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General considerations

All manipulations were performed under an inert atmosphere of dry argon by using vacuum line and Schlenk tube techniques. Solvents for all syntheses were either dried by standard methods and distilled under argon before use, or purified on an Innovative PURESOLV Solvent Purification System equipped with 4 Å MS columns, unless otherwise stated. Methyl ferrocenecarboxylate ^[1], 1,1'-dibromoferrocene ^[2], 1-bromo-1'-(phenylthio)ferrocene ^[3], (2,2-dibromoethenyl)ferrocene ^[4], methyl 4-ferrocenyl-benzoate ^[5], 1-formyl-1',2',3',4',5'-pentamethylferrocene ^[6] and 1-formyl-1',2,2',3,3',4,4',5-octamethylferrocene ^[7] were prepared according to previously reported procedures. Ferrocenecarboxylic acid **1a** was purchased from Sigma-Aldrich and used without further purification. Cp always refers to the ring that possesses the CO₂H or CO₂- substituent, and Cp' to the other ring.

1D- and 2D-NMR spectra were recorded on Bruker Avance300, Avance400 and Avance NEO 600 spectrometers. Chemical shifts (δ) for all nuclei are given in ppm. For ¹H and ¹³C, the residual peak of deuterated solvents was used as reference. Peaks are labeled as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). The proton and carbon assignments were performed by COSY, HSQC and ¹H-¹³C HMBC experiments.

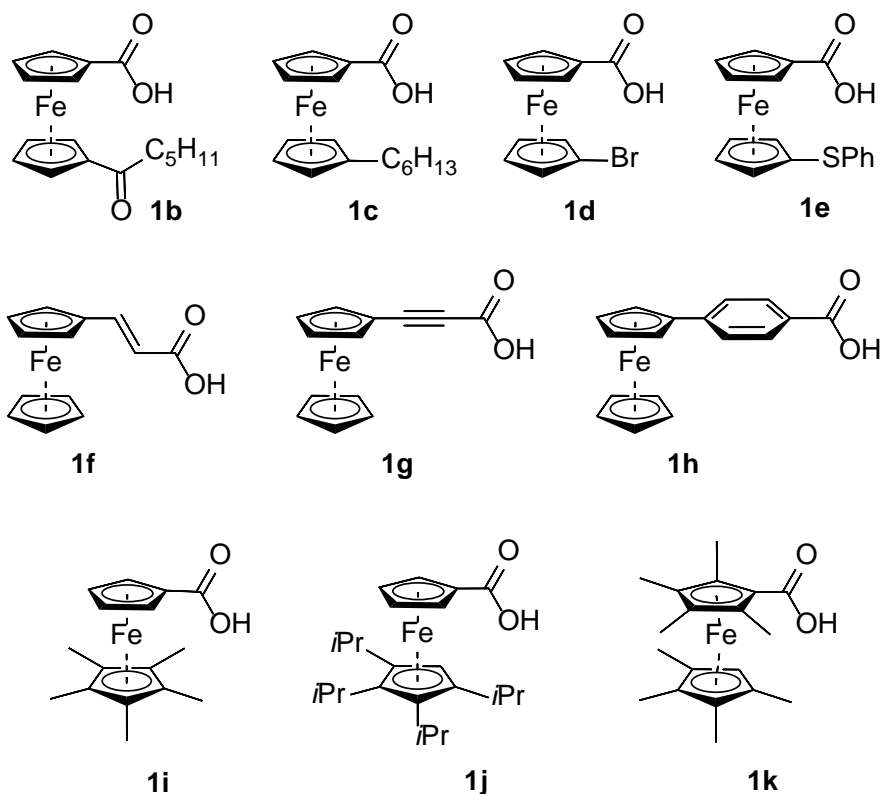
Electrospray (ES) mass spectra were recorded at the Université Paul Sabatier by the Service Commun de Spectrométrie de Masse on a MS/MS API-365 (Perkin Elmer Sciex).

Elemental analyses were carried out by the elemental analysis service of the LCC (Toulouse, France) using a PerkinElmer 2400 series II analyzer.

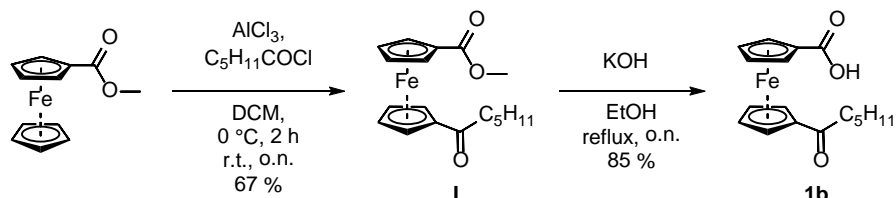
Electrochemical studies

Cyclic voltammetry (CV) and **square-wave voltammetry (SQW)** experiments were carried out with an Autolab PGSTAT100 potentiostat (Metrohm) controlled by GPES 4.09 software. Experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca 1cm² apparent surface. The working electrode was a platinum microdisk (0.5 mm diameter). The supporting electrolyte [*n*-Bu₄N][BF₄] (Sigma-Aldrich, 99 % electrochemical grade) was dried and degassed under argon. CH₂Cl₂ was freshly purified on an Innovative PURESOLV system equipped with 4 Å MS columns prior to use. The solutions used during the electrochemical studies were typically 10⁻³ M in analyte and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). All electrochemical data are referenced versus ferrocenium/ferrocene (FCH⁺/FCH) couple by adding ferrocene (10⁻³ M) at the end of the experiments.

Synthesis of ferrocenecarboxylic acids **1b-k**:



Synthesis of 1-carboxy-1'-(1-oxohexyl)ferrocene (**1b**):



1-(Methoxycarbonyl)-1'-(1-oxohexyl)ferrocene (**I**).^[8]

A suspension of AlCl_3 (2.67 g, 20.0 mmol, 2 equiv.) in DCM (24 mL) was cooled to 0 °C and stirred for 15 min under argon. A solution of *n*-hexanoyl chloride (1.7 mL, 12.0 mmol, 1.2 equiv.) in DCM (5 mL) was added dropwise and the resulting solution was stirred for 30 min. A solution of methyl ferrocenecarboxylate^[1] (2.42 g, 10.0 mmol, 1 equiv.) in DCM (15 mL) was added dropwise. After 2 h the cooling bath was removed and the reacting mixture was stirred at room temperature overnight. When the reaction was complete, the solution was poured onto ice-water mixture (≈ 100 mL). The organic phase was separated and the aqueous phase extracted with DCM (2 x 50 mL). The combined organic phases were washed with 5 % NaHCO_3 (1 x 100 mL) and brine (1 x 100 mL), dried (MgSO_4) and concentrated under reduced pressure. Purification of the solid residue by silica gel column chromatography (eluent EtOAc/hexane = 1:9, v/v) gave **I** as an orange-red solid: 2.3 g (67 %).

R_f (EtOAc/hexane = 1:9, v/v) 0.28;

MS (ESI, pos.) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{FeNaO}_3$ 365.1, found: 365.1;

Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{FeO}_3$ ($M_w = 342.22$): C, 63.18; H, 6.48. Found: C, 63.19; H, 6.66.

^1H NMR (400 MHz, CDCl_3) δ 4.80 (t, $J = 2.0$ Hz, 2H, 2 x CH Cp or Cp'), 4.78 (t, $J = 2.0$ Hz, 2H, 2 x CH Cp or Cp'), 4.49 (t, $J = 2.0$ Hz, 2H, 2 x CH Cp or Cp'), 4.40 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp or Cp'), 3.82

(s, 3H, CO₂CH₃), 2.68 (t, *J* = 7.5 Hz, 2H, COCH₂), 1.70 (m, 2H, COCH₂CH₂), 1.37 (m, 4H, CH₂CH₂CH₃), 0.93 (t, *J* = 6.7 Hz, 3H, CH₂CH₃).

¹³C NMR (101 MHz, CDCl₃) δ 203.96 (COCH₂), 170.99 (CO₂Me), 73.49 (2 x CH Cp or Cp'), 72.97 (2 x CH Cp or Cp'), 72.79 (C_{quat} Cp or Cp'), 71.65 (2 x CH Cp or Cp'), 70.85 (2 x CH Cp or Cp'), 51.90 (CO₂CH₃), 40.03 (COCH₂), 31.81 (CH₂CH₂CH₃), 24.14 (COCH₂CH₂), 22.73 (CH₂CH₃), 14.14 (CH₂CH₃) (one of C_{quat} is missing probably due to overlapping with other signal).

1-Carboxy-1'-(1-oxohexyl)ferrocene (**1b**).

A suspension of 1-(methoxycarbonyl)-1'-(1-oxohexyl)ferrocene (**1**) (1.03 g, 3.0 mmol, 1 equiv.) and KOH (1.01 g, 18.0 mmol, 6 equiv.) in EtOH (50 mL) was stirred under reflux overnight. When TLC analysis showed full consumption of the starting material, the reaction mixture was cooled to room temperature and poured onto an ice-water mixture (≈ 100 mL). The mixture was washed with diethyl ether (2 x 50 mL), acidified with concentrated HCl to pH 2 and extracted with diethyl ether (3 x 50 mL). The combined organic phases were washed with water (2 x 50 mL) and brine (1 x 50 mL), dried (MgSO₄) and concentrated under reduced pressure to give **1b** as an orange solid: 0.80 g (81 % yield).

R_f (EtOAc/hexane = 1:1 + 1% AcOH, v/v) 0.60;

HRMS (ESI, neg.) *m/z*: [M-H]⁻ calcd for C₁₇H₁₉FeO₃ 327.0684, found: 327.0690;

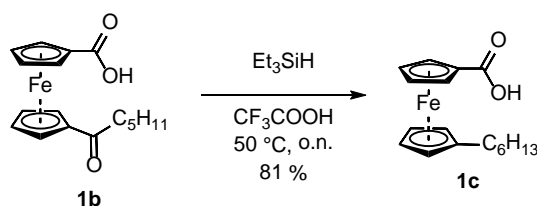
HRMS (ESI, pos.) *m/z*: [M+H]⁺ calcd for C₁₇H₂₁FeO₃ 329.0840, found: 329.0840;

Anal. Calcd for C₁₇H₁₉FeO₃ (M_w = 328.19): C, 62.22; H, 6.14. Found: C, 62.25; H, 6.28.

¹H NMR (400 MHz, *d*₆-acetone) δ 4.81 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp or Cp'), 4.75 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp or Cp'), 4.55 (t, *J* = 2.0 Hz, 2H, 2 x CH Cp or Cp'), 4.48 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp or Cp'), 2.77 (t, *J* = 7.3 Hz, 2H, COCH₂), 1.65 (m, 2H, COCH₂CH₂), 1.36 (m, 4H, CH₂CH₂CH₃), 0.91 (t, *J* = 6.7 Hz, 3H, CH₂CH₃).

¹³C NMR (101 MHz, *d*₆-acetone) δ 202.92 (COCH₂), 171.30 (CO₂H), 81.88 (C_{quat} Cp or Cp'), 74.18 (C_{quat} Cp or Cp'), 74.07 (2 x CH Cp or Cp'), 73.42 (2 x CH Cp or Cp'), 72.43 (2 x CH Cp or Cp'), 71.42 (2 x CH Cp or Cp'), 40.05 (COCH₂), 32.31 (CH₂CH₂CH₃), 24.50 (COCH₂CH₂), 23.28 (CH₂CH₃), 14.31 (CH₂CH₃).

Synthesis of 1-carboxy-1'-hexylferrocene (**1c**):^{[8],[9]}



Triethylsilane (0.7 mL, 4.4 mmol, 2.9 equiv.) was added dropwise to a solution of 1-carboxy-1'-(1-oxohexyl)ferrocene (**1b**) (492.3 mg, 1.5 mmol, 1 equiv.) in trifluoroacetic acid (1.5 mL) at 50 °C and the resulting mixture was stirred overnight. When TLC analysis showed full consumption of the starting material, the reaction was cooled to room temperature and poured onto an ice-water mixture (≈ 10 mL). The mixture was extracted with EtOAc (3 x 5 mL). The combined organic phases were washed with water (5 x 10 mL) and brine (1 x 10 mL), dried (MgSO₄) and concentrated under reduced pressure. Purification of the solid residue by silica gel column chromatography (eluent EtOAc/hexane = 1:1, v/v) gave **1c** as a red-orange solid: 381.6 mg (81 % yield).

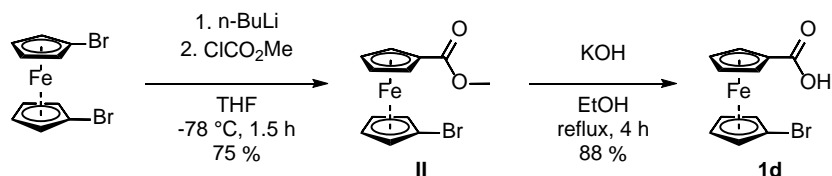
R_f (EtOAc/hexane = 1:1, v/v) 0.89;

HRMS (ESI, neg.) *m/z*: [M-H]⁻ calcd for C₁₇H₂₁FeO₂ 313.0891, found: 313.0890;

¹H NMR (400 MHz, CDCl₃) δ 4.78 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp), 4.41 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp), 4.13 (m, 2H, 2 x CH Cp'), 4.11 (m, 2H, 2 x CH Cp'), 2.29 (m, 2H, C₅H₄CH₂(CH₂)₄CH₃), 1.46 (m, 2H, C₅H₄CH₂CH₂(CH₂)₃CH₃), 1.28 (m, 6H, C₅H₄CH₂CH₂(CH₂)₃CH₃), 0.86 (t, *J* = 6.5 Hz, 3H, CH₃).

^{13}C NMR (101 MHz, CDCl_3) δ 177.89 (CO_2H), 91.43 (C_{quat} Cp'), 72.67 (2 x CH Cp), 71.23 (2 x CH Cp), 70.22 (C_{quat} Cp), 70.17 (2 x CH Cp'), 69.41 (2 x CH Cp'), 31.86 (one of $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 31.17 ($\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 29.33 (one of $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 28.49 ($\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 22.77 (one of $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 14.25 (CH_3).

Synthesis of 1-bromo-1'-carboxyferrocene (**1d**):^[10]



1-Bromo-1'-(methoxycarbonyl)ferrocene (**II**).

To a solution of 1,1'-dibromoferrocene ^[2] (343.8 mg, 1.0 mmol, 1.04 equiv.) in dry THF (2 mL), n-butyllithium (1.6 M in hexanes, 0.6 mL, 0.96 mmol, 1.0 equiv.) was added at $-25\text{ }^\circ\text{C}$. The resulting orange suspension was stirred for 30 min before being cooled to $-78\text{ }^\circ\text{C}$. A suspension of lithium salt was added via cannula to a precooled solution of methyl chloroformate (115 μL , 1.5 mmol, 1.5 equiv.) in dry THF (1 mL). The resulting solution was further stirred at room temperature for 2 h before water (5 mL) was added. The mixture was extracted with DCM (3 x 5 mL). The combined organic phases were washed with water (1 x 10 mL), brine (1 x 10 mL), dried (MgSO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (eluent EtOAc/hexane = 1:9, v/v) gave **II** as an orange solid: 232.5 mg (75 % yield).

R_f (EtOAc/hexane = 1:9, v/v) 0.60;

MS (ESI, pos.) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{FeNaO}_2$ 365.1, found: 365.1;

^1H NMR (400 MHz, CDCl_3) δ 4.85 (t, $J = 2.0$ Hz, 2H, 2 x CH Cp'), 4.43 (dt, $J = 3.9, 2.0$ Hz, 4H, 2 x CH Cp and 2 x CH Cp'), 4.13 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp), 3.82 (s, 3H, CH_3);

^{13}C NMR (101 MHz, CDCl_3) δ 170.89 (CO_2Me), 78.32 (C_{quat} Cp), 73.78 (2 x CH Cp), 73.53 (C_{quat} Cp'), 72.22 (2 x CH Cp'), 71.66 (2 x CH Cp'), 68.82 (2 x CH Cp), 51.70 (CH_3).

1-Bromo-1'-carboxyferrocene (**1d**).

Following the procedure for **1b**, ester hydrolysis was performed on 1-bromo-1'-(methoxycarbonyl)ferrocene (**II**) (186.3 mg, 0.58 mmol) to give **1d** as an orange solid: 143.2 mg (88 % yield).

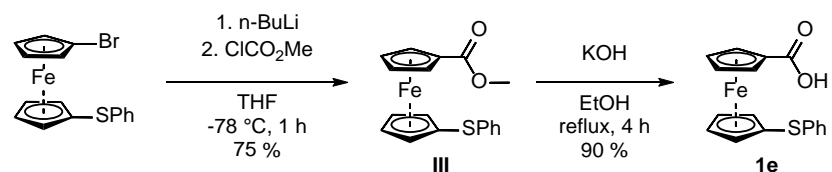
R_f (EtOAc/hexane = 1:1 + 1% AcOH, v/v) 0.69;

HRMS (ESI, neg.) m/z: $[\text{M}-\text{H}]^-$ calcd for $\text{C}_{11}\text{H}_8\text{BrFeO}_2$ 306.9057, found: 306.9062.

^1H NMR (400 MHz, CDCl_3) δ 10.36 (s, 1H, COOH), 4.91 (t, $J = 2.0$ Hz, 2H, 2 x CH Cp'), 4.51 (t, $J = 2.0$ Hz, 2H, 2 x CH Cp'), 4.49 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp), 4.20 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp).

^{13}C NMR (101 MHz, CDCl_3) δ 176.65 (CO_2H), 78.23 (C_{quat} Cp), 74.80 (2 x CH Cp'), 72.83 (2 x CH Cp'), 72.12 (C_{quat} Cp'), 72.04 (2 x CH Cp), 69.45 (2 x CH Cp).

Synthesis of 1-carboxy-1'-(phenylthio)ferrocene (**1e**):



1-(Methoxycarbonyl)-1'-(phenylthio)ferrocene (III).

To a solution of 1-bromo-1'-(phenylthio)ferrocene ^[3] (215.8 mg, 0.58 mmol, 1.0 equiv.) and TMEDA (87 μ L, 0.58 mmol, 1 equiv.) in dry THF (5 mL), n-butyllithium (1.6 M in hexanes, 0.4 mL, 0.61 mmol, 1.05 equiv.) was added at -78 °C. After 30 min, the resulting solution was added via cannula to a precooled solution of methyl chloroformate (70 μ L, 0.87 mmol, 1.5 equiv.) in dry THF (5 mL). The resulting solution was further stirred at room temperature for 2 h before water (5 mL) was added. The mixture was extracted with DCM (3 x 5 mL). The combined organic phases were washed with water (1 x 10 mL), brine (1 x 10 mL), dried (MgSO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (eluent dichloromethane) gave **II** as an orange solid: 143 mg (70 % yield).

R_f (EtOAc/hexane = 1:9, v/v) = 0.34;

HRMS (DCI-CH₄) m/z: [M]⁺ calcd for C₁₈H₁₆FeO₂S 352.0220, found: 352.0224;

Despite several attempts, correct elemental analyses could not be obtained for this compound.

¹H NMR (400 MHz, CDCl₃) δ 7.20-7.15 (m, 2H, 2 x *o*-CH Ph), 7.09-7.04 (m, 3H, 2 x *m*-CH Ph, *p*-CH Ph), 4.89 (p, *J* = 1.9 Hz, 2H, 2 x CH Cp), 4.47 (t, *J* = 2.0 Hz, 2H, 2 x CH Cp), 4.42 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp'), 4.37 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp'), 3.84 (s, 3H, CH₃);

¹³C NMR (101 MHz, CDCl₃) δ 171.40 (CO₂Me), 139.92 (C_{quat} Ph), 128.82 (2 x CH Ph), 126.47 (2 x CH Ph), 125.33 (*p*-CH Ph), 78.14 (C_{quat} Cp'), 76.31 (2 x CH Cp'), 73.03 (2 x CH Cp), 72.87 (C_{quat} Cp), 71.95 (2 x CH Cp'), 71.66 (2 x CH Cp), 51.88 (CH₃).

1-Carboxy-1'-(phenylthio)ferrocene (1e).

Following the procedure for **1b**, ester hydrolysis was performed on 1-(Methoxycarbonyl)-1'-(phenylthio)ferrocene (**III**) (75.0 mg, 0.21 mmol) to give **1e** as an orange solid: 71.0 mg (90% yield).

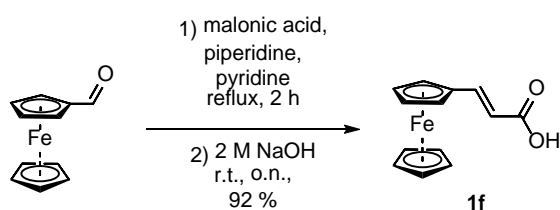
HRMS (DCI-CH₄) m/z: [M]⁺ calcd for C₁₇H₁₄FeO₂S 338.0064, found: 338.0074;

Despite several attempts, correct elemental analyses could not be obtained for this compound.

¹H NMR (400 MHz, CDCl₃) δ 7.19-7.15 (m, 2H, 2 x *o*-CH Ph), 7.09-7.04 (m, 3H, 2 x *m*-CH Ph, *p*-CH Ph), 4.94 (t, *J* = 2.0 Hz, 2H, 2 x CH Cp), 4.55 (t, *J* = 2.0 Hz, 2H, 2 x CH Cp), 4.47 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp'), 4.42 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp').

¹³C NMR (101 MHz, CDCl₃) δ 176.98 (CO₂H), 139.69 (C_{quat} Ph), 128.85 (2 x CH Ph), 126.63 (2 x CH Ph), 125.42 (CH Ph), 78.43 (C_{quat} Cp'), 76.45 (2 x CH Cp'), 73.85 (2 x CH Cp), 72.44 (2 x CH Cp'), 72.13 (2 x CH Cp), 71.40 (C_{quat} Cp).

Synthesis of 3-ferrocenylacrylic acid (1f):^[11]



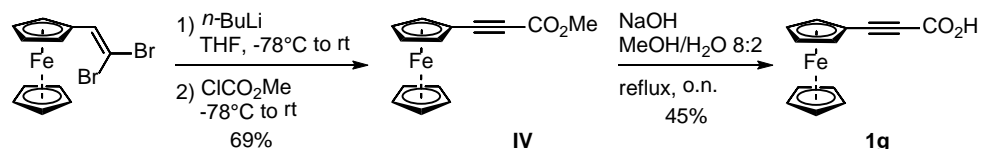
A solution of ferrocenecarboxaldehyde (1 g, 4.66 mmol, 1 equiv.), malonic acid (0.49 g, 4.66 mmol, 1 equiv.) and piperidine (0.40 g, 4.66 mmol) in pyridine (17 mL) was heated under reflux for 2 h. The resulting mixture was cooled to room temperature, diluted with aqueous 2 M NaOH (85 mL) and stirred overnight. Concentrated HCl was added until the formation of a precipitate. The mixture was extracted with CHCl₃ (3 x 30 mL). The combined organic phases were washed with water (1 x 50 mL), brine (1 x 50 mL), dried (MgSO₄) and concentrated under reduced pressure to give **1f** as dark-red powder: 1.1 g (92 % yield)

HRMS (ESI, neg.) m/z : $[M-H]^-$ calcd for $C_{13}H_{11}FeO_2$ 255.0108, found: 255.0112;

1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, $J_{HH} = 15.7$ Hz, 1H, $FcCH=CH$), 6.04 (d, $J_{HH} = 15.6$ Hz, 1H, $FcCH=CH$), 4.52 (t, $J_{HH} = 1.4$ Hz, 2H, 2 x CH Cp), 4.45 (t, $J_{HH} = 1.7$ Hz, 2H, 2 x CH Cp), 4.18 (s, 5H, 5 x CH Cp');

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.34 (CO_2H), 148.72 ($FcCH=CH$), 113.88 ($FcCH=CH$), 78.23 (C_{quat} Cp), 71.42 (2 x CH Cp), 69.91 (5 x CH Cp'), 69.03 (2 x CH Cp).

Synthesis of 3-ferrocenylpropionic acid (**1g**):



Methyl 3-ferrocenylpropionate (**IV**).

n -butyllithium (2.8 mL, 1.6M in hexane, 4.48 mmol, 2.2 equiv.) was added dropwise over 5 min to a solution of 2,2-dibromo-1-ferrocenyl ethylene [4] (0.75 g, 2.03 mmol, 1.0 equiv.) in dry THF (30 mL) at $-78^\circ C$. After 1 h, the mixture was allowed to warm to room temperature for 2 h, and then cooled to $-78^\circ C$ again. Methyl chloroformate (0.2 mL, 2.64 mmol, 1.3 equiv.) was added dropwise over 5 min and the cooling bath was removed. The mixture was stirred at room temperature for 1.5 h and then poured over NH_4Cl aq. (50 mL). The mixture was extracted with ethyl acetate (3 x 50 mL), the combined organic phases were washed with $NaHCO_3$ sat. aq. (50 mL), brine (50 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The brown residue was purified by column chromatography on silicagel (eluent: pentane/dichloromethane 1:1) to give **IV** as an orange crystalline solid: 0.38 g (69% yield).

HRMS (ESI, pos.) m/z : $[M]^+$ calcd for $C_{14}H_{12}FeO_2$ 268.0187, found: 268.0193;

1H NMR (400 MHz, $CDCl_3$) δ 4.59 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp), 4.34 (t, $J = 1.8$ Hz, 2H, 2 x CH Cp), 4.26 (s, 5H, 5 x CH Cp'), 3.81 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.72 (CO_2Me), 89.16 ($FcC\equiv C$), 77.95 ($FcC\equiv C$), 73.10 (2 x CH Cp), 70.56 (2 x CH Cp), 70.53 (5 x CH Cp'), 59.93 (C_{quat} Cp), 52.71 (CH_3).

3-ferrocenylpropionic acid (**1g**).

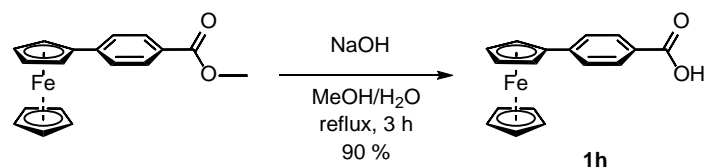
$NaOH$ (380 mg, 9.5 mmol, 6.8 equiv.) was added at room temperature to a stirred solution of methyl ester **IV** in a MeOH/ H_2O mixture (8 mL/2 mL). The suspension was stirred at reflux overnight and then poured onto an ice/water mixture. The aqueous phase was washed with ethyl acetate (3 x 50 mL) and acidified to pH 1 with aqueous 2M HCl . The aqueous phase was extracted with ethyl acetate (3 x 50 mL) and the combined organic phases were washed with brine (until the pH of brine was stable). The organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a mixture of the desired acid and ethynylferrocene. The solid was stirred in pentane, filtered, washed with pentane and dried to give acid **1g** as a red crystalline solid: 0.16 g (45% yield).

HRMS (DCI- CH_4) m/z : $[M+H]^+$ calcd for $C_{13}H_{11}FeO_2$ 255.0108, found: 255.0107;

1H NMR (400 MHz, d_6 -acetone) δ 4.63 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp), 4.43 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp), 4.30 (s, 5H, 5 x CH Cp').

^{13}C NMR (101 MHz, d_6 -acetone) δ 154.61 (CO_2H), 88.23 ($FcC\equiv C$), 79.11 ($FcC\equiv C$), 73.50 (2 x CH Cp), 71.29 (2 x CH Cp), 71.08 (5 x CH Cp'), 60.99 (C_{quat} Cp).

Synthesis of 4-ferrocenylbenzoic acid (**1h**): [5]



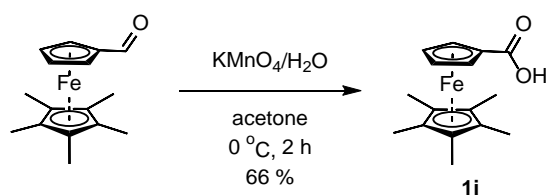
A suspension of methyl 4-ferrocenylbenzoate (200 mg, 0.6 mmol, 1 equiv.) and NaOH (27.5 mg, 0.68 mmol, 1.1 equiv.) in a water/methanol mixture (1:1, v/v 50 mL) was stirred under reflux for 3 h. When TLC analysis showed full consumption of the starting material, the reaction mixture was cooled to room temperature and washed with EtOAc (3 x 20 mL). The mixture was acidified with concentrated HCl to pH 2 and extracted with EtOAc (3 x 25 mL). The combined organic phases were washed with water (2 x 25 mL) and brine (1 x 25 mL), dried (MgSO₄) and concentrated under reduced pressure to give **1h** as an orange solid: 165.3 mg (90 % yield).

HRMS (ESI, neg.) m/z: [M-H]⁻ calcd for C₁₇H₁₃FeO₂ 305.0265, found: 305.0269;

¹H NMR (400 MHz, DMSO) δ 12.79 (br s, 1H, COOH), 7.86 (d, J_{HH} = 7.9 Hz, 2H, 2 x CH Ph), 7.63 (d, J_{HH} = 8.0 Hz, 2H, 2 x CH Ph), 4.87 (s, 2H, 2 x CH Cp), 4.42 (s, 2H, 2 x CH Cp), 4.02 (s, 5H, 5 x CH Cp[']);

¹³C NMR (101 MHz, DMSO) δ 167.33 (CO₂H), 144.60 (C_{quat}Fc Ph), 129.47 (2 x CH Ph), 127.82 (C_{quat}CO₂H Ph), 125.61 (2 x CH Ph), 82.91 (C_{quat} Cp), 69.72 (2 x CH Cp), 69.58 (5 x CH Cp[']), 66.78 (2 x CH Cp).

Synthesis of 1-carboxy-1',2',3',4',5'-pentamethylferrocene (1i):



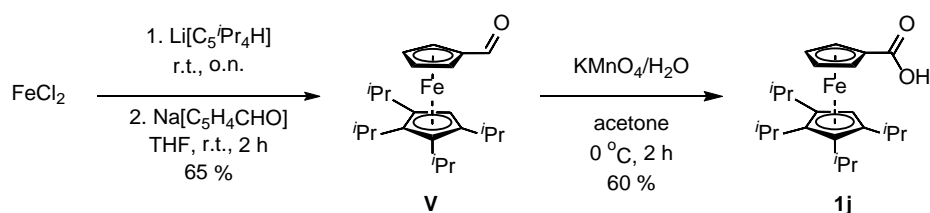
To a solution of 1-formyl-1',2',3',4',5'-pentamethylferrocene [6] (284.0 mg, 1.0 mmol, 1 equiv.) in acetone (10 mL) was added a solution of KMnO₄ (550.0 mg, 3.5 mmol, 3.5 equiv.) in water (2 mL). After 2 h, aqueous NaOH (20 % w/v, 1 mL) was added. The reaction mixture was filtered through Celite® and washed with aqueous NaOH (20 % w/v, 5 mL). The filtrate was washed with Et₂O (3 x 10 mL), acidified to pH 4 with aqueous HCl (2 M) and extracted with Et₂O (3 x 10 mL). The combined organic phases were washed with water (2 x 15 mL) and brine (1 x 15 mL), dried (MgSO₄) and concentrated under reduced pressure to give **1i** as an orange solid: 197.2 mg (66 % yield).

HRMS (ESI, neg.) m/z: [M-H]⁻ calcd for C₁₆H₁₉FeO₂ 299.0734, found: 299.0735.

¹H NMR (400 MHz, CDCl₃) δ 4.31 (t, J_{HH} = 1.8 Hz, 2H, 2 x CH Cp), 4.03 (t, J_{HH} = 1.9 Hz, 2H, 2 x CH Cp), 1.84 (s, 15H, 5 x CH₃).

¹³C NMR (101 MHz, CDCl₃) δ 177.52 (CO₂H), 81.68 (5 x C_{quat} Cp^{*}), 76.3 (2 x CH Cp), 73.25 (2 x CH Cp), 71.52 (C_{quat} Cp), 10.43 (5 x CH₃).

Synthesis of 1-carboxy-1',2',3',4'-tetraisopropylferrocene (1j):



1-Formyl-1',2',3',4'-tetraisopropylferrocene (V). A suspension of FeCl₂ (633.8 mg, 5.0 mmol, 1 equiv.) in dry THF (50 mL) was vigorously stirred in the dark for 1 h (Suspension A). A mixture of sodium cyclopentadienide (440.4 mg, 5.0 mmol, 1 equiv.) and methyl formate (0.45 mL, 7.5 mmol, 1.5 equiv.) in dry THF (8 mL) was stirred for 4 h at room temperature (Solution B). A suspension of lithium 1,2,3,4-tetraisopropylcyclopentadienide (1.32 g, 5.5 mmol, 1.1 equiv.) in dry THF (12 mL) was transferred via cannula to the suspension A and the resulting mixture was stirred for 1 h. Then, the deep-red solution B was added via cannula in the dark and the resulting mixture was stirred for 16 h. The solvents were then removed in vacuo, the residue was dissolved in a pentane/Et₂O mixture (1:1, v/v) and the resulting solution was filtered through a short pad of Celite® and concentrated in vacuo. Purification of the residue by silica gel column chromatography (eluent pentane/Et₂O = 2:1, v/v) gave **V** as a deep-red solid: 1.2 g (65 % yield).

MS (ESI, pos.) m/z: [M+Na]⁺ calcd for C₂₃H₃₄FeNaO 405.2, found: 405.2;

Anal. Calcd for C₂₃H₃₄FeO (M_w = 382.37): C, 72.25; H, 8.96. Found: C, 71.66; H, 9.12.

¹H NMR (400 MHz, CDCl₃) δ 9.99 (s, 1H, CHO), 4.65 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp), 4.57 (t, *J* = 2.0 Hz, 2H, 2 x CH Cp), 3.95 (s, 1H, CH Cp'), 2.74 (hept, *J* = 7.0 Hz, 4H, 4 x CH(CH₃)₂), 1.42 (d, *J* = 7.2 Hz, 6H, CH(CH₃)₂), 1.29 (dd, *J* = 11.4, 7.0 Hz, 12H, 2 x CH(CH₃)₂), 1.04 (d, *J* = 6.7 Hz, 6H, CH(CH₃)₂);

¹³C NMR (101 MHz, CDCl₃) δ 194.87 (CHO), 94.53 (2 x C_{quat} Cp'), 93.03 (2 x C_{quat} Cp'), 79.97 (C_{quat} Cp), 75.26 (2 x CH Cp), 71.05 (2 x CH Cp), 61.93 (CH Cp'), 26.21 (2 x CH₃), 26.02 (one of 2 x CH(CH₃)₂), 25.89 (one of 2 x CH(CH₃)₂), 24.36 (2 x CH₃), 24.23 (2 x CH₃), 23.35 (2 x CH₃).

1-Carboxy-1',2',3',4'-tetraisopropylferrocene (1j).

Following the procedure for **1i**, aldehyde oxidation was performed on 1-formyl-1',2',3',4'-tetraisopropylferrocene (**V**) (191.2 mg, 0.5 mmol) to give **1j** as a red solid: 119.5 mg (88 % yield).

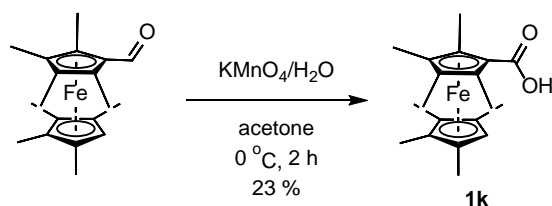
HRMS (ESI, neg.) m/z: [M-H]⁻ calcd for C₂₃H₃₃FeO₂ 397.1830, found: 397.1839.

Anal. Calcd for C₂₃H₃₄FeO₂ (M_w = 398.37): C, 69.35; H, 8.60. Found: C, 69.02; H, 8.55.

¹H NMR (400 MHz, CDCl₃) δ 4.69 (m, 2H, 2 x CH Cp), 4.42 (m, 2H, CH Cp), 3.93 (s, 1H, CH Cp'), 2.77 (hept, *J* = 7.1 Hz, 4H, 4 x CH(CH₃)₂), 1.42 (d, *J* = 7.1 Hz, 6H, CH(CH₃)₂), 1.32 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.27 (d, *J* = 7.1 Hz, 6H, CH(CH₃)₂), 1.03 (d, *J* = 6.7 Hz, 6H, CH(CH₃)₂).

¹³C NMR (101 MHz, CDCl₃) δ 178.67 (CO₂H), 94.25 (2 x C_{quat} Cp'), 92.47 (2 x C_{quat} Cp'), 73.85 (2 x CH Cp), 72.20 (2 x CH Cp), 71.80 (C_{quat} Cp), 62.23 (CH Cp'), 26.37 (2 x CH₃), 26.13 (2 x CH(CH₃)₂), 26.02 (2 x CH(CH₃)₂), 24.34 (2 x CH₃), 24.09 (2 x CH₃), 23.08 (2 x CH₃).

Synthesis of 1-carboxy-2,3,4,5,1',2',3',4'-octamethylferrocene (1k)



Following the procedure for **1i**, aldehyde oxidation was performed on 1-formyl-1',2,2',3,3',4,4',5-octamethylferrocene (326.0 mg, 1 mmol)^[7] to give **1k** as an orange solid: 80.0 mg (23 % yield).

HRMS (ESI, neg.) m/z: [M-H]⁻ calcd for C₁₉H₂₅FeO₂ 341.1204, found: 341.1209.

¹H NMR (400 MHz, CDCl₃) δ 3.44 (m, 1H, 1 x CH Cp), 1.98 (m, 6H, CH₃ Cp), 1.73 (m, 6H, CH₃ Cp), 1.57 (m, 12H, CH₃ Cp).

¹³C NMR (101 MHz, CDCl₃) δ 179.54 (CO₂H), 85.86 (2 x C_{quat} Cp or Cp'), 84.53 (2 x C_{quat} Cp or Cp'), 82.02 (4 x C_{quat} Cp or Cp'), 72.47 (C_{quat} Cp), 66.09 (CH Cp'), 11.39 (2 x CH₃ Cp or Cp'), 10.62 (2 x CH₃ Cp or Cp'), 9.98 (2 x CH₃ Cp or Cp'), 8.72 (2 x CH₃ Cp or Cp').

Synthesis of heteroleptic dirhodium(II) complex (3):

Dirhodium(II) tris[μ -acetato- κ O: κ O'] [μ -(2,2,2-trifluoroacetato- κ O: κ O')] (3). [12]

A suspension of $\text{Rh}_2(\text{OAc})_4$ (0.50 g, 1.13 mmol) in THF (12 mL) was sonicated for a few minutes until the solution became homogeneous. CF_3COOH (17 mL) was added and the resulting mixture was stirred at 55 °C for 2 h. Then, the reaction was quenched by addition of CH_3CN (15 mL), Celite® (\approx 1 g) was added and the reaction mixture was concentrated *in vacuo*. The solid residue was purified by column chromatography (flash silica gel, gradient EtOAc/hexane = 1:2 to 1:1, v/v) to give $\text{Rh}_2(\text{OAc})_3(\text{tfa})$ as a blue-green solid (0.56 g, 50 % yield).

R_f (EtOAc/hexane = 1:1, v/v) 0.24;

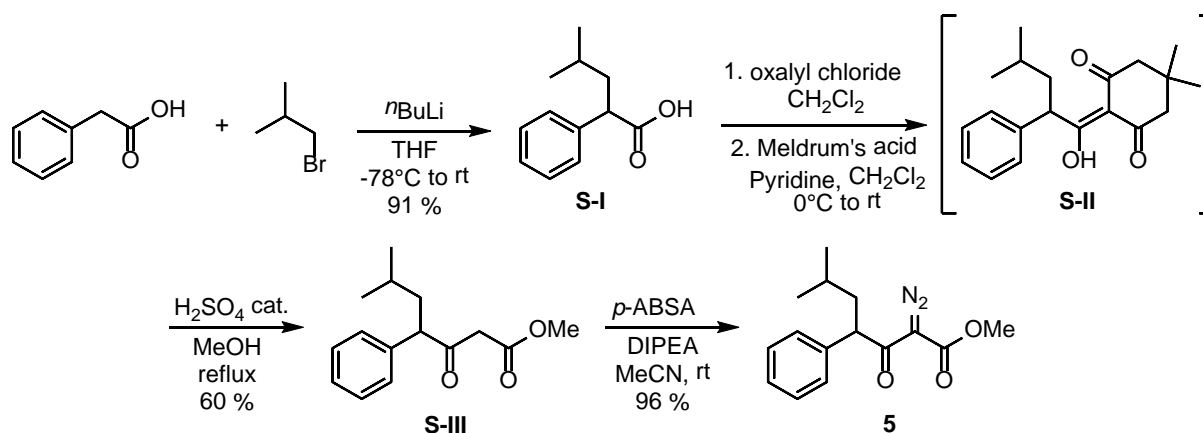
HRMS (DCI- CH_4) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_8\text{H}_{10}\text{F}_3\text{O}_8\text{Rh}_2$ 496.8438, found: 496.8445;

^1H NMR (400 MHz, Acetone) δ 1.81 (6H, 2 x *cis*- CH_3CO_2), 1.80 (3H, *trans*- CH_3CO_2);

^{13}C NMR (101 MHz, Acetone) δ 191.44 (*trans*- CH_3CO_2), 190.75 (2 x *cis*- CH_3CO_2), 22.28 (2 x *cis*- CH_3CO_2), 22.14 (*trans*- CH_3CO_2) (carbons of CF_3CO_2 are missing due to low intensity);

^{19}F NMR (377 MHz, Acetone) δ -75.73 (CF_3CO_2).

Synthesis of diazo substrate (5):^[13]



Synthesis of S-I: ^[14]

*n*BuLi (13.8 mL, 22 mmol, 2.2 equiv.) was added dropwise to a solution of phenylacetic acid (1.37 g, 10 mmol, 1.0 equiv.) in dry THF (40 mL) at -78°C. The mixture was stirred at room temperature for 1 h and cooled to -78°C again. 1-bromo-2-methylpropane (4.4 mL, 40 mmol, 4.0 equiv.) was then added and the reaction mixture was stirred at room temp. overnight. After completion of the reaction, the mixture was diluted with water and washed with Et₂O (3 x 20 mL). The solution was acidified to pH 4 by addition of aqueous 1M HCl and extracted with Et₂O (3 x 30 mL). The combined organic layers were washed with water and brine, dried (MgSO₄) and filtered. The organic solvent was removed *in vacuo* to yield **S-I** as a white solid (1.75 g, 91 yield).

¹H NMR (400 MHz, CDCl₃) δ 7.34-7.26 (m, 5H, CH Ph), 3.68 (t, 1H, *J*_{HH} = 7.8 Hz, PhCHCOOH), 1.98 (ddd, 1H, *J*_{HH} = 13.6 Hz, 7.9 Hz, 7.4 Hz, CH₂CH(CH₃)₂), 1.72 (ddd, 1H, *J*_{HH} = 13.6 Hz, 7.7 Hz, 6.7 Hz, CH₂CH(CH₃)₂), 1.56-1.46 (m, 1H, CH(CH₃)₂), 0.93 (d, 6H, *J*_{HH} = 6.6 Hz, CH(CH₃)₂), 0.92 (s, 3H, CH(CH₃)₂).

¹³C NMR (101 MHz, CDCl₃) δ 179.3 (COOH), 138.6 (C_{quat} Ph), 128.7 (*o*- or *m*-CH Ph), 128.1 (*o*- or *m*-CH Ph), 127.4 (*p*-CH Ph), 49.3 (PhCHCOOH), 42.0 (CH₂CH(CH₃)₂), 25.7 (CH₂CH(CH₃)₂), 22.6+22.2 (CH₂CH(CH₃)₂).

Synthesis of S-III: ^[15]

A solution of **S-I** (1.25g, 6.48 mmol, 1.0 equiv.) in dry dichloromethane (25 mL) was cooled to 0°C and oxalyl chloride (0.61 mL, 7.13 mmol, 1.1 equiv.) was added dropwise. The cooling bath was removed and the mixture was stirred at room temp. for 1.5 h. The solution was concentrated *in vacuo* and the solid residue was used without further purification.

The crude acyl chloride (6.48 mmol, 1.0 equiv.) was dissolved in dry dichloromethane (4 mL), and this solution was added over 1 h to a stirred solution of Meldrum's acid (935 mg, 6.48 mmol, 1.0 equiv.) and pyridine (1.3 mL, 16.2 mmol, 2.5 equiv.) in dry dichloromethane (12 mL) at 0°C. The temperature was maintained at 0°C for 1 h, then warmed to room temp. and stirred for 16 h. The reaction mixture was washed with aqueous 3M HCl (3 x 25 mL) then water (15 mL). The phases were separated, the organic phase was dried (MgSO₄), filtered and concentrated *in vacuo*. Crude **S-II** was dissolved in methanol (12 mL) and 5 drops of conc. H₂SO₄ were added. The mixture was heated at reflux temperature for 4 h, then the solvent was evaporated *in vacuo*. The crude residue was purified by column chromatography on silicagel (eluent: petroleum ether/ethyl acetate 10:1) to give **S-III** as a colorless oil (0.95 g, 60 % yield).

HRMS (DCI-CH₄) *m/z*: [M+H]⁺ calcd for C₁₅H₂₁O₃ 249.1491, found: 249.1494;

¹H NMR (300 MHz, CDCl₃) δ 7.38-7.21 (m, 5H, CH Ph), 3.89 (dd, *J* = 8.2 Hz, 6.7 Hz, 1H, PhCHC(O)), 3.72+3.68 (s, 3H, CO₂CH₃, enol+keto forms), 3.45 (d, AB syst., *J* = 15.5 Hz, 1H, C(O)CH₂CO₂Me), 3.32 (d, AB syst., *J* = 15.5 Hz, 1H, C(O)CH₂CO₂Me), 1.94 (ddd, 1H, *J*_{HH} = 13.8 Hz, 8.0 Hz, 6.7 Hz, CH₂CH(CH₃)₂), 1.66 (ddd, 1H, *J*_{HH} = 14.0 Hz, 8.2 Hz, 6.0 Hz, CH₂CH(CH₃)₂), 1.46-1.37 (m, 1H, CH(CH₃)₂), 0.91 (d, *J* = 6.6 Hz, 3H, CH(CH₃)₂), 0.89 (d, *J* = 6.6 Hz, 3H, CH(CH₃)₂).

^{13}C NMR (75.5 MHz, CDCl_3) δ 202.4 ($\text{CHC}(\text{O})\text{CH}_2$), 167.6 ($\text{CH}_2\text{CO}_2\text{CH}_3$), 138.1 (C_{quat} Ph), 129.1 (σ - or m -CH Ph), 128.5 (σ - or m -CH Ph), 127.6 (p -CH Ph), 56.9 ($\text{CH}_2\text{CO}_2\text{CH}_3$), 52.2 (CO_2CH_3), 47.8 ($\text{PhCHC}(\text{O})\text{CH}_2$), 40.6 ($\text{CH}_2\text{CH}(\text{CH}_3)_2$), 25.5 ($\text{CH}_2\text{CH}(\text{CH}_3)_2$), 22.9+22.1 ($\text{CH}_2\text{CH}(\text{CH}_3)_2$).

Synthesis of diazo substrate (5):

S-III (376 mg, 1.51 mmol, 1.0 equiv.) was placed in dry acetonitrile (5 mL) and cooled to 0°C . 4-acetobenzenesulfonyl azide (p -ABSA, 382 mg, 1.59 mmol, 1.05 equiv.) was added, then N,N -diisopropylethylamine (DIPEA, 0.4 mL, 2.30 mmol, 1.5 equiv.). The reaction mixture was warmed to room temperature and stirred for 3 h, then filtered. The precipitate was washed with dichloromethane, and the combined filtrate was concentrated in vacuo. The crude residue was purified by column chromatography on silicagel (eluent: DCM) to give **5** as a pale-yellow oil (399 mg, 96 % yield).

R_f (DCM) 0.9;

HRMS (DCI- CH_4) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_3$ 275.1396, found: 275.1406;

^1H NMR (400 MHz, CDCl_3) δ 7.37-7.21 (m, 5H, CH Ph), 4.97 (t, $J = 7.6$ Hz, 1H, $\text{PhCHC}(\text{O})$), 3.81 (s, 3H, CO_2CH_3), 1.99 (dt, 1H, $J_{\text{HH}} = 13.5$ Hz, 7.6 Hz, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.68 (ddd, 1H, $J_{\text{HH}} = 13.7$ Hz, 7.4 Hz, 6.6 Hz, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.49-1.39 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 0.91 (d, $J = 6.6$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.88 (d, $J = 6.6$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$).

^{13}C NMR (101 MHz, CDCl_3) δ 193.1 ($\text{CHC}(\text{O})\text{C}(\text{N}_2)$), 161.6 ($\text{C}(\text{N}_2)\text{CO}_2\text{CH}_3$), 139.2 (C_{quat} Ph), 128.9 (σ - or m -CH Ph), 128.7 (σ - or m -CH Ph), 127.3 (p -CH Ph), 52.3 (CO_2CH_3), 50.9 ($\text{PhCHC}(\text{O})\text{C}(\text{N}_2)$), 42.6 ($\text{CH}_2\text{CH}(\text{CH}_3)_2$), 26.1 ($\text{CH}_2\text{CH}(\text{CH}_3)_2$), 22.9+22.5 ($\text{CH}_2\text{CH}(\text{CH}_3)_2$). $\text{C}(\text{N}_2)\text{CO}_2\text{CH}_3$ not detected: under CDCl_3 signal.

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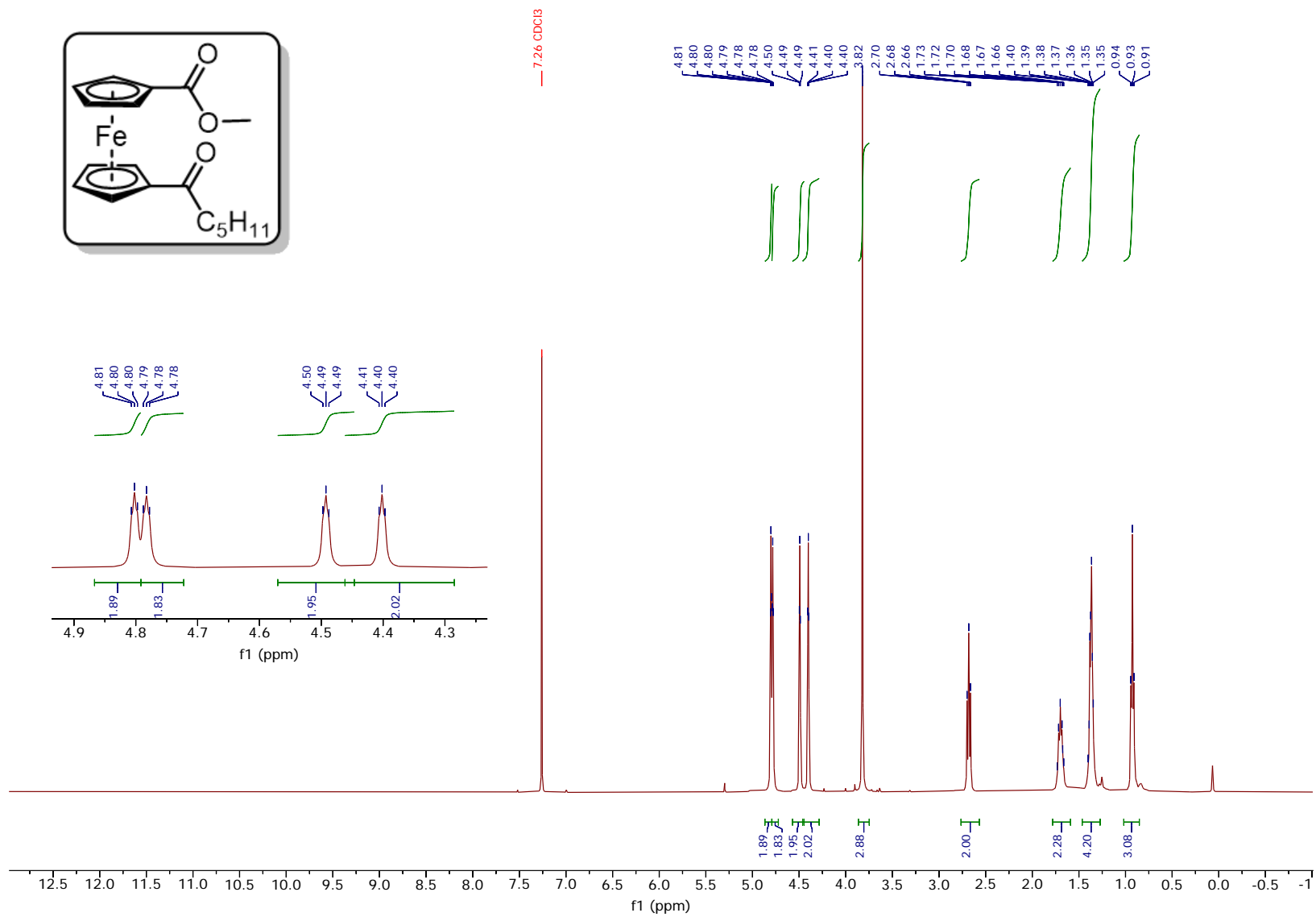


Figure S1. ^1H NMR of compound **I** in CDCl_3

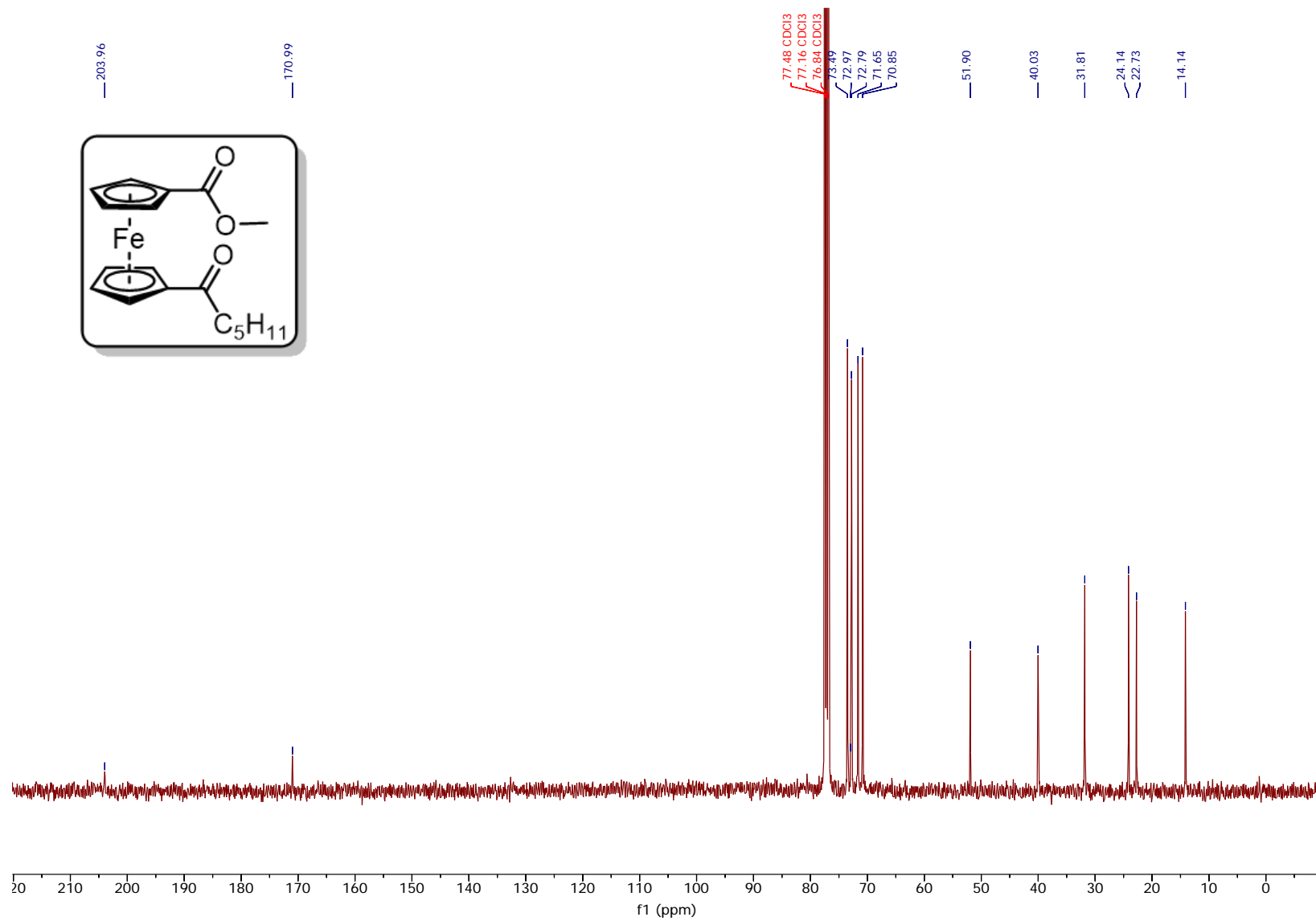


Figure S2. ^{13}C NMR of compound I in CDCl_3

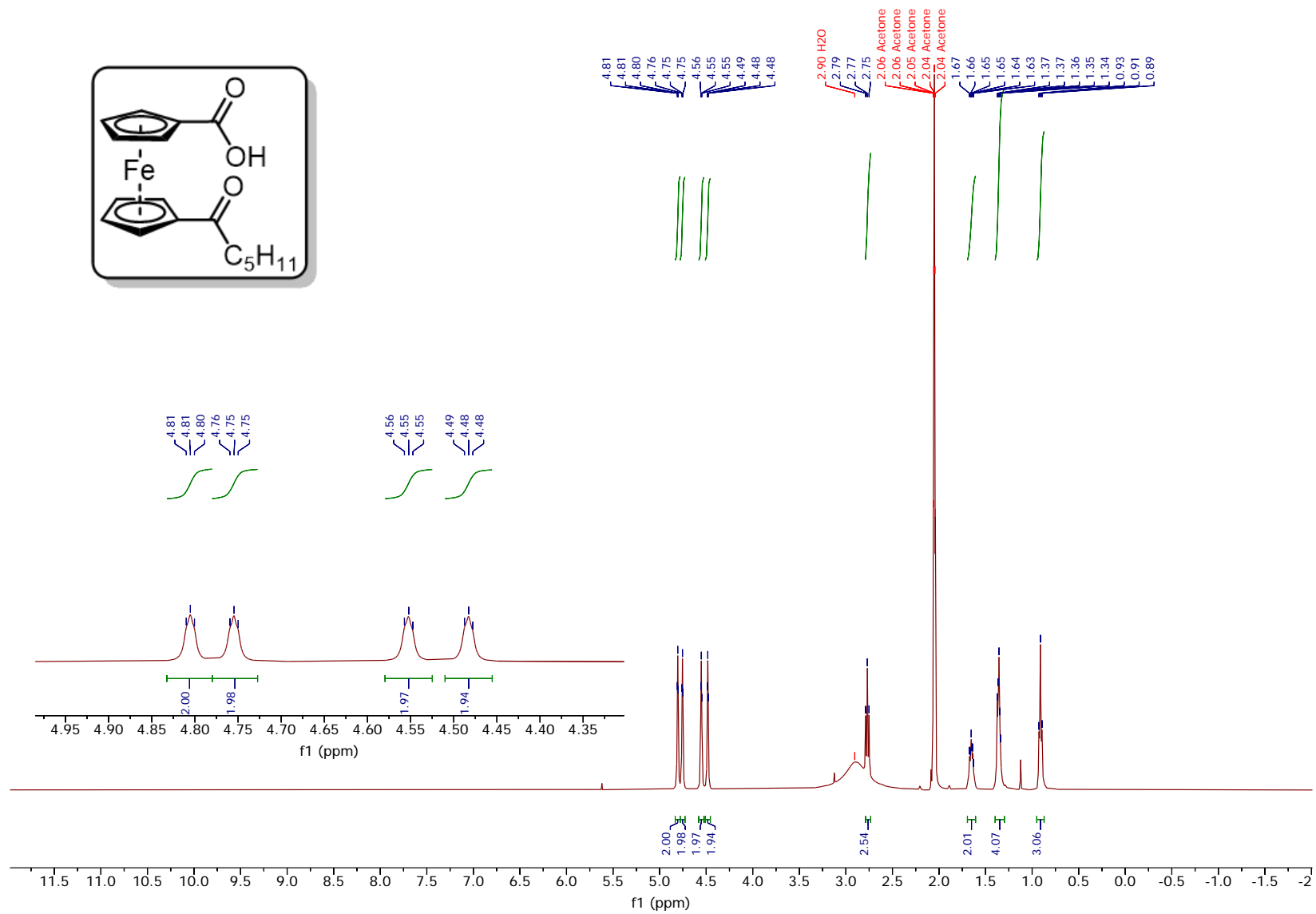


Figure S3. ^1H NMR of ligand **1b** in d_6 -acetone

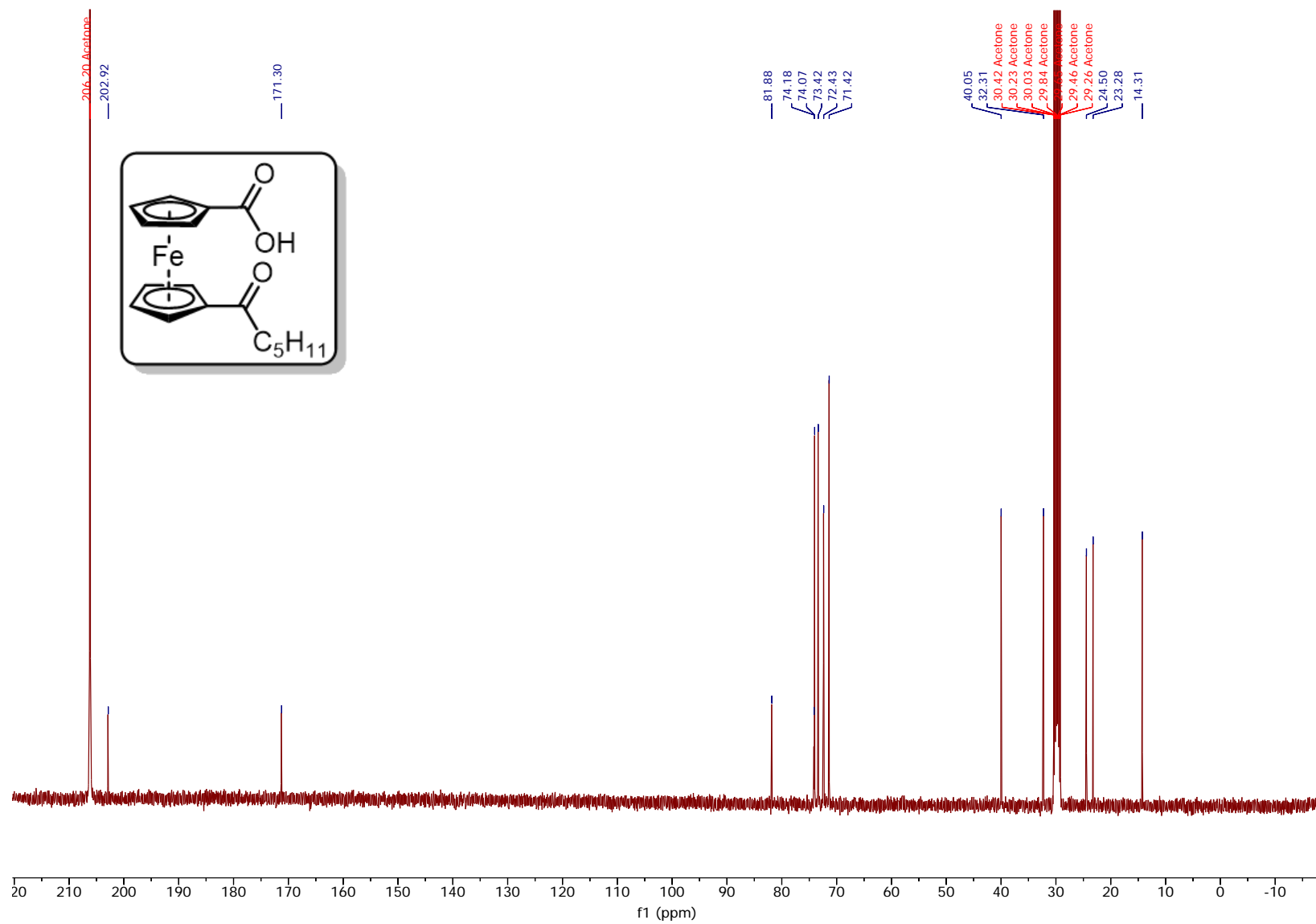


Figure S4. ^{13}C NMR of ligand **1b** in d_6 -acetone

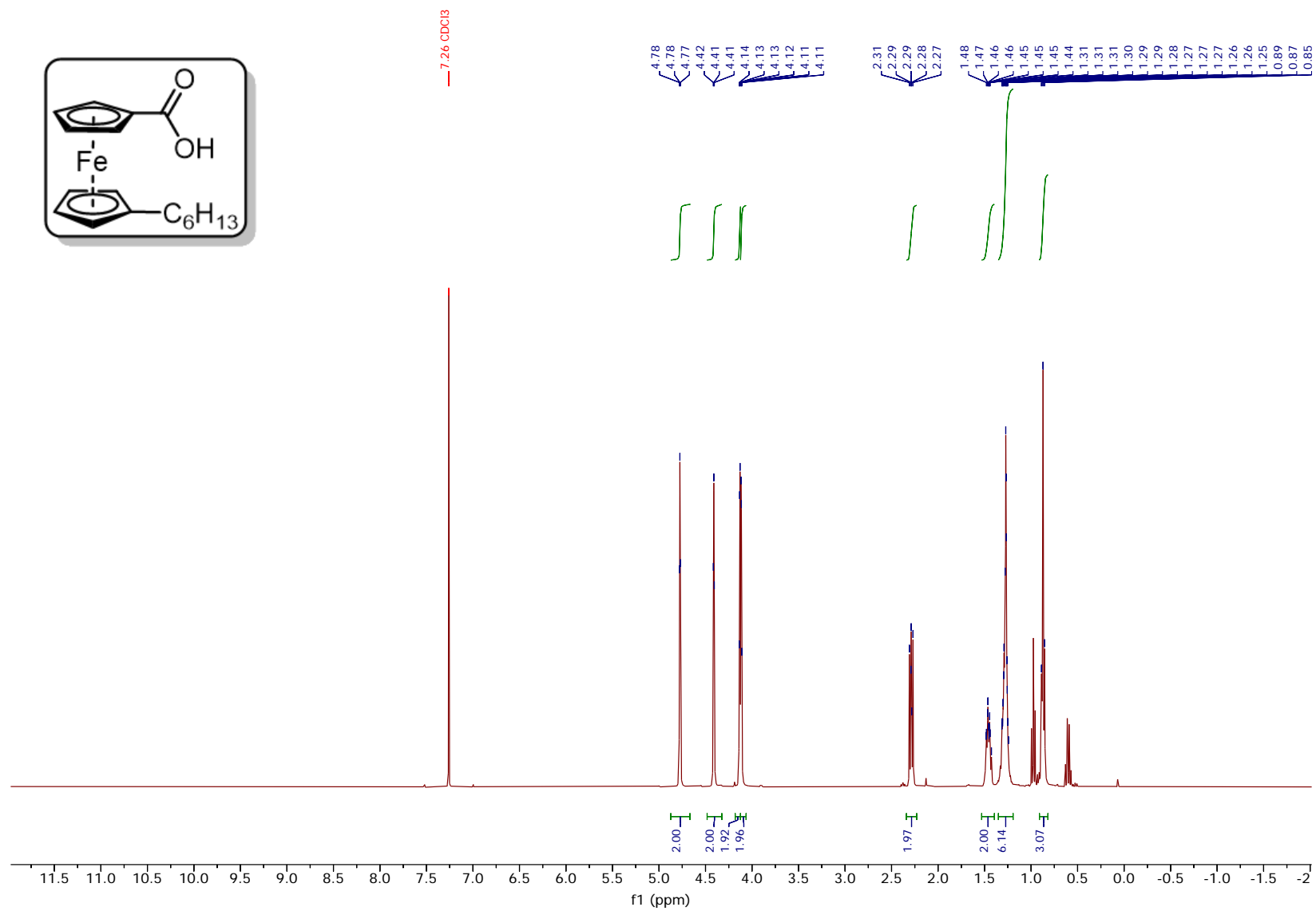


Figure S5. ¹H NMR of ligand **1c** in CDCl₃

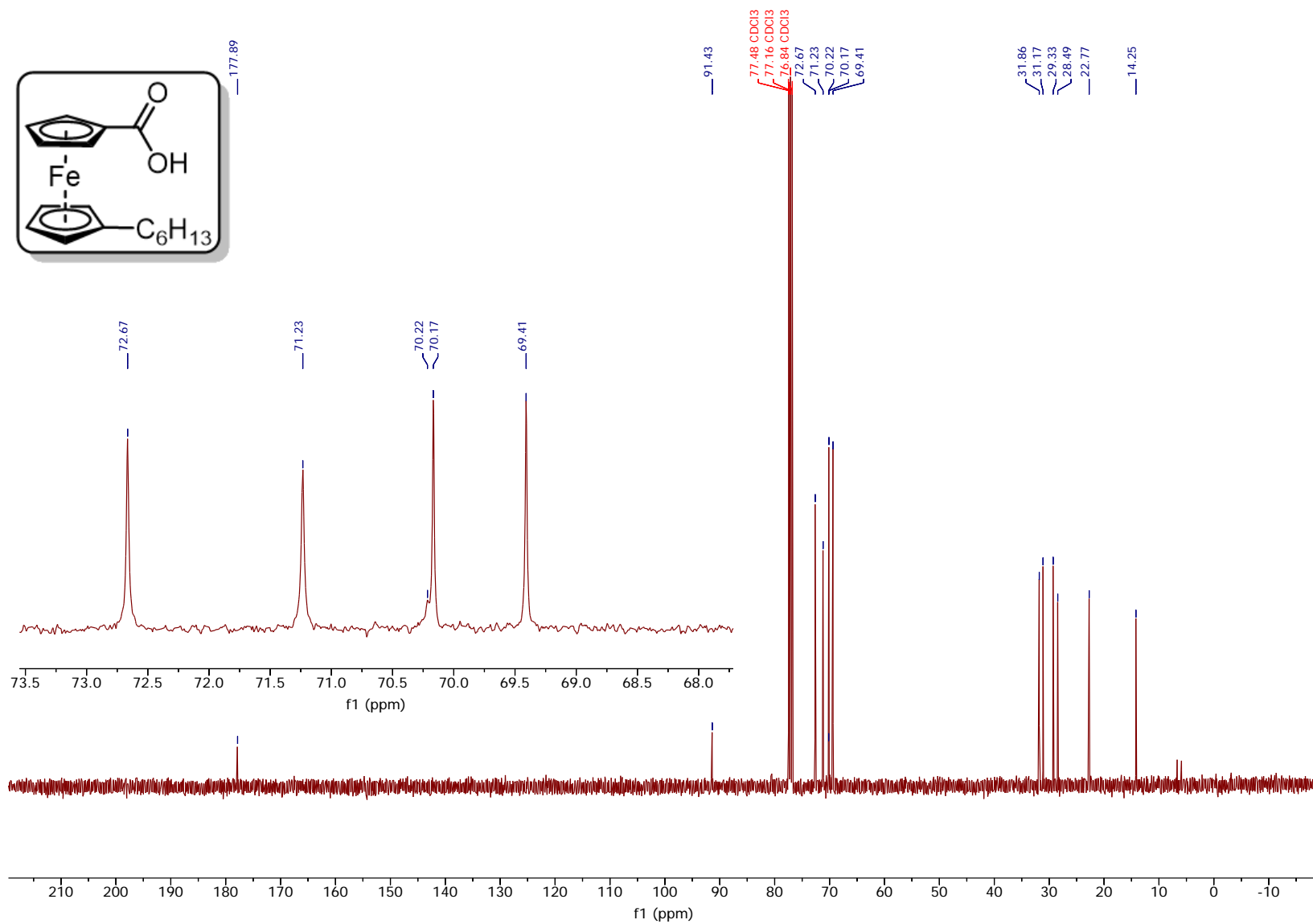


Figure S6. ^{13}C NMR of ligand **1c** in CDCl_3

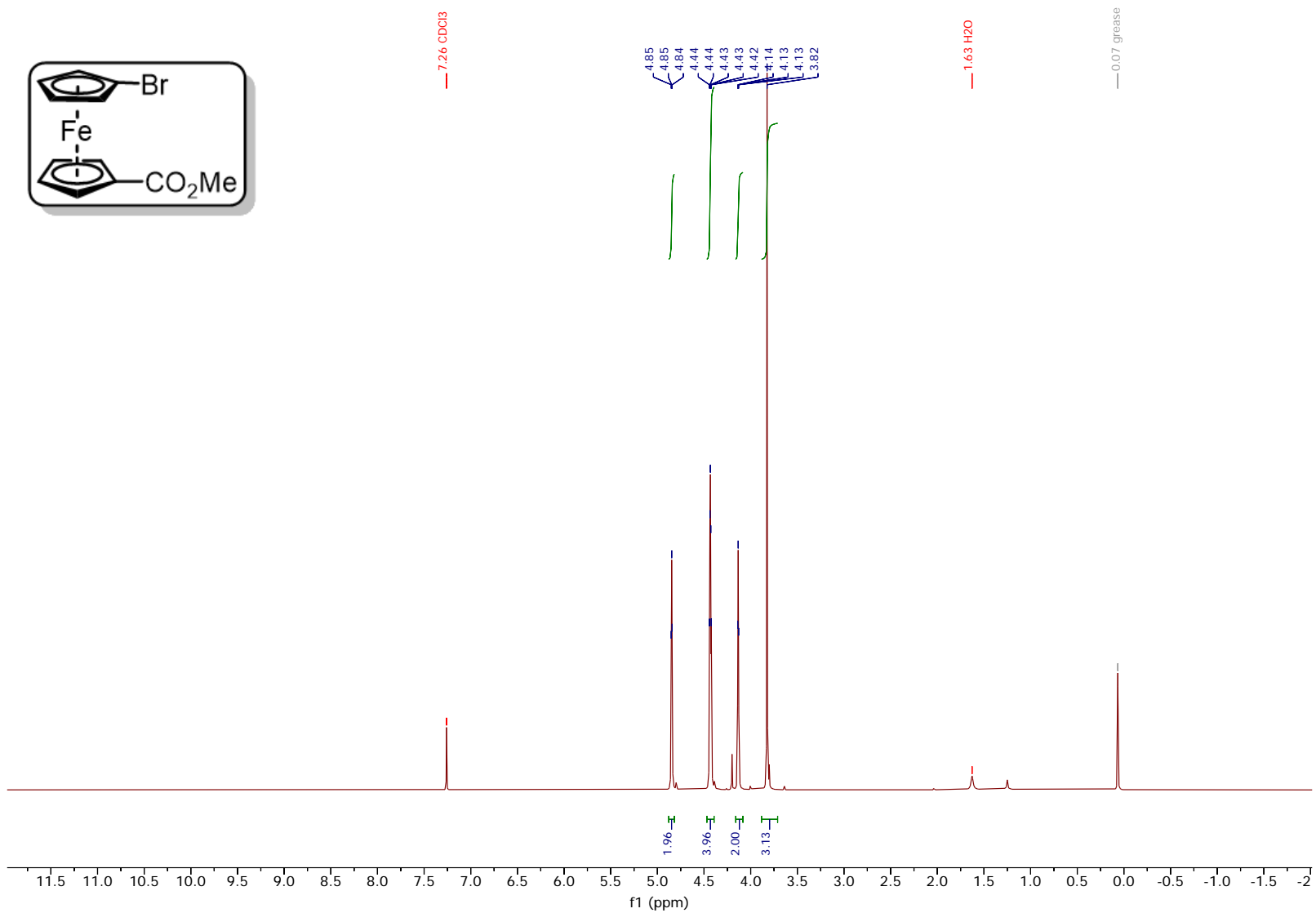


Figure S7. ^1H NMR of compound II in CDCl_3

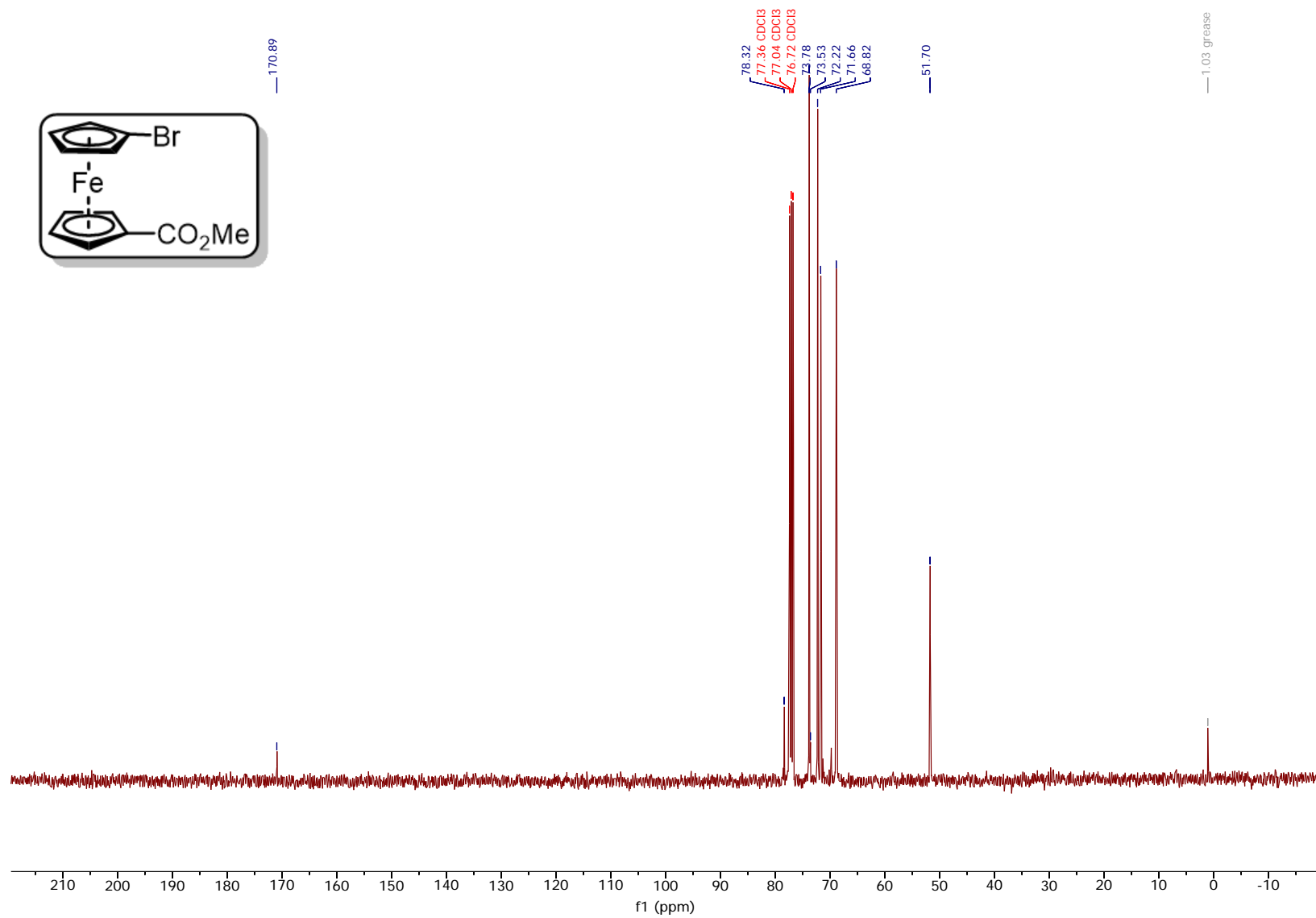


Figure S8. ^{13}C NMR of compound II in CDCl_3

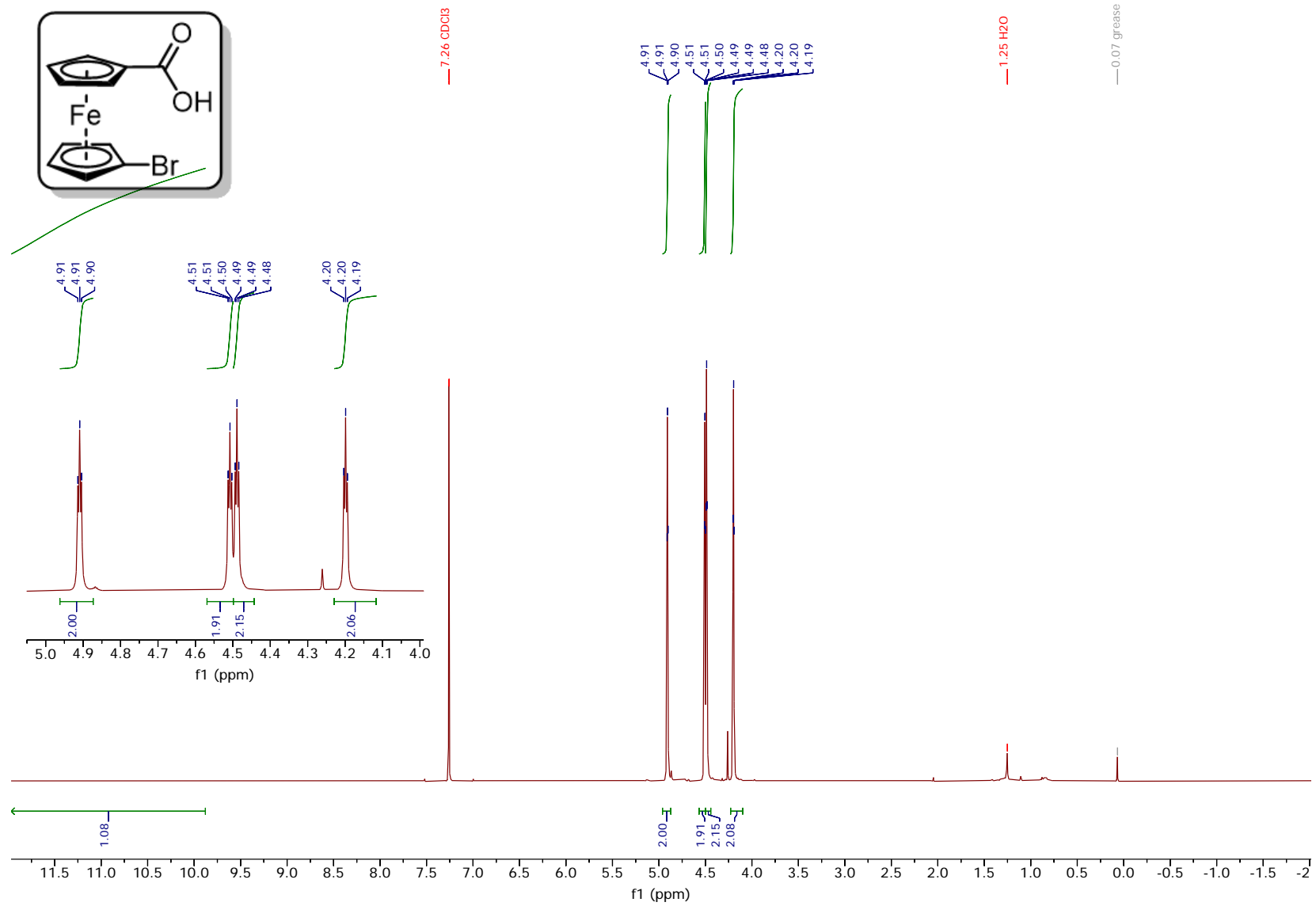


Figure S9. ^1H NMR of ligand **1d** in CDCl_3

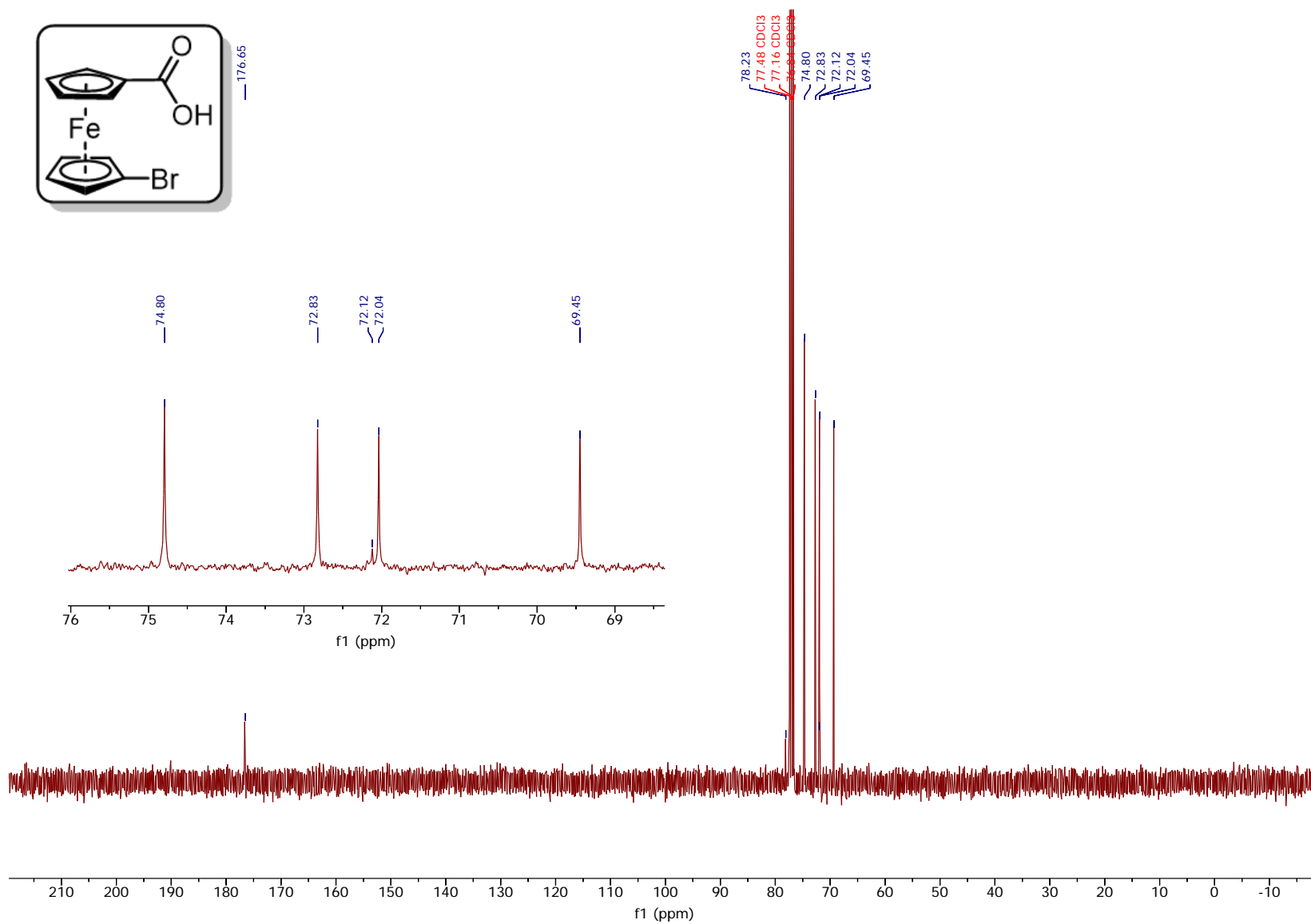


Figure S10. ^{13}C NMR of ligand **1d** in CDCl_3

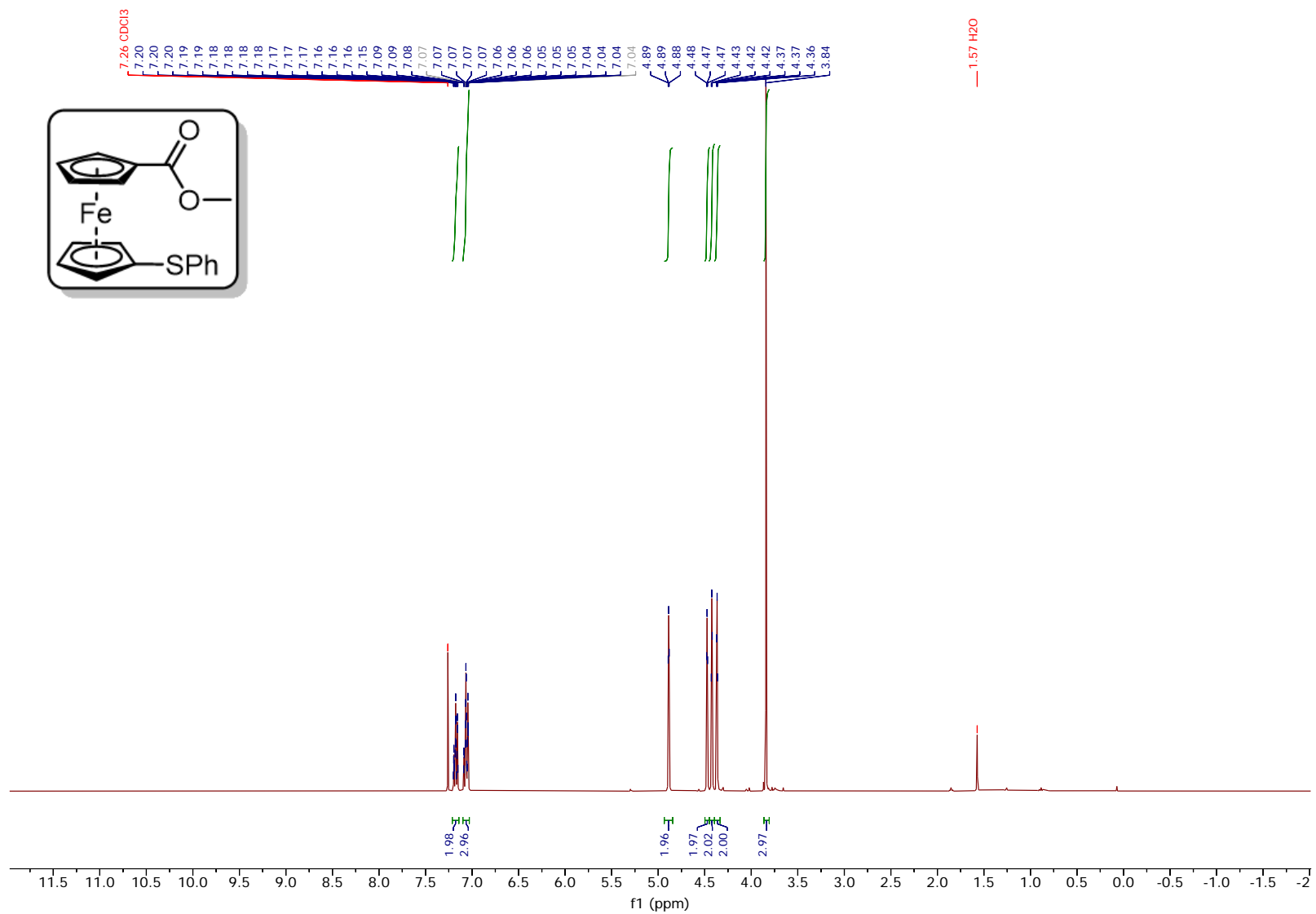


Figure S11. ¹H NMR of compound III in CDCl₃

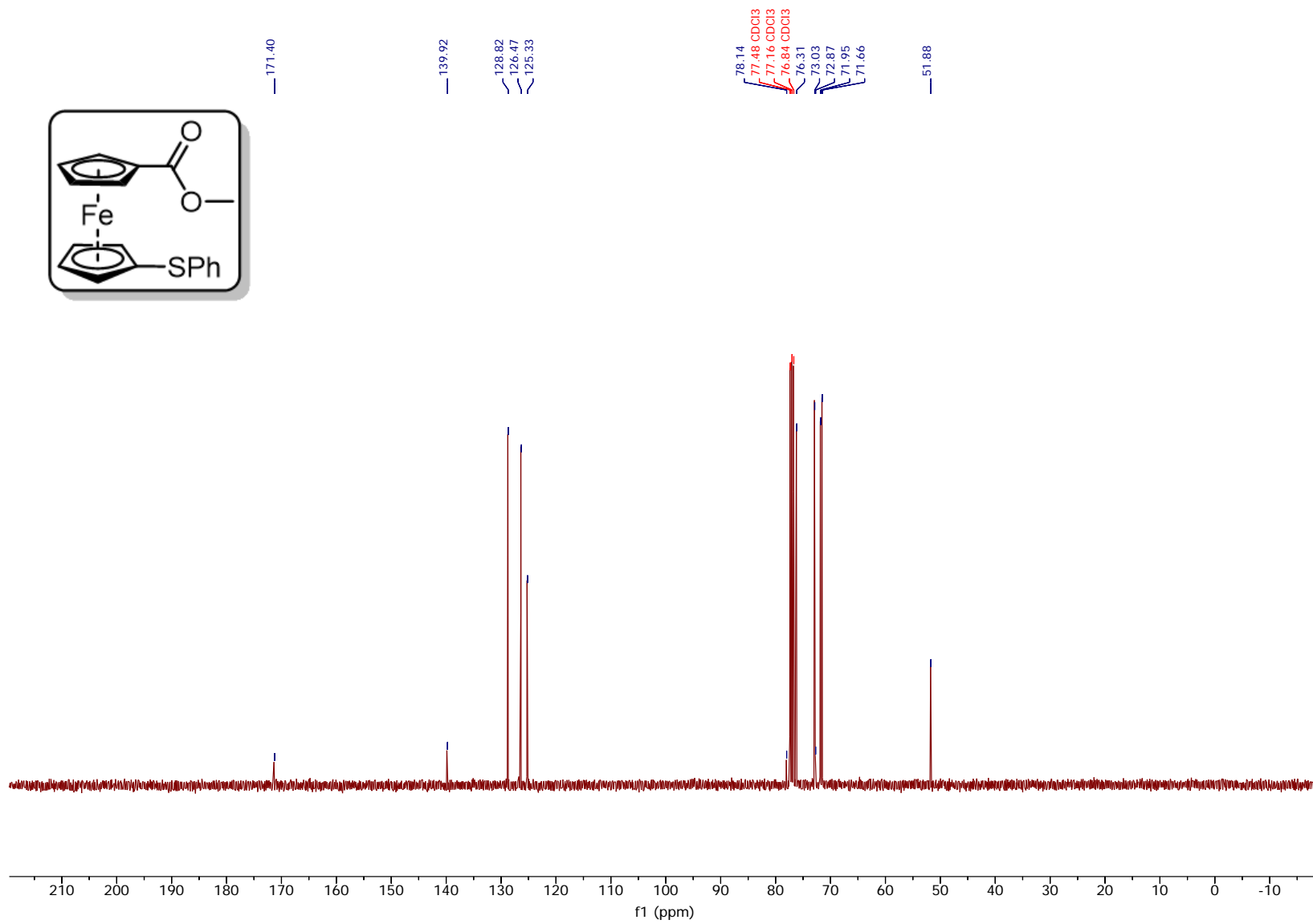


Figure S12. ^{13}C NMR of compound III in CDCl_3

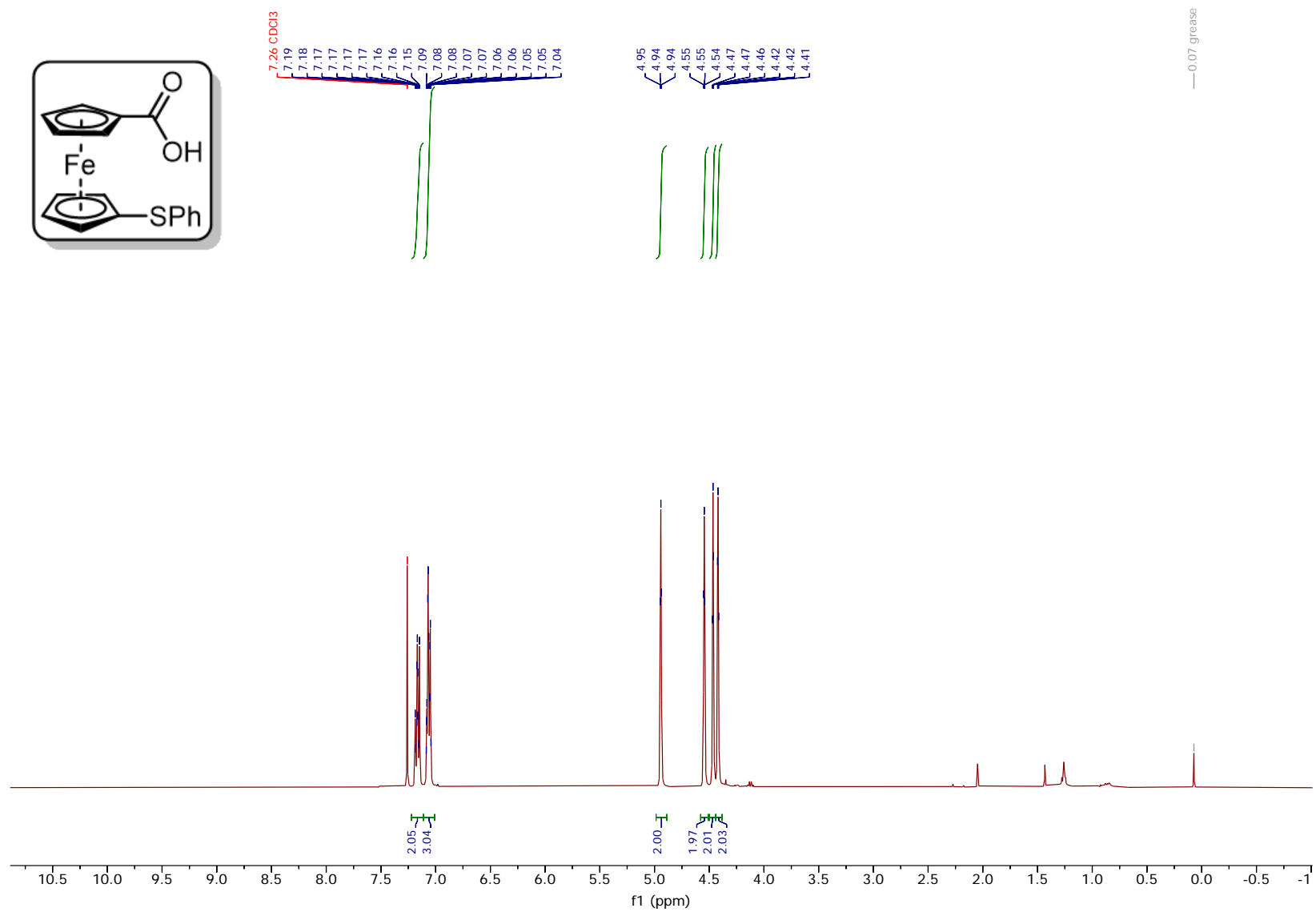


Figure S13. ¹H NMR of ligand **1e** in CDCl₃

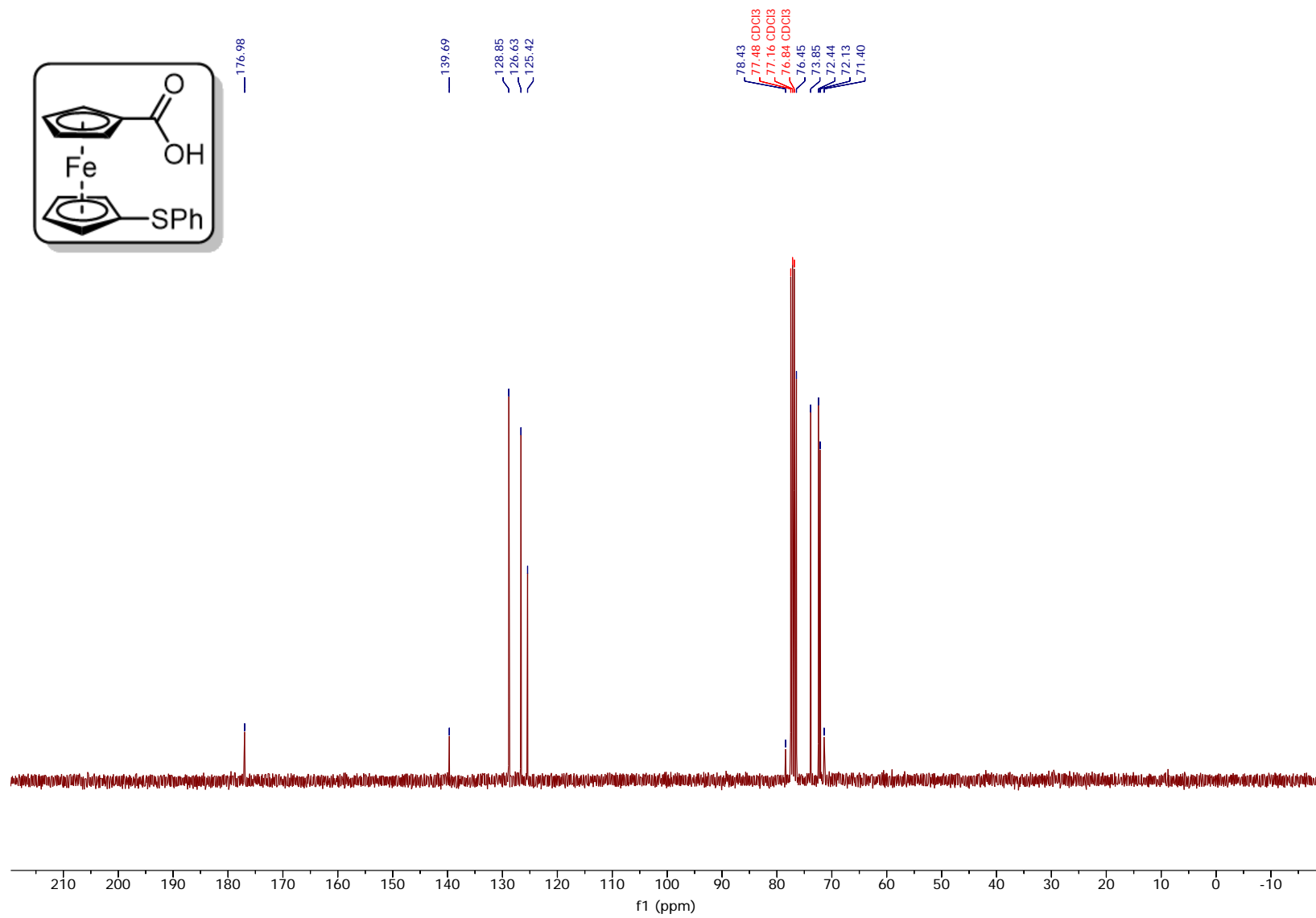


Figure S14. ^{13}C NMR of ligand **1e** in CDCl_3

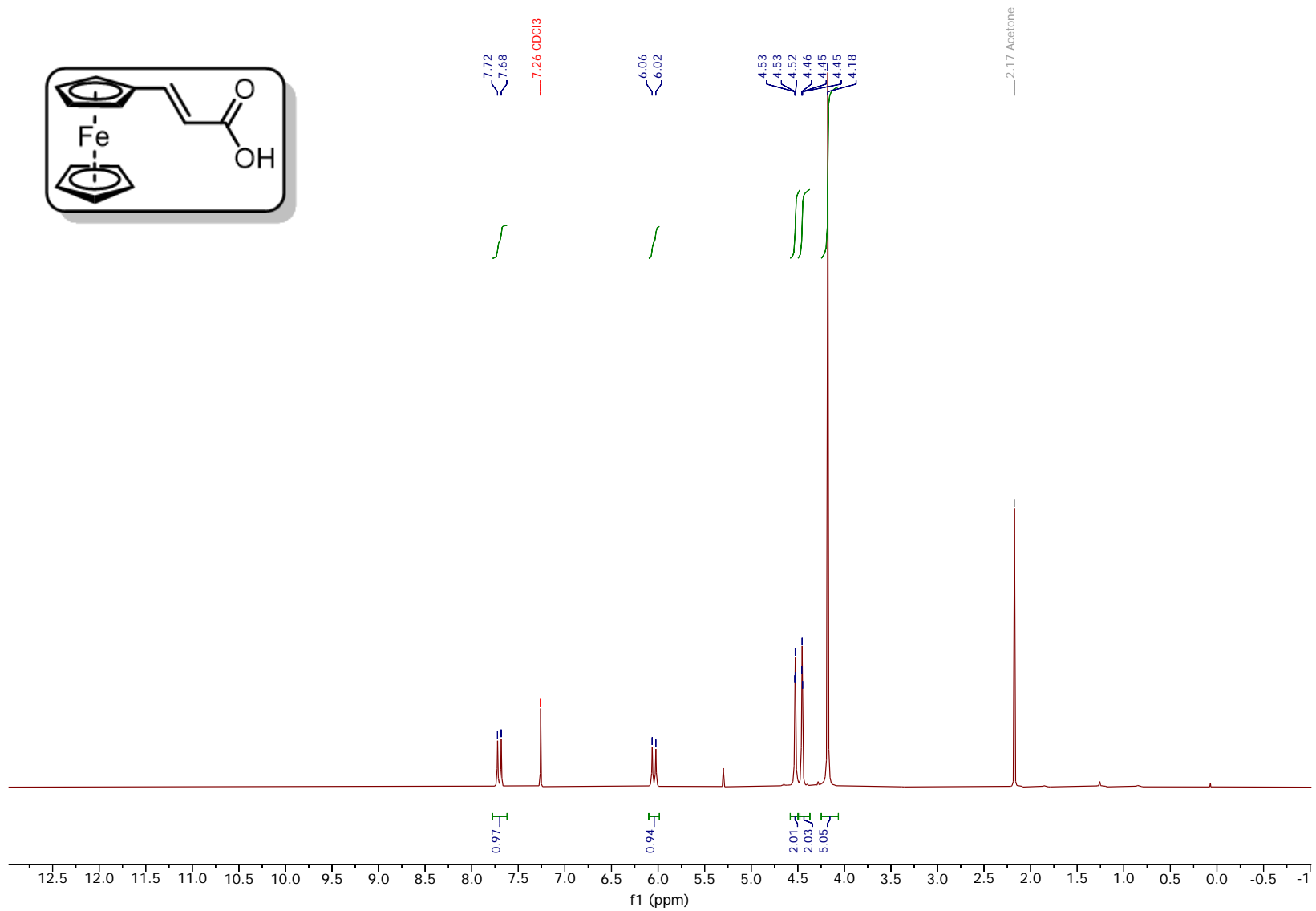


Figure S15. ¹H NMR of ligand **1f** in CDCl₃

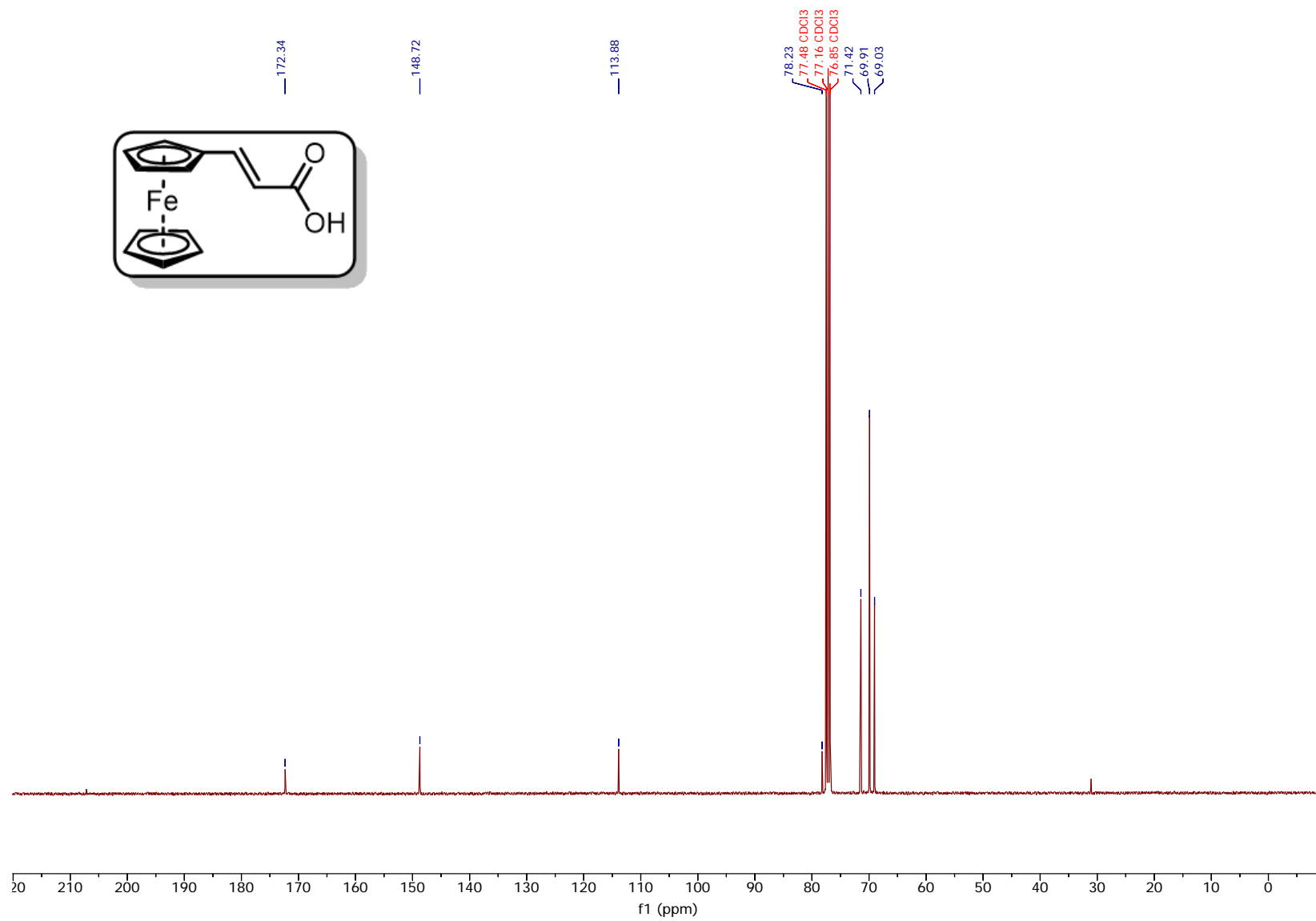


Figure S16. ^{13}C NMR of ligand **1f** in CDCl_3

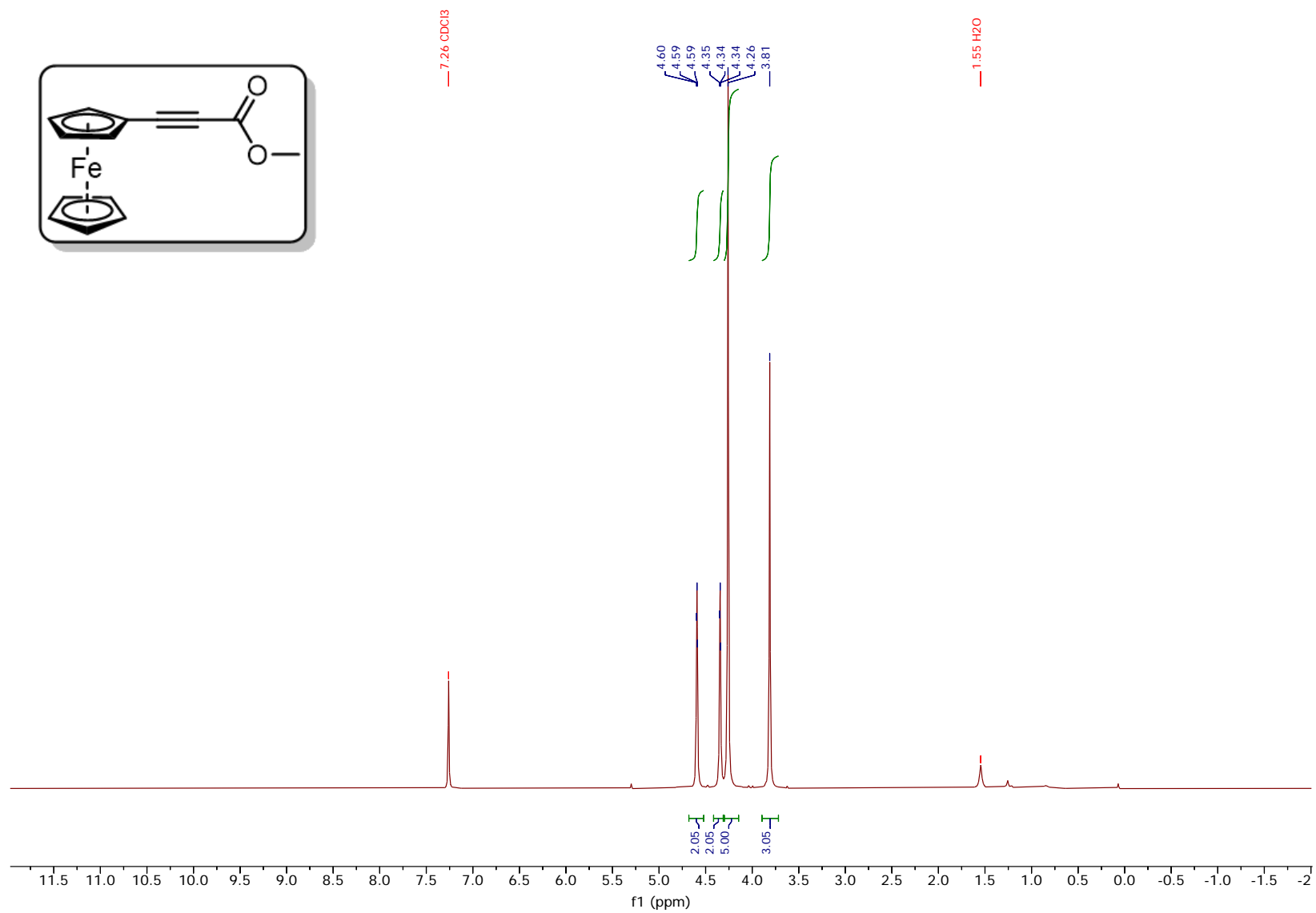


Figure S17. ¹H NMR of compound IV in CDCl₃

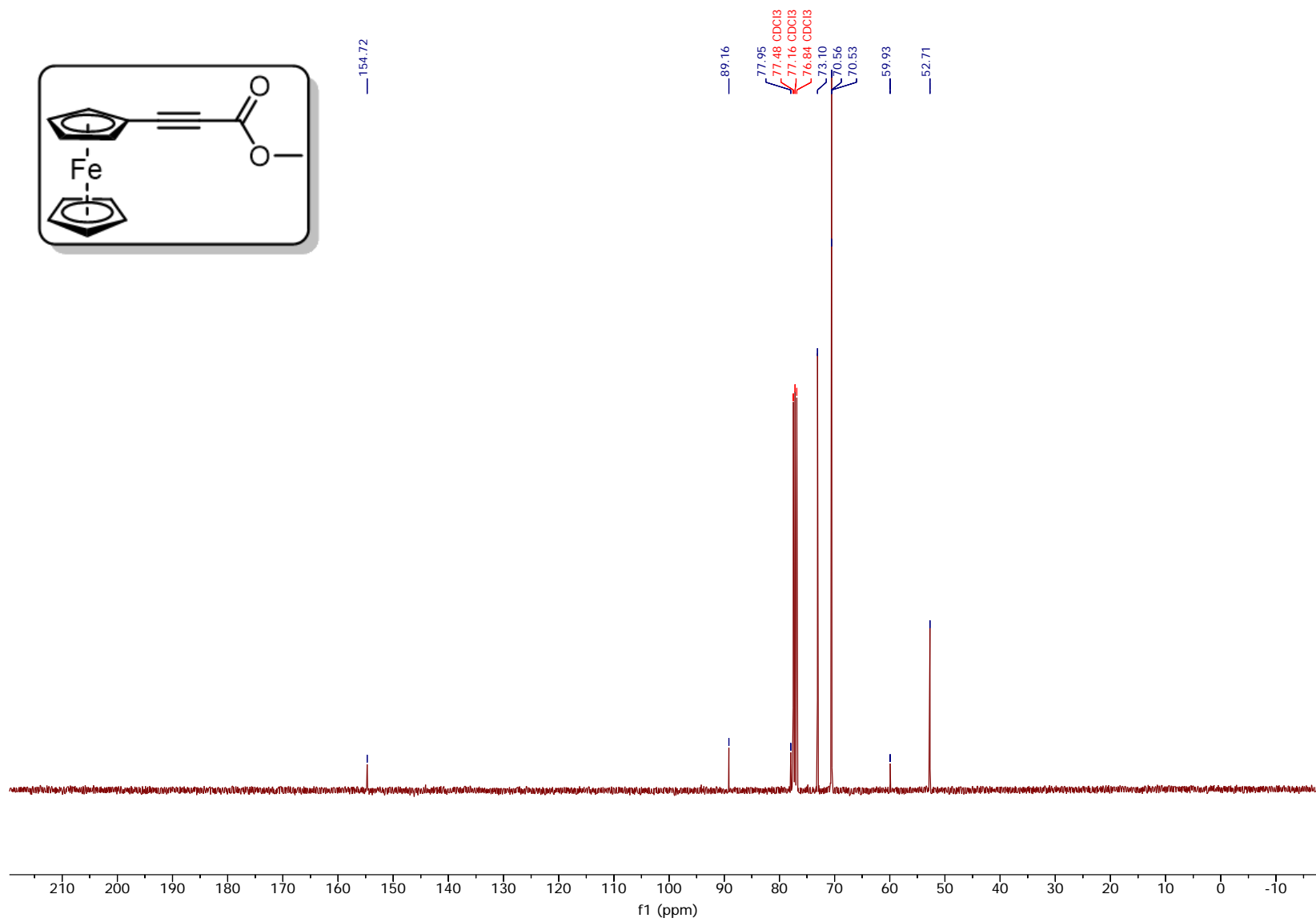


Figure S18. ^{13}C NMR of compound IV in CDCl_3

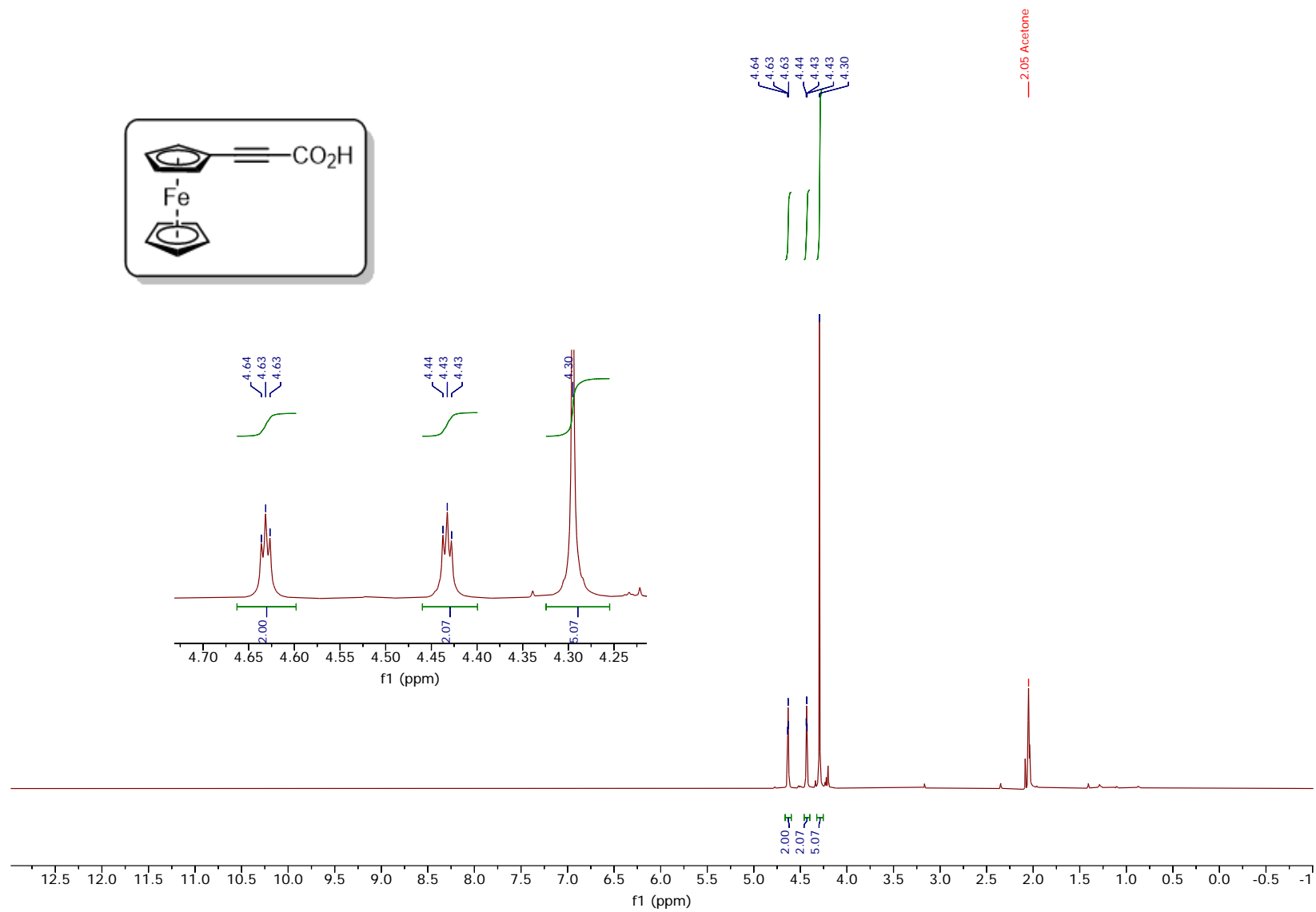


Figure S19. ^1H NMR of ligand **1g** in d_6 -acetone

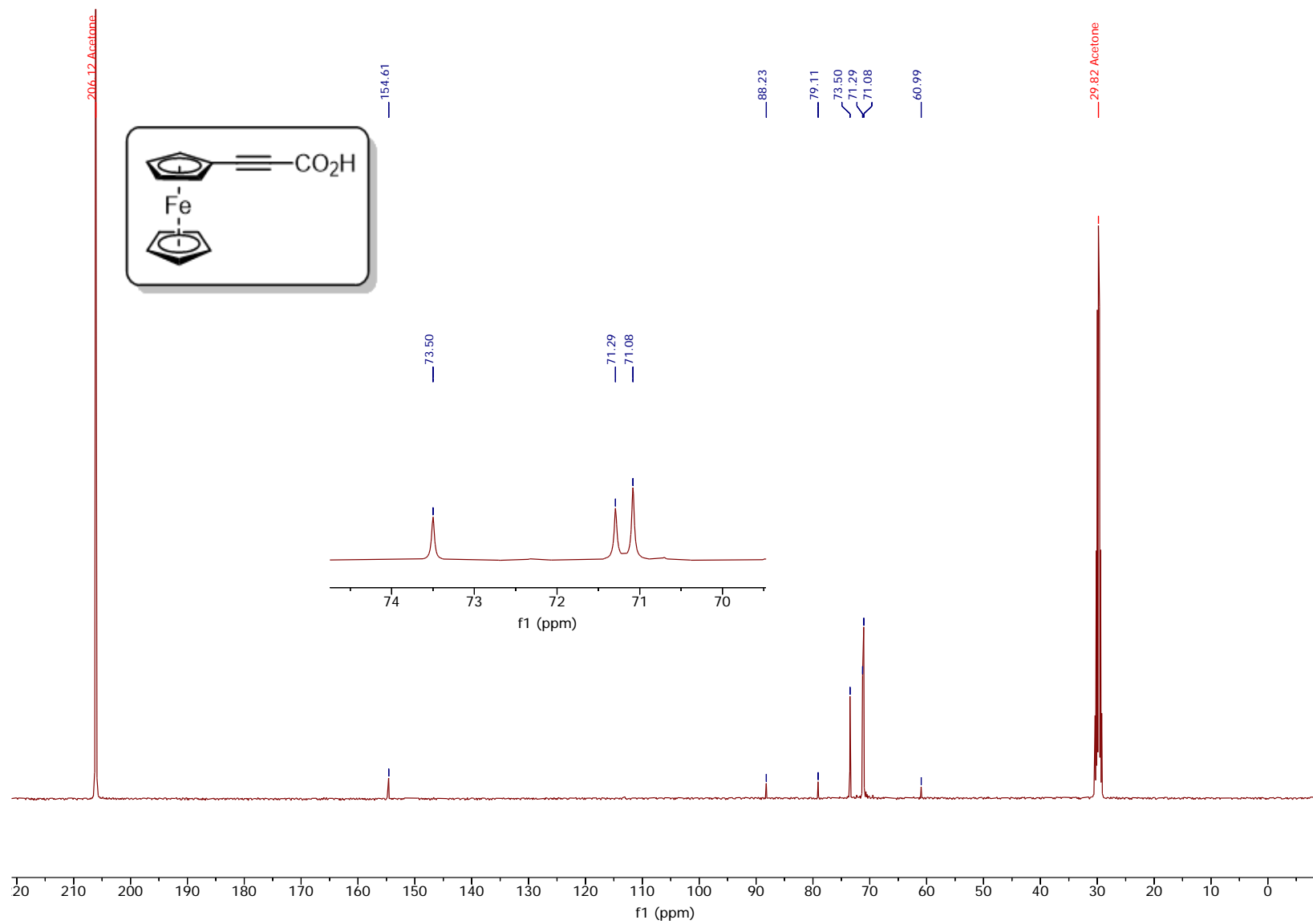


Figure S20. ^{13}C NMR of ligand **1g** in d_6 -acetone

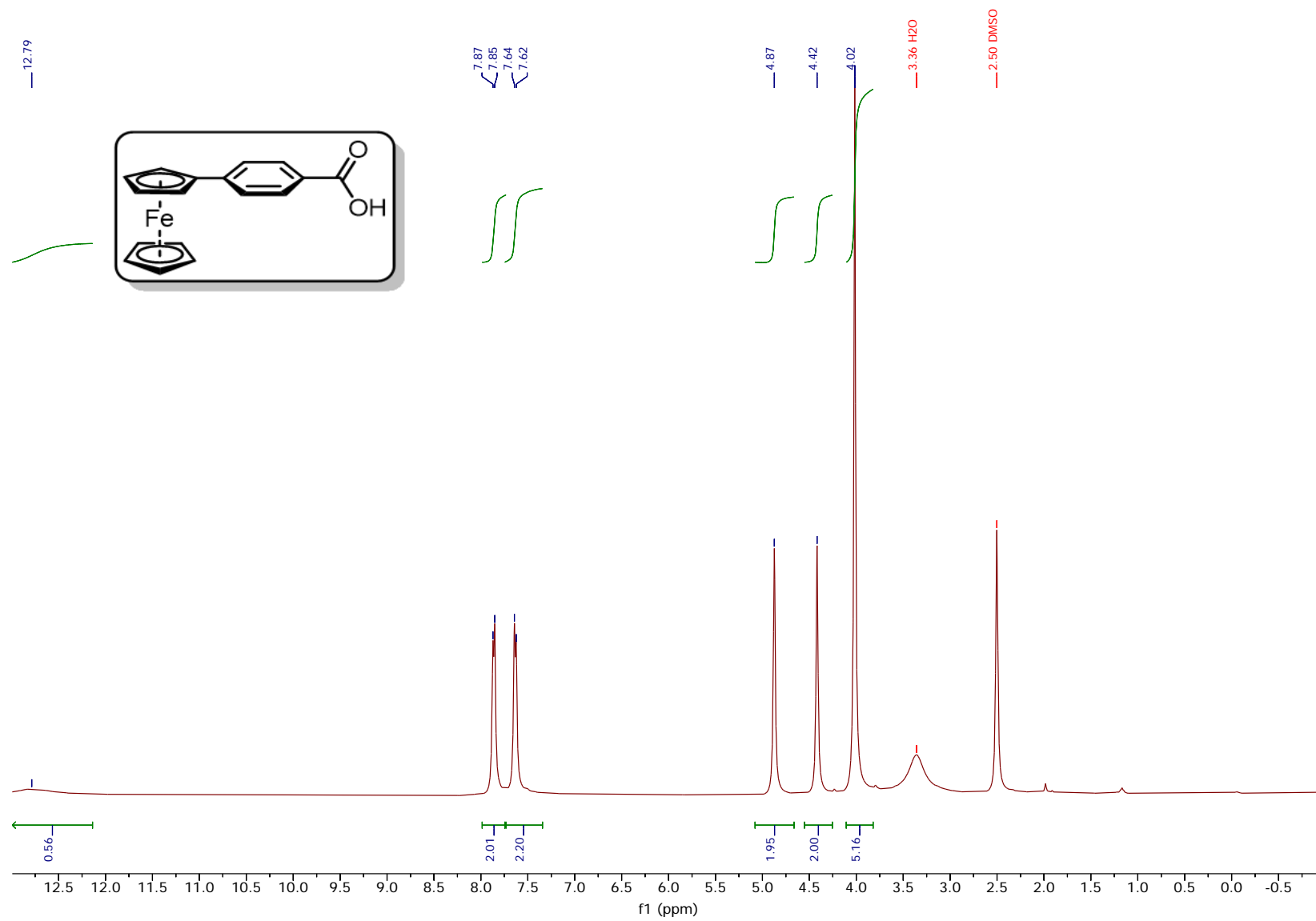


Figure S21. ¹H NMR of ligand **1h** in *d*₆-DMSO

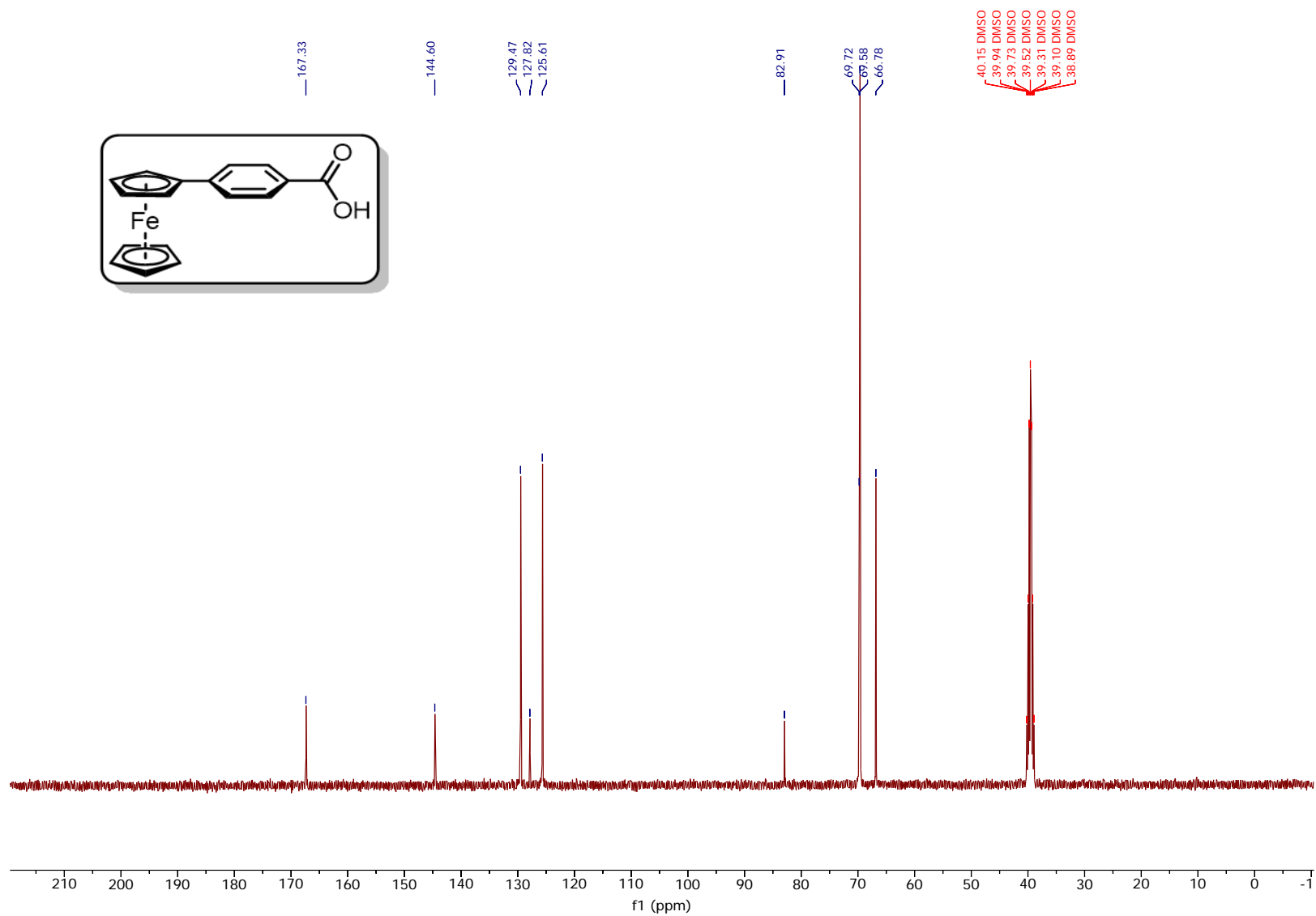


Figure S22. ^{13}C NMR of ligand **1h** in d_6 -DMSO

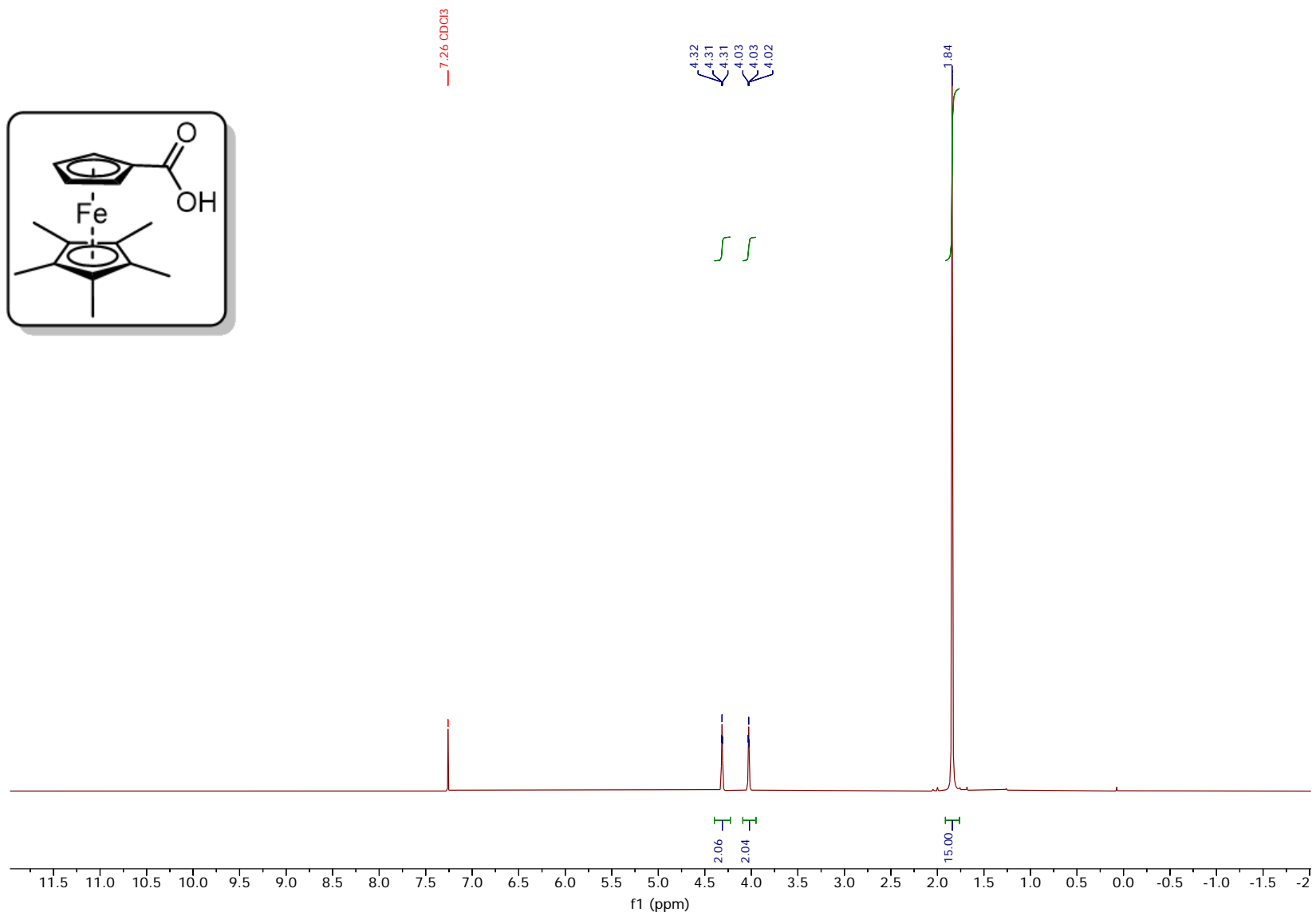


Figure S23. ^1H NMR of ligand **1i** in CDCl_3

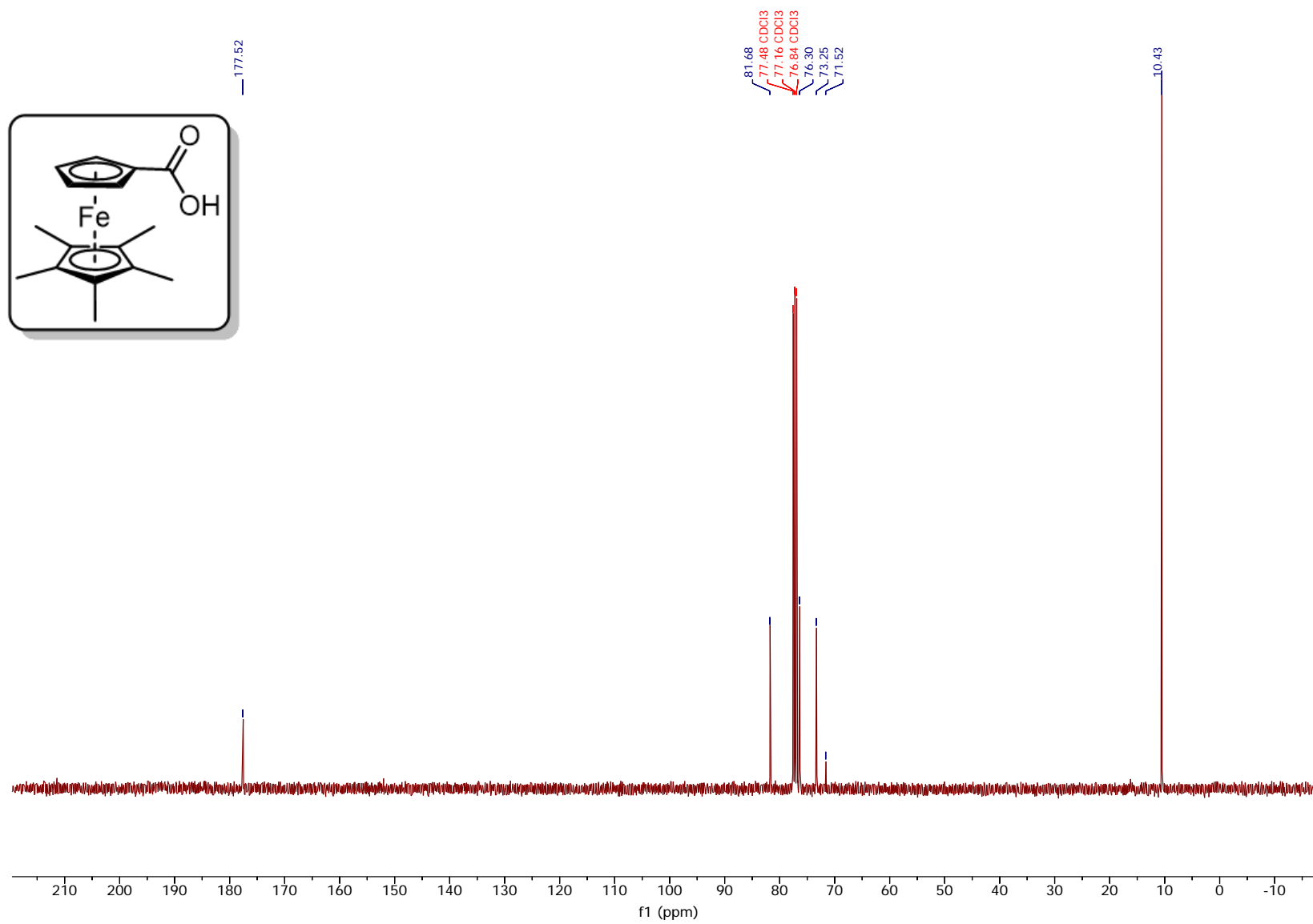


Figure S24. ^{13}C NMR of ligand **1i** in CDCl_3

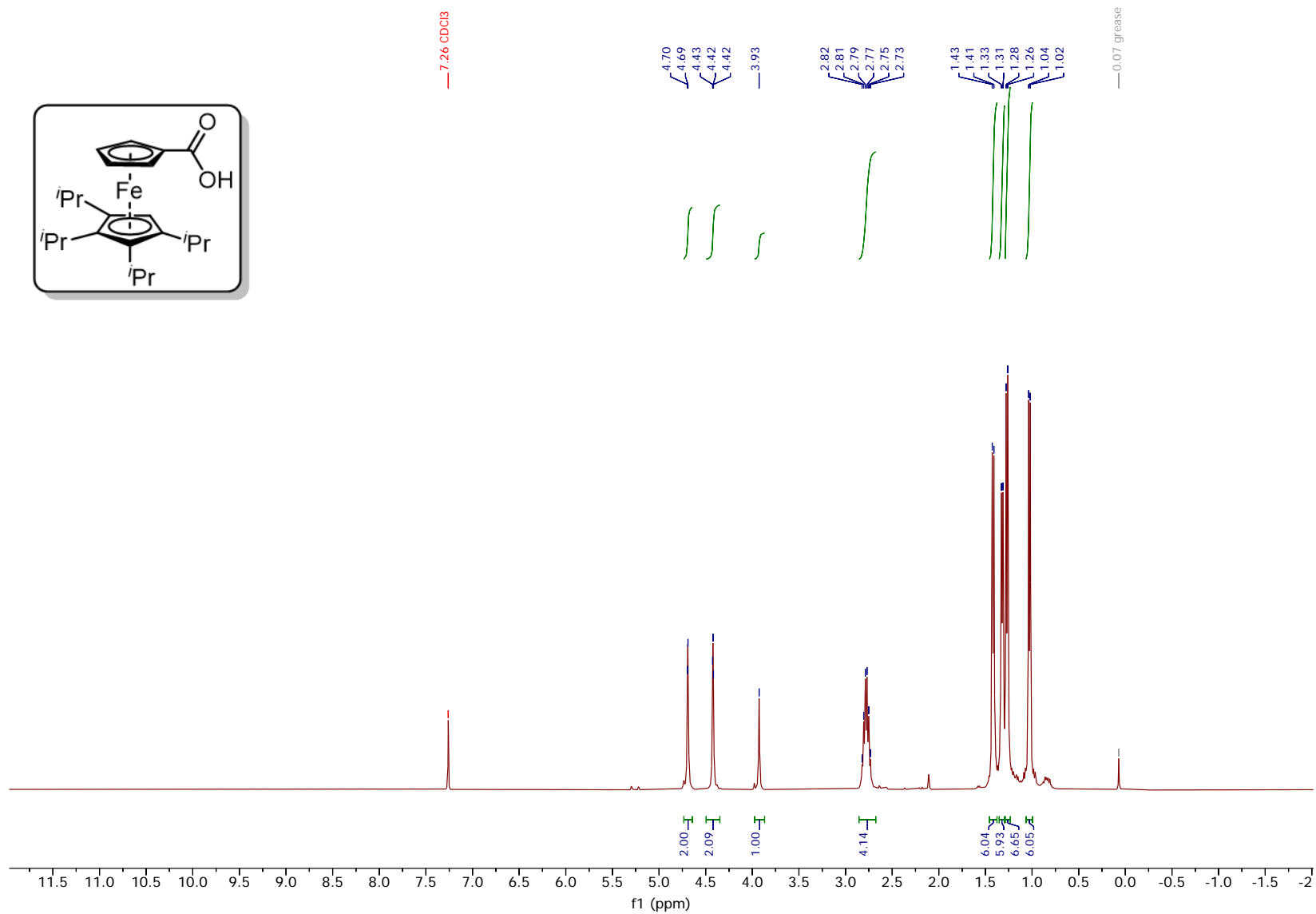


Figure S25. ^1H NMR of ligand **1j** in CDCl_3

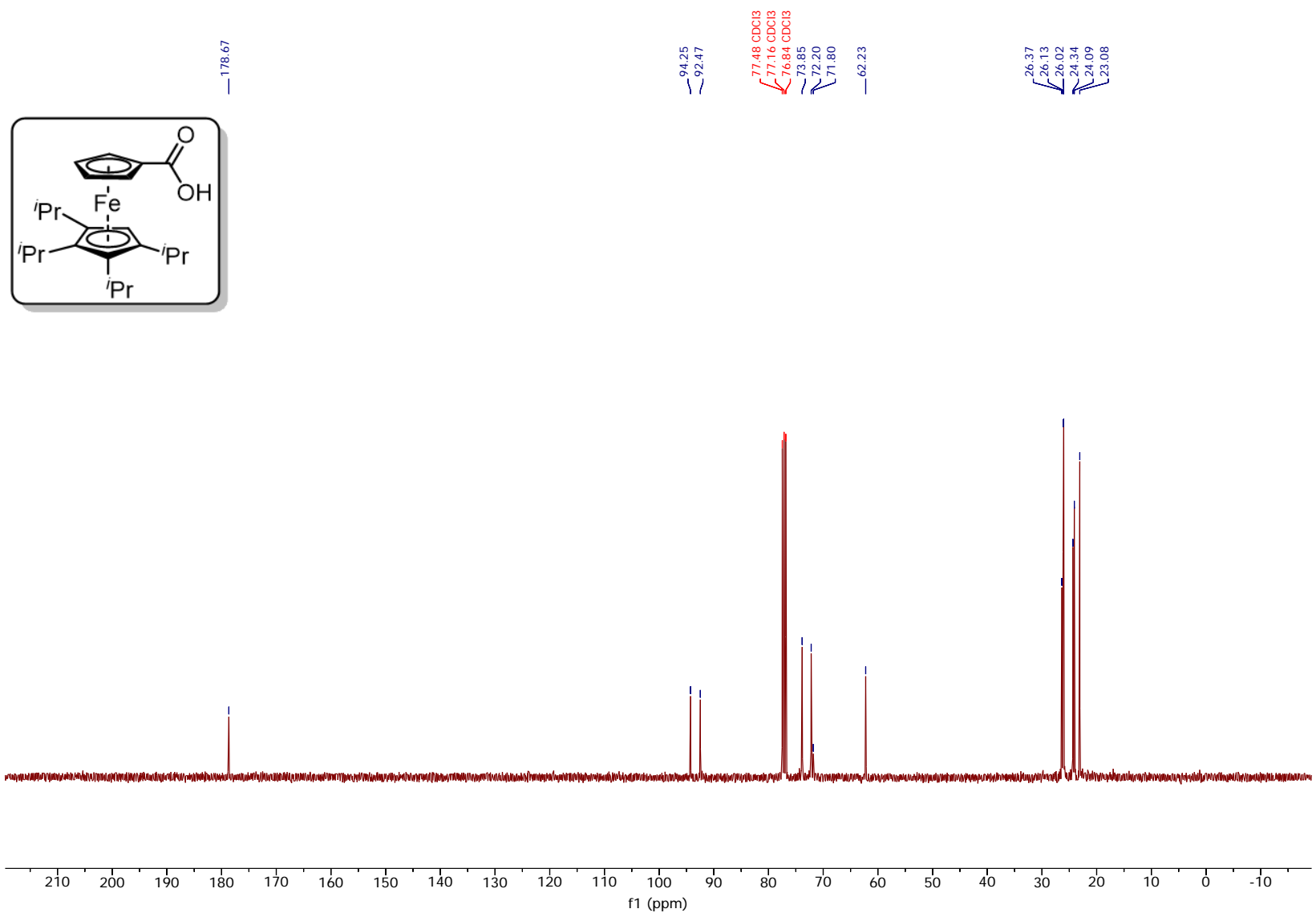


Figure S26. ^{13}C NMR of ligand **1j** in CDCl_3

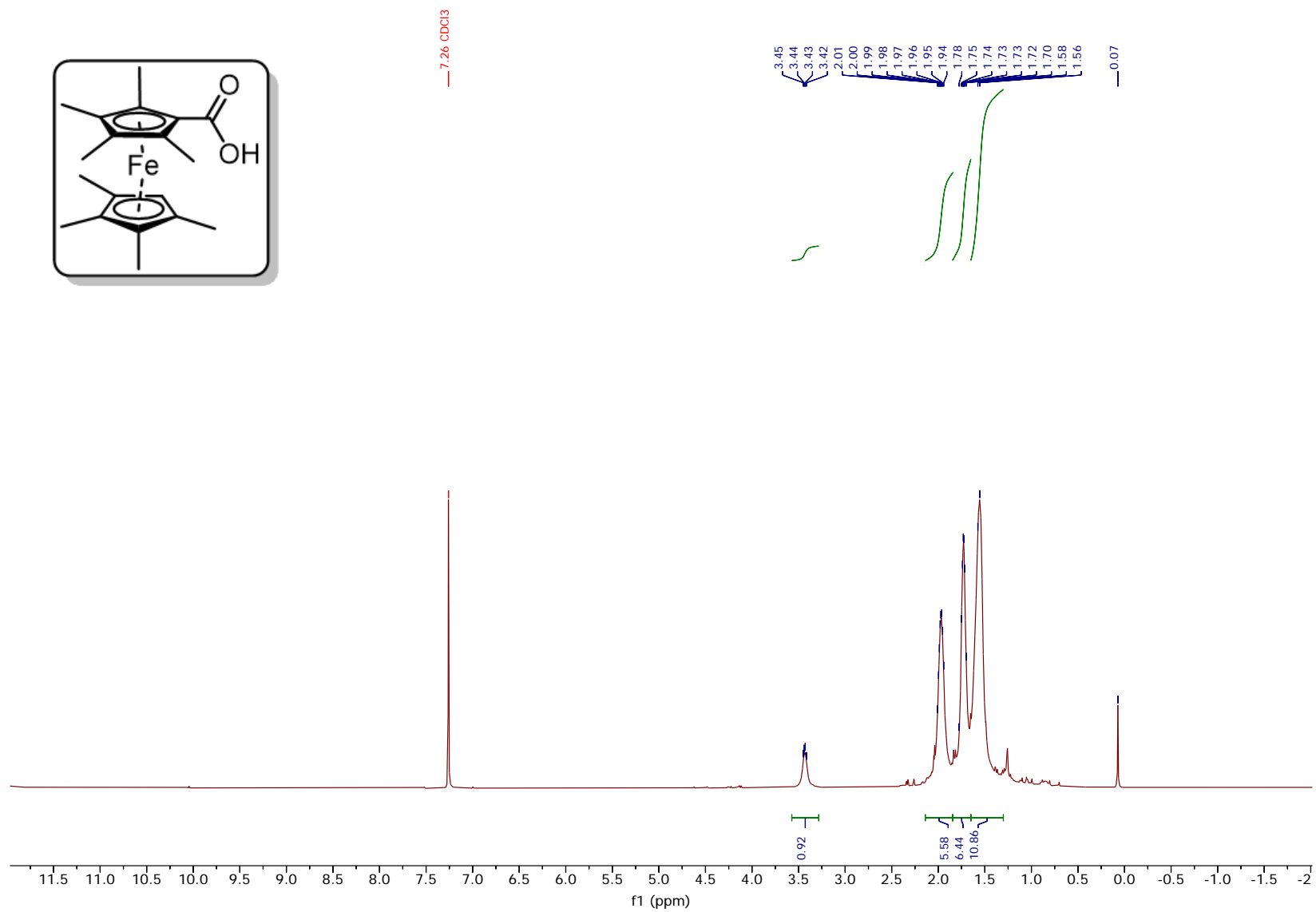
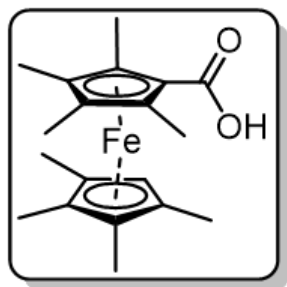


Figure S27. ¹H NMR of ligand **1k** in CDCl₃

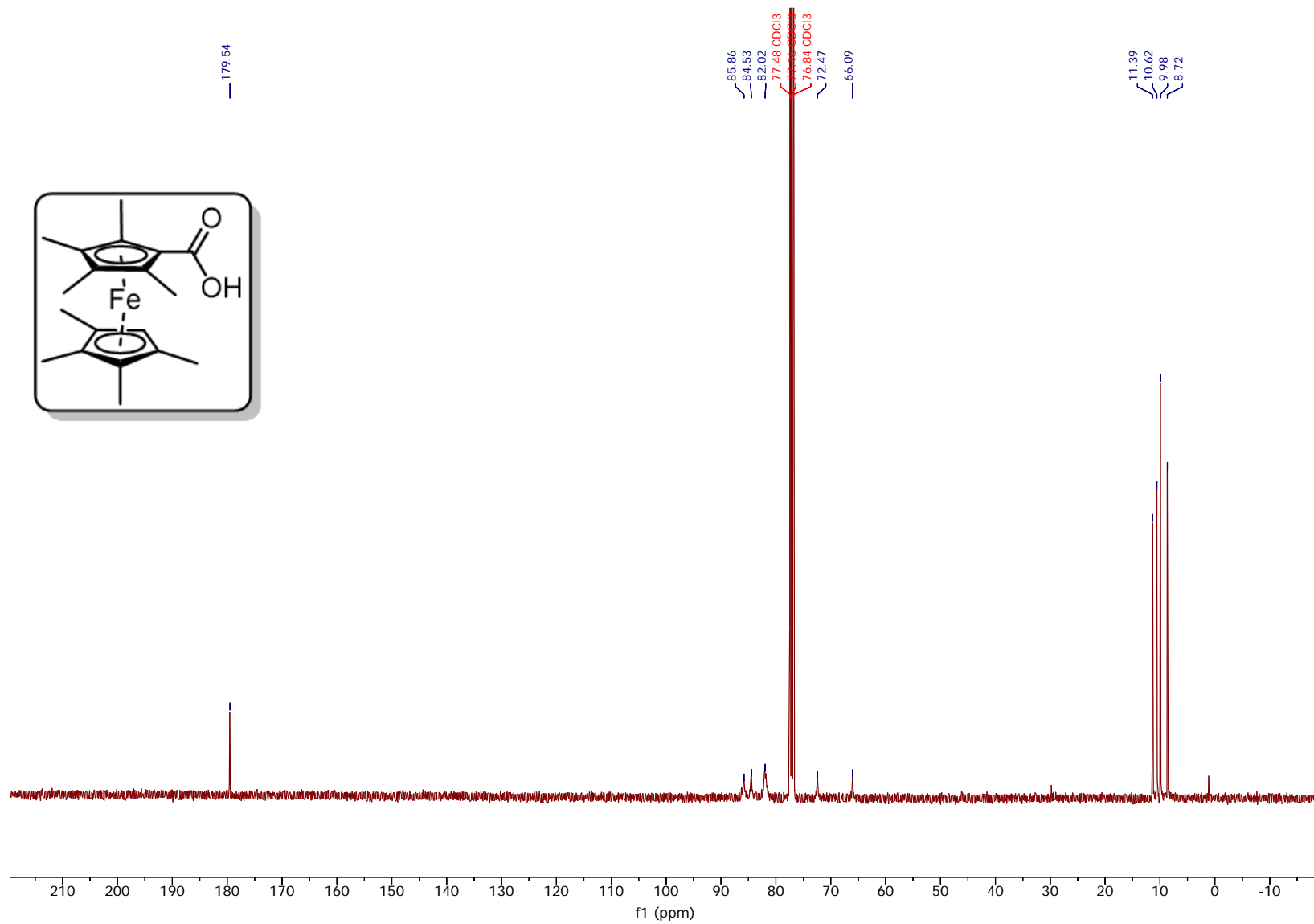


Figure S28. ^{13}C NMR of ligand **1k** in CDCl_3

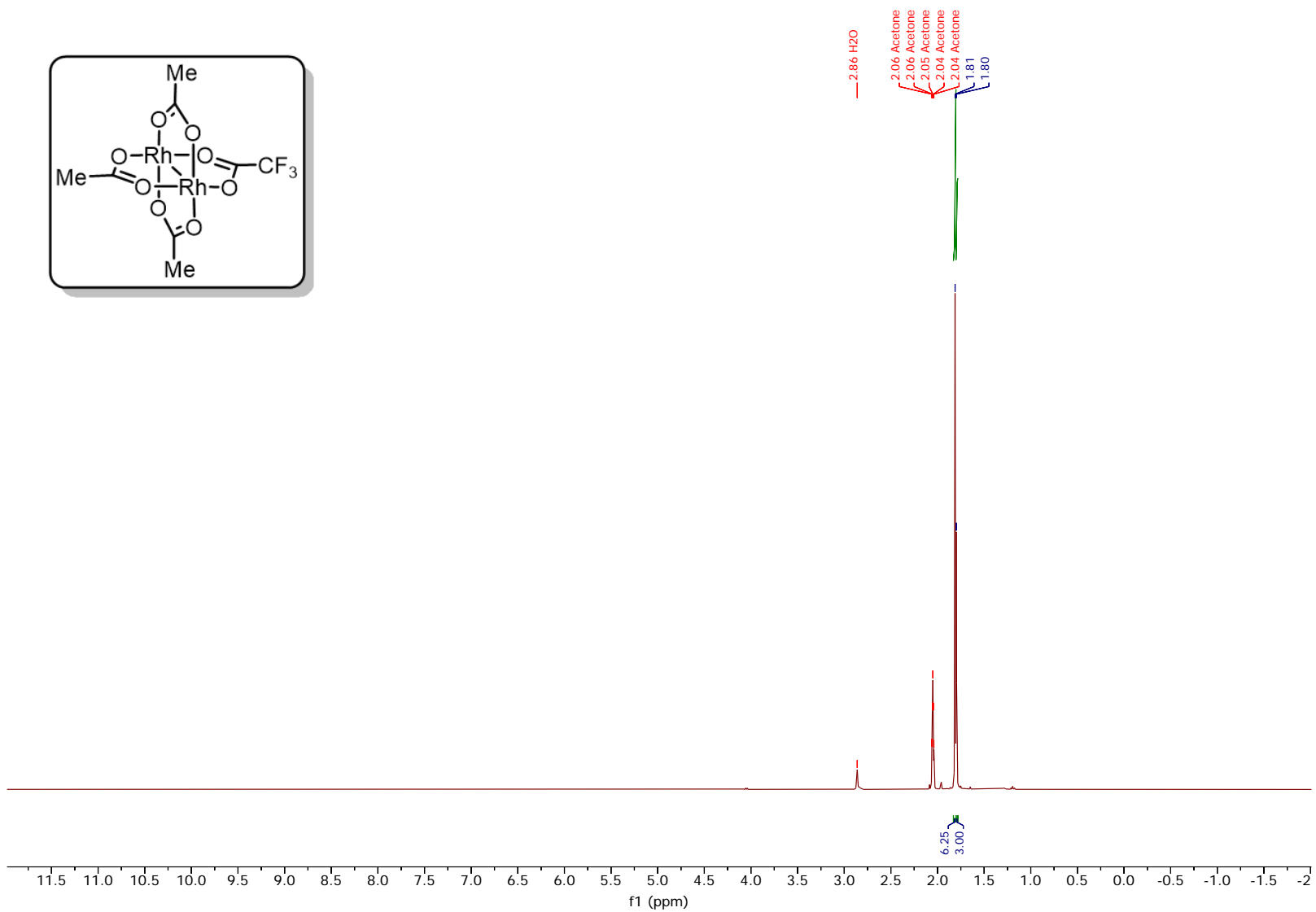


Figure S29. ¹H NMR of complex **3** in *d*₆-acetone.

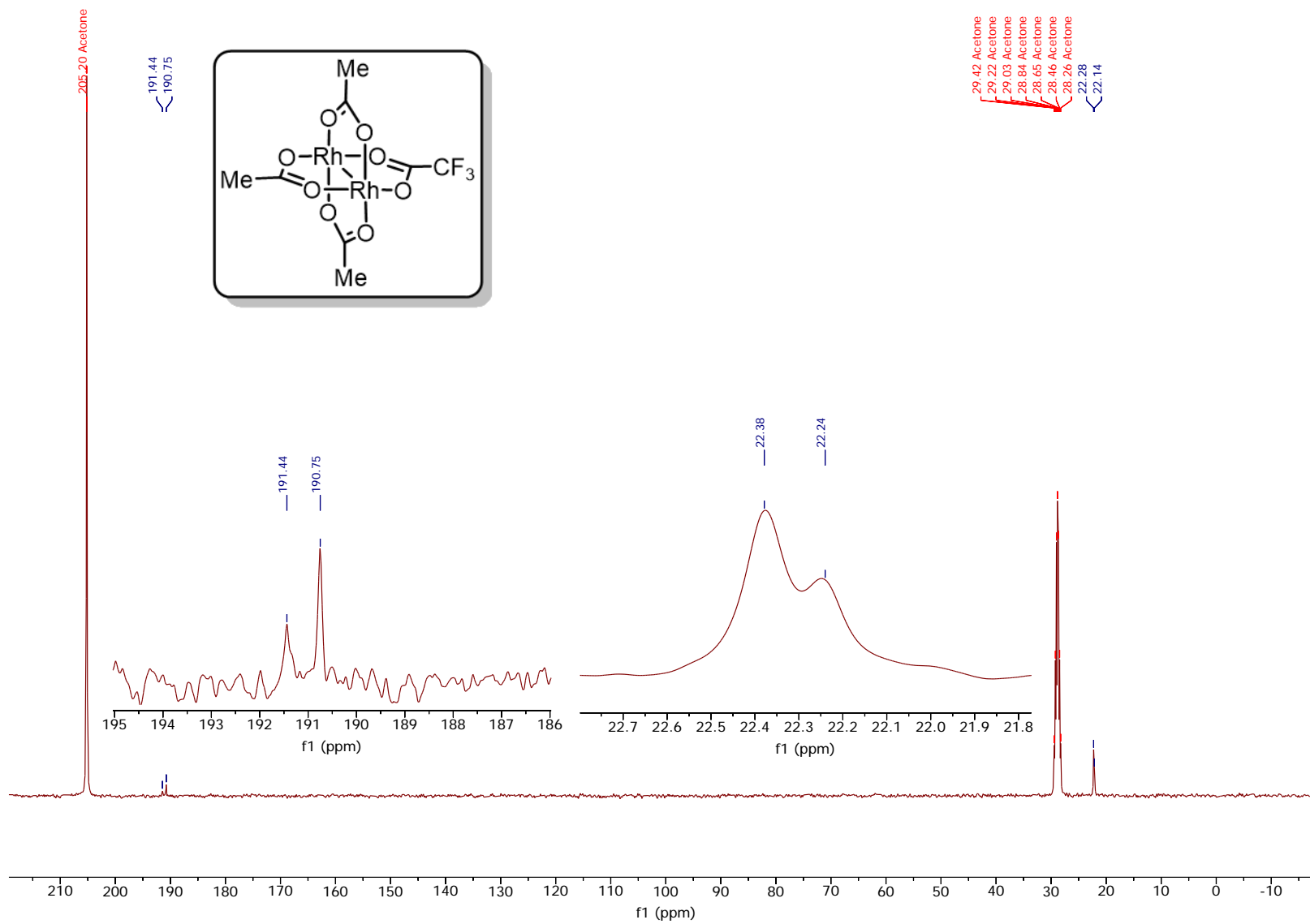


Figure S30. ^{13}C NMR of complex **3** in d_6 -acetone.

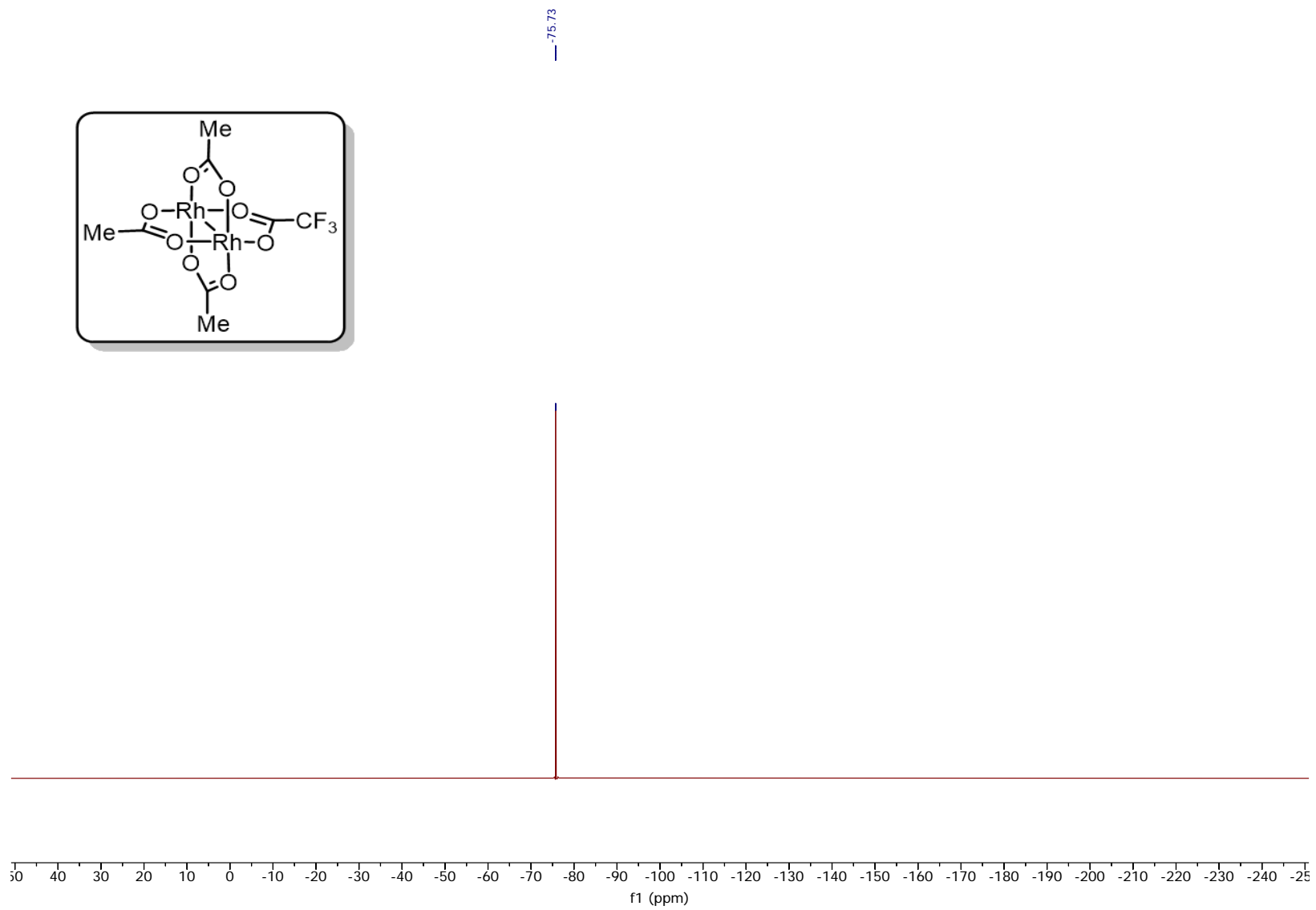


Figure S31. ^{19}F NMR of complex **3** in d_6 -acetone.

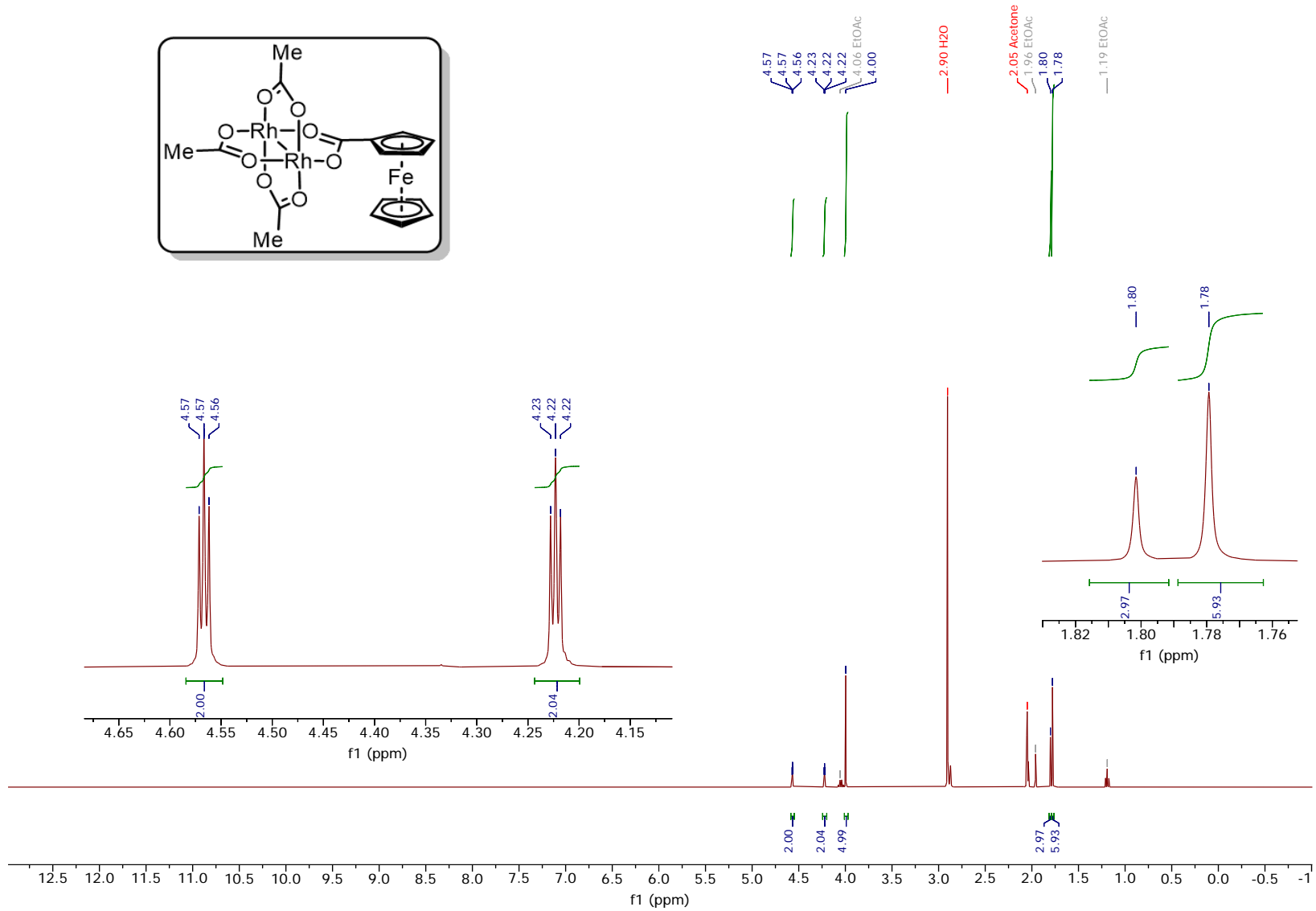


Figure S32. ^1H NMR of complex **4a** in d_6 -acetone

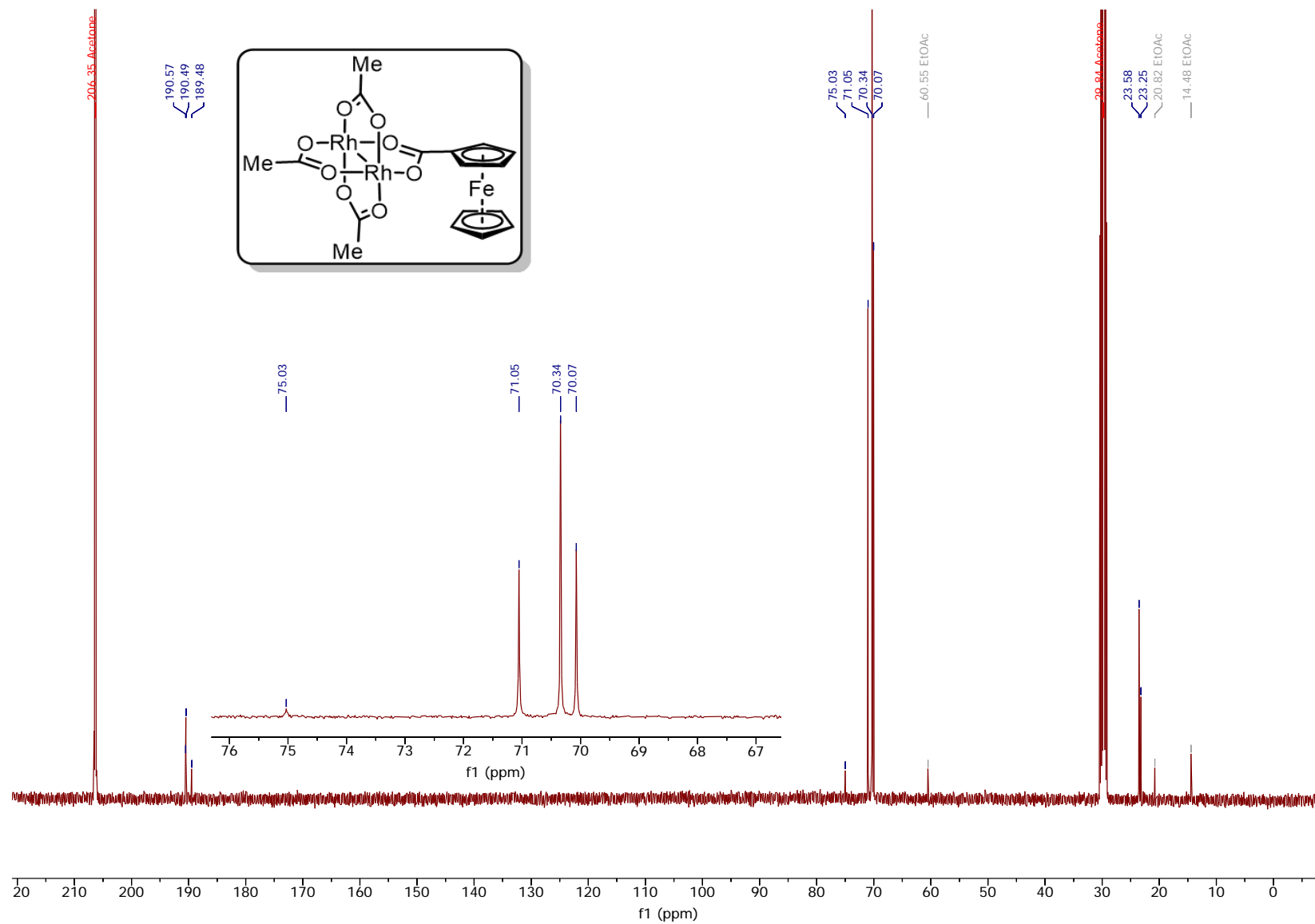


Figure S33. ¹³C NMR of complex **4a** in *d*₆-acetone

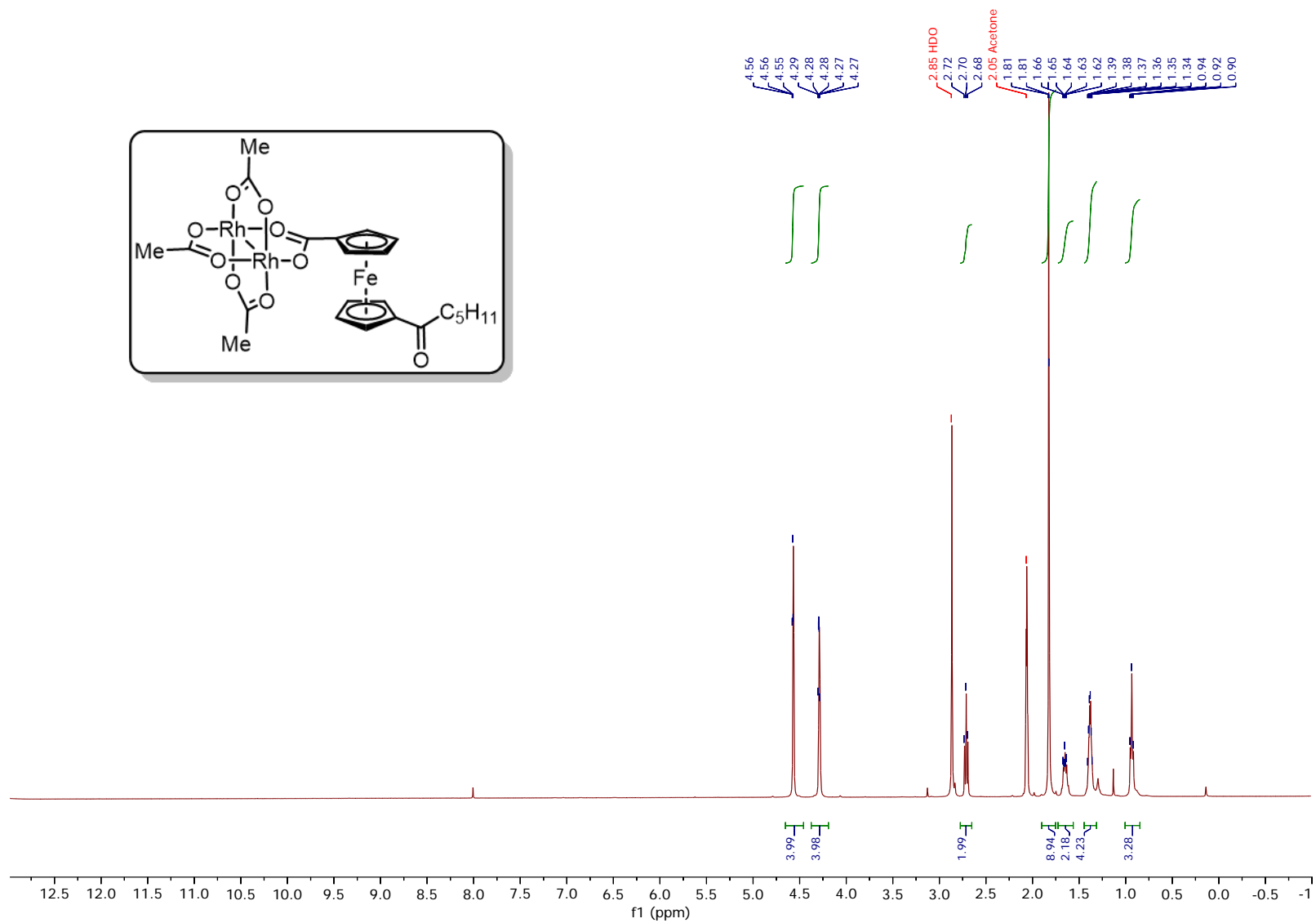


Figure S34. ^1H NMR of complex **4b** in d_6 -acetone

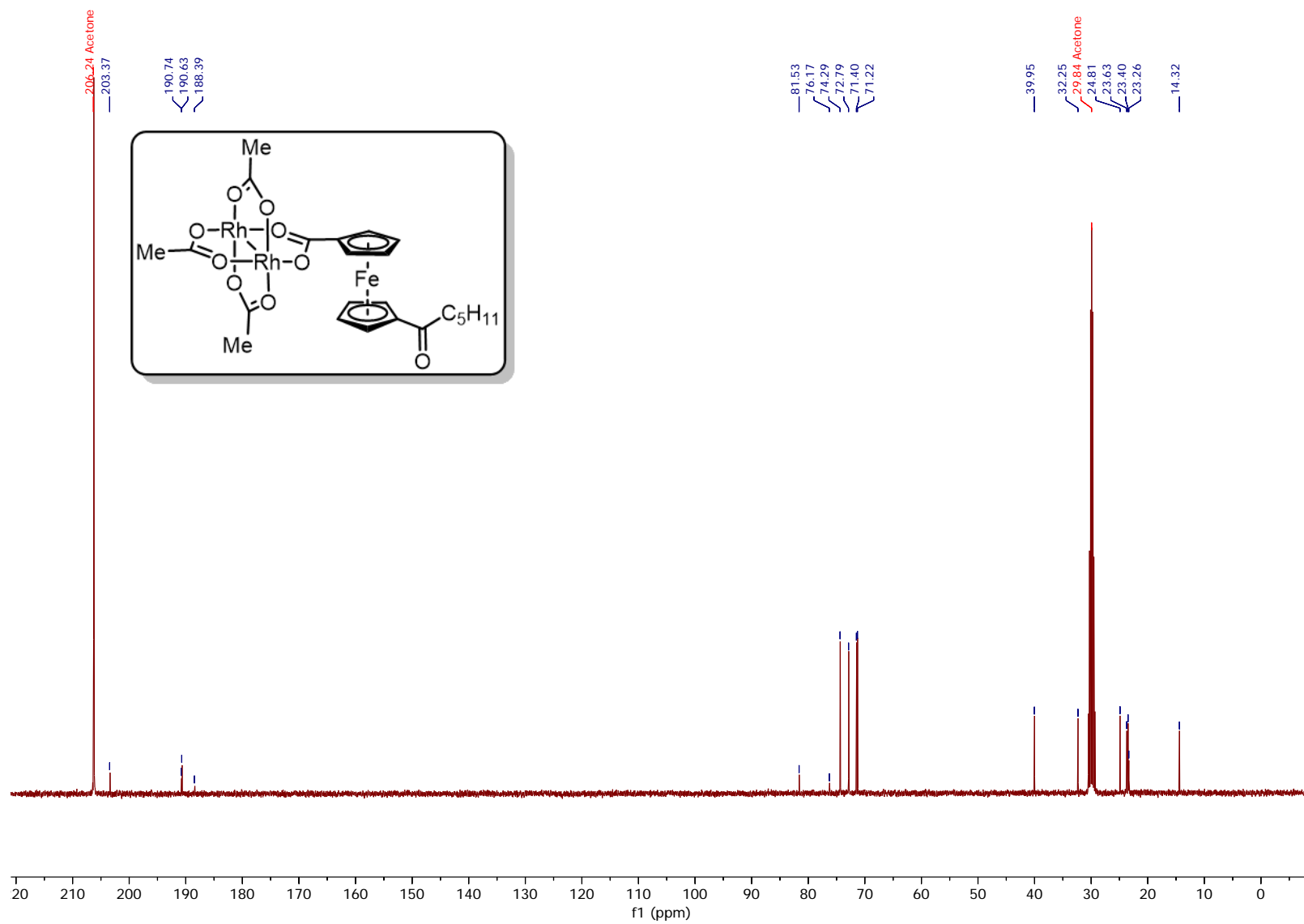


Figure S35. ^{13}C NMR of complex **4b** in d_6 -acetone

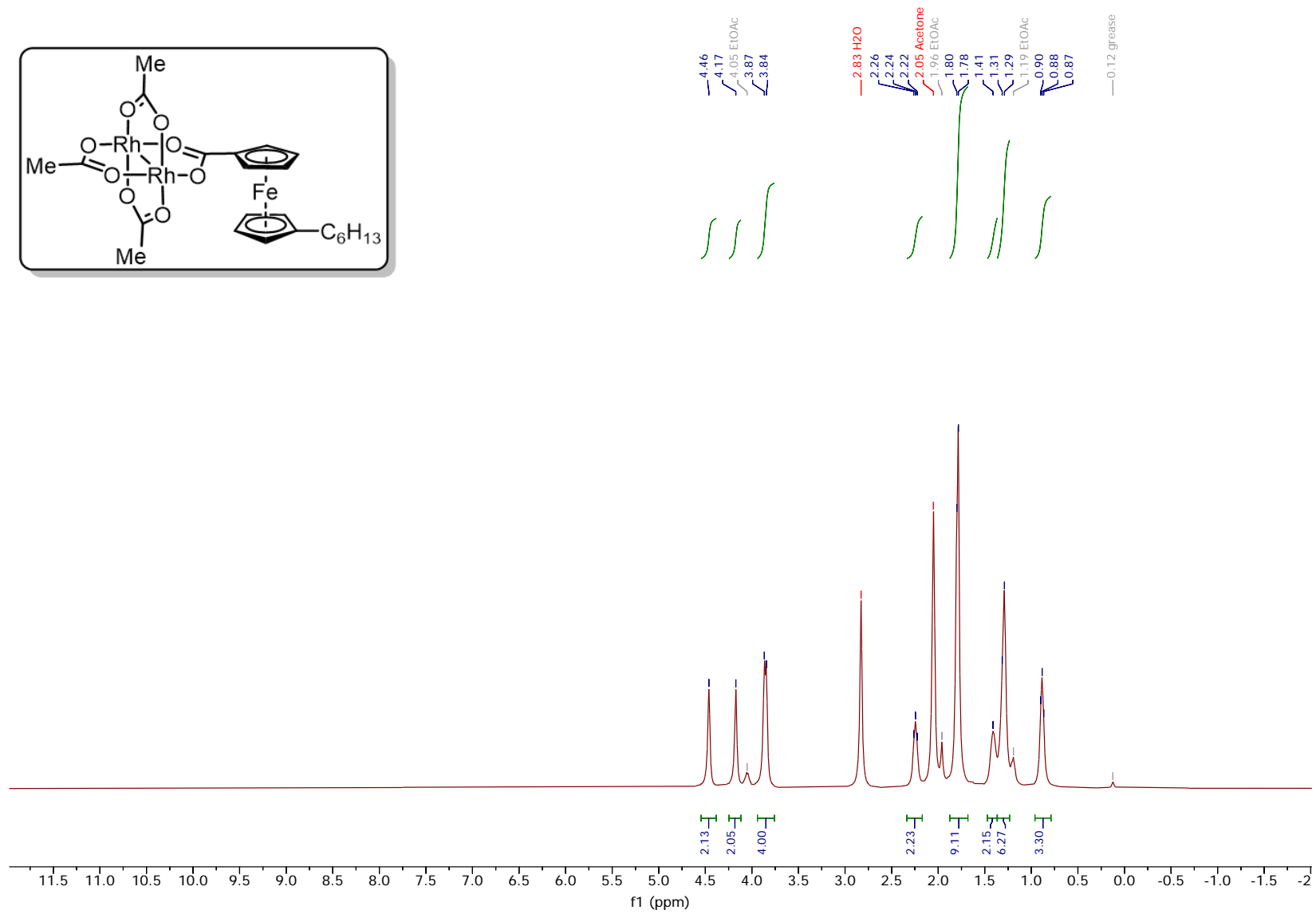
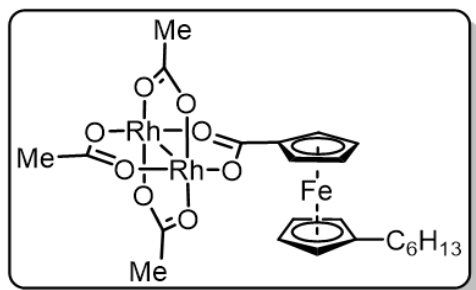


Figure S36. ^1H NMR of complex **4c** in d_6 -acetone

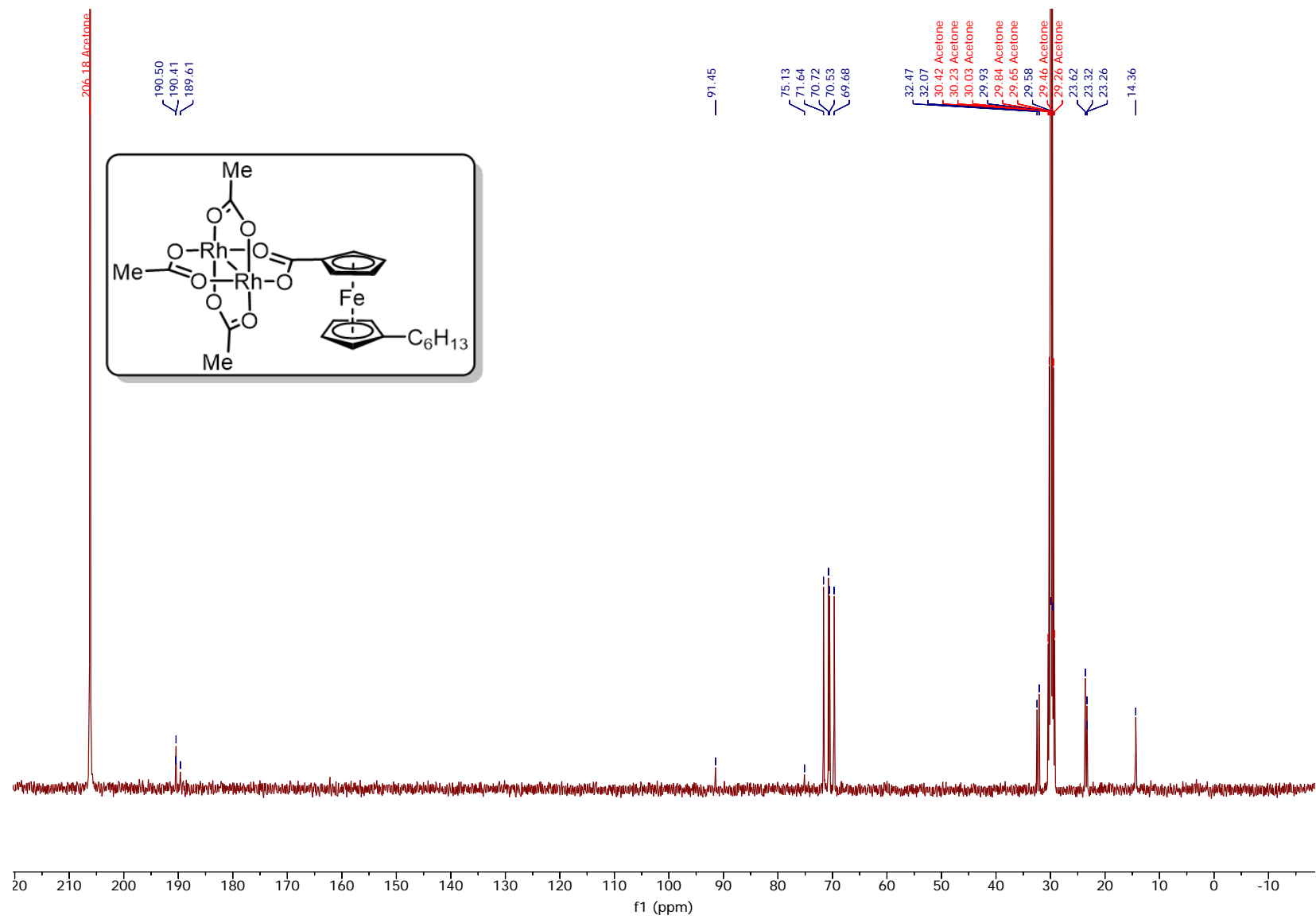


Figure S37. ^{13}C NMR of complex 4c in d_6 -acetone

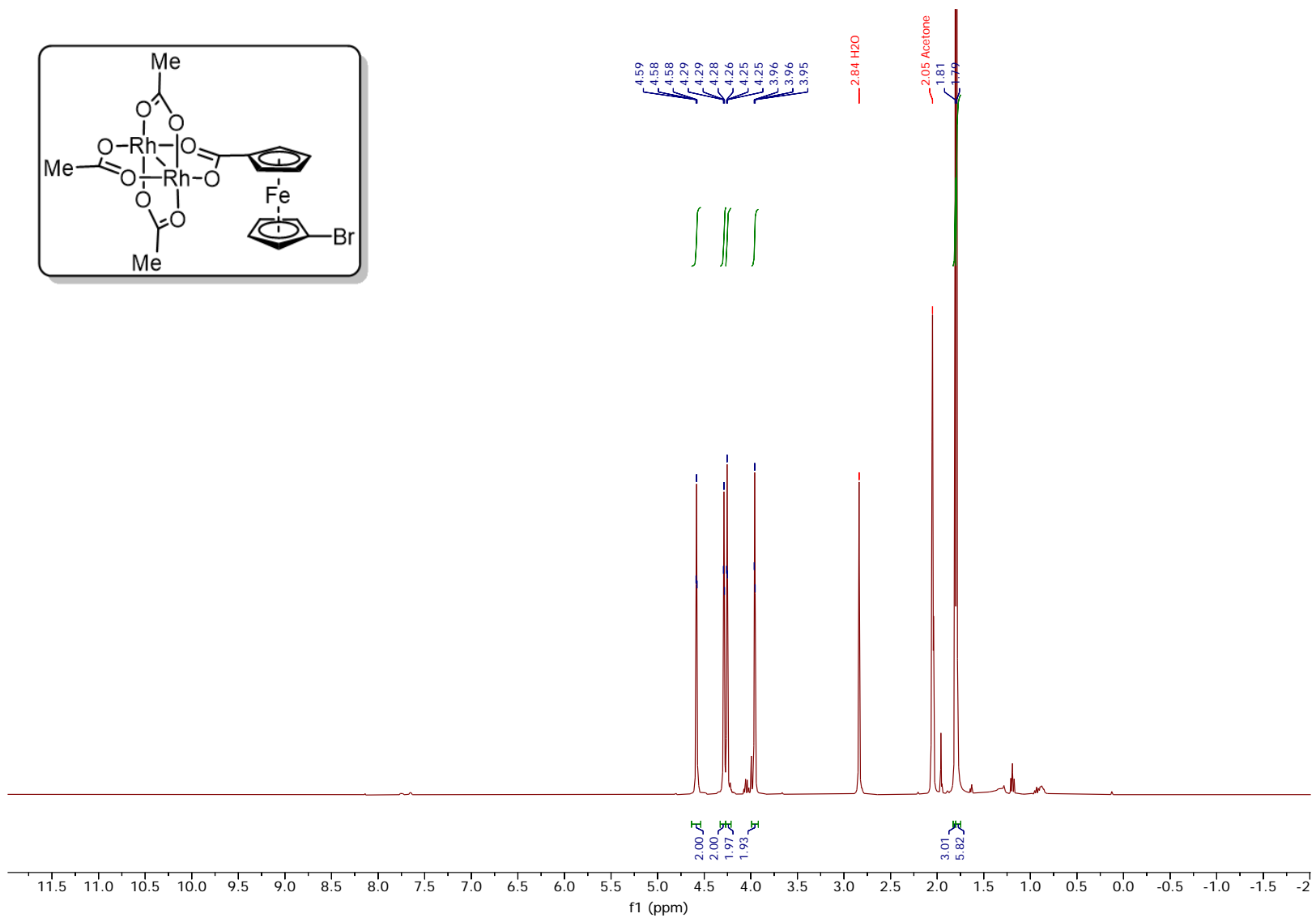


Figure S38. ^1H NMR of complex **4d** in d_6 -acetone

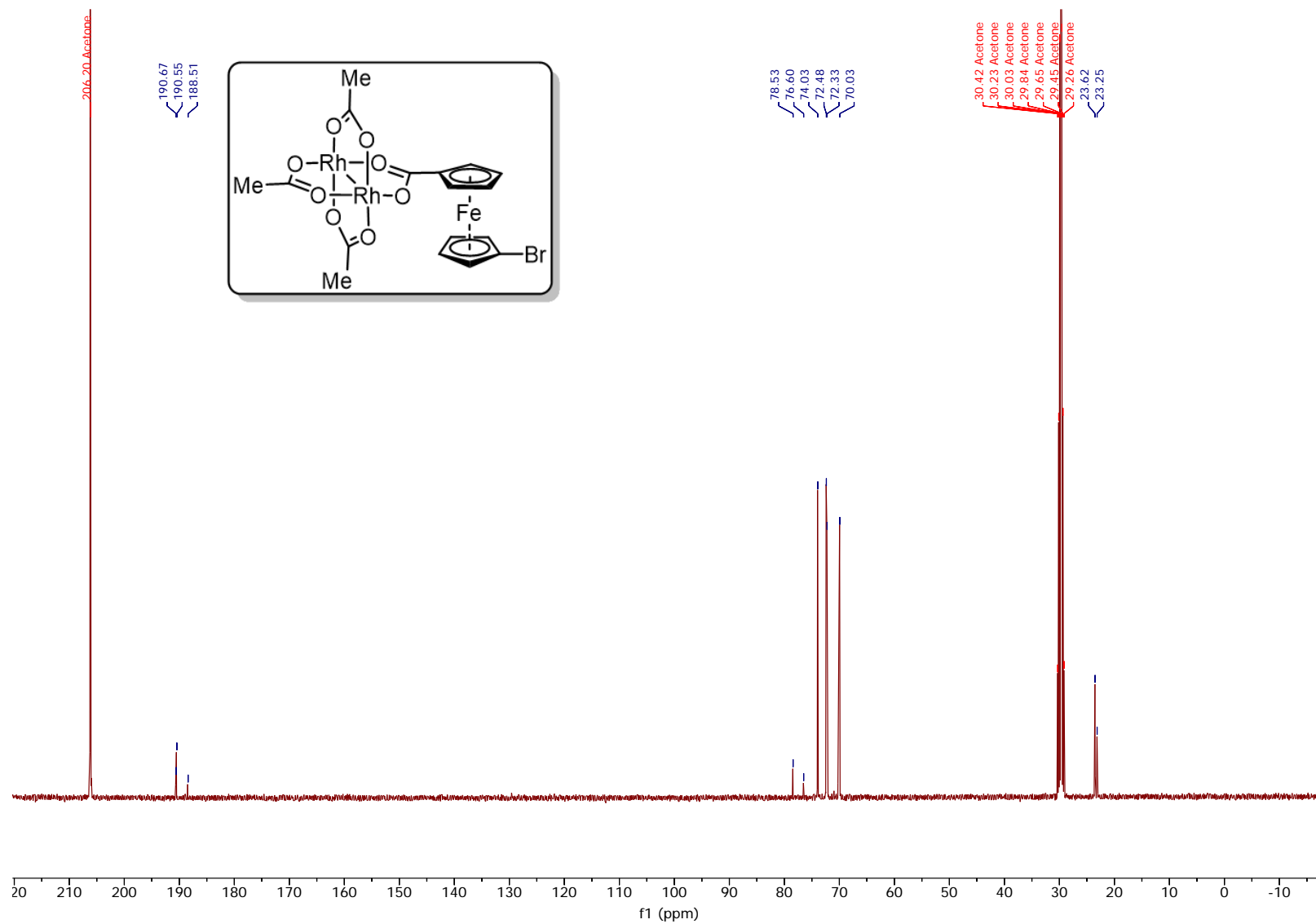


Figure S39. ¹³C NMR of complex 4d in *d*₆-acetone

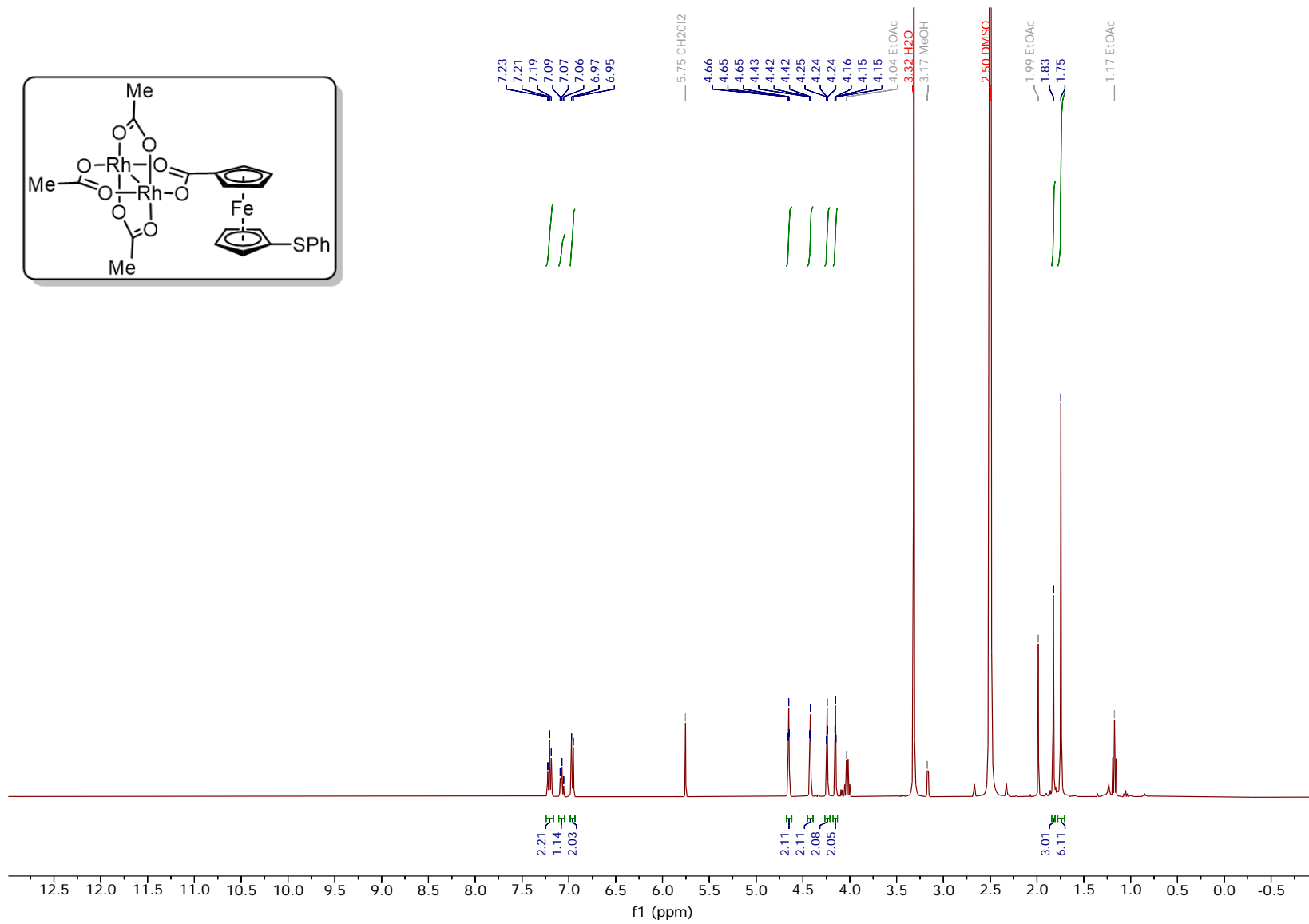


Figure S40. ^1H NMR of complex **4e** in d_6 -DMSO

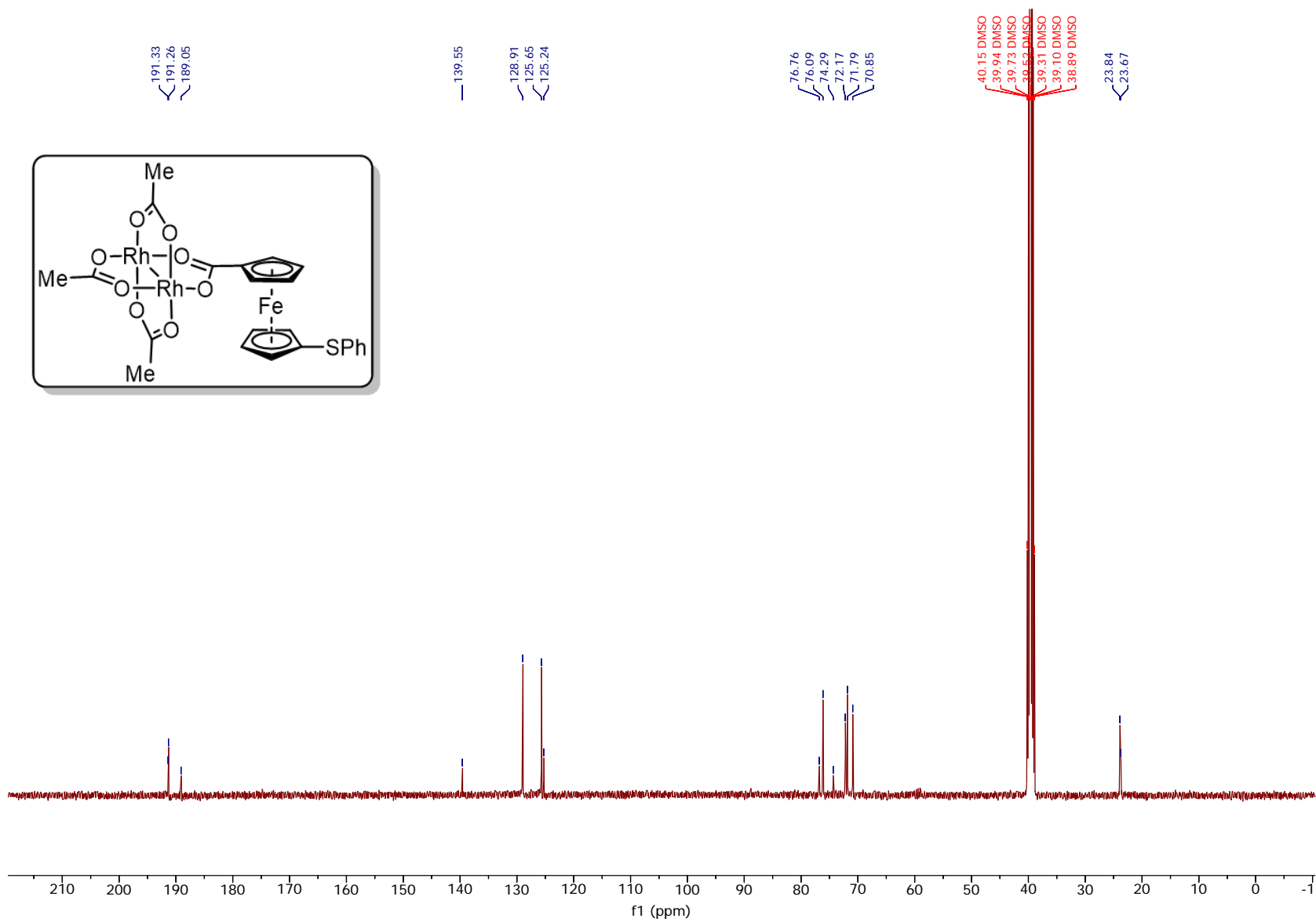


Figure S41. ^{13}C NMR of complex **4e** in d_6 -DMSO

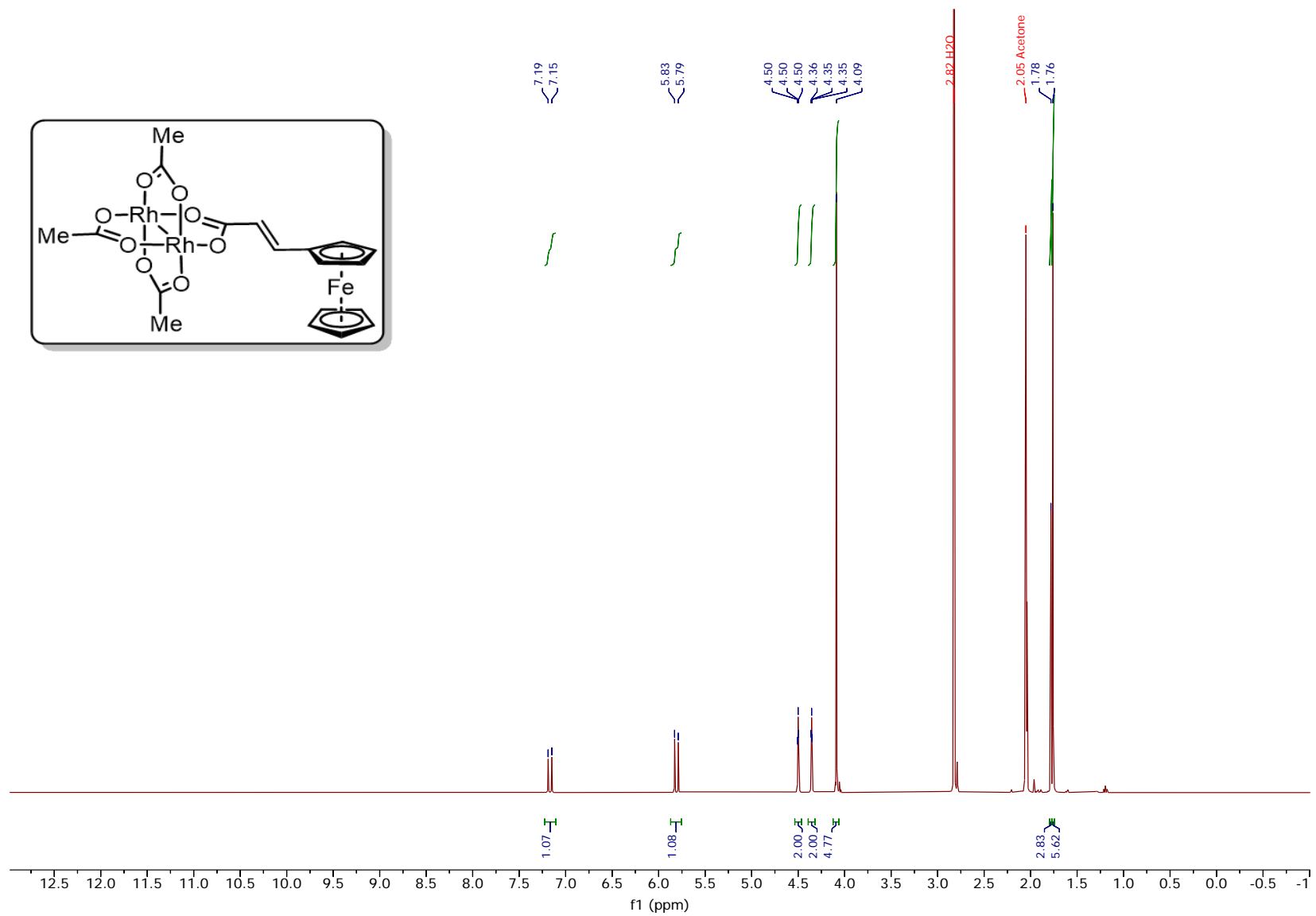


Figure S42. ^1H NMR of complex **4f** in d_6 -acetone

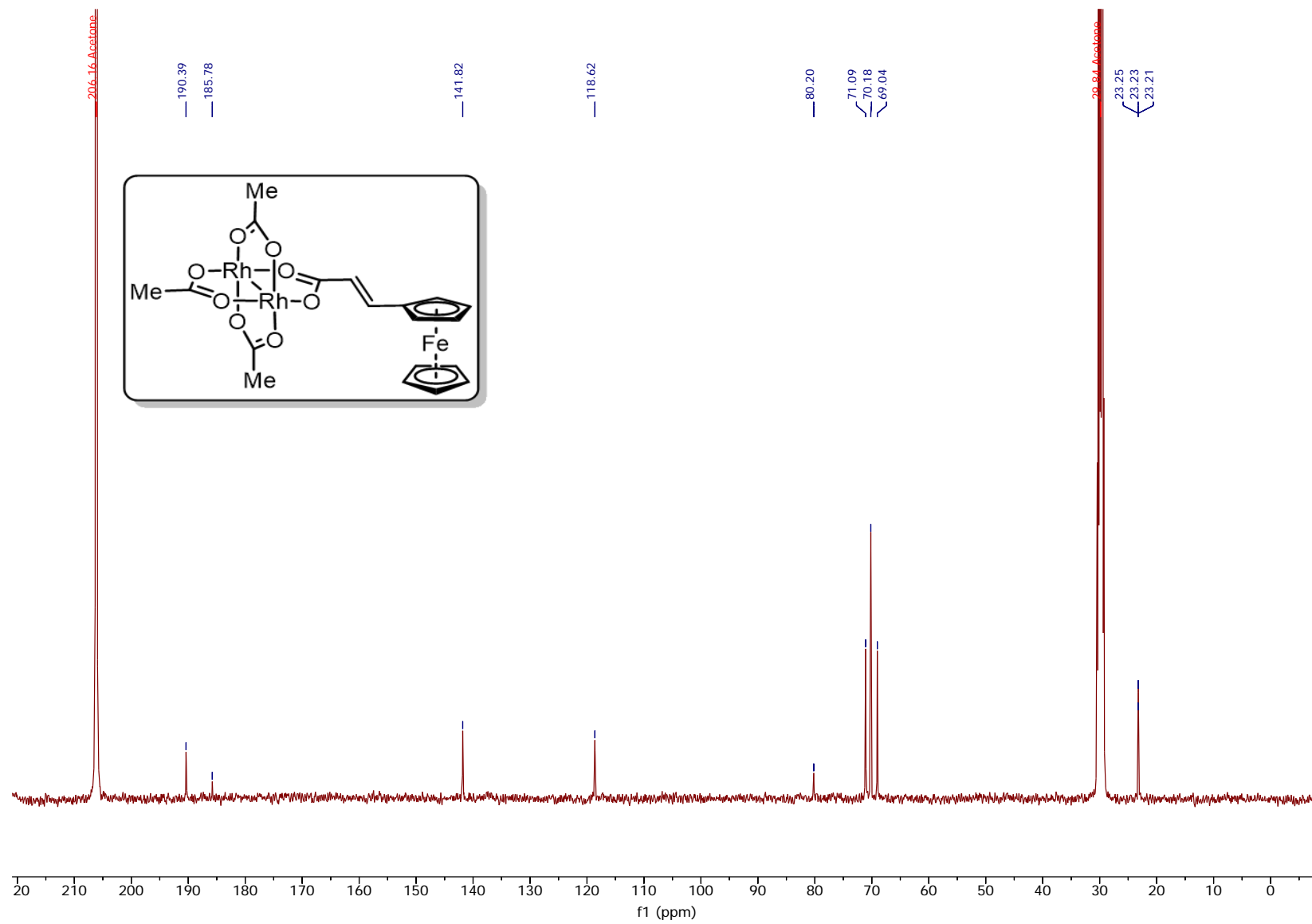


Figure S43. ^{13}C NMR of complex **4f** in d_6 -acetone

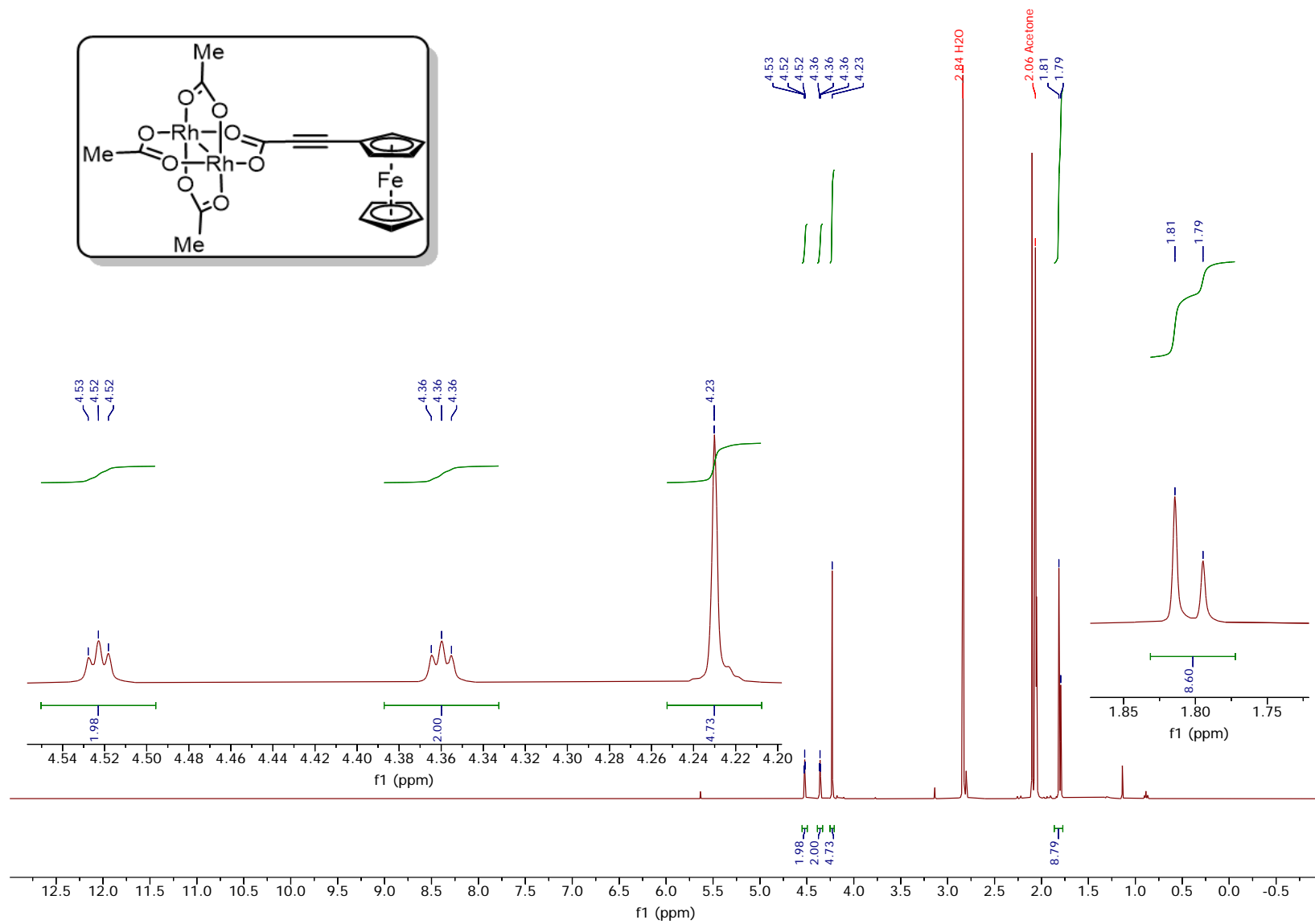


Figure S44. ^1H NMR of complex **4g** in d_6 -acetone

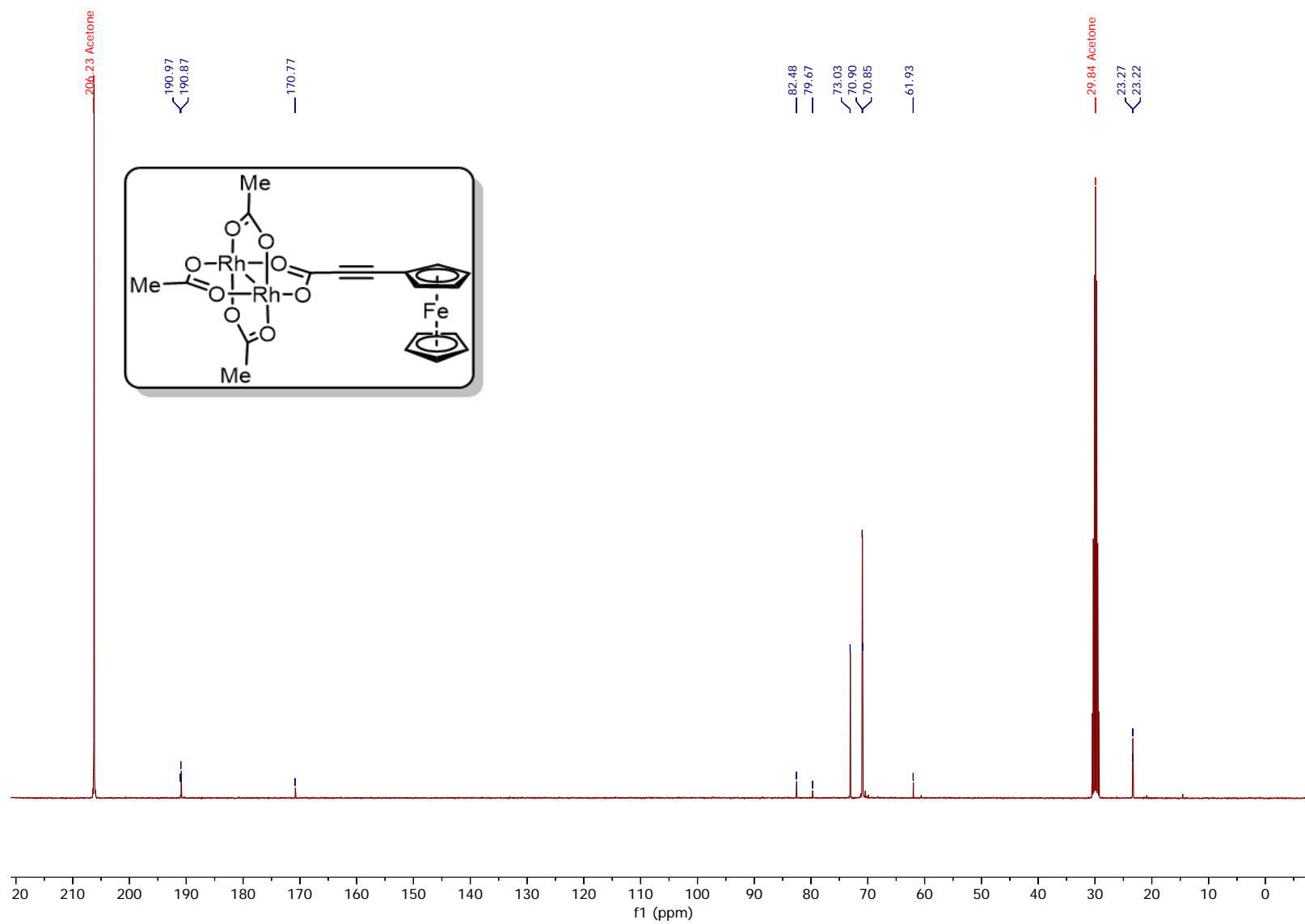


Figure S45. ^{13}C NMR of complex **4g** in d_6 -acetone

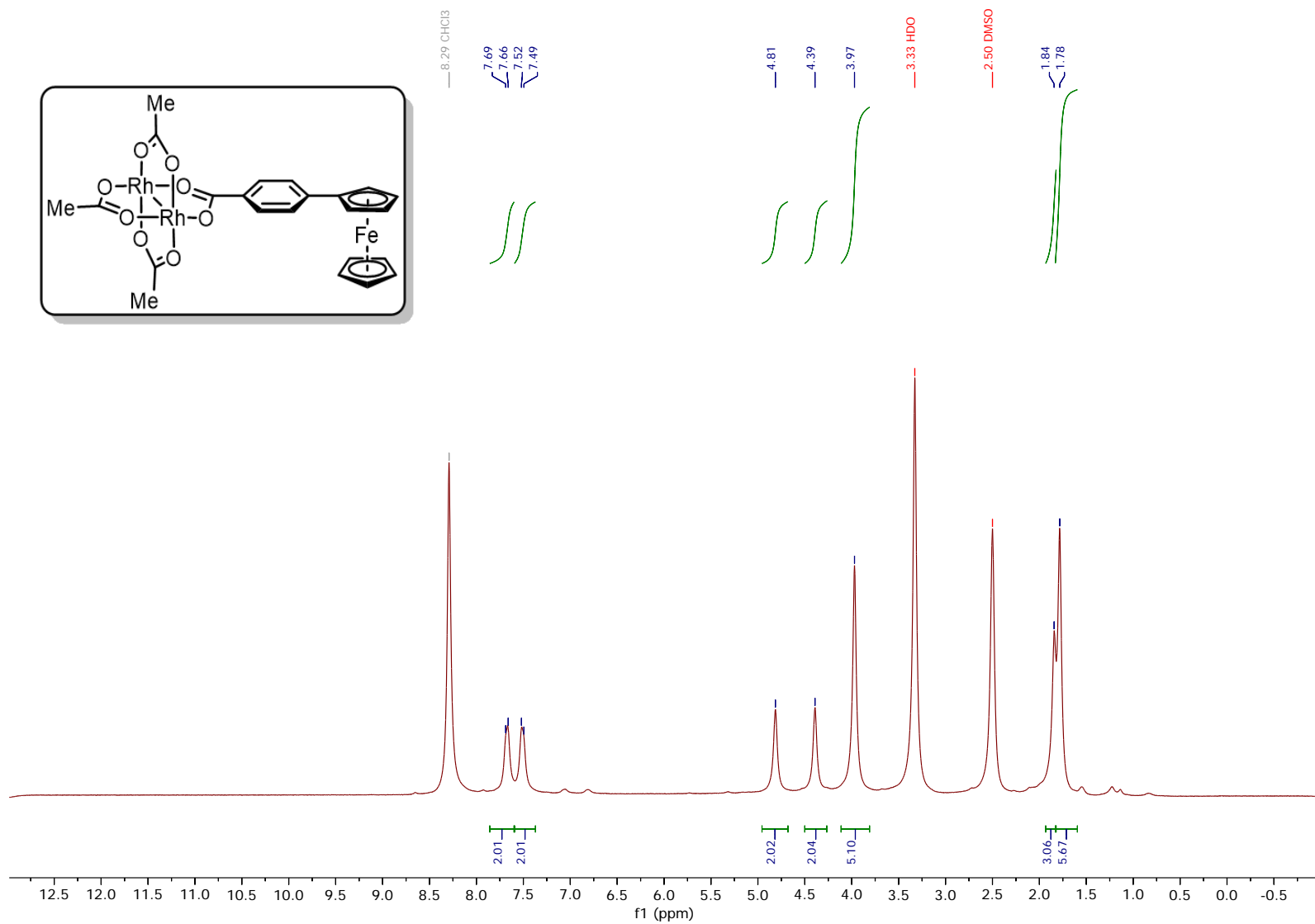


Figure S46. ^1H NMR of complex 4h in d_6 -DMSO

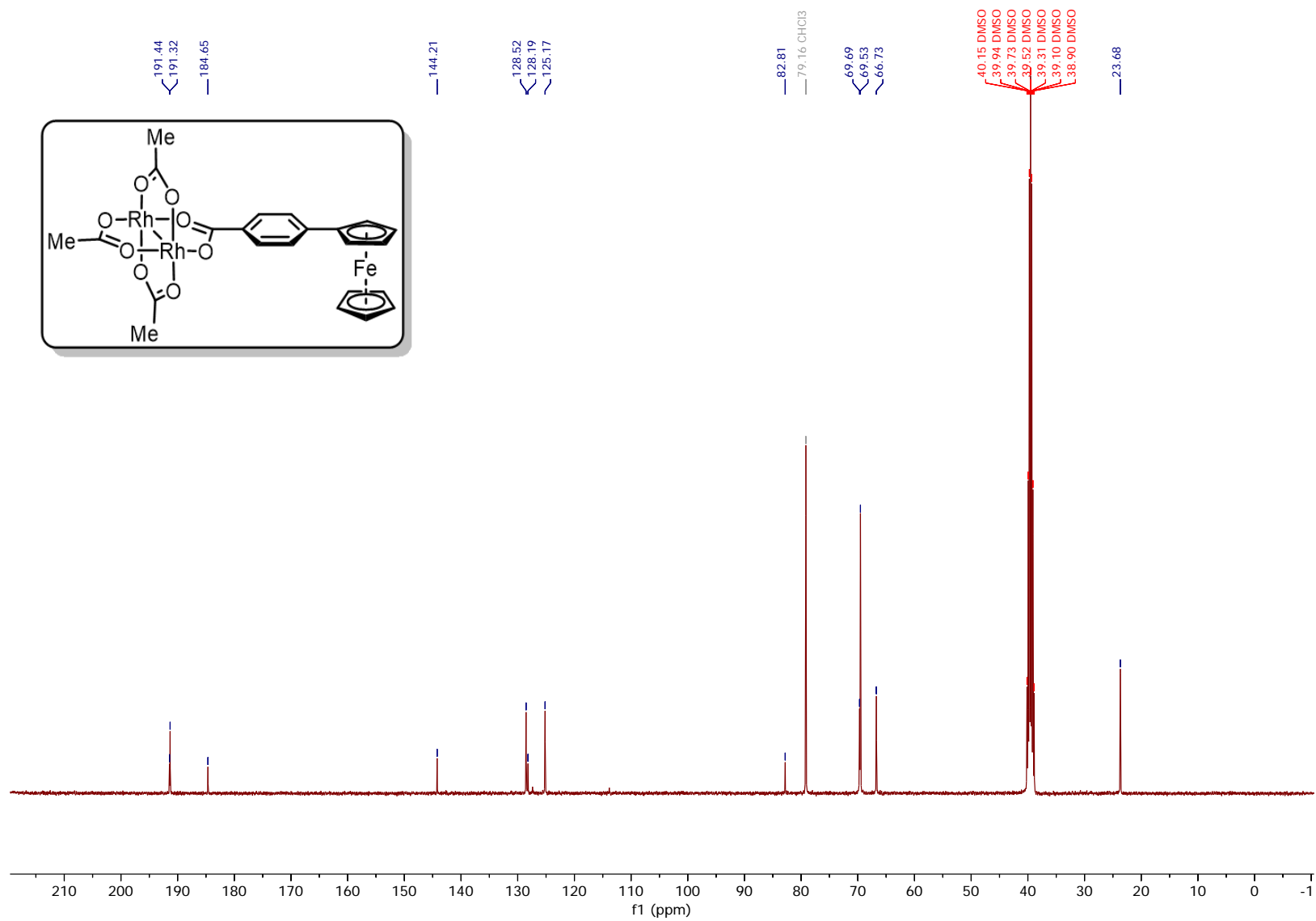


Figure S47. ¹³C NMR of complex **4h** in *d*₆-DMSO

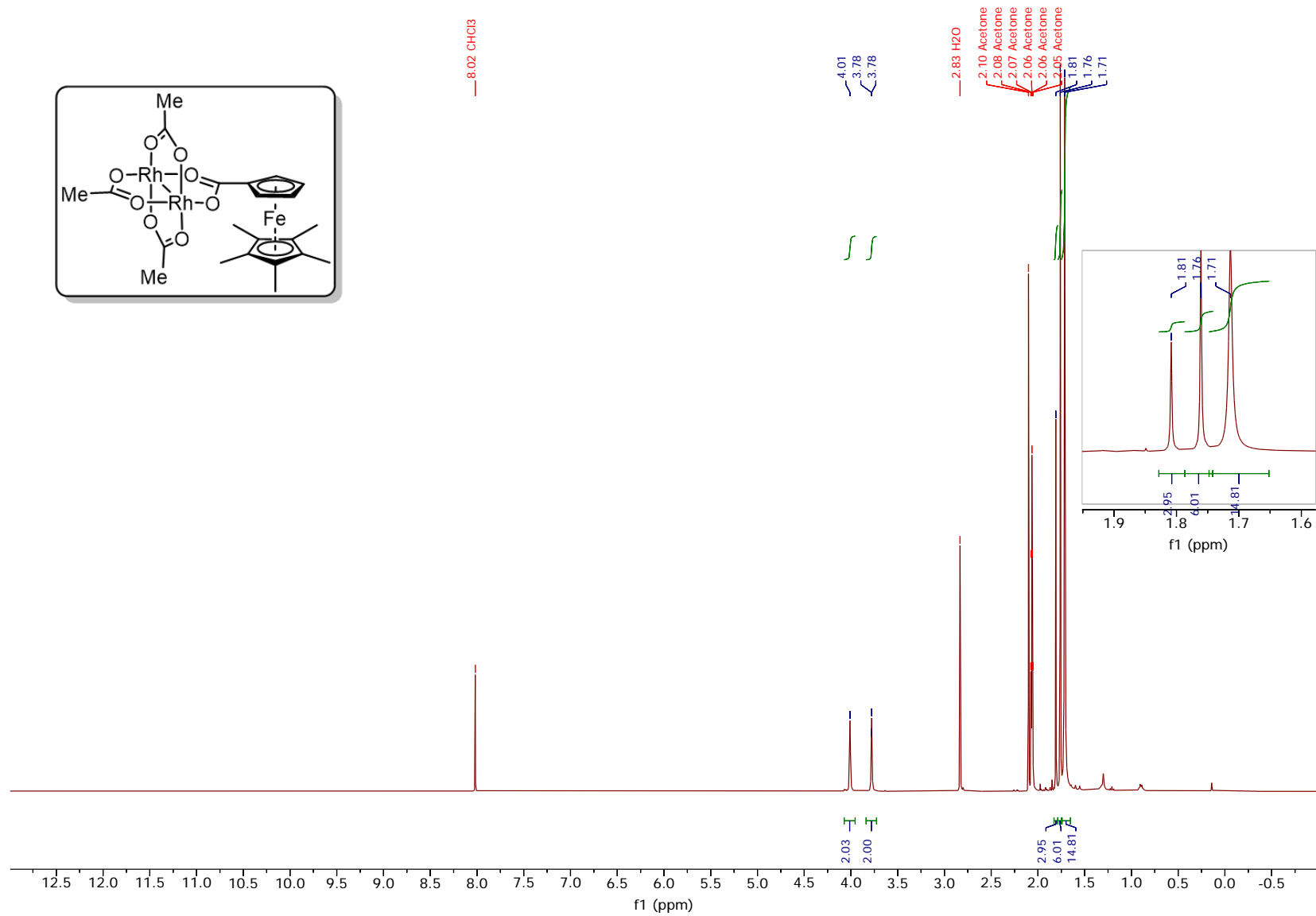


Figure S48. ¹H NMR of complex **4i** in *d*₆-acetone

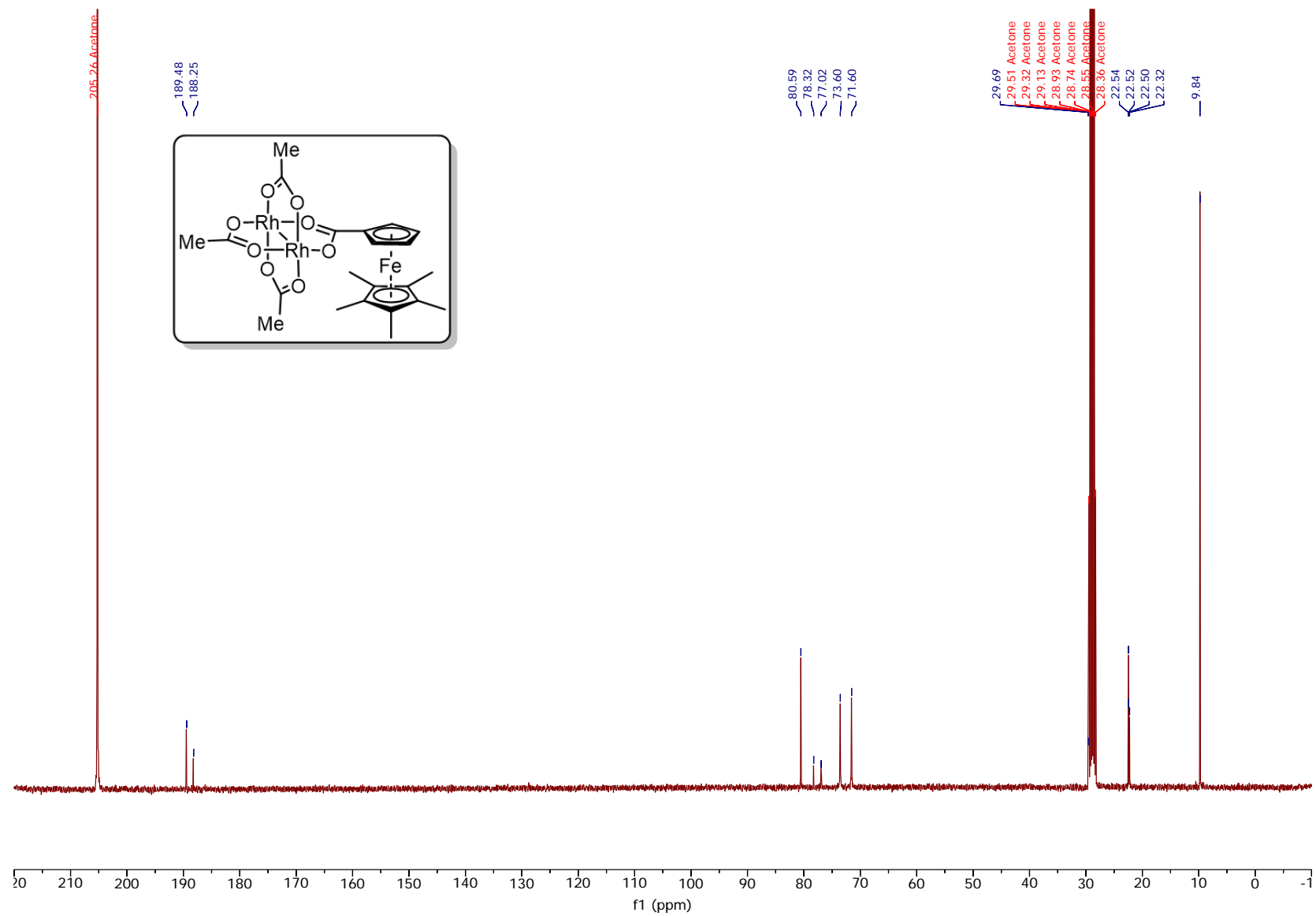


Figure S49. ¹³C NMR of complex **4i** in *d*₆-acetone

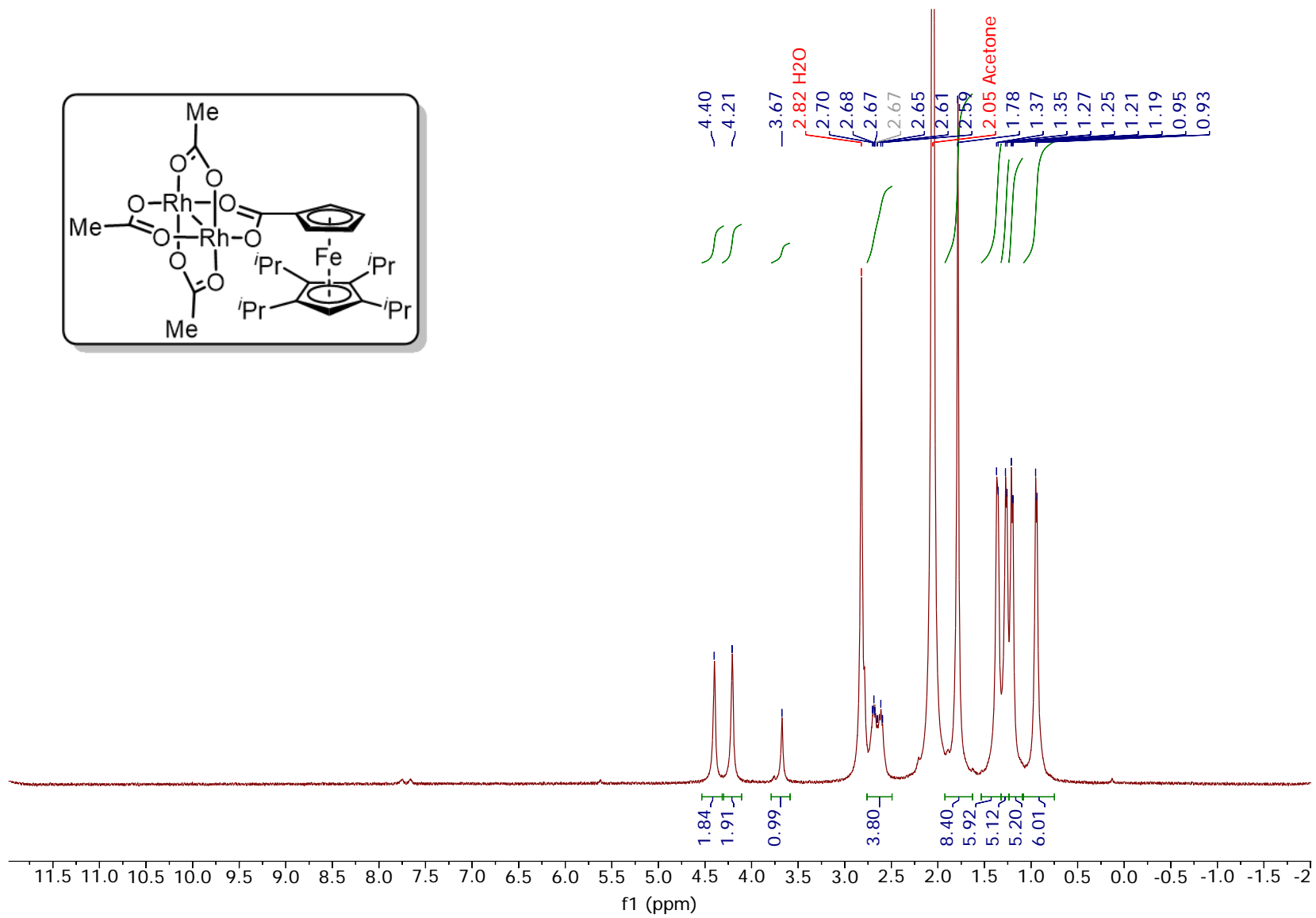


Figure S50. ¹H NMR of complex **4j** in *d*₆-acetone

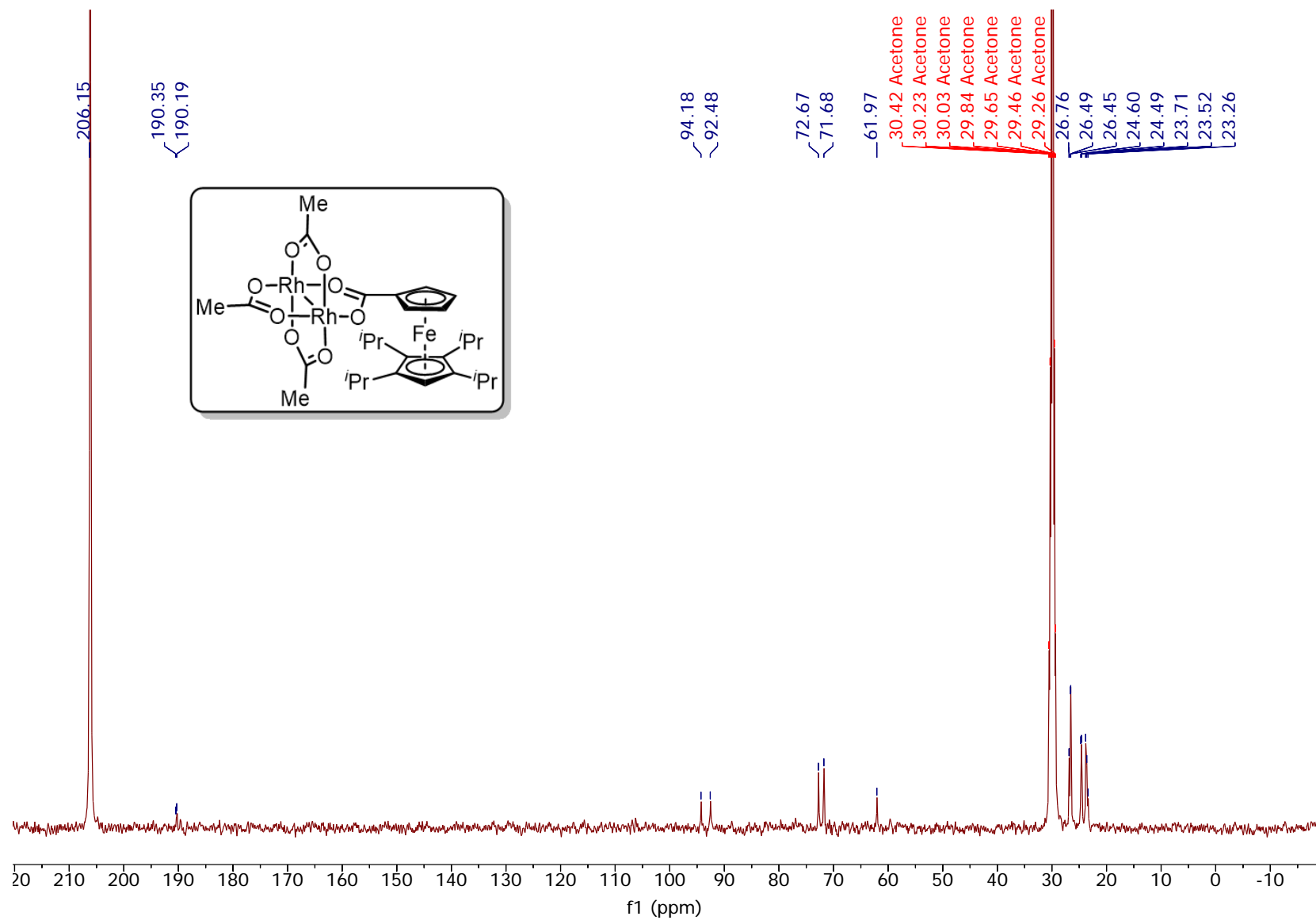


Figure S51. ¹³C NMR of complex **4j** in *d*₆-acetone

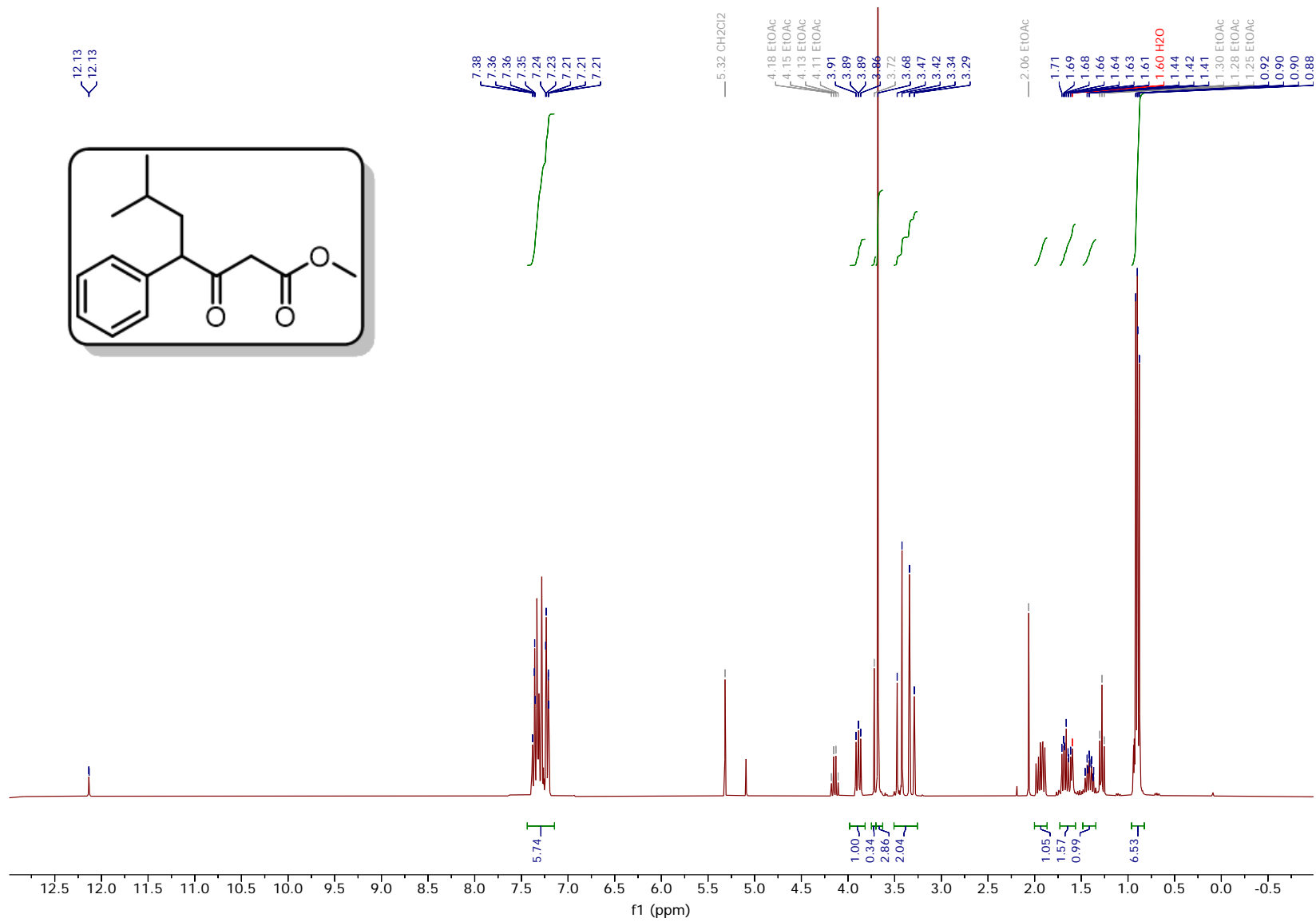


Figure S52. ¹H NMR of S-III in CDCl₃

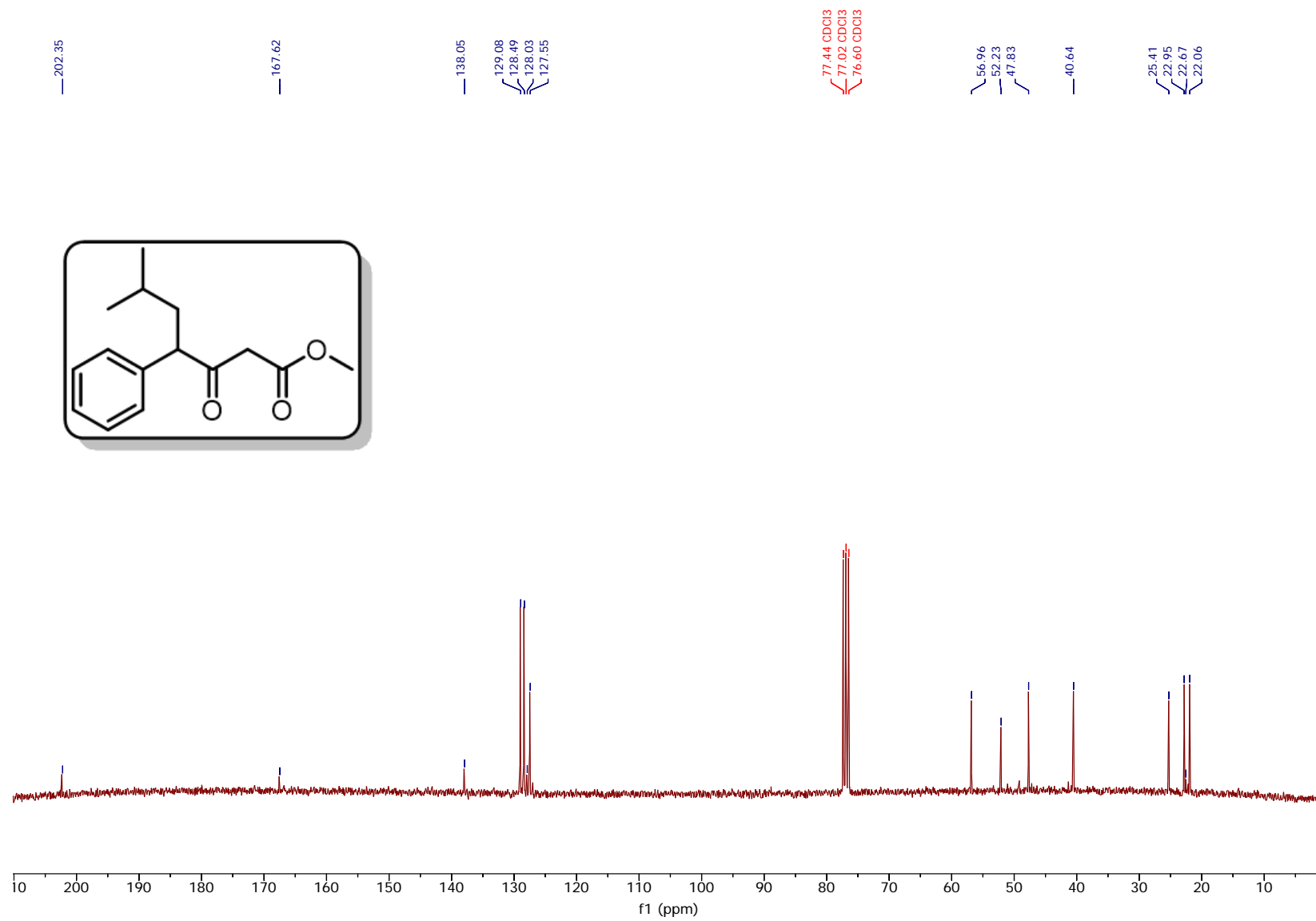


Figure S53. ^{13}C NMR of S-III in CDCl_3

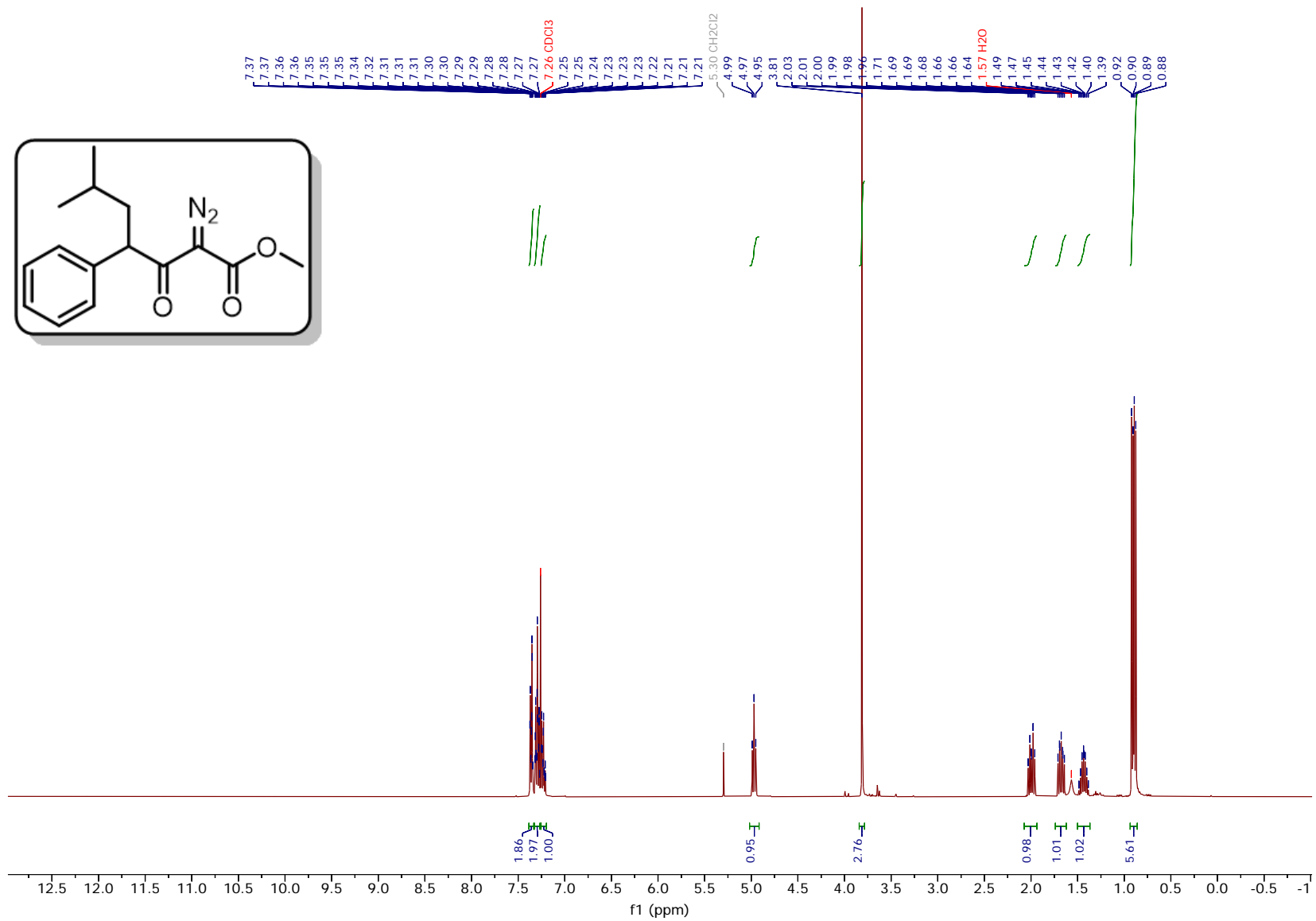


Figure S54. ¹H NMR of diazo compound **5** in CDCl₃

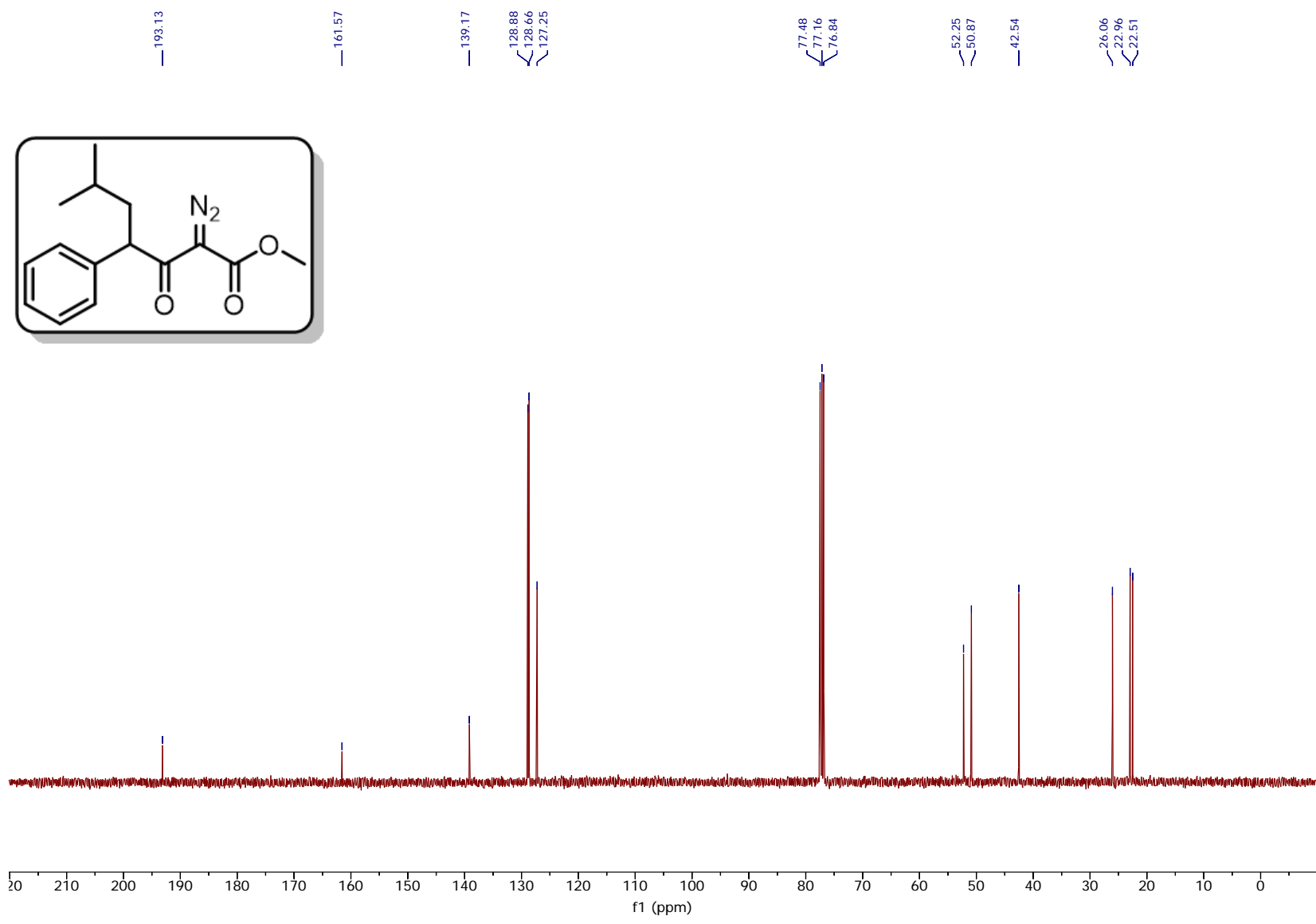


Figure S55. ¹³C NMR of diazo compound 5 in CDCl₃

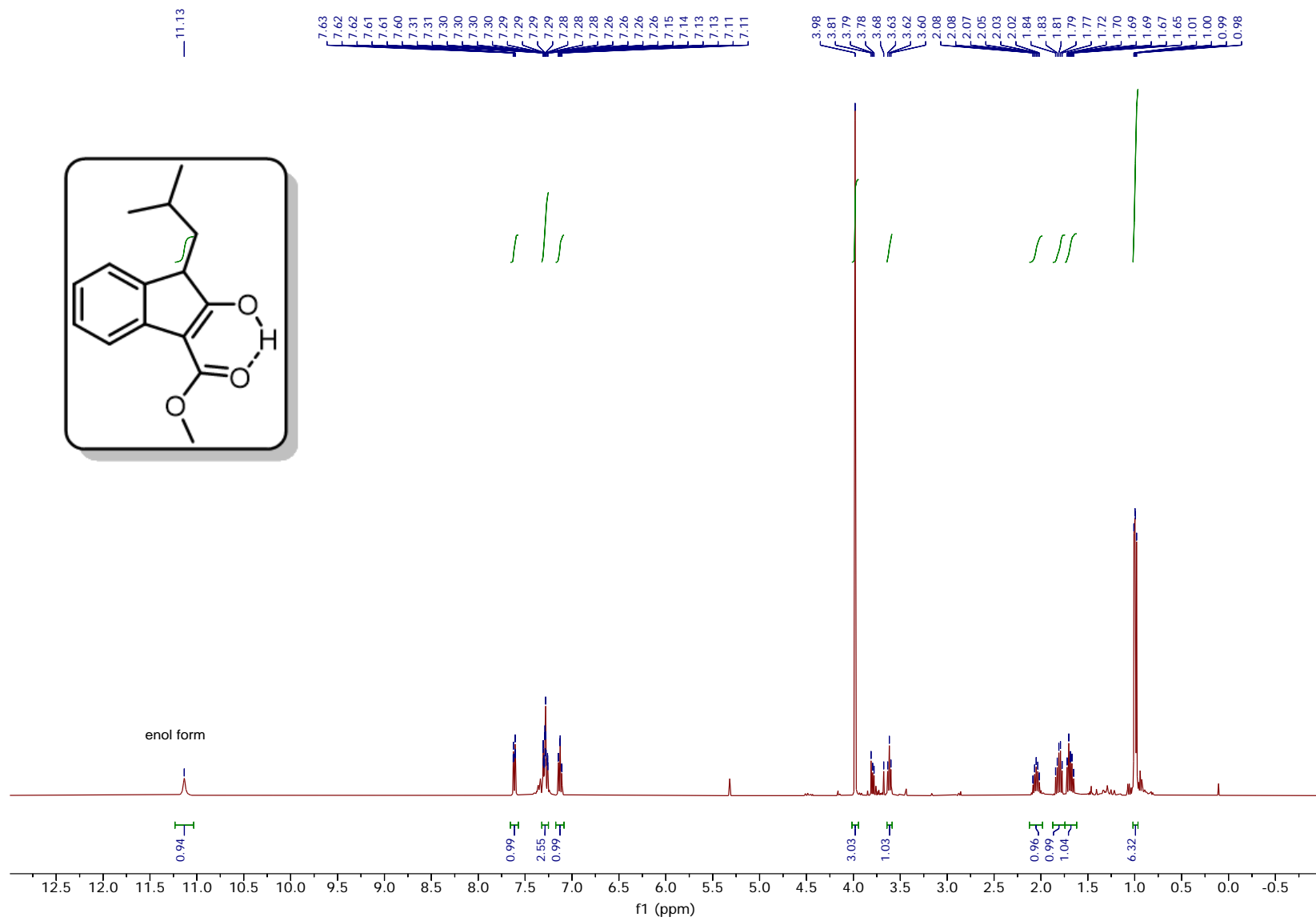


Figure S56. $^1\text{H NMR}$ of aromatic substitution product **6** in CDCl_3

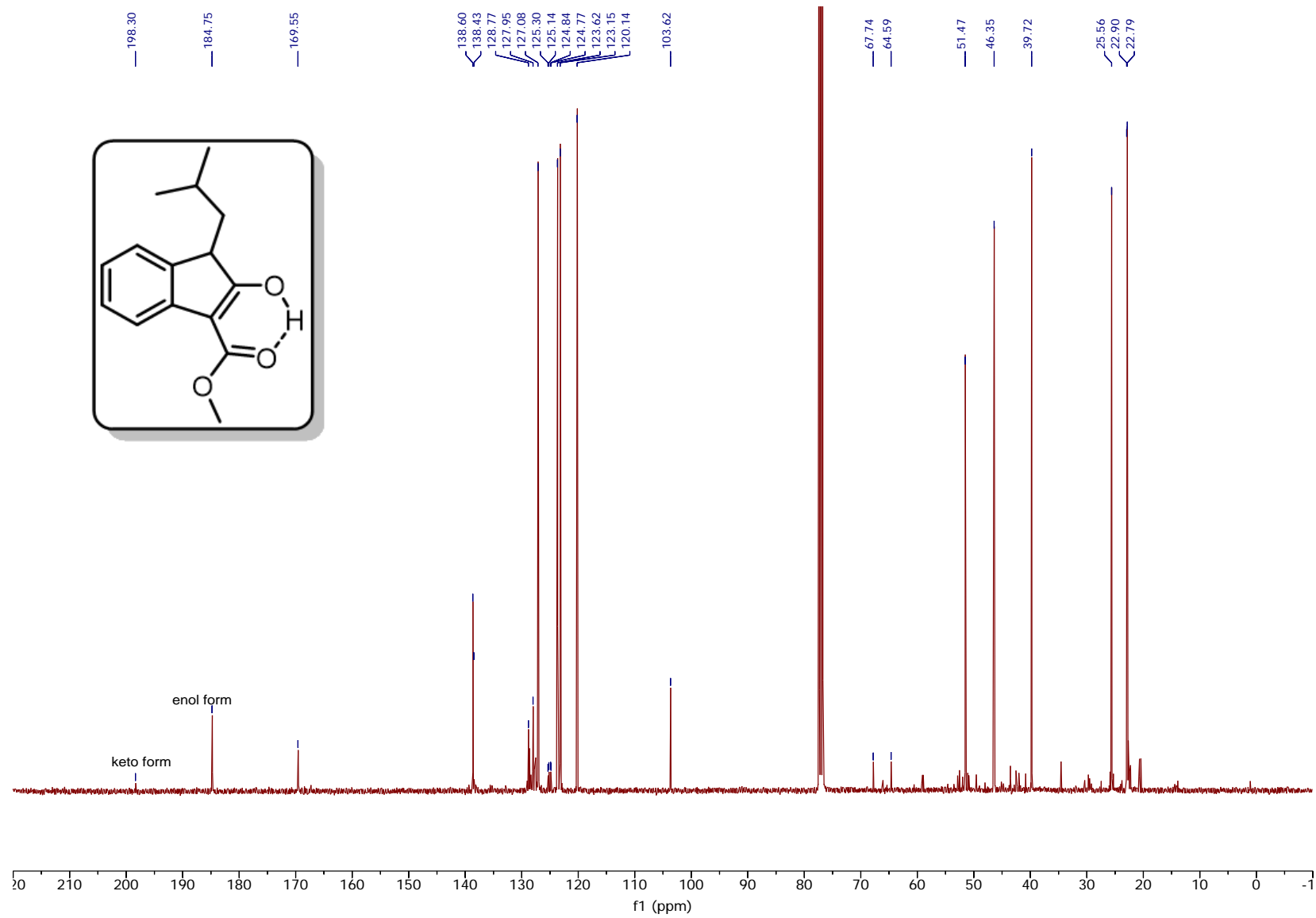


Figure S57. ^{13}C NMR of aromatic substitution product **6** in CDCl_3

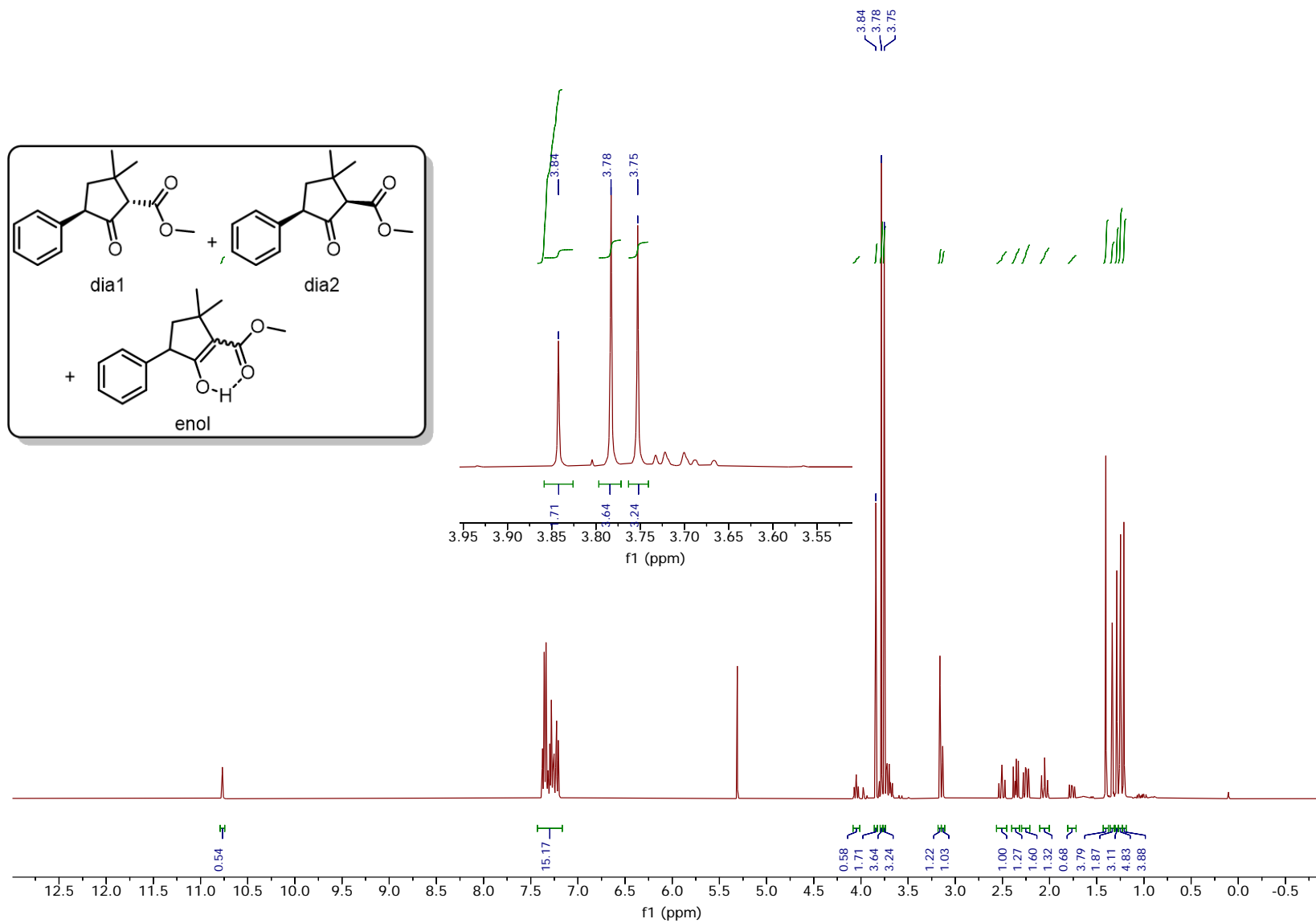


Figure S58. ¹H NMR of C-H aliphatic substitution product **7** in CDCl₃

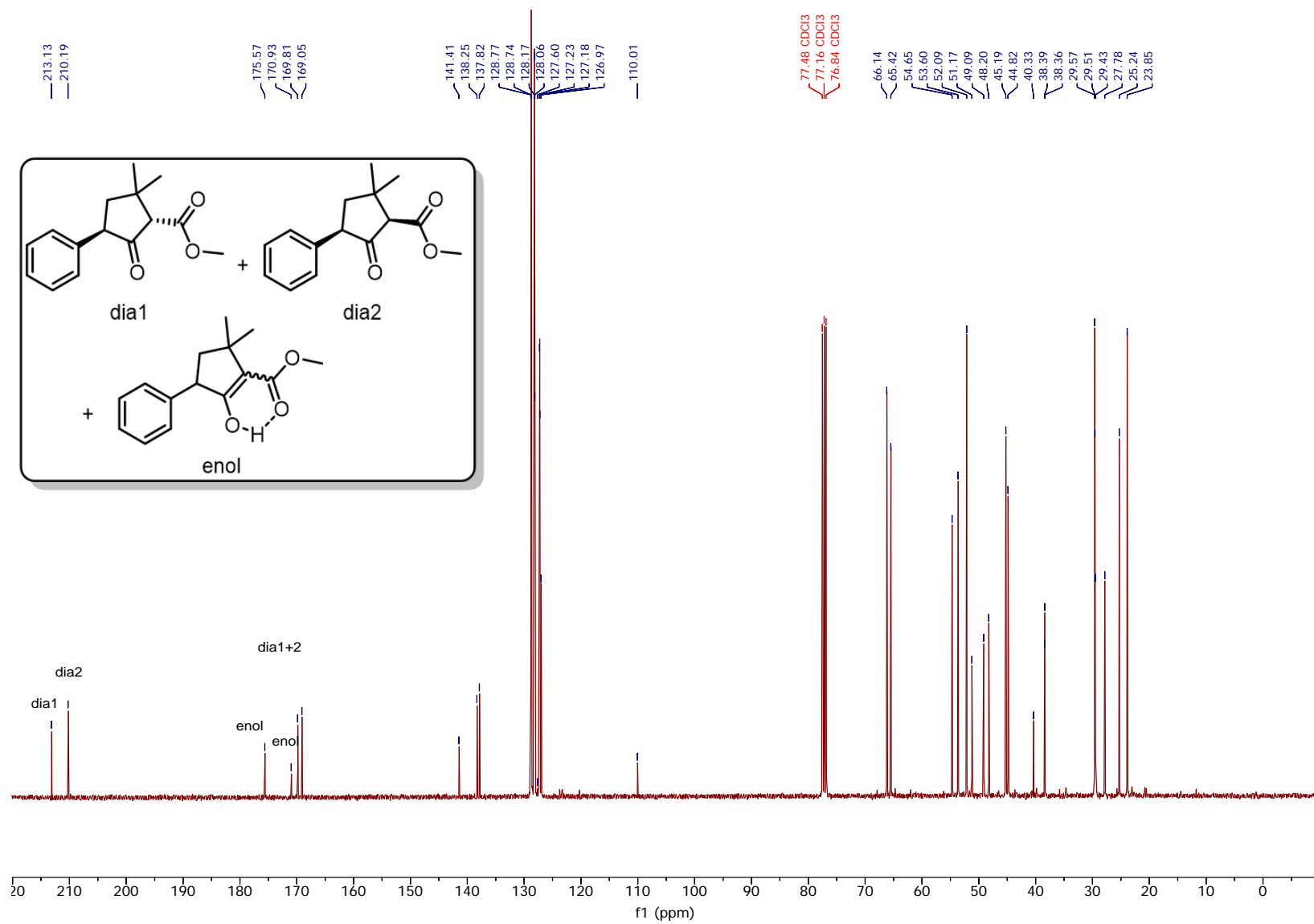


Figure S59. ¹³C NMR of C-H aliphatic substitution product **7** in CDCl₃

Electrochemical data for ferrocenecarboxylic acids 1a-k

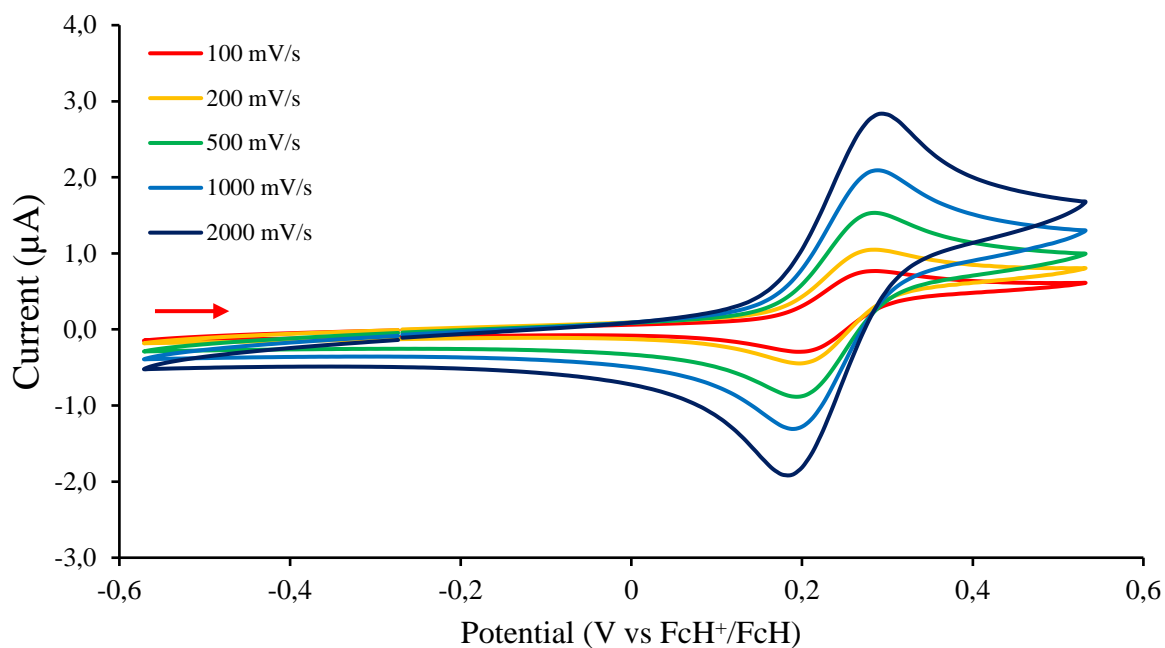


Figure S60. Cyclic voltammograms of **1a** on a Pt microelectrode, 1 mM in DCM with $[\text{n-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (100-2000 mV/s).

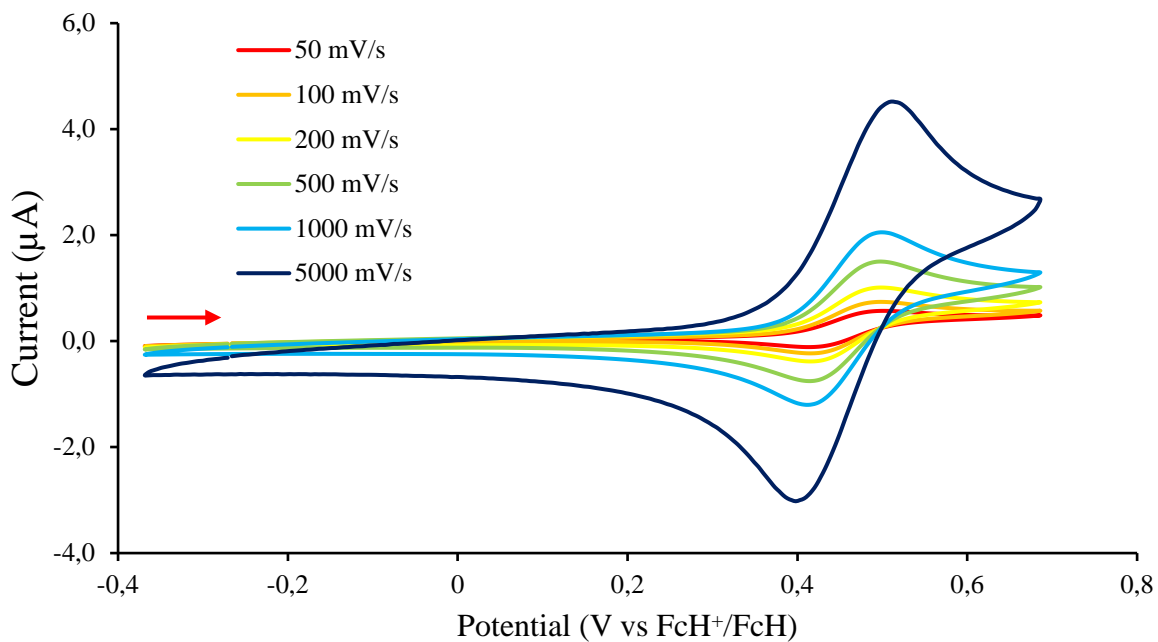


Figure S61. Cyclic voltammograms of **1b** on a Pt microelectrode, 1 mM in DCM with $[\text{n-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (50-5000 mV/s).

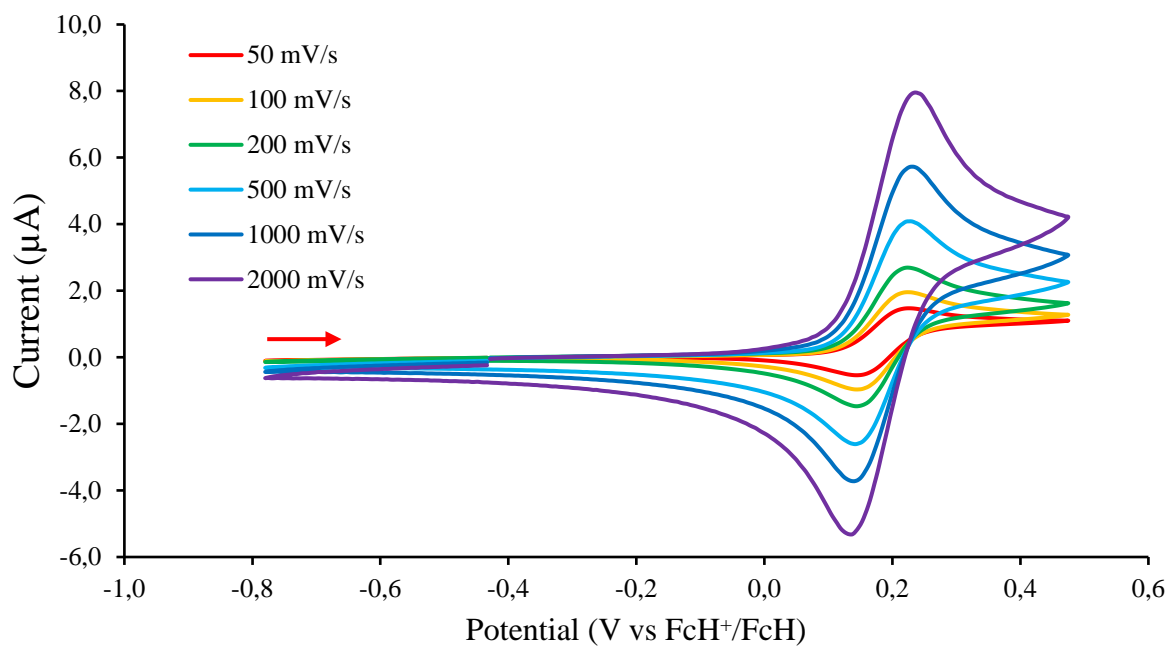


Figure S62. Cyclic voltammograms of **1c** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (50-2000 mV/s).

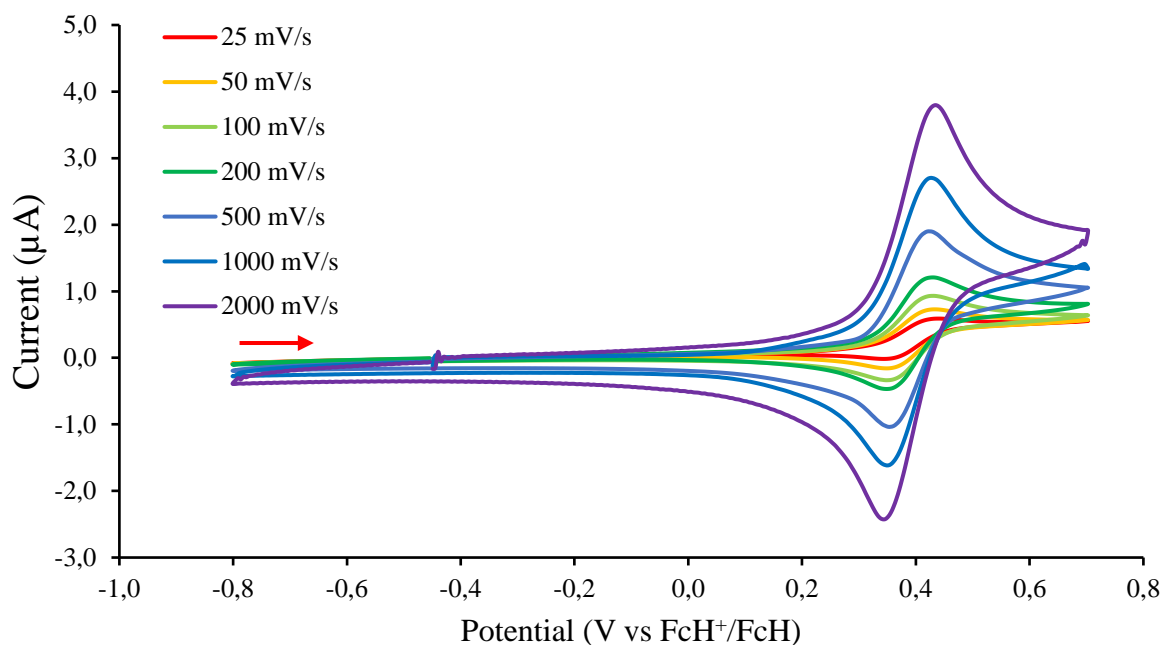


Figure S63. Cyclic voltammograms of **1d** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (25-2000 mV/s).

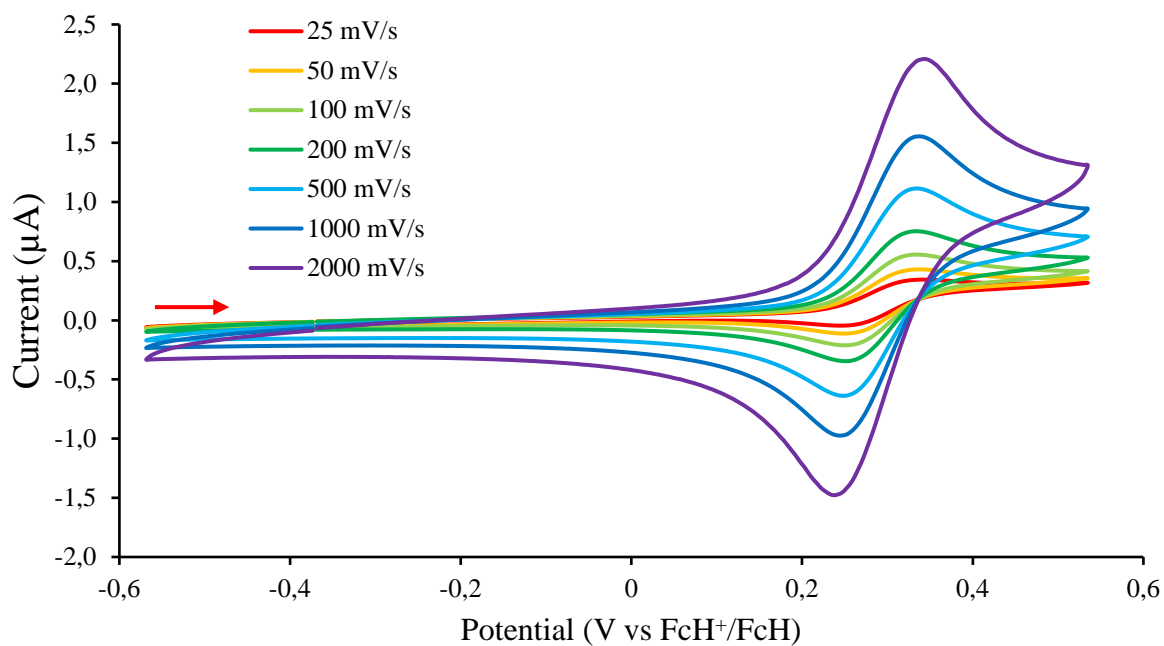


Figure S64. Cyclic voltammograms of **1e** on a Pt microelectrode, 1 mM in DCM with [n-Bu₄N][BF₄] (0.1 M) at different scan rates (25-2000 mV/s).

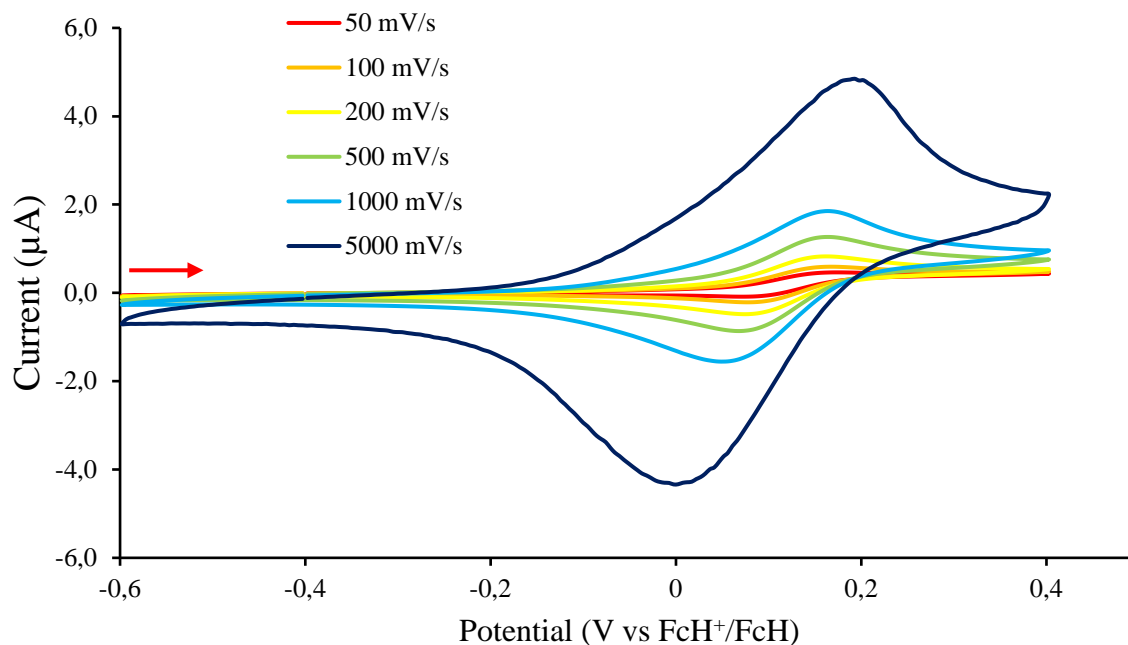


Figure S65: Cyclic voltammograms of **1f** on a Pt microelectrode, 1 mM in DCM with [n-Bu₄N][BF₄] (0.1 M) at different scan rates (50-5000 mV/s).

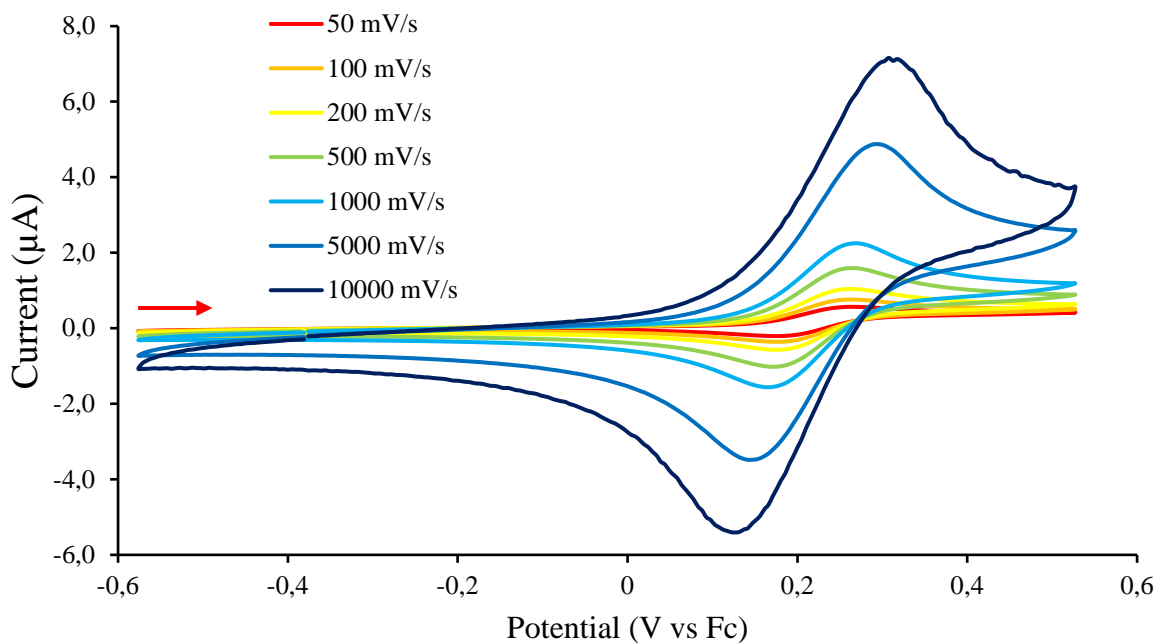


Figure S66: Cyclic voltammograms of **1g** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (50-10000 mV/s).

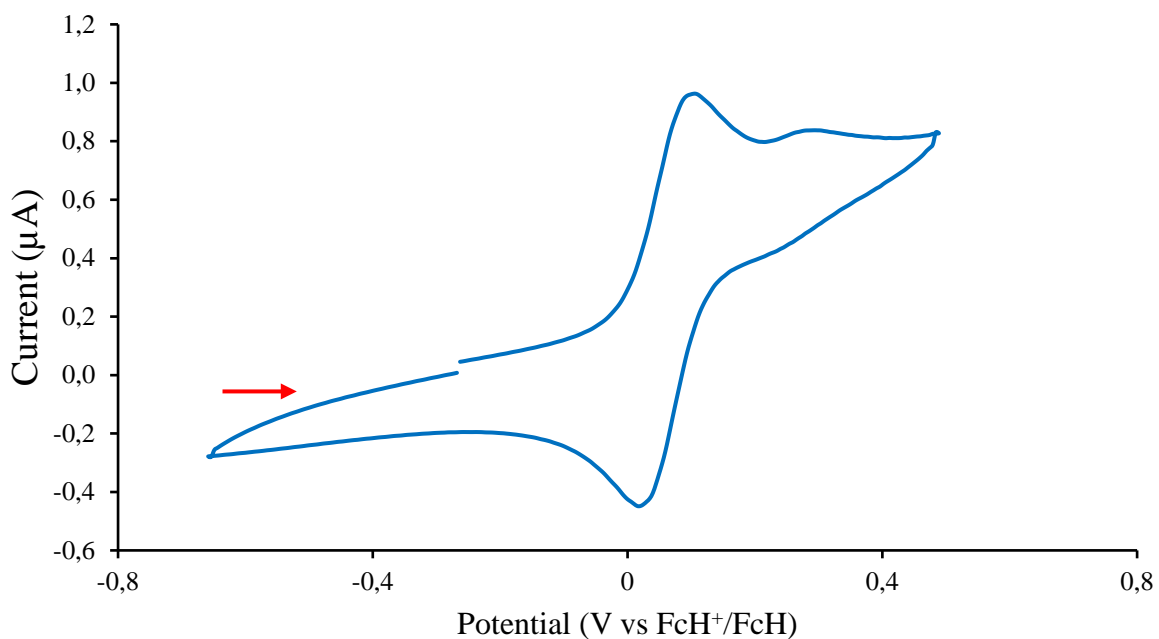


Figure S67: Cyclic voltammograms of **1h** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at a scan rate of 200 mV/s.

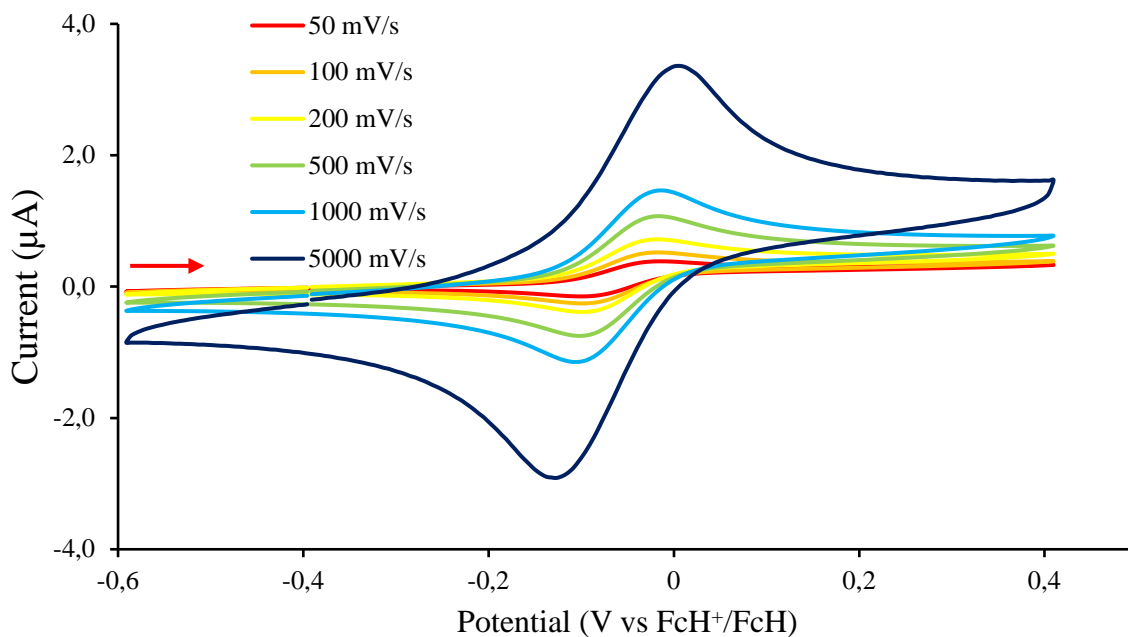


Figure S68: Cyclic voltammograms of **1i** on a Pt microelectrode, 1 mM in DCM with [n-Bu₄N][BF₄] (0.1 M) at different scan rates (50-5000 mV/s).

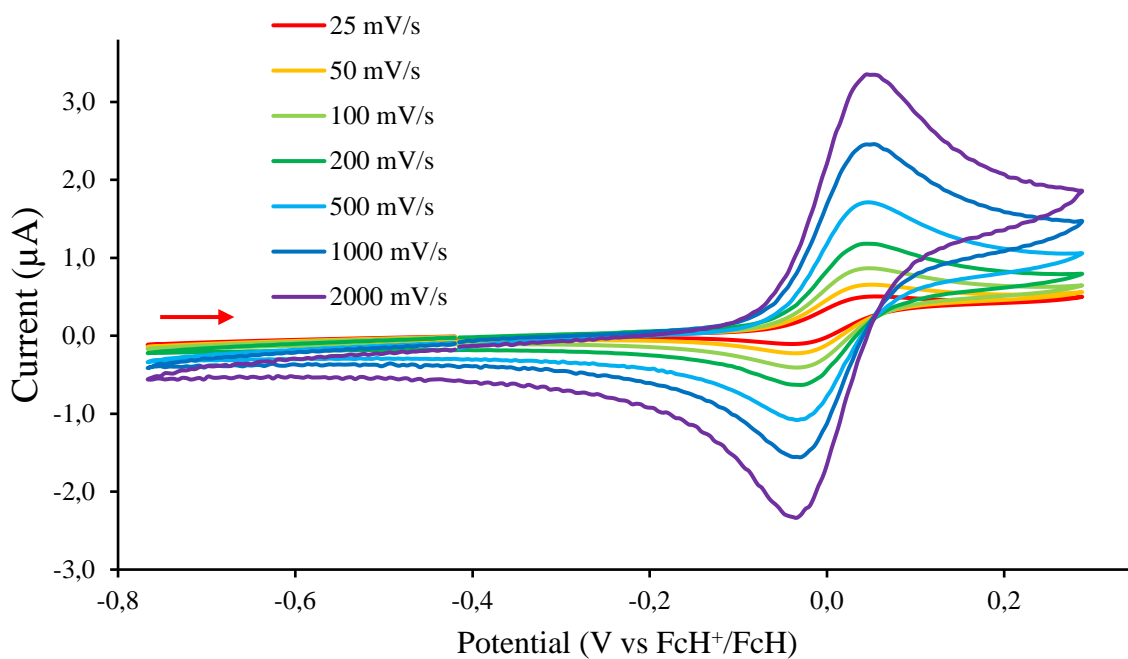


Figure S69: Cyclic voltammograms of **1j** on a Pt microelectrode, 1 mM in DCM with [n-Bu₄N][BF₄] (0.1 M) at different scan rates (25-2000 mV/s).

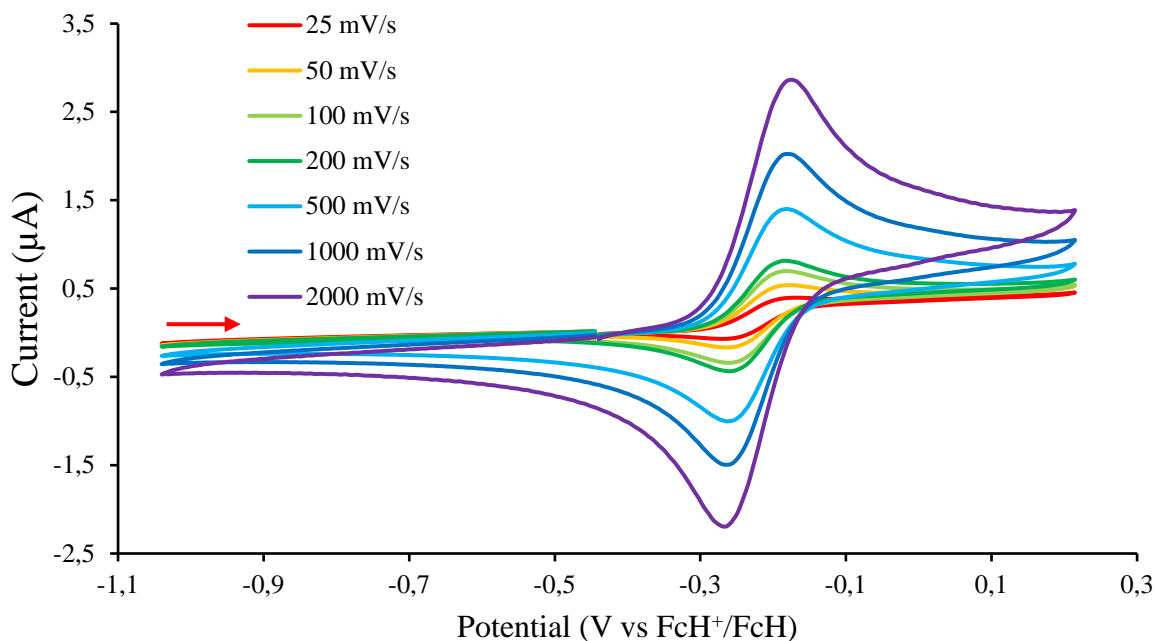


Figure S70: Cyclic voltammograms of **1k** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (25-2000 mV/s).

Electrochemical data for dirhodium(II) complexes 4a-j:

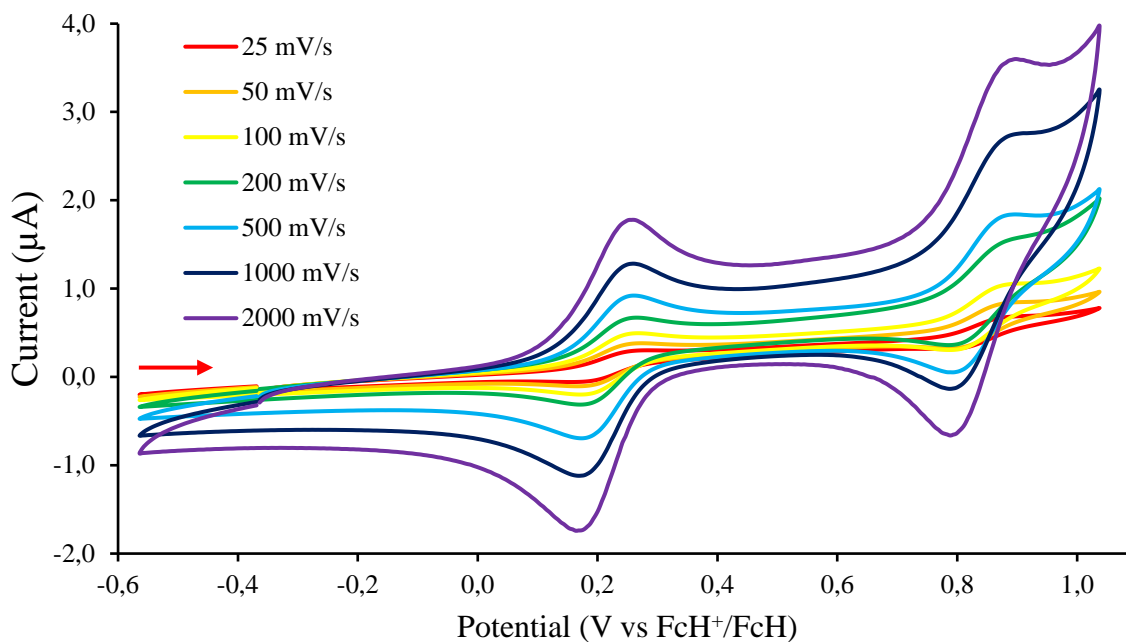


Figure S71: Cyclic voltammograms of **4a** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (25-2000 mV/s).

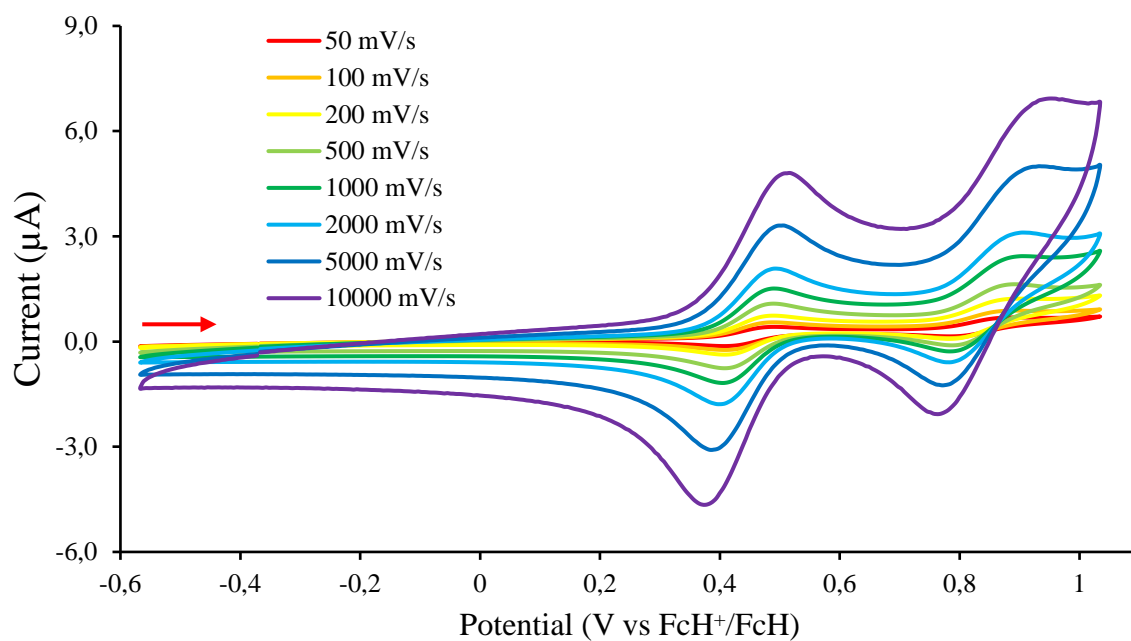


Figure S72: Cyclic voltammograms of **4b** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (50-10000 mV/s).

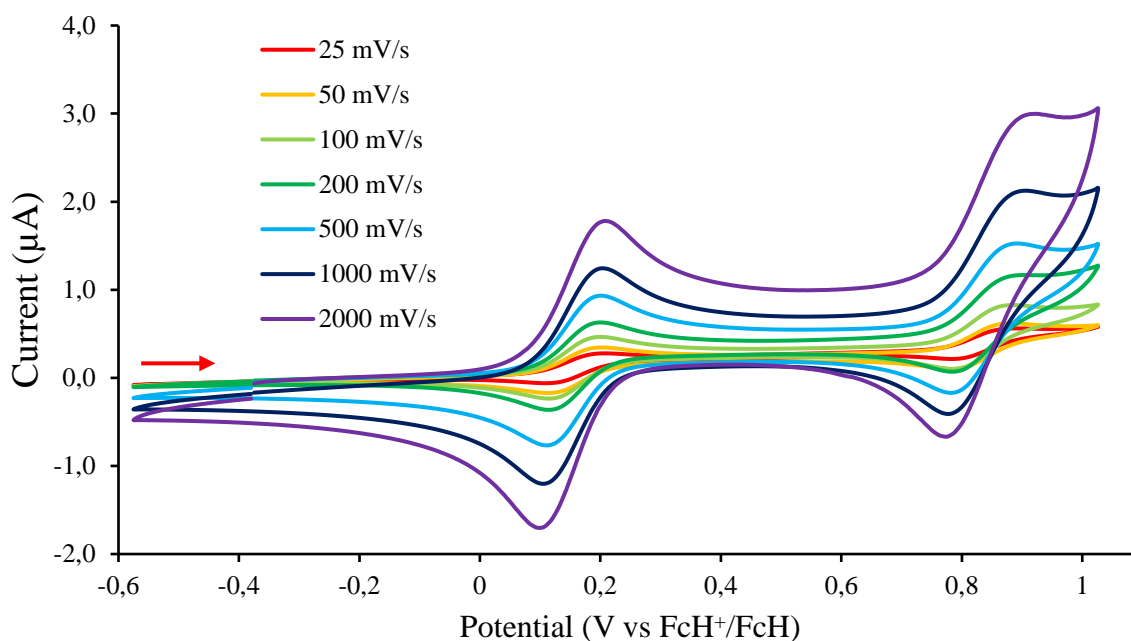


Figure S73: Cyclic voltammograms of **4c** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (25-2000 mV/s).

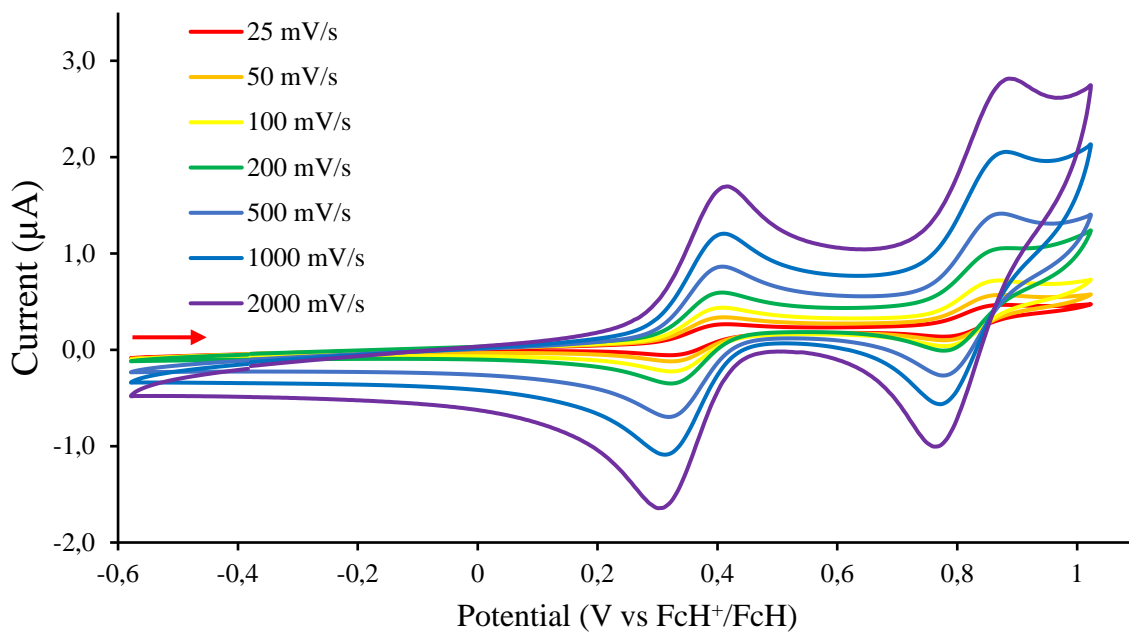


Figure S74: Cyclic voltammograms of **4d** on a Pt microelectrode, 1 mM in DCM with [n-Bu₄N][BF₄] (0.1 M) at different scan rates (25-2000 mV/s).

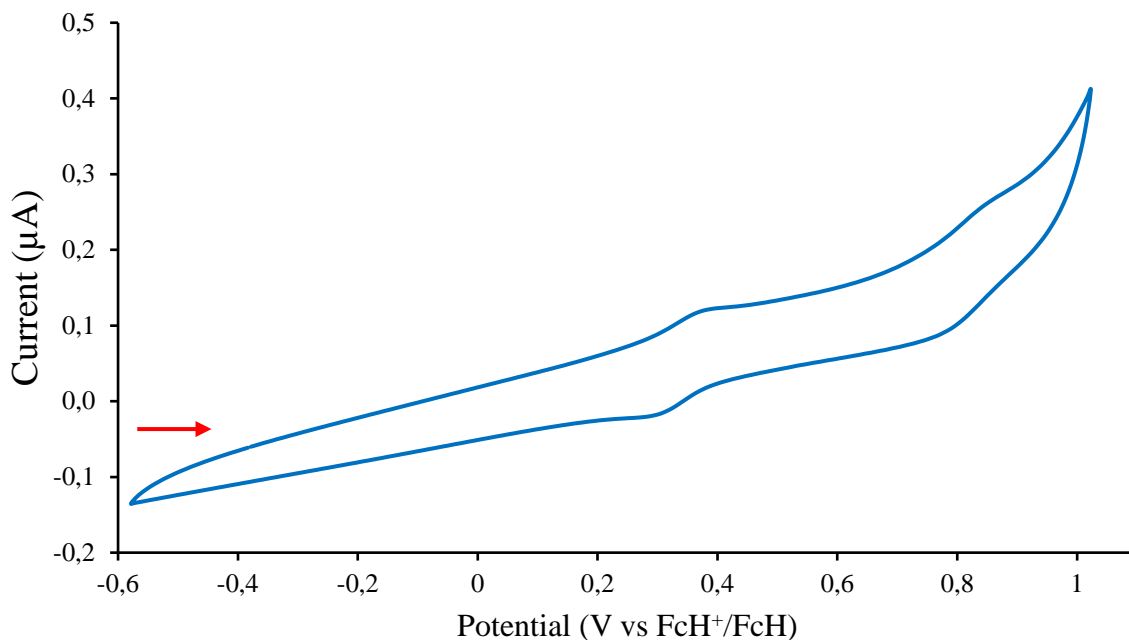


Figure S75: Cyclic voltammograms of **4e** on a Pt microelectrode, 1 mM in DCM with [n-Bu₄N][BF₄] (0.1 M) at a scan rate of 200 mV/s.

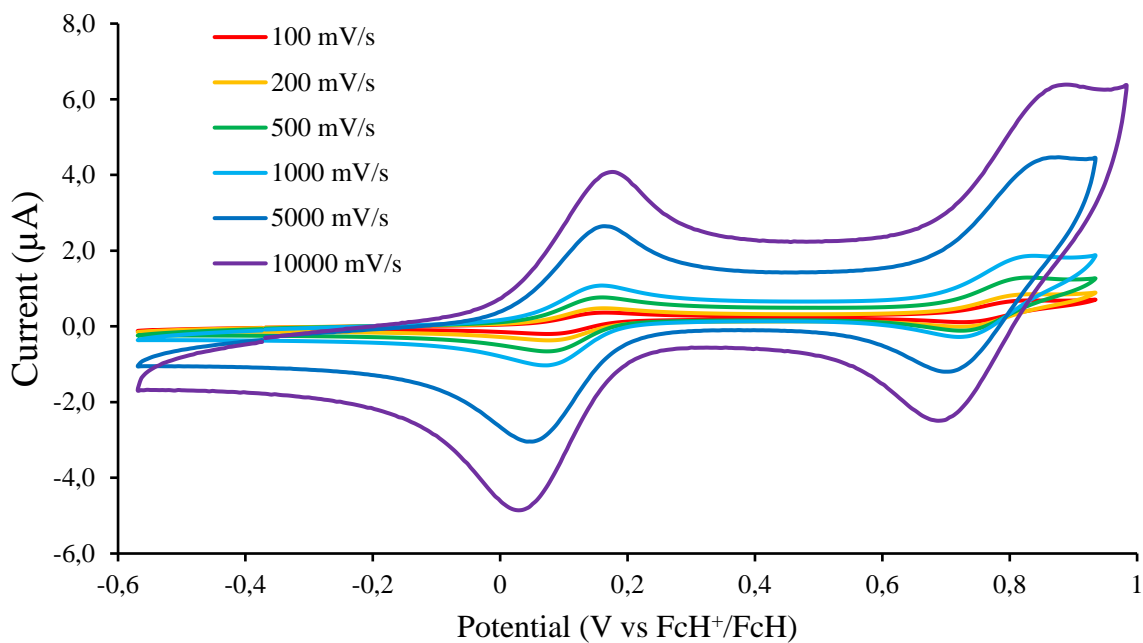


Figure S76: Cyclic voltammograms of **4f** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (100-10000 mV/s).

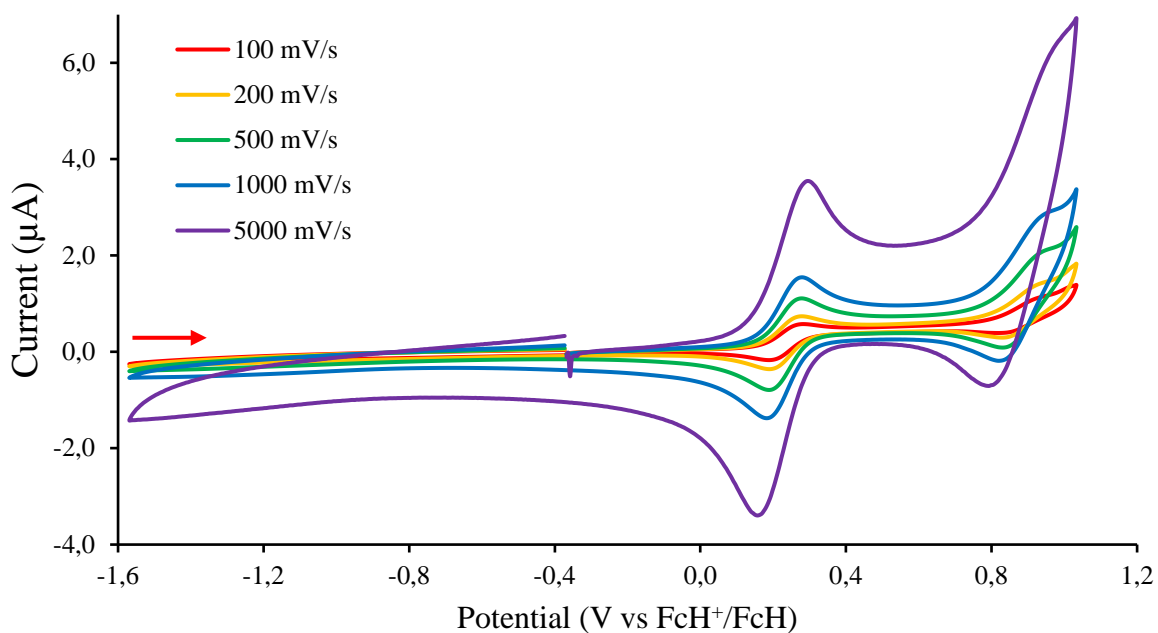


Figure S77: Cyclic voltammograms of **4g** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (100-5000 mV/s).

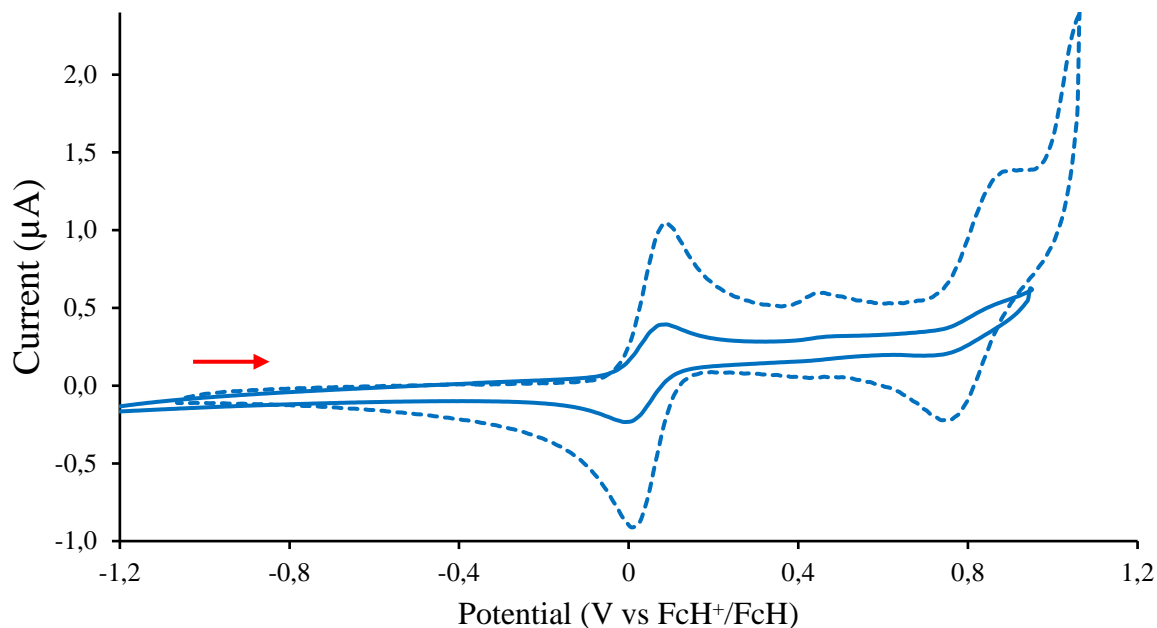


Figure S78: Cyclic voltammograms of **4h** on a Pt microelectrode (solid curve) or a glassy carbon electrode (dashed curve), 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at a scan rate of 200 mV/s.

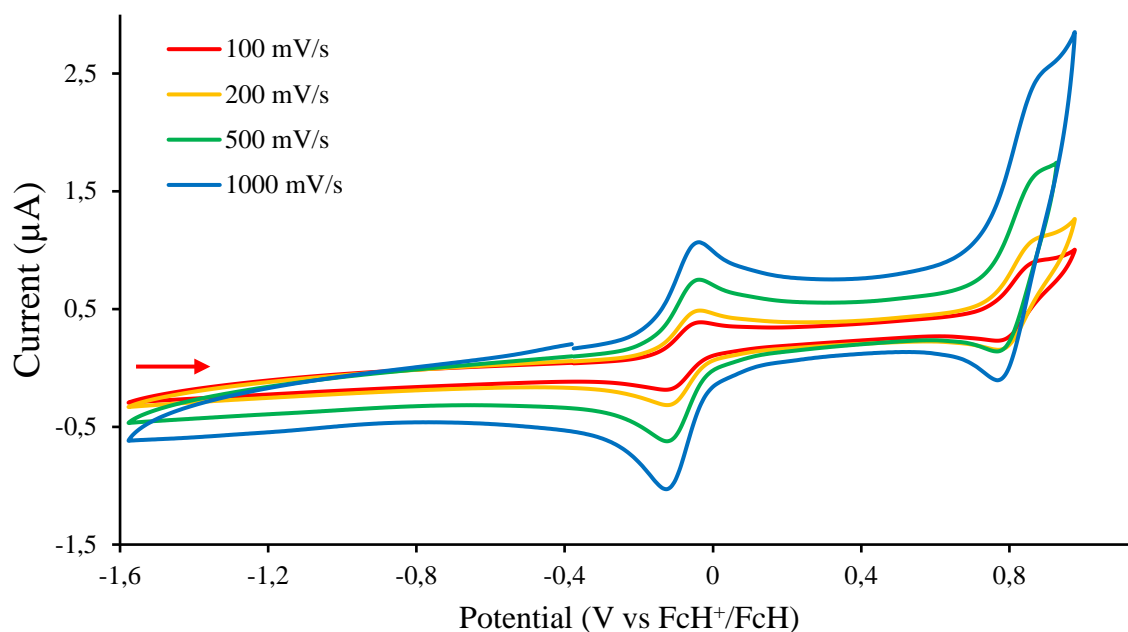


Figure S79: Cyclic voltammograms of **4i** on a Pt microelectrode, 1 mM in DCM with $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at different scan rates (100-1000 mV/s).

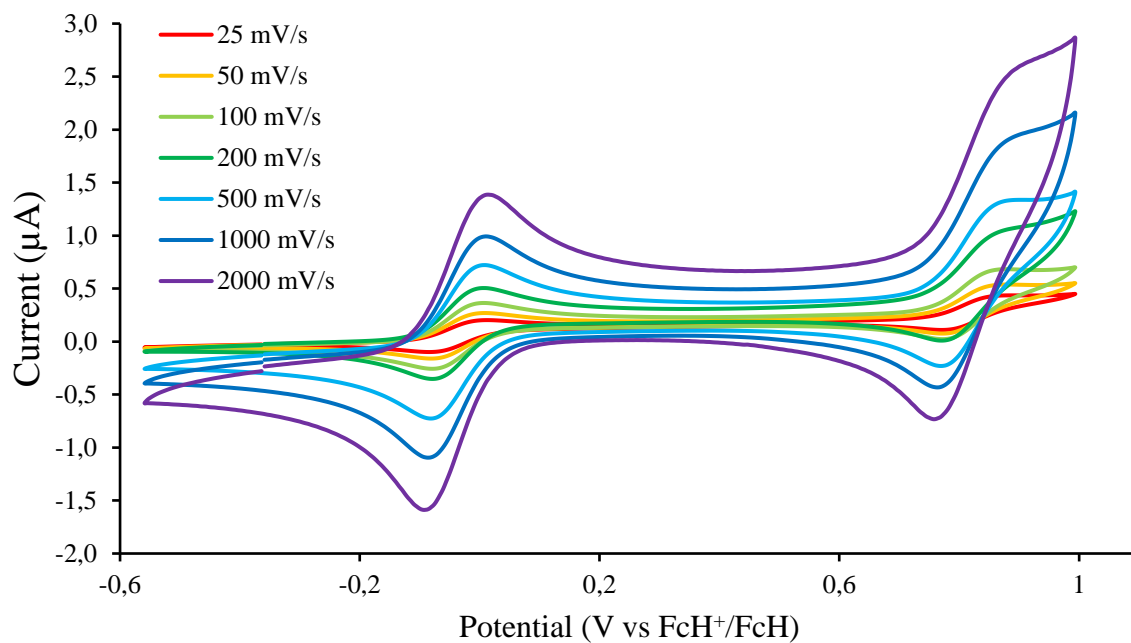


Figure S80: Cyclic voltammograms of **4j** on a Pt microelectrode, 1 mM in DCM with [n-Bu₄N][BF₄] (0.1 M) at different scan rates (25-2000 mV/s).