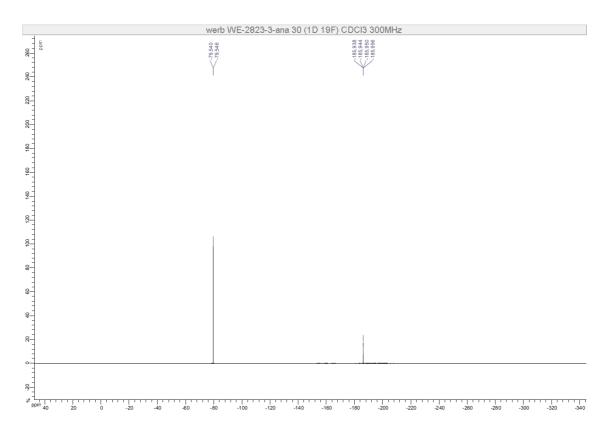


HSQC (500 MHz, CDCl₃)



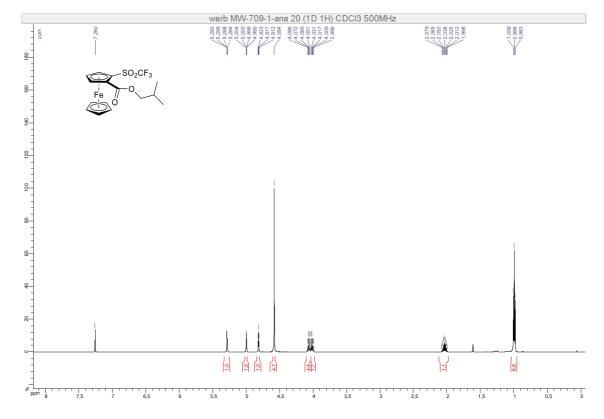


¹⁹F NMR (470 MHz, CDCl₃)

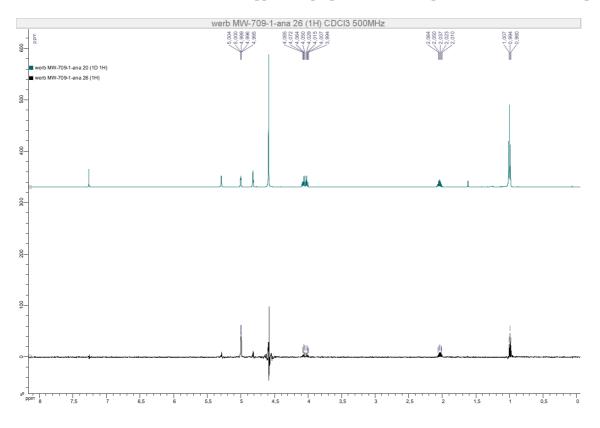


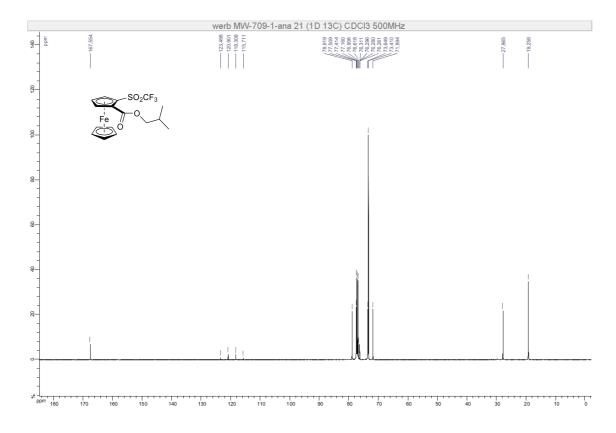
2-(Isobutoxycarbonyl)ferrocenetriflone (2d)

¹H NMR (500 MHz, CDCl₃)

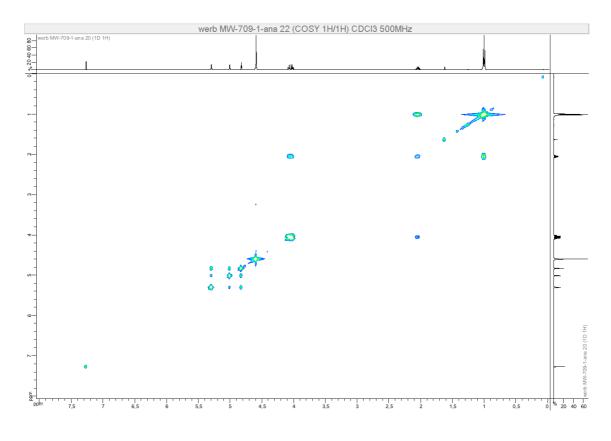


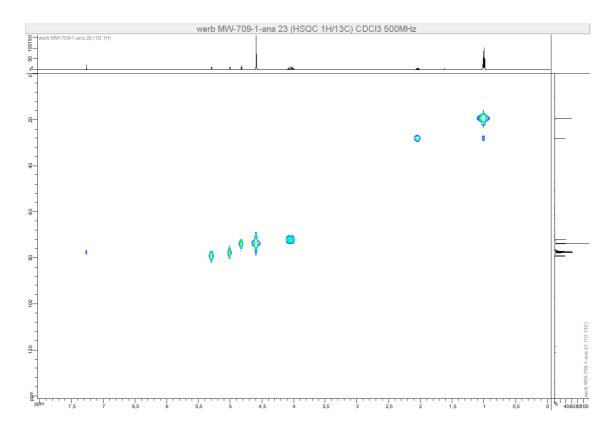
HOESY (500 MHz, CDCl₃) Irradiation at -76.8 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



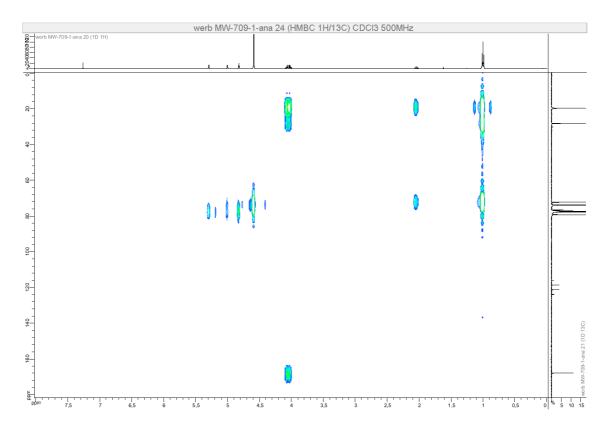


COSY (500 MHz, CDCl₃)

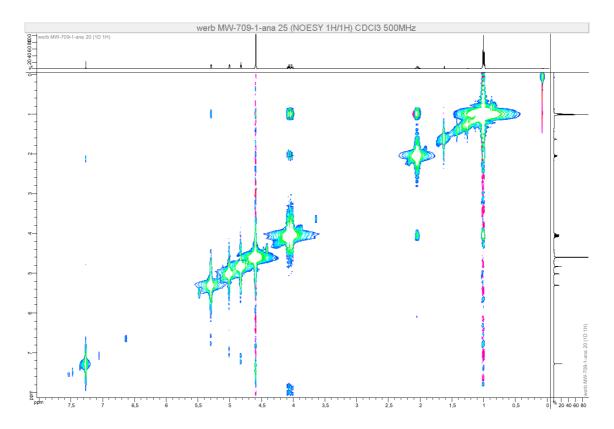




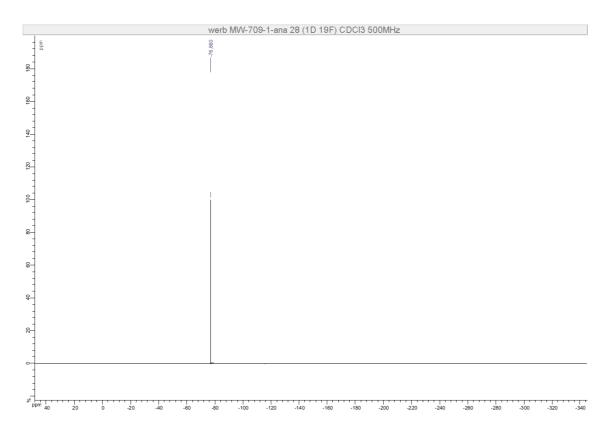
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

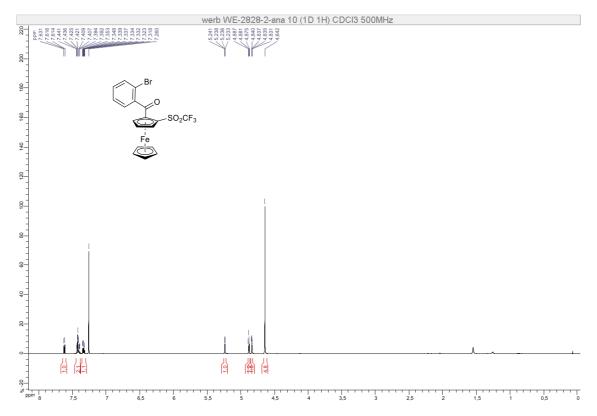


¹⁹F NMR (470 MHz, CDCl₃)

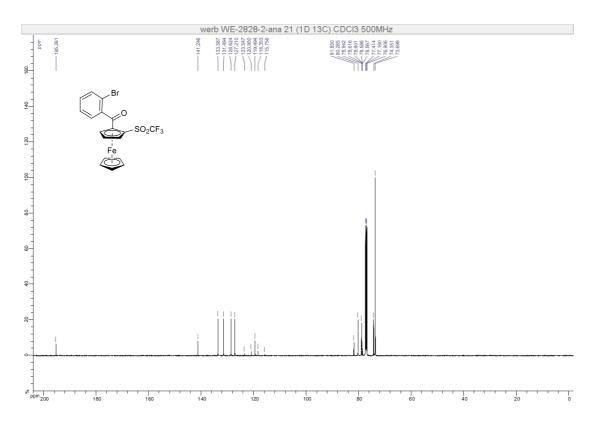


(S_P)-2-(2-Bromobenzoyl)ferrocenetriflone (S_P-2e)

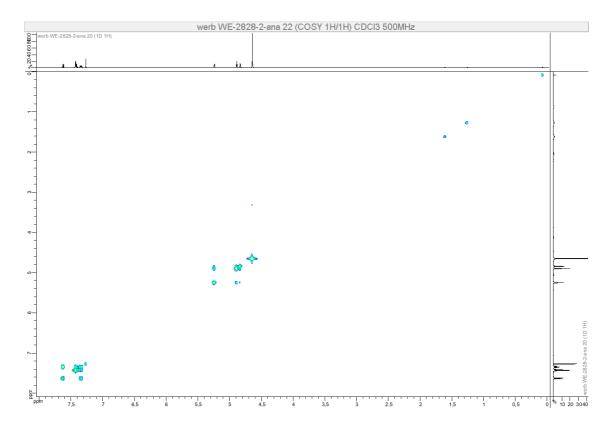
¹H NMR (500 MHz, CDCl₃)



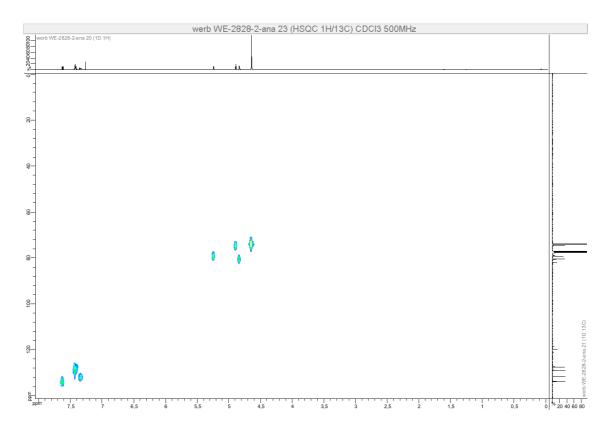
¹³C NMR (126 MHz, CDCl₃)

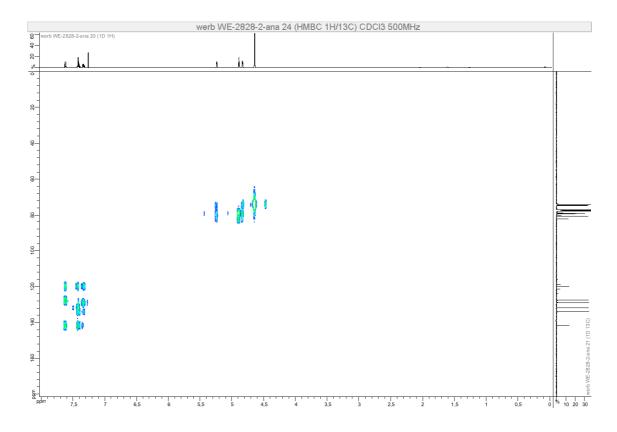


S54

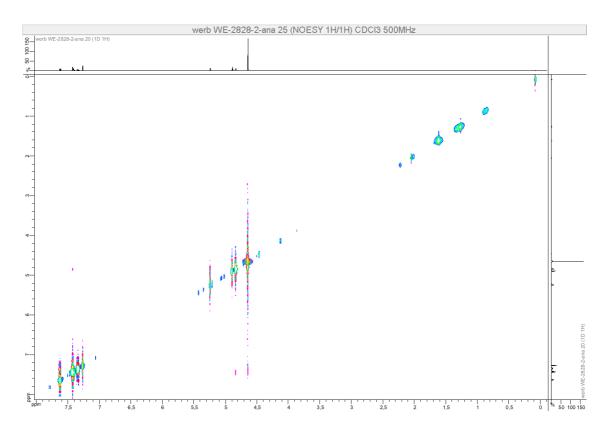


HSQC (500 MHz, CDCl₃)

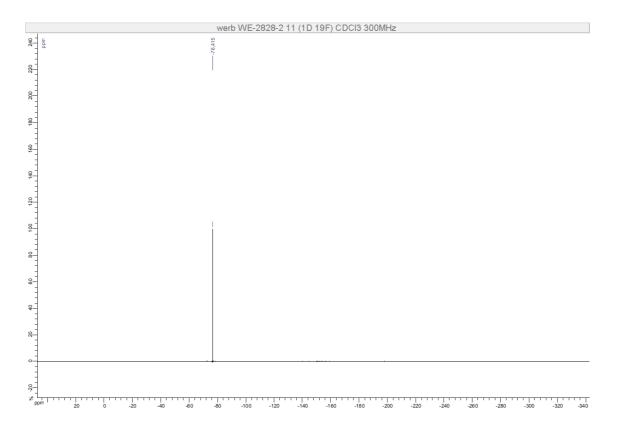




NOESY (500 MHz, CDCl₃)

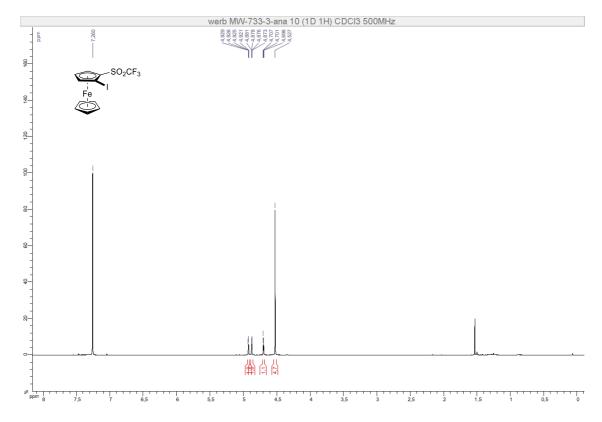


¹⁹F NMR (282 MHz, CDCl₃)

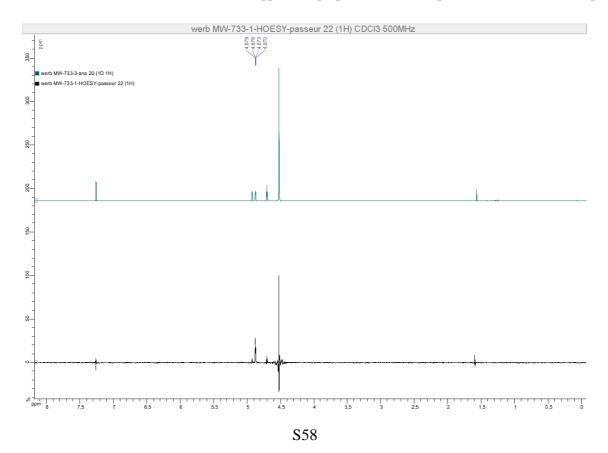


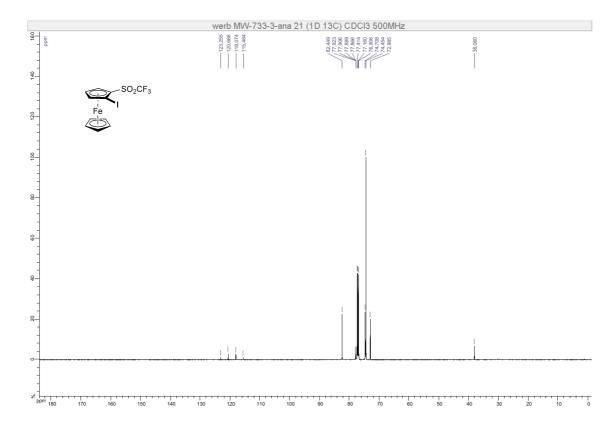
2-Iodoferrocenetriflone (2f)

¹H NMR (500 MHz, CDCl₃)

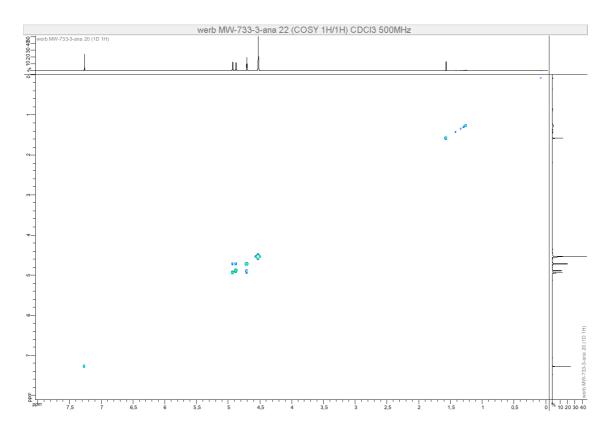


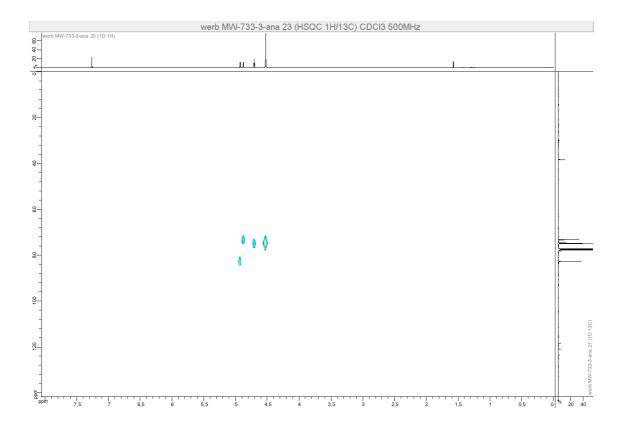
HOESY (500 MHz, $CDCl_3$) Irradiation at -78.2 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



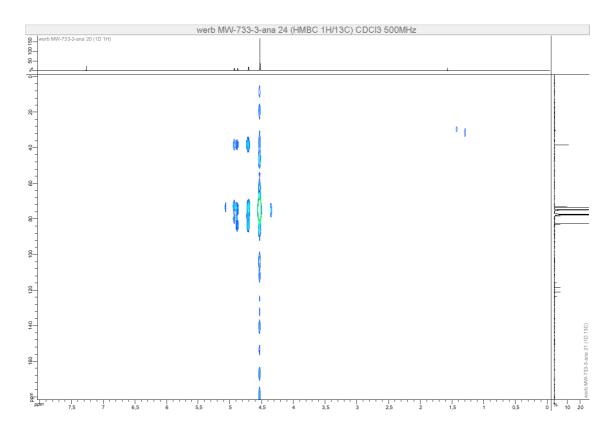


COSY (500 MHz, CDCl₃)

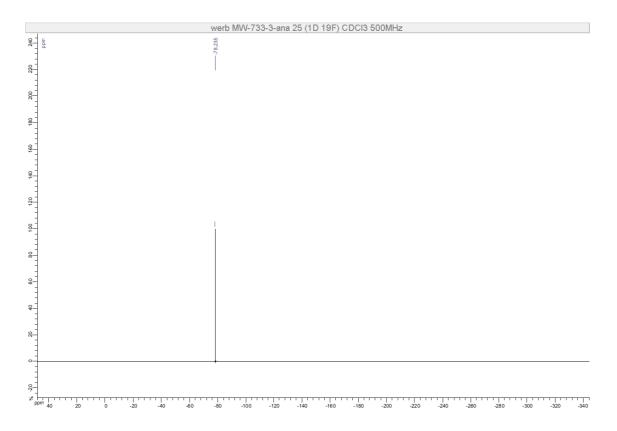




HMBC (500 MHz, CDCl₃)

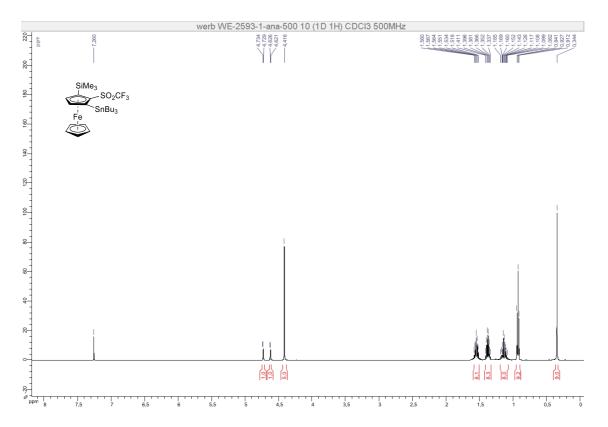


¹⁹F NMR (470 MHz, CDCl₃)

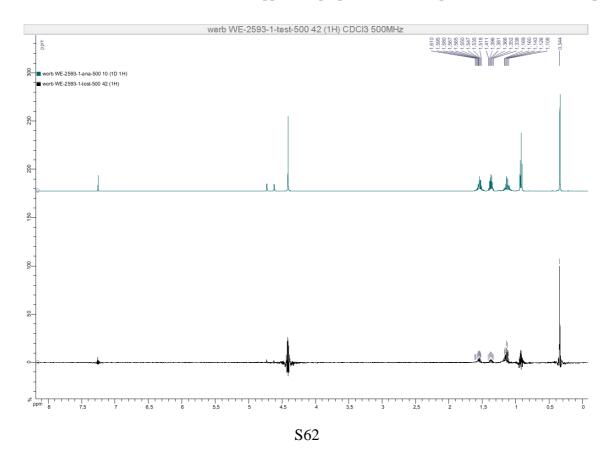


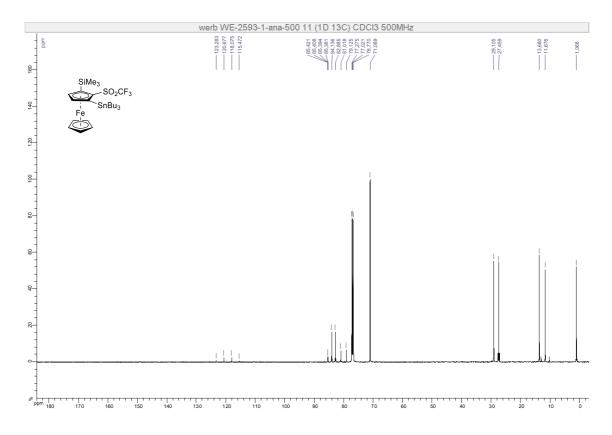
2-(Tributylstannyl)-5-(trimethylsilyl)ferrocenetriflone (3ba)

¹H NMR (500 MHz, CDCl₃)

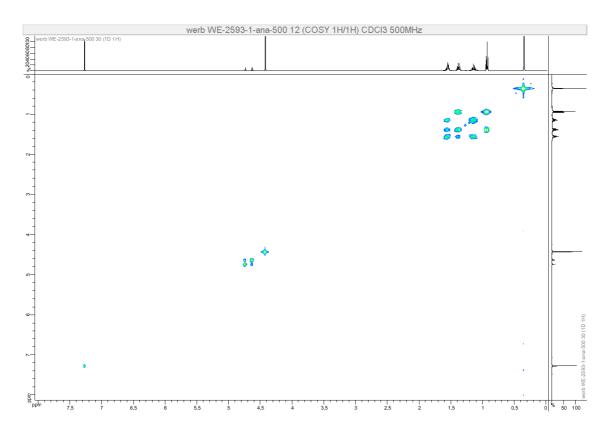


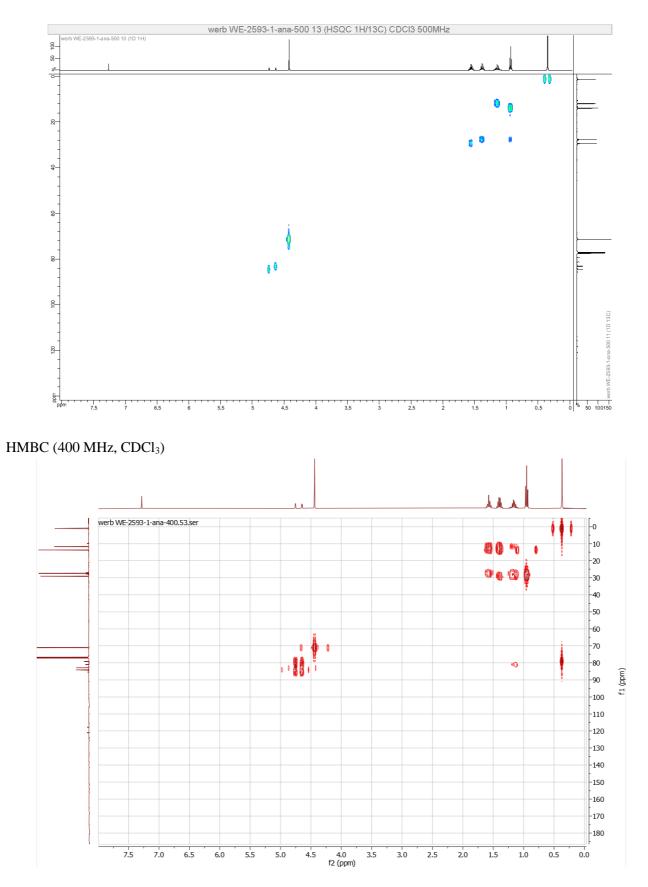
HOESY (500 MHz, CDCl₃) Irradiation at -76.7 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



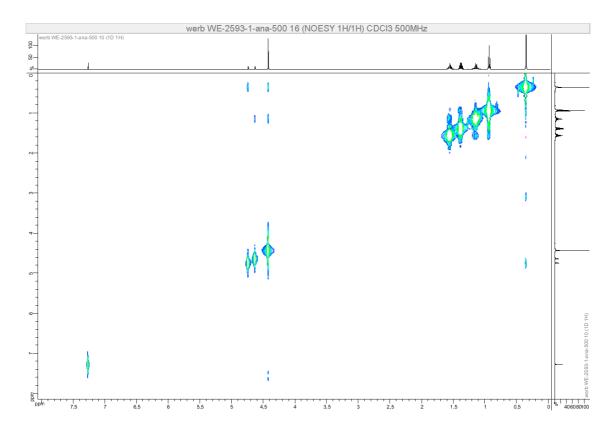


COSY (500 MHz, CDCl₃)

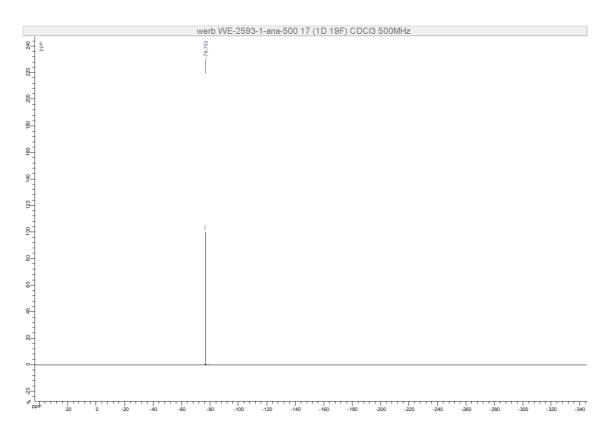




NOESY (500 MHz, CDCl₃)

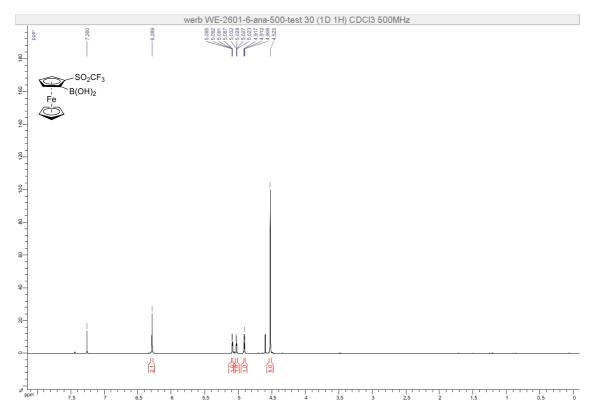


¹⁹F NMR (470 MHz, CDCl₃)

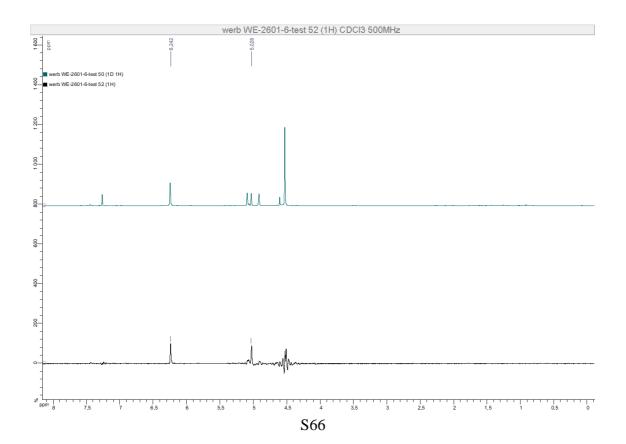


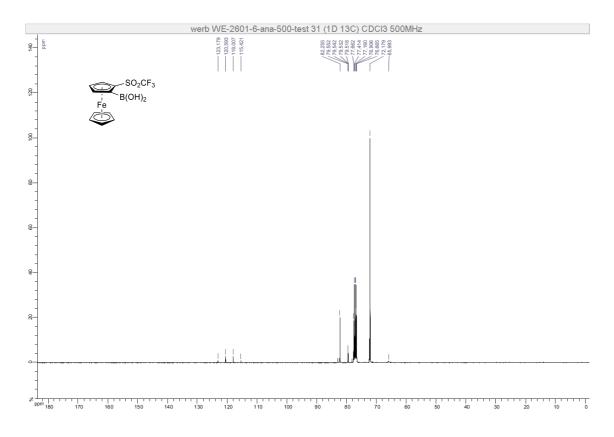
2-(Dihydroxyboryl)ferrocenetriflone (2g)

¹H NMR (500 MHz, CDCl₃)

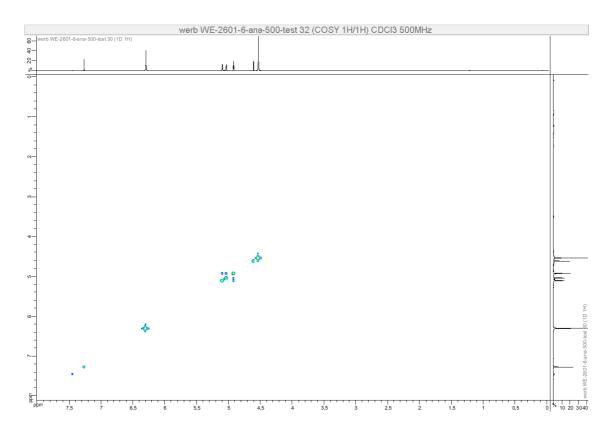


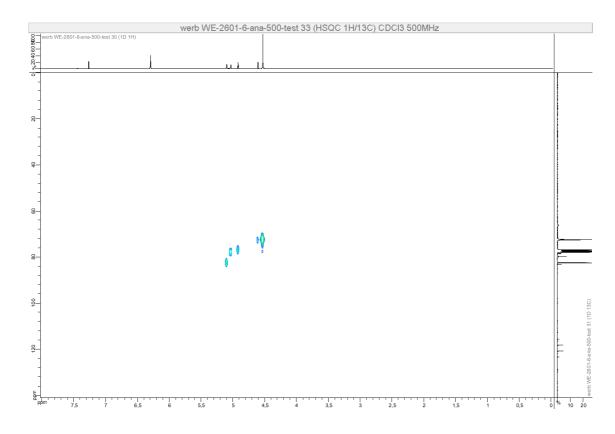
HOESY (500 MHz, CDCl₃) Irradiation at -79.2 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



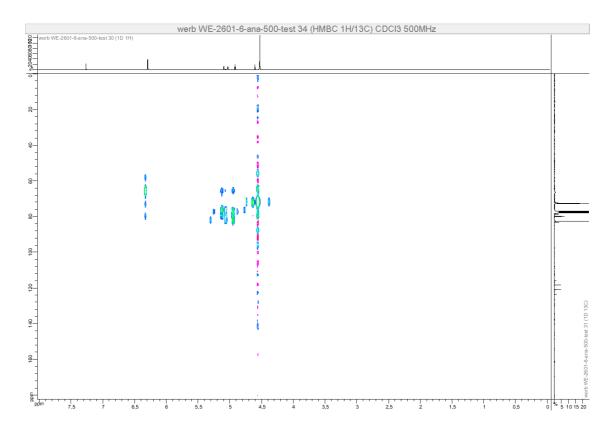


COSY (500 MHz, CDCl₃)

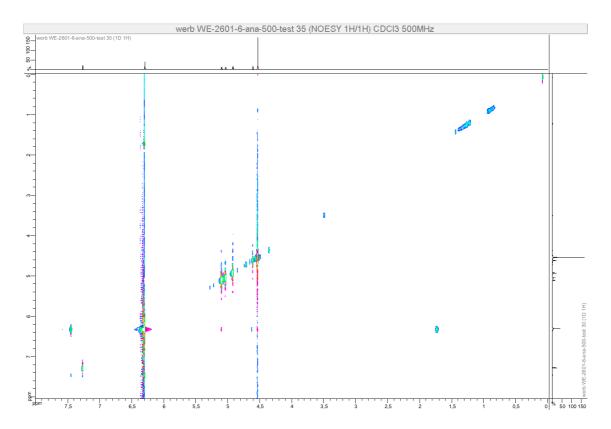




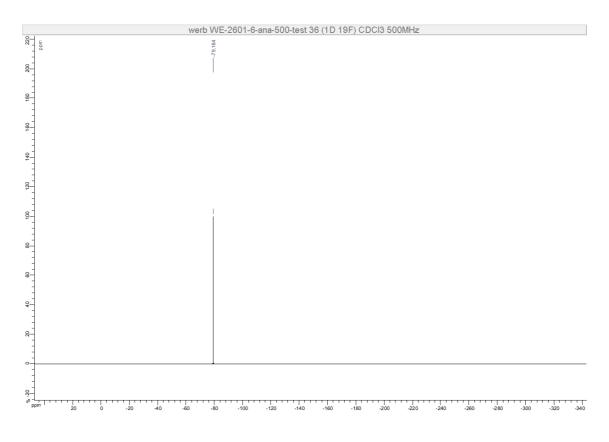
HMBC (500 MHz, CDCl₃)



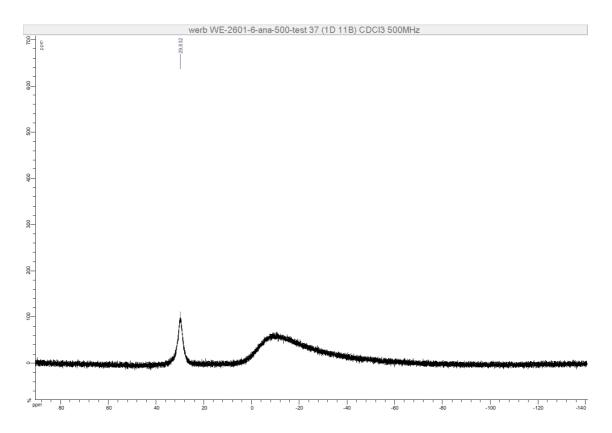
NOESY (500 MHz, CDCl₃)



¹⁹F NMR (470 MHz, CDCl₃)

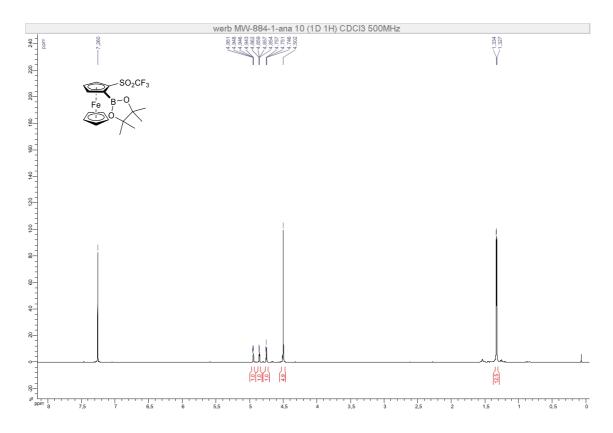


¹¹B NMR (160 MHz, CDCl₃)

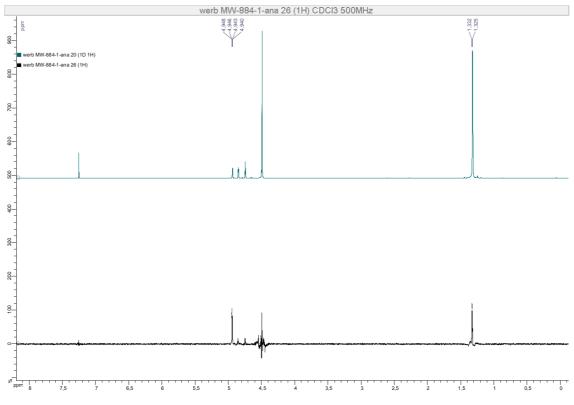


2-(4,4,5,5-Tetramethyl-1,3-dioxa-2-borolyl)ferrocenetriflone (2h)

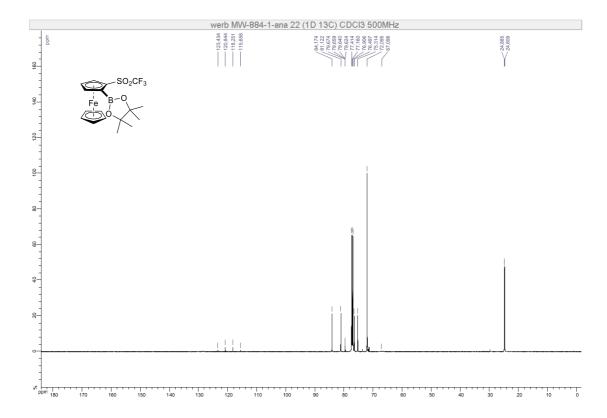
¹H NMR (500 MHz, CDCl₃)



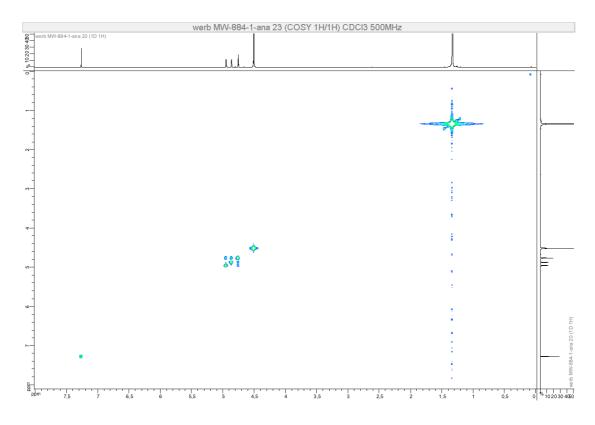
HOESY (500 MHz, CDCl₃) Irradiation at -78.4 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

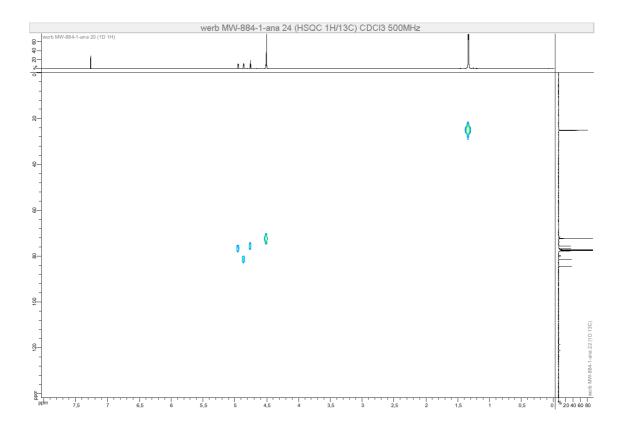


S71

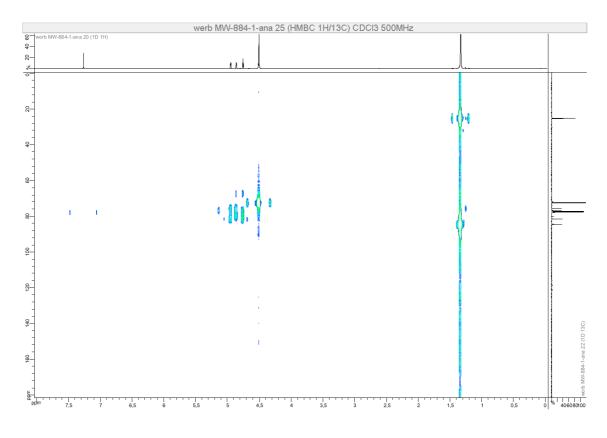


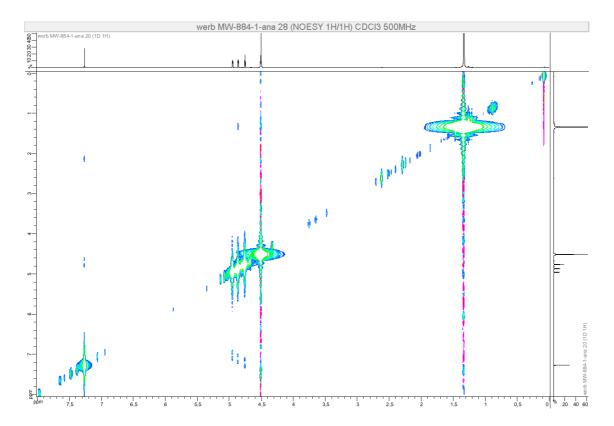
COSY (500 MHz, CDCl₃)



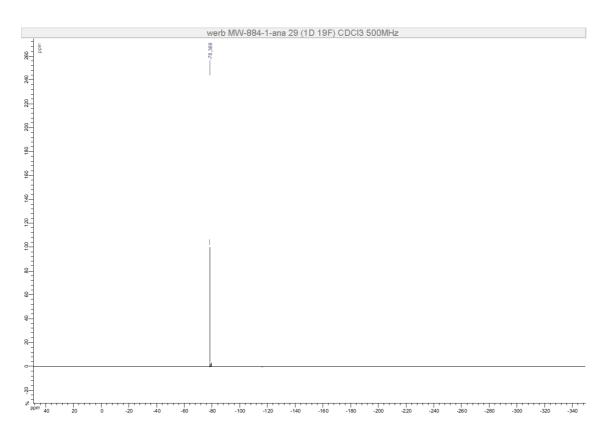


HMBC (500 MHz, CDCl₃)

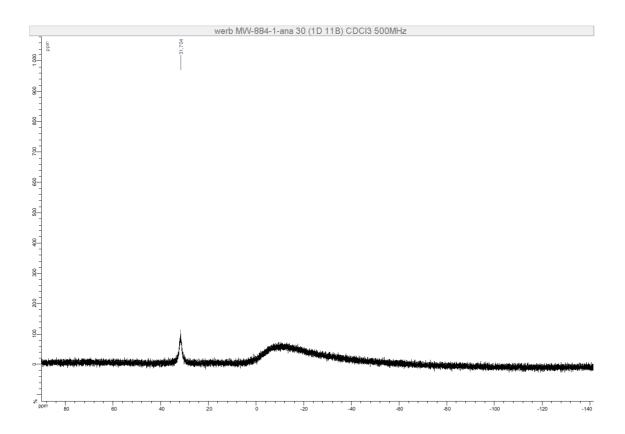




¹⁹F NMR (470 MHz, CDCl₃)

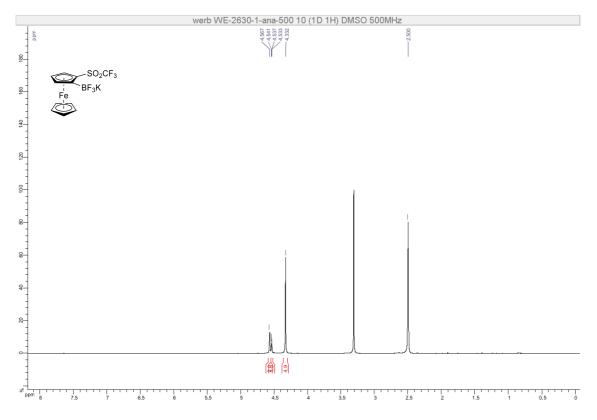


¹¹B NMR (160 MHz, CDCl₃)

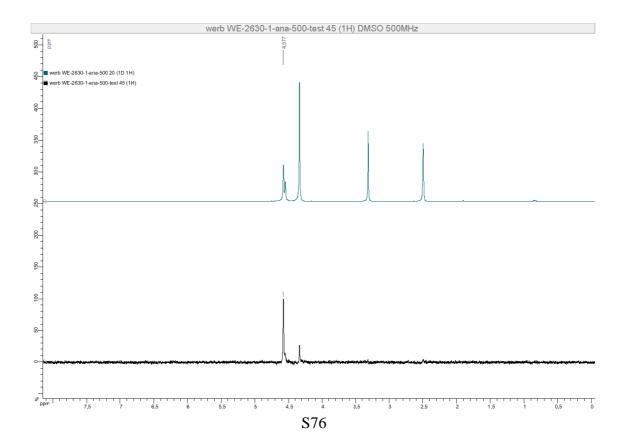


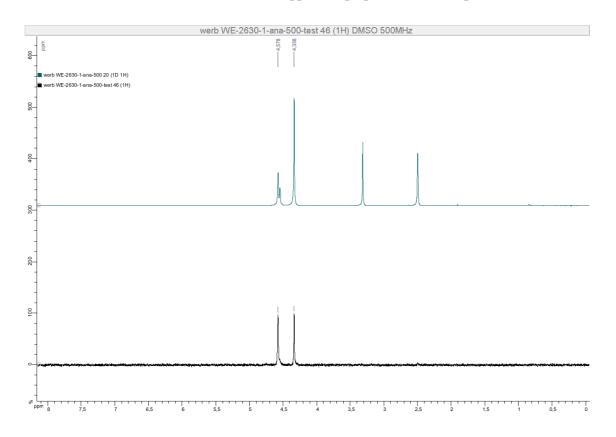
Potassium 2-(trifluoroboryl)ferrocenetriflone (2i)

¹H NMR (500 MHz, CDCl₃)



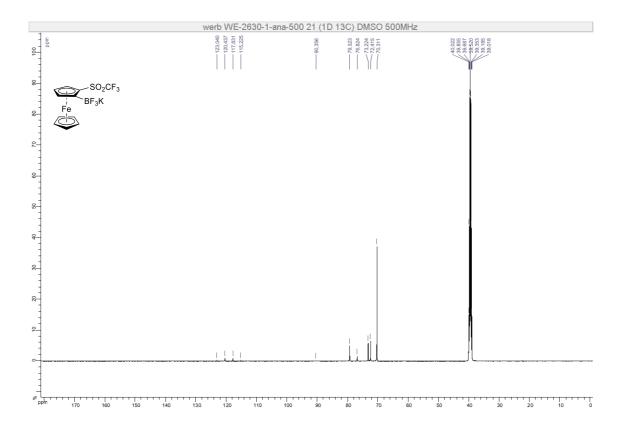
HOESY (500 MHz, CDCl₃) Irradiation at -78.4 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

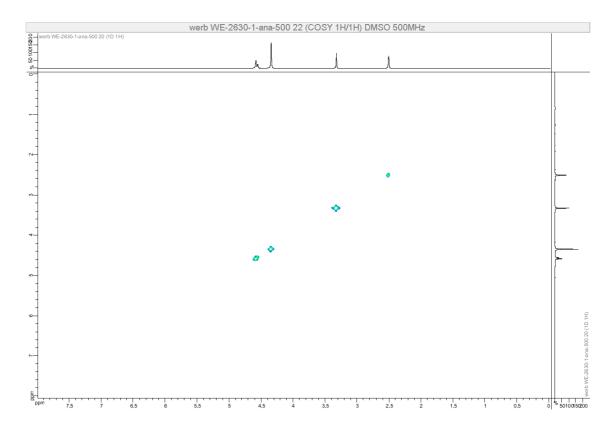


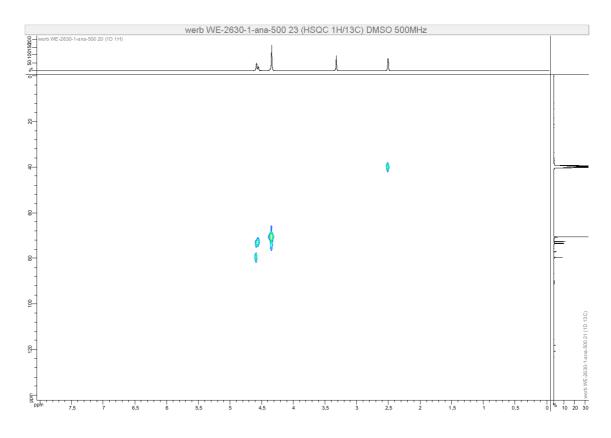


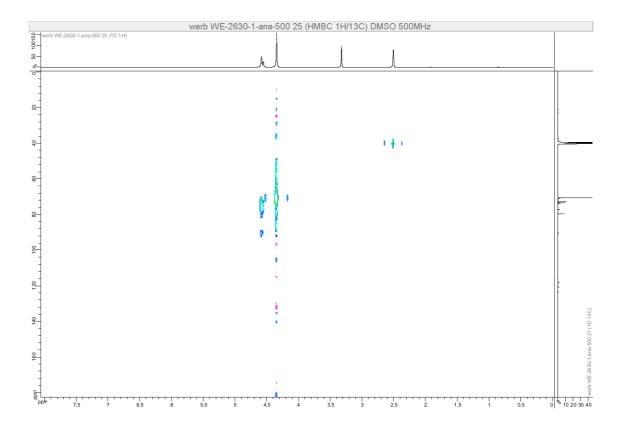
HOESY (500 MHz, CDCl₃) Irradiation at -132.5 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

¹³C NMR (126 MHz, CDCl₃)

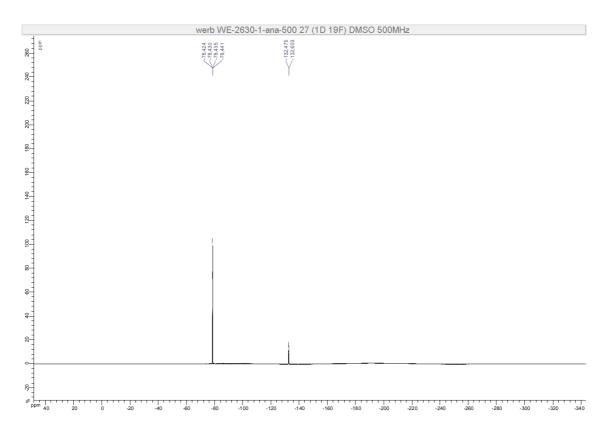




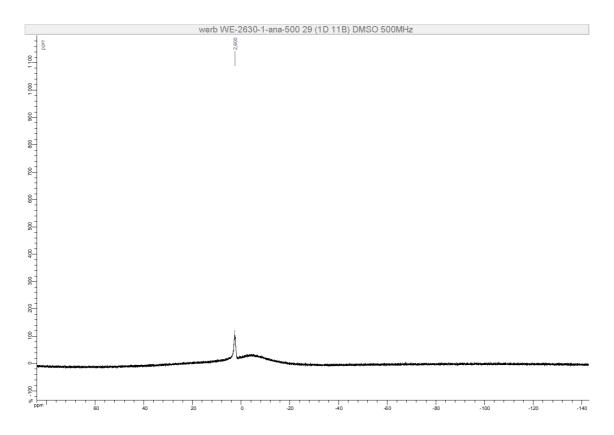




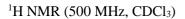
¹⁹F NMR (470 MHz, CDCl₃)

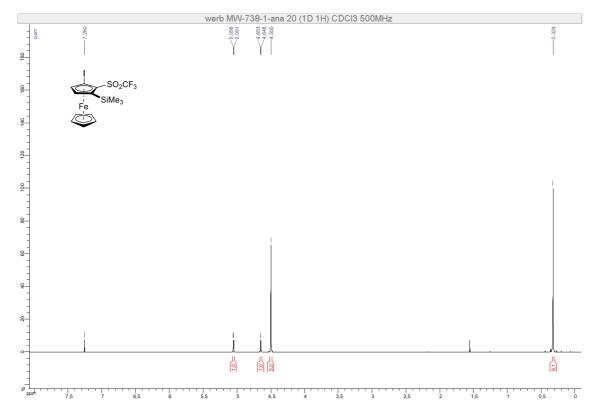


¹¹B NMR (160 MHz, CDCl₃)

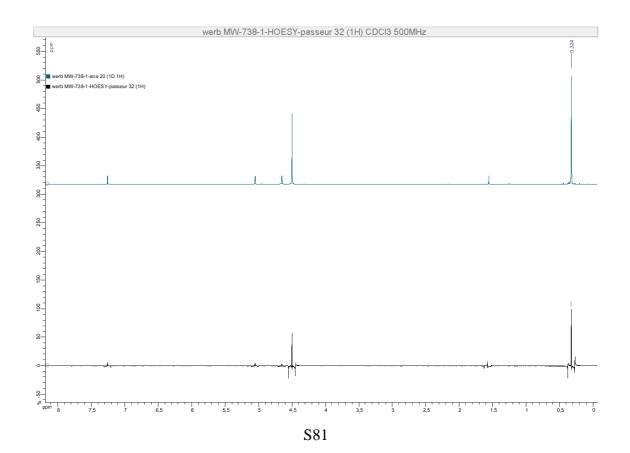


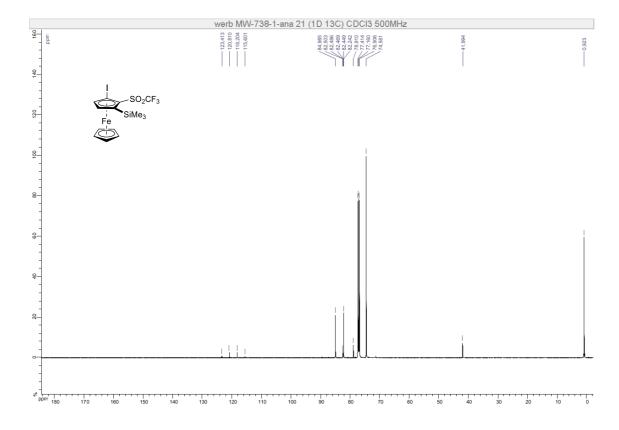
(*R*_P)-2-Iodo-5-(trimethylsilyl)ferrocenetriflone (*R*_P-3af)



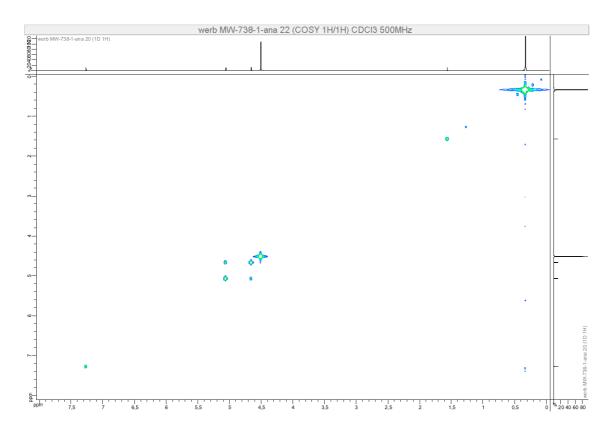


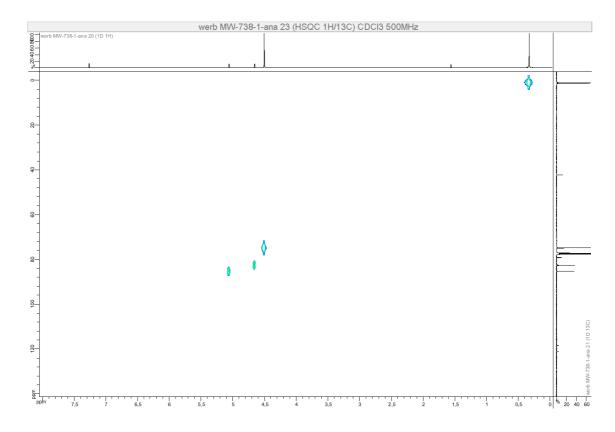
HOESY (500 MHz, CDCl₃) Irradiation at -75.8 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



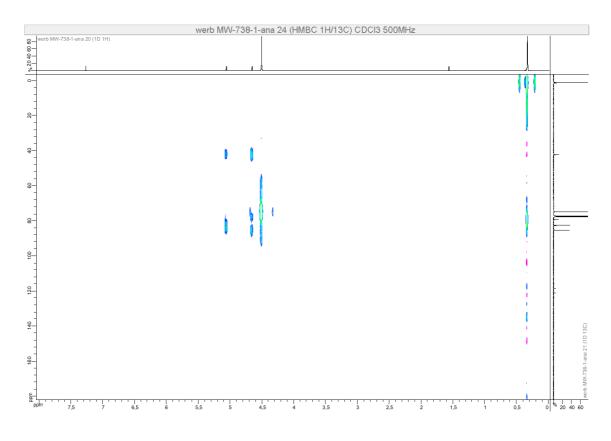


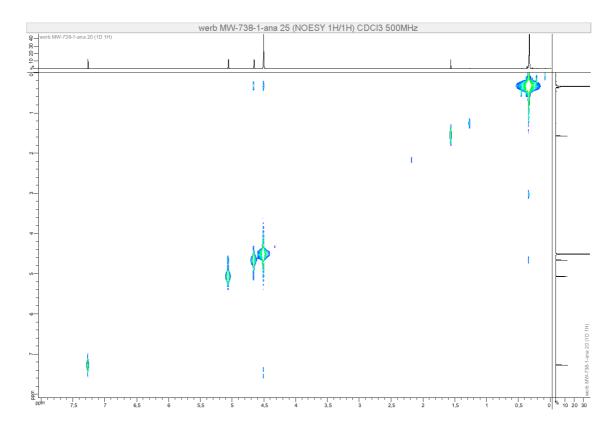
COSY (500 MHz, CDCl₃)



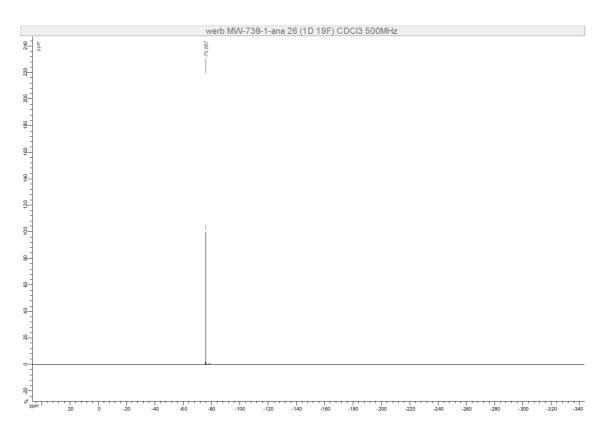


HMBC (500 MHz, CDCl₃)



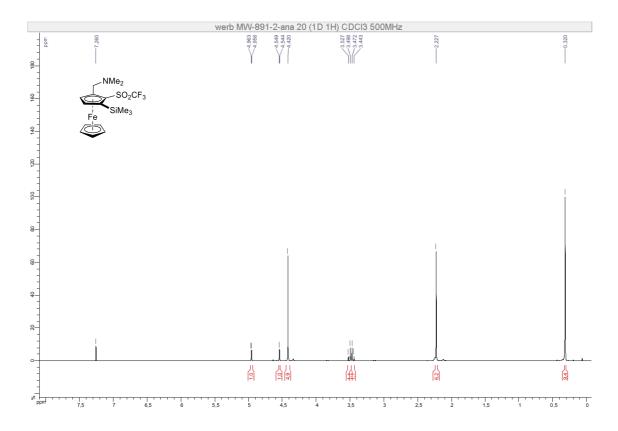


¹⁹F NMR (470 MHz, CDCl₃)

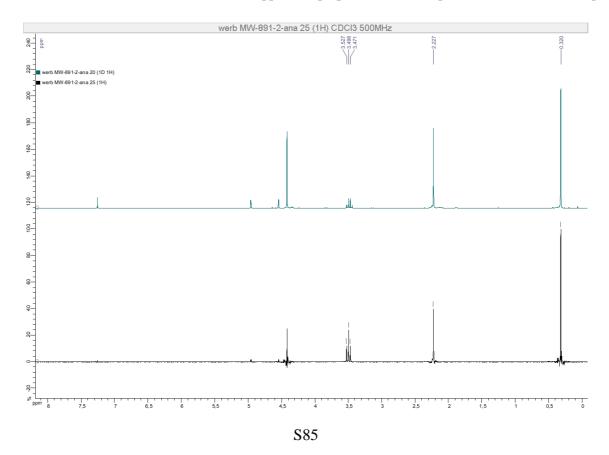


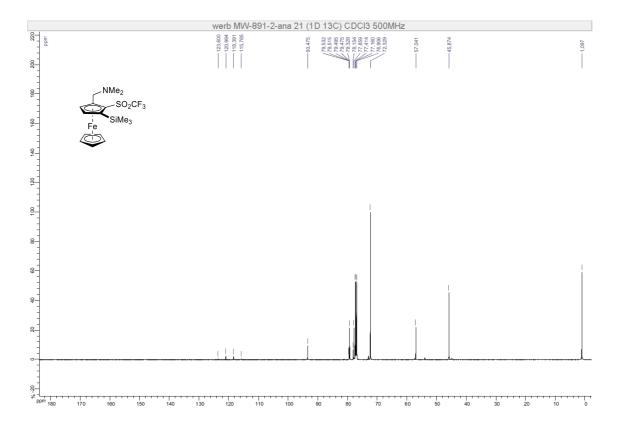
(*R*_P)-2-(Dimethylaminomethyl)-5-(trimethylsilyl)ferrocenetriflone (*R*_P-3aj)

¹H NMR (500 MHz, CDCl₃)

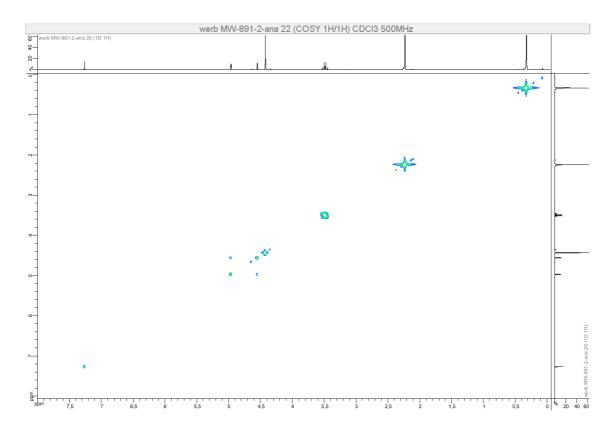


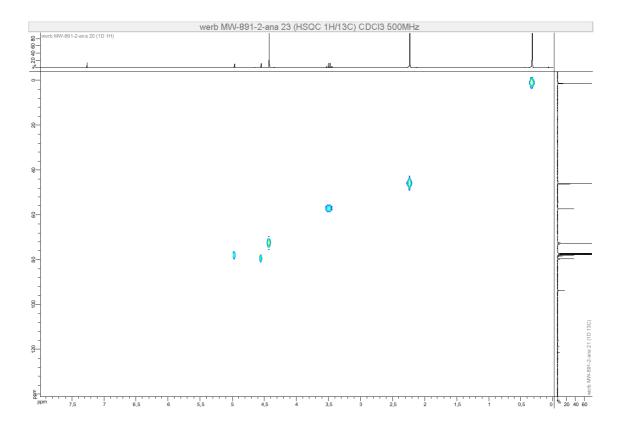
HOESY (500 MHz, CDCl₃) Irradiation at -75.9 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



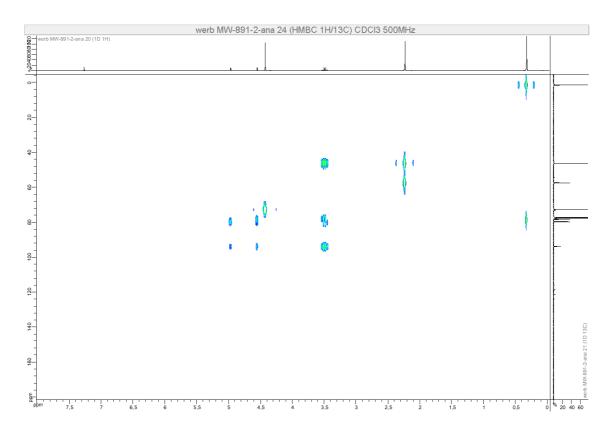


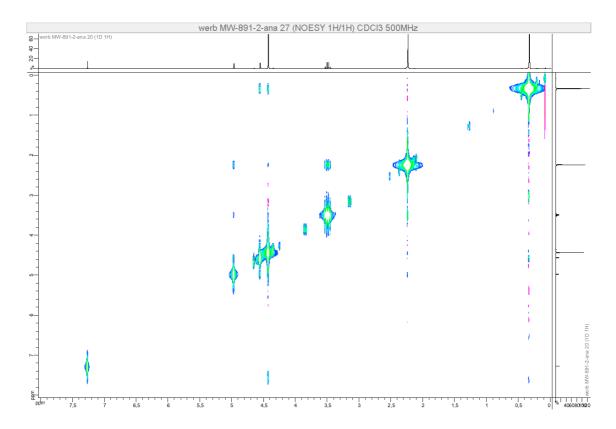
COSY (500 MHz, CDCl₃)



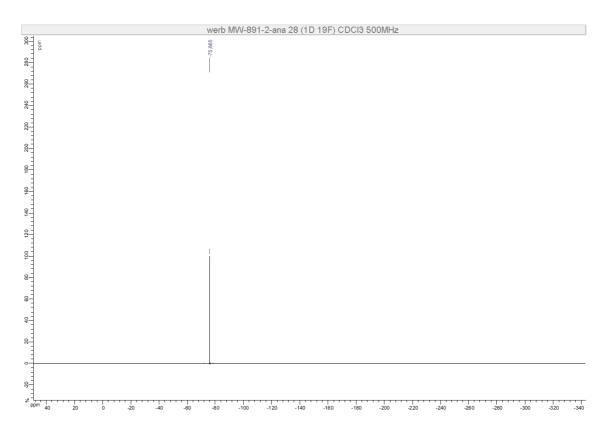


HMBC (500 MHz, CDCl₃)



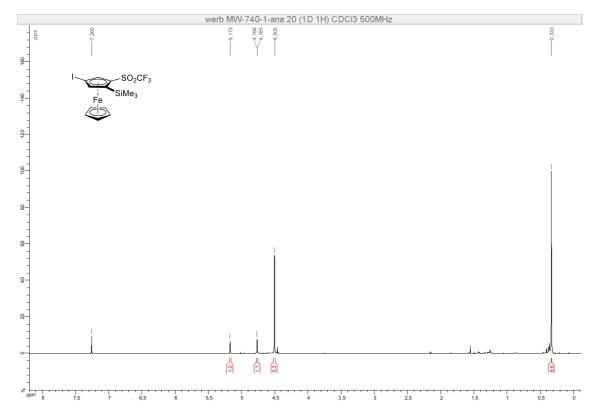


¹⁹F NMR (470 MHz, CDCl₃)

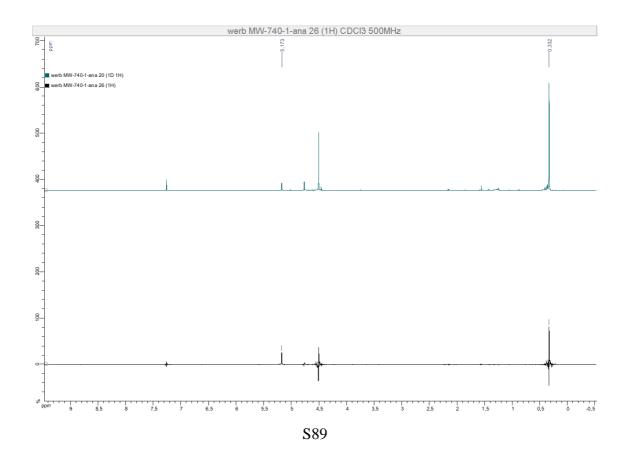


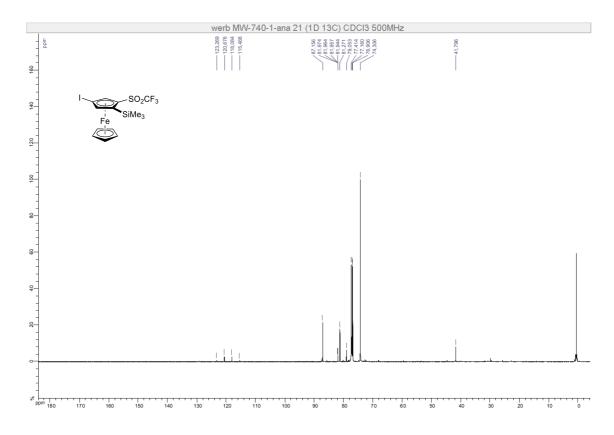
(*R*_P)-4-Iodo-2-(trimethylsilyl)ferrocenetriflone (*R*_P-4af)

¹H NMR (500 MHz, CDCl₃)

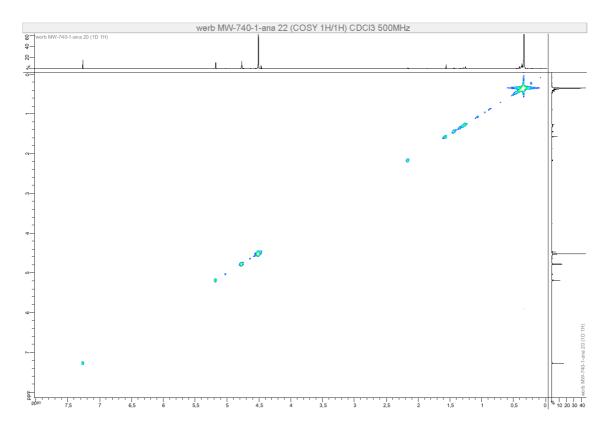


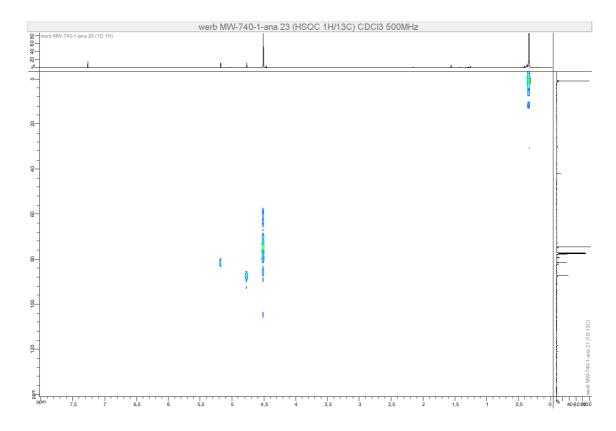
HOESY (500 MHz, CDCl₃) Irradiation at -78.3 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



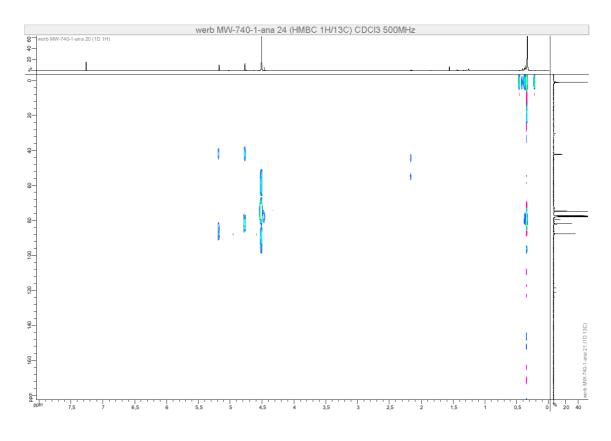


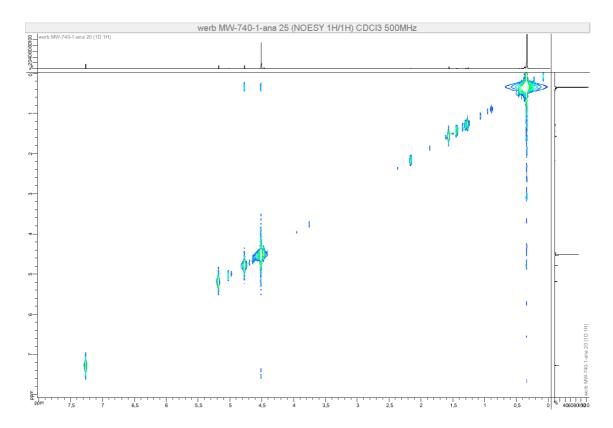
COSY (500 MHz, CDCl₃)



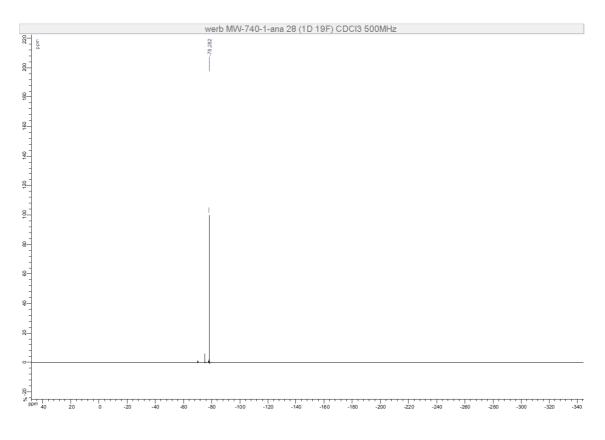


HMBC (500 MHz, CDCl₃)



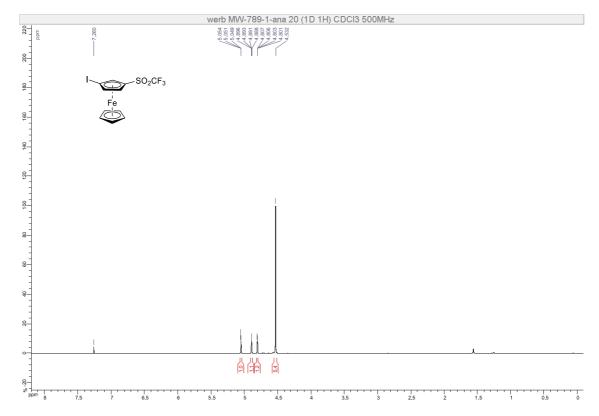


¹⁹F NMR (470 MHz, CDCl₃)

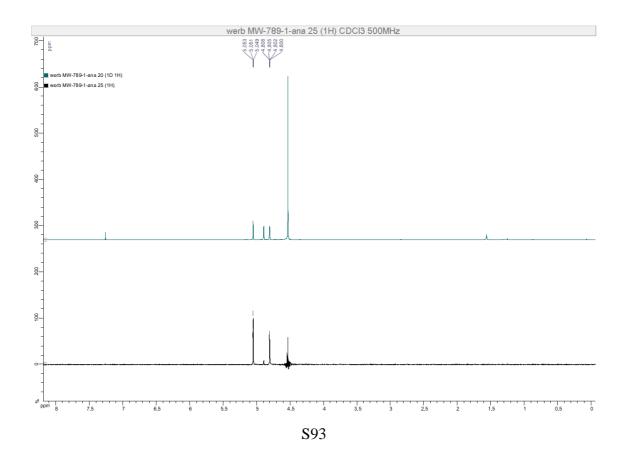


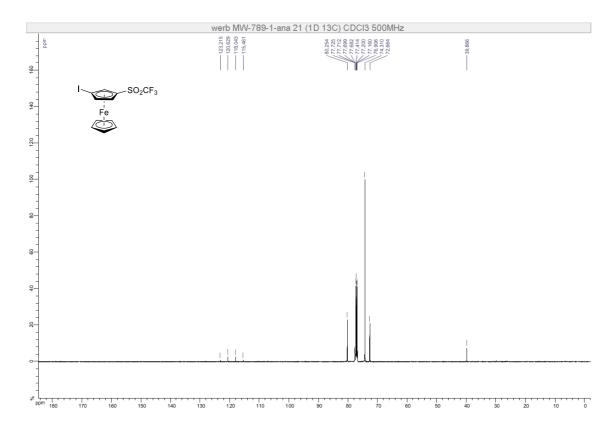
(*R*_P)-3-Iodoferrocenetriflone (*R*_P-5f)

¹H NMR (500 MHz, CDCl₃)

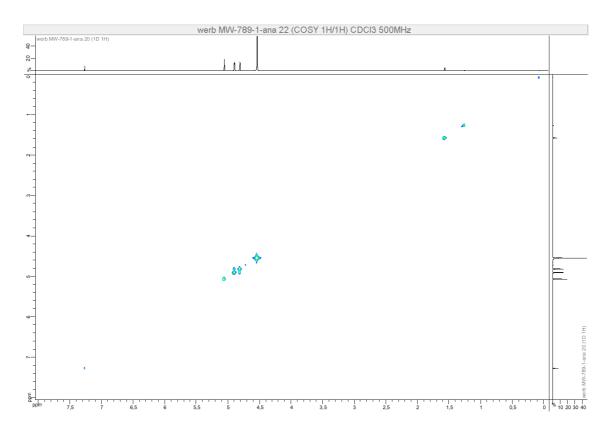


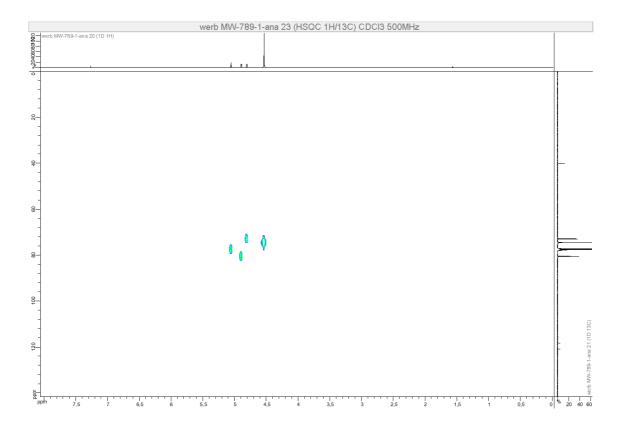
HOESY (500 MHz, CDCl₃) Irradiation at -79.1 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



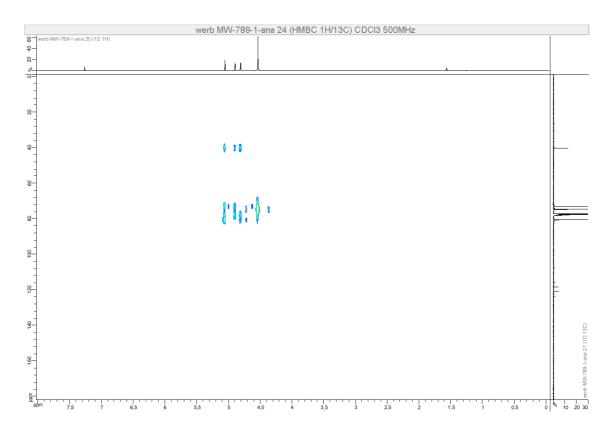


COSY (500 MHz, CDCl₃)

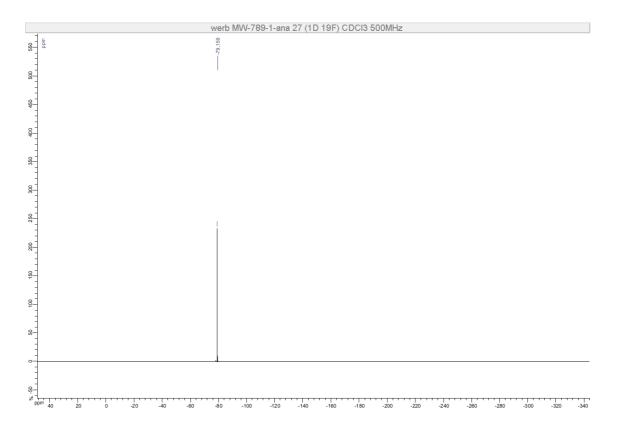




HMBC (500 MHz, CDCl₃)

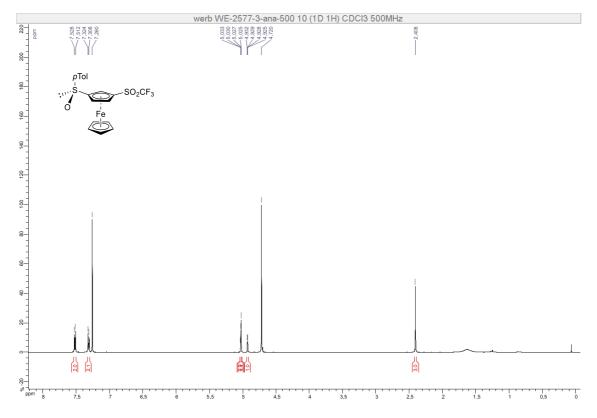


¹⁹F NMR (470 MHz, CDCl₃)

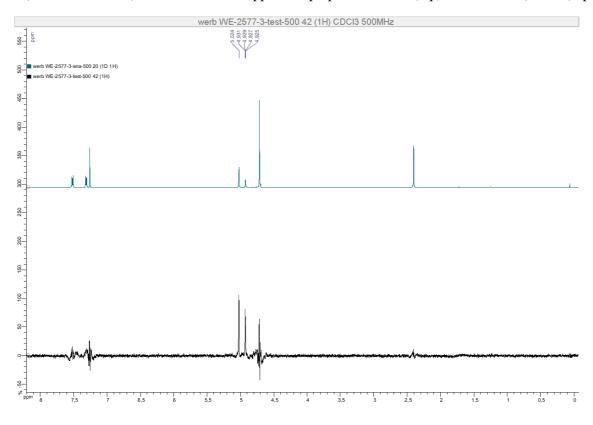


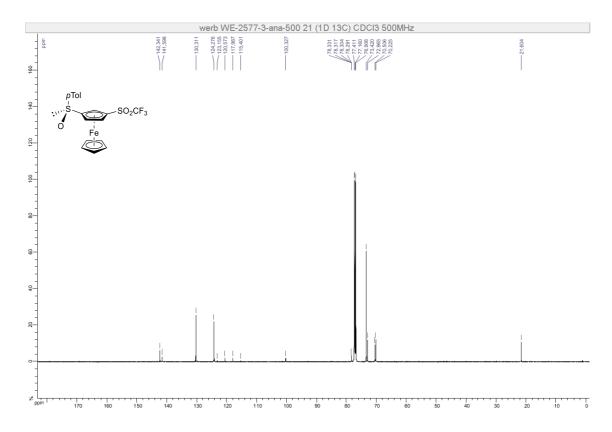
(S,S_P)-3-(4-Tolylsulfinyl)ferrocenetriflone (S_P-5k)

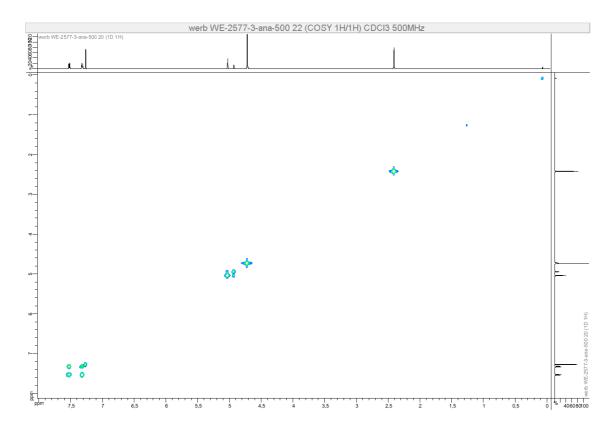
¹H NMR (500 MHz, CDCl₃)

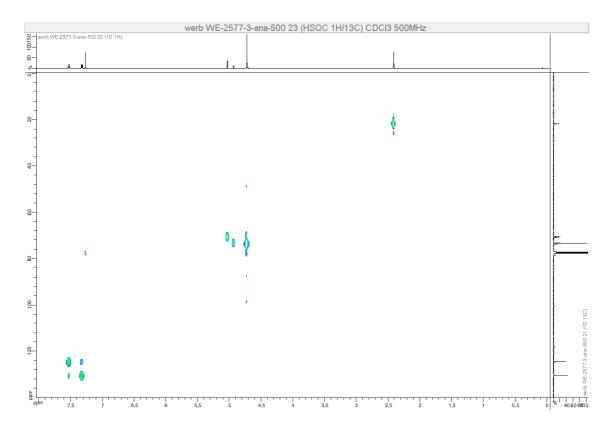


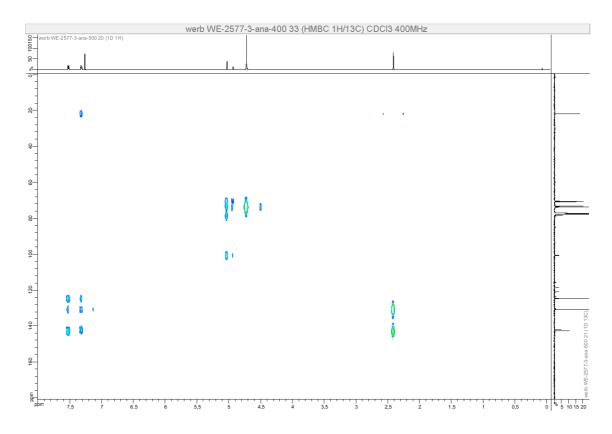
HOESY (500 MHz, CDCl₃) Irradiation at -78.9 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

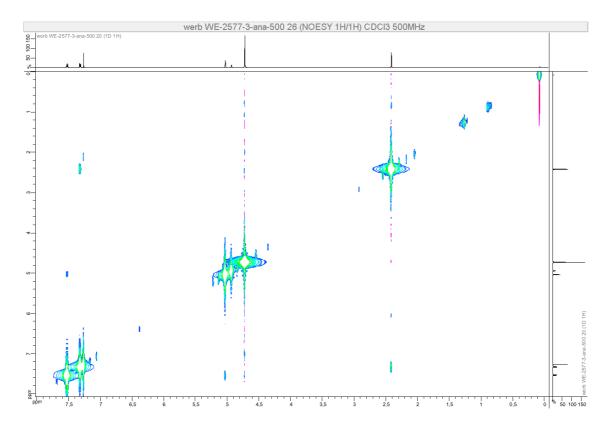




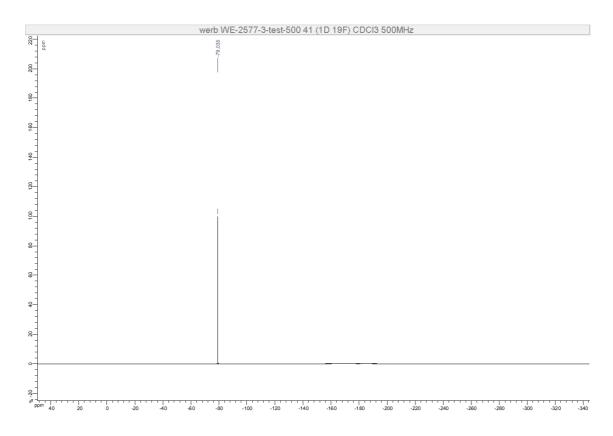






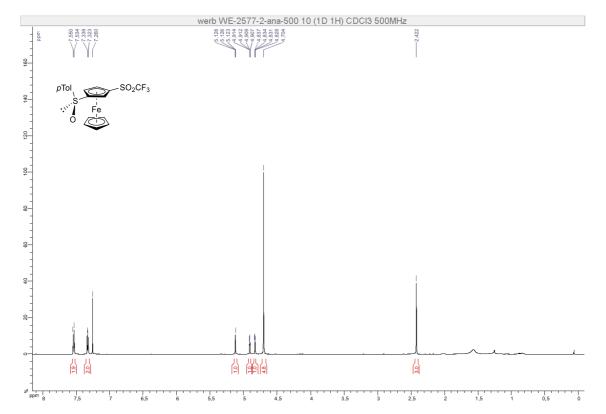


¹⁹F NMR (470 MHz, CDCl₃)

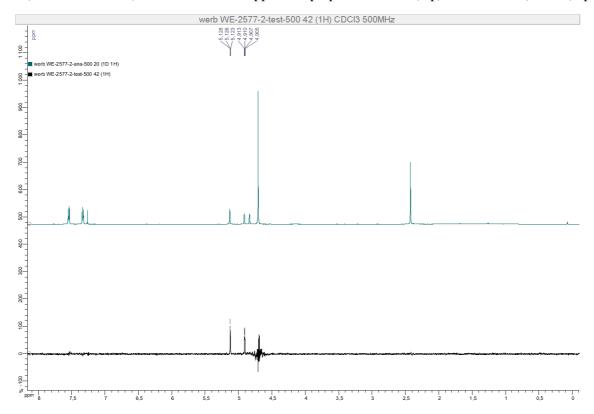


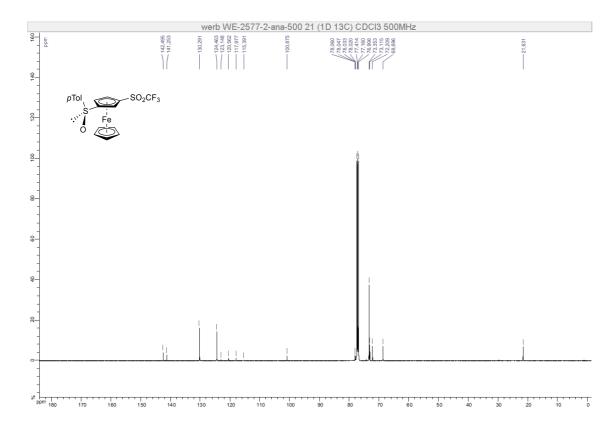
(S,R_P)-3-(4-Tolylsulfinyl)ferrocenetriflone (R_P-5k)

¹H NMR (500 MHz, CDCl₃)

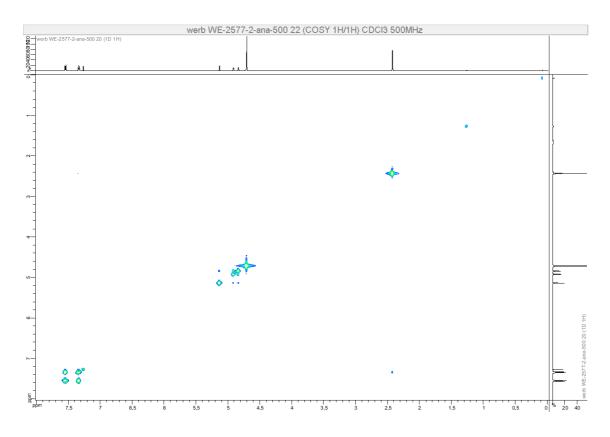


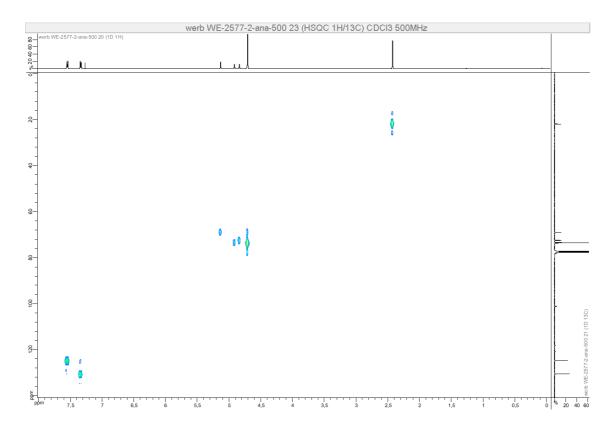
HOESY (500 MHz, CDCl₃) Irradiation at -78.9 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

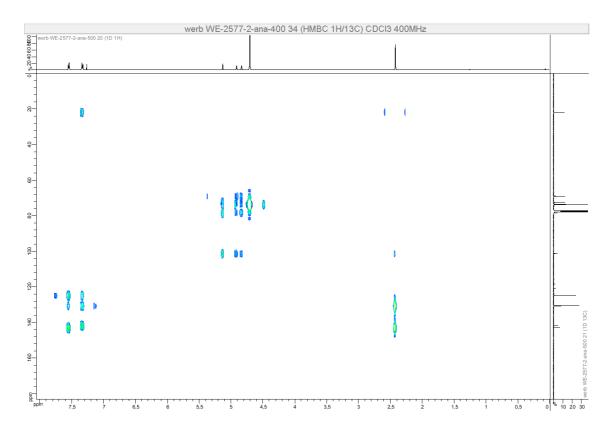


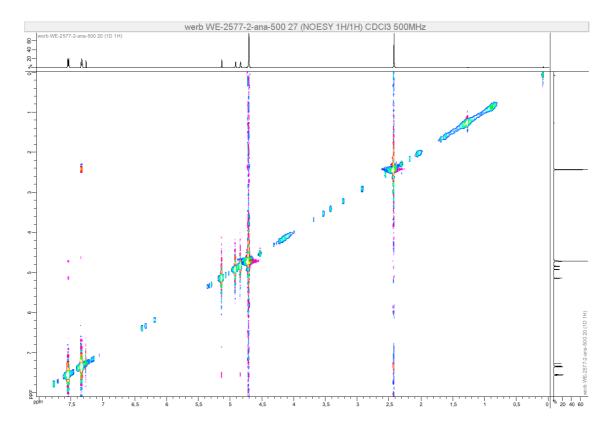


COSY (500 MHz, CDCl₃)

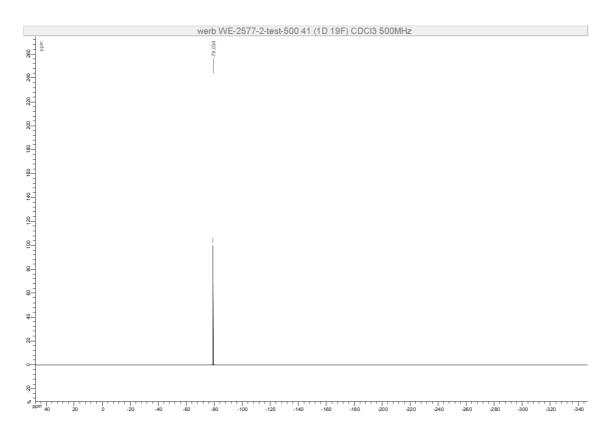






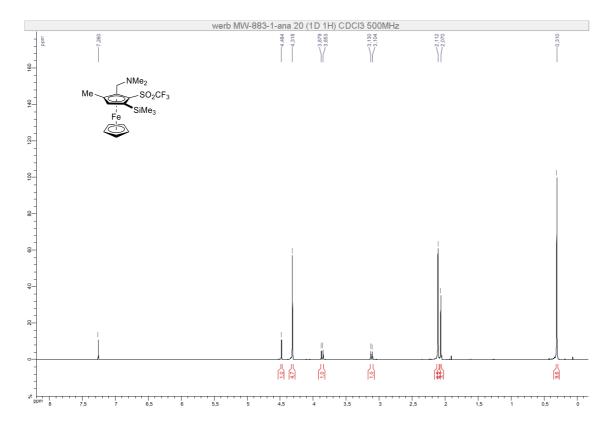


¹⁹F NMR (470 MHz, CDCl₃)

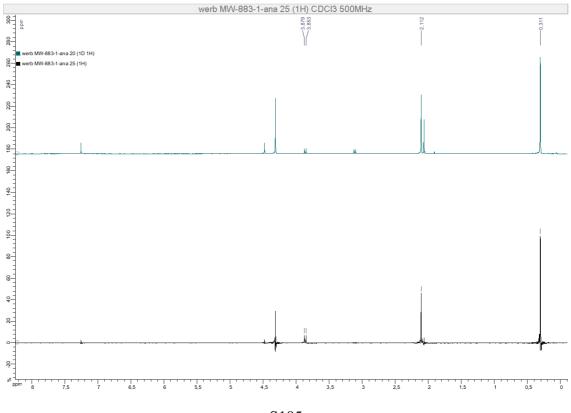


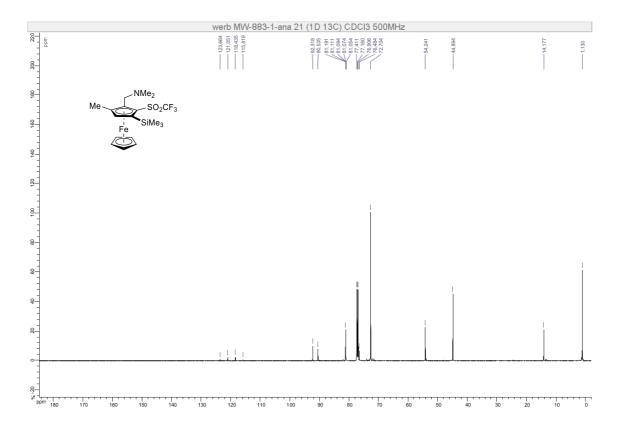
(*R*_P)-2-(Dimethylaminomethyl)-3-methyl-5-(trimethylsilyl)ferrocenetriflone (*R*_P-6)

¹H NMR (500 MHz, CDCl₃)

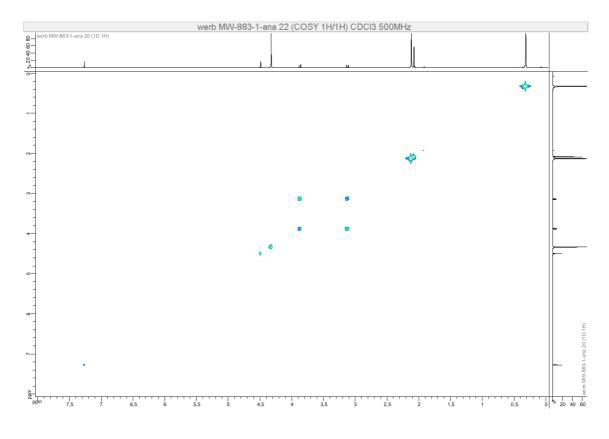


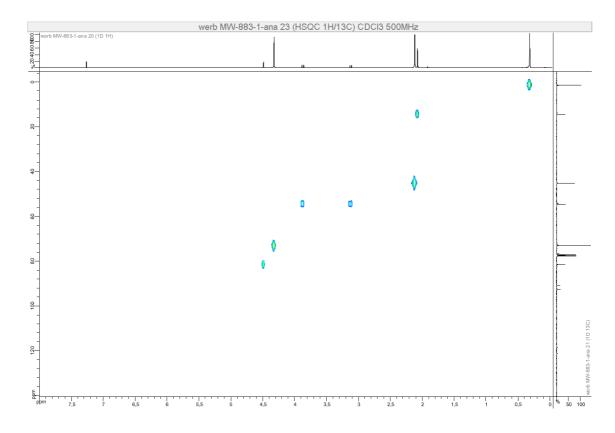
HOESY (500 MHz, CDCl₃) Irradiation at -72.8 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.



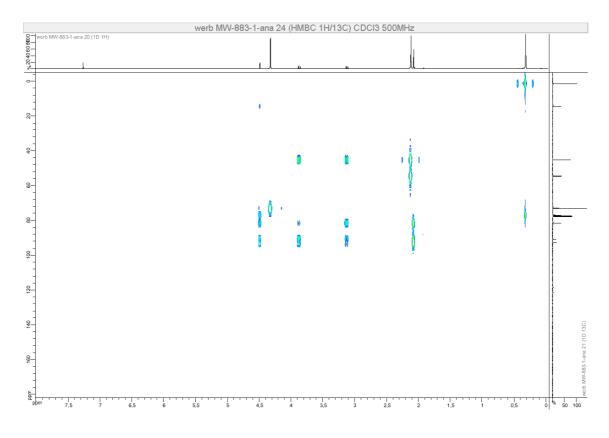


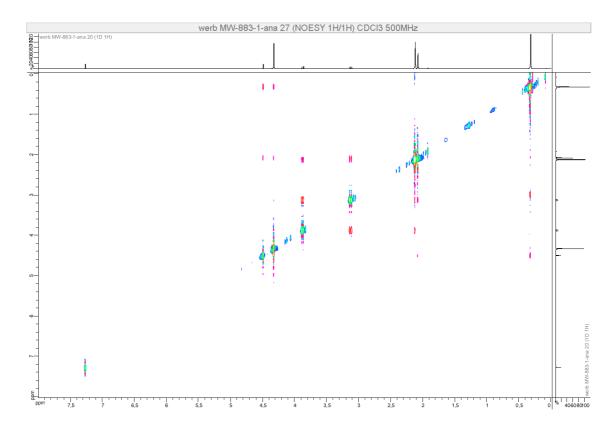
COSY (500 MHz, CDCl₃)



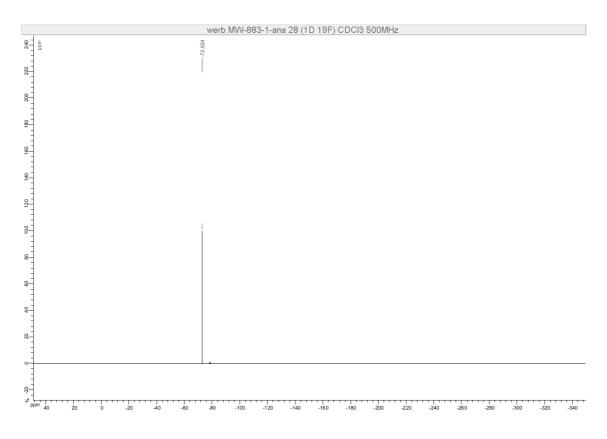


HMBC (500 MHz, CDCl₃)



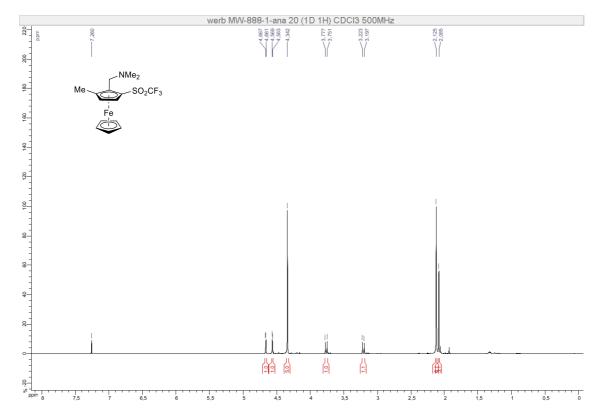


¹⁹F NMR (470 MHz, CDCl₃)

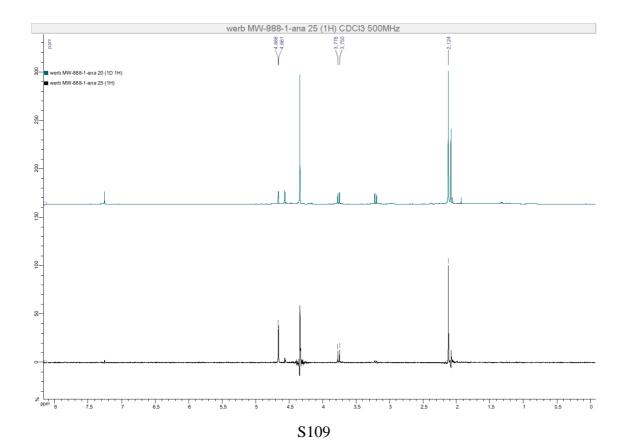


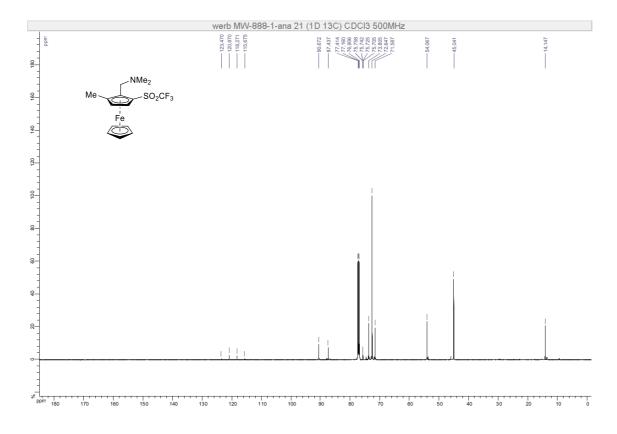
(S_P)-2-(Dimethylaminomethyl)-3-methylferrocenetriflone (S_P-7)

¹H NMR (500 MHz, CDCl₃)

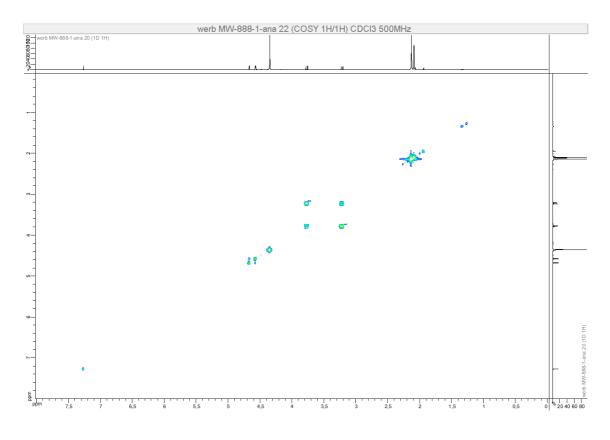


HOESY (500 MHz, CDCl₃) Irradiation at -77.2 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

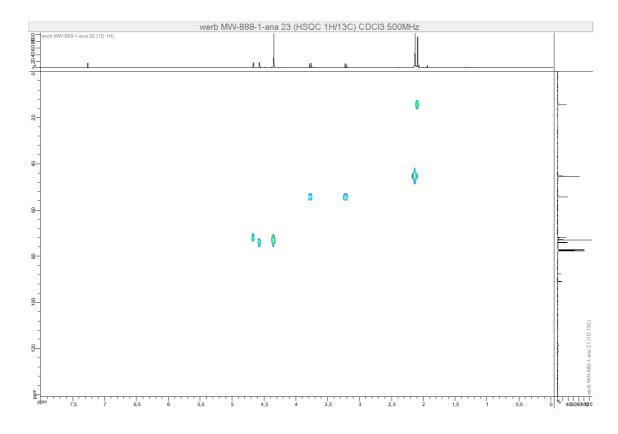




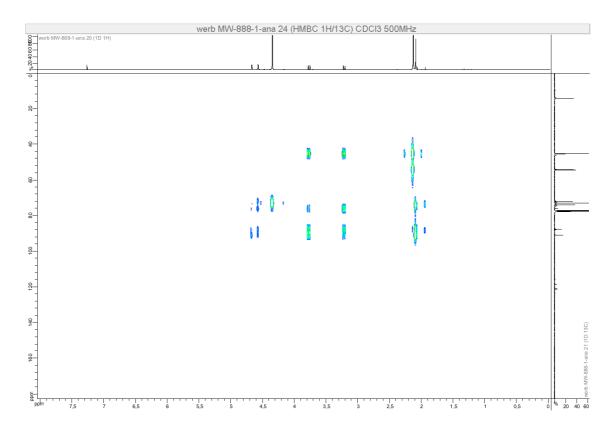
COSY (500 MHz, CDCl₃)



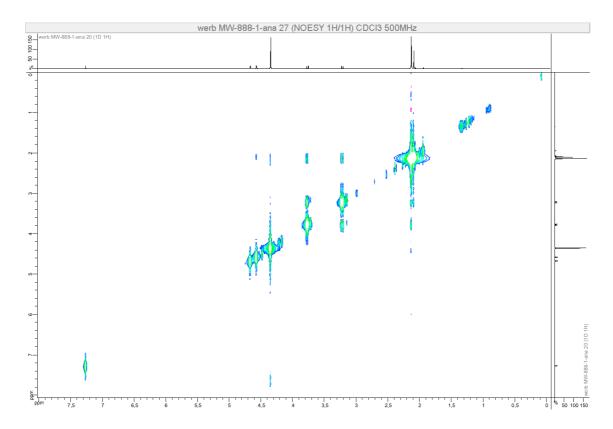
HSQC (500 MHz, CDCl₃)



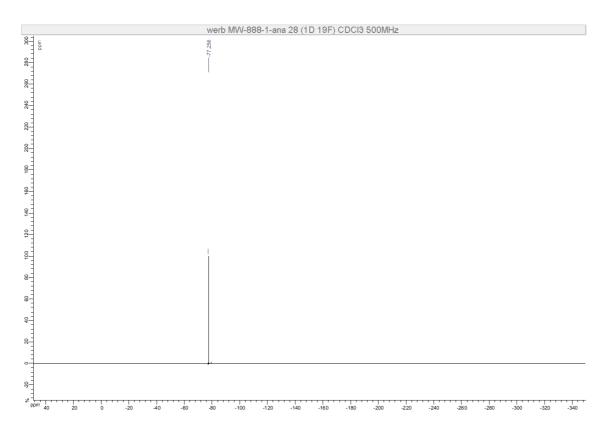
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

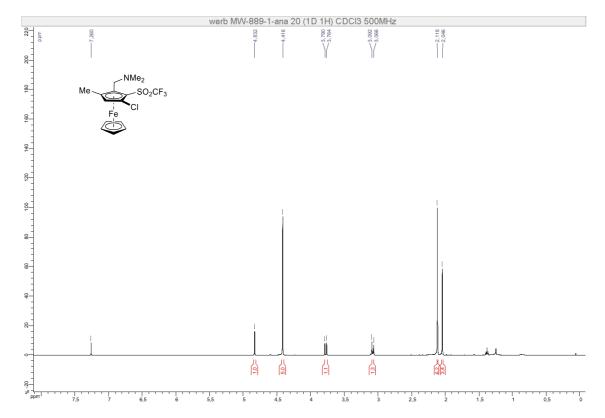


¹⁹F NMR (470 MHz, CDCl₃)

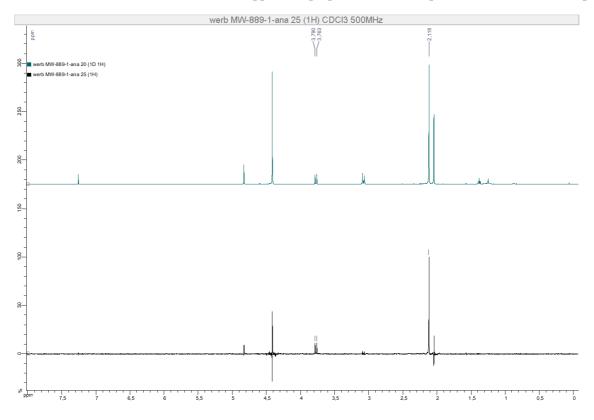


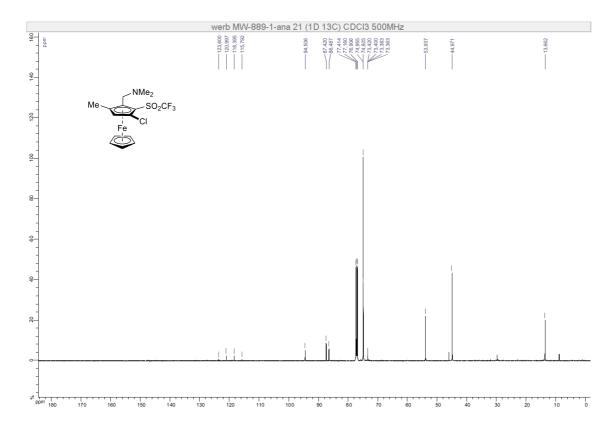
(S_P)-5-Chloro-2-(dimethylaminomethyl)-3-methylferrocenetriflone (S_P-8)

¹H NMR (500 MHz, CDCl₃)

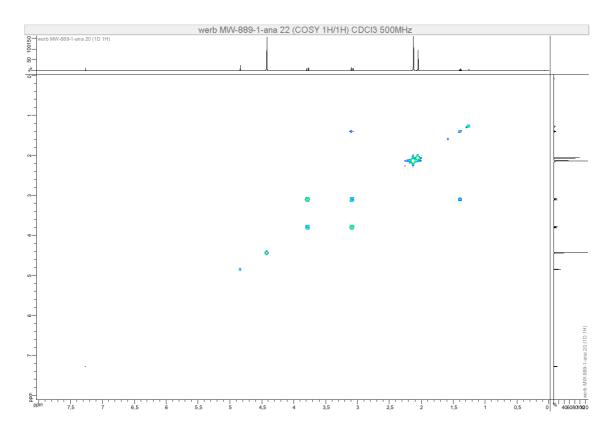


HOESY (500 MHz, CDCl₃) Irradiation at -76.4 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

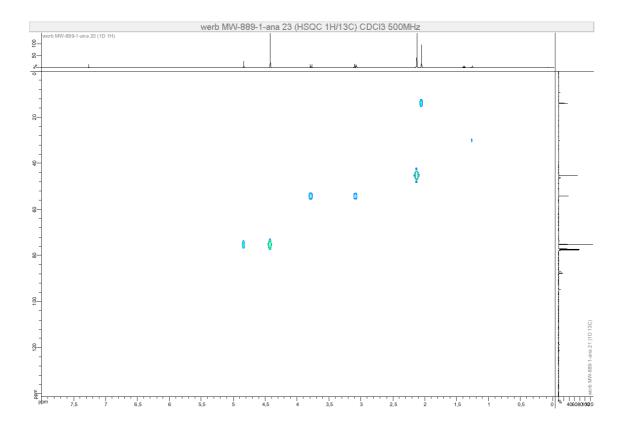




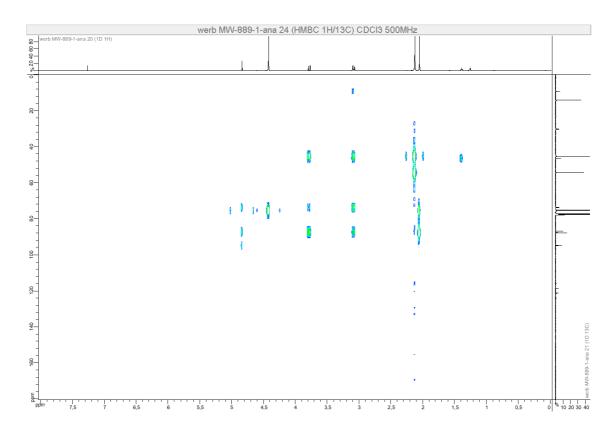
COSY (500 MHz, CDCl₃)



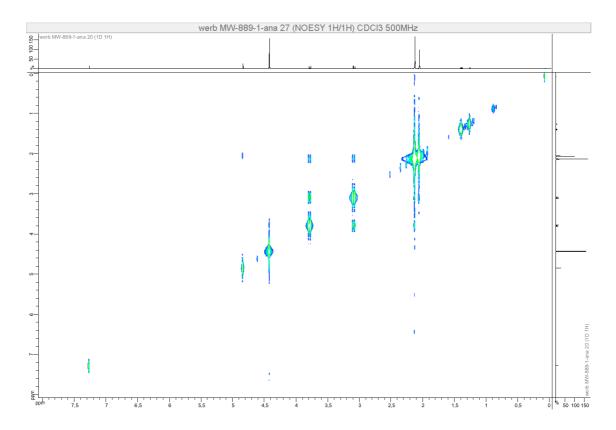
HSQC (500 MHz, CDCl₃)



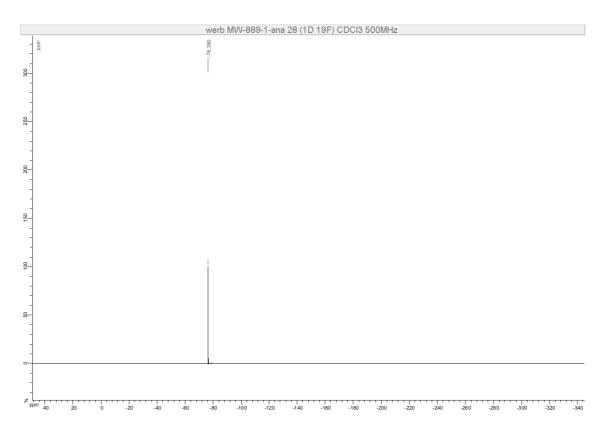
HMBC (500 MHz, CDCl₃)



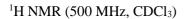
NOESY (500 MHz, CDCl₃)

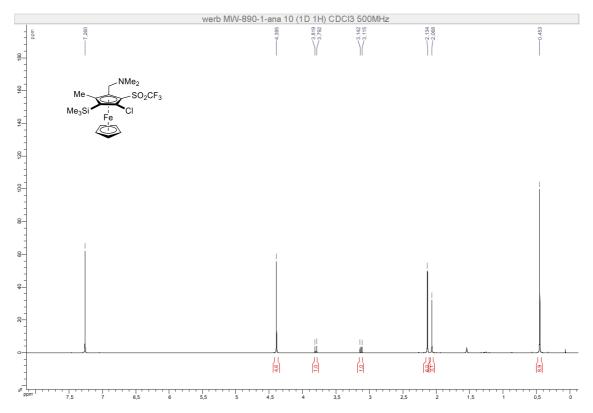


¹⁹F NMR (470 MHz, CDCl₃)

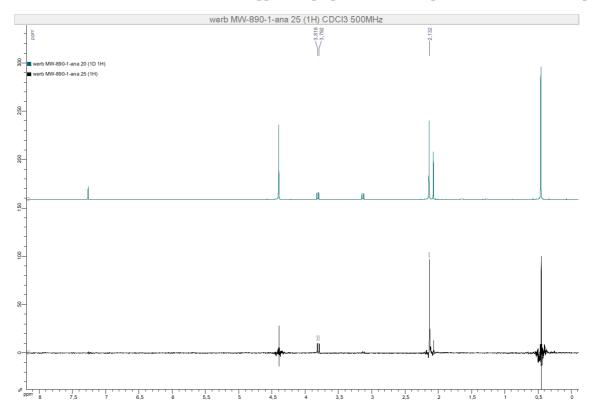


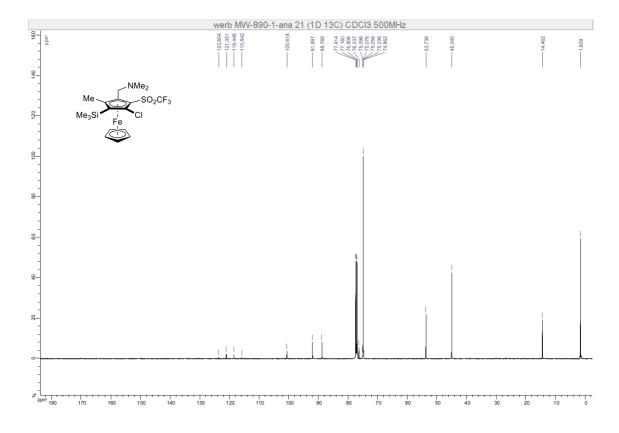
(S_P)-2-Chloro-5-(dimethylaminomethyl)-4-methyl-3-(trimethylsilyl)ferrocenetriflone (S_P-9)



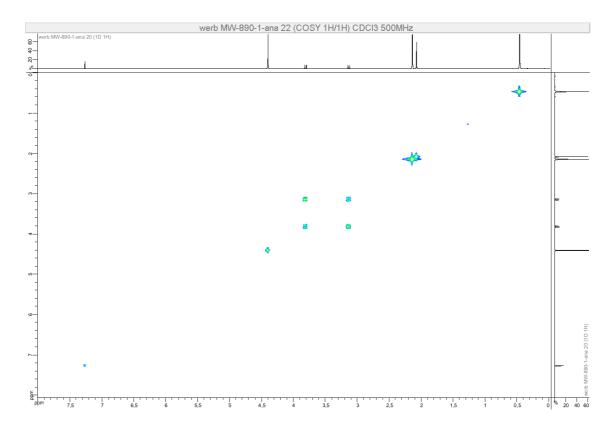


HOESY (500 MHz, $CDCl_3$) Irradiation at -182.6 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

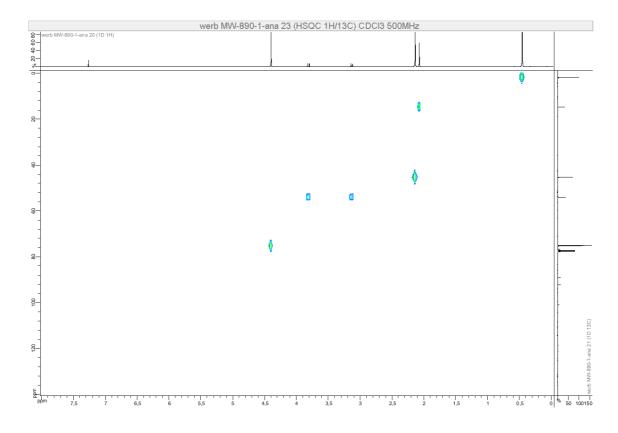




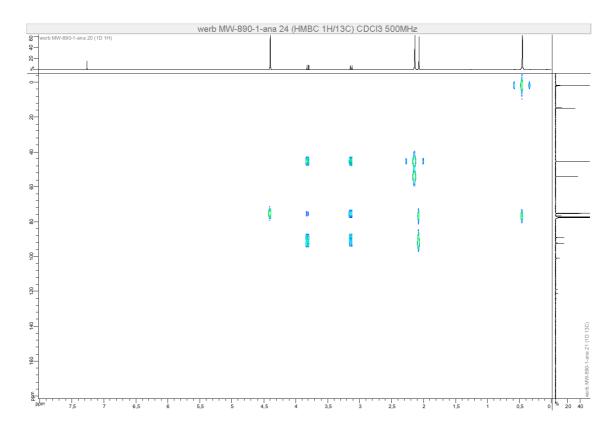
COSY (500 MHz, CDCl₃)



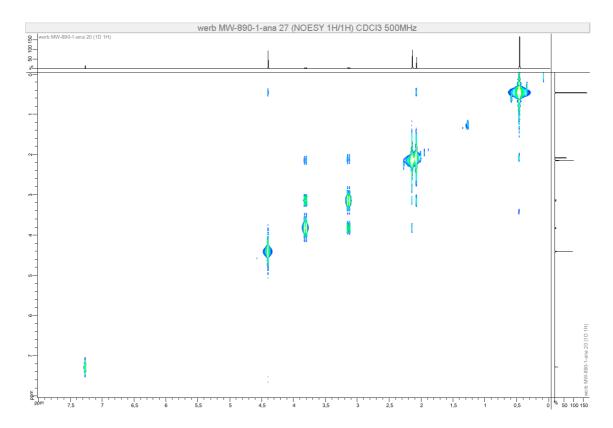
HSQC (500 MHz, CDCl₃)



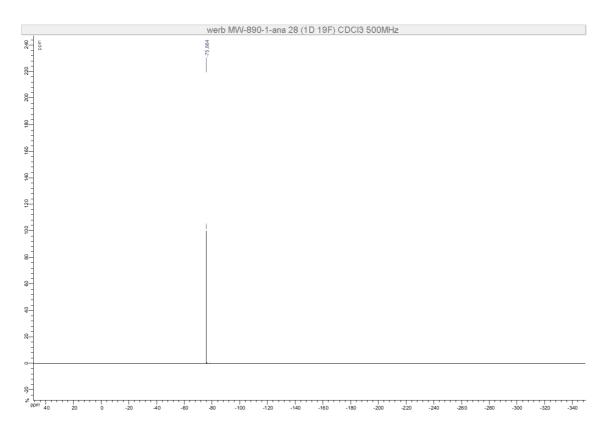
HMBC (500 MHz, CDCl₃)



NOESY (500 MHz, CDCl₃)

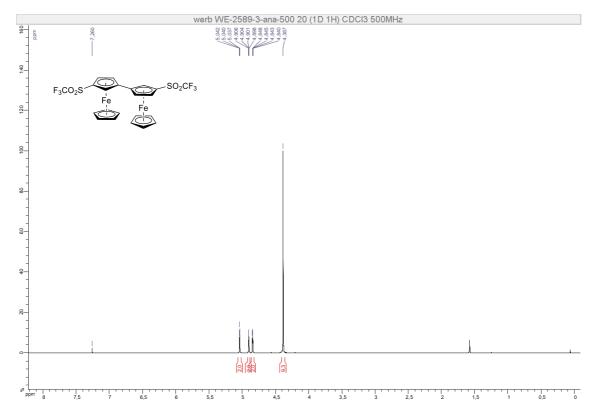


¹⁹F NMR (470 MHz, CDCl₃)

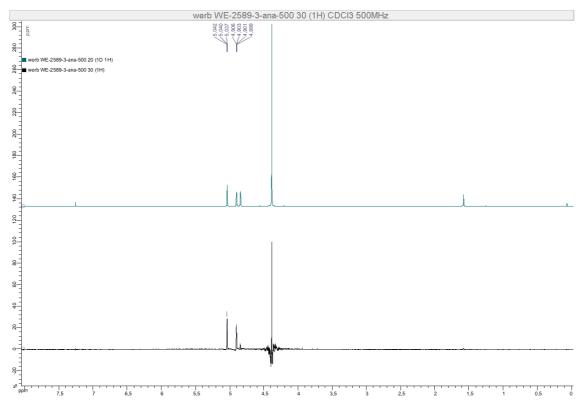


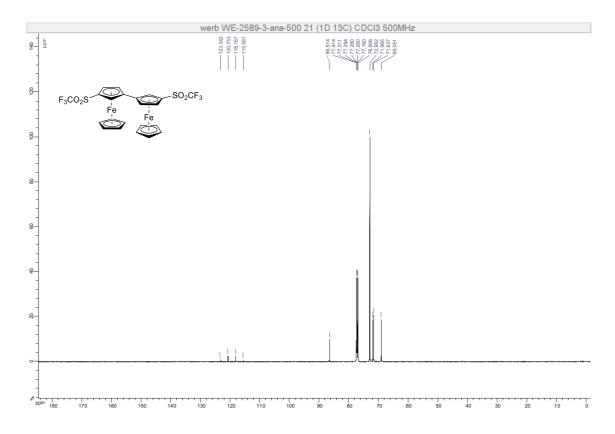
(S_P,S_P)-1,1'-Biferrocene-3,3'-bis(triflone) (S_P,S_P-5l)

¹H NMR (500 MHz, CDCl₃)

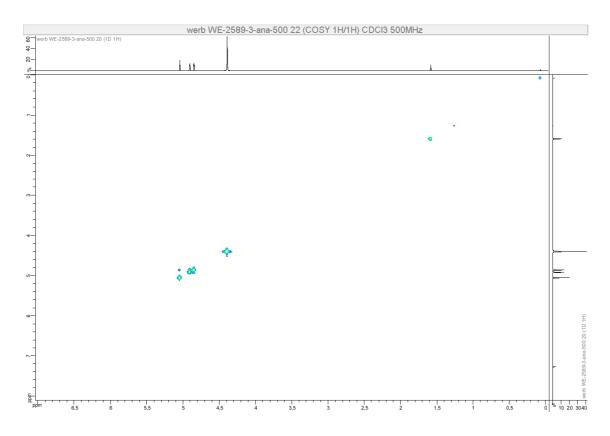


HOESY (500 MHz, CDCl₃) Irradiation at -79.2 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

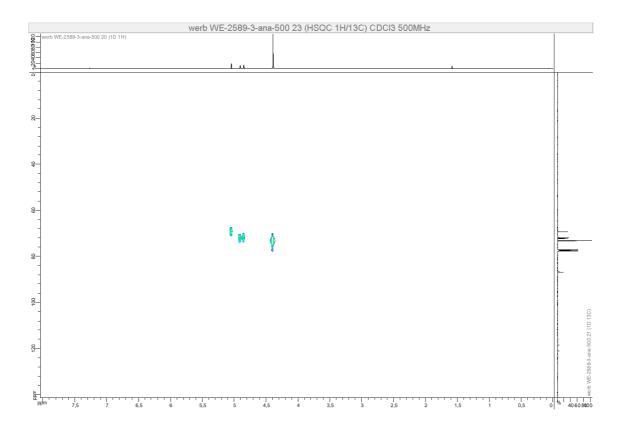




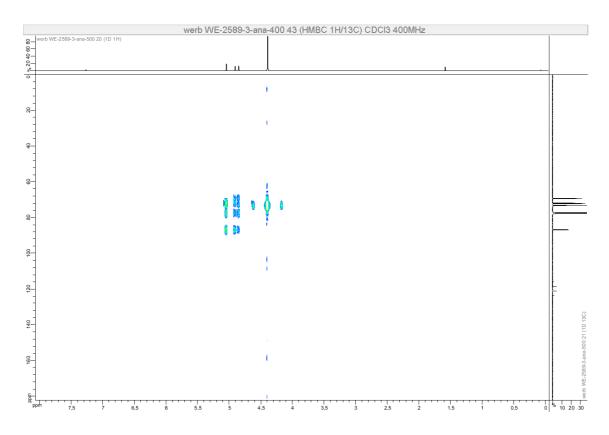
COSY (500 MHz, CDCl₃)



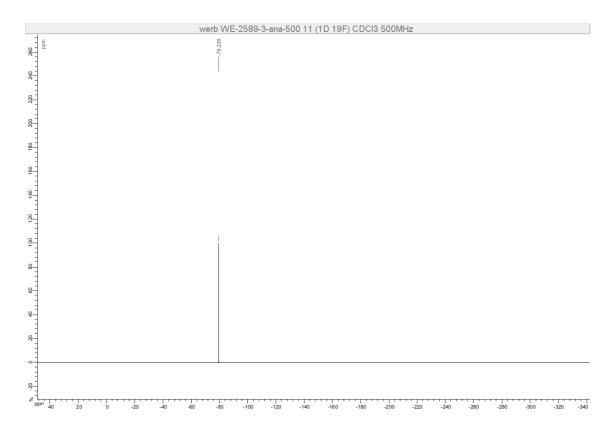
HSQC (500 MHz, CDCl₃)



HMBC (400 MHz, CDCl₃)

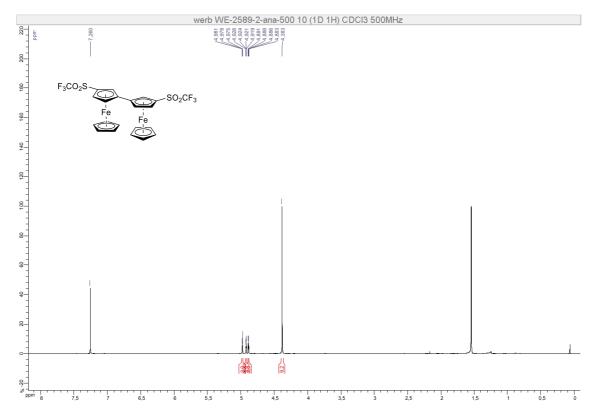


¹⁹F NMR (470 MHz, CDCl₃)

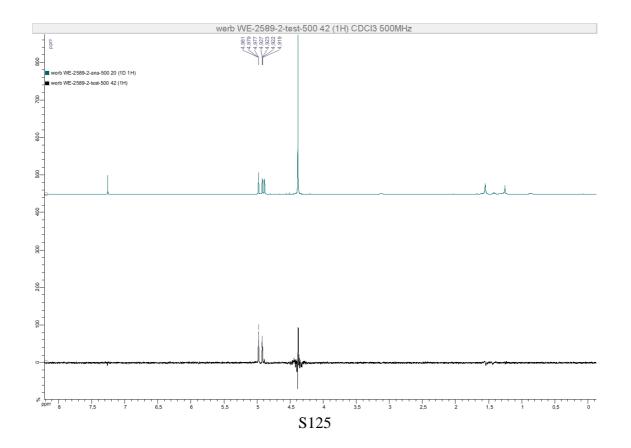


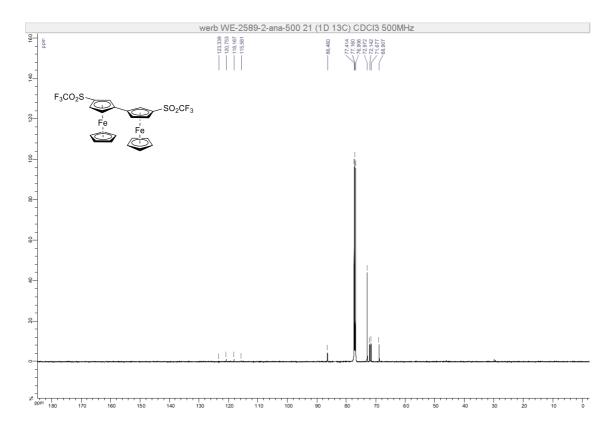
(*R*_P,*S*_P)-1,1'-Biferrocene-3,3'-bis(triflone) (*meso*-5l)

¹H NMR (500 MHz, CDCl₃)

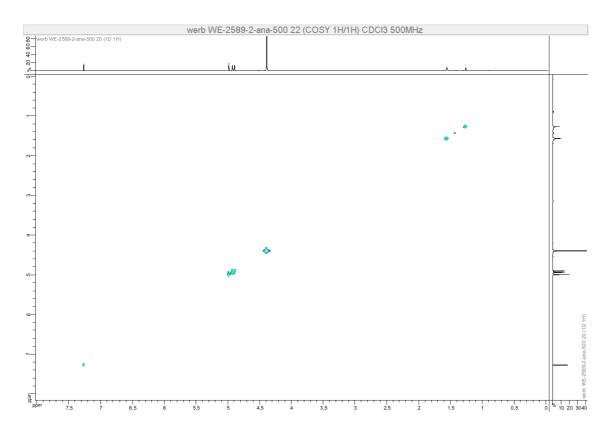


HOESY (500 MHz, CDCl₃) Irradiation at -79.1 ppm – Superposition of ¹H (top) and HOESY (bottom) spectra.

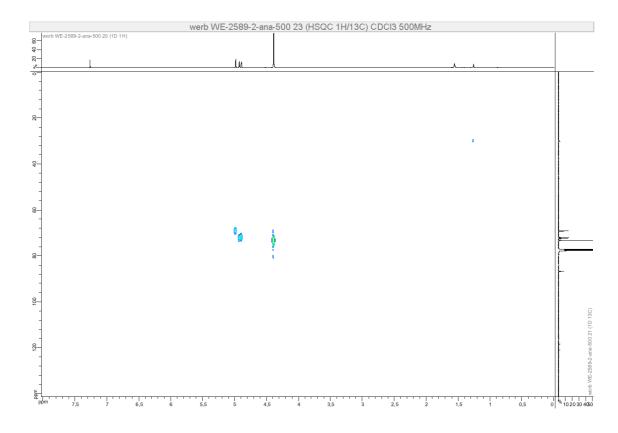




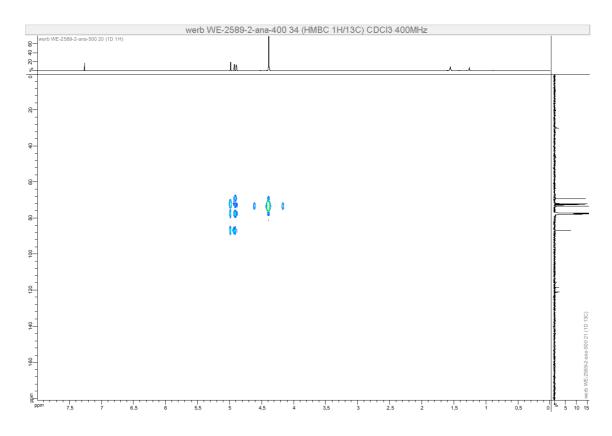
COSY (500 MHz, CDCl₃)



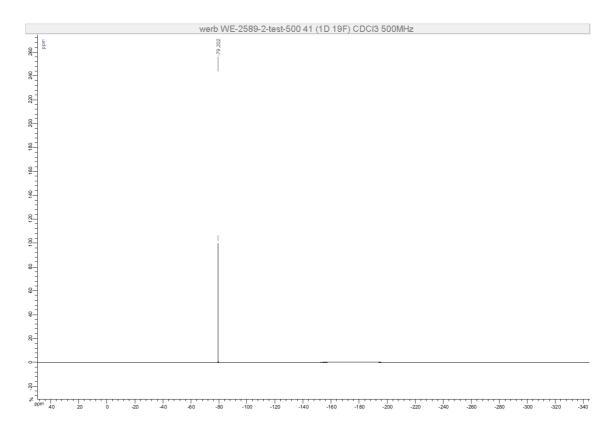
HSQC (500 MHz, CDCl₃)



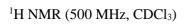
HMBC (400 MHz, CDCl₃)

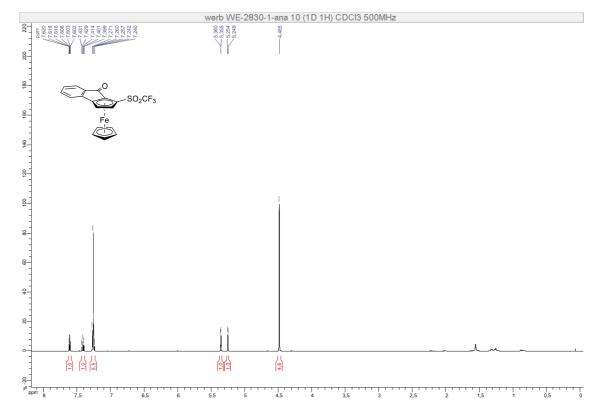


¹⁹F NMR (470 MHz, CDCl₃)

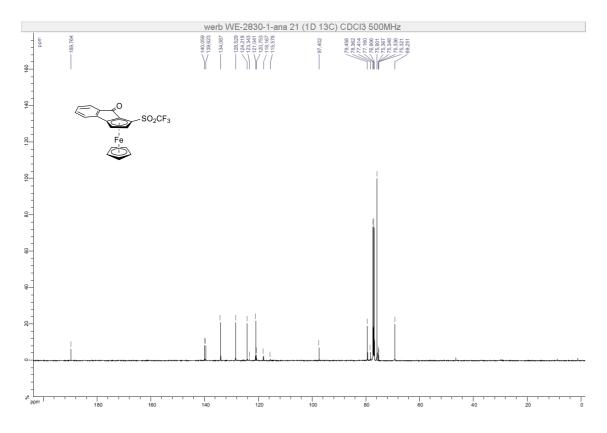


The ferrocenic analogue of fluorenone S_P-10



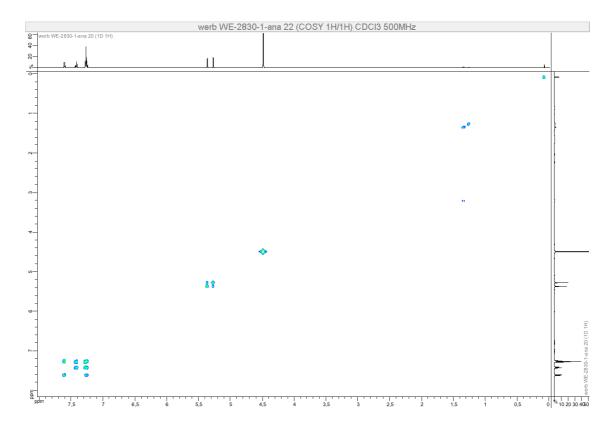


¹³C NMR (126 MHz, CDCl₃)

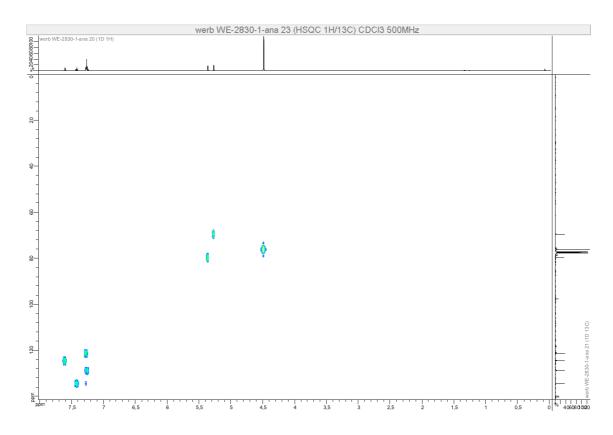


S129

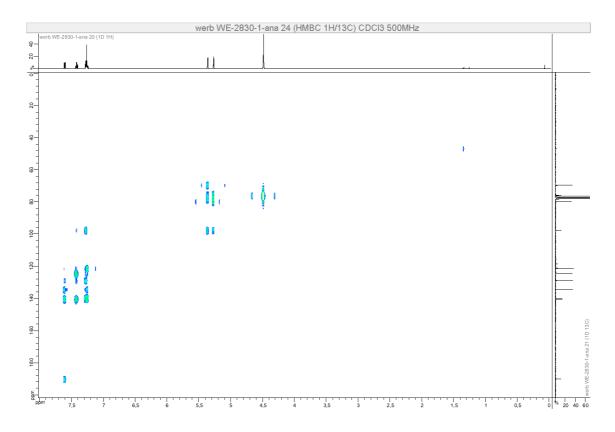
COSY (500 MHz, CDCl₃)



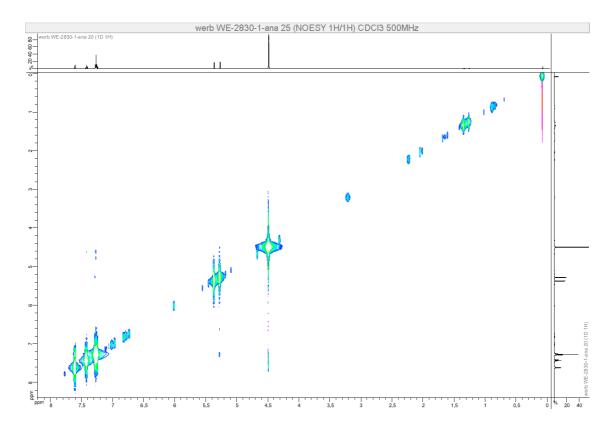
HSQC (500 MHz, CDCl₃)



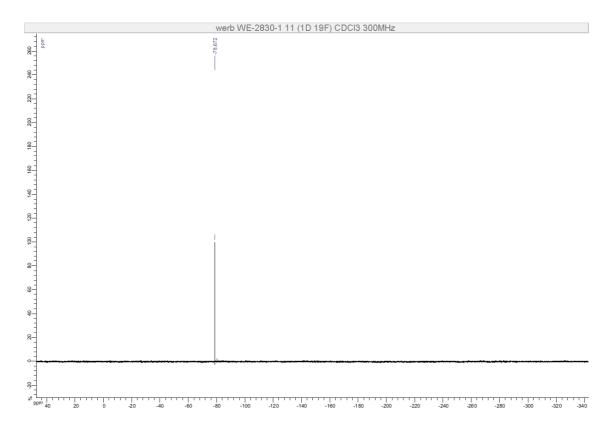
HMBC (500 MHz, CDCl₃)



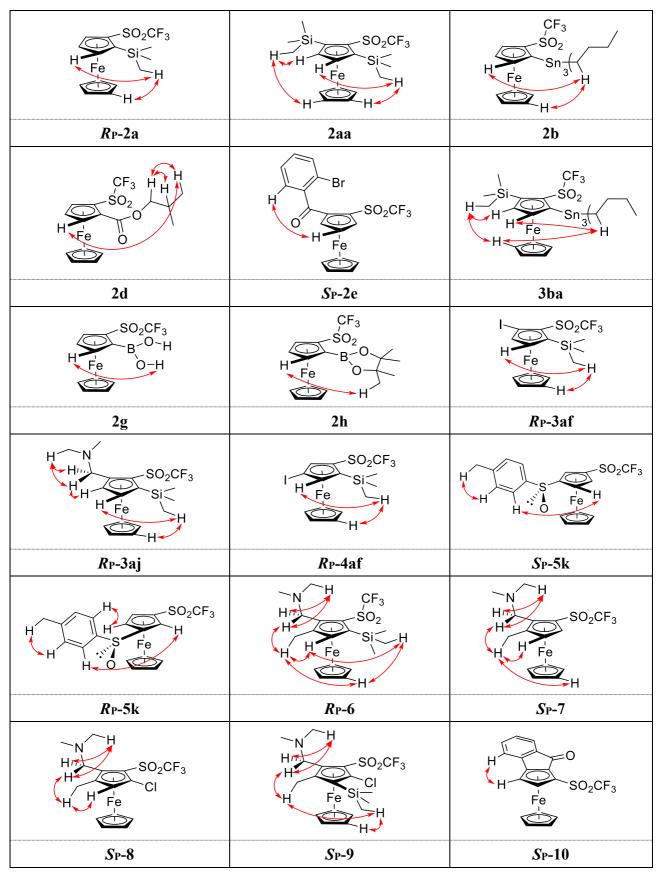
NOESY (500 MHz, CDCl₃)



¹⁹F NMR (282 MHz, CDCl₃)



E) Selected NMR NOESY correlations



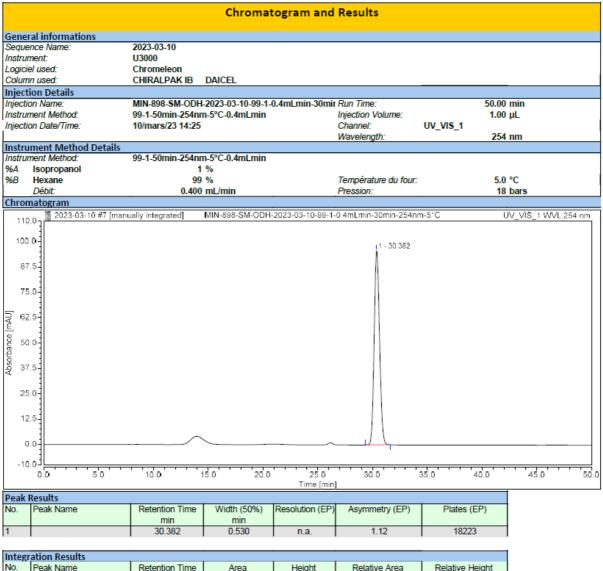
F) Selected NMR HOESY correlations

Fe H Fe	H F F Si SO ₂ H Fe	F H SO ₂ H Si Fe
1	2 aa	<i>R</i> _P -2a
F F F F F H S N H H H	F F H H H SO ₂ Fe O	F H F F F F F F F F F
2b	2d	2f
H F F F H SO_{2} SO_{3} H H H H	F H SO ₂ B(OH) ₂	H SO ₂ H SO ₂ Fe O O
3ba	2g	2h
H H F H F E F F K ⁺ K ⁺		H H H H H H H H H H H H H H H H H H H
2i	R _P -3af	<i>R</i> _Р -Зај
F H SO ₂ H Si Fe	F H F e H F e	<i>p</i> -Tol SO ₂ <i>h</i> Fe <i>b</i> Fe
R _P -4af	Rp-5f	Sp-5k

<i>p</i> -Tol S Fe O Fe	H F F F F F F F F F F F F F F F F F F F	H H H H H H H H H H H H H H H H H H H
<i>R</i> P-5k	<i>R</i> P-6	Sp-7
H H SO ₂ H CI Fe	H H H Me ₃ Si Fe	F F F F F F F F F F F F F F F F F F F
S _P -8	S _P -9	S _P ,S _P -51
F F F F F F F F F F F F F F F F F F F		
meso-51		

G) HPLC Data

Ferrocenetriflone (1)



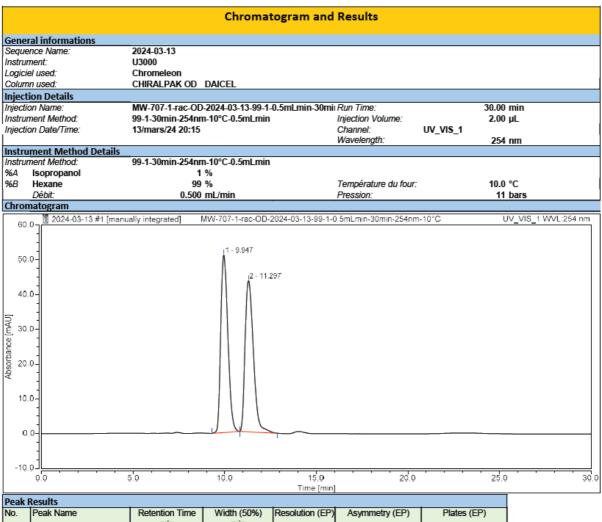
	ation results					
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		30.382	54.379	95.797	100.00	100.00
Total:			54.379	95.797	100.00	100.00

Ferrocenetriflone (1)

		Chroma	togram and	Results			
eneral information	IS						
Sequence Name:	2023-07-03						
nstrument:	U3000						
ogiciel used:	Chromeleon						
Column used:	CHIRALPAK IB-	3 DAICEL					
njection Details							
njection Name:		023-07-03-99-1-0.4				.00 min	
nstrument Method:		m-10°C-0.5mLmin	1	Injection Volume:		.00 µL	
njection Date/Time:	14/août/23 22:39			Channel: Wavelength:	UV_VIS_1	Ed non	
nstrument Method	Details			wavelengul.	2	254 nm	
nstrument Method:		m-10°C-0.5mLmin	1				
%A Isopropanol		1 %					
%B Hexane	9	9%		Température du four	: 1	0.0 °C	
Débit:	0.40	0 mL/min		Pression:		12 bars	
Chromatogram							
110.0	3 #19 [manually integrated]	WE-2559-2-OD-2	023-07-03-99-1-0	4mLmin-30min-254nm	-10°C	UV_VIS_1 WVL	:254 nr
10.0							
100.0				25.667			
1			Υ.	25.007			
87.5			Λ.				
1							
75.0							
_ 1							
2 62.5			11				
<u>e</u> ,]							
₿ 50.0-			11				
			11				
00 62.5 62.5 80 50.0 80 50.0 80 50.0 80 37.5							
2 37.5			1				
]							
25.0							
1							
12.5				1			
31			1	1			
0.0							
1				I			
-10.0	 						
0.0	5.0 10.0	15.0 20.0		30.0	35.0 40.0	45.0	5
			Time (mir]			
eak Results							
No. Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)		
	min	min					
1	25.667	1.096	n.a.	1.35	3039		
				-			
ntegration Results					_		
Deek Neme	Detention Time	Area	Lieisht	Deletive Area	Deletive Lleight		

Integra	ation Results					
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		25.667	111.160	95.843	100.00	100.00
Total:			111.160	95.843	100.00	100.00

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



No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)
		min	min			
1		9.947	0.427	1.74	1.31	3013
2		11.297	0.489	n.a.	1.38	2956

Integr	ation Results					
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		9.947	23.046	51.098	50.15	53.99
2		11.297	22.905	43.553	49.85	46.01
Total:			45.950	94.651	100.00	100.00

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

			Chroma	togram and	Results			
Gener	ral informations							
	nce Name:	2023-07-03						
nstrur		U3000						
.ogicie	el used:	Chromeleon						
Colum	n used:	CHIRALPAK IB-3	DAICEL					
nject	ion Details							
njectio	on Name:	RAC-MW-707-IB-2	023-07-03-99-1-0				30.00 min	
nstrur	nent Method:	99-1-30min-254nn	n-10°C-0.5mLmin		Injection Volume:		1.00 µL	
njectio	on Date/Time:	03/juil./23 20:45			Channel:	UV_VIS_1		
					Wavelength:		254 nm	
	ment Method Deta							
	nent Method:	99-1-30min-254nn						
6A	Isopropanol		%					
6B	Hexane	99			Température du four:		10.0 °C	
	Débit:	0.500	mL/min		Pression:		38 bars	
hron	natogram							
500	2023-07-03 #10		RAC-MW-707-IB-2	023-07-03-99-1-0.5	imLmin-30min-254nm-	10°C	UV_VIS_1	WVL:254 nn
400 [041] 200 200 100 0								
-50	.] <u>.</u>	5.0	10.0	15.0	20.0		25.0	
	¥+¥	¥1¥	1.11	Time [min]	20.0		11 V 1 V	Q.
Peak	Results							
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (E	P)	
		min	min	(LI)			· ·	
		10.913		2.78	1.43	20250		
1		10.913	0.181	2.78	1.45	202:30		

Integr	ation Results					
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		10.913	93.882	451.226	50.90	51.45
2		11.785	90.577	425.777	49.10	48.55
Total:			184.459	877.004	100.00	100.00

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

			Chromat	ogram and	Results			
Gener	al informations							
Seque	nce Name:	2024-06-03_2						
Instrun	nent:	U3000						
Logicie	el used:	Chromeleon						
Colum	n used:	CHIRALCEL IB3	DAICEL					
Iniecti	ion Details							
	on Name:	WE-2897-1-IB-2024	-06-06-99-1-40mir	n-5°C-254nm-0.5	Run Time:	3	0.00 min	
	nent Method:	99-1-30min-10°C-25			Injection Volume:		1.00 µL	
	on Date/Time:	04/juin/24 22:47			Channel:	UV_VIS_1		
1		•			Wavelength:	0.7.007.	254 nm	
Instru	ment Method Details				Tratolongan.		2011	
	nent Method:	99-1-30min-10°C-25	54nm-0.5mLmin					
%A	Isopropanol	1	%					
%B	Hexane	99			Température du four:		10.0 °C	
1	Débit:		mL/min		Pression:		38 bars	
Chron	natogram						00 5410	
	間 2024-06-03 2 #11 Ima	nually integrated	WE-2897-1-IB-202	24-06-06-99-1-40m	nin-5°C-254nm-0,5mLm	in	UV_VIS_1 WVL:254 nm	٦
400]]	nually integrated	VIE-2001-1-10-202		into 0-204mino,omen		00_010_10000.2041111	
	3							
350	-							
350	7							
	1							
300	퀴							
	1							
	1							
250	1		1 - 11.31	3				
5	1		1 1 1 2	~				
È 200	1		2 - 11	787				
Absorbance [mAU] 120	1							
aŭ	1							
문 150	-							
sq	1							
100	1							
100	1							
	1		- H H					
50	킈		11 11					
	1		N N					
	1		.///					
0	1							
	1							
-50	J							
	0.0 5	0	10.0	15.0	20.0		25.0 30	0.0
				Time [min]				
Peak I	Results							
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)		
		min	min	()	(<u> </u>			
1		11.313	0,100	2.52	0.80	71555		
2		11.787	0.122	n.a.	1.12	51747		

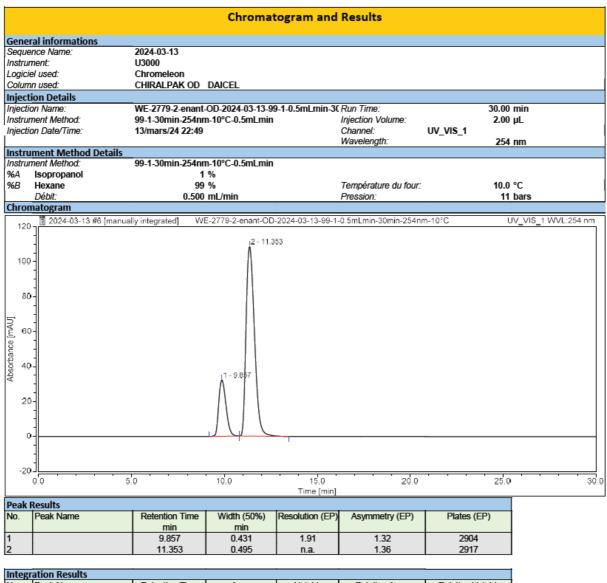
Integr	ation Results					
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		11.313	27.081	228.045	51.79	54.43
2		11.787	25.214	190.901	48.21	45.57
Total:			52.294	418.946	100.00	100.00

Deprotonation of 1 using BuLi·(+)-sparteine (1:1) in Et₂O at –80 $^\circ C$ and Me₃SiCl as the electrophile

120 100 100 100 100 100 100 100	min-3(Run Time: 30.00 min Injection Volume: 2.00 µL Channel: UV_VIS_1 Wavelength: 254 nm Température du four: 10.0 °C Pression: 12 bars 18-99-1-0.5mLmin-30min-254nm-10°C UV_VIS_1 WVL:254 nm
Sequence Name: 2024-03-18 Instrument: U3000 Logiciel used: Chromeleon Column used: CHIRALPAK OD DAICEL Injection Details Injection Data Injection Name: WE-2788-2-enant-OD-2024-03-18-99-1-0.5m Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin Infection Date/Time: 18/mars/24 22:39	Injection Volume: 2.00 µL Channel: UV_VIS_1 Wavelength: 254 nm Température du four: 10.0 °C Pression: 12 bars
Logiciel used: Chromeleon Column used: CHIRALPAK OD DAICEL Injection Datails Injection Name: WE-2788-2-enant-OD-2024-03-18-99-1-0.5m Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin 18/mars/24 22:39 Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin %A Isopropanol 1 % B Hexane 99 % Débit: 0.500 mL/min Chromatogram 120 100 100 100 100 100 100 100	Injection Volume: 2.00 µL Channel: UV_VIS_1 Wavelength: 254 nm Température du four: 10.0 °C Pression: 12 bars
Column used: CHIRALPAK OD DAICEL njection Details njection Name: WE-2788-2-enant-OD-2024-03-18-99-1-0.5m nstrument Method: 99-1-30min-254nm-10°C-0.5mLmin njection Date/Time: 18/mars/24 22:39 nstrument Method: 99-1-30min-254nm-10°C-0.5mLmin 64 Isopropanol 1 % 68 Hexane 99 % Débit: 0.500 mL/min hromatogram 120 2024-03-18 #4 [manually integrated] WE-2788-2-enant-OD-2024-03- 100 40 20 40 20 40 20 40 40 20 40 4	Injection Volume: 2.00 µL Channel: UV_VIS_1 Wavelength: 254 nm Température du four: 10.0 °C Pression: 12 bars
njection Details njection Name: WE-2788-2-enant-OD-2024-03-18-99-1-0.5m nstrument Method: 99-1-30min-254nm-10°C-0.5mLmin nstrument Method: 99-1-30min-254nm-10°C-0.5mLmin 64 Isopropanol 1 % 68 Hexane 99 % Débit: 0.500 mL/min hromatogram 120 100 60 60 60 -20 0 -20 0 -20 -20 -20 -20 -	Injection Volume: 2.00 µL Channel: UV_VIS_1 Wavelength: 254 nm Température du four: 10.0 °C Pression: 12 bars
Discriment WE-2788-2-enant-OD-2024-03-18-99-1-0.5m Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin Injection Date/Time: 18/mars/24 22:39 Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin Image: Strument Method: 99-1-30min-254nm-10°C-0.5mLmin Image: Strument Method: 99-1-30min-254nm-10°C-0.5mLmin Image: Strument 1 % 99 % Débit: 0.500 mL/min 0.500 mL/min Image: Strument Method: 99 % 0.500 mL/min Image: Strument Method: 99 % 0.500 mL/min Image: Strument Method: 92-2788-2-enant-OD-2024-03- 0.500 mL/min Image: Strument Method: 92-11.382 0.500 mL/min Image: Strument Method: 92-11.300	Injection Volume: 2.00 µL Channel: UV_VIS_1 Wavelength: 254 nm Température du four: 10.0 °C Pression: 12 bars
Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin njection Date/Time: 18/mars/24 22:39 Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin 64 Isopropanol 1 % 68 Hexane 99 % Débit: 0.500 mL/min Inormatogram 120 100 1 60 60 60 60 60 1 60 9 100 1 100 1 100 1 60 1 60 1 60 1 60 1 90 1 91 1 92 1 93 1 94 1 95 1 96 1 97 1 98 1 99 1 90 1 90 1 90 1 90 1 90 1	Injection Volume: 2.00 µL Channel: UV_VIS_1 Wavelength: 254 nm Température du four: 10.0 °C Pression: 12 bars
njection Date/Time: 18/mars/24 22:39 nstrument Method Details nstrument Method: 99-1-30min-254nm-10°C-0.5mLmin 64 Isopropanol 1 % 68 Hexane 99 % Débit: 0.500 mL/min hromatogram 120 120 120 120 120 120 120 120 120 12	Channel: UV_VIS_1 Wavelength: 254 nm Température du four: 10.0 °C Pression: 12 bars
Instrument Method Details Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin 64 Isopropanol 1 % 64 Hexane 99 % Débit: 0.500 mL/min Chromatogram WE-2788-2-enant-OD-2024-03- 120 2024-03-18 #4 [manually integrated] WE-2788-2-enant-OD-2024-03- 100 100 1-9.77 60 0 1-9.77 00 0 0 00 0 0 01 0 0 02 0 0 03 0 0 04 0 0 04 0 0 04 0 0 04 0 0 04 0 0 04 0 0 04 0 0 04 0 0 04 0 0 04 0 0 05 0 0 04 0 0 04 0	Wavelength: 254 nm Température du four: 10.0 °C Pression: 12 bars
nstrument Method: 99-1-30min-254nm-10°C-0.5mLmin 64 Isopropanol 1 % 68 Hexane 99 % Débit: 0.500 mL/min thromatogram 120 100 60 60 60 -20 -20	Température du four: 10.0 °C Pression: 12 bars
nstrument Method: 99-1-30min-254nm-10°C-0.5mLmin 6A Isopropanol 1 % 6B Hexane 99 % Débit: 0.500 mL/min hromatogram 120 100 - 100 - 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0 - 0 -	Pression: 12 bars
64 Isopropanol 1 % 68 Hexane 99 % Débit: 0.500 mL/min hromatogram 120 100 1 80 - 60 - 60 - 0 - 20 - 0 - 20 - 0 - - - 0 - - - 0 - - - 0 - - - 0 - - - 0 - 0 - 0 - - - 0 - - - - - - - - - - - - - - - - - - - - <td< td=""><td>Pression: 12 bars</td></td<>	Pression: 12 bars
6B Hexane 99 % Débit: 0.500 mL/min hromatogram 120 100 60 60 20 40 20 0 20	Pression: 12 bars
Image: Second	
120 2024-03-18 #4 [manually integrated] WE-2788-2-enant-OD-2024-03- 100	18-99-1-0.5mLmin-30min-254nm-10°C UV_VIS_1 WVL:254 nm
	18-99-1-0.5mLmin-30min-254nm-10°C UV_VIS_1 WVL:254 nm
-20	
Peak Results	
No. Peak Name Retention Time Width (50%) Resoluti min min min	15.0 20.0 25.0 30 e (min)
9.777 0.427 2.0 11.382 0.494 n.	on (EP) Asymmetry (EP) Plates (EP)

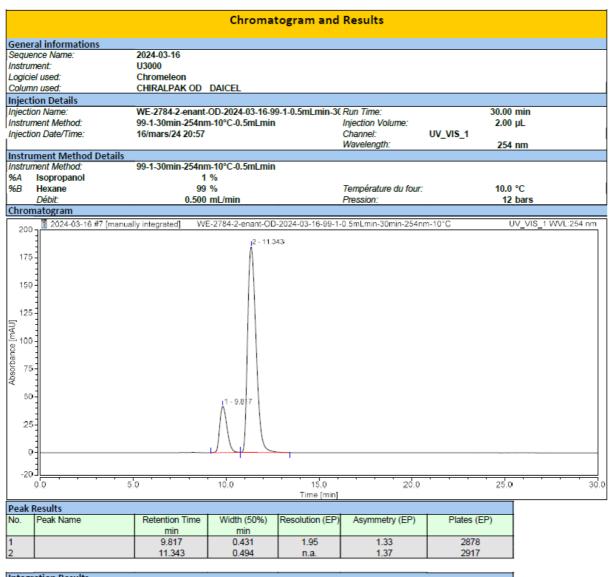
Integration Results							
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	
		min	mAU*min	mAU	%	%	
1		9.777	34.097	74.632	37.06	40.49	
2		11.382	57.908	109.691	62.94	59.51	
Total:			92.005	184.323	100.00	100.00	

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



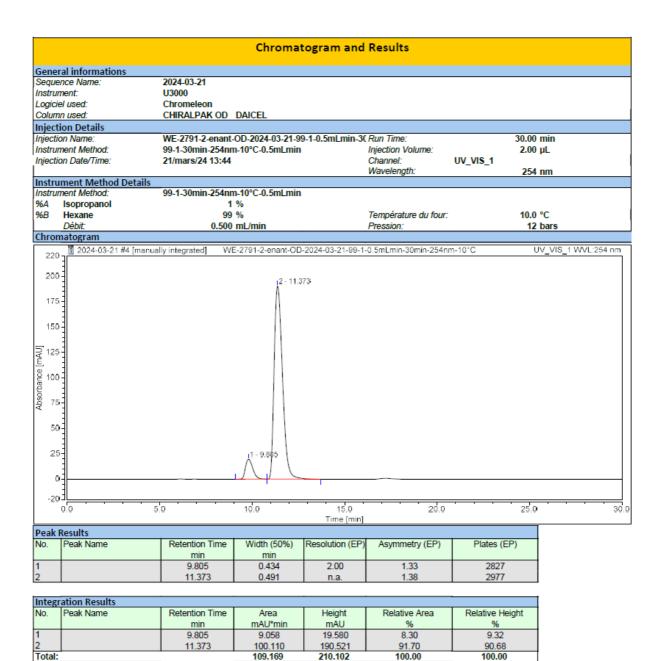
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		9.857	14.718	32.226	20.46	22.89
2		11.353	57.218	108.583	79.54	77.11
Total:		71.936	140.809	100.00	100.00	

Deprotonation of 1 using sBuLi·(+)-sparteine (1:1) in TBME at –80 $^{\circ}$ C and Me₃SiCl as the electrophile

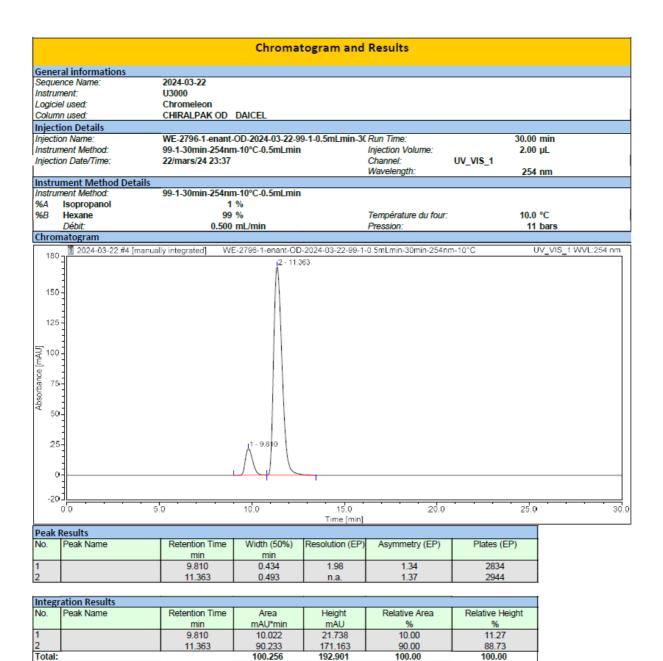


Integration Results						
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		9.817	19.005	41.484	16.28	18.32
2		11.343	97.709	184.912	83.72	81.68
Total:			116.714	226.396	100.00	100.00

Deprotonation of 1 using *s*BuLi·(+)-sparteine (1:1) in TBME at –100 °C and Me₃SiCl as the electrophile



Deprotonation of 1 using *s*BuLi·(+)-sparteine (1:0.4) in TBME at –100 °C and Me₃SiCl as the electrophile



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

			Chromat	togram and	Results			
ner	al informations							
	nce Name:	2024-04-06						
	nent:	U3000						
	el used:	Chromeleon						
	n used:	CHIRALPAK OD	H DAICEL					
	ion Details							
	on Name:	MW-906-rac-OD	H-2024-04-06-99-1-	0.4mLmin-30mir	Run Time:		30.00 min	
strun	nent Method:	99-1-30min-254r	nm-5°C-0.4mLmin		Injection Volume:		1.00 µL	
ectic	on Date/Time:	06/avr./24 18:54			Channel:	UV_VIS_1		
					Wavelength:		254 nm	
	ment Method Deta							
	nent Method:		m-5°C-0.4mLmin					
4	Isopropanol		1 %					
3	Hexane	-	9%		Température du four:		5.0 °C	
	Débit:	0.40	0_mL/min		Pression:	,	17 bars	
rom	natogram							
500	🛛 🛛 2024-04-06 #3 [m	nanually integrated]	MW-906-rac-ODH-2	2024-04-06-99-1-0	.4mLmin-30min-254nm	-5°C	UV_VIS_1	WVL:254 n
300 200 100	- - - - -							
-50	-							
	0.0	5.0	10.0	15.0 Time [min]	20.0		25.0	
ak F	Results							
	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (FP)	
).	reakiname	min	min					

	min	min			
1	9.095	0.142	2.65	1.12	22842
2	9.770	0.159	n.a.	1.12	20895

Integr	Integration Results										
No.	Peak Name Retention Time		Area	Height	Relative Area	Relative Height					
		min	mAU*min	mAU	%	%					
1		9.095	68.795	438.017	49.85	52.47					
2		9.770	69.211	396.766	50.15	47.53					
Total:			138.006	834.784	100.00	100.00					

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

			Chroma	togram and	Results		
Gener	al informations						
	nce Name:	2024-04-06					
Instrum		U3000					
	el used:	Chromeleon					
	n used:	CHIRALPAK ODH	DAICEL				_
	on Details						
	on Name:	WE-2826-1enant-		99-1-0.4mLmin-3		30.00	
	nent Method:	99-1-30min-254nn 06/avr./24 19:25	n-5°C-0.4mLmin		Injection Volume: Channel:	1.00	μL
Injecuo	on Date/Time:	00/avr./24 19:25			Wavelength:	UV_VIS_1	l nm
Instru	ment Method Details				wavelengin.	234	• 1011
	nent Method:	99-1-30min-254nn	n-5°C-0.4mLmin				
%A	Isopropanol	1	%				
%В	Hexane	99			Température du four:	5.0	0°C
	Débit:	0.400	mL/min		Pression:	18	bars
Chron	natogram						
800	2024-04-06 #4 [manua	ally integrated] W	E-2826-1enant-OD	H-2024-04-06-99-	1-0.4mLmin-30min-254	nm-5°C I	UV_VIS_1 WVL:254 nm
			2 - 9.748				
700	L.						
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5	1						
Ê 400	1						
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[NW 400 400 Absorbance 300	4		11				
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200	게						
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100	거		1 9,082				
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	, 1		MA L				
	1		1.1				
-100							
-100	0.0 5	0	10.0	15.0	20.0	25.0	0 30.0
				Time [min]			
Peak I	Results						
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)]
		min	min				1
1		9.082	0.141	2.63	1.30	22990	
2		9.748	0.158	n.a.	1.13	21067	1

Integr	ntegration Results										
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height					
		min	mAU*min	mAU	%	%					
1		9.082	12.878	80.645	9.19	9.81					
2		9.748	127.308	741.681	90.81	90.19					
Total:			140.186	822.326	100.00	100.00					

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

			Chromat	togram and	Results		
Gener	al informations						
	nce Name:	2024-05-16_3					
nstrun		U3000					
	l used:	Chromeleon					
	n used:	CHIRALPAK IC3	DAICEL				
njecti	on Details						
	on Name:		024-05-16-99-1-0.5	mLmin-30min-2	Run Time:) min
	nent Method:		m-5°C-0.5mLmin		Injection Volume:		θμL
njectio	on Date/Time:	17/mai/24 00:15			Channel:	UV_VIS_1	
	ment Method Detail	-			Wavelength:	254	4 nm
	ment Method:	99-1-30min-254n	m 5°C 0 5ml min				
	Isopropanol		1 %				
	Hexane		9%		Température du four:	51	0°C
00	Débit:) mL/min		Pression:		2 bars
hron	natogram	,					
	简 2024-05-16 3 #4 In	nanually integrated	WE-2823-3-IC3-2	024-05-16-99-1-0.5	5mLmin-30min-254nm-5	5°C	UV_VIS_1 WVL:254 nm
140]						
	-1						
120	1				1 - 17.377		
	-1				1-17.371		
	1				2 - 19.3	65	
100	1						
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- 80	1						
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3	-1						
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	0.0	5.0	10.0	15.0 Time (min)	20.0	25.	0 3
la F				Time [min]			1
eak	Results						
10.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	

INC	J.	reak Name	Retenuori nine	vviduri (50%)	Resolution (EP)	Asymmetry (EF)	Fiales (EF)
			min	min			
1			17.377	0.279	3.94	1.22	21547
2			19.365	0.316	n.a.	1.23	20743

Integr	Integration Results										
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height					
		min	mAU*min	mAU	%	%					
1		17.377	34.934	115.033	50.03	53.17					
2		19.365	34.894	101.308	49.97	46.83					
Total:			69.828	216.341	100.00	100.00					

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

			Chroma	togram and	Results		
Gener	ral informations						
Seque	nce Name:	2024-05-16_3					
Instrur	ment:	U3000					
	el used:	Chromeleon					
Colum	n used:	CHIRALPAK IC3	DAICEL				
	ion Details	_					
	on Name:	WE-2832-2-IC3-20	24-05-16-99-1-0.5	5mLmin-30min-2	Run Time:	30.00	
	ment Method:	99-1-30min-254nn	n-5°C-0.5mLmin		Injection Volume:	1.00	μL
Injectio	on Date/Time:	16/mai/24 23:44			Channel:	UV_VIS_1	
					Wavelength:	254	nm
	ment Method Details						
	ment Method:	99-1-30min-254nn					
%A	Isopropanol		%		To and the second second		
<u>%</u> В	Hexane	99			Température du four:		°C
Charan	Débit:	0.500	mL/min		Pression:	42	bars
Chron	natogram		M/E 0000 0 100 0	004.05.40.00.4.01	Factoria Officia Officia I	10	
160	2024-05-16_3 #3 [mar	ually integrated	WE-2832-2-IC3-2	024-05-16-99-1-0.	5mLmin-30min-254nm-	רַכָּ נ	JV_VIS_1 WVL:254 nm
	1						
140					1 - 17.392		
140	7				11.002		
	1						
120					1		
	-						
100	1						
	1						
AL	-						
Absorbance [mAU] 00 00	·1						
ano	1						
Ë 60					11		
psq	1						
40							
40	1						
					11		
20	-				2 - 19.4	35	
	1						
0	1			~			
	-				1 1		
	-						
-20		0	10.0	15.0	20.0		30.0
	0.0 5	.0	10.0	15.0 Time [min]	20.0	25.0	30.0
Deals I	Results			rine (init)			t
No.	Peak Name	Retention Time	Width (50%)	Decolution (CD)	Acummote (ED)	Plates (EP)	
NO.	reakiname			Resolution (EP)	Asymmetry (EP)	Plates (EP)	
1		min 17.392	min 0.283	4.04	1.24	20995	
2		19.435	0.315	4.04 n.a.	1.24	20995	

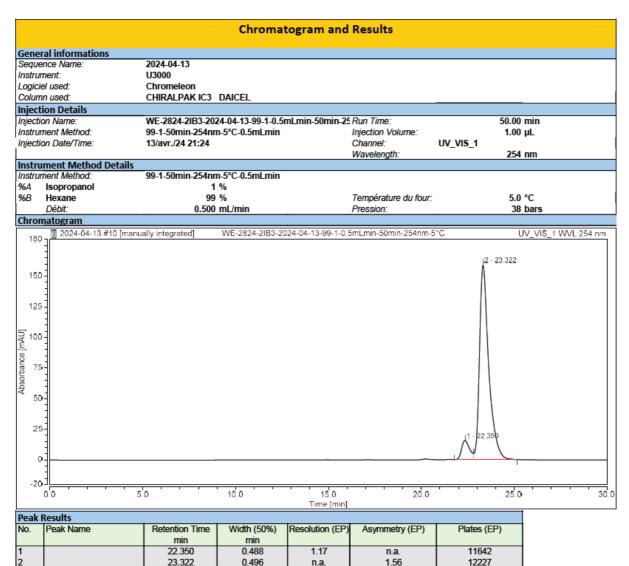
Integr	Integration Results										
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height					
		min	mAU*min	mAU	%	%					
1		17.392	42.383	137.856	89.34	90.27					
2		19.435	5.057	14.854	10.66	9.73					
Total:			47.441	152.710	100.00	100.00					

$(\pm) - 2 - (Isobutoxycarbonyl) ferrocenetriflone~(rac - 2d)$

			Chromat	togram and	Results		
Gen	eral informations						
	uence Name:	2024-04-13					
	rument:	U3000					
-	iciel used:	Chromeleon					
	imn used:	CHIRALPAK IC3	DAICEL				_
	ction Details						
	ction Name:	MW-709-IB3-2024		Lmin-50min-254			0 min
	rument Method:	99-1-50min-254nn 13/avr./24 20:33	0min-254nm-5°C-0.5mLmin Injection Volume: /24.20:33 Channel:) µL
Injec	ction Date/Time:	15/avr./24 20:55	4 20:33 Channel: Wavelength:			UV_VIS_1	4 nm
Inst	rument Method Details				wavelengul.	2.34	+ 1011
	rument Method:	99-1-50min-254nn					
%A	Isopropanol	1	%				
<u>%</u> B	Hexane	99	%		Température du four:	5.0	0 °C
	Débit:	0.500	mL/min		Pression:	2	5 bars
Chro	omatogram						
10	00.0 📊 2024-04-13 #9 [man]	ually integrated]	MW-709-IB3-20	024-04-13-99-1-0.5	5mLmin-50min-254nm-5	°Ç	UV_VIS_1 WVL:254 nm
Absorbance [mAU]	87.5 75.0 62.5 50.0 37.5 25.0 12.5					1 - 2129302.827	
	0.0	5.0	10.0	15.0 Time (min)	20.0	25.	0 30.0
	k Results						
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	
		min	min				4
1		21.830	0.479	1.20	n.a.	11498	
2		22.827	0.502	n.a.	n.a.	11451	

Integr	Integration Results											
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height						
		min	mAU*min	mAU	%	%						
1		21.830	46.962	89.042	47.34	50.01						
2		22.827	52.242	89.018	52.66	49.99						
Total:			99.204	178.059	100.00	100.00						

Deprotonation of 1 with sBuLi·(+)-sparteine using ClCO2iBu as the electrophile



Integr	ation Results					
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		22.350	7.844	15.711	7.84	8.99
2		23.322	92.162	159.047	92.16	91.01

174.758

100.00

100.00

100.006

Total:

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

			Chromat	ogram and I	Results			
Gene	ral informations							
	ence Name:	2024-04-11						
nstru	ment:	U3000						
.ogici	el used:	Chromeleon						
Colun	nn used:	CHIRALPAK IC3	DAICEL					
	tion Details							
	ion Name:	WE-2827-1-IB3-202					30.00 min	
	ment Method:	80-20-30min-254n	n-25°C		njection Volume:		2.00 µL	
njecti	ion Date/Time:	11/avr./24 10:28			Channel:	UV_VIS_1		
	<u> </u>				Wavelength:		254 nm	
	iment Method De		0500					
	ment Method:	80-20-30min-254ni						
%A	Isopropanol	20			To any factory at a f		25.0.00	
6В	Hexane	80			Température du four.		25.0 °C	
st	Débit:	1.000	mL/min	/	Pression:		80 bars	
nror	natogram		MIE 0007 4 15 2 22		1 1 00 1 051	0.500		
70	יר 0.0 🔞 2024-04-11	[manually integrated]	WE-2827-1-IB3-20	024-04-11-80-20-1r	mLmin-30min-254nm-	25°C	UV_VIS_1	WVL:254 nr
	1							
			1 - 9.515					
60	.0-		1					
]							
			1					
50	.0-		11	2	- 15.832			
	-		0	<u></u>	- 10.002			
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-10			· · · · · ·					
	0.0	5.0	10.0	15.0	20.0		25.0	3
				Time [min]				
Peak	Results							
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (I	EP)	
		min	min					
1		9.515	0.298	10.01	1.87	5653		

Integration Results										
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		9.515	22.931	62.719	50.00	58.09				
2		15.832	22.935	45.244	50.00	41.91				
Total:			45.866	107.963	100.00	100.00				

Deprotonation of 1 with $sBuLi \cdot (+)$ -sparteine using 2-BrC₆H₄C(O)Cl as the electrophile

			Chroma	togram and	Results			
Conc	ral informations							
	ence Name:	2024-04-11						
		2024-04-11 U3000						
	ment:	Chromeleon						
	iel used:							
	nn used:	CHIRALPAK IC3	DAICEL					
	tion Details				<u> </u>			
	ion Name:	WE-2835-1-IB3-202		mLmin-30min-25			30.00 min	
	ment Method:	80-20-30min-254nn	n-25°C		Injection Volume:		2.00 µL	
njecti	ion Date/Time:	11/avr./24 23:42			Channel:	UV_VIS_1		
					Wavelength:		254 nm	
	ument Method Det		- 2590					
	ment Method:	80-20-30min-254nn						
%A	Isopropanol	20 9			Town for the state of		25.0.00	
%В	Hexane	80 9			Température du four:		25.0 °C	
-1	Débit:	1.000 1	mL/min		Pression:		78 bars	
hroi	matogram							
140	2024-04-11 #26	[manually integrated]	NE-2835-1-IB3-2	024-04-11-80-20-1	mLmin-30min-254nm-2	25°Ç	UV_VIS_1 V	WL:254 nm
	´-							
	1		1 - 9.982					
120	p-1		1					
	-		Α					
	1							
100	거							
	1		11					
	-		11					
<u>⊇</u> 80	1		11					
<u></u>								
8 60	<u>, 1</u>		11					
5 0	2							
Apsonance (mAu)	-							
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	0.0	5.0	10.0	15.0	20.0		25.0	3
				Time [min]				
Peak	Results							
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (E	P)	
		min	min					
1		9.982	0.308	10.79	1.87	5812		

Integr	Integration Results										
No.	Peak Name	eak Name Retention Time		Height	Relative Area	Relative Height					
		min	mAU*min	mAU	%	%					
1		9.982	46.929	123.949	91.35	93.22					
2		16.683	4.443	9.020	8.65	6.78					
Total:			51.372	132.969	100.00	100.00					

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

			Chromat	togram and	Posulte		
			Chroma	logram and	Results		
	ral informations						
	ence Name:	2024-04-13					
Instru		U3000					
	el used:	Chromeleon					
	nn used:	CHIRALPAK IC3	DAICEL				
	ion Details						
	on Name:	WE-2835-4-IB3-20				30.00	
	ment Method:	80-20-30min-254n	m-25°C		Injection Volume:	2.00	μL
Injecti	on Date/Time:	13/avr./24 14:57			Channel:	UV_VIS_1	
Instra	ment Method Details				Wavelength:	254	nm
	ment Method:	80-20-30min-254n	m 25°C				
%A	Isopropanol	20					
%B	Hexane	80			Température du four:	25.0	۹C
100	Débit:		mL/min		Pression:		bars
Chro	natogram	11000			110001011.		buro
	間 2024-04-13 #2 [manus	ally integrated	WE-2835-4-IB3-20	24-04-13-80-20-1	mLmin-30min-254nm-2	5°C I	JV_VIS_1 WVL:254 nm
140						**	
	-		1 - 10.253				
120			10.200				
120	<u>'</u>]		Λ				
	1		1				
100	-1		11				
	1		11				
	1						
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dm)	-		- 11				
2 6	.1		11				
Dan 5	4		11				
Absorbance [mAU]							
Q 40	4						
	-						
	1						
20	-		1				
	1						
0	.1						
1	'l						
	-1						
-20	1						
	0.0 5	0	10.0	15.0	20.0	25.0	30.0
				Time [min]			
Peak	Results						
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	
		min	min				
1		10.253	0.310	n.a.	1.87	6042	

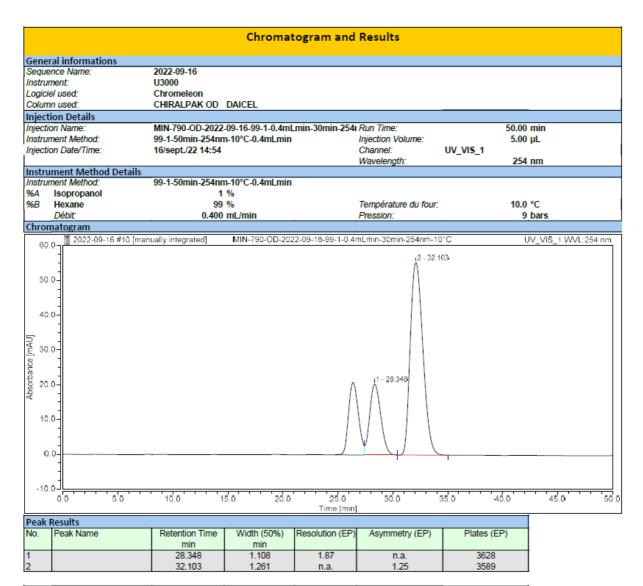
Integr	Integration Results										
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height					
		min	mAU*min	mĀU	%	%					
1		10.253	47.826	125.487	100.00	100.00					
Total:			47.826	125.487	100.00	100.00					

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

			Chroma	togram and	Results			
iene	eral informations							
equ	ence Name:	2022-09-16						
nstru	iment:	U3000						
ogic	iel used:	Chromeleon						
	nn used:	CHIRALPAK OD	DAICEL					
njec	tion Details							
nject	ion Name:	MIN-733-3-0D-202	22-09-16-99-1-0.4	_min-30min-254	Run Time:	50.0	0 min	
nstru	iment Method:	99-1-50min-254nn	n-10°C-0.4mLmin		Injection Volume:	5.0	0 µL	
nject	ion Date/Time:	16/sept./22 14:03			Channel:	UV_VIS_1		
					Wavelength:	25	4 nm	
	ument Method Detai							
	ment Method:	99-1-50min-254nn						
6A	Isopropanol		%					
6B	Hexane		%		Température du four:		0 °C	
	Débit:	0.400	mL/min		Pression:		9 bars	
hro	matogram							
).0 - 1 2022-09-16 #9 [m	nanually integrated]	MIN-733-3-OD-2	022-09-16-99-1-0	4Lmin-30min-254nm-1	0°C	UV_VIS_1 WVL:25	54 nr
40	0.0				12 - 32.	188		
	0.0							
	0.0 5.0	10.0 1	5.0 20.0	25.0 Time (min)	30.0	35.0 40.0	45.0	53
	Results					1	4	
lo.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)		
		28.398	1.092	1.91	1.28	3748	1	

Integr	Integration Results											
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height						
		min	mAU*min	mAU	%	%						
1		28.398	60.206	52.438	49.93	53.30						
2		32.188	60.380	45.937	50.07	46.70						
Total:			120.585	98.375	100.00	100.00						

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



Integr	Integration Results										
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height					
		min	mAU*min	mAU	%	%					
1		28.348	23.915	20.428	24.56	26.93					
2		32.103	73.472	55.430	75.44	73.07					
Total:			97.387	75.857	100.00	100.00					

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

	Chromatogram and Results										
			Chromat	togram and	Results						
Gener	ral informations										
	nce Name:	2023-08-16									
Instrur		U3000									
	el used:	Chromeleon									
	n used:	CHIRALPAK IB-3	DAICEL								
	ion Details			0.4	D	50.00					
	on Name: ment Method:	MW-828-2-ena-OE 99-1-30min-254nn				50.00 2.50					
	on Date/Time:	16/août/23 16:32	II-TU-C-0.5IIILIIIIII		Injection Volume: Channel:	UV_VIS_1	μc				
	un Daler nine.	10/000/25 10.52			Wavelength:		nm				
Instru	ment Method Details				Trat crongen.	2.54					
	ment Method:	99-1-30min-254nn	n-10°C-0.5mLmin								
%A	Isopropanol		%								
<u>%В</u>	Hexane	99			Température du four:	10.0					
	Débit:	0.400	mL/min		Pression:	9	bars				
Chron	natogram										
45.0	2023-08-16 #5 [manu	ally integrated] N	1W-828-2-ena-OD-	2023-08-16-99-1-0).4mLmin-50min-254nm	-10°C L	JV_VIS_1 WVL:254 nm				
	-				1 - 27.888						
40.0	-				Λ						
	-				11						
	-										
	4										
30.0	-										
5											
mA]										
8 22 4	.1										
8 20.0	'1										
sort	1										
Absorbance [mAU]	1										
	11										
10.0	24				2 - 31.507	,					
	-				\square						
	-				$I \setminus I \setminus$						
	-1				$I \setminus I \setminus$						
0.0	p	~~~~~			The second secon						
	-										
-5.0											
	0.0 5.0	10.0 15	5.0 20.0	25.0	30.0	35.0 40.0	45.0 50.0				
				Time [min]			T				
	Results										
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)					
4		min	min	1.60	4.24	2027					
1		27.888	1.191	1.68	1.31 1.31	3037					
2		31.507	1.348	n.a.	1.31	3029	1				

Integr	ation Results					
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		27.888	50.711	40.921	80.47	82.33
2		31.507	12.304	8.782	19.53	17.67
Total:			63.015	49.703	100.00	100.00

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

		Chromate	ogram and Results	
Seneral in	formations			
Sequence N		2023-08-25		
Instrument:		U3000		
Logiciel use		Chromeleon		
Column use		CHIRALPAK IB3 DAICEL		
niection D		CHINALPARIDS DAICEE		
njection Na		WE-2600-2-enan-OD-2023-08-26-99-	1-0.4mLmin-50r <i>Run Time:</i> 50.00 min	
instrument l		99-1-30min-254nm-10°C-0.5mLmin	Injection Volume: 2.00 µL	
njection Da		26/août/23 18:06	Channel: UV_VIS_1	
njecuon Da	uer mine.	20/40/0/23 10:00	Wavelength: 254 nm	
netrumon	t Method Detail	c	wavelengun. 254 him	
Instrument		99-1-30min-254nm-10°C-0.5mLmin		
	propanol	1 %		
%B Hex	•	99 %	Température du four: 10.0 °C	
Déb		0.400 mL/min	Pression: 10 bars	
hromato		0.400 IIIE/IIII		
	2023-08-25 #5 [mai	wally integrated WE 3600 3 epop OD 3	023-08-26-99-1-0.4mLmin-50min-254nm-10°C UV VIS 1 WVL:	054 mm
140 - 🔟 4	2023-06-25 #5 [mai	lually integrated VVE-2000-2-enall-QD-2	023-00-20-88-1-0.4IIIEIIIII-30IIIII-234IIII-10 C 0V_VIS_1 WVL.	294 nn
120 100 100 60 60 20 20 0			12 - 31.860	
-20 J 0.0 Peak Resul	5.0	10.0 15.0 20.0	25.0 30.0 35.0 40.0 45.0 Time (min)	50
	k Name		Resolution (EP) Asymmetry (EP) Plates (EP)	
		min min	4.00 4.04 0050	
1		28.310 1.205	1.69 1.34 3056	
>		31.860 1.268	n.a. 1.33 3499	

Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height			
		min	mAU*min	mAU	%	%			
1		28.310	151.356	119.684	96.32	96.41			
2		31.860	5.787	4.452	3.68	3.59			
Total:			157.143	124.136	100.00	100.00			

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

			Chromat	togram and	Results			
ene	eral informations							
	ence Name:	2022-10-17						
	iment:	U3000						
	iel used:	Chromeleon						
	nn used:	CHIRALPAK OD	DAICEL					
iject	tion Details							
ject	tion Name:	MIN-812-OD-2022	-10-17-99-1-0.5ml	_min-30min-254	Run Time:		30.00 min	
			Injection Volume:		5.00 µL			
nject	tion Date/Time:	17/oct./22 11:59			Channel:	UV_VIS_1		
					Wavelength:		254 nm	
	ument Method Details							
	iment Method:	99-1-30min-254nn						
6A								
6B	Hexane				Température du four:		10.0 °C	
	Débit:	0.500	mL/min		Pression:		12 bars	
	matogram							
3	2022-10-17 #5 [manually i	ntegratedj Iv	IIN-012-QD-2022-1	0-17-99-1-0.5mLn	nin-30min-254nm-10°C		0V_VR	S_1 WVL:254 r
			1					
			1 ^{-10.27} 2					
0.0	2.5 5.0	75 1	1 - 10.27e	15.0 Time [min]	17.5 20.0	22.5	25.0	27.5
	2.5 5.0 Results	7.5 1	0.0 12.5	Time (min)				27.5
0.0 • eak		7.5 1	$\wedge / $			22.5		27.5

1		10.272	0.390	1.55	1.24	3843
2		11.352	0.432	n.a.	1.27	3833
Integr	ation Results					
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		10.272	5.561	13.557	5.73	6.33
2		11.352	91.523	200.669	94.27	93.67
Total:			97.084	214.226	100.00	100.00

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

			Chroma	togram and	Results		
Gene	ral informations						
	ence Name:	2023-01-09					
Instru		U3000					
	iel used:	Chromeleon					
Colun	nn used:	CHIRALPAK OD	DAICEL				
	tion Details						
	ion Name:	MIN-868-OD-2023				30.00	
				Injection Volume:	1.00	μL	
Injecti			Channel: Wavelength:	UV_VIS_1 254	nm		
	ument Method Deta						
	ment Method:	99-1-30min-254nn		า			
%A	Isopropanol		%				
%B	Hexane	99			Température du four:		
-	Débit:	0.500	mL/min		Pression:	13	bars
Chron	matogram						
100),0 - 🛛 2023-01-09 #7	manually integrated]	MIN-868-QD-20	123-01-09-99-1-0.5	mLmin-30min-254nm-1	1°C (JV_VIS_1 WVL:254 nm
Absorbance [mAU] 55 25 25 75 75	7.5		1 - 10.193	.322			
	0.0	5.0	10.0	15.0 Time [min]	20.0	25.0	30.0
Dook	Results			rine (iiiii)			1
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	-
110.	Carriente	min	min	(LEF)	/ synnieuy (Li*)	riaco (LT)	
1		10,193	0.389	1.62	1.24	3807	1
2		11.322	0.431	n.a.	1.21	3817	
							•

Integr	Integration Results									
No.	Peak Name	lame Retention Time		Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		10.193	37.659	91.413	94.33	94.84				
2		11.322	2.264	4.975	5.67	5.16				
Total:			39.922	96.388	100.00	100.00				

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

	Chromatogra	am and Results	
eneral informations			
Sequence Name:	2023-06-28		
nstrument:	U3000		
oaiciel used:	Chromeleon		
olumn used:	CHIRALPAK IB-3 DAICEL		
njection Details			
jection Name:	WE-2559-1-IB-2023-06-28-99-1-0.5mLmin-	-30min-25 Run Time:	30.00 min
strument Method:	99-1-30min-254nm-10°C-0.5mLmin	Injection Volume:	1.00 μL
njection Date/Time:	28/juin/23 16:55	Channel: UV_VIS_1	
-	-	Wavelength:	254 nm
strument Method Detail			
strument Method:	99-1-30min-254nm-10°C-0.5mLmin		
6A Isopropanol	1 %		
6B Hexane	99 %	Température du four:	10.0 °C
Débit:	0.500 mL/min	Pression:	39 bars
hromatogram 2023-06-28 #5		8-99-1-0.5mLmin-30min-254nm-10°C	UV_VIS_1 WVL:254 nr
400 2023-06-28 #5	WE-2009-1-IB-2023-06-2	6-99-1-0.5mLmin-30min-254nm-10°C	0V_VIS_1 VVVL:254 Hr
1			
350-	1 - 10.797		
1			
300 -			
1			
250-			
-11			
200			
200			
150			
100			
-	[]		
50-			
507			
E	2 - 11.662		
0]	~ k_k/		
3			
-50			
0.0	5.0 10.0	15.0 20.0	25.0 3
		Time (min)	
eak Results			
o. Peak Name	Retention Time Width (50%) Resol	ution (EP) Asymmetry (EP) Plates	(EP)
	min min		

		11001	11001						
1		10.797	0.146	3.39	1.18	30424			
2		11.662	0.156	n.a.	1.15	31100			
Integration Results									
No	Poak Namo	Potention Time	Aroa	Hoight	Polativo Area	Polativo Hoight			

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height
		min	mAU*min	mAU	%	%
1		10.797	56.202	352.229	94.80	95.11
2		11.662	3.082	18.128	5.20	4.89
Total:			59.284	370.358	100.00	100.00

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

			Chromat	togram and	Poculte			
			chioma	togram and	Results			
	al informations							
	nce Name:	2023-07-03						
Instrun		U3000						
· ·	el used:	Chromeleon						
	n used:	CHIRALPAK IB-3 DA	ICEL					
	ion Details	-						
	on Name:	WE-2559-C1-IB-2023-				:	30.00 min	
	Instrument Method: 99-1-30min-254nm-10°C-0.5mLmin			Injection Volume:		1.00 µL		
Injectio	on Date/Time:	03/juil./23 18:41			Channel:	UV_VIS_1		
					Wavelength:		254 nm	
Instru	ment Method Details							
	nstrument Method: 99-1-30min-254nm-10°C-0.5mLmin							
%A								
%В	Hexane	99 %			Température du four:		10.0 °C	
Charan	Débit:	0.500 mL	/min		Pression:		38 bars	
Chron	natogram							
900	2023-07-03 #6	WE	-2559-C1-IB-2	023-06-28-99-1-0.5	5mLmin-30min-254nm-	10°C	UV_VIS_1 WVL	:254 nm
	1		1 - 10.96	R				
	1		1 - 10.00	0				
750	I							
750	(1)							
	1							
625	51							
			1					
	-1		, ji					
₹ 500	귀							
Absorbance [mAU]	1							
8	1							
8 375	5-							
sor	1							
PP	.1		- 11					
250	겝							
	1							
125			11					
125	~ 1		11					
	1		11					
	,il							
I .	- H							
-100	, 1							
-100		5.0	10.0	15,0	20.0		25.0	30.0
		r 1 m	1212	Time [min]	20.0		= V V	00.0
Peak P	Results			time (timi)				
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)		
	- Con Humo	min	min	(LT)	(LI)	riacos (Er)		
1		10.968	0.190	n.a.	1.42	18481		

Integr	Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		10.968	180.172	827.114	100.00	100.00				
Total:			180.172	827.114	100.00	100.00				

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

			Chroma	togram and	Results			
Gene	ral informations							
	nce Name:	2023-07-03 U3000						
Logici	el used:	Chromeleon						
Colum	olumn used: CHIRALPAK IB-3 DAICEL							
	ion Details	_						
	on Name:	WE-2559-C-OD-20				30.00		
	ment Method: on Date/Time:	99-1-30min-254nm 14/août/23 20:22	1-10°C-0.5mLmin		Injection Volume: Channel: Wavelength:	1.00 UV_VIS_1 254	μL	
Instru	nstrument Method Details					2.51		
	ment Method:	99-1-30min-254nm	n-10°C-0.5mLmin	1				
%A	Isopropanol		%					
%B	Hexane	99			Température du four:		-	
Chron	_Débit: natogram	0.500	mL/min		Pression:		bars	
CHIO	2023-07-03 #17 [manu	ally integrated	WE 2559 C OD 20	023 07 03 00 1 0 5	imLmin-30min-254nm-1	10°C	JV_VIS_1 WVL:254 nm	
140	2023-07-03 #17 [manu	any integrated		023-07-03-88-1-0.3	memm-30mm-234mm-		0V_VI3_1 VVVE.234 IIII	
120 100 [nyu] soucpauce 40 20 20 0			1 - 9,988					
-20	0.0 5	0	10.0	15.0 Time [min]	20.0	25.0	30.0	
Peak	Results							
No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)		
1		9.988	0.441	n.a.	1.35	2836	I	

Integr	Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		9.988	61.222	130.577	100.00	100.00				
Total:			61.222	130.577	100.00	100.00				

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

				Chroma	togram and	Results		
Gen	eral i	nformations						
		Name:	2023-08-18					
Instr	ument	t:	U3000					
Logic	ciel us	sed:	Chromeleon					
Colu	mn us	sed:	CHIRALPAK IB3	DAICEL				_
		Details						
	tion N		WE-2592-1-ODH-2		.4mLmin-30min-		30.00	
		t Method:	99-1-30min-254nn	n-5°C-0.4mLmin		Injection Volume:	1.00) µL
Injec	tion D)ate/Time:	18/août/23 13:29			Channel:	UV_VIS_1	
Inct		nt Method Details				Wavelength:	254	nm
		t Method:	99-1-30min-254nn	n.5°C-0.4ml min				
%A		propanol		%				
%B		xane	99			Température du four:	5.0	°C
1	Dé			mL/min		Pression:		bars
Chro	_	ogram						
	2	2023-08-18 #7 [manu	ally integrated	WE-2592-1-ODH-	2023-08-18-99-1-0).4mLmin-30min-254nm	1-5°C I	JV_VIS_1 WVL:254 nm
12	ר ⁰⁰		, , ,					
	- 11							
	<u>1</u>			1 - 9.012				
10	00			1				
	- 11							
2	300-							
	- 11			1				
AU.								
<u>E</u> *	500-							
92	- 11			1				
ę.								
Absorbance [mAU]	00-			1				
A	- 11							
				1				
2	200-			11				
	- 11			11				
				2 - 9.710				
	0-1-					_		
	- 11							
-2	500 J F		5.0	10.0	15.0	20.0	25.0	0 30.0
	0.0	9	5.0	10.0	15.0 Time [min]	20.0	25.0	0 30.0
Dool	(Resi	ulte			rine (min)			1
No.		ak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	+
140.	1.6	an Harris	min	min	(Coolution (ET)	, synnieuy (El)	riaco (Er)	
1			9.012	0,140	2.80	1.13	23026	1
2			9.710	0.155	n.a.	1.06	21816	
	_							-

Integr	ntegration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		9.012	157.182	1027.733	96.54	96.78				
2		9.710	5.627	34.239	3.46	3.22				
Total:			162.809	1061.972	100.00	100.00				

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

		Chromatogram and	Results		
General informati					
	2023-08-18				
Sequence Name:					
Instrument:	U3000				
Logiciel used:	Chromeleon				
Column used:	CHIRALPAK IB3 DAI	EL			
Injection Details					
Injection Name:		23-08-18-99-1-0.4mLmin-50		50.00 n	
Instrument Method:	99-1-30min-254nm-10°	2-0.5mLmin	Injection Volume:	2.50 µ	L
Injection Date/Time:	20/août/23 21:57		Channel:	UV_VIS_1	
			Wavelength:	254 n	m
Instrument Metho					
Instrument Method:	99-1-30min-254nm-10°	:-0.5mLmin			
%A Isopropano					
%B Hexane	99 %		Température du four:		-
Débit:	0.400 mL/r	in	Pression:	16 b	ars
Chromatogram					
140 - 2023-08-	18 #23 [manually integrated] WE-259	-1-enan-OD-2023-08-18-99-1-	0.4mLmin-50min-254nr	n-10°C UV	_VIS_1 WVL:254 nm
120 100 100 60 60 20 -20 0 0	50 100 150	20.0 25.0	30.0	2 - 34.477	45.0 50
Peak Results		Time (min)			
No. Peak Name		dth (50%) Resolution (EP)	Asymmetry (EP)	Plates (EP)	
	min	min		10112	
1	30.365	0.531 4.26	1.12	18148	
2	34.477	0.609 n.a.	1.04	17770	

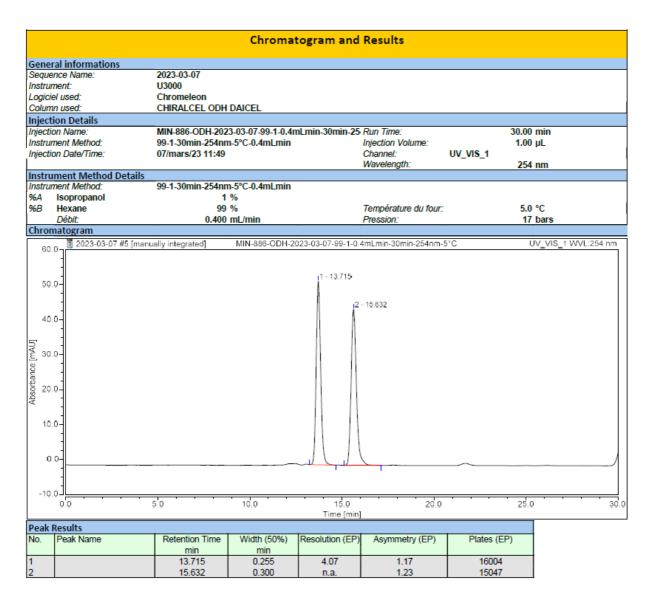
Integr	Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		30.365	68.916	120.934	96.45	96.84				
2		34.477	2.535	3.941	3.55	3.16				
Total:			71.452	124.875	100.00	100.00				

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

	Chromatogr	am and Results		
General informations				
Sequence Name:	2023-08-18			
nstrument:	U3000			
.ogiciel used:	Chromeleon			
Column used:	CHIRALPAK IB3 DAICEL			
njection Details	CHINALI ANIBO DAIGEE			
njection Name:	WE-2593-3-IB-2023-08-18-99-1-0.5mLmin	-30min_25 Run Time:	30.00 min	
nstrument Method:	99-1-30min-254nm-10°C-0.5mLmin	Injection Volume:	1.00 µL	
njection Date/Time:	18/août/23 19:11	Channel:	UV_VIS_1	
njoodon Dator nino.	10/00/02/3 13:11	Wavelength:	254 nm	
nstrument Method D	etails	marciengin.	204 1111	
nstrument Method:	99-1-30min-254nm-10°C-0.5mLmin			
6A Isopropanol	1 %			
%B Hexane	99 %	Température du four:	10.0 °C	
Débit:	0.500 mL/min	Pression:	31 bars	
Chromatogram	, , , , , , , , , , , , , , , , , , , ,		,	
間 2023-08-18 #	15 [manually integrated] WE-2593-3-IB-2023-08	-18-99-1-0.5mLmin-30min-254nm-1	10°C UV_VIS_1 WVL:25	54 pr
90.0				
1		1 - 13.950		
75.0-				
75.07				
1		1		
62.5		11		
1				
_ 1		11		
₹ 50.0-		11		
특 귀		11		
ê 1				
37.5				
004 50.0 -				
[₹] 25.0-				
20.07		1 \		
1				
12.5				
1		2 - 15.217		
0.0				
-10.0				
0.0	5.0 10.0	15.0 20.0	25.0	3
		Time [min]		
eak Results				
No. Peak Name	Retention Time Width (50%) Res	olution (EP) Asymmetry (EP)	Plates (EP)	
	min min			
1	13.950 0.377	2.12 1.84	7599	

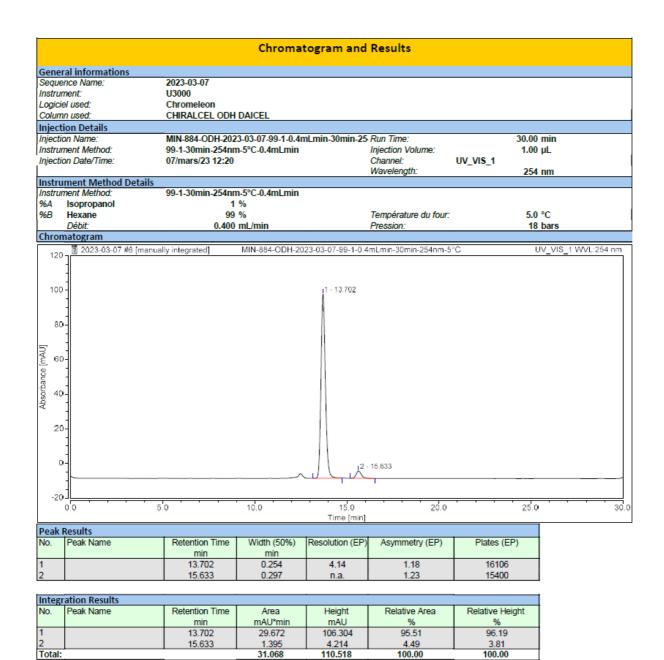
Integr	Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		13.950	35.970	80.441	96.95	96.32				
2		15.217	1.133	3.077	3.05	3.68				
Total:			37.103	83.518	100.00	100.00				

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



Integr	Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		13.715	14.721	52.497	49.65	54.03				
2		15.632	14.928	44.663	50.35	45.97				
Total:			29.649	97.160	100.00	100.00				

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

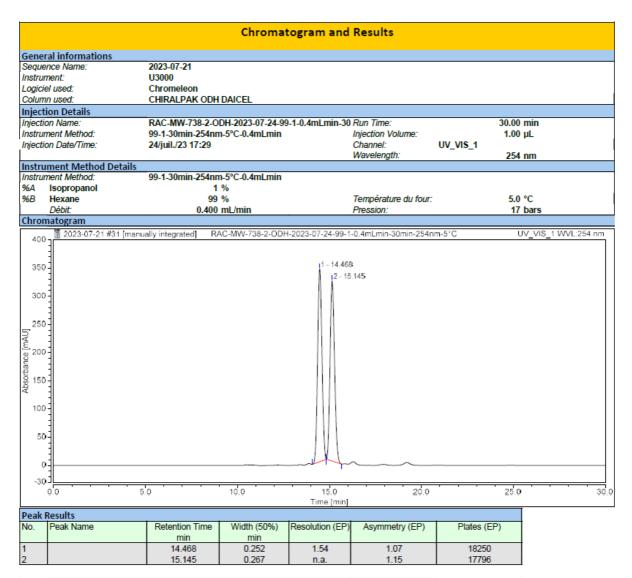


2-(4,4,5,5-Tetramethyl-1,3-dioxa-2-borolyl)ferrocenetriflone (2h) obtained by esterification of the boronic acid 2g

		Chroma	togram and	Results			
eneral informations							
equence Name:	2023-09-12						
strument:	U3000						
giciel used:	Chromeleon						
		DAICEI					
olumn used:	CHIRALCEL ODH	DAICEL					
jection Details							
jection Name:	WE-2627-enan-OD		-1-0.4mLmin-30r		3	0.00 min	
strument Method:	99-1-30min-254nn	n-5°C-0.4mLmin		Injection Volume:		1.00 µL	
jection Date/Time:	12/sept./23 16:55			Channel:	UV_VIS_1		
				Wavelength:		254 nm	
strument Method Detail	s						
strument Method:	99-1-30min-254nm	n-5°C-0.4mLmin					
A Isopropanol	1	%					
B Hexane	99	%		Température du four:		5.0 °C	
Débit:		mL/min		Pression:		18 bars	
romatogram	0.100				·		
2023-09-12 #4 [mail	nually integrated 1 - 56	E 2627 coop ODI	1 2023 00 42 00 4	-0.4mLmin-30min-254ni	m 5°C	UV VIS 1	AN/L-024
350 - 2023-09-12 #4 [mai	nually integrated j vi	L-2021-dilan-QDI	-2023-03-12-88-1-	-0.4mLmm-30mm-204m	11-3 Q	07_015_1	WVL.254 P
250 200 150 100 50				12 - 16.080 T			
	3.0 10.0	12.0	Time (min)	16.0 18.0	20.0 Plates (EP)	22.0	24.0
eak Results o. Peak Name	Retention Time	Width (50%)	Resolution (EP)	/ Synancu y (Li)			
	min	min					
			Resolution (EP)	1.03	13431	_	

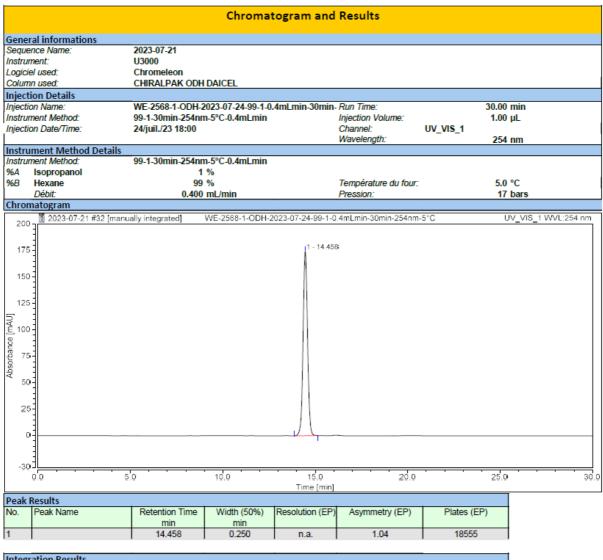
Integr	Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		14.128	99.733	319.541	98.98	99.02				
2		16.080	1.027	3.173	1.02	0.98				
Total:			100.760	322.714	100.00	100.00				

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



Integr	Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		14.468	91.463	341.974	50.14	51.66				
2		15.145	90.942	320.016	49.86	48.34				
Total:			182.405	661.991	100.00	100.00				

(*R*_P)-2-Iodo-5-(trimethylsilyl)ferrocenetriflone (*R*_P-3af)



Integr	Integration Results									
No.	Peak Name Retention Time		Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		14.458	47.658	174.101	100.00	100.00				
Total:			47.658	174.101	100.00	100.00				

$(\pm) - 4 - Iodo - 2 - (trimethylsilyl) ferrocenetriflone \ (rac - 4af)$

			Chromat	togram and	Results		
Gene	ral informations						
	ence Name:	2023-07-10					
Instrui	ment:	U3000					
Logicie	el used:	Chromeleon					
Colum	nn used:	CHIRALPAK IB-3	DAICEL				
	ion Details						
	on Name:	RAC-MW-785-IB-2		.5mLmin-30min-		30.00	
	ment Method:	99-1-30min-254nn	n-5°C-0.5mLmin		Injection Volume:	1.00	μL
Injecti	on Date/Time:	10/juil./23 13:45	10/juil./23 13:45		Channel:	UV_VIS_1	
1					Wavelength:	254	nm
	ment Method Details ment Method:	99-1-30min-254nn	5°C 0 Eml min				
%A	Isopropanol						
%B					Température du four:	5.0	°C
700	Débit:		mL/min		Pression:		bars
Chron	natogram	0.500			riession.	40	Dars
cinor	2023-07-10 #7 [manu	ally integrated	DAC MM/ 795 ID 2	022 07 10 00 1 0	.5mLmin-30min-254nm-	500	JV_VIS_1 WVL:254 nm
300) 1 2023-07-10 #7 [manu			.023-07-10-55-1-0	.5ITEITII1-30ITII1-254HITI-		0V_VI3_1 VVVL.2341111
	1		1 - 8.917				
	-	1	2 - 9.703				
250	1		1				
	-	1					
	1		8				
200	.1		- h				
200	1	1					
5	-						
Absorbance [mAU]	1						
등 150)-						
2 C	1						
ë	-	[
g 100	1						
<	-						
	1						
	-1						
50	'1						
	-						
			VI V				
0	,		4 m	~~~			
	-		1 - C				
-30	1						
	0.0	5.0	10.0	15.0	20.0	25.0	30.0
				Time [min]			-
Peak	Results						
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	1
		min	min				
1		8.917	0.178	2.54	1.62	13878	1
2		0.702	0 199		1.56	14760	1

2		9.703	0.188	n.a.	1.50	14760				
Integration Results										
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		8.917	58.241	279.325	49.72	51.14				
2		9.703	58.889	266.864	50.28	48.86				
Total:			117.130	546.189	100.00	100.00				

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

		Chroma	togram and	Results		
eneral informations						
equence Name:	2023-07-10					
strument:	U3000					
ogiciel used:	Chromeleon					
olumn used:	CHIRALPAK IB-3	DAICEL				
jection Details						
jection Name:	WE-2570-1-IB-20	23-07-10-99-1-0.5	mLmin-30min-25	Run Time:	30.00) min
nstrument Method:	99-1-30min-254n	m-5°C-0.5mLmin		Injection Volume:	1.00) µL
njection Date/Time:	10/juil./23 13:14			Channel:	UV_VIS_1	
-	-			Wavelength:		t nm
nstrument Method De						
strument Method:		m-5°C-0.5mLmin				
6A Isopropanol		1 %				
6B Hexane		9%		Température du four:	5.0	0°C
Débit:	0.50	0 mL/min		Pression:	40) bars
hromatogram						
450 - 2023-07-10 #6	[manually integrated]	WE-2570-1-IB-20	023-07-10-99-1-0.5	imLmin-30min-254nm-5	°C	UV_VIS_1 WVL:254 r
450						
		1 - 8.918				
400						
1						
350-		1				
1						
300		1				
1						
5 1						
250-		1				
ž 1		h				
200-						
2250 2200 2000						
		11				
100						
1						
50-						
]						
0						
		1.1				
-30 1	5.0	10.0	15.0	20.0	25.0	, · · · ·
0.0	0.0	10.0	15,0 Time [min]	20.0	25.0	,
			rine (minj			1
eak Results	Detertion T		Desch fing (CD)	Annual tracks	Distant (ED)	-
lo. Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	
	min	min		1.61	13463	4
	8.918	0.181	n.a.			

Integr	Integration Results										
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height					
		min	mAU*min	mAU	%	%					
1		8.918	86.202	406.498	100.00	100.00					
Total:			86.202	406.498	100.00	100.00					

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

			Chroma	togram and	Results		
Gonor	al informations						
	nce Name:	2023-07-20					
Instrun		U3000					
	giciel used: Chromeleon						
	n used:	CHIRALPAK IB-3	DAICEI				
	on Details	CHINALFAR ID-5	DAIGEL				
	n Name:	RAC-MW-789-IB-2	023-07-20-99-1-0	.5mLmin-30min-	Run Time:	30	.00 min
	nent Method:	99-1-30min-254nn			Injection Volume:		.00 µL
	n Date/Time:	20/juil./23 16:26			Channel:	UV_VIS_1	
					Wavelength:		254 nm
	ment Method Details						
Instrun	nent Method:	99-1-30min-254nn	n-5°C-0.5mLmin				
%A	Isopropanol		%				
%В	Hexane	99			Température du four:	:	5.0 °C
	Débit:	0.500	mL/min		Pression:		41 bars
Chron	natogram						
140	💈 2023-07-20 #10 [mai	nually integrated]	RAC-MW-789-IB-2	2023-07-20-99-1-0	5mLmin-30min-254nm-	·5°C	UV_VIS_1 WVL:254 nm
140]						
	-1				1 - 17.172		
120	-1				2 - 18.400		
	-						
	1						
100	-1						
]						
80	1						
	-1						
Absorbance [mAU] 05	1						
g 60	-1						
an	1 I						
ę ,,	-1						
80 40	1						
~	-1						
20	1						
	-1						
	1						
0		~				~	~
	1						
	-1						
-20	-11						
-30			· · · · ·				, , , , , , , , , , , , , , , , , , ,
	0.0	5.0	10.0	15.0 Time (min)	20.0	2	5.0 30.
				Time [min]			
	Results	Deteri T	MAGINE (COM)	Deset of the start	A		
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	
4		min 47,470	min	2.50	4.04	20000	
1		17.172	0.272	2.58	1.34	22009	
2		18.400	0.290	n.a.	1.35	22317	

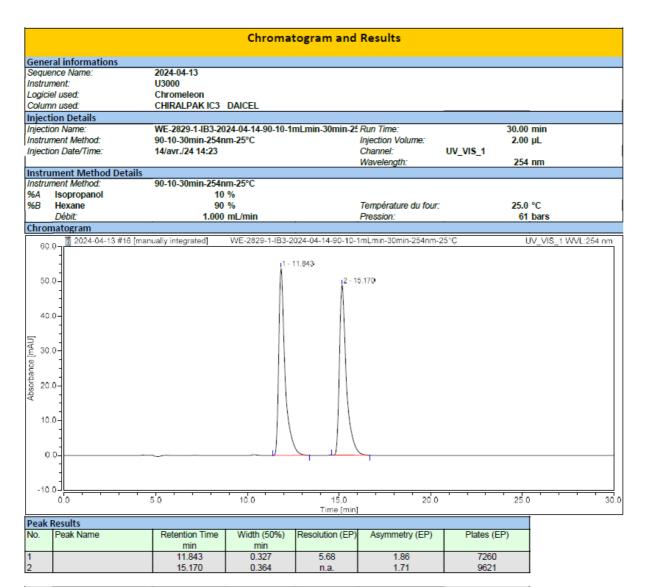
Integr	Integration Results									
No.	Peak Name	Area	Height	Relative Area	Relative Height					
		min	mAU*min	mAU	%	%				
1		17.172	38.232	124.885	50.29	51.61				
2		18.400	37.795	117.075	49.71	48.39				
Total:			76.026	241.960	100.00	100.00				

(*R*_P)-3-Iodoferrocenetriflone (*R*_P-5f)

			Chroma	togram and	Results		
Gener	al informations						
	nce Name:	2023-07-20					
nstrun	nent:	U3000					
	el used:	Chromeleon					
	n used:	CHIRALPAK IB-3	DAICEL				
	on Details						
	on Name:		3-07-20-99-1-0.5m			30.00	
	nent Method:	99-1-30min-254n	m-5°C-0.5mLmin		Injection Volume:	1.00	μL
njectio	on Date/Time:	20/juil./23 17:58			Channel:	UV_VIS_1	
netru	ment Method Deta	aile			Wavelength:	254	nm
	nent Method:	99-1-30min-254n	m_5°C_0 5ml min				
	Isopropanol		1 %				
6B	Hexane		9%		Température du four:	5.0	°C
	Débit:) mL/min		Pression:		bars
hron	natogram						
200	2023-07-20 #13 [manually integrated]	WE-2580-IB-20	23-07-20-99-1-0.5m	nLmin-30min-254nm-5°	c u	JV_VIS_1 WVL:254 nm
200	3						
	3				2 - 18.335		
175	1				2 - 18.335		
	1				1		
150	1				A		
	3						
125	3				11		
	1						
2	1				11		
โกษม] 2011 75	1						
5	1						
3 75	1						
20	3				11		
۲ 50	3				11		
	1				11		
	1				11		
25	1				11		
	1				1 17057		
0	1				~11-17,057		
	1						
	1						
-30	J <u> </u>	5.0	10.0	15.0	20.0	25.0	30
	0.0	0.0	10.0	Time [min]	20.0	20.0	30
)ook I	Doculto			time (tim)			[
PAK -	Results Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	
	IFEAK NAME	Retenuori Time	Width (50%)	(EP)	Asymmetry (EP)	Flates (EP)	
No.		min	min				
		min 17.057	min 0.255	2.76	1.32	24819	

Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height			
		min	mAU*min	mAU	%	%			
1		17.057	0.192	0.690	0.34	0.40			
2		18.335	56.366	173.737	99.66	99.60			
Total:			56.558	174.427	100.00	100.00			

The ferrocenic analogue of fluorenone *rac-10*



Integr	Integration Results									
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		11.843	21.552	53.752	50.28	52.37				
2		15.170	21.315	48.880	49.72	47.63				
Total:			42.867	102.632	100.00	100.00				

The ferrocenic analogue of fluorenone SP-10

			Chroma	togram and	Results		
Sener	ral informations						
	ence Name:	2024-04-13					
nstrur		U3000					
	el used:	Chromeleon					
	in used:	CHIRALPAK IC3	DAICEL				
	ion Details						
	on Name:	WE-2839-1-IB3-20	24-04-14-90-10-1	mLmin-30min-25	Run Time:	30.0	0 min
Instrur	ment Method:	90-10-30min-254n	m-25°C		Injection Volume:	2.0)0 µL
njectio	on Date/Time:	14/avr./24 14:54			Channel:	UV_VIS_1	
-					Wavelength:		54 nm
	iment Method Deta						
	ment Method:	90-10-30min-254n					
%A	Isopropanol	10					
%В	Hexane	90			Température du four:		.0 °C
	Débit:	1.000	mL/min		Pression:		51 bars
Chron	natogram						
350	🗑 2024-04-13 #17 [r	nanually integrated]	WE-2839-1-IB3-2	024-04-14-90-10-1r	mLmin-30min-254nm-2	5°Ç	UV_VIS_1 WVL:254 ni
250 200 150 150 50 0							
	0.0 Results	5.0	10.0	15.0 Time [min]	20.0	25	
No.	Peak Name	Retention Time	Width (50%)	Resolution (EP)	Asymmetry (EP)	Plates (EP)	-
1 0.	r call Name	min	min	(CSOIDIOT (EF)	(Symmetry (EP)	riaces (LP)	
1		15.102	0.359	n.a.	1.70	9822	-
		10.102	0.000			JOLL	
	ration Results						

Integr	Integration Results									
No.	D. Peak Name Retention Time		Area	Height	Relative Area	Relative Height				
		min	mAU*min	mAU	%	%				
1		15.102	121.981	286.303	100.00	100.00				
Total:			121.981	286.303	100.00	100.00				

H) Determination of the enantiomeric excess of RP-3aj, RP-6, SP-7, SP-8 and SP-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 μ mol) and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid (19 mg, 90 μ mol) were first dissolved in CDCl₃ (0.5 mL). The resulting solution for stirred for 1 min at rt before being filtrated over a 0.22 μ m 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 (${}^{3}J_{HP} = 16.2 \text{ Hz}$), 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 ¹⁹F NMR spectrum, with two signals at -76.4 and -76.8 ppm, also in a 1:1 ratio (Figure S20). In the ¹³C 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 (${}^{1}J_{CF} = 327 \text{ Hz}$), 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 ¹³C 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 ³¹P NMR spectrum (Figure S22).

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

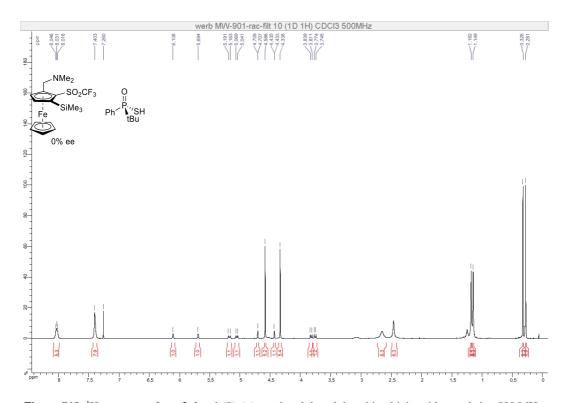


Figure S19. ¹H spectrum of *rac*-3aj and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

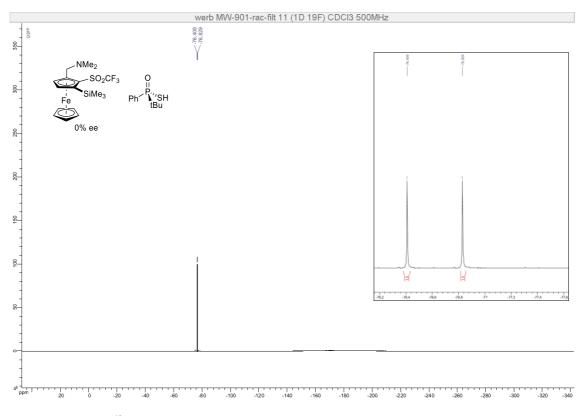


Figure S20. ¹⁹F spectrum of *rac-3aj* and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 470 MHz.

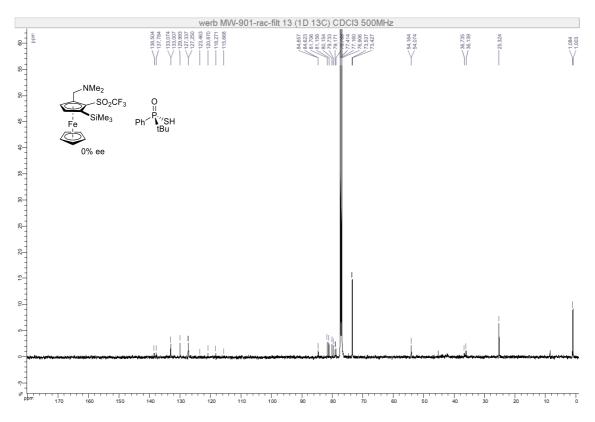


Figure S21. ¹³C spectrum of *rac-3aj* and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

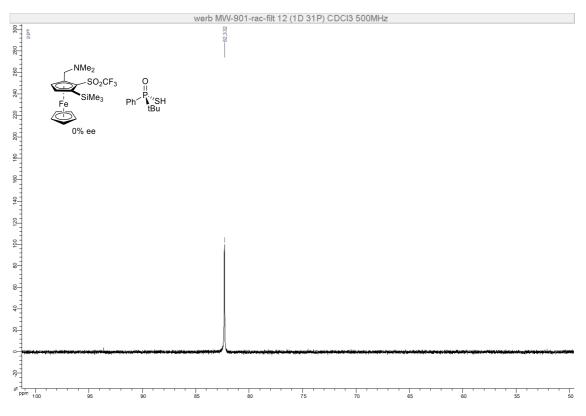


Figure S22. ³¹P spectrum of *rac-3aj* and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 202 MHz.

We then performed the same experiments starting from an expected enantiopure R_{P} -3aj, coming from R_{P} -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 R_{P} -3aj being > 99%, in good agreement with the HPLC results.

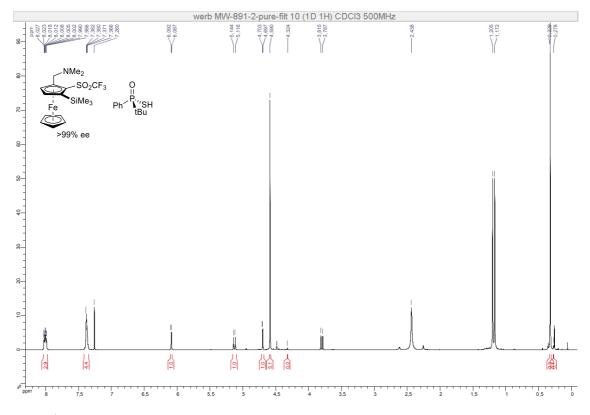


Figure S23. ¹H NMR spectrum of enantiopure *R*_P-3aj and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

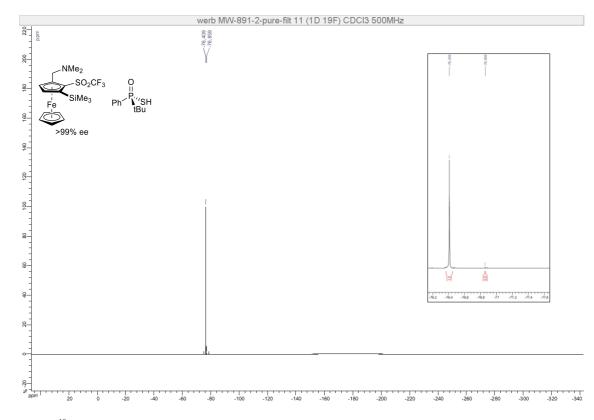


Figure S24. ¹⁹F NMR spectrum of enantiopure *R*_P-3aj and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 470 MHz.

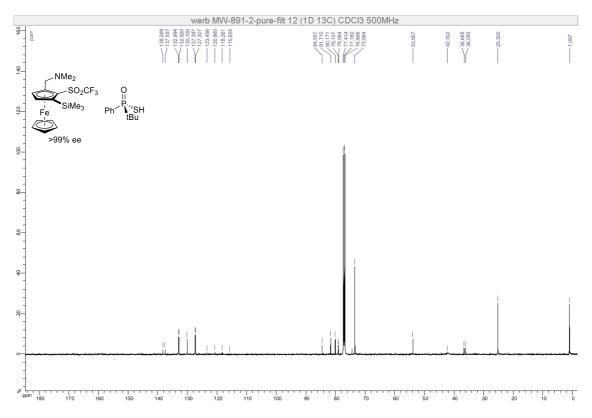


Figure S25. ¹³C NMR spectrum of enantiopure *R*_P-3aj and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

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 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, 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 ¹⁹F 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 ¹³C NMR spectrum (Figure S28), as only one diastereoisomer was observed.

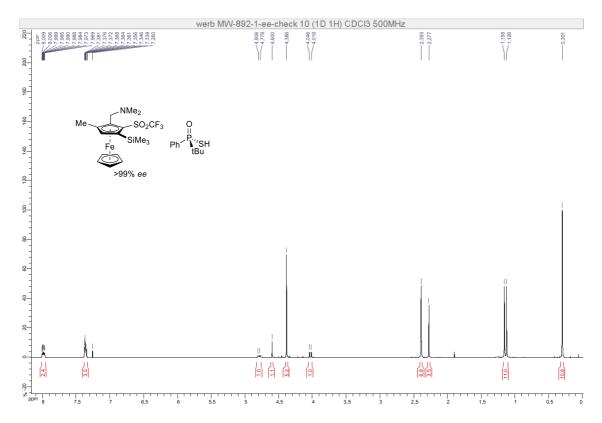


Figure S26. ¹H NMR spectrum of enantiopure R_{P-6} and (R)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

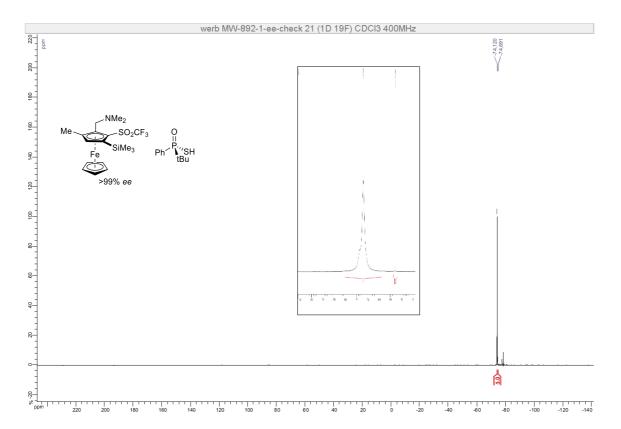


Figure S27. ¹⁹F NMR spectrum of enantiopure R_{P-6} and (R)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 376 MHz.

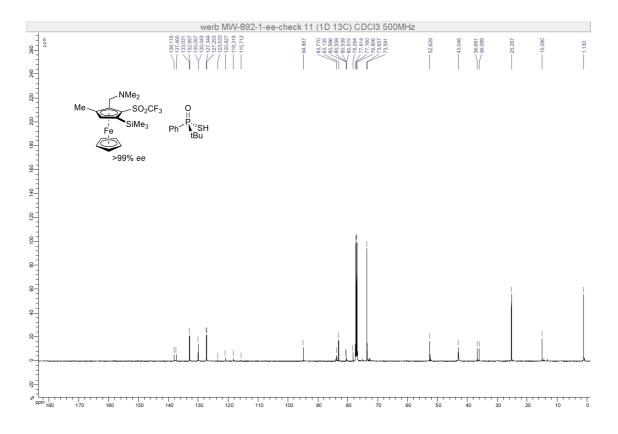


Figure S28. ¹³C NMR spectrum of enantiopure *R*_P-6 and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

We conducted the same experiments from S_{P} -7, concerned about a possible racemisation during the Bu₄NF induced desilylation, as previously observed. Thus, S_{P} -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 ¹⁹C NMR spectrum with no duplication of the main signals (Figure S31).

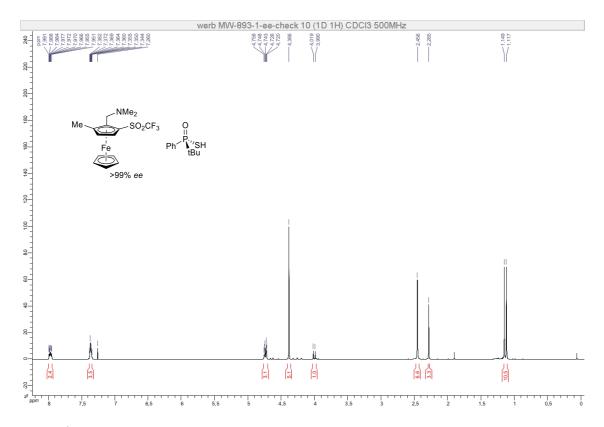


Figure S29. ¹H NMR spectrum of enantiopure S_{P-7} and (R)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

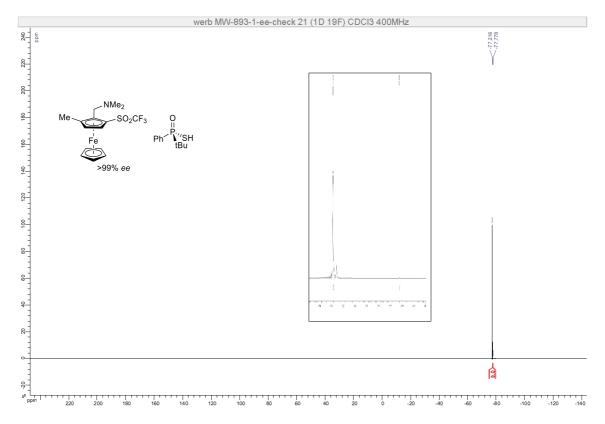


Figure S30. ¹⁹F NMR spectrum of enantiopure S_{P-7} and (R)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 376 MHz.

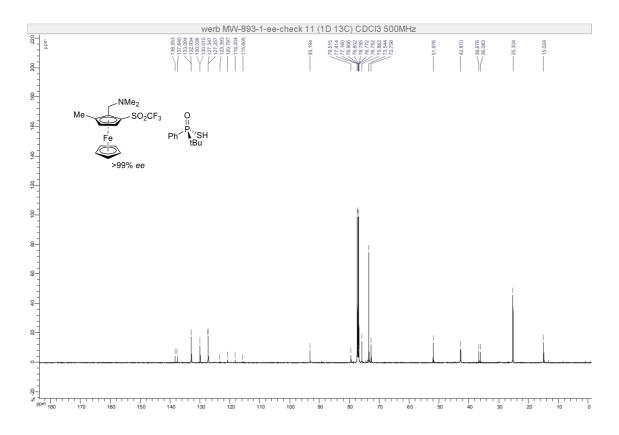


Figure S31. ¹³C NMR spectrum of enantiopure Sp-7 and (R)-(+)-tert-butylphenylphosphinothioic acid recorded at 125 MHz.

Next, *S*_P-8 (38 mg, 90 μ mol) and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid (19 mg, 90 μ mol) were dissolved in CDCl₃ (0.5 mL). The solution was stirred at rt for 1 min before being filtrated over a 0.22 μ m nylon syringe filter directly into a NMR tube.

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

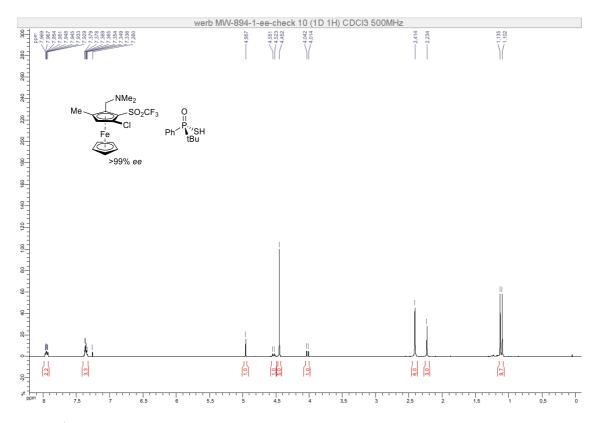


Figure S32. ¹H NMR spectrum of enantiopure S_{P-8} and (R)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 500 MHz.

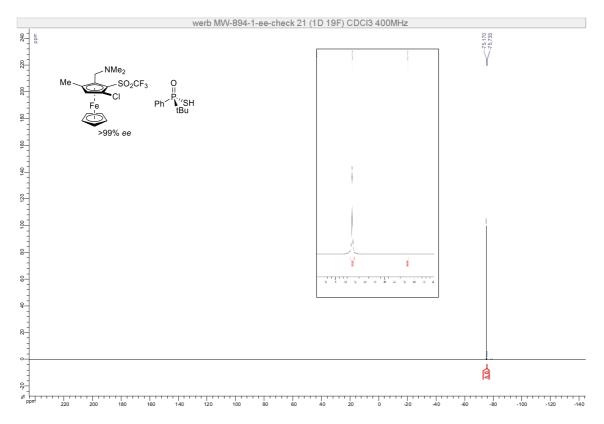


Figure S33. ¹⁹F NMR spectrum of enantiopure S_{P-8} and (R)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 376 MHz.

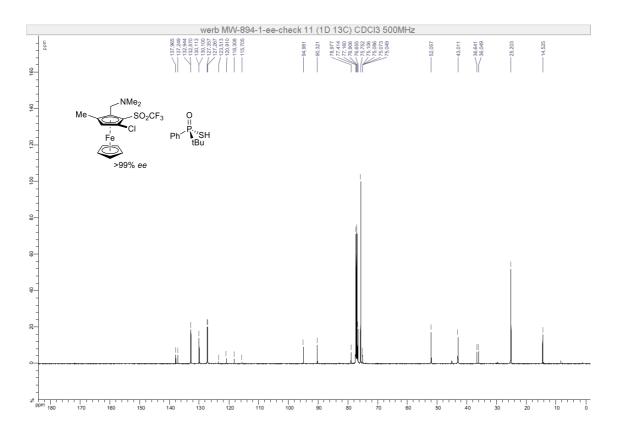


Figure S34. ¹³C NMR spectrum of enantiopure Sp-8 and (R)-(+)-tert-butylphenylphosphinothioic acid recorded at 125 MHz.

Finally, *S*_P-9 (45 mg, 90 μ mol) and (*R*)-(+)-*tert*-butylphenylphosphinothioic acid (19 mg, 90 μ mol) were dissolved in CDCl₃ (0.5 mL). The solution was stirred at rt for 1 min before being filtrated over a 0.22 μ m nylon syringe filter directly into an NMR tube.

No duplication of signals was noticed in the ¹H (Figure S35) and ¹³C (Figure S37) NMR spectra. In the ¹⁹F 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.

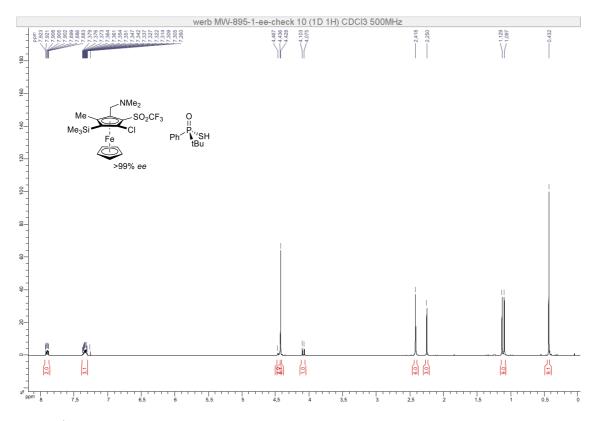


Figure S35. ¹H NMR spectrum of enantiopure S_{P-9} and (R)-(+)-tert-butylphenylphosphinothioic acid recorded at 500 MHz.

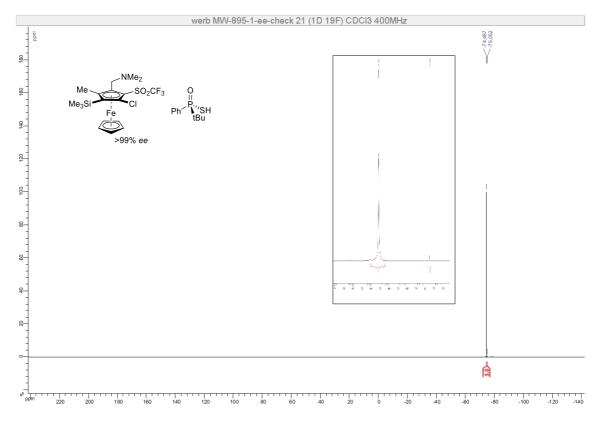


Figure S36. ¹⁹F NMR spectrum of enantiopure S_{P-9} and (R)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 376 MHz.

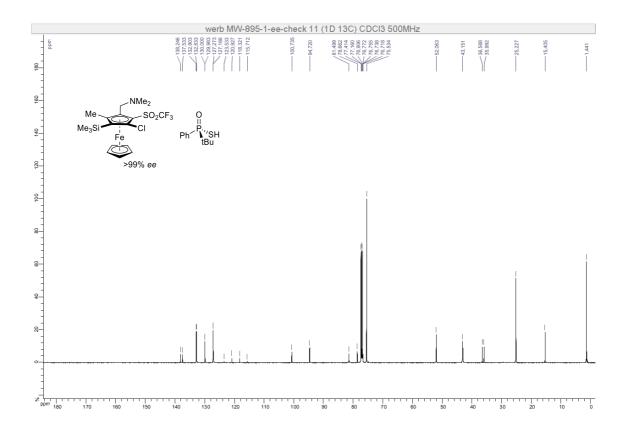


Figure S37. ¹³C NMR spectrum of enantiopure S_{P-9} and (R)-(+)-*tert*-butylphenylphosphinothioic acid recorded at 125 MHz.

I) Computational details for pKa 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 (R–H(g) \rightarrow R⁻(g) + H⁺(g)):

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

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

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

here furan with $pK_a(THF)$ 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	Х	Y	Ζ
Fe	1.64129	0.24585	0.00008
С	-0.34858	0.57680	0.00014
С	0.22401	1.17406	1.16540
С	1.15361	2.13901	0.71252
С	1.15358	2.13896	-0.71241
С	0.22397	1.17396	-1.16518
С	1.96244	-1.78877	-0.00024
С	2.55248	-1.19833	1.14992
С	3.51036	-0.24315	0.71063
С	3.51025	-0.24292	-0.71087
С	2.55227	-1.19794	-1.15032
Н	0.00218	0.90006	2.18618
Н	1.78820	2.74524	1.34354
Н	1.78819	2.74510	-1.34350
Н	0.00204	0.89992	-2.18593
Н	1.16689	-2.52064	-0.00030
Н	2.28800	-1.41174	2.17603
Н	4.10552	0.39873	1.34530
Н	4.10528	0.39920	-1.34542
Н	2.28759	-1.41100	-2.17645
S	-1.48280	-0.74580	0.00022
0	-1.41693	-1.44707	-1.27395
0	-1.41731	-1.44663	1.27465
С	-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]

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			C -3.90092800	-0.95575000	-0.72237000
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F	3.02238500	-1.40184500	2.41240300	H
				H
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Ene	ergy (RB3LY)	P): -2079.0483	312 hartree	C
Gił	bs Free Energ	gy: -2078.6343	367 hartree	C
				C
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Η	2.18491400	2.35825500	0.55710800	H
Η	3.19121600	-1.87357200	-3.06939000	L
	-3.04116500	0.35623300	0.21424000	S
	-3.76223000	-0.90995500	0.57209000	C
Η	-3.38520800	-1.20565100	1.55565500	C

С	-3.33768800	1.54685100	1.07433600
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С	-3.34411400	-1.99435400	-0.41385900
С	-3.78621600	-1.97903600	-1.74686400
С	-2.49044900	-3.02797400	-0.00313400
С	-3.38122700	-2.96860800	-2.64497900
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Η	-2.13094600	-3.05363500	1.02232300
С	-2.52907100	-3.99374000	-2.22268700
Η	-3.73122600	-2.93952400	-3.67307700
Η	-1.41484400	-4.80649300	-0.56192500
Η	-2.21108000	-4.76147200	-2.92208100
С	-2.67108200	2.76605200	0.45050600
С	-1.28812000	2.98599200	0.54871000
С	-3.44664800	3.69423600	-0.25898500
С	-0.70001200	4.10439100	-0.04684700
Η	-0.66256300	2.29213100	1.10398500
С	-2.86191100	4.81449600	-0.85744500
Η	-4.52127100	3.54319900	-0.33719900
С	-1.48485300	5.02249700	-0.75139800
Η	0.37087600	4.26163500	0.04244200
Η	-3.48175800	5.52334700	-1.39924000
Η	-1.02567300	5.89298400	-1.21096500
С	-5.29203000	-0.76435500	0.66618900
Η	-5.74393500	-1.73900000	0.87428200
Η	-5.58727500	-0.08307800	1.46981300
Η	-5.72126900	-0.39016400	-0.27016500
С	-2.91276600	1.30118700	2.52848700
Η	-3.04043800	2.22028900	3.10776000
Η	-3.52671400	0.52641600	2.99766300
Η	-1.86840100	0.98546400	2.60059700
Η	-3.31974600	0.60498400	-0.73674700
Η	3.57480300	-2.33753500	-0.43157300
Li	-1.02829600	-0.14590400	-0.04106000
S	1.09447200	-1.50205700	1.42877500
0	1.15460500	-2.91013900	1.84195700
0	-0.17023700	-0.73768900	1.64983500

С	2.31703400	-0.65454700	2.60547500
F	2.00541200	-1.00311300	3.85976200
F	2.25887400	0.68097000	2.50911600
F	3.57023500	-1.05664500	2.34186700

• INT1 (\mathbf{R}_p)

Energy (RB3LYP):	-2079.038384 hartree
Gibbs Free Energy:	-2078.629206 hartree

Fe	-3.17553000	-0.02725400	-1.07615000
С	-1.32380700	-0.74419800	-0.55224300
С	-1.76274100	-1.37695600	-1.77223400
С	-1.92405900	-0.33936800	-2.72837800
С	-1.59789600	0.90961400	-2.11126800
Н	-1.66099900	1.88321600	-2.57697100
С	-1.21687400	0.67434100	-0.76517000
С	-4.77851800	-0.83909200	-0.01023800
Н	-4.72260700	-1.74512800	0.57598300
С	-5.10345600	-0.75957100	-1.39608800
Н	-5.32909900	-1.59544600	-2.04421200
С	-5.02432700	0.61217500	-1.79084900
Н	-5.18014500	0.99646000	-2.78967600
С	-4.65392700	1.38001400	-0.64456000
Н	-4.47606200	2.44658300	-0.62511800
С	-4.49826300	0.48514500	0.45543200
Н	-4.19981200	0.75911200	1.45731100
Н	-2.27491400	-0.47233800	-3.74252600
N	3.37082700	0.99261000	-0.25616300
С	4.53555300	0.39151500	-0.89744700
Н	5.48448400	0.67219500	-0.39625000
С	3.38173700	2.44386400	-0.21035800
Η	3.45983100	2.89172600	-1.22200600
С	4.40413300	-1.11889200	-0.70470500
С	3.46688200	-1.86925300	-1.43789300
С	5.16191700	-1.78773100	0.27033500
С	3.29872100	-3.24100800	-1.20758700
Η	2.87676400	-1.37842000	-2.20735800

C 5.00282100	-3.15776100	0.50024600
Н 5.88468700	-1.22110100	0.85274200
C 4.06735100	-3.89031000	-0.23816200
Н 2.57192000	-3.80174900	-1.78983600
Н 5.60526600	-3.65201900	1.25796800
Н 3.93911200	-4.95427500	-0.05967200
C 2.05036800	2.93166800	0.35142300
C 1.64085900	2.58115200	1.64966000
C 1.20293100	3.75784900	-0.40134100
C 0.42864000	3.03831500	2.17518500
Н 2.28875900	1.95283600	2.25515600
C -0.00943800	4.22557300	0.11930600
Н 1.50251400	4.04145800	-1.40783500
C -0.40350700	3.86614500	1.41207300
Н 0.13892800	2.76018200	3.18551300
Н -0.64129200	4.87542800	-0.48169600
Н -1.33897500	4.23473900	1.82492800
C 4.72808600	0.75971000	-2.39133900
Н 5.57046200	0.21063900	-2.83059300
Н 4.93722300	1.82920600	-2.49980400
Н 3.82459600	0.54102000	-2.97225500
C 4.55185700	3.05803900	0.60905700
Н 4.48239100	4.15257000	0.64253100
Н 5.51748000	2.79993700	0.16129300
Н 4.54630900	2.67586100	1.63639600
Н -0.90844700	1.41748400	-0.04285600
Н -1.91814100	-2.43688400	-1.90966500
Li 2.23524400	-0.27618500	0.38140400
S -0.66881000	-1.66112600	0.79282700
C -1.61484600	-1.19616700	2.37005400
O -0.89951200	-3.09021000	0.58760700
O 0.68937600	-1.15493100	1.09534700
F -0.94825900	-1.70480800	3.40719000
F -2.84904900	-1.70970100	2.34881700
F -1.69126100	0.13405100	2.50077100

• TS (\mathbf{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
Н -0.14533900	-0.15981800	-3.37337500
C -0.00976100	-0.44969200	-1.16789000
C -4.23008200	-0.49507600	-1.65203300
Н -4.79417000	-1.38428700	-1.89936700
C -3.62600900	0.40262900	-2.58638700
Н -3.65366500	0.31333800	-3.66391900
С -2.93768200	1.41133200	-1.84319500
Н -2.34450500	2.21188500	-2.26268700
C -3.10857100	1.13510100	-0.45551000
Н -2.67568000	1.69766700	0.35867300
C -3.91051600	-0.04444300	-0.33760800
Н -4.21051900	-0.52191900	0.58343400
Н -1.69126700	-2.35358400	-3.45430000
N 2.07937700	1.26016400	-0.59321100
C 3.25455400	0.78692100	-1.35710500
Н 4.08957800	1.48418800	-1.19873800
C 1.69100100	2.66618300	-0.79537800
Н 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
Н 2.68598900	-1.87562100	-2.05965000
C 4.88467700	-1.63334300	1.12538800
Н 4.83889700	0.49831900	0.80778300
C 4.47799700	-2.88423000	0.65109300
Н 3.36467600	-3.92463800	-0.87332300
Н 5.50630900	-1.56123600	2.01375100
Н 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
Н 2.13164400	2.52686500	1.91586600
C -1.26634700	4.20122500	1.11863400
Н -0.76848800	3.86868400	-0.95130500
C -0.87144700	4.03697700	2.44876400
Н 0.67547200	3.29508600	3.75898000
Н -2.21261700	4.68309300	0.88719800
Н -1.50617600	4.38794200	3.25736700
C 3.04628000	0.69100200	-2.88119800
Н 3.96079300	0.35251400	-3.38233100
Н 2.78716300	1.67437600	-3.28761100
Н 2.23680300	0.00499400	-3.14282300
C 2.87145500	3.66047300	-0.89048300
Н 2.48735100	4.68456400	-0.93936100
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Н 3.52178800	3.58682000	-0.01112300
Н 1.03435400	0.50124600	-0.87287100
Н -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 (\mathbf{R}_p)

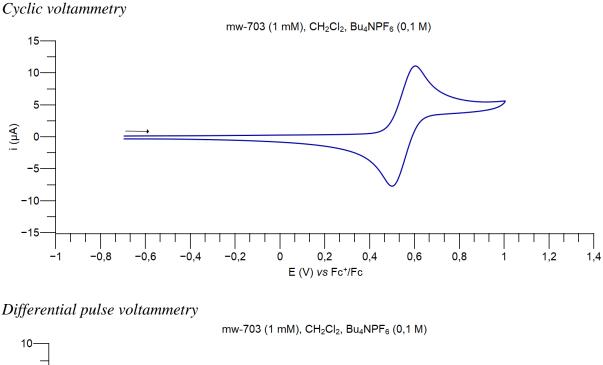
Energy (RB3LYP): -2079.048312 hartree Gibbs Free Energy: -2078.634361 hartree

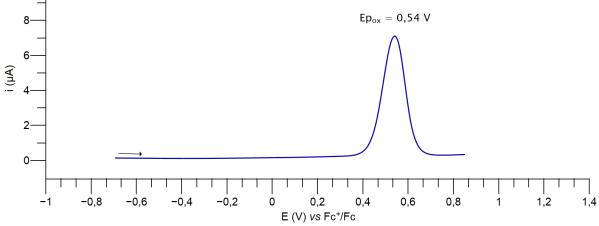
Fe -2.58754500	0.19355600	-1.25184500
C -1.57468000	-1.27283500	-0.23344900
C -2.72891200	-1.84405800	-0.88773700

С	-2.50335600	-1.61763000	-2.27169200
С	-1.24896900	-0.92543700	-2.41201500
Н	-0.85857800	-0.58905500	-3.36616700
С	-0.60669700	-0.69648000	-1.15224300
С	-4.43913400	1.09009700	-1.57895500
Н	-5.32316600	0.54147700	-1.87506800
С	-3.46127800	1.64318600	-2.46251700
Н	-3.47500100	1.58523800	-3.54242100
С	-2.43336700	2.23805000	-1.66590600
Н	-1.52771000	2.69708800	-2.03731200
С	-2.77563400	2.04869300	-0.29546600
Н	-2.18648500	2.35778000	0.55589900
С	-4.01668900	1.33754900	-0.23793200
Н	-4.53395200	1.02831300	0.65938500
Н	-3.19070100	-1.87707600	-3.06783400
N	3.04124500	0.35707600	0.21375700
С	3.76273600	-0.90877200	0.57218000
Н	3.38576500	-1.20414000	1.55586400
С	3.33729300	1.54811200	1.07351400
Н	4.41839800	1.74672000	1.06848600
С	3.34492500	-1.99370800	-0.41329600
С	3.78733300	-1.97908900	-1.74620400
С	2.49121900	-3.02715600	-0.00220500
С	3.38259700	-2.96916700	-2.64388700
Н	4.45826500	-1.19630200	-2.09254500
С	2.08582800	-4.02101200	-0.89805500
Η	2.13149800	-3.05228800	1.02319300
С	2.53039500	-3.99411000	-2.22123500
Η	3.73284000	-2.94062300	-3.67192000
Η	1.41584000	-4.80603700	-0.56028900
Н	2.21259700	-4.76224200	-2.92028100
С	2.66988900	2.76678200	0.44949400
С	1.28681700	2.98601400	0.54796400
С	3.44479000	3.69519600	-0.26040900
С	0.69797700	4.10393400	-0.04776300
Н	0.66176100	2.29201800	1.10364500
С	2.85931900	4.81500600	-0.85901700
Η	4.51947800	3.54471100	-0.33883500

С	1.48217400	5.02228700	-0.75272800
Н	-0.37298300	4.26062700	0.04167900
Н	3.47867000	5.52405900	-1.40112100
Н	1.02242100	5.89241000	-1.21241900
С	5.29247200	-0.76259900	0.66621500
Н	5.74473700	-1.73700100	0.87467400
Н	5.58748600	-0.08090200	1.46956800
Н	5.72157600	-0.38861100	-0.27028900
С	2.91276800	1.30263000	2.52782700
Н	3.03989400	2.22201900	3.10677000
Н	3.52733000	0.52845300	2.99718300
Н	1.86862700	0.98622000	2.60020300
Н	3.32007900	0.60561200	-0.73723300
Η	-3.57385100	-2.33924700	-0.42958100
Li	1.02829000	-0.14531000	-0.04091000
S	-1.09401300	-1.50107000	1.42998800
С	-2.31691600	-0.65275800	2.60579300
0	-1.15373800	-2.90874900	1.84458100
0	0.17048300	-0.73611700	1.65036000
F	-2.00542000	-1.00026700	3.86041900
F	-3.57001000	-1.05526500	2.34232500
F	-2.25894800	0.68269000	2.50838800

L) Voltammograms for compound 1





The measurements were done in dry, oxygen-free, CH_2Cl_2 , using Bu_4PF_6 (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	Epa ^[a]	Epc ^[a]	i pa/ i 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 = $100 \text{ mV} \cdot \text{s}^{-1}$. [a] For the ferrocene core, from CV experiments. [b] From DPV experiments.

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