From deprotometalation of ferrocenyl ketones to fused ferrocene structures

Madani Hedidi, William Erb,* Sirine Boussandel, Yury S. Halauko,* Vadim E. Matulis, Jean-Pierre Hurvois, Marielle Blot, Thierry Roisnel, Ali Samarat and Florence Mongin*

Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France

Laboratoire de Chimie des Matériaux, Catalyse et Réactivité, Département de Chimie, Faculté des Sciences Exactes et d'Informatique, Université Hassiba Benbouali de Chlef, Ouled Fares Chlef, BP 78C, 02180 Chlef, Algérie

University of Carthage, Faculty of Sciences of Bizerte, Laboratory of Hetero-Organic Compounds and Nanostructured Materials (LR18ES11), Zarzouna, 7021 Bizerte, Tunisia

Department of Chemistry, Belarusian State University, 14 Leningradskaya St., 220030 Minsk, Belarus

E-mails: florence.mongin@univ-rennes.fr (F. Mongin), hys@tut.by (Y. S. Halauko), william.erb@univ-rennes.fr (W. Erb)

Table of contents

A) Computational Details, Calculated NPA Charges and pK_a Values, Computed Gas Phase Acidities

Computational Details

In order to study the C–H acidity and related effects of the considered ferrocene ketones and their complexes, as well as to compare it with similar systems, we used the approach developed earlier and applied successfully, including ferrocene carboxamides [1] and ferrocenesulfoxides [2].

Correspondingly, all electronic structure calculations were carried out using standard DFT methods implemented in Gaussian 16 package [3]. We used the CAM-B3LYP hybrid functional [4]. The structures of stable conformers for each species were obtained by full geometry optimization without any symmetry constraints from different initial guesses (including XRD structures where available). The LANL2DZ basis set [5] with the effective core potential was used to describe 'heavy' atoms of Fe, Br and I, while the 6-31G(d) basis set [6] was used for the rest of the atoms during optimizations. Vibrational frequencies were calculated in order to characterize stationary points and calculate zero-point vibrational energies (ZPVE) and thermal corrections. The single point energies and NPA charges, in turn, were computed at the CAM-B3LYP/LANL2DZ + 6-311+G(d,p) level.

The Gibbs energies of isolated species were computed, and then gas-phase acidity ΔG_{acid} was defined as the Gibbs energy of deprotonation of the corresponding substrate R–H (R–H(g) → R^-(g) + H^+(g)):

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

The 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) in a modeled solvent media:

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

here furan with pK_a(THF) = 35.6 [7] was used as the probe compound. The solvent influence during calculations was accounted for with a help of polarized continuum model (IEF-PCM) [8] with the default parameters for THF in order to simulate the experimental conditions.

Calculated NPA Charges and pK_a Values

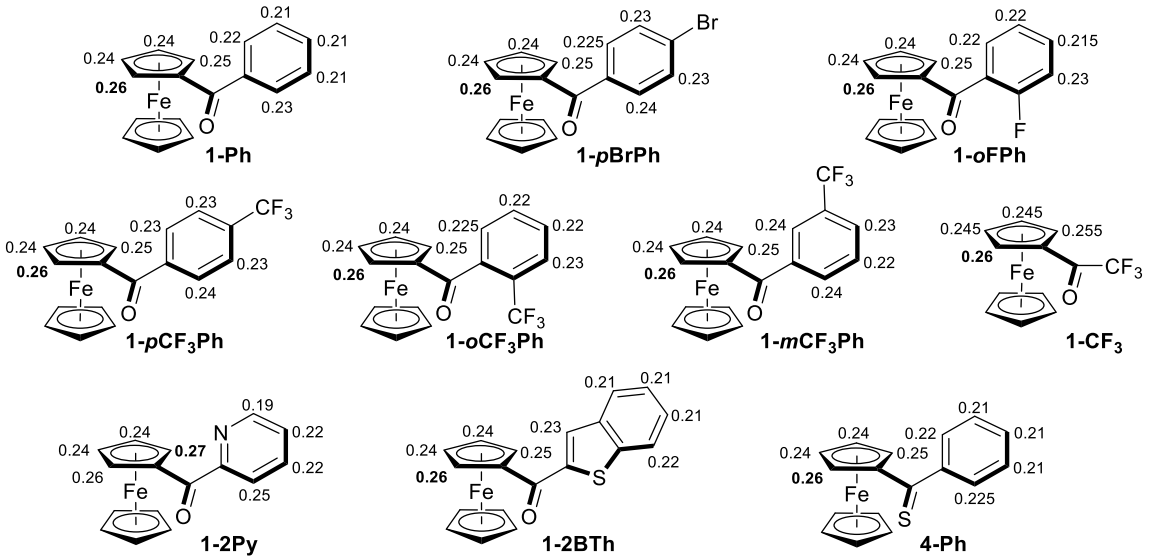


Figure S1. NPA charges on hydrogen atoms in isolated molecules of ferrocene ketones.

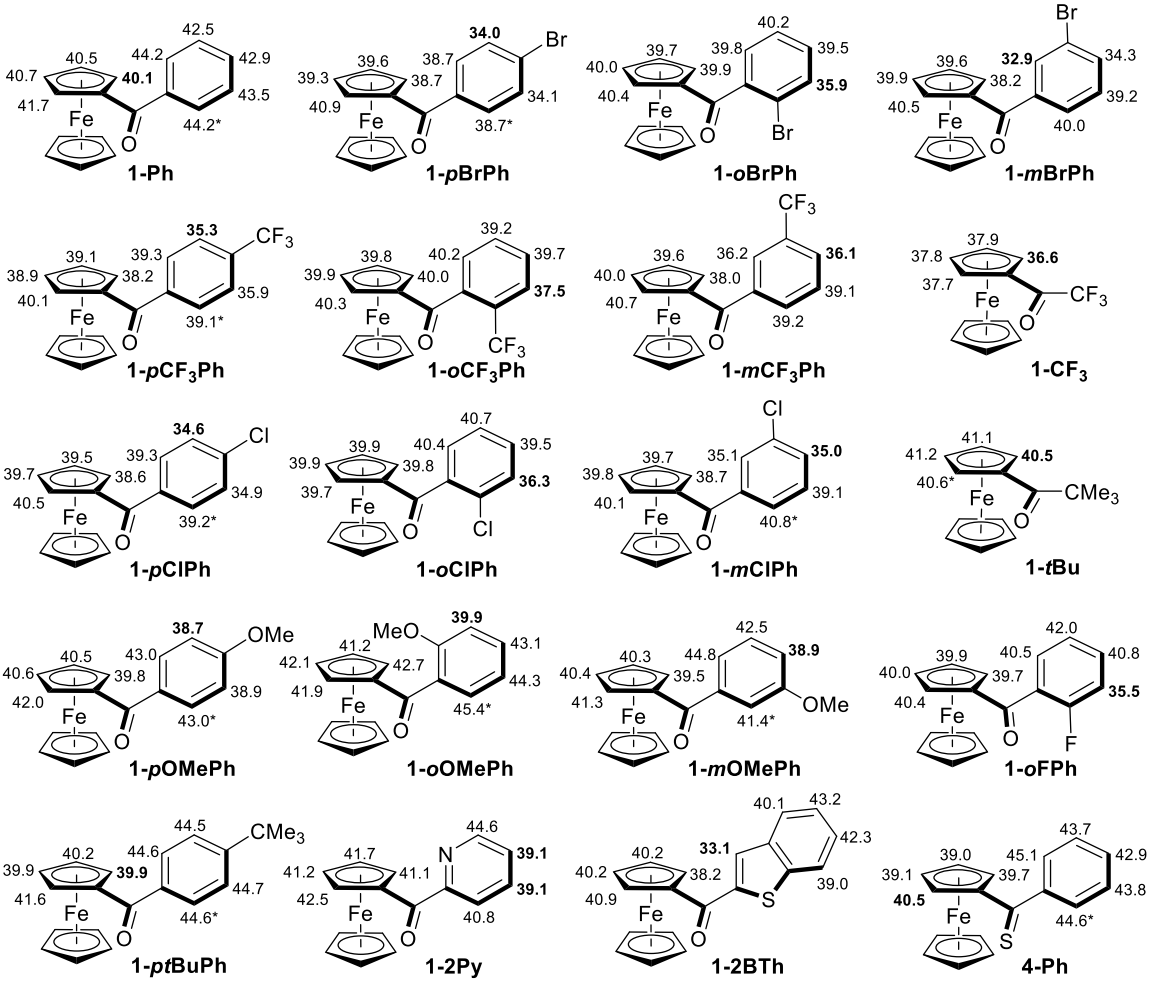


Figure S2. pK_a values calculated for ferrocene ketones in THF (an asterisk means that deprotonation in the corresponding position predicted to lead to interring rotation in order to reduce electron repulsion).

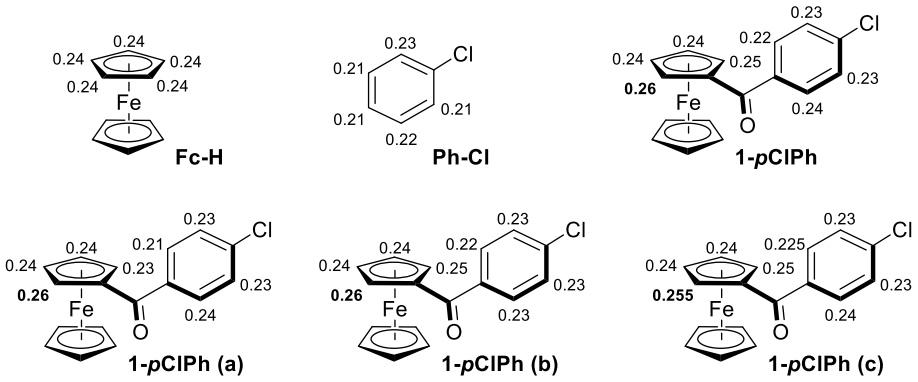


Figure S3. NPA charges of ferrocene, chlorobenzene and (4-chlorobenzoyl)ferrocene (**1-*p*ClPh**) (top); Impact of conformation on NPA charges: C=O in the plane of the two rings (dihedral angles of 0; **a**), in the plane of the ferrocene cyclopentadienyl (**b**), and in the plane of the phenyl (**c**) (bottom).

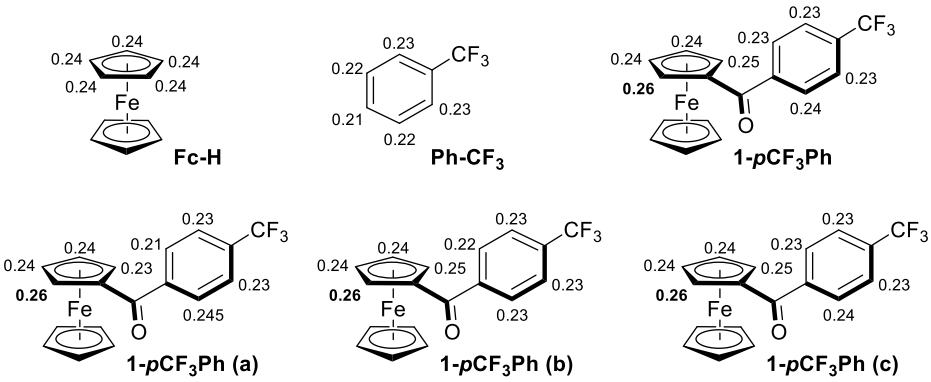


Figure S4. NPA charges of ferrocene, (trifluoromethyl)benzene and [4-(trifluoromethyl)benzoyl]-ferrocene (**1-*p*CF$_3$Ph**) (top); Impact of conformation on NPA charges: C=O in the plane of the two rings (dihedral angles of 0; **a**), in the plane of the ferrocene cyclopentadienyl (**b**), and in the plane of the phenyl (**c**) (bottom).

Computed Gas Phase Acidities

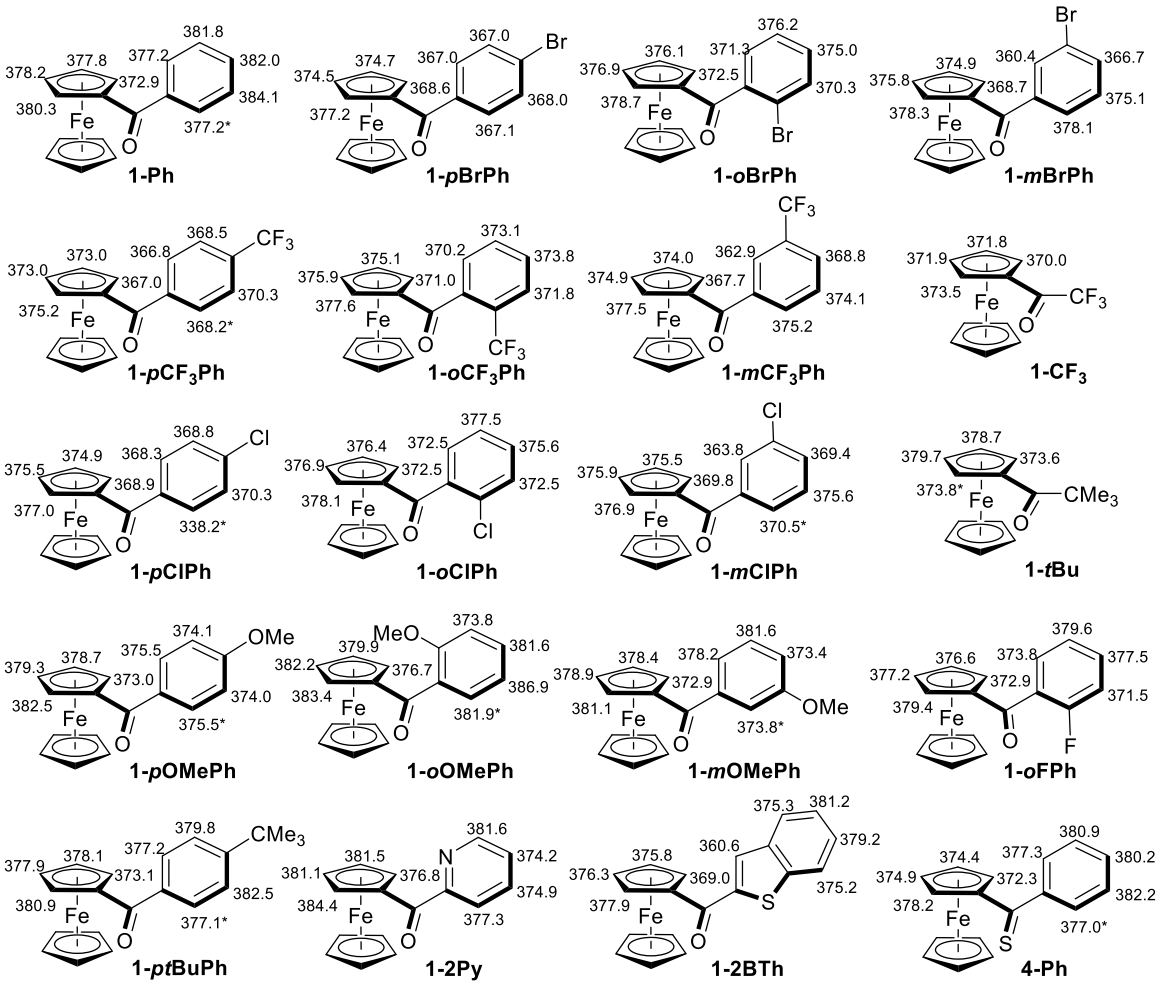


Figure S5. Computed gas phase acidities ($\Delta_{acid}G$, kcal·mol^{-1}) of the investigated ferrocene ketones.

B) General and Safety considerations, Crystallography and Electrochemistry

General

All reactions were carried out in Schlenk tubes under a dry argon atmosphere. Tetrahydrofuran (THF), Et_2O, toluene, xylene and dioxane were freshly distilled under argon from sodium-benzophenone. CH_2Cl_2, *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) were distilled under argon over CaH_2 prior to use. 2,2,6,6-Tetramethylpiperidine (TMPH), di[(*R*)-1-phenylethyl]amine ((*R*)-PEAH) and di[(*S*)-1-phenylethyl]amine ((*S*)-PEAH) were distilled over CaH_2 under reduced pressure and stored under argon. All alkyllithiums were titrated before use [9]. 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 aluminum backed plates pre-coated with silica gel (Merck, Silica Gel 60 F254) and visualized by exposure to UV light. Melting points were measured on a Kofler apparatus. Infrared (IR) spectra were taken on an ATR Perkin-Elmer Spectrum 100 spectrometer, and the main absorption wavenumbers are given in cm^{-1}. ^1H and $^{13}C\{^1H\}$ nuclear magnetic resonance (NMR) spectra were recorded at 300 K either on a Bruker Avance III HD spectrometer fitted with a BBFO probe at 500 MHz and 126 MHz respectively, or on a Bruker Avance III spectrometer fitted with a BBFO probe at 400 MHz and 100 MHz respectively, or on a Bruker Avance III spectrometer fitted with a BBFO probe at 300 MHz and 75.4 MHz respectively. ^1H chemical shifts (δ) are given in ppm relative to the solvent residual peak, and $^{13}C\{^1H\}$ chemical shifts (δ) are given in ppm relative to the central peak of the solvent signal [10]. Cp refers to the unsubstituted cyclopentadienyl ring of ferrocene. Specific rotations were determined from the observed rotation α measured on a Perkin Elmer 341 polarimeter (589 nm; 20 °C) using the equation $[\alpha] = (100 \cdot \alpha)/(l \cdot c)$ with the path length (l) given in dm and the concentrations (c) given in g/100 mL.

$ZnCl_2 \cdot$TMEDA was prepared as reported previously [11].

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 X-ray diffraction data of the compounds **1-*p*ClPh, 1-*m*BrPh, 2-*o*OMePh, 2-*p*OMePh, 2-*o*ClPh, 2-*p*ClPh, (*R*$_P$)-2-*o*BrPh, (*S*$_P$)-2-*o*BrPh, 2-*p*BrPh and 2-*p*CF$_3$Ph** were collected at the temperature indicated in the compound description by using a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector with monochromatized Mo-Kα radiation (λ = 0.71073 Å).

The X-ray diffraction data of the compounds **1-C≡CPh**, **1-*o*FPh** and **1-*o*OMePh** were collected at the temperature indicated in the compound description by using a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON III detector with monochromatized Mo-Kα radiation (λ = 0.71073 Å).

The X-ray diffraction data were collected at the temperature indicated in the compound description by using a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 70 with monochromatized Mo-Kα radiation (λ = 0.71073 Å) for **(*R*P)-2-Ph** and with monochromatized Cu-Kα radiation (λ = 1.54184 Å) for **1-*p*CF$_3$Ph** and compound **12**.

The X-ray diffraction data of the compounds **1-2BTh**, **1-*m*CF$_3$Ph** and **1-*o*CF$_3$Ph** were collected at the temperature indicated in the compound description by using a APEXII Kappa-CCD Bruker AXS diffractometer equipped with a CCD-LDI-APEX2 detector with monochromatized Mo-Kα radiation (λ = 0.71073 Å).

The X-ray diffraction data of the compounds **2'-2BTh**, **2"-2BTh** and **2'-2Py** were collected at the temperature indicated in the compound description by using a XtaLAB Synergy diffractometer equipped with a Hybrid Pixel Array detector with monochromatized Mo-Kα radiation (λ = 0.71073 Å).

The crystal structures were solved by dual-space algorithm using *SHELXT* program [12], and then refined with full-matrix least-square methods based on F^2 (*SHELXL* program) [13]. 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 2024.2.0.

Electrochemistry

Measurements were performed in dry, oxygen-free DMF for reduction studies and CH_2Cl_2 for oxidation studies 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 DMF of CH_2Cl_2 before use. The reference electrode was Ag/AgCl separated from the solution by a glass frit, while the counter electrode was a glassy carbon rod.

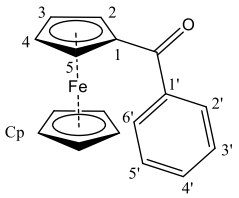
C) Procedures and Analyses of the Compounds

General procedure A for the synthesis of the ferrocene ketones [14, 15].

$AlCl_3$ (1.1 equiv) wad added portionwise to a solution of ferrocene and the acyl chloride (1.2 equiv) in dry CH_2Cl_2 (1 M) at 0 °C. After addition, the reaction mixture was warmed to rt and stirred for 1 h. The reaction mixture was cooled to 0 °C and water was added dropwise. After addition, the reaction mixture was stirred at rt for 10 min. Layers were separated and the product was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, 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) to give the title product.

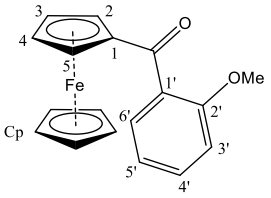
Benzoylferrocene (1-Ph)

It was prepared according to the general procedure A from ferrocene (3.7 g, 20 mmol), $AlCl_3$ (2.9 g) and PhCOCl (2.8 mL), and was isolated (eluent: petroleum ether-AcOEt-Et_3N 89:9:2) in 84% yield (4.9 g) as a red solid. Rf (petroleum ether-AcOEt 90:10) 0.30. Mp 110-111 °C. IR (ATR) ν 722, 803, 821, 852, 877, 952, 1002, 1025, 1057, 1166, 1288, 1311, 1332, 1375, 1410, 1439, 1450, 1577, 1598, 1624 (C=O), 2972, 3664 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.20 (s, 5H, Cp), 4.58 (s, 2H, H3 and H4), 4.90 (s, 2H, H2 and H5), 7.46 (t, 2H, J = 7.5 Hz, H3' and H5'), 7.54 (t, 1H, J = 7.4 Hz, H4'), 7.90 (d, 2H, J = 7.5 Hz, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.3 (5CH, Cp), 71.6 (2CH, C2 and C5), 72.7 (2CH, C3 and C4), 78.3 (C, C1, *C*-C(O)Ph), 128.2 (2CH, C2' and C6', or C3' and C5'), 128.3 (2CH, C2' and C6', or C3' and C5'), 131.6 (CH, C4'), 139.9 (C, C1'), 199.2 (C, C=O) ppm. These data are similar to those obtained for a commercial sample.



(2-Methoxybenzoyl)ferrocene (1-*o*OMePh)

It was prepared according to the general procedure A from ferrocene (2.8 g, 15 mmol), $AlCl_3$ (2.2 g) and 2-methoxybenzoyl chloride (2.7 mL), and was isolated (eluent: petroleum ether-AcOEt 90:10) in 65% yield (3.2 g) as a red solid. Rf (petroleum ether-AcOEt 80:20) 0.40. Mp 130-132 °C. IR (ATR) ν 660, 733, 755, 825, 859, 954, 1004, 1023, 1040, 1108, 1164, 1245, 1267, 1298, 1341, 1375, 1397, 1413, 1444, 1487, 1598, 1643 (C=O), 2837, 2942, 3099 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H, OMe), 4.22 (s, 5H, Cp), 4.52 (t, 2H, J = 2.0 Hz, H3 and H4), 4.74 (t, 2H, J = 1.9 Hz, H2 and H5), 6.98 (dd, 1H, J = 8.9 and 1.0 Hz, H3'), 7.02 (td, 1H, J = 7.4 and 1.0 Hz, H5'), 7.40-7.44 (m, 2H, H4' and H6') ppm. These data are close to those reported previously [16]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 55.7 (CH_3, OMe), 70.2 (5CH, Cp), 71.2 (2CH, C2 and C5), 72.6 (2CH, C3 and C4), 79.5 (C, C1, *C*-C(O)Ar), 111.6 (CH, C3'), 120.1 (CH, C5'), 128.5 (CH, C6'), 130.5 (C, C1'), 131.2 (CH, C4'), 156.6 (C, C2'), 199.6 (C, C=O) ppm.



*Crystal data for **1-oOMePh**.* $C_{18}H_{16}FeO_2$, M = 320.16, T = 150(2) K; monoclinic P $2_1/c$ (I.T.#14), a = 8.8454(3), b = 11.9401(4), c = 13.6967(4) Å, β = 96.6420(10) °, V = 1436.87(8) $Å^3$. Z = 4, d = 1.480 $g.cm^{-3}$, μ = 1.050 mm^{-1}. A final refinement on F^2 with 3252 unique intensities and 191 parameters converged at $\omega R(F^2)$ = 0.0730 (R_F = 0.0305) for 2833 observed reflections with $I > 2\sigma(I)$. CCDC 2490197.

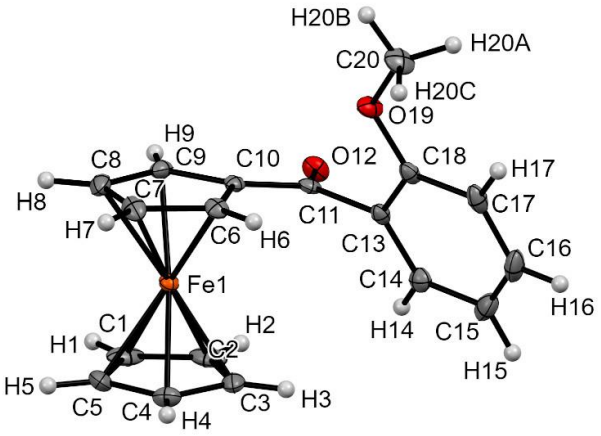
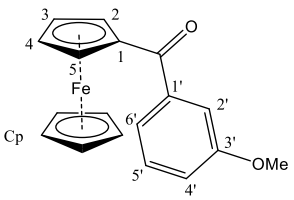


Figure S6. Molecular structure of compound **1-*o*OMePh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.464(3), C10−Cg2···Cg1−C3 = –42.05 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C9−C10−C11−O12 = –7.03(3), O12−C11−C13−C18 = –118.9(2).

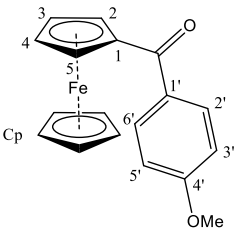
(3-Methoxybenzoyl)ferrocene (1-*m*OMePh)

It was prepared according to the general procedure A from ferrocene (1.0 g, 5.4 mmol), $AlCl_3$ (0.79 g) and 3-methoxybenzoyl chloride (0.76 mL), and was isolated (eluent: heptane-AcOEt 80:20) in 81% yield (1.2 g) as a red oil. IR (ATR) ν 694, 757, 784, 826, 890, 1003, 1041, 1107, 1150, 1245, 1289, 1376, 1442, 1485, 1579, 1637 (C=O), 3093 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.88 (s, 3H, OMe), 4.21 (s, 5H, Cp), 4.58 (t, 2H, *J* = 2.0 Hz, H3 and H4), 4.92 (t, 2H, *J* = 2.0 Hz, H2 and H5), 7.09 (ddd, 1H, *J* = 8.2, 2.7 and 1.0 Hz, H4'), 7.37 (t, 1H, *J* = 7.9 Hz, H5'), 7.42 (dd, 1H, *J* = 2.7 and 1.5 Hz, H2'), 7.50 (dt, 1H, *J* = 7.6 and 1.3 Hz, H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 55.3 (CH_3, OMe), 70.1 (5CH, Cp), 71.4 (2CH, C2 and C5), 72.5 (2CH, C3 and C4), 78.0 (C, C1, *C*-C(O)Ar), 113.1 (CH, C2'), 117.3 (CH, C4'), 120.5 (CH, C6'), 129.1 (CH, C5'), 140.9 (C, C1'), 159.3 (C, C3'), 198.5 (C, C=O) ppm. These data are similar to those reported previously [16].



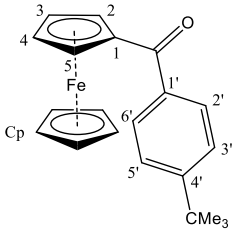
(4-Methoxybenzoyl)ferrocene (1-*p*OMePh)

It was prepared according to the general procedure A from ferrocene (1.0 g, 5.4 mmol), $AlCl_3$ (0.79 g) and 4-methoxybenzoyl chloride (0.73 mL), and was isolated (eluent: petroleum ether-AcOEt 80:20; Rf 0.40) in 80% yield (1.2 g) as a red solid. Mp 72-74 °C (lit. [17] 74-75 °C). IR (ATR) ν 711, 736, 769, 788, 824, 841, 954, 1003, 1025, 1049, 1106, 1160, 1184, 1250, 1286, 1305, 1334, 1353, 1376, 1397, 1414, 1440, 1509, 1569, 1597, 1627, 1709, 2047, 2838, 2935, 3093, 3933 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.89 (s, 3H, OMe), 4.20 (s, 5H, Cp), 4.56 (t, 2H, *J* = 1.9 Hz, H3 and H4), 4.89 (t, 2H, *J* = 1.9 Hz, H2 and H5), 6.96 (AA'BB', 2H, *J* = 8.9 Hz, C3' and C5'), 7.95 (AA'BB', 2H, *J* = 9.0 Hz, C2' and C6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 55.6 (CH_3, OMe), 70.3 (5CH, Cp), 71.6 (2CH, C2 and C5), 72.3 (2CH, C3 and C4), 78.9 (C, C1, *C*-C(O)Ar), 113.6 (2CH, C3' and C5'), 130.6 (2CH, C2' and C6'), 132.5 (C, C1'), 162.6 (C, C4'), 197.5 (C, C=O) ppm. The ^1H and ^{13}C NMR data are as reported previously, except the assignments of C2/C5 and C3/C4 [18].



(4-*tert*-Butylbenzoyl)ferrocene (1-*pt*BuPh)

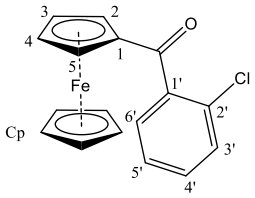
It was prepared according to the general procedure A from ferrocene (1.0 g, 5.4 mmol), $AlCl_3$ (0.79 g) and 4-*tert*-butylbenzoyl chloride (1.0 mL), and was isolated (eluent: heptane-AcOEt 80:20) in 59% yield (1.1 g) as a red solid. Mp 132-134 °C (lit. [19] 139-141 °C; lit. [20] 124-126 °C). IR (ATR) ν 668, 711, 731, 754, 775, 821, 838, 850, 876, 910, 953, 1002, 1015, 1026, 1049, 1106, 1170, 1198, 1266, 1287, 1312, 1334, 1376, 1398, 1407, 1441, 1558, 1604, 1624 (C=O), 1736, 2867, 2904, 2959, 3085 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.37 (s, 9H, *t*Bu), 4.21 (s, 5H, Cp), 4.57 (t, 2H, J = 2.0 Hz, H3 and H4), 4.92 (t, 2H, J = 2.0 Hz, H2 and H5), 7.48 (AA'BB', 2H, J = 8.8 Hz, H3' and H5'), 7.87 (AA'BB', 2H, J = 8.8 Hz, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.3 ($3CH_3$, C*Me*$_3$), 35.2 (C, *C*Me$_3$), 70.3 (5CH, Cp), 71.7 (2CH, C2 and C5), 72.4 (2CH, C3 and C4), 78.7 (C, C1, *C*-C(O)Ar), 125.3 (2CH, C3' and C5'), 128.3 (2CH, C2' and C6'), 137.2 (C, C1'), 155.2 (C, C4'), 198.8 (C, C=O) ppm. These NMR data are as reported, except the assignments of a few signals [21].



The title compound was also obtained as follows. To benzoylferrocene (**1-Ph**; 0.30 g, 1.0 mmol) in THF (2.5 mL) at –80 °C, was added dropwise *t*BuLi (1.4 M in pentane, 0.80 mL, 1.1 mmol). After 15 min stirring at this temperature, a solution of I_2 (0.28 g, 1.1 mmol) in THF (2 mL) was added and the reaction mixture was stirred for a further 15 min. A saturated aqueous solution of $Na_2S_2O_3$ (5 mL) was added, and the product was extracted with AcOEt. After drying the combined organic layers over anhydrous $MgSO_4$, the solvent was evaporated under reduced pressure, and the iodide was purified by column chromatography over silica gel (eluent: petroleum ether-AcOEt 80:20; Rf 0.75). The title product was isolated in 80% yield (0.275 g) as a red solid. The analyses are as above.

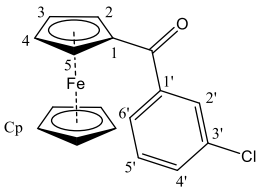
(2-Chlorobenzoyl)ferrocene (1-*o*ClPh)

It was prepared according to the general procedure A from ferrocene (1.0 g, 5.4 mmol), $AlCl_3$ (0.79 g) and 2-chlorobenzoyl chloride (0.68 mL), and was isolated (eluent: heptane-AcOEt 90:10) in 78% yield (1.1 g) as a red solid. Mp 98-100 °C (lit. [22] 97-99 °C). IR (ATR) ν 705, 738, 753, 825, 855, 955, 1004, 1027, 1039, 1063, 1107, 1180, 1273, 1291, 1339, 1353, 1375, 1397, 1413, 1444, 1470, 1590, 1644 (C=O), 3095 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.27 (s, 5H, Cp), 4.59 (t, 2H, J = 2.0 Hz, H3 and H4), 4.74 (t, 2H, J = 2.0 Hz, H2 and H5), 7.33 (td, 1H, J = 7.2 and 1.7 Hz, H5'), 7.39 (td, 1H, J = 7.5 and 2.0 Hz, H4'), 7.45 (dd, 1H, J = 7.5 and 1.6 Hz, H3'), 7.50 (dd, 1H, J = 7.0 and 2.1 Hz, H6') ppm. These data are close to those reported previously [22]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 69.9 (5CH, Cp), 70.8 (2CH, C2 and C5), 72.8 (2CH, C3 and C4), 78.1 (C, C1, *C*-C(O)Ar), 126.1 (CH, C4'), 128.4 (CH, C6'), 130.0 (CH, C5'), 130.5 (C, C2'), 130.6 (CH, C3'), 139.1 (C, C1'), 198.2 (C, C=O) ppm.



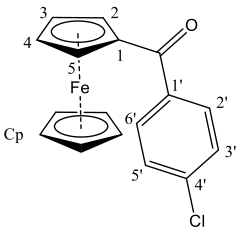
(3-Chlorobenzoyl)ferrocene (1-*m*ClPh)

It was prepared according to the general procedure A from ferrocene (1.0 g, 5.4 mmol), $AlCl_3$ (0.79 g) and 3-chlorobenzoyl chloride (0.69 mL), and was isolated (eluent: heptane-AcOEt 90:10) in 83% yield (1.2 g) as a red solid. Mp 98-100 °C (lit. [18] 96-98 °C). IR (ATR) ν 658, 686, 731, 756, 825, 878, 1003, 1029, 1050, 1079, 1107, 1175, 1286, 1335, 1353, 1377, 1412, 1444, 1567, 1592, 1637 (C=O), 3094 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.20 (s, 5H, Cp), 4.60 (t, 2H, J = 1.9 Hz, H3 and H4), 4.87 (t, 2H, J = 2.0 Hz, H2 and H5), 7.39 (t, 1H, J = 7.8 Hz, H5'), 7.50 (ddd, 1H, J = 8.0, 2.2 and 1.1 Hz, H4'), 7.76 (dt, 1H, J = 7.6 and 1.4 Hz, H6'), 7.91 (t, 1H, J = 1.8 Hz, H2') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.4 (5CH, Cp), 71.5 (2CH, C2 and C5), 72.9 (2CH, C3 and C4), 77.7 (C, C1, *C*-C(O)Ar), 126.2 (CH, C6'), 128.3 (CH, C2'), 129.7 (CH, C5'), 131.5 (CH, C4'), 134.3 (C, C3'), 141.3 (C, C1'), 197.6 (C, C=O) ppm. The ^1H and ^{13}C NMR data are as reported previously, except the assignments of C2/C5 and C3/C4 [18].



(4-Chlorobenzoyl)ferrocene (1-*p*ClPh)

It was prepared according to the general procedure A from ferrocene (1.0 g, 5.4 mmol), $AlCl_3$ (0.79 g) and 4-chlorobenzoyl chloride (0.51 mL), and was isolated (eluent: heptane-AcOEt 90:10) in 76% yield (1.1 g) as a red solid. Mp 114-116 °C (lit. [18] 115-116 °C). IR (ATR) ν 697, 732, 763, 825, 841, 855, 951, 1014, 1029, 1049, 1090, 1107, 1167, 1287, 1335, 1353, 1377, 1397, 1412, 1444, 1488, 1566, 1589, 1634 (C=O), 3096 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.20 (s, 5H, Cp), 4.60 (t, 2H, J = 2.0 Hz, H3 and H4), 4.88 (t, 2H, J = 2.0 Hz, H2 and H5), 7.45 (AA'BB', 2H, J = 8.5 Hz, H3' and H5'), 7.86 (AA'BB', 2H, J = 8.5 Hz, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.4 (5CH, Cp), 71.6 (2CH, C2 and C5), 72.9 (2CH, C3 and C4), 78.1 (C, C1, *C*-C(O)Ar), 128.7 (2CH, C3' and C5'), 129.7 (2CH, C2' and C6'), 137.9 (C, C1'), 138.2 (C, C4'), 197.9 (C, C=O) ppm. The ^1H and ^{13}C NMR data are as reported previously, except the assignments of C2/C5 and C3/C4 [18].



*Crystal data for **1**-**pClPh***. $C_{17}H_{13}ClFeO$, M = 324.57, T = 150(2) K; monoclinic P $2_1/n$ (I.T.#14), a = 6.1359(5), b = 27.961(2), c = 8.0162(7) Å, β = 103.056(3) °, V = 1339.75(19) $Å^3$. Z = 4, d = 1.609 $g.cm^{-3}$, μ = 1.315 mm^{-1}. A final refinement on F^2 with 3039 unique intensities and 181 parameters converged at $\omega R(F)^2$ = 0.0694 (R_F = 0.0305) for 2667 observed reflections with $I > 2\sigma$. CCDC 2490198.

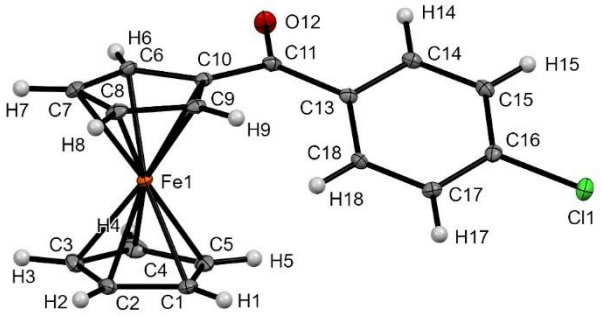
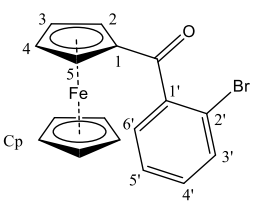


Figure S7. Molecular structure of compound **1-*p*ClPh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.482(3), C10−Cg2···Cg1−C5 = 6.78 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C6−C10−C11−O12 = 19.9(3), O12−C11−C13−C14 = 18.8(3).

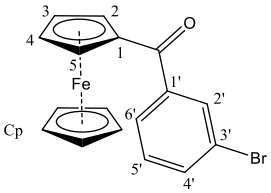
(2-Bromobenzoyl)ferrocene (1-*o*BrPh)

It was prepared according to the general procedure A from ferrocene (2.2 g, 12 mmol), $AlCl_3$ (1.8 g) and 4-bromobenzoyl chloride (1.9 mL), and was isolated (eluent: petroleum ether-AcOEt 90:10; Rf 0.31) in 78% yield (3.45 g) as a red solid. Mp 114-116 °C. IR (ATR) ν 683, 702, 731, 748, 778, 823, 853, 871, 954, 1003, 1024, 1056, 1107, 1179, 1269, 1289, 1339, 1353, 1374, 1397, 1442, 1466, 1563, 1586, 1646 (C=O), 3094, 3932 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.28 (s, 5H, Cp), 4.59 (t, 2H, J = 1.9 Hz, H3 and H4), 4.73 (t, 2H, J = 1.9 Hz, H2 and H5), 7.32 (ddd, 1H, J = 8.0, 7.4 and 1.8 Hz, H4'), 7.39 (td, 1H, J = 7.5 and 1.2 Hz, H5'), 7.50 (dd, 1H, J = 7.6 and 1.7 Hz, H6'), 7.64 (dd, 1H, J = 8.0 and 1.2 Hz, H3') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.3 (5CH, Cp), 71.3 (2CH, C2 and C5), 73.1 (2CH, C3 and C4), 78.4 (C, C1, *C*-C(O)Ar), 119.6 (C, C2'), 126.9 (CH, C5'), 128.8 (CH, C6'), 131.0 (CH, C4'), 133.6 (CH, C3'), 141.5 (C, C1'), 199.7 (C, C=O) ppm. These data are close to those reported previously [23].



(3-Bromobenzoyl)ferrocene (1-*m*BrPh)

It was prepared according to the general procedure A from ferrocene (1.0 g, 5.4 mmol), $AlCl_3$ (0.79 g) and 3-bromobenzoyl chloride (0.71 mL), and was isolated (eluent: heptane-AcOEt 90:10) in 68% yield (1.1 g) as a red solid. Mp 88-90 °C. IR (ATR) ν 683, 708, 728, 754, 824, 862, 963, 1002, 1029, 1049, 1107, 1173, 1285, 1335, 1353, 1377, 1410, 1445, 1562, 1636 (C=O), 1723, 2924, 3095 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.21 (s, 5H, Cp), 4.61 (t, 2H, J = 1.9 Hz, H3 and H4), 4.87 (t, 2H, J = 1.9 Hz, H2 and H5), 7.33 (t, 1H, J = 7.8 Hz, H5'), 7.66 (ddd, 1H, J = 7.9, 1.8 and 0.9 Hz, H4' or H6'), 7.80 (dt, 1H, J = 7.7 and 1.1 Hz, H4' or H6'), 8.09 (t, 1H, J = 1.7 Hz, H2') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.4 (5CH, Cp), 71.6 (2CH, C2 and C5), 73.0 (2CH, C3 and C4), 77.7 (C, C1, *C*-C(O)Ar), 122.4 (C, C3'), 126.7 (CH, C6'), 130.0 (CH, C5'), 131.3 (CH, C2'), 134.4 (CH, C4'), 141.6 (C, C1'), 197.7 (C, C=O) ppm. The ^1H and ^{13}C NMR data are as reported previously, except the assignments of C2/C5 and C3/C4 [18].



*Crystal data for **1**-**mBrPh***. $C_{17}H_{13}BrFeO$, M = 369.03, T = 150(2) K; triclinic P -1 (I.T.#2), a = 6.1415(6), b = 10.0793(8), c = 11.2942(11) Å, α = 89.031(3), β = 81.784(3), γ = 81.171(3) °, V = 683.75(11) $Å^3$. Z = 2, d = 1.792 $g.cm^{-3}$, μ = 4.015 mm^{-1}. A final refinement on F^2 with 3109 unique intensities and 181 parameters converged at $\omega R(F^2)$ = 0.0843 (R_F = 0.0294) for 2852 observed reflections with $I > 2\sigma(I)$. CCDC 2490199.

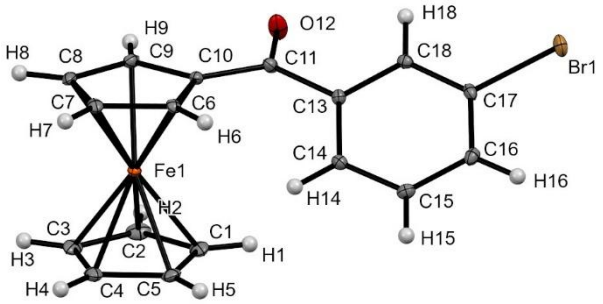
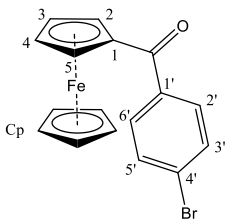


Figure S8. Molecular structure of compound **1-*m*BrPh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.474(3), C10−Cg2···Cg1−C1 = 7.58 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C9−C10−C11−O12 = 14.7(3), O12−C11−C13−C18 = 21.7(3).

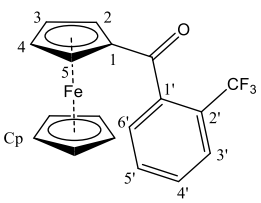
(4-Bromobenzoyl)ferrocene (1-*p*BrPh)

It was prepared according to the general procedure A from ferrocene (2.2 g, 12 mmol), $AlCl_3$ (1.8 g) and 4-bromobenzoyl chloride (3.2 g), and was isolated (eluent: petroleum ether-AcOEt-$CHCl_3$ 93:5:2 to 88:10:2) in 57% yield (2.5 g) as a red solid. Mp 120-122 °C (lit. [18] 117-119 °C). IR (ATR) ν 688, 732, 759, 824, 854, 951, 1010, 1028, 1047, 1069, 1107, 1167, 1284, 1302, 1335, 1353, 1376, 1393, 1412, 1442, 1482, 1561, 1584, 1630 (C=O), 3092, 3928 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.20 (s, 5H, Cp), 4.60 (t, 2H, J = 2.0 Hz, H3 and H4), 4.87 (t, 2H, J = 2.0 Hz, H2 and H5), 7.60-7.62 (m, 2H, H3' and H5'), 7.77-7.79 (m, 2H, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.4 (5CH, Cp), 71.6 (2CH, C2 and C5), 72.9 (2CH, C3 and C4), 77.9 (C, C1, *C*-C(O)Ar), 126.4 (C, C4'), 129.8 (2CH, C2' and C6'), 131.6 (2CH, C3' and C5'), 138.6 (C, C1'), 198.0 (C, C=O) ppm. The ^1H and ^{13}C NMR data are as reported previously, except the assignments of C2/C5 and C3/C4 [18].



[2-(Trifluoromethyl)benzoyl]ferrocene (1-*o*CF_3Ph)

It was prepared according to the general procedure A from ferrocene (1.9 g, 10 mmol), $AlCl_3$ (1.5 g) and 2-(trifluoromethyl)benzoyl chloride (1.8 mL), and was isolated (eluent: petroleum ether-AcOEt 90:10; Rf 0.36) in 46% yield (1.65 g) as a red solid. Mp 102-103 °C. IR (ATR) ν 738, 770, 792, 831, 850, 859, 888, 914, 952, 963, 1006, 1032, 1064, 1105, 1133, 1157, 1282, 1312, 1339, 1351, 1374, 1396, 1409, 1443, 1579, 1603, 1655 (C=O), 2973, 3121 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.27 (s, 5H, Cp), 4.58 (t, 2H, J = 2.0 Hz, H3 and H4), 4.67 (t, 2H, J = 2.0 Hz, H2 and H5), 7.58 (tq, 1H, J = 7.2 and 0.8 Hz, H4'), 7.63 (t, 1H, J = 7.0 Hz, H5'), 7.66 (d, 1H, J = 7.0 Hz, H6'), 7.73 (dd, 1H, J = 7.7 and 0.7 Hz, H3') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.3 (5CH, Cp), 71.1 (2CH, C2 and C5), 72.8 (2CH, C3 and C4), 79.1 (d, C, J = 1.9 Hz, C1, *C*-C(O)Ar), 123.8 (q, C, J = 274 Hz, CF_3), 126.9 (q, CH, J = 4.8 Hz, C3'), 127.7 (q, C, J = 32.2 Hz, C2', *C*-CF_3), 128.4 (CH, C6'), 129.8 (CH, C4'), 131.3 (CH, C5'), 139.5 (q, C, J = 2.2 Hz, C1'), 200.2 (C, C=O) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –57.5 ppm. Anal. Calcd for $C_{18}H_{13}F_3FeO$ (358.14): C, 60.37; H, 3.66. Found: C, 60.23; H, 3.55%.



Crystal data for ***1-oCF₃Ph***. $C_{18}H_{13}F_3FeO$, M = 358.13, T = 150(2) K; orthorhombic $P\,2_1\,2_1\,2_1$ (I.T.#19), a = 7.4381(6), b = 10.2075(10), c = 19.292(2) Å, V = 1464.7(3) $Å^3$. Z = 4, d = 1.624 $g.cm^{-3}$, μ = 1.063 mm^{-1}. A final refinement on F^2 with 3274 unique intensities and 209 parameters converged at $\omega R(F^2)$ = 0.1393 (R_F = 0.0488) for 2983 observed reflections with $I > 2\sigma$. CCDC 2490200.

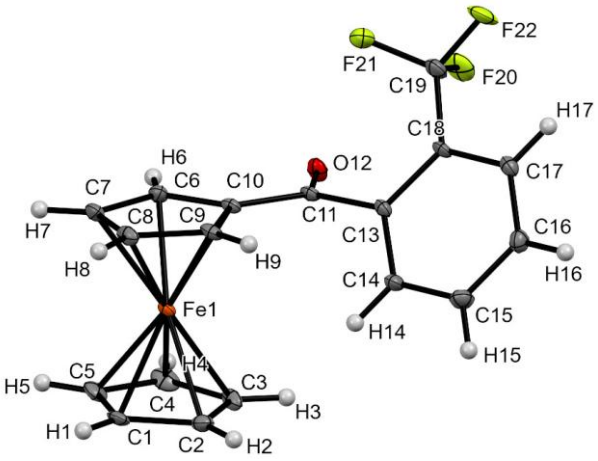
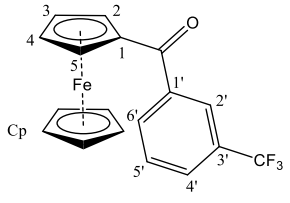


Figure S9. Molecular structure of compound **1-*o*CF_3Ph** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.471(8), C10−Cg2···Cg1−C3 = 7.58 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C6−C10−C11−O12 = 2.5(8), O12−C11−C13−C18 = 53.0(7).

[3-(Trifluoromethyl)benzoyl]ferrocene (1-*m*CF_3Ph)

It was prepared according to the general procedure A from ferrocene (1.2 g, 6.0 mmol), $AlCl_3$ (0.88 g) and 3-(trifluoromethyl)benzoyl chloride (1.1 mL), and was isolated (eluent: petroleum ether-AcOEt 95:5) in 42% yield (0.91 g) as a red solid. Rf (petroleum ether-AcOEt 90:10) 0.58. Mp 100-101 °C (lit. [24] 100 °C). IR (ATR) ν 755, 776, 823, 857, 927, 940, 972, 1002, 1028, 1072, 1097, 1108, 1155, 1276, 1329, 1377, 1435, 1455, 1607, 1629 (C=O), 1697, 2971, 3111 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.24 (s, 5H, Cp), 4.65 (t, 2H, J = 2.0 Hz, H3 and H4), 4.88 (t, 2H, J = 2.0 Hz, H2 and H5), 7.62 (tt, 1H, J = 7.8 and 0.8 Hz, H5'), 7.81 (dq, 1H, J = 7.7 and 0.7 Hz, H4'), 8.07 (dm, 1H, J = 7.7 Hz, H6'), 8.28 (hept, 1H, J = 0.8 Hz, H2') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.5 (5CH, Cp), 71.6 (2CH, C2 and C5), 73.2 (2CH, C3 and C4), 77.7 (C, C1, *C*-C(O)Ar), 124.0 (q, C, J = 272 Hz, CF_3), 125.3 (q, CH, J = 3.8 Hz, C2'), 128.2 (q, CH, J = 3.6 Hz, C4'), 129.1 (CH, C5'), 130.8



(q, C, J = 32.7 Hz, C3', *C*-CF_3), 131.5 (CH, C6'), 140.4 (C, C1'), 197.9 (C, C=O) ppm. These data are close to those reported previously [24]. $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –62.6 ppm.

Crystal data for ***1*-m*CF₃Ph***. $C_{18}H_{13}F_3FeO$, M = 358.13, T = 150(2) K; triclinic $P\,\bar{1}$ (I.T.#2), a = 6.1744(3), b = 10.1638(6), c = 11.9860(6) Å, α = 101.405(2), β = 97.354(2), γ = 99.850(2) °, V = 716.19(7) Å^3. Z = 2, d = 1.661 g.cm^{-3}, μ = 1.087 mm^{-1}. A final refinement on F^2 with 3232 unique intensities and 208 parameters converged at $\omega R(F)^2$ = 0.1138 (R_F = 0.0370) for 2853 observed reflections with $I > 2\sigma$. CCDC 2490201.

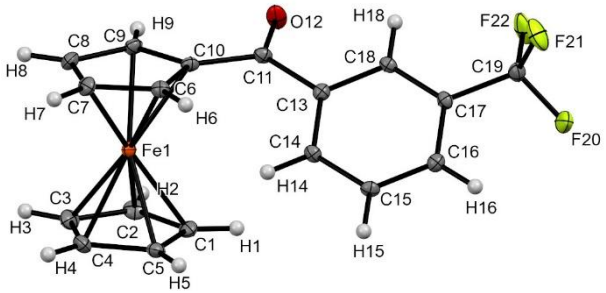
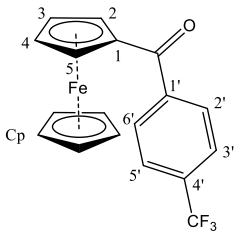


Figure S10. Molecular structure of compound **1-*m*CF₃Ph** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°] C10−C11 = 1.469(3), C10−Cg2···Cg1−C1 = 3.19 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C9−C10−C11−O12 = 18.0(3), O12−C11−C13−C18 = 20.2(3).

[4-(Trifluoromethyl)benzoyl]ferrocene (1-*p*CF₃Ph)

It was prepared according to the general procedure A from ferrocene (1.0 g, 5.4 mmol), $AlCl_3$ (0.79 g) and 4-(trifluoromethyl)benzoyl chloride (0.96 mL), and was isolated (eluent: petroleum ether-AcOEt 90:10; Rf 0.31) in 24% yield (0.46 g) as a red solid. Mp 166-168 °C. IR (ATR) ν 689, 721, 776, 824, 851, 953, 1016, 1029, 1053, 1070, 1108, 1160, 1294, 1327, 1379, 1408, 1451, 1509, 1574, 1628 (C=O), 3105 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.22 (s, 5H, Cp), 4.64 (t, 2H, J = 2.0 Hz, H3 and H4), 4.88 (t, 2H, J = 2.0 Hz, H2 and H5), 7.74 (AA'BB', 2H, J = 8.1 Hz, H3' and H5'), 7.98 (AA'BB', 2H, J = 8.0 Hz, H2' and H6') ppm. These NMR data are as reported [25]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.5 (5CH, Cp), 71.6 (2CH, C2 and C5), 73.2 (2CH, C3 and C4), 77.6 (C, C1, *C*-C(O)Ar), 123.9 (q, C, J = 272 Hz, CF_3), 125.5 (q, 2CH, J = 3.7 Hz, C3' and C5'), 128.4 (2CH, C2' and C6'), 133.1 (q, C, J = 32.6 Hz, C4'), 143.0 (C, C1'), 198.3 (C, C=O) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ –62.9 ppm.



Crystal data for ***1*-p*CF₃Ph***. $C_{18}H_{13}F_3FeO$, M = 358.13, T = 150(2) K; triclinic $P\,\bar{1}$ (I.T.#2), a = 6.1296(6), b = 10.1169(7), c = 12.0335(12) Å, α = 90.469(5), β = 99.276(6), γ = 98.812(5) °, V = 727.36(11) Å^3. Z = 2, d = 1.635 g.cm^{-3}, μ = 8.641 mm^{-1}. A final refinement on F^2 with 3026 unique intensities and 229 parameters converged at $\omega R(F)^2$ = 0.1183 (R_F = 0.0439) for 2870 observed reflections with $I > 2\sigma$. CCDC 2490202.

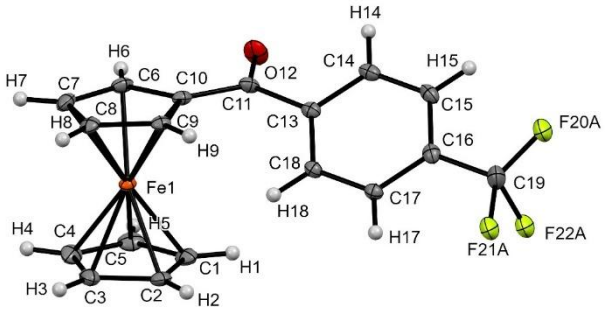
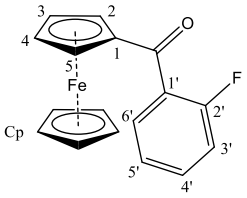


Figure S11. Molecular structure of compound **1-*p*CF$_3$Ph** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.469(4), C10−Cg2···Cg1−C1 = 4.71 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C6−C10−C11−O12 = 12.9(4), O12−C11−C13−C14 = 27.7(4).

(2-Fluorobenzoyl)ferrocene (1-*o*FPh)

It was prepared according to the general procedure A from ferrocene (3.35 g, 18 mmol), $AlCl_3$ (2.6 g) and 2-fluorobenzoyl chloride (2.6 mL), and was isolated (eluent: petroleum ether-AcOEt 90:10; Rf 0.35) in 80% yield (4.4 g) as a red solid. Mp 105-106 °C (lit. [24] 105 °C). IR (ATR) ν 719, 758, 775, 816, 833, 856, 949, 1005, 1048, 1099, 1152, 1173, 1220, 1258, 1296, 1340, 1375, 1412, 1451, 1481, 1610, 1639 (C=O), 2988, 3676 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.22 (s, 5H, Cp), 4.59 (t, 2H, J = 2.0 Hz, H3 and H4), 4.81 (td, 2H, J = 2.0 and 0.8 Hz, H2 and H5), 7.17 (ddd, 1H, J = 9.7, 8.3 and 1.1 Hz, H3'), 7.23 (td, 1H, J = 7.5 and 1.0 Hz, H5'), 7.47 (dddd, 1H, J = 8.3, 7.1, 5.1 and 1.8 Hz, H4'), 7.56 (td, 1H, J = 7.2 and 1.8 Hz, H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 70.4 (5CH, Cp), 71.2 (d, 2CH, J = 1.9 Hz, C2 and C5), 73.1 (2CH, C3 and C4), 78.7 (C, C1, *C*-C(O)Ar), 116.4 (d, CH, J = 21.9 Hz, C3'), 124.0 (d, CH, J = 3.4 Hz, C5'), 129.0 (d, C, J = 15.6 Hz, C1'), 129.2 (d, CH, J = 3.4 Hz, C6'), 132.1 (d, CH, J = 8.1 Hz, C4'), 159.3 (d, C, J = 251 Hz, C2', C-F), 196.5 (C, C=O) ppm. These data are close to those reported previously [24]. ^{19}F{^{1}H} NMR ($CDCl_3$) δ –113.4 ppm.



*Crystal data for **1-oFPh**.* $C_{17}H_{13}FFeO$, M = 308.12, T = 150(2) K; monoclinic P $2_1/n$ (I.T.#14), a = 10.8525(2), b = 7.37910(10), c = 16.4000(3) Å, β = 97.5520(10) °, V = 1301.95(4) Å^3. Z = 4, d = 1.572 g.cm^{-3}, μ = 1.161 mm^{-1}. A final refinement on F^2 with 2986 unique intensities and 181 parameters converged at $\omega R(F)^2$ = 0.0592 (R_F = 0.0224) for 2785 observed reflections with $I > 2\sigma$. CCDC 2490203.

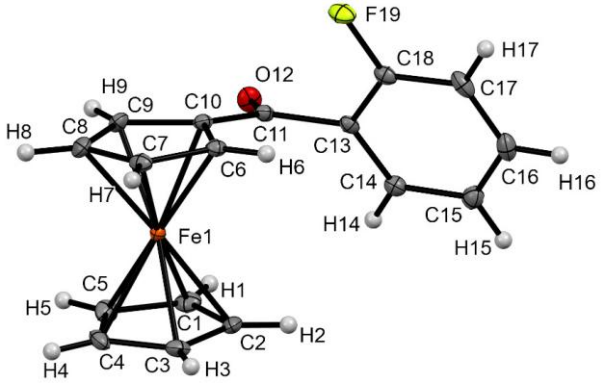
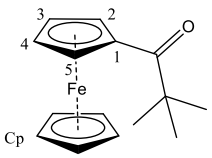


Figure S12. Molecular structure of compound **1-*o*FPh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.465(2), C10−Cg2···Cg1−C1 = -22.38 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C9−C10−C11−O12 = 4.6(2), O12−C11−C13−C18 = 119.1(1).

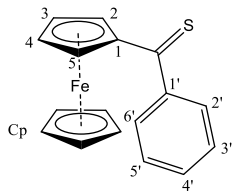
Pivaloylferrocene (1-*t*Bu)

It was prepared according to the general procedure A from ferrocene (1.0 g, 5.4 mmol), $AlCl_3$ (0.79 g) and pivaloyl chloride (0.80 mL), and was isolated (eluent: petroleum ether; Rf 0.63) in 53% yield (0.77 g) as an orange powder. Mp 91-92 °C (lit. [17] 92-93 °C). IR (ATR) ν 767, 802, 820, 878, 937, 969, 1002, 1022, 1034, 1066, 1107, 1212, 1284, 1329, 1364, 1378, 1397, 1412, 1436, 1459, 1477, 1533, 1643, 2871, 2930, 2969, 3090 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.33 (s, 9H, *t*Bu), 4.18 (s, 5H, Cp), 4.46 (t, 2H, J = 2.0 Hz, H3 and H4), 4.85 (t, 2H, J = 2.0 Hz, H2 and H5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 28.3 ($3CH_3$, C*Me*$_3$), 44.4 (C, *C*Me$_3$), 69.9 (5CH, Cp), 71.2 (2CH, C2 and C5), 71.3 (2CH, C3 and C4), 76.9 (C, C1, *C*-C(O)Ar), 210.5 (C, C=O) ppm. The NMR data are as reported [25].



*(Phenylcarbonothioyl)ferrocene (**4-Ph**)*

It was prepared as reported previously [26]. A solution of benzoylferrocene (**1-Ph**; 2.9 g, 10 mmol) and Lawesson's reagent (2.6 g, 6.5 mmol) in toluene (20 mL) was stirred at 65 °C for 15 min. The reaction mixture was cooled to rt. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt 95:5) gave the title product in 87% yield (2.7 g) as a purple powder. Rf (petroleum ether-AcOEt 91:9) 0.61. Mp 73-74 °C (lit. [26] 71-73 °C). IR (ATR) ν 767, 825, 839, 874, 932, 1005, 1028, 1053, 1064, 1085, 1107, 1175, 1241, 1279, 1292, 1313, 1325, 1351, 1373, 1399, 1429, 1444, 1592, 1643, 1981, 2988 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.16 (s, 5H, Cp), 4.82 (t, 2H, J = 2.0 Hz, H3 and H4), 5.04 (t, 2H, J = 2.0 Hz, H2 and H5), 7.36 (t, 2H, J = 7.6 Hz, H3' and H5'), 7.46 (t, 1H, J = 7.4 Hz, H4'), 7.66 (d, 2H, J = 7.2 Hz, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 72.3 (5CH, Cp), 72.8 (2CH, C2 and C5), 75.0 (2CH, C3 and C4), 89.5 (C, C1), 127.1 (2CH, C2' and C6'), 127.8 (2CH, C3' and C5'), 130.3 (CH, C4'), 149.1 (C, C1'), 238.9 (C, C=S) ppm. These data correspond to those reported [26].

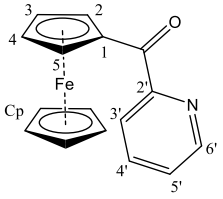


*N-Methoxy-N-methylferrocenecarboxamide (**1-NMeOMe**) [27]*

Oxalyl chloride (5.3 mL, 62.5 mmol) was added dropwise to a suspension of ferrocenecarboxylic acid (5.75 g, 25 mmol) and DMF (50 µL) in CH_2Cl_2 at rt. The reaction mixture was stirred for 15 min and the volatiles were removed under reduced pressure. CH_2Cl_2 (125 mL) was added, followed by *N*,*O*-dimethylhydroxylamine hydrochloride (3.7 g, 37.5 mmol) and pyridine (6.05 mL, 75 mmol). The reaction mixture was stirred at rt for 10 min and then kept at –20 °C for 16 h. The reaction mixture was washed with aqueous HCl (1 M), aqueous NaOH (1 M), water, dried over $MgSO_4$, and concentrated under reduced pressure to give the title product in 88% yield (6.1 g) as an orange solid. It was directly involved in the next step.

*(2-Pyridoyl)ferrocene (**1-2Py**)*

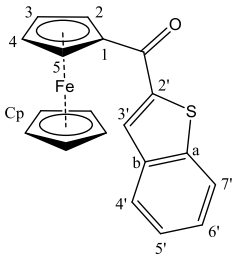
It was prepared by adapting a reported procedure [27]. A solution of 2-bromopyridine (0.715 mL, 1.2 g, 7.5 mmol) in Et_2O (9 mL) was added dropwise to a solution of *n*BuLi (1.5 M in hexanes, 5.85 mL, 7.5 mmol) in Et_2O (9 mL) at –80 °C. The reaction mixture was stirred at the same temperature for 2 h. This solution was cannulated onto a solution of **1-NMeOMe** (1.4 g, 5.0 mmol) in Et_2O (9 mL) at –80 °C. The reaction mixture was slowly warmed to –50 °C and aqueous NH_4Cl (saturated) was added. The reaction mixture was warmed to rt and the product was extracted with AcOEt. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt 95:5; Rf 0.27) gave the title product in 46% yield (1.0 g) as a red solid. Mp 94-95 °C. IR (ATR) ν 740, 758, 809, 829, 857, 879, 900, 953, 995, 1043, 1092, 1107, 1195, 1244, 1284, 1305, 1330, 1351, 1375, 1398, 1410, 1426, 1444, 1471, 1567, 1587, 1627 (C=O), 2988, 3060, 3677 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.13 (s, 5H, Cp), 4.63 (t, 2H, J = 2.0 Hz, H3 and H4), 5.37 (t, 2H, J =



2.0 Hz, H2 and H5), 7.45 (ddd, 1H, *J* = 7.6, 4.8 and 1.3 Hz, H5'), 7.86 (td, 1H, *J* = 7.7 and 1.8 Hz, H4'), 8.05 (dt, 1H, *J* = 7.8 and 1.1 Hz, H3'), 8.70 (ddd, 1H, *J* = 4.8, 1.8 and 0.9 Hz, H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.3 (5CH, Cp), 72.6 (2CH, C2 and C5), 73.1 (2CH, C3 and C4), 77.3 (C, C1, *C*-C(O)Ph), 122.8 (CH, C3'), 126.0 (CH, C5'), 136.9 (CH, C4'), 148.6 (CH, C6'), 156.2 (C, C2'), 196.1 (C, C=O) ppm. Anal. Calcd for $C_{16}H_{13}FeNO$ (291.13): C, 66.01; H, 4.50; N, 4.81. Found: C, 66.27; H, 4.54; N, 4.61%.

*(2-Benzothienoyl)ferrocene (**1-2BTh**)*

It was prepared by adapting a reported procedure [27]. *n*BuLi (1.25 M in hexanes, 6.0 mL, 7.5 mmol) was added to a solution of benzothiophene (1.0 g, 7.5 mmol) in THF at –20 °C, and the reaction mixture was stirred at the same temperature for 1 h. This solution was cannulated onto a solution of **1-NMeOMe** (1.4 g, 5.0 mmol) in THF (10 mL) at –20 °C, and the reaction mixture was stirred at the same temperature for 15 min. Aqueous NH_4Cl (saturated) was added. The reaction mixture was warmed to rt and was extracted with AcOEt. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt 95:5 to 90:10) gave the title product in 56% yield (0.97 g) as a red solid (0.97 g, 56%). Mp 157-158 °C (lit. [28] 157-159 °C). IR (ATR) ν 725, 742, 757, 785, 821, 840, 885, 944, 1005, 1026, 1048, 1067, 1108, 1135, 1192, 1294, 1328, 1381, 1445, 1514, 1599 (C=O), 2989, 3676 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.26 (s, 5H, Cp), 4.65 (t, 2H, *J* = 2.0 Hz, H3 and H4), 5.11 (t, 2H, *J* = 2.0 Hz, H2 and H5), 7.43 (ddd, 1H, *J* = 8.3, 7.1 and 1.2 Hz, H5'), 7.48 (ddd, 1H, *J* = 8.4, 7.1 and 1.3 Hz, H6'), 7.90-7.94 (m, 2H, H4' and H7'), 8.14 (d, 1H, *J* = 0.8 Hz, H3') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.6 (5CH, Cp), 71.2 (2CH, C2 and C5), 72.8 (2CH, C3 and C4), 78.8 (C, C1, *C*-C(O)Ar), 122.9 (CH, C7'), 125.1 (CH, C5'), 125.7 (CH, C4'), 127.0 (CH, C6'), 128.4 (CH, C3'), 139.2 (C, Cb), 141.7 (C, Ca), 143.8 (C, C2'), 190.7 (C, C=O) ppm. The NMR data are as reported [27].



*Crystal data for **1-2BTh**.* $C_{19}H_{14}FeOS$, *M* = 346.21, *T* = 150(2) K; monoclinic *P* $2_1/c$ (I.T.#14), *a* = 9.9165(3), *b* = 12.8474(3), *c* = 11.6381(3) Å, β = 100.4620(10) °, *V* = 1458.06(7) $Å^3$. *Z* = 4, *d* = 1.577 $g.cm^{-3}$, μ = 1.175 mm^{-1}. A final refinement on F^2 with 2920 unique intensities and 199 parameters converged at $\omega R(F^2)$ = 0.1353 (R_F = 0.0403) for 2592 observed reflections with $I > 2\sigma(I)$. CCDC 2490204.

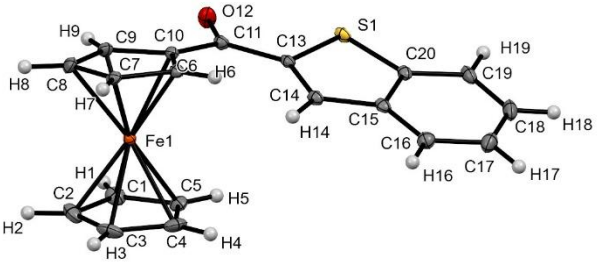
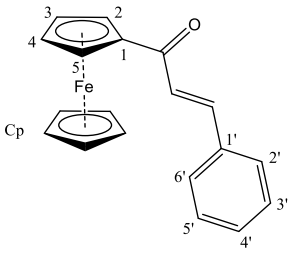


Figure S13. Molecular structure of compound **1-2BTh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.476(3), C10−Cg2···Cg1−C5 = 7.33 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C9−C10−C11−O12 = 15.7(3), O12−C11−C13−S1 = 8.8(3).

*(E)-(Cinnamoyl)ferrocene (**1-CH=CHPh**)*

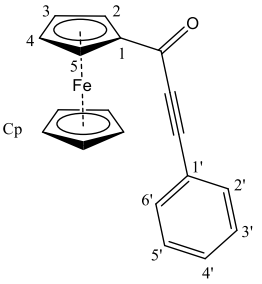
It was prepared as reported previously [29]. An aqueous solution of NaOH (50%, 2.6 mL, 50 mmol) was added dropwise to a solution of acetylferrocene (2.3 g, 10 mmol) and benzaldehyde (1.2 mL, 12 mmol) in EtOH (30 mL) at rt, and the reaction mixture was stirred for 2 h. The resulting solids were filtrated, washed with water and dissolved in AcOEt. The organic layer was dried over $MgSO_4$, and

concentrated under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt 90:10; Rf 0.40) gave the title product in 75% yield (2.4 g) as a red solid. Mp 135-136 °C (lit. [29] 139-141 °C). IR (ATR) ν 725, 758, 764, 822, 844, 858, 912, 924, 980, 992, 1031, 1067, 1079, 1204, 1239, 1288, 1322, 1340, 1353, 1377, 1411, 1447, 1457, 1496, 1574, 1596, 1647 (C=O), 3087 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.22 (s, 5H, Cp), 4.60 (t, 2H, J = 1.9 Hz, H3 and H4), 4.92 (t, 2H, J = 1.9 Hz, H2 and H5), 7.14 (d, 1H, J = 15.6 Hz, C*H*=CHPh), 7.40-7.45 (m, 3H, H3', H4' and H5'), 7.64-7.67 (m, 2H, H2' and H6'), 7.80 (d, 1H, J = 15.6 Hz, CH=C*H*Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 69.9 (2CH, C2 and C5), 70.2 (5CH, Cp), 72.9 (2CH, C3 and C4), 80.8 (C, C1), 123.1 (CH, *C*H=CH-Ph), 128.4 (2CH, C2' and C6'), 129.1 (2CH, C3' and C5'), 130.2 (CH, C4'), 135.3 (C, C1'), 140.9 (CH, CH=*C*H-Ph), 193.0 (C, C=O) ppm.



*(Phenylpropioloyl)ferrocene (**1-C≡CPh**)*

It was prepared as reported previously [30]. Trifluoroacetic anhydride (TFAA; 3.8 mL, 27.5 mmol) was added to a solution of phenylpropiolic acid (4.0 g, 27.5 mmol) in CH_2Cl_2 (125 mL) at rt, and the reaction mixture was stirred for 1 min. Ferrocene (4.65 g, 25 mmol) and triflic acid (8.9 mL, 0.10 mol) were sequentially added, and the reaction mixture was stirred at rt for 2 h. Water was added and the product was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt 90:10; Rf 0.32) gave the title product in 53% yield (4.2 g) as a dark red solid. Mp 109-110 °C. IR (ATR) ν 749, 780, 824, 844, 895, 994, 1002, 1029, 1072, 1107, 1229, 1295, 1338, 1353, 1374, 1411, 1448, 1488, 1605 (C=O), 2204, 2987, 3087 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.30 (s, 5H, Cp), 4.64 (t, 2H, J = 2.0 Hz, H3 and H4), 5.01 (t, 2H, J = 2.0 Hz, H2 and H5), 7.41-7.45 (m, 2H, H3' and H5'), 7.46-7.50 (m, 1H, H4'), 7.65-7.68 (m, 2H, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.7 (7CH, Cp, C2 and C5), 73.4 (2CH, C3 and C4), 80.7 (C, C1), 87.9 (C, *C*≡C-Ph), 89.7 (C, C≡*C*-Ph), 120.8 (C, C1'), 128.8 (2CH, C3' and C5'), 130.5 (CH, C4'), 132.9 (2CH, C2' and C6'), 181.3 (C, C=O) ppm. The NMR data are as reported [30].



*Crystal data for **1-C≡CPh***. $C_{19}H_{14}FeO$, M = 314.15, T = 150(2) K; orthorhombic $P\ n\ a\ 2_1$ (I.T.#33), a = 21.6675(12), b = 5.9808(4), c = 10.9996(7) Å, V = 1425.43(15) $Å^3$. Z = 4, d = 1.464 $g.cm^{-3}$, μ = 1.052 mm^{-1}. A final refinement on F^2 with 3127 unique intensities and 191 parameters converged at $\omega R(F^2)$ = 0.0831 (R_F = 0.0422) for 2557 observed reflections with $I > 2\sigma$. CCDC 2490205.

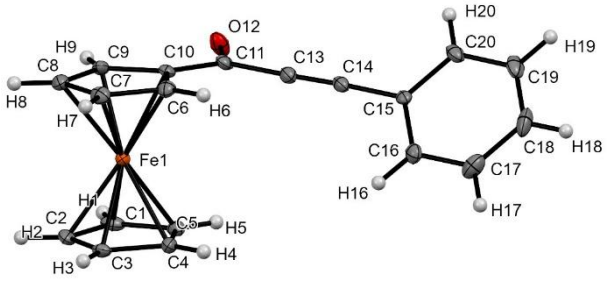
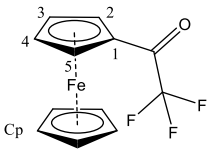


Figure S14. Molecular structure of compound **1-C≡CPh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.470(7), C10−Cg2···Cg1−C5 = 5.08 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C9−C10−C11−O12 = 8.3(8).

*[(Trifluoromethyl)carbonyl]ferrocene (**1-CF$_3$**)*

It was prepared as reported previously [31]. *t*BuLi (1.6 M solution in pentane, 33 mL, 50 mmol) was added dropwise to a solution of ferrocene (4.65 g, 25 mmol) and *t*BuOK (0.28 g, 2.5 mmol) in THF (180 mL) at –80 °C. After addition, the reaction was stirred at the same temperature for 1 h. *N*-Methyl-*N*-methoxytrifluoroacetamide (4.85 mL, 50 mmol) was added, and the reaction mixture was warmed to rt. Aqueous HCl (1 M) was added and the product was extracted with AcOEt. The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt-Et_3N 94:5:1) gave the title product in 71% yield (5.1 g) as a red solid. Rf (petroleum ether-AcOEt 90:10) 0.66. Mp < 50 °C. IR (ATR) ν 729, 765, 824, 839, 849, 876, 960, 1006, 1033, 1051, 1106, 1133, 1186, 1218, 1320, 1380, 1413, 1459, 1531, 1688 (C=O), 2971, 3097, 3665 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.30 (s, 5H, Cp), 4.75 (t, 2H, J = 2.0 Hz, H3 and H4), 4.98 (br s, 2H, H2 and H5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 70.8 (5CH, Cp), 70.8 (q, 2CH, J = 2.2 Hz, C2 and C5), 70.9 (q, C, J = 31.5 Hz, C1), 74.6 (2CH, C3 and C4), 116.9 (q, C, J = 291 Hz, CF_3), 186.5 (q, C, J = 35.1 Hz, C=O) ppm; ^{19}F{^{1}H} NMR ($CDCl_3$) δ –72.1 ppm. These data are similar to those reported in $(CD_3)_2SO$ [31].

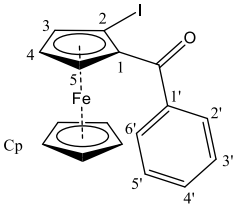


General procedure B for the deprotolithiation-iodination sequence on ferrocene ketones [32, 33].

A solution of *n*BuLi in hexane (1.1 equiv) was added dropwise to a solution of TMPH (1.2 equiv) in THF (0.36 M) at –15 °C and the reaction mixture was stirred for 5 min. This LiTMP solution was cooled to –20 °C and cannulated onto a solution of the ferrocene ketone and $ZnCl_2$·TMEDA (1.0 equiv) in THF (0.33 M). The reaction mixture was stirred for 1 h at –20 °C and a solution of I_2 (1.1 equiv) in THF (0.55 M) was added. The reaction mixture was warmed to rt, an aqueous saturated solution of $Na_2S_2O_3$ was added, and the product was extracted with AcOEt. The combined organic layers were washed with water, dried over $MgSO_4$, 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) to give the title product.

1-Benzoyl-2-iodoferrocene (2-Ph)

It was prepared according to the general procedure B from benzoylferrocene (**1-Ph**; 0.435 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 95:5; Rf 0.44) in 72% yield (0.45 g) as a red solid. Mp 65-66 °C (lit. [34] 83 °C). IR (ATR) ν 717, 799, 826, 836, 857, 896, 934, 985, 1004, 1030, 1048, 1066, 1104, 1152, 1178, 1190, 1250, 1317, 1348, 1368, 1419, 1448, 1576, 1597, 1630 (C=O), 1794, 2163, 3071, 3108 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.24 (s, 5H, Cp), 4.53 (t, 1H, J = 2.6 Hz, H4), 4.62 (dd, 1H, J = 2.8 and 1.4 Hz, H5), 4.85 (dd, 1H, J = 2.5 and 1.4 Hz, H3), 7.45 (t, 2H, J = 7.5 Hz, H3' and H5'), 7.55 (tt, 1H, J = 7.4 and 1.3 Hz, H4'), 7.85 (dd, 2H, J = 8.3 and 1.3 Hz, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 41.1 (C, C2, C-I), 71.6 (CH, C5), 72.5 (CH, C4), 73.4 (5CH, Cp), 77.8 (C, C1, *C*-C(O)Ar), 80.2 (CH, C3), 128.3 (2CH, C3' and C5'), 128.8 (2CH, C2' and C6'), 132.1 (CH, C4'), 139.3 (C, C1'), 197.9 (C, C=O) ppm. These data are as reported [34]. 12% of the starting **1-Ph** were recovered.



*Crystal data for (**R$_P$**)-**2-Ph***. $C_{17}H_{13}FeIO$, M = 416.02, T = 156(2) K; orthorhombic P 2_1 2_1 2_1 (I.T.#19), a = 7.9159(3), b = 10.5508(3), c = 17.0486(6) Å, V = 1423.88(8) Å^3. Z = 4, d = 1.941 g.cm^{-3}, μ = 3.218 mm^{-1}. A final refinement on F^2 with 3236 unique intensities and 181 parameters converged at $\omega R(F^2)$ = 0.0324 (R_F = 0.0134) for 3205 observed reflections with $I > 2\sigma$. CCDC 2490206.

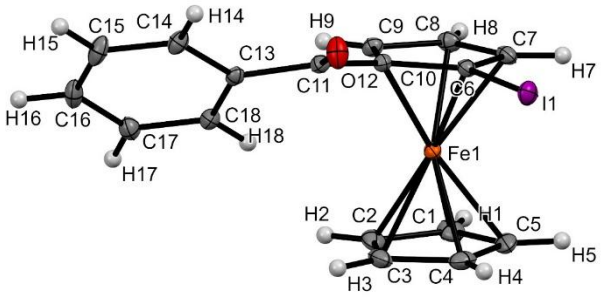
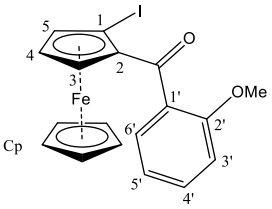


Figure S15. Molecular structure of compound **(*R*P)-2-Ph** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.475(3), C6−I1 = 2.082(2), C10−Cg2···Cg1−C3 = 2.74 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), Cg2−C6−I1 = 175.62, C6−C10−C11−O12 = 15.8(4), O12−C11−C13−C14 = 25.9(3).

1-Iodo-2-(2-methoxybenzoyl)ferrocene (2-*o*OMePh)

It was prepared according to the general procedure B, but using 1.5 equivalents of LiTMP and I_2, from (2-methoxybenzoyl)ferrocene (**1-*o*OMePh**; 0.32 g, 1.0 mmol) and was isolated (eluent: petroleum ether-AcOEt 95:5 to 90:10) in 94% yield (0.41 g) as a red solid. Rf (petroleum ether-AcOEt 90:10) 0.32. Mp 154-156 °C. IR (ATR) ν 660, 734, 754, 827, 866, 989, 1004, 1023, 1041, 1108, 1163, 1181, 1248, 1283, 1322, 1352, 1370, 1421, 1435, 1462, 1487, 1597, 1652, 2836, 2941, 3098 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.81 (s, 3H, OMe), 4.23 (s, 5H, Cp), 4.48 (t, 1H, J = 2.7 Hz, H4), 4.51 (dd, 1H, J = 2.8 and 1.5 Hz, H5), 4.83 (dd, 1H, J = 2.5 and 1.5 Hz, H3), 6.96 (dd, 1H, J = 8.4 and 1.0 Hz, H3'), 7.02 (td, 1H, J = 7.5 and 0.9 Hz, H5'), 7.39 (dd, 1H, J = 7.5 and 1.7 Hz, H6'), 7.43 (ddd, 1H, J = 8.3, 7.4 and 1.8 Hz, H4') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 39.1 (C, C2, C-I), 55.7 (CH_3, OMe), 72.1 (CH, C5), 73.0 (CH, C4), 73.2 (5CH, Cp), 77.2 (C, C1, *C*-C(O)Ar), 81.0 (CH, C3), 111.6 (CH, C3'), 120.3 (CH, C5'), 128.7 (CH, C6'), 130.3 (C, C1'), 131.5 (CH, C4'), 156.9 (C, C2'), 198.9 (C, C=O) ppm. Anal. Calcd for $C_{18}H_{15}FeIO_2$ (446.07): C, 48.47; H, 3.39. Found: C, 48.53; H, 3.56%. Using 1.1 equiv of LiTMP and I_2 from **1-*o*OMePh** (2.5 mmol) led to the title product in 89% yield while 9% of the starting **1-*o*OMePh** were recovered.



*Crystal data for **2-oOMePh***. $C_{18}H_{15}FeIO_2$, M = 446.05, T = 150(2) K; orthorhombic *P n a* 2_1 (I.T.#33), a = 14.4336(16), b = 7.3603(7), c = 30.087(3) Å, V = 3196.3(6) $Å^3$. Z = 8, d = 1.854 $g.cm^{-3}$, μ = 2.879 mm^{-1}. A final refinement on F^2 with 7371 unique intensities and 268 parameters converged at $\omega R(F^2)$ = 0.0823 (R_F = 0.0328) for 7239 observed reflections with $I > 2\sigma(I)$. CCDC 2490207.

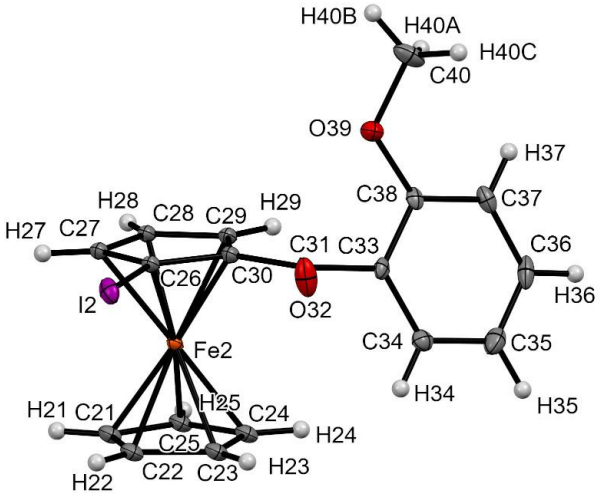
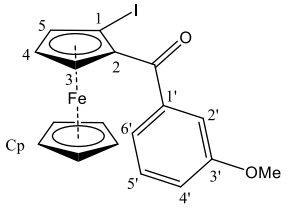


Figure S16. Molecular structure of compound **2-*o*OMePh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C30−C31 = 1.492(7), C26−I2 = 2.096(4), C30−Cg4···Cg3−C23 = 22.47 (Cg3 being the centroid of the C21−C22−C23−C24−C25 ring and Cg4 the one of the C26−C27−C28−C29−C30 ring), Cg4−C26−I2 = 176.92, C26−C30−C31−O32 = –10.1(8), O32−C31−C33−C38 = –105.7(7).

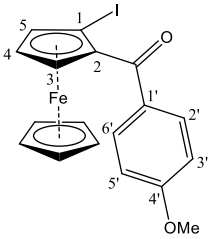
1-Iodo-2-(3-methoxybenzoyl)ferrocene (2-*m*OMePh)

It was prepared according to the general procedure, but using 1.5 equivalents of LiTMP and I_2, from (3-methoxybenzoyl)ferrocene (**1-*m*OMePh**; 0.32 g, 1.0 mmol), and was isolated (eluent: heptane-AcOEt 70:30) in 82% yield (0.37 g) as a red oil. IR (ATR) ν 692, 754, 784, 808, 903, 1002, 1040, 1108, 1167, 1237, 1264, 1288, 1318, 1352, 1371, 1429, 1450, 1484, 1579, 1646, 2935, 3100 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.86 (s, 3H, OMe), 4.24 (s, 5H, Cp), 4.52 (t, 1H, J = 2.6 Hz, H4), 4.64 (dd, 1H, J = 2.5 and 1.3 Hz, H3), 4.85 (dd, 1H, J = 2.0 and 1.4 Hz, H5), 7.09 (dd, 1H, J = 8.1 and 1.8 Hz, H4'), 7.35 (t, 1H, J = 7.8 Hz, H5'), 7.40-7.44 (m, 2H, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 41.0 (C, C1, C-I), 55.5 (CH_3, OMe), 71.6 (CH, C3), 72.5 (CH, C4), 73.3 (5CH, Cp), 77.6 (C, C2, *C*-C(O)Ar), 80.2 (CH, C5), 113.4 (CH, C2'), 118.2 (CH, C4'), 121.4 (CH, C6'), 129.2 (CH, C5'), 140.4 (C, C1'), 159.4 (C, C3'), 197.5 (C, C=O) ppm.



1-Iodo-2-(4-methoxybenzoyl)ferrocene (2-*p*OMePh)

It was prepared according to the general procedure B from (4-methoxybenzoyl)ferrocene (**1-*p*OMePh**; 0.48 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 90:10) in 67% yield (0.45 g) as a red solid. Rf (petroleum ether-AcOEt 80:20) 0.52. Mp 130-132 °C. IR (ATR) ν 708, 768, 789, 843, 865, 986, 1003, 1027, 1108, 1169, 1250, 1314, 1352, 1371, 1423, 1459, 1508, 1573, 1598, 1639, 2838, 2934, 3097 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.88 (s, 3H, OMe), 4.24 (s, 5H, Cp), 4.50 (t, 1H, J = 2.6 Hz, H4), 4.61 (dd, 1H, J = 2.7 and 1.4 Hz, H3), 4.80 (dd, 1H, J = 2.5 and 1.4 Hz, H5), 6.94 (AA'BB', 2H, J = 8.8 Hz, H3' and H5'), 7.89 (AA'BB', 2H, J = 8.8 Hz, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 41.6 (C, C1, C-I), 55.6 (CH_3, OMe), 71.2 (CH, C3), 71.8 (CH, C4), 73.3 (5CH, Cp), 79.4 (CH, C5), 79.6 (C, C2, *C*-C(O)Ar), 113.5 (2CH, C3' and C5'), 131.4 (2CH, C2' and C6'), 131.9 (C, C1'), 163.1 (C, C4'), 195.9 (C, C=O) ppm. Anal. Calcd for $C_{18}H_{15}FeIO_2$ (446.07): C, 48.47; H, 3.39. Found: C, 48.36; H, 3.21%. 12% of the starting **1-*p*OMePh** were recovered. Using 1.5 equiv of LiTMP and I_2 led to the title product in 91% yield.



Crystal data for ***2-*p*OMePh***. $C_{18}H_{15}FeIO_2$, M = 446.05, T = 150(2) K; monoclinic P $2_1/c$ (I.T.#14), a = 15.653(3), b = 7.4790(11), c = 13.326(2) Å, β = 99.338(6) °, V = 1539.4(4) $Å^3$. Z = 4, d = 1.925

g.cm^{-3}, μ = 2.989 mm^{-1}. A final refinement on F^2 with 3523 unique intensities and 200 parameters converged at $\omega R(F^2)$ = 0.0521 (R_F = 0.0224) for 3292 observed reflections with $I > 2\sigma(I)$. CCDC 2490208.

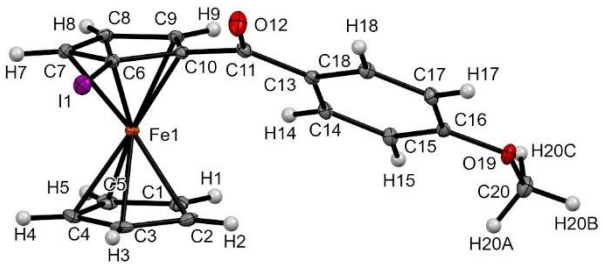
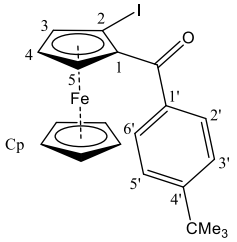


Figure S17. Molecular structure of compound **2-*p*OMePh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.490(3), C6−I1 = 2.089(2), C10−Cg2···Cg1−C2 = 3.12 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), Cg2−C6−I1 = 178.23, C6−C10−C11−O12 = –33.5(3), O12−C11−C13−C18 = –1.1(3).

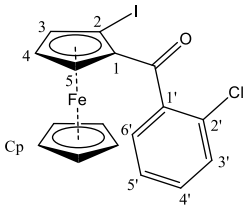
1-(4-*tert*-Butylbenzoyl)-2-iodoferrocene (2-*pt*BuPh)

It was prepared according to the general procedure B, but using 2 equivalents of LiTMP and I_2, from (4-*tert*-butylbenzoyl)ferrocene (**1-*pt*BuPh**; 0.35 g, 1.0 mmol), and was isolated (eluent: heptane-AcOEt 70:30) in 94% yield (0.44 g) as a red oil. IR (ATR) ν 764, 824, 880, 937, 996, 1056, 1079, 1108, 1211, 1263, 1301, 1365, 1392, 1416, 1460, 1477, 1662 (C=O), 2870, 2930, 2968, 3099 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9H, *t*Bu), 4.24 (s, 5H, Cp), 4.51 (t, 1H, J = 2.6 Hz, H4), 4.64 (dd, 1H, J = 2.7 and 1.4 Hz, H5), 4.83 (dd, 1H, J = 2.5 and 1.4 Hz, H3), 7.46 (AA'BB', 2H, J = 8.6 Hz, H3' and H5'), 7.82 (AA'BB', 2H, J = 8.5 Hz, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 31.2 (3CH_3, C*Me*$_3$), 35.1 (C, *C*Me$_3$), 41.3 (C, C2, C-I), 71.4 (CH, C5), 72.1 (CH, C4), 73.2 (5CH, Cp), 78.2 (C, C1, *C*-C(O)Ar), 79.8 (CH, C3), 125.1 (2CH, C3' and C5'), 128.8 (2CH, C2' and C6'), 136.4 (C, C1'), 155.7 (C, C4'), 197.1 (C, C=O) ppm. Anal. Calcd for $C_{21}H_{21}FeIO$ (472.15): C, 53.42; H, 4.48. Found: C, 53.29; H, 4.63%.



1-(2-Chlorobenzoyl)-2-iodoferrocene (2-*o*ClPh)

It was prepared according to the general procedure B from (2-chlorobenzoyl)ferrocene (**1-*o*ClPh**; 0.32 g, 1.0 mmol), and was isolated (eluent: petroleum ether-CH_2Cl_2 70:30) in 64% yield (0.28 g) as a red solid. Mp 128-130 °C. IR (ATR) ν 705, 736, 752, 828, 859, 910, 988, 1004, 1040, 1056, 1074, 1108, 1159, 1190, 1246, 1271, 1287, 1321, 1353, 1370, 1421, 1468, 1518, 1591, 1655 (C=O), 2854, 2925, 3098 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.28 (s, 5H, Cp), 4.48 (dd, 1H, J = 2.8 and 1.5 Hz, H5), 4.54 (t, 1H, J = 2.7 Hz, H4), 4.90 (dd, 1H, J = 2.5 and 1.5 Hz, H3), 7.34 (td, 1H, J = 7.0 and 2.0 Hz, H5'), 7.40 (td, 1H, J = 7.8 and 1.8 Hz, H4'), 7.43-7.47 (m, 2H, H3' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 39.1 (C, C2, C-I), 72.1 (CH, C5), 73.3 (5CH, Cp), 73.4 (CH, C4), 76.4 (C, C1, *C*-C(O)Ar), 81.4 (CH, C3), 126.5 (CH, C4'), 128.9 (CH, C6'), 130.3 (CH, C5'), 131.1 (CH, C3'), 131.3 (C, C2'), 139.3 (C, C1'), 198.1 (C, C=O) ppm.



Crystal data for ***2-oClPh***. $C_{17}H_{12}ClFeIO$, M = 450.47, T = 150(2) K; monoclinic P 2$_1$ (I.T.#4), a = 9.4977(14), b = 7.6673(10), c = 10.8013(15) Å, β = 106.599(5) °, V = 753.79(18) Å^3. Z = 2, d = 1.985 g.cm^{-3}, μ = 3.219 mm^{-1}. A final refinement on F^2 with 3391 unique intensities and 191 parameters converged at $\omega R(F^2)$ = 0.0630 (R_F = 0.0246) for 3341 observed reflections with $I > 2\sigma(I)$. CCDC 2490209.

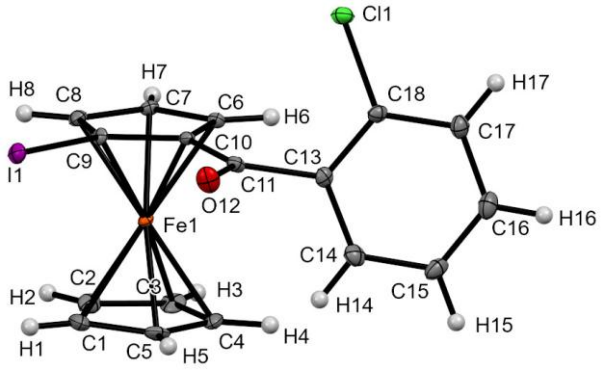
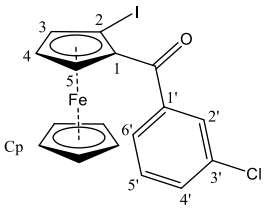


Figure S18. Molecular structure of compound **2-*o*ClPh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.462(8), C9−I1 = 2.090(4), C10−Cg2···Cg1−C5 = 21.60 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), Cg2−C9−I1 = 177.11, C9−C10−C11−O12 = –8.9(9), O12−C11−C13−C18 = –108.7(7).

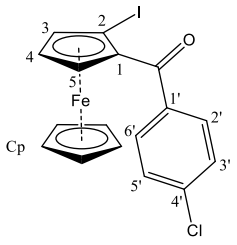
1-(3-Chlorobenzoyl)-2-iodoferrocene (2-*m*ClPh)

It was prepared according to the general procedure B from (3-chlorobenzoyl)ferrocene (**1-*m*ClPh**; 0.32 g, 1.0 mmol), and was isolated (eluent: heptane-AcOEt 70:30) in 55% yield (0.25 g) as a red oil. IR (ATR) ν 658, 684, 730, 751, 803, 827, 876, 1002, 1048, 1067, 1107, 1157, 1187, 1246, 1315, 1352, 1370, 1423, 1471, 1567, 1591, 1645 (C=O), 2928, 3094, 3933 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.25 (s, 5H, Cp), 4.56 (t, 1H, *J* = 2.6 Hz, H4), 4.60 (dd, 1H, *J* = 2.6 and 1.3 Hz, H5), 4.88 (dd, 1H, *J* = 2.3 and 1.4 Hz, H3), 7.39 (t, 1H, *J* = 7.8 Hz, H5'), 7.52 (ddd, 1H, *J* = 8.0, 1.7 and 1.0 Hz, H4'), 7.72 (d, 1H, *J* = 7.7 Hz, H6'), 7.87 (t, 1H, *J* = 1.6 Hz, H2') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 40.7 (C, C2, C-I), 71.7 (CH, C5), 72.8 (CH, C4), 73.4 (5CH, Cp), 77.0 (C, C1, *C*-C(O)Ar), 80.6 (CH, C3), 126.9 (CH, C6'), 128.8 (CH, C2'), 129.7 (CH, C5'), 132.0 (CH, C4'), 134.4 (C, C3'), 140.8 (C, C1'), 196.6 (C, C=O) ppm. Anal. Calcd for $C_{17}H_{12}ClFeIO$ (450.48): C, 45.33; H, 2.69. Found: C, 45.36; H, 2.68%. The rest was starting **1-*m*ClPh** and degradation. Using 1.5 equivalents of LiTMP and I_2 led to the title product in 46% yield.



1-(4-Chlorobenzoyl)-2-iodoferrocene (2-*p*ClPh)

It was prepared according to the general procedure B from (4-chlorobenzoyl)ferrocene (**1-*p*ClPh**; 0.32 g, 1.0 mmol), and was isolated (eluent: heptane-AcOEt 70:30) in 51% yield (0.24 g) as an orange solid. Mp 88-89 °C. IR (ATR) ν 696, 734, 760, 829, 862, 987, 1003, 1014, 1067, 1089, 1107, 1173, 1190, 1253, 1316, 1352, 1371, 1420, 1486, 1586, 1646, 2924, 3094 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.24 (s, 5H, Cp), 4.54 (t, 1H, *J* = 2.6 Hz, H4), 4.58 (dd, 1H, *J* = 2.7 and 1.4 Hz, H5), 4.86 (dd, 1H, *J* = 2.4 and 1.4 Hz, H3), 7.43 (AA'BB', 2H, *J* = 8.5 Hz, H3' and H5'), 7.81 (AA'BB', 2H, *J* = 8.5 Hz, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 41.0 (C, C2, C-I), 71.4 (CH, C5), 72.6 (CH, C4), 73.4 (5CH, Cp), 77.5 (C, C1, *C*-C(O)Ar), 80.3 (CH, C3), 128.6 (2CH, C3' and C5'), 132.2 (2CH, C2' and C6'), 137.4 (C, C1'), 138.4 (C, C4'), 196.6 (C, C=O) ppm. Anal. Calcd for $C_{17}H_{12}ClFeIO$ (450.48): C, 45.33; H, 2.69. Found: C, 45.28; H, 2.84%. The rest was starting **1-*p*ClPh**.



Crystal data for ***2-pClPh***. $C_{17}H_{12}ClFeIO$, *M* = 450.47, *T* = 150(2) K; triclinic *P* –1 (I.T.#2), *a* = 7.2961(9), *b* = 13.7201(15), *c* = 15.8285(19) Å, α = 95.716(4), β = 100.525(4), γ = 93.277(4) °, *V* = 1545.5(3) Å^3. *Z* = 4, *d* = 1.936 g.cm^{-3}, μ = 3.140 mm^{-1}. A final refinement on F^2 with 7016 unique intensities and 313 parameters converged at $\omega R(F^2)$ = 0.1690 (R_F = 0.0681) for 6206 observed reflections with $I > 2\sigma(I)$. CCDC 2490210.

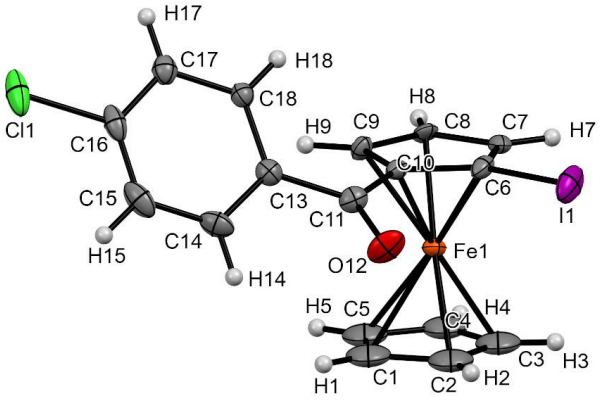
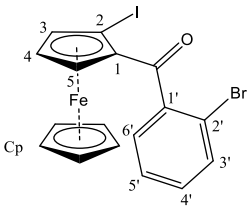


Figure S19. Molecular structure of compound **2-*p*ClPh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.476(9), C6−I1 = 2.080(7), C10−Cg2···Cg1−C1 = 3.30 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), Cg2−C9−I1 = 176.10, C6−C10−C11−O12 = –22(1), O12−C11−C13−C14 = –29(1).

1-(2-Bromobenzoyl)-2-iodoferrocene (2-*o*BrPh)

It was prepared according to the general procedure B from (2-bromobenzoyl)ferrocene (**1-*o*BrPh**; 0.55 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 97:3 to 95:5) in 62% yield (0.46 g) as a red solid. Rf (petroleum ether-AcOEt 95:5) 0.44. Mp 126-128 °C. IR (ATR) ν 685, 731, 749, 828, 858, 910, 988, 1003, 1027, 1071, 1108, 1190, 1246, 1269, 1286, 1321, 1352, 1370, 1420, 1465, 1587, 1653 (C=O), 3095 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.29 (s, 5H, Cp), 4.47 (dd, 1H, J = 2.8 and 1.5 Hz, H5), 4.54 (t, 1H, J = 2.7 Hz, H4), 4.90 (dd, 1H, J = 2.5 and 1.5 Hz, H3), 7.31 (ddd, 1H, J = 8.0, 7.3 and 1.8 Hz, H4'), 7.39 (td, 1H, J = 7.4 and 1.2 Hz, H5'), 7.44 (ddd, 1H, J = 7.5, 1.8 and 0.5 Hz, H6'), 7.61 (ddd, 1H, J = 7.9, 1.2 and 0.4 Hz, H3') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 39.3 (C, C2, C-I), 72.2 (CH, C5), 73.3 (5CH, Cp), 73.4 (CH, C4), 76.4 (C, C1, *C*-C(O)Ar), 81.4 (CH, C3), 120.0 (C, C2'), 127.0 (CH, C5'), 129.1 (CH, C6'), 131.2 (CH, C4'), 133.5 (CH, C3'), 141.2 (C, C1'), 199.0 (C, C=O) ppm. Anal. Calcd for $C_{17}H_{12}BrFeIO$ (494.94): C, 41.26; H, 2.44. Found: C, 41.28; H, 2.56%. A second fraction containing a mixture of the title product (5%) and the starting **1-*o*BrPh** (9%) was also recovered.



Crystal data for ***(R$_P$)-2-oBrPh***. $C_{17}H_{12}BrFeIO$, M = 494.93, T = 150(2) K; tetragonal P 4_3 (I.T.#78), a = 10.7426(15), c = 13.643(2) Å, V = 1574.4(5) $Å^3$. Z = 4, d = 2.088 $g.cm^{-3}$, μ = 5.451 mm^{-1}. A final refinement on F^2 with 3496 unique intensities and 155 parameters converged at $\omega R(F^2)$ = 0.0945 (R_F = 0.0485) for 3044 observed reflections with $I > 2\sigma(I)$. CCDC 2490211.

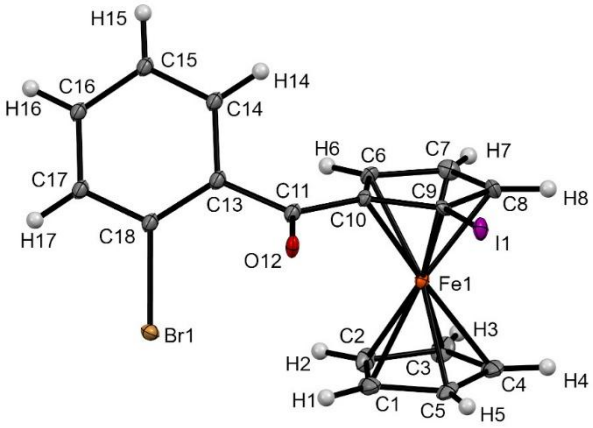


Figure S20. Molecular structure of compound **(*R*P)-2-*o*BrPh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.47(2), C9−I1 = 2.08(1), C10−Cg2···Cg1−C1 = –5.75 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), Cg2−C9−I1 = 173.72, C9−C10−C11−O12 = –11(2), O12−C11−C13−C14 = 124(1).

Crystal data for ***(S*P*)-2-o*BrPh***. $C_{17}H_{12}BrFeIO$, M = 494.93, T = 150(2) K; tetragonal $P\,4_1$ (I.T.#76), a = 10.7559(8), c = 13.6557(10) Å, V = 1579.8(3) Å^3. Z = 4, d = 2.081 g.cm^{-3}, μ = 5.432 mm^{-1}. A final refinement on F^2 with 3466 unique intensities and 191 parameters converged at $\omega R(F^2)$ = 0.0524 (R_F = 0.0228) for 3326 observed reflections with $I > 2\sigma(I)$. CCDC 2490212.

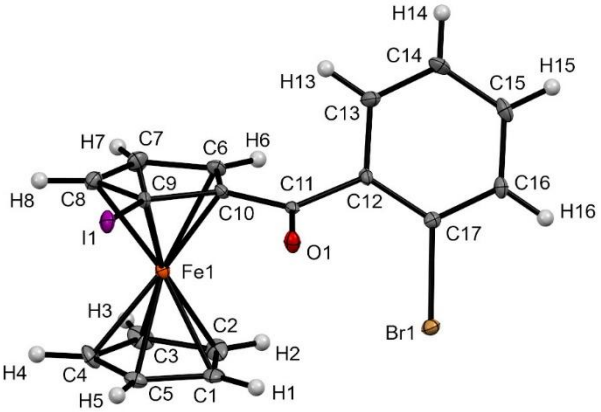
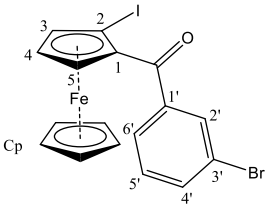


Figure S21. Molecular structure of compound **(*S*P)-2-*o*BrPh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.470(6), C9−I1 = 2.086(5), C10−Cg2···Cg1−C1 = 5.29 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), Cg2−C9−I1 = 173.86, C9−C10−C11−O1 = 11.6(7), O1−C11−C12−C13 = –123.9(5).

1-(3-Bromobenzoyl)-2-iodoferrocene (2-*m*BrPh)

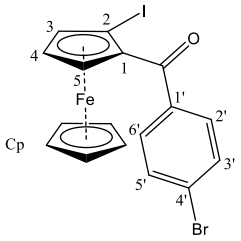
It was prepared according to the general procedure B from (3-bromobenzoyl)ferrocene (**1-*m*BrPh**; 0.37 g, 1.0 mmol), and was isolated (eluent: petroleum ether-CH_2Cl_2 70:30) in 41% yield (0.20 g) as a red oil. IR (ATR) ν 682, 712, 729, 751, 829, 871, 1003, 1069, 1108, 1185, 1248, 1316, 1352, 1371, 1424, 1469, 1561, 1647 (C=O), 3093 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.25 (s, 5H, Cp), 4.56 (t, 1H, J = 2.7 Hz, H4), 4.60 (dd, 1H, J = 2.8 and 1.4 Hz, H5), 4.88 (dd, 1H, J = 2.5 and 1.4 Hz, H3), 7.34 (t, 1H, J = 7.8 Hz, H5'), 7.68 (ddd, 1H, J = 8.0, 2.0 and 1.0 Hz, H4' or H6'), 7.76 (dt, 1H, J = 7.7 and 1.3 Hz, H4' or H6'), 8.05 (t, 1H, J = 1.8 Hz, H2') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 40.6 (C, C2, C-I), 71.7 (CH, C5), 72.8 (CH, C4), 73.4 (5CH, Cp), 77.0 (C, C1, *C*-C(O)Ar), 80.5



(CH, C3), 122.4 (C, C3'), 127.3 (CH, C6'), 129.9 (CH, C5'), 131.7 (CH, C2'), 134.9 (CH, C4'), 140.9 (C, C1'), 196.4 (C, C=O) ppm. Anal. Calcd for $C_{17}H_{12}BrFeIO$ (494.94): C, 41.26; H, 2.44. Found: C, 41.48; H, 2.27%. The rest was starting material and degradation.

1-(4-Bromobenzoyl)-2-iodoferrocene (2-*p*BrPh)

It was prepared according to the general procedure B from (4-bromobenzoyl)ferrocene (**1-*p*BrPh**; 0.55 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 95:5) in 26% yield (0.20 g) as a red solid. Rf (petroleum ether-AcOEt 90:10) 0.61. Mp 104-106 °C. IR (ATR) ν 688, 729, 757, 824, 860, 909, 986, 1011, 1045, 1070, 1107, 1130, 1154, 1174, 1190, 1252, 1318, 1371, 1394, 1420, 1482, 1584, 1645 (C=O), 2923, 3093 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.23 (s, 5H, Cp), 4.54 (t, 1H, J = 2.6 Hz, H4), 4.58 (dd, 1H, J = 2.8 and 1.4 Hz, H5), 4.87 (dd, 1H, J = 2.5 and 1.4 Hz, H3), 7.60 (AA'BB', 2H, J = 8.5 Hz, H3' and H5'), 7.73 (AA'BB', 2H, J = 8.5 Hz, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 41.0 (C, C2, C-I), 71.5 (CH, C5), 72.7 (CH, C4), 73.4 (5CH, Cp), 77.6 (C, C1, *C*-C(O)Ar), 80.4 (CH, C3), 127.1 (C, C4'), 130.4 (2CH, C2' and C6'), 131.6 (2CH, C3' and C5'), 138.0 (C, C1'), 196.9 (C, C=O) ppm.



*Crystal data for **2-pBrPh**.* $C_{17}H_{12}BrFeIO$, M = 494.93, T = 150(2) K; monoclinic P $2_1/c$ (I.T.#14), a = 15.656(3), b = 7.7588(12), c = 12.784(2) Å, β = 98.732(6) °, V = 1534.9(4) $Å^3$. Z = 4, d = 2.142 $g.cm^{-3}$, μ = 5.592 mm^{-1}. A final refinement on F^2 with 3523 unique intensities and 191 parameters converged at $\omega R(F^2)$ = 0.1003 (R_F = 0.0334) for 3242 observed reflections with $I > 2\sigma(I)$. CCDC 2490213.

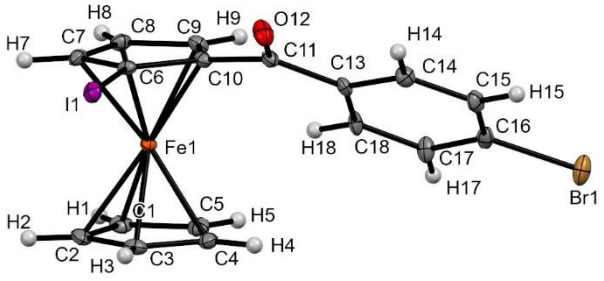
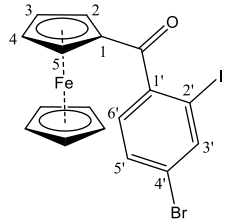


Figure S22. Molecular structure of compound **2-*p*BrPh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.491(5), C6−I1 = 2.080(3), C10−Cg2···Cg1−C4 = 3.99 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), Cg2−C6−I1 = 178.02, C6−C10−C11−O12 = 31.2(5), O12−C11−C13−C14 = 5.1(5).

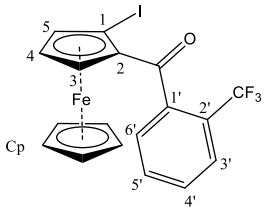
(4-Bromo-2-iodobenzoyl)ferrocene (2'-*p*BrPh) was also obtained (eluent: petroleum ether-AcOEt 90:10; Rf 0.48) in an estimated 52% yield, but as a mixture with 10% recovered **1-*p*BrPh**, as a red glue. It was identified by NMR: ^1H NMR ($CDCl_3$) δ 4.30 (s, 5H, Cp), 4.62 (t, 2H, J = 2.0 Hz, H3 and H4), 4.72 (t, 2H, J = 2.0 Hz, H2 and H5), 7.36 (d, 1H, J = 8.1 Hz, H6'), 7.57 (dd, 1H, J = 8.1 and 1.8 Hz, H5'), 8.09 (d, 1H, J = 1.8 Hz, H3') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.3 (5CH, Cp), 71.5 (2CH, C2 and C5), 73.3 (2CH, C3 and C4), 77.6 (C, C1, *C*-C(O)Ar), 93.3 (C, C2', C-I), 124.3 (C, C4'), 129.4 (CH, C6'), 130.8 (CH, C5'), 142.3 (CH, C3'), 143.5 (C, C1'), 200.2 (C, C=O) ppm. The rest was starting **1-*p*BrPh** and degradation.



1-Iodo-2-[2-(trifluoromethyl)benzoyl]ferrocene (2-*o*CF_3Ph)

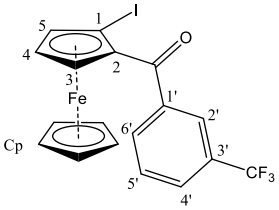
It was prepared according to the general procedure B from 2-(trifluoromethyl)benzoylferrocene (**1-*o*CF_3Ph**; 0.43 g, 1.2 mmol), and was obtained (eluent: petroleum ether-AcOEt 95:5; Rf 0.28) in an estimated 70% yield as a mixture (red glue) with **1-*o*CF_3Ph** (17%). It was identified by NMR. ^1H NMR ($CDCl_3$) δ 4.28 (s, 5H, Cp), 4.43 (dd, 1H, J = 2.8 and 1.5 Hz, H3), 4.53 (t, 1H, J = 2.7 Hz, H4),

4.87 (dd, 1H, *J* = 2.5 and 1.4 Hz, H5), 7.53 (dd, 1H, *J* = 7.0 and 1.8 Hz, H6'), 7.58-7.61 (m, 2H, H4' and H5'), 7.74 (dd, 1H, *J* = 7.2 and 1.9 Hz, H3') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 39.6 (C, C1, C-I), 71.8 (CH, C3), 73.0 (CH, C4), 73.3 (5CH, Cp), 77.8 (C, C2, *C*-C(O)Ar), 80.9 (CH, C5), 123.8 (q, C, *J* = 274 Hz, CF_3), 126.9 (q, CH, *J* = 4.8 Hz, C3'), 127.7 (q, C, *J* = 32.2 Hz, C2'), 128.8 (CH, C6'), 130.1 (CH, C4' or C5'), 131.4 (CH, C4' or C5'), 139.2 (d, C, *J* = 2.3 Hz, C1'), 199.2 (C, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ –57.5 ppm. Anal. Calcd for $C_{18}H_{12}F_3FeIO$ (484.04): C, 44.67; H, 2.50. Found: C, 44.83; H, 2.70%. 17% of the starting **1-*o*CF₃Ph** were recovered.

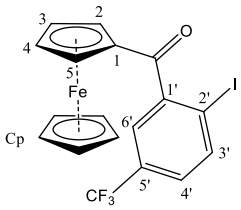


1-Iodo-2-[3-(trifluoromethyl)benzoyl]ferrocene (2-*m*CF₃Ph)

It was prepared according to the general procedure B from 3-(trifluoromethyl)benzoylferrocene (**1-*m*CF₃Ph**; 0.43 g, 1.2 mmol), and was obtained (eluent: petroleum ether-AcOEt 95:5; Rf 0.64) in an estimated 41% yield as a mixture (red glue) with [2-iodo-5-(trifluoromethyl)benzoyl]ferrocene (**2'-*m*CF₃Ph**; estimated 10% yield). It was identified by NMR. ^1H NMR ($CDCl_3$) δ 4.27 (s, 5H, Cp), 4.59 (d, 2H, *J* = 1.9 Hz, H3 and H4), 4.91 (t, 1H, *J* = 1.9 Hz, H5), 7.61 (t, 1H, *J* = 7.8 Hz, H5'), 7.82 (d, 1H, *J* = 7.8 Hz, H4'), 8.04 (d, 1H, *J* = 7.8 Hz, H6'), 8.22 (s, 1H, H2') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 40.4 (C, C1, C-I), 71.9 (CH, C3 or C4), 73.1 (CH, C3 or C4), 73.5 (5CH, Cp), 77.0 (C, C2, *C*-C(O)Ar), 80.8 (CH, C5), 123.9 (d, C, *J* = 273 Hz, CF_3), 125.7 (q, CH, *J* = 3.8 Hz, C2'), 128.6 (q, CH, *J* = 3.7 Hz, C4'), 129.1 (CH, C5'), 130.8 (q, C, *J* = 32.6 Hz, C3'), 132.0 (CH, C6'), 139.8 (C, C1'), 196.7 (C, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ –62.7 ppm.

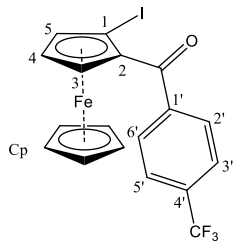


[2-Iodo-5-(trifluoromethyl)benzoyl]ferrocene (2'-*m*CF₃Ph) was similarly identified by NMR. ^1H NMR ($CDCl_3$) δ 4.32 (s, 5H, Cp), 4.66 (t, *J* = 1.9 Hz, 2H), 4.70 (t, *J* = 1.9 Hz, 2H), 7.40 (dd, 1H, *J* = 9.3 and 1.3 Hz, H4'), 7.79 (d, 1H, *J* = 2.2 Hz, H6'), 8.06 (d, 1H, *J* = 8.3 Hz, H3') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.4 (5CH, Cp), 70.5 (2CH, C2 and C5), 73.5 (2CH, C3 and C4), 77.2 (C, C1, *C*-C(O)Ar), 97.0 (C, C2', C-I), 123.8 (d, C, *J* = 273 Hz, CF_3), 125.0 (q, CH, *J* = 3.6 Hz, C6'), 127.3 (q, CH, *J* = 3.6 Hz, C4'), 130.3 (q, C, *J* = 33.1 Hz, C5'), 140.9 (CH, C3'), 145.5 (C, C1'), 200.0 (C, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ –62.9 ppm.



1-Iodo-2-[4-(trifluoromethyl)benzoyl]ferrocene (2-*p*CF₃Ph)

It was prepared according to the general procedure B from 4-(trifluoromethyl)benzoylferrocene (**1-*p*CF₃Ph**; 0.43 g, 1.2 mmol), and was isolated (eluent: petroleum ether-AcOEt 95:5; Rf 0.45) in 54% yield (0.31 g) as a red solid. Mp 106-108 °C. IR (ATR) ν 686, 722, 772, 829, 851, 867, 989, 1018, 1068, 1108, 1128, 1167, 1253, 1320, 1372, 1408, 1424, 1510, 1578, 1650, 2925, 3099 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.25 (s, 5H, Cp), 4.57-4.58 (m, 2H, H3 and H4), 4.92 (dd, 1H, *J* = 2.3 and 1.6 Hz, H5), 7.73 (AA'BB', 2H, *J* = 8.2 Hz, H3' and H5'), 7.94 (AA'BB', 2H, *J* = 8.0 Hz, H2' and H6') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 40.6 (C, C1, C-I), 71.7 (CH, C3), 73.1 (CH, C4), 73.5 (5CH, Cp), 76.7 (C, C2, *C*-C(O)Ar), 81.0 (CH, C5), 123.9 (d, C, *J* = 273 Hz, CF_3), 125.4 (q, 2CH, *J* = 3.7 Hz, C3' and C5'), 128.9 (2CH, C2' and C6'), 133.4 (d, C, *J* = 32.7 Hz, C4'), 142.4 (C, C1'), 197.3 (C, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ –62.9 ppm. Anal. Calcd for $C_{18}H_{12}F_3FeIO$ (484.04): C, 44.67; H, 2.50. Found: C, 44.85; H, 2.78%.



Crystal data for ***2-pCF₃Ph***. $C_{18}H_{12}F_3FeIO$, *M* = 484.03, *T* = 150(2) K; monoclinic *P n* (I.T.#7), *a* = 9.8470(18), *b* = 7.7662(14), *c* = 11.3185(19) Å, β = 109.221(5) °, *V* = 817.3(3) $Å^3$. *Z* = 2, *d* = 1.967 $g.cm^{-3}$, μ = 2.844 mm^{-1}. A final refinement on F^2 with 3354 unique intensities and 217 parameters converged at $\omega R(F^2)$ = 0.1001 (R_F = 0.0386) for 3332 observed reflections with $I > 2\sigma(I)$. CCDC 2490214.

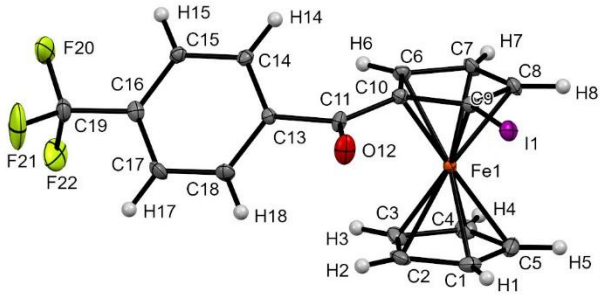
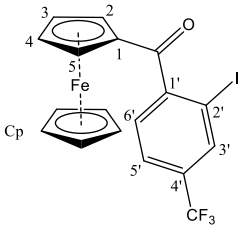


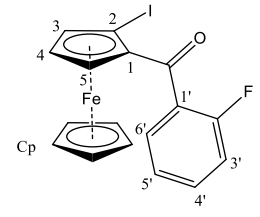
Figure S23. Molecular structure of compound **2-*p*CF$_3$Ph** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.49(1), C9−I1 = 2.082(7), C10−Cg2···Cg1−C2 = 3.35 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), Cg2−C9−I1 = 175.11, C9−C10−C11−O12 = –3(1), O12−C11−C13−C14 = –138.0(8).

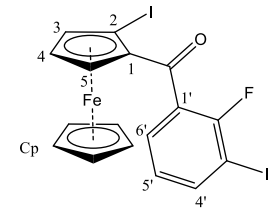
[2-Iodo-4-(trifluoromethyl)benzoyl]ferrocene (2'-*p*CF$_3$Ph) was similarly obtained (Rf 0.31) in an estimated 11% yield as a mixture with 6% starting **1-*p*CF$_3$Ph**, and was identified by NMR: ^{1}H NMR ($CDCl_3$) δ 4.31 (s, 5H, Cp), 4.64-4.65 (m, 2H, H3 and H4), 4.71 (t, 2H, J = 2.0 Hz, H2 and H5), 7.59 (d, 1H, J = 7.9 Hz, H6'), 7.70 (dd, 1H, J = 8.1 and 1.9 Hz, H5'), 8.16 (s, 1H, H3') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 70.4 (5CH, Cp), 71.4 (2CH, C2 and C5), 73.5 (2CH, C3 and C4), 77.3 (C, C1, *C*-C(O)Ar), 92.4 (C, C2', C-I), 122.7 (d, C, J = 273 Hz, CF_3), 124.7 (q, CH, J = 3.6 Hz, C5'), 128.4 (CH, C6'), 132.8 (q, C, J = 33.2 Hz, C4'), 137.0 (q, CH, J = 3.9 Hz, C3'), 148.2 (C, C1'), 200.3 (C, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ –62.9 ppm. These data correspond to those reported [35].



1-(2-Fluorobenzoyl)-2-iodoferrocene (2-*o*FPh)

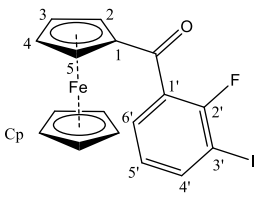
It was prepared according to the general procedure B from (2-fluorobenzoyl)ferrocene (**1-*o*FPh**; 0.46 g, 1.5 mmol), and obtained (eluent: petroleum ether-AcOEt 97:3 to 95:5) in an estimated 41% yield [Rf (petroleum ether-AcOEt 95:5) 0.34]. ^{1}H NMR ($CDCl_3$) δ 4.24 (s, 5H, Cp), 4.52-4.54 (m, 2H, H4 and H5), 4.90 (dd, 1H, J = 2.5 and 1.5 Hz, H3), 7.15 (ddd, 1H, J = 9.6, 8.3 and 1.0 Hz, H3'), 7.23 (td, 1H, J = 7.5 and 1.1 Hz, H5'), 7.45-7.50 (m, 1H, H4'), 7.53 (td, 1H, J = 7.3 and 1.8 Hz, H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 39.4 (C, C2, C-I), 71.9 (CH, C4 or C5), 73.4 (5CH, Cp), 73.4 (CH, C4 or C5), 76.5 (C, C1, *C*-C(O)Ar), 81.4 (CH, C3), 116.4 (d, CH, J = 21.6 Hz, C3'), 124.1 (d, CH, J = 3.5 Hz, C5'), 128.7 (d, C, J = 15.4 Hz, C1'), 129.5 (d, CH, J = 3.2 Hz, C6'), 132.4 (d, CH, J = 8.4 Hz, C4'), 159.5 (d, C, J = 251 Hz, C2'), 195.8 (C, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ –113.1 ppm] as a mixture (red glue) with 18% **1-(2-fluoro-3-iodobenzoyl)-2-iodoferrocene (2"-*o*FPh)** [Rf (petroleum ether-AcOEt 95:5) 0.34]. ^{1}H NMR ($CDCl_3$) δ 4.25 (s, 5H, Cp), 4.51 (dt, 1H, J = 2.9 and 1.5 Hz, H5), 4.56 (t, 1H, J = 2.7 Hz, H4), 4.92 (dd, 1H, J = 2.5 and 1.4 Hz, H3), 7.00 (t, 1H, J = 7.7 Hz, H5'), 7.45-7.50 (m, 1H, H6'), 7.88 (ddd, 1H, J = 7.7, 5.8 and 1.7 Hz, H4') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 39.2 (C, C2, C-I), 71.9 (CH, C5), 73.4 (5CH, Cp), 73.7 (CH, C4), 76.2 (C, C1, *C*-C(O)Ar), 81.7 (CH, C3), 82.6 (d, C, J = 26.4 Hz, C3', C-I), 125.7 (d, CH, J = 4.3 Hz, C5'), 129.1 (d, C, J = 18.8 Hz, C1'), 129.5 (d, CH, J = 3.2 Hz, C6'), 141.6 (d, CH, J = 2.0 Hz, C4'), 158.2 (d, C, J = 249 Hz, C2'), 194.8 (C, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ –93.1 ppm].





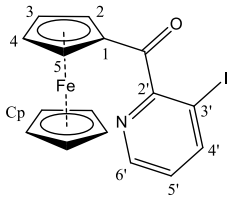
(2-Fluoro-3-iodobenzoyl)ferrocene (2'-*o*FPh) was similarly obtained (Rf 0.29) in an estimated 6% yield as a mixture (red glue) with 20% starting material, and identified by NMR. ^{1}H NMR ($CDCl_3$) δ 4.23 (s, 5H, Cp), 4.62 (t, 2H, J = 2.0 Hz, H3 and H4), 4.79 (td, 2H, J = 2.0 and 0.8 Hz, H2 and H5), 7.00 (t, 1H, J = 7.7 Hz, H5'), 7.50 (ddd, 1H, J = 7.4, 6.1 and 1.5 Hz, H6'), 7.88 (ddd, 1H, J = 7.7, 5.9

and 1.7 Hz, H4') ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 70.4 (5CH, Cp), 71.2 (2CH, C2 and C5), 73.4 (2CH, C3 and C4), 78.2 (C, C1, *C*-C(O)Ar), 82.6 (d, C, J = 26.6 Hz, C3', C-I), 125.6 (d, CH, J = 4.3 Hz, C5'), 129.0 (d, CH, J = 15.7 Hz, C6'), 129.3 (d, C, J = 3.3 Hz, C1'), 141.4 (CH, C4'), 158.1 (d, C, J = 250 Hz, C2'), 195.4 (C, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ –93.4 ppm.



(3-Iodo-2-pyridoyl)ferrocene (2'-2Py)

It was prepared according to the general procedure B from (2-pyridoyl)ferrocene (**1-2Py**; 0.29 g, 1.0 mmol), and was isolated (eluent: petroleum ether-AcOEt 90:10; Rf 0.19) in 20% yield (85 mg) as a red solid. Mp 114-115 °C. IR (ATR) ν 758, 808, 824, 859, 872, 956, 1012, 1026, 1045, 1071, 1107, 1188, 1216, 1238, 1262, 1294, 1338, 1372, 1386, 1412, 1455, 1548, 1564, 1633 (C=O), 2852, 2922, 3045, 3099, 3357 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.33 (s, 5H, Cp), 4.62 (t, 2H, J = 2.0 Hz, H3 and H4), 4.83 (t, 2H, J = 2.0 Hz, H2 and H5), 7.11 (dd, 1H, J = 8.1 and 4.6 Hz, H5'), 8.26 (dd, 1H, J = 8.0 and 1.5 Hz, H4'), 8.62 (dd, 1H, J = 4.7 and 1.4 Hz, H6') ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 70.5 (5CH, Cp), 71.6 (2CH, C2 and C5), 73.3 (2CH, C3 and C4), 76.7 (C, C1, *C*-C(O)Ar), 89.7 (C, C3', C-I), 125.5 (CH, C5'), 147.7 (2CH, C4' and C6'), 158.7 (C, C2'), 198.3 (C, C=O) ppm. Anal. Calcd for $C_{16}H_{12}FeINO$ (417.03): C, 46.08; H, 2.90; N, 3.36. Found: C, 45.89; H, 2.78; N, 3.52%. 3% of the starting **1-2Py** were recovered.



*Crystal data for **2'-2Py**.* $C_{16}H_{12}FeINO$, M = 417.02, T = 150(2) K; orthorhombic P 2_1 2_1 2_1 (I.T.#19), a = 11.1000(3), b = 11.7680(4), c = 22.4934(6) Å, V = 2938.20(15) $Å^3$. Z = 8, d = 1.885 $g.cm^{-3}$, μ = 3.121 mm^{-1}. A final refinement on F^2 with 7880 unique intensities and 336 parameters converged at $\omega R(F^2)$ = 0.0566 (R_F = 0.0283) for 7137 observed reflections with $I > 2\sigma$. CCDC 2490215.

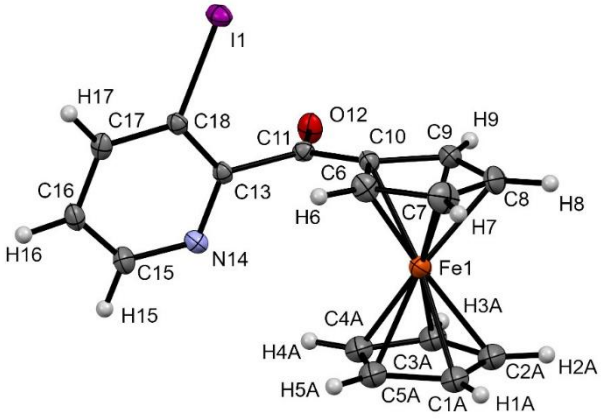
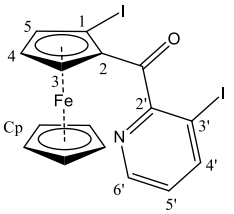


Figure S24. Molecular structure of compound **2'-2Py** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.458(6), C10−Cg2···Cg1−C5 = -11.92 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C9−C10−C11−O12 = –9.4(7), O12−C11−C13−C18 = –100.0(5).

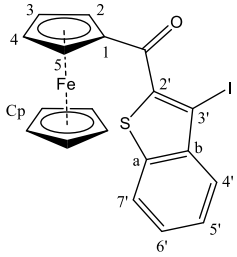
1-Iodo-2-(3-iodo-2-pyridoyl)ferrocene (2"-2Py) was similarly obtained (Rf 0.15) in an estimated 8% yield as a mixture (red solid) with (3-iodo-2-pyridoyl)ferrocene (**2'-2Py**, 6% yield). It was identified by NMR. ^{1}H NMR ($CDCl_3$) δ 4.37 (s, 5H, Cp), 4.60 (t, 1H, J = 2.7 Hz, H4), 4.73 (dd, 1H, J = 2.9 and 1.5 Hz, H5), 4.89 (dd, 1H, J = 2.5 and 1.5 Hz, H3), 7.12 (dd, 1H, J = 8.1 and 4.6 Hz, H5'), 8.21 (dd, 1H, J = 8.1 and 1.4 Hz, H4'), 8.62 (dd, 1H, J = 4.6 and 1.4 Hz, H6') ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 39.6 (C, C1, C-I), 72.2 (CH, C5), 73.7 (5CH, Cp), 73.9 (CH, C4), 75.3 (C, C2,



C-C(O)Ar), 81.4 (CH, C3), 90.4 (C, C3', C-I), 125.6 (CH, C5'), 147.3 (CH, C4'), 147.9 (CH, C6'), 158.7 (C, C2'), 198.5 (C, C=O) ppm.

(3-Iodo-2-benzothienoyl)ferrocene (2'-2BTh)

It was prepared according to the general procedure B from (2-benzothienoyl)ferrocene (**1-2BTh**; 0.35 g1.0 mmol), and was isolated (eluent: petroleum ether-AcOEt 96:4) in 51% yield (0.24 g) as a red solid. Rf (petroleum ether-AcOEt 95:5) 0.29. Mp 163-164 °C. IR (ATR) ν 717, 741, 755, 823, 834, 852, 896, 955, 1005, 1028, 1069, 1107, 1134, 1163, 1244, 1265, 1296, 1334, 1352, 1374, 1442, 1453, 1494, 1628 (C=O), 3101 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.35 (s, 5H, Cp), 4.67 (t, 2H, J = 2.0 Hz, H3 and H4), 5.05 (t, 2H, J = 2.0 Hz, H2 and H5), 7.51 (td, 1H, J = 7.2 and 1.7 Hz, H6'), 7.54 (dd, 1H, J = 7.1 and 1.6 Hz, H5'), 7.85-7.87 (m, 1H, H7'), 7.95-7.97 (m, 1H, H4') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.7 (5CH, Cp), 71.8 (2CH, C2 and C5), 73.4 (2CH, C3 and C4), 78.8 (C, C1, *C*-C(O)Ar), 83.2 (C, C3', C-I), 122.5 (CH, C7'), 126.1 (CH, C6'), 127.4 (CH, C5'), 127.5 (CH, C4'), 137.8 (C, C2'), 138.9 (Cb), 141.2 (Ca), 192.4 (C, C=O) ppm. Anal. Calcd for $C_{19}H_{13}FeIOS$ (472.12): C, 48.34; H, 2.78; S, 6.79. Found: C, 48.13; H, 2.56; S, 6.72%. 13% of the starting **1-2BTh** were recovered.



*Crystal data for **2'-2BTh***. $C_{19}H_{13}FeIOS$, M = 472.10, T = 150(2) K; monoclinic C 2/c (I.T.#15), a = 13.5622(5), b = 7.6491(2), c = 31.4758(9) Å, β = 101.084(3) °, V = 3204.35(17) $Å^3$. Z = 8, d = 1.957 $g.cm^{-3}$, μ = 2.999 mm^{-1}. A final refinement on F^2 with 3663 unique intensities and 208 parameters converged at $\omega R(F)^2$ = 0.0514 (R_F = 0.0234) for 3178 observed reflections with $I > 2\sigma$. CCDC 2490216.

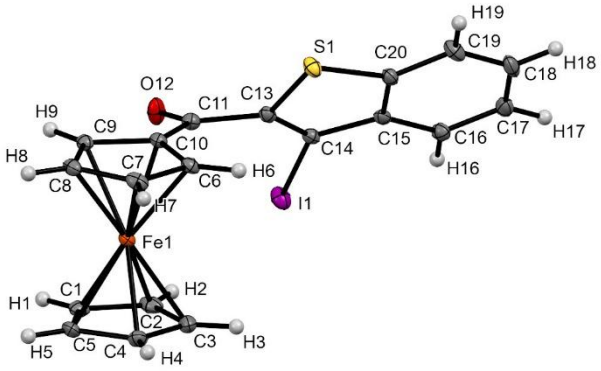
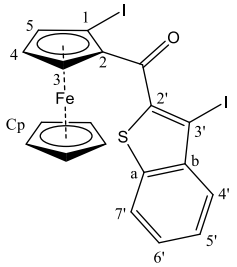


Figure S25. Molecular structure of compound **2'-2BTh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.470(4), C10−Cg2···Cg1−C2 = 3.77 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C6−C10−C11−O12 = –16.7(4), O12−C11−C13−S1 = 137.9(2).

1-Iodo-2-(3-iodo-2-benzothienoyl)ferrocene (2"-2BTh) was similarly obtained (Rf 0.36) in 7% yield (43 mg) as a red solid. Mp 165-166 °C. IR (ATR) ν 728, 755, 768, 814, 832, 845, 855, 895, 1007, 1035, 1056, 1108, 1122, 1233, 1306, 1350, 1368, 1410, 1451, 1477, 1637 (C=O), 2167 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.35 (s, 5H, Cp), 4.59 (t, 1H, J = 2.7 Hz, H4), 4.83 (dd, 1H, J = 2.9 and 1.4 Hz, H3), 4.95 (dd, 1H, J = 2.5 and 1.4 Hz, H5), 7.51 (td, 1H, J = 7.2 and 1.6 Hz, H6'), 7.53 (td, 1H, J = 7.2 and 1.6 Hz, H5'), 7.83-7.85 (m, 1H, H7'), 7.93-7.95 (m, 1H, H4') ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 40.2 (C, C1, C-I), 72.7 (CH, C3), 73.2 (CH, C4), 73.7 (5CH, Cp), 77.5 (C, C2, *C*-C(O)Ar), 81.3 (CH, C5), 83.8 (C, C3', C-I), 122.6 (CH, C7'), 126.2 (CH, C6'), 127.5 (CH, C5'), 127.6 (CH, C4'), 138.3 (C, C2'), 139.1 (Cb), 141.2 (Ca), 192.1 (C, C=O) ppm. Anal. Calcd for $C_{19}H_{12}FeI_2OS$ (598.02): C, 38.16; H, 2.02; S, 5.36. Found: C, 38.13; H, 1.98; S, 5.31%.



Crystal data for ***2"-2BTh***. $C_{19}H_{12}FeI_2OS$, M = 598.00, T = 150(2) K; monoclinic $P\ 2_1/c$ (I.T.#14), a = 16.7511(5), b = 8.1541(2), c = 13.8559(4) Å, β = 112.091(3) °, V = 1753.64(9) Å^3. Z = 4, d = 2.265 g.cm^{-3}, μ = 4.503 mm^{-1}. A final refinement on F^2 with 4019 unique intensities and 217 parameters converged at $\omega R(F^2)$ = 0.0493 (R_F = 0.0222) for 3627 observed reflections with $I > 2\sigma(I)$. CCDC 2490217.

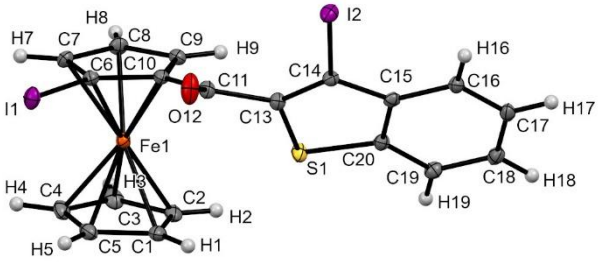
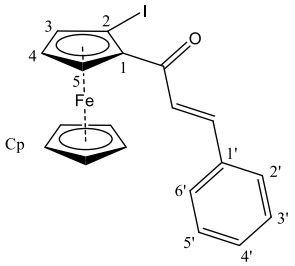


Figure S26. Molecular structure of compound **2"-2BTh** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.470(4), C6−I1 = 2.085(3), C10−Cg2···Cg1−C1 = 1.39 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C6−C10−C11−O12 = –16.7(4), O12−C11−C13−S1 = 137.9(2).

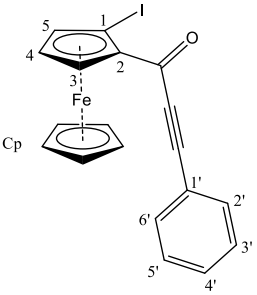
(*E*)-1-Cinnamoyl-2-iodoferrocene (2-CH=CHPh)

It was prepared according to the general procedure B from (*E*)-(cinnamoyl)ferrocene (**1-CH=CHPh**; 0.79 g, 2.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 97:3 to 96:4) in 25% yield (0.28 g) as a red solid. Rf (petroleum ether-AcOEt 95:5) 0.23. Mp 147-148 °C. IR (ATR) ν 718, 759, 771, 825, 846, 873, 931, 980, 990, 1002, 1028, 1073, 1094, 1106, 1159, 1207, 1229, 1285, 1305, 1327, 1350, 1373, 1426, 1450, 1497, 1575, 1594, 1652, 2190, 3034 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.25 (s, 5H, Cp), 4.59 (t, 1H, J = 2.7 Hz, H4), 4.85 (dd, 1H, J = 2.5 and 1.5 Hz, H3), 4.88 (dd, 1H, J = 2.8 and 1.5 Hz, H5), 7.39-7.46 (m, 3H, H3', H4' and H5'), 7.45 (d, 1H, J = 15.6 Hz, C*H*=CH-Ph), 7.66 (dd, 2H, J = 7.3 and 2.0 Hz, H2' and H6'), 7.81 (d, 1H, J = 15.6 Hz, CH=C*H*-Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 39.2 (C, C2, C-I), 70.1 (CH, C5), 73.1 (5CH, Cp), 73.3 (CH, C4), 79.2 (C, C1, *C*-C(O)Ar), 81.1 (CH, C3), 123.6 (CH, *C*H=CH-Ph), 128.5 (2CH, C2' and C6'), 129.1 (2CH, C3' and C5'), 130.4 (CH, C4'), 135.3 (C, C1'), 141.6 (CH, CH=*C*H-Ph), 192.3 (C, C=O) ppm. HRMS (ESI; Maxis 4G, 90:10 CH_3OH-CH_2Cl_2): m/z [M+Na]$^+$ calcd for $C_{19}H_{15}OINa^{56}Fe$: 464.94093; found: 464.9406 (1 ppm).



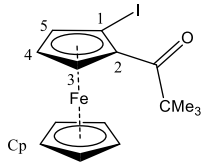
1-Iodo-2-(phenylpropioloyl)ferrocene (2-C≡CPh)

It was prepared according to the general procedure B from (phenylpropioloyl)ferrocene (**1-C≡CPh**; 0.47 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 97:3) in 48% yield (0.32 g) as a red glue. Rf (petroleum ether-AcOEt 95:5) 0.23. IR (ATR) ν 742, 754, 780, 826, 916, 999, 1026, 1046, 1089, 1107, 1156, 1177, 1224, 1267, 1286, 1324, 1351, 1370, 1387, 1422, 1443, 1488, 1623 (C=O), 2200, 3098 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.31 (s, 5H, Cp), 4.64 (t, 1H, J = 2.7 Hz, H4), 4.89 (dd, 1H, J = 2.6 and 1.5 Hz, H5), 5.07 (dd, 1H, J = 2.8 and 1.5 Hz, H3), 7.41-7.45 (m, 2H, H3' and H5'), 7.47-7.50 (m, 1H, H4'), 7.68-7.71 (m, 2H, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 38.3 (C, C1, C-I), 72.0 (CH, C3), 73.6 (5CH, Cp), 73.9 (CH, C4), 78.4 (C, C2, *C*-C(O)Ar), 81.8 (CH, C5), 88.0 (C, *C*≡C-Ph), 91.0 (C, C≡*C*-Ph), 120.7 (C, C1'), 128.8 (2CH, C3' and C5'), 130.7 (CH, C4'), 132.9 (2CH, C2' and C6'), 180.2 (C, C=O) ppm. Anal. Calcd for $C_{19}H_{13}FeIO$ (440.06): C, 51.86; H, 2.98. Found: C, 51.99; H, 3.00%. 19% of the starting **2-C≡CPh** were recovered.



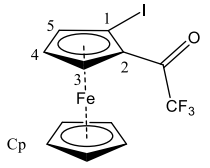
1-Iodo-2-pivaloylferrocene (2-*t*Bu)

It was prepared according to the general procedure B from pivaloylferrocene (**1-*t*Bu**; 0.405 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 95:5) in 75% yield (0.45 g) as a red solid. Mp < 50 °C. IR (ATR) ν 710, 733, 772, 824, 849, 865, 987, 1003, 1025, 1056, 1107, 1156, 1182, 1202, 1254, 1315, 1370, 1421, 1463, 1562, 1603, 1644 (C=O), 2961, 3091 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.29 (s, 9H, *t*Bu), 4.21 (s, 5H, Cp), 4.44 (t, 1H, *J* = 2.7 Hz, H4), 4.63 (dd, 1H, *J* = 2.8 and 1.3 Hz, H3), 4.71 (dd, 1H, *J* = 2.5 and 1.3 Hz, H5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 28.0 ($3CH_3$, C*Me*$_3$), 43.2 (C, C1, C-I), 45.2 (C, *C*Me$_3$), 68.0 (CH, C3), 71.8 (CH, C4), 73.0 (5CH, Cp), 77.6 (C, C2, *C*-C(O)*t*Bu), 78.6 (CH, C5), 209.4 (C, C=O) ppm. Anal. Calcd for $C_{15}H_{17}FeIO$ (396.05): C, 45.49; H, 4.33. Found: C, 45.32; H, 4.41%. 20% of the starting **1-*t*Bu** were recovered. Using 2 equivalents of LiTMP and I_2 from **1-*t*Bu** (1.0 mmol) led to the title product in 95% yield.



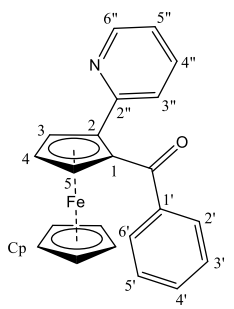
1-Iodo-2-(trifluoromethylcarbonyl)ferrocene (2-CF_3)

It was prepared according to the general procedure B from [(trifluoromethyl)carbonyl]ferrocene (**1-CF_3**; 0.42 g, 1.5 mmol), and was obtained (eluent: petroleum ether-AcOEt 95:5) in an estimated 38% yield as a mixture (red glue) with **1-CF_3** (18%). It was identified by NMR. ^1H NMR ($CDCl_3$) δ 4.31 (s, 5H, Cp), 4.74 (t, 1H, *J* = 2.8 Hz, H4), 4.88-4.90 (m, 1H, H3), 5.05 (dd, 1H, *J* = 2.6 and 1.3 Hz, H5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 38.4 (C, C1, C-I), 68.2 (C, C2, *C*-C(O)CF_3), 71.3 (q, CH, *J* = 3.9 Hz, C3), 73.8 (5CH, Cp), 75.4 (CH, C4), 82.7 (CH, C5), 116.5 (d, C, *J* = 292 Hz, CF_3), 185.4 (q, C, *J* = 35.2 Hz, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ –71.8 ppm. Using 2 equivalents of LiTMP and I_2 only led to the title product in an estimated 8% yield due to major formation of an unidentified product (and to the recovery of 10% of the starting **1-CF_3**).



*1-Benzoyl-2-(2-pyridyl)ferrocene (**3-Ph**)*

*n*BuLi (1.4 M in hexane, 1.2 mL, 1.65 mmol) was added dropwise to a solution of TMPH (0.28 mL, 1.65 mmol) in THF (4.5 mL) at –15 °C and the reaction mixture was stirred for 5 min. This LiTMP solution was cooled to –20 °C and cannulated onto a solution of the ferrocene ketone (0.435mg, 1.5 mmol) and $ZnCl_2$·TMEDA (0.38 g, 1.5 mmol) in THF (4.5 mL). The reaction mixture was stirred for 1 h at –20 °C. 2-Chloropyridine (0.16 mL, 1.65 mmol), $PdCl_2$ (21 mg, 0.12 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (dppf; 66.5 mg, 0.12 mmol) were added and the reaction mixture was stirred at 80 °C for 16 h. The reaction mixture was cooled to rt and Et_2O was added. The reaction mixture was extracted with aqueous HCl (1 M). The combined aqueous layers were washed with Et_2O, basified with solid K_2CO_3 until pH 12 and extracted with AcOEt. The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt-Et_3N 83:15:2) led to the title product in 37% yield (0.20 g) as a red glue. Rf (petroleum ether-AcOEt 85:15) 0.30. IR (ATR) ν 720, 744, 785, 820, 851, 872, 895, 931, 983, 1001, 1026, 1046, 1107, 1151, 1168, 1245, 1293, 1346, 1419, 1448, 1487, 1519, 1564, 1586, 1642 (C=O), 3082 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.23 (s, 5H, Cp), 4.60 (t, 1H, *J* = 2.6 Hz, H4), 4.76 (dd, 1H, *J* = 2.6 and 1.5 Hz, H5), 5.11 (dd, 1H, *J* = 2.6 and 1.5 Hz, H3), 7.04 (ddd, 1H, *J* = 7.4, 4.9 and 1.3 Hz, H5"), 7.33 (t, 2H, *J* = 7.8 Hz, H3' and H5'), 7.45 (tt, 1H, *J* = 7.0 and 1.6 Hz, H4'), 7.48 (td, 1H, *J* = 7.4 and 1.8 Hz, H4"), 7.54 (dt, 1H, *J* = 7.9 and 1.1 Hz, H3"), 7.80-7.82 (m, 2H, H2' and H6'), 8.42 (ddd, 1H, *J* = 4.9, 1.9 and 1.0 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 70.3 (CH, C4), 71.9 (5CH, Cp), 72.6 (CH, C5), 74.5 (CH, C3), 81.3 (C, C1, *C*-C(O)Ph), 88.2 (C, C2), 121.1 (CH, C5"), 124.1 (CH, C3"), 128.1 (2CH, C3' and C5'), 129.0 (2CH, C2' and C6'), 132.0 (CH, C4'), 135.3 (CH, C4"), 139.5 (C,



C1'), 148.8 (CH, C6"), 157.5 (C, C2"), 198.8 (C, C=O) ppm. Anal. Calcd for $C_{22}H_{17}FeNO$ (367.23): C, 71.96; H, 4.67; N, 3.81. Found: C, 72.09; H, 4.35; N, 3.98%.

General procedure C for the asymmetric deprotolithiation-zincation-iodination sequence on ferrocene ketones.

A solution of *n*BuLi in hexane (2.2 equiv) was added dropwise to a solution of (*S*)-PEAH (2.2 equiv) in THF (0.75 M) at –15 °C and the reaction mixture was stirred for 5 min. This (*S*)-PEALi solution was cooled to –20 °C and cannulated onto a solution of the ferrocene ketone and $ZnCl_2$·TMEDA (1.0 equiv) in THF (0.33 M). The reaction mixture was stirred for 1 h at –20 °C and a solution of I_2 (2.2 equiv) in THF (0.55 M) was added. The reaction mixture was warmed to rt, an aqueous saturated solution of $Na_2S_2O_3$ was added, and the product was extracted with AcOEt. The combined organic layers were washed with water, dried over $MgSO_4$, 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) to give the title product.

1-Benzoyl-2-iodoferrocene (2-Ph)

It was prepared according to the general procedure C from benzoylferrocene (**1-Ph**; 0.435 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 95:5) in 69% yield (0.43 g) as a red solid. The *er* (69:31) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 85:15, 1.0 mL·min^{-1}, 25 °C, λ = 254 nm, t (major) = 11.81 min, t (minor) = 13.87 min.

1-Iodo-2-(2-methoxybenzoyl)ferrocene (2-*o*OMePh)

It was prepared according to the general procedure C from (2-methoxybenzoyl)ferrocene (**1-*o*OMePh**; 0.48 g, 1.5 mmol) and was isolated (eluent: petroleum ether-AcOEt 90:10) in 61% yield (0.41 g) as a red solid. The *er* (73:27) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 80:20, 1.0 mL·min^{-1}, 20 °C, λ = 254 nm, t (major) = 21.34 min, t (minor) = 24.03 min. 31% of **2OMePh** were recovered.

1-Iodo-2-(4-methoxybenzoyl)ferrocene (2-*p*OMePh)

It was prepared according to the general procedure C from (4-methoxybenzoyl)ferrocene (**1-*p*OMePh**; 0.48 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 90:10) in 68% yield (0.46 g) as a red solid. The *er* (66:34) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 80:20, 1.0 mL·min^{-1}, 20 °C, λ = 254 nm, t (major) = 21.39 min, t (minor) = 23.80 min. 6% of **1-*p*OMePh** were recovered.

1-(2-Bromobenzoyl)-2-iodoferrocene (2-*o*BrPh)

It was prepared according to the general procedure C from (2-bromobenzoyl)ferrocene (**1-*o*BrPh**; 0.55 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 97:3 to 95:5) in 37% yield (0.28 g) as a red solid. The *er* (70:30) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 99:1, 1.0 mL·min^{-1}, 20 °C, λ = 254 nm, t (major) = 100.79 min, t (minor) = 117.75 min. 29% of **1-*o*BrPh** were recovered.

1-(4-Bromobenzoyl)-2-iodoferrocene (2-*p*BrPh)

It was prepared according to the general procedure C from (4-bromobenzoyl)ferrocene (**1-*p*BrPh**; 0.55 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 95:5) in 24% yield (0.18 g) as a red solid. The *er* (71:29) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 90:10, 1.0 mL·min^{-1}, 20 °C, λ = 254 nm, t (major) = 12.33 min, t (minor) = 17.62 min. A second fraction containing a mixture of **1-*p*BrPh** (15%) and **2-*p*BrPh** (50%) was also obtained.

1-Iodo-2-[2-(trifluoromethyl)benzoyl]ferrocene (2-*o*CF$_3$Ph)

It was prepared according to the general procedure C from 2-(trifluoromethyl)benzoylferrocene (**1-*o*CF$_3$Ph**; 0.43 g, 1.2 mmol), and was obtained (eluent: petroleum ether-AcOEt 90:10) in an estimated 49% yield as a mixture with **1-*o*CF$_3$Ph** (26%). The *er* (51:49) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IA-3 column, hexane-isopropanol 99:1, 0.8 mL·min^{-1}, 5 °C, λ = 254 nm, t (major) = 32.44 min, t (minor) = 35.26 min.

1-Iodo-2-[3-(trifluoromethyl)benzoyl]ferrocene (2-*m*CF$_3$Ph)

It was prepared according to the general procedure C from 3-(trifluoromethyl)benzoylferrocene (**1-*m*CF$_3$Ph**; 0.43 g, 1.2 mmol), and was obtained (eluent: petroleum ether-AcOEt 90:10) in an estimated 50% yield as a mixture with [2-iodo-5-(trifluoromethyl)benzoyl]ferrocene (**2'-*m*CF$_3$Ph**; estimated 8% yield). The *er* (71:29) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 95:5, 1.0 mL·min^{-1}, 20 °C, λ = 254 nm, t (major) = 9.27 min, t (minor) = 12.92 min.

1-Iodo-2-[4-(trifluoromethyl)benzoyl]ferrocene (2-*p*CF$_3$Ph)

It was prepared according to the general procedure C from 4-(trifluoromethyl)benzoylferrocene (**1-*p*CF$_3$Ph**; 0.43 g, 1.2 mmol), and was isolated (eluent: petroleum ether-AcOEt 95:5) in 54% yield (0.31 g) as a red solid. The *er* (73:27) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 80:20, 1.0 mL·min^{-1}, 20 °C, λ = 254 nm, t (major) = 6.28 min, t (minor) = 9.14 min. A second fraction containing a mixture of [2-iodo-4-(trifluoromethyl)benzoyl]ferrocene (**2'-*p*CF$_3$Ph**; 16%) and **1-*p*CF$_3$Ph** (11%) was also obtained.

1-(2-Fluorobenzoyl)-2-iodoferrocene (2-*o*FPh)

It was prepared according to the general procedure C from (2-fluorobenzoyl)ferrocene (**1-*o*FPh**; 0.46 g, 1.5 mmol), and obtained (eluent: petroleum ether-AcOEt 97:3 to 95:5) in an estimated 42% yield as a mixture with 15% **1-(2-fluoro-3-iodobenzoyl)-2-iodoferrocene (2"-*o*FPh)**. The *er* (76:24) of the title product in favor of the R_p enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 99:1, 1.0 mL·min^{-1}, 20 °C, λ = 254 nm, t (major) = 86.46 min, t (minor) = 133.34 min. The *er* (64:36) of **2"-*o*FPh** in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 99:1, 1.0 mL·min^{-1}, 20 °C, λ = 254 nm, t (major) = 75.07 min, t (minor) = 100.35 min. A second fraction containing a mixture of (2-fluoro-3-iodobenzoyl)ferrocene (**2'-*o*FPh**; 23%) and **1-*o*FPh** (12%) was also obtained.

1-Iodo-2-pivaloylferrocene (2-*t*Bu)

It was prepared according to the general procedure C from pivaloylferrocene (**1-*t*Bu**; 0.405 g, 1.5 mmol), and was isolated (eluent: petroleum ether-AcOEt 95:5) in 51% yield (0.31 g) as a red solid. The *er* (68:32) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 99:1, 1.0 mL·min^{-1}, 20 °C, λ = 254 nm, t (major) = 12.44 min, t (minor) = 14.39 min. 32% of **1-*t*Bu** were recovered.

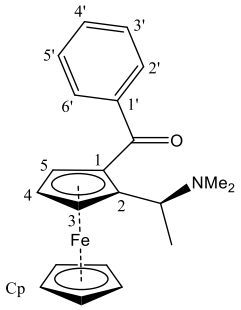
1-Iodo-2-(trifluoromethylcarbonyl)ferrocene (2-CF$_3$)

It was prepared according to the general procedure C from [(trifluoromethyl)carbonyl]ferrocene (**1-CF$_3$**; 0.85 g, 3.0 mmol), but using *n*BuLi (1.25 M in hexanes, 2.6 mL, 3.3 mmol), (*S*)-PEAH (755 µL, 3.3 mmol), $ZnCl_2$·TMEDA (0.76 g, 3.0 mmol) and I_2 (0.84 g, 3.3 mmol), and was obtained (eluent: petroleum ether-AcOEt 96:4) in an estimated 13% yield as a mixture with **1-CF$_3$** (24%). The *er* (80:20) in favor of the R_P enantiomer was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 99:1, 0.8 mL·min^{-1}, 5 °C, λ = 254 nm, t (major) = 12.08 min, t (minor) = 13.03 min. When the title product was prepared according to the general procedure C from [(trifluoromethyl)-

carbonyl]ferrocene (**1-CF$_3$**; 0.85 g, 3.0 mmol), it was similarly obtained in an estimated 6% yield as a mixture with **1-CF$_3$** (5%). The *er* (62:38) in favor of the R_P enantiomer was determined similarly.

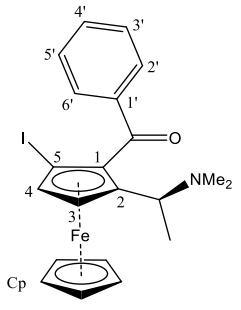
*(S,R$_P$)-1-Benzoyl-2-[1-(dimethylamino)ethyl]ferrocene (**R$_P$-5**)*

It was prepared by adapting a reported procedure [36]. To [(*S*)-1-(dimethylamino)ethyl]ferrocene (0.81 g, 2.0 mmol) in Et_2O (4 mL) at 0 °C, was added *s*BuLi (1.1 M in cyclohexane; 3.1 mL, 3.4 mmol), and the reaction mixture was stirred for 3 h at this temperature. *N*-Methoxy-*N*-methylbenzamide (0.51 mL, 3.4 mmol) was next added at –80 °C, and the reaction mixture stirred at 0 °C for 30 min. H_2O (5 mL) was added, and the product was extracted with AcOEt. After drying the combined organic layers over anhydrous $MgSO_4$, the solvent was evaporated under reduced pressure. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt-Et_3N 88:10:2; Rf 0.24). The title product was isolated in 99% yield (0.72 g) as a red solid. Mp 68 °C. IR (ATR) ν 660, 698, 734, 773, 800, 822, 833, 850, 878, 930, 958, 1007, 1043, 1063, 1081, 1106, 1154, 1183, 1220, 1255, 1305, 1319, 1360, 1374, 1417, 1429, 1448, 1474, 1576, 1596, 1634 (C=O), 2768, 2818, 2852, 2930, 3090 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.61 (d, 3H, *J* = 7.0 Hz, CH*Me*), 2.04 (s, 6H, NMe_2), 4.14 (s, 5H, Cp), 4.43 (t, 1H, *J* = 2.6 Hz, H4), 4.46 (dd, 1H, *J* = 2.7 and 1.4 Hz, H5), 4.57 (dd, 1H, *J* = 2.6 and 1.4 Hz, H3), 4.72 (q, 1H, *J* = 7.0 Hz, C*H*Me), 7.44 (t, 2H, *J* = 7.5 Hz, H3' and H5'), 7.53 (tt, 1H, *J* = 7.4 and 1.4 Hz, H4'), 7.78-7.81 (m, 2H, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 17.5 (CH_3, CH*Me*), 40.7 ($2CH_3$, NMe_2), 54.5 (CH, *C*HMe), 69.5 (CH, C4), 71.0 (5CH, Cp), 71.4 (CH, C5), 71.9 (CH, C3), 77.1 (C, C1, *C*-C(O)Ph), 92.3 (C, C2), 128.2 (2CH, C3' and C5'), 128.5 (2CH, C2' and C6'), 131.7 (CH, C4'), 140.5 (C, C1'), 200.7 (C, C=O) ppm. These data are similar to those reported for the *R*,*S*$_P$ enantiomer [37]. $[\alpha]_D^{20}$ +443.5 (*c* 0.34, $CHCl_3$).



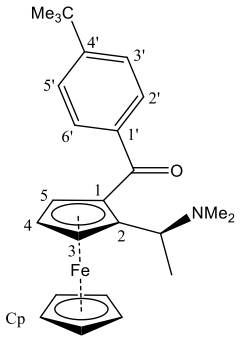
*(S,R$_P$)-1-Benzoyl-2-[1-(dimethylamino)ethyl]-5-iodoferrocene (**R$_P$-6**)*

To a stirred, cooled (-15 °C) solution of TMPH (0.27 mL, 1.6 mmol) in THF (4 mL) was added dropwise *n*BuLi (1.2 M in hexane; 1.3 mL, 1.6 mmol). After 5 min, this solution of LiTMP was cooled to –20 °C and slowly cannulated to a solution of $ZnCl_2$·TMEDA (0.20 g, 0.80 mmol) and (*S*,*R*$_P$)-1-benzoyl-2-[1-(dimethylamino)ethyl]ferrocene (**R$_P$-5**; 0.29 g, 0.80 mmol) in THF (4 mL) cooled at the same temperature. After 1 h at –20 °C, a solution of I_2 (0.41 g, 1.6 mmol) in THF (2 mL) was added and the reaction mixture was warmed to rt. Aa saturated aqueous solution of $Na_2S_2O_3$ (10 mL) was then added, and the product was extracted with AcOEt. After drying the combined organic layers over anhydrous $MgSO_4$, the solvent was evaporated under reduced pressure, and the iodide was purified by column chromatography over silica gel (eluent: petroleum ether-AcOEt-Et_3N 88:10:2; Rf 0.55). It was isolated in 20% yield (78 mg) as a yellow solid. Mp 102 °C. IR (ATR) ν 689, 707, 740, 793, 819, 839, 876, 899, 929, 949, 1001, 1025, 1047, 1078, 1100, 1160, 1179, 1192, 1222, 1267, 1289, 1372, 1409, 1450, 1582, 1599, 1661 (C=O), 2779, 2825, 2928, 3089 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.31 (d, 3H, *J* = 6.9 Hz, CH*Me*), 1.86 (s, 6H, NMe_2), 4.02 (q, 1H, *J* = 6.8 Hz, C*H*Me), 4.27 (s, 5H, Cp), 4.35 (d, 1H, *J* = 2.5 Hz, H3), 4.60 (d, 1H, *J* = 2.5 Hz, H4), 7.38 (t, 2H, *J* = 7.65 Hz, H3' and H5'), 7.50 (tt, 1H, *J* = 7.4 and 1.3 Hz, H4'), 7.69-7.72 (m, 2H, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 12.4 (CH_3, CH*Me*), 38.4 (C, C5, C-I), 40.1 ($2CH_3$, NMe_2), 55.4 (CH, *C*HMe), 68.4 (CH, C3), 74.1 (5CH, Cp), 74.2 (CH, C4), 89.7 (C, C1, *C*-C(O)Ph), 95.4 (C, C2), 128.0 (2CH, C3' and C5'), 129.9 (2CH, C2' and C6'), 132.5 (C, C4'), 138.2 (C, C1'), 197.5 (C, C=O) ppm. $[\alpha]_D^{20}$ +325 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{21}H_{22}FeINO$ (487.16): C, 51.78; H, 4.55; N, 2.88. Found: C, 51.72; H, 4.29; N, 2.83%. 20% of **R$_P$-5** were recovered.



(S,R$_P$*)-1-(4-tert-Butylbenzoyl)-2-[1-(dimethylamino)ethyl]ferrocene (**R**$_P$**-7**)*

To (*S*,*R*$_P$)-1-benzoyl-2-[1-(dimethylamino)ethyl]ferrocene (***R*$_P$-5**; 0.30 g, 0.80 mmol) in THF (2 mL) at –80 °C, was added dropwise *t*BuLi (1.6 M in pentane, 0.55 mL, 0.88 mmol). After 15 min stirring at this temperature, a solution of I_2 (0.22 g, 0.88 mmol) in THF (1 mL) was added and the reaction mixture was stirred for a further 15 min. A saturated aqueous solution of $Na_2S_2O_3$ (5 mL) was added, and the product was extracted with AcOEt. After drying the combined organic layers over anhydrous $MgSO_4$, the solvent was evaporated under reduced pressure, and the iodide was purified by column chromatography over silica gel (eluent: petroleum ether-AcOEt-Et_3N 78:20:2; Rf 0.30). The title product was isolated in 61% yield (0.20 g) as a red oil. IR (ATR) ν 666, 703, 749, 775, 822, 853, 885, 955, 1002, 1047, 1065, 1107, 1156, 1192, 1224, 1255, 1304, 1314, 1364, 1418, 1435, 1543, 1579, 1604, 1640 (C=O), 2775, 2818, 2870, 2965 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 9H, *t*Bu), 1.62 (d, 3H, *J* = 7.0 Hz, CH*Me*), 2.03 (s, 6H, NMe_2), 4.14 (s, 5H, Cp), 4.42 (t, 1H, *J* = 2.7 Hz, H4), 4.50 (dd, 1H, *J* = 2.6 and 1.3 Hz, H5), 4.55 (dd, 1H, *J* = 2.6 and 1.4 Hz, H3), 4.72 (q, 1H, *J* = 7.0 Hz, C*H*Me), 4.92 (t, 2H, *J* = 2.0 Hz, H2 and H5), 7.44 (AA'BB', 2H, *J* = 8.4 Hz, H3' and H5'), 7.74 (AA'BB', 2H, *J* = 8.3 Hz, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 17.8 (CH_3, CH*Me*), 31.3 ($3CH_3$, C*Me*$_3$), 35.1 (C, *C*Me$_3$), 40.8 ($2CH_3$, NMe_2), 54.6 (CH, *C*HMe), 69.3 (CH, C4), 71.0 (5CH, Cp), 71.3 (CH, C5), 71.7 (CH, C3), 77.7 (C, C1, *C*-C(O)Ar), 91.9 (C, C2), 125.1 (2CH, C3' and C5'), 128.6 (2CH, C2' and C6'), 137.7 (C, C1'), 155.4 (C, C4'), 200.3 (C, C=O) ppm. $[\alpha]_D^{20}$ +466 (*c* 0.50, $CHCl_3$). HRMS (ESI, 90:10 MeOH-CH_2Cl_2), *m/z*: 440.0309 (0 ppm) found (calcd for $C_{21}H_{23}NO^{79}Br^{56}Fe$, $[M+H]^+$, requires 440.03069).

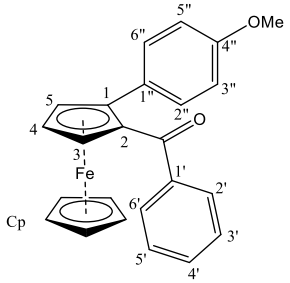


General procedure D for the Suzuki-Miyaura cross-coupling.

1-Benzoyl-2-iodoferrocene (**2-Ph**; 0.21 g, 0.50 mmol), the boronic acid (1.0 mmol), bis(dibenzylideneacetone)palladium ($Pd(dba)_2$, 14 mg, 25 µmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (Sphos, 41 mg, 0.10 mmol) and CsF (0.15 g, 1.0 mmol) were placed in a dried Schlenk tube, subjected to three cycles of vacuum/argon. Toluene (5 mL) was added and the reaction mixture was stirred overnight at 110 °C in a pre-heated oil bath. The reaction mixture was cooled to rt and water was added. The reaction mixture was extracted with AcOEt and the combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent given in the product description) led to the product.

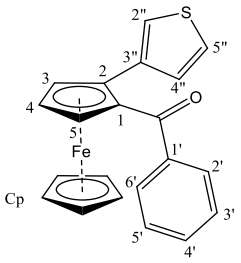
1-Anisyl-2-benzoylferrocene (8a)

The title product was obtained by following the general procedure D and using anisylboronic acid (0.15 g, 1.0 mmol). Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt 95:5 to 90:10) afforded the title product in 67% yield (0.13 g) as an orange glue. Rf (eluent: petroleum ether-AcOEt 90:10) 0.44. IR (ATR) ν 731, 752, 824, 851, 871, 893, 980, 1001, 1029, 1106, 1132, 1175, 1242, 1293, 1343, 1405, 1423, 1436, 1447, 1520, 1576, 1609, 1642 (C=O), 2834, 2934, 3005 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3H, OMe), 4.21 (s, 5H, Cp), 4.52 (t, 1H, *J* = 2.6 Hz, H4), 4.68 (dd, 1H, *J* = 2.6 and 1.5 Hz, H3), 4.74 (dd, 1H, *J* = 2.6 and 1.6 Hz, H5), 6.78 (AA'BB', 2H, *J* = 8.8 Hz, H3" and H5"), 7.36 (t, 2H, *J* = 7.7 Hz, H3' and H5'), 7.43 (AA'BB', 2H, *J* = 8.7 Hz, H2" and H6"), 7.47 (tt, 1H, *J* = 7.4 and 1.3 Hz, H4'), 7.81-7.83 (m, 2H, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 55.4 (CH_3), 69.7 (CH, C4), 71.7 (5CH, Cp), 73.0 (CH, C3), 73.3 (CH, C5), 78.2 (C, C2, *C*-C(O)Ph), 91.8 (C, C1), 113.2 (2CH, C3" and C5"), 128.1 (2CH, C3' and C5'), 129.0 (2CH, C2' and C6'), 129.5 (C, C1'), 130.9 (2CH, C2" and C6"), 131.9 (CH, C4'), 139.7 (C, C1"), 158.6 (C, C4"), 199.2 (C, C=O) ppm. Anal. Calcd for $C_{24}H_{20}FeO_2$ (396.27): C, 72.74; H, 5.09. Found: C, 72.87; H, 5.28%. 14% of the starting **2-Ph** were recovered.



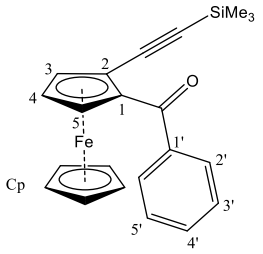
1-Benzoyl-2-(3-thienyl)ferrocene (8b)

The title product was obtained by following the general procedure D and using 2-thiopheneboronic acid (0.13 g). Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt 90:10; Rf 0.55) afforded the title product in an estimated 40% yield as a mixture (red glue) with the starting **2-Ph** (34%). It was identified by NMR. ^{1}H NMR ($CDCl_3$) δ 4.20 (s, 5H, Cp), 4.53 (t, 1H, *J* = 2.5 Hz, H4), 4.67 (dd, 1H, *J* = 2.7 and 1.5 Hz, H5), 4.79 (dd, 1H, *J* = 2.5 and 1.6 Hz, H3), 7.19 (dd, 1H, *J* = 5.0 and 3.0 Hz, H5"), 7.25 (dd, 1H, *J* = 5.0 and 1.3 Hz, H4"), 7.37-7.40 (m, 3H, H3', H5' and H2"), 7.49 (tt, 1H, *J* = 7.4 and 1.3 Hz, H4'), 7.82-7.86 (m, 2H, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 69.9 (CH, C4), 71.7 (5CH, Cp), 72.9 (CH, C3), 73.4 (CH, C5), 78.3 (C, C1, *C*-C(O)Ph), 85.6 (C, C2), 122.5 (CH, C2"), 124.2 (CH, C5"), 128.1 (2CH, C3' and C5'), 128.9 (2CH, C2' and C6'), 129.6 (CH, C4"), 132.0 (CH, C4'), 137.8 (C, C3"), 139.8 (C, C1'), 199.4 (C, C=O) ppm.



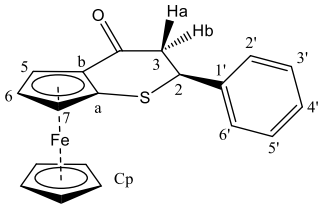
*1-Benzoyl-2-(trimethylsilylethinyl)ferrocene (**9**)*

1-Benzoyl-2-iodoferrocene (**2-Ph**; 0.42 g, 1.0 mmol), Pd(P*t*Bu$_3$)$_2$ (20 mg, 40 µmol) and CuI (7.6 mg, 40 µmol) were placed in a dried Schlenk tube, subjected to three cycles of vacuum/argon. Trimethylsilylacetylene (0.28 mL, 2.0 mmol), degassed THF-iPr_2NEt (3:1, 1.5 mL) mixture were added and the reaction mixture was stirred at 20 °C for 16 h. The reaction mixture was filtrated over a pad of celite, washed with AcOEt and the combined filtrates were concentrated under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt 97:3 to 96:4) gave the title product in 21% yield (81 mg) as an orange oil. Rf (petroleum ether-AcOEt 90:10) 0.63. IR (ATR) ν 728, 758, 838, 888, 913, 1003, 1017, 1075, 1107, 1179, 1231, 1248, 1274, 1337, 1411, 1447, 1579, 1599, 1646 (C=O), 2153, 2245, 2958 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.26 (s, 5H, Cp), 4.52 (t, 1H, *J* = 2.7 Hz, H4), 4.79 (dd, 1H, *J* = 2.6 and 1.5 Hz, H3), 4.83 (dd, 1H, *J* = 2.7 and 1.5 Hz, H5), 7.42 (t, 2H, *J* = 7.6 Hz, H3' and H5'), 7.52 (ddt, 1H, *J* = 8.0, 6.9 and 1.3 Hz, H4'), 7.86-7.88 (m, 2H, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 67.1 (C, C2), 71.2 (CH, C4), 72.6 (5CH, Cp), 73.9 (CH, C5), 76.3 (CH, C3), 80.9 (C, C1, *C*-C(O)Ph), 95.1 (C, C≡*C*-$SiMe_3$), 102.6 (C, *C*≡C-$SiMe_3$), 128.1 (2CH, C3' and C5'), 129.0 (2CH, C2' and C6'), 131.9 (CH, C4'), 139.5 (C, C1'), 198.6 (C, C=O) ppm. Anal. Calcd for $C_{22}H_{22}FeOSi$ (386.35): C, 68.39; H, 5.74. Found: C, 68.17; H, 5.73%. 55% of the starting **2-Ph** were recovered.



*2-Phenyl-2,3-dihydrothiopyrano[2,3]ferrocen-4-one (**10**)*

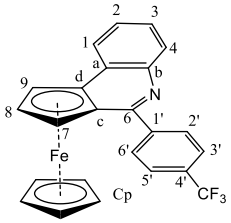
(*E*)-1-Cinnamoyl-2-iodoferrocene (**2-CH=CHPh**; 0.11 g, 0.25 mmol), potassium ethylxanthate (80 mg, 0.50 mmol) and $Cu(OAc)_2.2H_2O$ (25 mg, 0.12 mmol) were placed in a dried tube under air. DMSO (1 mL) was added and the reaction mixture was heated at 70 °C in a pre-heated oil bath for 16 h. The reaction mixture was filtrated over a pad of celite, washed with petroleum ether-AcOEt to give the crude product. Purification by preparative thin-layer chromatography (eluent: petroleum ether-AcOEt 95:5; Rf 0.20) gave the title product in 47% yield (41 mg) and 85:15 diastereoisomeric ratio as an orange solid. Mp 158-159 °C. IR (ATR) ν 772, 812, 833, 853, 914, 1000, 1036, 1049, 1077, 1100, 1158, 1176, 1277, 1313, 1373, 1398, 1410, 1434, 1452, 1493, 1665 (C=O), 2919, 3106 cm^{-1}. ^{1}H NMR (main diastereoisomer; $CDCl_3$) δ 2.91 (dd, 1H, *J* = 16.8 and 12.9 Hz, C*Ha*Hb), 3.15 (dd, 1H, *J* = 16.8 and 2.6 Hz, CHa*Hb*), 4.33 (s, 5H, Cp), 4.63 (t, 1H, *J* = 2.6 Hz, H6), 4.78 (dd, 1H, *J* = 2.5 and 1.3 Hz, H7), 4.94 (dd, 1H, *J* = 12.9 and 2.7 Hz, H2), 4.99 (dd, 1H, *J* = 2.7 and 1.3 Hz, H5), 7.34 (tt, 1H, *J* = 7.2 and 1.4 Hz, H4'), 7.39 (t, 2H, *J* = 7.3 Hz, H3' and H5'), 7.44 (dd, 2H, *J* = 7.1 and 1.7 Hz, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 48.2 and 48.3 (CH and CH_2, C2 and C3), 65.8 (CH, C5), 70.9 (C, Cb), 71.0 (CH, C6), 71.4 (5CH, Cp), 71.7 (CH, C7), 91.5 (C, Ca), 127.7 (2CH, C2' and C6'), 128.5 (CH, C4'), 129.1 (2CH, C3' and C5'),



139.0 (C, C1'), 201.5 (C, C=O) ppm. Anal. Calcd for $C_{19}H_{16}FeOS$ (348.24): C, 65.53; H, 4.63; S, 9.21. Found: C, 65.37; H, 4.47; S, 9.11%.

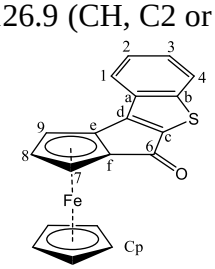
*6-[4-(Trifluoromethyl)phenyl]ferroceno[c]quinoline (**11**)*

1-Iodo-2-[4-(trifluoromethyl)benzoyl]ferrocene (**2-*p*CF$_3$Ph**; 0.19 g, 0.39 mmol), 2-aminophenylboronic acid hydrochloride (0.27 g, 1.6 mmol), Cs_2CO_3 (0.25 g, 0.78 mmol), CsF (0.12 g, 0.78 mmol), $Pd(dba)_2$ (11 mg, 0.020 mmol) and PPh_3 (20.5 mg, 0.080 mmol) were placed in a dried Schlenk tube, subjected to three cycles of vacuum/argon. Dioxane (4 mL) was added and the reaction mixture was stirred overnight at 110 °C in a pre-heated oil bath. The reaction mixture was cooled to rt and water was added. The reaction mixture was extracted with AcOEt and the combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to give the crude product. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt-Et_3N 89:10:1; Rf 0.50) gave the title product in 88% yield (0.15 g) as a red solid. Mp 138-140 °C. IR (ATR) ν 722, 751, 758, 779, 827, 851, 914, 997, 1017, 1043, 1068, 1107, 1142, 1162, 1239, 1325, 1357, 1404, 1429, 1467, 1477, 1519, 1540, 1562, 1620, 3055 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 5H, Cp), 4.50 (t, 1H, J = 2.6 Hz, H8), 5.03 (dd, 1H, J = 2.6 and 1.1 Hz, H7), 5.51 (dd, 1H, J = 2.6 and 1.1 Hz, H9), 7.53 (td, 1H, J = 7.4 and 1.5 Hz, H2), 7.57 (td, 1H, J = 7.5 and 1.7 Hz, H3), 7.86 (d, 2H, J = 8.0 Hz, H3' and H5'), 8.01 (dd, 1H, J = 7.8 and 1.6 Hz, H1), 8.03 (dd, 1H, J = 8.0 and 1.3 Hz, H4), 8.28 (d, 2H, J = 7.4 Hz, H2' and H6') ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 63.0 (CH, C9), 65.4 (CH, C7), 69.8 (5CH, Cp), 72.5 (CH, C8), 77.4 (C, Cc), 85.9 (C, Cd), 122.9 (CH, C1), 124.3 (q, C, J = 272 Hz, CF_3), 125.8 (q, 2CH, J = 3.8 Hz, C3' and C5'), 127.3 (2CH, C2 and C3), 128.2 (C, Ca), 128.7 (2CH, C2' and C6'), 130.3 (CH, C4), 131.5 (q, C, J = 32.4 Hz, C4'), 143.5 (C, Cb or C1'), 143.6 (C, Cb or C1'), 165.0 (C, C6) ppm. ^{19}F NMR ($CDCl_3$) δ –62.6 ppm. Anal. Calcd for $C_{24}H_{16}F_3FeN$ (431.24): C, 66.85; H, 3.74; N, 3.25. Found: C, 66.91; H, 3.81; S, 3.47%. 10% of the starting **2-*p*CF$_3$Ph** were recovered.



*Compound **12***

(3-Iodo-2-benzothienoyl)ferrocene (**2'-2BTh**; 165 mg, 0.35 mmol), $Pd(OAc)_2$ (2.0 mg, 8.75 µmol), (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(S)-BINAP; 11 mg, 17.5 µmol], Cs_2CO_3 (0.17 g, 0.52 mmol) and pivalic acid (11 mg, 0.10 mmol) were placed in a dried Schlenk tube, subjected to three cycles of vacuum/argon. *p*-Xylene (2 mL) was added and the reaction mixture was stirred overnight at 60 °C in a pre-heated oil bath. The reaction mixture was cooled to rt. Purification by column chromatography over silica gel (eluent: petroleum ether-AcOEt 90:10; Rf 0.33) gave the title product in 92% yield (0.11 g) and 99.4% *ee* as a purple solid. Mp 175-176 °C. IR (ATR) ν 707, 732, 746, 800, 820, 868, 916, 1003, 1023, 1058, 1075, 1105, 1160, 1178, 1216, 1230, 1265, 1345, 1355, 1410, 1425, 1444, 1485, 1594, 1663 -C=O), 1957, 3018 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.22 (s, 5H, Cp), 4.87 (dd, 1H, J = 2.2 and 0.8 Hz, H9), 4.97-4.99 (m, 2H, H7 and H8), 7.39 (dd, 1H, J = 7.1 and 1.7 Hz, H3), 7.43 (dd, 1H, J = 7.2 and 1.6 Hz, H2), 7.74-7.78 (m, 1H, H1), 7.80-7.84 (m, 1H, H4) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 66.6 (CH, C9), 68.2 (CH, C7 or C8), 73.7 (5CH, Cp), 72.5 (CH, C7 or C8), 79.4 (C, Cf), 84.5 (C, Ce), 123.1 (CH, C1), 124.7 (CH, C4), 125.6 (CH, C2 or C3), 126.9 (CH, C2 or C3), 131.8 (C, Ca), 138.2 (C, Cc), 147.2 (C, Cd), 147.2 (C, Cc), 149.7 (C, Cb), 189.5 (C, C=O) ppm. $[\alpha]_D^{20}$ +205.5 (*c* 0.033, $CHCl_3$). Anal. Calcd for $C_{19}H_{12}FeOS$ (344.21): C, 66.30; H, 3.51; S, 9.31. Found: C, 66.22; H, 3.48; S, 9.26%. Using *rac*-BINAP led to compound **12** in 87% yield (0.105 g). Using (*S*)-BINAP, the *er* (> 99:1) was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 70:30, 1.0 mL·min^{-1}, 25 °C, λ = 220 nm, t (major) = 17.89 min, t (minor) = 15.89 min.



*Crystal data for **12***. $C_{19}H_{12}FeOS$, M = 344.20, T = 150(2) K; triclinic P 1 (I.T.#1), a = 8.0313(4), b = 8.9523(4), c = 11.1807(5) Å, α = 67.899(2), β = 76.526(2), γ = 77.126(2) °, V = 716.12(6) Å^3. Z = 2, d = 1.596 g.cm^{-3}, μ = 9.772 mm^{-1}. A final refinement on F^2 with 5049 unique intensities and 398

parameters converged at $\omega R(F^2)$ = 0.1081 (R_F = 0.0417) for 4925 observed reflections with $I > 2\sigma(I)$. CCDC 2490218.

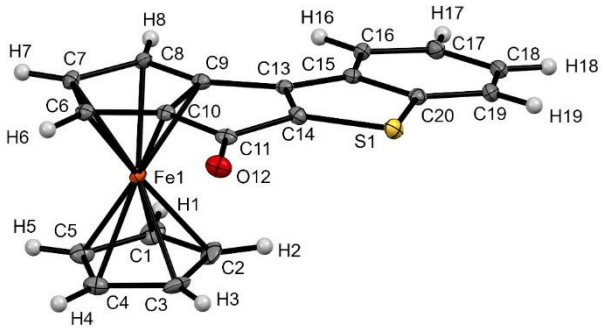
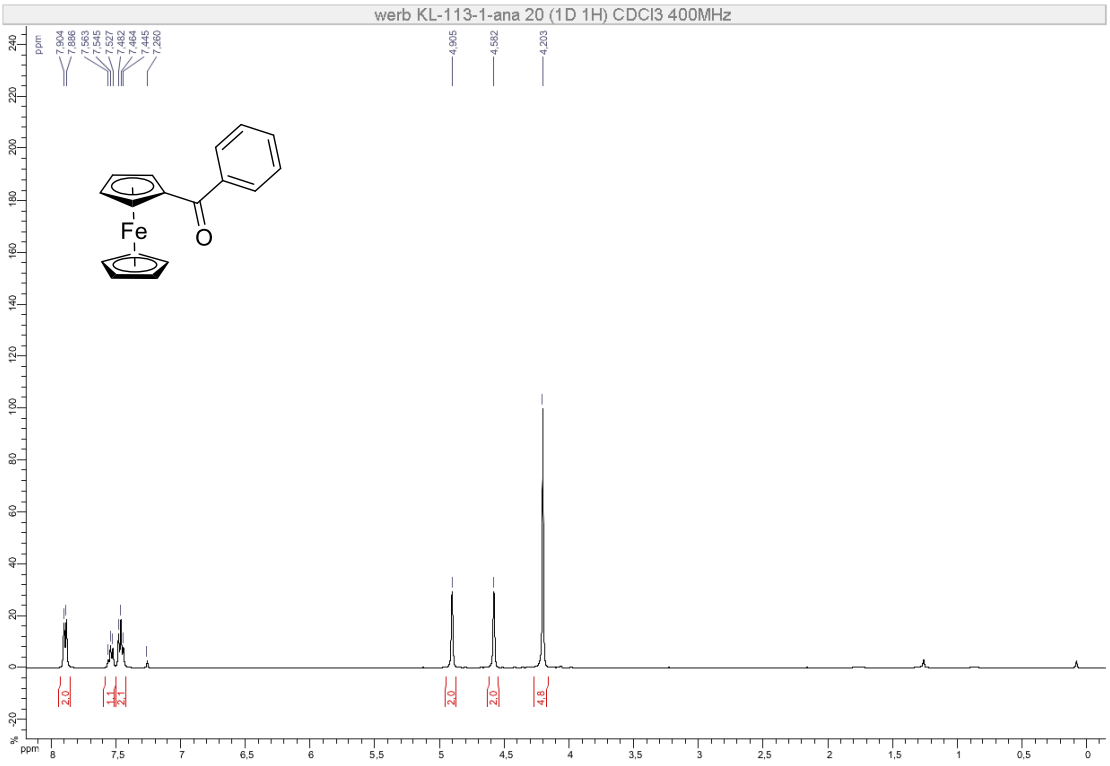


Figure S27. Molecular structure of compound **12** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C10−C11 = 1.501(6), C10−Cg2···Cg1−C3 = –0.60 (Cg1 being the centroid of the C1−C2−C3−C4−C5 ring and Cg2 the one of the C6−C7−C8−C9−C10 ring), C6−C10−C11−O12 = –1.4(9), O12−C11−C13−S1 = 4.8(8).

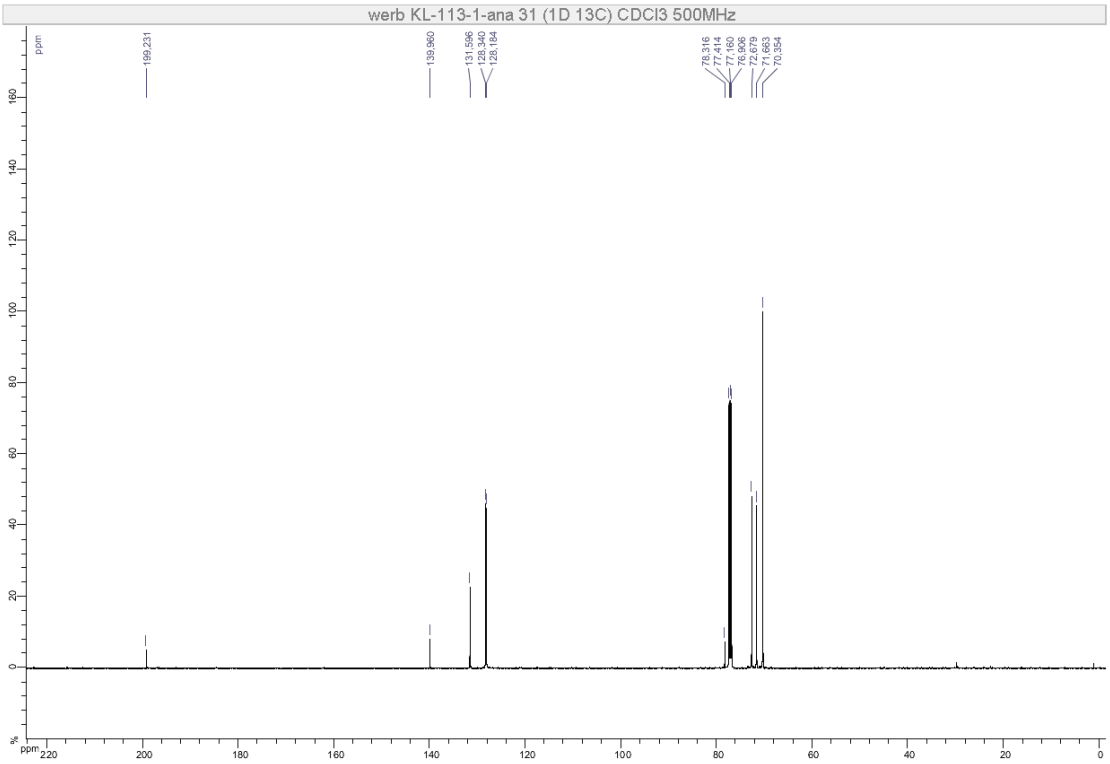
D) NMR Spectra

Benzoylferrocene (1-Ph)

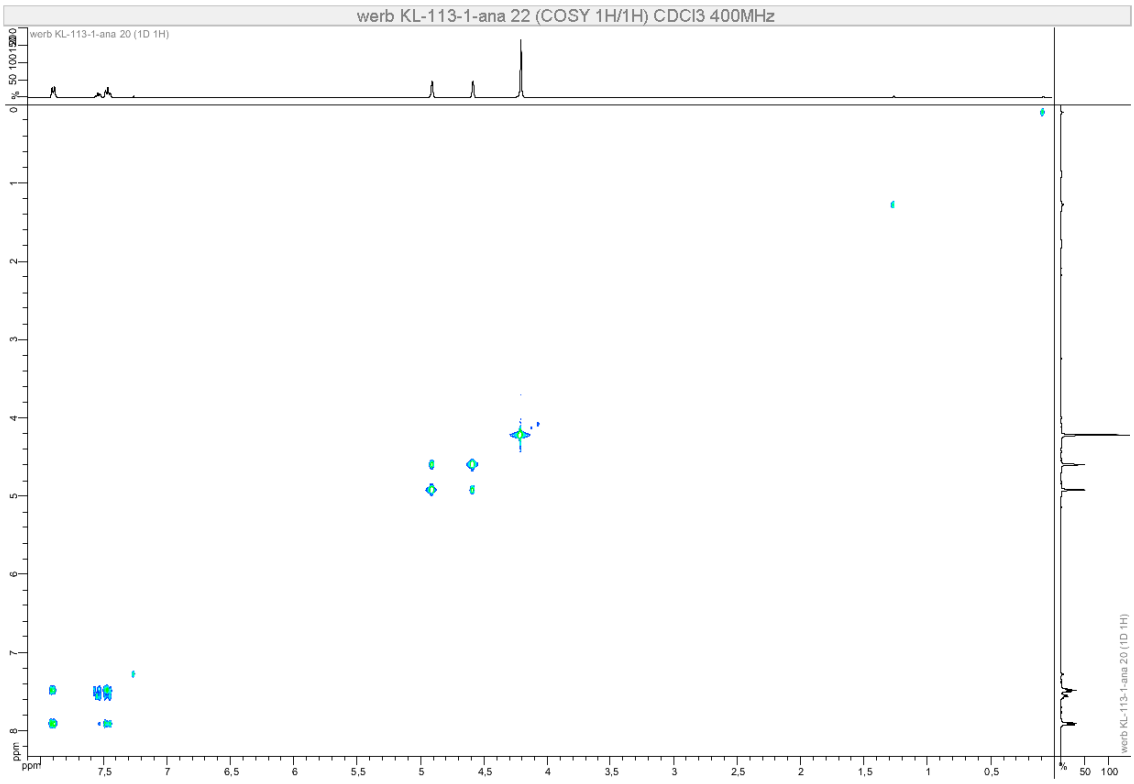
^{1}H NMR (400 MHz, $CDCl_3$)



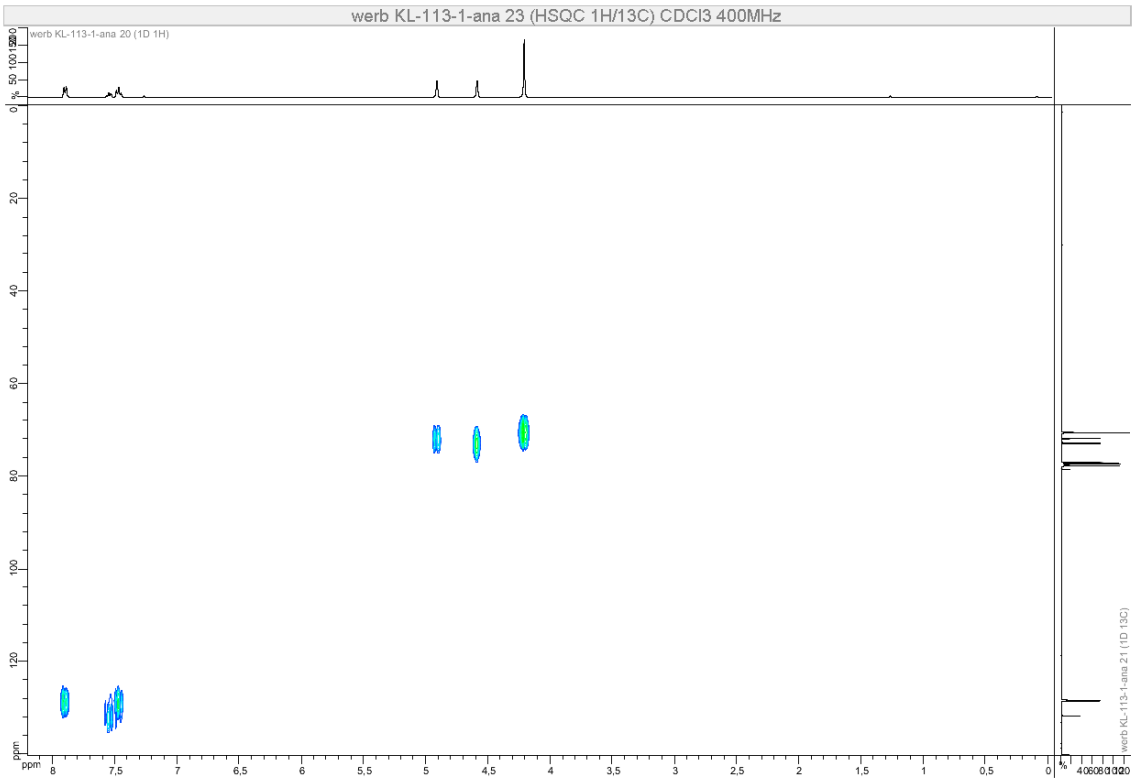
^{13}C NMR (126 MHz, $CDCl_3$)



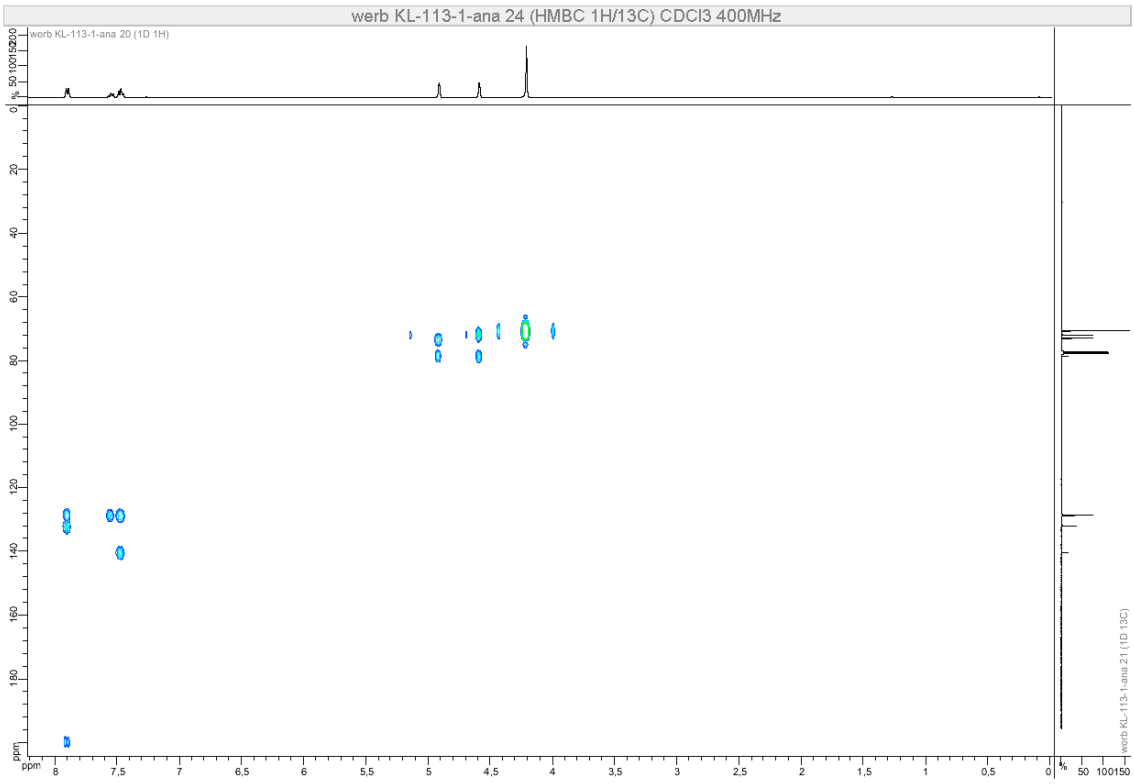
COSY (400 MHz, $CDCl_3$)



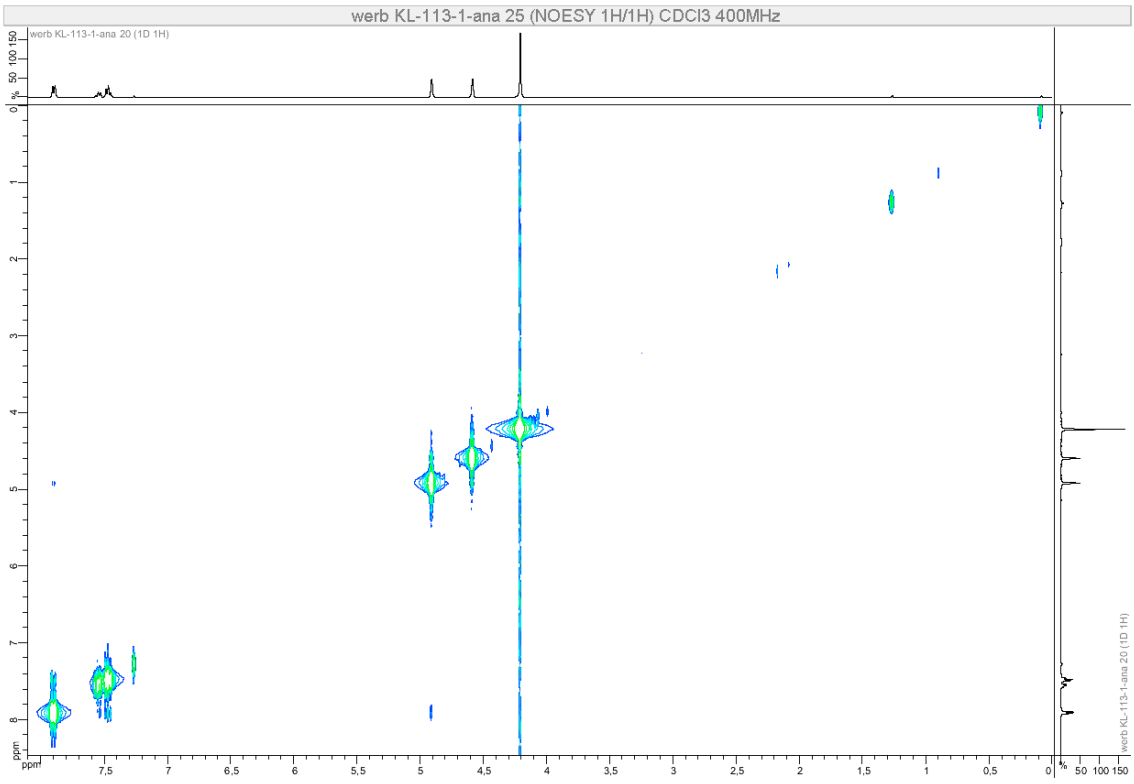
HSQC (400 MHz, $CDCl_3$)



HMBC (400 MHz, $CDCl_3$)

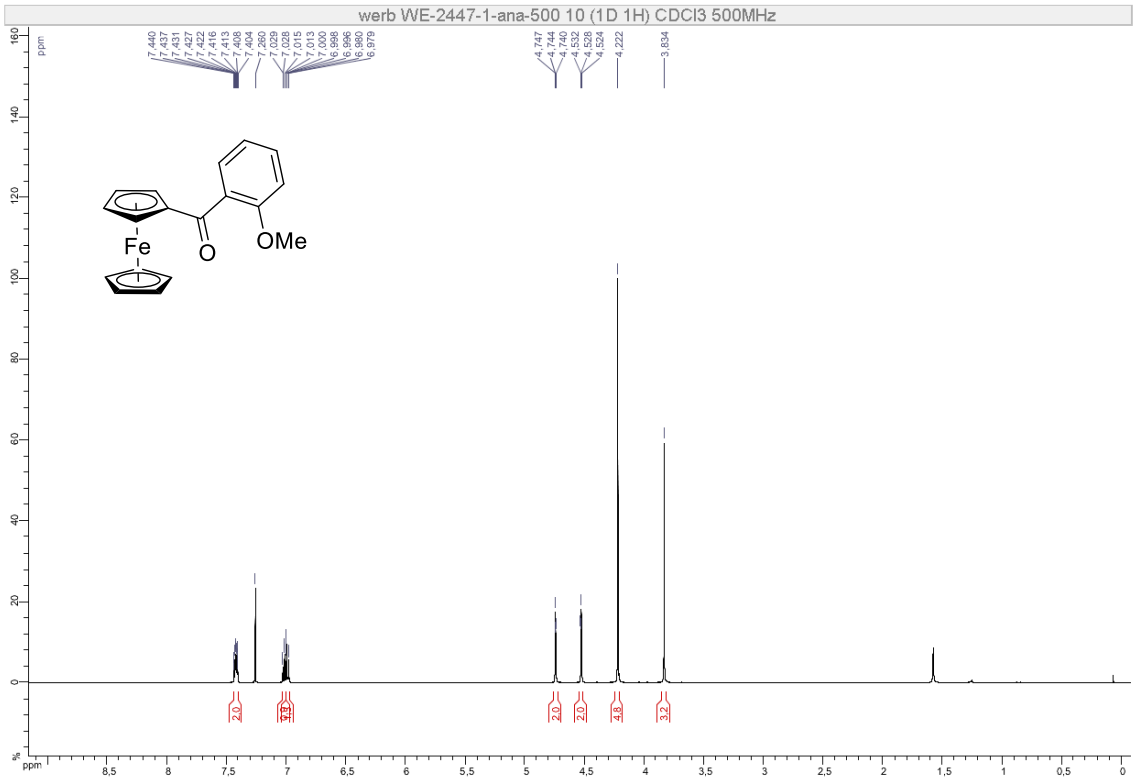


NOESY (400 MHz, $CDCl_3$)

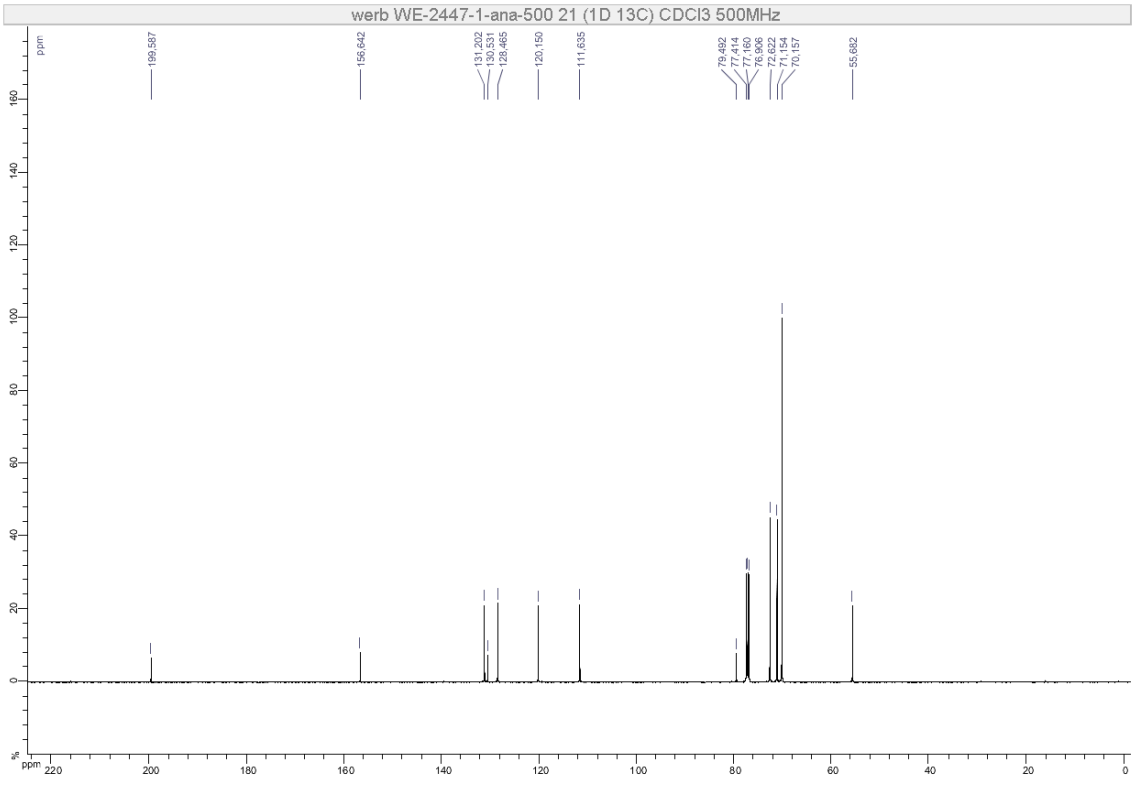


(2-Methoxybenzoyl)ferrocene (1-*o*OMePh)

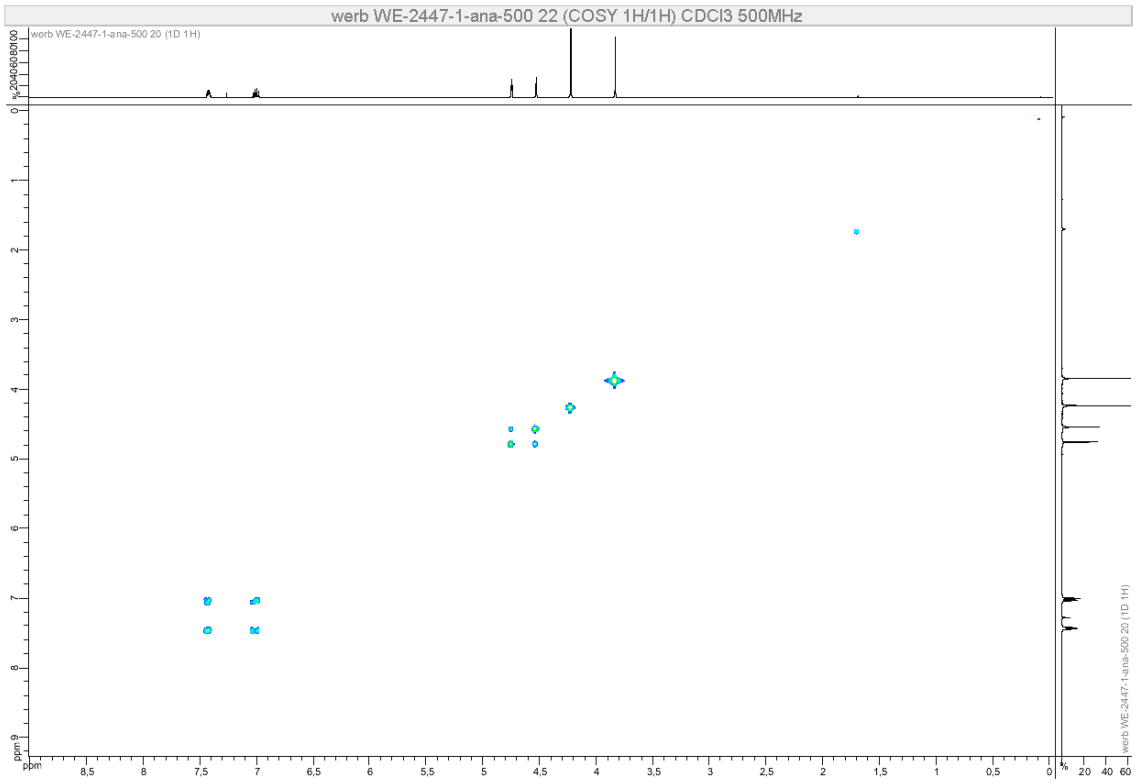
^{1}H NMR (500 MHz, $CDCl_3$)



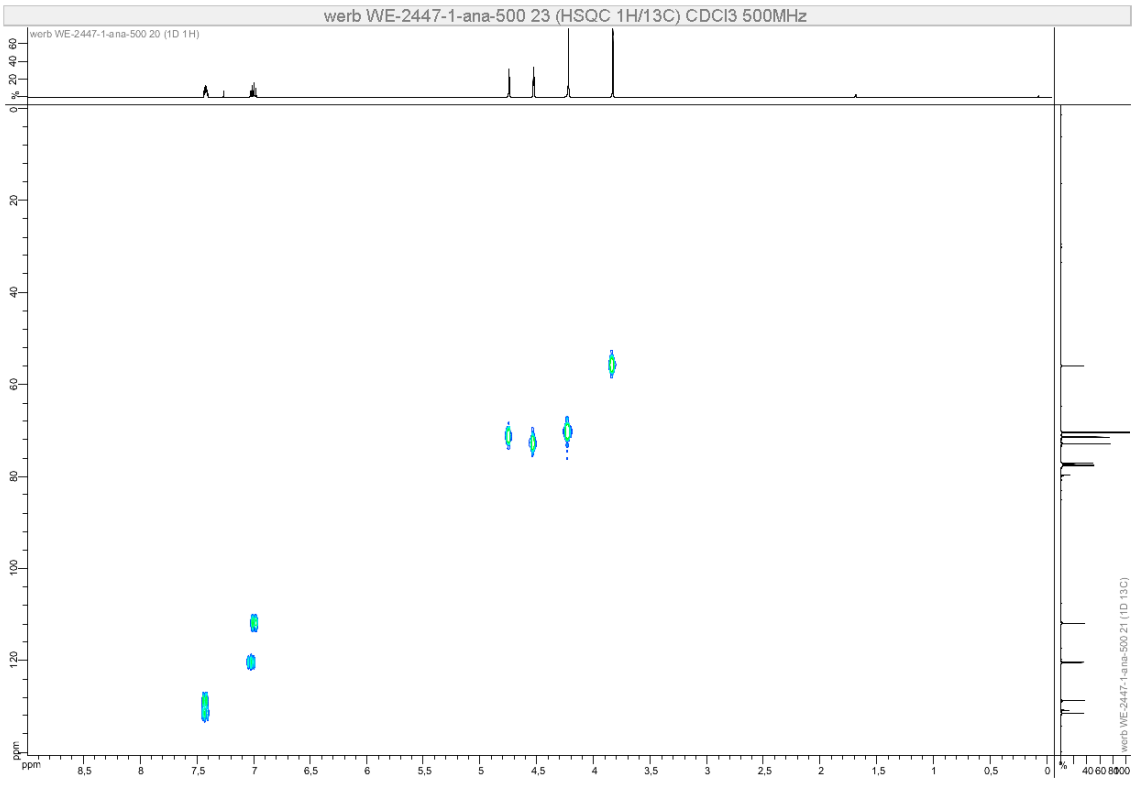
^{13}C NMR (126 MHz, $CDCl_3$)



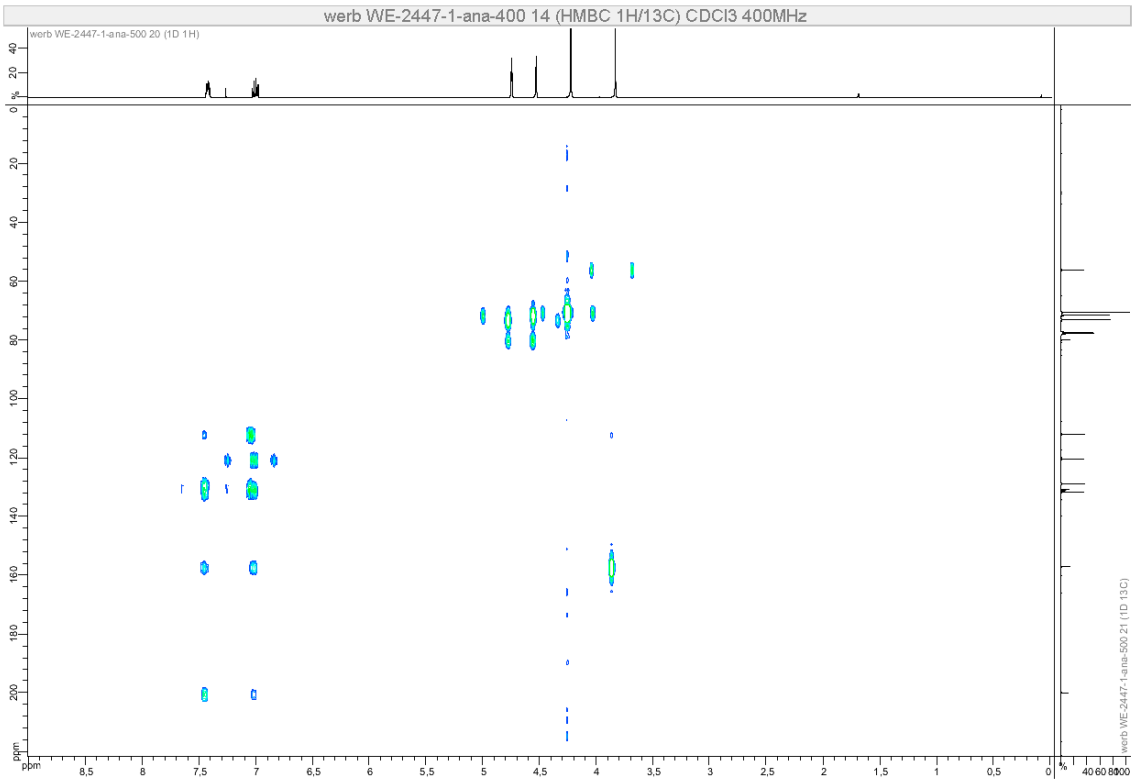
COSY (500 MHz, $CDCl_3$)



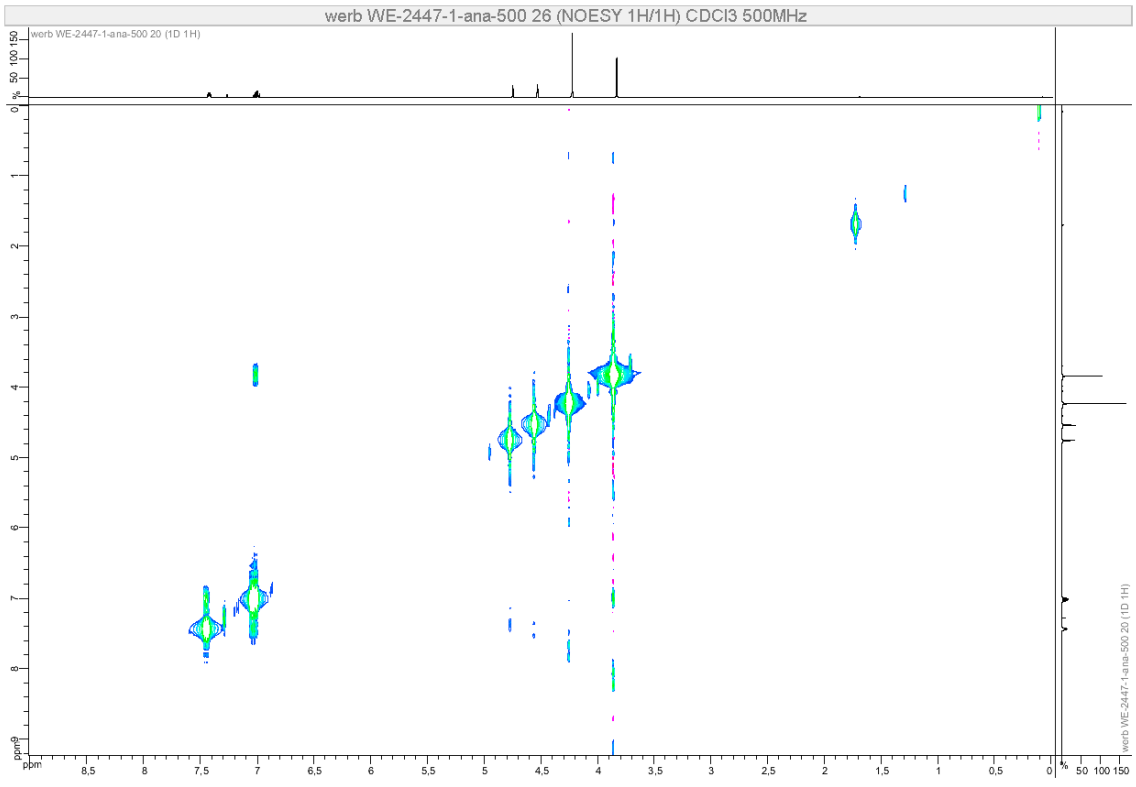
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

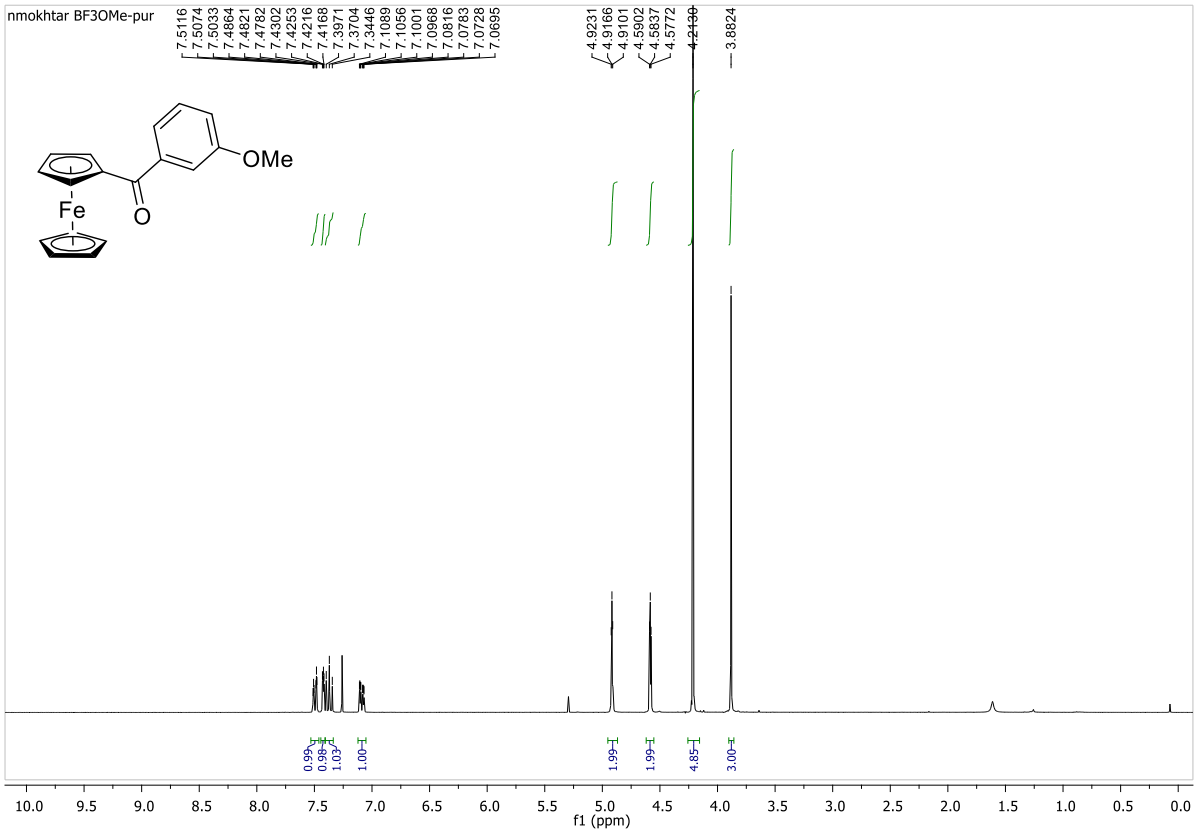


NOESY (500 MHz, $CDCl_3$)

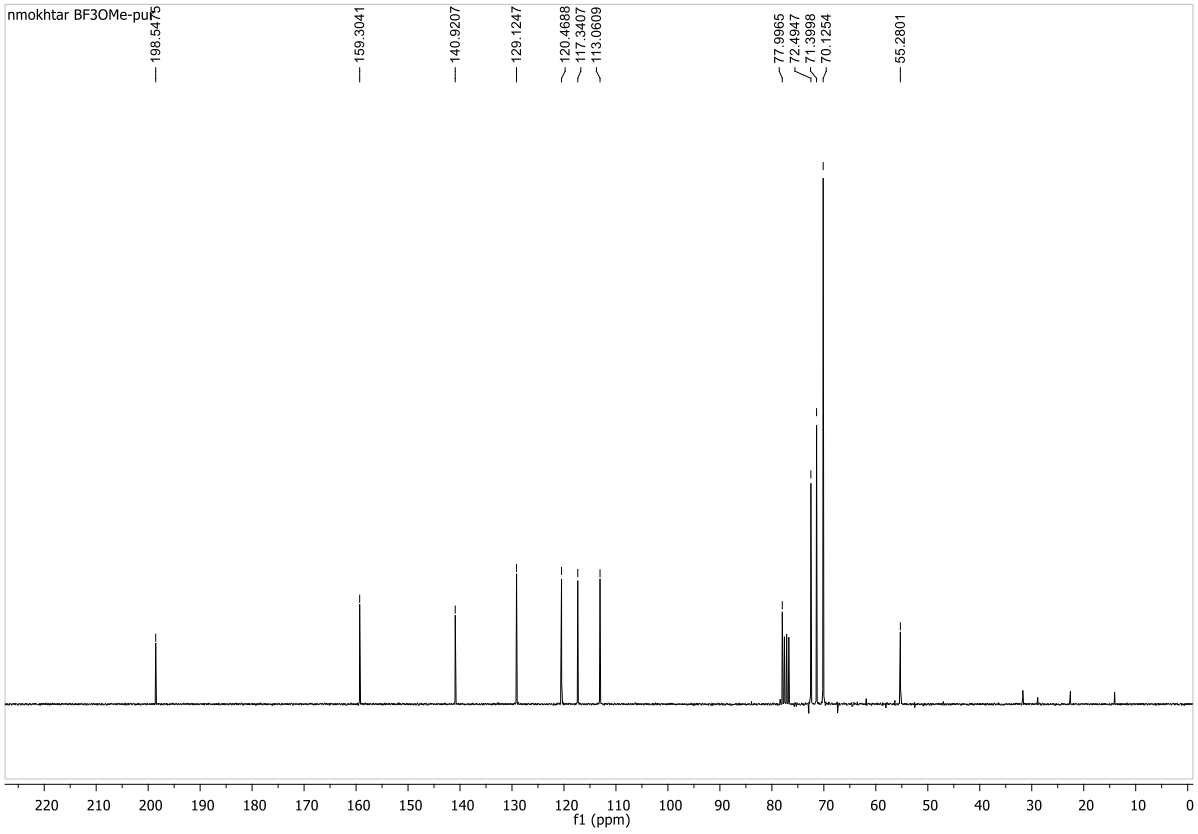


(3-Methoxybenzoyl)ferrocene (1-*m*OMePh)

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

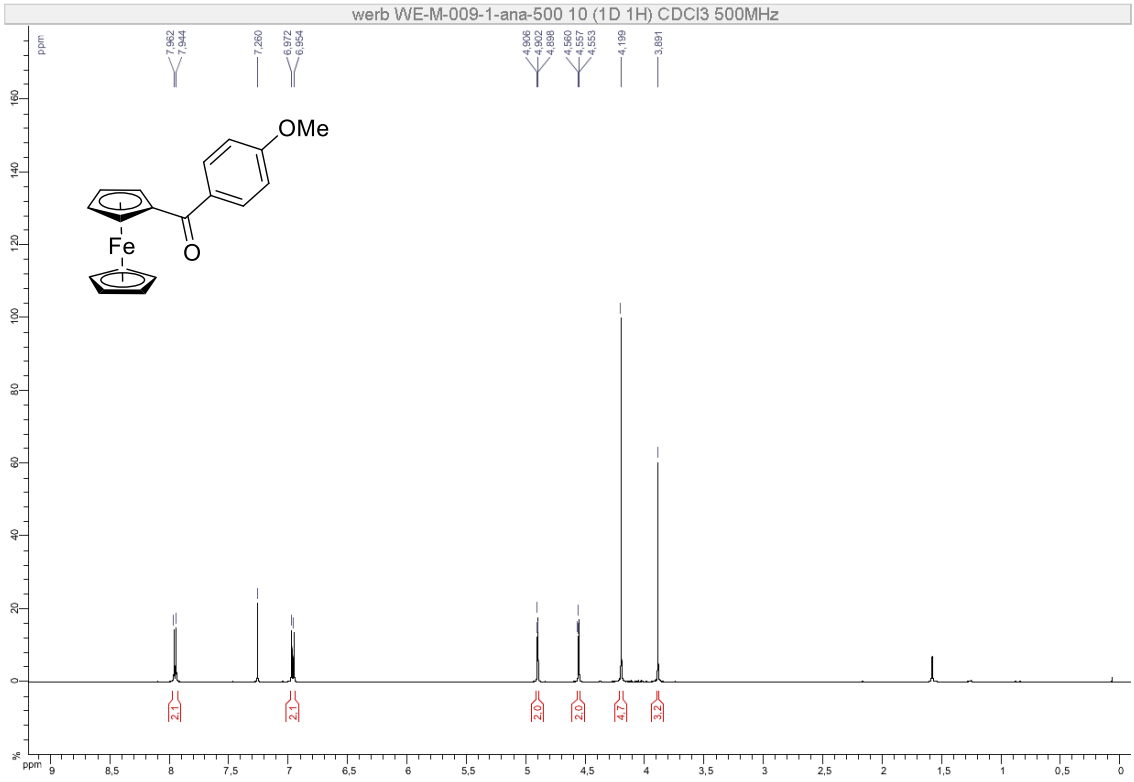


^{13}C NMR (75 MHz, $CDCl_3$)

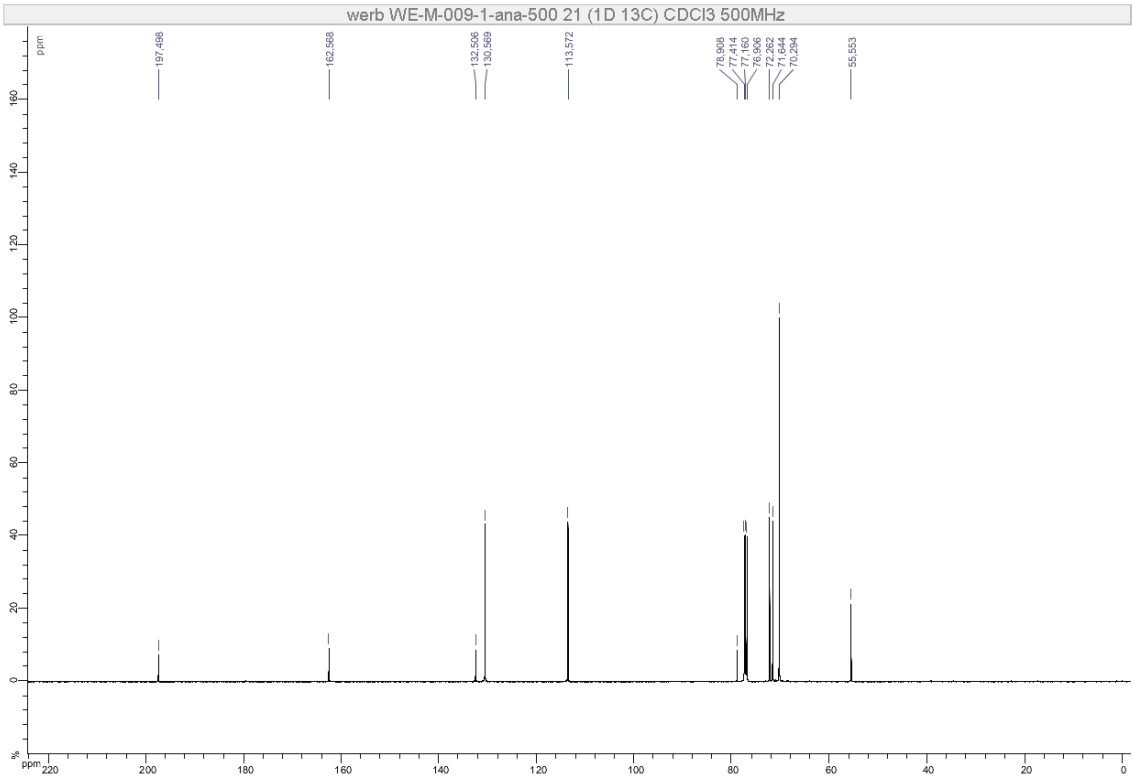


(4-Methoxybenzoyl)ferrocene (1-*p*OMePh)

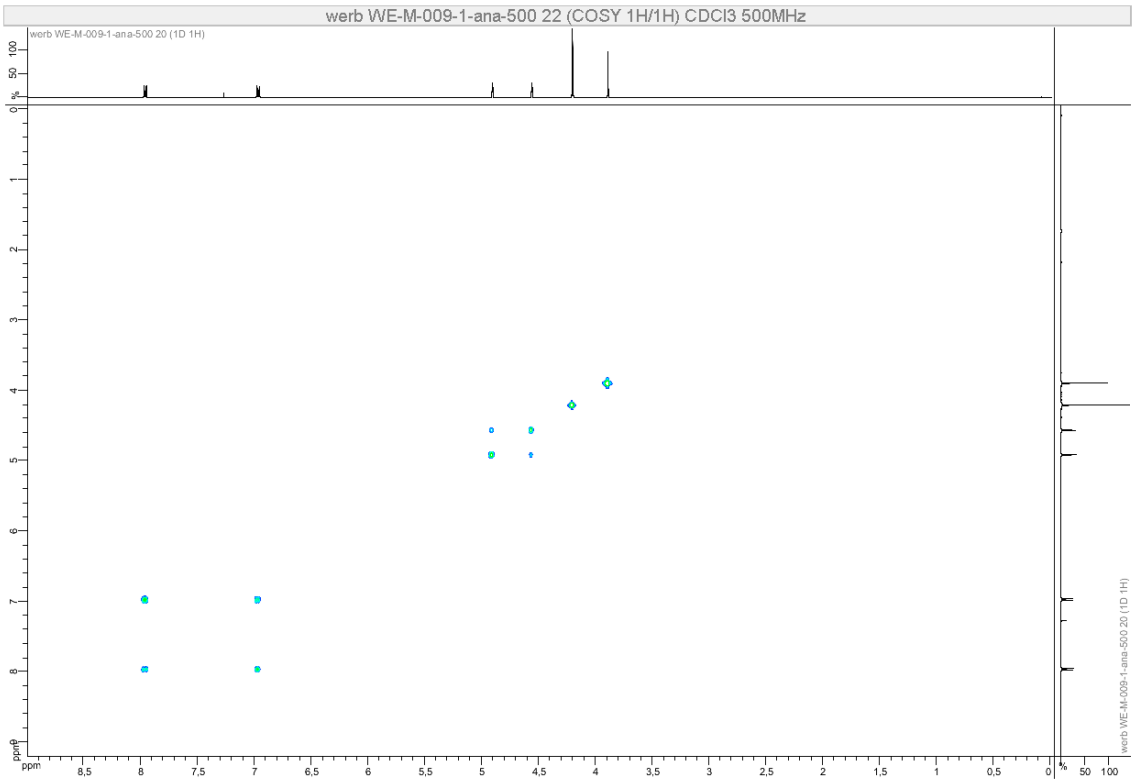
^{1}H NMR (500 MHz, $CDCl_3$)



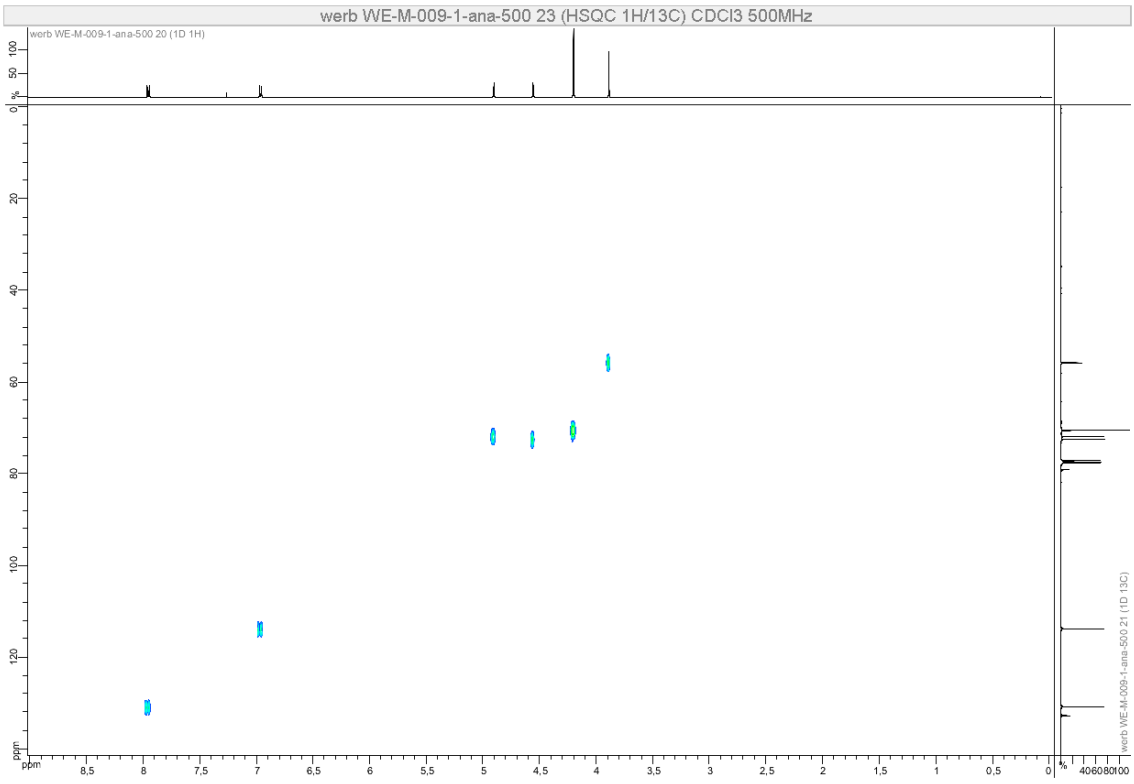
^{13}C NMR (126 MHz, $CDCl_3$)



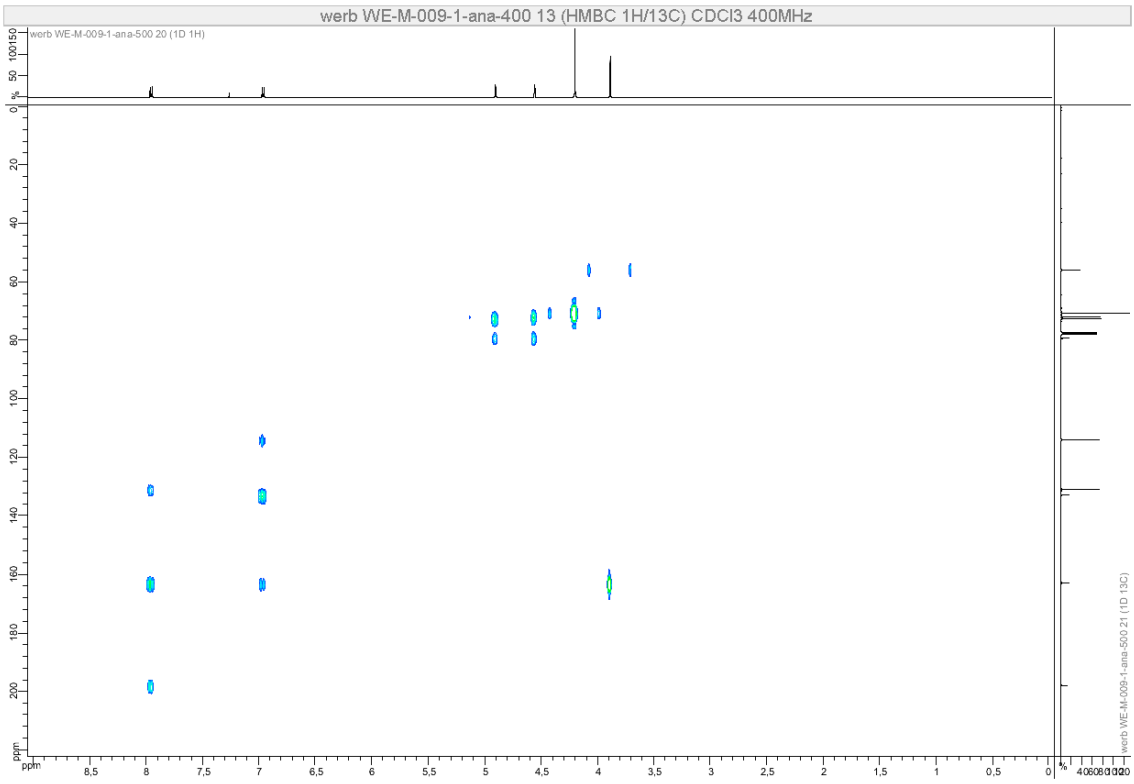
COSY (500 MHz, $CDCl_3$)



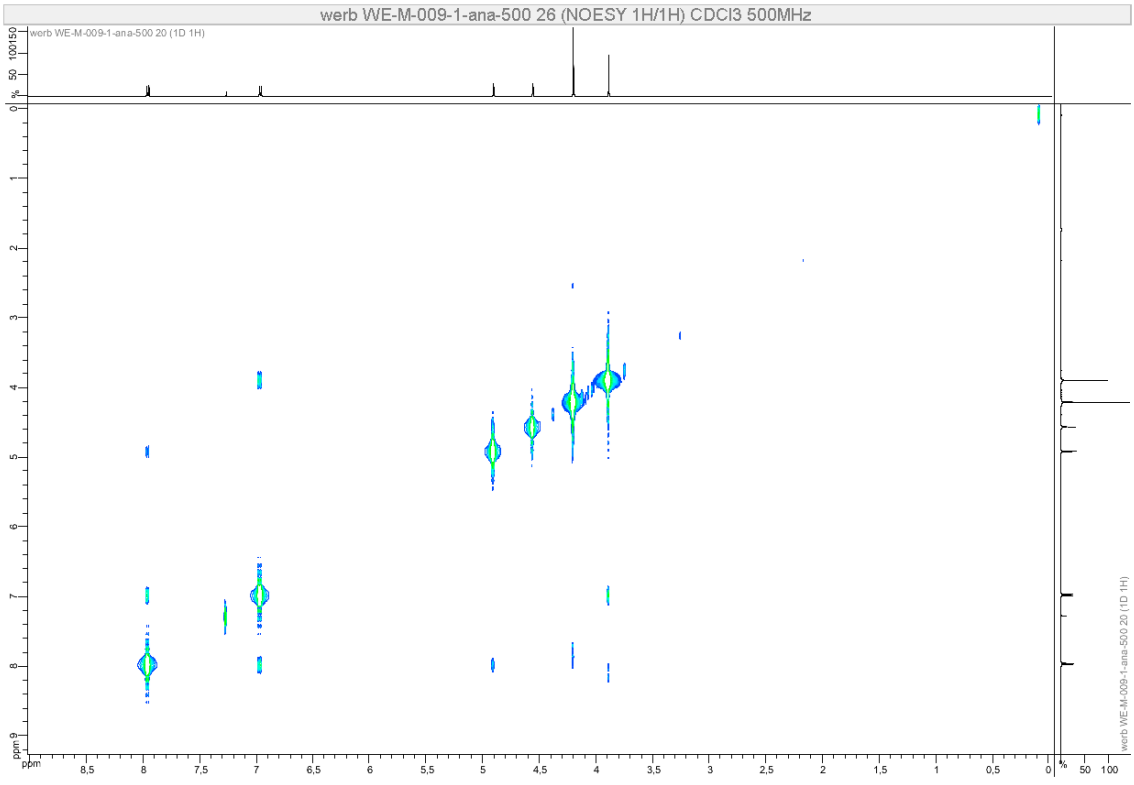
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

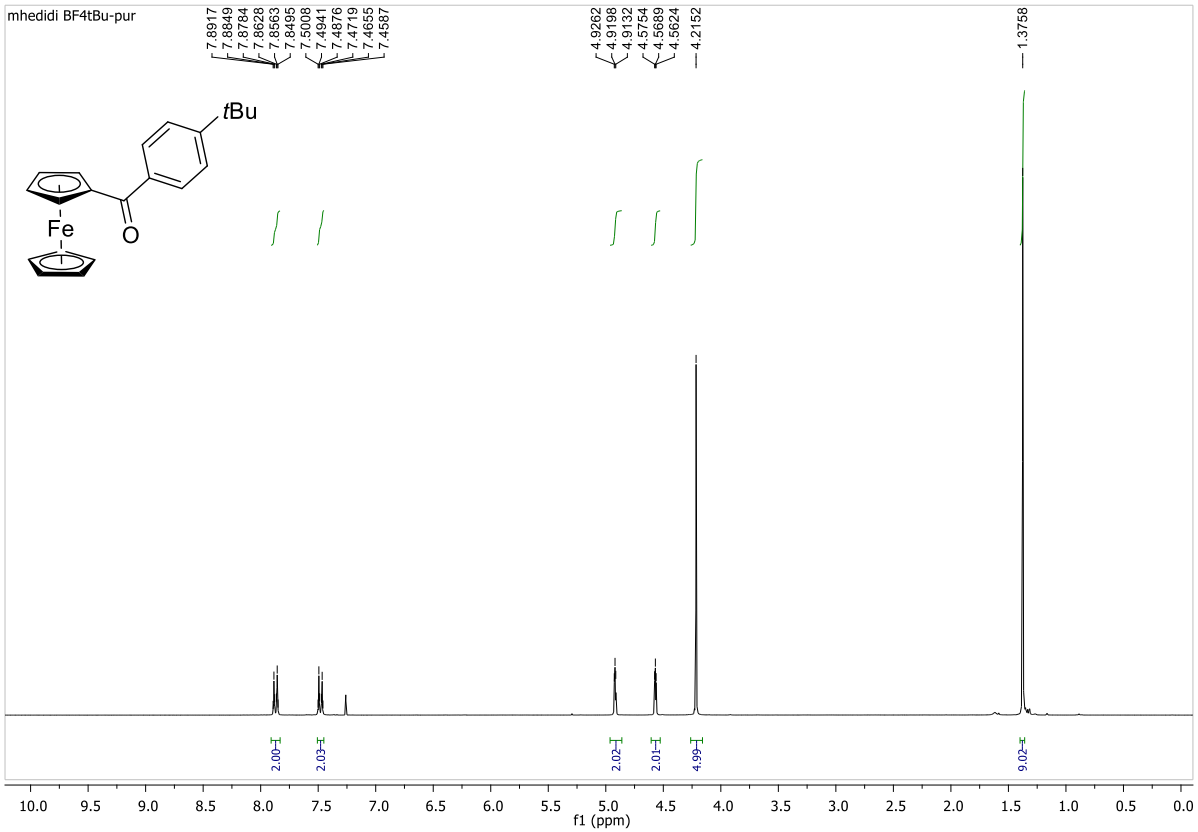


NOESY (500 MHz, $CDCl_3$)

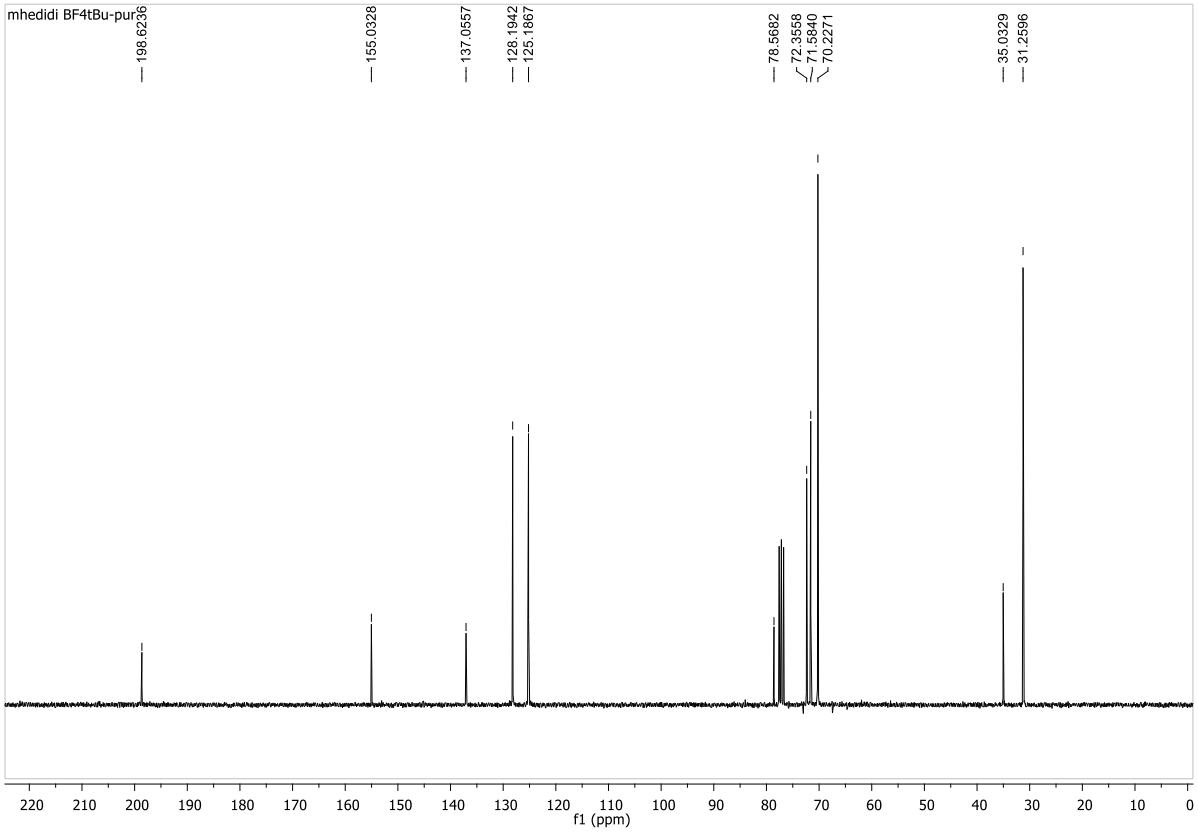


(4-*tert*-Butylbenzoyl)ferrocene (1-*pt*BuPh)

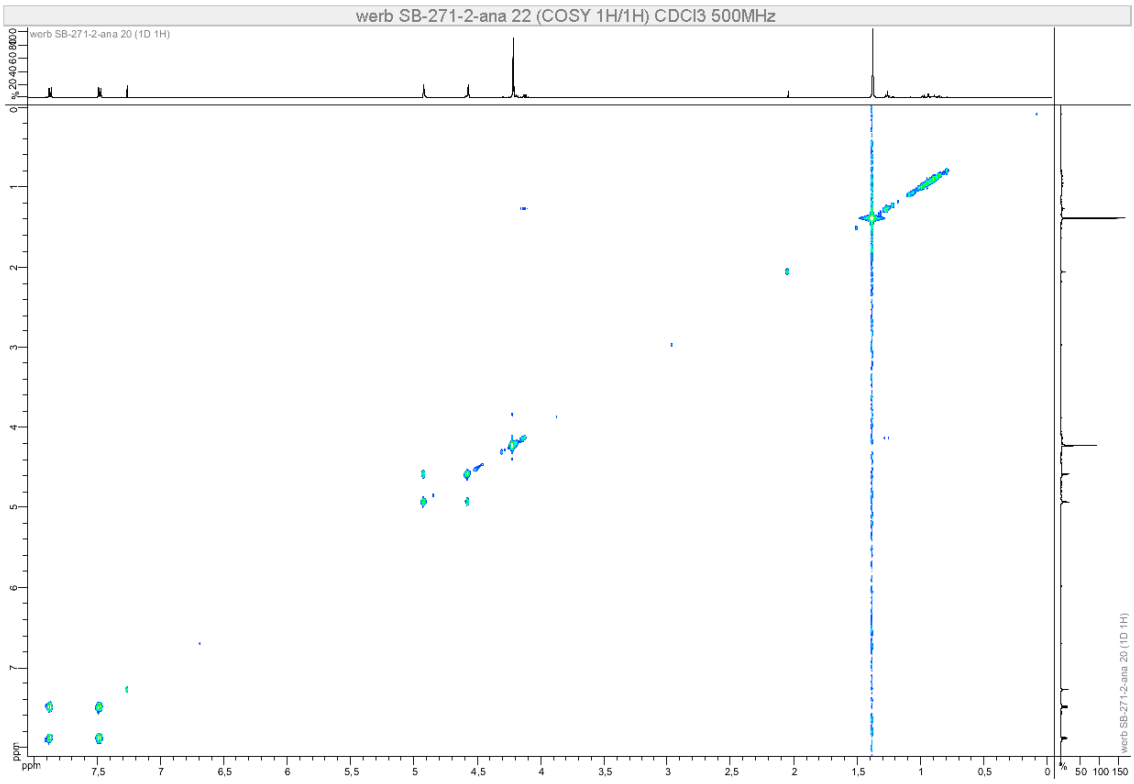
^{1}H NMR (300 MHz, $CDCl_3$)



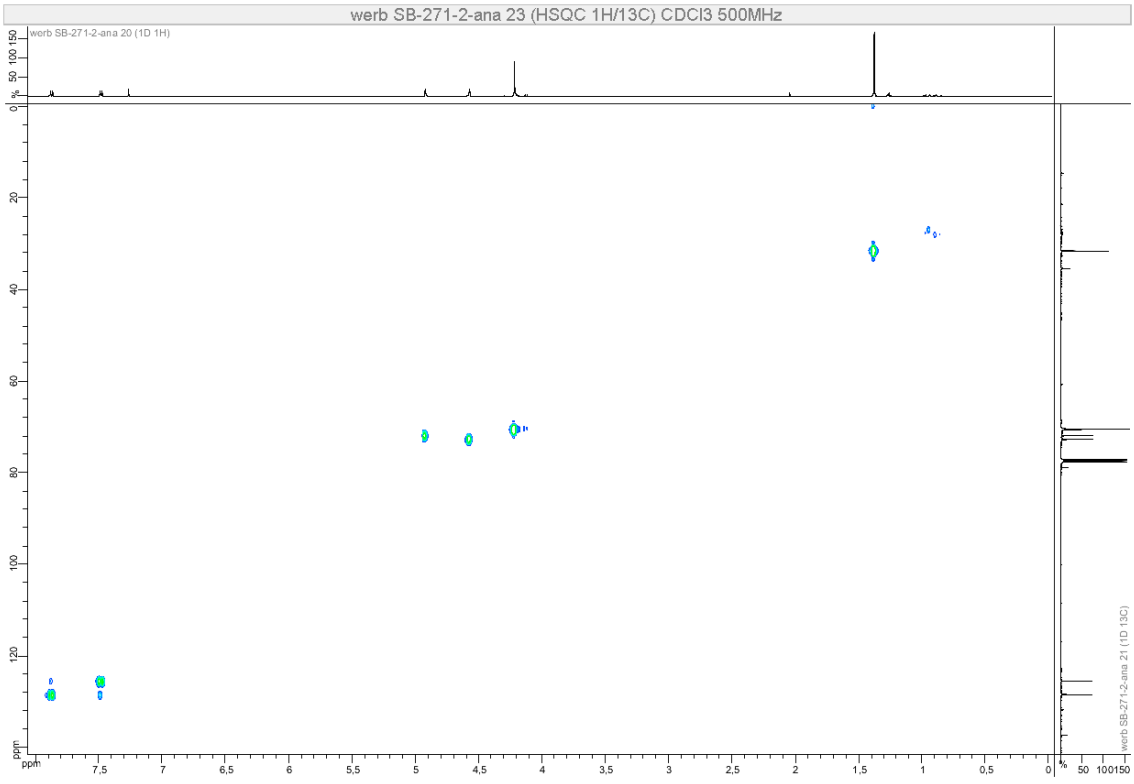
^{13}C NMR (75 MHz, $CDCl_3$)



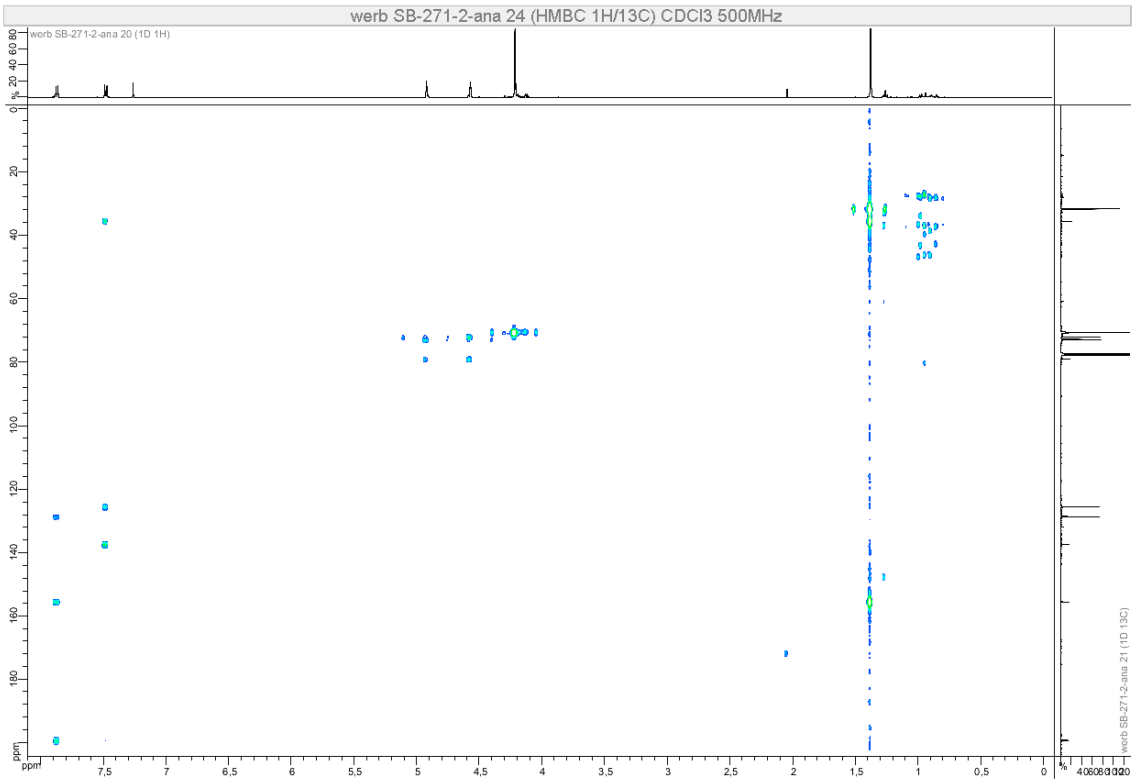
COSY (500 MHz, $CDCl_3$)



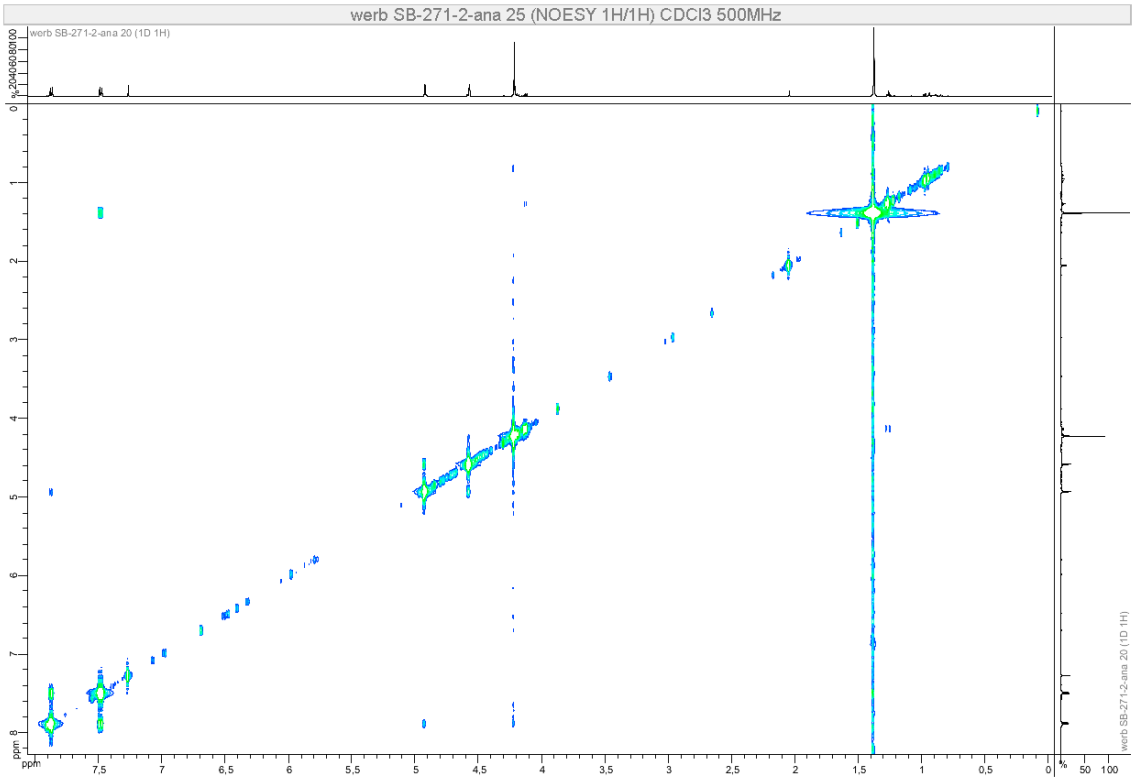
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

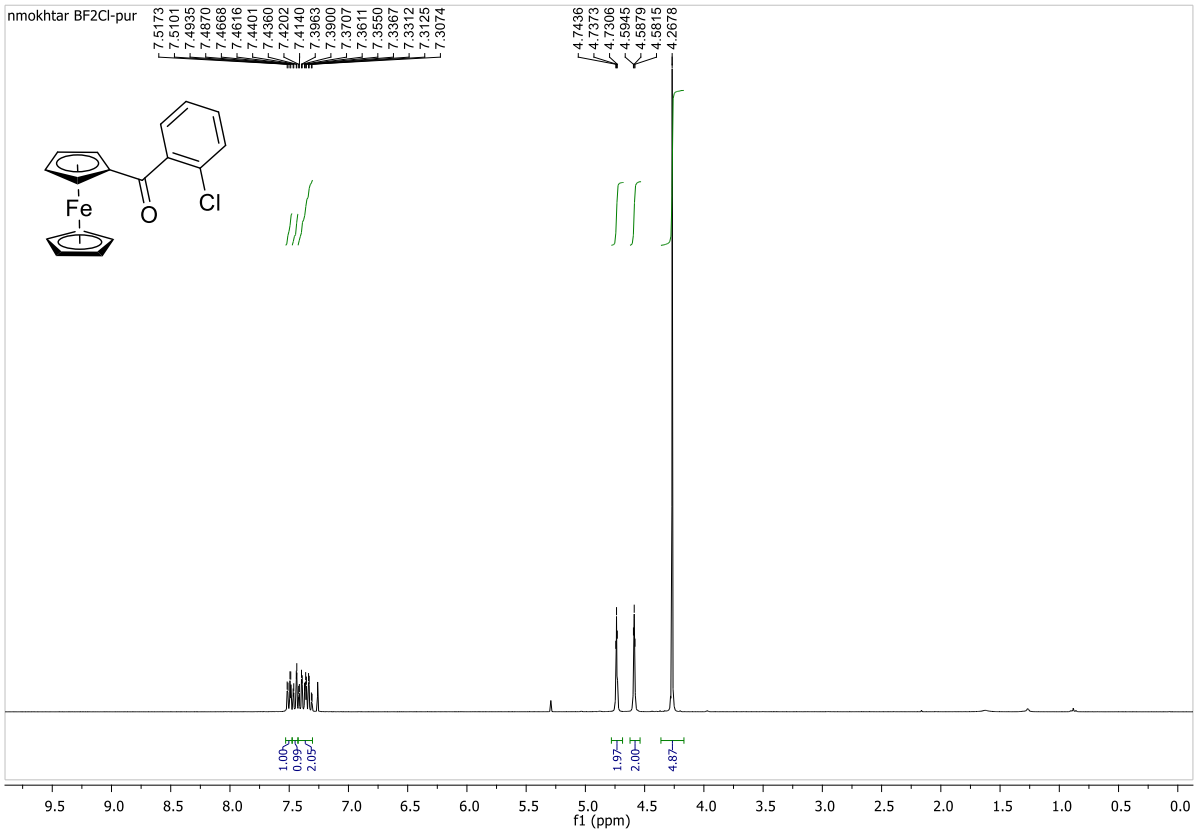


NOESY (500 MHz, $CDCl_3$)

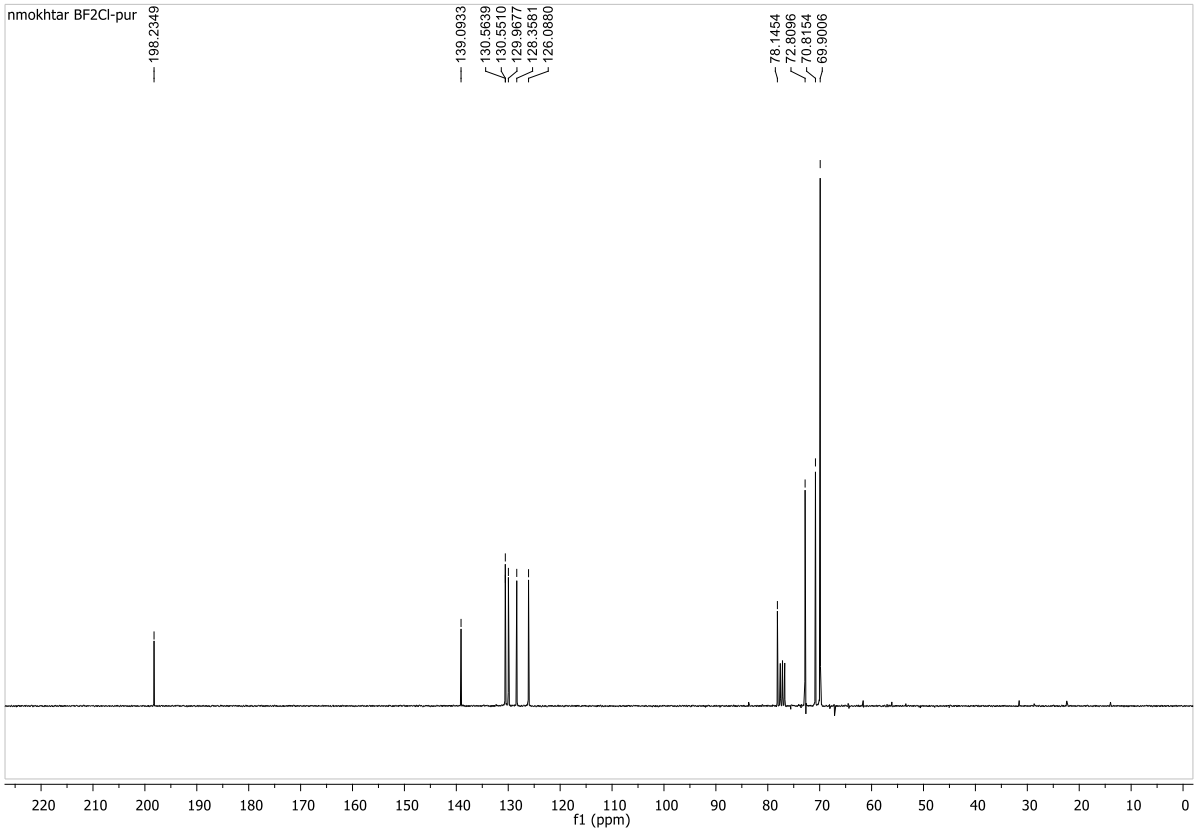


(2-Chlorobenzoyl)ferrocene (1-*o*ClPh)

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

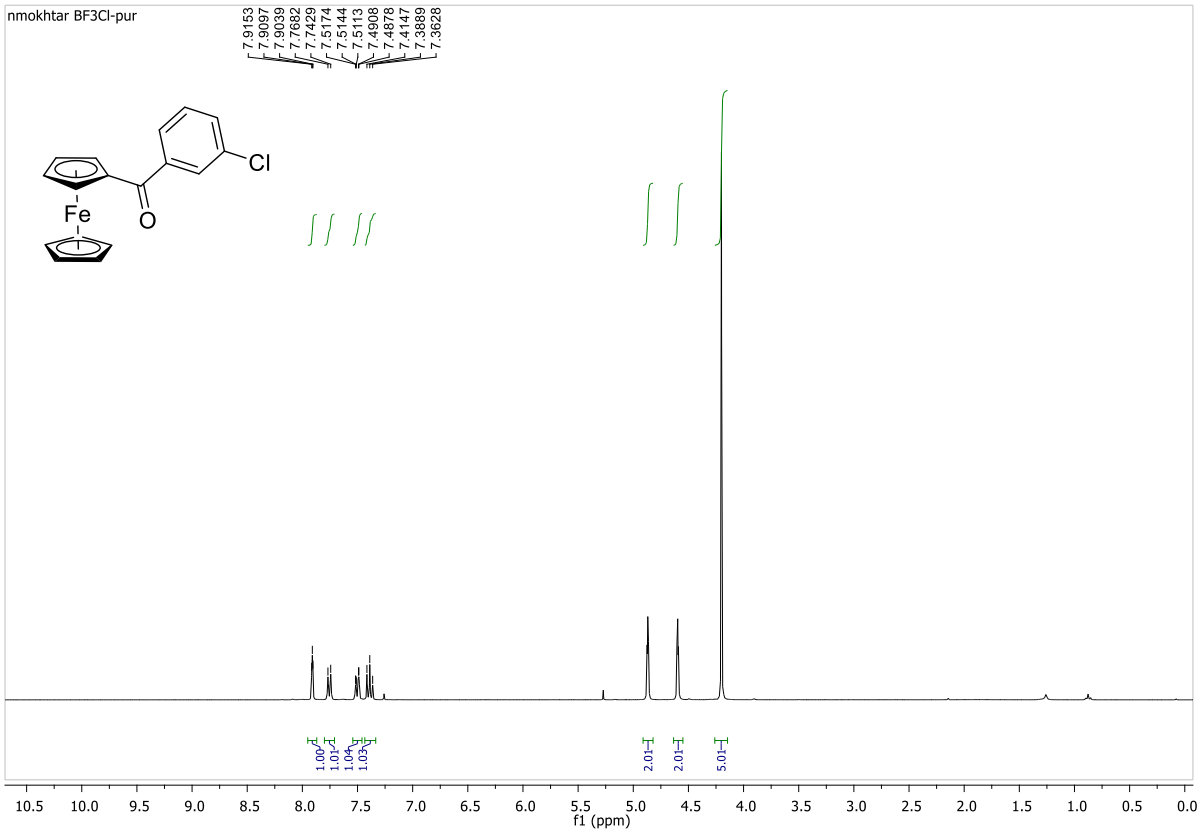


^{13}C NMR (75 MHz, $CDCl_3$)

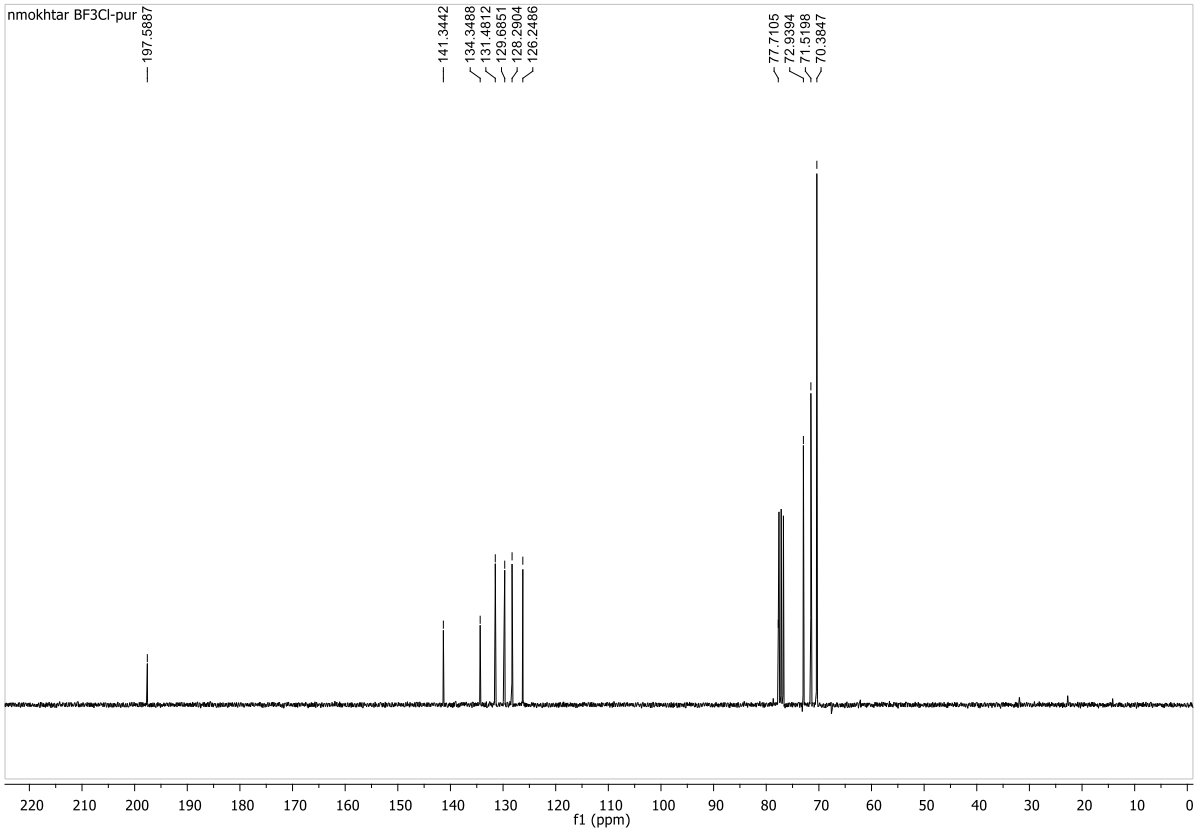


(3-Chlorobenzoyl)ferrocene (1-*m*ClPh)

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

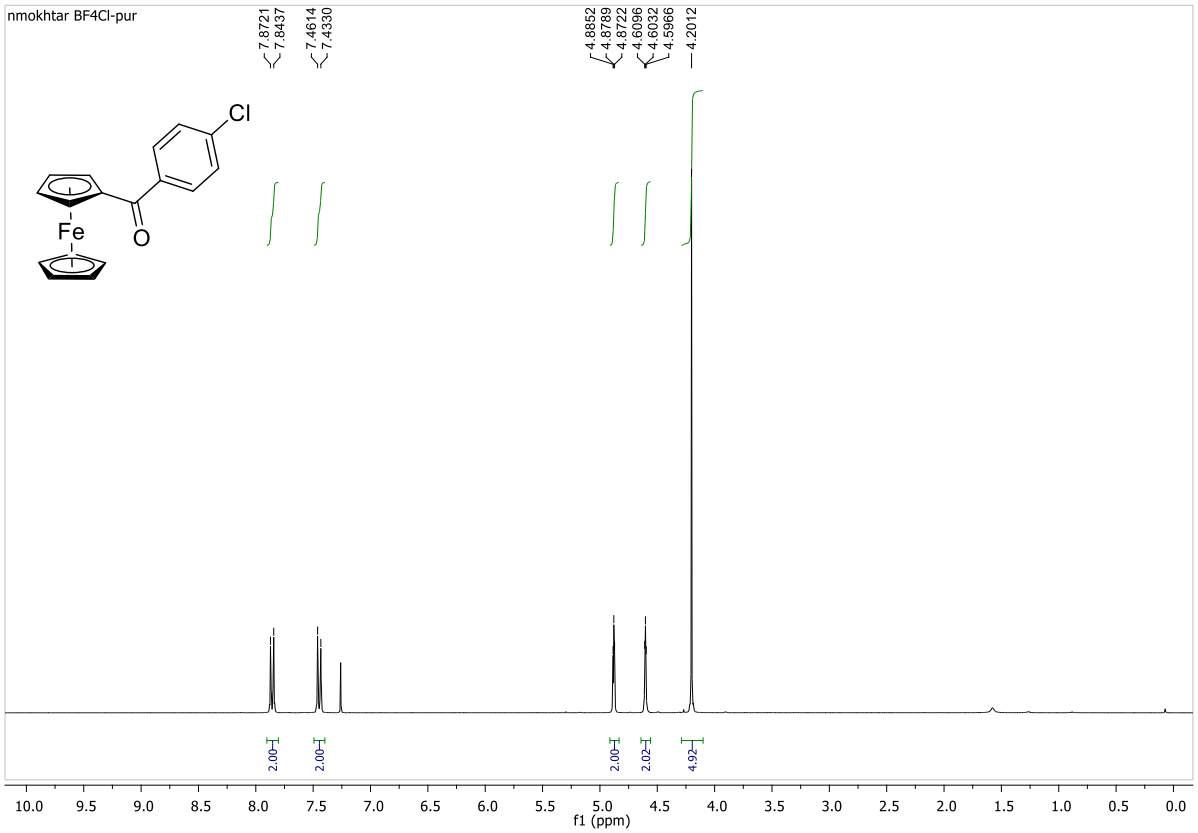


^{13}C NMR (75 MHz, $CDCl_3$)

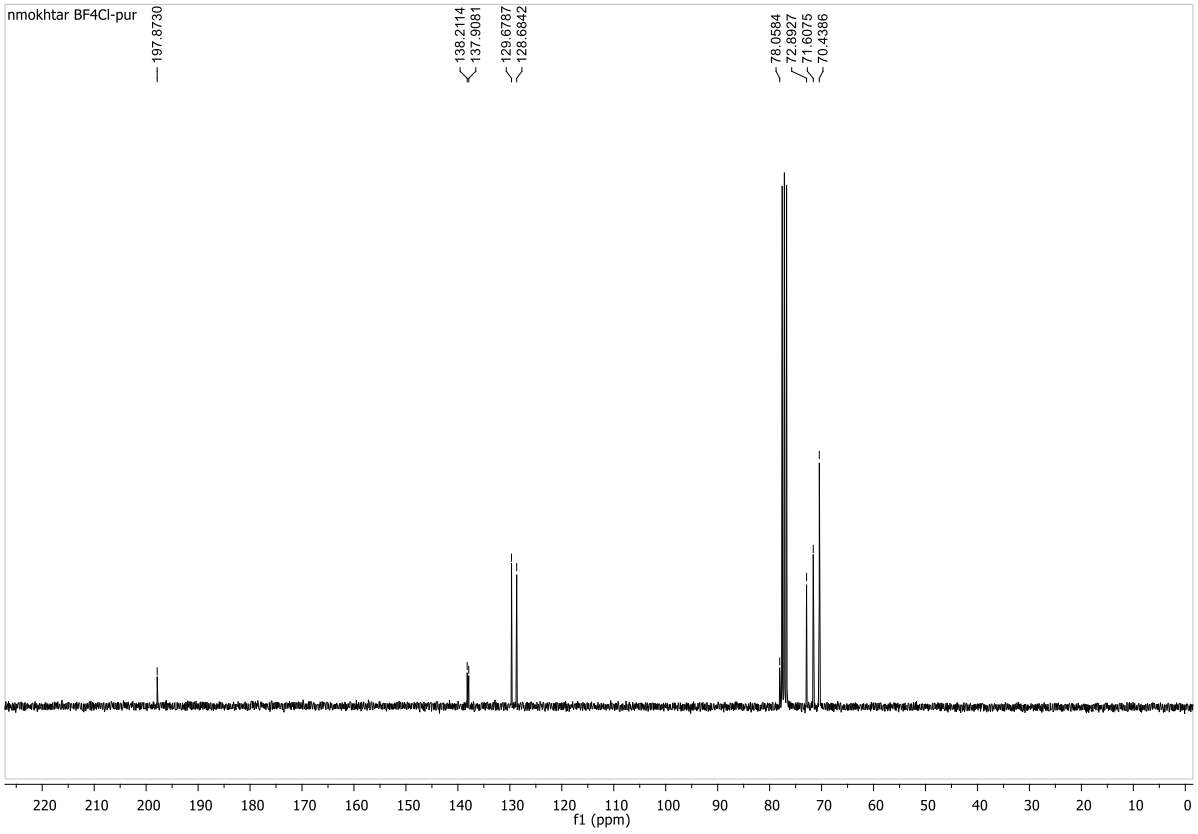


(4-Chlorobenzoyl)ferrocene (1-*p*ClPh)

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

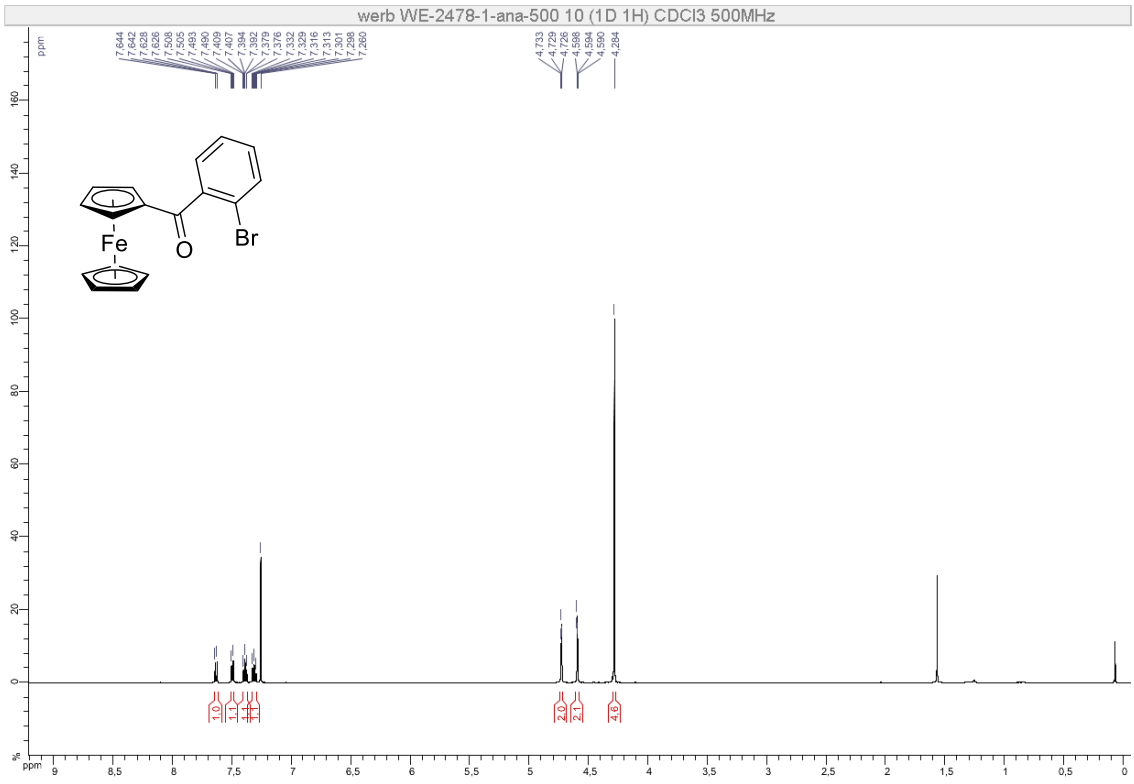


^{13}C NMR (75 MHz, $CDCl_3$)

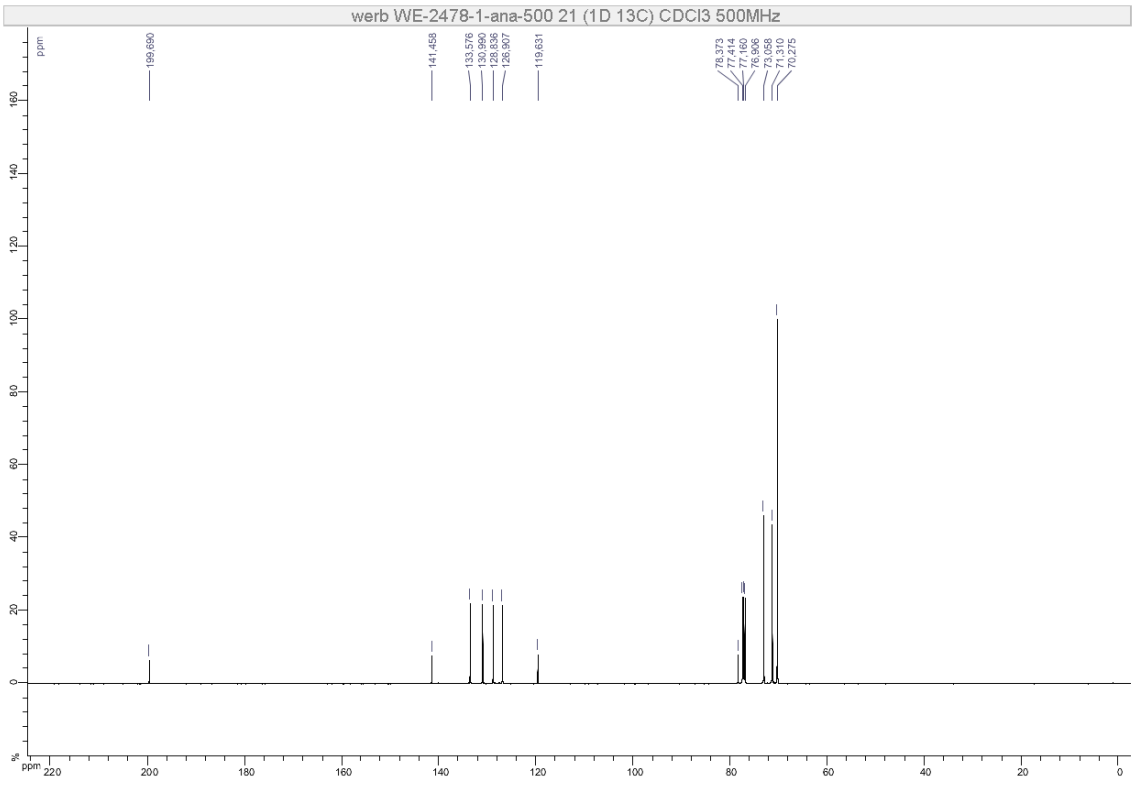


(2-Bromobenzoyl)ferrocene (1-*o*BrPh)

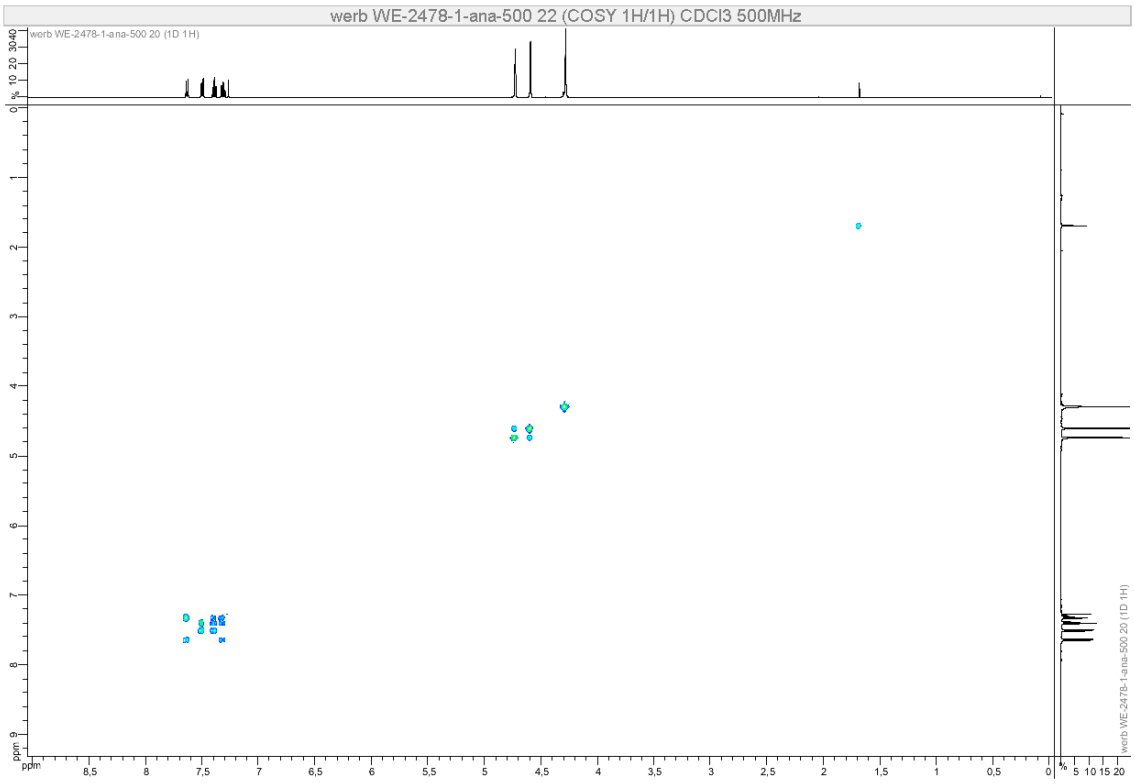
^{1}H NMR (500 MHz, $CDCl_3$)



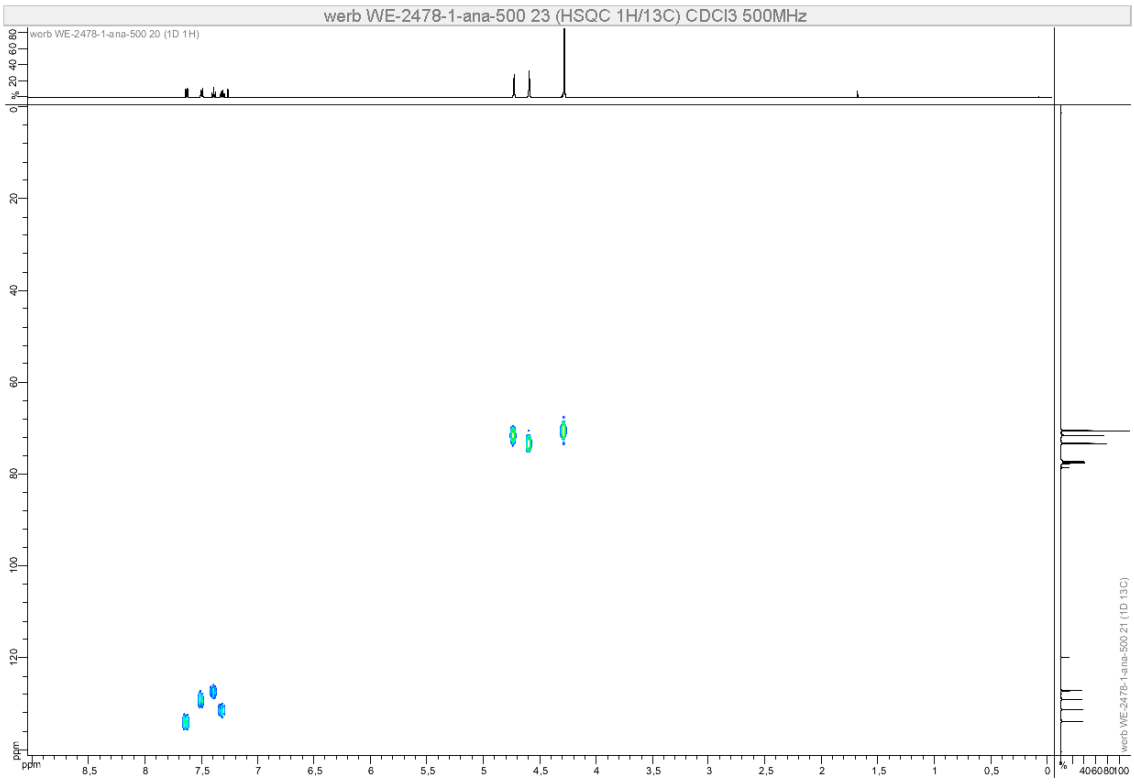
^{13}C NMR (126 MHz, $CDCl_3$)



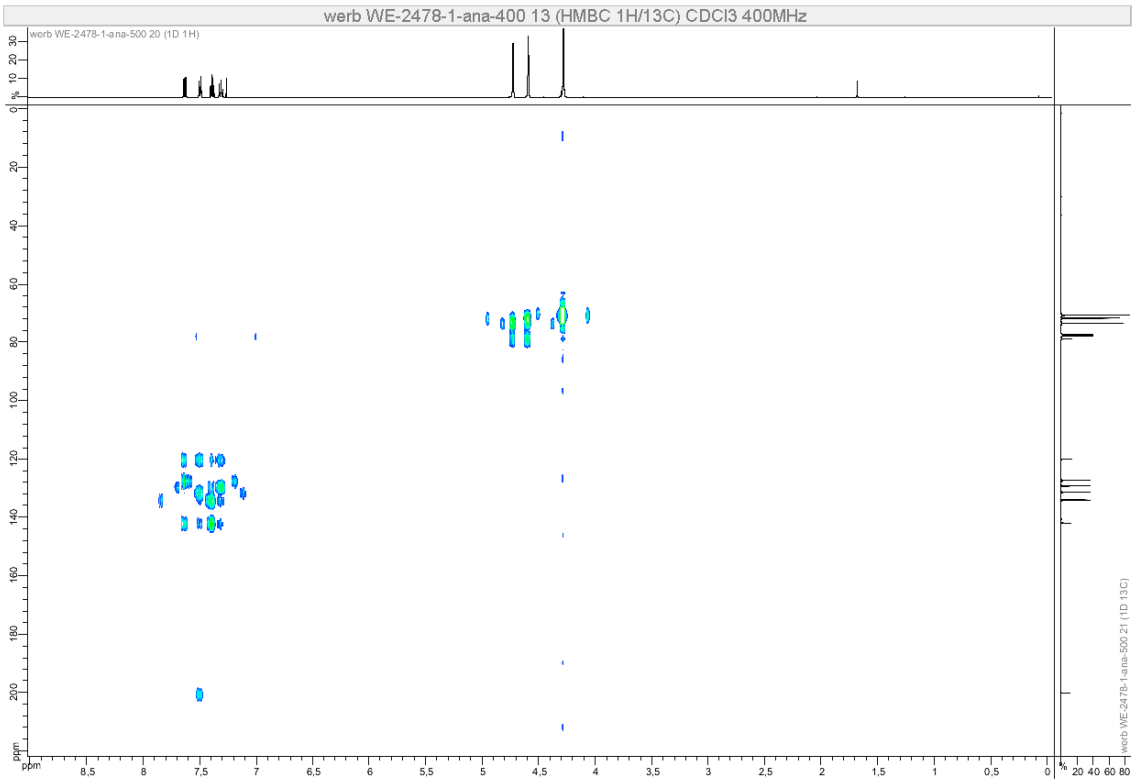
COSY (500 MHz, $CDCl_3$)



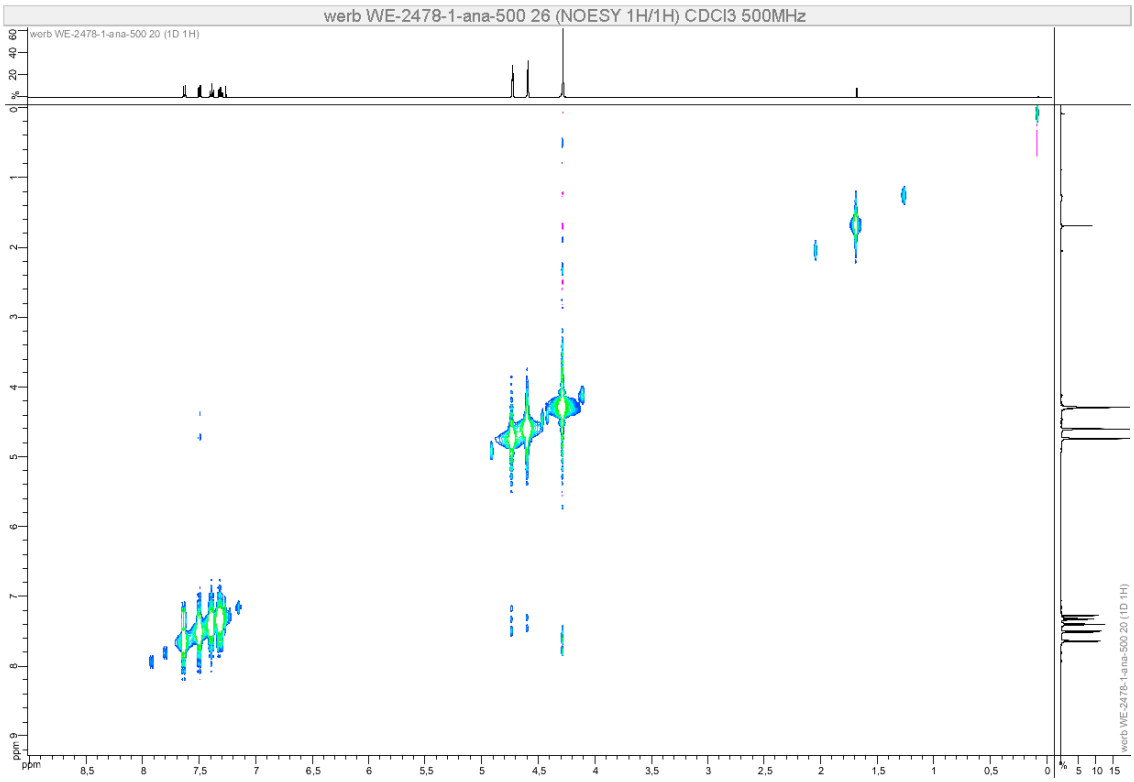
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

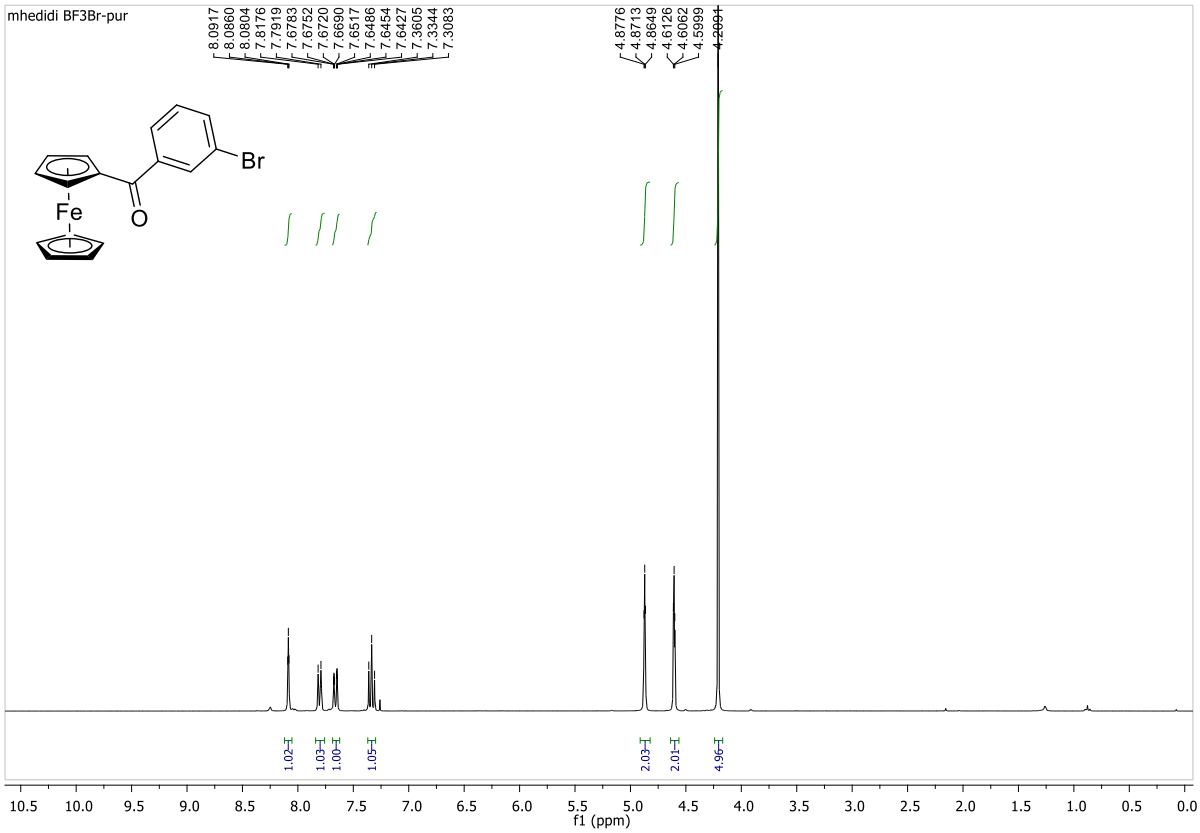


NOESY (500 MHz, $CDCl_3$)

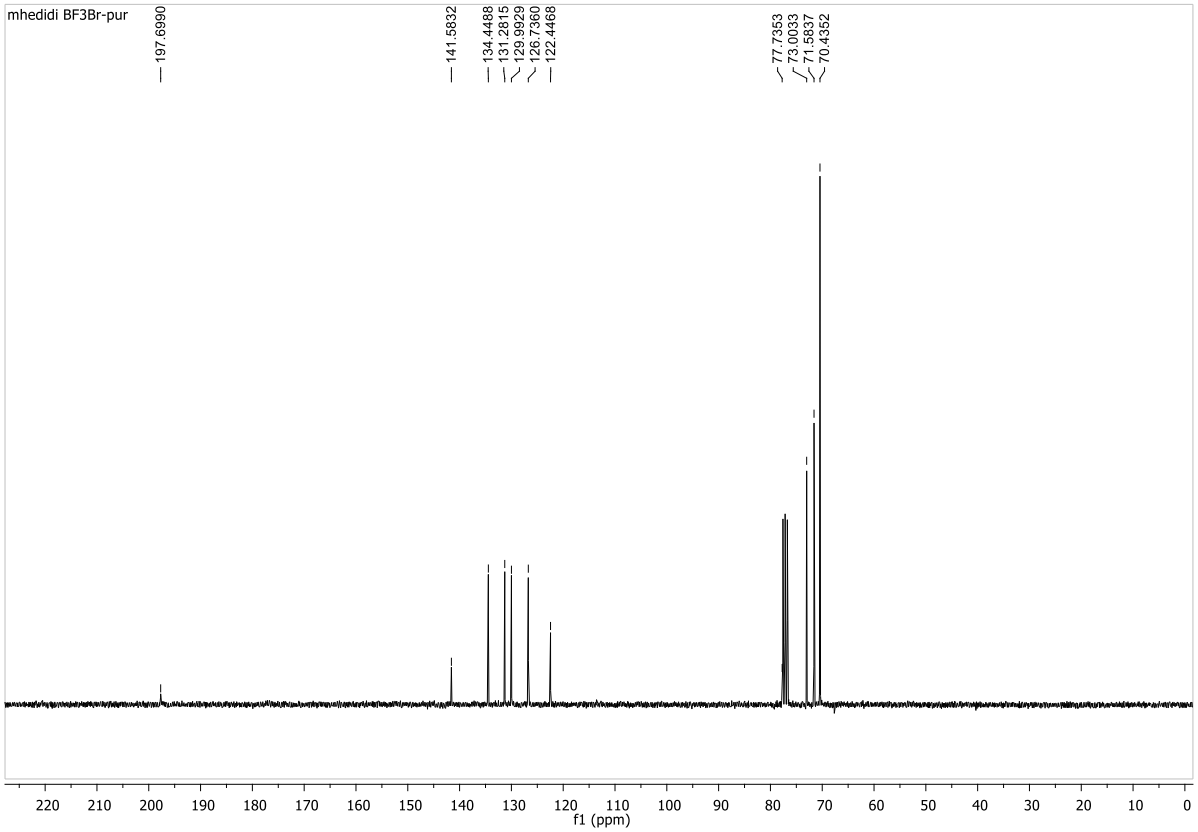


(3-Bromobenzoyl)ferrocene (1-*m*BrPh)

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

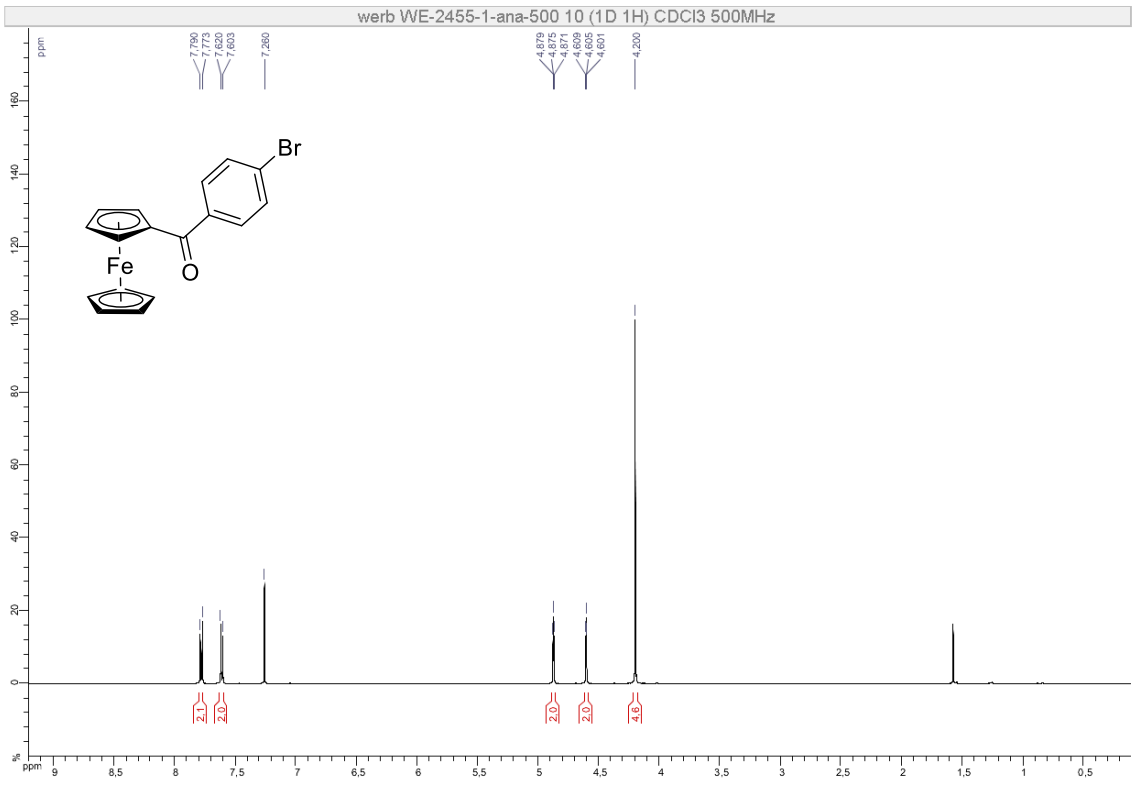


^{13}C NMR (75 MHz, $CDCl_3$)

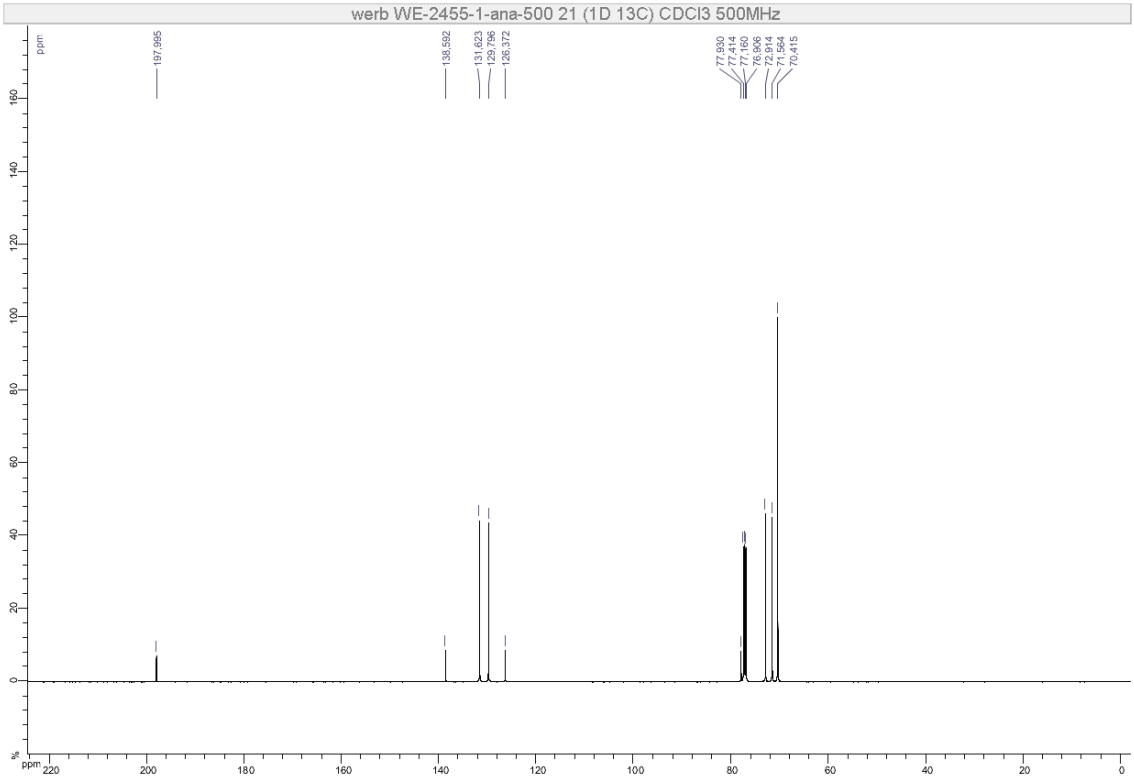


(4-Bromobenzoyl)ferrocene (1-*p*BrPh)

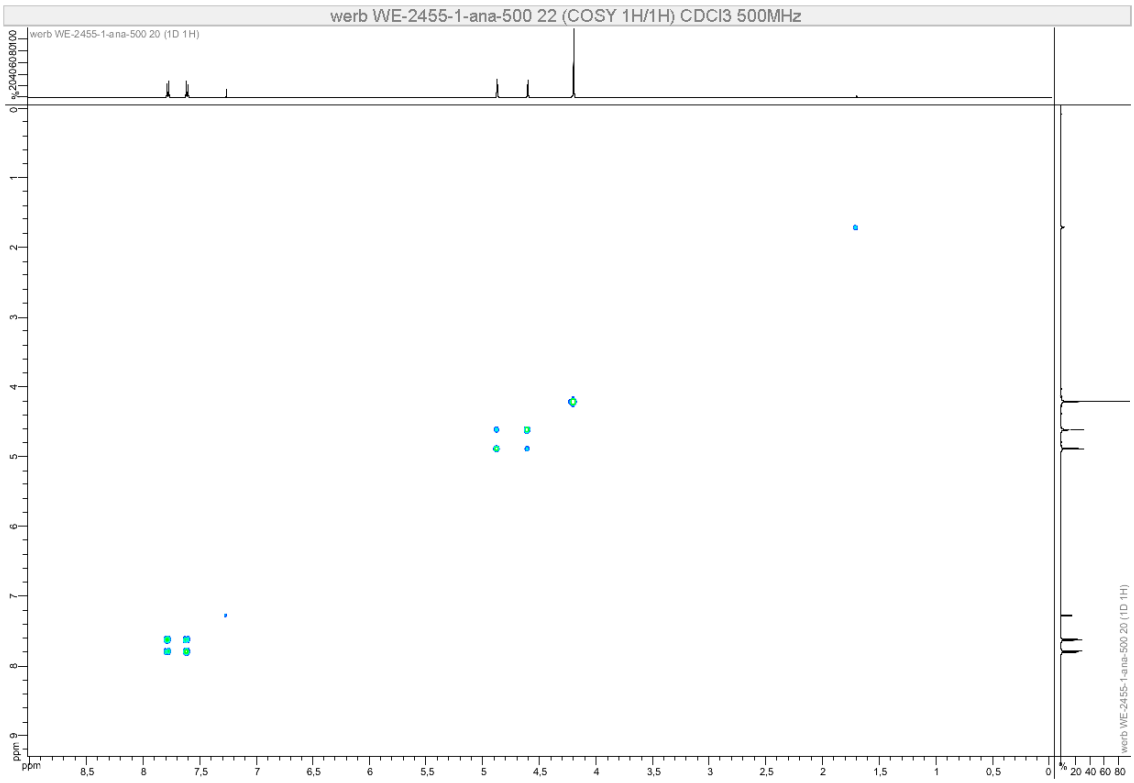
^{1}H NMR (500 MHz, $CDCl_3$)



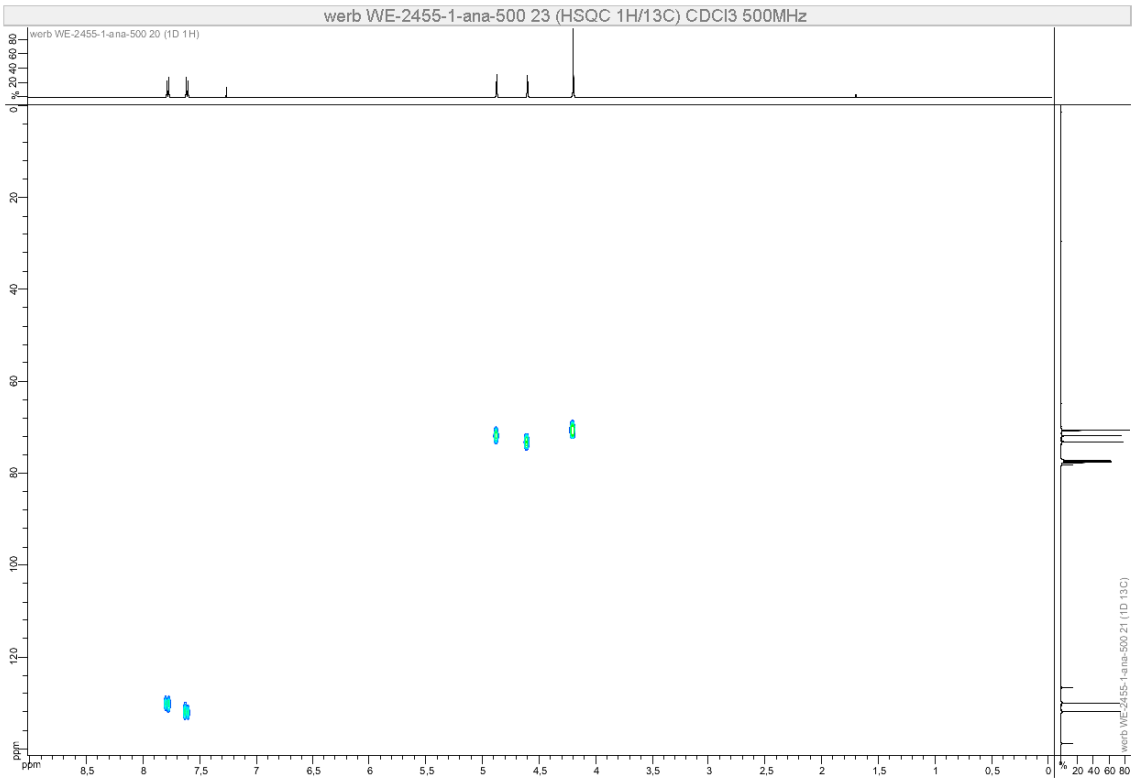
^{13}C NMR (126 MHz, $CDCl_3$)



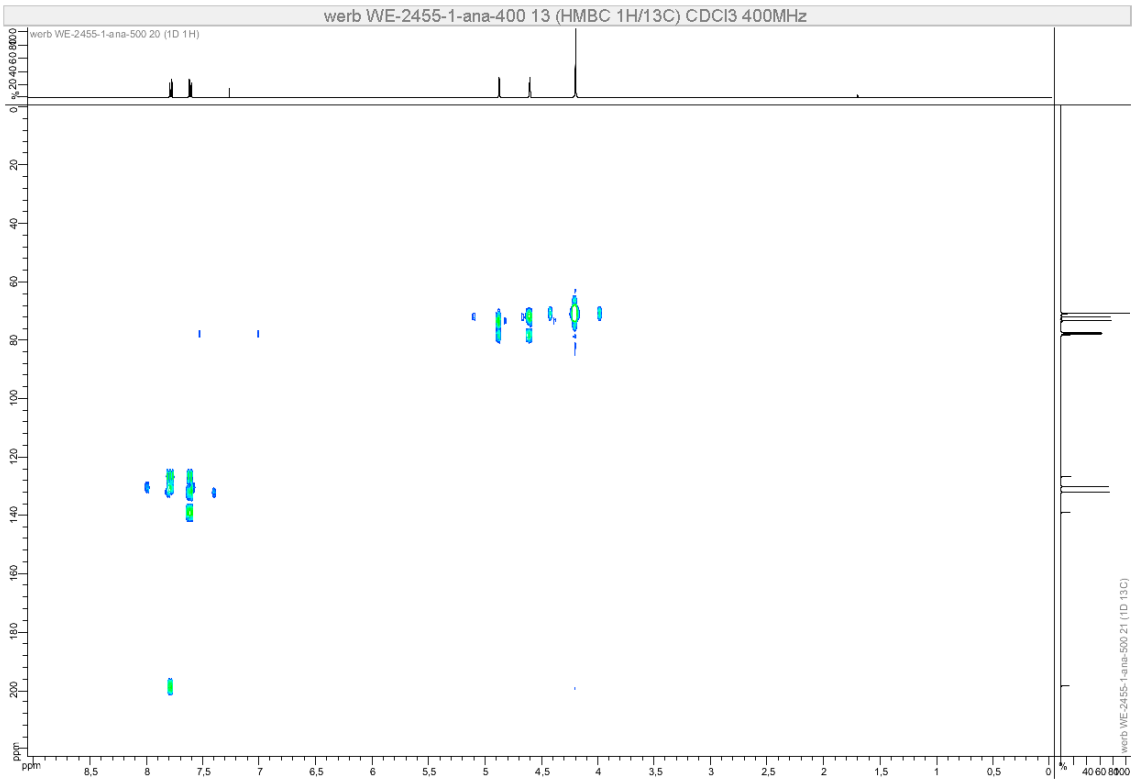
COSY (500 MHz, $CDCl_3$)



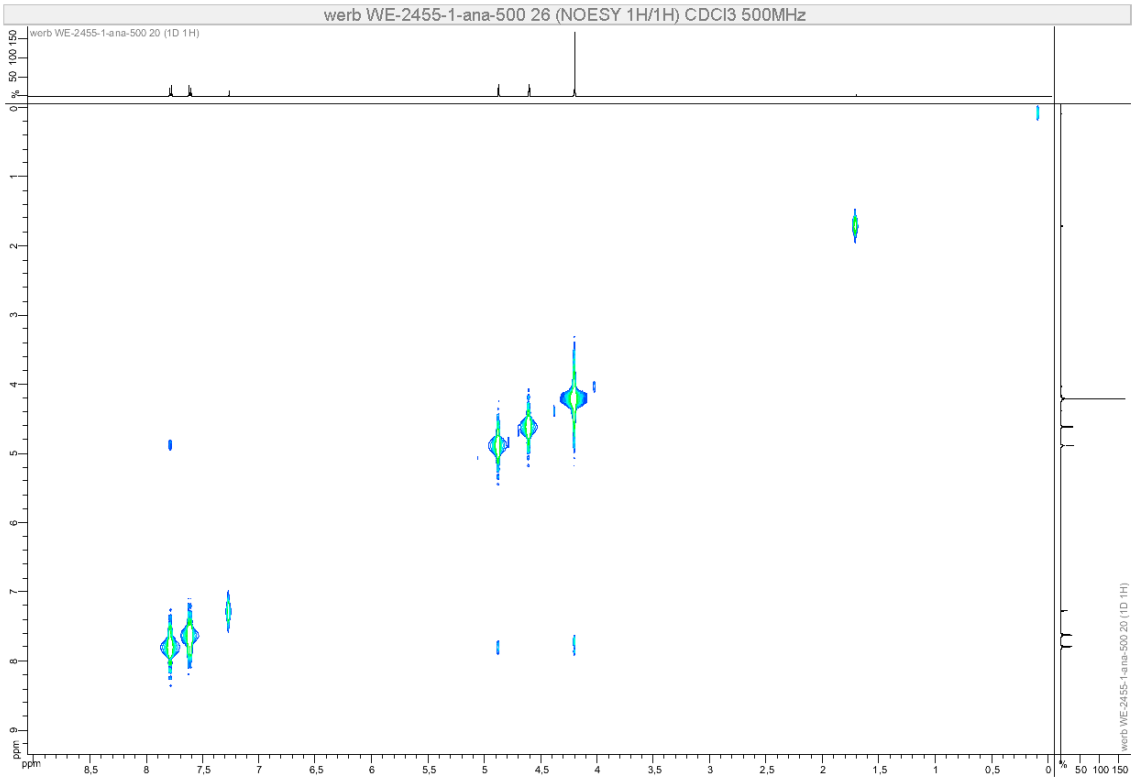
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

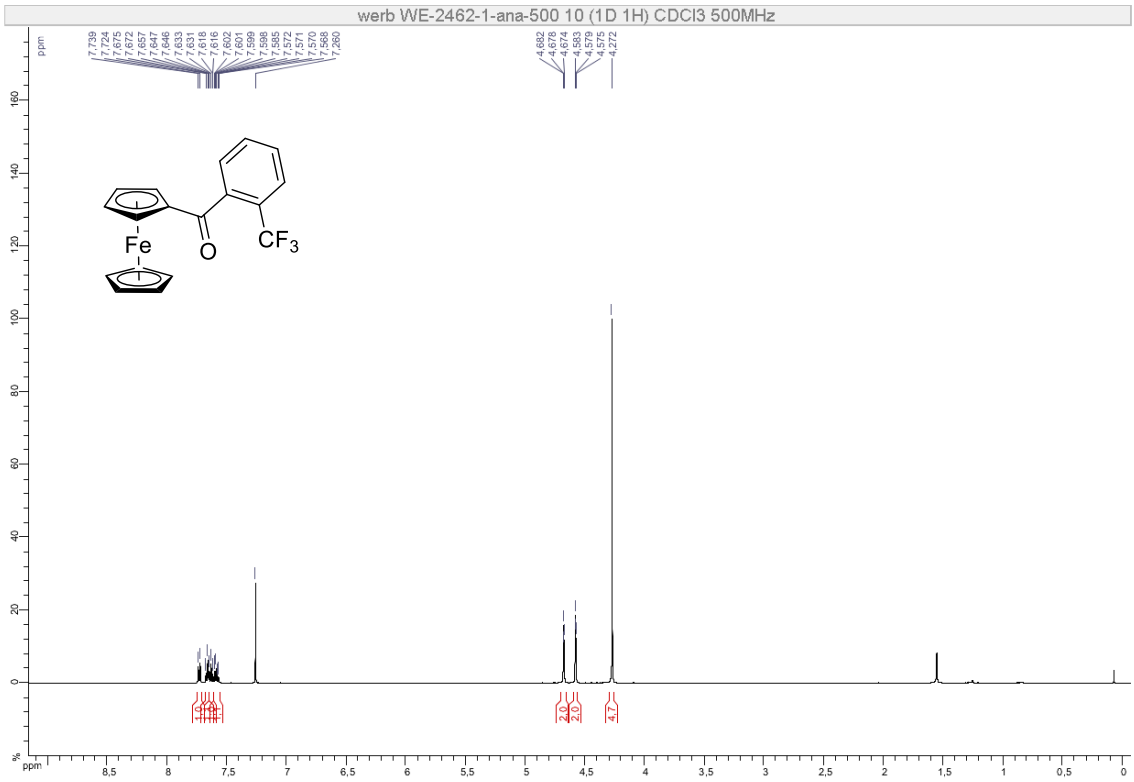


NOESY (500 MHz, $CDCl_3$)

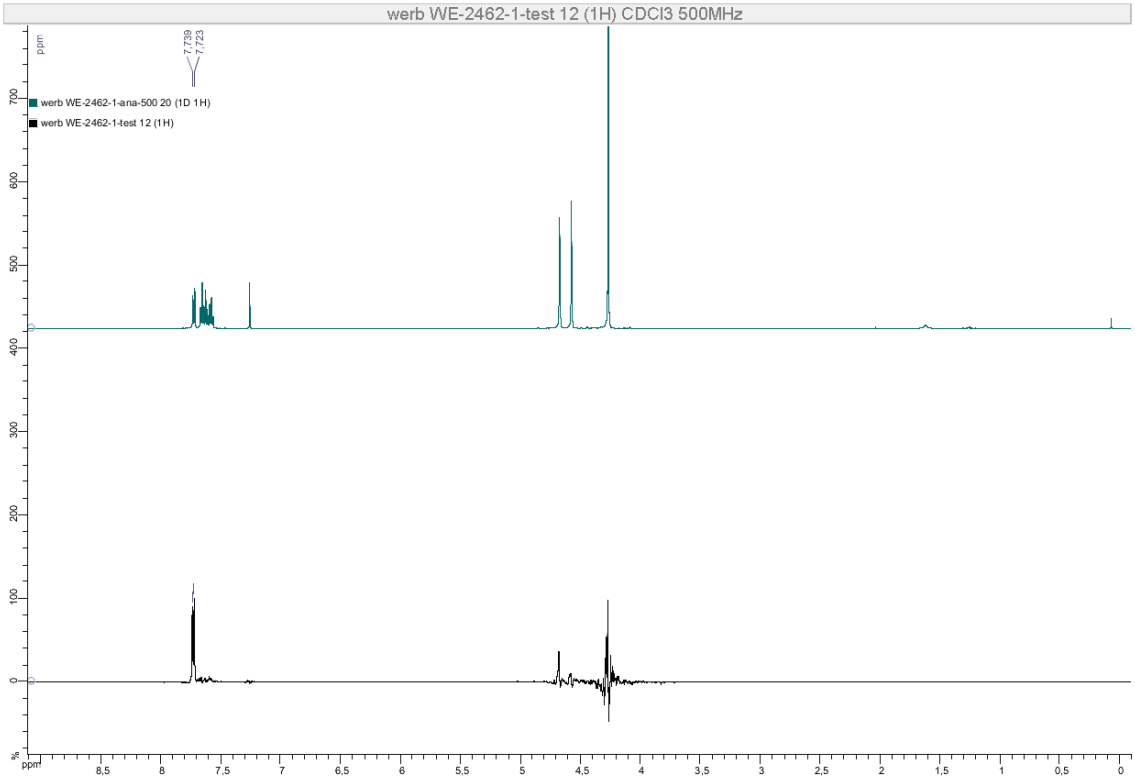


[2-(Trifluoromethyl)benzoyl]ferrocene (1-*o*CF_3Ph)

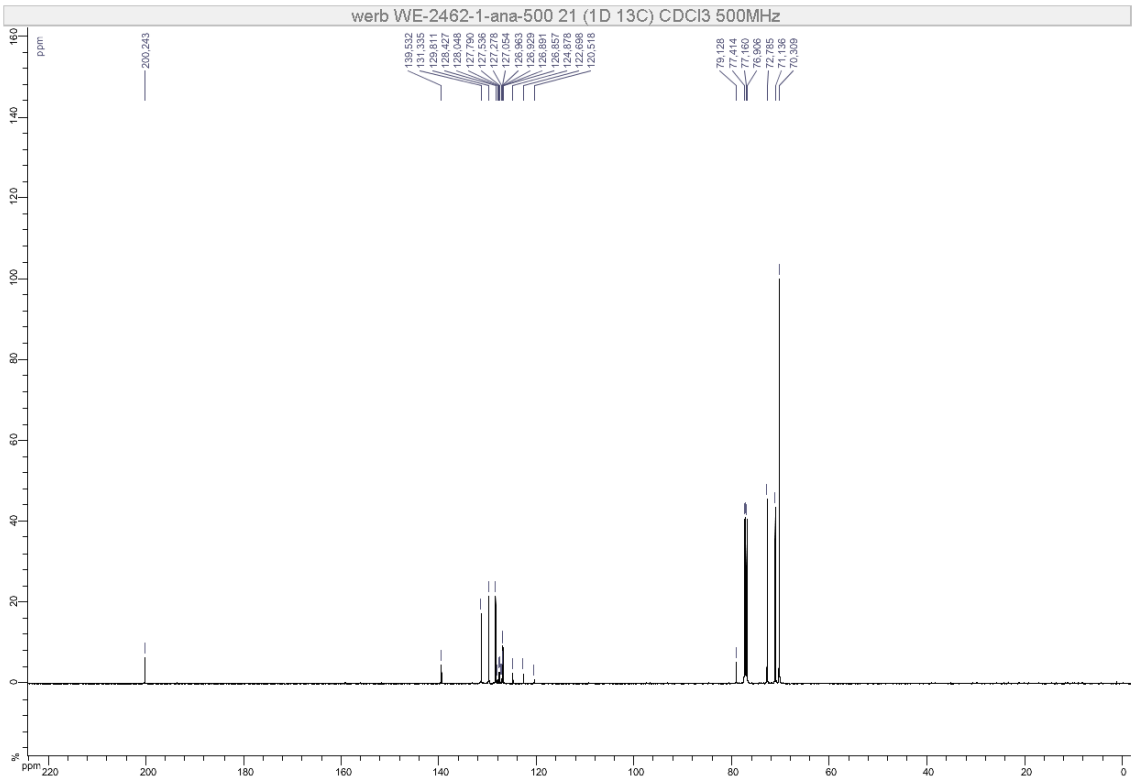
^{1}H NMR (500 MHz, $CDCl_3$)



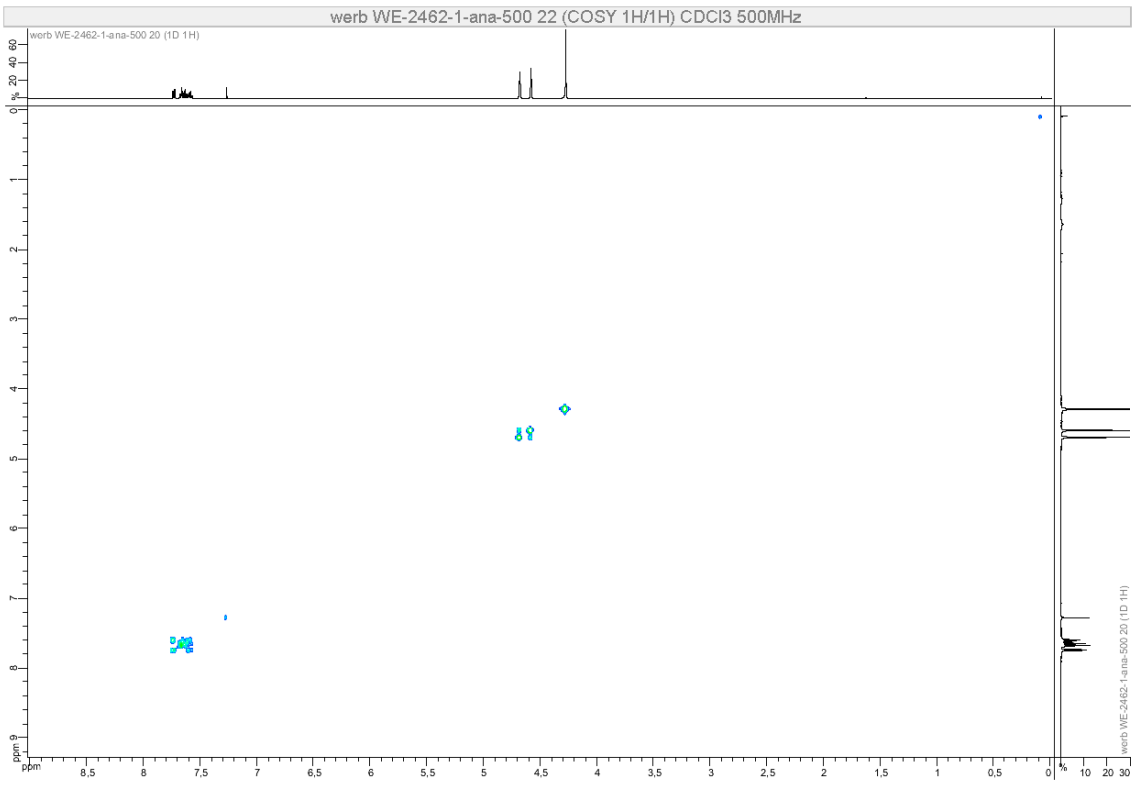
HOESY (500 MHz, $CDCl_3$) Irradiation at –57.5 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



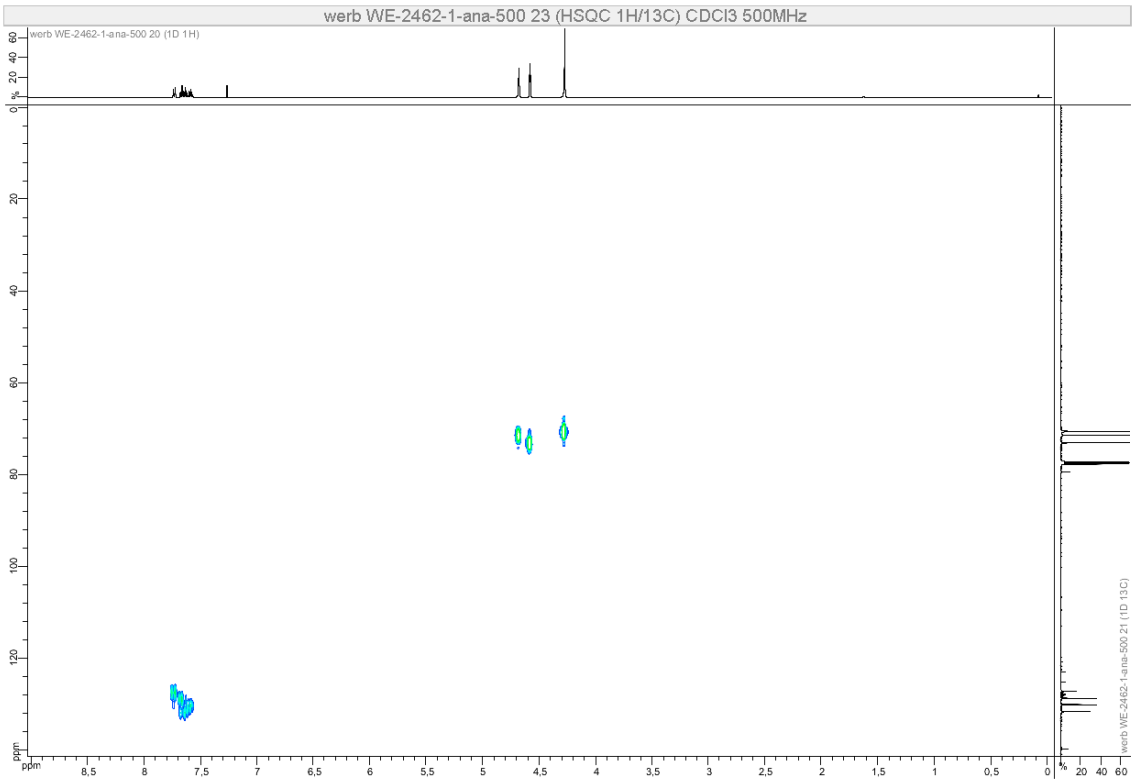
^{13}C NMR (126 MHz, $CDCl_3$)



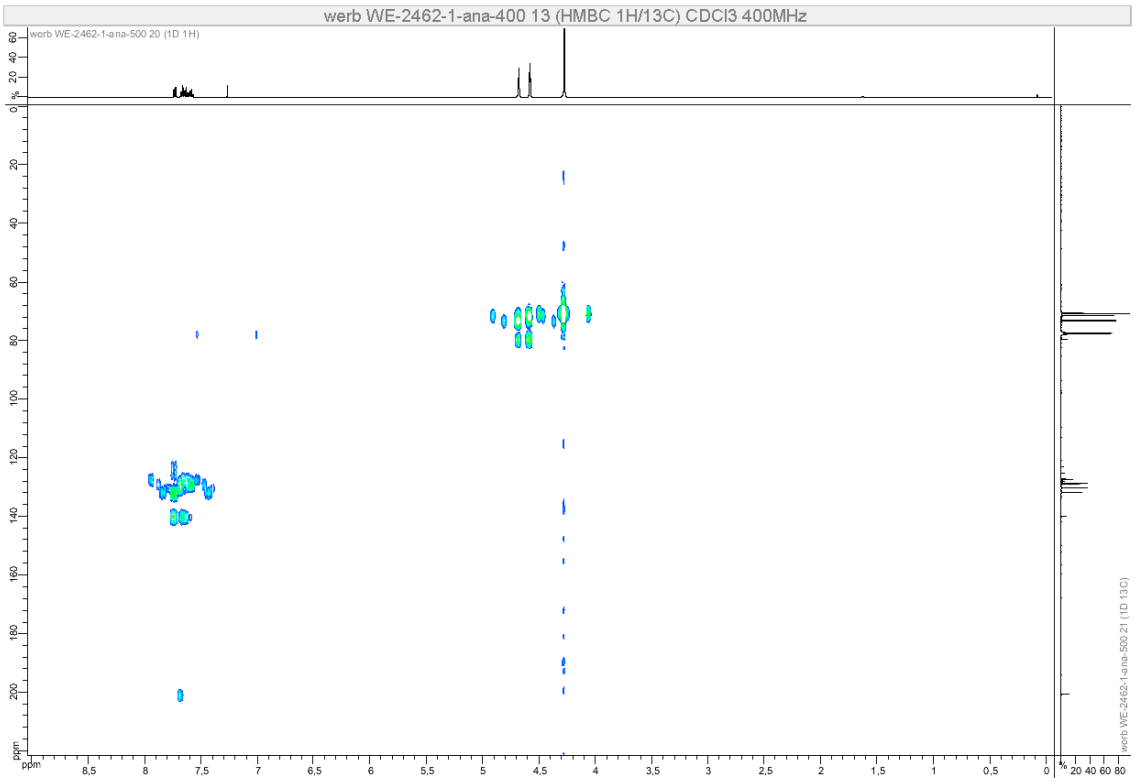
COSY (500 MHz, $CDCl_3$)



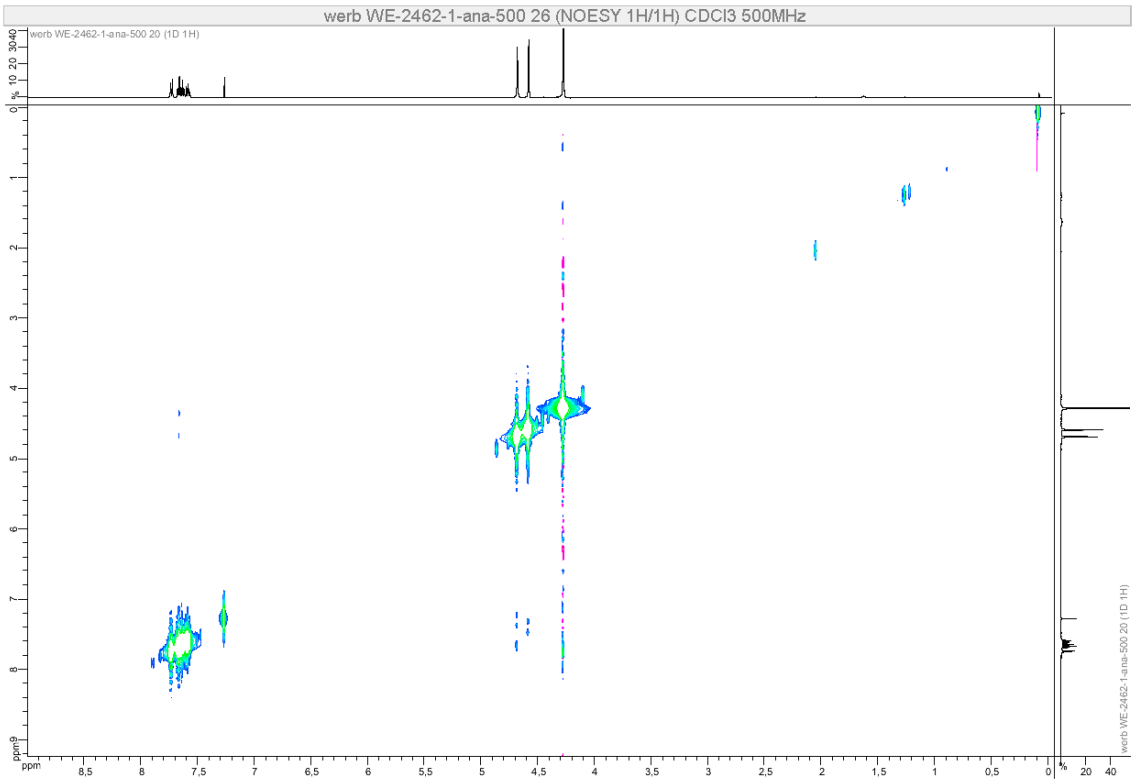
HSQC (500 MHz, $CDCl_3$)



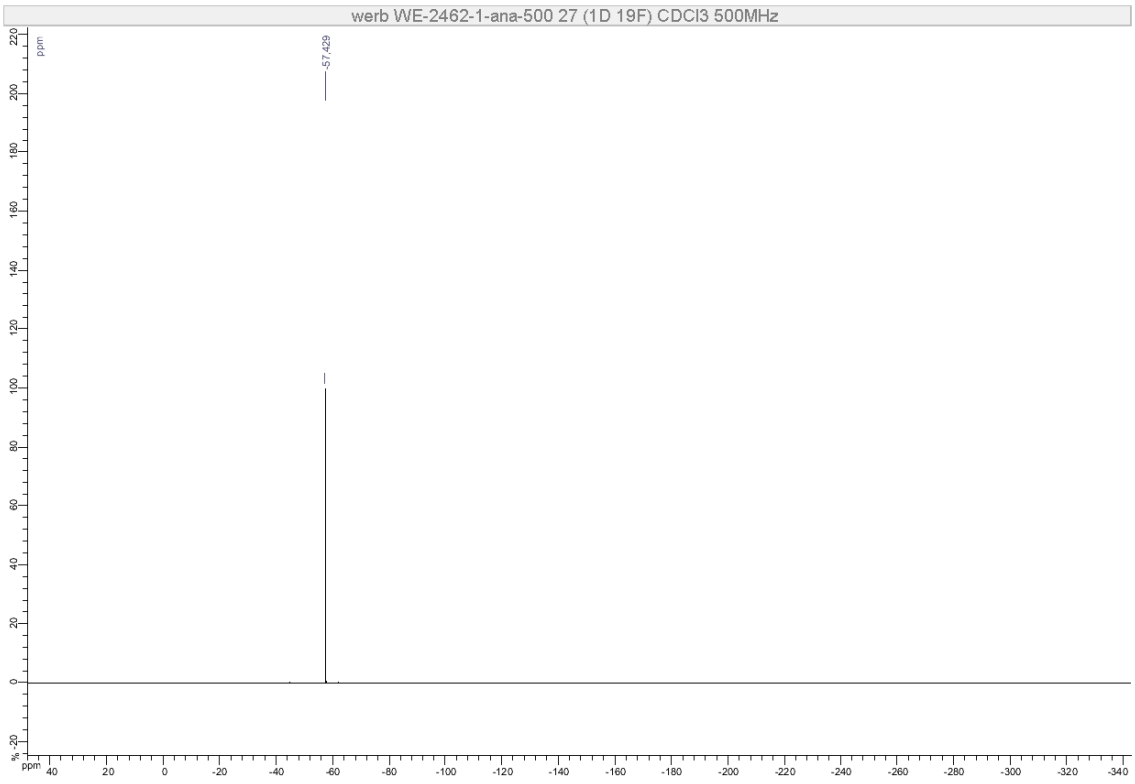
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

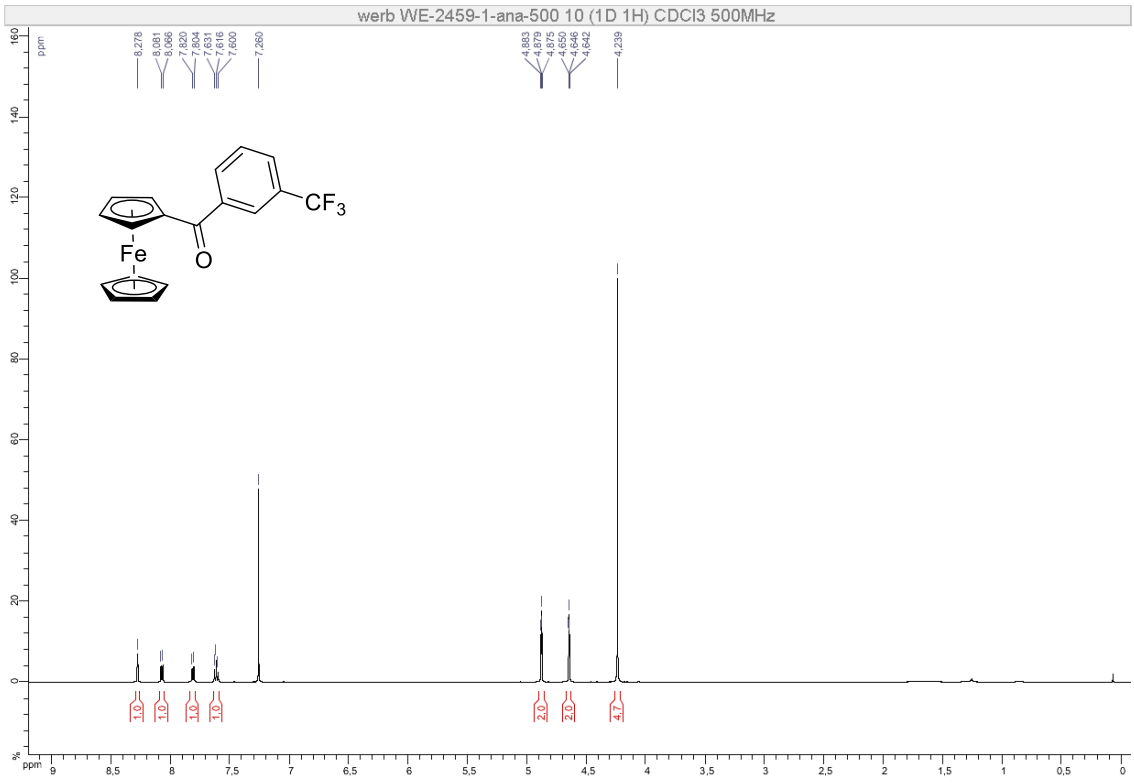


^{19}F NMR (470 MHz, $CDCl_3$)

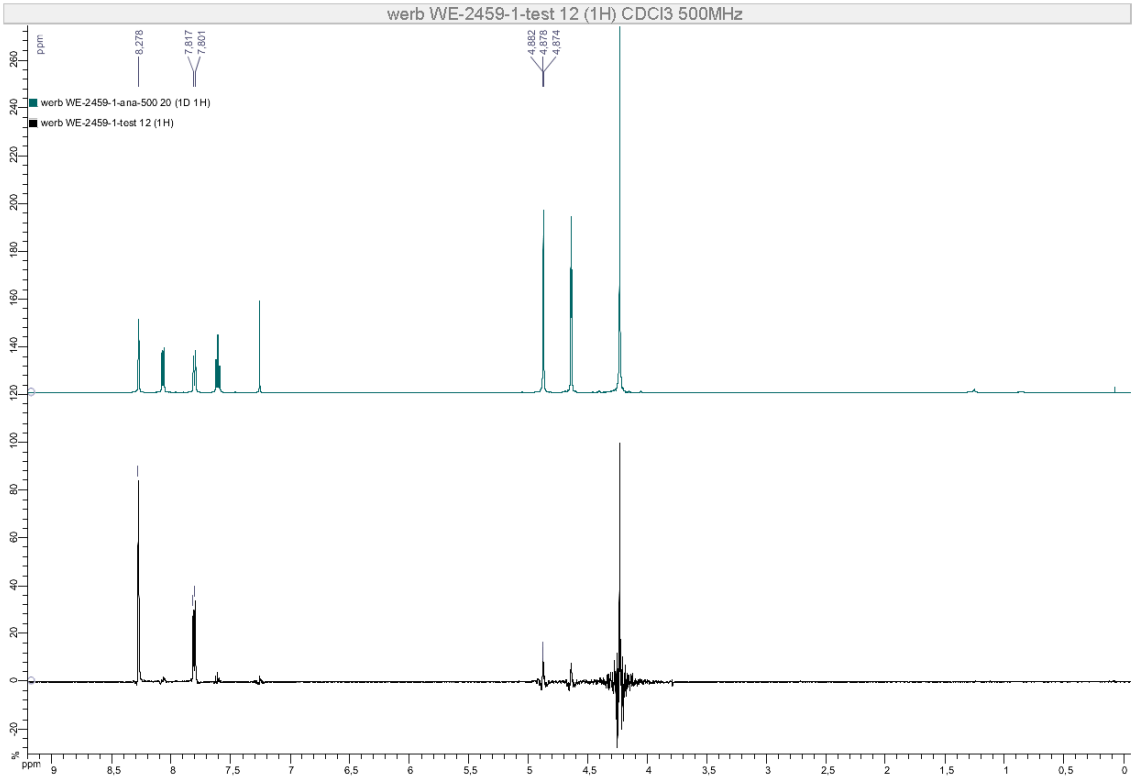


[3-(Trifluoromethyl)benzoyl]ferrocene (1-*m*CF_3Ph)

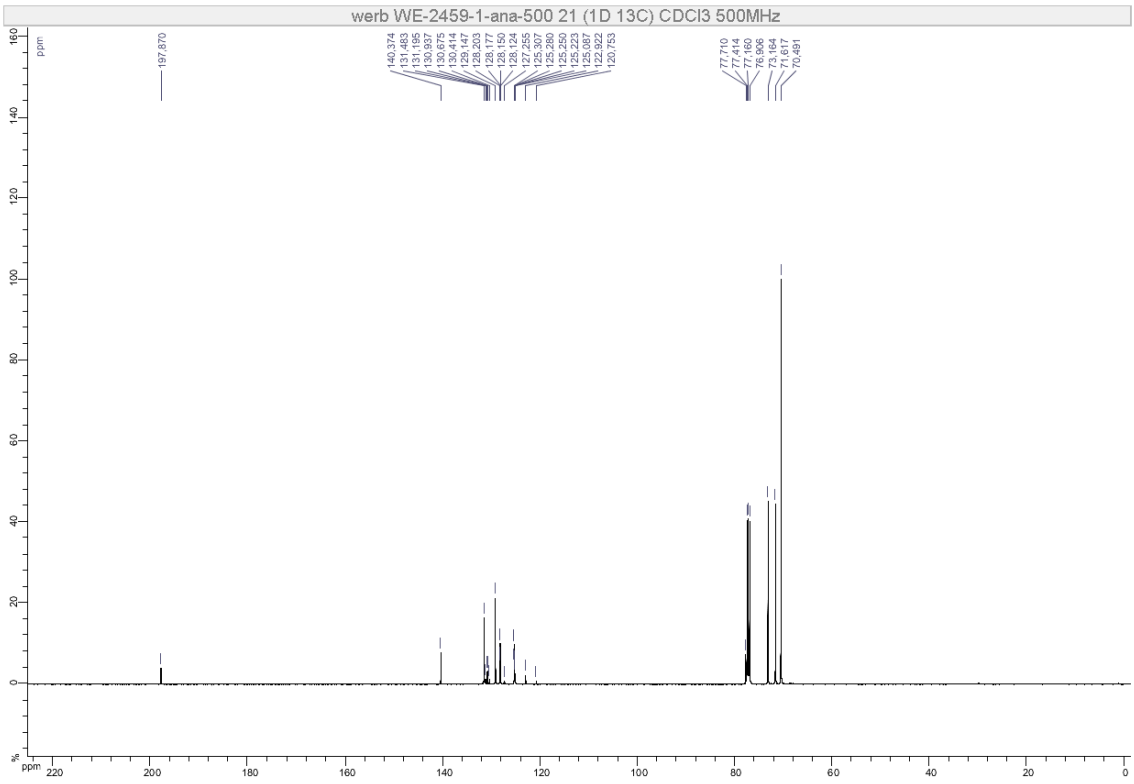
^{1}H NMR (500 MHz, $CDCl_3$)



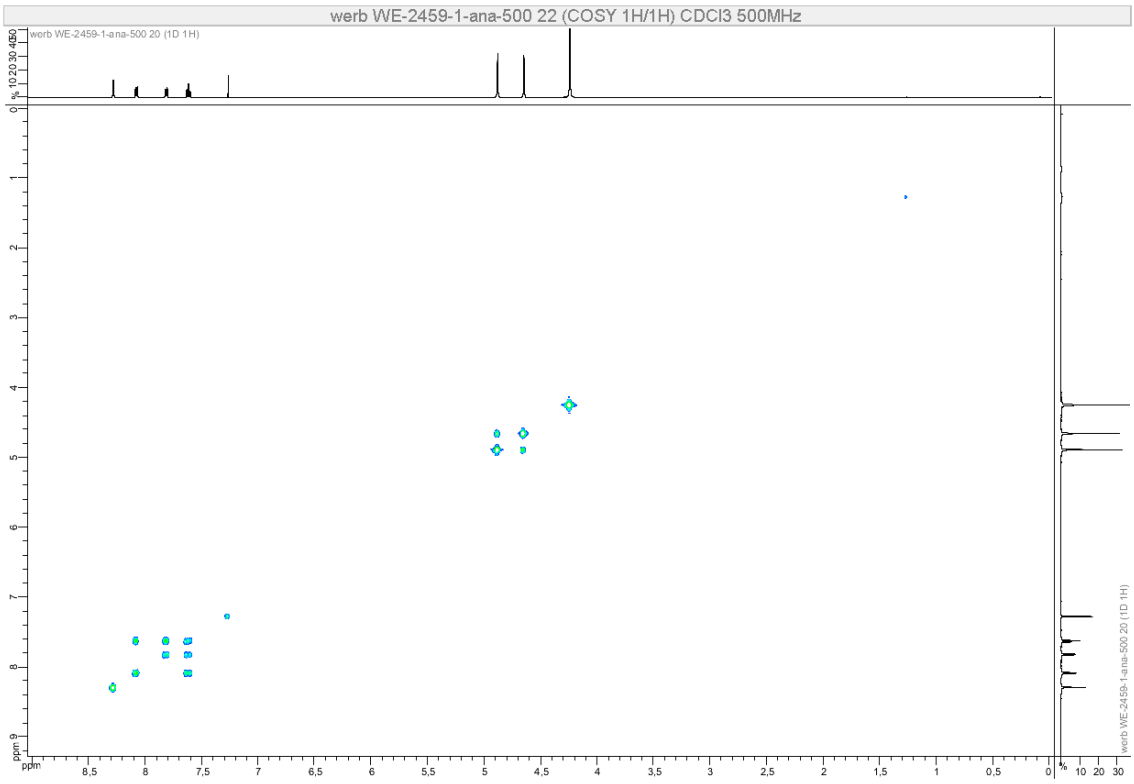
HOESY (500 MHz, $CDCl_3$) Irradiation at –62.6 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



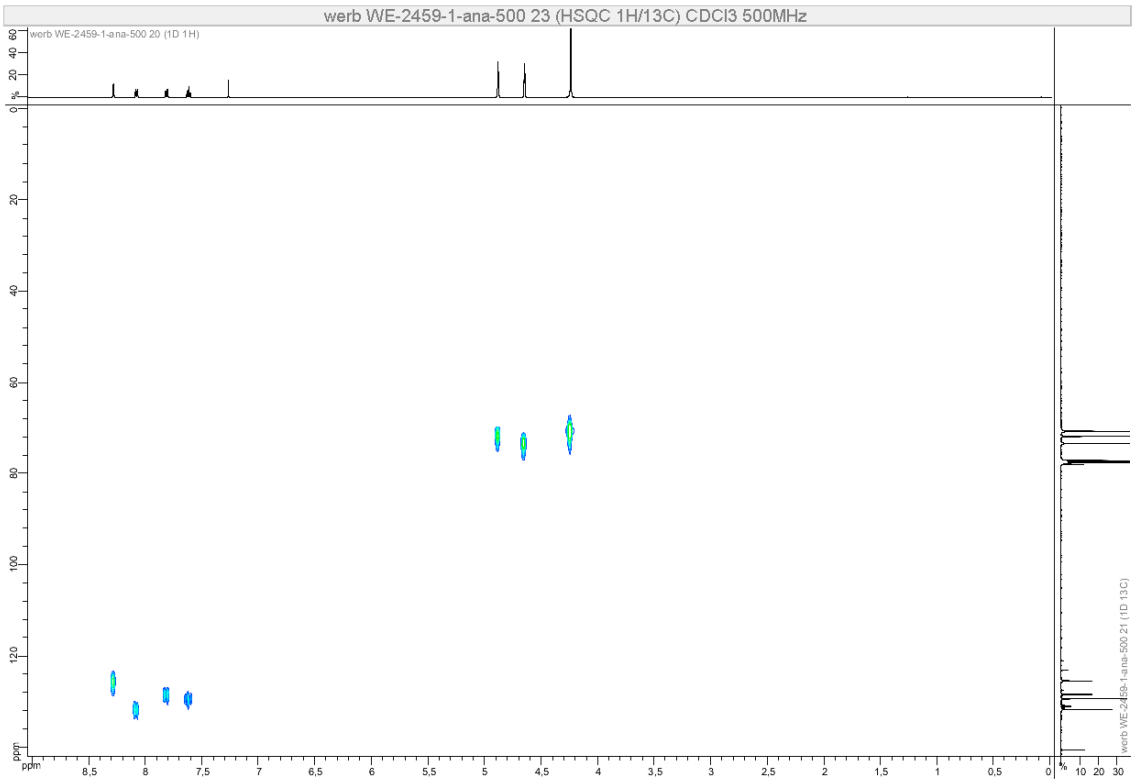
^{13}C NMR (126 MHz, $CDCl_3$)



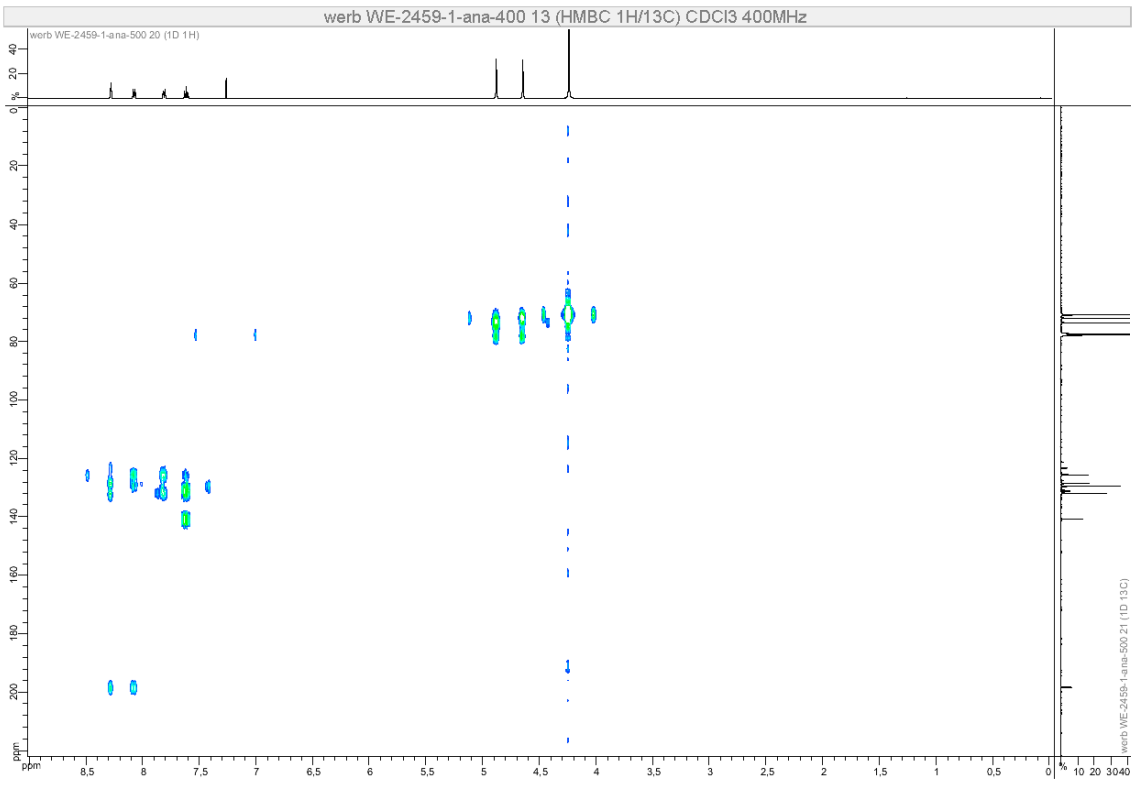
COSY (500 MHz, $CDCl_3$)



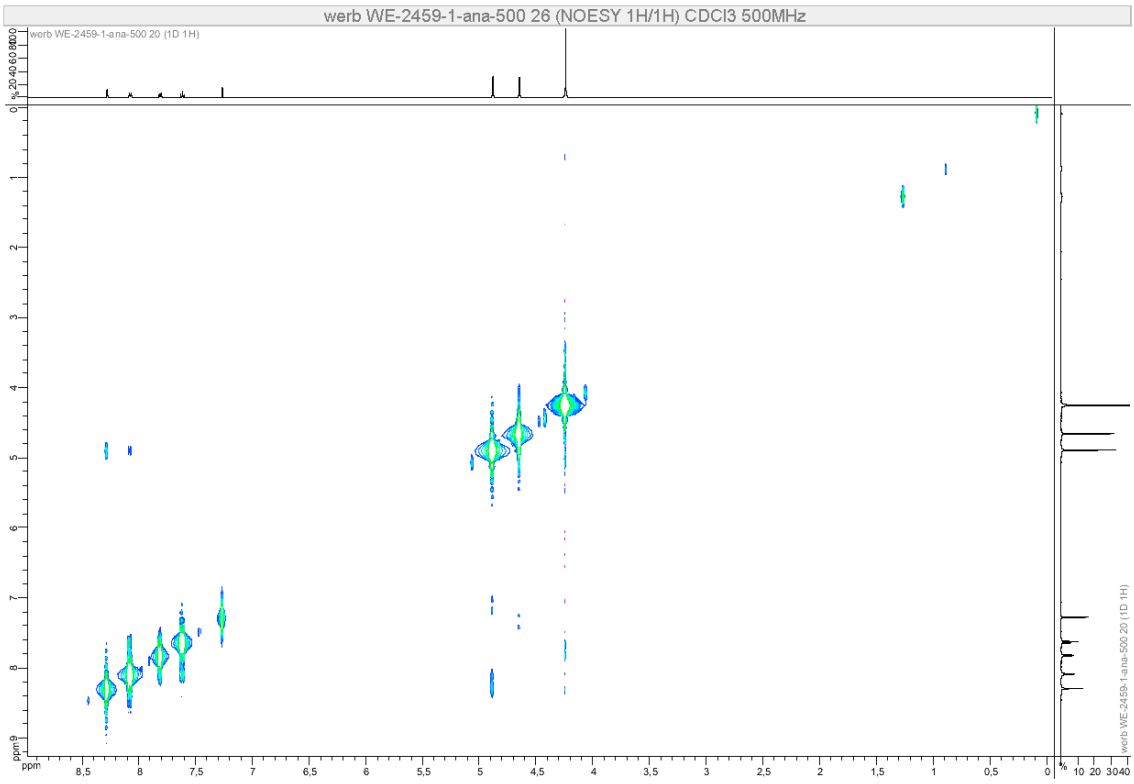
HSQC (500 MHz, $CDCl_3$)



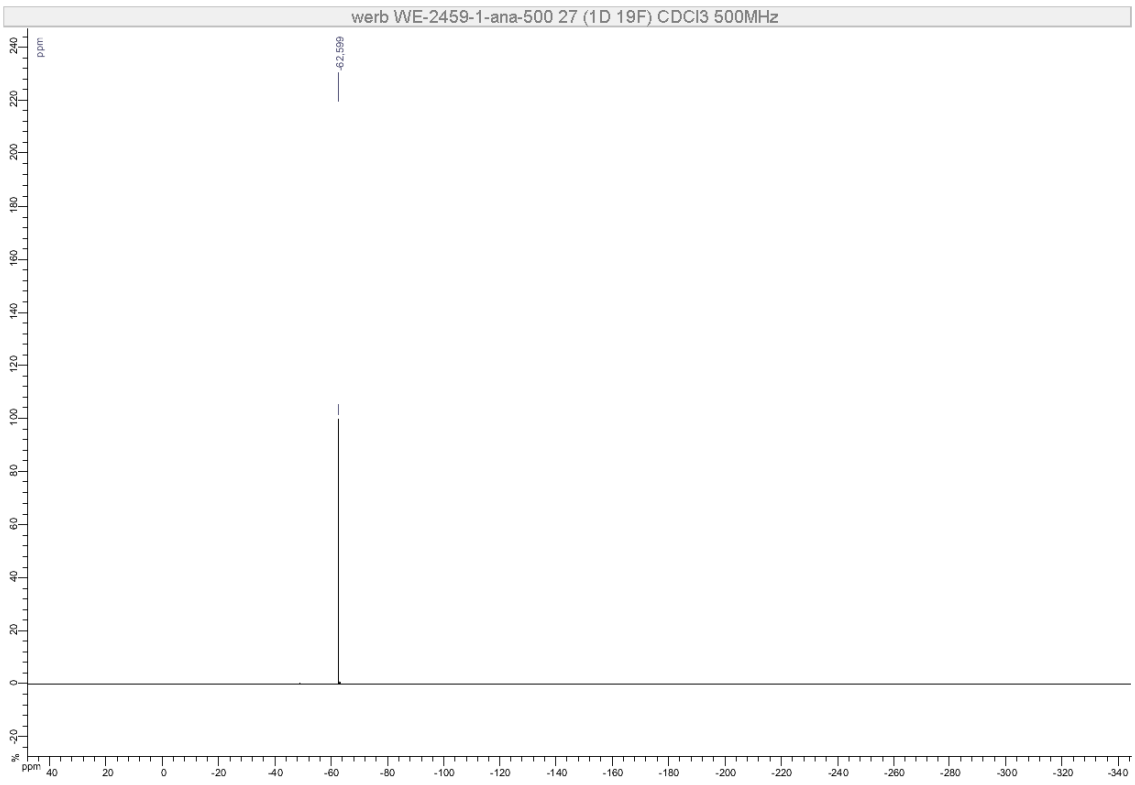
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

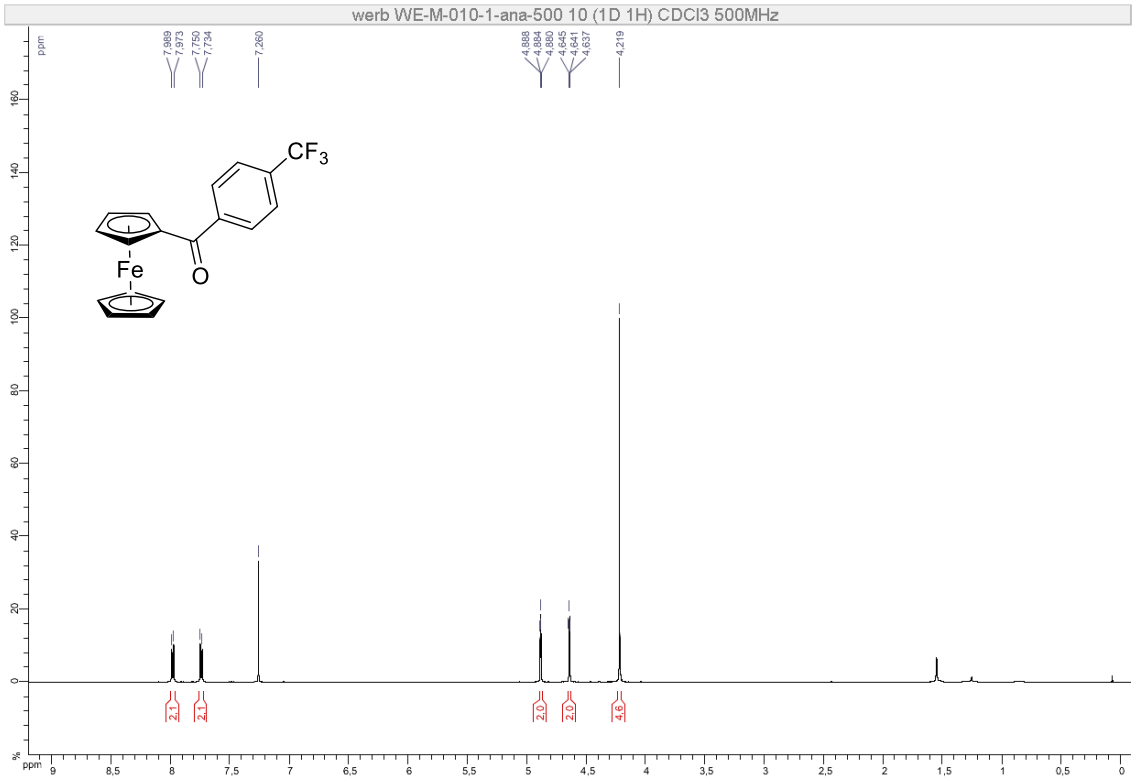


^{19}F NMR (470 MHz, $CDCl_3$)

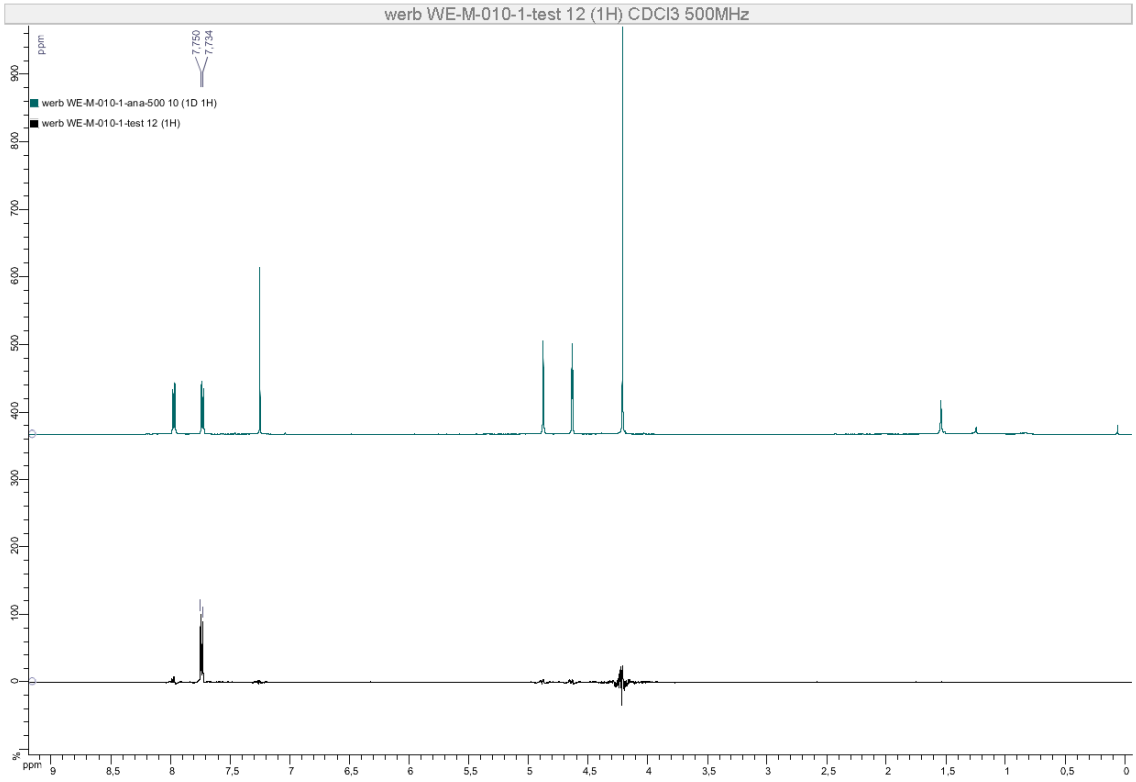


(4-(Trifluoromethyl)benzoyl)ferrocene (1-*p*CF_3Ph)

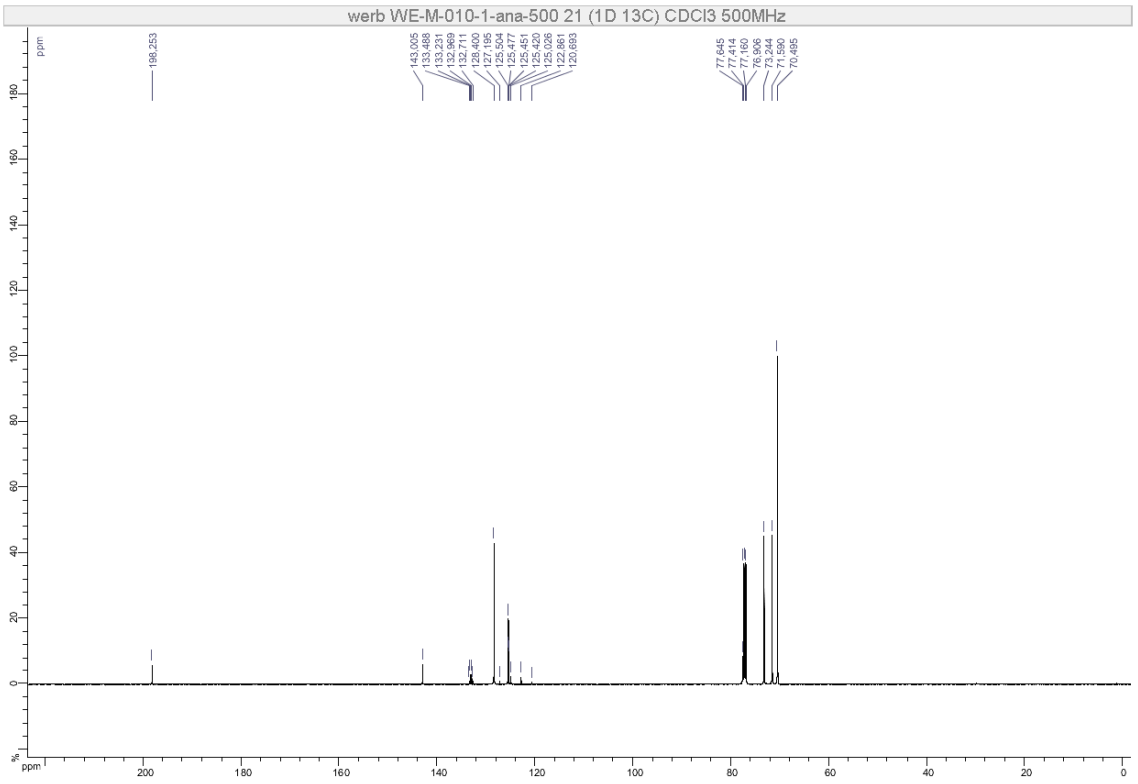
^{1}H NMR (500 MHz, $CDCl_3$)



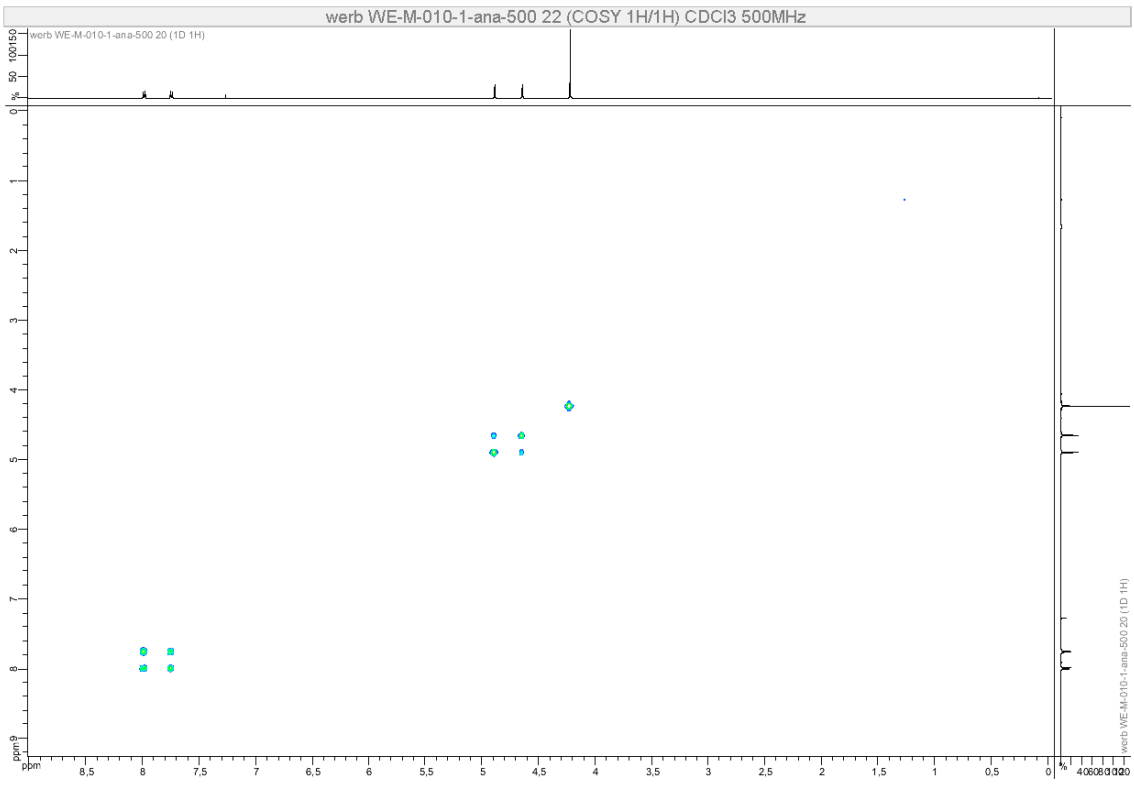
HOESY (500 MHz, $CDCl_3$) Irradiation at –62.9 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



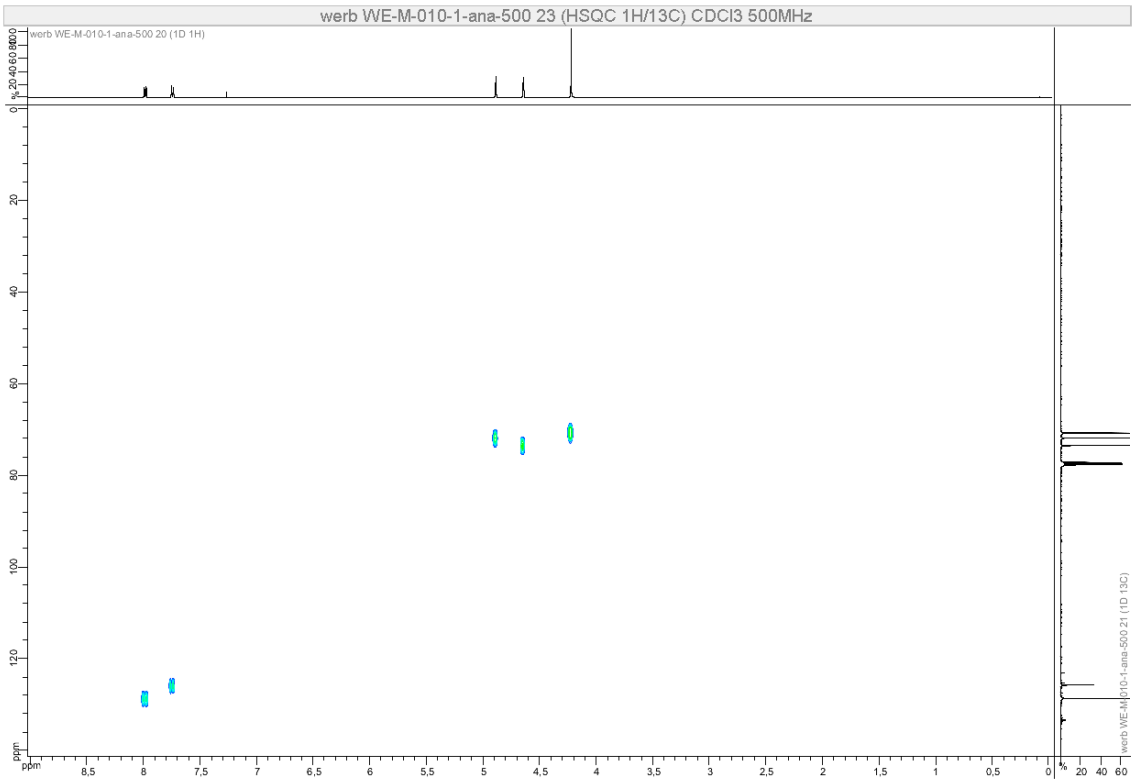
^{13}C NMR (126 MHz, $CDCl_3$)



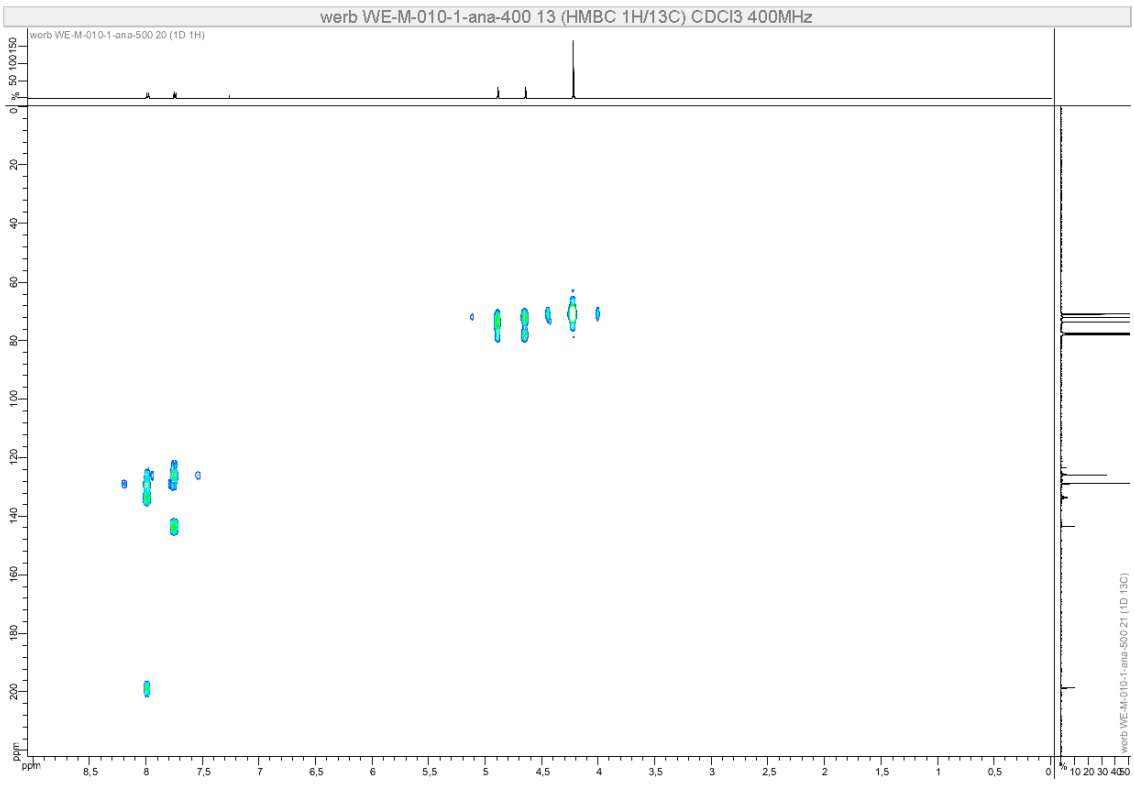
COSY (500 MHz, $CDCl_3$)



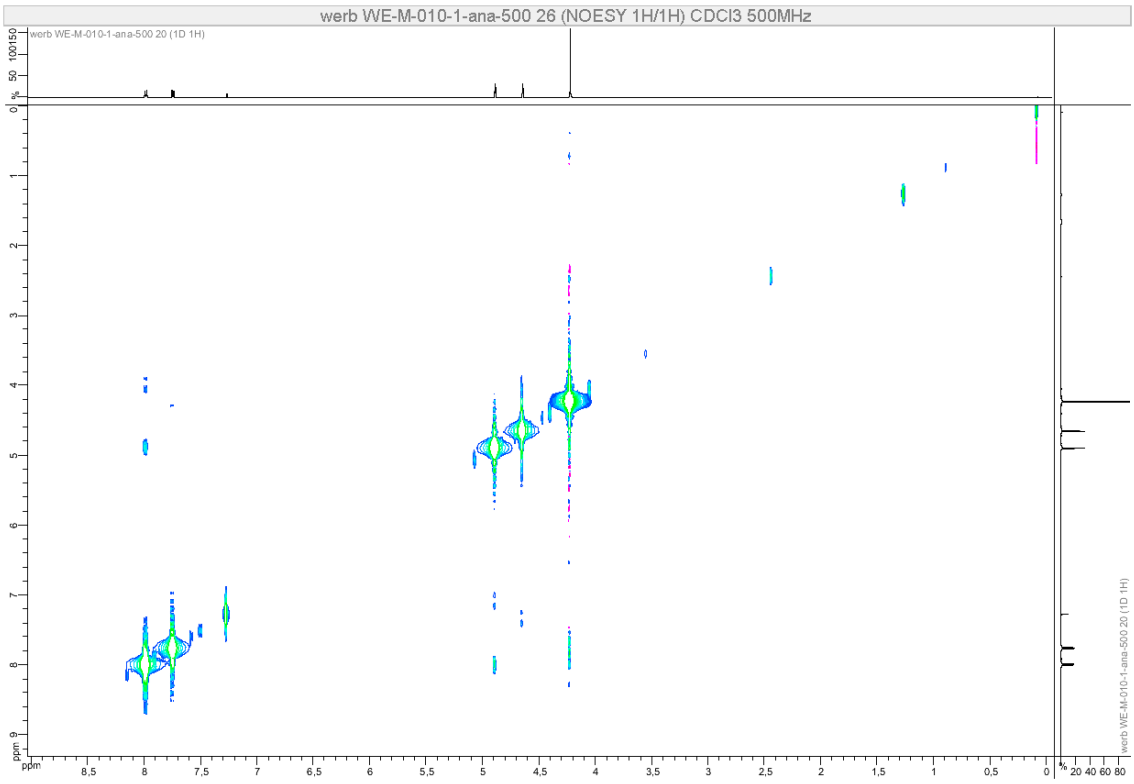
HSQC (500 MHz, $CDCl_3$)



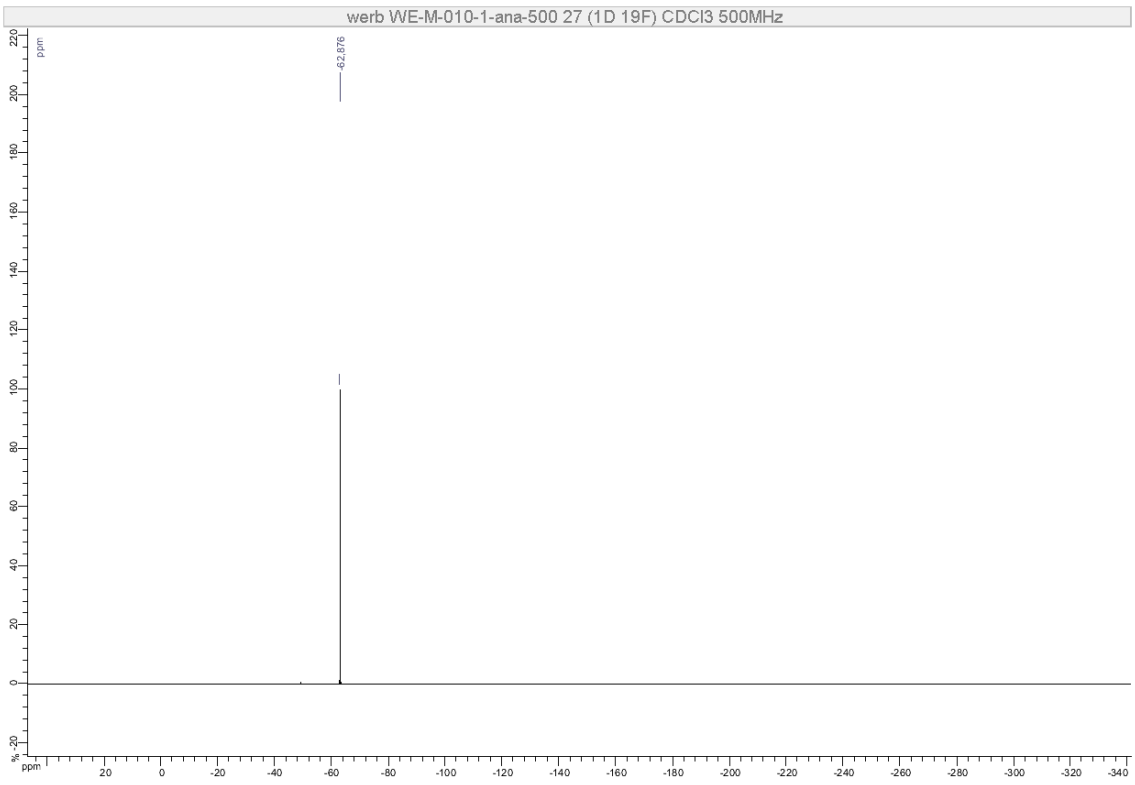
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

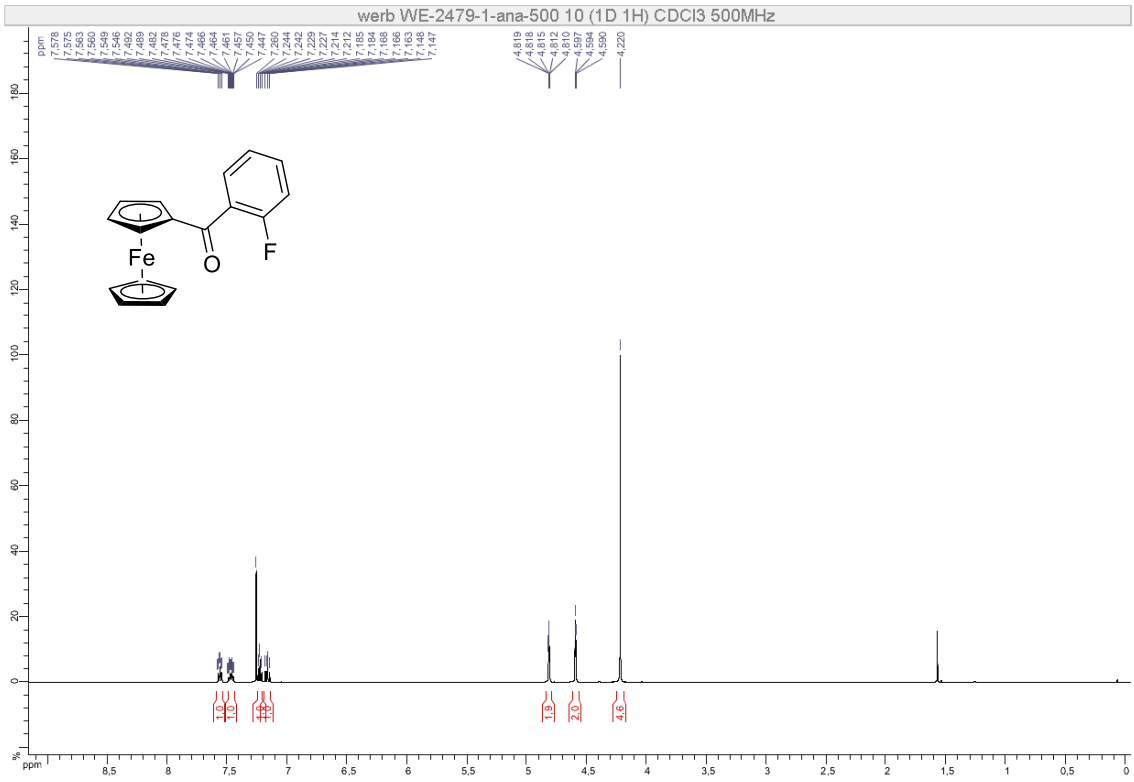


^{19}F NMR (470 MHz, $CDCl_3$)

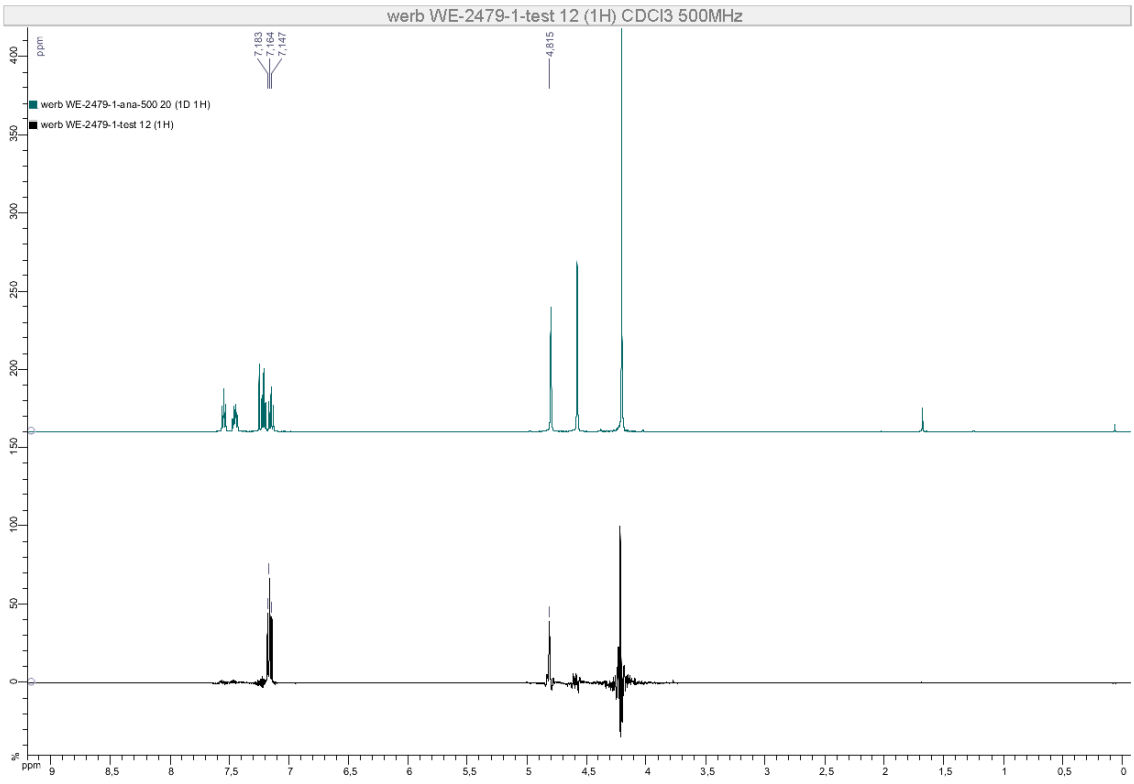


(2-Fluorobenzoyl)ferrocene (1-*o*FPh)

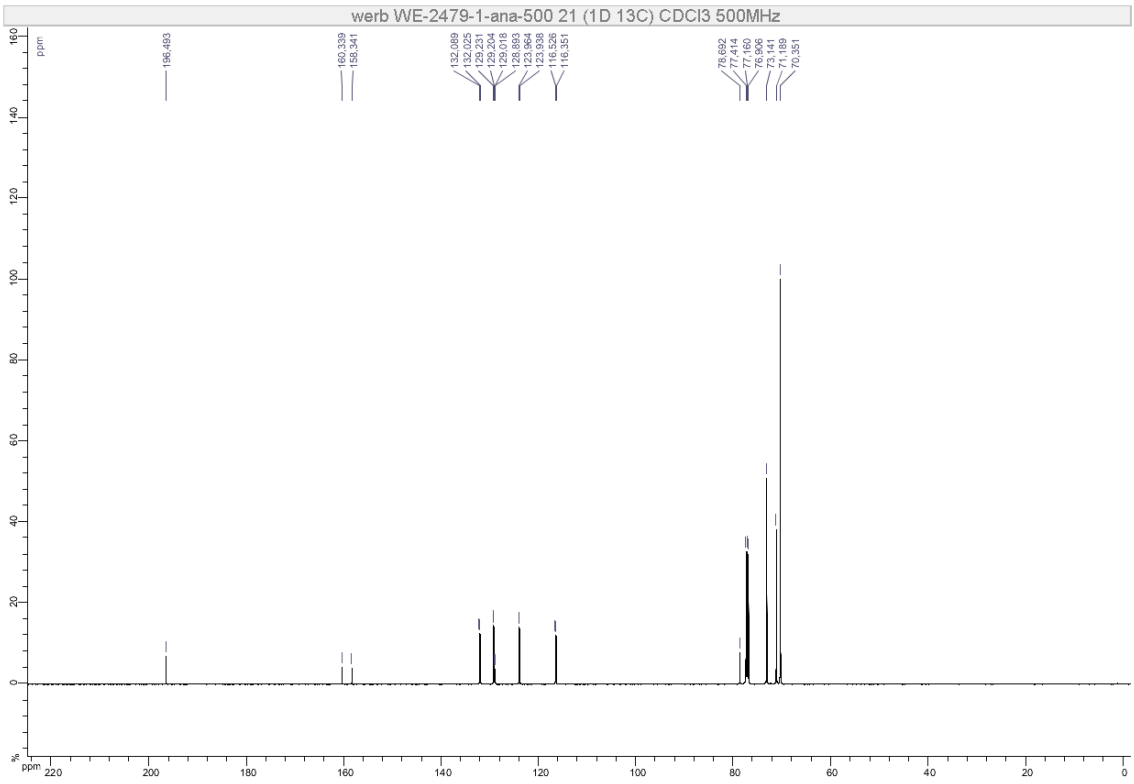
^{1}H NMR (500 MHz, $CDCl_3$)



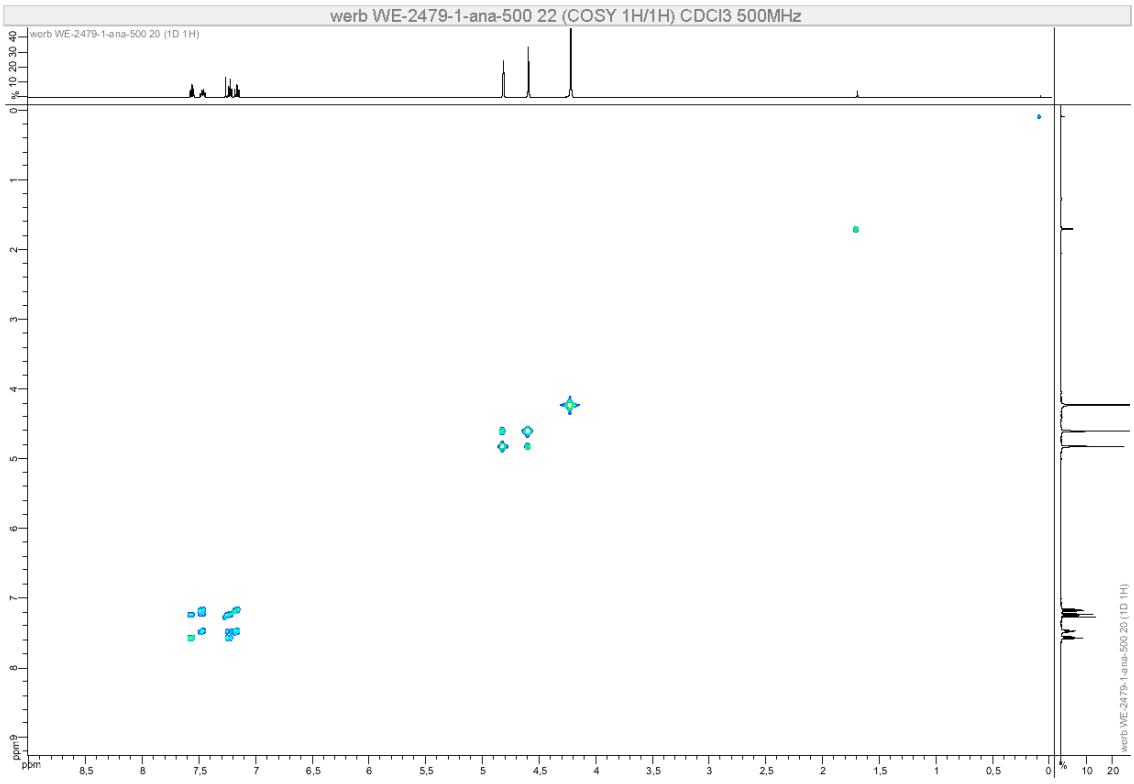
HOESY (500 MHz, $CDCl_3$) Irradiation at –113.4 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra



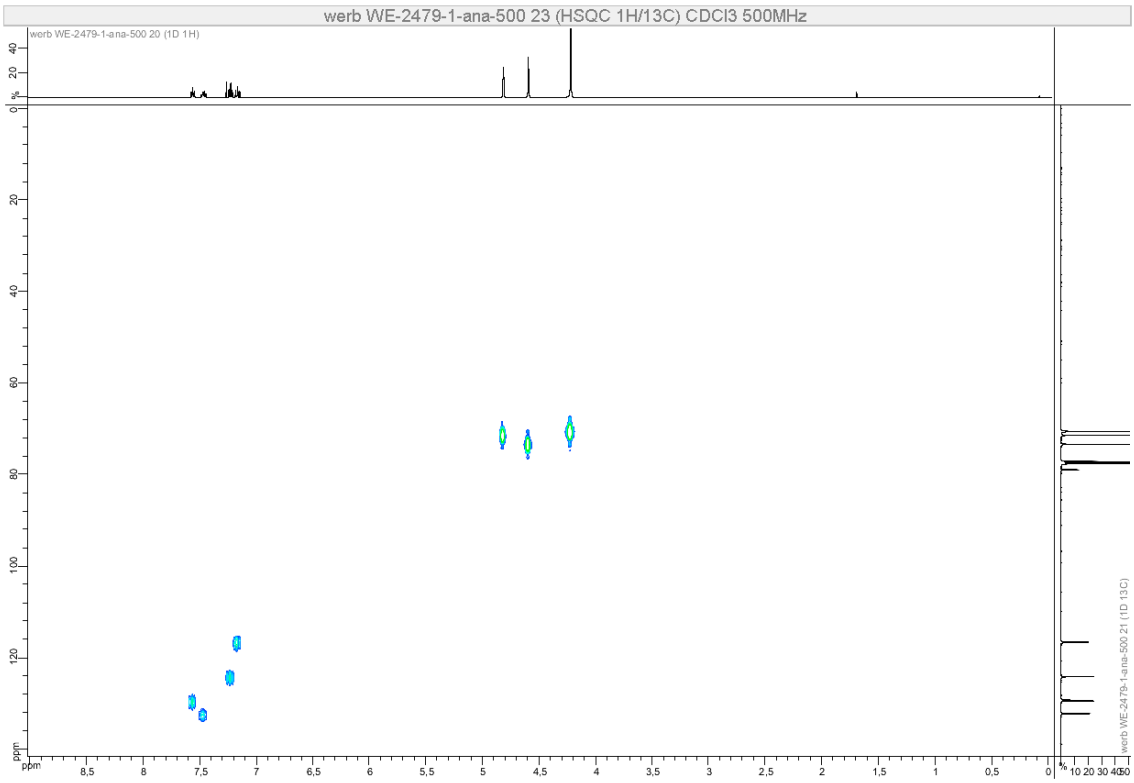
^{13}C NMR (126 MHz, $CDCl_3$)



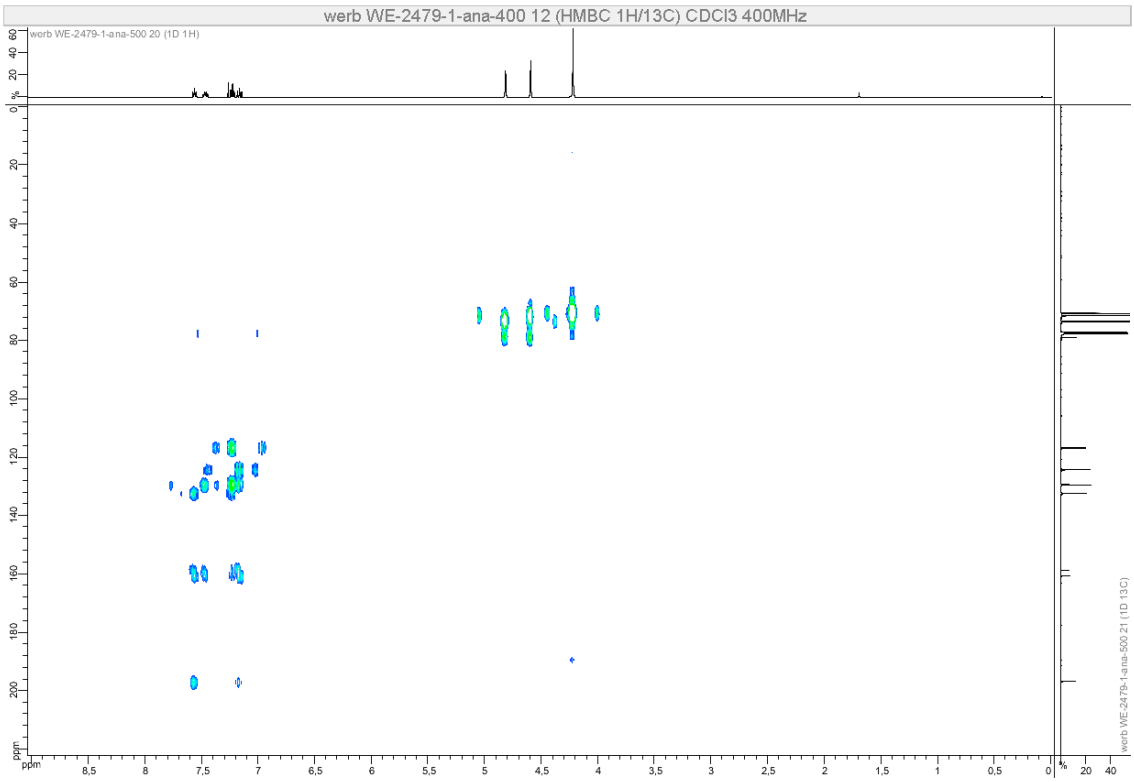
COSY (500 MHz, $CDCl_3$)



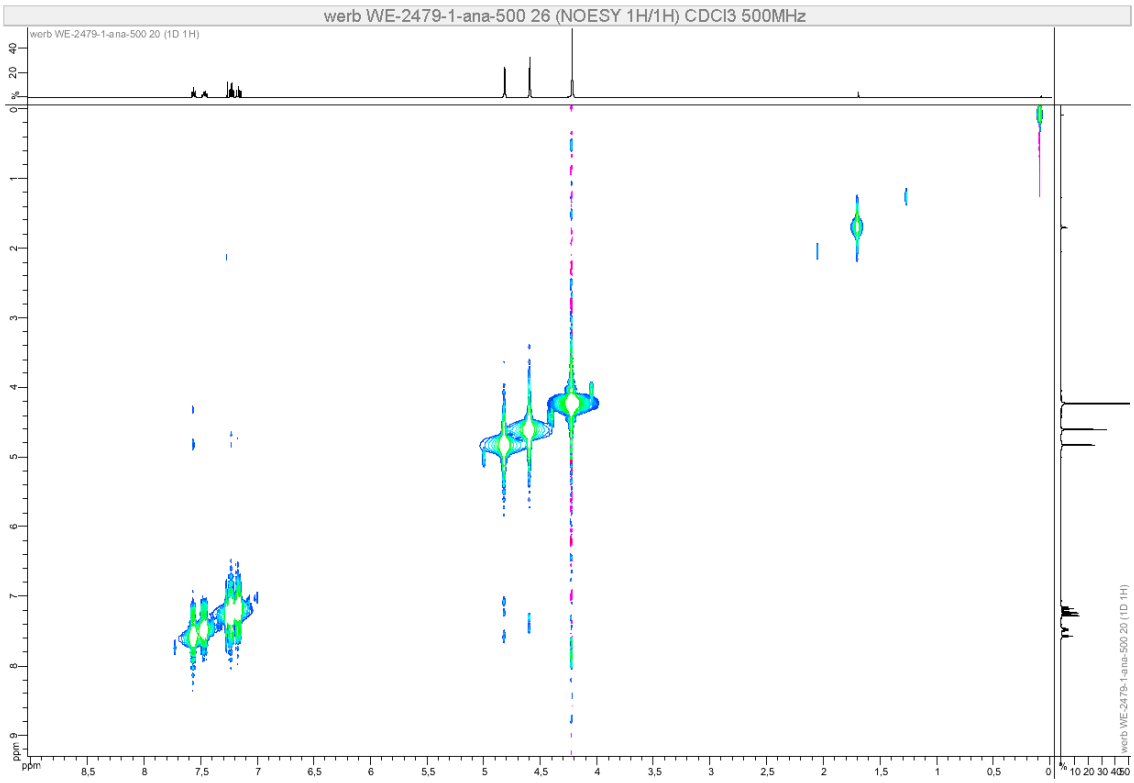
HSQC (500 MHz, $CDCl_3$)



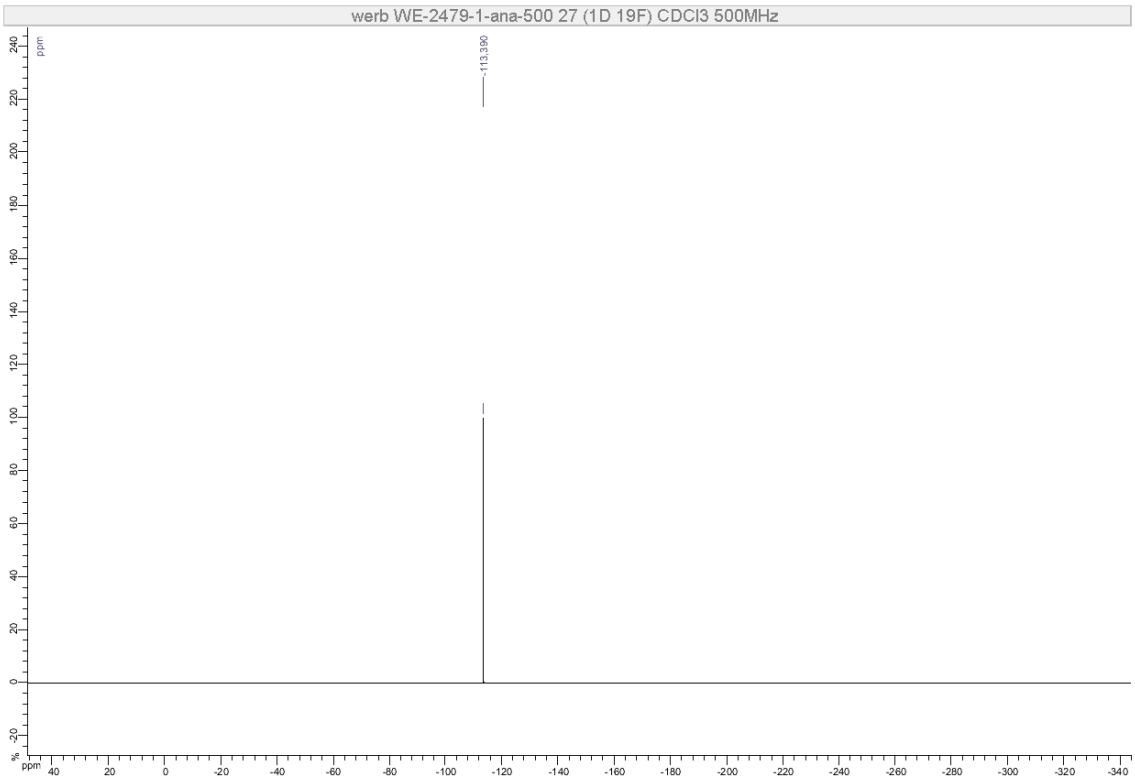
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

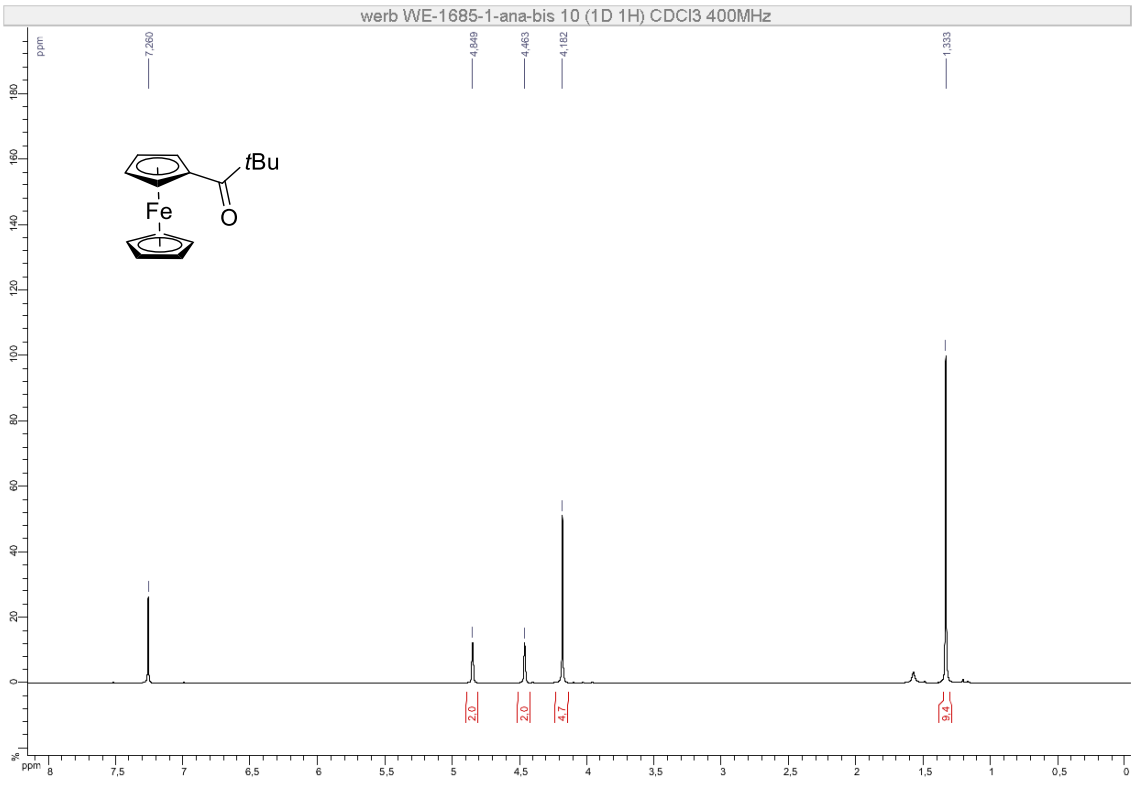


^{19}F NMR (471 MHz, $CDCl_3$)

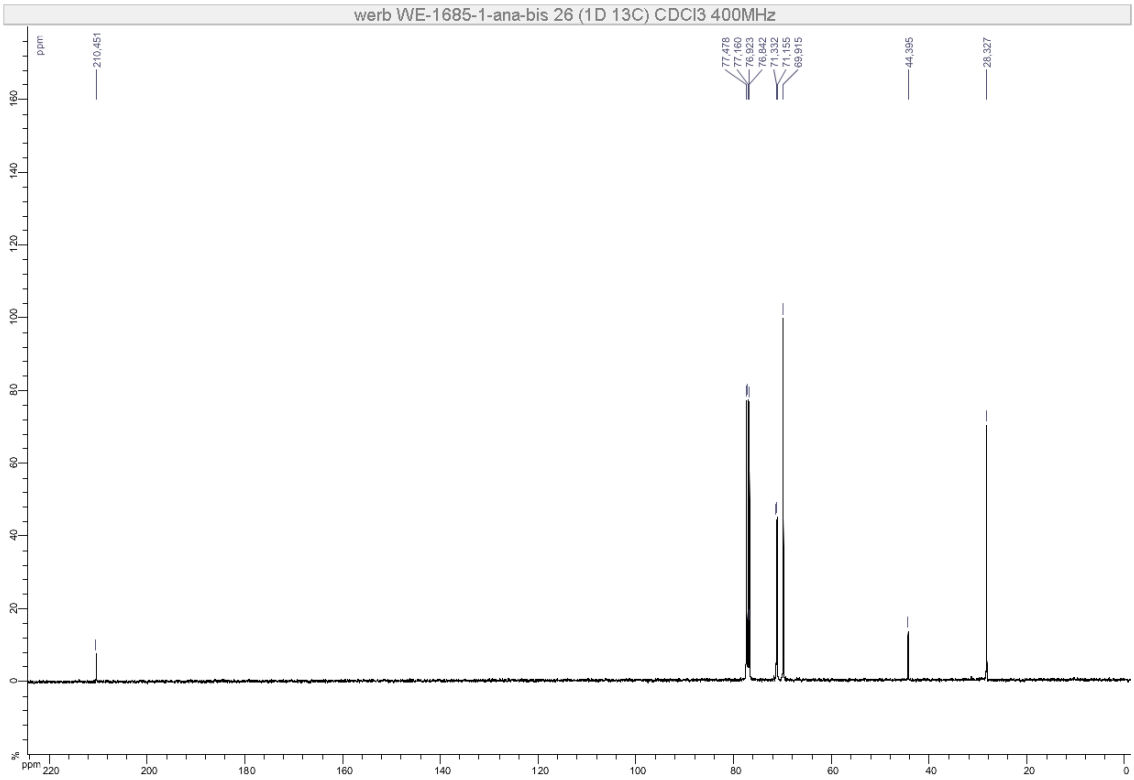


Pivaloylferrocene (1-*t*Bu)

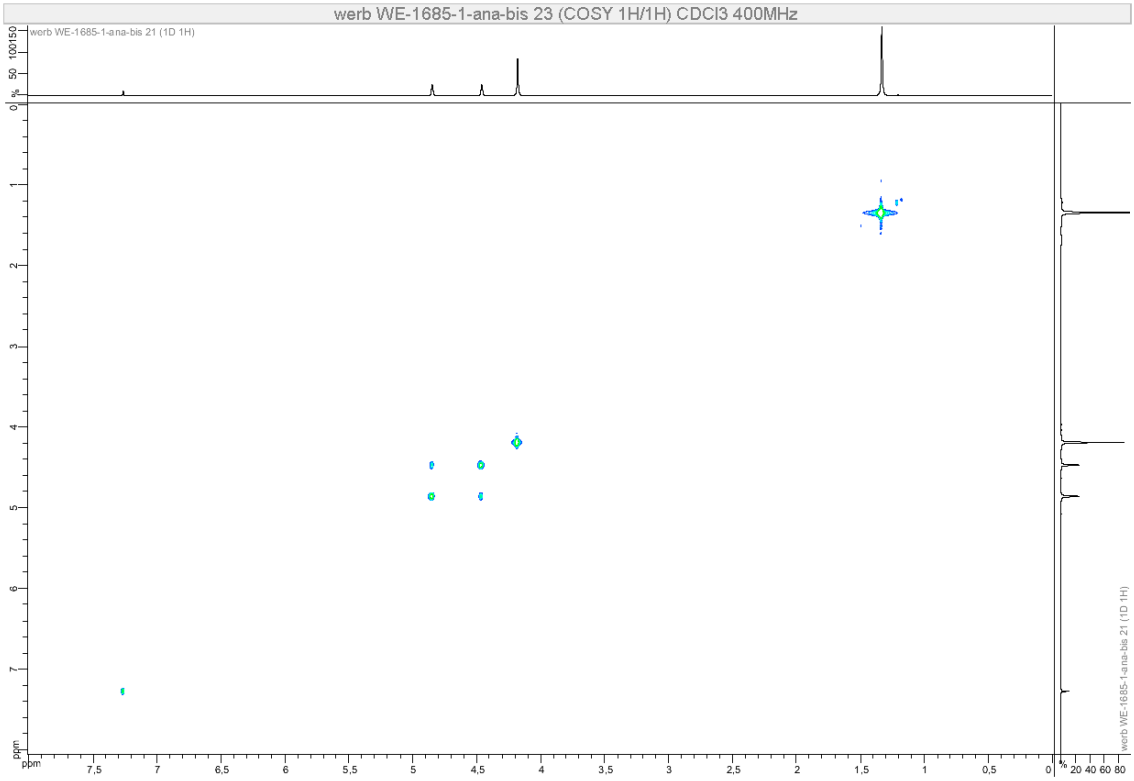
^{1}H NMR (400 MHz, $CDCl_3$)



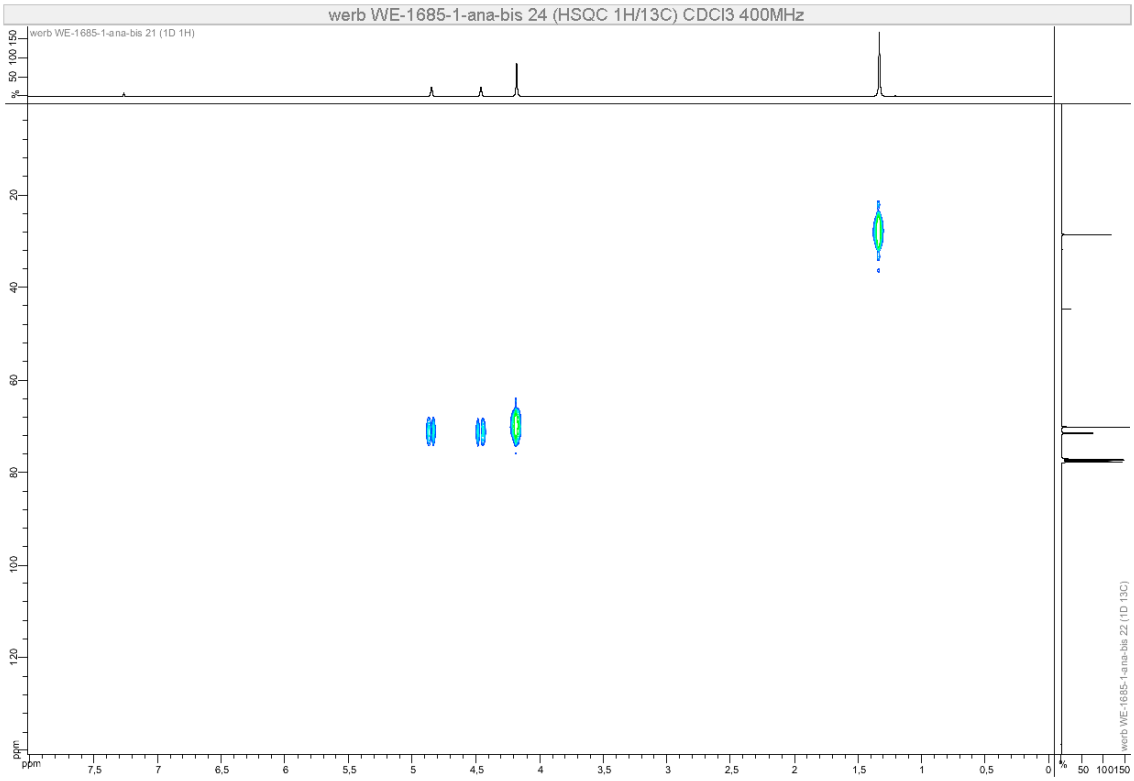
^{13}C NMR (101 MHz, $CDCl_3$)



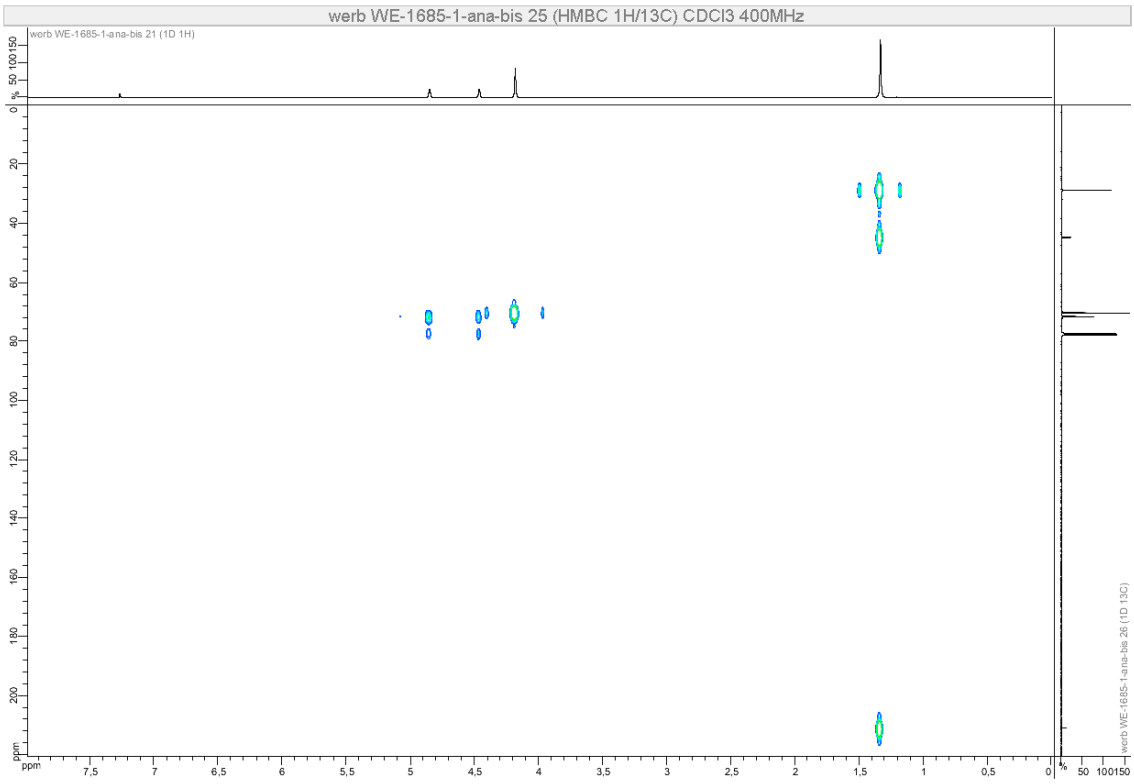
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

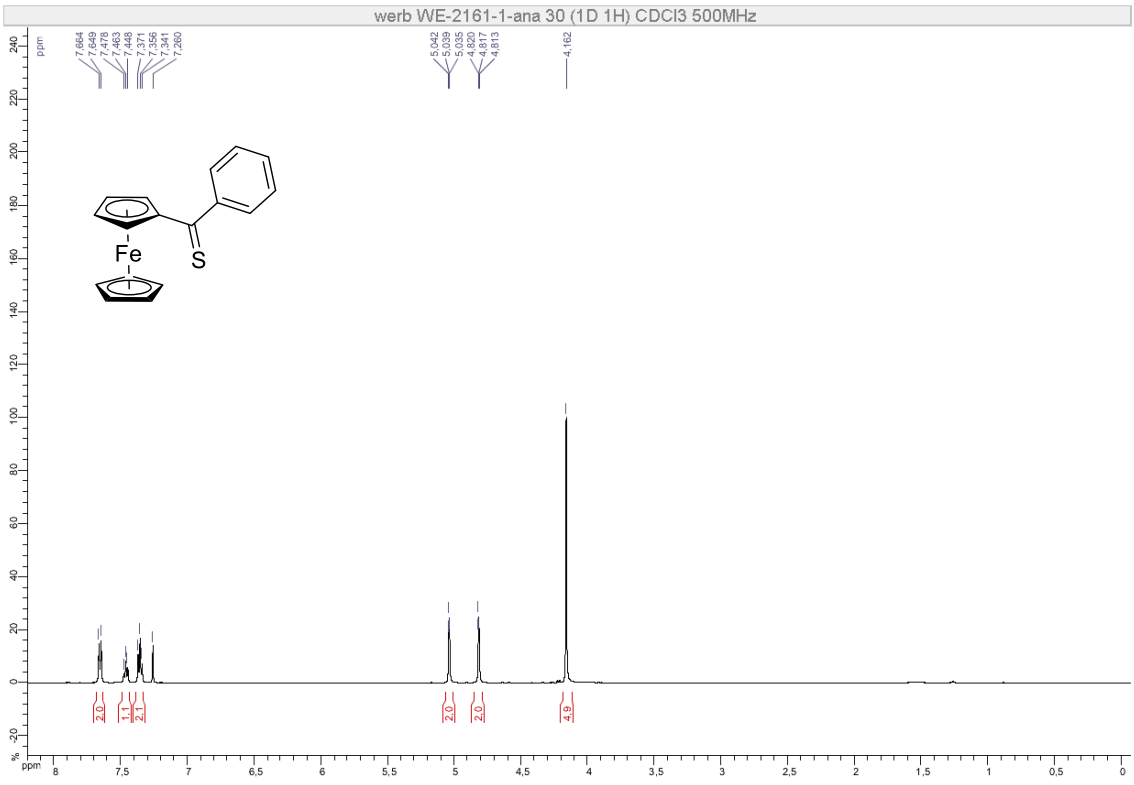


HMBC (500 MHz, $CDCl_3$)

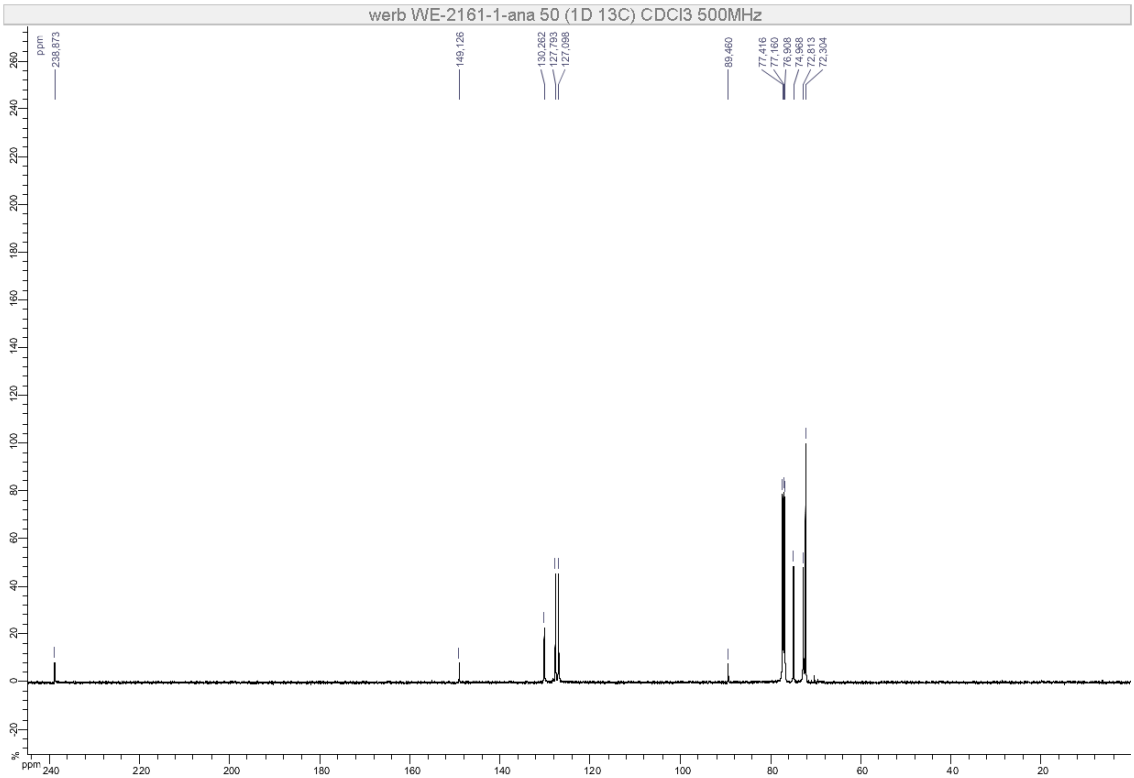


(Phenylcarbonothioyl)ferrocene (4-Ph)

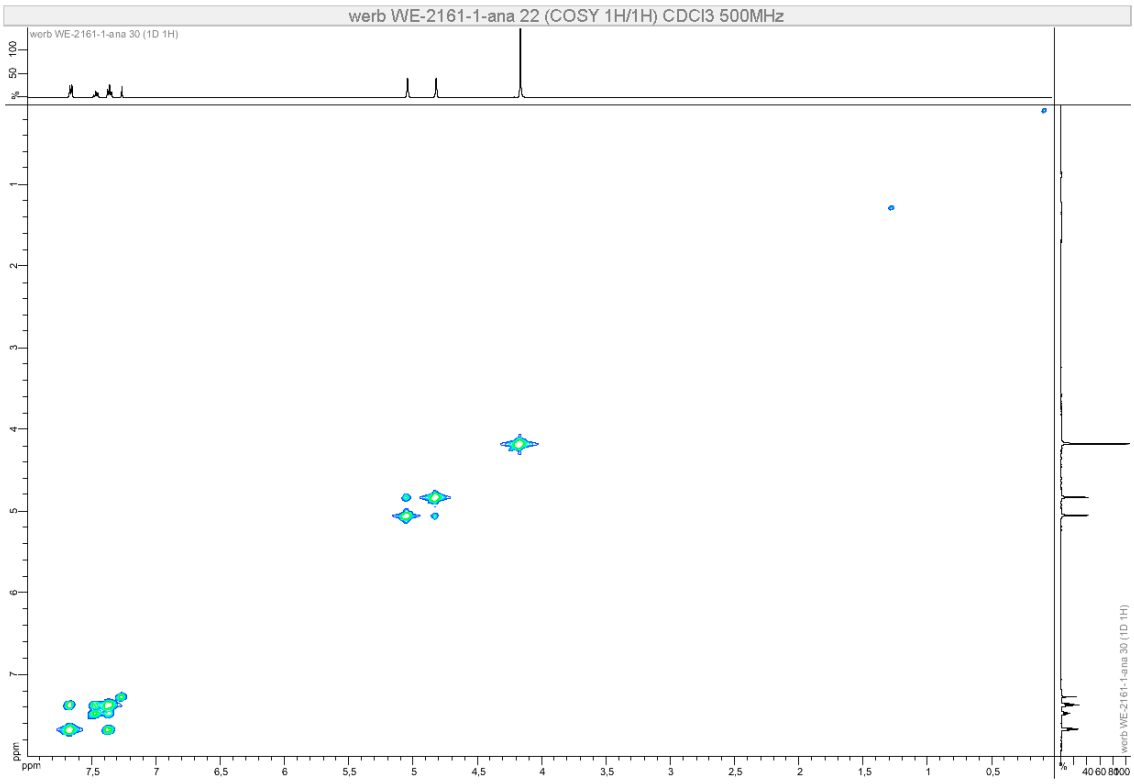
^{1}H NMR (500 MHz, $CDCl_3$)



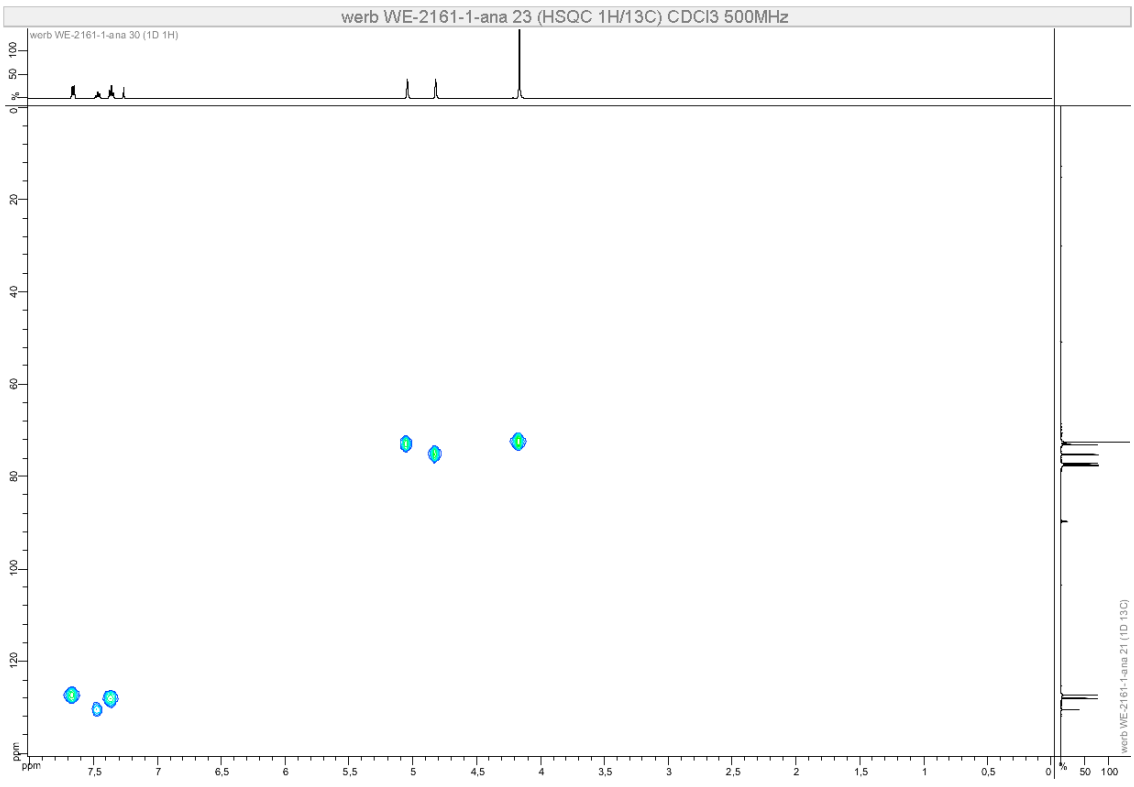
^{13}C NMR (126 MHz, $CDCl_3$)



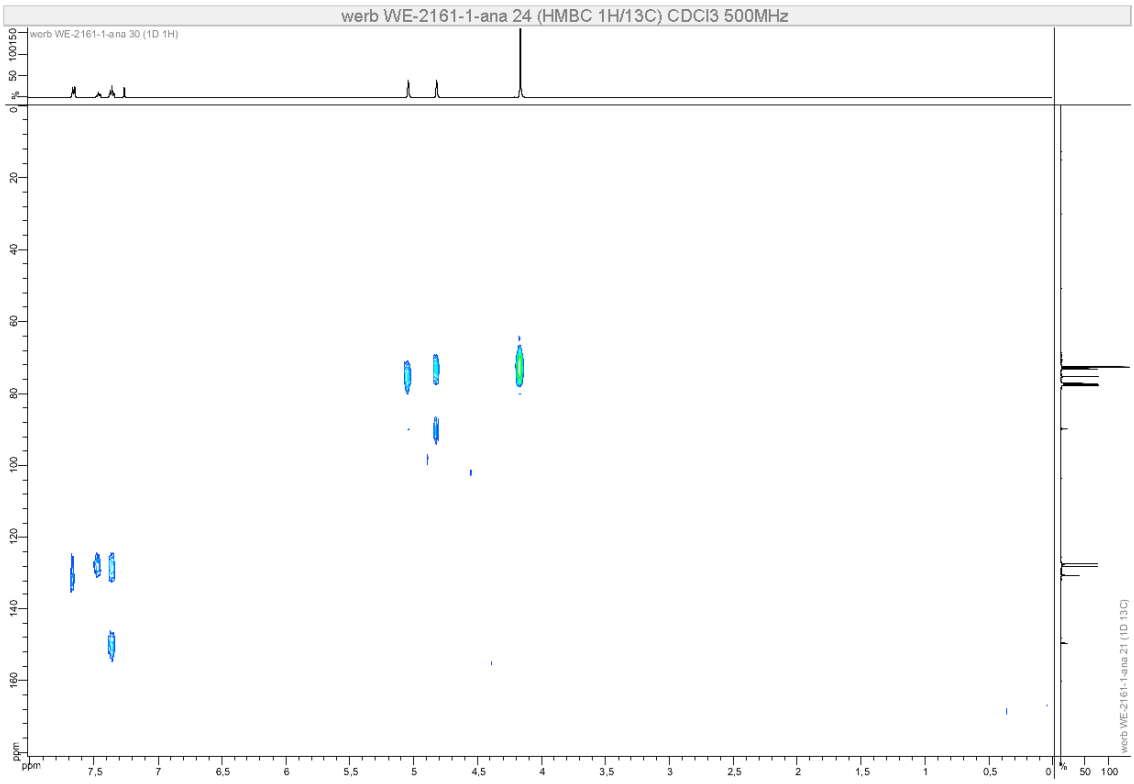
COSY (500 MHz, $CDCl_3$)



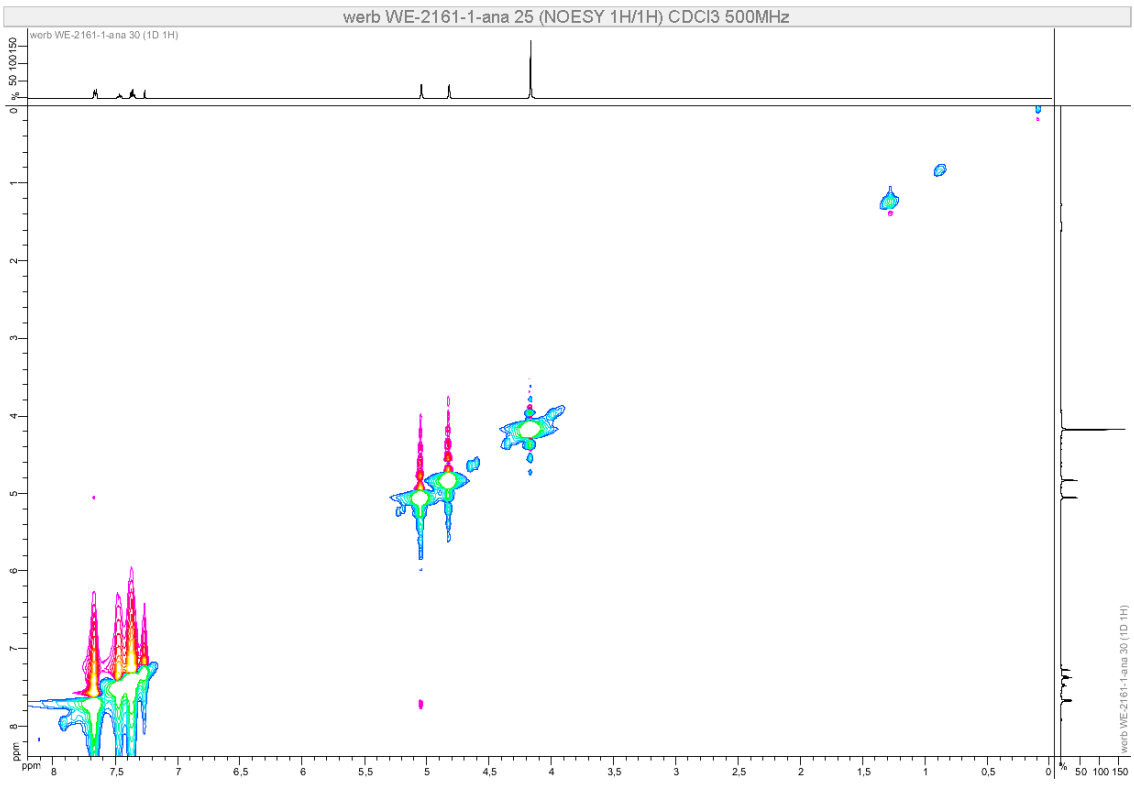
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

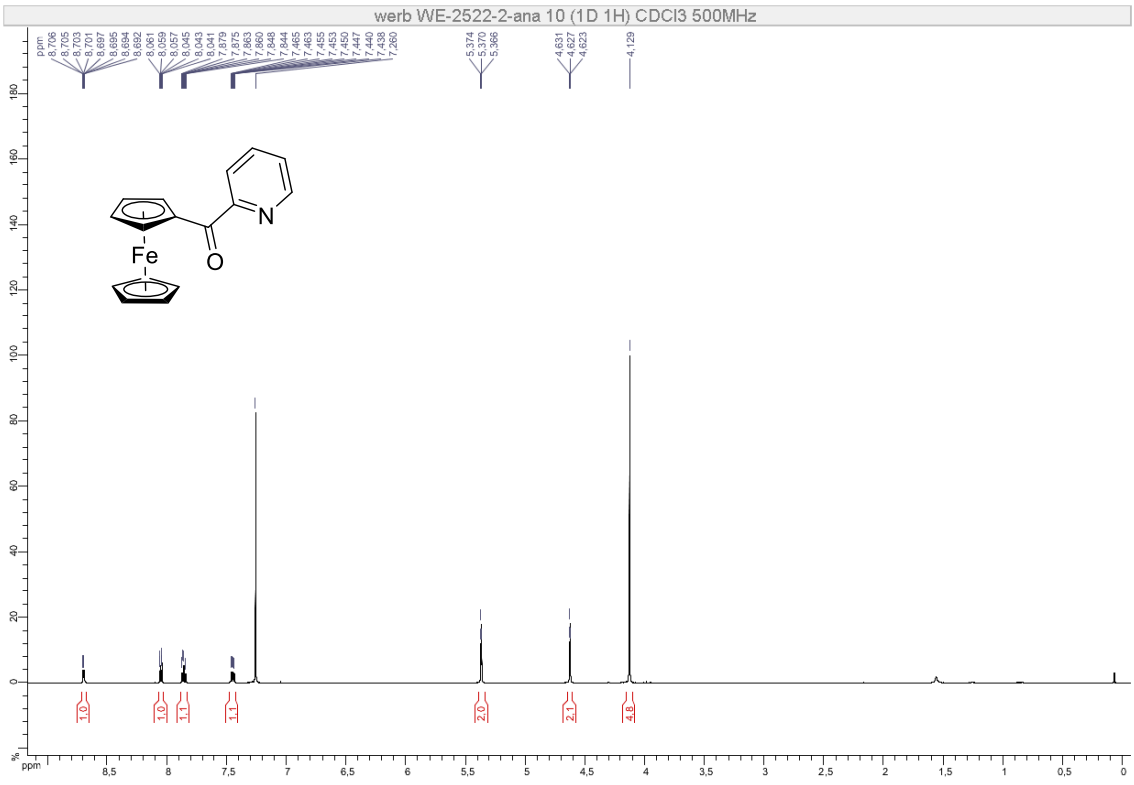


NOESY (500 MHz, $CDCl_3$)

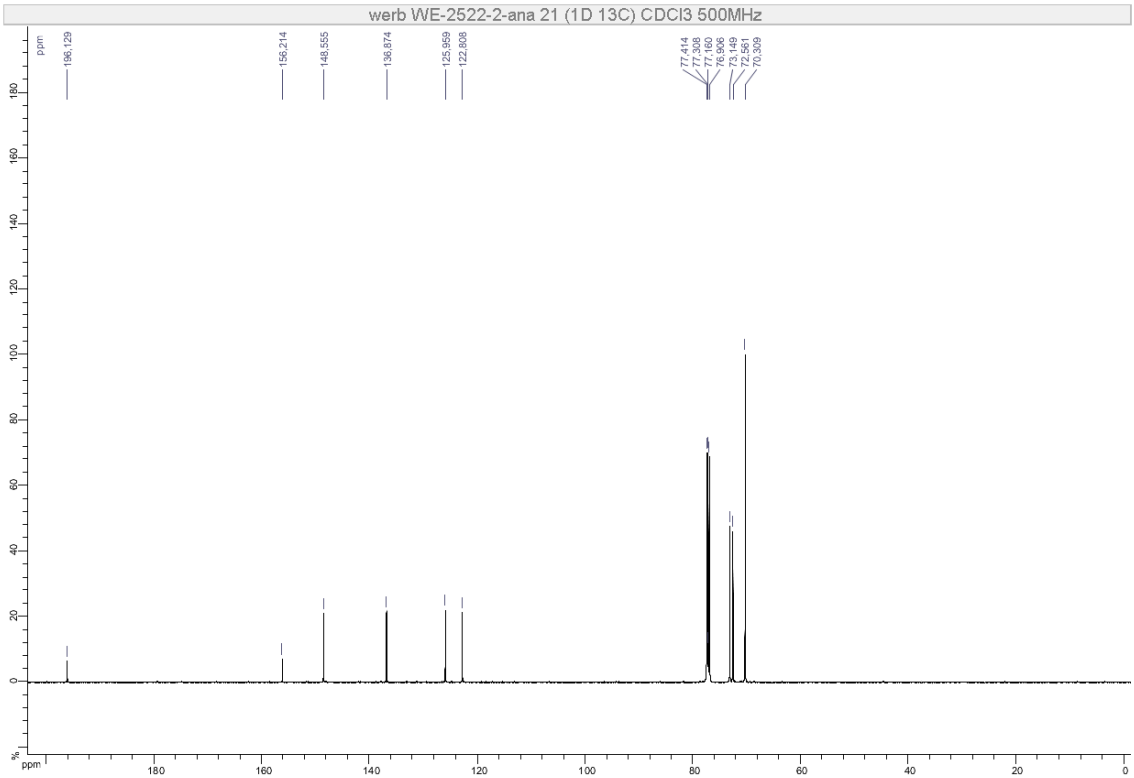


(2-Pyridoyl)ferrocene (1-2Py)

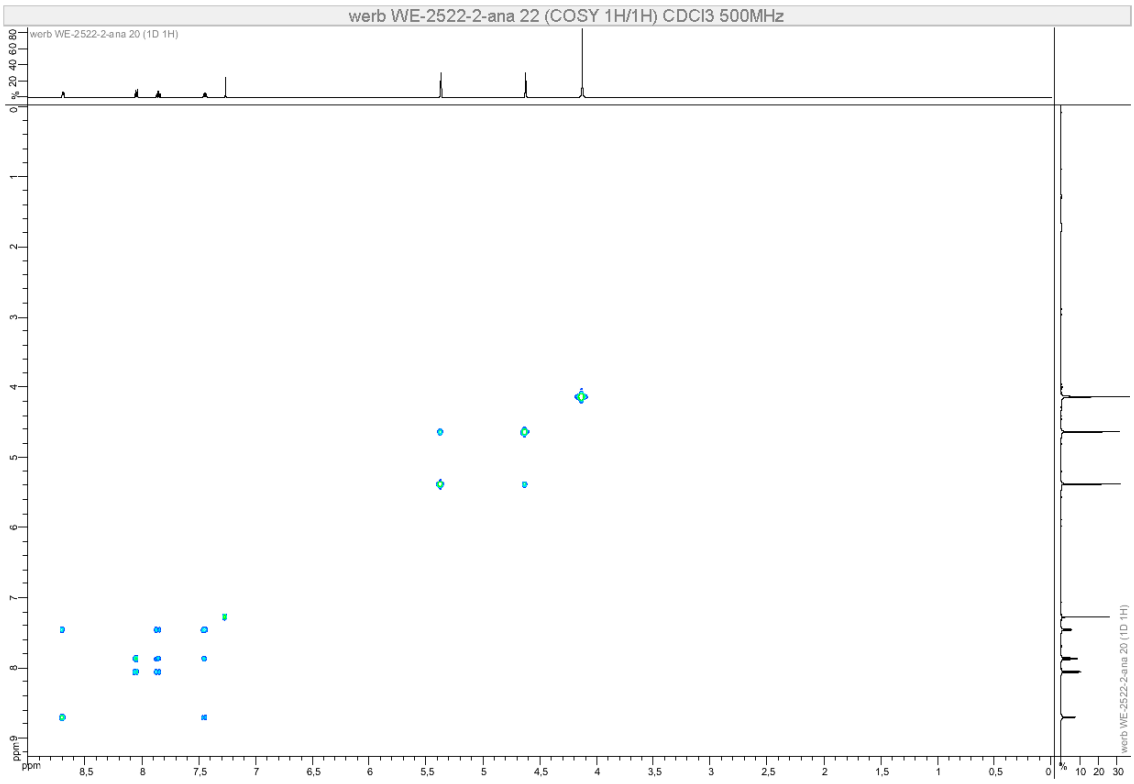
^{1}H NMR (500 MHz, $CDCl_3$)



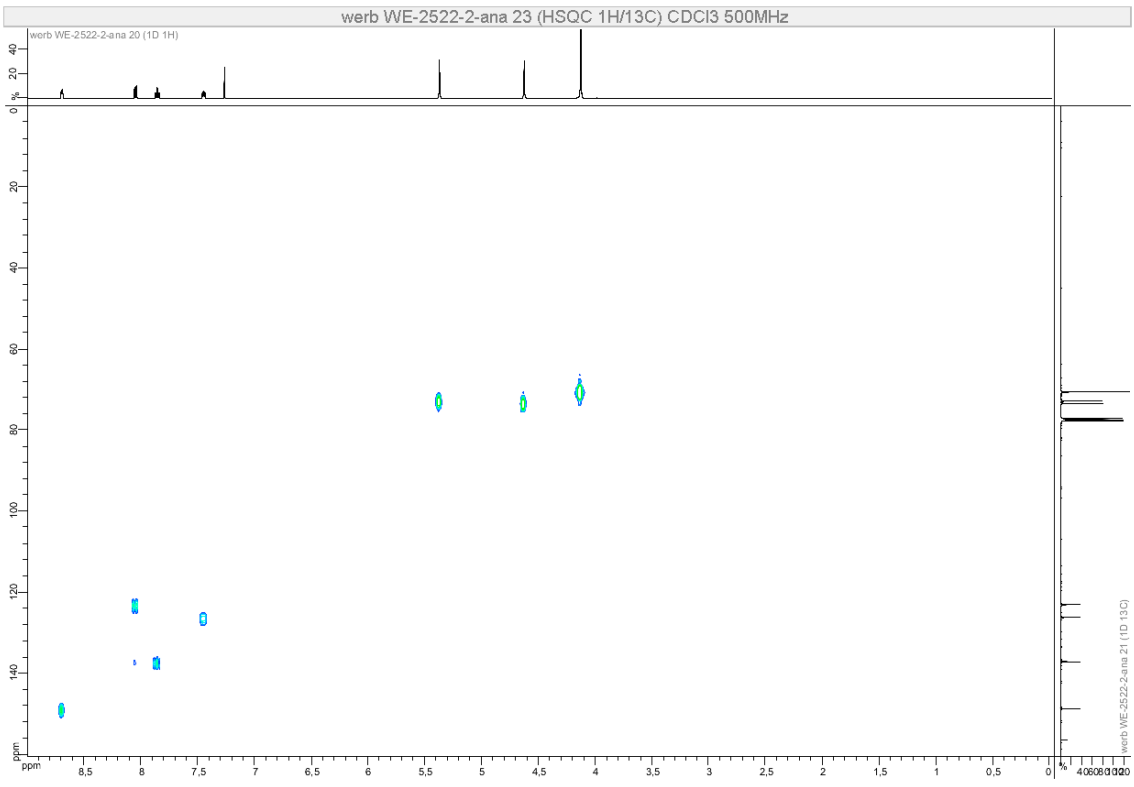
^{13}C NMR (126 MHz, $CDCl_3$)



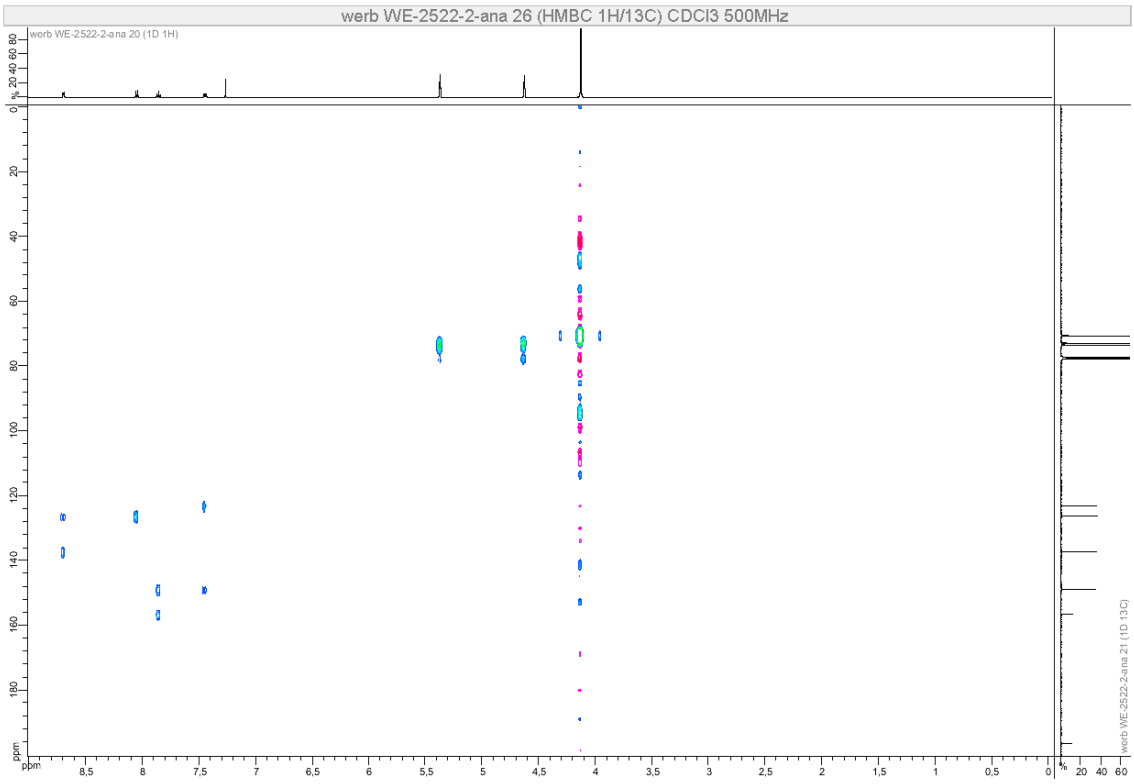
COSY (500 MHz, $CDCl_3$)



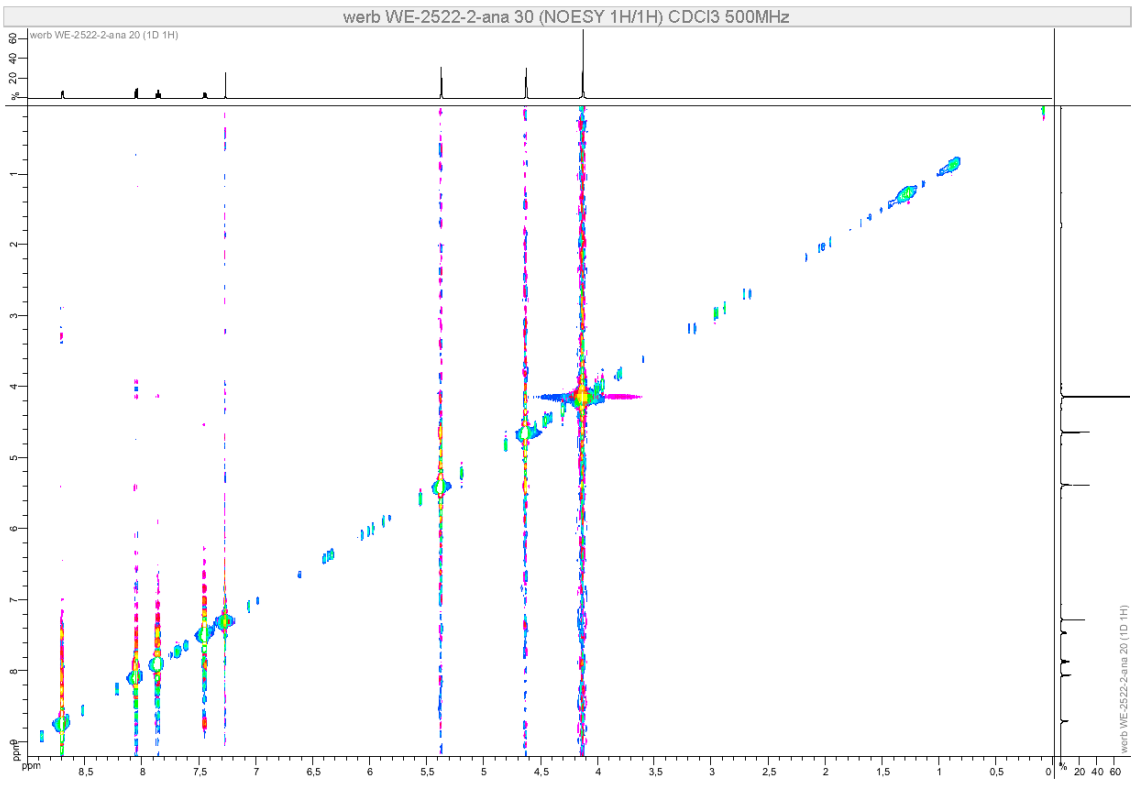
HSQC (500 MHz, $CDCl_3$)



HMBC (400 MHz, $CDCl_3$)

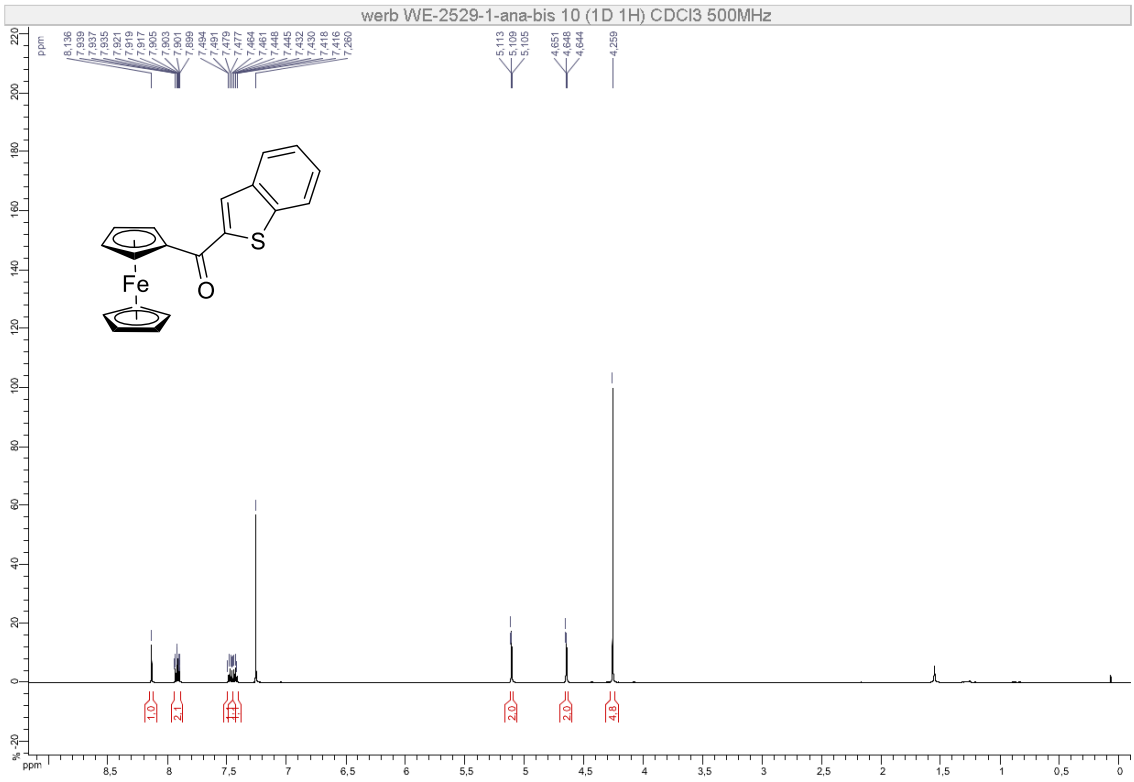


NOESY (400 MHz, $CDCl_3$)

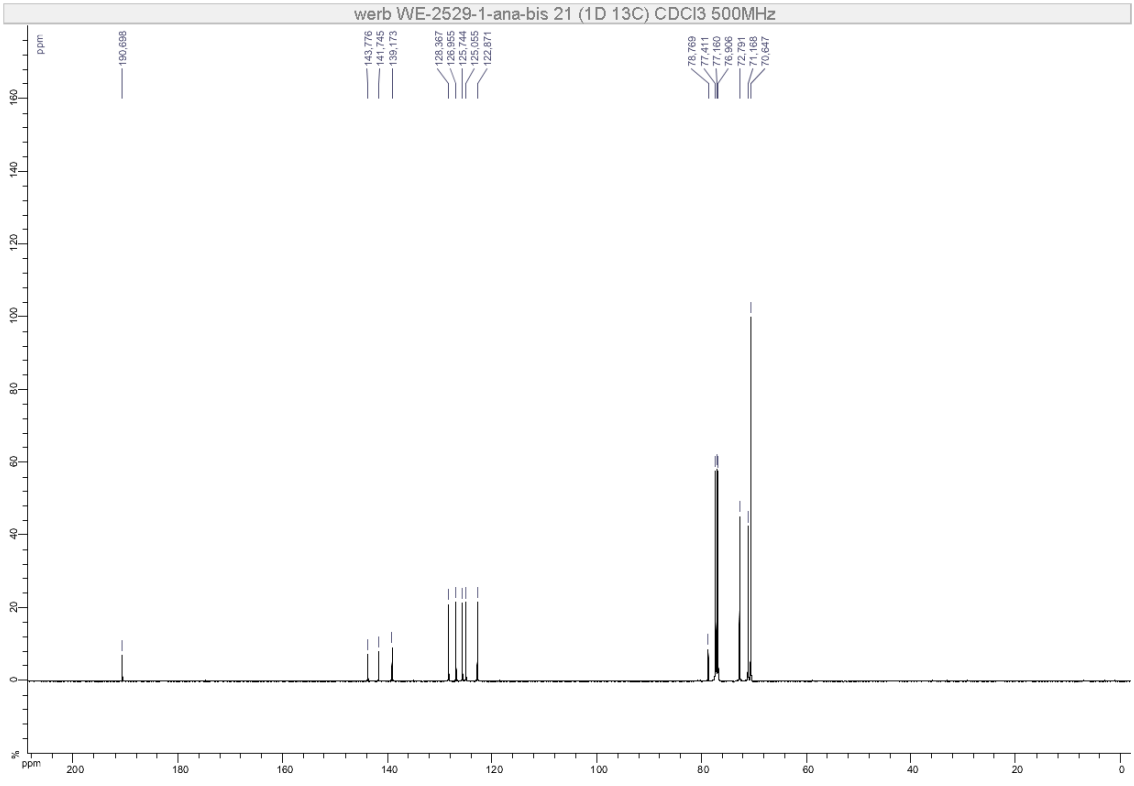


(2-Benzothienoyl)ferrocene (1-2BTh)

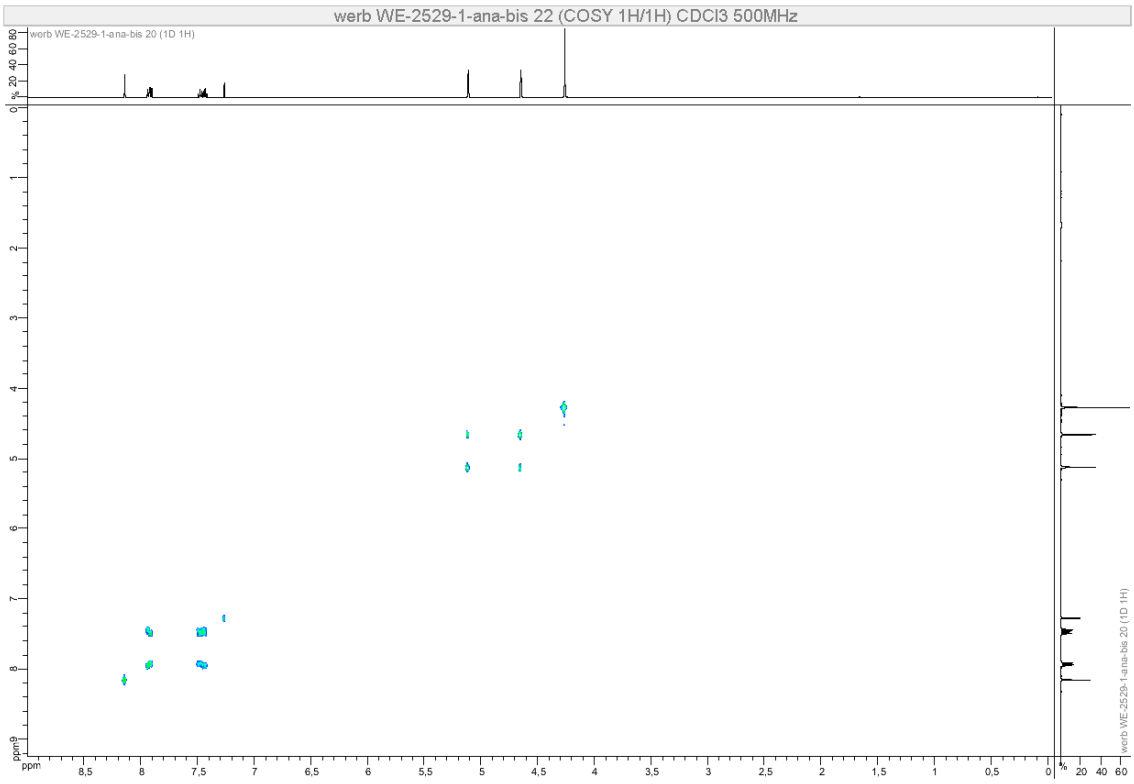
^{1}H NMR (500 MHz, $CDCl_3$)



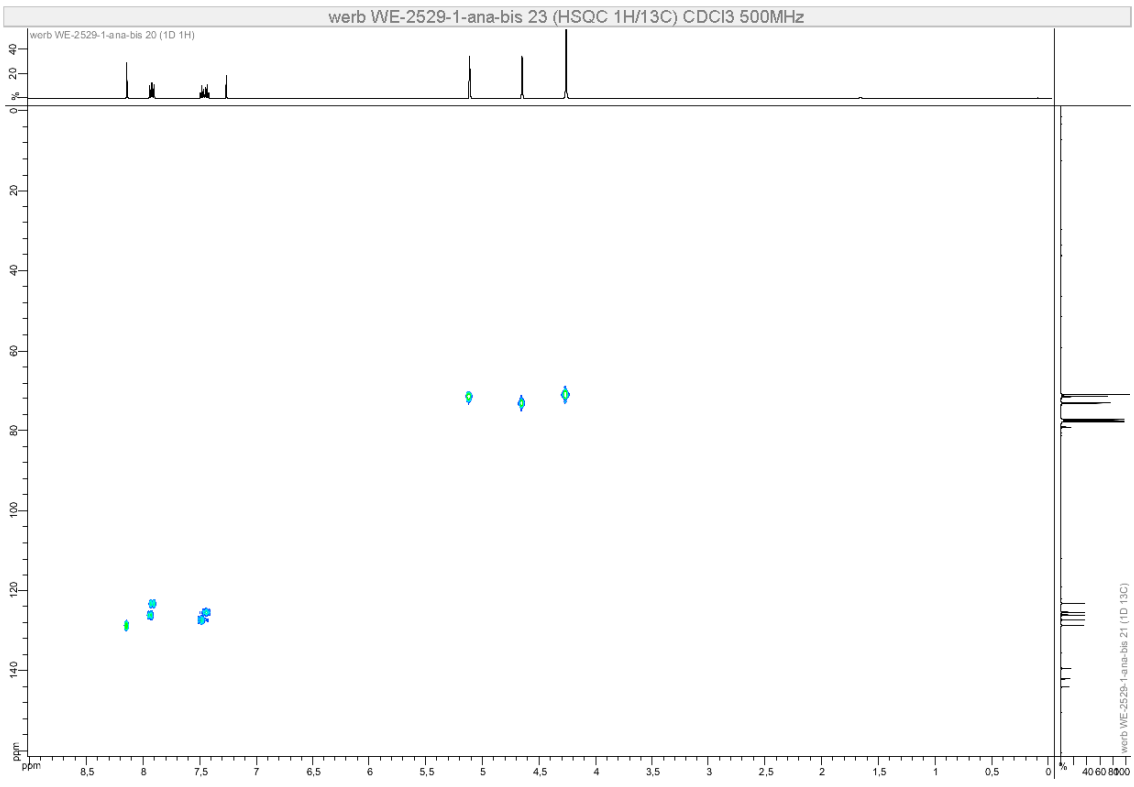
^{13}C NMR (126 MHz, $CDCl_3$)



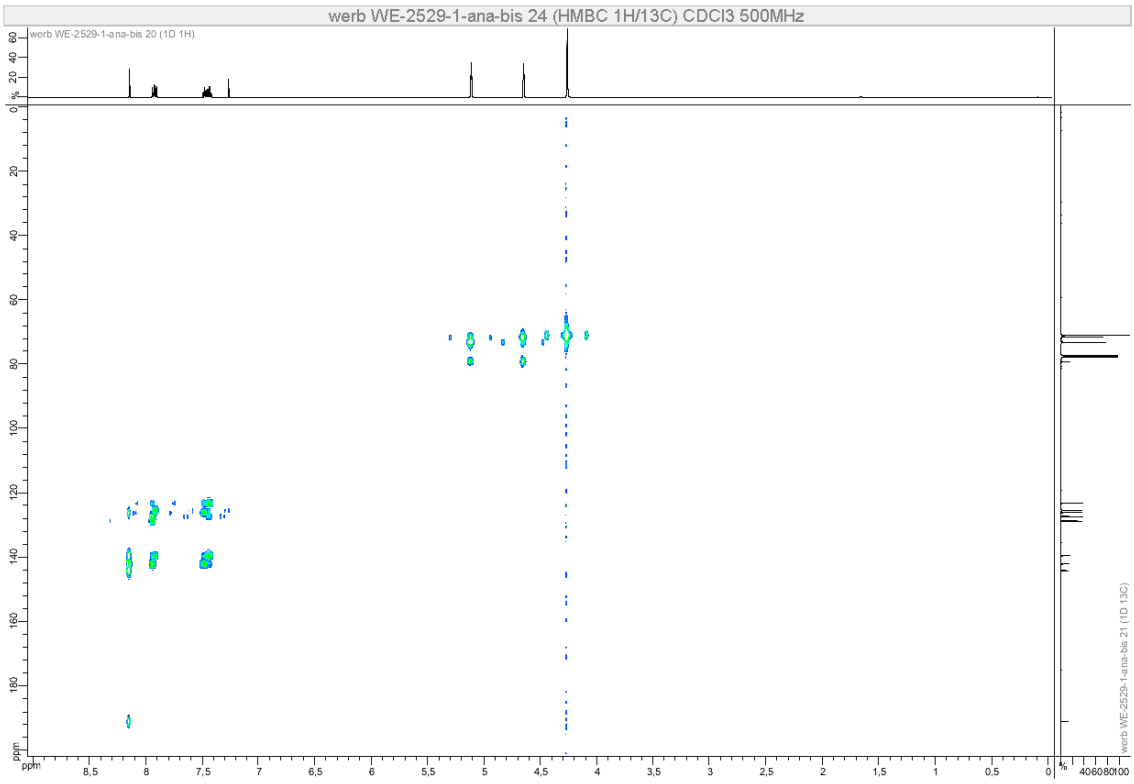
COSY (500 MHz, $CDCl_3$)



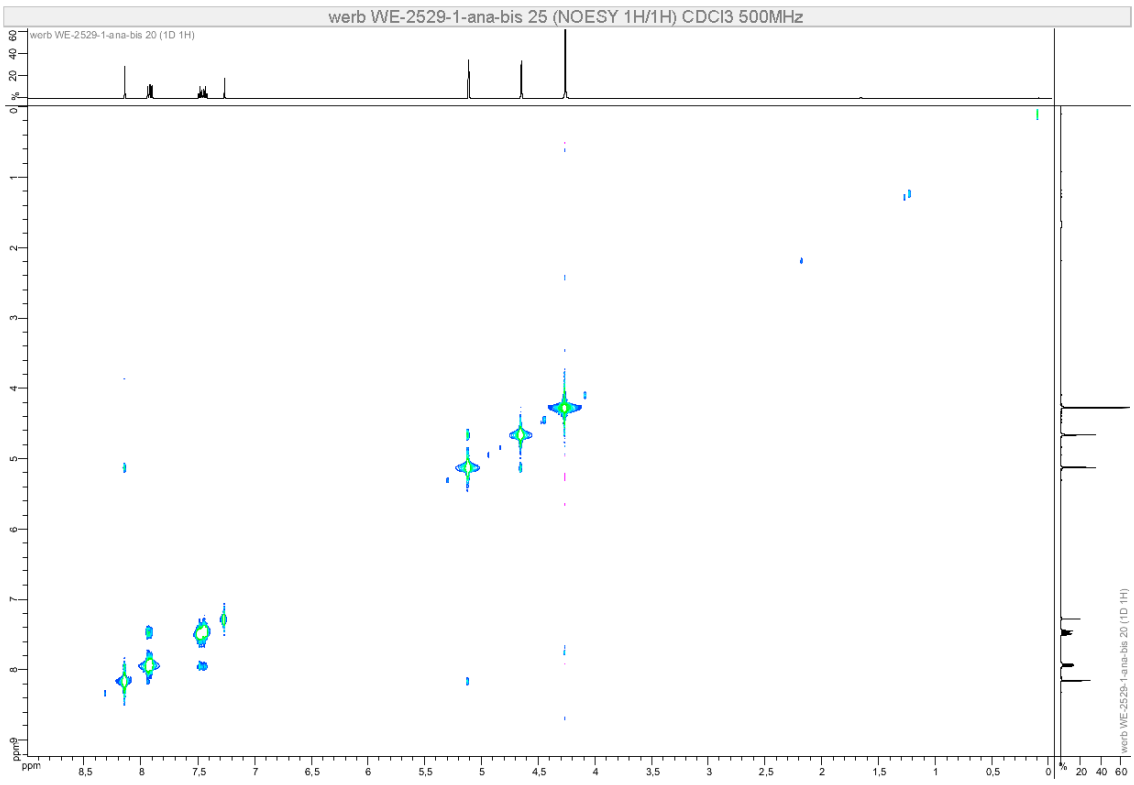
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

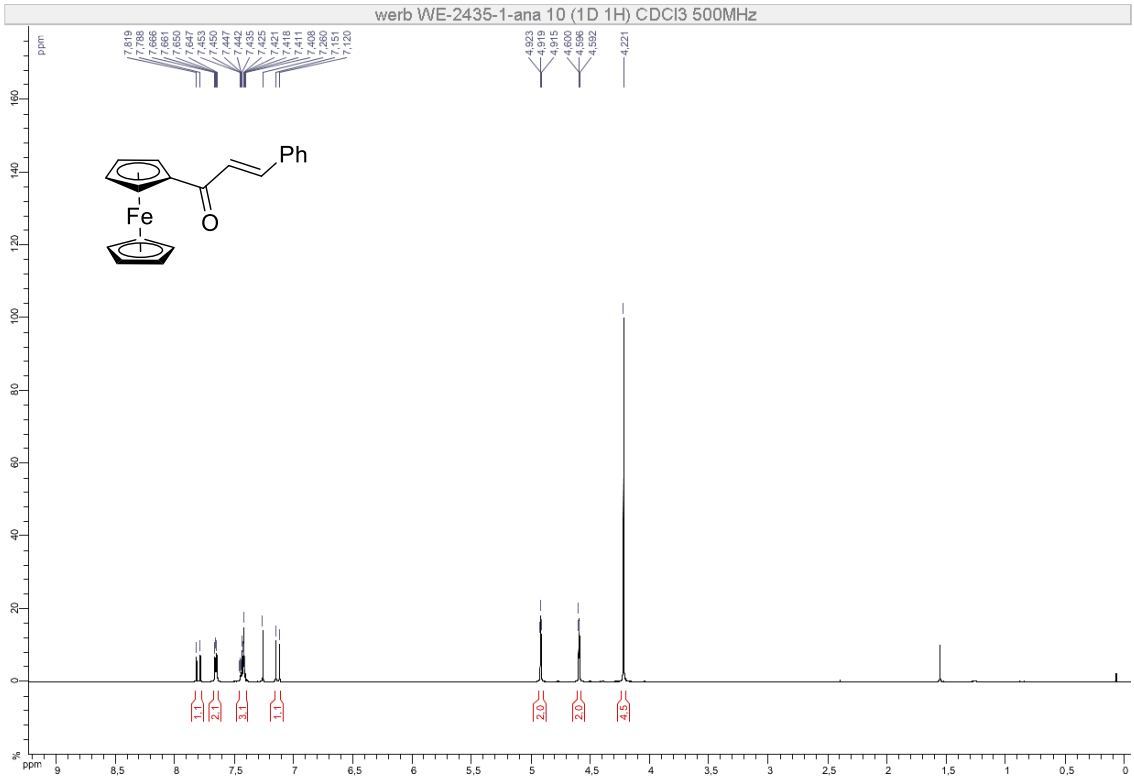


NOESY (500 MHz, $CDCl_3$)

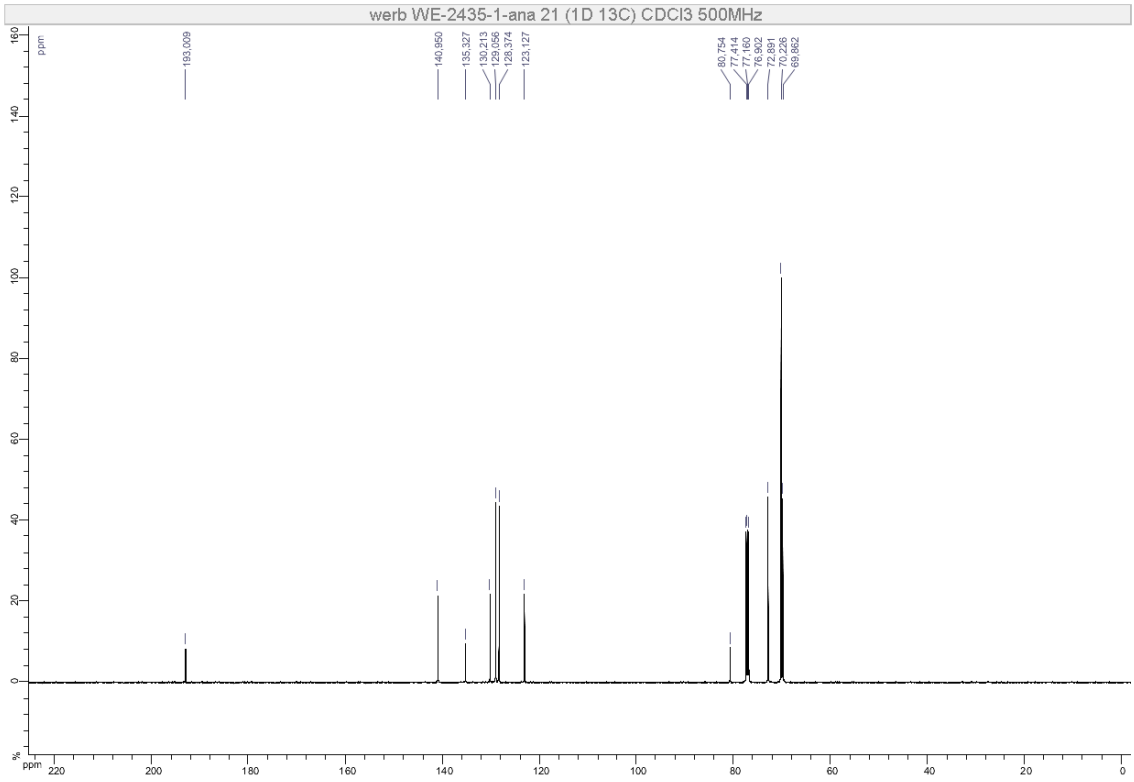


(*E*)-(Cinnamoyl)ferrocene (1-CH=CHPh)

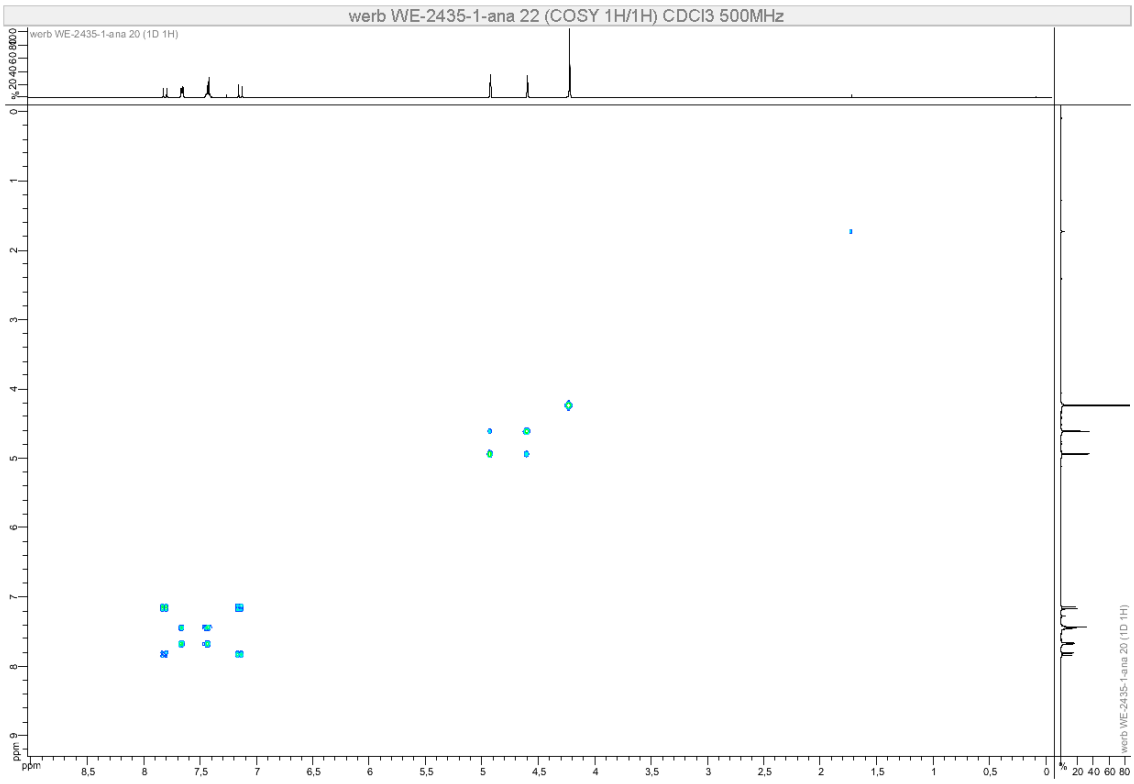
^{1}H NMR (500 MHz, $CDCl_3$)



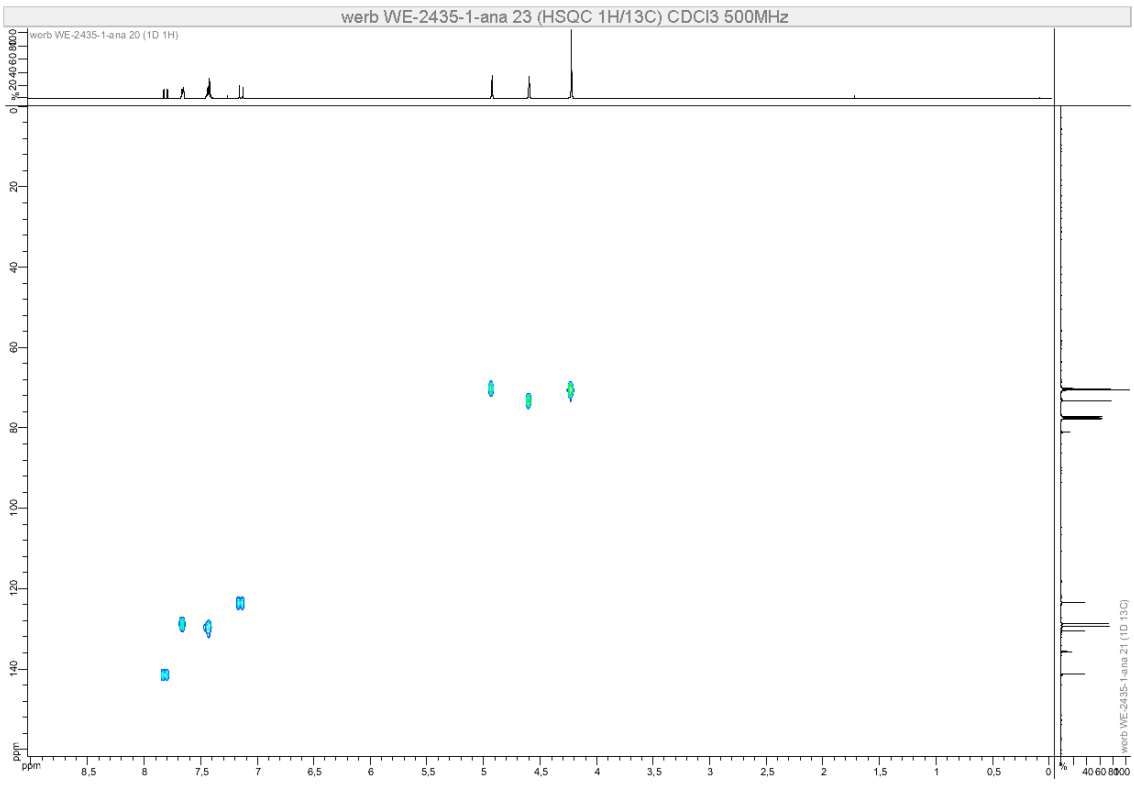
^{13}C NMR (126 MHz, $CDCl_3$)



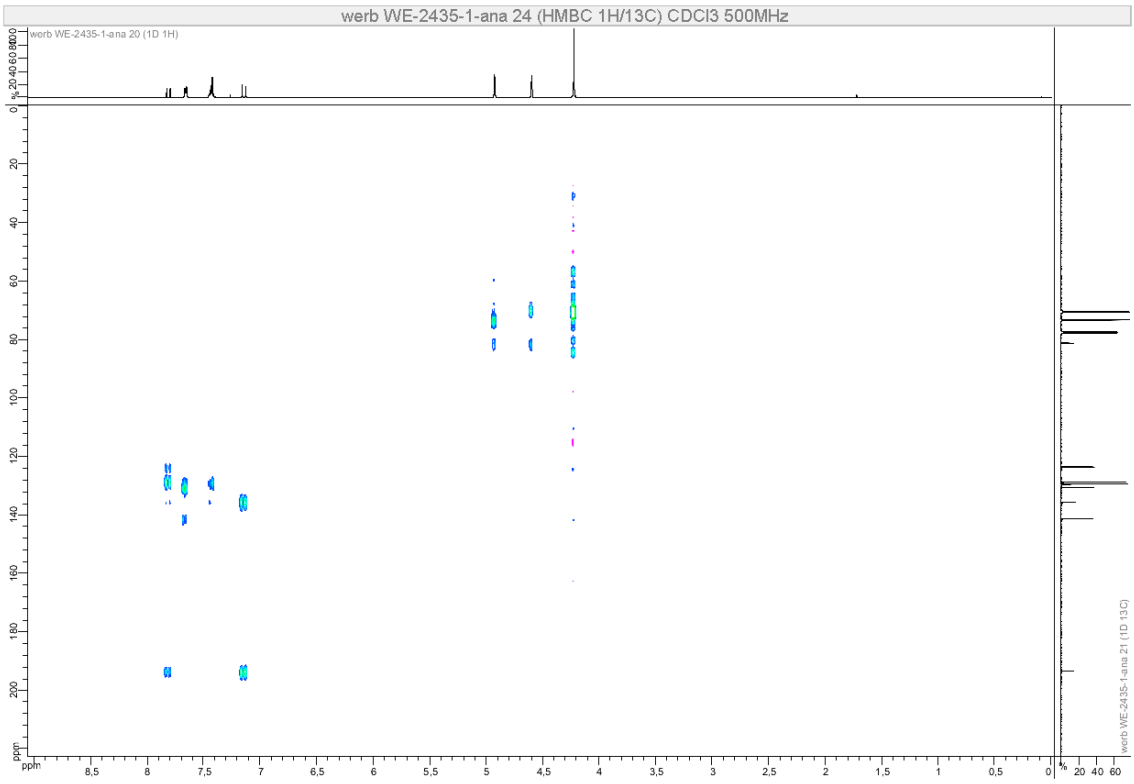
COSY (500 MHz, $CDCl_3$)



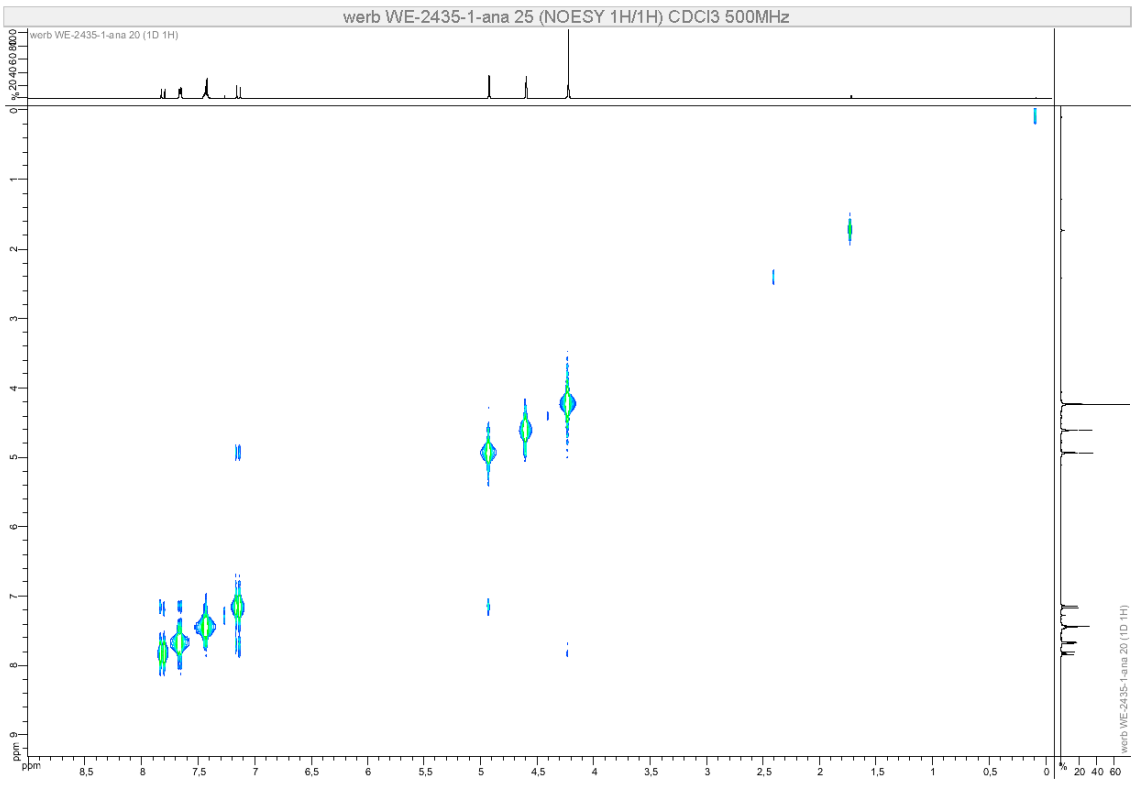
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

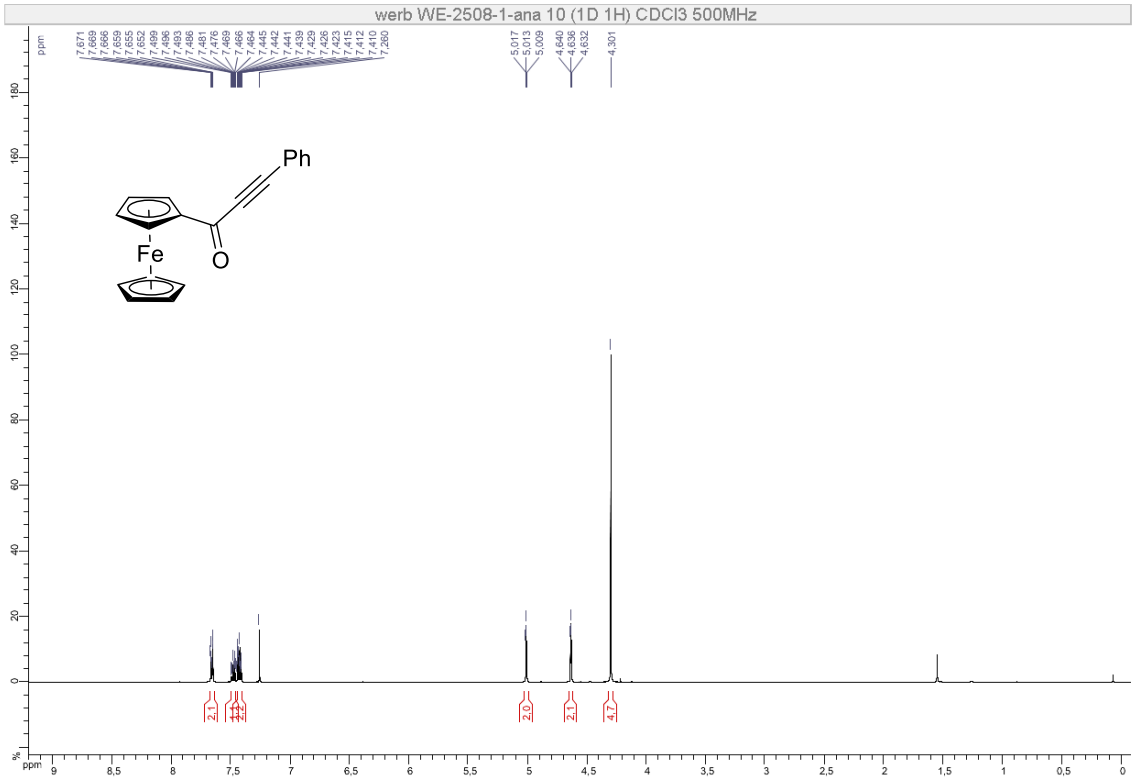


NOESY (500 MHz, $CDCl_3$)

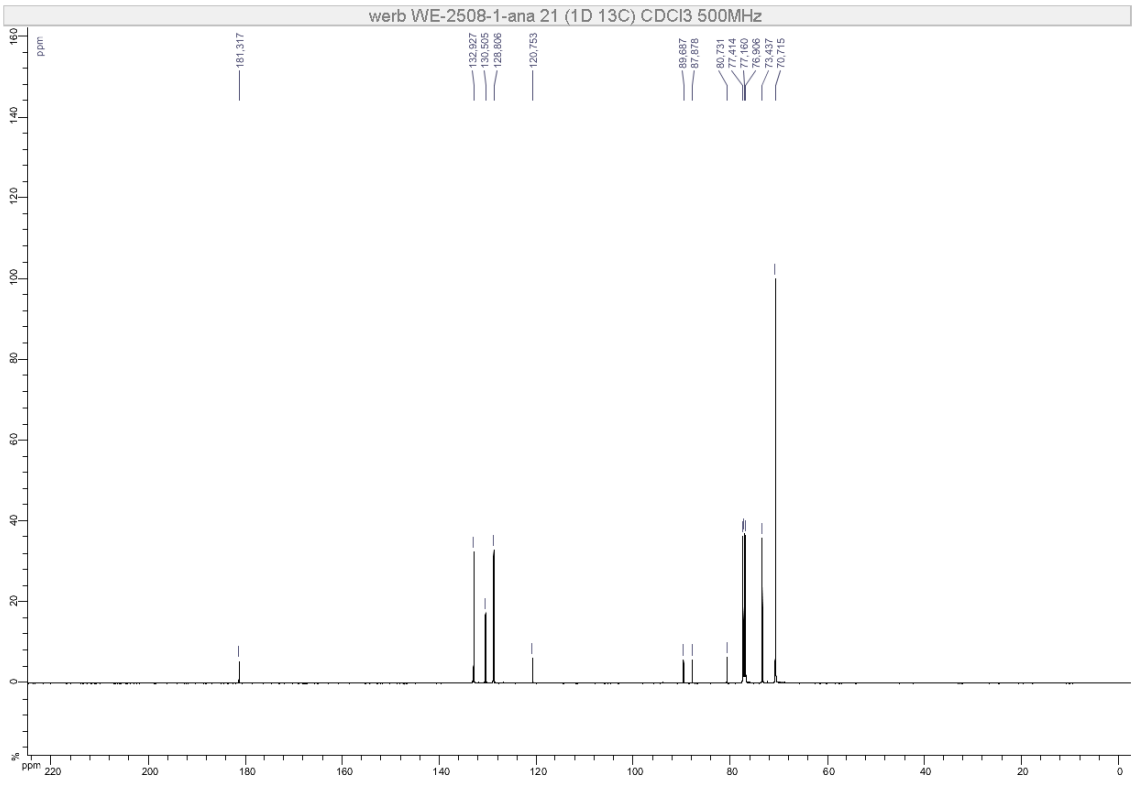


(Phenylpropioloyl)ferrocene (1-C≡CPh)

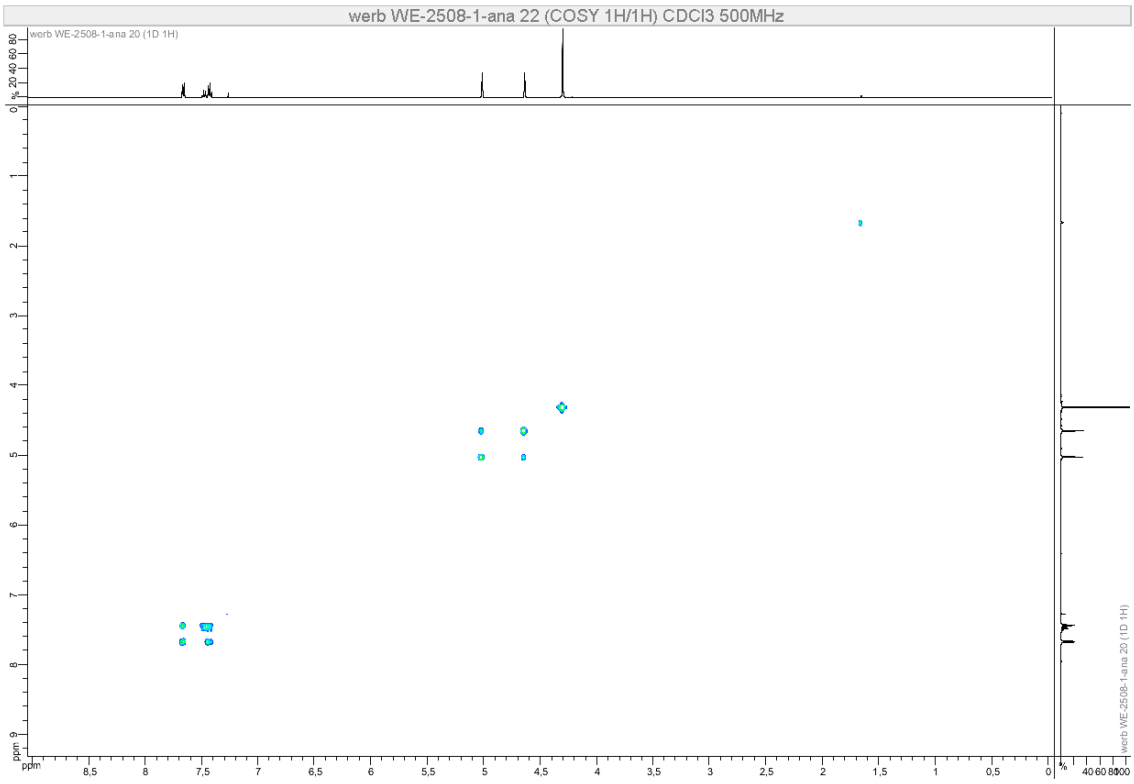
^{1}H NMR (500 MHz, $CDCl_3$)



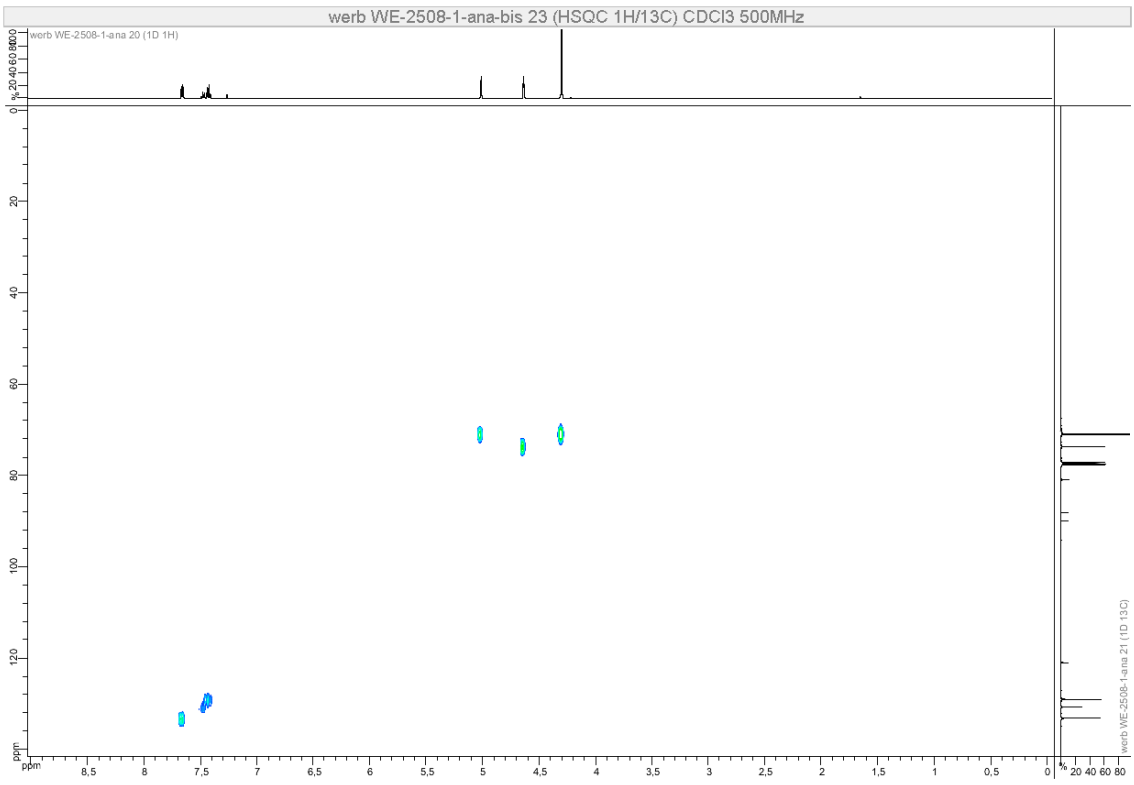
^{13}C NMR (126 MHz, $CDCl_3$)



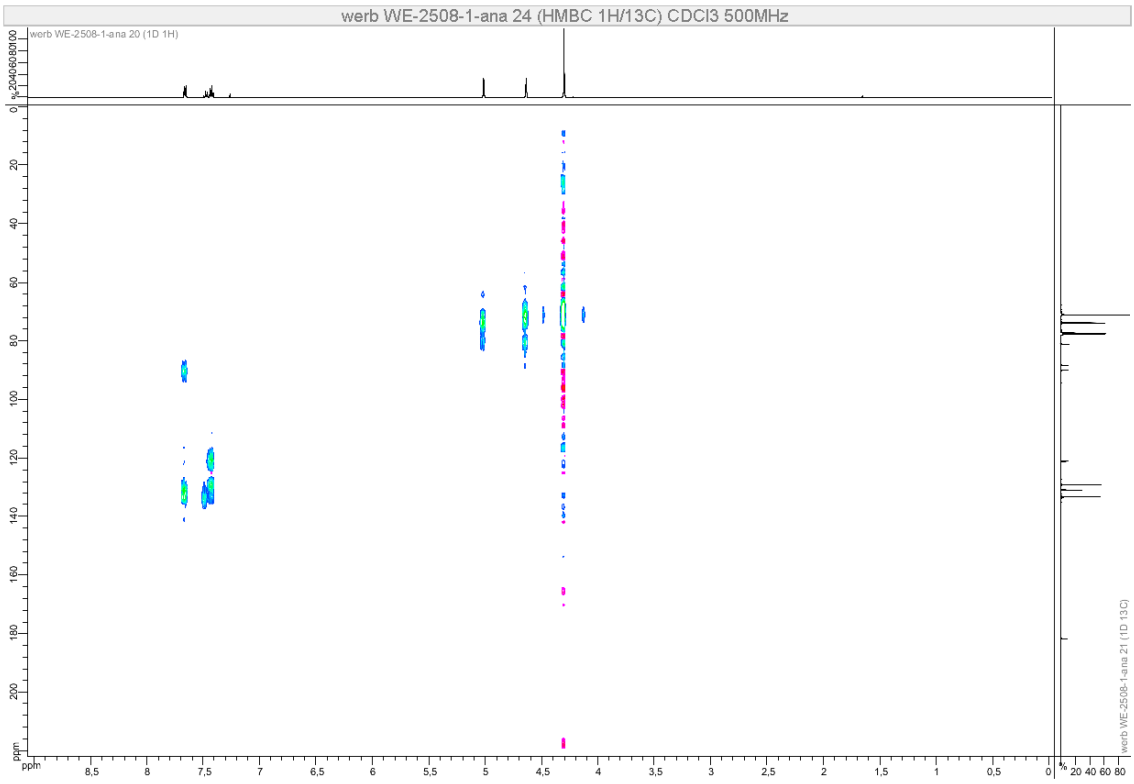
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

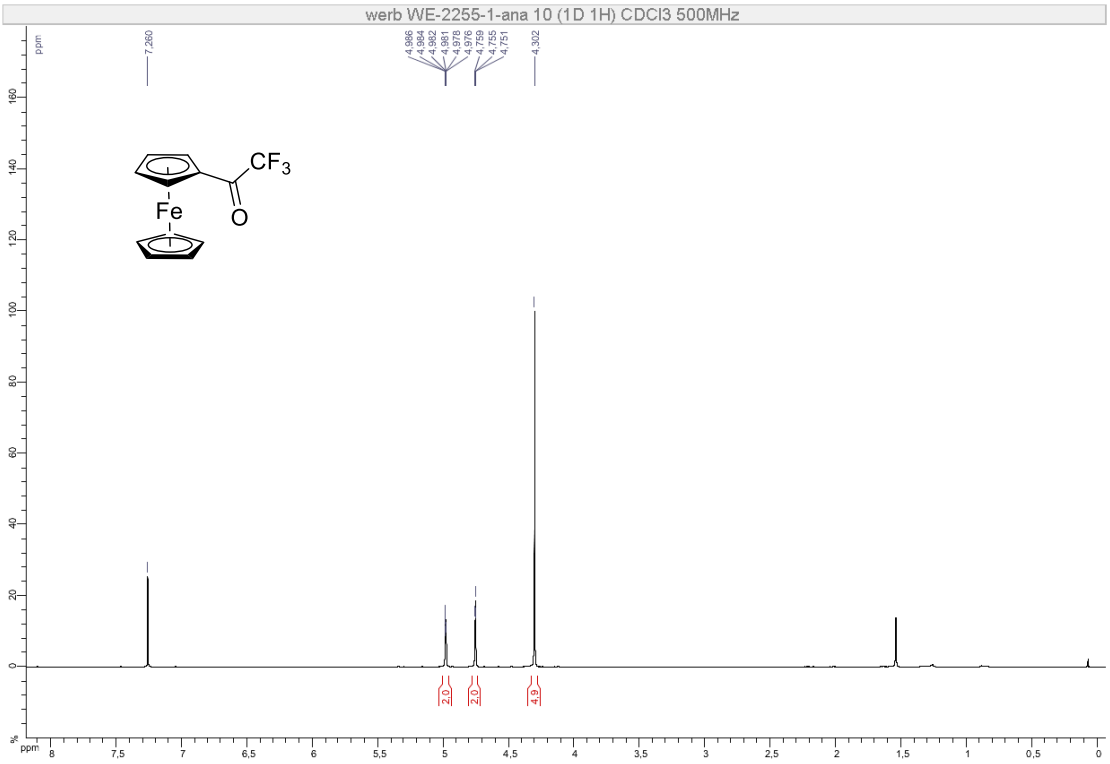


HMBC (500 MHz, $CDCl_3$)

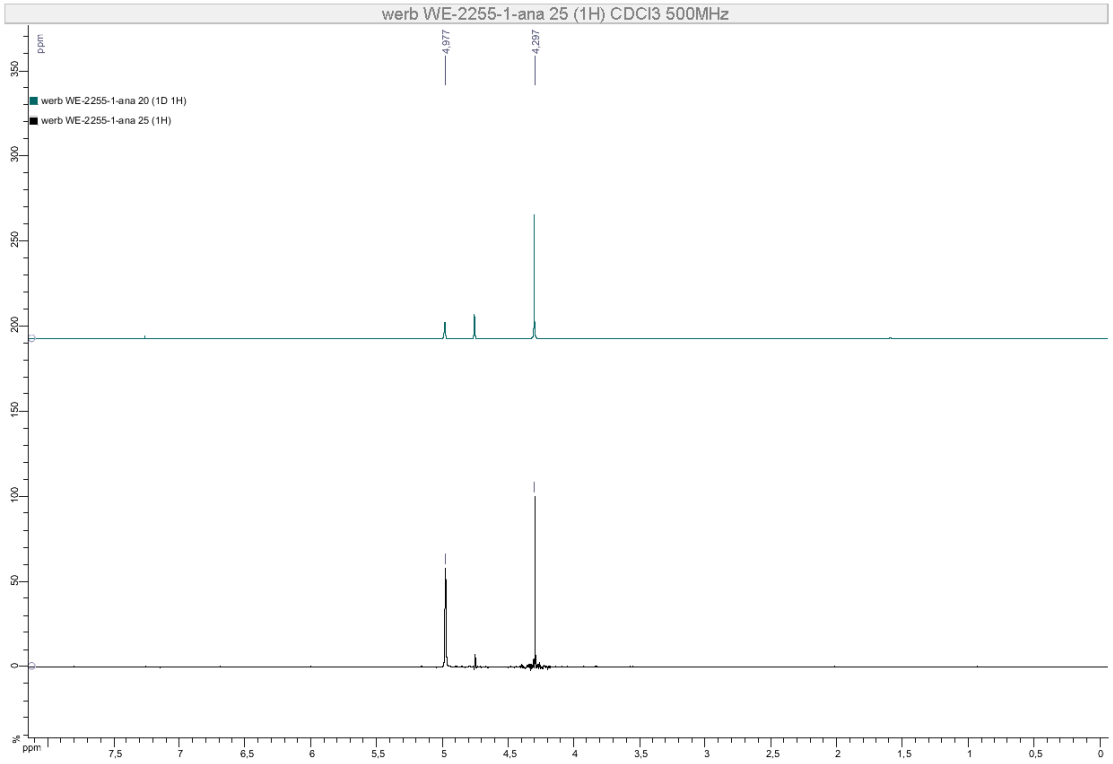


[(Trifluoromethyl)carbonyl]ferrocene (1-CF_3)

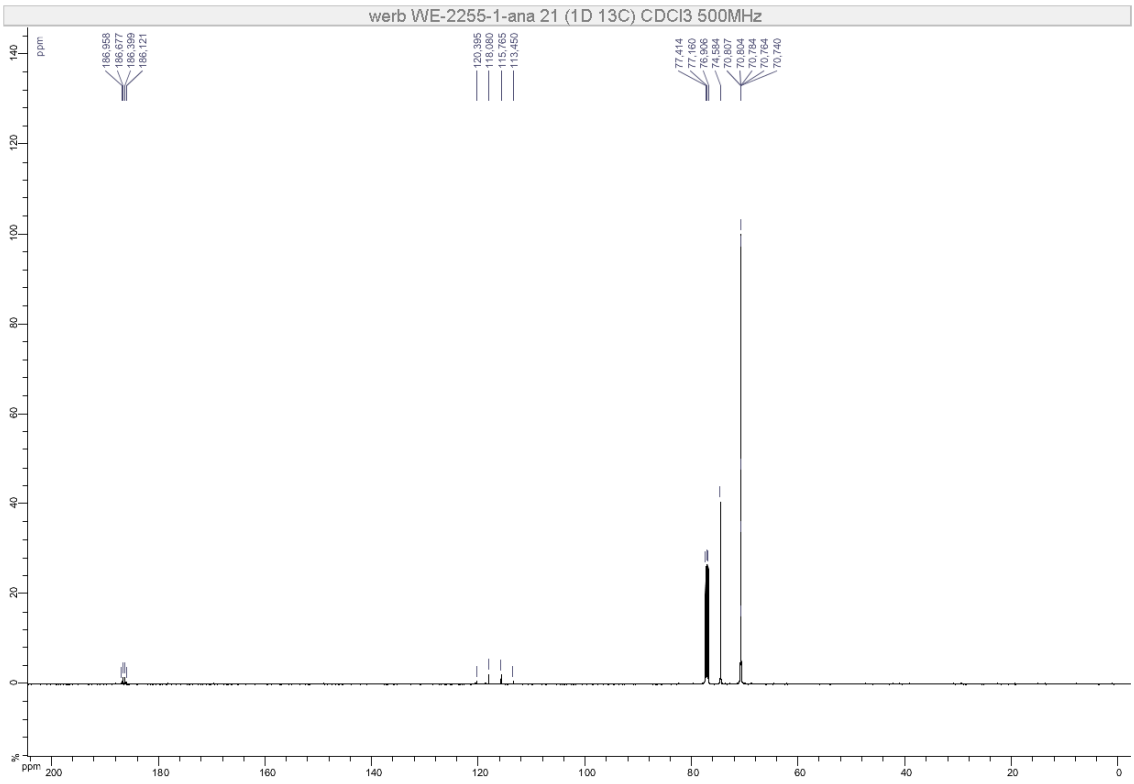
^{1}H NMR (500 MHz, $CDCl_3$)



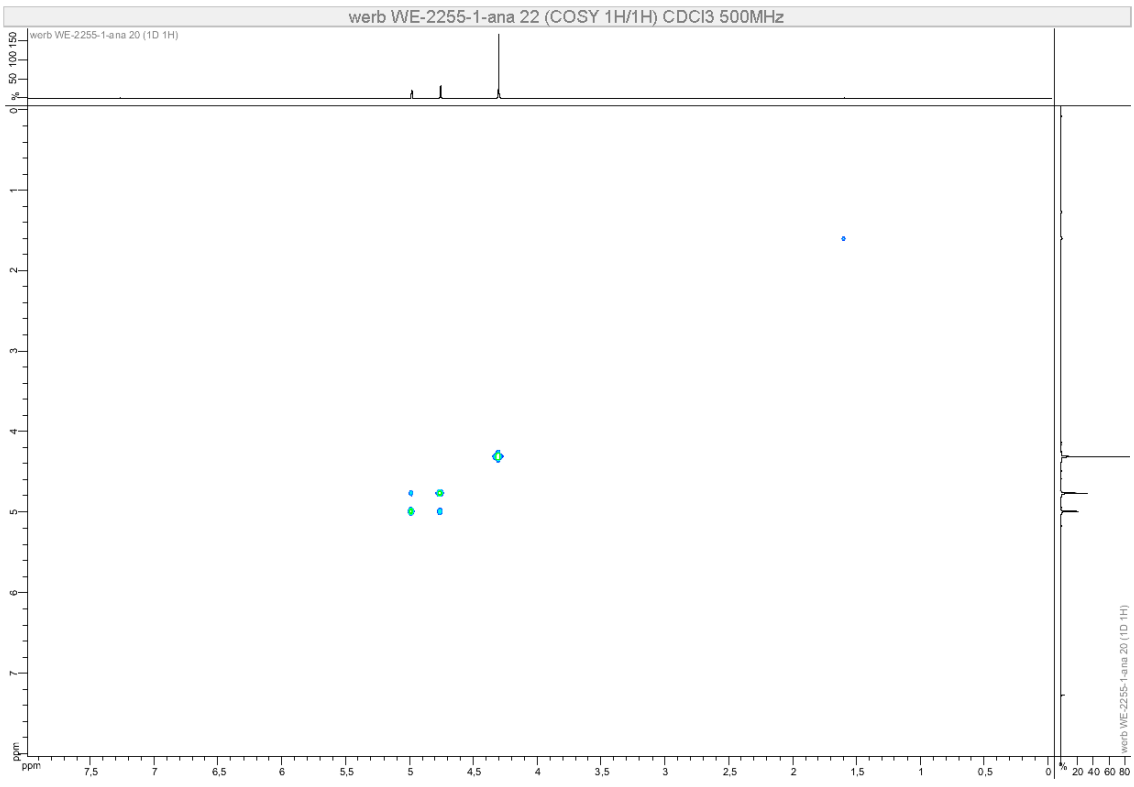
HOESY (500 MHz, $CDCl_3$) Irradiation at –72.1 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



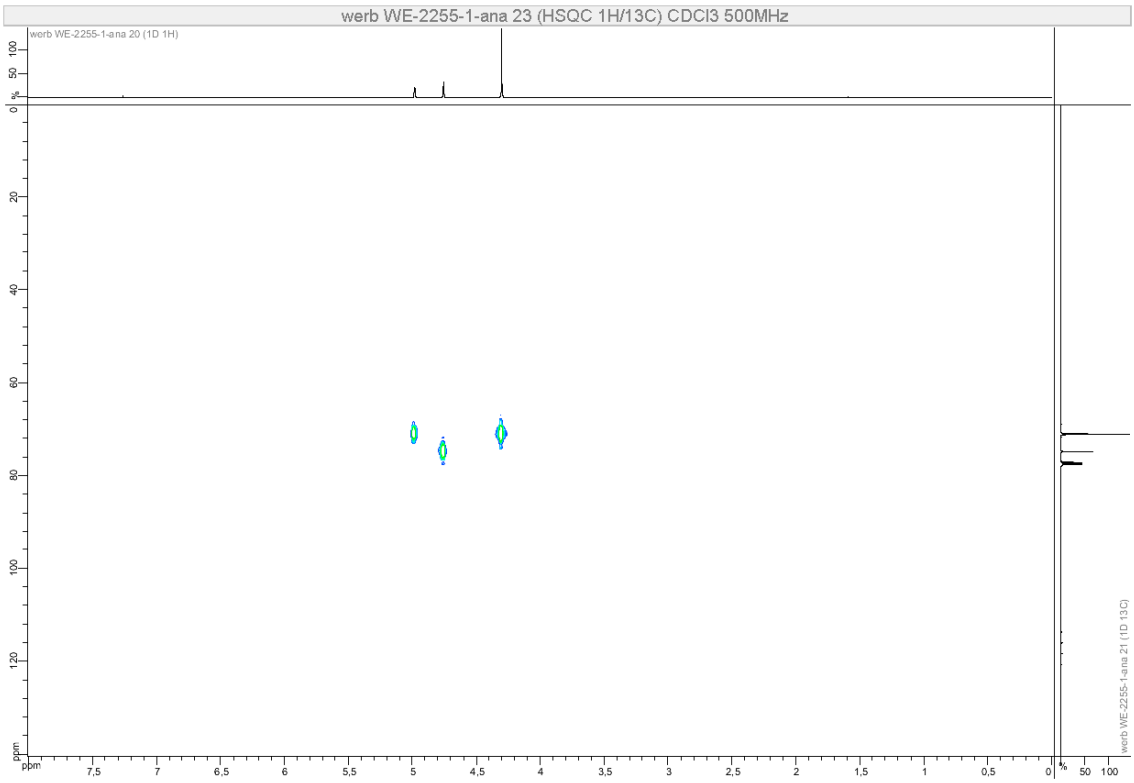
^{13}C NMR (126 MHz, $CDCl_3$)



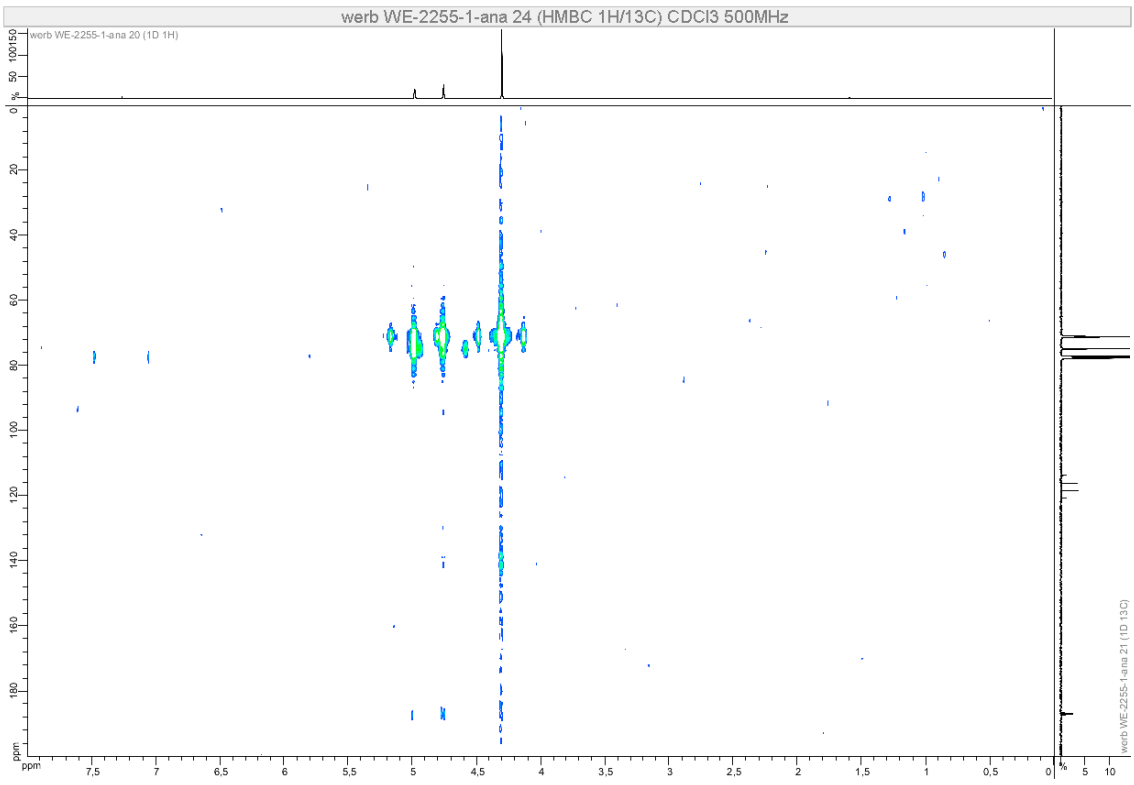
COSY (500 MHz, $CDCl_3$)



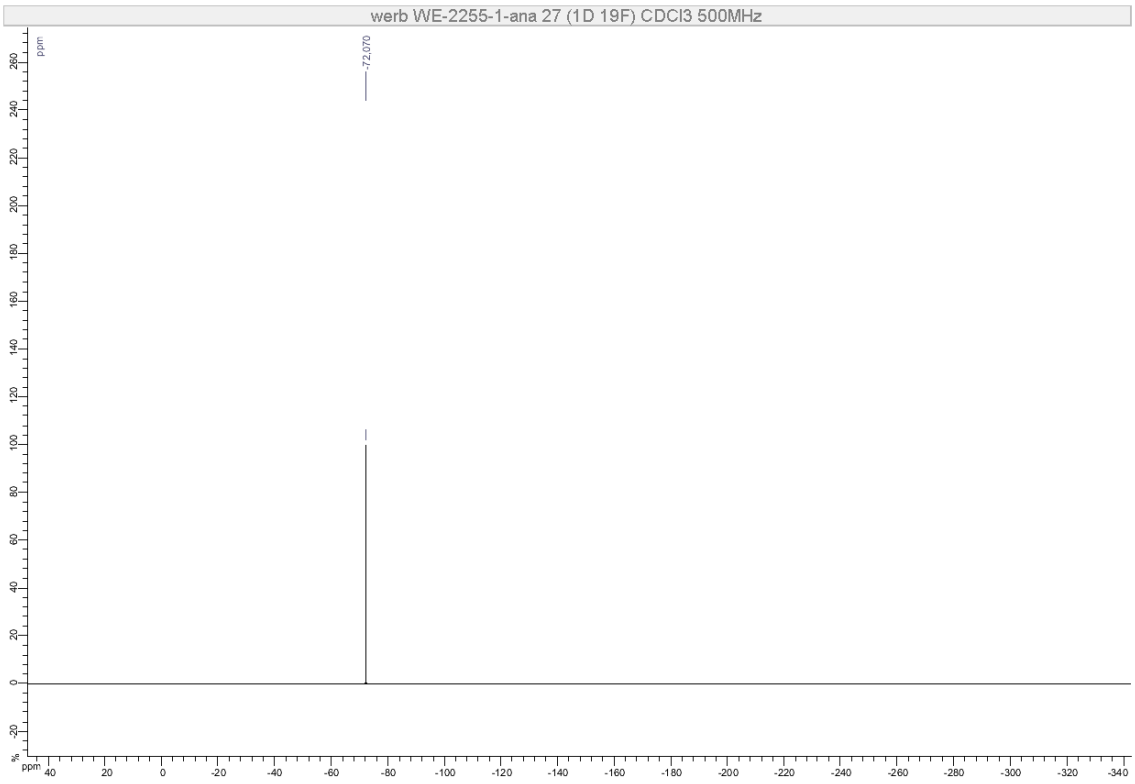
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

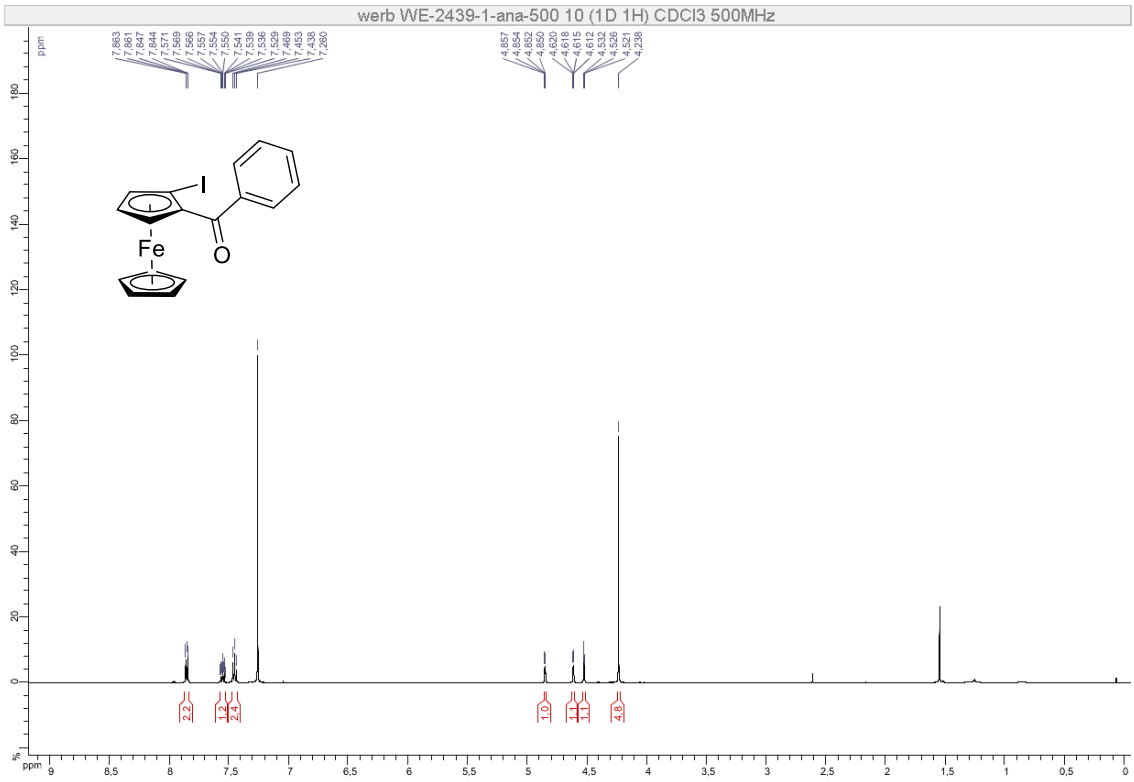


^{19}F NMR (471 MHz, $CDCl_3$)

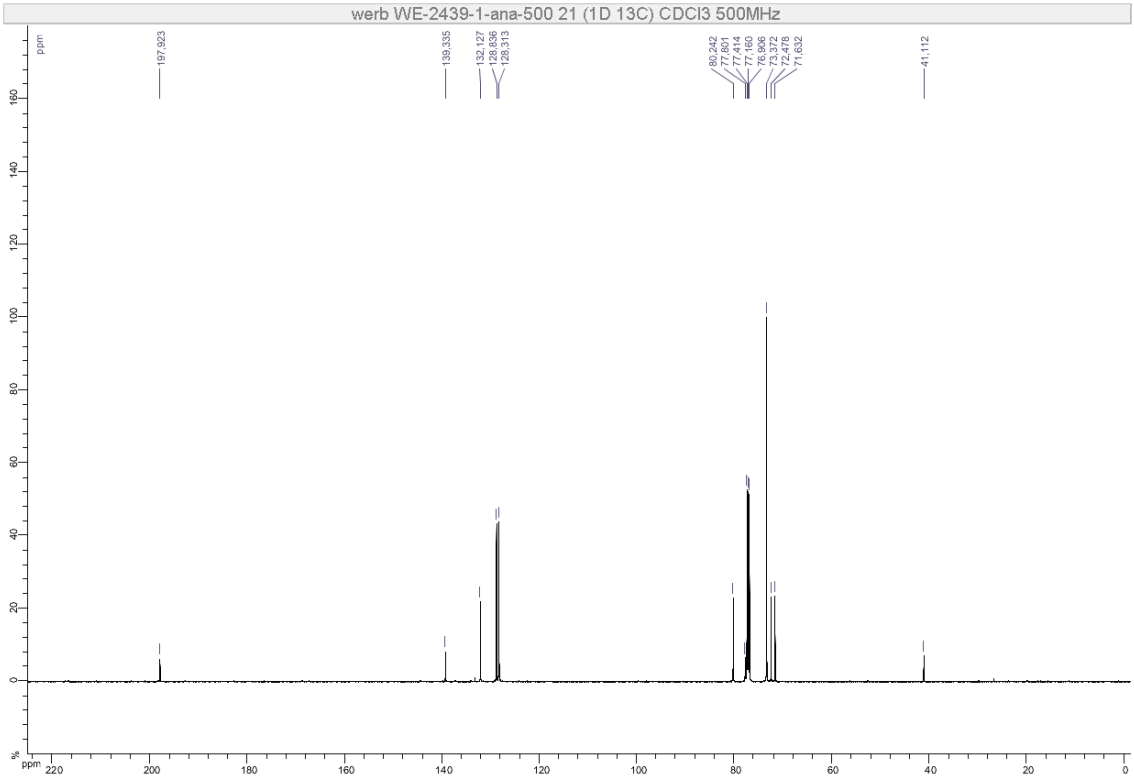


1-Benzoyl-2-iodoferrocene (2-Ph)

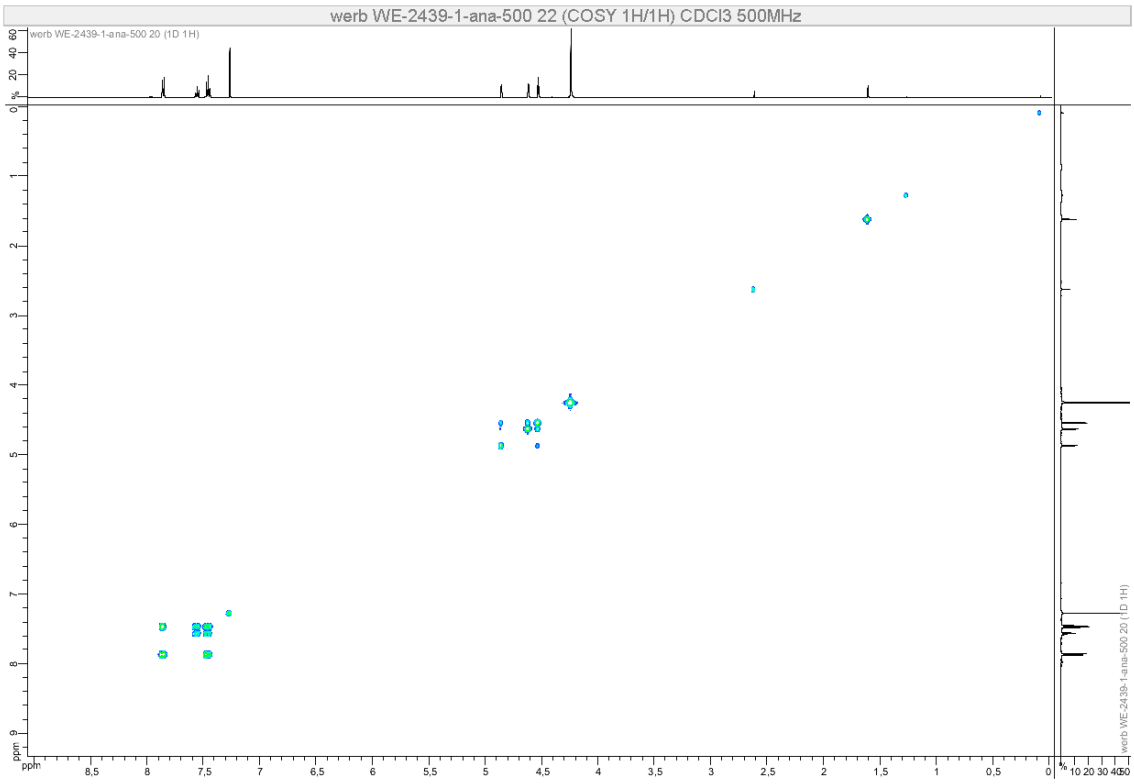
^{1}H NMR (500 MHz, $CDCl_3$)



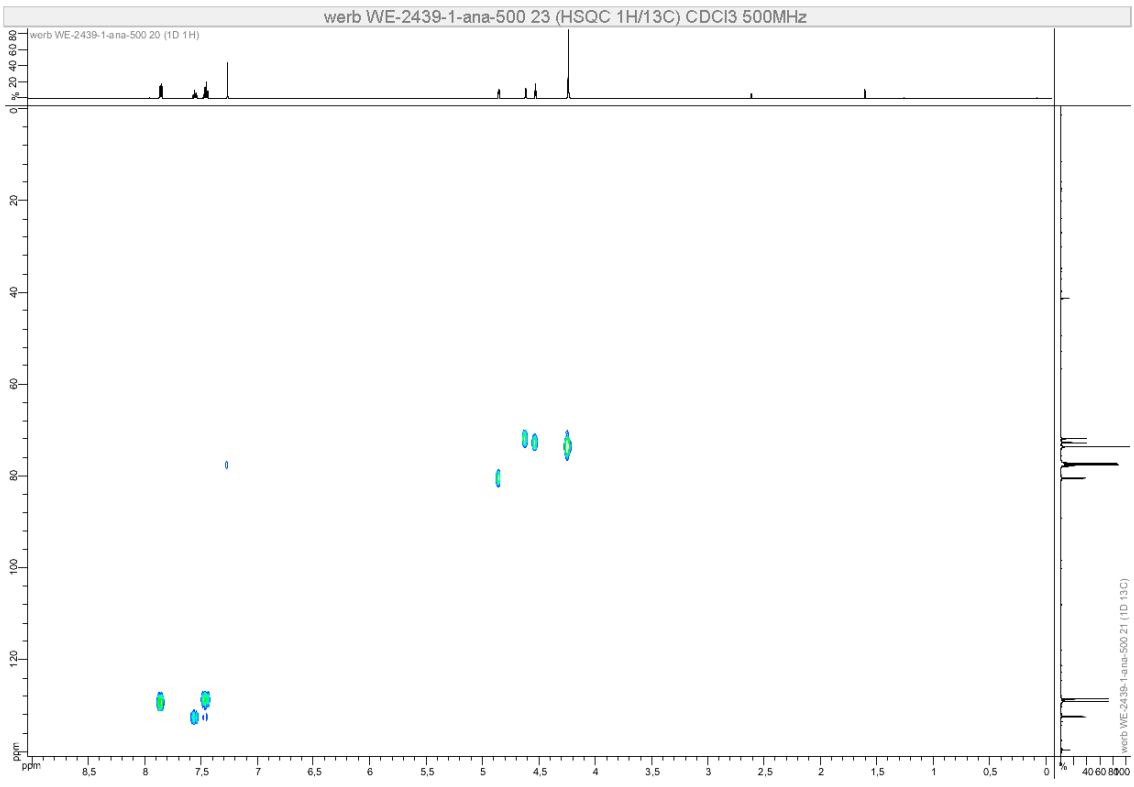
^{13}C NMR (126 MHz, $CDCl_3$)



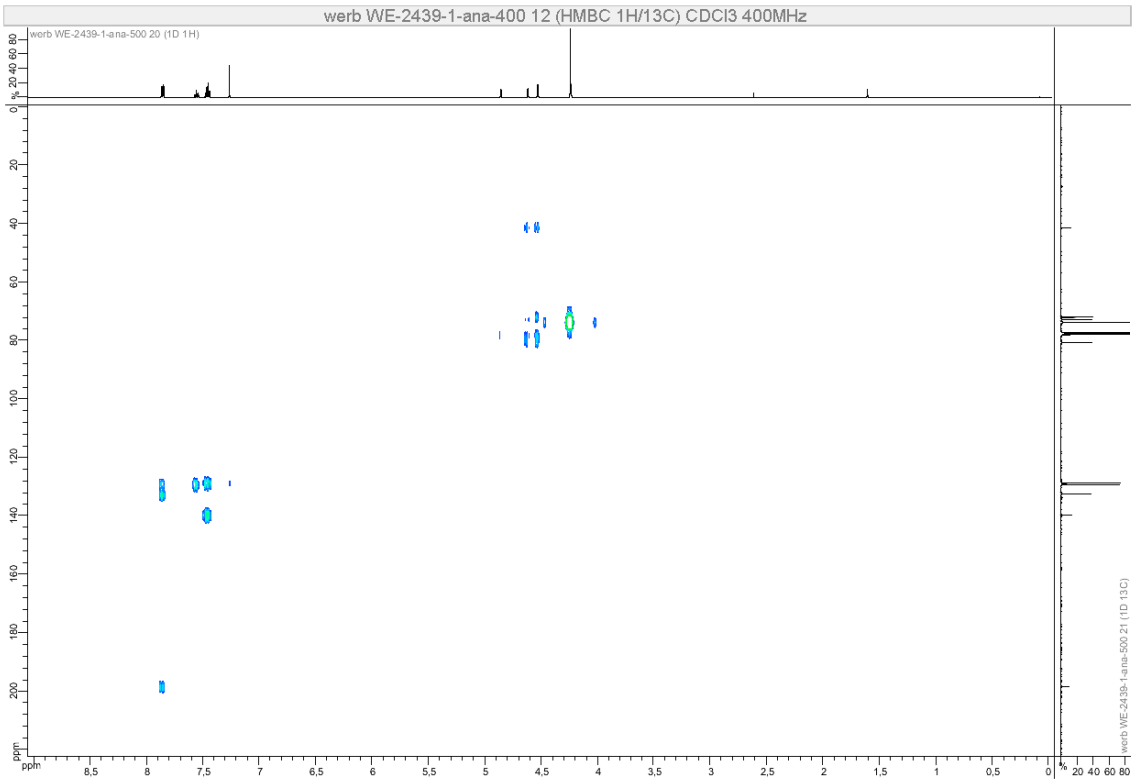
COSY (500 MHz, $CDCl_3$)



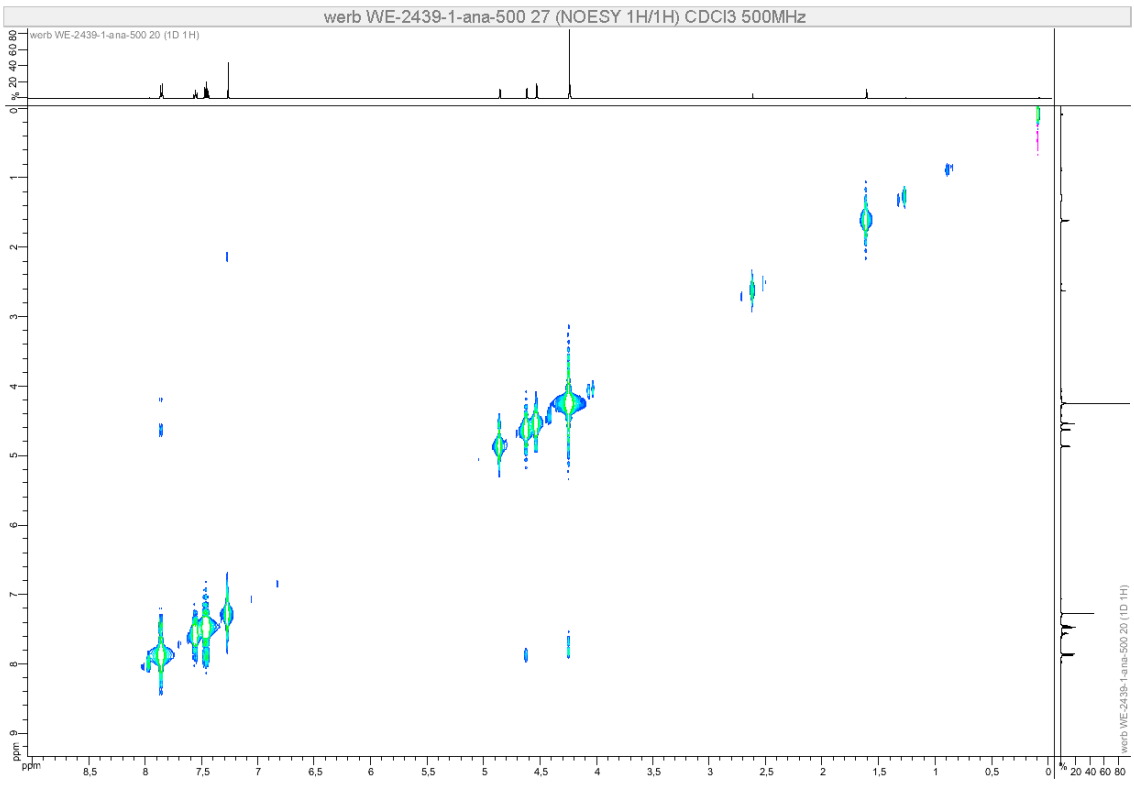
HSQC (500 MHz, $CDCl_3$)



HMBC (400 MHz, $CDCl_3$)

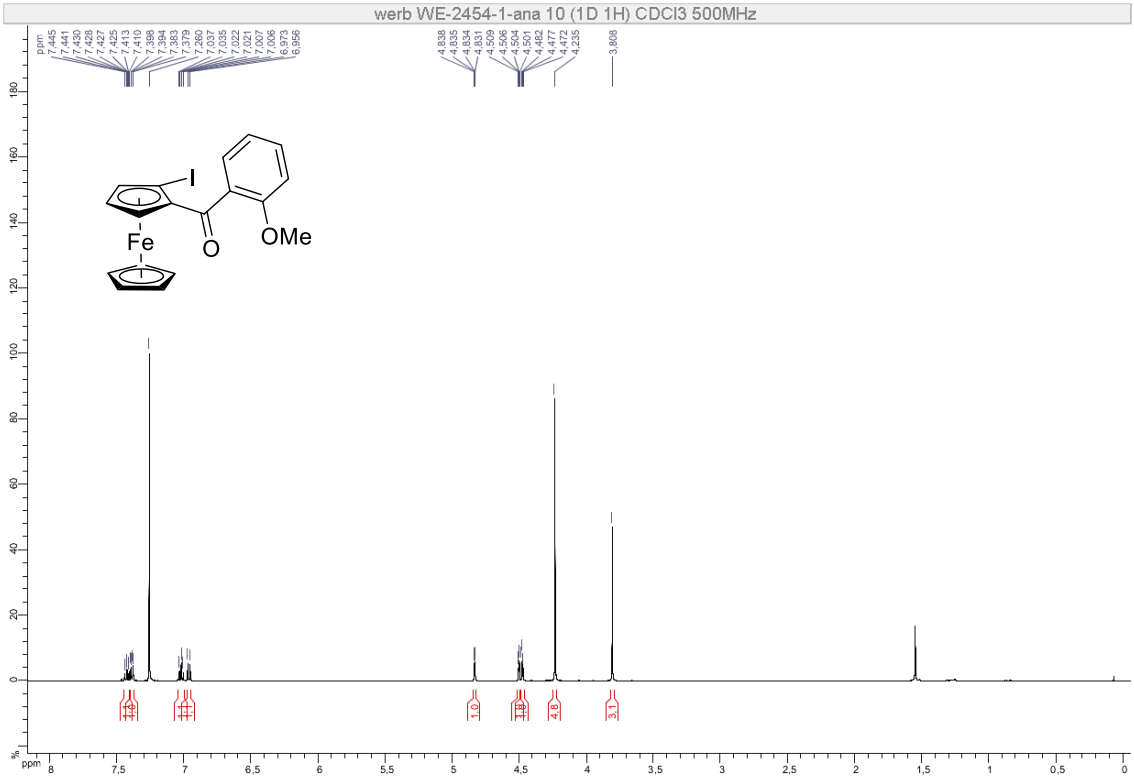


NOESY (500 MHz, $CDCl_3$)

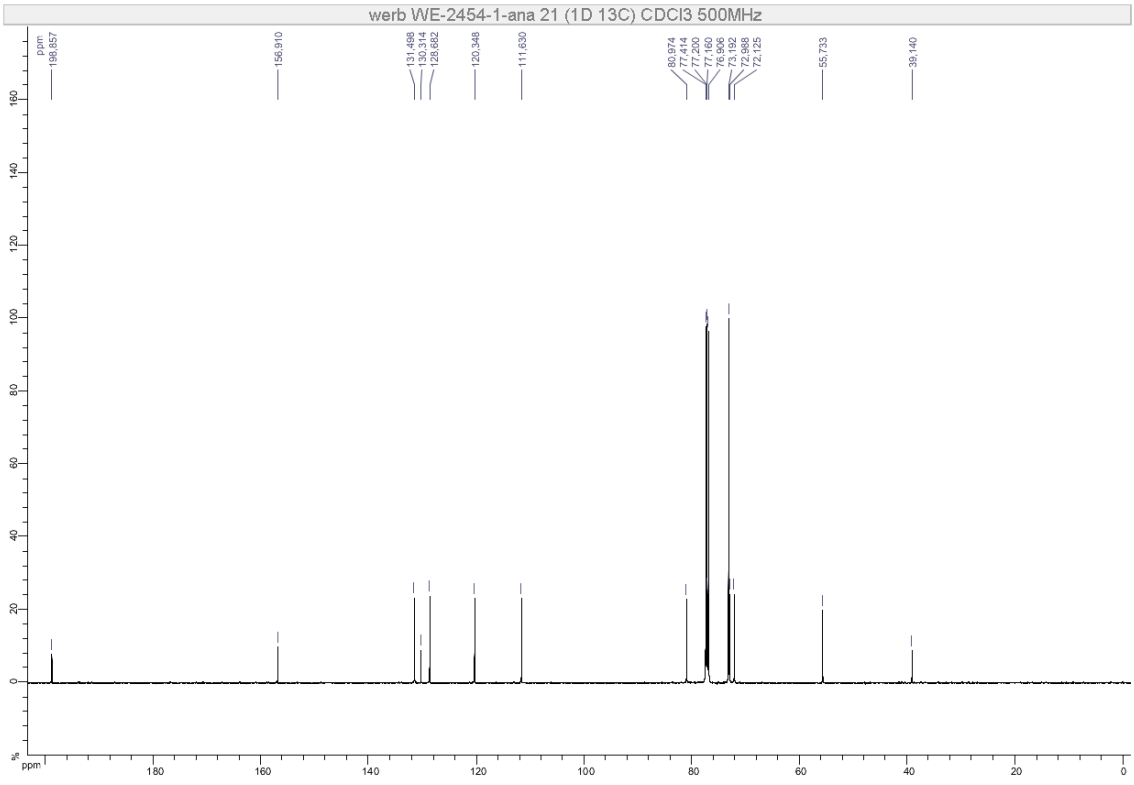


1-Iodo-2-(2-methoxybenzoyl)ferrocene (2-*o*OMePh)

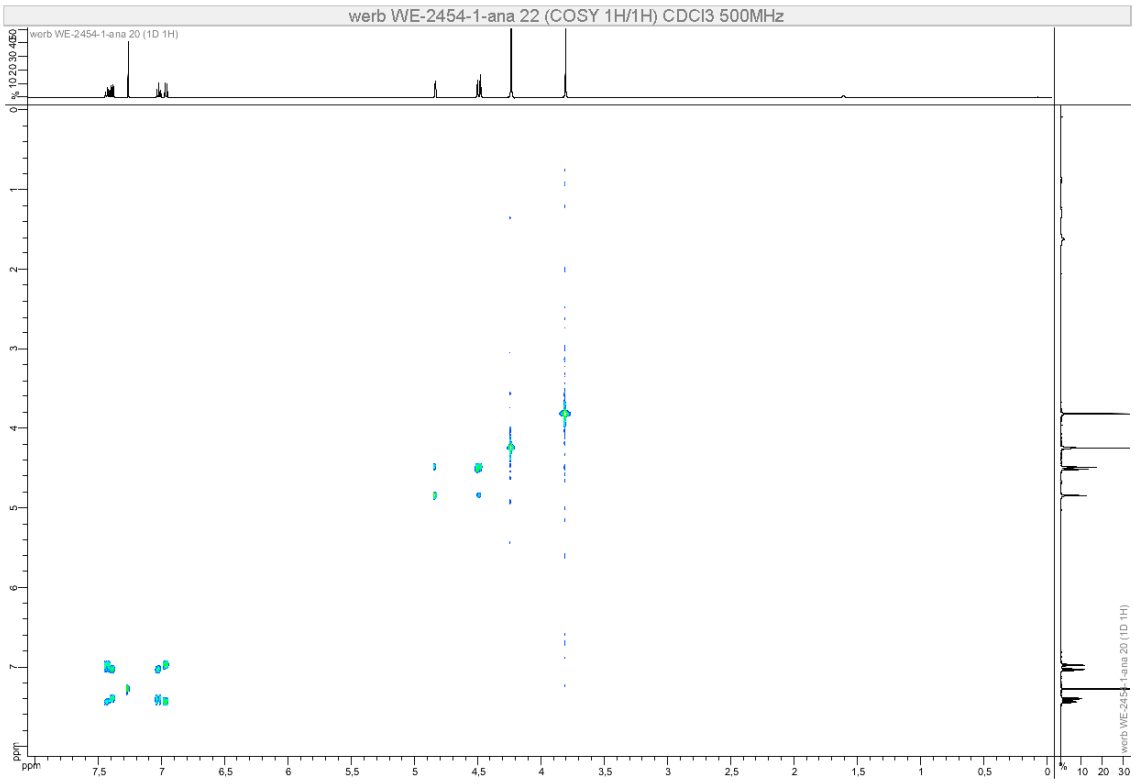
^{1}H NMR (500 MHz, $CDCl_3$)



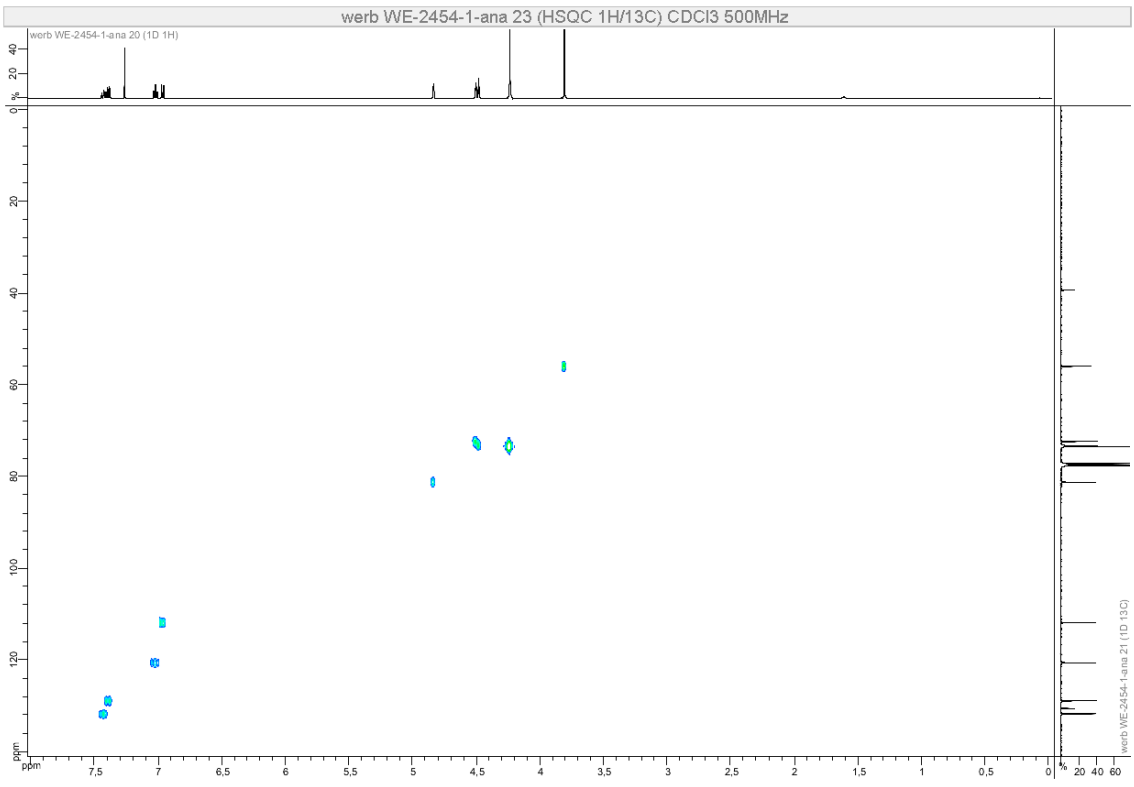
^{13}C NMR (126 MHz, $CDCl_3$)



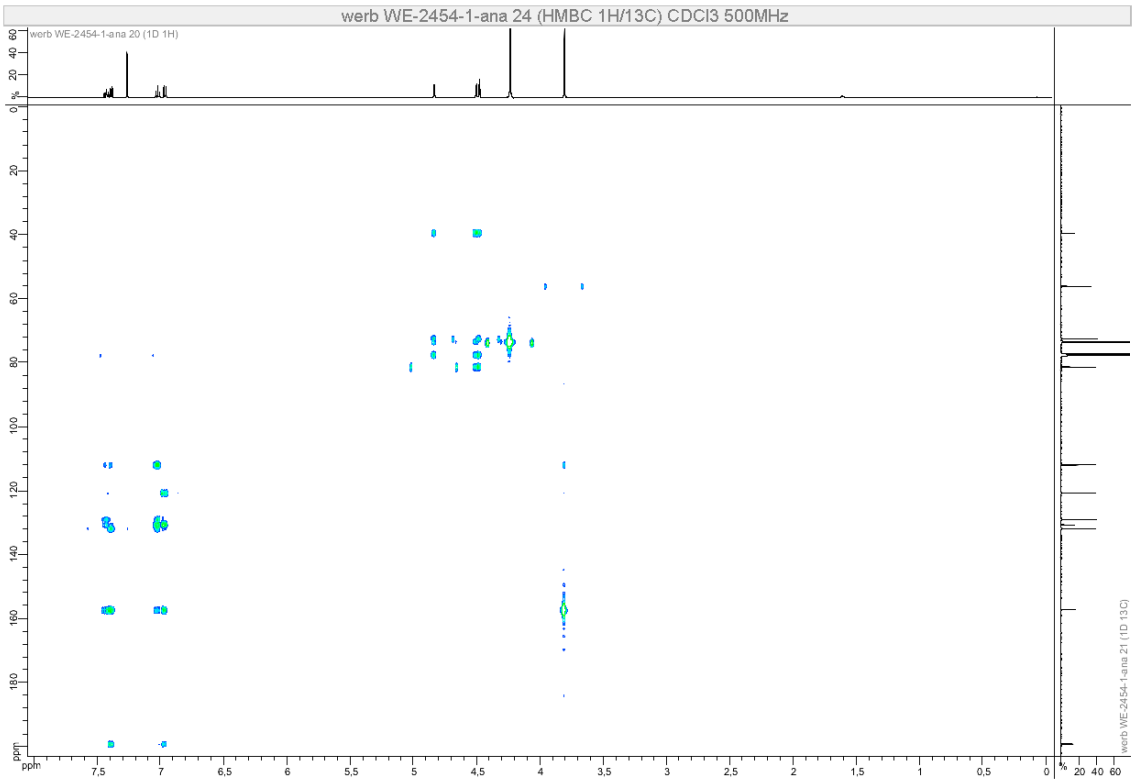
COSY (500 MHz, $CDCl_3$)



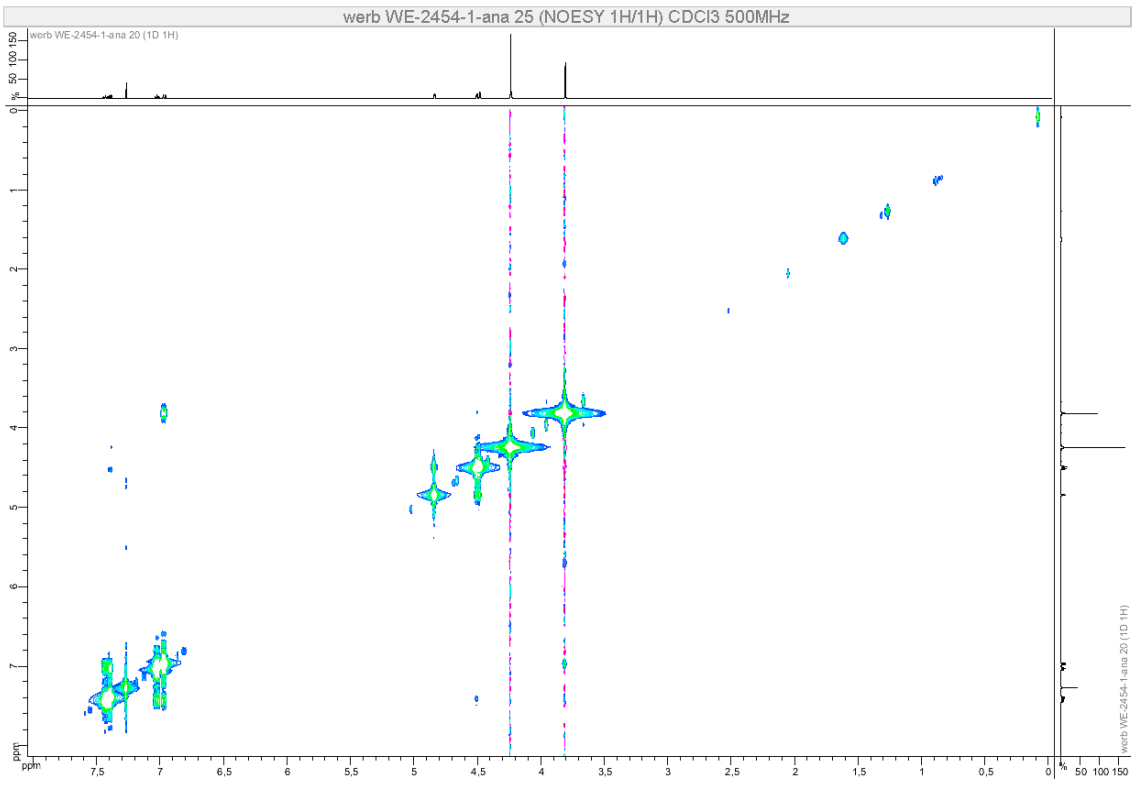
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

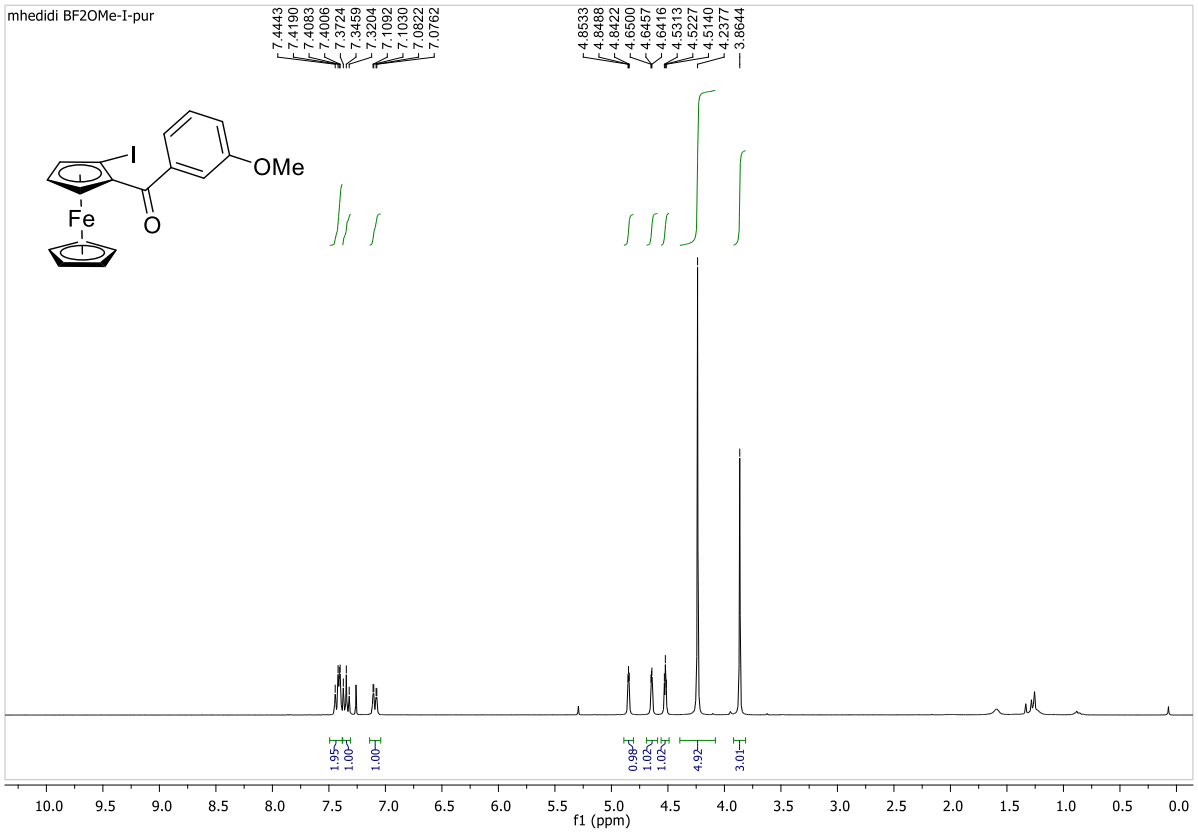


NOESY (500 MHz, $CDCl_3$)

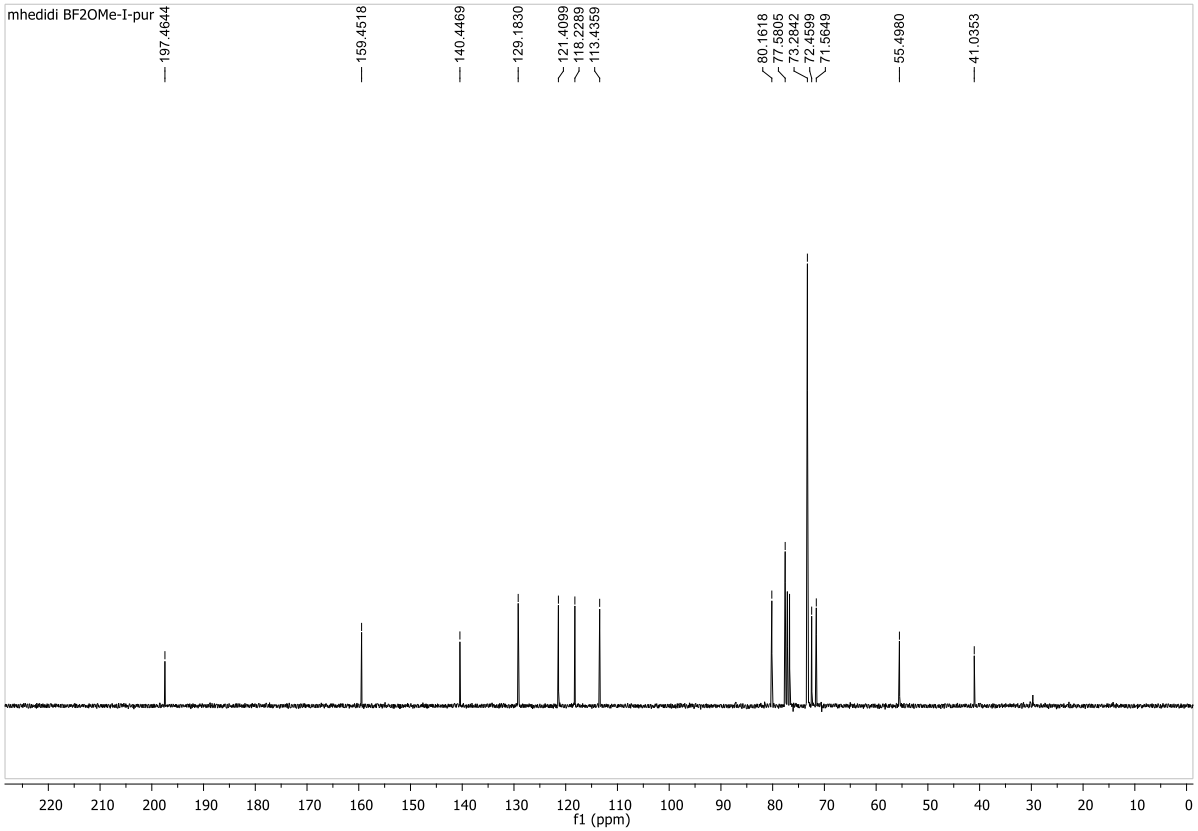


1-Iodo-2-(3-methoxybenzoyl)ferrocene (2-*m*OMePh)

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

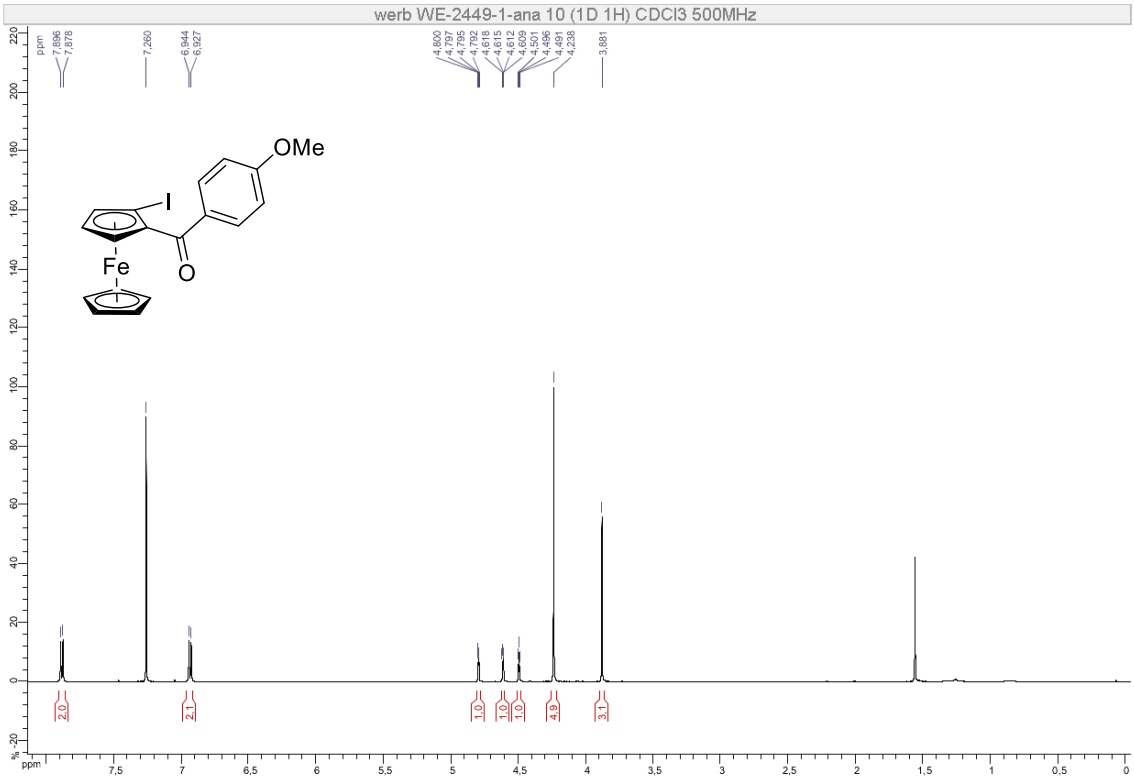


^{13}C NMR (75 MHz, $CDCl_3$)

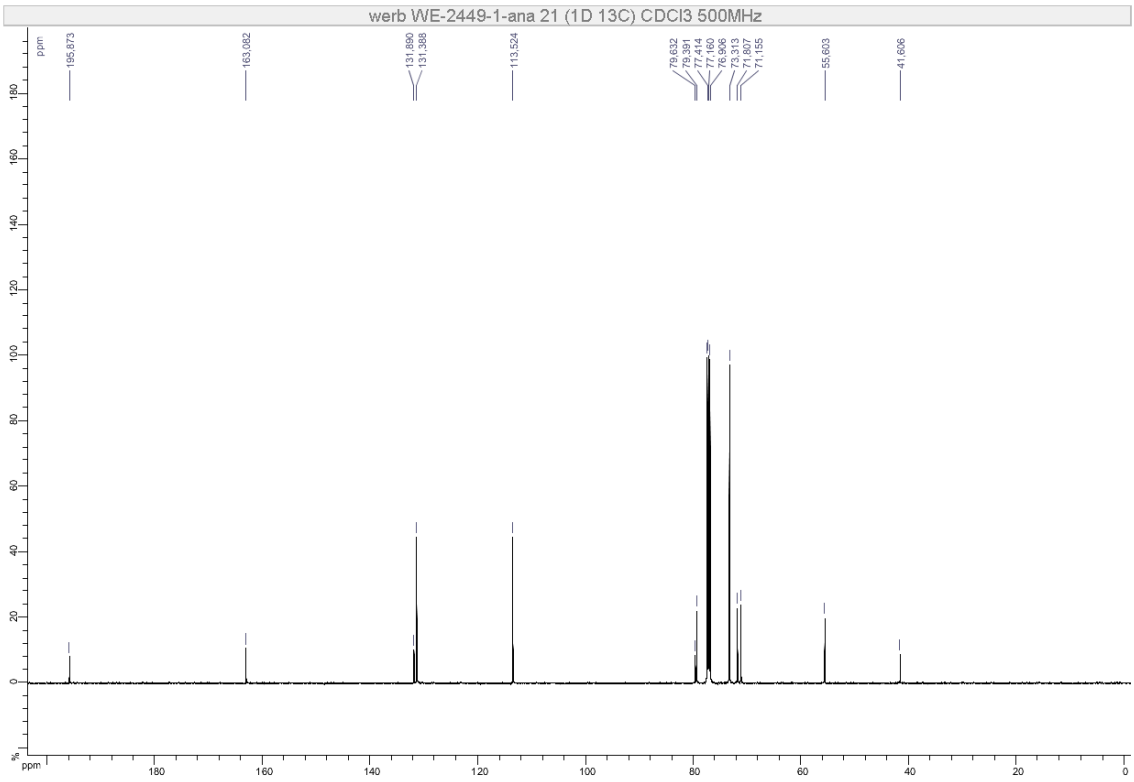


1-Iodo-2-(4-methoxybenzoyl)ferrocene (2-*p*OMePh)

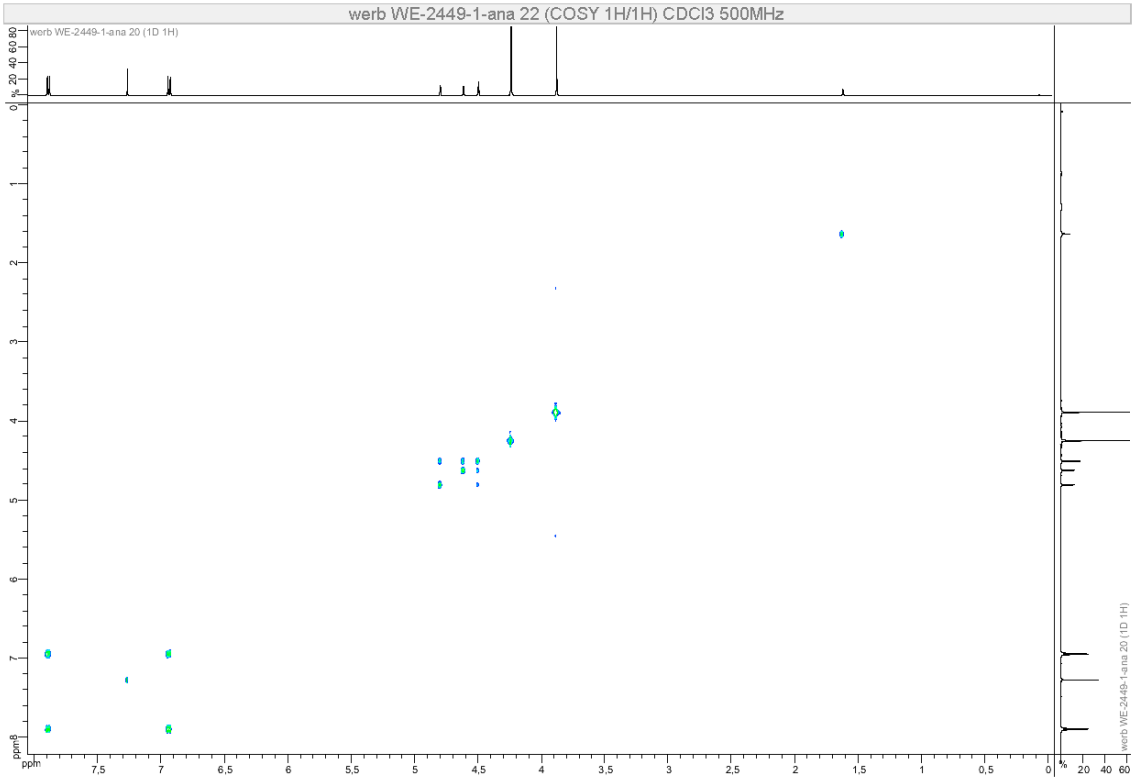
^{1}H NMR (500 MHz, $CDCl_3$)



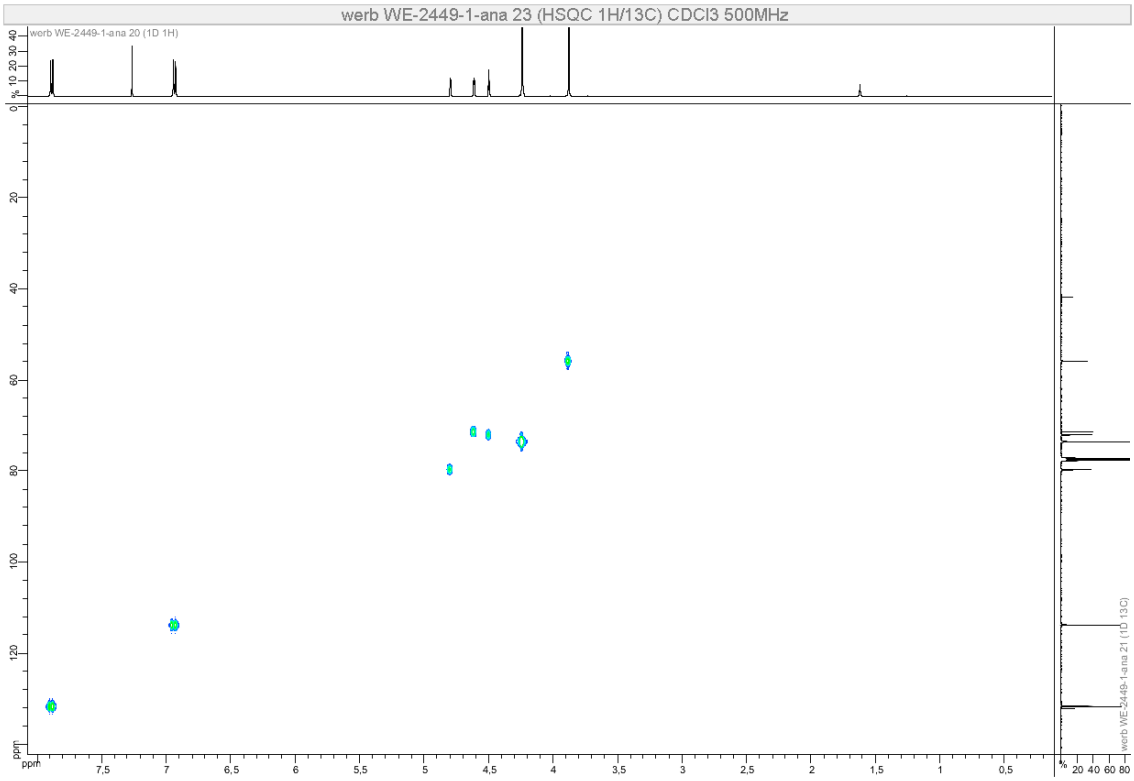
^{13}C NMR (126 MHz, $CDCl_3$)



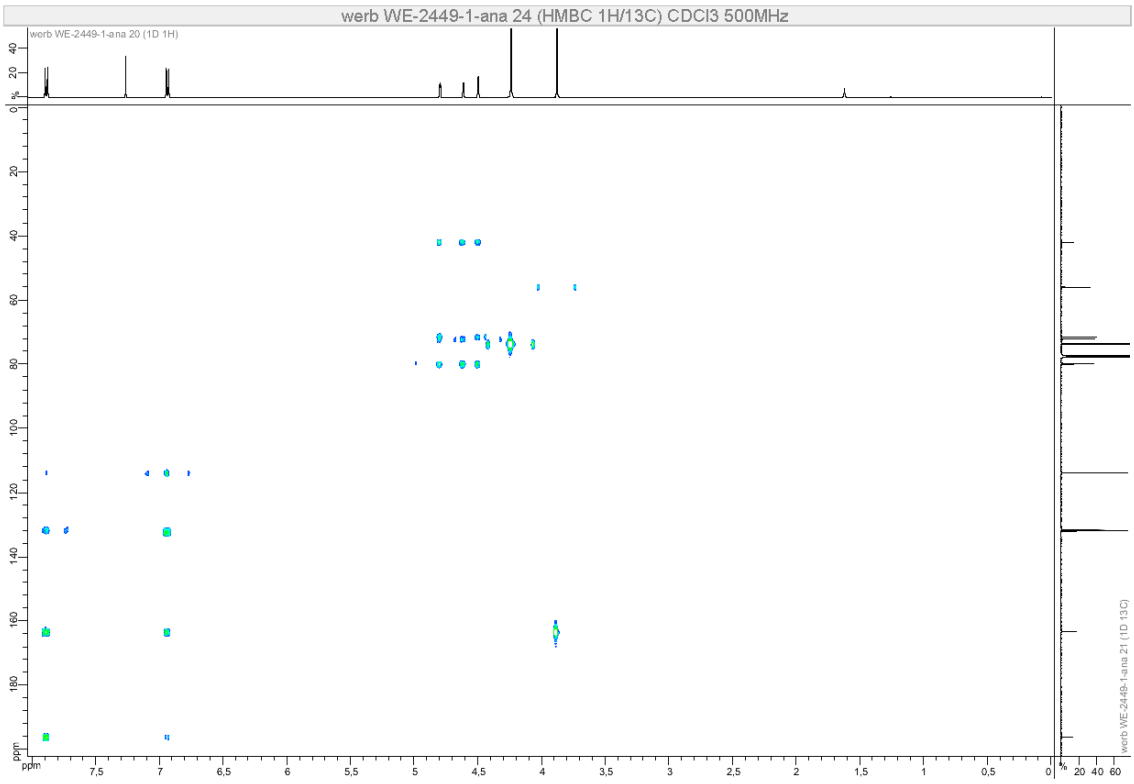
COSY (500 MHz, $CDCl_3$)



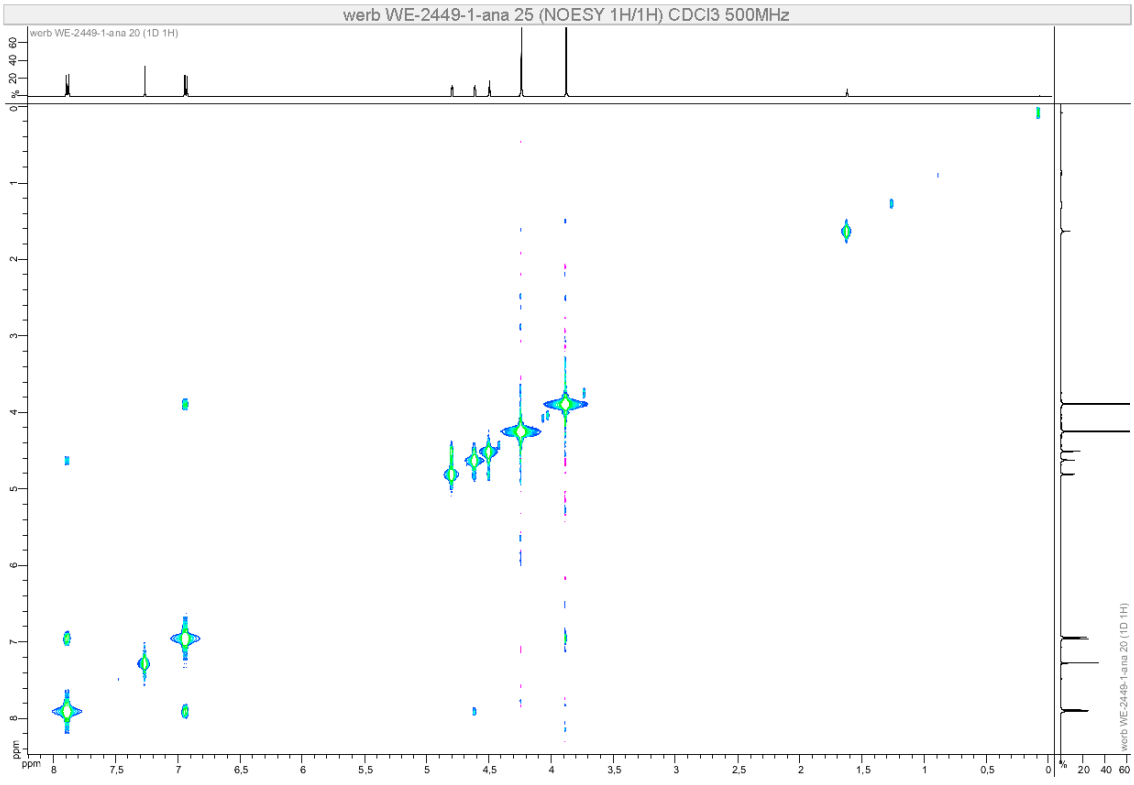
HSQC (500 MHz, $CDCl_3$)



HMBC (400 MHz, $CDCl_3$)

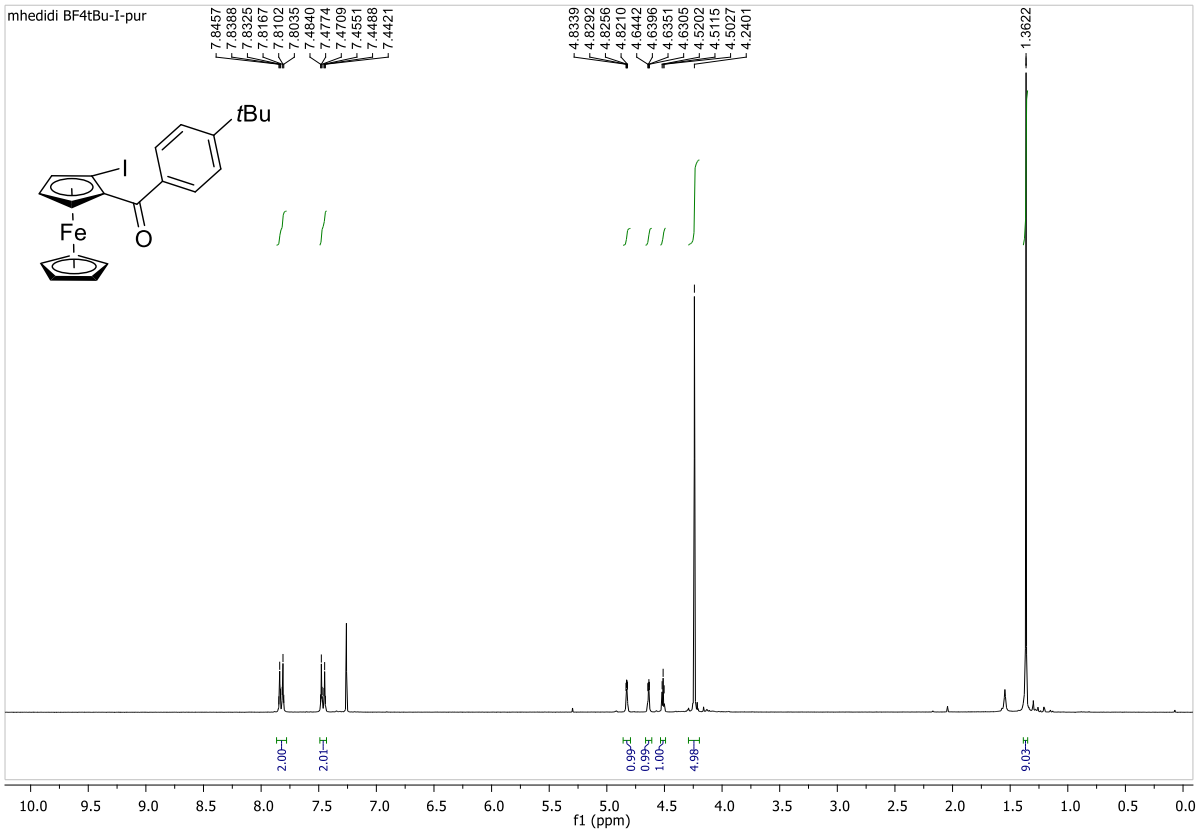


NOESY (500 MHz, $CDCl_3$)

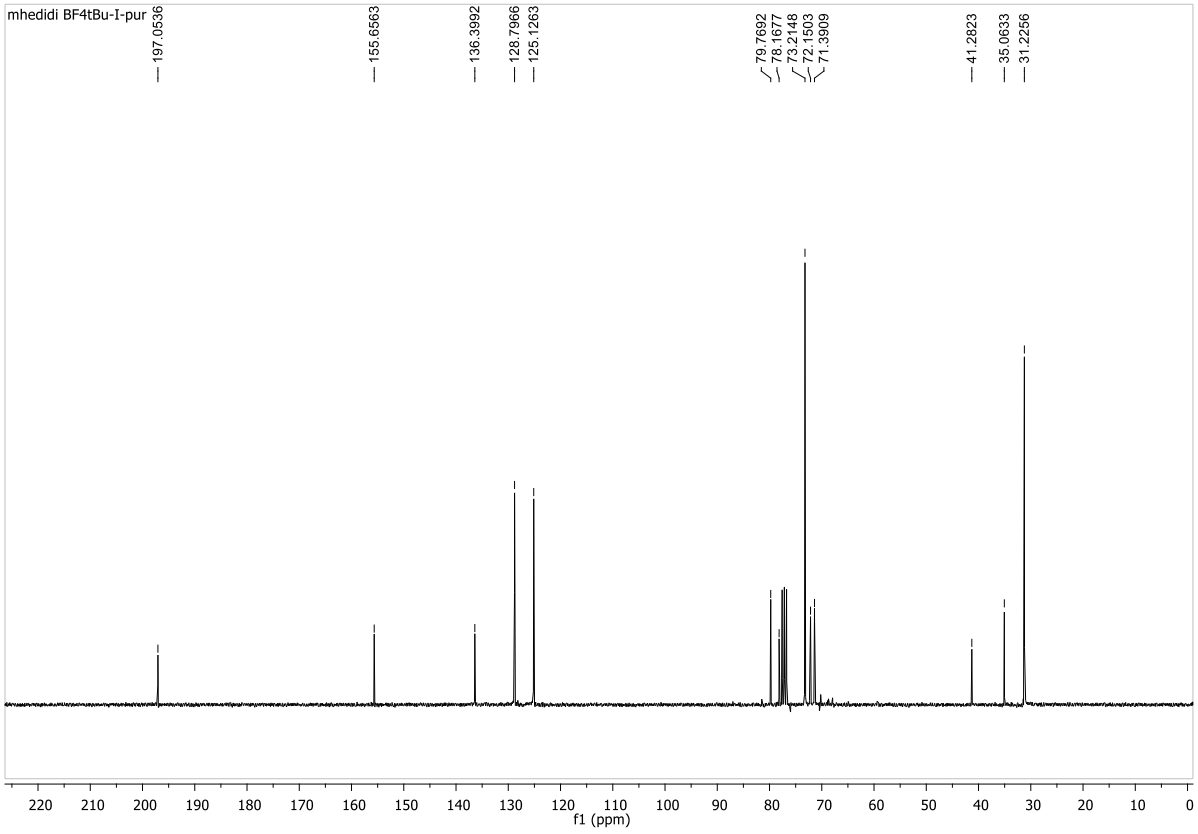


1-(4-*tert*-Butylbenzoyl)-2-iodoferrocene (2-*pt*BuPh)

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

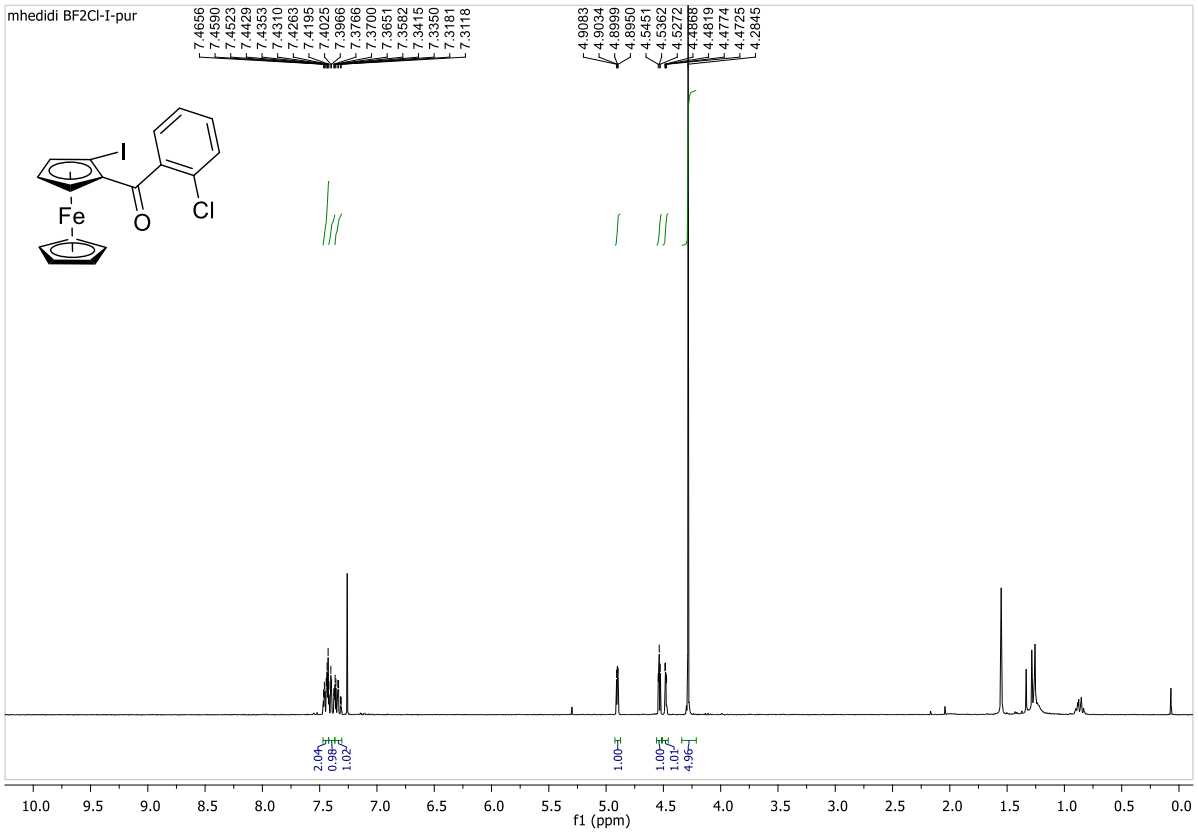


^{13}C NMR (75 MHz, $CDCl_3$)

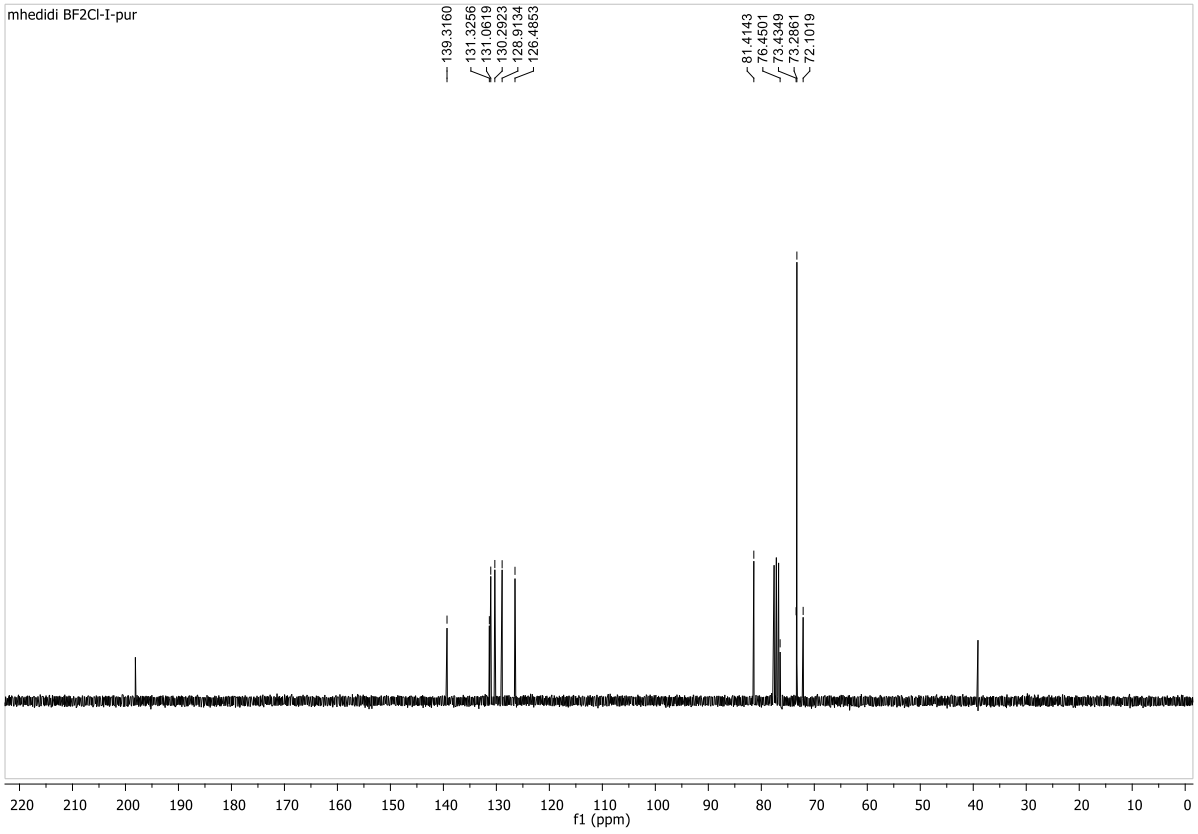


1-(2-Chlorobenzoyl)-2-iodoferrocene (2-*o*ClPh)

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

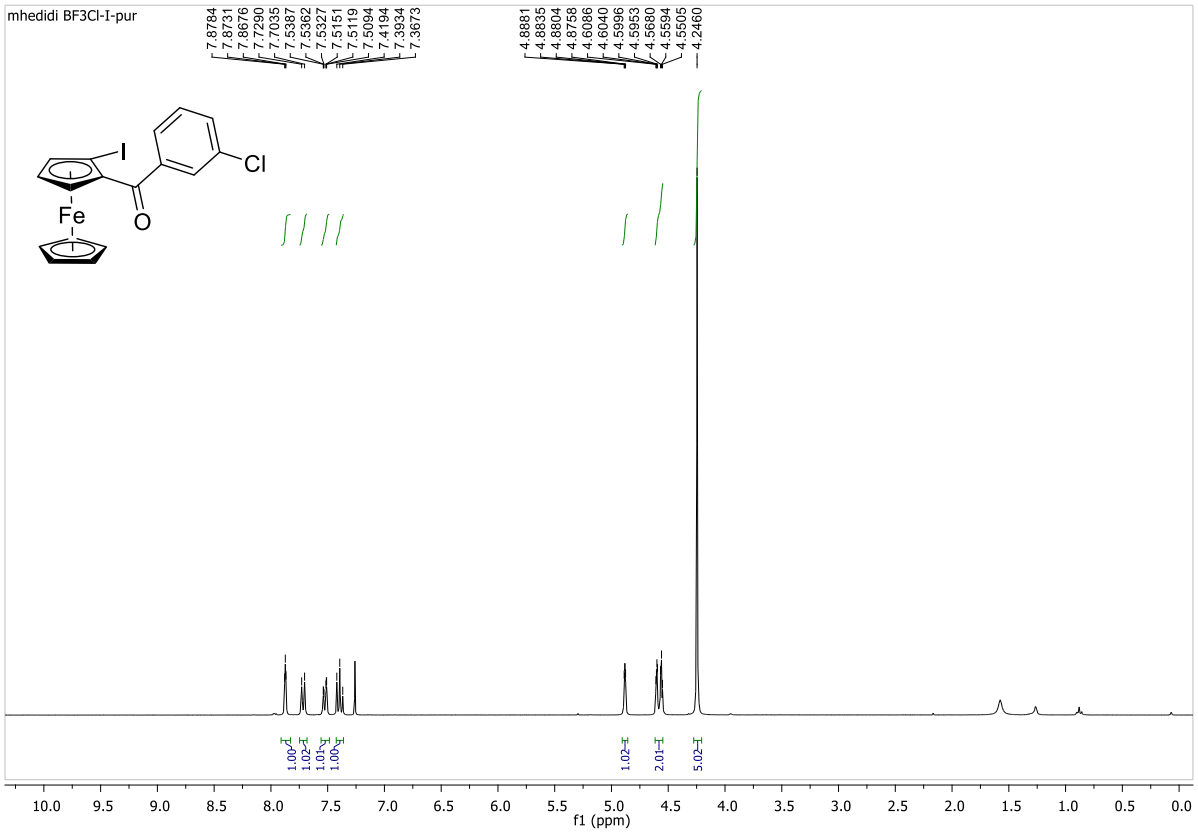


^{13}C NMR (75 MHz, $CDCl_3$)

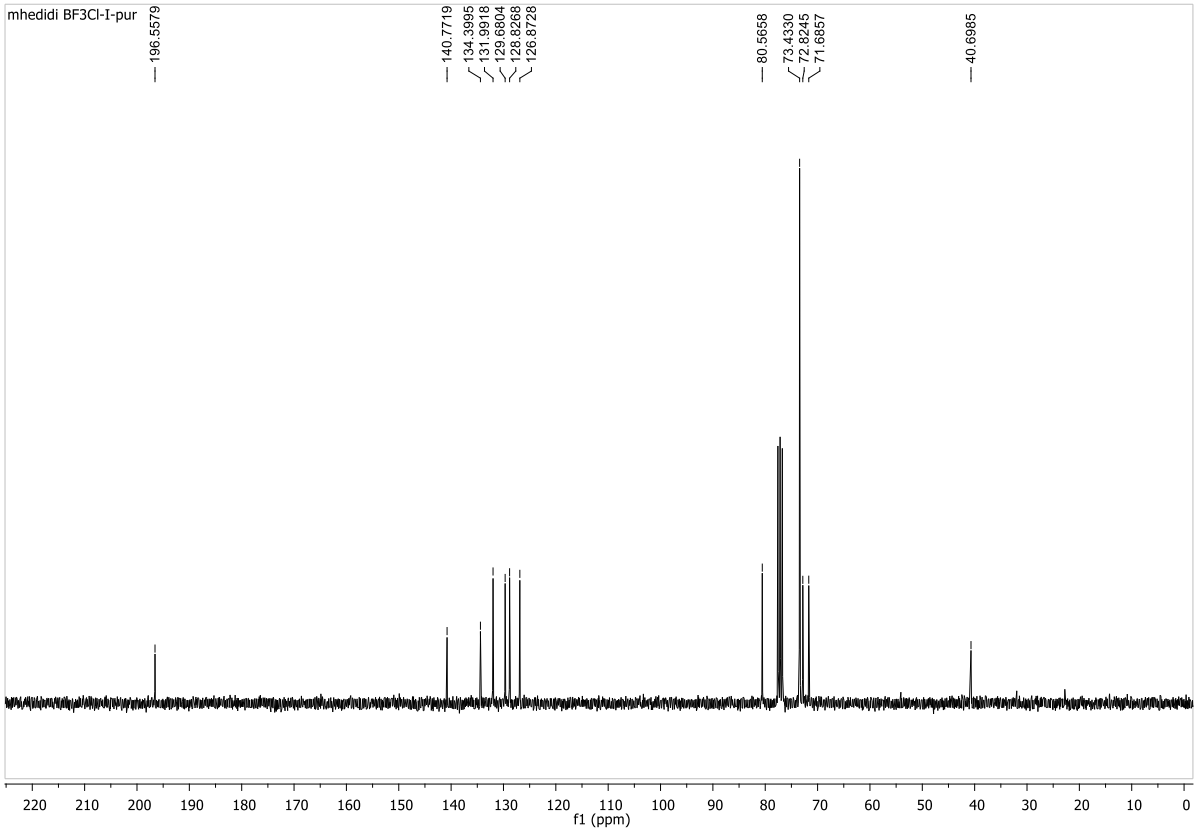


1-(3-Chlorobenzoyl)-2-iodoferrocene (2-*m*ClPh)

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

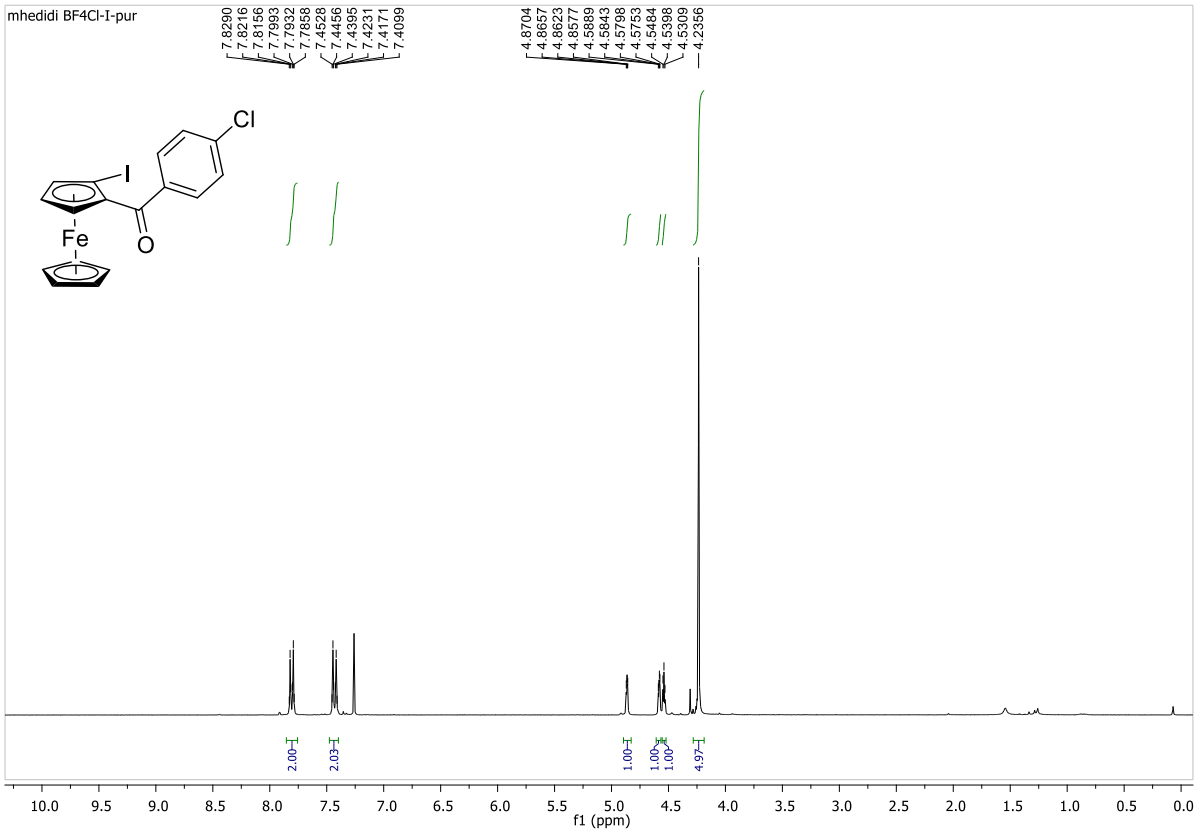


^{13}C NMR (75 MHz, $CDCl_3$)

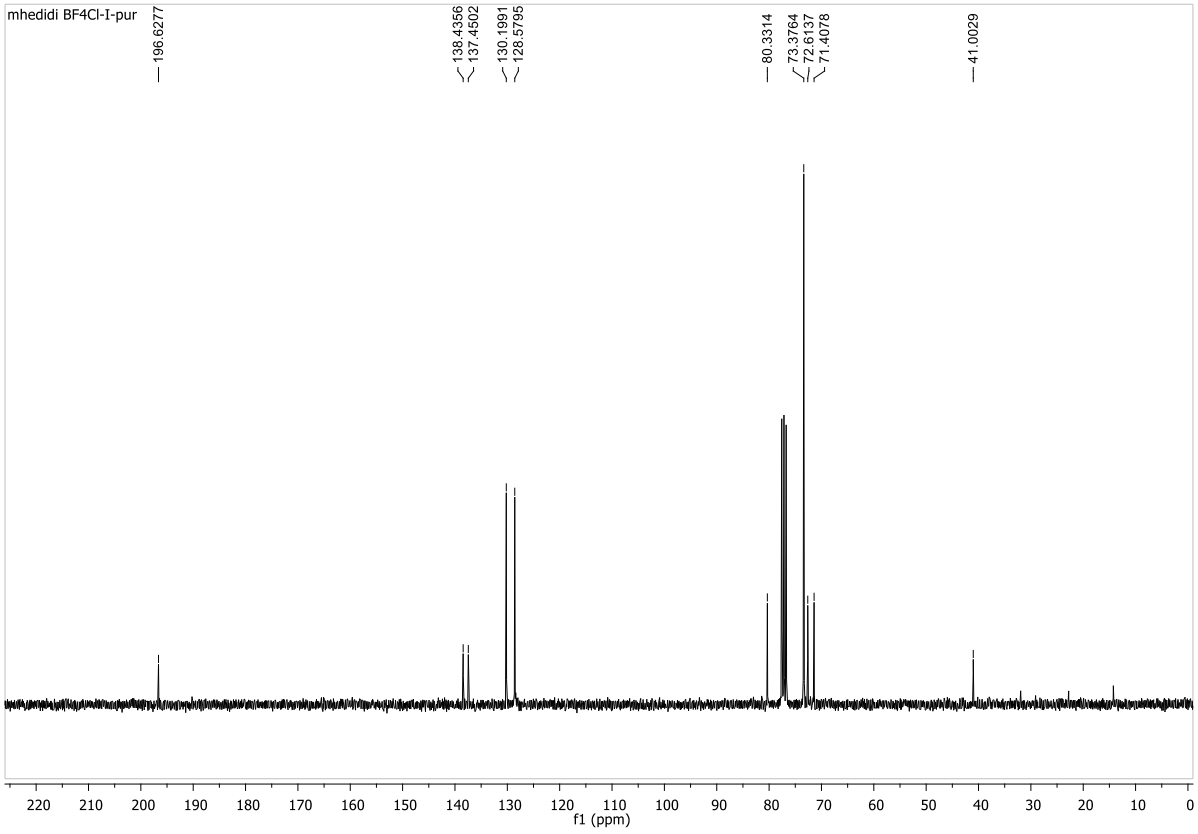


1-(4-Chlorobenzoyl)-2-iodoferrocene (2-*p*ClPh)

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

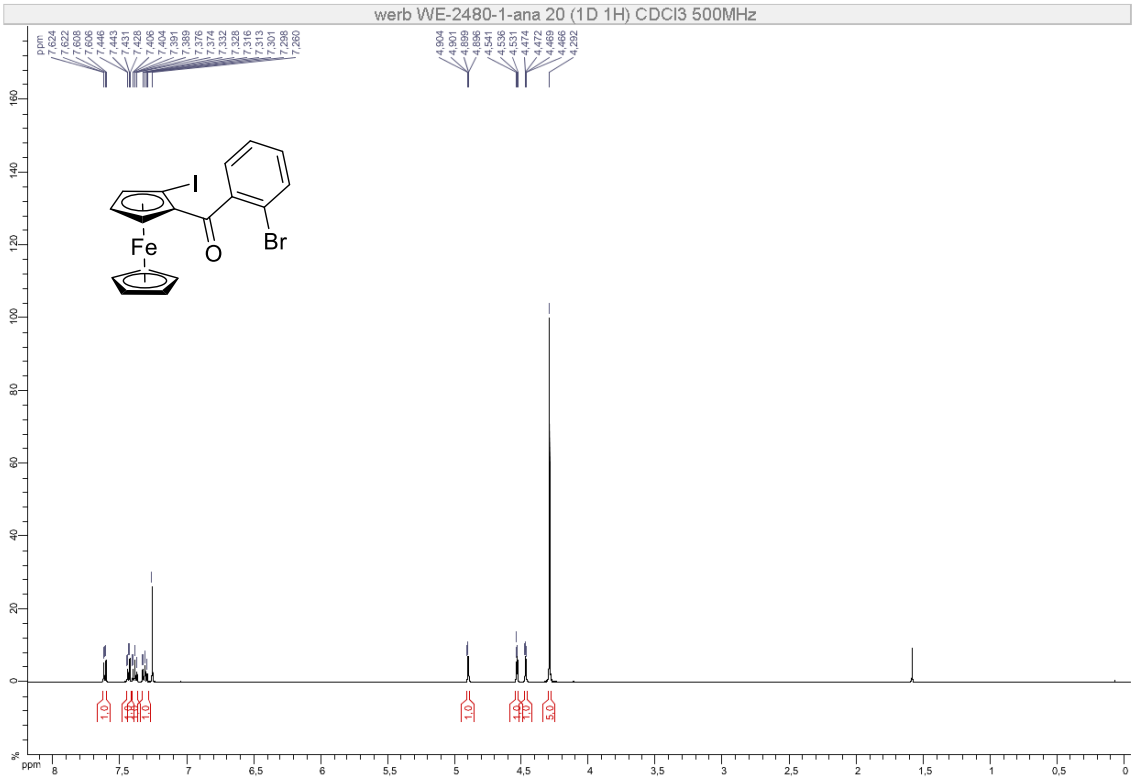


^{13}C NMR (75 MHz, $CDCl_3$)

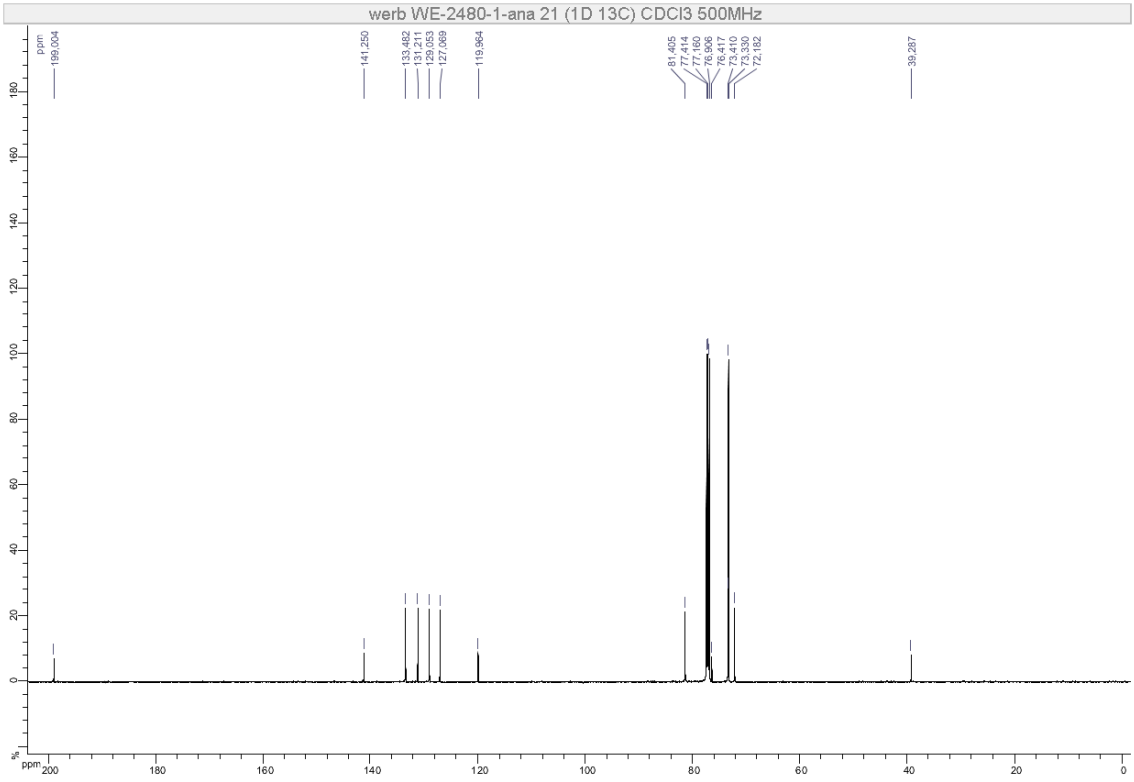


1-(2-Bromobenzoyl)-2-iodoferrocene (2-*o*BrPh)

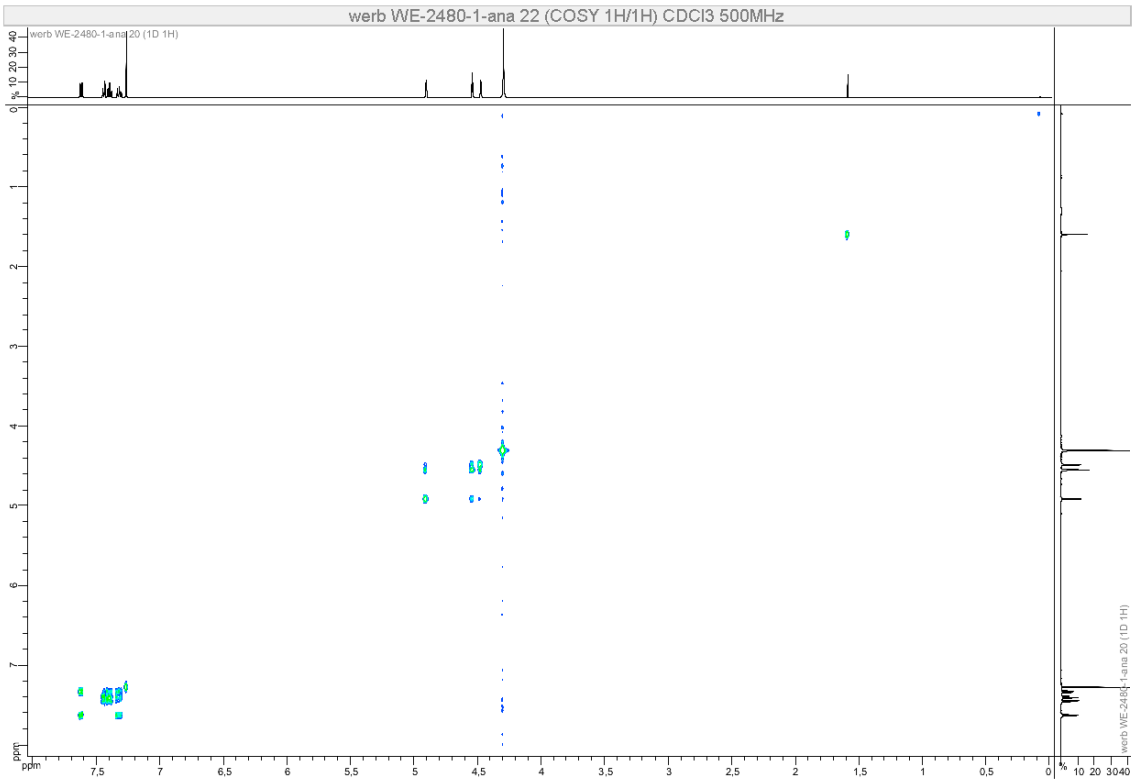
^{1}H NMR (500 MHz, $CDCl_3$)



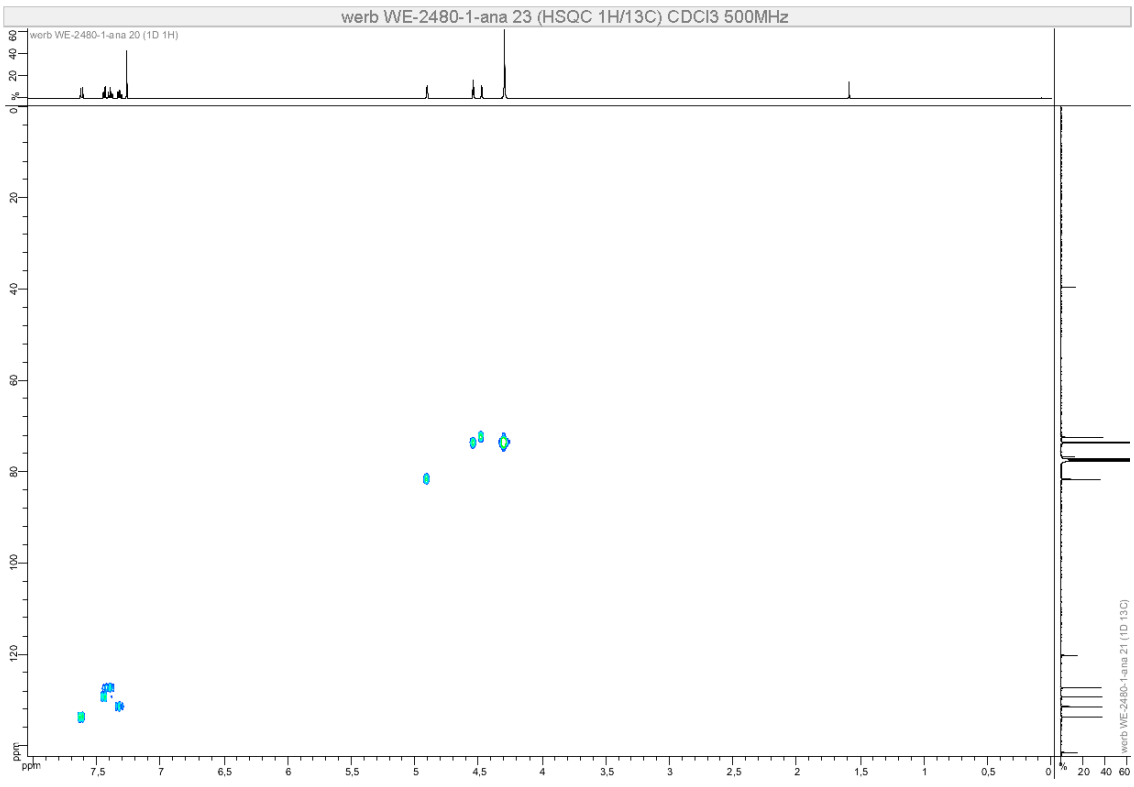
^{13}C NMR (126 MHz, $CDCl_3$)



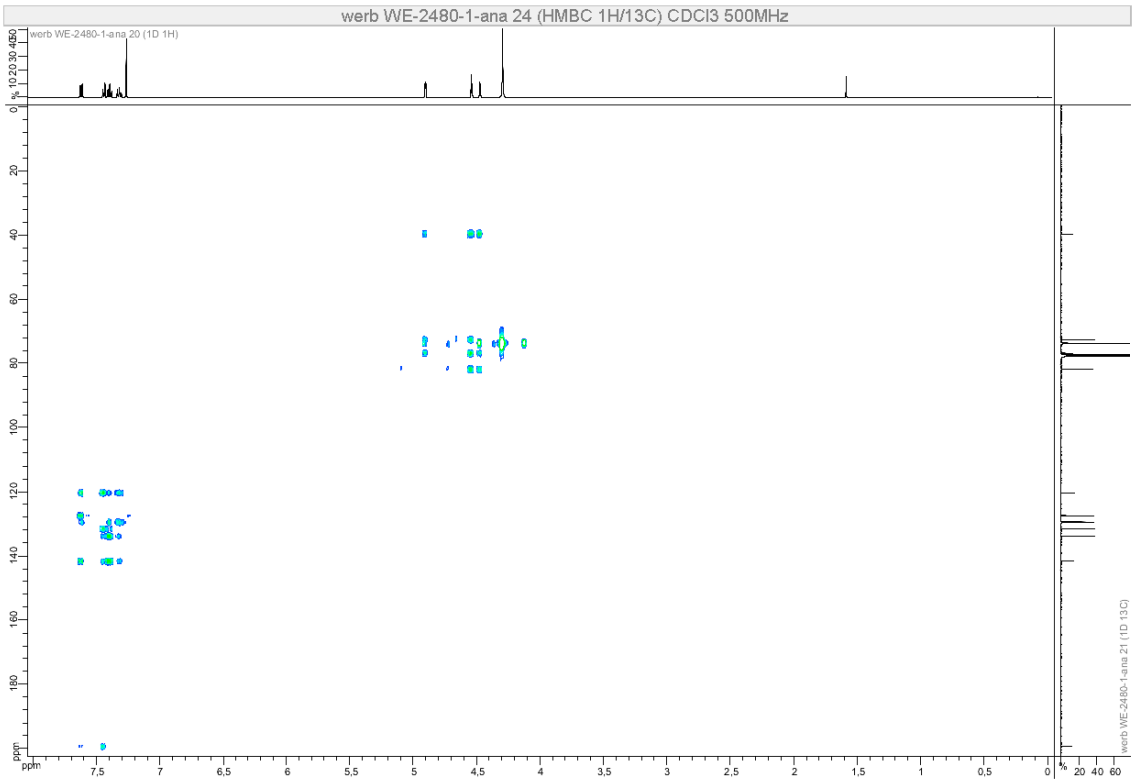
COSY (500 MHz, $CDCl_3$)



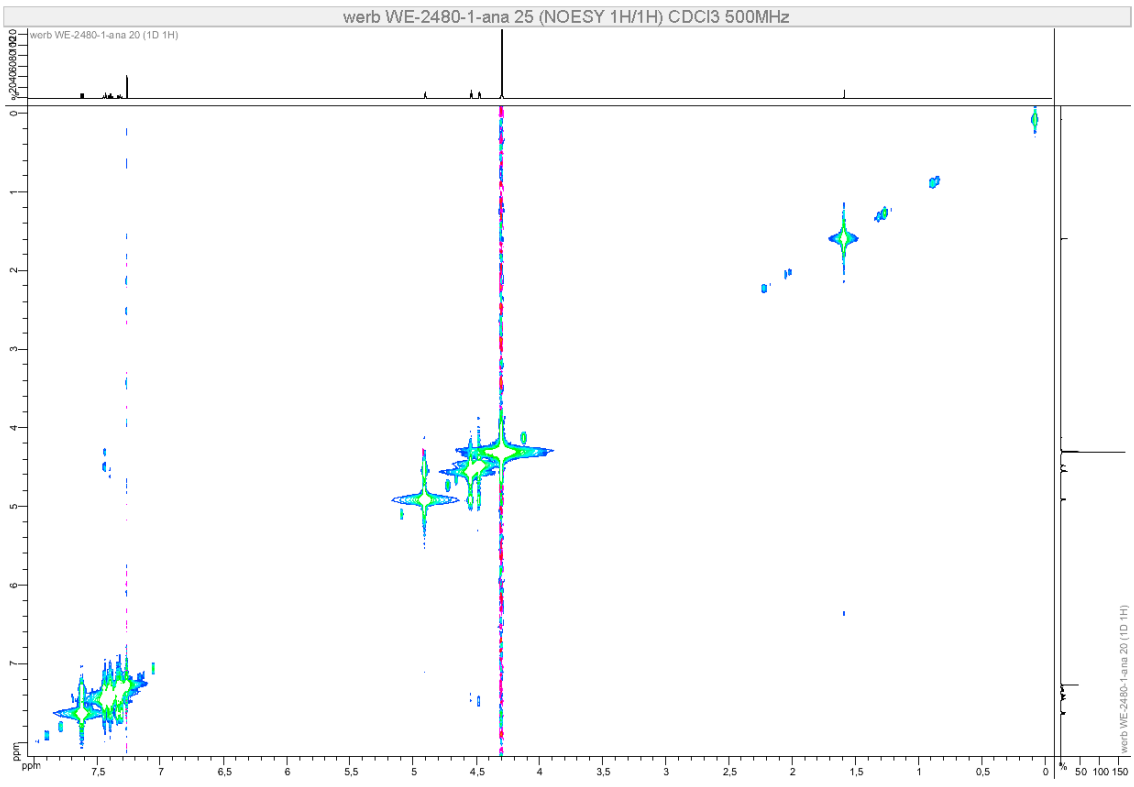
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

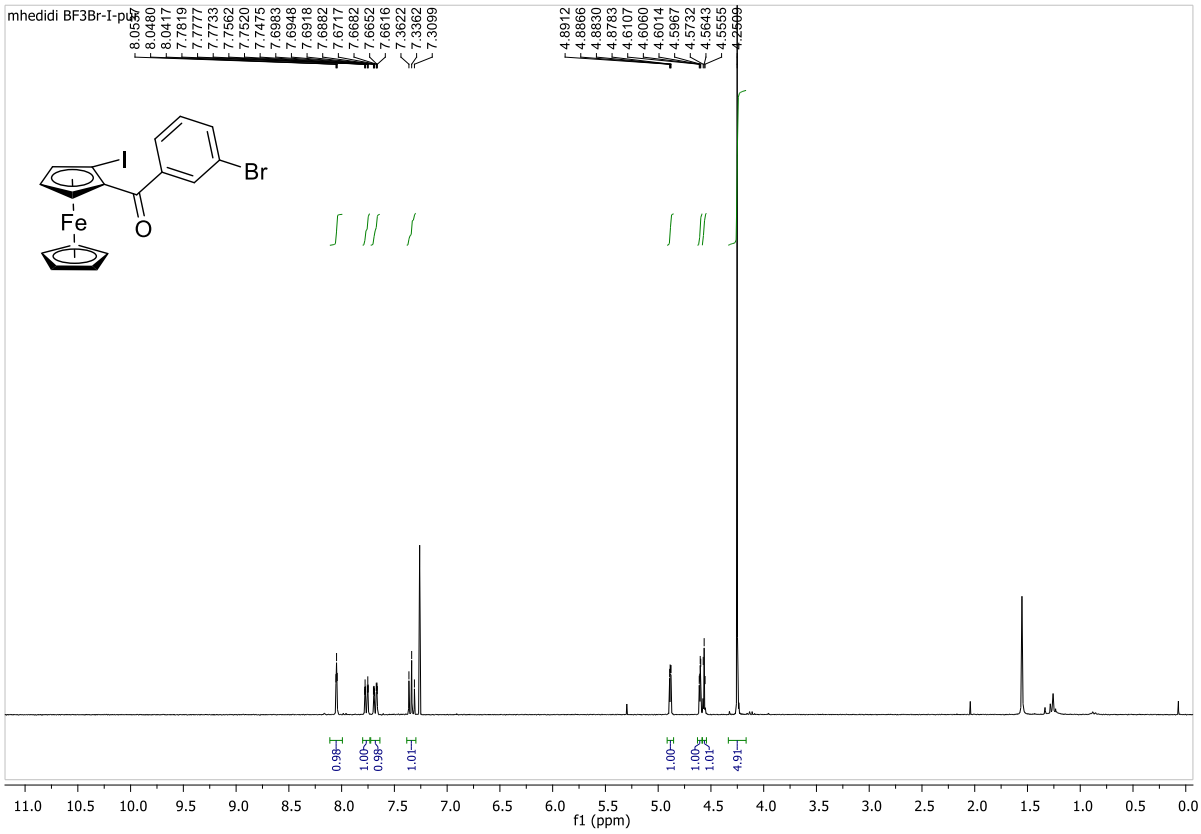


NOESY (500 MHz, $CDCl_3$)

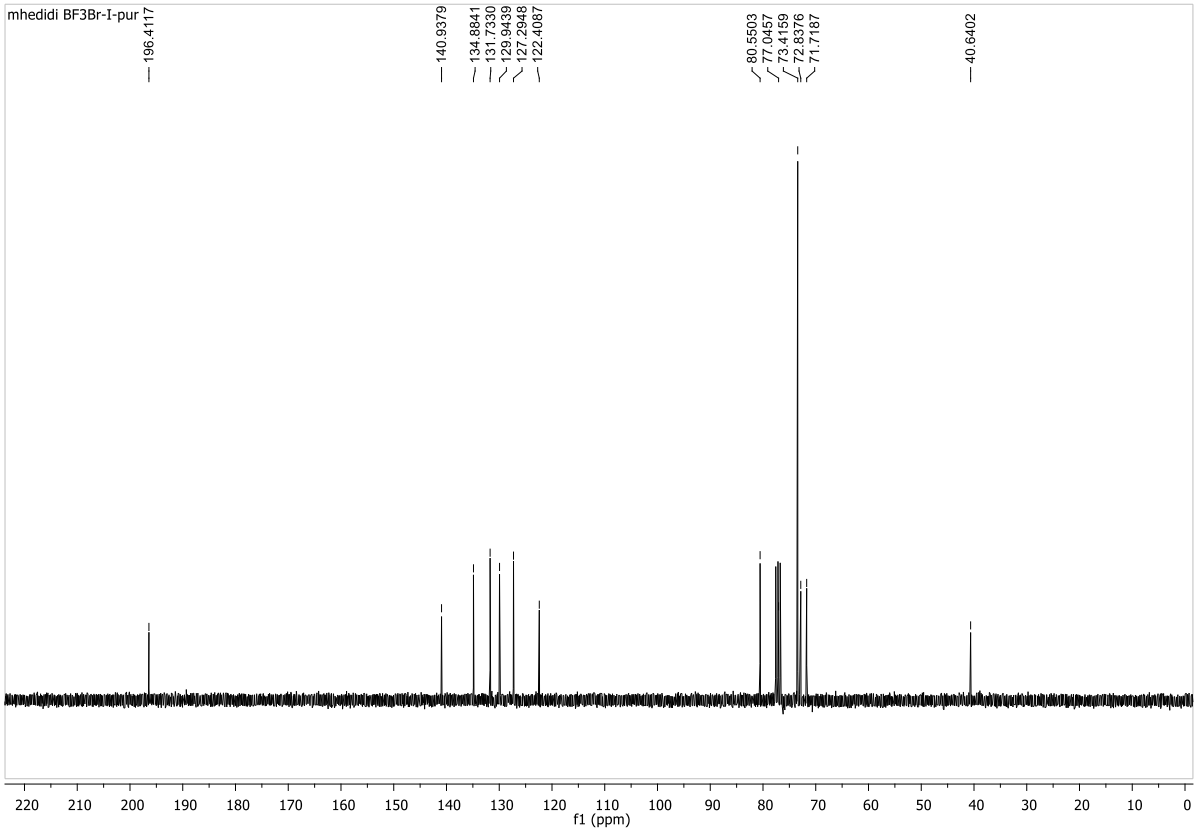


1-(3-Bromobenzoyl)-2-iodoferrocene (2-*m*BrPh)

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

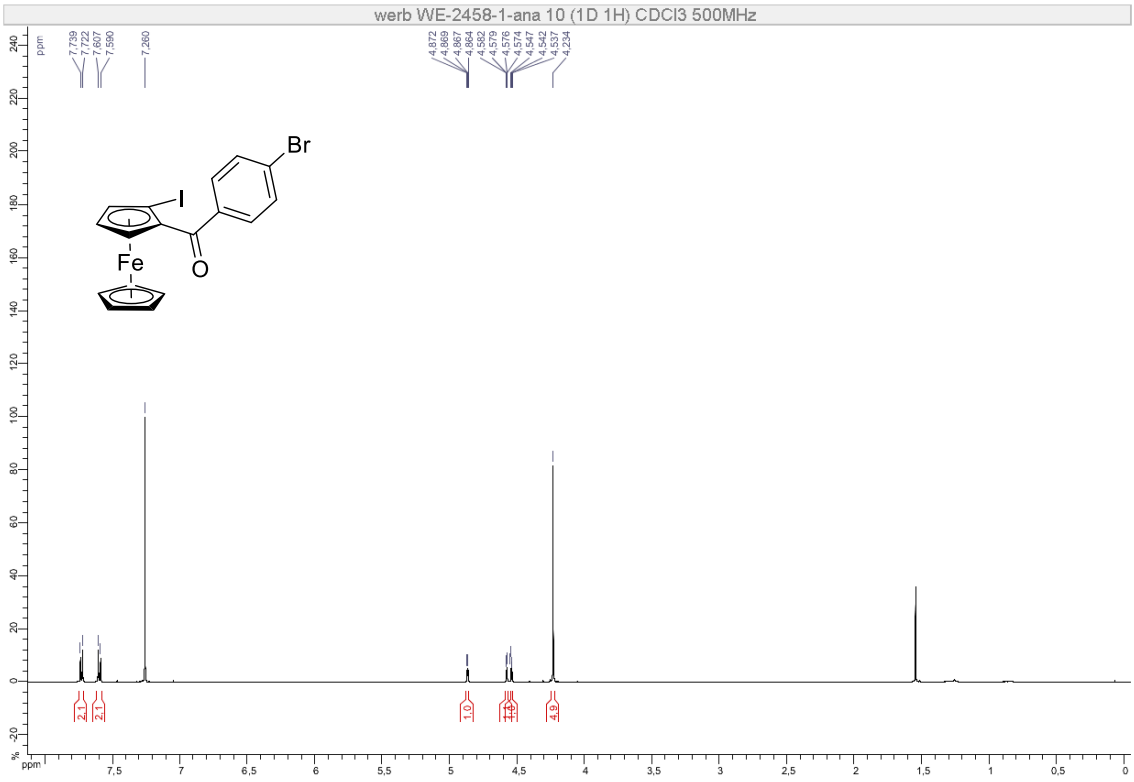


^{13}C NMR (75 MHz, $CDCl_3$)

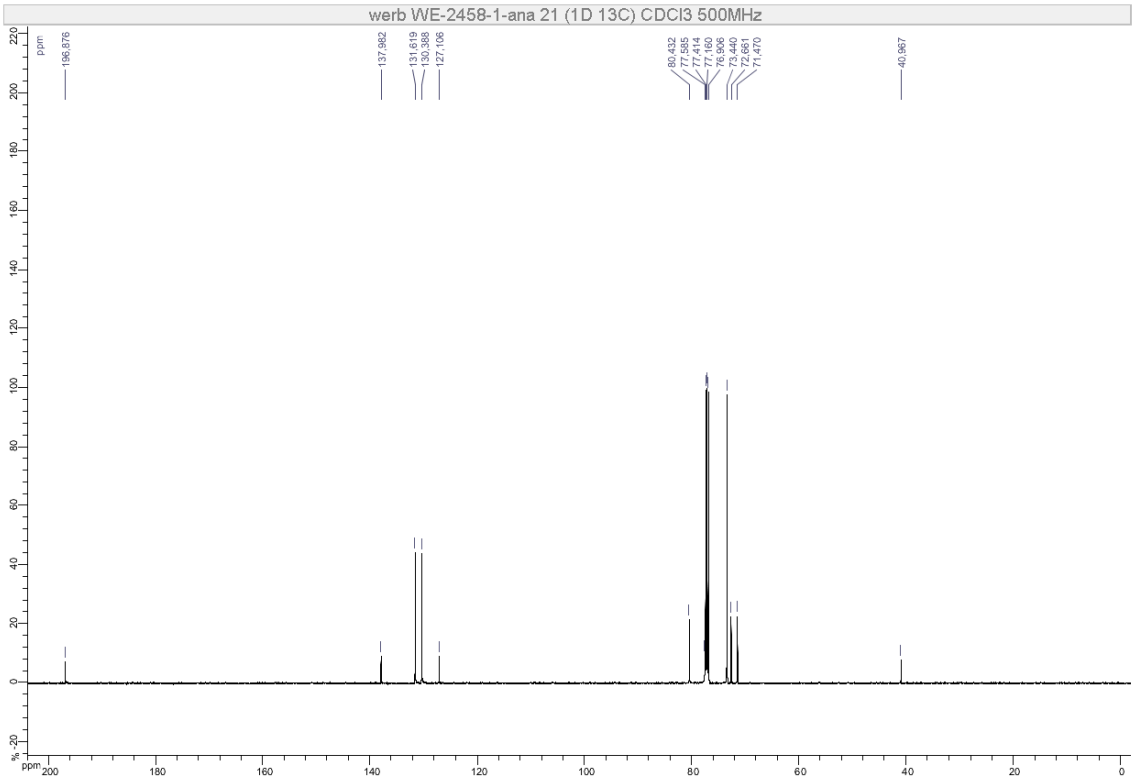


1-(4-Bromobenzoyl)-2-iodoferrocene (2-*p*BrPh)

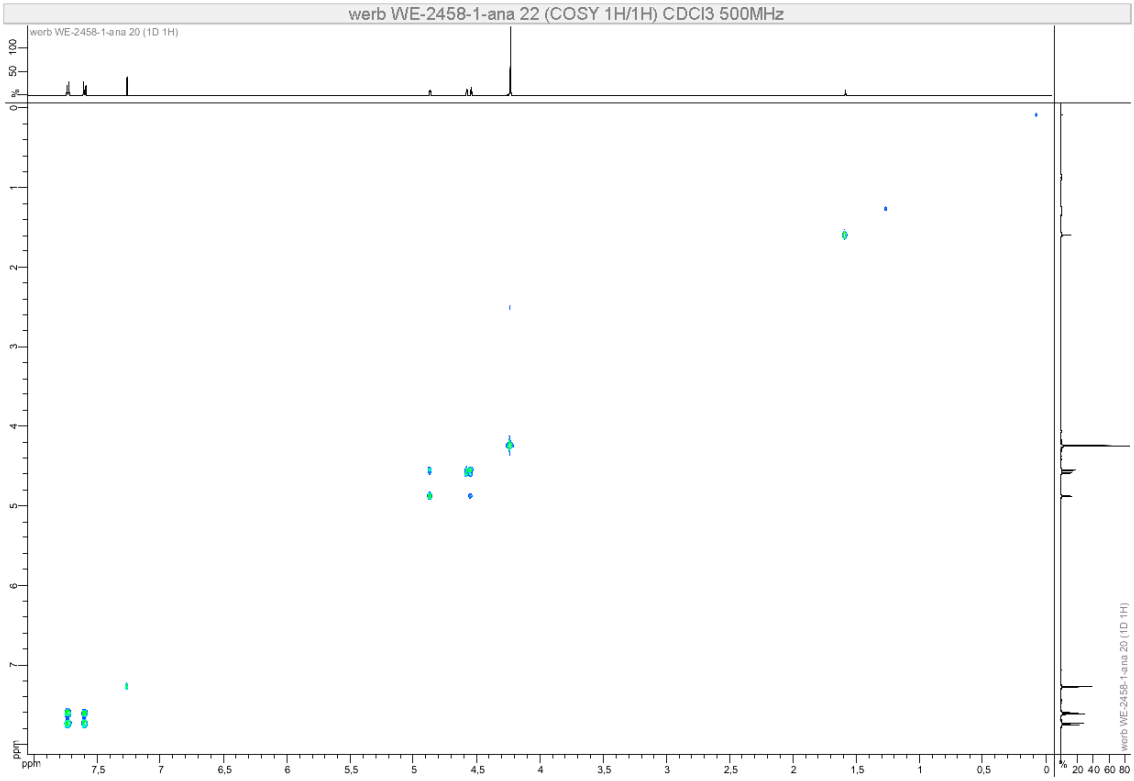
^{1}H NMR (500 MHz, $CDCl_3$)



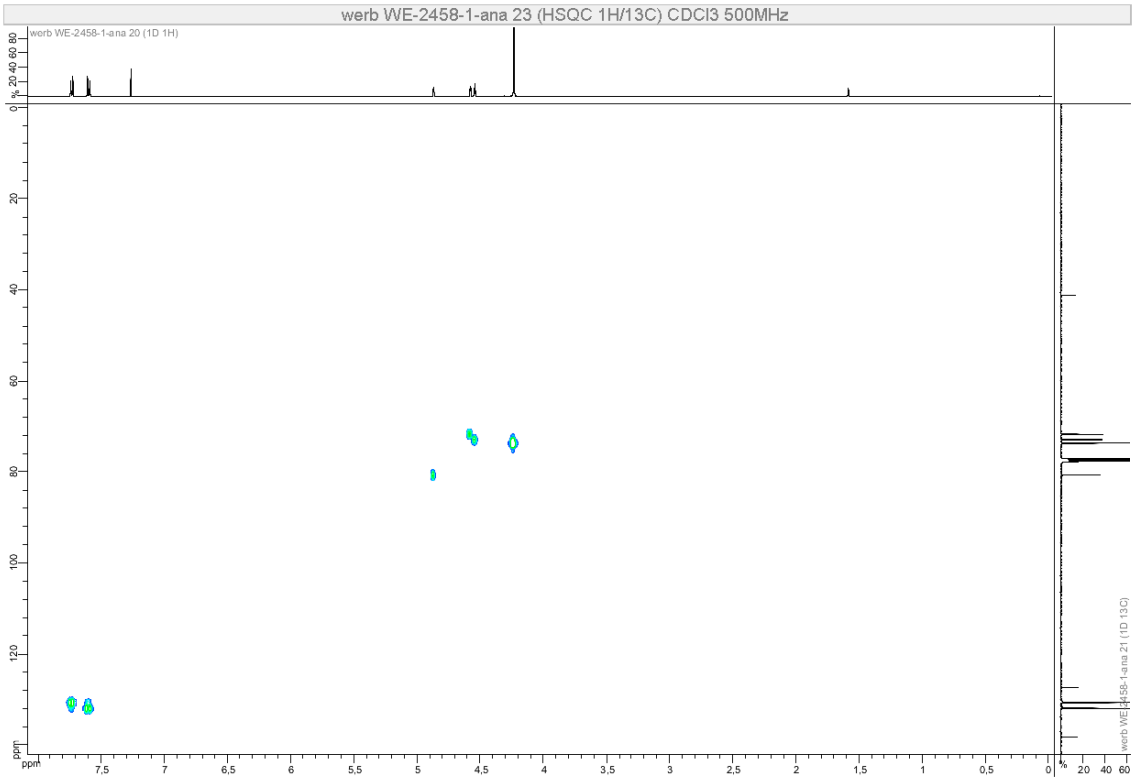
^{13}C NMR (126 MHz, $CDCl_3$)



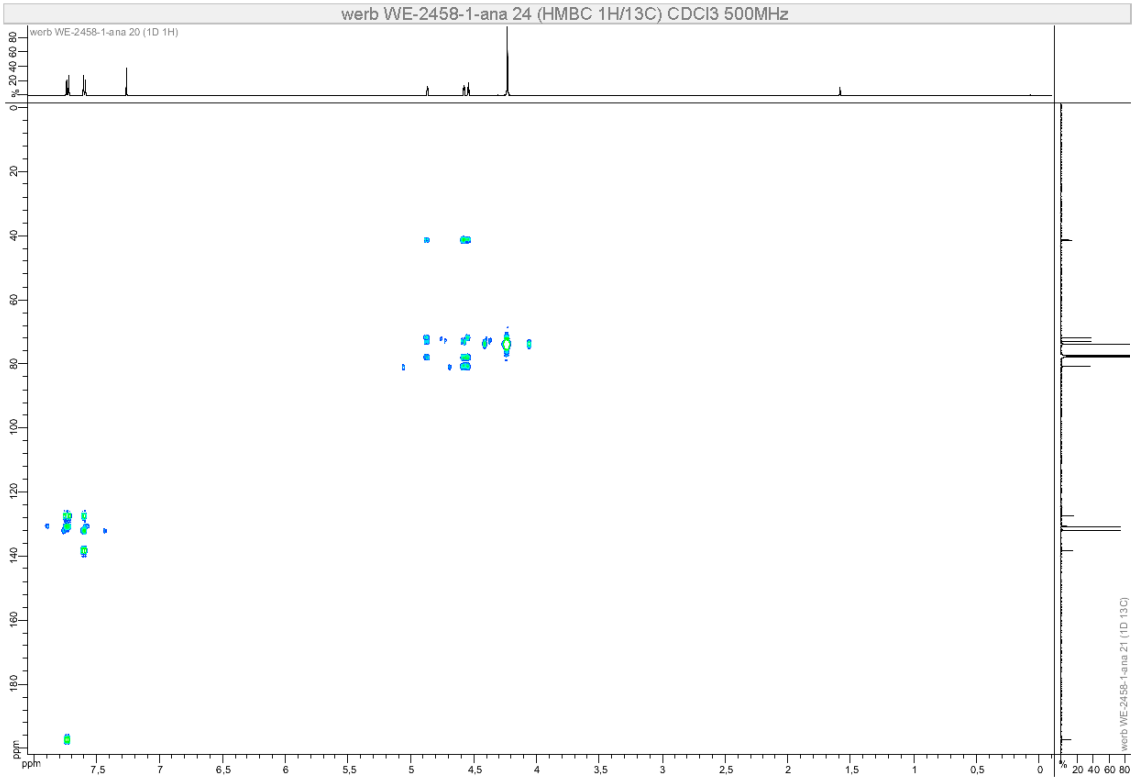
COSY (500 MHz, $CDCl_3$)



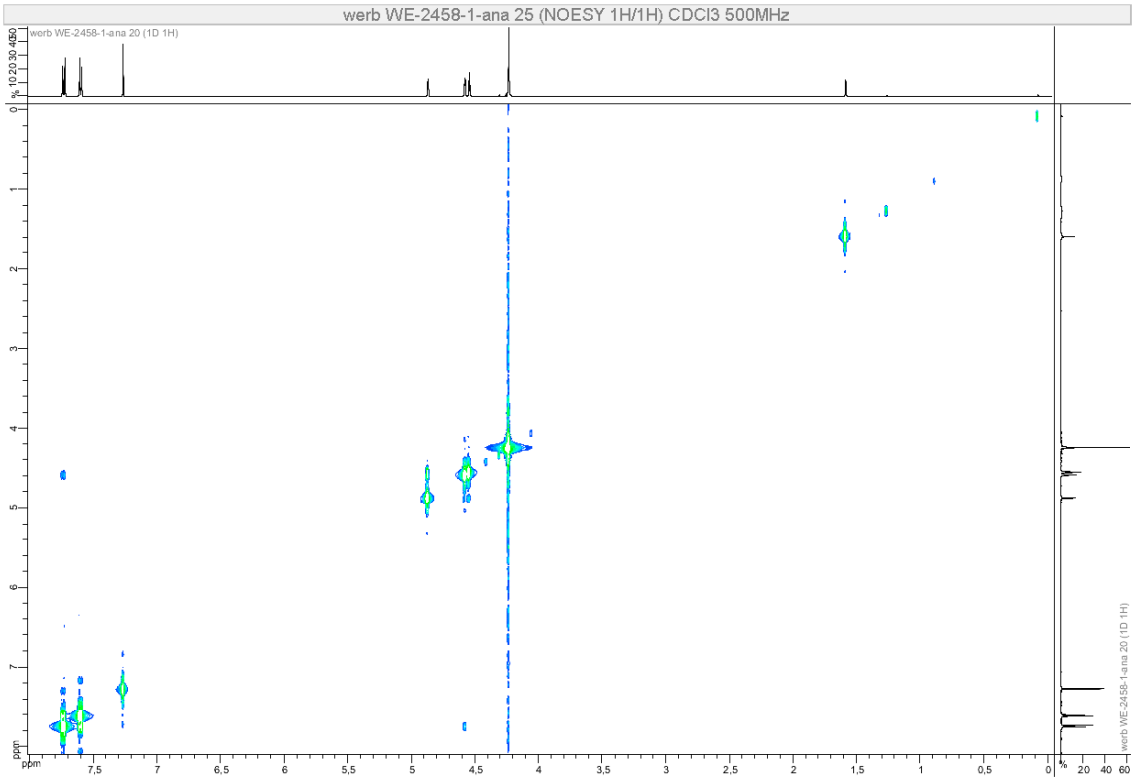
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

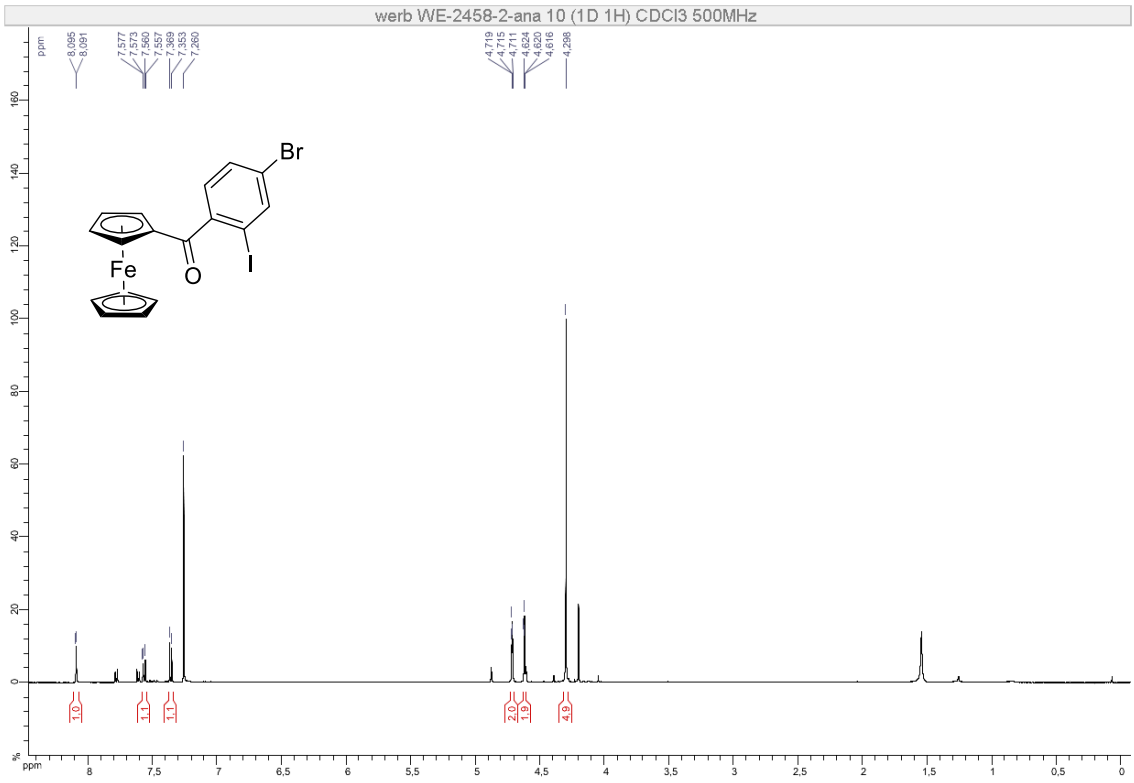


NOESY (500 MHz, $CDCl_3$)

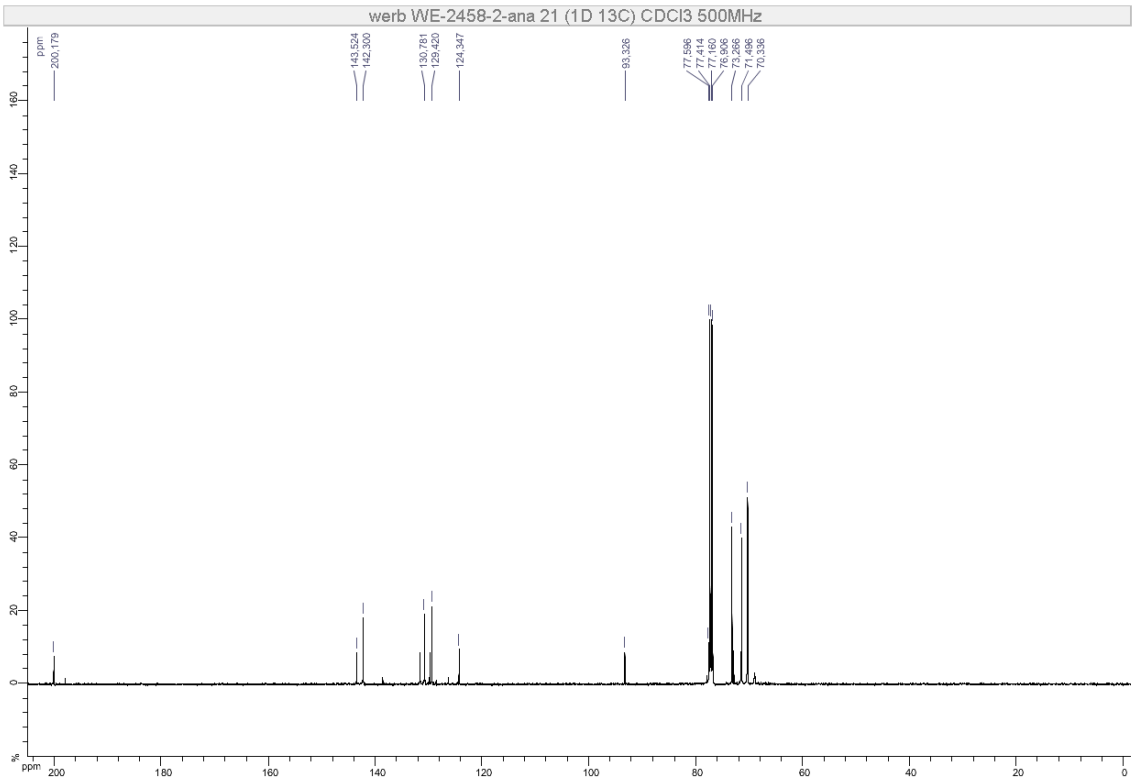


(4-Bromo-2-iodobenzoyl)ferrocene (2'-*p*BrPh)

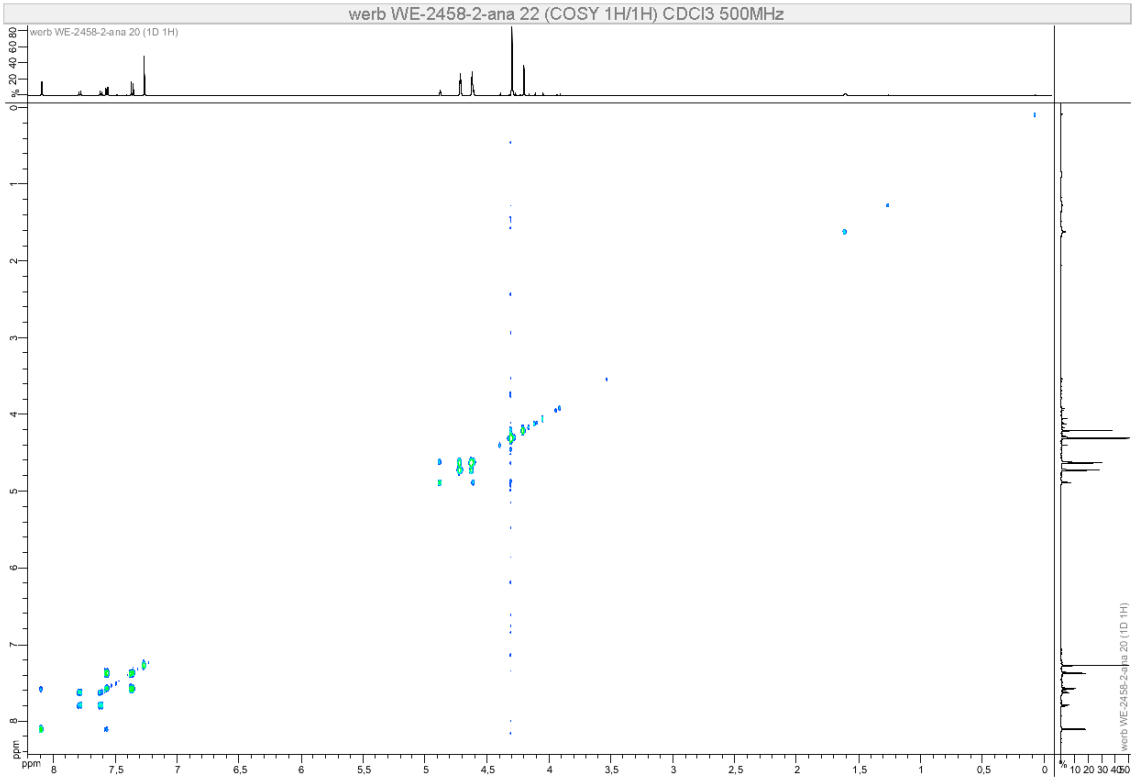
^{1}H NMR (500 MHz, $CDCl_3$)



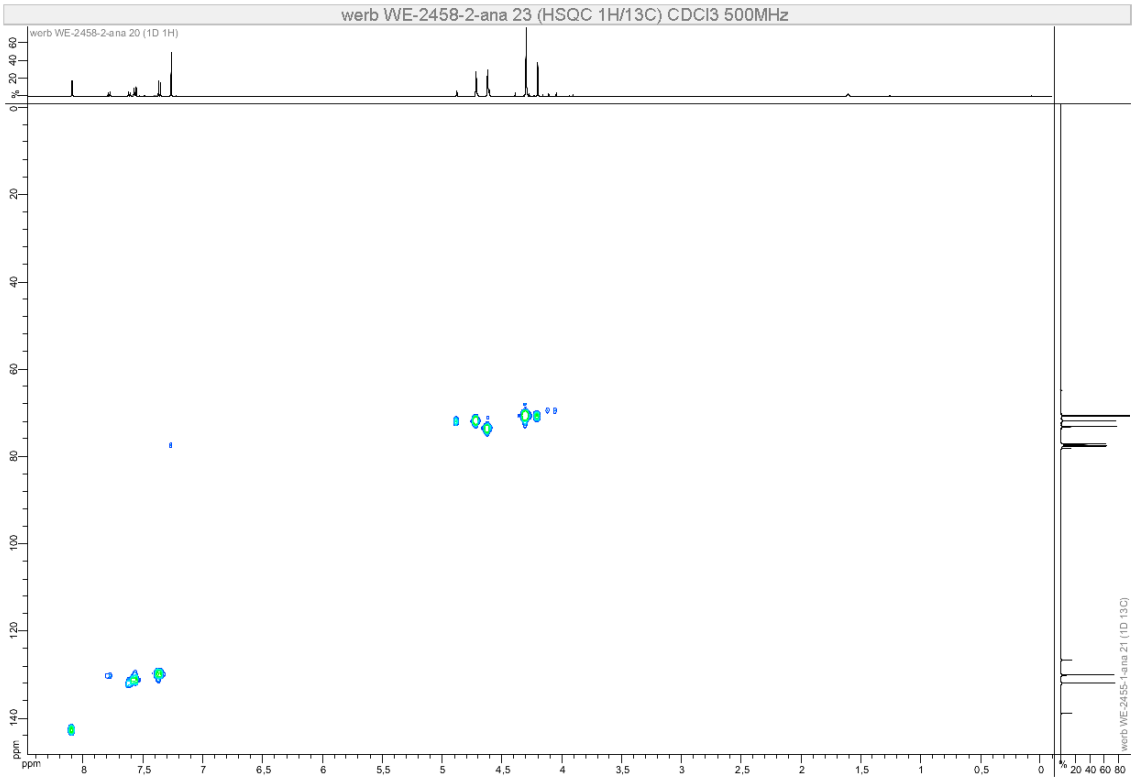
^{13}C NMR (126 MHz, $CDCl_3$)



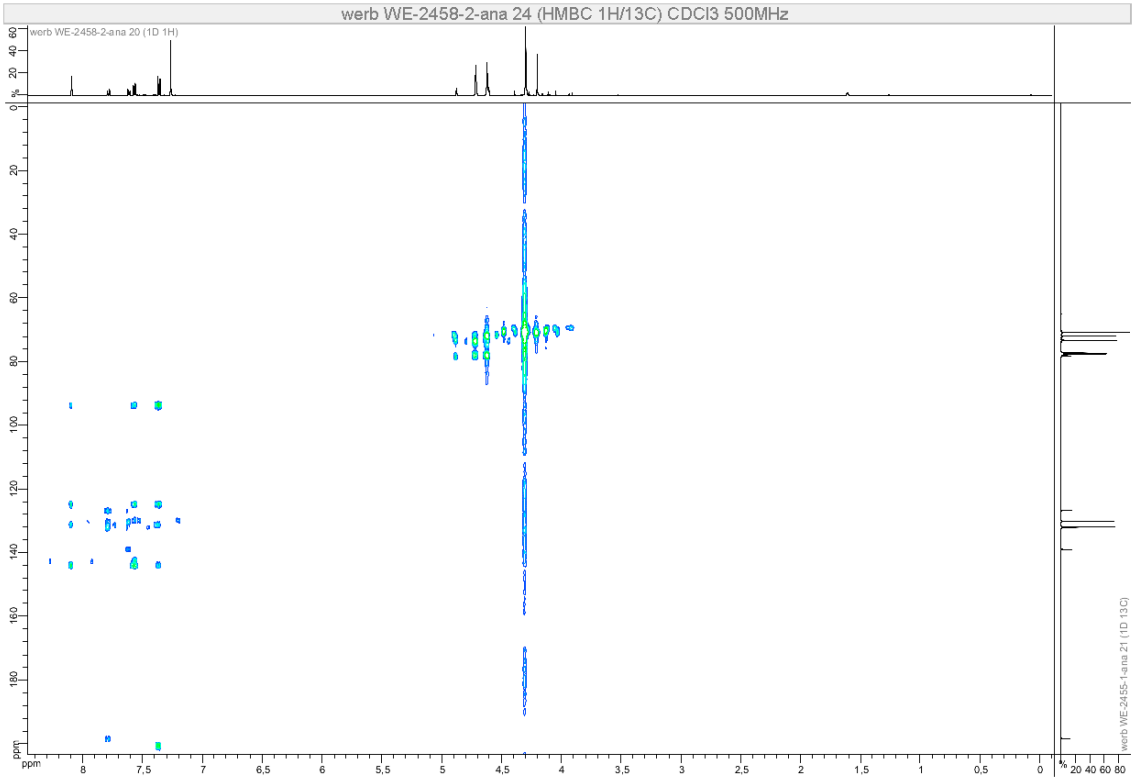
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

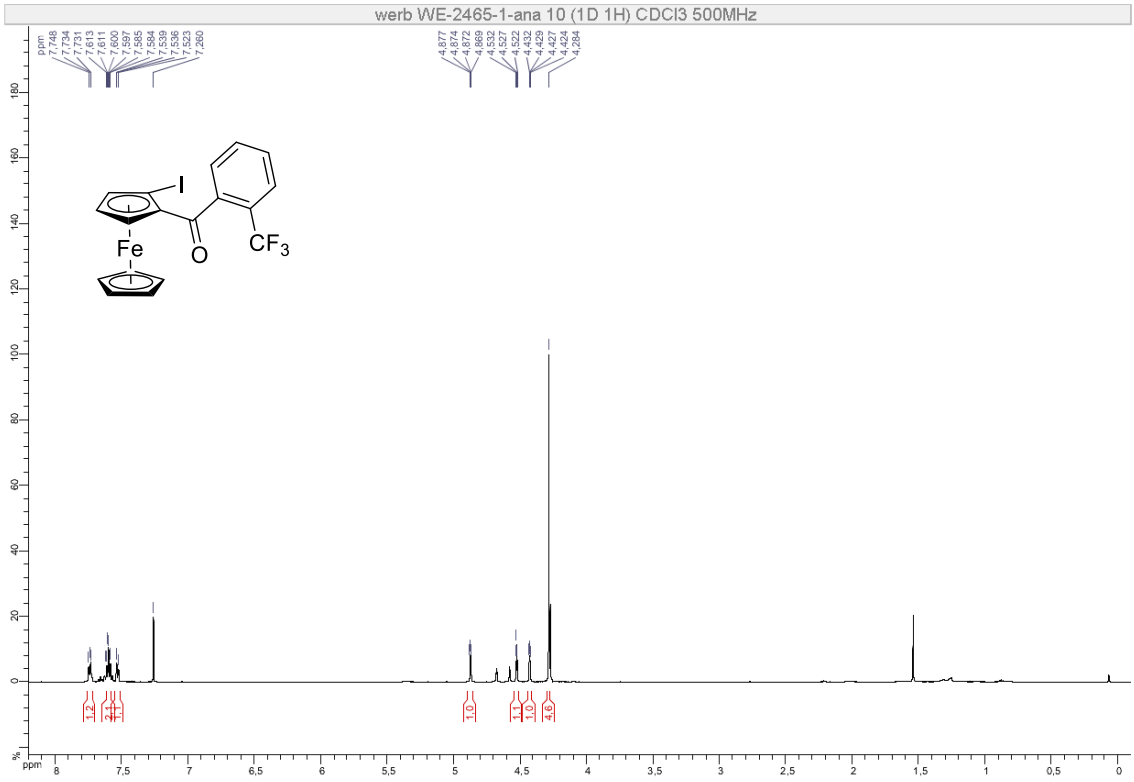


HMBC (500 MHz, $CDCl_3$)

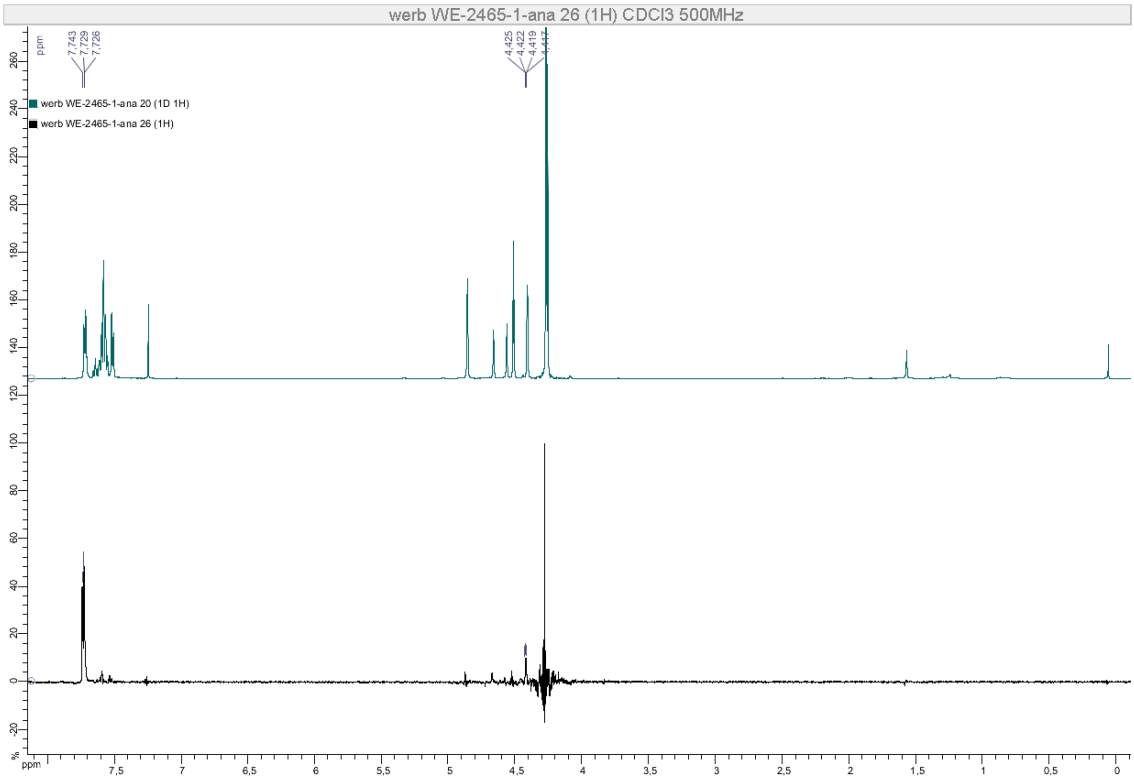


1-Iodo-2-[2-(trifluoromethyl)benzoyl]ferrocene (2-*o*CF_3Ph), mixture with 1-*o*CF_3Ph

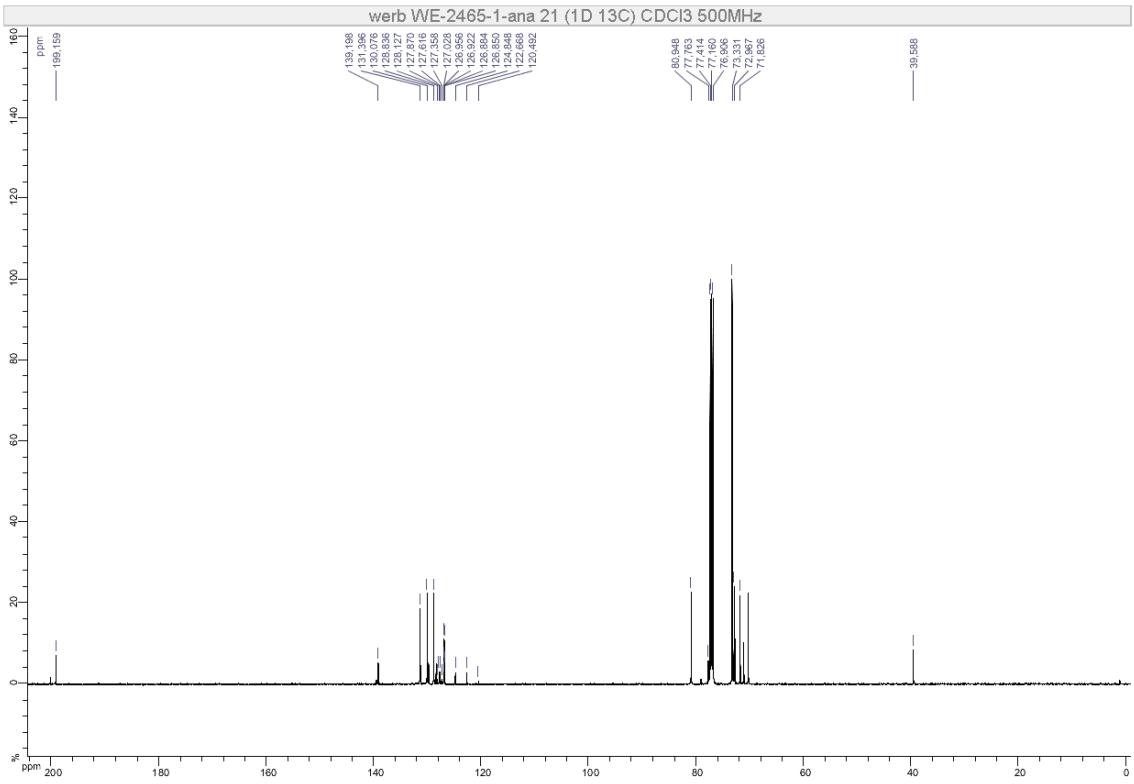
^{1}H NMR (500 MHz, $CDCl_3$)



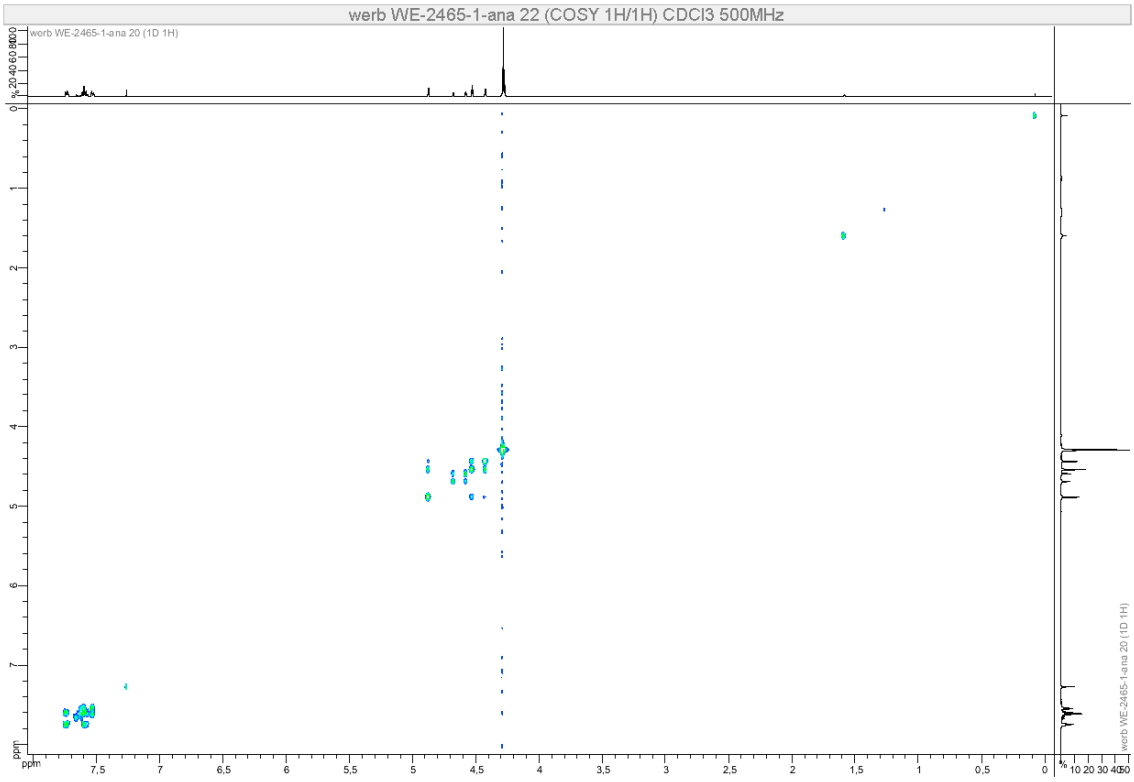
HOESY (500 MHz, $CDCl_3$) Irradiation at –57.5 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



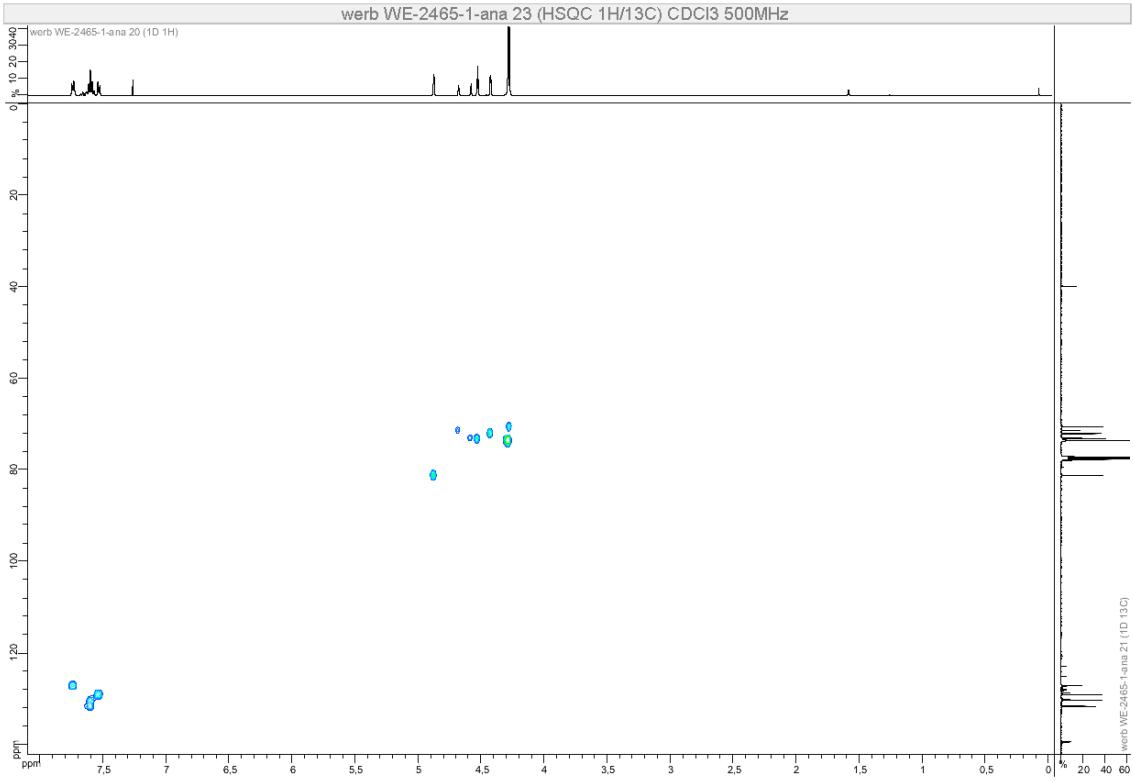
^{13}C NMR (126 MHz, $CDCl_3$)



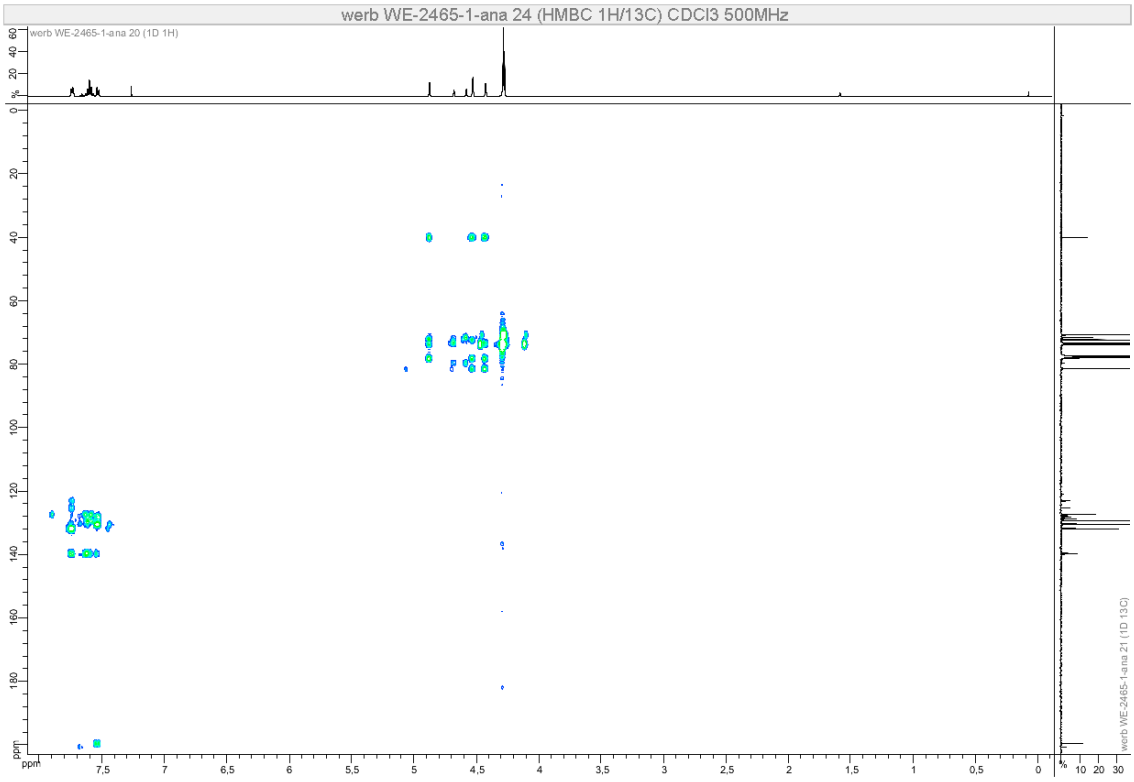
COSY (500 MHz, $CDCl_3$)



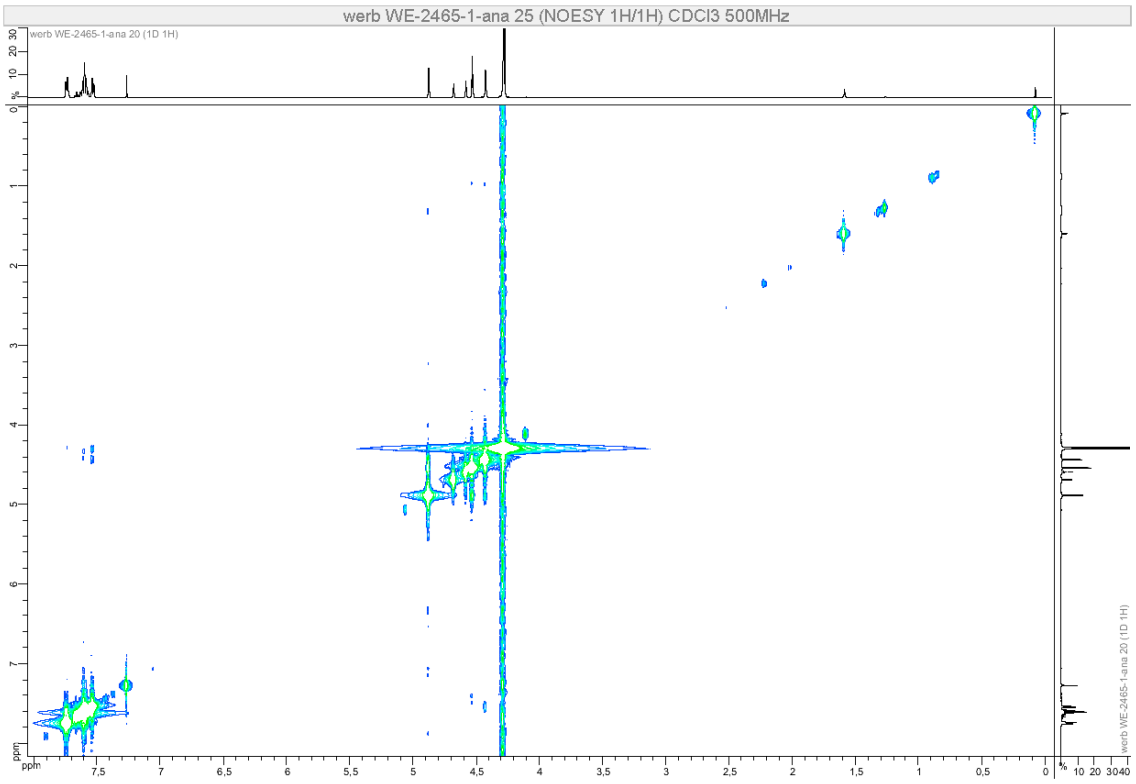
HSQC (500 MHz, $CDCl_3$)



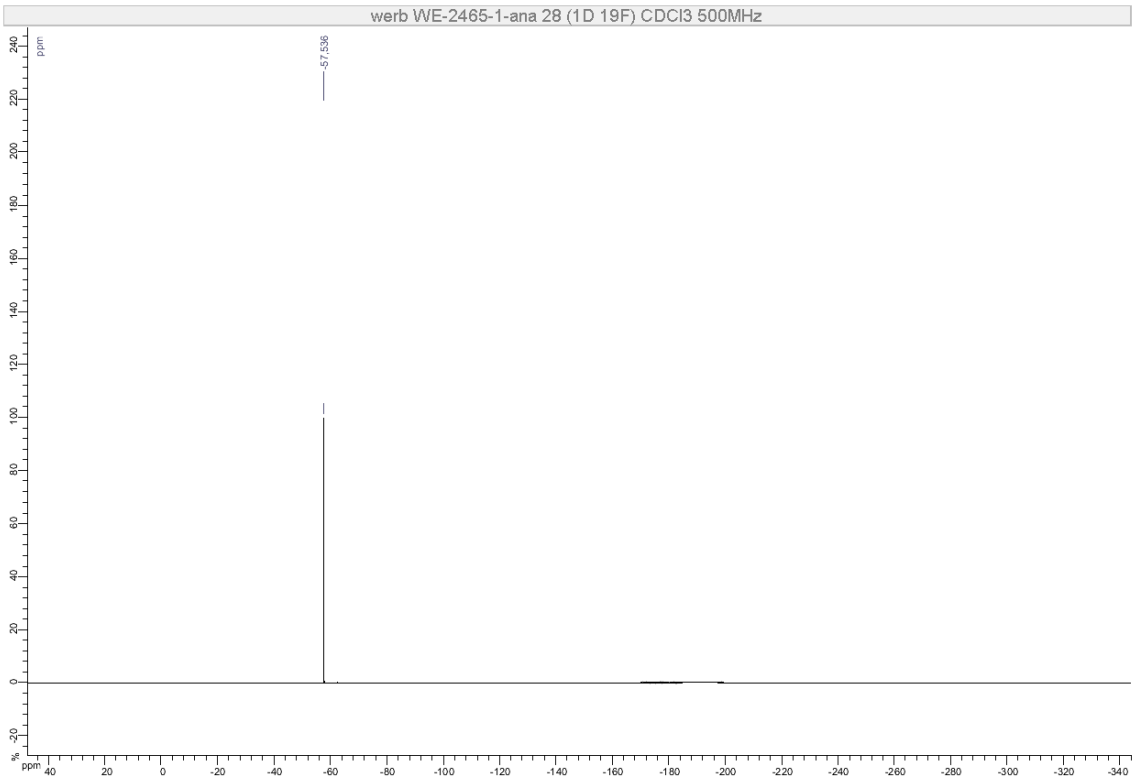
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

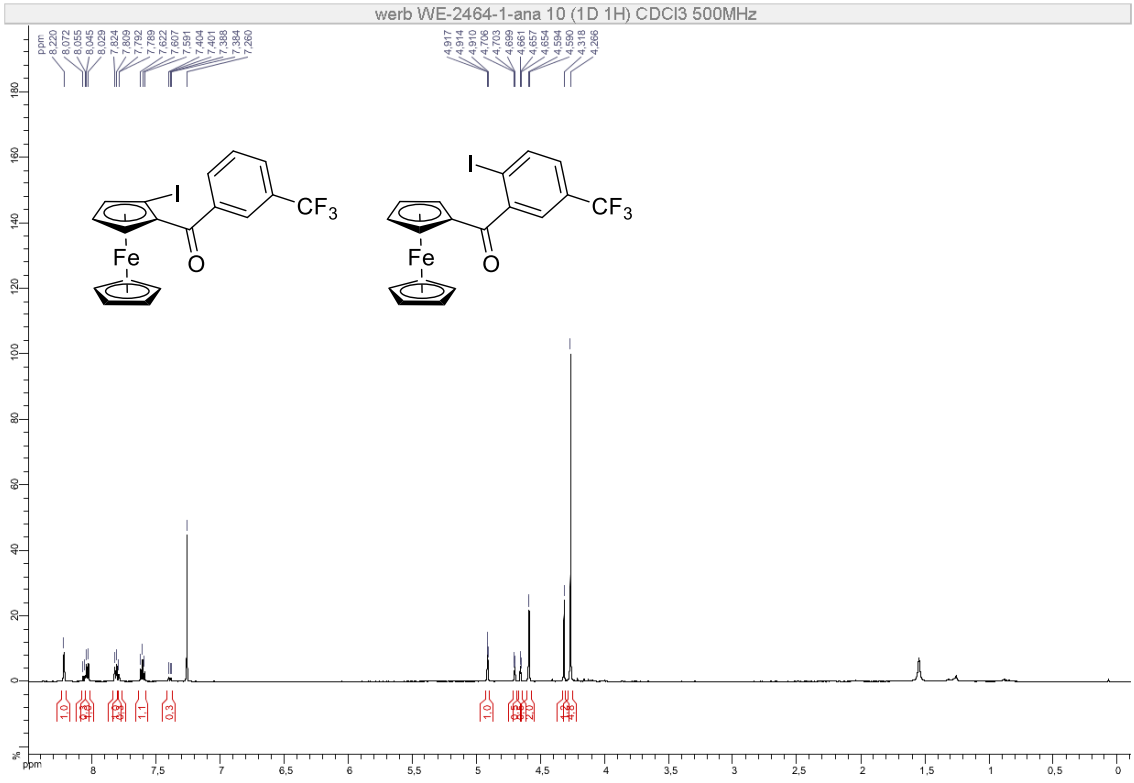


^{19}F NMR (470 MHz, $CDCl_3$)

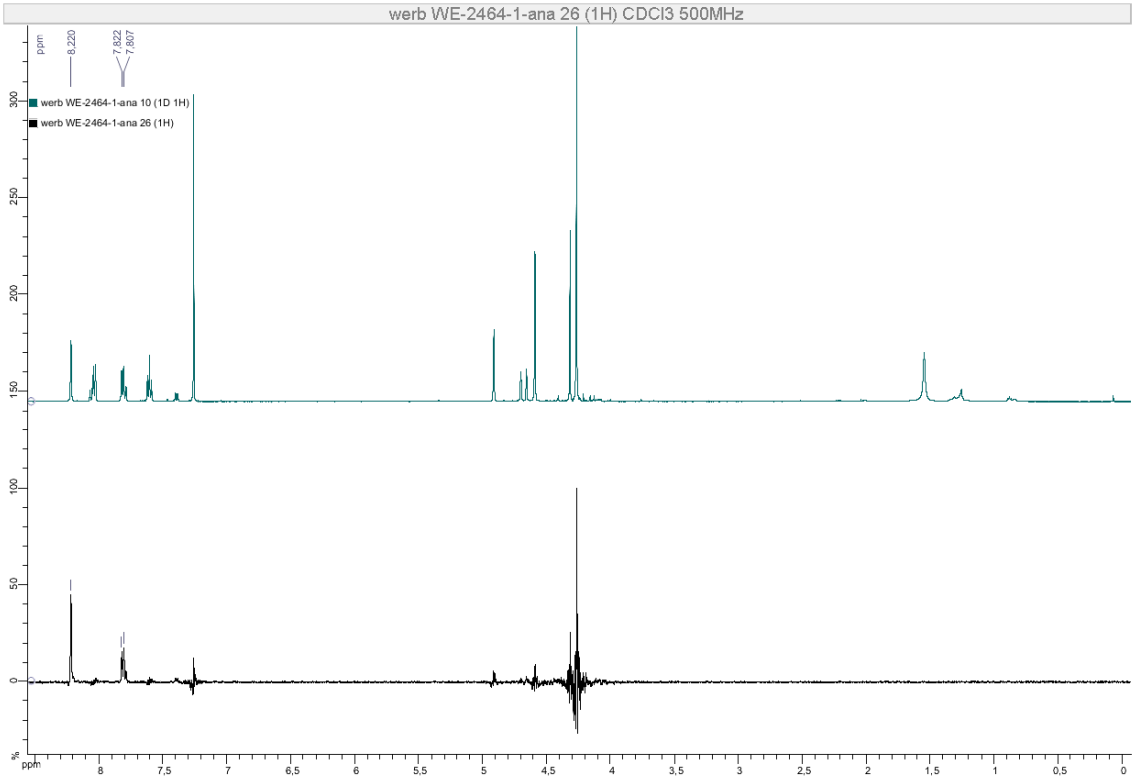


1-Iodo-2-[3-(trifluoromethyl)benzoyl]ferrocene (2-*m*CF_3Ph), mixture with 2-iodo-5-(trifluoromethyl)benzoyl]ferrocene (2'-*m*CF_3Ph)

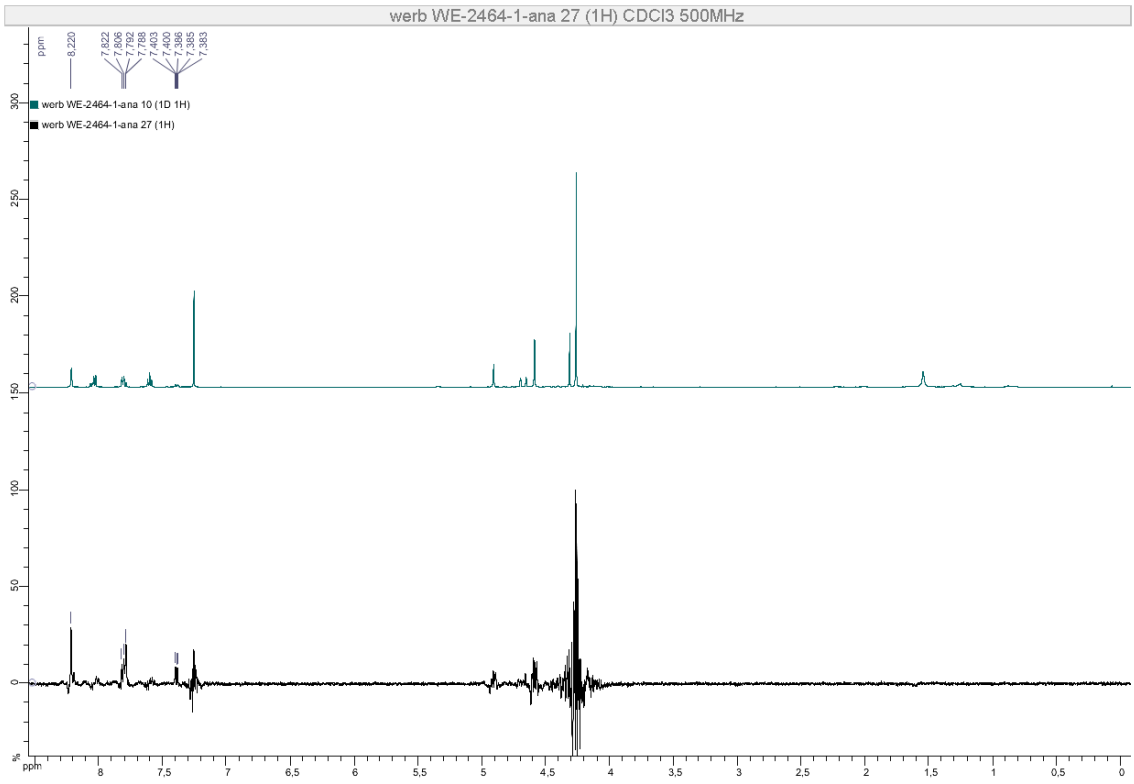
^{1}H NMR (500 MHz, $CDCl_3$)



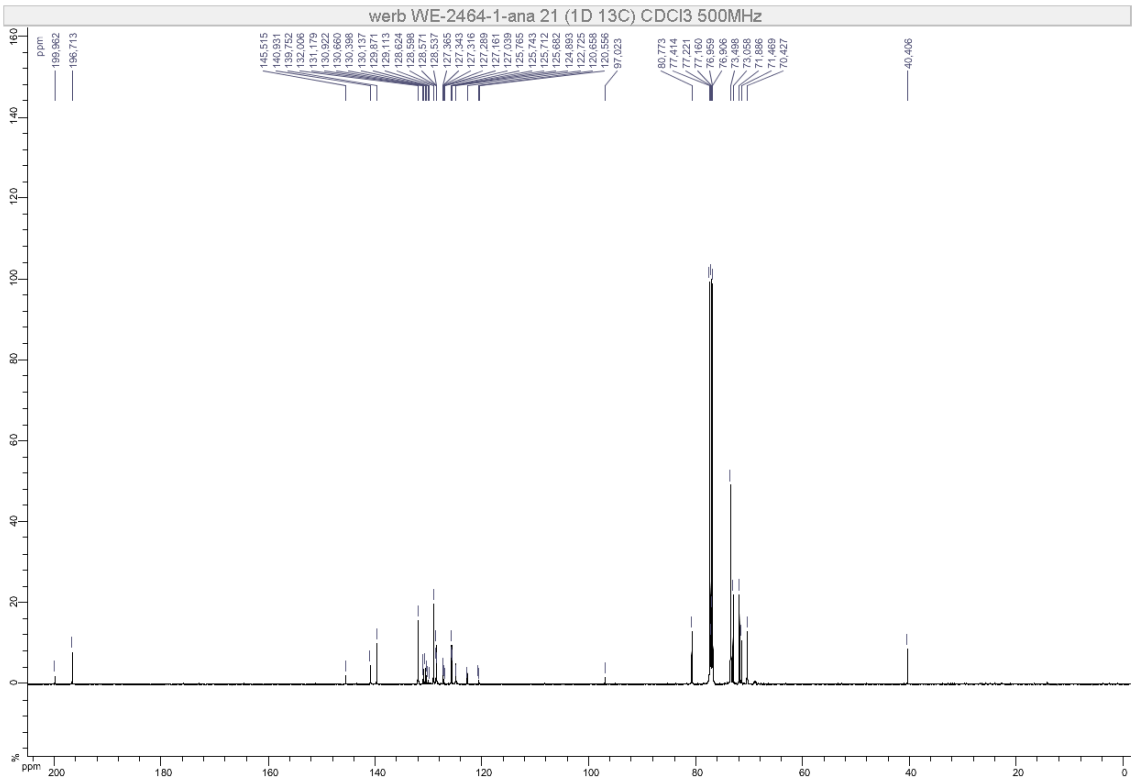
HOESY (500 MHz, $CDCl_3$) Irradiation at –62.6 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



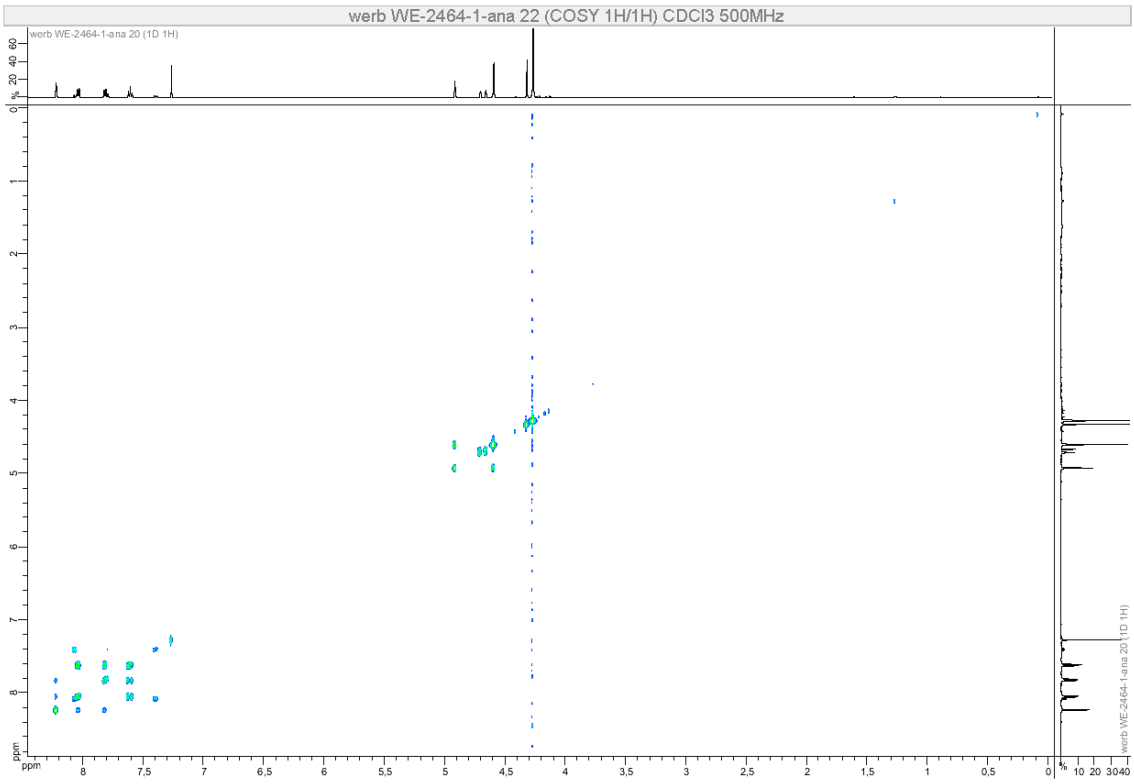
HOESY (500 MHz, $CDCl_3$) Irradiation at –62.9 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



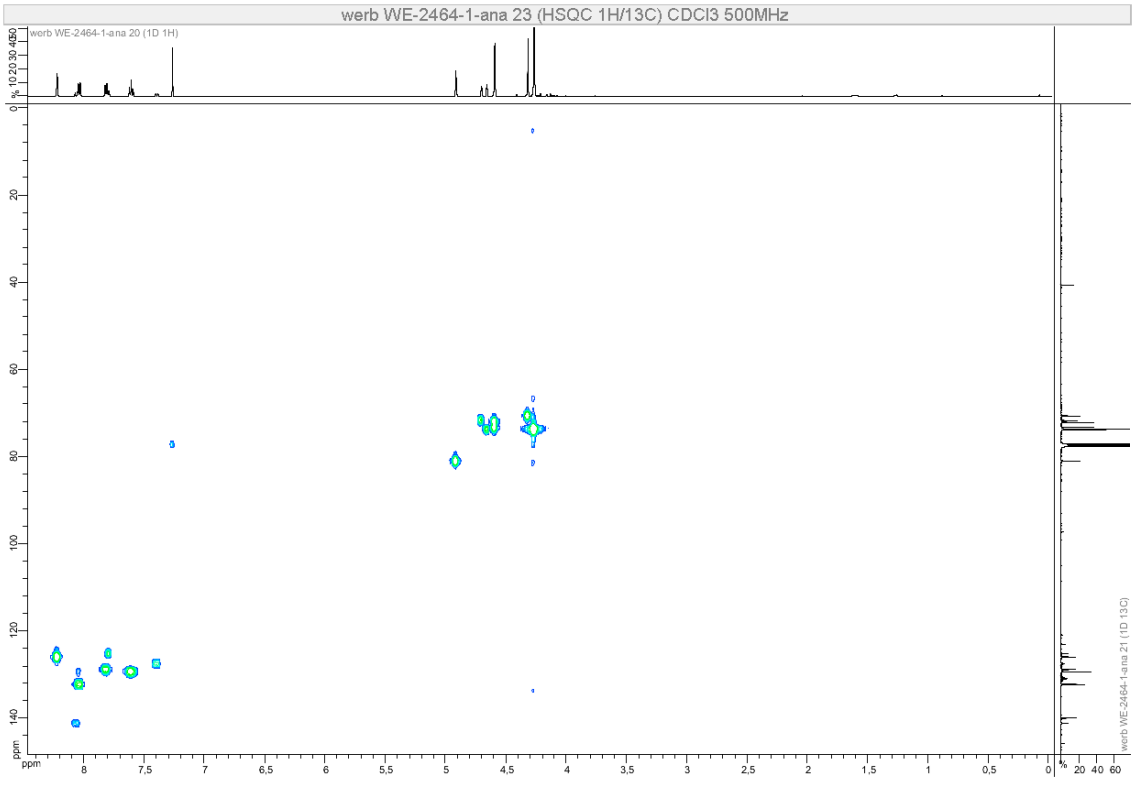
^{13}C NMR (126 MHz, $CDCl_3$)



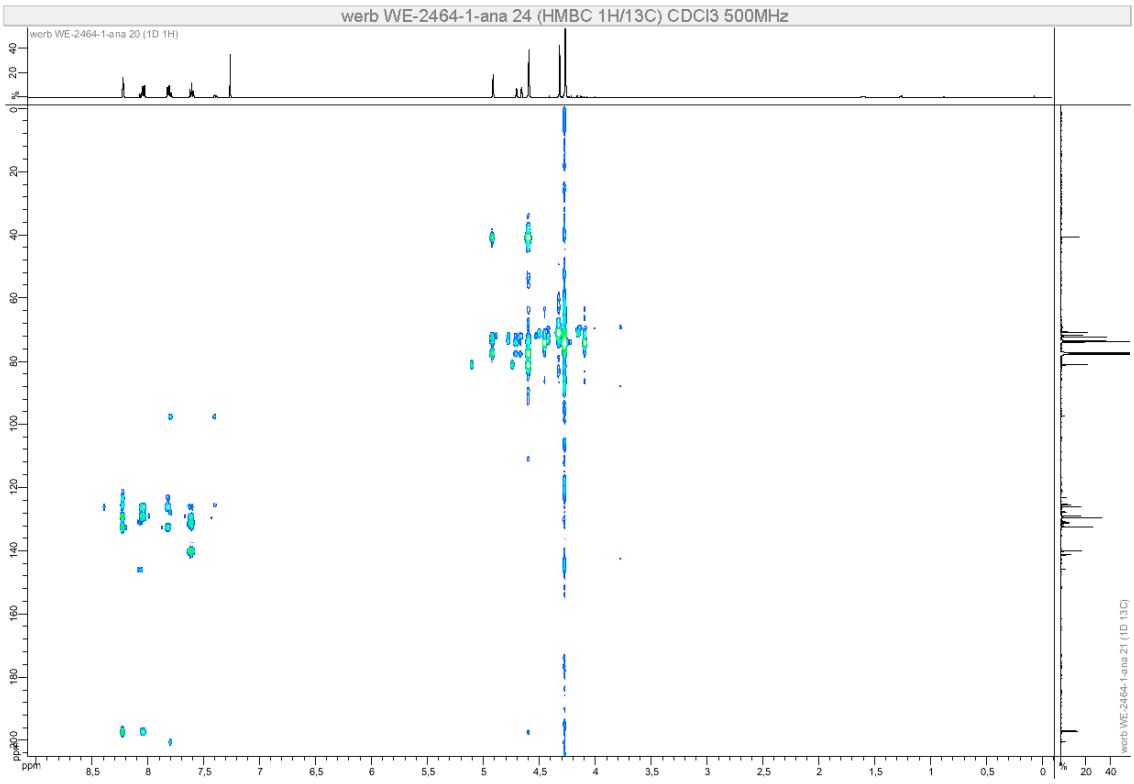
COSY (500 MHz, $CDCl_3$)



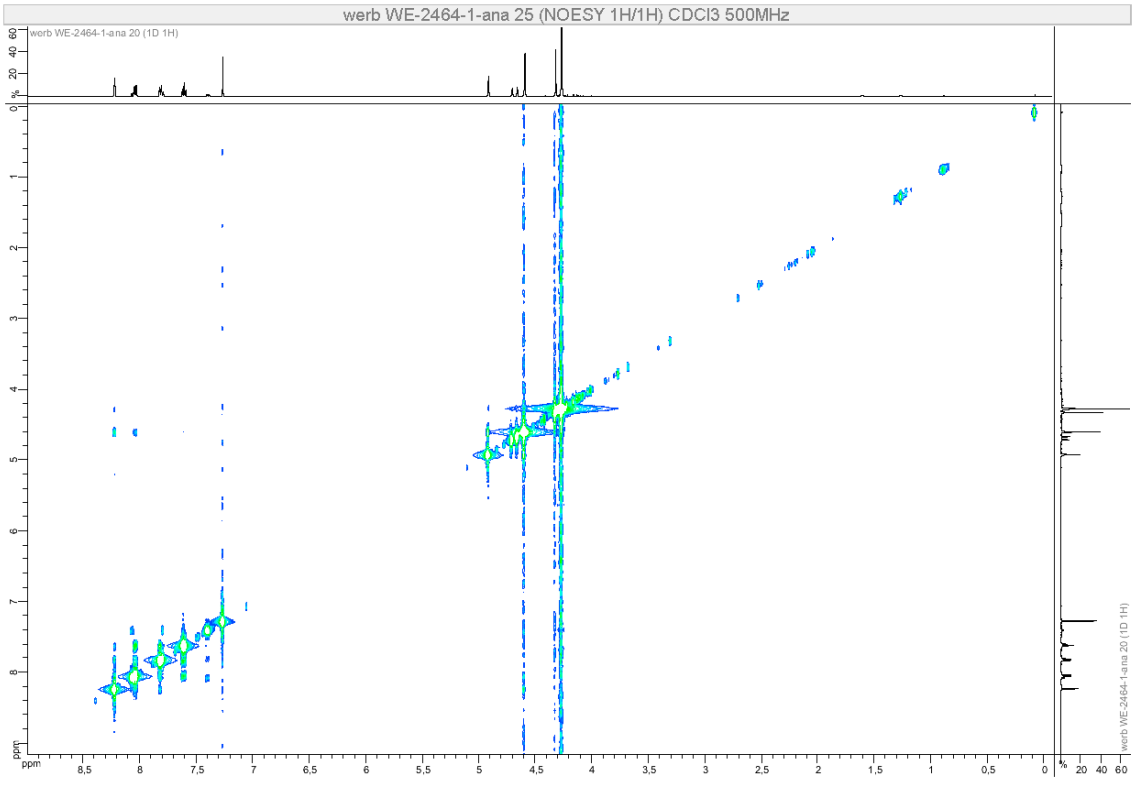
HSQC (500 MHz, $CDCl_3$)



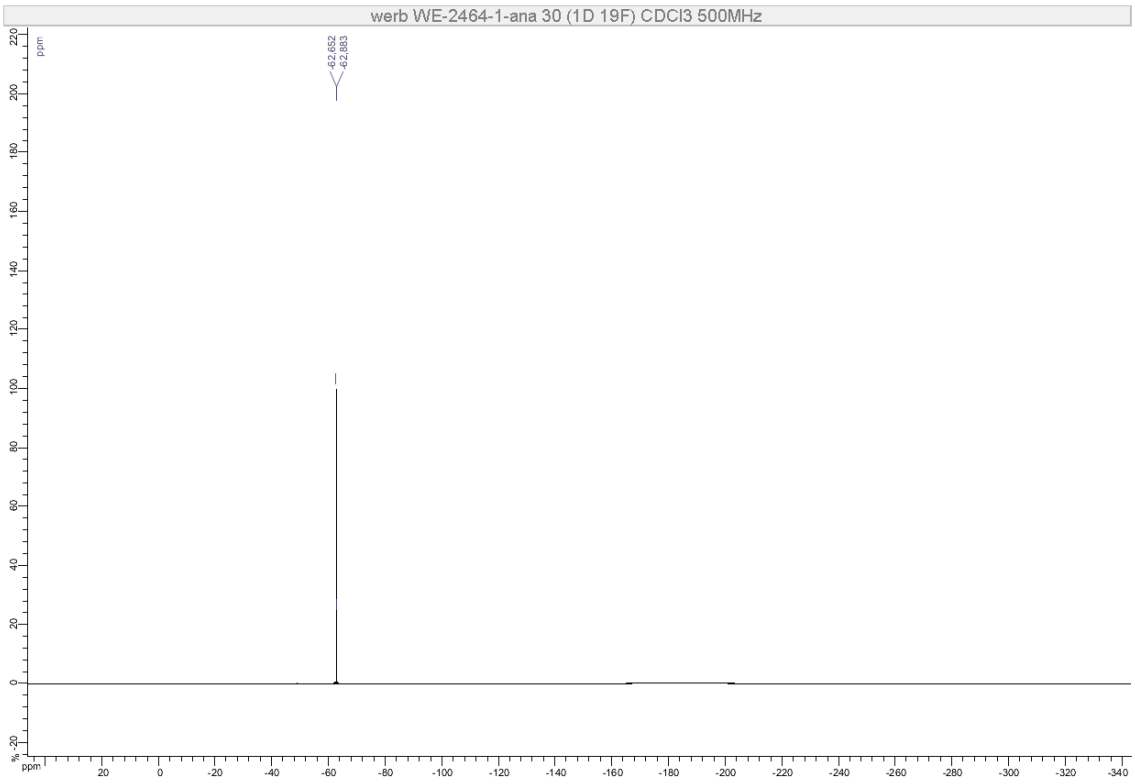
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

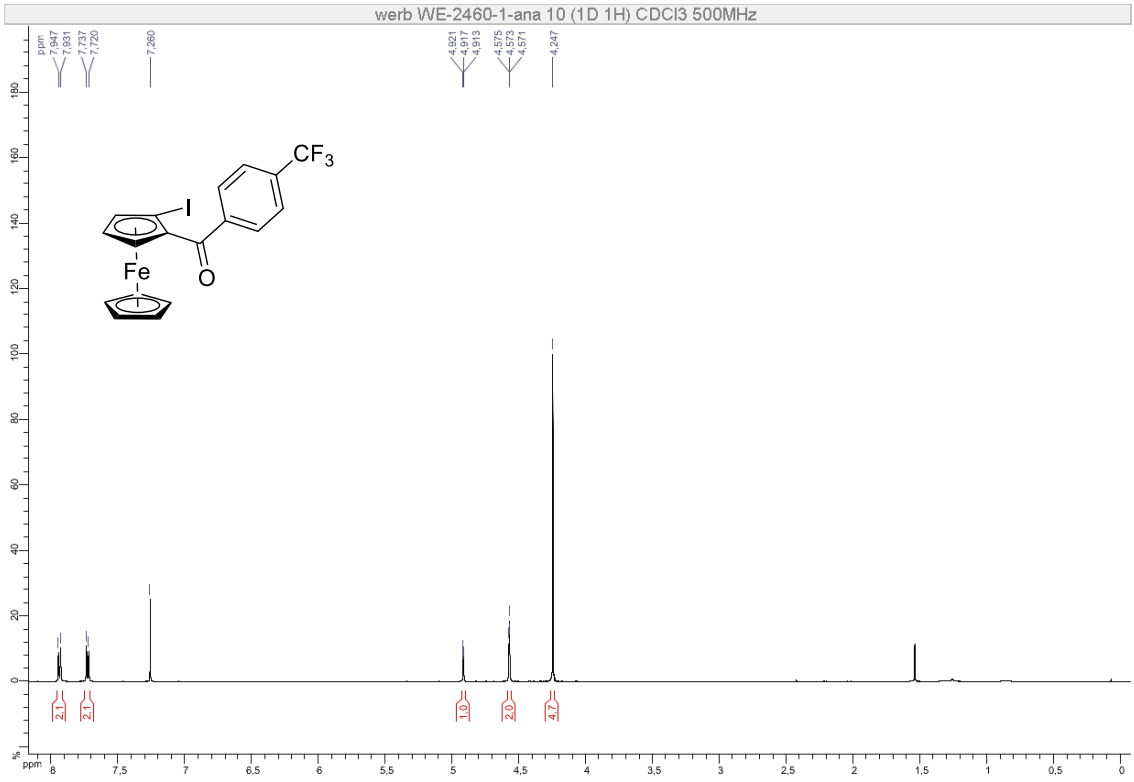


^{19}F NMR (470 MHz, $CDCl_3$)

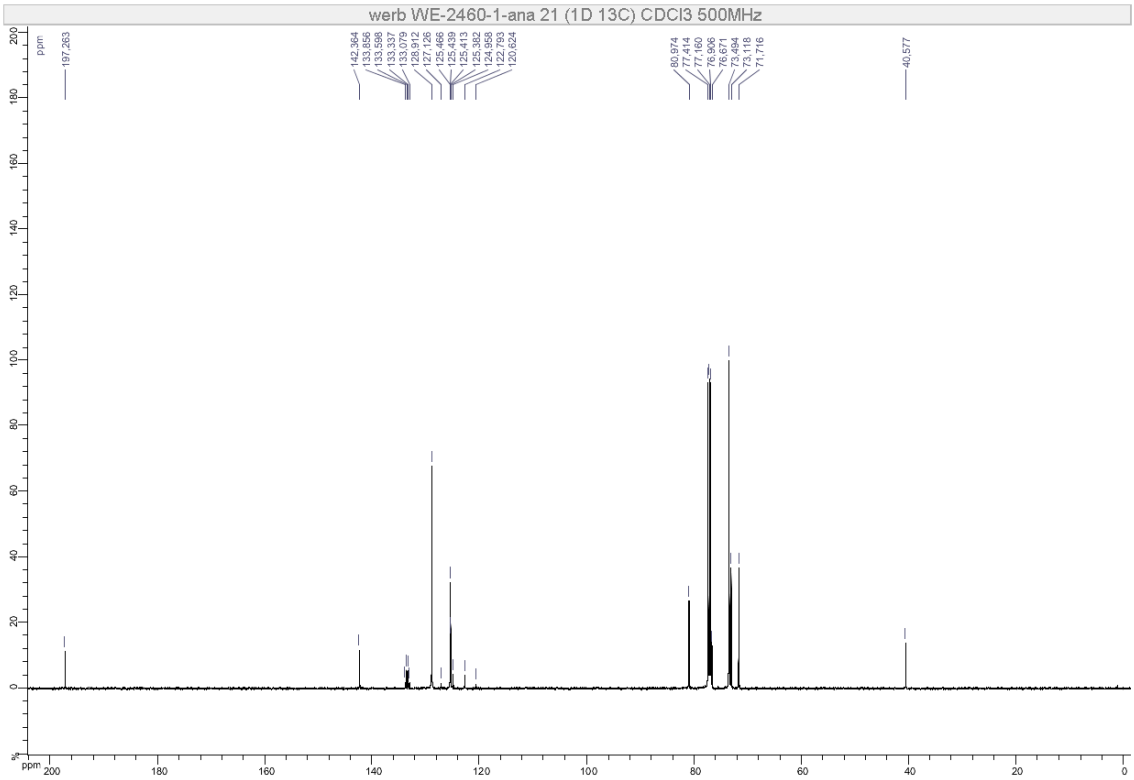


1-Iodo-2-[4-(trifluoromethyl)benzoyl]ferrocene (2-*p*CF_3Ph)

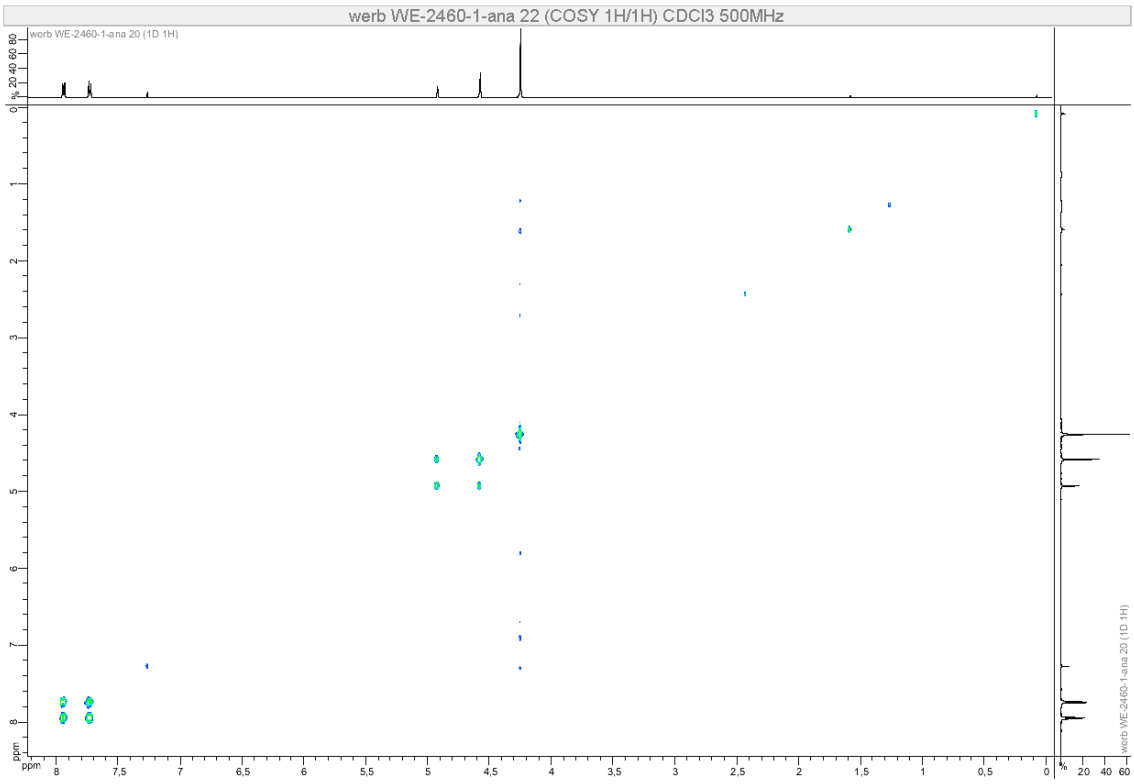
^{1}H NMR (500 MHz, $CDCl_3$)



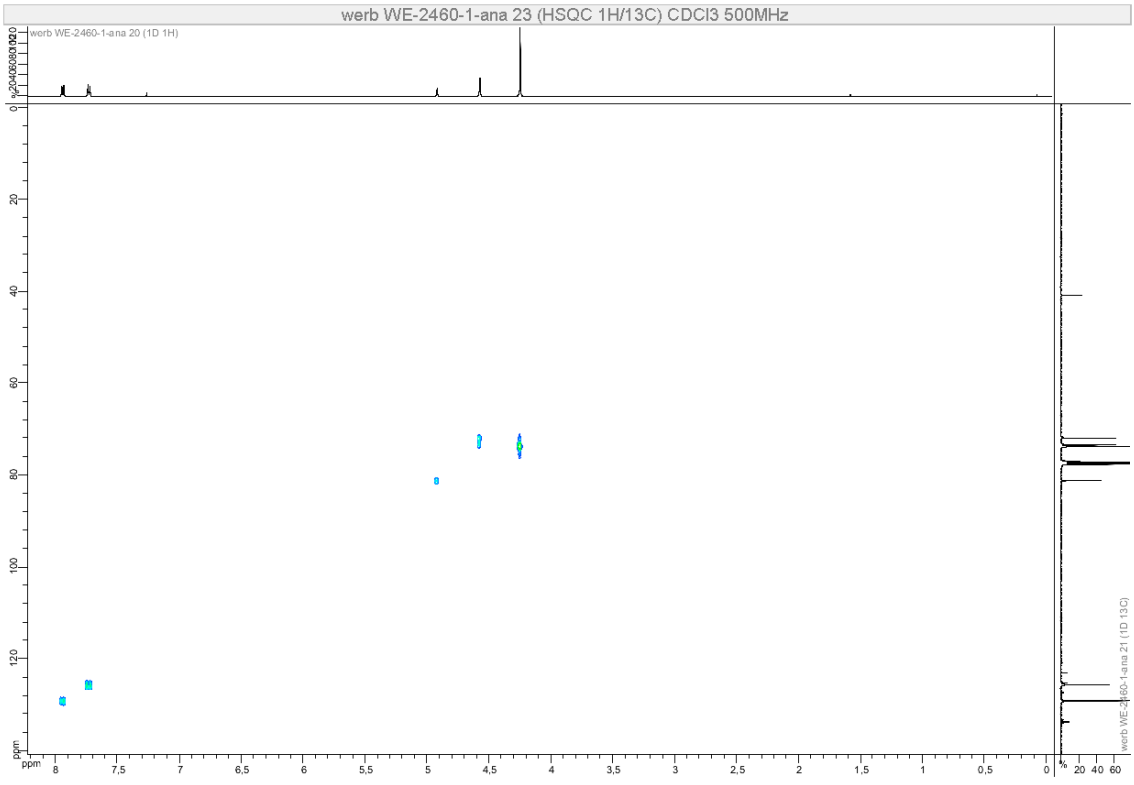
^{13}C NMR (126 MHz, $CDCl_3$)



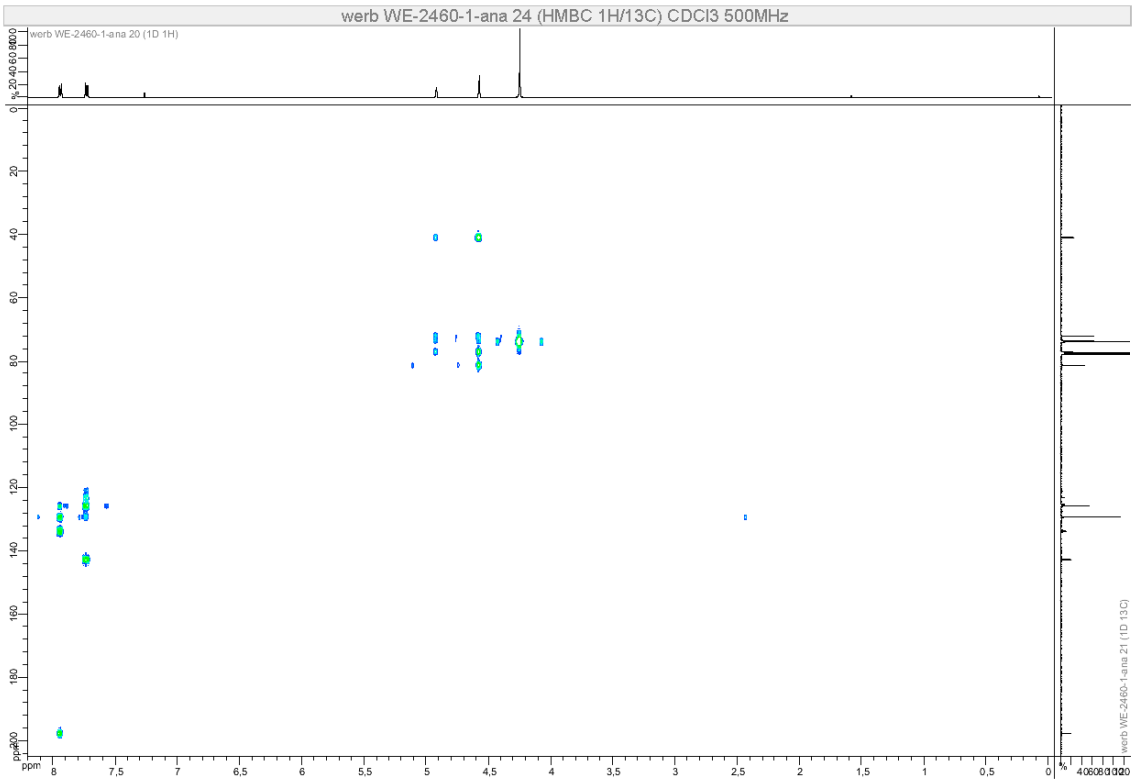
COSY (500 MHz, $CDCl_3$)



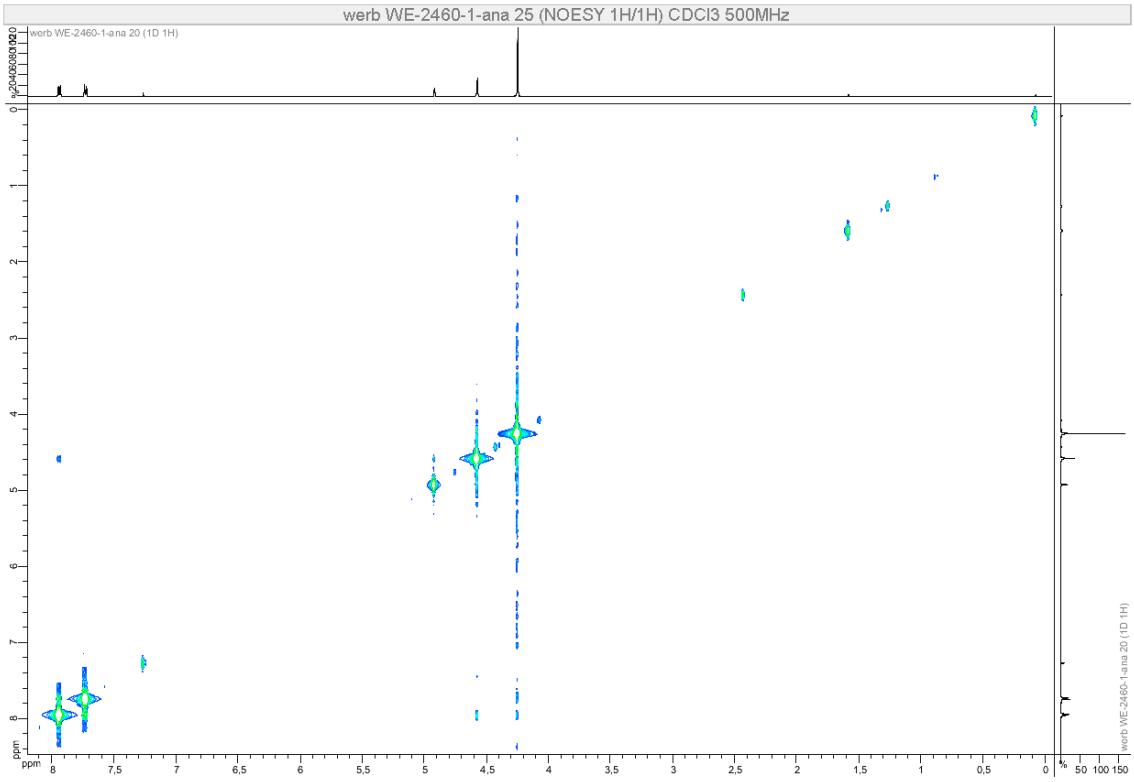
HSQC (500 MHz, $CDCl_3$)



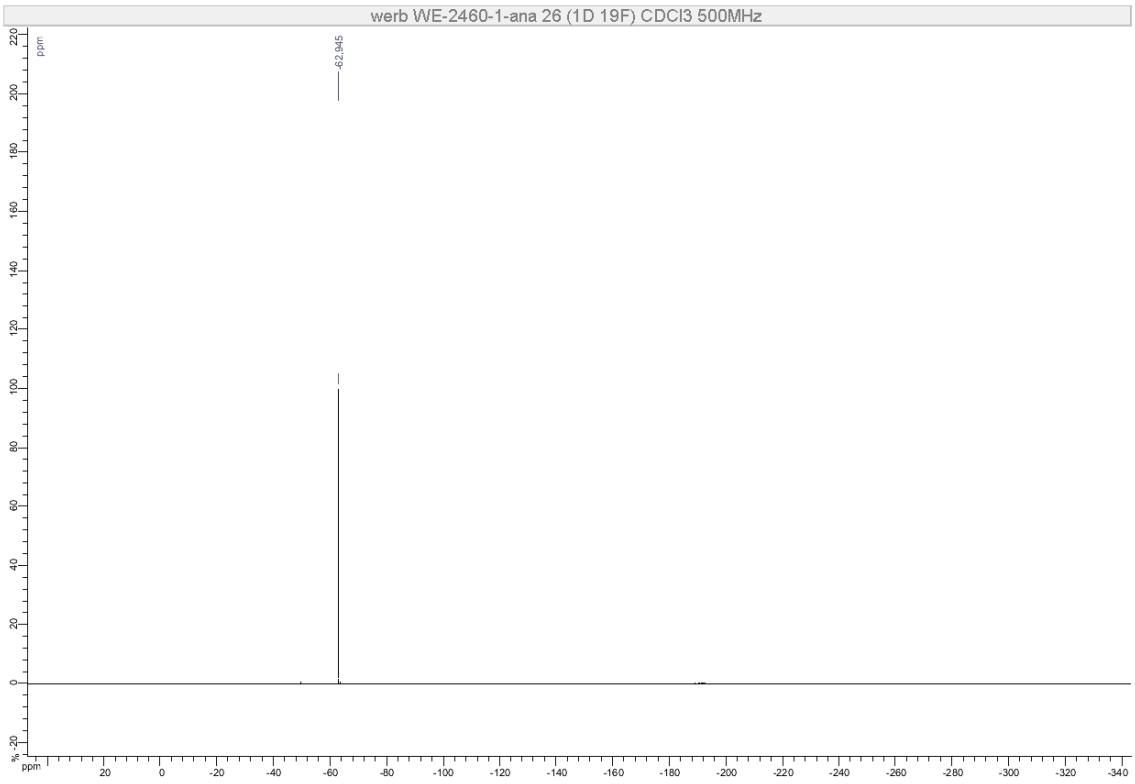
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

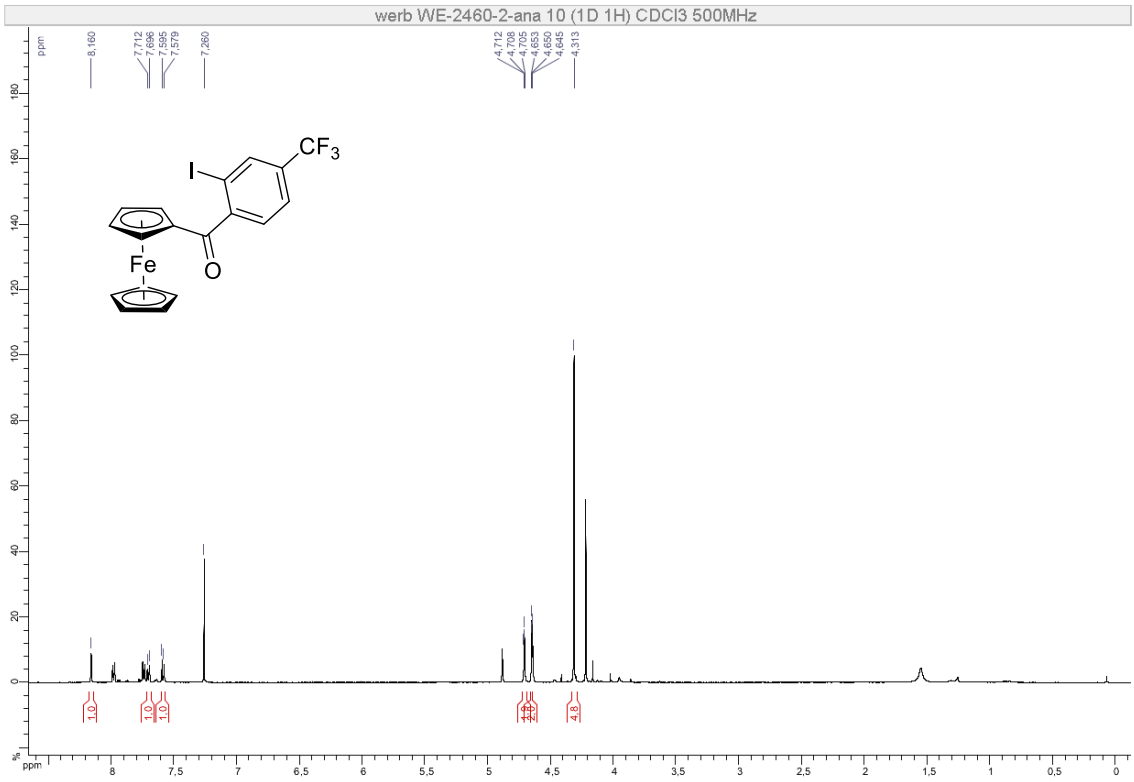


^{19}F NMR (470 MHz, $CDCl_3$)

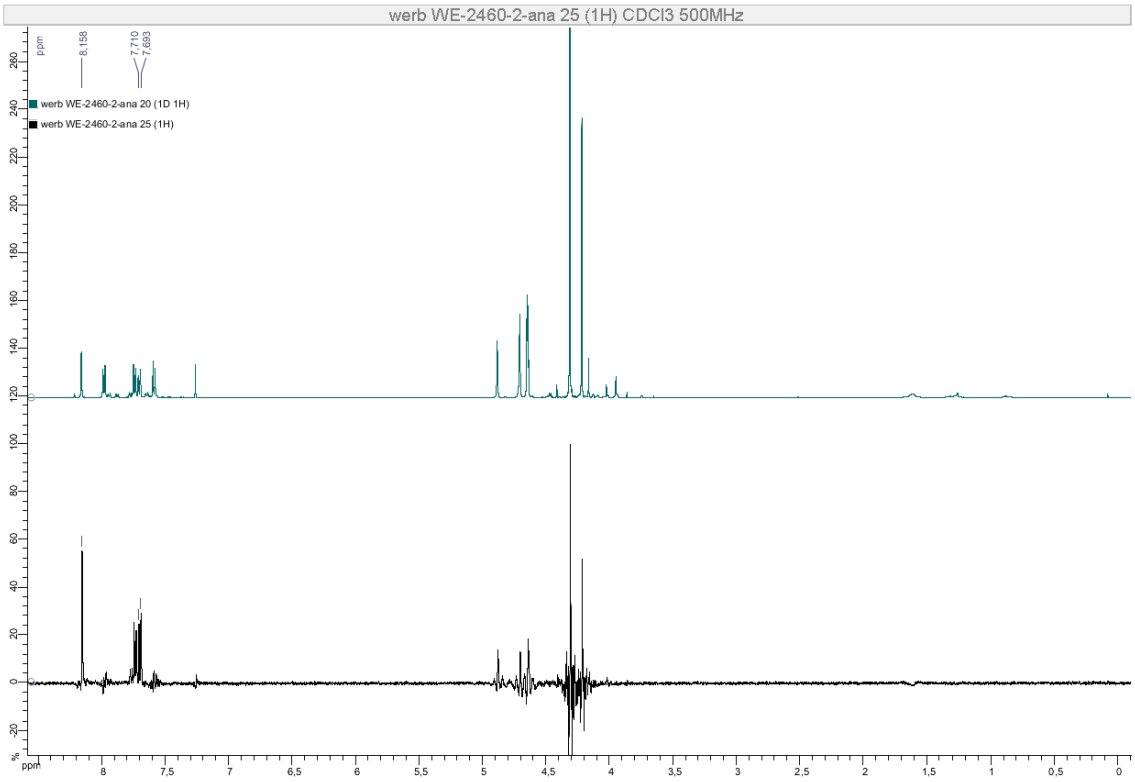


[2-Iodo-4-(trifluoromethyl)benzoyl]ferrocene (2'-*p*CF_3Ph), mixture with 1-*p*CF_3Ph

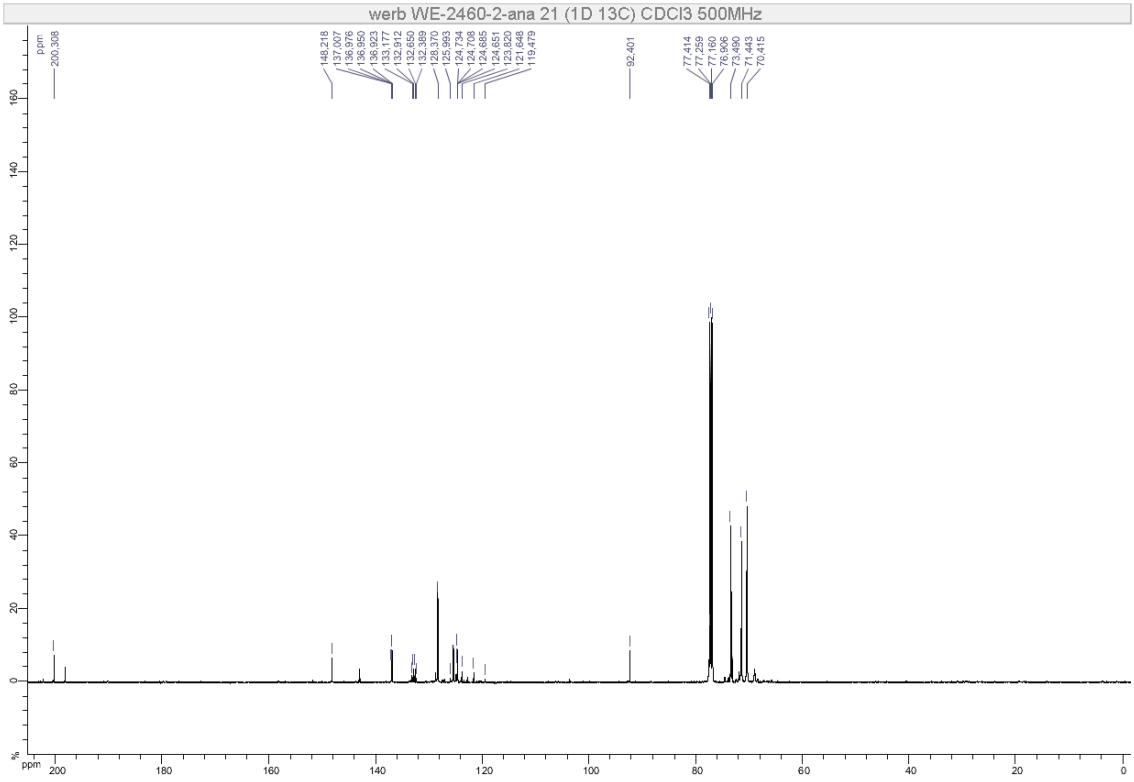
^{1}H NMR (500 MHz, $CDCl_3$)



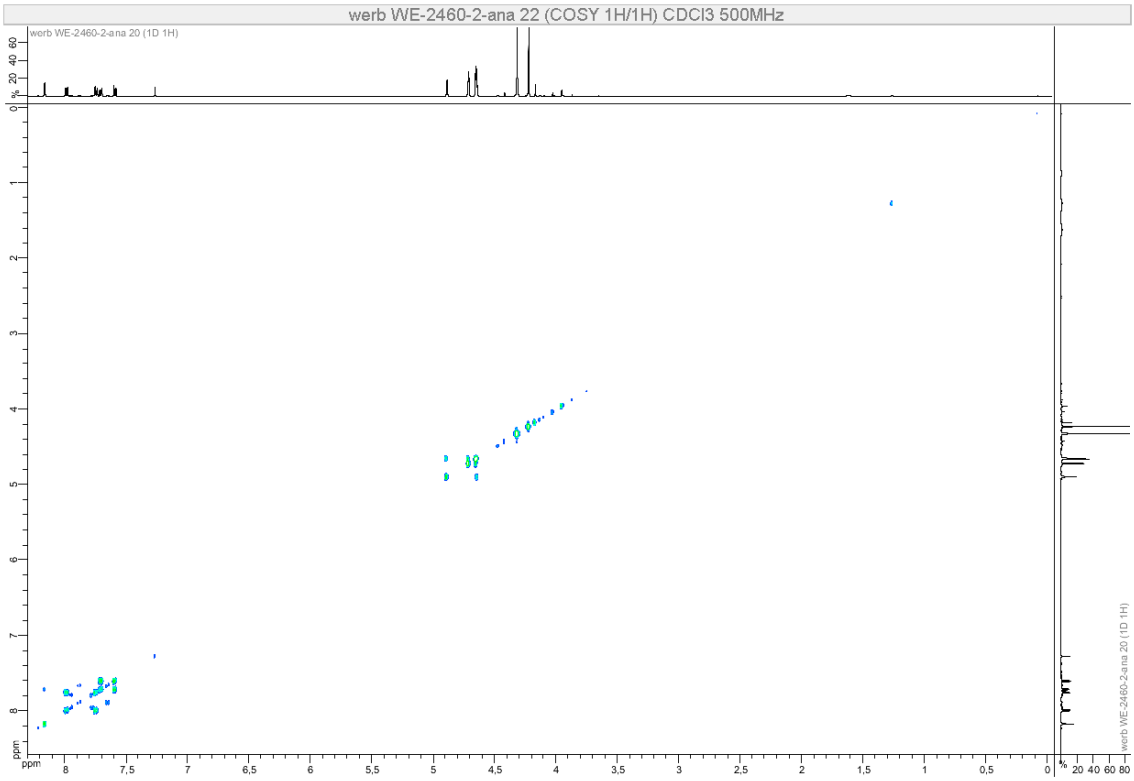
HOESY (500 MHz, $CDCl_3$) Irradiation at –62.8 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



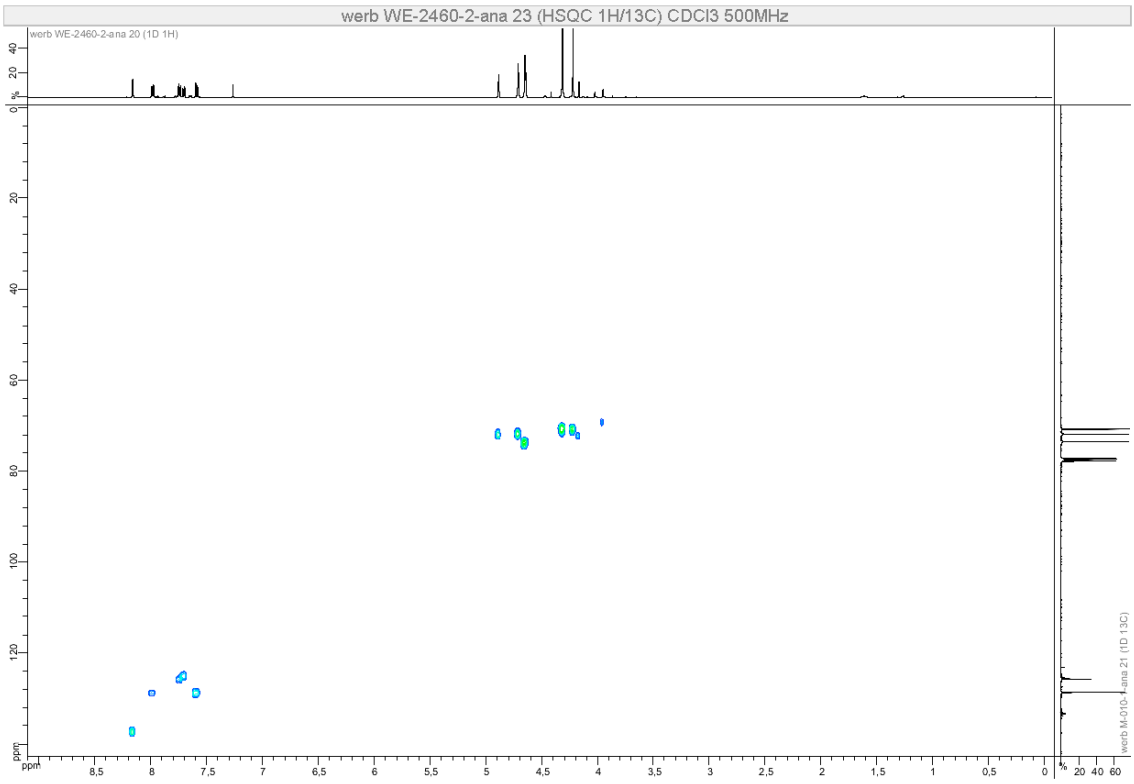
^{13}C NMR (126 MHz, $CDCl_3$)



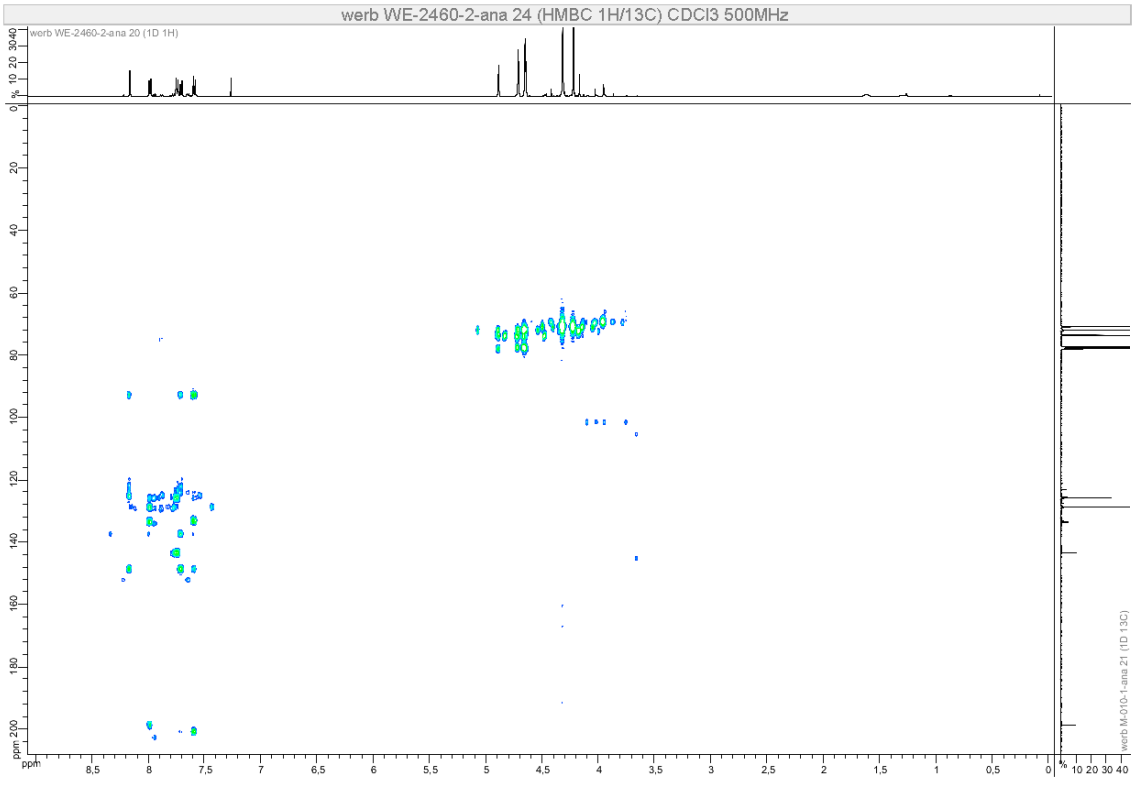
COSY (500 MHz, $CDCl_3$)



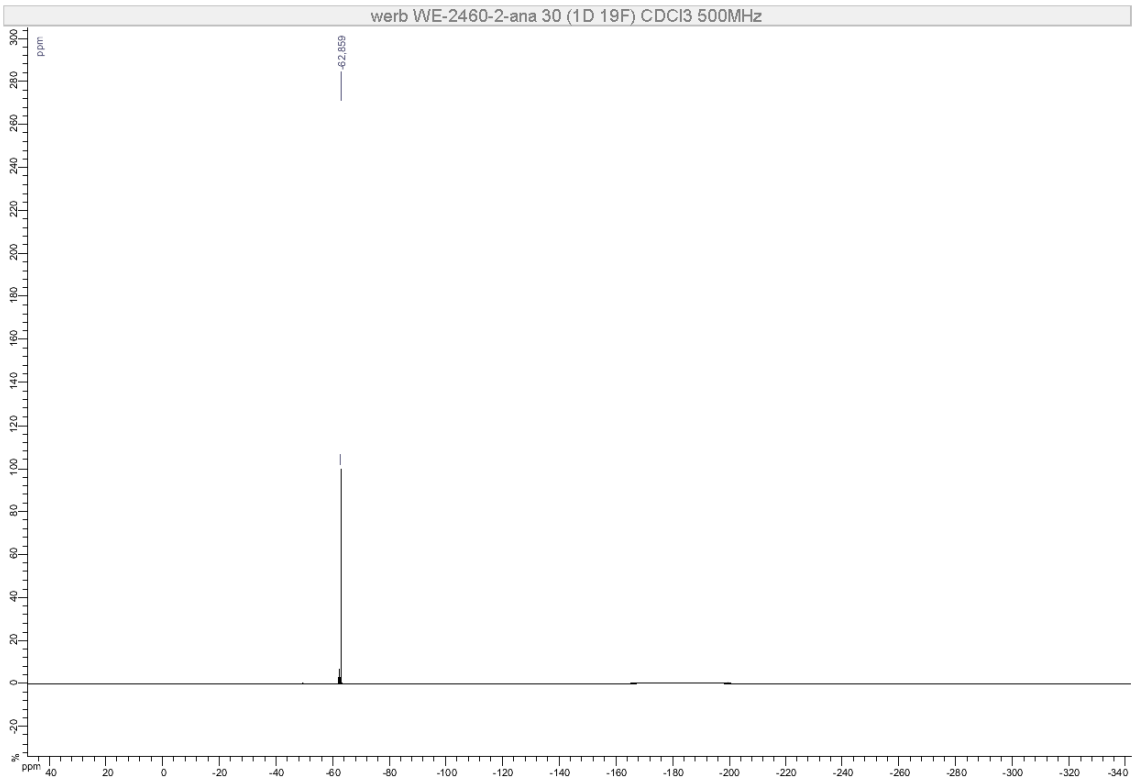
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

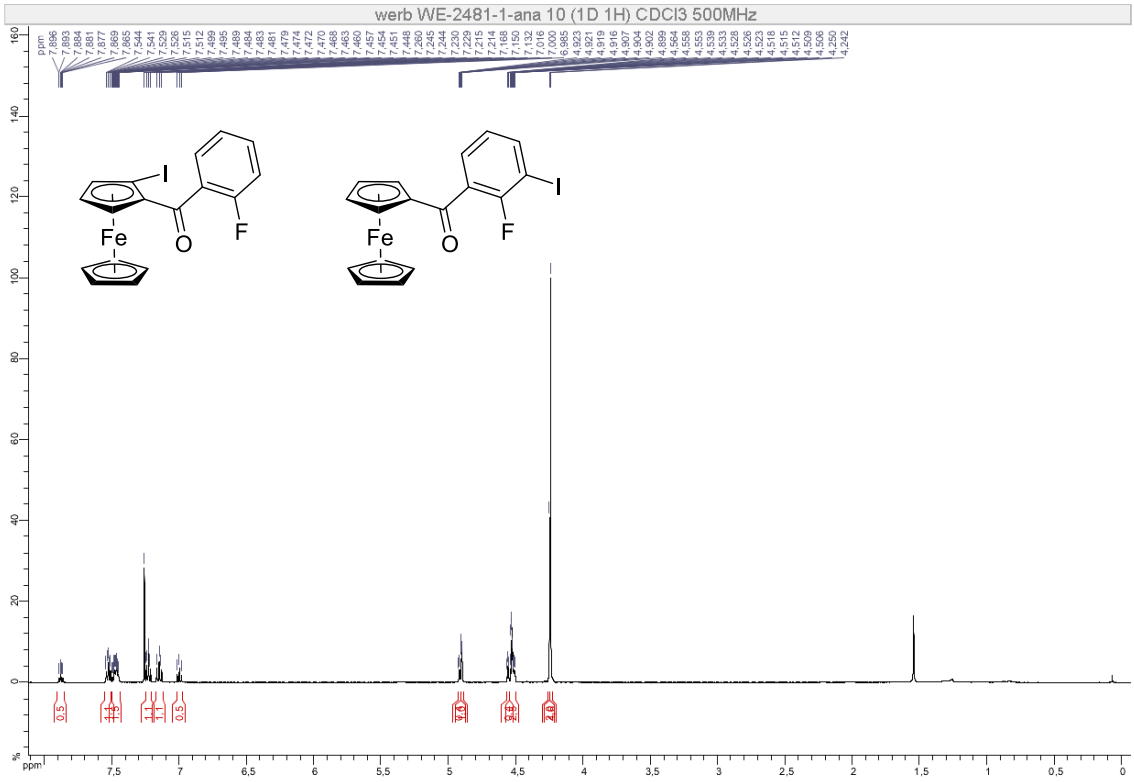


^{19}F NMR (470 MHz, $CDCl_3$)

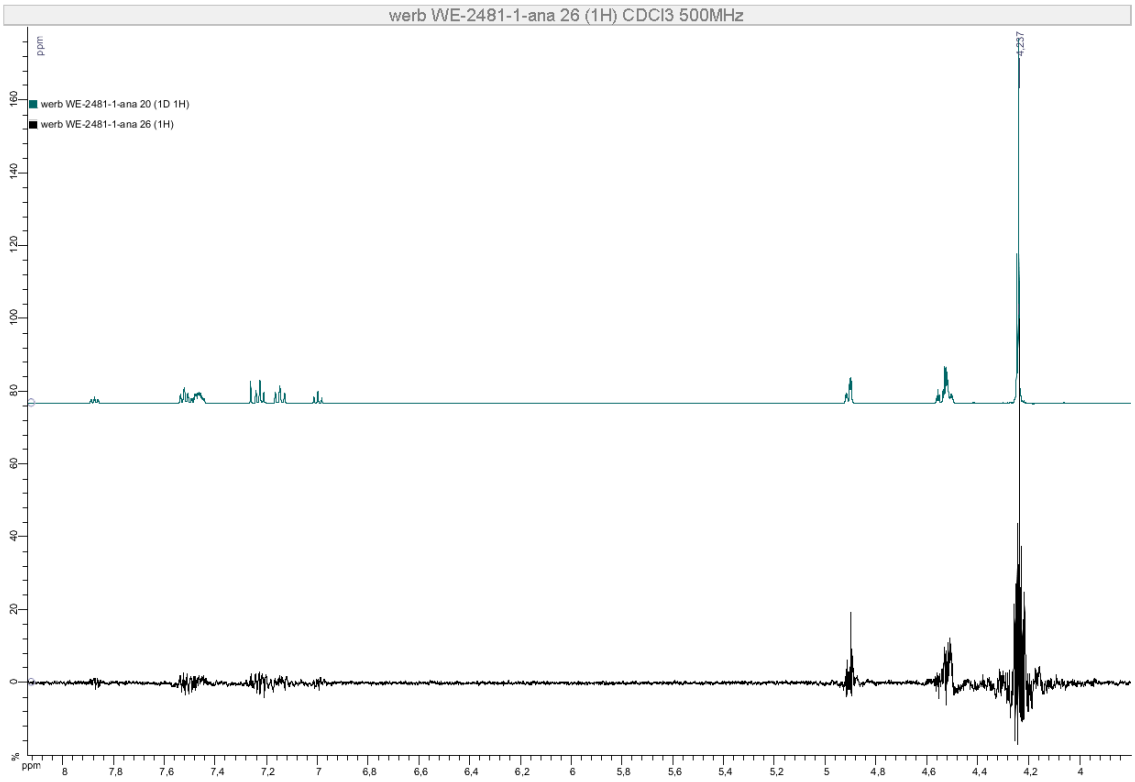


1-(2-Fluorobenzoyl)-2-iodoferrocene (2-*o*FPh), mixture with 1-(2-fluoro-3-iodobenzoyl)-2-iodoferrocene (2”-*o*FPh)

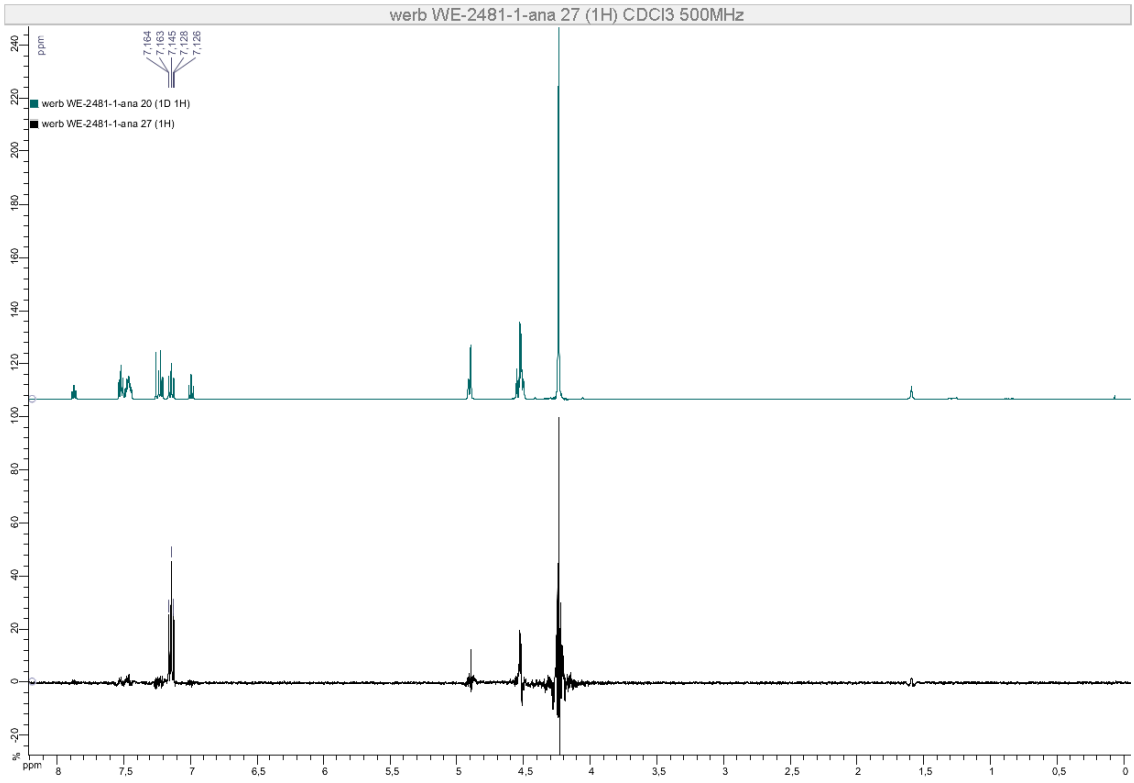
^{1}H NMR (500 MHz, $CDCl_3$)



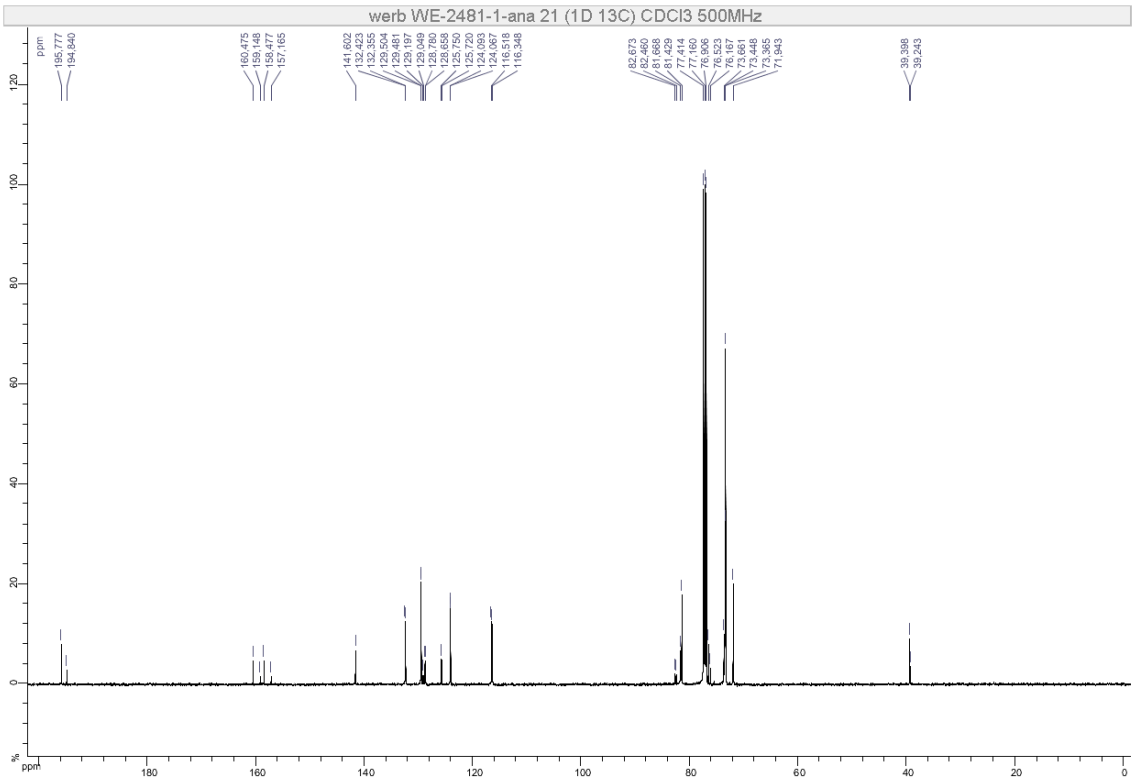
HOESY (500 MHz, $CDCl_3$) Irradiation at –93.2 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



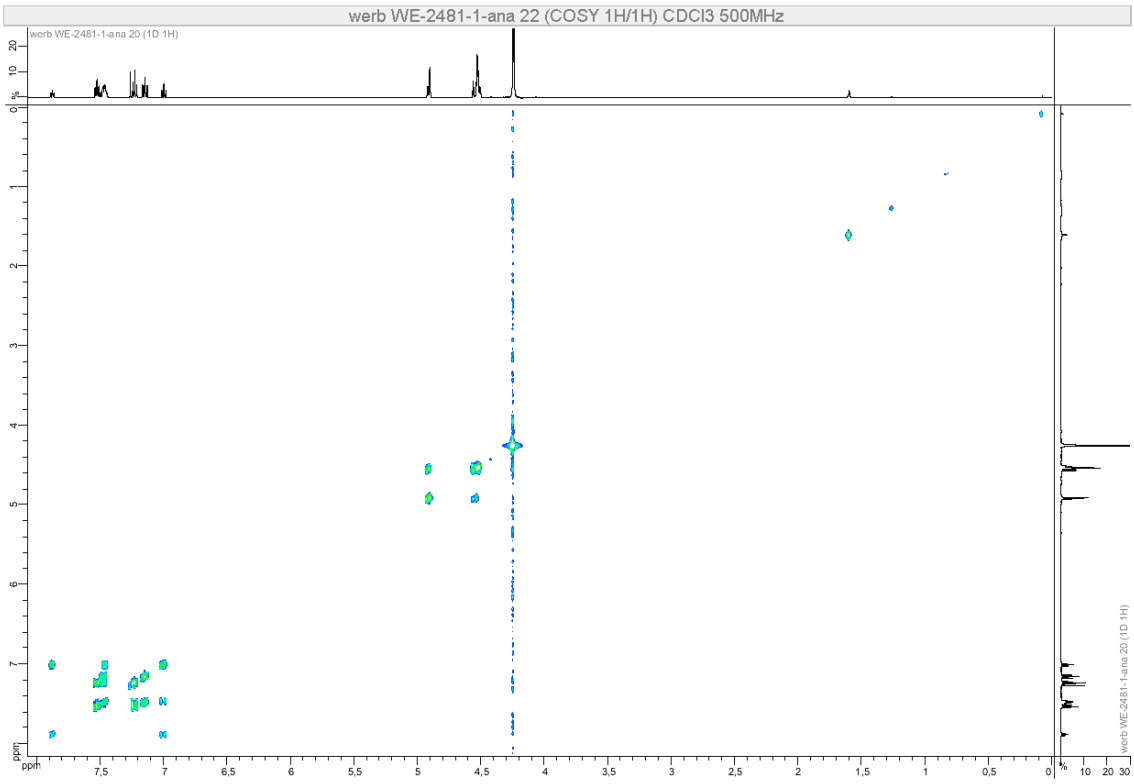
HOESY (500 MHz, $CDCl_3$) Irradiation at –113.0 ppm – Superposition of ^1H (top) and HOESY (bottom) spectra.



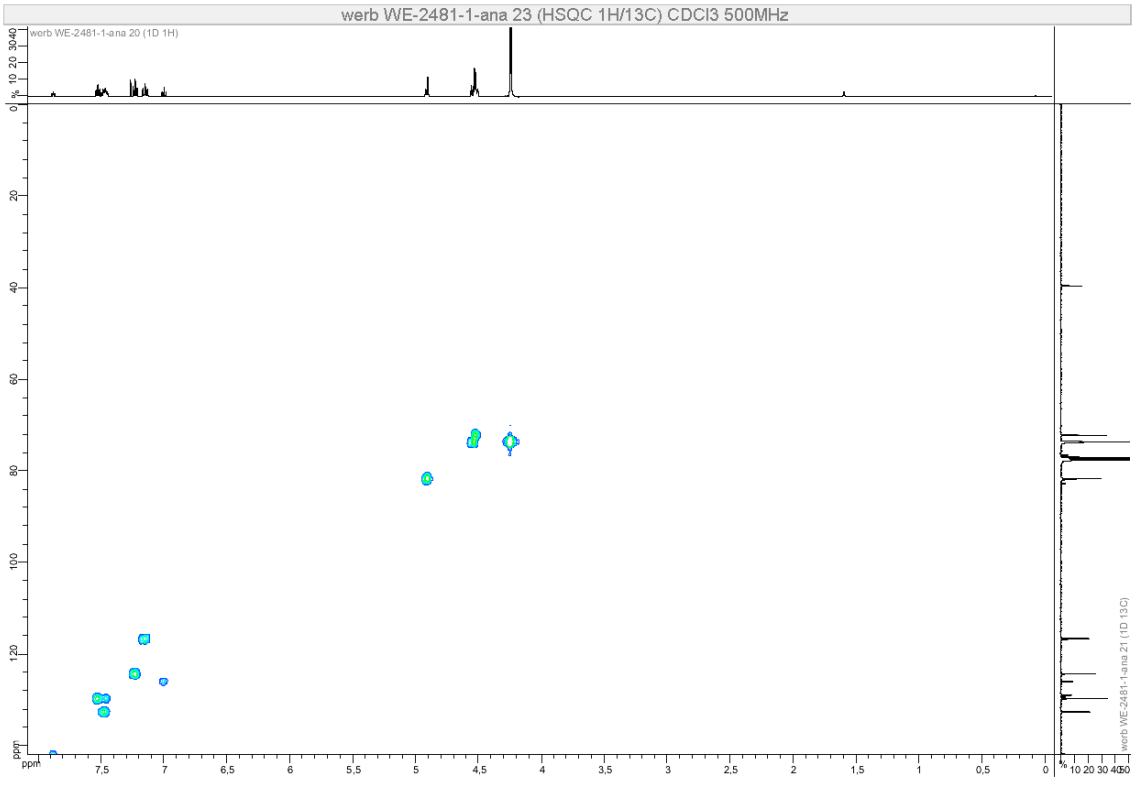
^{13}C NMR (126 MHz, $CDCl_3$)



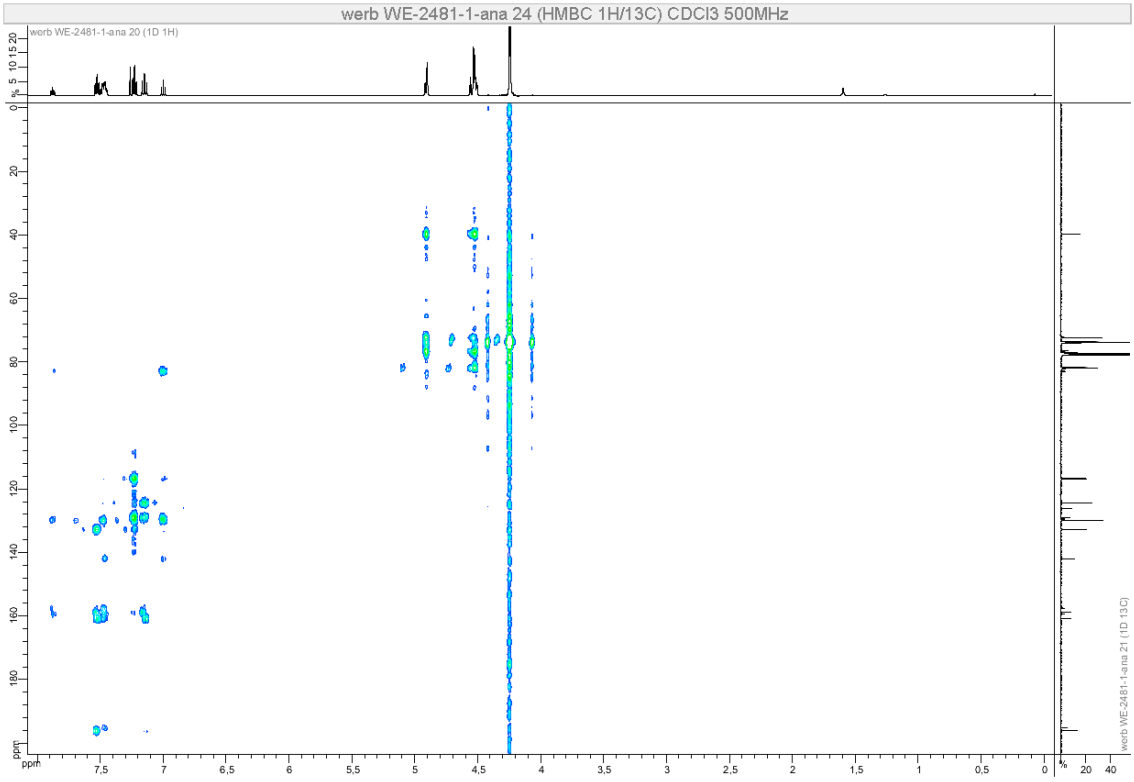
COSY (500 MHz, $CDCl_3$)



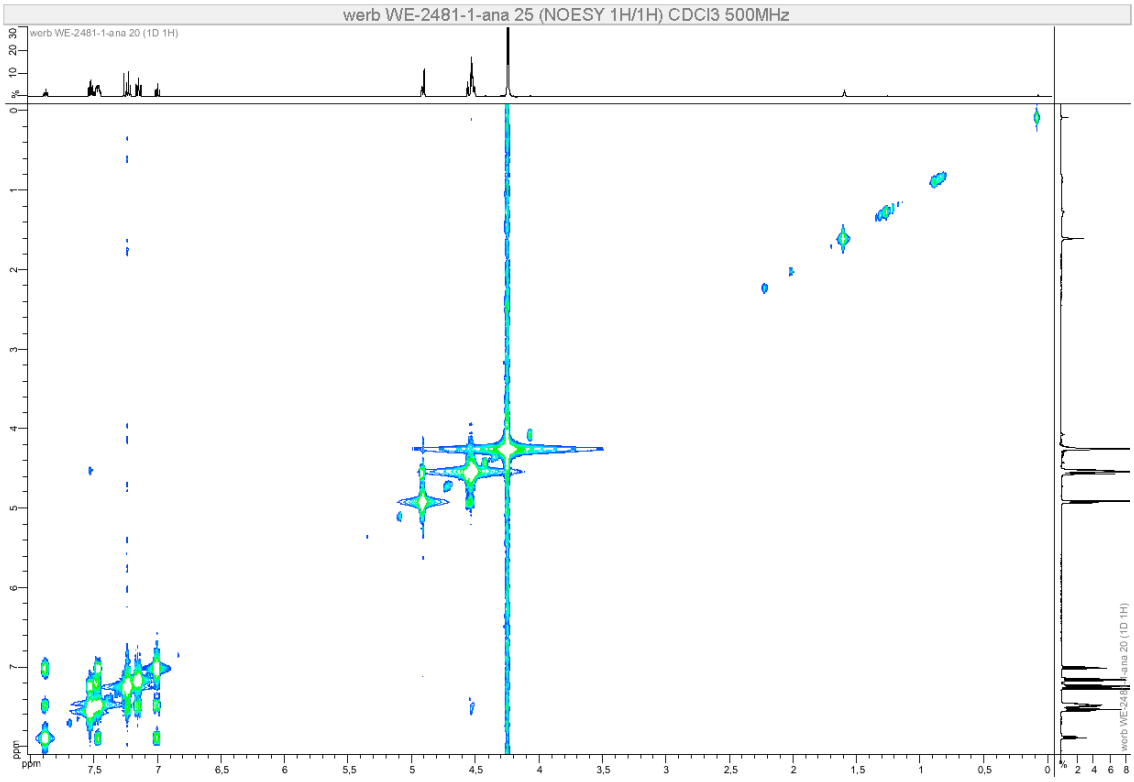
HSQC (500 MHz, $CDCl_3$)



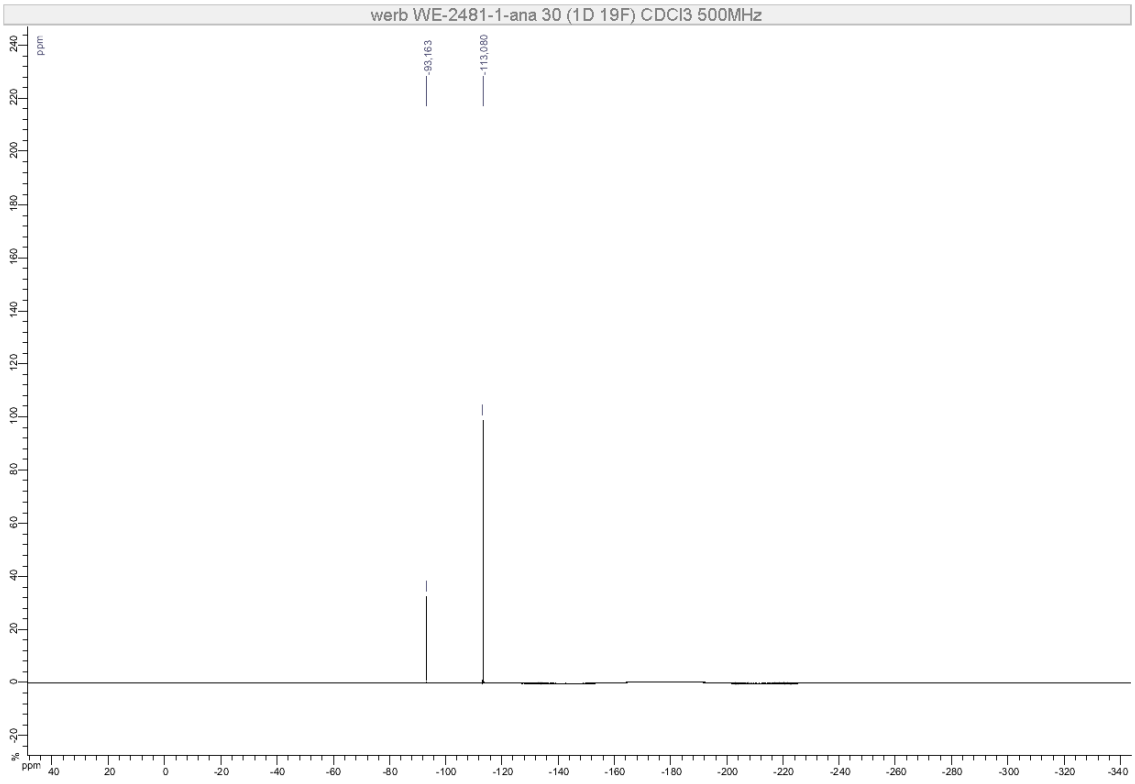
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

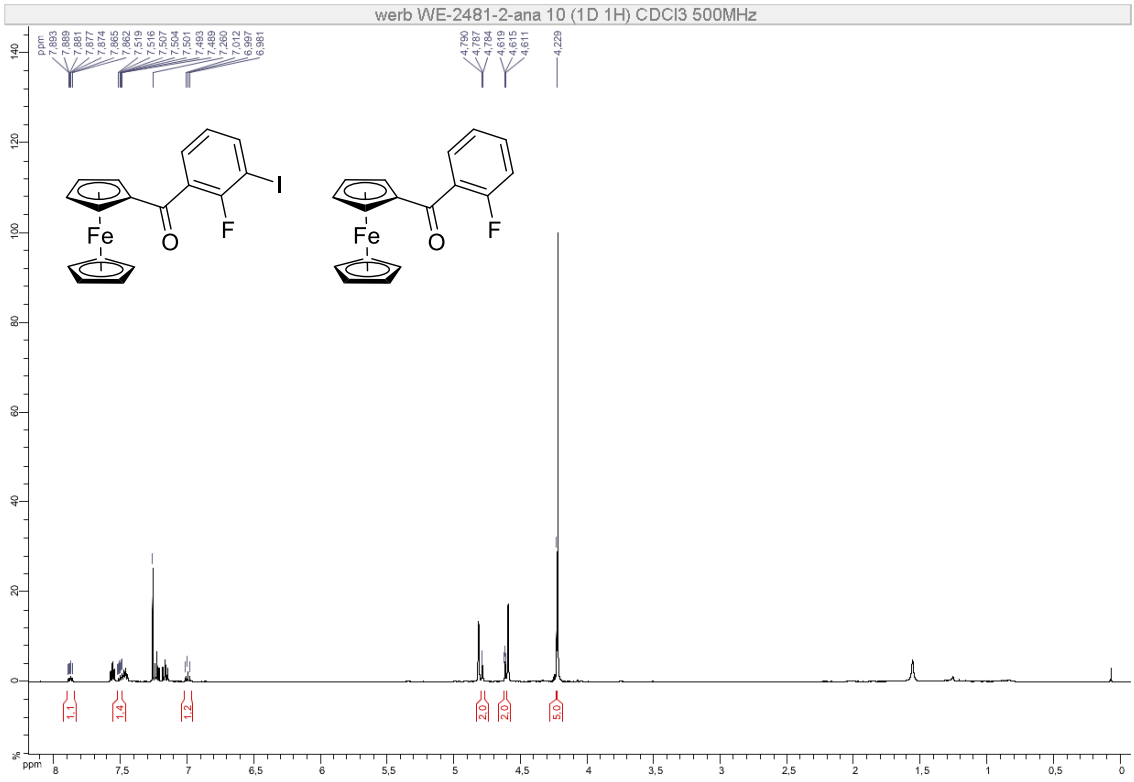


^{19}F NMR (470 MHz, $CDCl_3$)

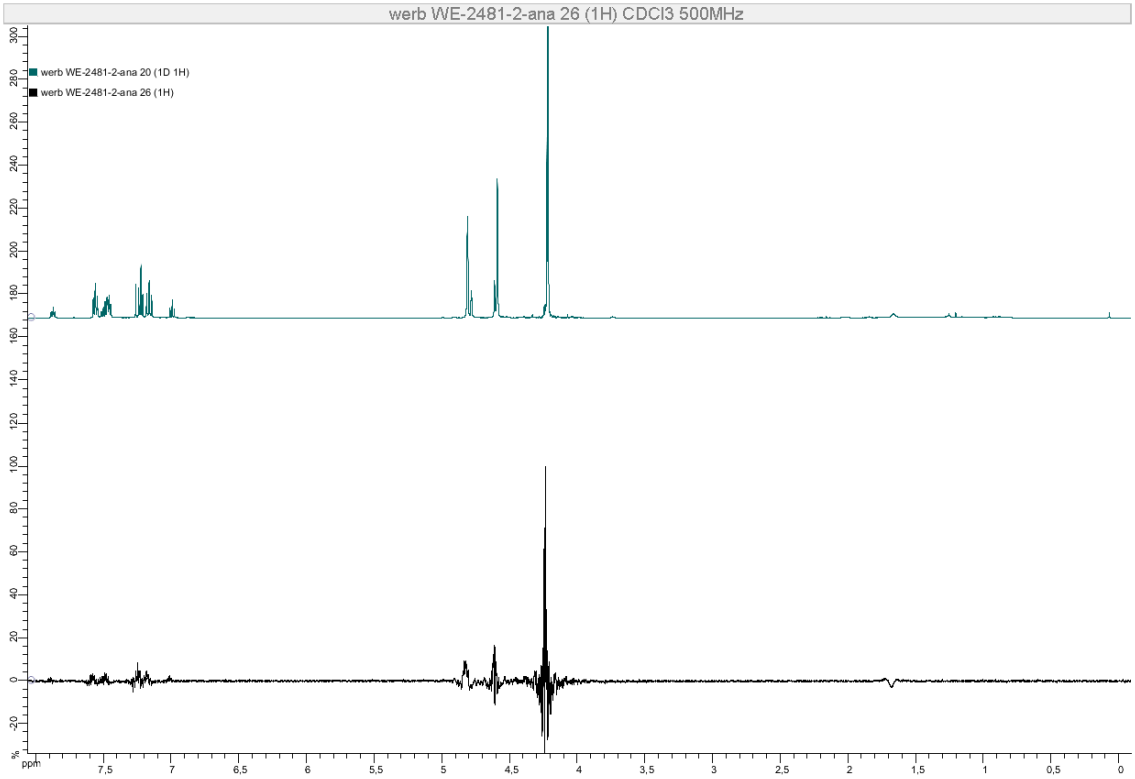


(2-Fluoro-3-iodobenzoyl)ferrocene (2'-*o*FPh), mixture with 1-*o*FPh

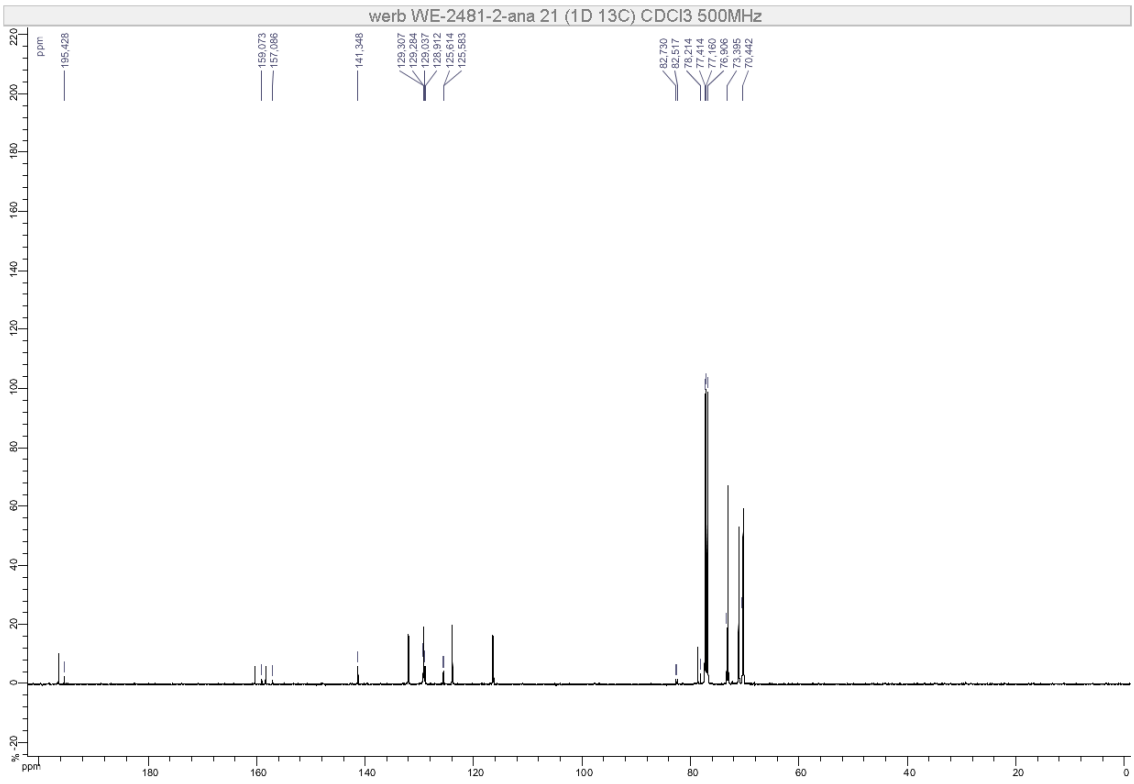
^{1}H NMR (500 MHz, $CDCl_3$)



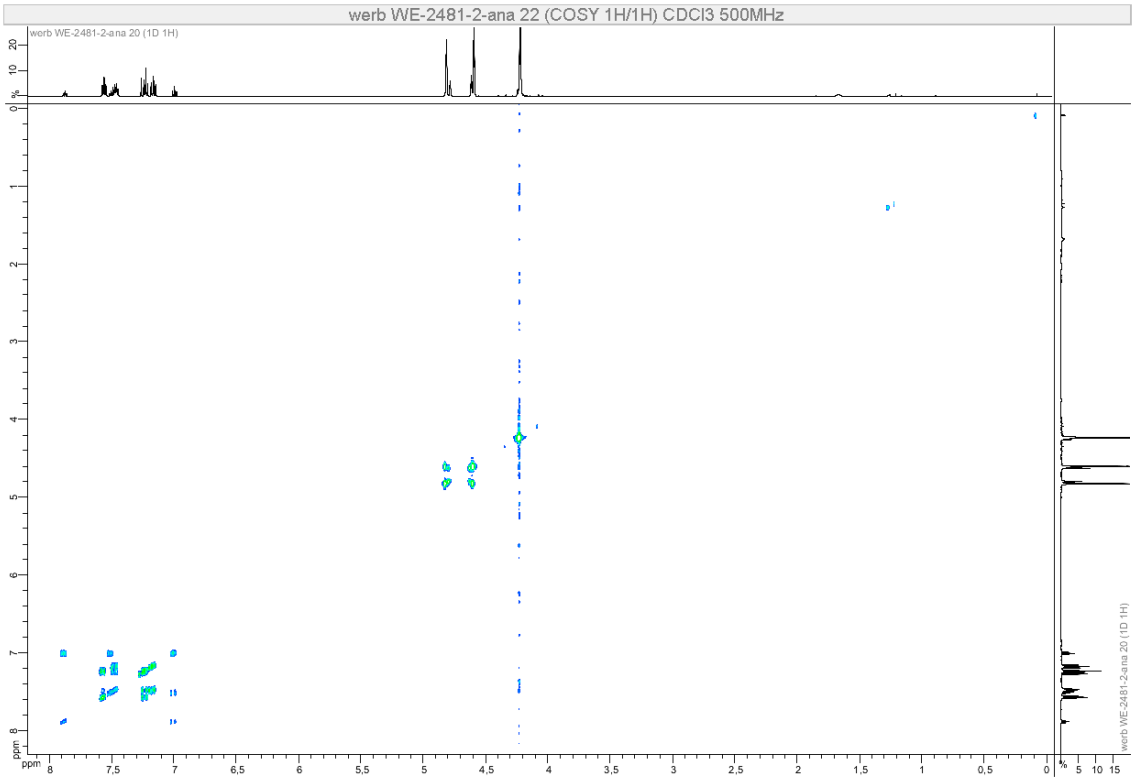
HOESY (500 MHz, $CDCl_3$) Irradiation at –93.4 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



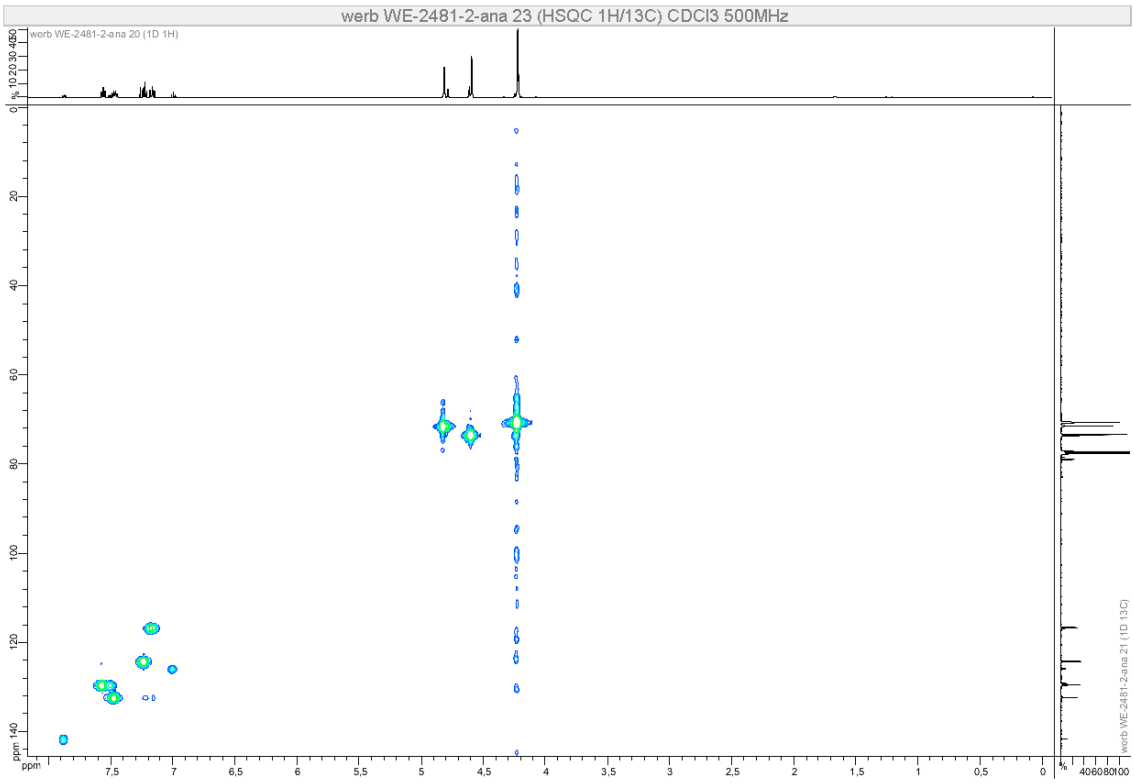
^{13}C NMR (126 MHz, $CDCl_3$)



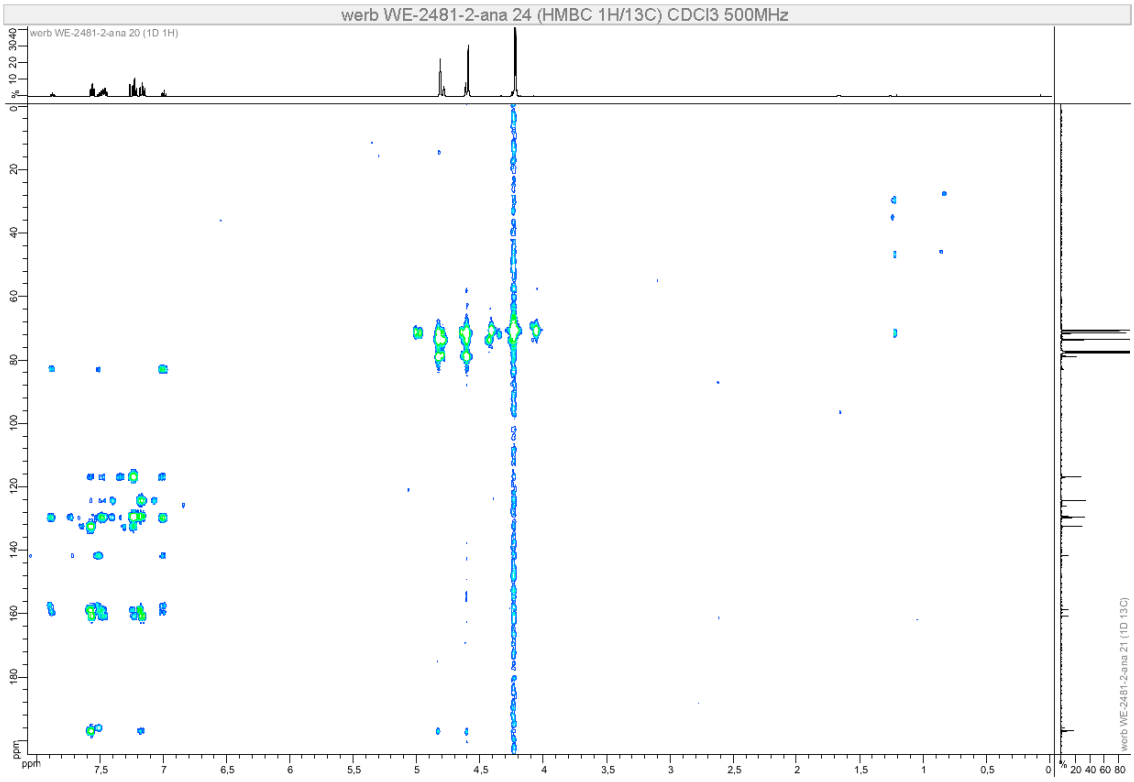
COSY (500 MHz, $CDCl_3$)



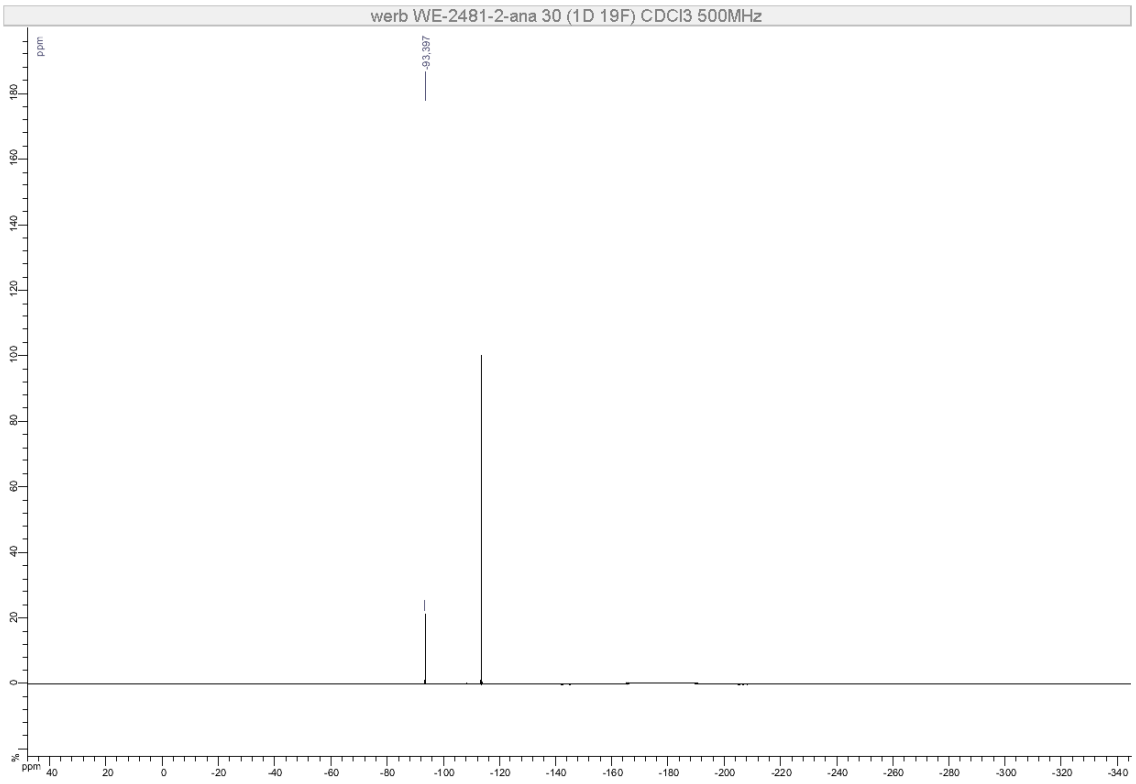
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

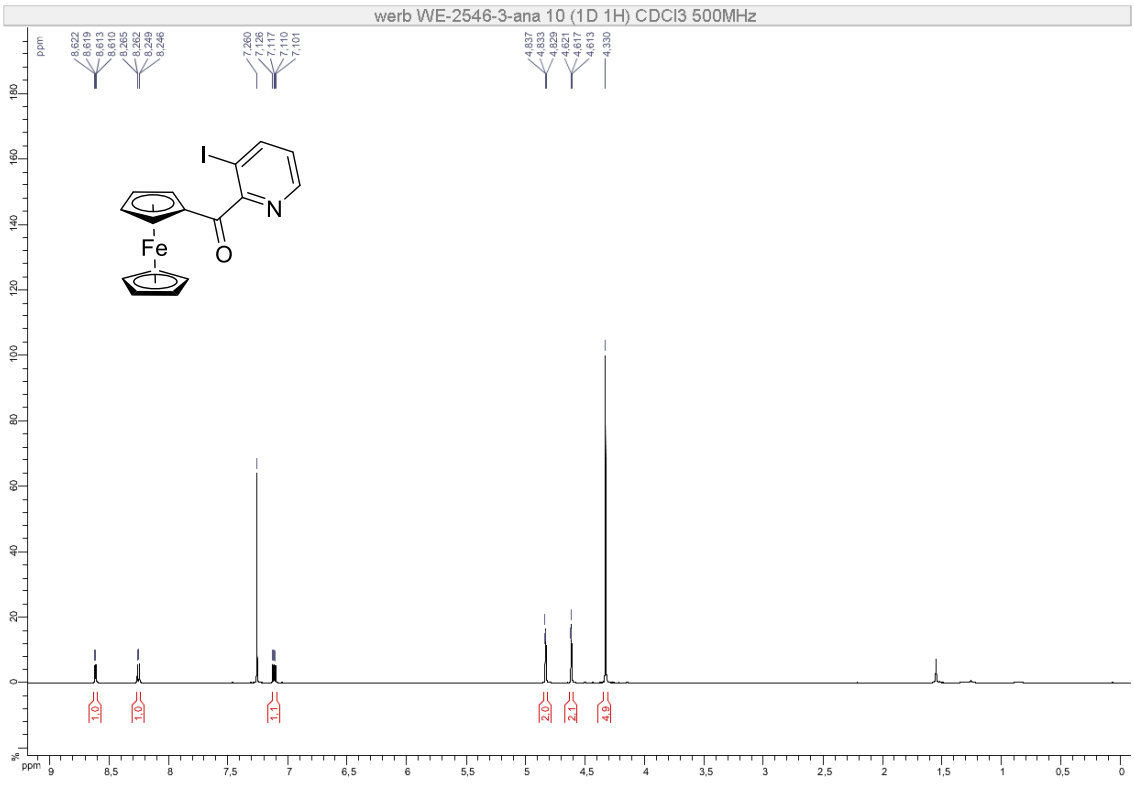


^{19}F NMR (470 MHz, $CDCl_3$)

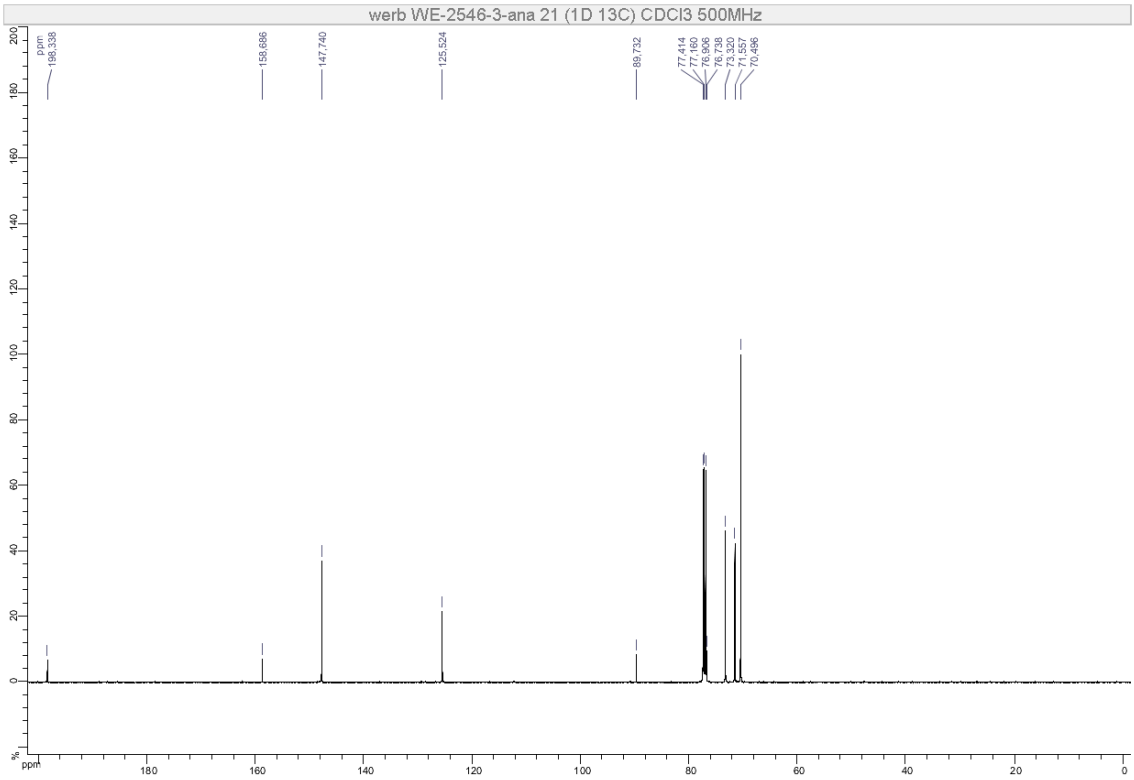


(3-Iodo-2-pyridoyl)ferrocene (2'-2Py)

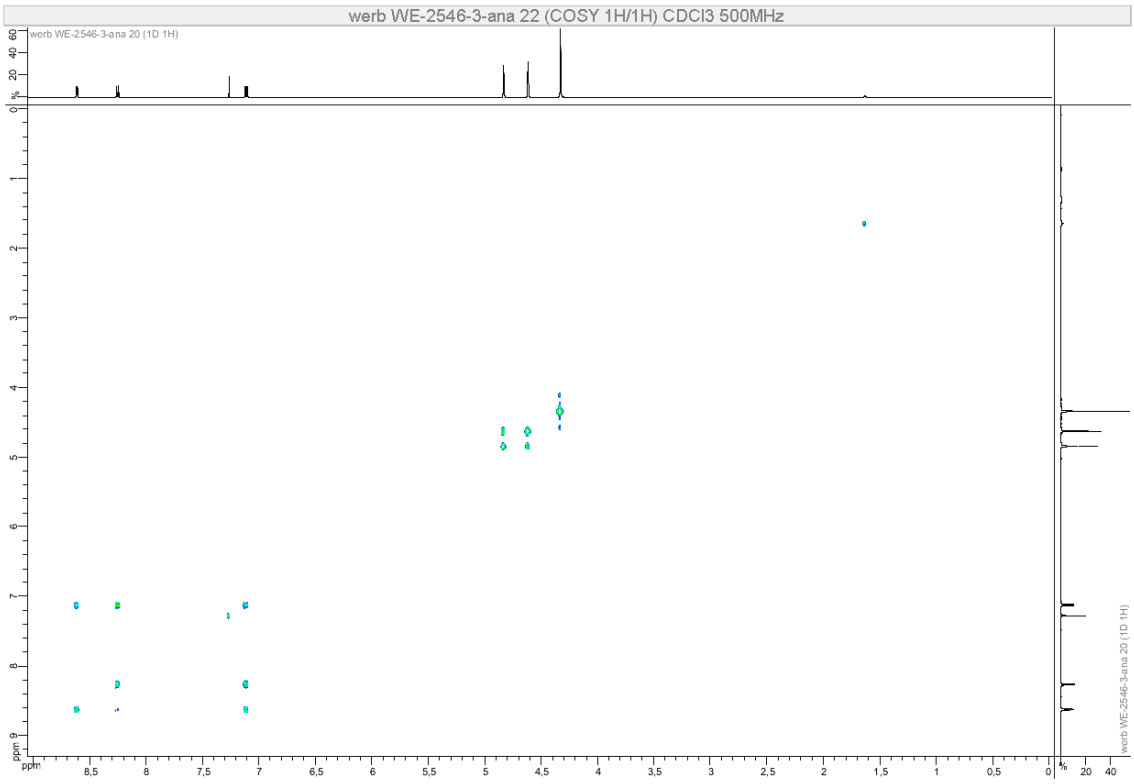
^{1}H NMR (500 MHz, $CDCl_3$)



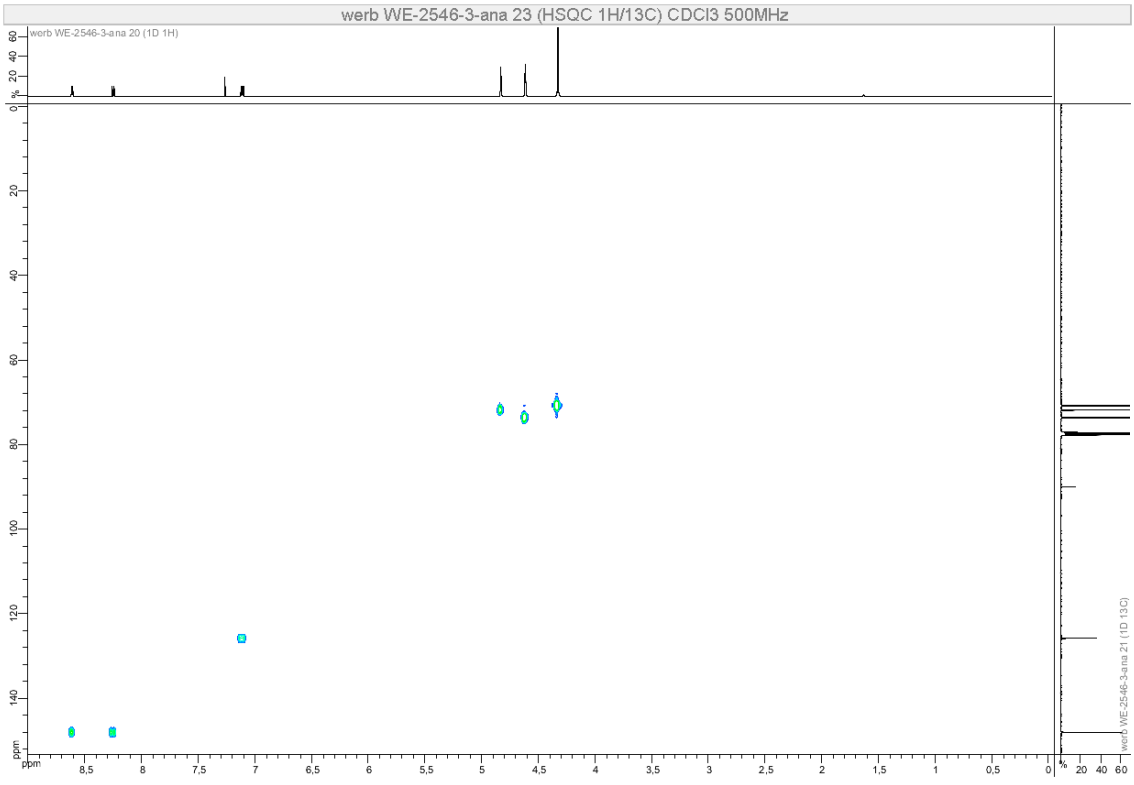
^{13}C NMR (126 MHz, $CDCl_3$)



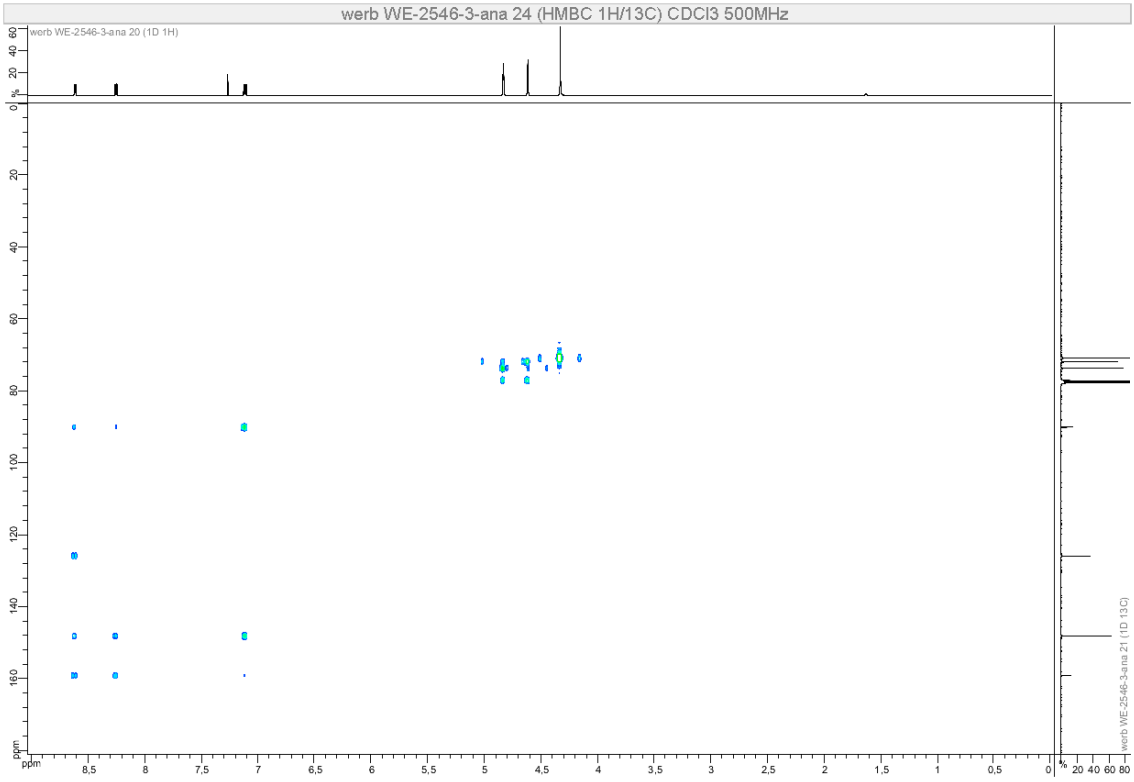
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

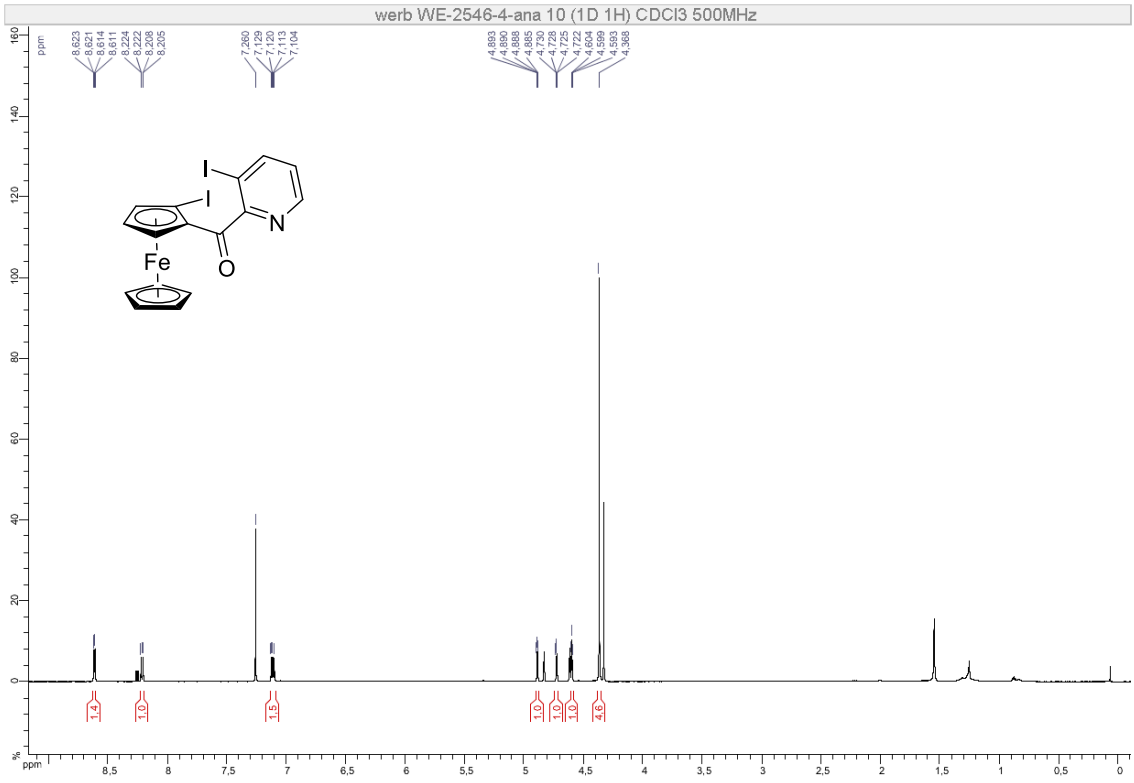


HMBC (500 MHz, $CDCl_3$)

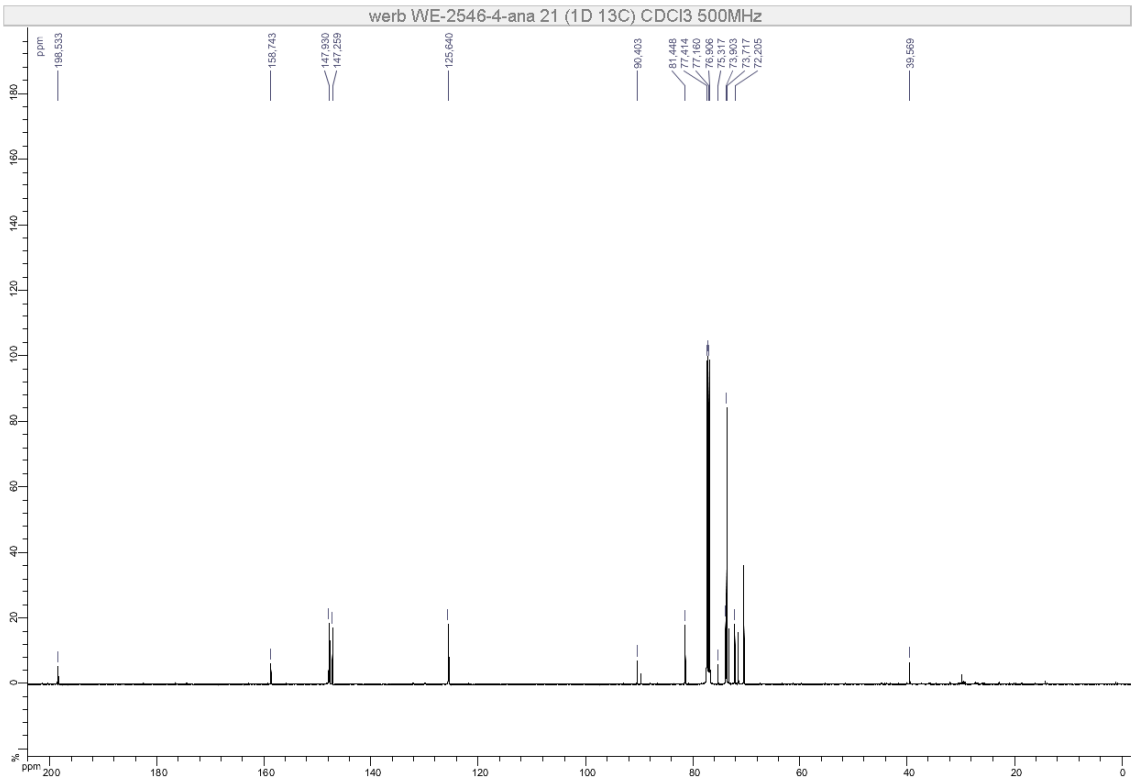


1-Iodo-2-(3-iodo-2-pyridoyl)ferrocene (2”-2Py)

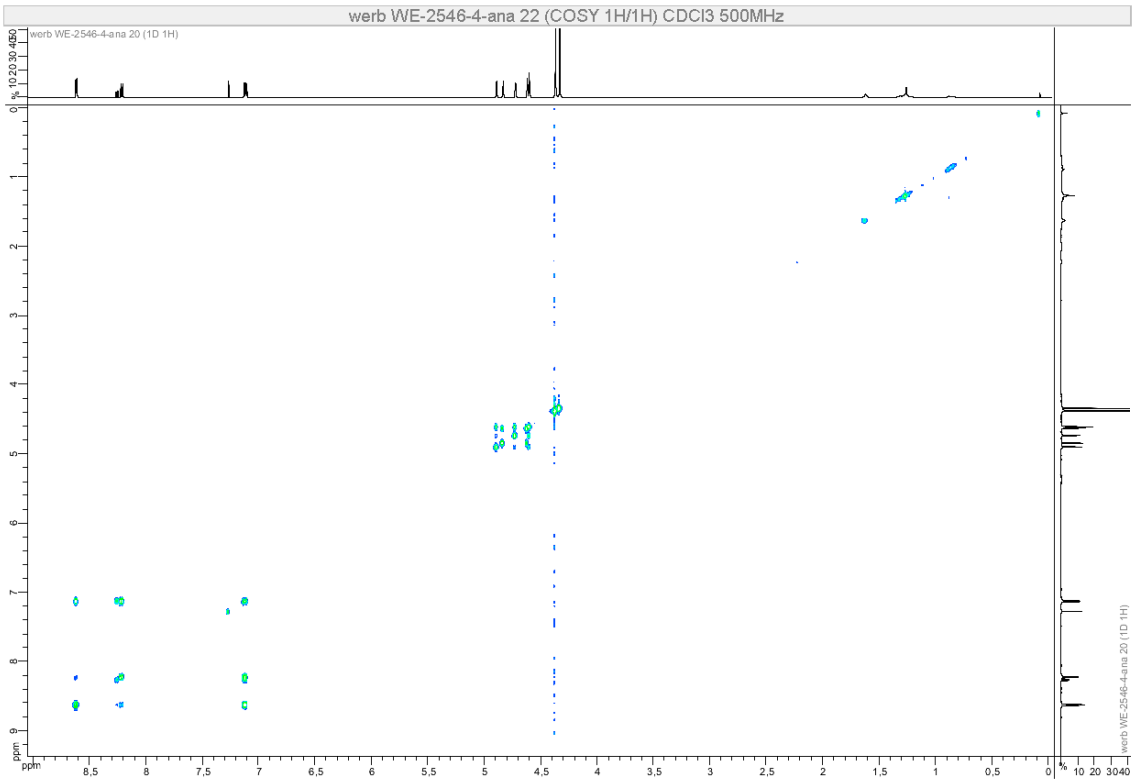
^{1}H NMR (500 MHz, $CDCl_3$)



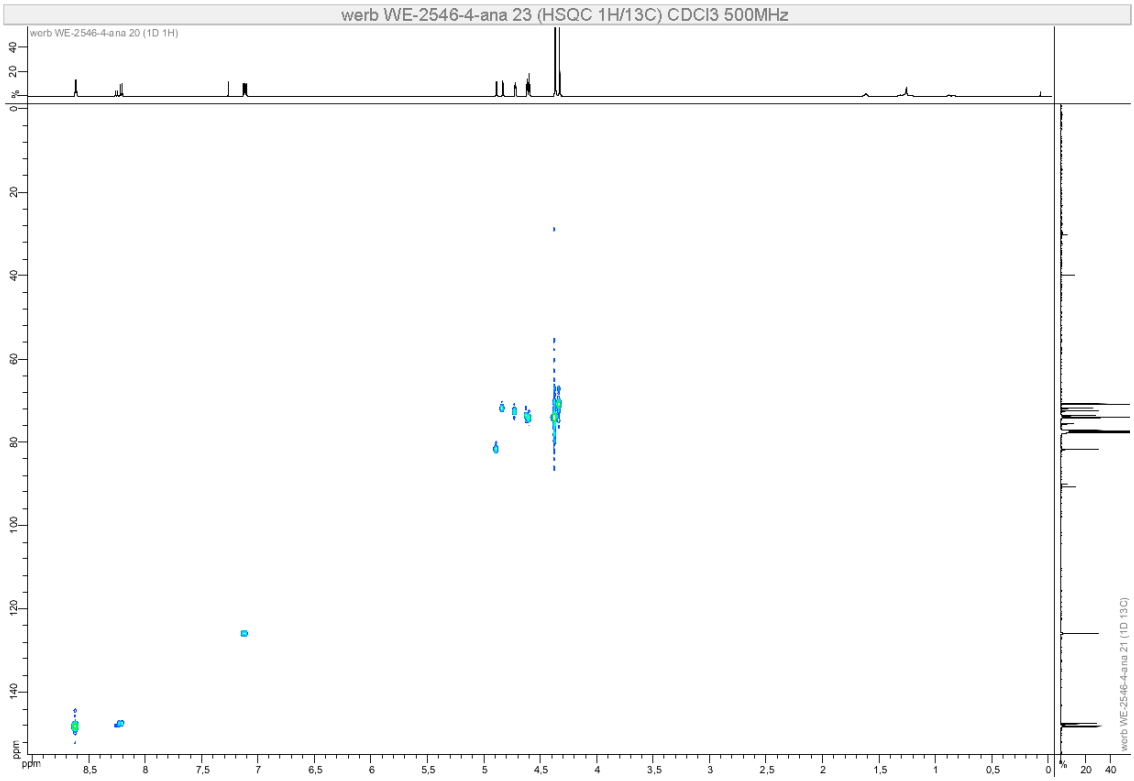
^{13}C NMR (126 MHz, $CDCl_3$)



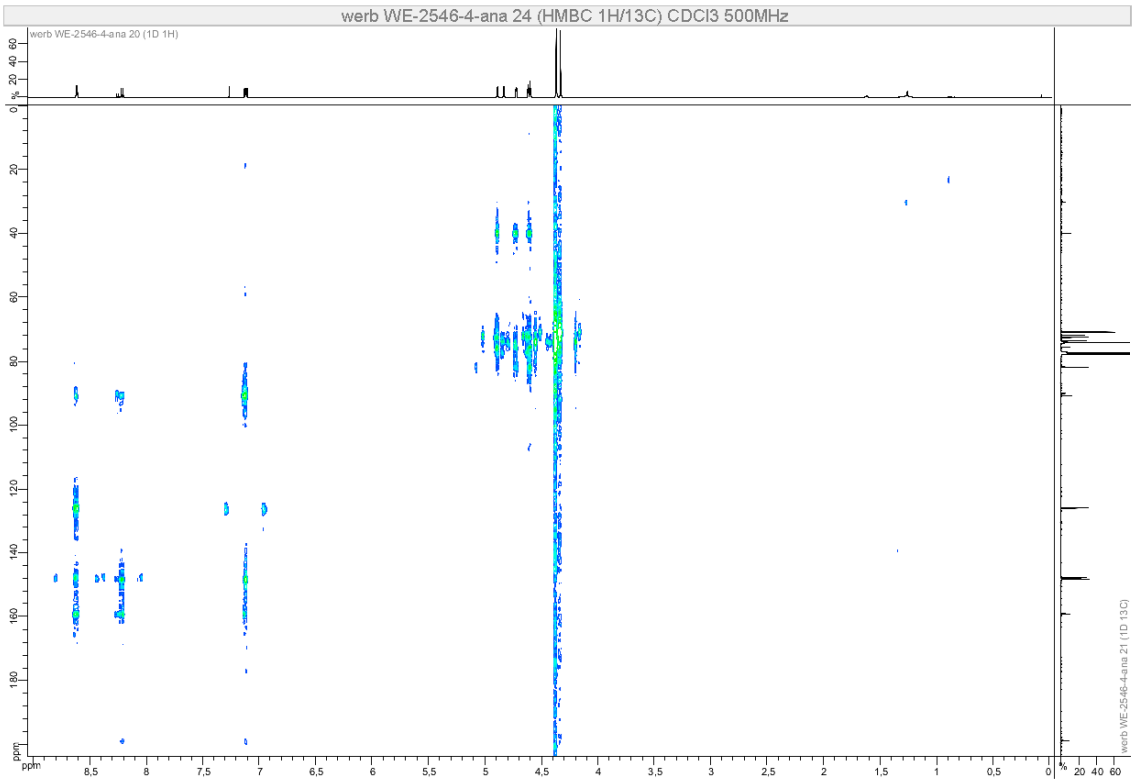
COSY (500 MHz, $CDCl_3$)



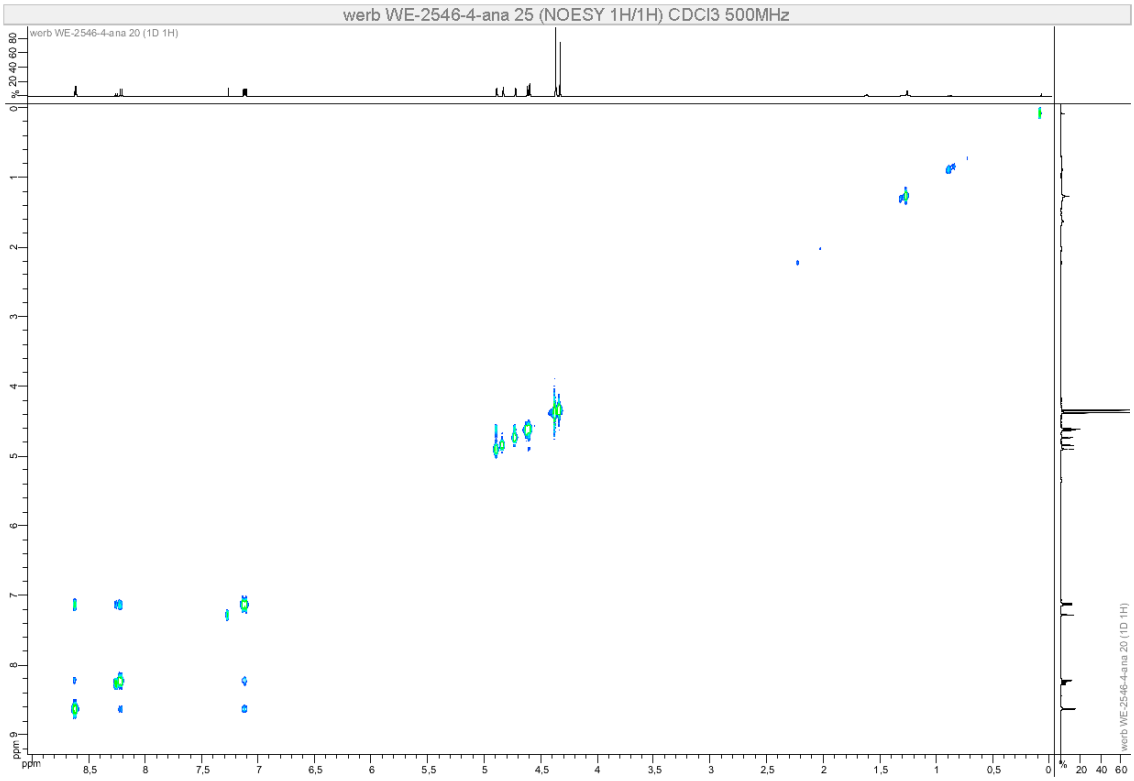
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

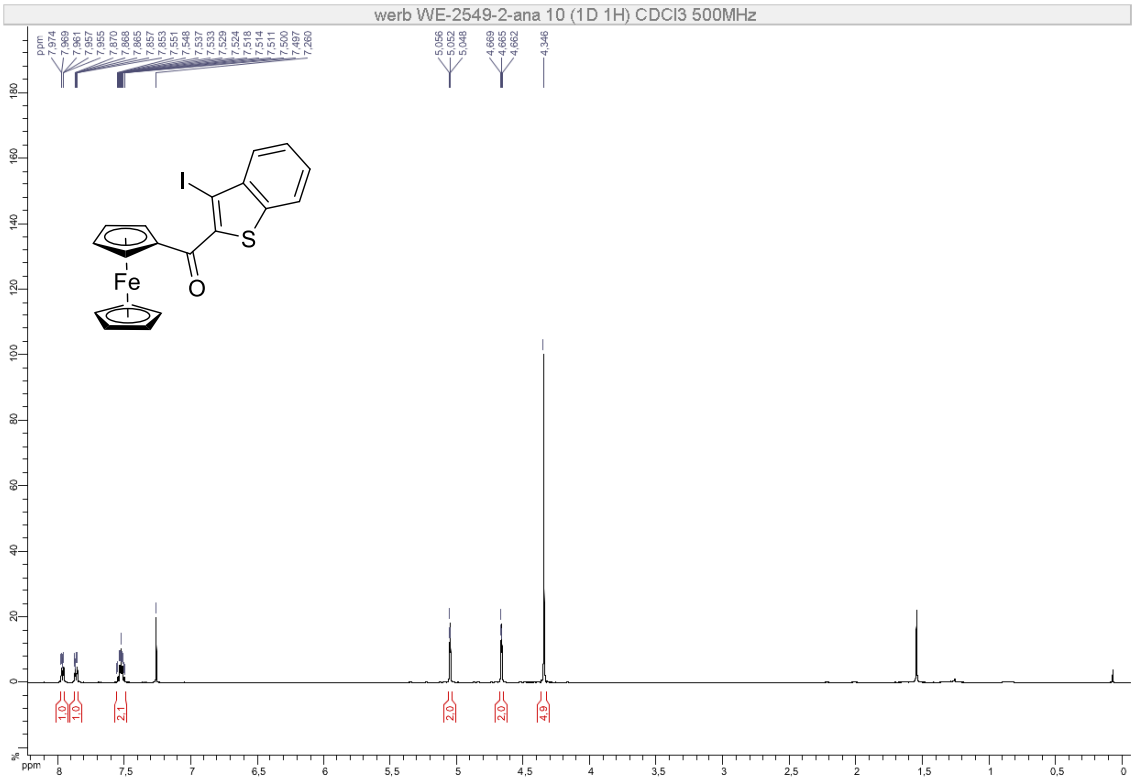


NOESY (500 MHz, $CDCl_3$)

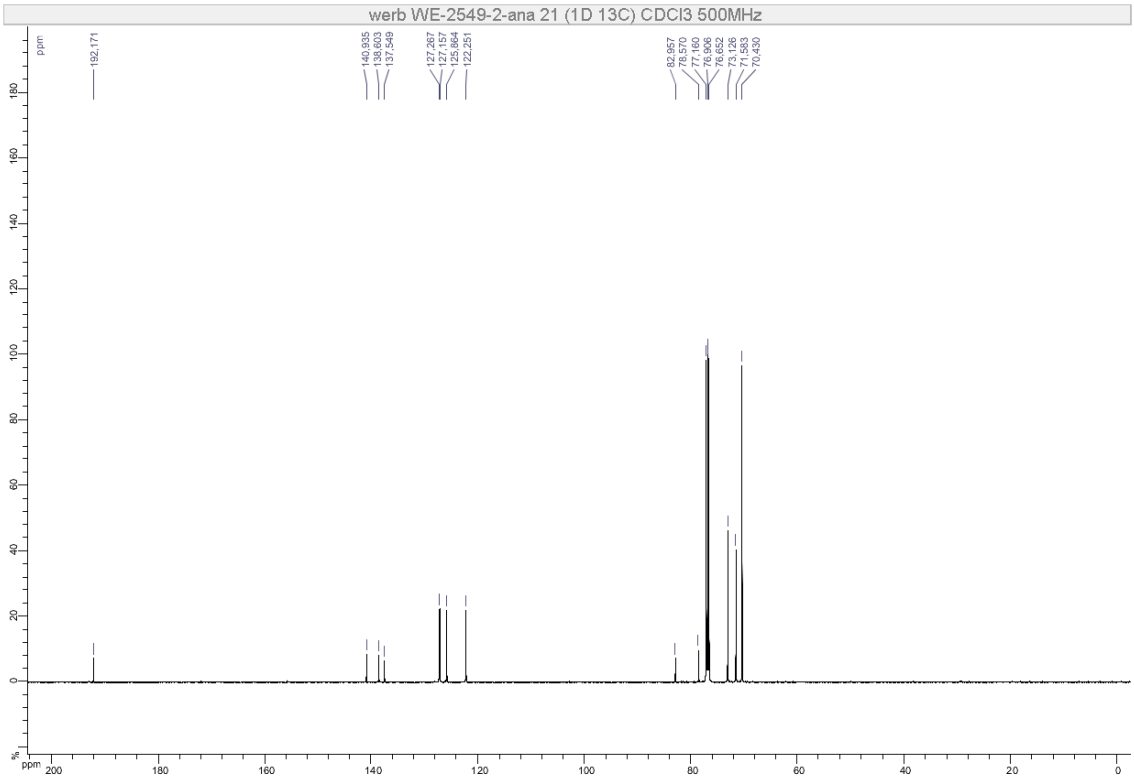


(3-Iodo-2-benzothienoyl)ferrocene (2'-2BTh)

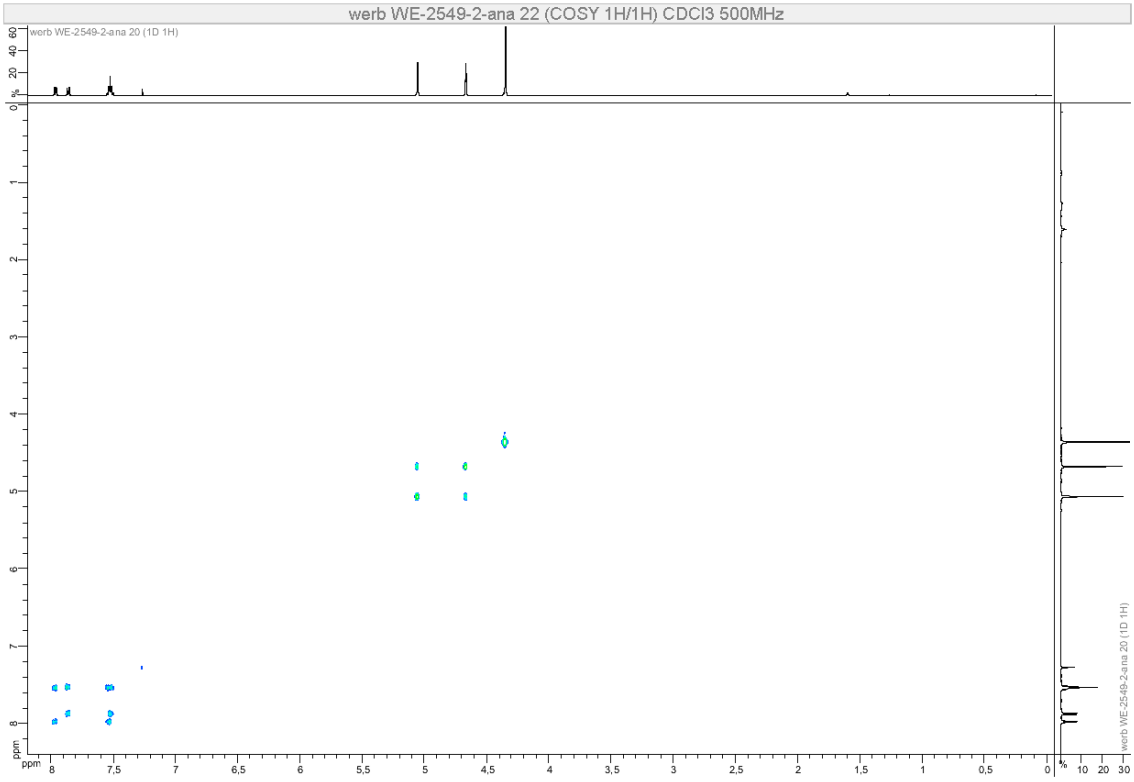
^{1}H NMR (500 MHz, $CDCl_3$)



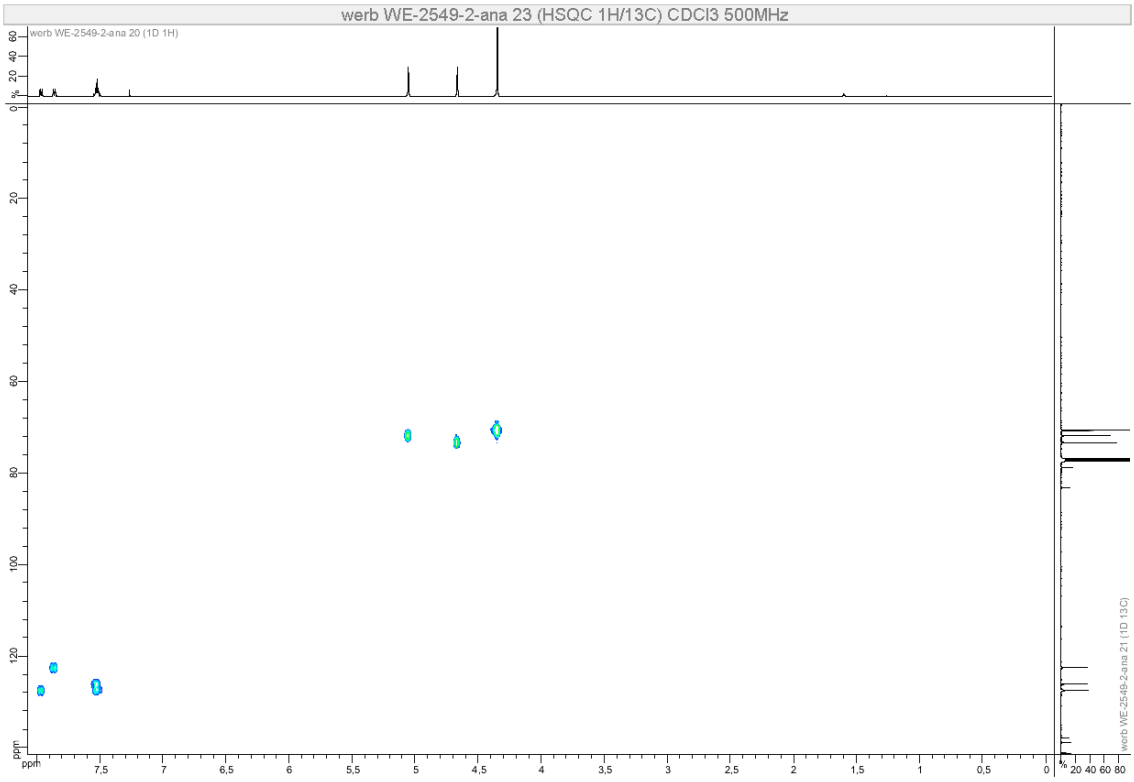
^{13}C NMR (126 MHz, $CDCl_3$)



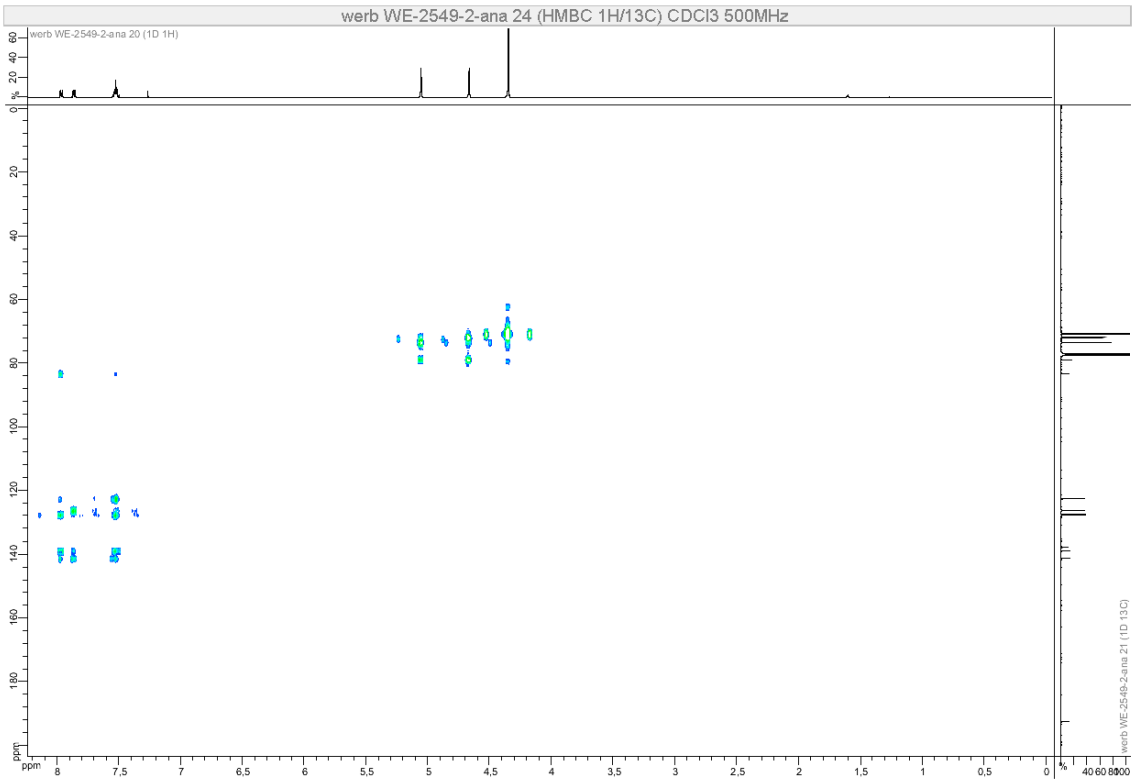
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

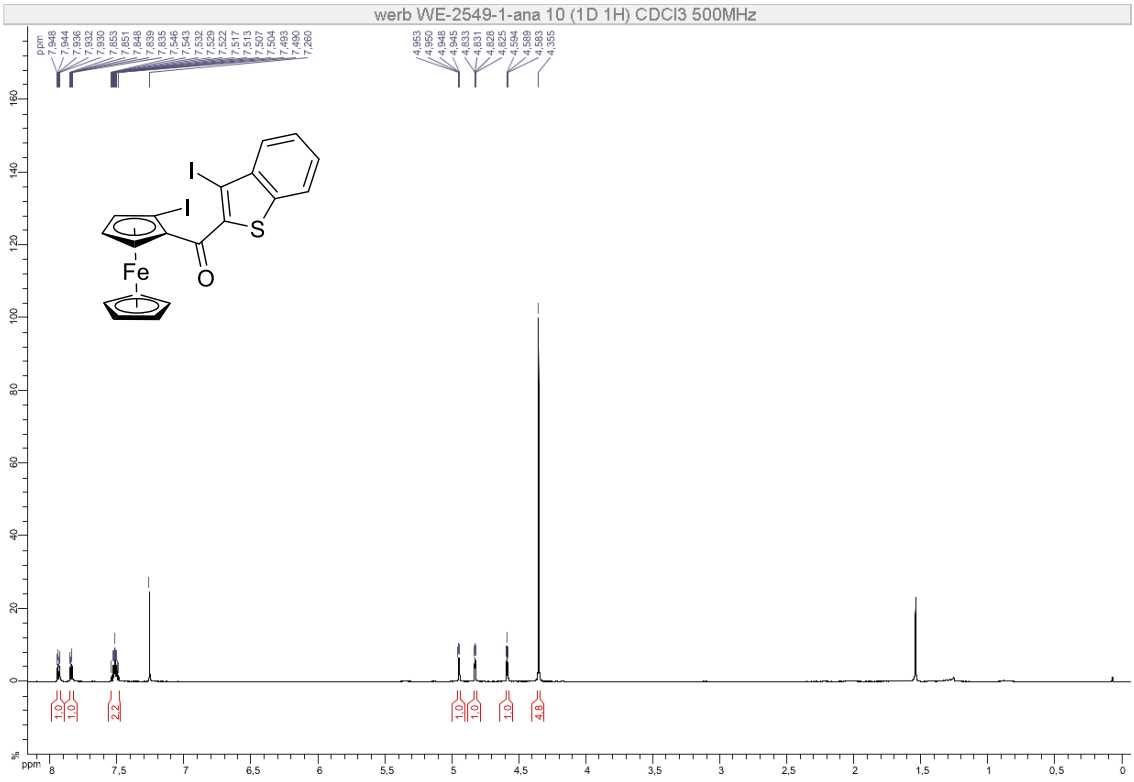


HMBC (500 MHz, $CDCl_3$)

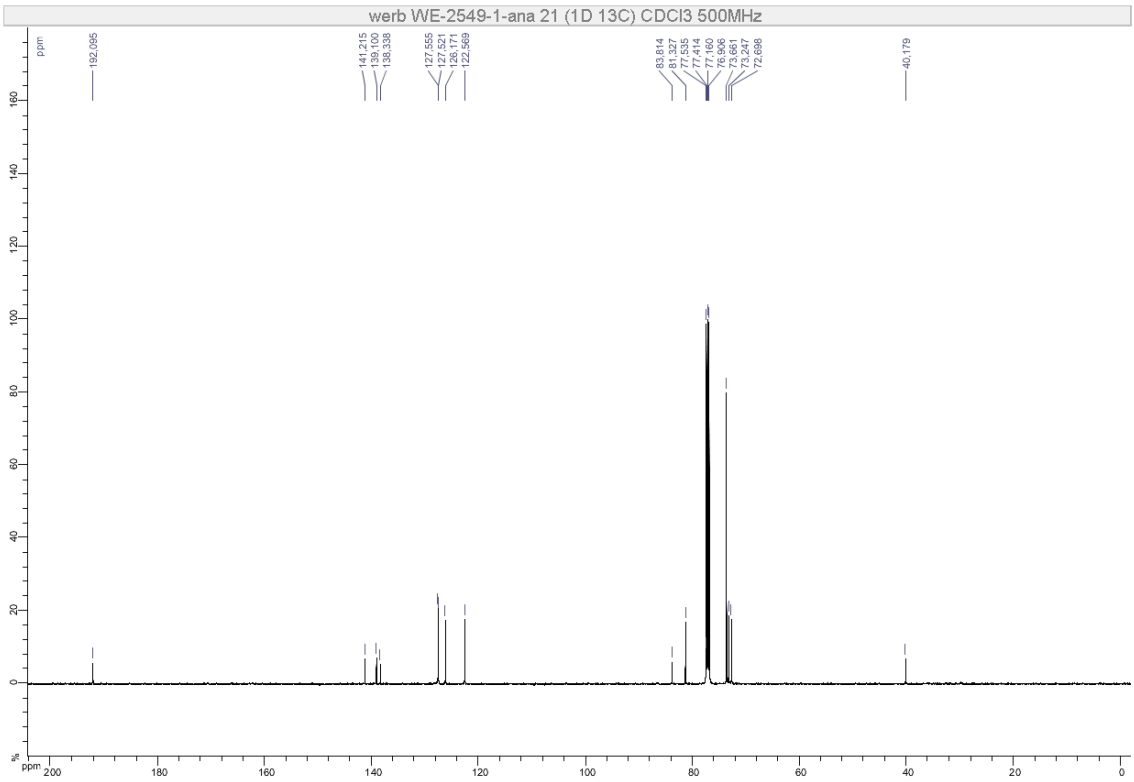


1-Iodo-2-(3-iodo-2-benzothienoyl)ferrocene (2”-2BTh)

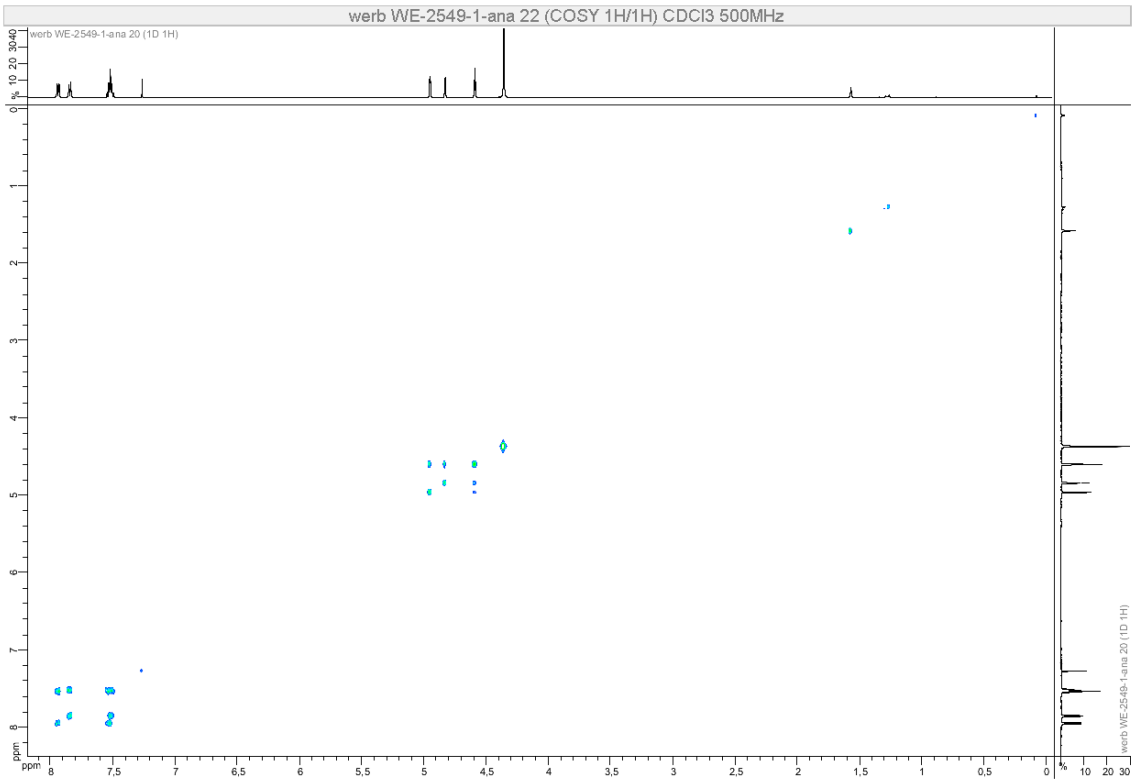
^{1}H NMR (500 MHz, $CDCl_3$)



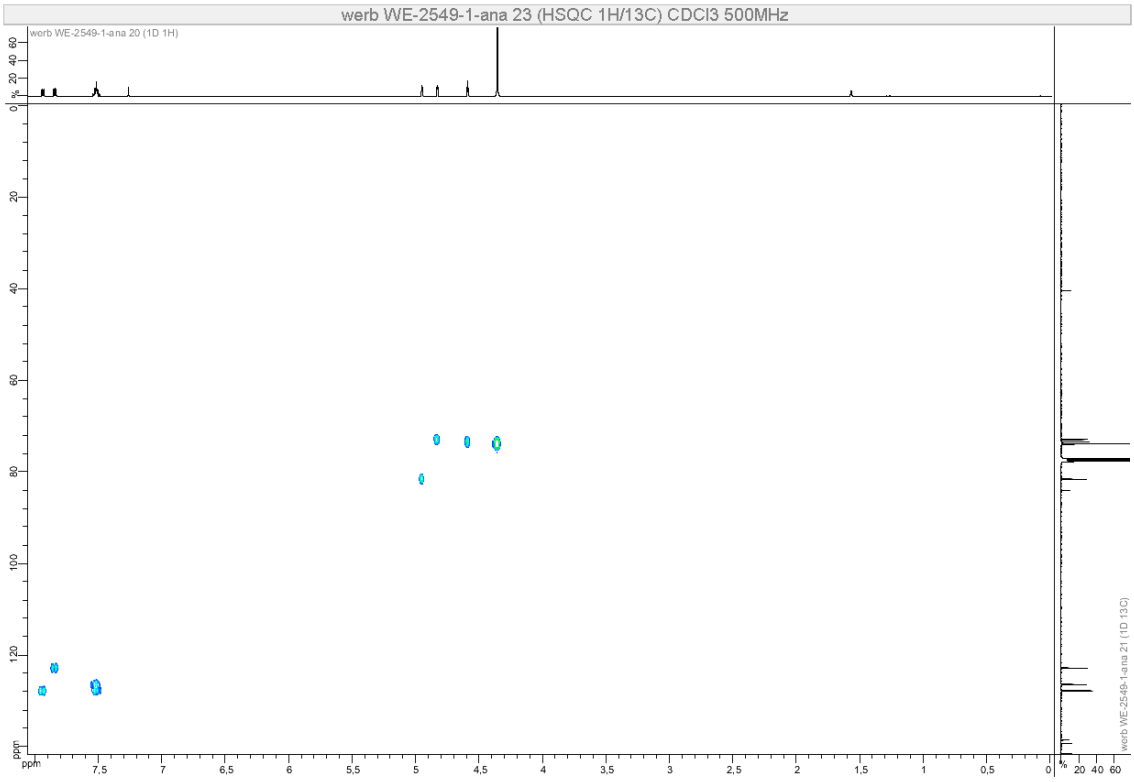
^{13}C NMR (126 MHz, $CDCl_3$)



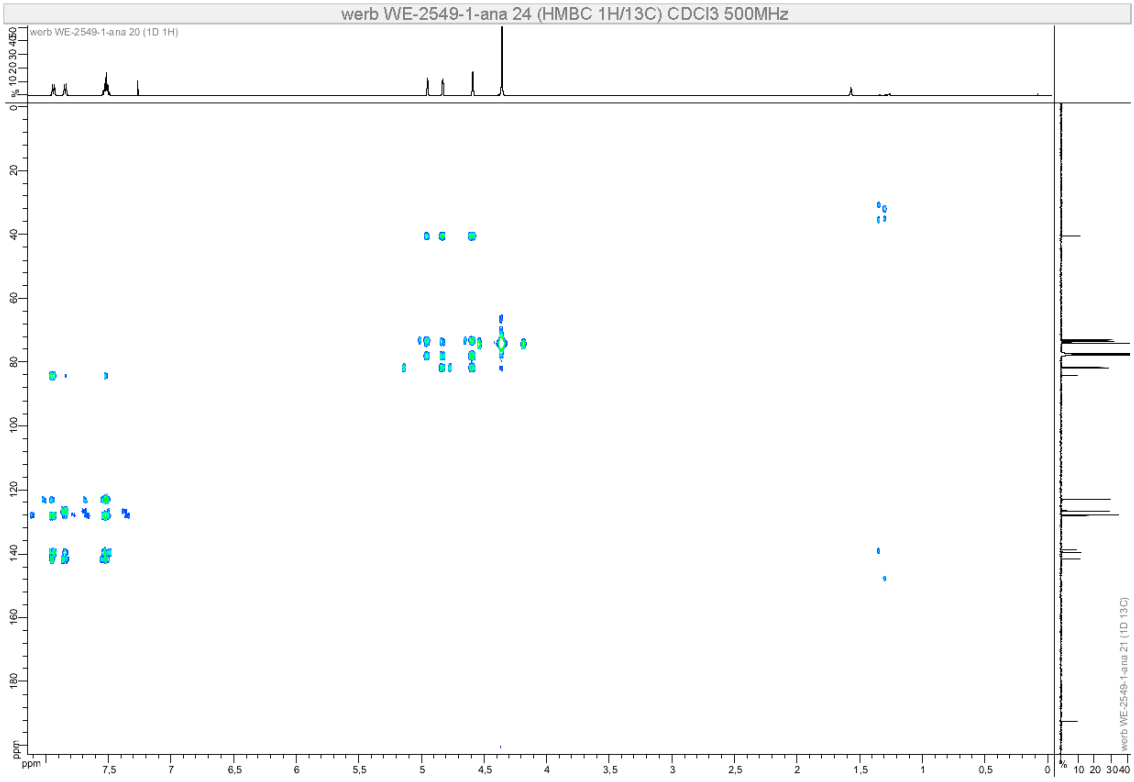
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

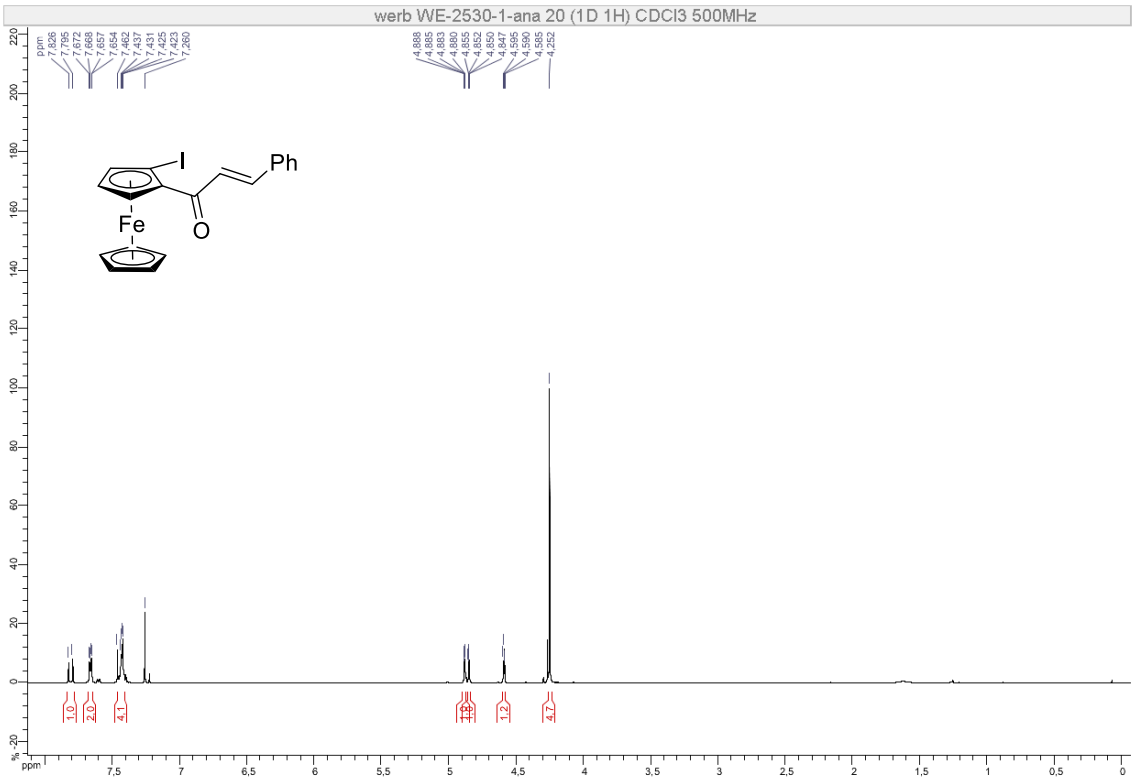


HMBC (500 MHz, $CDCl_3$)

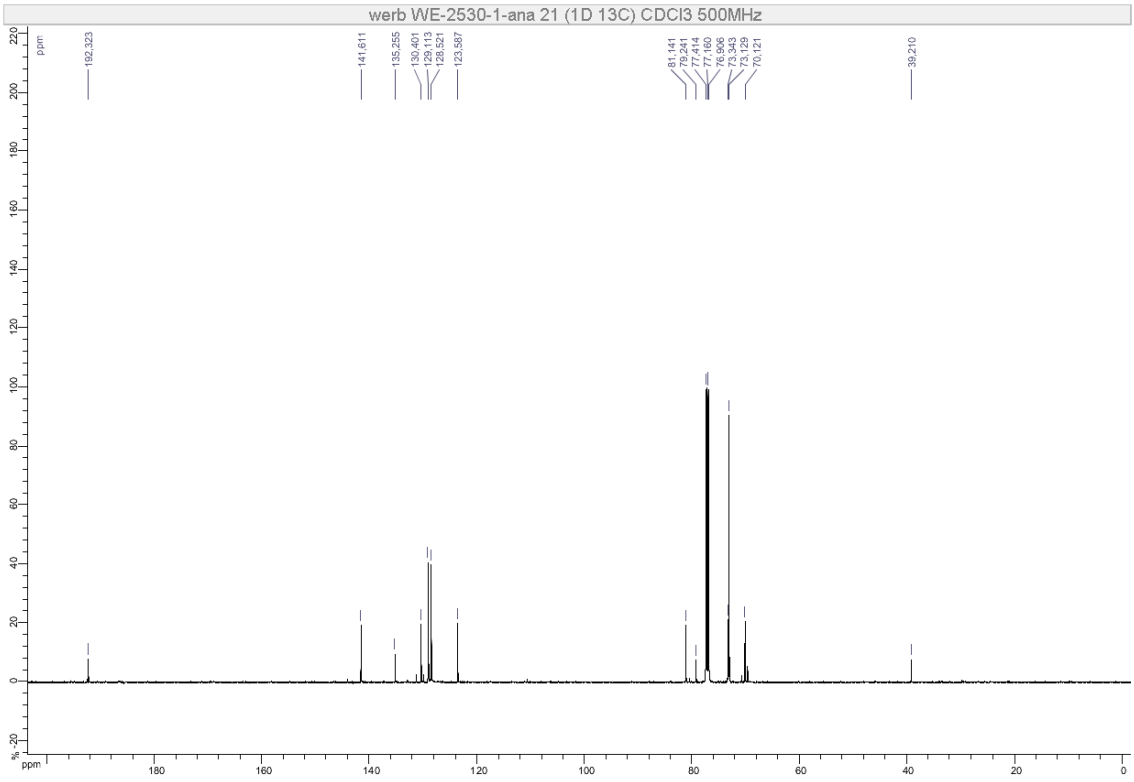


(*E*)-1-Cinnamoyl-2-iodoferrocene (2-CH=CHPh)

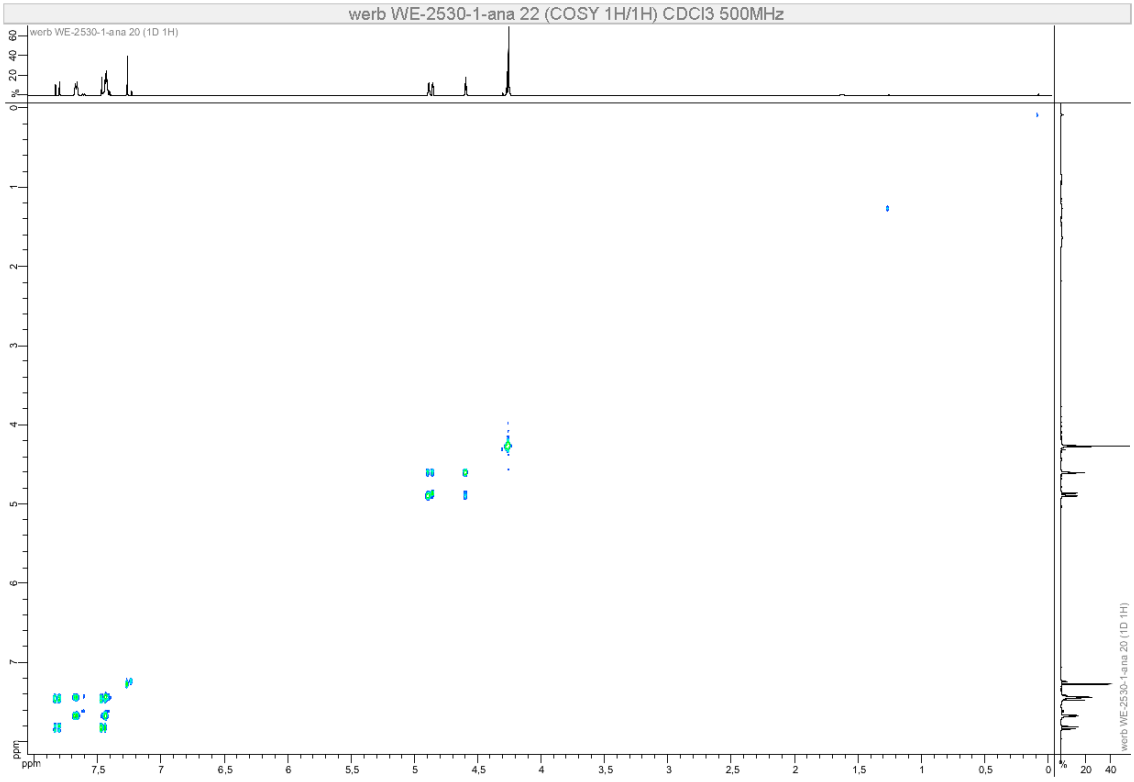
^{1}H NMR (500 MHz, $CDCl_3$)



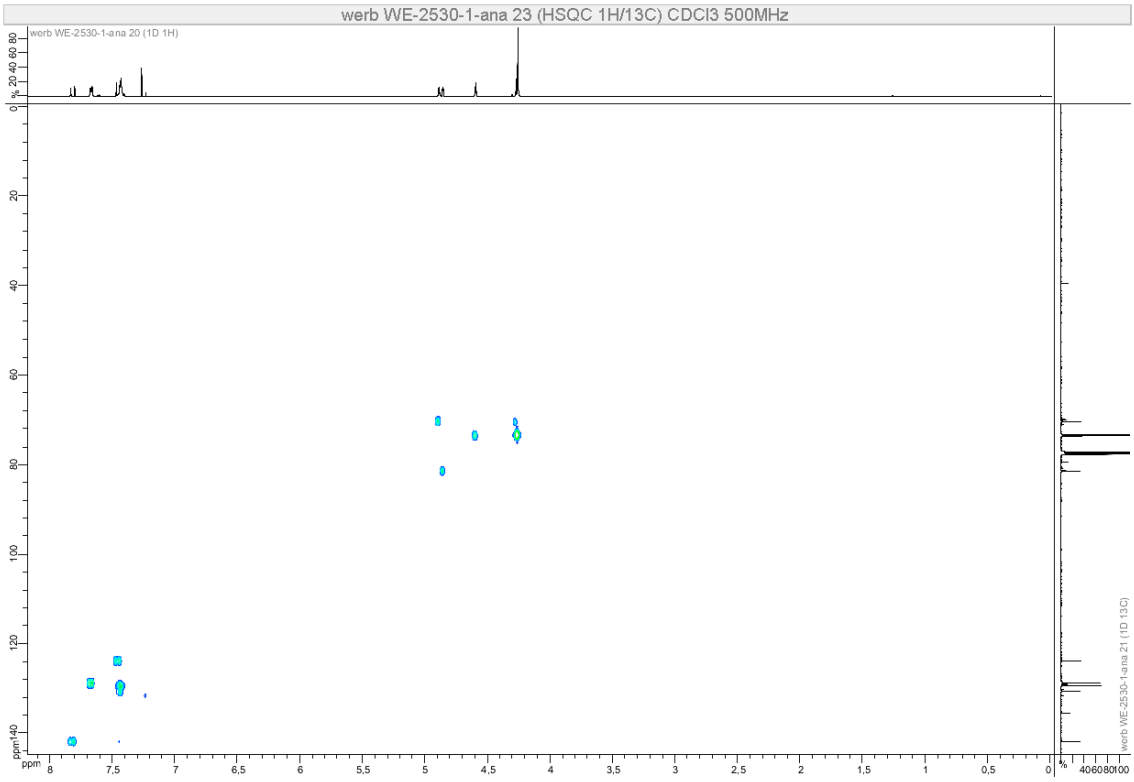
^{13}C NMR (126 MHz, $CDCl_3$)



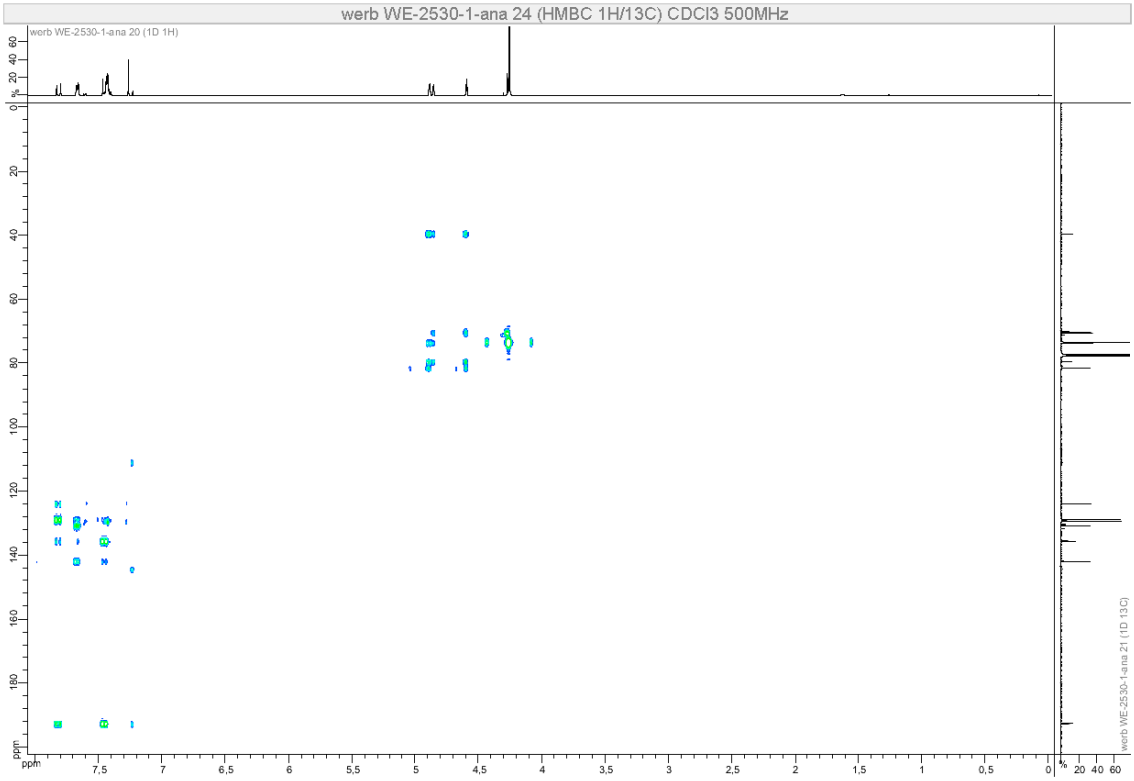
COSY (500 MHz, $CDCl_3$)



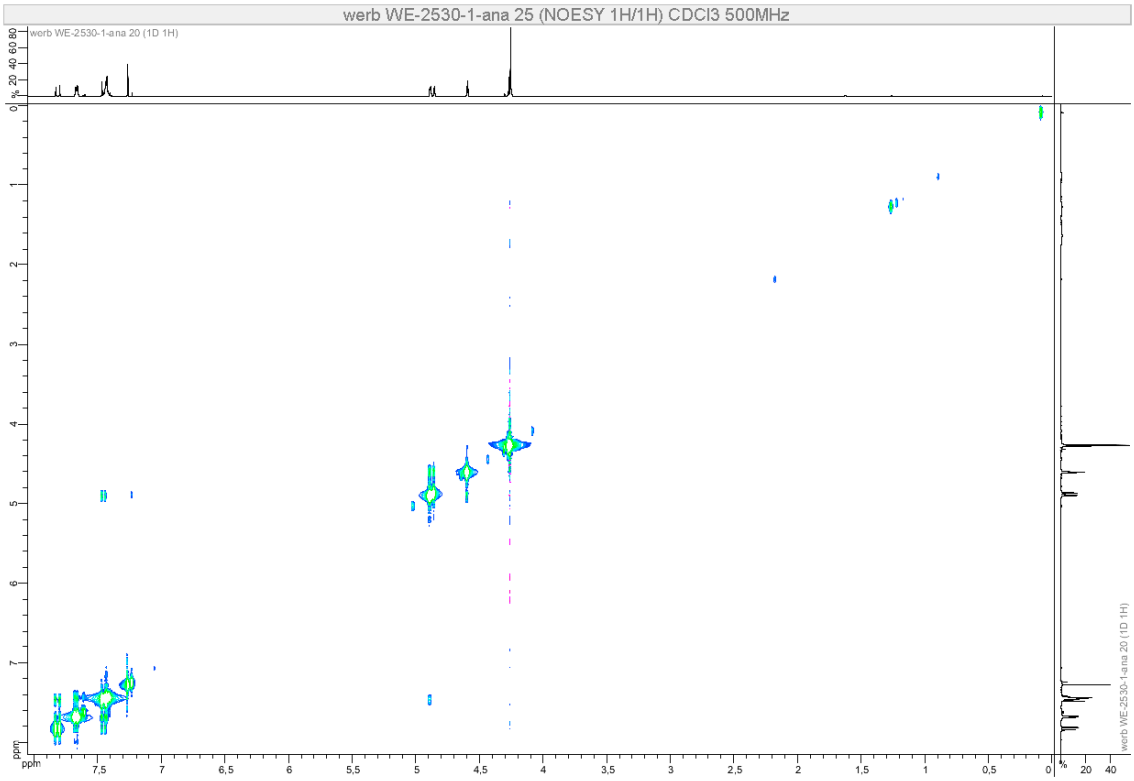
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

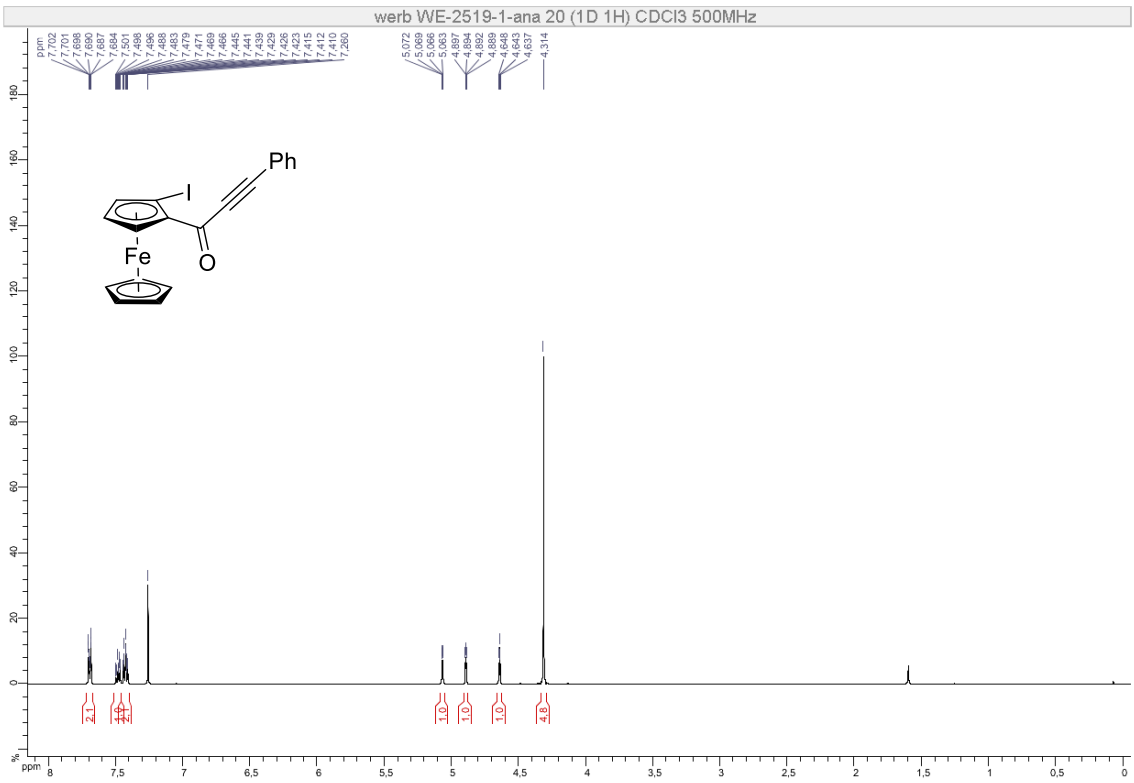


NOESY (500 MHz, $CDCl_3$)

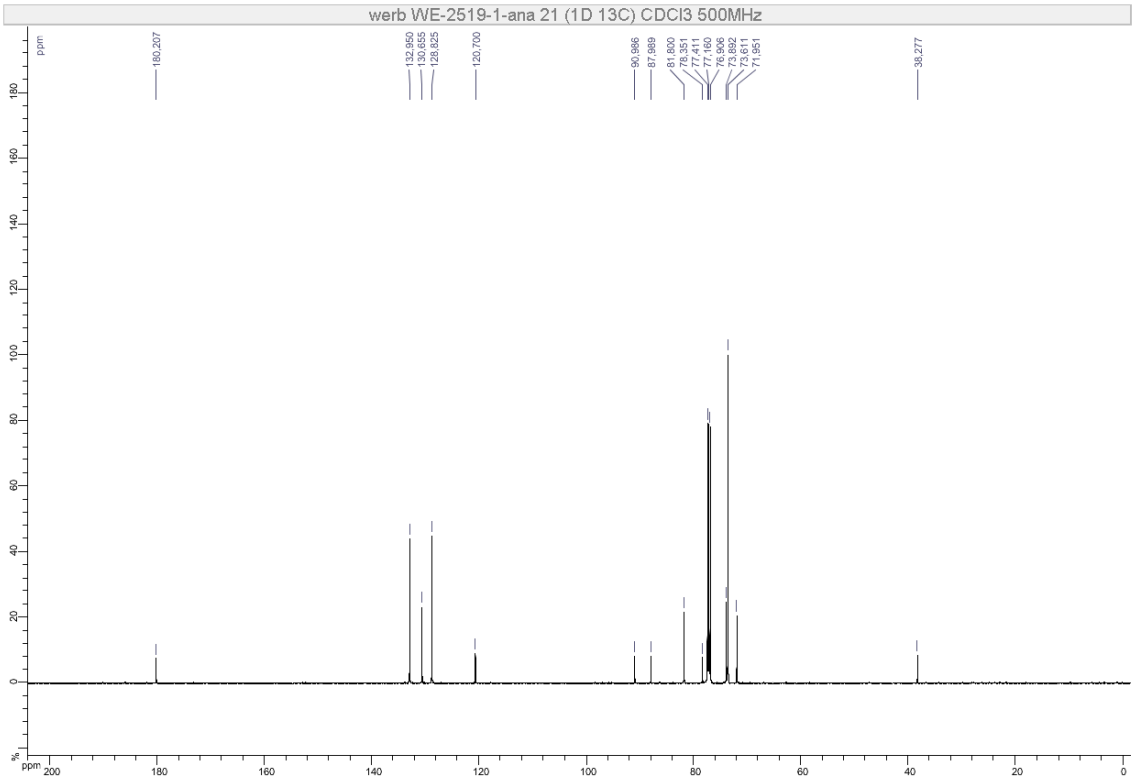


1-Iodo-2-(phenylpropioloyl)ferrocene (2-C≡CPh)

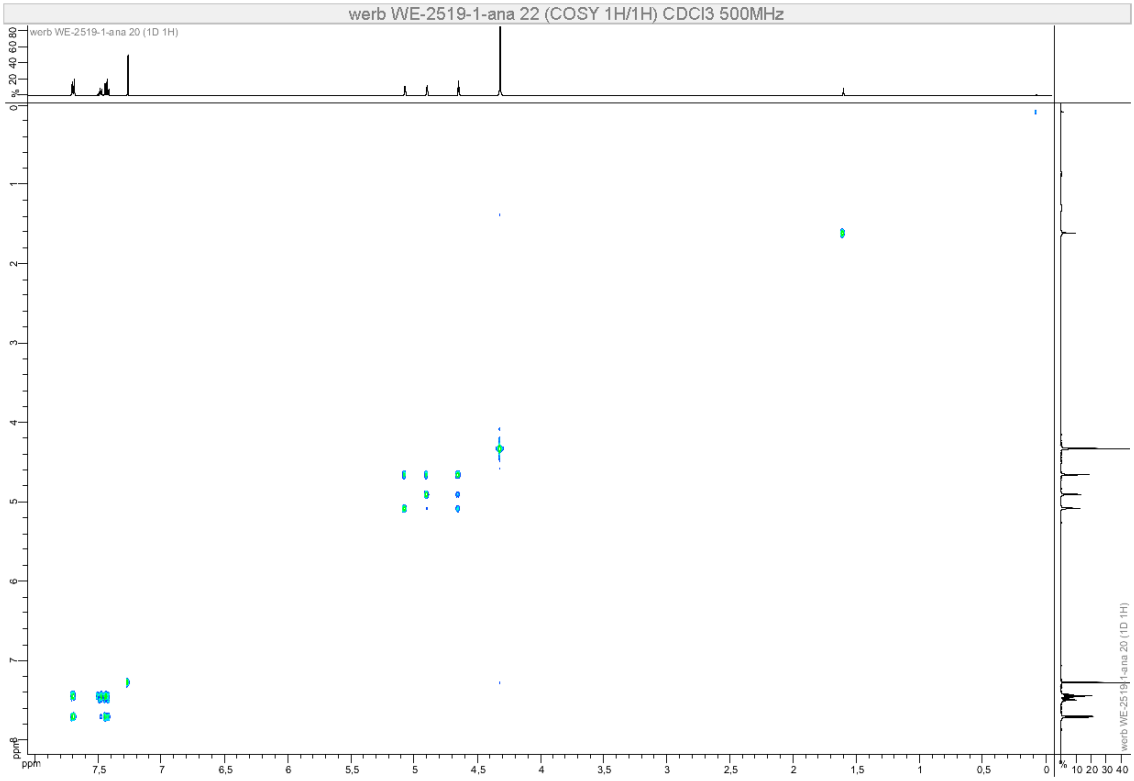
^{1}H NMR (500 MHz, $CDCl_3$)



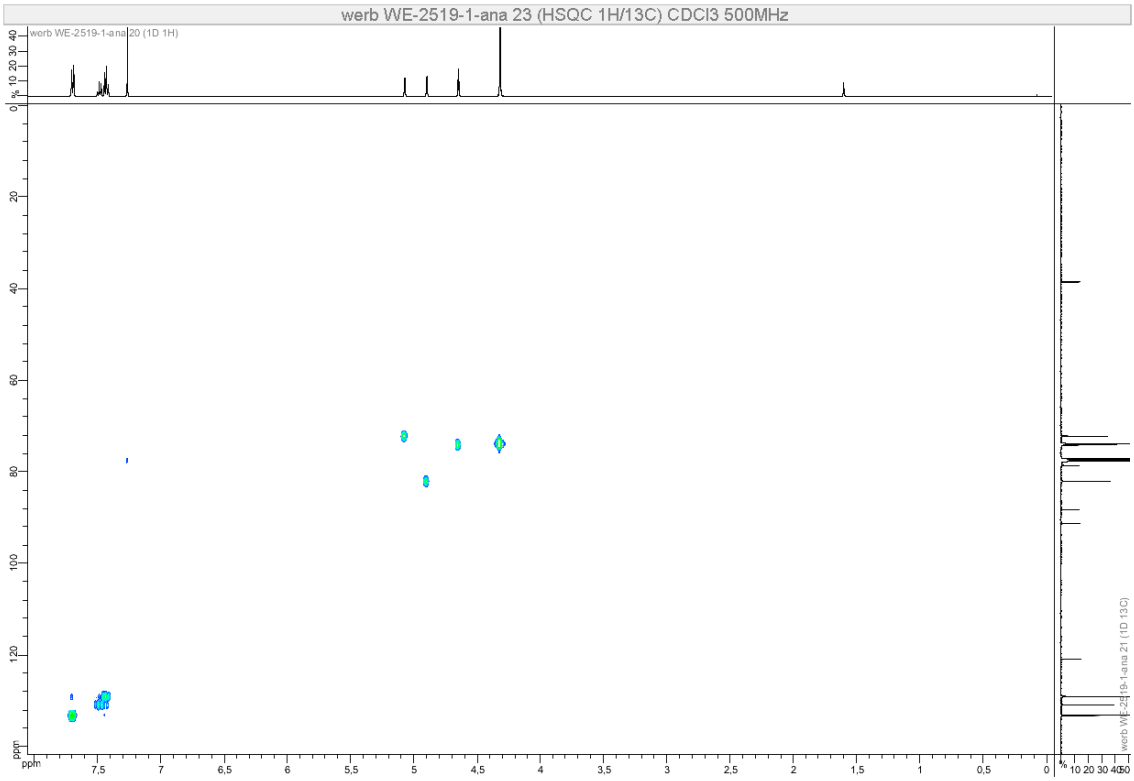
^{13}C NMR (126 MHz, $CDCl_3$)



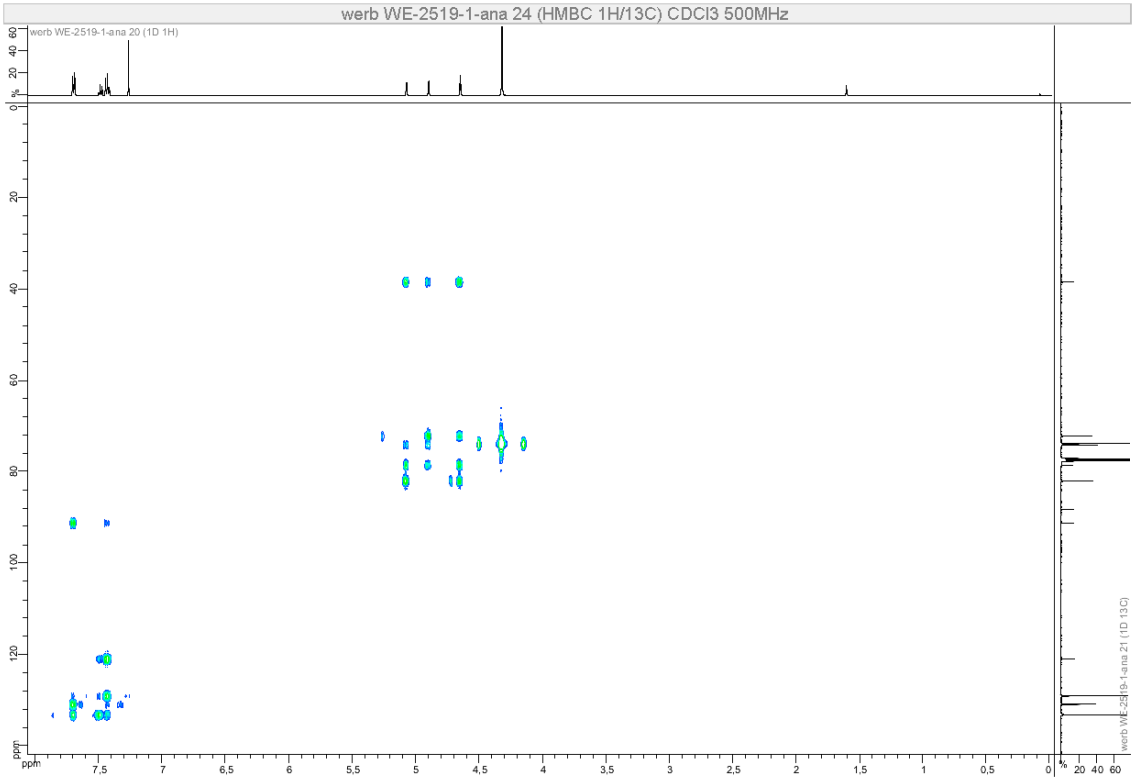
COSY (500 MHz, $CDCl_3$)



HSQC (500 MHz, $CDCl_3$)

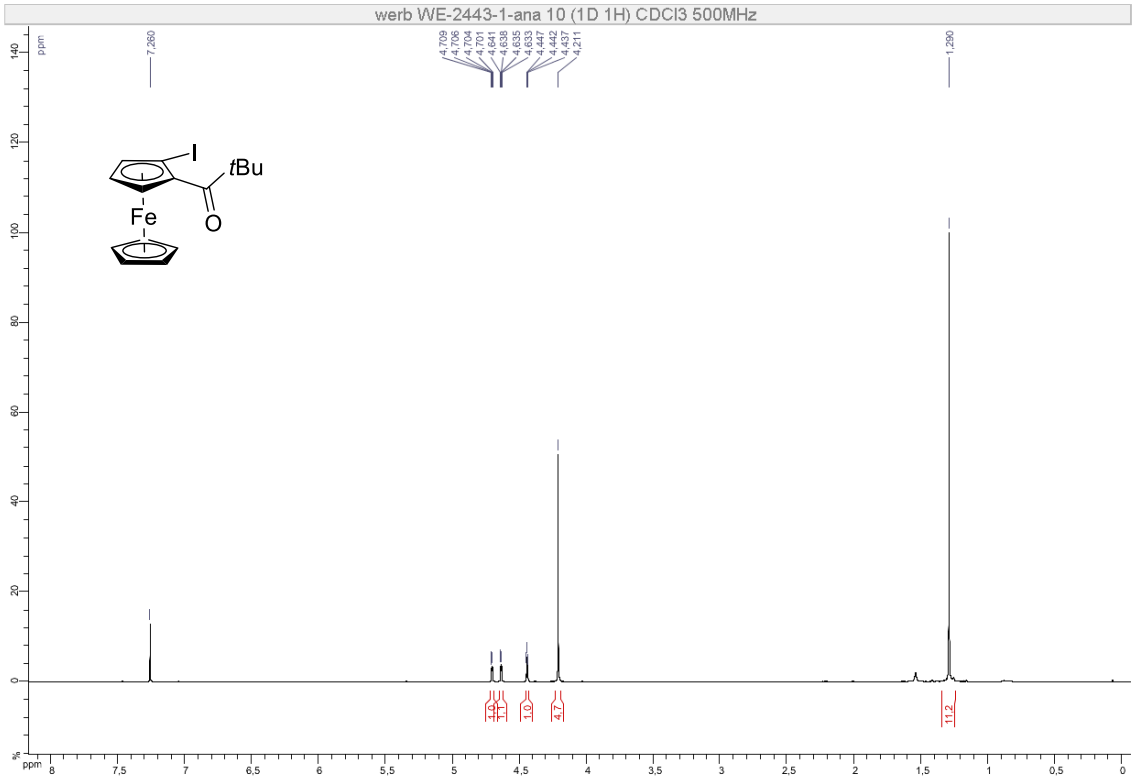


HMBC (500 MHz, $CDCl_3$)

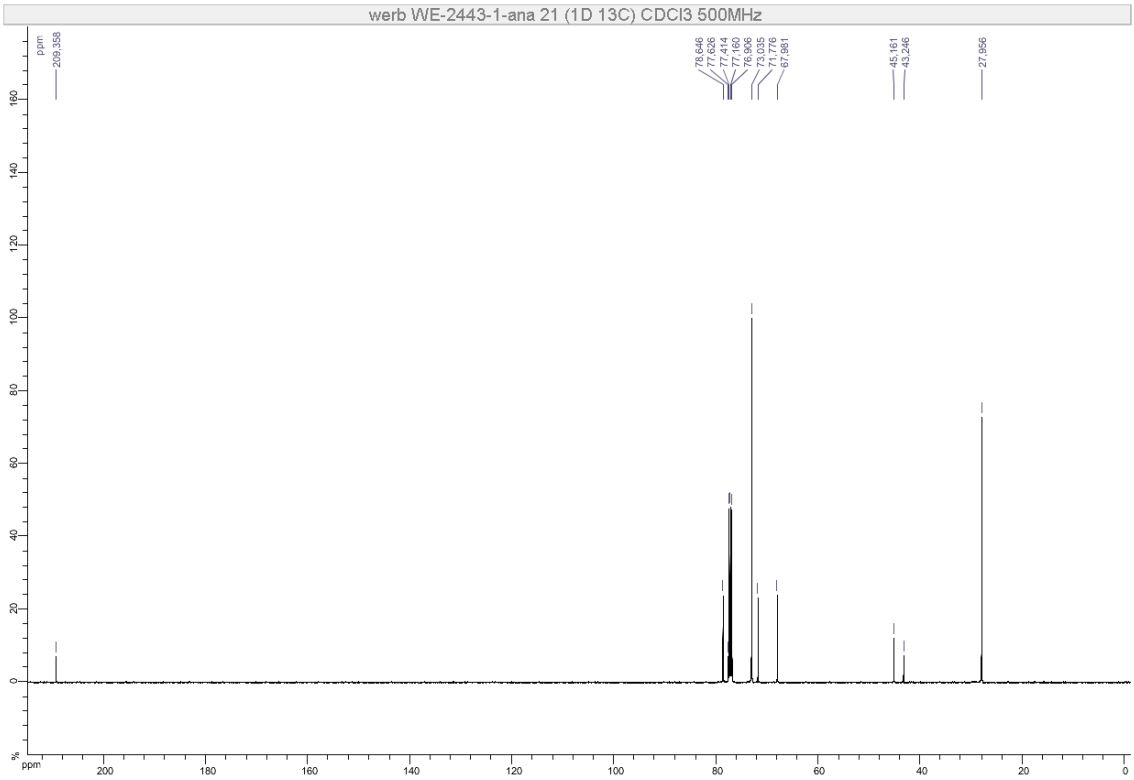


1-Iodo-2-pivaloylferrocene (2-*t*Bu)

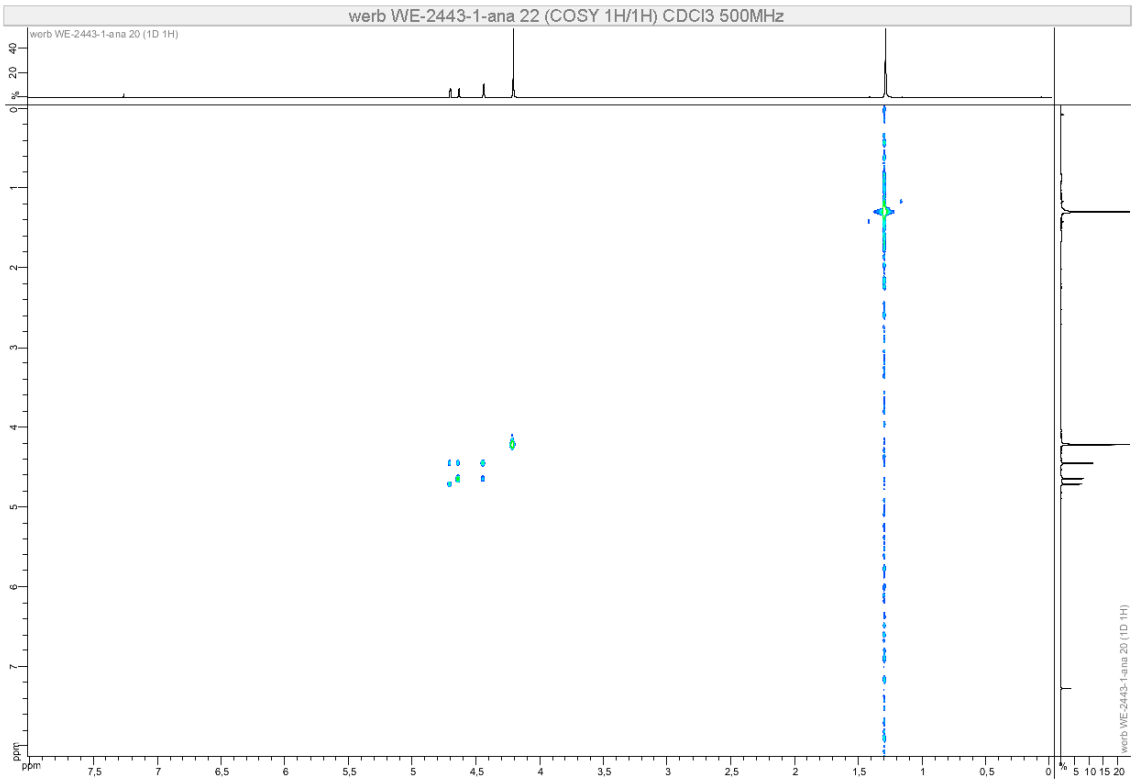
^{1}H NMR (500 MHz, $CDCl_3$)



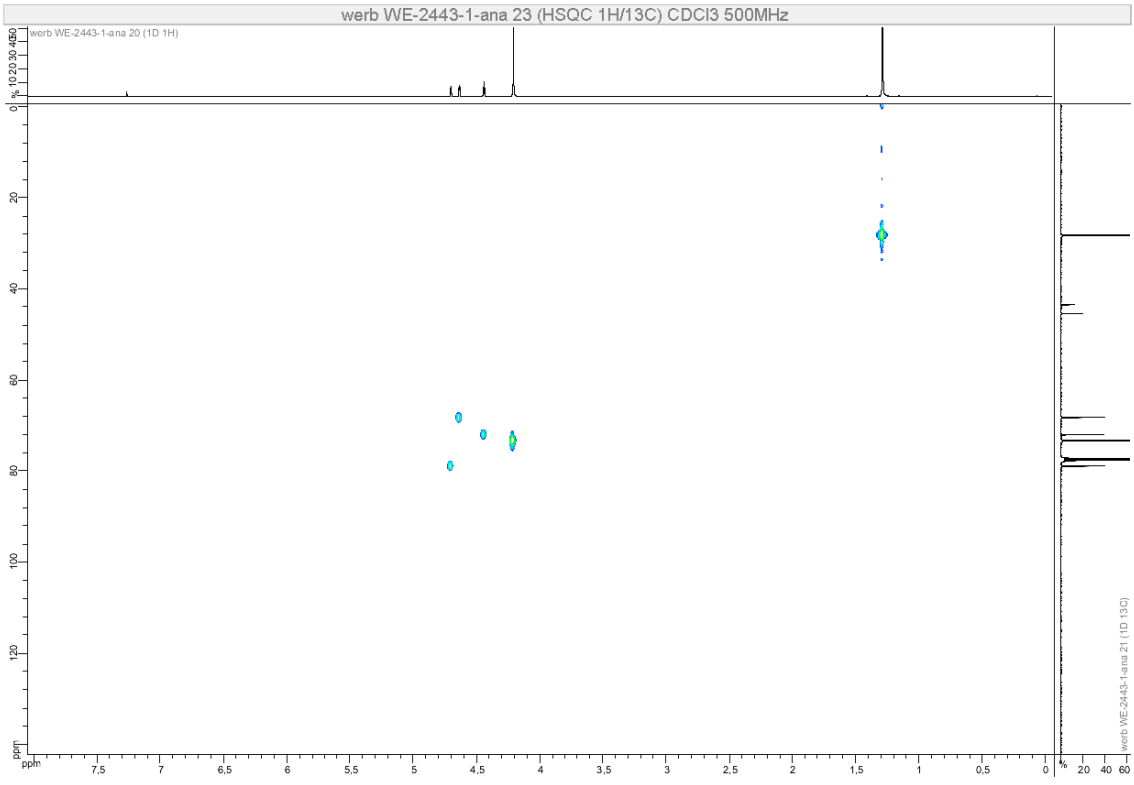
^{13}C NMR (126 MHz, $CDCl_3$)



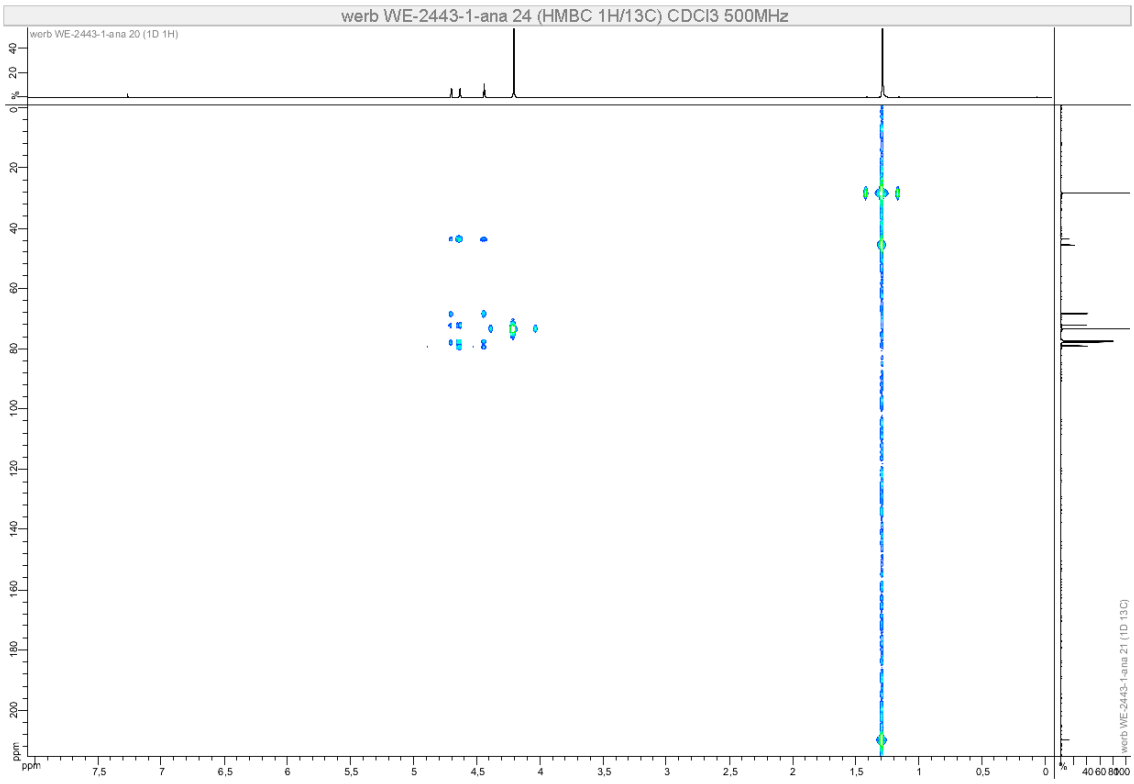
COSY (500 MHz, $CDCl_3$)



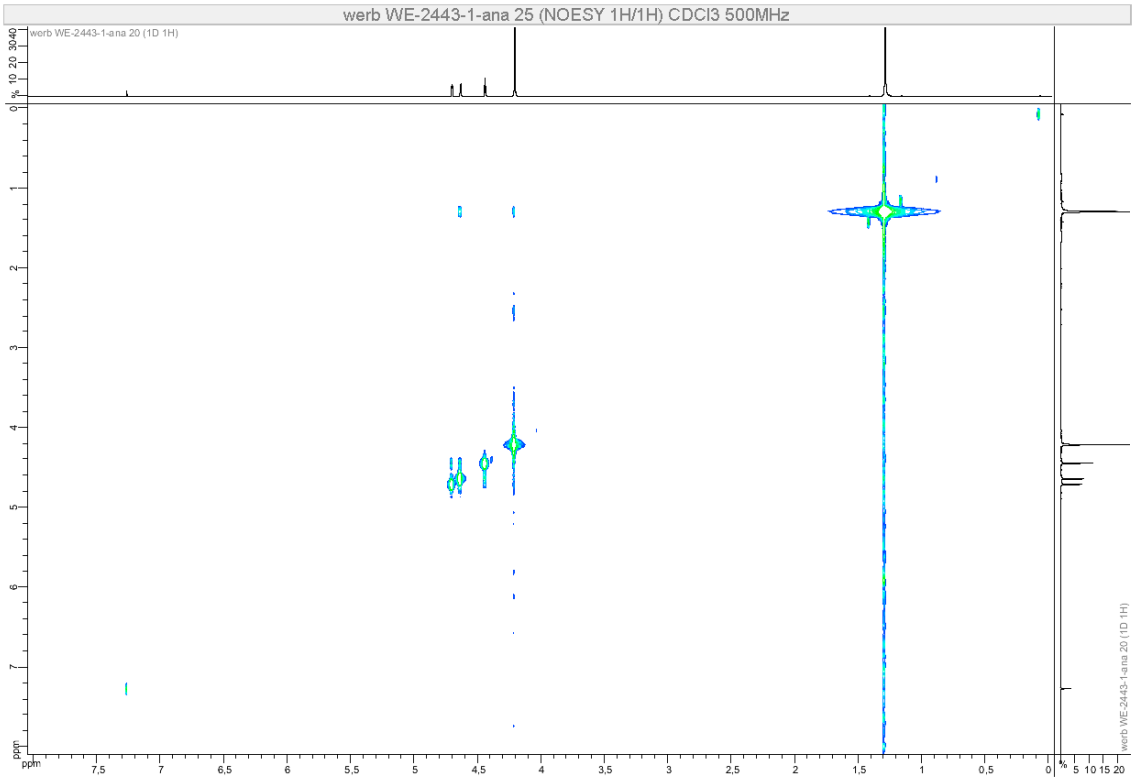
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

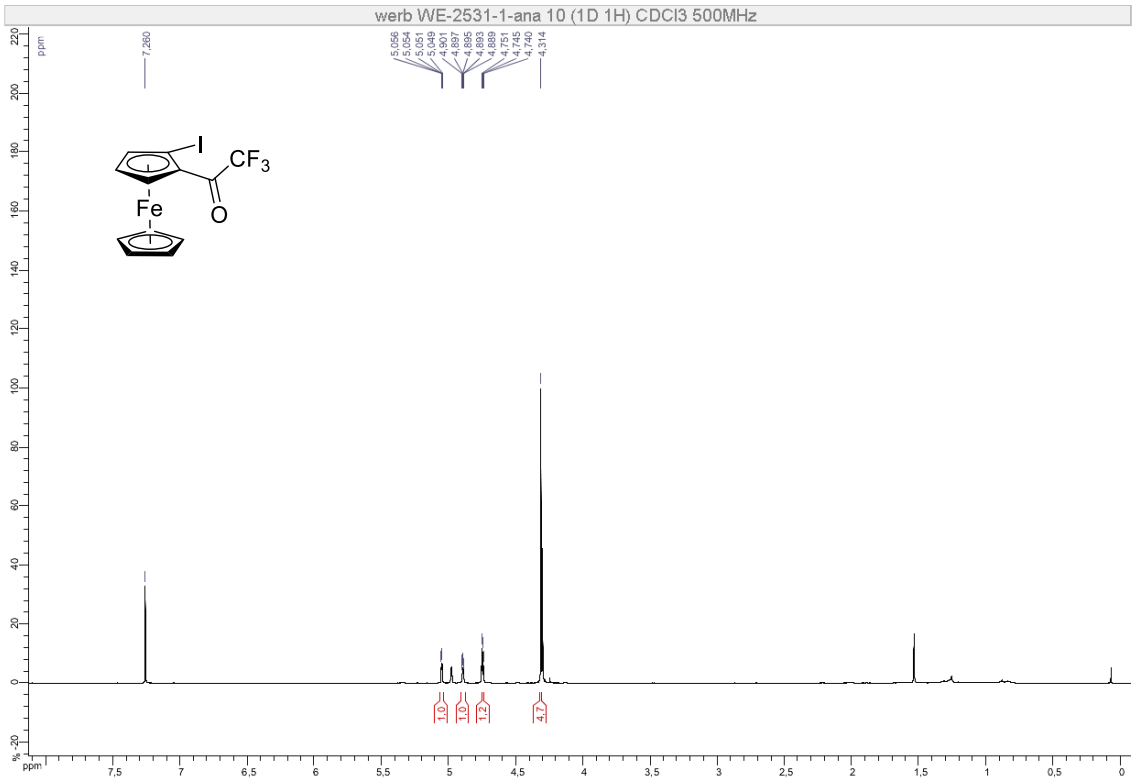


NOESY (500 MHz, $CDCl_3$)

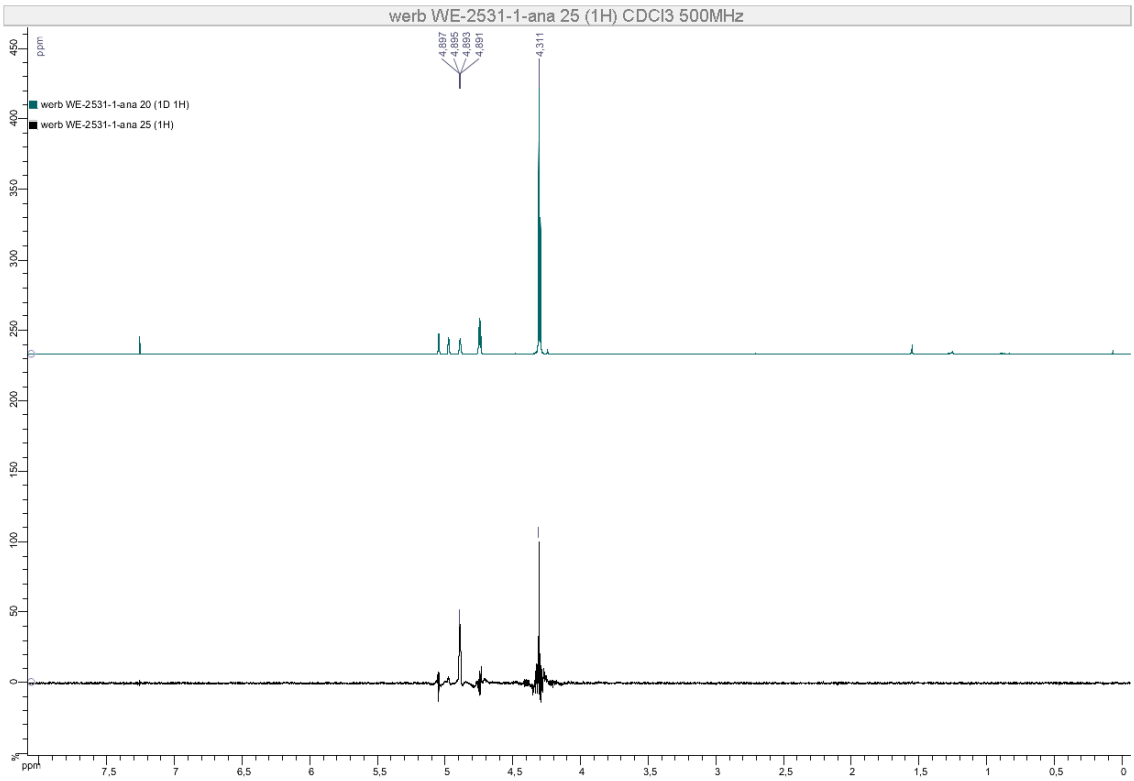


1-Iodo-2-(trifluoromethylcarbonyl)ferrocene (2-CF_3)

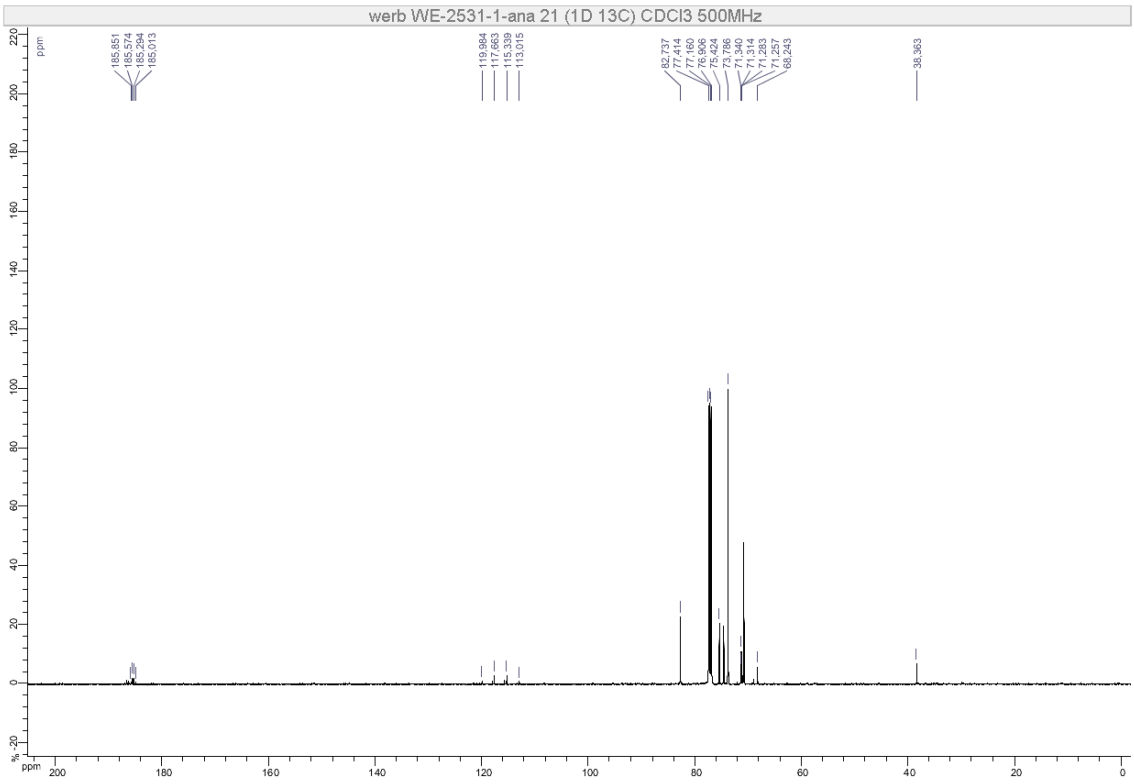
^{1}H NMR (500 MHz, $CDCl_3$)



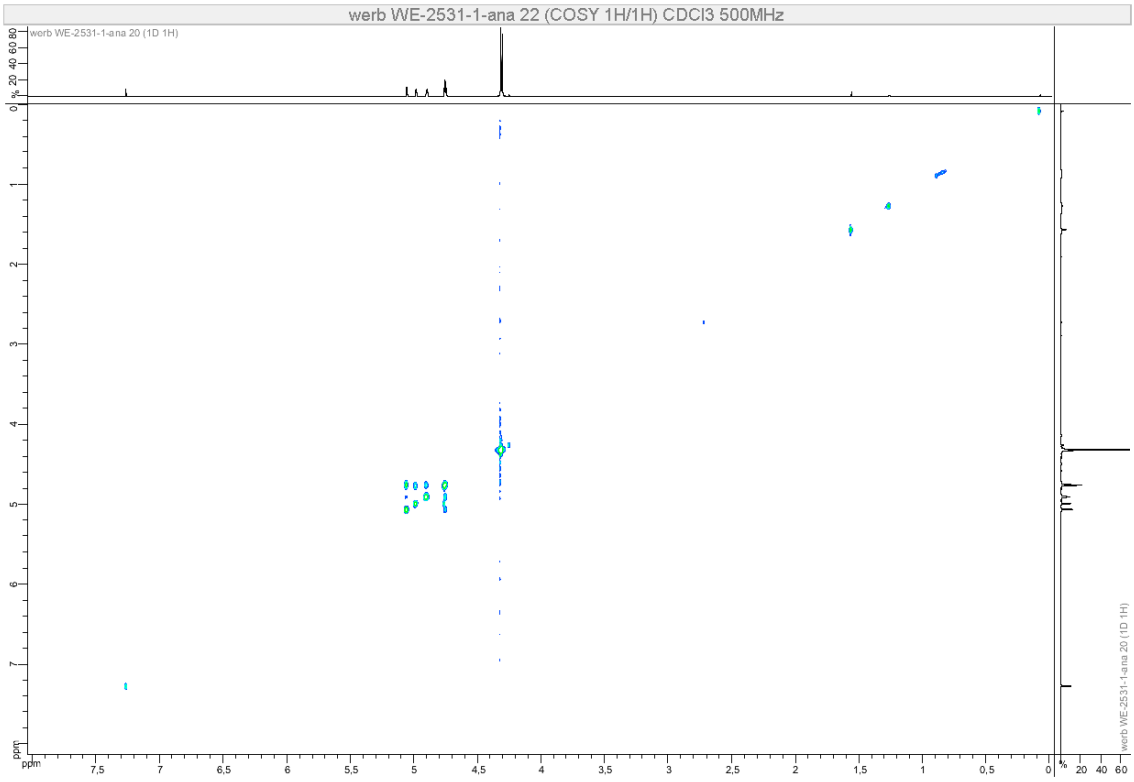
HOESY (500 MHz, $CDCl_3$) Irradiation at –71.8 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



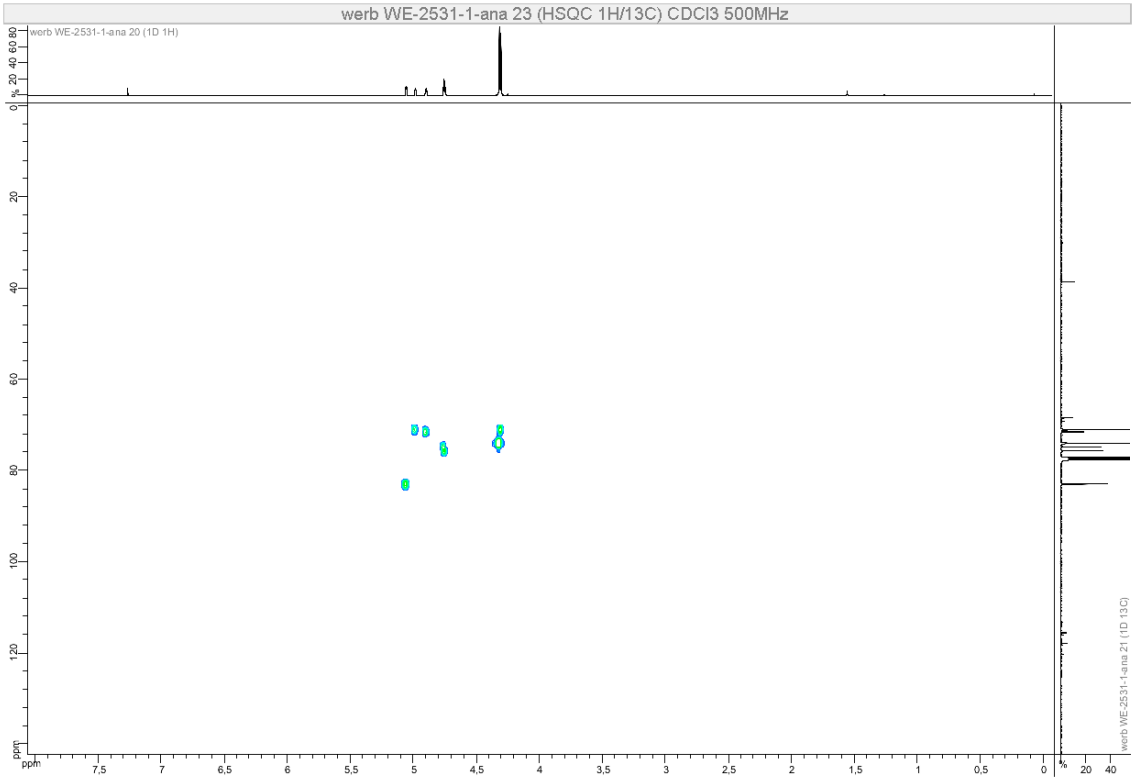
^{13}C NMR (126 MHz, $CDCl_3$)



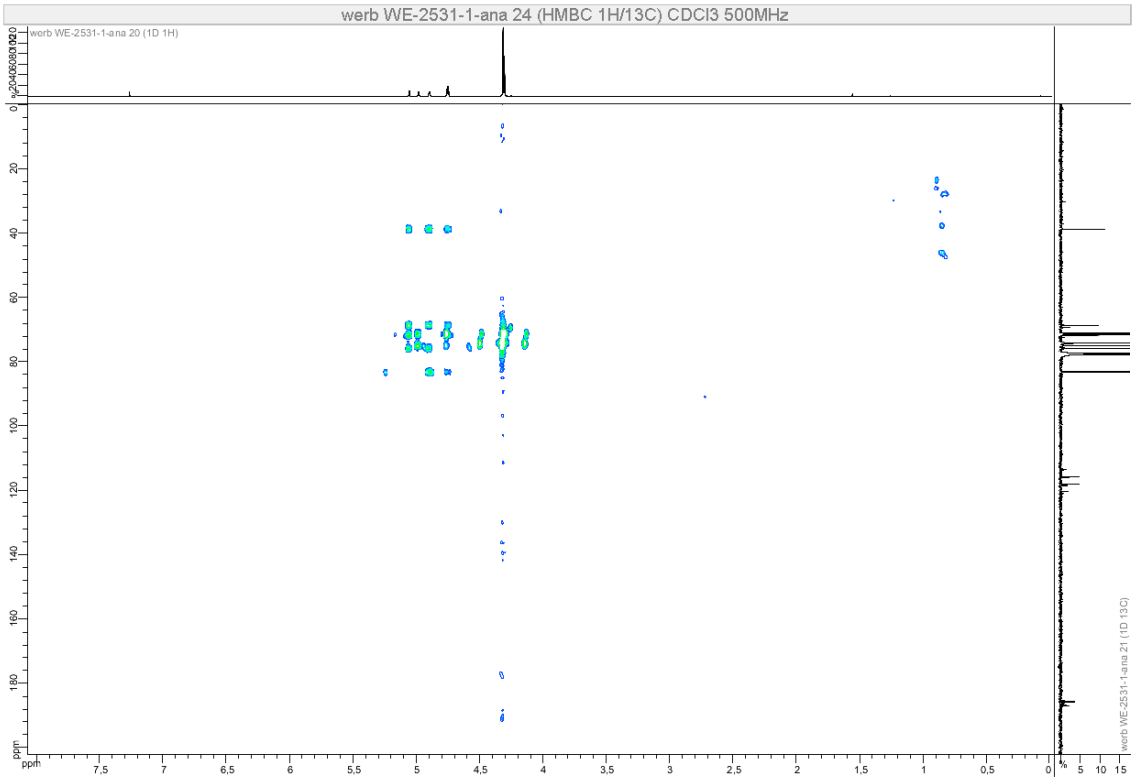
COSY (500 MHz, $CDCl_3$)



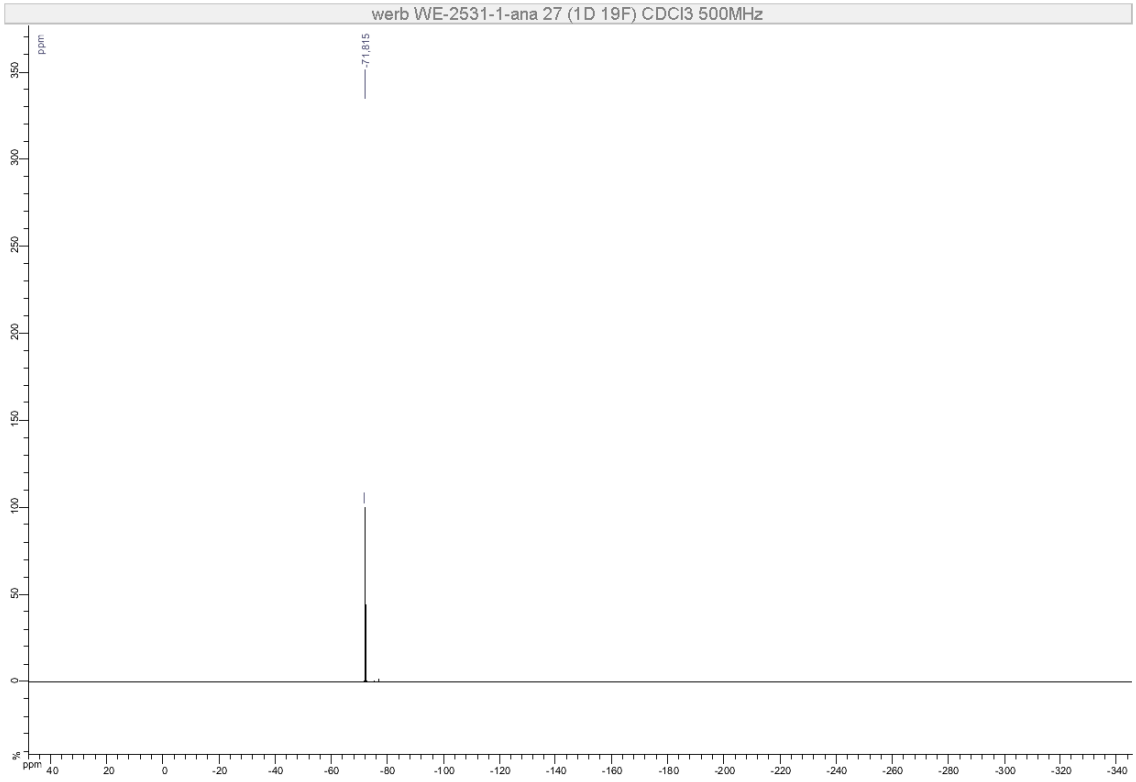
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

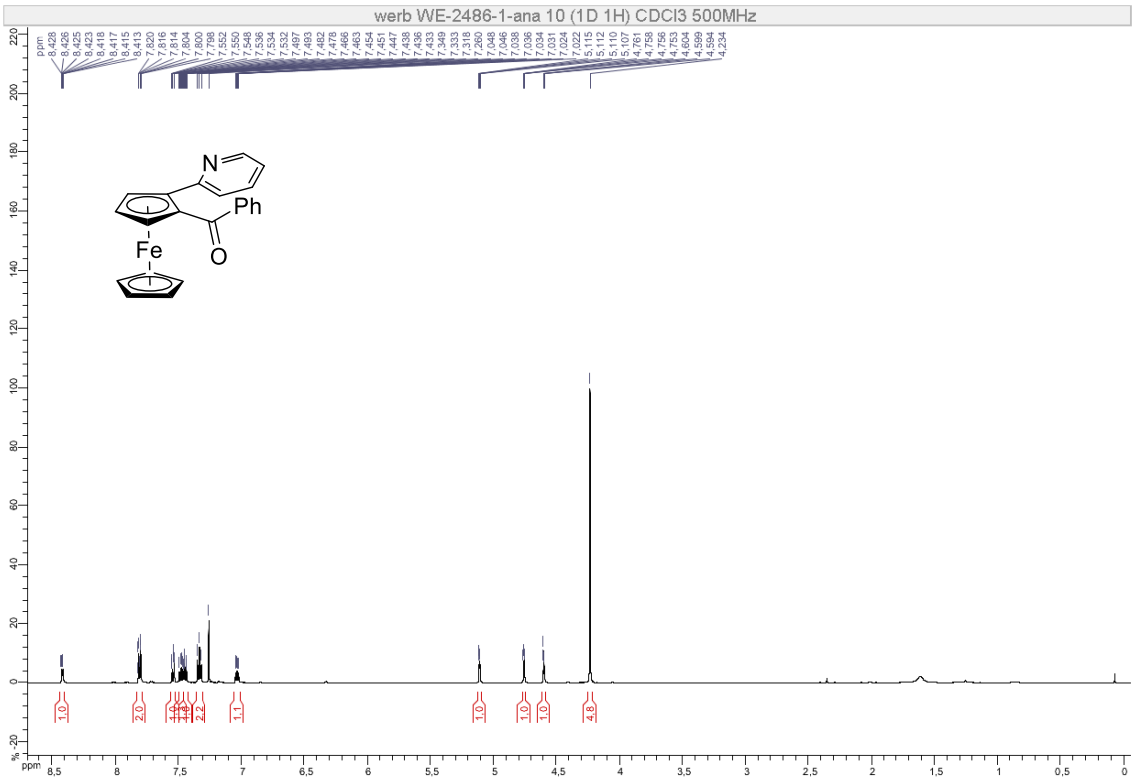


^{19}F NMR (470 MHz, $CDCl_3$)

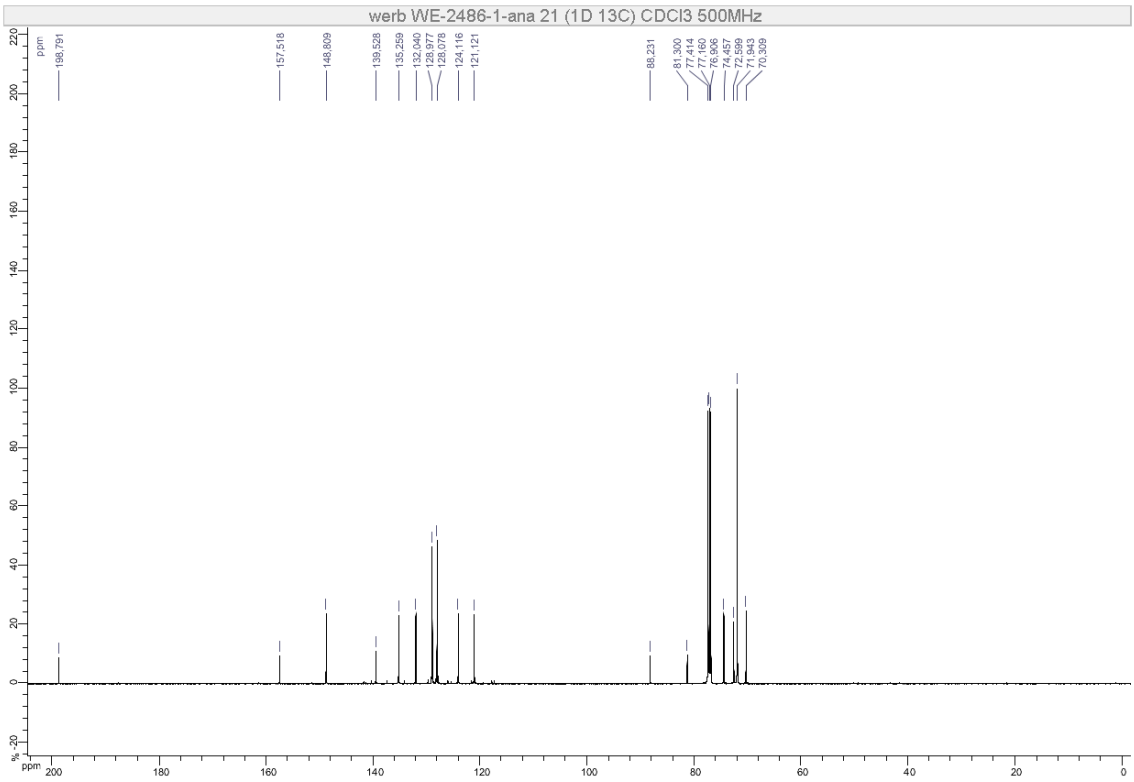


1-Benzoyl-2-(2-pyridyl)ferrocene (3-Ph)

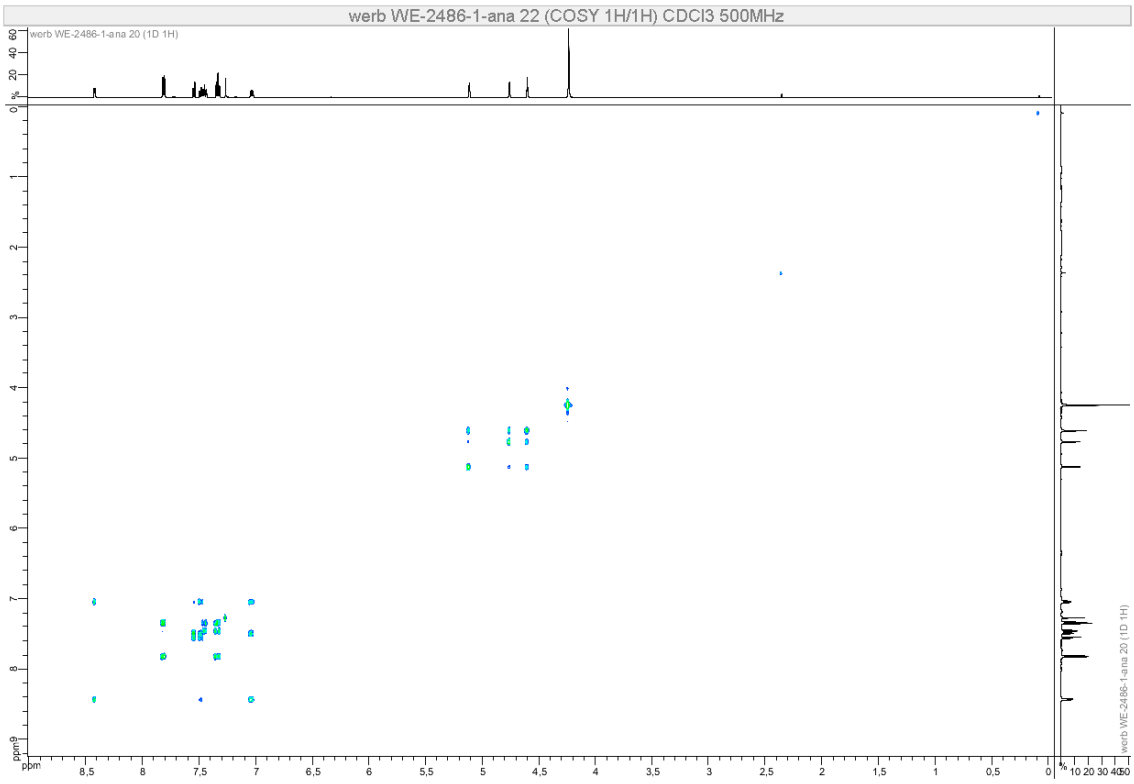
^{1}H NMR (500 MHz, $CDCl_3$)



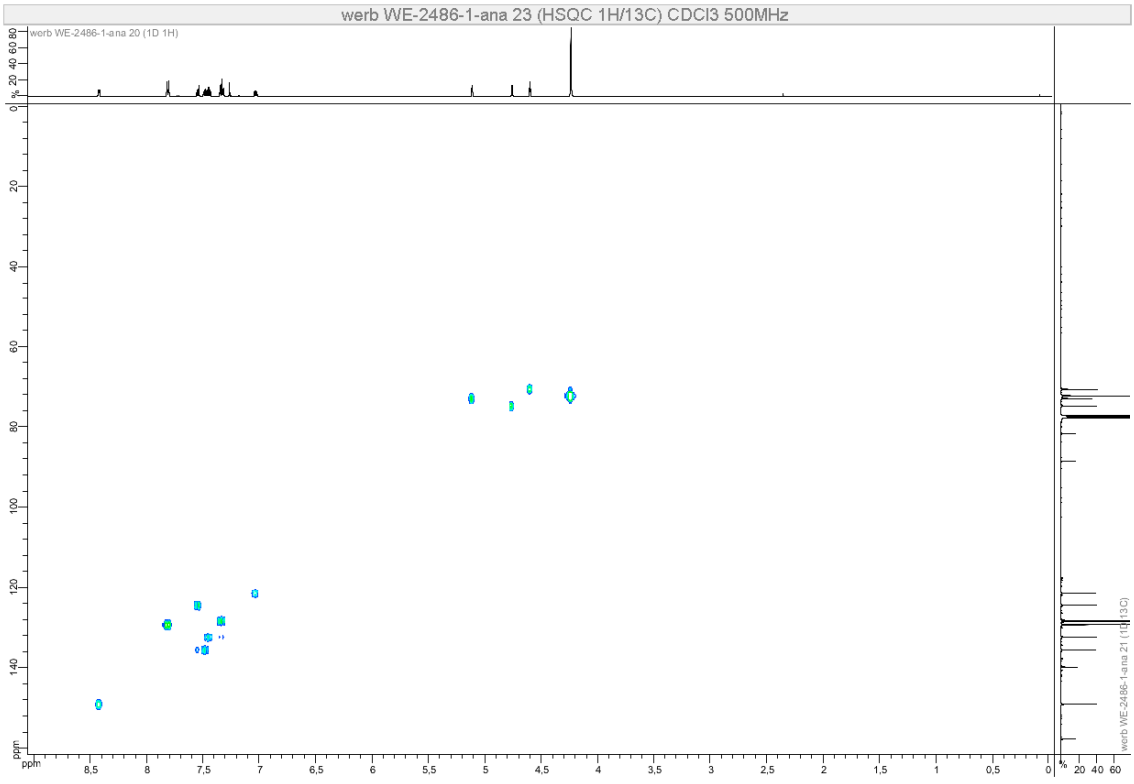
^{13}C NMR (126 MHz, $CDCl_3$)



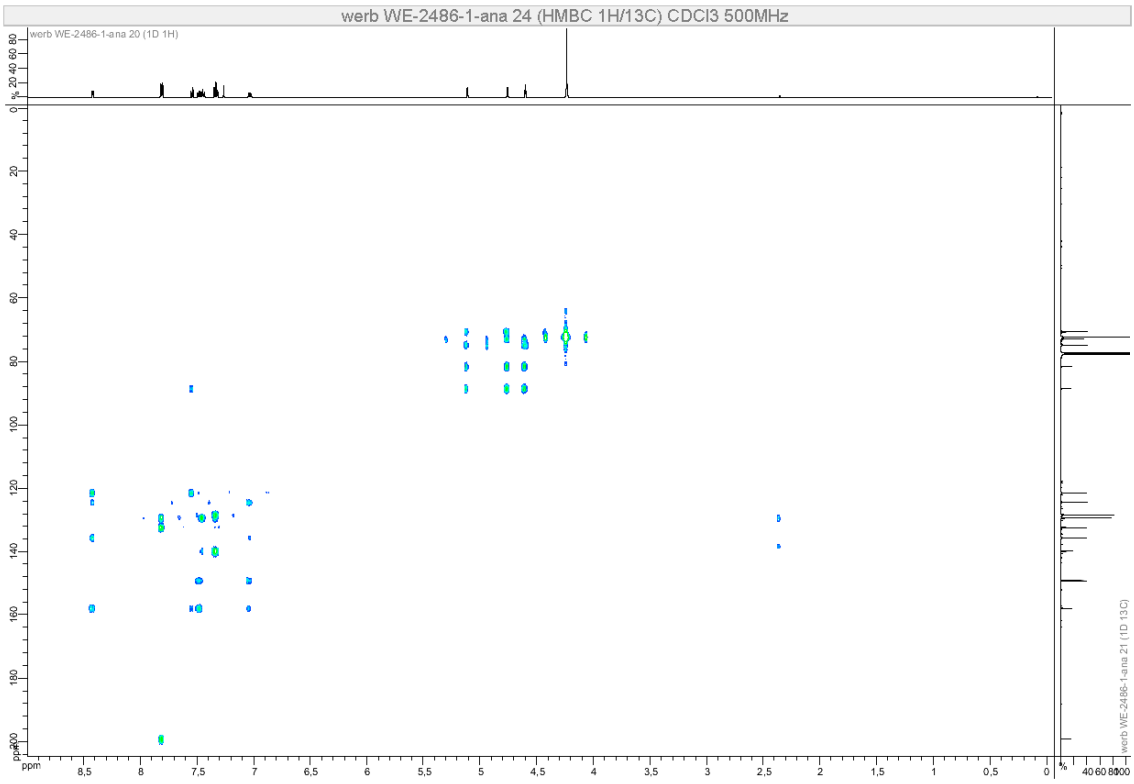
COSY (500 MHz, $CDCl_3$)



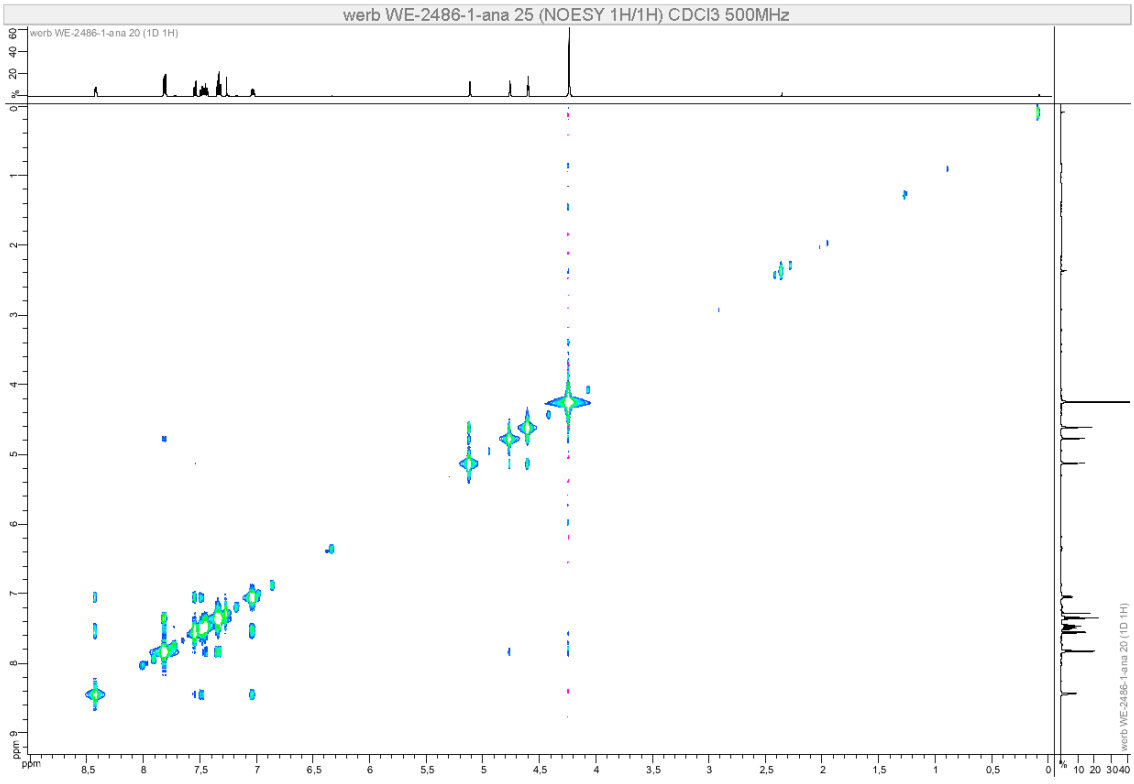
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

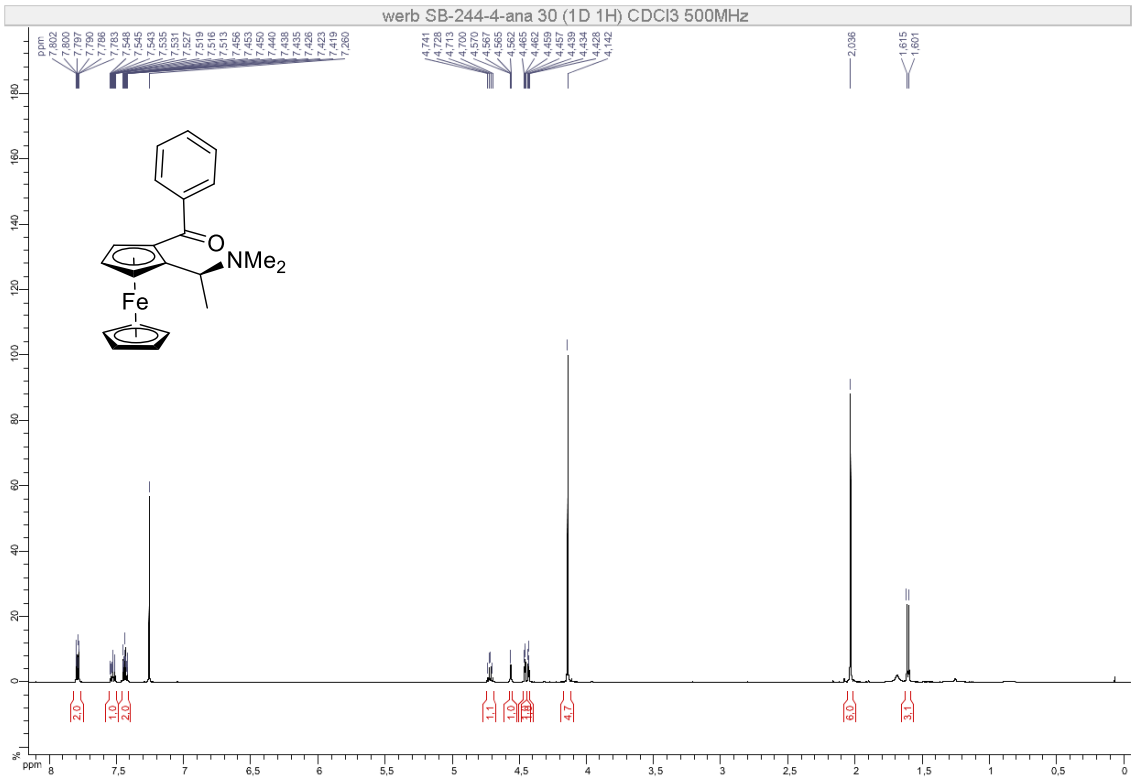


NOESY (500 MHz, $CDCl_3$)

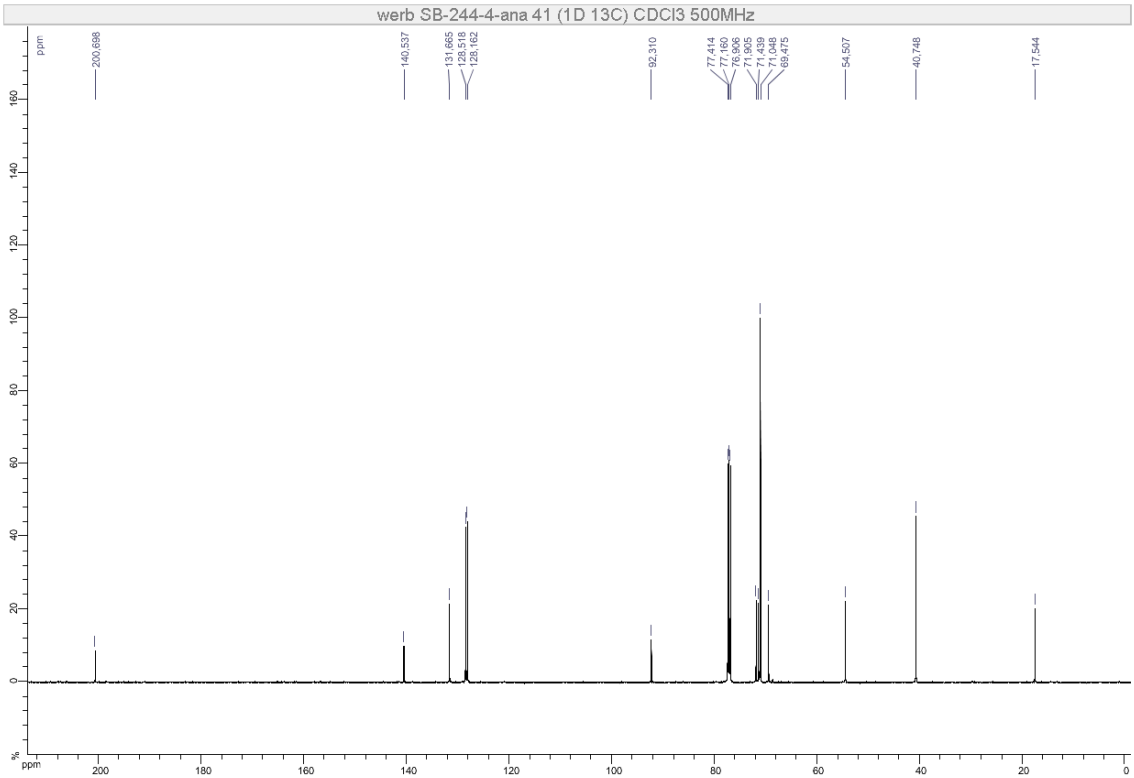


(*S*,*R*$_P$)-1-Benzoyl-2-[1-(dimethylamino)ethyl]ferrocene (*R*$_P$-5)

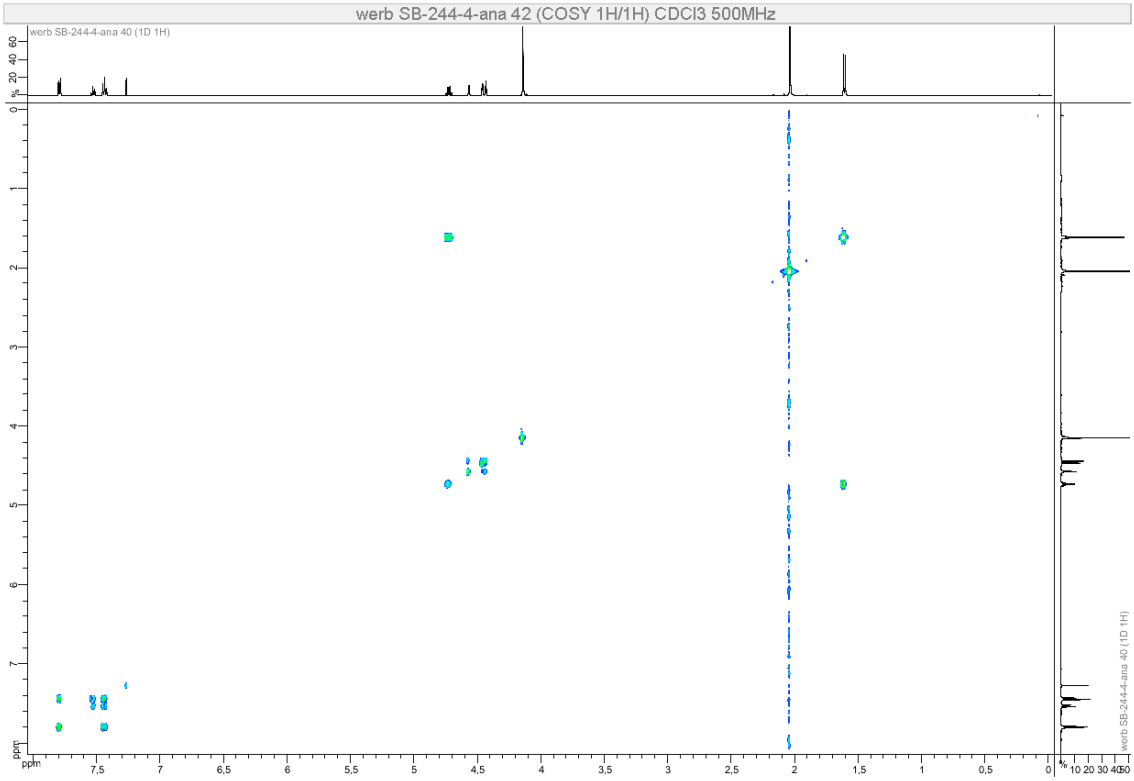
^{1}H NMR (500 MHz, $CDCl_3$)



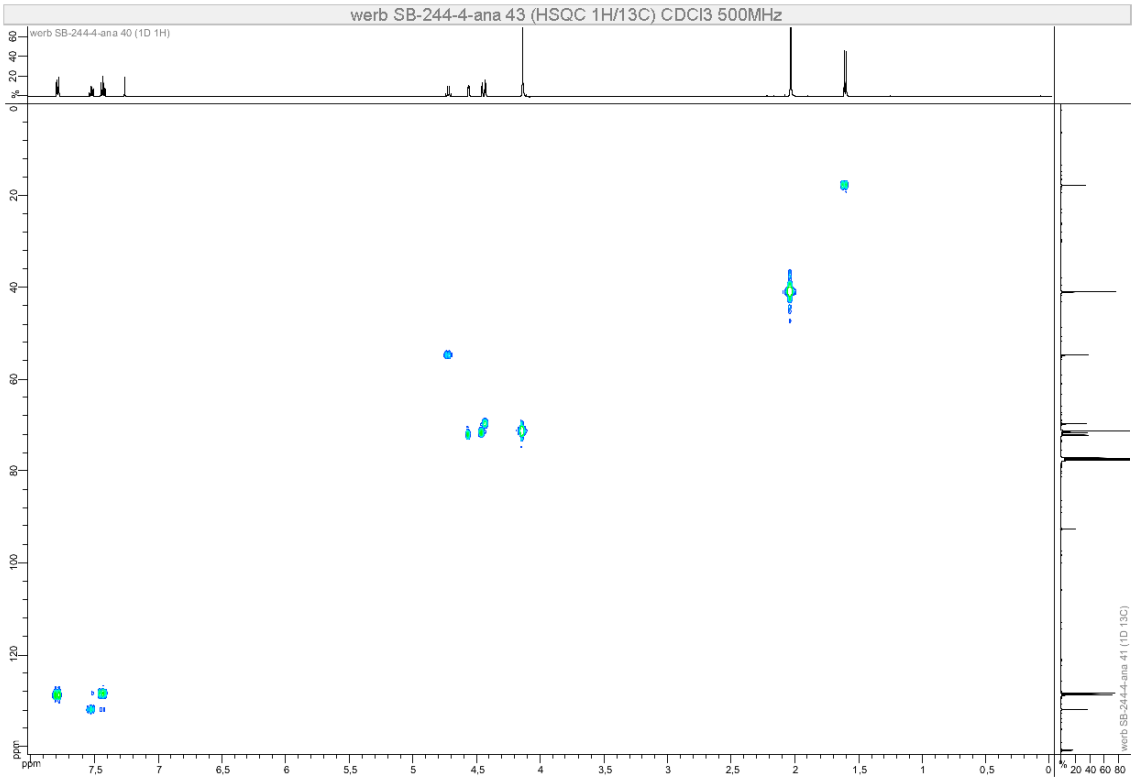
^{13}C NMR (126 MHz, $CDCl_3$)



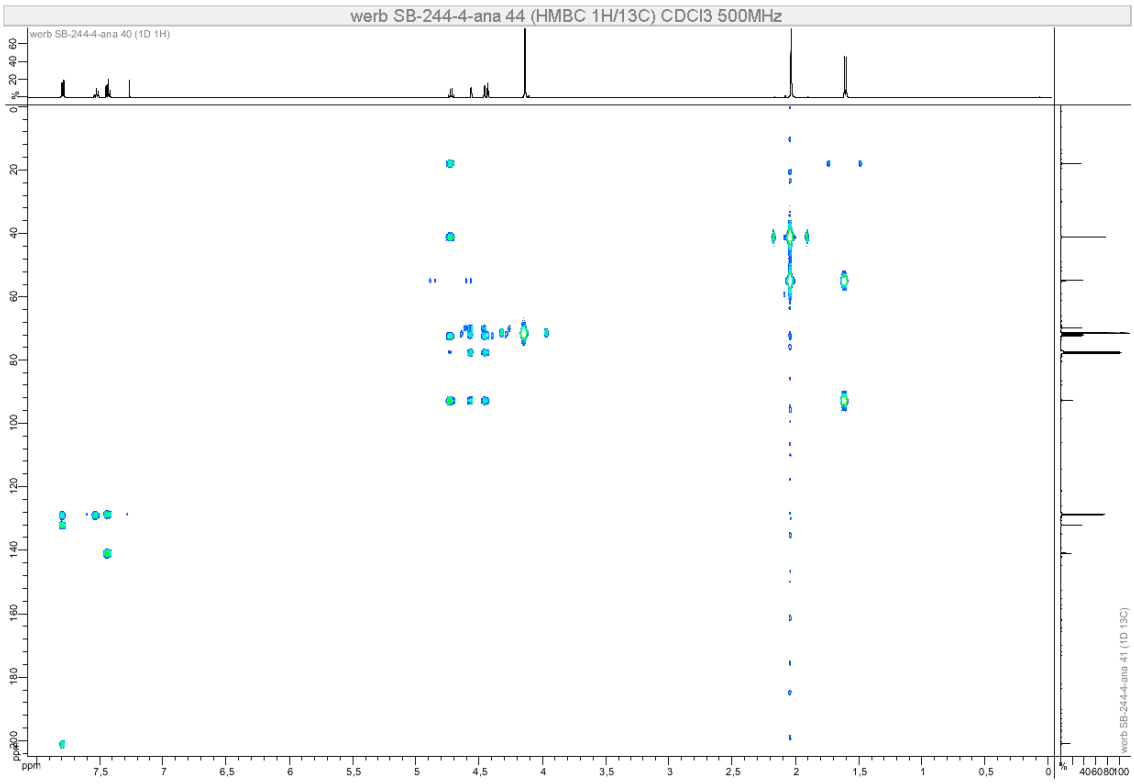
COSY (500 MHz, $CDCl_3$)



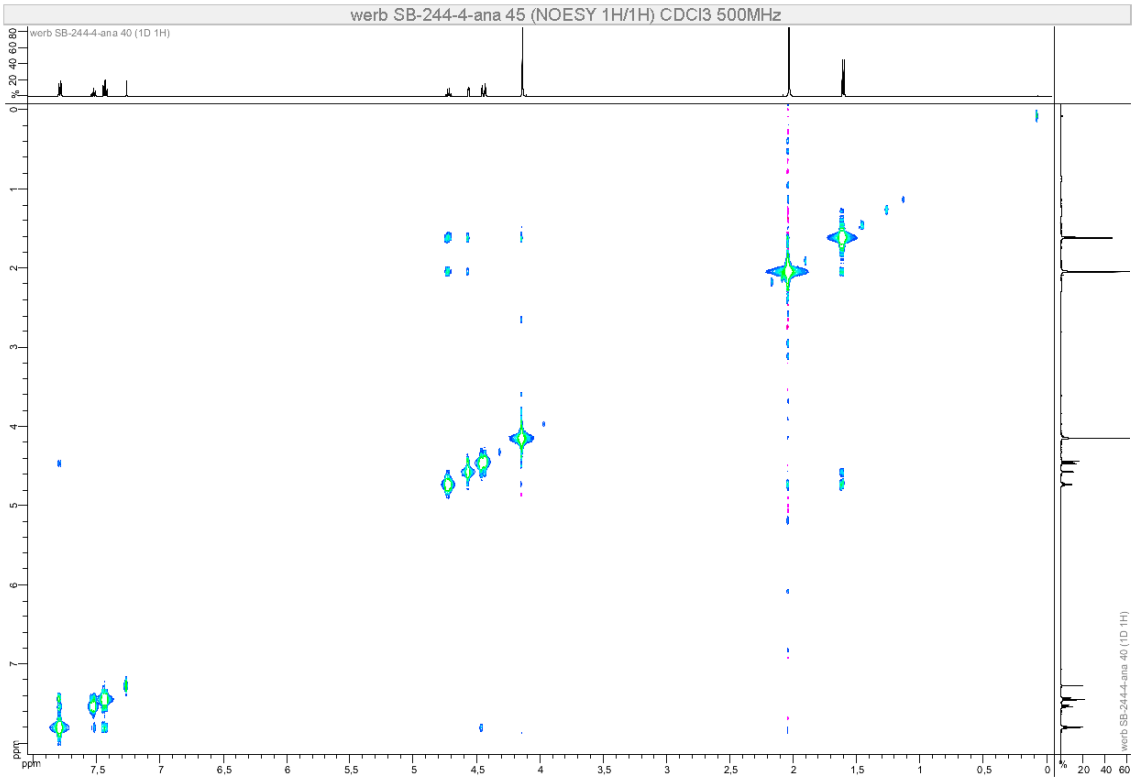
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

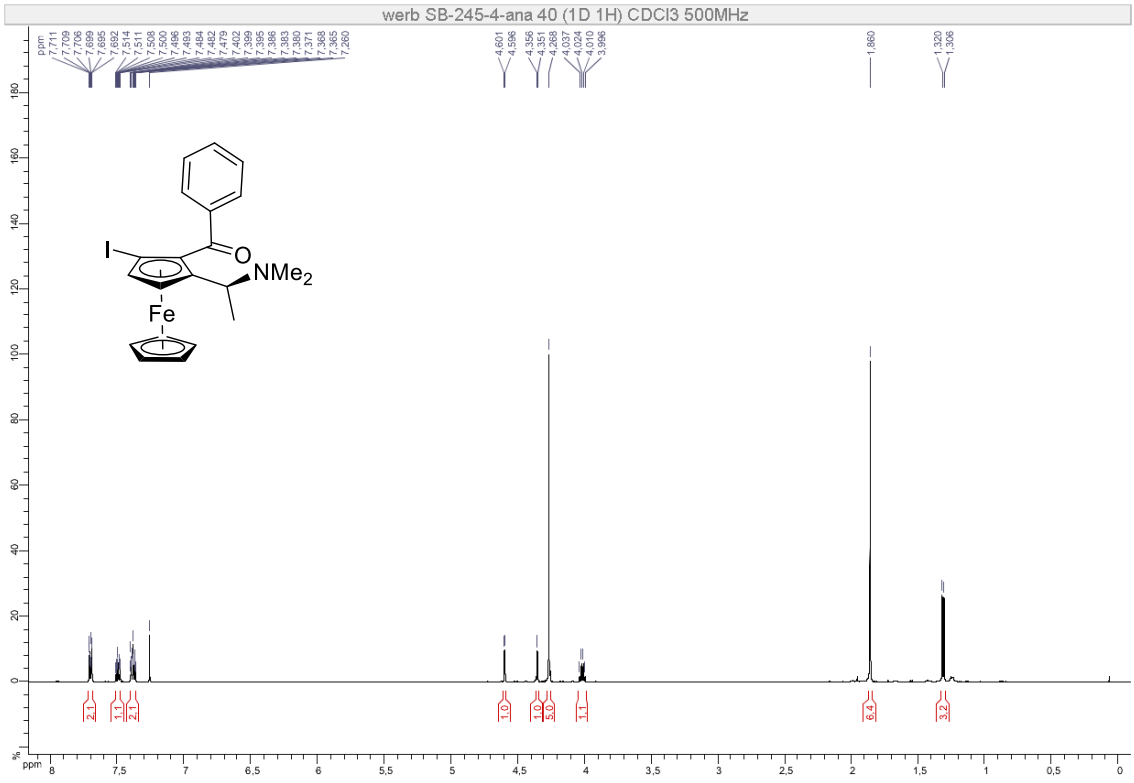


NOESY (500 MHz, $CDCl_3$)

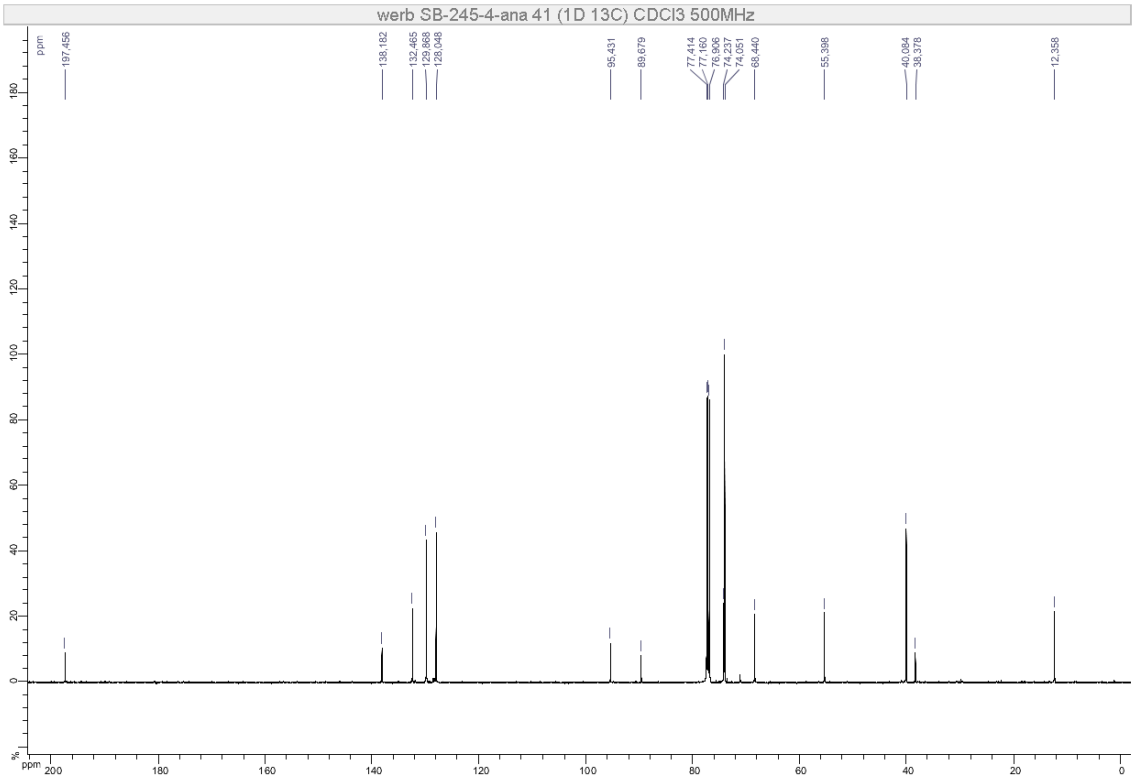


(*S*,*R*$_P$)-1-Benzoyl-2-[1-(dimethylamino)ethyl]-5-iodoferrocene (*R*$_P$-6)

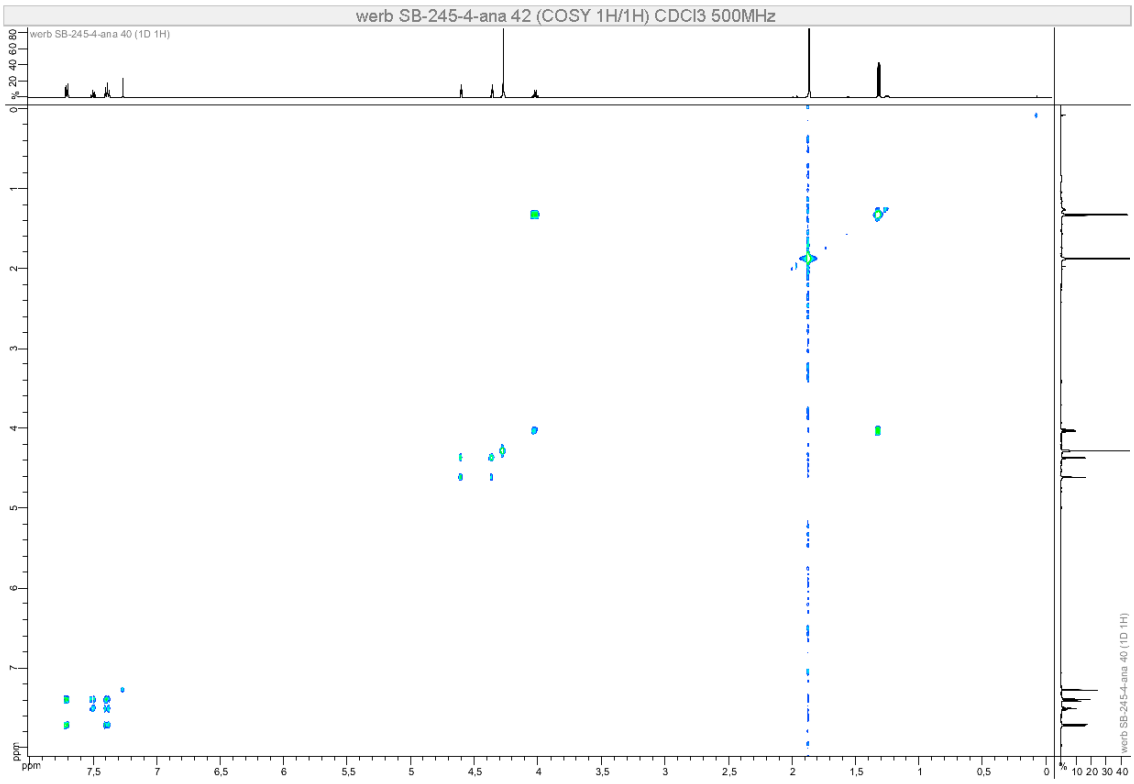
^{1}H NMR (500 MHz, $CDCl_3$)



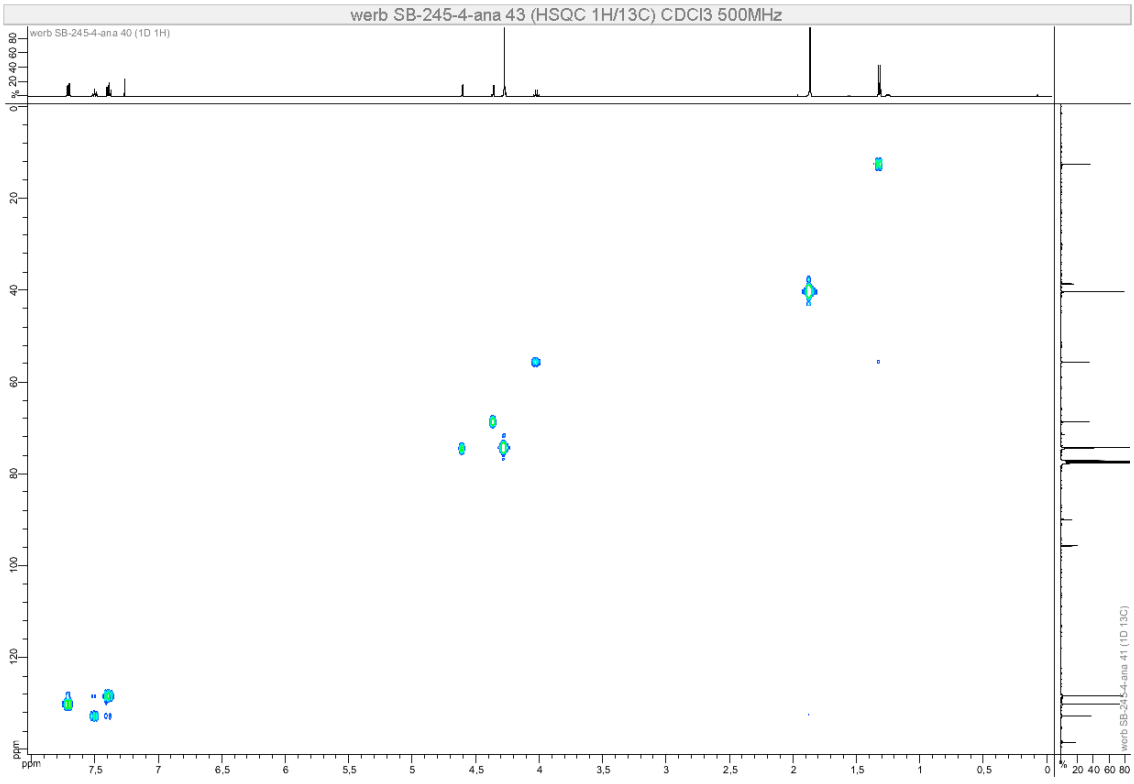
^{13}C NMR (126 MHz, $CDCl_3$)



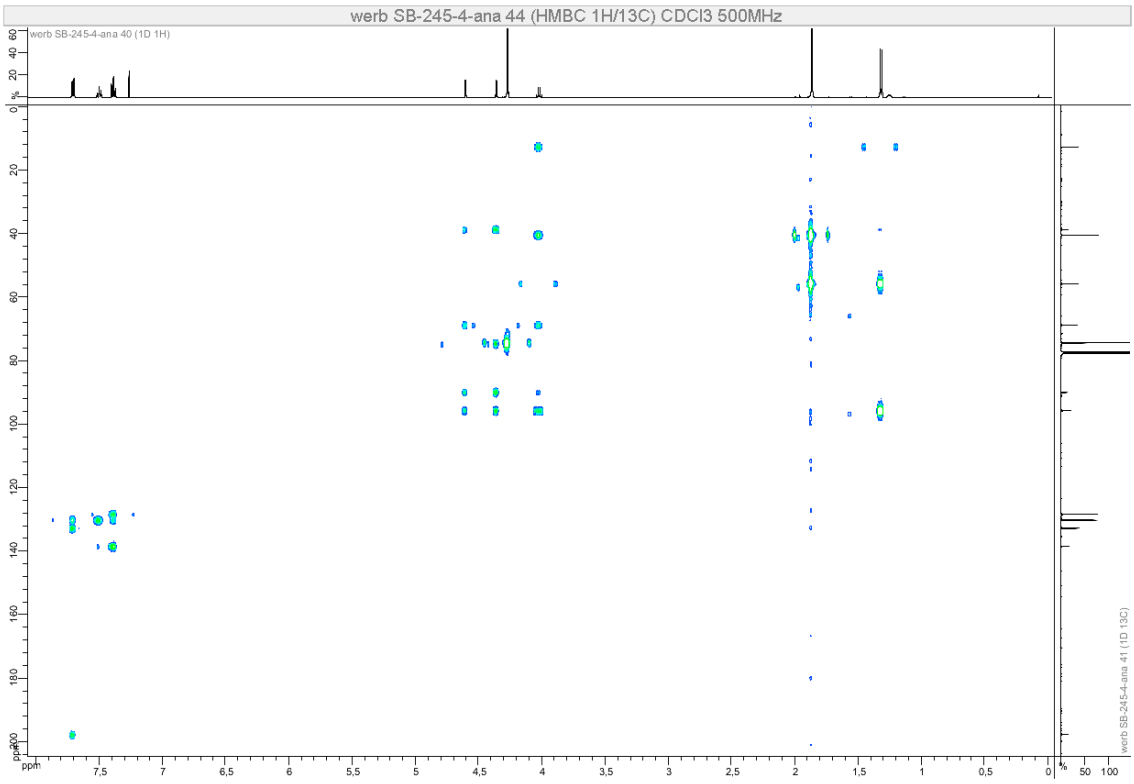
COSY (500 MHz, $CDCl_3$)



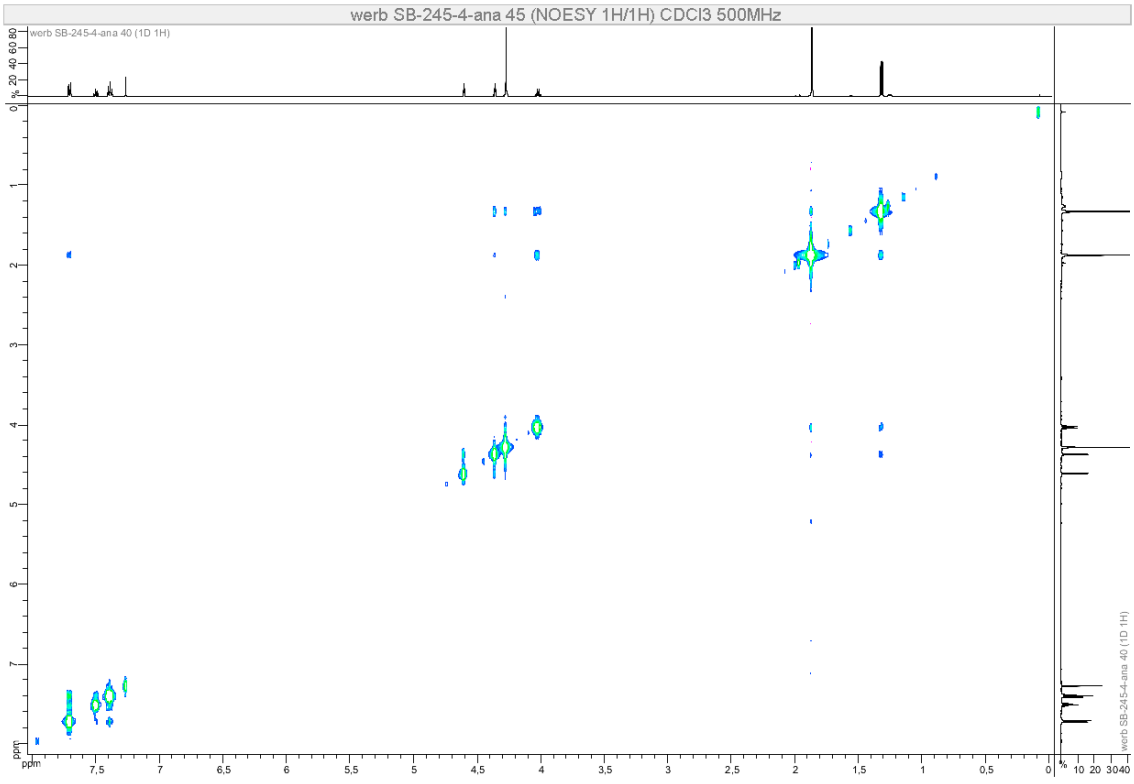
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

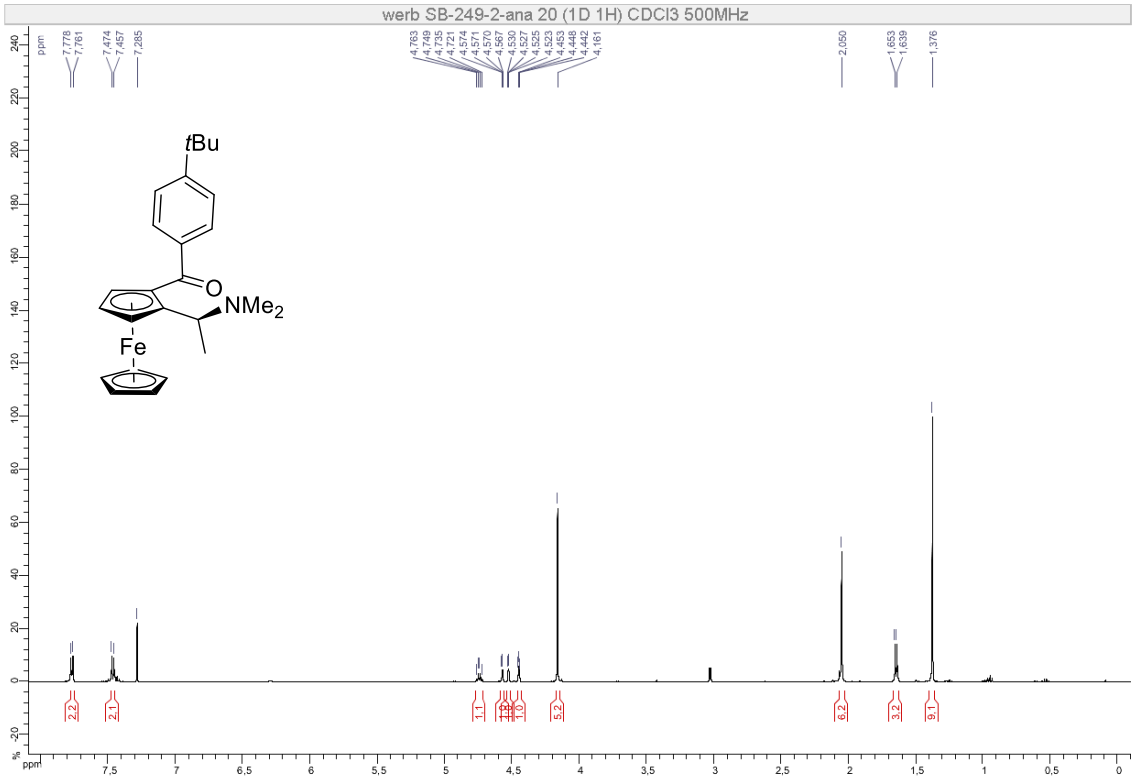


NOESY (500 MHz, $CDCl_3$)

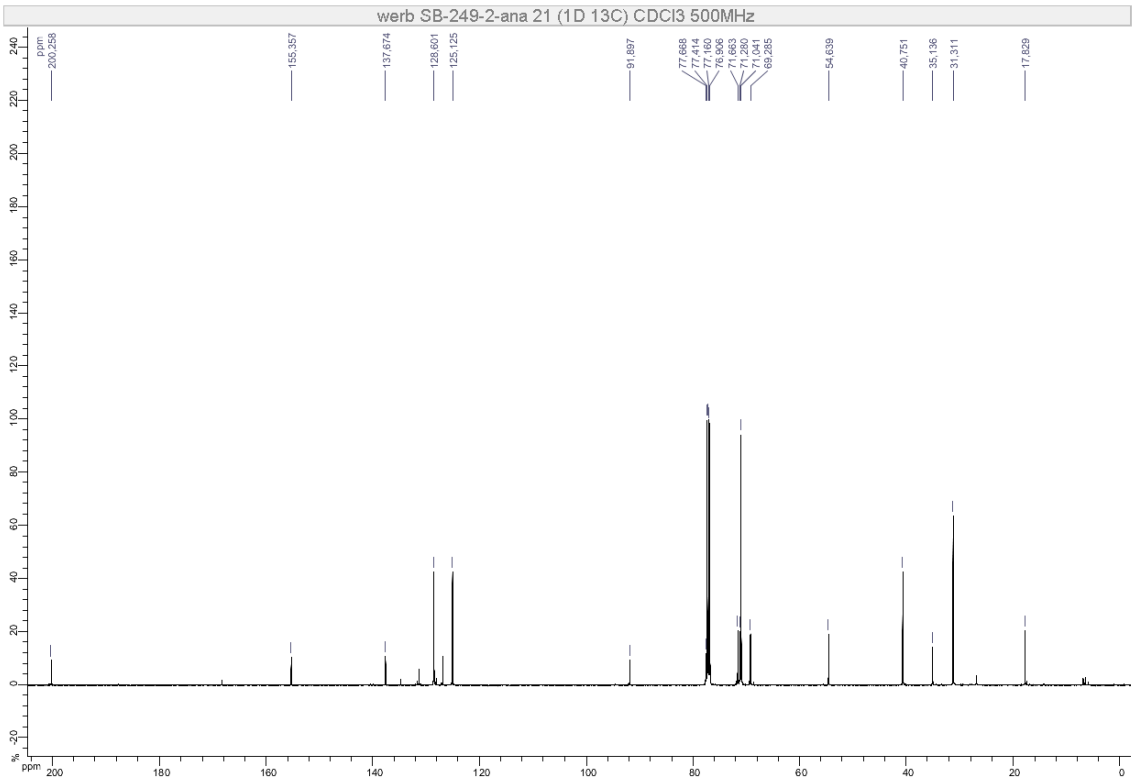


(*S*,*R*$_P$)-1-(4-*tert*-Butylbenzoyl)-2-[1-(dimethylamino)ethyl]ferrocene (*R*$_P$-7)

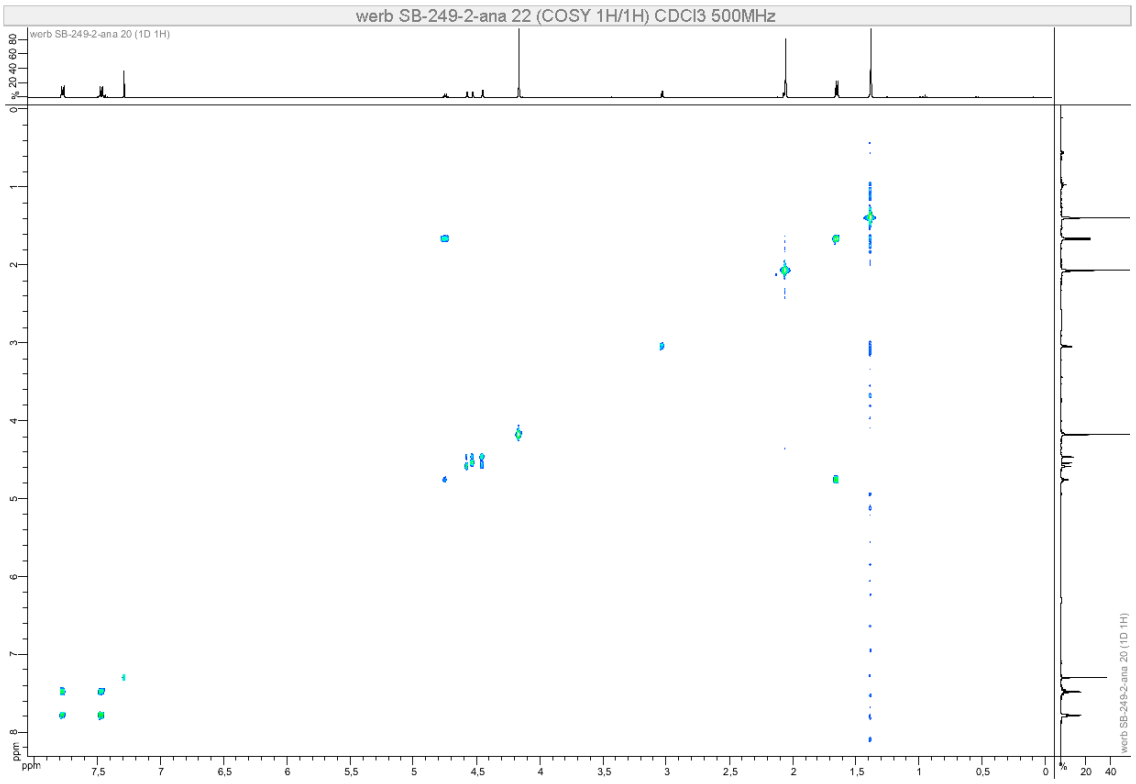
^{1}H NMR (500 MHz, $CDCl_3$)



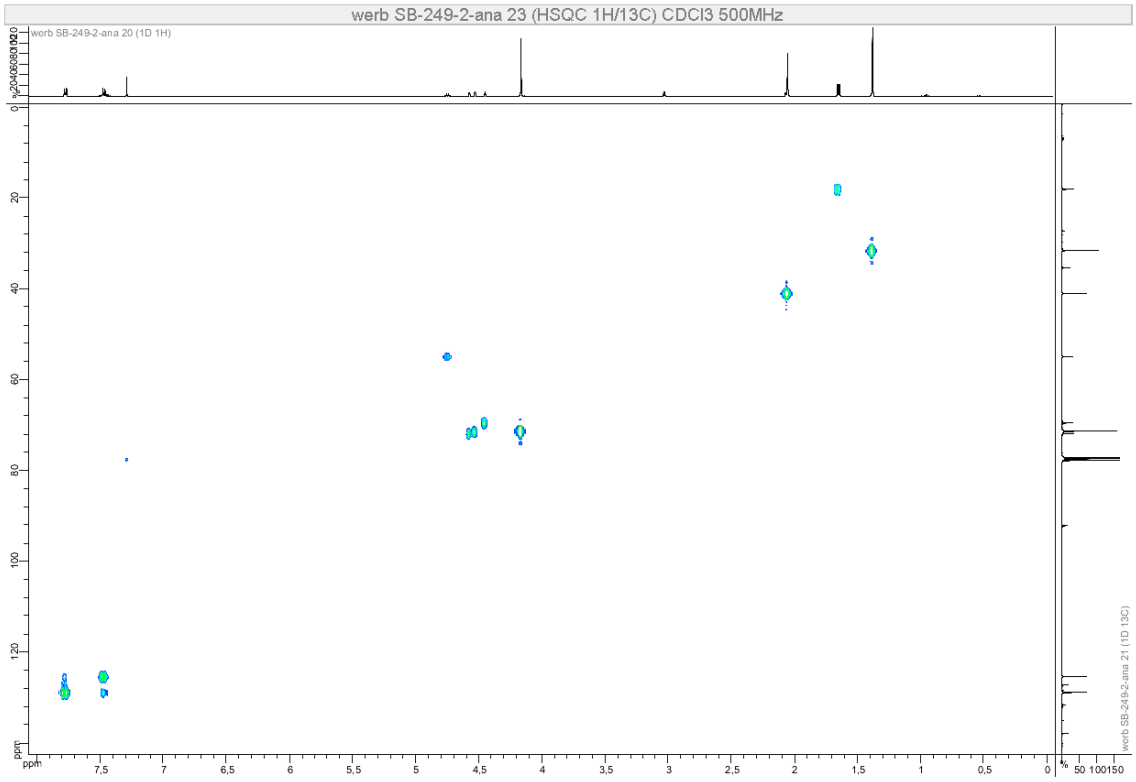
^{13}C NMR (126 MHz, $CDCl_3$)



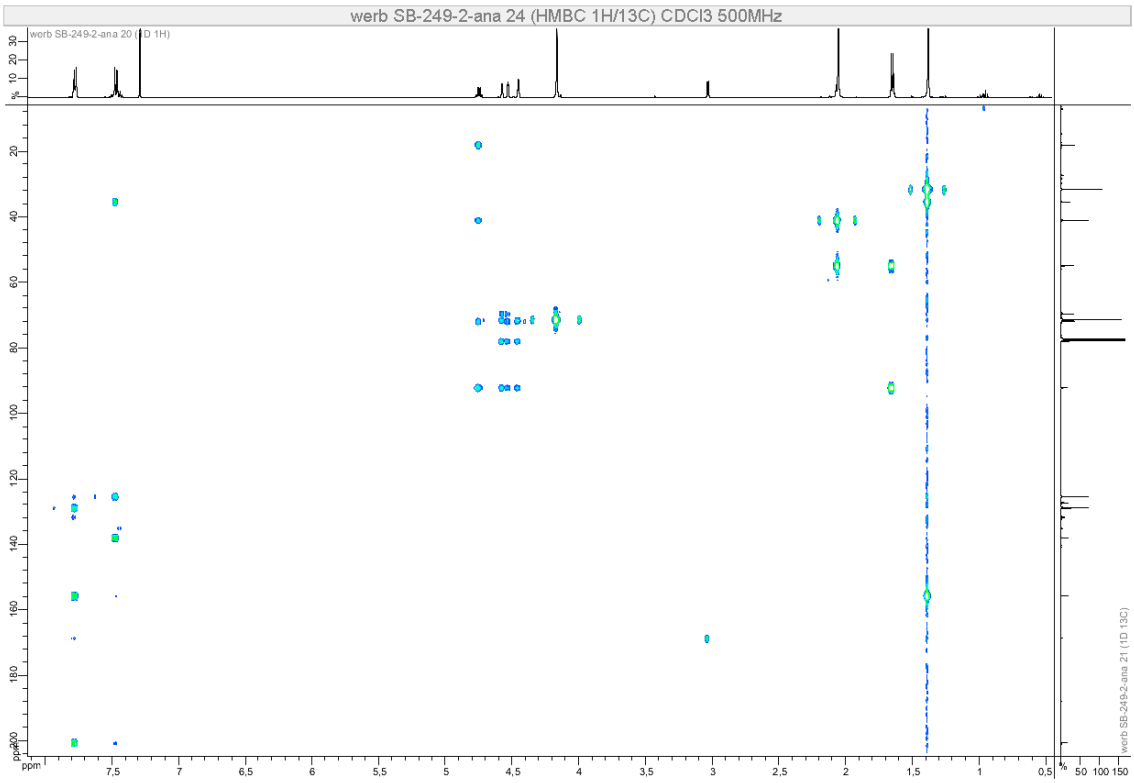
COSY (500 MHz, $CDCl_3$)



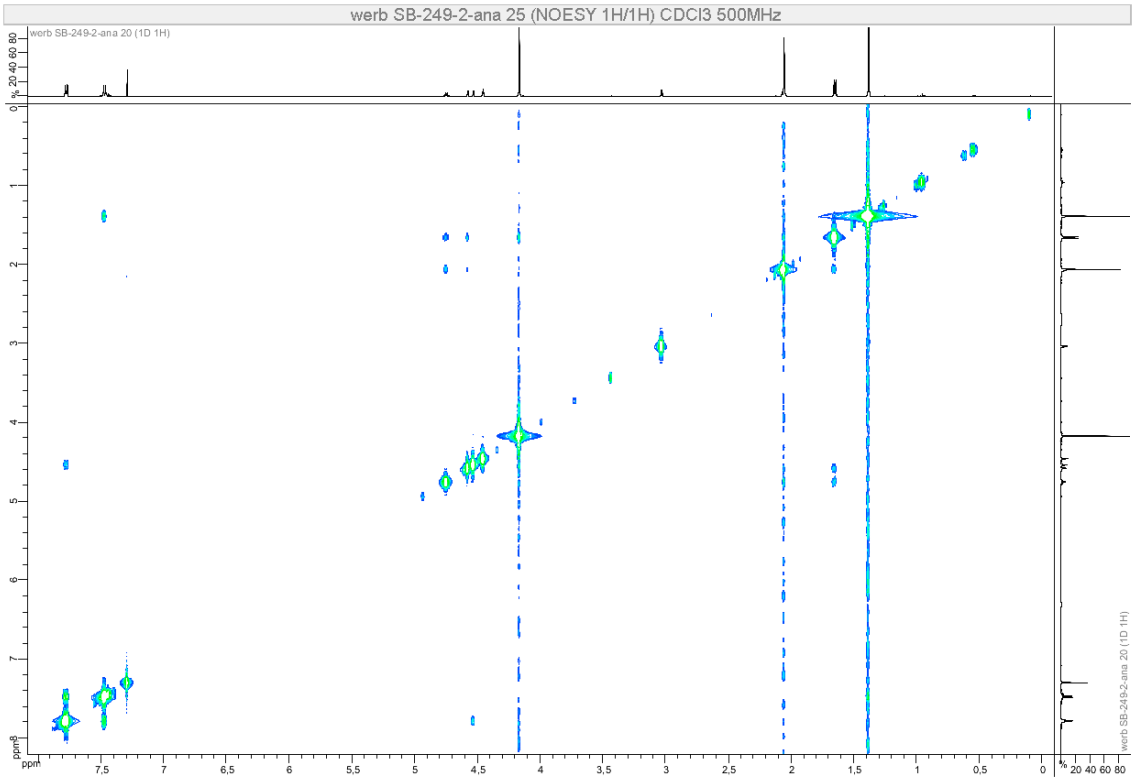
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

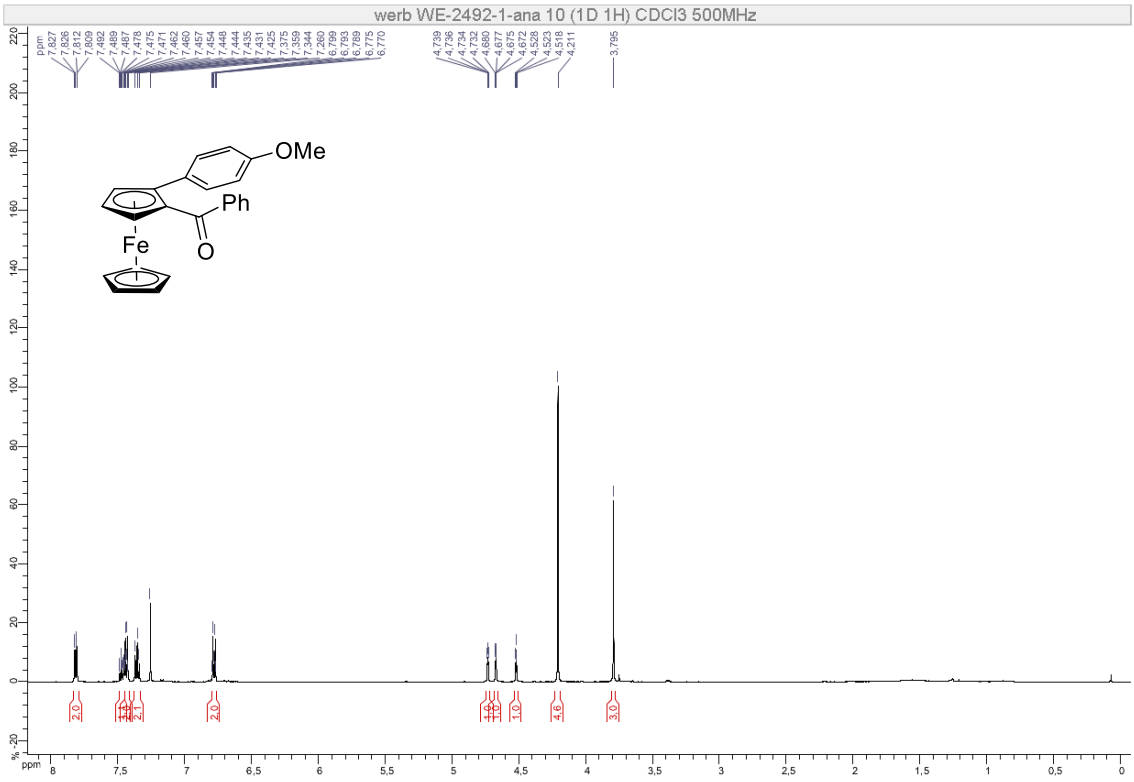


NOESY (500 MHz, $CDCl_3$)

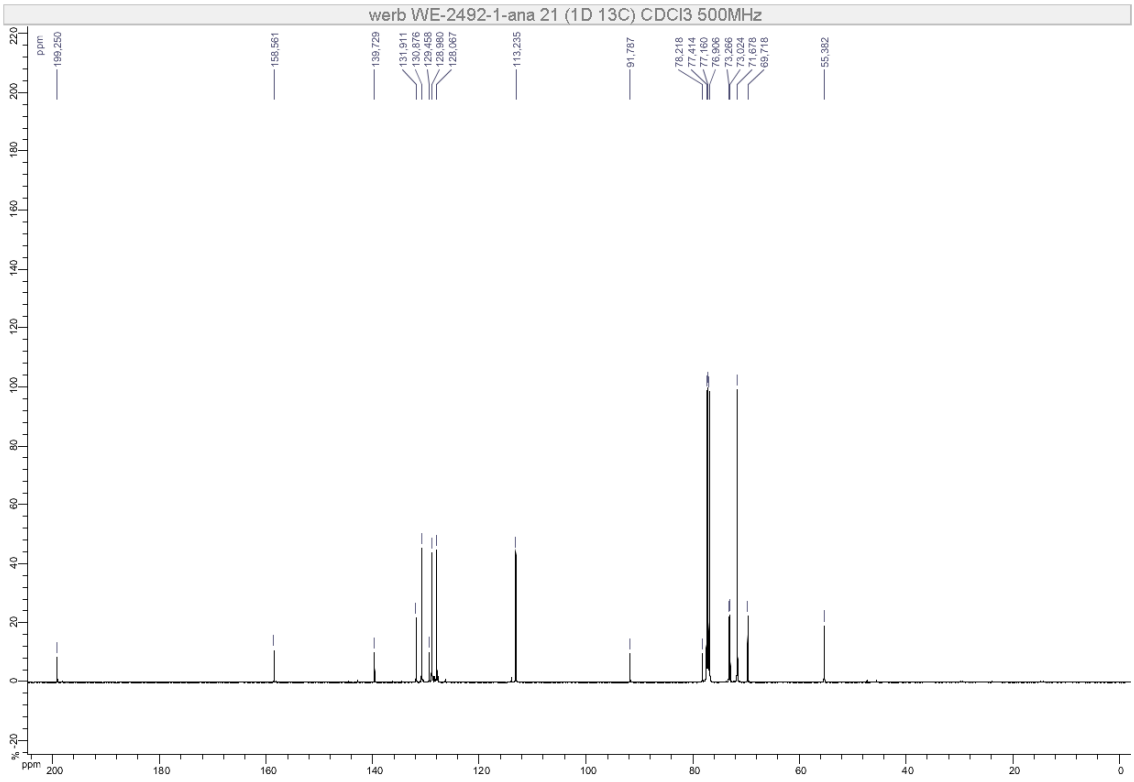


1-Anisyl-2-benzoylferrocene (8a)

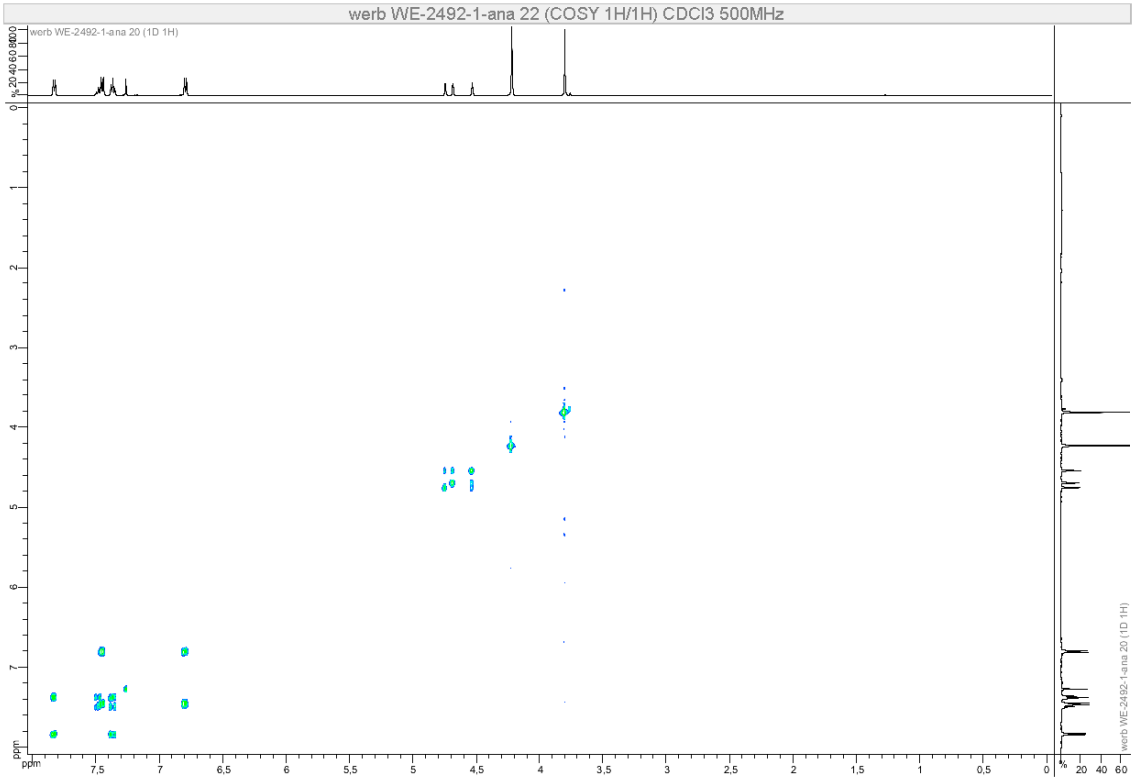
^{1}H NMR (500 MHz, $CDCl_3$)



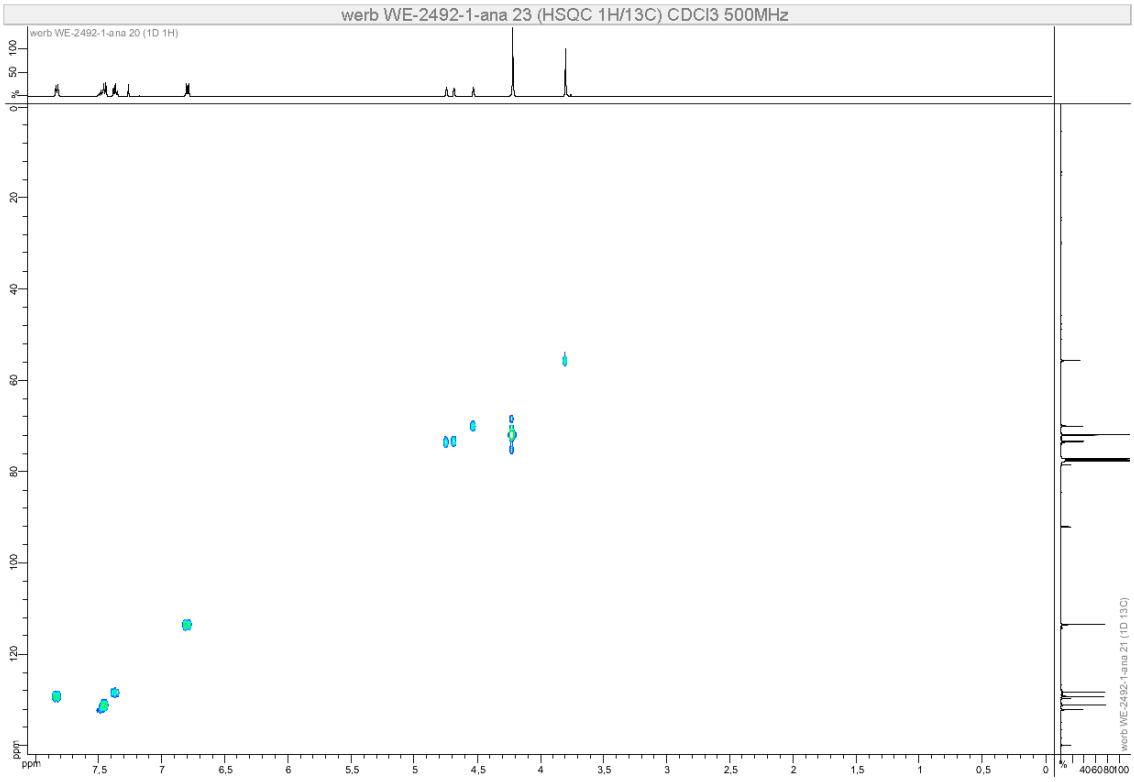
^{13}C NMR (126 MHz, $CDCl_3$)



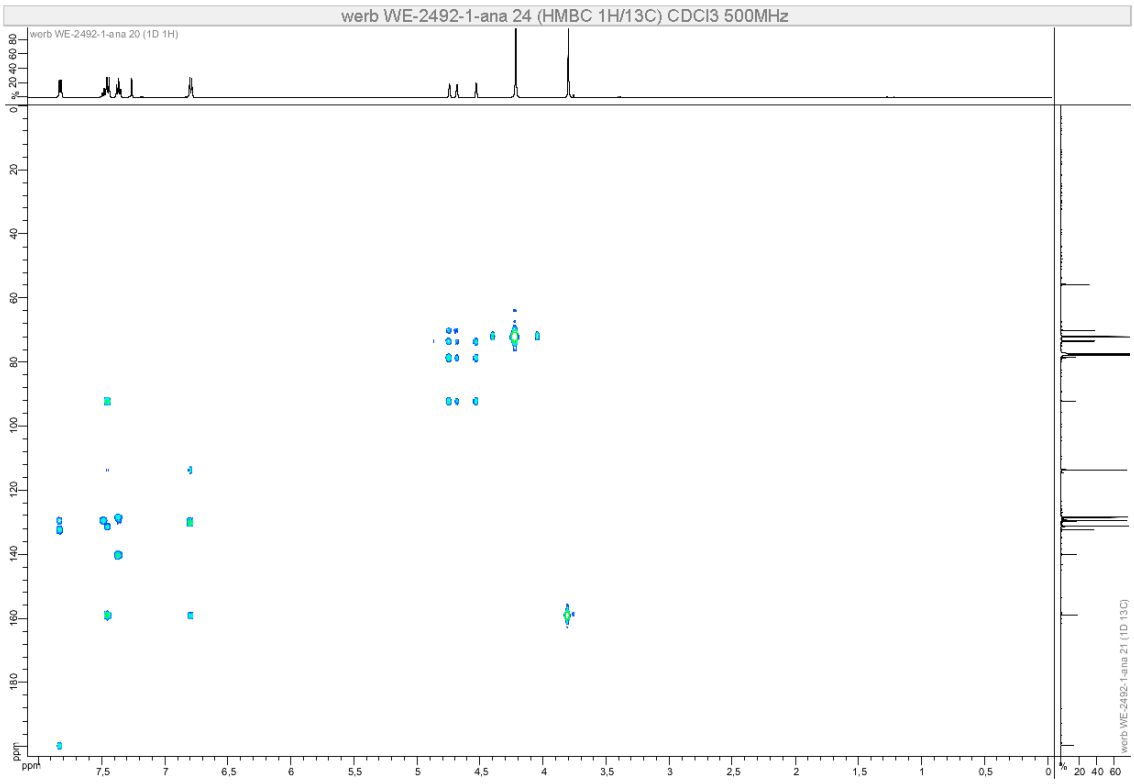
COSY (500 MHz, $CDCl_3$)



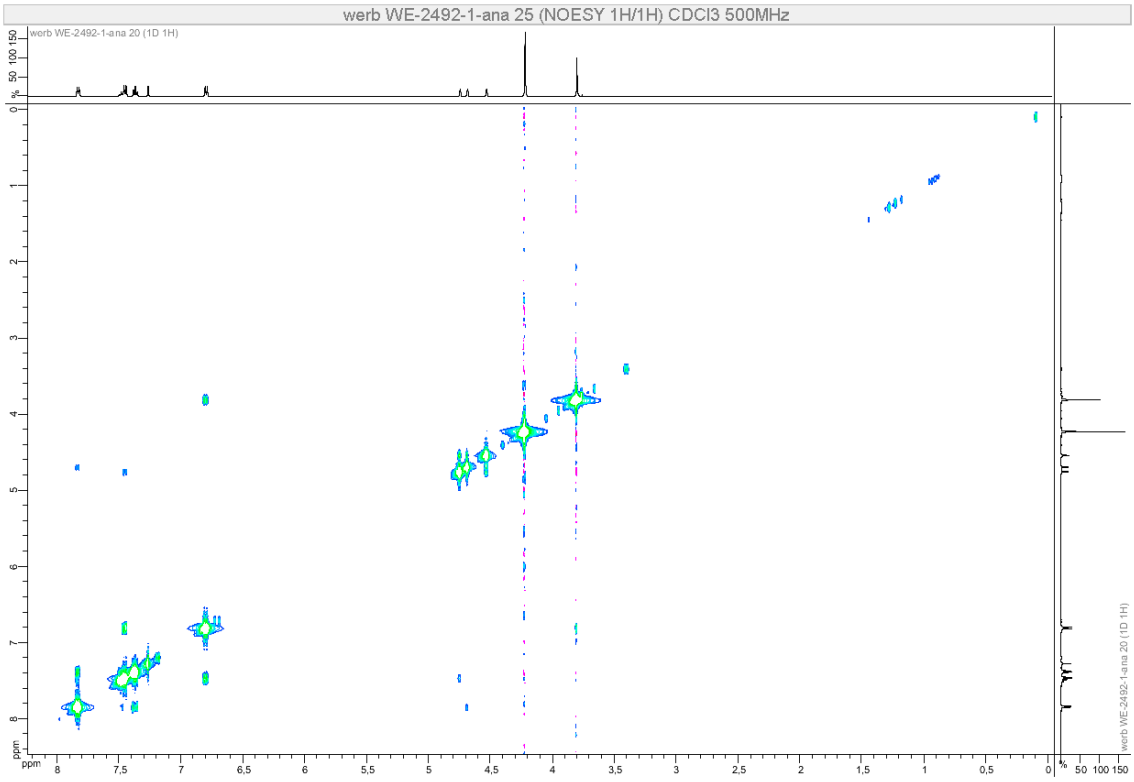
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

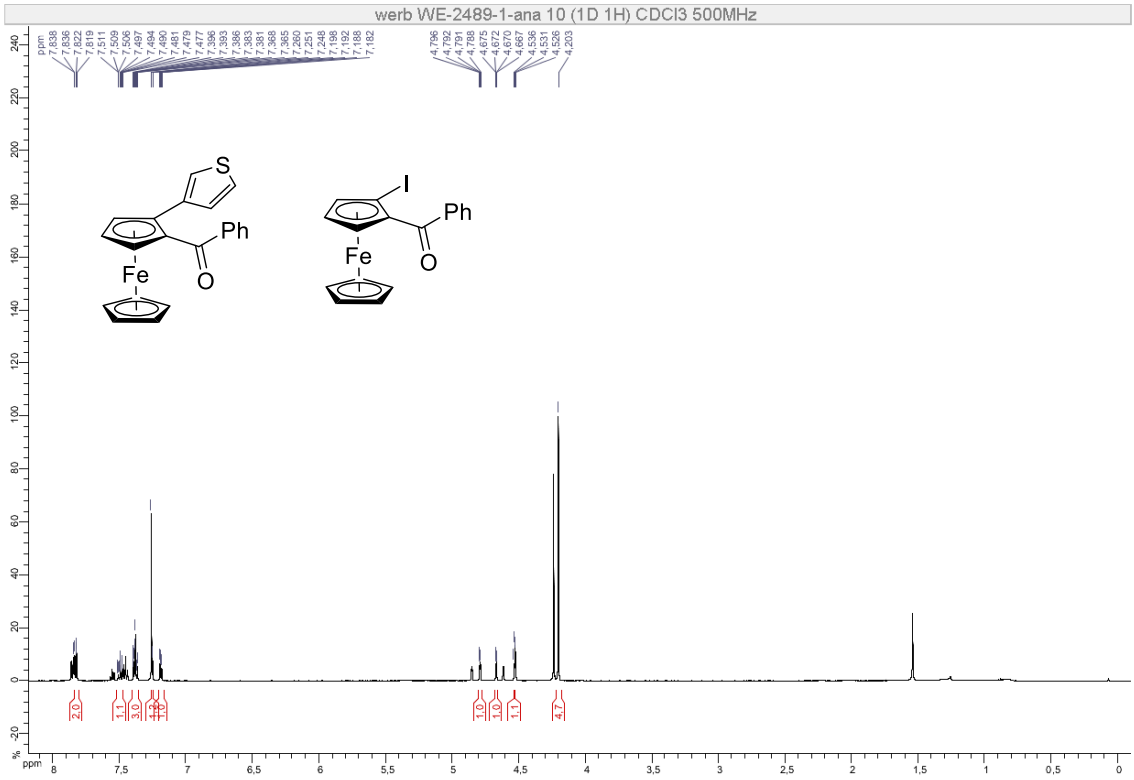


NOESY (500 MHz, $CDCl_3$)

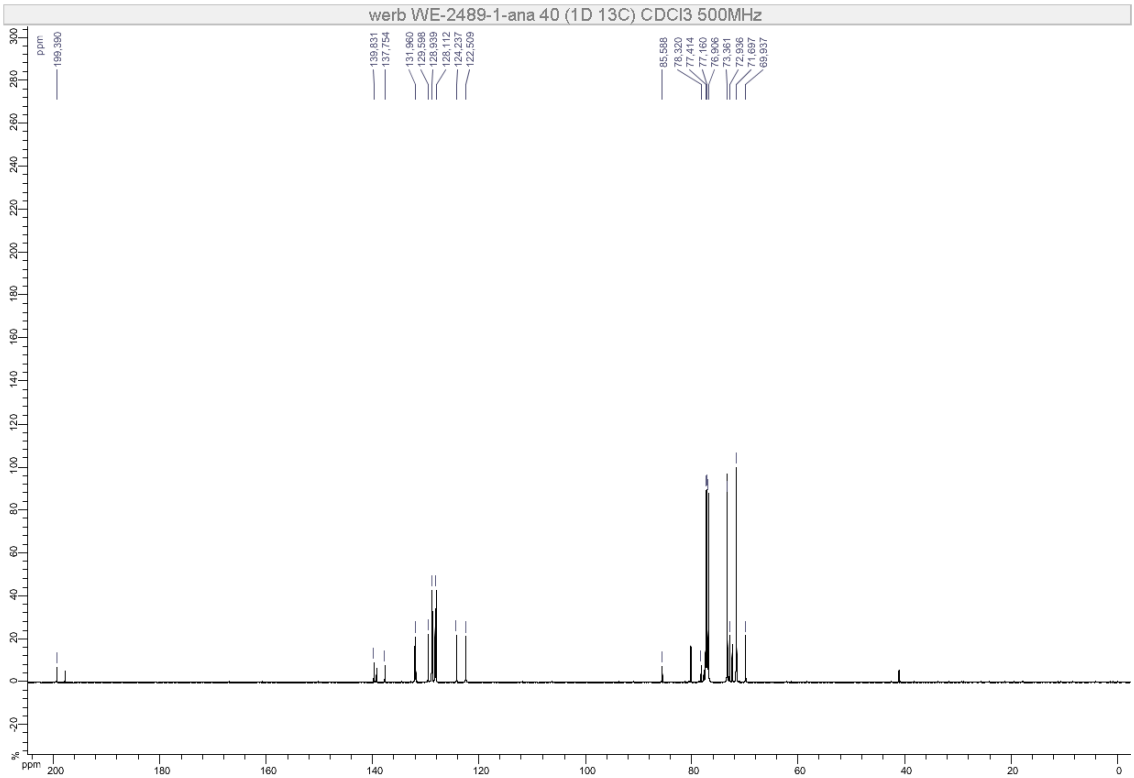


1-Benzoyl-2-(3-thienyl)ferrocene (8b), mixture with 2-Ph

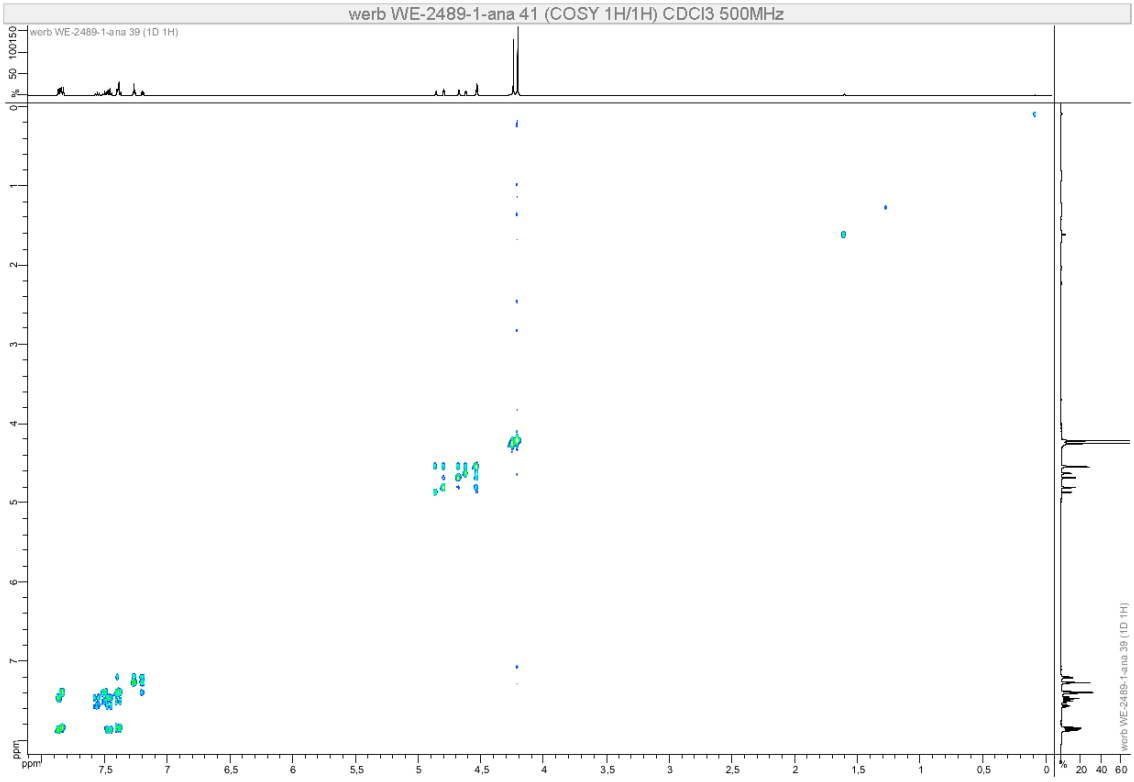
^{1}H NMR (500 MHz, $CDCl_3$)



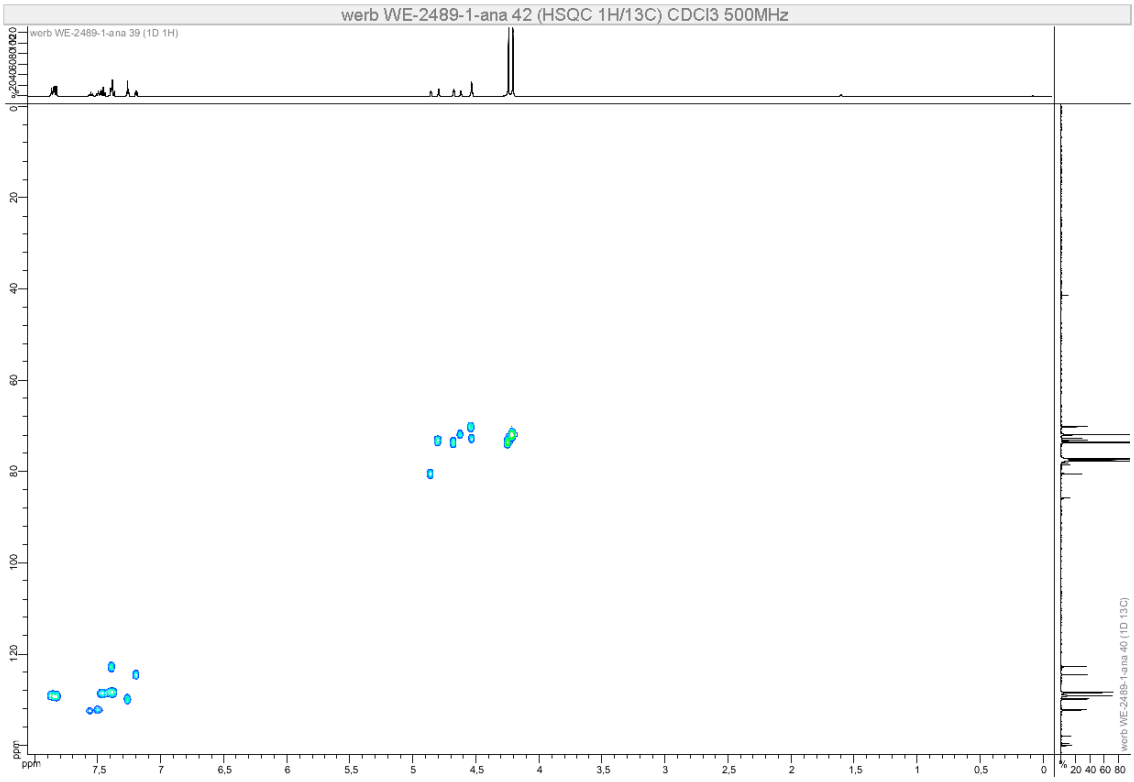
^{13}C NMR (126 MHz, $CDCl_3$)



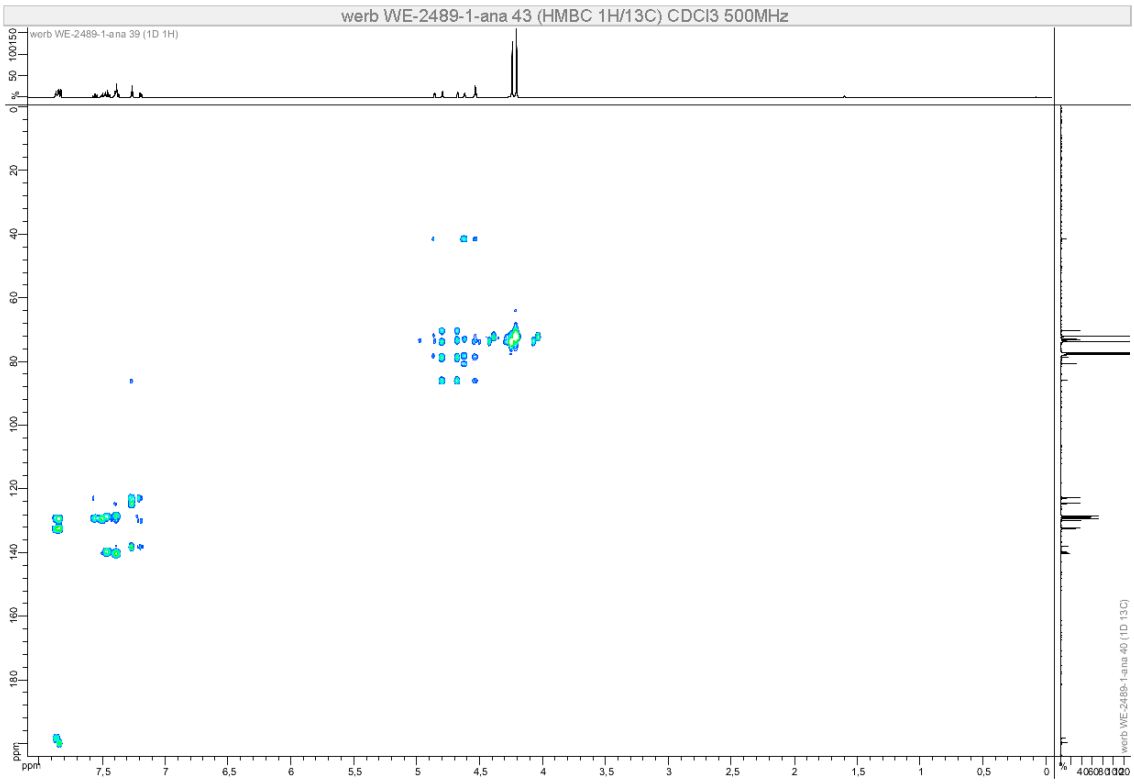
COSY (500 MHz, $CDCl_3$)



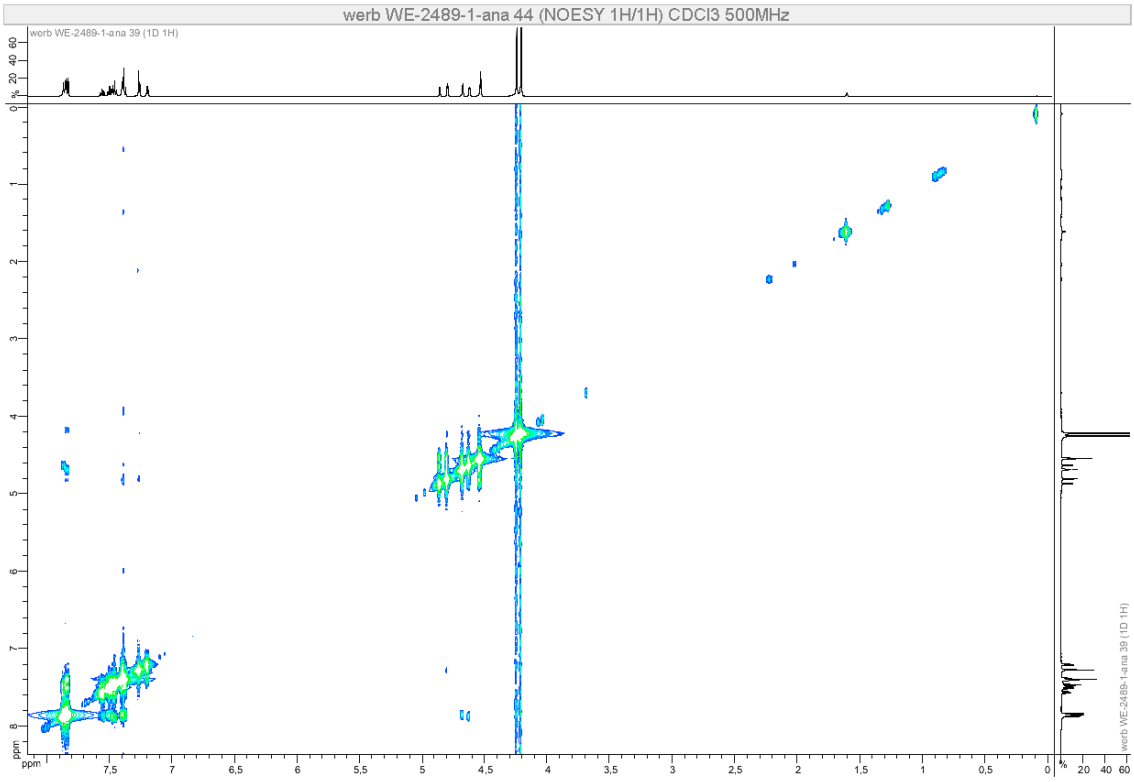
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

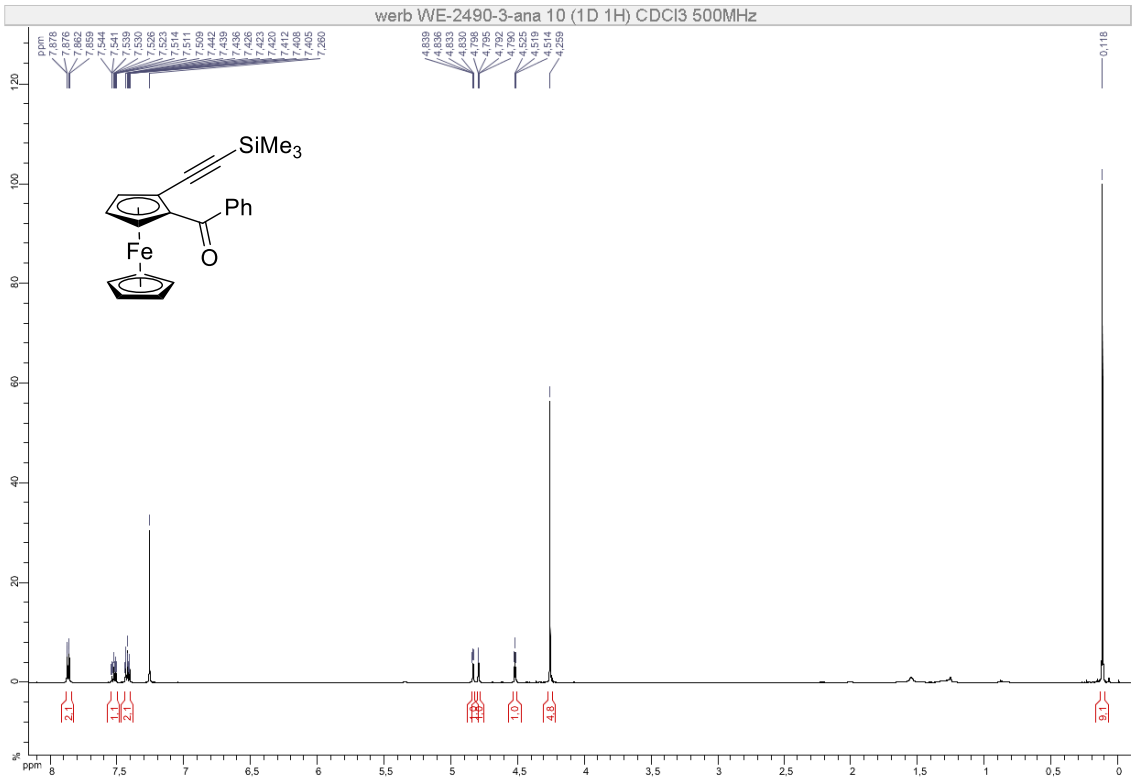


NOESY (500 MHz, $CDCl_3$)

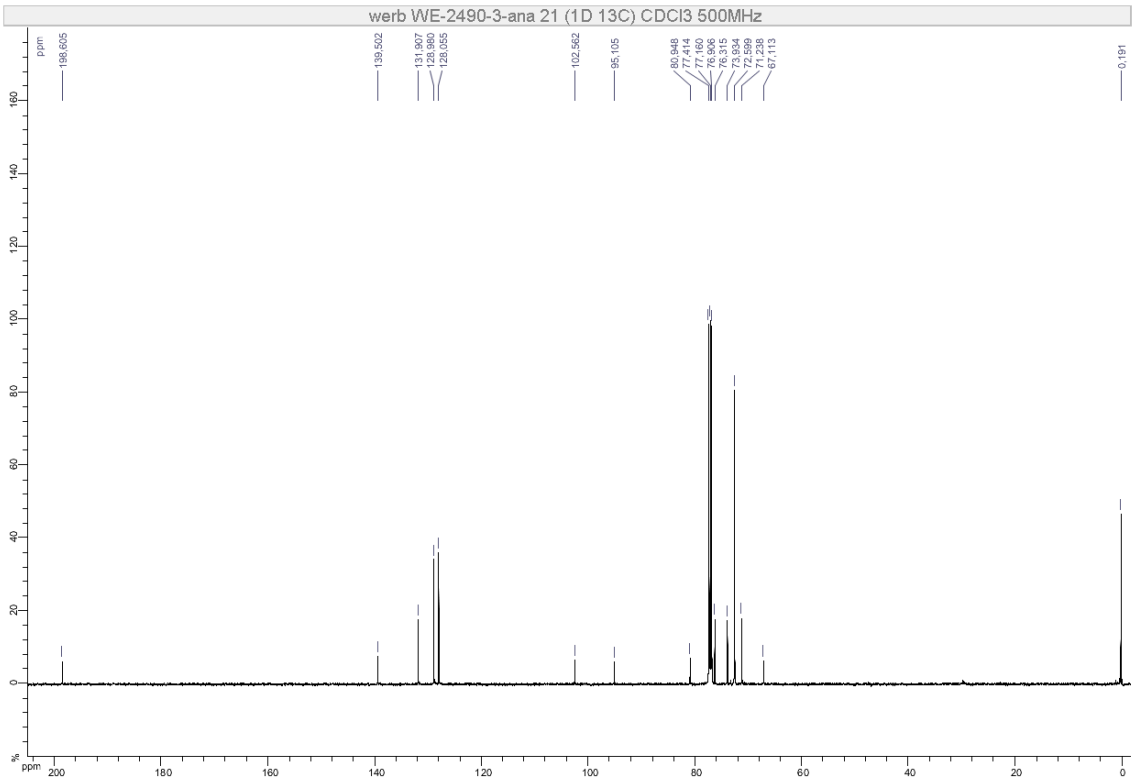


1-Benzoyl-2-(trimethylsilylethinyl)ferrocene (9)

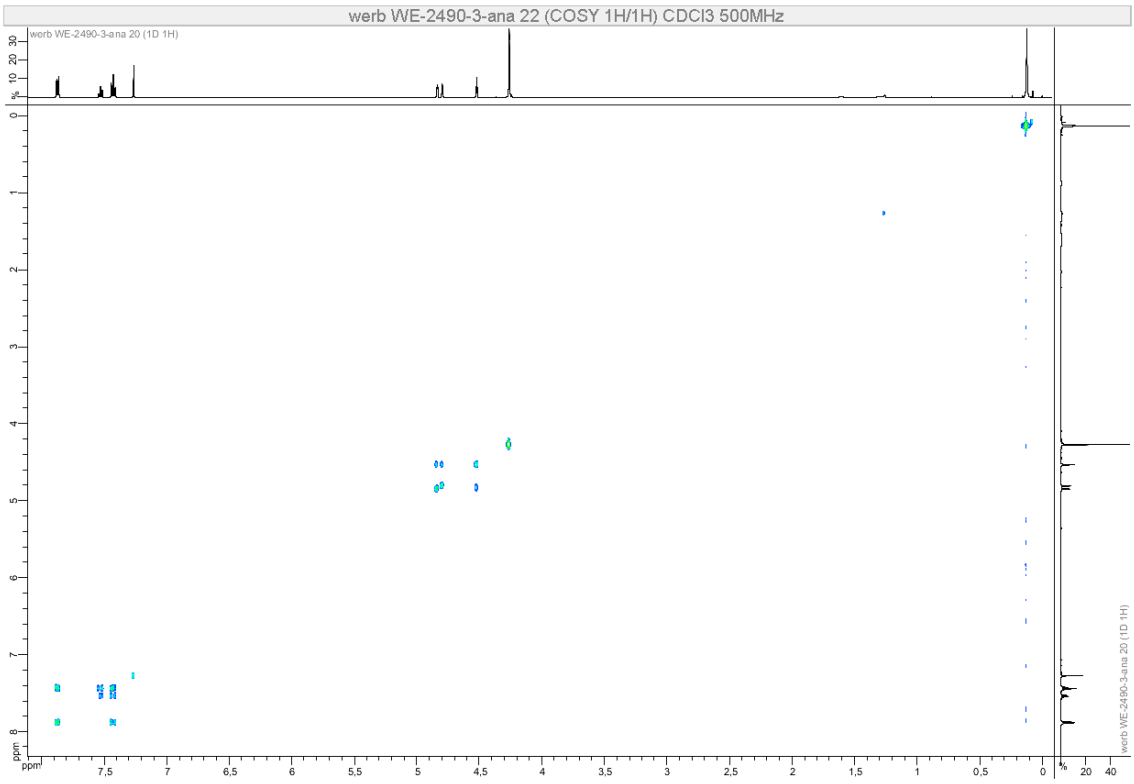
^{1}H NMR (500 MHz, $CDCl_3$)



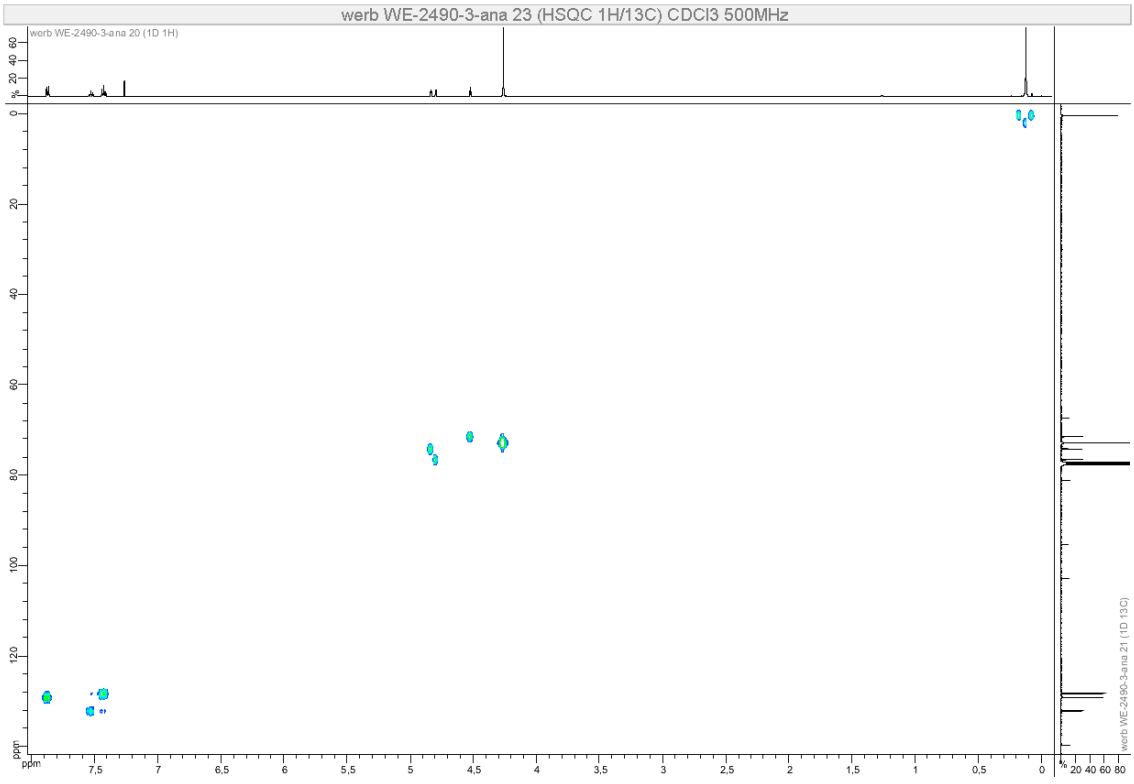
^{13}C NMR (126 MHz, $CDCl_3$)



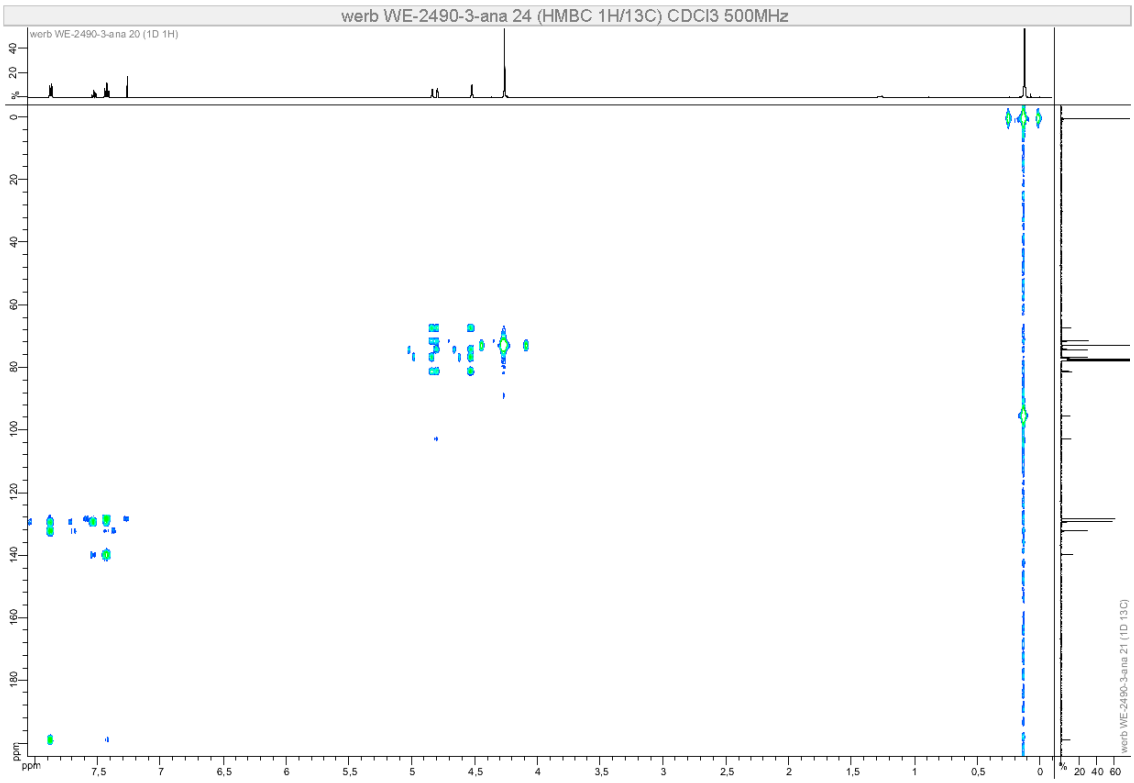
COSY (500 MHz, $CDCl_3$)



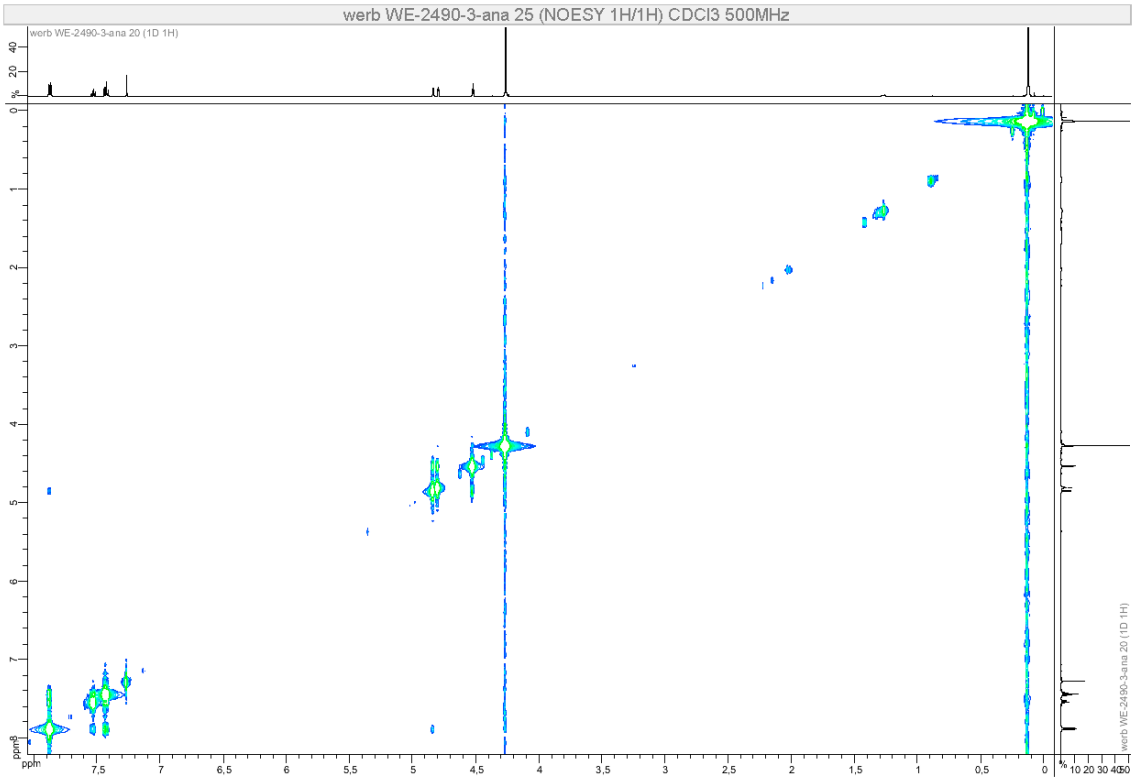
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

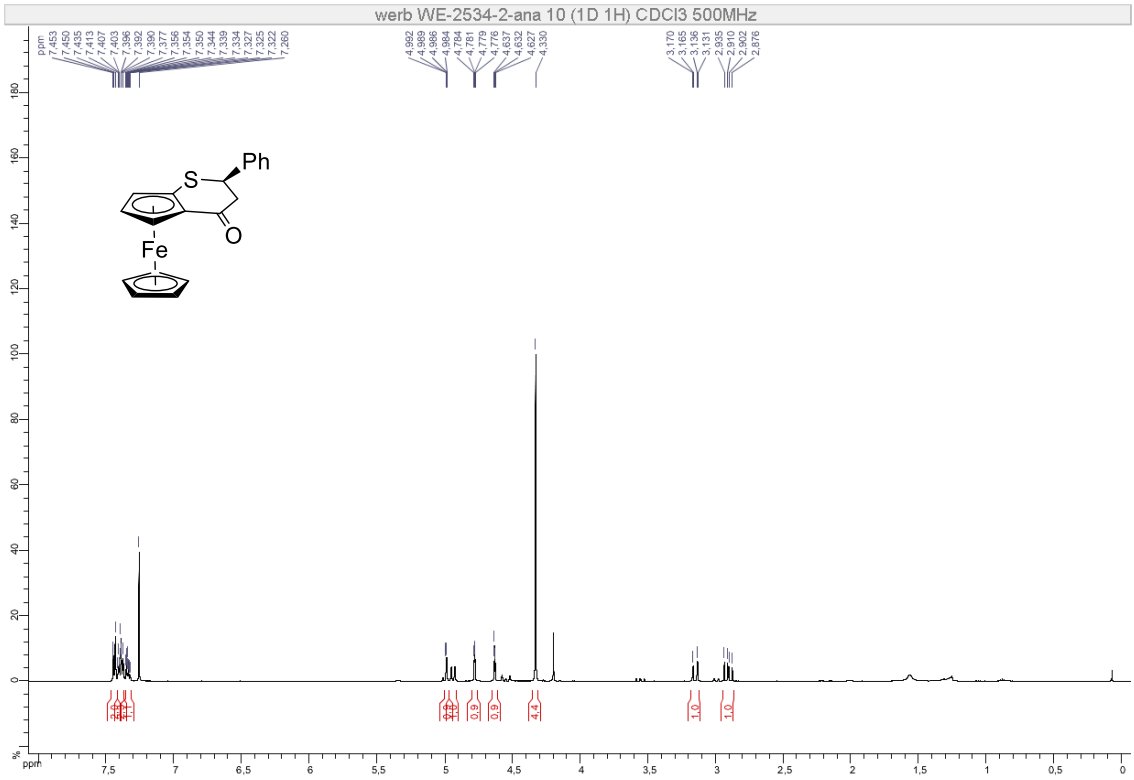


NOESY (500 MHz, $CDCl_3$)

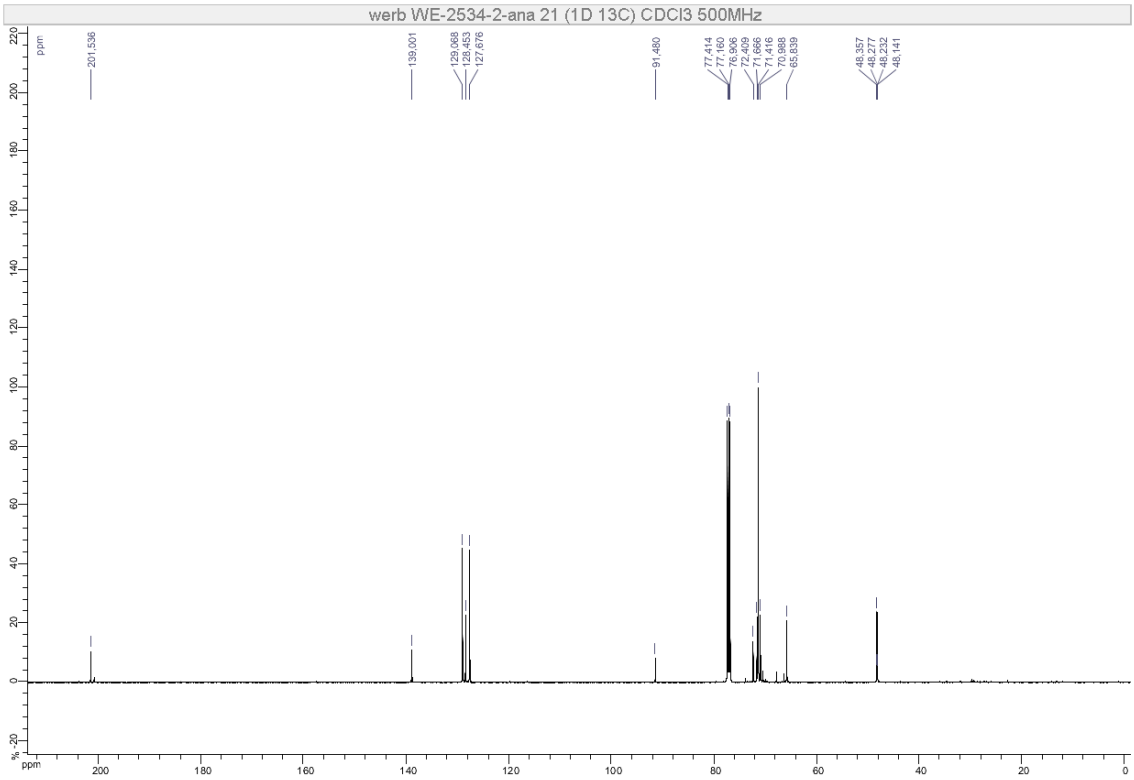


2-Phenyl-2,3-dihydrothiopyrano[2,3]ferrocene-4-one (10), stereoisomeric mixture

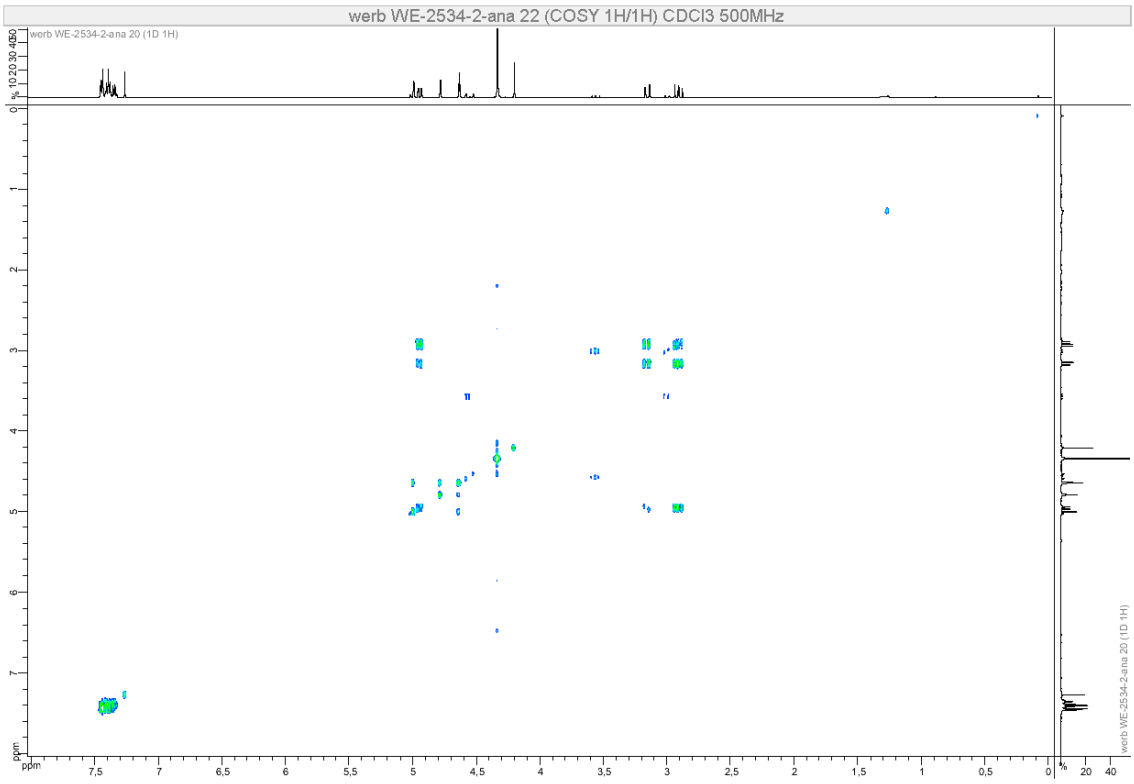
^{1}H NMR (500 MHz, $CDCl_3$)



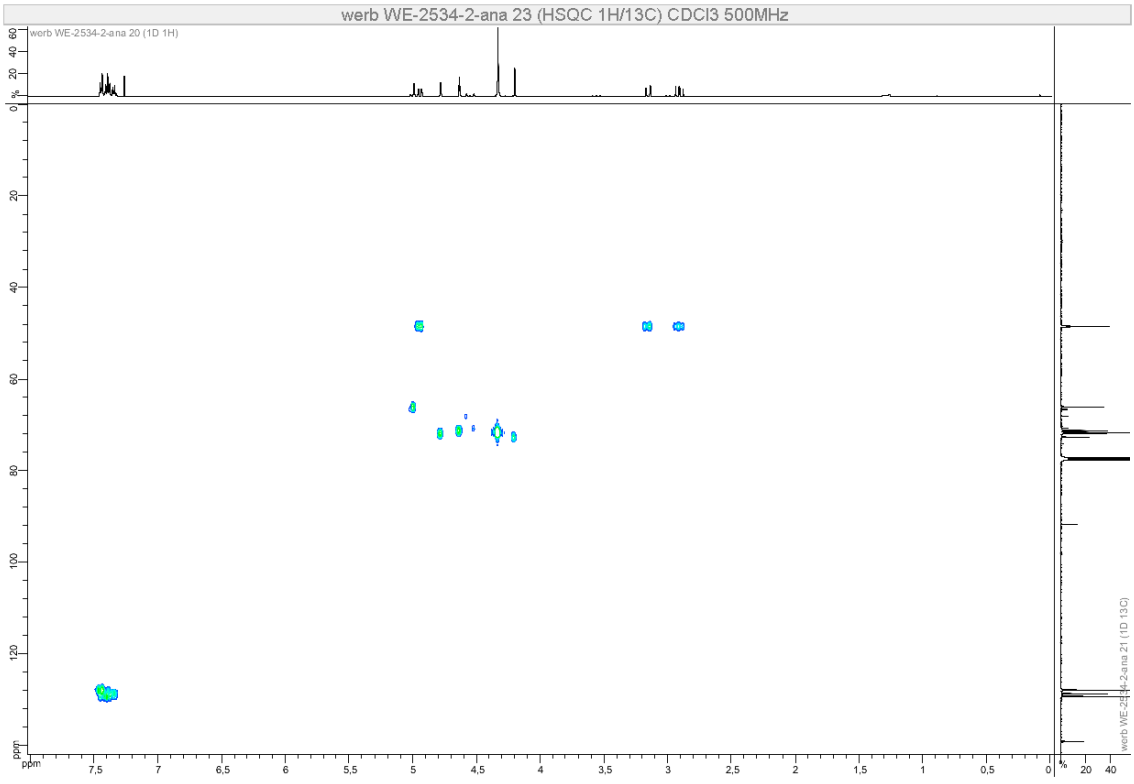
^{13}C NMR (126 MHz, $CDCl_3$)



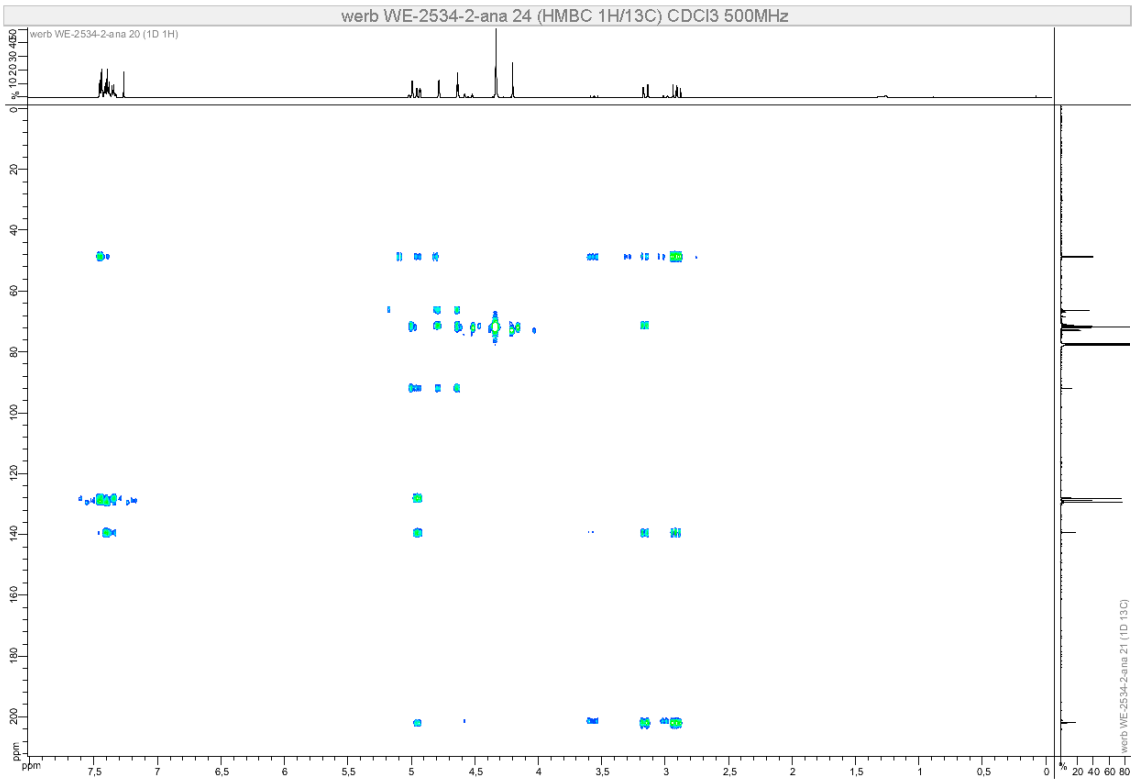
COSY (500 MHz, $CDCl_3$)



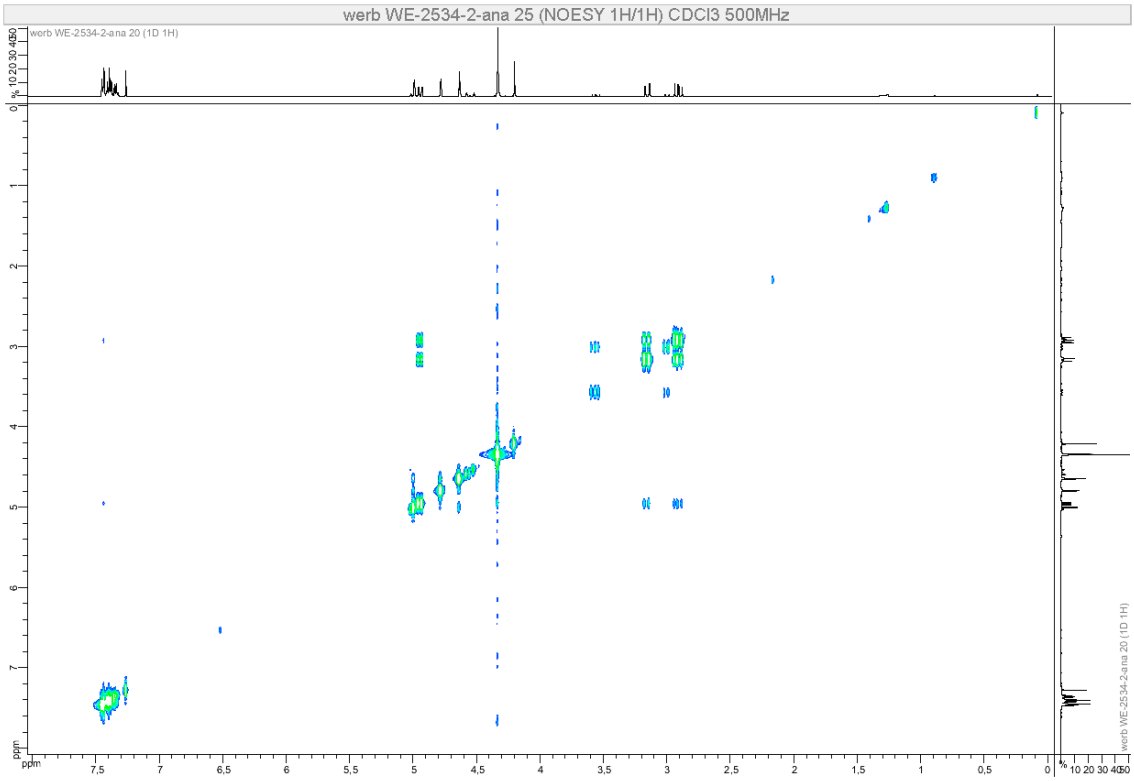
HSQC (500 MHz, $CDCl_3$)



HMBC (500 MHz, $CDCl_3$)

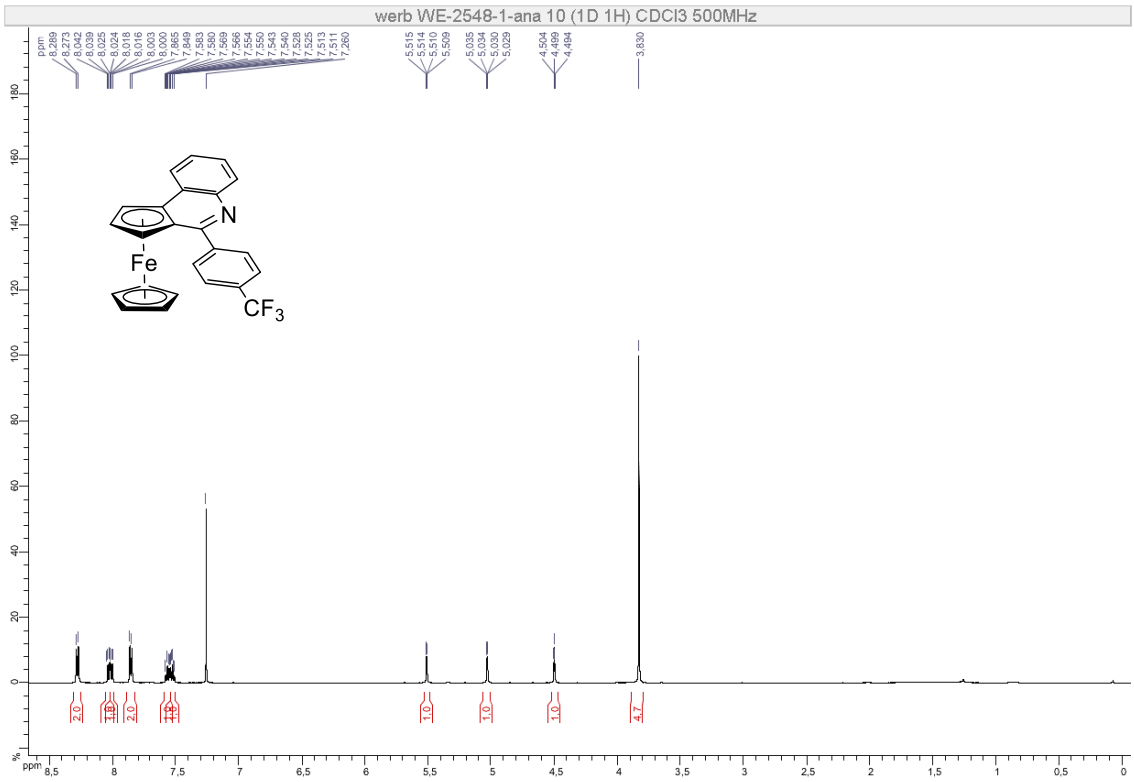


NOESY (500 MHz, $CDCl_3$)

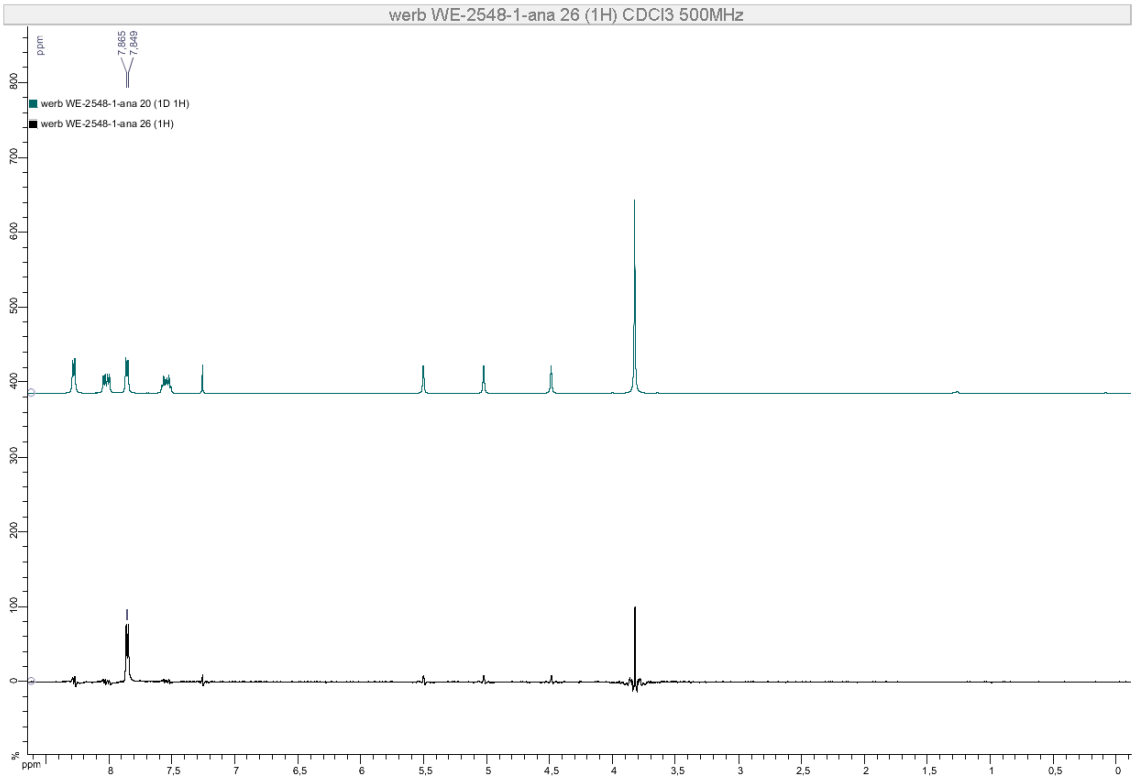


6-[4-(Trifluoromethyl)phenyl]ferroceno[*c*]quinoline (11)

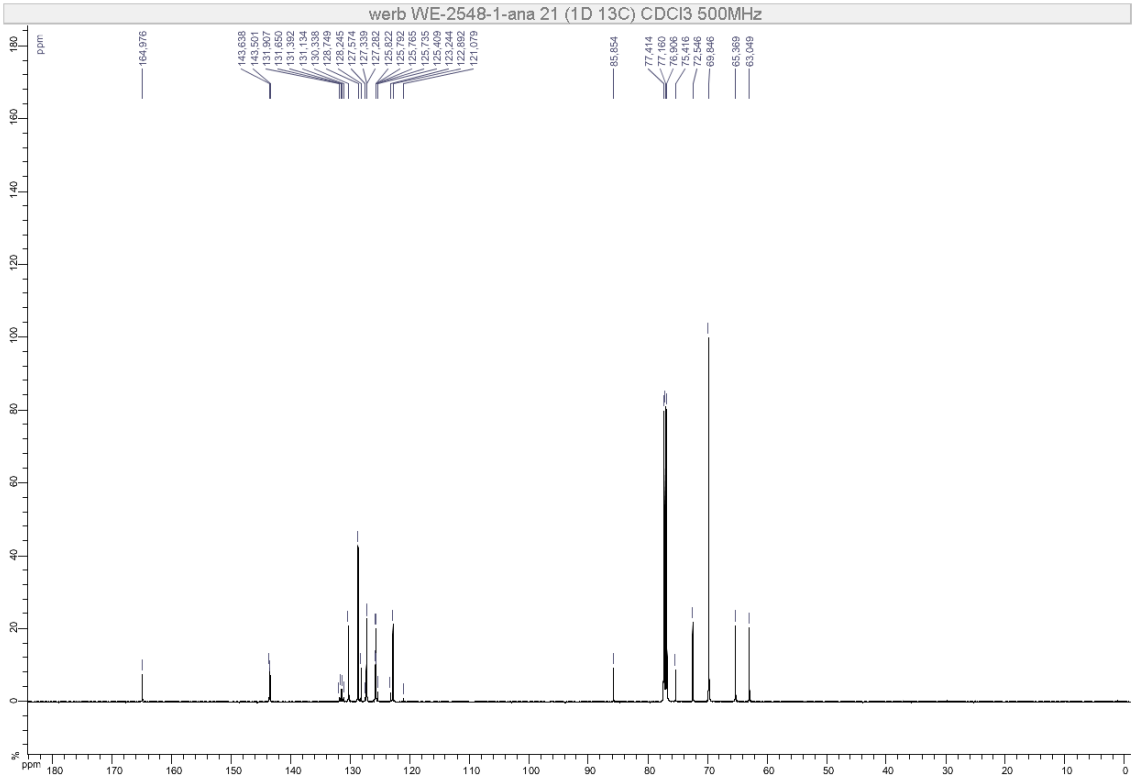
^{1}H NMR (500 MHz, $CDCl_3$)



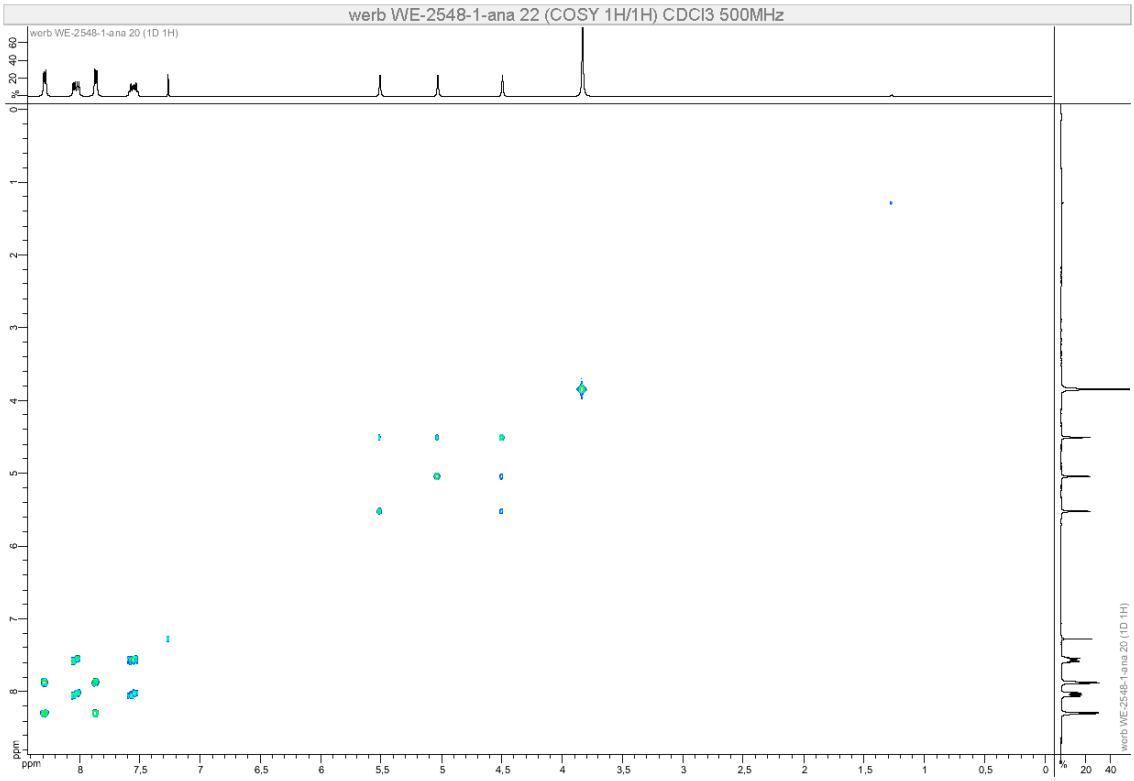
HOESY (500 MHz, $CDCl_3$) Irradiation at –62.6 ppm – Superposition of ^{1}H (top) and HOESY (bottom) spectra.



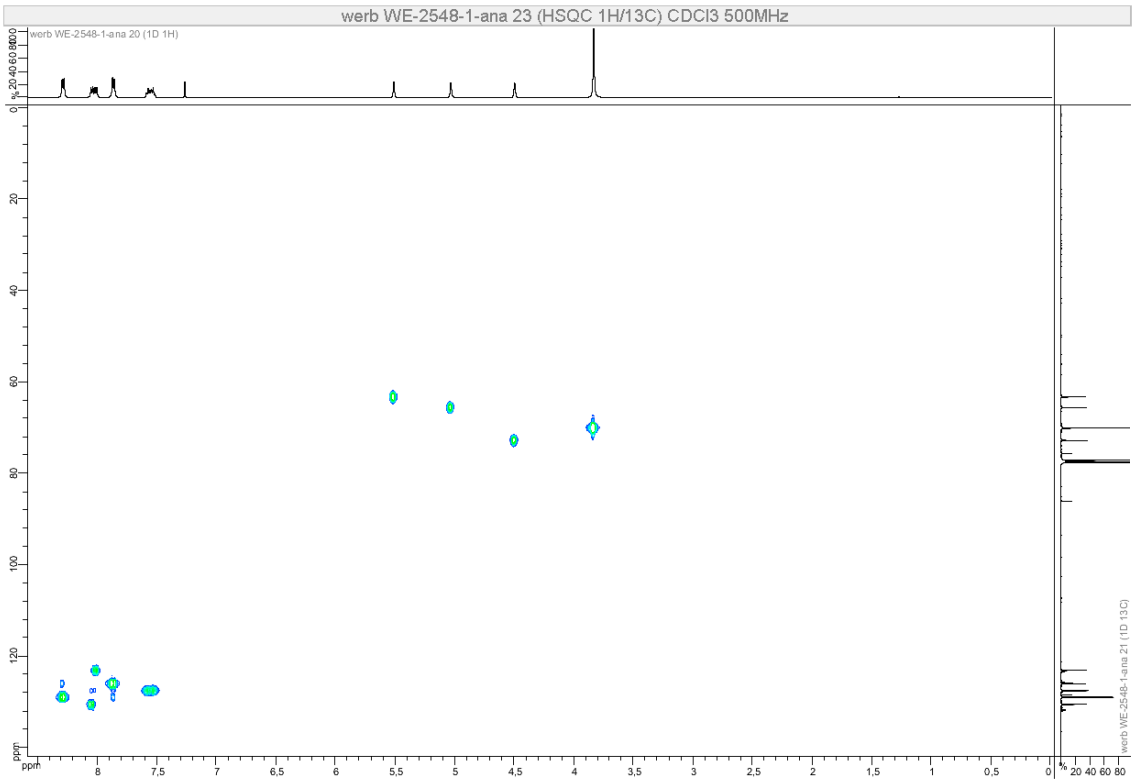
^{13}C NMR (126 MHz, $CDCl_3$)



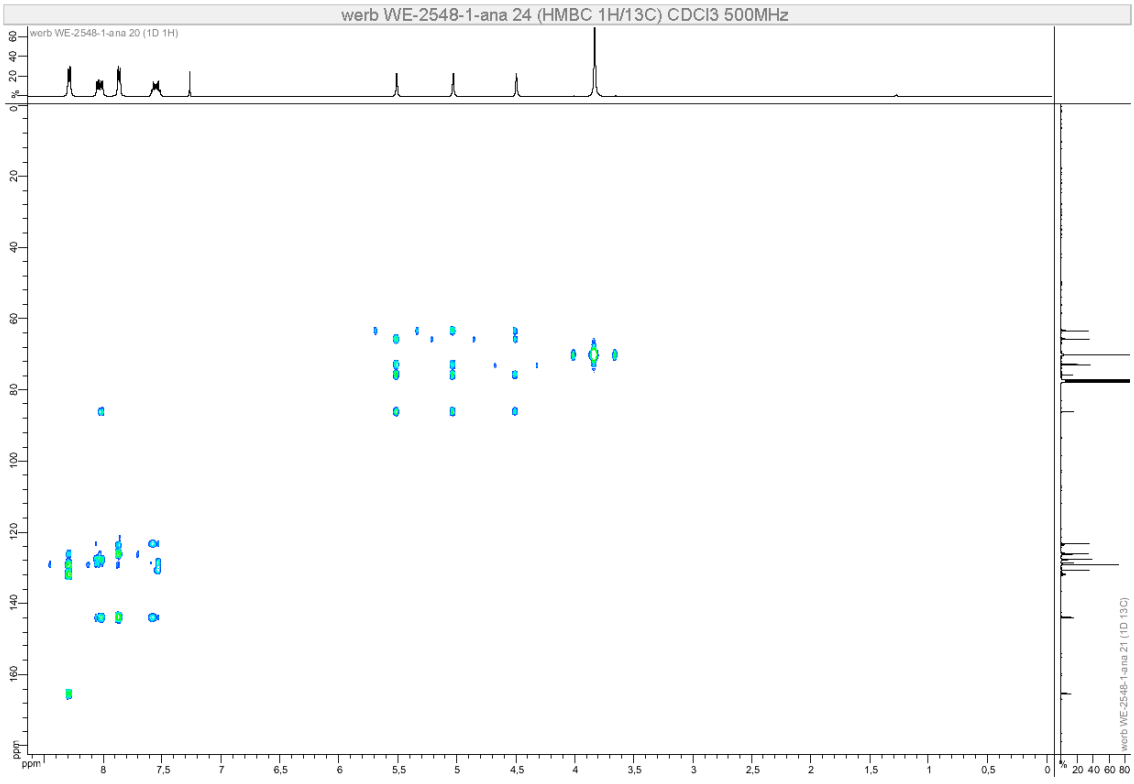
COSY (500 MHz, $CDCl_3$)



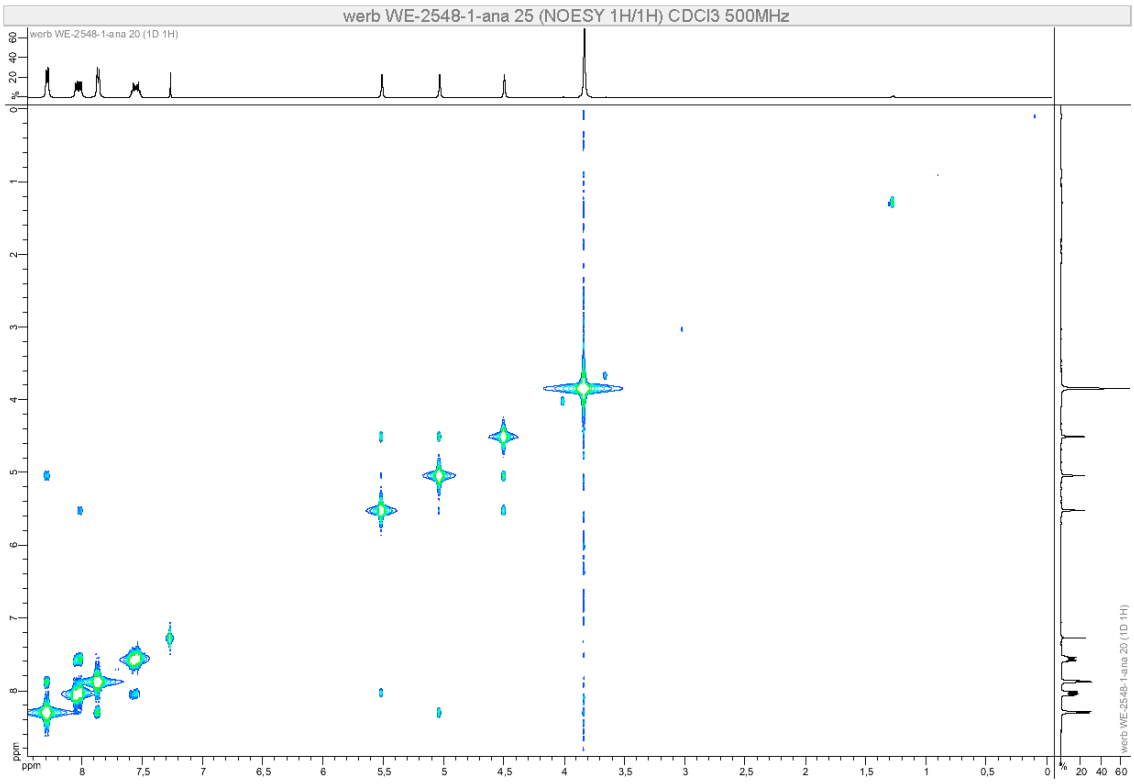
HSQC (500 MHz, $CDCl_3$)



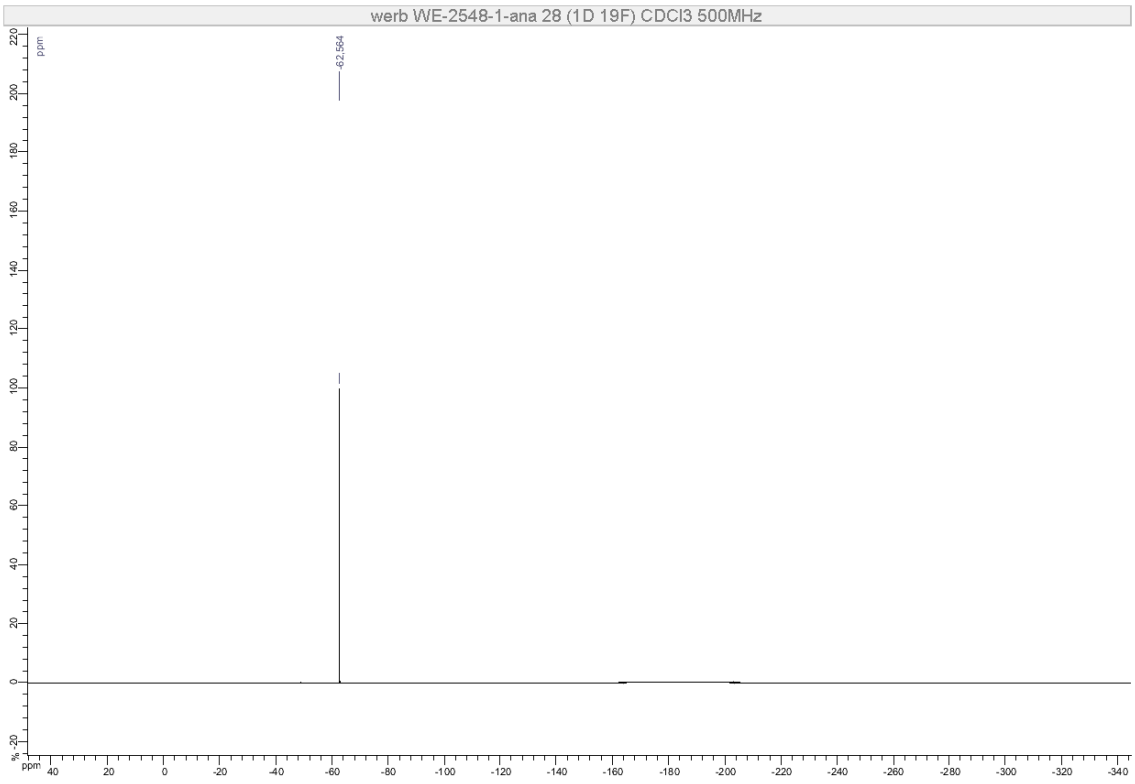
HMBC (500 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)

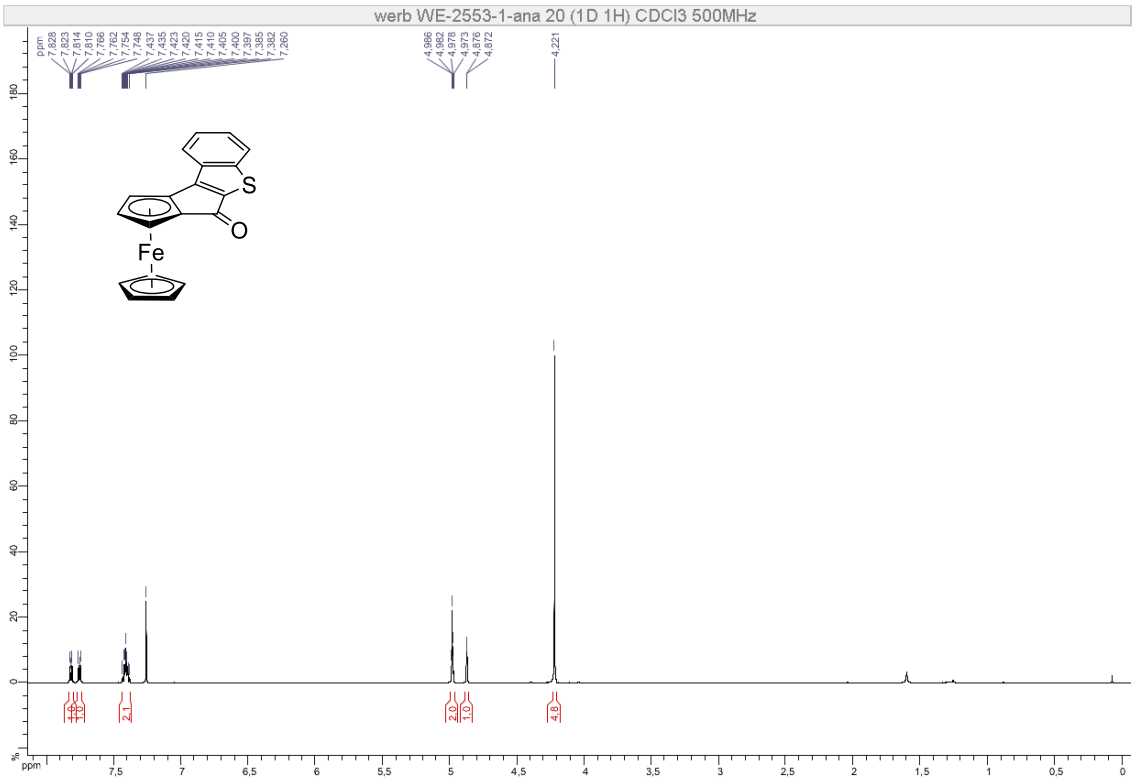


^{19}F NMR (470 MHz, $CDCl_3$)

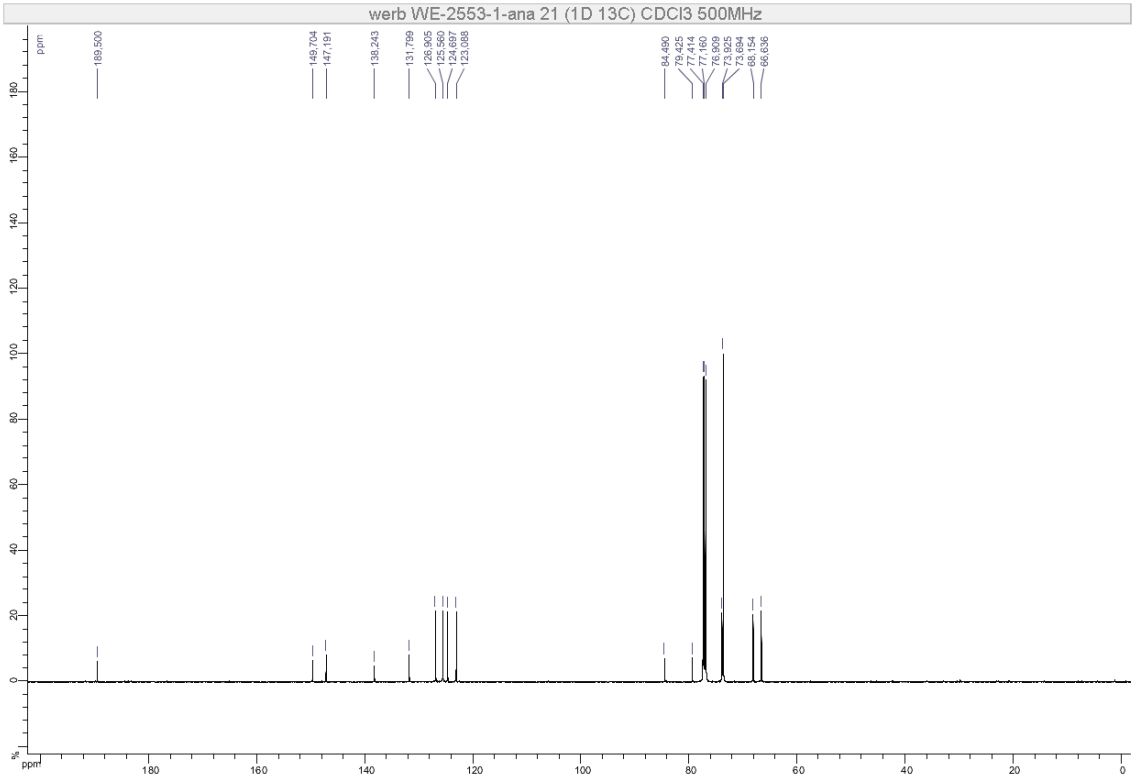


Compound 12

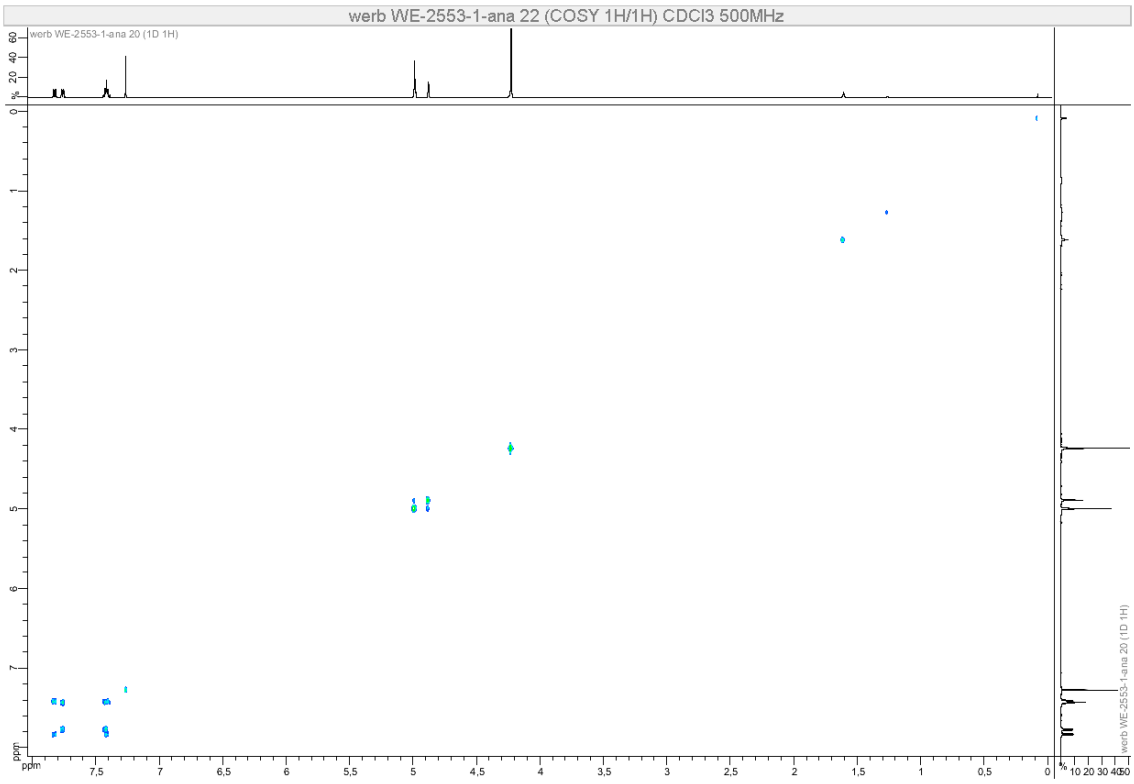
^{1}H NMR (500 MHz, $CDCl_3$)



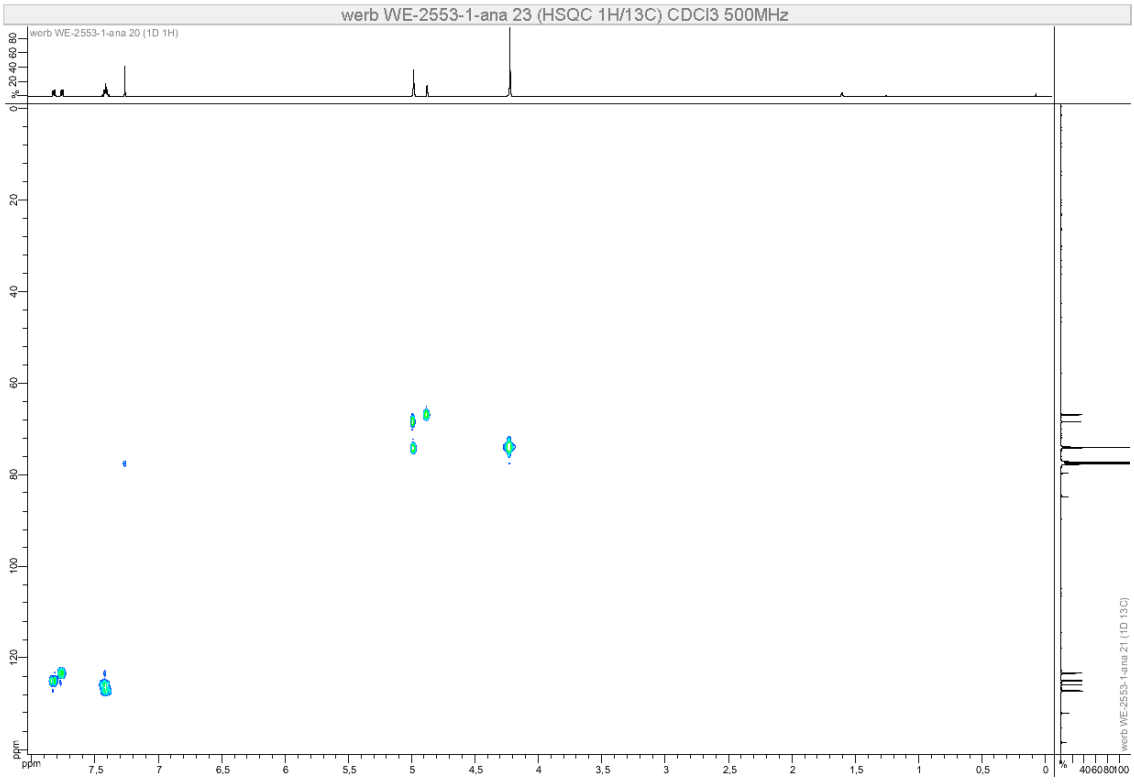
^{13}C NMR (126 MHz, $CDCl_3$)



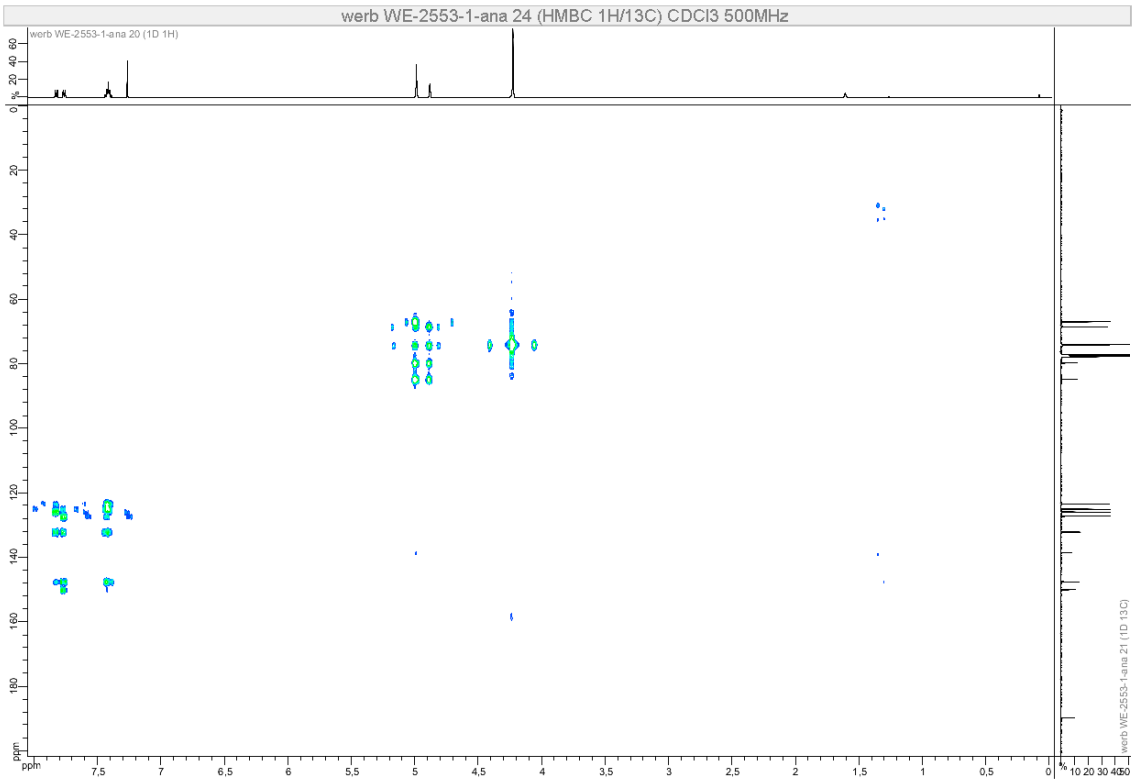
COSY (500 MHz, $CDCl_3$)



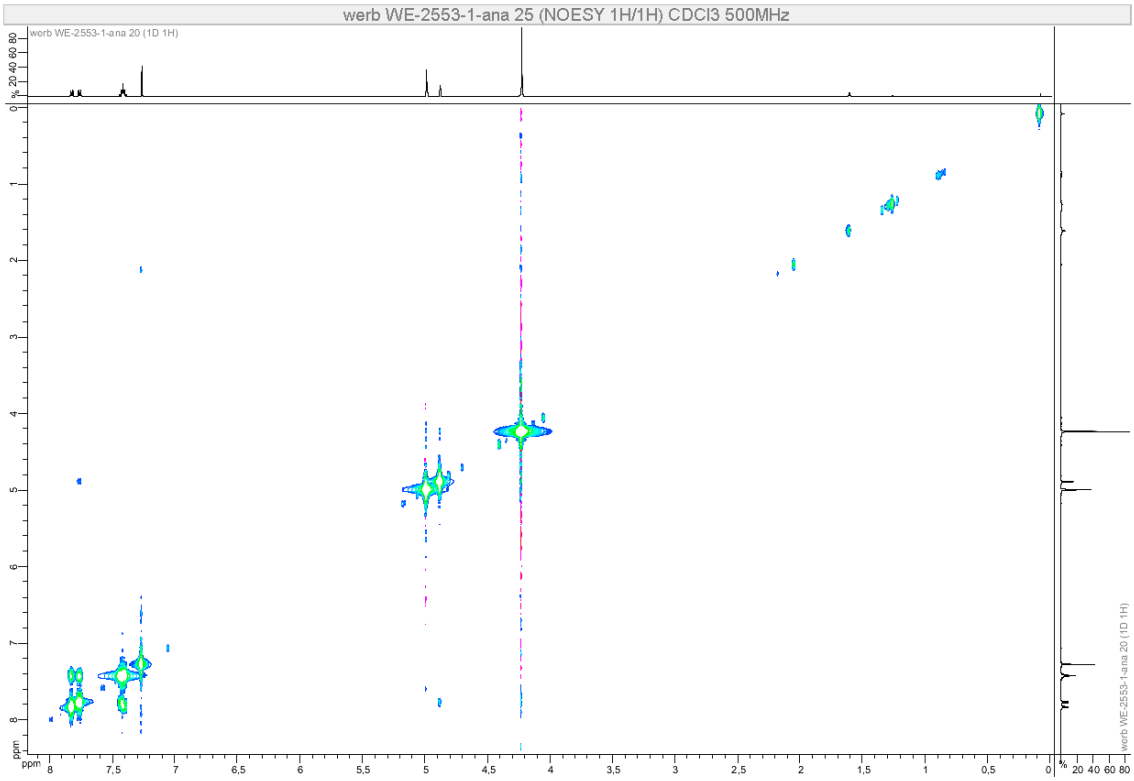
HSQC (500 MHz, $CDCl_3$)



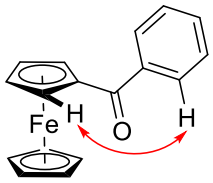
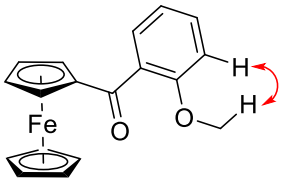
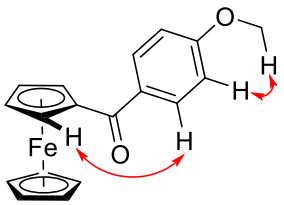
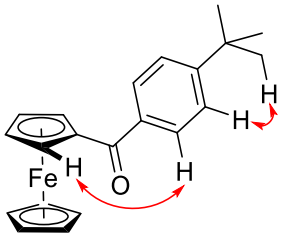
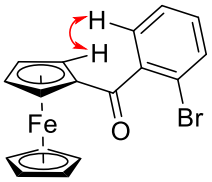
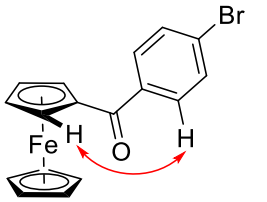
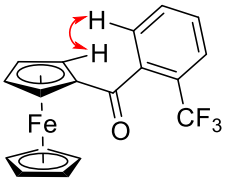
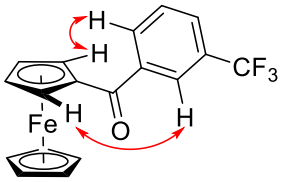
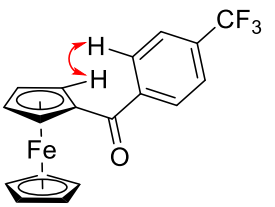
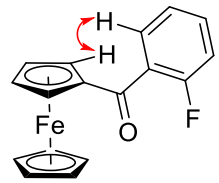
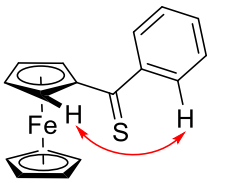
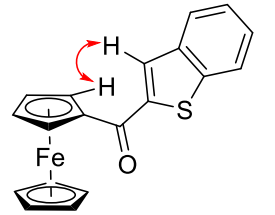
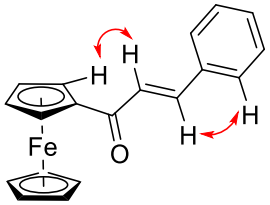
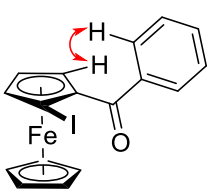
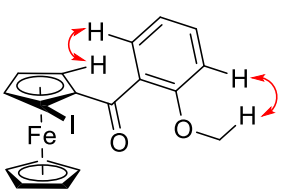
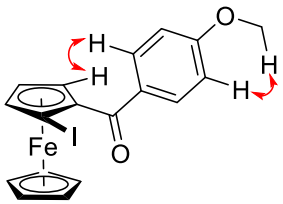
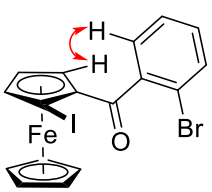
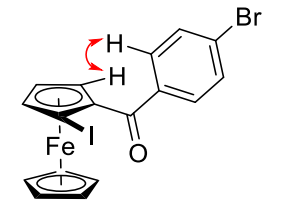
HMBC (500 MHz, $CDCl_3$)

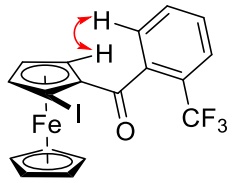
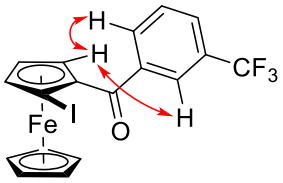
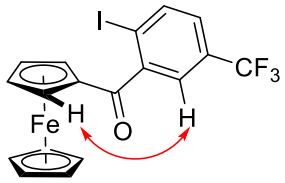
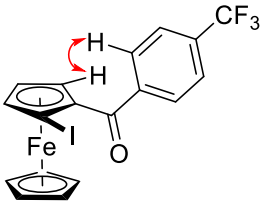
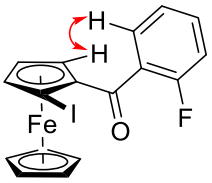
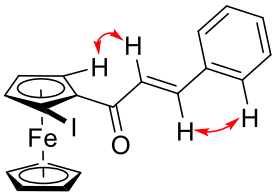
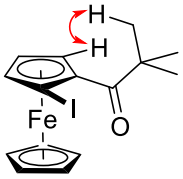
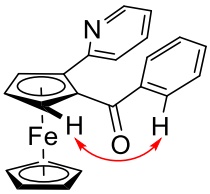
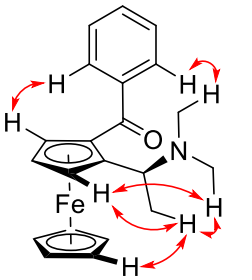
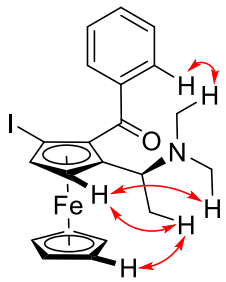
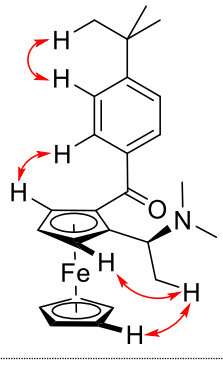
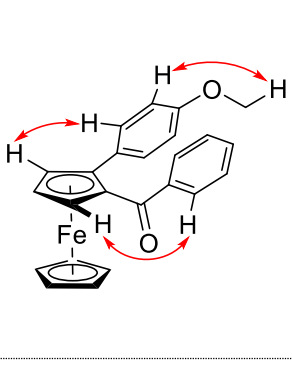
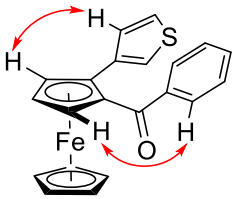
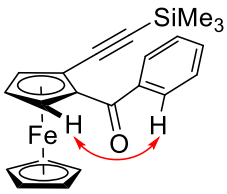
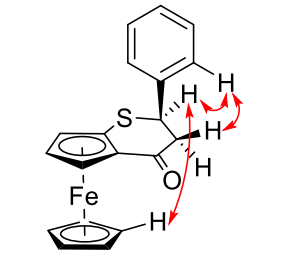


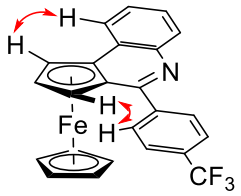
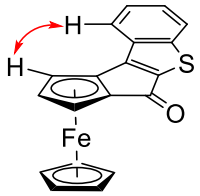
NOESY (500 MHz, $CDCl_3$)



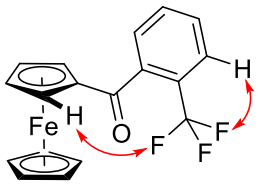
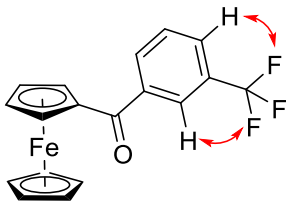
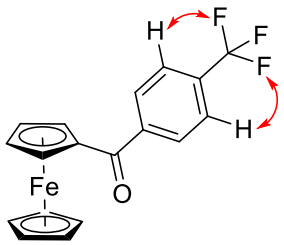
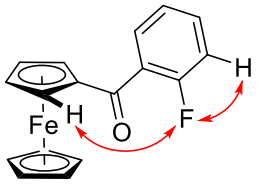
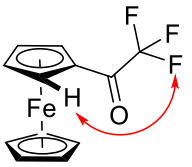
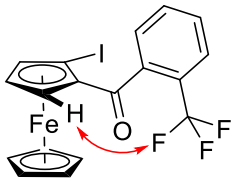
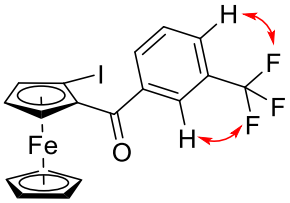
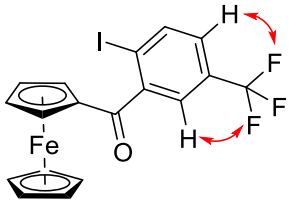
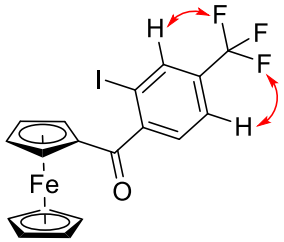
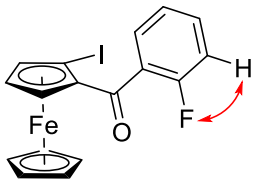
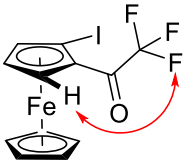
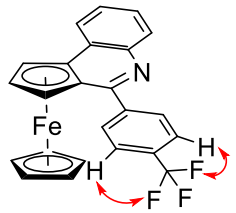
E) Selected NMR NOESY Correlations

		
1-Ph	**1-*o*OMePh**	**1-*p*OMePh**
		
1-*pt*BuPh	**1-*o*BrPh**	**1-*p*BrPh**
		
1-*o*CF$_3$Ph	**1-*m*CF$_3$Ph**	**1-*p*CF$_3$Ph**
		
1-*o*FPh	**4-Ph**	**1-2BTh**
		
1-CH=CHPh	**2-Ph**	**2-*o*OMePh**
		
2-*p*OMePh	**2-*o*BrPh**	**2-*p*BrPh**

		
2-*o*CF$_3$Ph	**2-*m*CF$_3$Ph**	**2'-*m*CF$_3$Ph**
		
2-*p*CF$_3$Ph	**2-*o*FPh**	**2-CH=CHPh**
		
2-*t*Bu	**3-Ph**	***R*$_P$-5**
		
***R*$_P$-6**	***R*$_P$-7**	**8a**
		
8b	**9**	**10**

	
11	**12**

F) Selected NMR HOESY Correlations

		
1-*o*CF$_3$Ph	**1-*m*CF$_3$Ph**	**1-*p*CF$_3$Ph**
		
1-*o*FPh	**1-CF$_3$**	**2-*o*CF$_3$Ph**
		
2-*m*CF$_3$Ph	**2'-*m*CF$_3$Ph**	**2'-*p*CF$_3$Ph**
		
2-*o*FPh	**2-CF$_3$**	**11**

G) HPLC data

(±)-1-Benzoyl-2-iodoferrocene (*rac*-2-Ph)

Chromatogram and Results

General informations

Sequence Name:	2023-04-03_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

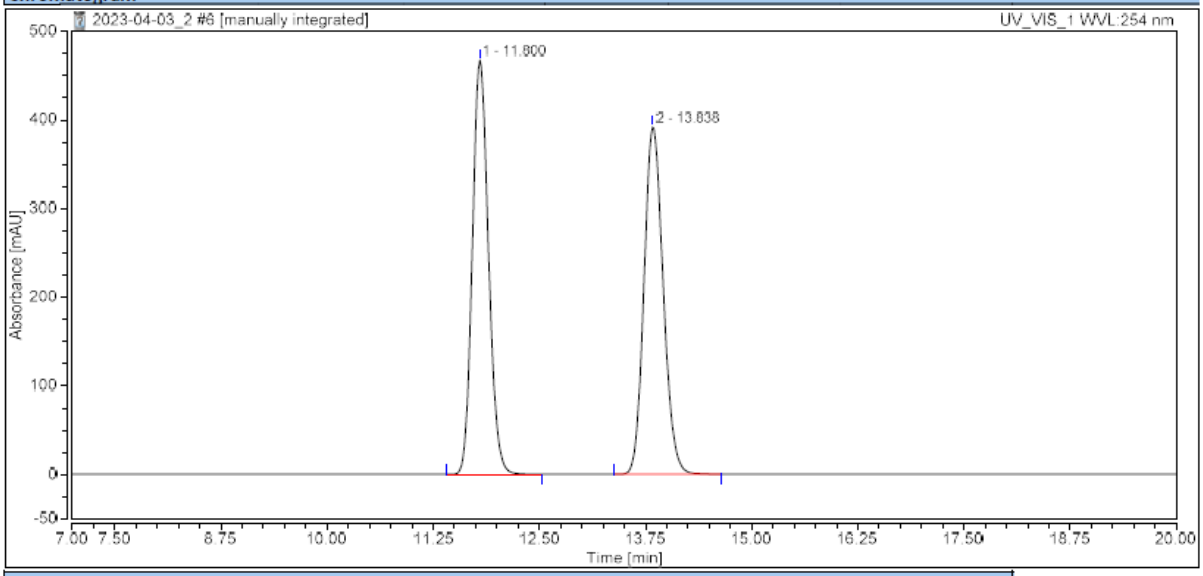
Injection Details

Injection Name:	RAC-WE-2407-2-IC-2023-04-03-85-15-1mLmin-30mi	*Run Time:*	30.00 min
Instrument Method:	85-15-30min-254nm-25°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	03/avr./23 14:45	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	85-15-30min-254nm-25°C		
%A Isopropanol	15 %		
%B Hexane	85 %	*Température du four:*	25.0 °C
Débit:	1.000 mL/min	*Pression:*	82 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		11.800	0.203	5.40	1.14	18705
2		13.838	0.243	n.a.	1.13	18039

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		11.800	102.714	467.801	49.99	54.38
2		13.838	102.768	392.495	50.01	45.62
Total:			**205.482**	**860.296**	**100.00**	**100.00**

Enantioenriched 1-benzoyl-2-iodoferrocene using (*S*)-PEALi (2-Ph)

Chromatogram and Results

General informations

Sequence Name:	2023-03-30
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

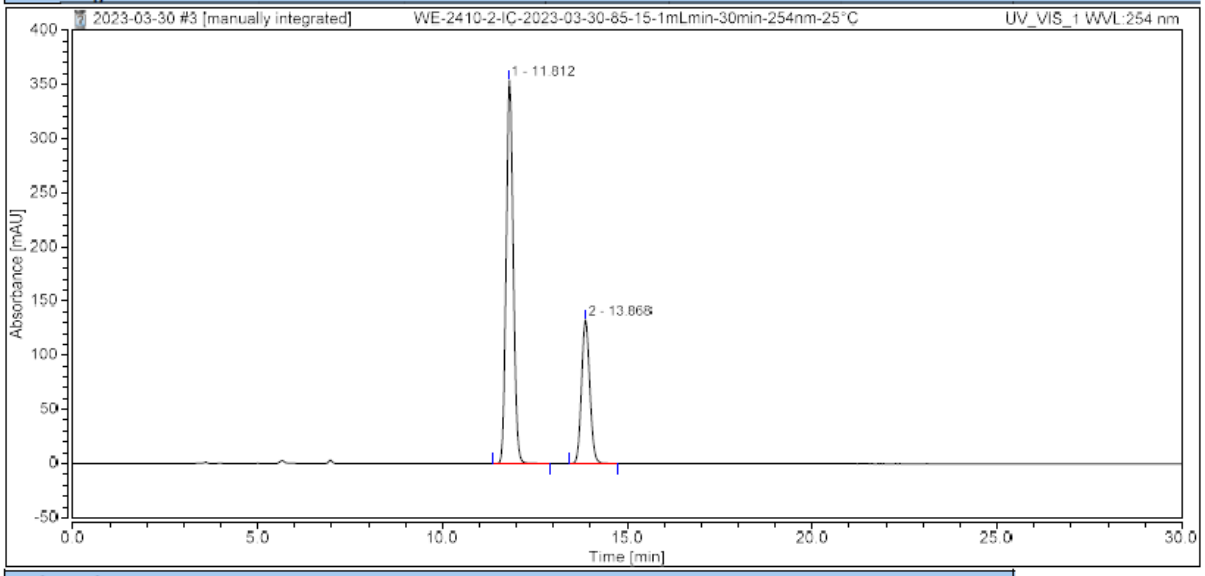
Injection Details

Injection Name:	WE-2410-2-IC-2023-03-30-85-15-1mLmin-30min-254	*Run Time:*	50.00 min
Instrument Method:	85-15-50min-254nm-25°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	30/mars/23 11:08	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	85-15-50min-254nm-25°C				
%A	Isopropanol	15 %			
%B	Hexane	85 %	*Température du four:*	25.0 °C	
	Débit:	1.000 mL/min	*Pression:*	81 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		11.812	0.202	5.48	1.12	18861
2		13.868	0.241	n.a.	1.10	18378

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		11.812	77.399	354.034	69.20	72.73
2		13.868	34.448	132.776	30.80	27.27
Total:			**111.847**	**486.809**	**100.00**	**100.00**

Enantioenriched 1-benzoyl-2-iodoferrocene obtained by crystallization (2-Ph)

Chromatogram and Results

General informations

Sequence Name:	**2023-06-01**
Instrument:	**U3000**
Logiciel used:	**Chromeleon**
Column used:	**CHIRALCEL IC3 DAICEL**

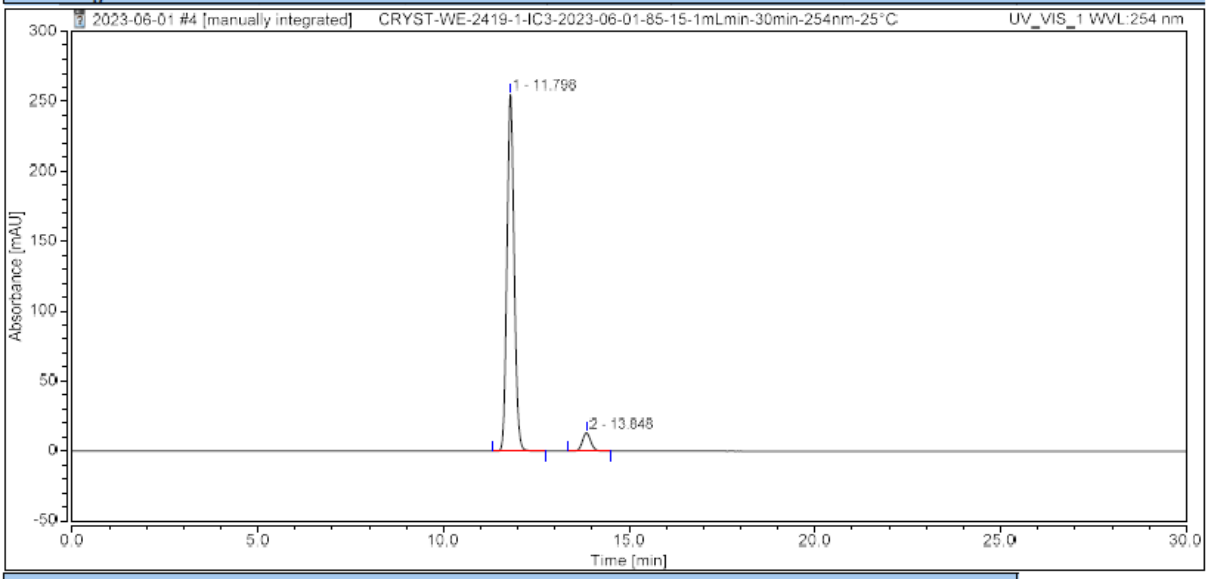
Injection Details

Injection Name:	**CRYST-WE-2419-1-IC3-2023-06-01-85-15-1mLmin-3**	*Run Time:*	**30.00 min**
Instrument Method:	**85-15-30min-254nm-25°C**	*Injection Volume:*	**2.00 µL**
Injection Date/Time:	**01/juin/23 22:15**	*Channel:*	**UV_VIS_1**
		Wavelength:	**254 nm**

Instrument Method Details

Instrument Method:		**85-15-30min-254nm-25°C**			
%A	**Isopropanol**	**15 %**			
%B	**Hexane**	**85 %**	*Température du four:*	**25.0 °C**	
	Débit:	**1.000 mL/min**	*Pression:*	**81 bars**	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		11.798	0.203	5.44	1.13	18694
2		13.848	0.242	n.a.	1.10	18194

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		11.798	56.155	254.994	94.28	95.13
2		13.848	3.409	13.065	5.72	4.87
Total:			**59.564**	**268.059**	**100.00**	**100.00**

1-Iodo-2-(2-methoxybenzoyl)ferrocene (*rac*-2-*o*OMePh)

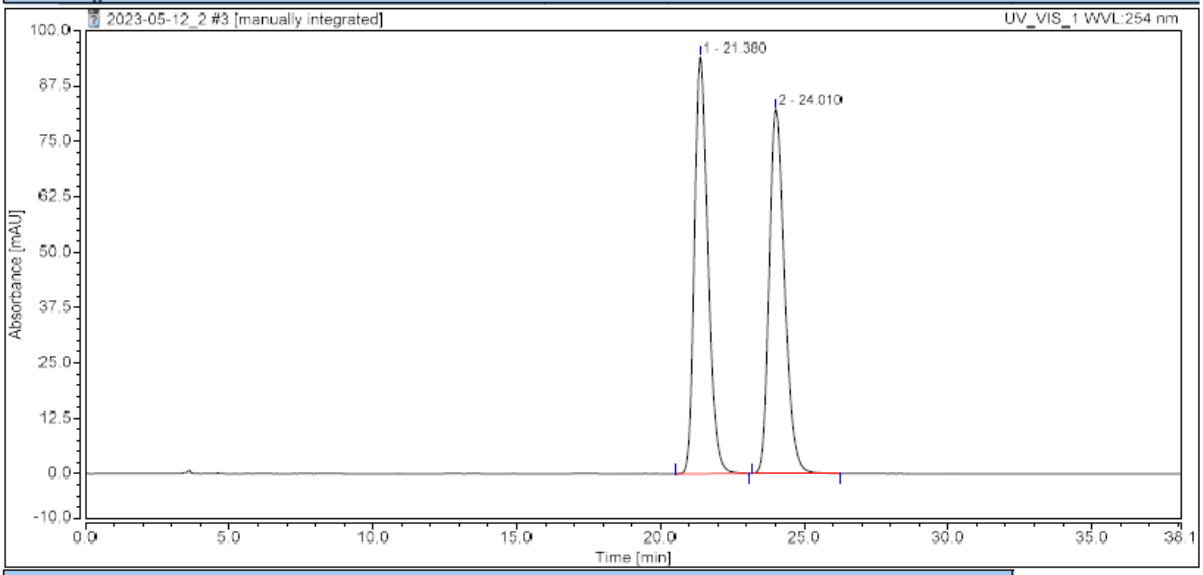
Chromatogram and Results

General informations	
Sequence Name:	2023-05-12_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

Injection Details			
Injection Name:	RAC-WE-2454-1-IC3-2023-05-12-80-20-1mLmin-30n	*Run Time:*	38.10 min
Instrument Method:	80-20-50min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	12/mai/23 15:26	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details					
Instrument Method:		80-20-50min-254nm-20°C			
%A	Isopropanol	20 %			
%B	Hexane	80 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	93 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		21.380	0.499	2.90	1.27	10175
2		24.010	0.570	n.a.	1.26	9819

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		21.380	51.037	94.041	50.01	53.34
2		24.010	51.016	82.258	49.99	46.66
Total:			**102.053**	**176.299**	**100.00**	**100.00**

Enantioenriched 1-iodo-2-(2-methoxybenzoyl)ferrocene using (*S*)-PEALi (2-*o*OMePh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-12_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

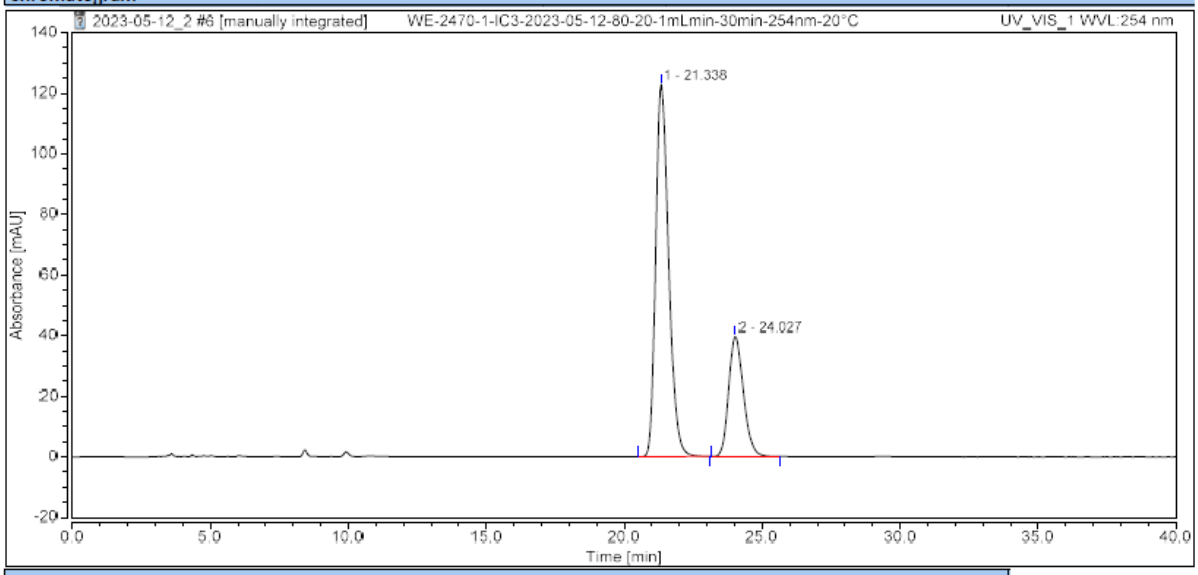
Injection Details

Injection Name:	WE-2470-1-IC3-2023-05-12-80-20-1mLmin-30min-25	*Run Time:*	40.00 min
Instrument Method:	80-20-40min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	12/mai/23 17:37	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	80-20-40min-254nm-20°C		
%A	Isopropanol	20 %	
%B	Hexane	80 %	
	Débit:	1.000 mL/min	*Température du four:* 20.0 °C
			Pression: 93 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		21.338	0.499	2.96	1.30	10115
2		24.027	0.571	n.a.	1.20	9822

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		21.338	66.746	122.876	73.09	75.60
2		24.027	24.568	39.668	26.91	24.40
Total:			**91.314**	**162.544**	**100.00**	**100.00**

1-Iodo-2-(4-methoxybenzoyl)ferrocene (*rac*-2-*p*OMePh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-12_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

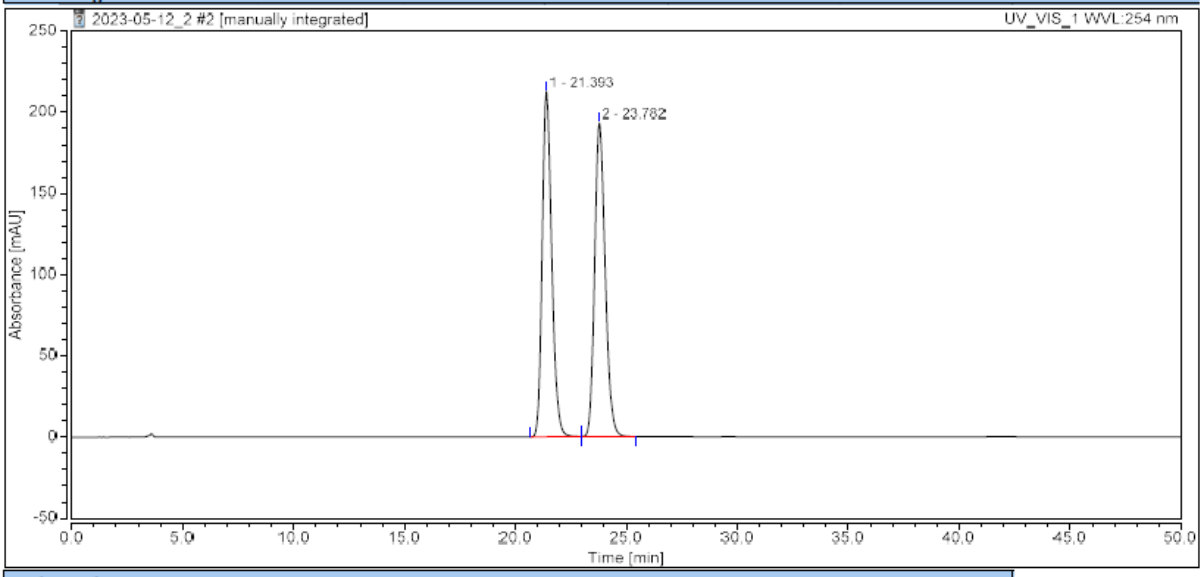
Injection Details

Injection Name:	RAC-WE-2449-1-IC3-2023-05-12-80-20-1mLmin-30n	*Run Time:*	50.00 min
Instrument Method:	80-20-50min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	12/mai/23 14:36	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		80-20-50min-254nm-20°C			
%A	Isopropanol	20 %			
%B	Hexane	80 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	93 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		21.393	0.463	2.89	1.24	11841
2		23.782	0.511	n.a.	1.21	11996

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		21.393	106.594	212.511	50.00	52.42
2		23.782	106.581	192.884	50.00	47.58
Total:			**213.175**	**405.395**	**100.00**	**100.00**

Enantioenriched 1-iodo-2-(4-methoxybenzoyl)ferrocene using (*S*)-PEALi (2-*p*OMePh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-12_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

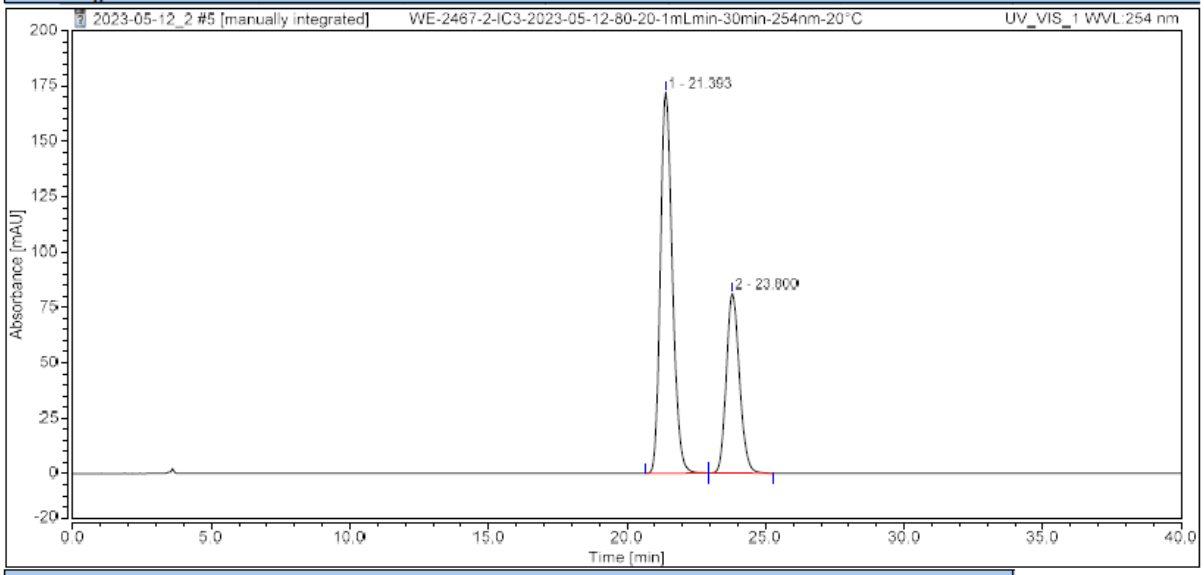
Injection Details

Injection Name:	WE-2467-2-IC3-2023-05-12-80-20-1mLmin-30min-25	*Run Time:*	40.00 min
Instrument Method:	80-20-40min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	12/mai/23 16:56	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		80-20-40min-254nm-20°C			
%A	Isopropanol	20 %			
%B	Hexane	80 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	93 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		21.393	0.462	2.93	1.23	11886
2		23.800	0.508	n.a.	1.16	12174

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		21.393	86.166	172.101	65.93	67.97
2		23.800	44.530	81.111	34.07	32.03
Total:			**130.695**	**253.212**	**100.00**	**100.00**

1-(2-Bromobenzoyl)-2-iodoferrocene (*rac*-2-*o*BrPh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-16
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

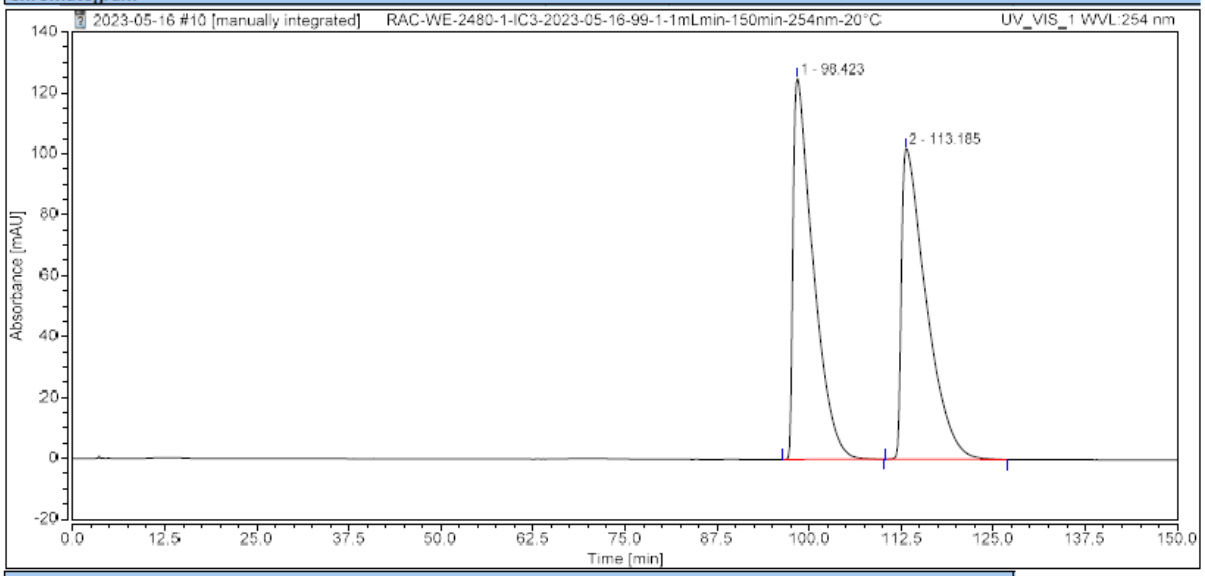
Injection Details

Injection Name:	RAC-WE-2480-1-IC3-2023-05-16-99-1-1mLmin-150n	*Run Time:*	150.00 min
Instrument Method:	99-1-150min-254nm-20°C	*Injection Volume:*	5.00 µL
Injection Date/Time:	16/mai/23 17:07	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-150min-254nm-20°C			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	75 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		98.423	2.844	2.74	3.24	6633
2		113.185	3.506	n.a.	3.57	5775

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		98.423	393.360	125.190	49.81	55.07
2		113.185	396.363	102.160	50.19	44.93
Total:			**789.723**	**227.350**	**100.00**	**100.00**

Enantioenriched 1-(2-bromobenzoyl)-2-iodoferrocene using (*S*)-PEALi (2-*o*BrPh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-16
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

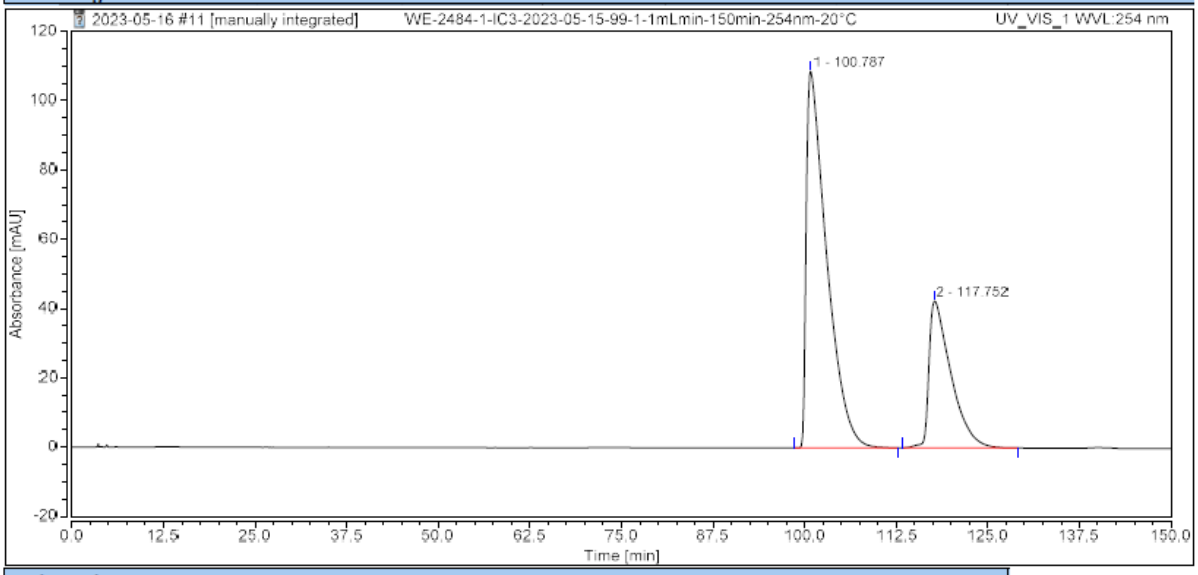
Injection Details

Injection Name:	WE-2484-1-IC3-2023-05-15-99-1-1mLmin-150min-25	*Run Time:*	150.00 min
Instrument Method:	99-1-150min-254nm-20°C	*Injection Volume:*	5.00 µL
Injection Date/Time:	16/mai/23 19:38	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-150min-254nm-20°C			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	74 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		100.787	2.872	3.35	3.36	6821
2		117.752	3.101	n.a.	2.46	7990

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		100.787	346.986	108.731	70.27	71.95
2		117.752	146.797	42.394	29.73	28.05
Total:			**493.783**	**151.125**	**100.00**	**100.00**

Enantiopure 1-(2-bromobenzoyl)-2-iodoferrocene after crystallization ((*R*P)-2-*o*BrPh)

Chromatogram and Results

General informations

Sequence Name:	2025-08-01
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK OD DAICEL

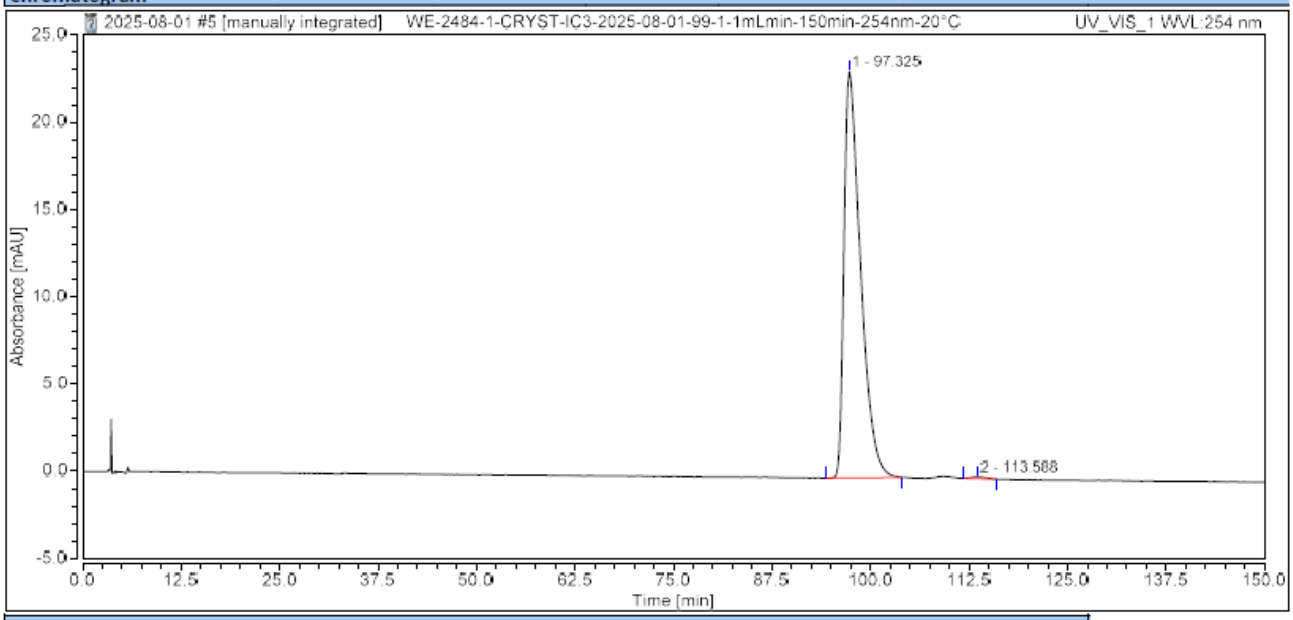
Injection Details

Injection Name:	WE-2484-1-CRYST-IC3-2025-08-01-99-1-1mLmin-15	*Run Time:*	150.00 min
Instrument Method:	99-1-150min-254nm-20°C	*Injection Volume:*	5.00 µL
Injection Date/Time:	01/août/25 22:38	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-150min-254nm-20°C			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	74 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		97.325	2.207	4.61	1.84	10769
2		113.588	1.954	n.a.	1.20	18727

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		97.325	56.540	23.296	99.59	99.53
2		113.588	0.230	0.110	0.41	0.47
Total:			**56.770**	**23.406**	**100.00**	**100.00**

1-(4-Bromobenzoyl)-2-iodoferrocene (*rac*-2-*p*BrPh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-15
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

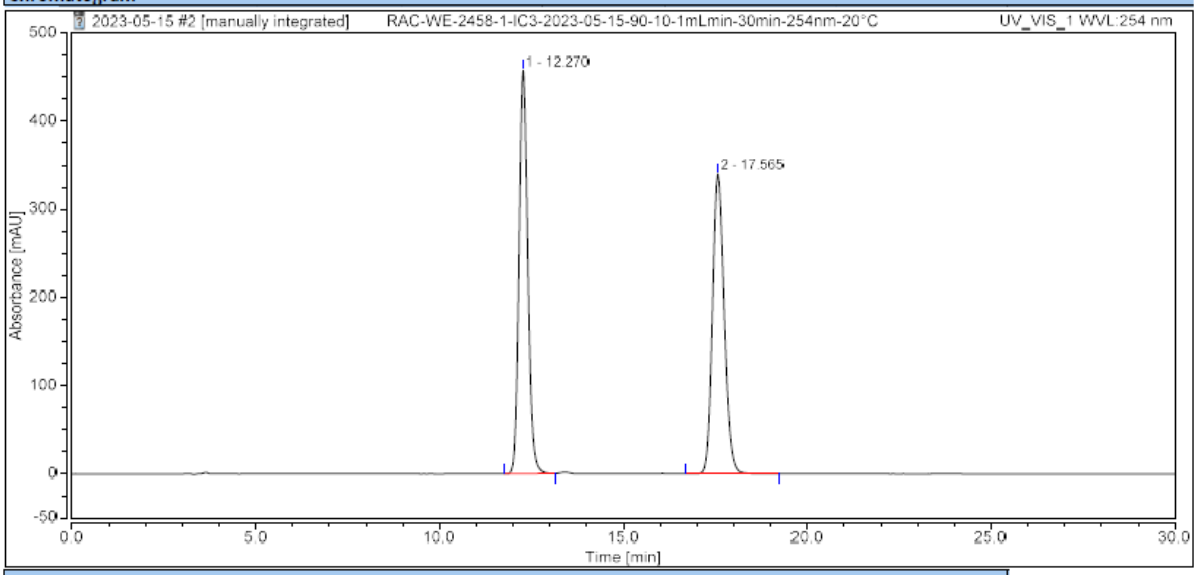
Injection Details

Injection Name:	RAC-WE-2458-1-IC3-2023-05-15-90-10-1mLmin-30n	*Run Time:*	30.00 min
Instrument Method:	90-10-30min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	15/mai/23 10:15	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		90-10-30min-254nm-20°C			
%A	Isopropanol	10 %			
%B	Hexane	90 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	80 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		12.270	0.254	10.47	1.14	12958
2		17.565	0.343	n.a.	1.17	14533

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		12.270	126.816	456.982	50.02	57.33
2		17.565	126.721	340.063	49.98	42.67
Total:			**253.537**	**797.045**	**100.00**	**100.00**

Enantioenriched 1-(4-bromobenzoyl)-2-iodoferrocene e using (*S*)-PEALi (2-*p*BrPh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-15
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

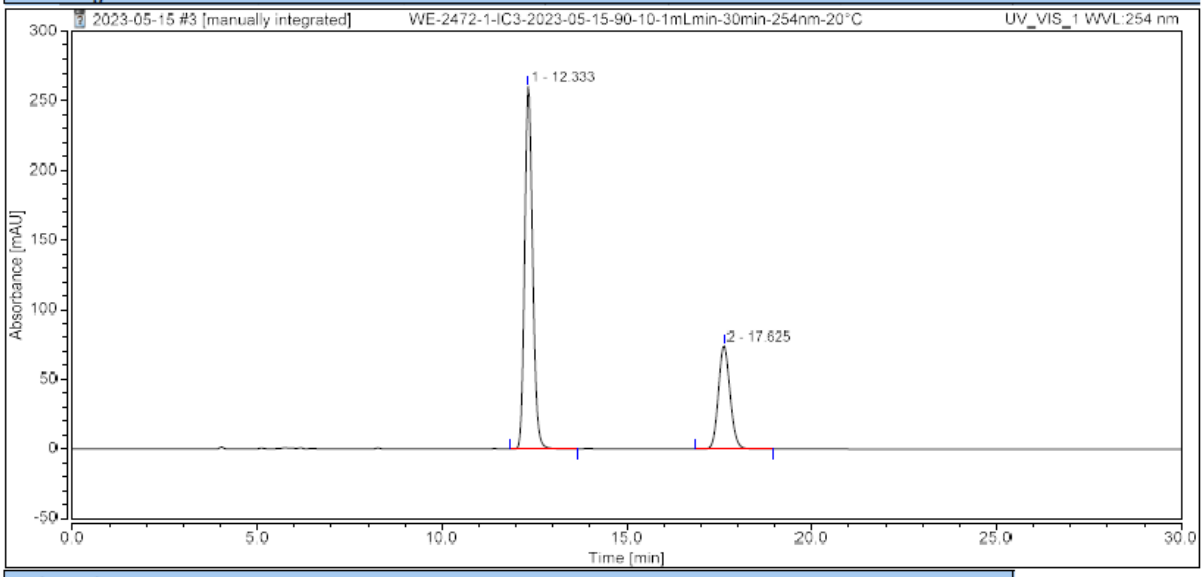
Injection Details

Injection Name:	WE-2472-1-IC3-2023-05-15-90-10-1mLmin-30min-25	*Run Time:*	30.00 min
Instrument Method:	90-10-30min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	15/mai/23 10:46	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		90-10-30min-254nm-20°C			
%A	Isopropanol	10 %			
%B	Hexane	90 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	80 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		12.333	0.231	10.96	1.16	15835
2		17.625	0.339	n.a.	1.12	14955

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		12.333	65.640	260.528	70.59	77.81
2		17.625	27.342	74.283	29.41	22.19
Total:			**92.982**	**334.811**	**100.00**	**100.00**

2-(Trifluoromethyl)benzoylferrocene (1-*o*CF_3Ph)

Chromatogram and Results

General informations

Sequence Name:	2023-05-25
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA DAICEL

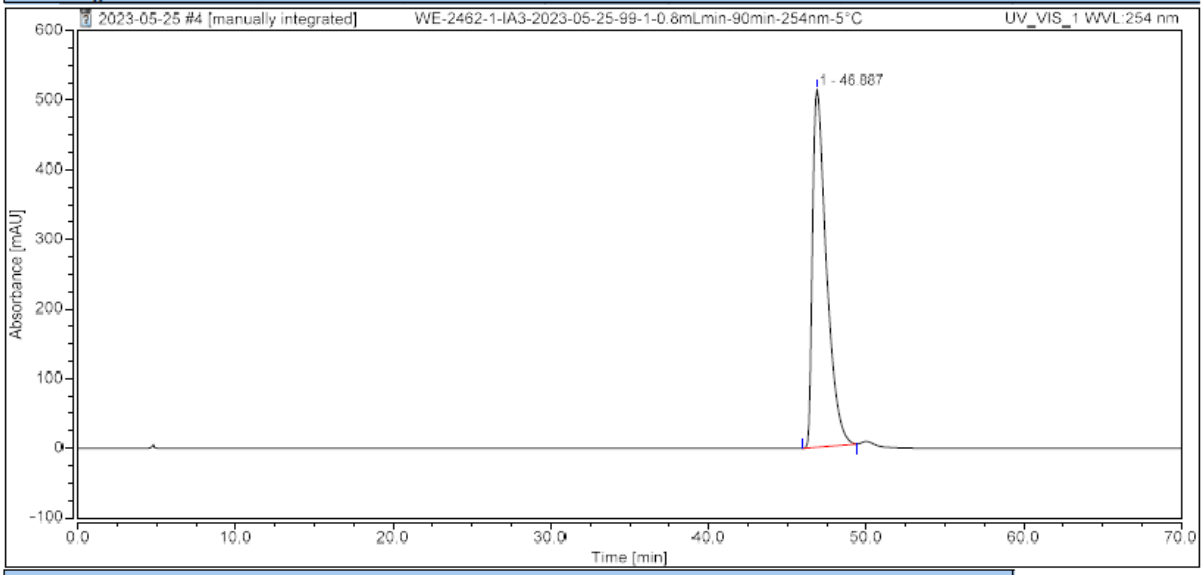
Injection Details

Injection Name:	WE-2462-1-IA3-2023-05-25-99-1-0.8mLmin-90min-2	*Run Time:*	90.00 min
Instrument Method:	99-1-90min-254nm-5°C-0.8mLmin	*Injection Volume:*	1.00 µL
Injection Date/Time:	25/mai/23 12:58	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-90min-254nm-5°C-0.8mLmin			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	5.0 °C	
	Débit:	0.800 mL/min	*Pression:*	73 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		46.887	0.932	n.a.	1.99	14027

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		46.887	527.393	513.836	100.00	100.00
Total:			**527.393**	**513.836**	**100.00**	**100.00**

1-Iodo-2-[2-(trifluoromethyl)benzoyl]ferrocene (*rac*-2-*o*CF_3Ph)

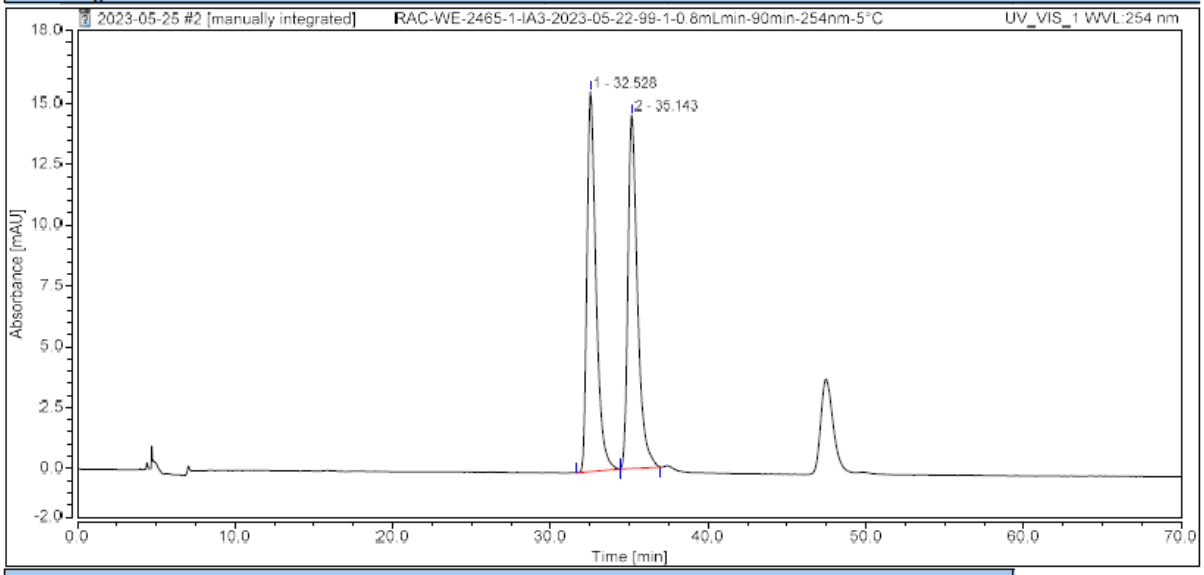
Chromatogram and Results

General informations	
Sequence Name:	2023-05-25
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA DAICEL

Injection Details			
Injection Name:	RAC-WE-2465-1-IA3-2023-05-22-99-1-0.8mLmin-90r	*Run Time:*	90.00 min
Instrument Method:	99-1-90min-254nm-5°C-0.8mLmin	*Injection Volume:*	1.00 µL
Injection Date/Time:	25/mai/23 09:56	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details				
Instrument Method:	99-1-90min-254nm-5°C-0.8mLmin			
%A	Isopropanol	1 %		
%B	Hexane	99 %	*Température du four:*	5.0 °C
	Débit:	0.800 mL/min	*Pression:*	73 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		32.528	0.589	2.54	1.58	16885
2		35.143	0.626	n.a.	1.57	17443

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		32.528	10.324	15.594	50.14	51.78
2		35.143	10.265	14.520	49.86	48.22
Total:			**20.589**	**30.115**	**100.00**	**100.00**

Enantioenriched 1-iodo-2-[2-(trifluoromethyl)benzoyl]ferrocene using (*S*)-PEALi (2-*o*CF_3Ph)

Chromatogram and Results

General informations

Sequence Name:	2023-05-25
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IA DAICEL

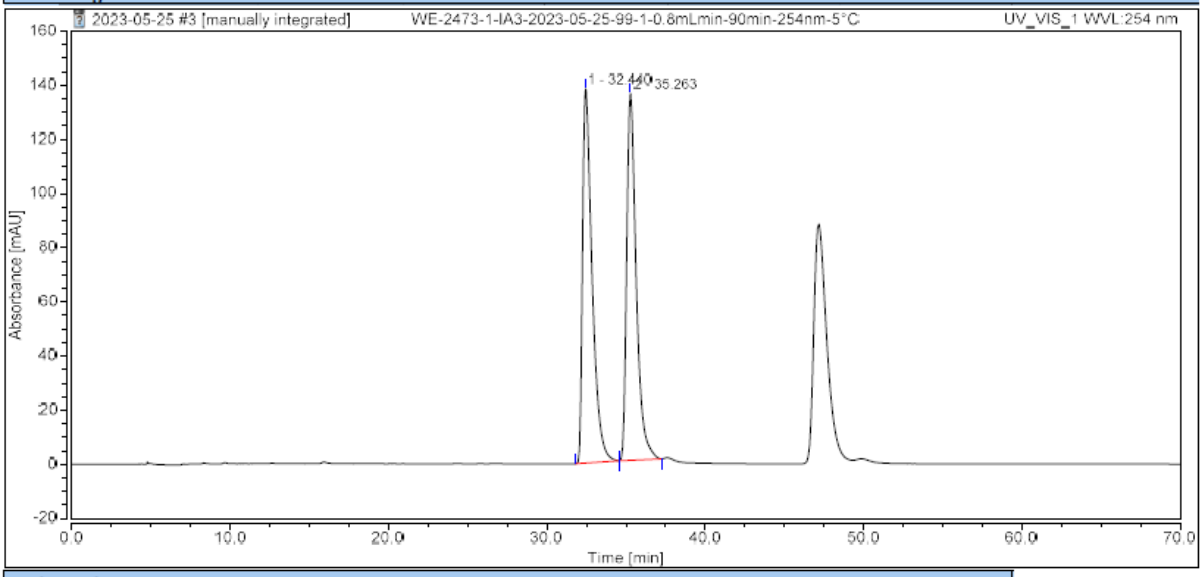
Injection Details

Injection Name:	WE-2473-1-IA3-2023-05-25-99-1-0.8mLmin-90min-2	*Run Time:*	90.00 min
Instrument Method:	99-1-90min-254nm-5°C-0.8mLmin	*Injection Volume:*	1.00 µL
Injection Date/Time:	25/mai/23 11:27	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-90min-254nm-5°C-0.8mLmin			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	5.0 °C	
	Débit:	0.800 mL/min	*Pression:*	73 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		32.440	0.623	2.69	1.96	15015
2		35.263	0.615	n.a.	1.60	18199

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		32.440	96.512	138.335	50.59	50.50
2		35.263	94.248	135.594	49.41	49.50
Total:			**190.760**	**273.929**	**100.00**	**100.00**

1-Iodo-2-[3-(trifluoromethyl)benzoyl]ferrocene (*rac*-2-*m*CF_3Ph)

Chromatogram and Results

General informations

Sequence Name:	2023-05-23
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

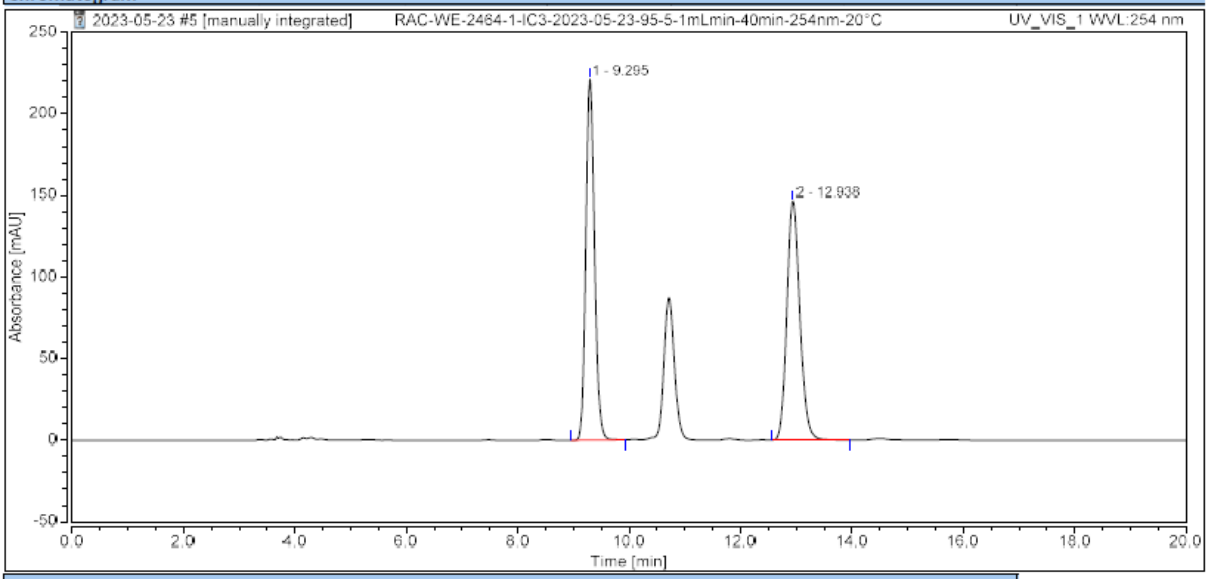
Injection Details

Injection Name:	RAC-WE-2464-1-IC3-2023-05-23-95-5-1mLmin-40mi	*Run Time:*	40.00 min
Instrument Method:	95-5-40min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	23/mai/23 11:35	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		95-5-40min-254nm-20°C			
%A	Isopropanol	5 %			
%B	Hexane	95 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	76 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		9.295	0.166	10.38	1.14	17445
2		12.938	0.249	n.a.	1.16	15015

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		9.295	39.786	221.009	50.15	60.17
2		12.938	39.554	146.299	49.85	39.83
Total:			**79.340**	**367.307**	**100.00**	**100.00**

Enantioenriched 1-iodo-2-[3-(trifluoromethyl)benzoyl]ferrocene using (*S*)-PEALi (2-*m*CF_3Ph)

Chromatogram and Results

General informations

Sequence Name:	2023-05-23
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

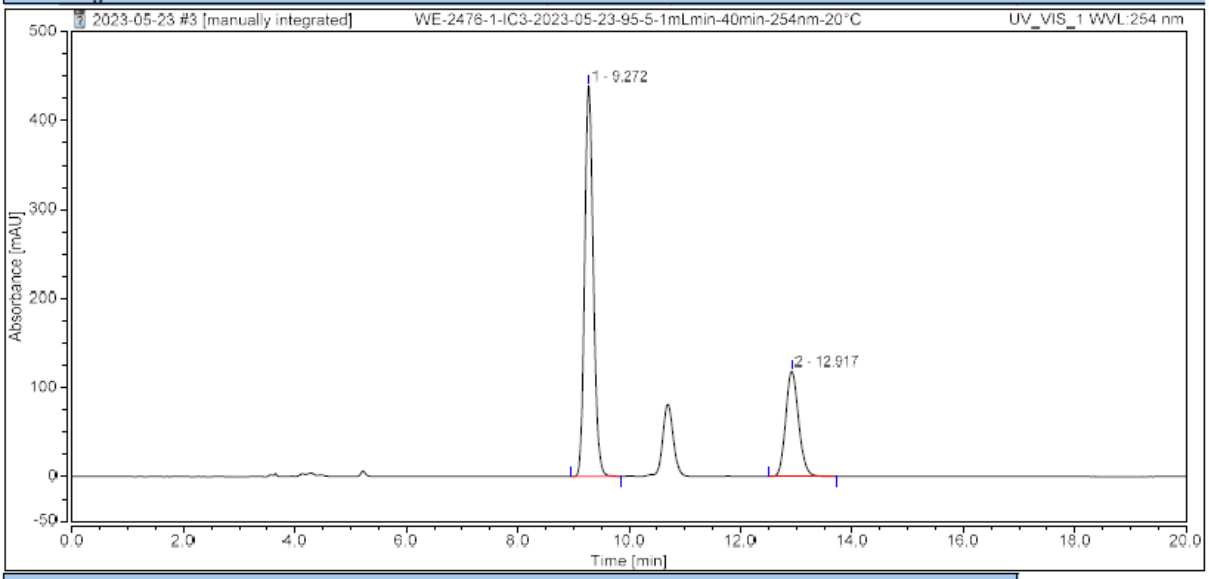
Injection Details

Injection Name:	WE-2476-1-IC3-2023-05-23-95-5-1mLmin-40min-254	*Run Time:*	40.00 min
Instrument Method:	95-5-40min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	23/mai/23 10:30	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	95-5-40min-254nm-20°C				
%A	Isopropanol	5 %			
%B	Hexane	95 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	76 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		9.272	0.165	10.41	1.16	17499
2		12.917	0.248	n.a.	1.15	15008

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		9.272	78.557	438.851	71.06	78.71
2		12.917	31.992	118.679	28.94	21.29
Total:			**110.549**	**557.530**	**100.00**	**100.00**

1-Iodo-2-[4-(trifluoromethyl)benzoyl]ferrocene (*rac*-2-*p*CF_3Ph)

Chromatogram and Results

General informations

Sequence Name:	2023-05-12_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

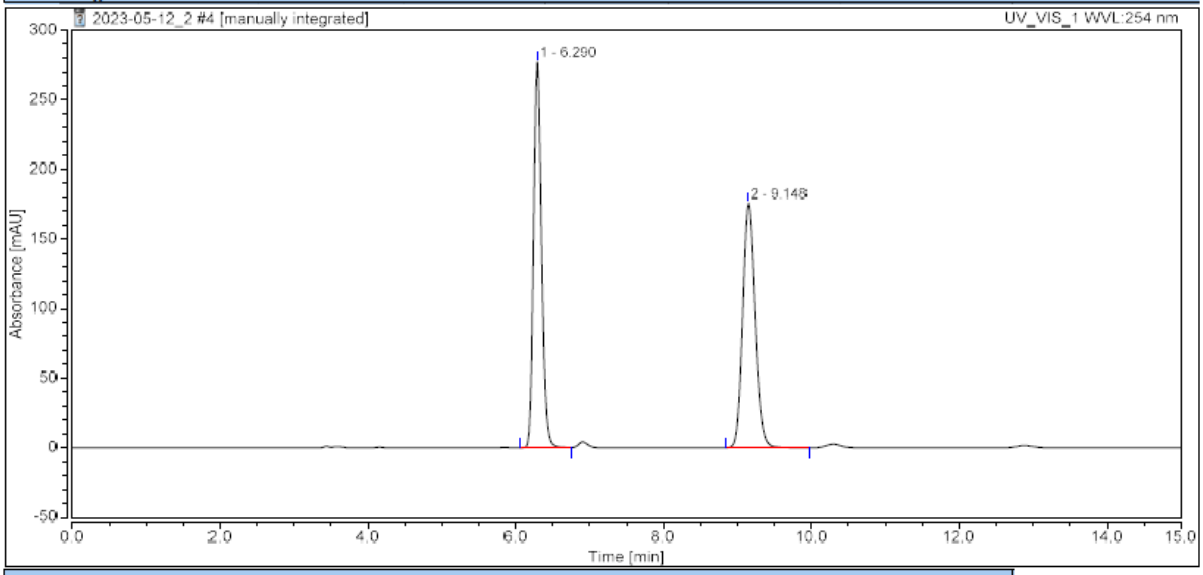
Injection Details

Injection Name:	RAC-WE-2460-1-IC3-2023-05-12-80-20-1mLmin-30n	*Run Time:*	50.00 min
Instrument Method:	80-20-50min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	12/mai/23 16:06	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		80-20-50min-254nm-20°C			
%A	Isopropanol	20 %			
%B	Hexane	80 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	93 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		6.290	0.115	11.35	1.19	16617
2		9.148	0.182	n.a.	1.14	13967

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		6.290	34.663	277.249	49.97	61.21
2		9.148	34.702	175.680	50.03	38.79
Total:			**69.365**	**452.929**	**100.00**	**100.00**

Enantioenriched 1-iodo-2-[4-(trifluoromethyl)benzoyl]ferrocene using (*S*)-PEALi (2-*p*CF_3Ph)

Chromatogram and Results

General informations

Sequence Name:	2023-05-12_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

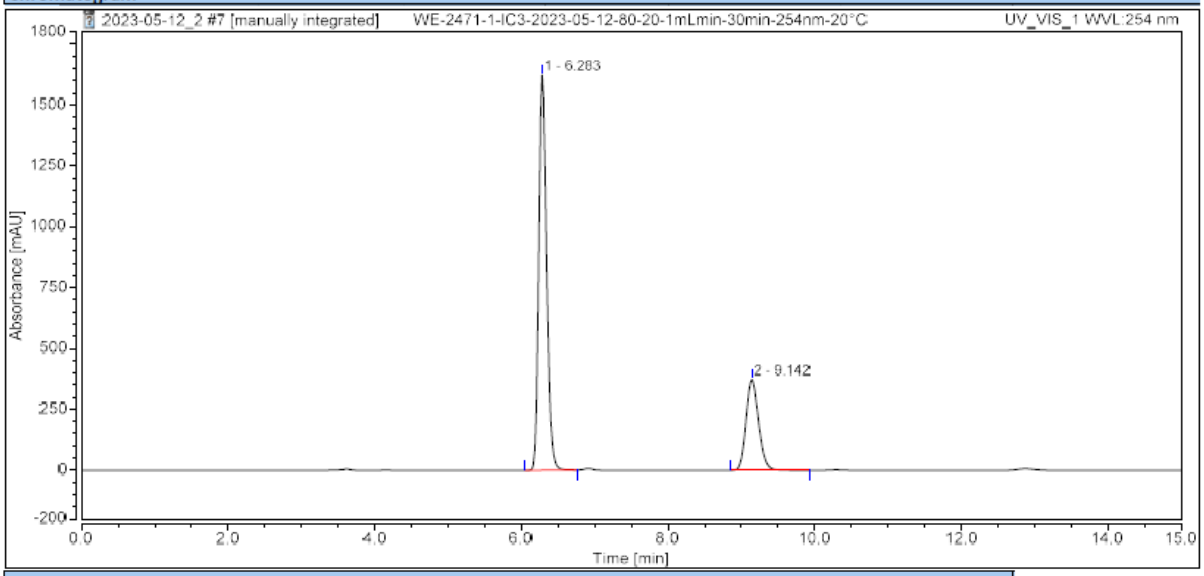
Injection Details

Injection Name:	WE-2471-1-IC3-2023-05-12-80-20-1mLmin-30min-25	*Run Time:*	30.00 min
Instrument Method:	80-20-30min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	12/mai/23 18:18	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		80-20-30min-254nm-20°C			
%A	Isopropanol	20 %			
%B	Hexane	80 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	93 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		6.283	0.114	11.35	1.23	16691
2		9.142	0.183	n.a.	1.16	13873

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		6.283	202.201	1622.751	73.26	81.31
2		9.142	73.820	372.928	26.74	18.69
Total:			**276.021**	**1995.679**	**100.00**	**100.00**

1-(2-Fluorobenzoyl)-2-iodoferrocene (*rac*-2-*o*FPh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-16
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

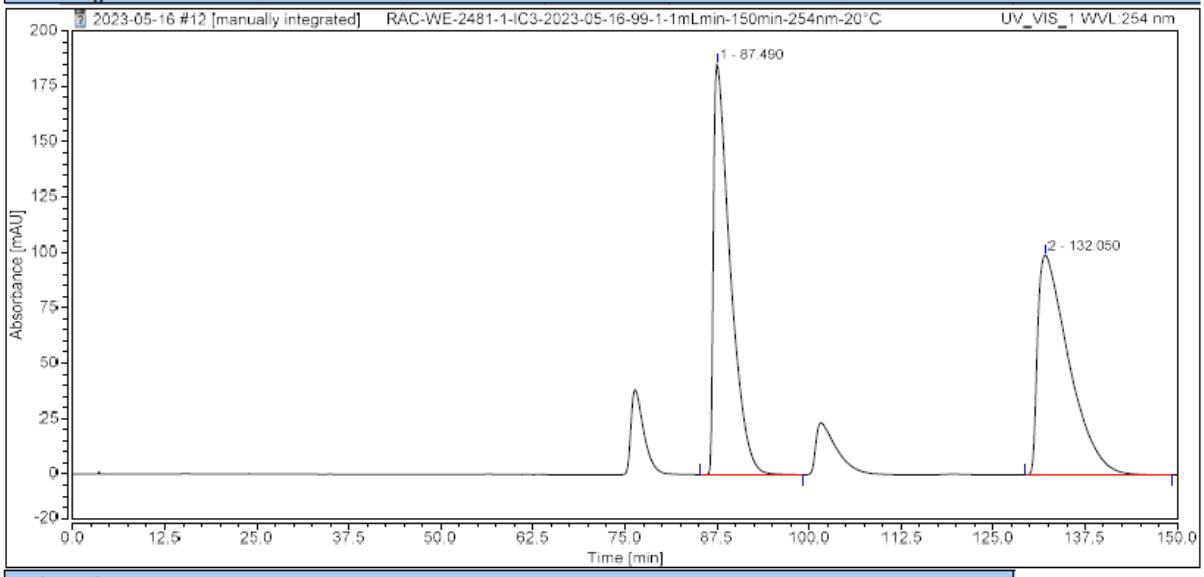
Injection Details

Injection Name:	RAC-WE-2481-1-IC3-2023-05-16-99-1-1mLmin-150n	*Run Time:*	150.00 min
Instrument Method:	99-1-150min-254nm-20°C	*Injection Volume:*	5.00 µL
Injection Date/Time:	16/mai/23 22:09	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	99-1-150min-254nm-20°C				
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	74 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		87.490	2.365	7.67	3.22	7583
2		132.050	4.493	n.a.	2.93	4785

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		87.490	488.672	185.574	50.02	65.12
2		132.050	488.238	99.382	49.98	34.88
Total:			**976.911**	**284.956**	**100.00**	**100.00**

Enantioenriched 1-(2-fluorobenzoyl)-2-iodoferrocene using (*S*)-PEALi (2-*o*FPh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-16
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

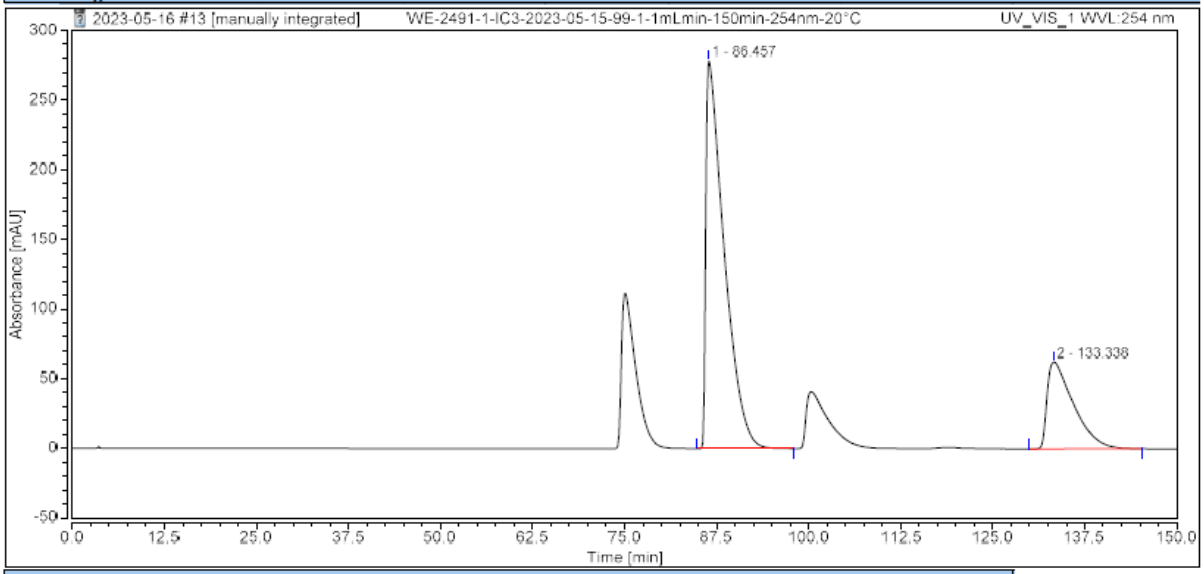
Injection Details

Injection Name:	WE-2491-1-IC3-2023-05-15-99-1-1mLmin-150min-25	*Run Time:*	150.00 min
Instrument Method:	99-1-150min-254nm-20°C	*Injection Volume:*	5.00 µL
Injection Date/Time:	17/mai/23 00:39	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:	99-1-150min-254nm-20°C		
%A	Isopropanol	1 %	
%B	Hexane	99 %	
	Débit:	1.000 mL/min	*Température du four:* 20.0 °C
			Pression: 74 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		86.457	2.603	8.63	4.05	6114
2		133.338	3.809	n.a.	2.57	6788

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		86.457	802.858	278.333	75.65	81.71
2		133.338	258.382	62.317	24.35	18.29
Total:			**1061.240**	**340.649**	**100.00**	**100.00**

1-(2-Fluoro-3-iodobenzoyl)-2-iodoferrocene (*rac*-2”-*o*FPh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-16
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

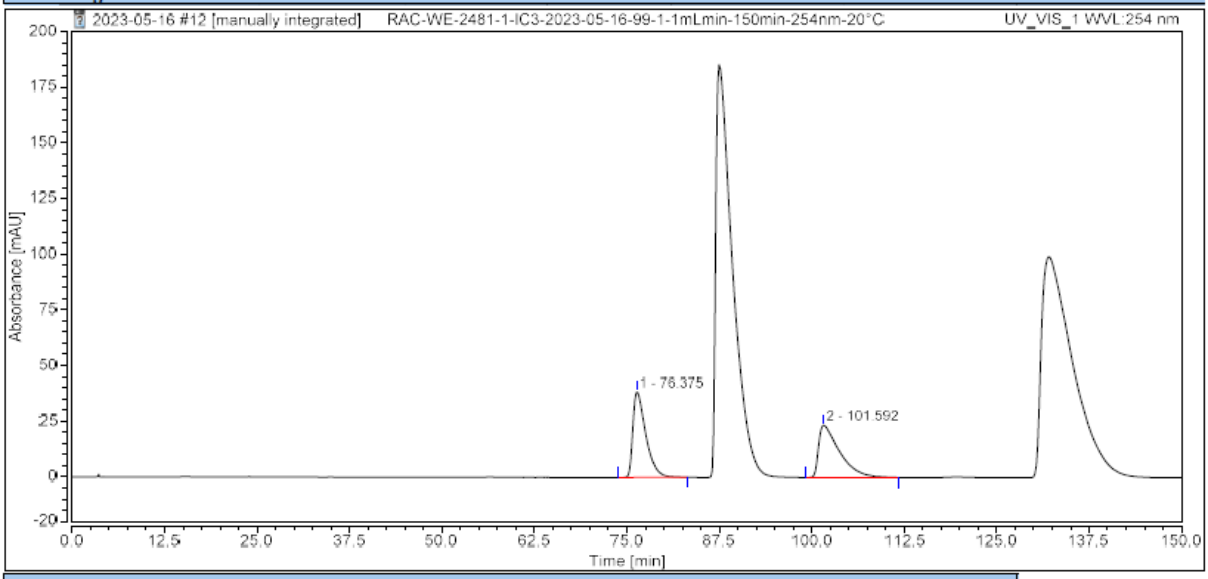
Injection Details

Injection Name:	RAC-WE-2481-1-IC3-2023-05-16-99-1-1mLmin-150n	*Run Time:*	150.00 min
Instrument Method:	99-1-150min-254nm-20°C	*Injection Volume:*	5.00 µL
Injection Date/Time:	16/mai/23 22:09	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-150min-254nm-20°C		
%A	Isopropanol	1 %		
%B	Hexane	99 %	*Température du four:*	20.0 °C
	Débit:	1.000 mL/min	*Pression:*	74 bars

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		76.375	1.815	6.29	1.92	9813
2		101.592	2.913	n.a.	2.78	6736

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		76.375	77.513	38.467	50.31	62.15
2		101.592	76.566	23.423	49.69	37.85
Total:			**154.079**	**61.890**	**100.00**	**100.00**

Enantioenriched 1-(2-fluoro-3-iodobenzoyl)-2-iodoferrocene using (*S*)-PEALi (2”-*o*FPh)

Chromatogram and Results

General informations

Sequence Name:	2023-05-16
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

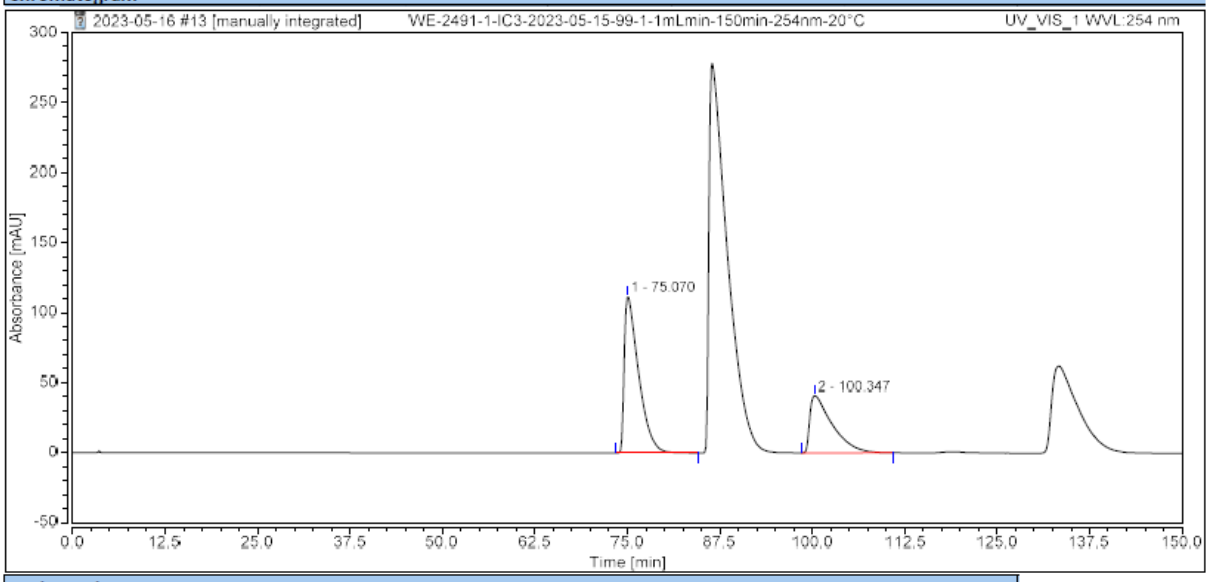
Injection Details

Injection Name:	WE-2491-1-IC3-2023-05-15-99-1-1mLmin-150min-25	*Run Time:*	150.00 min
Instrument Method:	99-1-150min-254nm-20°C	*Injection Volume:*	5.00 µL
Injection Date/Time:	17/mai/23 00:39	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-150min-254nm-20°C			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	74 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		75.070	2.037	5.82	2.67	7521
2		100.347	3.088	n.a.	3.27	5849

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		75.070	252.308	112.003	63.95	73.27
2		100.347	142.236	40.860	36.05	26.73
Total:			**394.544**	**152.863**	**100.00**	**100.00**

1-Iodo-2-pivaloylferrocene (*rac*-2-*t*Bu)

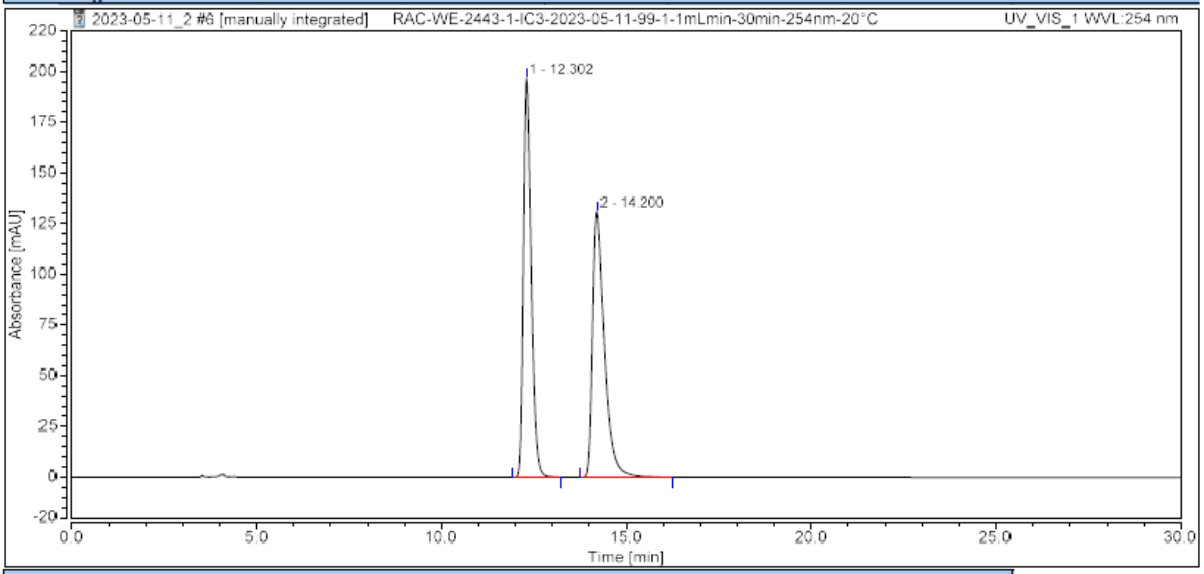
Chromatogram and Results

General informations	
Sequence Name:	2023-05-11_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

Injection Details			
Injection Name:	RAC-WE-2443-1-IC3-2023-05-11-99-1-1mLmin-30mi	*Run Time:*	50.00 min
Instrument Method:	99-1-50min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	11/mai/23 19:20	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details					
Instrument Method:	99-1-50min-254nm-20°C				
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	74 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		12.302	0.226	4.06	1.37	16366
2		14.200	0.325	n.a.	1.71	10569

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		12.302	48.542	196.832	50.06	60.05
2		14.200	48.424	130.952	49.94	39.95
Total:			**96.966**	**327.784**	**100.00**	**100.00**

Enantioenriched 1-Iodo-2-pivaloylferrocene using (*S*)-PEALi (2-*t*Bu)

Chromatogram and Results

General informations

Sequence Name:	2023-05-11_2
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

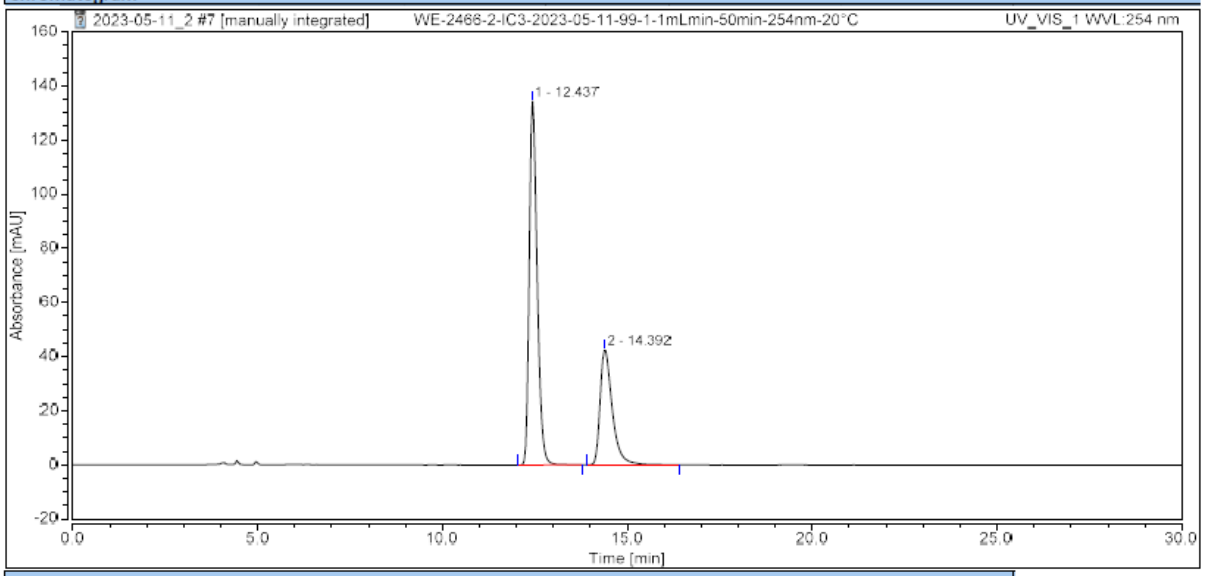
Injection Details

Injection Name:	WE-2466-2-IC3-2023-05-11-99-1-1mLmin-50min-254	*Run Time:*	50.00 min
Instrument Method:	99-1-50min-254nm-20°C	*Injection Volume:*	1.00 µL
Injection Date/Time:	11/mai/23 20:10	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-50min-254nm-20°C			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	20.0 °C	
	Débit:	1.000 mL/min	*Pression:*	74 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		12.437	0.228	4.15	1.33	16491
2		14.392	0.328	n.a.	1.57	10667

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		12.437	33.511	134.359	67.58	75.89
2		14.392	16.075	42.678	32.42	24.11
Total:			**49.587**	**177.038**	**100.00**	**100.00**

(Trifluoromethylcarbonyl)ferrocene (*rac*-1-CF_3)

Chromatogram and Results

General informations

Sequence Name:	2023-04-03
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

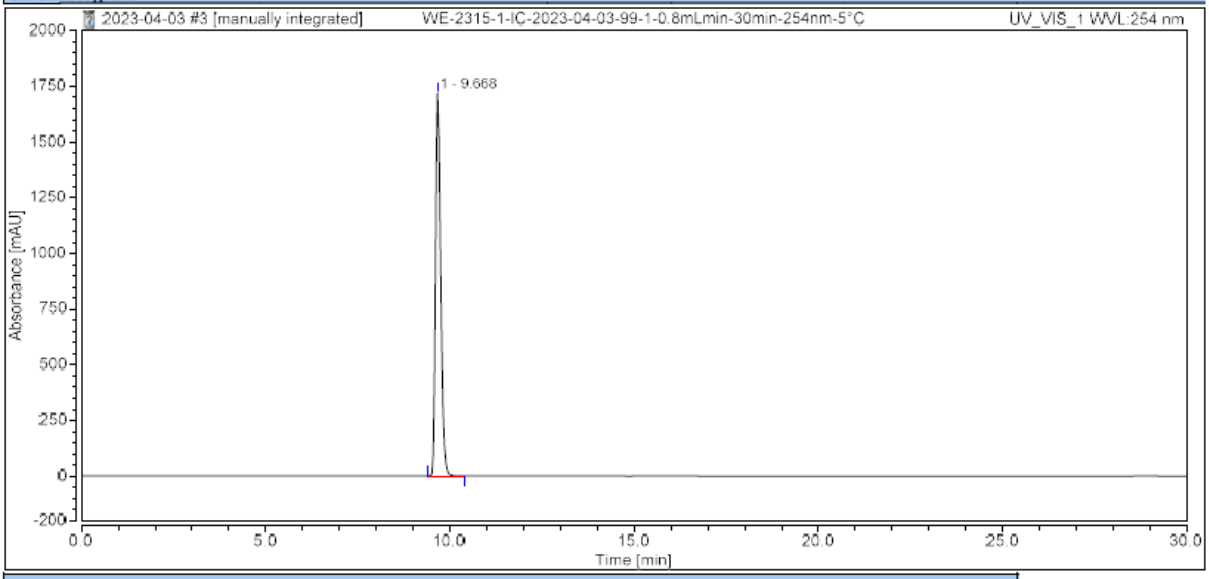
Injection Details

Injection Name:	WE-2315-1-IC-2023-04-03-99-1-0.8mLmin-30min-25	*Run Time:*	30.00 min
Instrument Method:	99-1-30min-254nm-5°C-0.8mLmin	*Injection Volume:*	1.00 µL
Injection Date/Time:	03/avr./23 10:37	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-30min-254nm-5°C-0.8mLmin			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	5.0 °C	
	Débit:	0.800 mL/min	*Pression:*	68 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		9.668	0.151	n.a.	1.31	22807

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		9.668	282.496	1721.198	100.00	100.00
Total:			**282.496**	**1721.198**	**100.00**	**100.00**

1-Iodo-2-(trifluoromethylcarbonyl)ferrocene (*rac*-2-CF_3)

Chromatogram and Results

General informations

Sequence Name:	2023-06-02
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALCEL IC3 DAICEL

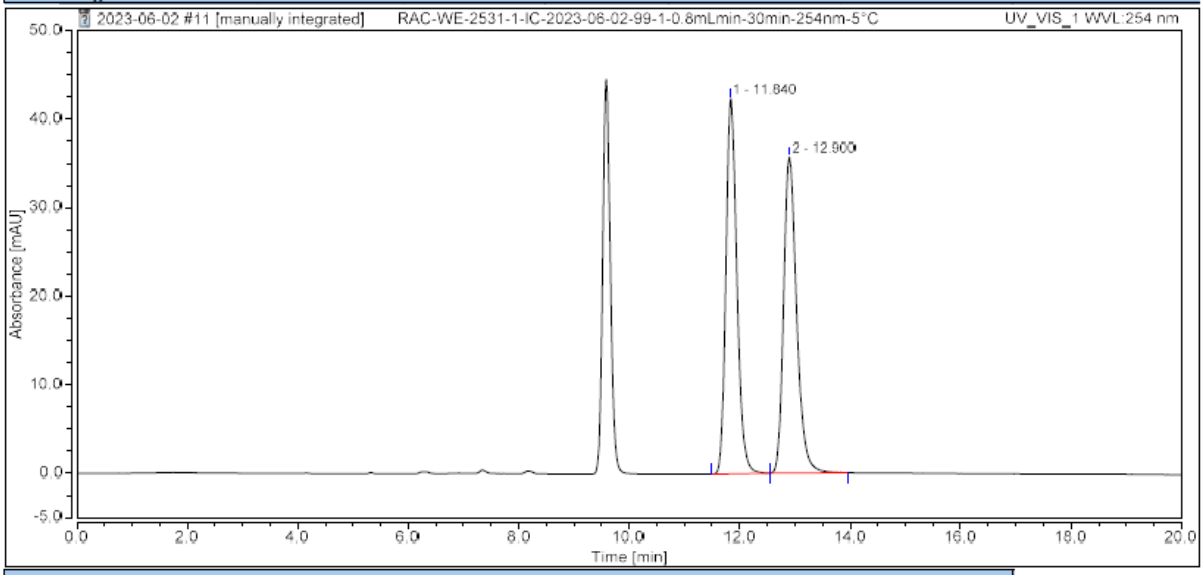
Injection Details

Injection Name:	RAC-WE-2531-1-IC-2023-06-02-99-1-0.8mLmin-30m	*Run Time:*	30.00 min
Instrument Method:	99-1-30min-254nm-5°C-0.8mLmin	*Injection Volume:*	1.00 µL
Injection Date/Time:	02/juin/23 15:13	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-30min-254nm-5°C-0.8mLmin			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	5.0 °C	
	Débit:	0.800 mL/min	*Pression:*	68 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		11.840	0.210	2.75	1.23	17646
2		12.900	0.246	n.a.	1.29	15264

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		11.840	9.750	42.382	50.06	54.29
2		12.900	9.728	35.686	49.94	45.71
Total:			**19.478**	**78.068**	**100.00**	**100.00**

Enantioenriched 1-iodo-2-(trifluoromethylcarbonyl)ferrocene using (*S*)-PEALi (2-CF_3)

Chromatogram and Results

General informations

Sequence Name:	2023-06-09
Instrument:	U3000
Logiciel used:	Chromeleon
Column used:	CHIRALPAK IC DAICEL

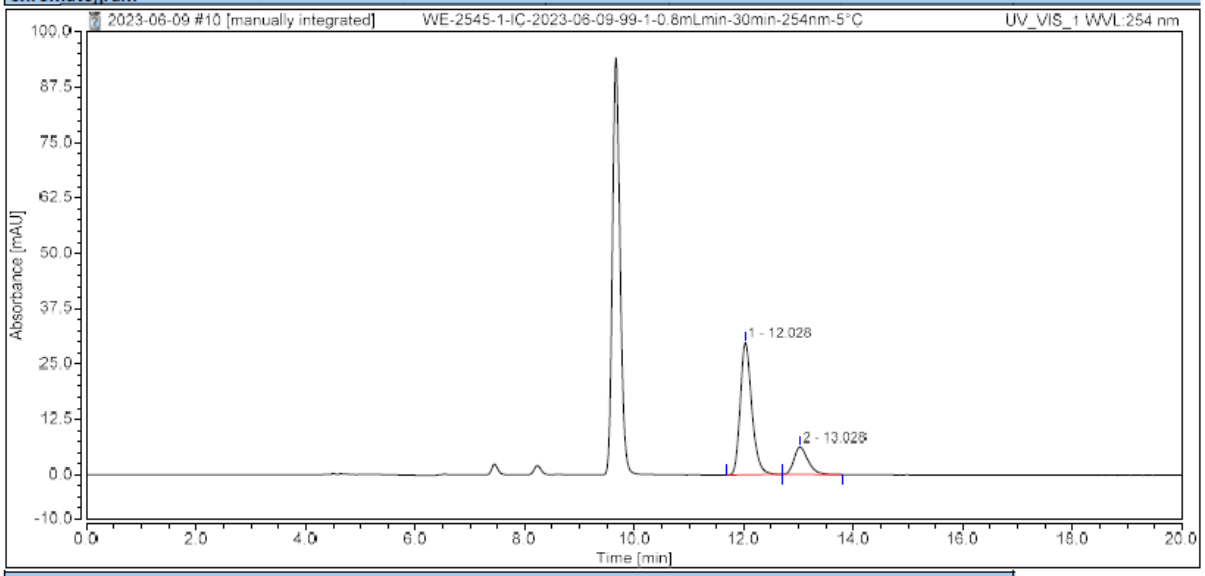
Injection Details

Injection Name:	WE-2545-1-IC-2023-06-09-99-1-0.8mLmin-30min-25	*Run Time:*	30.00 min
Instrument Method:	99-1-30min-254nm-5°C-0.8mLmin	*Injection Volume:*	1.00 µL
Injection Date/Time:	09/juin/23 14:21	*Channel:*	UV_VIS_1
		Wavelength:	254 nm

Instrument Method Details

Instrument Method:		99-1-30min-254nm-5°C-0.8mLmin			
%A	Isopropanol	1 %			
%B	Hexane	99 %	*Température du four:*	5.0 °C	
	Débit:	0.800 mL/min	*Pression:*	67 bars	

Chromatogram



Peak Results

No.	Peak Name	Retention Time min	Width (50%) min	Resolution (EP)	Asymmetry (EP)	Plates (EP)
1		12.028	0.221	2.41	1.27	16356
2		13.028	0.268	n.a.	1.33	13055

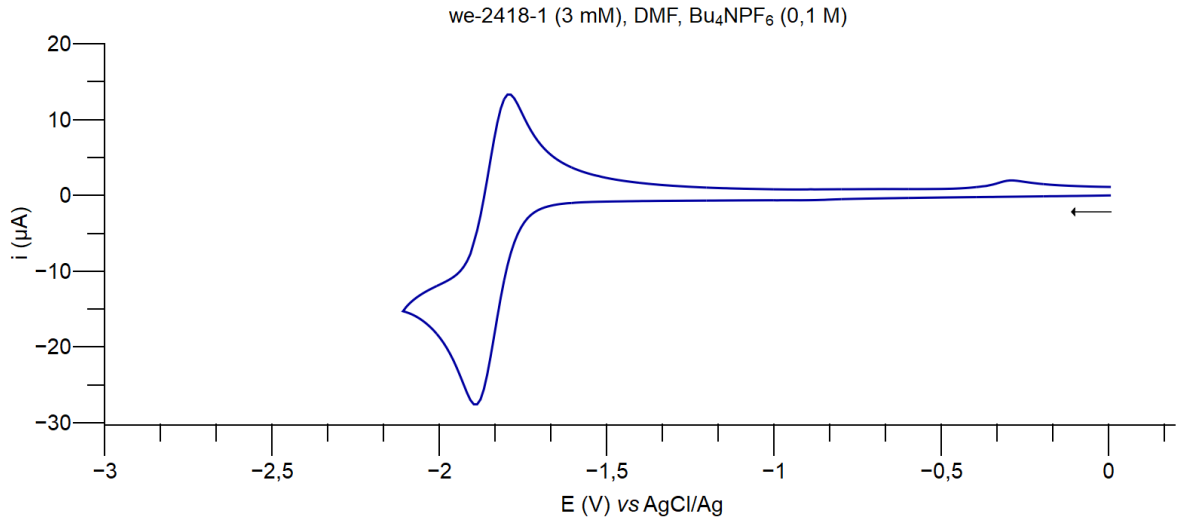
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %
1		12.028	7.320	29.953	79.77	82.79
2		13.028	1.857	6.229	20.23	17.21
Total:			**9.177**	**36.181**	**100.00**	**100.00**

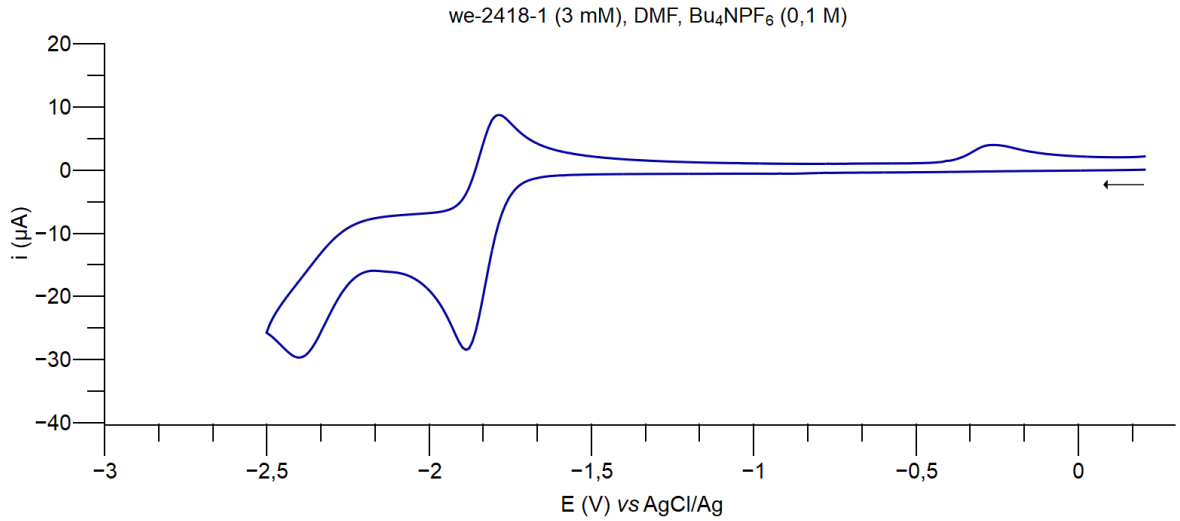
H) Electrochemical study

Compound 1-Ph

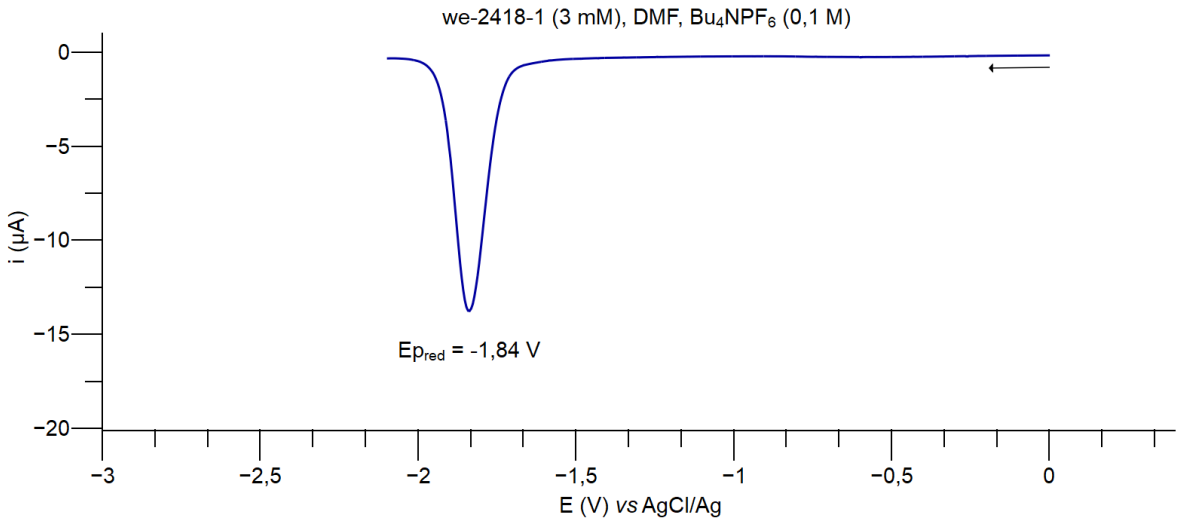
Cyclic voltammetry for ketone reduction in DMF



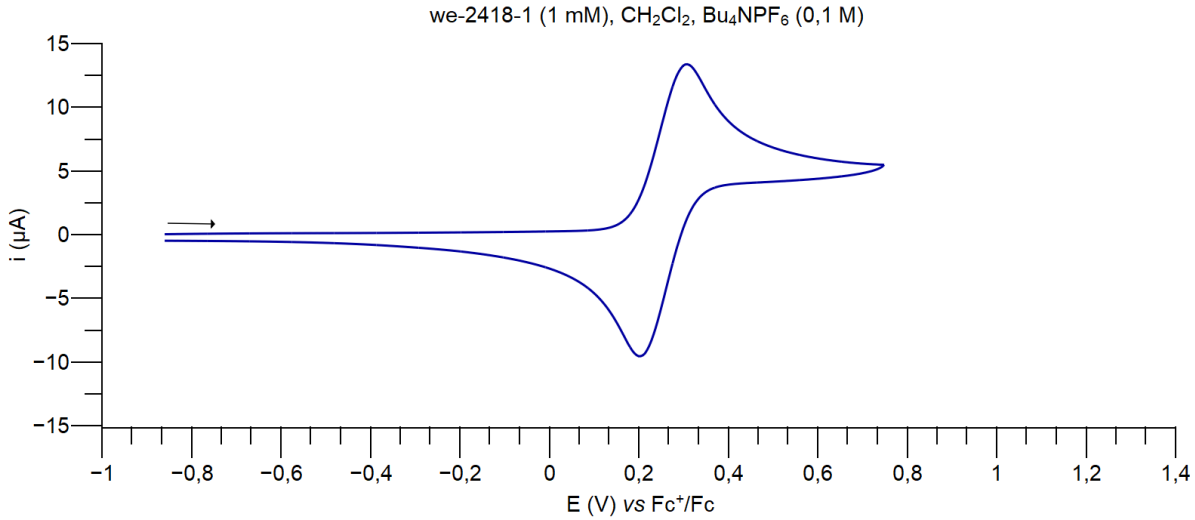
Full cyclic voltammetry for ketone reduction in DMF



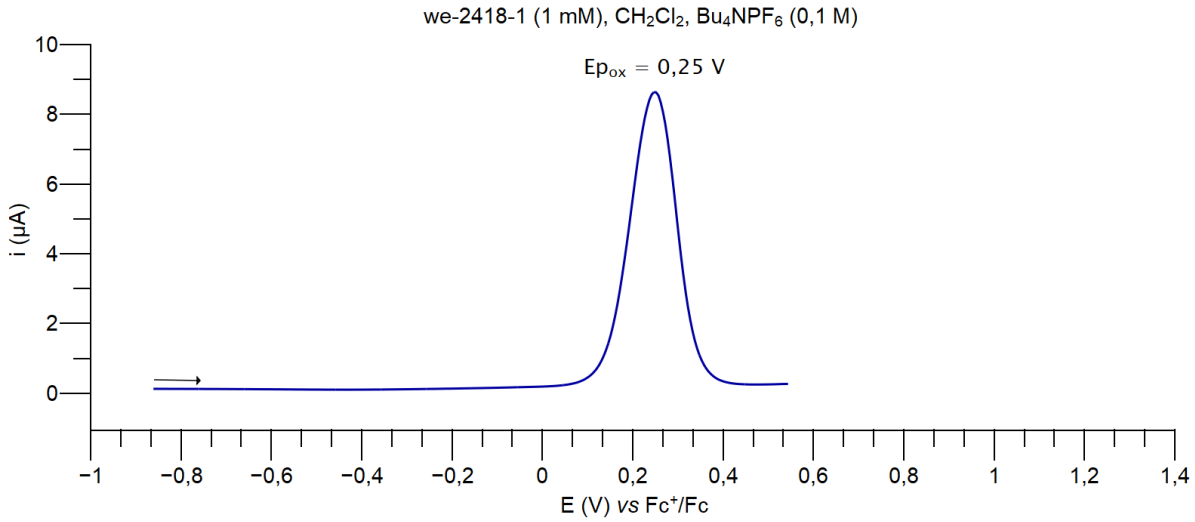
Differential pulse voltammetry for ketone reduction in DMF



Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

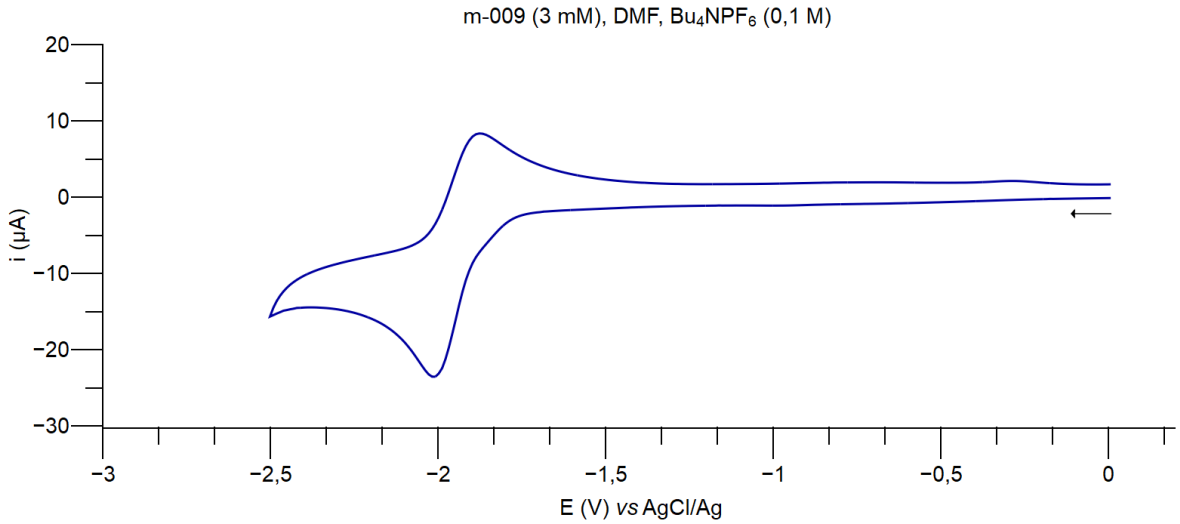


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

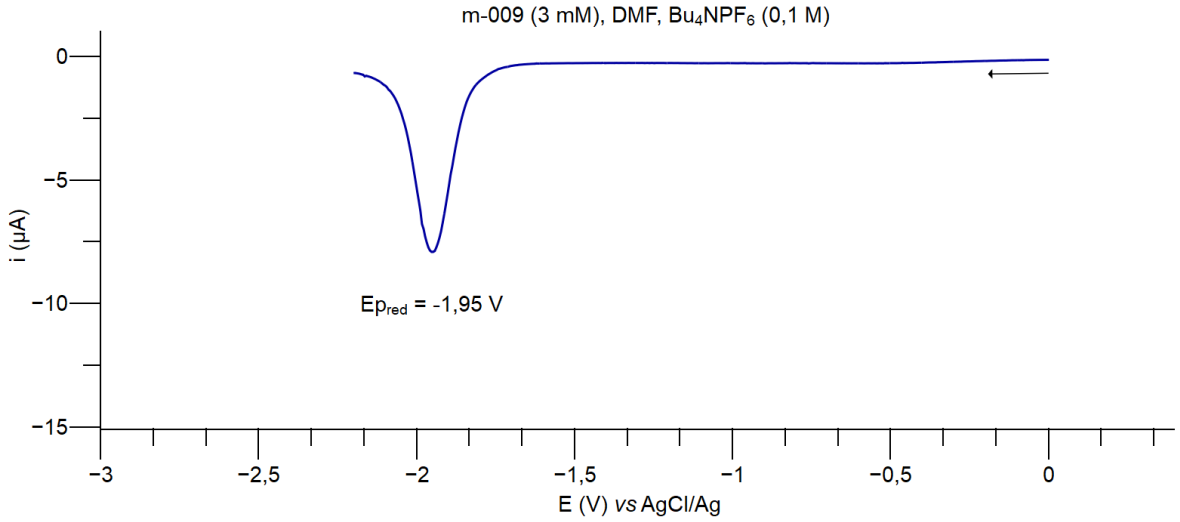


Compound 1-*p*OMePh

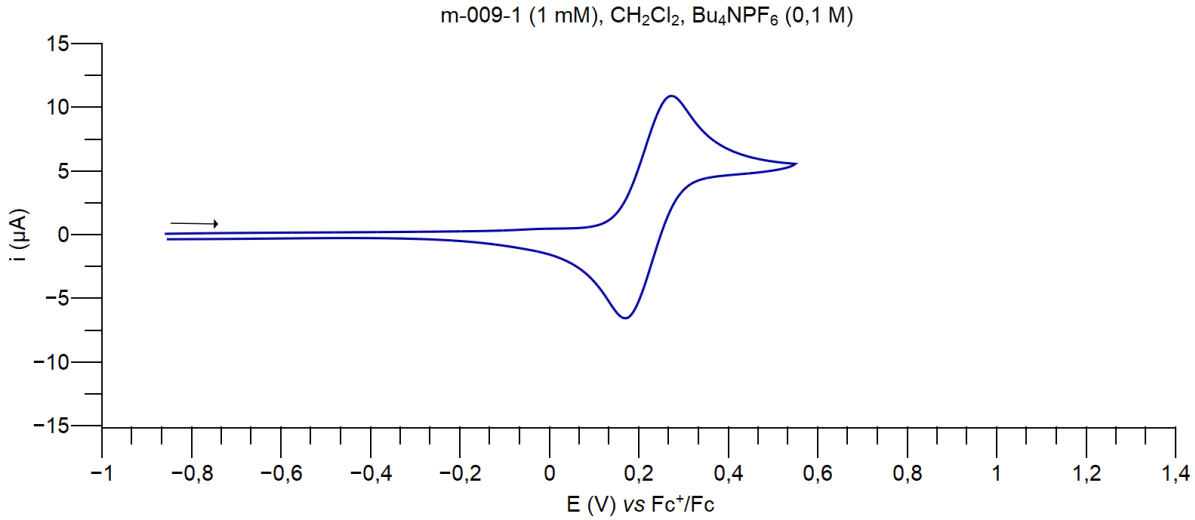
Cyclic voltammetry for ketone reduction in DMF



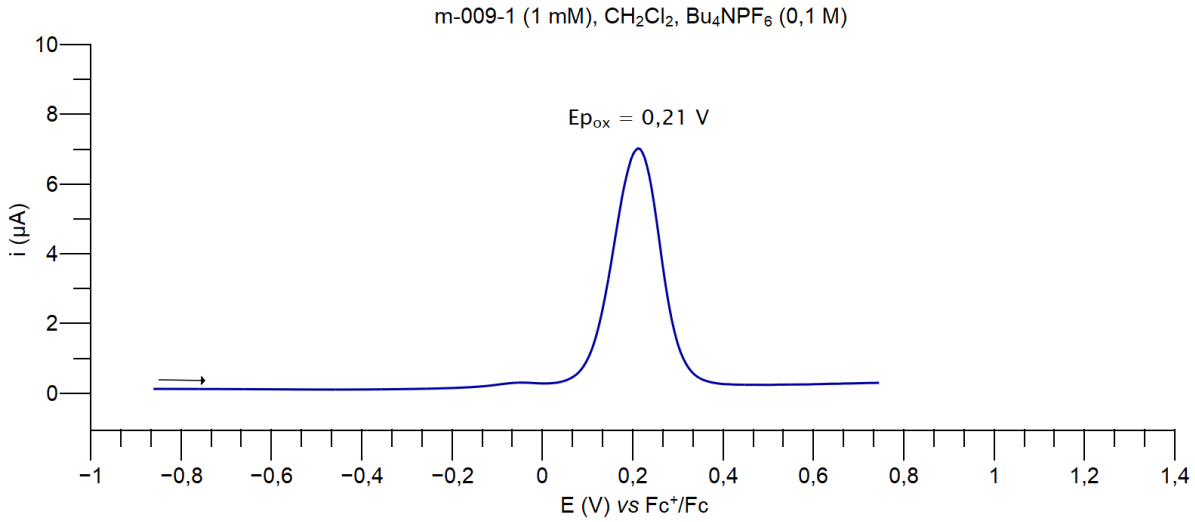
Differential pulse voltammetry for ketone reduction in DMF



Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

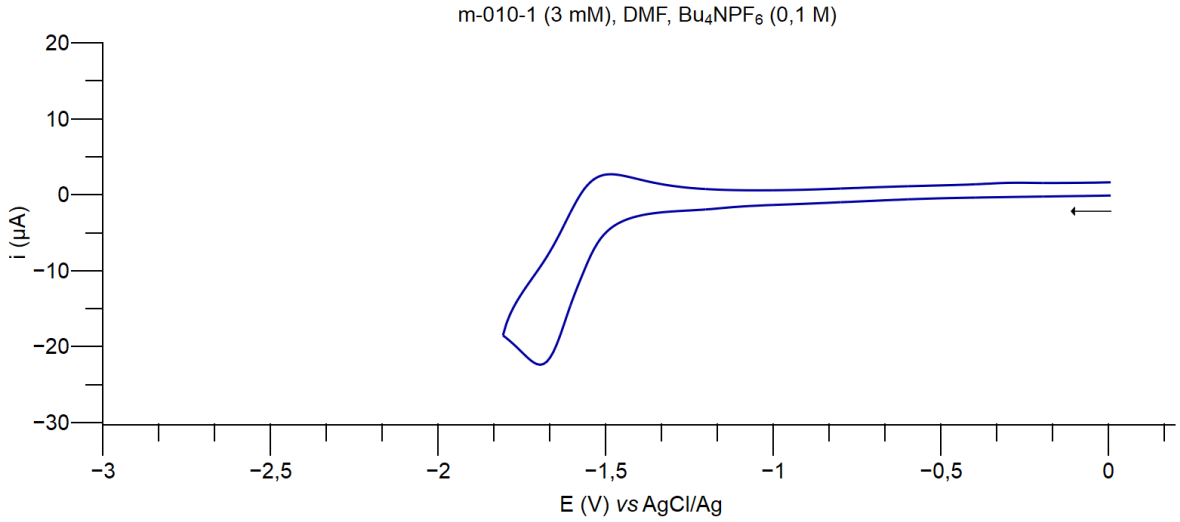


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

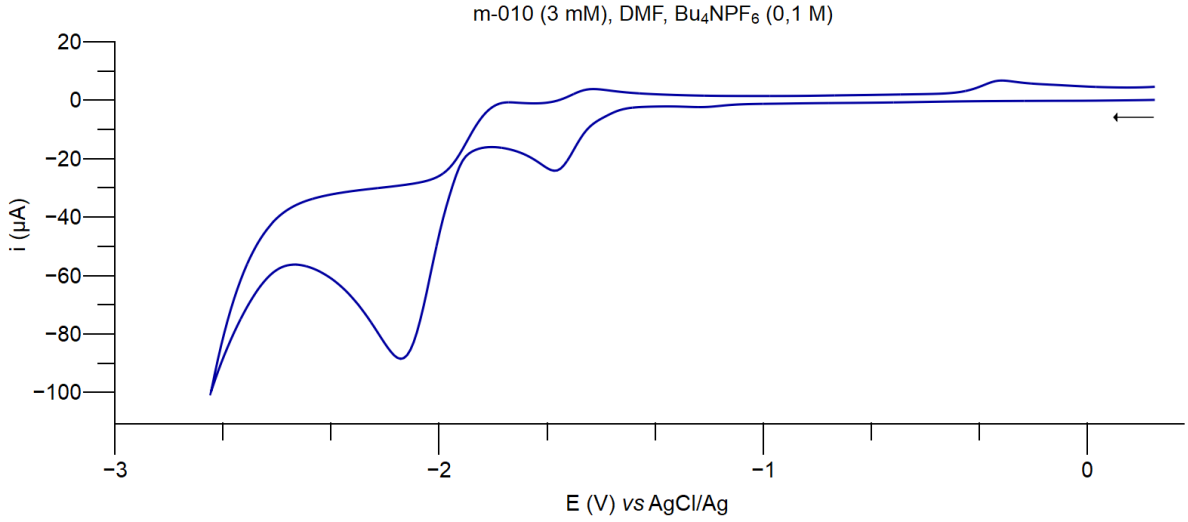


Compound 1-*p*CF_3Ph

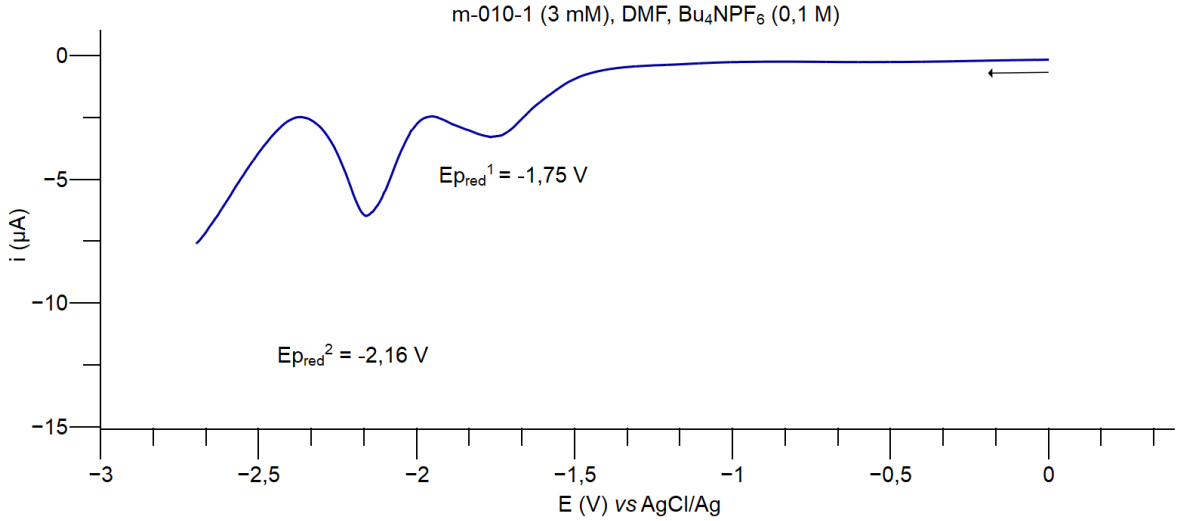
Cyclic voltammetry for ketone reduction in DMF



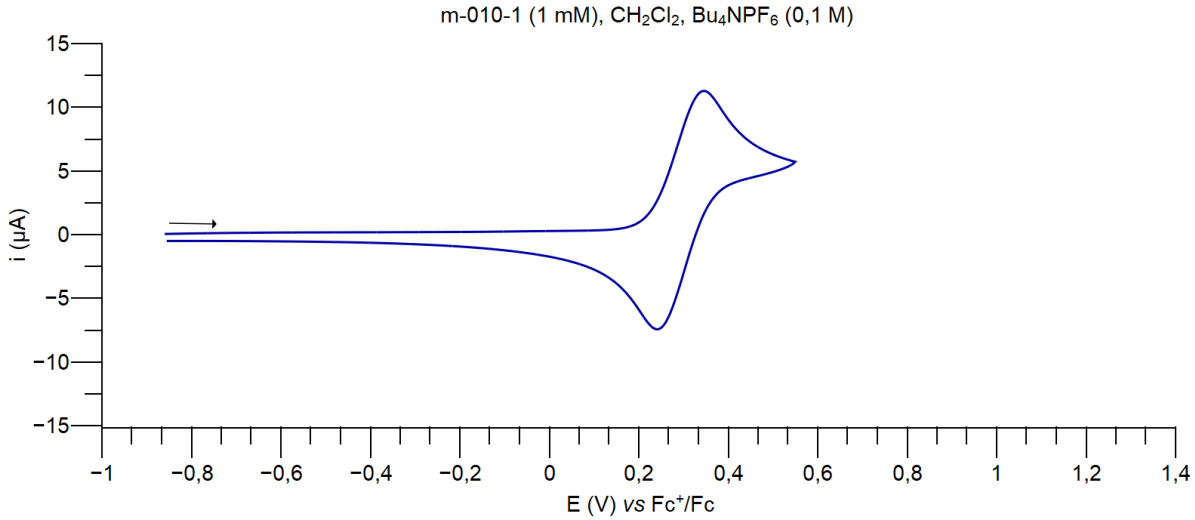
Full cyclic voltammetry for ketone reduction in DMF



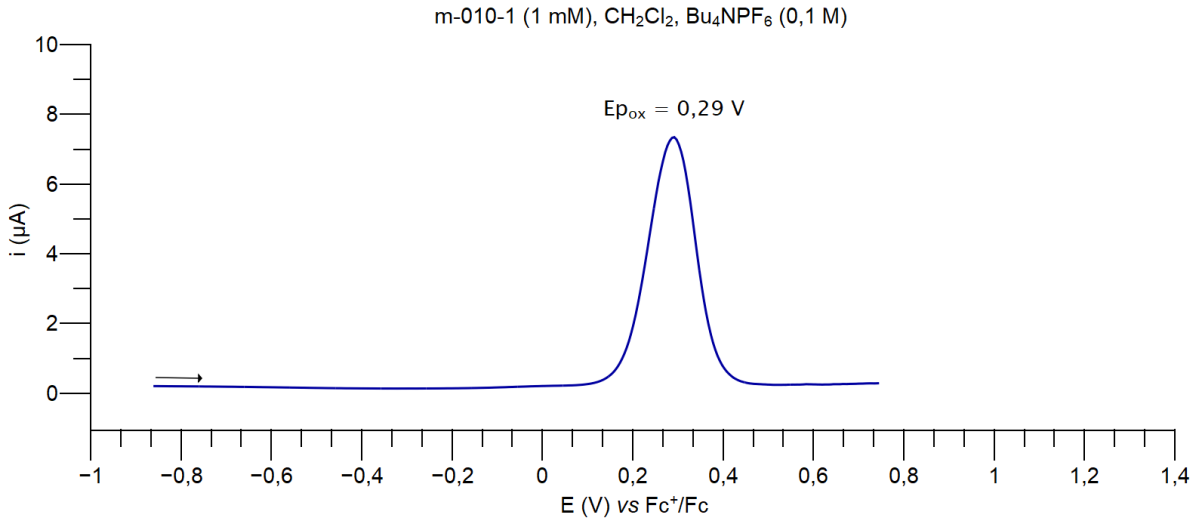
Differential pulse voltammetry for ketone reduction in DMF



Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

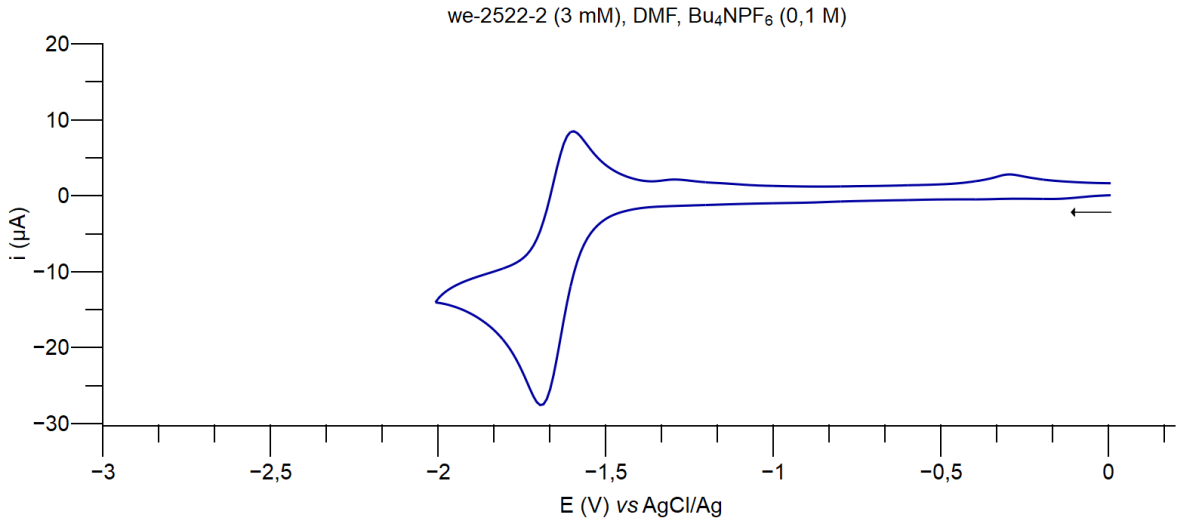


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

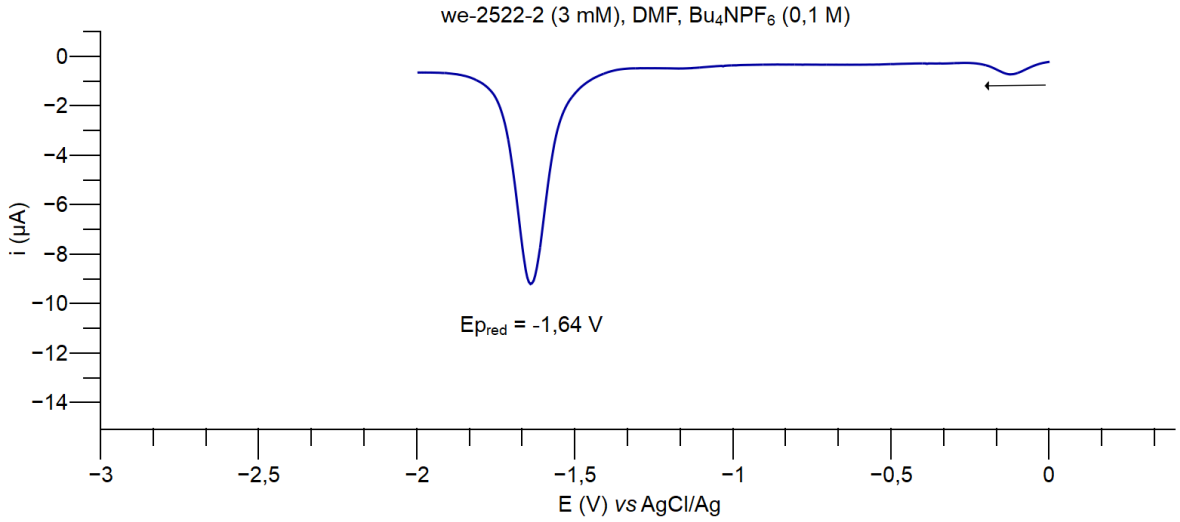


Compound 1-2Py

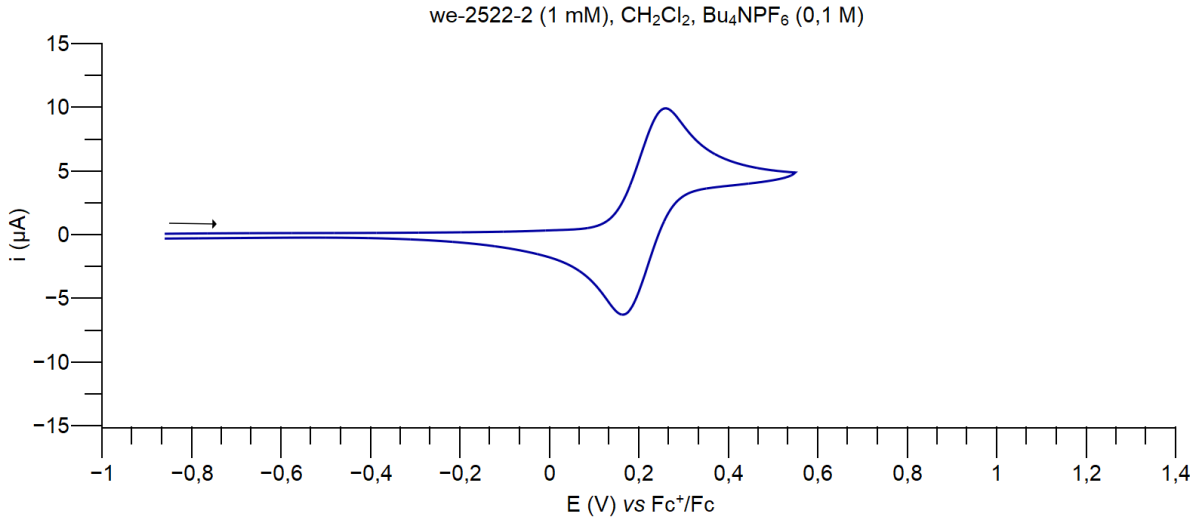
Cyclic voltammetry for ketone reduction in DMF



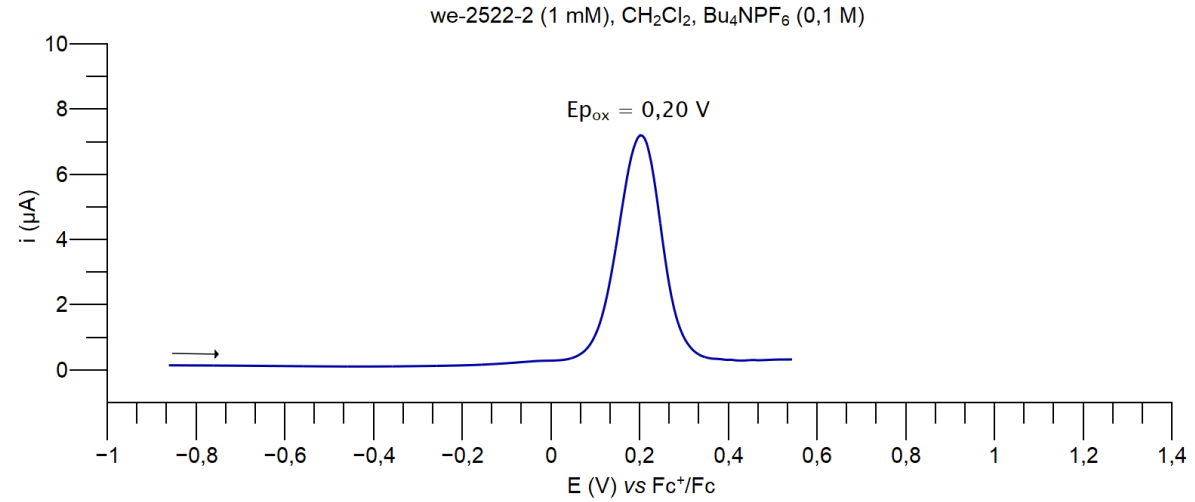
Differential pulse voltammetry for ketone reduction in DMF



Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

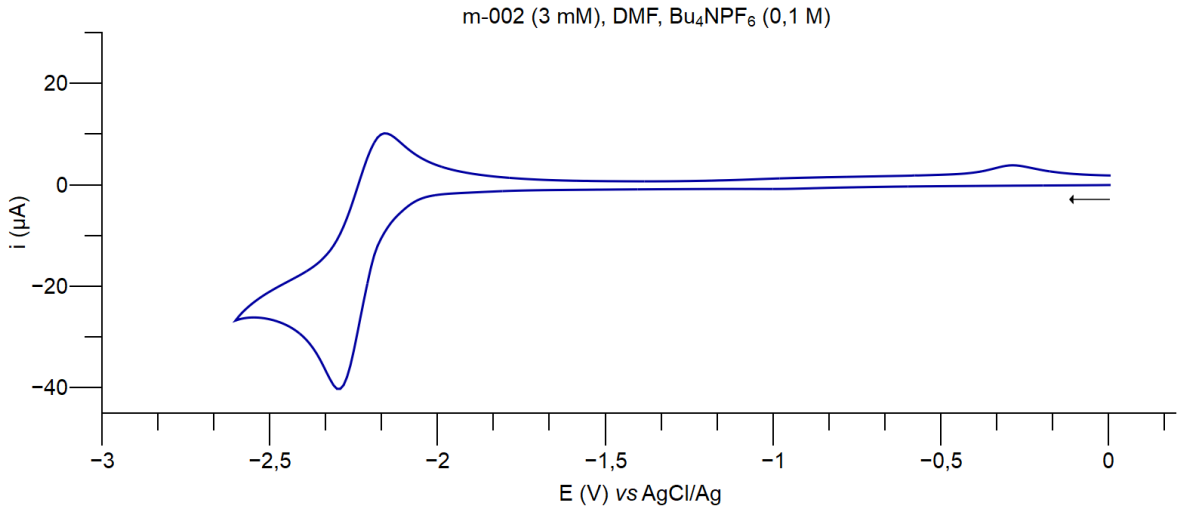


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

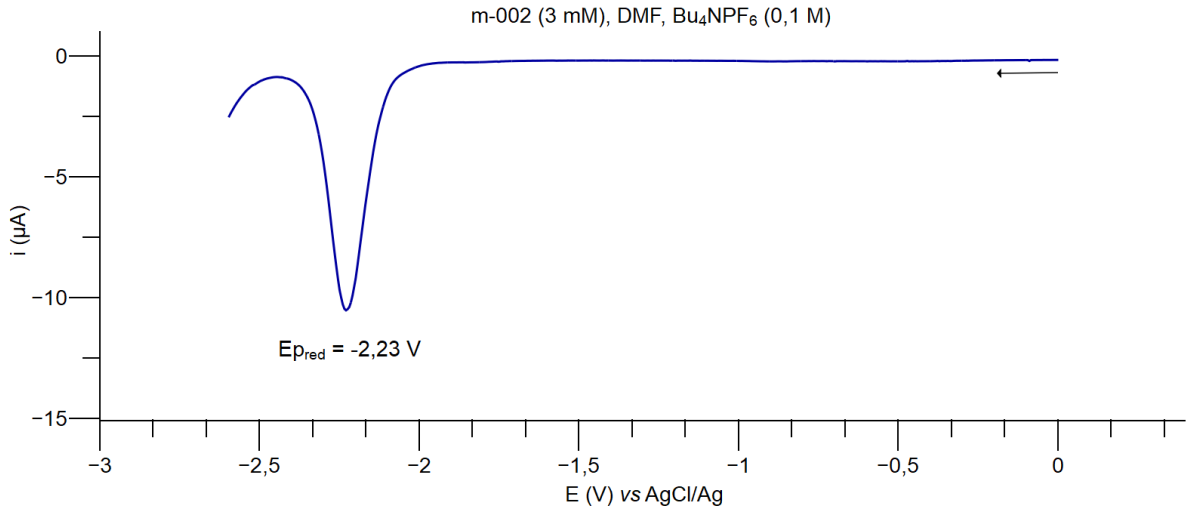


Compound 1-*t*Bu

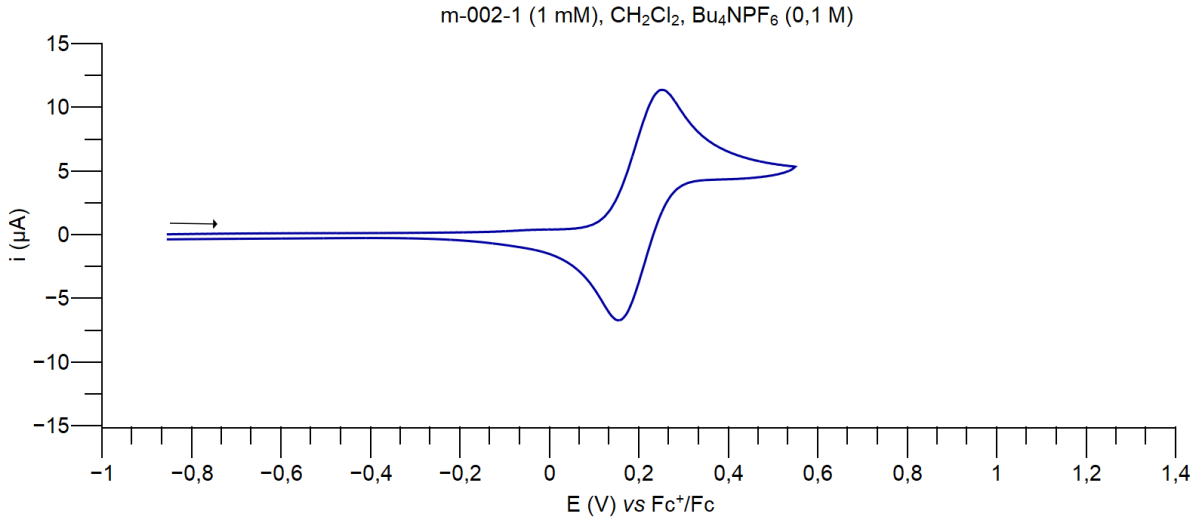
Cyclic voltammetry for ketone reduction in DMF



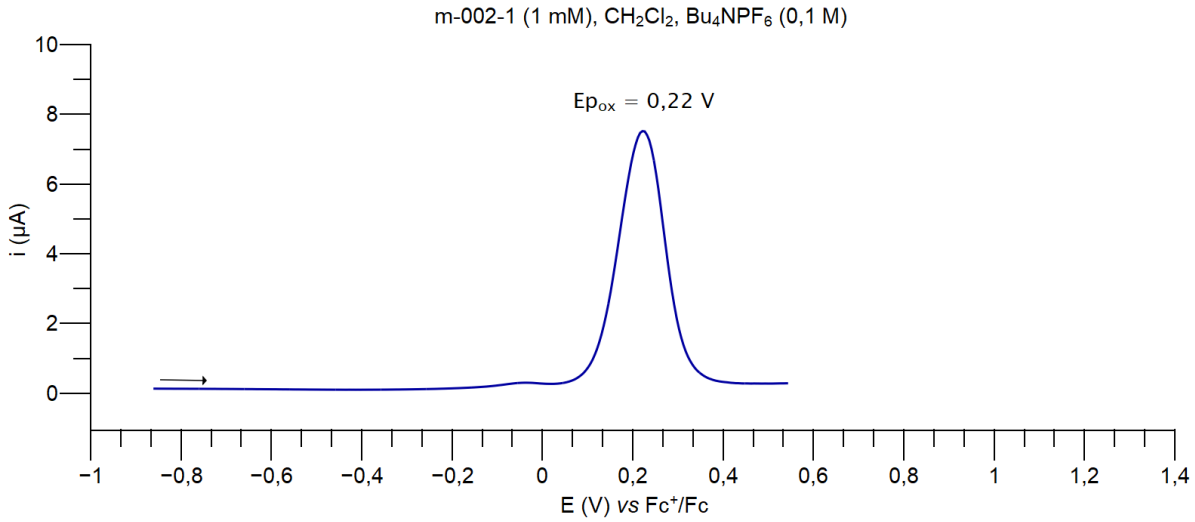
Differential pulse voltammetry for ketone reduction in DMF



Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

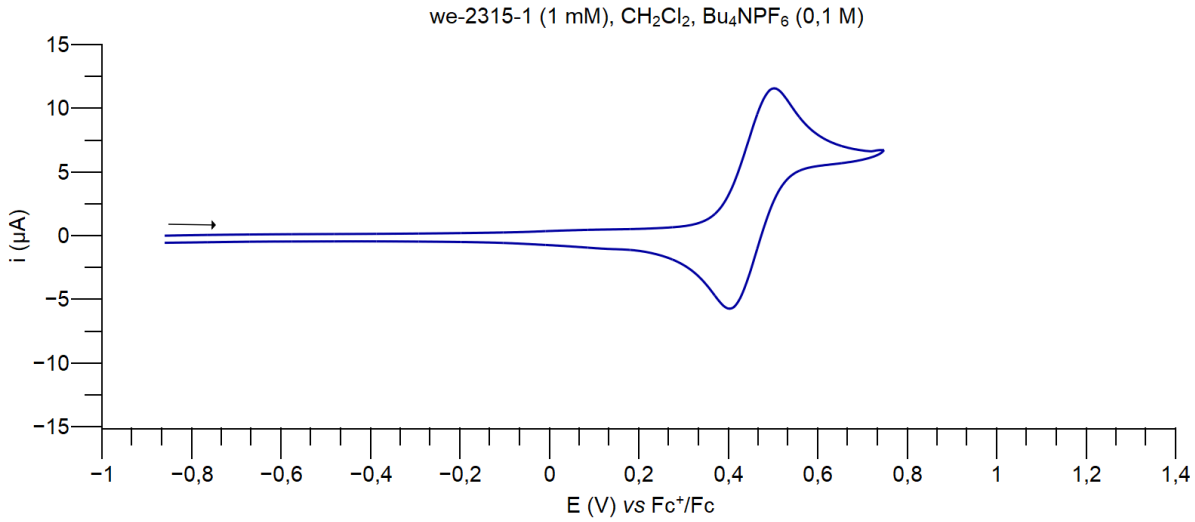


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

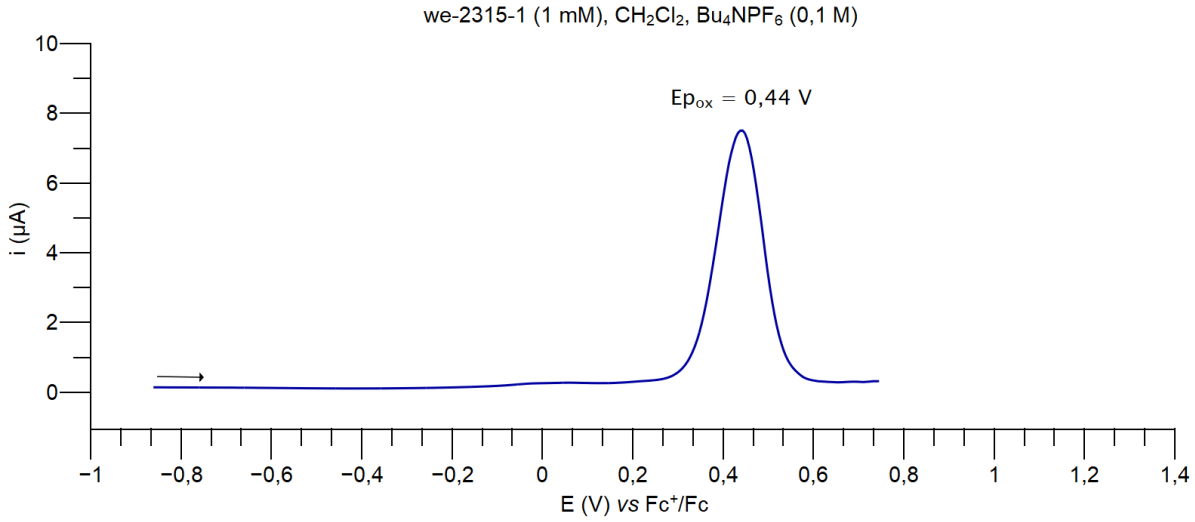


Compound 1-CF_3

Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

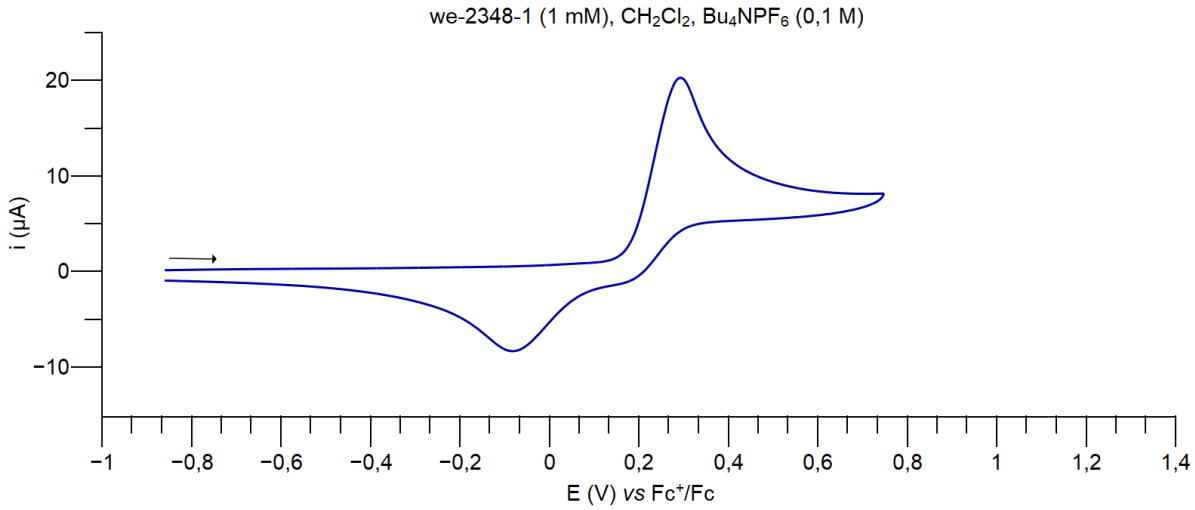


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

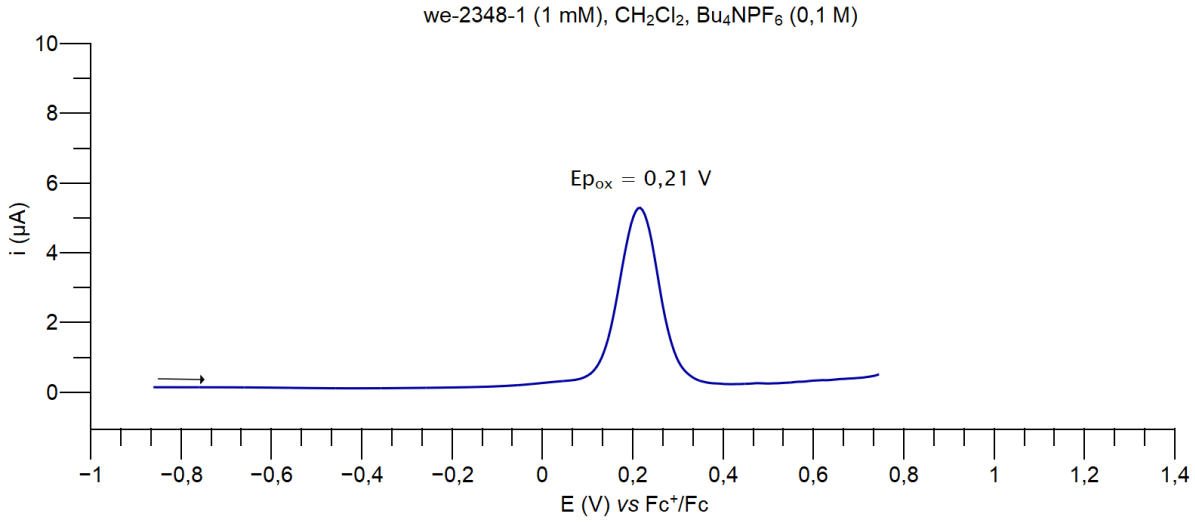


Compound 4-Ph

Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

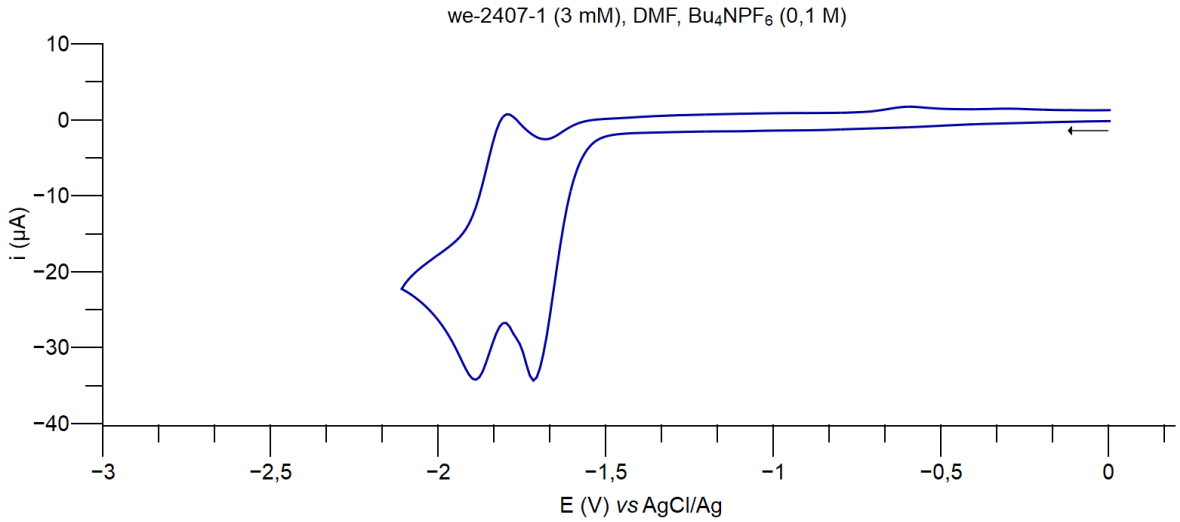


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

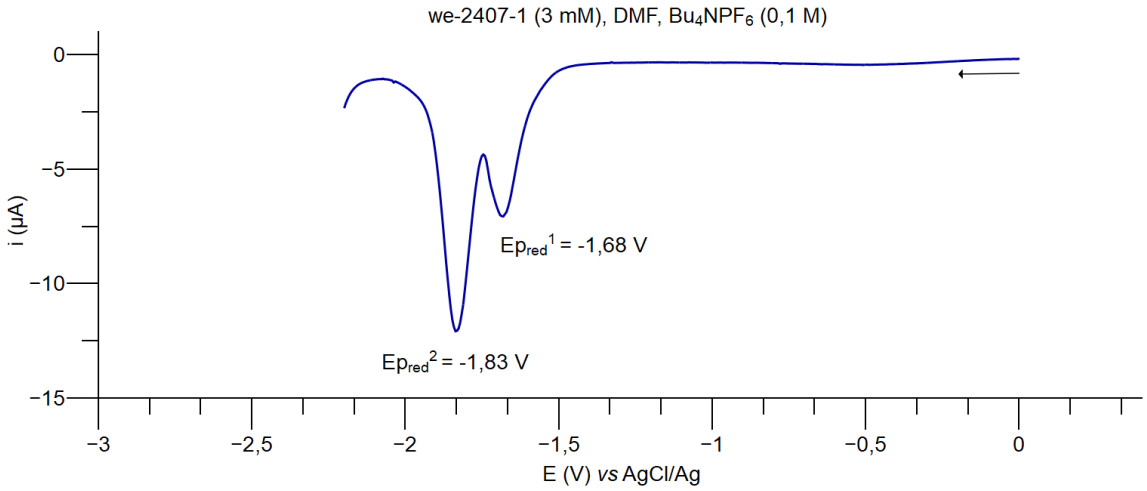


Compound 2-Ph

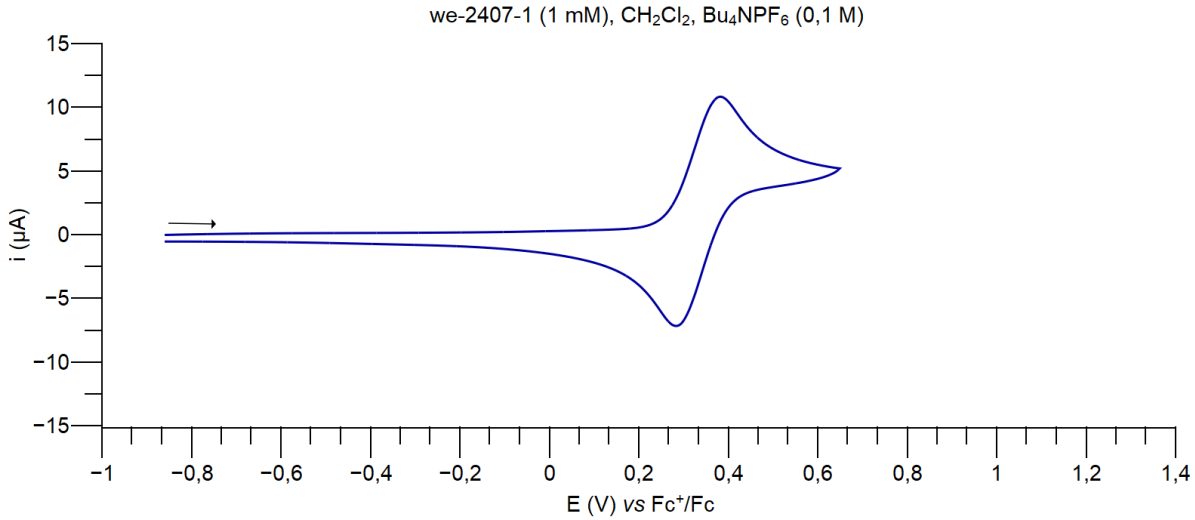
Cyclic voltammetry for ketone reduction in DMF



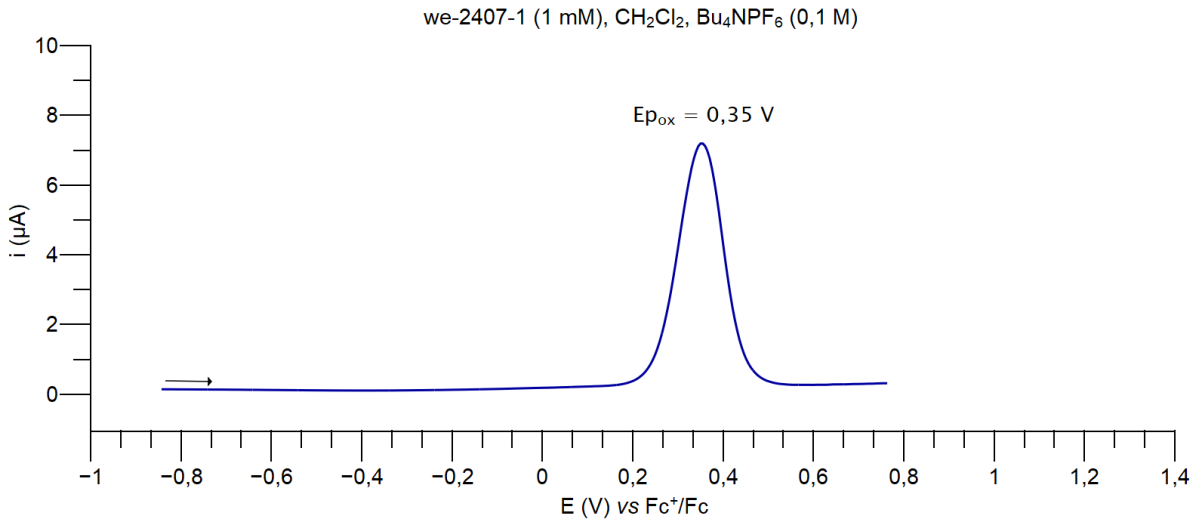
Differential pulse voltammetry for ketone reduction in DMF



Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

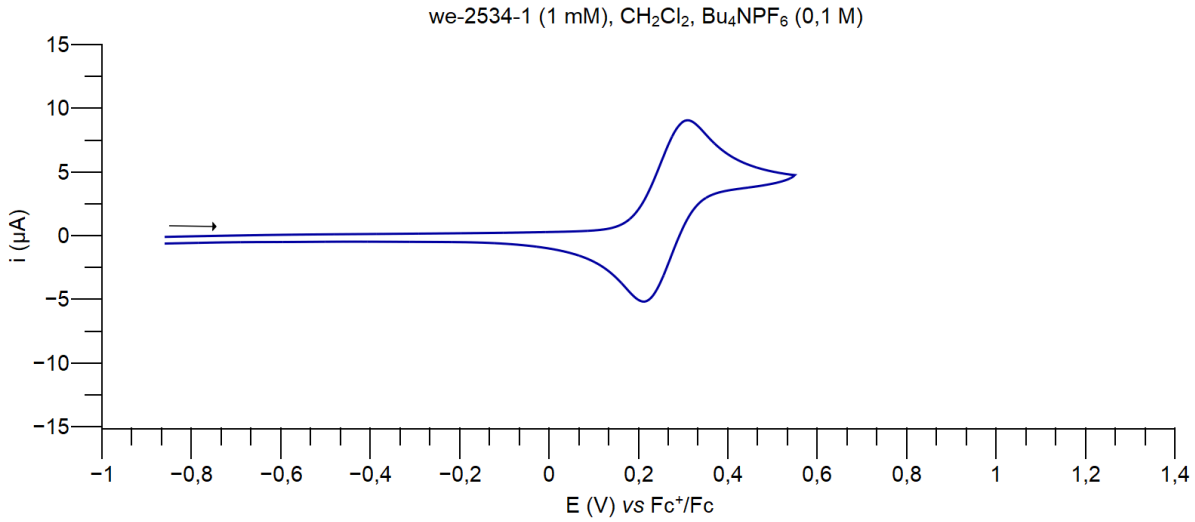


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

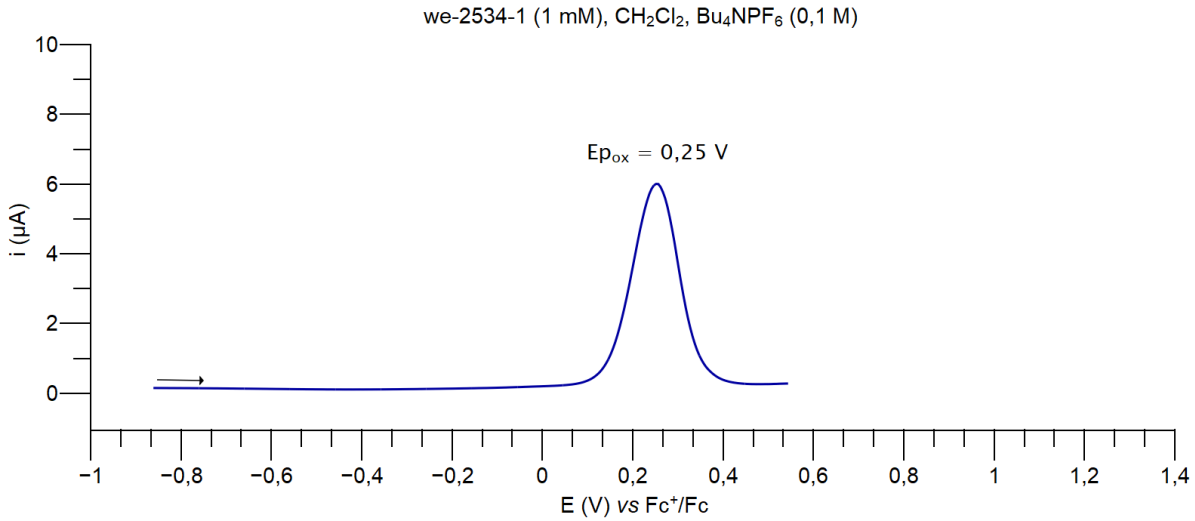


Compound 10

Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

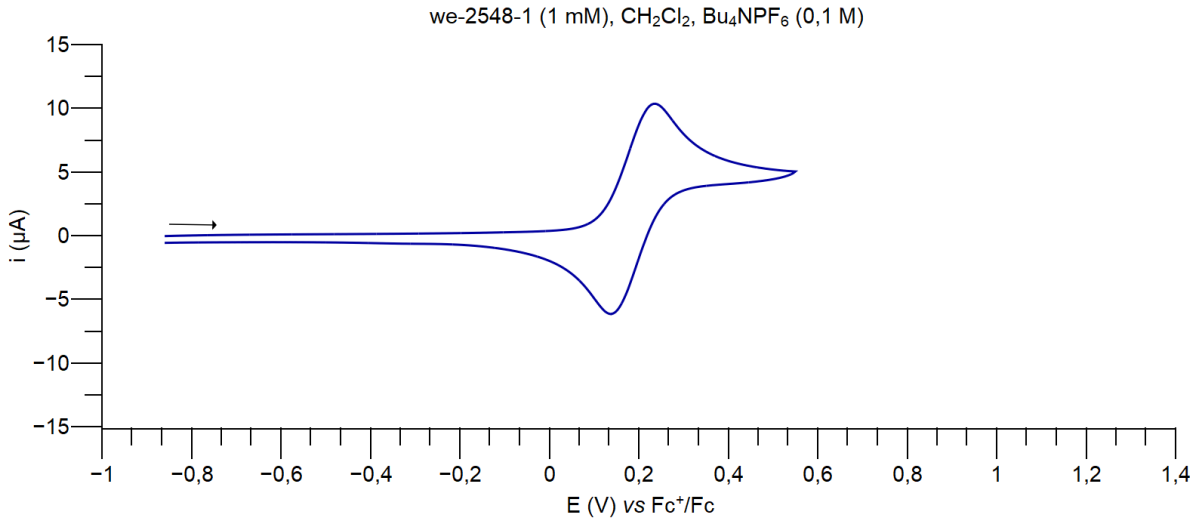


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

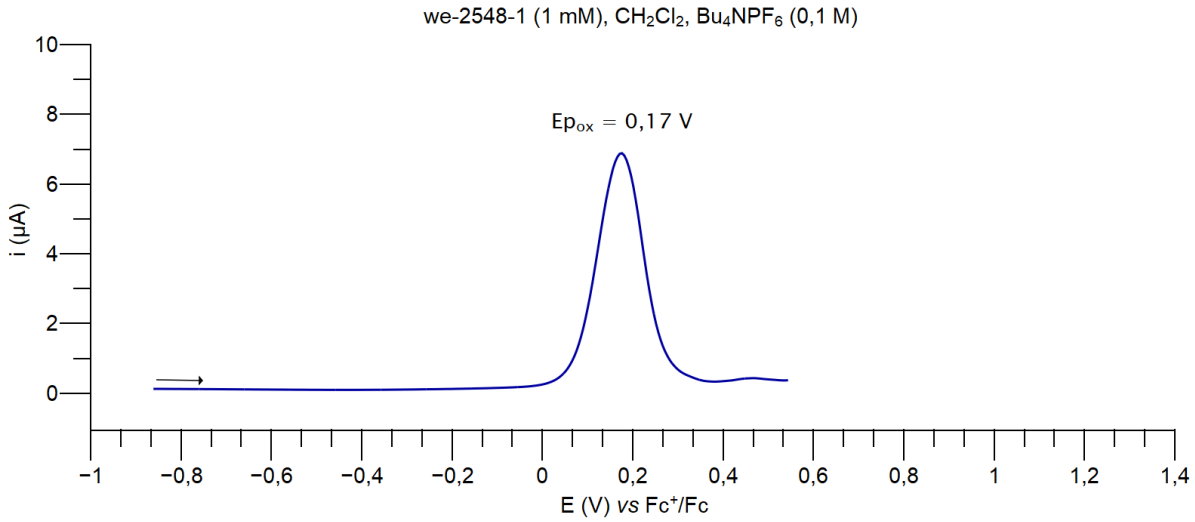


Compound 11

Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2

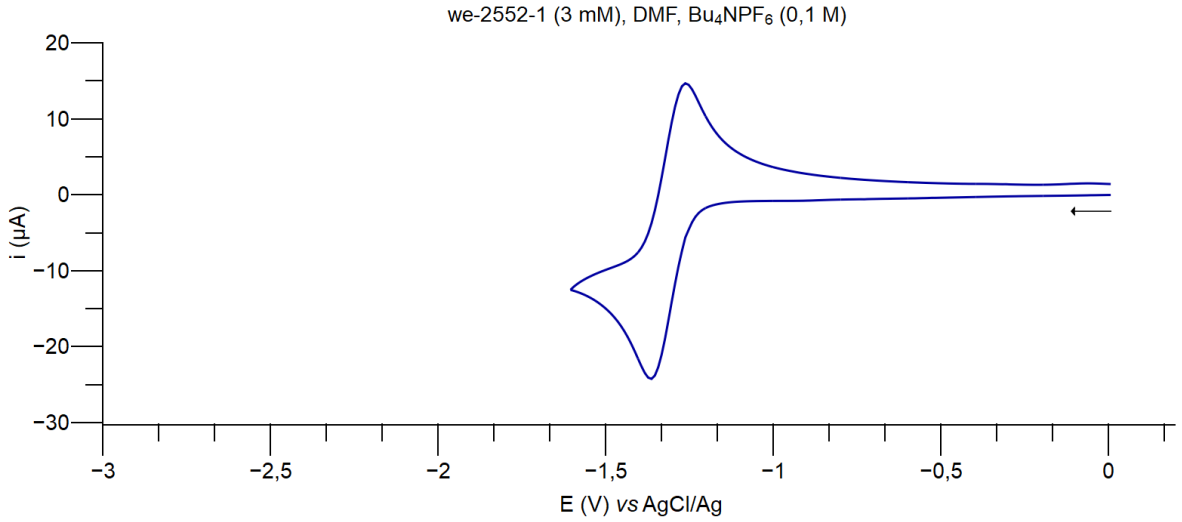


Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2

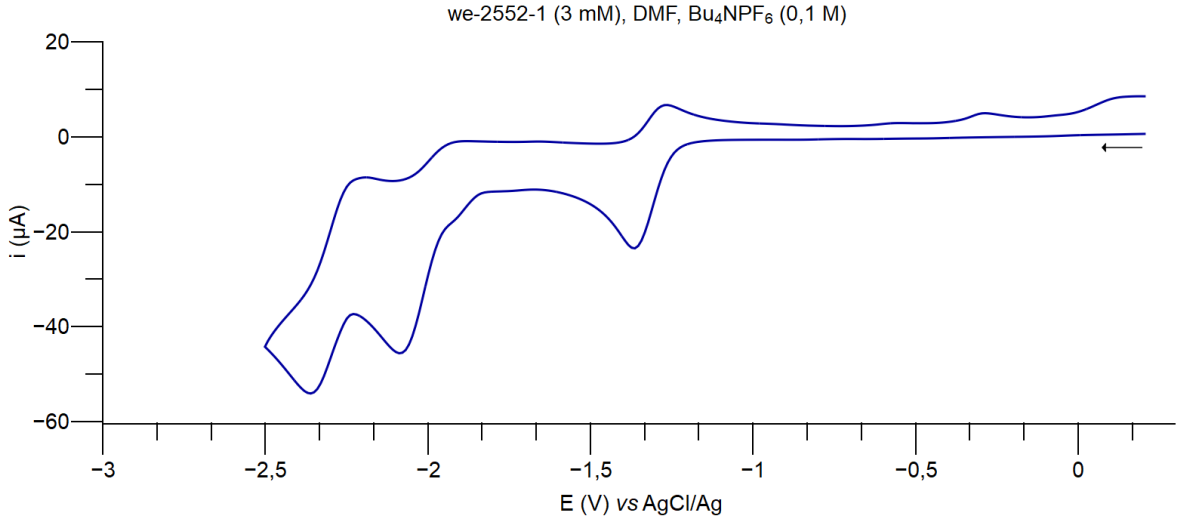


Compound 12

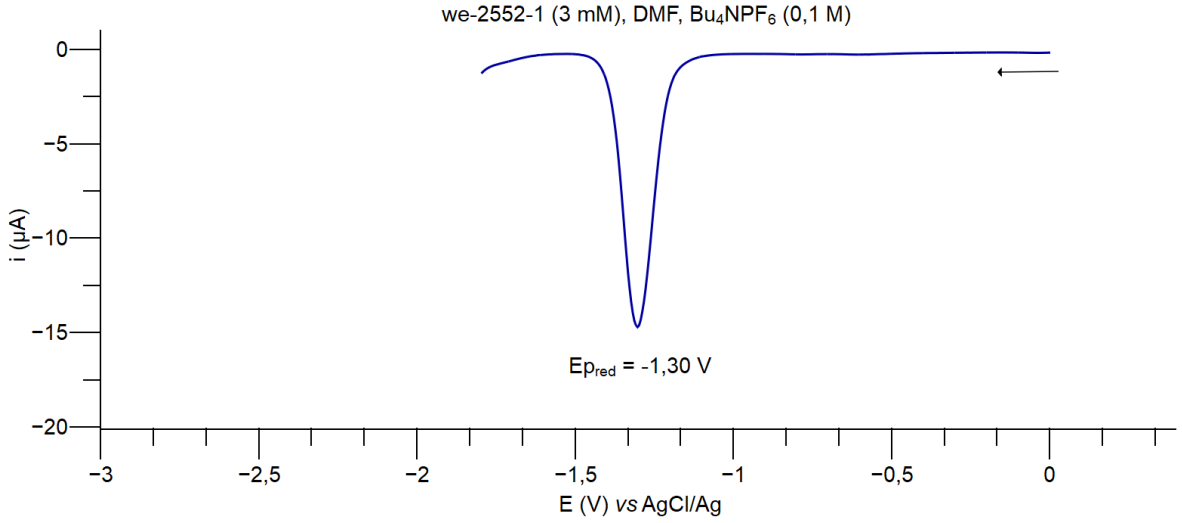
Cyclic voltammetry for ketone reduction in DMF



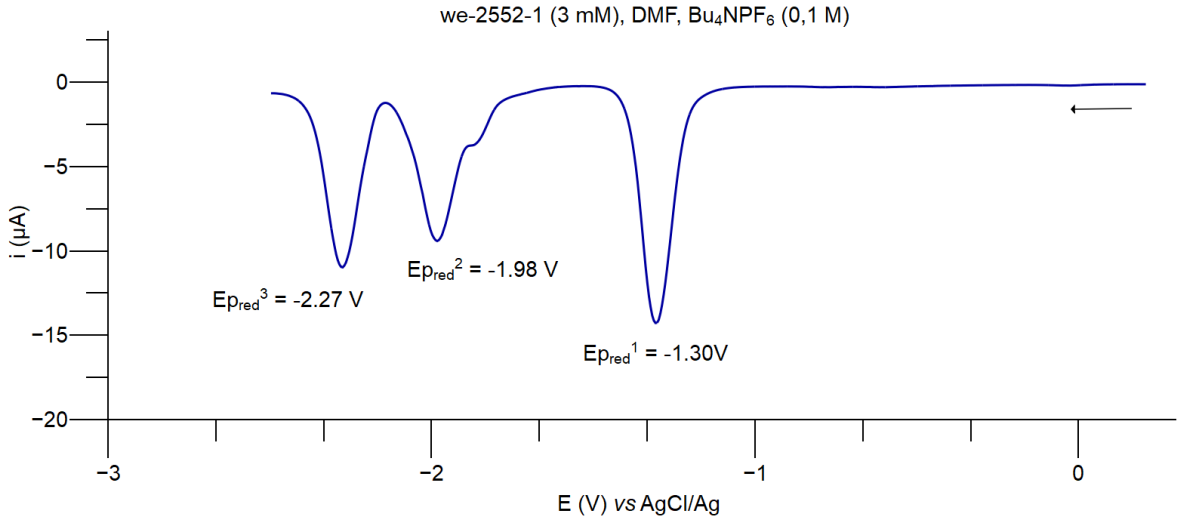
Full cyclic voltammetry for ketone reduction in DMF



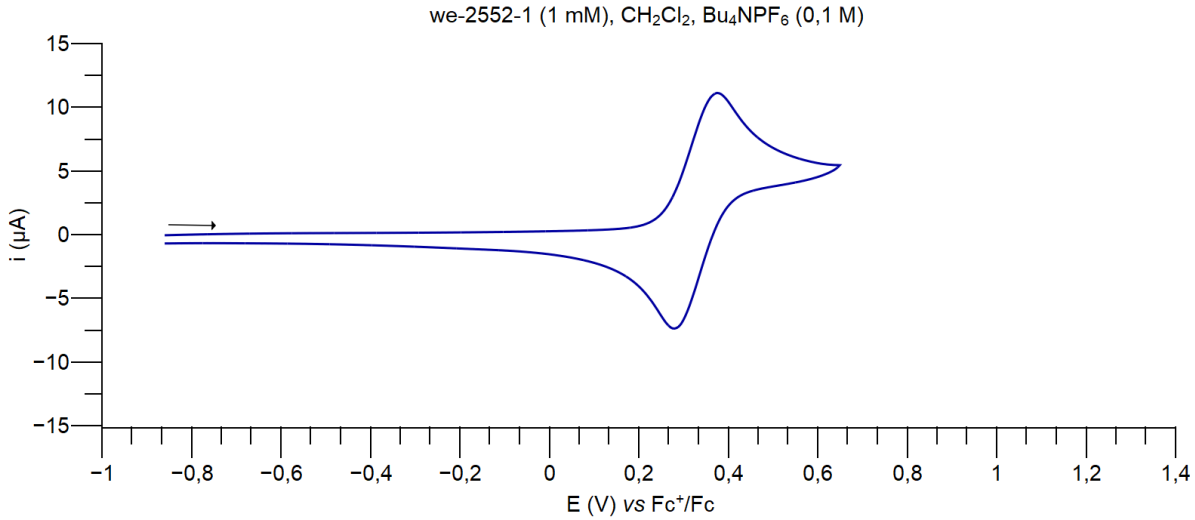
Differential pulse voltammetry for ketone reduction in DMF



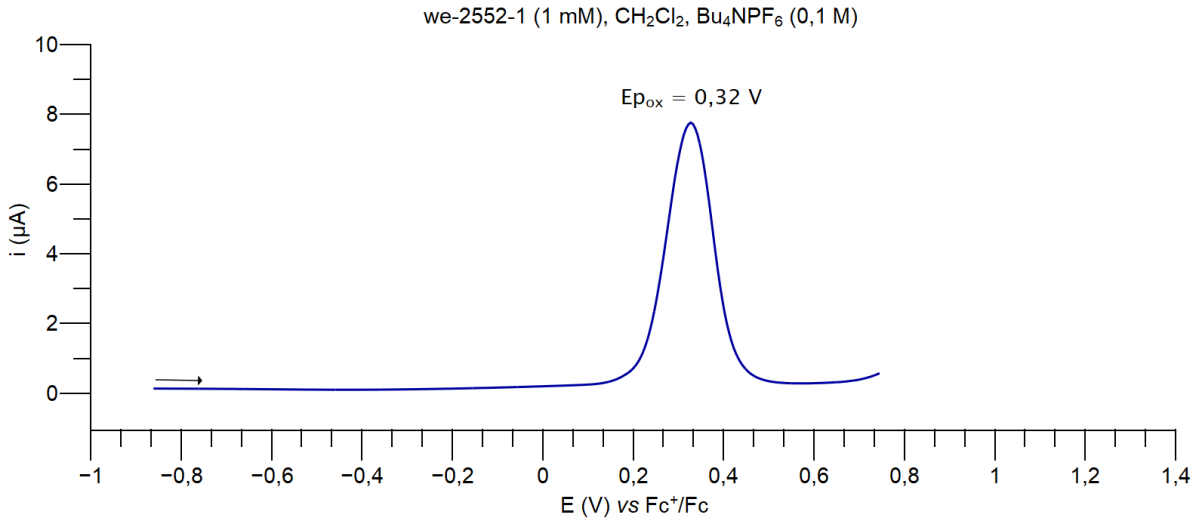
Full differential pulse voltammetry for ketone reduction in DMF



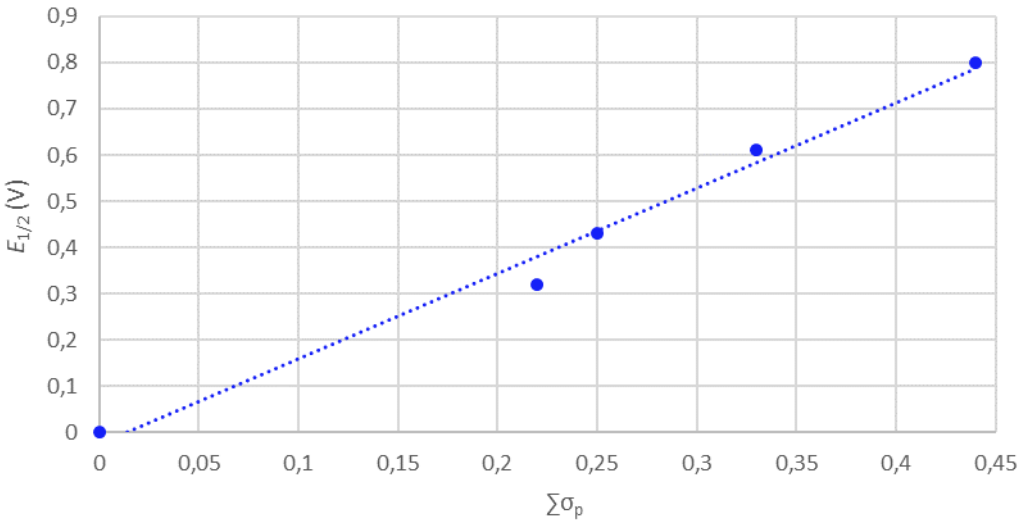
Cyclic voltammetry for ferrocene oxidation in CH_2Cl_2



Differential pulse voltammetry for ferrocene oxidation in CH_2Cl_2



Plot 1. $E_{1/2}$ (V) *vs*. $\Sigma\sigma_p$ for ferrocene **FcH** and compounds **1-*t*Bu**, **1-Ph**, **2-Ph** and **1-CF$_3$**. Regression line equation $E_{1/2} = 1.8466\ \Sigma\alpha_p - 0.026$ ($R^2 = 0.9857$).



I) References

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