

SUPPLEMENTARY INFORMATION FOR

**Mild access to planar-chiral *ortho*-condensed aromatic ferrocenes via
enantioselective cationic gold(I)-catalyzed cycloisomerization of
ortho-alkynylaryl ferrocenes**

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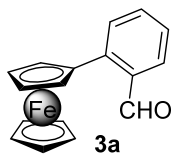
Experimental Procedures

General. Melting points were obtained in open capillary tubes and are uncorrected. ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ at 300 and 75 MHz, respectively. All reactions were monitored by thin layer chromatography that was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230-400 mesh) of Merck. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry nitrogen. Ethyl ether, CH₂Cl₂ and THF were dried over 4Å molecular sieves. All other reagent quality solvents were used without purification. For routine workup, extraction was carried out with ethyl acetate, and solvent drying with MgSO₄.

General procedure A. Suzuki Coupling

To a mixture of commercially available ferrocenyl boronic acid (**1**) (470 mg, 2 mmol), Pd(PPh₃)₄ (107 mg, 0.093 mmol) and K₃PO₄ (690 mg, 3.2 mmol), a solution of the corresponding commercially available 2-bromoaryl aldehydes **2a-k** (0.93 mmol) in toluene (15 mL) was added. The resulting suspension was refluxed overnight and filtered through Celite. After solvent evaporation and flash chromatography, the pure 2-formylaryl ferrocenes **3a-k** were obtained.

2-Formylphenyl-ferrocene (**3a**)



Compound **3a** was obtained from 2-bromobenzaldehyde (**2a**) following *general procedure A* (eluent heptane/EtOAc 5:1), in 67% yield.

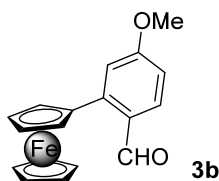
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.33 (s, 1H), 7.76 (d, $J = 7.9$ Hz, 2H), 7.44 (td, $J = 7.7, 1.4$ Hz, 1H), 7.23 (t, $J = 7.5$ Hz, 1H), 4.40 (broad s, 2H), 4.30 (broad s, 2H), 4.04 (s, 5H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.5, 143.0, 134.0, 132.9, 131.6, 127.2, 126.3, 83.4, 70.9 (2C), 69.8 (5C), 69.2 (2C).

MS (EI): m/z (%) 290 (M^+ , 15), 152 (100).

HRMS (EI): Calculated for $\text{C}_{17}\text{H}_{14}\text{FeO}$ (M^+) 290.0394, found 290.0385.

2-Formyl-5-methoxyphenyl-ferrocene (**3b**)



Compound **3b** was obtained from 2-bromo-4-methoxybenzaldehyde (**2b**) following *general procedure A*, (eluent hexane/EtOAc, 5:1), in 92% yield.

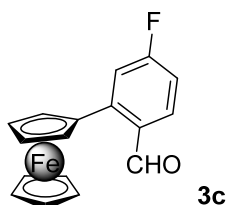
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.36 (s, 1H), 7.90 (d, $J = 8.7$ Hz, 1H), 7.36 (d, $J = 2.4$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 4.55 (broad s, 2H), 4.43 (broad s, 2H), 4.19 (s, 5H), 3.96 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.1, 163.1, 145.5, 129.9, 128.0, 116.3, 112.6, 83.7, 71.1 (2C), 69.9 (5C), 69.1 (2C), 55.5.

MS (EI): m/z (%) 320 (M^+ , 100), 182 (18), 139 (27).

HRMS (EI): Calculated for $C_{18}H_{16}O_2Fe$ (M^+) 320.0500, found 320.0507.

5-Fluoro-2-formylphenyl-ferrocene (**3c**)



Compound **3c** was obtained from 2-bromo-4-fluorobenzaldehyde (**2c**) following *general procedure A* (eluent heptane/EtOAc 5:1), in 57% yield.

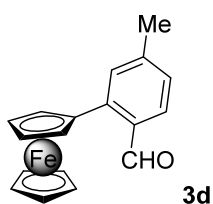
1H NMR (300 MHz, $CDCl_3$): δ 10.34 (s, 1H), 7.87 (dd, $J = 8.7, 6.2$ Hz, 1H), 7.49 (dd, $J = 10.0, 2.5$ Hz, 1H), 7.08 – 6.90 (dt, $J = 2.4, 11.1$ Hz, 1H), 4.52 (broad s, 2H), 4.40 (broad s, 2H), 4.14 (s, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 190.7, 165.1 (d, $J = 253.5$ Hz), 146.4 (d, $J = 9.6$ Hz), 130.6 (d, $J = 2.5$ Hz), 130.3 (d, $J = 10.0$ Hz), 117.6 (d, $J = 22.3$ Hz), 114.0 (d, $J = 22.2$ Hz), 82.1, 70.9 (2C), 69.9 (5C), 69.4 (2C).

MS (EI): m/z (%) 308 (M^+ , 18), 242 (22), 170 (100).

HRMS (EI): Calculated for $C_{17}H_{13}FFeO$ (M^+) 308.0300, found 308.0292.

2-Formyl-5-methylphenyl-ferrocene (**3d**)



Compound **3d** was obtained from 2-bromo-4-methylbenzaldehyde (**2d**) following *general procedure A* (eluent hexane/EtOAc 5:1), in 98% yield.

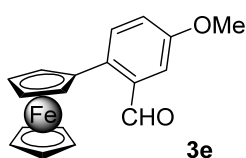
1H NMR (300 MHz, $CDCl_3$): δ 10.36 (s, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 2.1$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 4.24 (broad s, 2H), 4.20 (broad s, 2H), 4.08 (s, 5H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 192.1, 143.6, 142.9, 133.7, 131.9, 128.4, 127.4, 83.5, 70.8 (2C), 69.7 (5C), 69.0 (2C), 21.8.

MS (EI): m/z (%) 304 (M^+ , 100), 166 (45).

HRMS (EI): Calculated for $\text{C}_{18}\text{H}_{16}\text{FeO}$ (M^+) 304.0551, found 304.0563.

2-Formyl-4-methoxyphenyl-ferrocene (3e)



Compound **3e** was obtained from 2-bromo-5-methoxybenzaldehyde (**2e**) following *general procedure A*, (eluent hexane/EtOAc 20:1), in 63% yield.

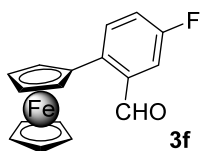
^1H NMR (300 MHz, CDCl_3): δ 10.40 (s, 1H), 7.78 (d, J = 8.6 Hz, 1H), 7.34 (d, J = 2.9 Hz, 1H), 7.13 (dd, J = 8.6, 2.9 Hz, 1H), 4.49 (broad s, 2H), 4.38 (broad s, 2H), 4.17 (s, 5H), 3.90 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 192.2, 158.0, 135.7, 134.6, 133.0, 121.2, 109.0, 83.5, 70.7 (2C), 69.7 (5C), 68.9 (2C), 55.4.

MS (EI): m/z (%) 320 (M^+ , 100), 292 (20), 277 (30), 249 (18).

HRMS (EI): Calculated for $\text{C}_{18}\text{H}_{16}\text{FeO}_2$ (M^+) 320.0501, found 320.0500

4-Fluoro-2-formylphenyl-ferrocene (3f)



Compound **3f** was obtained from 2-bromo-5-fluorobenzaldehyde (**2f**) following **general procedure A** (eluent hexane/EtOAc 15:1), in 89% yield.

¹H NMR (300 MHz, CDCl₃): δ 10.34 (d, *J* = 3.2 Hz, 1H), 7.84 (dd, *J* = 8.7, 5.2 Hz, 1H), 7.51 (dd, *J* = 9.0, 2.9 Hz, 1H), 7.29 – 7.20 (m, 1H), 4.48 (broad s, 2H), 4.39 (broad s, 2H), 4.14 (s, 5H).

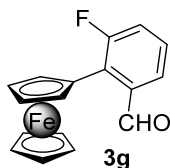
¹³C NMR (75 MHz, CDCl₃): δ 191.2, 161.2 (d, *J* = 246.7 Hz), 139.0, 135.4, 133.7, 120.4 (d, *J* = 21.7 Hz), 113.0 (d, *J* = 21.7 Hz), 82.8, 70.9 (2C), 69.8 (5C), 69.2 (2C).

¹⁹F NMR (282 MHz, CDCl₃): δ -114.92.

MS (EI): *m/z* (%) 308 (M⁺, 98), 242 (57), 170 (100).

HRMS (EI): Calculated for C₁₇H₁₃FFeO (M⁺) 308.0288, found 308.0298.

6-Fluoro-2-formylphenyl-ferrocene (**3g**)



Compound **3g** was obtained from 2-bromo-3-fluorobenzaldehyde (**2g**) following **general procedure A** (eluent heptane/EtOAc 5:1), in 55% yield.

¹H NMR (300 MHz, CDCl₃): δ 10.28 (s, 1H), 7.66 (dd, *J* = 8.6, 4.0 Hz, 1H), 7.37 – 7.28 (m, 2H), 4.56 (broad s, 2H), 4.45 (broad s, 2H), 4.15 (s, 5H).

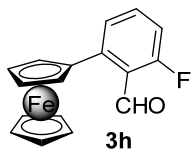
¹³C NMR (75 MHz, CDCl₃): δ 191.8, 160.4 (d, *J* = 249.0 Hz), 136.8, 130.3 (d, *J* = 13.5 Hz), 127.3 (d, *J* = 9.0 Hz), 123.7, 120.3 (d, *J* = 23.2 Hz), 75.4, 71.5 (2C), 69.9 (5C), 69.5 (2C).

¹⁹F NMR (282 MHz, CDCl₃): δ -106.98.

MS (EI): *m/z* (%) 308 (M⁺, 19), 170 (100).

HRMS (EI): Calculated for C₁₇H₁₃FFeO (M⁺) 308.0300, found 308.0302.

3-Fluoro-2-formylphenyl-ferrocene (3h)



Compound **3h** was obtained from 2-bromo-6-fluorobenzaldehyde (**2h**) following **general procedure A**, (eluent hexane/EtOAc 5:1), in 53% yield.

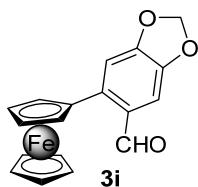
¹H NMR (300 MHz, CDCl₃): δ 10.23 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.39 (m, 1H), 7.04 – 6.95 (m, 1H), 4.54 (broad s, 2H), 4.42 (broad s, 2H), 4.15 (s, 5H).

¹³C NMR (75 MHz, CDCl₃): δ 189.9, 161.3 (d, *J* = 259.5 Hz), 144.5, 133.4 (d, *J* = 10.7 Hz), 127.2, 123.5, 114.0 (d, *J* = 22.3 Hz), 82.9, 71.0 (2C), 70.0 (5C), 69.5 (2C).

MS (EI): *m/z* (%) 308 (M⁺, 48), 170 (100).

HRMS (EI): Calculated for C₁₇H₁₃FFeO (M⁺) 308.0300, found 308.0288.

2-Formyl-4,5-(methylenedioxy)phenyl-ferrocene (3i)



Compound **3i** was obtained from 6-bromo-3,4-(methylenedioxy)benzaldehyde (**2i**) following **general procedure A** (eluent heptane/EtOAc 5:1), in 89% yield.

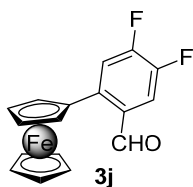
¹H NMR (300 MHz, CDCl₃): δ 10.17 (s, 1H), 7.30 (broad s, 2H), 6.06 (s, 2H), 4.47 (broad s, 2H), 4.37 (broad s, 2H), 4.17 (s, 5H).

¹³C NMR (75 MHz, CDCl₃): δ 190.4, 151.7, 146.9, 140.5, 129.2, 110.8, 105.8, 101.8, 83.8, 70.9 (2C), 69.7 (5C), 68.9 (2C).

MS (EI): *m/z* (%) 334 (M⁺, 98), 269 (57).

HRMS (EI): Calculated for $C_{18}H_{14}FeO_3$ (M^+) 334.0292, found 334.0300.

4,5-Difluoro-2-formylphenyl-ferrocene (**3j**)



Compound **3j** was obtained from 2-bromo-4,5-difluorobenzaldehyde (**2j**) following *general procedure A* (eluent heptane/EtOAc 5:1), in 75% yield.

1H NMR (300 MHz, $CDCl_3$): δ 10.29 (d, $J = 3.2$ Hz, 1H), 7.70 – 7.58 (m, 2H), 4.50 (broad s, 2H), 4.43 (broad s, 2H), 4.17 (s, 5H).

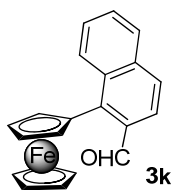
^{13}C NMR (75 MHz, $CDCl_3$): δ 189.7, 153.0 (dd, $J = 257.3, 13.6$ Hz), 149.1 (dd, $J = 251.3, 13.5$ Hz), 141.3 (d, $J = 11.2$ Hz), 130.8, 120.0 (d, $J = 18.0$ Hz), 115.9 (d, $J = 17.2$ Hz), 81.6, 70.9 (2C), 69.9 (5C), 69.5 (2C).

^{19}F NMR (282 MHz, $CDCl_3$): δ -128.99 (d, $J = 21.8$ Hz), -138.90 (d, $J = 21.8$ Hz).

MS (EI): m/z (%) 326 (M^+ , 18), 260 (20), 188 (100).

HRMS (EI): Calculated for $C_{17}H_{12}F_2FeO$ (M^+) 326.0206, found 326.0207.

2-Formylnaphthyl-ferrocene (**3k**)



Compound **3k** was obtained from 1-bromo-2-naphthaldehyde (**2k**) following *general procedure A* (eluent hexane/EtOAc 5:1), in 79% yield.

¹H NMR (300 MHz, CDCl₃): δ 9.55 (d, *J* = 8.3 Hz, 1H), 8.04 – 7.79 (m, 3H), 7.72 – 7.56 (m, 2H), 7.34 (broad s, 1H), 4.65 (broad s, 2H), 4.57 (broad s, 2H), 4.24 (s, 5H).

¹³C NMR (75 MHz, CDCl₃): δ 193.5, 141.8, 135.9, 133.6, 132.0, 128.5, 128.3, 128.1, 127.6, 125.4, 123.1, 81.1, 73.4 (2C), 69.9 (5C), 68.9 (2C).

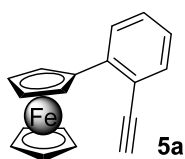
MS (EI): *m/z* (%) 340 (M⁺, 100), 252 (20).

HRMS (EI): Calculated for C₂₁H₁₆FeO (M⁺) 340.0541, found 340.0551.

General procedure B. Seyferth-Gilbert homologation

The corresponding 2-formylaryl ferrocenes **3a-k** (0.550 mmol), dimethyl (1-diazo-2-oxopropyl)-phosphonate (Ohira-Bestmann reagent) (318 mg, 1.65 mmol) and K₂CO₃ (381 mg, 2.76 mmol) were suspended in dry MeOH (5 mL) and stirred for 20 h at r.t. After evaporation of the solvent, the crude was partitioned between CH₂Cl₂ and brine. The combined organic layers were dried (Na₂SO₄), evaporated, and the residue purified by flash chromatography, affording pure 2-alkynylaryl ferrocenes **5a-k**.

2-Ethynylphenyl-ferrocene (5a)



Compound **5a** was obtained from 2-formylphenyl-ferrocene (**3a**) following **general procedure B** (eluent hexane/EtOAc 5:1), in 98% yield.

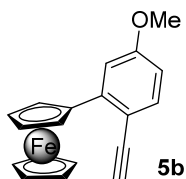
¹H NMR (300 MHz, CDCl₃): δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 4.95 (broad s, 2H), 4.32 (broad s, 2H), 4.11 (s, 5H), 3.27 (s, 1H).

¹³C NMR (75 MHz, CDCl₃): δ 141.4, 134.6, 129.0, 128.5, 125.5, 119.5, 84.4, 84.3, 81.1, 69.7 (5C), 69.0 (2C), 68.6 (2C).

MS (EI): m/z (%) 286 (M^+ , 90), 165 (100).

HRMS (EI): Calculated for $C_{18}H_{24}Fe$ (M^+) 286.0445, found 286.0457.

2-Ethynyl-5-methoxyphenyl-ferrocene (**5b**)



Compound **5b** was obtained from 2-formyl-5-methoxyferrocene (**3b**) following *general procedure B*, (eluent hexane to hexane/EtOAc, 5:1), in 44% yield.

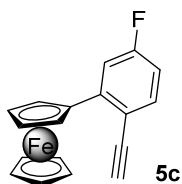
1H NMR δ (300 MHz, $CDCl_3$): 7.35 (d, J = 8.6 Hz, 1H), 7.04 (d, J = 2.6 Hz, 1H), 6.64 (dd, J = 8.6 and 2.7 Hz, 1H), 4.87 (broad s, 2H), 4.25 (broad s, 2H), 4.04 (s, 5H), 3.78 (s, 3H), 3.17 (s, 1H).

^{13}C NMR δ (75 MHz, $CDCl_3$): 159.5, 143.1, 136.1, 114.5, 112.1, 111.4, 84.4, 84.3, 79.8, 69.8 (5C), 69.1 (2C), 68.7 (2C), 55.3

MS (EI): m/z (%) 316 (M^+ , 100).

HRMS (EI): Calculated for $C_{19}H_{16}OFe$ (M^+) 316.0551, found 316.0561.

2-Ethynyl-5-fluorophenyl-ferrocene (**5c**)



Compound **5c** was obtained from 5-fluoro-2-formylphenyl-ferrocene (**3c**) following *general procedure B* (eluent heptane/EtOAc 5:1), in 64% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.46 (dd, *J* = 8.5, 6.1 Hz, 1H), 7.27 (dd, *J* = 10.5, 2.3 Hz, 1H), 6.86 (td, *J* = 8.2, 2.6 Hz, 1H), 4.96 (broad s, 2H), 4.36 (broad s, 2H), 4.12 (s, 5H), 3.29 (s, 1H).

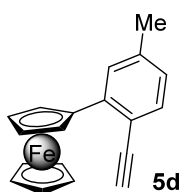
¹³C NMR (75 MHz, CDCl₃): δ 162.4 (d, *J* = 248.7 Hz), 144.5, 144.4, 136.5 (d, *J* = 8.9 Hz), 115.3 (d, *J* = 22.7 Hz), 112.9 (d, *J* = 22.2 Hz), 83.5, 83.2, 80.8, 69.8 (5C), 69.0 (4C).

¹⁹F NMR (282 MHz, CDCl₃): δ -111.13.

MS (EI): *m/z* (%) 304 (M⁺, 100), 246 (20).

HRMS (EI): Calculated for C₁₈H₁₃FFe (M⁺) 304.0351, found 304.0345.

2-Ethynyl-5-methylphenyl-ferrocene (5d)



Compound **5d** was obtained from 2-formyl-5-methylphenyl-ferrocene (**3d**) following **general procedure B** (eluent hexane), in 87% yield.

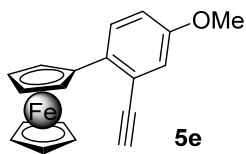
¹H NMR (300 MHz, CDCl₃): δ 7.38 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 4.95 (broad s, 2H), 4.32 (broad s, 2H), 4.11 (s, 5H), 3.29 (s, 1H), 2.38 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 141.1, 138.4, 134.6, 129.4, 126.5, 116.6, 84.5, 84.5, 80.6, 69.7 (5C), 68.8 (2C), 68.5 (2C), 21.5.

MS (EI): *m/z* (%) 300 (M⁺, 100), 178 (20).

HRMS (EI): Calculated for C₁₉H₁₆Fe (M⁺) 300.0601, found 300.0606.

2-Ethynyl-4-methoxyphenyl-ferrocene (**5e**)



Compound **5e** was obtained from 2-formyl-4-methoxyphenyl-ferrocene (**3e**) following *general procedure B* (eluent hexane/EtOAc 10:1), in 85% yield.

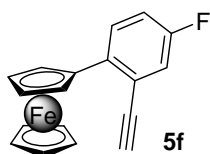
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.54 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 2.6 Hz, 1H), 6.87 (dd, J = 8.6, 2.6 Hz, 1H) 4.90 (broad s, 2H), 4.32 (broad s, 2H), 4.13 (s, 5H), 3.82 (s, 3H), 3.28 (s, 1H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 157.1, 133.7, 130.2, 120.0, 118.2, 115.9, 84.6, 84.1, 80.9, 69.6 (5C), 68.6 (2C), 68.2 (2C), 55.3.

MS (EI): m/z (%) 316 (M^+ , 100), 152 (31).

HMRS (EI): Calculated for $\text{C}_{19}\text{H}_{16}\text{FeO}$ (M^+) 316.0551, found 316.0556.

2-Ethynyl-4-fluorophenyl-ferrocene (**5f**)



Compound **5f** was obtained from 4-fluoro-2-formylphenyl-ferrocene (**3f**) following *general procedure B* (eluent hexane), in 86% yield.

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.56 (dd, J = 8.7, 5.8 Hz, 1H), 7.17 (dd, J = 9.1, 2.6 Hz, 1H), 7.01 (td, J = 8.5, 2.6 Hz, 1H), 4.89 (broad s, 2H), 4.34 (broad s, 2H), 4.12 (s, 5H), 3.34 (s, 1H).

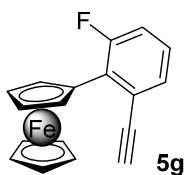
$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 160.2 (d, J = 243.7 Hz), 137.6 (d, J = 3.0 Hz), 130.6 (d, J = 8.3 Hz), 120.9, 120.6 (d, J = 23.2 Hz), 116.2 (d, J = 21.0 Hz), 83.8, 83.1, 82.0, 69.7 (5C), 68.9 (2C), 68.6 (2C).

^{19}F NMR (282 MHz, CDCl_3): δ -117.22.

MS (EI): m/z (%) 304 (M^+ , 100).

HMRS (EI): Calculated for $\text{C}_{18}\text{H}_{13}\text{FFe}$ (M^+) 304.0351, found 304.0364.

2-Ethynyl-6-fluorophenyl-ferrocene (5g)



Compound **5g** was obtained from 6-fluoro-2-formylphenyl-ferrocene (**3g**) following *general procedure B* (eluent heptane/EtOAc 5:1), in 65% yield.

^1H NMR (300 MHz, CDCl_3): δ 7.27 (dd, $J = 7.6, 1.0$ Hz, 1H), 7.20 – 7.05 (m, 2H), 4.96 (broad s, 2H), 4.37 (broad s, 2H), 4.09 (s, 5H), 3.30 (s, 1H).

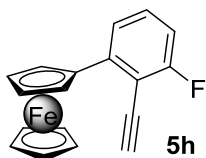
^{13}C NMR (75 MHz, CDCl_3): δ 160.1 (d, $J = 247.5$ Hz), 130.7, 129.3, 126.5 (d, $J = 9.8$ Hz), 122.1, 116.5 (d, $J = 24.0$ Hz), 83.7, 83.6, 81.8, 70.3 (2C), 69.7 (5C), 68.5 (2C).

^{19}F NMR (282 MHz, CDCl_3): δ -107.82.

MS (EI+): m/z (%) 304 (M^+ , 100), 183 (26).

HRMS: Calculated for $\text{C}_{18}\text{H}_{13}\text{FFe}$ (M^+) 304.0351, found 304.0349.

2-Ethynyl-3-fluorophenyl-ferrocene (5h)



Compound **5h** was obtained from 2-formyl-3-fluorophenyl-ferrocene (**3h**) following *general procedure B* (eluent hexane/AcOEt 5:1), in 53% yield.

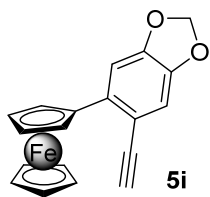
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.29 (d, $J = 7.9$ Hz, 1H), 7.25 - 7.20 (m, 1H), 6.85 (td, $J = 8.7, 1.1$ Hz, 1H), 4.88 (broad s, 2H), 4.28 (broad s, 2H), 4.03 (s, 5H), 3.50 (s, 1H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 165.8 (d, $J = 250.2$ Hz), 144.2, 129.3 (d, $J = 9.3$ Hz), 124.3 (d, $J = 3.2$ Hz), 112.3 (d, $J = 22.0$ Hz), 108.5, 87.0, 86.9, 83.2, 69.8 (5C), 69.1 (2C), 69.00 (2C).

MS (EI): m/z (%) 304 (M^+ , 100), 183 (19).

HMRS (EI): Calculated for $\text{C}_{18}\text{H}_{13}\text{Fe}$ (M^+) 304.0351, found 304.0356.

2-Ethynyl-4,5-(methylenedioxy)phenyl-ferrocene (**5i**)



Compound **5i** was obtained from 2-formyl-4,5-(methylenedioxy)phenyl-ferrocene (**3i**) following the *general procedure B* (eluent hexane), in 60% yield.

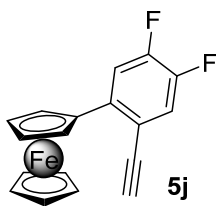
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.09 (s, 1H), 6.90 (s, 1H), 5.99 (s, 2H), 4.85 (broad s, 2H), 4.30 (broad s, 2H), 4.12 (s, 5H), 3.20 (s, 1H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 148.2, 145.5, 136.7, 113.2, 112.4, 109.0, 101.4, 84.8, 84.2, 79.6, 69.6 (5C), 69.1 (2C), 68.3 (2C).

MS (EI): m/z (%) 330 (M^+ , 100), 216 (15).

HRMS (EI): Calculated for $\text{C}_{19}\text{H}_{14}\text{FeO}_2$ (M^+) 330.0343, found 330.0353.

4,5-Difluoro-2-ethynylphenyl-ferrocene (**5j**)



Compound **5j** was obtained from 4,5-difluoro-2-formylphenyl-ferrocene (**3j**) following **general procedure B** (eluent heptane/EtOAc 5:1), in 79% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.38 (dd, *J* = 11.8, 8.1 Hz, 1H), 7.28 (dd, *J* = 10.6, 8.2 Hz, 1H), 4.91 (broad s, 2H), 4.36 (broad s, 2H), 4.13 (s, 5H), 3.32 (s, 1H).

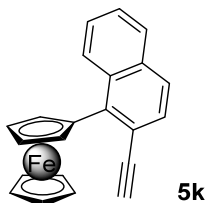
¹³C NMR (75 MHz, CDCl₃): δ 149.2 (dd, *J* = 251.2, 12.9 Hz), 146.6 (dd, *J* = 248.5, 13.4 Hz), 138.5 (dd, *J* = 6.5, 3.6 Hz), 121.7 (dd, *J* = 18.3, 1.1 Hz), 116.3 (d, *J* = 18.3 Hz), 114.6 (dd, *J* = 7.1, 3.5 Hz), 81.6, 81.3, 80.7, 68.7 (5C), 67.9 (2C), 67.9 (2C).

¹⁹F NMR (282 MHz, CDCl₃): δ -135.38 (d, *J* = 22.2 Hz), -141.01 (d, *J* = 22.2 Hz).

MS (EI+): *m/z* (%) 322 (M⁺, 100), 201 (34).

HRMS: Calculated for C₁₈H₁₂F₂Fe (M⁺) 322.0256, found 322.0256.

2-Ethynylnaphthyl-ferrocene (**5k**)



Compound **5k** was obtained from 2-formylnaphthyl-ferrocene (**3k**) following **general procedure B** (eluent hexane/AcOEt 5:1), in 61% yield.

¹H NMR (300 MHz, CDCl₃): δ 9.43 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.47 (m, 3H), 4.98 (broad s, 2H), 4.45 (broad s, 2H), 4.21 (s, 5H), 3.33 (s, 1H).

¹³C NMR (75 MHz, CDCl₃): δ 138.7, 133.7, 131.7, 130.7, 128.3, 127.5, 126.7, 126.4, 125.2, 119.5, 85.7, 83.2, 82.1, 72.1 (2C), 69.8 (5C), 67.8 (2C).

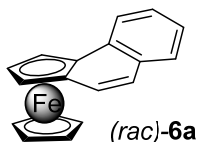
MS (EI): *m/z* (%) 336 (M⁺, 100).

HRMS (EI): Calculated for C₂₂H₁₆Fe (M⁺) 336.0601, found 336.0806.

General procedure C. PtCl₂-catalyzed cycloisomerization

In a high-necked-schlenck flask, a solution of the corresponding alkyne (0.15 mmol) and PtCl₂ (4 mg, 0.015 mmol) in dry toluene (2.2 mL), under an argon atmosphere, was heated at 100 °C for the time indicated in each case. The crude mixture was filtered through celite and washed with hexane. After solvent removal, the corresponding *ortho*-condensed aromatic ferrocenes, which didn't need further purification, were obtained in practically quantitative yield. Pure analytical samples could be obtained by flash chromatography using a short pad of neutralized silica gel eluting with hexane.

(rac)-Ferrocene[3]helicene (6a).



Compound (*rac*)-**6a** was obtained from 2-ethynylphenyl-ferrocene (**5a**) following **general procedure C** (4 h).

¹H NMR (500 MHz, CDCl₃): δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.41 (m, 2H), 7.18 (d, *J* = 9.1 Hz, 1H), 5.27 (broad s, 1H), 4.82 (broad s, 1H), 4.23 (broad s, 1H), 3.74 (s, 5H).

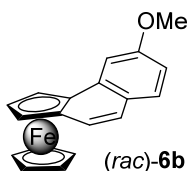
¹³C NMR (126 MHz, CDCl₃): δ 135.1, 131.9, 128.6, 127.5, 126.6, 125.2 (2C), 123.3, 83.9, 83.0, 69.3 (5C), 69.2, 64.0, 61.1.

MS (EI): *m/z* (%) 286 (M⁺, 90), 165 (100).

HRMS: Calculated for C₁₈H₂₄Fe (M⁺) 286.0445, found 286.0457.

HPLC: Daicel Chiralpak IB, hexano / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, $R_t = 19.3$ min, $R_t = 21.6$ min, $T = 25$ °C).

(rac)-8-Methoxyferrocene[3]helicene (6b)



Compound (rac)-6b was obtained from 2-ethynyl-1-ferrocenyl-5-methoxybenzene (5b) following **general procedure C** (5 h).

¹H NMR (500 MHz, CDCl₃): δ 7.55 (d, $J = 8.4$ Hz, 1H), 7.43 (broad s, 1H), 7.22 (d, $J = 8.9$ Hz, 1H), 7.11 (d, $J = 8.9$ Hz, 1H), 7.02 (d, $J = 7.4$ Hz, 1H), 5.19 (broad s, 1H), 4.81 (broad s, 1H), 4.22 (broad s, 1H), 3.98 (s, 3H), 3.74 (s, 5H).

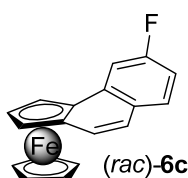
¹³C NMR (126 MHz, CDCl₃): δ 158.5, 136.7, 129.9, 125.9, 124.8, 124.5, 113.0, 106.5, 84.5, 82.6, 69.3 (5C), 69.1, 63.9, 61.0, 55.5.

MS (EI): m/z (%) 316 (M^+ , 90), 195 (98), 152 (100).

HRMS: Calculated for C₁₉H₁₆OFe (M^+) 316.0551, found 316.0553.

HPLC: Daicel Chiralpak IB, hexane / 2-propanol 96:4; 0.4 mL min⁻¹, 254 nm, $R_t = 15.2$ min, $R_t = 40.4$ min, $T = 25$ °C

(rac)-8-Fluoroferrocene[3]helicene (6c)



Compound (*rac*)-**6c** was obtained from 2-ethynyl-1-ferrocenyl-5-fluorobenzene (**5c**) following **general procedure C** (3 h).

¹H NMR δ (500 MHz, CDCl₃): 7.68 – 7.53 (m, 2H), 7.34 (d, *J* = 9.1 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 5.20 (broad s, 1H), 4.83 (broad s, 1H), 4.25 (broad s, 1H), 3.75 (s, 5H).

¹³C NMR δ (126 MHz, CDCl₃): 161.6 (d, *J* = 245.6 Hz), 137.2 (d, *J* = 8.8 Hz), 130.3 (d, *J* = 8.9 Hz), 128.3, 126.4, 124.4, 113.1 (d, *J* = 22.9 Hz), 108.9 (d, *J* = 21.8 Hz), 84.2, 82.2, 69.5, 69.4 (5C), 64.3, 61.3.

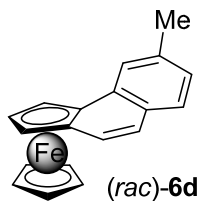
¹⁹F NMR δ (282 MHz, CDCl₃): -114.17.

MS (EI): *m/z* (%) 304 (M⁺, 100), 183 (30).

HRMS: Calculated for C₁₈H₁₃FFe (M⁺) 304.0351, found 304.0354.

HPLC: Daicel Chiralpak IA, CO₂ /MeOH 98:2; 1.0 mL min⁻¹, 254 nm, *R*_t = 41.7 min, *R*_t = 49.3 min, *T* = 25 °C

(*rac*)-8-Methylferrocene-[3]-helicene (**6d**)



Compound (*rac*)-**6d** was obtained from 2-ethynyl-1-ferrocenyl-5-methylbenzene (**5d**) following **general procedure C** (6 h).

¹H NMR (300 MHz, CDCl₃): δ 7.78 (broad s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.22 (m, 2H), 7.15 (d, *J* = 7.9 Hz, 1H), 5.26 (broad s, 1H), 4.83 (broad s, 1H), 4.22 (broad s, 1H), 3.75 (s, 5H), 2.55 (s, 3H).

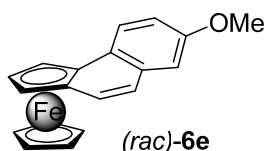
¹³C NMR (75 MHz, CDCl₃): δ 136.4, 135.1, 129.6, 128.4, 126.6, 126.2, 125.1, 123.4, 84.2, 82.9, 69.3 (5C), 69.02, 63.9, 60.9, 21.8.

MS (EI): *m/z* (%) 300 (M⁺, 100), 179 (13).

HRMS: Calculated for C₁₉H₁₆ (M⁺) 300.0601, found 300.0592.

HPLC: Daicel Chiralpak IB, hexane / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, $R_t = 15.8$ min, $R_t = 21.8$ min, $T = 25$ °C.

(rac)-7-Methoxyferrocene-[3]-helicene (6e).



Compound (rac)-6e was obtained from 2-ethynyl-4-methoxyphenyl-ferrocene (5e) following **general procedure C** (10 h).

¹H NMR (500 MHz, CDCl₃): δ 7.91 (d, $J = 8.4$ Hz, 1H), 7.38 (d, $J = 9.0$ Hz, 1H), 7.11 (m, 3H), 5.20 (broad s, 1H), 4.77 (broad s, 1H), 4.18 (broad s, 1H), 3.92 (s, 3H), 3.73 (s, 5H).

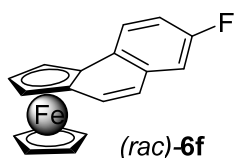
¹³C NMR (126 MHz, CDCl₃): δ 157.5, 133.2, 128.4, 128.1, 124.9, 124.6, 115.2, 111.0, 83.8, 83.0, 69.2 (5C), 68.8, 63.7, 60.6, 55.4.

MS (EI): m/z (%) 316 (M^+ , 100), 273 (52), 215 (47),

HRMS: Calculated for C₁₉H₁₆FeO (M^+) 316.0551, found 316.0543.

HPLC: Daicel Chiralpak IC, hexane / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, $R_t = 30.4$ min, $R_t = 33.5$ min, $T = 25$ °C.

(rac)-7-Fluoroferrocene-[3]-helicene (6f).



Compound (rac)-6f was obtained from 2-ethynyl-4-fluorophenyl-ferrocene (5f) following **general procedure C** (5 h).

¹H NMR (500 MHz, CDCl₃): δ 7.95 (dd, *J* = 8.4, 5.7 Hz, 1H), 7.44 (d, *J* = 9.1 Hz, 1H), 7.30 (dd, *J* = 9.7, 2.1 Hz, 1H), 7.20 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.10 (d, *J* = 9.1 Hz, 1H), 5.24 (broad s, 1H), 4.81 (broad s, 1H), 4.23 (broad s, 1H), 3.74 (s, 5H).

¹³C NMR (126 MHz, CDCl₃): δ 160.8 (d, *J* = 243.0 Hz), 133.4 (d, *J* = 8.3 Hz), 131.1, 129.3, 124.9 (d, *J* = 8.4 Hz), 124.3, 114.5 (d, *J* = 22.9 Hz), 113.7 (d, *J* = 21.0 Hz), 83.2, 83.0, 69.3 (5C), 69.3, 64.1, 61.0.

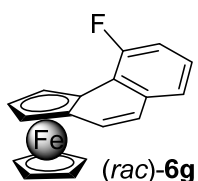
¹⁹F NMR (282 MHz, CDCl₃): δ -117.21.

MS (EI): *m/z* (%) 304 (M⁺, 100), 183 (54).

HRMS: Calculated for C₁₈H₁₃FFe (M⁺) 304.0351, found 304.0343.

HPLC-SFC: Daicel Chiralpak IA, CO₂/MeOH 98:2; 1.0 mL min⁻¹, 254 nm, *R*_t = 33.1 min, *R*_t = 36.7 min, *T* = 25 °C.

(rac)-9-Fluoro-ferrocene-[3]helicene (6g)



Compound (*rac*)-**6g** was obtained from 2-ethynyl-1-ferrocenyl-6-fluorobenzene (**5g**) following **general procedure C** (3h).

¹H NMR (500 MHz, CDCl₃): δ 7.47 – 7.39 (m, 2H), 7.34 (td, *J* = 7.9 and 5.3 Hz, 1H), 7.22 – 7.12 (m, 2H), 5.53 (broad s, 1H), 4.81 (broad s, 1H), 4.25 (broad s, 1H), 3.78 (s, 5H).

¹³C NMR (126 MHz, CDCl₃): δ 159.9 (d, *J* = 248.0 Hz), 134.6 (d, *J* = 5.6 Hz), 129.0, 125.4 (d, *J* = 8.6 Hz), 124.3, 124.1, 123.7, 112.6 (d, *J* = 21.3 Hz), 83.6, 78.4, 70.0, 69.2 (5C), 65.7, 63.9.

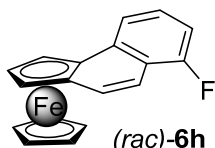
¹⁹F NMR δ (282 MHz, CDCl₃): -117.13.

MS (EI): *m/z* (%) 304 (M⁺, 100), 183 (30).

HRMS: Calculated for $C_{18}H_{13}Fe$ (M^+) 304.0351, found 304.0355.

HPLC: Daicel Chiralpak IA, CO₂/ MeOH 98:2; 1.0 mL min⁻¹, 254 nm, $R_t = 37.9$ min, $R_t = 41.6$ min, $T = 25$ °C

(rac)-6-Fluoro-ferrocene-[3]helicene (6h).



Compound (rac)-6h was obtained from 2-ethynyl-1-ferrocenyl-3-fluorobenzene (5h) following **general procedure C** (15 h).

¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, $J = 7.9$ Hz, 1H), 7.54 – 7.38 (m, 3H), 7.14 (dd, $J = 9.9, 8.5$ Hz, 1H), 5.30 (broad s, 1H), 4.90 (broad s, 1H), 4.31 (broad s, 1H), 3.80 (s, 5H).

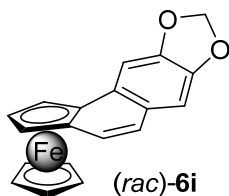
¹³C NMR (126 MHz, CDCl₃): δ 159.6 (d, $J = 249.2$ Hz), 137.3, 128.3, 127.1 (d, $J = 8.9$ Hz), 120.6 (d, $J = 14.7$ Hz), 118.9, 116.5, 110.7 (d, $J = 21.3$ Hz), 83.8, 82.2, 69.7, 69.4 (5C), 64.4, 61.6.

MS (EI): m/z (%) 304 (M^+ , 100), 163 (10).

HRMS: Calculated for $C_{18}H_{13}Fe$ (M^+) 304.0351, found 304.0342.

HPLC: Daicel Chiralpak IC, hexano / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, $R_t = 14.3$ min, $R_t = 15.3$ min, $T = 25$ °C.

(rac)-7,8-(Methylenedioxy)ferrocene-[3]-helicene (6i)



Compound (rac)-6i was obtained from 2-ethynyl-4,5-(methylenedioxy)phenyl-ferrocene (5i) following **general procedure C** (5 h).

¹H NMR (300 MHz, CDCl₃): δ 7.38 (s, 1H), 7.24 (s, 1H), 7.03 (m, 2H), 6.03 (m, 2H), 5.11 (broad s, 1H), 4.77 (broad s, 1H), 4.13 (broad s, 1H), 3.70 (s, 5H).

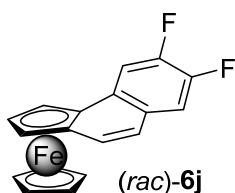
¹³C NMR (75 MHz, CDCl₃): δ 147.2, 146.1, 130.1, 126.9, 125.5, 124.9, 107.3, 102.5, 101.0, 84.1, 83.9, 69.1 (5C), 68.9, 63.4, 60.4.

MS (EI+): *m/z* (%) 330 (M⁺, 100), 264 (25), 215 (25).

HRMS: Calculated for C₁₉H₁₄O₂Fe (M⁺) 330.0343, found 330.0334.

HPLC: Daicel Chiralpak IC, hexano / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, *R*_t = 22.1 min, *R*_t = 29.8 min, *T* = 25 °C.

(rac)-7,8-Difluoro-ferrocene-[3]helicene (6j)



Compound (*rac*)-**6j** was obtained from 2-ethynyl-1-ferrocenyl-4,5-difluorobenzene (**5j**) following **general procedure C** (8 h).

¹H NMR (300 MHz, CDCl₃): δ 7.65 (dd, *J* = 11.1 and 7.8 Hz, 1H), 7.32 (m, 2H), 6.98 (d, *J* = 9.2 Hz, 1H), 5.09 (broad s, 1H), 4.76 (broad s, 1H), 4.17 (broad s, 1H), 3.68 (s, 5H).

¹³C NMR (75 MHz, CDCl₃): δ 149.6 (dd, *J* = 246.7 and 13.5 Hz), 148.6 (dd, *J* = 244.5 and 13.5 Hz), 132.1, 128.5, 128.3, 123.5, 115.9 (d, *J* = 17.0 Hz), 111.0 (d, *J* = 17.7 Hz), 83.5, 82.2, 69.6, 69.4 (5C), 64.3, 61.2.

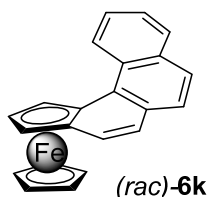
¹⁹F NMR δ (282 MHz, CDCl₃): -138.21 (d, *J* = 21.4 Hz), -141.25 (d, *J* = 21.5 Hz).

MS (EI): *m/z* (%) 322 (M⁺, 100).

HRMS: Calculated for C₁₈H₁₂F₂Fe (M⁺) 322.0256, found 322.0255.

HPLC: Daicel Chiralpak IA, hexane / 2-propanol 100:0; 0.4 mL min⁻¹, 254 nm, *R*_t = 17.5 min, *R*_t = 22.3 min, *T* = 25 °C.

(rac)-Ferrocene-[4]helicene (6k).



Compound (*rac*)-**6k** was obtained from 2-ethynyl-1-naphthylferrocene (**5k**) following **general procedure C** (15 h).

¹H NMR δ (500 MHz, CDCl₃): 9.17 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.63 (m, 2H), 7.37 (d, *J* = 8.9 Hz, 1H), 5.79 (broad s, 1H), 5.03 (broad s, 1H), 4.34 (broad s, 1H), 3.76 (s, 5H).

¹³C NMR δ (126 MHz, CDCl₃): 133.2, 131.9, 131.1, 130.9, 128.8, 128.5, 127.9, 126.3, 126.1, 126.1, 125.7, 125.5, 86.7, 82.3, 70.8, 68.9 (5C), 65.6, 64.0.

MS (EI): *m/z* (%) 336 (M⁺, 50), 154 (88), 57 (100).

HRMS: Calculated for C₂₂H₁₆Fe (M⁺) 336.0601, found 336.0596.

HPLC: Daicel Chiralpak IC, hexano / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, *R_t* = 28.2 min, *R_t* = 30.2 min, *T* = 25 °C).

Synthesis of chiral gold complex (R)-DTBM-Segphos-(AuCl)₂

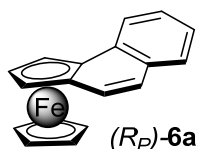
To a solution of commercially available Me₂S·AuCl (40 mg, 0.136 mmol) in CH₂Cl₂ (8.4 mL) cooled to 0 °C, a solution of commercially available chiral phosphine (*R*)-DTBM-Segphos (80 mg, 0.068 mmol) in CH₂Cl₂ (4.2 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred overnight. After evaporation of the solvent, the desired gold(I) complex was obtained.

General procedure D. Enantioselective Au(I)-Catalyzed Cycloisomerization

A solution of (*R*)-DTBM-Segphos-(AuCl)₂ (14 mg, 0.0089 mmol) and commercially available AgSbF₆ (6.5 mg, 0.0178 mmol) in dry toluene (0.2 mL), in the dark and under argon atmosphere, was stirred at room

temperature for 5 min. After cooling to 0 °C, a solution of the corresponding 2-alkynylaryl ferrocene **5a-k** (0.089 mmol) in toluene (0.5 mL) was slowly added and the resulting mixture stirred at the same temperature for the time indicated in each case. Then, hexane (0.6 mL) was added and the mixture filtered through celite to remove the metal residues. After evaporation of the solvent and flash chromatography using neutralized silica gel (eluent hexane), the corresponding pure enantioenriched *ortho*-condensed aromatic ferrocenes were obtained.

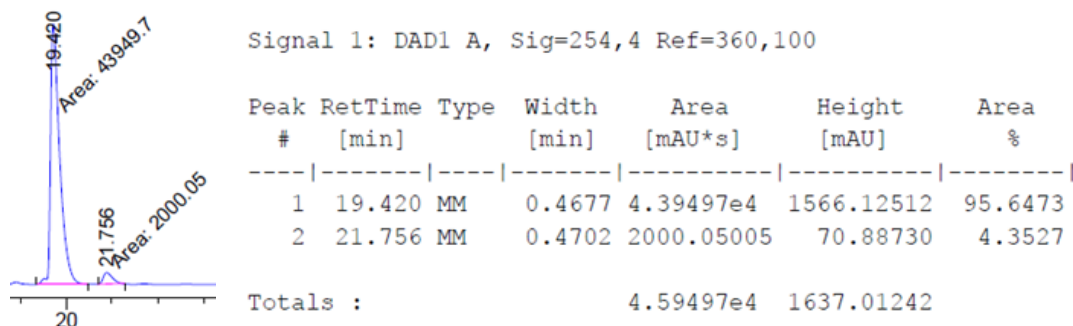
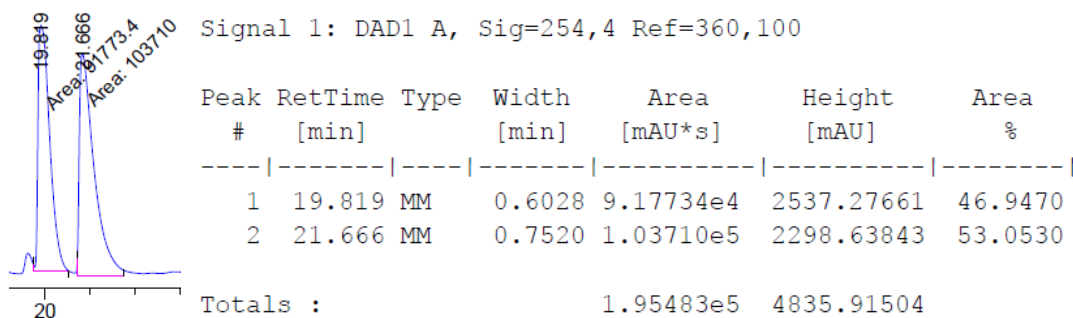
(*R_p*)-Ferrocene[3]helicene (6a).



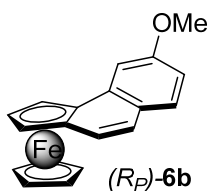
Compound (*R_p*)-**6a** was obtained from 2-ethynylphenyl-ferrocene (**5a**) following **general procedure D** (4 h), in 92% yield.

$[\alpha]_D^{20} = +932$ ($c = 0.040$, CHCl_2), 91% *ee*.

HPLC: Daicel Chiralpak IB, hexano / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, $R_t = 21.2$ min, $T = 25$ °C).



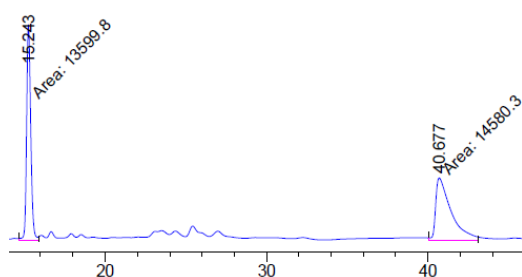
(*R_p*)-8-Methoxyferrocene[3]helicene (6b)



Compound (*R_p*)-**6b** was obtained from 2-ethynyl-1-ferrocenyl-5-methoxybenzene **5b** following *general procedure D* (3 h), in 83% yield.

$[\alpha]_D^{20} = +2750$ (*c* 0.007, CH₂Cl₂), 83% *ee*.

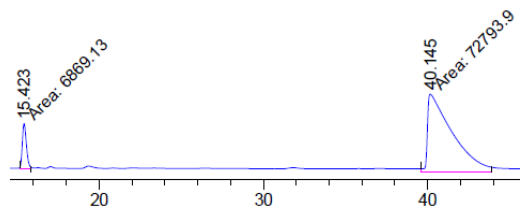
HPLC: Daicel Chiralpak IB, hexane / 2-propanol 96:4; 0.4 mL min⁻¹, 254 nm, *R_t* = 40.1 min, *T* = 25 °C



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.243	MM	0.2973	1.35998e4	762.46027	47.5026
2	40.677	MM	1.1031	1.45803e4	220.29704	50.9277
3	63.752	BB	0.9566	449.40881	5.53897	1.5697

Totals : 2.86295e4 988.29628

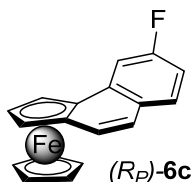


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.423	MM	0.2884	6869.13184	396.99210	8.6227
2	40.145	MM	1.7547	7.27939e4	691.43701	91.3773

Totals : 7.96630e4 1088.42911

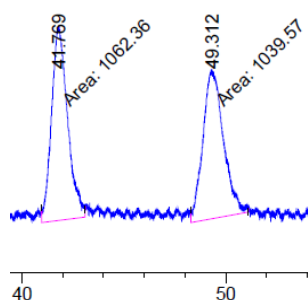
(*R_p*)-8-Fluoroferrrocene[3]helicene (6c)



Compound (*R_p*)-**6c** was obtained from 2-ethynyl-1-ferrocenyl-5-fluorobenzene **5c** following *general procedure D* (3 h), in 85% yield.

$[\alpha]_D^{20} = +3260$ (c 0.08, CH_2Cl_2), 92% *ee*.

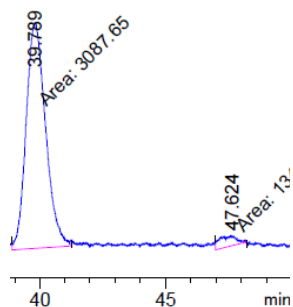
HPLC: Daicel Chiralpak IA, CO_2 /MeOH 98:2; 1.0 mL min^{-1} , 254 nm, $R_t = 39.8$ min, $T = 25$ °C



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.769	MM	0.9126	1062.35681	19.40245	50.5420
2	49.312	MM	1.1660	1039.57288	14.85958	49.4580

Totals : 2101.92969 34.26203

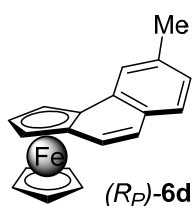


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.789	MM	0.8940	3087.65381	57.56224	95.8298
2	47.624	MM	0.8409	134.36462	2.66326	4.1702

Totals : 3222.01843 60.22549

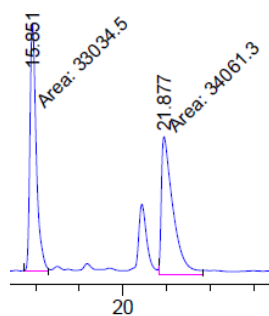
(*R*_p)-8-Methylferrocene-[3]-helicene (6d)



Compound (*R*_p)-**6d** was obtained from 2-ethynyl-1-ferrocenyl-5-methylbenzene (**5d**) following **general procedure D** (6 h), in 84% yield.

$[\alpha]_D^{20} = +980$ ($c = 0.012$, CHCl_2), 91% *ee*.

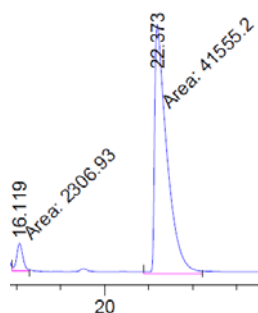
HPLC: Daicel Chiralpak IB, hexane / 2-propanol 97:3; 0.3 mL min^{-1} , 254 nm, $R_t = 22.4$ min, $T = 25$ °C.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.851	MM	0.3372	3.30345e4	1632.65222	49.2349
2	21.877	MM	0.6242	3.40613e4	909.45093	50.7651

Totals : 6.70958e4 2542.10315

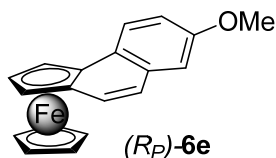


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.119	MM	0.3285	2306.92676	117.05837	5.2595
2	22.373	MM	0.6544	4.15552e4	1058.39600	94.7405

Totals : 4.38621e4 1175.45437

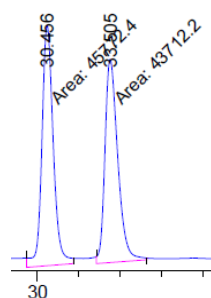
(*R_p*)-7-methoxyferrocene-[3]-helicene (**6e**).



Compound (*R_p*)-**6e** was obtained from 2-ethynyl-4-methoxyphenyl-ferrocene (**5e**) following **general procedure D** (5 h), in 90% yield.

$[\alpha]_D^{20} = +1545$ ($c = 0.016$, CHCl_2), 81% *ee*.

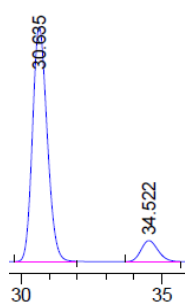
HPLC: Daicel Chiralpak IC, hexane / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, $R_t = 30.6$ min, $T = 25$ °C.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.456	MM	0.6384	4.57724e4	1194.90332	51.1512
2	33.505	MM	0.7210	4.37122e4	1010.43073	48.8488

Totals : 8.94846e4 2205.33405

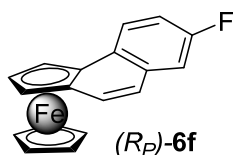


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.635	BB	0.5647	3.53884e4	976.79785	90.5963
2	34.522	BB	0.6548	3673.22925	87.67911	9.4037

Totals : 3.90616e4 1064.47696

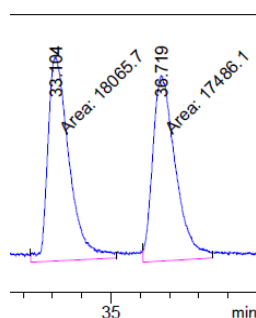
(R_p)-7-Fluoroferrocene-[3]-helicene (6f).



Compound (R_p)-6f was obtained from 2-ethynyl-4-fluorophenyl-ferrocene (5f) following **general procedure D** (5 h), in 82% yield.

[α]_D²⁰ = +432 (c = 0.032, CHCl₂), 89% ee.

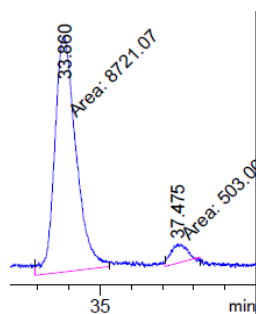
HPLC-SFC: Daicel Chiralpak IA, CO₂/MeOH 98:2; 1.0 mL min⁻¹, 254 nm, R_t = 33.9 min, T = 25 °C.



Signal 3: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.104	MM	0.8444	1.80657e4	356.57330	50.8151
2	36.719	MM	0.9036	1.74861e4	322.53961	49.1849

Totals : 3.55517e4 679.11292

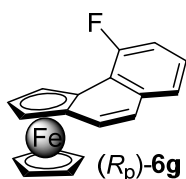


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.860	MM	0.7867	8721.06738	184.75812	94.5468
2	37.475	MM	0.5629	503.00848	14.89272	5.4532

Totals : 9224.07587 199.65084

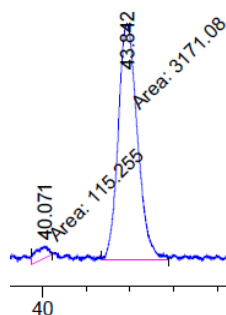
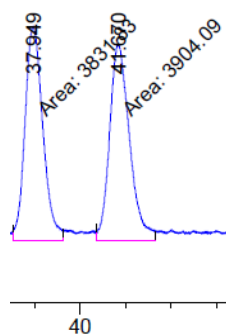
9-Fluoro-ferrocene-[3]helicene (6g)



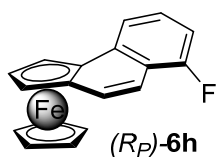
Compound (*R_p*)-6g was obtained from 2-ethynyl-1-ferrocenyl-6-fluorobenzene 5g following **general procedure D** (3h), in 74% yield.

$[\alpha]_D^{20} = +2710$ ($c = 0.07$, CHCl_2), 93% *ee*.

HPLC: Daicel Chiralpak IA, CO_2/MeOH 98:2; 1.0 mL min^{-1} , 254 nm, $R_t = 43.8 \text{ min}$, $T = 25 \text{ }^\circ\text{C}$.



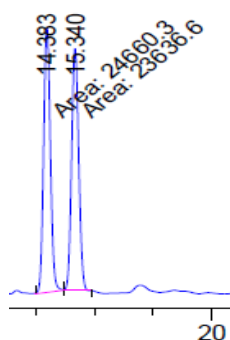
(*R_p*)-6-Fluoro-ferrocene-[3]helicene (6h).



Compound (*R_p*)-**6h** was obtained from 2-ethynyl-1-ferrocenyl-3-fluorobenzene **5h** following **general procedure D** (15 h), in 79% yield.

$[\alpha]_D^{20} = +660$ (c 0.055, CHCl₂), 68% *ee*.

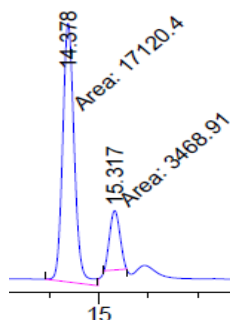
HPLC: Daicel Chiralpak IC, hexano / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, *R_t* = 14.4 min, *T* = 25 °C.



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.383	MM	0.2668	2.46603e4	1540.64343	51.0598
2	15.340	MM	0.2805	2.36366e4	1404.24182	48.9402

Totals : 4.82968e4 2944.88525

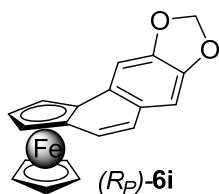


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.366	MM	0.2615	5496.23340	350.27203	83.6724
2	15.301	MM	0.2290	1072.52002	78.07485	16.3276

Totals : 6568.75342 428.34689

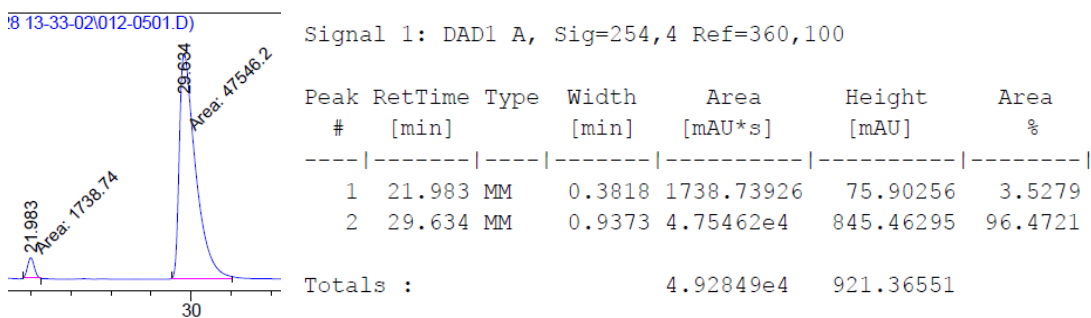
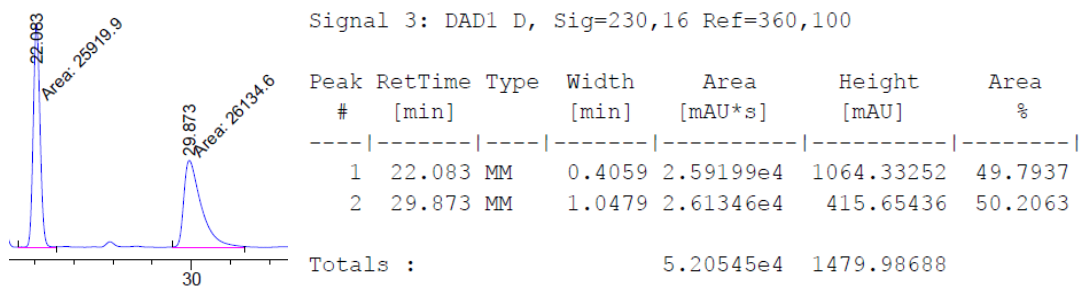
(*R_p*)-7,8-(Methylenedioxy)ferrocene-[3]-helicene (**6i**)



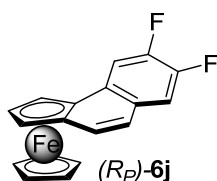
Compound (*R_p*)-**6i** was obtained from 2-ethynyl-4,5-(methylenedioxy)phenyl-ferrocene (**5i**) following **general procedure D** (5 h), in 85% yield.

$[\alpha]_D^{20} = +2444$ ($c = 0.037$, CH_2Cl_2), 93% *ee*.

HPLC: Daicel Chiralpak IC, hexano / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, $R_t = 29.6$ min, $T = 25$ °C.



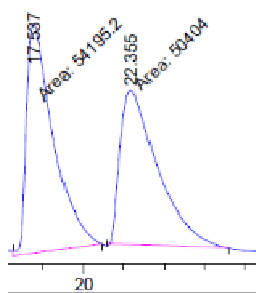
(*R_p*)-7,8-Difluoro-ferrocene-[3]helicene (6j).



Compound (*R_p*)-**6j** was obtained from 2-ethynyl-1-ferrocenyl-4,5-difluorobenzene **5j** following **general procedure D** (4 h), in 83% yield.

$[\alpha]_D^{20} = +2774$ ($c 0.042$, CH_2Cl_2), 87% *ee*.

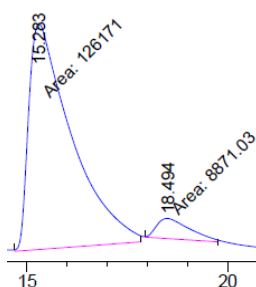
HPLC: Daicel Chiralpak IA, hexane / 2-propanol 100:0; 0.4 mL min⁻¹, 254 nm, $R_t = 15.3$ min, $T = 25$ °C



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.537	MM	1.5453	5.41952e4	584.52600	51.8122
2	22.355	MM	2.1539	5.04040e4	390.01868	48.1878

Totals : 1.04599e5 974.54468

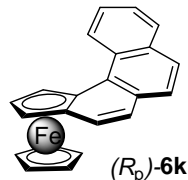


Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.283	MM	1.2391	1.26171e5	1697.06177	93.4309
2	18.494	MM	0.9695	8871.03223	152.49930	6.5691

Totals : 1.35042e5 1849.56107

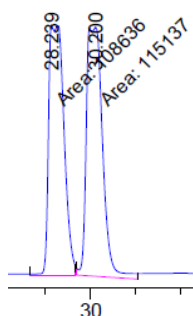
(*R_p*)-Ferrocene-[4]helicene (6k).



Compound (*R_p*)-6k was obtained from (*R_p*)-2-ethynyl-1-naphthylferrocene **5k** following **general procedure D** (15 h), in 88% yield.

$[\alpha]_D^{20} = +1974$ (c 0.017, CH₂Cl₂), 93% ee.

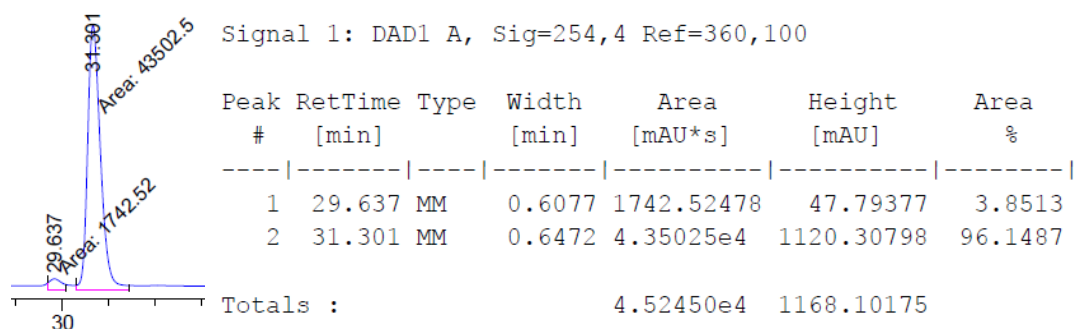
HPLC: Daicel Chiralpak IC, hexano / 2-propanol 97:3; 0.3 mL min⁻¹, 254 nm, *R_t* = 31.3 min, *T* = 25 °C).



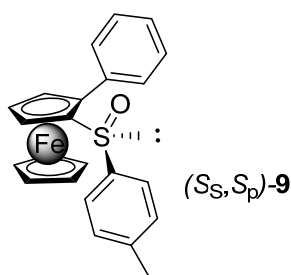
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.239	MM	0.7834	1.08636e5	2311.23120	48.5475
2	30.200	MM	0.8326	1.15137e5	2304.80396	51.4525

Totals : 2.23773e5 4616.03516



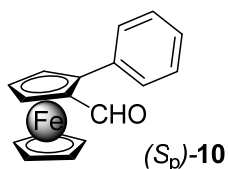
(*S_S*,*S_p*)-2-Phenyl-1-(*p*-tolylsulfinyl)ferrocene (9**).¹**



To a mixture of (*S_S*,*S_p*)-2-(*p*-tolylsulfinyl)ferrocenyl boronic acid (**7**) (94 mg, 0.25 mmol), PdCl₂(dppf) (11 mg, 0.015 mmol) and NaOH (39 mg, 1 mmol), iodobenzene (101 μL, 0.9 mmol), toluene (3.3 mL) and water (0.6 mL) were added. The resulting suspension was refluxed overnight. After workup and flash chromatography (eluent hexane/EtOAc/CH₂Cl₂ 79:22:8), pure compound (*S_S*,*S_p*)-**9** was obtained, as an orange solid, in 79% yield.

¹H NMR (300 MHz, CDCl₃): δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.19 (m, 5H), 4.66 (broad s, 1H), 4.34 (broad s, 1H), 4.07 (s, 5H), 4.05 (broad s, 1H), 2.36 (s, 3H).

(*S_p*)-1-Formyl-2-phenylferrocene (10**).²**



(1) V. E. Albrow, A. J. Blake, R. Fryatt, C. Wilson, S. Woodward, *Eur. J. Org. Chem.* **2006**, 2549.

(2) M. R. Buchmeiser, N. Schuler, G. Kaltenhauser, K. -H. Ongania, I. Lagoja, K. Wurst, H. Schottenberger, *Macromolecules* **1998**, *31*, 3175.

To a solution of the sulfoxide (S_S, S_P)-**9** (376 mg, 0.94 mmol) in THF (9.8 mL) at $-78\text{ }^\circ\text{C}$, *tert*-BuLi (0.82 mL, 1.4 mmol, 1.7 M in pentane) was added dropwise during 10 min. The resulting solution was stirred for 10 min at the same temperature before addition of dry *N,N*-dimethyl formamide (DMF) (0.82 mL, 10.4 mmol). After stirring at $-78\text{ }^\circ\text{C}$ for 2 h, the solution was quenched with water. After workup, the residue was concentrated *in vacuo* and purified by flash chromatography (eluent hexane/EtOAc 5:1) affording the pure aldehyde (S_P)-**10**, as orange oil, in 64% yield.

$[\alpha]_D^{20} = -697$ ($c = 0.070$, CH_2Cl_2).

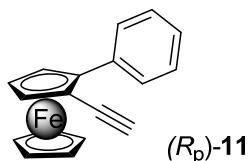
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.21 (s, 1H), 7.53 (d, $J = 7.8$, Hz, 2H), 7.41 – 7.29 (m, 3H), 5.00 (broad s, 1H), 4.84 (broad s, 1H), 4.71 (broad s, 1H), 4.26 (s, 5H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 193.1, 136.0, 129.7 (2C), 128.3 (2C), 127.3, 92.7, 75.07, 72.0, 71.1 (5C), 70.0, 68.5.

MS (FAB+): m/z (%) 290 (M^+ , 43), 57 (30).

HRMS: Calculated for $\text{C}_{17}\text{H}_{14}\text{FeO}$ (M^+) 290.0394, found 290.0397.

(R_P)-2-Ethynyl-1-phenylferrocene (11**).**³



A solution of PPh_3 (390 mg, 1.5 mmol) and CBr_4 (250 mg, 0.75 mmol) in CH_2Cl_2 (15 mL) was stirred for 10 min at $0\text{ }^\circ\text{C}$. Then, a solution of (S_P)-1-formyl-2-phenylferrocene (**10**) (174 mg, 0.60 mmol) in CH_2Cl_2 (15 mL) was added, and the reaction mixture was stirred for 2 h at this temperature. After filtration over silica gel and solvent elimination, Et_2O (20 mL) and THF (10 mL) were added under nitrogen. The solution was cooled at $-78\text{ }^\circ\text{C}$ and *n*-BuLi 2.5 M (0.86 mL, 2.09 mmol) was added dropwise. After 30 min, the mixture was allowed to warm to room temperature, stirred for 1 h and hydrolyzed with water. After workup and solvent elimination, the crude was purified by flash chromatography (eluent hexane) affording pure ethynyl compound (R_P)-**11**, in 60% yield.

(3) H. Lehner, K. Schoegl, *Monatsh. Chem.* **1970**, *101*, 895

$[\alpha]_D^{20} = -434$ ($c = 0.08$, CH_2Cl_2).

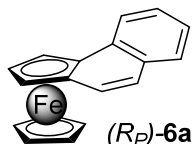
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.81 (d, $J = 7.3$ Hz, 2H), 7.33 (m, 3H), 4.62 (broad s, 2H), 4.33 (broad s, 1H), 4.16 (s, 5H), 2.90 (s, 1H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 137.6, 128.0 (2C), 127.8 (2C), 126.6, 88.0, 82.6, 76.3, 73.2, 71.6 (5C), 70.3, 68.6, 68.4.

MS (EI): m/z (%) 286 (M^+ , 100), 121 (15).

HRMS: Calculated for $\text{C}_{18}\text{H}_{14}\text{Fe}$ (M^+) 286.0445, found 286.0435.

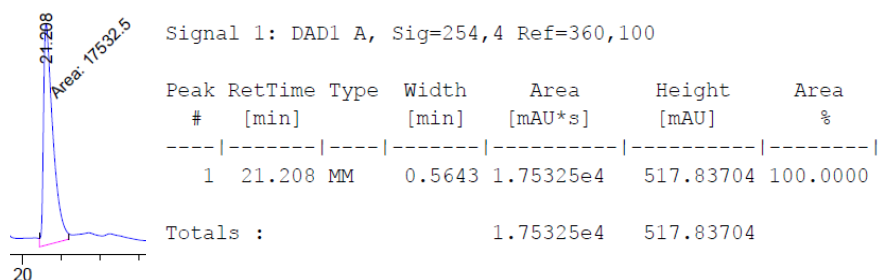
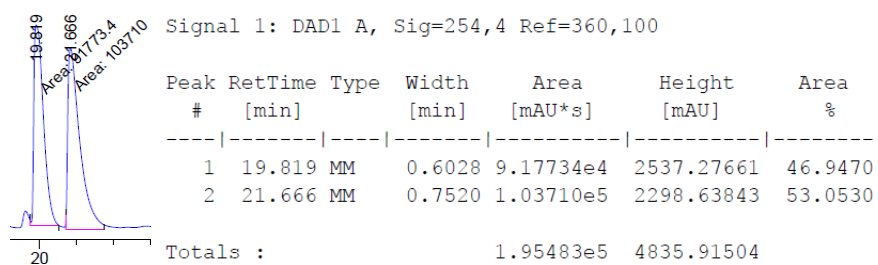
(R_p)-Ferrocene[3]helicene (6a).



Compound (R_p)-**6a** was obtained from (R_p)-2-ethynyl-1-phenylferrocene (**11**) following **general procedure C** (1.5 h).

$[\alpha]_D^{20} = +1037$ ($c = 0.013$, CH_2Cl_2), >98% *ee*.

HPLC: Daicel Chiralpak IB, hexano / 2-propanol 97:3; 0.3 mL min^{-1} , 254 nm, $R_t = 21.2$ min, $T = 25$ °C).



X-Ray Crystallography for (*rac*)-6a (CCDC-1469767)

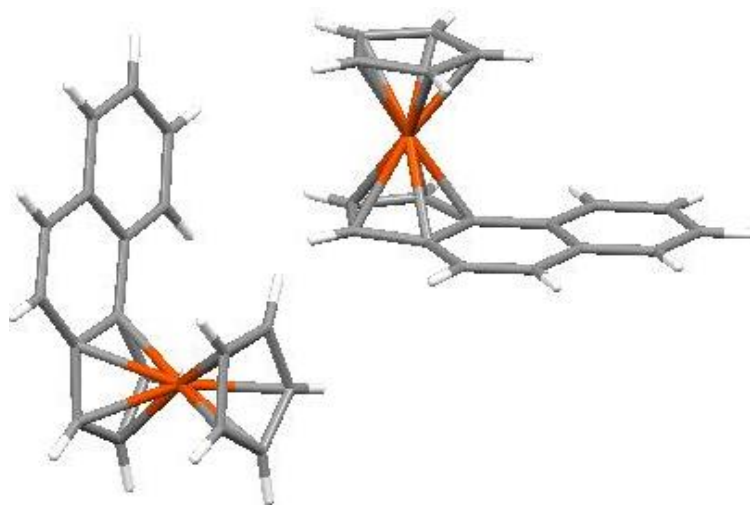


Table. Crystal data and structure refinement for (*rac*)-6a.

Identification code	<i>(rac)</i> -6a	
Chemical formula	C ₁₈ H ₁₄ Fe	
Formula weight	286.14	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal size	0.04 x 0.20 x 0.32 mm	
Crystal habit	clear dark orange plate	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.4447(4) Å	α = 90°
	b = 19.4178(11) Å	β = 91.4960(10)°
	c = 9.8391(6) Å	γ = 90°
Volume	2567.8(2) Å ³	
Z	8	
Density (calculated)	1.480 Mg/cm ³	
Absorption coefficient	1.155 mm ⁻¹	
F(000)	1184	

Theta range for data collection	1.84 to 25.37°	
Index ranges	-16<=h<=14, -23<=k<=23, -11<=l<=11	
Reflections collected	32723	
Independent reflections	4683 [R(int) = 0.0521]	
Coverage of independent reflections	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9553 and 0.7089	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4683 / 0 / 343	
Goodness-of-fit on F²	1.034	
Δ/σ_{\max}	0.001	
Final R indices	3631 data; I>2σ(I)	R1 = 0.0308, wR2 = 0.0699
	all data	R1 = 0.0469, wR2 = 0.0777
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0371P) ² +0.3877P] where P=(F _o ² +2F _c ²)/3	
Largest diff. peak and hole	0.301 and -0.243 eÅ ⁻³	
R.M.S. deviation from mean	0.049 eÅ ⁻³	

X-Ray Crystallography for (*R_p*)-6e (CCDC-1469768)

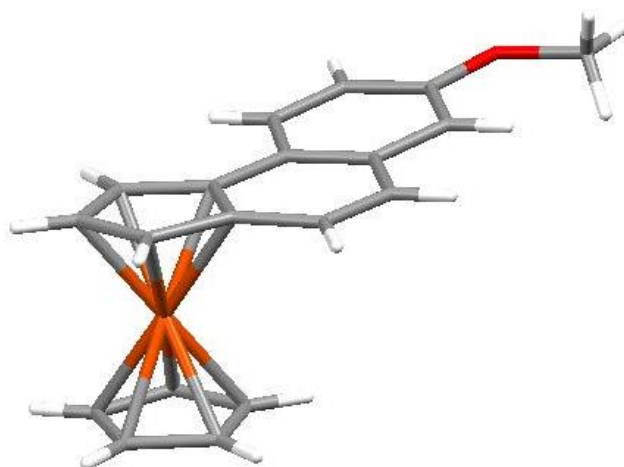


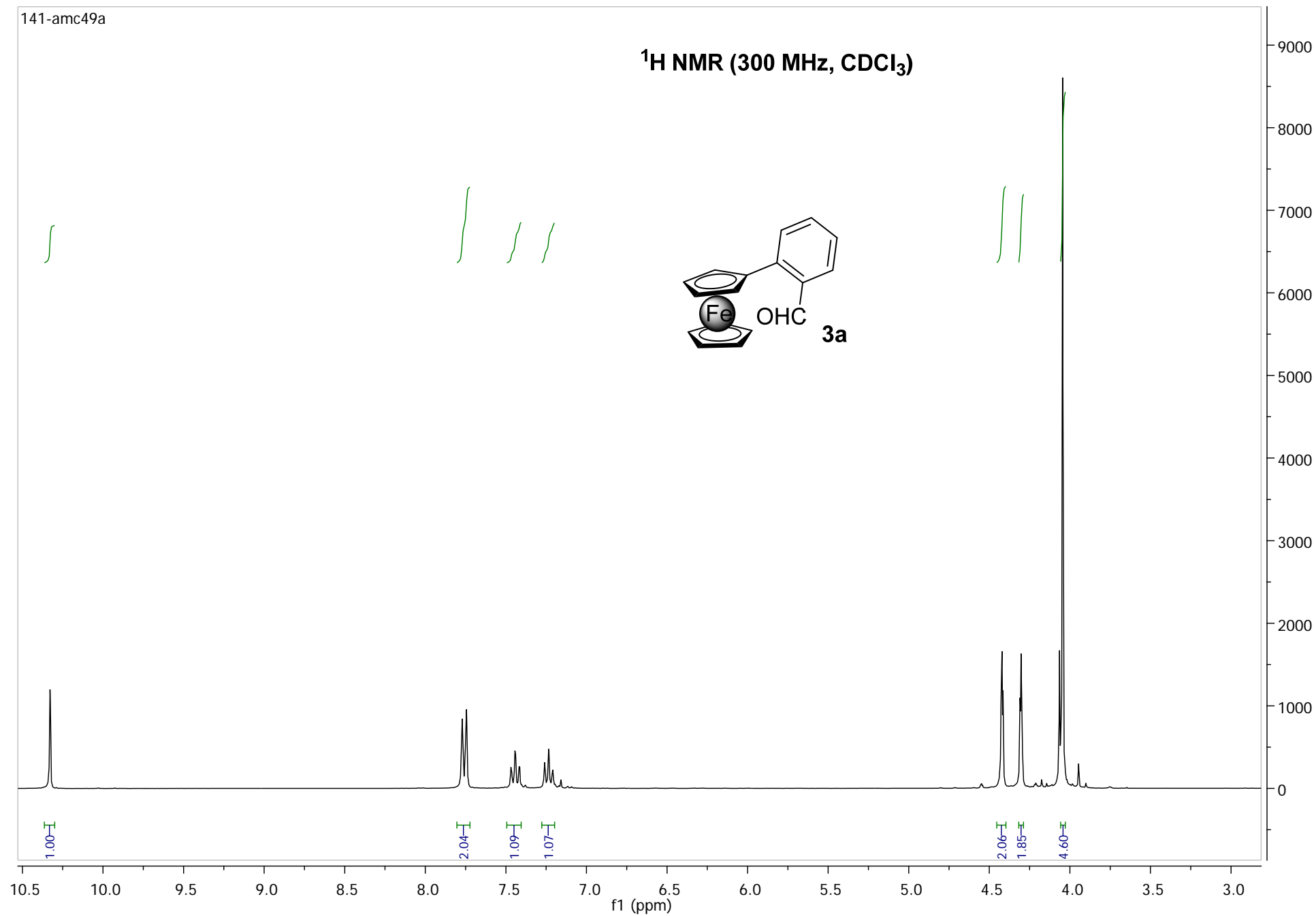
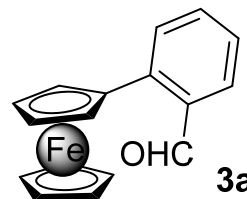
Table. Crystal data and structure refinement for (*R_p*)-6e.

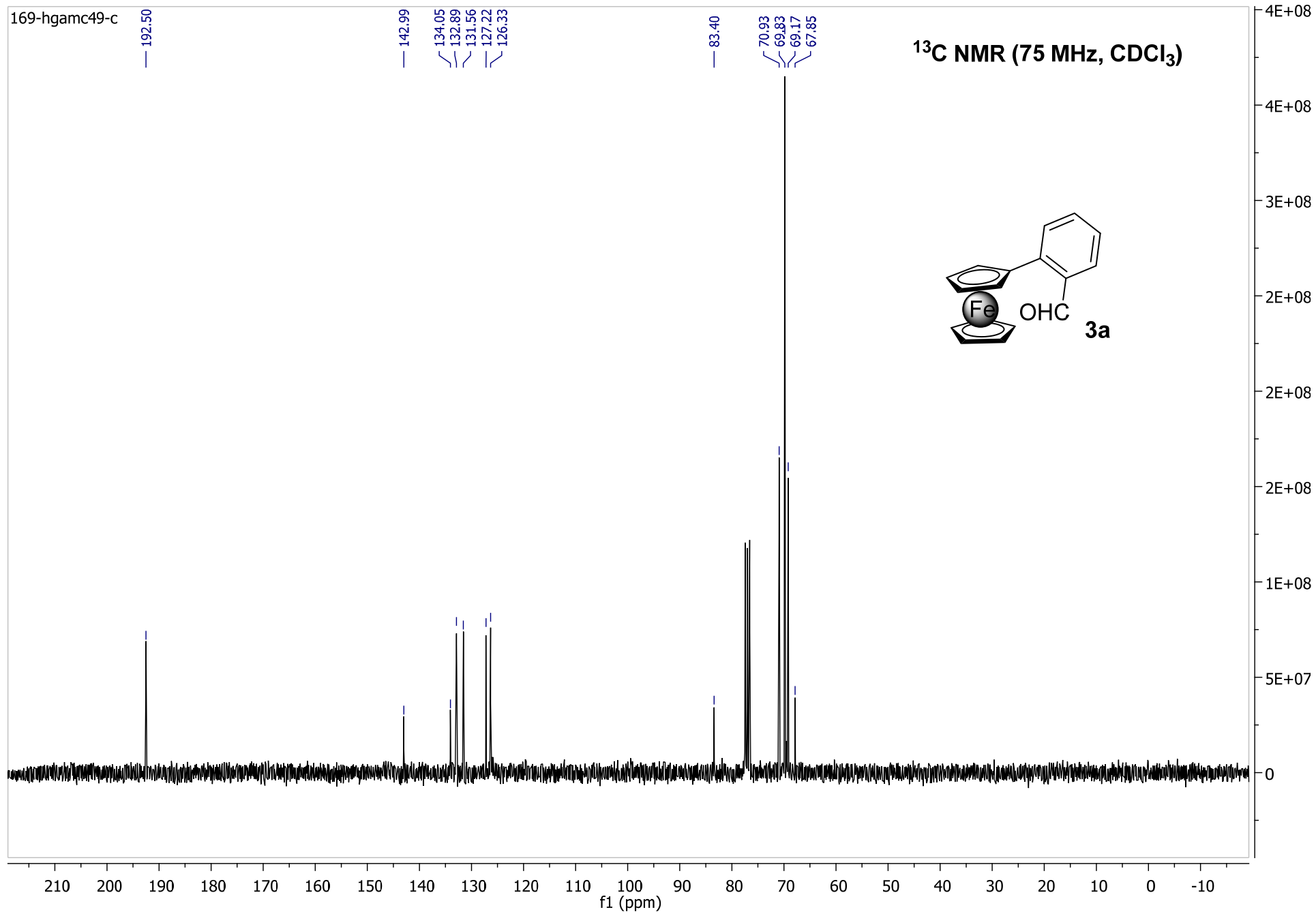
Identification code	<i>(R_p</i>)-6e	
Chemical formula	C ₁₉ H ₁₆ FeO	
Formula weight	316.17	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal size	0.02 x 0.14 x 0.18 mm	
Crystal habit	clear light red plate	
Crystal system	tetragonal	
Space group	P 41 21 2	
Unit cell dimensions	a = 7.8273(13) Å	α = 90°
	b = 7.8273(13) Å	β = 90°
	c = 47.227(9) Å	γ = 90°
Volume	2893.4(9) Å ³	
Z	8	
Density (calculated)	1.452 Mg/cm ³	
Absorption coefficient	1.037 mm ⁻¹	
F(000)	1312	

Theta range for data collection	1.72 to 25.45°	
Index ranges	-7<=h<=7, -9<=k<=8, -48<=l<=57	
Reflections collected	10547	
Independent reflections	2679 [R(int) = 0.1009]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9796 and 0.8353	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2679 / 0 / 191	
Goodness-of-fit on F²	1.031	
Δ/σ_{\max}	0.001	
Final R indices	1829 data; I>2σ(I)	R1 = 0.0751, wR2 = 0.1647
	all data	R1 = 0.1172, wR2 = 0.1839
Weighting scheme	w=1/[σ ² (F _o ²)+(0.1000P) ² +0.0000P] where P=(F _o ² +2F _c ²)/3	
Absolute structure parameter	-0.0(1)	
Largest diff. peak and hole	0.335 and -0.441 eÅ ⁻³	
R.M.S. deviation from mean	0.083 eÅ ⁻³	

141-amc49a

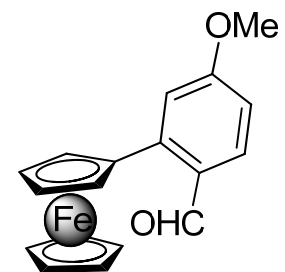
¹H NMR (300 MHz, CDCl₃)



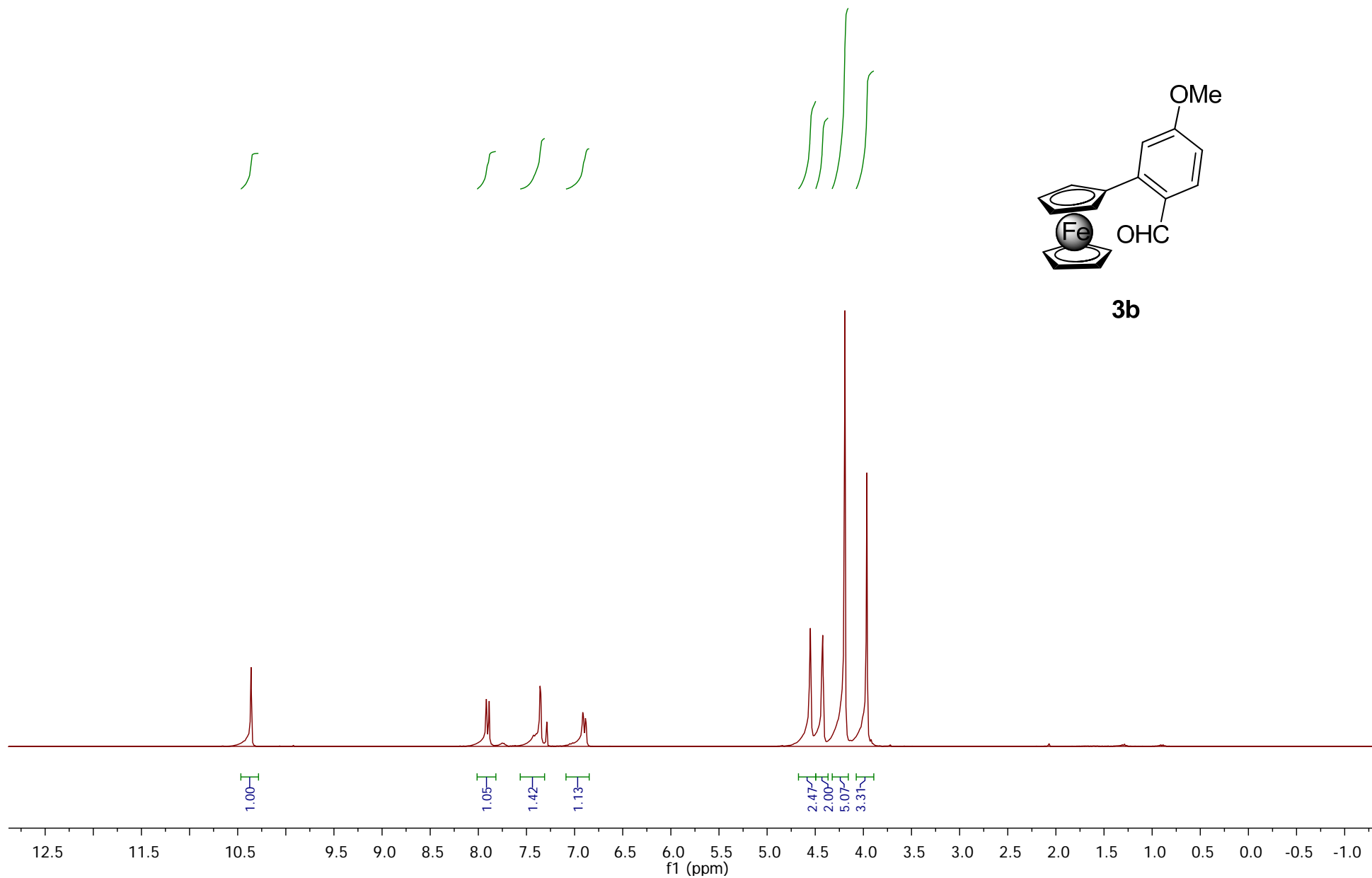


hgc1_09

^1H NMR (300 MHz, CDCl_3)



3b



S-41

hgc1_09

— 191.13

— 163.15

— 145.55

— 129.89
— 128.04

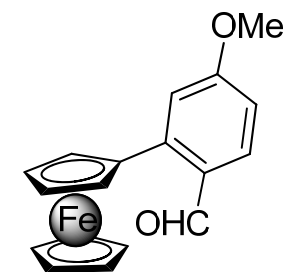
— 116.33
— 112.56

— 83.72

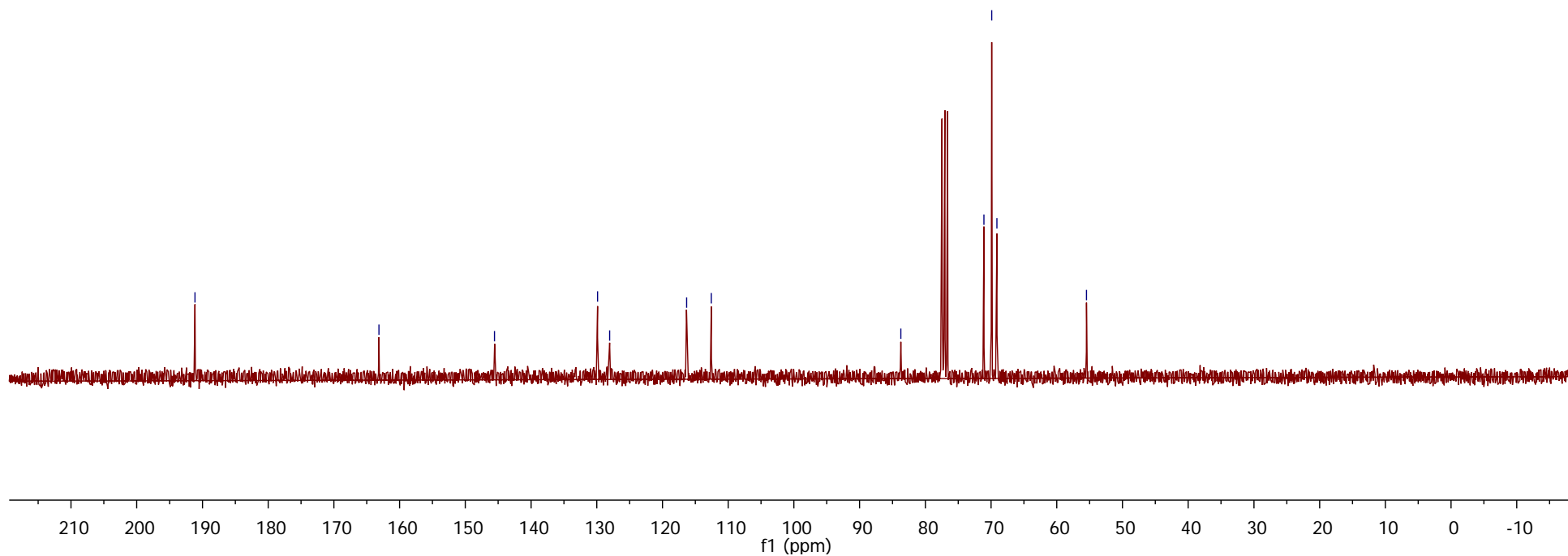
— 71.09
— 69.90
— 69.11

— 55.48

¹³C NMR (75 MHz, CDCl₃)



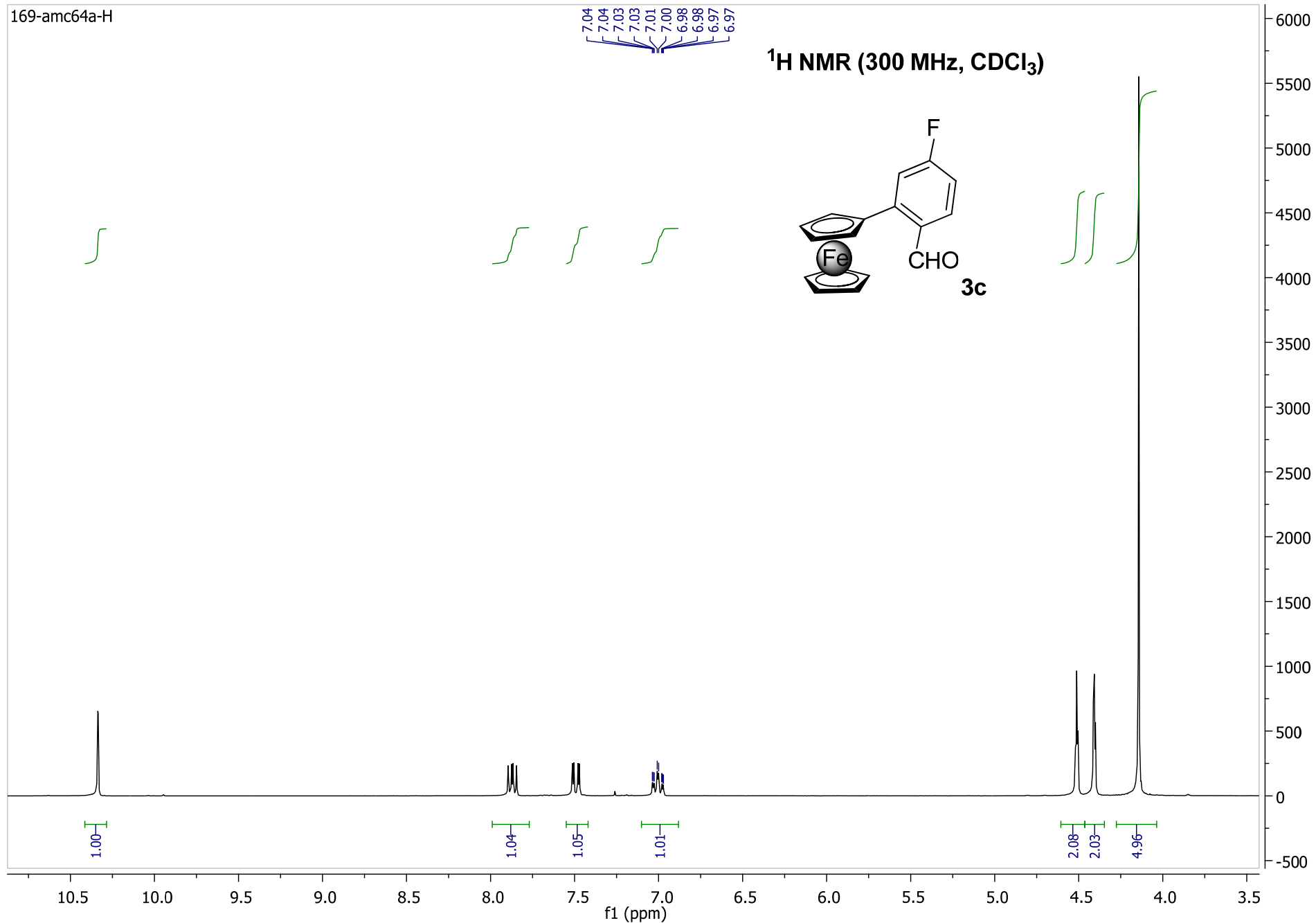
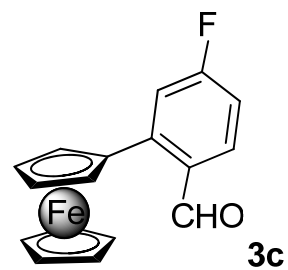
3b

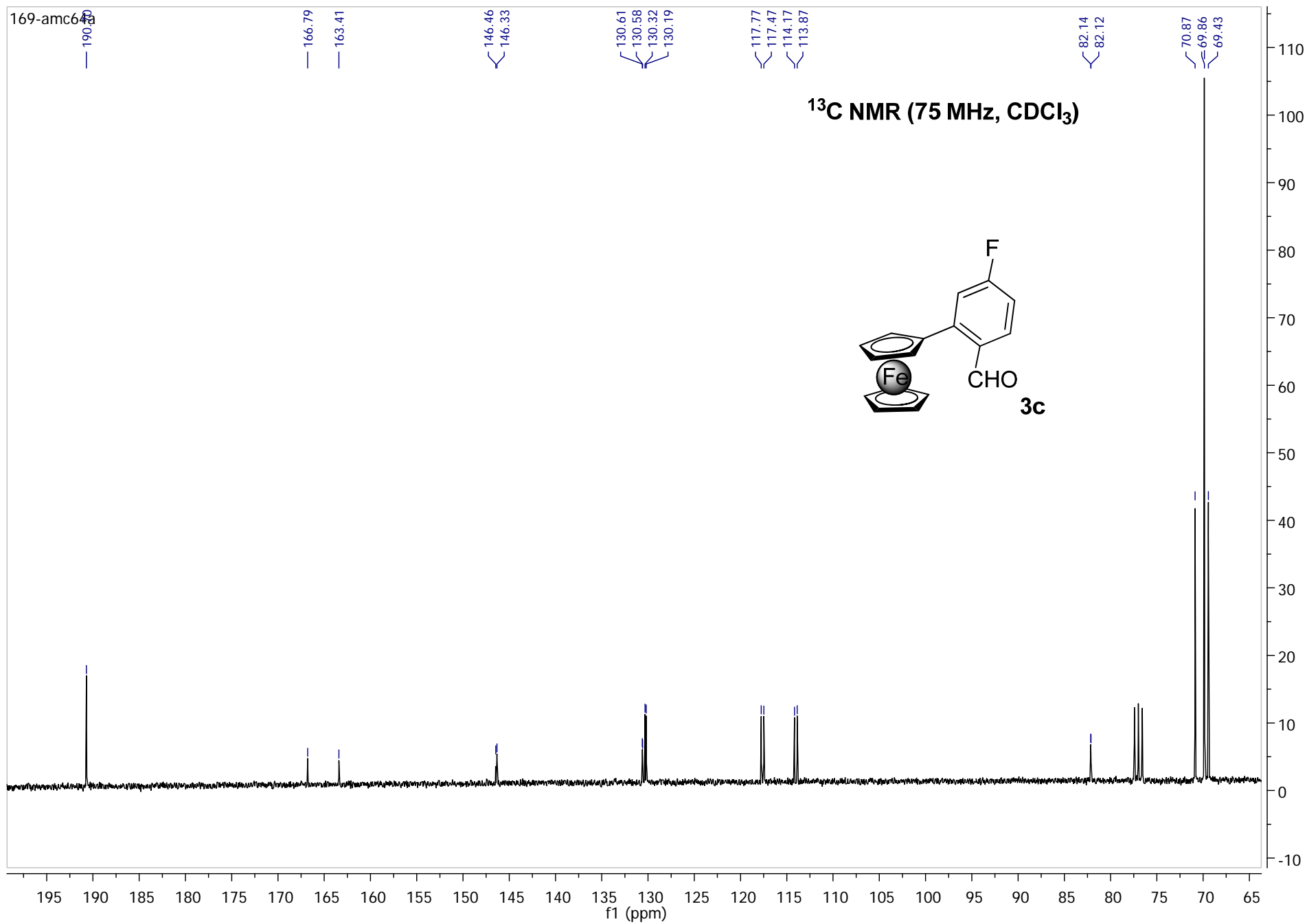


169-amc64a-H

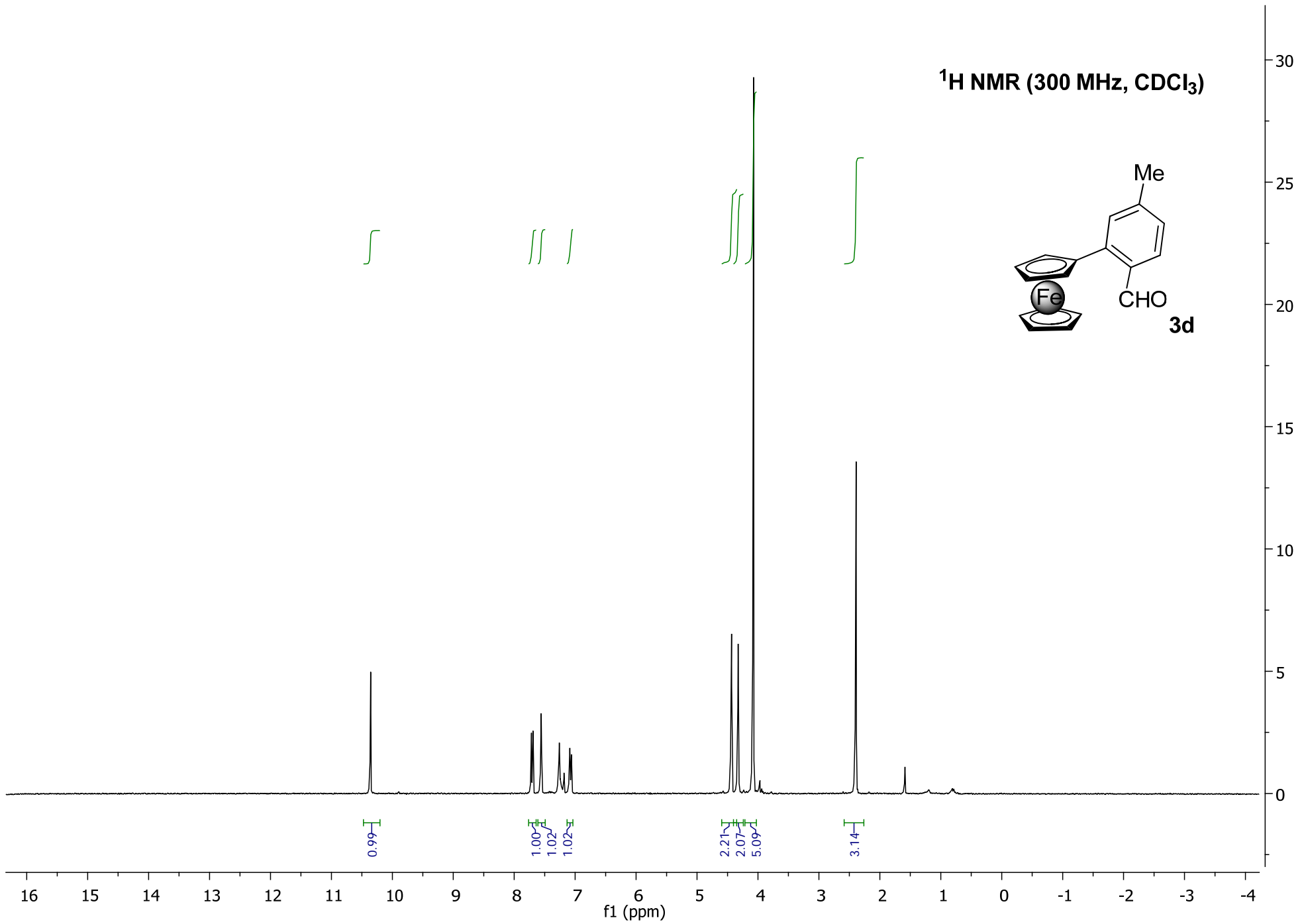
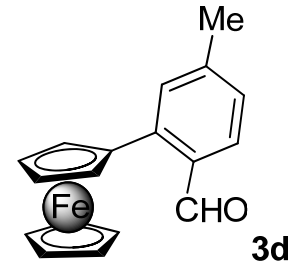
7.04
7.04
7.03
7.03
7.01
7.00
6.98
6.98
6.97
6.97

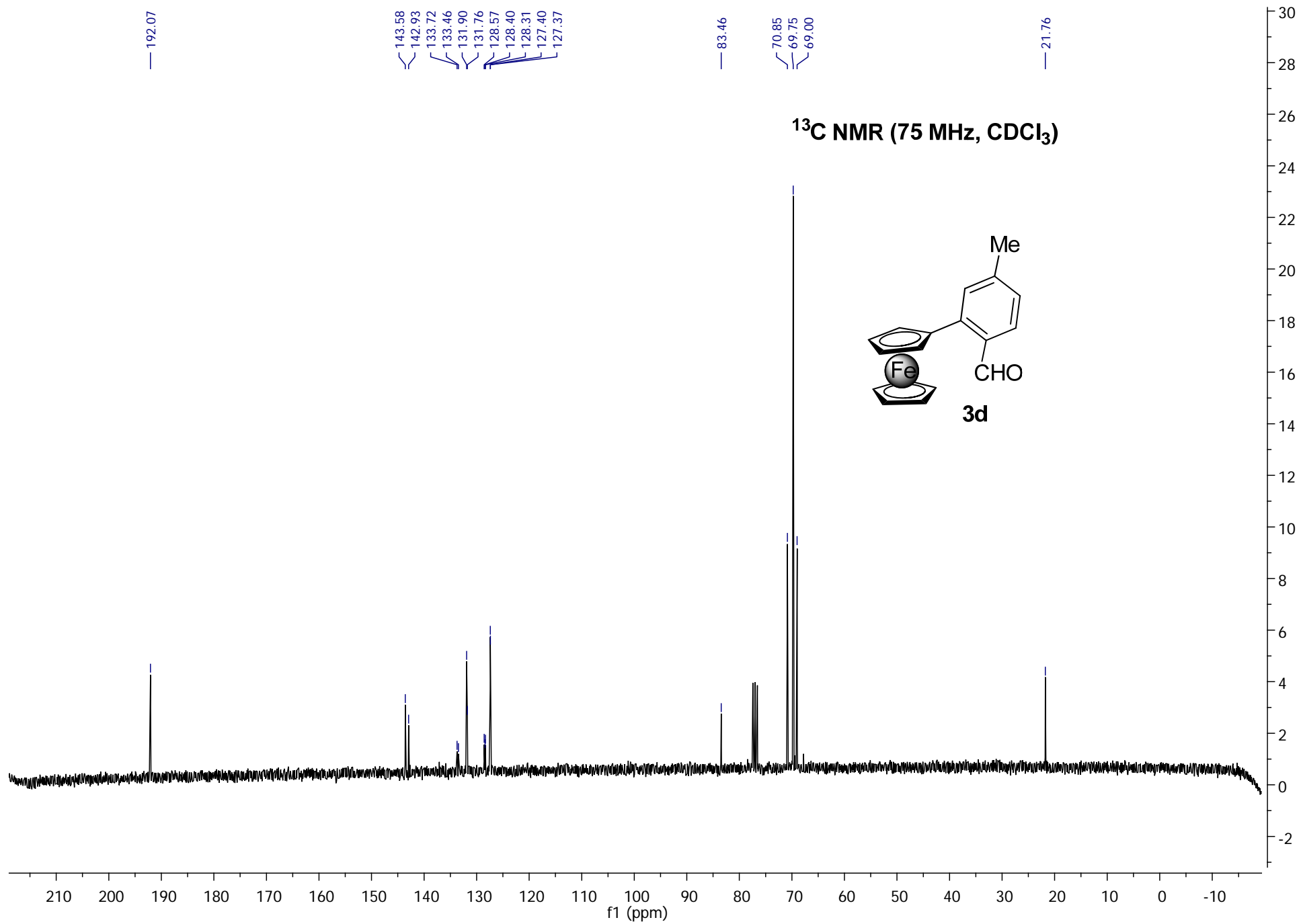
¹H NMR (300 MHz, CDCl₃)





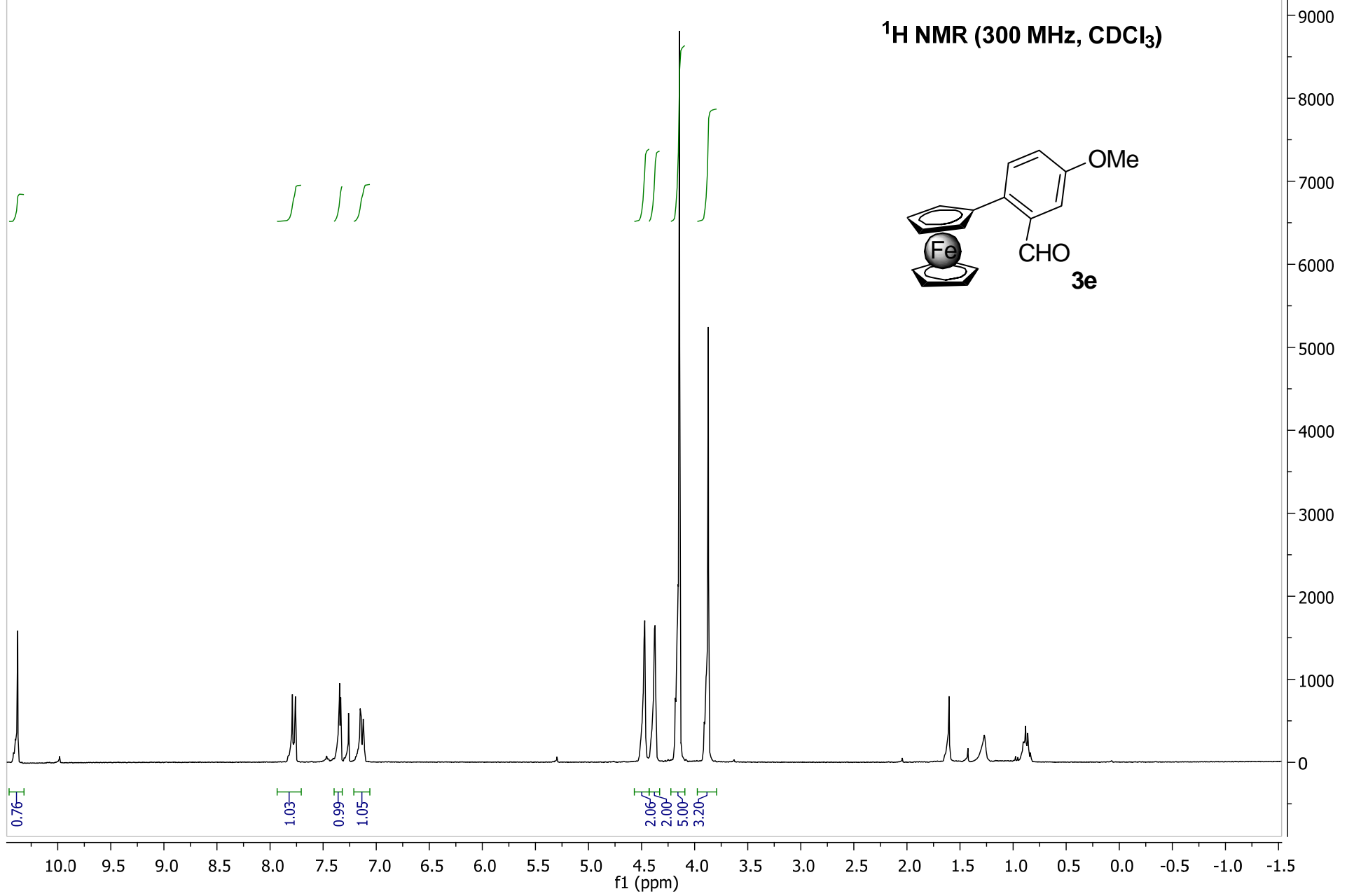
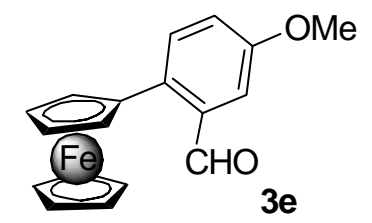
¹H NMR (300 MHz, CDCl₃)

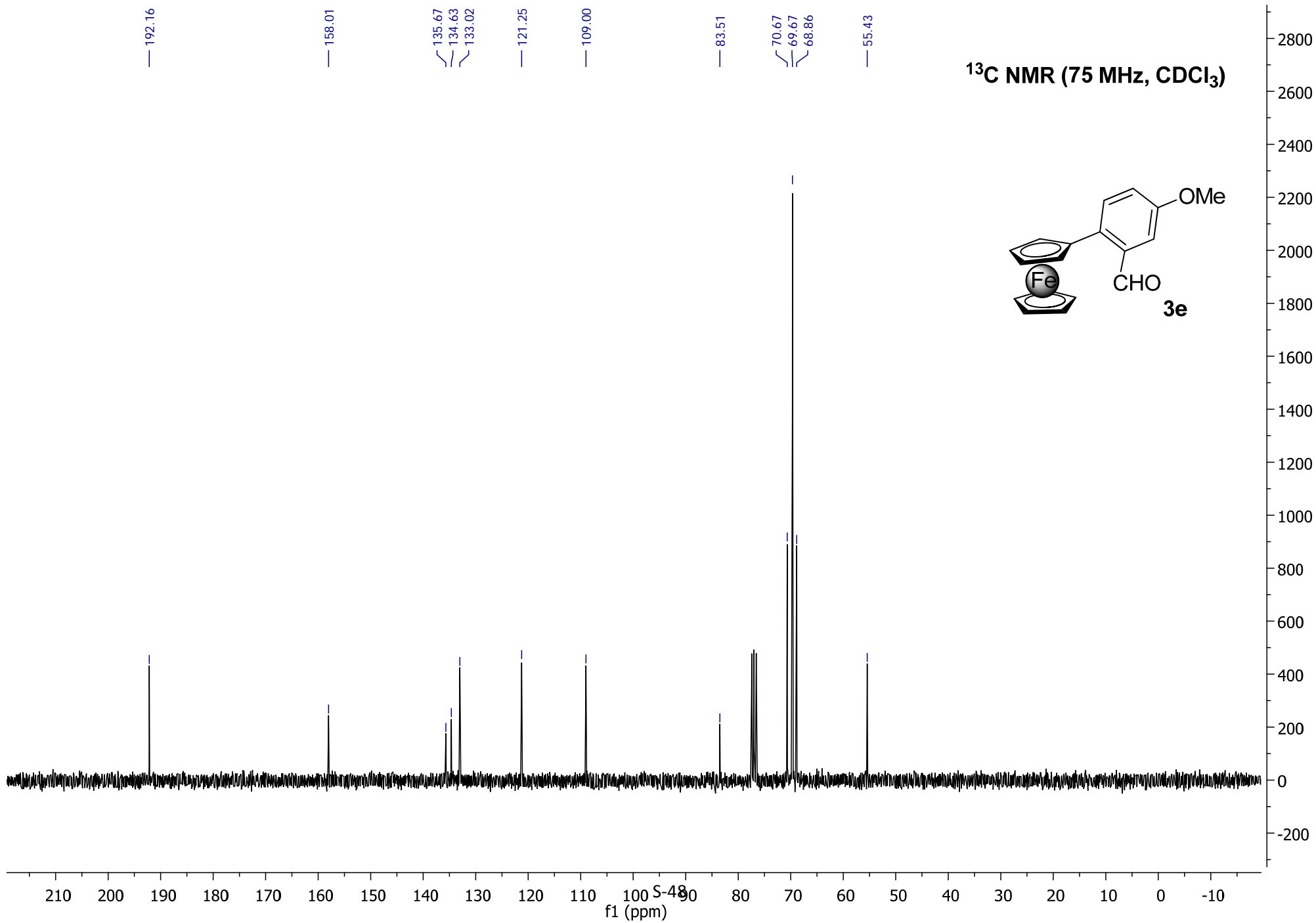




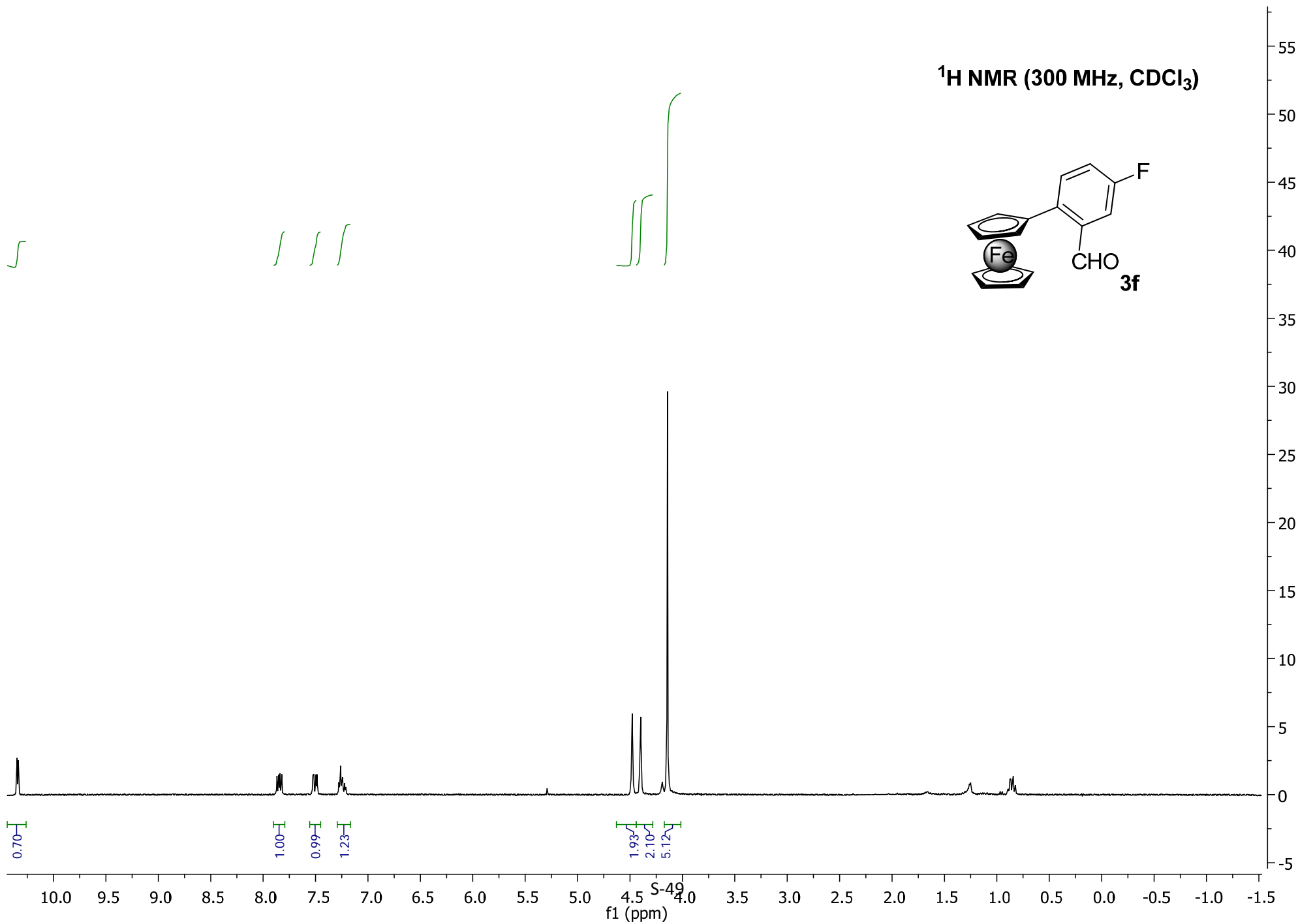
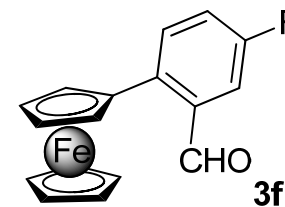
061-amc21a

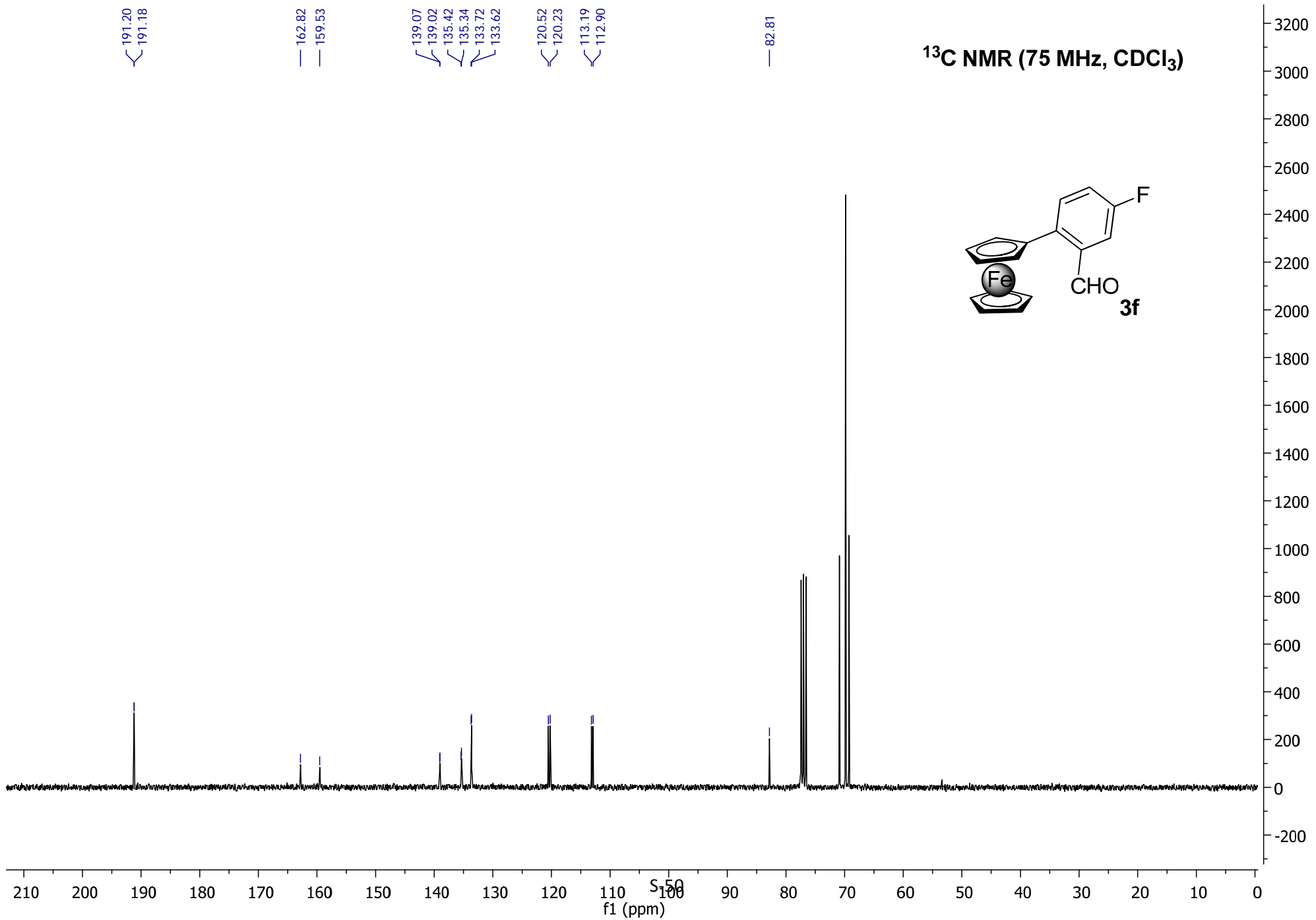
¹H NMR (300 MHz, CDCl₃)





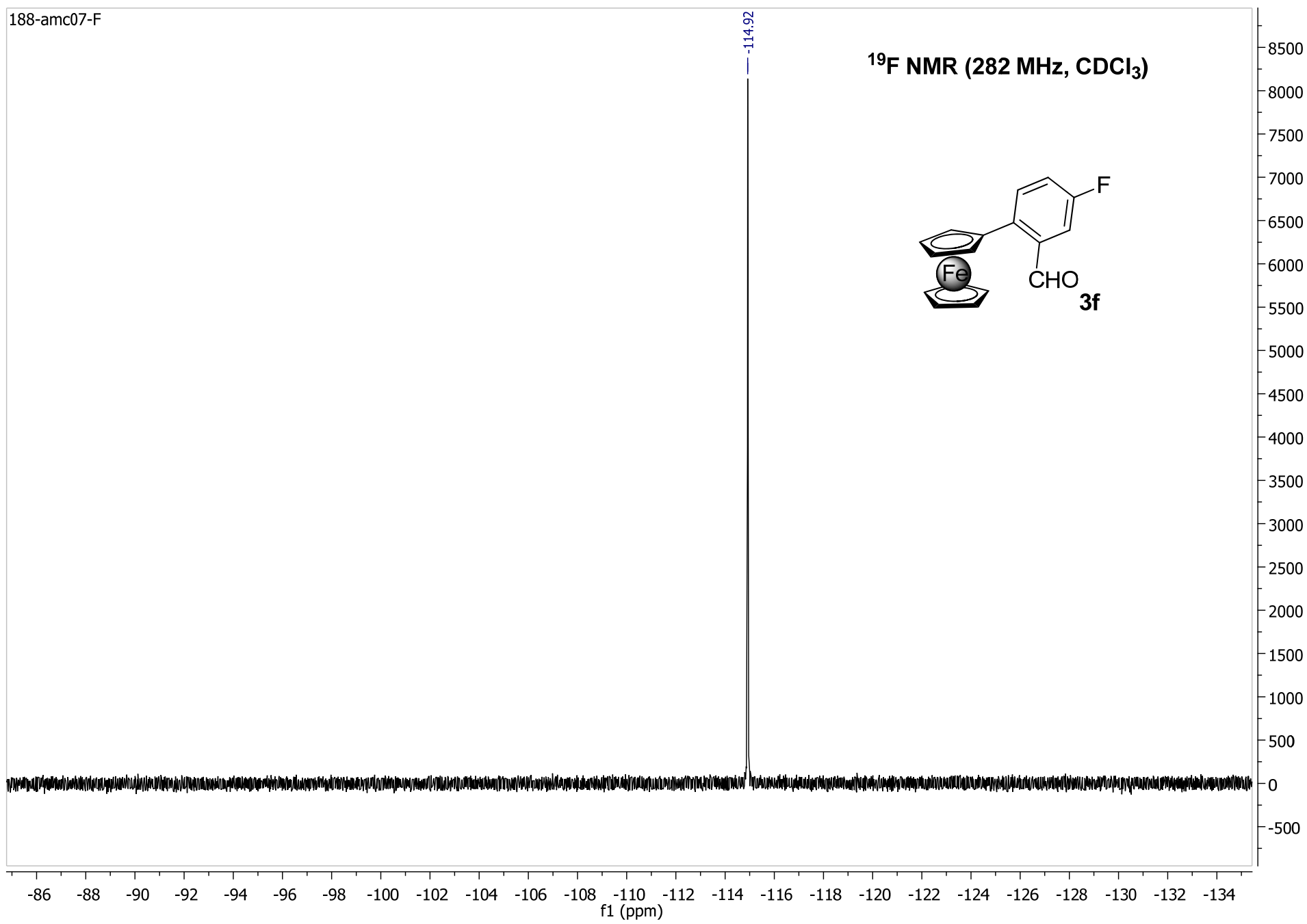
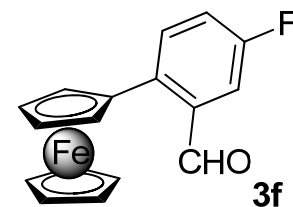
¹H NMR (300 MHz, CDCl₃)





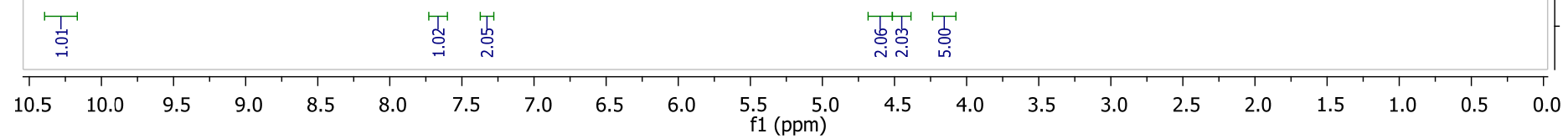
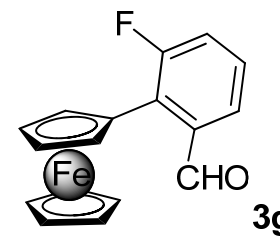
188-amc07-F

¹⁹F NMR (282 MHz, CDCl₃)



155-amc56a

^1H NMR (300 MHz, CDCl_3)



S-52

174-amc63-C

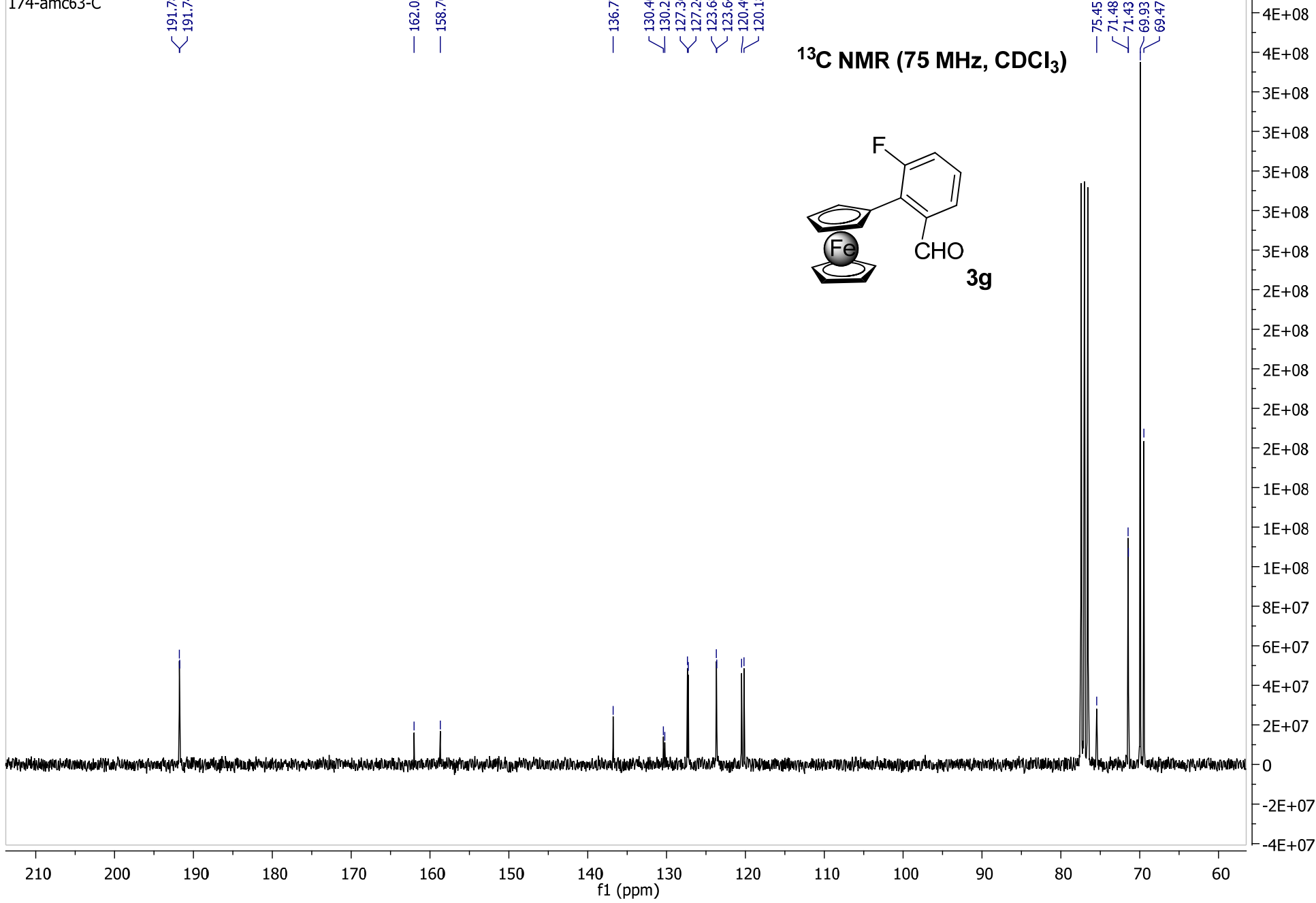
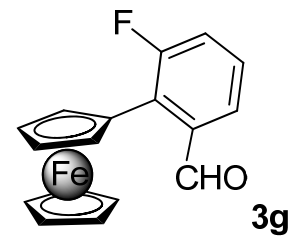
191.78
191.74

162.02
158.70

136.77
130.40
130.22
127.36
127.24
123.68
123.64
120.49
120.18

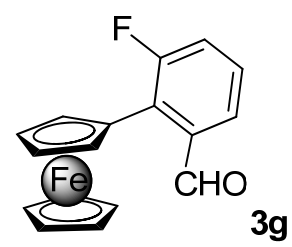
¹³C NMR (75 MHz, CDCl₃)

75.45
71.48
71.43
69.93
69.47

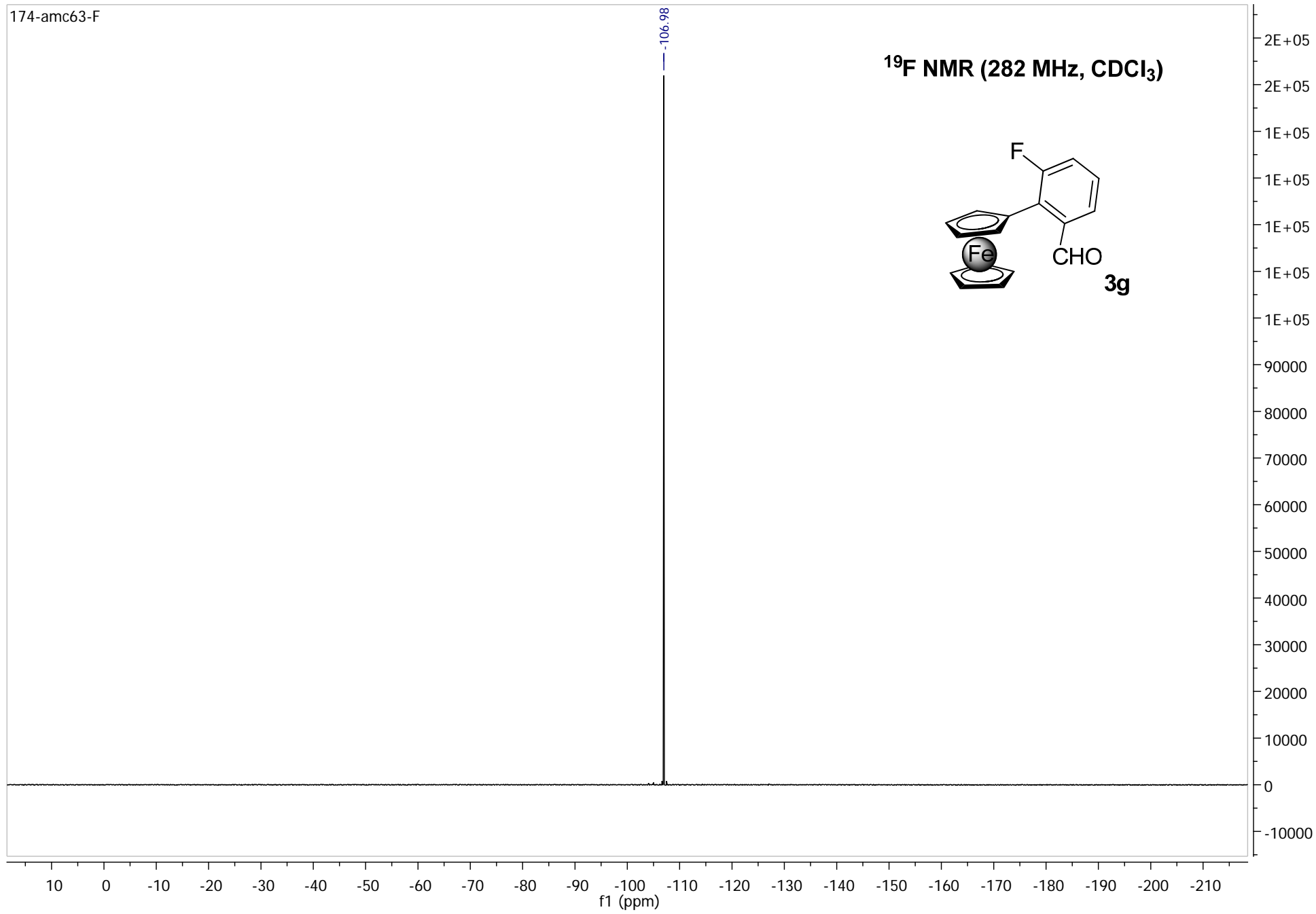


174-amc63-F

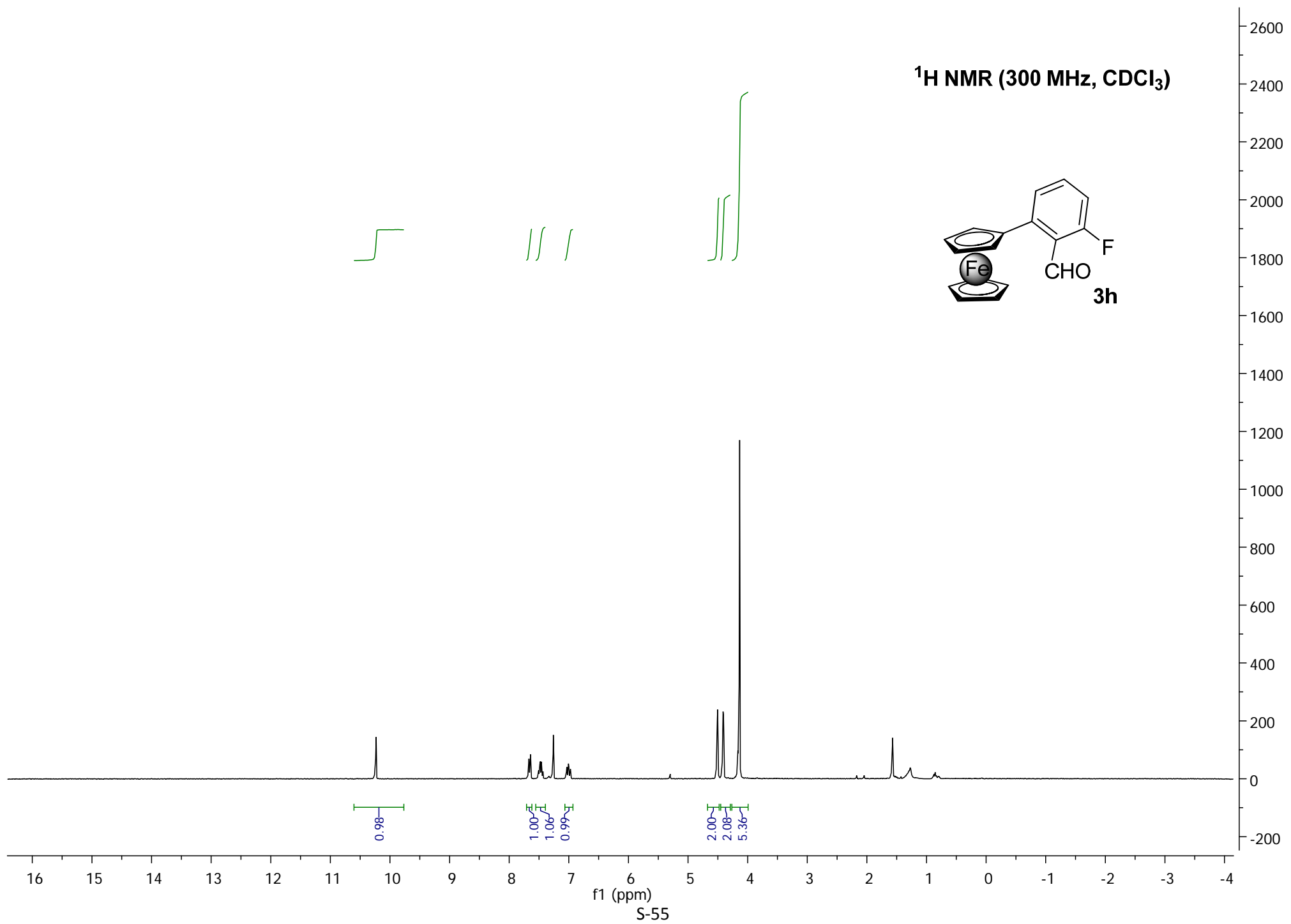
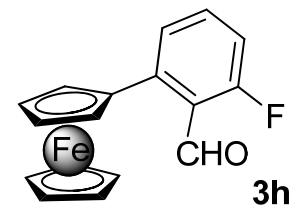
¹⁹F NMR (282 MHz, CDCl₃)



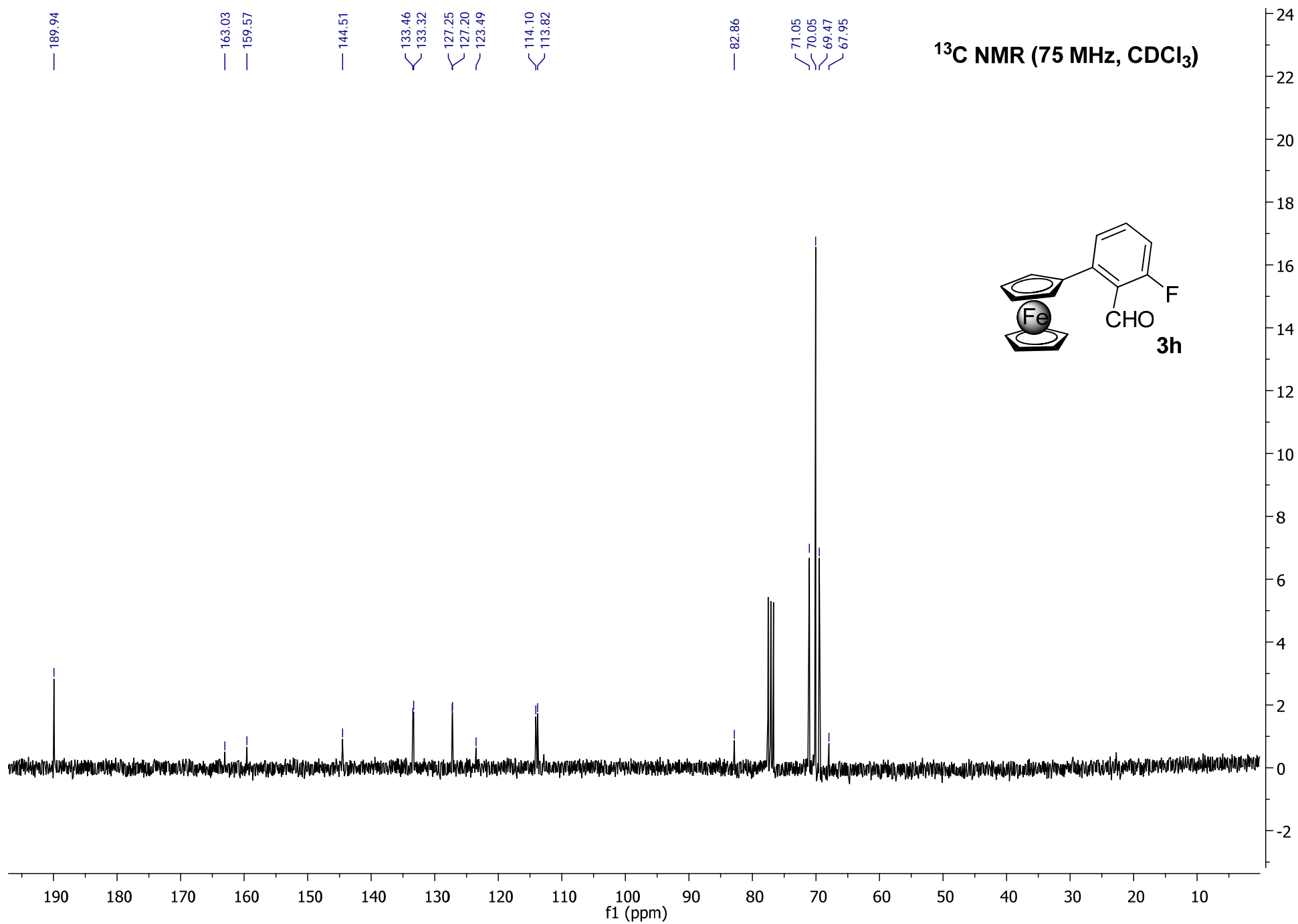
-106.98



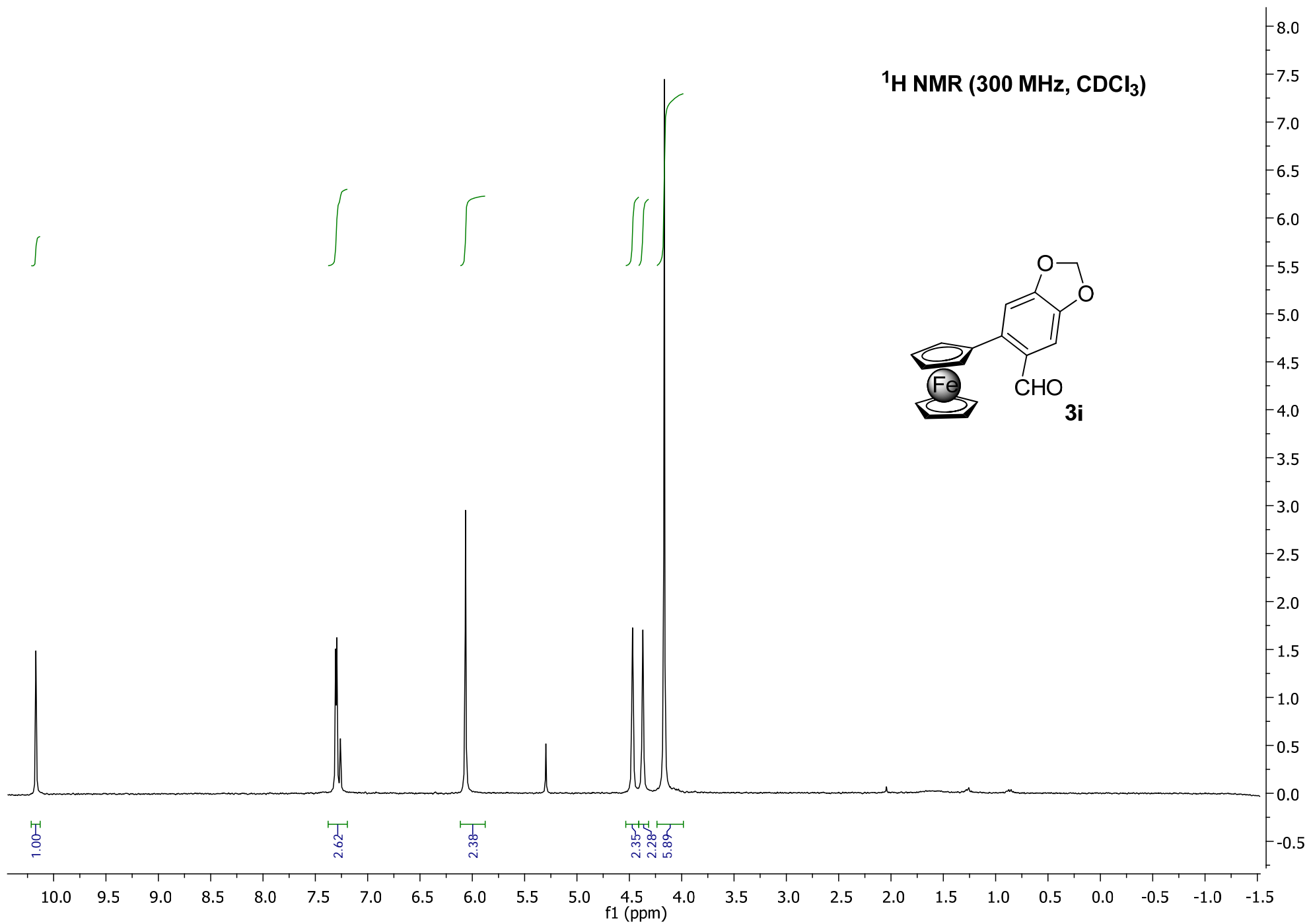
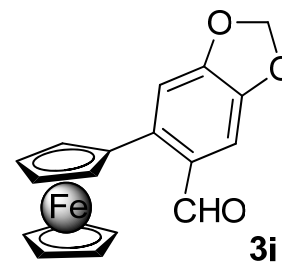
¹H NMR (300 MHz, CDCl₃)

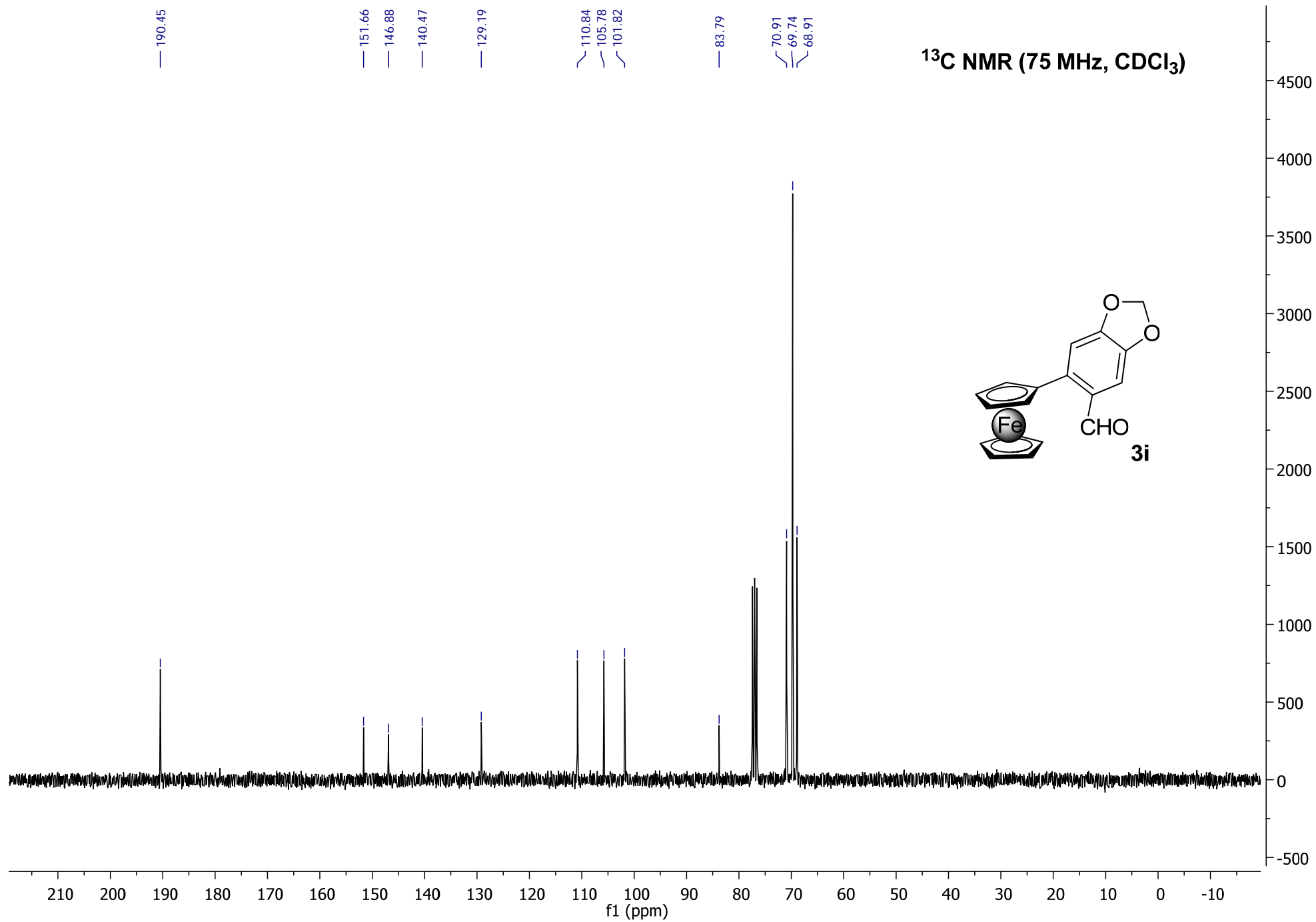


S-55



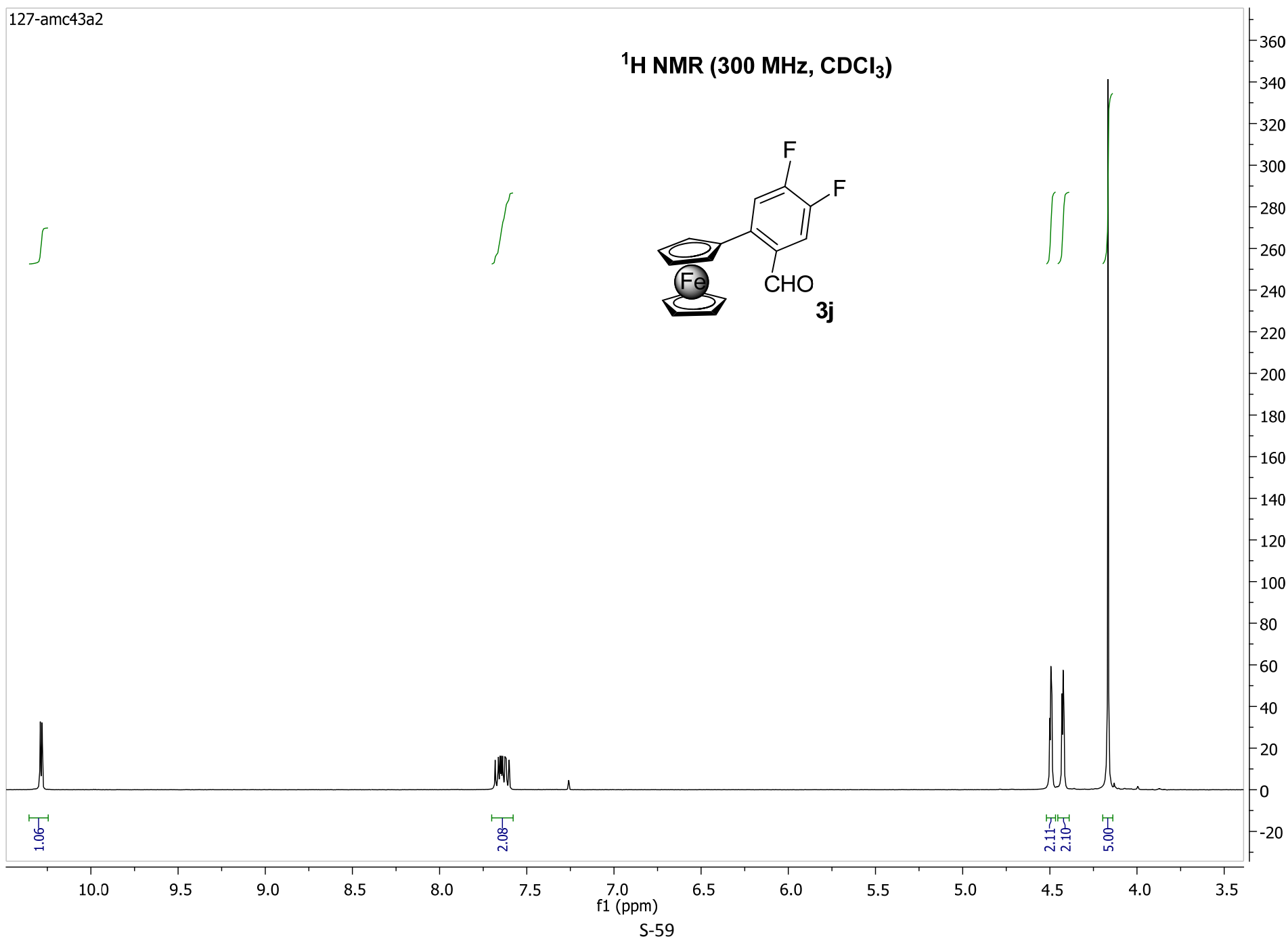
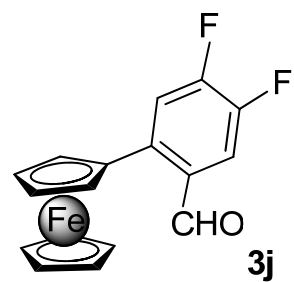
¹H NMR (300 MHz, CDCl₃)

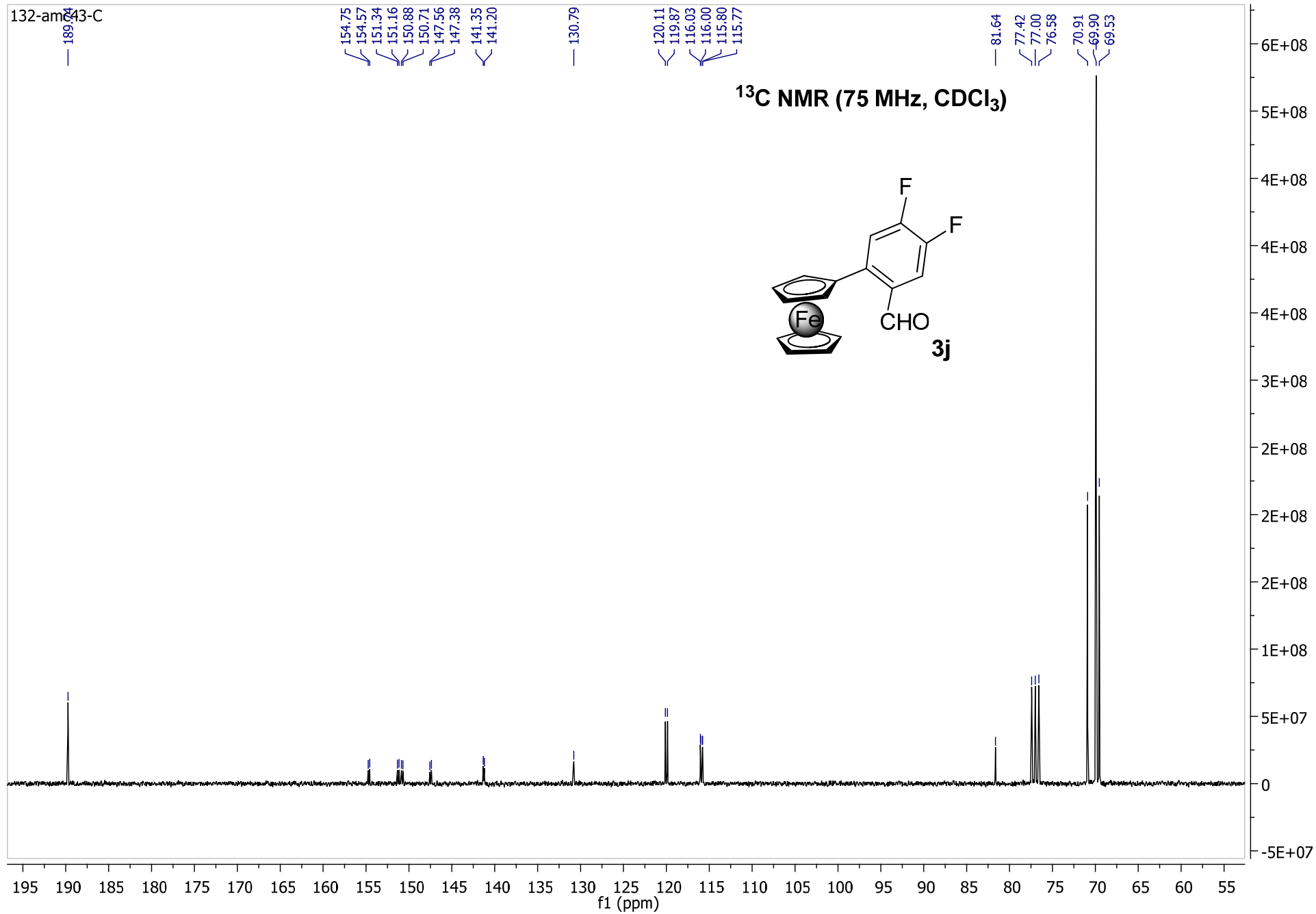




127-amc43a2

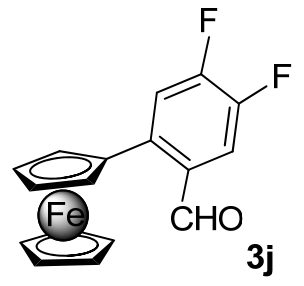
¹H NMR (300 MHz, CDCl₃)





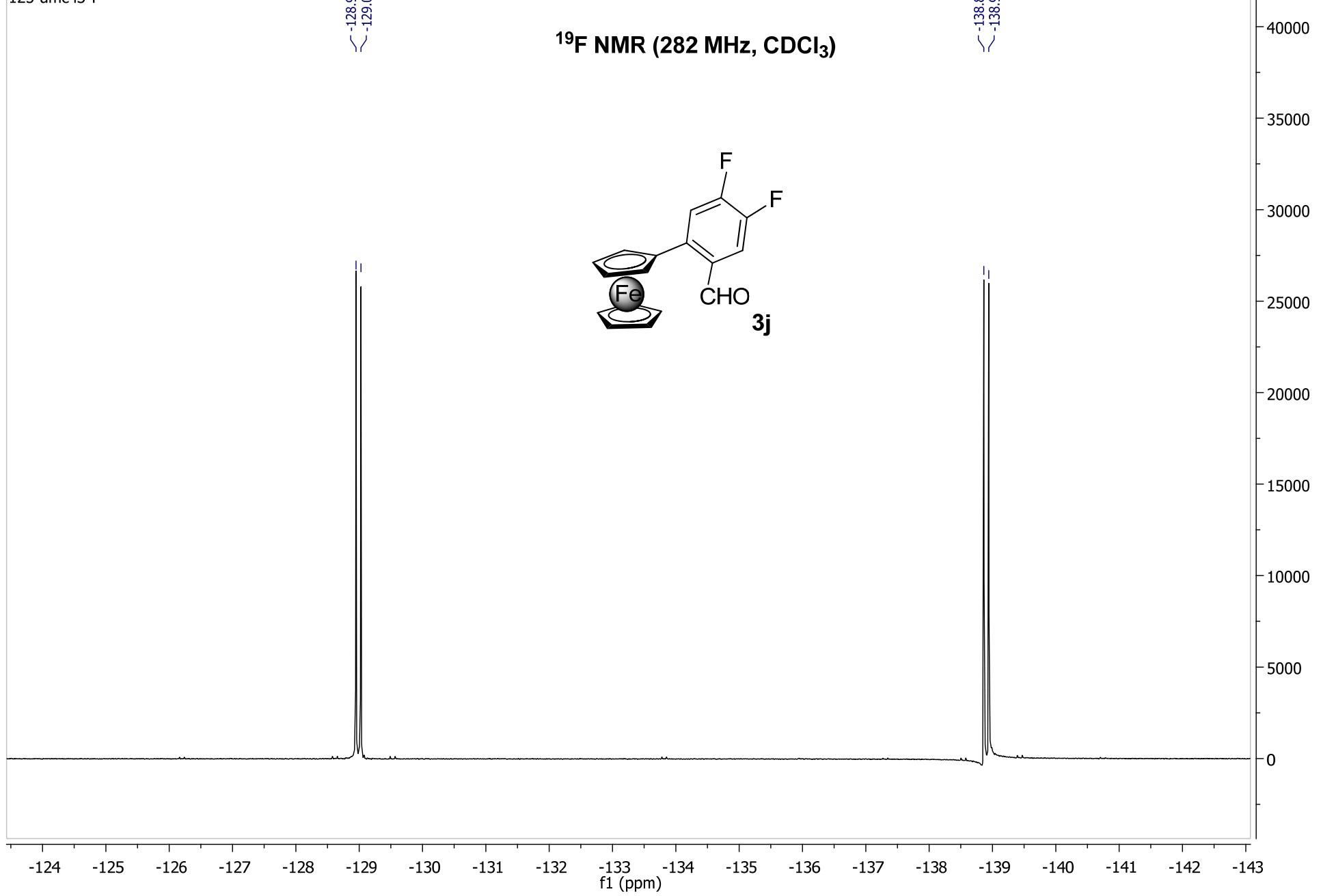
125-amc43-F

¹⁹F NMR (282 MHz, CDCl₃)

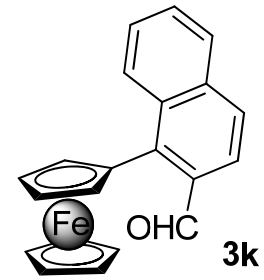
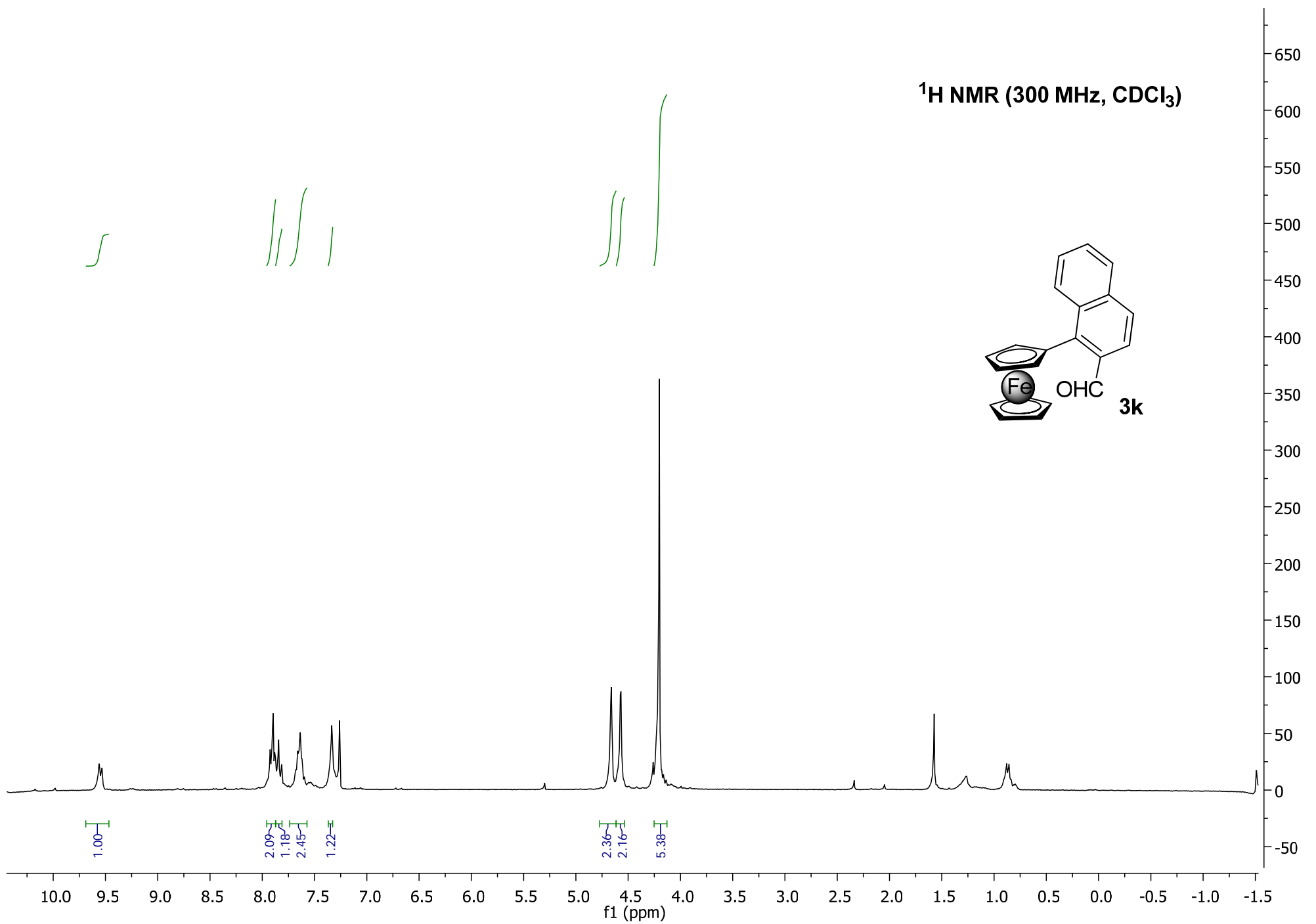


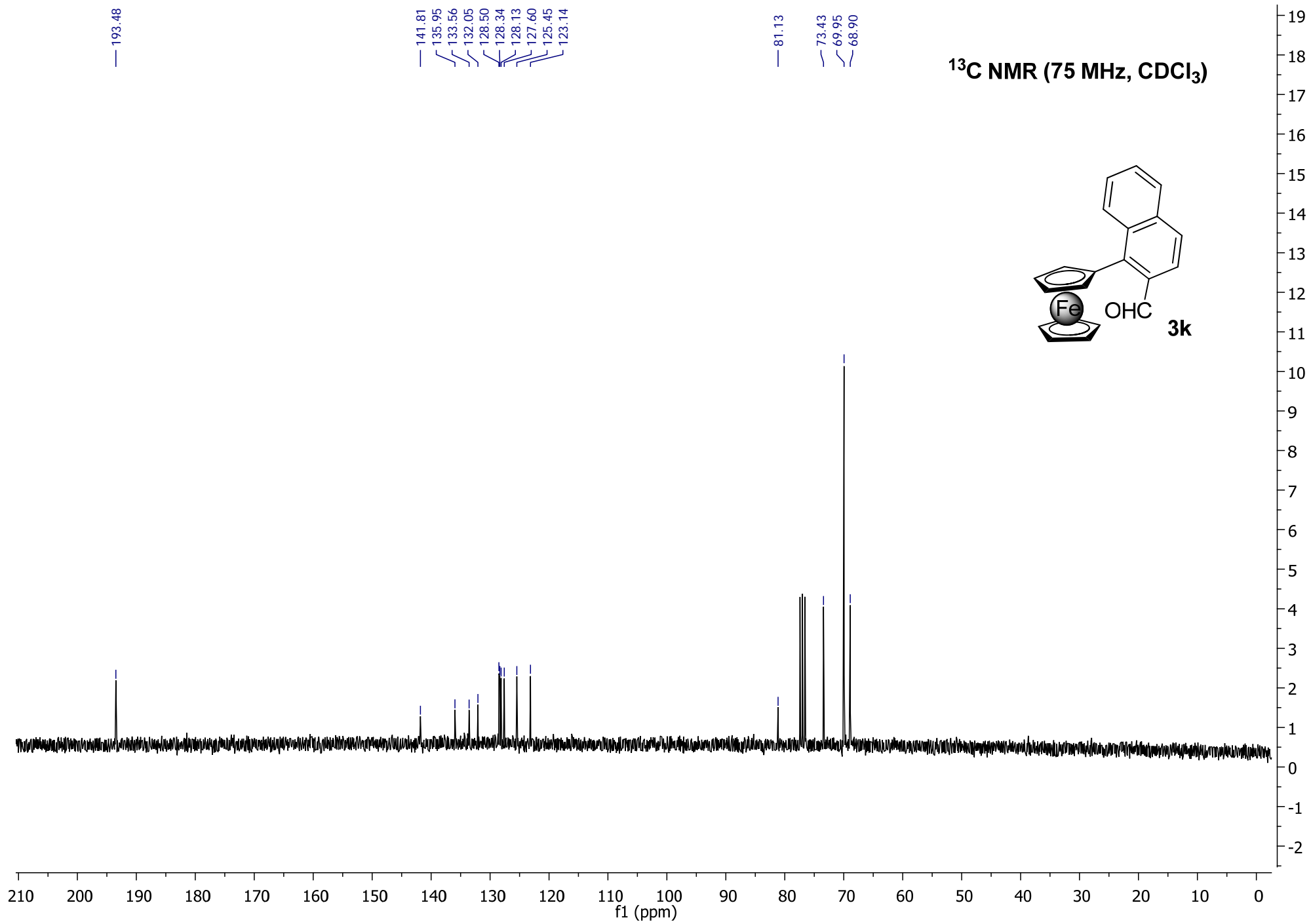
-128.95
-129.03

-138.86
-138.94

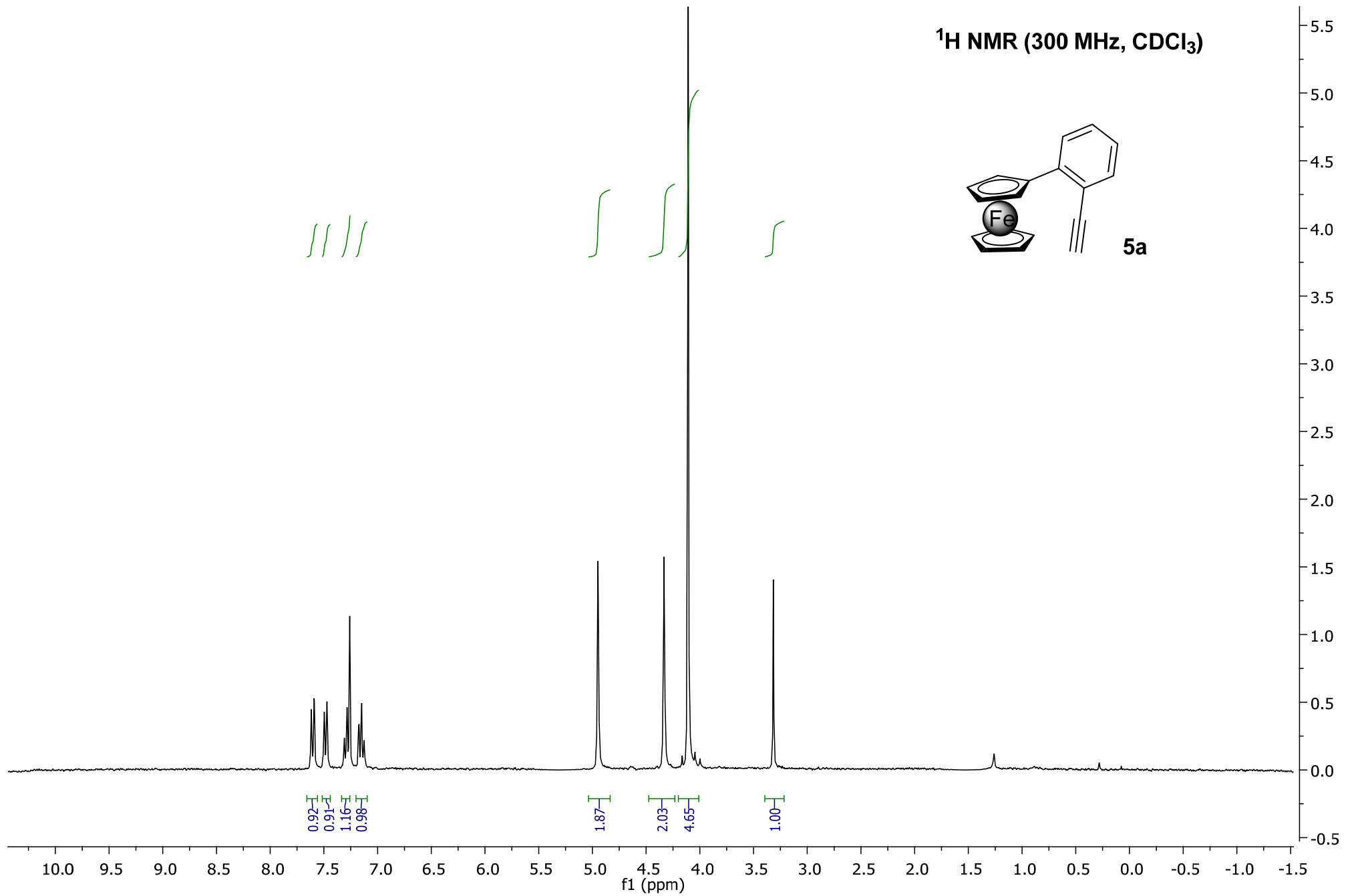
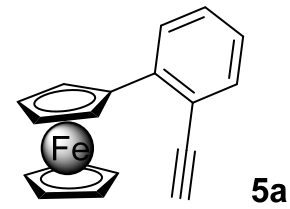


¹H NMR (300 MHz, CDCl₃)

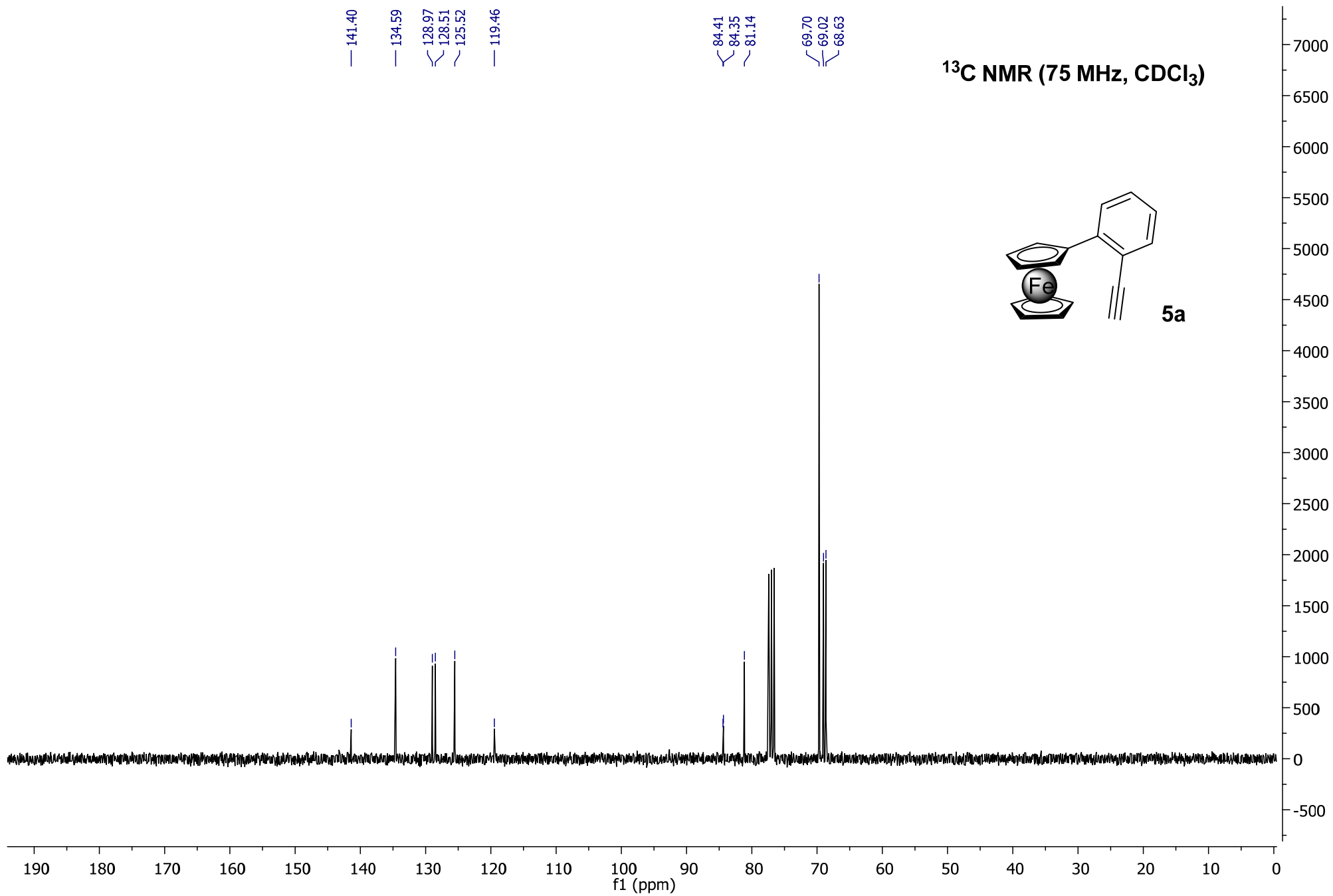


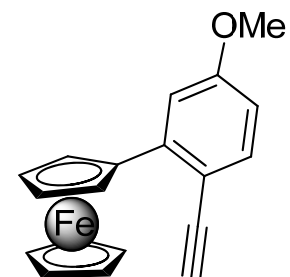


^1H NMR (300 MHz, CDCl_3)

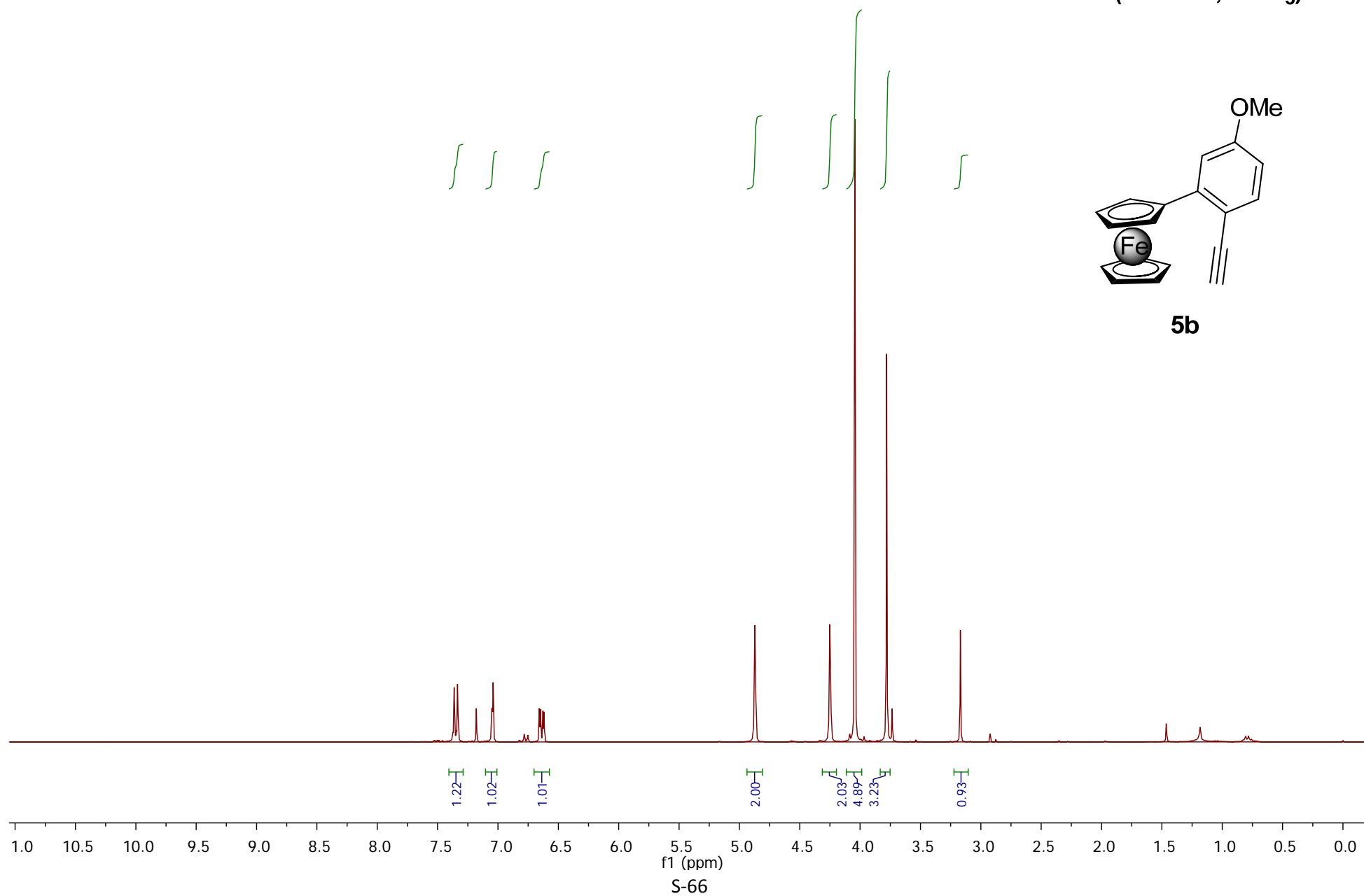


S-64



^1H NMR (300 MHz, CDCl_3)

5b



hg01_13

— 159.52

— 143.14

— 136.09

— 114.48

— 112.12

— 111.39

— 84.42

— 79.82

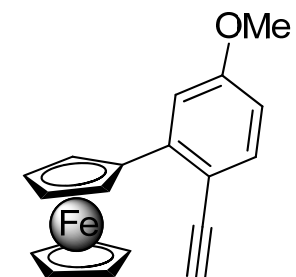
— 69.79

— 69.06

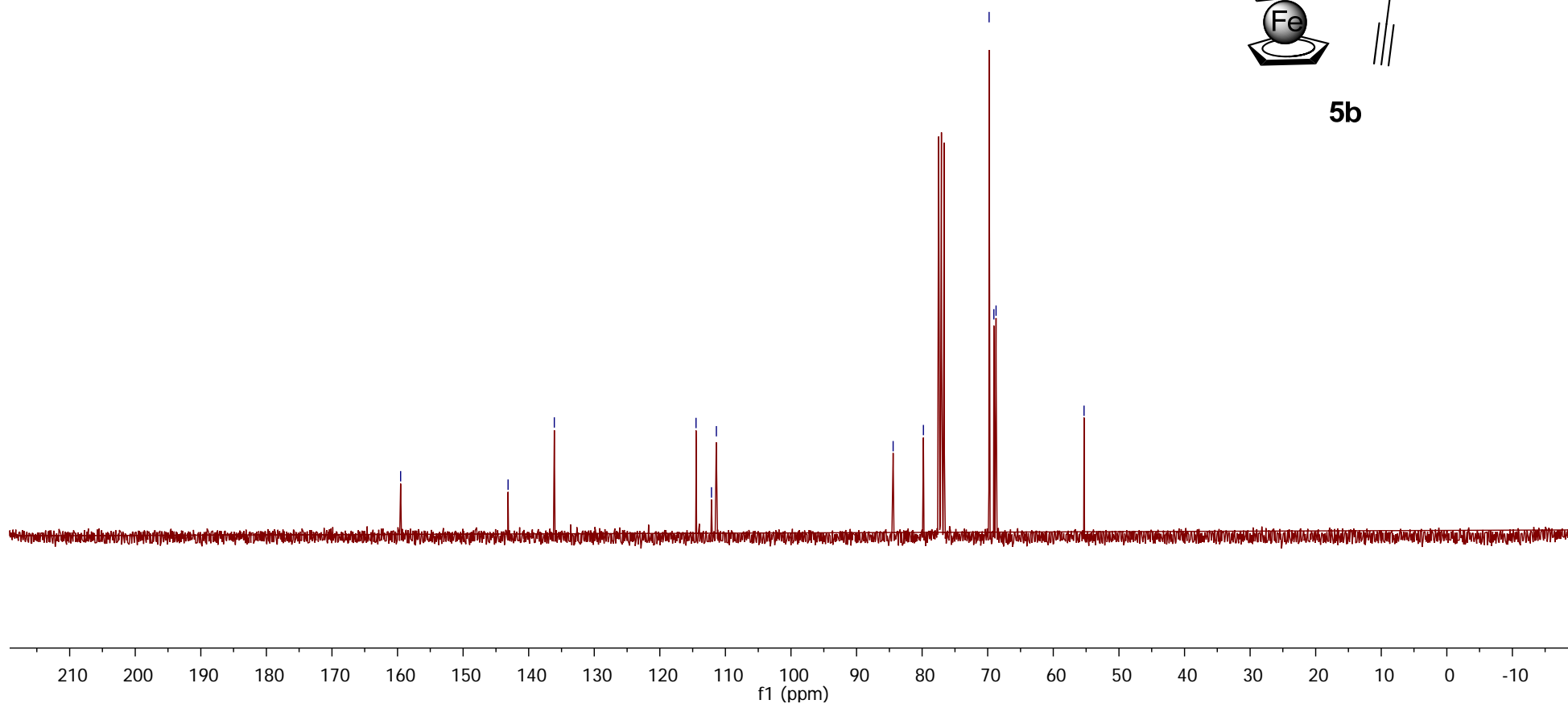
— 68.73

— 55.31

¹³C NMR (75 MHz, CDCl₃)



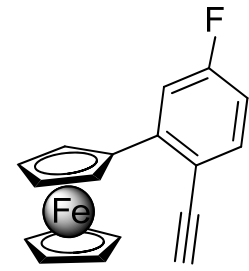
5b



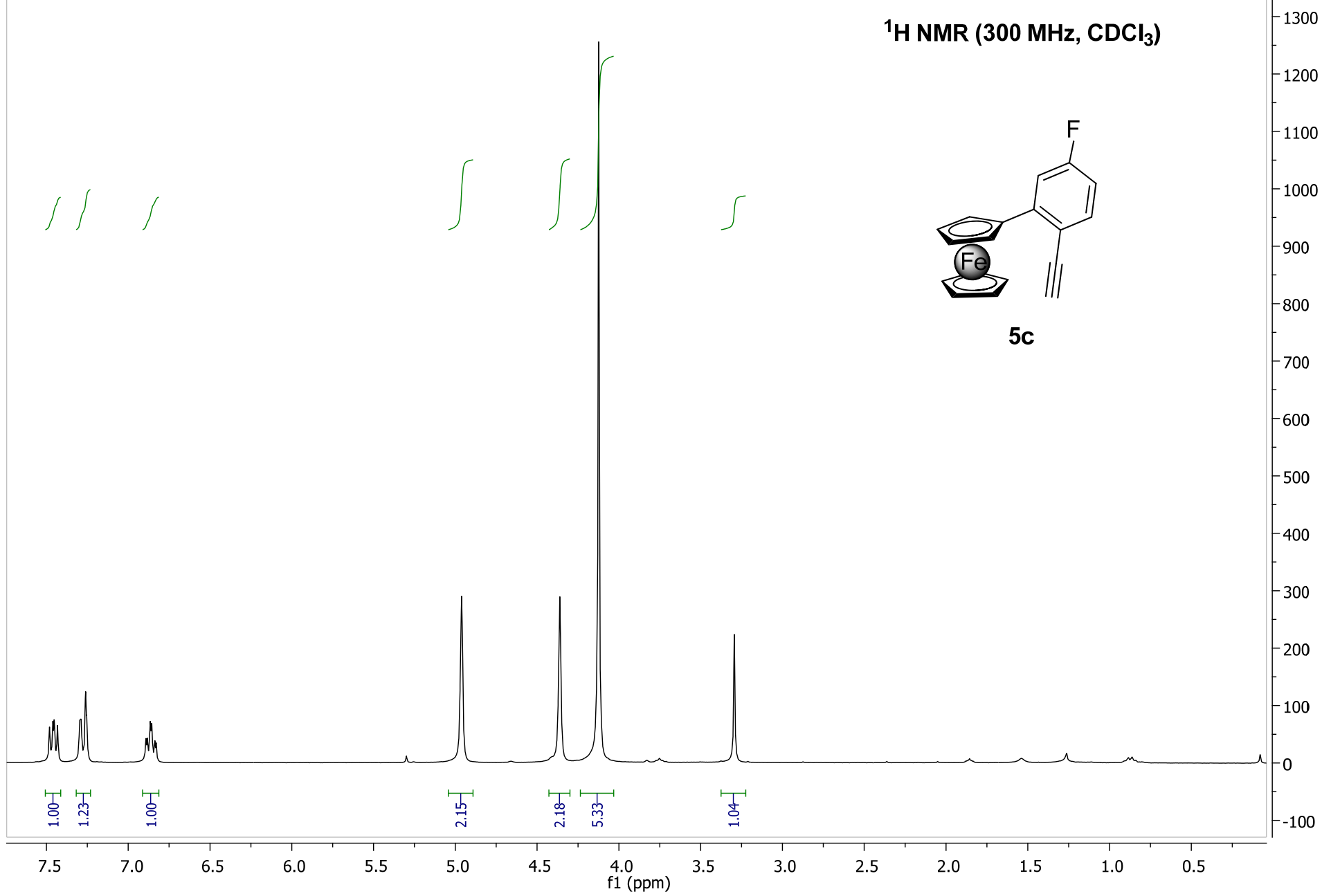
S-67

amc67-H

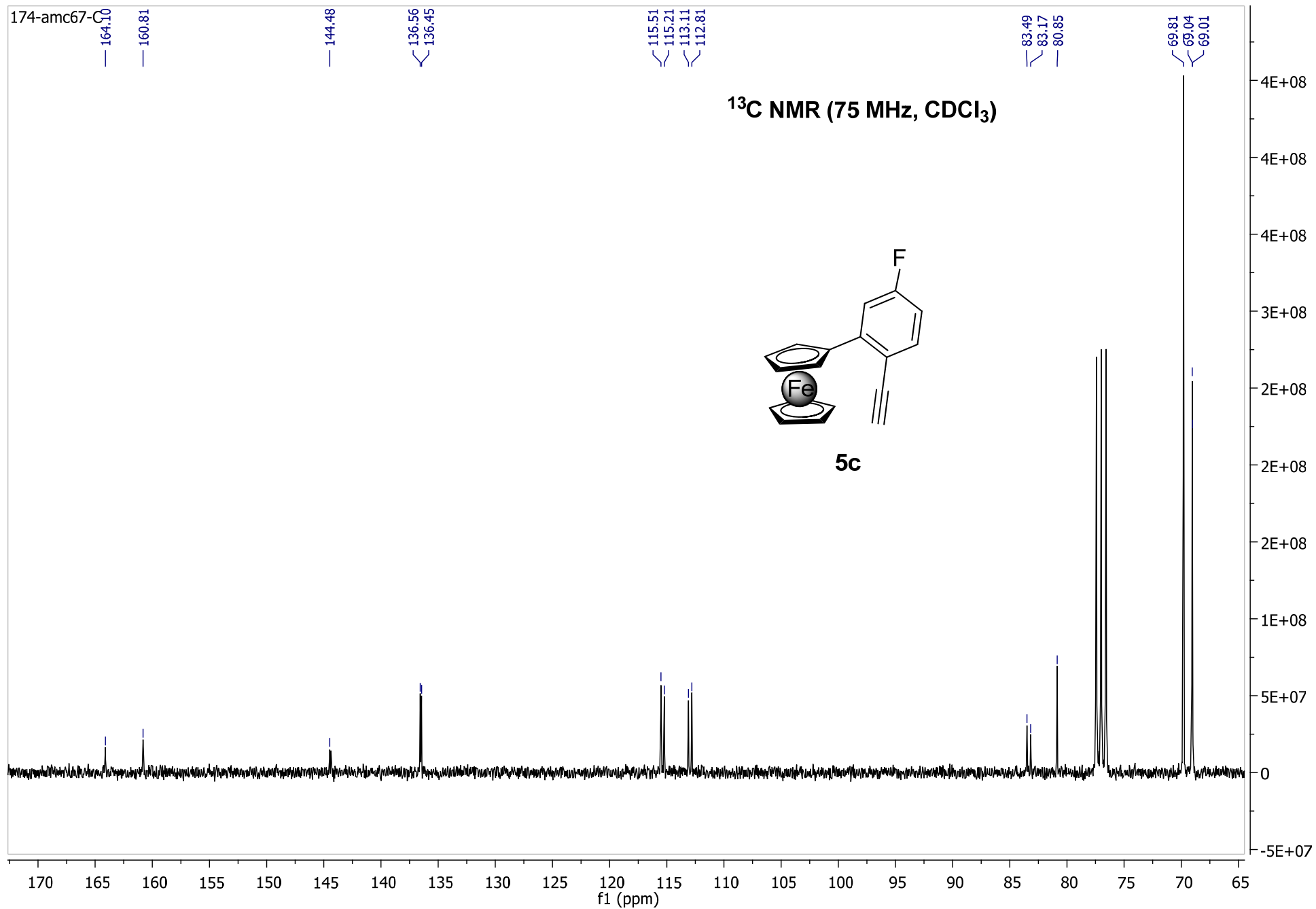
¹H NMR (300 MHz, CDCl₃)



5c

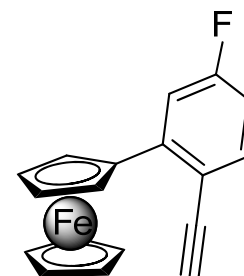


S-68

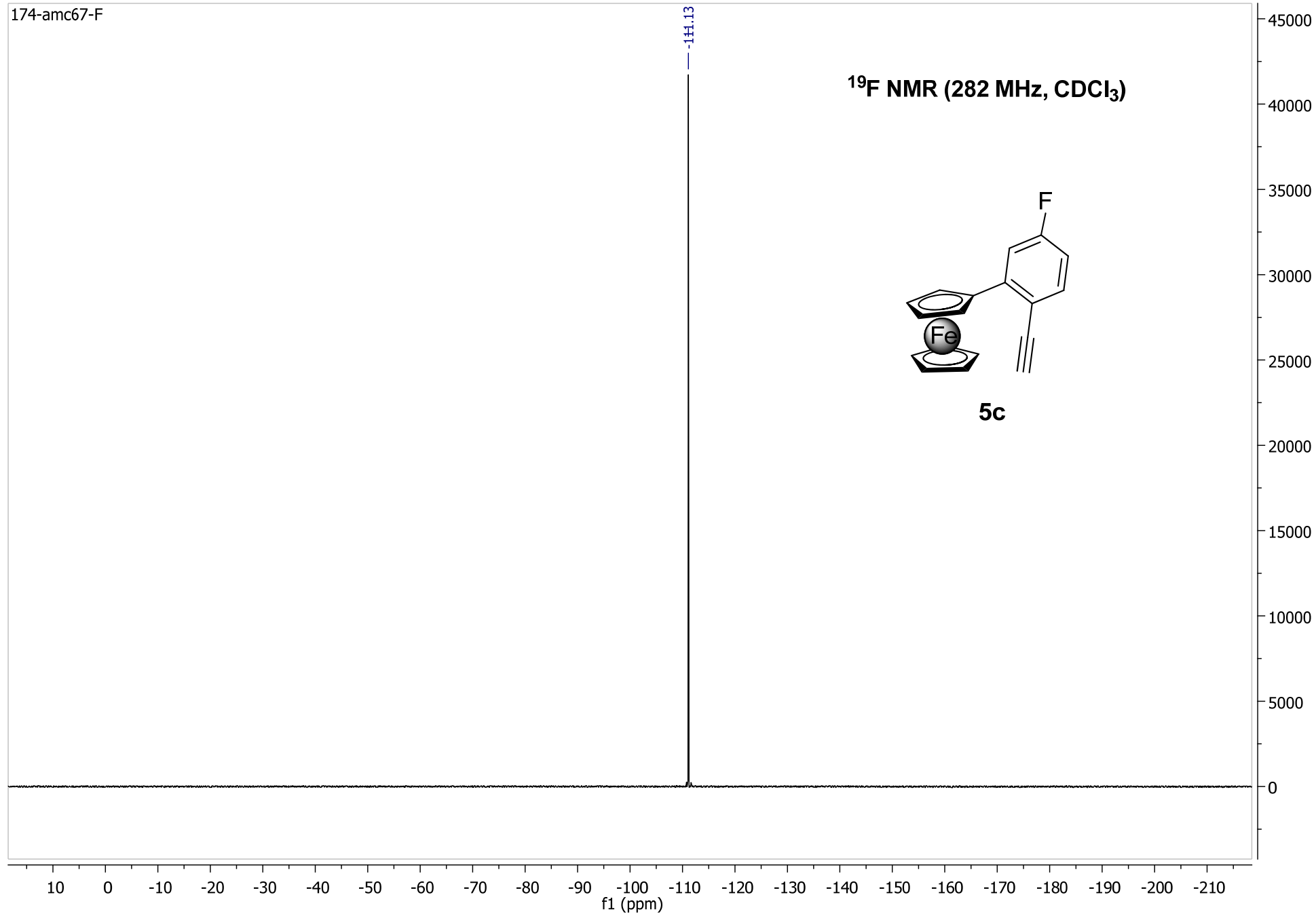


174-amc67-F

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

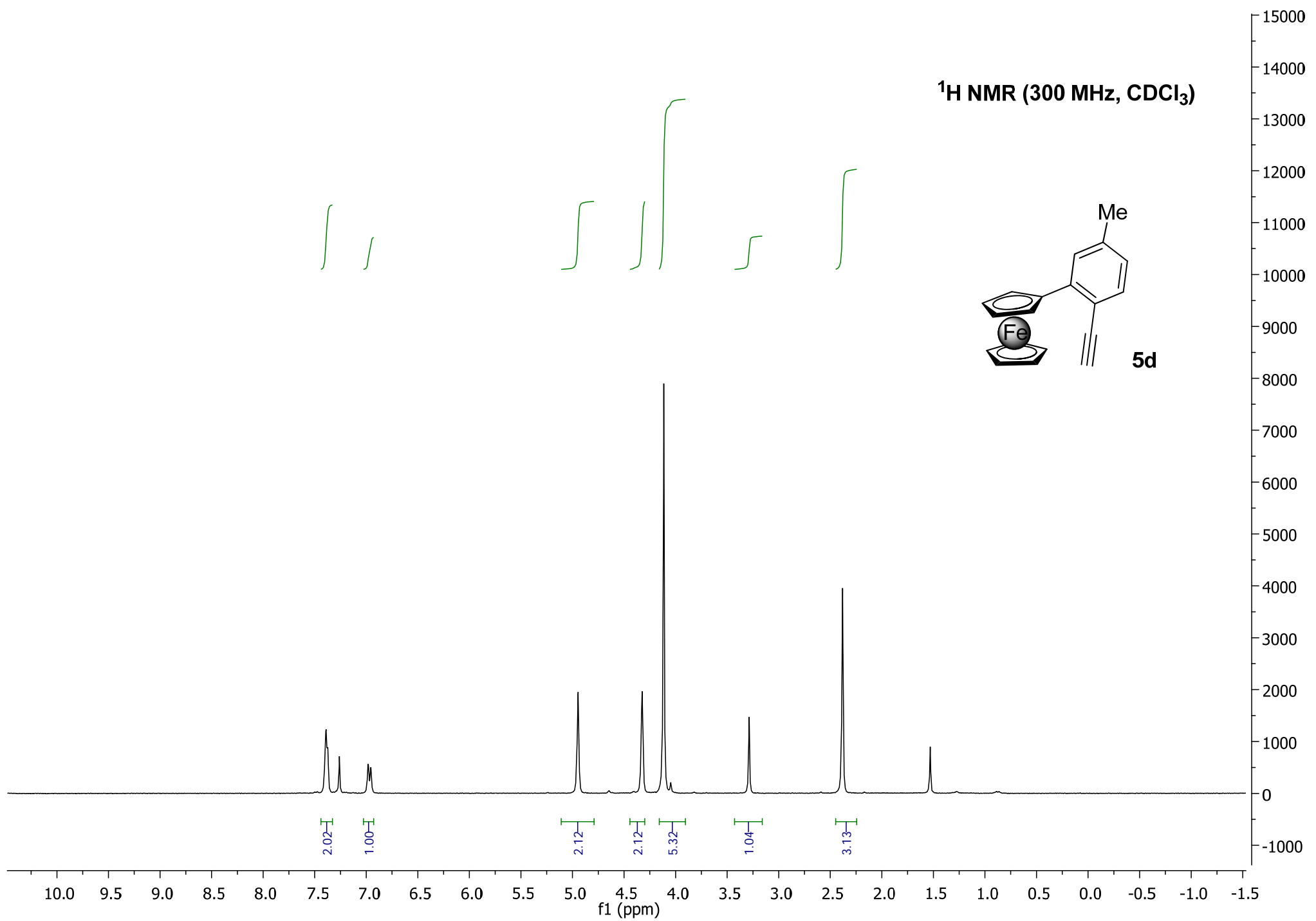
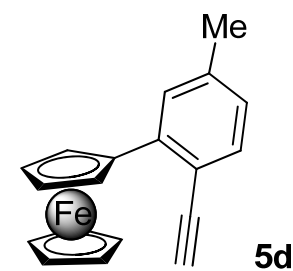


5c



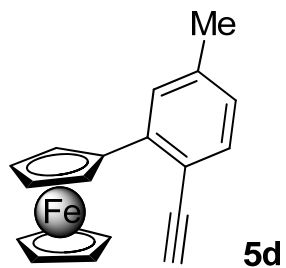
S-70

¹H NMR (300 MHz, CDCl₃)

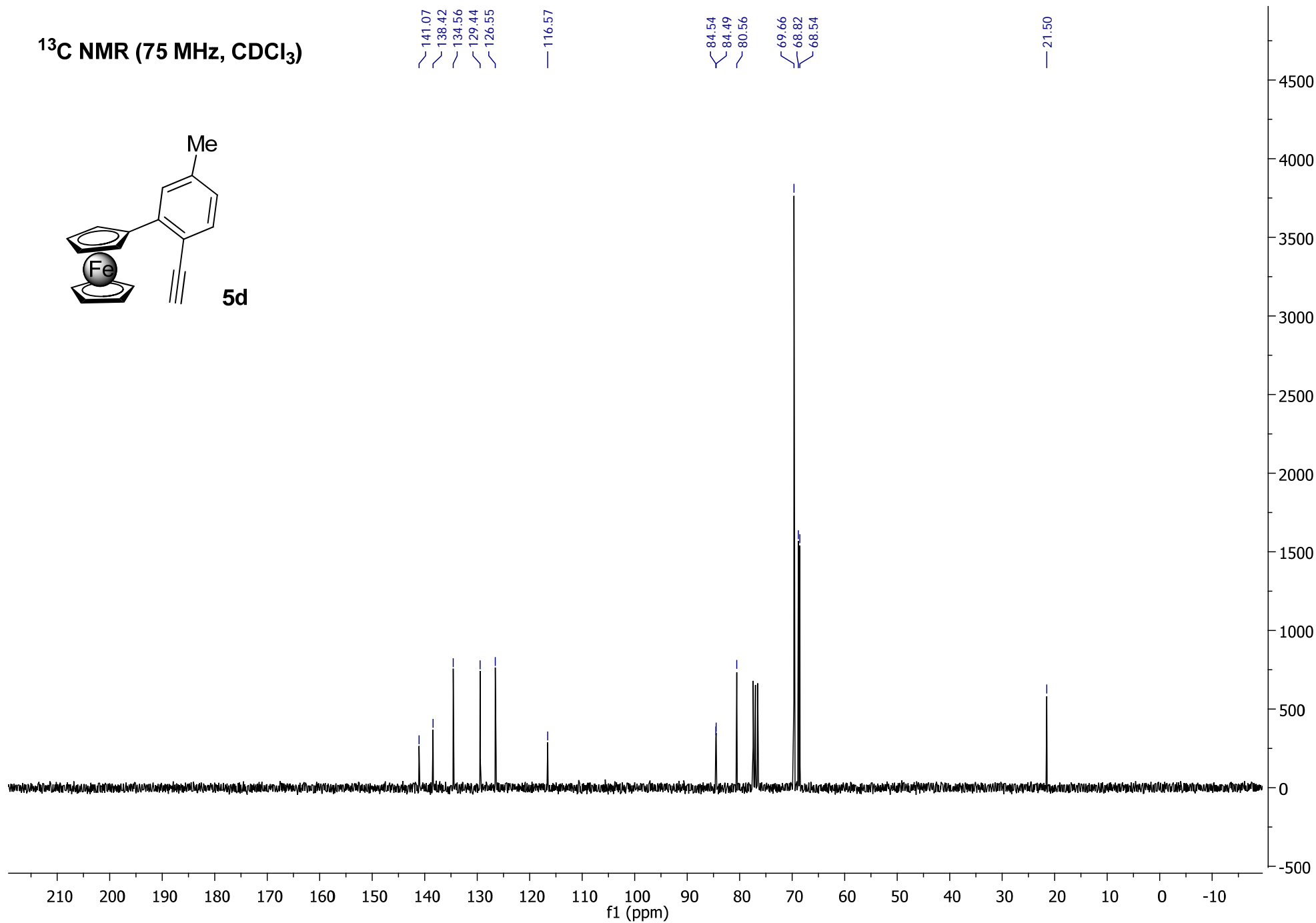


S-71

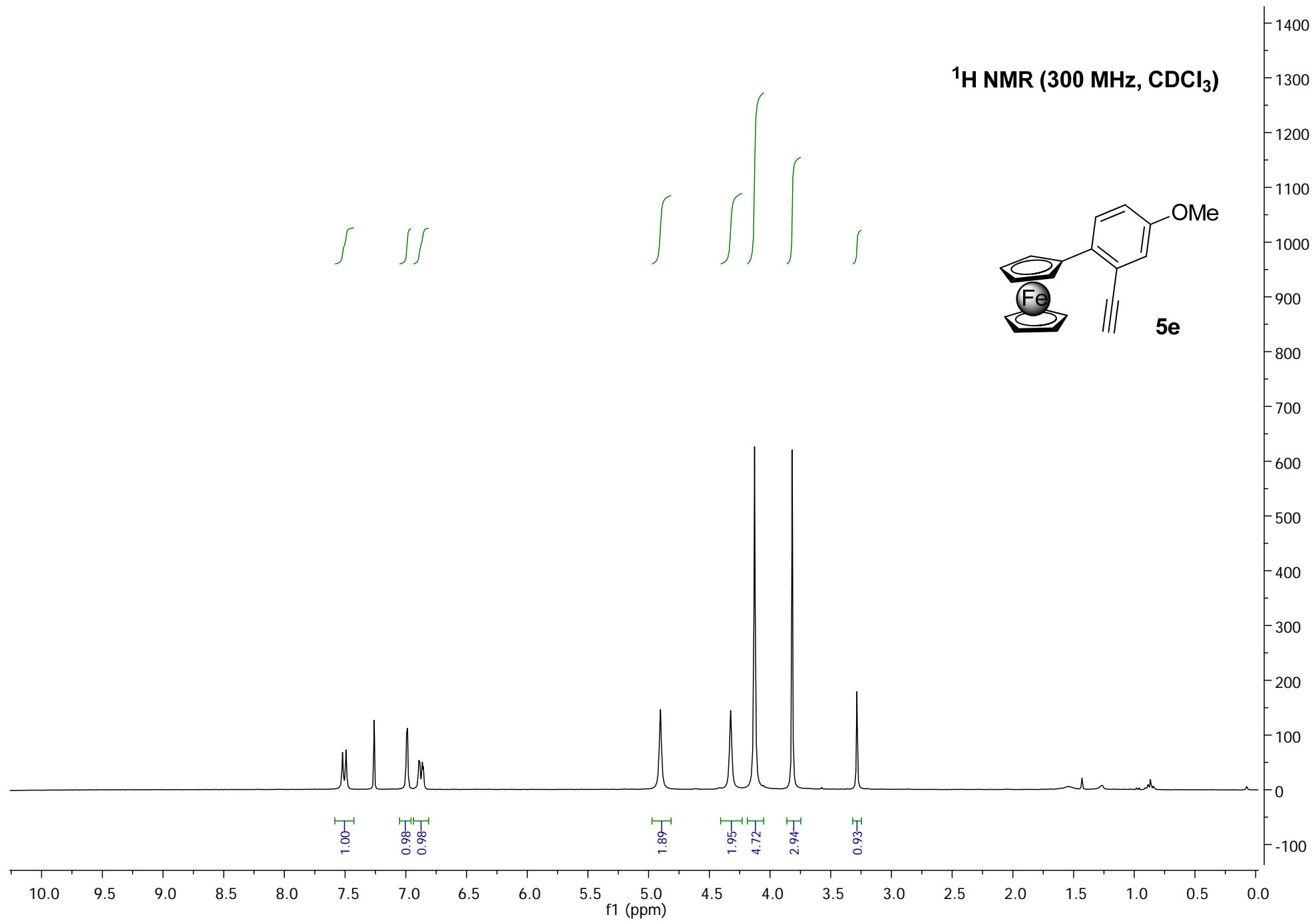
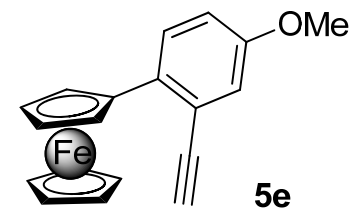
¹³C NMR (75 MHz, CDCl₃)

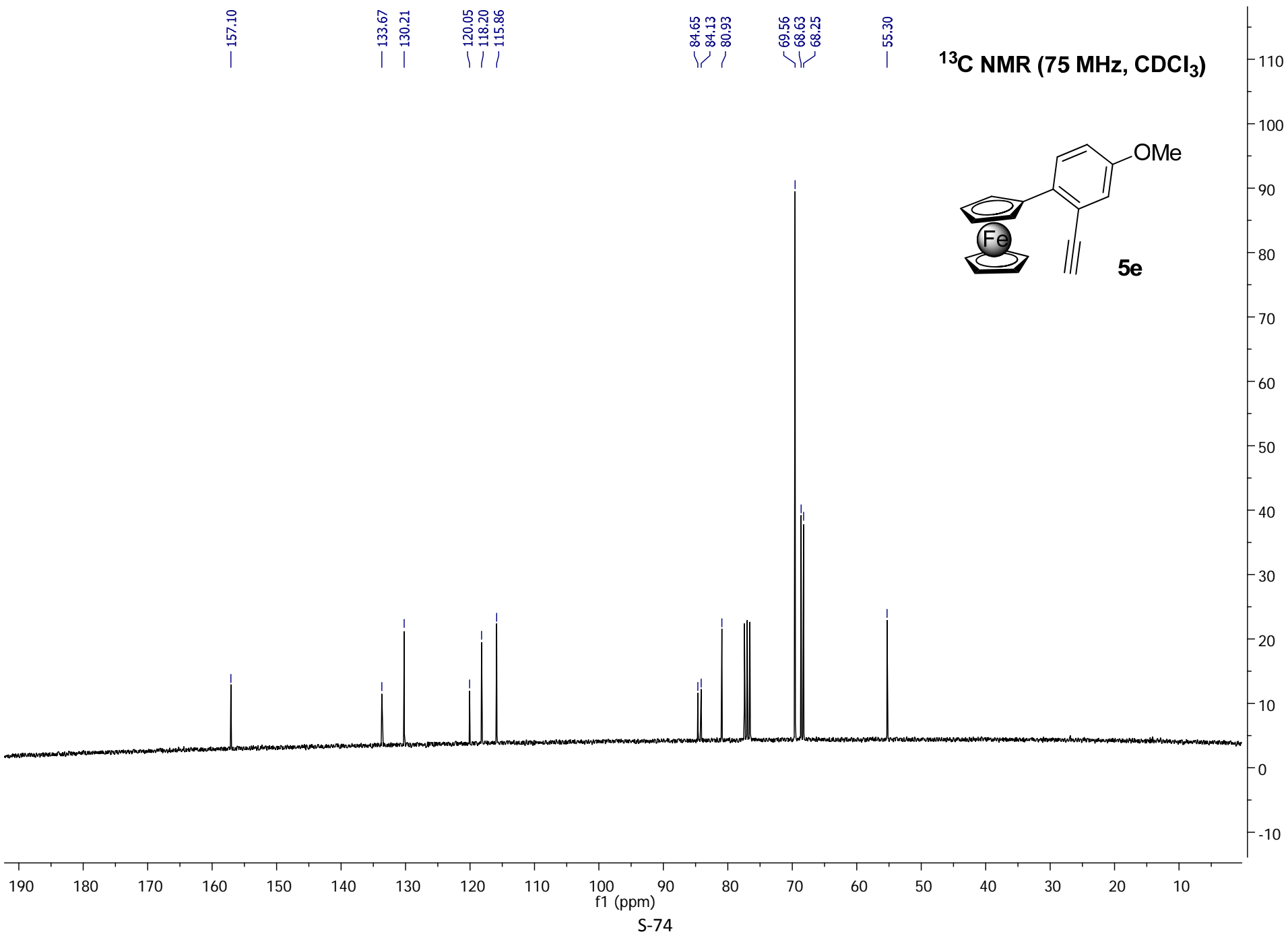


141.07
138.42
134.56
129.44
126.55
116.57
84.54
84.49
80.56
69.66
68.82
68.54
21.50



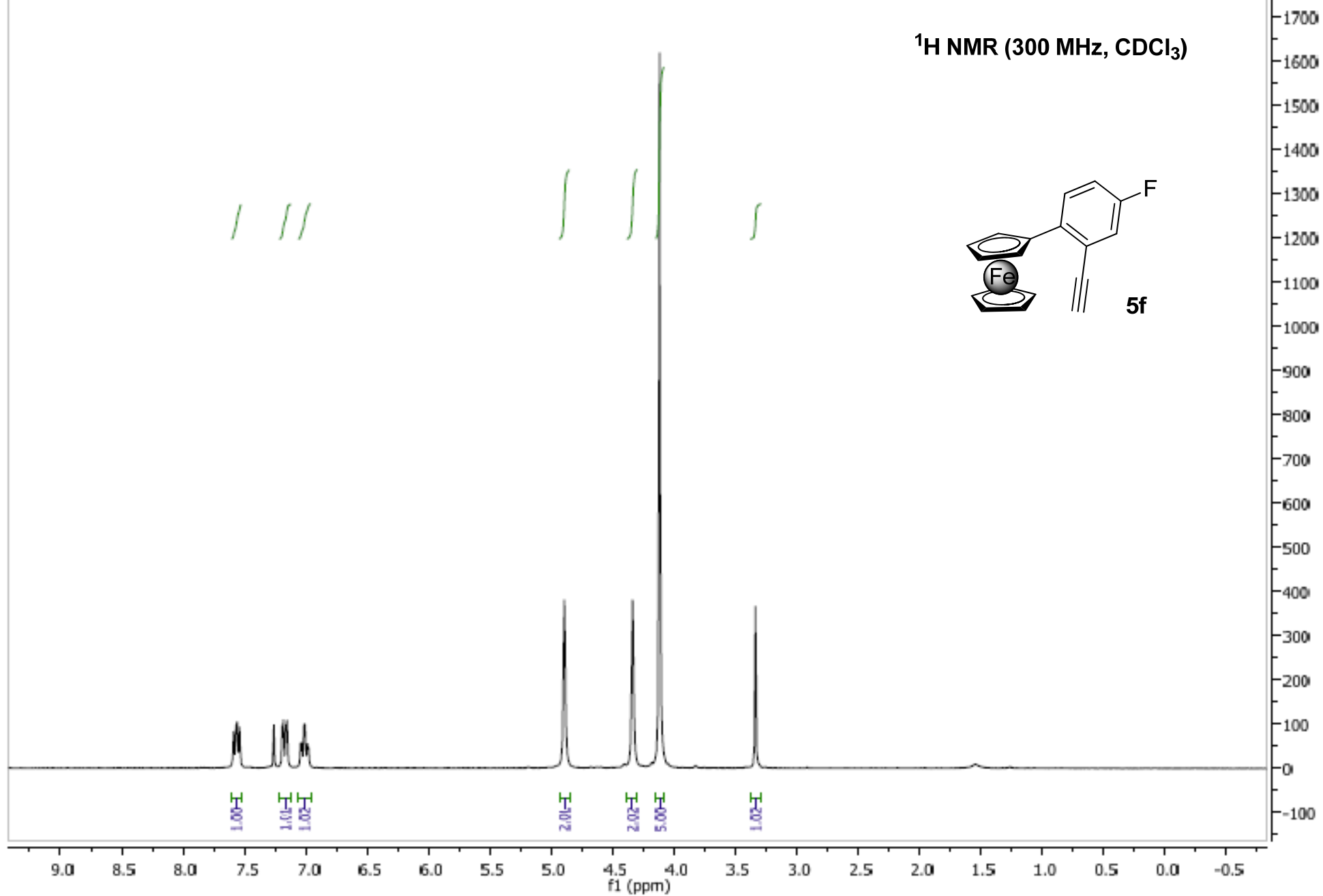
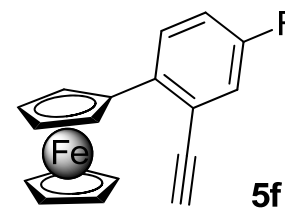
¹H NMR (300 MHz, CDCl₃)





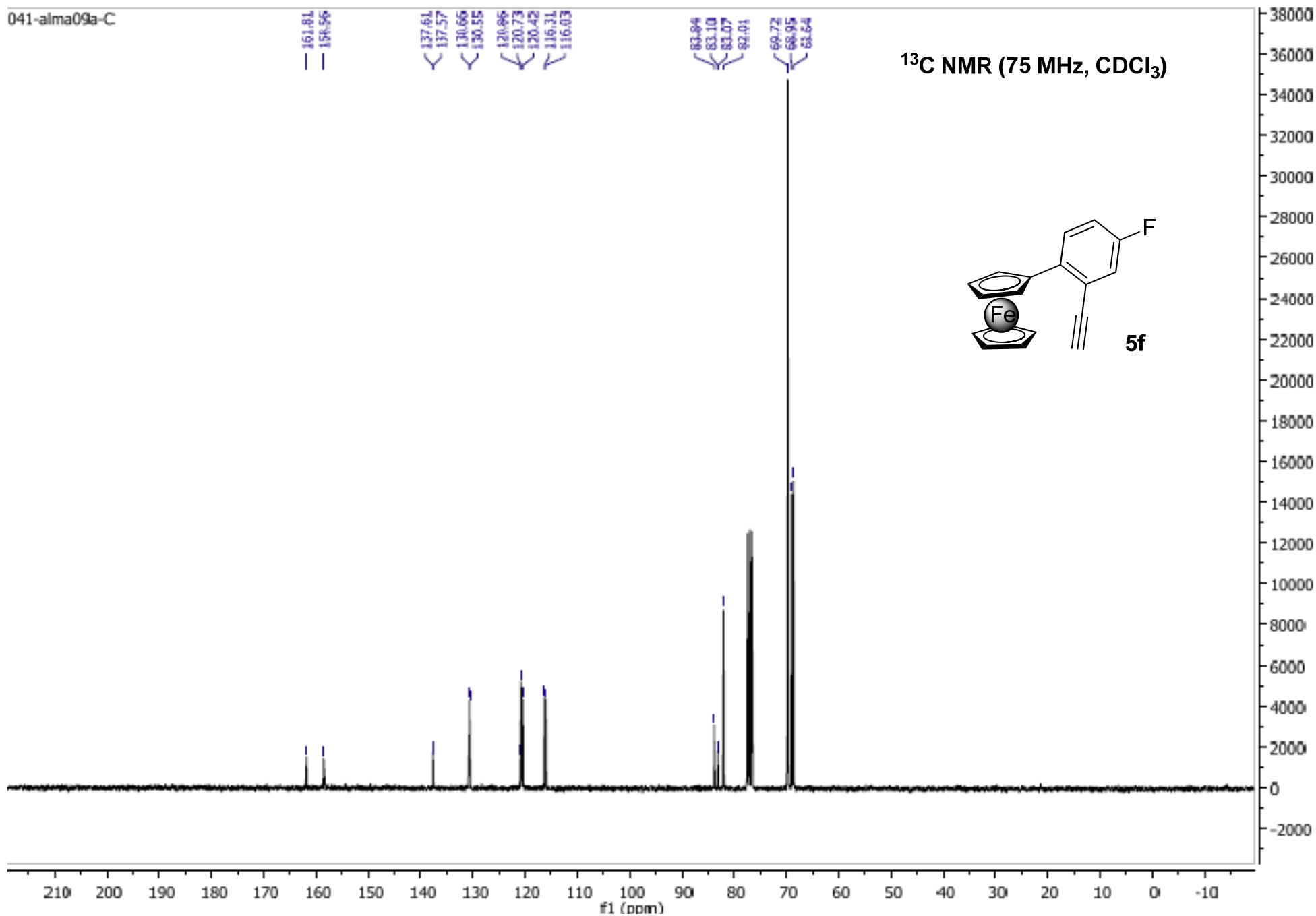
040-aiima09a

^1H NMR (300 MHz, CDCl_3)

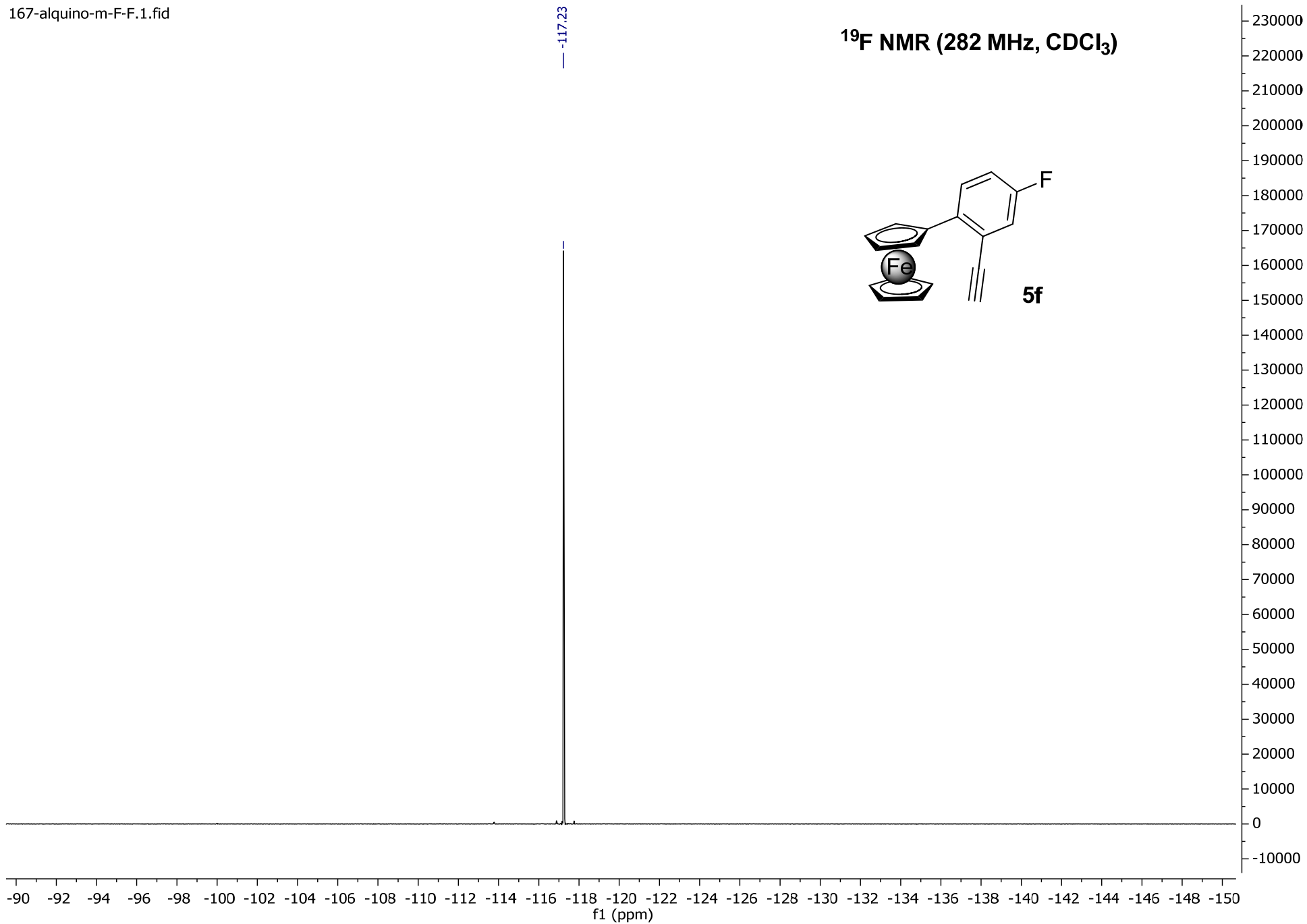
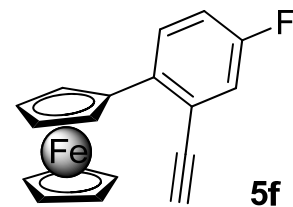


S-75

041-alma09a-C

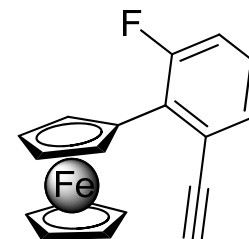


¹⁹F NMR (282 MHz, CDCl₃)

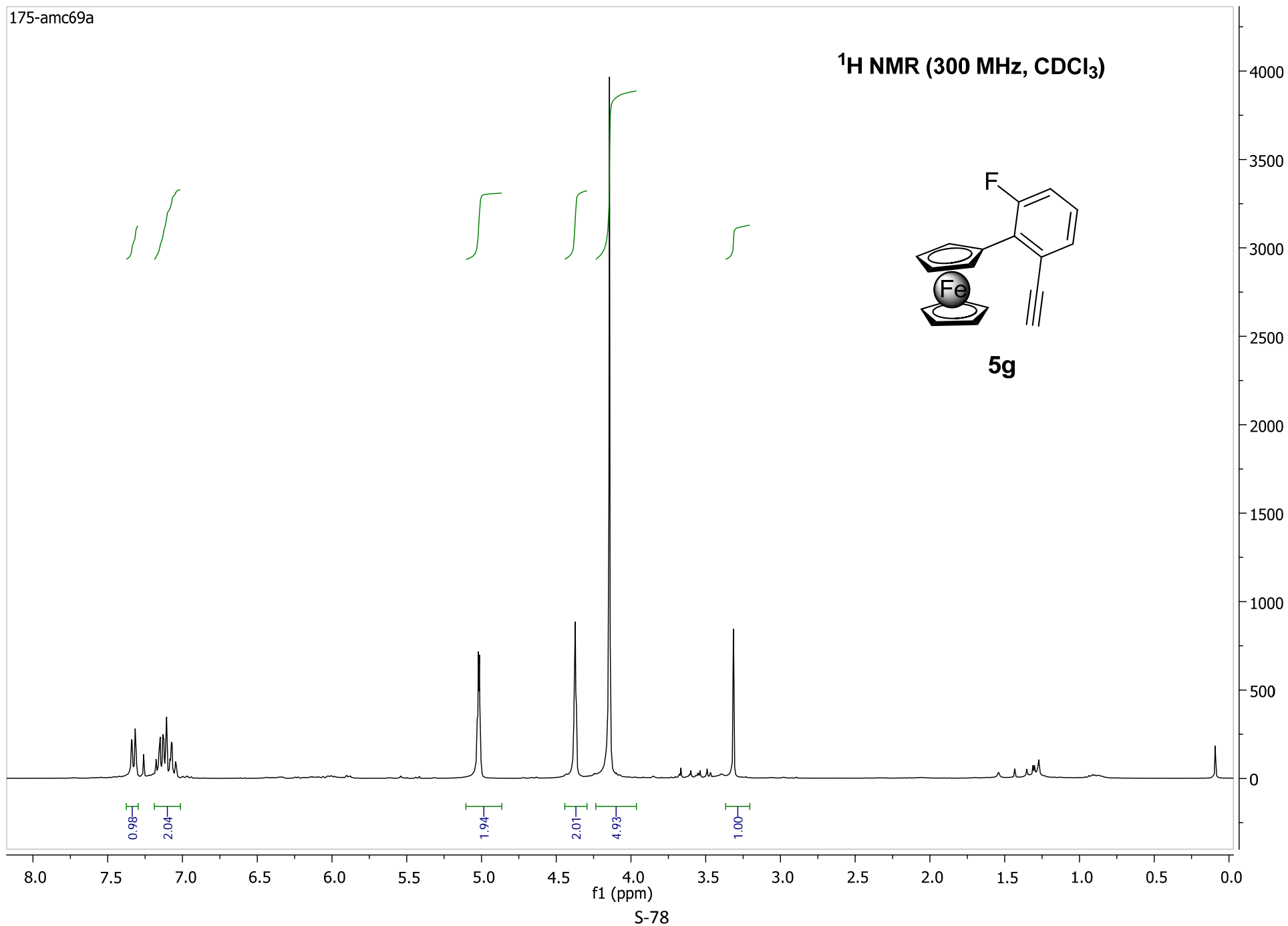


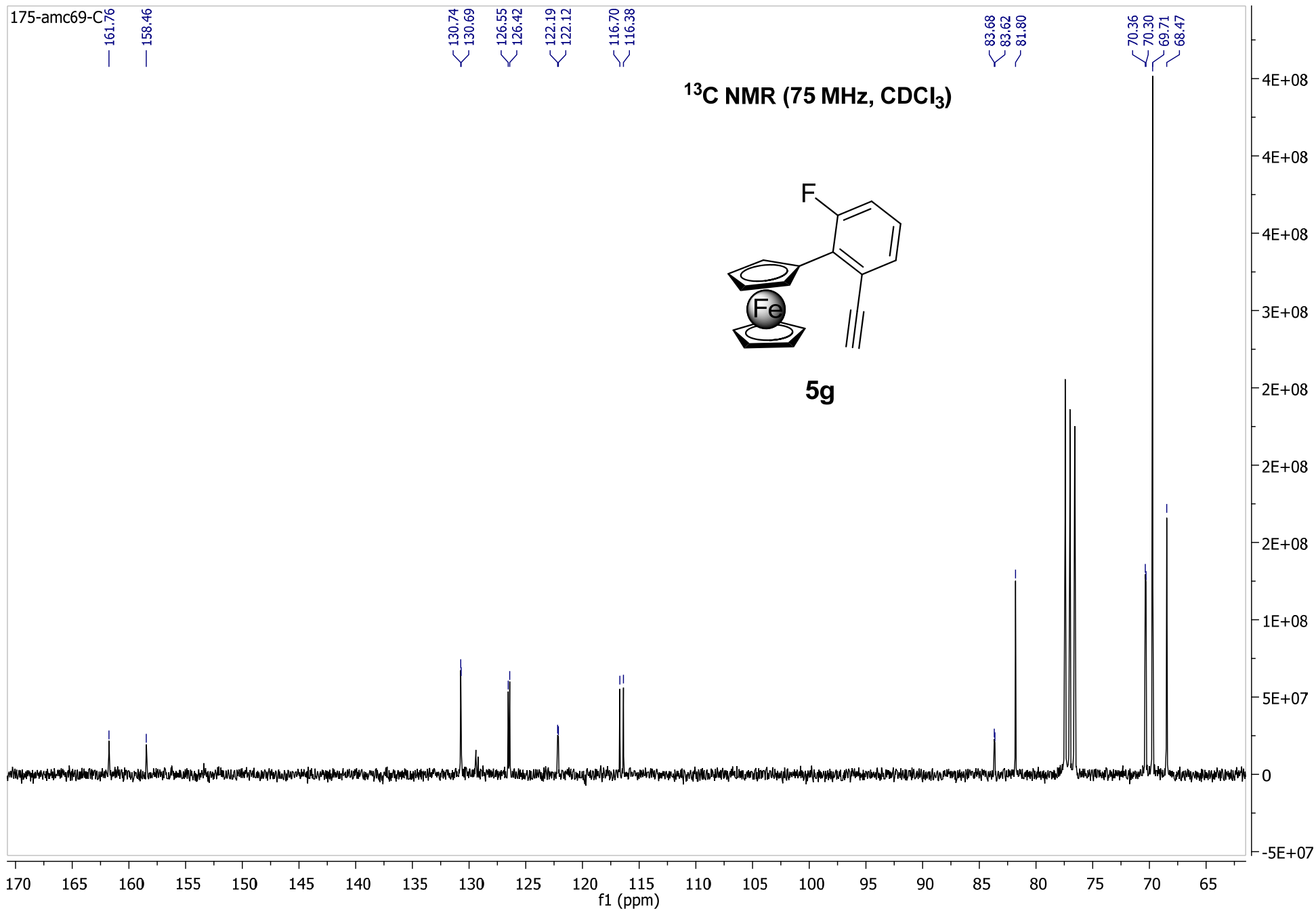
175-amc69a

^1H NMR (300 MHz, CDCl_3)



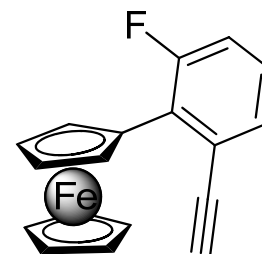
5g





188-amc69-F

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



5g

-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145

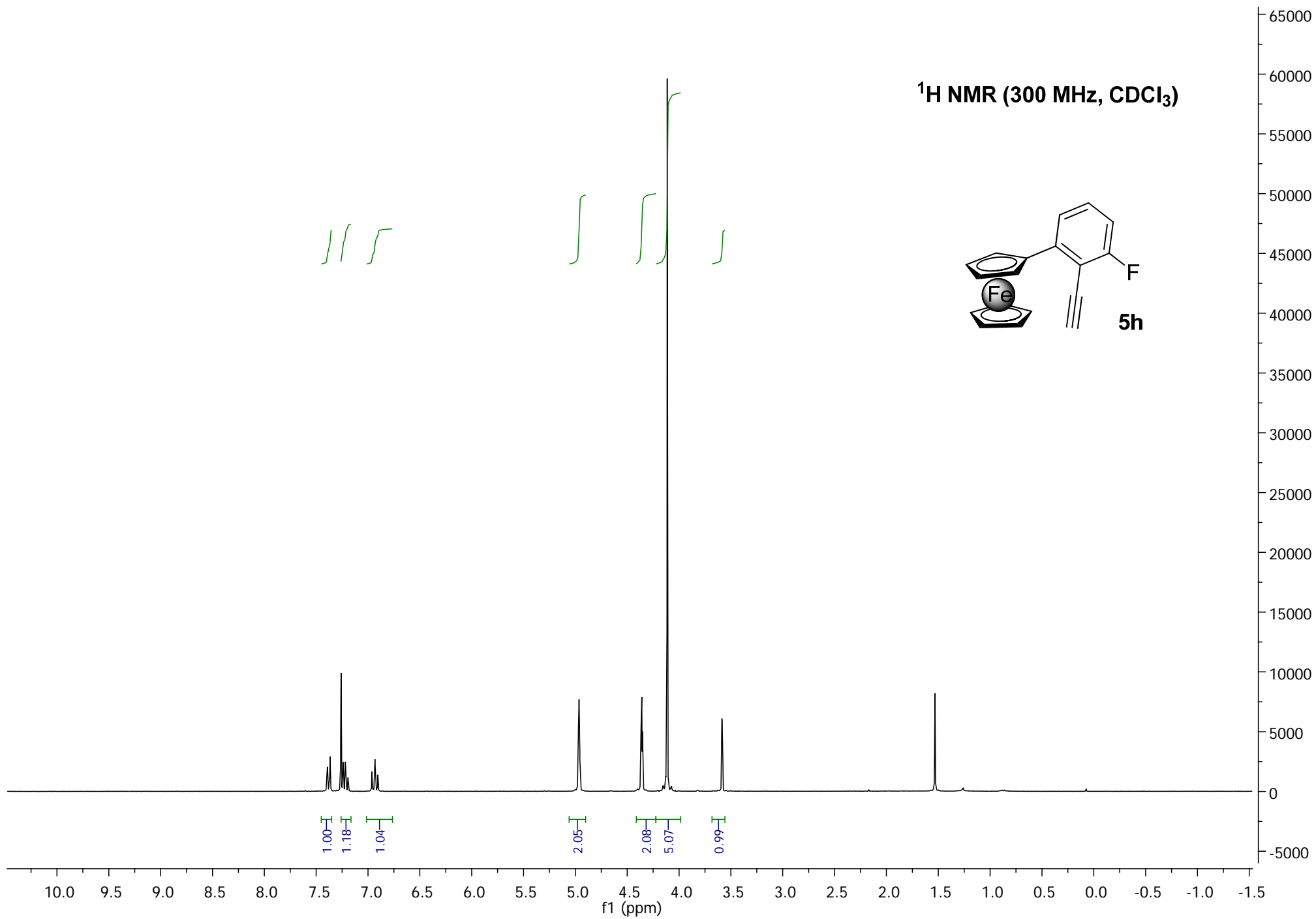
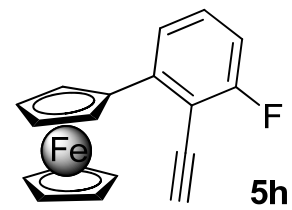
f1 (ppm)

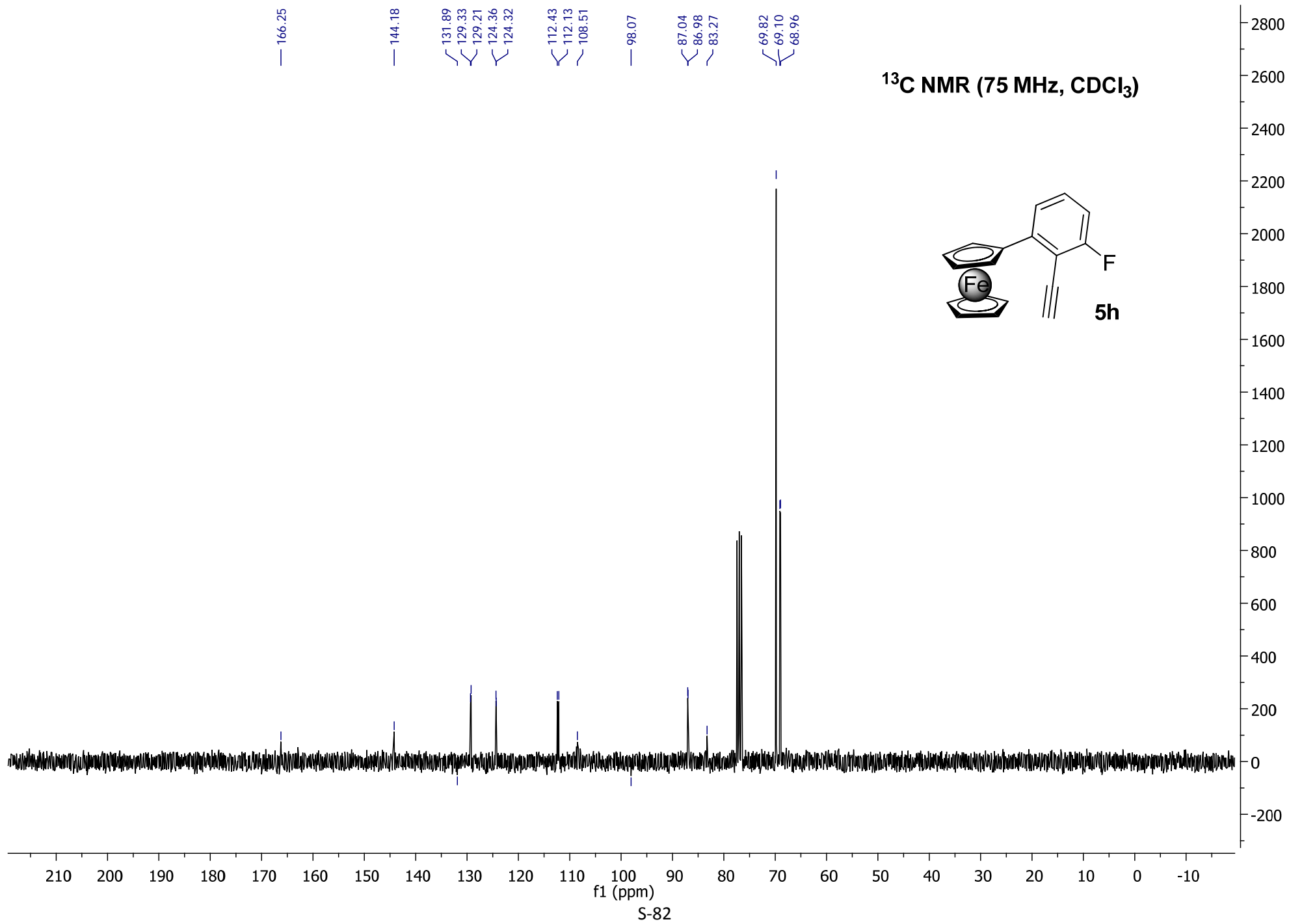
S-80

0
5000
10000
15000
20000
25000
30000
35000
40000

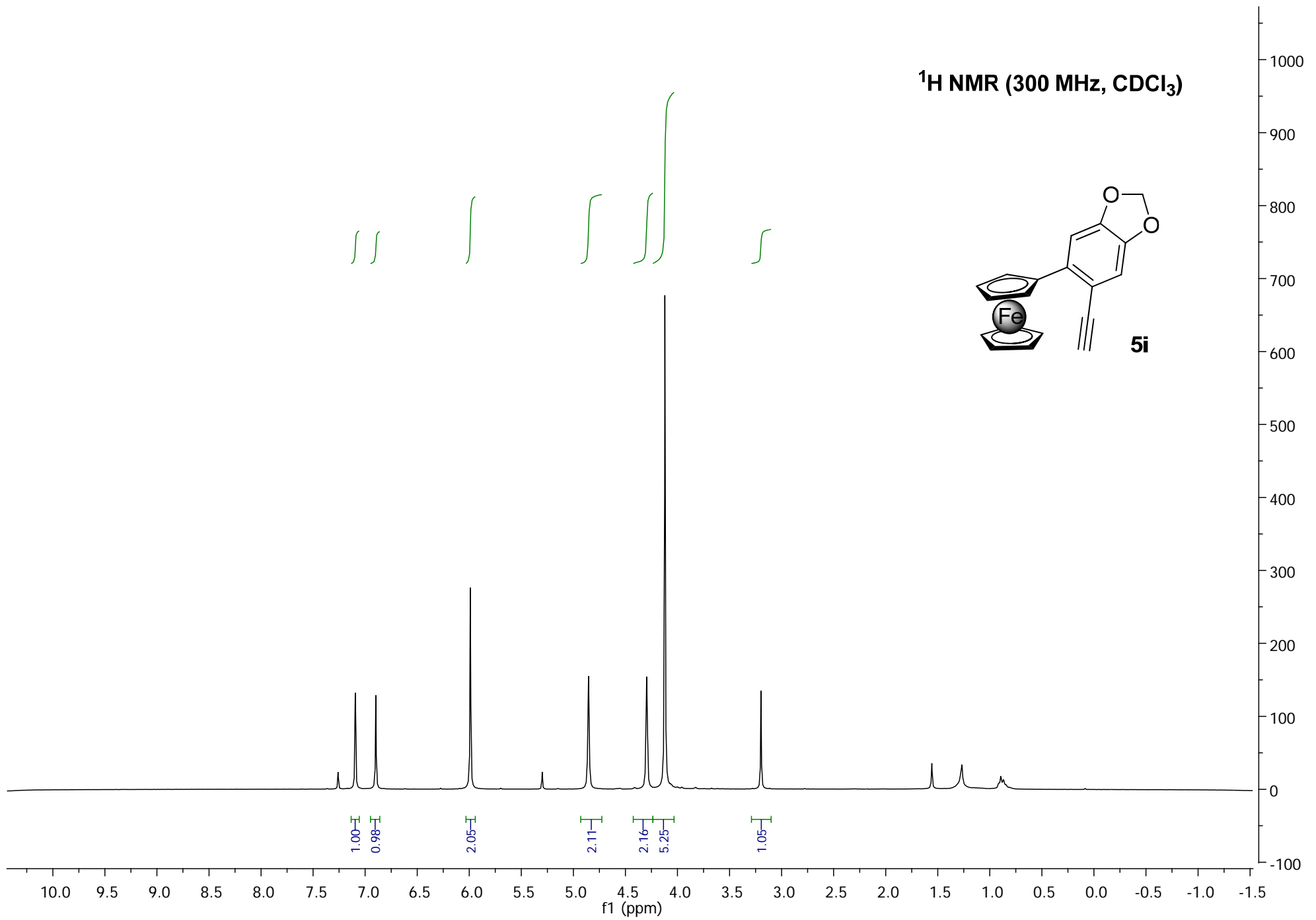
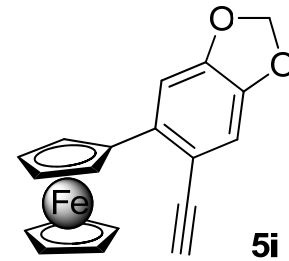
-107.82

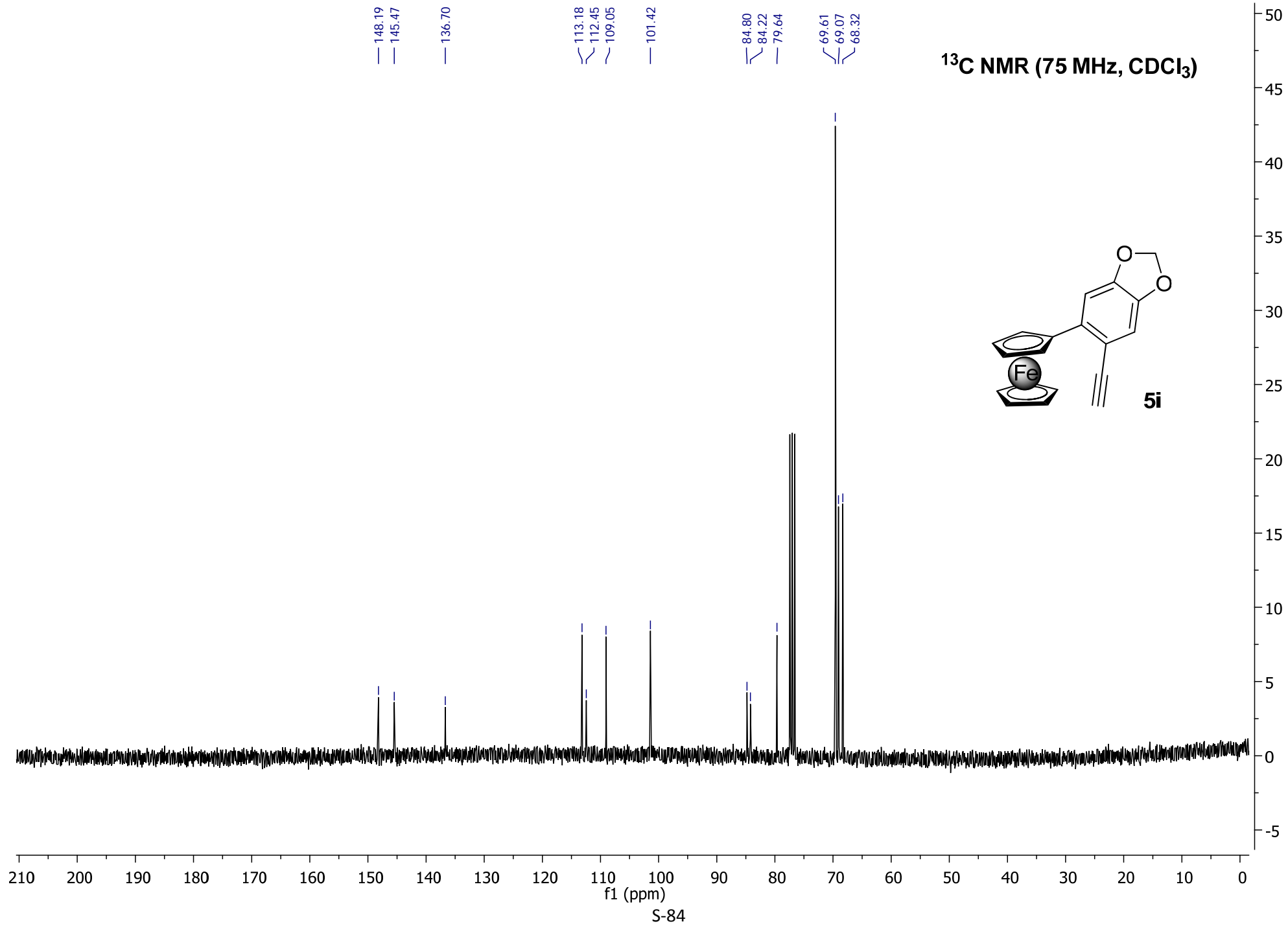
¹H NMR (300 MHz, CDCl₃)





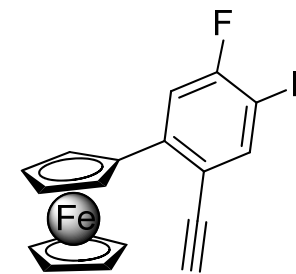
¹H NMR (300 MHz, CDCl₃)



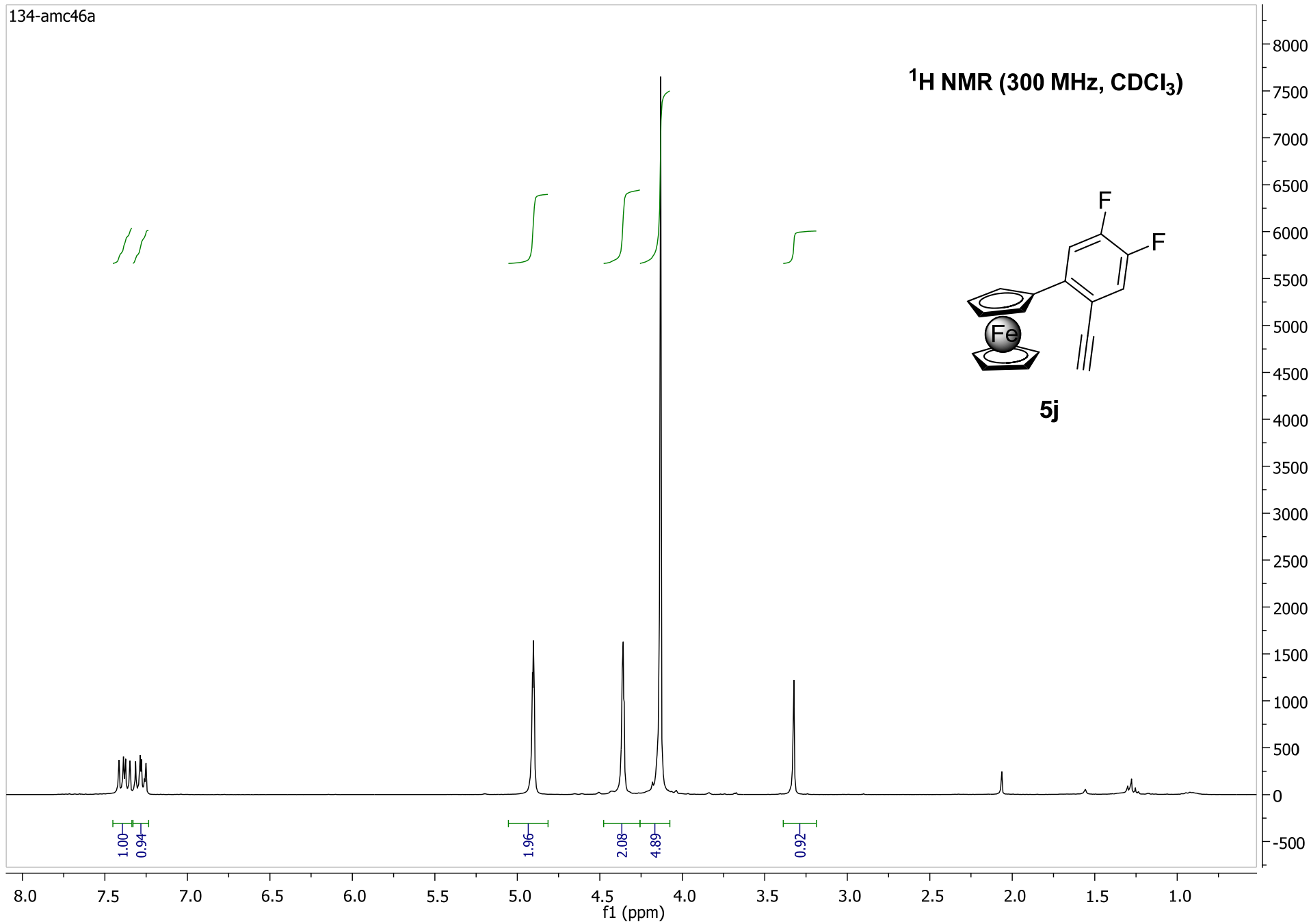


134-amc46a

¹H NMR (300 MHz, CDCl₃)



5j



S-85

3818t-amc46
amc46

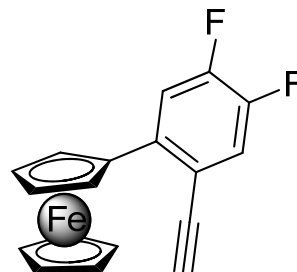
150.94
150.77
148.38
148.20
147.62
147.44
145.09
144.91
138.53
138.48
138.44
138.39

121.86
121.84
121.61
121.60
116.42
116.18
114.66
114.62
114.57
114.52

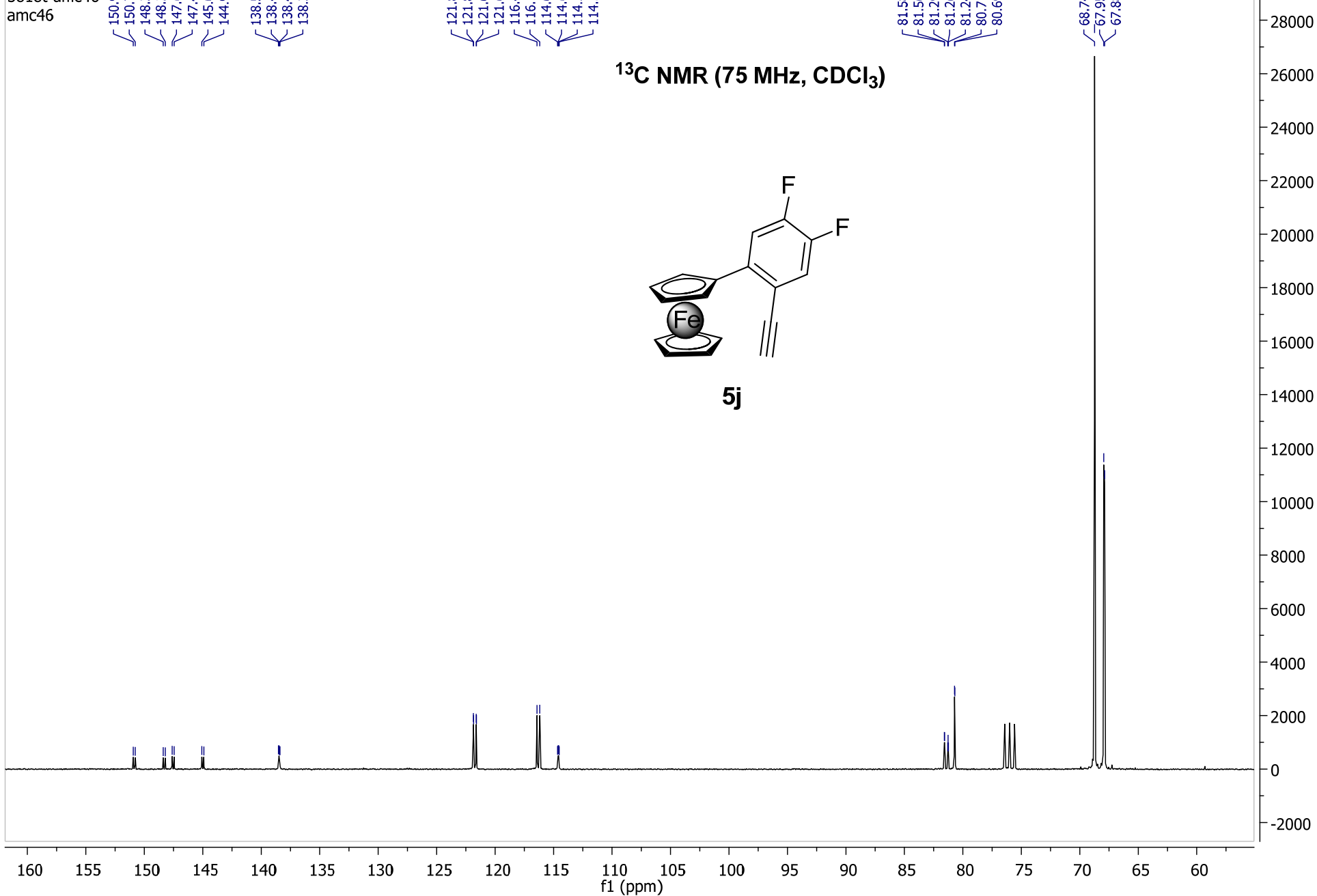
81.58
81.56
81.29
81.26
81.24
80.71
80.69

68.74
67.95
67.88

¹³C NMR (75 MHz, CDCl₃)

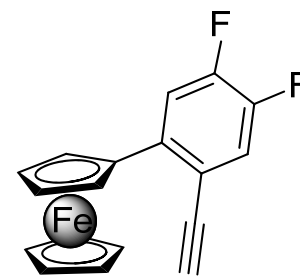


5j

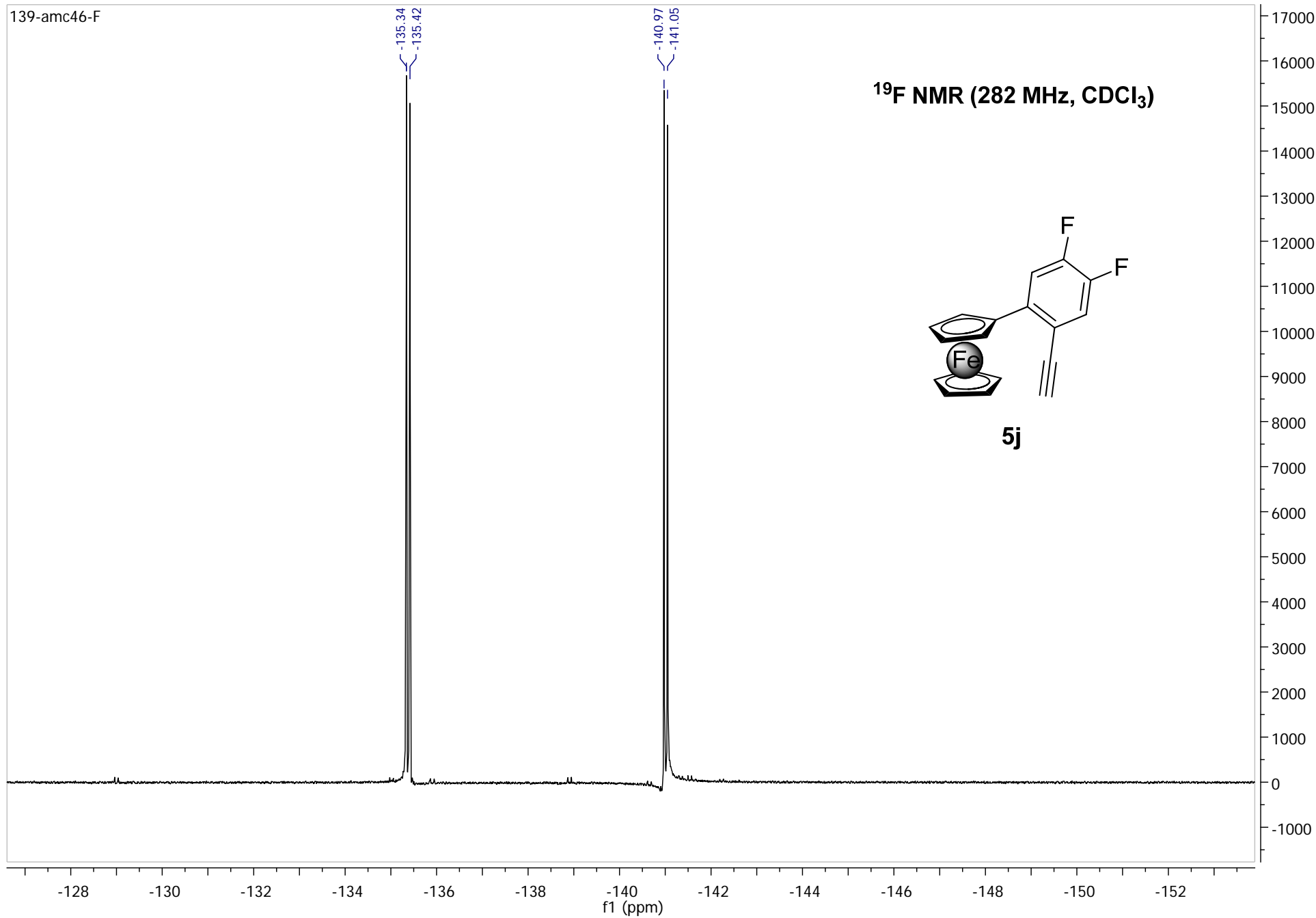


139-amc46-F

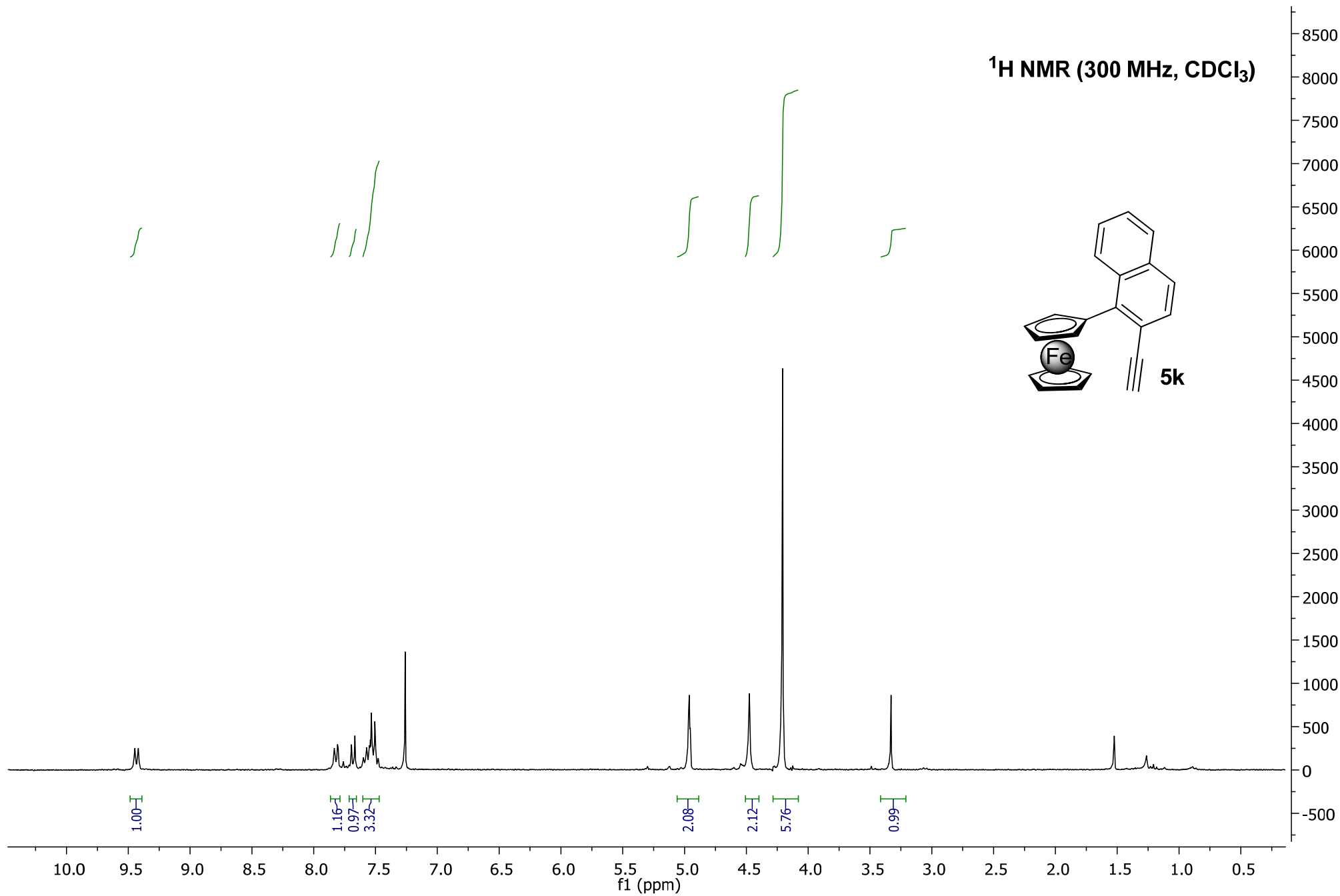
¹⁹F NMR (282 MHz, CDCl₃)



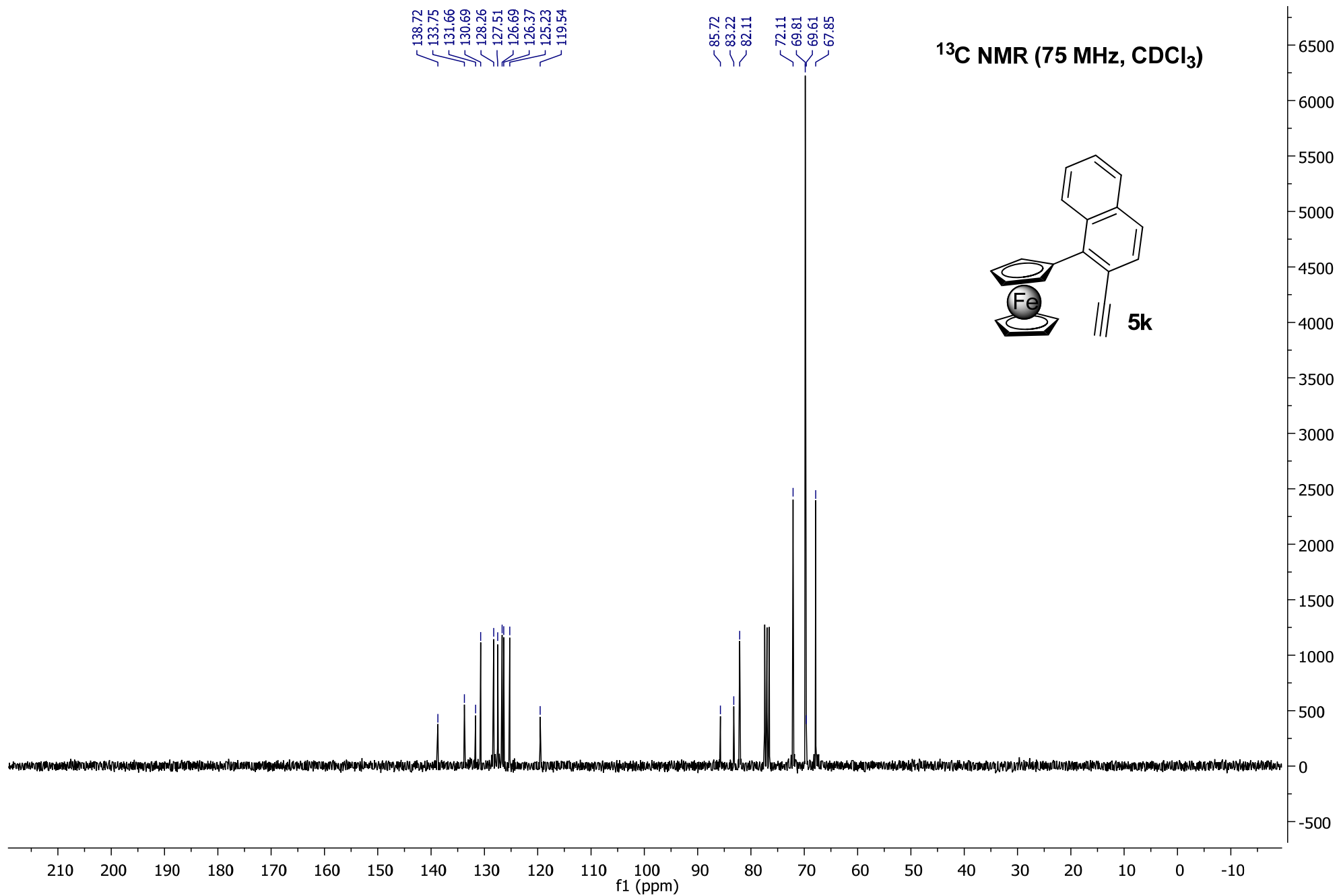
5j



S-87

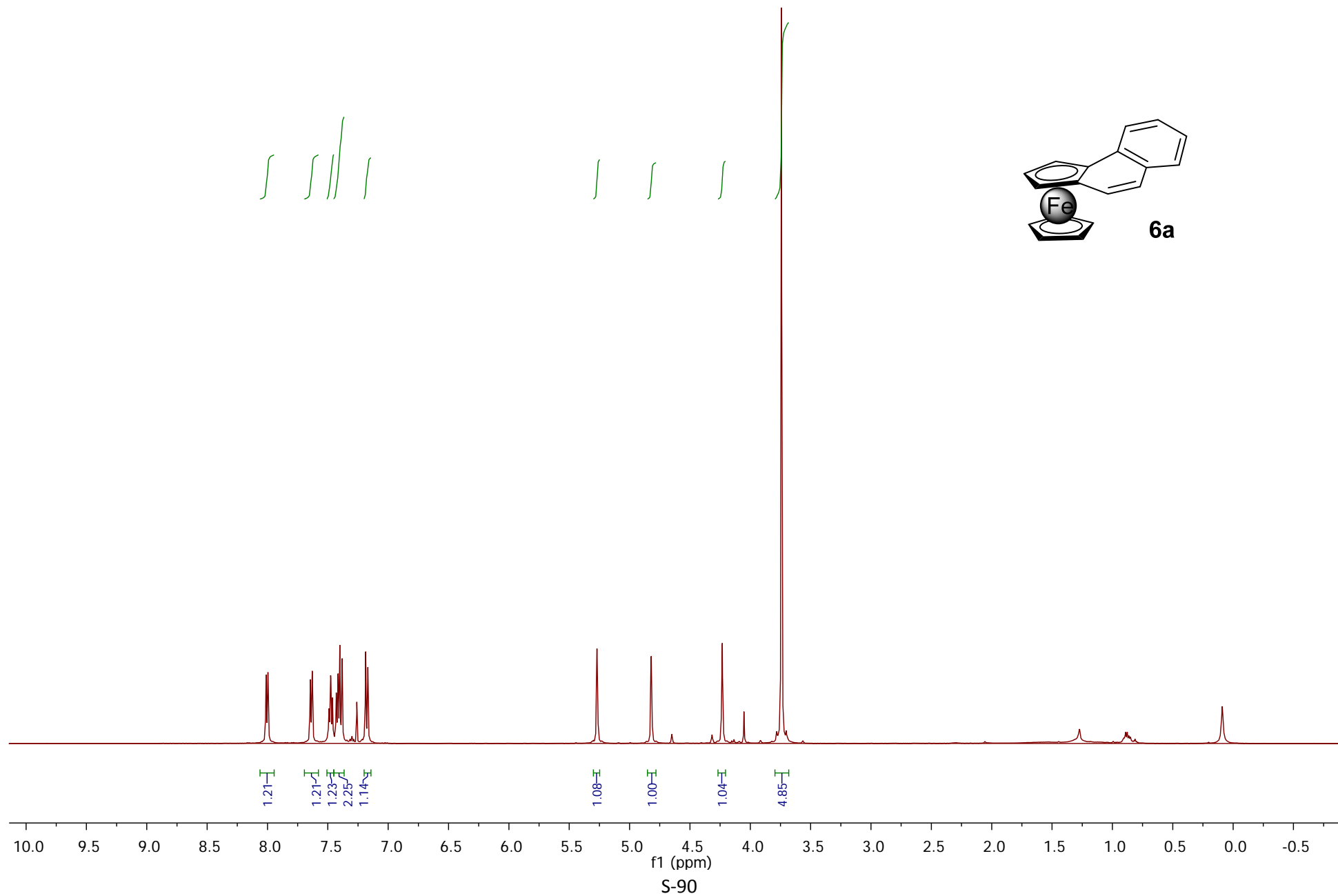
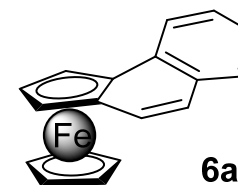


S-88



11104q-hgh3p2
hgH[3]_P2
PROTON CDCl3 C:\sidi 2

¹H NMR (300 MHz, CDCl₃)



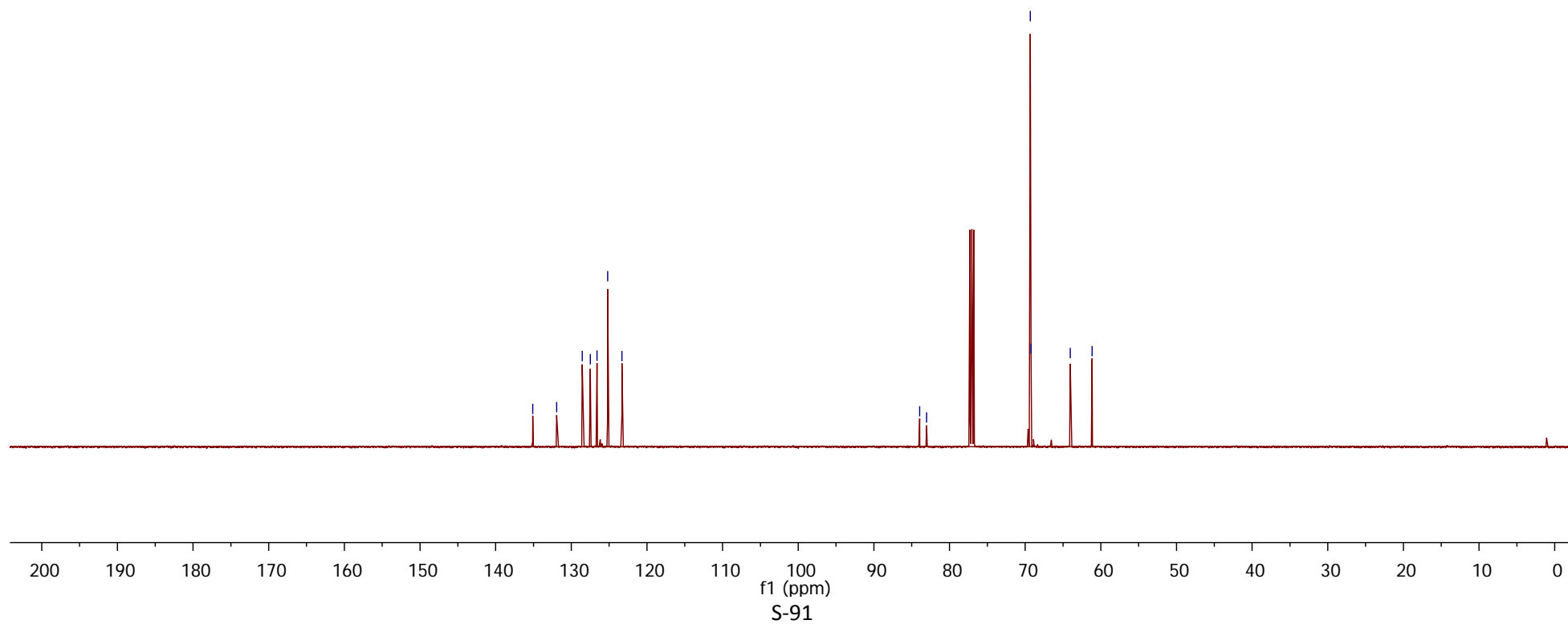
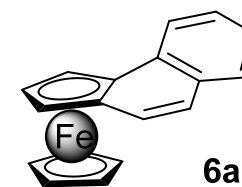
11104q-hgh3p2
hgH[3]_P2
C13CPD CDCl3 C:\ \ sisi 2

135.09
131.93
128.56
127.49
126.60
125.20
123.30

83.95
83.04

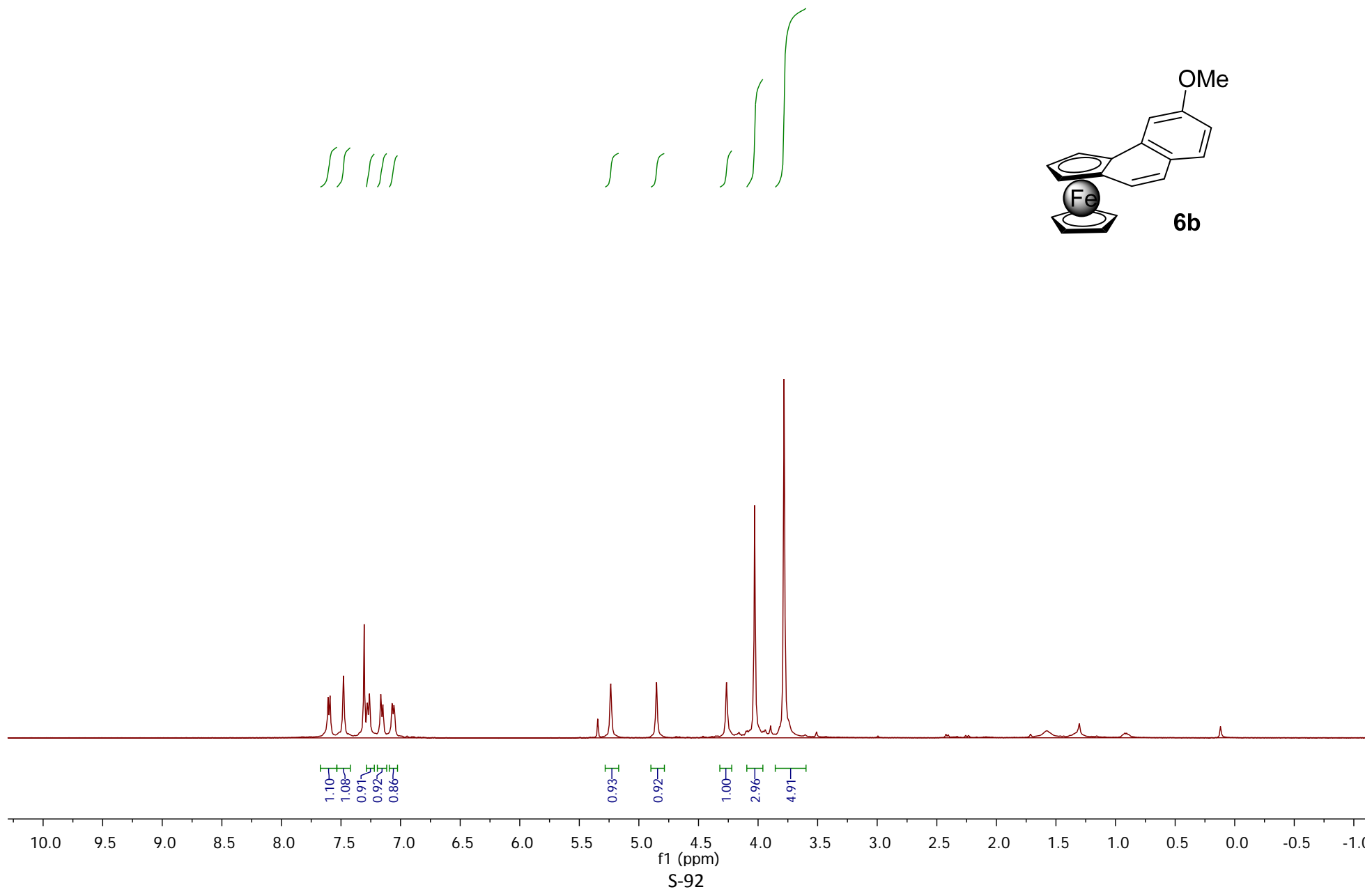
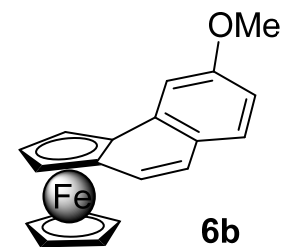
69.32
69.21
64.04
61.15

¹³C NMR (75 MHz, CDCl₃)

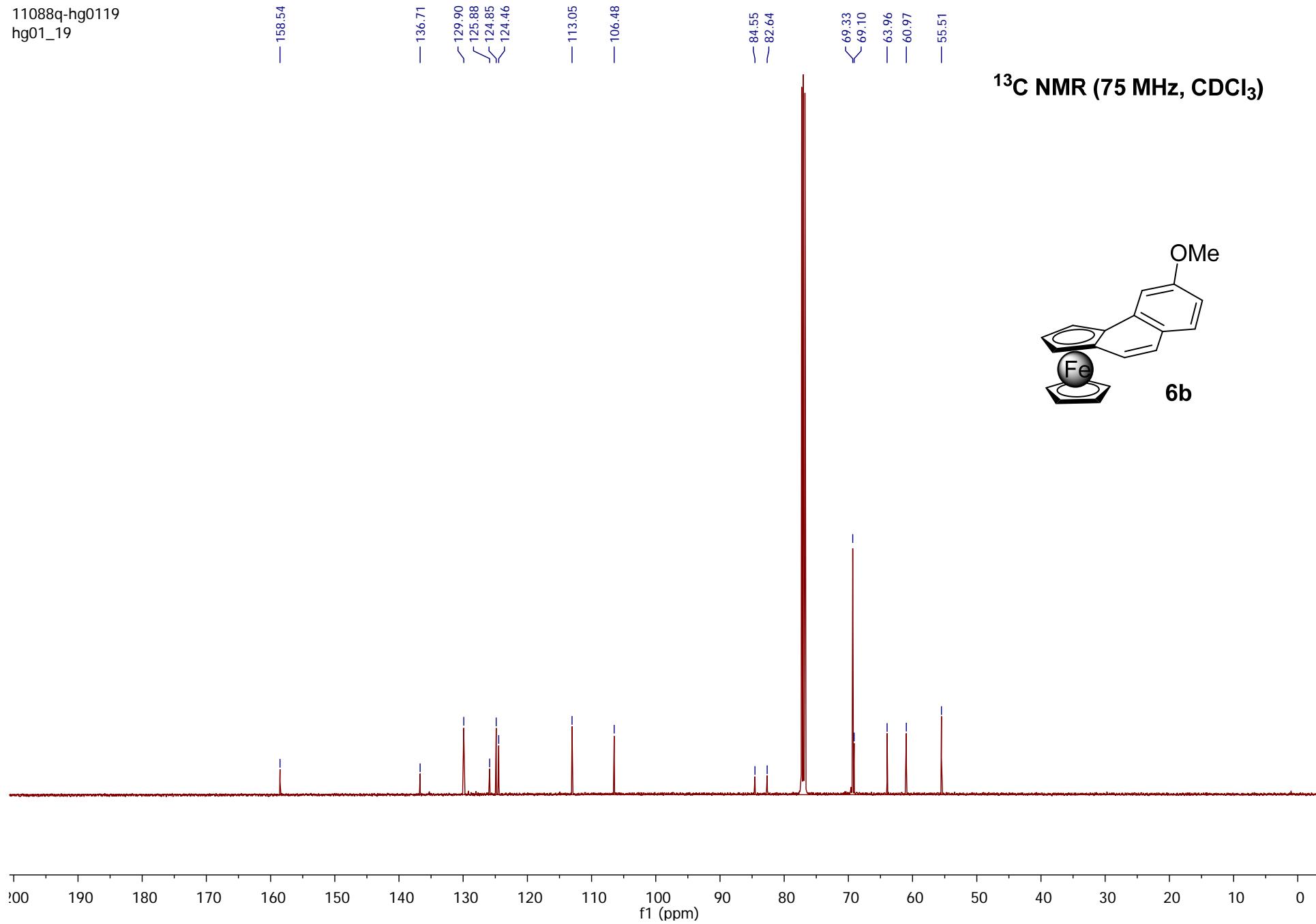


11088q-hg0119
hg01_19

^1H NMR (300 MHz, CDCl_3)

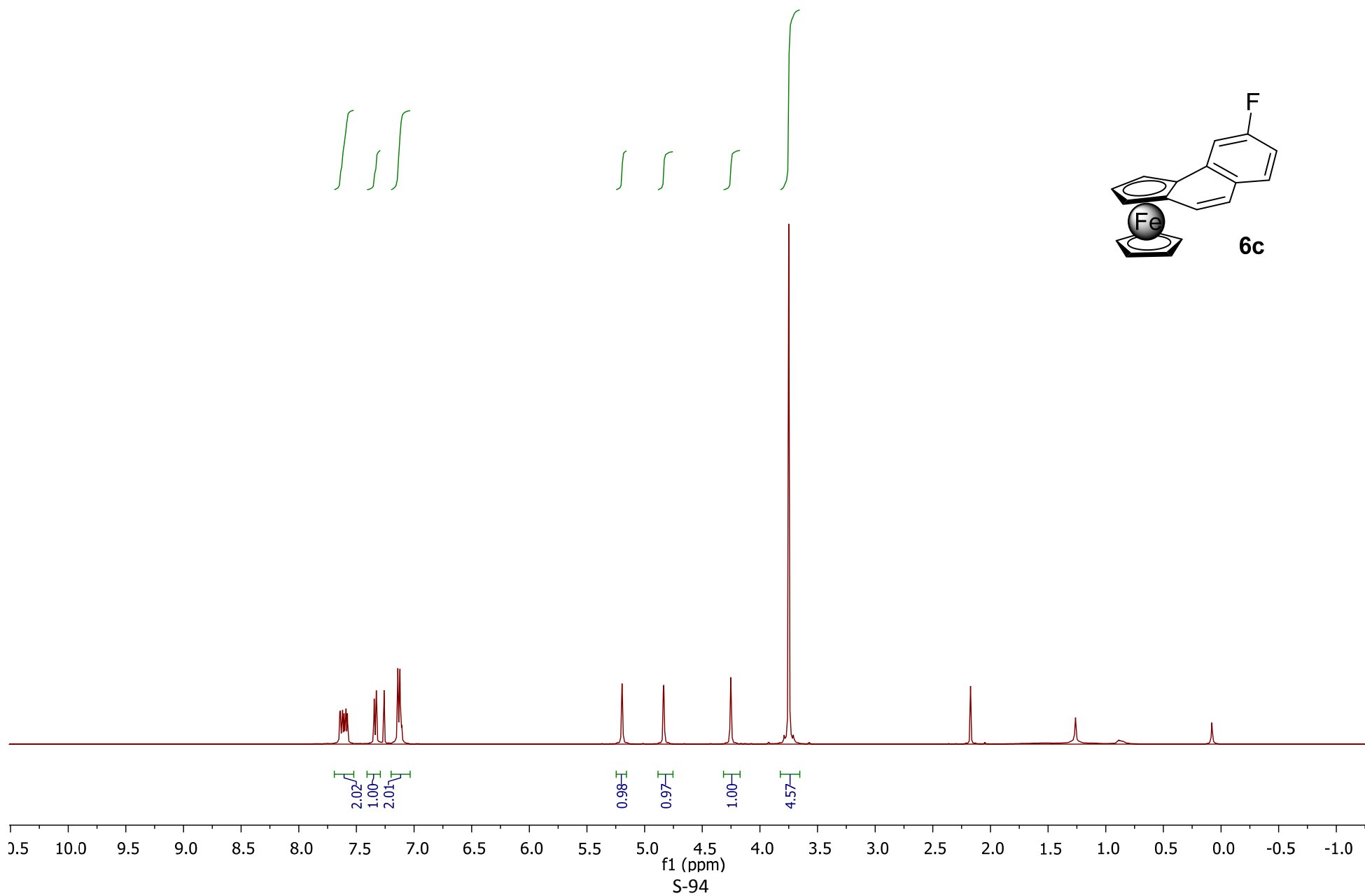
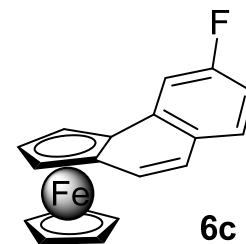


11088q-hg0119
hg01_19



11092q-hg0138
hg01_38
PROTON CDCl3 C:\\ sidi 3

^1H NMR (300 MHz, CDCl_3)



11092q-hg0138
hg01_38
C13CPD CDCl3 C:\sidi 3

162.62
160.67

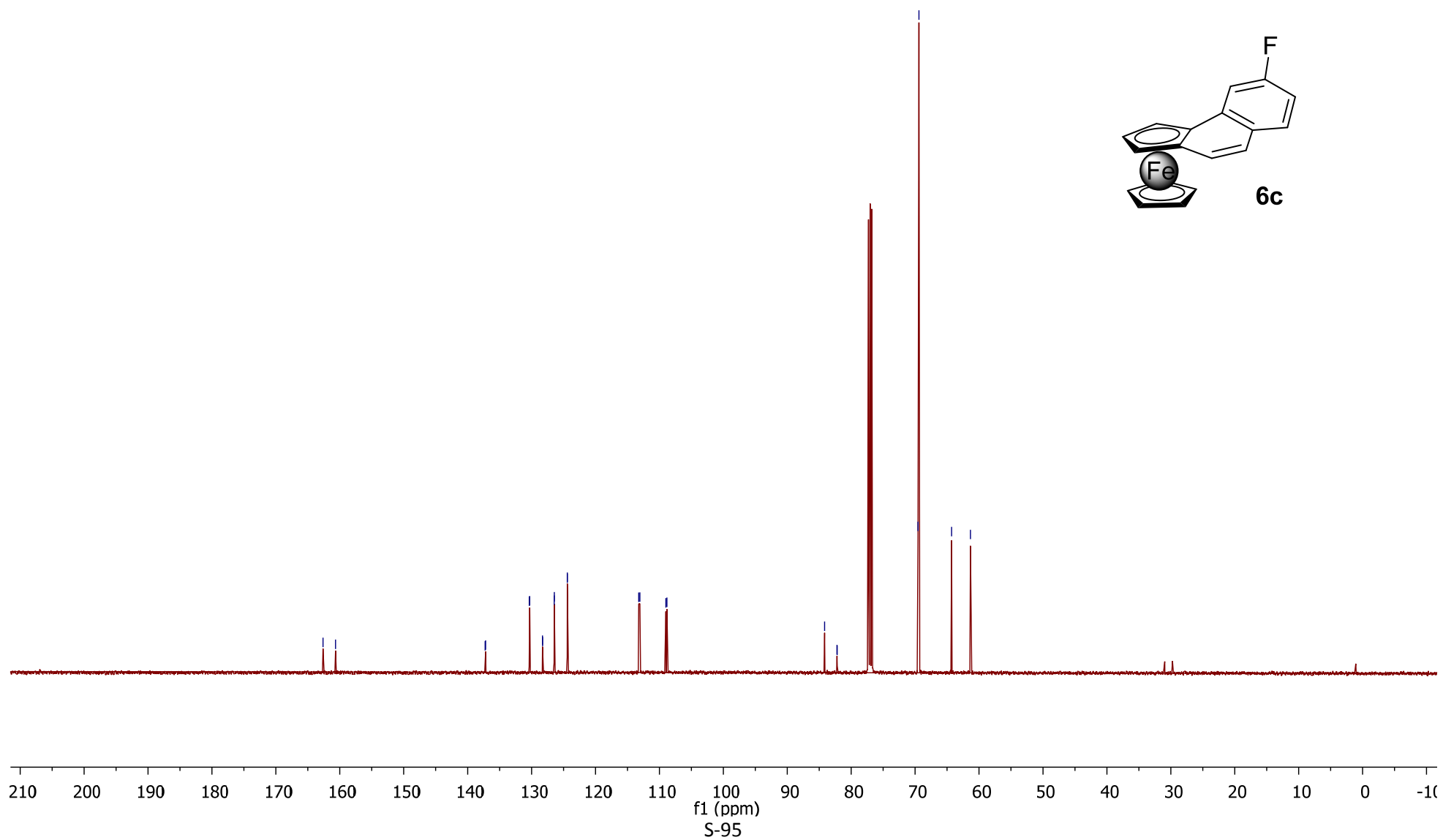
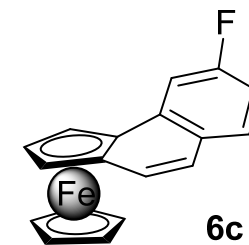
137.26
137.19

130.36
130.28
126.46
126.44
124.41
124.44
113.06
108.99
108.82

84.16
82.22
82.19

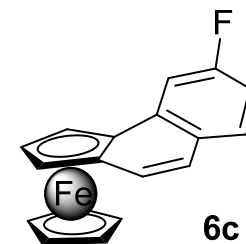
69.55
69.40
64.28
61.34

¹³C NMR (75 MHz, CDCl₃)

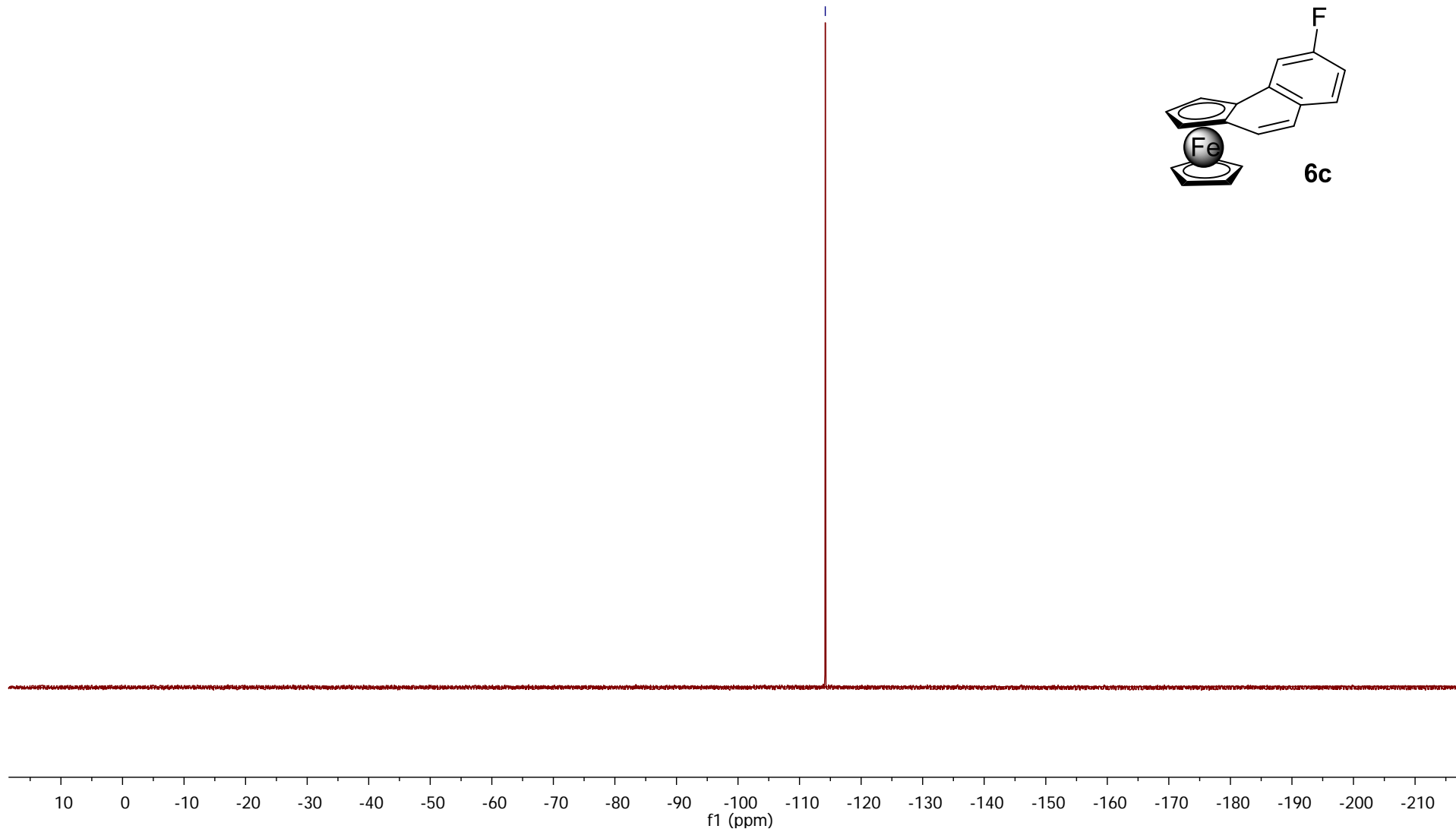


hg01_38-F

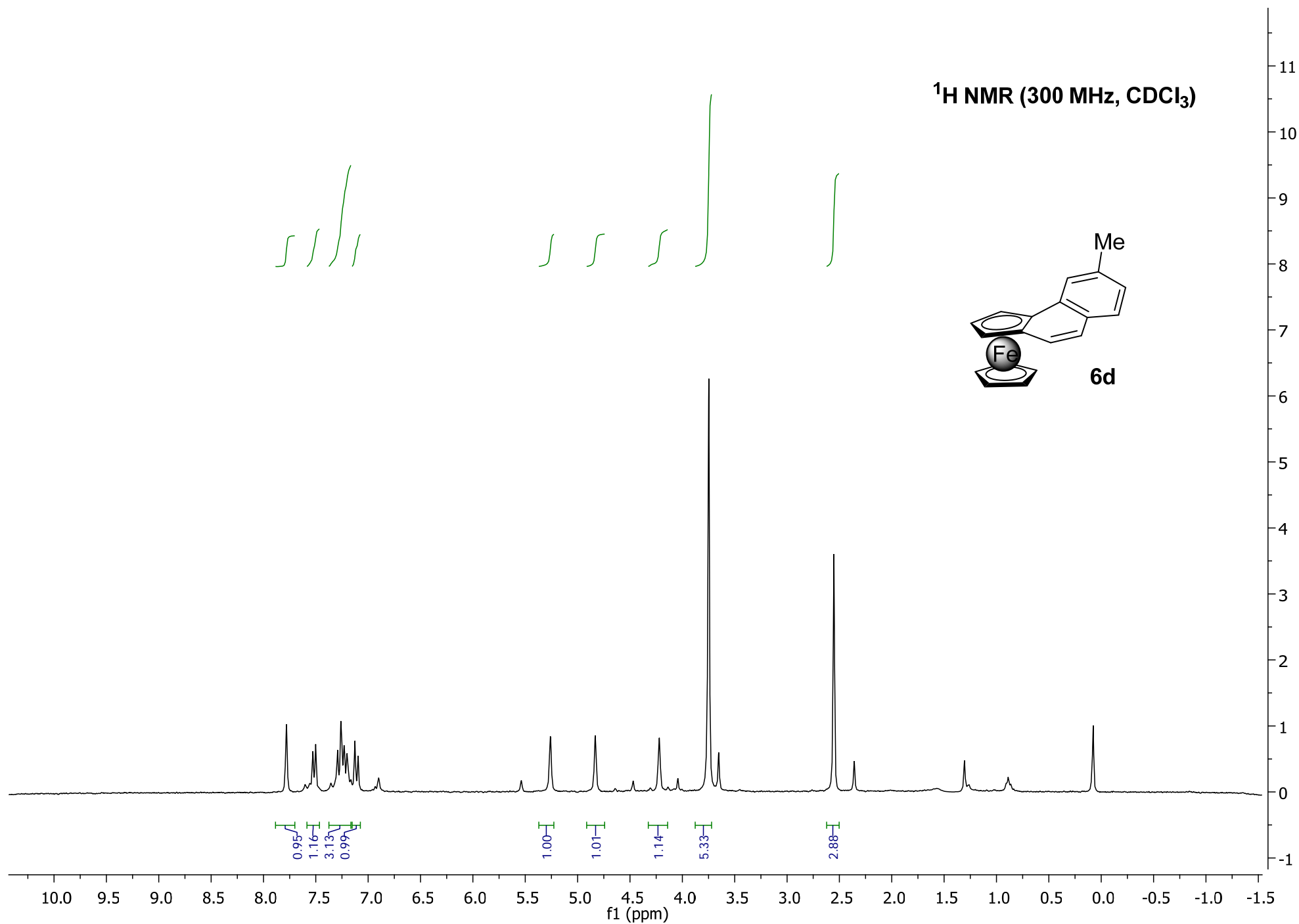
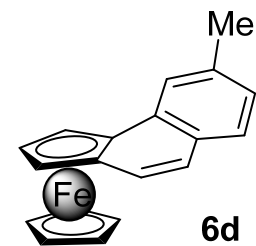
^{19}F NMR (282 MHz, CDCl_3)



-114.17

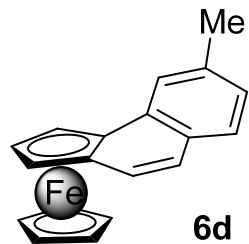


¹H NMR (300 MHz, CDCl₃)



S-97

¹³C NMR (75 MHz, CDCl₃)

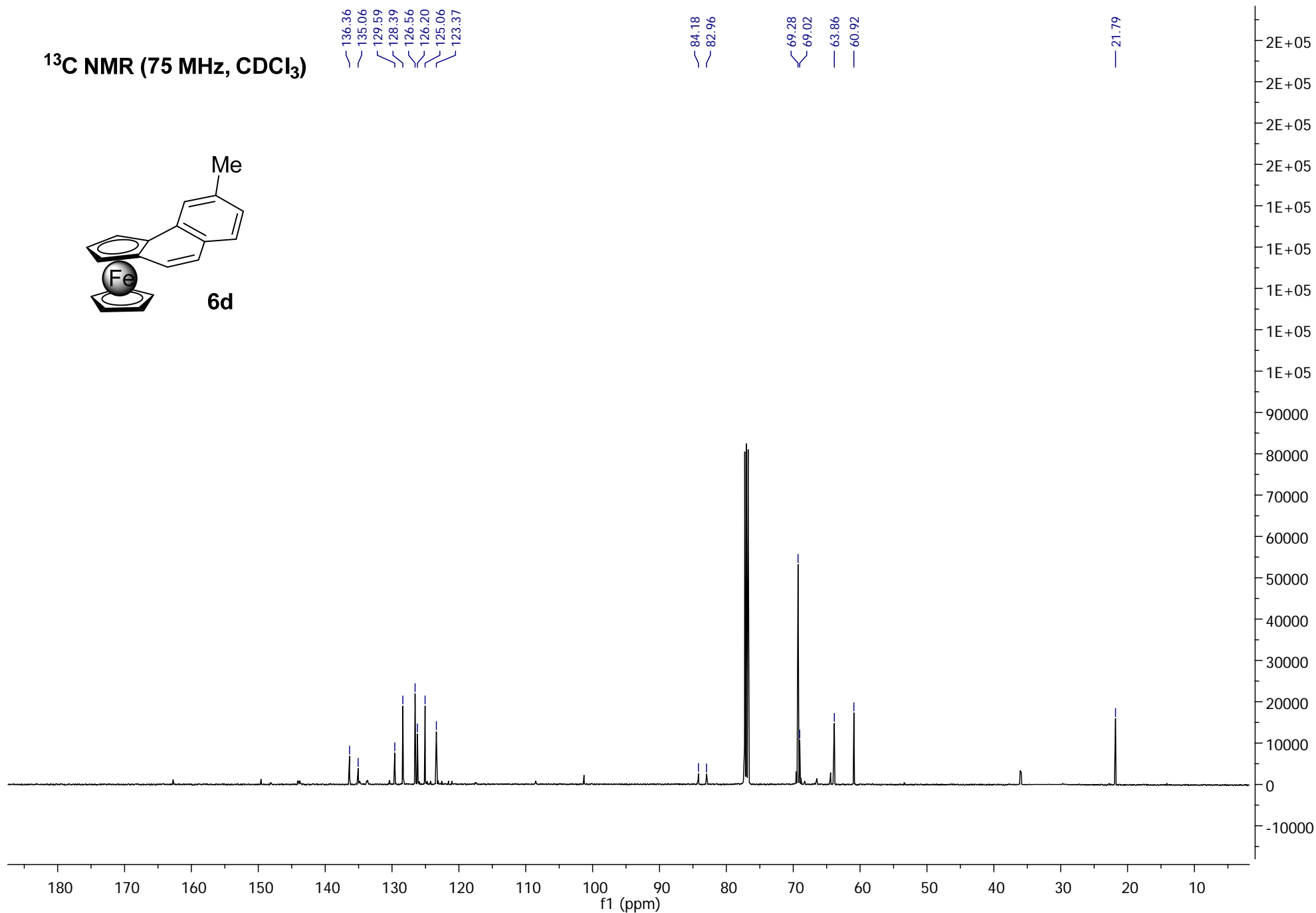


136.36
135.06
129.59
128.39
126.56
126.20
125.06
123.37

84.18
82.96

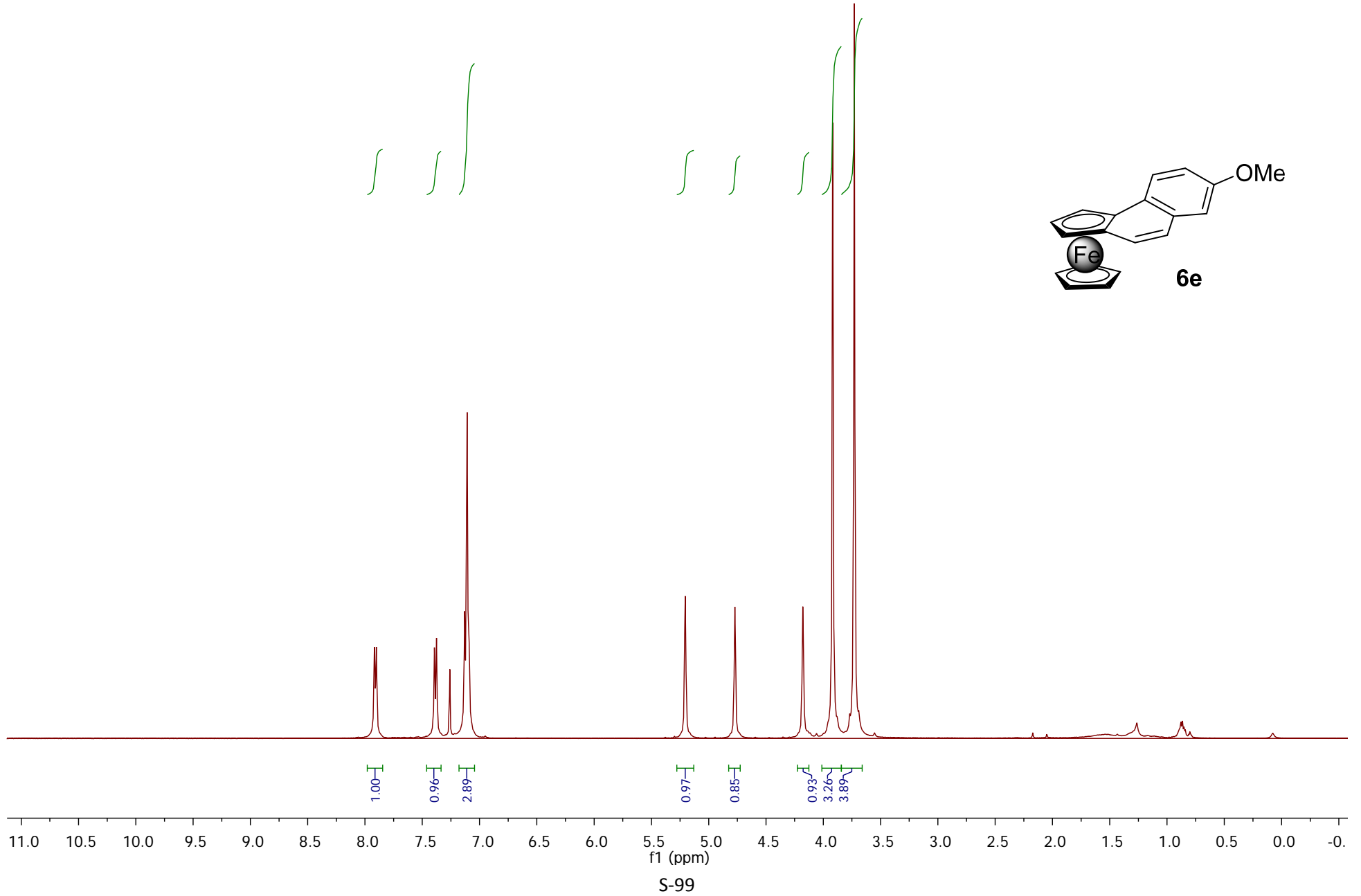
69.28
69.02
63.86
60.92

21.79



11105q-hgmomep3
hgmOMe_P3
PROTON CDCl3 C:\ sidi 3

¹H NMR (300 MHz, CDCl₃)



11105q-hgmomep3
hgmOMe_P3
C13CPD CDCl3 C:\sidi 3

157.50

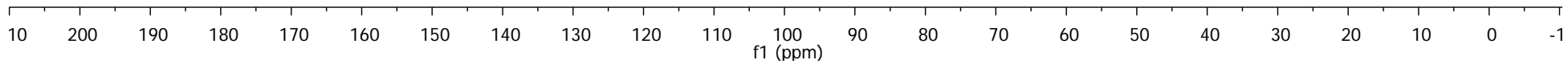
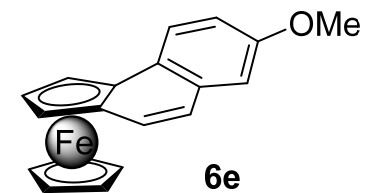
133.17
128.39
128.07
124.94
124.57

115.18
110.99

83.84
83.00

69.22
68.82
63.69
60.58
55.40

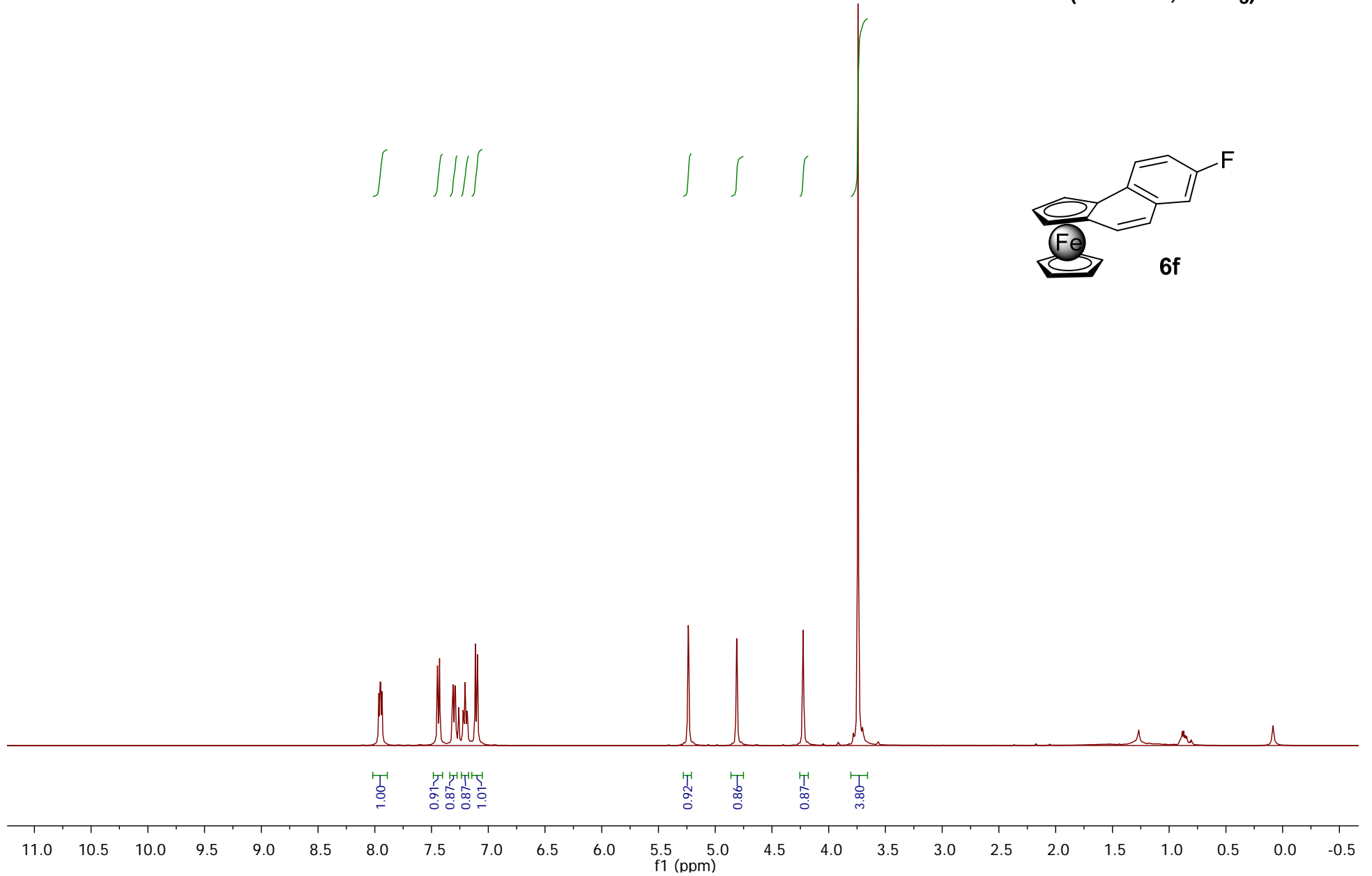
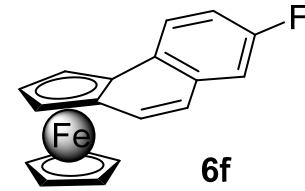
¹³C NMR (75 MHz, CDCl₃)



S-100

11108q-hgmfp6
hgmF_P6
PROTON CDCl3 C:\ sidi 6

¹H NMR (300 MHz, CDCl₃)



S-101

11108q-hgmfp6
hgmF_P6
C13CPD CDCl3 C:\sidi 6

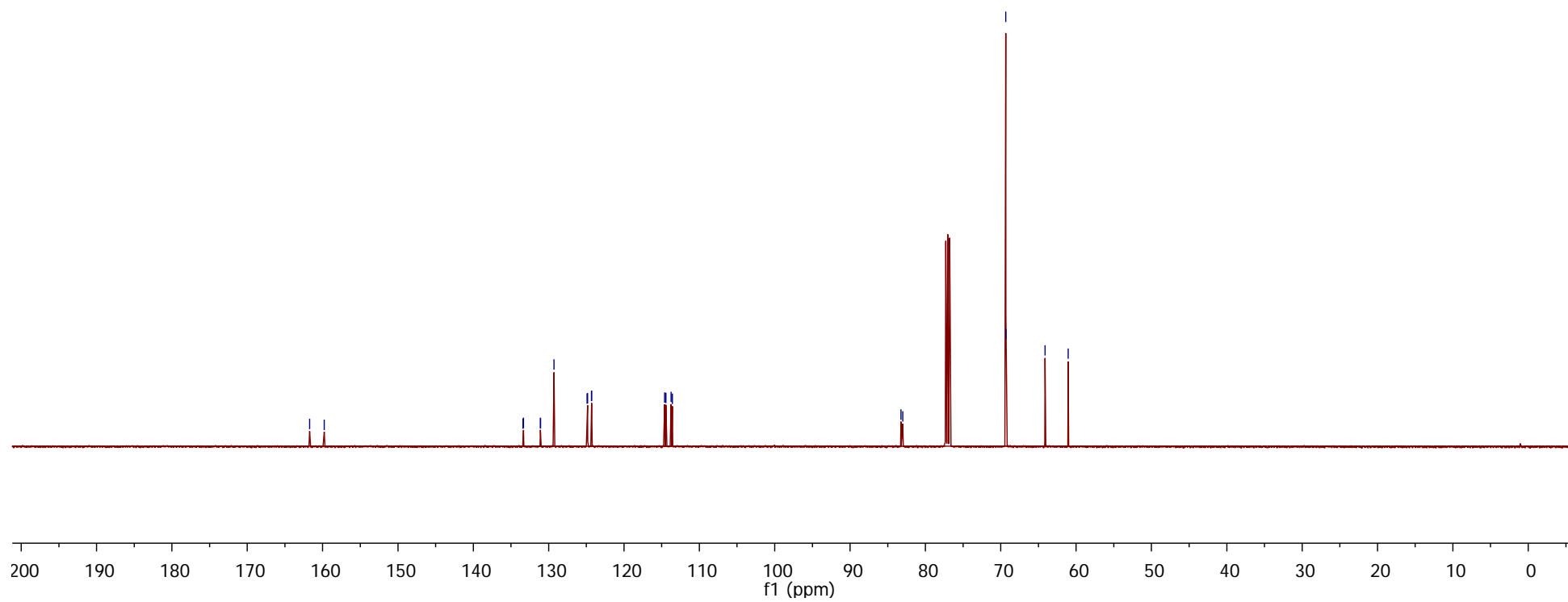
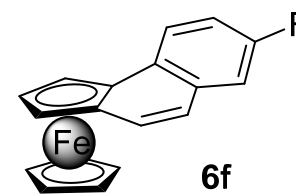
161.72
159.79

133.41
133.35
131.09
131.07
129.29
124.91
124.84
124.32
124.29
114.62
114.44
113.75
113.59

83.25
83.01

69.33
69.30
64.12
61.05

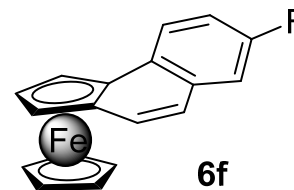
^{13}C NMR (75 MHz, CDCl_3)



S-102

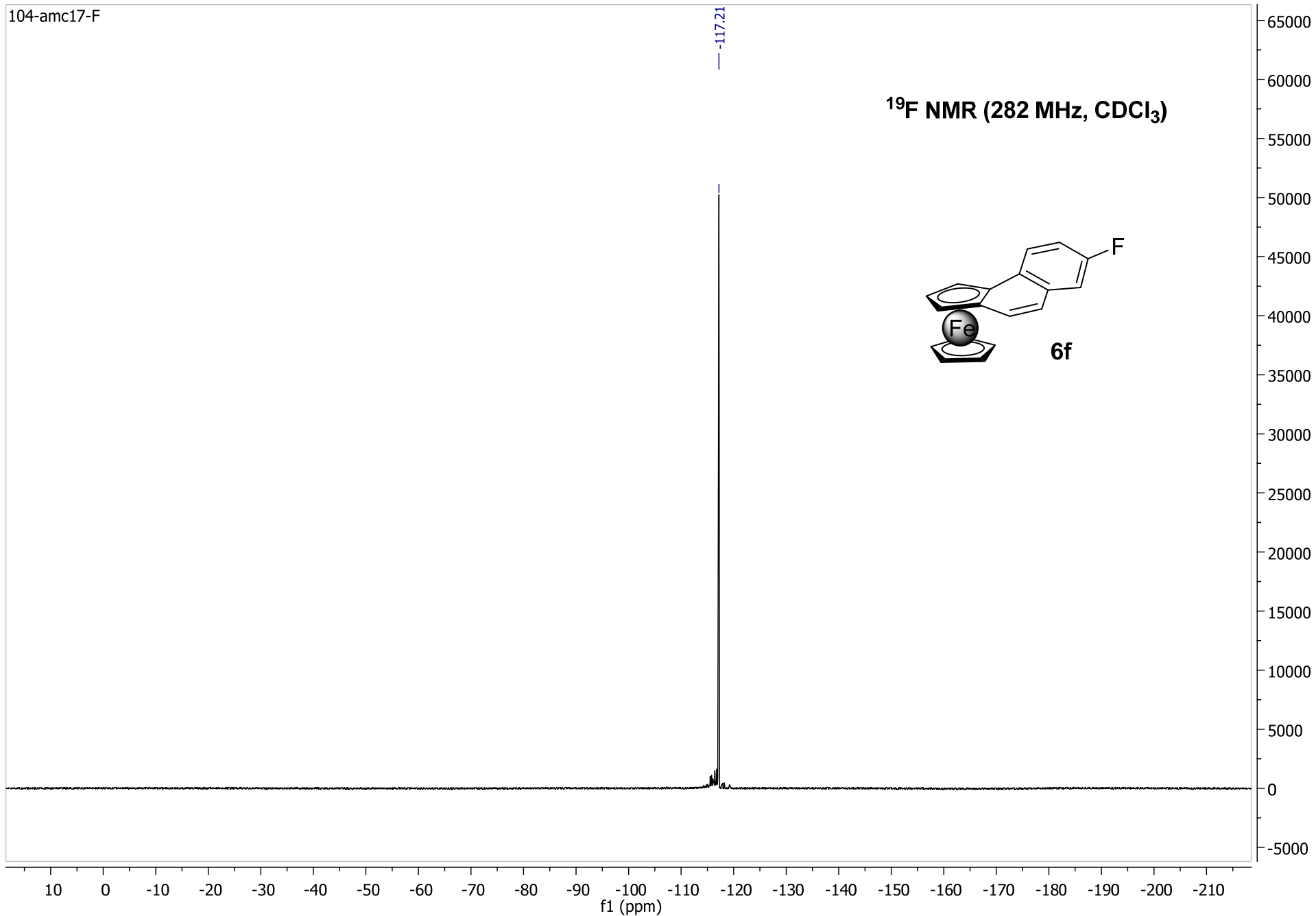
104-amc17-F

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



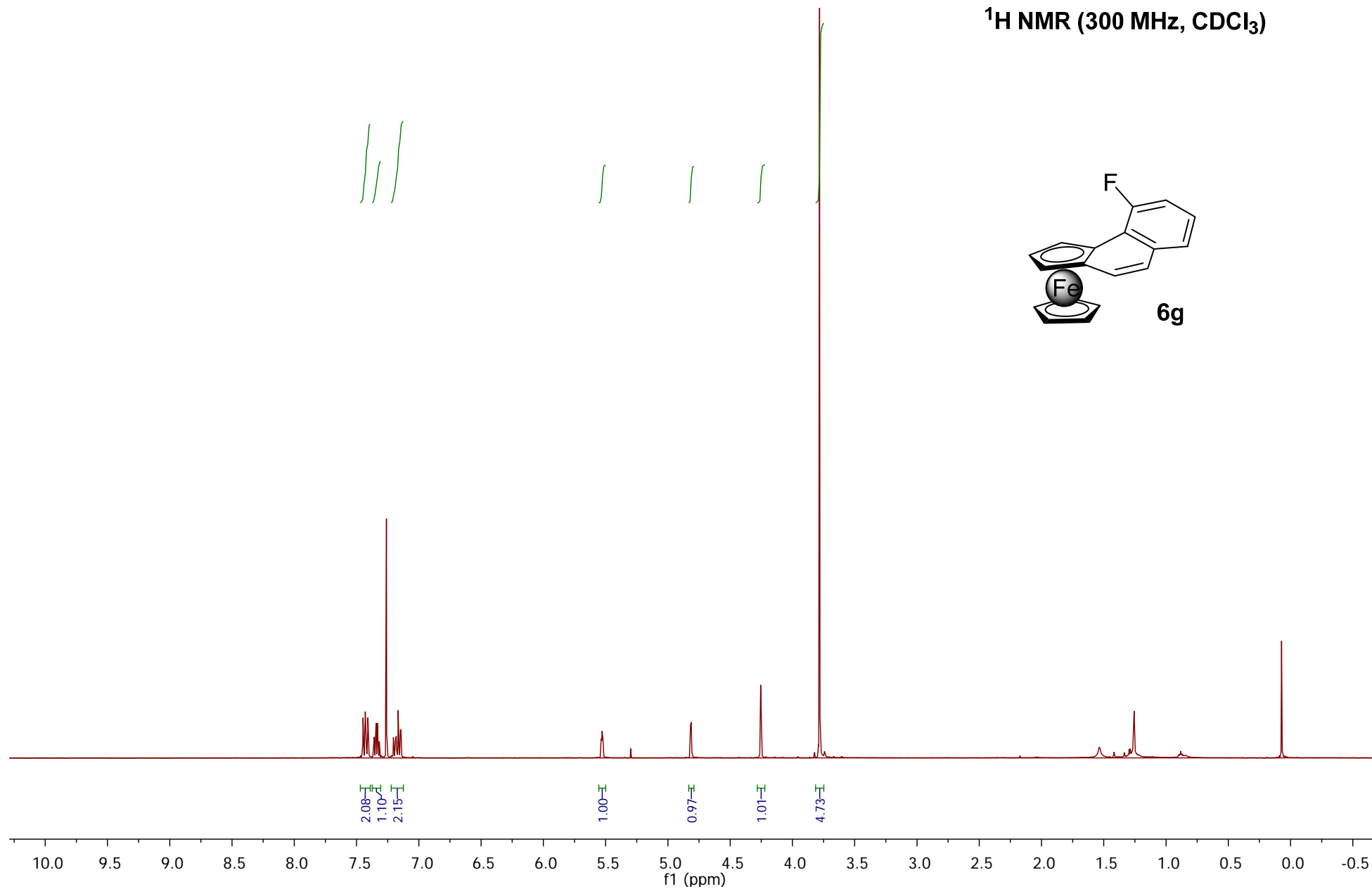
6f

-117.21



11113q-hg0160
hg01_60
PROTON CDCl3 C:\sidi 1

¹H NMR (300 MHz, CDCl₃)



S-104

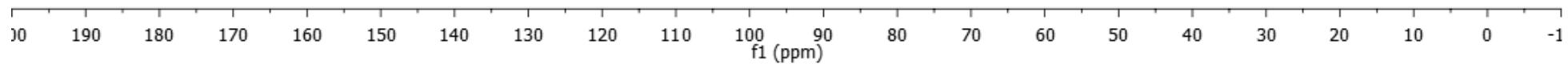
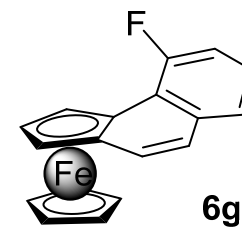
11113q-hg0160
hg01_60
C13CPD CDCl3 C:\sidi 1

160.88
158.91

134.58
134.53
129.03
125.37
124.33
124.30
124.13
122.71
112.54

83.64
78.41
70.01
69.99
69.25
65.71
65.63
63.93

¹³C NMR (75 MHz, CDCl₃)

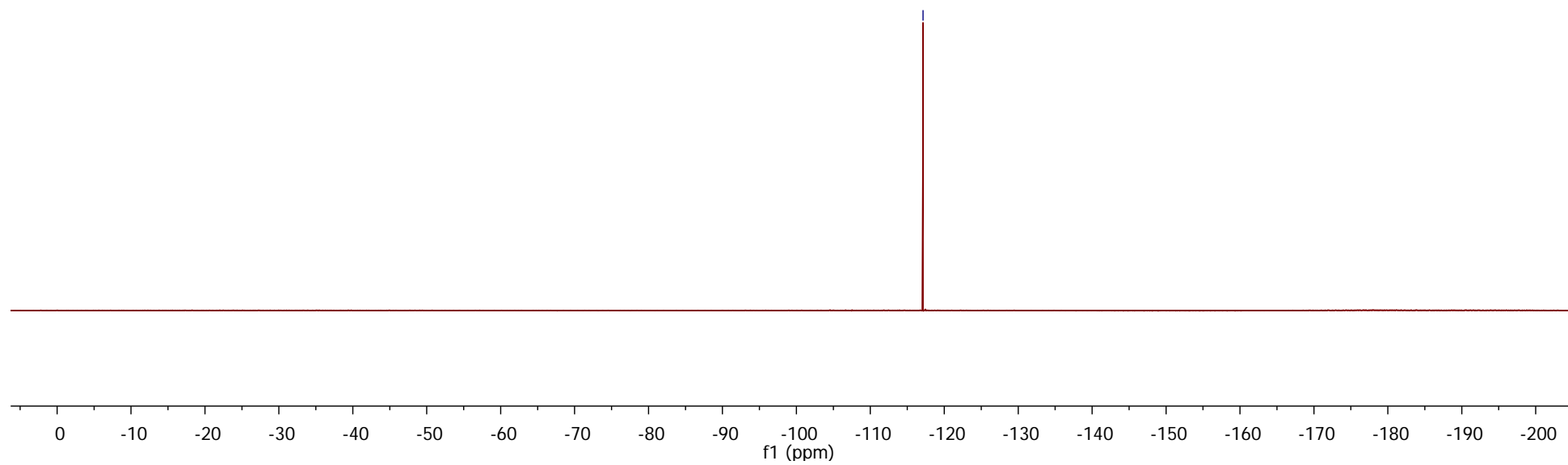
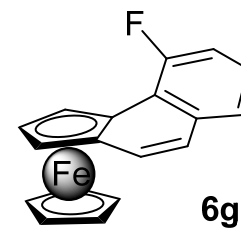


S-105

11113q-hg0160
hg01_60
F19CPD CDCl3 C:\ sidi 1

— -117.13

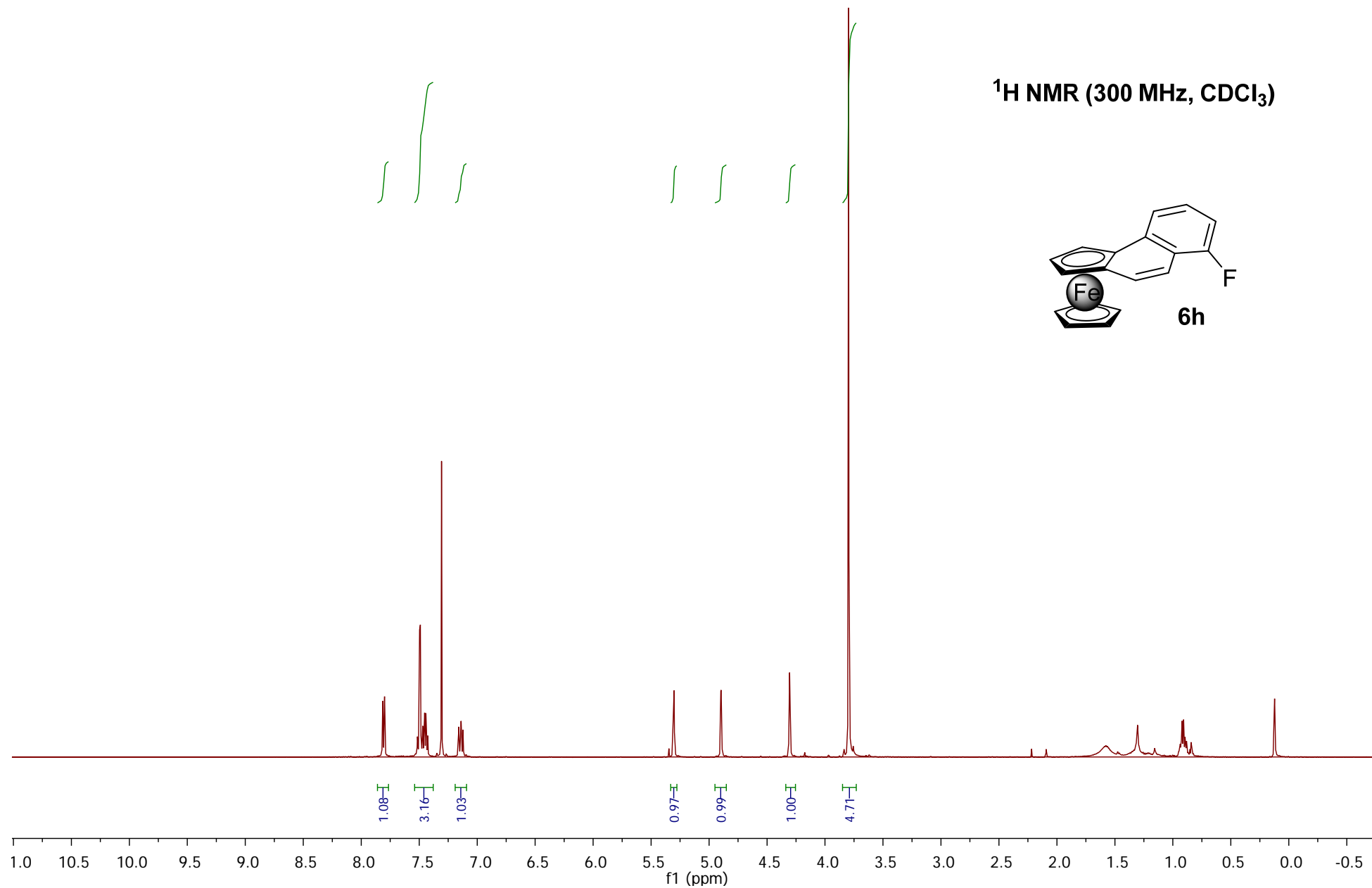
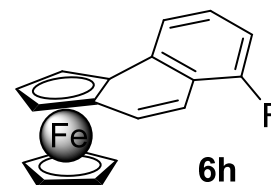
^{19}F NMR (282 MHz, CDCl_3)



S-106

11106q-hgofp4
hgoF_P4
PROTON CDCl3 C:\ \ sidi 4

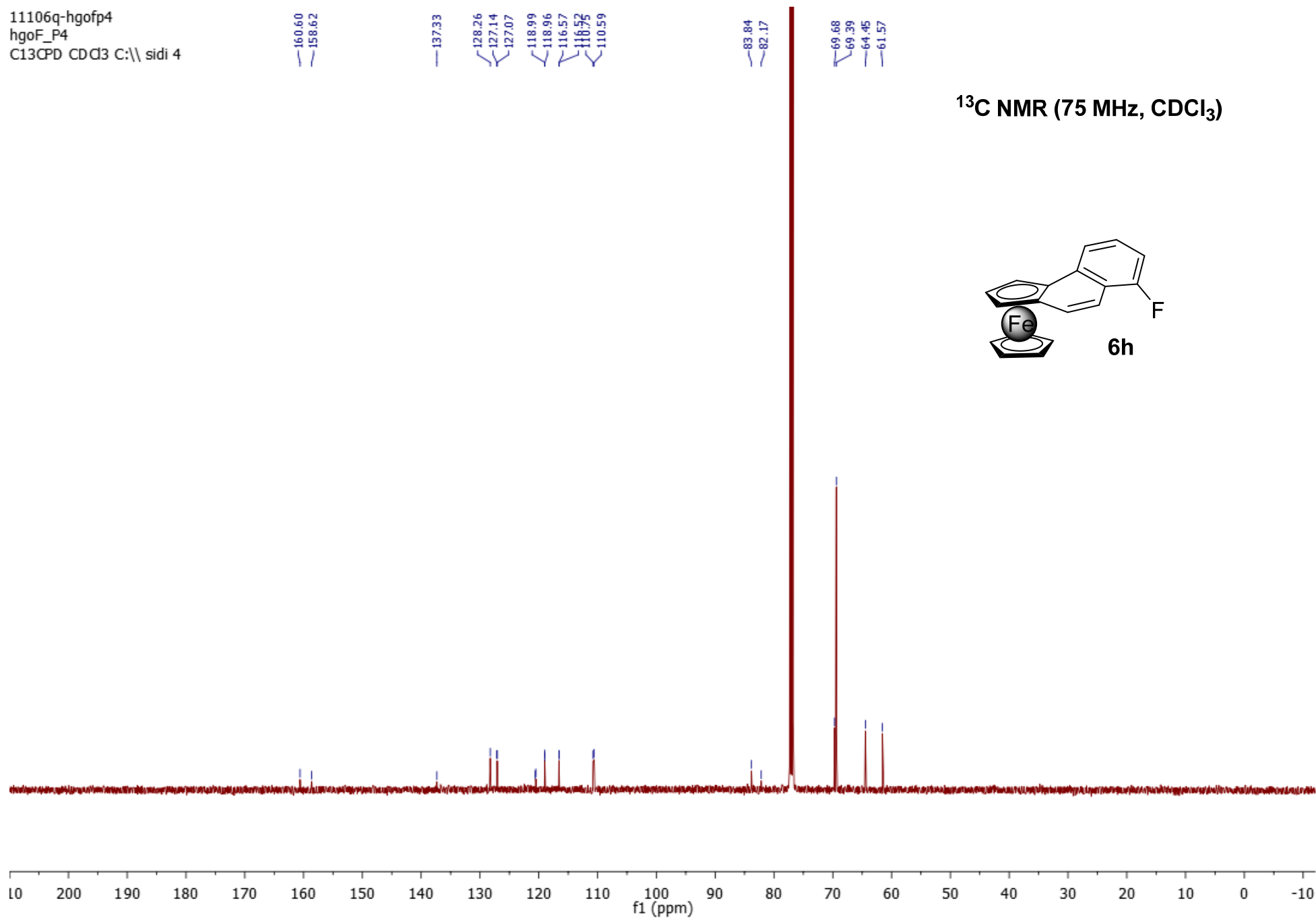
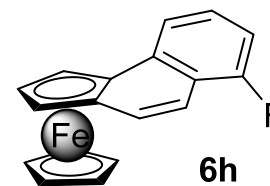
^1H NMR (300 MHz, CDCl_3)



S-107

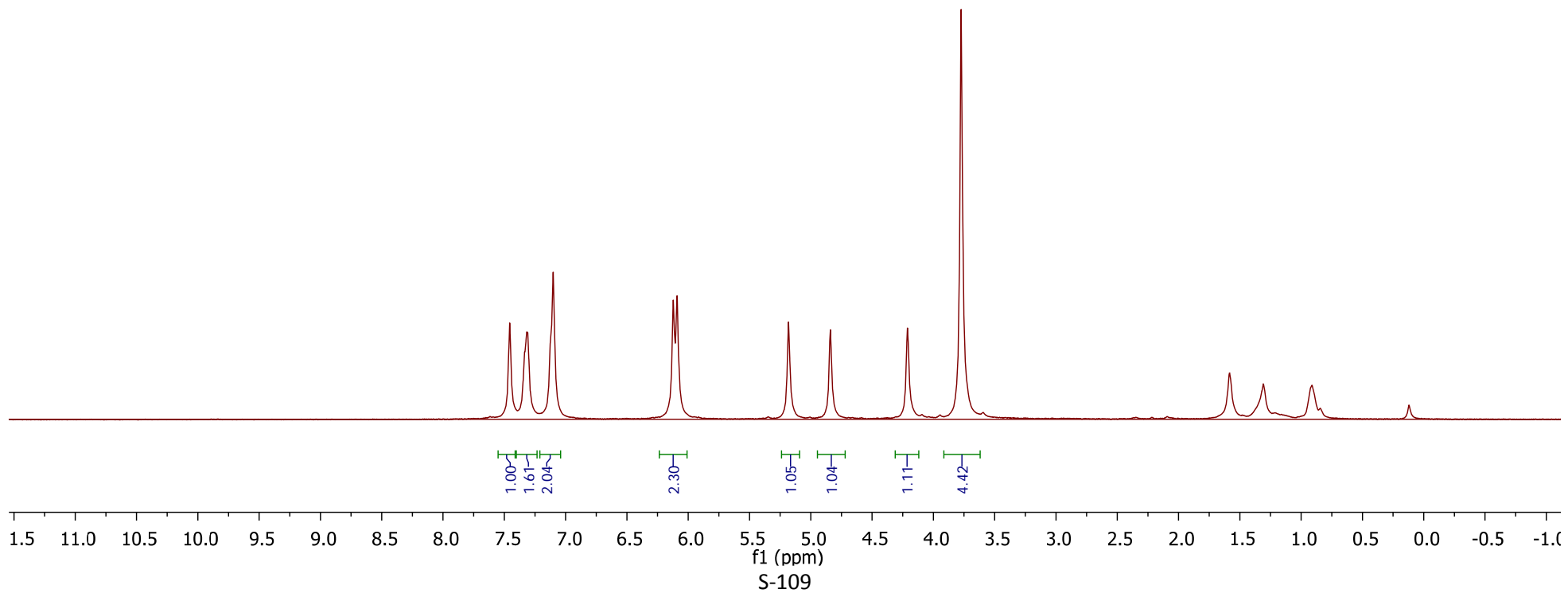
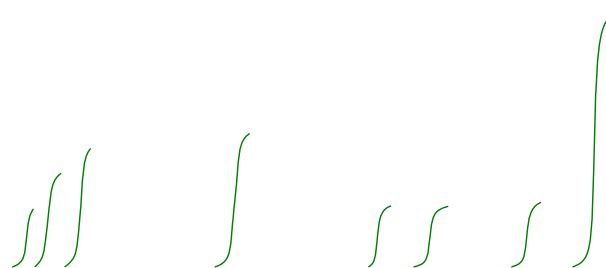
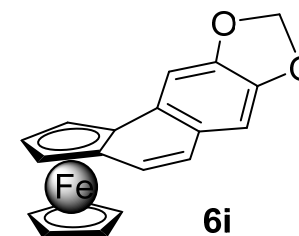
11106q-hgofp4
hgoF_P4
C13CPD CDCl3 C:\sidi 4

¹³C NMR (75 MHz, CDCl₃)



11109q-hgmdioxop7
hgmdioxo_P7
PROTON CDCl3 C:\\ sisi 7

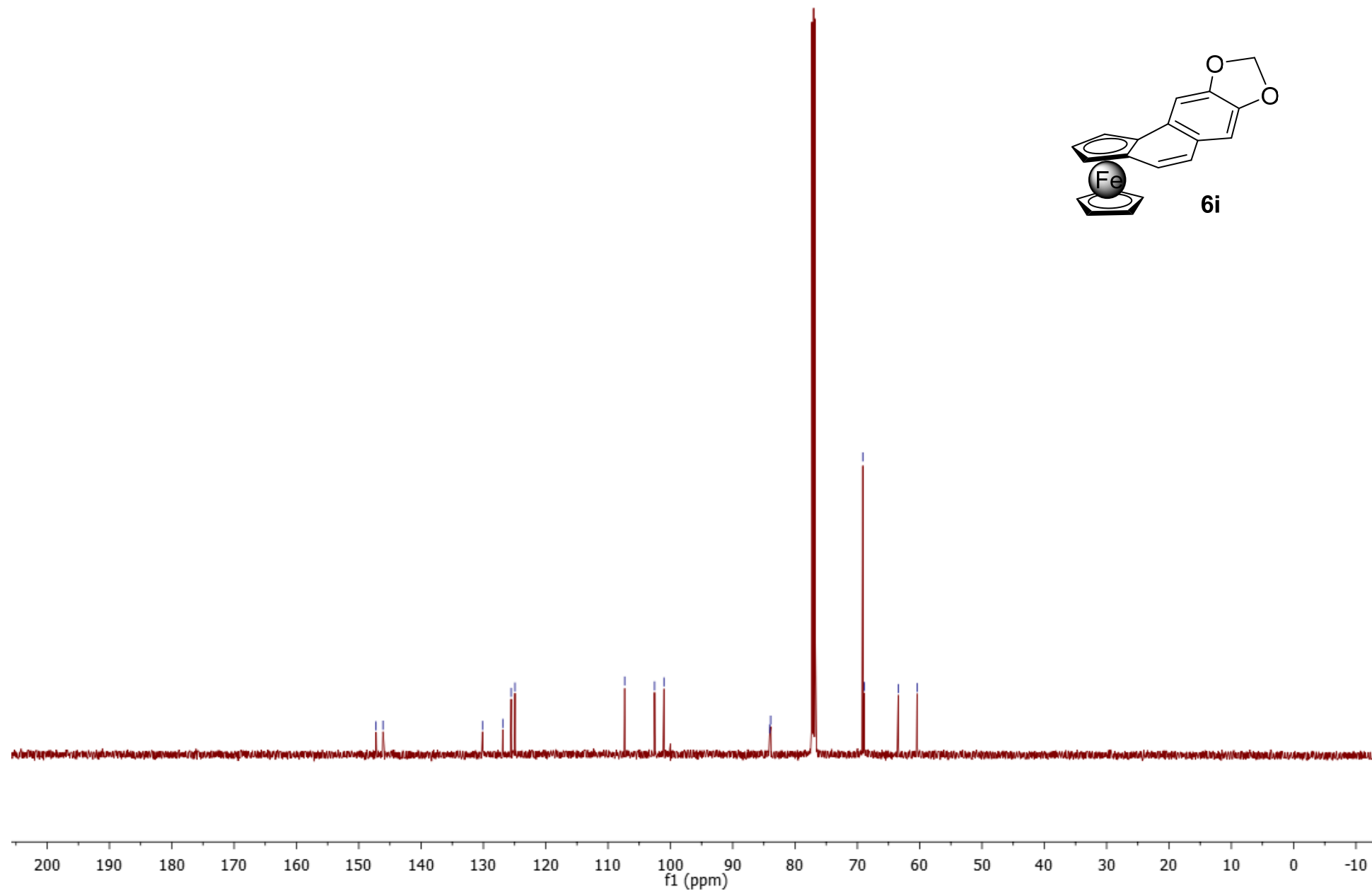
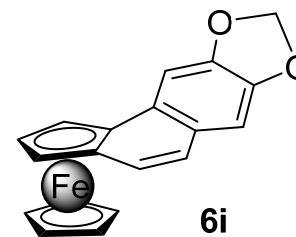
¹H NMR (300 MHz, CDCl₃)



11109q-hgmdioxop7
hgmdioxo_P7
C13CPD CDCl3 C:\sidi 7

147.23
146.11
130.14
126.90
125.54
124.94
107.33
102.54
101.03
84.07
83.91
69.13
68.90
63.44
60.41

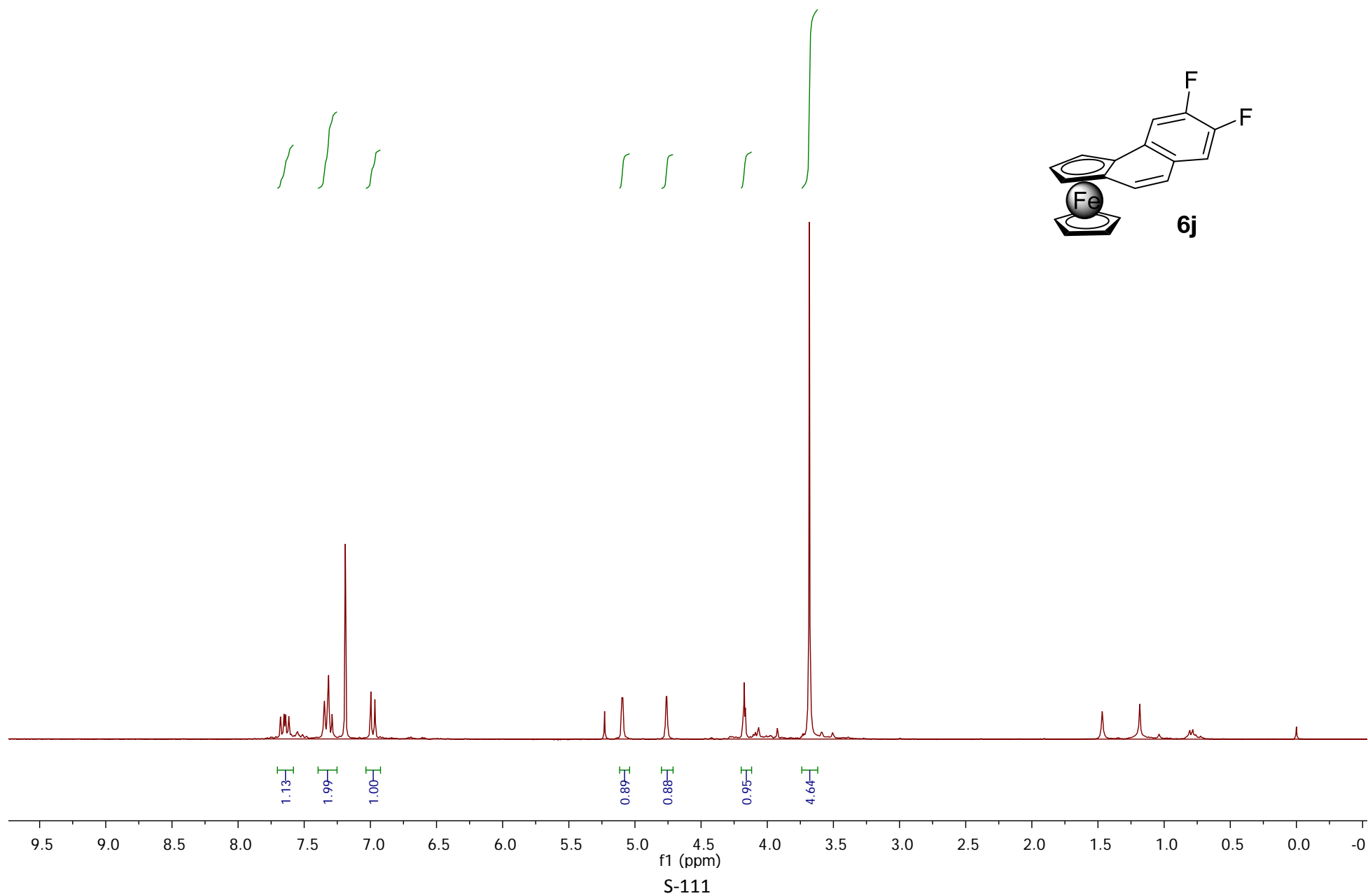
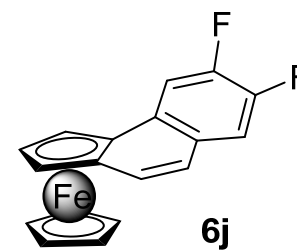
¹³C NMR (75 MHz, CDCl₃)



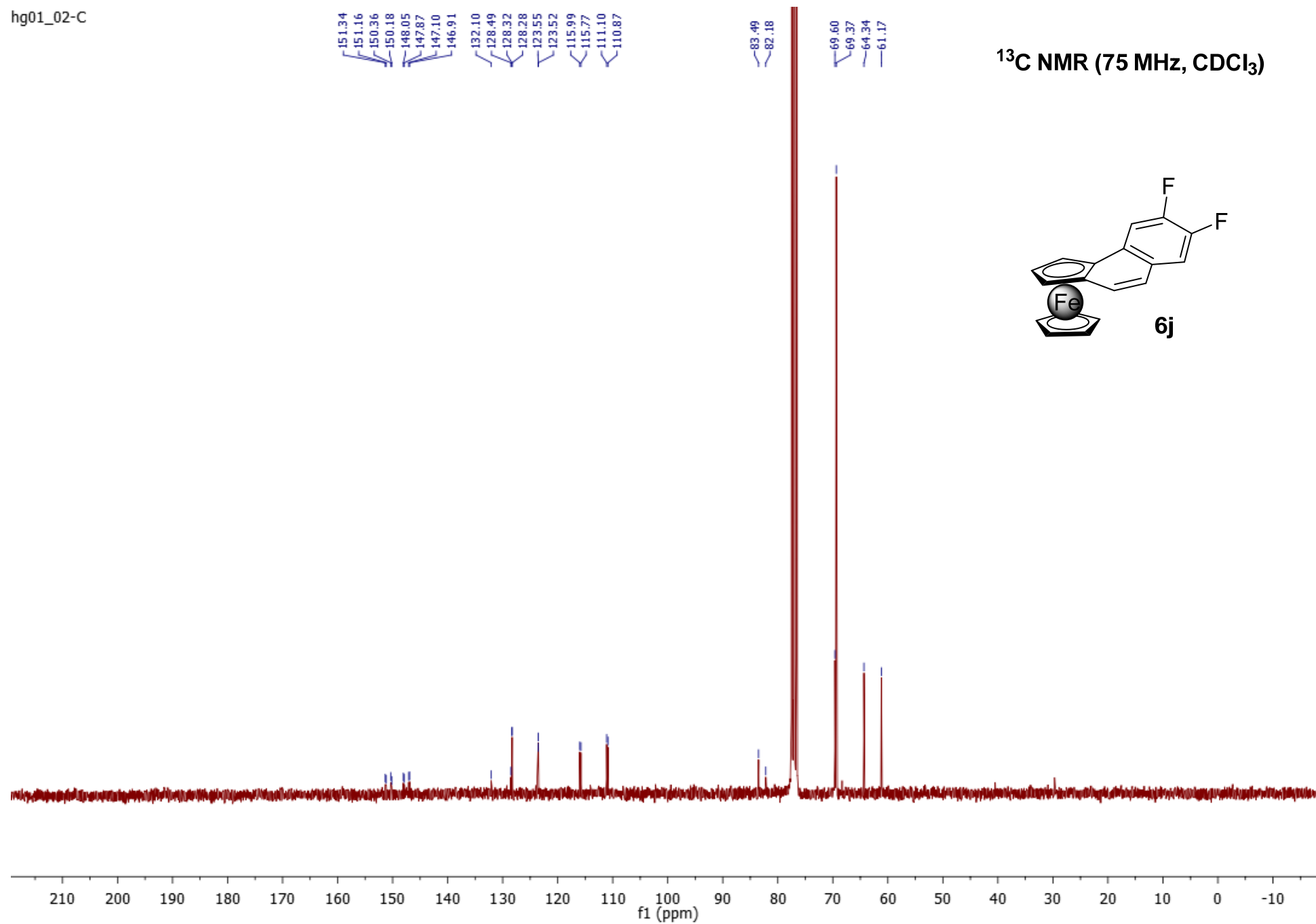
S-110

hg01_02

¹H NMR (300 MHz, CDCl₃)



hg01_02-C

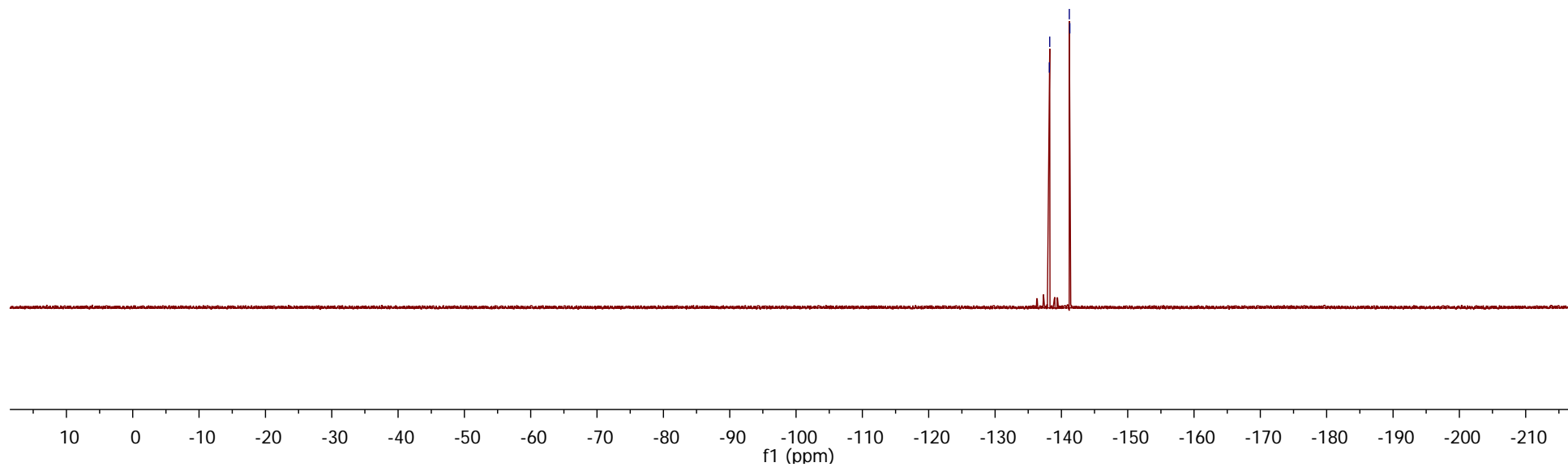
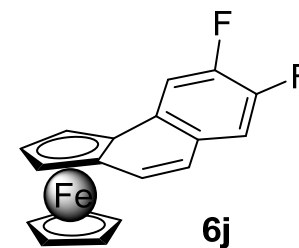


S-112

hg01_02-F

-138.18
-138.25
-141.21
-141.28

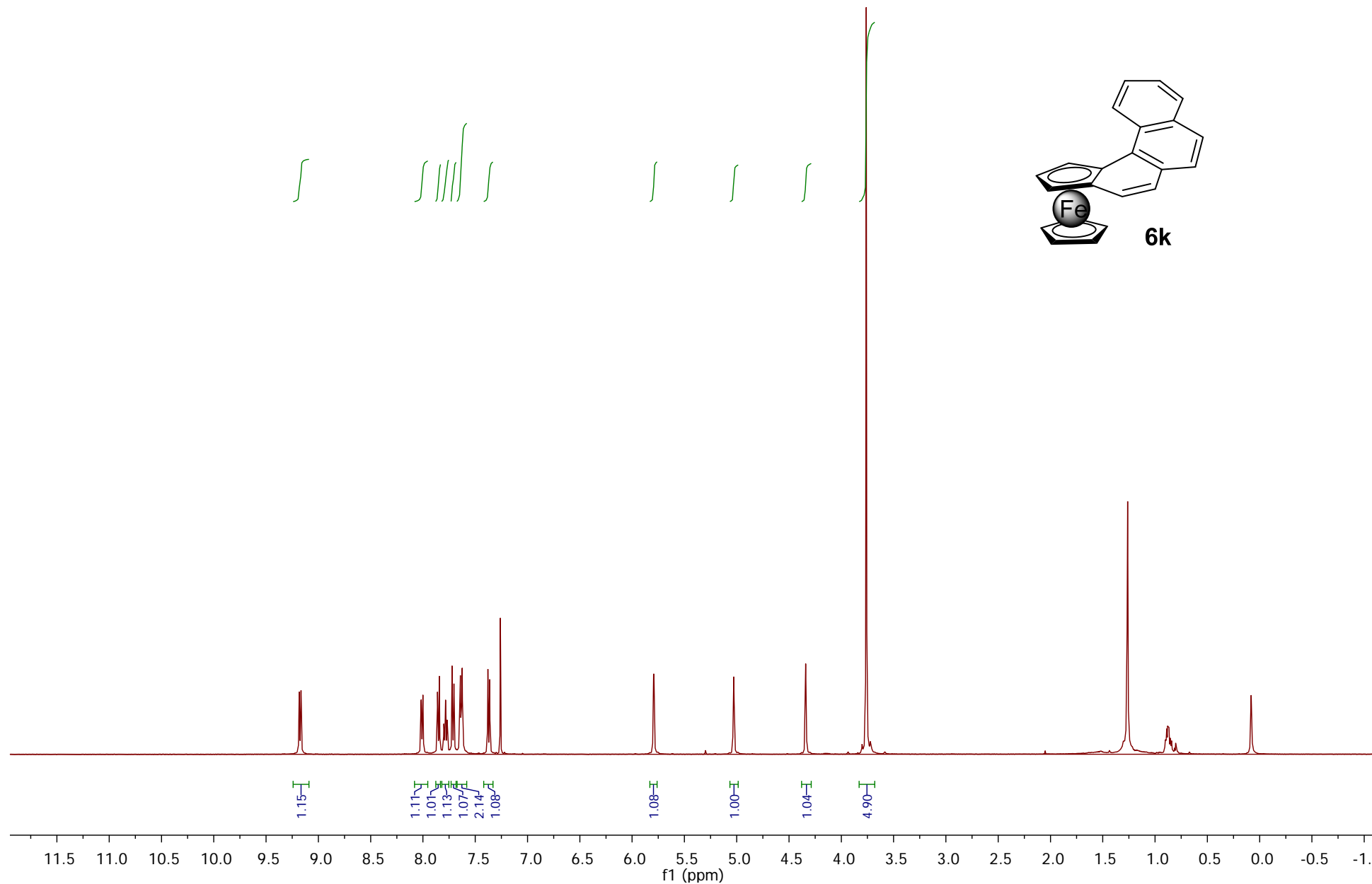
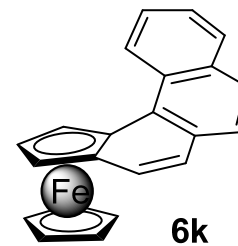
¹⁹F NMR (282 MHz, CDCl₃)



S-113

11103q-hgh4p1
hgH[4]_P1
PROTON CDCl3 C:\ sidi 1

¹H NMR (300 MHz, CDCl₃)



S-114

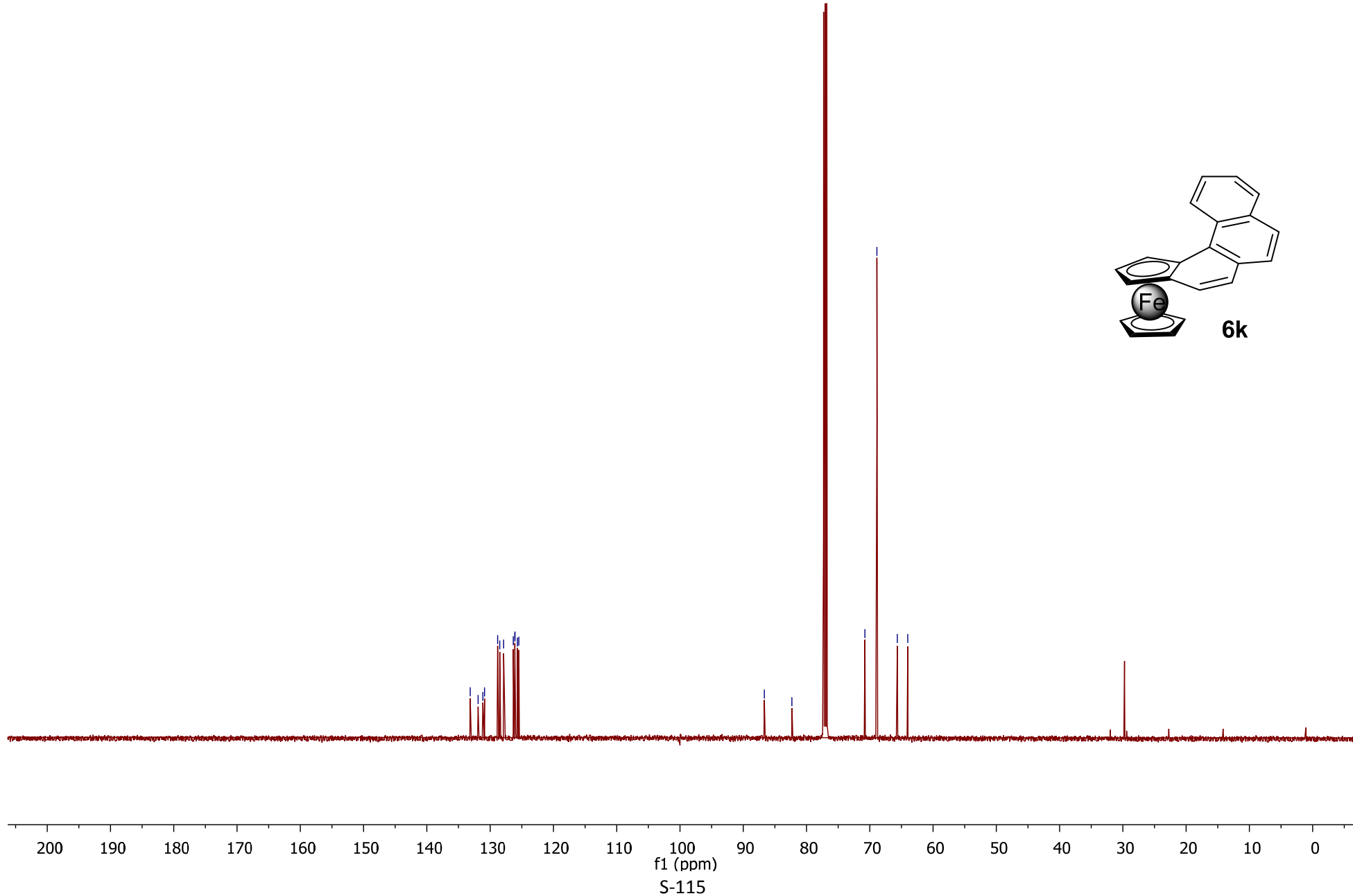
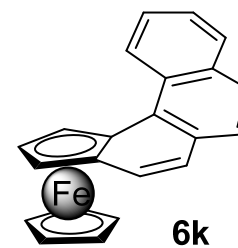
11103q-hgh4p1
hgH[4]_P1
C13CPD CDCl3 C:\sidi 1

133.16
131.91
131.14
130.89
128.82
128.49
127.87
126.34
126.10
126.08
125.69
125.46

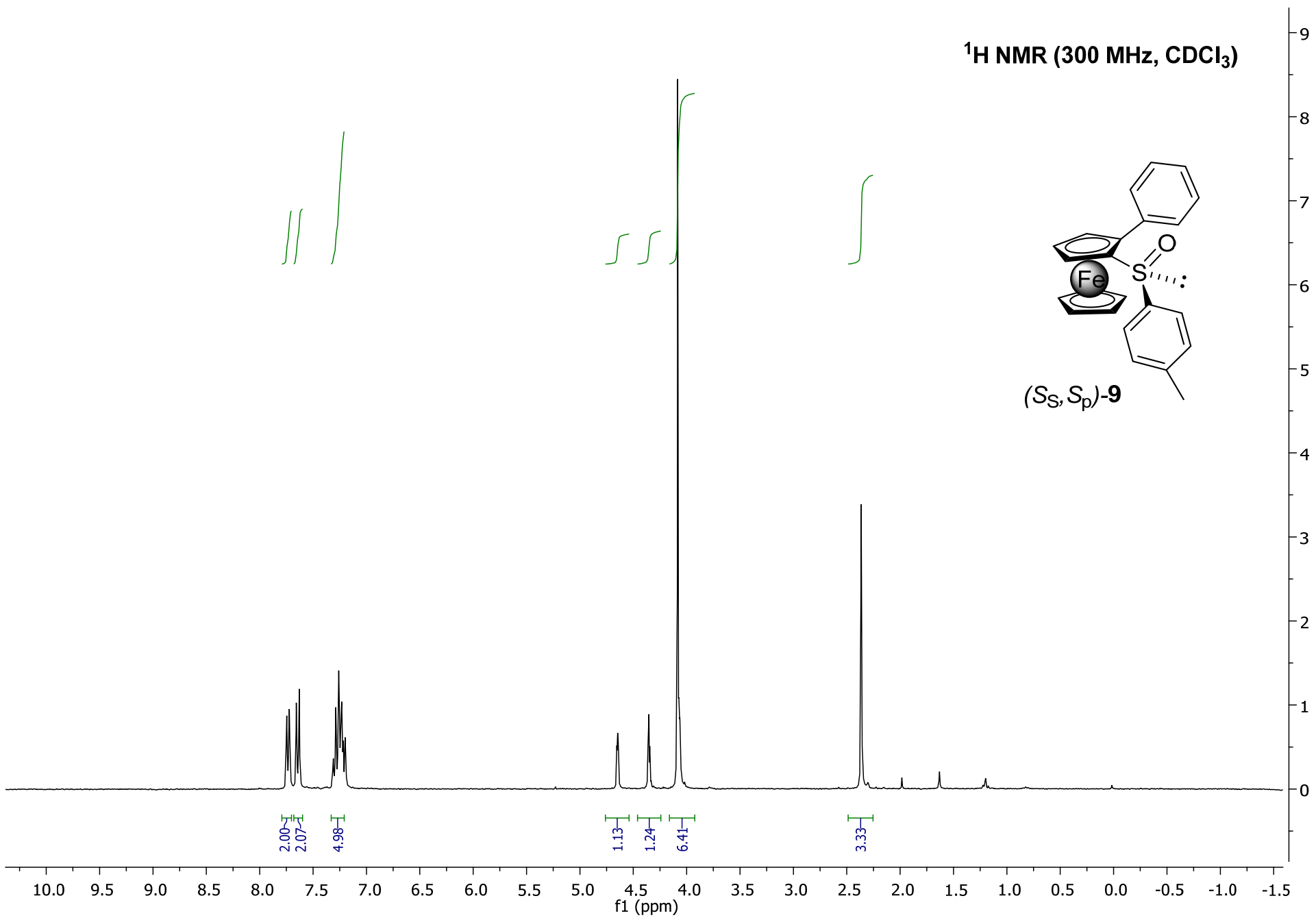
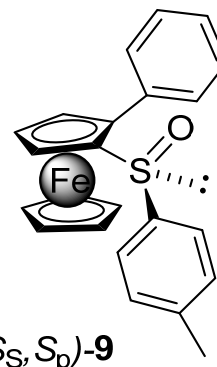
86.66
82.30

70.77
68.86
65.65
64.00

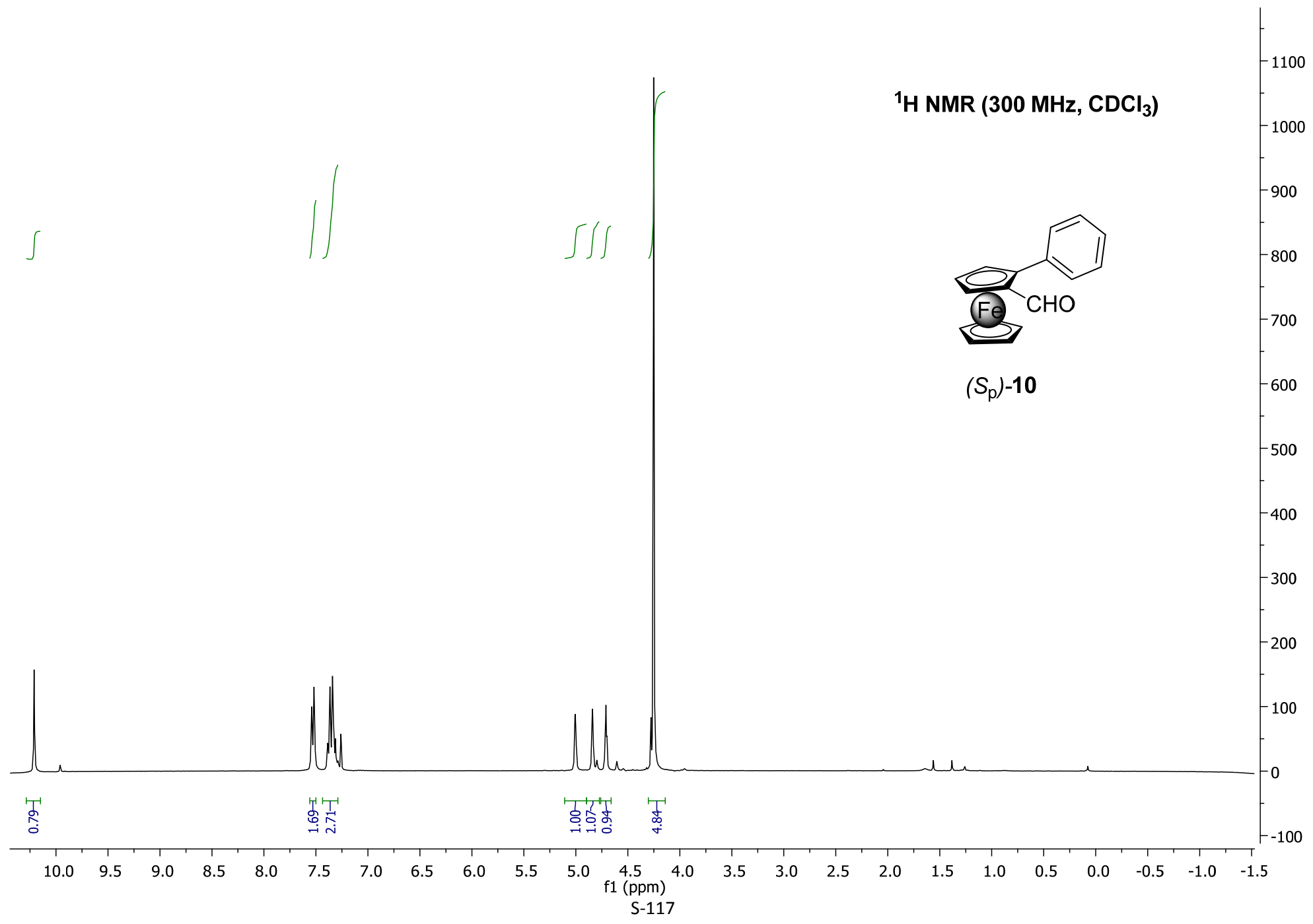
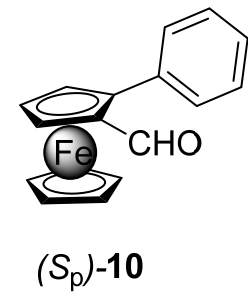
¹³C NMR (75 MHz, CDCl₃)



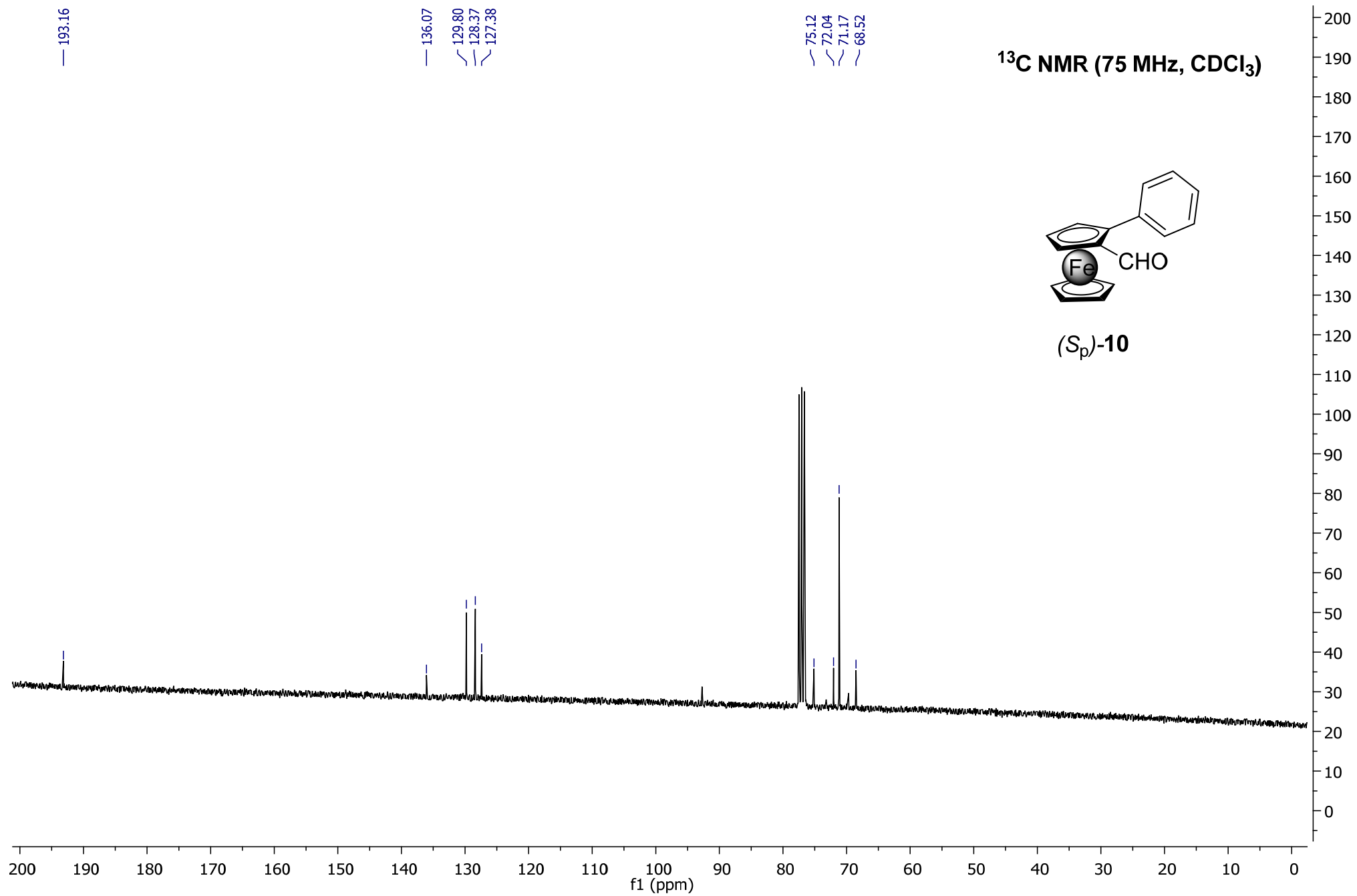
¹H NMR (300 MHz, CDCl₃)



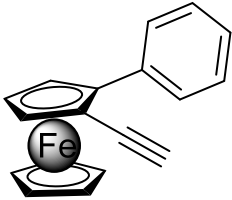
¹H NMR (300 MHz, CDCl₃)



S-117



¹H NMR (300 MHz, CDCl₃)



(*R_p*)-11

