Supporting Information

Fluoro- and Chloroferrocene: From 2- to 3-substituted Derivatives

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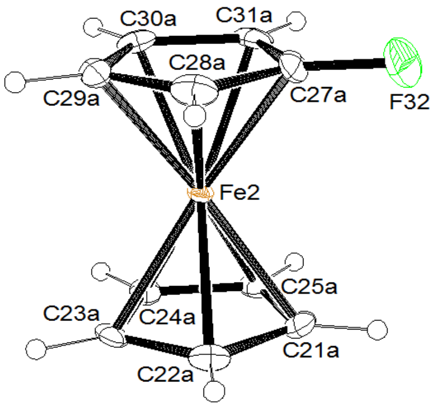
Experimental section

General Considerations. All reactions were performed under argon atmosphere using standard Schlenk techniques. THF was distilled over sodium/benzophenone. Column chromatography separations were achieved on silica gel (40-63 or 60-200 μm). Melting points were measured on a Kofler apparatus. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer. ^{1}H, ^{13}C and ^{19}F Nuclear Magnetic Resonance (NMR) spectra were in general recorded on (i) a Bruker Avance III spectrometer at 300, 75 and 282 MHz, respectively, or/and (ii) a Bruker Avance III HD at 500, 126 and 470 MHz, respectively. The ^{31}P NMR spectrum was recorded on a Bruker Avance III HD at 162 MHz. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ^{13}C chemical shifts are relative to the central peak of the solvent signal.[1]

Crystallography. For **1a**, **3b**, **3c**, **3f**, **3g**, **3h**, **3i**, **3j**, **3k**, **3l**, **3m'**, **3o**, **3fb** and **3fb-mig**, the X-ray diffraction data were collected using D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector at the temperature given in the crystal data. The samples were studied with monochromatized Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator). The structures were solved by dual-space algorithm using the *SHELXT* program,[2] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[3] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except C_{16}-linked hydrogen atoms of **3f** and O-linked hydrogen atom of **3i**, **3j** and **3k** that were introduced in the structural model through Fourier difference maps analysis, 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 ORTEP-3 (version 2.02; 30% probability level).[4] Chloroferrocene was prepared as described previously.[5]

Fluoroferrocene (1a). To a stirred solution of ferrocene (9.3 g, 50 mmol) and potassium *tert*-butoxide (0.70 g, 6.25 mmol) in THF (330 mL) at -75 °C was added dropwise *t*BuLi (~1.9 M in pentane, 100 mmol). After 1 h at the same temperature, the resulting mixture was transferred into a solution of *N*-fluorobenzenesulfonimide (39 g, 125 mmol) in THF (200 mL) cooled at -20 °C, and the mixture was stirred for 10 min. After preliminary column chromatography over alumina gel surmounted by cotton wool (eluent: petroleum ether), the product was purified by column chromatography over silica gel (eluent: petroleum ether-CH_2Cl_2 1:3) and, if necessary to remove remaining traces of unreacted ferrocene, washed with aqueous 0.2 M $FeCl_3$ (1 to 3 x 140 mL) and water (3 x 140 mL). Drying the organic phase over $MgSO_4$ and concentration under reduced pressure afforded **1a** in an average 50% yield as an orange powder: mp 114-115 °C (lit.[6] 116-118 °C); ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 3.79 (td, 2H, J = 2.0 and 1.3 Hz, H_3 and H_4), 4.27 (s, 5H, Cp), 4.31 (dt, 2H, J = 2.9 and 2.0 Hz, H_2 and H_5); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -188.85. These data are analogous to those previously reported.[7] **Crystal data for 1a.** $C_{10}H_9FFe$, M = 204.02, T = 150(2) K, monoclinic, $P\ 2_1/n$, a = 17.983(3), b = 7.4966(10), c = 19.410(3) Å, β = 111.210(5) °, V = 2439.6(6) Å^3, Z = 12, d = 1.666 g cm^{-3}, μ = 1.801 mm^{-1}. A final refinement on F^2 with 5425 unique intensities and 346 parameters converged at $\omega R(F^2)$ = 0.1150 ($R(F)$ = 0.0542) for 3970 observed reflections with $I > 2\sigma(I)$. CCDC 1841221.

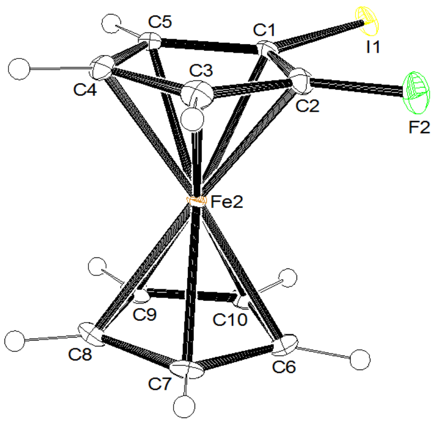


***N,N*-Diisopropyl-2-fluoroferrocenecarboxamide (2a, racemic mixture).** To a stirred, cooled (-75 °C) solution of *N,N*-diisopropylferrocenecarboxamide (0.63 g, 2.0 mmol) in THF (4 mL) was added *s*BuLi (~1.3 M in cyclohexane, 2.4 mmol). After 1 h at the same temperature, the resulting mixture was transferred into a solution of *N*-fluorobenzenesulfonimide (1.6 g, 5.0 mmol) in THF (8 mL) cooled at -20 °C, and the mixture was stirred for 10 min. After addition of water (10 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (3 x 20 mL) and brine (20 mL), drying over $MgSO_4$ and concentration under reduced pressure, the product was purified by column chromatography over silica gel (eluent: petroleum ether-EtOAc 70:30; R_f = 0.59) to afford **2a** in 17% yield as a yellow powder: mp 101 °C; IR (ATR): 678, 810, 1041, 1134, 1209, 1329, 1370, 1445, 1477, 1625, 2928, 2968, 2986, 3088 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 1.08-1.25 (br m, 6H, CH_3), 1.49 (br s, 6H, CH_3), 3.43 (br s, 1H, C*H*Me_2), 3.85 (br s, 1H, H_4), 4.10 (br s, 1H, C*H*Me_2), 4.14 (br s, 1H, H_5), 4.33 (br s, 1H, H_3), 4.37 (s, 5H, Cp); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 20.7 (CH_3), 21.1 (2CH_3), 21.4 (CH_3), 46.3 (*C*HMe_2), 50.6 (*C*HMe_2), 55.8 (d, J = 15.8 Hz, CH, C_3), 60.2 (d, J = 3.7 Hz, CH, C_4), 63.9 (d, J = 2.4 Hz, CH, C_5), 71.3 (5CH, Cp), 73.6 (d, J = 11.9 Hz, *C*-C=O), 132.9 (d, J = 271 Hz, C-F), 165.7 (d, J = 3.2 Hz, C=O); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -186.1. Anal. Calcd for $C_{17}H_{22}FFeNO$: C, 61.65; H, 6.70; N, 4.23. Found: C, 61.58; H, 6.76; N, 4.31. ***N,N*-Diisopropyl-2-(phenylsulfonyl)ferrocenecarboxamide (2b, racemic mixture)** was similarly isolated (R_f (petroleum ether-EtOAc 70:30) = 0.34) in 43% yield as a yellow powder: mp 130 °C; IR (ATR): 689, 725, 752, 814, 1086, 1144, 1165, 1204, 1307, 1327, 1371, 1446, 1640, 2394, 2932, 2975 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 0.70 (d, 3H, J = 5.9 Hz, CH_3), 0.96 (d, 3H, J = 6.4 Hz, CH_3), 1.50 (br s, 6H, 2CH_3), 3.35 (br s, 1H, C*H*Me_2), 3.51 (br s, 1H, C*H*Me_2), 4.30 (s, 5H, Cp), 4.38 (t, 1H, J = 2.5 Hz, Cp-H), 4.41 (dd, 1H, J = 2.5 and 1.5 Hz, Cp-H), 4.86 (dd, 1H, J = 2.6 and 1.5 Hz, Cp-H), 7.49-7.56 (m, 3H, Ph), 8.02-8.05 (m, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 19.8 (CH_3), 20.4 (CH_3), 20.8 (CH_3), 21.2 (CH_3), 46.1 (*C*HMe_2), 50.2 (*C*HMe_2), 68.1 (CH, C_3), 69.8 and 70.0 (2CH, C_4 and C_5), 72.5 (5CH, Cp), 89.7 and 91.0 (2C, C_1 and C_2), 127.8 (2CH, Ph), 128.9 (2CH, Ph), 133.0 (CH, $C_{4'}$), 143.4 (C, $C_{1'}$), 164.0 (C=O). Anal. Calcd for $C_{23}H_{27}FeNO_3S$: C, 60.93; H, 6.00; N, 3.09. Found: C, 61.10; H, 6.21; N, 2.96.

General procedure 1. To a stirred, cooled (-75 °C) solution of fluoroferrocene (**1a**, 0.41 g, 2.0 mmol) in THF (2 mL) were successively added *s*BuLi (~1.3 M in cyclohexane, 2.4 mmol) and, 1 h later, the required electrophile before warming to room temperature. The mixture was treated as specified in the product description.

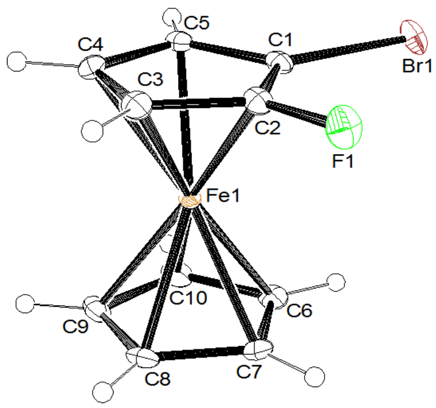
1-Deuterio-2-fluoroferrocene (3a, racemic mixture). The general procedure 1 using as electrophile D_2O (0.3 mL) gave **3a** after extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (3 x 20 mL) and brine (20 mL), drying over $MgSO_4$ and concentration under reduced pressure 98% yield (>95% D) as a yellow powder: R_f (eluent: petroleum ether-Et_2O 90:10) = 0.79); mp 114 °C; IR (ATR): 798, 925, 999, 1017, 1104, 1165, 1230, 1369, 1409, 1456, 2924, 3101 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 3.80 (t, 2H, J = 1.6 Hz, H_4 and H_5), 4.27 (s, 5H, Cp), 4.31 (q, 1H, J = 2.3 Hz, H_3); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 56.0 (m, C, C-D), 56.2 (d, J = 15.2 Hz, C_3), 61.1 (d, J = 3.7 Hz, 2CH, C_4 and C_5), 69.5 (5CH, Cp), 135.8 (d, J = 268 Hz, C-F); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -189.0.

1-Fluoro-2-iodoferrocene (3b, racemic mixture). The general procedure 1 using as electrophile iodine (0.58 g, 2.2 mmol) in THF (2 mL) gave **3b** after addition of an aqueous saturated solution of $Na_2S_2O_3$ (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with aqueous 0.2 M $FeCl_3$ (4 x 20 mL), water (3 x 20 mL) and brine (20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 95:5; R_f = 0.74) in 96% yield as an orange powder: mp 57 °C; IR (ATR): 797, 819, 835, 964, 998, 1018, 1056, 1104, 1246, 1362, 1408, 1453, 1732, 3080 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 3.93 (br s, 1H, H_4), 4.12 (s, 1H, H_5), 4.27 (s, 5H, Cp), 4.39 (br s, 1H, H_3); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 28.9 (d, J = 20.5 Hz, C-I), 55.3 (d, J = 15.6 Hz, CH, C_5), 62.2 (d, J = 3.1 Hz, CH, C_4), 67.5 (d, J = 1.4 Hz, CH, C_3), 72.4 (5CH, Cp), 135.4 (d, J = 270 Hz, C-F); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -186.8. Anal. Calcd for $C_{10}H_8FFeI$: C, 36.41; H, 2.44. Found: C, 36.50; H, 2.67. **Crystal data for 3b.** $C_{10}H_8FFeI$, M = 329.91, T = 150(2) K, monoclinic, $P\,2_1/c$, a = 6.6830(4), b = 19.1020(11), c = 7.5510(3) Å, β = 99.525(2) °, V = 950.66(9) Å^3, Z = 4, d = 2.305 g cm^{-3}, μ = 4.793 mm^{-1}. A final refinement on F^2 with 2113 unique intensities and 118 parameters converged at $\omega R(F^2)$ = 0.0723 ($R(F)$ = 0.0286) for 2050 observed reflections with $I > 2\sigma(I)$. CCDC 1841222.



1-Bromo-2-fluoroferrocene (3c, racemic mixture). The general procedure 1 using as electrophile tetrabromomethane (0.73 g, 2.2 mmol) in THF (2 mL) gave **3c** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (3 x 20 mL) and brine (20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 90:10; R_f = 0.75) in 92% yield as an orange powder: mp 45 °C; IR (ATR): 796, 820, 835, 975, 999, 1020, 1060, 1104, 1253, 1366, 1409, 1462, 1733, 2853, 2923, 3110 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 291 K) δ 3.81 (td, 1H, *J* = 2.8 and 1.5 Hz, H_4), 4.14 (ddd, 1H, *J* = 2.8, 1.5 and 0.6 Hz, H_5), 4.31 (s, 5H, Cp), 4.29-4.35 (m, 1H, H_3); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 54.8 (d, *J* = 14.6 Hz, CH, C_3), 59.4 (d, *J* = 3.3 Hz, CH, C_4), 63.8 (CH, C_5), 66.4 (d, *J* = 17.5 Hz, C-Br), 72.1 (5CH, Cp), 132.8 (d, *J* = 271.5 Hz, C-F); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -191.1. The NMR data are analogous to those reported previously.[8]

Crystal data for 3c. $C_{10}H_8BrFFe$, M = 282.92, T = 150(2) K, monoclinic, $P\,2_1/c$, a = 6.4541(11), b = 19.159(3), c = 7.4818(12) Å, β = 99.658(6) °, V = 912.0(3) $Å^3$, Z = 4, d = 2.060 g cm^{-3}, μ = 5.992 mm^{-1}. A final refinement on F^2 with 2096 unique intensities and 118 parameters converged at $\omega R(F^2)$ = 0.0739 ($R(F)$ = 0.0309) for 1858 observed reflections with $I > 2\sigma(I)$. CCDC 1841223.

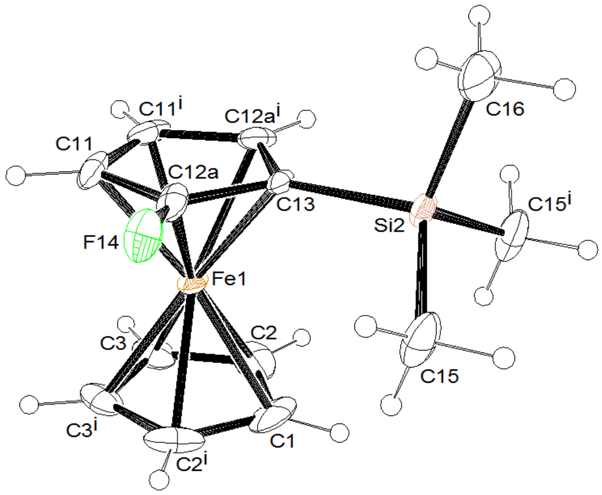


1-Chloro-2-fluoroferrocene (3d, racemic mixture). The general procedure 1 using as electrophile hexachloroethane (0.52 g, 2.2 mmol) in THF (2 mL) gave **3d** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (3 x 20 mL) and brine (20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 90:10; R_f = 0.76) in 92% yield as an orange powder: mp 59-61 °C; IR (ATR): 803, 824, 841, 986, 1000, 1018, 1067, 1106, 1257, 1369, 1410, 1466, 1732, 1787, 2853, 2924, 3104 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 3.74 (br s, 1H, H_4), 4.13 (br s, 1H, H_5), 4.30 (t, 1H, *J* = 3.4 Hz, H_3), 4.32 (s, 5H, Cp); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 54.3 (d, *J* = 13.9 Hz, CH, C_3), 57.7 (d, *J* = 3.4 Hz, CH, C_4), 61.9

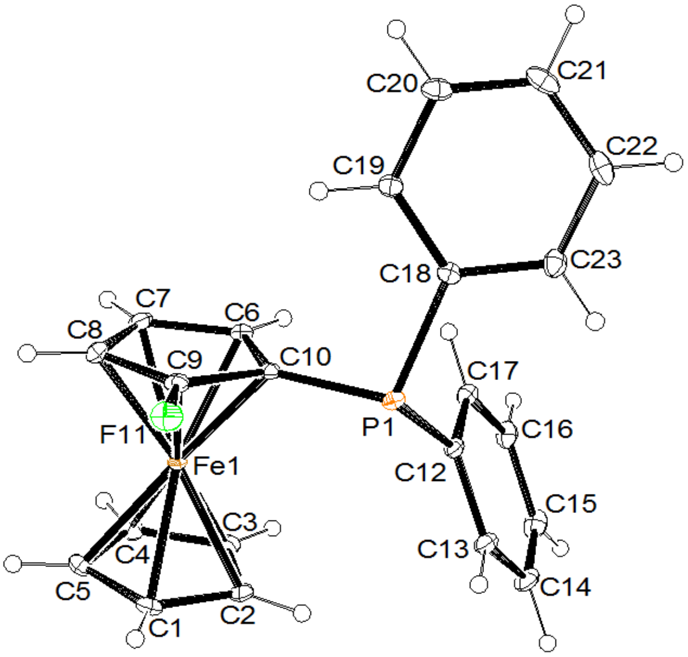
(CH, C_5), 71.7 (5CH, Cp), 80.9 (d, J = 15.1 Hz, C-Cl), 131.5 (d, J = 272 Hz, C-F); ^{19}F NMR (470 MHz, $CDCl_3$, 298 K) δ -193.5. Anal. Calcd for $C_{10}H_8ClFFe$: C, 50.37; H, 3.38. Found: C, 50.42; H, 3.43.

1,2-Difluoroferrocene (3e). The general procedure 1, but with transfer of the lithioferrocene onto the electrophile, using as electrophile *N*-fluorobenzenesulfonimide (0.69 g, 2.2 mmol) in THF (2 mL) gave **3e** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (3 x 20 mL) and brine (20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: heptane-CH_2Cl_2 50:50 to 0:100; R_f (heptane-CH_2Cl_2 50:50) = 0.85) in 72% yield as a yellow powder: mp 112 °C; IR (ATR): 694, 750, 814, 837, 1005, 1175, 1277, 1315, 1335, 1402, 1455, 1487, 1507, 1587, 2855, 2921, 2956, 3038 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 3.46 (t, 1H, J = 1.5 Hz, H_4), 4.08 (br s, 2H, H_3 and H_5), 4.36 (s, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 50.7-51.3 (m, 2CH), 51.5-51.8 (m, CH), 70.9 (d, J = 21.5 Hz, 5CH, Cp), 123.6 (dd, J = 272 and 13.4 Hz, 2C, C-F); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -202.3. These data are analogous to those reported previously.[9]

1-Fluoro-2-(trimethylsilyl)ferrocene (3f, racemic mixture). The general procedure 1 using as electrophile chlorotrimethylsilane (0.25 mL, 2.2 mmol) gave **3f** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (3 x 20 mL) and brine (3 x 20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 90:10; R_f = 0.85) in 96% yield as an orange powder: mp 42-43 °C; IR (ATR): 695, 754, 812, 837, 857, 991, 1000, 1023, 1072, 1153, 1246, 1332, 1420, 1430, 2899, 2956, 3101 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 0.30 (s, 9H, $SiMe_3$), 3.68 (s, 1H, H_3), 3.93 (t, 1H, J = 2.6 Hz, H_4), 4.24 (s, 5H, Cp), 4.42 (t, 1H, J = 3.2 Hz, H_5); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ -0.20 (3CH_3, $SiMe_3$), 58.2 (d, J = 17.7 Hz, CH, C_5), 59.5 (d, J = 20.7 Hz, *C*-$SiMe_3$), 63.6 (d, J = 3.8 Hz, CH, C_4), 66.0 (d, J = 6.2 Hz, CH, C_3), 69.5 (5CH, Cp), 140.0 (d, J = 266 Hz, C, C-F); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -182.9. Anal. Calcd for $C_{13}H_{17}FFeSi$: C, 56.53; H, 6.20. Found: C, 56.66; H, 6.22. **Crystal data for 3f.** $C_{13}H_{17}FFeSi$, M = 276.20, T = 150(2) K, orthorhombic, $P\,n\,m\,a$, a = 11.110(3), b = 11.222(4), c = 10.604(3) Å, V = 1322.1(7) Å^3, Z = 4, d = 1.388 g cm^{-3}, μ = 1.214 mm^{-1}. A final refinement on F^2 with 1586 unique intensities and 90 parameters converged at $\omega R(F^2)$ = 0.0694 ($R(F)$ = 0.0365) for 1261 observed reflections with $I > 2\sigma(I)$. CCDC 1841224.



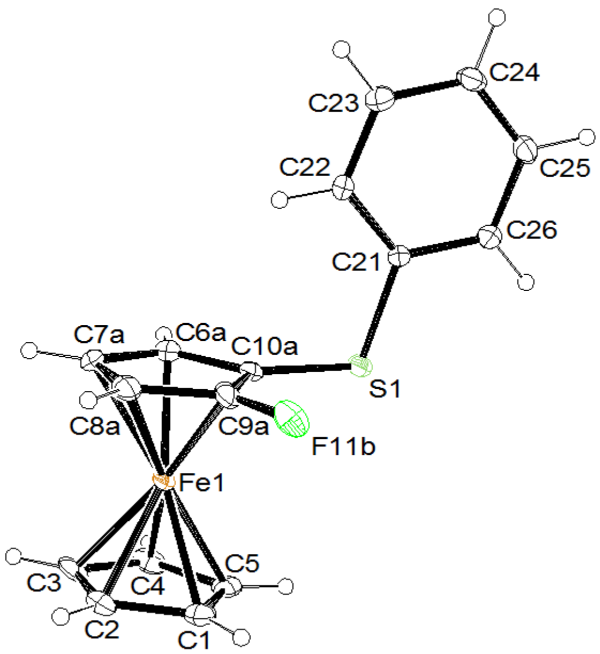
1-(Diphenylphosphino)-2-fluoroferrocene (3g, racemic mixture). The general procedure 1 using as electrophile chlorodiphenylphosphine (0.40 mL, 2.2 mmol) gave **3g** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 90:10; R_f = 0.69) in 16% yield as an orange powder: mp 137-138 °C; IR (ATR): 699, 739, 751, 804, 824, 986, 1002, 1025, 1108, 1159, 1236, 1335, 1409, 1437, 1476, 1585, 3052, 3071 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 3.52-3.53 (m, 1H, H_5), 3.96-3.97 (m, 1H, H_4), 4.16 (s, 5H, Cp), 4.53-4.55 (m, 1H, H_3), 7.29-7.39 (m, 8H, Ph), 7.49-7.53 (m, 2H, Ph); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 58.5 (dd, J = 15.7 and 1.9 Hz, CH, C_3), 62.8 (d, J = 4.2 Hz, CH, C_4), 64.3 (dd, J = 14.5 and 11.1 Hz, C, C_1), 65.5 (t, J = 3.0 Hz, CH, C_5), 70.5 (5CH, Cp), 128.3 (CH, $C_{4'}$), 128.4 (d, J = 2.0 Hz, 2CH, Ph), 128.4 (d, J = 3.9 Hz, 2CH, Ph), 129.2 (CH, $C_{4'}$), 132.8 (d, J = 19.1 Hz, 2CH, Ph), 134.5 (d, J = 20.7 Hz, 2CH, Ph), 137.00 (d, J = 8.4 Hz, C, $C_{1'}$), 138.7 (d, J = 9.7 Hz, C, $C_{1'}$), 138.7 (dd, J = 271.5 and 15.7 Hz, C-F); ^{19}F NMR (470 MHz, $CDCl_3$, 298 K) δ -185.9; ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ -23.9. Anal. Calcd for $C_{22}H_{18}FFeP$: C, 68.07; H, 4.67. Found: C, 68.12; H, 4.91. **Crystal data for 3g.** $C_{22}H_{18}FFeP$, M = 388.18, T = 150(2) K, monoclinic, $P\,2_1/n$, a = 8.4999(2), b = 17.4245(5), c = 11.9000(4) Å, β = 104.5910(10) °, V = 1705.63(9) Å^3, Z = 4, d = 1.512 g cm^{-3}, μ = 0.989 mm^{-1}. A final refinement on F^2 with 3861 unique intensities and 226 parameters converged at $\omega R(F^2)$ = 0.0656 ($R(F)$ = 0.0252) for 3551 observed reflections with $I > 2\sigma(I)$. CCDC 1841227.



The product **3g·BH$_3$** was also obtained by treating the crude by a THF 1 M solution of BH$_3$·THF (10 mmol) at room temperature overnight. After removal of the solvent and chromatography over silica gel (eluent: petroleum ether-CH$_2$Cl$_2$ 80:20; R$_f$ = 0.17), **3g·BH$_3$** was identified by NMR: ^{1}H NMR (300 MHz, CDCl$_3$, 291 K) δ 0.68-1.83 (br s, 3H, BH$_3$), 4.13-4.17 (m, 1H, Cp-H), 4.15 (s, 5H, Cp), 4.25-4.28 (m, 1H, Cp-H), 4.59-4.61 (m, 1H, Cp-H), 7.34-7.54 (m, 8H), 7.83-7.90 (m, 2H); ^{19}F NMR (282 MHz, CDCl$_3$, 291 K) δ -182. 5 (d, *J* = 8.5 Hz); IR (ATR): 694, 738, 812, 824, 951, 996, 1027, 1054, 1106, 1131, 1170, 1342, 1411, 1436, 1482, 2373, 2388, 2928, 2968 cm^{-1}. By following a protocol reported previously,[10] it was then converted into **3g**, which was isolated in an overall 61% yield.

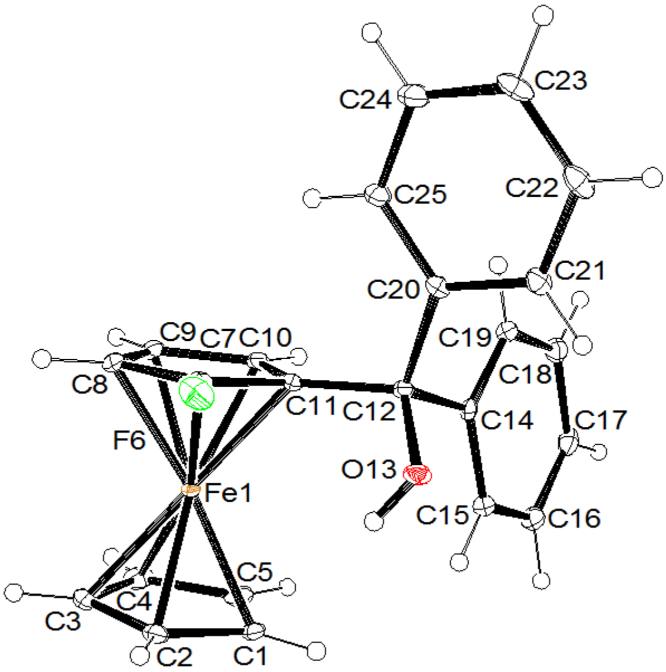
1-Fluoro-2-(phenylthio)ferrocene (3h, racemic mixture). The general procedure 1 using as electrophile phenyl disulfide (0.48 g, 2.2 mmol) in THF (2 mL) gave **3h** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), drying over MgSO$_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et$_2$O 90:10; R$_f$ = 0.70) in 97% yield as an orange powder: mp 101-102 °C; IR (ATR): 655, 689, 736, 815, 826, 897, 991, 1000, 1018, 1106, 1164, 1244, 1342, 1409, 1441, 1450, 1476, 1581 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, 291 K) δ 4.11 (td, 1H, *J* = 2.8 and 1.7 Hz, H$_4$), 4.24 (ddd, 1H, *J* = 2.6, 1.5 and 1.0 Hz, H$_3$), 4.46 (s, 5H, Cp), 4.64 (ddd, 1H, *J* = 3.5, 2.8 and 1.5 Hz, H$_5$), 7.17-7.36 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$, 291 K) δ 57.6 (d, *J* = 14.9 Hz, CH, C$_5$), 61.9 (d, *J* = 4.0 Hz, CH, C$_4$), 64.7 (d, *J* = 15.8 Hz, C, C$_2$), 68.5 (CH, C$_3$), 71.1 (5CH, Cp), 125.6 (CH, C$_{4'}$), 126.7 (2CH, Ph), 128.9 (2CH, Ph), 136.5

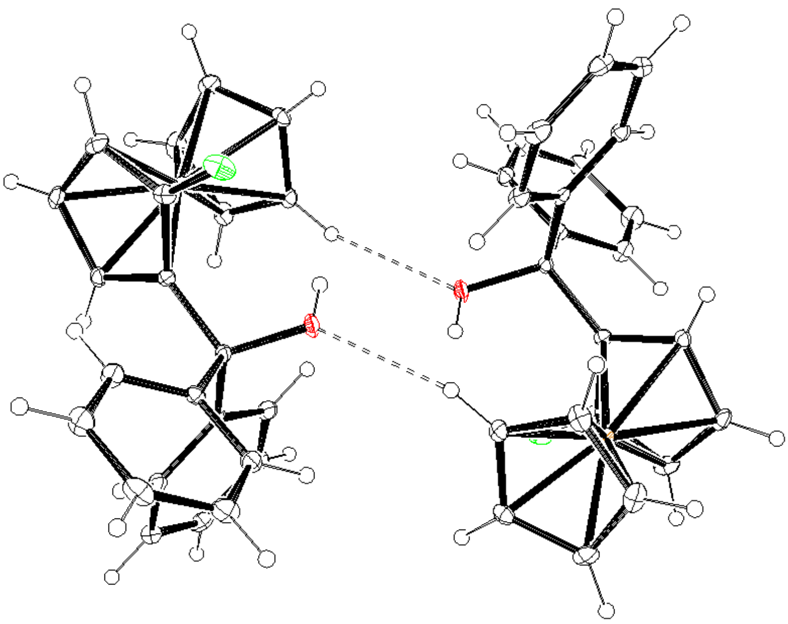
(d, J = 272 Hz, C-F), 139.1 (C, Ph); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -188.2. Anal. Calcd for $C_{16}H_{13}FFeS$: C, 61.56; H, 4.20. Found: C, 61.68; H, 4.31. **Crystal data for 3h.** $C_{16}H_{13}FFeS$, M = 312.17, T = 150(2) K, orthorhombic, $P\ 2_1\ 2_1\ 2_1$, a = 7.3559(7), b = 9.0886(9), c = 19.6427(16) Å, V = 1313.2(2) Å^3, Z = 4, d = 1.579 g cm^{-3}, μ = 1.299 mm^{-1}. A final refinement on F^2 with 3000 unique intensities and 181 parameters converged at $\omega R(F^2)$ = 0.0960 ($R(F)$ = 0.0377) for 2895 observed reflections with $I > 2\sigma(I)$. CCDC 1841228.



2-Fluoro-α,α-diphenylferrocenemethanol (3i, racemic mixture). The general procedure 1 using as electrophile benzophenone (0.40 g, 2.2 mmol) in THF (2 mL) gave **3i** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 90:10; R_f = 0.55) in an estimated 71% yield (due to remaining benzophenone). A pure fraction was nevertheless obtained as an orange powder: mp 127-129 °C; IR (ATR): 702, 757, 808, 1010, 1032, 1108, 1153, 1320, 1414, 1445, 1461, 1493, 1661, 3056, 3551 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 3.41 (s, 2H, OH and H_5), 3.83 (s, 1H, H_4), 4.32 (s, 5H, Cp), 4.45 (s, 1H, H_3), 7.26-7.83 (m, 10H, Ph); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 57.1 (d, J = 15.4 Hz, CH, C_3), 59.2 (d, J = 4.7 Hz, CH, C_4), 64.7 (d, J = 2.3 Hz, CH, C_5), 70.3 (5CH, Cp), 85.6 (d, J = 8.1 Hz, C, C_1), 127.1 (CH, Ph), 127.1 (2CH, Ph), 127.3 (2CH, Ph), 127.4 (CH, Ph), 127.5 (2CH, Ph), 128.0 (2CH, Ph), 133.4 (d, J = 271 Hz, C-F), 145.2 (C, Ph), 147.0 (C, Ph); ^{19}F NMR (470 MHz, $CDCl_3$, 298 K) δ -187.7. Anal. Calcd for

$C_{23}H_{19}FFeO$: C, 71.52; H, 4.96. Found: C, 71.69; H, 5.10. **Crystal data for 3i.** $C_{23}H_{19}FFeO$, M = 386.23, T = 150(2) K, triclinic, P -1, a = 8.4417(11), b = 9.1109(12), c = 12.5792(15) Å, α = 95.968(4), β = 103.721(4), γ = 110.768(4) °, V = 859.76(19) Å^3, Z = 2, d = 1.492 g cm^{-3}, μ = 0.896 mm^{-1}. A final refinement on F^2 with 3941 unique intensities and 238 parameters converged at $\omega R(F^2)$ = 0.0913 ($R(F)$ = 0.0354) for 3685 observed reflections with $I > 2\sigma(I)$. CCDC 1841229.

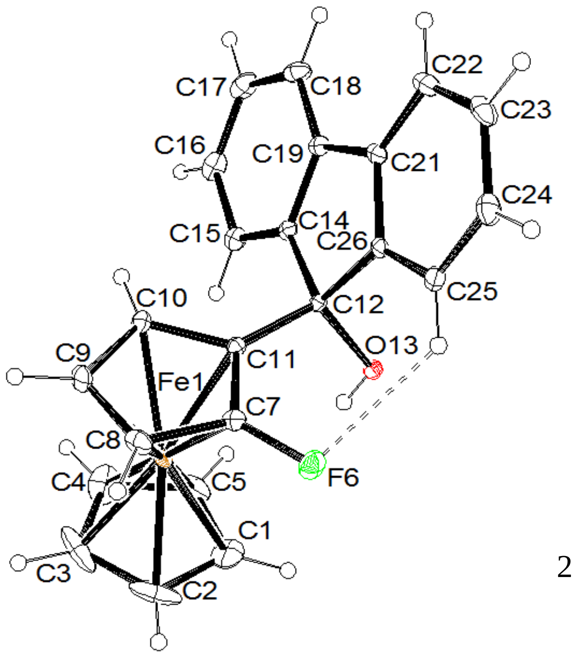




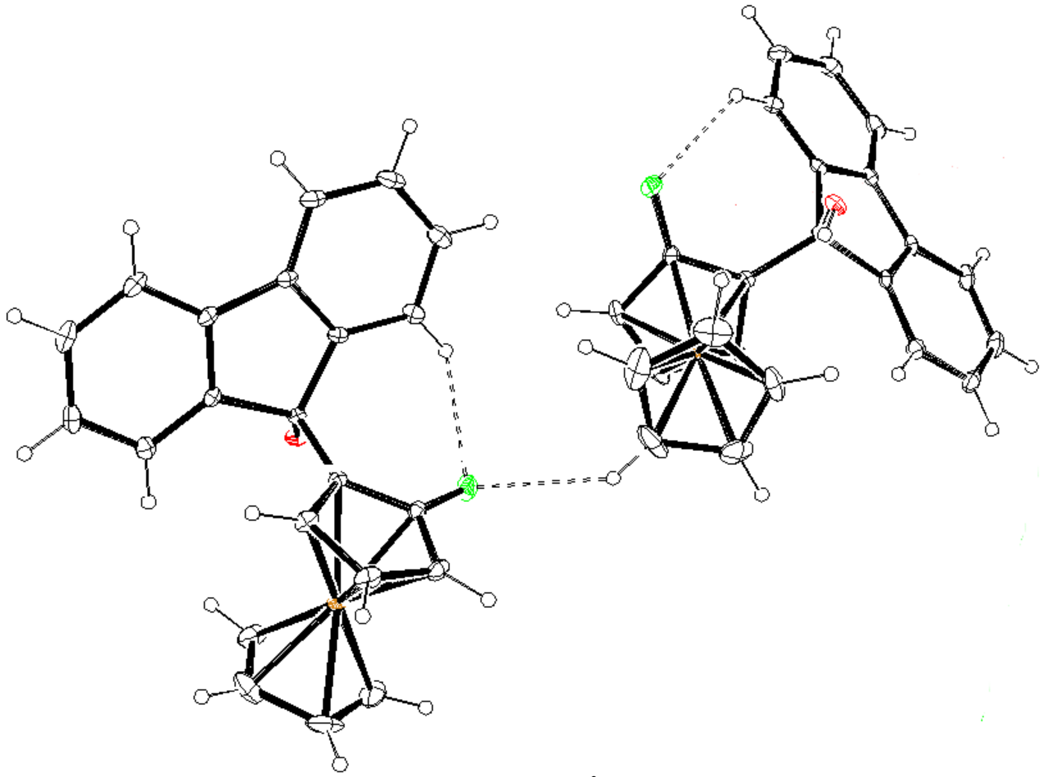
2.517 Å

9-(2-Fluoroferrocenyl)-9-fluorenol (3j, racemic mixture). The general procedure 1 using as electrophile fluorenone (0.40 g, 2.2 mmol) in THF (2 mL) gave **3j** after addition of water (20 mL), extraction with

AcOEt (3 x 20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 90:10; R_f = 0.28) in 72% yield as an orange powder: mp 130 °C; IR (ATR): 655, 730, 748, 768, 809, 817, 889, 1004, 1019, 1033, 1105, 1193, 1289, 1330, 1365, 1412, 1448, 1606, 1668, 3069, 3537 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 3.11 (s, 1H, OH), 3.48 (br s, 1H, H_5), 3.71 (br s, 1H, H_4), 4.41 (s, 5H, Cp), 4.45 (br s, 1H, H_3), 7.28-7.53 (m, 4H, H_{10}, $H_{10'}$, H_{11} and $H_{11'}$), 7.68 (d, 1H, *J* = 7.1 Hz, H_{12}), 7.73 (dd, 1H, *J* = 6.1 and 2.4 Hz, $H_{12'}$), 7.83 (d, 1H, *J* = 7.2 Hz, $H_{9'}$), 7.97 (d, 1H, *J* = 5.9 Hz, H_9); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 57.1 (d, *J* = 15.9 Hz, CH, C_3), 58.8 (d, *J* = 4.4 Hz, CH, C_4), 62.4 (d, *J* = 2.6 Hz, CH, C_5), 70.2 (5CH, Cp), 80.1 (d, *J* = 3.2 Hz, C-OH), 81.4 (d, *J* = 9.8 Hz, C, C_1), 119.8 (CH, C_{12}), 119.9 (CH, $C_{12'}$), 124.3 (d, *J* = 5.1 Hz, CH, $C_{9'}$), 124.8 (d, *J* = 2.4 Hz, CH, C_9), 127.6 (CH, $C_{11'}$), 128.0 (CH, C_{11}), 128.9 (CH, $C_{10'}$), 129.1 (CH, C_{10}), 133.2 (d, *J* = 271 Hz, C-F), 138.6 (C, $C_{8'}$), 139.4 (C, C_8), 148.2 (C, $C_{13'}$), 149.2 (C, C_{13}); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -186.0. Anal. Calcd for $C_{23}H_{17}FFeO$: C, 71.90; H, 4.46. Found: C, 72.05; H, 4.57. **Crystal data for 3j.** $C_{23}H_{17}FFeO$, *M* = 384.21, *T* = 150(2) K, monoclinic, *P* $2_1/c$, *a* = 11.4134(9), *b* = 11.6979(10), *c* = 13.3112(12) Å, β = 108.703(3) °, *V* = 1683.4(2) $Å^3$, *Z* = 4, *d* = 1.516 g cm^{-3}, μ = 0.915 mm^{-1}. A final refinement on F^2 with 3822 unique intensities and 238 parameters converged at $\omega R(F^2)$ = 0.0776 ($R(F)$ = 0.0316) for 3367 observed reflections with $I > 2\sigma(I)$. CCDC 1841230.



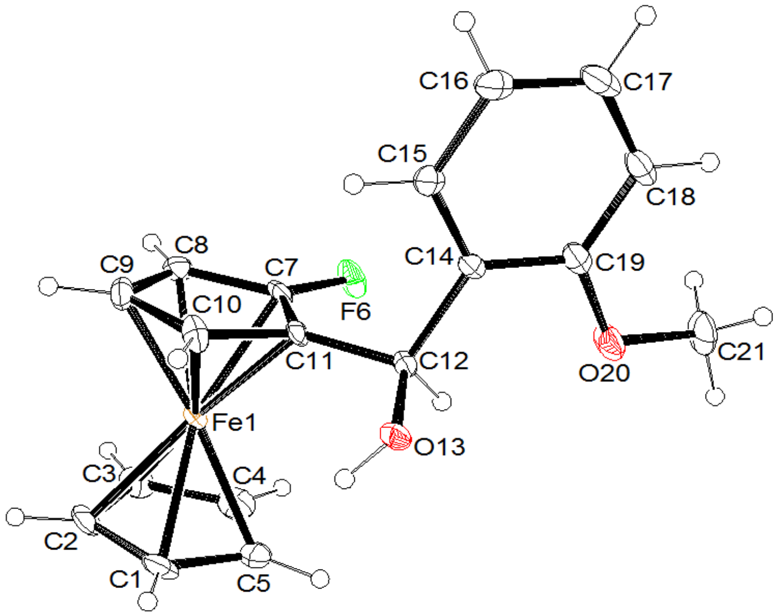
2.405 Å



2.519 Å

2-Fluoro-α-(2-methoxyphenyl)ferrocenemethanol (3k, major diastereoisomer, S_P-*S* and R_P-*R* racemic mixture). The general procedure 1 using as electrophile 2-anisaldehyde (0.27 mL, 2.2 mmol) gave **3k** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-CH_2Cl_2 90:10 to 50:50; R_f (petroleum ether-Et_2O 90:10) = 0.07; R_f (petroleum ether-CH_2Cl_2 70:30) = 0.06) in 63% yield as a yellow powder: mp 124 °C; IR (ATR): 758, 819, 988, 1001, 1025, 1047, 1104, 1162, 1238, 1285, 1448, 1488, 1586, 1598, 2837, 2933, 2961, 3447 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 3.05 (d, 1H, *J* = 4.8 Hz, OH), 3.80 (s, 1H, H_4), 3.86 (s, 3H, OMe), 3.96 (s, 1H, H_5), 4.33 (s, 1H, H_3), 4.37 (s, 5H, Cp), 5.99 (d, 1H, *J* = 4.5 Hz, C*H*-OH), 6.87 (d, 1H, *J* = 8.2 Hz, Ar), 6.92 (t, 1H, *J* = 7.5 Hz, Ar), 7.22-7.28 (m, 2H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 55.5 (CH_3, OMe), 56.1 (d, *J* = 14.8 Hz, CH, C_3), 59.4 (d, *J* = 4.2 Hz, CH, C_4), 60.3 (CH, *C*H-OH), 65.5 (d, *J* = 3.1 Hz, CH, C_5), 70.1 (5CH, Cp), 80.1 (d, *J* = 11.3 Hz, C, C_1), 110.7 (CH, Ar), 120.8 (CH, Ar), 127.4 (CH, Ar), 128.9 (CH, Ar), 131.1 (C, $C_{1'}$), 134.1 (d, *J* = 270 Hz, C-F), 156.7 (C, $C_{2'}$); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -190.9. Anal. Calcd for $C_{18}H_{17}FFeO_2$: C, 63.55; H, 5.04.

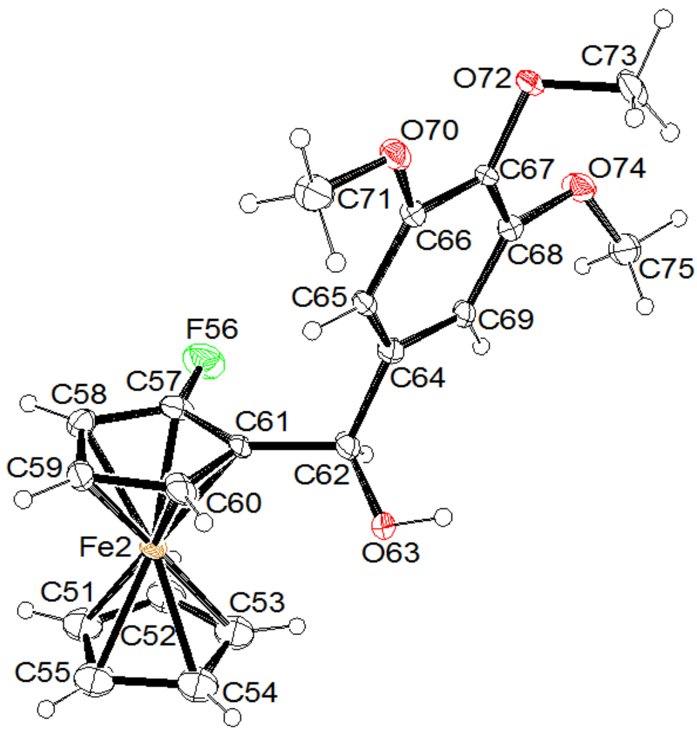
Found: C, 63.48; H, 5.25. **Crystal data for 3k.** $C_{18}H_{17}FFeO_2$, M = 340.16, T = 150(2) K, tetragonal, $P\ 4_3\ 2_1\ 2$, a = 7.9670(5), c = 46.209(2) Å, V = 2933.1(4) Å^3, Z = 8, d = 1.541 g cm^{-3}, μ = 1.043 mm^{-1}. A final refinement on F^2 with 3278 unique intensities and 204 parameters converged at $\omega R(F^2)$ = 0.0782 ($R(F)$ = 0.0371) for 3063 observed reflections with $I > 2\sigma(I)$. CCDC 1841231.

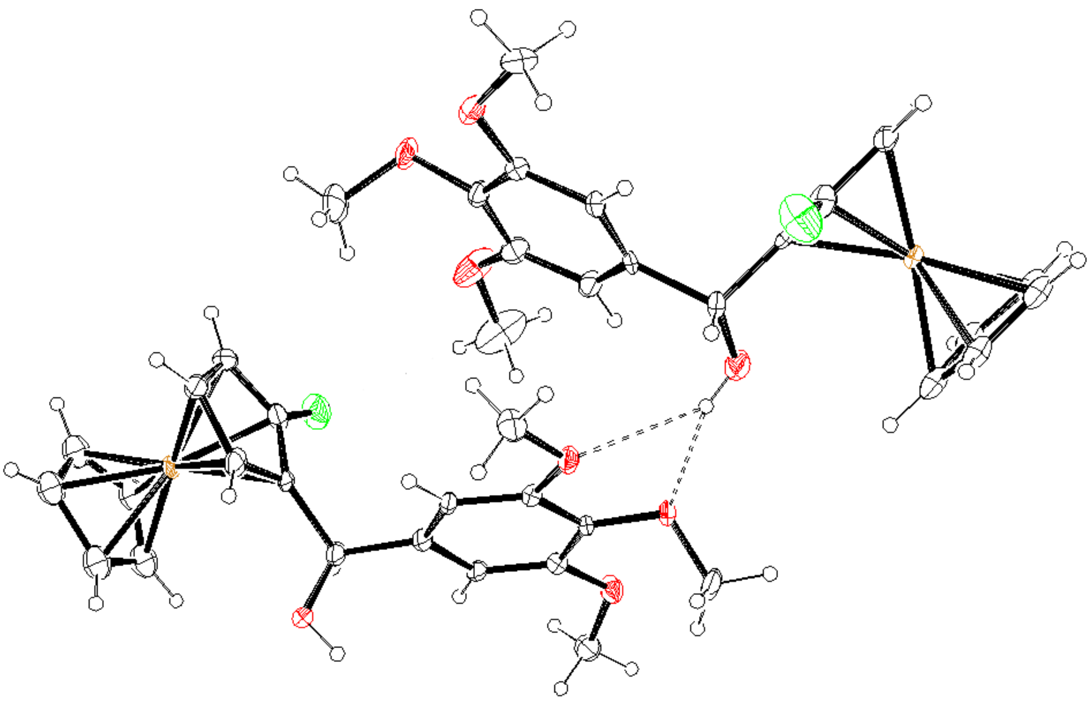


The **minor diastereoisomer (3k', *S*P-*R* and *R*P-*S* racemic mixture)** was similarly obtained (R_f (petroleum ether-CH_2Cl_2 70:30) = 0.06) in 25% yield as a yellow powder: mp 102 °C; IR (ATR): 661, 759, 822, 1000, 1015, 1104, 1128, 1161, 1186, 1237, 1286, 1445, 1470, 1490, 1586, 1598, 2845, 2922, 2948, 3520 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 3.16 (d, 1H, J = 6.8 Hz, OH), 3.74 (s, 1H, H_4), 3.76 (s, 1H, H_5), 3.89 (d, 3H, J = 1.7 Hz, OMe), 4.21 (d, 5H, J = 2.1 Hz, Cp), 4.34 (s, 1H, H_3), 5.94 (d, 1H, J = 6.7 Hz, C*H*-OH), 6.93 (d, 1H, J = 8.2 Hz, Ar), 7.00 (t, 1H, J = 7.5 Hz, Ar), 7.29 (t, 1H, J = 7.9 Hz, Ar), 7.44 (d, 1H, J = 7.1 Hz, Ar); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 55.4 (CH_3, OMe), 56.5 (d, J = 14.9 Hz, CH, C_3), 59.5 (d, J = 4.5 Hz, CH, C_4), 61.8 (d, J = 2.5 Hz, CH, *C*H-OH), 67.8 (d, J = 2.4 Hz, CH, C_5), 70.1 (5CH, Cp), 78.3 (d, J = 10.1 Hz, C, C_1), 110.8 (CH, Ar), 120.9 (CH, Ar), 128.2 (CH, Ar), 128.9 (CH, Ar), 130.7 (C, Ar), 134.0 (d, J = 271 Hz, C-F), 156.6 (C, Ar); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -190.2. Anal. Calcd for $C_{18}H_{17}FFeO_2$: C, 63.55; H, 5.04. Found: C, 63.62; H, 5.30.

2-Fluoro-α-(3,4,5-trimethoxyphenyl)ferrocenemethanol (3l, major diastereoisomer, *S*P-*S* and *R*P-*R* racemic mixture). The general procedure 1 using as electrophile 3,4,5-trimethoxybenzaldehyde (0.43 g, 2.2

mmol) in THF (2 mL) gave **3l** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: heptane-AcOEt 90:10) in 50% yield as a yellow powder: R_f (eluent: Et_2O-petroleum ether 60:40) = 0.35; R_f (eluent: CH_2Cl_2) = 0.17; mp 103 °C; IR (ATR): 707, 810, 841, 961, 1000, 1106, 1120, 1231, 1332, 1421, 1448, 1505, 1592, 2839, 2937, 3101, 3482 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 2.55 (s, 1H, OH), 3.79 (s, 3H, OMe), 3.80 (s, 1H, H_4), 3.81 (s, 6H, 2OMe), 3.93 (s, 1H, H_5), 4.35 (s, 6H, H_3 and Cp), 5.65 (s, 1H, C*H*-OH), 6.61 (s, 2H, $H_{2'}$ and $H_{6'}$); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 56.1 (2CH_3, 2OMe), 56.3 (d, J = 14.9 Hz, CH, C_3), 58.9 (d, J = 2.2 Hz, CH, C_5), 59.6 (d, J = 4.1 Hz, CH, C_4), 60.8 (CH_3, OMe), 69.1 (d, J = 3.4 Hz, CH, *C*H-OH), 69.9 (5CH, Cp), 81.3 (d, J = 11.1 Hz, C, C_1), 102.8 (2CH, $C_{2'}$ and $C_{6'}$), 134.0 (d, J = 270 Hz, C-F), 137.2 (C, Ar), 138.7 (C, Ar), 153.1 (2C, $C_{3'}$ and $C_{5'}$); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -191.6. Anal. Calcd for $C_{20}H_{21}FFeO_4$: C, 60.02; H, 5.29. Found: C, 60.13; H, 5.44. **Crystal data for 3l.** $C_{20}H_{21}FFeO_4$, M = 400.22, T = 150(2) K, monoclinic, $P\ c$, a = 13.0179(10), b = 10.2447(7), c = 14.9685(11) Å, β = 114.620(2) °, V = 1814.8(2) $Å^3$, Z = 4, d = 1.465 g cm^{-3}, μ = 0.863 mm^{-1}. A final refinement on F^2 with 7881 unique intensities and 430 parameters converged at $\omega R(F^2)$ = 0.1558 ($R(F)$ = 0.0627) for 7025 observed reflections with $I > 2\sigma(I)$. CCDC 1841232.



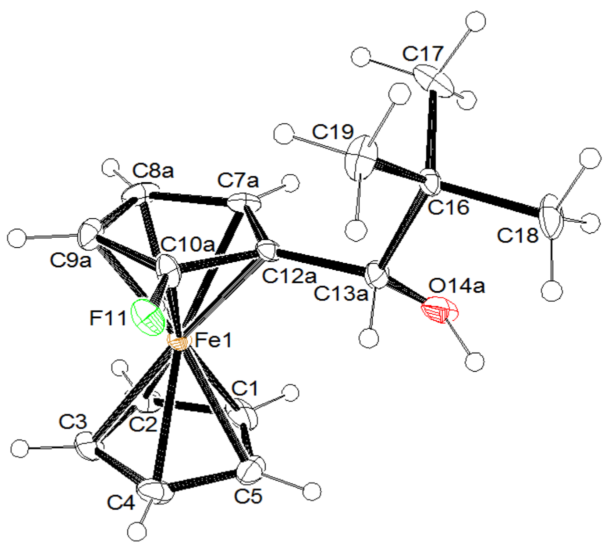


2.508 and 2.169 Å

The **minor diastereoisomer (3l', S_P-*R* and R_P-*S* racemic mixture)** was similarly isolated (remaining traces of other ferrocene compounds): 39% estimated yield; R_f (eluent: CH_2Cl_2) = 0.13; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 2.49 (s, 1H, OH), 3.84 (s, 3H, OMe), 3.87 (s, 6H, 2OMe), ~3.8 (2H, H_4 and H_5), 4.25 (s, 5H, Cp), 4.36 (d, 1H, *J* = 2.2 Hz, H_3), 5.60 (d, 1H, *J* = 2.9 Hz, C*H*-OH), 6.72 (s, 2H, $H_{2'}$ and $H_{6'}$); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 56.2 (br s, 2CH_3, 2OMe), 56.8 (d, *J* = 14.8 Hz, CH, C_3), 59.7 (d, *J* = 4.3 Hz, CH, C_4), 60.9 (CH_3, OMe), 61.7 (d, *J* = 2.6 Hz, CH, C_5), 70.0 (5CH, Cp), 71.5 (d, *J* = 2.6 Hz, CH, *C*H-OH), 79.2 (d, *J* = 10.0 Hz, C, C_1), 103.7 (2CH, $C_{2'}$ and $C_{6'}$), 133.6 (d, *J* = 271 Hz, C-F), 137.5 (C, Ar), 138.4 (C, Ar), 153.1 (2C, $C_{3'}$ and $C_{5'}$); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -190.3. Anal. Calcd for $C_{20}H_{21}FFeO_4$: C, 60.02; H, 5.29. Found: C, 60.27; H, 5.33.

2-Fluoro-α-(*tert*-butyl)ferrocenemethanol (3m, major diastereoisomer, S_P-*R* and R_P-*S* racemic mixture). The general procedure 1 using as electrophile pivaldehyde (0.25 mL, 2.2 mmol) gave **3m** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 90:10) in 63% yield as an orange powder: R_f (heptane-Et_2O 90:10) = 0.25; mp 67 °C; IR (ATR): 666, 774, 811, 997, 1049, 1104, 1182, 1235, 1366, 1393, 1455, 1479, 2869, 2952, 2970, 3101, 3481 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291

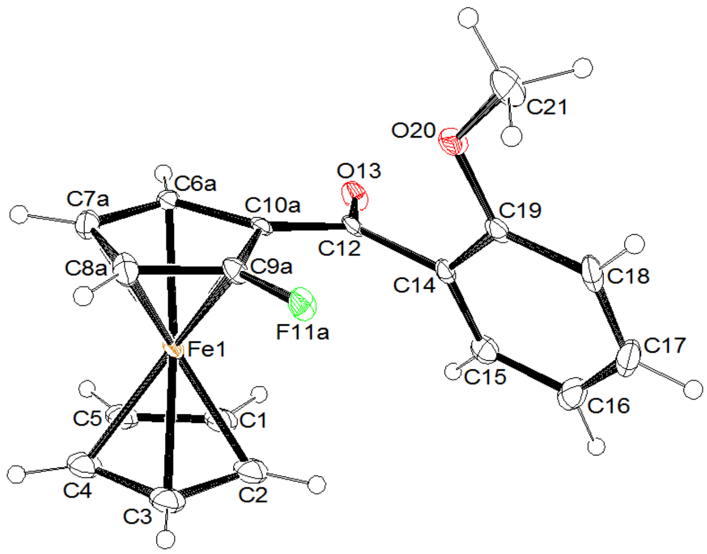
K) δ 0.88 (d, 9H, J = 0.7 Hz, CMe_3), 2.00 (d, 1H, J = 1.6 Hz, OH), 3.76-3.82 (m, 1H, H_4), 3.91-3.96 (m, 1H, H_5), 4.29 (s, 5H, Cp), 4.35 (d, 1H, J = 1.6 Hz, C*H*-OH), 4.36 (dd, 1H, J = 2.8 and 1.6 Hz, H_3); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 25.7 ($3CH_3$, C*Me*$_3$), 35.8 (C, *C*Me$_3$), 56.0 (d, J = 15.3 Hz, CH, C_3), 59.5 (CH, C4 or C5), 59.6 (CH, C4 or C5), 69.7 (5CH, Cp), 74.4 (d, J = 3.9 Hz, CH, *C*H-OH), 79.2 (d, J = 11.6 Hz, C, C_1), 135.2 (d, J = 269 Hz, C-F); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -188.7. Anal. Calcd for $C_{15}H_{19}FFeO$: C, 62.09; H, 6.60. Found: C, 62.27; H, 6.73. The **minor diastereoisomer (3m', *R*$_P$-*R* and *S*$_P$-*S* racemic mixture)** was similarly isolated in 36% yield as an orange powder: R_f (heptane-Et_2O 90:10) = 0.37; mp 68 °C; IR (ATR): 666, 773, 811, 997, 1049, 1104, 1182, 1234, 1294, 1364, 1393, 1454, 1480, 1724, 2868, 2955, 3101, 3484 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 0.90 (d, 9H, J = 0.9 Hz, CMe_3), 2.33 (dd, 1H, J = 4.7 and 2.9 Hz, OH), 3.76-3.81 (m, 2H, H_4 and H_5), 4.00 (d, 1H, J = 4.7 Hz, C*H*-OH), 4.30-4.33 (m, 1H, H_3), 4.32 (s, 5H, Cp); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 26.1 ($3CH_3$, C*Me*$_3$), 36.3 (C, *C*Me$_3$), 56.8 (d, J = 16.0 Hz, CH, C_3), 59.6 (CH, C_4), 64.1 (CH, C_5), 70.2 (5CH, Cp), 77.6 (d, J = 8.4 Hz, C, C_1), 78.9 (CH, *C*H-OH), 134.0 (d, J = 270 Hz, C-F); ^{19}F NMR (470 MHz, $CDCl_3$, 298 K) δ -187.0. Anal. Calcd for $C_{15}H_{19}FFeO$: C, 62.09; H, 6.60. Found: C, 62.18; H, 6.67. **Crystal data for 3m'.** $C_{15}H_{19}FFeO$, M = 290.15, T = 150(2) K, orthorhombic, $P\ 2_1\ 2_1\ 2_1$, a = 6.0435(2), b = 10.1248(3), c = 21.5858(8) Å, V = 1320.82(8) Å^3, Z = 4, d = 1.459 g cm^{-3}, μ = 1.138 mm^{-1}. A final refinement on F^2 with 2994 unique intensities and 176 parameters converged at $\omega R(F^2)$ = 0.1093 ($R(F)$ = 0.0434) for 2890 observed reflections with $I > 2\sigma(I)$. CCDC 1841233.



2-Fluoroferrocenecarboxaldehyde (3n, racemic mixture). The general procedure 1 using as electrophile dimethylformamide (0.19 mL, 2.2 mmol) gave **3n** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (3 x 20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 90:10; R_f = 0.17) in 97% yield as a red powder: mp 128-130 °C; IR (ATR): 771, 813, 827, 1003, 1015, 1094, 1104, 1202, 1286, 1341, 1384, 1400, 1411, 1455, 1675, 2836, 3079, 3103 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 4.28 (q, 1H, J = 2.4 Hz, H_4), 4.38 (s, 5H, Cp), 4.51 (t, 1H, J = 2.1 Hz, H_5), 4.70 (q, 1H, J = 2.3 Hz, H_3), 10.2 (s, 1H, CHO); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 60.6 (d, J = 12.9 Hz, CH, C_3), 61.7 (CH, C_5), 65.1 (d, J = 3.9 Hz, CH, C_4), 67.1 (d, J = 8.2 Hz, *C*-CHO), 71.2 (5CH, Cp), 137.15 (d, J = 279 Hz, C-F), 191.1 (d, J = 2.9 Hz, *C*HO); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -189.4. Anal. Calcd for $C_{11}H_9FFeO$: C, 56.94; H, 3.91. Found: C, 57.02; H, 3.99.

1-Fluoro-2-(2-methoxybenzoyl)ferrocene (3o, racemic mixture). The general procedure 1 (but with warming to -40 °C instead of room temperature after addition of the electrophile) using as electrophile 2-methoxybenzoyl chloride (0.33 mL, 2.2 mmol) gave **3o** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (3 x 20 mL) and brine (20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: CH_2Cl_2-petroleum ether 90:10; R_f = 0.12) in 60% yield as a red powder: mp 153 °C; IR (ATR): 674, 730, 756, 816, 918, 1014, 1099, 1162, 1182, 1224, 1246, 1270, 1297, 1306, 1443, 1454, 1489, 1582, 1598, 1634, 1727, 2841, 2926 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 3.80 (s, 3H, OMe), 4.17 (s, 1H, H_4), 4.31 (s, 5H, Cp), 4.46 (s, 1H, H_3), 4.63 (s, 1H, H_5), 6.95-7.04 (m, 2H, $H_{3'}$ and $H_{5'}$), 7.42-7.46 (m, 2H, $H_{4'}$ and $H_{6'}$); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 55.7 (CH_3, OMe), 60.4 (d, J = 14.8 Hz, CH, C_5), 63.8 (d, J = 4.2 Hz, CH, C_4), 65.4 (CH, C_3), 67.6 (d, J = 7.1 Hz, C_2), 71.5 (5CH, Cp), 111.4 (CH, $C_{3'}$), 120.4 (CH, $C_{5'}$), 128.4 (CH, $C_{6'}$), 130.6 (C, $C_{1'}$), 131.6 (CH, $C_{4'}$), 134.8 (d, J = 279 Hz, C-F), 157.0 (C, $C_{2'}$), 198.2 (d, J = 3.9 Hz, *C*=O); ^{19}F NMR (470 MHz, $CDCl_3$, 298 K) δ -183.8. Anal. Calcd for $C_{18}H_{15}FFeO_2$: C, 63.93; H, 4.47. Found: C, 64.01; H, 4.54. **Crystal data for 3o.** $C_{18}H_{15}FFeO_2$, M = 338.15, T = 150(2) K, monoclinic, $P\ 2_1/c$, a = 8.8223(18), b = 12.218(2), c = 13.536(3) Å, β = 95.984(8) °, V = 1451.1(5) $Å^3$, Z = 4, d = 1.548 g cm^{-3}, μ =

1.054 mm^{-1}. A final refinement on F^2 with 3277 unique intensities and 180 parameters converged at $\omega R(F^2)$ = 0.1925 ($R(F)$ = 0.0750) for 2735 observed reflections with $I > 2\sigma(I)$. CCDC 1841234.



2-Fluoroferrocenecarboxylic acid (3p, racemic mixture). The general procedure 1 using as electrophile carbon dioxide in excess (gas) gave **3p** after washing the organic phase with aqueous 1M HCl (2 x 20 mL) and water (2 x 20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 50:50; R_f = 0.32) in 72% yield as an orange powder: mp > 150 °C (deg.); IR (ATR): 664, 760, 812, 830, 941, 1002, 1087, 1164, 1239, 1296, 1410, 1463, 1486, 1668, 2579, 2855 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 291 K) δ 4.14 (td, 1H, J = 2.9 and 1.6 Hz, H_4), 4.37 (s, 5H, Cp), 4.53 (t, 1H, J = 2.4 Hz, H_5), 4.64 (td, 1H, J = 2.8 and 1.6 Hz, H_3), OH not seen; ^{13}C NMR (101 MHz, $(CD_3)_2CO$, 296 K) δ 60.2 (d, J = 14.4 Hz, CH, C_3), 63.6 (d, J = 4.2 Hz, CH, C_4), 65.1 (CH, C_5), 71.8 (5CH, Cp), 71.8 (C, C_1), 135.8 (d, J = 277.5 Hz, C-F), 170.9 (CO_2H); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -184.4; ^{19}F NMR (376 MHz, $(CD_3)_2CO$, 296 K) δ -186.0. Anal. Calcd for $C_{11}H_9FFeO_2$: C, 53.27; H, 3.66. Found: C, 53.38; H, 3.79.

2-Fluoro-1-iodo-3-(trimethylsilyl)ferrocene (3fb, racemic mixture). To a stirred, cooled (-75 °C) solution of fluoroferrocene (**1a**, 0.41 g, 2.0 mmol) in THF (2 mL) were successively added *s*BuLi (~1.3 M in cyclohexane, 2.4 mmol) and, 1 h later, chlorotrimethylsilane (0.25 mL, 2.2 mmol) before warming to room temperature. The mixture was next cooled again (-75 °C) before addition of *s*BuLi (~1.3 M in cyclohexane, 2.4 mmol) and, 1 h later, iodine (0.63 g, 2.4 mmol) in THF (2 mL) before warming to room temperature.

After addition of an aqueous saturated solution of $Na_2S_2O_3$ (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with aqueous 0.4 M $FeCl_3$ (20 mL), water (3 x 20 mL) and brine (20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether-Et_2O 90:10; R_f = 0.83), **3fb** was isolated in 83% yield as an orange powder: mp 62 °C; IR (ATR): 694, 751, 814, 837, 1004, 1077, 1134, 1175, 1276, 1316, 1329, 1402, 1454, 1487, 1507, 1587, 2855, 2921, 2956, 3038 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 291 K) δ 0.29 (s, 9H, $SiMe_3$), 3.79 (dd, 1H, J = 2.7 and 1.8 Hz, H_4), 4.22 (s, 5H, Cp), 4.22-4.24 (m, 1H, H_5); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ -0.38 ($3CH_3$, $SiMe_3$), 30.7 (d, J = 22.9 Hz, C-I), 59.3 (d, J = 20.8 Hz, C-$SiMe_3$), 66.8 (d, J = 5.7 Hz, CH, C_4), 69.9 (CH, C_5), 72.5 (5CH, Cp), 139.1 (d, J = 269 Hz, C-F); ^{19}F NMR (282 MHz, $CDCl_3$, 291 K) δ -181.7. Anal. Calcd for $C_{13}H_{16}FFeISi$: C, 38.83; H, 4.01. Found: C, 39.02; H, 4.19. **Crystal data for 3fb.** $C_{13}H_{16}FFeISi$, M = 402.10, T = 150(2) K, orthorhombic, $P\,n\,a\,2_1$, a = 18.2207(17), b = 12.3664(12), c = 6.6897(6) Å, V = 1507.4(2) $Å^3$, Z = 4, d = 1.772 g cm^{-3}, μ = 3.116 mm^{-1}. A final refinement on F^2 with 3271 unique intensities and 149 parameters converged at $\omega R(F^2)$ = 0.0609 ($R(F)$ = 0.0334) for 2641 observed reflections with $I > 2\sigma(I)$. CCDC 1841225.

General procedure 2. To a stirred, cooled (-75 °C) solution of the required chloroferrocene (2.0 mmol) in THF (2 mL) was added *s*BuLi (~1.3 M in cyclohexane, 2.4 mmol). After 1 h at -75 °C, the temperature was raised to -15 °C. The required electrophile was introduced at -15 °C, and the mixture was stirred during warming to room temperature. The mixture was treated as specified in the product description.

1-Chloro-2-iodoferrocene (6b, racemic mixture). The general procedure 2 starting from chloroferrocene (**5a**, 0.44 g) and using as electrophile iodine (0.58 g, 2.2 mmol) in THF (2 mL) gave **6b** after addition of an aqueous saturated solution of $Na_2S_2O_3$ (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (2 x 20 mL) and brine (20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether; R_f (heptane) = 0.48) in 80% yield as an orange oil: IR (ATR): 829, 912, 1002, 1107, 1196, 1342, 1393, 3095 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 291 K) δ 4.15 (t, 1H, J = 2.5 Hz, H_4), 4.23 (s, 5H, Cp), 4.37 (dd, 1H, J = 2.7 and 1.4 Hz, H_3), 4.50 (dd, 1H, J = 2.6

and 1.4 Hz, H_5); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 43.4 (C-I), 67.1 and 67.3 (2CH, C_4 and C_5), 72.9 (CH, C_3), 73.4 (5CH, Cp), 96.7 (C-Cl). The NMR data are as reported previously.[5]

1-Chloro-2-(trimethylsilyl)ferrocene (6f, racemic mixture). The general procedure 2 starting from chloroferrocene (**5a**, 0.44 g) and using as electrophile chlorotrimethylsilane (0.25 mL, 2.2 mmol) gave **6f** after addition of water (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (2 x 20 mL) and brine (20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether; R_f (heptane) = 0.75) in 96% yield as an orange oil: IR (ATR): 694, 756, 820, 837, 944, 1002, 1108, 1146, 1192, 1248, 1295, 1374, 1402, 2956 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 291 K) δ 0.33 (s, 9H, $SiMe_3$), 3.98 (br s, 1H, H_3), 4.20 (m, 1H, H_4), 4.23 (s, 5H, Cp), 4.54 (br s, 1H, H_5); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ -0.07 ($3CH_3$, $SiMe_3$), 68.3 (CH, C_4), 70.5 (5CH, Cp), 70.6 (*C*-$SiMe_3$), 71.1 and 71.8 (2CH, C_3 and C_5), 98.1 (C-Cl). Anal. Calcd for $C_{13}H_{17}ClFeSi$: C, 53.35; H, 5.86. Found: C, 53.47; H, 5.93.

2-Chloro-1-iodo-3-(trimethylsilyl)ferrocene (6fb, racemic mixture). The general procedure 2 starting from 1-chloro-2-(trimethylsilyl)ferrocene (**6f**, 0.59 g) and using as electrophile iodine (0.58 g, 2.2 mmol) in THF (2 mL) gave **6fb** after addition of an aqueous saturated solution of $Na_2S_2O_3$ (20 mL), extraction with AcOEt (3 x 20 mL), washing of the organic phase with water (2 x 20 mL) and brine (20 mL), drying over $MgSO_4$, concentration under reduced pressure and chromatography over silica gel (eluent: petroleum ether; R_f (heptane) = 0.79) in 70% yield as an orange oil: IR (ATR): 693, 754, 819, 950, 1002, 1108, 1125, 1202, 1247, 1275, 1314, 1365, 1387, 1408, 2896, 2955, 3097 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 291 K) δ 0.32 (s, 9H, $SiMe_3$), 4.06 (d, 1H, J = 2.5 Hz, H_4), 4.20 (s, 5H, Cp), 4.49 (d, 1H, J = 2.5 Hz, H_5); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ -0.33 ($3CH_3$, $SiMe_3$), 46.3 (C-I), 70.4 (*C*-$SiMe_3$), 72.5 (CH), 73.4 (5CH, Cp), 74.9 (CH), 101.6 (C-Cl). Anal. Calcd for $C_{13}H_{16}ClFeISi$: C, 37.31; H, 3.85. Found: C, 37.44; H, 3.84.

General procedure 3. To a stirred, cooled (0 °C) solution of H-TMP (0.19 mL, 1.1 mmol) in THF (2 mL) was added BuLi (~1.6 M in hexane, 1.1 mmol). The mixture was stirred for 5 min at 0 °C before introduction of the required iodoferrocene (1.0 mmol) at -50 °C. After 2 h at -50 °C, MeOH (2.0 mL) and aqueous 1M HCl (10 mL) were successively added. Extraction with AcOEt (3 x 15 mL), drying over $MgSO_4$, concentration under reduced pressure, and purification by column chromatography over silica gel (the eluent is given in the product description) led to the expected product.

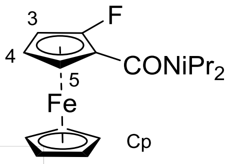
1-Fluoro-4-iodo-2-(trimethylsilyl)ferrocene (3fb-mig, racemic mixture). The general procedure 3 (eluent: heptane; R_f = 0.57) applied to 2-fluoro-1-iodo-3-(trimethylsilyl)ferrocene (**3fb**, 0.40 g) gave **3fb-mig** in 77% yield as an orange powder: mp 35-37 °C; IR (ATR): 811, 835, 872, 1021, 1140, 1225, 1244, 1339, 1410, 1423, 2924, 2955 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 0.28 (s, 9H, $SiMe_3$), 3.97 (t, 1H, J = 1.4 Hz, H_3), 4.26 (s, 5H, Cp), 4.69 (dd, 1H, J = 3.7 and 1.4 Hz, H_5); ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ -0.26 ($3CH_3$, $SiMe_3$), 35.0 (d, J = 2.0 Hz, C-I), 61.7 (d, J = 21.4 Hz, *C*-$SiMe_3$), 64.6 (d, J = 17.2 Hz, CH, C_5), 72.3 (d, J = 6.0 Hz, CH, C_3), 72.7 (5CH, Cp), 138.7 (d, J = 272 Hz, C-F); ^{19}F NMR (470 MHz, $CDCl_3$, 298 K) δ -180.1. Anal. Calcd for $C_{13}H_{16}FFeISi$: C, 38.83; H, 4.01. Found: C, 39.10; H, 4.18. **Crystal data for 3fb-mig.** $C_{13}H_{16}FFeISi$, M = 402.10, T = 150(2) K, monoclinic, $C\,2/c$, a = 36.679(4), b = 6.8411(7), c = 11.5528(13) Å, β = 93.263(5) °, V = 2894.2(5) $Å^3$, Z = 8, d = 1.846 g cm^{-3}, μ = 3.245 mm^{-1}. A final refinement on F^2 with 3247 unique intensities and 157 parameters converged at $\omega R(F^2)$ = 0.1542 ($R(F)$ = 0.0654) for 2828 observed reflections with $I > 2\sigma(I)$. CCDC 1841226.

1-Chloro-3-iodoferrocene (6b-mig, racemic mixture).[5] The general procedure 3 (eluent: petroleum ether; R_f (heptane) = 0.53) applied to 1-chloro-2-iodoferrocene (**6b**, 0.35 g) gave **6b-mig** in 23% yield as an orange oil: IR (ATR): 823, 867, 890, 1002, 1028, 1107, 1194, 1338, 1362, 1404, 3105 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 291 K) δ 4.27 (s, 5H, Cp), 4.35 (dd, 1H, J = 2.3 and 1.1 Hz, H_4), 4.42 (dd, 1H, J = 2.4 and 1.2 Hz, H_5), 4.68 (br s, 1H, H_2); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ 37.0 (C-I), 69.0 (CH, C_5), 72.7 (CH), 73.5 (5CH, Cp), 74.0 (CH), 92.6 (C-Cl). Anal. Calcd for $C_{10}H_8ClFeI$: C, 34.68; H, 2.33. Found: C, 34.79; H, 2.09.

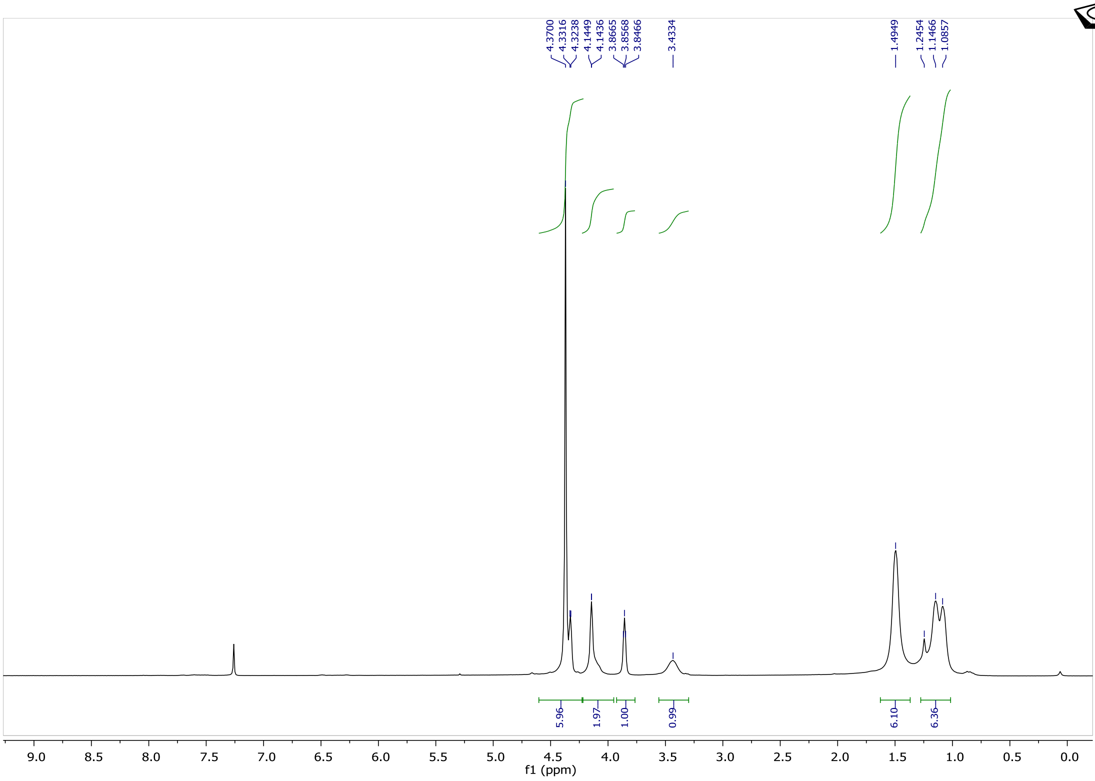
1-Chloro-4-iodo-2-(trimethylsilyl)ferrocene (6fb-mig, racemic mixture). The general procedure 3 (eluent: petroleum ether; R_f (heptane) = 0.62) applied to 1-chloro-3-iodo-2-(trimethylsilyl)ferrocene (**6fb**, 0.42 g) gave **6fb-mig** in 87% yield as an orange oil: IR (ATR): 756, 839, 873, 964, 1207, 1249, 1273, 1364, 2956 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 291 K) δ 0.33 (s, 9H, $SiMe_3$), 4.22 (d, 1H, J = 1.3 Hz, H_3), 4.24 (s, 5H, Cp), 4.78 (d, 1H, *J* = 1.3 Hz, H_5); ^{13}C NMR (75 MHz, $CDCl_3$, 291 K) δ -0.18 (3CH_3, $SiMe_3$), 39.1 (C-I), 72.5 (*C*-$SiMe_3$), 73.5 (5CH, Cp), 76.7 (CH), 77.9 (CH), 97.7 (C-Cl). Anal. Calcd for $C_{13}H_{16}ClFeISi$: C, 37.31; H, 3.85. Found: C, 37.59; H, 3.82.

NMR spectra

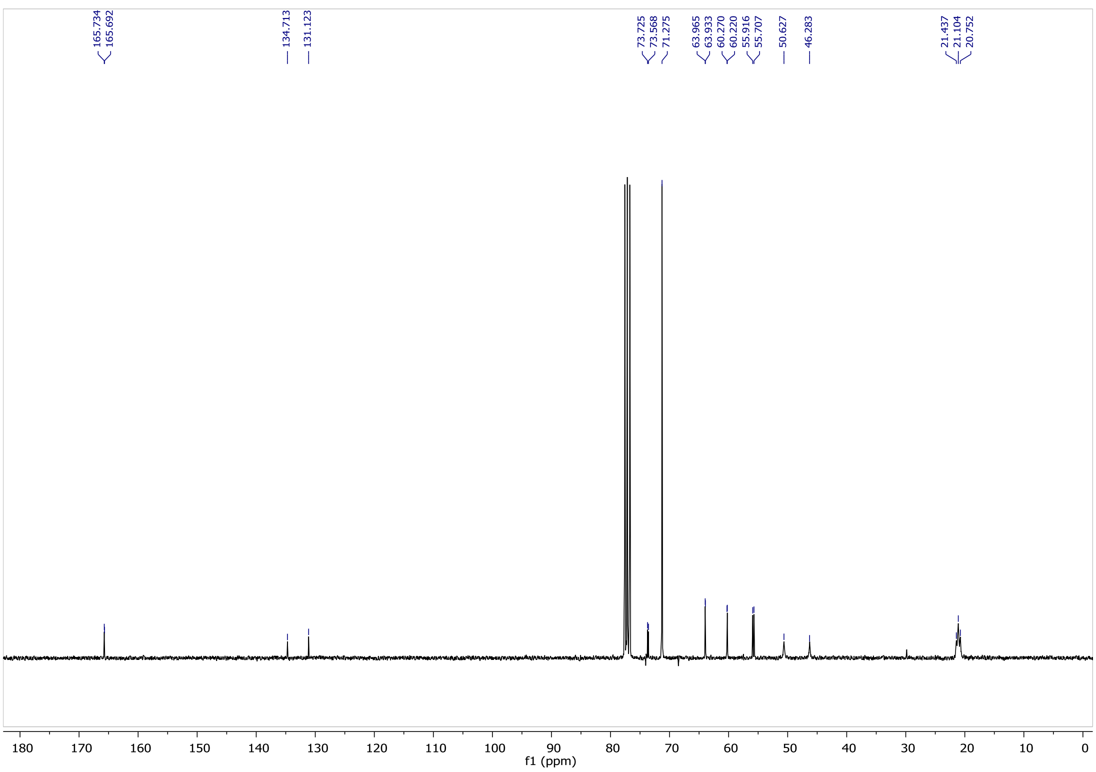
Compound 2a (racemic mixture)



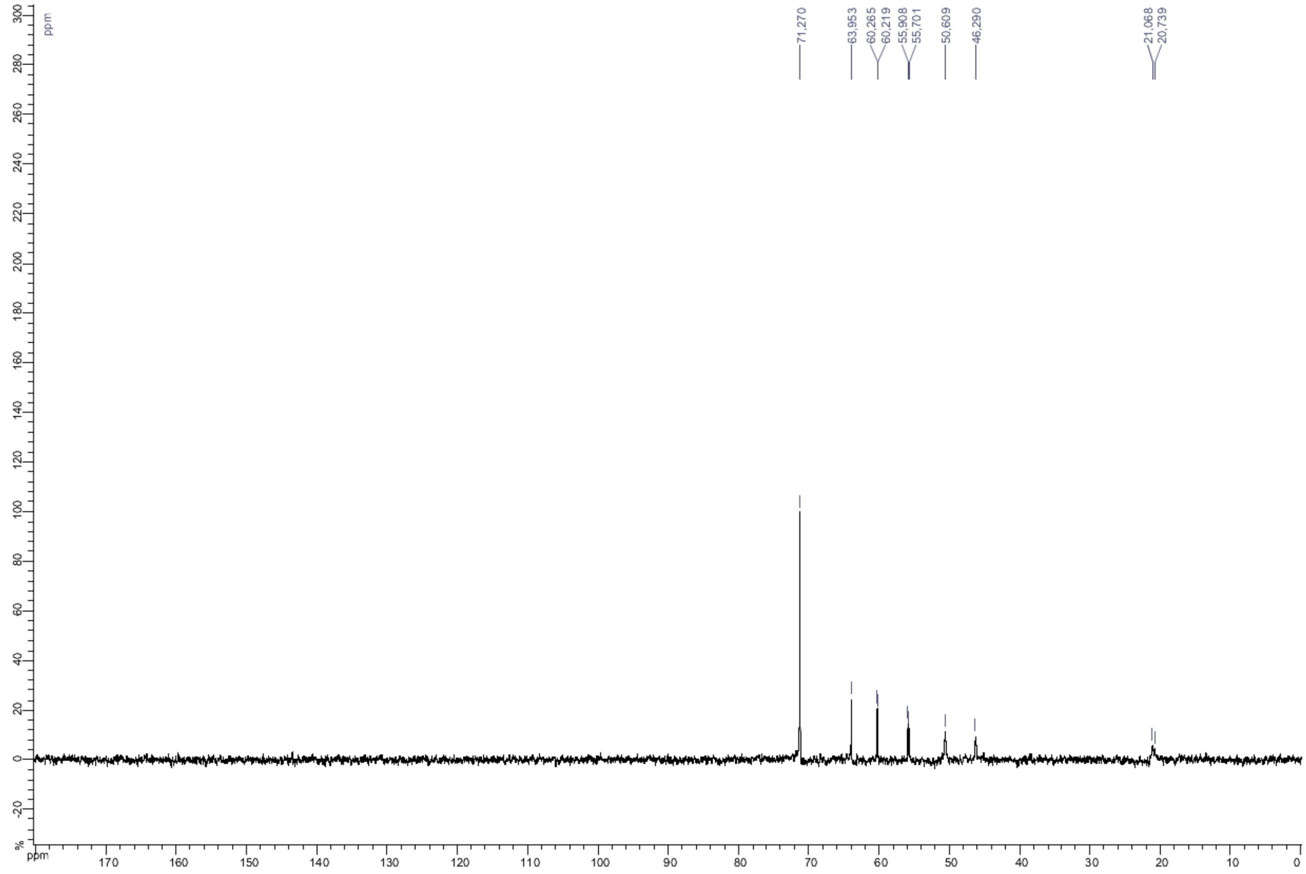
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



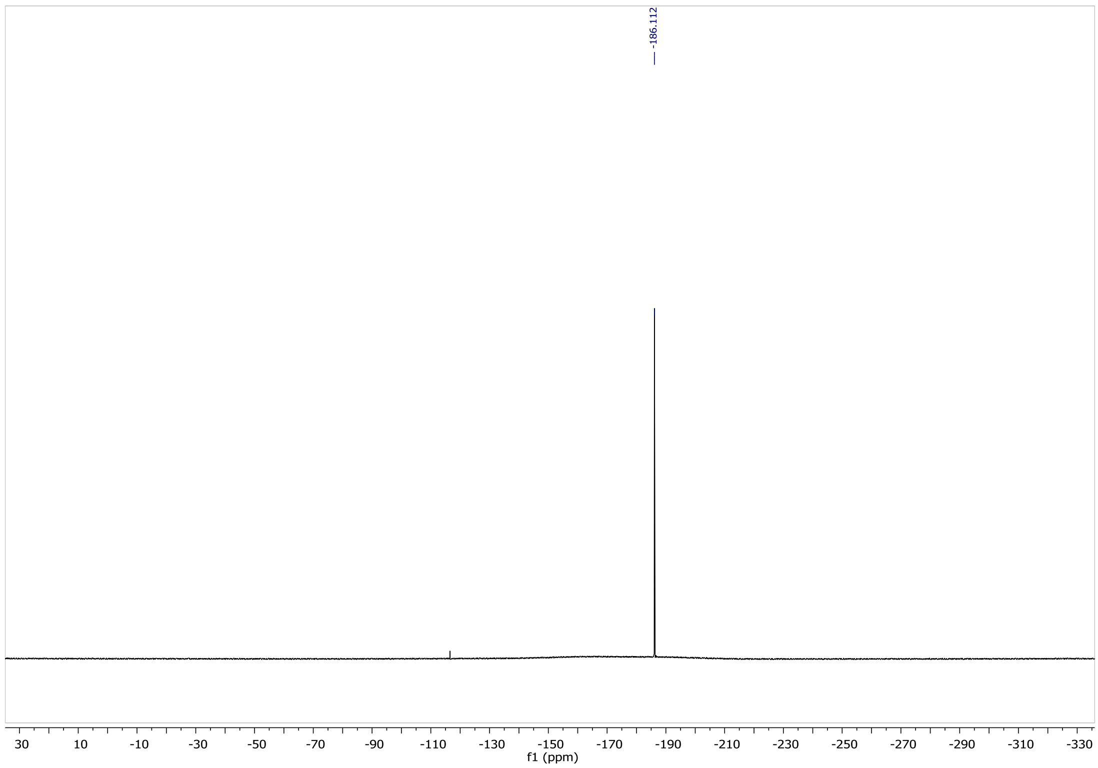
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



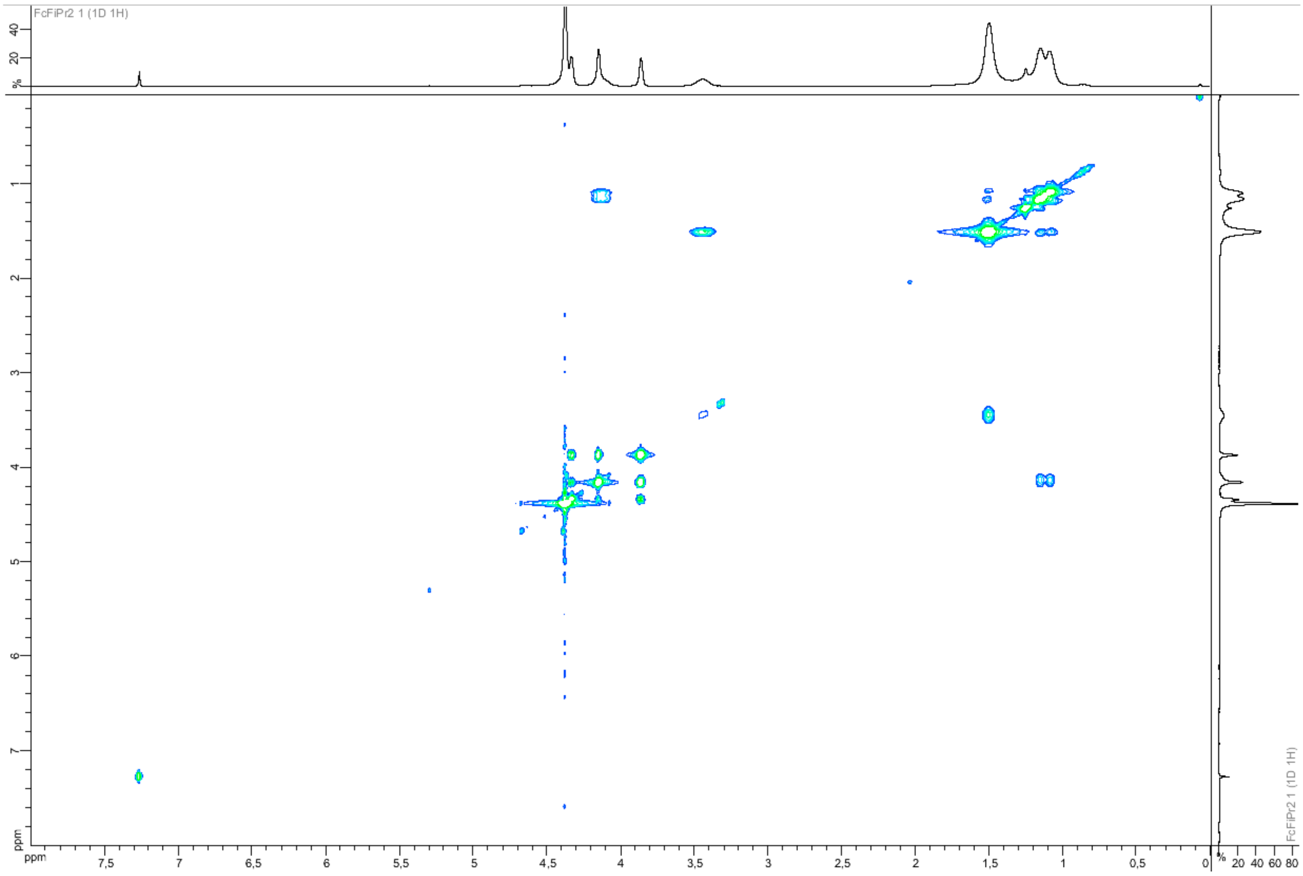
DEPT 135 (75 MHz, $CDCl_3$, 291 K)



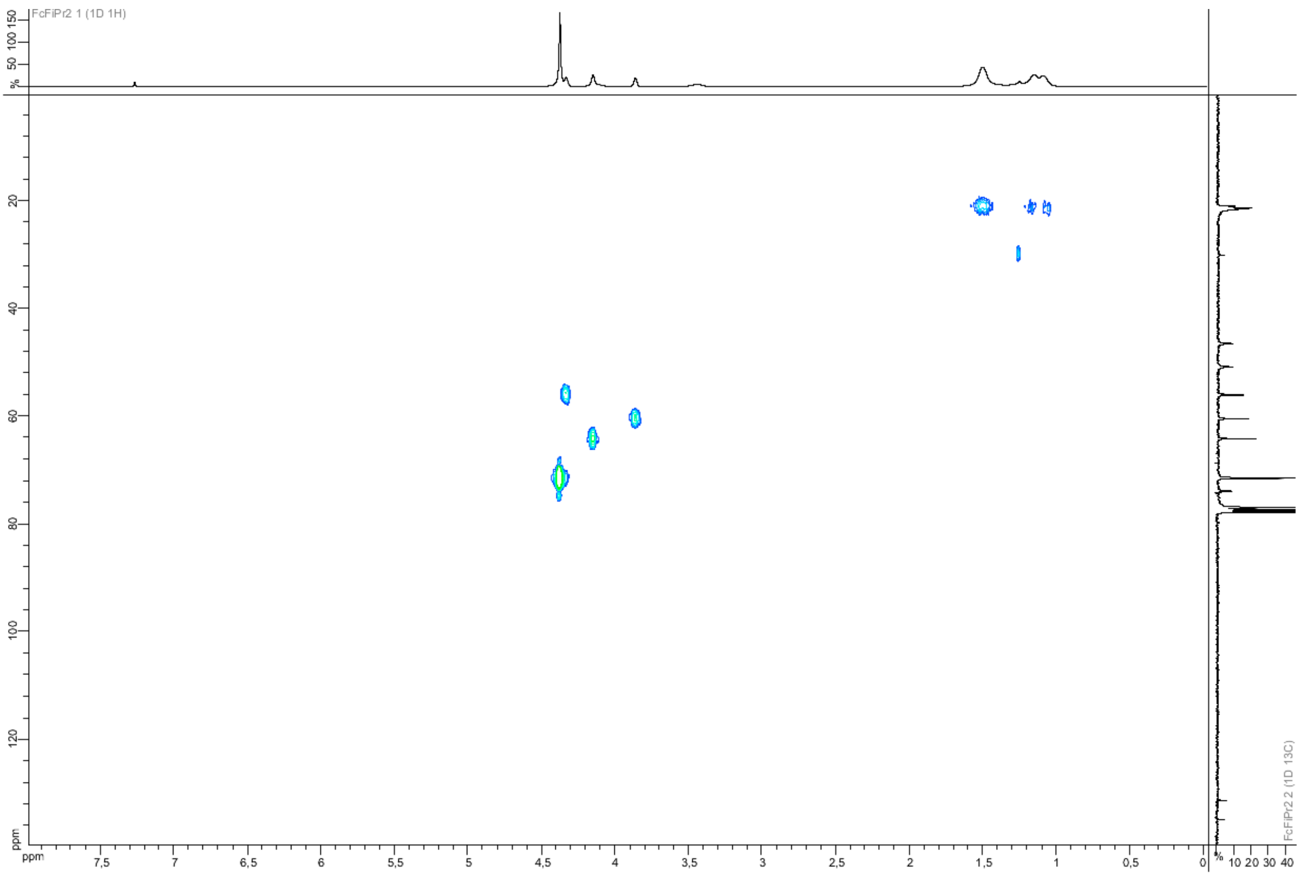
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



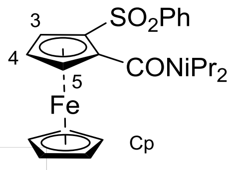
COSY (300 MHz, $CDCl_3$, 291 K)



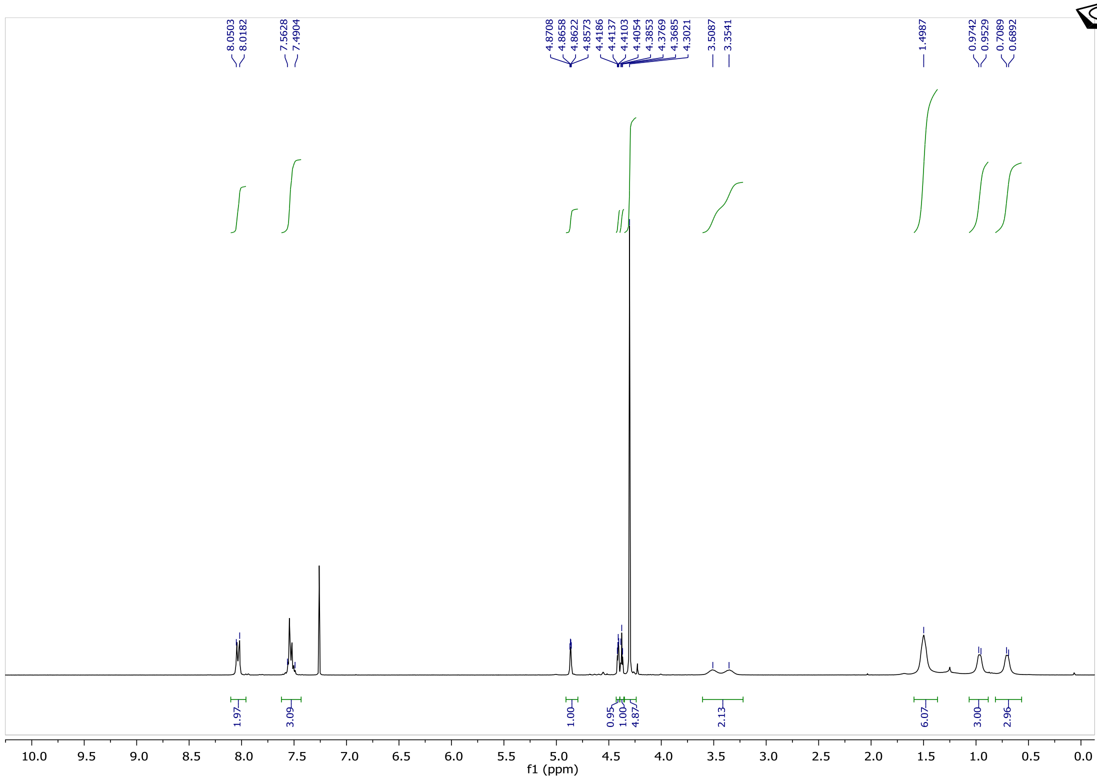
HSQC (300 MHz, $CDCl_3$, 291 K)



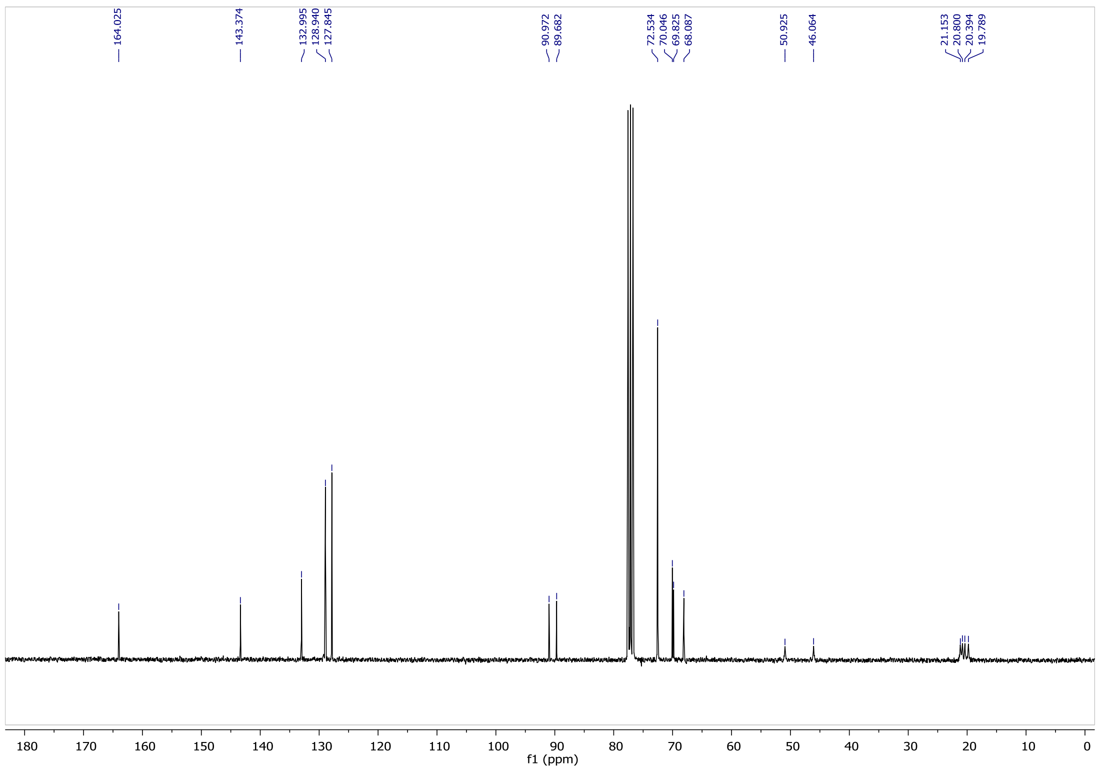
Compound 2b (racemic mixture)



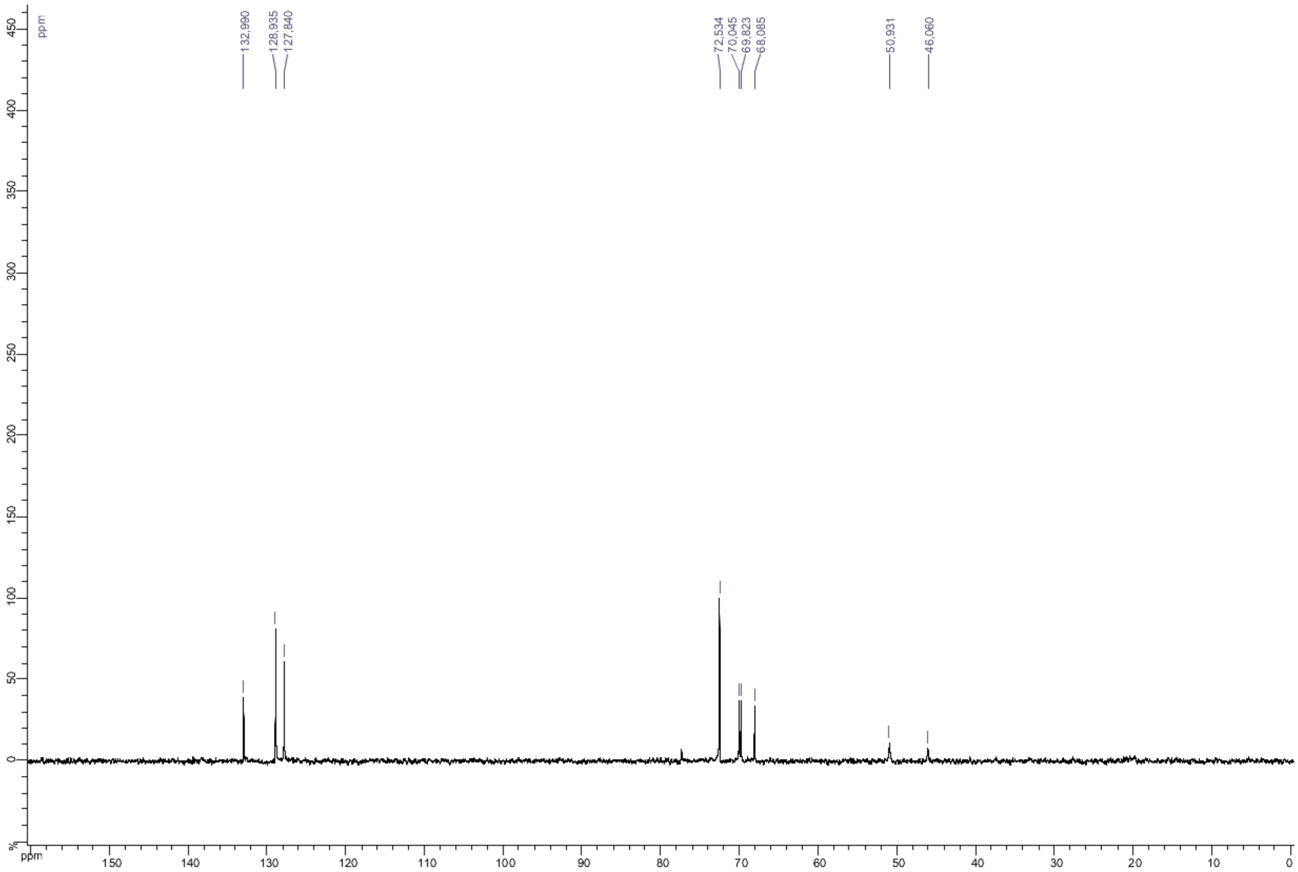
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



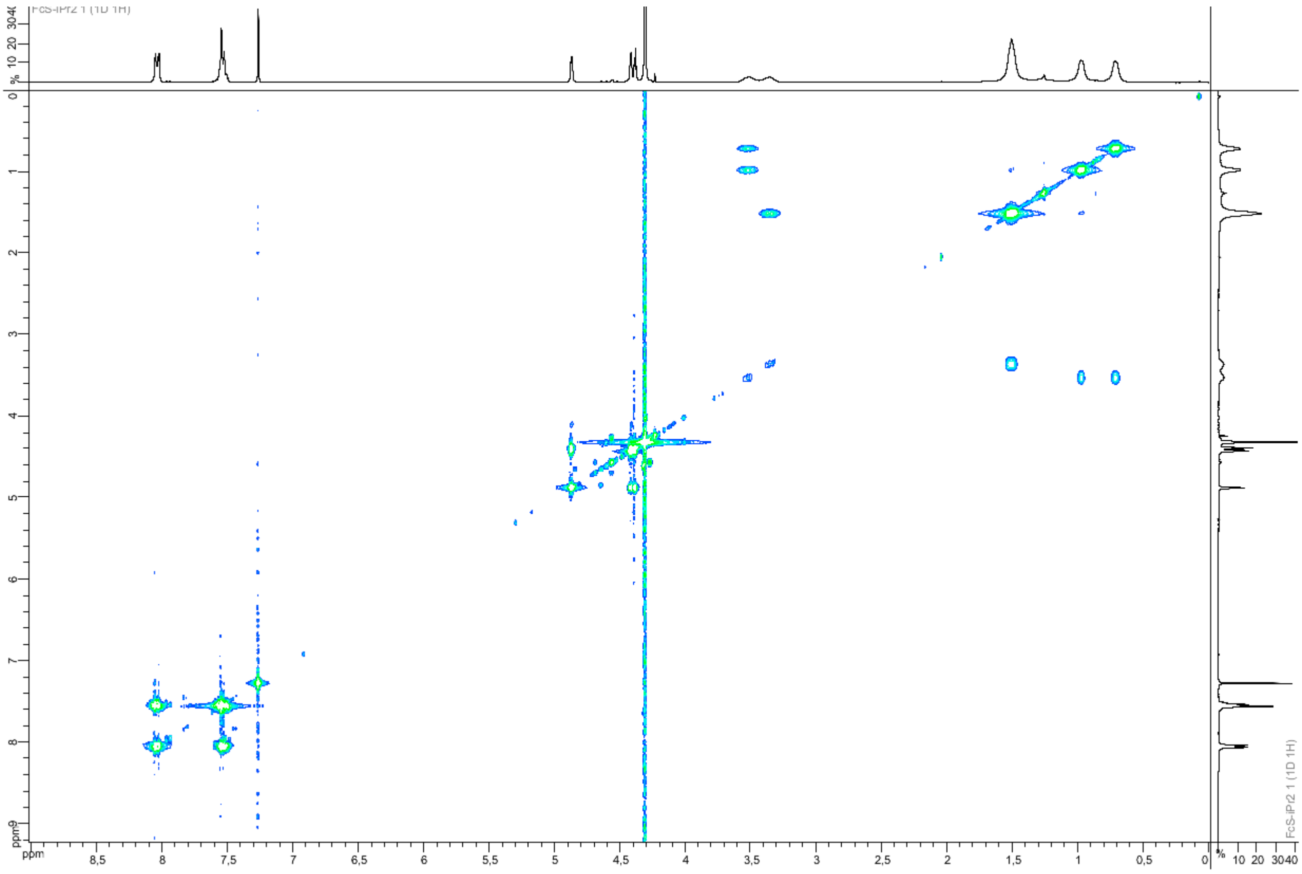
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



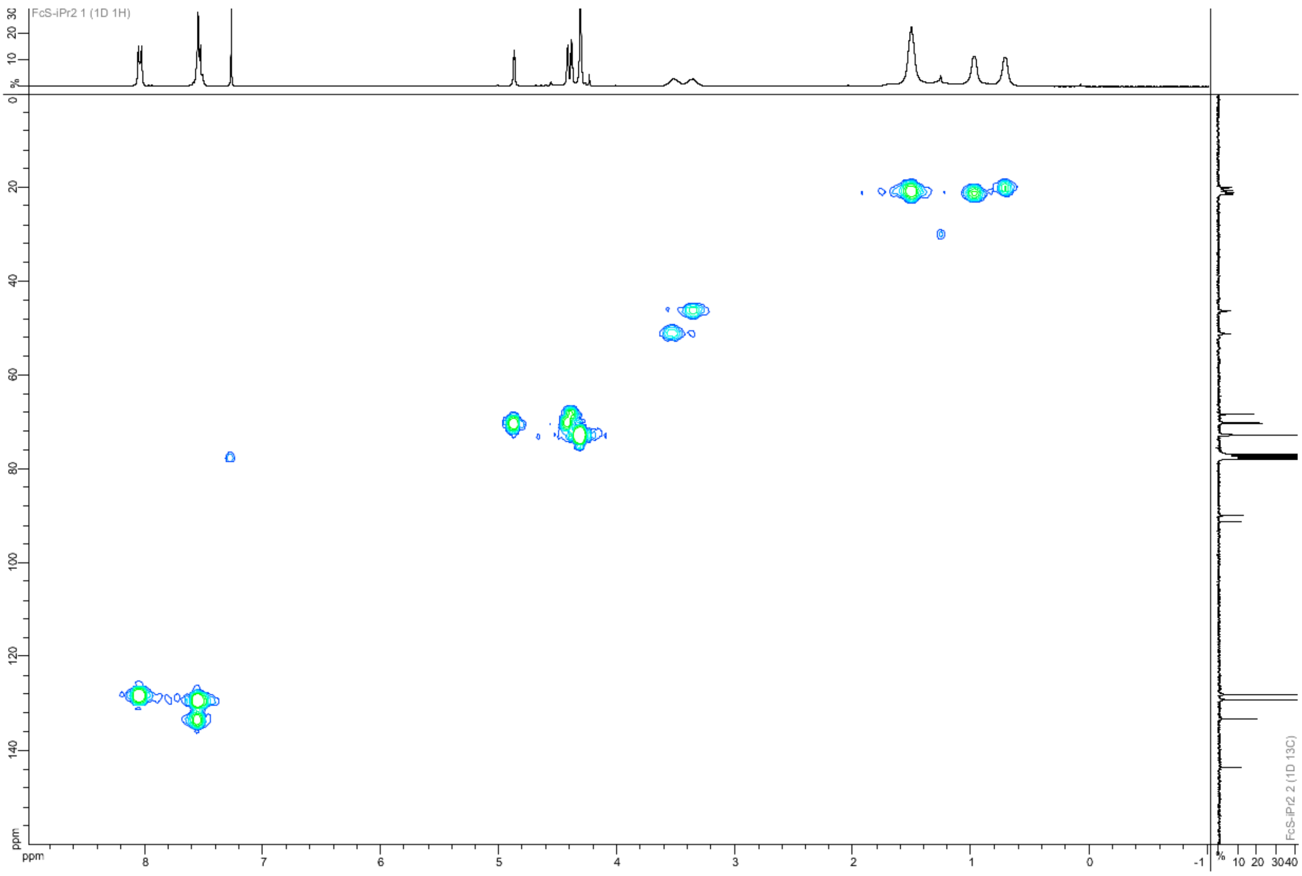
DEPT 135 (75 MHz, $CDCl_3$, 291 K)



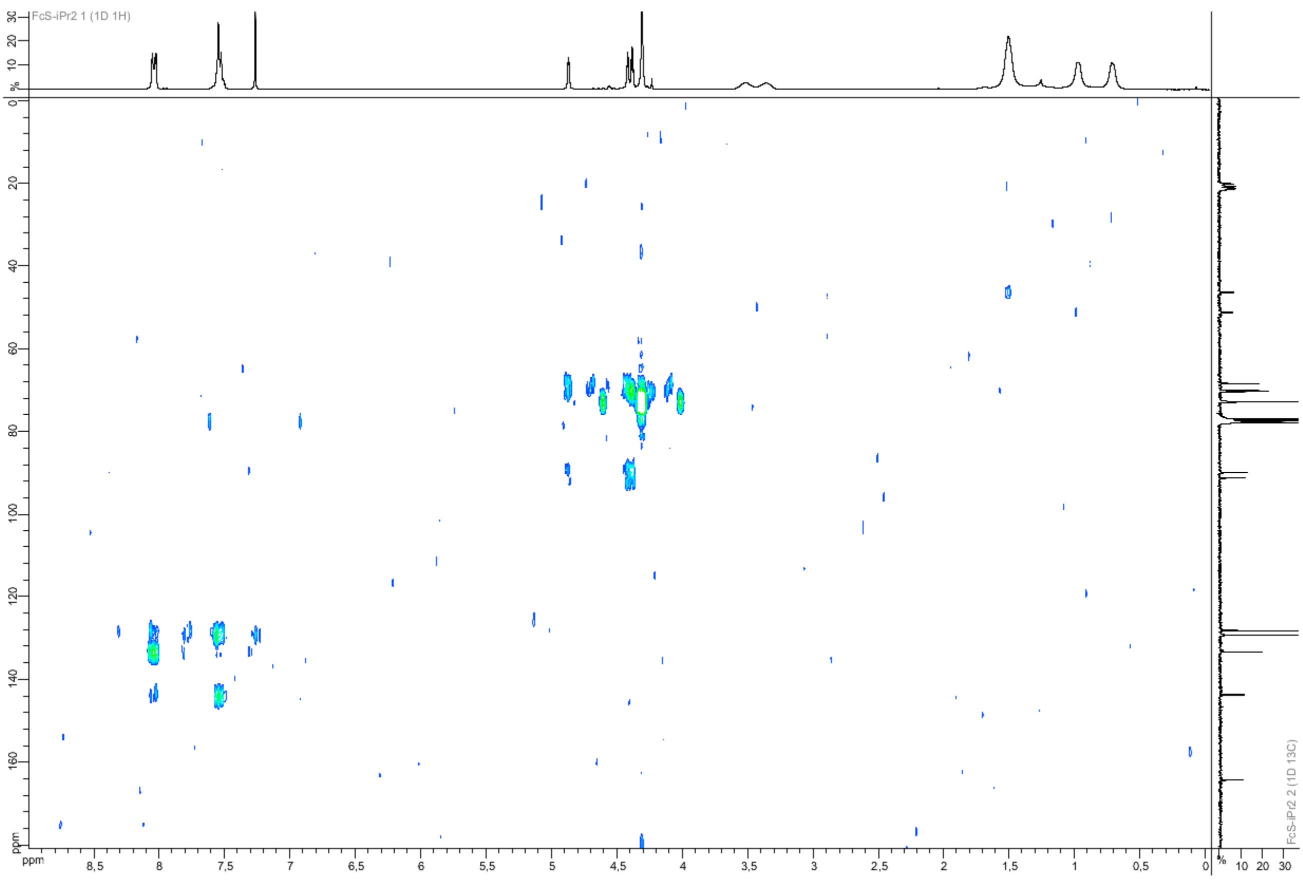
COSY (300 MHz, $CDCl_3$, 291 K)



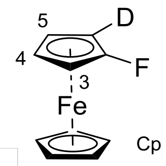
HSQC (300 MHz, $CDCl_3$, 291 K)



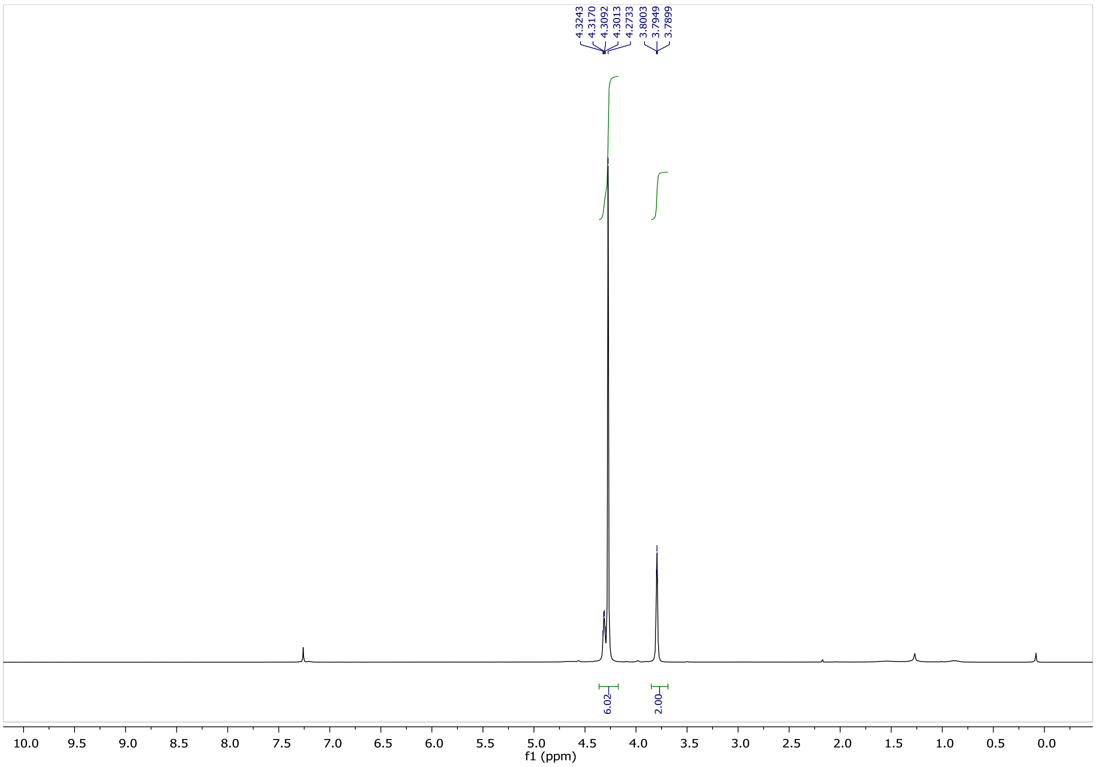
HMBC (300 MHz, $CDCl_3$, 291 K)



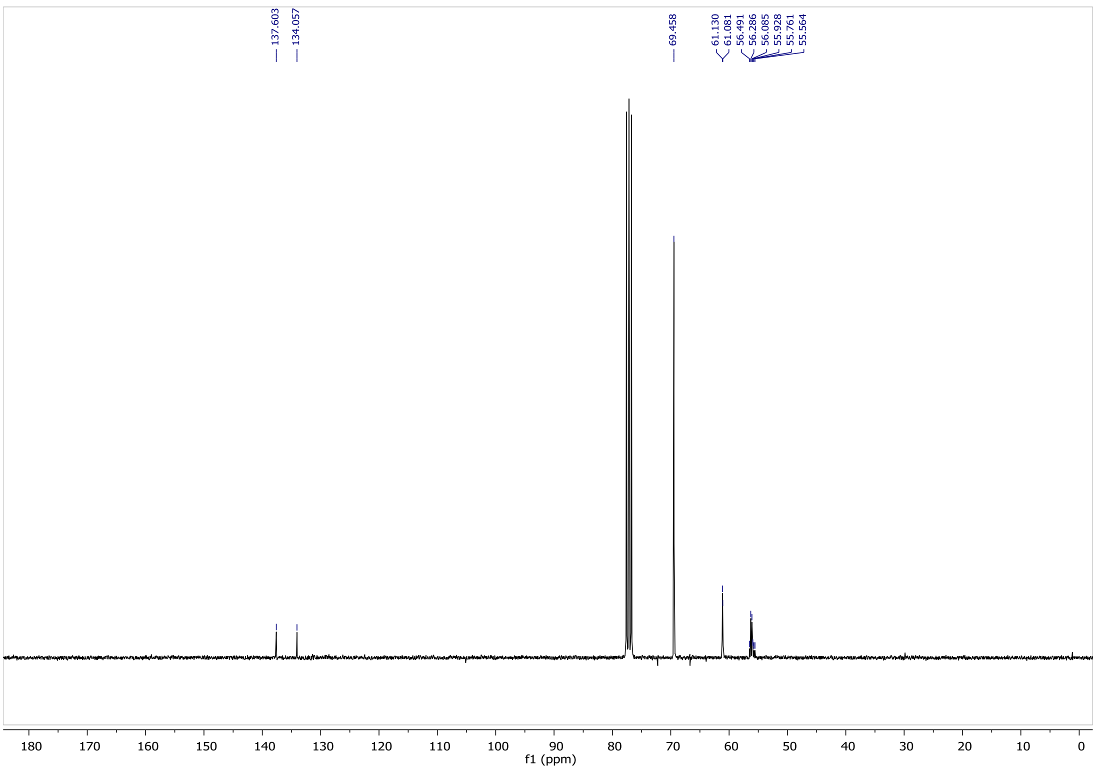
Compound 3a (racemic mixture)



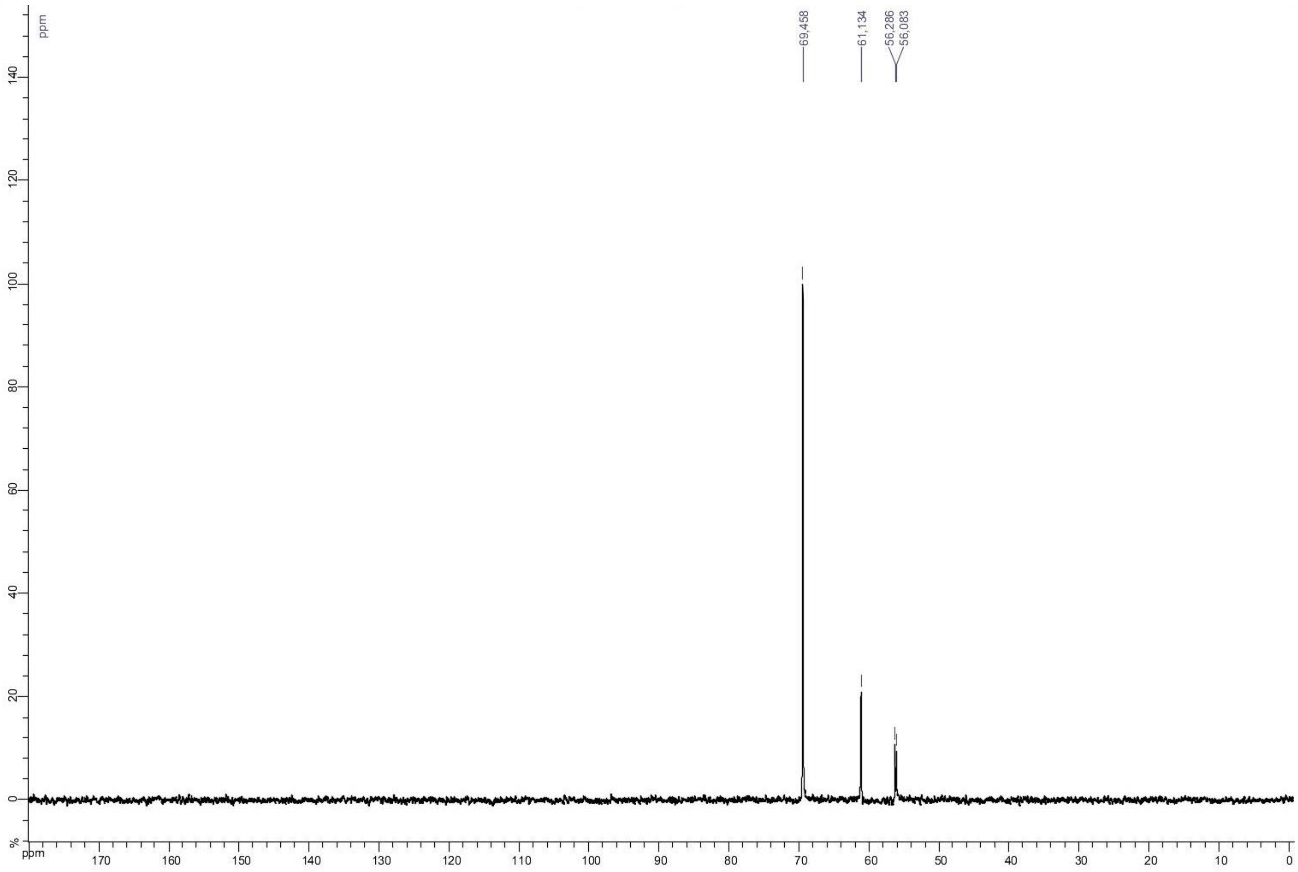
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



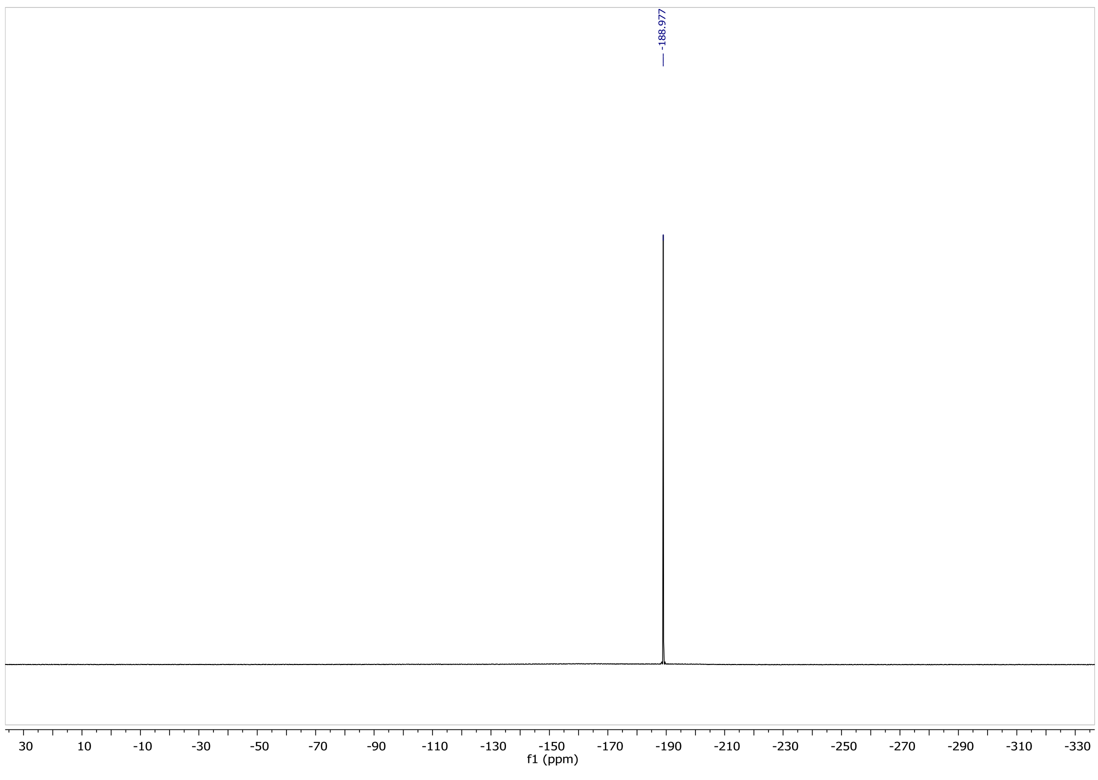
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



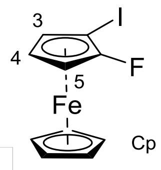
DEPT-135 (75 MHz, $CDCl_3$, 291 K)



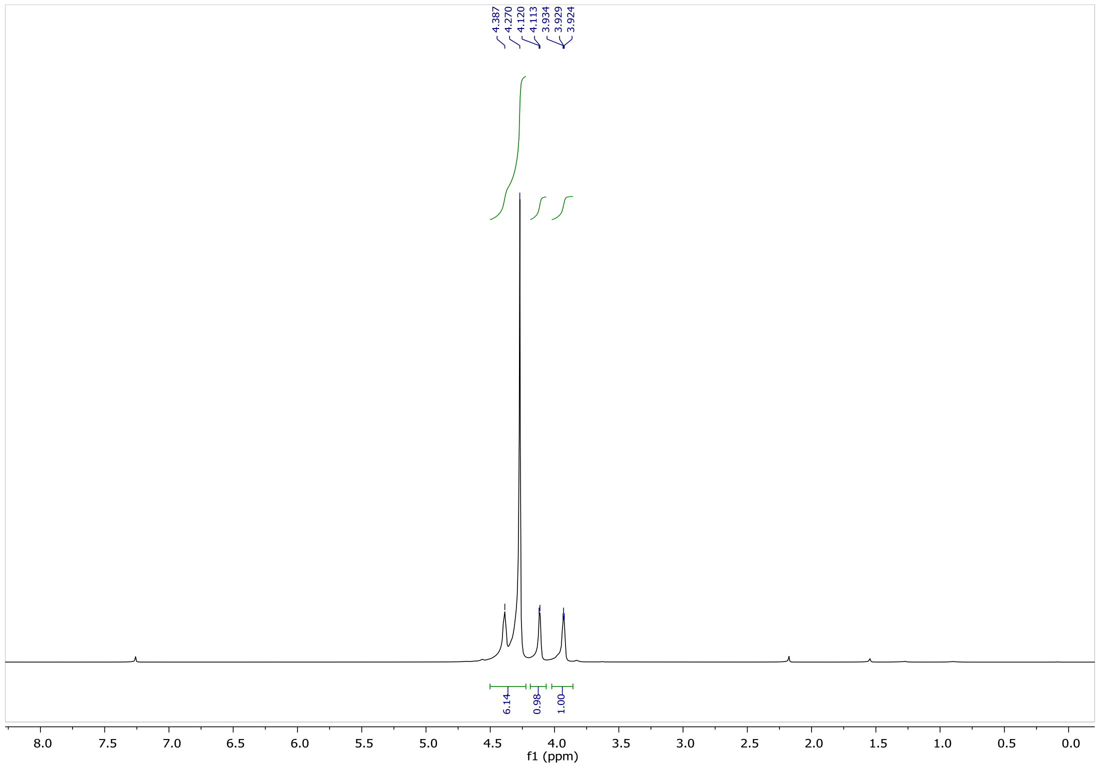
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



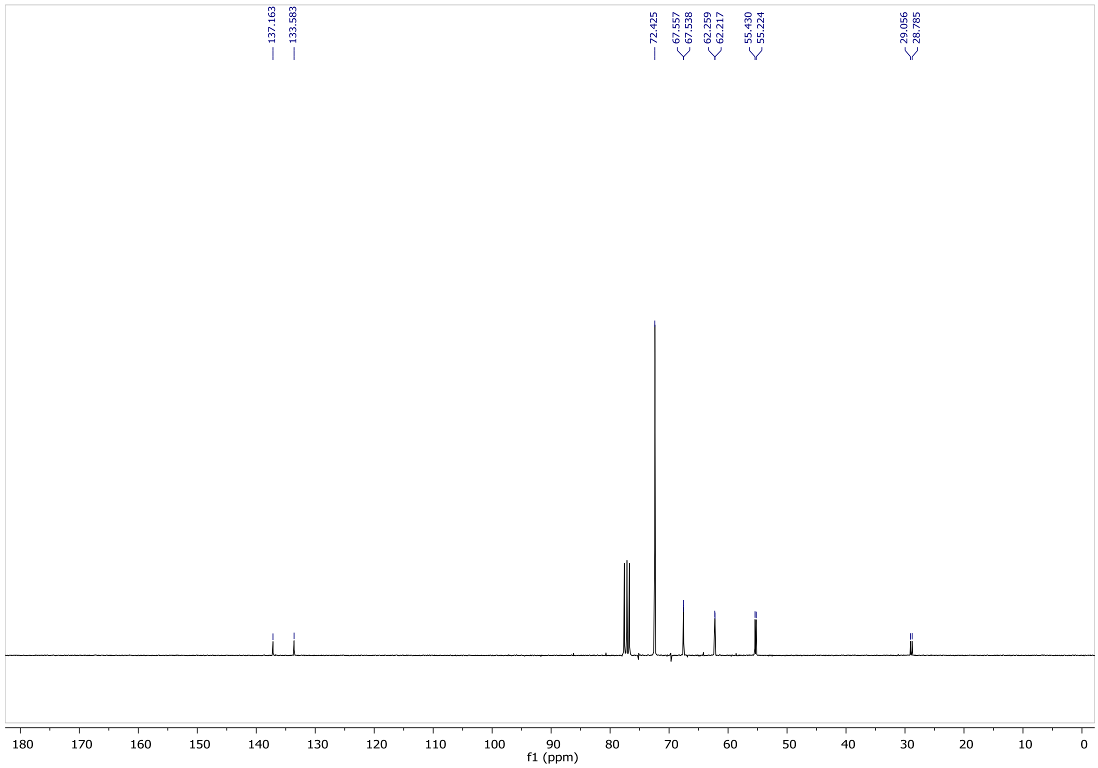
Compound 3b (racemic mixture)



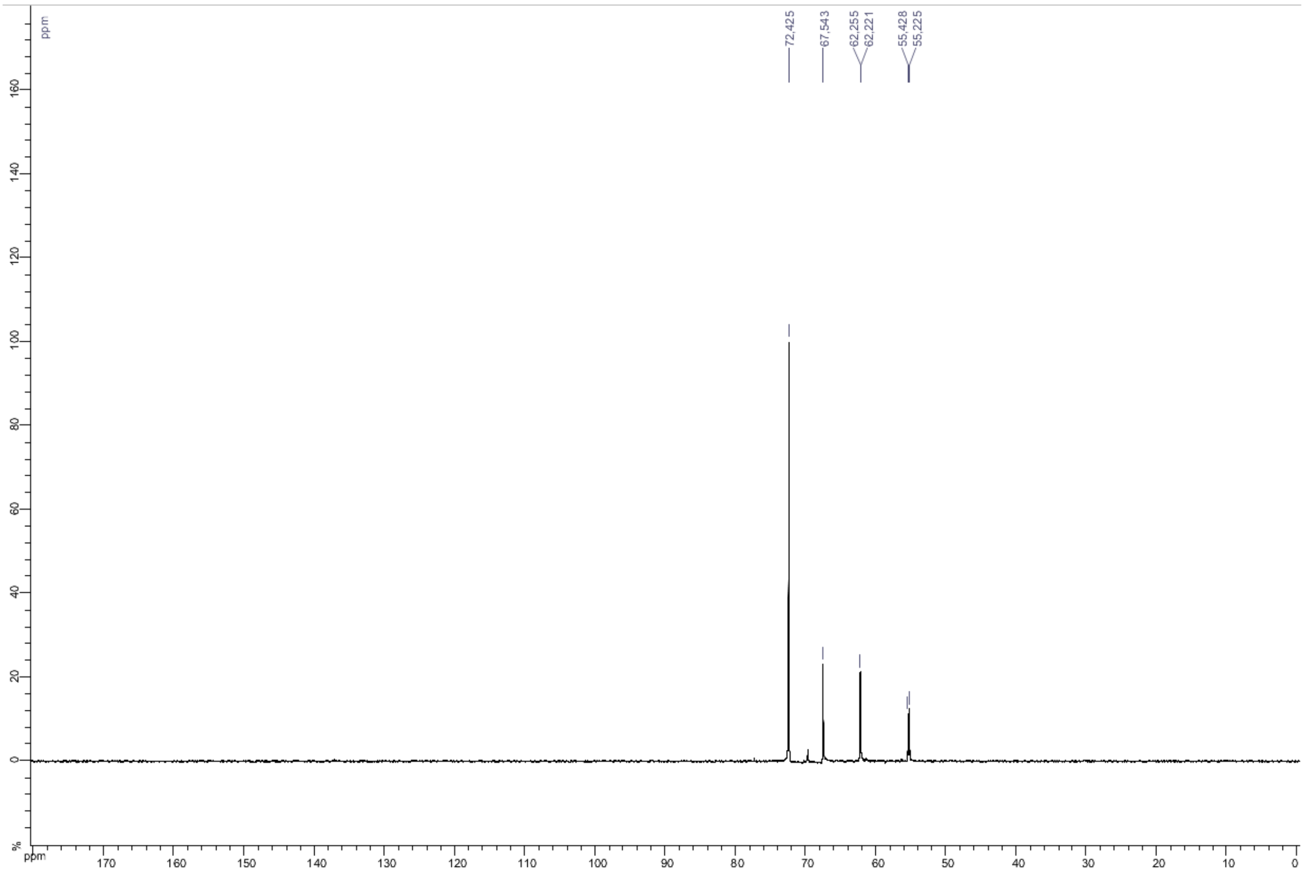
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



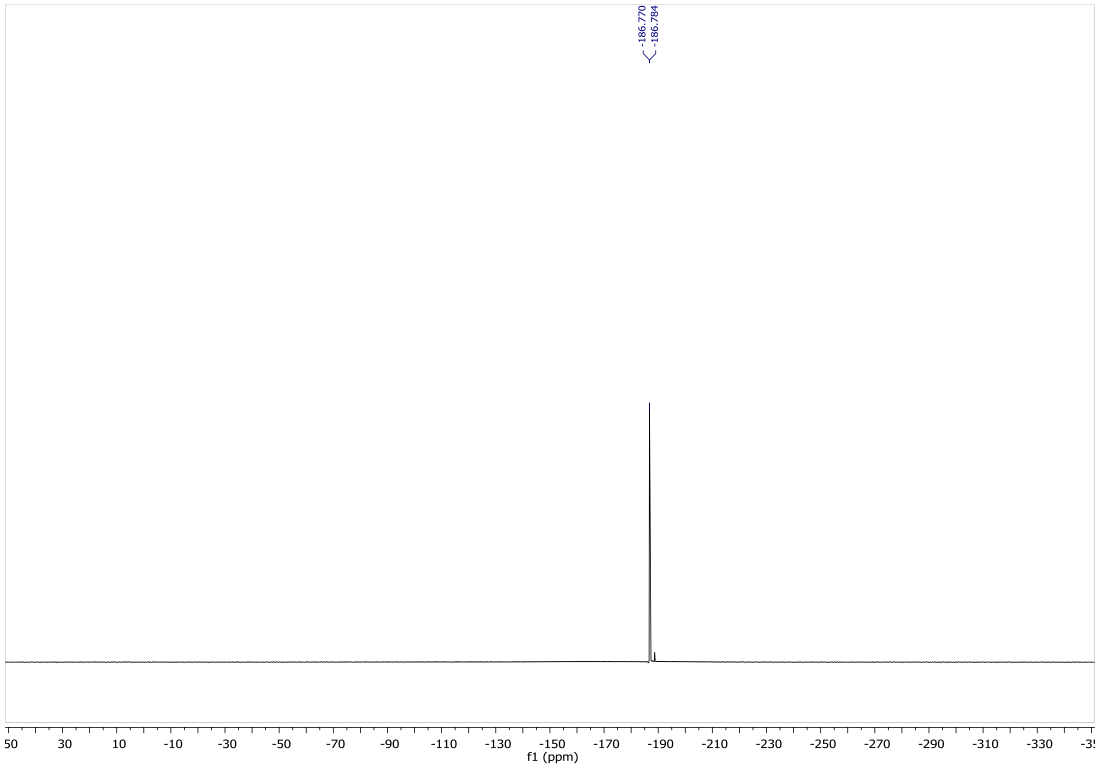
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



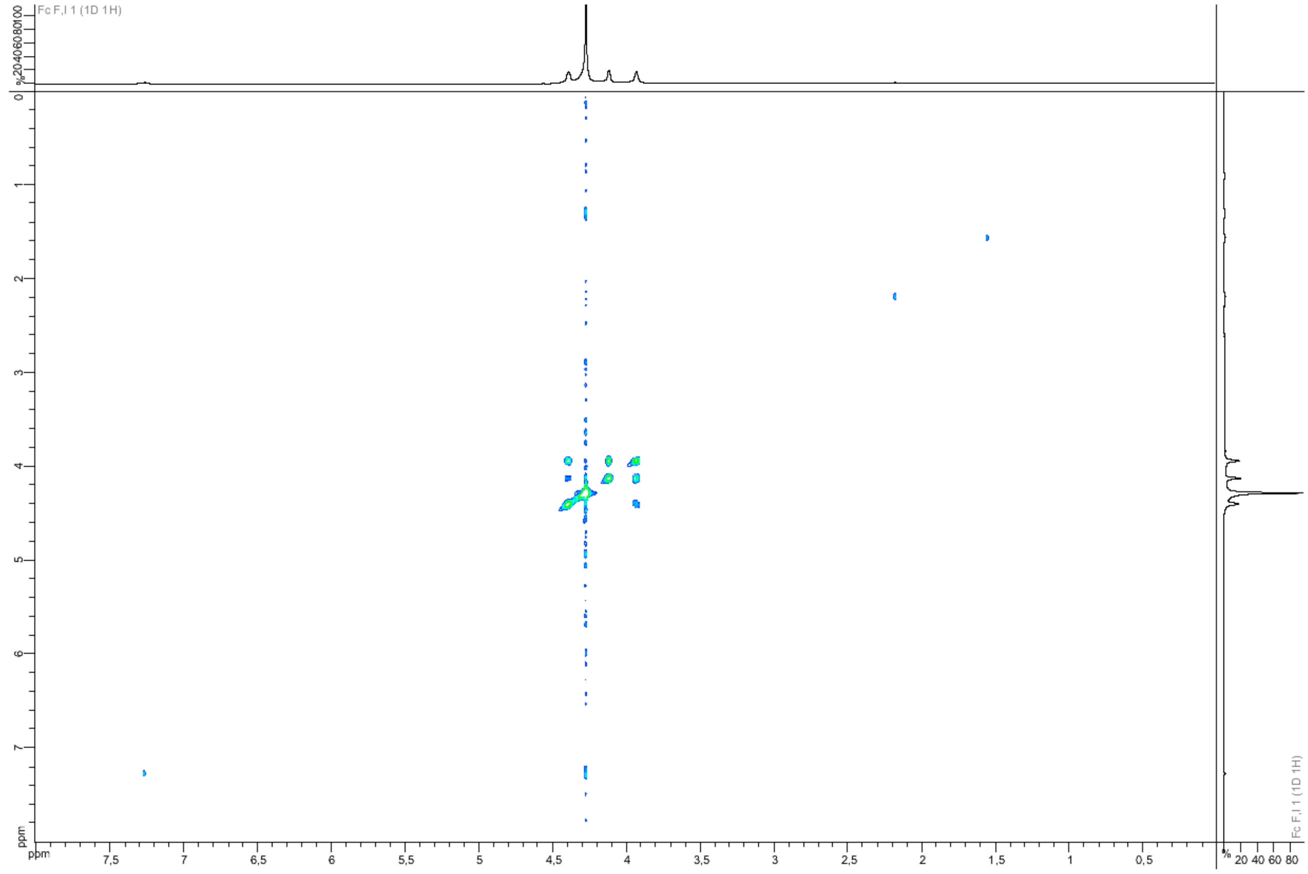
DEPT-135 (75 MHz, $CDCl_3$, 291 K)



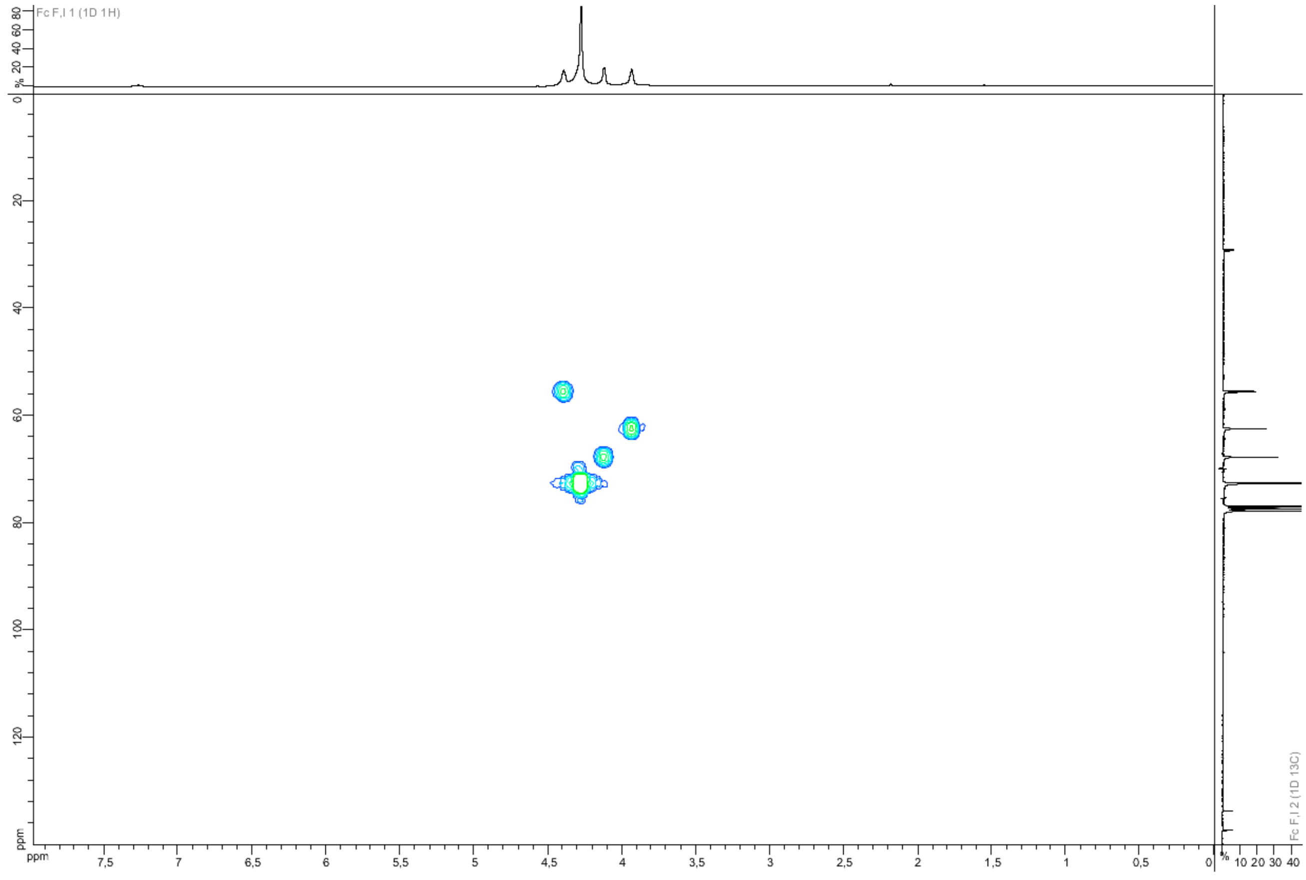
[19]F NMR (282 MHz, $CDCl_3$, 291 K)



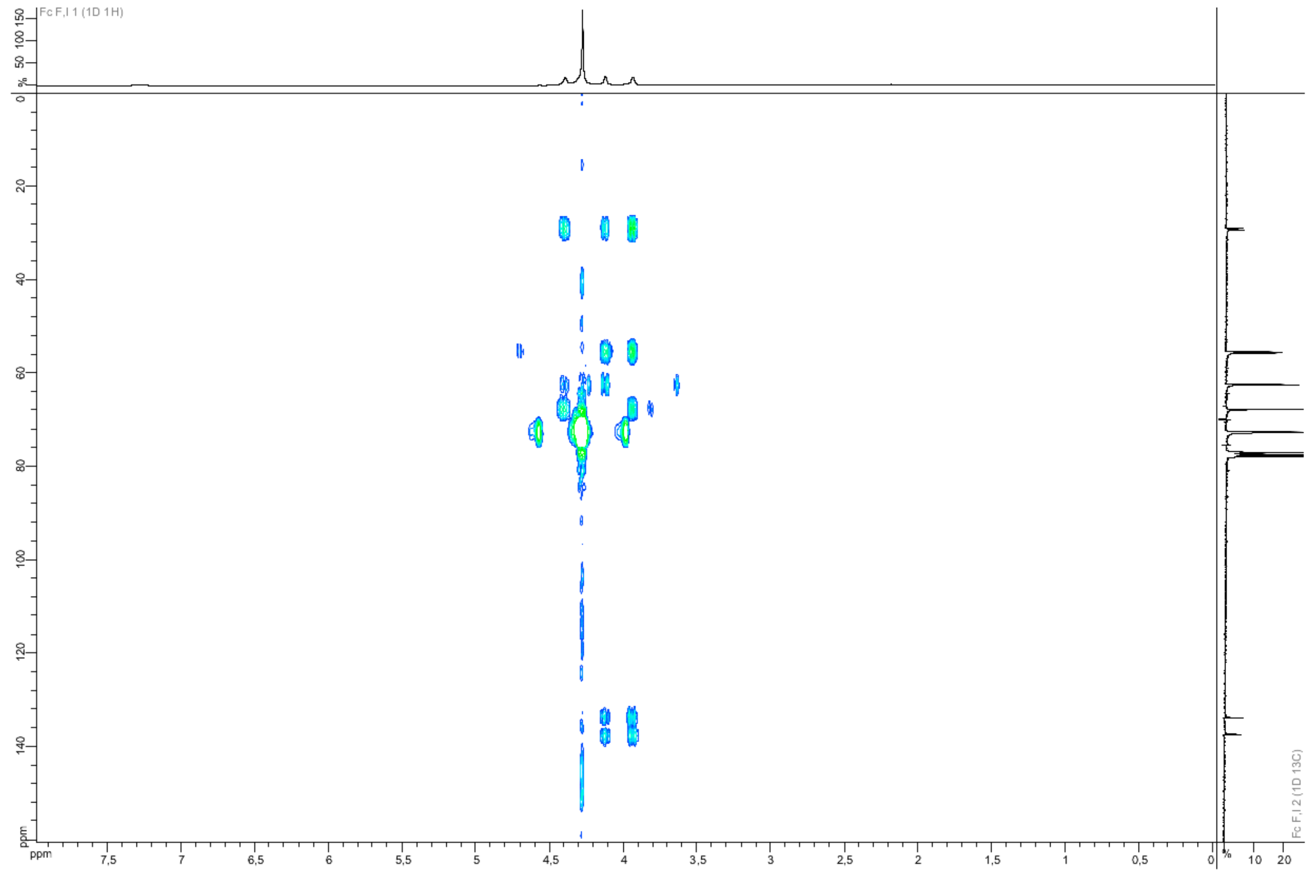
COSY (300 MHz, $CDCl_3$, 291 K)



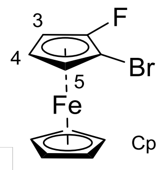
HSQC (300 MHz, $CDCl_3$, 291 K)



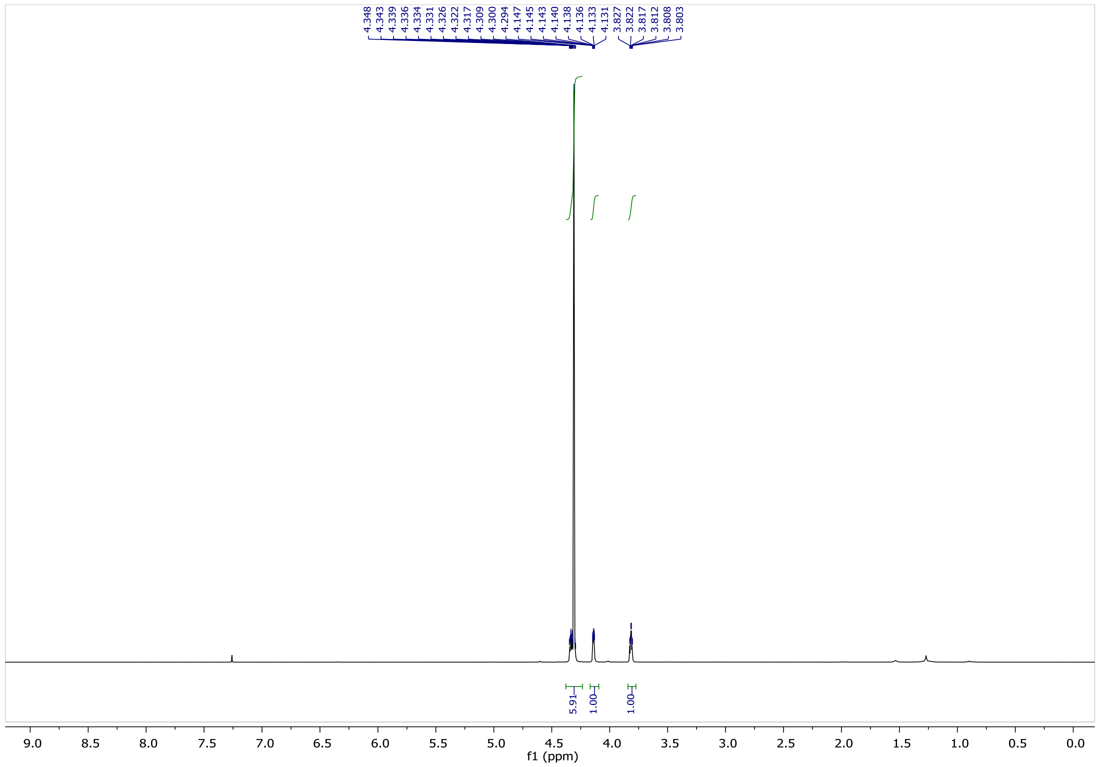
HMBC (300 MHz, $CDCl_3$, 291 K)



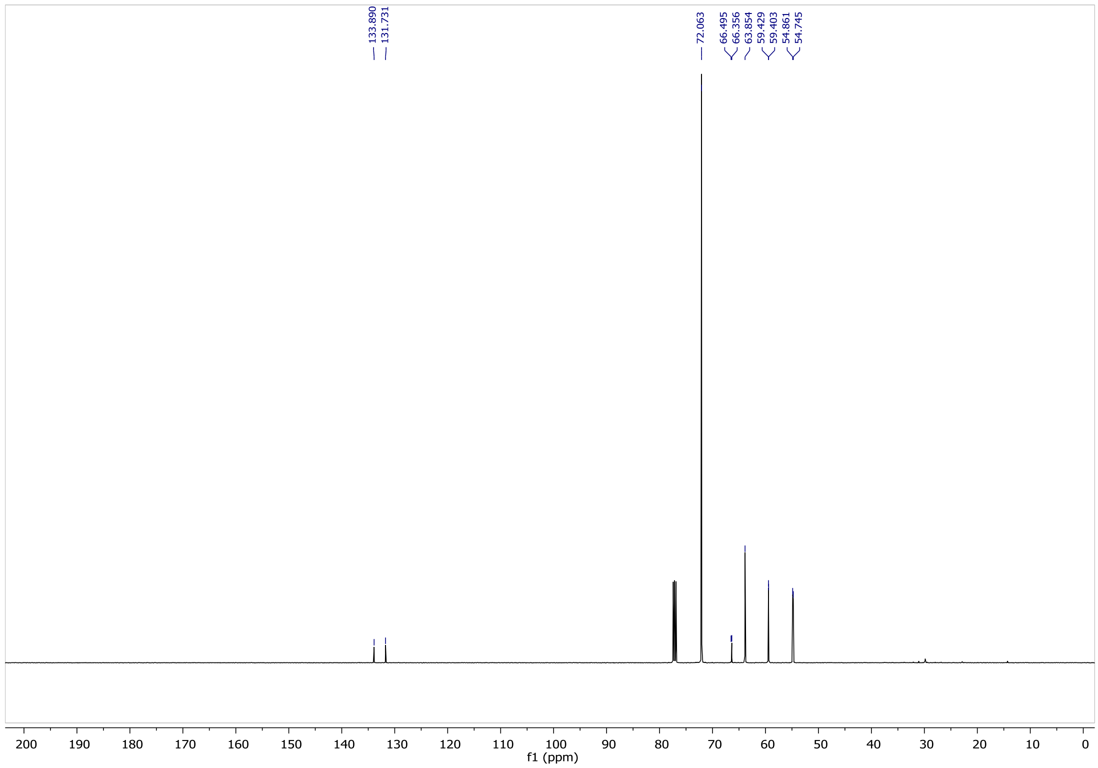
Compound 3c (racemic mixture)



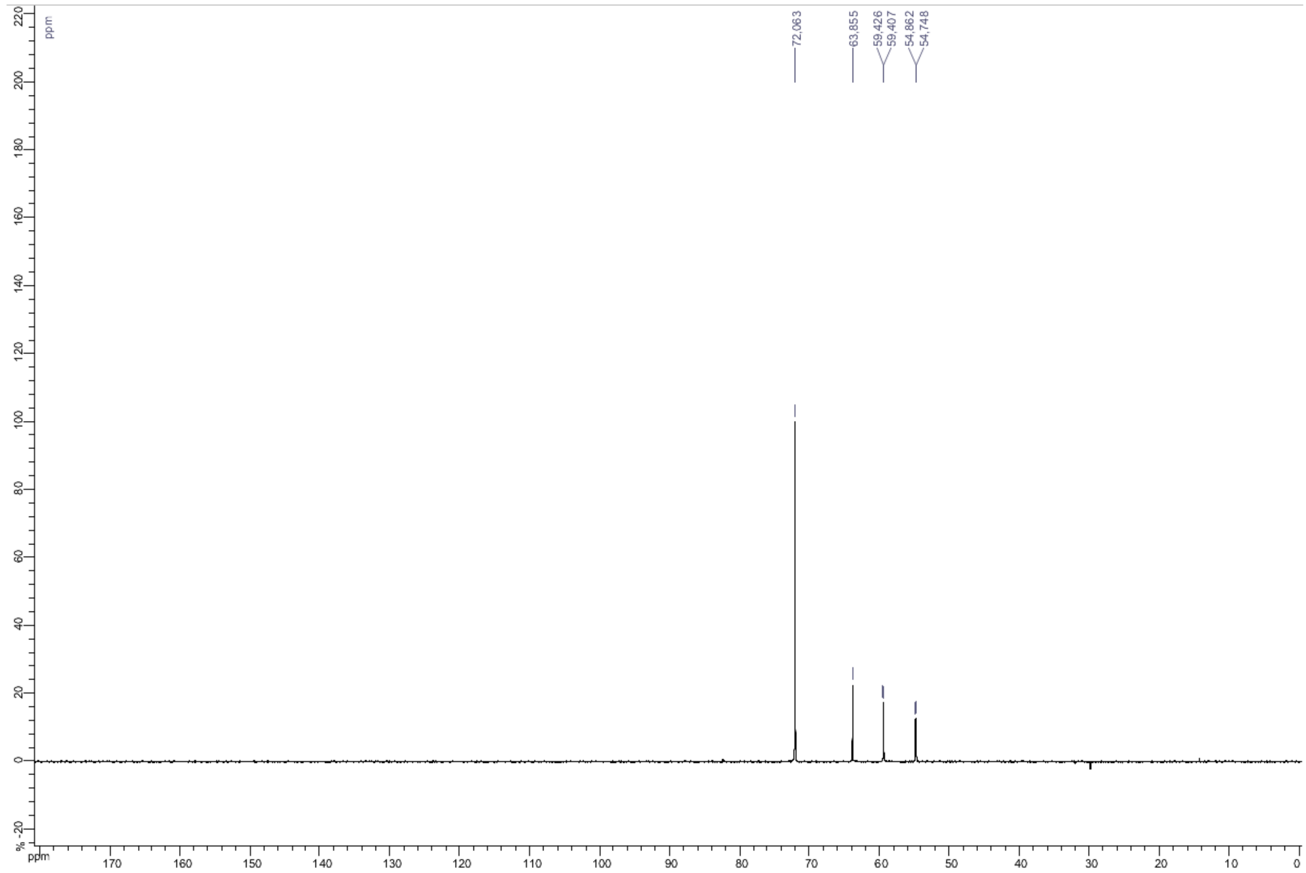
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



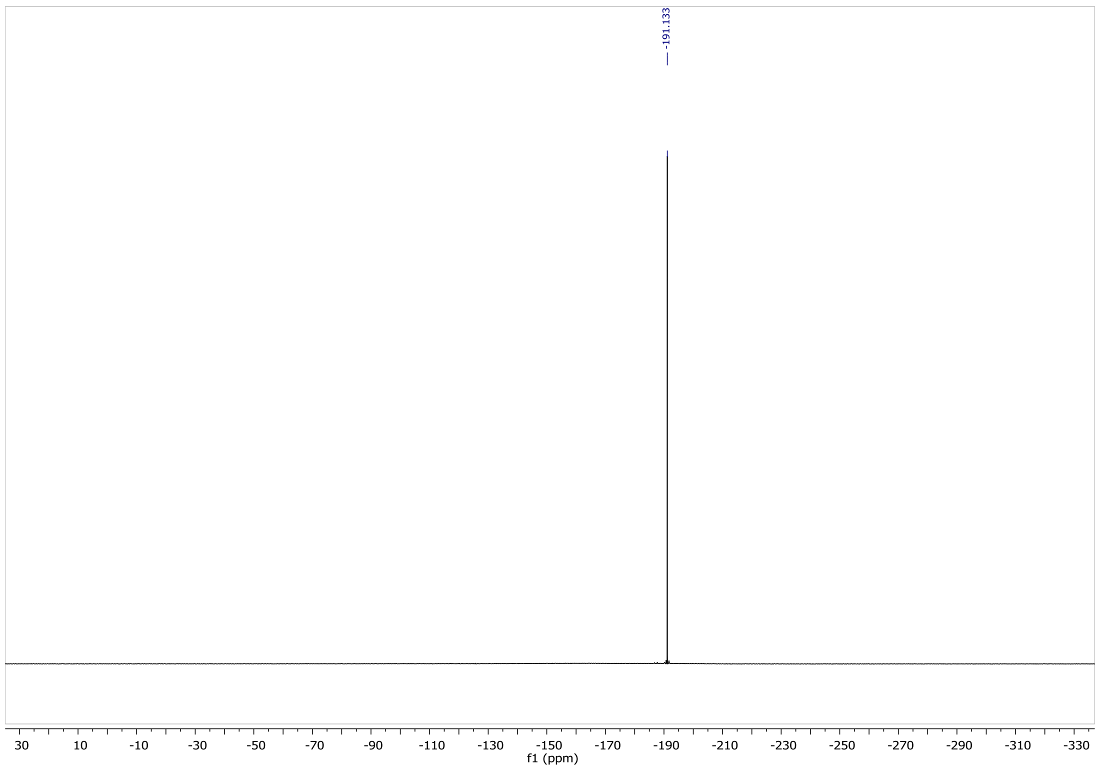
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



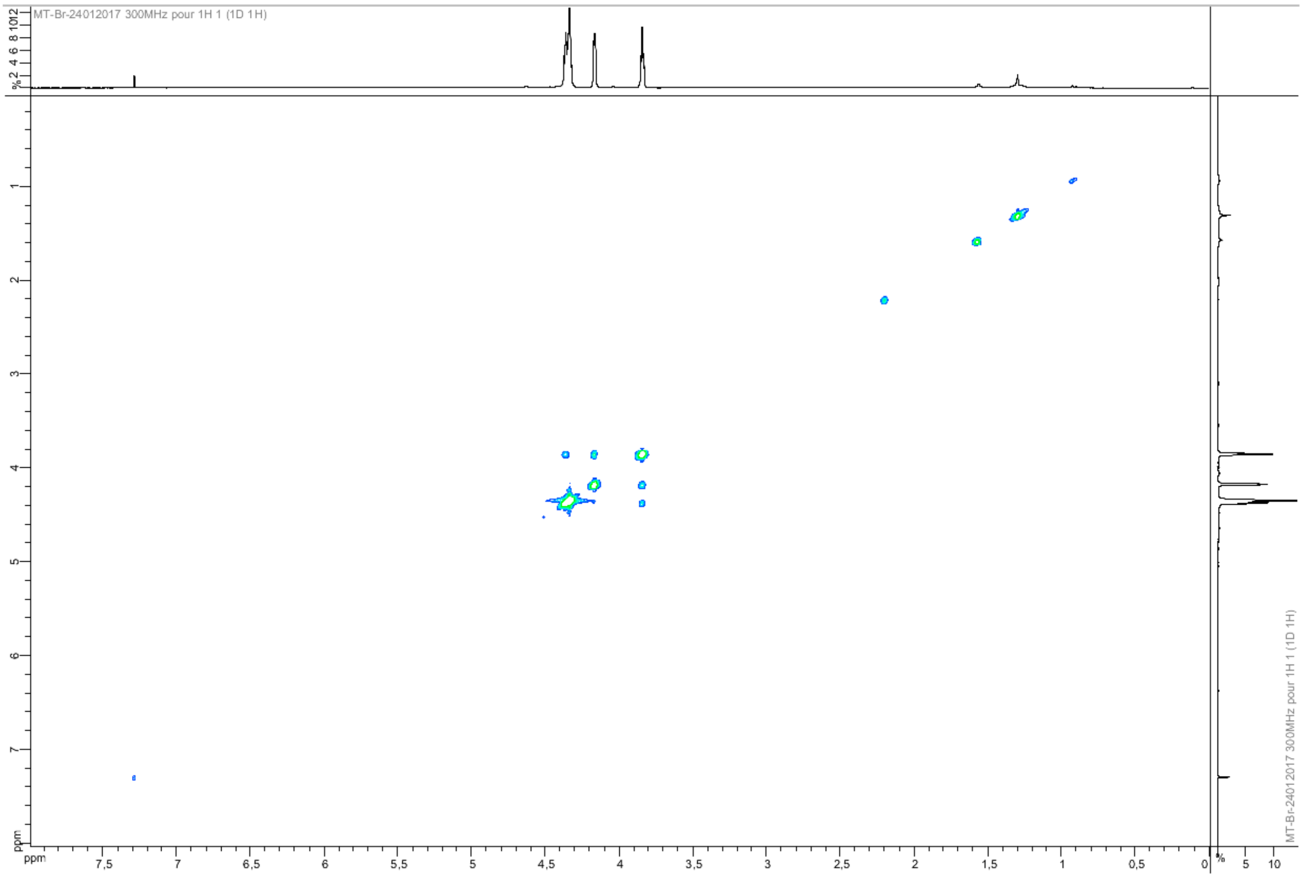
DEPT-135 (126 MHz, $CDCl_3$, 291 K)



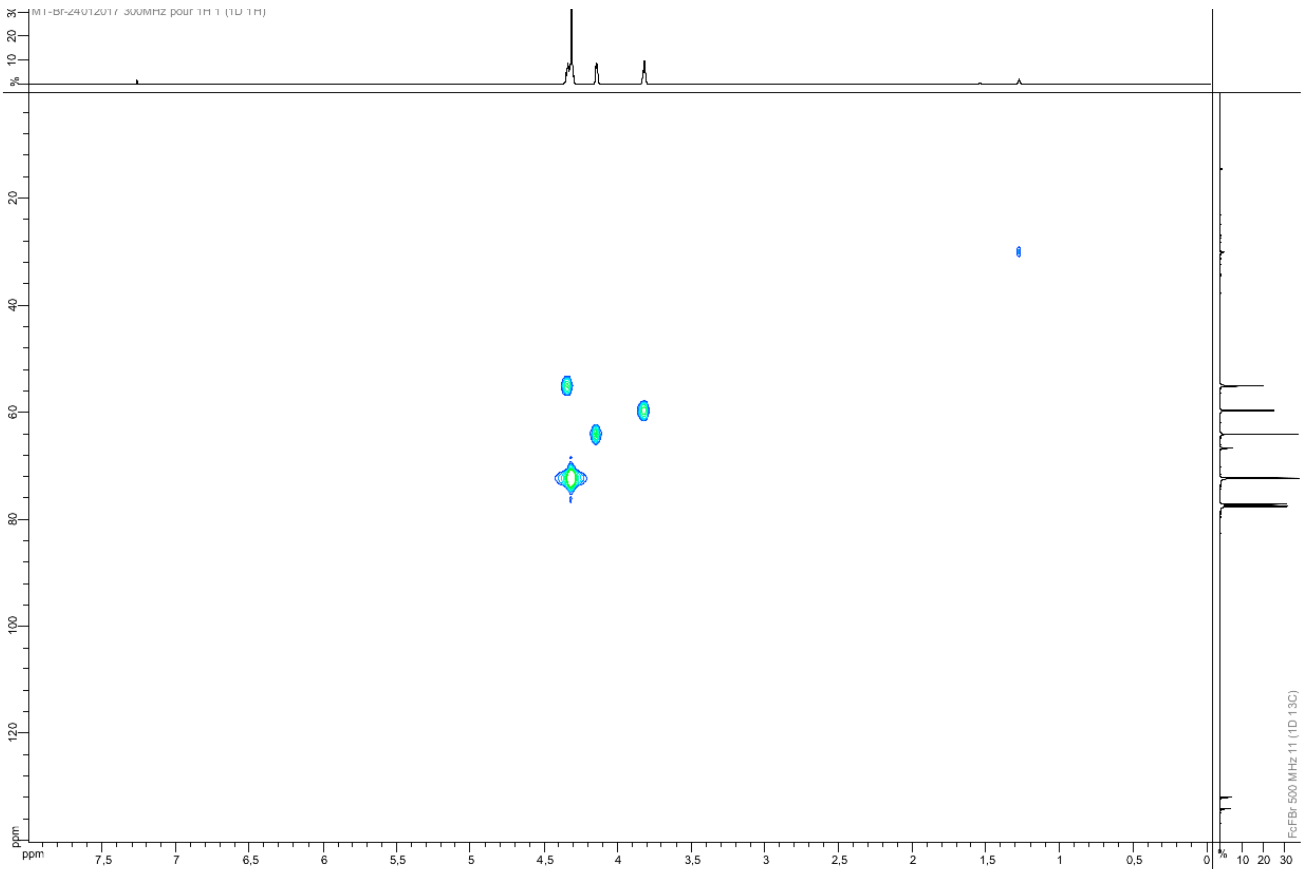
[19]F NMR (282 MHz, $CDCl_3$, 291 K)



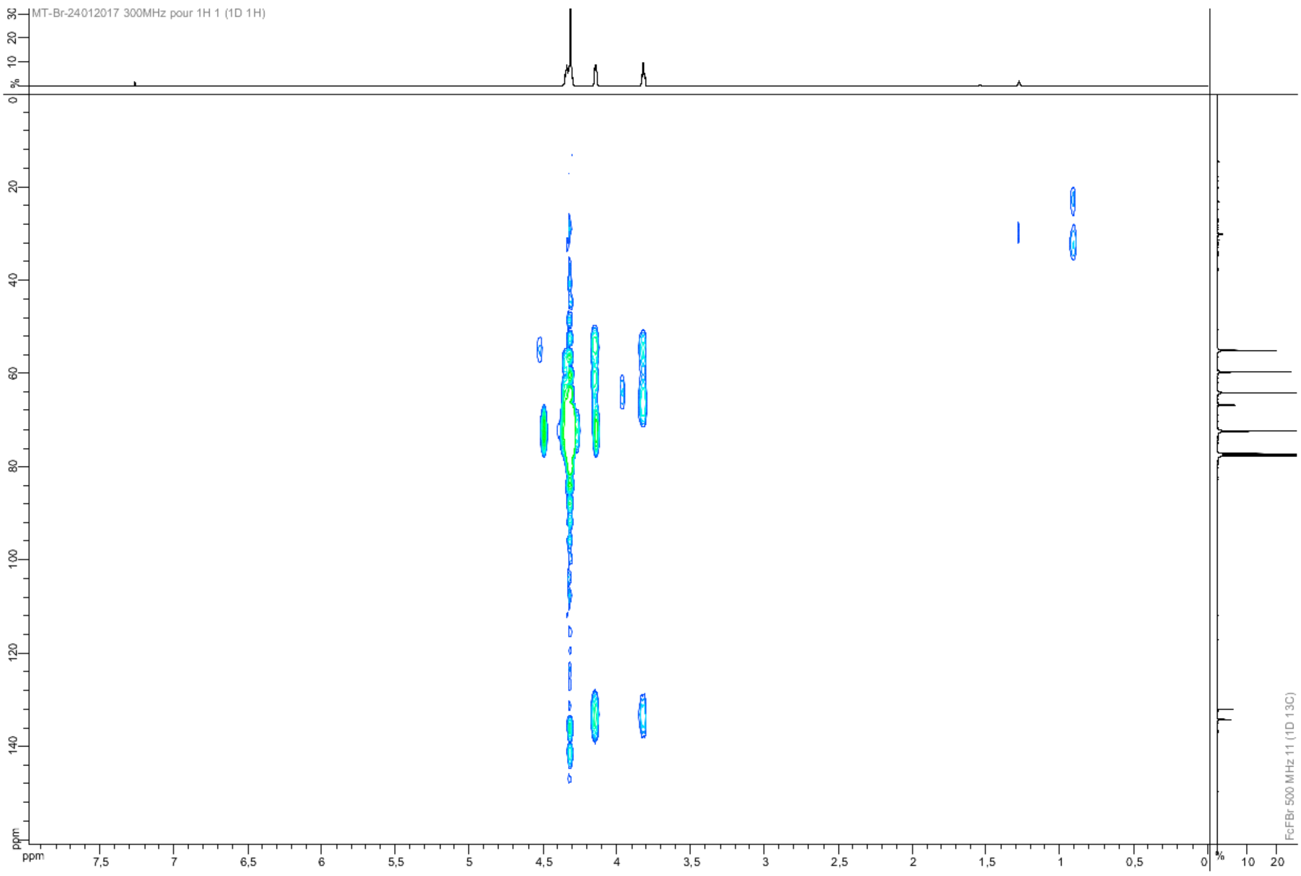
COSY (500 MHz, $CDCl_3$, 291 K)



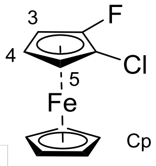
HSQC (500 MHz, $CDCl_3$, 291 K)



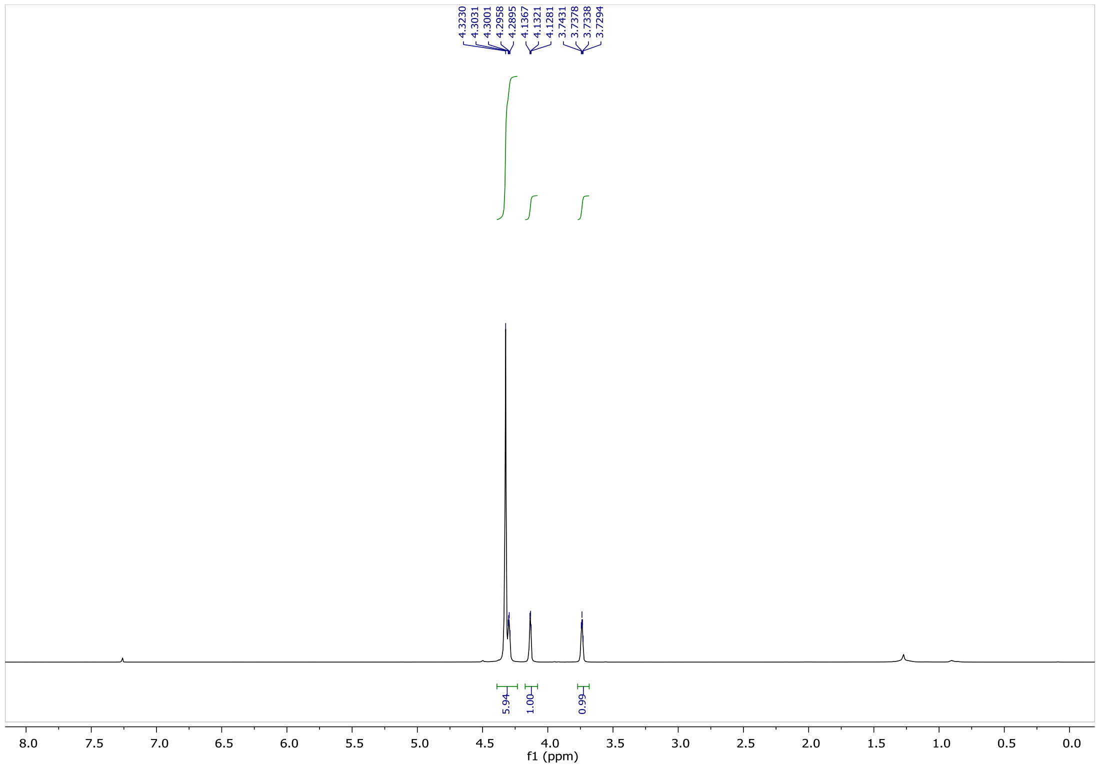
HMBC (500 MHz, $CDCl_3$, 291 K)



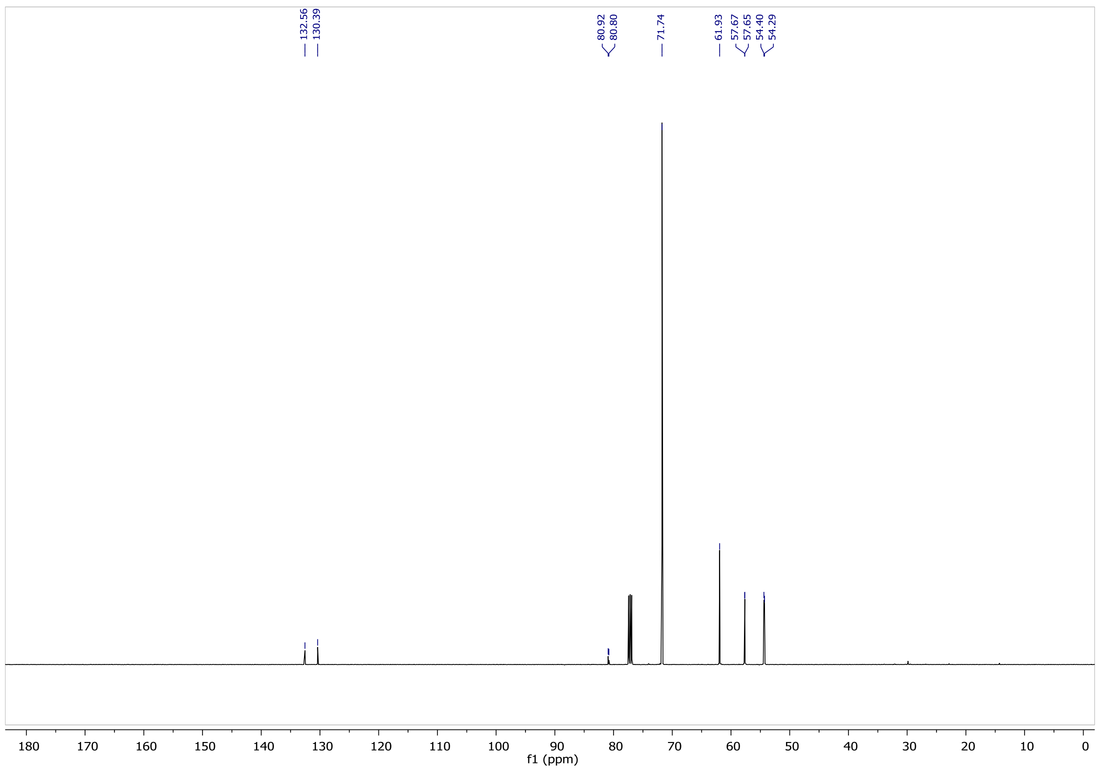
Compound 3d (racemic mixture)



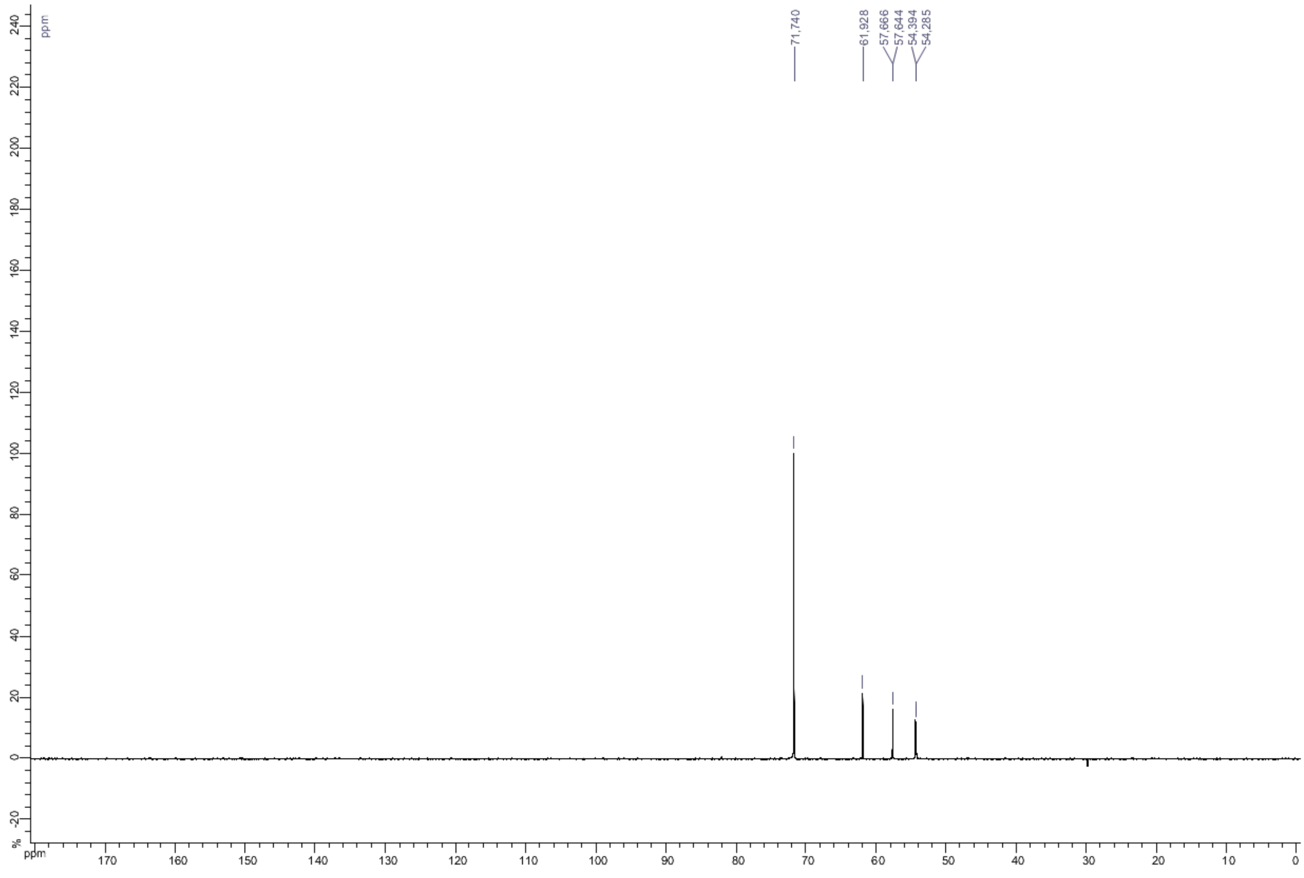
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



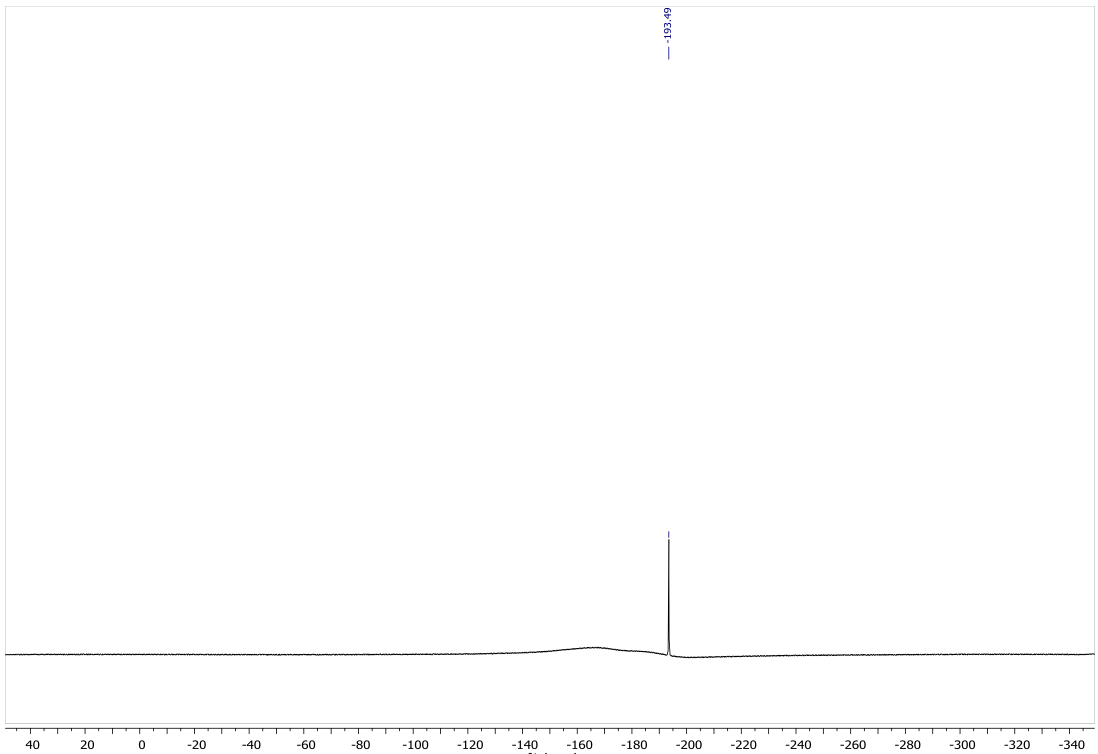
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



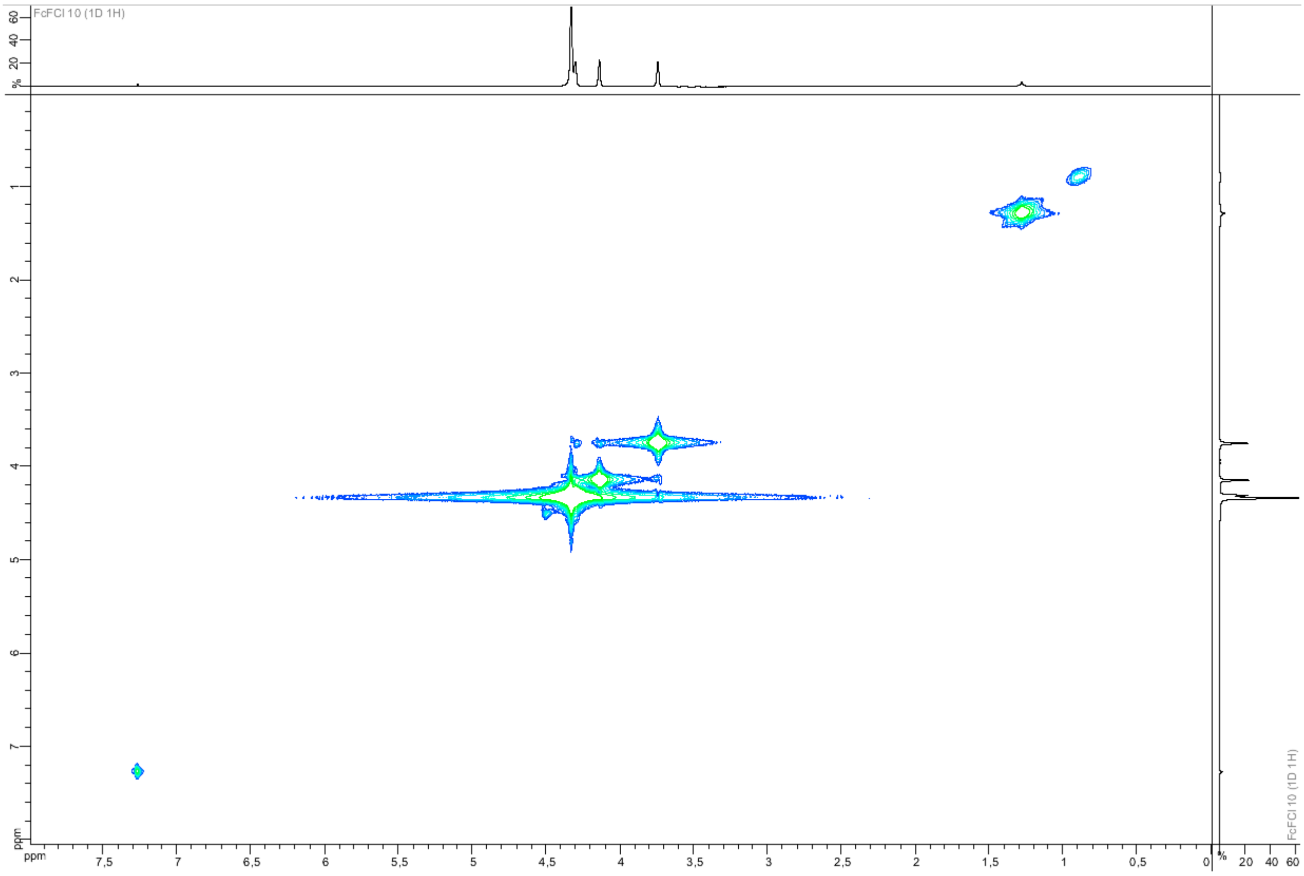
DEPT-135 (126 MHz, $CDCl_3$, 291 K)



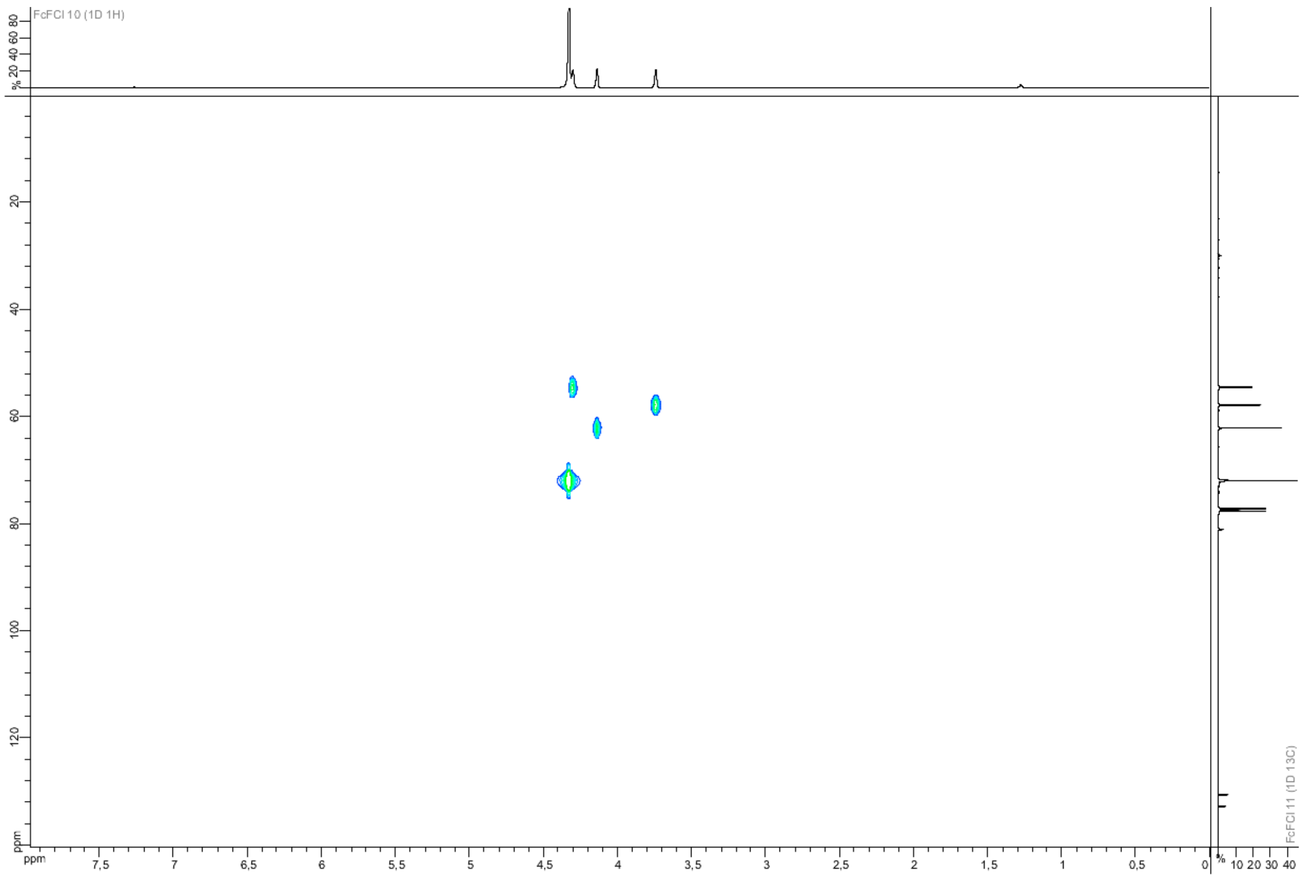
[19]F NMR (470 MHz, $CDCl_3$, 298 K)



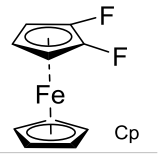
COSY (500 MHz, $CDCl_3$, 291 K)



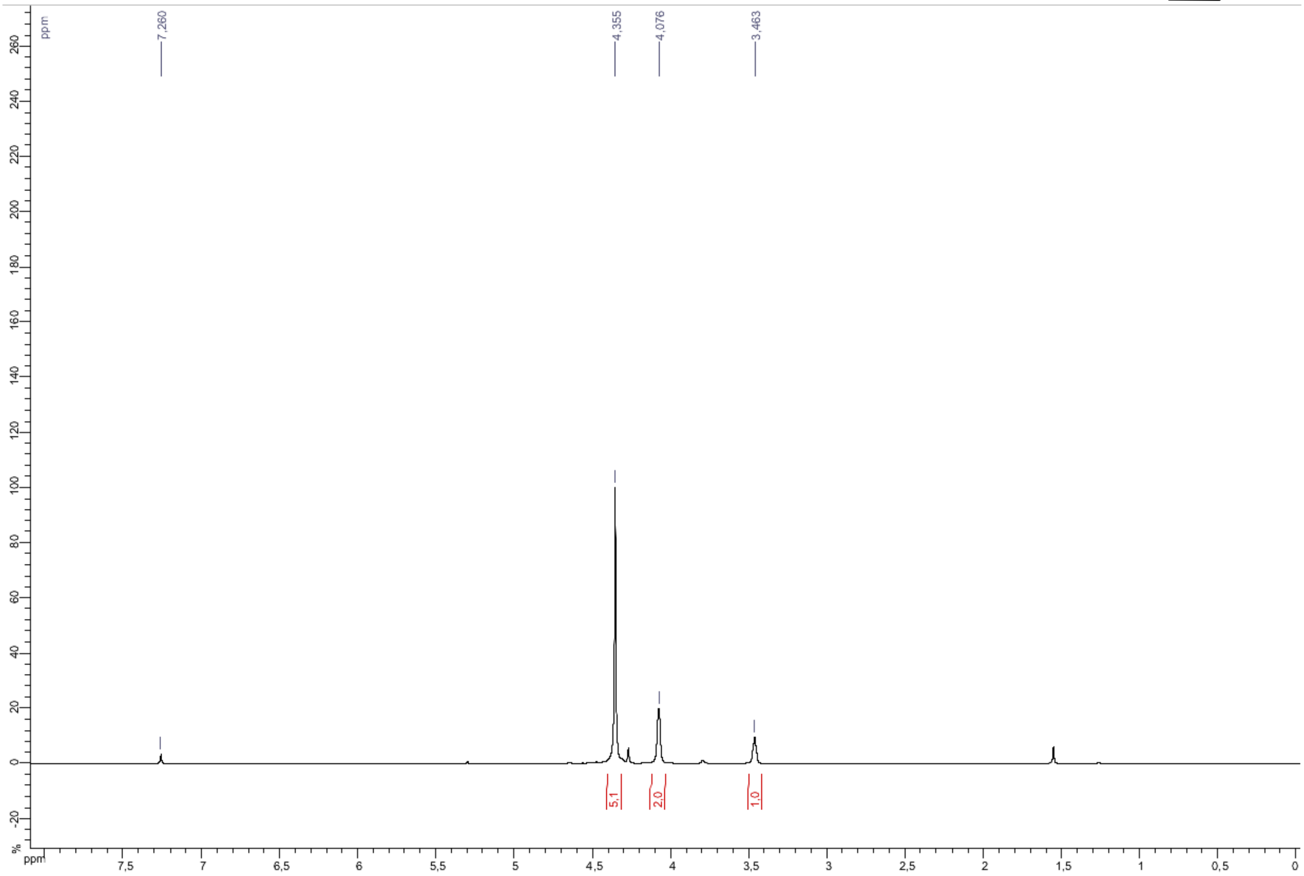
HSQC (500 MHz, $CDCl_3$, 291 K)



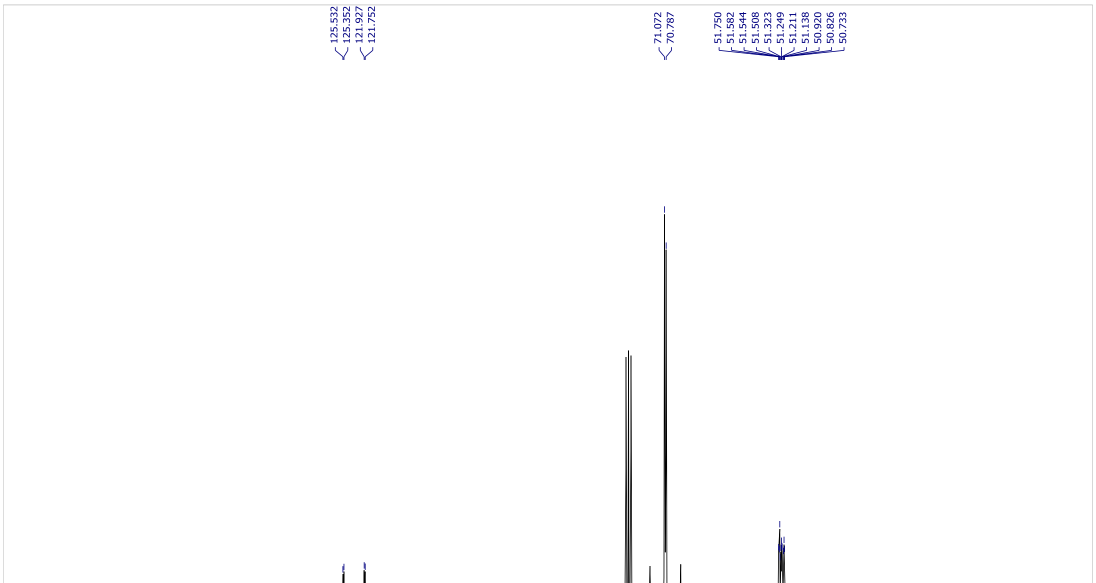
Compound 3e



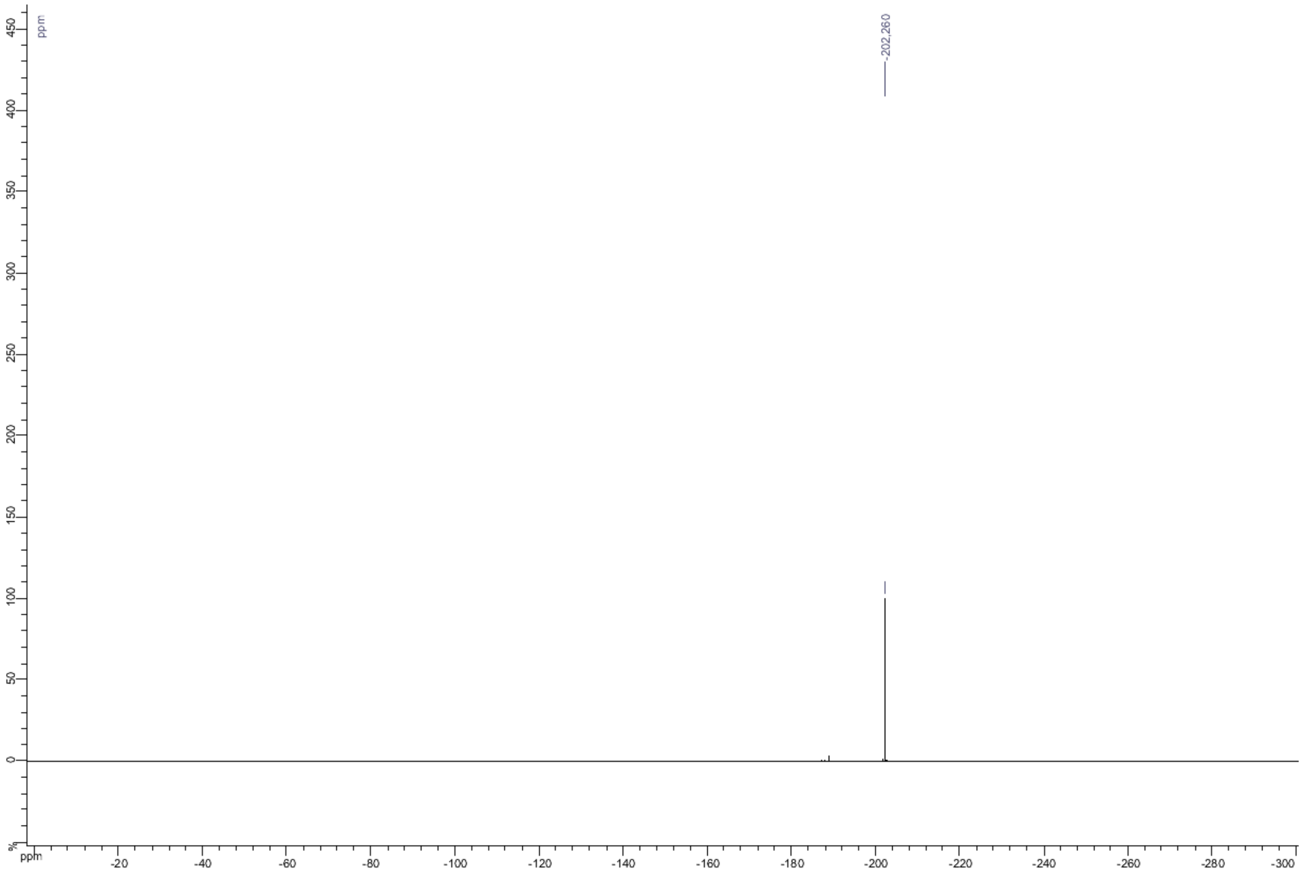
^{1}H NMR (300 MHz, $CDCl_3$, 298 K)



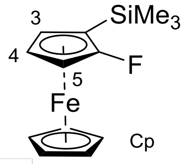
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



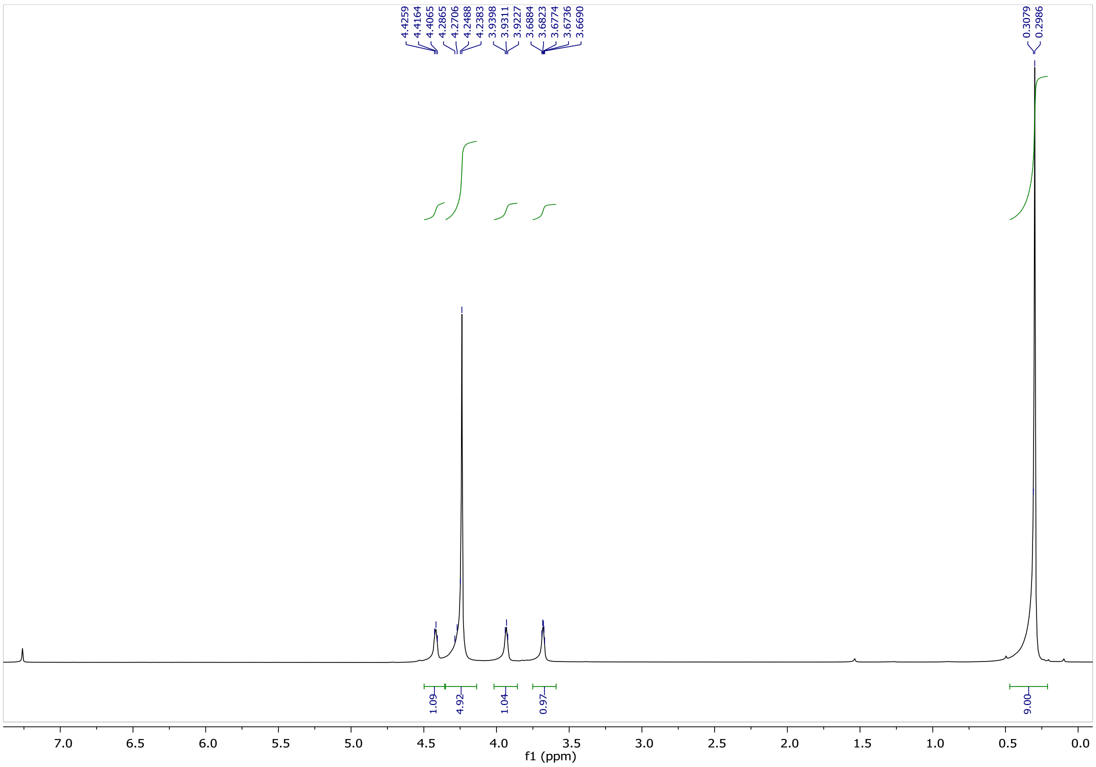
^{19}F NMR (282 MHz, $CDCl_3$, 298 K)



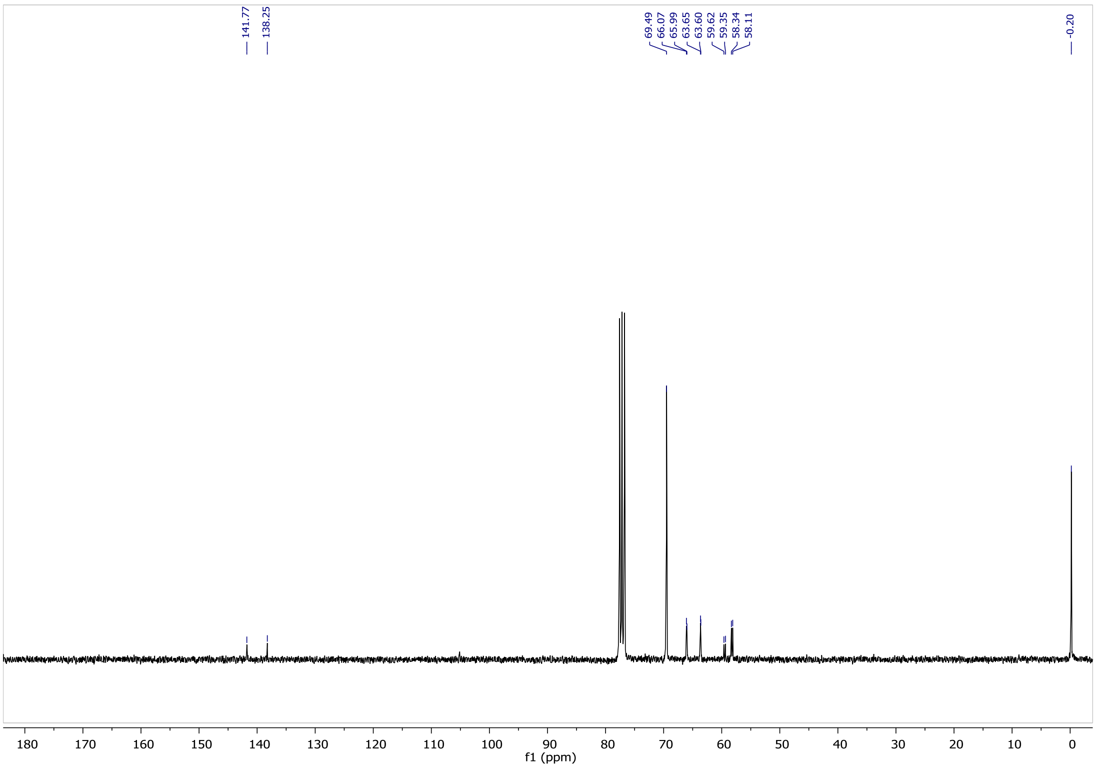
Compound 3f (racemic mixture)



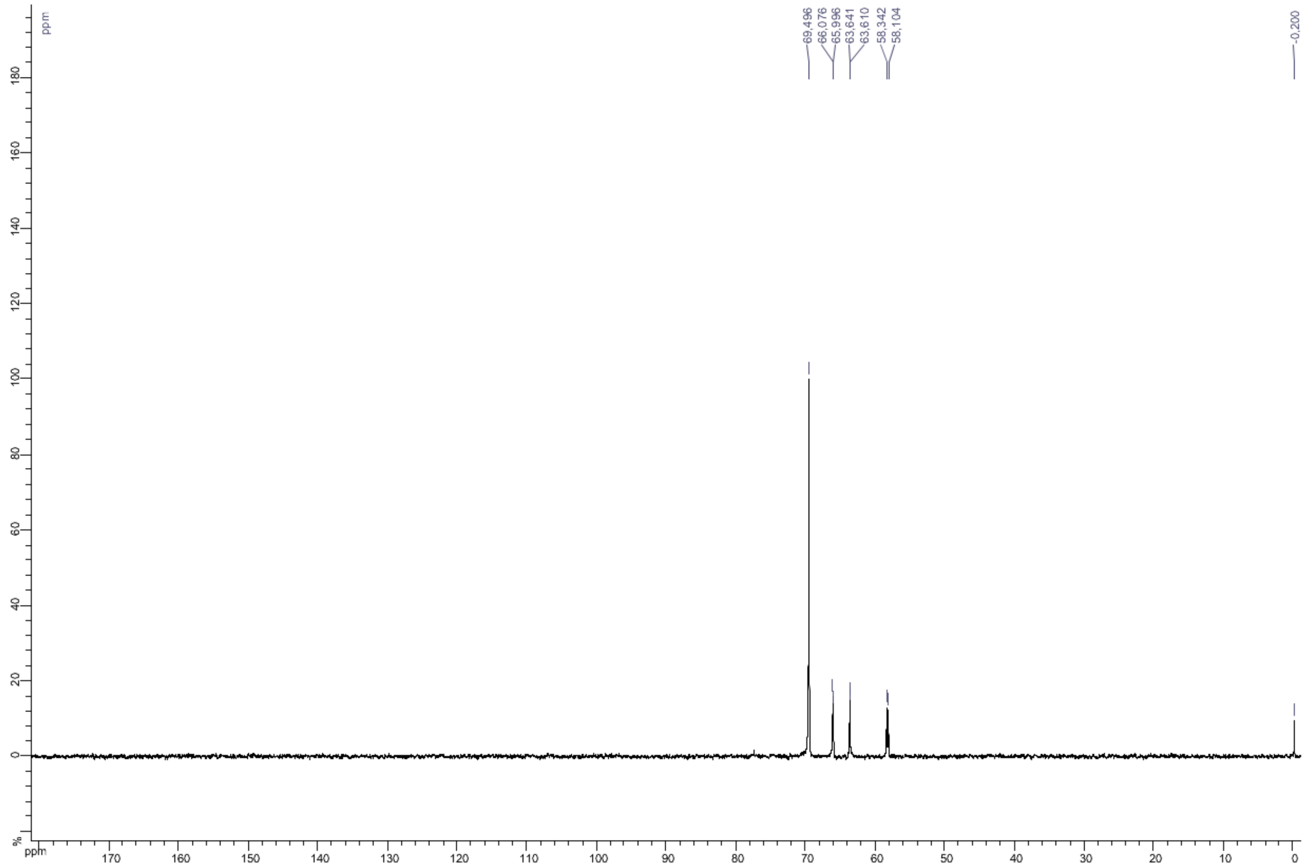
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



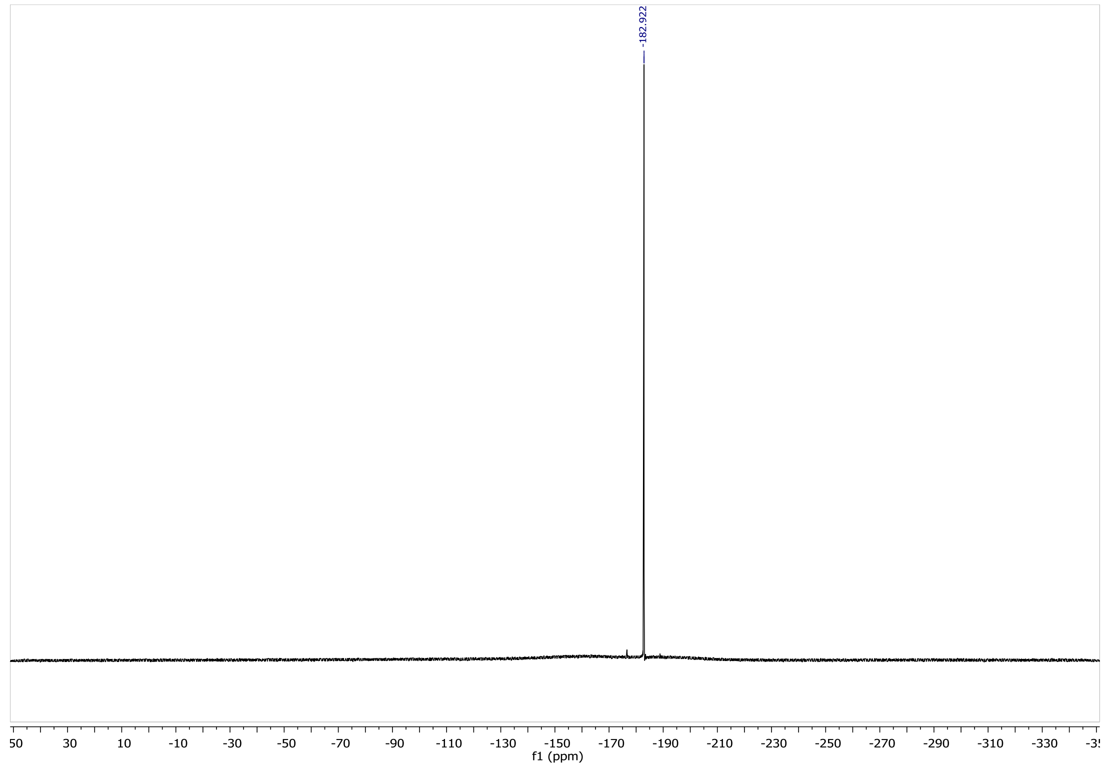
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



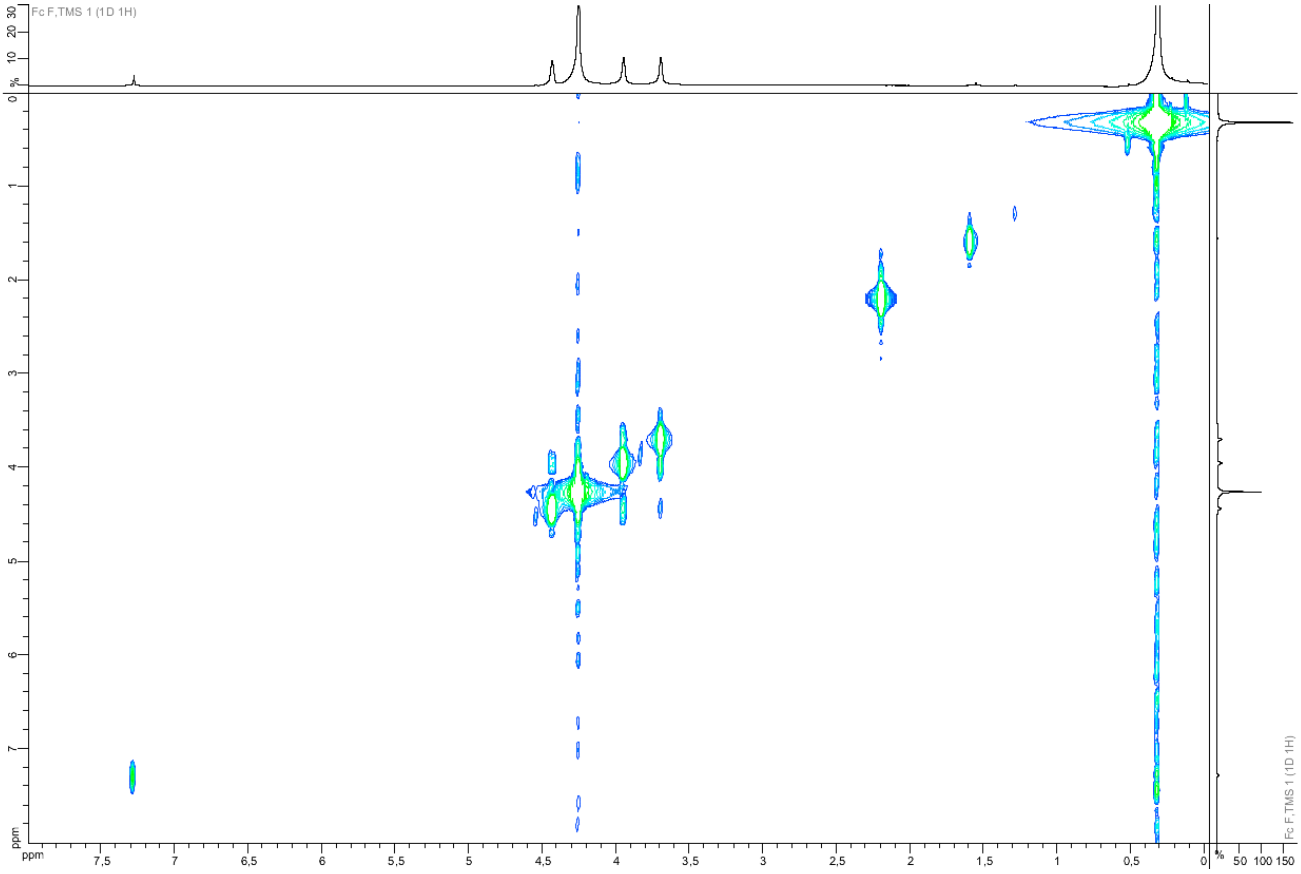
DEPT-135 (75 MHz, $CDCl_3$, 291 K)



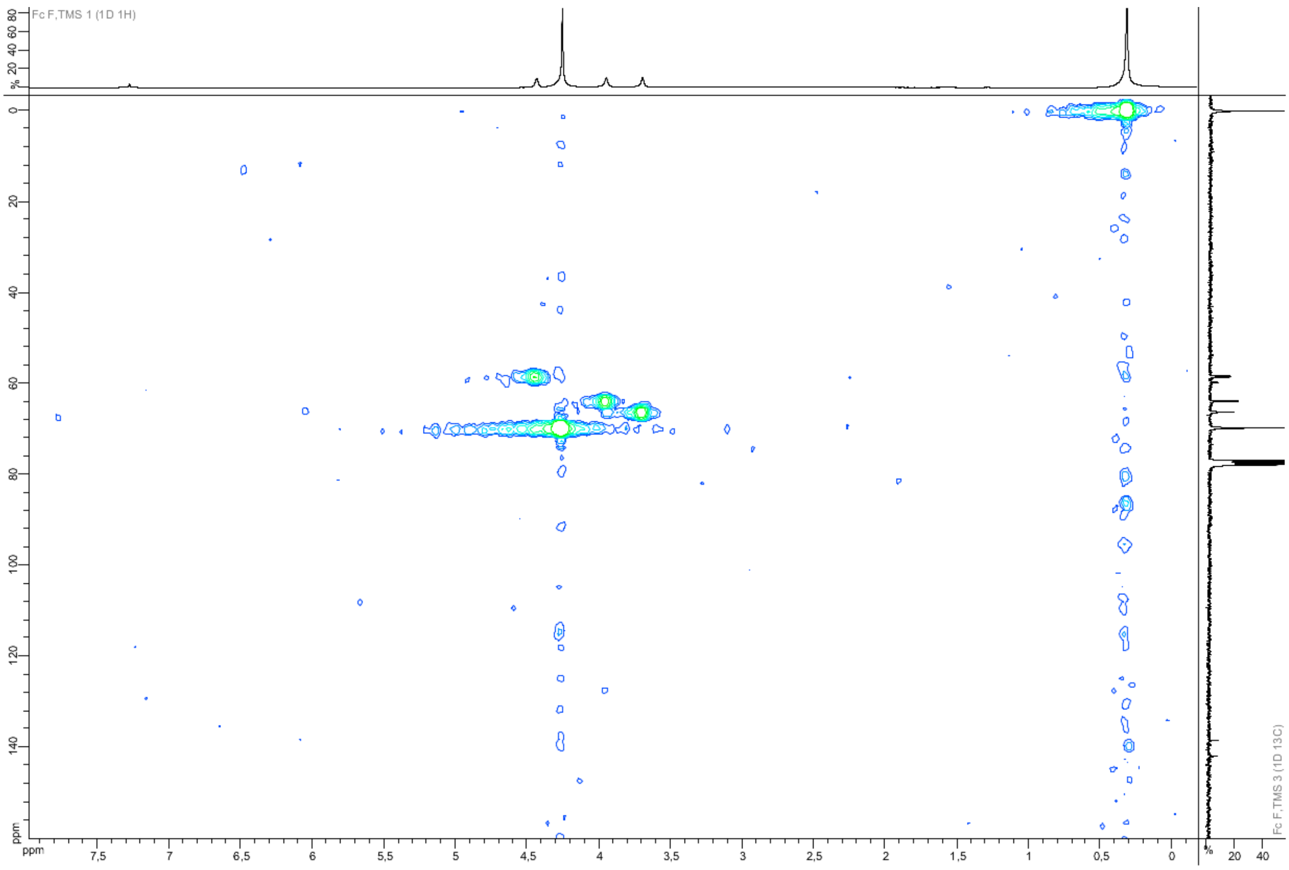
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



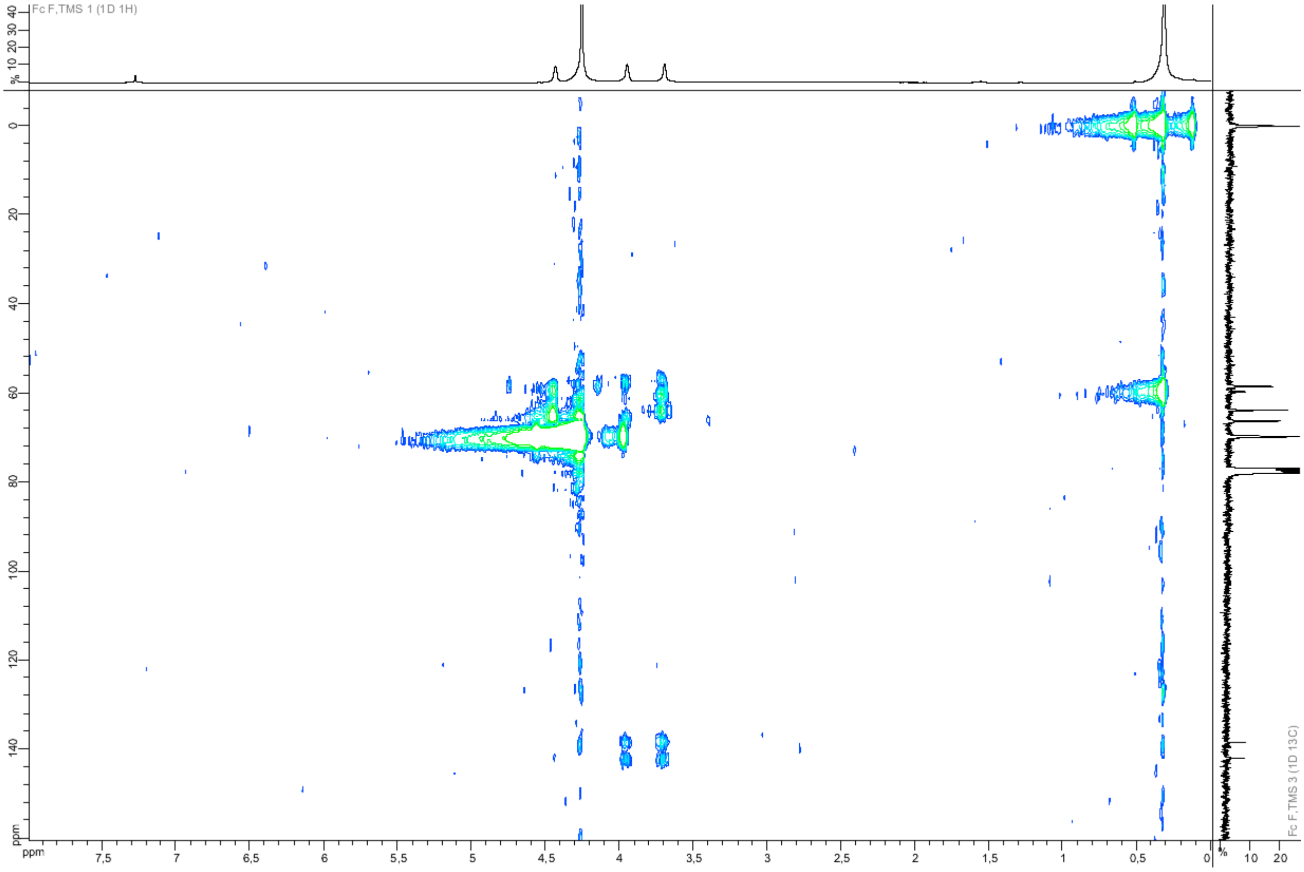
COSY (300 MHz, $CDCl_3$, 291 K)



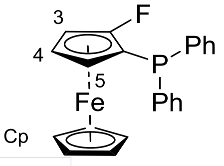
HSQC (300 MHz, $CDCl_3$, 291 K)



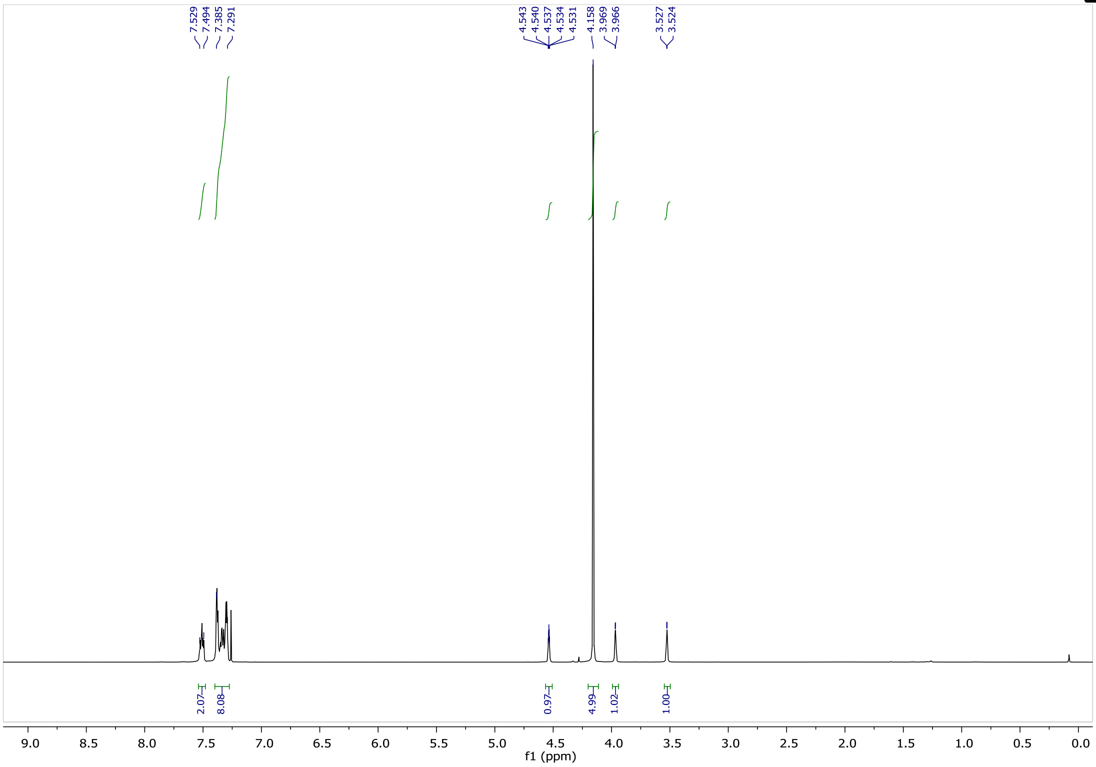
HMBC (300 MHz, $CDCl_3$, 291 K)



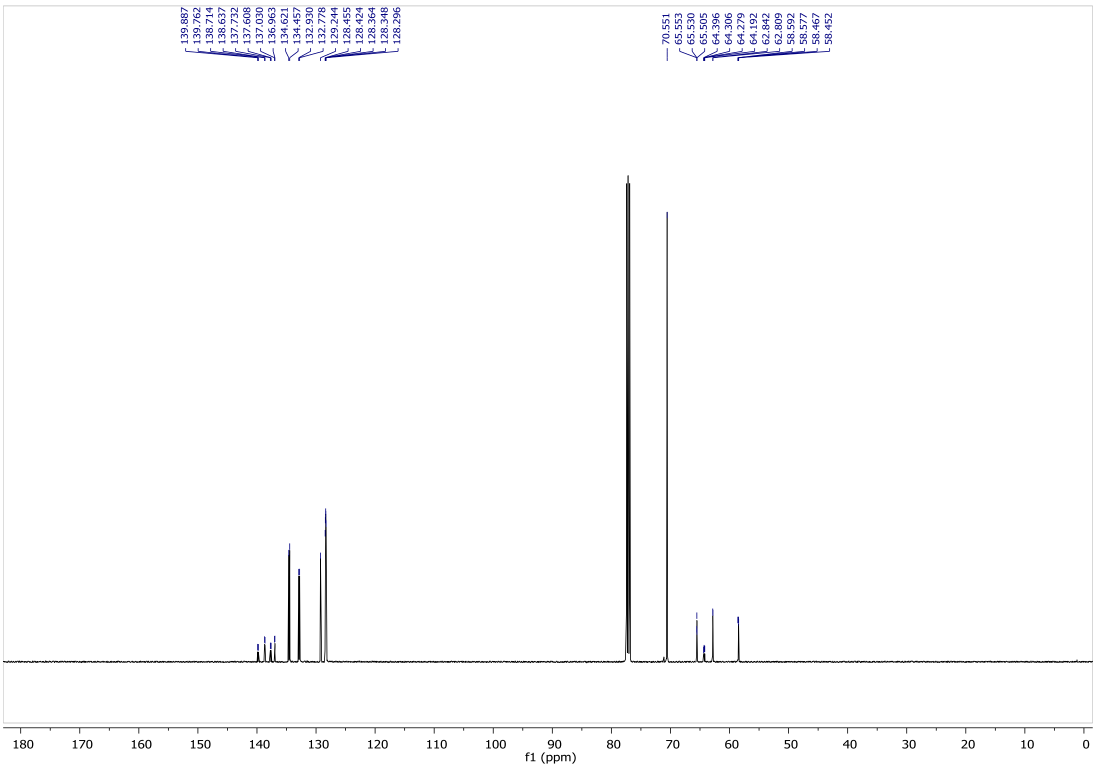
Compound 3g (racemic mixture)



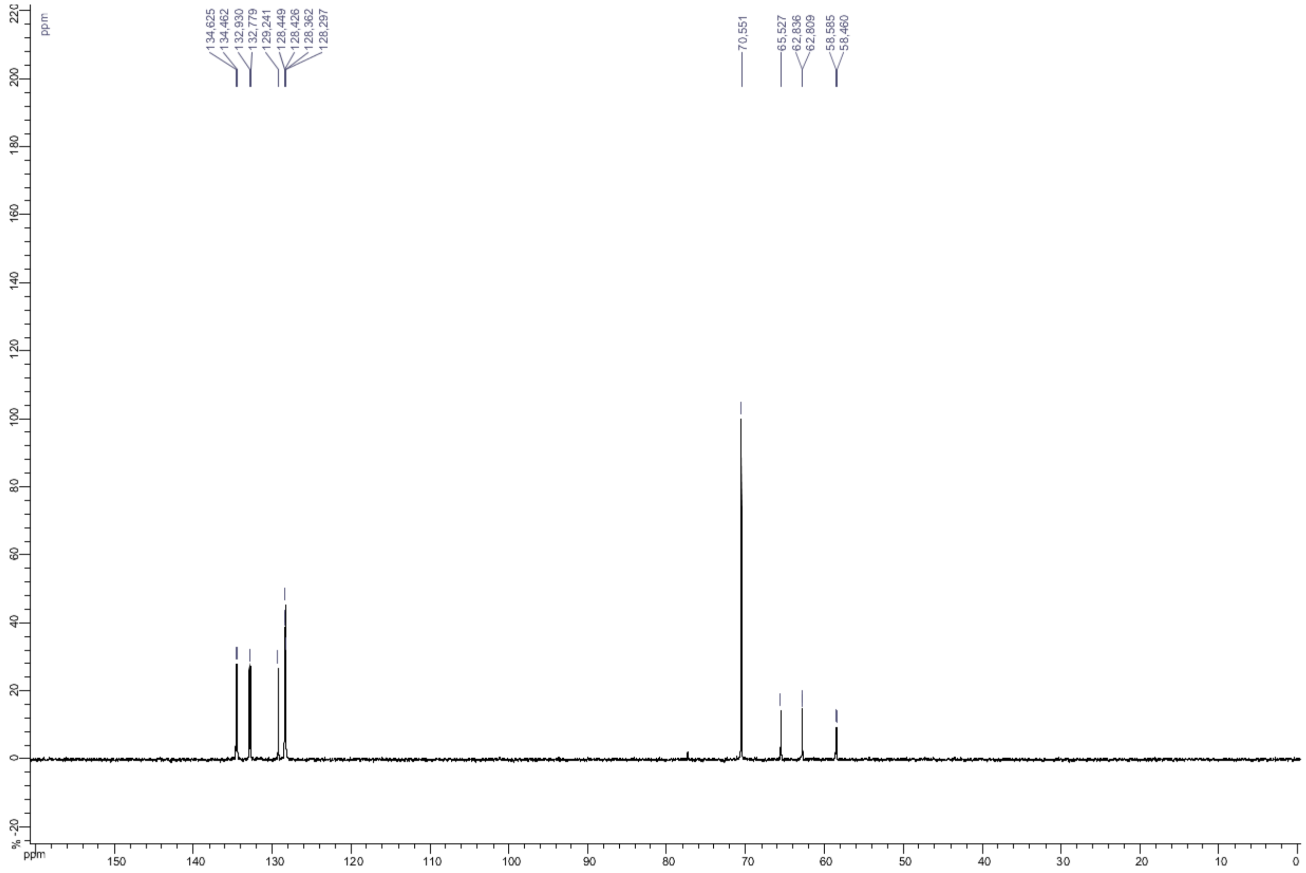
[1]H NMR (500 MHz, $CDCl_3$, 298 K)



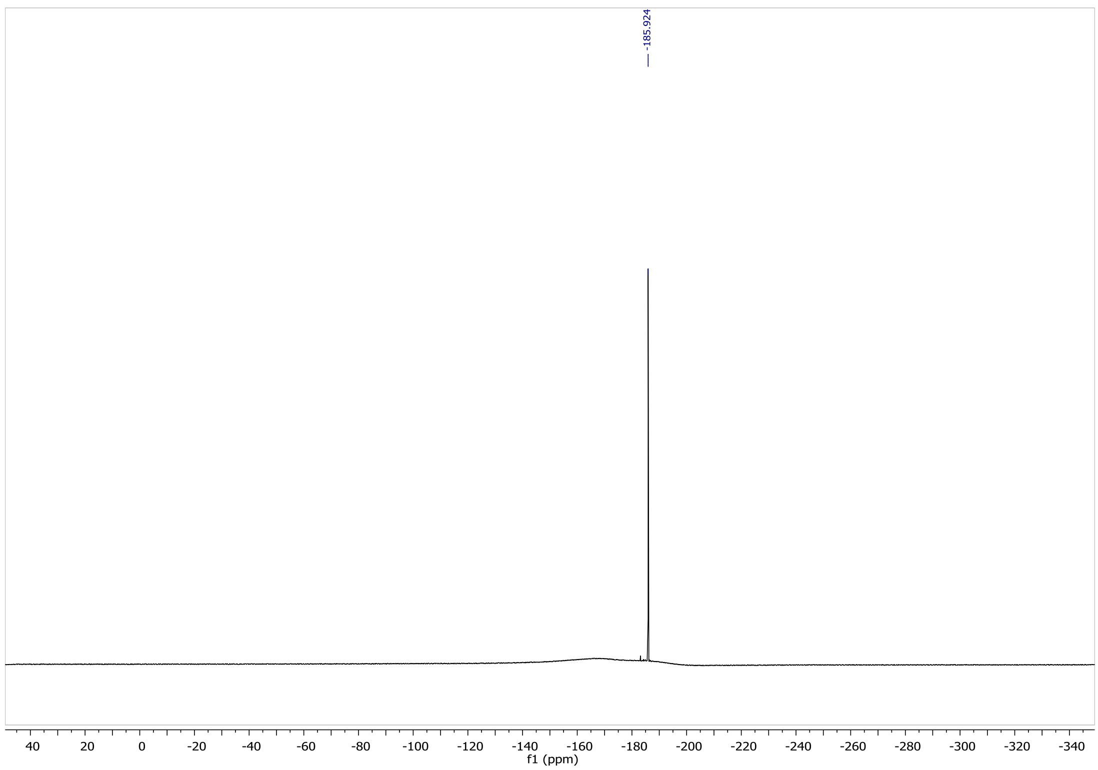
[13]C NMR (126 MHz, $CDCl_3$, 298 K)



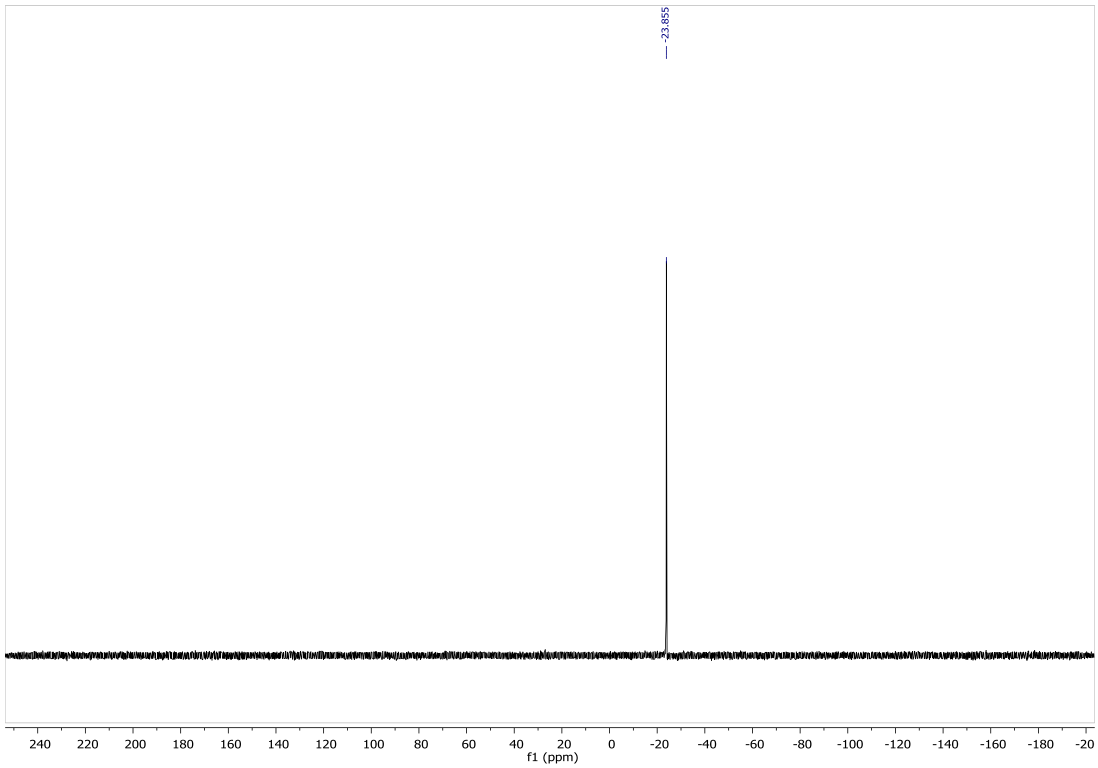
DEPT 135 (126 MHz, $CDCl_3$, 298 K)



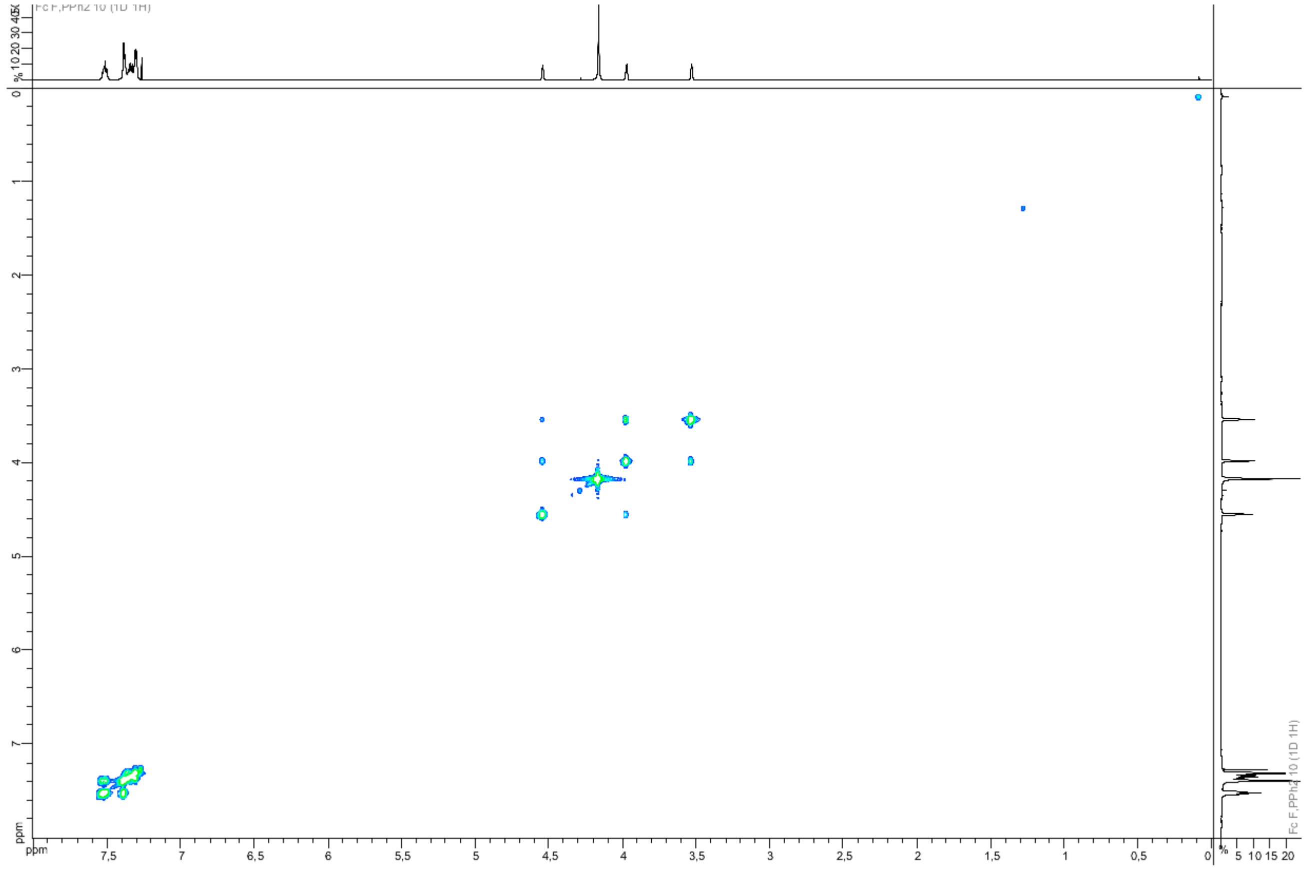
^{19}F NMR (470 MHz, $CDCl_3$, 298 K)



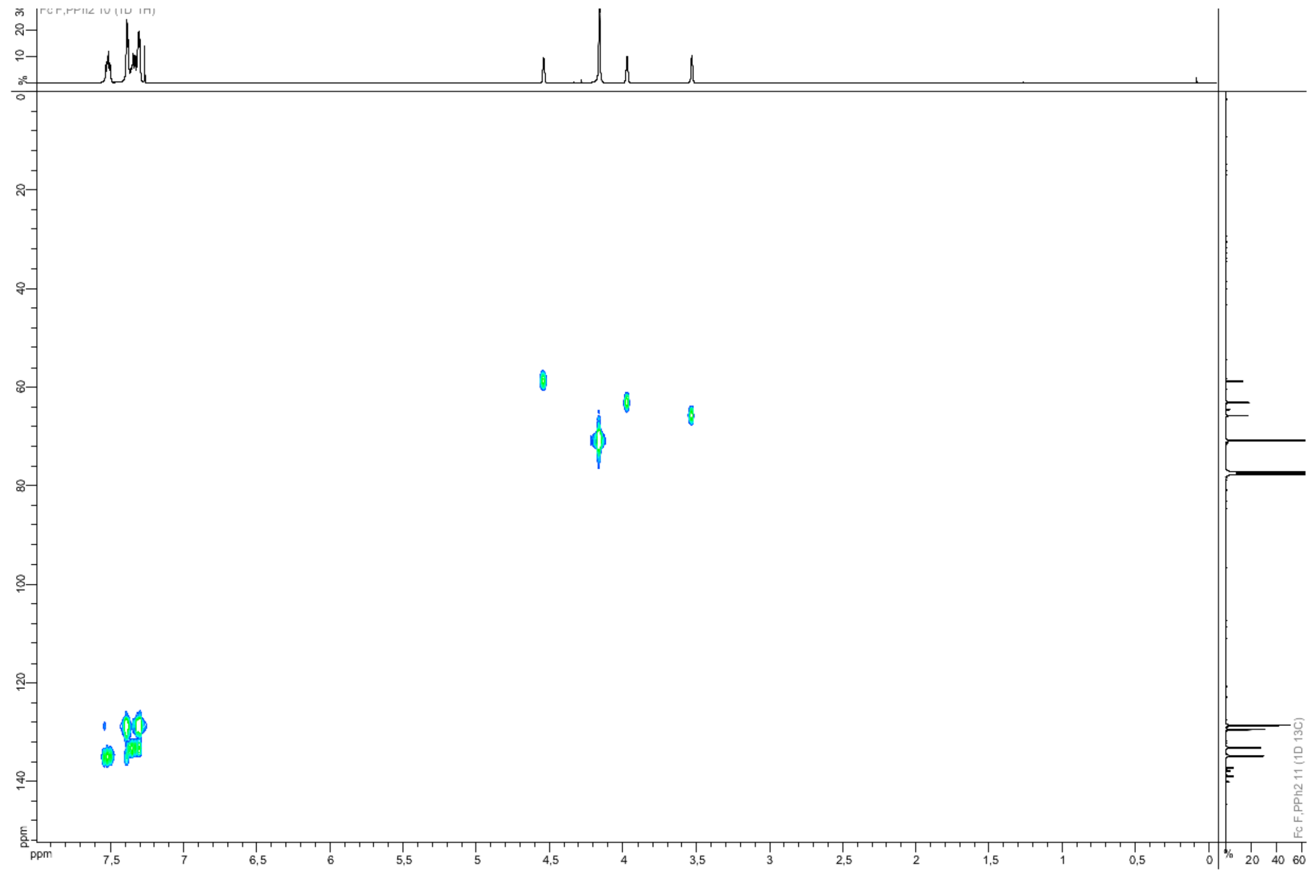
^{31}P NMR (162 MHz, $CDCl_3$, 298 K)



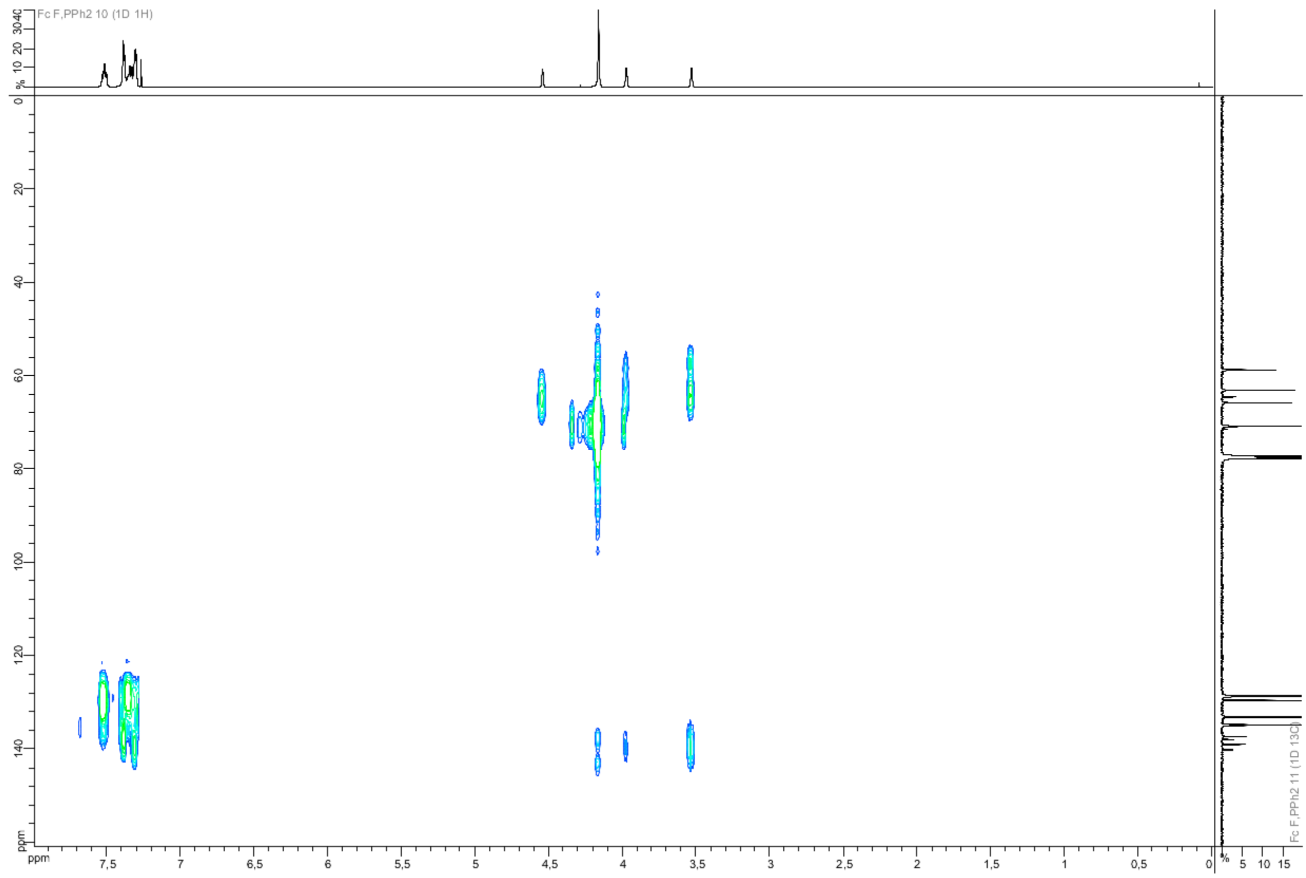
COSY (500 MHz, $CDCl_3$, 298 K)



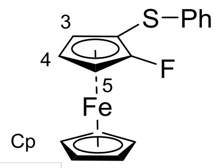
HSQC (500 MHz, $CDCl_3$, 298 K)



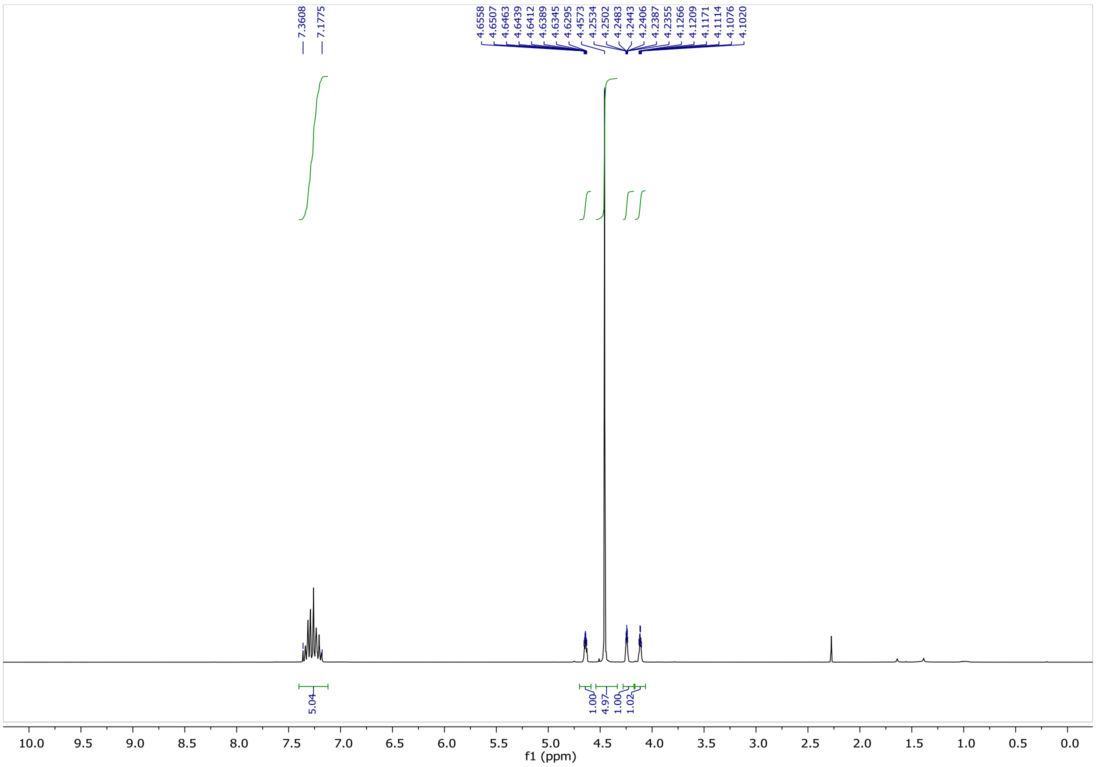
HMBC (500 MHz, $CDCl_3$, 298 K)



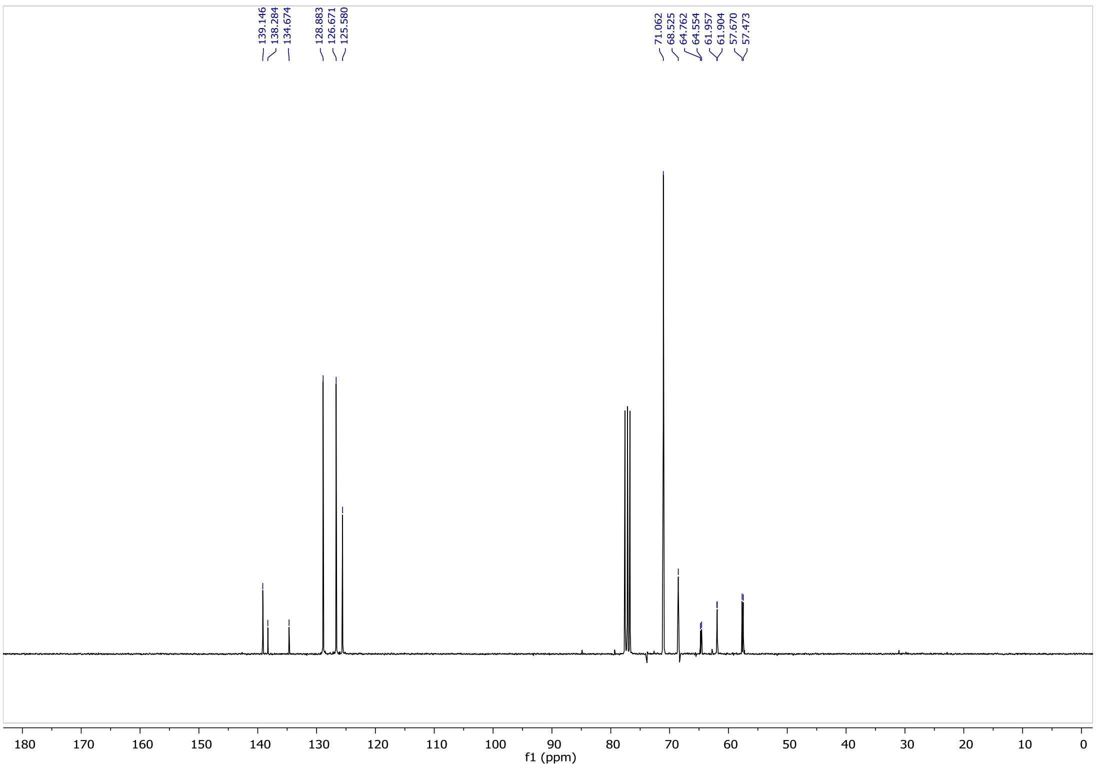
Compound 3h (racemic mixture)



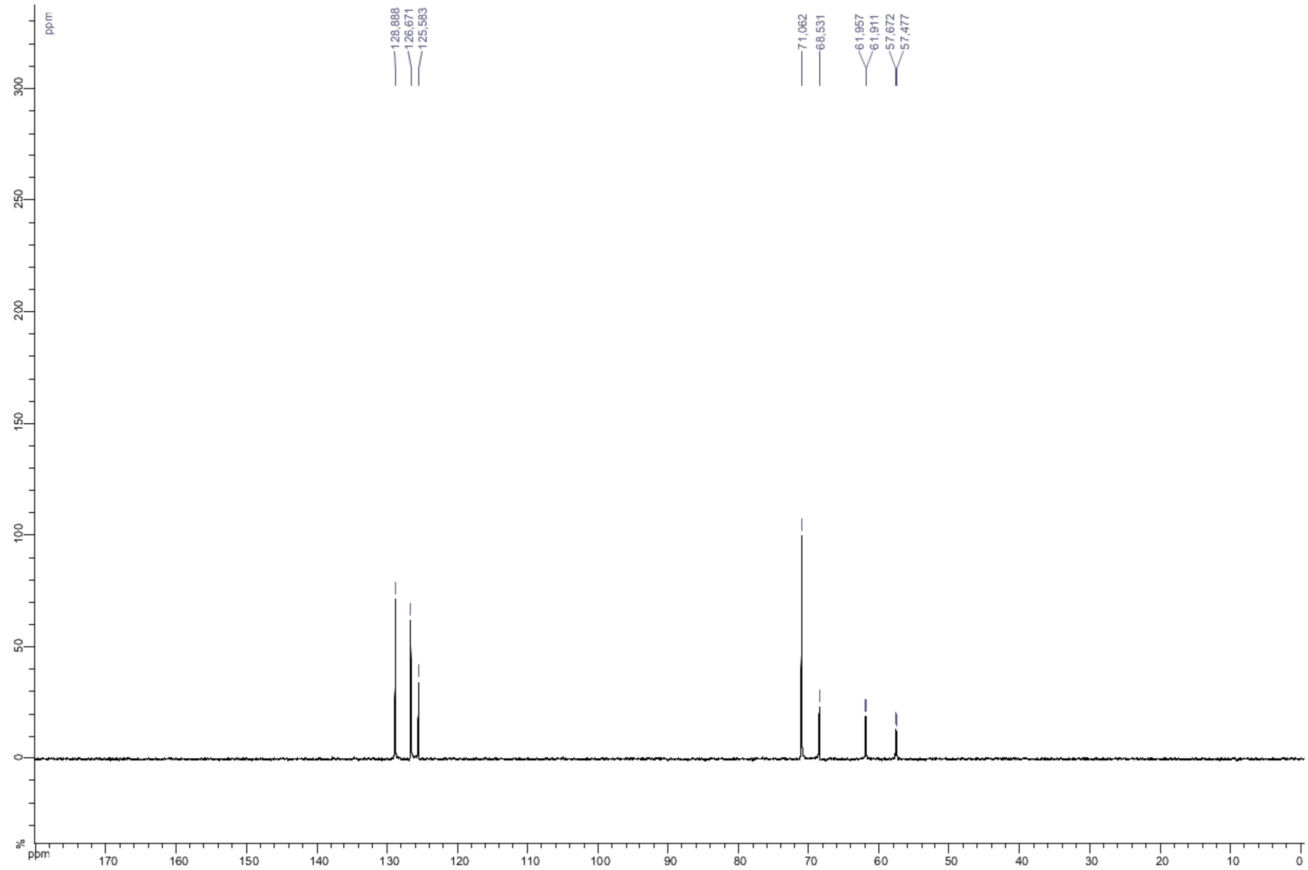
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



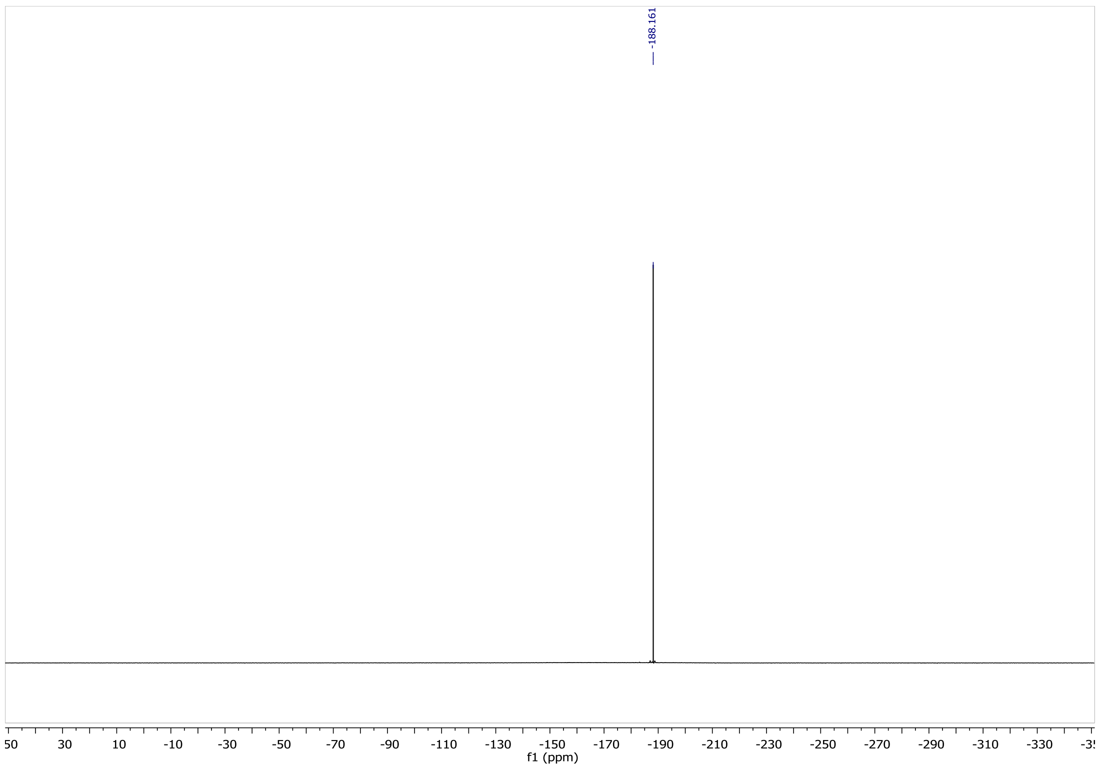
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



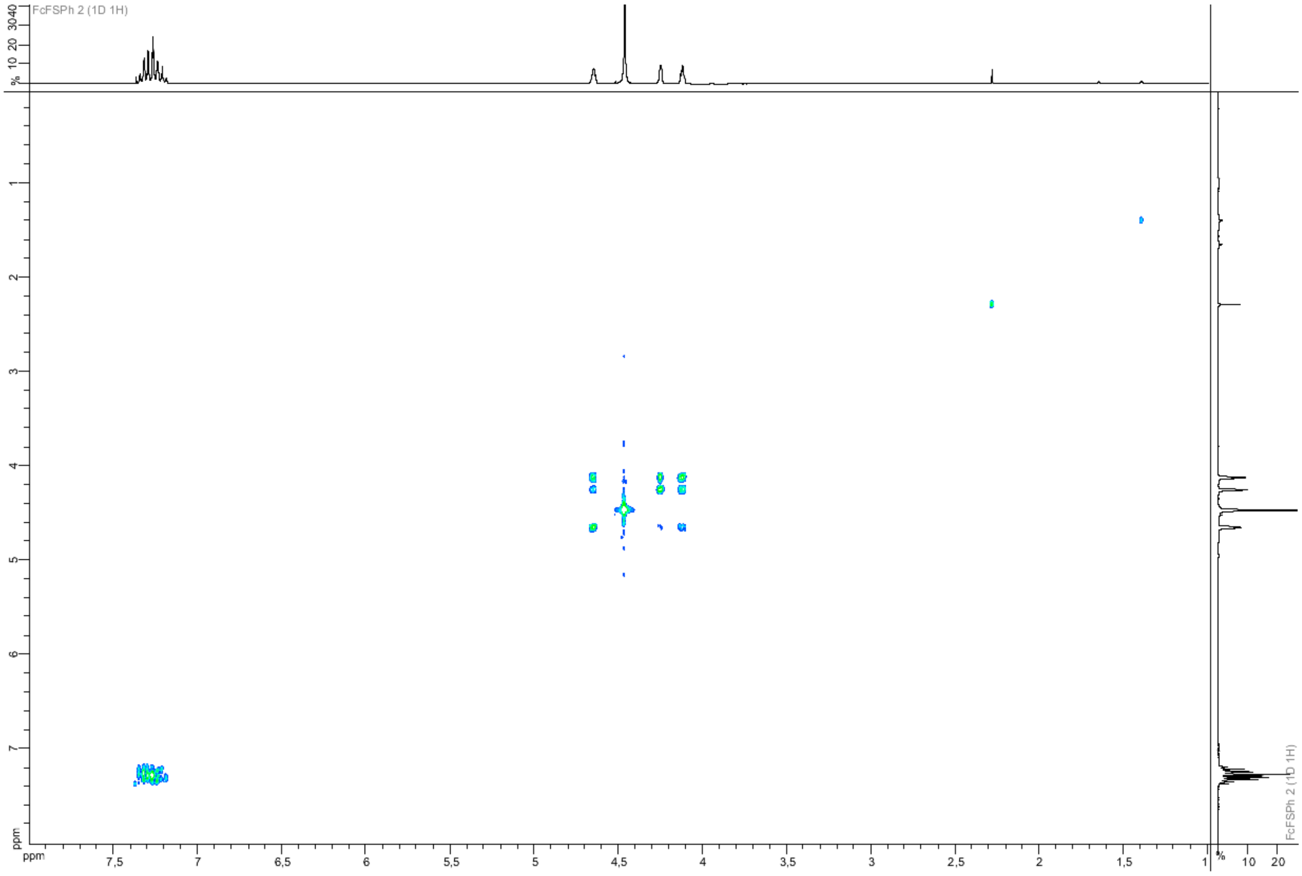
DEPT 135 (75 MHz, $CDCl_3$, 291 K)



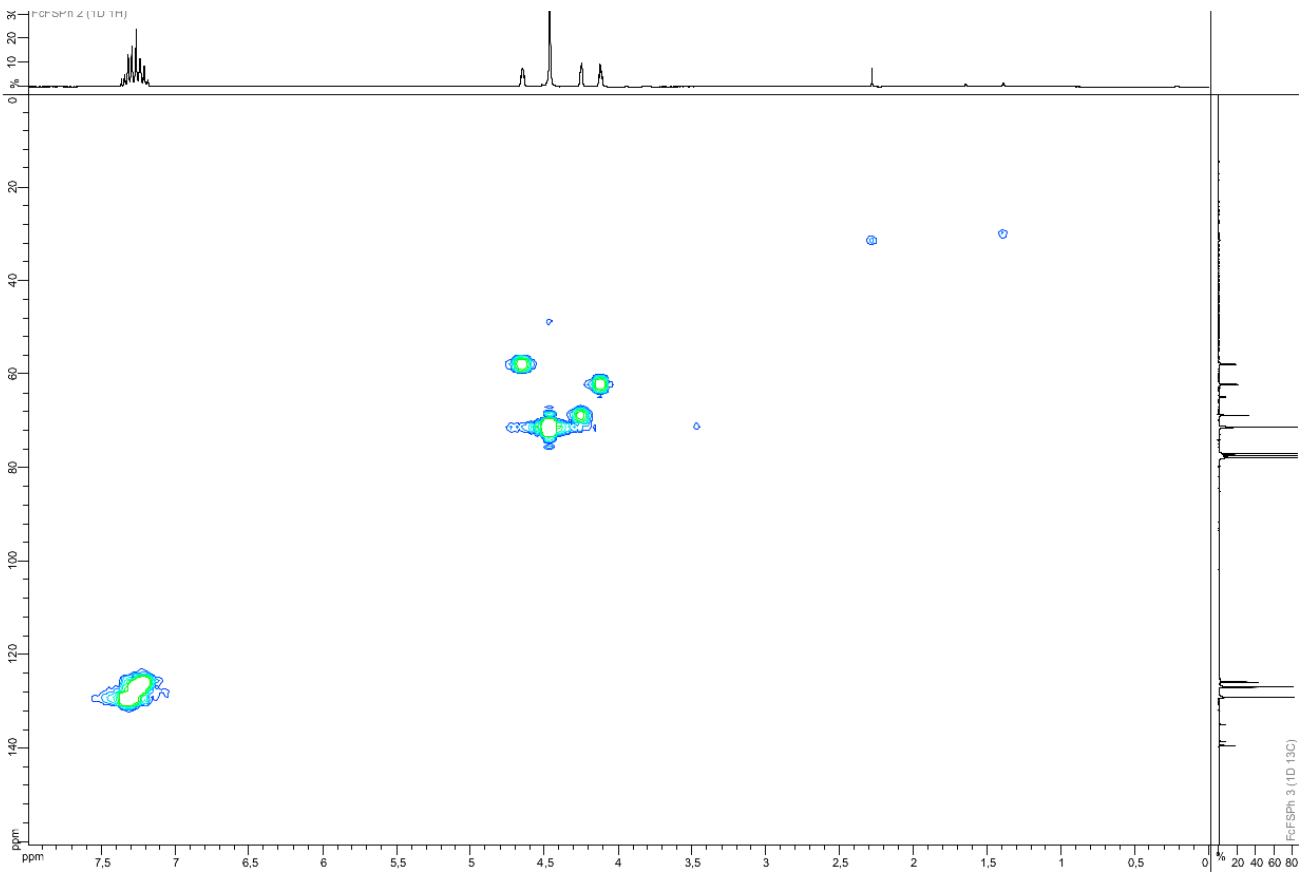
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



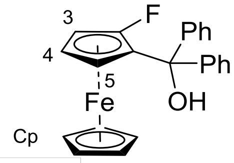
COSY (300 MHz, $CDCl_3$, 298 K)



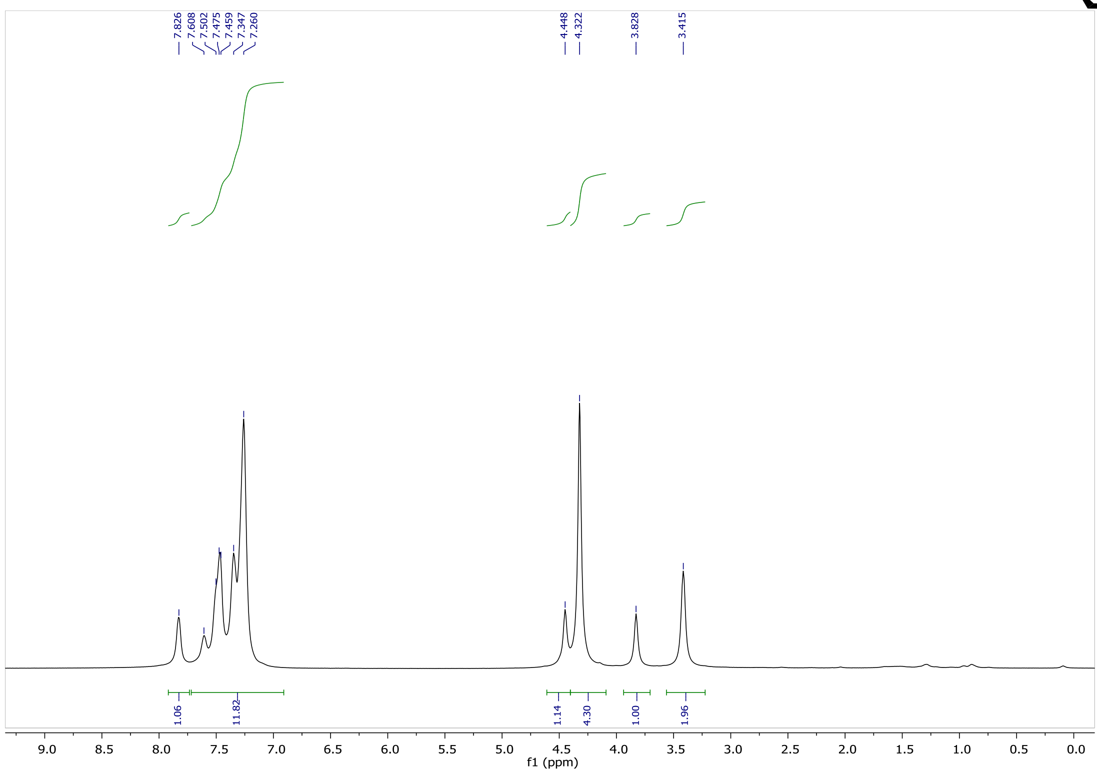
HSQC (300 MHz, $CDCl_3$, 298 K)



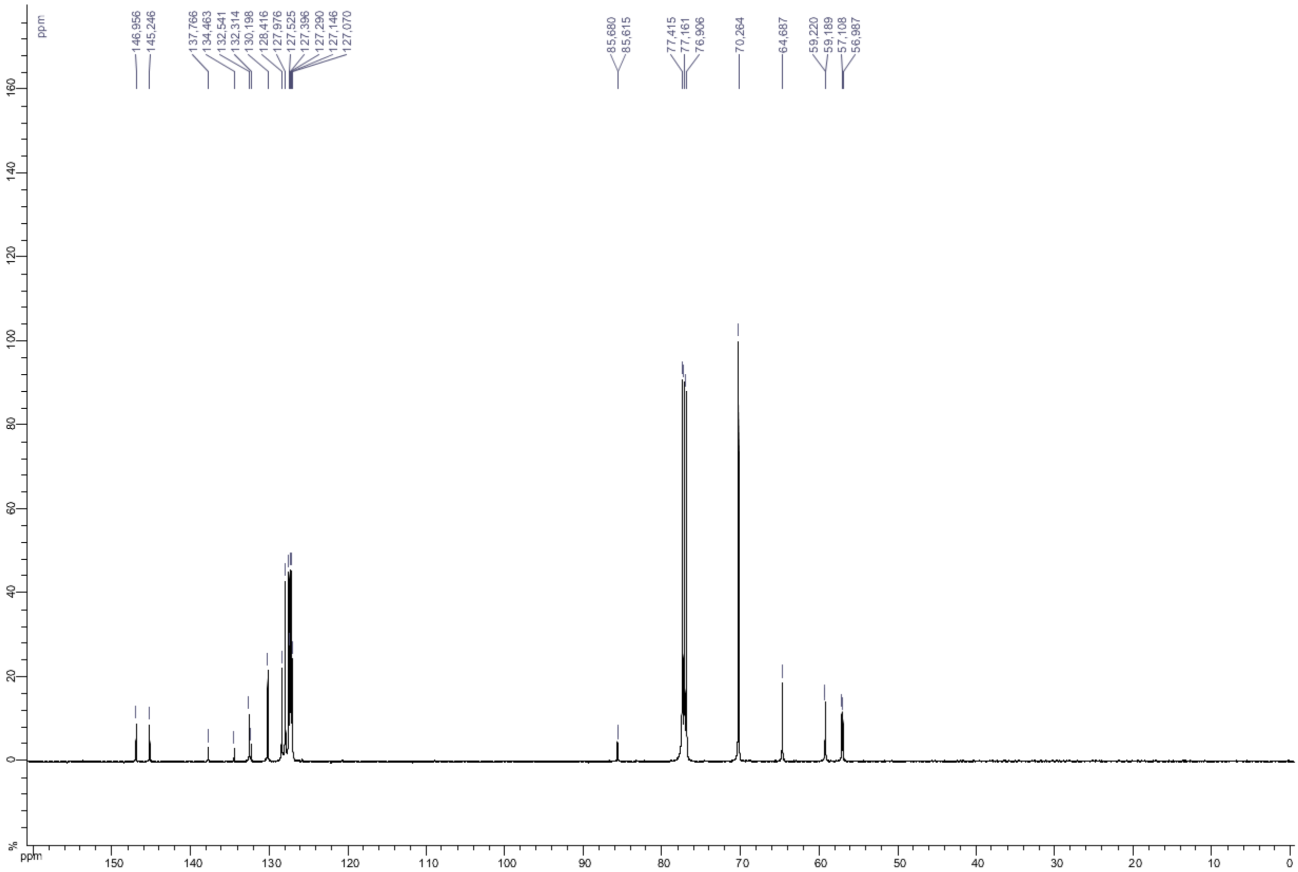
Compound 3i (racemic mixture; together with remaining benzophenone)



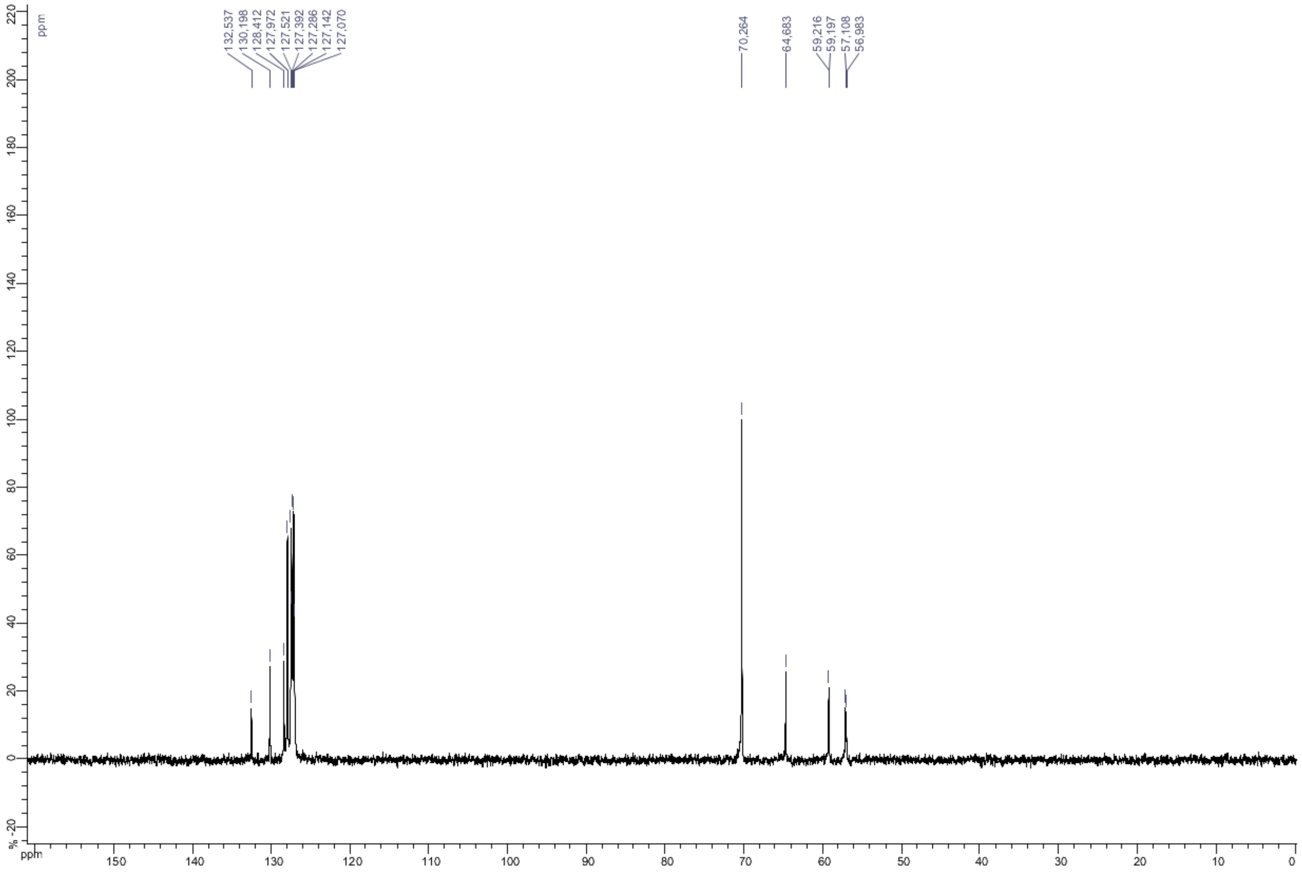
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



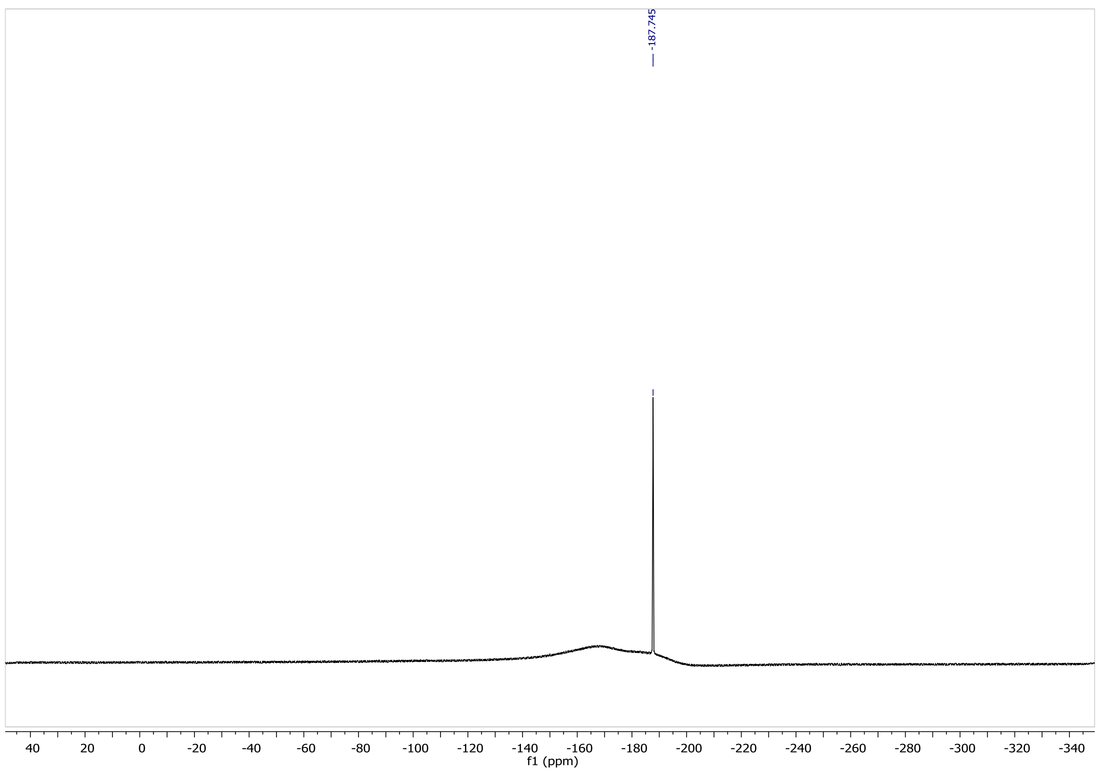
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



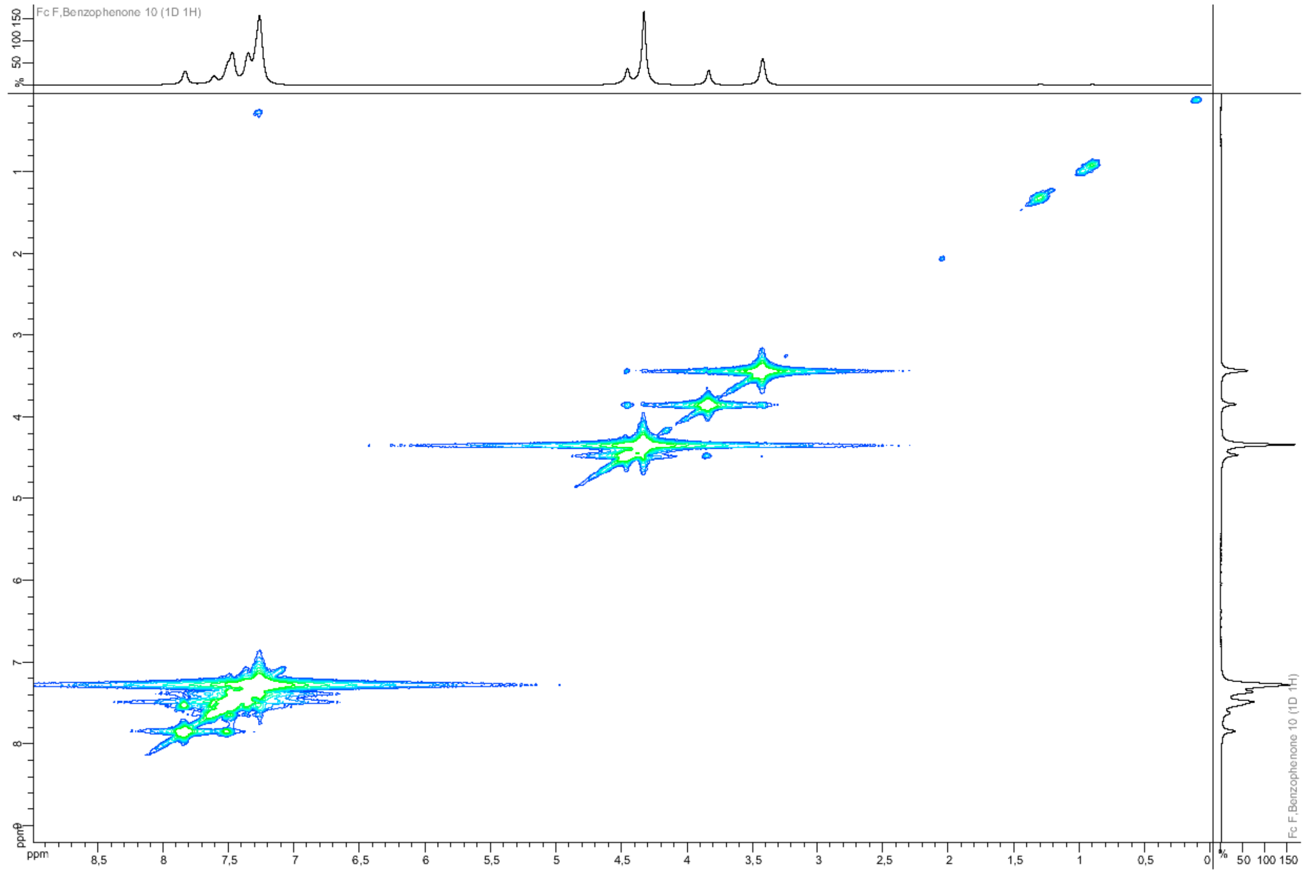
DEPT 135 (126 MHz, $CDCl_3$, 298 K)



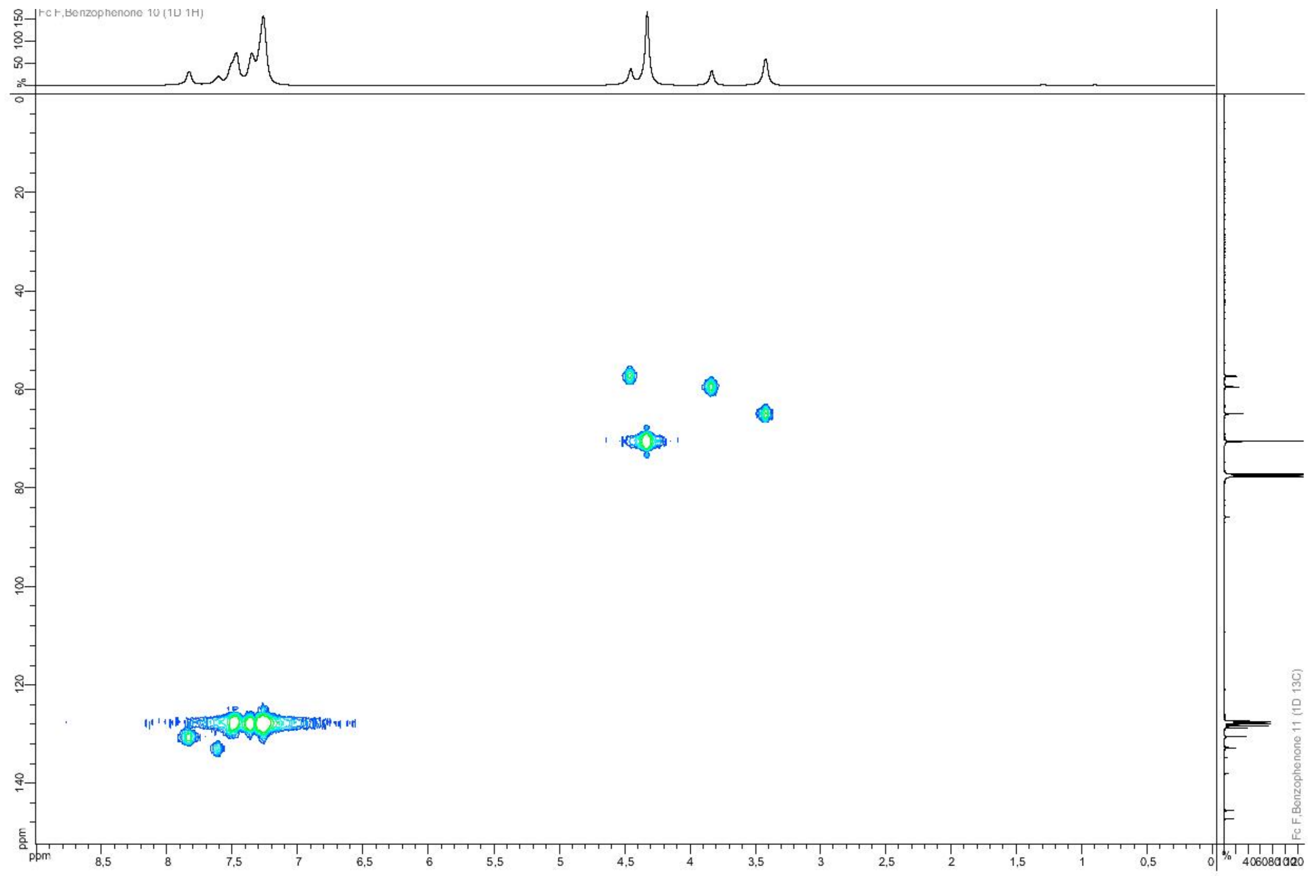
^{19}F NMR (470 MHz, $CDCl_3$, 298 K)



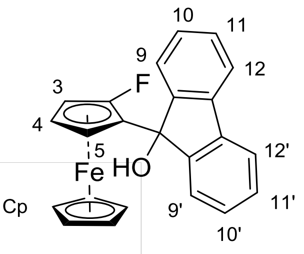
COSY (500 MHz, $CDCl_3$, 298 K)



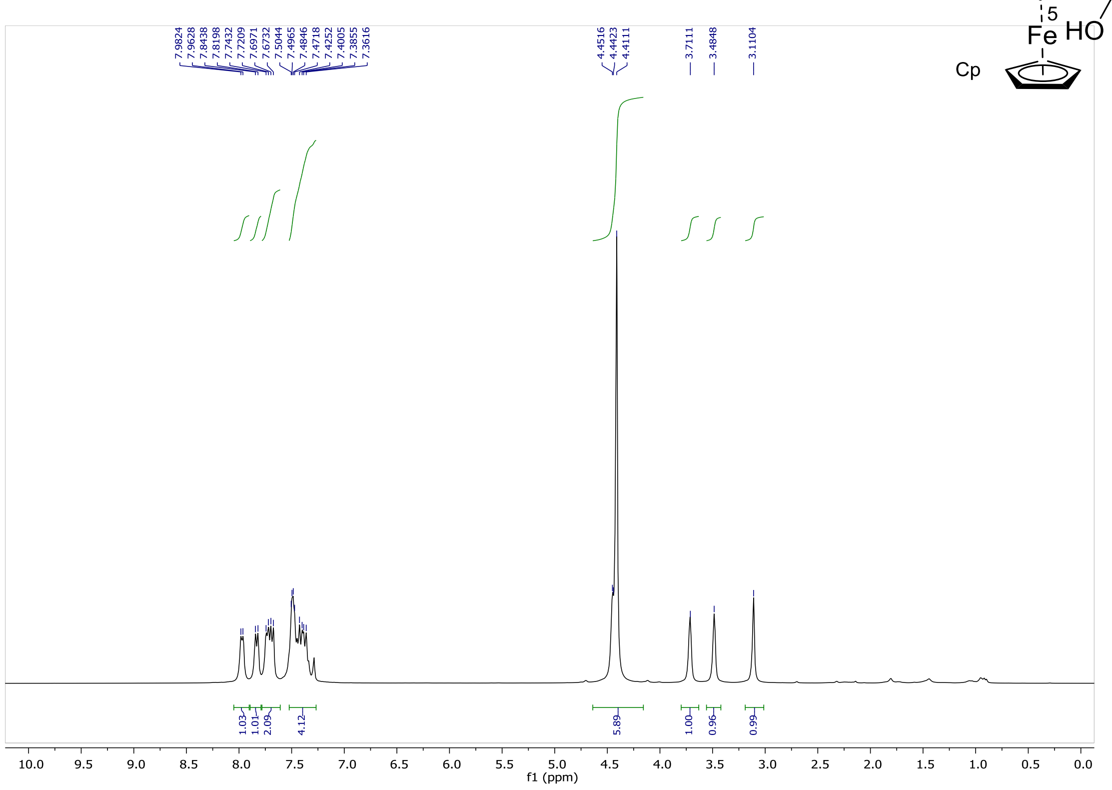
HSQC (500 MHz, $CDCl_3$, 298 K)



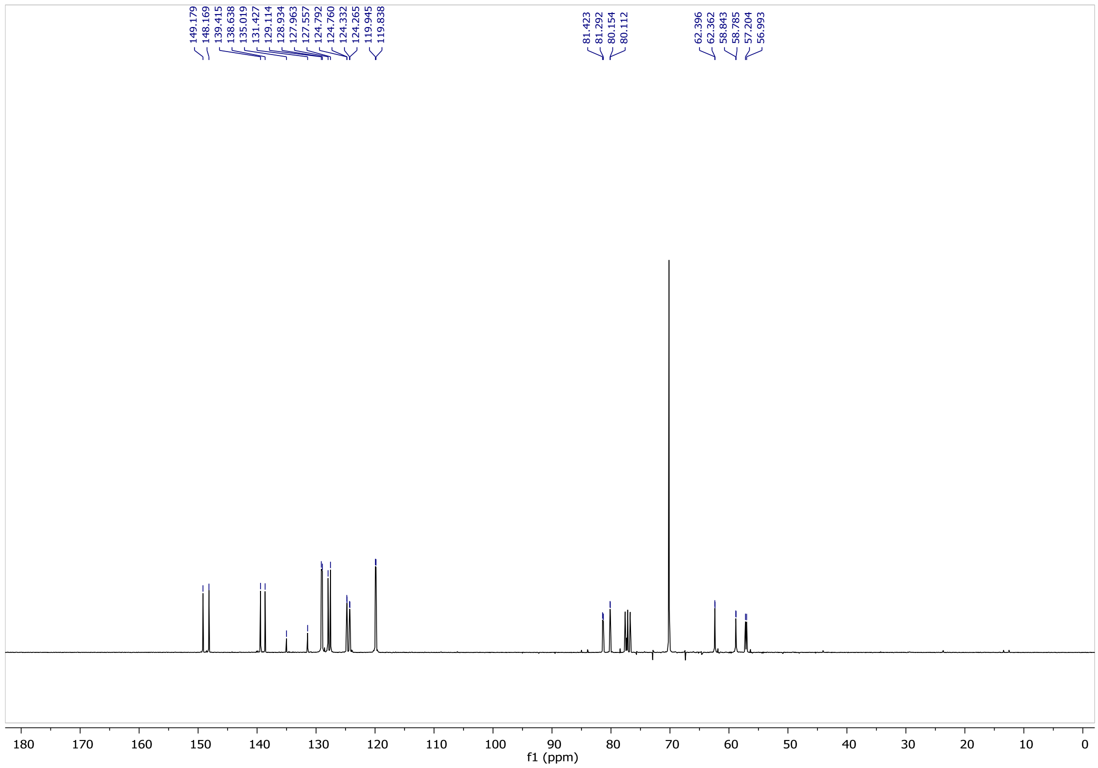
Compound 3j (racemic mixture)



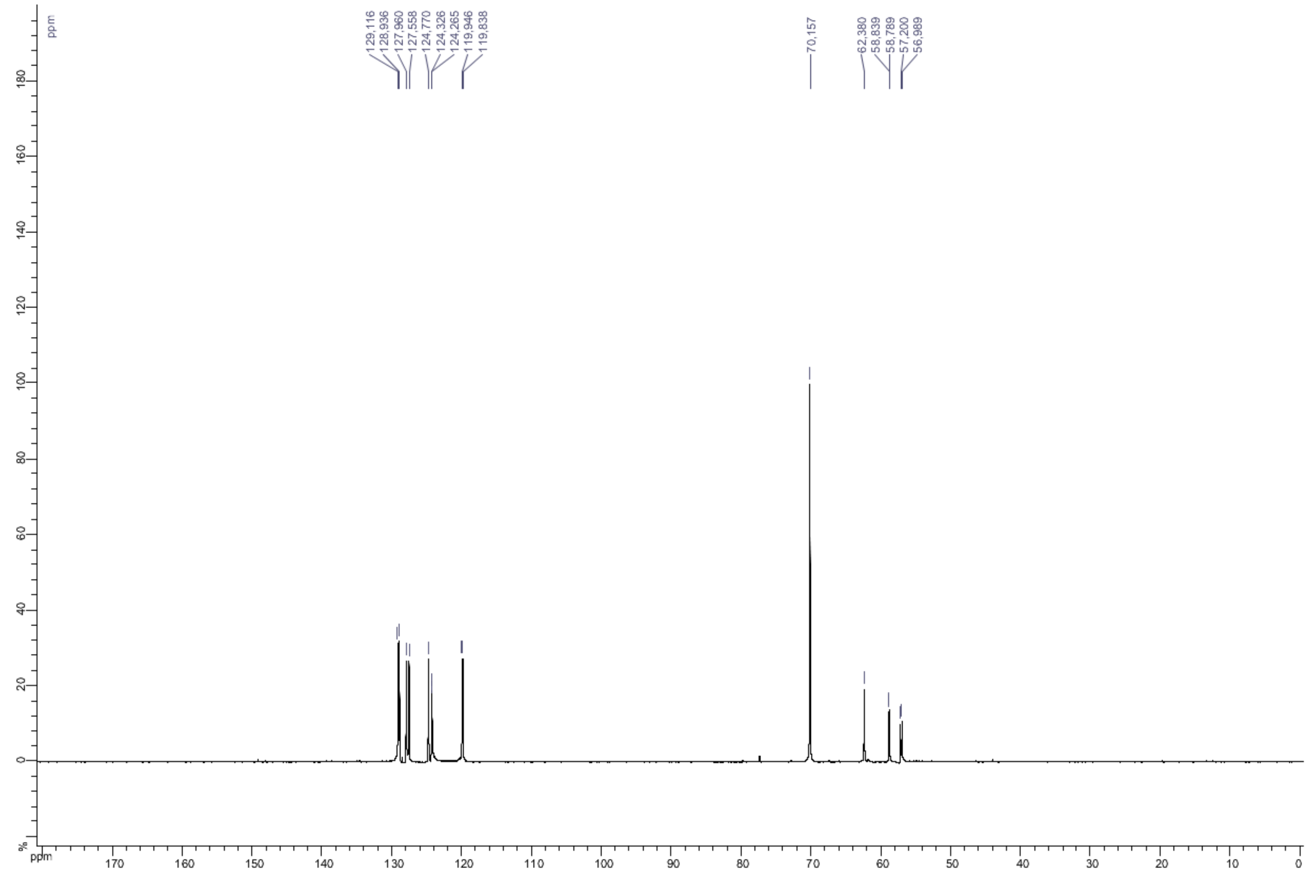
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



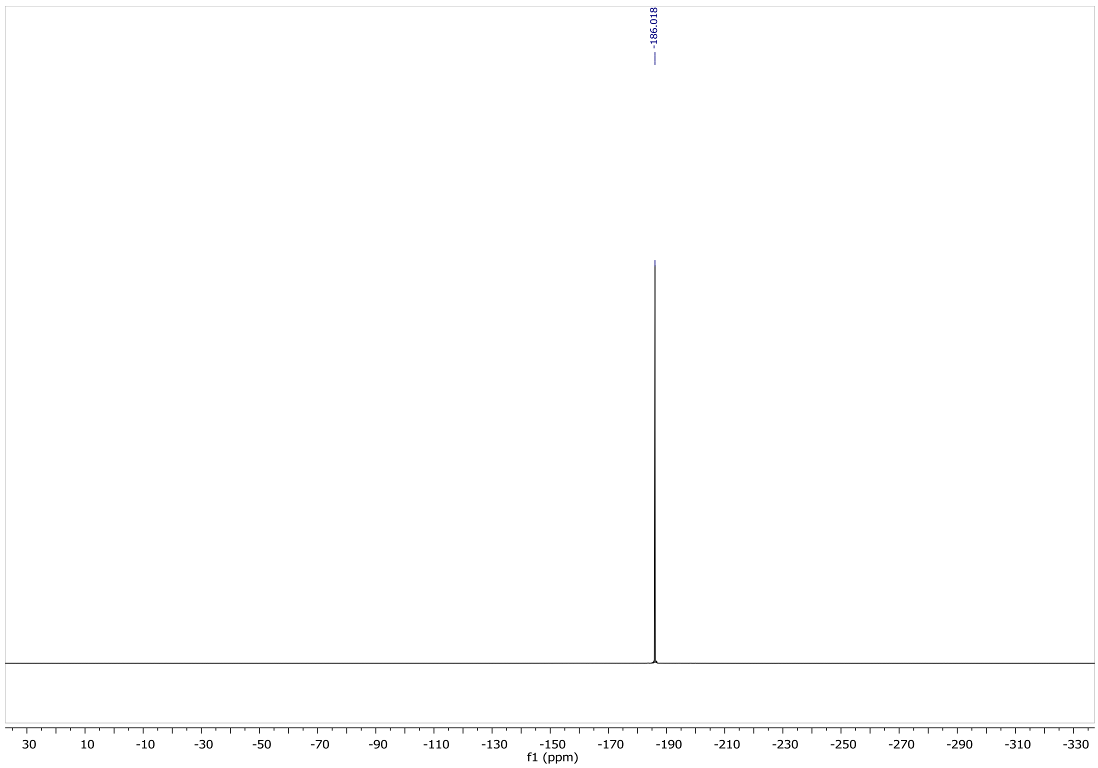
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



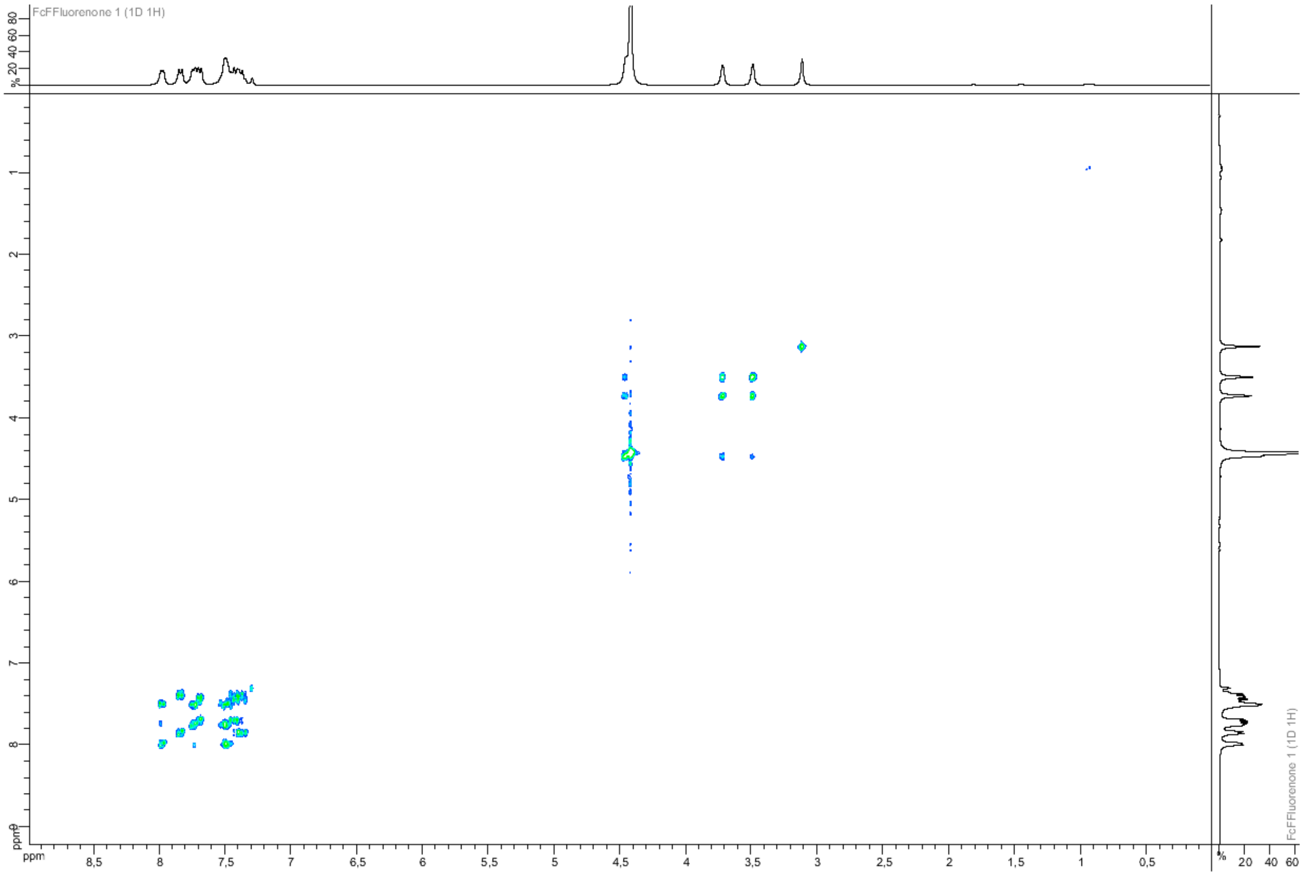
DEPT 135 (75 MHz, $CDCl_3$, 291 K)



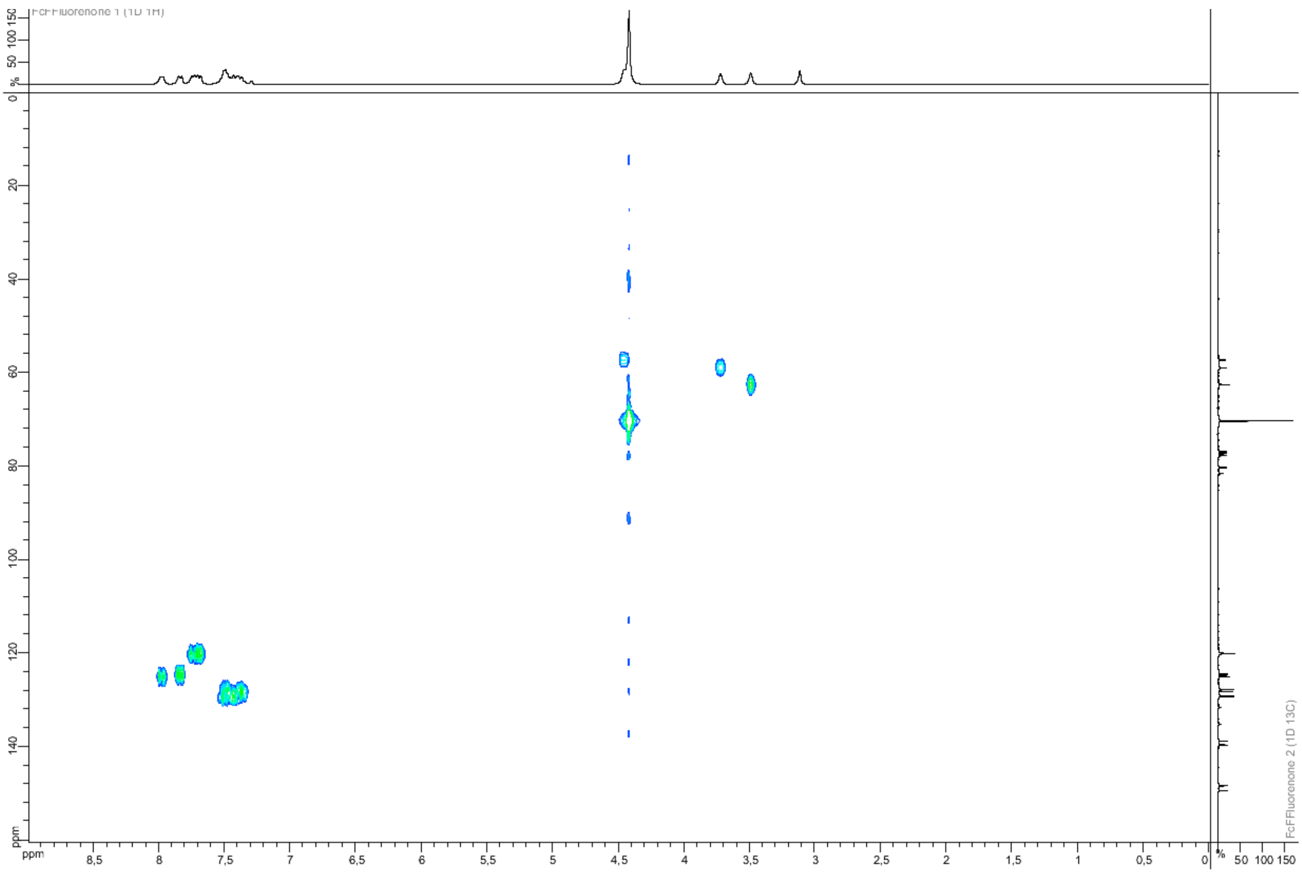
[19]F NMR (282 MHz, $CDCl_3$, 291 K)



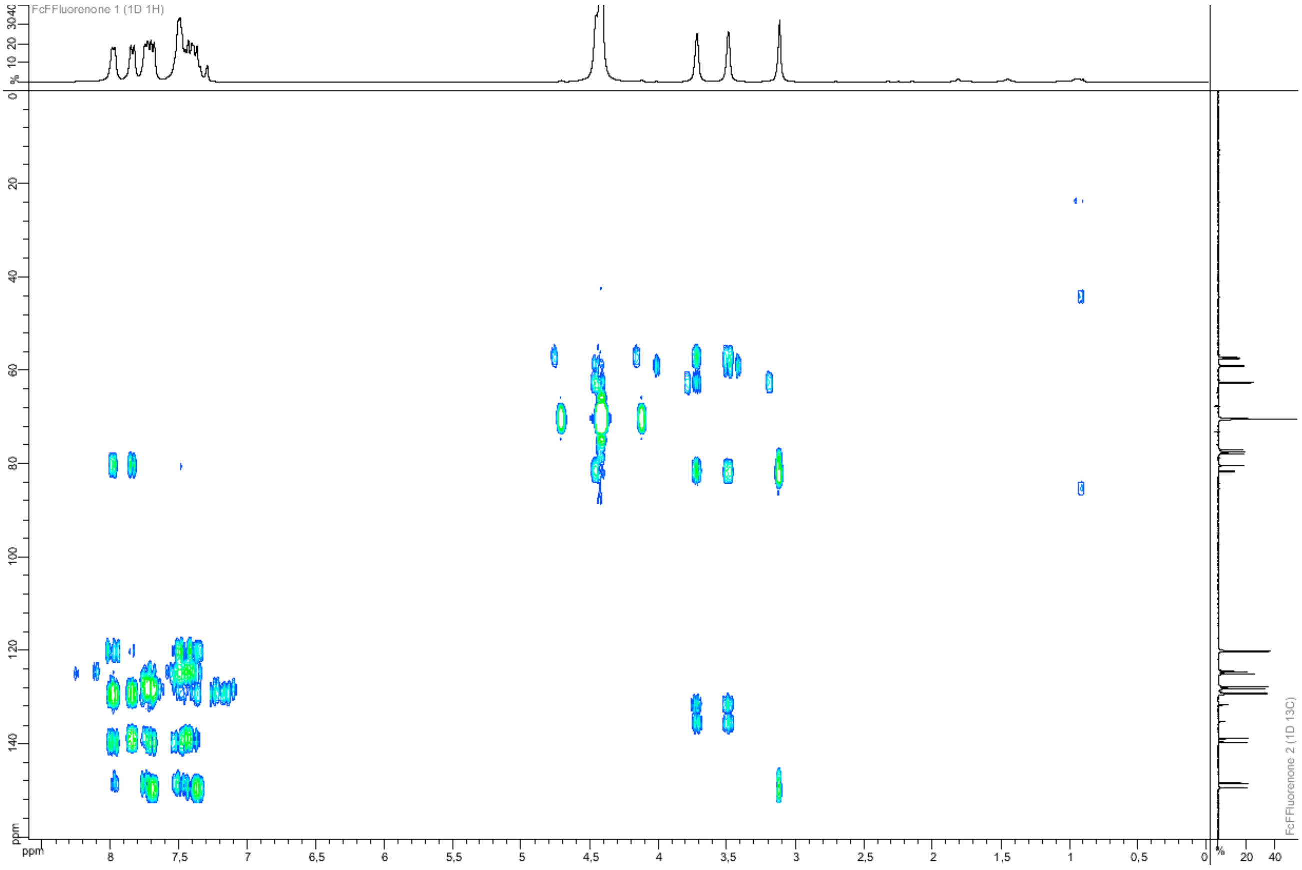
COSY (300 MHz, $CDCl_3$, 298 K)



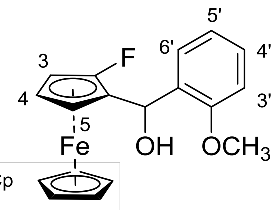
HSQC (300 MHz, $CDCl_3$, 298 K)



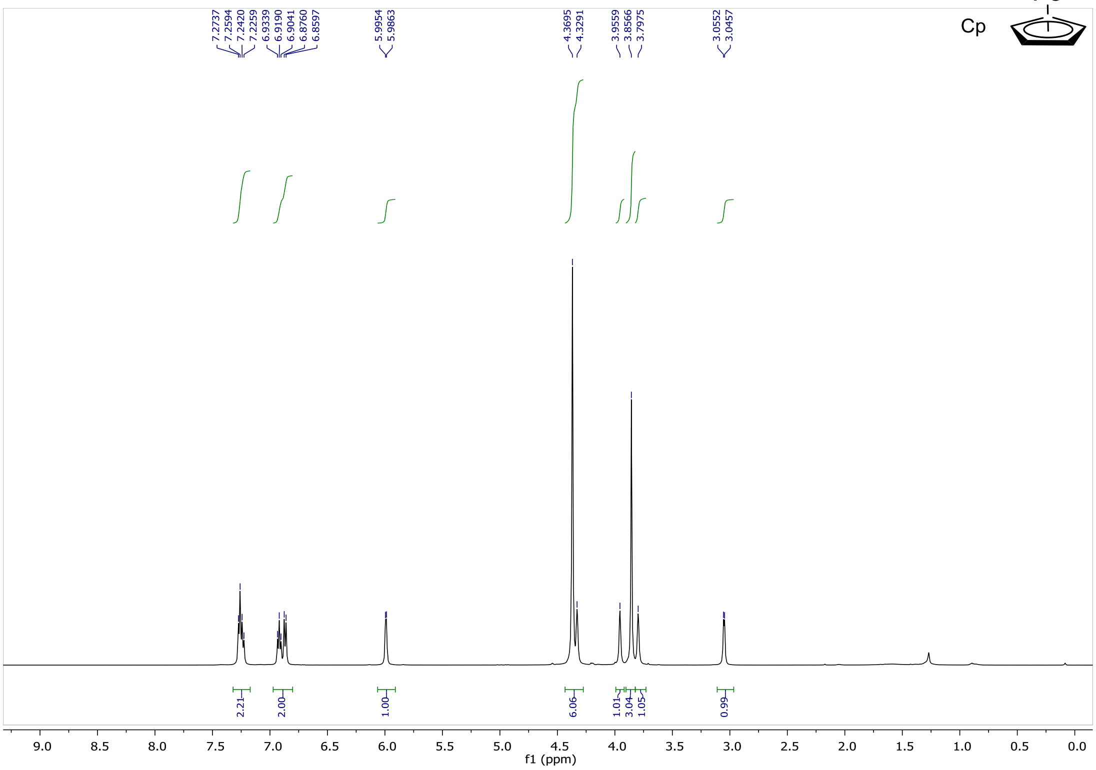
HMBC (300 MHz, $CDCl_3$, 298 K)



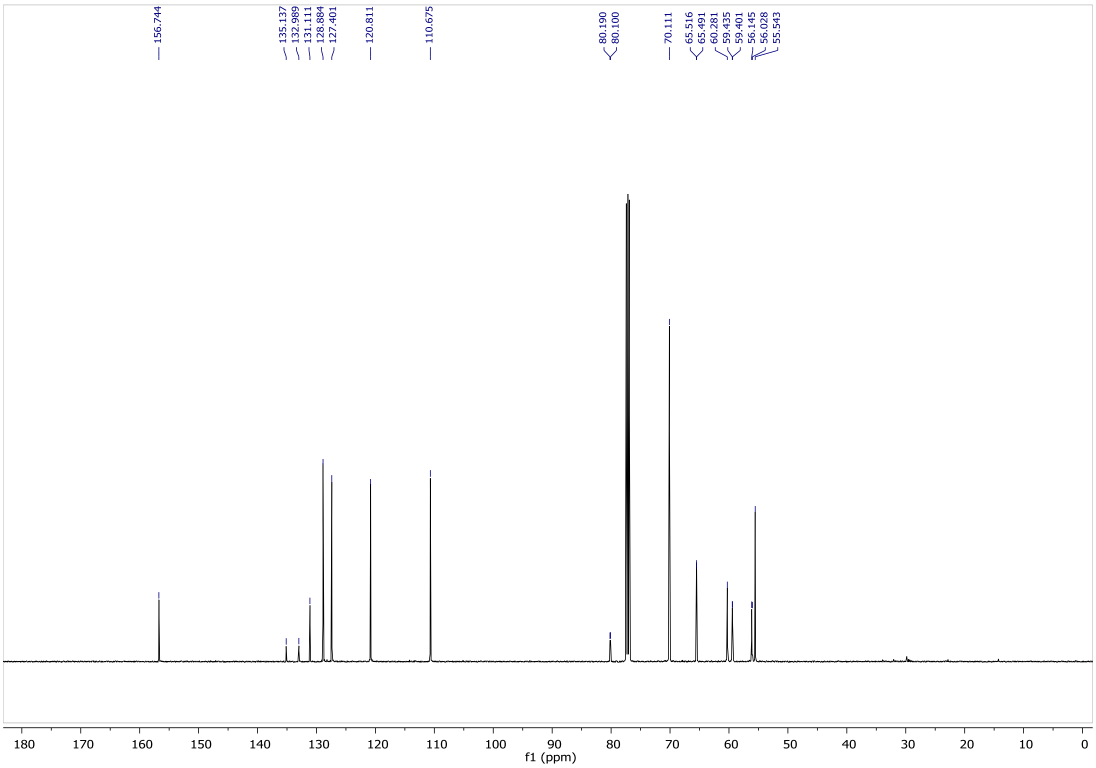
Compound 3k (major diastereoisomer, racemic mixture)



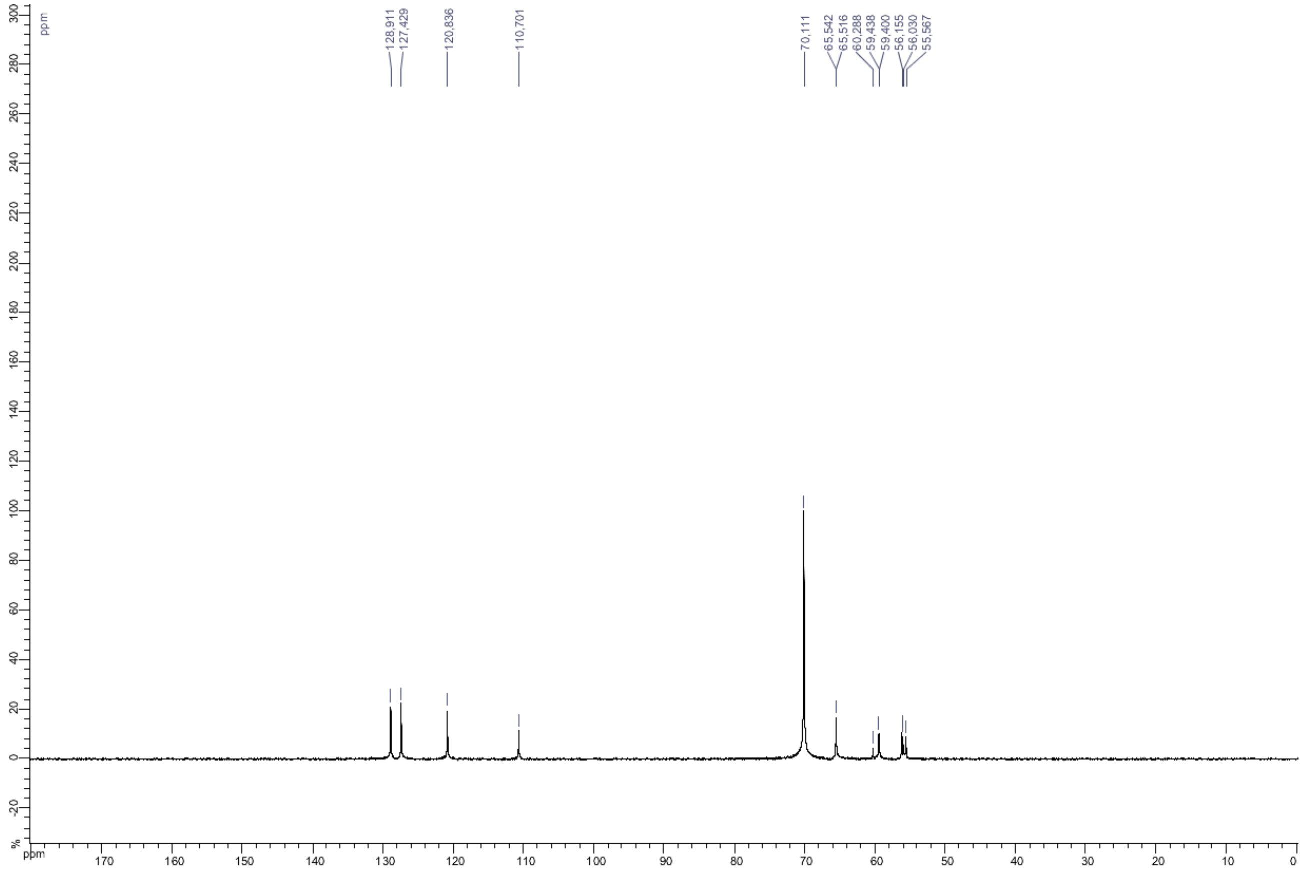
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



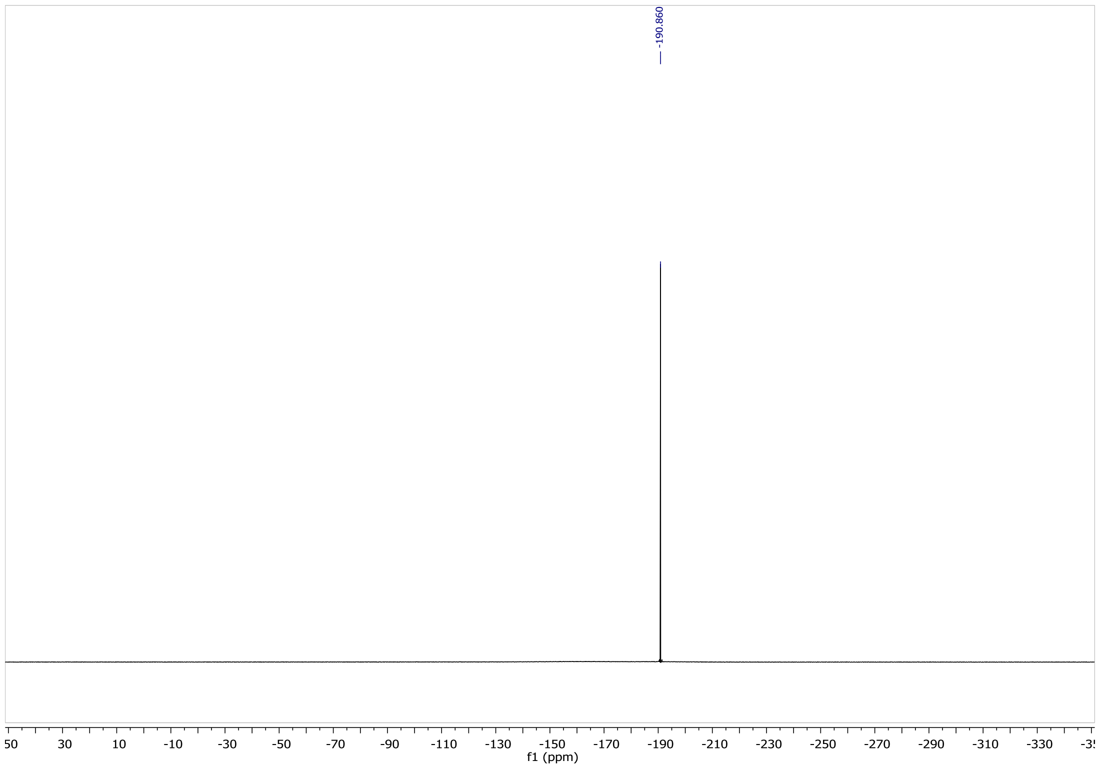
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



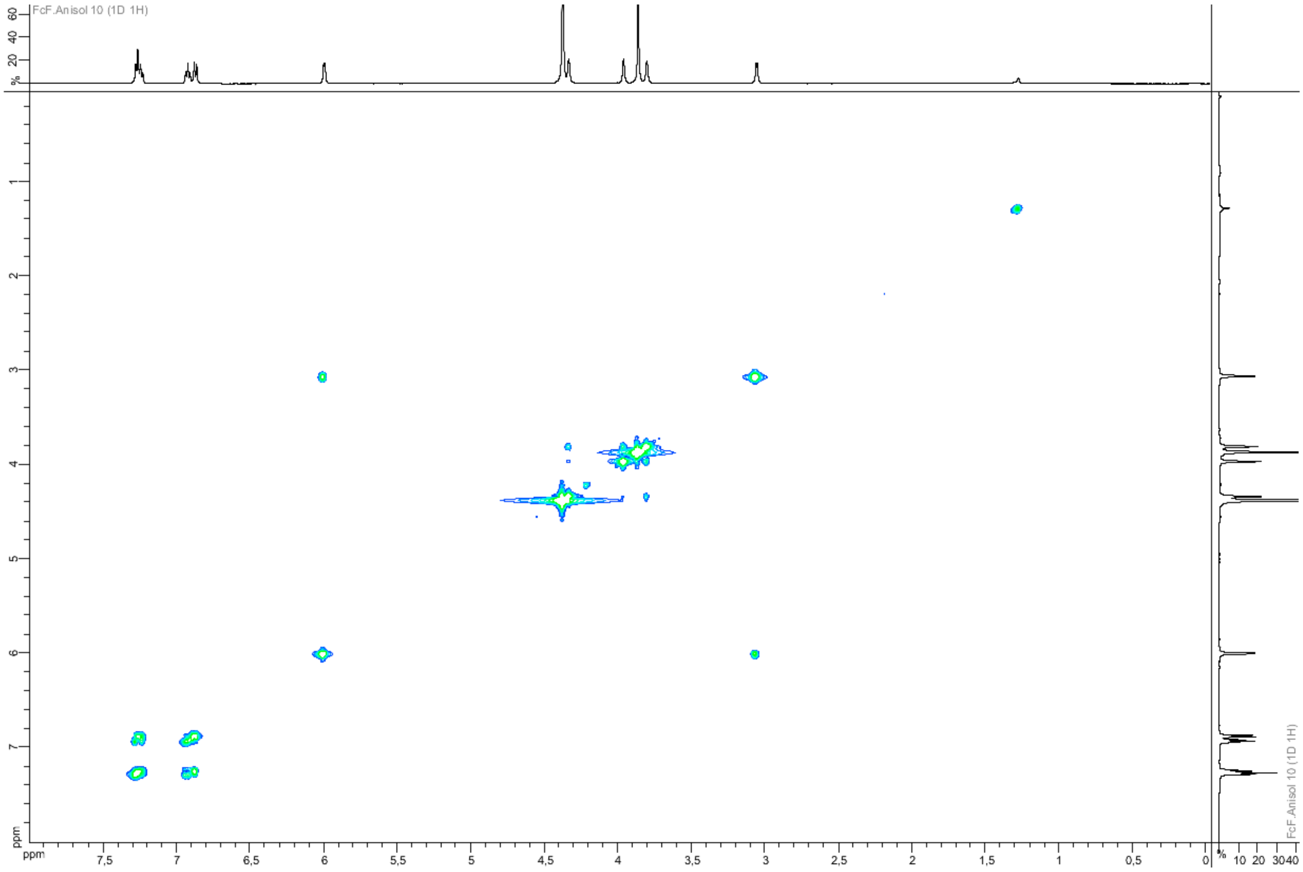
DEPT 135 (126 MHz, $CDCl_3$, 298 K)



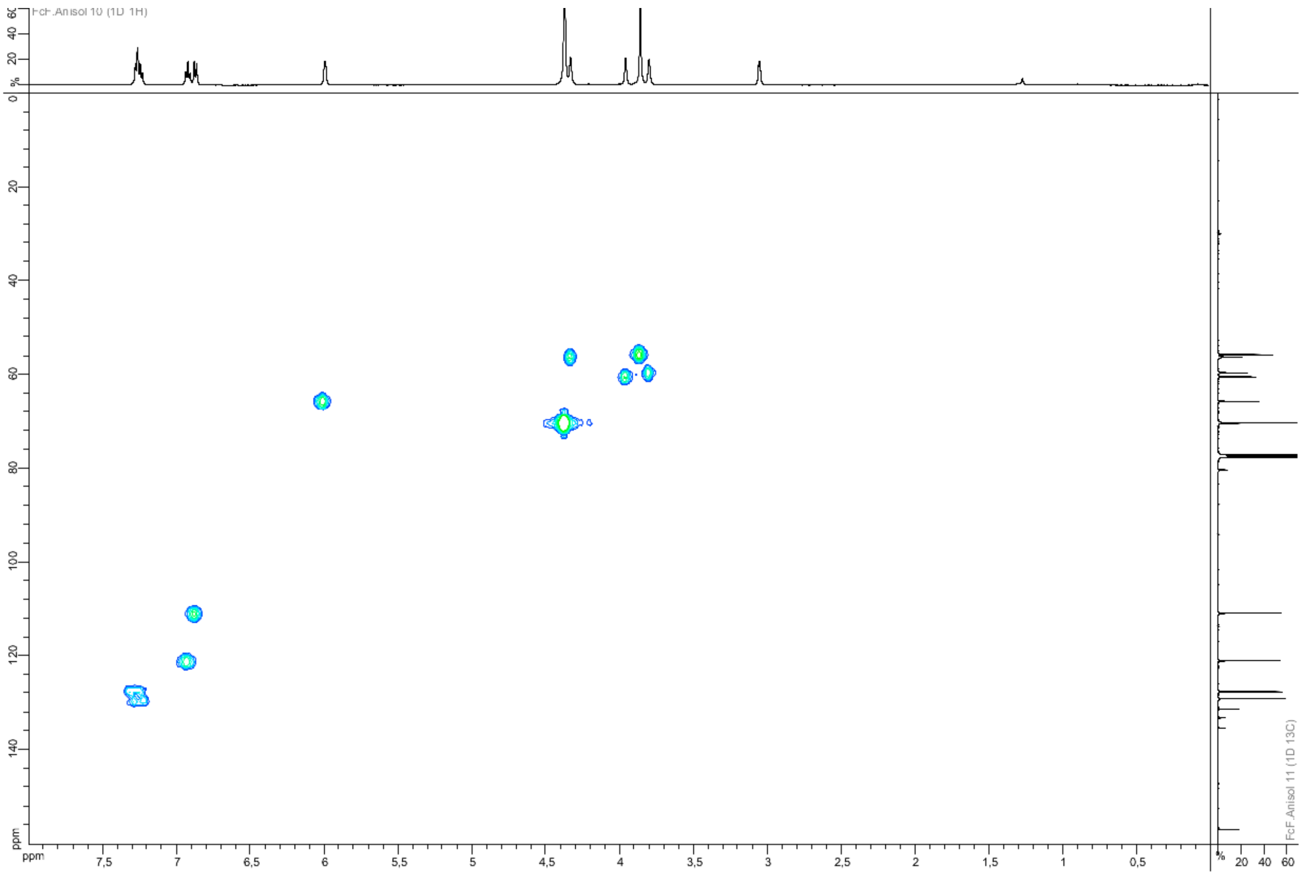
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



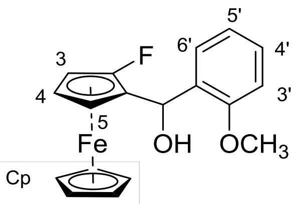
COSY (500 MHz, $CDCl_3$, 298 K)



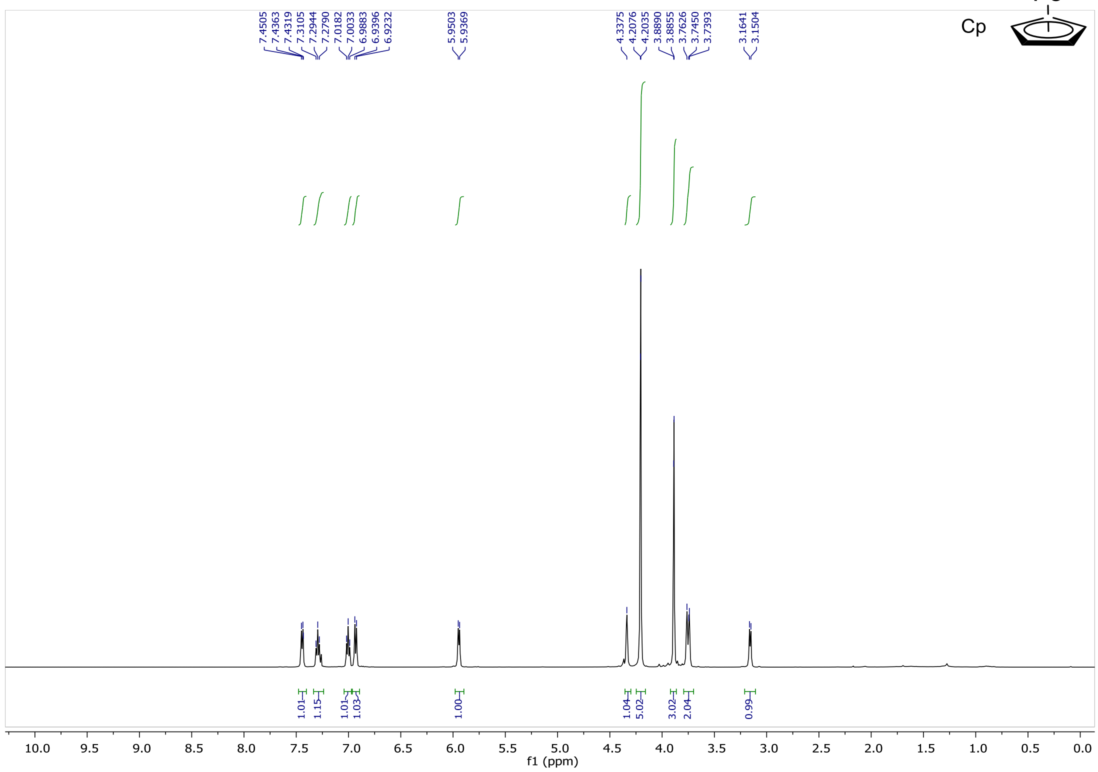
HSQC (500 MHz, $CDCl_3$, 298 K)



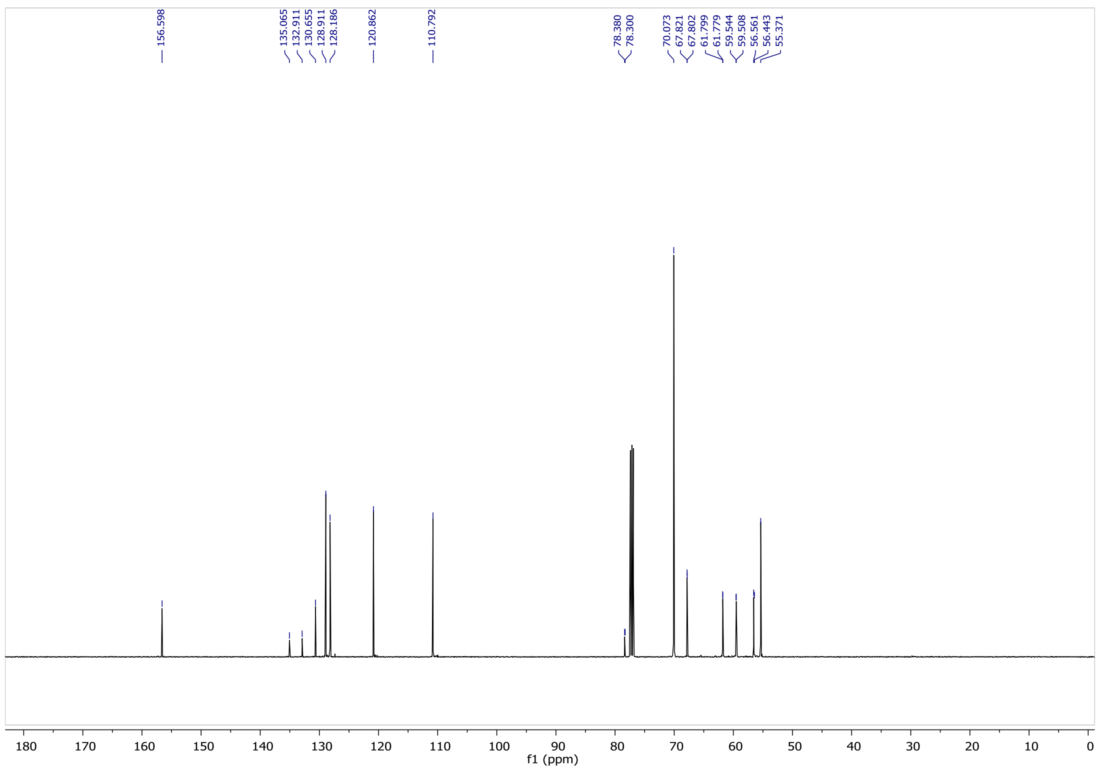
Compound 3k' (minor diastereoisomer, racemic mixture)



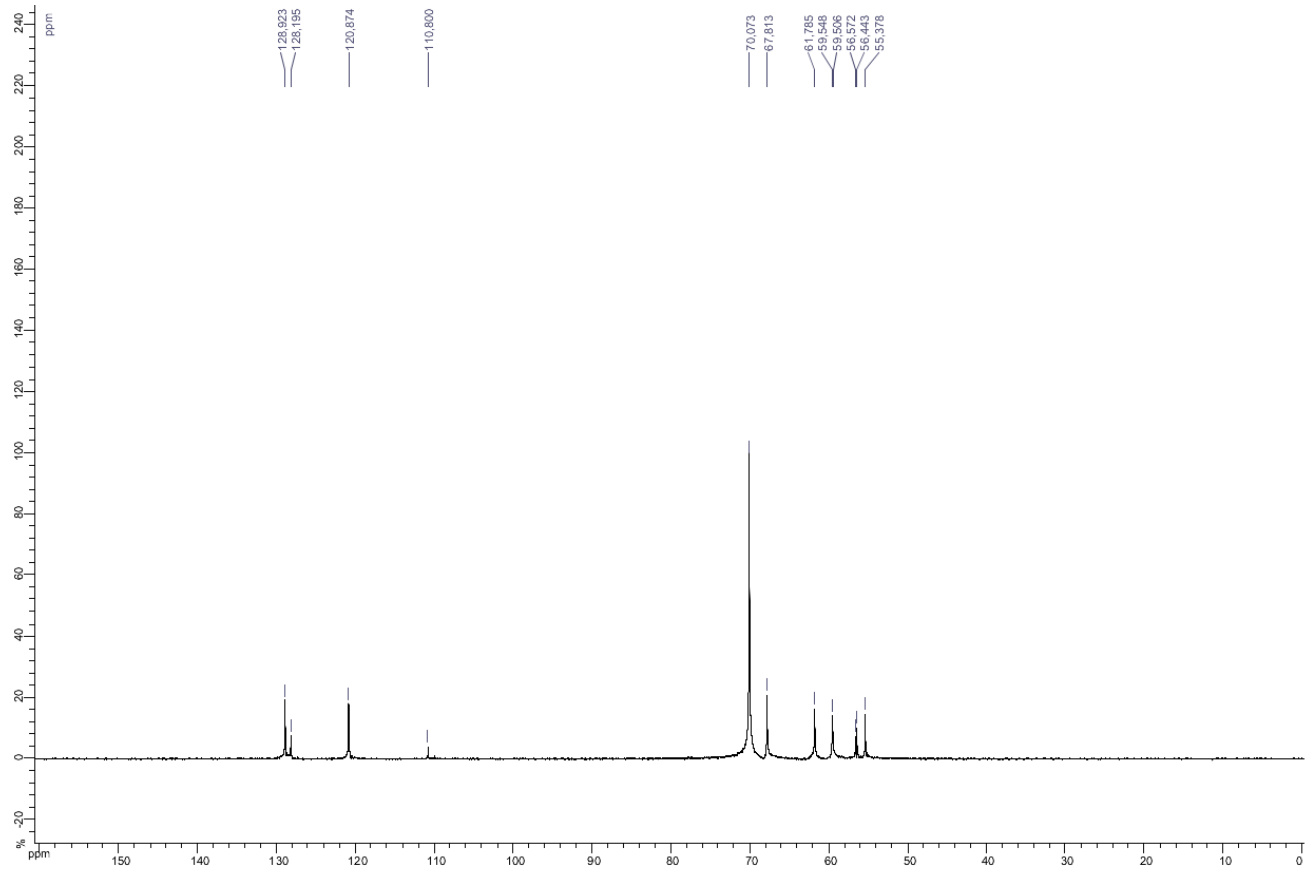
^1H NMR (500 MHz, $CDCl_3$, 298 K)



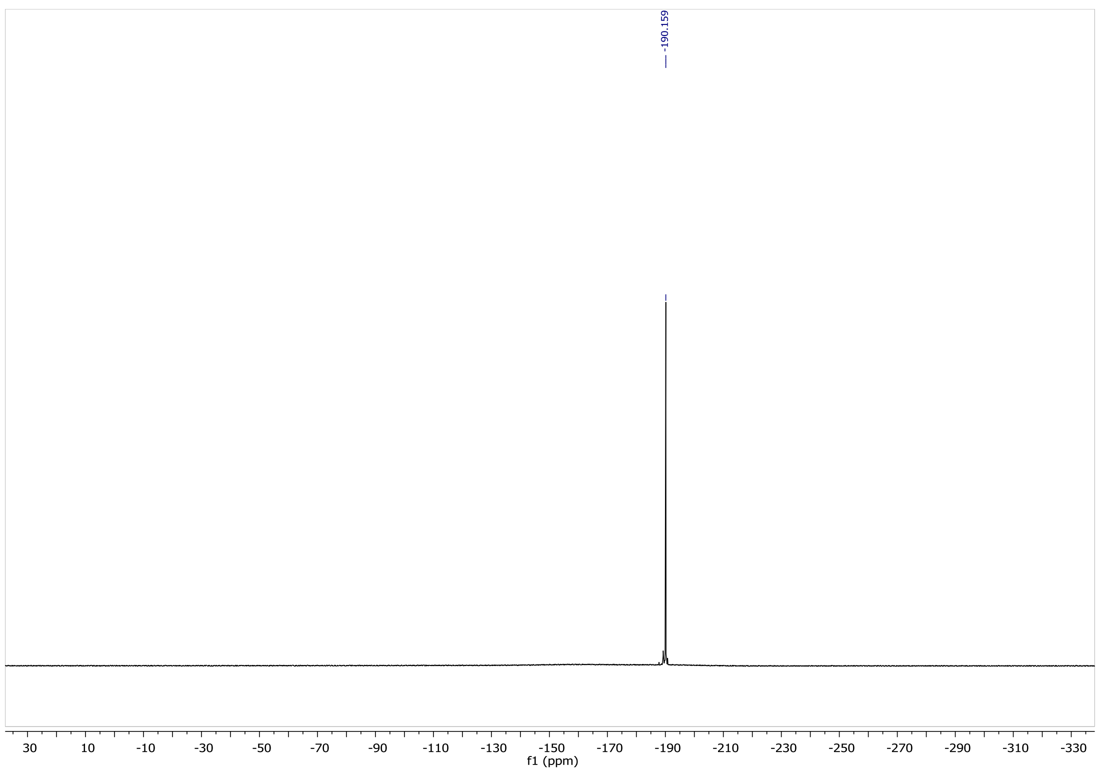
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



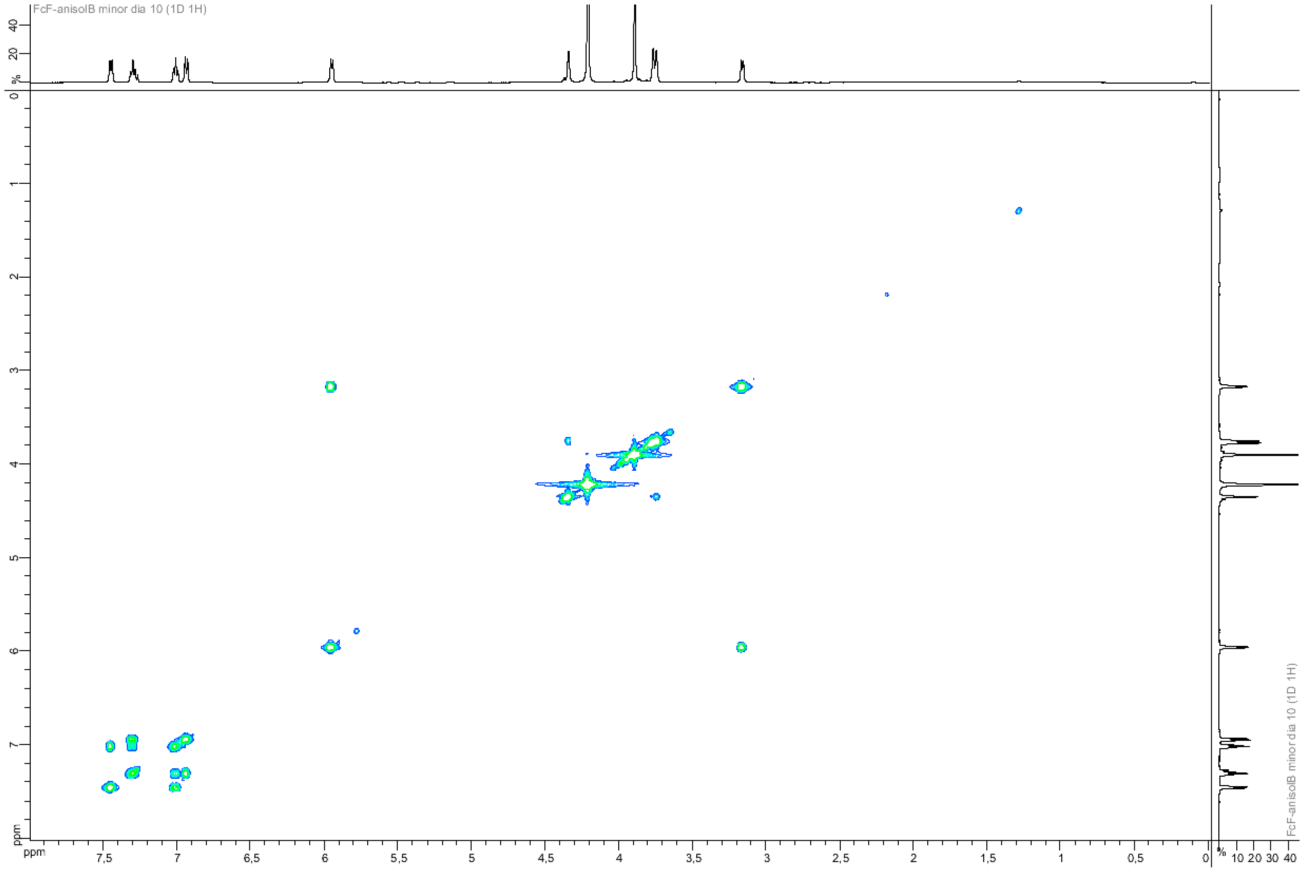
DEPT 135 (126 MHz, $CDCl_3$, 298 K)



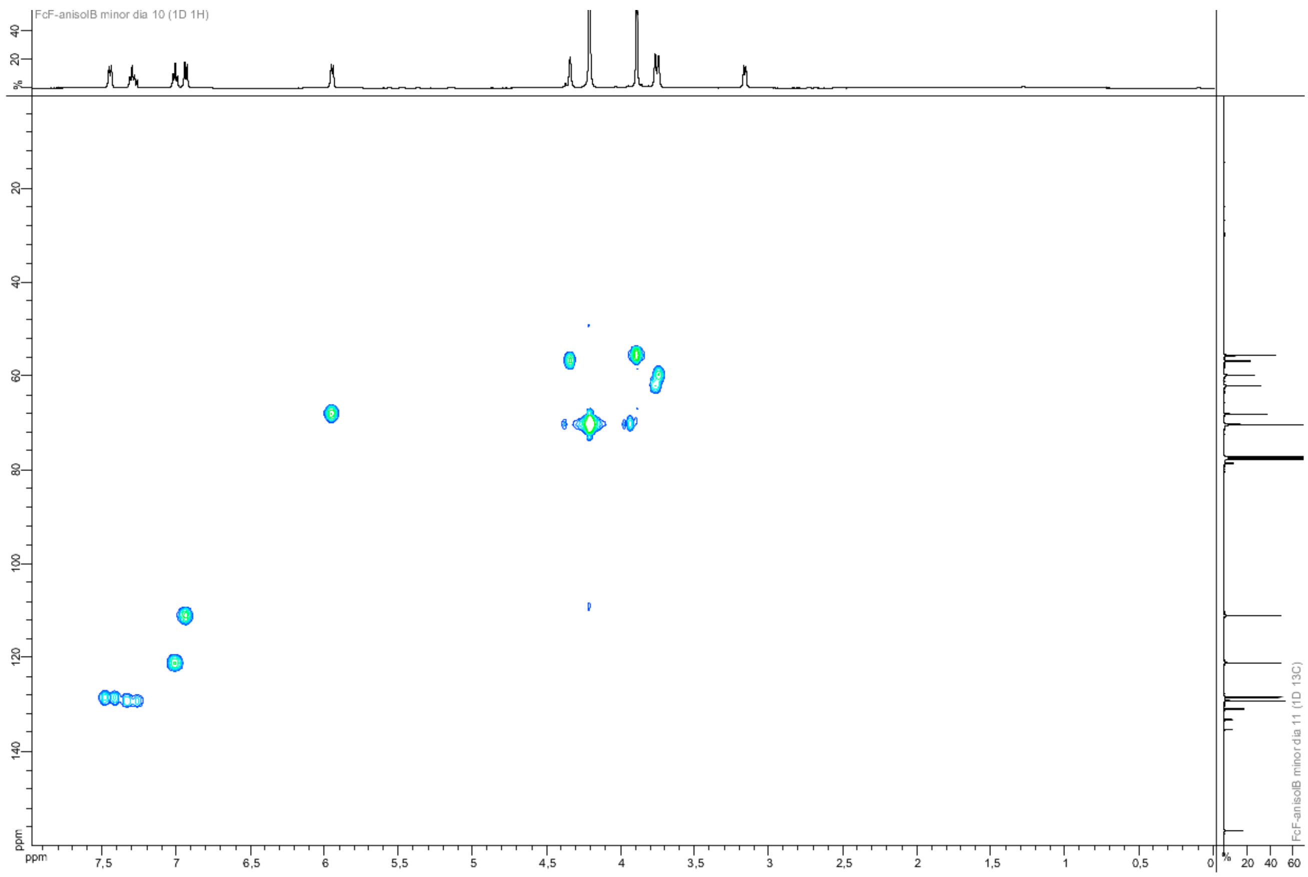
[19]F NMR (282 MHz, $CDCl_3$, 291 K)



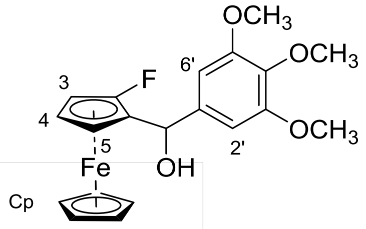
COSY (500 MHz, $CDCl_3$, 298 K)



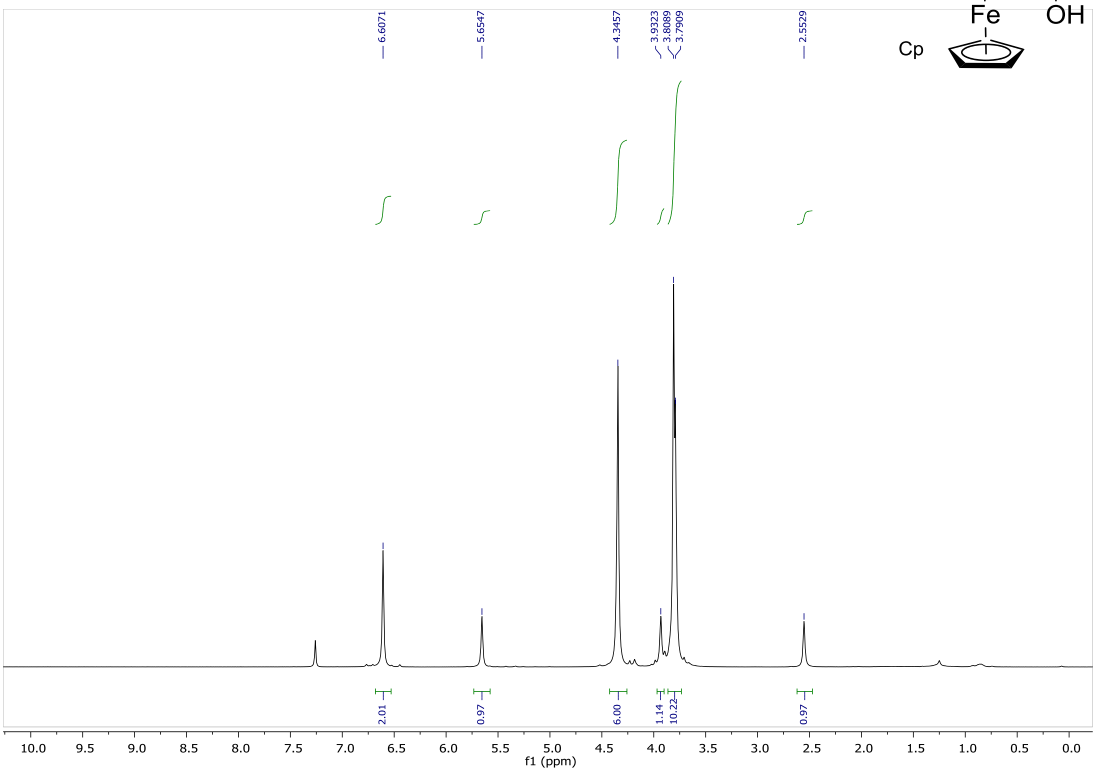
HSQC (500 MHz, $CDCl_3$, 298 K)



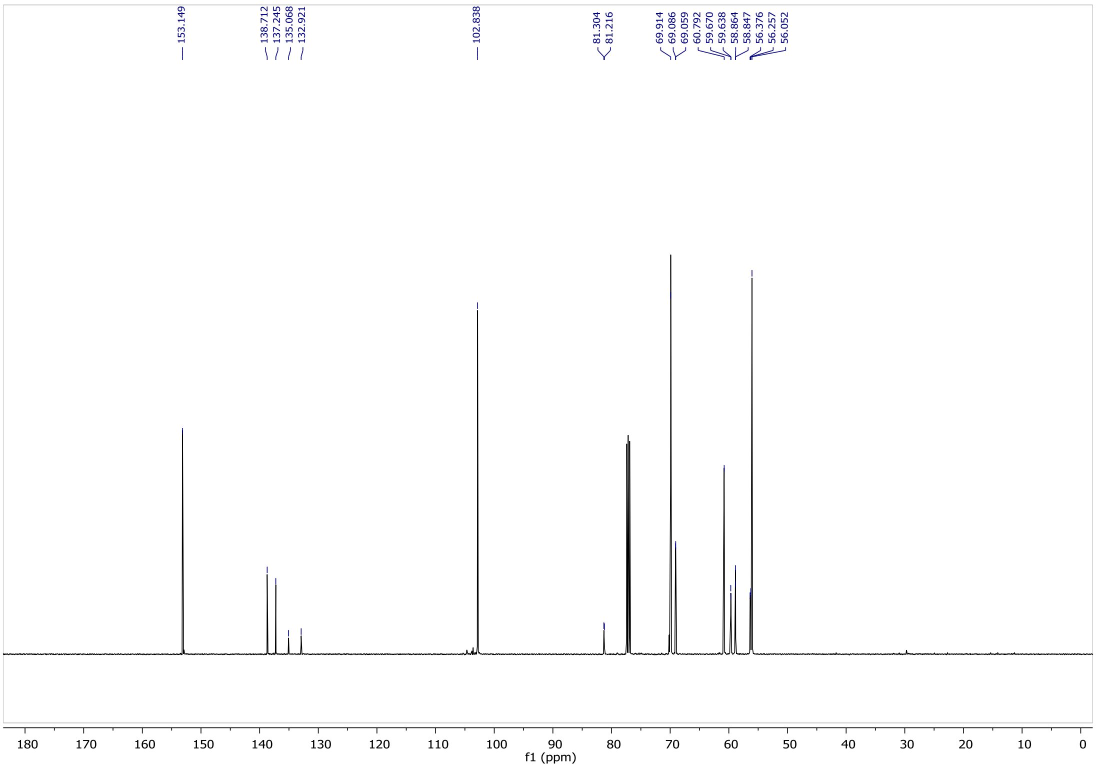
Compound 3l (major diastereoisomer, racemic mixture)



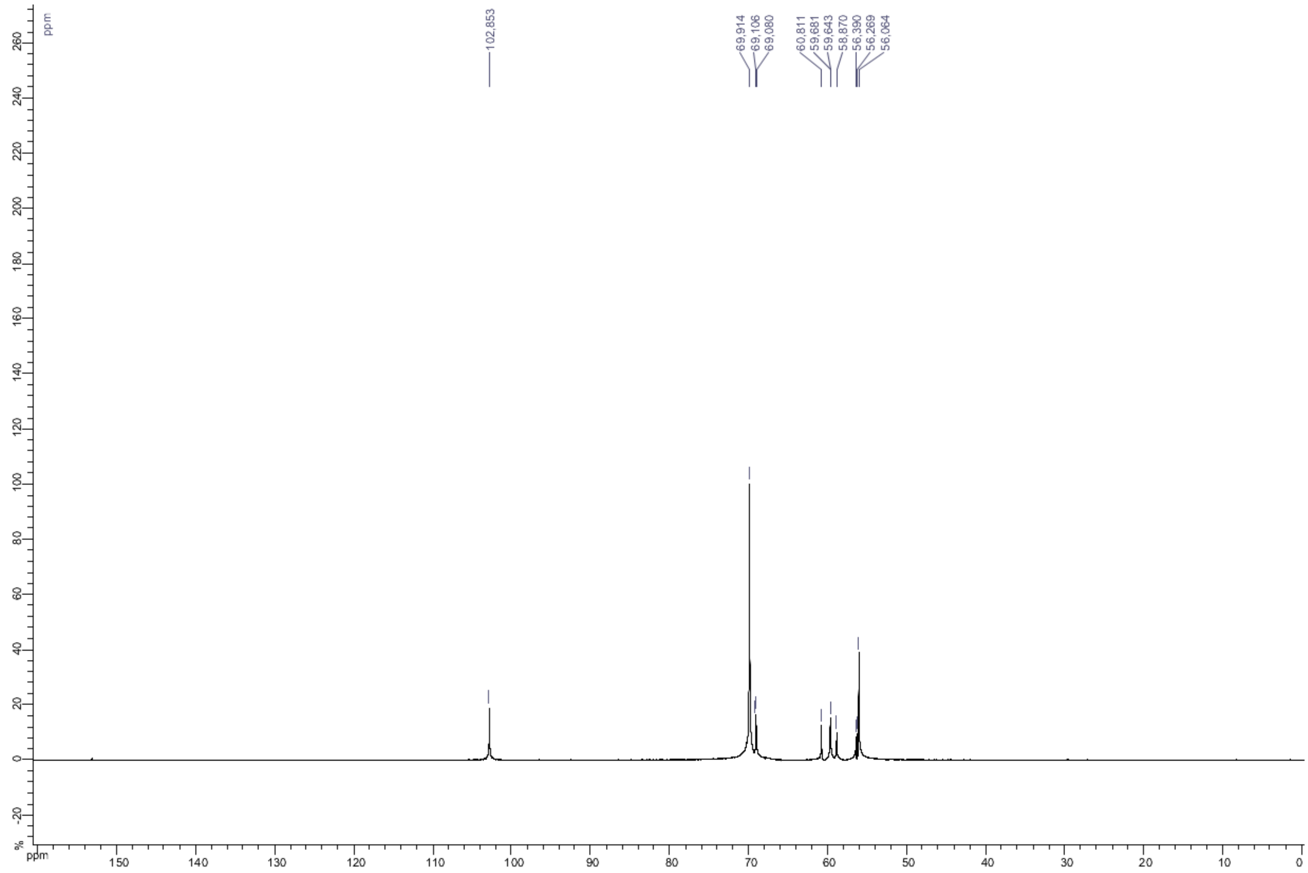
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



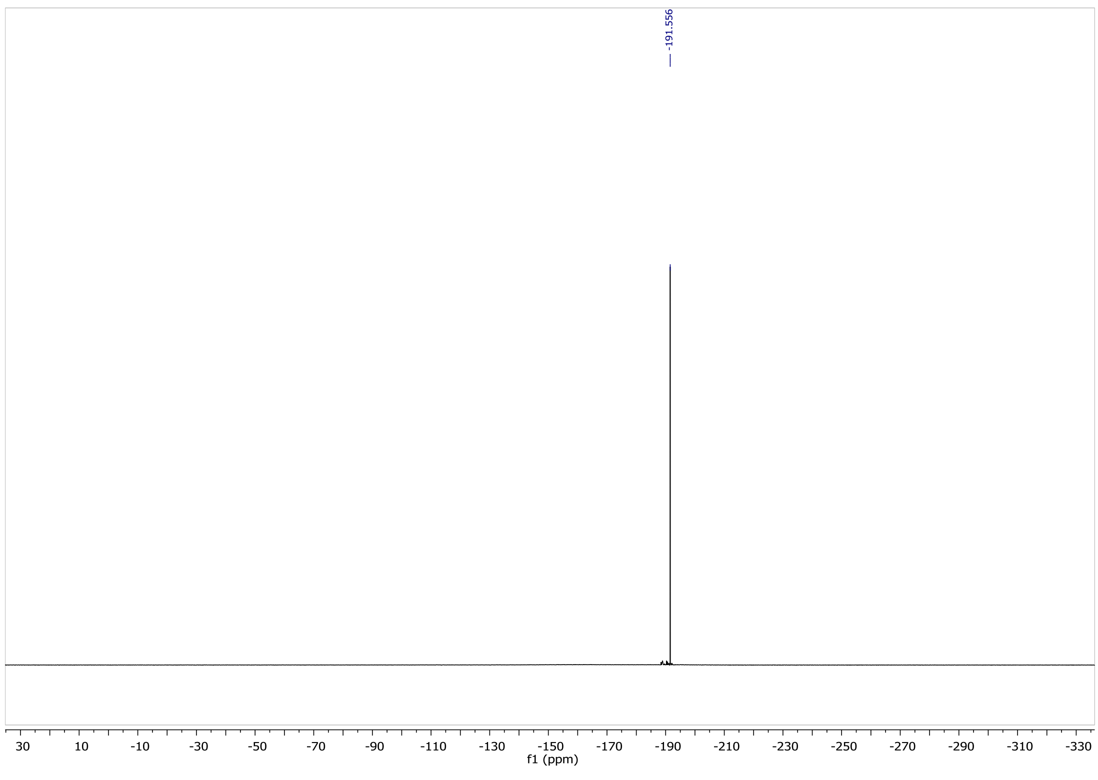
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



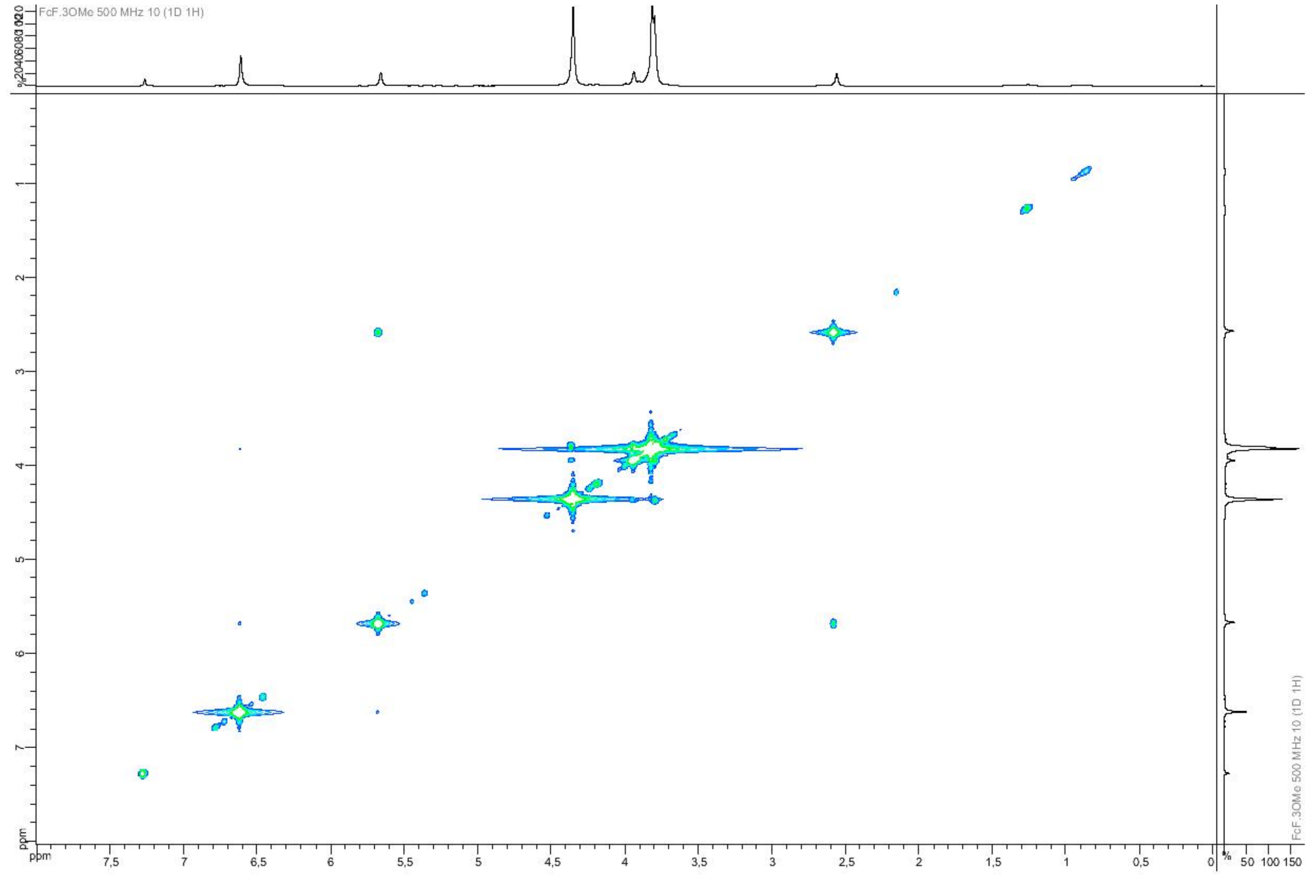
DEPT 135 (126 MHz, $CDCl_3$, 298 K)



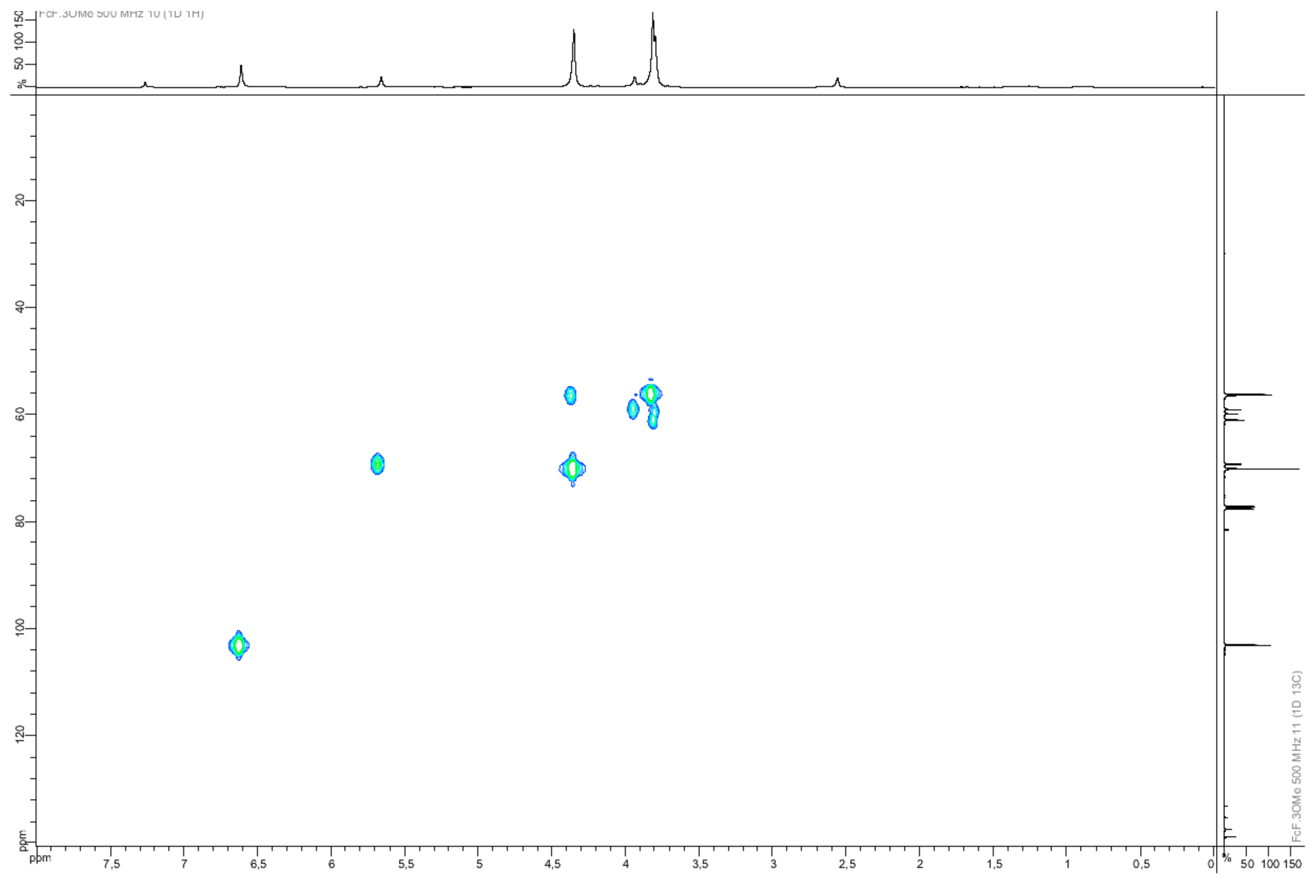
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



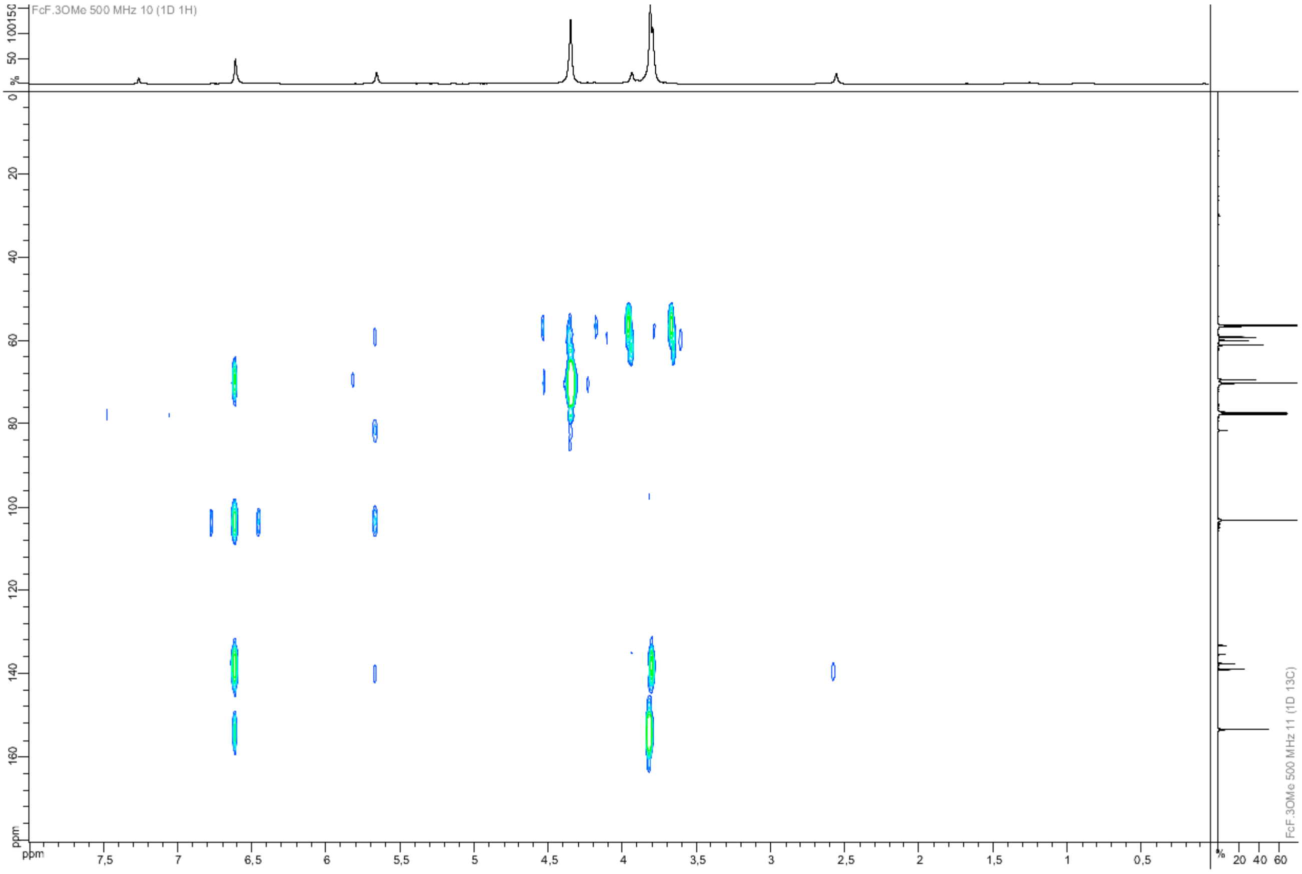
COSY (500 MHz, $CDCl_3$, 298 K)



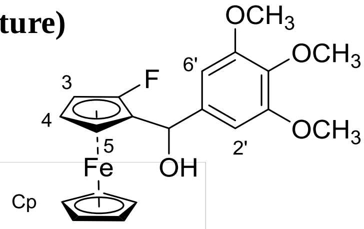
HSQC (500 MHz, $CDCl_3$, 298 K)



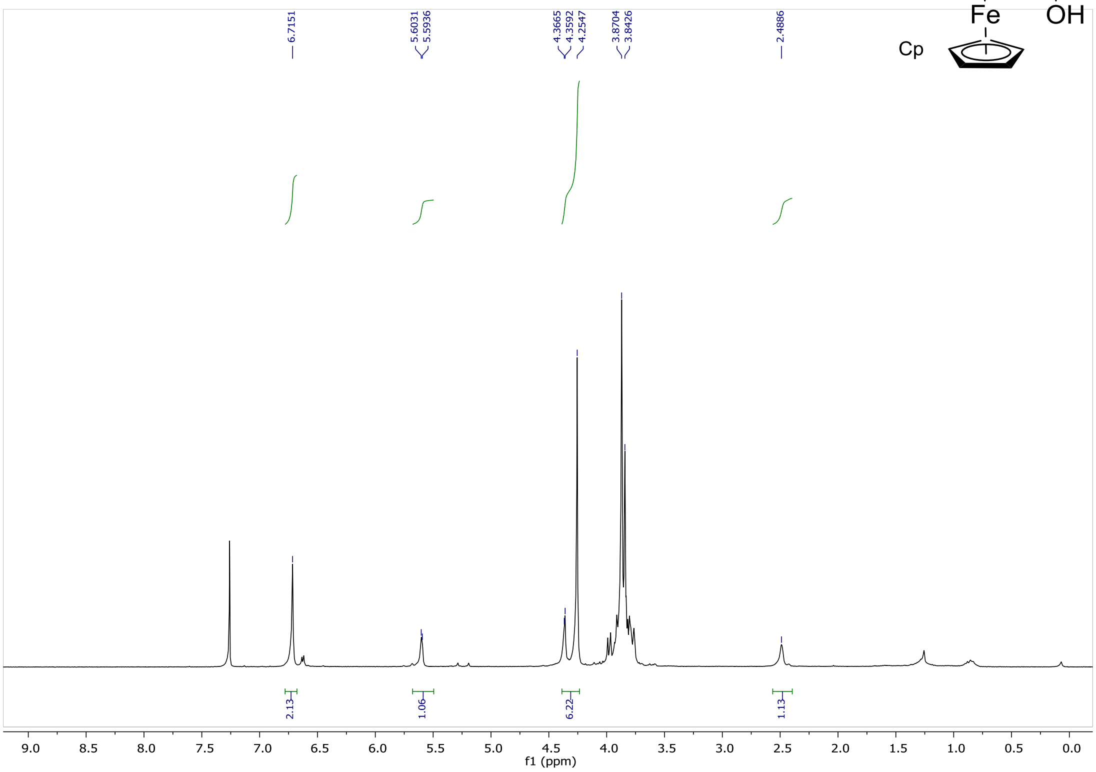
HMBC (500 MHz, $CDCl_3$, 298 K)



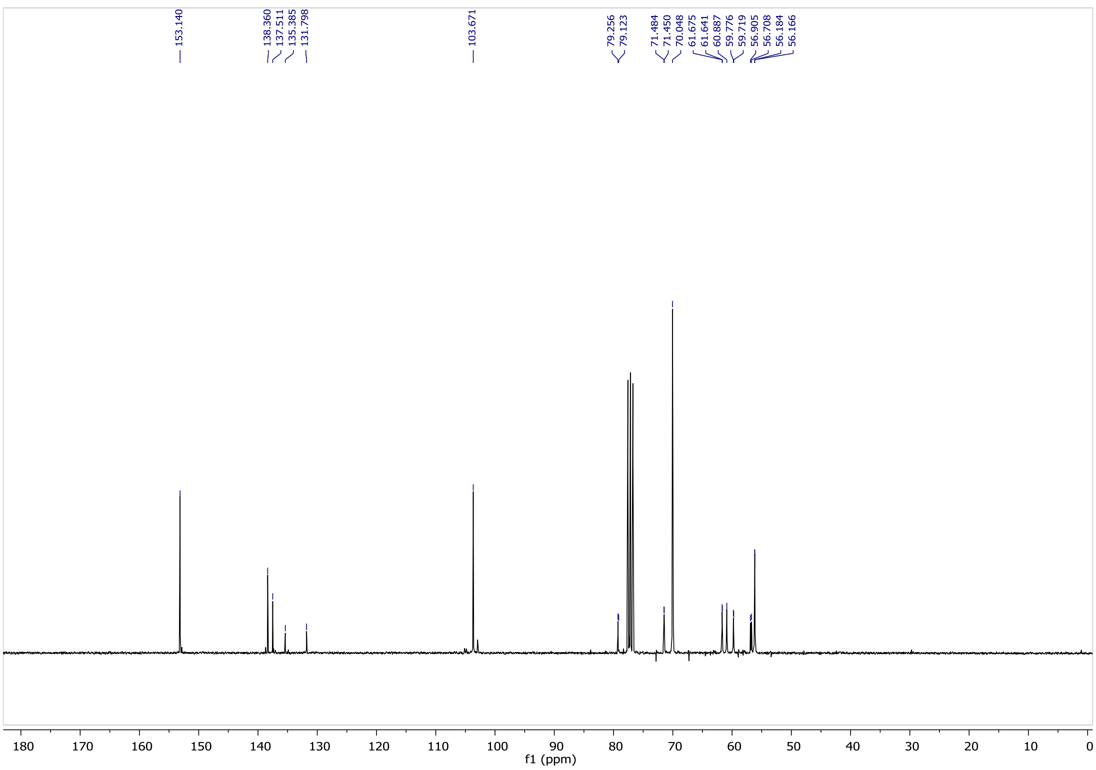
Compound 3l’ (minor diastereoisomer containing impurities, racemic mixture)



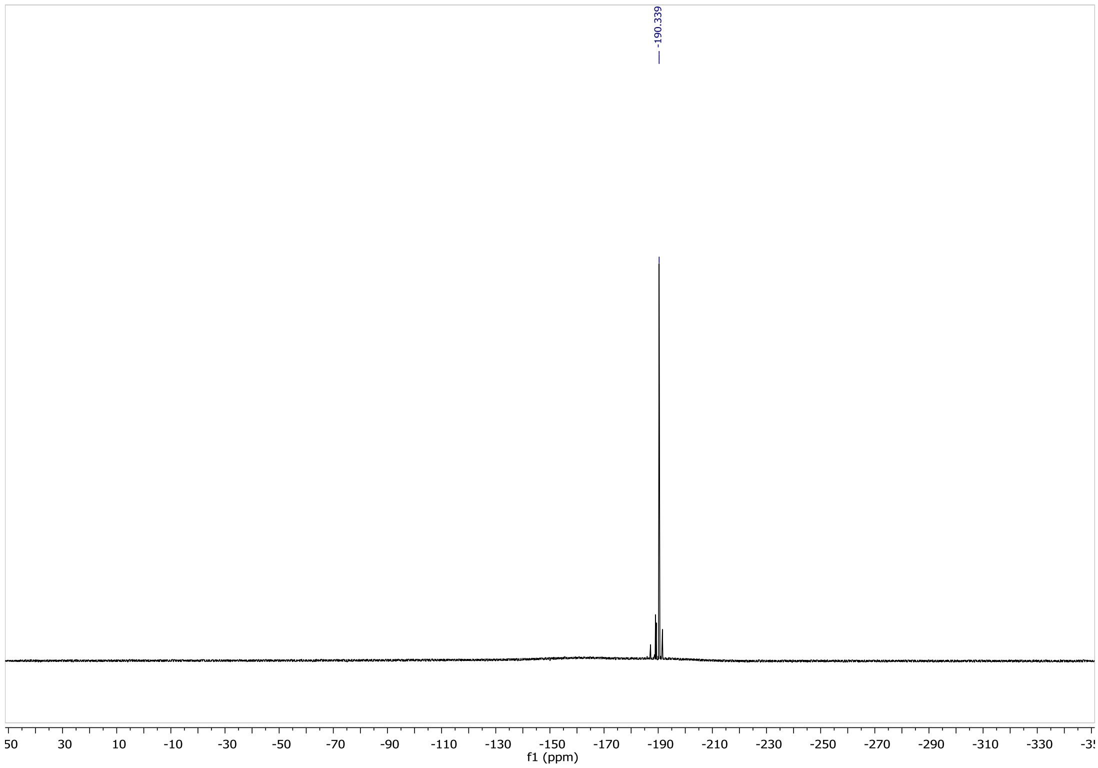
^{1}H NMR (300 MHz, CDCl$_3$, 291 K)



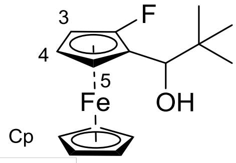
^{13}C NMR (75 MHz, CDCl$_3$, 291 K)



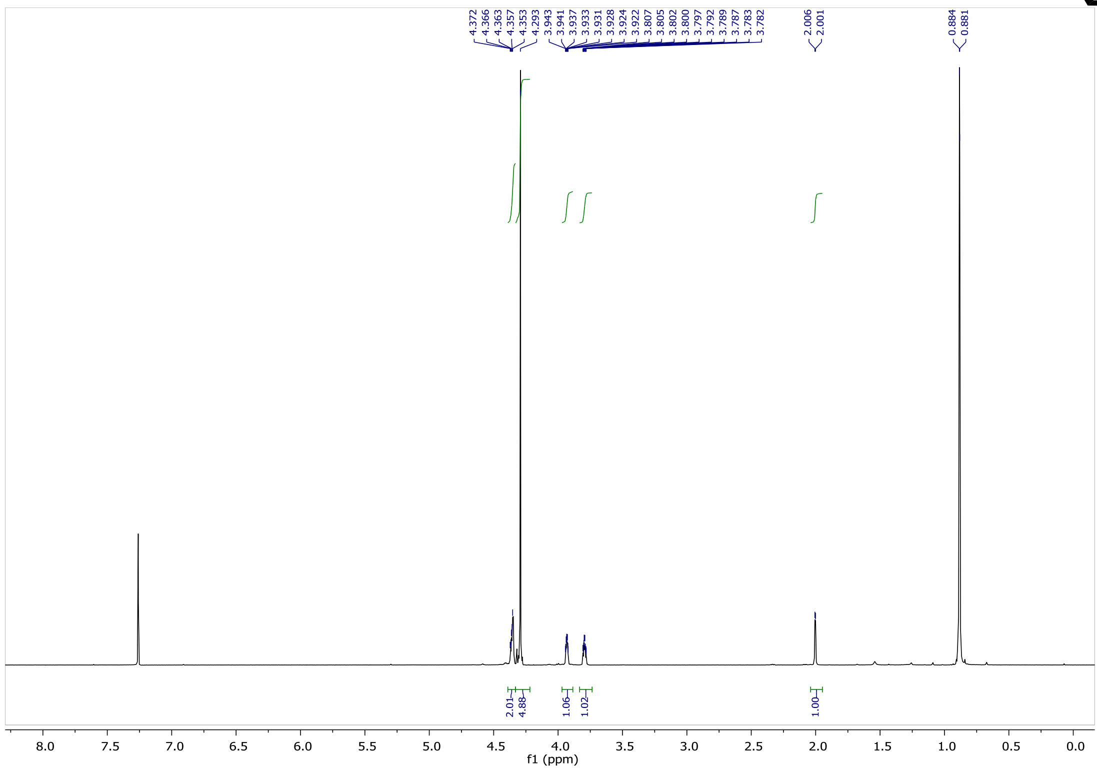
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



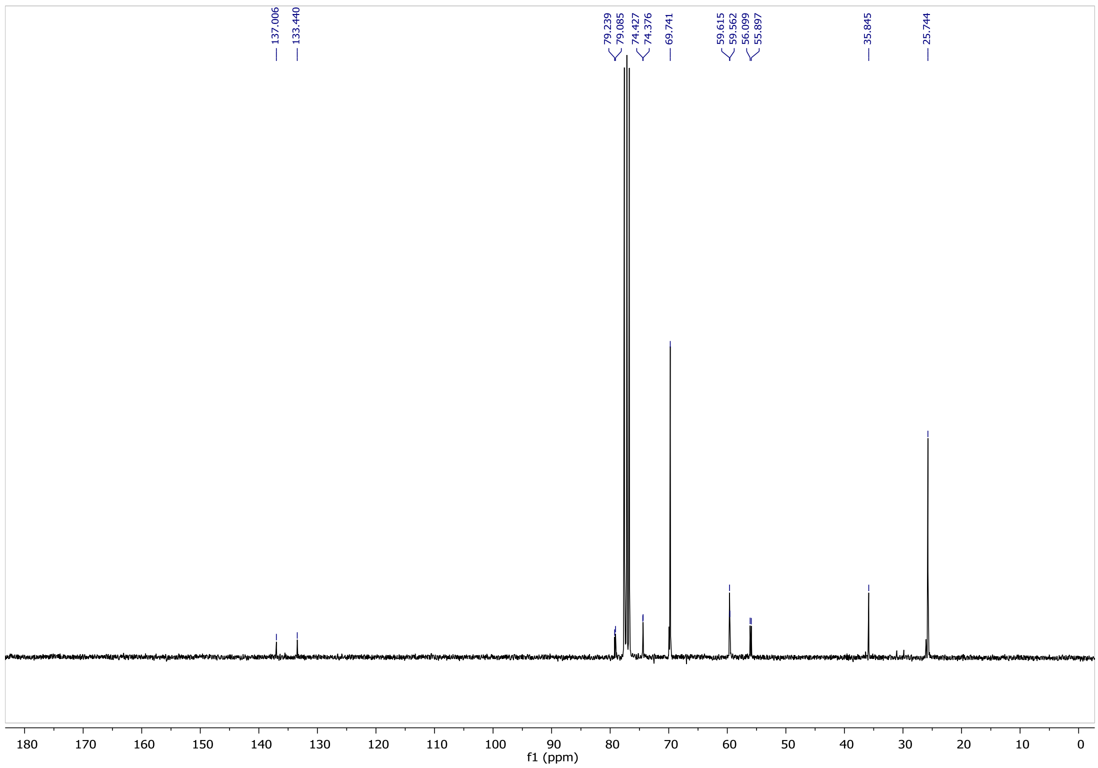
Compound 3m (major diastereoisomer, racemic mixture)



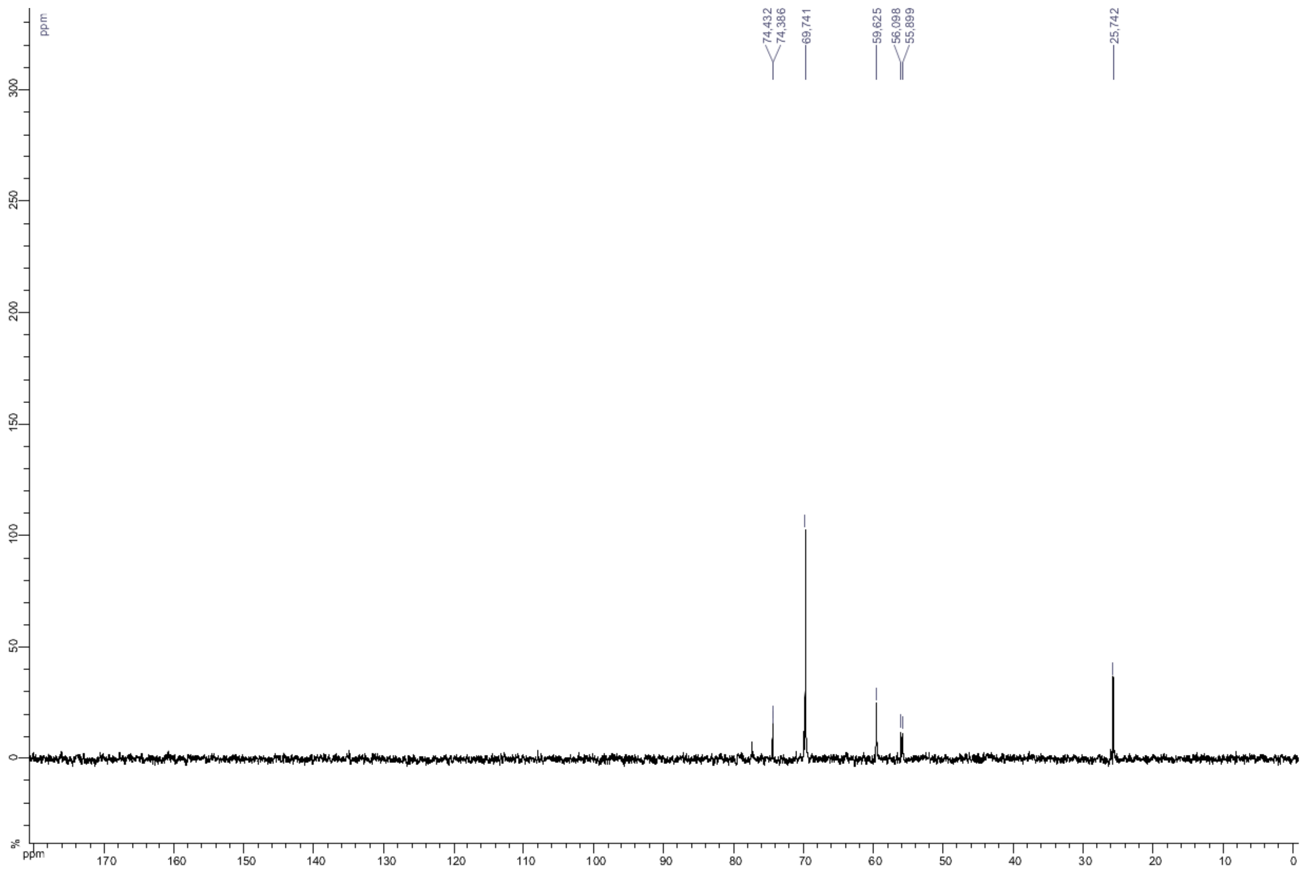
[1]H NMR (300 MHz, $CDCl_3$, 291 K)



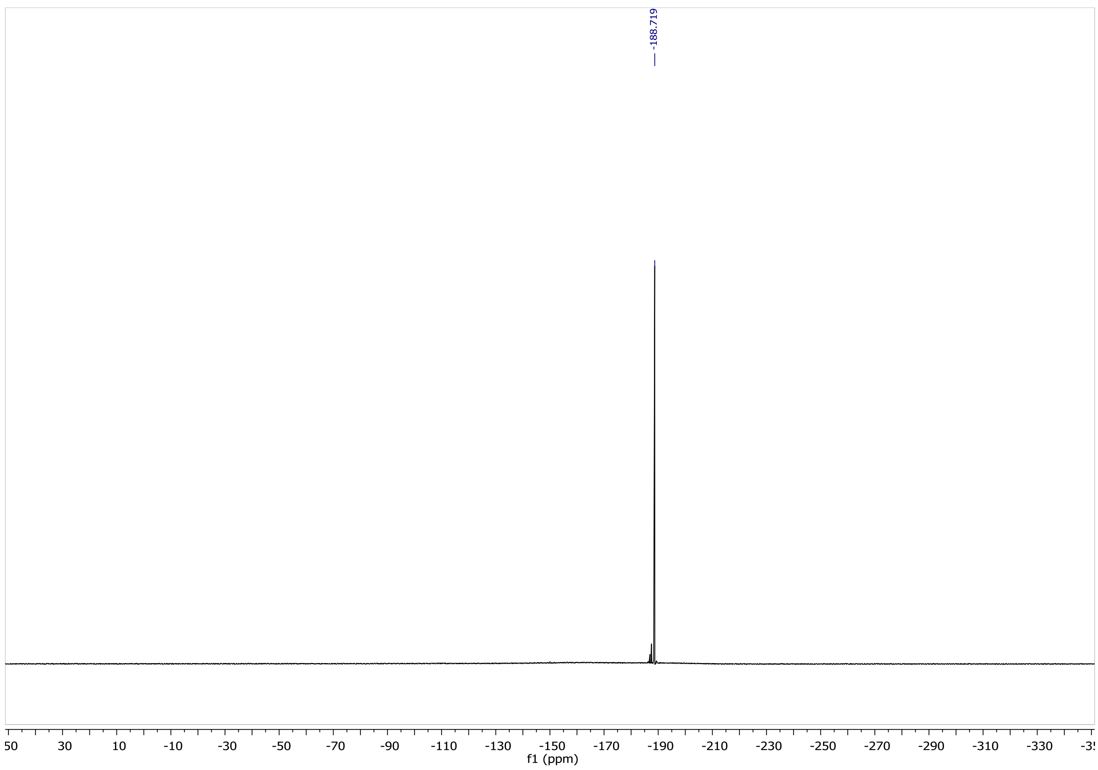
[13]C NMR (75 MHz, $CDCl_3$, 291 K)



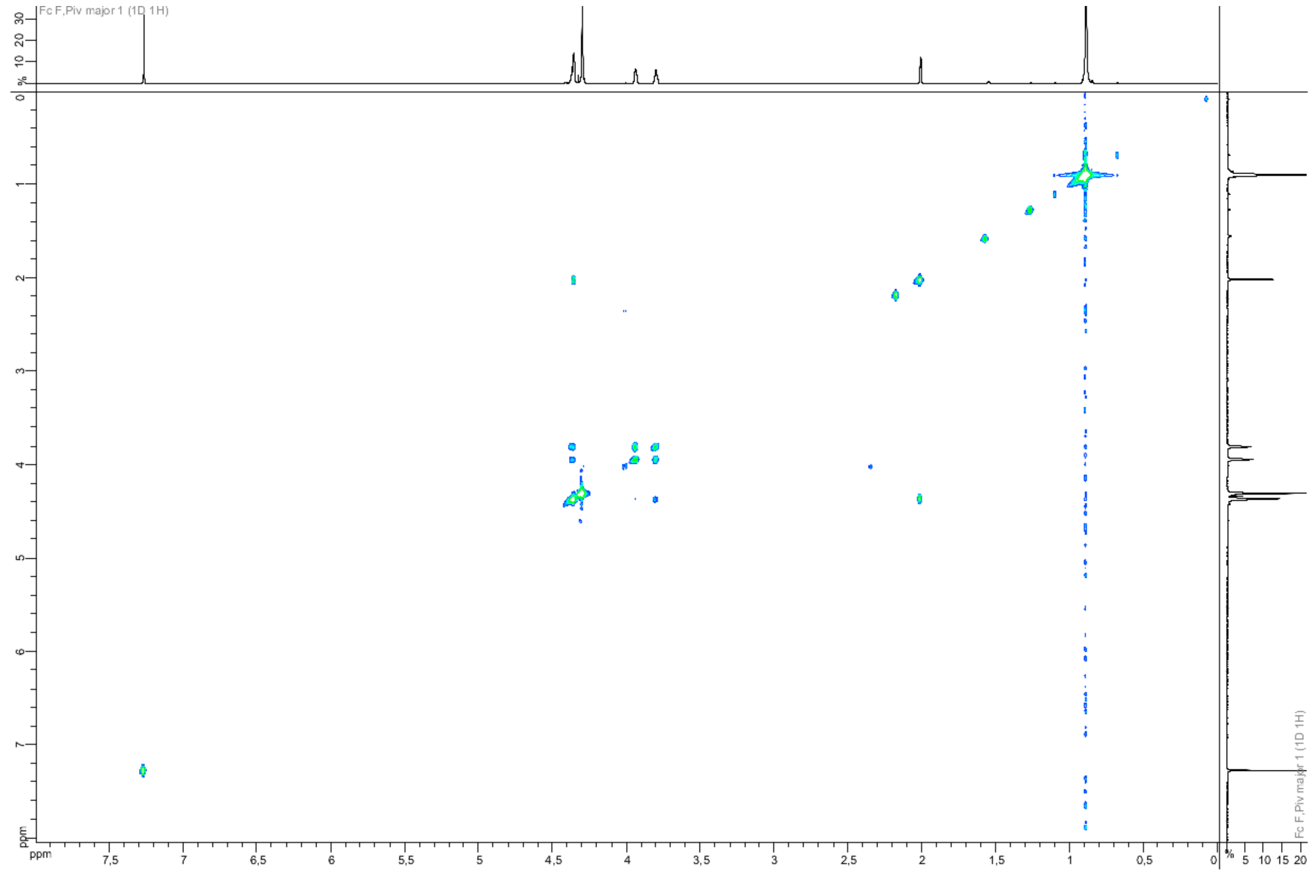
DEPT 135 (75 MHz, $CDCl_3$, 291 K)



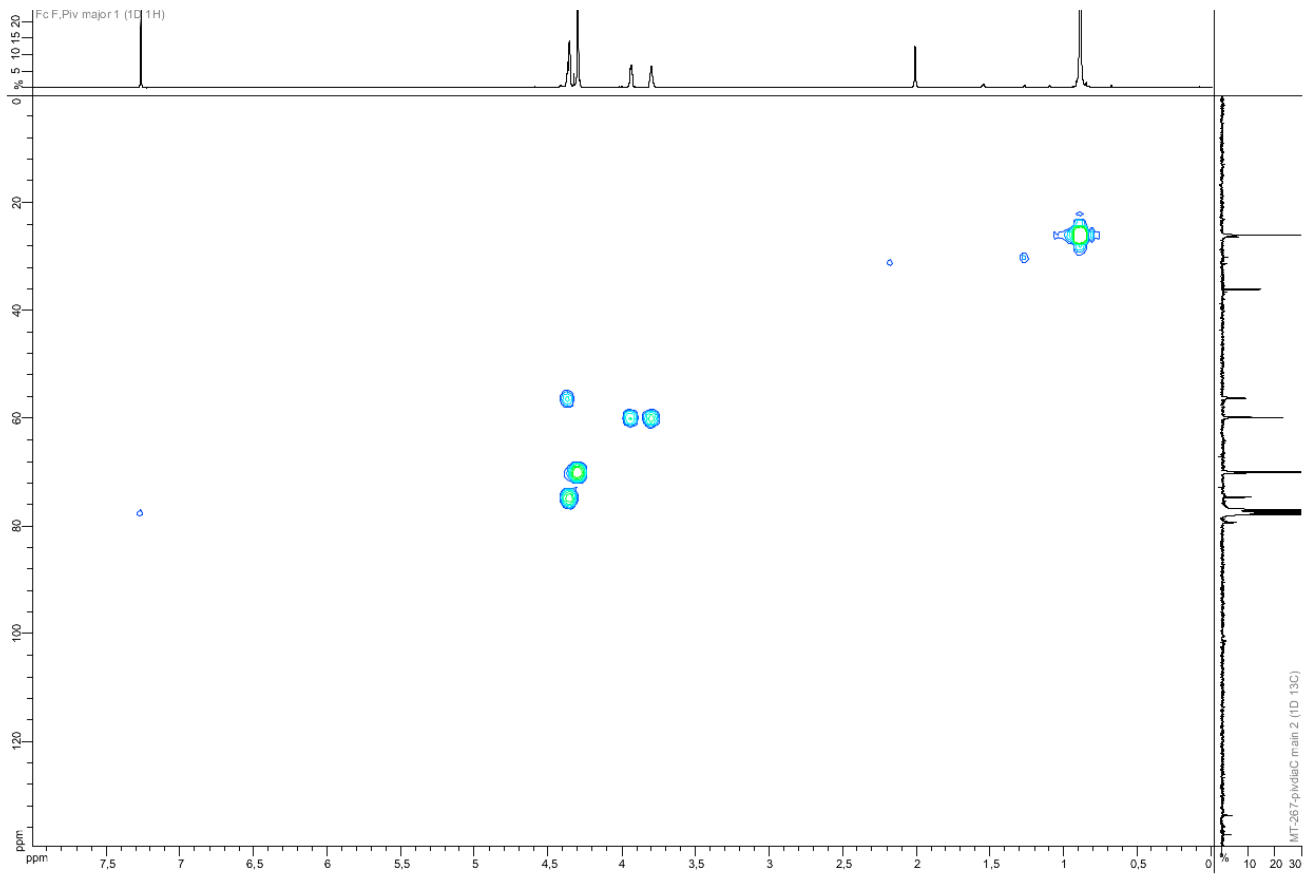
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



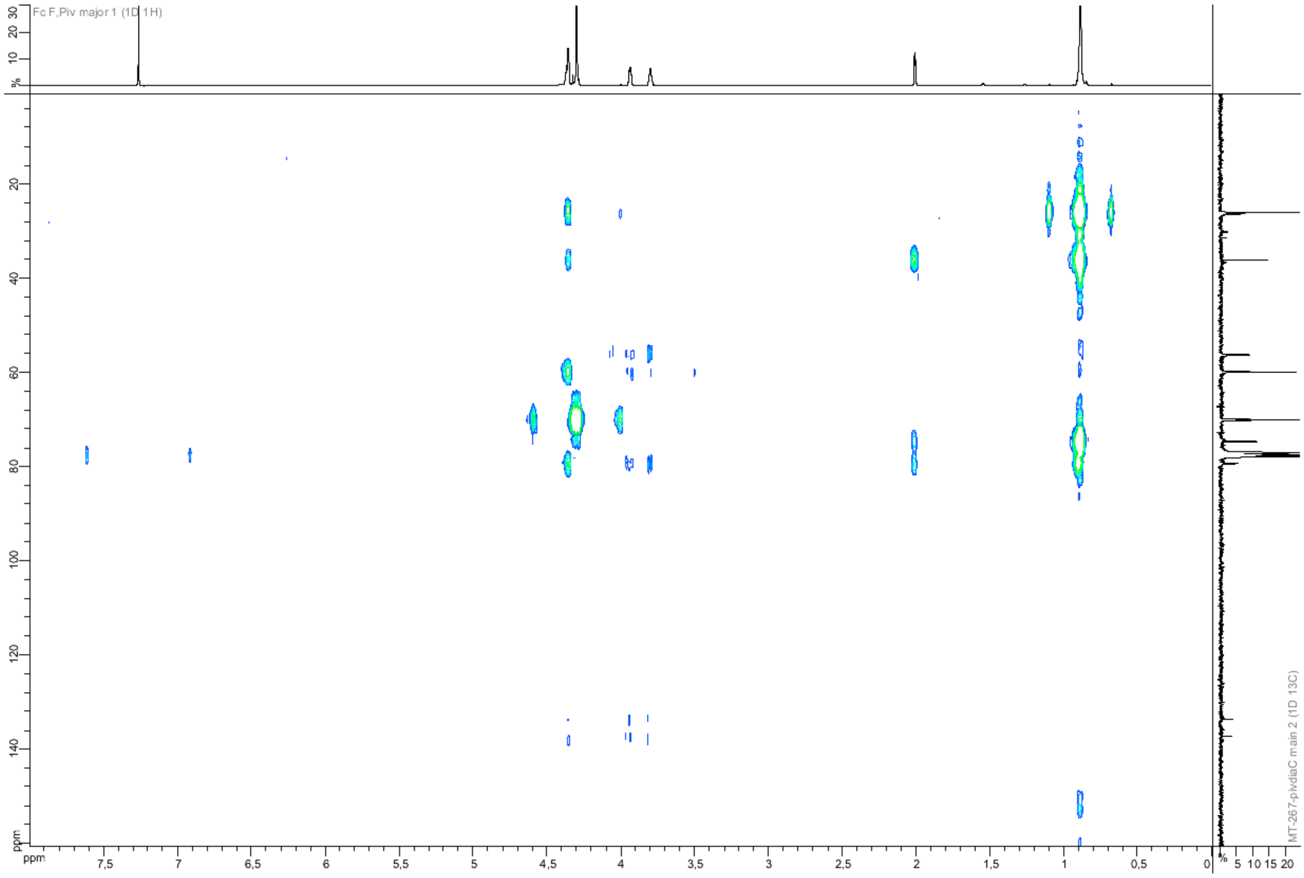
COSY (300 MHz, $CDCl_3$, 298 K)



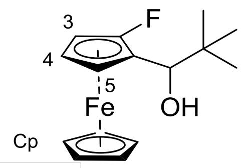
HSQC (500 MHz, $CDCl_3$, 298 K)



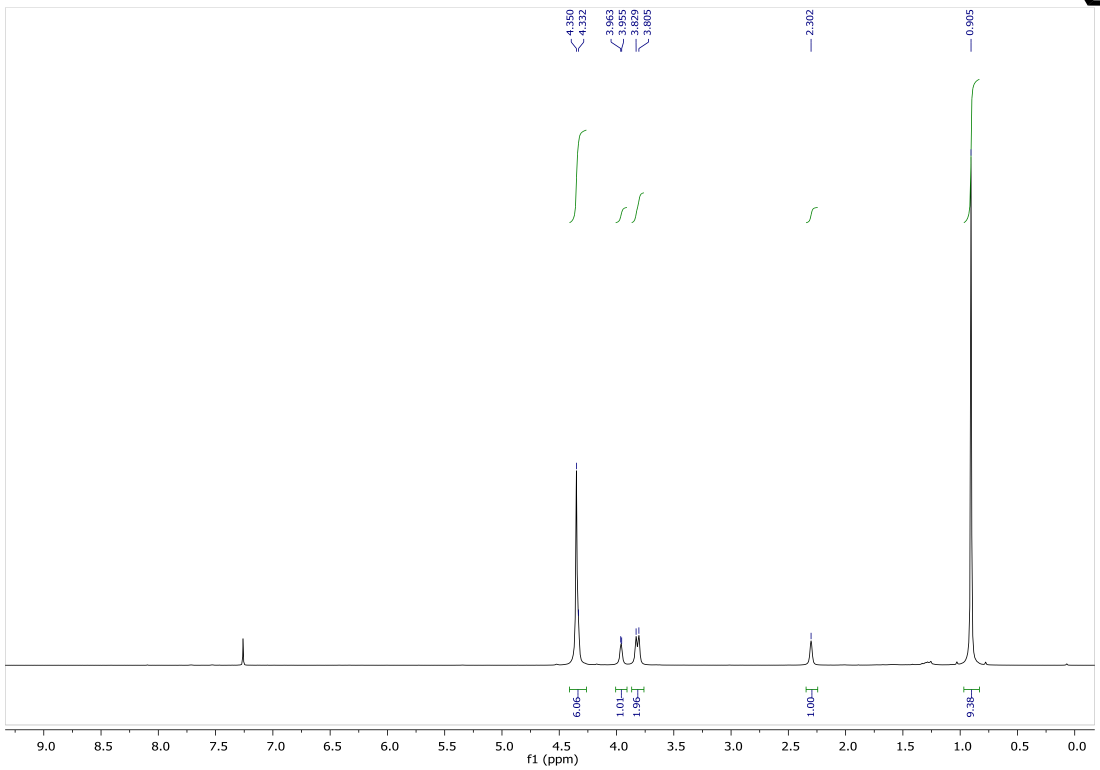
HMBC (500 MHz, $CDCl_3$, 298 K)



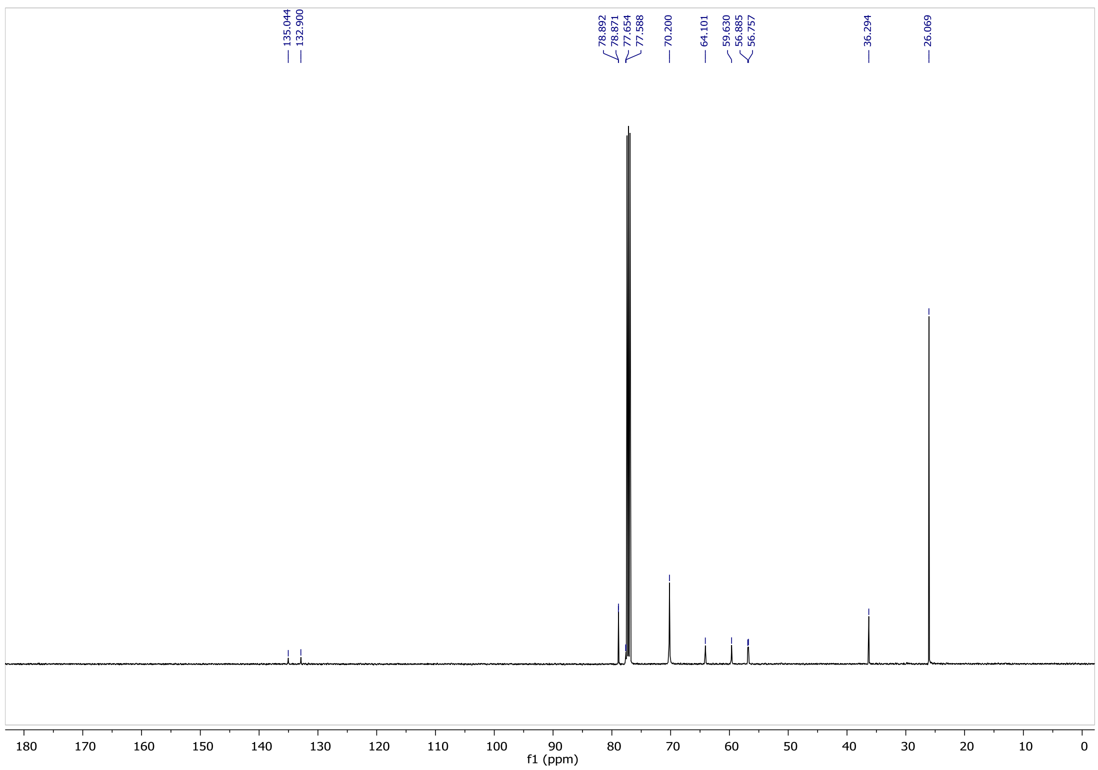
Compound 3m' (minor diastereoisomer, racemic mixture)



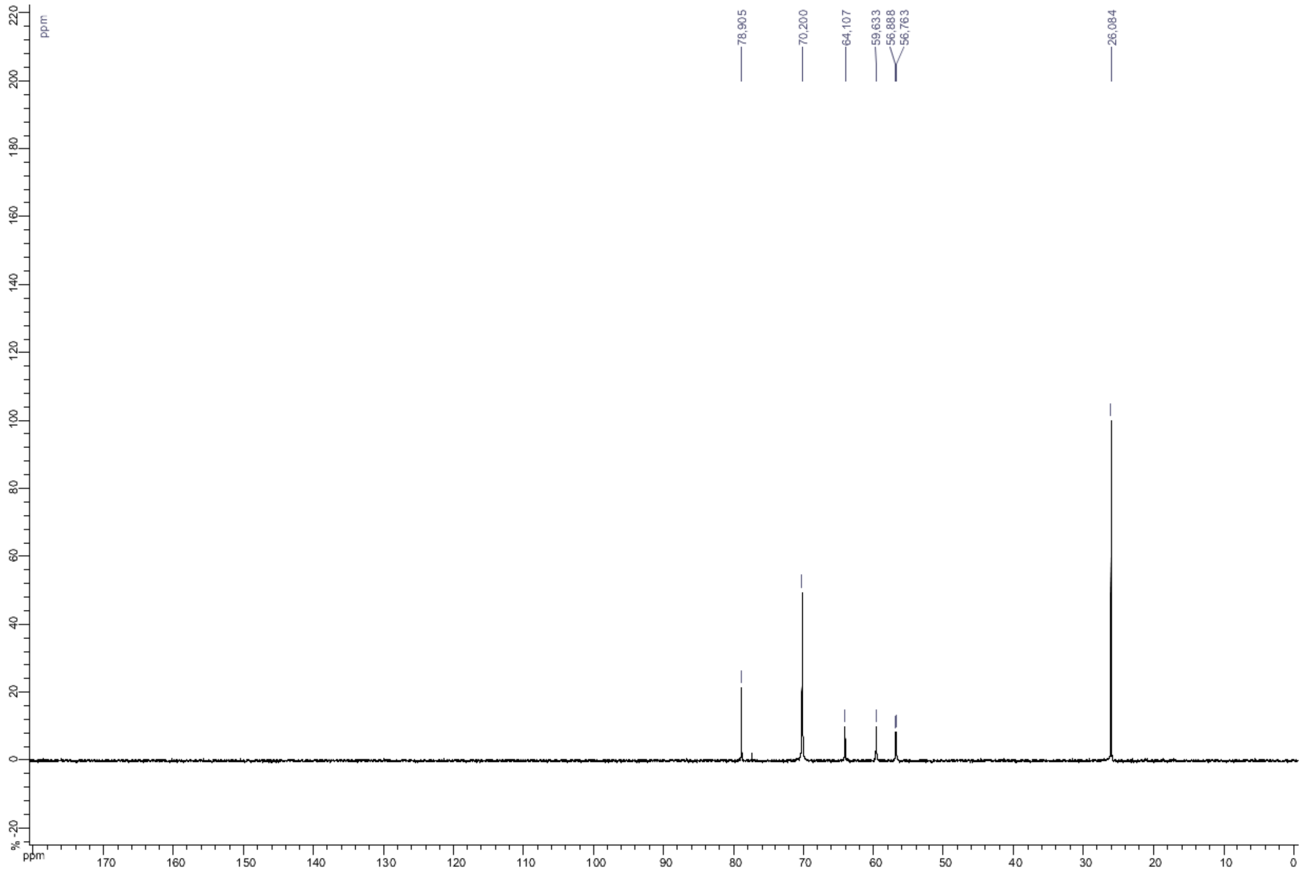
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



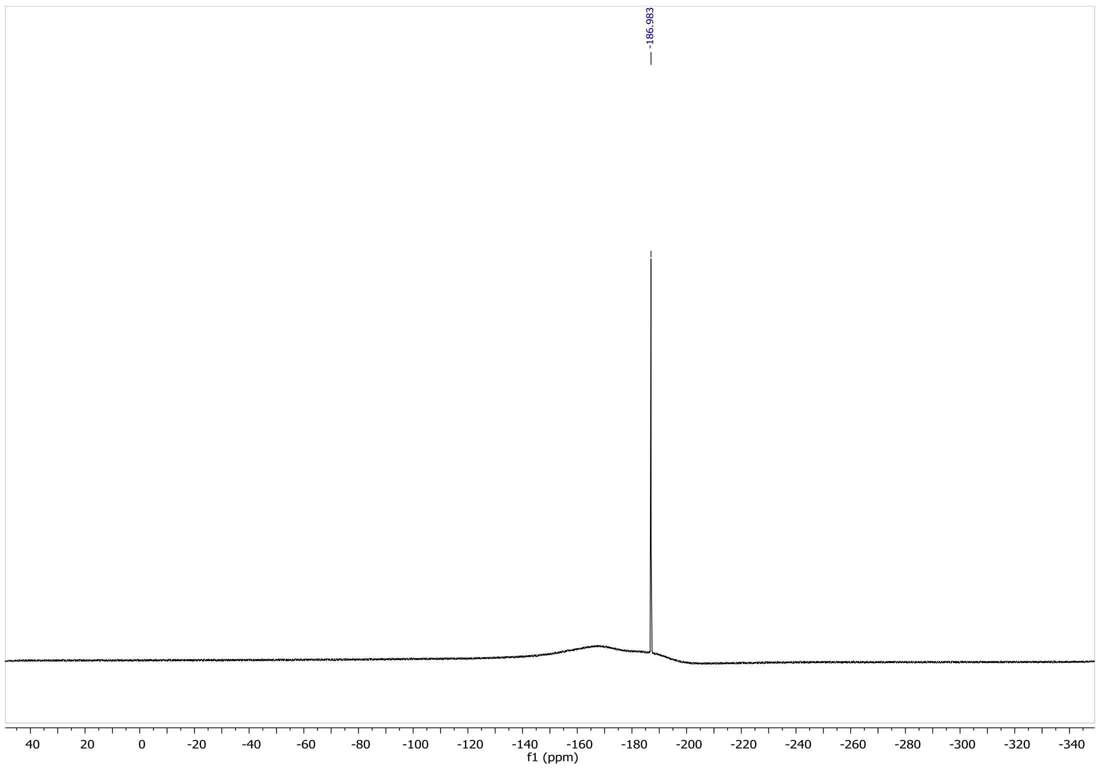
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



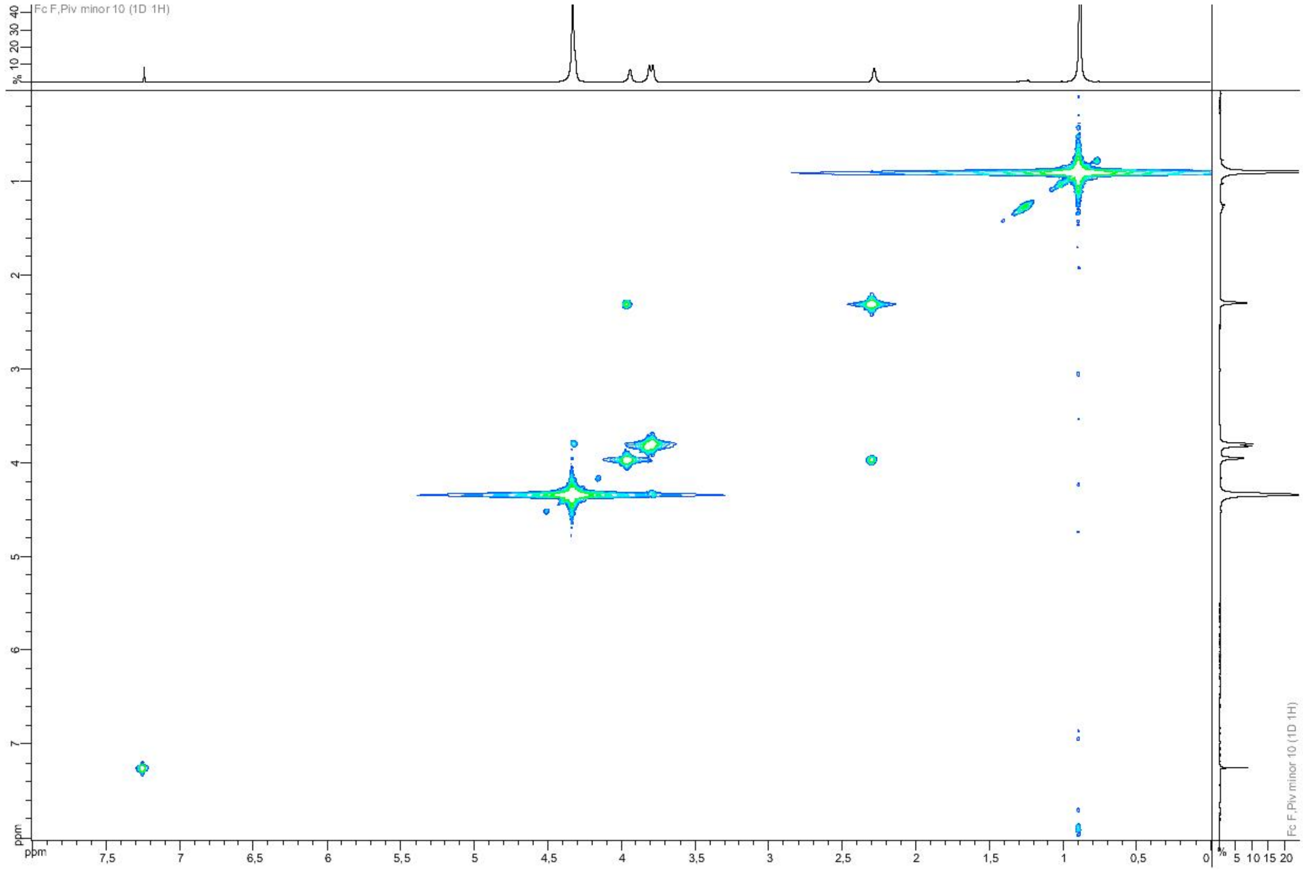
DEPT 135 (126 MHz, $CDCl_3$, 298 K)



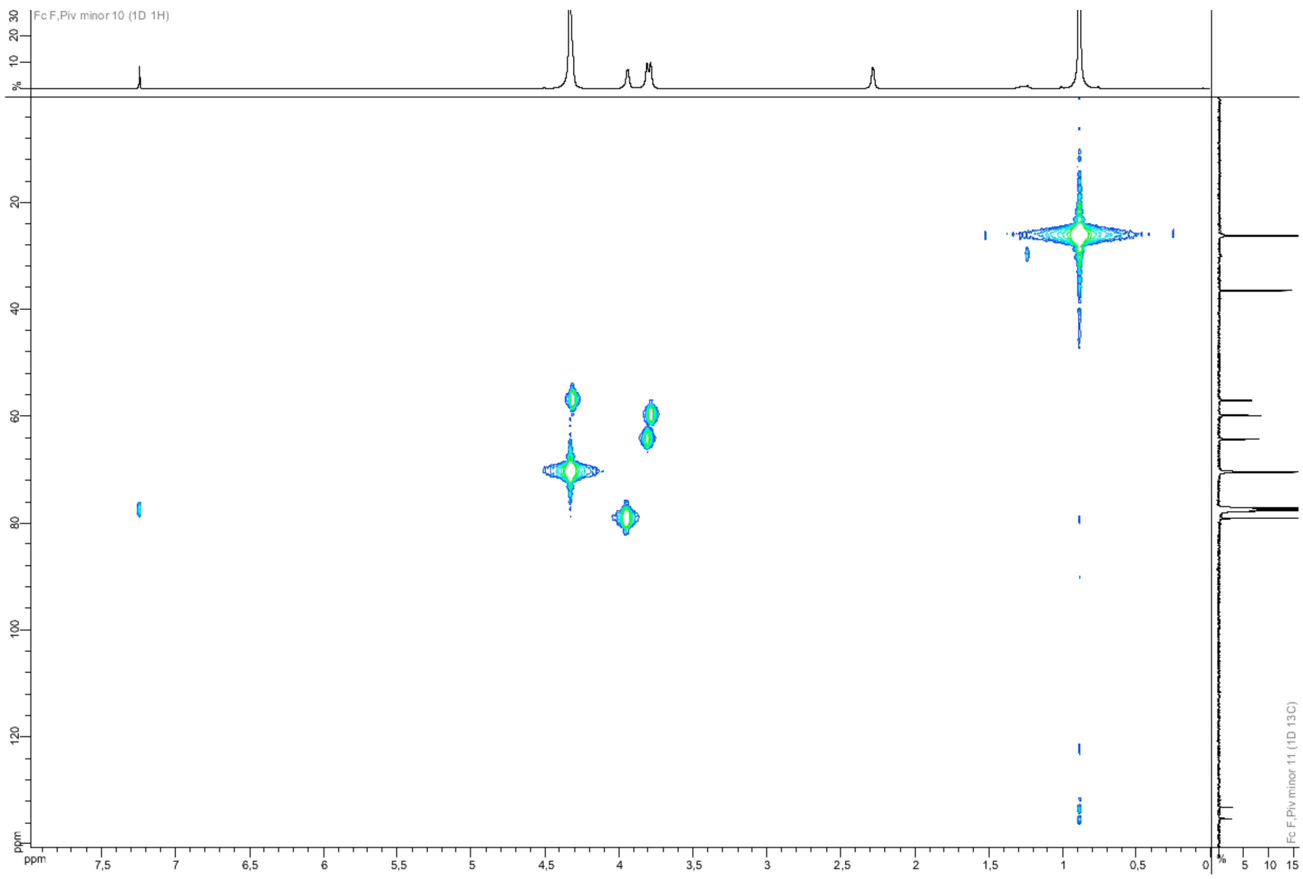
^{19}F NMR (470 MHz, $CDCl_3$, 298 K)



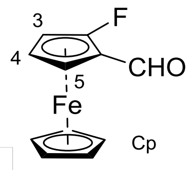
COSY (500 MHz, $CDCl_3$, 298 K)



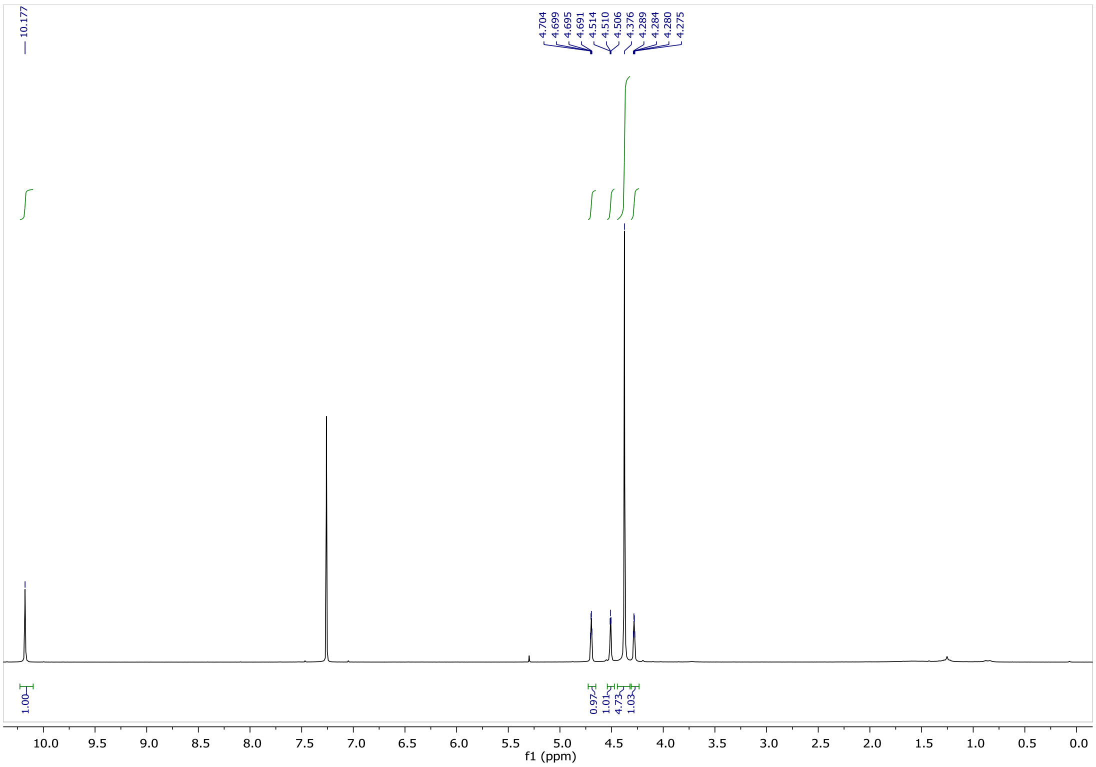
HSQC (500 MHz, $CDCl_3$, 298 K)



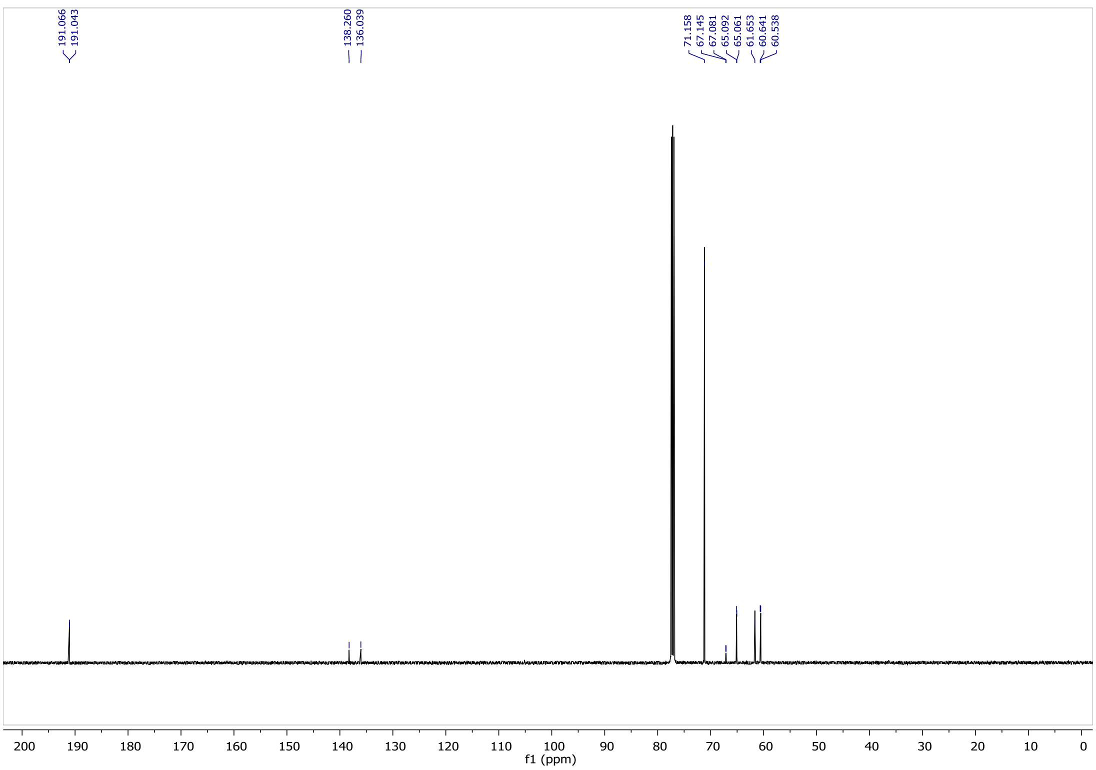
Compound 3n (racemic mixture)



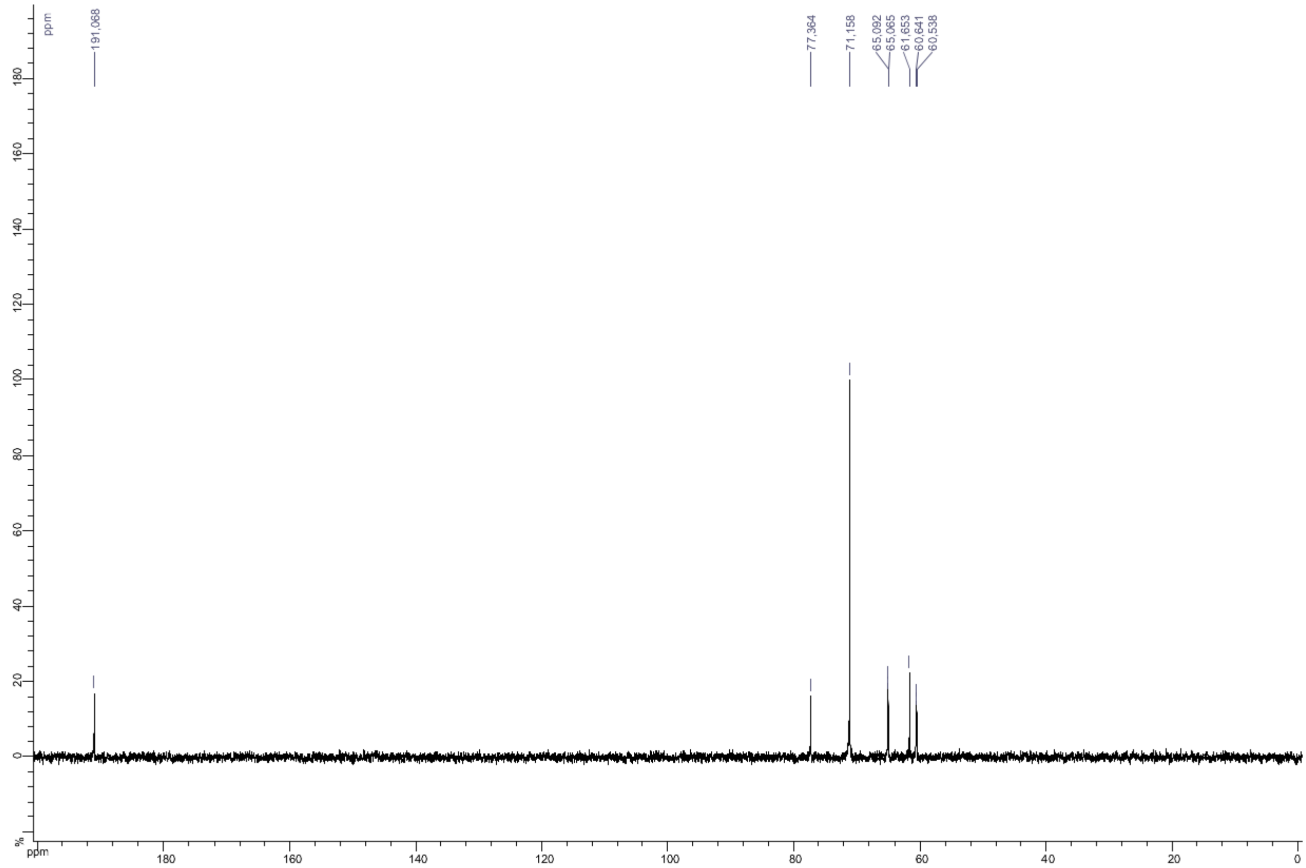
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



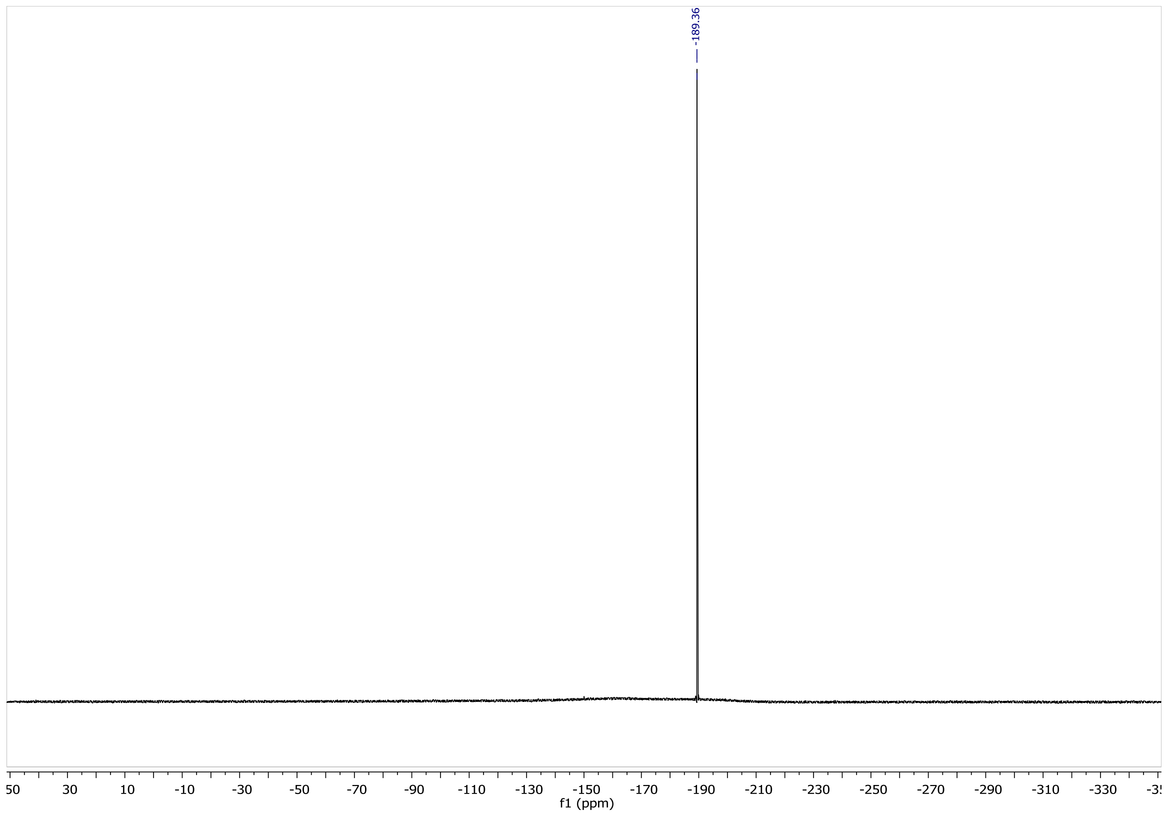
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



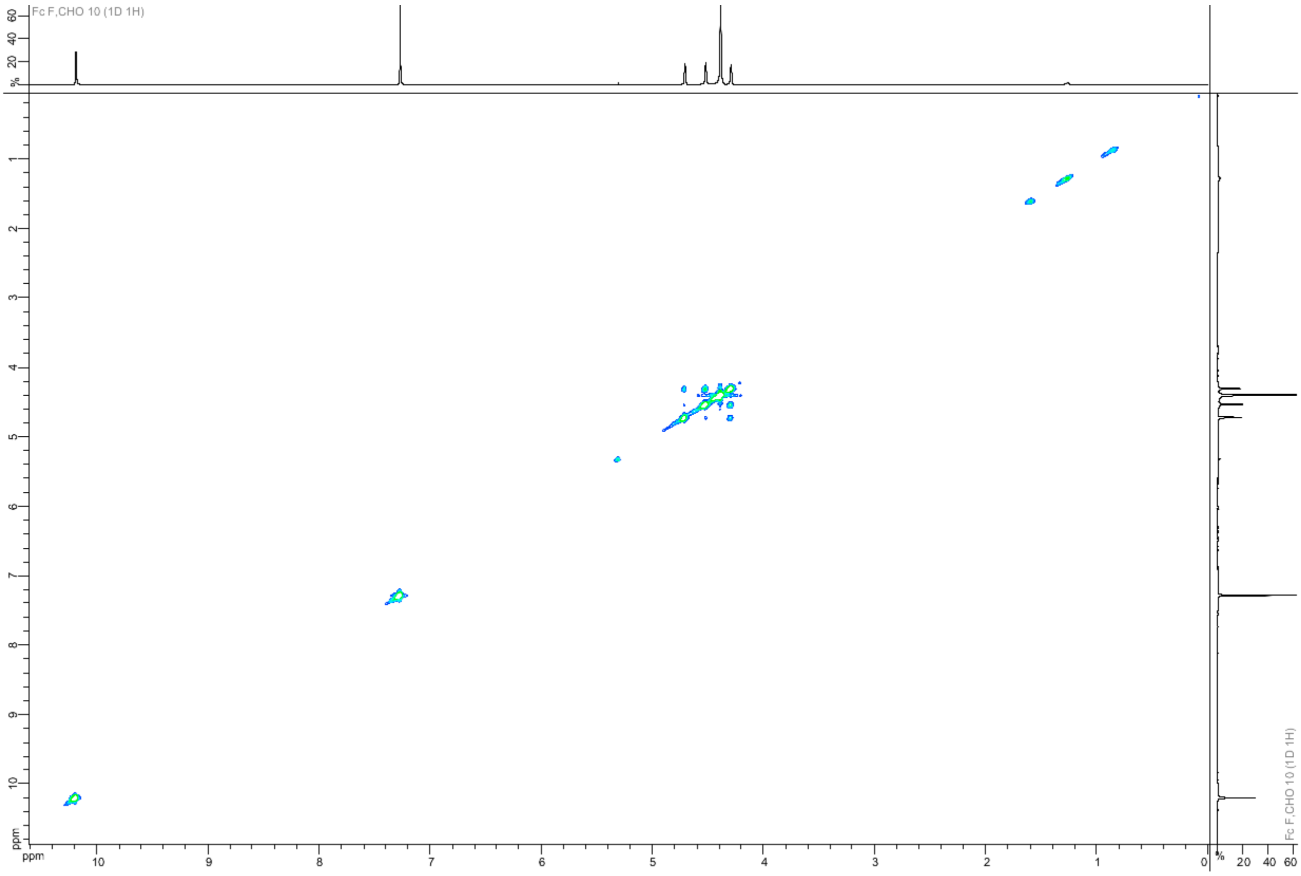
DEPT 135 (126 MHz, $CDCl_3$, 298 K)



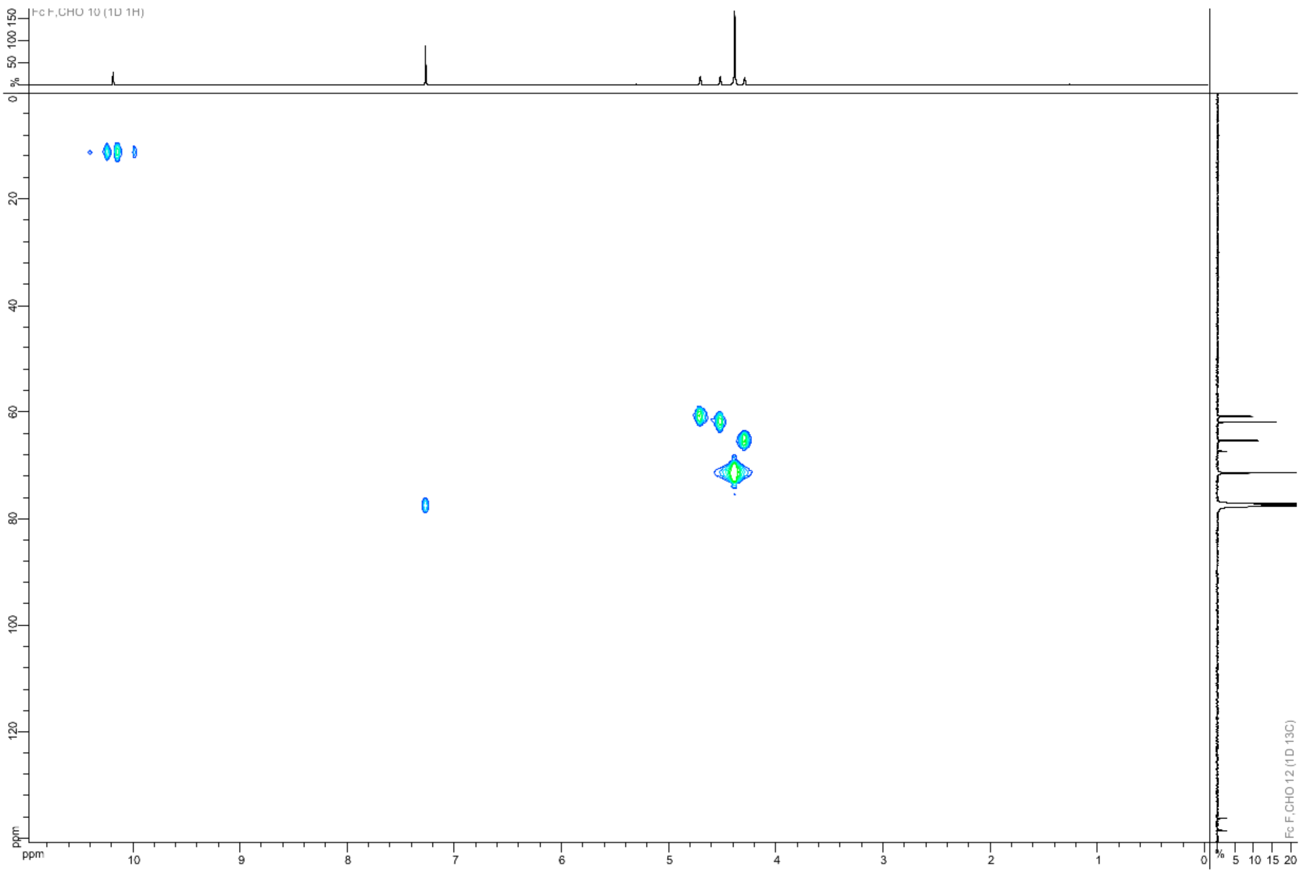
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



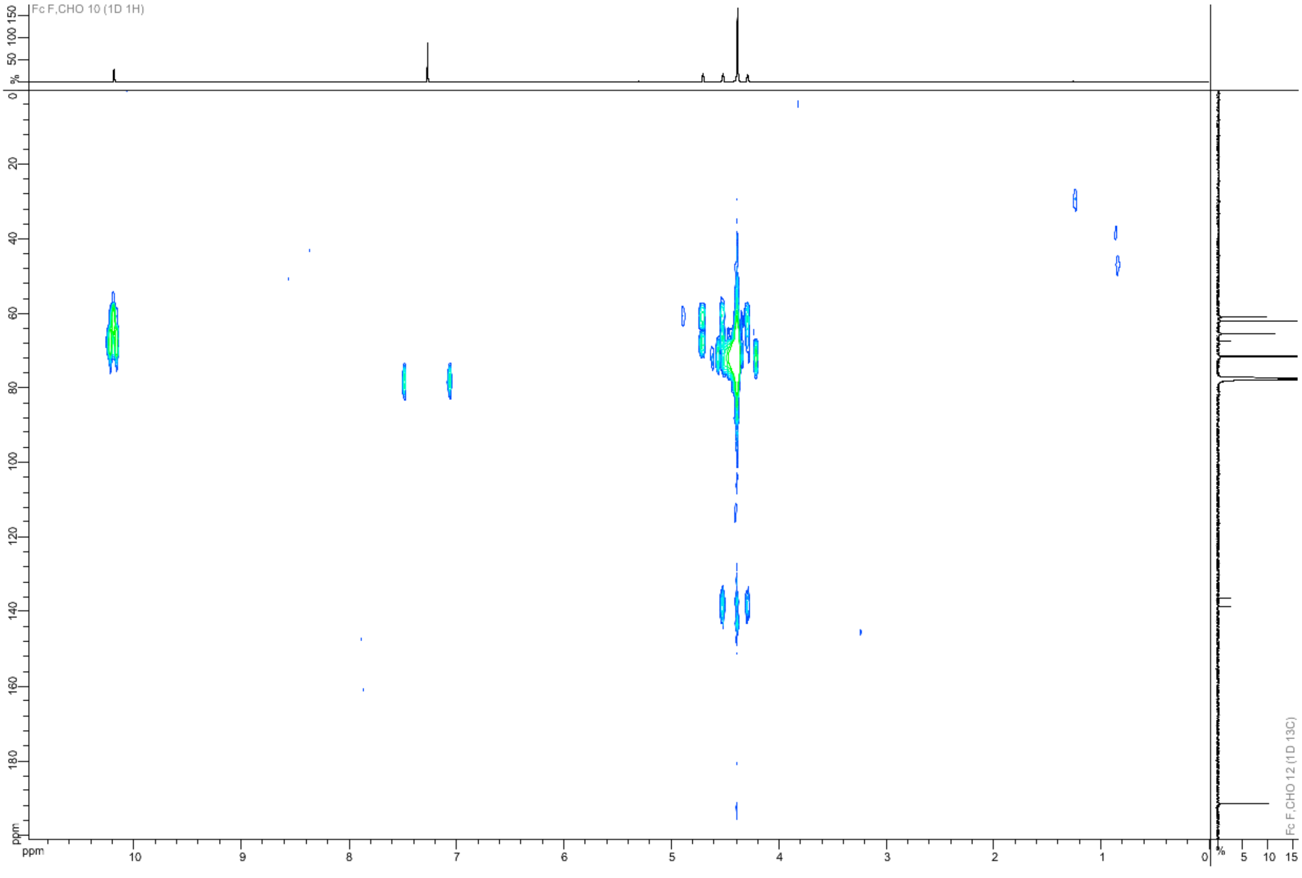
COSY (500 MHz, $CDCl_3$, 298 K)



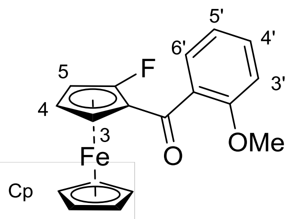
HSQC (500 MHz, $CDCl_3$, 298 K)



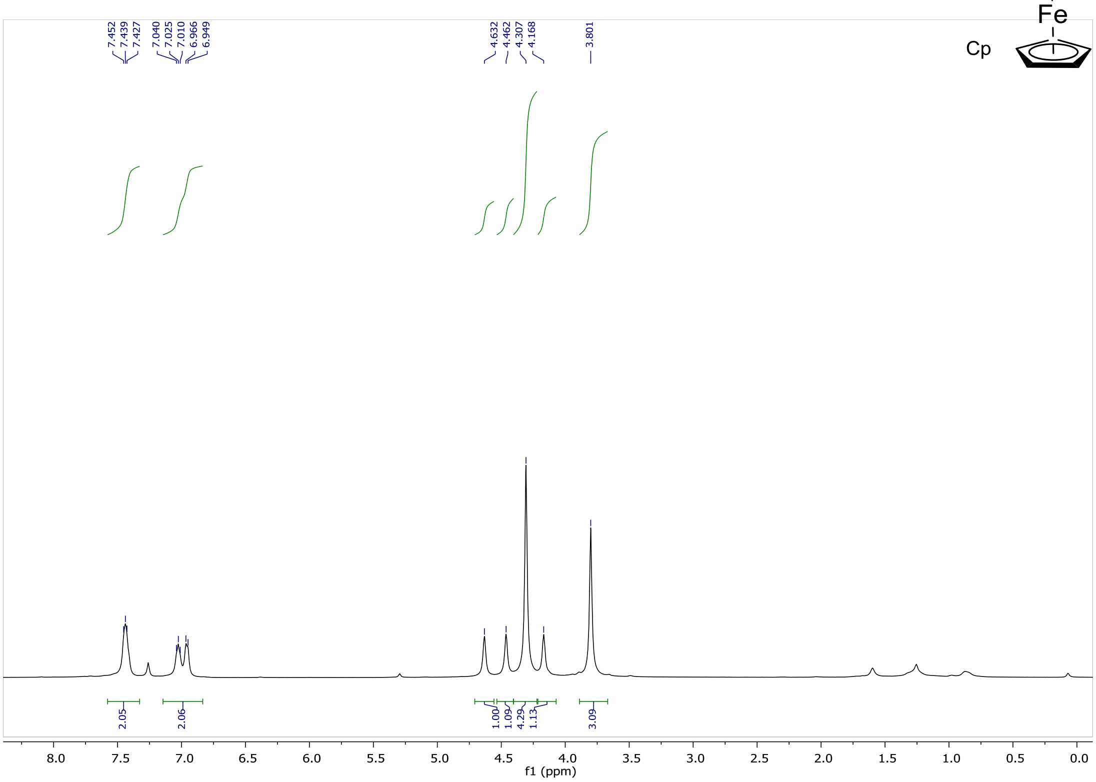
HMBC (500 MHz, $CDCl_3$, 298 K)



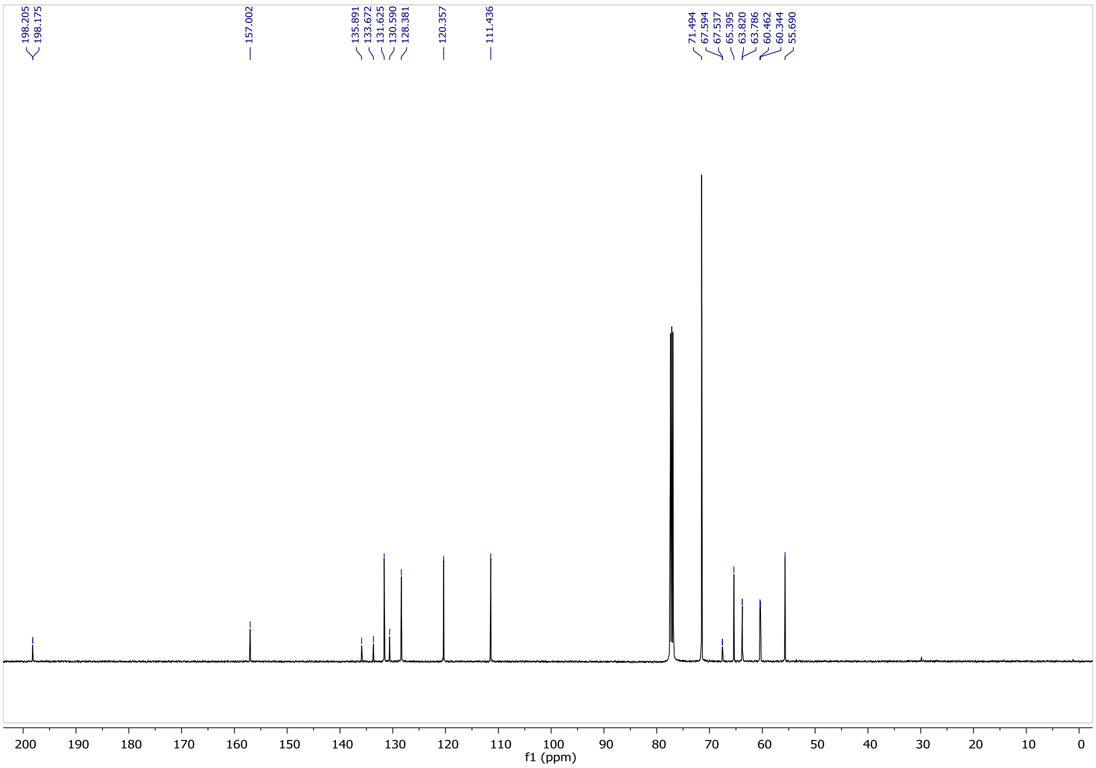
Compound 3o (racemic mixture)



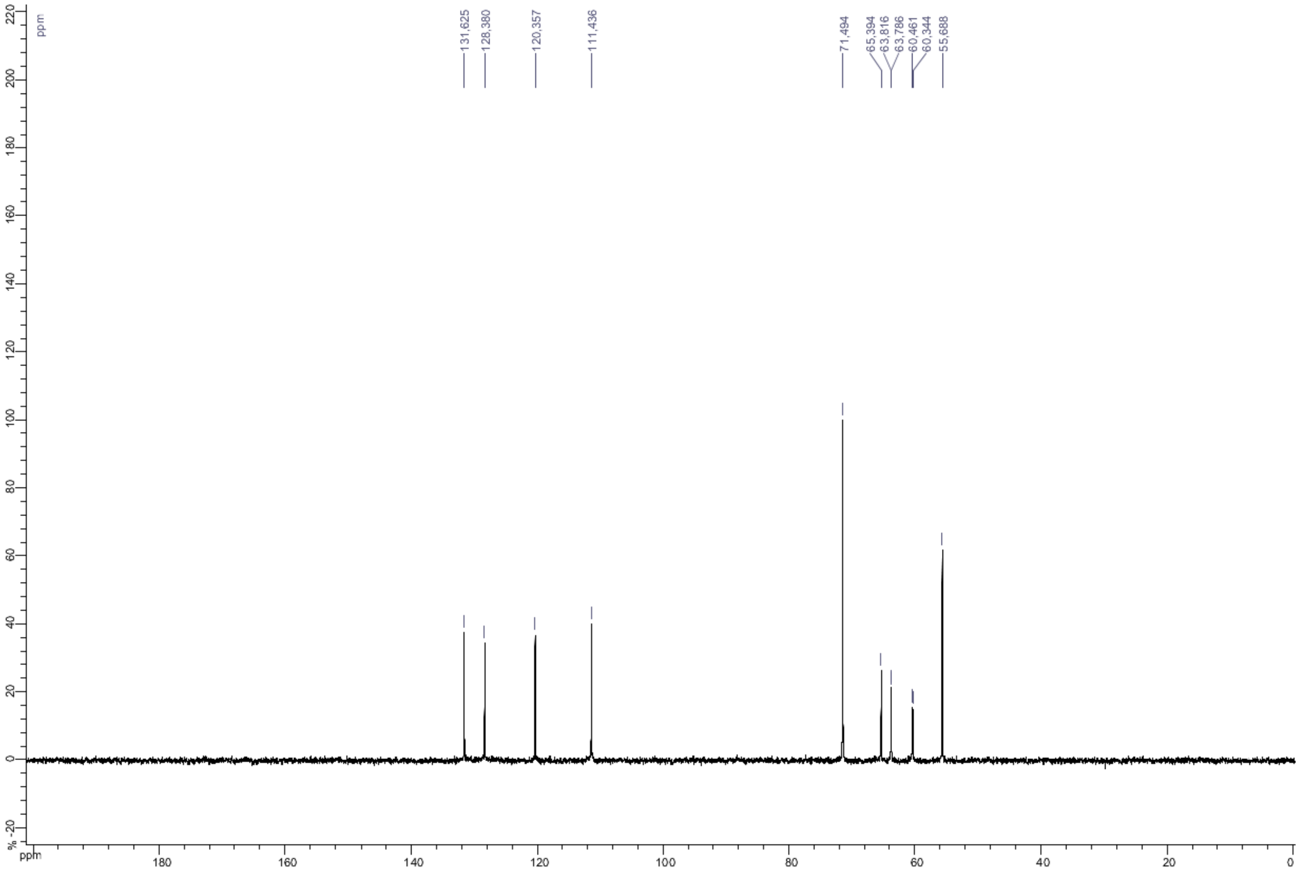
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



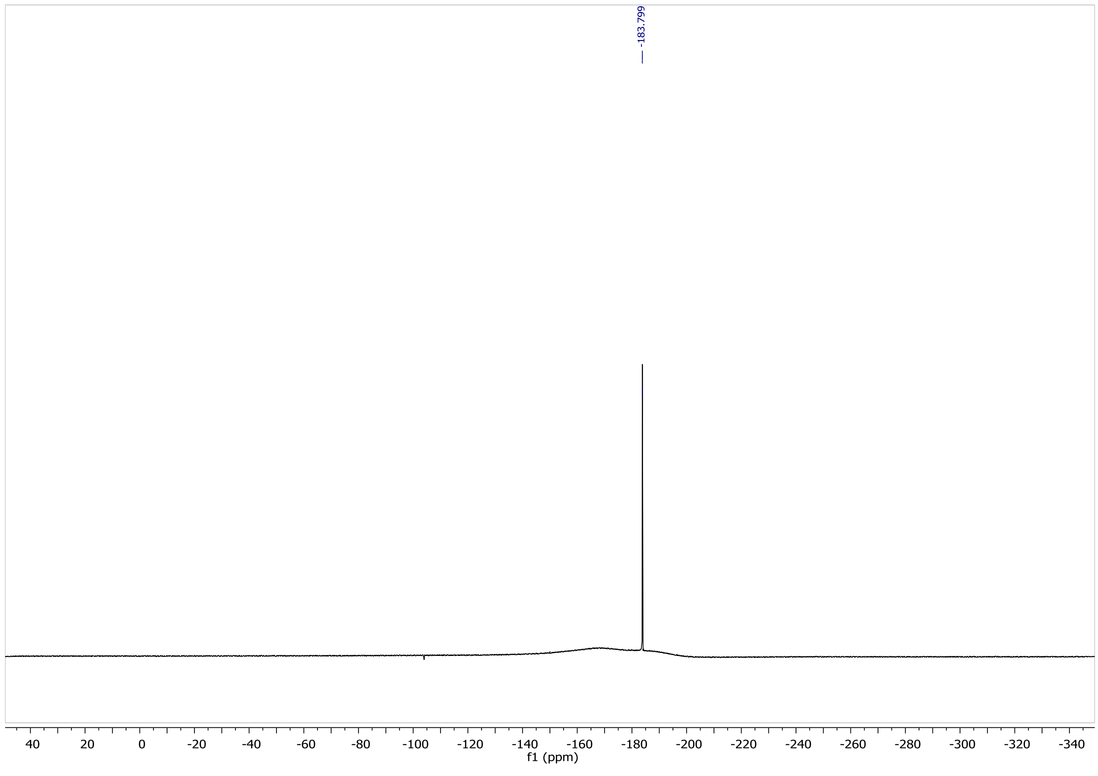
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



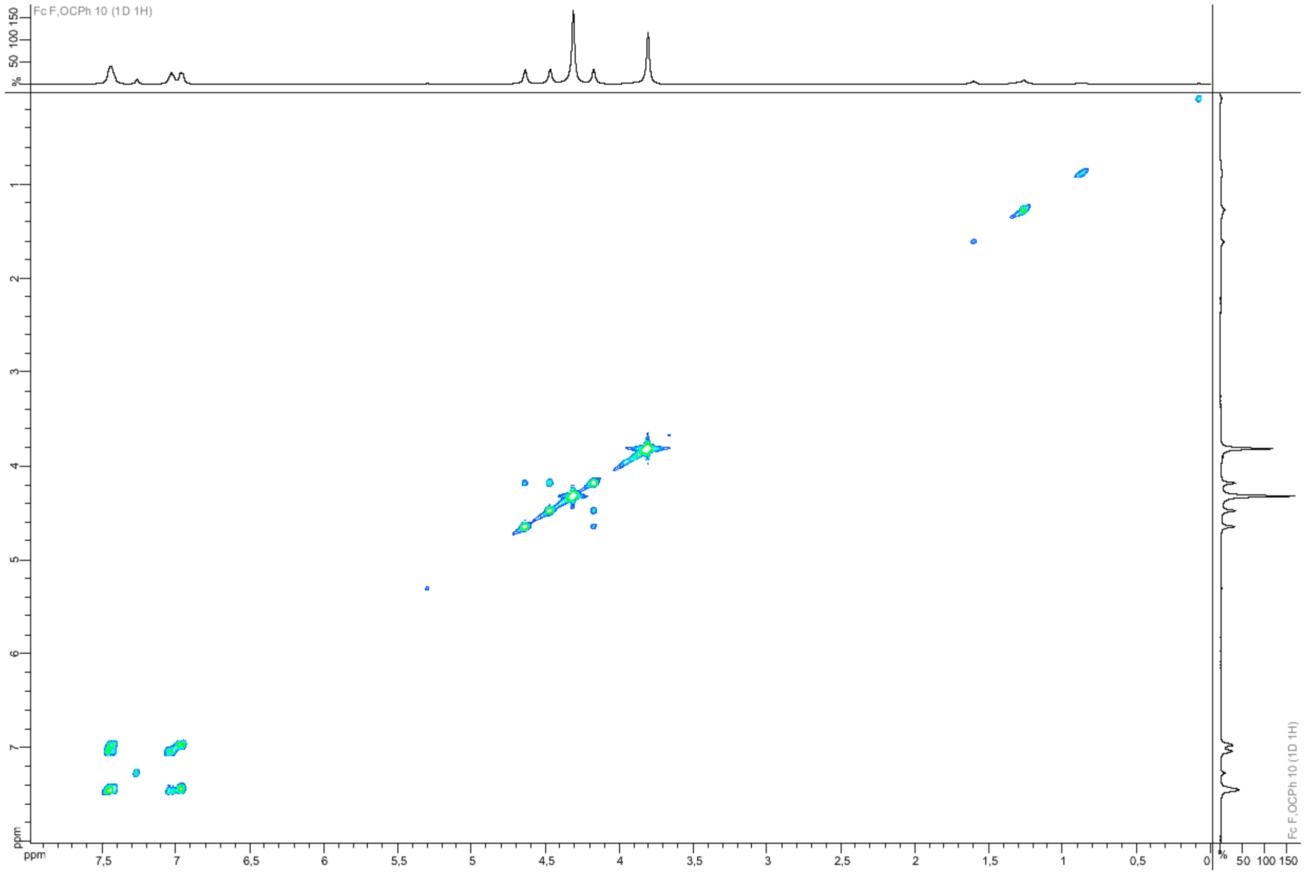
DEPT 135 NMR (126 MHz, $CDCl_3$, 298 K)



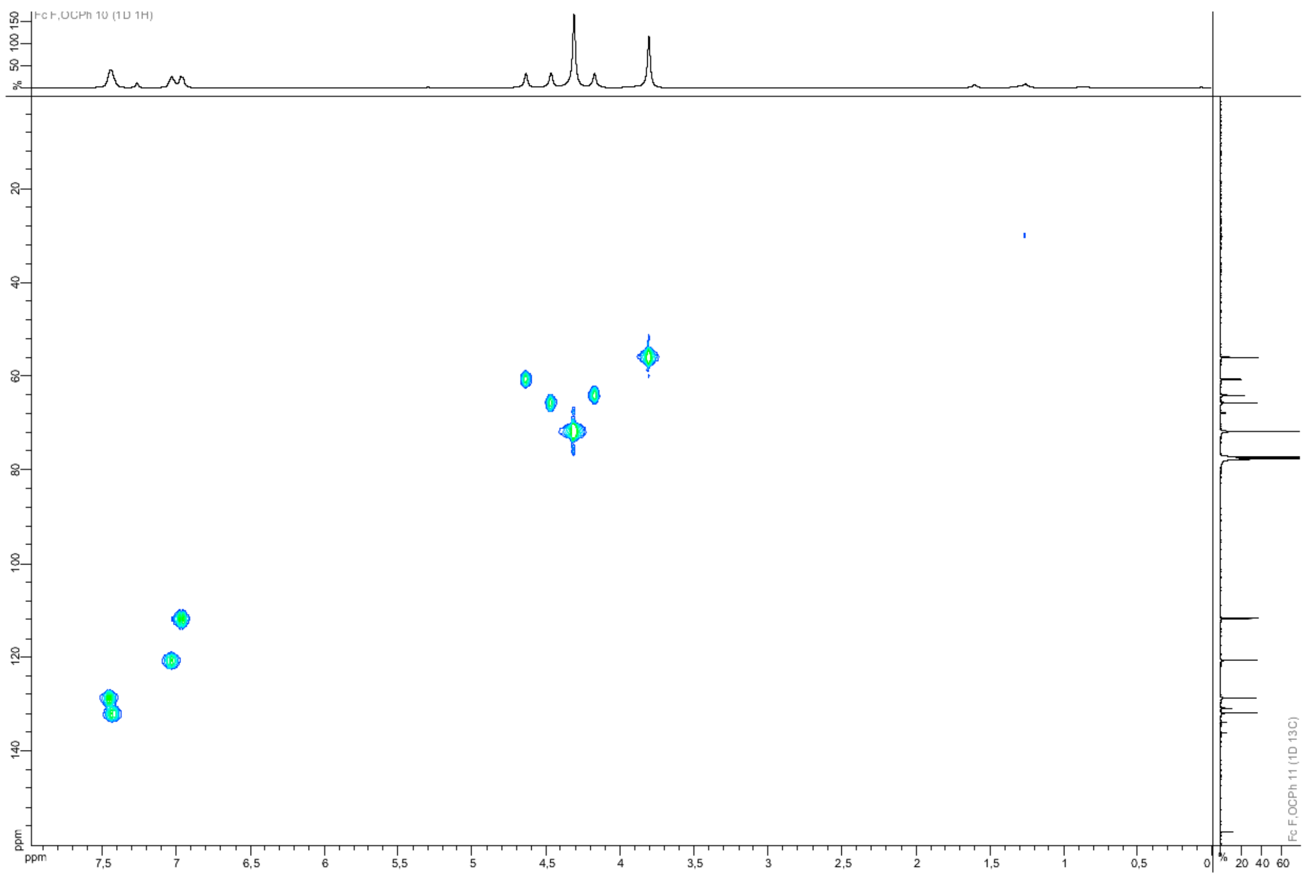
^{19}F NMR (470 MHz, $CDCl_3$, 298 K)



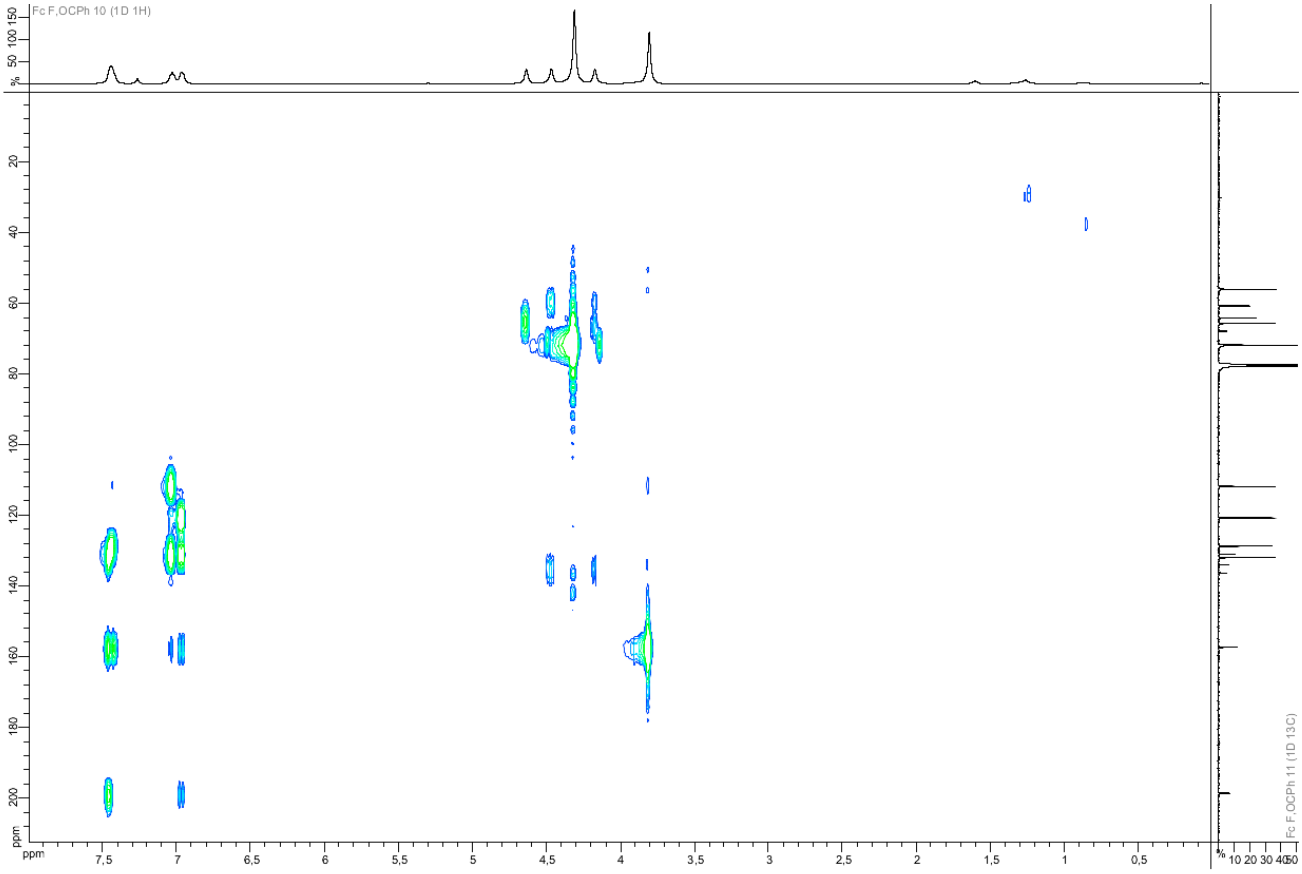
COSY (500 MHz, $CDCl_3$, 298 K)



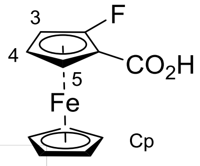
HSQC (500 MHz, $CDCl_3$, 298 K)



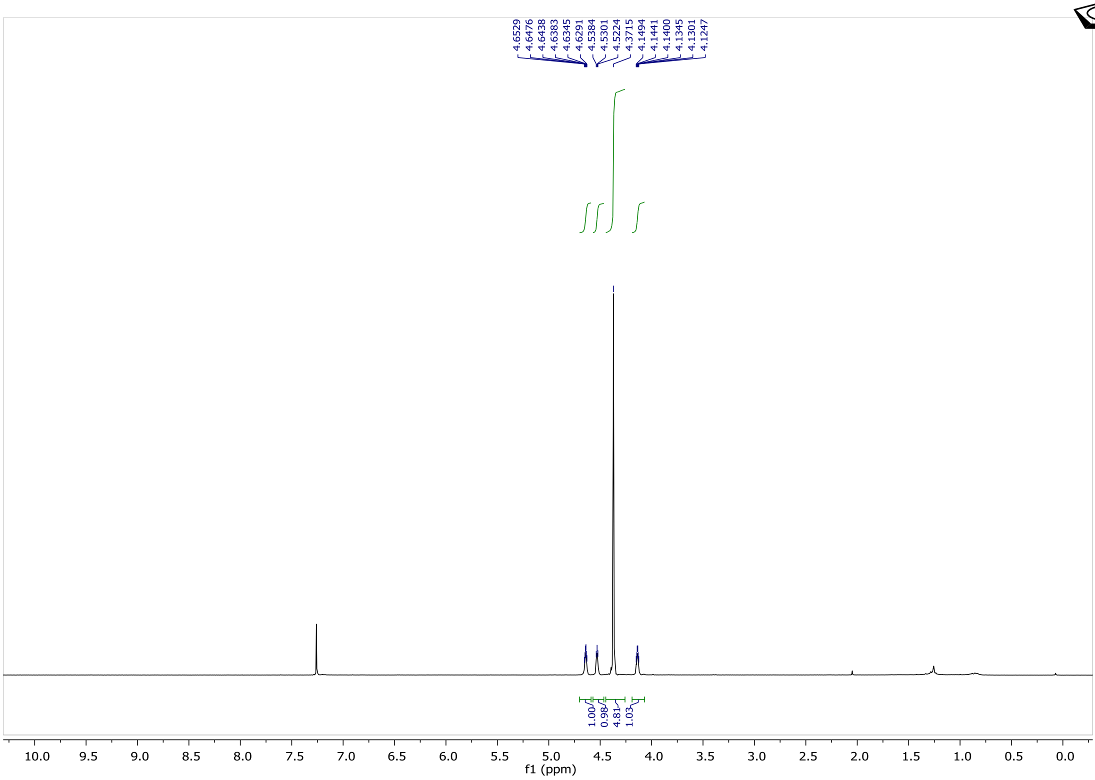
HMBC (500 MHz, $CDCl_3$, 298 K)



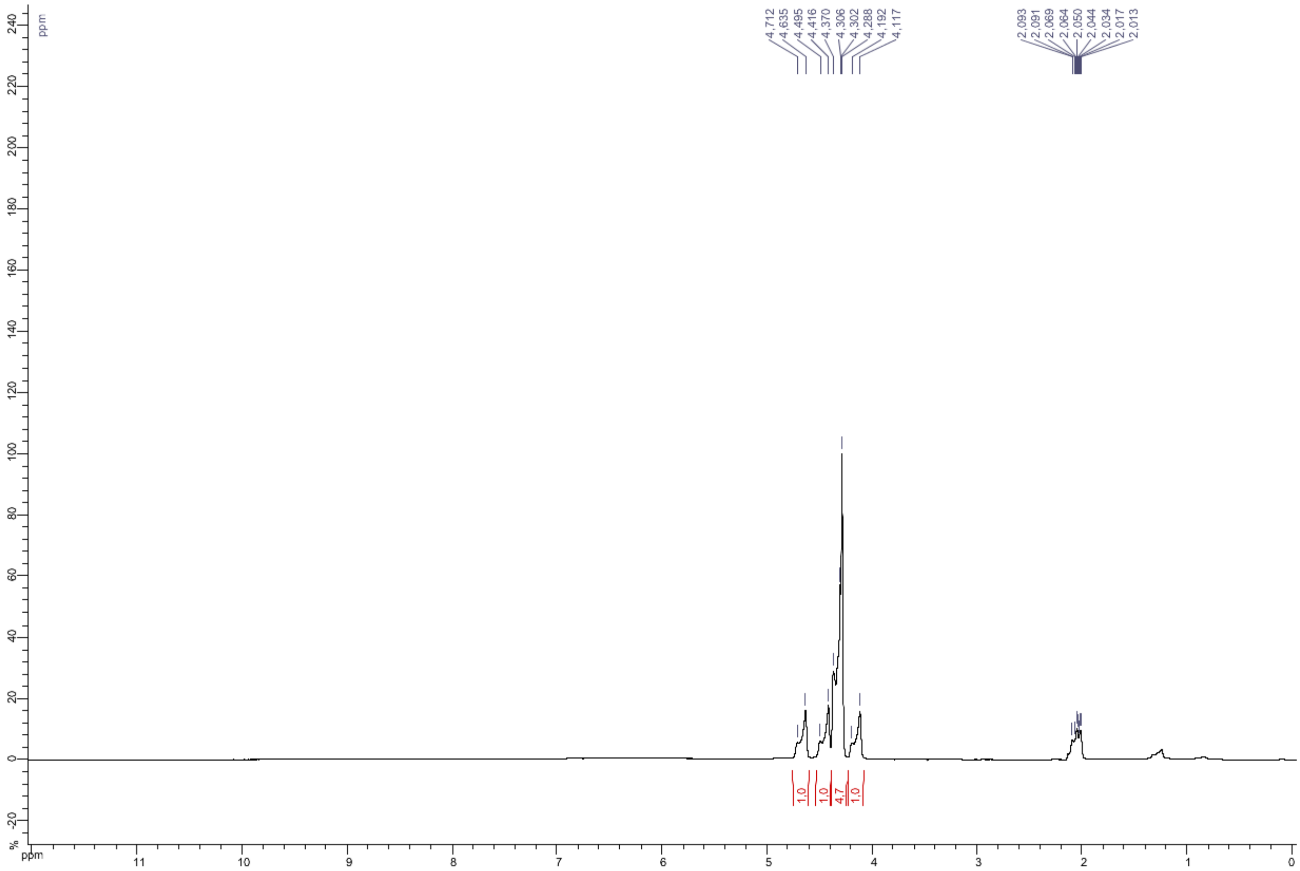
Compound 3p (racemic mixture)



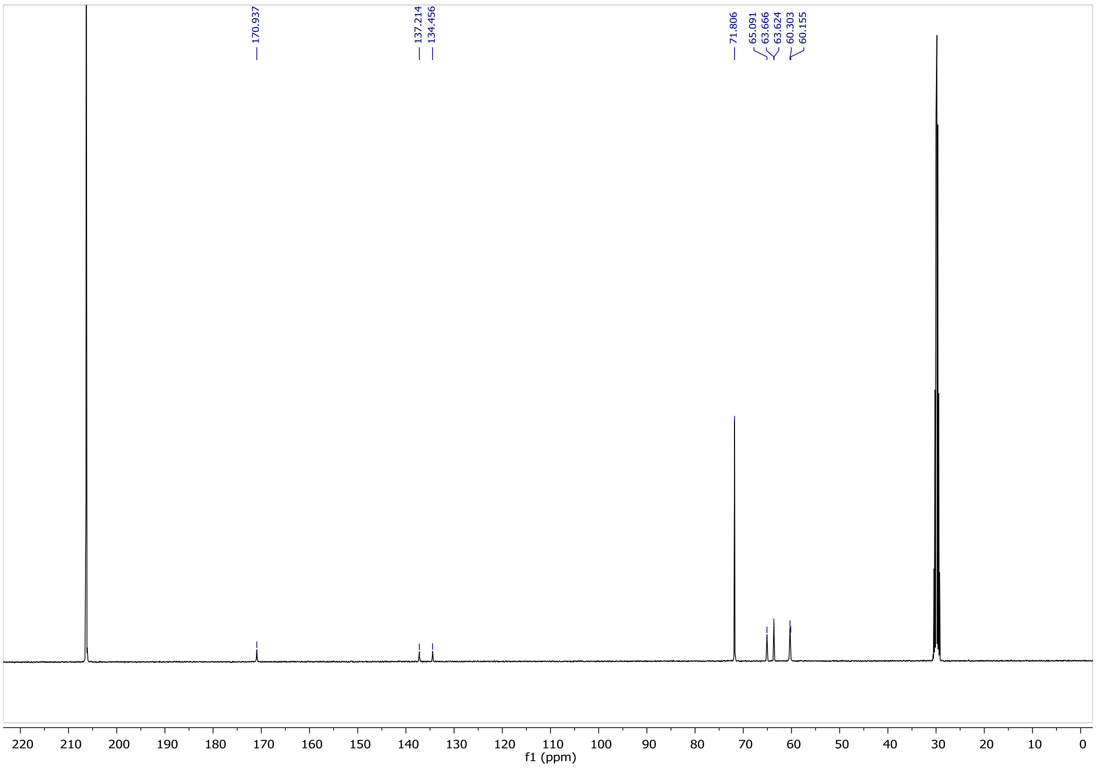
[1]H NMR (300 MHz, $CDCl_3$, 291 K)



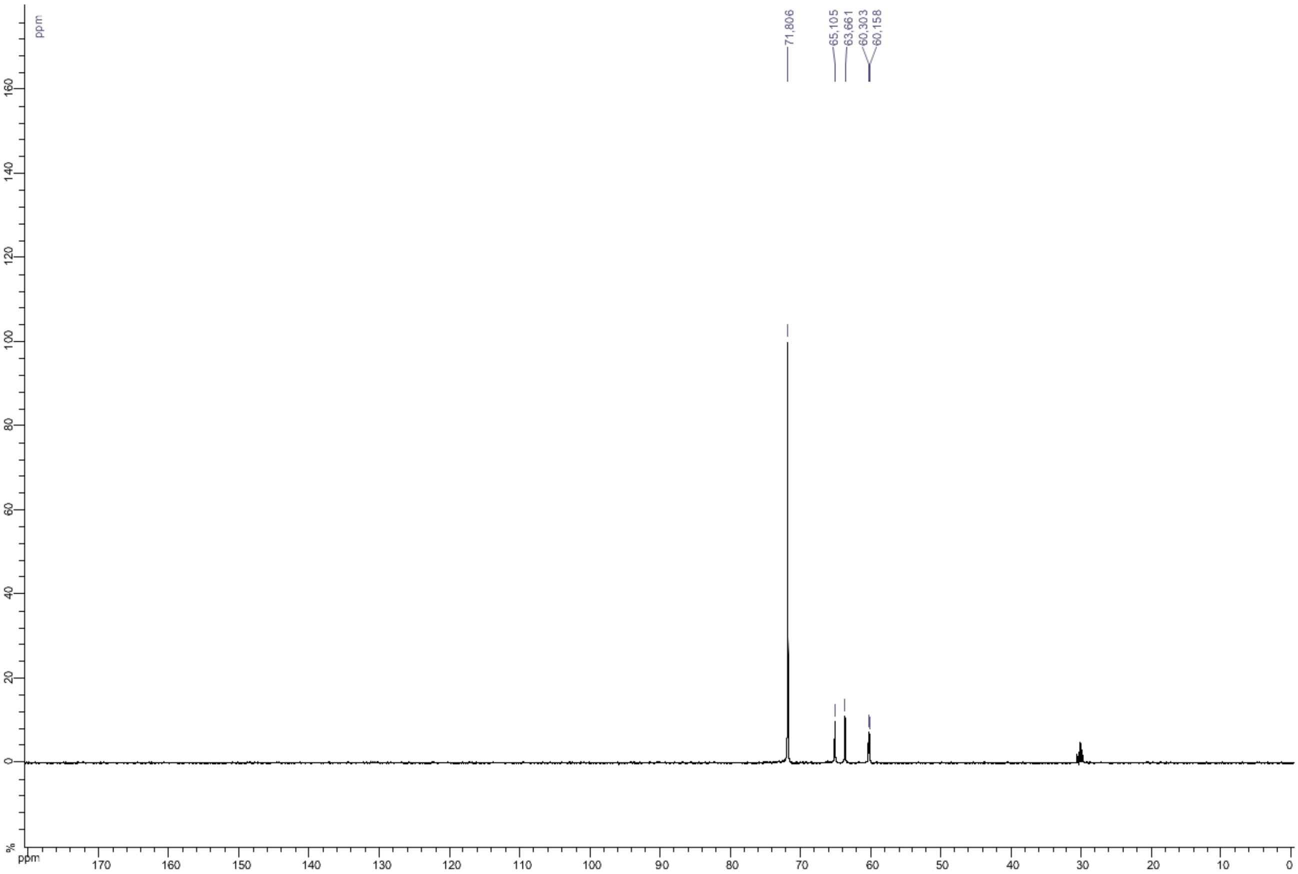
[1]H NMR (400 MHz, $(CD_3)_2CO$, 298 K)



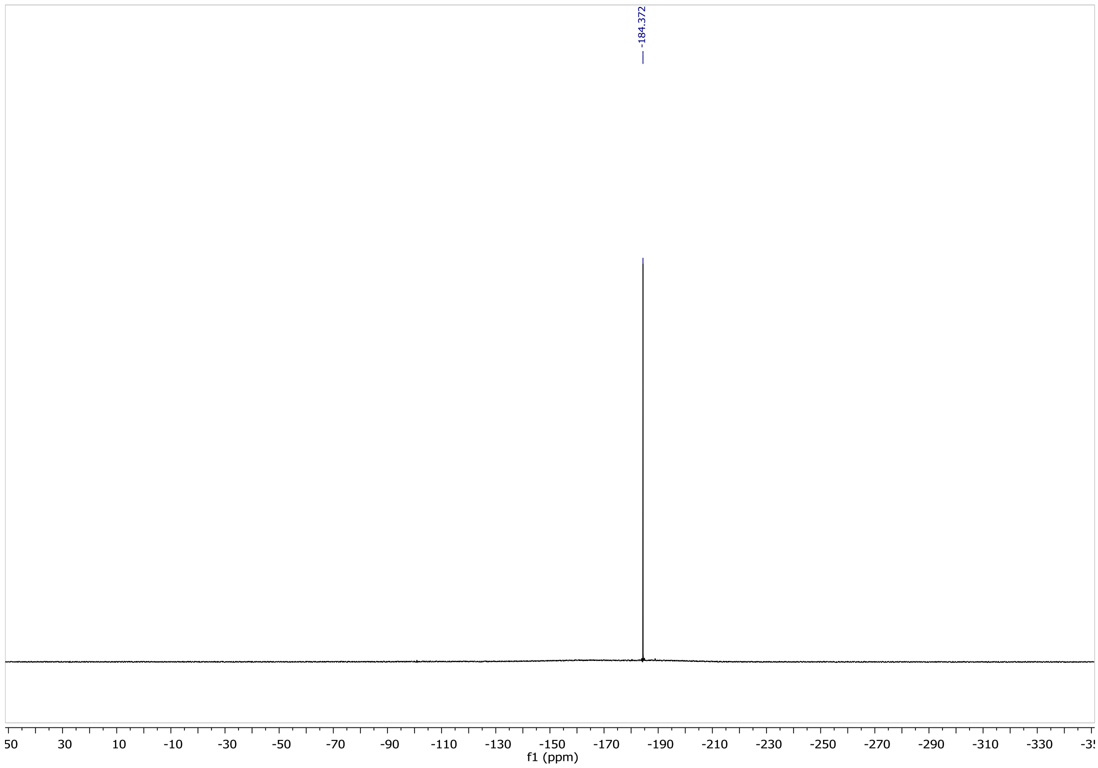
^{13}C NMR (101 MHz, $(CD_3)_2CO$, 298 K)



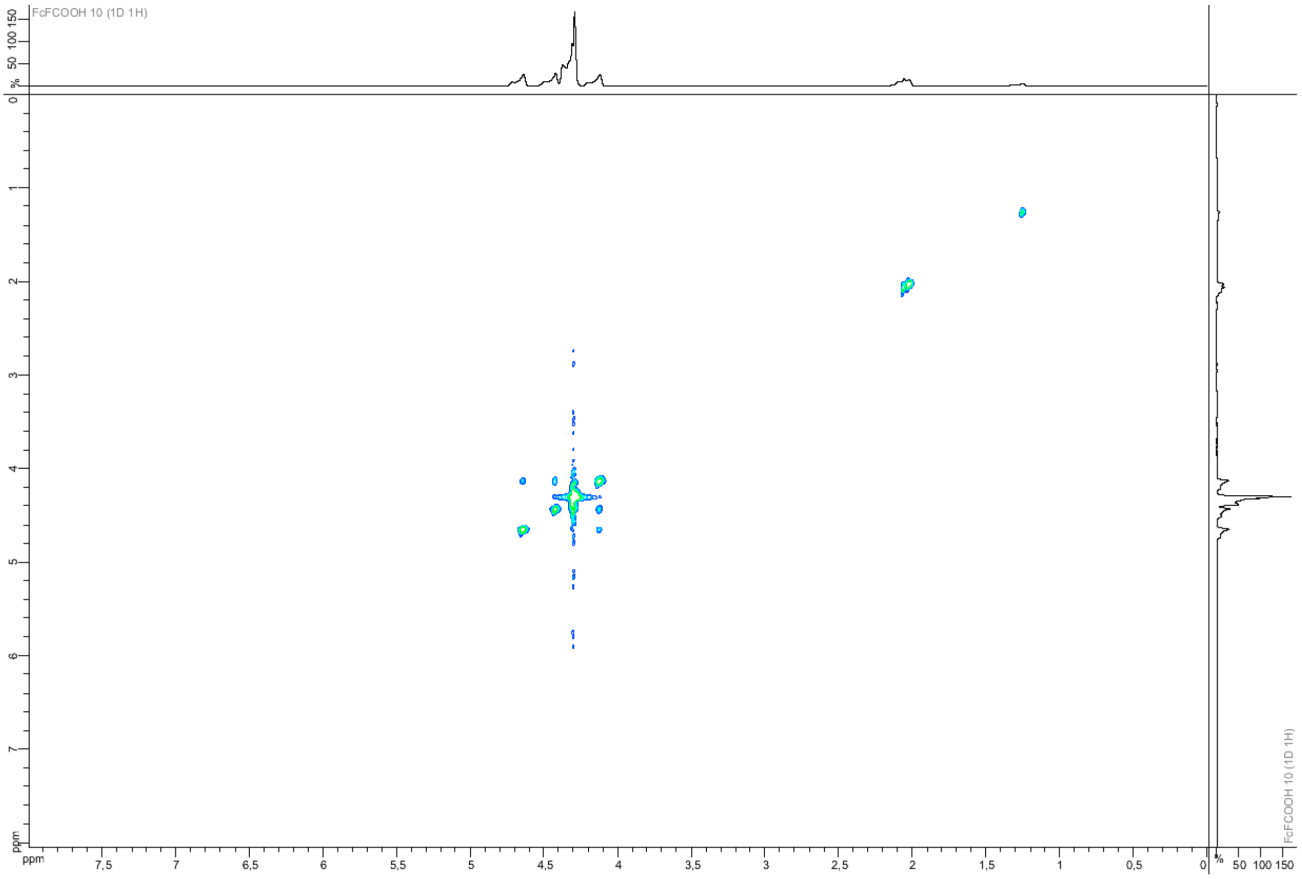
DEPT 135 (101 MHz, $(CD_3)_2CO$, 298 K)



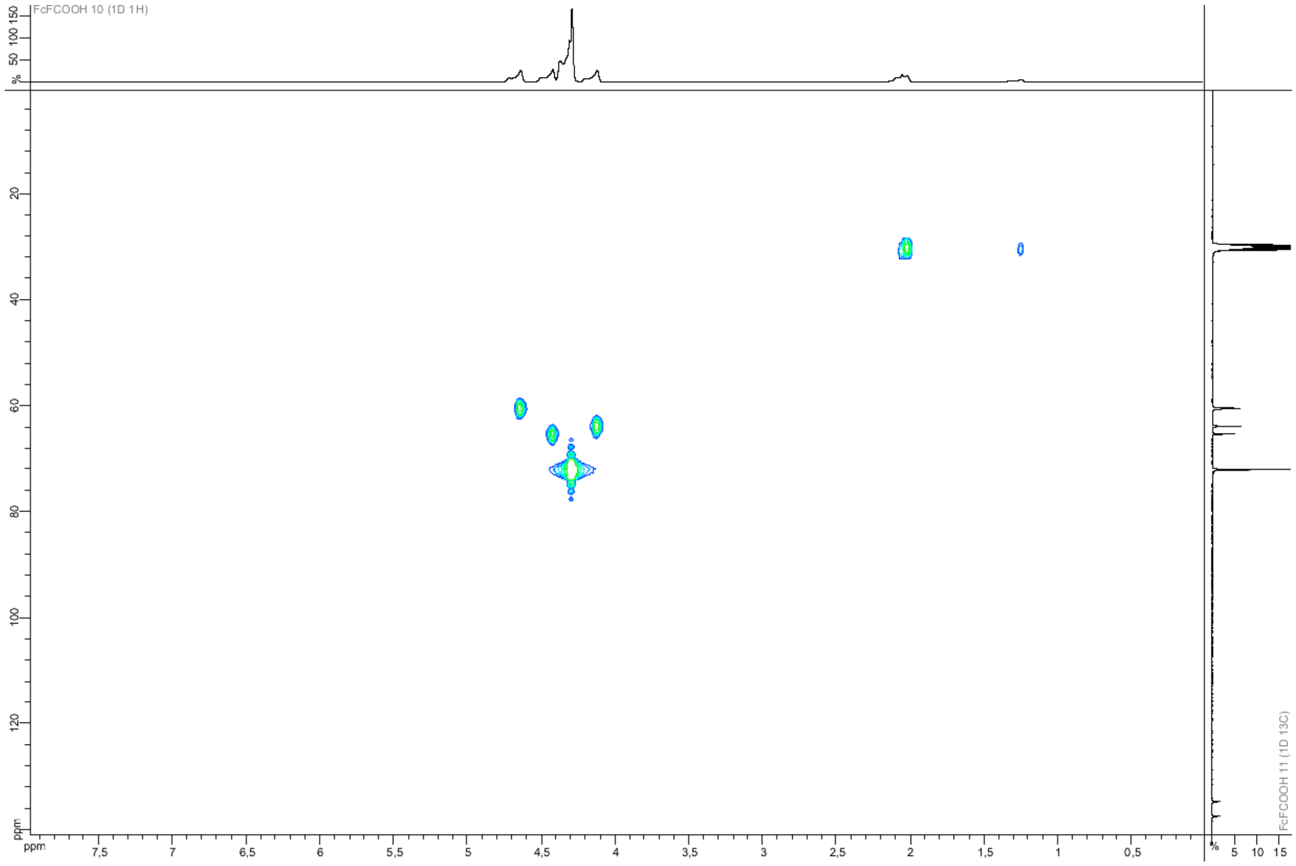
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



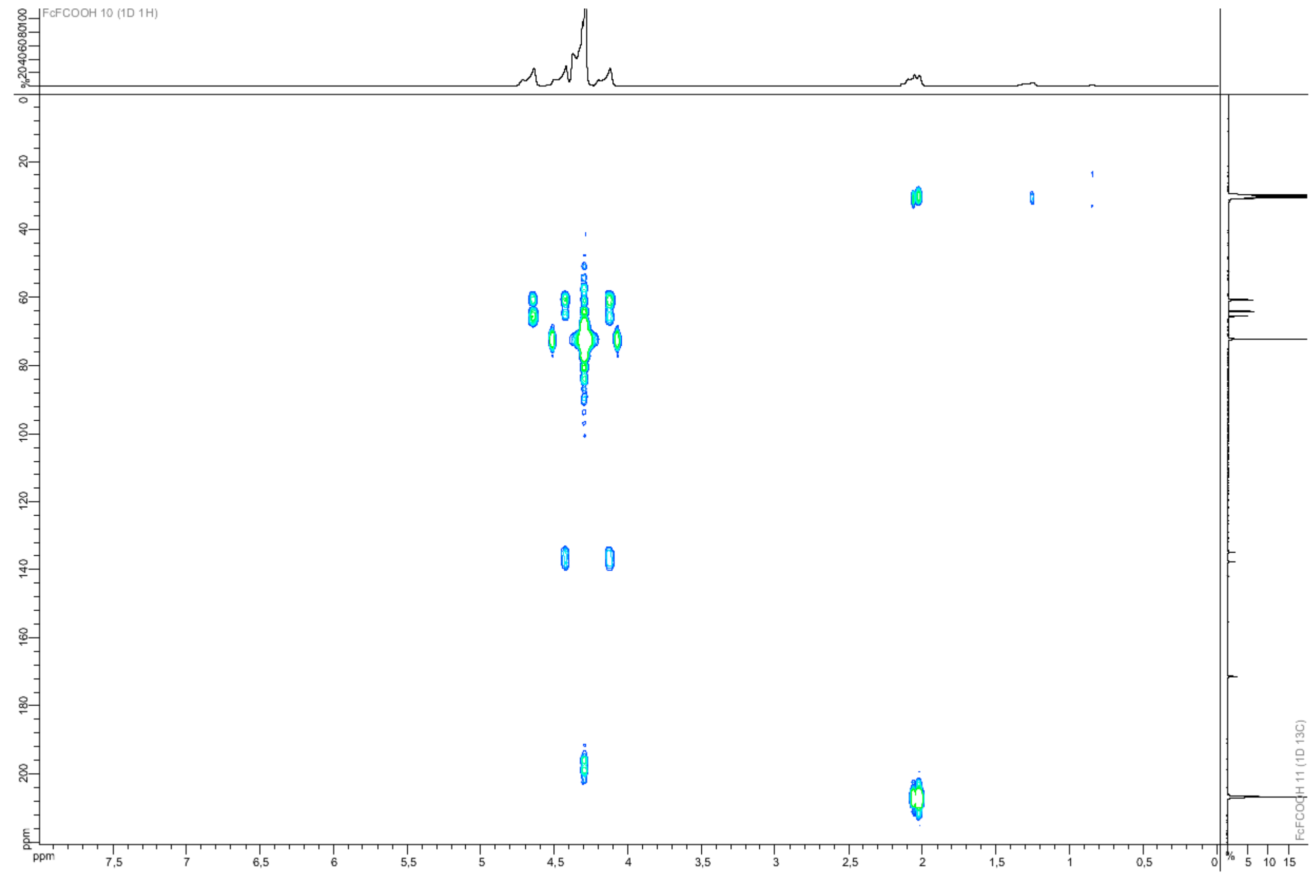
COSY (400 MHz, $(CD_3)_2CO$, 298 K)



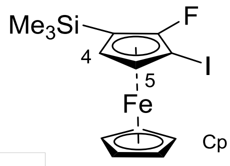
HSQC (400 MHz, $(CD_3)_2CO$, 298 K)



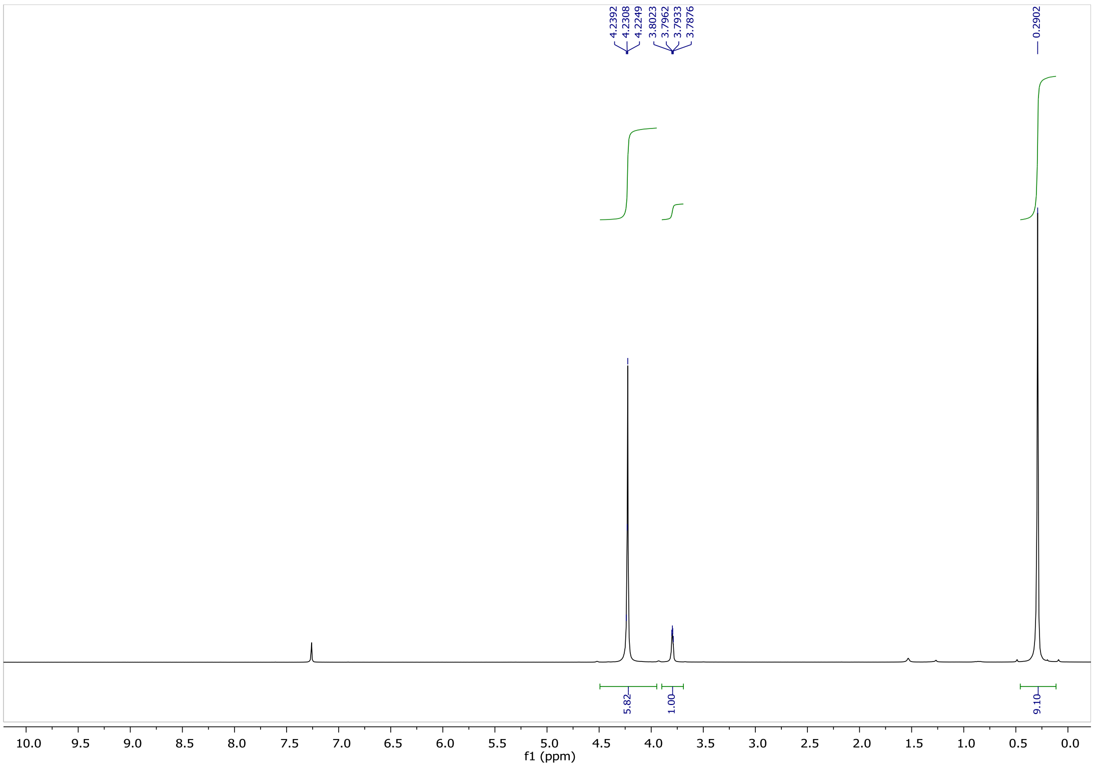
HMBC (400 MHz, $(CD_3)_2CO$, 298 K)



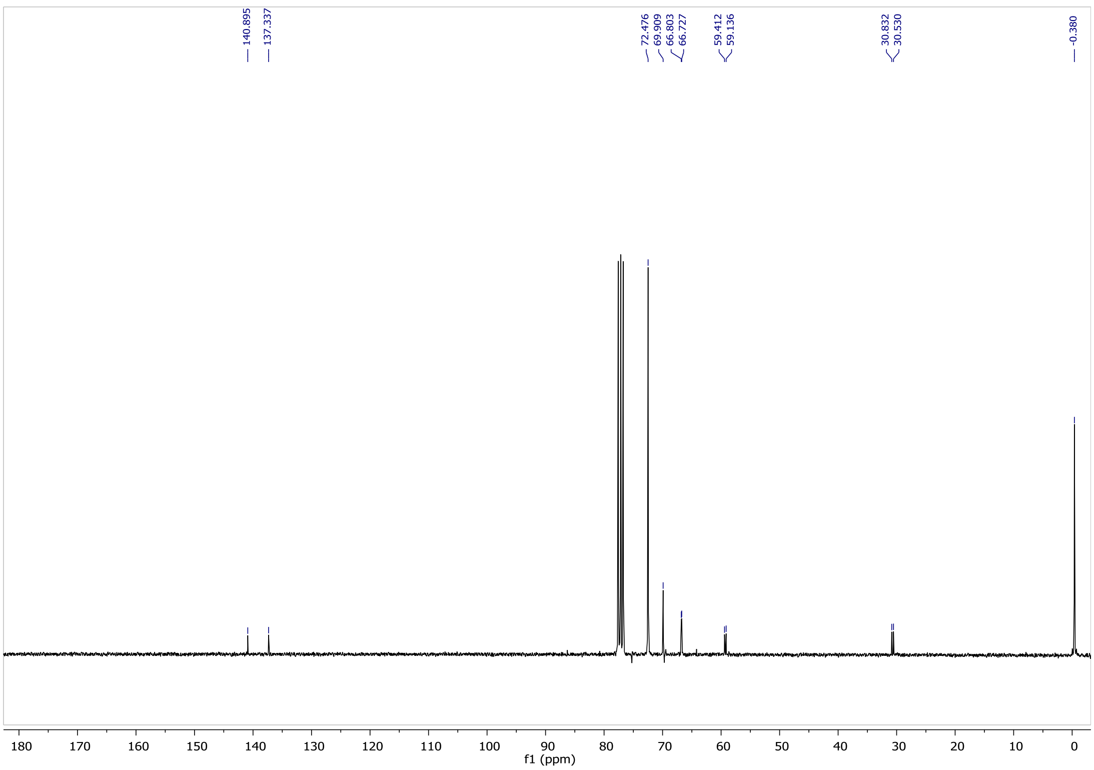
Compound 3fb (racemic mixture)



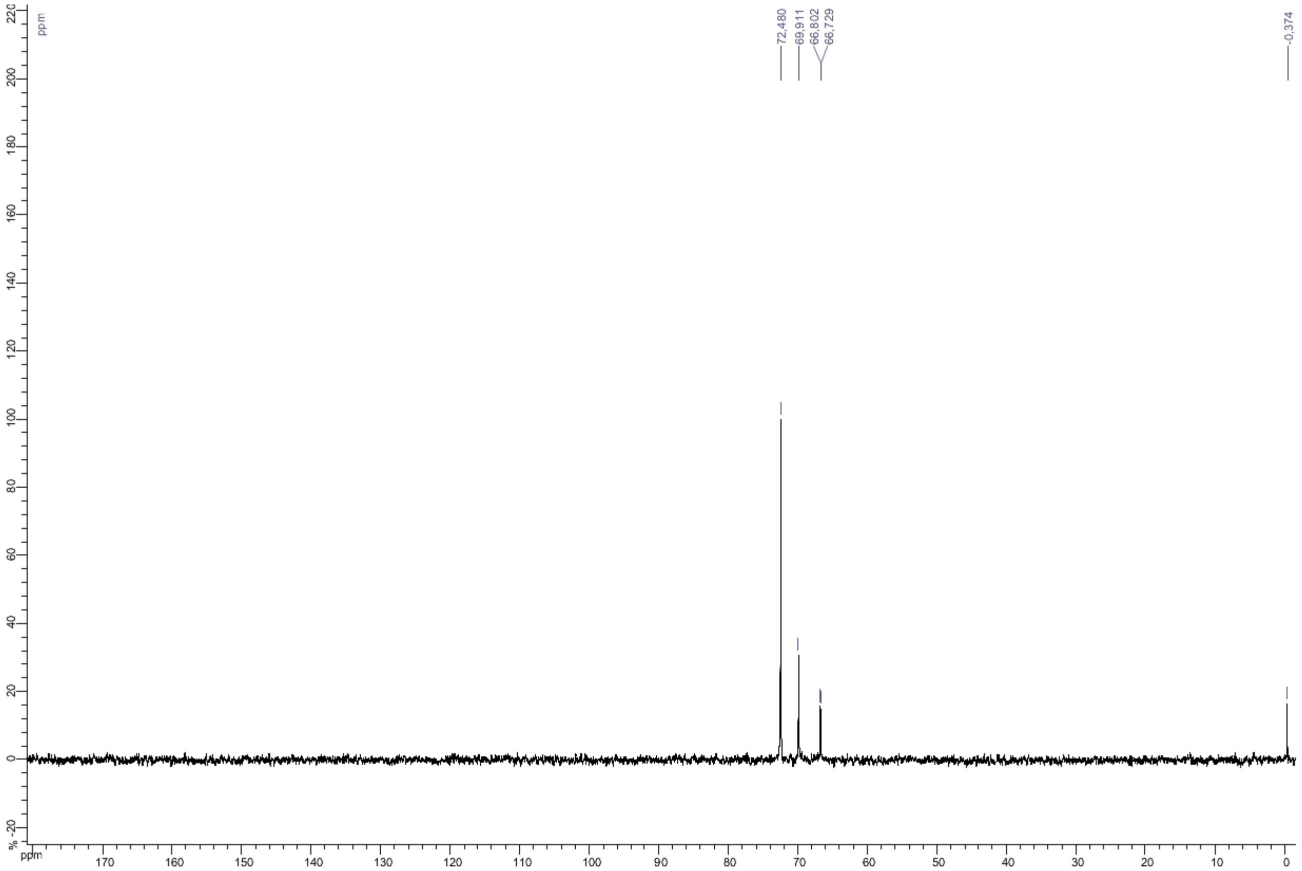
[1]H NMR (300 MHz, $CDCl_3$, 291 K)



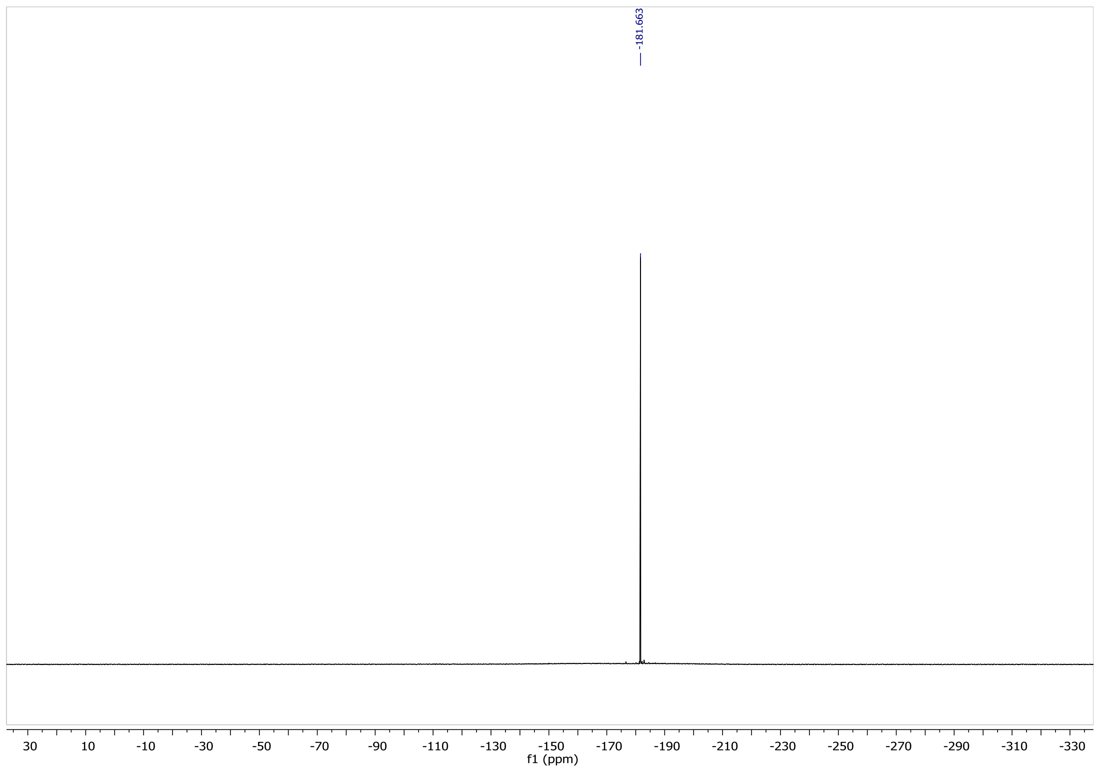
[13]C NMR (75 MHz, $CDCl_3$, 291 K)



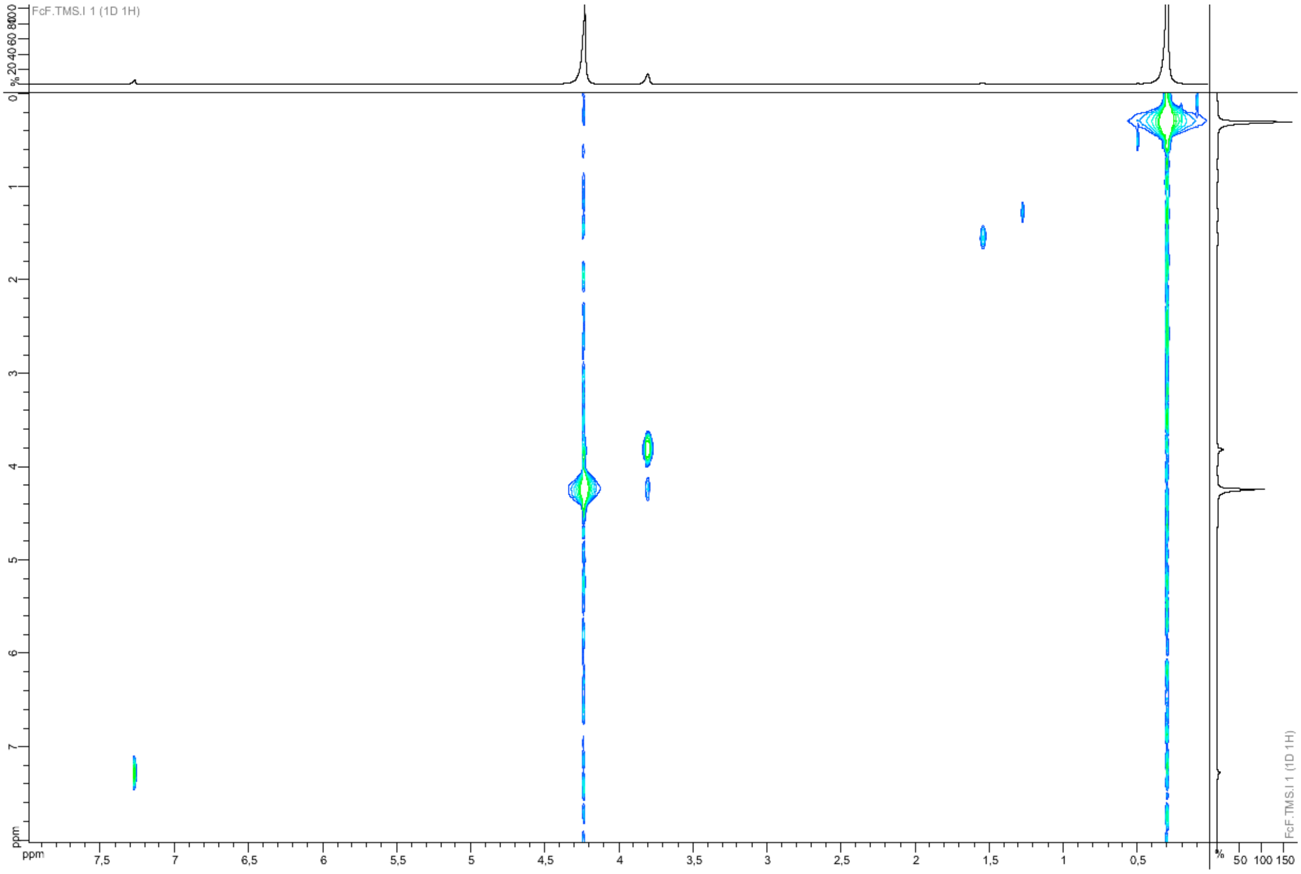
DEPT 135 (75 MHz, $CDCl_3$, 291 K)



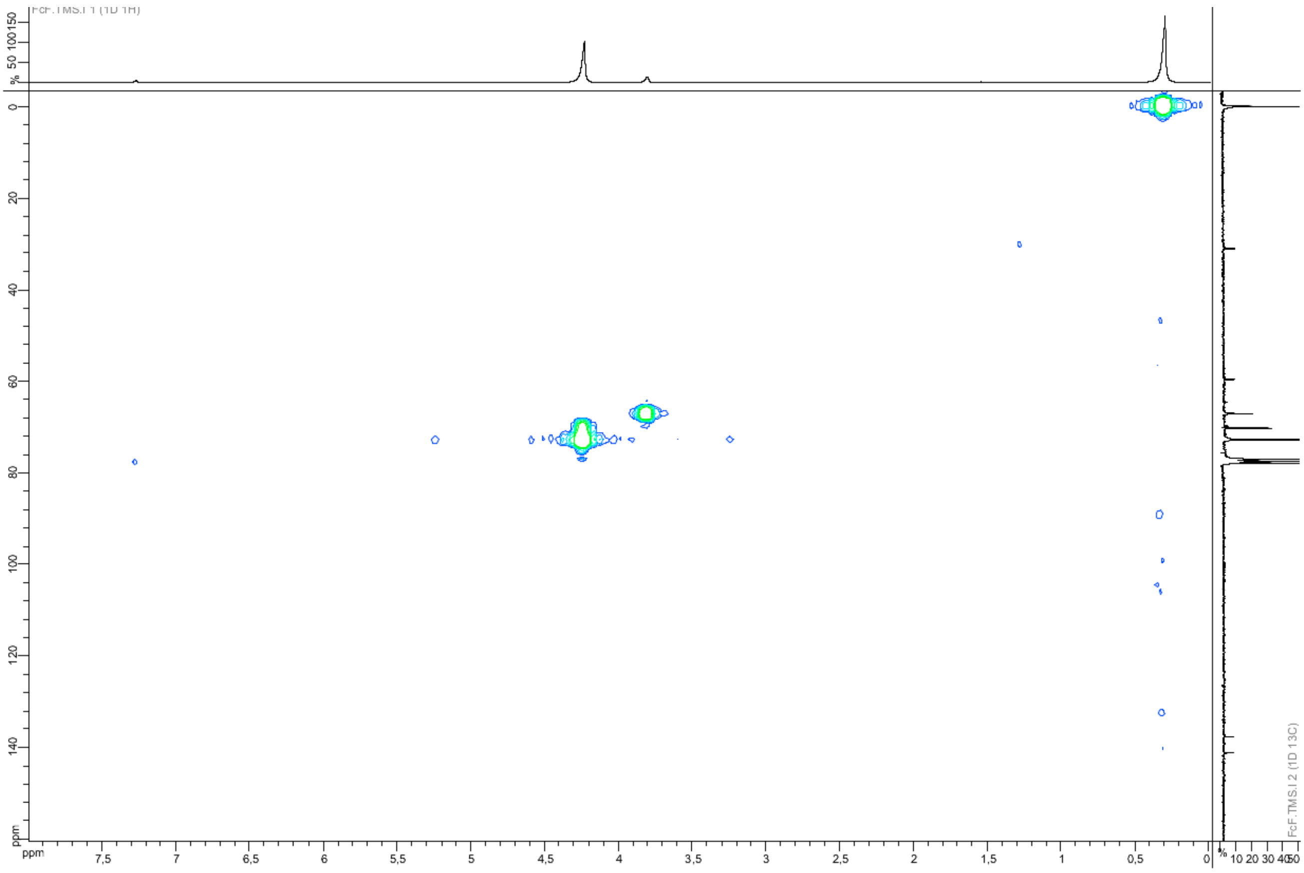
^{19}F NMR (282 MHz, $CDCl_3$, 291 K)



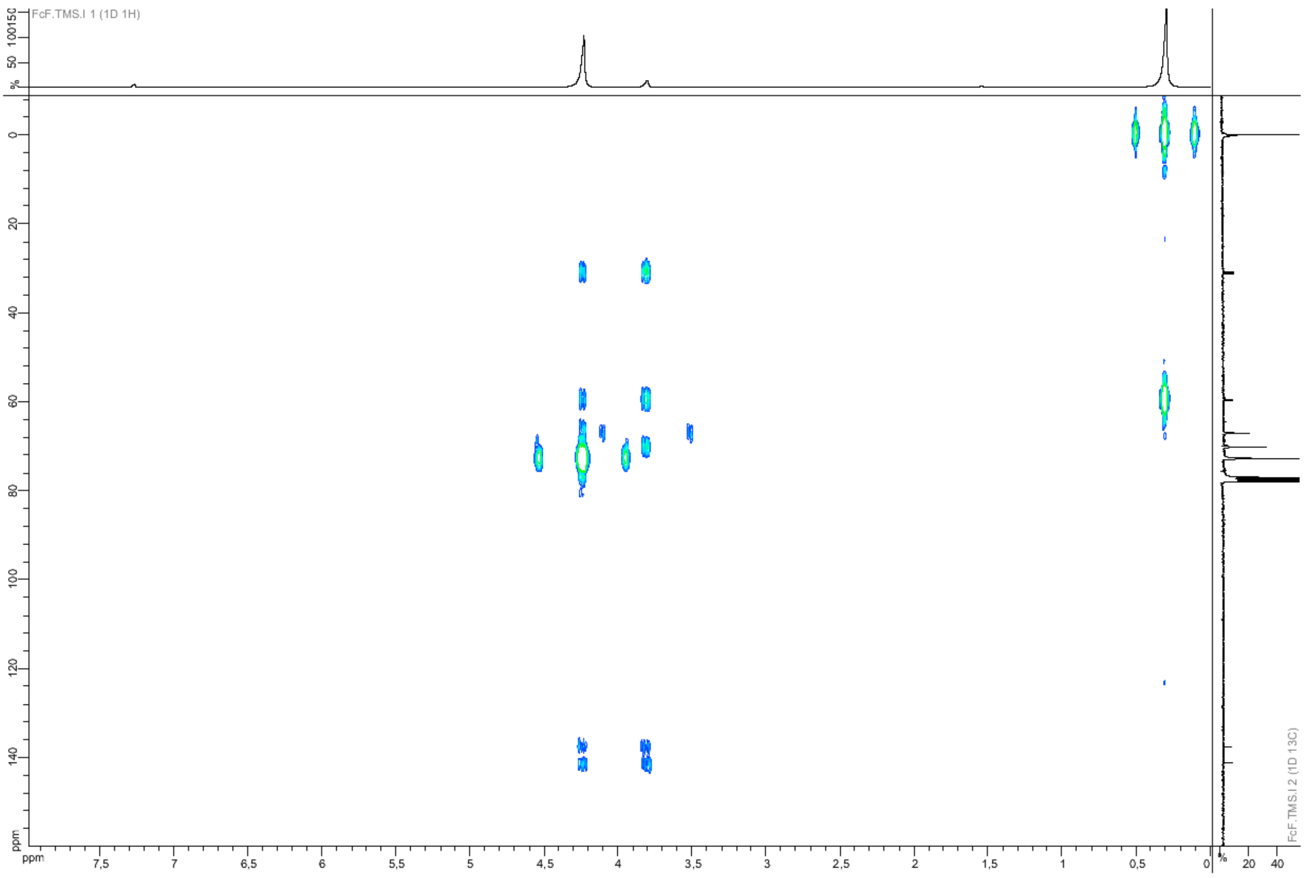
COSY (300 MHz, $CDCl_3$, 291 K)



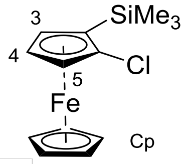
HSQC (300 MHz, $CDCl_3$, 291 K)



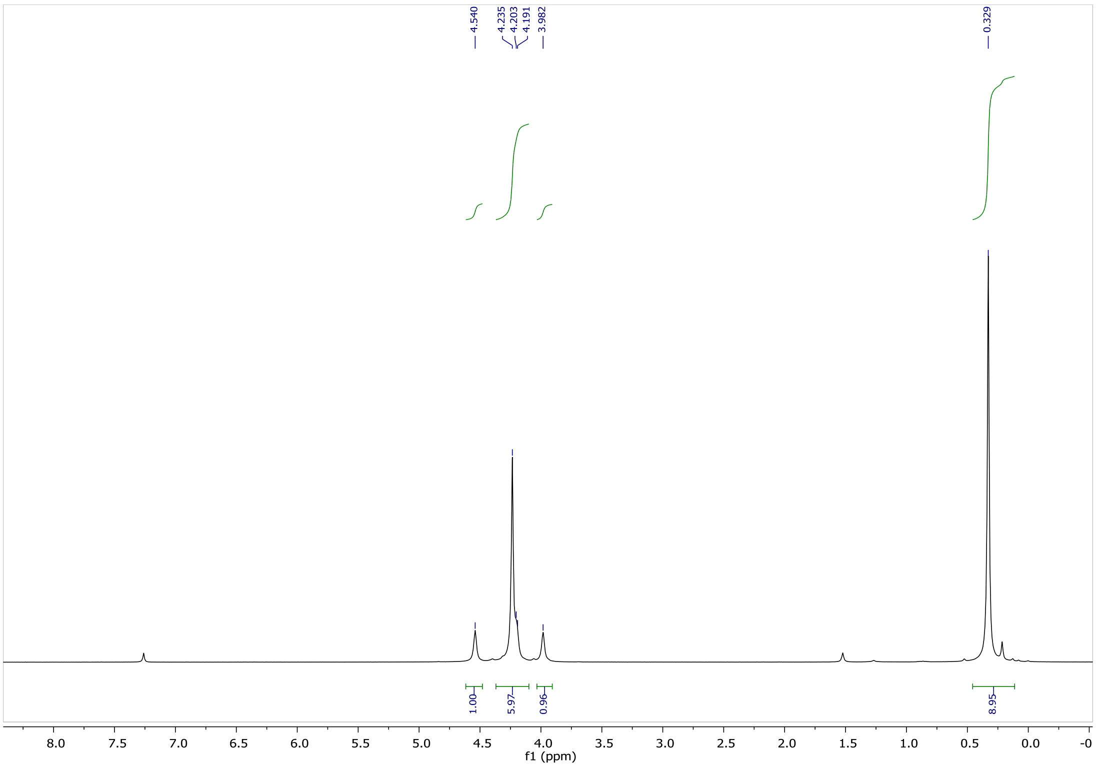
HMBC (300 MHz, $CDCl_3$, 291 K)



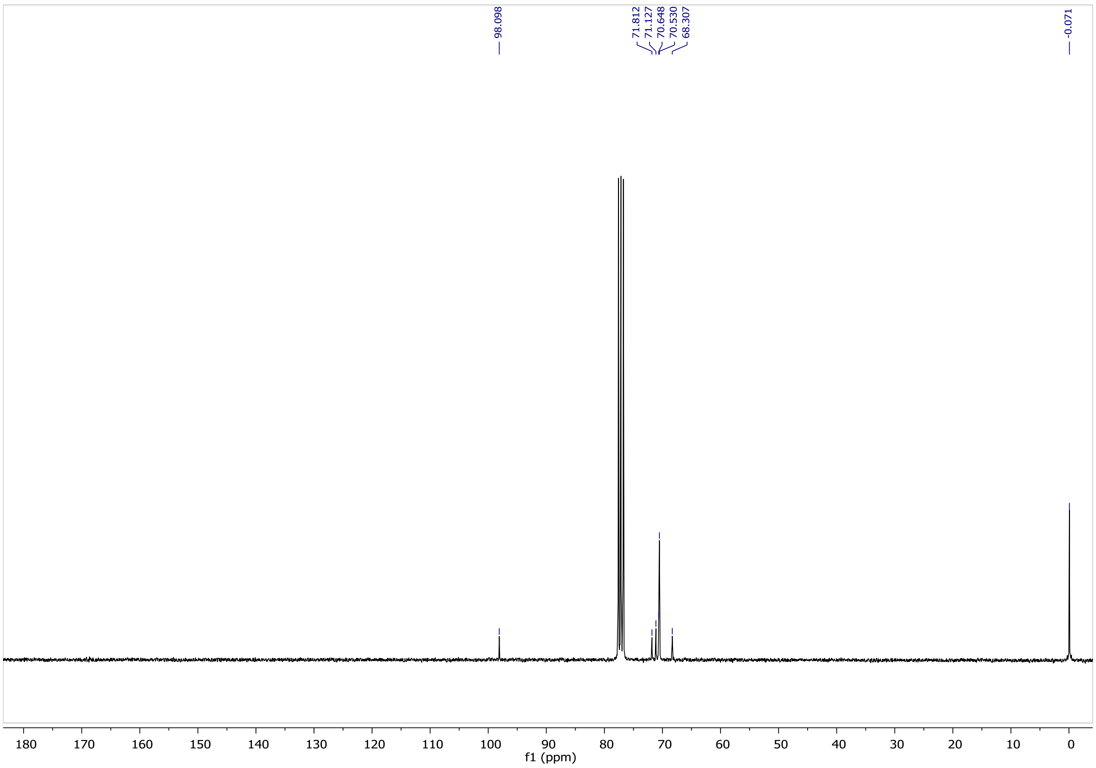
Compound 6f (racemic mixture)



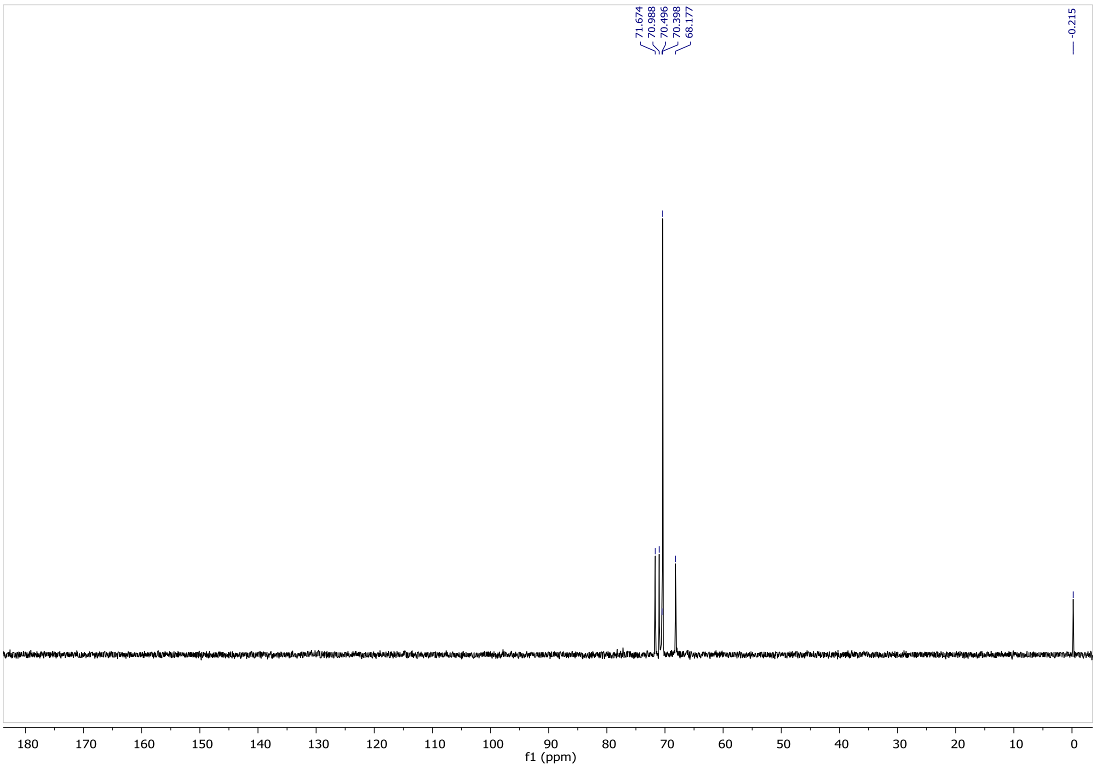
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



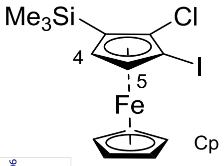
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



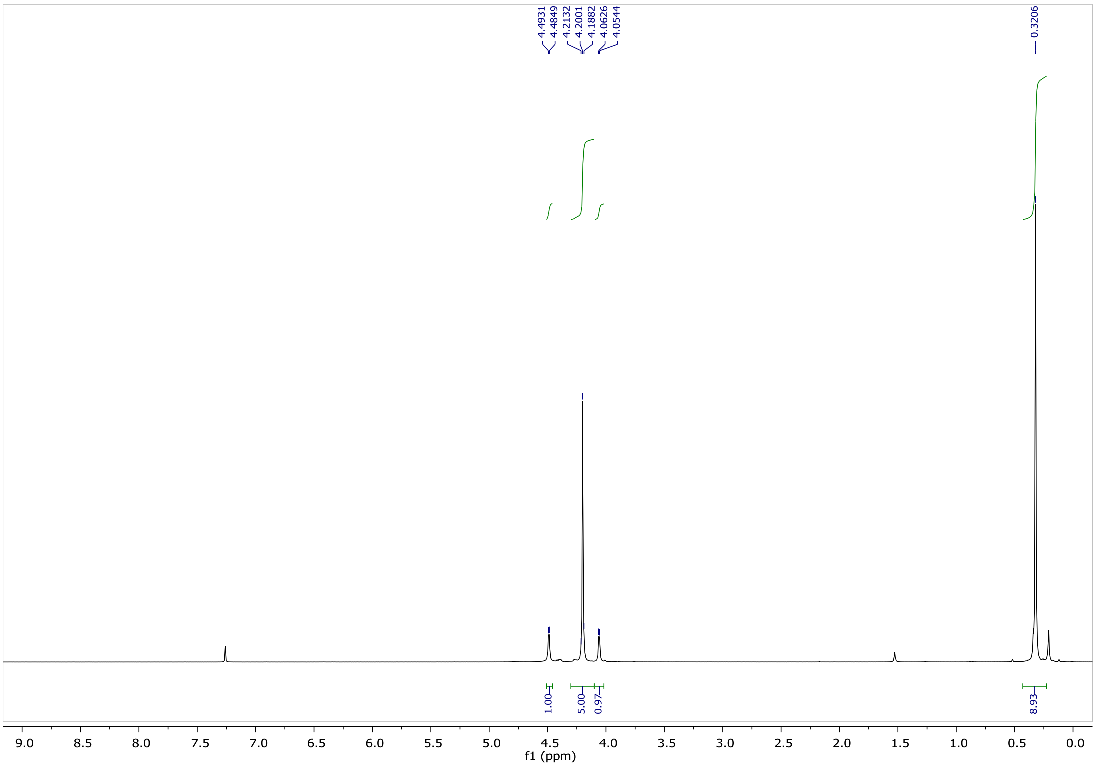
DEPT-135 (75 MHz, $CDCl_3$, 291 K)



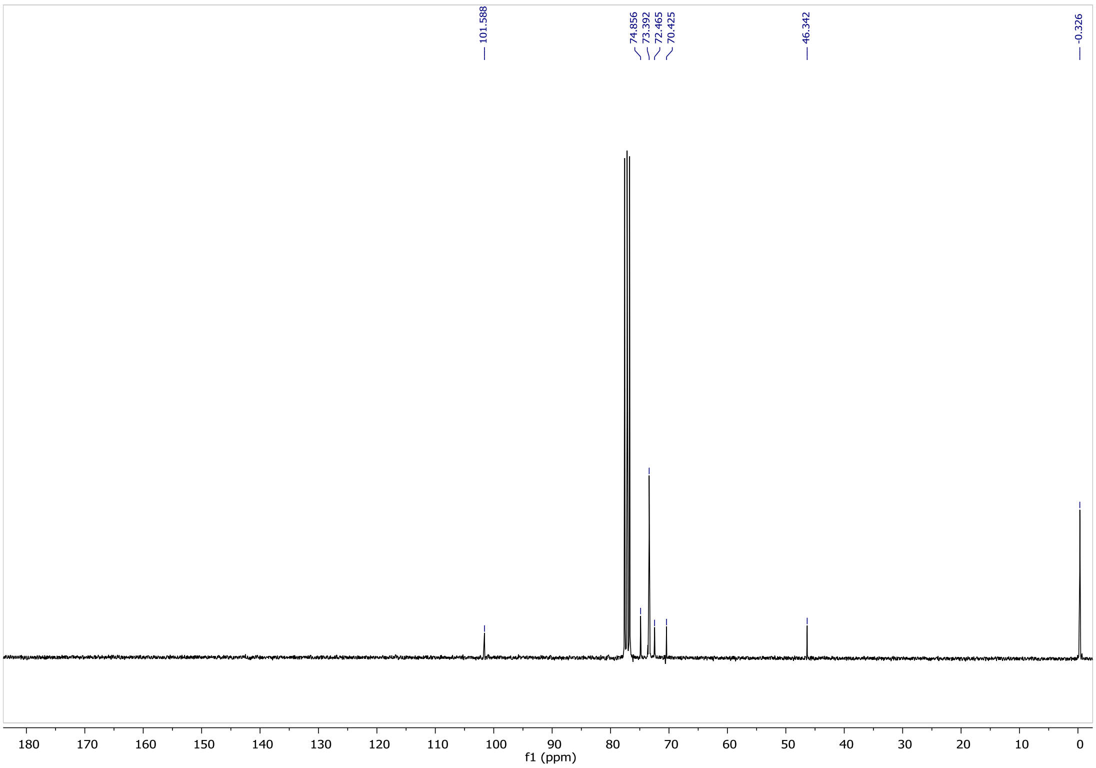
Compound 6fb (racemic mixture)



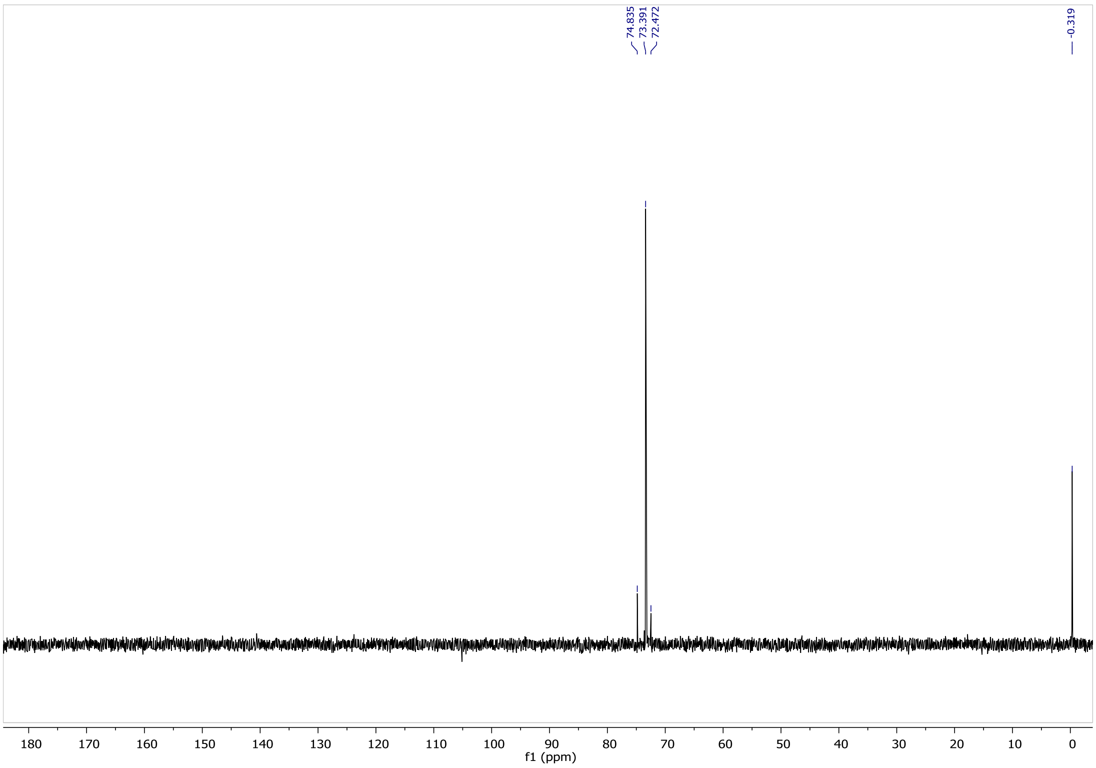
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



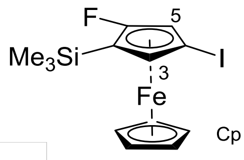
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



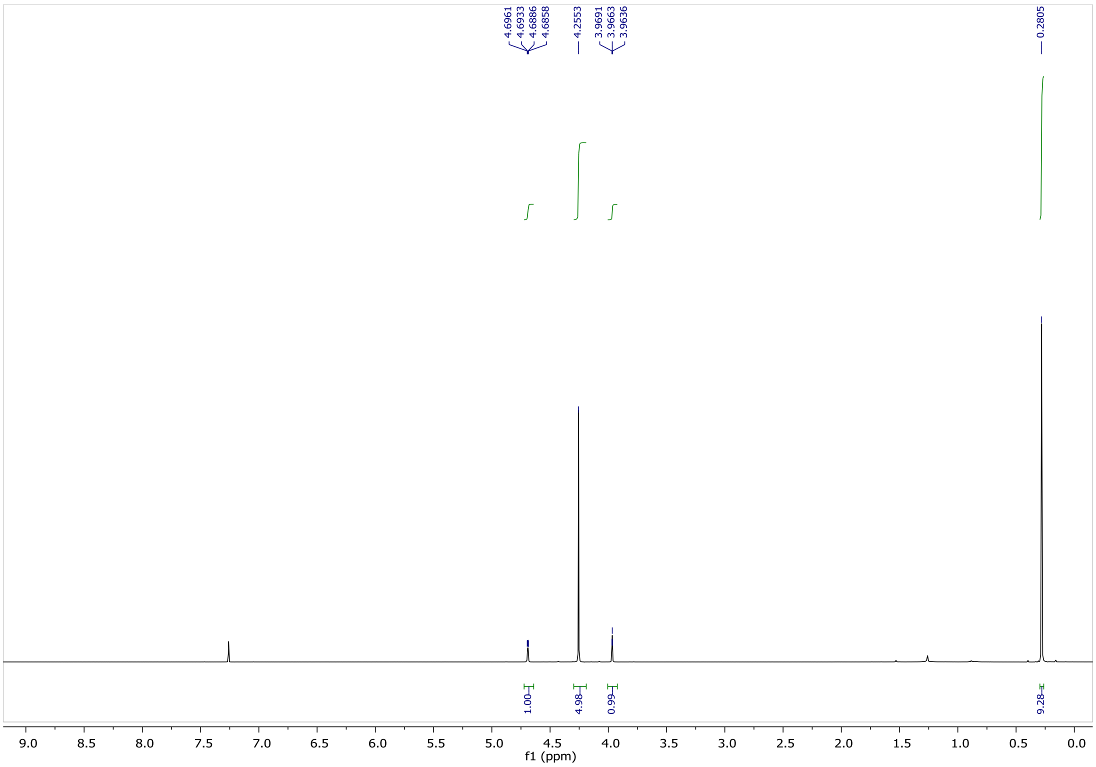
DEPT-135 (75 MHz, $CDCl_3$, 291 K)



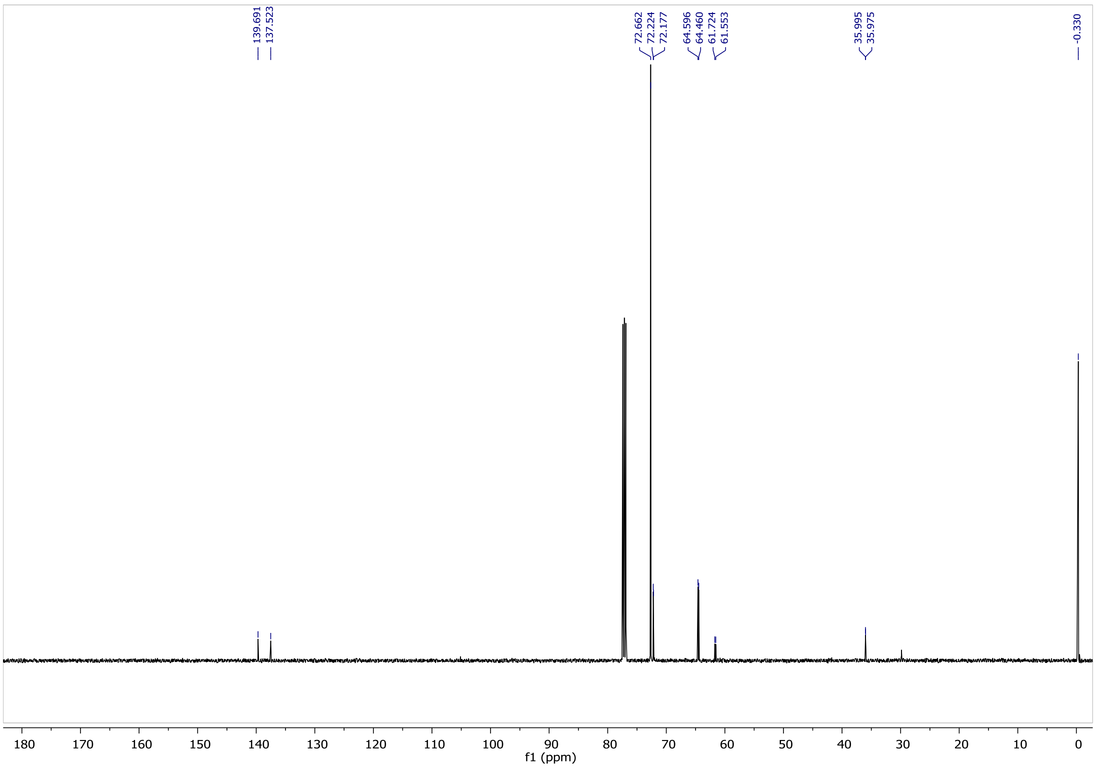
Compound 3fb-mig (racemic mixture)



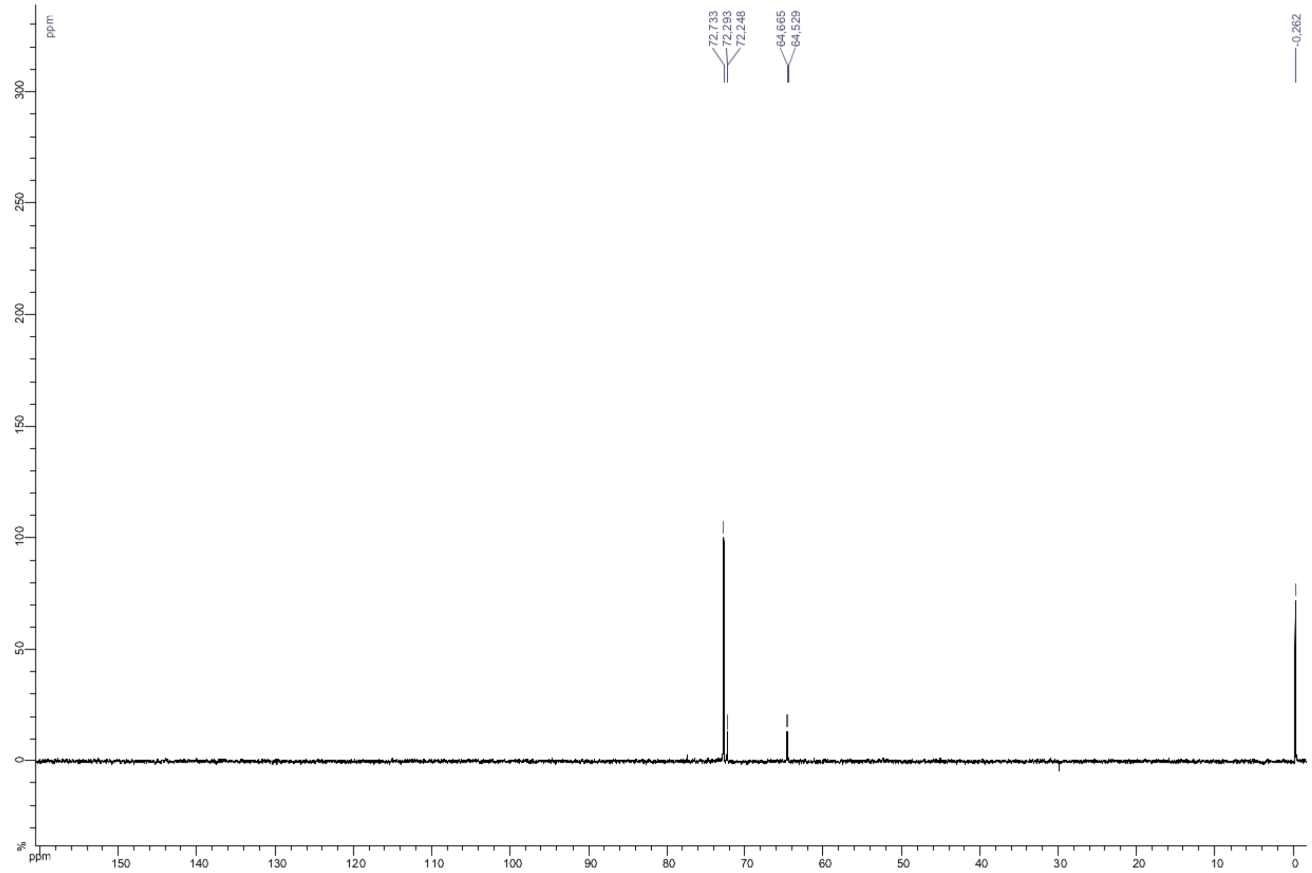
^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



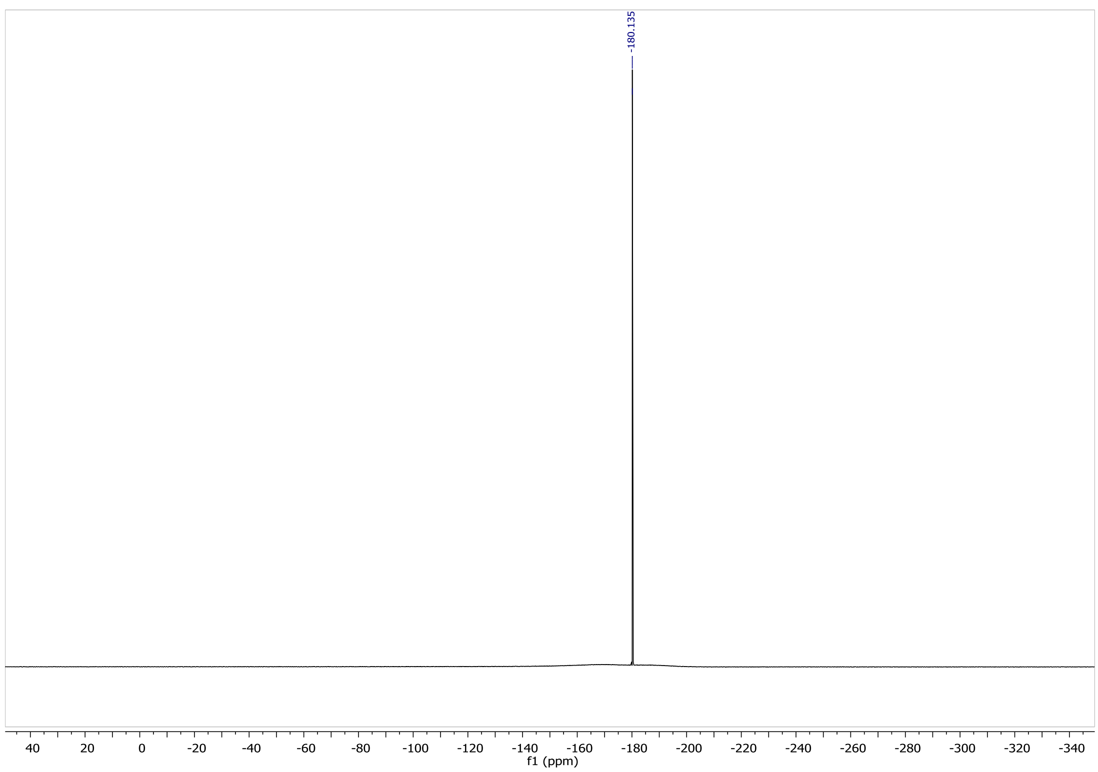
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



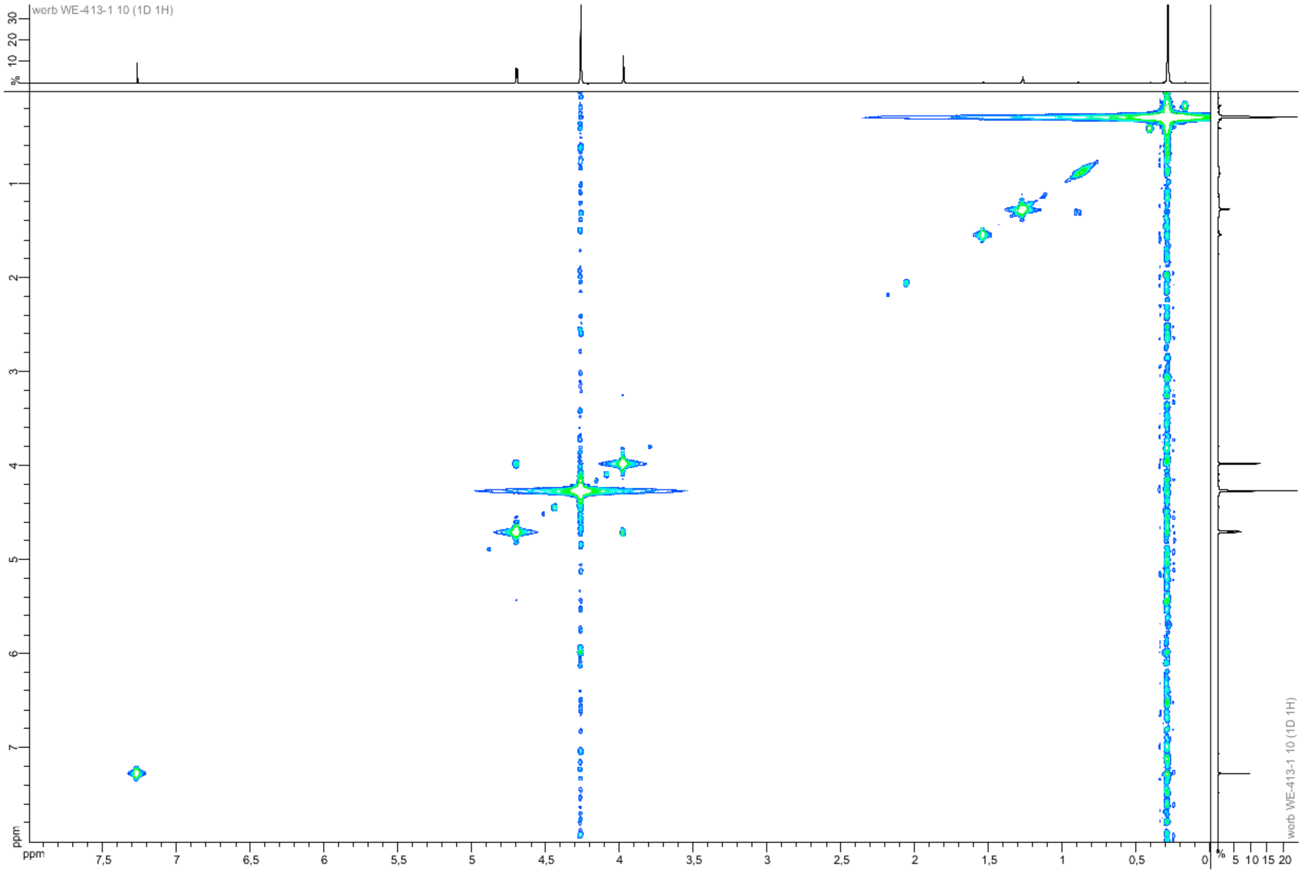
DEPT 135 (126 MHz, $CDCl_3$, 298 K)



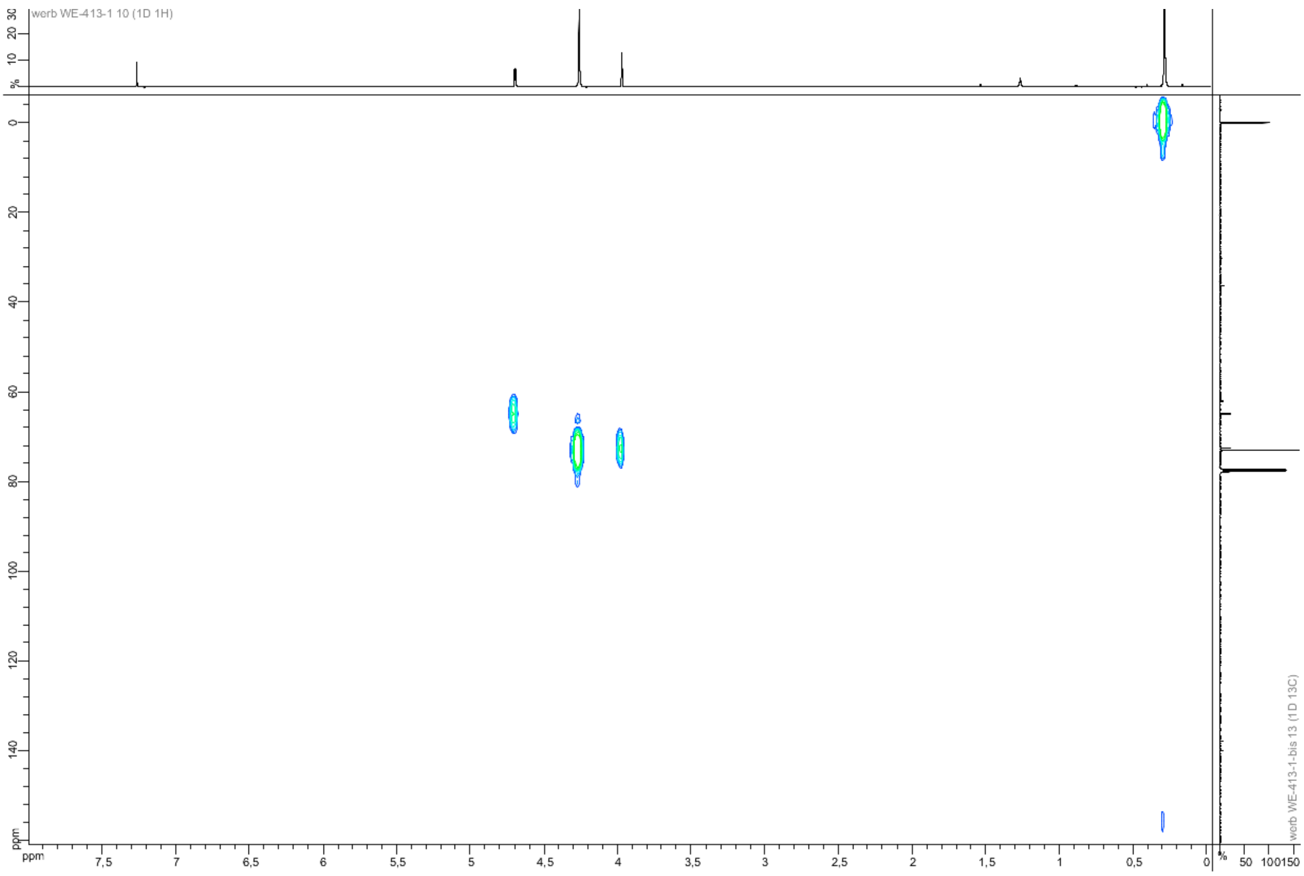
^{19}F NMR (470 MHz, $CDCl_3$, 298 K)



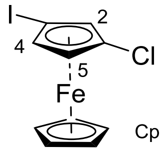
COSY (500 MHz, $CDCl_3$, 291 K)



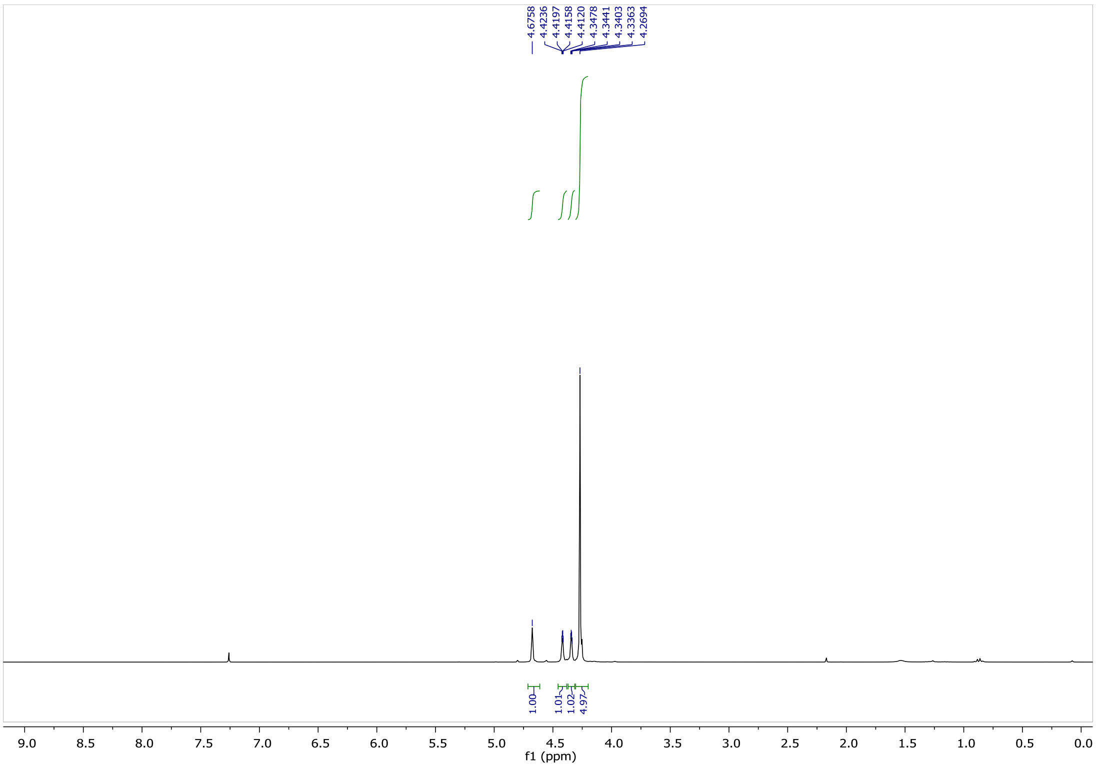
HSQC (500 MHz, $CDCl_3$, 291 K)



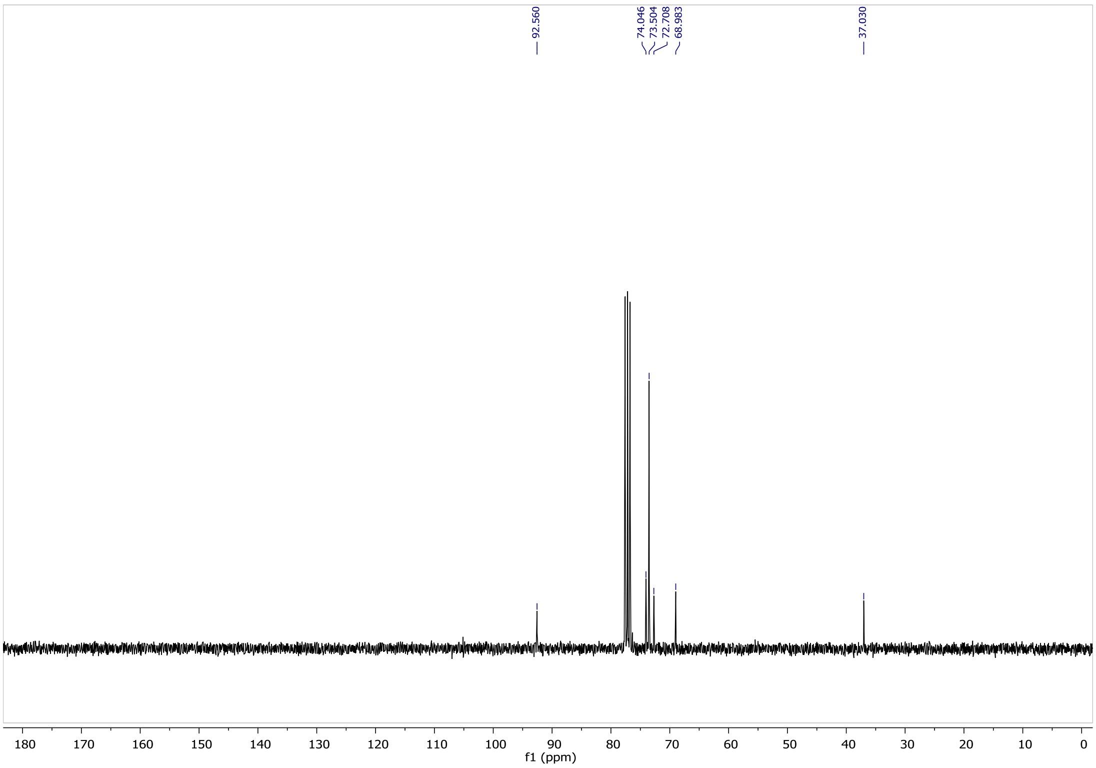
Compound 6b-mig (racemic mixture)



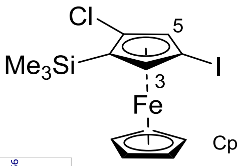
^{1}H NMR (300 MHz, $CDCl_3$, 291 K)



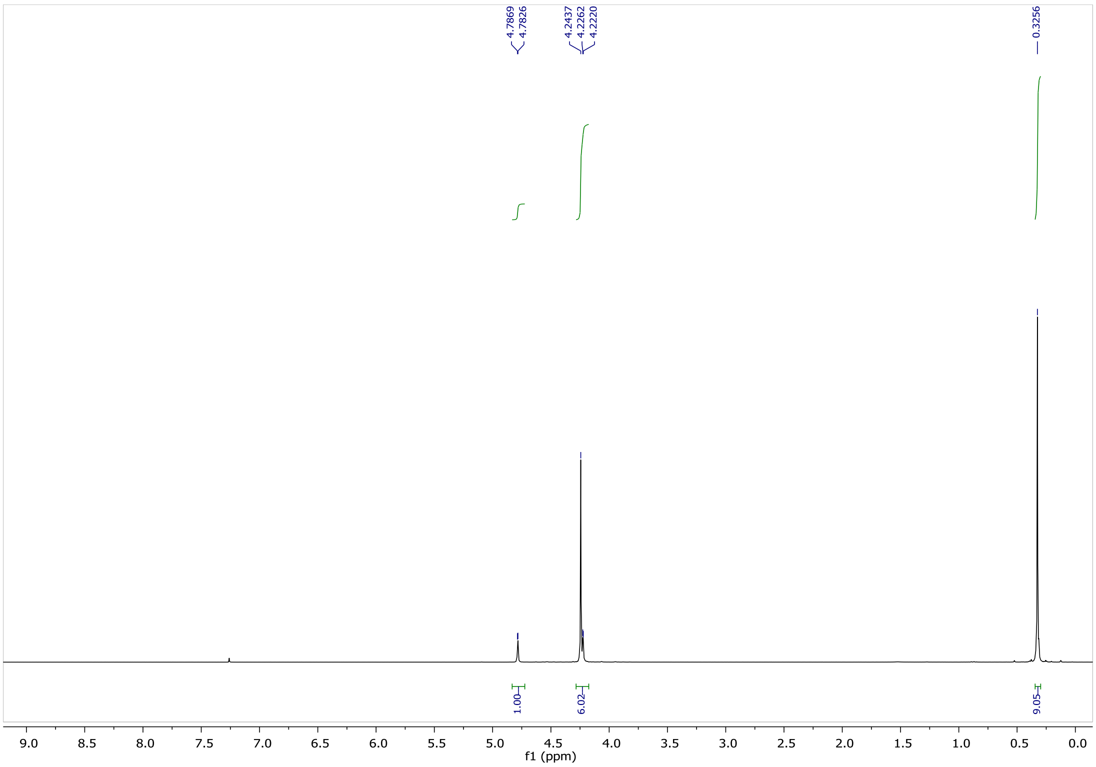
^{13}C NMR (75 MHz, $CDCl_3$, 291 K)



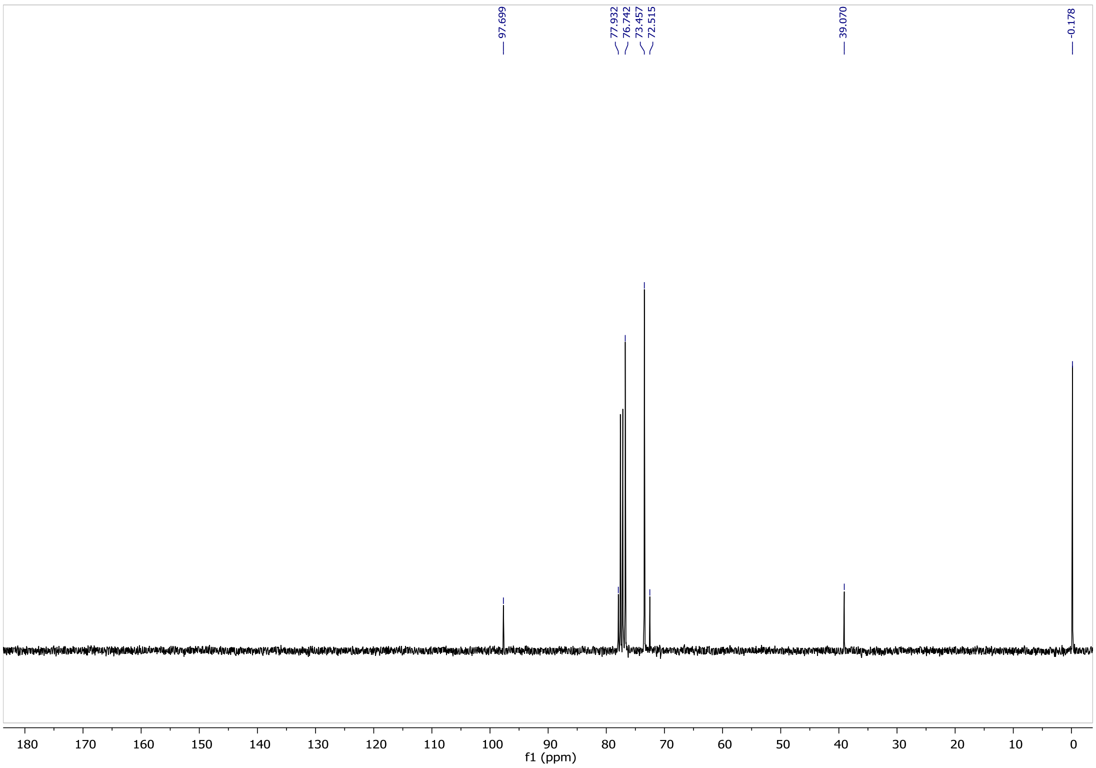
Compound 6fb-mig (racemic mixture)



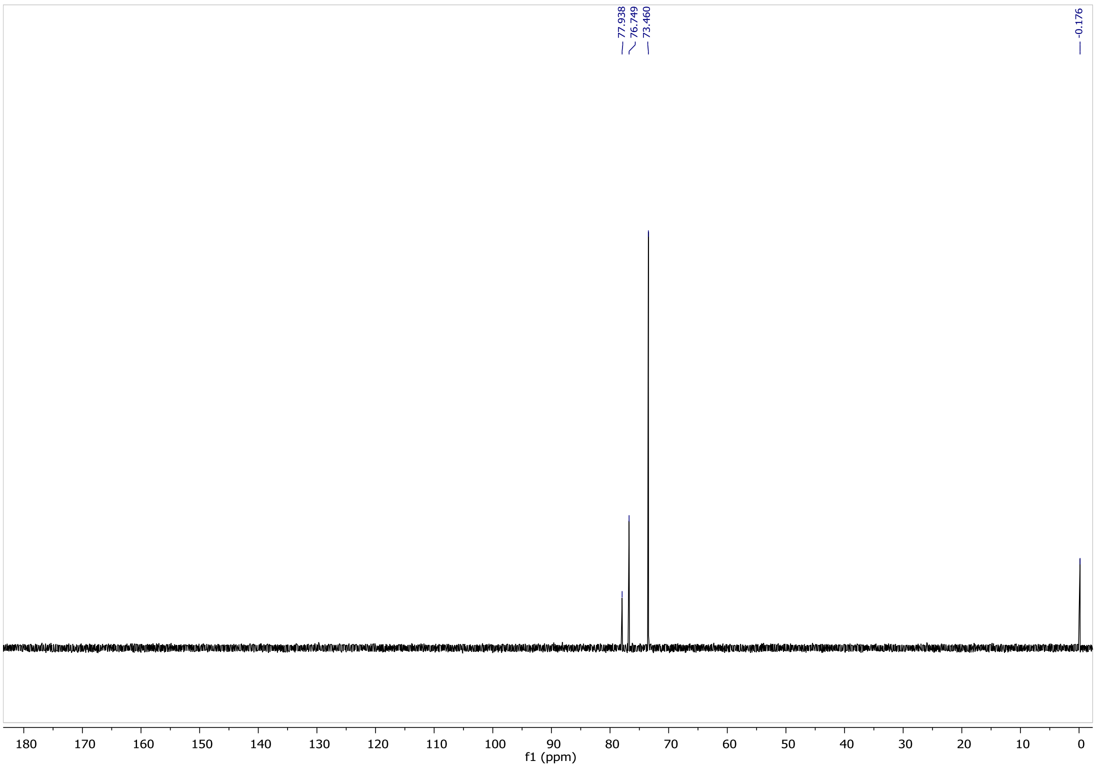
[1]H NMR (300 MHz, $CDCl_3$, 291 K)



[13]C NMR (75 MHz, $CDCl_3$, 291 K)



DEPT-135 (75 MHz, $CDCl_3$, 291 K)



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