Rhodium(II)-Catalyzed C-H Carboxylation of Ferrocenes with CO_2

Hong Lv,[a] Xinchao Wang,[a] Yanzhao Hao,[a] Chao Ma,[a] Shangda Li,[*a] Gang Li[*a,b] and Jian Zhang[a]

[a]State Key Laboratory of Structural Chemistry, and Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Center for Excellence in Molecular Synthesis, Fujian Institute of Research on the Structure of Matter, University of Chinese Academy of Sciences, Fuzhou 350100, China.
[b]Frontiers Science Center for Transformative Molecules, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.
*Email: sdli@fjirsm.ac.cn; gangli@fjirsm.ac.cn.

Table of content

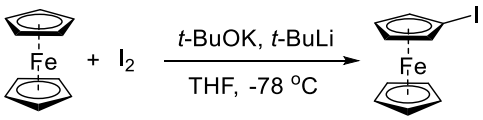
1. General Information

Unless otherwise noted, commercial available reagents were purchased from commercial suppliers (such as Strem, Alfa Aesar, J&K Chemical Co, Energy Chemical, Bide Pharmatech Ltd. and Adamas) and used as received. $Rh_2(OAc)_4$ was purchased from Sinocompound. Sensitive reagents, such as *t*-BuOK, were stored and weighed in a glove box. CO_2 was provided by Linde Gas (Xiamen) and its purity was ≥99.995%. $^{13}CO_2$ was provided by Dateng Chemistry (Wuhan) Co., Ltd. and its purity was ≥99.9%. Solvents were generally dried over 4Å molecular sieves. The reaction vessels used for C–H functionalization were 25 mL Schlenk sealed tube (Synthware). Purification of products was performed by flash chromatography (FC) using silica gel or preparative thin layer chromatography. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz and 101 MHz, respectively) or a JEOL ECZ600S spectrometer (600 MHz and 151 MHz, respectively). Chemical shifts are reported parts per million (ppm) referenced to Chloroform-*d* (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm) for ^1H NMR; Chloroform-*d* (δ 77.16 ppm) for ^{13}C NMR. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = double doublet of doublets, dt = doublet of triplet, td = triplet of doublet and m = multiplet. To distinguish, some ^{13}C NMR chemical shifts retain two decimal places. High-resolution mass spectra (HRMS) were obtained on an Thermo Scientific LTQ Orbitrap mass spectrometry equipped with an ESI source from keecloud Biotech. The determination of ee value was performed via chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Agilent SuperNova X-ray diffractionmeter.

2. Experimental Section

2.1 Preparation and characterization of substrates.

2.1.1 Preparation of ferrocene iodide.

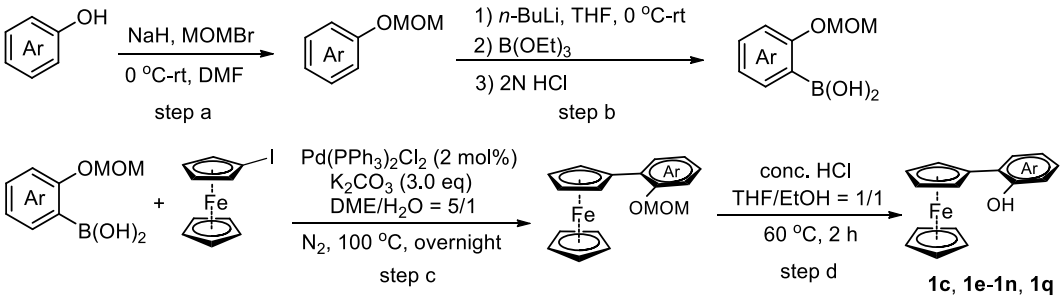


An oven-dried three-necked flask was charged with ferrocene (9.67 g, 52 mmol), *t*-BuOK (0.67 g, 5.98 mmol) and anhydrous THF (300 mL) under N_2 atmosphere. The solution was cooled to -78 °C and *t*-BuLi (100 mL, 1.3 M in pentane, 2.5 equiv) was

added dropwise while stirring (be careful!). After 0.5 h at -78 °C, an orange precipitate was formed. Stirring was continued for another 1.5 h and then solid iodine (33.5 g, 132 mmol) was added to the suspension. After kept at -78 °C for 15 min, the mixture was allowed to slowly warm to room temperature and stirred for 5 h. The reaction was quenched with 200 mL of saturated $Na_2S_2O_3$ solution, and extracted with EtOAc (100 mL × 3). The combined organic extracts were concentrated using a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to give ferrocene iodide as a red solid (10.39 g, 64%).[S1]

2.1.2 Preparation of substrates.[S2, S3]

Rout 1 (for **1c**, **1e-1n**, **1q**)



Step a: To an oven-dried Schlenk flask equipped with a magnetic stir bar was added NaH (1.73 g, 26 mmol, 60% in mineral oil) and anhydrous DMF (40 mL). After cooled to 0 °C under an ice-bath, phenols (20 mmol) and bromomethyl methyl ether (2.06 mL, 24 mmol) were added successively. Then the ice bath was removed and the mixture was stirred at room temperature for 2 h. Afterwards, the reaction was carefully quenched with ice-water (100 mL) at 0 °C. The mixture was extracted with EtOAc (30 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 10/1) to give MOM-protected phenols (100% yield).

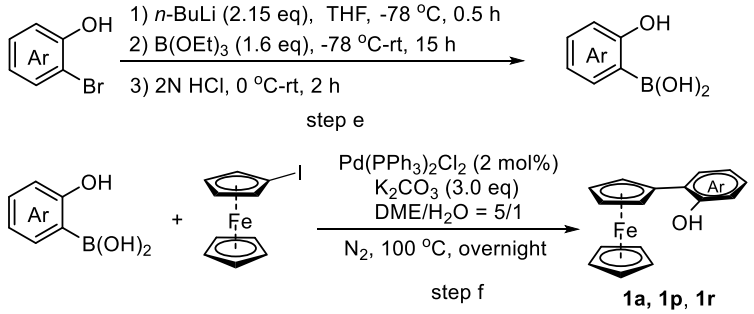
Step b: To a solution of MOM-protected phenols (20 mmol) in anhydrous THF (70 mL) was added *n*-BuLi (2.5 M in hexane, 9.6 mL, 24 mmol) at 0 °C under N_2 atmosphere. The mixture was stirred at room temperature for 2 h. After re-cooled to 0 °C, $B(OEt)_3$ (4.76 mL, 28 mmol) was added and the solution was stirred at room temperature for another 1 h. Afterwards, the mixture was quenched with 2 N HCl and stirred at room temperature for 24 h. The solution was extracted with EtOAc (30 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified through flash silica-gel chromatography to obtain corresponding boronic acid (petroleum ether/EtOAc = 2/1 to 1/2).

Step c: To an oven-dried Schlenk tube (120 mL) was added corresponding boronic acid (4.5 mmol), iodoferrocene (936 mg, 3 mmol), K_2CO_3 (1.24 g, 9 mmol),

$Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol), DME (25 mL) and H_2O (5 mL). The solution was degassed and heated at 100 °C overnight under N_2 atmosphere. Afterwards, the reaction was cooled to room temperature and diluted with H_2O (50 mL). The mixture was extracted with EtOAc (40 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified through flash silica-gel chromatography to obtain MOM-protected substrates (petroleum ether/EtOAc = 100/1 to 50/1).

Step d: The MOM-protected substrate was dissolved in EtOH (7.5 mL) and THF (7.5 mL) in a Schlenk tube. Then conc. HCl (2.0 mL) was added to the solution. The mixture was heated at 60 °C for 2 h. After cooled to room temperature, saturated aqueous $NaHCO_3$ (10 mL) was added and the system was extracted with EtOAc (30 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified through flash silica-gel chromatography to obtain the final substrates (petroleum ether/EtOAc = 80/1 to 10/1).

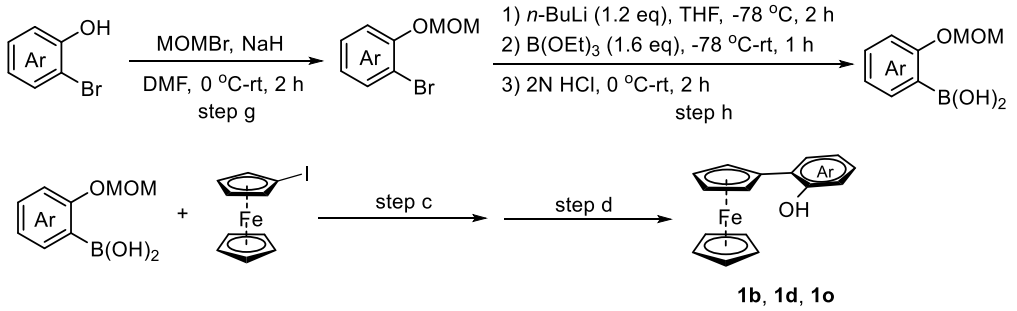
Rout 2 (for **1a**, **1p**, **1r**)



Step e: To a solution of corresponding *o*-bromophenol (15 mmol) in anhydrous THF (45 mL) was added *n*-BuLi (12 mL, 2.5 M in hexane, 30 mmol) at -78 °C under N_2 atmosphere. The mixture was stirred at -78 °C for 3 h, followed by addition of $B(OEt)_3$ (4.08 mL, 24 mmol). Then the mixture was stirred at room temperature for 15 h. After re-cooled to 0 °C, the reaction was quenched with 2 N HCl (50 mL) and then stirred at room temperature for another 2 h. Afterwards, the solution was extracted with EtOAc (30 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified through flash silica-gel chromatography to obtain corresponding boronic acid (petroleum ether/EtOAc = 2/1 to 1/2).

Step f: Similar procedure as Step c.

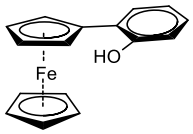
Rout 3 (for **1b**, **1d**, **1o**)



1b, **1d**, **1o**

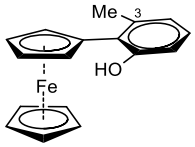
Step g: Similar procedure as Step a.

Step h: To a solution of MOM-protected *o*-bromophenols (15 mmol) in anhydrous THF (50 mL) was added *n*-BuLi (7.2 mL, 2.5 M in hexane, 18 mmol) at -78 °C under N_2 atmosphere. The mixture was stirred at -78 °C for 2 h, and then $B(OEt)_3$ (4.08 mL, 24 mmol) was added. The solution was allowed to slowly warm to room temperature and stirring was continued for another 1 h. Then the reaction was re-cooled to 0 °C and quenched with 2 N HCl (30 mL). After stirring at room temperature for 2 h, the solution was extracted with EtOAc (30 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified through flash silica-gel chromatography (petroleum ether/EtOAc = 2/1) to obtain corresponding boronic acid.



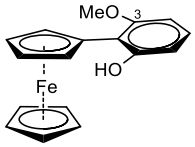
1a: 2-ferrocenylphenol.

1a was prepared from route 2 [Note: (2-hydroxyphenyl)boronic acid was purchased from commercial supplier], dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 3H), 6.98 (d, *J* = 8.58 Hz, 1H), 6.87 (t, *J* = 7.46 Hz, 1H), 4.54 (t, 2H), 4.43 (t, 2H), 4.26 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 129.5, 128.5, 123.0, 120.3, 115.8, 82.2, 69.6, 69.3, 67.5. HRMS (m/z, ESI): calcd for $C_{16}H_{14}FeO^+$ (M^+) 278.0389, found 278.0389.



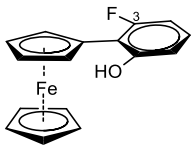
1b: 3-methyl-2-ferrocenylphenol.

1b was prepared from route 3, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.13 (t, *J* = 7.81 Hz, 1H), 6.87 (d, *J* = 8.08 Hz, 1H), 6.75 (d, *J* = 7.49 Hz, 1H), 4.48 (t, *J* = 1.86 Hz, 2H), 4.40 (t, *J* = 1.83 Hz, 2H), 4.32 (s, 5H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.1, 138.1, 128.0, 122.3, 120.6, 113.1, 80.2, 69.9, 69.4, 69.0, 21.7. HRMS (m/z, ESI): calcd for $C_{17}H_{16}FeO^+$ (M^+) 292.0545, found 292.0546.



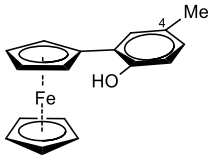
1c: 3-methoxy-2-ferrocenylphenol.

1c was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.14 (t, *J* = 8.23 Hz, 1H), 6.65 (d, *J* = 8.31 Hz, 1H), 6.47 (d, *J* = 8.42 Hz, 1H), 4.67 (s, 2H), 4.52 (s, 2H), 4.34 (s, 5H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.9, 155.0, 128.4, 110.8, 108.7, 102.8, 70.2, 69.7, 69.3, 55.8. HRMS (m/z, ESI): calcd for $C_{17}H_{16}FeO_2^+$ (M^+) 308.0494, found 308.0491.



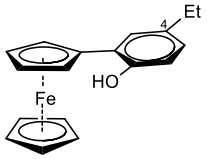
1d: 3-fluoro-2-ferrocenylphenol.

1d was prepared from route 3, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.20 – 7.10 (m, 1H), 6.81 (d, *J* = 8.22 Hz, 1H), 6.66 (t, 1H), 4.59 (t, *J* = 1.97 Hz, 2H), 4.48 (t, *J* = 1.89 Hz, 2H), 4.29 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.6 (d, $J_{C\text{-}F}$ = 246.5 Hz), 155.1 (d, $J_{C\text{-}F}$ = 5.5 Hz), 128.3 (d, $J_{C\text{-}F}$ = 10.7 Hz), 111.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 111.3 (d, $J_{C\text{-}F}$ = 16.3 Hz), 107.4 (d, $J_{C\text{-}F}$ = 23.1 Hz), 74.5, 69.6, 69.4, 69.1 (d, $J_{C\text{-}F}$ = 3.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.4. HRMS (m/z, ESI): calcd for $C_{16}H_{13}FFeO^+$ (M^+) 296.0294, found 296.0296.



1e: 4-methyl-2-ferrocenylphenol.

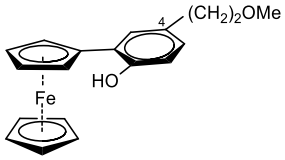
1e was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.01 (d, *J* = 8.09 Hz, 3H), 6.87 (d, *J* = 7.90 Hz, 1H), 4.55 (s, 2H), 4.44 (s, 2H), 4.27 (s, 5H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.3, 129.9, 129.4, 129.1, 122.6, 115.6, 82.7, 69.7, 69.4, 67.6, 20.6. HRMS (m/z, ESI): calcd for $C_{17}H_{16}FeO^+$ (M^+) 292.0545, found 292.0552.



1f: 4-ethyl-2-ferrocenylphenol.

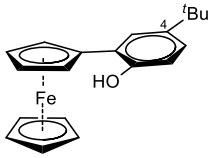
1f was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 – 7.01 (m, 3H), 6.90 (dt, *J* = 8.67, 1.20 Hz, 1H), 4.53 (t, *J* = 1.86 Hz, 2H), 4.42 (t, 2H), 4.26 (s, 5H), 2.58 (q, *J* = 7.60 Hz, 2H), 1.22 (t, *J* = 7.60 Hz, 3H). ^{13}C NMR (101 MHz,

Chloroform-*d*) δ 151.5, 135.9, 128.9, 127.9, 122.5, 115.6, 82.6, 69.5, 69.3, 67.5, 28.1, 16.0. HRMS (m/z, ESI): calcd for $C_{18}H_{18}FeO^+$ (M^+) 306.0702, found 306.0700.



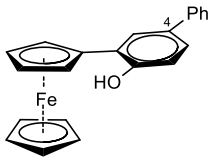
1g: 4-(2-methoxyethyl)-2-ferrocenylphenol.

1g was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (t, *J* = 6.16 Hz, 3H), 6.90 (d, *J* = 8.80 Hz, 1H), 4.52 (t, *J* = 1.79 Hz, 2H), 4.41 (t, *J* = 1.78 Hz, 2H), 4.25 (s, 5H), 3.58 (t, *J* = 7.16 Hz, 2H), 3.36 (s, 3H), 2.81 (t, *J* = 7.15 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.0, 130.5, 129.9, 128.8, 122.8, 115.7, 82.4, 74.0, 69.6, 69.3, 67.5, 58.8, 35.4. HRMS (m/z, ESI): calcd for $C_{19}H_{21}FeO_2^+$ ($M+H^+$) 337.0880, found 337.0874.



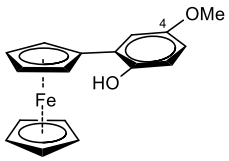
1h: 4-*tert*-butyl-2-ferrocenylphenol.

1h was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.18 (m, 2H), 7.06 (s, 1H), 6.90 (d, *J* = 8.31 Hz, 1H), 4.52 (t, *J* = 1.83 Hz, 2H), 4.41 (t, *J* = 1.82 Hz, 2H), 4.26 (s, 5H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.2, 142.9, 126.6, 125.5, 122.0, 115.2, 83.1, 69.5, 69.3, 67.6, 34.2, 31.7. HRMS (m/z, ESI): calcd for $C_{20}H_{22}FeO^+$ (M^+) 334.1015, found 334.1014.



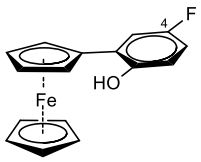
1i: 4-phenyl-2-ferrocenylphenol.

1i was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.23 Hz, 2H), 7.47 – 7.37 (m, 4H), 7.32 – 7.21 (m, 2H), 7.03 (d, *J* = 9.02 Hz, 1H), 4.57 (t, *J* = 1.78 Hz, 2H), 4.44 (t, *J* = 1.79 Hz, 2H), 4.27 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.1, 140.9, 133.5, 128.8, 128.2, 127.2, 126.84, 126.77, 123.3, 116.2, 82.3, 69.8, 69.4, 67.6. HRMS (m/z, ESI): calcd for $C_{22}H_{18}FeO^+$ (M^+) 354.0702, found 354.0702.



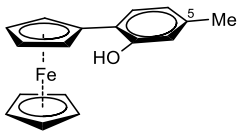
1j: 4-methoxy-2-ferrocenylphenol.

1j was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.90 (d, *J* = 8.38 Hz, 1H), 6.82 – 6.74 (m, 3H), 4.56 (t, 2H), 4.42 (t, *J* = 1.82 Hz, 2H), 4.25 (s, 5H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.2, 147.6, 123.7, 116.4, 114.7, 113.7, 82.4, 69.6, 69.3, 67.6, 55.9. HRMS (m/z, ESI): calcd for $C_{17}H_{16}FeO_2^+$ (M^+) 308.0494, found 308.0491.



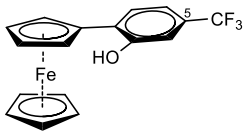
1k: 4-fluoro-2-ferrocenylphenol.

1k was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 – 6.73 (m, 4H), 4.55 (s, 2H), 4.45 (s, 2H), 4.26 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.8 (d, J_{C-F} = 237.4 Hz), 149.5 (d, J_{C-F} = 2.0 Hz), 124.4 (d, J_{C-F} = 8.0 Hz), 116.6 (d, J_{C-F} = 8.3 Hz), 115.5 (d, J_{C-F} = 23.6 Hz), 114.6 (d, J_{C-F} = 23.1 Hz), 81.6, 70.0, 69.5, 67.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.7. HRMS (m/z, ESI): calcd for $C_{16}H_{13}FFeO^+$ (M^+) 296.0294, found 296.0299.



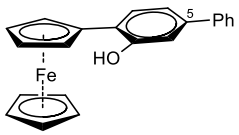
1l: 5-methyl-2-ferrocenylphenol.

1l was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (s, 1H), 7.11 (d, *J* = 7.76 Hz, 1H), 6.82 (s, 1H), 6.70 (d, *J* = 7.80 Hz, 1H), 4.51 (t, *J* = 1.87 Hz, 2H), 4.41 (t, *J* = 1.83 Hz, 2H), 4.25 (s, 5H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.3, 138.7, 129.3, 121.2, 119.8, 116.4, 82.4, 69.4, 69.2, 67.4, 21.4. HRMS (m/z, ESI): calcd for $C_{17}H_{16}FeO^+$ (M^+) 292.0545, found 292.0552.



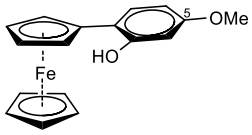
1m: 5-trifluoromethyl-2-ferrocenylphenol.

1m was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.31 (d, *J* = 7.95 Hz, 1H), 7.21 (s, 1H), 7.11 (d, *J* = 7.83 Hz, 1H), 4.56 (t, 2H), 4.48 (t, 2H), 4.27 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.6, 130.4 (q, J_{C-F} = 32.61 Hz), 129.7, 127.3, 124.2 (q, J_{C-F} = 271.92 Hz), 117.0 (q, J_{C-F} = 3.93 Hz), 112.9 (q, J_{C-F} = 3.93 Hz), 80.6, 70.2, 69.5, 67.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.6. HRMS (m/z, ESI): calcd for $C_{17}H_{13}F_3FeO^+$ (M^+) 346.0262, found 346.0262.



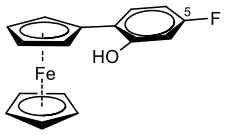
1n: 5-phenyl-2-ferrocenylphenol.

1n was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.19 Hz, 2H), 7.41 (t, *J* = 7.52 Hz, 2H), 7.31 (t, *J* = 7.35 Hz, 1H), 7.22 (t, *J* = 8.46 Hz, 2H), 7.08 (d, *J* = 7.62 Hz, 1H), 4.53 (t, 2H), 4.40 (t, 2H), 4.24 (s, 5H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.8, 141.6, 140.7, 129.8, 128.9, 127.5, 127.0, 122.2, 119.1, 114.4, 81.9, 69.7, 69.3, 67.5. HRMS (m/z, ESI): calcd for $C_{22}H_{18}FeO^{+}$ (M^{+}) 354.0702, found 354.0704.



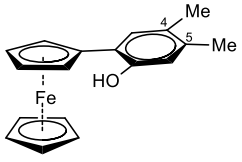
1o: 5-methoxy-2-ferrocenylphenol.

1o was prepared from route 3, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (s, 1H), 7.11 (d, *J* = 8.45 Hz, 1H), 6.57 (d, *J* = 2.54 Hz, 1H), 6.45 (dd, *J* = 8.46, 2.56 Hz, 1H), 4.47 (t, 2H), 4.39 (t, 2H), 4.25 (s, 5H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.3, 154.5, 130.0, 115.2, 106.5, 101.4, 82.5, 69.3, 69.2, 67.2, 55.5. HRMS (m/z, ESI): calcd for $C_{17}H_{16}FeO_2^{+}$ (M^{+}) 308.0494, found 308.0490.



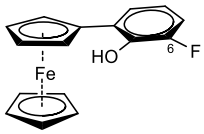
1p: 5-fluoro-2-ferrocenylphenol.

1p was prepared from route 2, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.14 (dd, *J* = 8.50, 6.51 Hz, 1H), 6.71 (dd, *J* = 10.14, 2.59 Hz, 1H), 6.63 – 6.51 (m, 1H), 4.49 (t, *J* = 1.82 Hz, 2H), 4.43 (t, *J* = 1.83 Hz, 2H), 4.26 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1 (d, $J_{C\text{-}F}$ = 244.8 Hz), 154.6 (d, $J_{C\text{-}F}$ = 12.3 Hz), 130.2 (d, $J_{C\text{-}F}$ = 9.8 Hz), 118.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 107.3 (d, $J_{C\text{-}F}$ = 21.6 Hz), 103.3 (d, $J_{C\text{-}F}$ = 24.8 Hz), 81.7, 69.7, 69.3, 67.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.7. HRMS (m/z, ESI): calcd for $C_{16}H_{13}FFeO^{+}$ (M^{+}) 296.0294, found 296.0299.



1q: 4,5-dimethyl-2-ferrocenylphenol.

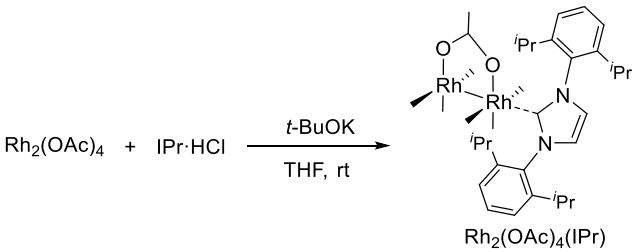
1q was prepared from route 1, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.97 (s, 2H), 6.79 (s, 1H), 4.51 (t, *J* = 1.80 Hz, 2H), 4.40 (t, *J* = 1.85 Hz, 2H), 4.25 (s, 5H), 2.24 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.4, 137.1, 130.4, 128.2, 119.8, 117.0, 82.6, 69.4, 69.2, 67.4, 19.8, 18.9. HRMS (m/z, ESI): calcd for $C_{18}H_{18}FeO^{+}$ (M^{+}) 306.0702, found 306.0701.



1r: 6-fluoro-2-ferrocenylphenol.

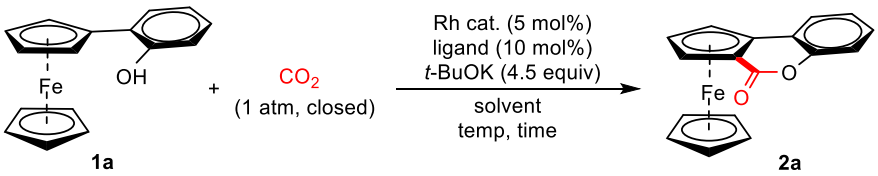
1r was prepared from route 2, dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 – 6.97 (m, 2H), 6.82 – 6.75 (m, 1H), 6.74 (d, *J* = 2.43 Hz, 1H), 4.63 (t, *J* = 1.88 Hz, 2H), 4.41 (t, *J* = 1.90 Hz, 2H), 4.22 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.6 (d, $J_{C\text{-}F}$ = 240.3 Hz), 141.5 (d, $J_{C\text{-}F}$ = 12.9 Hz), 126.3 (d, $J_{C\text{-}F}$ = 2.4 Hz), 124.4 (d, $J_{C\text{-}F}$ = 3.1 Hz), 119.8 (d, $J_{C\text{-}F}$ = 7.7 Hz), 114.2 (d, $J_{C\text{-}F}$ = 18.4 Hz), 81.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 69.6, 69.4, 67.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -138.8. HRMS (m/z, ESI): calcd for $C_{16}H_{13}FFeO^{+}$ (M^{+}) 296.0294, found 296.0285.

2.1.3 Preparation of $Rh_2(OAc)_4(IPr)$.



Complex $Rh_2(OAc)_4(IPr)$ was prepared according to literature procedure.[S4] To a solution of $Rh_2(OAc)_4$ (300 mg, 0.68 mmol) and IPr·HCl (540 mg, 1.38 mmol) in anhydrous THF (10 mL) was added *t*-BuOK (157 mg, 1.4 mmol) under N_2 atmosphere. The mixture was stirred at room temperature for 5 h. Color change from blue to red was observed during the course. Upon the removal of THF, the residual was purified *via* column chromatography using petroleum ether/EtOAc = 2/1 to afford analytical pure purple crystals (350 mg) in 60% yield.

2.2 More condition screenings for optimization.



General procedure: In a glove box, to an oven-dried 25 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added Rh precursor (5 mol%), ligand (10 mol%) and *t*-BuOK (4.5 eq, note: base should be dry). After taken out of the glove box, **1a** (27.8 mg, 0.1 mmol) dissolved in anhydrous mesitylene (1 mL) was added, then the tube was evacuated under vacuum and charged with CO_2 (1

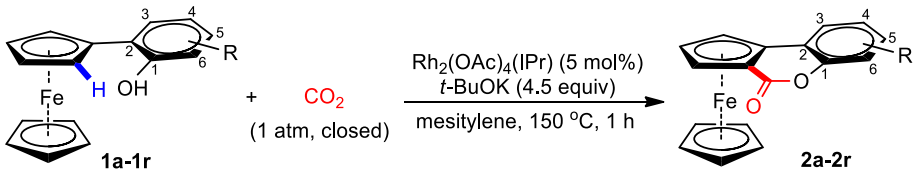
atm, × 3). Afterwards, the tube was capped and then placed into a preheated hotplate (100-150 °C). The reaction was stirred vigorously (Note: good stirring is important!) for 1-24 h and cooled to room temperature. Mesitylene was removed by vacuum pump evaporation under reduced pressure, then the reaction was diluted with EtOAc (20 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional 10 mL of EtOAc. The filtrate was concentrated in *vacuo*, and crude ^{1}H NMR spectrum was made by using CH_2Br_2 as internal standard.

Table S1: Screening of reaction conditions[a]

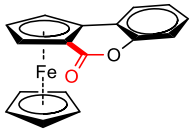
Entry	Rh Cat.	Ligand	Solvent	Temp (°C)	Time (h)	2a (%)
1	$Rh_2(OAc)_4$	IMes·HCl	DMF	150	24	0
2	$Rh_2(OAc)_4$	IMes·HCl	diglyme	150	24	0
3	$Rh_2(OAc)_4$	IMes·HCl	DMA	150	24	0
4	$Rh_2(OAc)_4$	IPr·HCl	diglyme	150	24	0
5	$Rh_2(OAc)_4$	SPhos	diglyme	150	24	0
6	$Rh_2(OAc)_4$	PCy_3	diglyme	150	24	0
7	$Rh_2(OAc)_4$	IPr·HCl	DMF	150	24	0
8	$Rh_2(OAc)_4$	SPhos	DMF	100	24	0
9	$[RhCl(cod)]_2$	PPh_3	DMF	150	24	0
10	$[RhCl(cod)]_2$	PPh_3	diglyme	150	24	0
11	$[RhCl(cod)]_2$	PPh_3	DMA	150	24	0
12	$Rh_2(OAc)_4$	IPr·HCl	mesitylene	150	2	64
13	$Rh_2(OAc)_4$	IPr·HCl	mesitylene	130	1	30
14	$Rh_2(OAc)_4$	IPr·HCl	mesitylene	120	1	0
15	$Rh_2(OAc)_4$	IPr·HCl	mesitylene	100	1	0
16[b]	$Rh_2(OAc)_4$	IPr·HCl	mesitylene	150	1	18
17	-	IPr·HCl	mesitylene	150	1	0
18	$Rh_2(OAc)_4$(IPr)	-	mesitylene	120	1	13
19	$Rh_2(OAc)_4$(IPr)	-	*tert*-butylbenzene	150	1	59
20	$Rh_2(OAc)_4$(IPr)	-	*p*-xylene	150	1	49
21	$Rh_2(OAc)_4$(IPr)	-	toluene	150	1	13
22	$Rh_2(OAc)_4$(IPr)	-	chlorobenzene	150	1	13
23	$Rh_2(OAc)_4$(IPr)	-	diglyme	150	1	26
24	$Rh_2(OAc)_4$(IPr)	-	MeCN	150	1	3
25[c]	$Rh_2(OAc)_4$(IPr)	-	mesitylene	150	1	65

[a]Reaction conditions: **1a** (0.1 mmol), CO_2 (1 atm, closed), $Rh_2(OAc)_4$ (5 mol%), ligand (10 mol%), *t*-BuOK (4.5 equiv), solvent (1 mL), 100-150 °C. Yield was determined by ^{1}H NMR with CH_2Br_2 as internal standard. [b]*t*-BuOK (2.0 equiv). [c]1 mol% $Rh_2(OAc)_4$(IPr) was used.

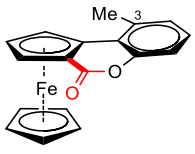
2.3 General procedure and characterization of products.



General procedure: In a glove box, to an oven-dried 25 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added $Rh_2(OAc)_4(IPr)$ (8.3 mg, 0.01 mol) and *t*-BuOK (101 mg, 0.9 mmol) (Note: *t*-BuOK should be dry). After taken out of the glove box, substrate **1** (0.2 mmol) dissolved in anhydrous mesitylene (2 mL) was added and the tube was evacuated under vacuum and charged with CO_2 (1 atm, × 3). Afterwards, the tube was capped and then placed into a preheated hotplate (150 °C). The reaction was stirred vigorously (Note: good stirring is important!) for 1 h and cooled to room temperature. Mesitylene was removed by vacuum pump evaporation under reduced pressure, then the reaction was diluted with EtOAc (20 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional 10 mL of EtOAc. The filtrate was concentrated in vacuo, and purified by preparative thin layer chromatography using petroleum ether/EtOAc (10/1 to 5/1) as the eluent to afford the desired products.

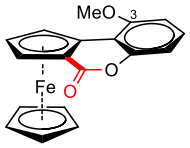


2a: 6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 47.4 mg; yield: 78%; dark red oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 7.66, 1.60 Hz, 1H), 7.32 (td, *J* = 8.24, 7.23, 1.60 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.20 (td, *J* = 7.65, 7.24, 1.29 Hz, 1H), 5.19 (dd, *J* = 2.60, 1.17 Hz, 1H), 5.16 (dd, *J* = 2.57, 1.17 Hz, 1H), 4.65 (t, *J* = 2.58 Hz, 1H), 4.07 (s, 5H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.6, 151.4, 128.1, 124.5, 123.2, 121.6, 117.4, 83.5, 73.1, 71.4, 68.4, 65.3, 64.6. HRMS (m/z, ESI): calcd for $C_{17}H_{13}FeO_2^+$ ($M+H^+$) 305.0260, found 305.0254.

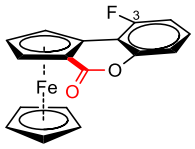


2b: 3-methyl-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 34 mg; yield: 54%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.36 Hz, 1H), 7.14 (d, 1H), 7.03 (d, *J* = 7.28 Hz, 1H), 5.24 (ddd, *J* = 17.60, 2.72, 1.18 Hz, 2H), 4.65 (t, *J* = 2.71 Hz, 1H), 4.07 (s, 5H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 151.8, 134.8, 127.3, 126.7, 120.6, 115.6, 82.9, 73.4,

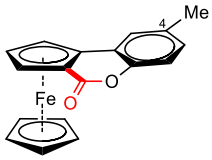
71.1, 69.6, 68.5, 64.9, 22.5. HRMS (m/z, ESI): calcd for $C_{18}H_{15}FeO_2^+$ ($M+H^+$) 319.0416, found 319.0412.



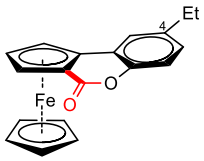
2c: 3-methoxy-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 46 mg; yield: 70%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (t, *J* = 8.3 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.51 (dd, *J* = 2.6, 1.3 Hz, 1H), 5.14 (dd, *J* = 2.7, 1.3 Hz, 1H), 4.61 (t, *J* = 2.6 Hz, 1H), 4.05 (s, 5H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 156.5, 152.2, 127.7, 111.2, 110.0, 106.1, 81.4, 73.2, 71.0, 70.5, 67.7, 63.7, 56.1. HRMS (m/z, ESI): calcd for $C_{18}H_{15}FeO_3^+$ ($M+H^+$) 335.0365, found 335.0366.



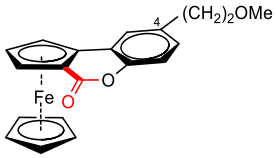
2d: 3-fluoro-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 37 mg; yield: 58%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.22 (m, 1H), 7.09 (d, *J* = 8.39 Hz, 1H), 6.97 (t, *J* = 9.03 Hz, 1H), 5.37 (dd, *J* = 5.92, 1.25 Hz, 1H), 5.20 (dd, *J* = 2.65, 1.26 Hz, 1H), 4.69 (t, *J* = 2.64 Hz, 1H), 4.11 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 158.8 (d, J_{C-F} = 249.1 Hz), 152.1 (d, J_{C-F} = 7.3 Hz), 127.7 (d, J_{C-F} = 9.7 Hz), 113.1 (d, J_{C-F} = 3.3 Hz), 111.5 (d, J_{C-F} = 20.2 Hz), 111.0 (d, J_{C-F} = 20.5 Hz), 78.7, 73.7 (d, J_{C-F} = 1.8 Hz), 71.3, 69.4 (d, J_{C-F} = 8.0 Hz), 68.4, 63.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.8. HRMS (m/z, ESI): calcd for $C_{17}H_{12}FFeO_2^+$ ($M+H^+$) 323.0165, found 323.0166.



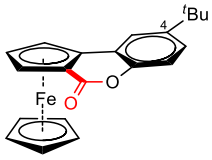
2e: 4-methyl-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 41 mg; yield: 64%; dark red oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.14 (d, *J* = 8.35 Hz, 1H), 7.09 (dd, *J* = 8.33, 2.07 Hz, 1H), 5.16 (dd, *J* = 2.64, 1.16 Hz, 1H), 5.11 (dd, *J* = 2.57, 1.16 Hz, 1H), 4.62 (t, *J* = 2.58 Hz, 1H), 4.05 (s, 5H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.7, 149.4, 134.0, 128.8, 123.2, 121.1, 117.0, 83.6, 73.0, 71.3, 68.3, 65.1, 64.5, 21.0. HRMS (m/z, ESI): calcd for $C_{18}H_{15}FeO_2^+$ ($M+H^+$) 319.0416, found 319.0417.



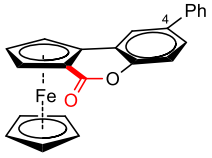
2f: 4-ethyl-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 46.2 mg; yield: 70%; dark red oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.21 – 7.08 (m, 2H), 5.15 (d, *J* = 17.26 Hz, 2H), 4.63 (t, 1H), 4.05 (s, 5H), 2.70 (q, *J* = 7.89 Hz, 2H), 1.28 (t, *J* = 7.54 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.8, 149.5, 140.5, 127.7, 122.1, 121.2, 117.1, 83.7, 73.0, 71.3, 68.3, 65.2, 64.5, 28.4, 15.9. HRMS (m/z, ESI): calcd for $C_{19}H_{17}FeO_2^+$ ($M+H^+$) 333.0573, found 333.0577.



2g: 4-(2-methoxyethyl)-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 55 mg; yield: 75%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (s, 1H), 7.17 (t, *J* = 1.46 Hz, 2H), 5.16 (dd, *J* = 2.63, 1.17 Hz, 1H), 5.13 (dd, *J* = 2.63, 1.17 Hz, 1H), 4.63 (t, *J* = 2.61 Hz, 1H), 4.05 (s, 5H), 3.63 (t, *J* = 6.85 Hz, 2H), 3.36 (s, 3H), 2.92 (t, *J* = 6.88 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 149.9, 135.3, 128.5, 123.3, 121.3, 117.2, 83.5, 73.6, 73.0, 71.3, 68.3, 65.2, 64.5, 58.9, 35.8. HRMS (m/z, ESI): calcd for $C_{20}H_{19}FeO_3^+$ ($M+H^+$) 363.0678, found 363.0664.

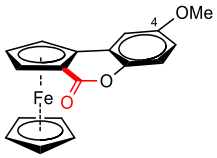


2h: 4-*tert*-butyl-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 42 mg; yield: 58%; dark red oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.34 (d, *J* = 8.70 Hz, 1H), 7.19 (d, *J* = 8.57 Hz, 1H), 5.16 (s, 2H), 4.64 (t, *J* = 2.78 Hz, 1H), 4.06 (s, 5H), 1.38 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.9, 149.3, 147.5, 125.4, 120.7, 119.5, 116.8, 84.0, 72.9, 71.3, 68.3, 65.1, 64.5, 34.6, 31.6. HRMS (m/z, ESI): calcd for $C_{21}H_{21}FeO_2^+$ ($M+H^+$) 361.0886, found 361.0886.

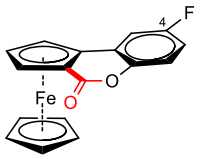


2i: 4-phenyl-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 63 mg; yield: 84%; dark red oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 2.15 Hz, 1H), 7.64 (dd, *J* = 8.09, 1.03 Hz, 2H), 7.54 (dd, *J* = 8.47, 2.23 Hz, 1H), 7.49 (t, *J* = 7.74 Hz, 2H), 7.41 – 7.38 (m, 1H), 7.33 (d, *J* = 8.46 Hz, 1H), 5.20 (t, *J* = 2.52 Hz, 2H), 4.68 (t, *J* = 2.56 Hz, 1H), 4.09 (s, 5H). ^{13}C NMR (151 MHz,

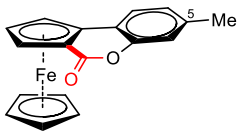
Chloroform-*d*) δ 167.5, 150.8, 140.2, 137.6, 129.0, 127.6, 127.2, 126.9, 121.9, 121.5, 117.7, 83.3, 73.2, 71.4, 68.5, 65.3, 64.5. HRMS (m/z, ESI): calcd for $C_{23}H_{17}FeO_2^+$ ($M+H^+$) 381.0573, found 381.0572.



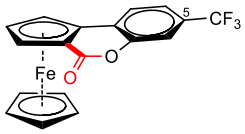
2j: 4-methoxy-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 48 mg; yield: 72%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.95 Hz, 1H), 7.05 (d, *J* = 2.98 Hz, 1H), 6.85 (dd, *J* = 8.95, 2.95 Hz, 1H), 5.16 (dd, *J* = 2.64, 1.14 Hz, 1H), 5.10 (dd, *J* = 2.62, 1.16 Hz, 1H), 4.63 (t, *J* = 2.61 Hz, 1H), 4.05 (s, 5H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 156.2, 145.5, 122.4, 118.1, 113.7, 107.4, 83.3, 73.0, 71.4, 68.5, 65.3, 64.7, 55.9. HRMS (m/z, ESI): calcd for $C_{18}H_{15}FeO_3^+$ ($M+H^+$) 335.0365, found 335.0364.



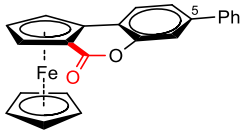
2k: 4-fluoro-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 44 mg; yield: 69%; dark red oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (dd, *J* = 8.38, 2.90 Hz, 1H), 7.23 (dd, *J* = 8.98, 4.61 Hz, 1H), 7.06 – 6.98 (m, 1H), 5.21 (dd, *J* = 2.66, 1.17 Hz, 1H), 5.12 (dd, *J* = 2.62, 1.16 Hz, 1H), 4.69 (t, *J* = 2.60 Hz, 1H), 4.09 (s, 5H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.1, 159.2 (d, J_{C-F} = 243.0 Hz), 147.3 (d, J_{C-F} = 1.7 Hz), 123.2 (d, J_{C-F} = 8.9 Hz), 118.7 (d, J_{C-F} = 8.8 Hz), 114.8 (d, J_{C-F} = 23.9 Hz), 109.2 (d, J_{C-F} = 24.6 Hz), 82.4, 73.4, 71.5, 68.8, 65.6, 64.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.0. HRMS (m/z, ESI): calcd for $C_{17}H_{12}FFeO_2^+$ ($M+H^+$) 323.0165, found 323.0164.



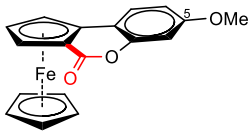
2l: 5-methyl-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 43 mg; yield: 68%; dark red oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.75 Hz, 1H), 7.06 (s, 1H), 7.00 (d, *J* = 6.89 Hz, 1H), 5.15 (dd, *J* = 2.61, 1.15 Hz, 1H), 5.11 (dd, *J* = 2.57, 1.16 Hz, 1H), 4.61 (t, *J* = 2.59 Hz, 1H), 4.04 (s, 5H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.8, 151.3, 138.5, 125.4, 122.9, 118.4, 117.7, 83.9, 72.8, 71.3, 68.1, 65.0, 64.2, 21.5. HRMS (m/z, ESI): calcd for $C_{18}H_{15}FeO_2^+$ ($M+H^+$) 319.0416, found 319.0414.



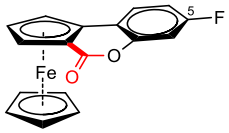
2m: 5-trifluoromethyl-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 62 mg; yield: 84%; dark red oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.98 Hz, 1H), 7.48 (s, 1H), 7.43 (d, *J* = 7.07 Hz, 1H), 5.23 (dd, *J* = 2.67, 1.15 Hz, 1H), 5.19 (dd, *J* = 2.65, 1.16 Hz, 1H), 4.73 (t, *J* = 2.63 Hz, 1H), 4.09 (s, 5H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.5, 150.9, 129.8 (q, J_{C-F} = 33.2 Hz), 125.8, 123.7 (q, J_{C-F} = 272.7 Hz), 123.6, 121.1 (q, J_{C-F} = 3.8 Hz), 114.6 (q, J_{C-F} = 4.0 Hz), 81.4, 73.8, 71.6, 69.2, 66.1, 64.7. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.3. HRMS (m/z, ESI): calcd for $C_{18}H_{12}F_3FeO_2^+$ ($M+H^+$) 373.0133, found 373.0132.



2n: 5-phenyl-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 61 mg; yield: 80%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.57 (m, 3H), 7.51 – 7.41 (m, 4H), 7.39 (t, *J* = 7.29 Hz, 1H), 5.20 (dd, *J* = 2.63, 1.16 Hz, 1H), 5.16 (dd, *J* = 2.55, 1.19 Hz, 1H), 4.66 (t, *J* = 2.60 Hz, 1H), 4.09 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 151.7, 141.1, 139.8, 129.1, 127.9, 127.0, 123.5, 123.1, 120.5, 115.6, 83.2, 73.2, 71.4, 68.5, 65.3, 64.4. HRMS (m/z, ESI): calcd for $C_{23}H_{17}FeO_2^+$ ($M+H^+$) 381.0573, found 381.0561.

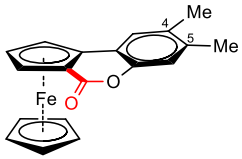


2o: 5-methoxy-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 47 mg; yield: 70%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.45 Hz, 1H), 6.83 – 6.75 (m, 2H), 5.12 (dd, *J* = 2.66, 1.11 Hz, 1H), 5.07 (dd, *J* = 2.54, 1.15 Hz, 1H), 4.59 (t, *J* = 2.62 Hz, 1H), 4.04 (s, 5H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 159.8, 152.4, 123.8, 113.7, 111.5, 102.4, 84.5, 72.6, 71.2, 67.8, 64.6, 63.4, 55.7. HRMS (m/z, ESI): calcd for $C_{18}H_{15}FeO_3^+$ ($M+H^+$) 335.0365, found 335.0364.

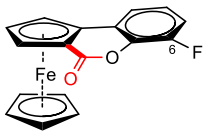


2p: 5-fluoro-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 42 mg; yield: 65%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 8.57, 6.02 Hz, 1H), 7.03 – 6.86 (m, 2H), 5.14 (ddd, *J* = 19.72, 2.62, 1.19 Hz,

2H), 4.65 (t, J = 2.63 Hz, 1H), 4.06 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 162.0 (d, $J_{C\text{-}F}$ = 247.5 Hz), 152.0 (d, $J_{C\text{-}F}$ = 12.1 Hz), 124.1 (d, $J_{C\text{-}F}$ = 9.5 Hz), 117.7 (d, $J_{C\text{-}F}$ = 3.2 Hz), 111.9 (d, $J_{C\text{-}F}$ = 22.3 Hz), 105.2 (d, $J_{C\text{-}F}$ = 25.6 Hz), 83.1, 73.1, 71.4, 68.3, 65.2, 63.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.8. HRMS (m/z, ESI): calcd for $C_{17}H_{12}FFeO_2^+$ ($M+H^+$) 323.0165, found 323.0165.



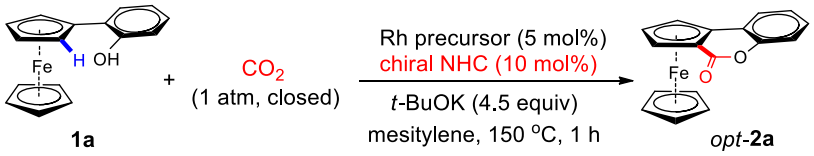
2q: 4,5-dimethyl-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 47 mg; yield: 70%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (s, 1H), 7.03 (s, 1H), 5.14 (dd, J = 2.61, 1.16 Hz, 1H), 5.09 (dd, J = 2.56, 1.13 Hz, 1H), 4.60 (t, J = 2.58 Hz, 1H), 4.05 (s, 5H), 2.30 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 149.6, 137.1, 132.8, 123.7, 118.4, 118.1, 84.1, 72.7, 71.3, 68.1, 64.8, 64.4, 20.1, 19.5. HRMS (m/z, ESI): calcd for $C_{19}H_{17}FeO_2^+$ ($M+H^+$) 333.0573, found 333.0573.



2r: 6-fluoro-6*H*-benzo[*b*]ferroceno[*d*]pyran-6-one.
Quality: 29 mg; yield: 44%; dark red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, J = 6.75 Hz, 1H), 7.19 – 7.00 (m, 2H), 5.18 (d, J = 21.53 Hz, 2H), 4.69 (t, J = 2.70 Hz, 1H), 4.09 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 150.3 (d, $J_{C\text{-}F}$ = 250.4 Hz), 139.4 (d, $J_{C\text{-}F}$ = 11.1 Hz), 124.4 (d, $J_{C\text{-}F}$ = 7.3 Hz), 123.9 (d, $J_{C\text{-}F}$ = 41.2 Hz), 118.2 (d, $J_{C\text{-}F}$ = 3.8 Hz), 114.9 (d, $J_{C\text{-}F}$ = 18.0 Hz), 82.6, 73.4, 71.5, 68.9, 65.9, 64.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -131.6. HRMS (m/z, ESI): calcd for $C_{17}H_{12}FFeO_2^+$ ($M+H^+$) 323.0165, found 323.0166.

2.4. Asymmetric C-H carboxylation with CO_2.

2.4.1 General procedure and details of HPLC analysis for *opt*-2a.

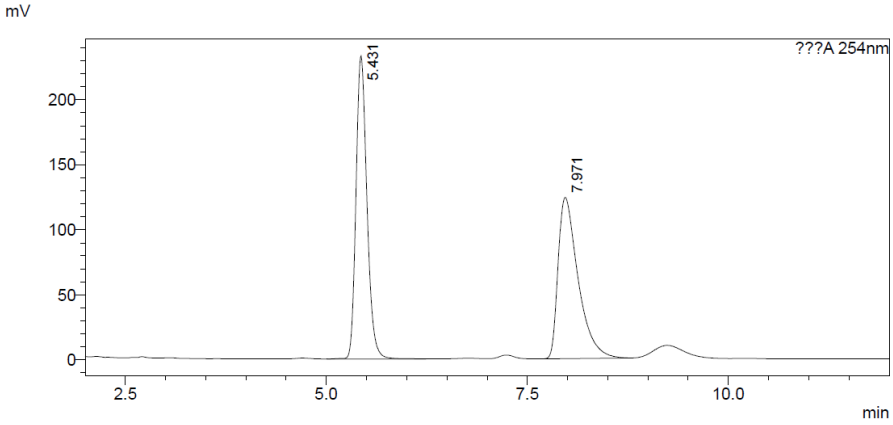


General procedure: In a glove box, to an oven-dried 25 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added Rh precursor (0.005 mol), chiral NHC ligand (0.01 mol) and *t*-BuOK (4.5 equiv) (Note: base should be dry). After taken out of the glove box, **1a** (27.8 mg, 0.1 mmol) dissolved in anhydrous

mesitylene (1 mL) was added, then the tube was evacuated under vacuum and charged with CO_2 (1 atm, × 3). Afterwards, the tube was capped and then placed into a preheated hotplate (150 ^oC). The reaction was stirred vigorously (Note: good stirring is important!) for 1 h and cooled to room temperature. Remove mesitylene by vacuum pump evaporation under reduced pressure and then the reaction was diluted with EtOAc (20 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional 10 mL of EtOAc. The combined organic filtrate was concentrated in vacuo. For the residue, yield was determined through crude ^1H NMR spectrum by using CH_2Br_2 as internal standard; the ee value was determined through HPLC analysis after purification.

Analytical method for HPLC: Chiralcel AD-H column, (hexane/isopropanol = 90/10, flow = 1.0 mL/min, 254 nm) with tr_1 = 5.43 min, tr_2 = 7.97 min.
Chromatogram for the optimal reaction condition was listed below.

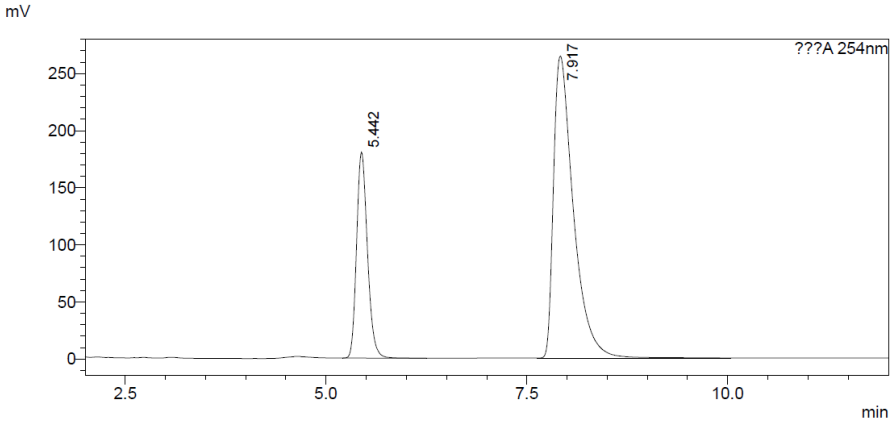
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.431	2222381	233070	50.939			
2	7.971	2140478	123960	49.061			
Total		4362859	357030				



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.442	1707020	180552	27.328			
2	7.917	4539346	264487	72.672			
Total		6246367	445039				

2.4.2 More condition screenings.

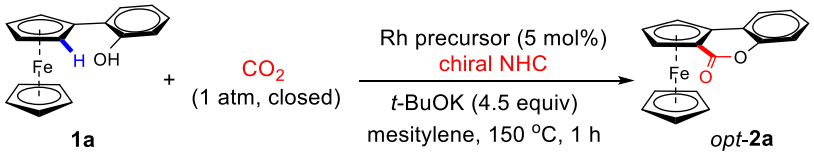
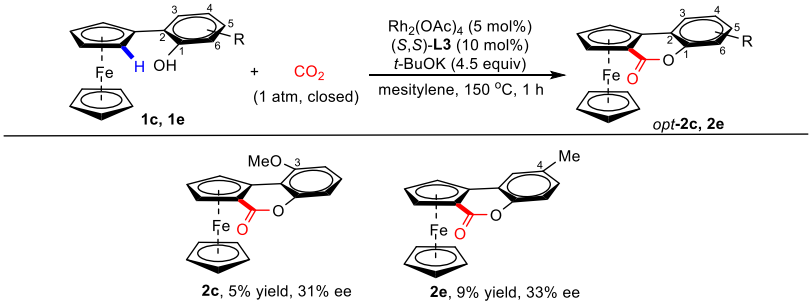


Table S2: Screening of reaction conditions[a]

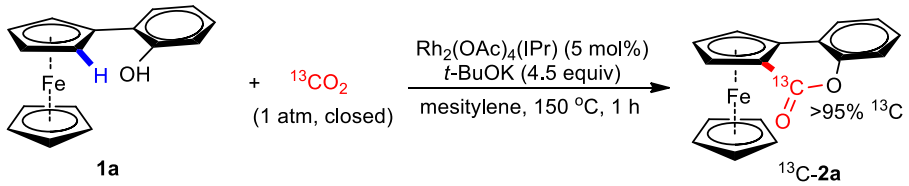
Entry	Rh Cat.	Ligand	Temp (°C)	yield (%)	Ee (%)
1	$Rh_2(TFA)_4$	(*S*,*S*)-**L3** (10 mol%)	140	10	38
2	$Rh_2(TFA)_4$	(*S*,*S*)-**L3** (10 mol%)	130	5	44
3	$Rh_2(TFA)_4$	(*S*,*S*)-**L3** (10 mol%)	120	-	-
4[b]	$Rh_2(TFA)_4$	(*S*,*S*)-**L3** (10 mol%)	150	-	-
5[c]	$Rh_2(TFA)_4$	(*S*,*S*)-**L3** (10 mol%)	150	-	-
6[d]	$Rh_2(TFA)_4$	(*S*,*S*)-**L3** (10 mol%)	150	58	48
7[e]	$Rh_2(TFA)_4$	(*S*,*S*)-**L3** (10 mol%)	150	49	46
8	$Rh_2(TFA)_4$	(*S*,*S*)-**L3** (15 mol%)	150	29	39
9	$Rh_2(TFA)_4$	(*S*,*S*)-**L3** (20 mol%)	150	31	40

[a]Reaction conditions: **1a** (0.1 mmol), CO_2 (1 atm, closed), Rh precursor (5 mol%), chiral ligand, *t*-BuOK (4.5 equiv), mesitylene (1 mL), 150 °C, 1 h. Yield was determined by ^1H NMR with CH_2Br_2 as internal standard; enantiomeric ratios of **2a** were determined by HPLC analysis on a chiral stationary phase. [b]Pre-complexing at 100 °C for 0.5 h without CO_2 inflation. [c]Pre-complexing at 120 °C for 0.5 h without CO_2 inflation. [d]Pre-complexing at 100 °C for 0.5 h with CO_2 inflation. [e]Pre-complexing at 120 °C for 0.5 h with CO_2 inflation.

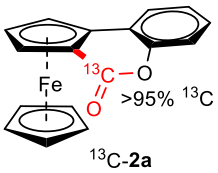
2.4.3 Substrates expansion with 1c and 1e.



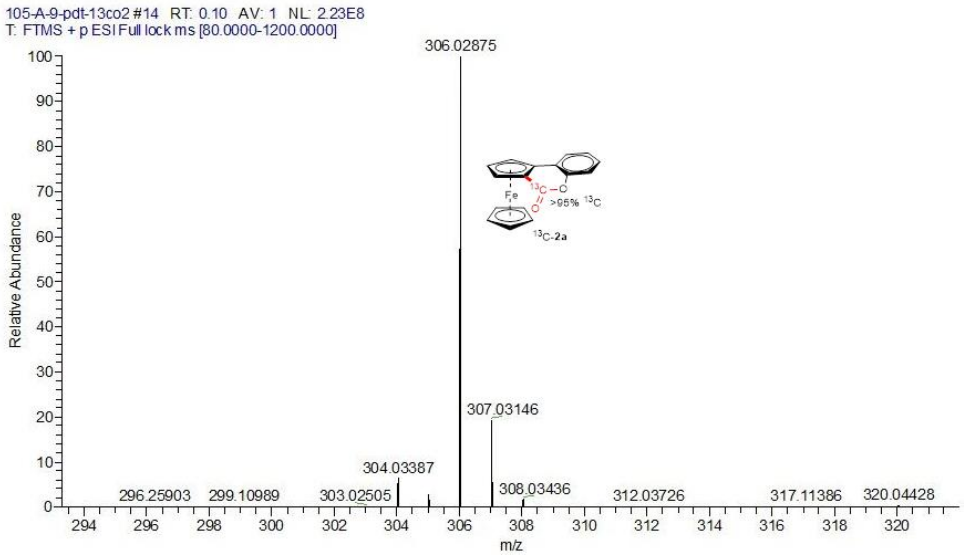
2.5 ^{13}C-Labeling experiments.



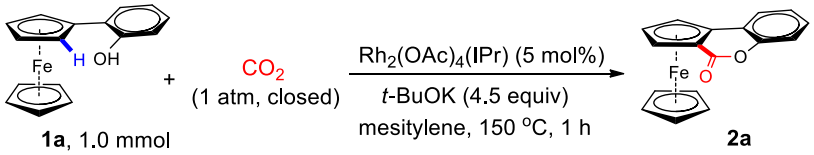
General procedure: In a glove box, to an oven-dried 25 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added $[Rh_2(OAc)_4](IPr)$ (8.3 mg, 0.01 mol) and *t*-BuOK (101 mg, 0.9 mmol) (Note: should be dry) was added successively. After taken out of the glove box, **1a** (56 mg, 0.2 mmol) dissolved in mesitylene (2 mL) was added, then the tube was evacuated under vacuum and charged with $^{13}CO_2$. Afterwards, the tube was capped and then placed into a preheated hotplate (150 °C). The reaction was stirred vigorously (Note: good stirring is important!) for 1 h and cooled to room temperature. Remove mesitylene by vacuum pump evaporation under reduced pressure and then the reaction was diluted with EtOAc (20 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional 10 mL of EtOAc. The filtrate was concentrated in vacuo, and purified by preparative thin layer chromatography using petroleum ether/EtOAc (5/1) as the eluent to afford the ^{13}C-**2a** (43 mg, 70% yield; >95% ^{13}C abundance, calculated from GC-MS).



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.61 Hz, 1H), 7.33 (t, *J* = 7.16 Hz, 1H), 7.27 (d, *J* = 7.19 Hz, 1H), 7.21 (t, *J* = 7.37 Hz, 1H), 5.19 (dd, *J* = 2.68, 1.22 Hz, 1H), 5.16 (dd, *J* = 2.58, 1.33 Hz, 1H), 4.66 (t, *J* = 2.43 Hz, 1H), 4.07 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6 (^{13}C carbanyl group), 151.3 (d, *J* = 2.3 Hz), 128.1, 124.5, 123.1, 121.6 (d, *J* = 2.4 Hz), 117.4 (d, *J* = 3.3 Hz), 83.5 (d, *J* = 3.4 Hz), 73.1 (d, *J* = 5.0 Hz), 71.4, 68.4 (d, *J* = 4.2 Hz), 65.3 (d, *J* = 3.4 Hz), 64.5 (d, *J* = 81.5 Hz). HRMS (m/z , ESI): calcd for $^{13}CC_{16}H_{13}FeO_2^+$ $(M+H)^+$ 306.0293, found 306.0288.



2.6 Scaled-up synthesis.



General procedure: In a glove box, to an oven-dried 100 mL Schlenk sealed tube (with a Teflon cap) equipped with a magnetic stir bar was added $[Rh_2(OAc)_4](IPr)$ (42 mg, 0.05 mol) and *t*-BuOK (505 mg, 4.5 mmol) (Note: base should be dry) was added successively. After taken out of the glove box, **1a** (278 mg, 1 mmol) dissolved in anhydrous mesitylene (10 mL) was added, then the tube was evacuated under vacuum and charged with CO_2 (1 atm, × 3). Afterwards, the tube was capped and then placed into a preheated hotplate (150 °C). The reaction was stirred vigorously (Note: good stirring is important!) for 1 h and cooled to room temperature. Remove mesitylene by vacuum pump evaporation under reduced pressure and then the reaction was diluted with EtOAc (40 mL) and filtered through a short pad of Celite. The tube and Celite pad were washed with an additional 15 mL of EtOAc. Finally, the resulting residue was purified by flash silica gel chromatography using petroleum ether/EtOAc (5/1) as the eluent to afford **2a** (225 mg, 74% yield).

3. X-Ray Crystallographic Spectrum of 2c and 2i.

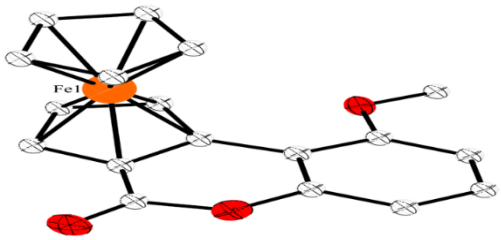


Figure S1. The crystal structure of **2c** (CCDC 2211993).

Table S3. Crystal data and structure refinement for **2c**

Identification code	LV-0922_auto
Empirical formula	$C_{18}H_{14}FeO_3$
Formula weight	43.03
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	10.4854(4)
b/Å	11.7036(4)
c/Å	12.3518(4)
α/°	72.325(3)
β/°	79.087(3)
γ/°	75.017(3)
Volume/Å^3	1384.97(9)
Z	2
ρ_{calc}g/cm^3	2.682
μ/mm^{-1}	36.987
F(000)	1096.0
Crystal size/mm^3	0.1 × 0.2 × 0.2
Radiation	Ga-Kα (λ = 1.3405)
2Θ range for data collection/°	6.578 to 120.544
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 14, -14 ≤ l ≤ 15
Reflections collected	16150
Independent reflections	6127 [R_{int} = 0.0409, R_{sigma} = 0.0384]
Data/restraints/parameters	6127/0/399
Goodness-of-fit on F^2	0.699
Final R indexes [I>=2σ (I)]	R_1 = 0.0372, wR_2 = 0.0983
Final R indexes [all data]	R_1 = 0.0403, wR_2 = 0.1013
Largest diff. peak/hole / e Å^{-3}	0.85/-0.58

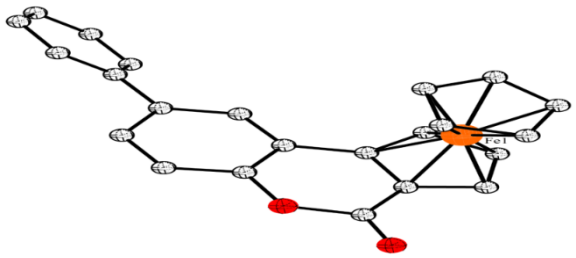


Figure S2. The crystal structure of **2i** (CCDC 2211992).

Table S4. Crystal data and structure refinement for **2i**

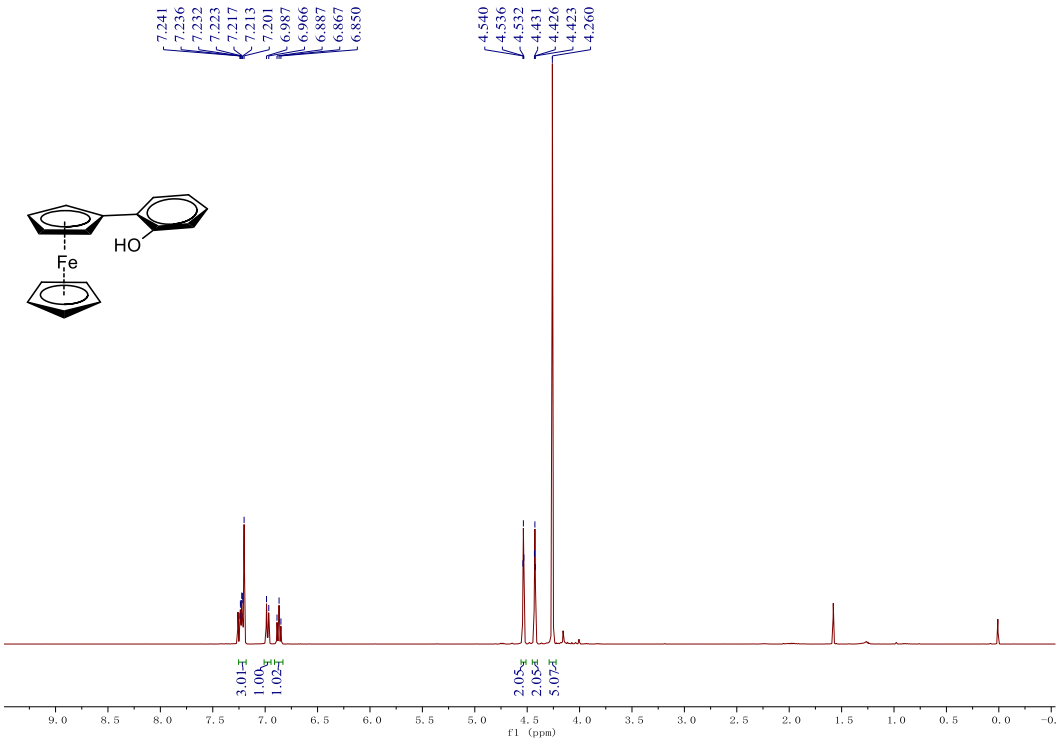
Identification code	LH-0918_auto
Empirical formula	$C_{23}H_{16}FeO_2$
Formula weight	200.12
Temperature/K	200.15
Crystal system	triclinic
Space group	P-1
a/Å	6.7731(6)
b/Å	10.9956(11)
c/Å	12.2301(6)
α/°	72.319(7)
β/°	75.206(6)
γ/°	77.254(8)
Volume/Å^3	828.85(13)
Z	2
ρ_{calc}g/cm^3	1.604
μ/mm^{-1}	5.146
F(000)	416.0
Crystal size/mm^3	0.1 × 0.2 × 0.3
Radiation	Ga-Kα (λ = 1.3405)
2Θ range for data collection/°	6.734 to 111.04
Index ranges	$-8 \le h \le 8$, $-13 \le k \le 12$, $-14 \le l \le 14$
Reflections collected	8809
Independent reflections	3091 [R_{int} = 0.0560, R_{sigma} = 0.0550]
Data/restraints/parameters	3091/0/235
Goodness-of-fit on F^2	0.899
Final R indexes [I>=2σ (I)]	R_1 = 0.0569, wR_2 = 0.1523
Final R indexes [all data]	R_1 = 0.0716, wR_2 = 0.1803
Largest diff. peak/hole / e Å^{-3}	1.20/-0.69

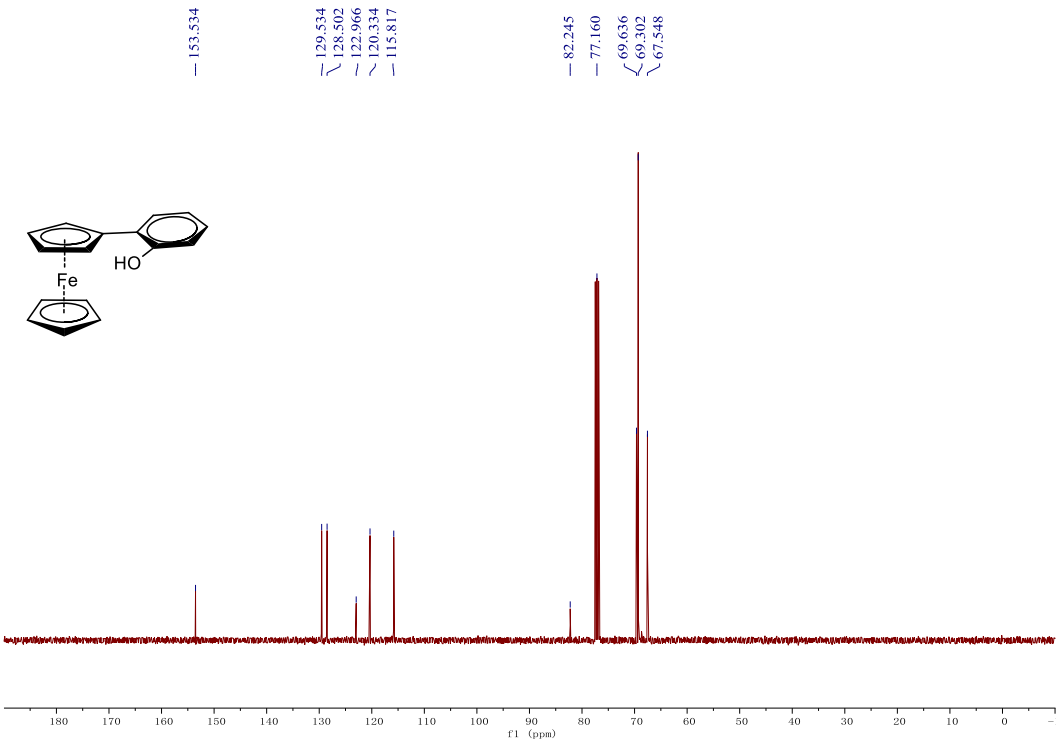
4. References

[S1] M. Roemer and C. A. Nijhuis, *Dalton Trans.*, 2014, **43**, 11815–11818.
[S2] Z. Cai, S. Li, Y. Gao and G. Li, *Adv. Synth. Catal.*, 2018, **360**, 4005–4011.
[S3] X. Zhang, X. Huang, W. Gao, Y. Zhou, M. Liu and H. Wu, *Adv. Synth. Catal.*, 2020, **362**, 5639–5644.
[S4] J. Na, B. Y. Lee, N.-N. Bui, S. Mho and H.-Y. Jang, *Journal of Organometallic Chemistry*, 2007, **692**, 5523–5527

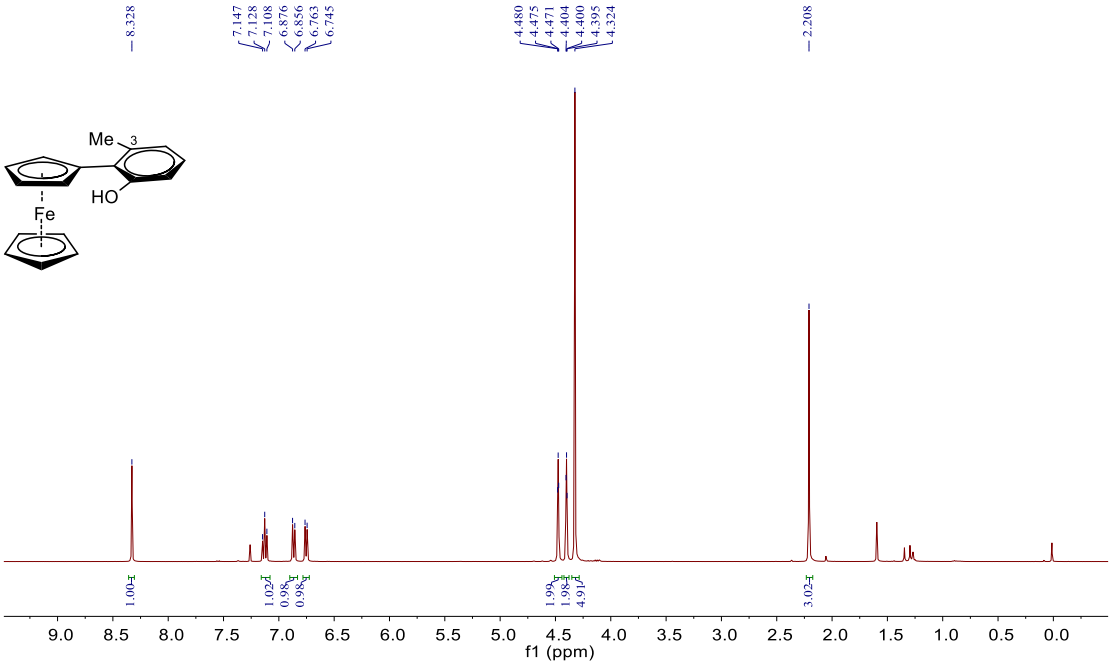
5. NMR Spectra of Compounds

1a





1b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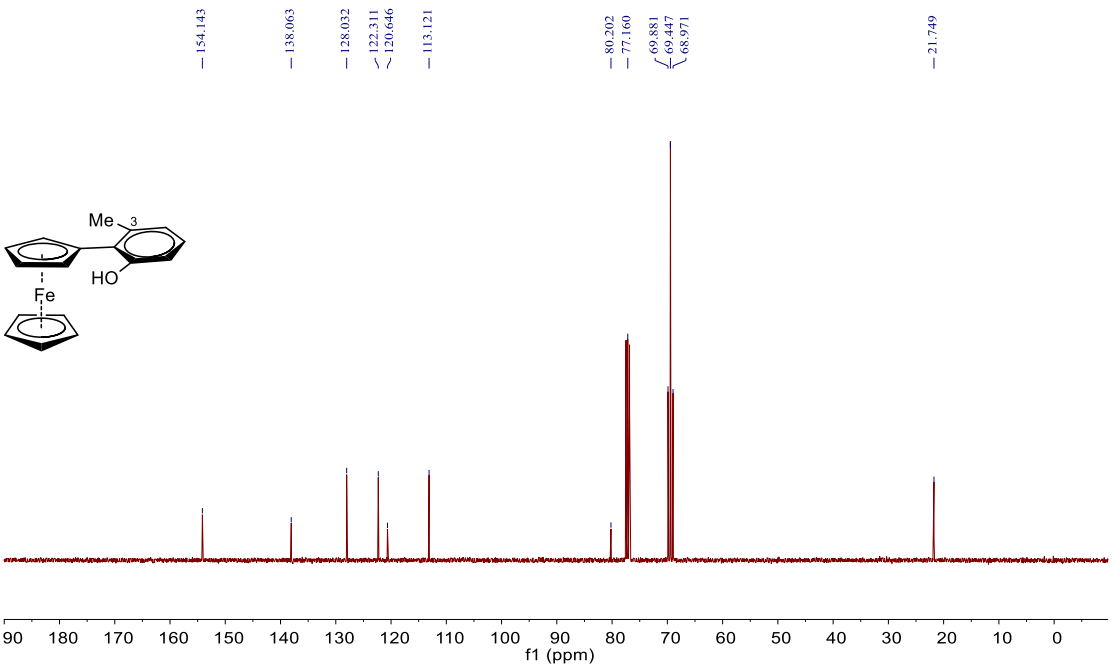
7.128
7.108
6.876
6.856
6.763
6.745
4.480
4.475
4.471
4.404
4.400
4.395
4.324
2.208
Me
3
HO
Fe
1.00
1.02
0.98
0.98
1.98
1.98
4.91
3.02
f1 (ppm)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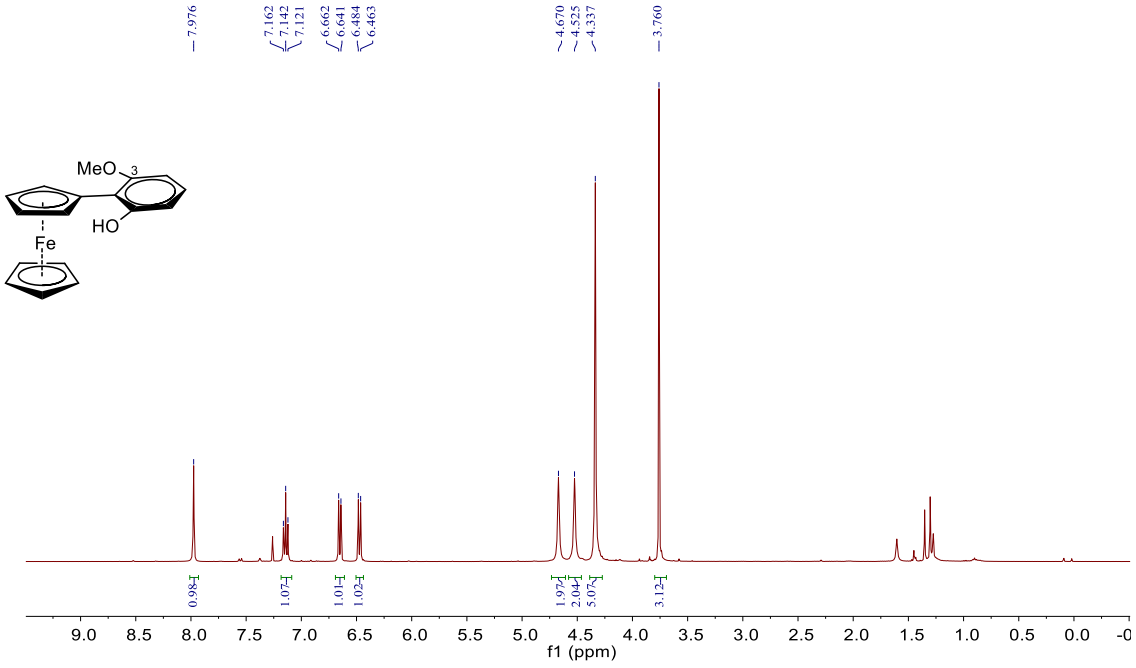
138.063
128.032
122.311
120.646
113.121
80.202
77.160
69.881
69.447
68.971
21.749
Me
3
HO
Fe
f1 (ppm)

1c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6.662
6.641
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4.337
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3
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Fe
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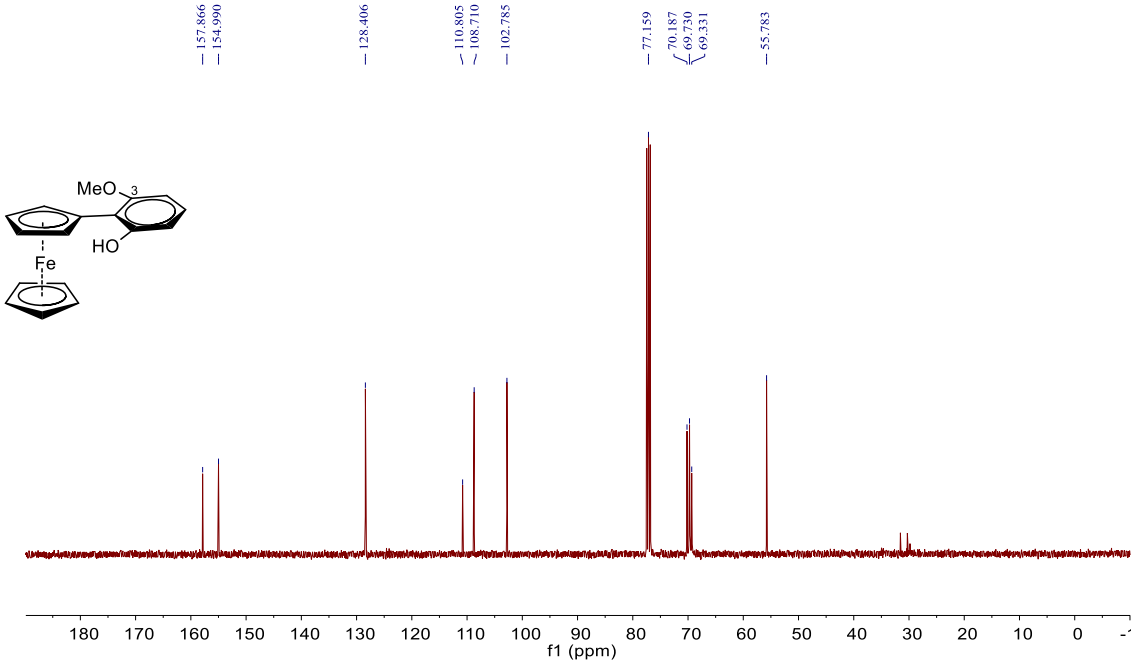
1.01
1.02
1.97
2.04
5.07
3.12
f1 (ppm)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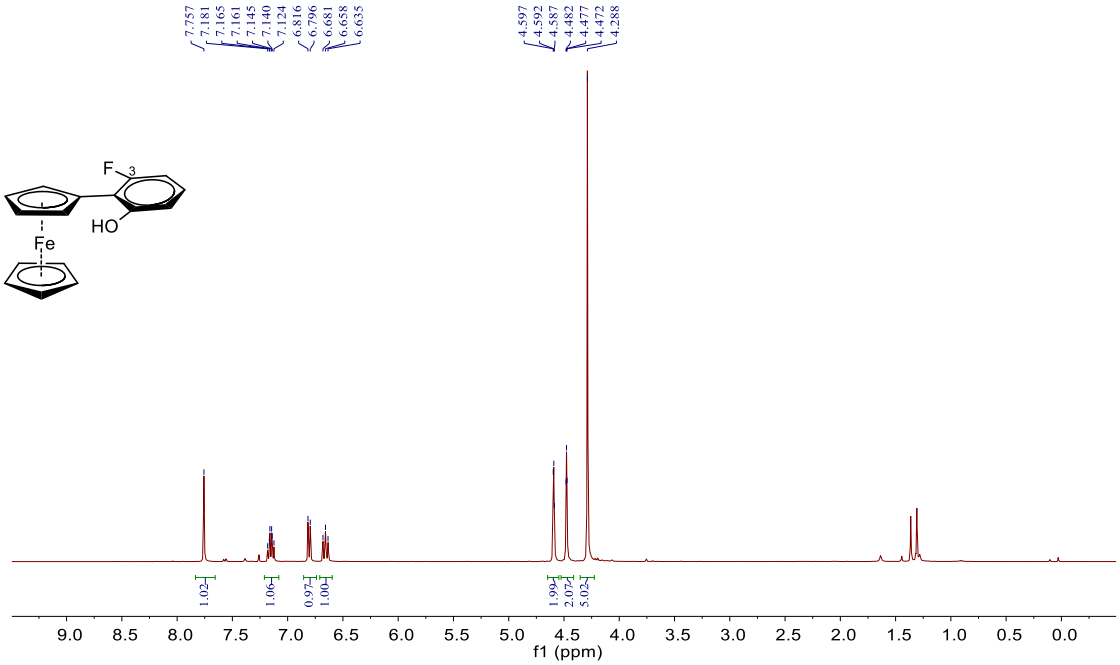
3
HO
Fe
f1 (ppm)

1d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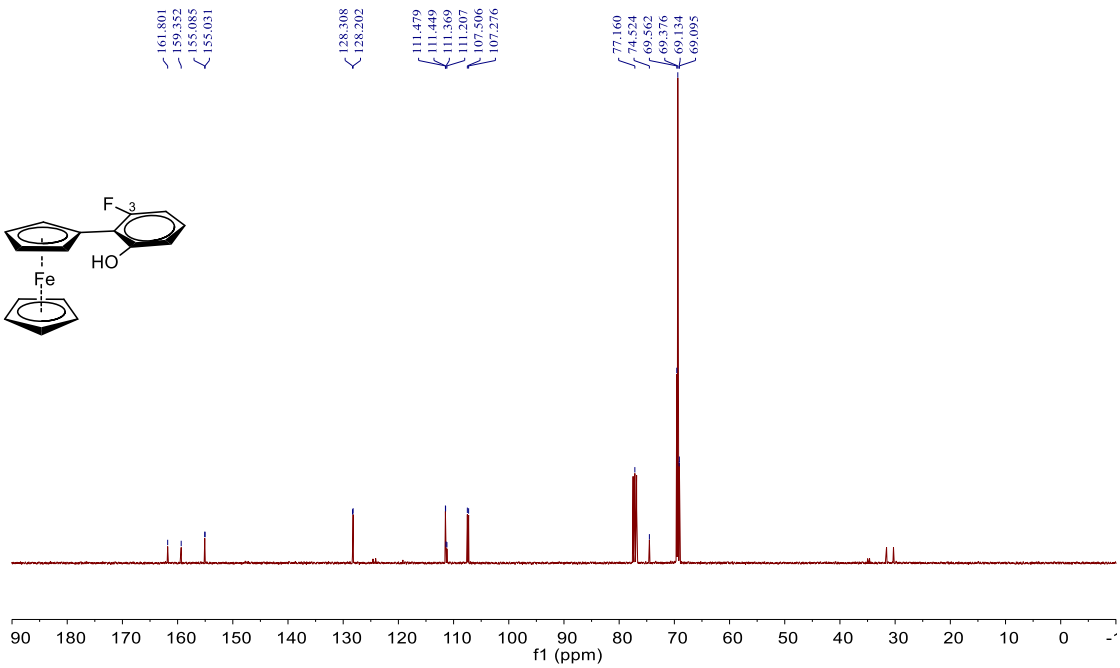
7.165
7.161
7.145
7.140
7.124
6.816
6.796
6.681
6.658
6.635
4.597
4.592
4.587
4.482
4.477
4.472
4.288
F
3
HO
Fe
1.02
1.06
0.97
1.00
1.99
2.07
5.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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155.031
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111.479
111.449
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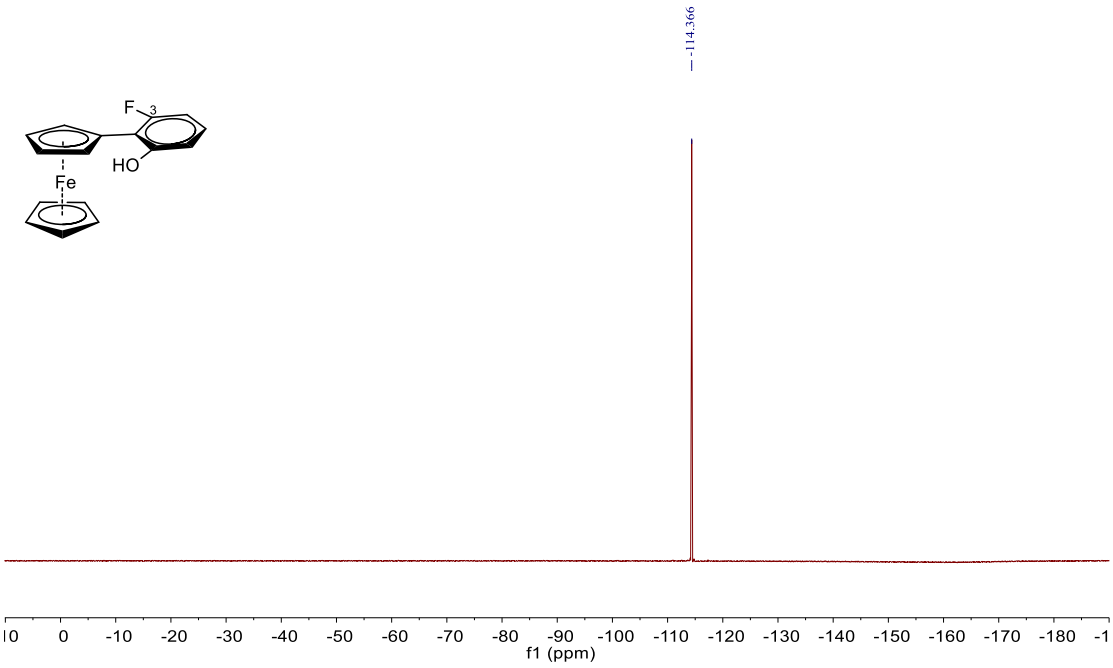
111.207
107.506
107.276
77.160
74.524
69.562
69.376
69.134
69.095
F
3
HO
Fe
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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F
3
HO
Fe
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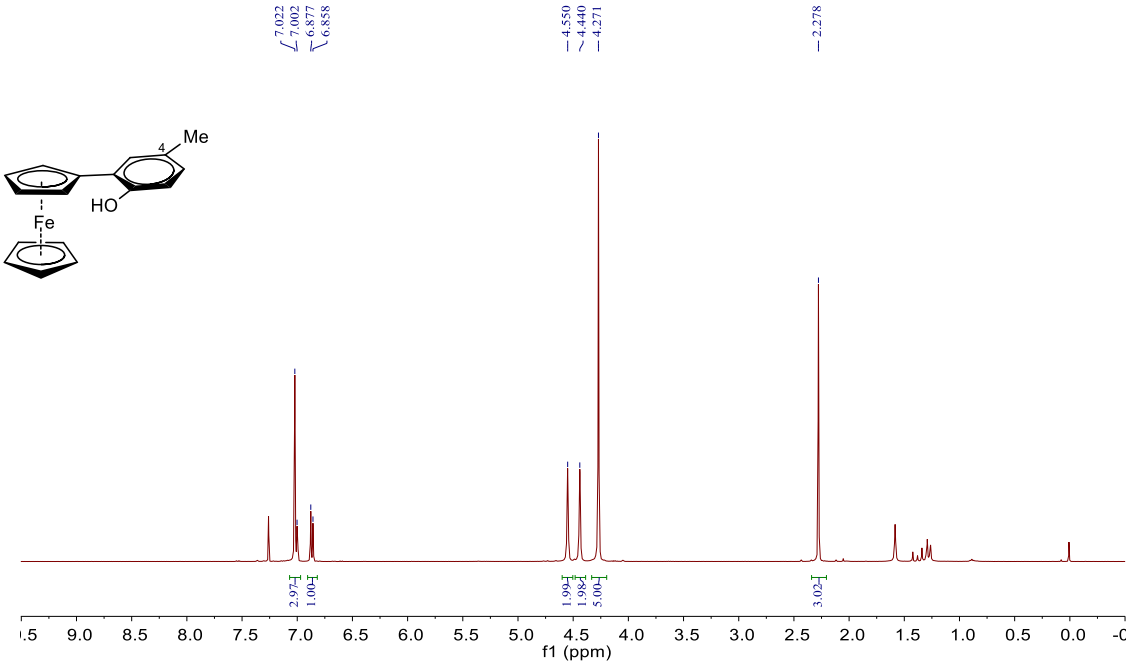
f1 (ppm)

1e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4
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Fe
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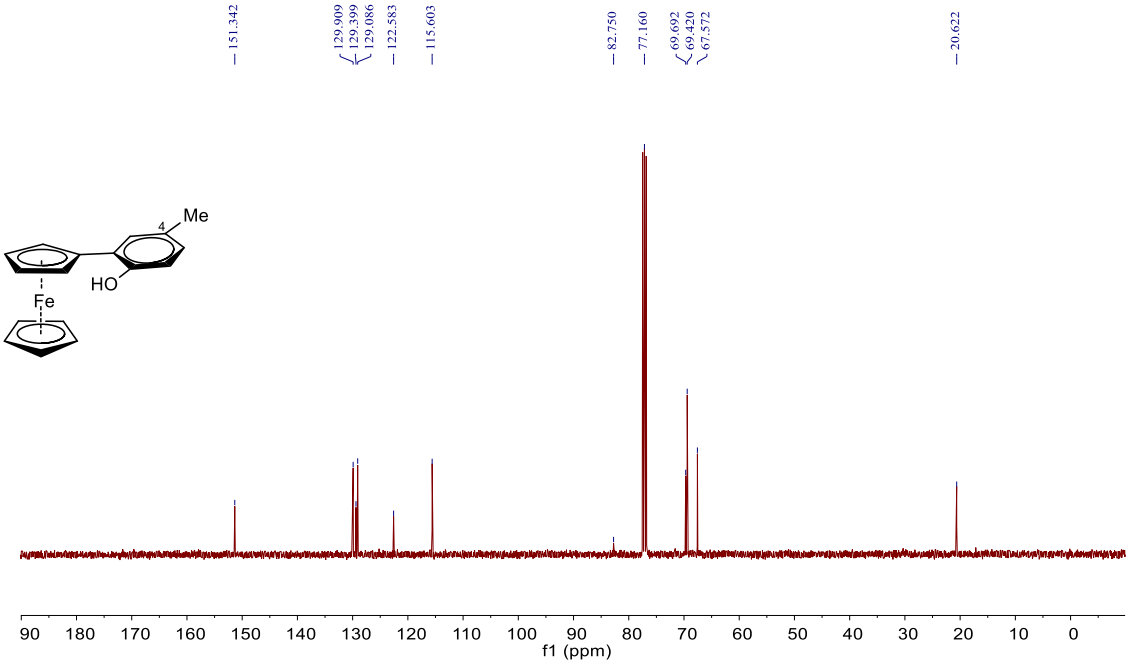
1.98
5.00
3.02
f1 (ppm)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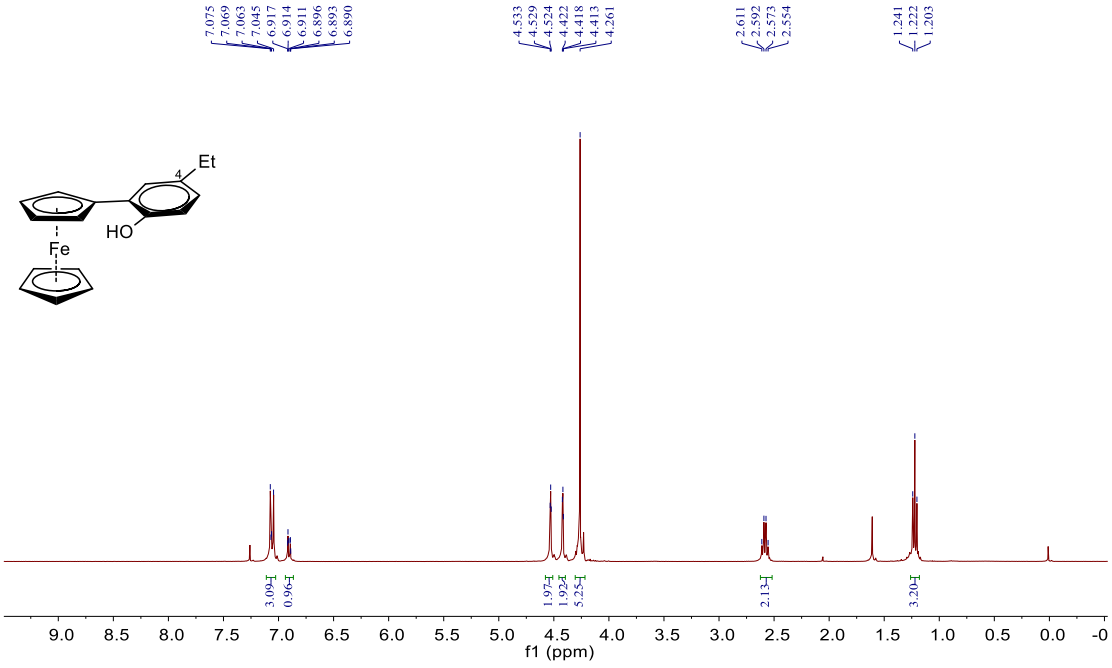
Me
4
HO
Fe
f1 (ppm)

1f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4.529
4.524
4.422
4.418
4.413
4.261
2.611
2.592
2.573
2.554
1.241
1.222
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Et
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HO
Fe
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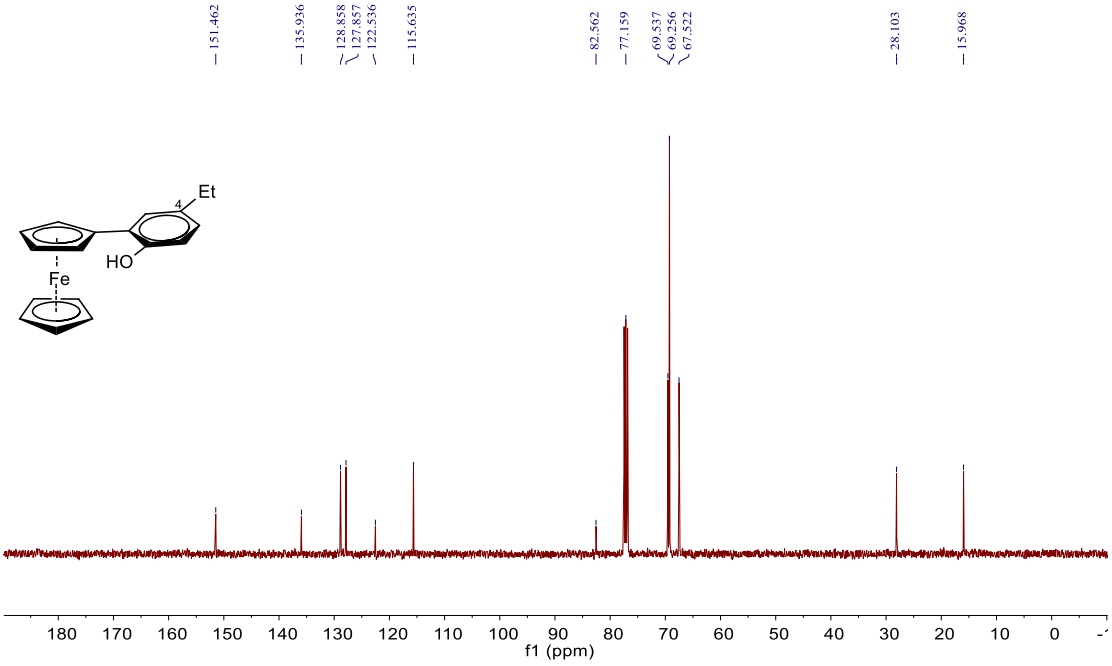
f1 (ppm)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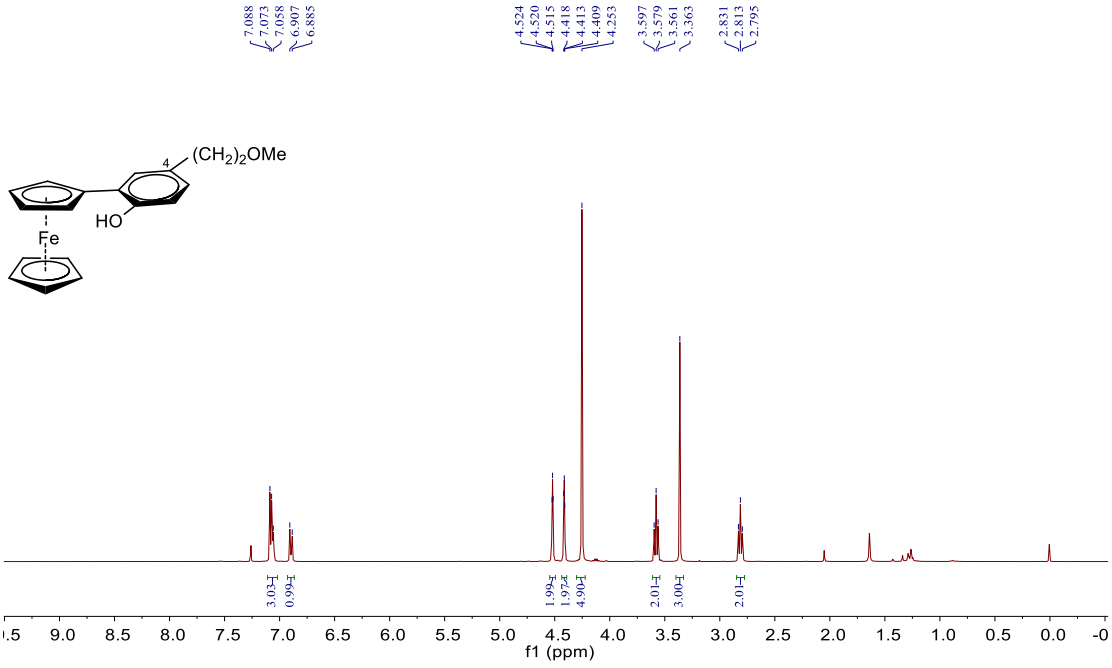
Et
4
HO
Fe
f1 (ppm)

1g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4.515
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3.579
3.561
3.363
2.831
2.813
2.795
4
(CH2)2OMe
HO
Fe
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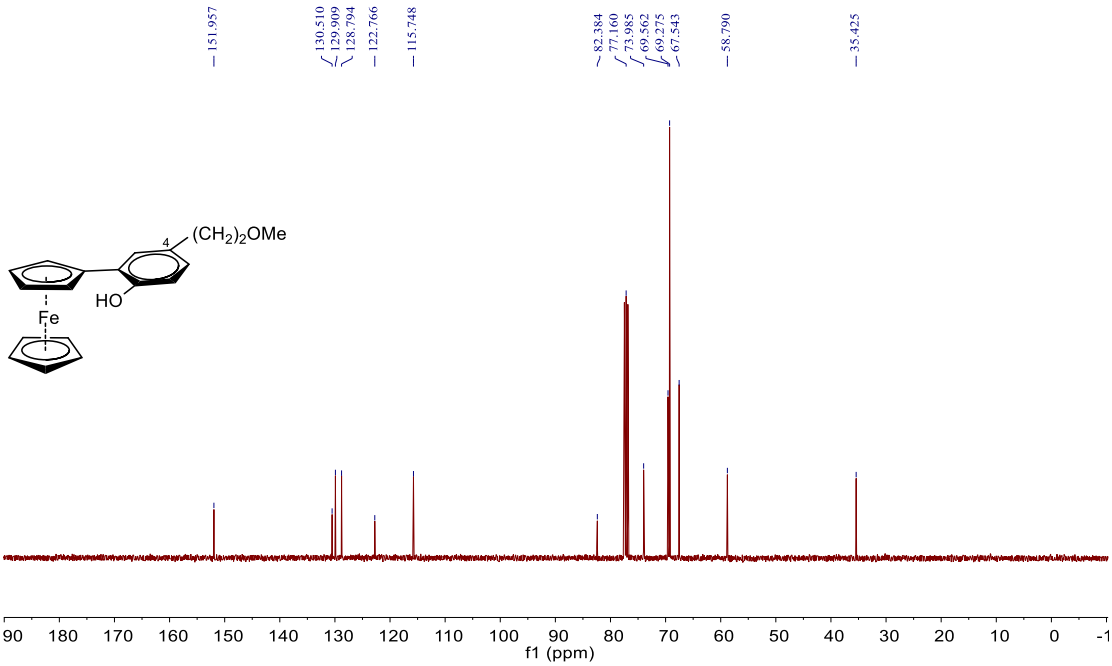
2.01
3.00
2.01
f1 (ppm)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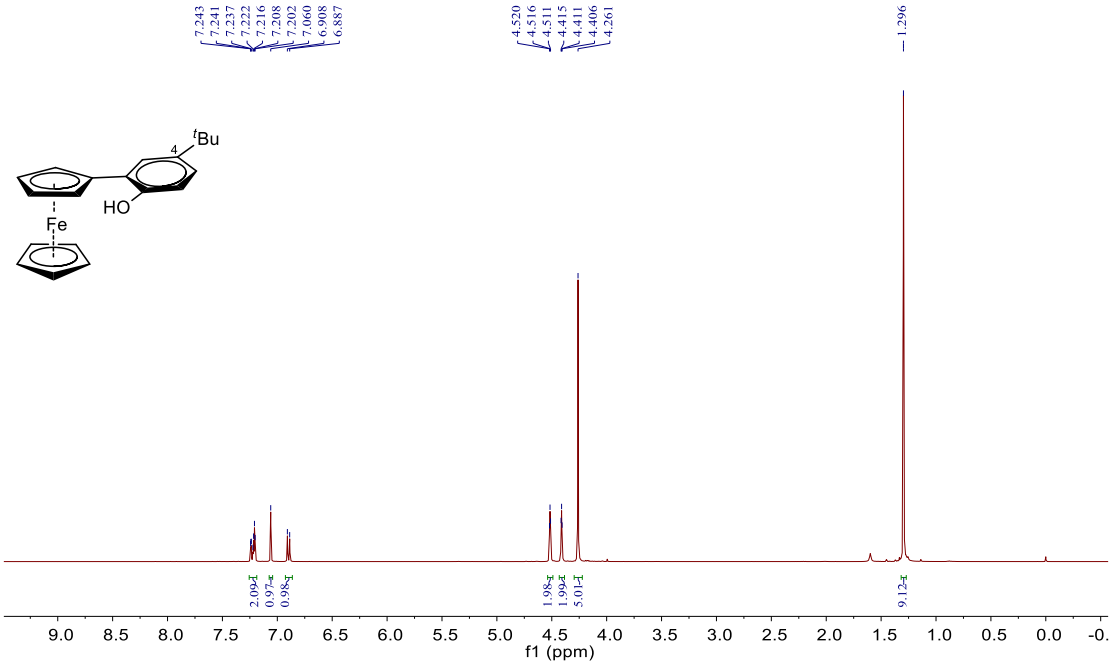
(CH2)2OMe
HO
Fe
f1 (ppm)

1h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7.202
7.060
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6.887
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4.516
4.511
4.415
4.411
4.406
4.261
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4
HO
Fe
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0.98
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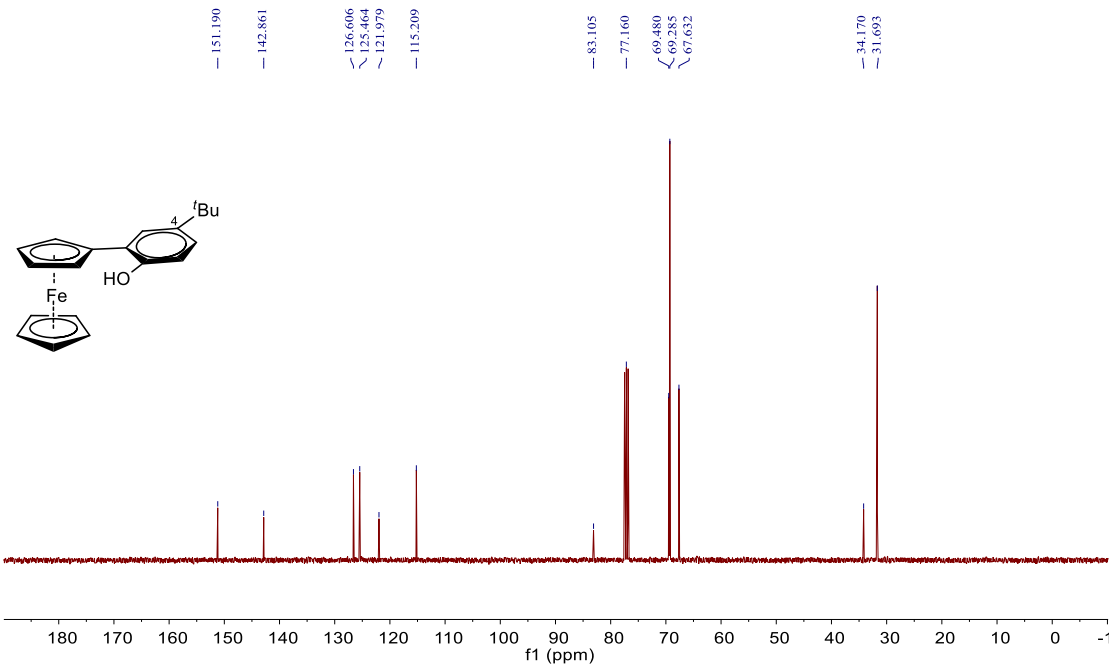
1.99
5.01
9.12
f1 (ppm)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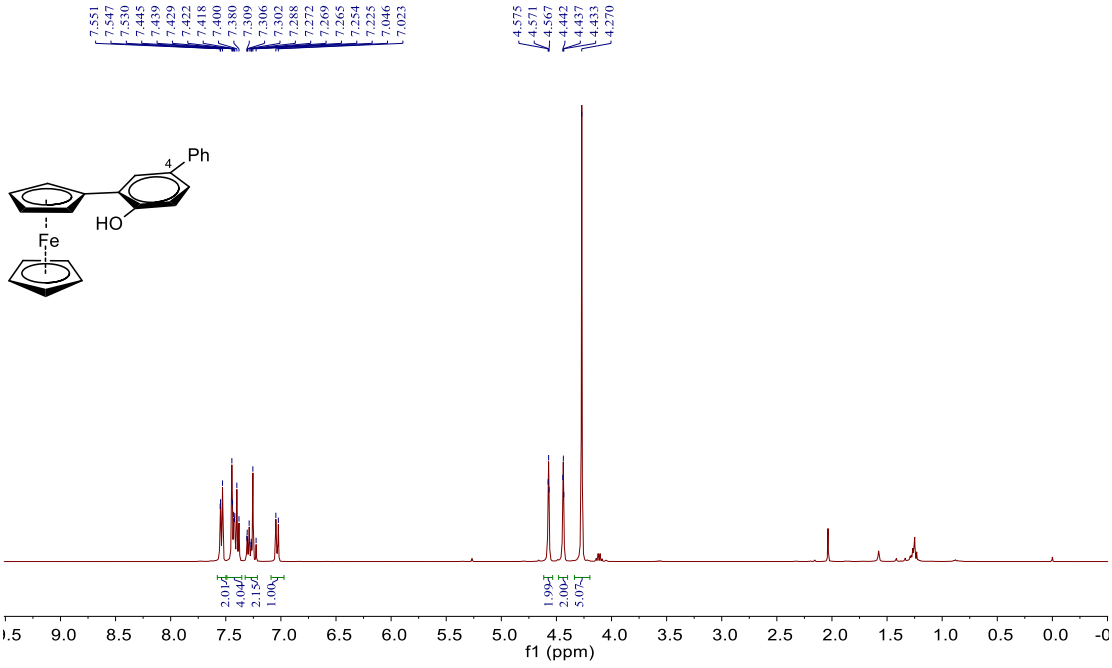
tBu
4
HO
Fe
f1 (ppm)

1i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7.288
7.272
7.269
7.265
7.254
7.225
7.046
7.023
4.575
4.571
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4.442
4.437
4.433
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HO
Fe
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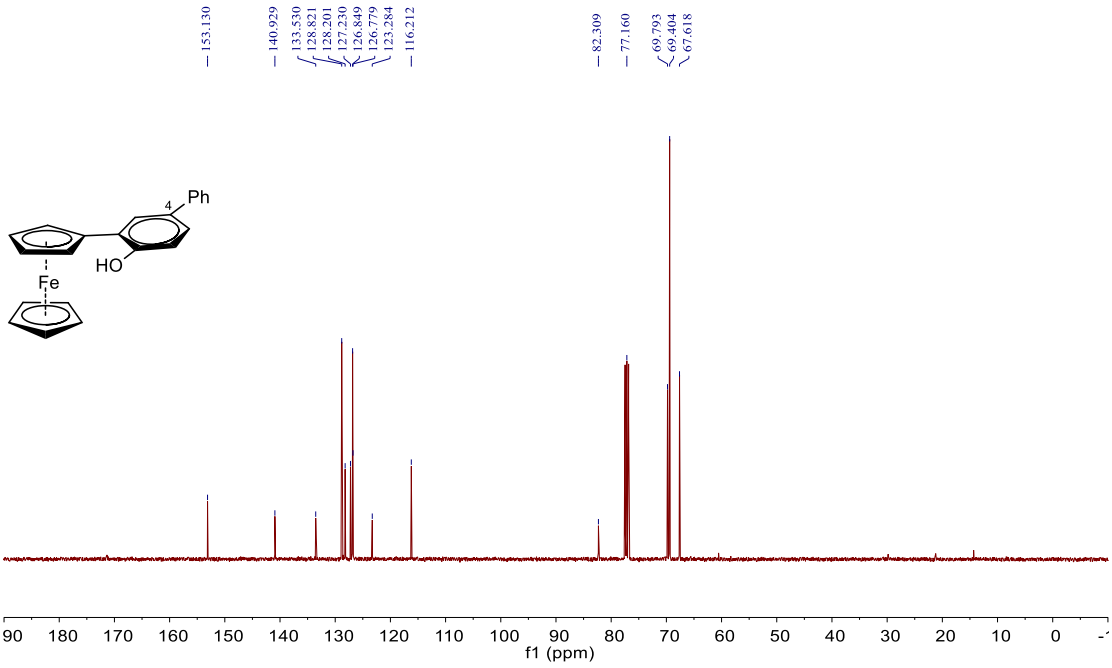
5.07
f1 (ppm)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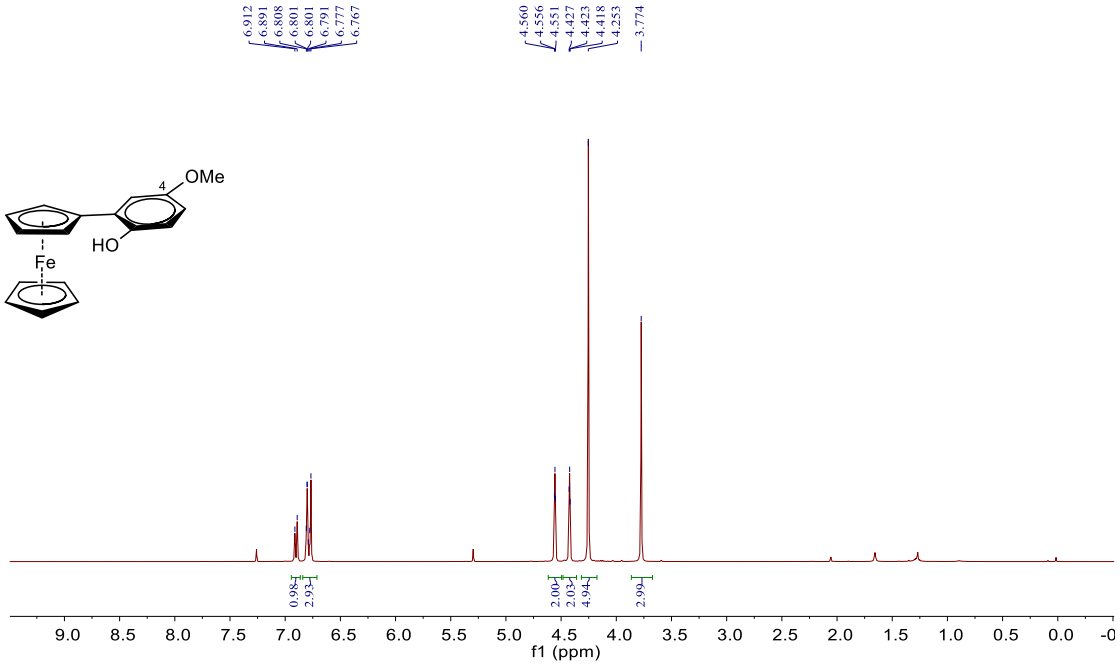
Ph
4
HO
Fe
f1 (ppm)

1j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4.418
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4
HO
Fe
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2.03
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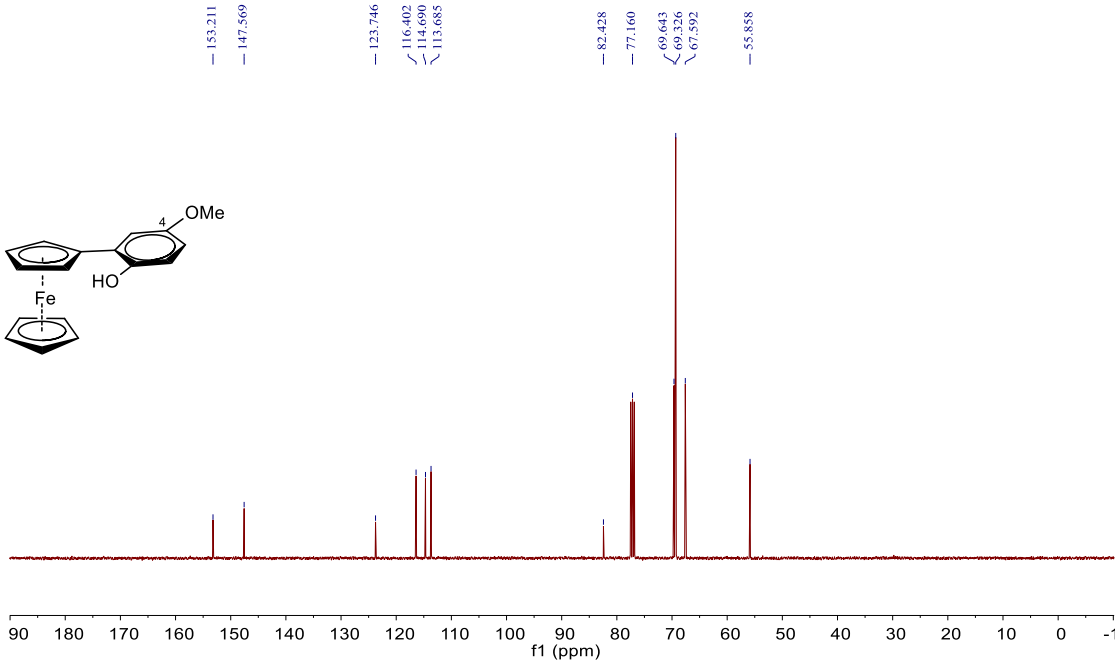
f1 (ppm)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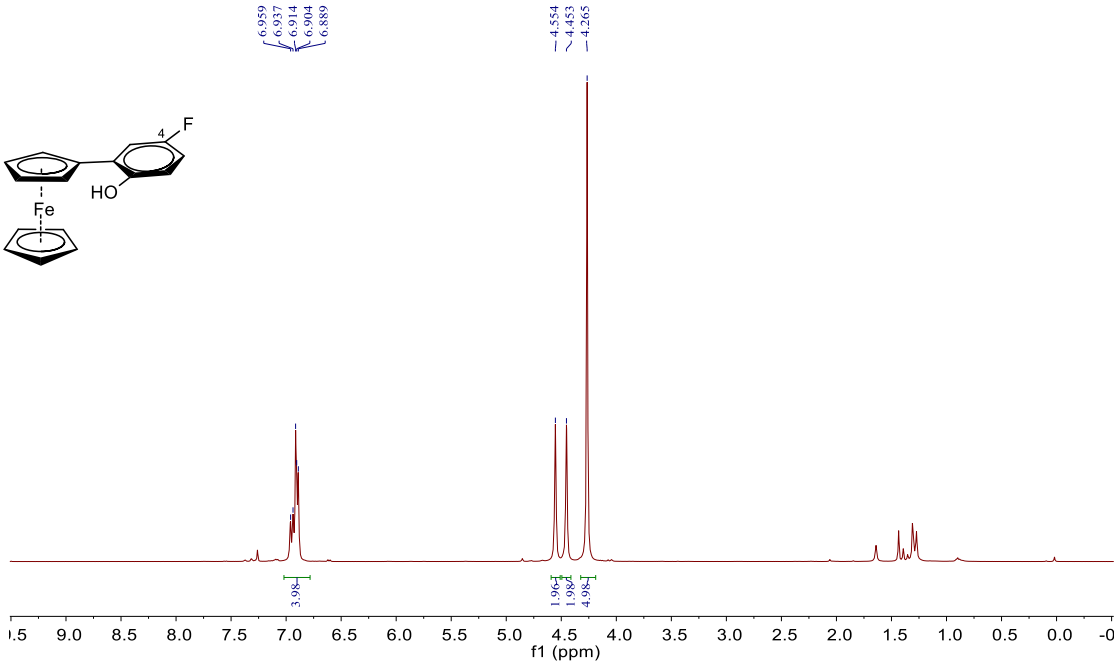
OMe
4
HO
Fe
f1 (ppm)

1k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F
4
HO
Fe
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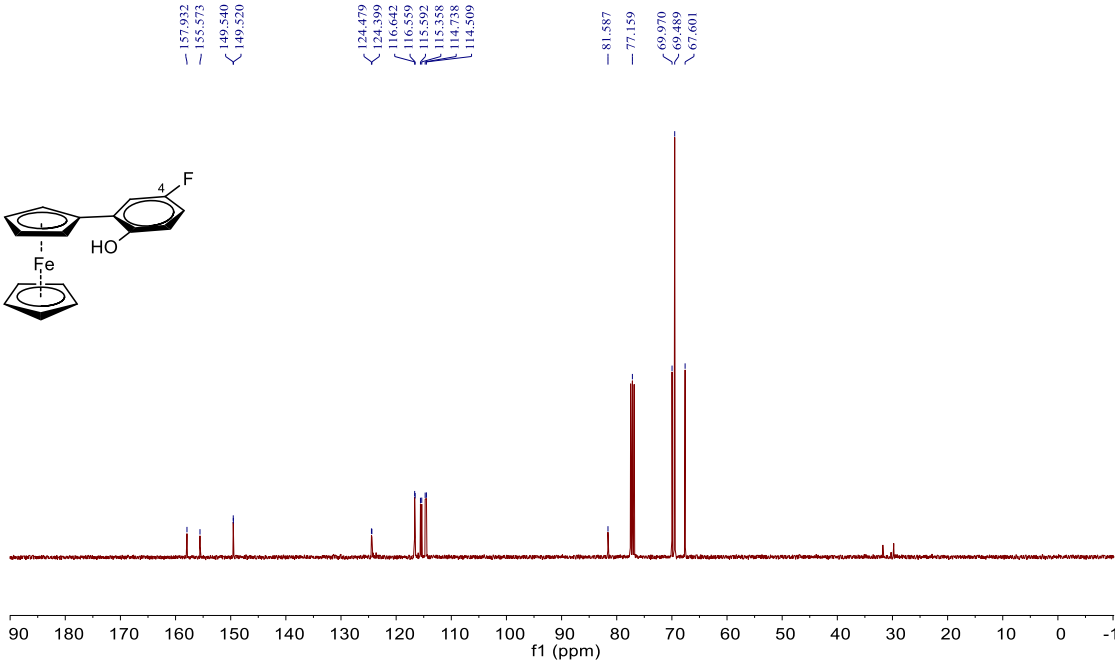
1.98
4.98
f1 (ppm)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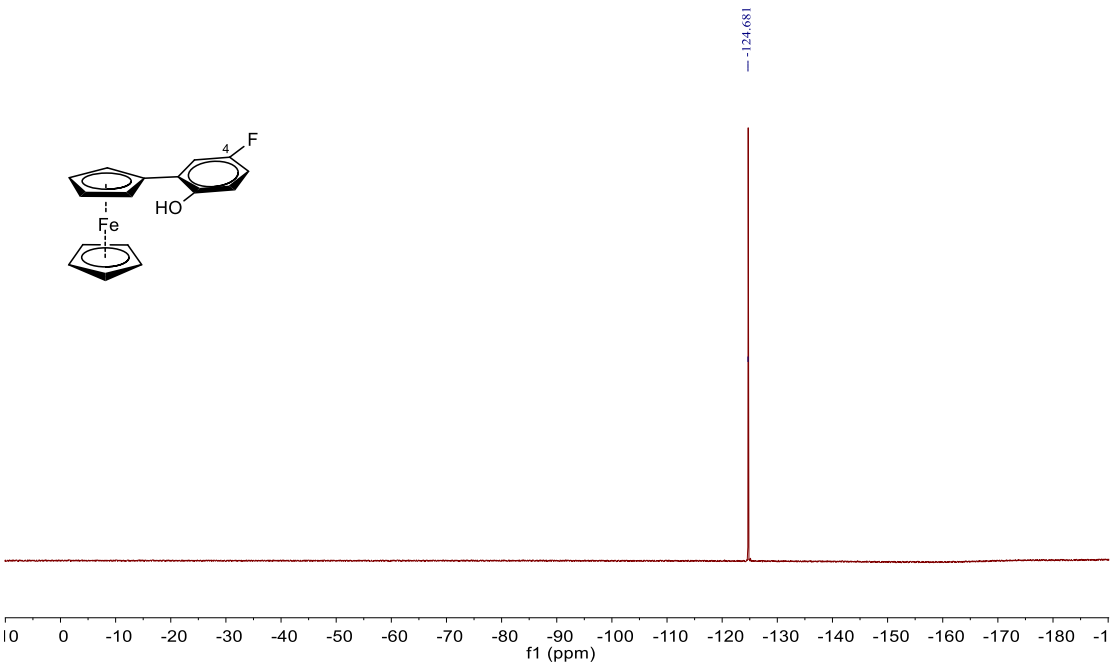
69.489
67.601
F
4
HO
Fe
f1 (ppm)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F
4
HO
Fe
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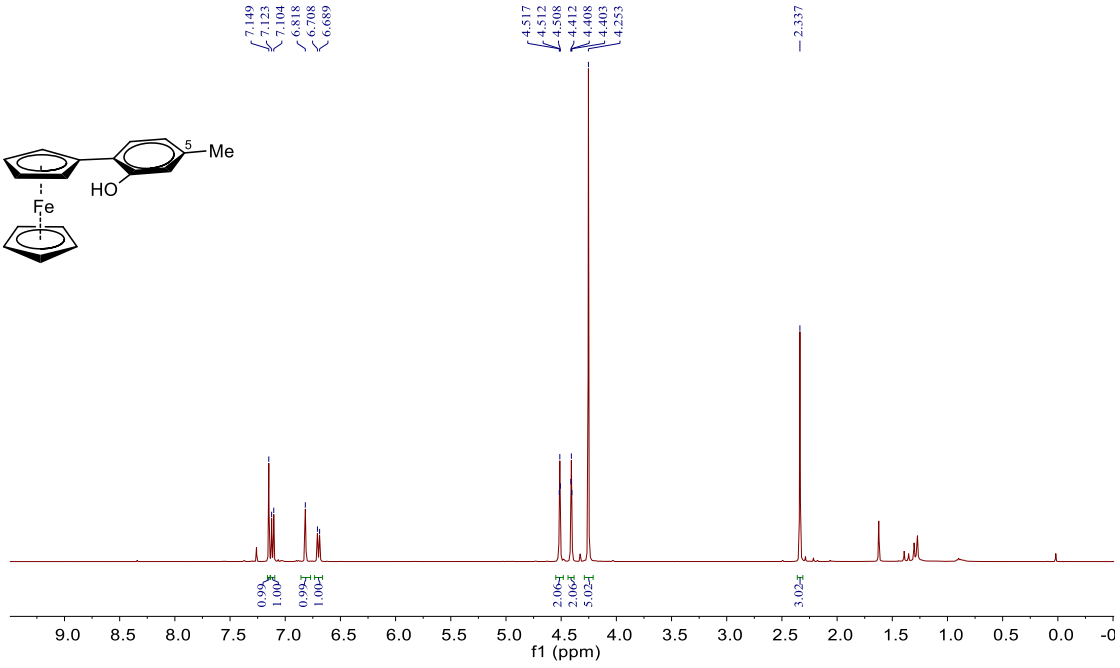
f1 (ppm)

1l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4.253
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Me
HO
Fe
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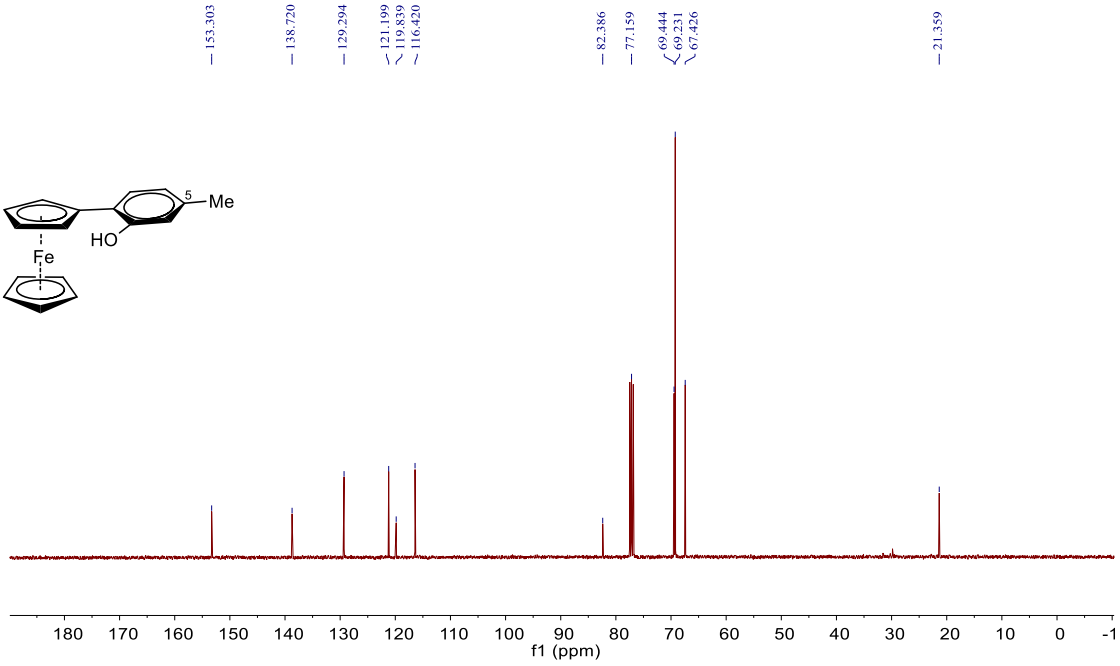
0.99
1.00
2.06
2.06
5.02
3.02
f1 (ppm)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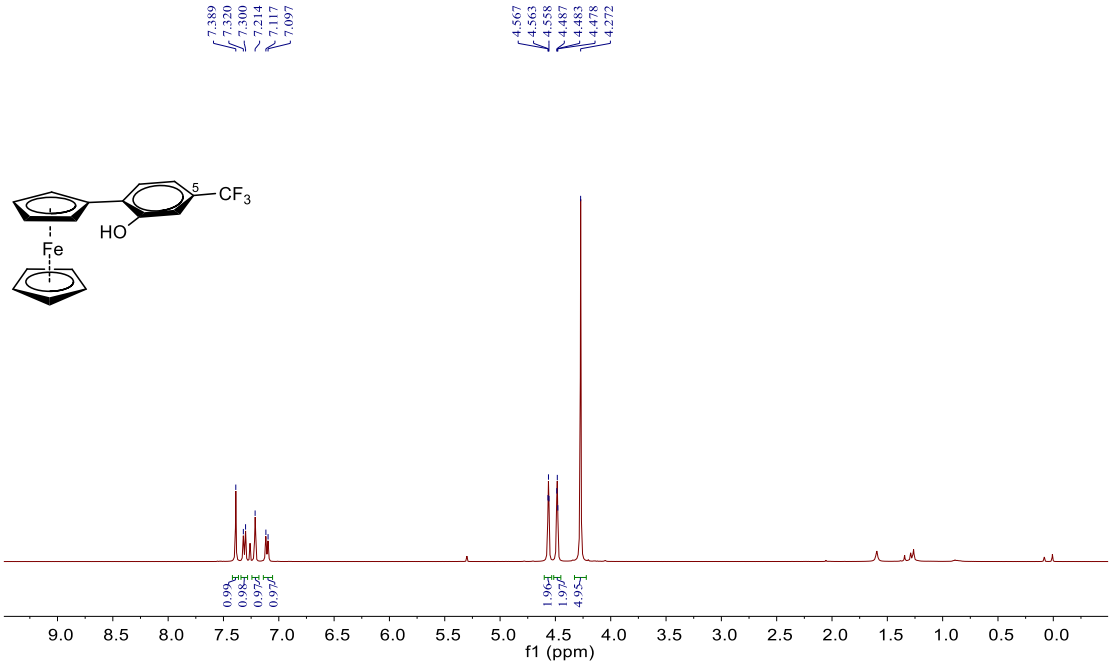
21.359
Me
HO
Fe
f1 (ppm)

1m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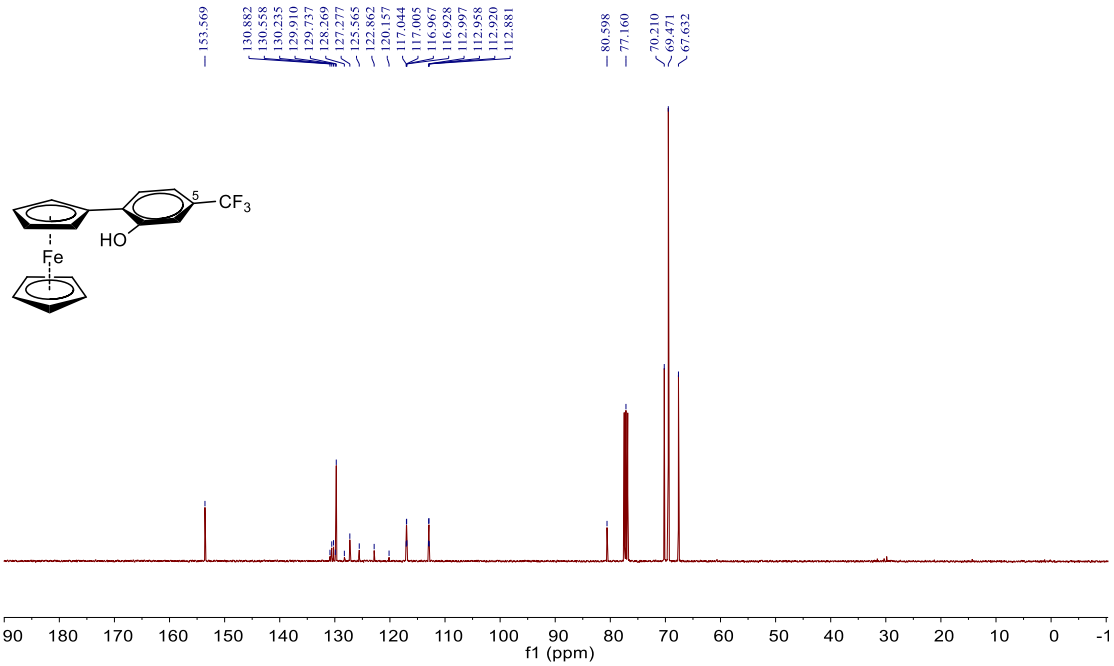
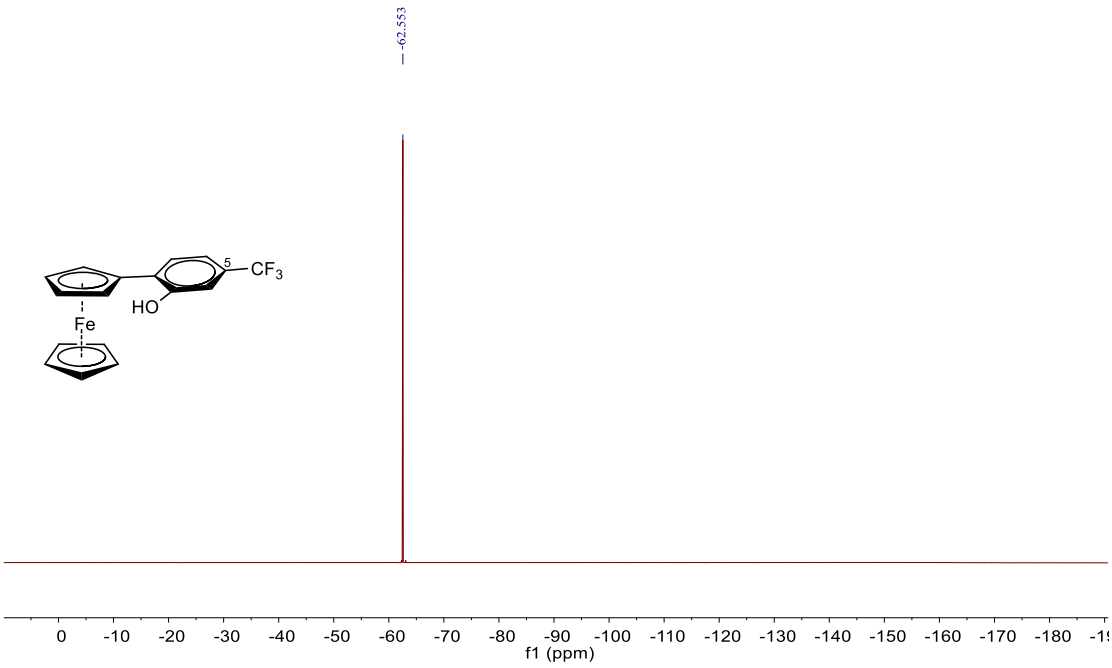
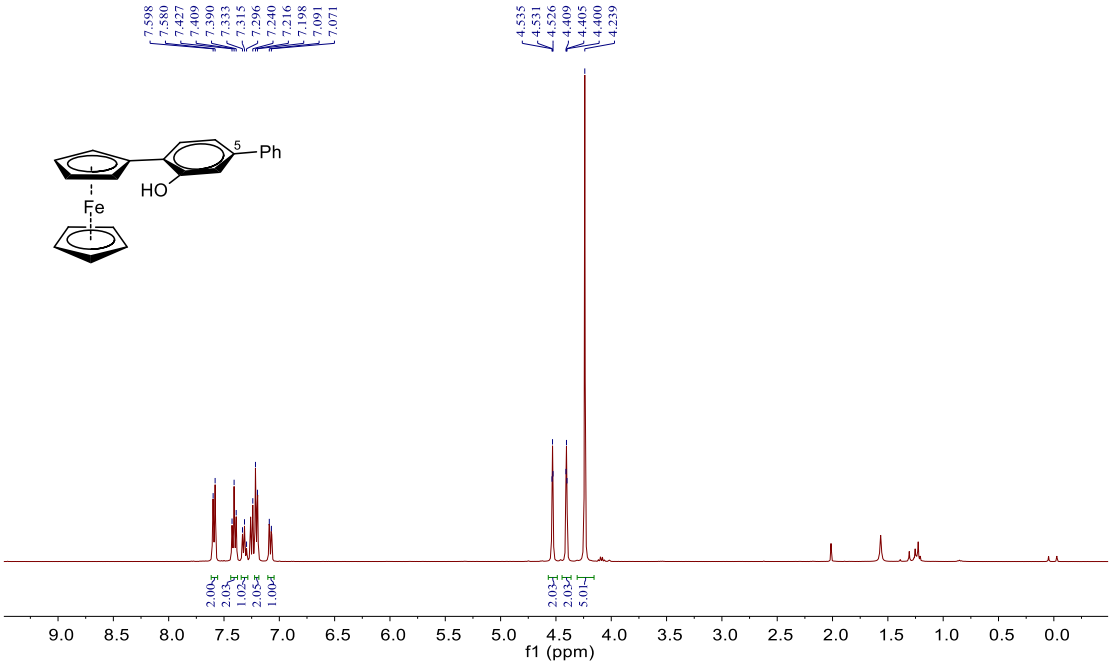
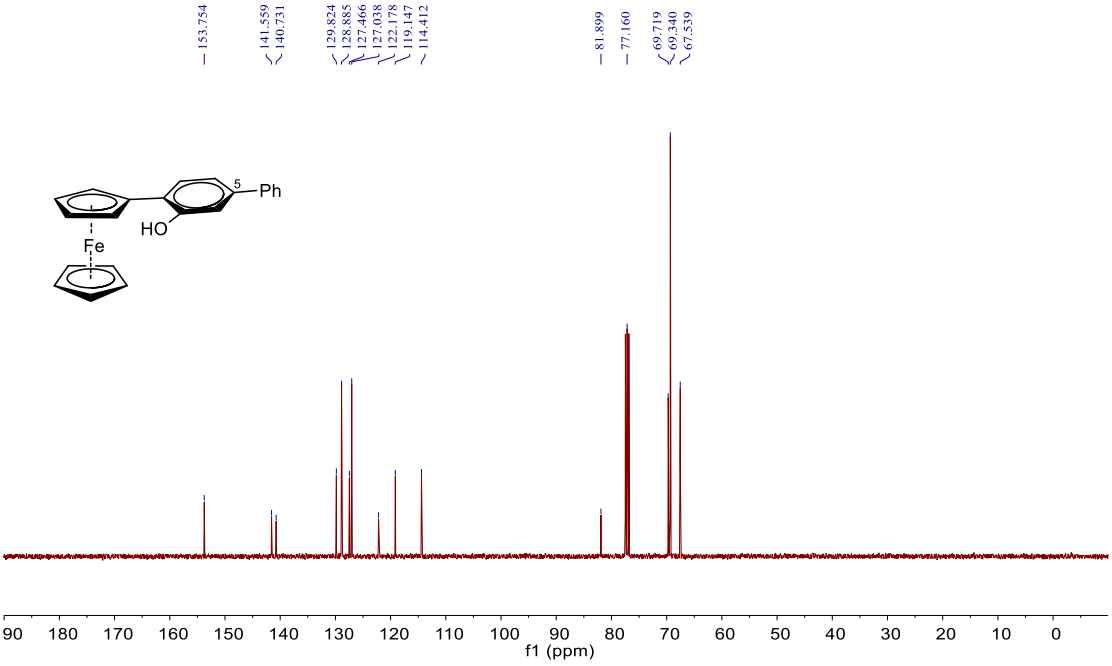
7.320
7.300
7.214
7.117
7.097
4.567
4.563
4.558
4.487
4.483
4.478
4.272
CF3
HO
Fe
0.98
0.98
0.97
0.97
1.96
1.97
4.95
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


153.569
130.882
130.558
130.235
129.910
129.737
128.269
127.277
125.565
122.862
120.157
117.044
117.005
116.967
116.928
112.997
112.958
112.920
112.881
80.598
77.160
70.210
69.471
67.632
CF3
HO
Fe
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

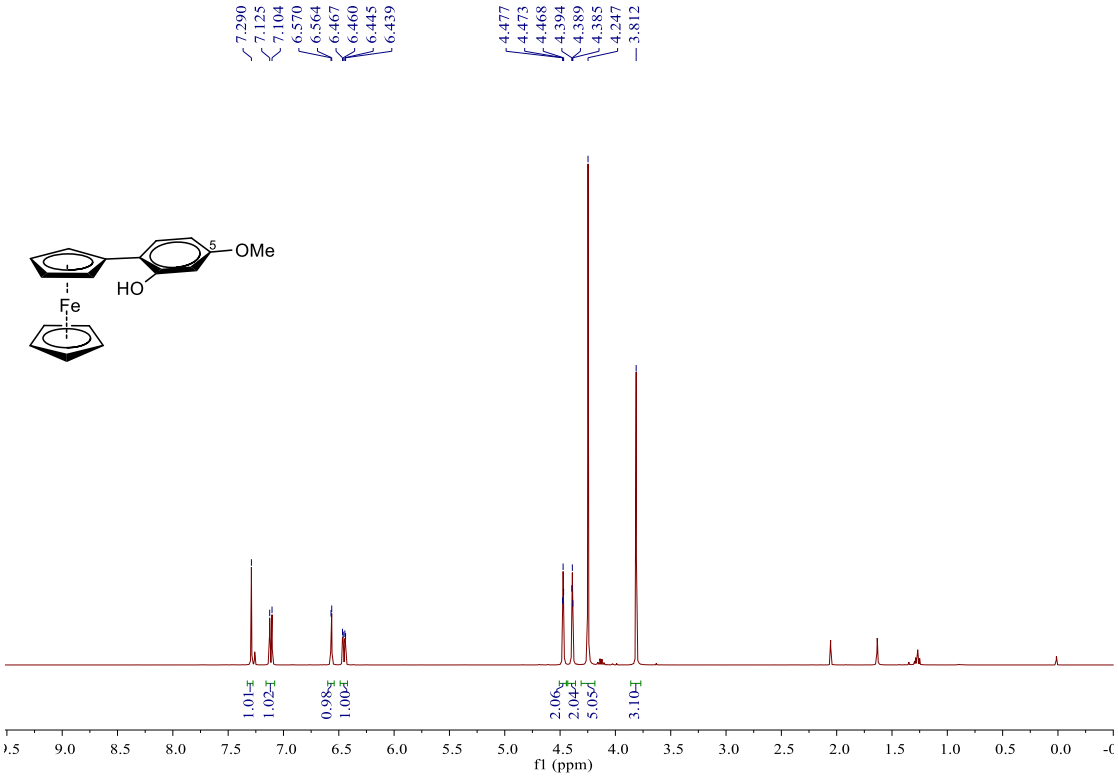

-62.553
5
CF3
HO
Fe
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

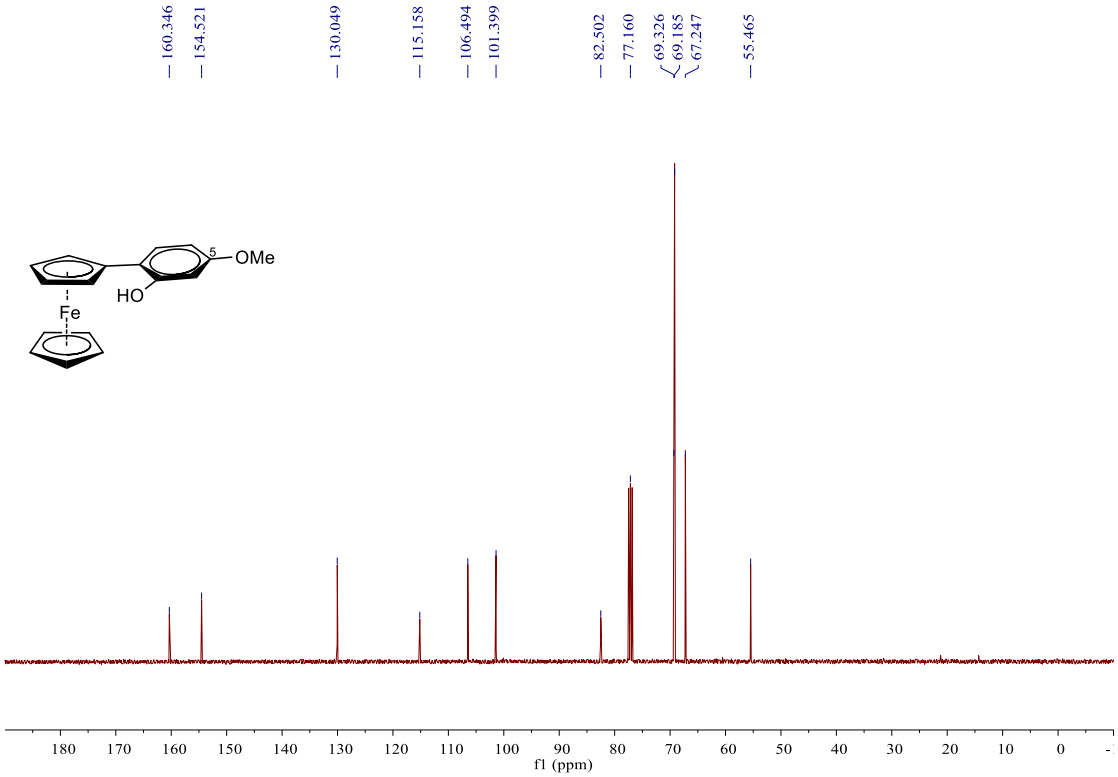
1n


7.598
7.580
7.427
7.409
7.390
7.333
7.315
7.296
7.240
7.216
7.198
7.091
7.071
4.535
4.531
4.526
4.409
4.405
4.400
4.239
5
Ph
HO
Fe
2.00
2.03
1.02
2.05
1.00
2.03
2.03
5.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

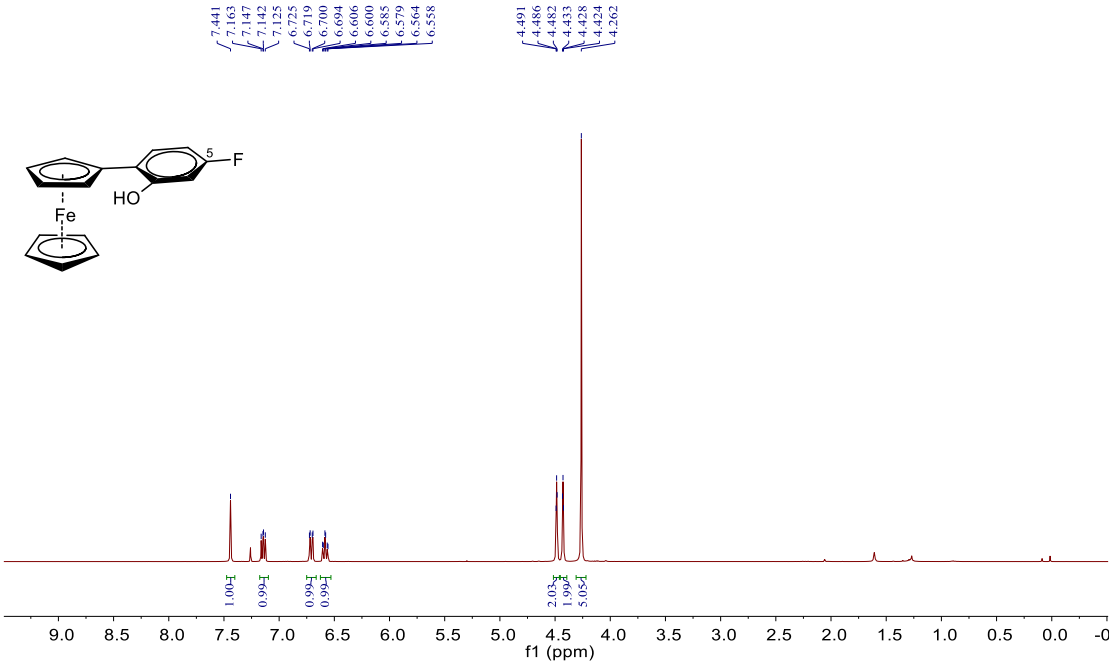

153.754
141.559
140.731
129.824
128.885
127.466
127.038
122.178
119.147
114.412
81.899
77.160
69.719
69.340
67.539
5
Ph
HO
Fe
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

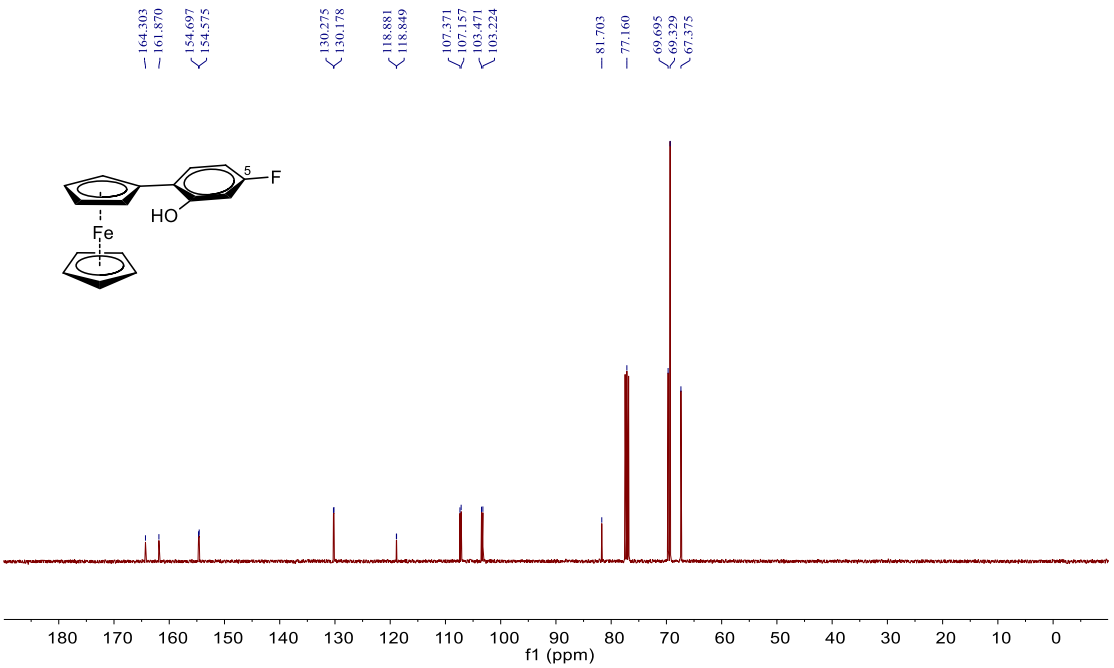
1o

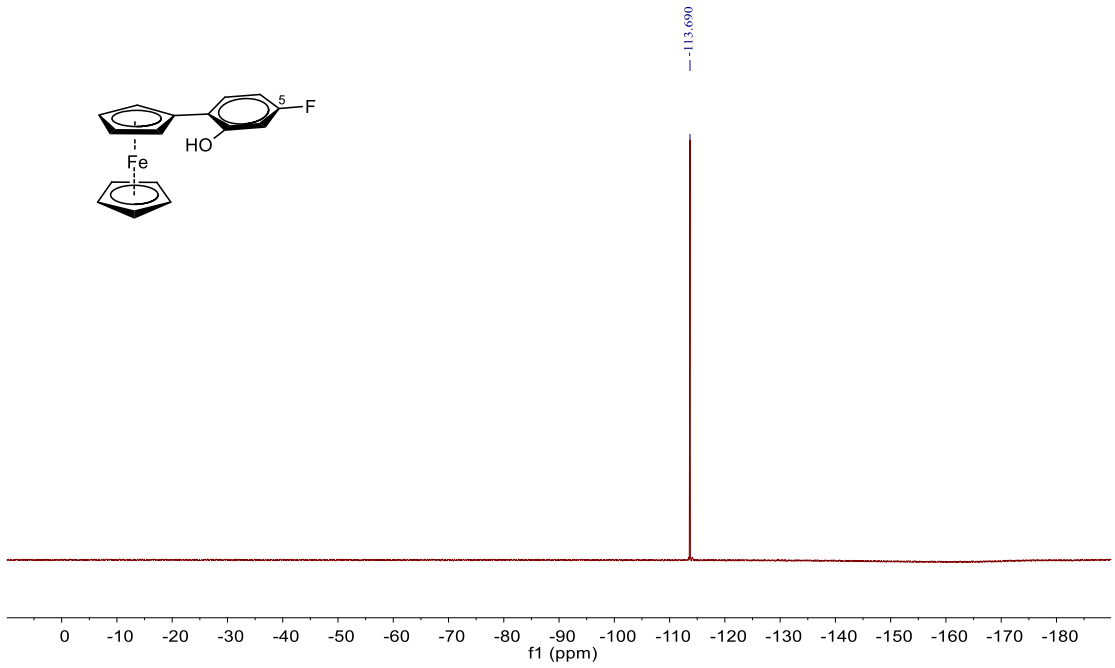

7.290
7.125
7.104
6.570
6.564
6.467
6.460
6.445
6.439
4.477
4.473
4.468
4.394
4.389
4.385
4.247
3.812
OMe
HO
Fe
1.01
1.02
0.98
1.00
2.06
2.04
5.05
3.10
f1 (ppm)


160.346
154.521
130.049
115.158
106.494
101.399
82.502
77.160
69.326
69.185
67.247
55.465
OMe
HO
Fe
f1 (ppm)

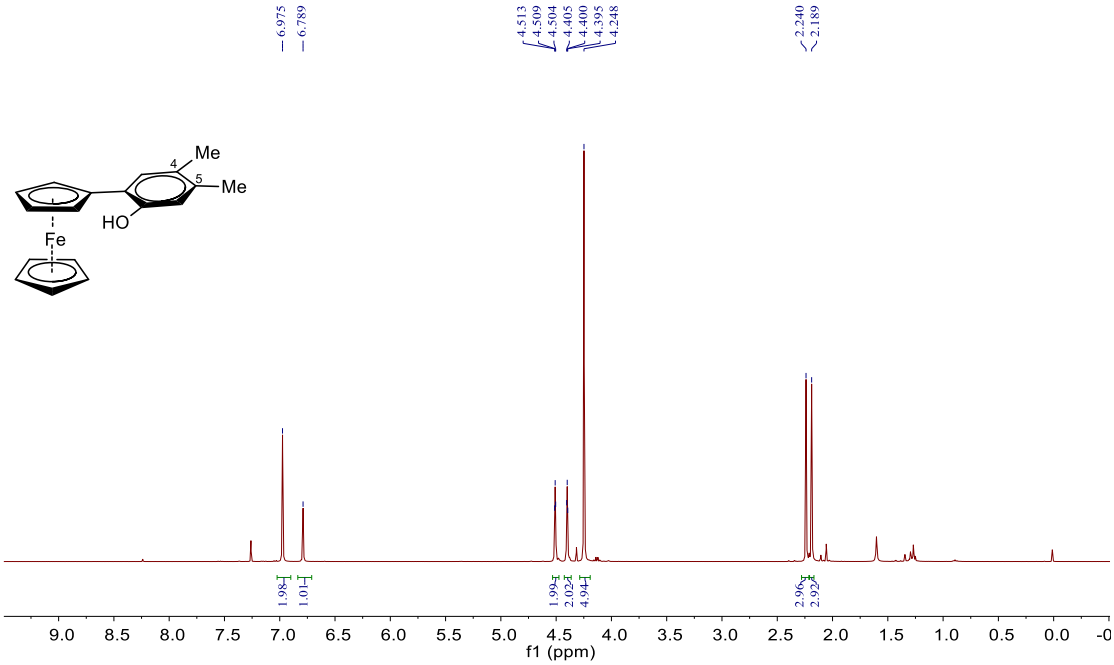
1p

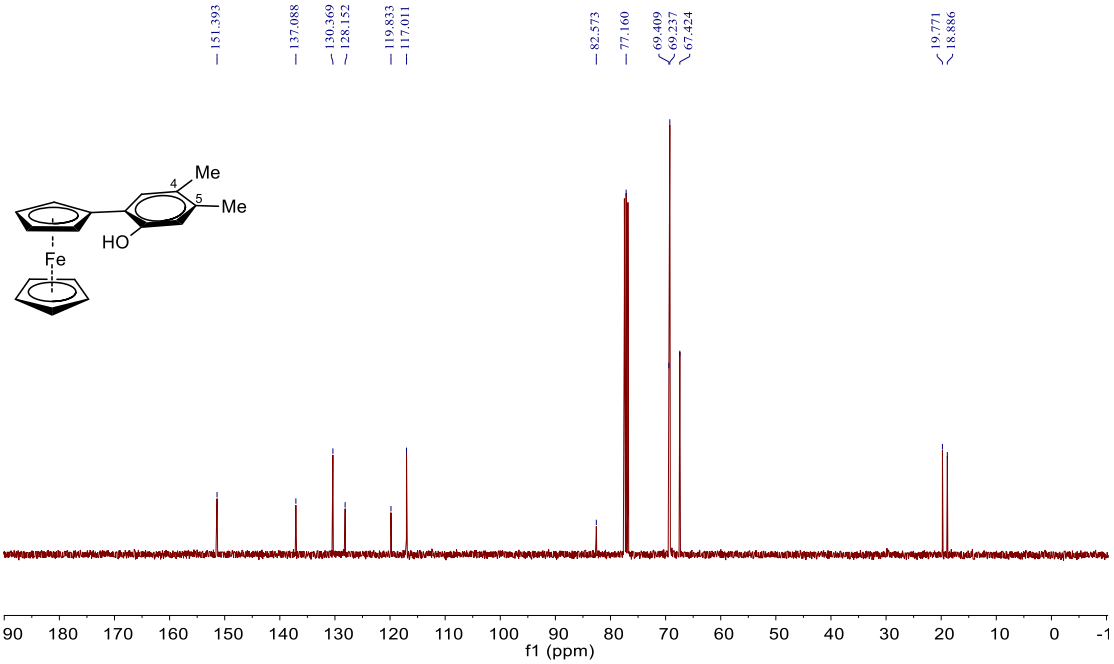

7.441
7.163
7.147
7.142
7.125
6.725
6.719
6.700
6.694
6.606
6.600
6.585
6.579
6.564
6.558
4.491
4.486
4.482
4.433
4.428
4.424
4.262
5
F
HO
Fe
1.00
0.99
0.99
0.99
2.03
1.99
5.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.303
161.870
154.697
154.575
130.275
130.178
118.881
118.849
107.371
107.157
103.471
103.224
81.703
77.160
69.695
69.329
67.375
5
F
HO
Fe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

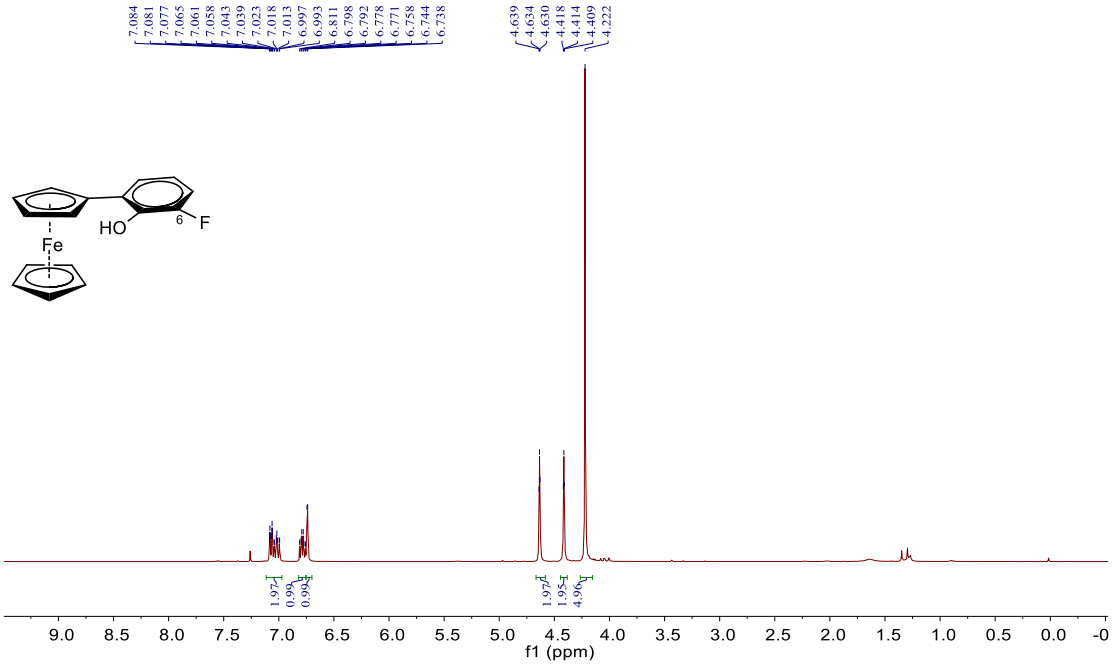

-113.690
5
F
HO
Fe
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

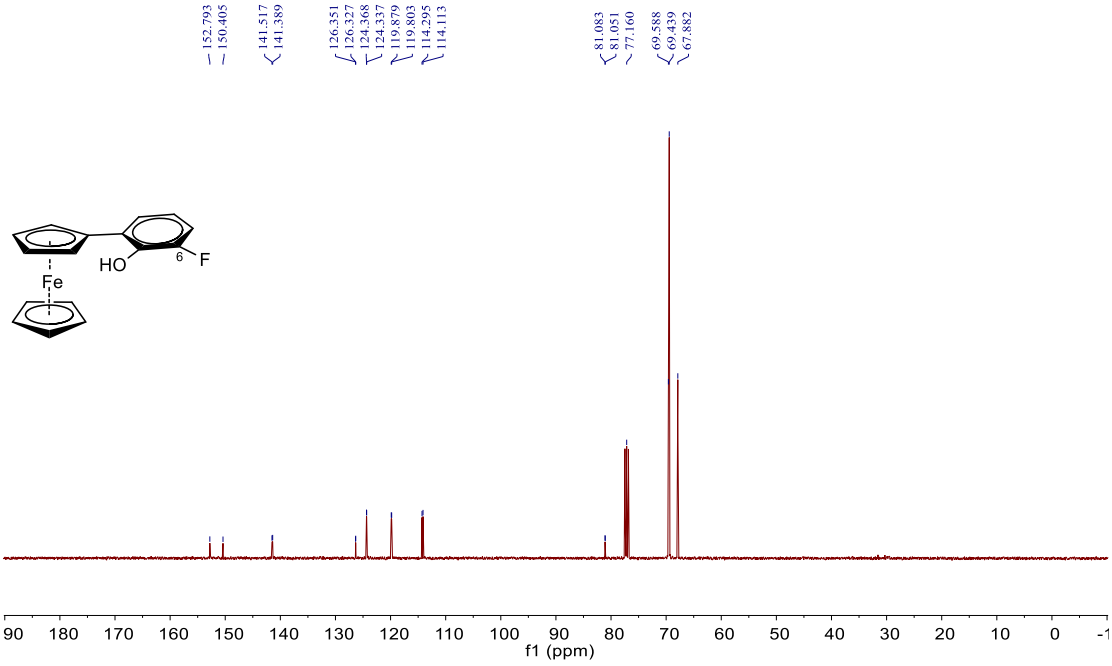
1q

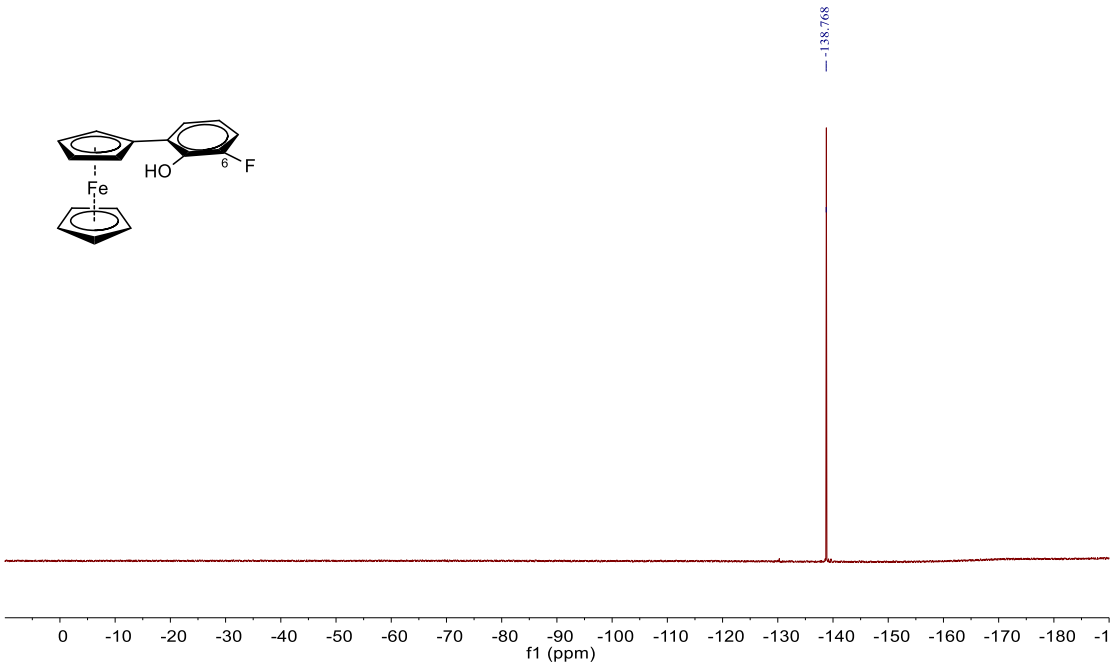

6.975
6.789
4.513
4.509
4.504
4.405
4.400
4.395
4.248
2.240
2.189
Me
Me
HO
Fe
1.98
1.01
1.99
2.02
4.94
2.96
2.92
f1 (ppm)


151.393
137.088
130.369
128.152
119.833
117.011
82.573
77.160
69.409
69.237
67.424
19.771
18.886
Me
Me
HO
Fe
f1 (ppm)

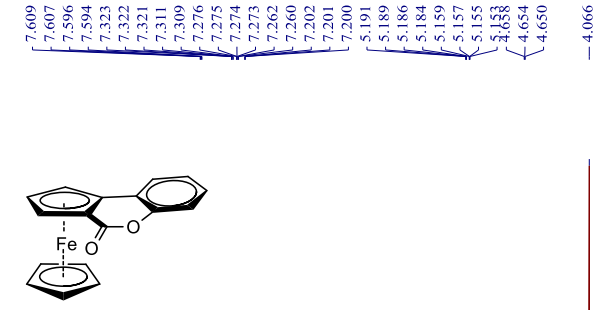
1r


7.084
7.081
7.077
7.065
7.061
7.058
7.043
7.039
7.023
7.018
7.013
6.997
6.993
6.811
6.798
6.792
6.778
6.771
6.758
6.744
6.738
4.639
4.634
4.630
4.418
4.414
4.409
4.222
HO
6
F
Fe
1.97
0.99
0.99
1.97
1.95
4.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

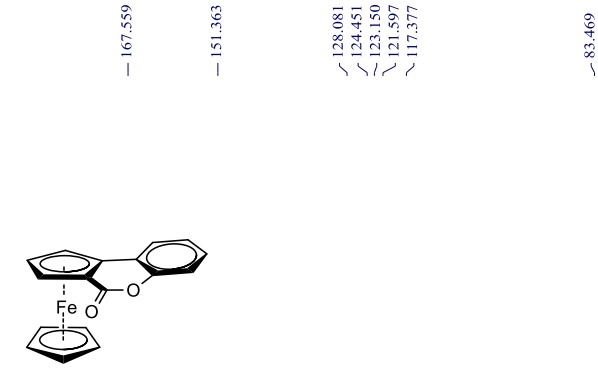

152.793
150.405
141.517
141.389
126.351
126.327
124.368
124.337
119.879
119.803
114.295
114.113
81.083
81.051
77.160
69.588
69.439
67.882
HO
6
F
Fe
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


-138.768
HO
6
F
Fe
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-1
f1 (ppm)

2a

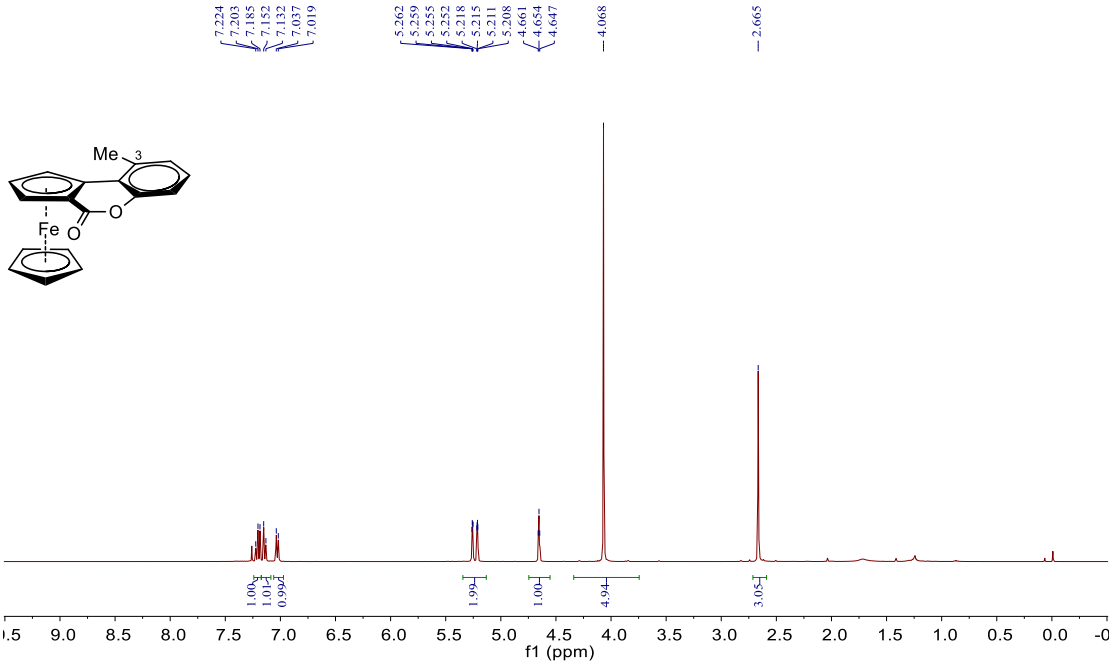

7.609
7.607
7.596
7.594
7.323
7.322
7.321
7.311
7.309
7.276
7.275
7.274
7.273
7.262
7.260
7.202
7.201
7.200
5.191
5.189
5.186
5.184
5.159
5.157
5.155
4.654
4.650
4.066
Fe
O
O

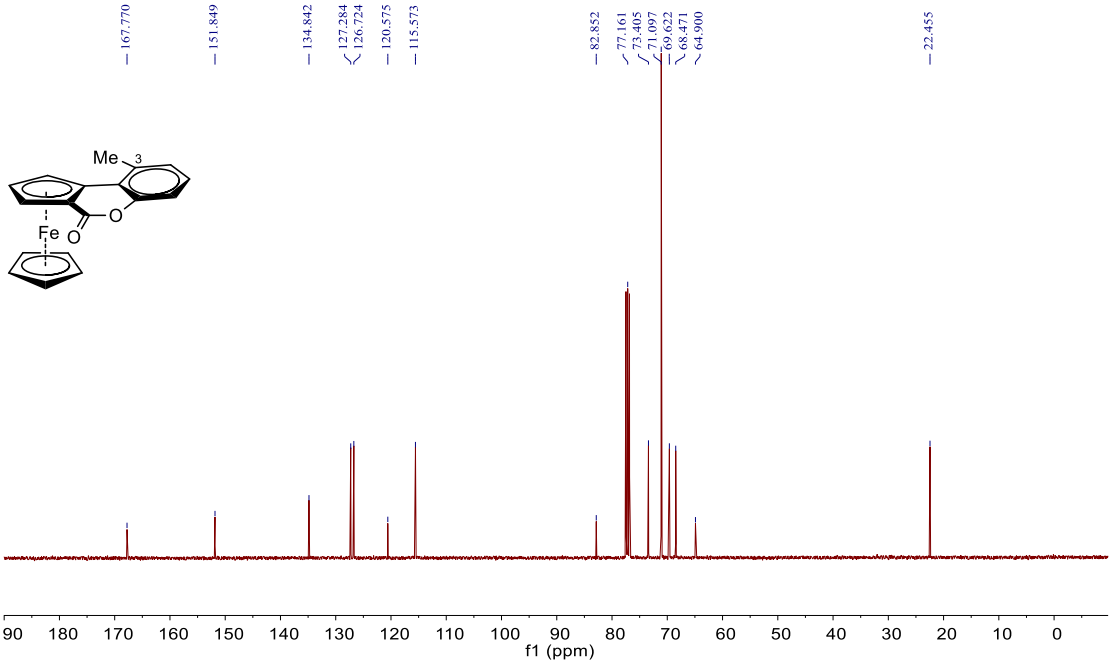
1.00
1.03
1.19
1.02
1.00
1.00
1.04
5.10
f1 (ppm)


167.559
151.363
128.081
124.451
123.150
121.597
117.377
83.469
77.160
73.085
71.366
68.434
65.313
64.571
Fe
O
O

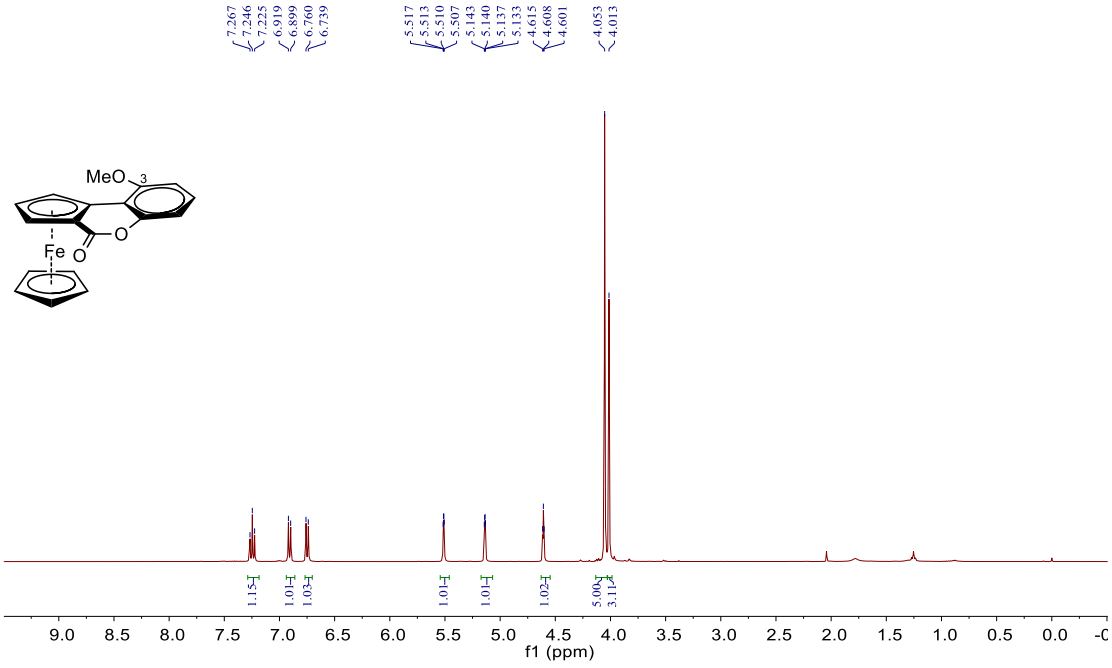
f1 (ppm)

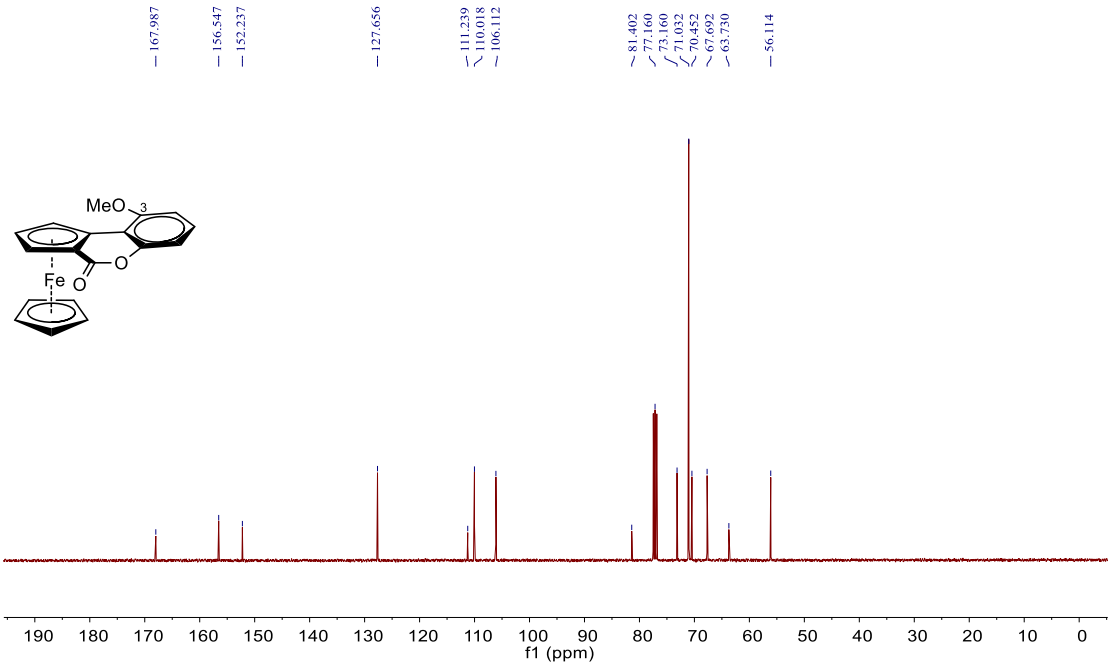
2b


7.224
7.203
7.185
7.152
7.132
7.037
7.019
5.262
5.259
5.255
5.252
5.218
5.215
5.211
5.208
4.661
4.654
4.647
4.068
2.665
Me
3
Fe
O
O
1.00
1.01
0.99
1.99
1.00
4.94
3.05
f1 (ppm)

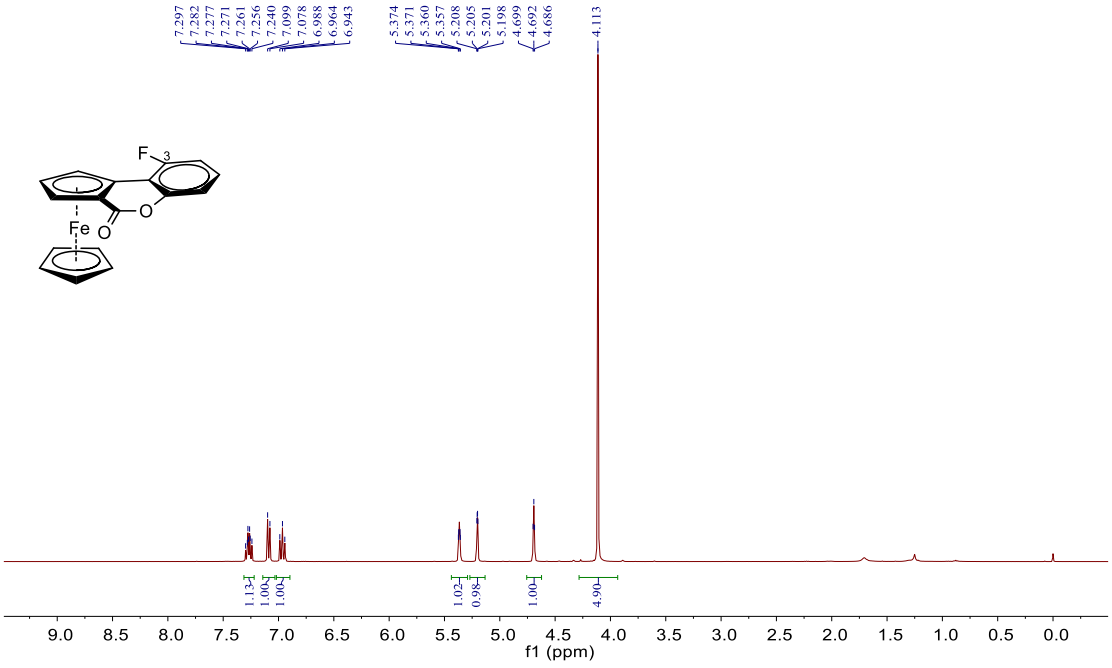

167.770
151.849
134.842
127.284
126.724
120.575
115.573
82.852
77.161
73.405
71.097
69.622
68.471
64.900
22.455
Me
3
Fe
O
O
f1 (ppm)

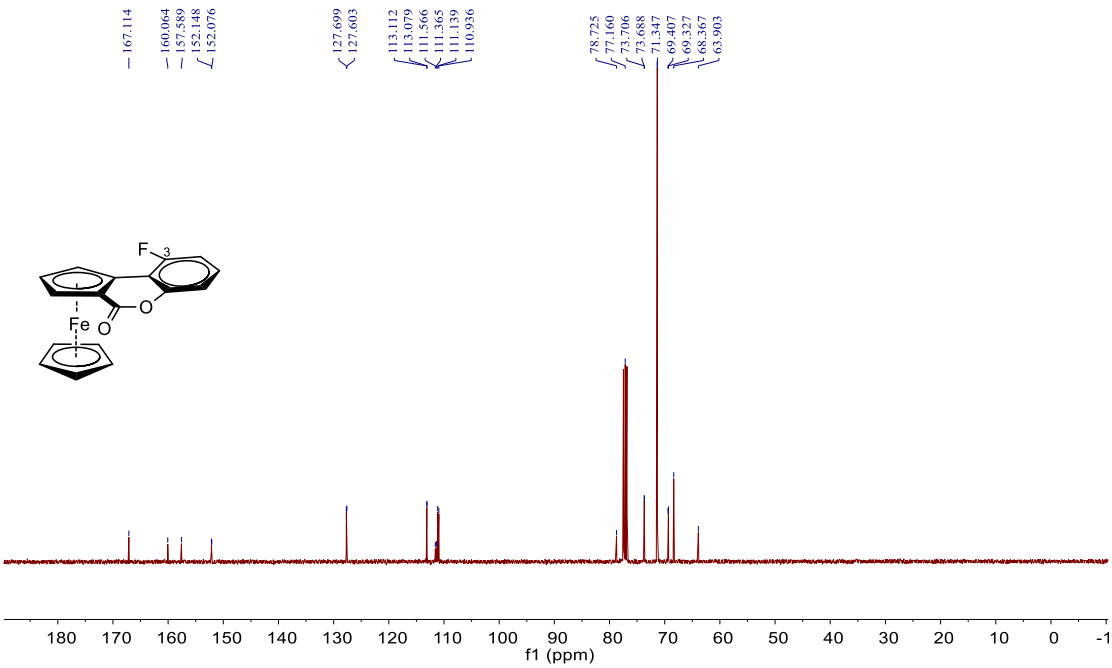
2c

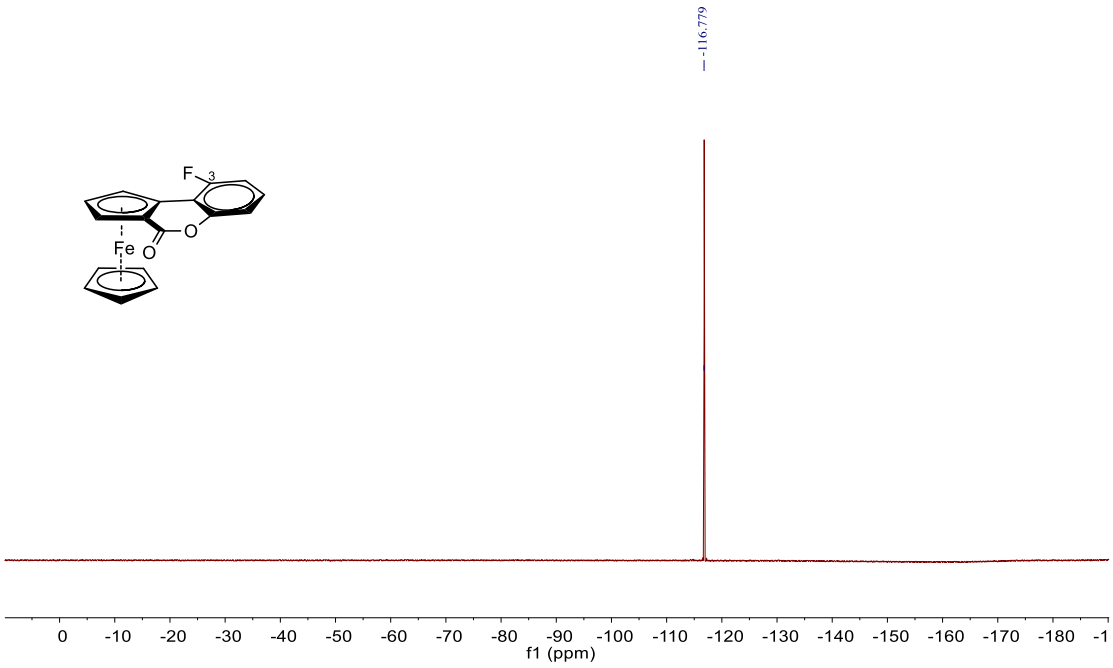

7.267
7.246
7.225
6.919
6.899
6.760
6.739
5.517
5.513
5.510
5.507
5.143
5.140
5.137
5.133
4.615
4.608
4.601
4.053
4.013
MeO
3
O
Fe
O
1.15
1.01
1.03
1.01
1.01
1.02
5.00
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.987
156.547
152.237
127.656
111.239
110.018
106.112
81.402
77.160
73.160
71.032
70.452
67.692
63.730
56.114
MeO
3
O
Fe
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

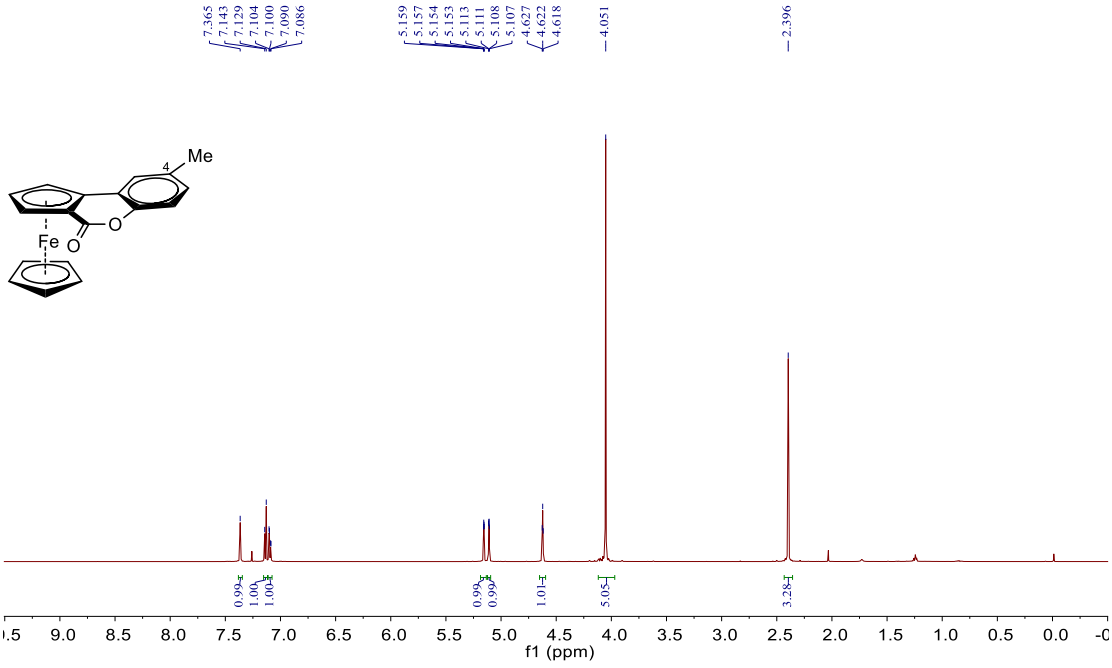
2d

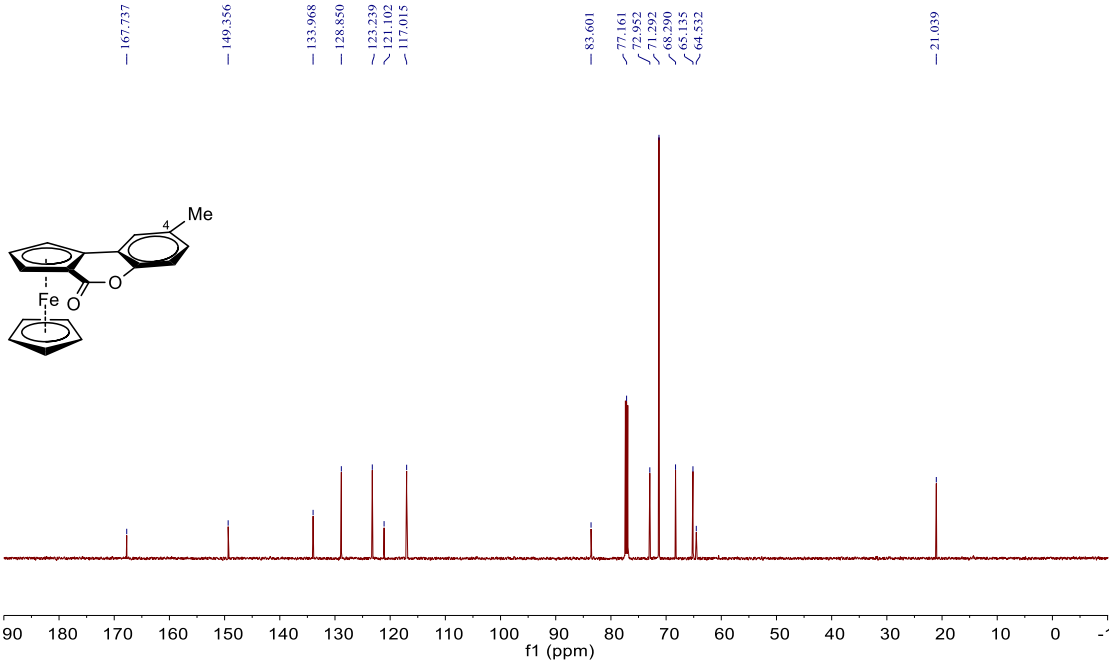

7.297
7.282
7.277
7.271
7.261
7.256
7.240
7.099
7.078
6.988
6.964
6.943
5.374
5.371
5.360
5.357
5.208
5.205
5.201
5.198
4.699
4.692
4.686
4.113
F3
O
Fe
O
1.13
1.00
1.00
1.00
1.02
0.98
1.00
4.90
f1 (ppm)


167.114
160.064
157.589
152.148
152.076
127.699
127.603
113.112
113.079
111.566
111.365
111.139
110.936
78.725
77.160
73.706
73.688
71.347
69.407
69.327
68.367
63.903
F3
O
Fe
O
f1 (ppm)

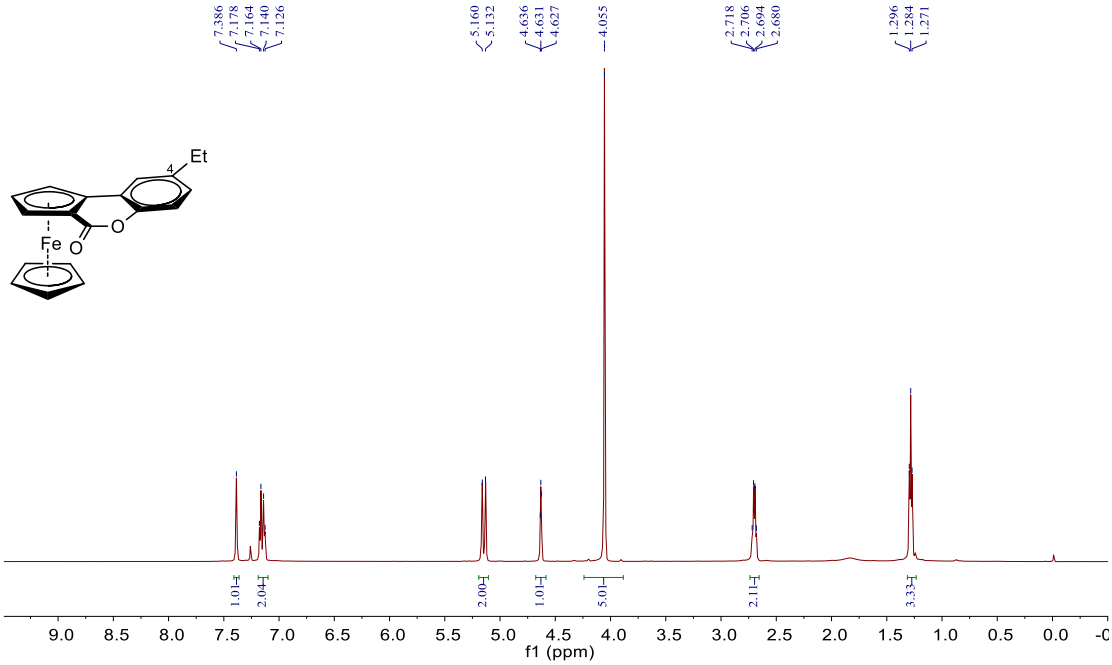

-116.779
F
3
Fe
O
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-1
f1 (ppm)

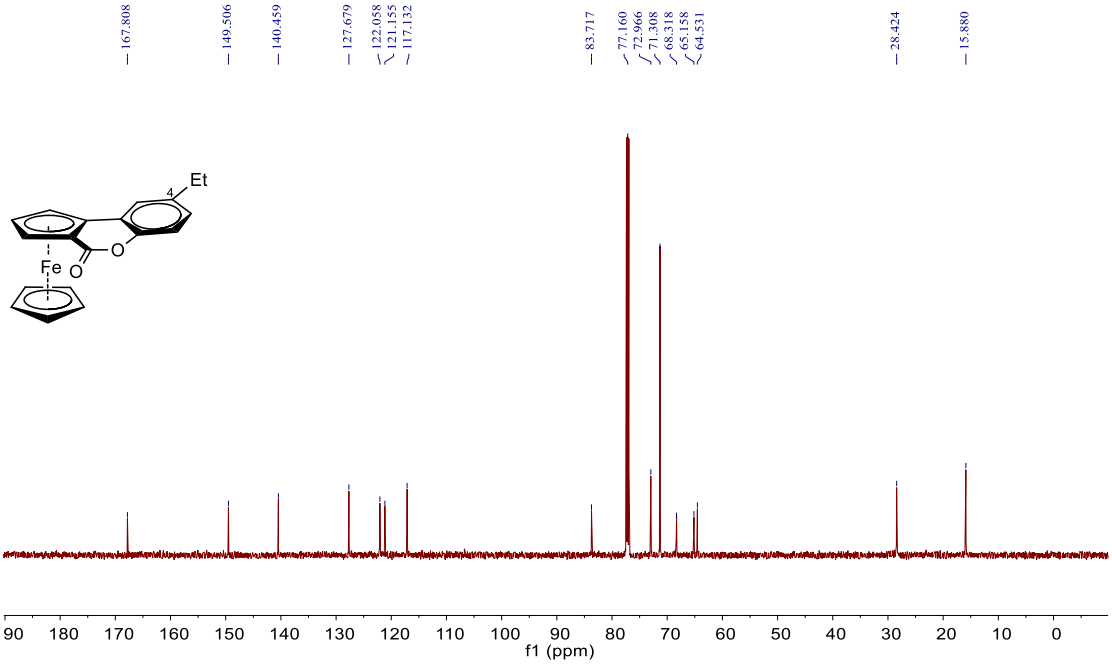
2e


7.365
7.143
7.129
7.104
7.100
7.090
7.086
5.159
5.157
5.154
5.153
5.113
5.111
5.108
5.107
4.627
4.622
4.618
4.051
2.396
Me
4
O
Fe
O
0.99
1.00
1.00
0.99
0.99
1.01
5.05
3.28
f1 (ppm)

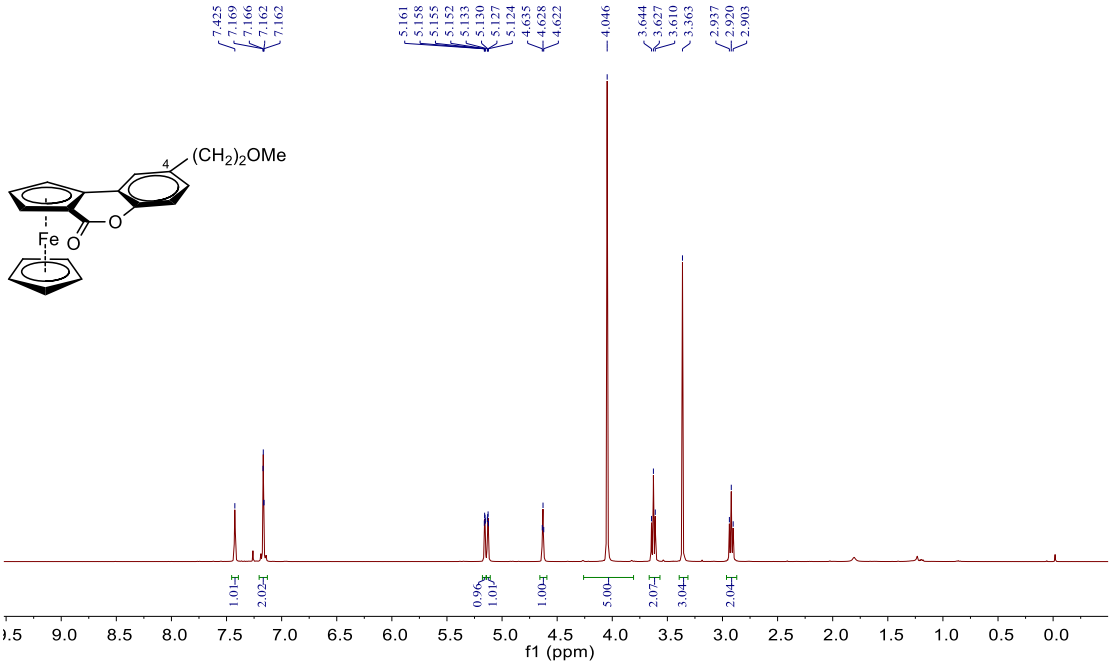

167.737
149.356
133.968
128.850
123.239
121.102
117.015
83.601
77.161
72.952
71.292
68.290
65.135
64.532
21.039
Me
4
O
Fe
O
f1 (ppm)

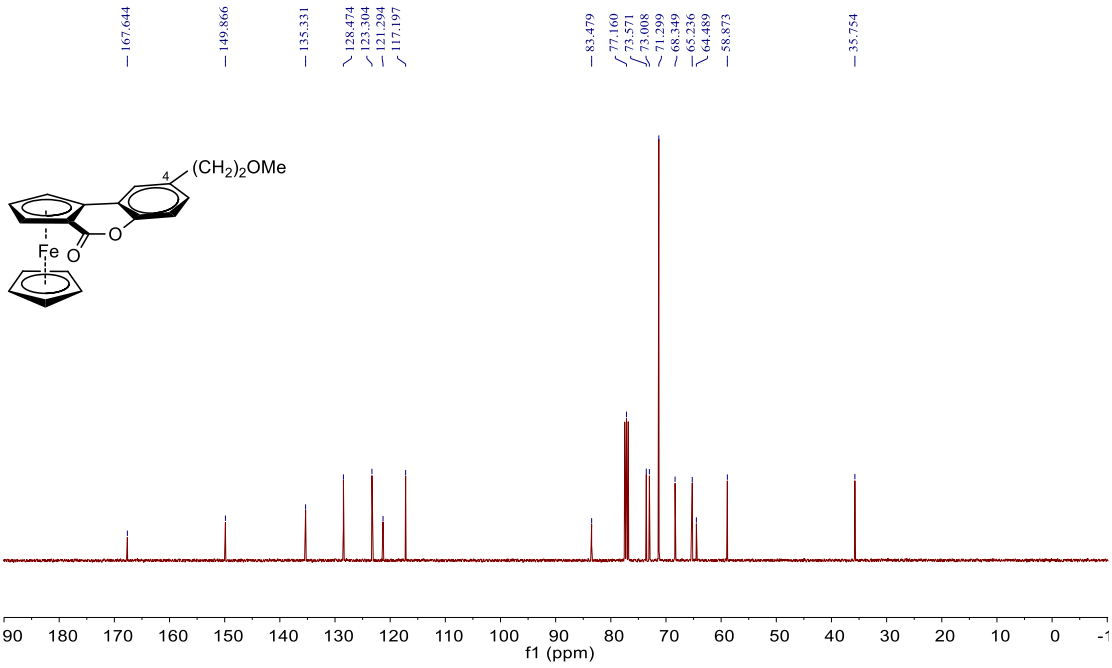
2f


7.386
7.178
7.164
7.140
7.126
5.160
5.132
4.636
4.631
4.627
4.055
2.718
2.706
2.694
2.680
1.296
1.284
1.271
Et
4
O
Fe
O
1.01
2.04
2.00
1.01
5.01
2.11
3.33
f1 (ppm)

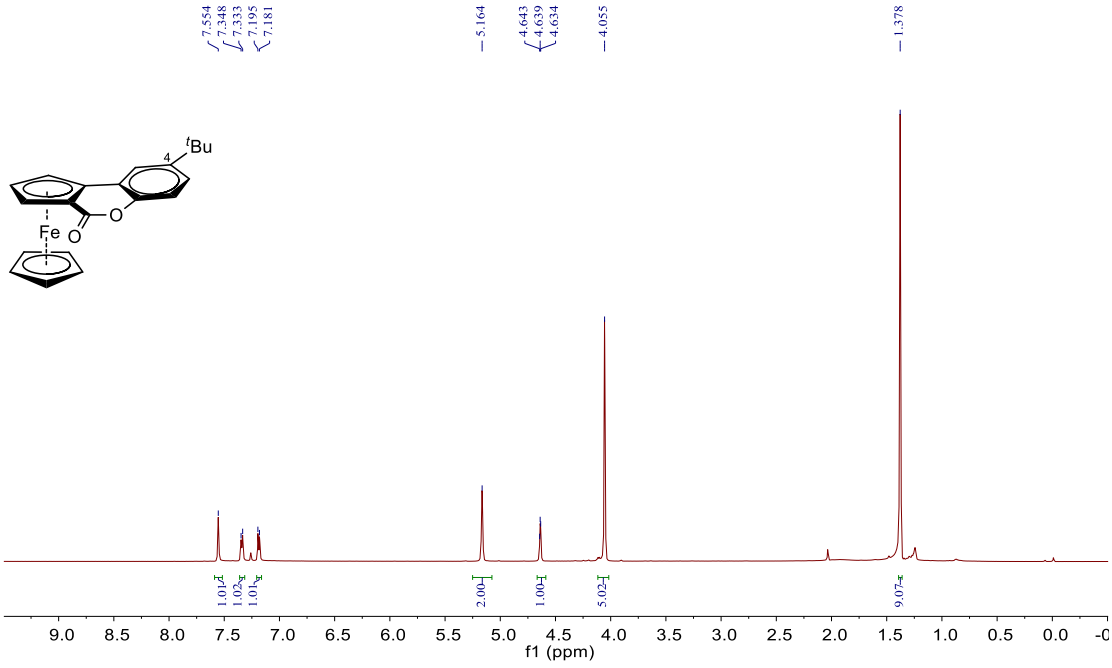

167.808
149.506
140.459
127.679
122.058
121.155
117.132
83.717
77.160
72.966
71.308
68.318
65.158
64.531
28.424
15.880
Et
4
O
Fe
O
f1 (ppm)

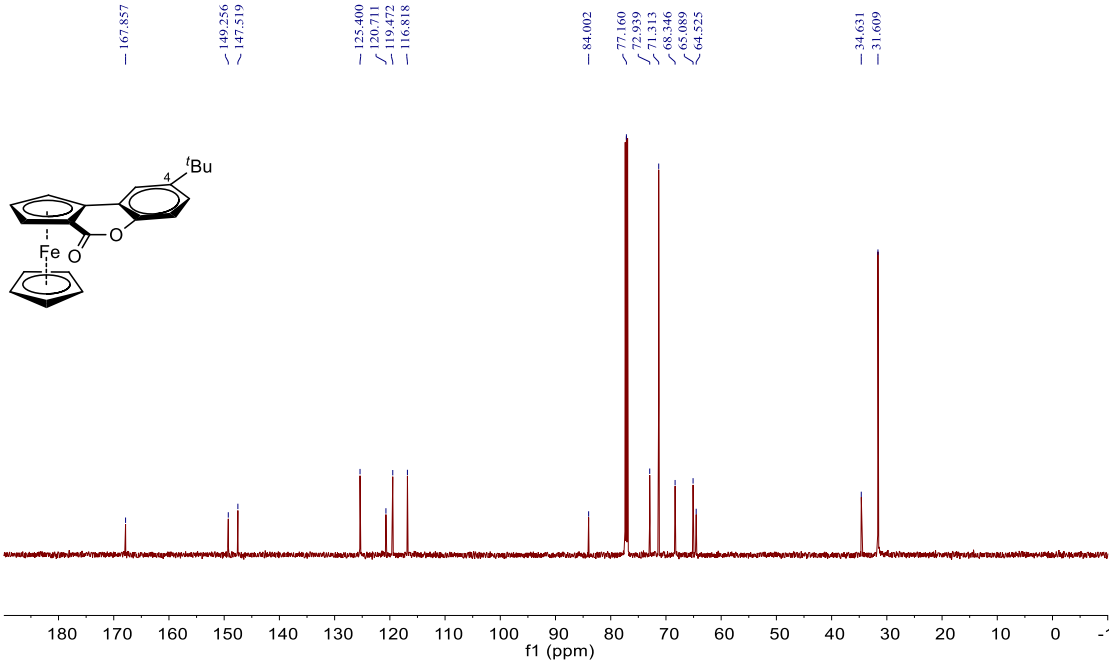
2g


7.425
7.169
7.166
7.162
7.162
5.161
5.158
5.155
5.152
5.133
5.130
5.127
5.124
4.635
4.628
4.622
4.046
3.644
3.627
3.610
3.363
2.937
2.920
2.903
4
(CH2)2OMe
Fe
O
O
1.01
2.02
0.96
1.01
1.00
5.00
2.07
3.04
2.04
f1 (ppm)

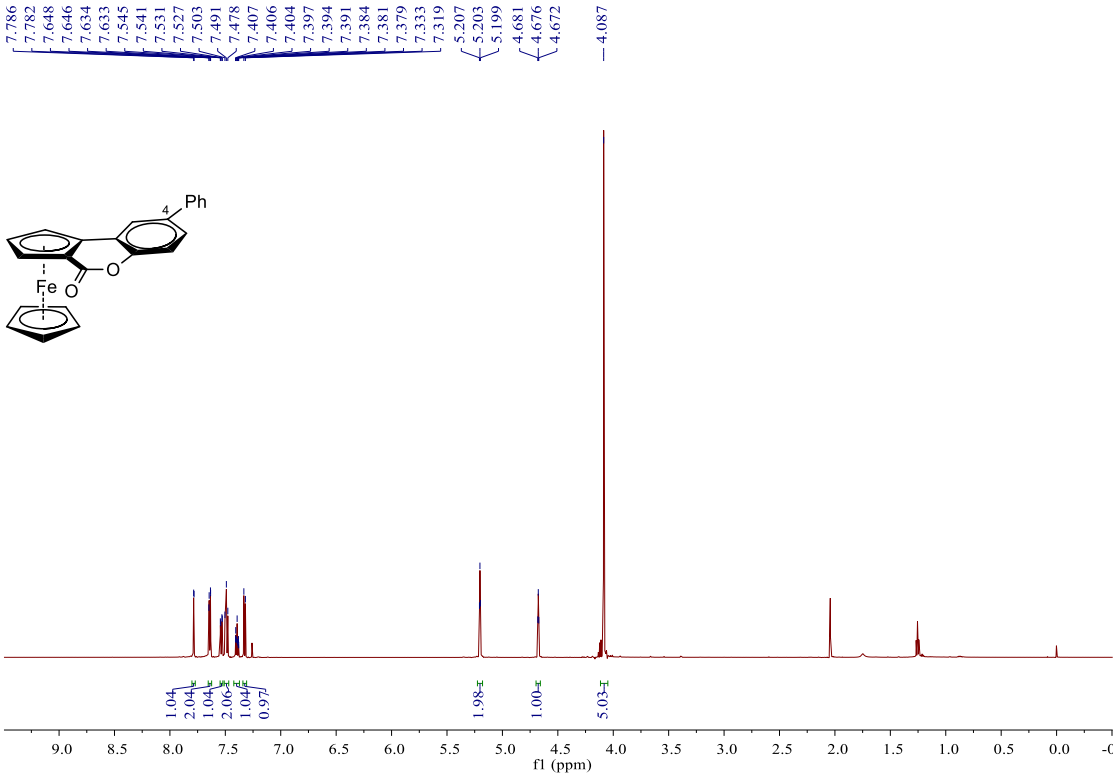

167.644
149.866
135.331
128.474
123.304
121.294
117.197
83.479
77.160
73.571
73.008
71.299
68.349
65.236
64.489
58.873
35.754
4
(CH2)2OMe
Fe
O
O
f1 (ppm)

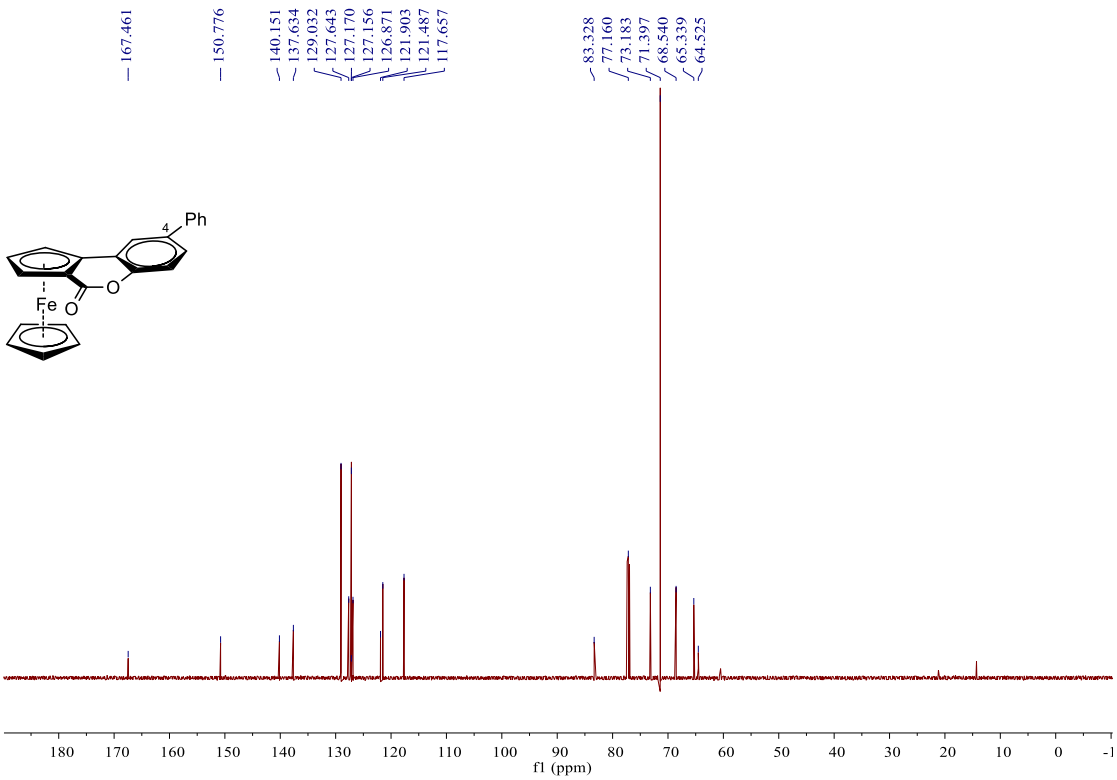
2h


7.554
7.348
7.333
7.195
7.181
5.164
4.643
4.639
4.634
4.055
1.378
tBu
4
O
Fe
O
1.01
1.02
1.01
2.00
1.00
5.02
9.07
f1 (ppm)

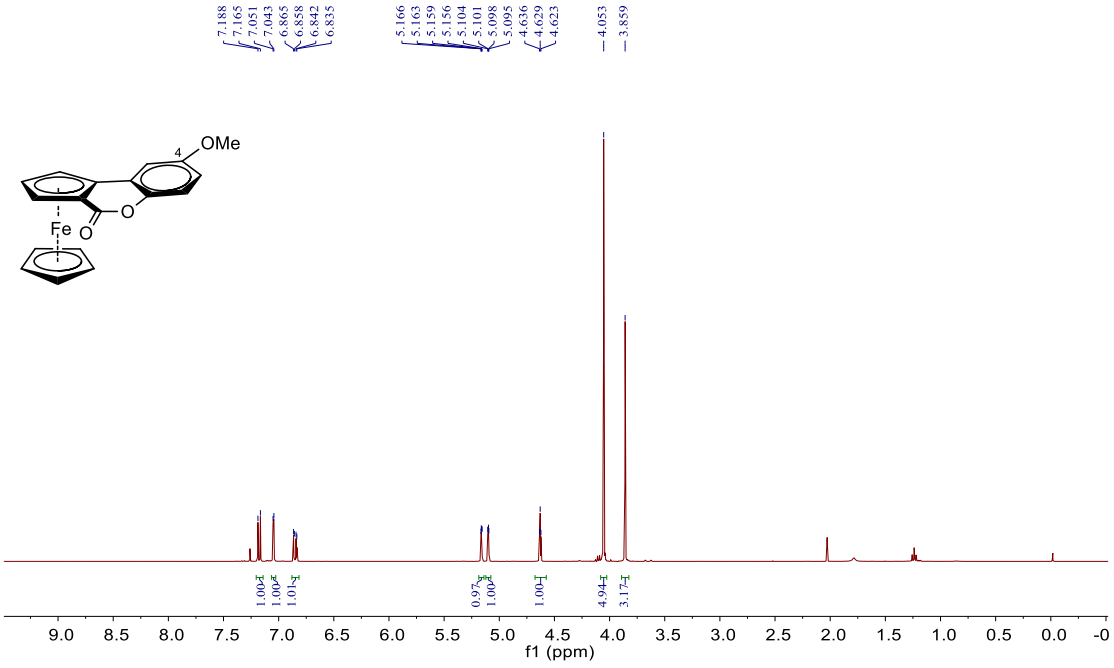

167.857
149.256
147.519
125.400
120.711
119.472
116.818
84.002
77.160
72.939
71.313
68.346
65.089
64.525
34.631
31.609
tBu
4
O
Fe
O
f1 (ppm)

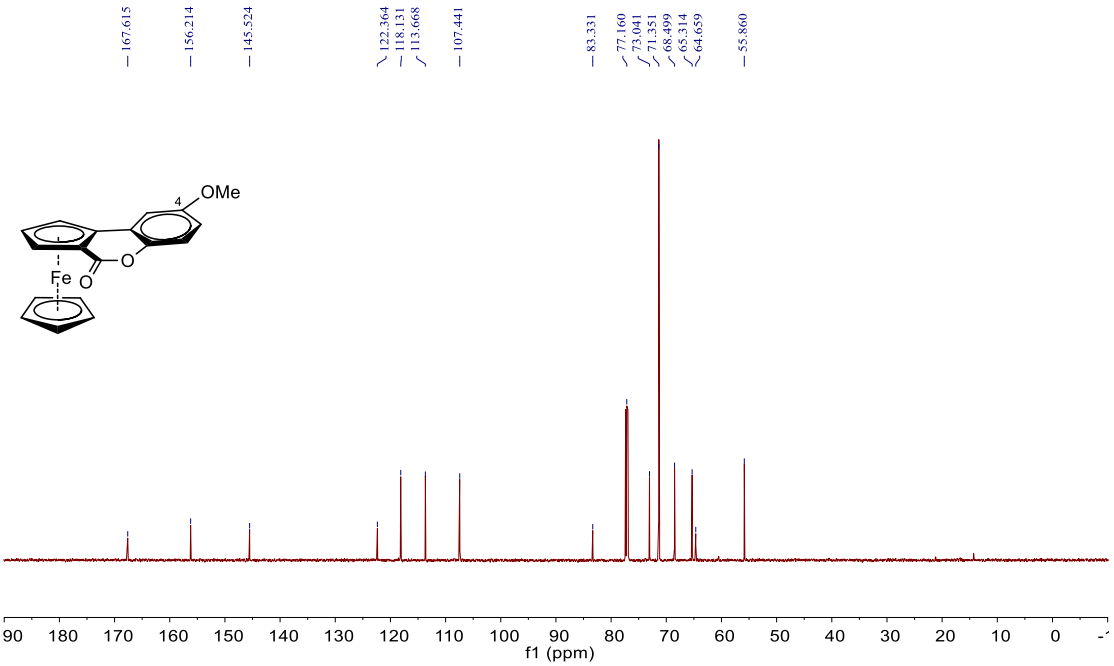
2i


7.786
7.782
7.648
7.646
7.634
7.633
7.545
7.541
7.531
7.527
7.503
7.491
7.478
7.407
7.406
7.404
7.397
7.394
7.391
7.384
7.381
7.379
7.333
7.319
5.207
5.203
5.199
4.681
4.676
4.672
4.087
Ph
4
Fe
O
O
1.04
2.04
1.04
2.06
1.04
0.97
1.98
1.00
5.03
f1 (ppm)

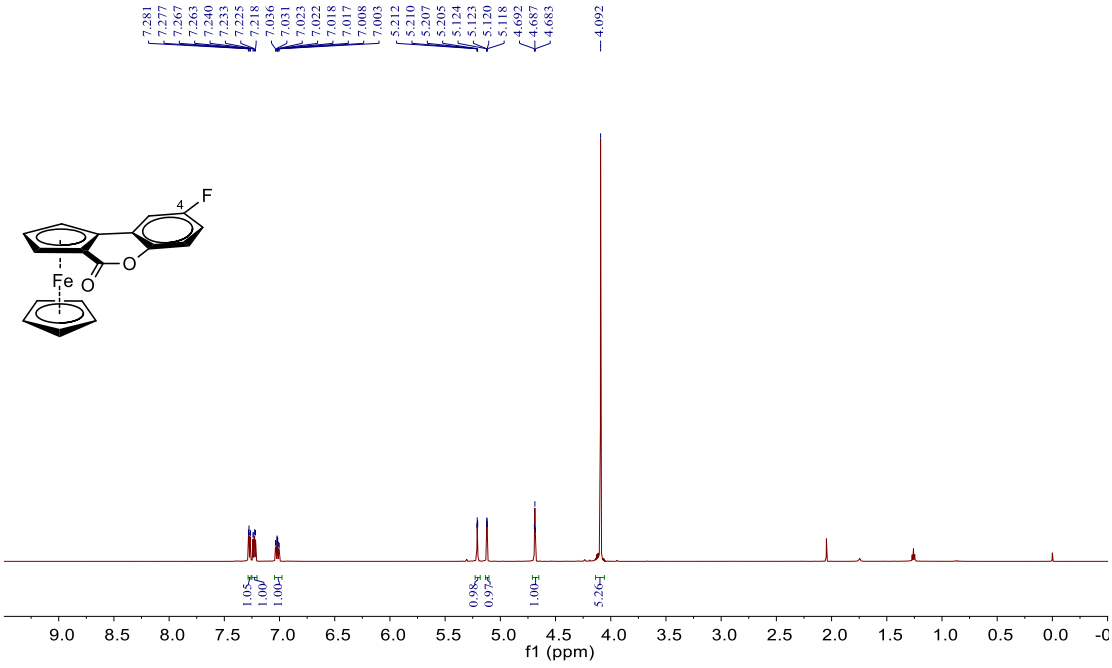

167.461
150.776
140.151
137.634
129.032
127.643
127.170
127.156
126.871
121.903
121.487
117.657
83.328
77.160
73.183
71.397
68.540
65.339
64.525
Ph
4
Fe
O
O
f1 (ppm)

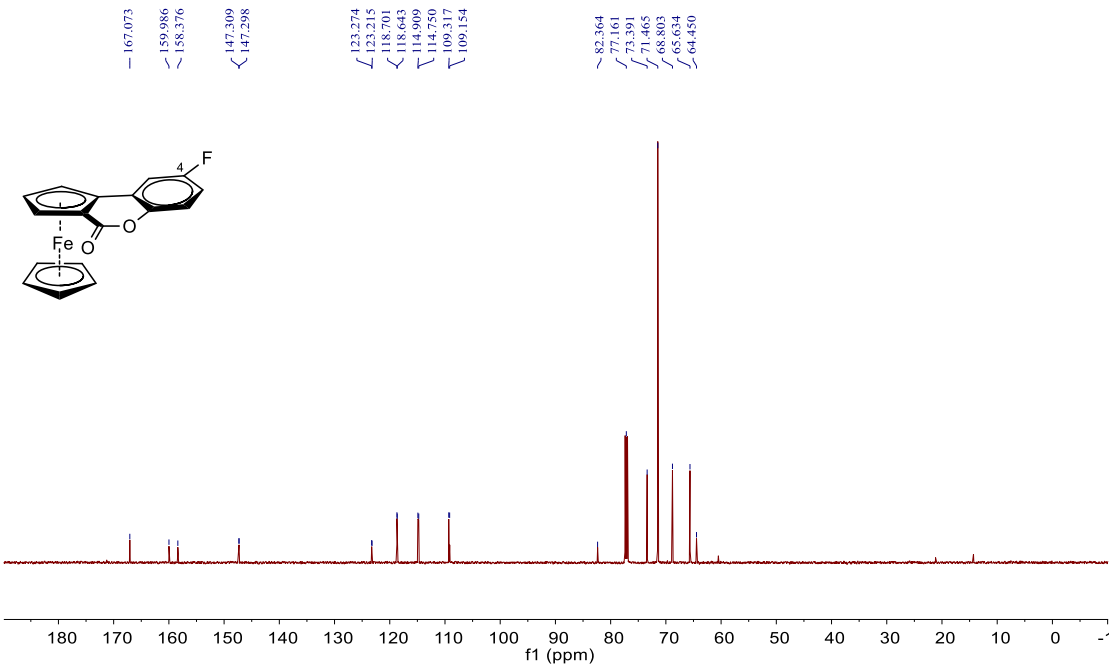
2j

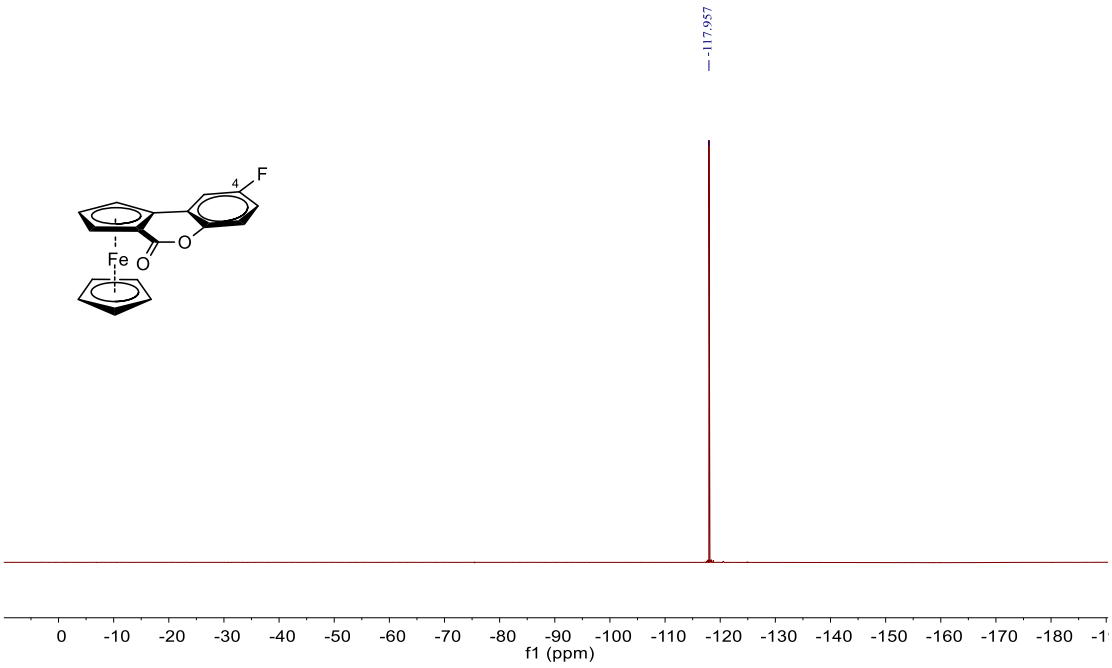

7.188
7.165
7.051
7.043
6.865
6.858
6.842
6.835
5.166
5.163
5.159
5.156
5.104
5.101
5.098
5.095
4.636
4.629
4.623
4.053
3.859
OMe
4
O
Fe
O
1.00
1.00
1.01
0.97
1.00
1.00
4.94
3.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


167.615
156.214
145.524
122.364
118.131
113.668
107.441
83.331
77.160
73.041
71.351
68.499
65.314
64.659
55.860
OMe
4
O
Fe
O
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)

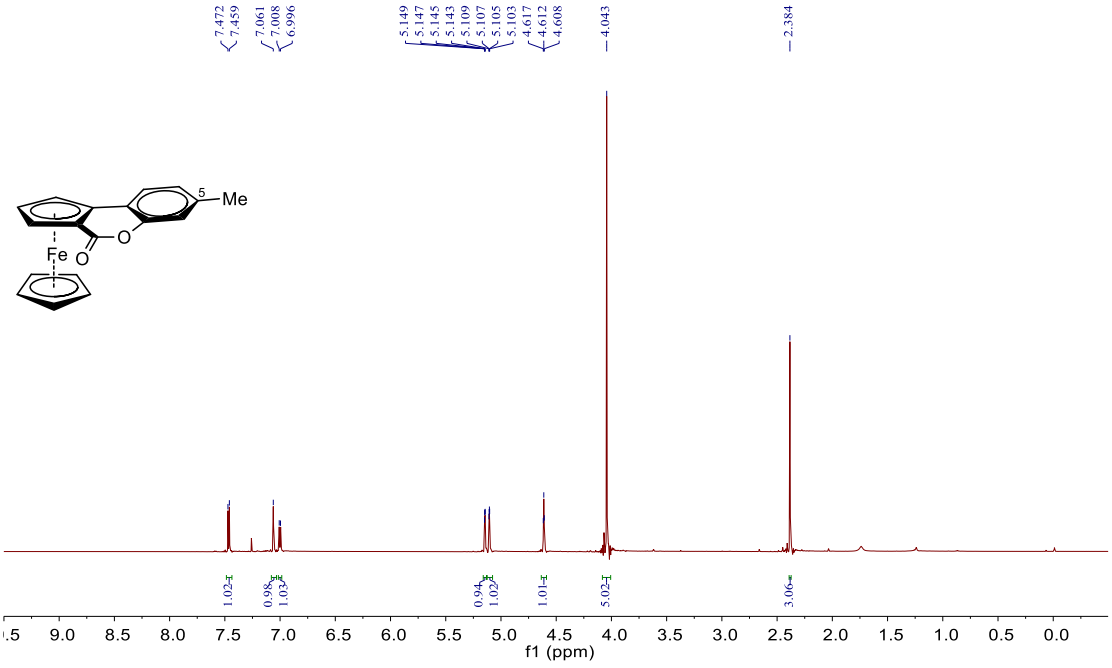
2k

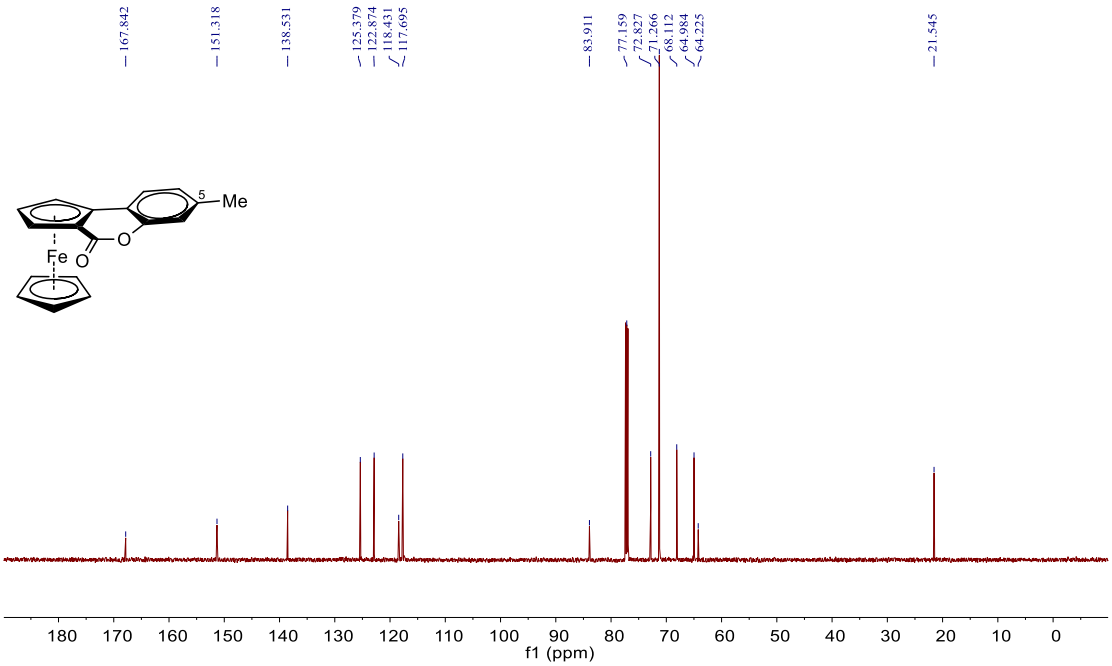

7.281
7.277
7.267
7.263
7.240
7.233
7.225
7.218
7.036
7.031
7.023
7.022
7.018
7.017
7.008
7.003
5.212
5.210
5.207
5.205
5.124
5.123
5.120
5.118
4.692
4.687
4.683
4.092
F
4
O
Fe
O
1.05
1.00
1.00
0.98
0.97
1.00
5.26
f1 (ppm)


167.073
159.986
158.376
147.309
147.298
123.274
123.215
118.701
118.643
114.909
114.750
109.317
109.154
82.364
77.161
73.391
71.465
68.803
65.634
64.450
F
4
O
Fe
O
f1 (ppm)

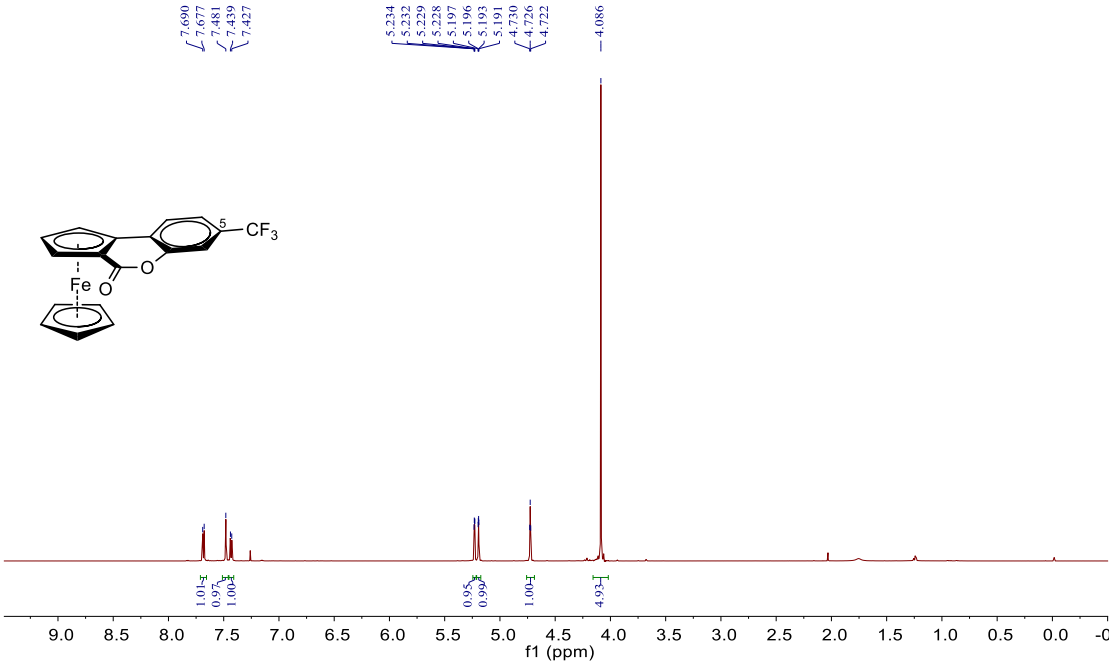

-117.957
F
4
O
Fe
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

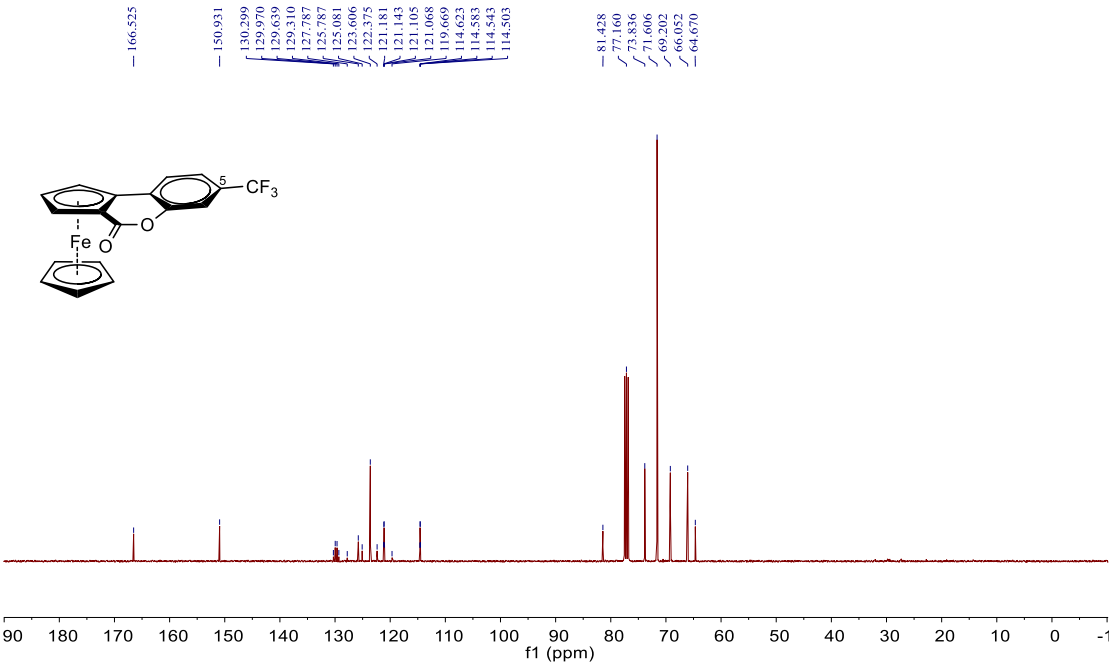
2l

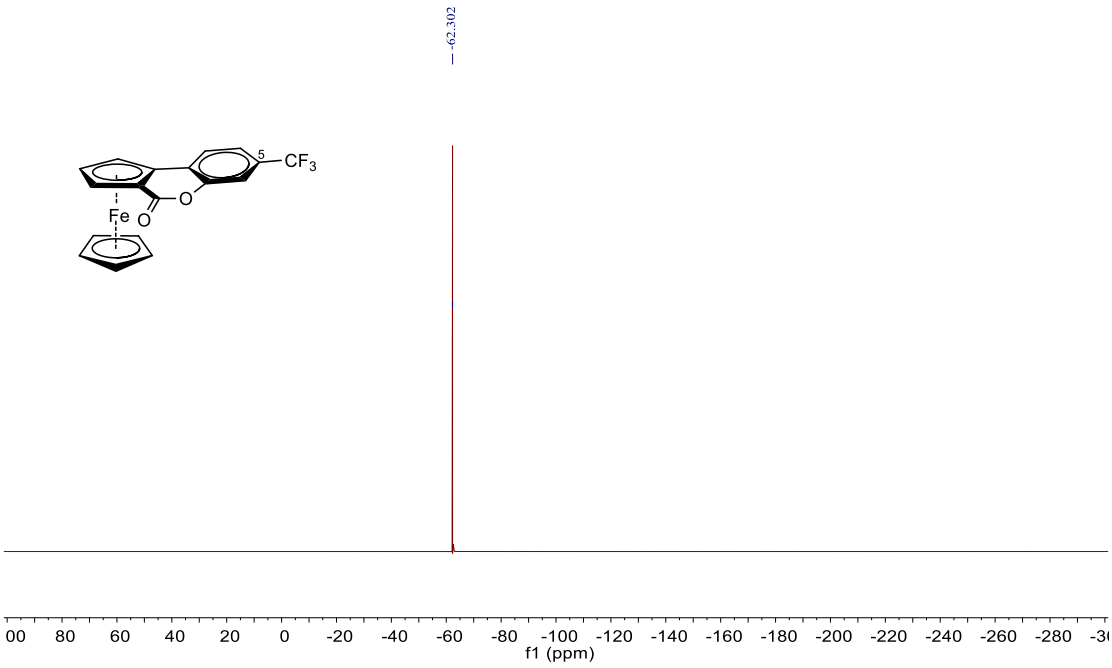

7.472
7.459
7.061
7.008
6.996
5.149
5.147
5.145
5.143
5.109
5.107
5.105
5.103
4.617
4.612
4.608
4.043
2.384
Me
5
O
Fe
O
1.02
0.98
1.03
0.94
1.02
1.01
5.02
3.06
f1 (ppm)


167.842
151.318
138.531
125.379
122.874
118.431
117.695
83.911
77.159
72.827
71.266
68.112
64.984
64.225
21.545
Me
5
O
Fe
O
f1 (ppm)

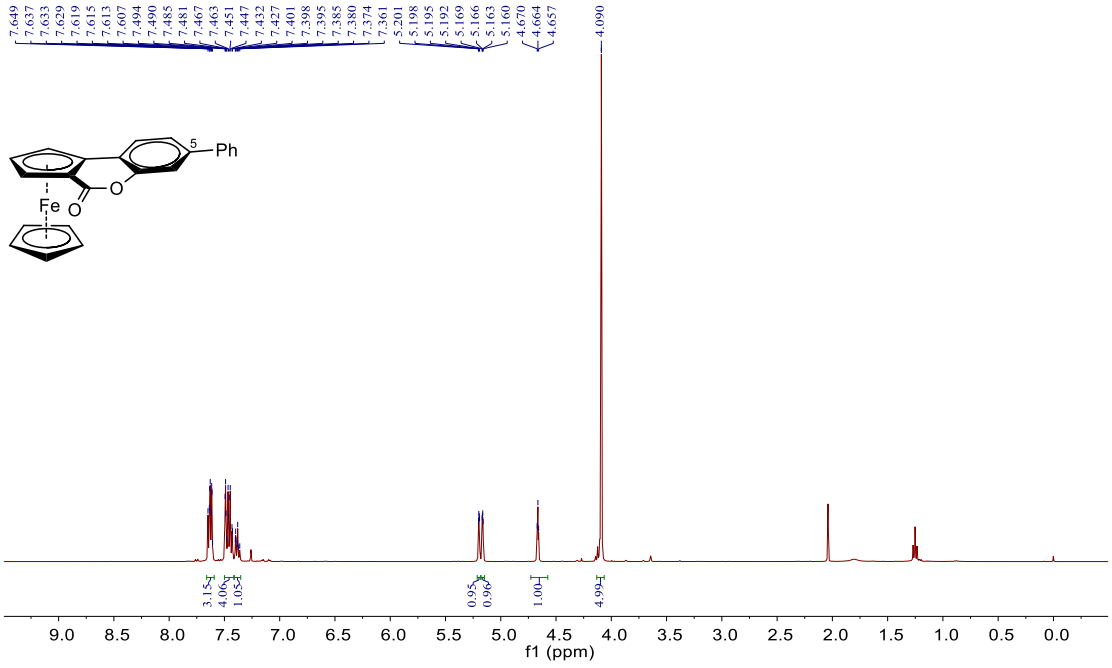
2m

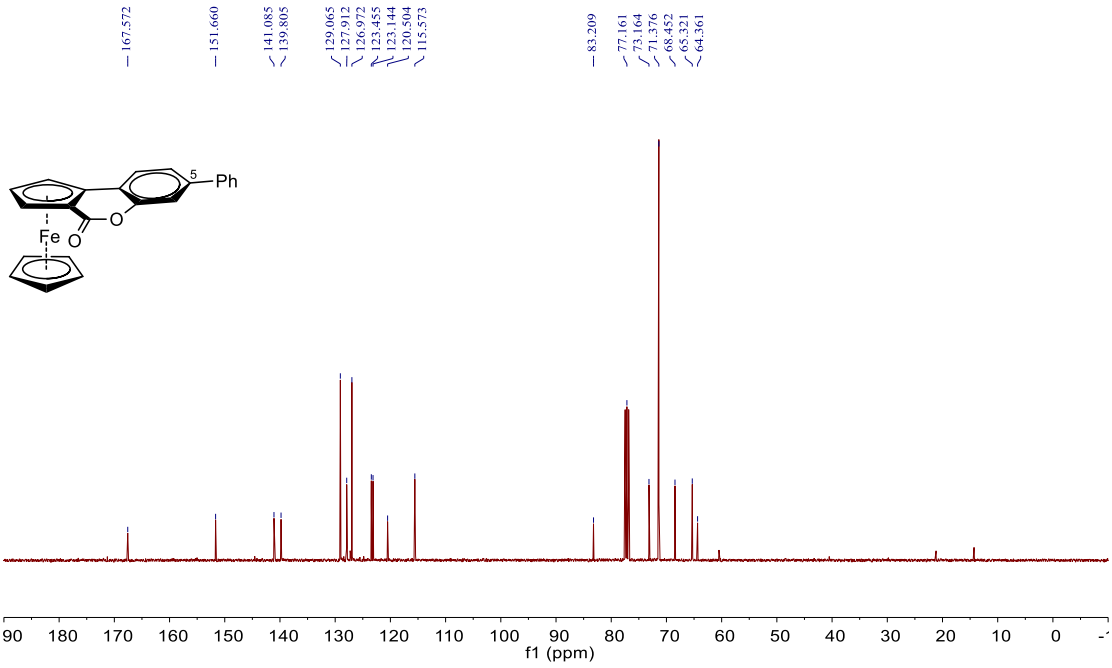

7.690
7.677
7.481
7.439
7.427
5.234
5.232
5.229
5.228
5.197
5.196
5.193
5.191
4.730
4.726
4.722
4.086
1.01
0.97
1.00
0.95
0.99
1.00
4.93
CF3
5
O
Fe
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.525
150.931
130.299
129.970
129.639
129.310
127.787
125.787
125.081
123.606
122.375
121.181
121.143
121.105
121.068
119.669
114.623
114.583
114.543
114.503
81.428
77.160
73.836
71.606
69.202
66.052
64.670
CF3
5
O
Fe
O
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

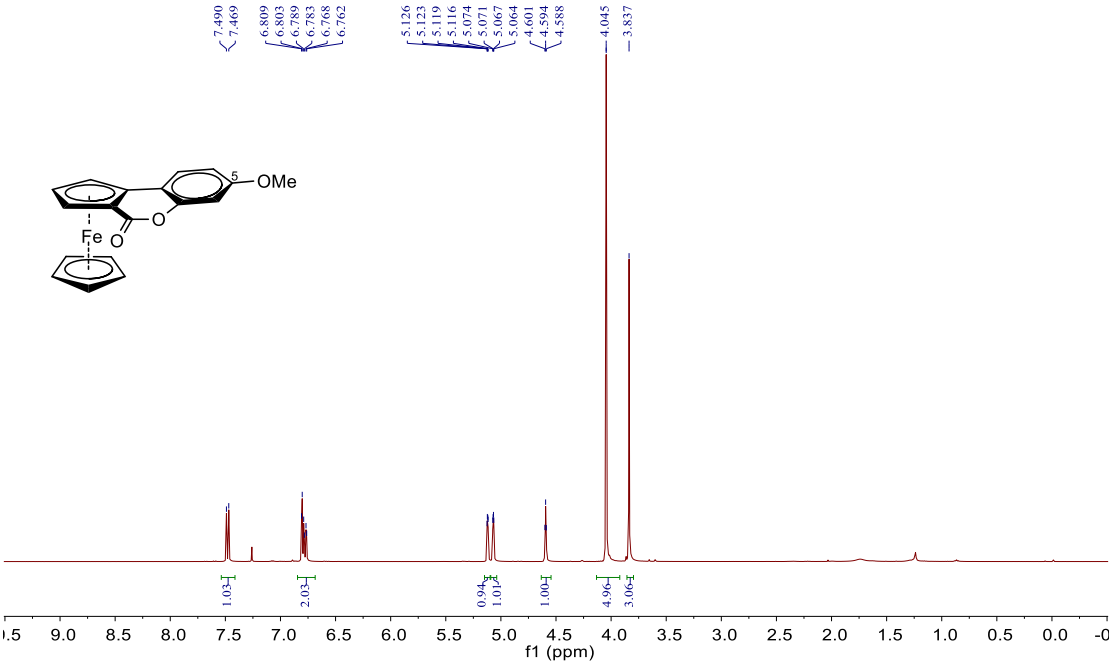

-62.302
5
CF3
O
Fe
O
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -3
f1 (ppm)

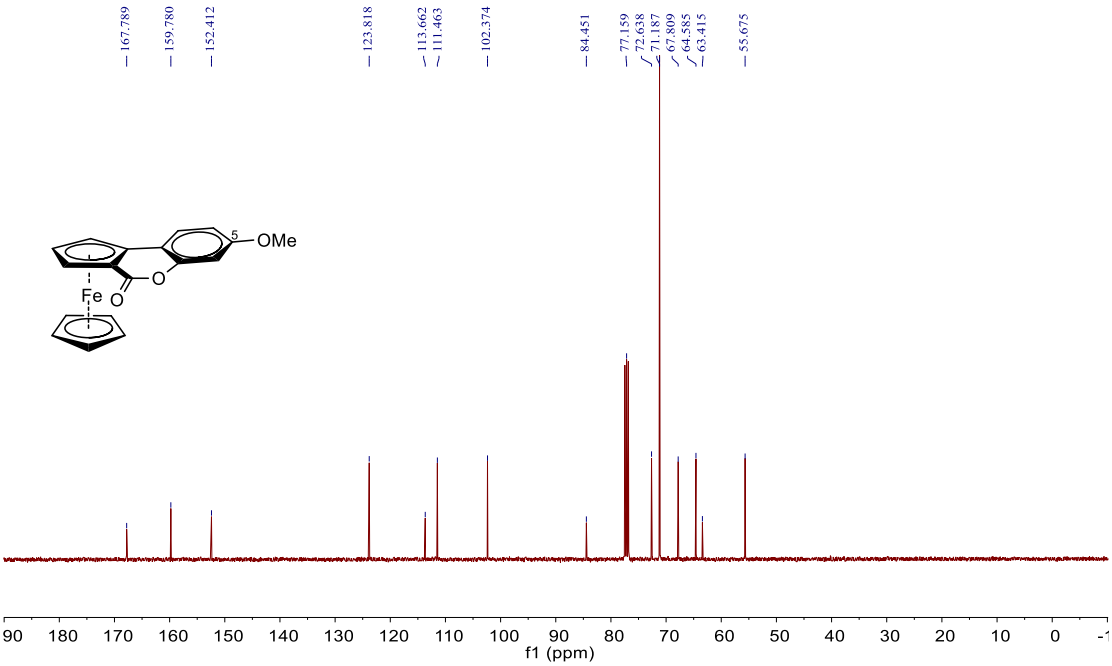
2n


7.649
7.637
7.633
7.629
7.619
7.615
7.613
7.607
7.494
7.490
7.485
7.481
7.467
7.463
7.451
7.447
7.432
7.427
7.401
7.398
7.395
7.385
7.380
7.374
7.361
5.201
5.198
5.195
5.192
5.169
5.166
5.163
5.160
4.670
4.664
4.657
4.090
Ph
5
O
Fe
O
3.15
4.06
1.05
0.95
0.96
1.00
4.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

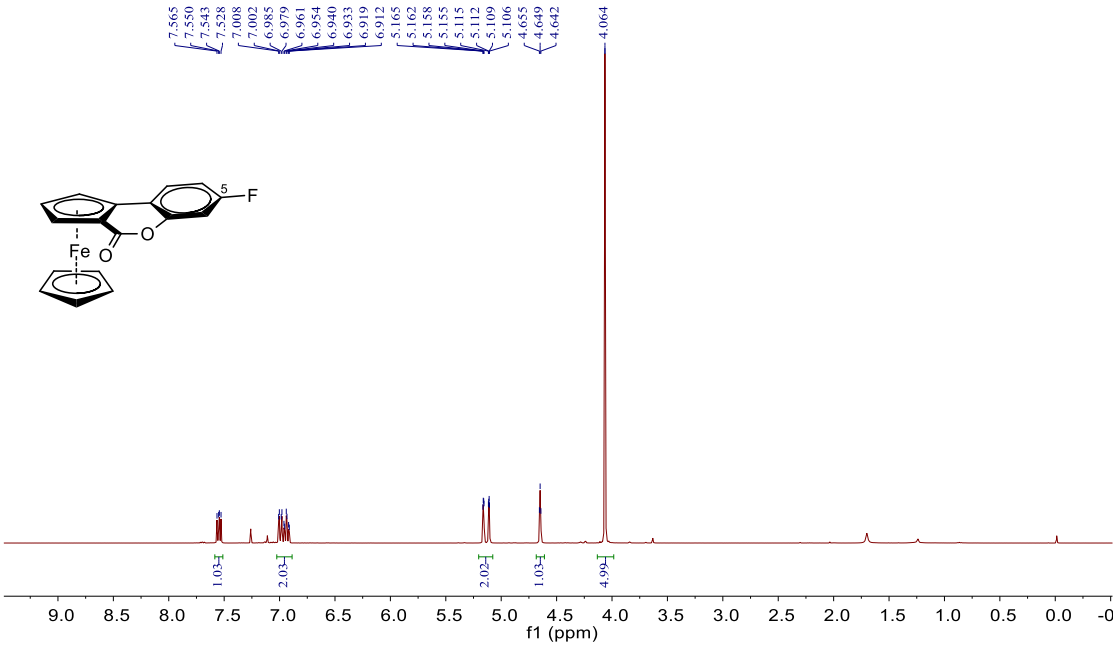

167.572
151.660
141.085
139.805
129.065
127.912
126.972
123.455
123.144
120.504
115.573
83.209
77.161
73.164
71.376
68.452
65.321
64.361
Ph
5
O
Fe
O
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

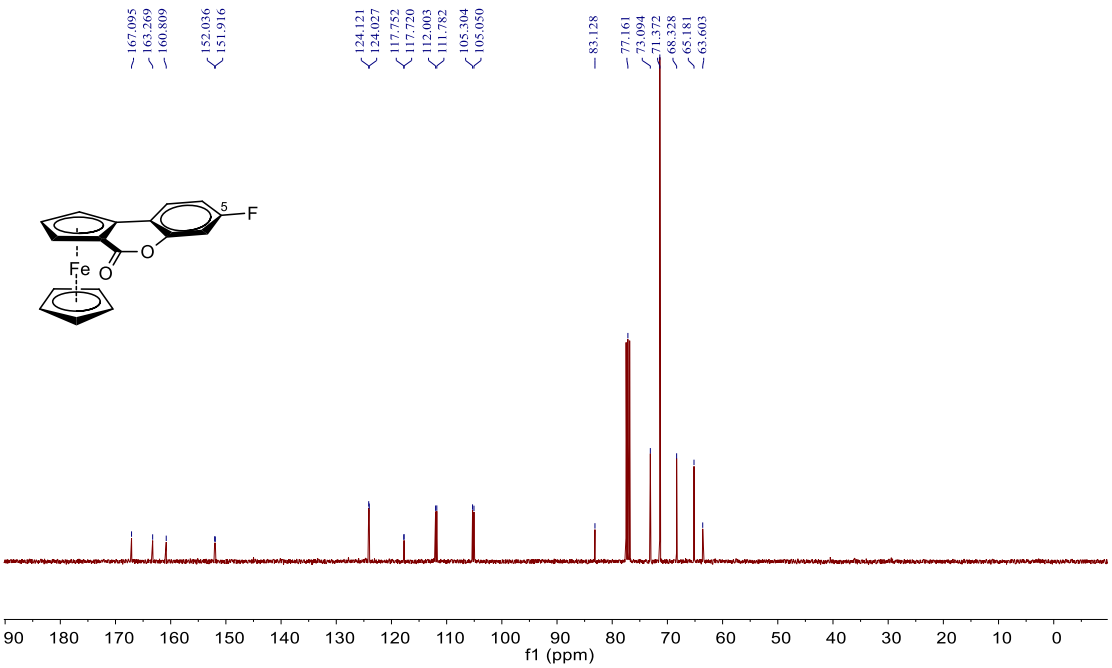
2o

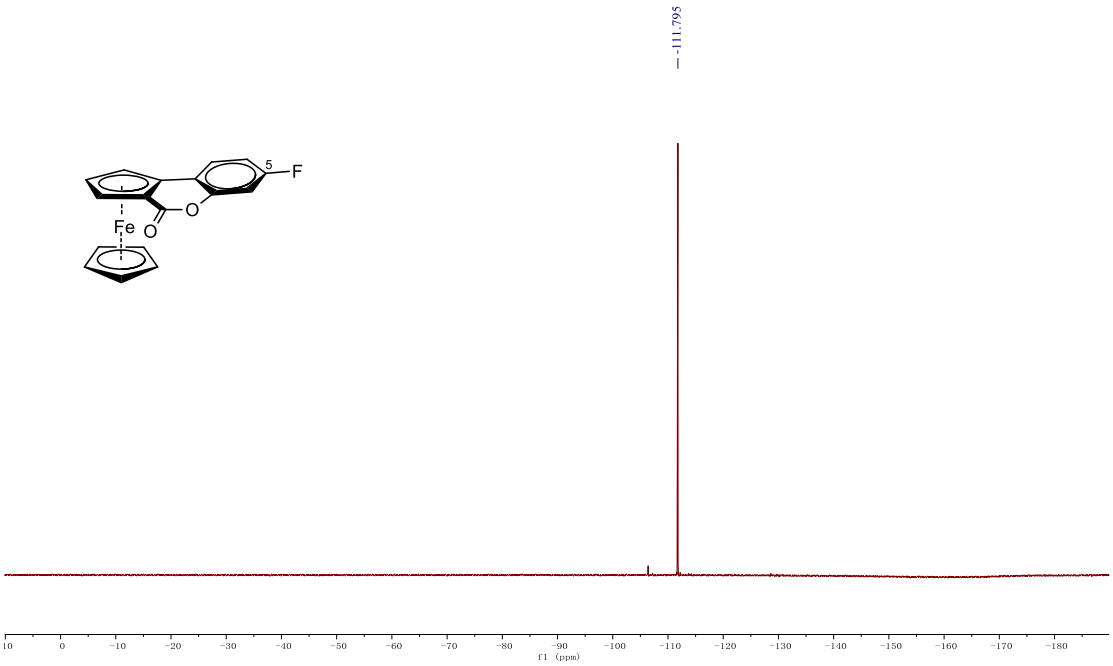

7.490
7.469
6.809
6.803
6.789
6.783
6.768
6.762
5.126
5.123
5.119
5.116
5.074
5.071
5.067
5.064
4.601
4.594
4.588
4.045
3.837
OMe
Fe
O
1.03
2.03
0.94
1.01
1.00
4.96
3.06
f1 (ppm)


167.789
159.780
152.412
123.818
113.662
111.463
102.374
84.451
77.159
72.638
71.187
67.809
64.585
63.415
55.675
OMe
Fe
O
f1 (ppm)

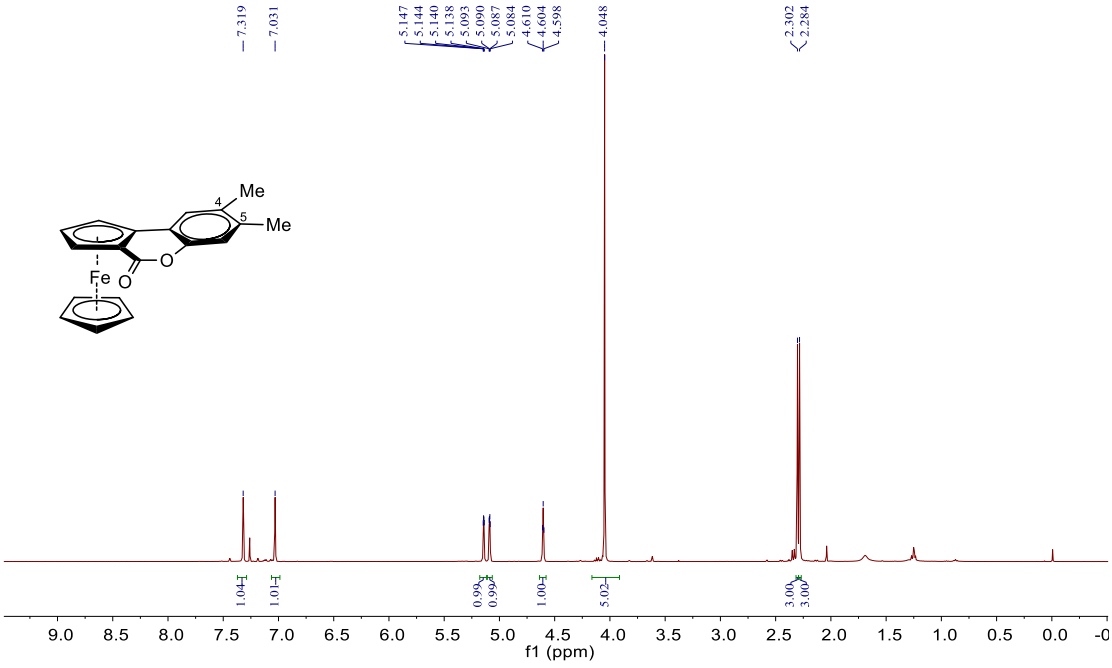
2p

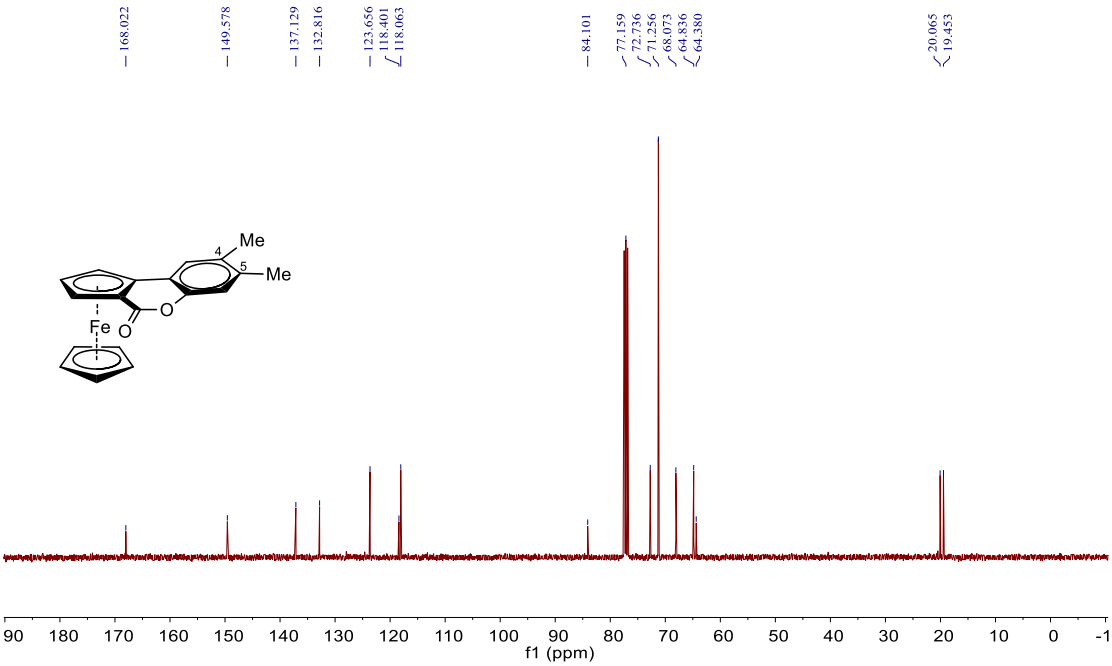

7.565
7.550
7.543
7.528
7.008
7.002
6.985
6.979
6.961
6.954
6.940
6.933
6.919
6.912
5.165
5.162
5.158
5.155
5.115
5.112
5.109
5.106
4.655
4.649
4.642
4.064
F
O
Fe
1.03
2.03
2.02
1.03
4.99
f1 (ppm)


167.095
163.269
160.809
152.036
151.916
124.121
124.027
117.752
117.720
112.003
111.782
105.304
105.050
83.128
77.161
73.094
71.372
68.328
65.181
63.603
F
O
Fe
f1 (ppm)

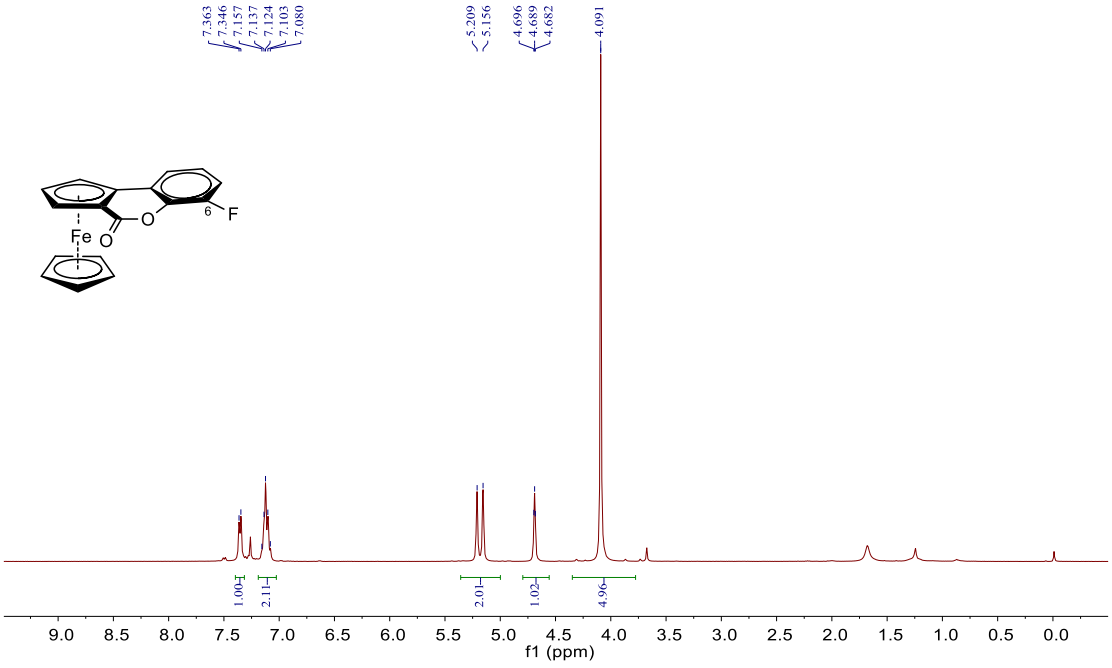

-111.795
5
F
O
Fe
O
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
f1 (ppm)

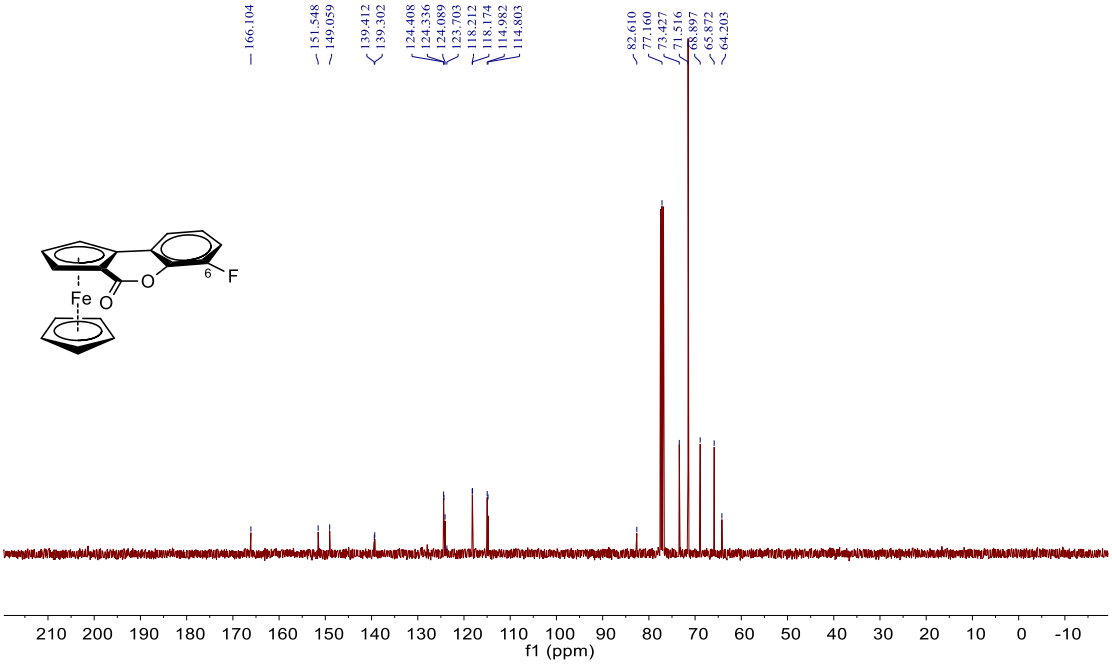
2q


7.319
7.031
5.147
5.144
5.140
5.138
5.093
5.090
5.087
5.084
4.610
4.604
4.598
4.048
2.302
2.284
Me
Me
4
5
O
Fe
O
1.04
1.01
0.99
0.99
1.00
5.02
3.00
3.00
f1 (ppm)


168.022
149.578
137.129
132.816
123.656
118.401
118.063
84.101
77.159
72.736
71.256
68.073
64.836
64.380
20.065
19.453
Me
Me
4
5
O
Fe
O
f1 (ppm)

2r


7.363
7.346
7.157
7.137
7.124
7.103
7.080
5.209
5.156
4.696
4.689
4.682
4.091
Fe
O
O
6
F
1.00
2.11
2.01
1.02
4.96
f1 (ppm)


166.104
151.548
149.059
139.412
139.302
124.408
124.336
124.089
123.703
118.212
118.174
114.982
114.803
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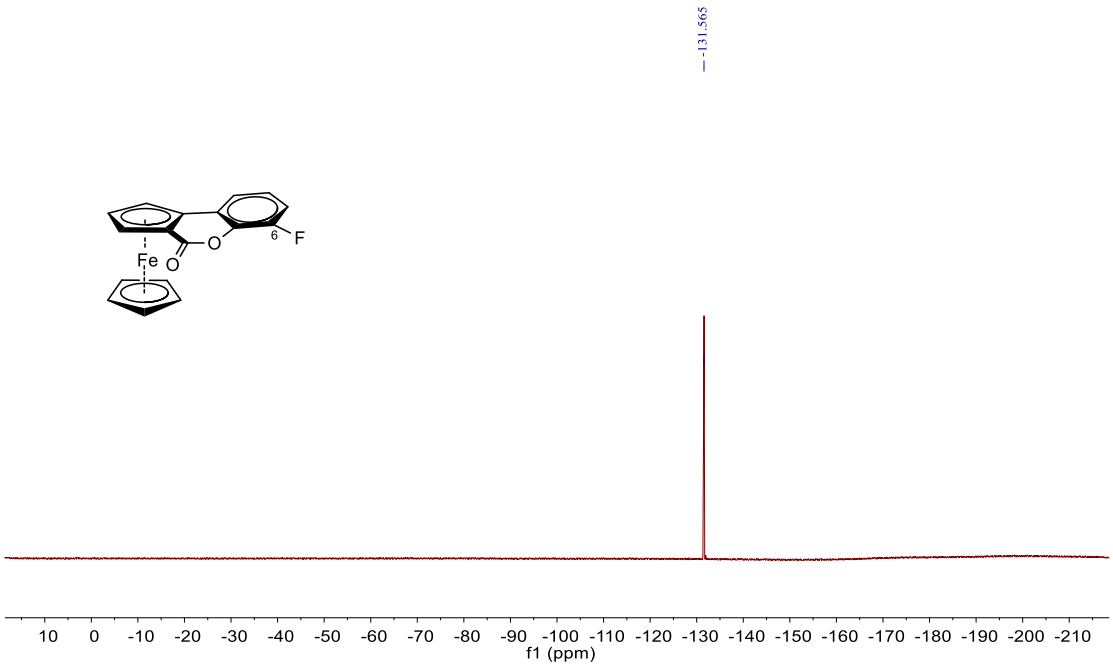
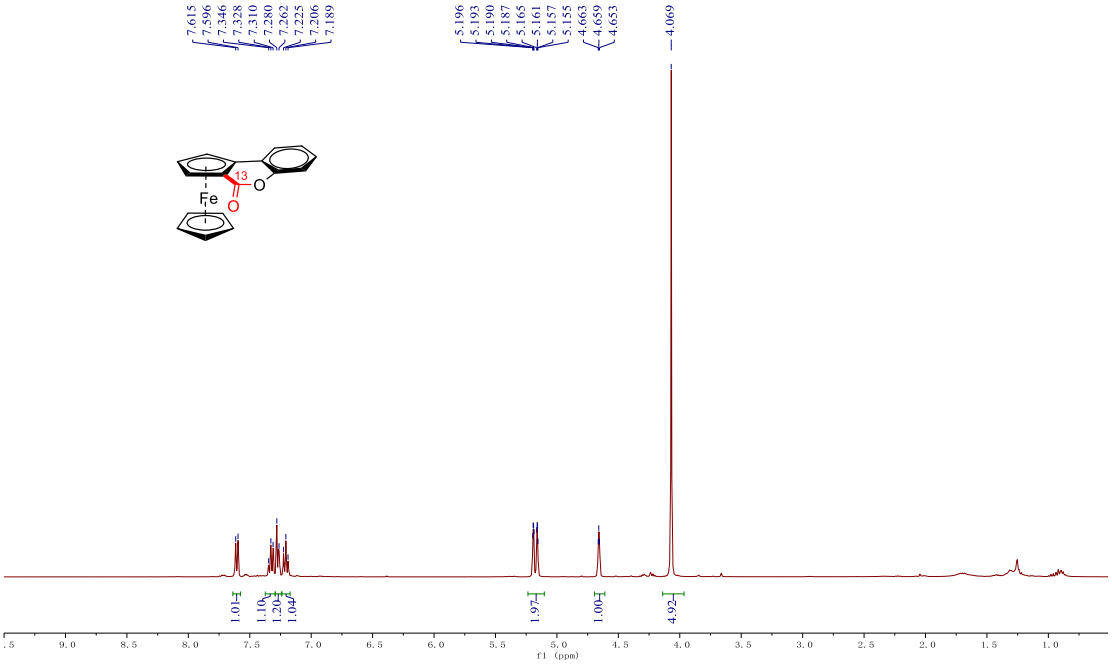
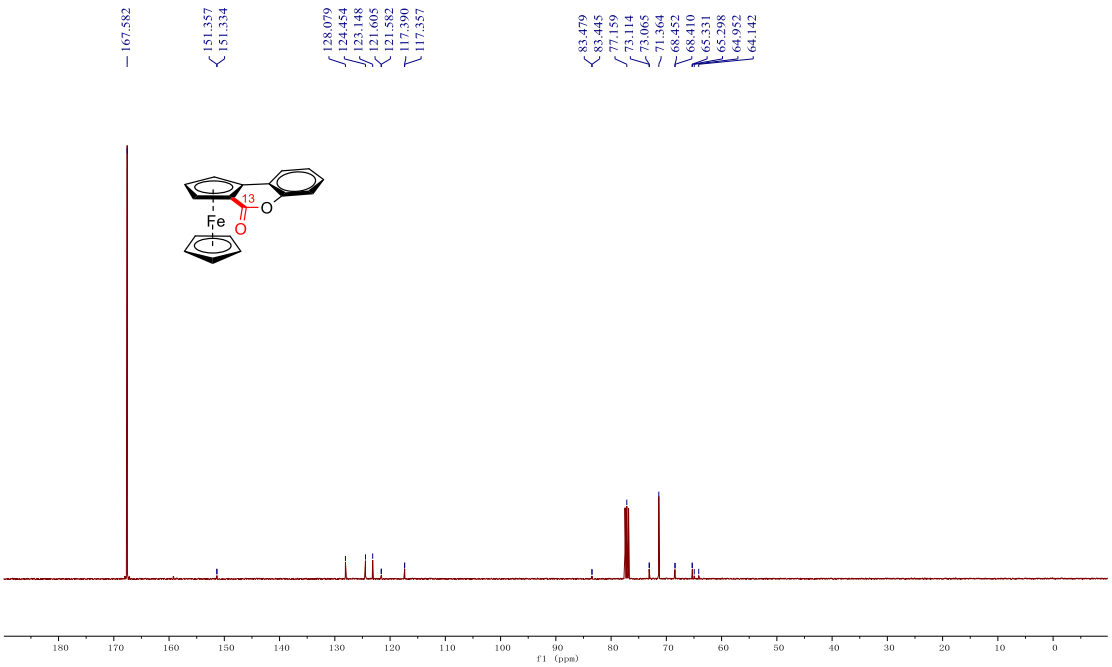
73.427
71.516
68.897
65.872
64.203
Fe
O
O
6
F
f1 (ppm)


-131.565
Fe
O
O
6
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^{13}C-**2a**


7.615
7.596
7.346
7.328
7.310
7.280
7.262
7.225
7.206
7.189
5.196
5.193
5.190
5.187
5.165
5.161
5.157
5.155
4.663
4.659
4.653
4.069
Fe
O
13
O
1.01
1.10
1.20
1.04
1.97
1.00
4.92
f1 (ppm)


167.582
151.357
151.334
128.079
124.454
123.148
121.605
121.582
117.390
117.357
83.479
83.445
77.159
73.114
73.065
71.364
68.452
68.410
65.331
65.298
64.952
64.142
Fe
O
13
O
f1 (ppm)