
Supplementary information

Iridium(I)-catalyzed enantioselective five- and six-membered C–H silylation of ferrocenes

Fang Gao, Hexin Sun, Hongpeng Zhang, Dongbing Zhao

Table of Contents

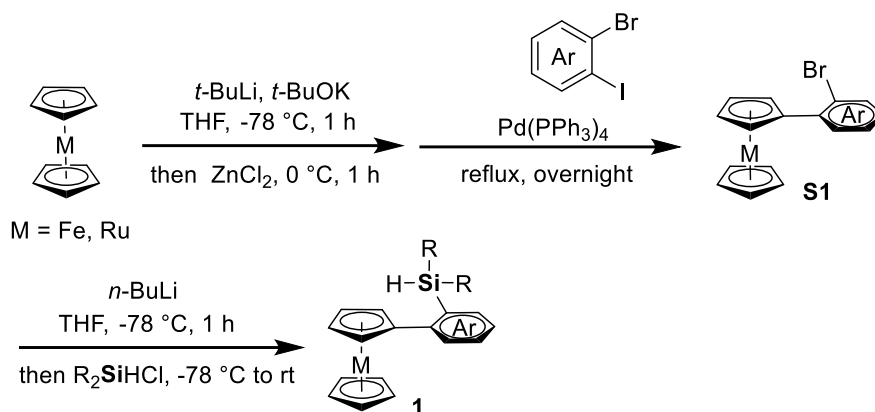
1. General Information	2
2. Iridium-Catalyzed 5-Membered Enantioselective C–H Silylation of Ferrocenes.....	3
2.1 General procedures for the synthesis of substrate 1	3
2.2 Characterization of substrates 1	4
2.3 Reaction condition optimization.....	12
2.4 General procedure for the Ir-catalyzed asymmetric C–H silylation of Ferrocenes 1	14
2.5 Characterization of products 2	15
3. Iridium-Catalyzed 6-Membered Enantioselective C–H Silylation of Ferrocenes.....	24
3.1 General procedures for the synthesis of starting materials 3	24
3.2 Characterization of starting materials 3	26
3.3 General procedure for the Ir-catalyzed asymmetric 6-membered C–H silylation	33
3.4 Characterization of products 4	34
4. Applications of Product 4a	46
4.1 Ligand synthesis.....	46
4.2 Applications of chiral ligands FcL1 and FcL2	49
5. References.....	51
6. NMR Spectra.....	52
7. HPLC Traces.....	155

1. General Information

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware. Unless otherwise mentioned, all other reagents were purchased from commercial sources and were used without further purification. Solvent was purified according to the procedure from the book named "Purification of Laboratory Chemicals". Flash column chromatography was performed on silica gel (particle size 200-300 mesh). NMR spectra were recorded on a Bruker 400MHz spectrometer and were calibrated using residual solvent as an internal reference (CDCl_3 : 7.26 ppm for ^1H NMR and 77 ppm for ^{13}C NMR; CD_3COCD_3 : 2.05 ppm for ^1H NMR and 29.84 ppm for ^{13}C NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Enantiomeric excesses (ee values) of the products were determined by chiral HPLC analysis using a Thermo U3000 instrument (n-hexane/iPrOH as eluent) with a Daicel chiralcel® OD-H or OD-3 or IA-3 or IC-3 Column (column temperature 25 °C). Optical rotation was measured on IP-digi300/2 apparatus with a sodium lamp (589 nm) at 25 °C. Melting points were determined on a X-4B melting point apparatus. High-resolution mass spectra were recorded on an IonSpec FT-ICR mass spectrometer or Agilent 6520 Q-TOF LC-MS with ESI resource. Absolute configurations were determined by comparison of specific rotations with literature data. Racemic compounds were prepared by use of (*rac*)-4-phenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole as the ligand under the same reaction condition.

2. Iridium-Catalyzed 5-Membered Enantioselective C–H Silylation of Ferrocenes

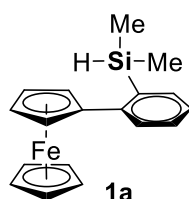
2.1 General procedures for the synthesis of substrate **1**¹⁻³



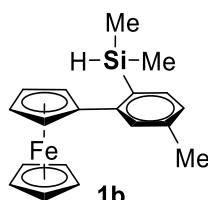
The stirred solution of metallocene (20 mmol) in THF (60 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ under N_2 , *t*-BuOK (10 mol%, 224 mg) was added followed by dropwise addition of *t*-BuLi (42 mmol, 1.6 M, 26 mL). After being stirred at this temperature for 1 h, ZnCl_2 (42 mmol, 5.7 g) was added in one portion and the system was gradually warmed to room temperature in 1 h. $\text{Pd}(\text{PPh}_3)_4$ (1.0 mmol, 1.15 g) and 2-bromiodobenzene derivatives (20 mmol) were added sequentially. The stirring was continued for additional 4 h after being heated to $60\text{ }^{\circ}\text{C}$. The reaction was quenched with 2N HCl aq. (50 mL), the organic phase was separated, sequentially washed with water (50 mL), brine (50 mL) and dried with MgSO_4 . The mixture was filtered and concentrated under reduced pressure. Column chromatography on silica gel by using hexane as eluent provided the aryl bromide **S1**.

The aryl bromide **S1** (5 mmol) was dissolved in THF (25 mL) and cooled to $-78\text{ }^{\circ}\text{C}$ under N_2 . *n*-BuLi (5.5 mmol, 2.5 M, 2.2 mL) was added dropwise and the mixture was stirred for additional 10 min. The reaction system was allowed to warm to room temperature after the addition of silane chloride (6 mmol) and stirred overnight. After the reaction was finished, the reaction mixture was quenched with water (5 mL) and the volatile compound was removed under reduced pressure. The residue was extracted with DCM for three times ($30\text{ mL} \times 3$). The combined organic layer was separated, washed with brine (30 mL), dried with Na_2SO_4 . The mixture was filtered and concentrated under reduced pressure. Column chromatography on silica gel by using hexane as eluent provided the substrate **1**.

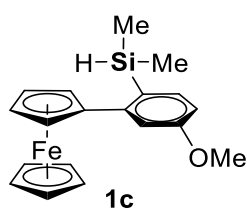
2.2 Characterization of substrates 1



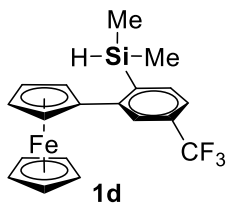
According to general procedure, **1a** was obtained in 42% yield as dark orange solid. $R_f = 0.5$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.98 (d, $J = 7.7$ Hz, 1H), 7.47 – 7.39 (m, 2H), 7.24 (t, $J = 7.4$ Hz, 1H), 4.53 – 4.49 (m, 3H), 4.31 (t, $J = 1.9$ Hz, 2H), 4.18 (s, 5H), 0.09 (d, $J = 3.8$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 145.88, 136.72, 135.28, 132.08, 129.84, 126.54, 92.24, 71.14, 70.20, 68.53, -2.78.



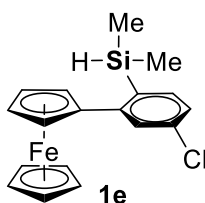
According to general procedure, **1b** was obtained in 47% yield as dark orange solid. $R_f = 0.5$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.80 (s, 1H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.07 (ddd, $J = 7.6, 1.8, 0.8$ Hz, 1H), 4.49 – 4.45 (m, 3H), 4.29 (t, $J = 1.9$ Hz, 2H), 4.17 (s, 5H), 2.40 (s, 3H), 0.07 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 145.84, 139.44, 135.47, 133.21, 132.79, 127.43, 92.30, 71.07, 70.20, 68.43, -2.72.



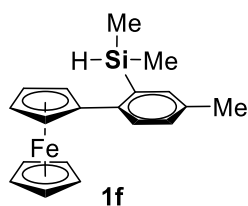
According to general procedure, **1c** was obtained in 36% yield as dark orange solid. $R_f = 0.5$ (Hexane/Ethyl acetate = 20:1). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.54 (d, $J = 2.6$ Hz, 1H), 7.36 (d, $J = 8.3$ Hz, 1H), 6.84 (dd, $J = 8.3, 2.6$ Hz, 1H), 4.51 (t, $J = 1.8$ Hz, 2H), δ 4.48 – 4.45 (m, 1H), 4.30 (t, $J = 1.8$ Hz, 2H), 4.20 (s, 5H), 3.90 (s, 3H), 0.06 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 161.26, 147.72, 136.86, 127.71, 117.66, 112.59, 92.35, 71.18, 70.20, 70.19, 68.49, 55.33, -2.61.



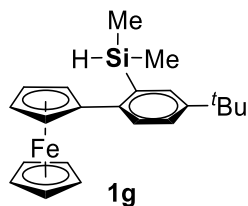
According to general procedure, **1d** was obtained in 22% yield as dark orange solid. $R_f = 0.5$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 8.25 (s, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.56 (d, $J = 8.9$ Hz, 1H), 4.59 (t, $J = 1.9$ Hz, 2H), 4.53 – 4.50 (m, 1H), 4.39 (t, $J = 1.8$ Hz, 2H), 4.20 (s, 5H), 0.14 (d, $J = 3.8$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 147.46, 142.22, 136.23, 131.13 (q, $J = 31.8$ Hz), 128.32 (q, $J = 3.8$ Hz), 125.38 (q, $J = 272.7$ Hz), 122.63 (q, $J = 3.8$ Hz), 71.41, 70.36, 69.15, 69.13, -3.14.



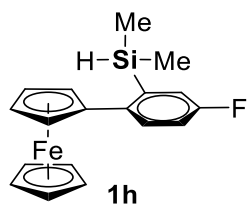
According to general procedure, **1e** was obtained in 25% yield as dark orange oil. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.96 (d, $J = 2.2$ Hz, 1H), 7.45 (d, $J = 8.1$ Hz, 1H), 7.28 (dd, $J = 8.0, 2.2$ Hz, 1H), 4.55 (t, $J = 1.9$ Hz, 2H), 4.50 – 4.44 (m, 1H), 4.36 (t, $J = 1.8$ Hz, 2H), 4.20 (s, 5H), 0.10 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 148.57, 137.12, 135.67, 135.41, 131.69, 126.55, 90.73, 71.27, 70.37, 68.97, -2.97.



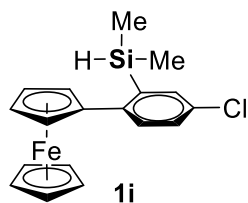
According to general procedure, **1f** was obtained in 42% yield as dark orange solid. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.86 (d, $J = 7.8$ Hz, 1H), 7.27 – 7.21 (m, 2H), 4.50 – 4.45 (m, 3H), 4.28 (t, $J = 1.8$ Hz, 2H), 4.16 (s, 4H), 2.32 (s, 3H), 0.08 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 142.77, 136.50, 135.91, 135.66, 132.06, 130.58, 92.22, 71.07, 70.14, 68.37, 21.13, -2.73.



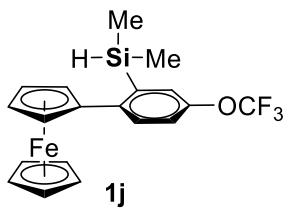
According to general procedure, **1g** was obtained in 34% yield as dark orange solid. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.90 (d, $J = 8.1$ Hz, 1H), 7.51 – 7.46 (m, 2H), 4.53–4.48 (m, 1H), 4.46 (t, $J = 1.8$ Hz, 2H), 4.29 (t, $J = 1.9$ Hz, 2H), 4.17 (s, 5H), 1.35 (s, 9H), 0.10 (d, $J = 3.8$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 148.71, 142.82, 136.13, 131.93, 131.90, 126.92, 92.20, 71.09, 70.13, 68.38, -2.69.



According to general procedure, **1h** was obtained in 30% yield as dark orange solid. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 8.08 – 8.01 (m, 1H), 7.18 – 7.13 (m, 2H), 4.50–4.43 (m, 3H), 4.31 (t, $J = 1.9$ Hz, 2H), 4.19 (s, 5H), 0.11 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 161.88 (d, $J = 246.1$ Hz), 141.90 (d, $J = 3.2$ Hz), 139.81 (d, $J = 3.9$ Hz), 134.26 (d, $J = 7.0$ Hz), 121.02 (d, $J = 19.1$ Hz), 116.49 (d, $J = 21.1$ Hz), 91.32, 71.23, 70.20, 68.58, -3.08.

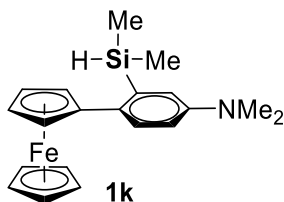


According to general procedure, **1i** was obtained in 42% yield as dark orange solid. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.99 (d, $J = 8.2$ Hz, 1H), 7.43 – 7.39 (m, 2H), 4.50 – 4.46 (m, 3H), 4.33 (t, $J = 1.8$ Hz, 2H), 4.19 (s, 5H), 0.12 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 144.84, 139.61, 134.55, 133.99, 132.23, 129.71, 90.85, 71.20, 70.32, 68.83, -3.07.



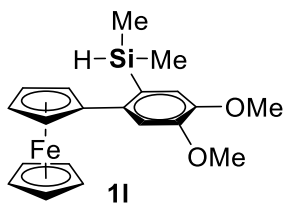
According to general procedure, **1j** was obtained in 26% yield as dark orange oil. $R_f = 0.4$ (Hexane).

$^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 8.11 (d, $J = 8.5$ Hz, 1H), 7.37 – 7.31 (m, 2H), 4.52 (t, $J = 1.8$ Hz, 2H), 4.49 (p, $J = 3.8$ Hz, 1H), 4.35 (t, $J = 1.8$ Hz, 2H), 4.21 (s, 5H), 0.12 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 147.92, 145.36, 139.81, 134.05, 127.16, 122.27, 121.48 (q, $J = 255.2$ Hz), 90.81, 71.30, 70.32, 68.86, -3.12.



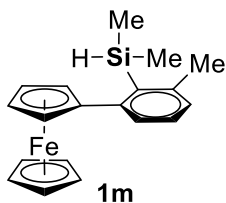
According to general procedure, **1k** was obtained in 20% yield as dark orange solid. $R_f = 0.3$

(Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.80 (dt, $J = 8.6, 1.2$ Hz, 1H), 6.85 – 6.82 (m, 2H), 4.48 (p, $J = 3.7$ Hz, 1H), 4.40 (t, $J = 1.9$ Hz, 2H), 4.23 (t, $J = 1.8$ Hz, 2H), 4.15 (s, 5H), 2.95 (s, 6H), 0.09 (d, $J = 3.8$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 149.48, 136.68, 133.06, 132.82, 119.14, 114.37, 92.74, 70.81, 69.93, 67.98, 40.68, -2.66.

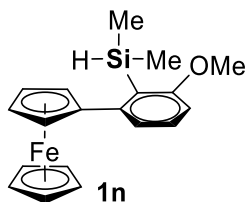


According to general procedure, **1l** was obtained in 26% yield as dark orange solid. $R_f = 0.4$

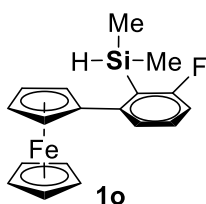
(Hexane/Ethyl acetate = 10:1). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.57 (s, 1H), 6.95 (s, 1H), 4.48 – 4.44 (m, 3H), 4.27 (t, $J = 1.8$ Hz, 2H), 4.20 (s, 5H), 3.95 (s, 3H), 3.83 (s, 3H), 0.08 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 150.66, 148.39, 139.15, 127.45, 118.64, 116.30, 92.68, 71.08, 70.09, 68.31, 56.22, 55.86, -2.60.



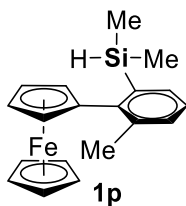
According to general procedure, **1m** was obtained in 28% yield as dark orange solid. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.85 (d, $J = 7.6$ Hz, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 7.4$ Hz, 1H), 4.41 (t, $J = 1.8$ Hz, 2H), 4.32 – 4.27 (m, 3H), 4.15 (s, 5H), 2.45 (s, 3H), 0.11 (d, $J = 4.0$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 146.31, 144.32, 136.28, 130.63, 129.23, 128.80, 94.48, 71.66, 70.15, 68.21, 23.62, -1.66.



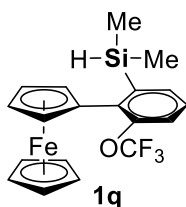
According to general procedure, **1n** was obtained in 21% yield as dark orange solid. $R_f = 0.3$ (Hexane/Ethyl acetate = 20:1). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.58 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.34 (t, $J = 8.0$ Hz, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 4.40 (t, $J = 1.8$ Hz, 2H), 4.24 (t, $J = 1.8$ Hz, 2H), 4.19 (p, $J = 3.8$ Hz, 1H), 4.12 (s, 5H), 3.82 (s, 3H), 0.20 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 165.50, 147.37, 130.76, 125.58, 125.21, 108.47, 92.00, 71.65, 70.17, 68.01, 55.69, -2.22.



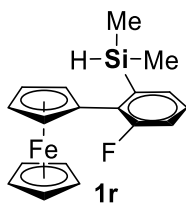
According to general procedure, **1o** was obtained in 36% yield as dark orange oil. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.83 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.42 – 7.40 (m, 1H), 6.95 (t, $J = 8.7$ Hz, 1H), 4.45 (t, $J = 1.9$ Hz, 2H), 4.31 – 4.30 (m, 3H), 4.16 (s, 5H), 0.24 (d, $J = 2.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 168.35 (d, $J = 237.9$ Hz), 148.36 (d, $J = 10.5$ Hz), 131.59 (d, $J = 9.9$ Hz), 128.83 (d, $J = 2.5$ Hz), 123.53 (d, $J = 28.9$ Hz), 113.03 (d, $J = 26.8$ Hz), 91.23, 71.62, 70.33, 68.48, -2.35.



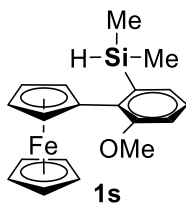
According to general procedure, **1p** was obtained in 29% yield as dark orange oil. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.35 – 7.33 (m, 1H), 7.29 – 7.24 (m, 1H), 7.17 (t, $J = 7.4$ Hz, 1H), 4.52 – 4.48 (m, 3H), 4.42 (t, $J = 1.9$ Hz, 2H), 4.18 (s, 5H), 2.93 (s, 3H), 0.02 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 142.13, 138.54, 136.48, 133.20, 132.23, 125.71, 90.61, 70.80, 69.27, 67.67, 21.07, -2.61.



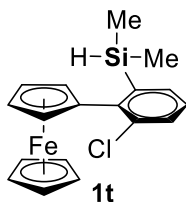
According to general procedure, **1q** was obtained in 15% yield as dark orange solid. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.51 – 7.49 (m, 1H), 7.43 (d, $J = 6.2$ Hz, 2H), 4.58 – 4.49 (m, 3H), 4.47 – 4.40 (m, 2H), 4.18 (s, 5H), 0.10 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 147.67, 142.20, 137.55, 134.55, 128.14, 122.0 (q, $J = 256.5$ Hz), 121.30 (d, $J = 1.7$ Hz), 84.83, 71.28, 70.21, 69.13, -2.34.



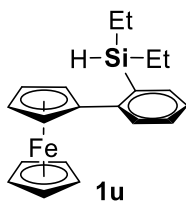
According to general procedure, **1r** was obtained in 12% yield as dark orange oil. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.34-7.32 (m, 2H), 7.26 – 7.16 (m, 1H), 4.60 – 4.55 (m, 3H), 4.38 (t, $J = 1.9$ Hz, 2H), 4.15 (s, 5H), 0.12 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 161.17 (d, $J = 249.6$ Hz), 140.74, 132.53 (d, $J = 10.8$ Hz), 131.92 (d, $J = 3.5$ Hz), 128.44 (d, $J = 7.7$ Hz), 117.65 (d, $J = 23.9$ Hz), 83.55 70.98 (d, $J = 1.8$ Hz), 70.25, 68.93, -2.52.



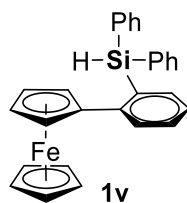
According to general procedure, **1s** was obtained in 22% yield as dark orange solid. $R_f = 0.3$ (Hexane/Ethyl acetate = 20:1). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.28 (t, $J = 7.8$ Hz, 1H), 7.11 – 7.08 (m, 2H), 4.59 – 4.51 (m, 3H), 4.30 (t, $J = 1.9$ Hz, 2H), 4.09 (s, 5H), 4.01 (s, 3H), 0.07 (d, $J = 3.6$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 157.85, 139.22, 133.02, 128.15, 127.78, 112.53, 87.13, 71.29, 69.98, 68.15, 55.43, -2.11.



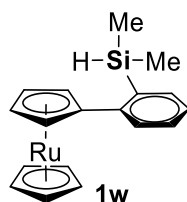
According to general procedure, **1t** was obtained in 14% yield as dark orange oil. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.51 – 7.46 (m, 2H), 7.27 (t, $J = 7.6$ Hz, 1H), 4.64 (t, $J = 1.9$ Hz, 2H), 4.55 – 4.51 (m, 1H), 4.44 (t, $J = 1.9$ Hz, 2H), 4.21 (s, 5H), 0.06 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 142.62, 142.22, 135.12, 134.73, 132.54, 127.80, 88.77, 71.62, 70.44, 68.81, -2.08.



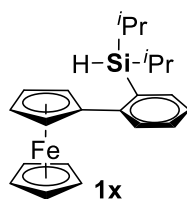
According to general procedure, **1u** was obtained in 40% yield as dark orange oil. $R_f = 0.5$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.99 (d, $J = 7.7$ Hz, 1H), 7.46 – 7.39 (m, 2H), 7.24 (td, $J = 7.4, 1.2$ Hz, 1H), 4.47 (t, $J = 1.9$ Hz, 2H), 4.30 (t, $J = 1.8$ Hz, 2H), 4.24 (p, $J = 3.3$ Hz, 1H), 4.18 (s, 5H), 0.86 (t, $J = 7.8$ Hz, 6H), 0.64 – 0.60 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 146.12, 136.14, 134.75, 132.22, 129.80, 126.42, 92.24, 71.18, 70.19, 68.45, 8.66, 4.50.



According to general procedure, **1v** was obtained in 40% yield as dark orange solid. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 8.06 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.49 – 7.34 (m, 11H), 7.29 – 7.26 (m, 1H), 7.21 – 7.19 (m, 1H), 5.40 (s, 1H), 4.41 (t, $J = 1.9$ Hz, 2H), 4.14 (t, $J = 1.8$ Hz, 2H), 4.08 (s, 5H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 147.27, 137.61, 136.44, 136.42, 135.28, 132.25, 132.04, 130.49, 130.44, 128.84, 126.32, 90.78, 71.12, 70.20, 68.62.



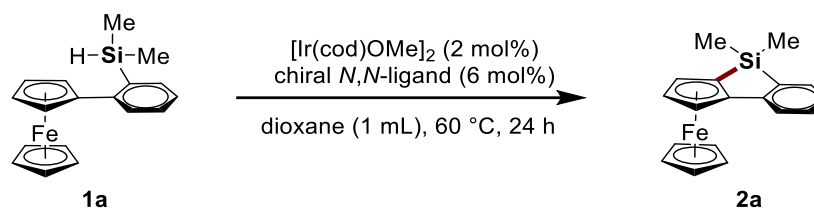
According to general procedure, **1w** was obtained in 22% yield as colorless oil. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.63 (dd, $J = 7.5, 1.3$ Hz, 1H), 7.46 (dd, $J = 7.1, 1.5$ Hz, 1H), 7.30 (td, $J = 7.5, 1.6$ Hz, 1H), 7.23 (td, $J = 7.4, 1.4$ Hz, 1H), 4.81 (t, $J = 1.7$ Hz, 2H), 4.63 (t, $J = 1.7$ Hz, 2H), 4.61 (s, 5H), 4.55 – 4.50 (m, 1H), 0.19 (d, $J = 3.8$ Hz, 7H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 144.45, 137.14, 134.90, 134.15, 129.72, 126.90, 97.88, 74.21, 72.08, 70.35, -2.75.



According to general procedure, **1x** was obtained in 38% yield as dark orange oil. $R_f = 0.4$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 8.02 (dd, $J = 7.8, 0.7$ Hz, 1H), 7.46 – 7.39 (m, 2H), 7.25 (td, $J = 7.4, 1.3$ Hz, 1H), 4.45 (t, $J = 1.8$ Hz, 2H), 4.29 (t, $J = 1.8$ Hz, 2H), 4.17 (s, 5H), 3.93 (t, $J = 3.9$ Hz, 1H), 1.14 – 1.05 (m, 2H), 0.98 (d, $J = 7.1$ Hz, 6H), 0.87 (d, $J = 7.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 146.18, 136.61, 134.56, 132.44, 129.61, 126.21, 92.30, 71.55, 70.17, 68.32, 19.71, 19.55, 12.40.

2.3 Reaction condition optimization

Table S1 Chiral ligands screening for the enantioselective C–H silylation of **1a**^[a]



entry	ligand	yield (%) ^[b]	ee (%) ^[c]	entry	ligand	yield (%) ^[b]	ee (%) ^[c]
1	L1	96	95	8	L8	93	88
2	L2	99	98	9	L9	94	97
3	L3	93	73	10	L10	95	91
4	L4	93	80	11	L11	96	81
5	L5	96	61	12	L12	92	79
6	L6	90	96	13	L13	N.R	N.R
7	L7	97	66	14	L14	N.R	N.R

[a] The reaction was conducted with **1a** (0.2 mmol), [Ir(cod)OMe]₂ (2 mol%), chiral *N,N*-ligand (6 mol%) in dioxane (1 mL) at 60 °C under N₂ for 24 h. [b] Yields were determined by NMR using TCE as internal standard. [c] Ee values were determined by chiral HPLC.

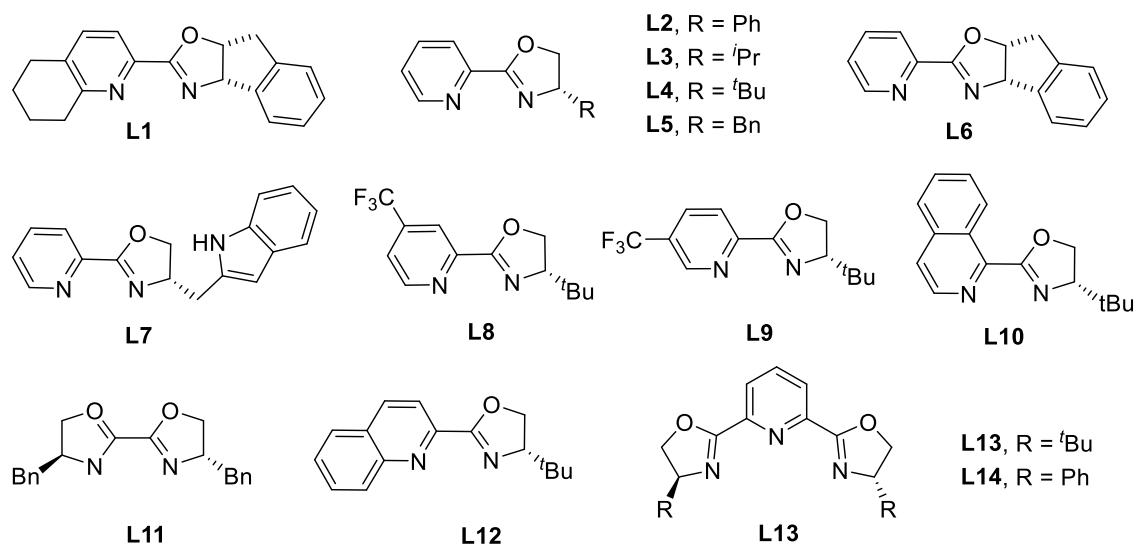
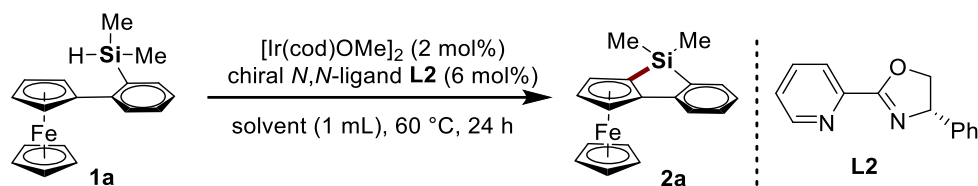
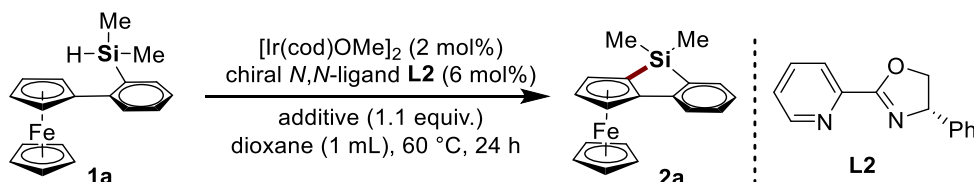


Table S2 Solvent screening for the enantioselective C–H silylation of **1a**^[a]

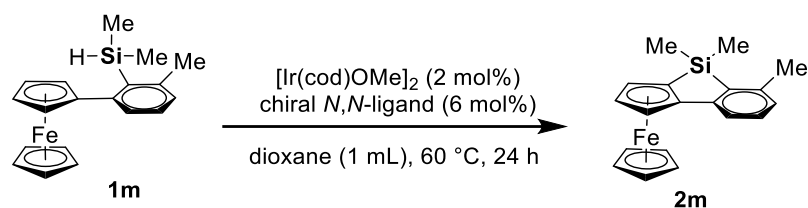
entry	solvent	yield (%) ^[b]	ee (%) ^[c]
1	THF	95	93
2	toluene	92	91
3	benzene	93	95
4	DCE	83	82
5	DME	85	89
6	DMA	38	71
7	DMSO	N.R.	N.R.
8	PhCF ₃	85	90
9	cyclohexane	91	91
10	MTBE	90	91
11	CH ₃ CN	82	81

[a] The reaction was conducted with **1a** (0.2 mmol), $[\text{Ir}(\text{cod})\text{OMe}]_2$ (2 mol%), chiral *N,N*-ligand **L2** (6 mol%) in solvent (1 mL) at 60 °C under N₂ for 24 h. [b] Yields were determined by NMR using TCE as internal standard. [c] Ee values were determined by chiral HPLC. N.R.: no reaction.

Table S3 Additive screening for the enantioselective C–H silylation of **1a**^[a]

entry	additive	yield (%) ^[b]	ee (%) ^[c]
1	cyclohexene	96	88
2	cod	96	92
3	styrene	95	92
4	cyclooctene	96	83
5	tbe	97	90
6	nbe	96	90
7	none	99	98

[a] The reaction was conducted with **1a** (0.2 mmol), $[\text{Ir}(\text{cod})\text{OMe}]_2$ (2 mol%), chiral *N,N*-ligand **L2** (6 mol%), additive (1.1 equiv.) in dioxane (1 mL) at 60 °C under N₂ for 24 h. [b] Yields were determined by NMR using TCE as internal standard. [c] Ee values were determined by chiral HPLC.

Table S4 Optimization for the enantioselective C–H silylation of C3-substituted substrate **1m**^[a]

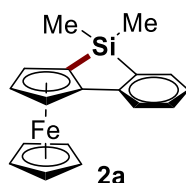
entry	ligand	yield (%) ^[b]	ee (%) ^[c]	entry	ligand	yield (%) ^[b]	ee (%) ^[c]
1	L1	90	85	8	L8	90	87
2	L2	85	92	9	L9	91	88
3	L3	90	76	10	L10	94	90
4	L4	92	80	11	L11	85	77
5	L5	88	57	12	L12	92	83
6	L6	98	95	13	L13	N.R	N.R
7	L7	82	65	14	L14	N.R	N.R

[a]The reaction was conducted with **1a** (0.2 mmol), [Ir(cod)OMe]₂ (2 mol%), chiral *N,N*-ligand (6 mol%) in dioxane (1 mL) at 60 °C under N₂ for 24 h. [b] Yields were determined by NMR using TCE as internal standard. [c] Ee values were determined by chiral HPLC.

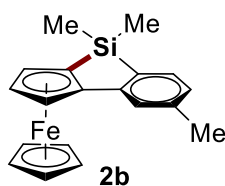
2.4 General procedure for the Ir-catalyzed asymmetric C–H silylation of Ferrocenes **1**

In a N₂ flushed glovebox, an oven-dried 8 mL tube equipped with a Teflon-coated magnetic stir bar was charged with [Ir(cod)OMe]₂ (2.6 mg, 0.004 mmol, 2 mol%), chiral *N,N*-ligand (0.012 mmol, 6 mol%) and anhydrous 1,4-dioxane (0.5 mL). The resulting mixture was stirred in the glovebox at room temperature for 1 hour, followed by addition of the starting material **1** (0.2 mmol, 1 equiv) in 1,4-dioxane (0.5 mL). The reaction tube was capped, removed from the glove box and the reaction mixture was stirred at 60 °C for 24 h. Then, the reaction mixture was cooled to room temperature, concentrated under vacuum and subjected to silica gel column chromatography to deliver the planar chiral ferrocene sioles **2**. The ee value of the product was determined by chiral HPLC analysis. Chiral *N,N*-ligand **L2** was used for the synthesis of planar chiral ferrocene sioles **2a–l** and **2u–w** under the reaction. On the other hand, chiral *N,N*-ligand **L6** was used for the Ir-catalyzed enantioselective C–H silylation of C3 or C6-substituted substrates **1m–t**. Product **2u** was synthesized at 90 °C for 48h. Product **2v** was synthesized at 100 °C for 24 h.

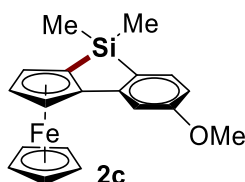
2.5 Characterization of products 2



According to general procedure, **2a** was obtained in 99% yield and 98% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.49 (d, $J = 7.2$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.27 (td, $J = 7.5, 1.3$ Hz, 1H), 7.11 (td, $J = 7.3, 1.1$ Hz, 1H), 4.88 (dd, $J = 2.2, 0.9$ Hz, 1H), 4.54 (t, $J = 2.3$ Hz, 1H), 4.39 (d, $J = 2.1$ Hz, 1H), 3.97 (s, 5H), 0.69 (s, 3H), 0.28 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 148.72, 142.75, 133.28, 130.31, 126.06, 121.69, 97.82, 74.04, 72.29, 71.32, 70.35, 64.97, -0.62, -1.58. **HPLC analysis (IA-3)**: Hexane/Isopropanol = 100:0, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_R = 10.4$ min (major) and $t_R = 13.2$ min (minor). $[\alpha]_D^{25} = 349$ ($c = 0.538$, acetone).

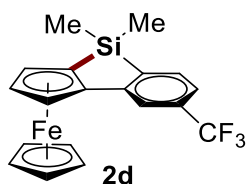


According to general procedure, **2b** was obtained in 99% yield and 98% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.37 (d, $J = 7.3$ Hz, 1H), 7.25 (s, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 4.86 (dd, $J = 2.3, 0.9$ Hz, 1H), 4.52 (t, $J = 2.3$ Hz, 1H), 4.37 (dd, $J = 2.2, 0.8$ Hz, 1H), 3.96 (s, 5H), 2.32 (s, 3H), 0.67 (s, 3H), 0.26 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 148.91, 139.89, 139.21, 133.19, 126.99, 122.49, 97.88, 73.90, 72.65, 71.24, 70.31, 64.82, 21.69, -0.51, -1.49. **HPLC analysis (OD-3)**: Hexane/Isopropanol = 99:1, 1 mL/min, 254 nm UV detector, 98% ee, $t_R = 8.4$ min (major) and $t_R = 10.6$ min (minor). $[\alpha]_D^{25} = 169.5$ ($c = 0.56$, acetone).

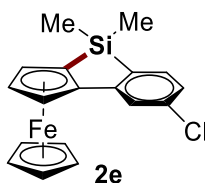


According to general procedure, **2c** was obtained in 83% yield and 97% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/Ethyl acetate = 20:1). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.39 (d, $J = 7.9$ Hz, 1H), 7.04

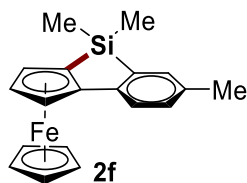
(d, $J = 2.3$ Hz, 1H), 6.71 (dd, $J = 7.9, 2.4$ Hz, 1H), 4.90 (dd, $J = 2.3, 0.9$ Hz, 1H), 4.53 (t, $J = 2.3$ Hz, 1H), 4.38 (dd, $J = 2.3, 0.9$ Hz, 1H), 3.99 (s, 5H), 3.83 (s, 3H), 0.67 (s, 3H), 0.27 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) δ 162.49, 150.73, 134.27, 133.36, 111.66, 107.97, 97.52, 73.94, 73.31, 71.35, 70.38, 65.00, 55.34, -0.39, -1.36. **HPLC analysis** (OD-3): Hexane/Isopropanol = 90:10, 1 mL/min, 254 nm UV detector, 97% ee, $t_{\text{R}} = 7.9$ min (major) and $t_{\text{R}} = 12.4$ min (minor). $[\alpha]_{\text{D}}^{25} = 98.6$ ($c = 0.46$, acetone).



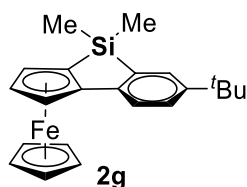
According to general procedure, **2d** was obtained in 94% yield and 99% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane). ^1H NMR (400 MHz, CD_3COCD_3) δ 7.70 – 7.68 (m, 2H), 7.42 (d, $J = 7.7$ Hz, 1H), 5.07 (d, $J = 2.3$ Hz, 1H), 4.62 (t, $J = 2.3$ Hz, 1H), 4.48 (d, $J = 2.2$ Hz, 1H), 4.01 (s, 5H), 0.73 (s, 3H), 0.32 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) δ 150.42, 148.21 (d, $J = 1.4$ Hz), 133.85, 131.98 (q, $J = 31.5$ Hz), 125.62 (q, $J = 271.6$ Hz), 122.28 (q, $J = 3.9$ Hz), 117.60 (q, $J = 3.7$ Hz), 96.09, 74.84, 72.62, 71.99, 70.57, 65.68, -0.90, -1.86. **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{17}\text{F}_3\text{FeSi}$ $[\text{M}]^+$ 386.0401, found 386.0393. **HPLC analysis** (IA-3): Hexane/Isopropanol = 100:0, 0.5 mL/min, 254 nm UV detector, 99% ee, $t_{\text{R}} = 11.3$ min (major) and $t_{\text{R}} = 9.6$ min (minor). $[\alpha]_{\text{D}}^{25} = 393.9$ ($c = 0.595$, acetone).



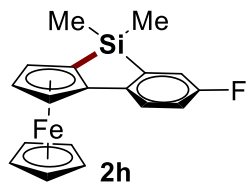
According to general procedure, **2e** was obtained in 92% yield and 98% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane). ^1H NMR (400 MHz, CD_3COCD_3) δ 7.47 (d, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 2.0$ Hz, 1H), 7.13 (dd, $J = 7.7, 1.9$ Hz, 1H), 4.96 (dd, $J = 2.3, 0.8$ Hz, 1H), 4.57 (t, $J = 2.3$ Hz, 1H), 4.43 (dd, $J = 2.3, 0.8$ Hz, 1H), 4.00 (s, 5H), 0.69 (s, 3H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) δ 151.50, 141.36, 136.26, 134.62, 125.73, 121.57, 96.17, 74.54, 72.87, 71.81, 70.49, 65.43, -0.71, -1.66. **HPLC analysis** (OD-3): Hexane/Isopropanol = 99:1, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_{\text{R}} = 8.3$ min (major) and $t_{\text{R}} = 9.0$ min (minor). $[\alpha]_{\text{D}}^{25} = 111.7$ ($c = 0.68$, acetone).



According to general procedure, **2f** was obtained in 97% yield and 98% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.31 – 7.29 (m, 2H), 7.08 (d, $J = 7.8$ Hz, 1H), 4.83 (dd, $J = 2.3, 0.8$ Hz, 1H), 4.50 (t, $J = 2.2$ Hz, 1H), 4.36 (dd, $J = 2.2, 0.8$ Hz, 1H), 3.96 (s, 5H), 2.27 (s, 3H), 0.68 (s, 3H), 0.27 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 145.67, 142.91, 135.14, 134.08, 131.03, 121.53, 98.13, 73.78, 72.13, 71.09, 70.30, 64.67, 21.34, -0.59, -1.54. **HPLC analysis (OD-H):** Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_R = 12.3$ min (major) and $t_R = 11.7$ min (minor). $[\alpha]_D^{25} = 359.9$ ($c = 0.515$, acetone).

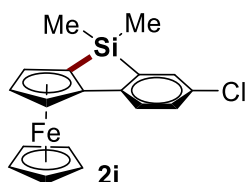


According to general procedure, **2g** was obtained in 97% yield and 98% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.58 (dd, $J = 1.6, 0.8$ Hz, 1H), 7.35 – 7.31 (m, 2H), 4.83 (dd, $J = 2.2, 0.8$ Hz, 1H), 4.51 (t, $J = 2.3$ Hz, 1H), 4.36 (dd, $J = 2.3, 0.8$ Hz, 1H), 3.96 (s, 5H), 1.32 (s, 9H), 0.69 (s, 3H), 0.27 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 148.44, 145.64, 142.53, 129.98, 127.33, 121.30, 98.01, 73.75, 72.35, 71.07, 70.23, 70.13, 64.67, 35.11, 31.78, -0.49, -1.38. **HPLC analysis (OD-H):** Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_R = 8.5$ min (major) and $t_R = 7.9$ min (minor). $[\alpha]_D^{25} = 353.2$ ($c = 0.6$, acetone).

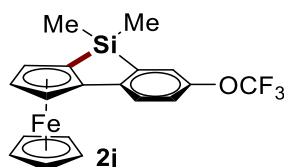


According to general procedure, **2h** was obtained in 92% yield and 98% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.42 (dd, $J = 8.3, 4.9$ Hz, 1H), 7.26 (dd, $J = 8.3, 2.6$ Hz, 1H),

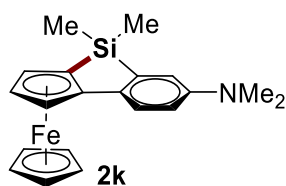
7.03 – 6.98 (m, 1H), 4.87 (dd, $J = 2.3, 0.9$ Hz, 1H), 4.53 (t, $J = 2.3$ Hz, 1H), 4.39 (dd, $J = 2.2, 0.8$ Hz, 1H), 3.98 (s, 5H), 0.70 (s, 3H), 0.29 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) δ 162.20 (d, $J = 243.8$ Hz), 145.92 (d, $J = 4.8$ Hz), 144.58 (d, $J = 2.5$ Hz), 122.89 (d, $J = 7.4$ Hz), 119.80 (d, $J = 19.8$ Hz), 116.79 (d, $J = 22.4$ Hz), 97.05, 74.08, 72.13, 71.43, 70.36, 64.91, -0.78, -1.70. **HPLC analysis** (OD-H): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_{\text{R}} = 10.5$ min (major) and $t_{\text{R}} = 9.9$ min (minor). $[\alpha]_{\text{D}}^{25} = 263.9$ (c = 0.57, acetone).



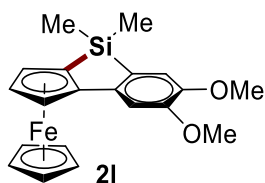
According to general procedure, **2i** was obtained in 90% yield and 96% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane). ^1H NMR (400 MHz, CD_3COCD_3) δ 7.49 (d, $J = 2.2$ Hz, 1H), 7.40 (d, $J = 8.1$ Hz, 1H), 7.27 (dd, $J = 8.1, 2.2$ Hz, 1H), 4.90 (dd, $J = 2.3, 0.8$ Hz, 1H), 4.56 (t, $J = 2.3$ Hz, 1H), 4.42 (dd, $J = 2.2, 0.8$ Hz, 1H), 3.99 (s, 5H), 0.71 (s, 3H), 0.31 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) δ 147.63, 145.77, 133.07, 131.45, 130.14, 123.02, 96.50, 74.46, 72.34, 71.70, 70.50, 65.29, -0.79, -1.73. **HPLC analysis** (OD-H): Hexane/Isopropanol = 99.7:0.3, 1 mL/min, 254 nm UV detector, 96% ee, $t_{\text{R}} = 6.6$ min (major) and $t_{\text{R}} = 6.2$ min (minor). $[\alpha]_{\text{D}}^{25} = 423.5$ (c = 0.48, acetone).



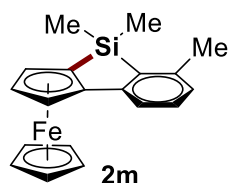
According to general procedure, **2j** was obtained in 97% yield and 97% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane). ^1H NMR (400 MHz, CD_3COCD_3) δ 7.49 (d, $J = 8.3$ Hz, 1H), 7.44 (d, $J = 1.2$ Hz, 1H), 7.21 – 7.18 (m, 1H), 4.93 (dd, $J = 2.3, 0.8$ Hz, 1H), 4.58 (t, $J = 2.3$ Hz, 1H), 4.44 (dd, $J = 2.3, 0.8$ Hz, 1H), 4.00 (s, 5H), 0.72 (s, 3H), 0.32 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) δ 148.18, 147.85 (d, $J = 2$ Hz), 145.77, 125.85, 123.07, 122.73, 121.50 (q, $J = 255.53$ Hz), 96.27, 74.55, 72.61, 71.83, 70.50, 65.41, -0.84, -1.75. **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{17}\text{F}_3\text{FeOSi}$ $[\text{M}]^+$ 402.0350, found 402.0349. **HPLC analysis** (OD-3): Hexane/Isopropanol = 99.7:0.3, 0.5 mL/min, 254 nm UV detector, 97% ee, $t_{\text{R}} = 10.2$ min (major) and $t_{\text{R}} = 9.5$ min (minor). $[\alpha]_{\text{D}}^{25} = 290.3$ (c = 0.495, acetone).



According to general procedure, **2k** was obtained in 96% yield and 97% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.26 (dd, $J = 8.3, 0.5$ Hz, 1H), 6.98 (d, $J = 2.6$ Hz, 1H), 6.68 (dd, $J = 8.4, 2.7$ Hz, 1H), 4.73 (dd, $J = 2.2, 0.8$ Hz, 1H), 4.44 (t, $J = 2.2$ Hz, 1H), 4.29 (dd, $J = 2.2, 0.8$ Hz, 1H), 3.95 (s, 5H), 2.94 (s, 6H), 0.68 (s, 3H), 0.27 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 149.96, 143.80, 136.16, 122.24, 117.91, 114.69, 99.65, 73.08, 71.22, 70.47, 70.08, 63.64, 40.93, -0.42, -1.32. **HRMS (ESI)** calcd for C₂₀H₂₄FeNSi [M+H]⁺ 362.1022, found 362.1025. **HPLC analysis (IA-3)**: Hexane/Isopropanol = 99:1, 0.5 mL/min, 254 nm UV detector, 97% ee, $t_R = 9.3$ min (major) and $t_R = 9.6$ min (minor). $[\alpha]_D^{25} = 388.3$ (c = 0.062, acetone).

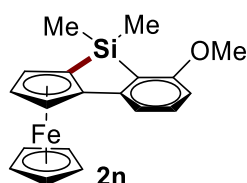


According to general procedure, **2l** was obtained in 80% yield and 98% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/Ethyl acetate = 10:1). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.11 (s, 1H), 7.10 (s, 1H), 4.82 (d, $J = 2.2$ Hz, 1H), 4.46 (t, $J = 2.2$ Hz, 1H), 4.32 (d, $J = 2.1$ Hz, 1H), 3.97 (s, 5H), 3.85 (s, 3H), 3.81 (s, 3H), 0.66 (s, 3H), 0.26 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 152.19, 148.79, 141.93, 133.45, 117.12, 106.52, 98.66, 73.34, 72.18, 71.01, 70.27, 69.20, 64.42, 56.31, 56.03, 30.42, -0.48, -1.36. **HPLC analysis (ID)**: Hexane/Isopropanol = 95:5, 1 mL/min, 254 nm UV detector, 98% ee, $t_R = 6.7$ min (major) and $t_R = 11.1$ min (minor). $[\alpha]_D^{25} = 208.2$ (c = 0.37, acetone).

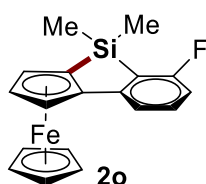


According to general procedure, **2m** was obtained in 98% yield and 95% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane).

¹H NMR (400 MHz, CD₃COCD₃) δ 7.28 – 7.21 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 4.85 (dd, *J* = 2.3, 0.9 Hz, 1H), 4.51 (t, *J* = 2.2 Hz, 1H), 4.38 (dd, *J* = 2.3, 0.8 Hz, 1H), 3.97 (s, 5H), 2.39 (s, 3H), 0.75 (s, 3H), 0.33 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 148.71, 143.38, 141.31, 130.76, 127.06, 119.30, 97.87, 73.84, 72.17, 71.14, 70.31, 64.96, 22.21, -1.08, -1.25. **HRMS (ESI)** calcd for C₁₉H₂₀FeSi [M]⁺ 332.0684, found 332.0682. **HPLC analysis (IA-3):** Hexane/Isopropanol = 100:0, 0.5 mL/min, 254 nm UV detector, 95% ee, *t_R* = 11.6 min (major) and *t_R* = 14.6 min (minor). **[α]_D²⁵** = 428.4 (c = 0.24, acetone).

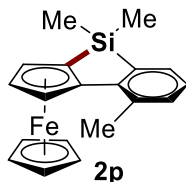


According to general procedure, **2n** was obtained in 98% yield and 97% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. *R_f* = 0.3 (Hexane/DCM = 5:1). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.28 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 4.83 (dd, *J* = 2.3, 0.8 Hz, 1H), 4.50 (t, *J* = 2.3 Hz, 1H), 4.35 (dd, *J* = 2.2, 0.8 Hz, 1H), 3.97 (s, 5H), 3.81 (s, 3H), 0.68 (s, 3H), 0.27 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 164.40, 150.33, 132.69, 128.28, 115.14, 108.16, 97.53, 73.87, 72.97, 71.27, 70.32, 65.11, 55.45, -1.12, -1.48. **HRMS (ESI)** calcd for C₁₉H₂₀FeOSi [M]⁺ 348.0633, found 348.0630. **HPLC analysis (IA-3):** Hexane/Isopropanol = 99.7:0.3, 0.5 mL/min, 254 nm UV detector, 97% ee, *t_R* = 9.4 min (major) and *t_R* = 10.0 min (minor). **[α]_D²⁵** = 658.1 (c = 0.63, acetone).

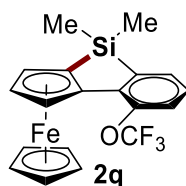


According to general procedure, **2o** was obtained in 93% yield and 97% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. *R_f* = 0.4 (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.34 – 7.29 (m, 1H), 7.25 – 7.23 (m, 1H), 6.82 – 6.77 (m, 1H), 4.91 (dd, *J* = 2.3, 0.9 Hz, 1H), 4.56 (t, *J* = 2.3 Hz, 1H), 4.43 (dd, *J* = 2.2, 0.9 Hz, 1H), 4.00 (s, 5H), 0.75 (s, 3H), 0.35 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 167.02 (d, *J* = 239.4 Hz), 151.78 (d, *J* = 12.7 Hz), 133.36 (d, *J* = 8.1 Hz), 126.80 (d, *J* = 35.0 Hz), 118.16 (d, *J* = 2.7 Hz), 112.43 (d, *J* = 25.1 Hz), 96.67 (d, *J* = 1.9 Hz), 74.59, 72.36, 71.67, 70.51, 65.50, -0.94, -1.50. **HRMS (ESI)**

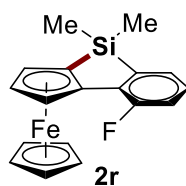
calcd for C₁₈H₁₇FeSi [M]⁺ 336.0433, found 336.0431. **HPLC analysis** (OD-3): Hexane/Isopropanol = 99:1, 0.5 mL/min, 254 nm UV detector, 97% ee, t_R = 10.4 min (major) and t_R = 8.9 min (minor). [α]_D²⁵ = 507.3 (c = 0.54, acetone).



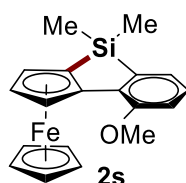
According to general procedure, **2p** was obtained in 97% yield and 84% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. R_f = 0.4 (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.33 (dd, *J* = 6.9, 1.5, 0.7 Hz, 1H), 7.14 – 6.97 (m, 2H), 4.88 (dd, *J* = 2.3, 0.8 Hz, 1H), 4.56 (t, *J* = 2.3 Hz, 1H), 4.41 (dd, *J* = 2.3, 0.8 Hz, 1H), 3.99 (s, 5H), 2.50 (s, 3H), 0.66 (s, 3H), 0.26 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 146.97, 143.20, 132.66, 132.54, 130.86, 126.05, 97.65, 74.52, 72.74, 71.28, 70.08, 68.90, 21.49, -0.71, -1.57. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 84% ee, t_R = 11.0 min (major) and t_R = 12.4 min (minor). [α]_D²⁵ = 114.6 (c = 0.70, acetone).



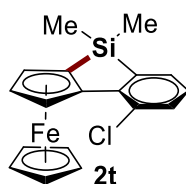
According to general procedure, **2q** was obtained in 97% yield and 99% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. R_f = 0.4 (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.51 – 7.46 (m, 1H), 7.25 – 7.24 (m, 2H), 4.93 (d, *J* = 2.2 Hz, 1H), 4.63 (t, *J* = 2.3 Hz, 1H), 4.48 (dd, *J* = 2.3, 0.9 Hz, 1H), 4.03 (s, 5H), 0.72 (s, 3H), 0.31 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 147.02, 144.77 (q, *J* = 1.3 Hz), 140.70, 132.07, 127.61, 122.07 (q, *J* = 1.3 Hz), 121.08 (q, *J* = 128.3 Hz), 93.08, 75.11, 72.59, 72.57, 71.73, 70.38, 68.66, -0.83, -1.69. **HRMS (ESI)** calcd for C₁₉H₁₇F₃FeOSi [M]⁺ 402.0345, found 402.0340. **HPLC analysis** (OD-H): Hexane/Isopropanol=100:0, 0.5 mL/min, 254 nm UV detector, 99% ee, t_R = 10.3 min (major) and t_R = 11.7 min (minor). [α]_D²⁵ = 343.4 (c = 0.41, acetone).



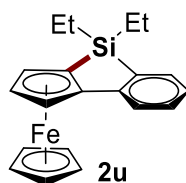
According to general procedure, **2r** was obtained in 97% yield and 95% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.32 – 7.31 (m, 1H), 7.19 – 7.14 (ddd, $J = 8.2, 6.9, 4.7$ Hz, 1H), 7.06 – 7.01 (ddd, $J = 10.6, 8.2, 1.0$ Hz, 1H), 4.92 (td, $J = 2.5, 0.9$ Hz, 1H), 4.58 (t, $J = 2.3$ Hz, 1H), 4.43 (dd, $J = 2.3, 0.9$ Hz, 1H), 4.01 (s, 5H), 0.71 (s, 3H), 0.30 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 158.76 (d, $J = 248.6$ Hz), 146.61 (d, $J = 1.5$ Hz), 134.84 (d, $J = 12.3$ Hz), 129.26 (d, $J = 3.3$ Hz), 127.95 (d, $J = 5.9$ Hz), 117.19 (d, $J = 20.5$ Hz), 93.00 (d, $J = 2.2$ Hz), 74.69 (d, $J = 1.0$ Hz), 72.06, 71.47, 70.35, 68.26 (d, $J = 5.0$ Hz), -0.78, -1.63. **HRMS (ESI)** calcd for C₁₈H₁₇FFeSi [M]⁺ 336.0433, found 336.0430. **HPLC analysis** (OD-H): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 95% ee, $t_R = 9.2$ min (major) and $t_R = 8.7$ min (minor). $[\alpha]_D^{25} = 452.8$ (c = 0.57, acetone).



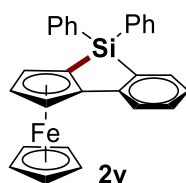
According to general procedure, **2s** was obtained in 97% yield and 96% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/DCM = 5:1). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.16 – 7.08 (m, 2H), 6.95 (dd, $J = 8.0, 1.2$ Hz, 1H), 5.06 (dd, $J = 2.2, 0.9$ Hz, 1H), 4.49 (t, $J = 2.2$ Hz, 1H), 4.34 (dd, $J = 2.3, 0.9$ Hz, 1H), 3.95 (s, 5H), 3.95 (s, 3H), 0.67 (s, 3H), 0.27 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 155.81, 144.51, 136.18, 127.52, 125.48, 113.09, 95.99, 73.97, 71.37, 70.81, 70.12, 69.51, 55.68, -0.67, -1.53. **HRMS (ESI)** calcd for C₁₉H₂₀FeOSi [M]⁺ 348.0633, found 348.0631. **HPLC analysis** (OD-H): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 6.0$ min (major) and $t_R = 5.8$ min (minor). $[\alpha]_D^{25} = -6.2$ (c = 0.53, acetone).



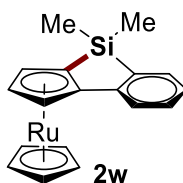
According to general procedure, **2t** was obtained in 95% yield and 81% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.44 (dd, $J = 6.9, 1.1$ Hz, 1H), 7.31 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.13 (t, $J = 7.4$ Hz, 1H), 5.31 (dd, $J = 2.3, 0.9$ Hz, 1H), 4.61 (t, $J = 2.4$ Hz, 1H), 4.46 (dd, $J = 2.4, 0.9$ Hz, 1H), 4.03 (s, 5H), 0.69 (s, 3H), 0.30 (s, 3H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 146.51, 146.01, 131.78, 131.64, 129.27, 127.37, 95.07, 75.01, 72.88, 71.84, 70.36, 69.75, -0.85, -1.69. **HRMS (ESI)** calcd for C₁₈H₁₇ClFeSi [M]⁺ 352.0132, found 352.0130. **HPLC analysis (OD-H):** Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 81% ee, $t_R = 10.6$ min (major) and $t_R = 8.8$ min (minor). $[\alpha]_D^{25} = 3.9$ ($c = 0.543$, acetone).



According to general procedure, **2u** was obtained in 59% yield and 86% ee as dark orange oil under the modified optimized condition by use of **L2** as the chiral ligand at 90 °C for 48 h. $R_f = 0.3$ (Hexane). **¹H NMR (400 MHz, CD₃COCD₃)** δ 7.47 – 7.41 (m, 1H), 7.27 (td, $J = 7.5, 1.3$ Hz, 1H), 7.10 (td, $J = 7.3, 1.1$ Hz, 1H), 4.90 (d, $J = 2.3$ Hz, 1H), 4.55 (t, $J = 2.3$ Hz, 1H), 4.37 (d, $J = 2.3$ Hz, 1H), 3.97 (s, 5H), 1.36 (t, $J = 7.8$ Hz, 3H), 1.25 – 1.11 (m, 2H), 0.86 – 0.78 (m, 5H). **¹³C NMR (101 MHz, CD₃COCD₃)** δ 149.31, 141.12, 133.89, 130.36, 125.99, 121.85, 98.10, 74.10, 71.65, 70.97, 70.40, 64.95, 8.22, 7.85, 5.91, 5.58. **HPLC analysis (OD-3):** Hexane/Isopropanol = 99:1, 1 mL/min, 254 nm UV detector, 86% ee, $t_R = 14.8$ min (major) and $t_R = 10.7$ min (minor). $[\alpha]_D^{25} = 290.2$ ($c = 0.37$, acetone).



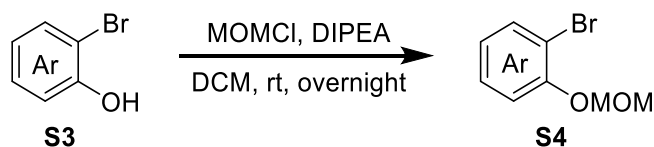
According to general procedure, **2v** was obtained in 98% yield and 86% ee as dark orange oil under the modified optimized condition by use of **L2** as the chiral ligand at 100 °C for 24 h. $R_f = 0.3$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 8.00 – 7.97 (m, 2H), 7.79 (d, $J = 7.3$, 1H), 7.56 – 7.48 (m, 6H), 7.39 – 7.21 (m, 5H), 5.01 (dd, $J = 2.2$, 1.0 Hz, 1H), 4.66 (dd, $J = 2.6$, 1.6 Hz, 2H), 3.66 (s, 5H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 149.81, 138.82, 136.50, 135.96, 135.61, 134.91, 131.03, 130.77, 130.39, 128.94, 128.68, 126.46, 122.21, 98.08, 74.69, 71.72, 70.84, 69.74, 65.38. **HPLC analysis** (OD-H): Hexane/Isopropanol = 99:1, 1 mL/min, 254 nm UV detector, 86% ee, $t_R = 12.7$ min (major) and $t_R = 8.0$ min (minor). $[\alpha]_D^{25} = 296.2$ ($c = 0.67$, acetone).



According to general procedure, **2w** was obtained in 92% yield and 98% ee as colorless oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane). $^1\text{H NMR}$ (400 MHz, CD_3COCD_3) δ 7.42 (dt, $J = 7.0$, 1.0 Hz, 1H), 7.29 (dt, $J = 7.6$, 0.9 Hz, 1H), 7.19 (td, $J = 7.5$, 1.3 Hz, 1H), 7.05 (td, $J = 7.2$, 1.1 Hz, 1H), 5.24 (dd, $J = 2.2$, 0.7 Hz, 1H), 4.77 (t, $J = 2.2$ Hz, 1H), 4.72 (dd, $J = 2.1$, 0.7 Hz, 1H), 4.38 (s, 5H), 0.50 (s, 3H), 0.36 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CD_3COCD_3) δ 147.86, 141.99, 133.32, 130.15, 126.22, 121.28, 101.24, 77.21, 75.11, 72.72, 72.10, 66.86, -0.03, -1.40. **HPLC analysis** (OD-3): Hexane/Isopropanol = 99:1, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_R = 6.0$ min (major) and $t_R = 4.3$ min (minor). $[\alpha]_D^{25} = 178.1$ ($c = 0.524$, acetone).

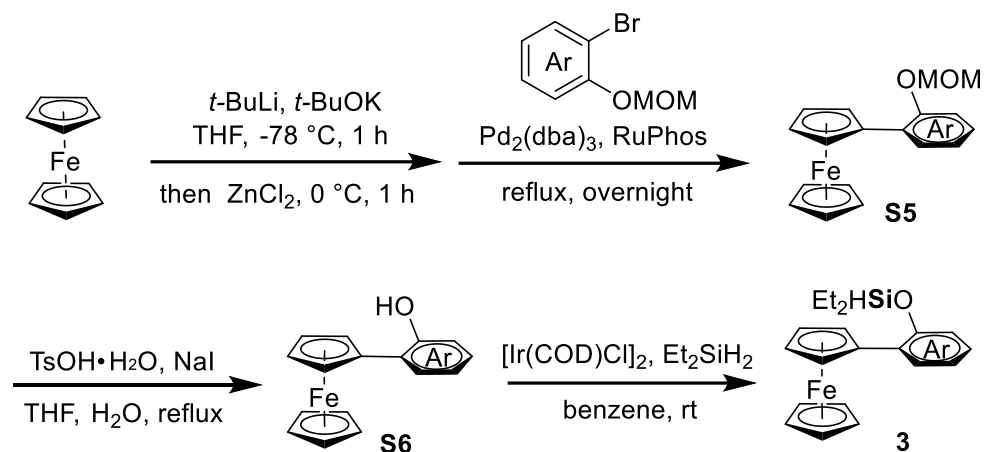
3. Iridium-Catalyzed 6-Membered Enantioselective C–H Silylation of Ferrocenes

3.1 General procedures for the synthesis of starting materials **3**^{1, 2, 4, 5}



To a solution of substituted phenol **S3** (20 mmol, 1 equiv) and DIPEA (6.6 mL, 40 mmol, 2 equiv) in DCM (50 mL), MOMCl (2.3 mL, 2.4g, 30 mmol, 1.5 equiv) was added dropwise at 0 °C.

After addition, the solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was then diluted with DCM (100 mL) and washed with sat NH₄Cl aq solution (30 mL × 3). The organic layer was separated, washed with brine (50 mL), dried with Na₂SO₄, filtered and concentrated under reduced pressure to yield the crude product **S4**. The crude product **S4** was directly used for next step without any further purification.



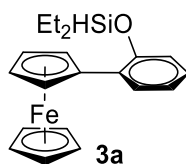
The stirred solution of ferrocene (20 mmol) in THF (60 mL) was cooled to -78 °C under N₂, *t*-BuOK (10 mol%, 224 mg) was added followed by dropwise addition of *t*-BuLi (42 mmol, 1.6 M, 26 mL). After being stirred at this temperature for 1 h, ZnCl₂ (42 mmol, 5.7 g) was added in one portion and the system was gradually warmed to room temperature in 1 h. Then, the aryl bromide **S4** (20 mmol, 1 equiv), Pd₂(dba)₃ (0.183g, 0.02 mmol, 1 mol%) and RuPhos (0.38g, 0.08 mmol, 4 mol%) were added sequentially and the mixture is refluxed overnight (If the aryl bromide **S4** contains a chloro-group on phenyl ring, Pd(PPh₃)₄ (1.15 g, 1 mmol, 0.05 equiv) was used as the catalyst instead of Pd₂(dba)₃/RuPhos system during the coupling reaction). The solution was cooled and quenched with sat NH₄Cl aq solution (10 mL) and extracted with DCM for three times (100 mL × 3). The combined organic layer was separated, washed with brine (50 mL), dried with Na₂SO₄, filtered and concentrated under reduced pressure. The crude product **S5** was purified by column chromatography on silica gel using hexane/DCM as eluent.

A two-necked flask equipped with a magnetic stir bar and a reflux condenser was charged with **S5** (10 mmol, 1 equiv), NaI (14.9 g, 100 mmol, 10 equiv), TsOH·H₂O (3.8 g, 20 mmol, 2 equiv) and evacuated and backfilled with N₂ for three times. Degassed THF (80 mL) and water (20 mL) was added to the flask via syringe. The mixture was refluxed until the starting material **S5** had been

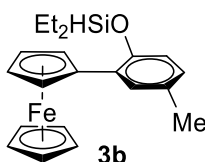
completely consumed as judged by TLC analysis. The volatiles were removed under vacuum, and the residue was extracted with DCM for three times (50 mL \times 3). The combined organic layer was separated, washed with brine (50 mL), dried with Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane/DCM as eluent to deliver the product **S6**.

Following the literature procedure,^{6,7} a flame-dried flask was charged with [Ir(cod)Cl]₂ (33.6 mg, 0.05 mmol, 0.5 mol%) and Et₂SiH₂ (15 mmol, 1.5 equiv) under N₂ and stirred at room temperature until the brown solid was completely dissolved. **S6** (10 mmol, 1 equiv) in benzene (20 mL) was added dropwise to the flask under N₂. The mixture was stirred at room temperature until the starting material **S6** had been completely consumed as judged by NMR analysis (typically 10–72 h). The volatiles were removed under vacuum to afford the hydrosilane product **3** with almost quantitative yield, which was directly used for next step without any further purification.

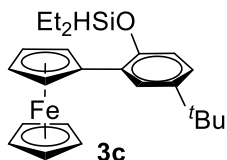
3.2 Characterization of starting materials **3**



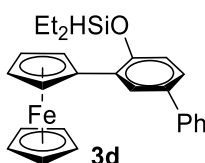
According to the general procedure, **3a** was obtained in almost quantitative yield as dark orange oil. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.81 – 4.80 (m, 1H), 4.76 (s, 2H), 4.29 (s, 2H), 4.08 (s, 5H), 1.06 – 0.97 (m, 6H), 0.87 – 0.81 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 152.74, 129.75, 129.18, 126.70, 121.32, 118.57, 82.65, 69.37, 68.94, 68.15, 6.62, 5.15.



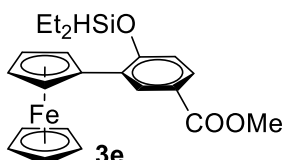
According to general procedure, **3b** was obtained in almost quantitative yield as dark orange oil. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 4.77 – 4.75 (m, 3H), 4.31 (s, 2H), 4.10 (s, 5H), 2.32 (s, 3H), 1.01 (t, *J* = 7.7 Hz, 6H), 0.83 – 0.80 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 150.56, 130.28, 130.13, 128.63, 127.31, 118.31, 82.82, 69.34, 68.82, 68.09, 20.72, 6.64, 5.15.



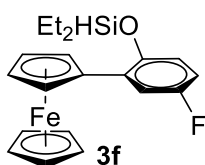
According to general procedure, **3c** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.63 (d, $J = 2.6$ Hz, 1H), 7.11 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 4.76 – 4.74 (m, 1H), 4.72 (t, $J = 1.9$ Hz, 2H), 4.27 (s, 2H), 4.07 (s, 5H), 1.36 (s, 9H), 1.02 (t, $J = 7.9$ Hz, 6H), 0.86 – 0.77 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.44, 143.59, 128.09, 127.18, 123.64, 117.86, 83.61, 69.34, 69.12, 67.94, 34.09, 31.57, 6.63, 5.19.



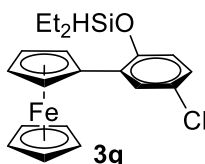
According to general procedure, **3d** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 2.4$ Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.37 – 7.32 (m, 2H), 6.96 (d, $J = 8.3$ Hz, 1H), 4.85 – 4.79 (m, 3H), 4.31 (s, 2H), 4.10 (s, 5H), 1.06 (t, $J = 7.8$ Hz, 6H), 0.90 – 0.84 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.35, 140.91, 134.26, 129.44, 128.68, 128.37, 126.68, 125.42, 118.77, 82.60, 69.38, 68.94, 68.25, 6.63, 5.16.



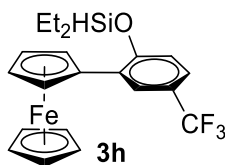
According to general procedure, **3e** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.27 (d, $J = 2.3$ Hz, 1H), 7.79 (dd, $J = 8.5, 2.3$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 1H), 4.87 – 4.85 (m, 1H), 4.79 (t, $J = 1.9$ Hz, 2H), 4.31 (t, $J = 1.9$ Hz, 2H), 4.06 (s, 5H), 3.92 (s, 3H), 1.06 – 0.99 (m, 6H), 0.90 – 0.84 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.95, 156.73, 131.35, 129.51, 128.37, 123.17, 118.11, 81.50, 69.45, 68.85, 68.53, 51.95, 6.56, 5.07.



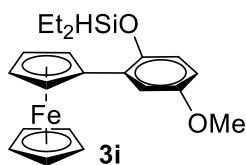
According to general procedure, **3f** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26 – 7.23 (m, 1H), 7.82 – 7.65 (m, 2H), 4.74 – 4.73 (m, 3H), 4.31 (s, 2H), 4.08 (s, 5H), 1.03 – 0.95 (m, 6H), 0.83 – 0.76 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.39 (d, $J = 238.1$ Hz), 148.74 (d, $J = 1.6$ Hz), 131.04 (d, $J = 8.0$ Hz), 119.33 (d, $J = 8.6$ Hz), 115.52 (d, $J = 23.5$ Hz), 112.89 (d, $J = 23.0$ Hz), 81.48, 69.49, 68.99, 68.53, 6.57, 5.07.



According to general procedure, **3g** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (s, 1H), 7.04 (d, $J = 9.3$ Hz, 1H), 6.80 (d, $J = 8.6$ Hz, 1H), 4.76 – 4.75 (m, 3H), 4.32 (s, 2H), 4.09 (s, 5H), 1.01 (t, $J = 7.9$ Hz, 6H), 0.84 – 0.78 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.33, 131.31, 129.05, 126.30, 126.13, 119.63, 81.20, 69.47, 68.87, 68.56, 6.57, 5.04.

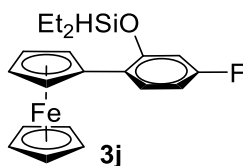


According to general procedure, **3h** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.34 (d, $J = 8.4$ Hz, 1H), 6.94 (d, $J = 8.5$ Hz, 1H), 4.84 – 4.76 (m, 3H), 4.33 (s, 2H), 4.07 (s, 5H), 1.04 (t, $J = 8.0$ Hz, 6H), 0.89 – 0.83 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.37, 130.35, 126.80 (q, $J = 3.5$ Hz), 124.5 (q, $J = 272.4$ Hz), 123.68 (q, $J = 3.9, 3.5$ Hz), 123.58 (q, $J = 32.3$ Hz), 118.53, 81.24, 69.55, 68.99, 68.73, 6.59, 5.12.

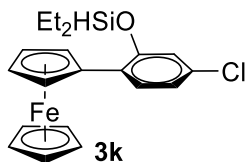


According to general procedure, **3i** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.14 (d, $J = 3.1$ Hz, 1H), 6.80 (d, $J = 8.7$ Hz, 1H), 6.66 (dd, $J = 8.8, 3.1$ Hz, 1H), 4.74 – 4.70 (m, 3H), 4.27 (t, $J = 1.9$ Hz, 2H), 4.07 (s, 5H), 3.82 (s, 3H), 1.00 (t, $J = 7.9$ Hz, 6H), 0.87 – 0.73 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.78, 146.82, 130.12,

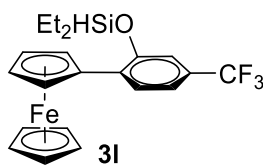
119.12, 115.17, 111.48, 82.52, 69.41, 69.04, 68.24, 55.59, 6.62, 5.12.



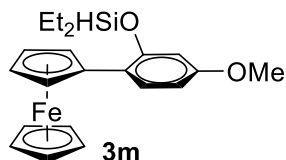
According to general procedure, **3j** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (t, $J = 7.8$ Hz, 1H), 6.72 – 6.62 (m, 2H), 4.80 – 4.79 (m, 1H), 4.69 (t, $J = 1.9$ Hz, 2H), 4.27 (t, $J = 1.9$ Hz, 2H), 4.07 (s, 5H), 1.04 (t, $J = 7.7$ Hz, 6H), 0.87 – 0.81 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.31 (d, $J = 245.6$ Hz), 153.51 (d, $J = 10.4$ Hz), 130.32 (d, $J = 9.6$ Hz), 125.23 (d, $J = 3.5$ Hz), 108.29 (d, $J = 21.0$ Hz), 105.92 (d, $J = 22.9$ Hz), 82.18, 69.34, 68.67, 68.09, 6.54, 5.01.



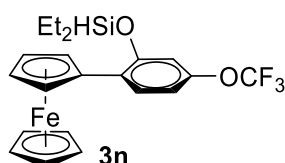
According to general procedure, **3k** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (d, $J = 2.7$ Hz, 1H), 7.04 (dd, $J = 8.7, 2.7$ Hz, 1H), 6.80 (d, $J = 8.6$ Hz, 1H), 4.77 (s, 1H), 4.73 (s, 2H), 4.30 (s, 2H), 4.08 (s, 5H), 1.04 – 0.95 (m, 6H), 0.85 – 0.79 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.35, 131.32, 129.08, 126.33, 126.13, 119.65, 81.26, 69.51, 68.90, 68.59, 6.58, 5.05.



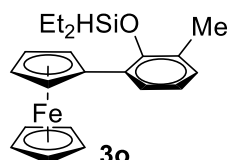
According to general procedure, **3l** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, $J = 8.1$ Hz, 1H), 7.19 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.10 (d, $J = 1.9$ Hz, 1H), 4.84 – 4.81 (m, 1H), 4.78 (t, $J = 1.8$ Hz, 3H), 4.34 (t, $J = 1.9$ Hz, 2H), 4.07 (s, 4H), 1.02 – 0.97 (m, 6H), 0.88 – 0.81 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.69, 133.79, 129.85, 128.46 (q, $J = 32.6$ Hz), 124.08 (q, $J = 272.7$ Hz), 117.98 (q, $J = 3.8$ Hz), 115.34 (q, $J = 3.8$ Hz), 80.77, 69.55, 69.18, 68.86, 6.52, 5.05.



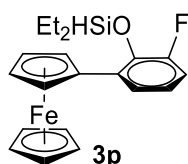
According to general procedure, **3m** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.6$ Hz, 1H), 6.55 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.48 (d, $J = 2.5$ Hz, 1H), 4.81 – 4.78 (m, 1H), 4.68 (t, $J = 1.8$ Hz, 2H), 4.24 (t, $J = 1.8$ Hz, 2H), 4.07 (s, 5H), 3.81 (s, 3H), 1.05 – 1.02 (m, 6H), 0.86 – 0.80 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.59, 153.54, 130.18, 121.53, 106.75, 104.81, 83.21, 69.28, 68.42, 67.80, 55.26, 6.61, 5.10.



According to general procedure, **3n** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 (dd, $J = 8.5, 1.6$ Hz, 1H), 6.84 (d, $J = 8.6$ Hz, 1H), 6.76 (s, 1H), 4.80 – 4.79 (m, 1H), 4.71 (s, 2H), 4.30 (s, 2H), 4.08 (s, 5H), 1.05 – 0.96 (m, 6H), 0.87 – 0.81 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.28, 147.38 (q, $J = 1.9$ Hz), 130.18, 128.34, 120.45 (q, $J = 257.0$ Hz), 113.63, 111.43, 81.50, 69.43, 68.86, 68.38, 6.52, 5.02.

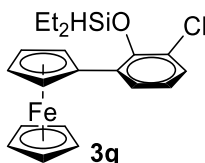


According to general procedure, **3o** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 (dd, $J = 7.7, 1.9$ Hz, 1H), 7.02 – 6.99 (m, 1H), 6.93 (t, $J = 7.5$ Hz, 1H), 4.62 (t, $J = 1.9$ Hz, 2H), 4.42 – 4.41 (m, 1H), 4.27 (t, $J = 1.9$ Hz, 2H), 4.09 (s, 5H), 2.28 (s, 3H), 0.87 – 0.83 (m, 6H), 0.56 – 0.47 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.17, 129.83, 129.11, 128.80, 128.61, 121.49, 84.21, 70.20, 69.47, 69.44, 67.73, 17.33, 6.48, 5.26.

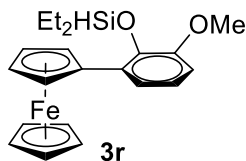


According to general procedure, **3p** was obtained in almost quantitative yield as dark orange

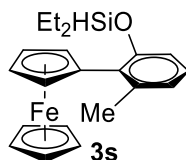
oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 (d, $J = 7.6$ Hz, 1H), 6.94 – 6.86 (m, 2H), 4.73 – 4.68 (m, 3H), 4.30 (s, 2H), 4.07 (s, 5H), 0.99 – 0.95 (m, 6H), 0.89 – 0.76 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.32 (d, $J = 241.0$ Hz), 140.51 (d, $J = 13.4$ Hz), 132.22, 124.76, 121.02 (d, $J = 8.3$ Hz), 113.16 (d, $J = 19.7$ Hz), 81.63 (d, $J = 2.6$ Hz), 69.47, 69.15, 68.38, 6.45, 5.52.



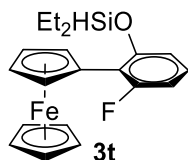
According to general procedure, **3q** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.19 (dd, $J = 7.9, 1.7$ Hz, 1H), 6.92 (t, $J = 7.8$ Hz, 1H), 4.65 (t, $J = 1.8$ Hz, 2H), 4.52 – 4.50 (m, 1H), 4.29 (t, $J = 1.8$ Hz, 2H), 4.07 (s, 5H), 0.86 (t, $J = 7.9$ Hz, 6H), 0.64 – 0.59 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.82, 132.30, 129.12, 129.10, 127.41, 127.38, 126.09, 122.07, 82.63, 69.99, 69.55, 68.17, 6.44, 5.36.



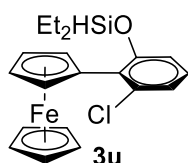
According to general procedure, **3r** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.19 (d, $J = 7.9$ Hz, 1H), 6.88 (t, $J = 7.9$ Hz, 1H), 6.72 (d, $J = 7.9$ Hz, 1H), 4.77 (s, 2H), 4.70 – 4.68 (m, 1H), 4.28 (s, 2H), 4.07 (s, 5H), 3.84 (s, 3H), 0.96 (t, $J = 7.9$ Hz, 6H), 0.80 – 0.69 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.33, 142.15, 129.84, 121.77, 120.73, 108.92, 82.48, 69.36, 69.13, 68.10, 55.27, 6.72, 6.01.



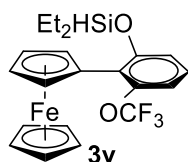
According to general procedure, **3s** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.04 (t, $J = 7.8$ Hz, 1H), 6.85 (d, $J = 7.2$ Hz, 1H), 6.76 (d, $J = 8.1$ Hz, 1H), 4.71 – 4.68 (m, 1H), 4.59 (t, $J = 1.9$ Hz, 2H), 4.30 (t, $J = 1.9$ Hz, 2H), 4.13 (s, 5H), 2.94 (s, 3H), 1.0 – 0.96 (m, 6H), 0.81 – 0.74 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.93, 138.29, 127.42, 126.32, 124.59, 116.40, 81.92, 71.18, 69.25, 67.08, 22.42, 6.69, 5.21.



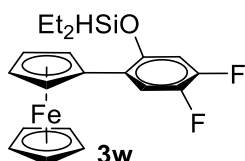
According to general procedure, **3t** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.08 – 7.03 (m, 1H), 6.77 – 6.69 (m, 2H), 4.81 (s, 2H), 4.72 (s, 1H), 4.30 (s, 2H), 4.11 (s, 5H), 1.00 – 0.96 (m, 6H), 0.80 – 0.74 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.17 (d, $J = 248.0$ Hz), 154.34 (d, $J = 7.6$ Hz), 126.37 (d, $J = 11.3$ Hz), 118.15 (d, $J = 14.1$ Hz), 114.51, 109.18 (d, $J = 24.0$ Hz), 75.96, 70.26 (d, $J = 4.9$ Hz), 69.38, 67.95, 6.53, 5.01.



According to general procedure, **3u** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.09 – 6.98 (m, 2H), 6.81 (dd, $J = 7.8, 1.6$ Hz, 1H), 4.81 (t, $J = 1.9$ Hz, 1H), 4.64 – 4.62 (m, 1H), 4.32 (t, $J = 1.9$ Hz, 1H), 4.16 (s, 5H), 1.06 – 0.94 (m, 6H), 0.75 – 0.69 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.82, 134.12, 127.87, 126.72, 124.38, 117.66, 79.49, 71.32, 69.51, 67.43, 6.53, 5.00.

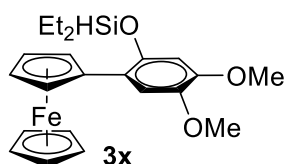


According to general procedure, **3v** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.14 (t, $J = 8.2$ Hz, 1H), 6.99 – 6.95 (m, 1H), 6.85 (dd, $J = 8.1, 1.2$ Hz, 1H), 4.77 – 4.74 (m, 3H), 4.33 (t, $J = 1.9$ Hz, 2H), 4.13 (s, 5H), 1.04 – 0.99 (m, 6H), 0.88 – 0.74 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.79, 147.77, 126.41, 120.77 (q, $J = 258.6$ Hz), 116.78, 112.74 (q, $J = 2.2$ Hz), 76.46, 70.67, 69.35, 67.96, 6.52, 5.07.

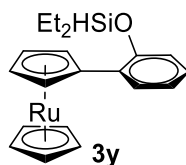


According to general procedure, **3w** was obtained in almost quantitative yield as dark orange

oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 (dd, $J = 11.8, 9.2$ Hz, 1H), 6.71 (dd, $J = 11.6, 7.1$ Hz, 1H), 4.75 – 4.73 (m, 1H), 4.67 (t, $J = 1.9$ Hz, 2H), 4.29 (t, $J = 1.9$ Hz, 2H), 4.08 (s, 5H), 1.04 – 0.94 (m, 6H), 0.86 – 0.76 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.45 (dd, $J = 7.5, 2.3$ Hz), 147.96 (dd, $J = 248.5, 14.0$ Hz), 145.09 (dd, $J = 240.1, 12.8$ Hz), 126.03 (d, $J = 9.3$ Hz), 116.94 (d, $J = 18.8$ Hz), 107.62 (d, $J = 18.5$ Hz), 81.08, 69.46, 68.83, 68.45, 6.49, 4.96.



According to general procedure, **3x** was obtained in almost quantitative yield as dark orange oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.99 (s, 1H), 6.36 (s, 1H), 4.61 – 4.56 (m, 1H), 4.56 (t, $J = 1.9$ Hz, 2H), 4.14 (t, $J = 1.8$ Hz, 2H), 3.96 (s, 5H), 3.81 (s, 3H), 3.76 (s, 3H), 0.91 – 0.86 (m, 6H), 0.71 – 0.59 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.74, 146.54, 143.49, 120.29, 113.10, 103.68, 83.32, 69.29, 68.66, 67.87, 56.50, 55.92, 6.62, 5.16.



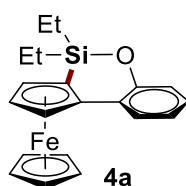
Compound **3y** was synthesized by a modified literature's procedure,⁸ which has been described in our previous report. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 (dd, $J = 7.7, 1.8$ Hz, 10H), 7.07 (ddd, $J = 8.1, 7.3, 1.8$ Hz, 1H), 6.89 – 6.82 (m, 2H), 5.07 (t, $J = 1.7$ Hz, 2H), 4.75 (p, $J = 2.4$ Hz, 1H), 4.63 (t, $J = 1.7$ Hz, 2H), 4.49 (s, 5H), 1.03 – 0.95 (m, 6H), 0.86 – 0.73 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.56, 130.78, 128.42, 127.14, 121.12, 118.49, 87.53, 72.01, 71.23, 70.11, 6.59, 5.15.

3.3 General procedure for the Ir-catalyzed asymmetric 6-membered C–H silylation

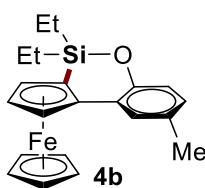
In a N_2 flushed glovebox, an oven-dried 8 mL tube equipped with a Teflon-coated magnetic stir bar was charged with $[\text{Ir}(\text{cod})\text{OMe}]_2$ (2.6 mg, 0.004 mmol, 2 mol%), chiral *N, N*-ligand **L2** or **L6** (0.012 mmol, 6 mol%) and anhydrous 1,4-dioxane (0.5 mL). The resulting mixture was stirred in the glovebox at room temperature for 1 hour, followed by addition of the starting material **3** (0.2 mmol, 1 equiv) in 1,4-dioxane (0.5 mL). The reaction tube was capped, removed from the glove box and the reaction mixture was stirred at 60 °C for 24 h. Then, the reaction mixture was cooled

to room temperature, concentrated under vacuum and subjected to silica gel column chromatography to deliver the planar chiral ferrocene sioles **2**. The ee value of the product was determined by chiral HPLC analysis. **L2** was employed as the chiral ligand for the enantioselective 6-membered C–H silylation of substrates **3a–n** as well as **3w–y**. On the other hand, **L6** was utilized as the chiral ligand for the enantioselective 6-membered C–H silylation of C3 or C6-substituted substrates **3o–v**.

3.4 Characterization of products **4**

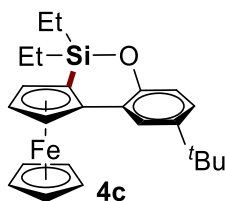


According to general procedure, **4a** was obtained in 93% yield and 98% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.11 – 7.09 (m, 1H), 6.94 – 6.87 (m, 2H), 4.96 (dd, $J = 2.4, 1.1$ Hz, 1H), 4.53 (t, $J = 2.4$ Hz, 1H), 4.28 (dd, $J = 2.3, 1.0$ Hz, 1H), 4.04 (s, 5H), 1.31 – 1.18 (m, 5H), 0.86 – 0.72 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.42, 127.10, 125.57, 124.89, 120.70, 119.58, 86.80, 71.70, 71.53, 69.82, 65.40, 64.33, 7.75, 7.48, 6.31, 6.26. **HPLC analysis** (IC-3): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_R = 8.0$ min (major) and $t_R = 9.7$ min (minor). $[\alpha]_D^{25} = 304$ ($c = 0.867$, DCM).

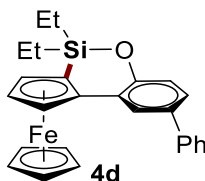


According to general procedure, **4b** was obtained in 93% yield and 96% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21 (d, $J = 2.2$ Hz, 1H), 6.94 – 6.91 (m, 1H), 6.84 (d, $J = 8.2$ Hz, 1H), 4.96 (d, $J = 1.6$ Hz, 1H), 4.53 (t, $J = 2.3$ Hz, 1H), 4.29 (d, $J = 1.6$ Hz, 1H), 4.06 (s, 5H), 2.33 (s, 3H), 1.33 – 1.15 (m, 5H), 0.87 – 0.69 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.26, 129.65, 127.82, 125.26, 125.09, 119.24, 87.09, 71.67, 71.47, 69.83, 65.27, 64.46, 20.73, 7.67, 7.39, 6.32, 6.30. **HPLC analysis** (OD-3): Hexane/Isopropanol = 99.7:0.3, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 10.4$ min (major) and $t_R = 12.3$ min (minor). $[\alpha]_D^{25} = 111.6$ ($c = 0.645$,

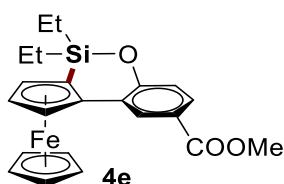
DCM).



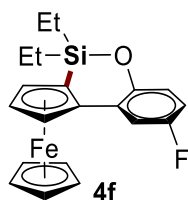
According to general procedure, **4c** was obtained in 82% yield and 97% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/DCM = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (d, $J = 2.5$ Hz, 1H), 7.13 (dd, $J = 8.5$, 2.5 Hz, 1H), 6.85 (d, $J = 8.5$ Hz, 1H), 4.98 (dd, $J = 2.4$, 1.1 Hz, 1H), 4.52 (t, $J = 2.4$ Hz, 1H), 4.27 (dd, $J = 2.3$, 1.1 Hz, 1H), 4.04 (s, 5H), 1.35 (s, 9H), 1.32 – 1.16 (m, 5H), 0.87 – 0.69 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.08, 143.18, 124.45, 124.08, 121.60, 118.87, 87.38, 71.68, 71.39, 69.81, 65.26, 64.37, 34.08, 31.61, 7.66, 7.52, 6.32, 6.31. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 97% ee, $t_R = 11.5$ min (major) and $t_R = 9.1$ min (minor). $[\alpha]_D^{25} = -29.7$ ($c = 0.72$, DCM).



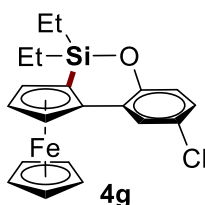
According to general procedure, **4d** was obtained in 87% yield and 96% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 3:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 – 7.60 (m, 3H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.35 – 7.31 (m, 2H), 6.99 (d, $J = 8.3$ Hz, 1H), 5.04 (s, 1H), 4.57 (s, 1H), 4.33 (s, 1H), 4.07 (s, 5H), 1.33 – 1.18 (m, 5H), 0.89 – 0.74 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.13, 141.16, 133.75, 128.65, 126.74, 126.57, 125.89, 125.84, 123.48, 119.90, 86.71, 71.84, 71.68, 69.90, 65.43, 64.41, 7.76, 7.47, 6.31, 6.29. **HRMS (ESI)** calcd for $\text{C}_{26}\text{H}_{26}\text{FeOSi}$ $[\text{M}]^+$ 438.1102, found 438.1103. **HPLC analysis** (OD-3): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 11.9$ min (major) and $t_R = 10.6$ min (minor). $[\alpha]_D^{25} = 36.2$ ($c = 0.46$, DCM).



According to general procedure, **4e** was obtained in 84% yield and 95% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/Ethyl acetate = 20:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 (d, $J = 2.2$ Hz, 1H), 7.79 (dd, $J = 8.5, 2.2$ Hz, 1H), 6.94 (d, $J = 8.5$ Hz, 1H), 5.07 (dd, $J = 2.4, 1.1$ Hz, 1H), 4.57 (t, $J = 2.4$ Hz, 1H), 4.30 (dd, $J = 2.4, 1.0$ Hz, 1H), 4.03 (s, 5H), 3.91 (s, 3H), 1.30 – 1.16 (m, 5H), 0.82 – 0.70 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.12, 156.58, 128.80, 126.81, 125.91, 122.64, 119.60, 85.64, 71.99, 71.94, 69.92, 65.83, 63.89, 51.88, 7.81, 7.48, 6.23, 6.14. **HPLC analysis** (OD-3) Hexane/Isopropanol=99:1, 0.5 mL/min, 254 nm UV detector, 95% ee, $t_R = 13.6$ min (major) and $t_R = 18.2$ min (minor). $[\alpha]_D^{25} = -72.1$ (c = 0.65, DCM).

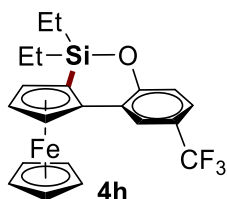


According to general procedure, **4f** was obtained in 92% yield and 95% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.07 (dd, $J = 9.6, 3.0$ Hz, 1H), 6.86 – 6.75 (m, 2H), 4.89 (d, $J = 2.2$ Hz, 1H), 4.55 (t, $J = 2.3$ Hz, 1H), 4.30 (d, $J = 2.1$ Hz, 1H), 4.05 (s, 5H), 1.30 – 1.12 (m, 5H), 0.84 – 0.68 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.17 (d, $J = 236.6$ Hz), 148.35, 126.99 (d, $J = 7.9$ Hz), 120.18 (d, $J = 8.5$ Hz), 113.26 (d, $J = 23.4$ Hz), 110.79 (d, $J = 24.0$ Hz), 85.77 (d, $J = 0.7$ Hz), 72.06, 71.86, 69.92, 65.64, 64.50, 7.70, 7.40, 6.27, 6.23. **HPLC analysis** (IC-3): Hexane/Isopropanol = 99.8:0.2, 0.5 mL/min, 254 nm UV detector, 95% ee, $t_R = 9.1$ min (major) and $t_R = 10.5$ min (minor). $[\alpha]_D^{25} = 257.3$ (c = 0.225, DCM).

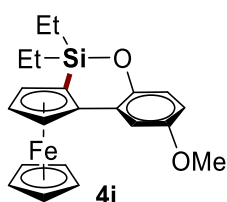


According to general procedure, **4g** was obtained in 92% yield and 96% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 4:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 (d, $J = 2.7$ Hz, 1H), 7.06 (dd, $J = 8.6,$

2.7 Hz, 1H), 6.86 (d, $J = 8.6$ Hz, 1H), 4.92 (dd, $J = 2.5, 1.0$ Hz, 1H), 4.56 (t, $J = 2.4$ Hz, 1H), 4.30 (dd, $J = 2.5, 1.1$ Hz, 1H), 4.06 (s, 5H), 1.32 – 1.16 (m, 5H), 0.84 – 0.69 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.00, 127.57, 126.71, 125.44, 124.33, 120.78, 85.46, 72.06, 71.94, 69.94, 65.55, 64.37, 7.72, 7.40, 6.25, 6.20. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_{\text{R}} = 14.7$ min (major) and $t_{\text{R}} = 11.8$ min (minor). $[\alpha]_{\text{D}}^{25} = -11.4$ (c = 0.47, DCM).

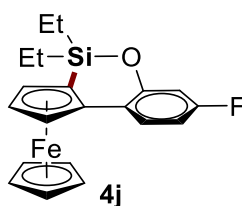


According to general procedure, **4h** was obtained in 89% yield and 95% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 2.3$ Hz, 1H), 7.37 (dd, $J = 8.6, 2.3$ Hz, 1H), 7.01 (d, $J = 8.5$ Hz, 1H), 5.01 (dd, $J = 2.5, 1.0$ Hz, 1H), 4.60 (t, $J = 2.4$ Hz, 1H), 4.34 (dd, $J = 2.4, 1.0$ Hz, 1H), 4.07 (s, 5H), 1.33 – 1.21 (m, 5H), 0.86 – 0.72 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.98, 126.49, 124.58 (q, $J = 272.7$ Hz), 123.97 (q, $J = 4.1$ Hz), 122.97 (q, $J = 32.7$ Hz), 121.91 (q, $J = 3.4$ Hz), 119.86, 85.21, 72.14 (d, $J = 4.3$ Hz), 69.97, 65.66, 64.23, 7.77, 7.46, 6.21, 6.15. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 95% ee, $t_{\text{R}} = 10.9$ min (major) and $t_{\text{R}} = 9.3$ min (minor). $[\alpha]_{\text{D}}^{25} = 221.2$ (c = 0.64, DCM).

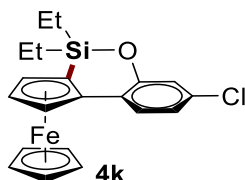


According to general procedure, **4i** was obtained in 93% yield and 96% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/Ethyl acetate = 20:1). ^1H NMR (400 MHz, CDCl_3) δ 6.93 (d, $J = 3.1$ Hz, 1H), 6.84 (d, $J = 8.7$ Hz, 1H), 6.66 (dd, $J = 8.8, 2.9$ Hz, 1H), 4.93 (s, 1H), 4.55 (s, 1H), 4.31 (s, 1H), 4.06 (s, 5H), 3.81 (s, 3H), 1.29 – 1.13 (m, 5H), 0.84 – 0.67 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.46, 146.54, 126.30, 119.77, 111.95, 110.33, 86.69, 71.86, 71.58, 69.86, 65.44, 64.69, 55.64, 7.63, 7.34,

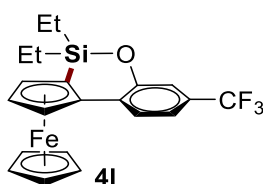
6.31, 6.28. **HPLC analysis** (IC-3): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 11.6$ min (major) and $t_R = 12.8$ min (minor). $[\alpha]_D^{25} = 67.7$ ($c = 0.55$, DCM).



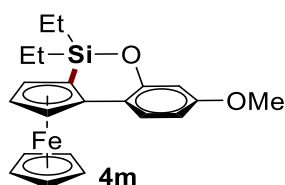
According to general procedure, **4j** was obtained in 88% yield and 96% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/DCM = 5:1). **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 7.34 (dd, $J = 8.6, 6.7$ Hz, 1H), 6.69 – 6.59 (m, 2H), 4.90 (dd, $J = 2.4, 1.1$ Hz, 1H), 4.52 (t, $J = 2.4$ Hz, 1H), 4.27 (dd, $J = 2.4, 1.0$ Hz, 1H), 4.04 (s, 5H), 1.31 – 1.16 (m, 5H), 0.85 – 0.72 (m, 5H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 161.94 (d, $J = 243.9$ Hz), 153.48 (d, $J = 12.2$ Hz), 125.41 (d, $J = 9.8$ Hz), 121.68 (d, $J = 3.1$ Hz), 107.75 (d, $J = 21.3$ Hz), 106.93 (d, $J = 23.3$ Hz), 86.43, 71.54, 71.46, 69.82, 65.23, 63.46, 7.72, 7.42, 6.23, 6.18. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 14.0$ min (major) and $t_R = 12.9$ min (minor). $[\alpha]_D^{25} = 231.4$ ($c = 0.38$, DCM).



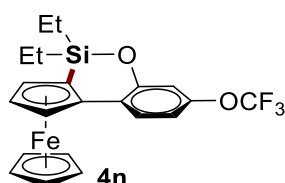
According to general procedure, **4k** was obtained in 90% yield and 96% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/DCM = 5:1). **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 7.35 (s, 1H), 7.05 (d, $J = 8.5$ Hz, 1H), 6.85 (d, $J = 8.6$ Hz, 1H), 4.92 (s, 1H), 4.56 (s, 1H), 4.31 (s, 1H), 4.06 (s, 5H), 1.29 – 1.12 (m, 5H), 0.83 – 0.65 (m, 5H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 151.00, 127.56, 126.72, 125.42, 124.33, 120.76, 85.57, 72.12, 72.01, 70.01, 65.57, 64.40, 7.69, 7.38, 6.25, 6.20. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 12.4$ min (major) and $t_R = 10.6$ min (minor). $[\alpha]_D^{25} = -10.6$ ($c = 0.63$, DCM).



According to general procedure, **4l** was obtained in 81% yield and 92% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 (dd, $J = 8.1, 1.0$ Hz, 1H), 7.17 (s, 1H), 7.12 – 7.10 (m, 1H), 4.98 (dd, $J = 2.5, 1.1$ Hz, 1H), 4.59 (t, $J = 2.4$ Hz, 1H), 4.33 (dd, $J = 2.4, 1.0$ Hz, 1H), 4.04 (s, 5H), 1.32 – 1.16 (m, 5H), 0.84 – 0.71 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.26, 129.86, 128.77 (q, $J = 33.7$ Hz), 125.04, 124.22 (q, $J = 272.7$ Hz), 122.87, 117.32 (q, $J = 3.8$ Hz), 116.61 (q, $J = 3.9$ Hz), 84.85, 72.33 (d, $J = 9.8$ Hz), 70.02, 65.94, 64.75, 7.76, 7.47, 6.22, 6.17. **HPLC analysis** (IC-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 92% ee, $t_R = 9.5$ min (major) and $t_R = 10.3$ min (minor). $[\alpha]_D^{25} = 292.2$ ($c = 0.64$, DCM).

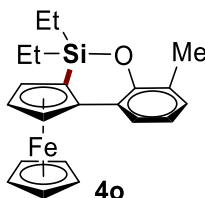


According to general procedure, **4m** was obtained in 90% yield and 97% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/Ethyl acetate = 20:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.5$ Hz, 1H), 6.53 (d, $J = 2.5$ Hz, 1H), 6.49 (dd, $J = 8.5, 2.6$ Hz, 1H), 4.93 (s, 1H), 4.53 (s, 1H), 4.30 (s, 1H), 4.07 (s, 5H), 3.81 (s, 3H), 1.31 – 1.13 (m, 5H), 0.91 – 0.69 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.21, 153.49, 125.44, 117.90, 107.26, 104.63, 88.09, 71.30, 71.27, 69.89, 64.81, 63.01, 55.16, 7.61, 7.39, 6.27, 6.24. **HPLC analysis** (IC-3): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 97% ee, $t_R = 11.5$ min (major) and $t_R = 15$ min (minor). $[\alpha]_D^{25} = 255.8$ ($c = 0.44$, DCM).

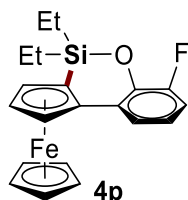


According to general procedure, **4n** was obtained in 86% yield and 96% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 (d, $J = 8.5$ Hz, 1H), 6.81 (s, 1H), 6.75 (d, $J = 7.6$ Hz, 1H), 4.93 (dd, $J = 2.4, 1.1$ Hz, 1H), 4.55 (t, $J = 2.4$ Hz, 1H), 4.29 (dd, $J = 2.4, 1.1$ Hz, 1H), 4.05 (s, 5H), 1.32 – 1.14 (m, 5H), 0.89 – 0.68 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.09, 147.95, 125.28, 124.60, 120.46 (q, $J = 256.6$ Hz), 113.06, 112.30, 85.64, 71.86, 71.78, 69.90,

65.50, 63.89, 7.74, 7.46, 6.22, 6.17. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 11.5$ min (major) and $t_R = 10.5$ min (minor). $[\alpha]_D^{25} = 307.8$ (c = 0.26, DCM).

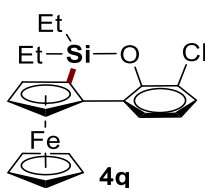


According to general procedure, **4o** was obtained in 90% yield and 92% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.5$ (Hexane/DCM = 5:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.26 – 7.18 (m, 1H), 6.98 (d, $J = 7.2$ Hz, 1H), 6.78 (t, $J = 7.4$ Hz, 1H), 5.01 (s, 1H), 4.58 (s, 1H), 4.36 (s, 1H), 4.09 (s, 5H), 2.27 (s, 3H), 1.29 – 1.08 (m, 5H), 0.90 – 0.69 (m, 5H). **¹³C NMR (101 MHz, CDCl₃)** δ 150.69, 128.54, 127.85, 124.82, 122.76, 119.93, 88.28, 71.90, 71.89, 70.22, 65.73, 64.67, 16.58, 7.60, 7.32, 6.31, 6.27. **HRMS (ESI)** calcd for C₂₁H₂₄FeOSi [M]⁺ 376.0945, found 376.0942. **HPLC analysis** (IC-3): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 92% ee, $t_R = 7.7$ min (major) and $t_R = 8.2$ min (minor). $[\alpha]_D^{25} = 348.9$ (c = 0.45, DCM).



According to general procedure, **4p** was obtained in 85% yield and 96% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM=5:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.14 (d, $J = 7.8$ Hz, 1H), 6.93 – 6.88 (m, 1H), 6.80 – 6.75 (m, 1H), 4.97 (s, 1H), 4.58 (s, 1H), 4.35 (s, 1H), 4.07 (s, 5H), 1.31 – 1.14 (m, 5H), 0.87 – 0.71 (m, 5H). **¹³C NMR (101 MHz, CDCl₃)** δ 153.59 (d, $J = 243.1$ Hz), 140.58 (d, $J = 12.3$ Hz), 128.32 (d, $J = 2.0$ Hz), 120.09 (d, $J = 7.7$ Hz), 119.89 (d, $J = 3.2$ Hz), 113.71 (d, $J = 19.1$ Hz), 85.83 (d, $J = 3.2$ Hz), 72.10, 71.84, 69.98, 65.87, 64.39, 7.80, 7.51, 6.27, 6.20. **HRMS (ESI)** calcd for C₂₀H₂₁FFeOSi [M]⁺ 380.0695, found 380.0693 **HPLC analysis** (OD-3): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 11.8$ min (major) and $t_R = 11.1$ min

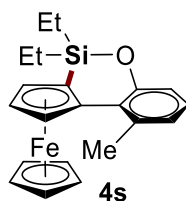
(minor). $[\alpha]_D^{25} = 282.8$ ($c = 0.78$, DCM).



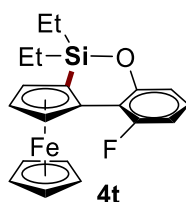
According to general procedure, **4q** was obtained in 94% yield and 90% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.20 (dd, $J = 7.9, 1.5$ Hz, 1H), 6.79 (t, $J = 7.8$ Hz, 1H), 4.95 (s, 1H), 4.56 (t, $J = 2.0$ Hz, 1H), 4.32 (s, 1H), 4.06 (s, 5H), 1.33 – 1.17 (m, 5H), 0.87 – 0.68 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.13, 127.52, 124.44, 123.27, 120.74, 86.10, 71.96, 71.93, 69.93, 65.77, 64.53, 7.71, 7.32, 6.18, 6.16. **HRMS (ESI)** calcd for $\text{C}_{20}\text{H}_{21}\text{ClFeOSi}$ $[\text{M}]^+$ 396.0400, found 396.0398. **HPLC analysis (OD-3)**: Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 90% ee, $t_R = 12.5$ min (major) and $t_R = 11.3$ min (minor). $[\alpha]_D^{25} = 416.6$ ($c = 0.57$, DCM).



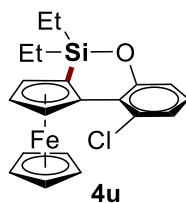
According to general procedure, **4r** was obtained in 98% yield and 96% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/Ethyl acetate = 20:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.03 (dd, $J = 7.7, 1.7$ Hz, 1H), 6.84 – 6.75 (m, 2H), 4.94 (s, 1H), 4.53 (s, 1H), 4.31 (s, 1H), 4.06 (s, 5H), 3.89 (s, 3H), 1.35 – 1.17 (m, 5H), 0.88 – 0.67 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.17, 141.95, 126.34, 120.13, 117.35, 110.26, 86.80, 71.76, 71.45, 69.78, 65.72, 64.45, 56.22, 7.64, 7.42, 6.32, 6.27. **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{25}\text{FeO}_2\text{Si}$ $[\text{M}]^+$ 393.0968, found 393.0962. **HPLC analysis (IA-3)**: Hexane/Isopropanol = 90:10, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 7.7$ min (major) and $t_R = 8.0$ min (minor). $[\alpha]_D^{25} = 431.1$ ($c = 0.34$, DCM).



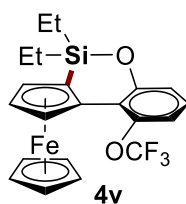
According to general procedure, **4s** was obtained in 89% yield and 98% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 7.02 (t, $J = 7.7$ Hz, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.78 (d, $J = 7.4$ Hz, 1H), 5.13 (s, 1H), 4.58 (s, 1H), 4.32 (s, 1H), 4.08 (s, 5H), 2.61 (s, 3H), 1.31 – 1.08 (m, 5H), 0.86 – 0.67 (m, 5H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 153.63, 135.70, 126.33, 125.27, 124.32, 118.12, 86.86, 71.62, 71.38, 70.19, 69.93, 66.77, 24.00, 6.90, 6.85, 6.40, 6.36. **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{24}\text{FeOSi}$ $[\text{M}]^+$ 376.0945, found 376.0940. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_R = 8.0$ min (major) and $t_R = 8.6$ min (minor). $[\alpha]_D^{25} = 154.5$ ($c = 0.326$, DCM).



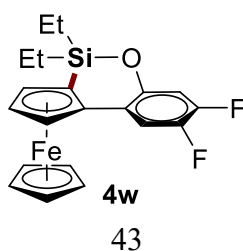
According to general procedure, **4t** was obtained in 84% yield and 96% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 7.01 (q, $J = 8.1$ Hz, 1H), 6.73 (d, $J = 8.1$ Hz, 1H), 6.68 – 6.63 (m, 1H), 5.32 (s, 1H), 4.59 (s, 1H), 4.32 (s, 1H), 4.09 (s, 5H), 1.28 – 1.12 (m, 5H), 0.86 – 0.71 (m, 5H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 160.39 (d, $J = 246.6$ Hz), 153.96 (d, $J = 7.4$ Hz), 126.29 (d, $J = 11.4$ Hz), 115.45 (d, $J = 3.0$ Hz), 114.99 (d, $J = 15.0$ Hz), 108.07 (d, $J = 23.6$ Hz), 81.52 (d, $J = 1.7$ Hz), 72.20 (d, $J = 3.1$ Hz), 71.25 (d, $J = 1.3$ Hz), 70.22, 70.06, 69.86, 7.54, 7.50, 6.30, 6.20. **HRMS (ESI)** calcd for $\text{C}_{20}\text{H}_{21}\text{FFeOSi}$ $[\text{M}]^+$ 380.0690, found 380.0688. **HPLC analysis** (OD-3): Hexane/Isopropanol = 99.5:0.5, 0.5 mL/min, 254 nm UV detector, 96% ee, $t_R = 11.8$ min (major) and $t_R = 11.1$ min (minor). $[\alpha]_D^{25} = 287.9$ ($c = 0.616$, DCM).



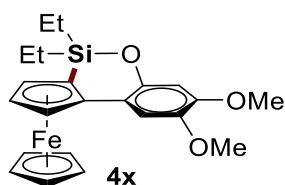
According to general procedure, **4u** was obtained in 92% yield and 98% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.04 – 7.00 (m, 2H), 6.92 – 6.88 (m, 1H), 5.79 (dd, $J = 2.5, 1.0$ Hz, 1H), 4.59 (t, $J = 2.5$ Hz, 1H), 4.32 (dd, $J = 2.4, 1.0$ Hz, 1H), 4.09 (s, 5H), 1.31 – 1.15 (m, 5H), 0.88 – 0.70 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.40, 131.41, 126.60, 125.24, 123.90, 118.89, 83.97, 71.97, 71.59, 71.05, 69.98, 66.31, 7.08, 6.91, 6.33, 6.27. **HRMS (ESI)** calcd for $\text{C}_{20}\text{H}_{21}\text{ClFeOSi}$ $[\text{M}]^+$ 396.0400, found 396.0399. **HPLC analysis** (OD-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_R = 10.1$ min (major) and $t_R = 11$ min (minor). $[\alpha]_D^{25} = 14.7$ ($c = 0.29$, DCM).



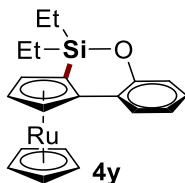
According to general procedure, **4v** was obtained in 93% yield and 98% ee as dark orange oil under the optimized condition by use of **L6** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.09 (t, $J = 8.1$ Hz, 1H), 6.92 – 6.87 (m, 2H), 5.34 (s, 1H), 4.59 (t, $J = 2.3$ Hz, 1H), 4.31 (s, 1H), 4.07 (s, 5H), 1.38 – 1.09 (m, 5H), 0.84 – 0.65 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.28, 146.38 (q, $J = 1.4$ Hz), 126.26, 120.73 (d, $J = 258.2$ Hz), 120.47, 118.51, 113.35 (q, $J = 1.6$ Hz), 81.62, 72.50, 71.56, 70.19, 69.94, 65.47, 7.48, 7.16, 6.29, 6.17. **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{21}\text{F}_3\text{FeO}_2\text{Si}$ $[\text{M}]^+$ 446.0612, found 446.0610. **HPLC analysis** (OD-3): Hexane/Isopropanol = 100:0, 0.5 mL/min, 254 nm UV detector, 98% ee, $t_R = 9.9$ min (major) and $t_R = 10.7$ min (minor). $[\alpha]_D^{25} = 201.5$ ($c = 0.423$, DCM).



According to general procedure, **4w** was obtained in 80% yield and 91% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/DCM = 5:1). **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 7.15 (dd, $J = 11.4, 9.0$ Hz, 1H), 6.73 (dd, $J = 11.7, 7.2$ Hz, 1H), 4.83 (dd, $J = 2.5, 1.0$ Hz, 1H), 4.53 (t, $J = 2.4$ Hz, 1H), 4.28 (dd, $J = 2.4, 1.0$ Hz, 1H), 4.05 (s, 5H), 1.30 – 1.14 (m, 5H), 0.84 – 0.68 (m, 5H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 148.57 (dd, $J = 247.5, 14.0$ Hz), 148.36 (d, $J = 9.8$ Hz), 144.99 (dd, $J = 239.0, 13.0$ Hz), 122.02 (dd, $J = 5.5, 1.6$ Hz), 112.16 (d, $J = 19.2$ Hz), 108.49 (d, $J = 19.1$ Hz), 85.42, 71.92, 71.76, 69.93, 65.48, 63.84, 7.69, 7.38, 6.19, 6.15. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 91% ee, $t_R = 14.7$ min (major) and $t_R = 14.3$ min (minor). $[\alpha]_D^{25} = 237.2$ ($c = 0.135$, DCM).



According to general procedure, **4x** was obtained in 91% yield and 94% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.3$ (Hexane/Ethyl acetate = 10:1). **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 6.87 (s, 1H), 6.54 (s, 1H), 4.85 (s, 1H), 4.49 (s, 1H), 4.24 (s, 1H), 4.04 (s, 5H), 3.90 (s, 3H), 3.87 (s, 3H), 1.30 – 1.12 (m, 5H), 0.65 – 0.66 (m, 5H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 148.43, 146.79, 143.16, 116.29, 108.34, 103.89, 87.76, 71.33, 71.04, 69.74, 64.76, 63.33, 56.69, 55.75, 7.60, 7.39, 6.27, 6.24. **HPLC analysis** (IA-3): Hexane/Isopropanol = 98:2, 0.5 mL/min, 254 nm UV detector, 94% ee, $t_R = 13.7$ min (major) and $t_R = 11.3$ min (minor). $[\alpha]_D^{25} = 203.4$ ($c = 0.59$, DCM).

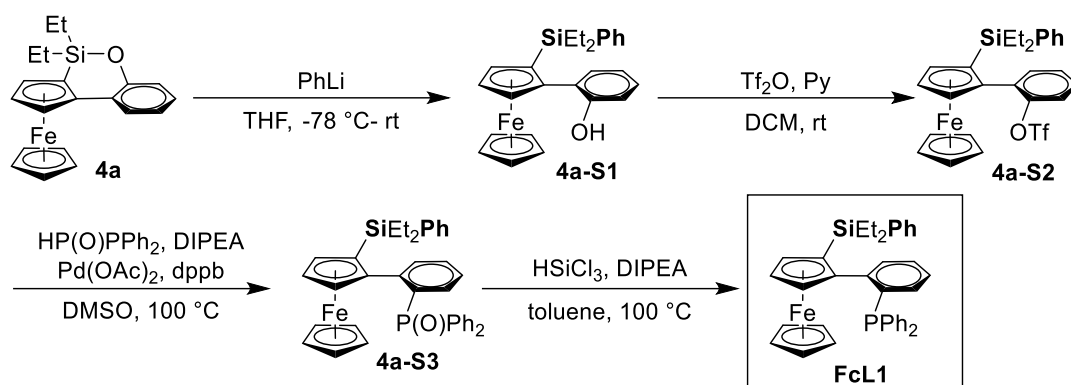


According to general procedure, **4y** was obtained in 90% yield and 97% ee as dark orange oil under the optimized condition by use of **L2** as the chiral ligand at 60 °C for 24 h. $R_f = 0.4$ (Hexane/DCM = 5:1). **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 7.37 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.08 – 7.05 (m, 1H), 6.90 – 6.83 (m, 2H), 5.34 (dd, $J = 2.3, 0.9$ Hz, 1H), 4.85 (t, $J = 2.3$ Hz, 1H), 4.64 (dd, $J = 2.3, 0.9$ Hz, 1H), 4.48 (s, 5H), 1.21 – 1.09 (m, 4H), 0.97 – 0.81 (m, 6H). **$^{13}\text{C NMR}$ (101 MHz,**

CDCl₃) δ 152.14, 127.02, 124.71, 124.63, 120.54, 119.41, 89.80, 73.36, 72.81, 71.73, 68.16, 67.58, 8.84, 7.59, 6.38, 6.15. **HPLC analysis** (IA-3): Hexane/Isopropanol = 99.9:0.1, 0.5 mL/min, 254 nm UV detector, 97% ee, t_R = 11.2 min (major) and t_R = 13.2 min (minor). $[\alpha]_D^{25}$ = 213.9 (c = 0.75, DCM).

4. Applications of Product 4a

4.1 Ligand synthesis⁹



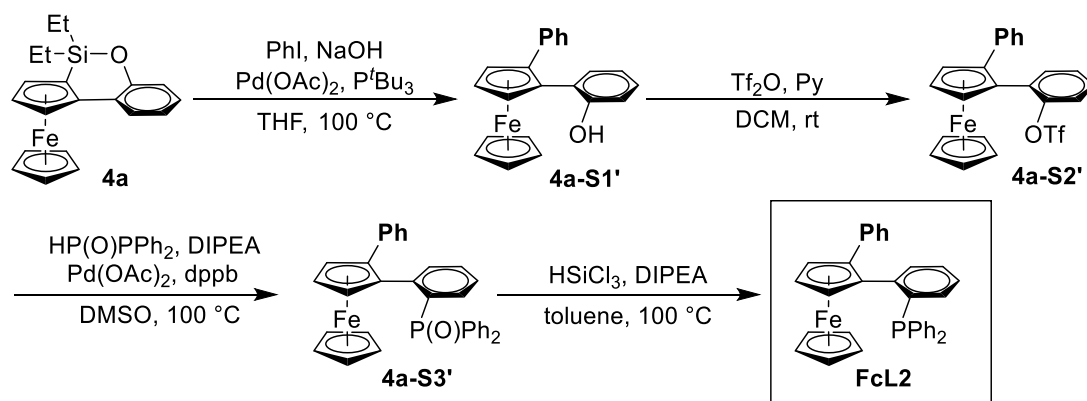
A flame-dried Schlenk tube containing a stir bar was charged with **4a** (1.86 g, 5 mmol, 1 equiv). The tube was then evacuated and backfilled with N₂ for three times, followed by addition of 25 mL of THF. The solution was cooled to -78 °C and PhLi (10 mL, 1 mol/L in Et₂O, 2 equiv) was added dropwise. The reaction mixture was stirred for 30 min at -78 °C and then allowed to warm to room temperature for additional 30 min. After completion of the reaction, the reaction mixture was quenched with NH₄Cl solution (3 mL), extracted with Et₂O (30 mL × 3), washed with brine (30 mL), dried over Na₂SO₄, filtered and concentrated in vacuum. The crude residue was purified by flash column chromatography on silica gel (Hexane/DCM, 90/10), affording the product **4a-S1**.

To a solution of ferrocenyl-phenol **4a-S1** (10 mmol, 1 equiv) and pyridine (3.3 mL, 20 mmol, 2 equiv) in DCM (25 mL), Tf₂O (1.2 mL, 15 mmol, 1.5 equiv) was added dropwise at 0 °C and the mixture was stirred at room temperature overnight. After the reaction was finished, the reaction mixture was diluted with DCM (100 mL) and washed with 1N HCl solution (30 mL × 3). The organic layer was separated, washed with brine (50 mL), dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to deliver the product **4a-S2**.

A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with Pd(OAc)₂ (112.5 mg, 0.5 mmol, 0.1 equiv), dppb (213.3 mg, 0.5 mmol, 0.1 equiv), HP(O)Ph₂ (2.02 g, 10 mmol, 1 equiv) and ArOTf (5 mmol, 1 equiv). The tube was evacuated and backfilled with N₂ for three times, followed by addition of the DIPEA (3.3 mL, 20 mmol, 4 equiv) and DMSO (25 mL). The reaction mixture was heated to 100 °C with continuously stirring for 18 h. After the reaction was finished,

the reaction mixture was cooled to room temperature, diluted with EtOAc (50 mL) and washed with 1N HCl solution (15 mL × 3) and brine (30 mL × 3). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to yield the product **4a-S3**.

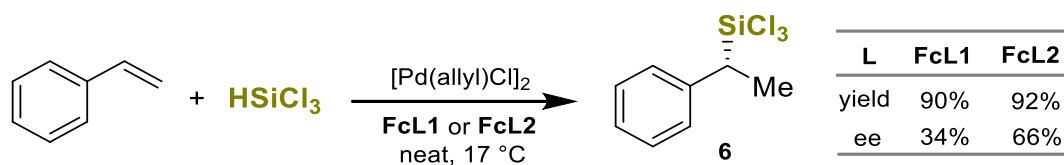
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with ArP(O)Ph₂ **4a-S3** (5 mmol, 1 equiv). The tube was evacuated and backfilled with N₂ for three times, followed by addition of DIPEA (8.3 mL, 50 mmol, 10 equiv) and toluene (25 mL). The reaction mixture was cooled to 0 °C and HSiCl₃ (2.6 mL, 25 mmol, 5 equiv) was added dropwise to the stirred solution. After addition, the reaction mixture was heated to 90 °C with continuously stirring for 24 h. After the reaction was finished, an aqueous solution of NaOH was added dropwise to the stirred solution at 0 °C. Then, the reaction mixture was extracted with Et₂O (30 mL × 3), washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuum. The crude residue was purified by flash column chromatography on silica gel (Hexane/DCM, 90/10), affording the phosphine ligand **FcL1**. **FcL1** was obtained in 56 % yield over 4steps as orange solid. $R_f = 0.4$ (Hexane/DCM = 4:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.74 – 7.71 (m, 1H), 7.45 – 7.36 (m, 2H), 7.29 – 7.21 (m, 6H), 7.18 – 7.06 (m, 7H), 6.92 – 6.88 (m, 2H), 6.83 – 6.80 (m, 1H), 4.20 (t, $J = 2.4$ Hz, 1H), 4.09 (s, 1H), 3.93 (s, 5H), 3.83 (t, $J = 1.9$ Hz, 1H), 1.03 – 0.61 (m, 10H). **¹³C NMR (101 MHz, CDCl₃)** δ 138.85 (d, $J = 13.9$ Hz), 138.25 (d, $J = 12.4$ Hz), 137.91 (d, $J = 13.7$ Hz), 137.22, 134.83, 134.04, 133.99, 133.94, 133.74, 133.68, 133.49, 133.42, 128.66, 128.36, 128.30, 128.17, 128.11, 127.95, 127.73, 127.42, 126.92, 96.32, 96.22, 74.94, 74.70, 74.61, 71.57, 69.26, 7.77, 7.66, 4.53, 4.46. (The complicate C-P splittings were observed from 134.04 ppm to 126.92 ppm). **³¹P NMR (162 MHz, CDCl₃)** δ -15.64. **HRMS (ESI)** calcd for C₃₈H₃₇FePSi [M]⁺ 608.1746, found 608.1750. $[\alpha]_D^{25} = 42.0$ (c = 0.12, CHCl₃).



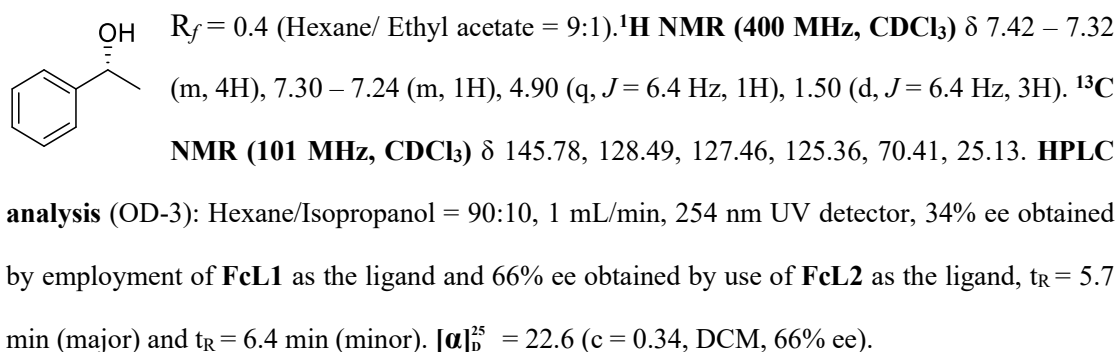
A flame-dried Schlenk tube containing a stirbar was charged with Pd(OAc)₂ (112.5 mg, 0.5 mmol, 0.1 equiv), P'^tBu₃ (202 mg, 1 mmol, 0.2 equiv), NaOH (0.6 g, 15 mmol, 3 equiv) and **4a** (1.86 g, 5 mmol, 1 equiv) in glovebox, followed by addition of PhI (3.06 g, 15 mmol, 3 equiv) and THF (25 mL). The reaction tube was capped, removed from the glove box and the reaction mixture was stirred at 100 °C for 24 h. Then, the reaction mixture was cooled to room temperature and then quenched with 1N HCl solution (30 mL), extracted with Et₂O (30 mL × 3), washed with brine (30 mL), dried over Na₂SO₄, filtered and concentrated in vacuum. The crude residue was purified by flash column chromatography on silica gel (Hexane/DCM, 90/10) to deliver the ferrocenyl-phenol **4a-S1'**.

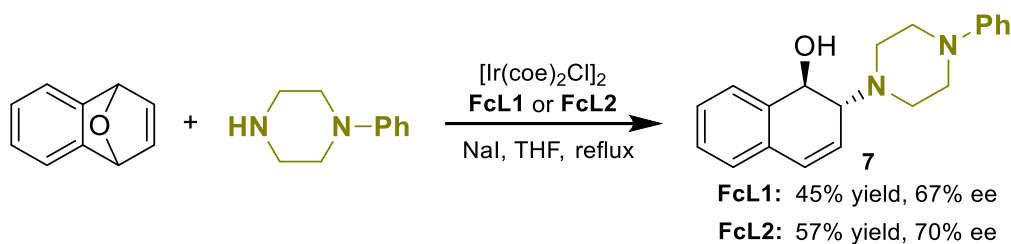
As described in the synthesis of **FcL1**, the ferrocenyl-phenol **4a-S1'** was transformed to the phosphine ligand **FcL2** by 3-steps. Notably, to ensure the ee value of the **FcL2**, **4a-S3'** underwent recrystallization (in CH₃OH) before reduction. **FcL2** was obtained in 38% yield over 4 steps as orange solid. *R_f* = 0.4 (Hexane/DCM = 3:1). ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.91 (m, 1H), 7.28–7.18 (m, 4H), 7.14 – 7.01 (m, 11H), 6.95 – 6.74 (m, 3H), 4.51 (t, *J* = 1.5 Hz, 1H), 4.20 (d, *J* = 2.4 Hz, 1H), 4.17 (s, 1H), 4.09 (s, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 143.09, 142.80, 138.58, 138.52, 138.38, 137.80, 137.77, 137.67, 137.63, 133.72, 133.65, 133.63, 133.55, 133.50, 133.46, 133.43, 128.95, 128.22, 128.15, 128.13, 128.05, 127.99, 127.50, 126.97, 125.63, 89.23 (d, *J* = 9.9 Hz), 87.89 (d, *J* = 2.3 Hz), 72.71 (d, *J* = 8.0 Hz), 70.46, 68.66, 66.54. (The complicate C-P splittings were observed from 143.09 ppm to 89.23 ppm). ³¹P NMR (162 MHz, CDCl₃) δ -13.58. HRMS (ESI) calcd for C₃₄H₂₇FeP [M]⁺ 522.1194, found 522.1186. [*α*]_D²⁵ = 159.0 (c = 0.18, CHCl₃).

4.2 Applications of chiral ligands **FcL1** and **FcL2**



Following the literature's procedure,¹⁰ a flame-dried Schlenk tube containing a stirbar was charged with allylpalladium chloride dimer (1.5 mg, 0.00625 mmol, 0.125 mol %), the chiral ligand **FcL1** or **FcL2** (0.025 mmol, 0.5 mol %) and styrene (520 mg, 5 mmol, 1 equiv) in glovebox. The resulting mixture was stirred in the glovebox at room temperature for 1 hour, followed by the dropwise addition of the trichlorosilane (1.6 mL, 10 mmol, 2 equiv) at 0 °C. After addition, the reaction mixture was allowed to warm to room temperature and the tube was capped, removed from the glove box. The reaction mixture was stirred at room temperature (17 °C) for 24 h and then was subjected to bulb-to-bulb distillation, giving 1-(trichlorosilyl)-1-phenylethane **6** as colorless oil. To determine the ee value of product **6**, the Fleming-Tamao oxidation was carried out: To a mixture of the hydrosilylation product **6** (177 mg, 0.741 mmol, 1 equiv), KF (258 mg, 4.446 mmol, 6 equiv), KHCO₃ (445 mg, 4.446 mmol, 6 equiv) in THF (15 mL) and MeOH (15 mL) was added H₂O₂ (0.89 mL, 30%) at room temperature. The mixture was stirred at room temperature for 17 h. To the mixture was added sat. Na₂S₂O₃ aq. Organic materials were extracted with ether, washed with water and brine, and dried over Na₂SO₄. After evaporation of the solvent, the residue was subjected to bulb-to-bulb distillation, giving enantioenriched 1-arylethanol. The enantiomeric excesses of the alcohol was determined by HPLC on a chiral stationary phase. The absolute configurations were assigned on the basis of the optical rotation.





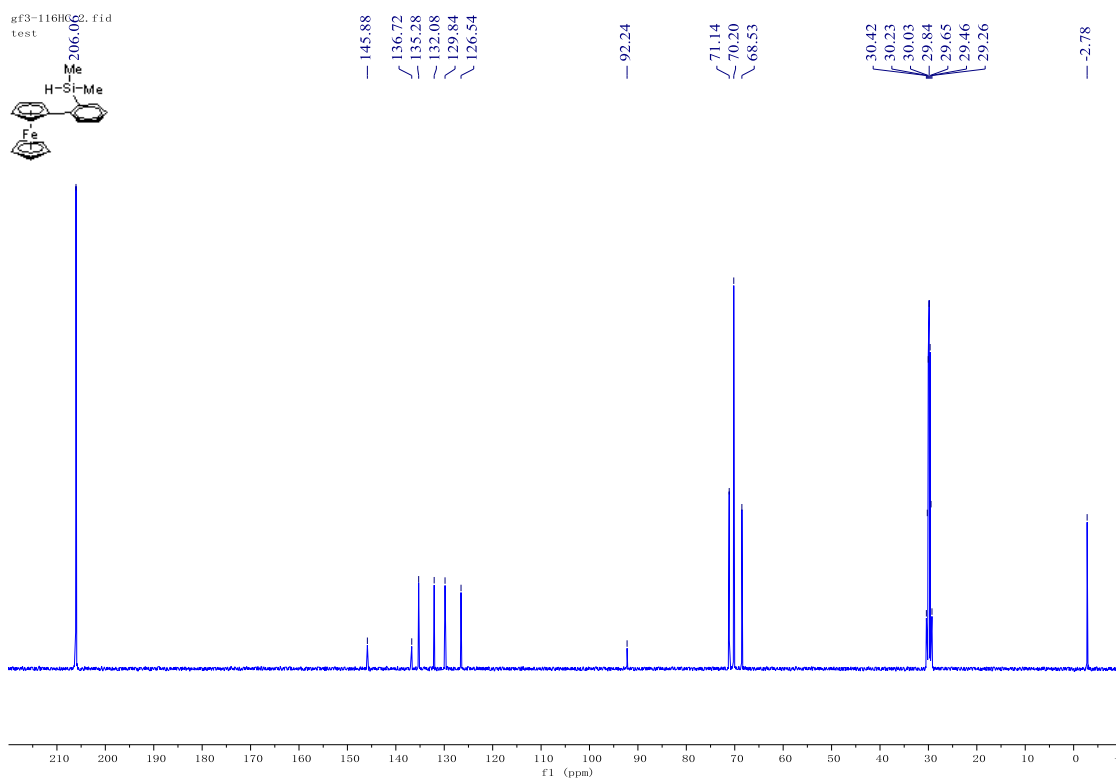
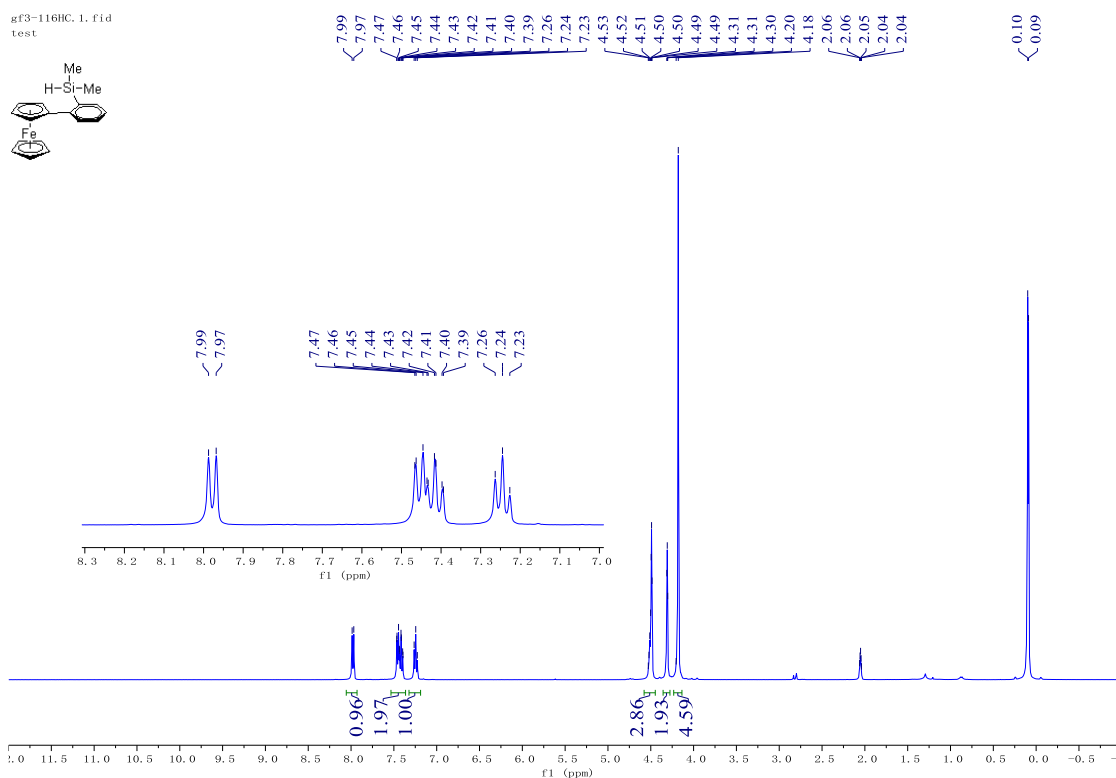
Following a modified literature's procedure,¹¹ a flame-dried Schlenk tube containing a stirbar was charged with $[\text{Ir}(\text{coe})_2\text{Cl}]_2$ (3.8 mg, 0.004 mmol, 2 mol%), the chiral ligand **FcL1** or **FcL2** (0.01 mmol, 5 mol%) and THF (0.6 mL) in glovebox. After 1 h stirring at room temperature, oxabenzonorbornadiene (28.8 mg, 0.2 mmol, 1 equiv), 1-phenylpiperazine (97.3 mg, 0.6 mmol, 3 equiv), NaI (6 mg, 0.04 mmol, 0.2 equiv) and THF (0.6 mL) was added to the Schlenk tube and the reaction mixture was allowed to stirred at reflux for 18 h. After the reaction was finished, the crude residue was purified by flash column chromatography on silica gel to afford the product **7** in 45% yield for **FcL1** and in 57% yield for **FcL2** as white solid. $R_f = 0.3$ (Hexane/ Ethyl acetate = 7:3). **¹H NMR (400 MHz, CDCl₃)** δ 7.59 (d, $J = 7.2$ Hz, 1H), 7.30 – 7.22 (m, 5H), 7.09 (d, $J = 7.1$ Hz, 1H), 6.95 (d, $J = 8.2$ Hz, 2H), 6.88 (t, $J = 7.3$ Hz, 1H), 6.56 (dd, $J = 9.9, 2.6$ Hz, 1H), 6.14 (dd, $J = 10.0, 2.5$ Hz, 1H), 4.93 (d, $J = 11.7$ Hz, 1H), 3.53 (dt, $J = 11.8, 2.7$ Hz, 1H), 3.33 – 3.19 (m, 4H), 3.02 – 2.97 (m, 2H), 2.76 – 2.70 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 151.16, 136.89, 131.66, 129.63, 129.14, 127.97, 127.51, 126.26, 124.84, 124.57, 123.96, 120.03, 116.29, 67.66, 67.60, 49.71, 48.97. **HPLC analysis (OD-3):** Hexane/Isopropanol = 90:10, 1 mL/min, 254 nm UV detector, 67% ee for **FcL1** and 70% ee for **FcL2**, $t_R = 11.6$ min (major) and $t_R = 13.5$ min (minor). $[\alpha]_D^{25} = -49.5$ (c = 0.13, CHCl₃, 70% ee).

5. References

1. Zhang QW, An K, Liu LC, Yue Y, He W. Rhodium-catalyzed Enantioselective Intramolecular C-H Silylation for the Syntheses of Planar-chiral Metallocene Siloles. *Angew Chem Int Ed.* 2015; 54(23): 6918-6921. [\[DOI\]](#)
2. Murai M, Matsumoto K, Takeuchi Y, Takai K. Rhodium-Catalyzed Synthesis of Benzosilolometallobenes via the Dehydrogenative Silylation of C(*sp*²) - H Bonds. *Org Lett.* 2015; 17(12): 3102–3105. [\[DOI\]](#)
3. Milne, JE, Buchwald, SL. An Extremely Active Catalyst for the Negishi Cross-Coupling Reaction. *J Am Chem Soc.* 2004; 126(40): 13028–13032. [\[DOI\]](#)
4. Arnold, R, Matchett, SA, Rosenblum, M. Preparation and properties of stacked oligomeric and polymeric metallocenes. *Organometallics* 1988; 7(11): 2261–2266. [\[DOI\]](#)
5. Stemper, J, Isaac, K, Duret, V, Retailleau, P, Voituriez, A, Betzer, J-F, Marinetti, A. [3,3]Paracyclophanes as planar chiral scaffolds for the synthesis of new phosphoric acids. *Chem Commun.* 2013, 49(54), 6084-6086. [\[DOI\]](#)
6. Simmons, E M, Hartwig, J F. Iridium-Catalyzed Arene Ortho-Silylation by Formal Hydroxyl-Directed C–H Activation. *J Am Chem Soc.* 2010; 132(48): 17092-17095. [\[DOI\]](#)
7. Lee, T, Hartwig, JF. Rhodium-Catalyzed Enantioselective Silylation of Cyclopropyl C–H Bonds. *Angew Chem Int Ed.* 2016; 55(30): 8723-8727. [\[DOI\]](#)
8. Zhao WT, Lu ZQ, Zheng H, Xue XS, Zhao D. Rhodium-Catalyzed 2-Arylphenol-Derived Six-Membered Silacyclization: Straightforward Access toward Dibenzooxasilines and Silicon-Containing Planar Chiral Metallocenes. *ACS Catal.* 2018; 8(9): 7997–8005. [\[DOI\]](#)
9. J. H. Xie, L. X. Wang, Y. Fu, S. F. Zhu, B. M. Fan, H. F. Duan, Q. L. Zhou, Synthesis of Spiro Diphosphines and Their Application in Asymmetric Hydrogenation of Ketones. *J Am Chem Soc.* 2003; 125(15): 4404–4405. [\[DOI\]](#)
10. Guo, XX, Xie, JH, Hou, GH, Shi, WH, Wang, LX, Zhou, QL. Asymmetric palladium-catalyzed hydrosilylation of styrenes using efficient chiral spiro phosphoramidite ligands. *Tetrahedron: Asymmetry* 2004; 15(14): 2231-2234. [\[DOI\]](#)
11. Luo, R, Liao, J, Xie, L, Tang, W, Chan, ASC. Asymmetric ring-opening of oxabenzonorbornadiene with amines promoted by a chiral iridium-monophosphine catalyst. *Chem Commun.* 2013; 49(85): 9959-9961. [\[DOI\]](#)

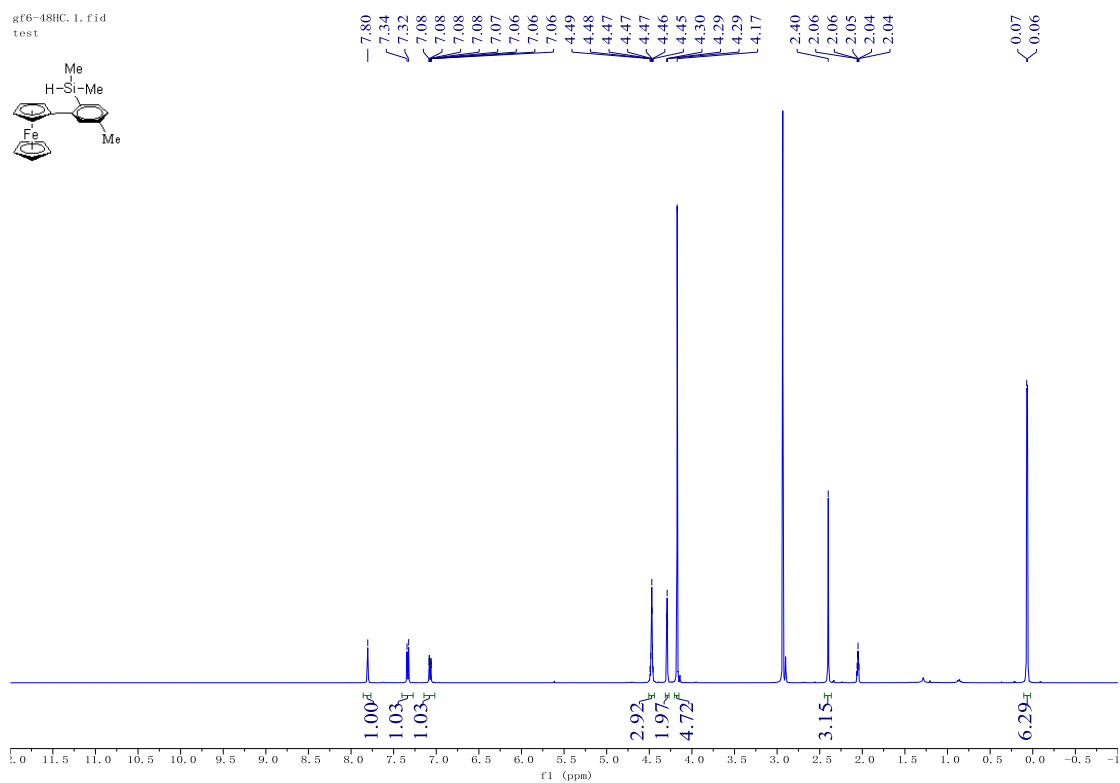
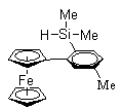
6. NMR Spectra

Compound 1a

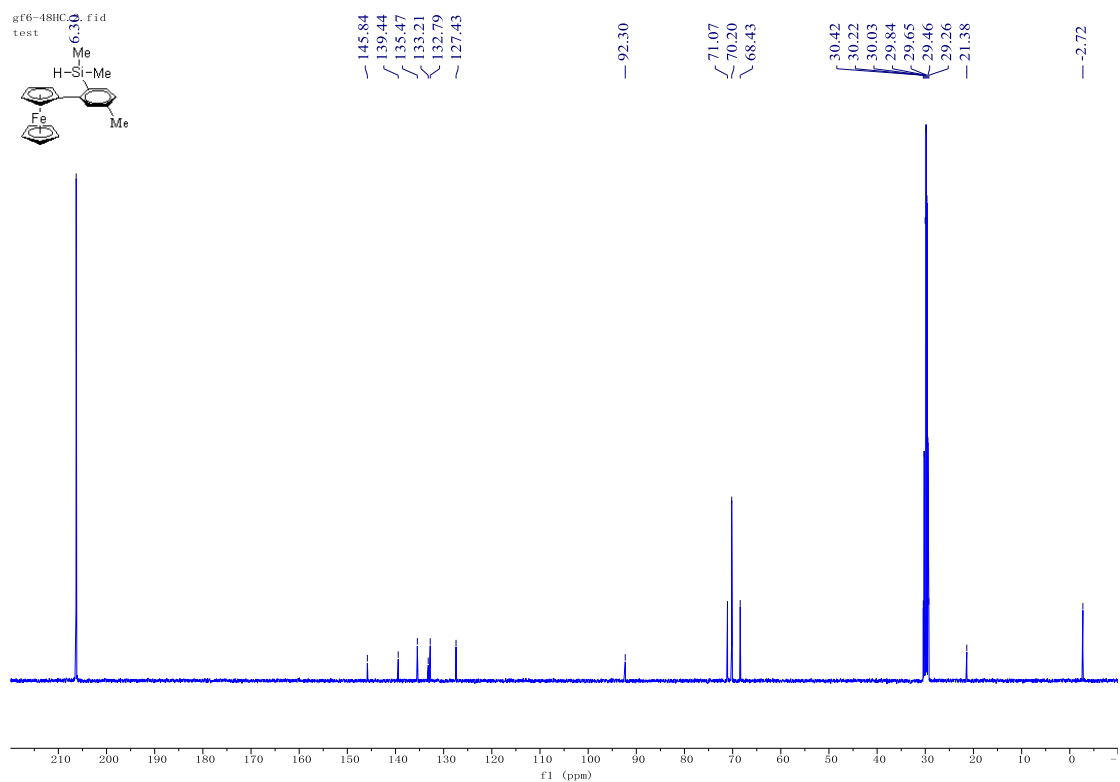
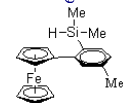


Compound 1b

gf6-48HC.1.fid
test

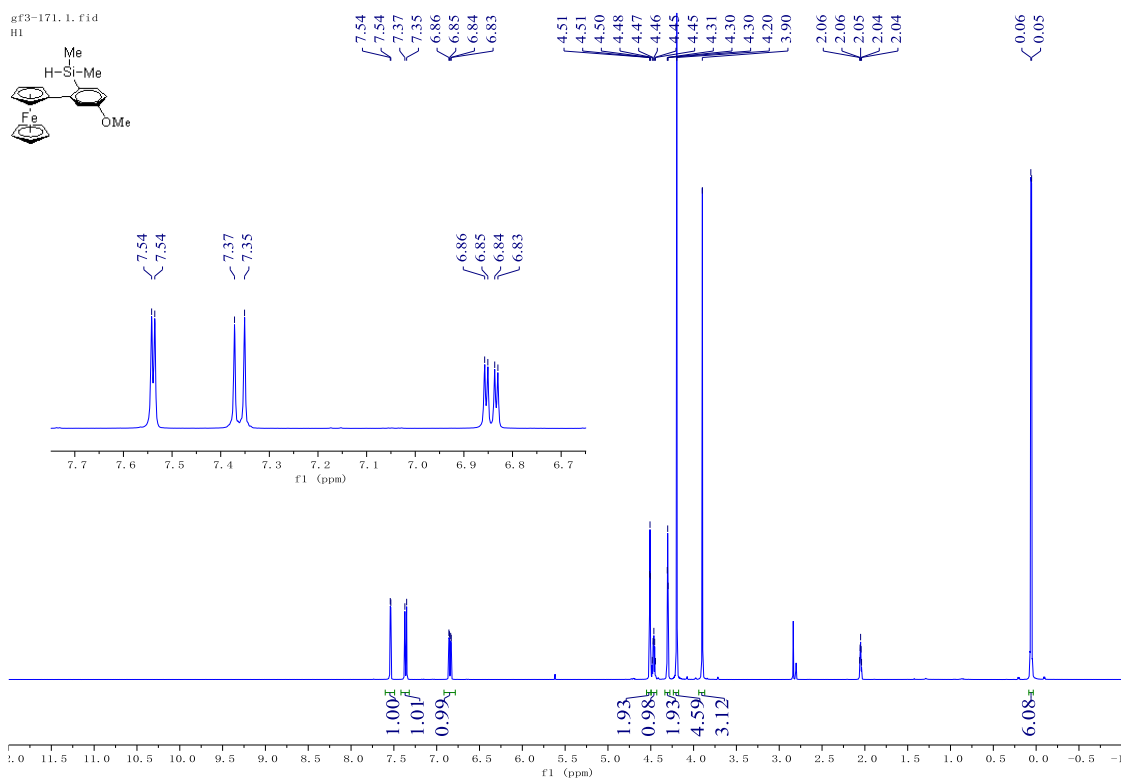
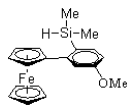


gf6-48HC.2.fid
test

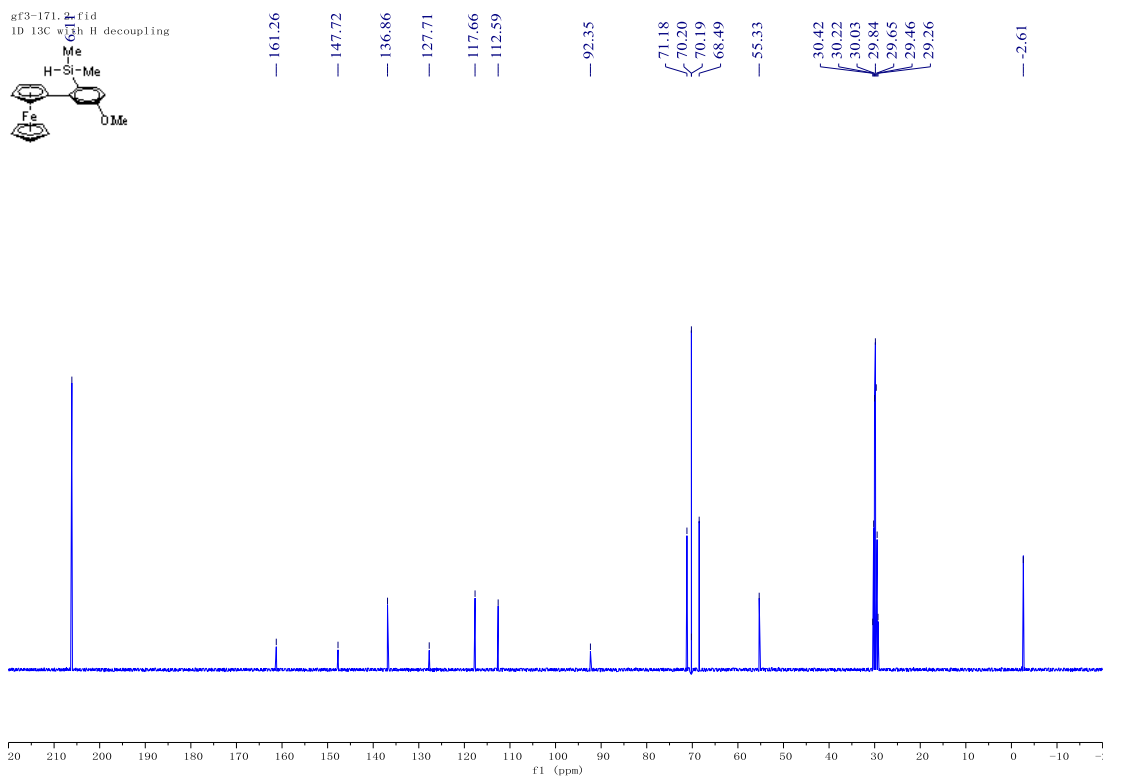
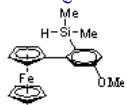


Compound 1c

gf3-171.1.fid
H1

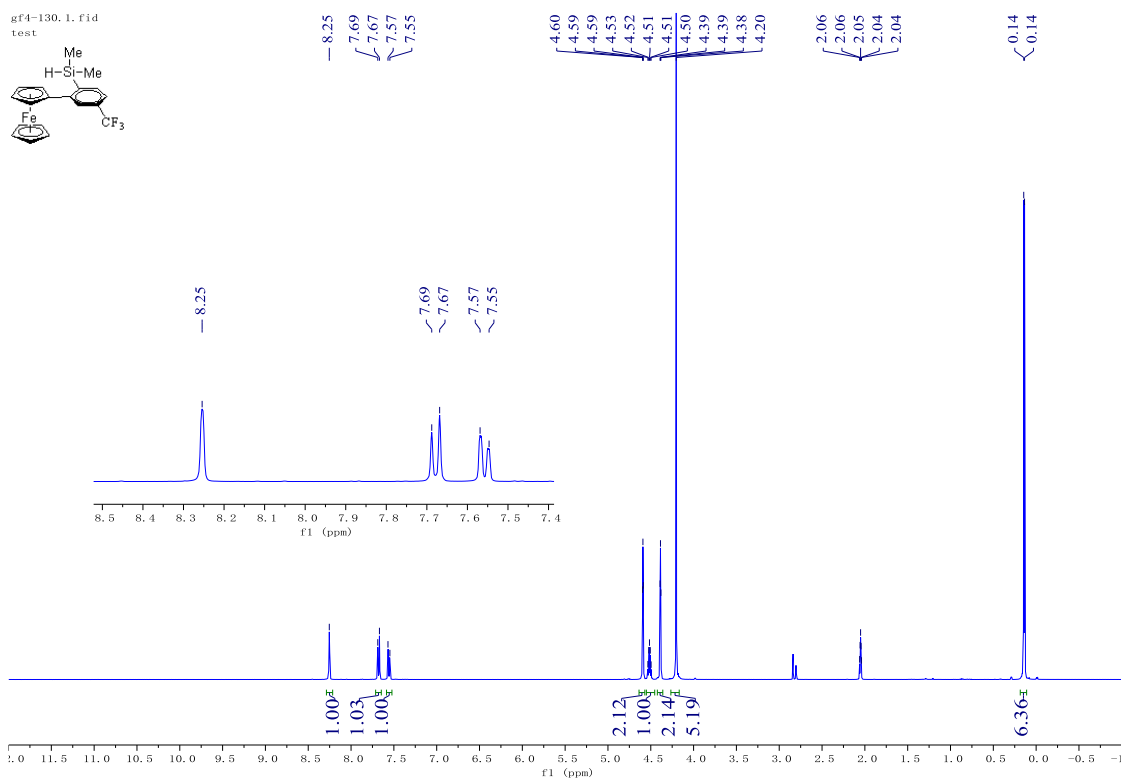
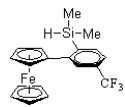


gf3-171.2.fid
ID 13C w/1h H decoupling

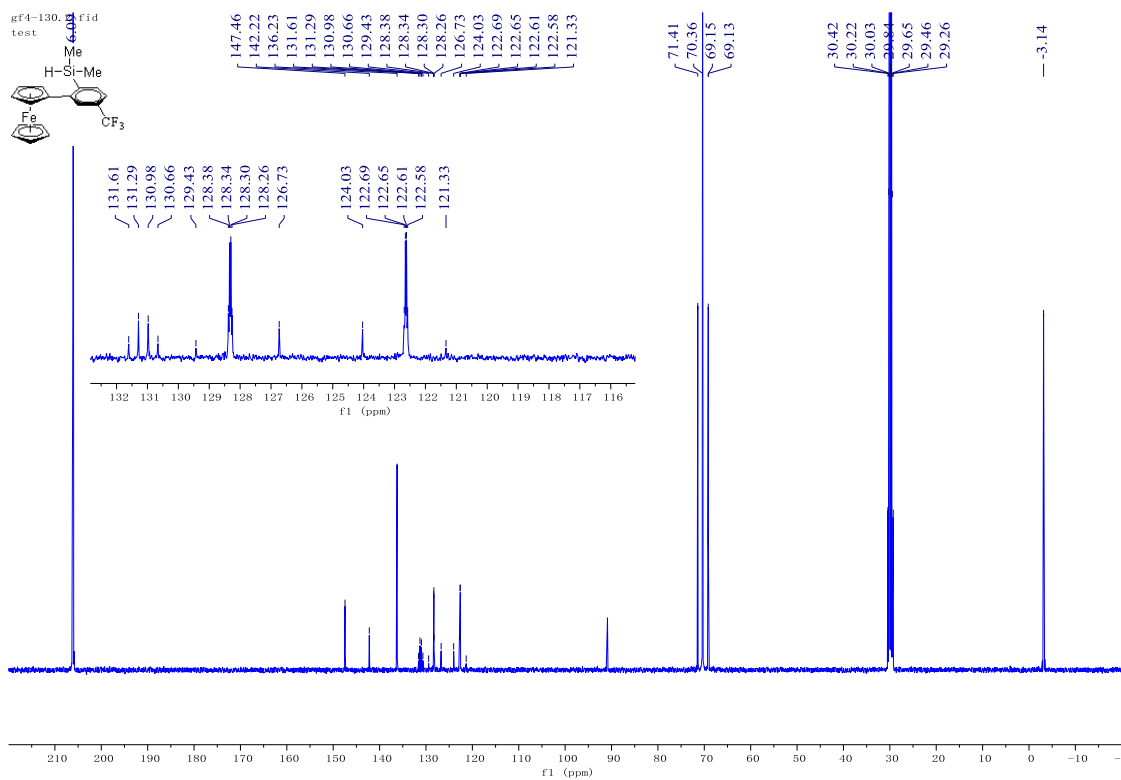
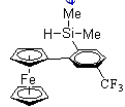


Compound 1d

gf4-130, 1.fid
test

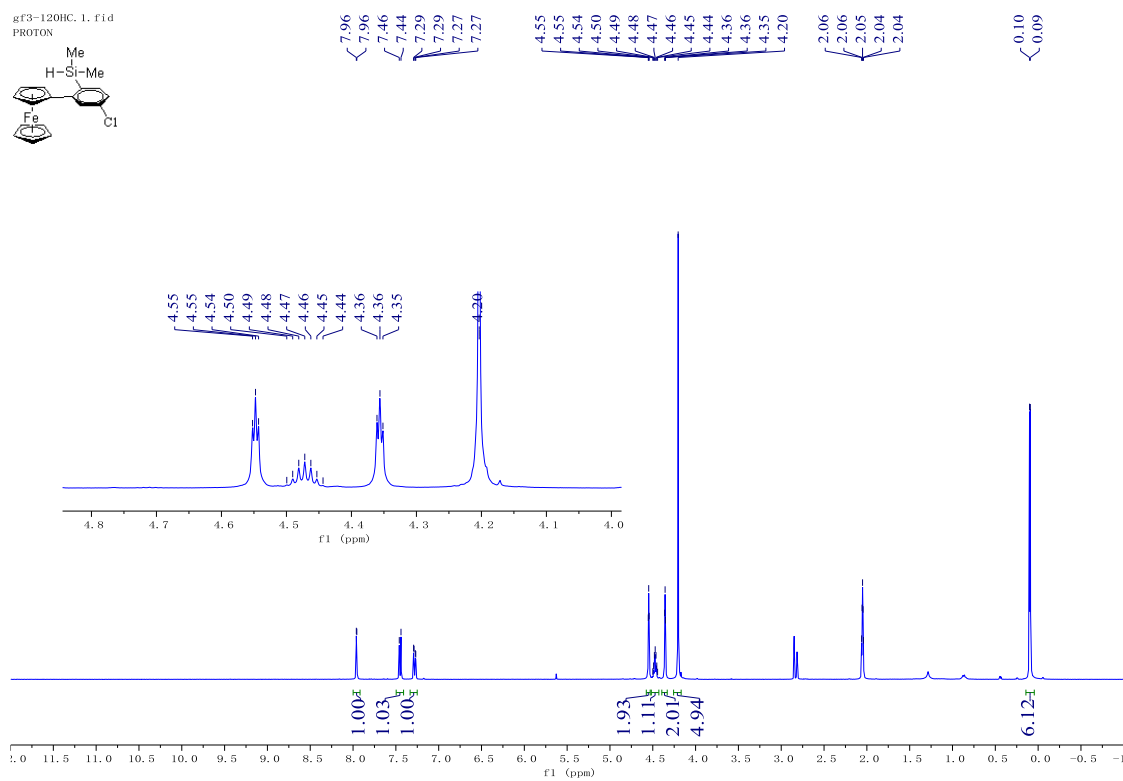
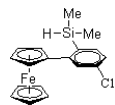


gf4-130, 1.fid
test

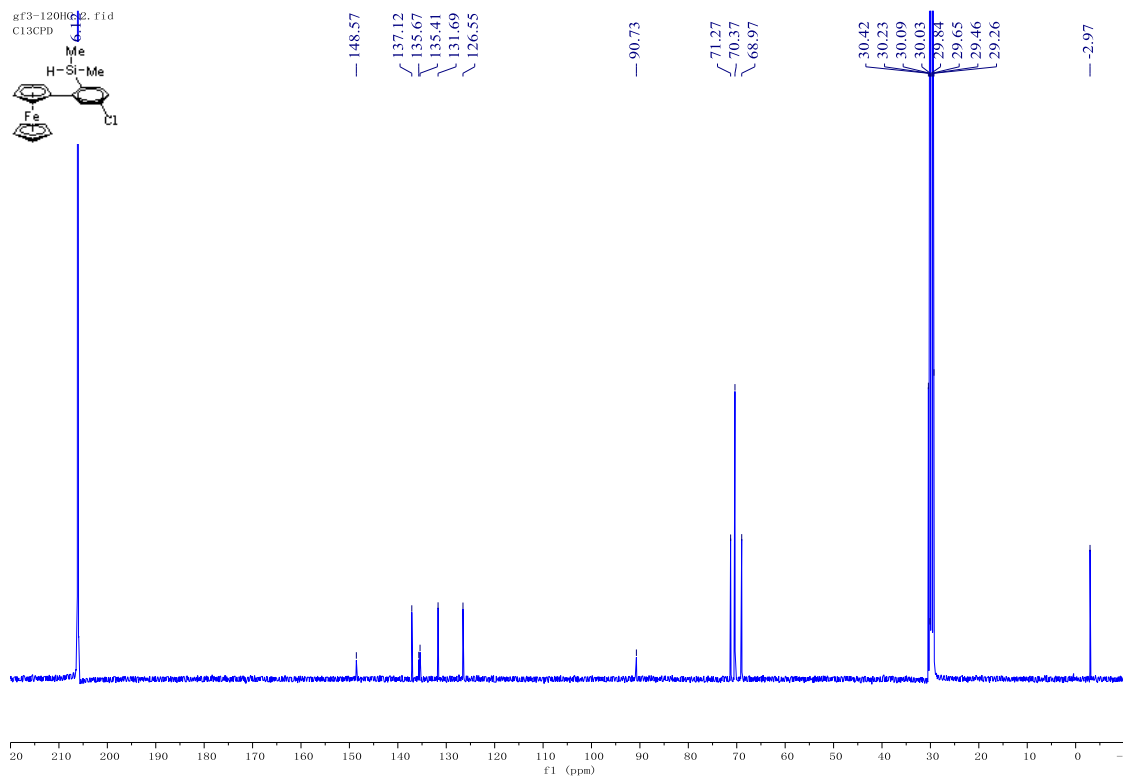
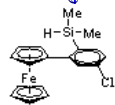


Compound 1e

gf3-120HC.1.fid
PROTON

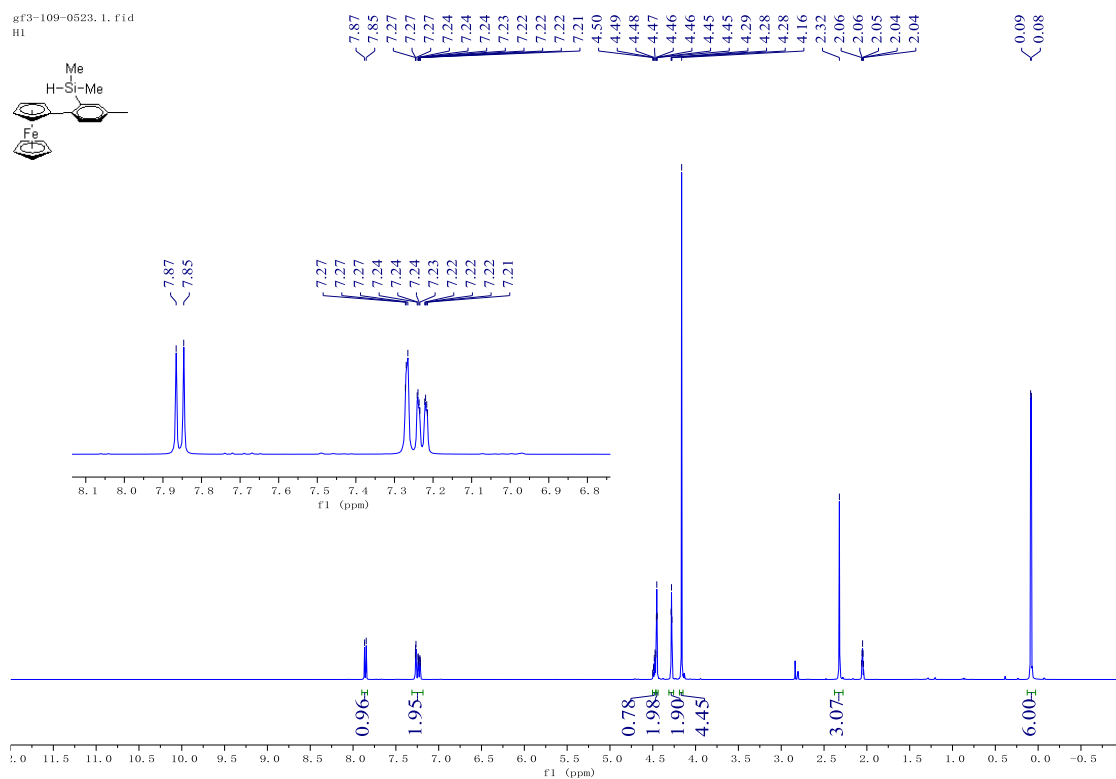
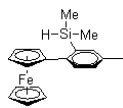


gf3-120HC.2.fid
C13CPD

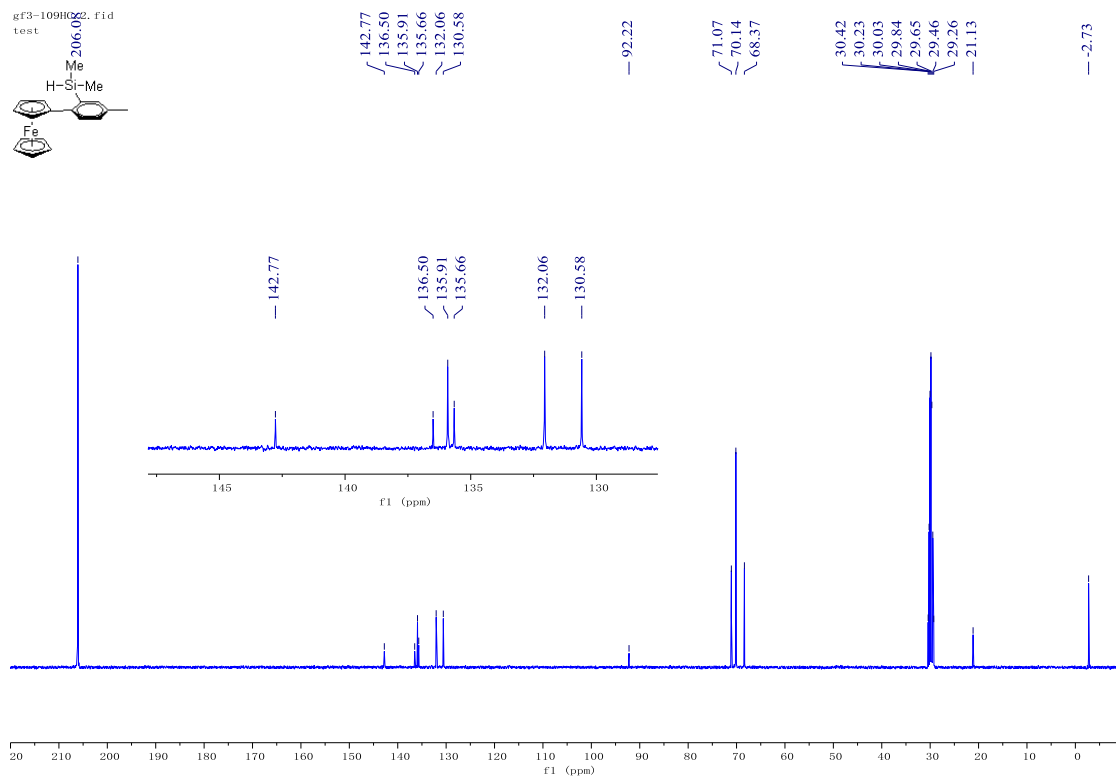
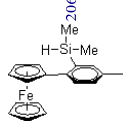


Compound 1f

gf3-109-0523. 1. fid
H1

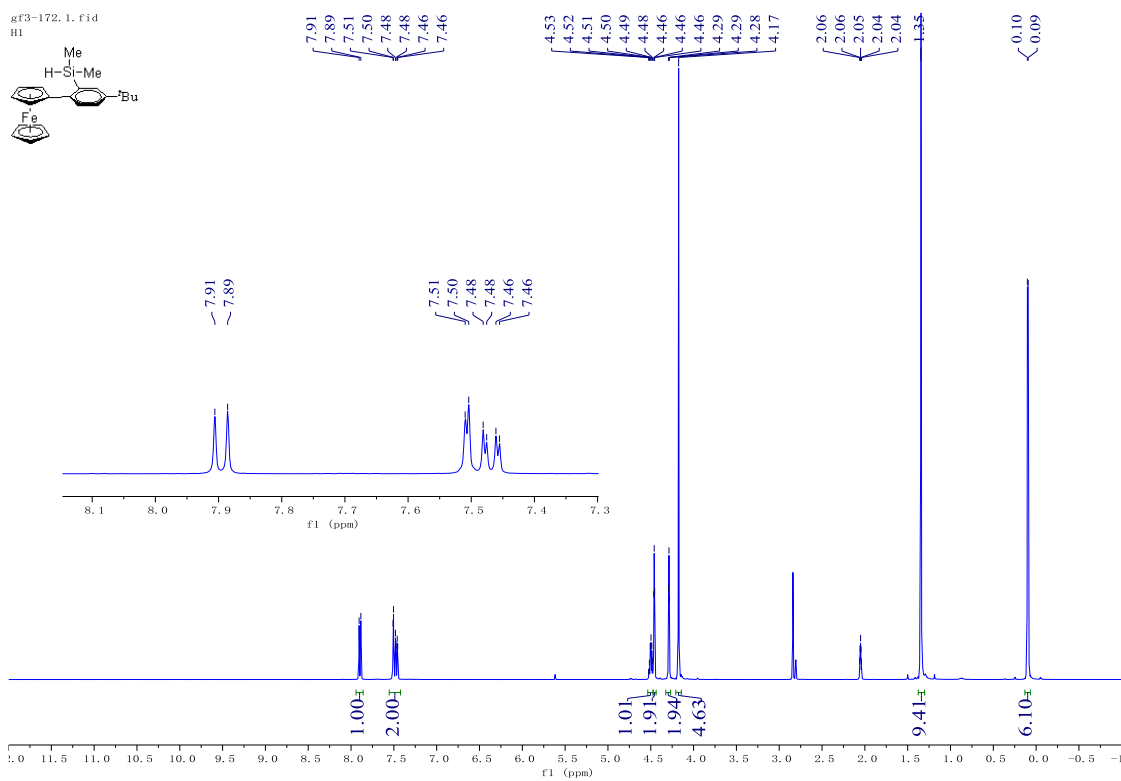
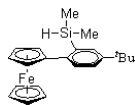


gf3-109H022. fid
test

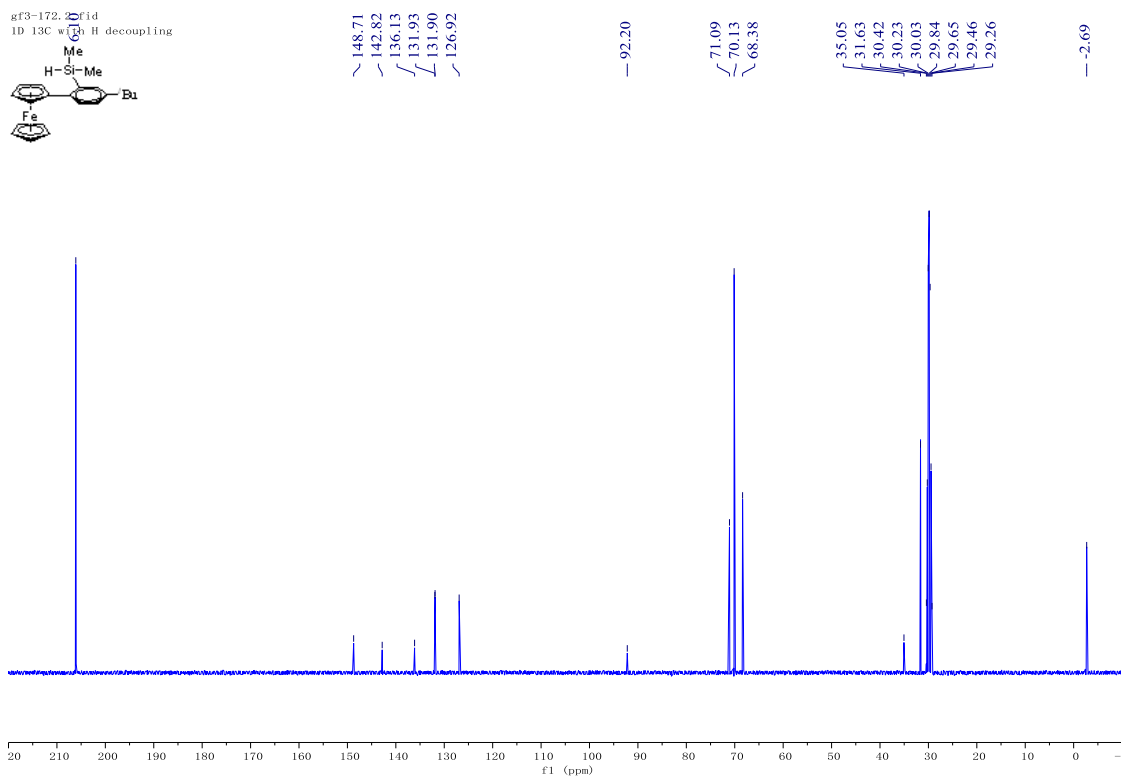
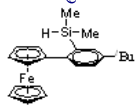


Compound 1g

gf3-172. 1.fid
H1

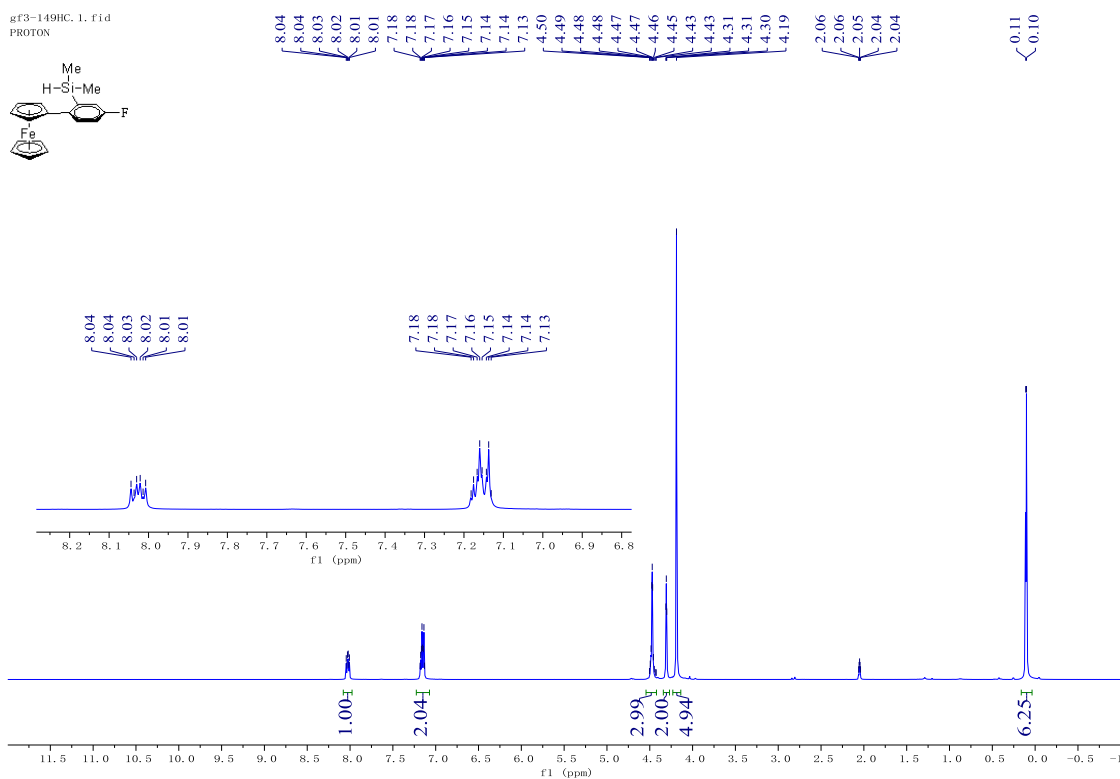
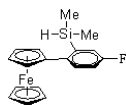


gf3-172. 2.fid
ID 13C w/13H decoupling

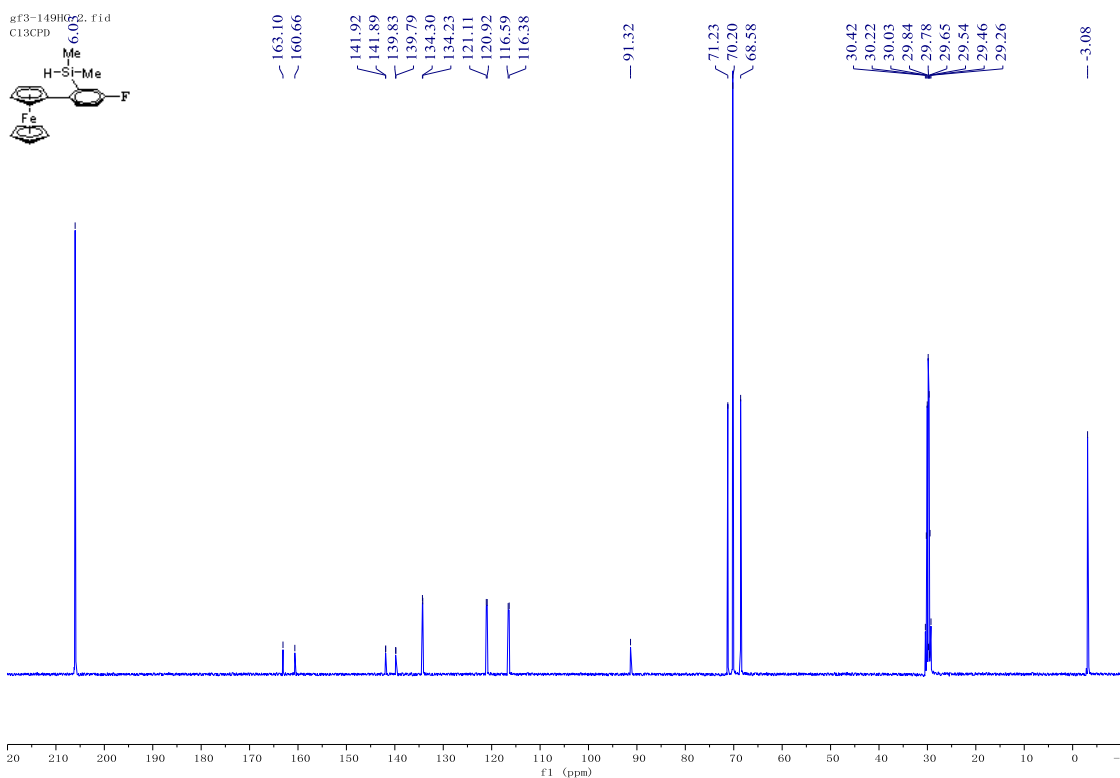
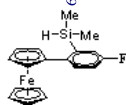


Compound 1h

gF3-149HC.1.fid
PROTON

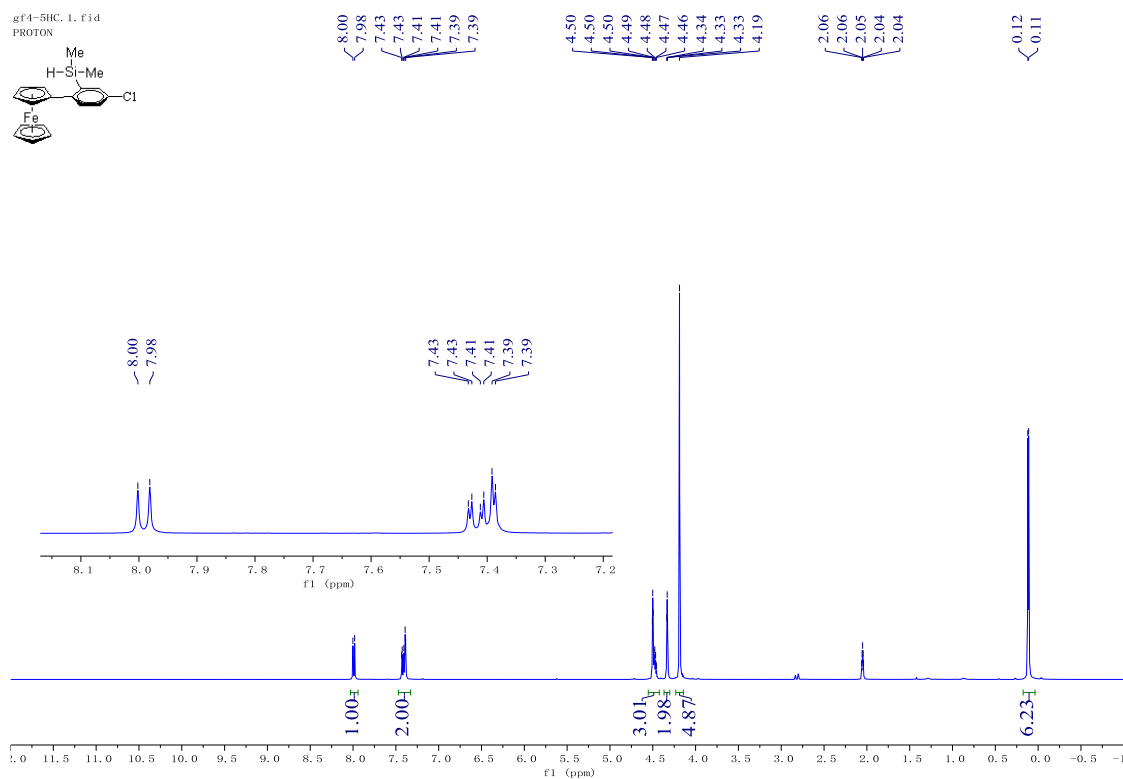
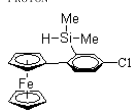


gF3-149HG2.fid
C13CPD

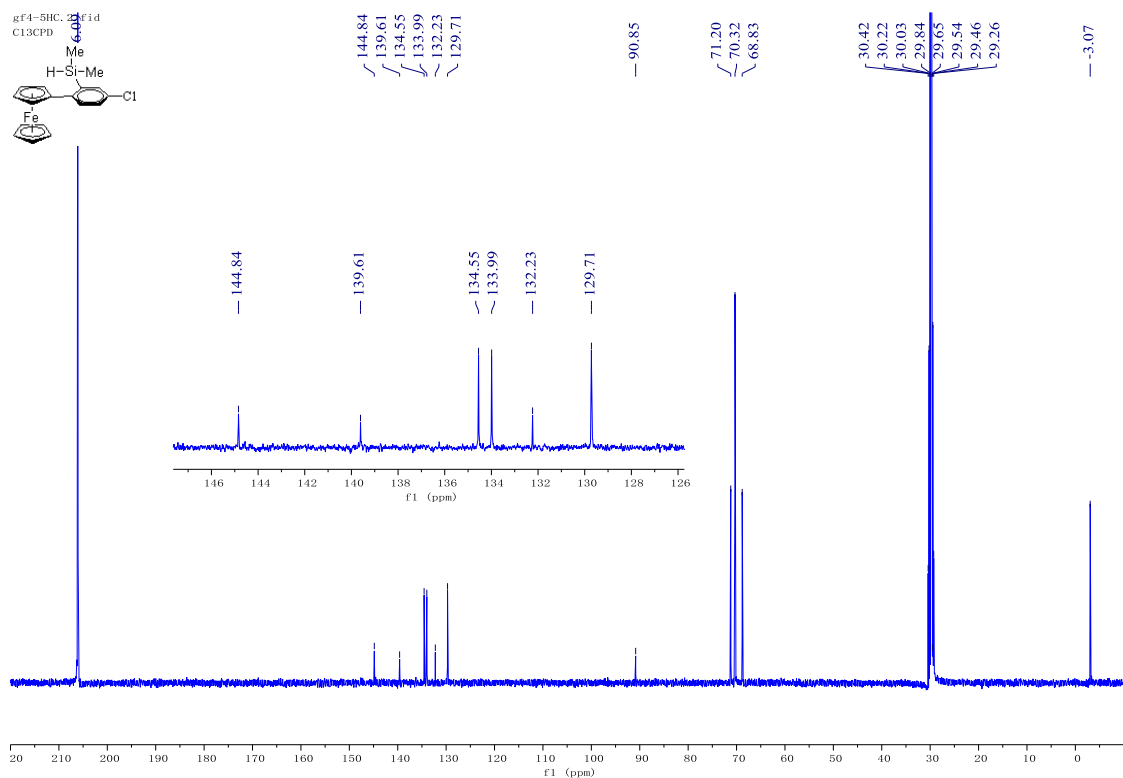
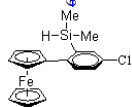


Compound 1i

gF4-5HC, 1.fid
PROTON

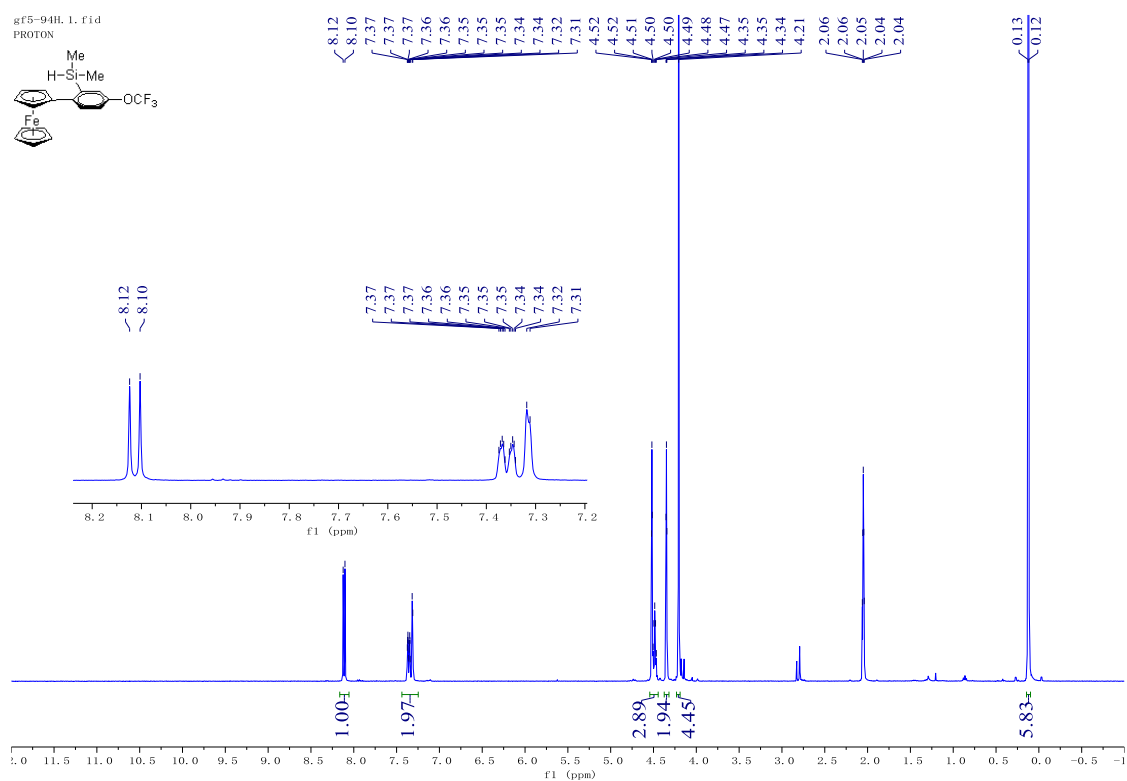
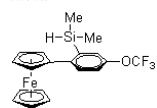


gF4-5HC, 2.fid
C13CPD

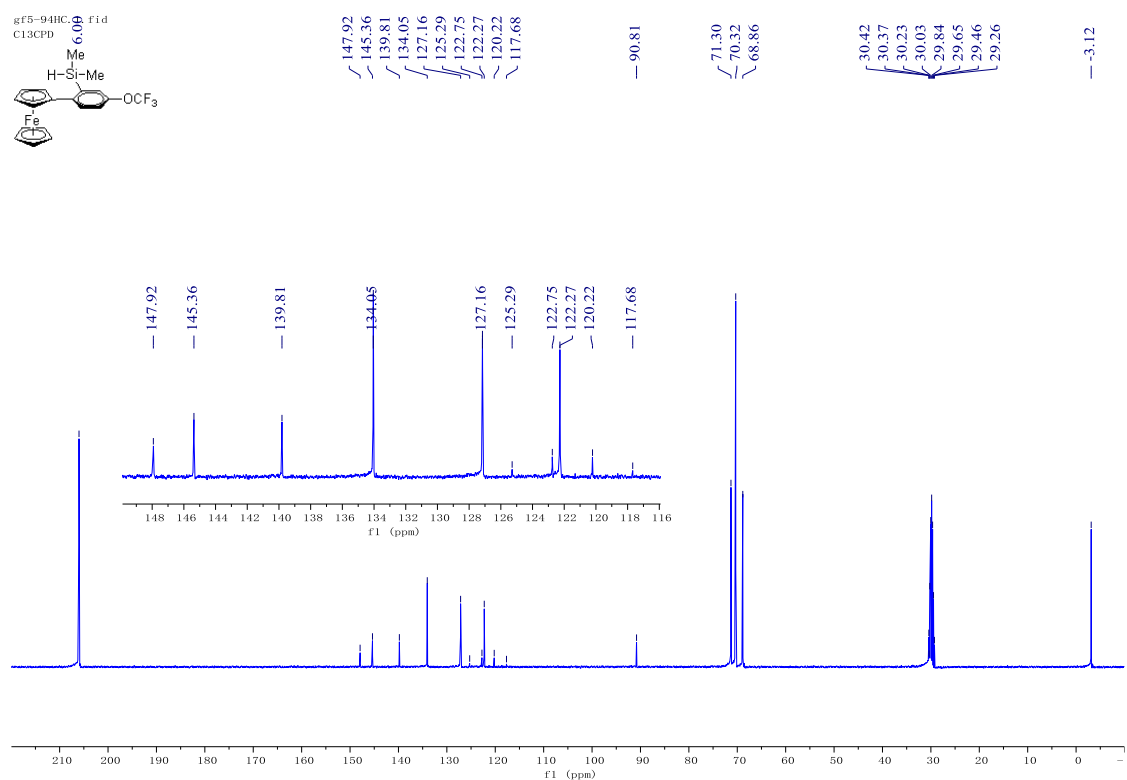
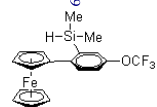


Compound 1j

gF5-94H. 1. fid
PROTON

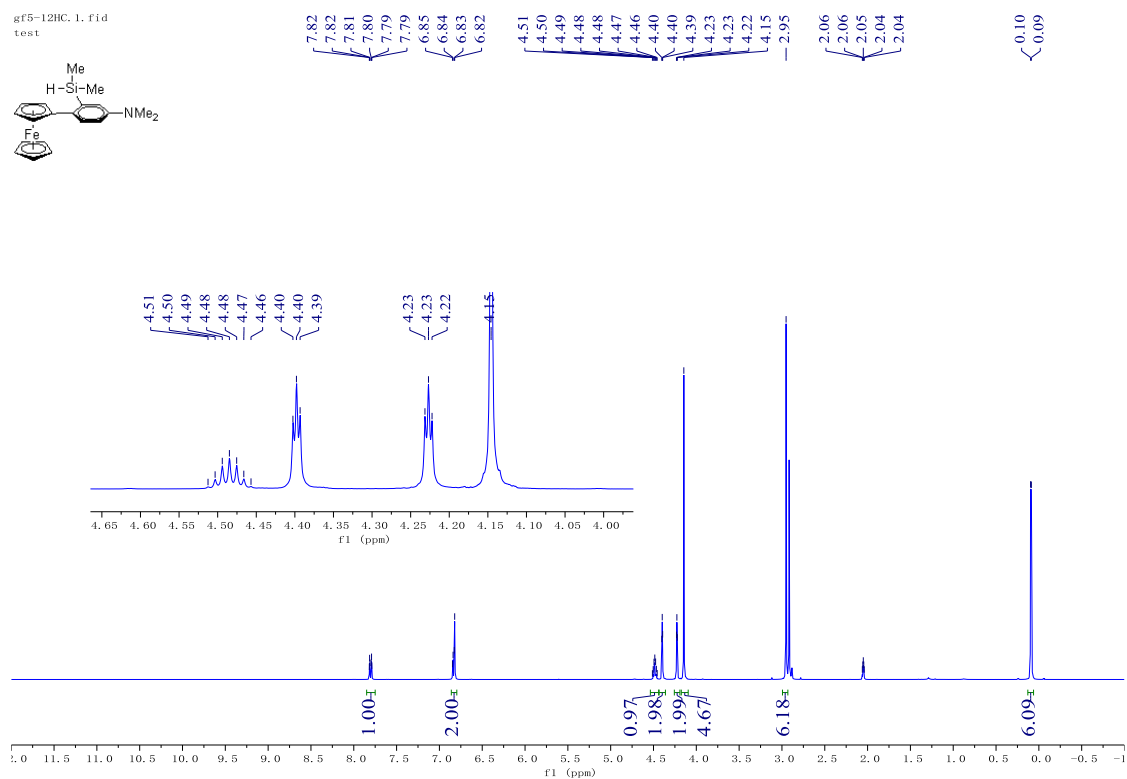
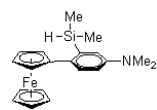


gF5-94HC. fid
C13CPD

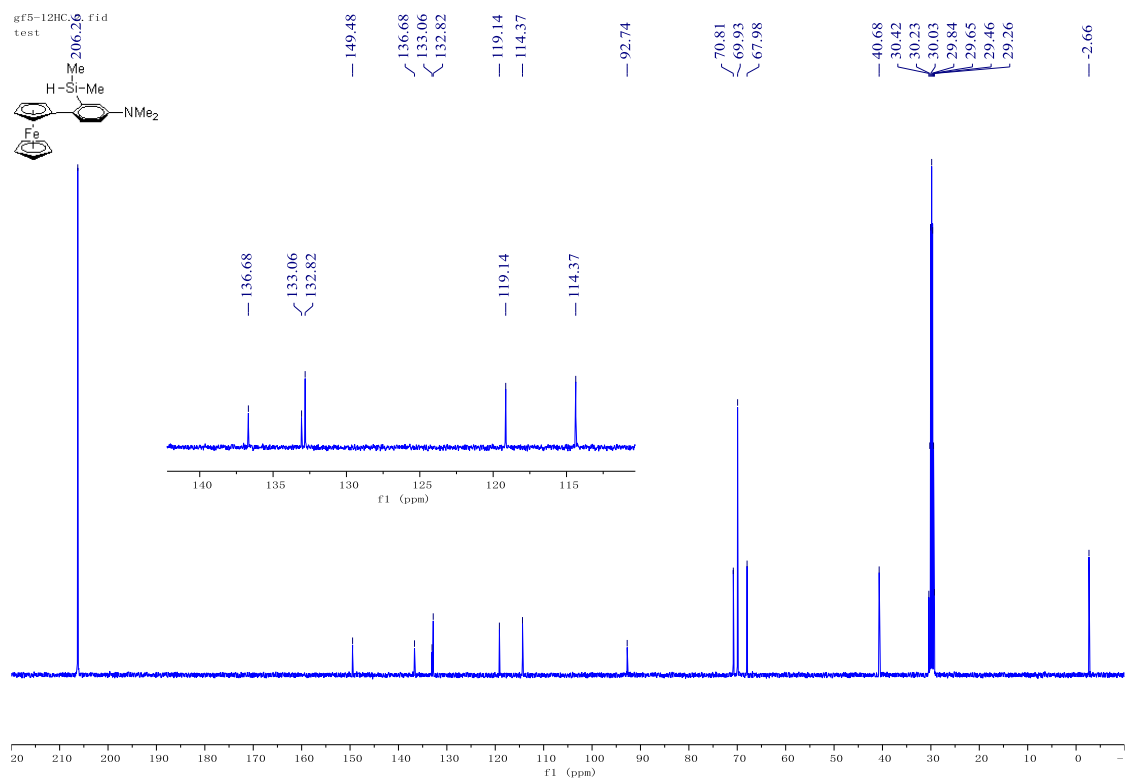
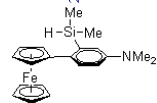


Compound 1k

gF5-12HC.1.fid
test

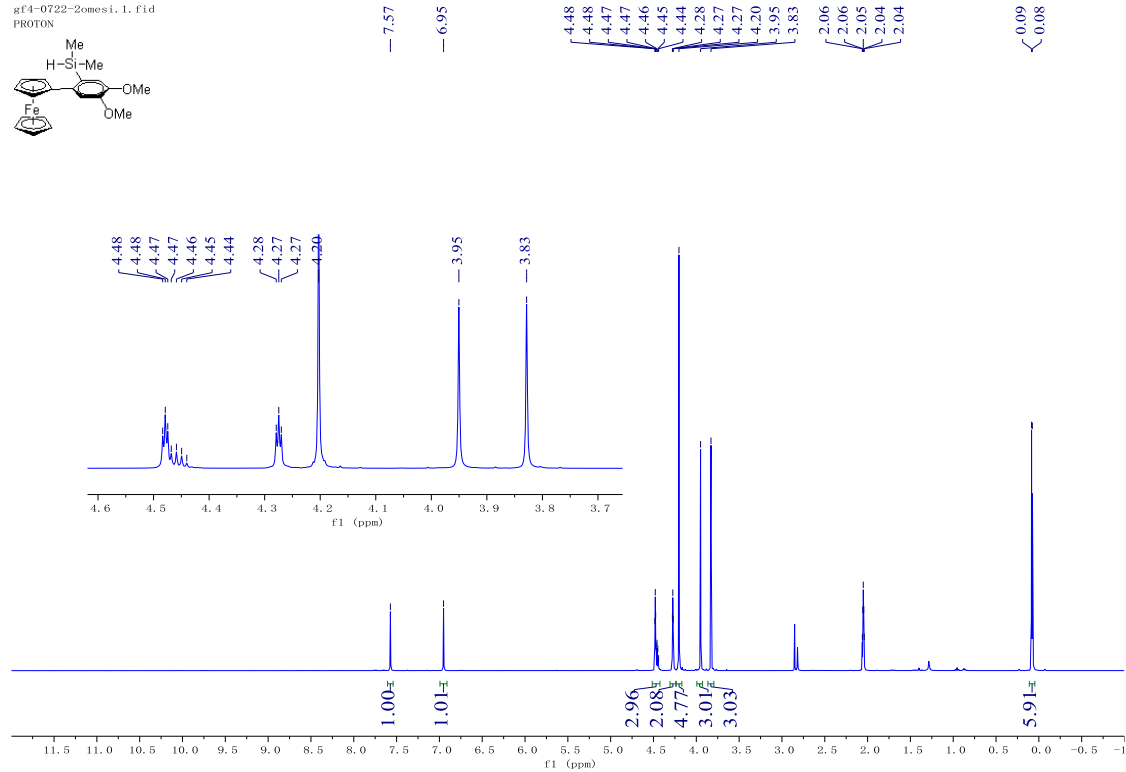
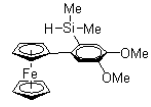


gF5-12HC.26.fid
test

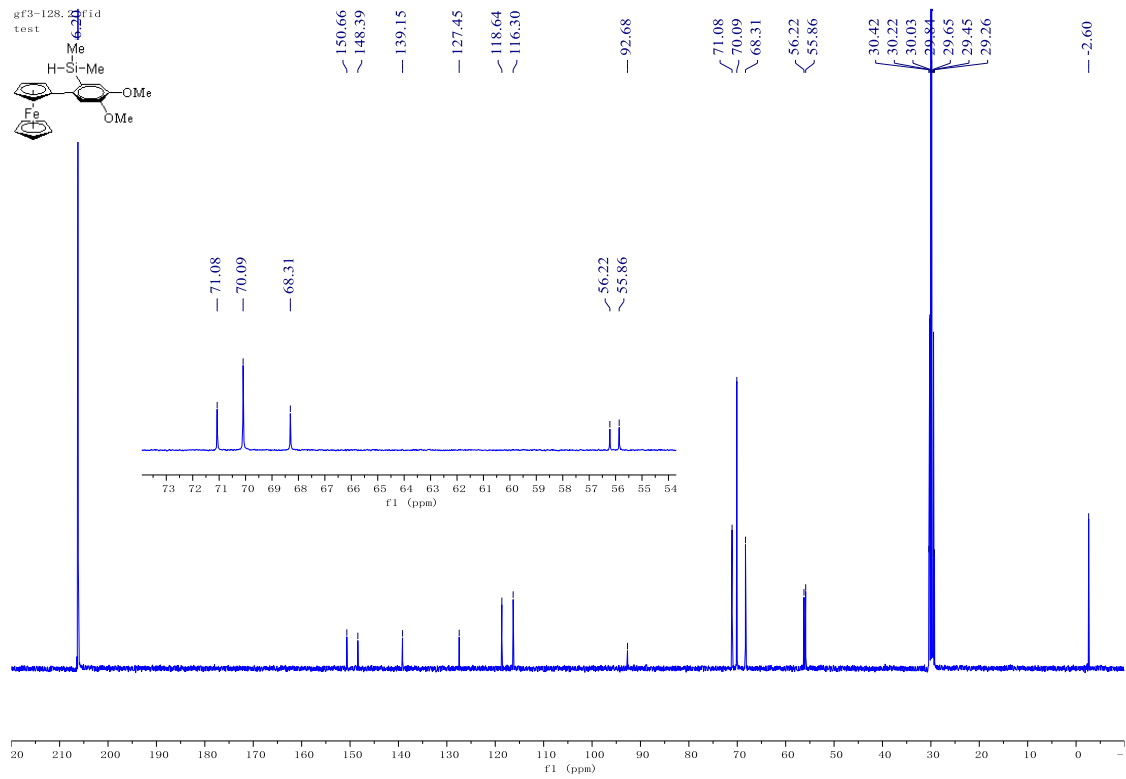
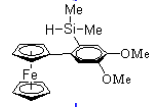


Compound 11

gf4-0722-20mesi.1.fid
PROTON

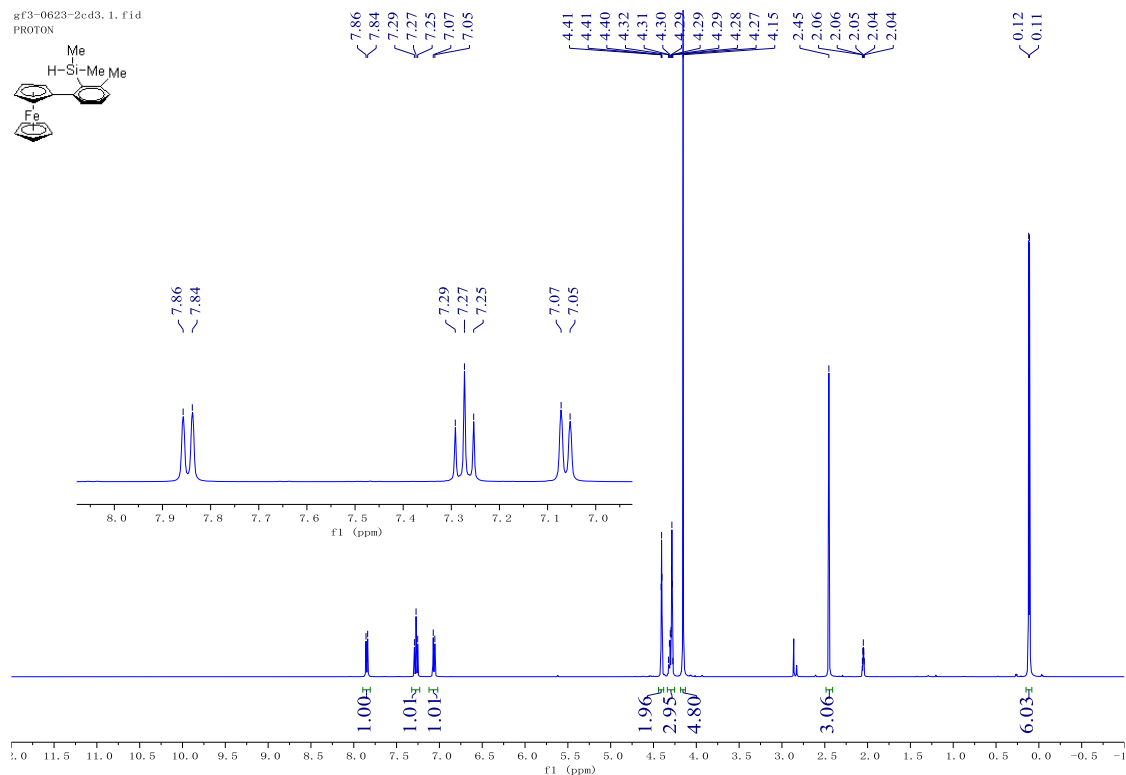
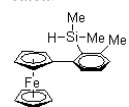


gf3-128.20.fid
test

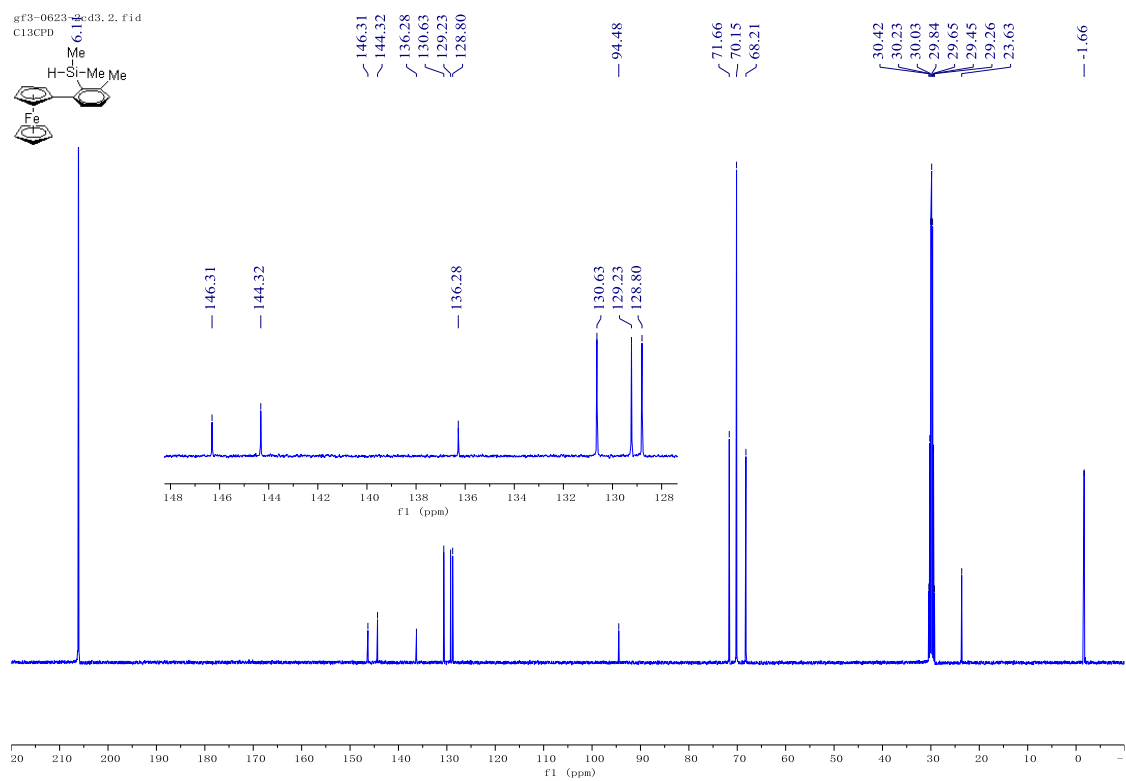
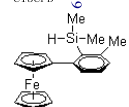


Compound 1m

gF3-0623-2cd3.1.fid
PROTON

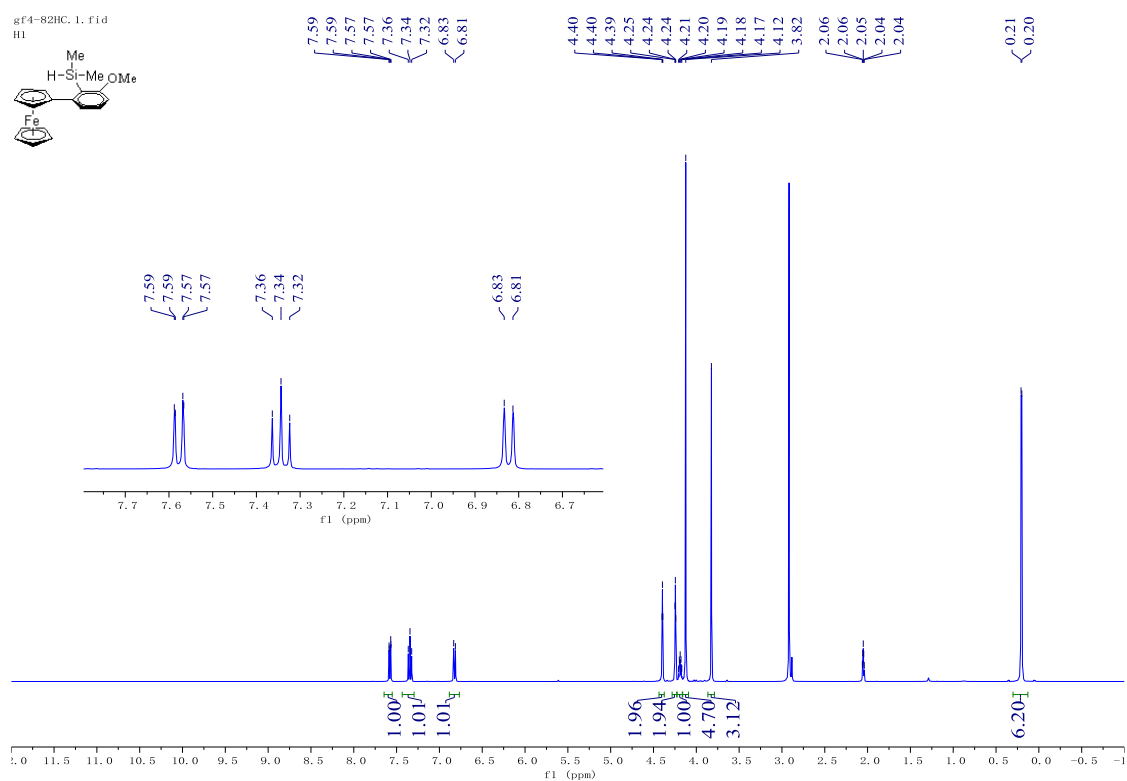
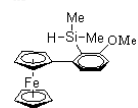


gF3-0623-2cd3.2.fid
C13CPD

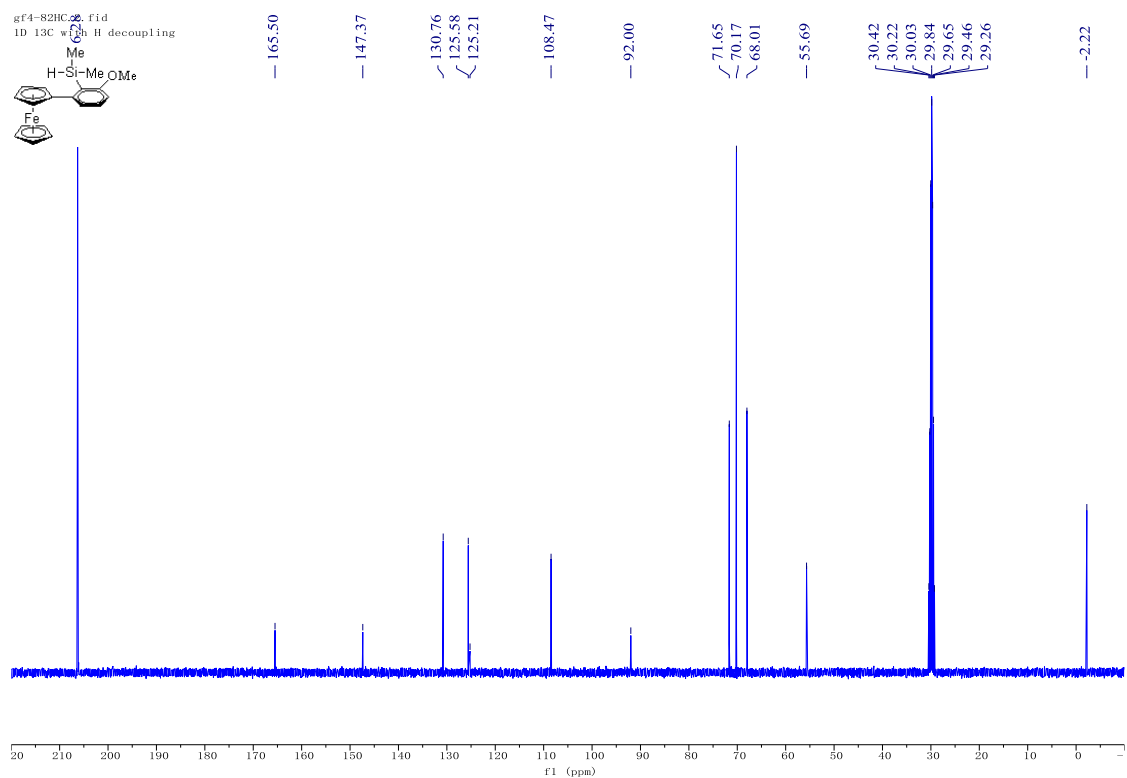
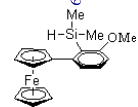


Compound 1n

gf4-82HC.1.fid
H1

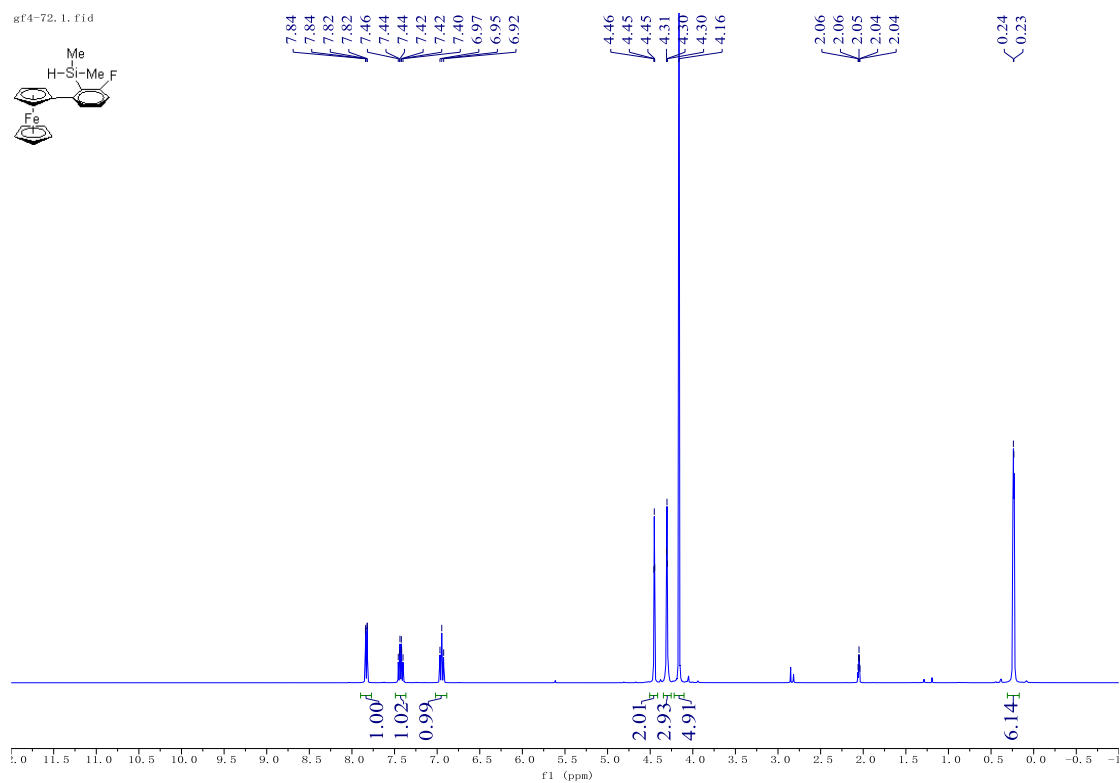
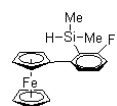


gf4-82HC.2.fid
ID 13C w/CH H decoupling

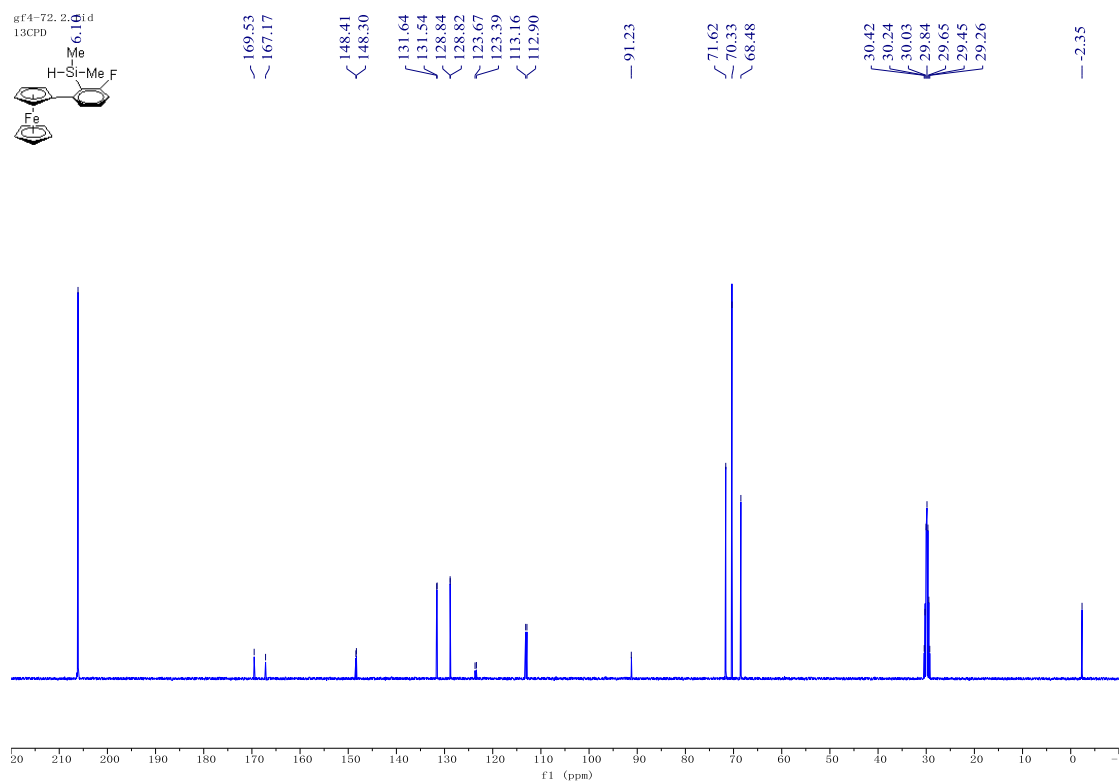
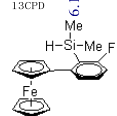


Compound 1o

gF4-72.1.fid

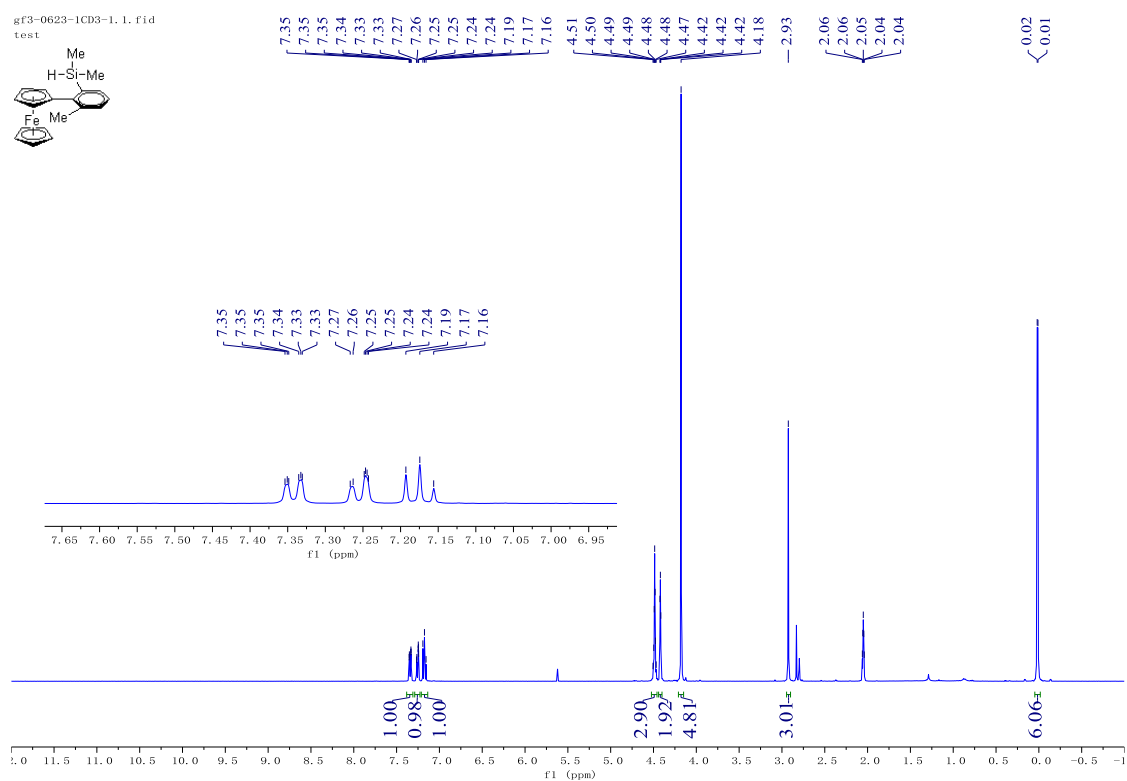
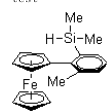


gF4-72.2.fid

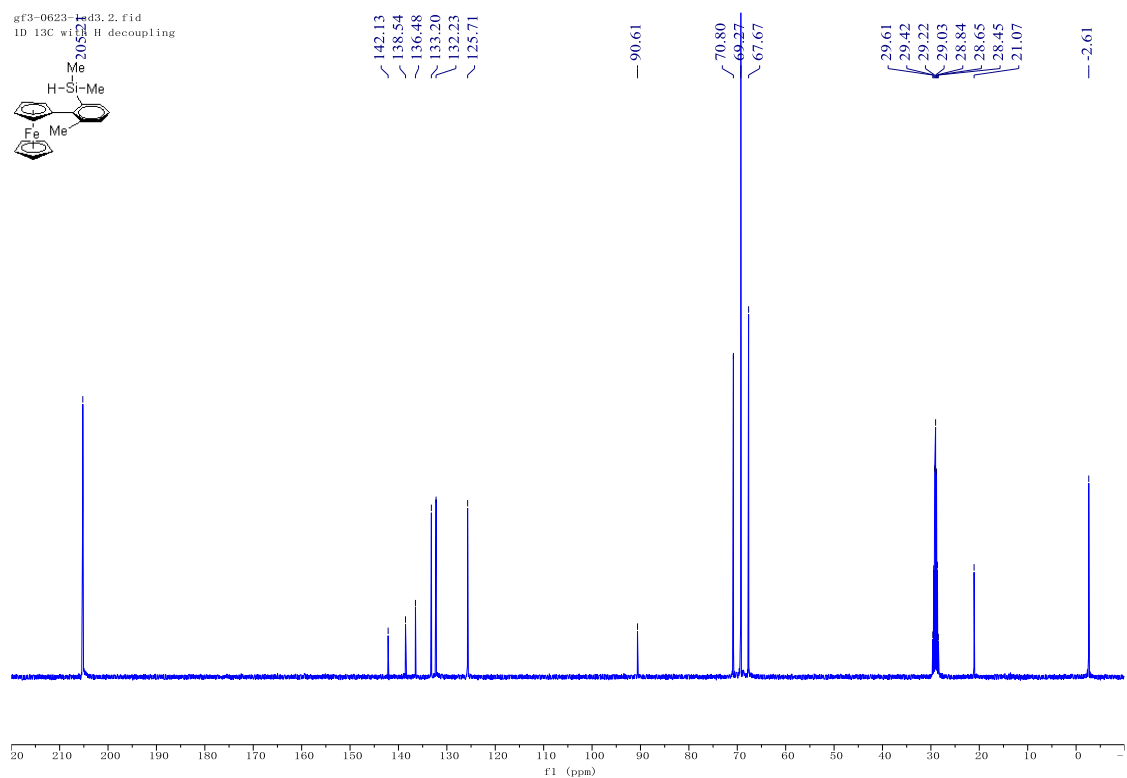
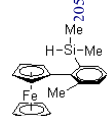


Compound 1p

gF3-0623-1CD3-1.1.fid
test

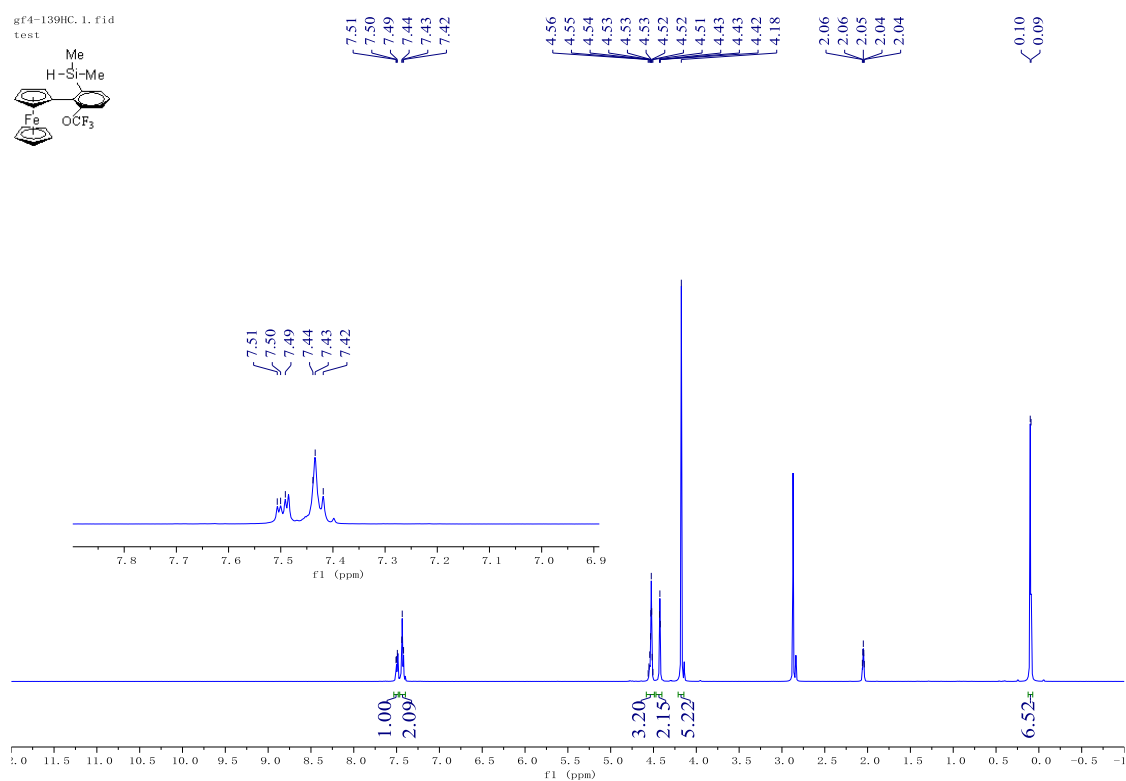
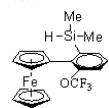


gF3-0623-1CD3.2.fid
ID 13C with H decoupling

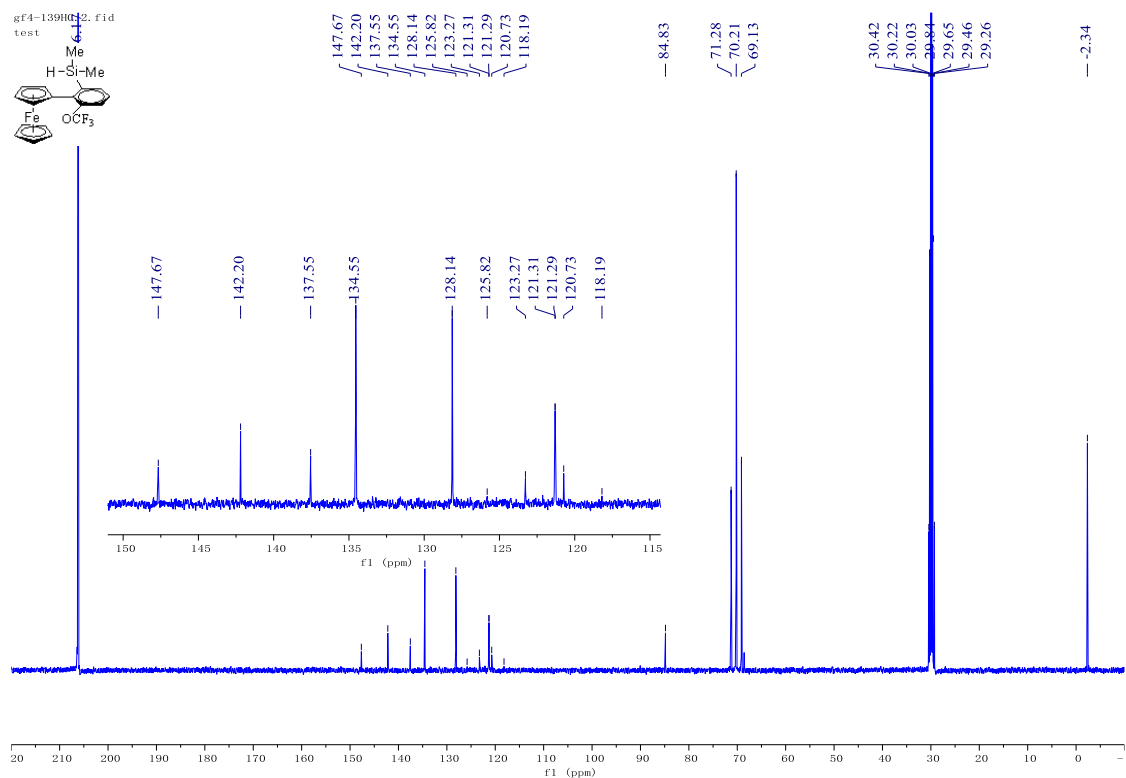
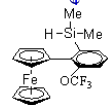


Compound 1q

gF4-139HC.1.fid
test

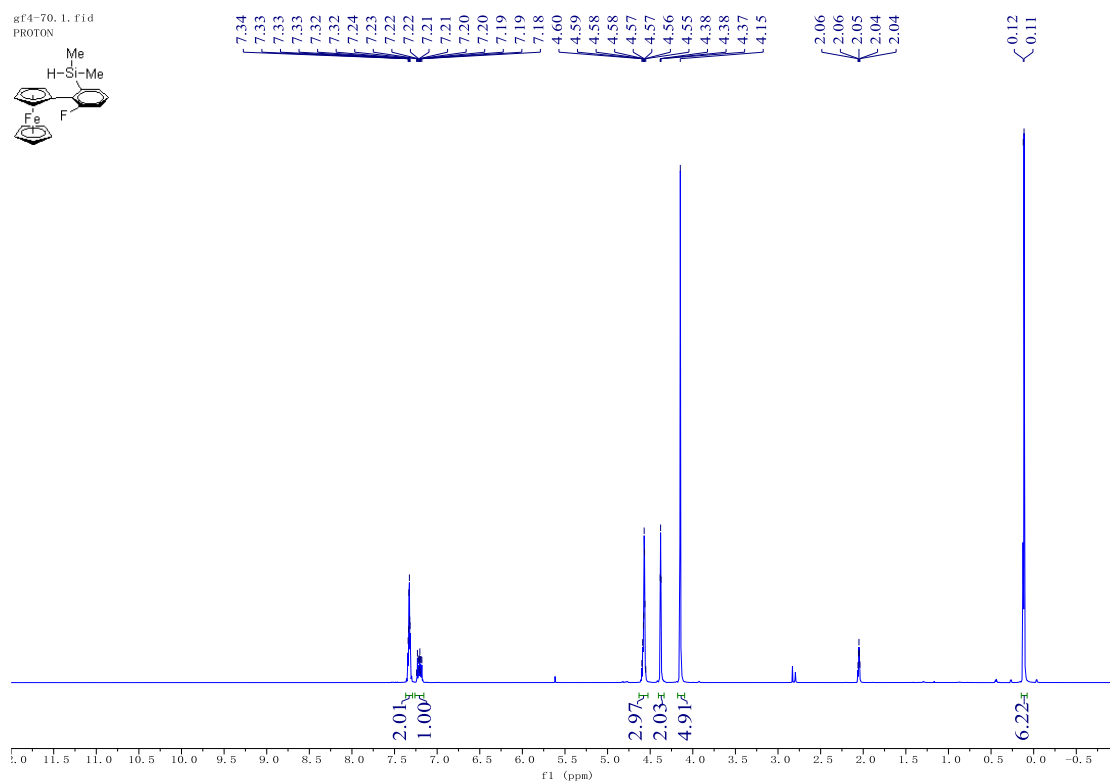
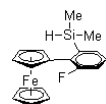


gF4-139HC2.fid
test

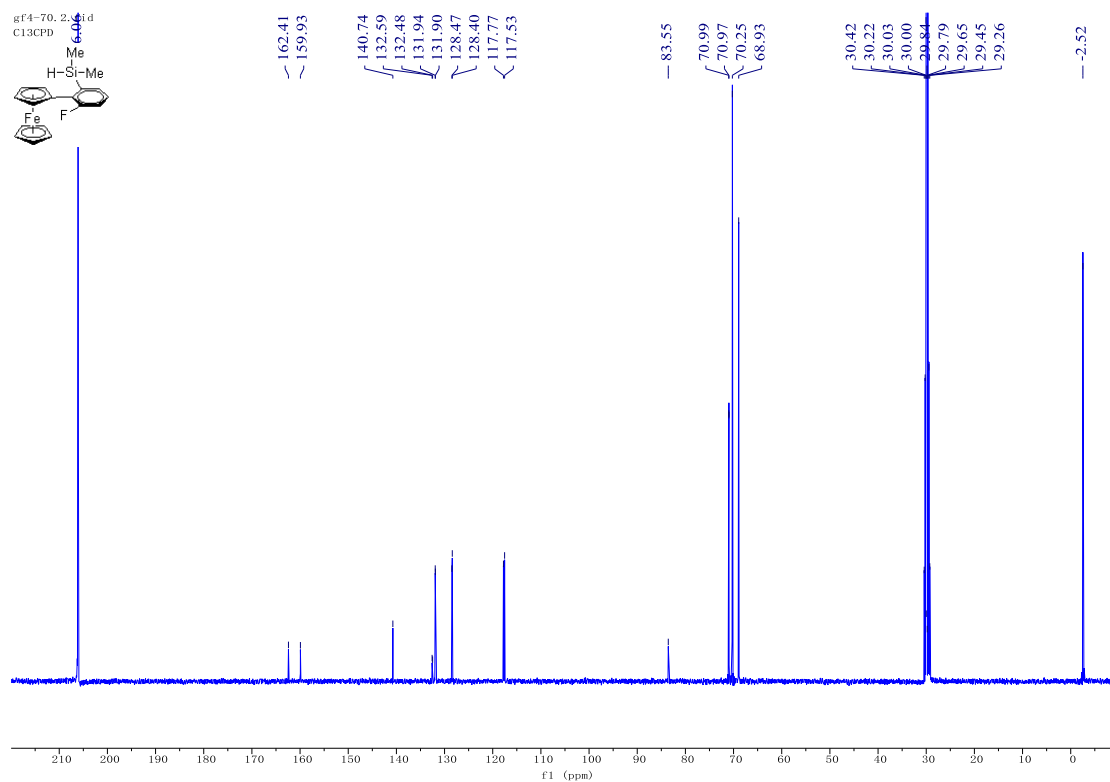
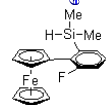


Compound 1r

gF4-70.1.fid
PROTON

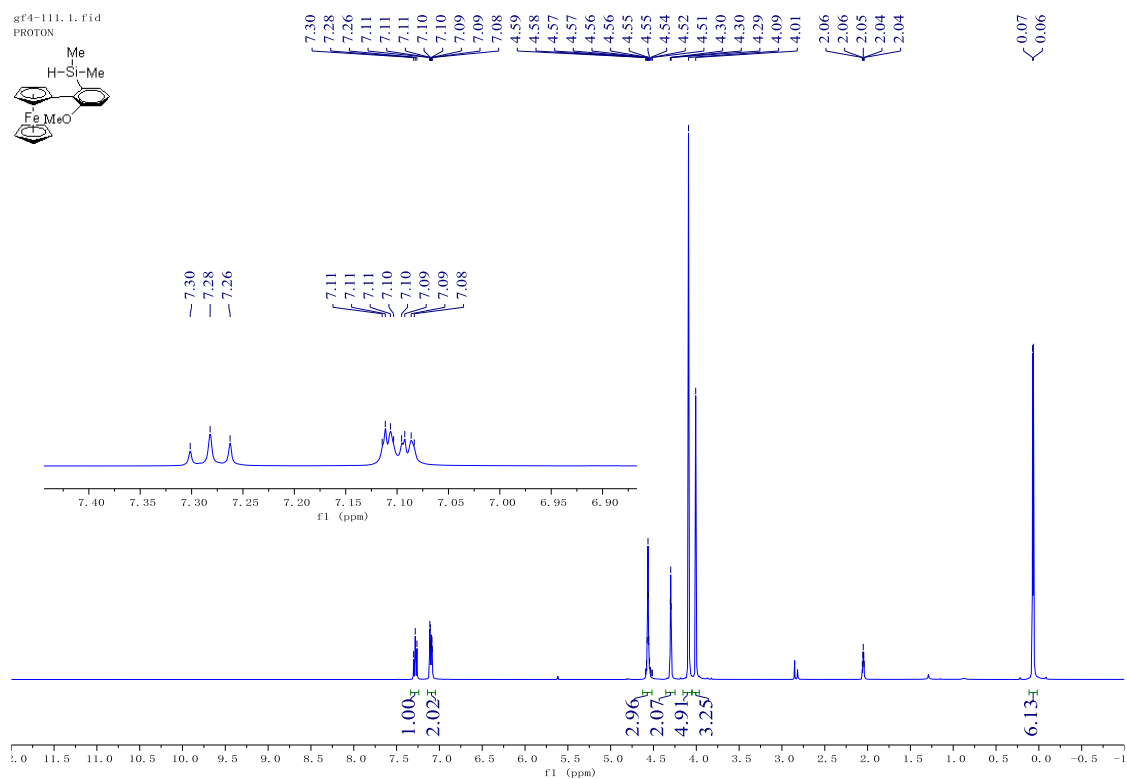
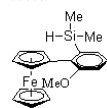


gF4-70.2.fid
C13CPD

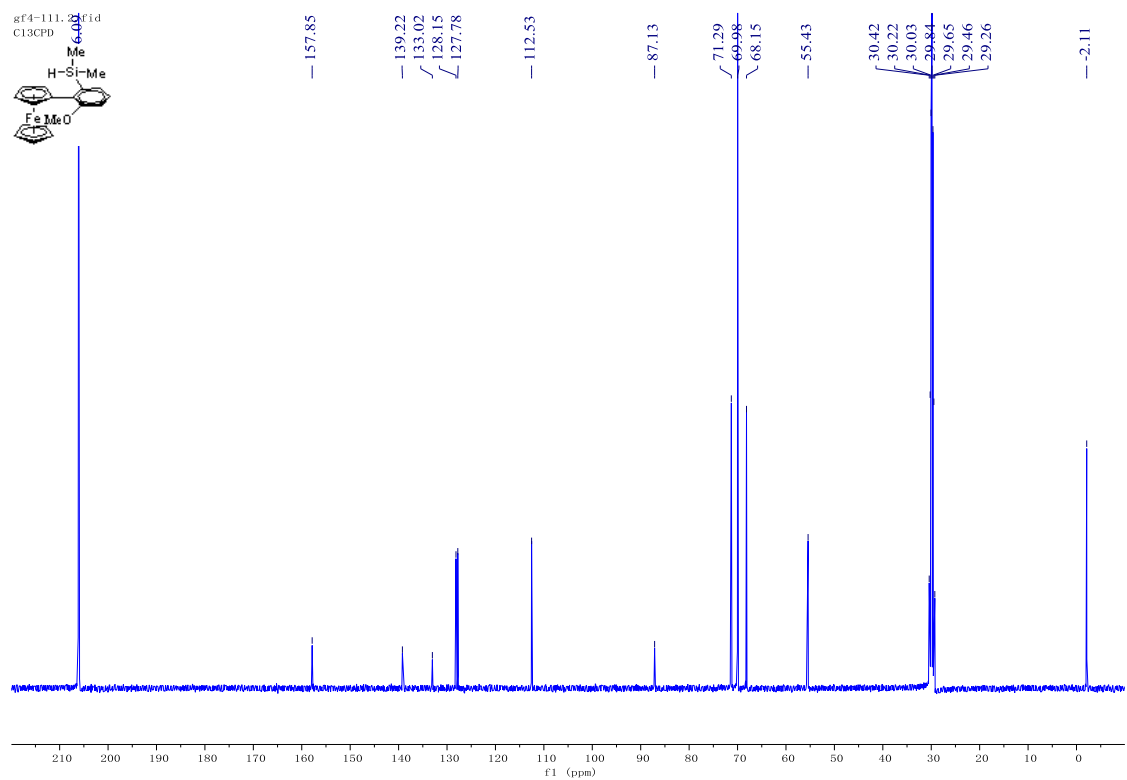
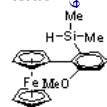


Compound 1s

gF4-111.1.fid
PROTON

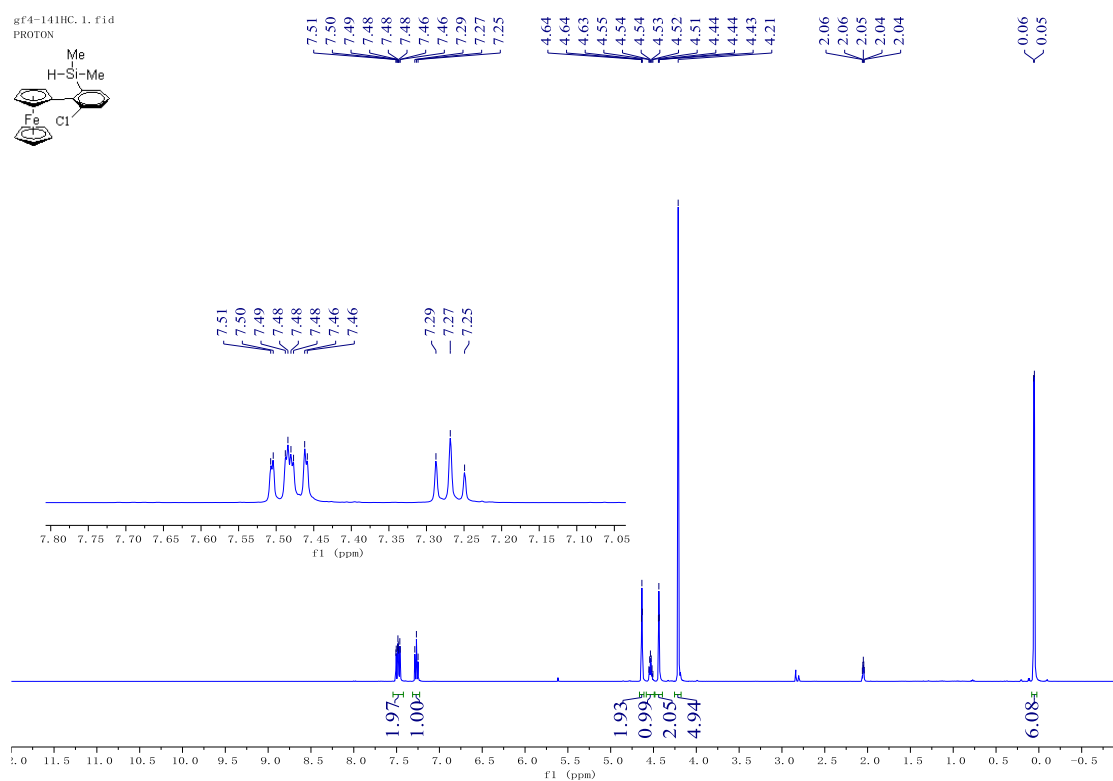
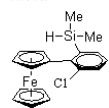


gF4-111.2.fid
C13CPD

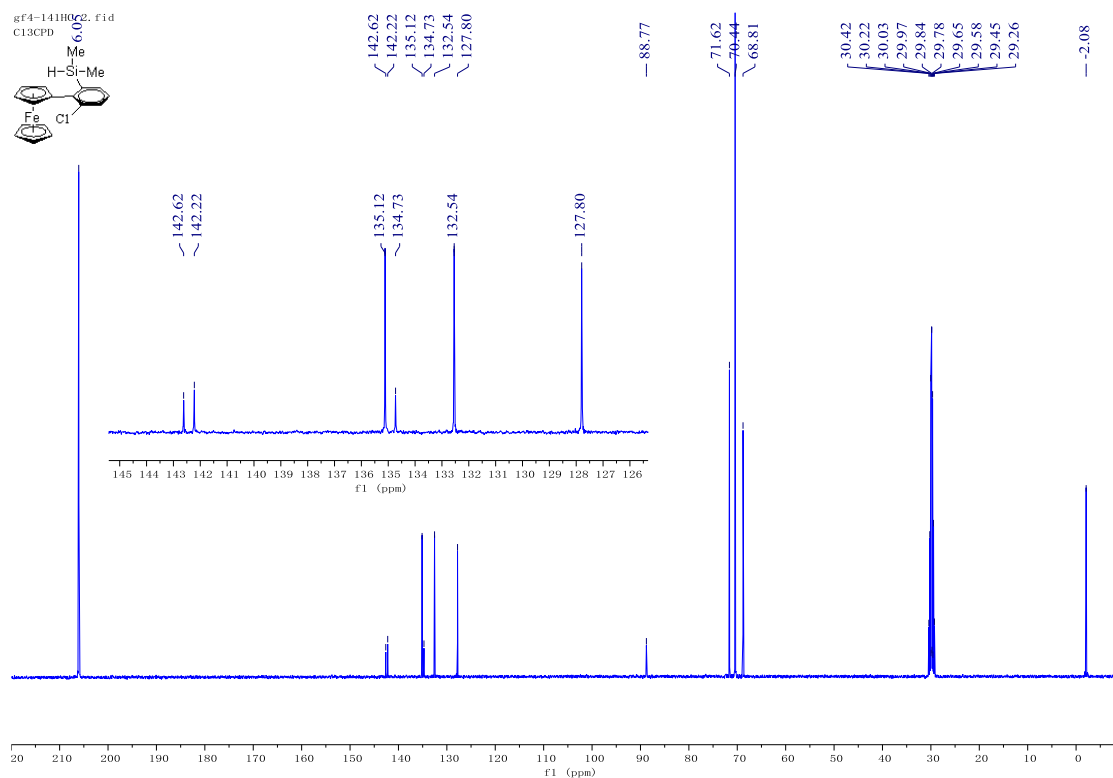
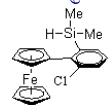


Compound 1t

gF4-141HC.1.f1d
PROTON

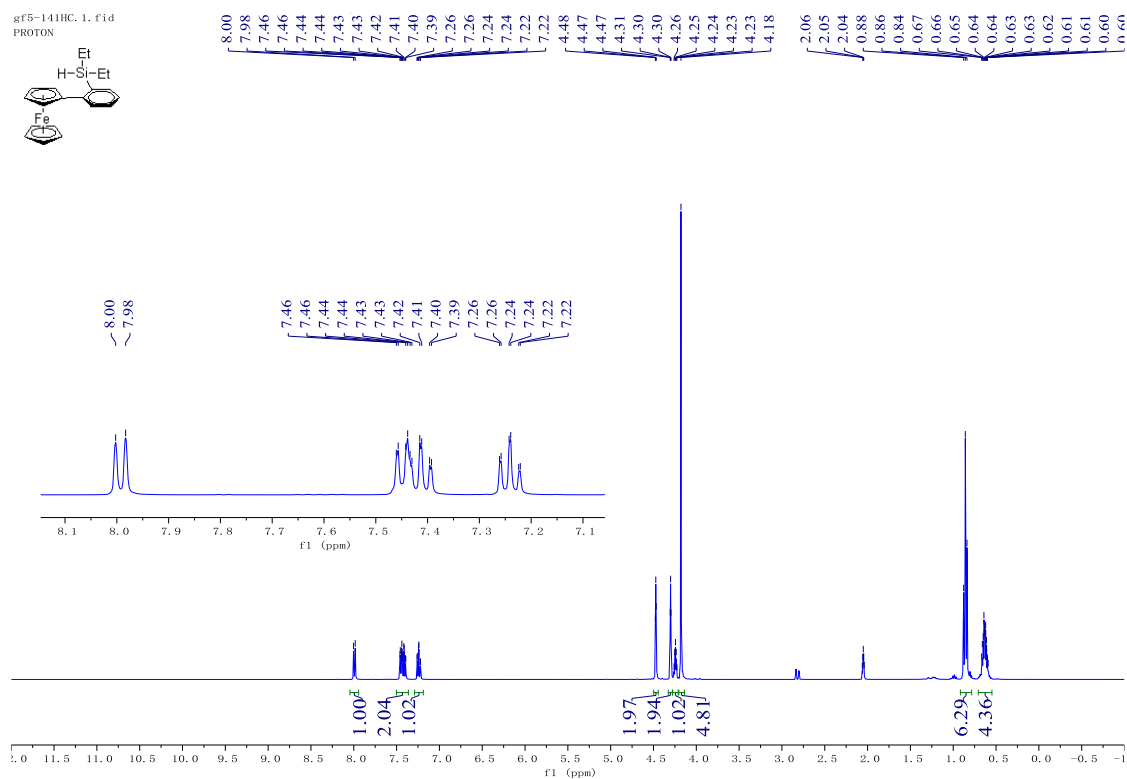
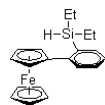


gF4-141HC2.f1d
C13CPD

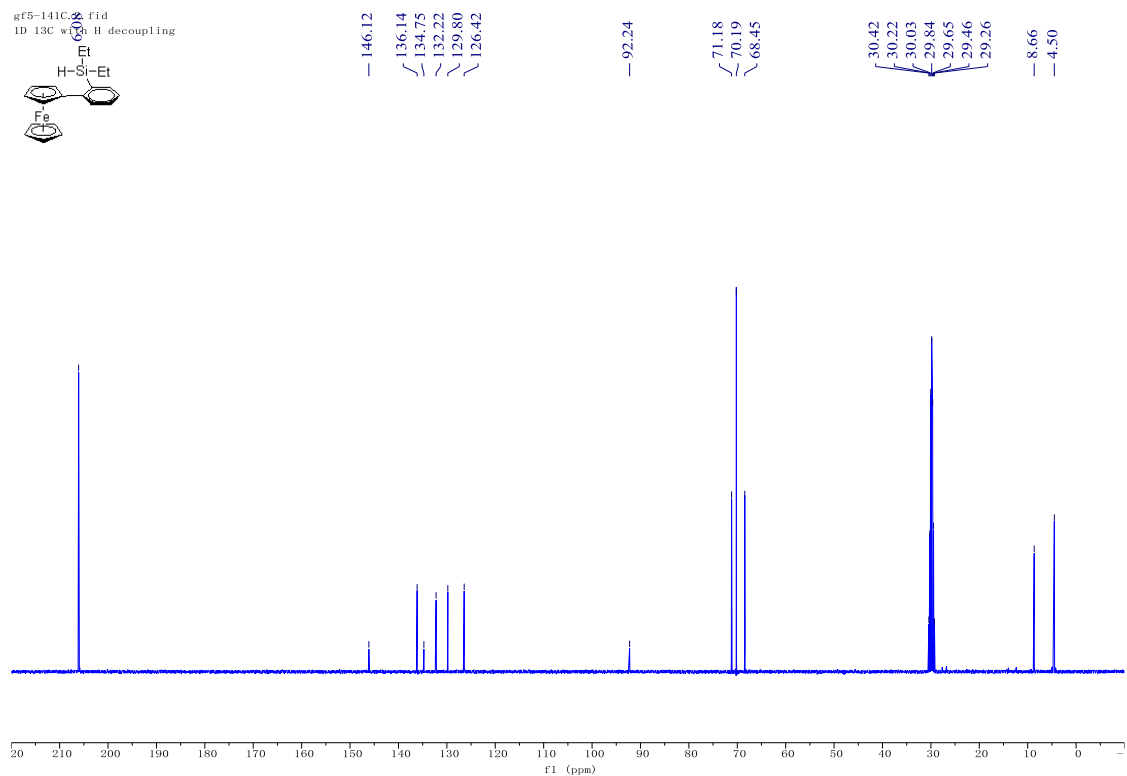
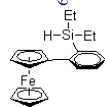


Compound 1u

gF5-141HC.1.f1d
PROTON

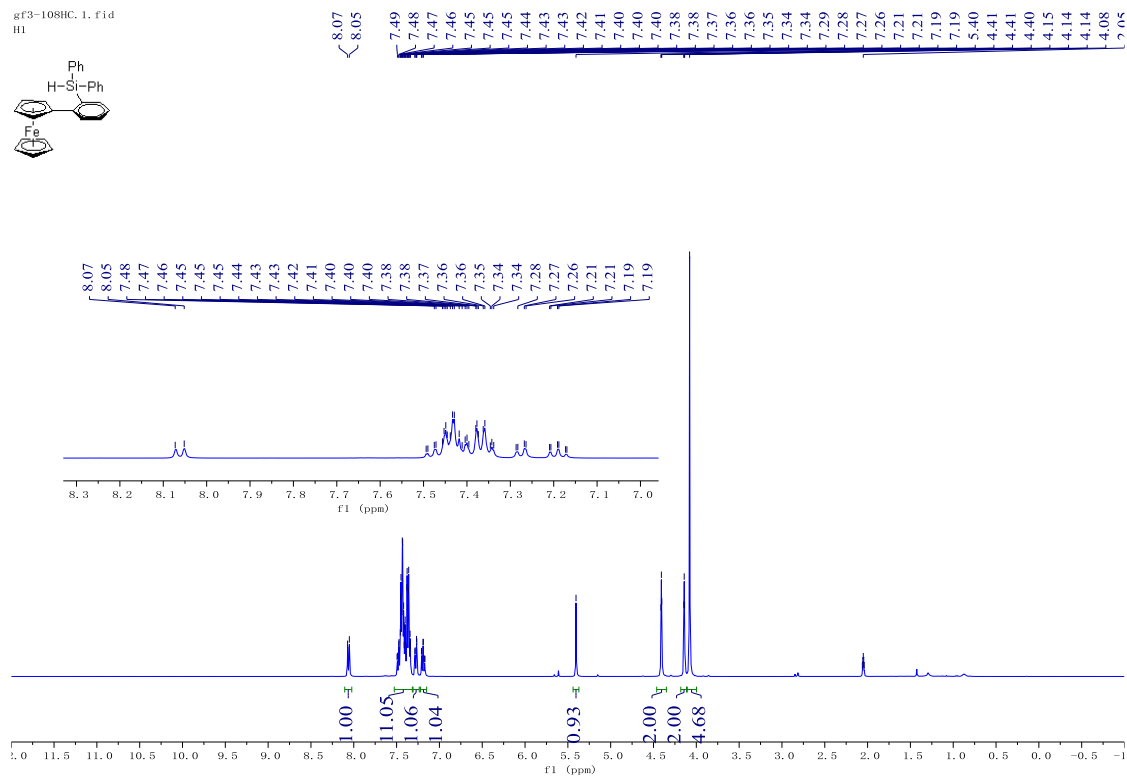
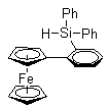


gF5-141C.2.f1d
1D 13C w/3H H decoupling

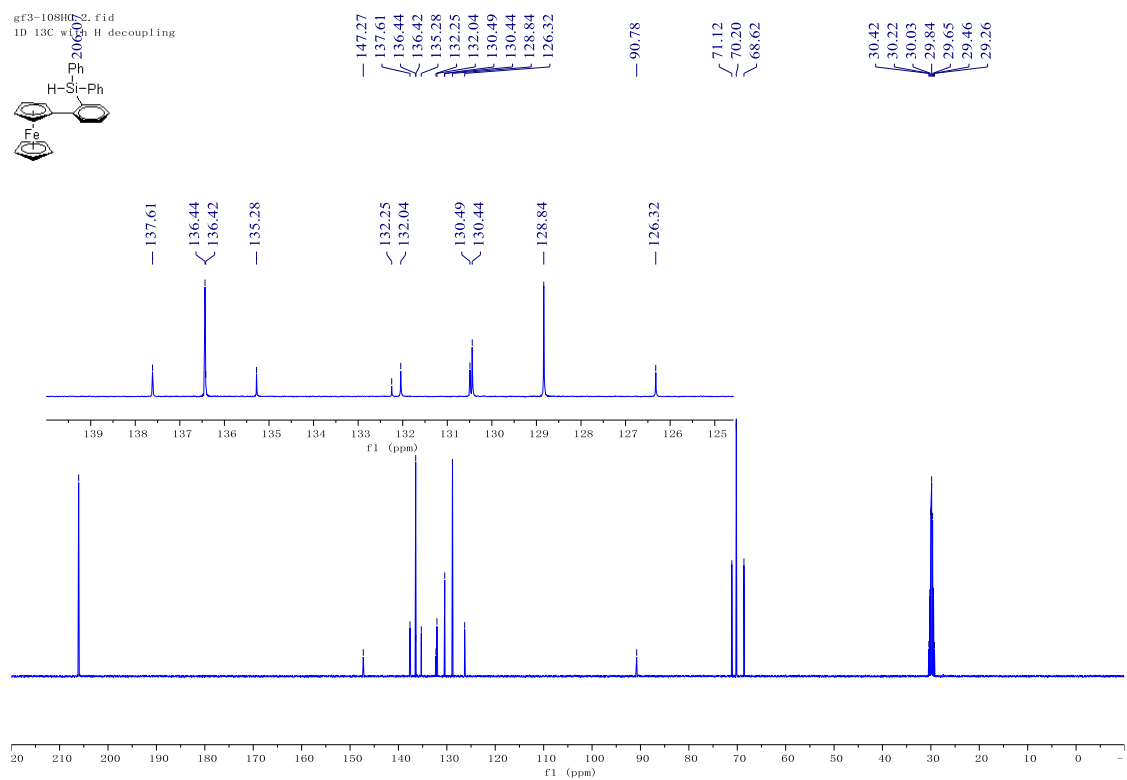
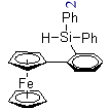


Compound 1v

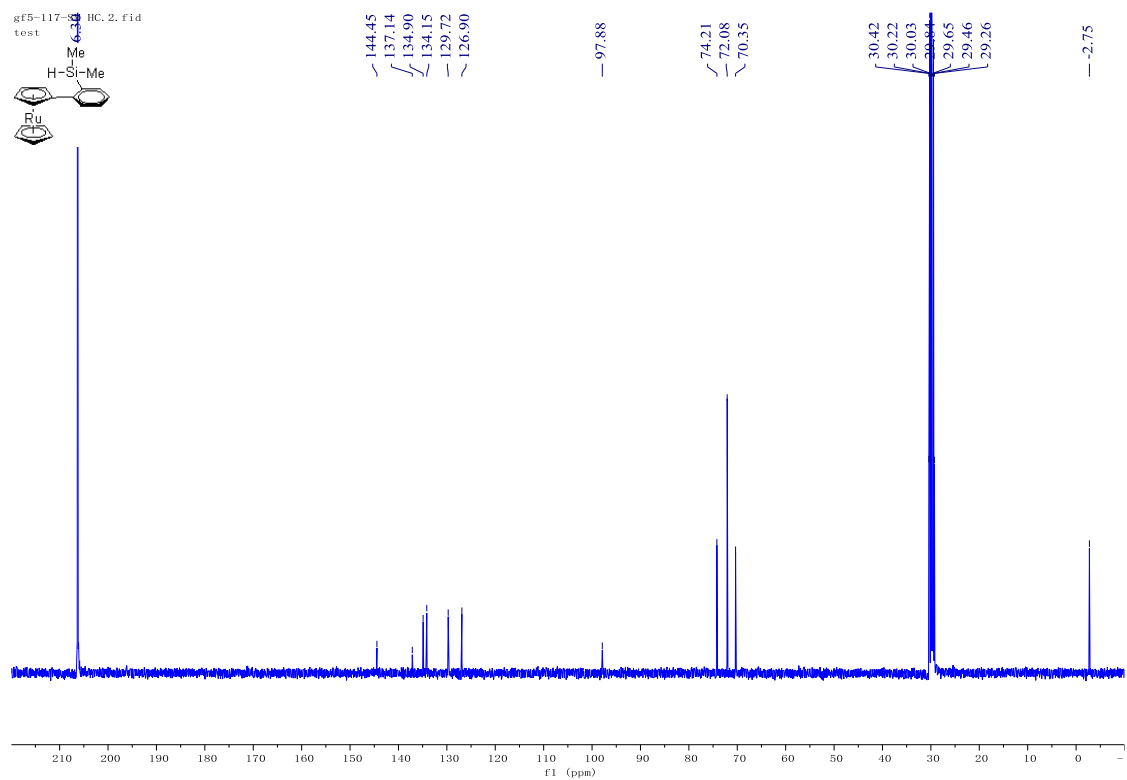
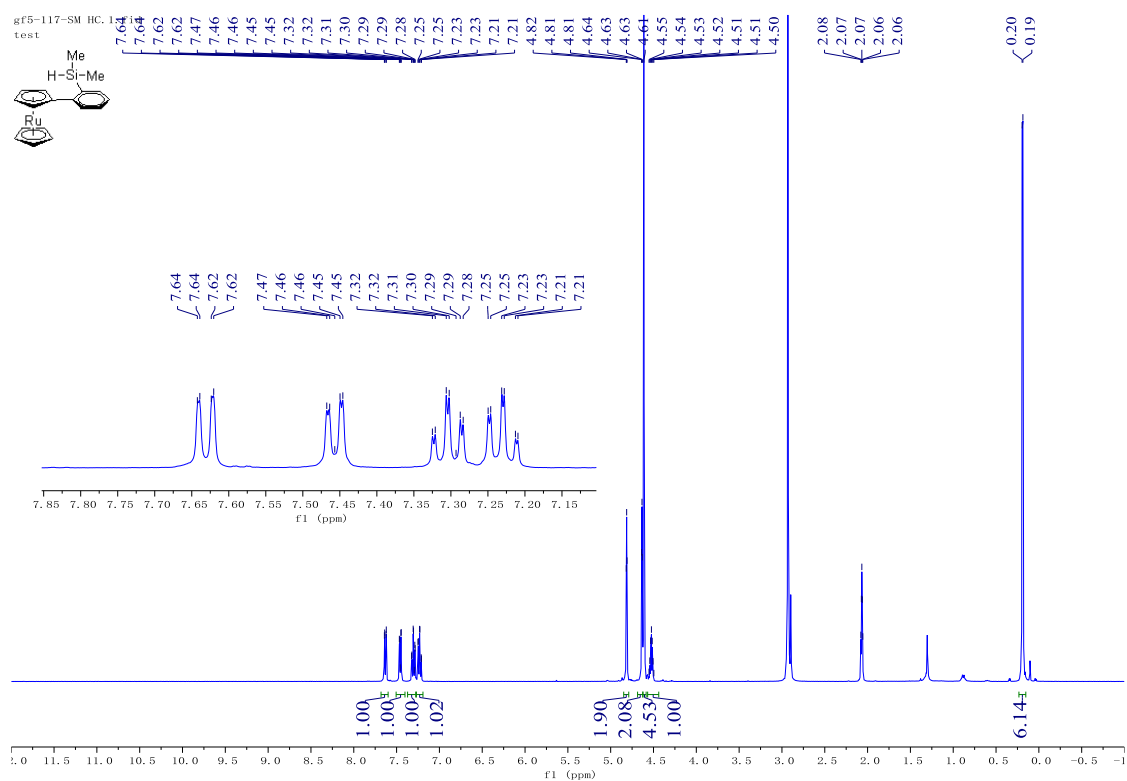
gf3-108HC.1.fid
H1



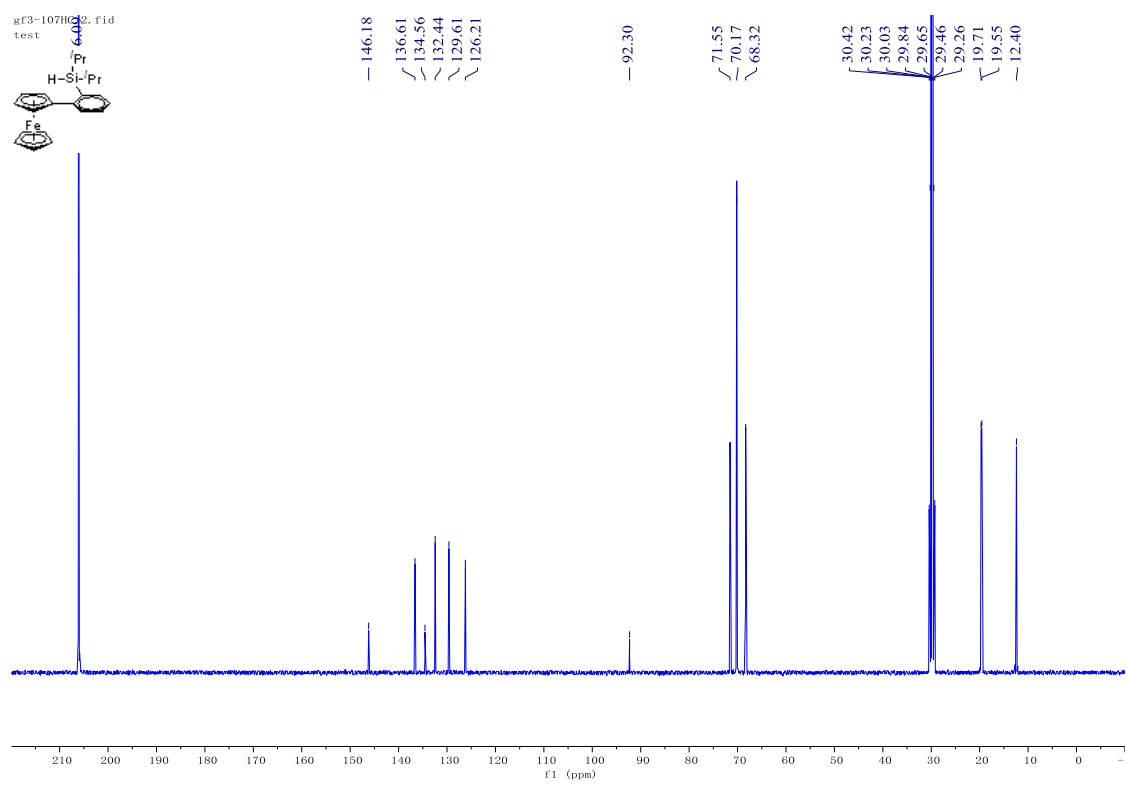
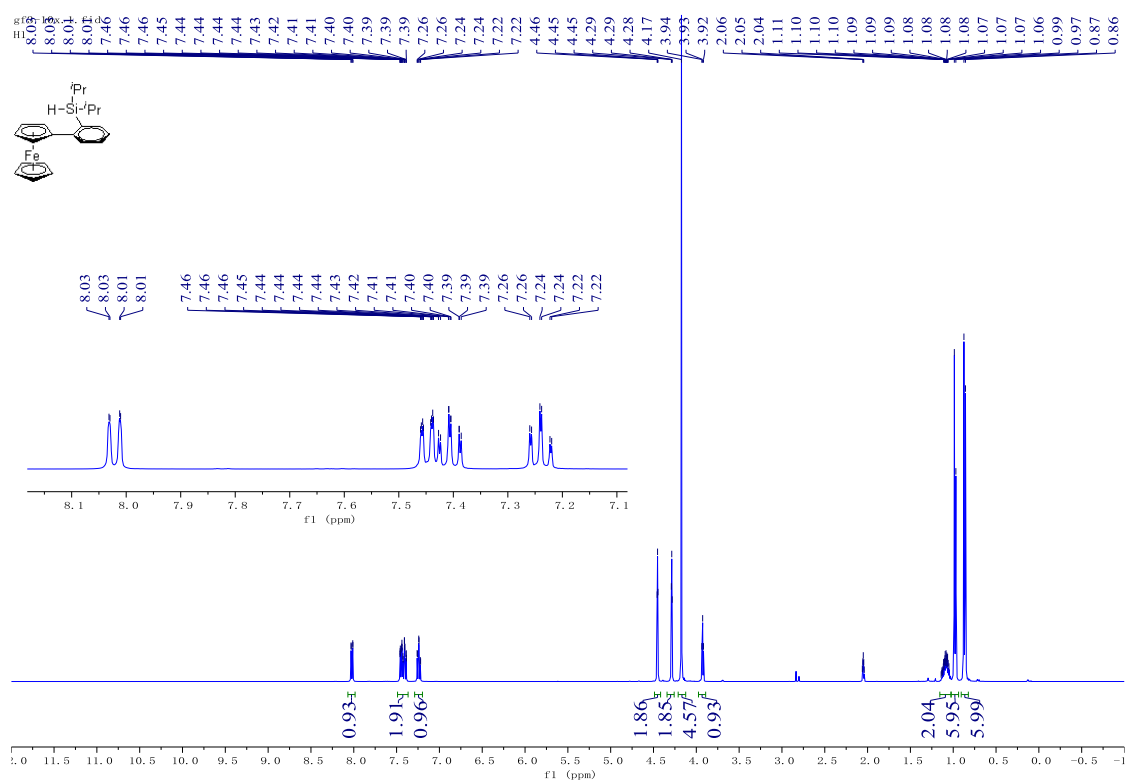
gf3-108HC.2.fid
ID 13C w/CPH H decoupling



Compound 1w

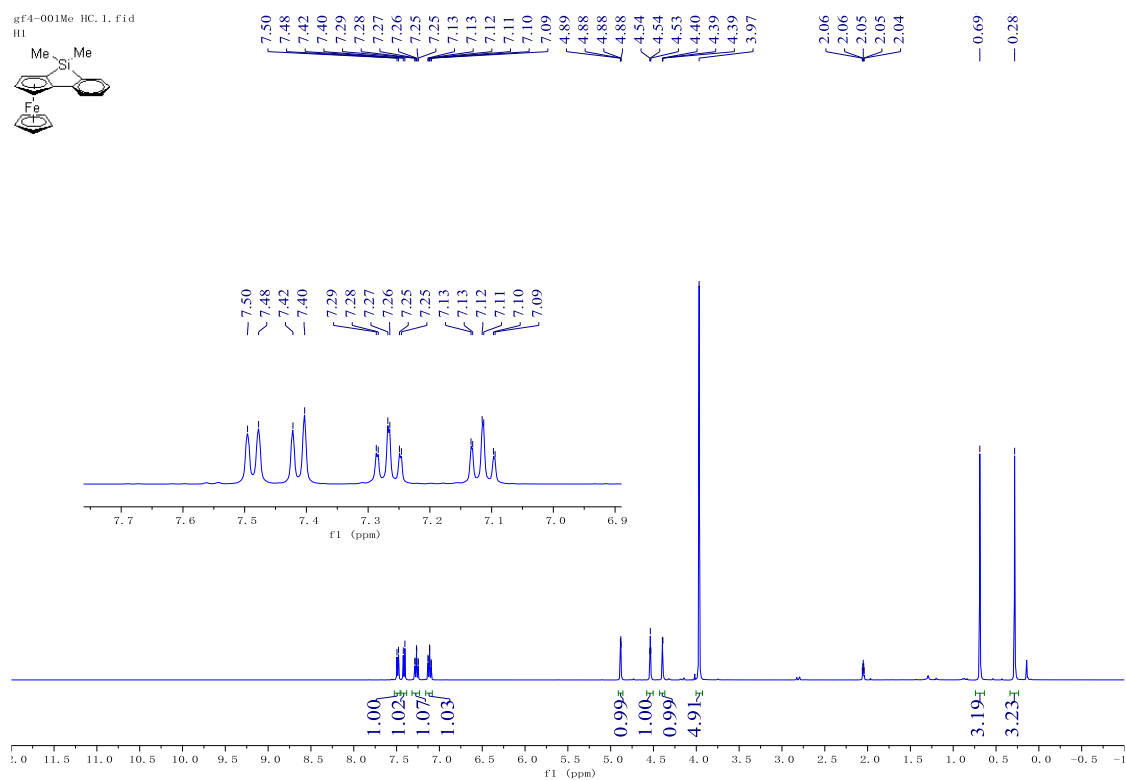
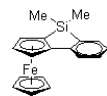


Compound 1x

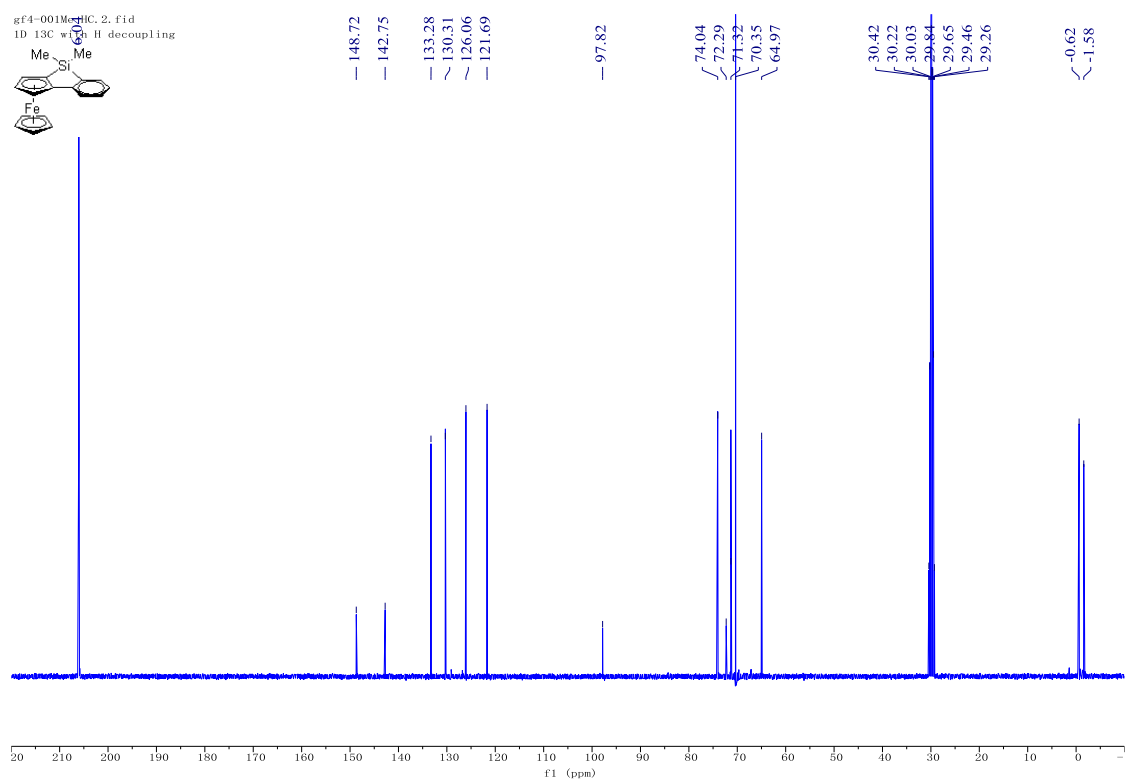
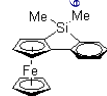


Compound 2a

gF4-001Me HC. 1. fid
H1

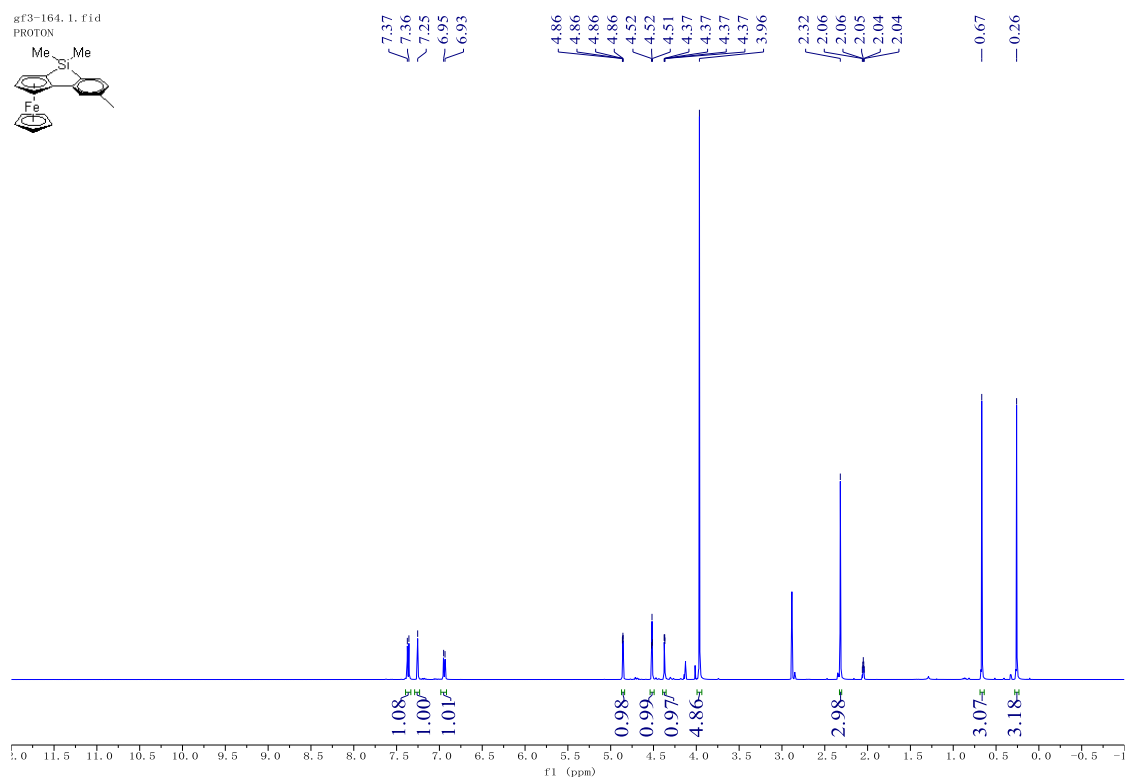
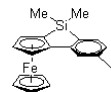


gF4-001Me HC. 2. fid
ID 13C with H decoupling

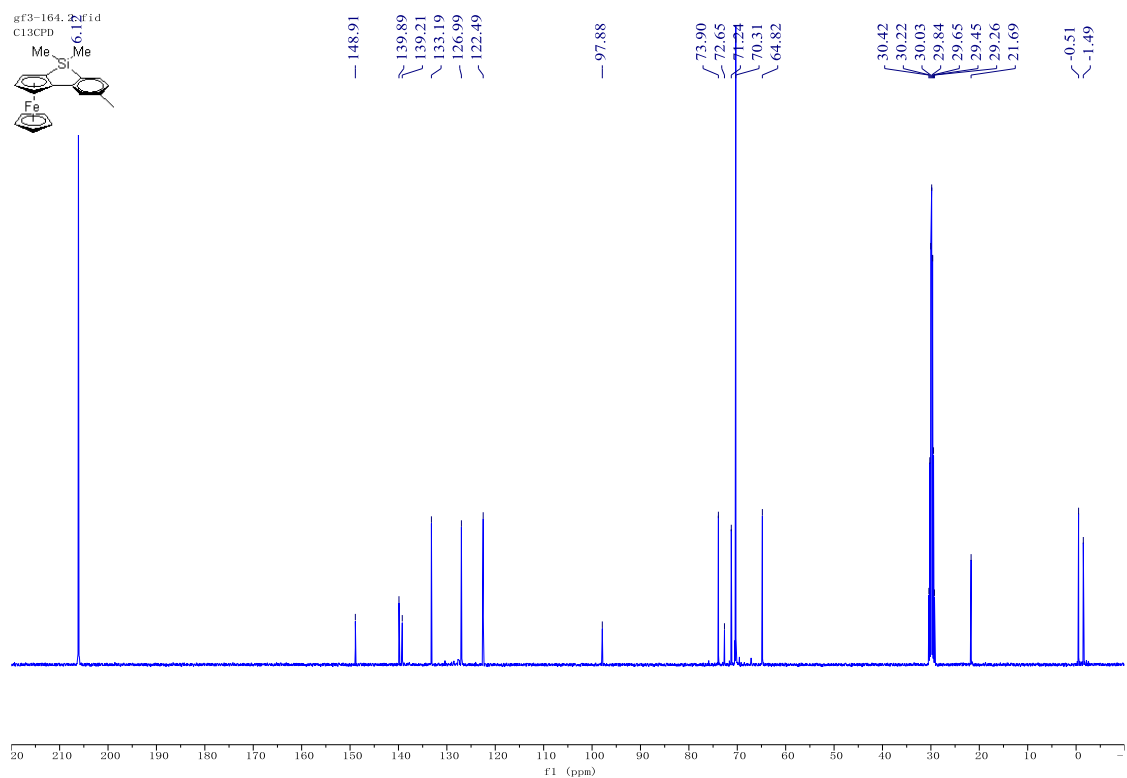
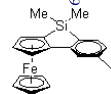


Compound 2b

gF3-164. 1. fid
PROTON

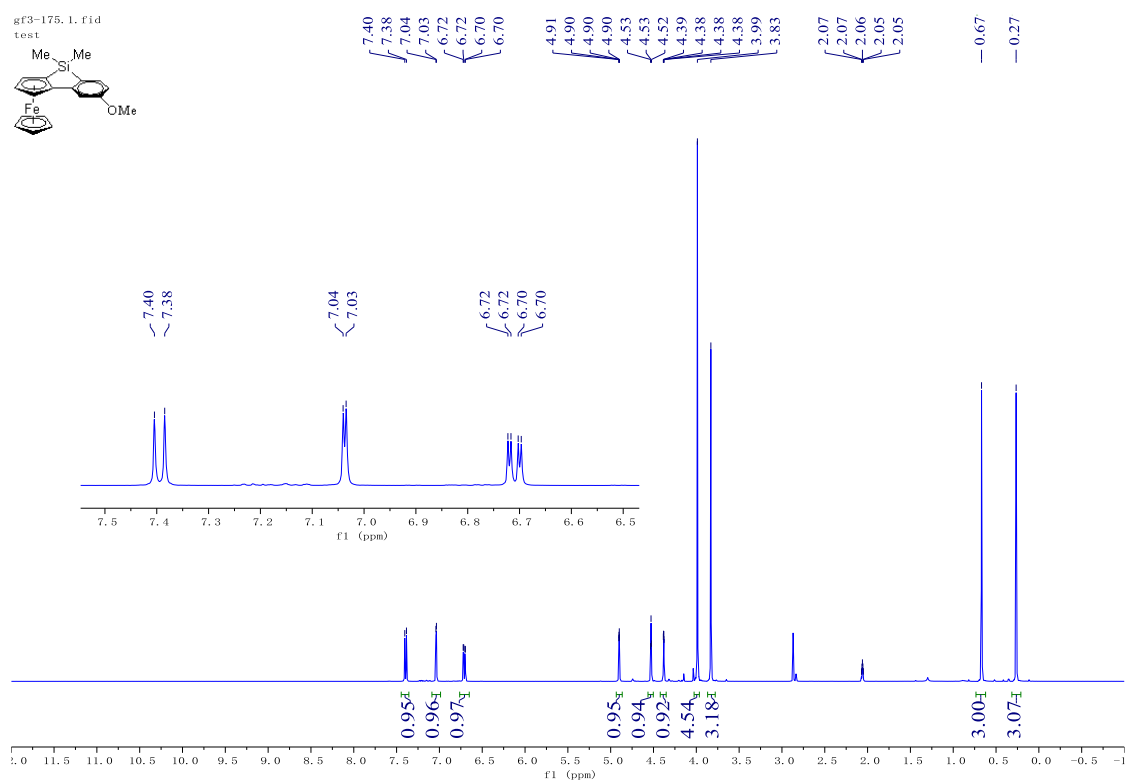
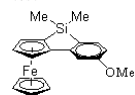


gF3-164. 2. fid
C13CPD

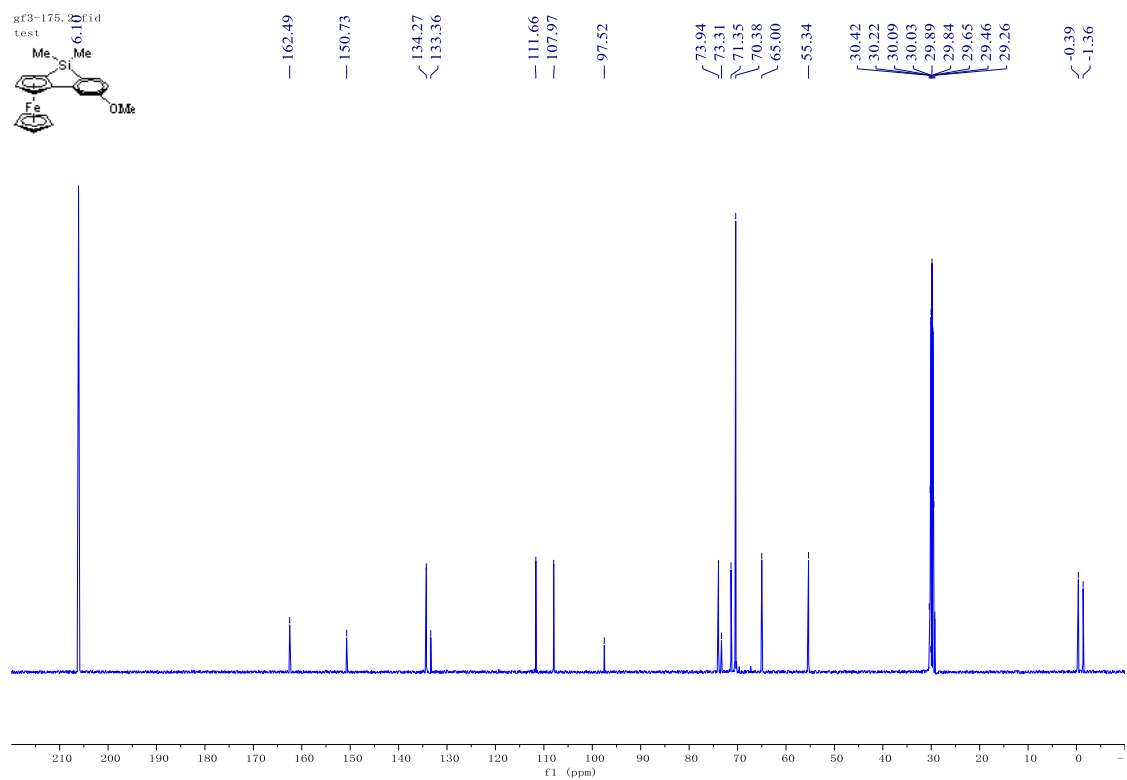
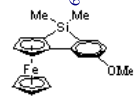


Compound 2c

gf3-175.1.fid
test

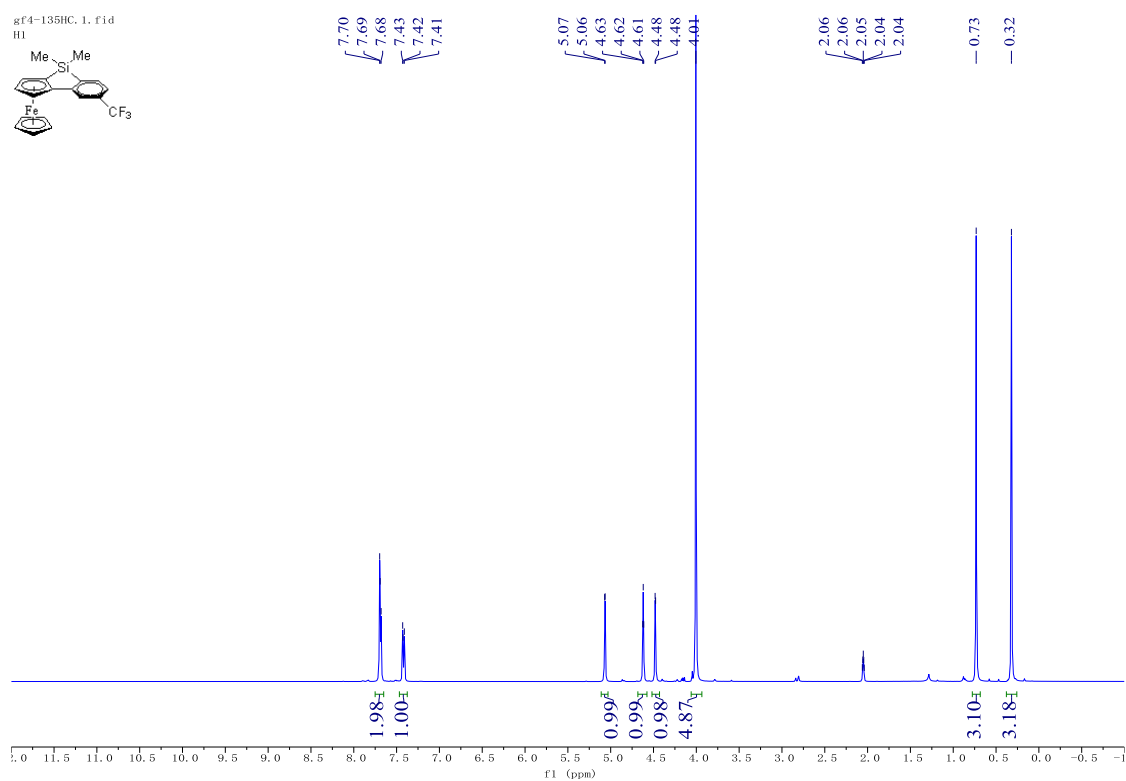
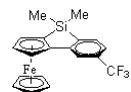


gf3-175.2.fid
test

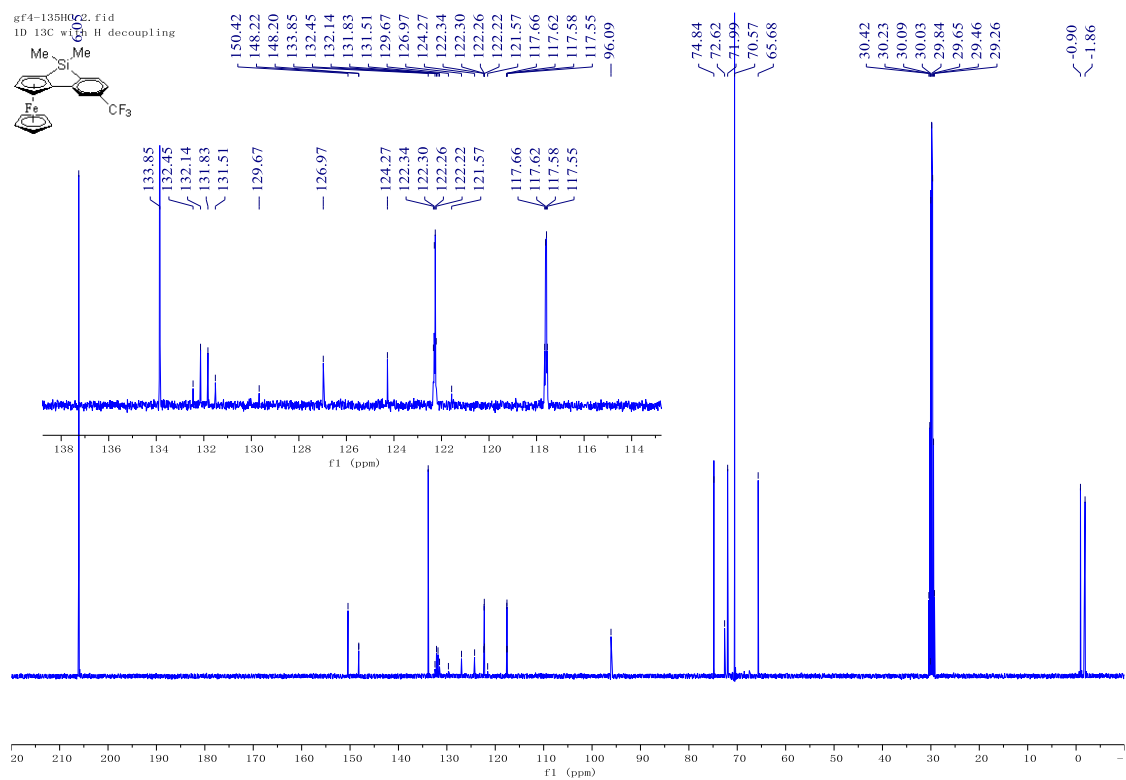
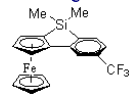


Compound 2d

gf4-135HC.1.fid
H1

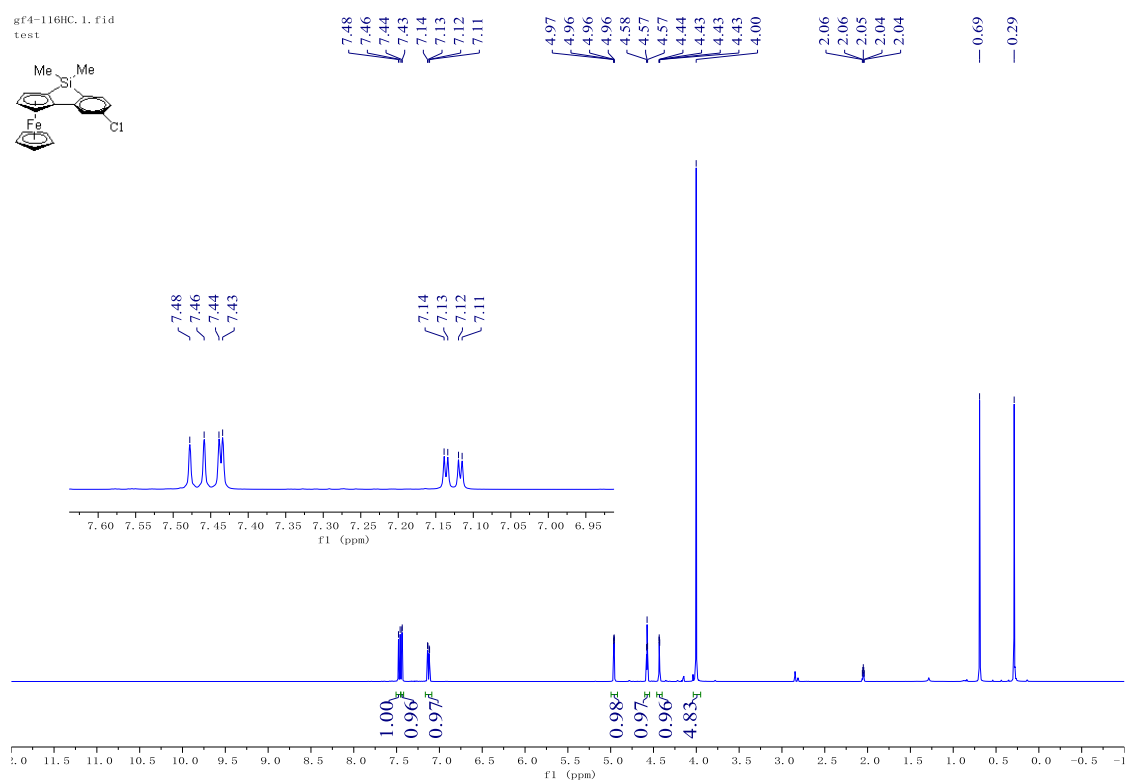
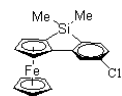


gf4-135H02.fid
ID 13C w/1H decoupling

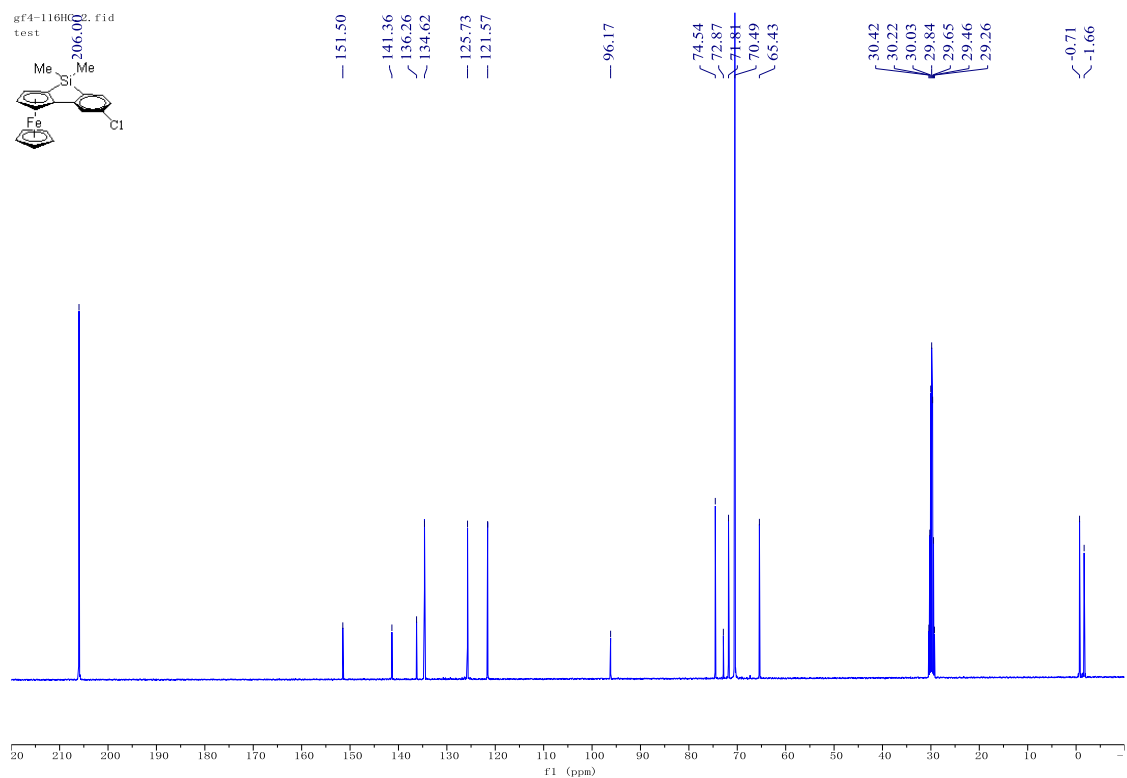
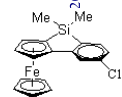


Compound 2e

gf4-116HC.1.fid
test

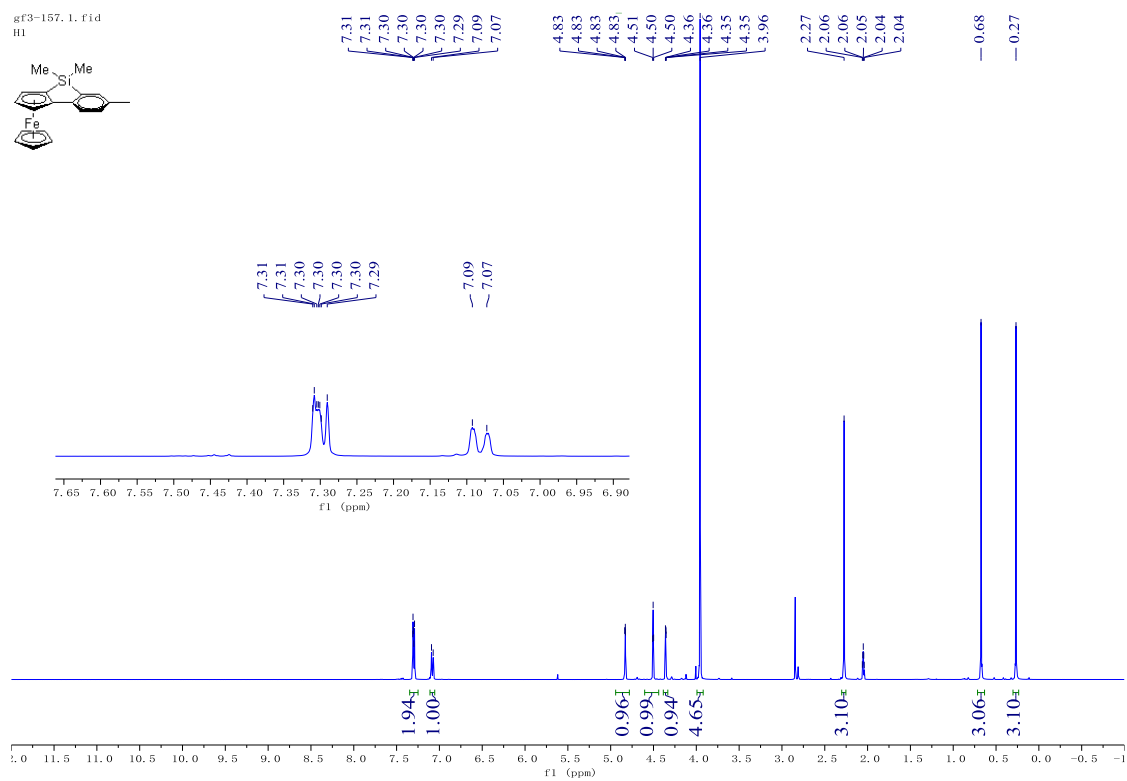
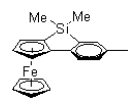


gf4-116HC2.fid
test

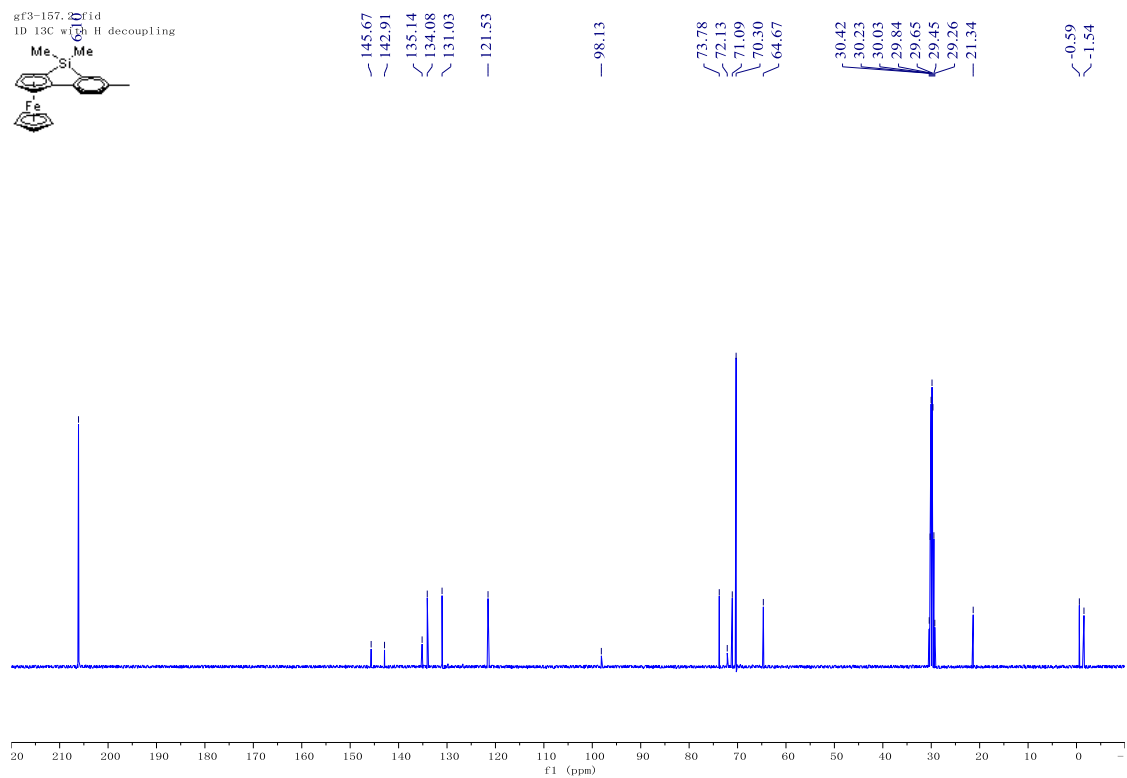
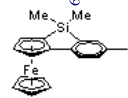


Compound 2f

gf3-157.1.fid
H1

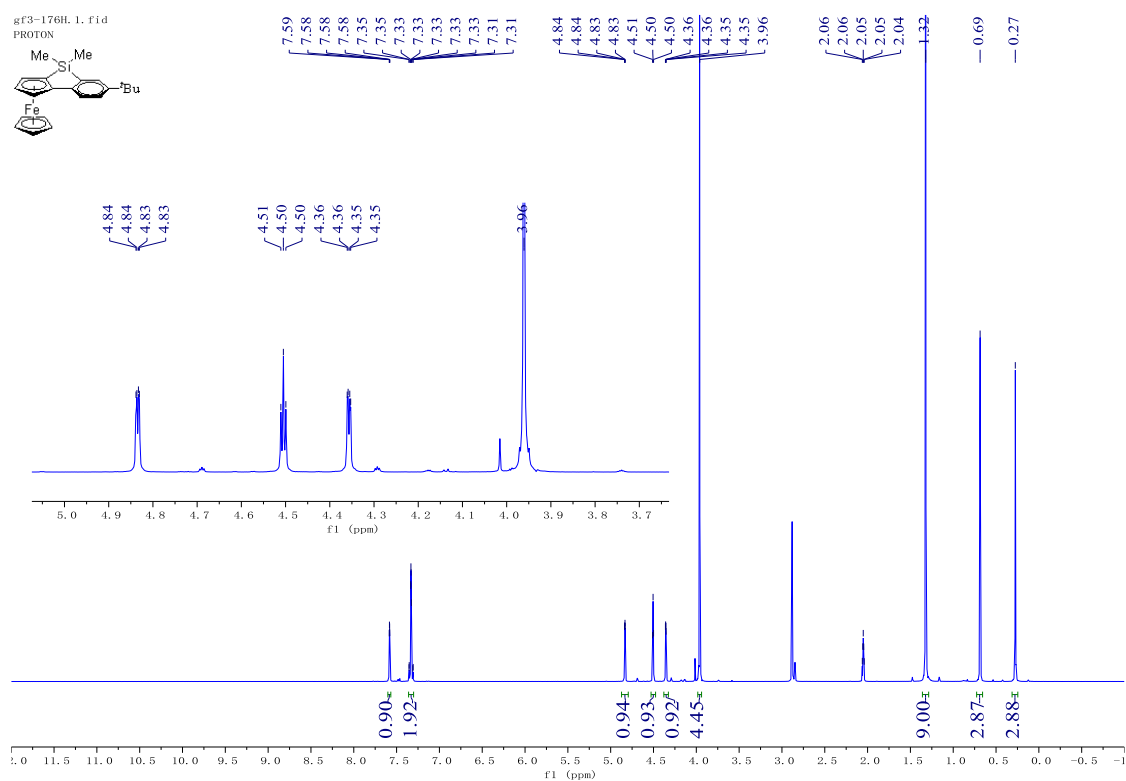
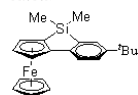


gf3-157.2.fid
ID 13C w/3H H decoupling

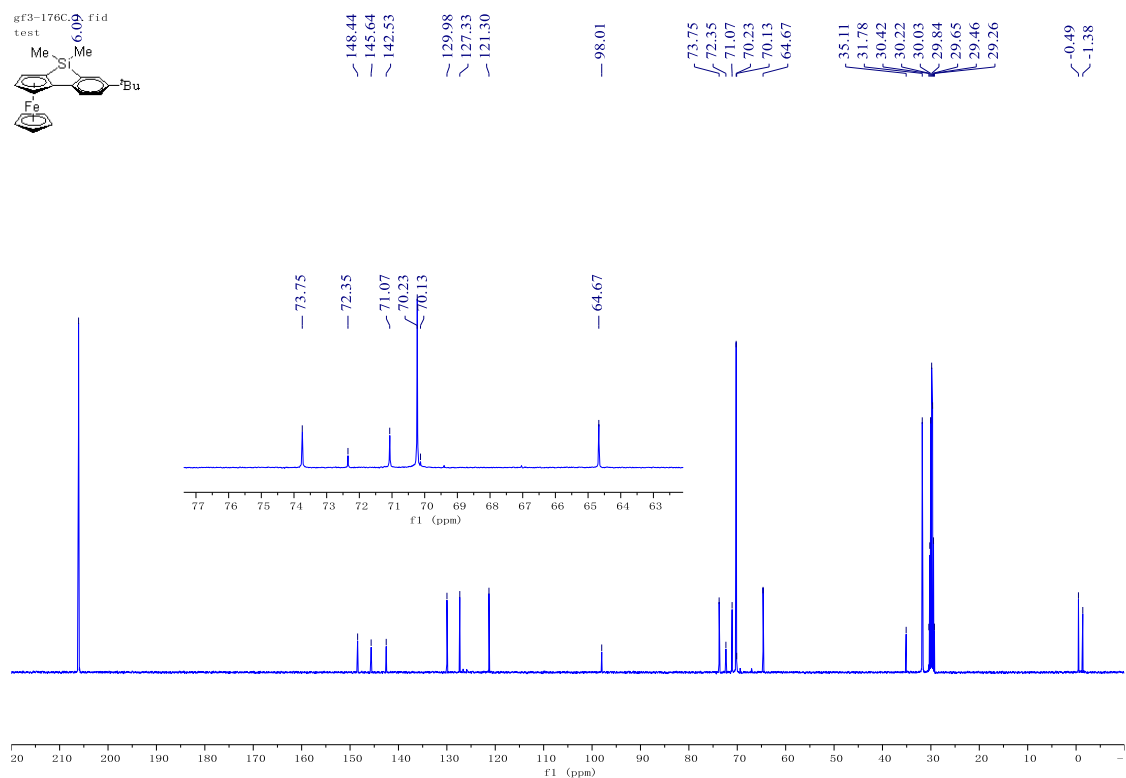
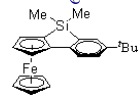


Compound 2g

gF3-176H.1.fid
PROTON

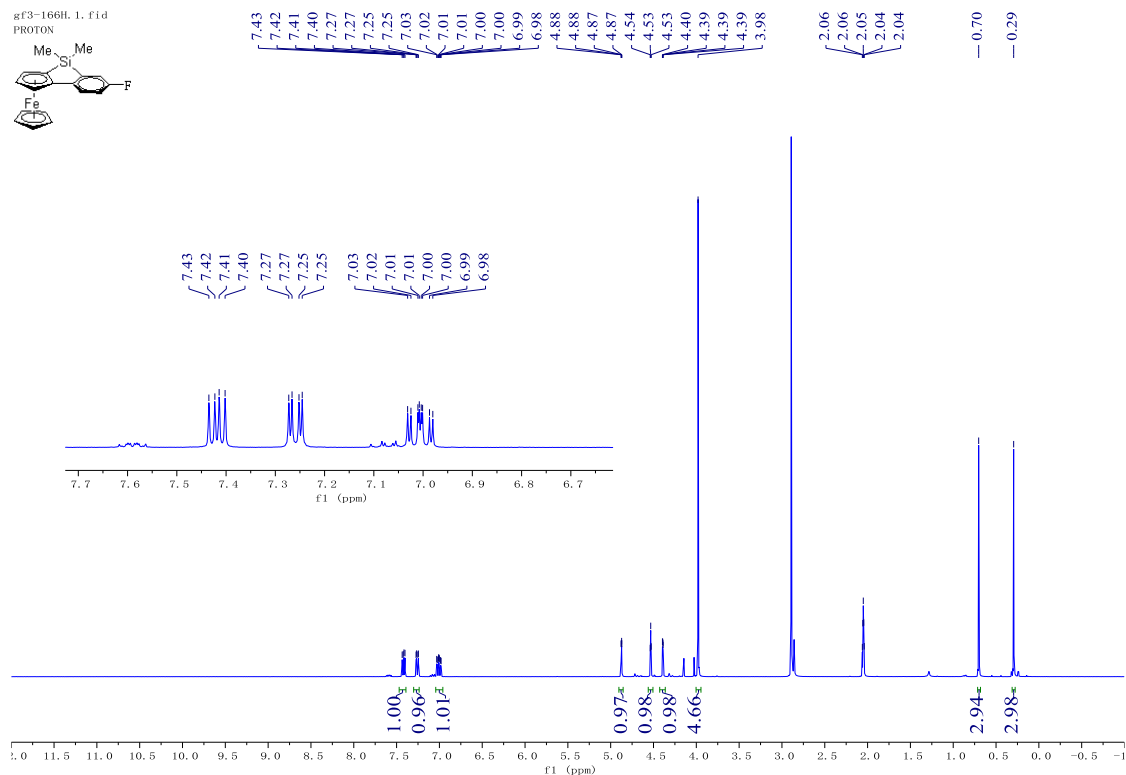
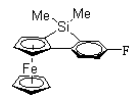


gF3-176C.fid
test

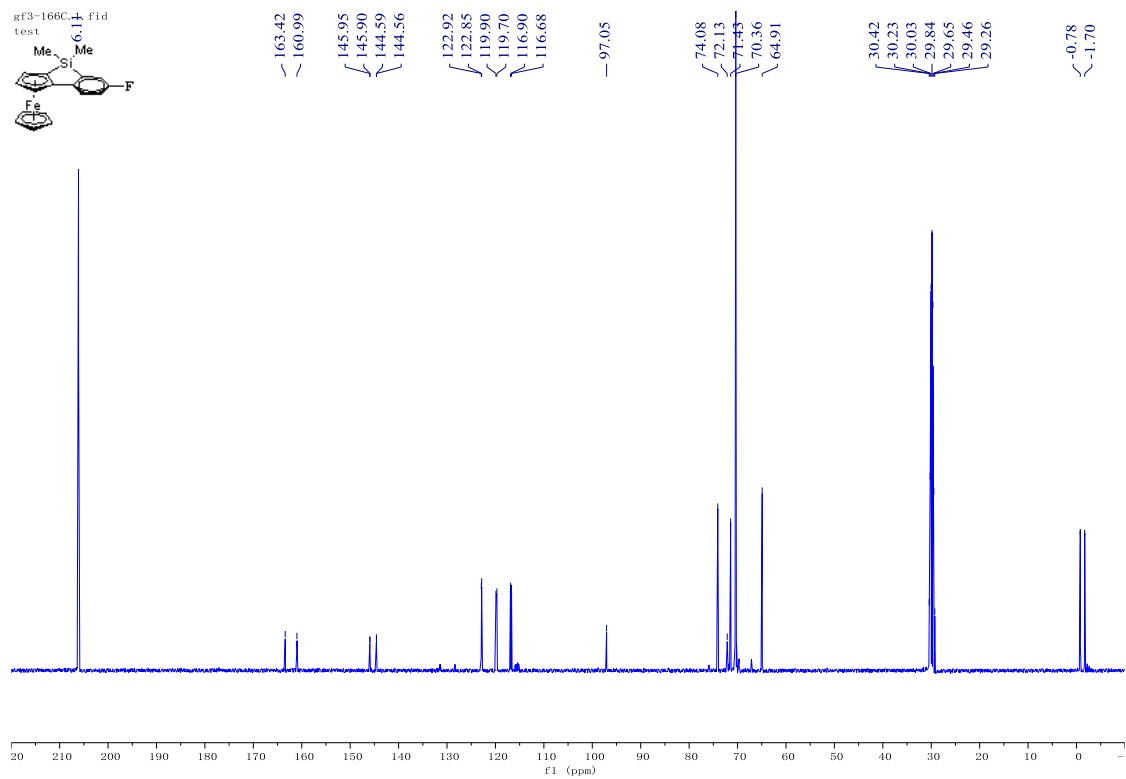
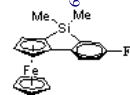


Compound 2h

gF3-166H.1.fid
PROTON

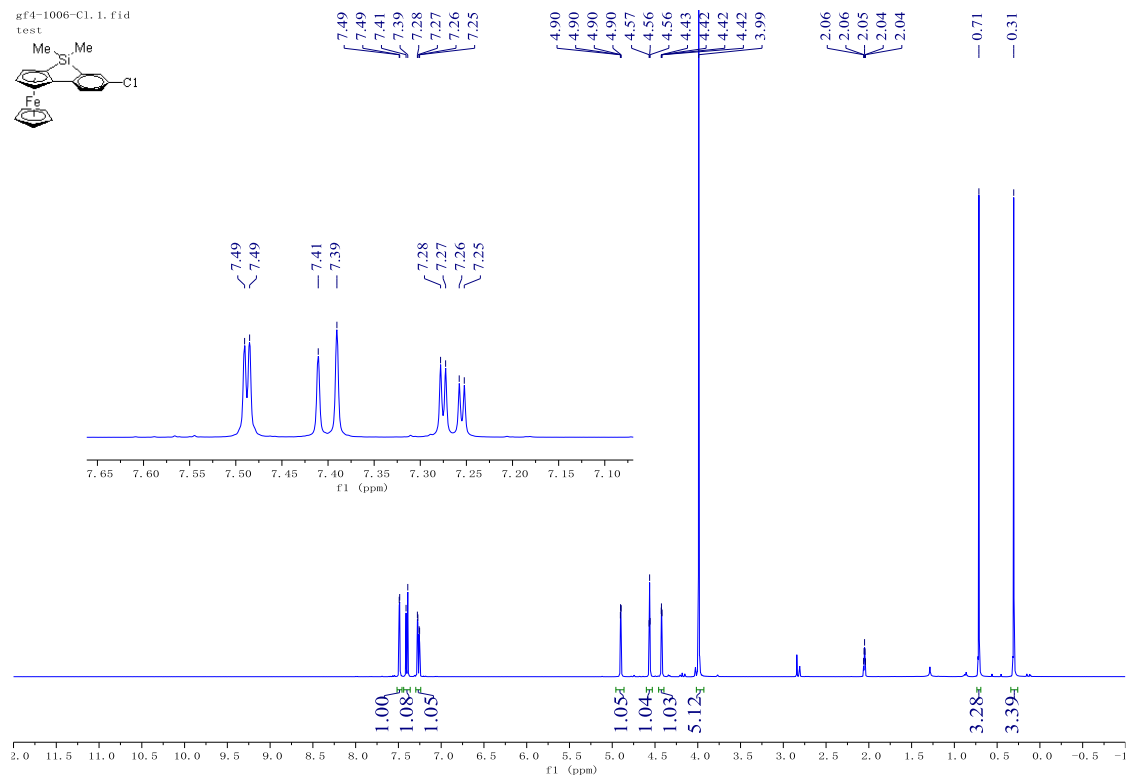
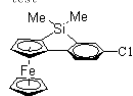


gF3-166C.1.fid
test

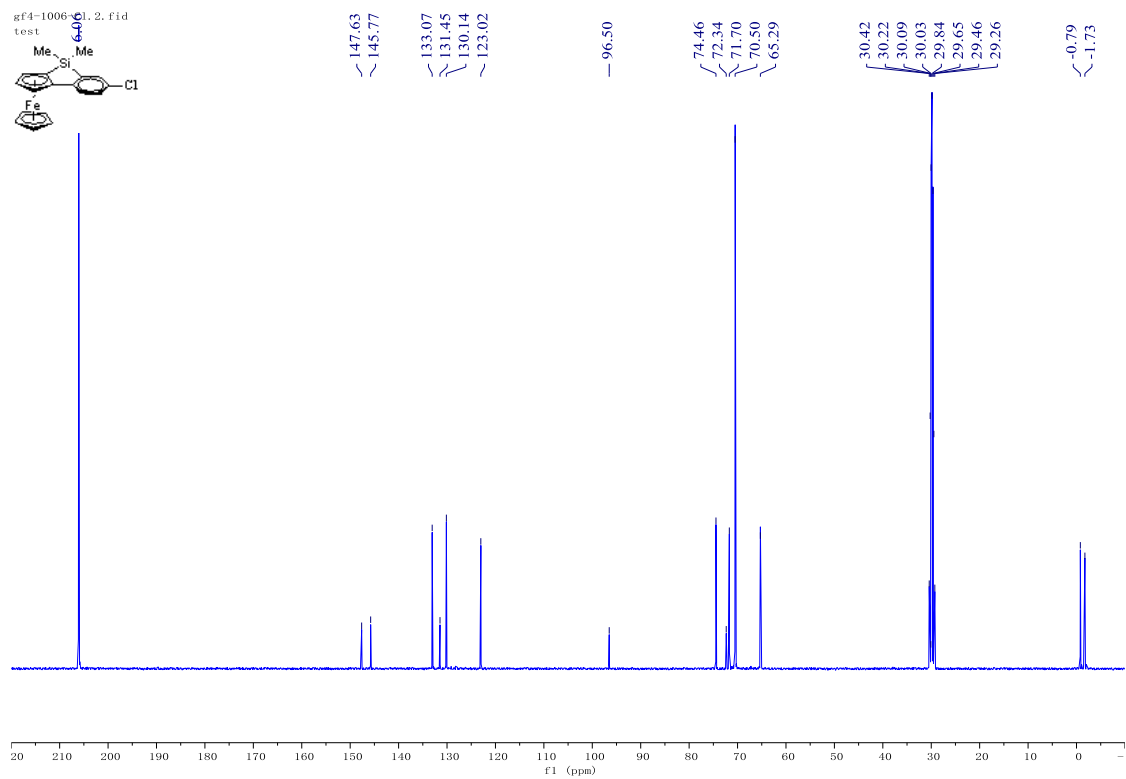


Compound 2i

gf4-1006-Cl. 1. fid
test

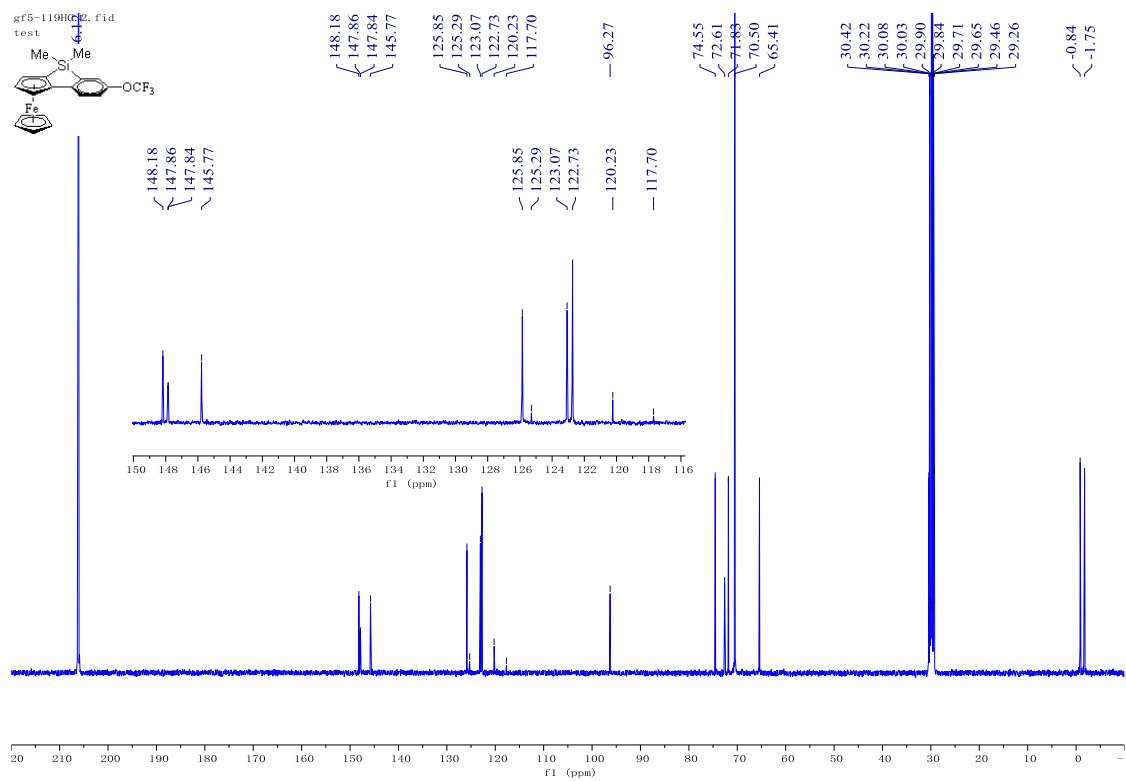
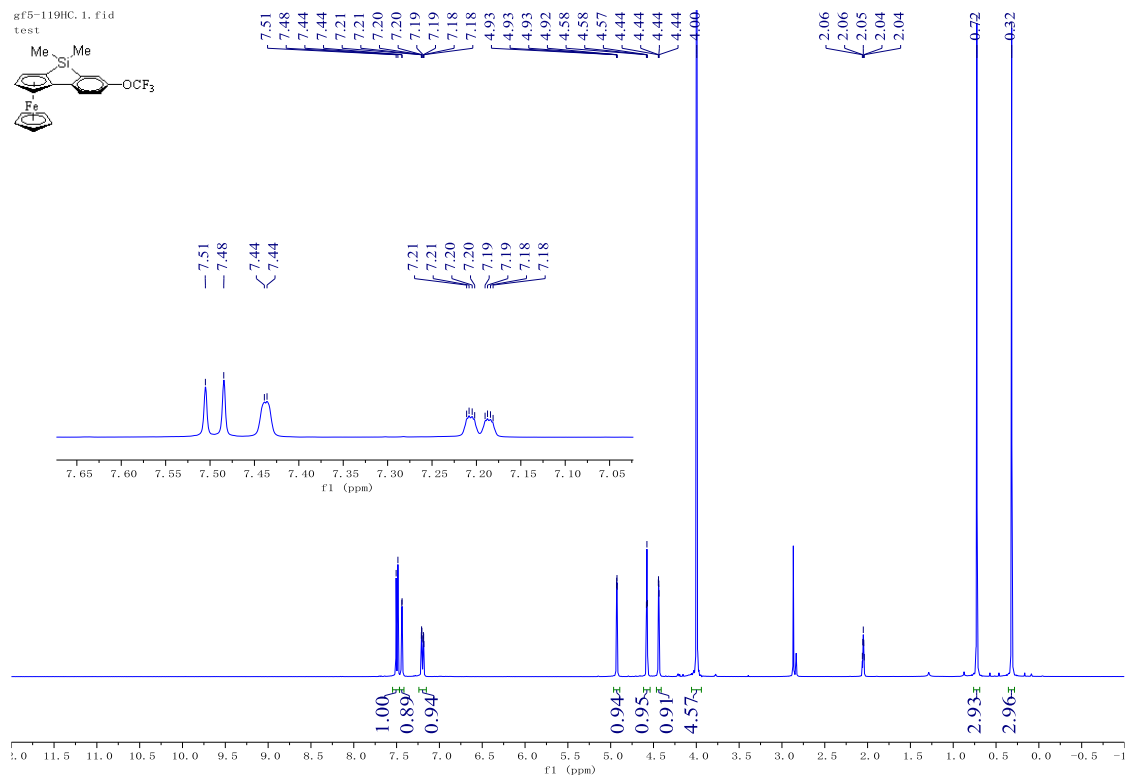
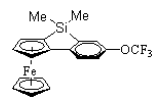


gf4-1006-Cl. 2. fid
test



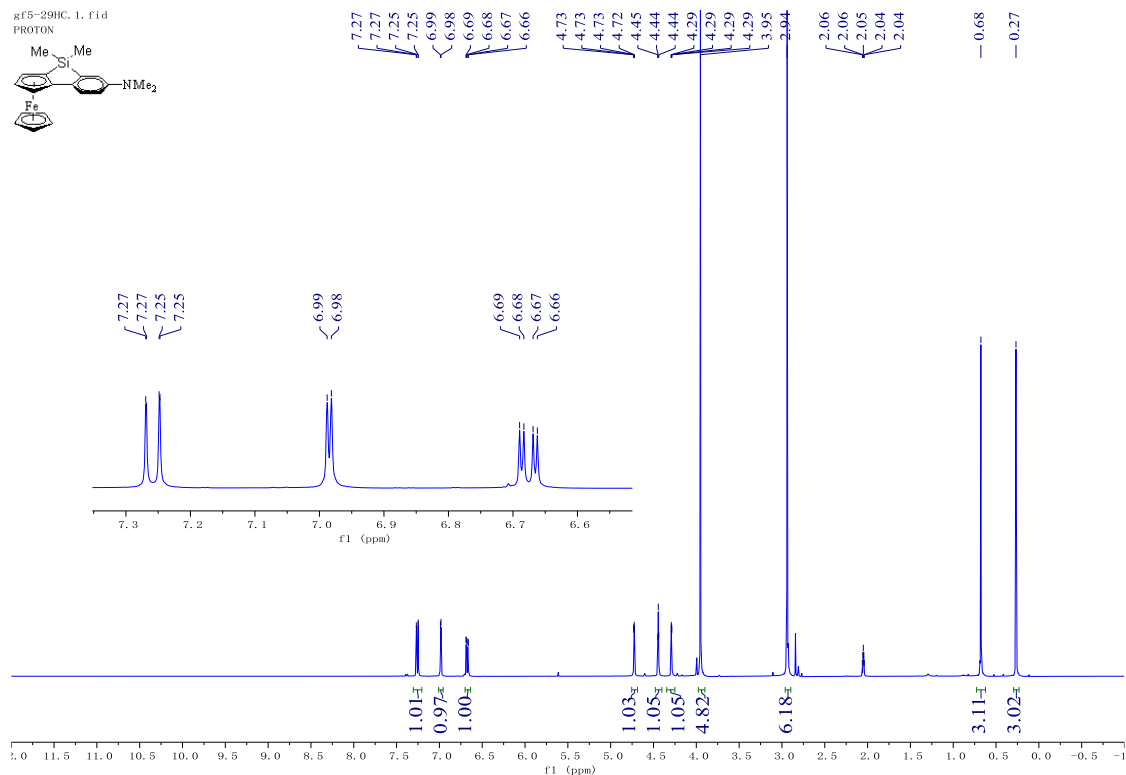
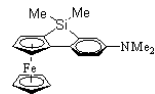
Compound 2j

gf5-119HC.1.fid
test

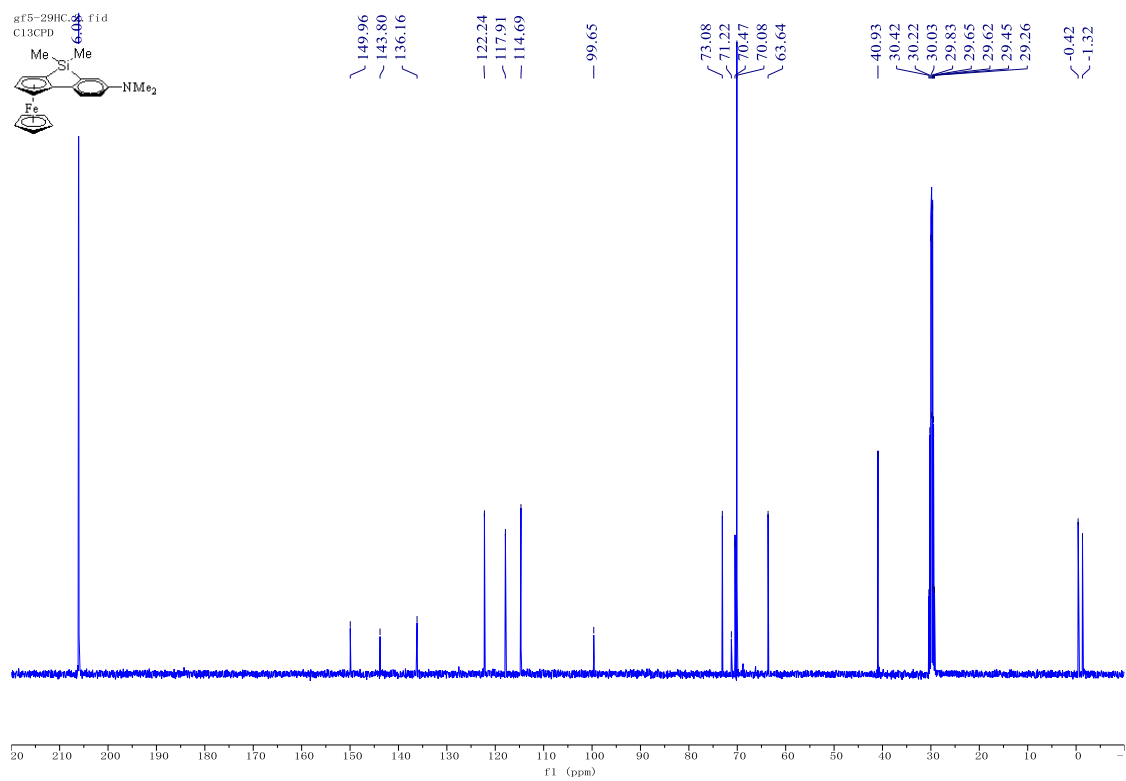
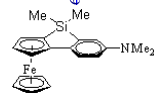


Compound 2k

gF5-29HC.1.fid
PROTON

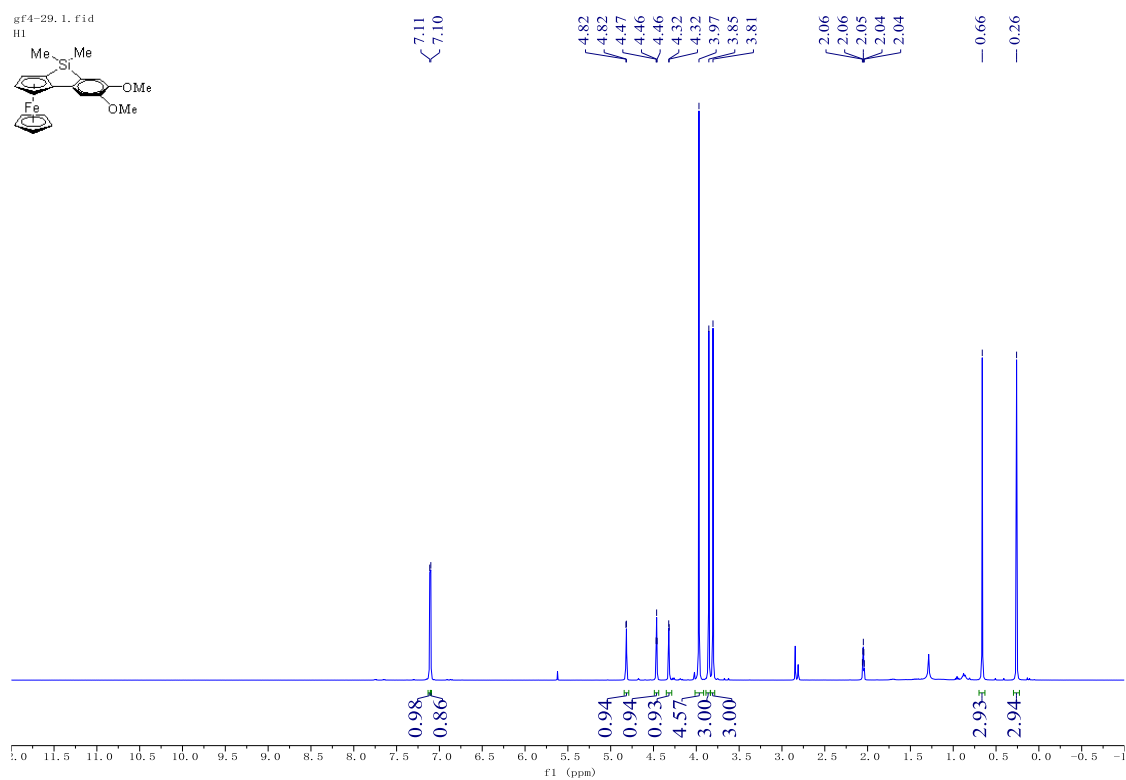
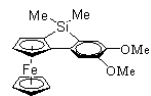


gF5-29HC.4.fid
C13CPD

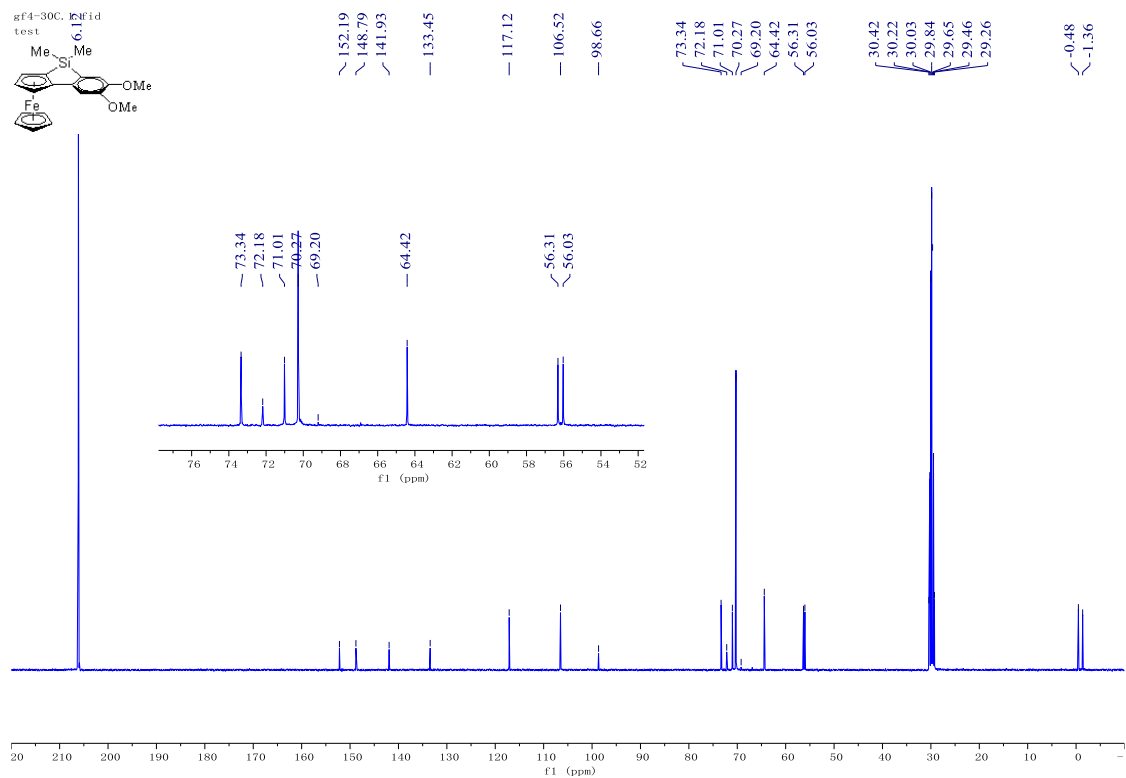
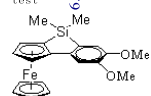


Compound 2l

gF4-29.1.f1d
H1

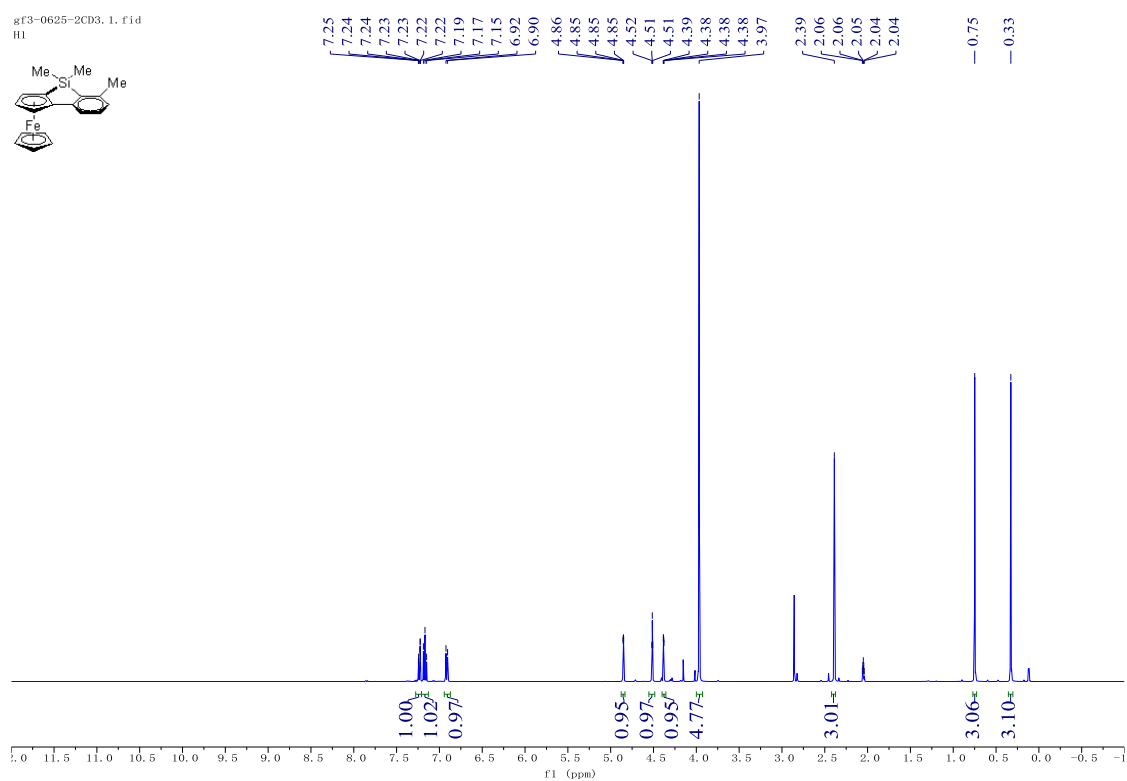
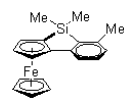


gF4-30C.f1d
test

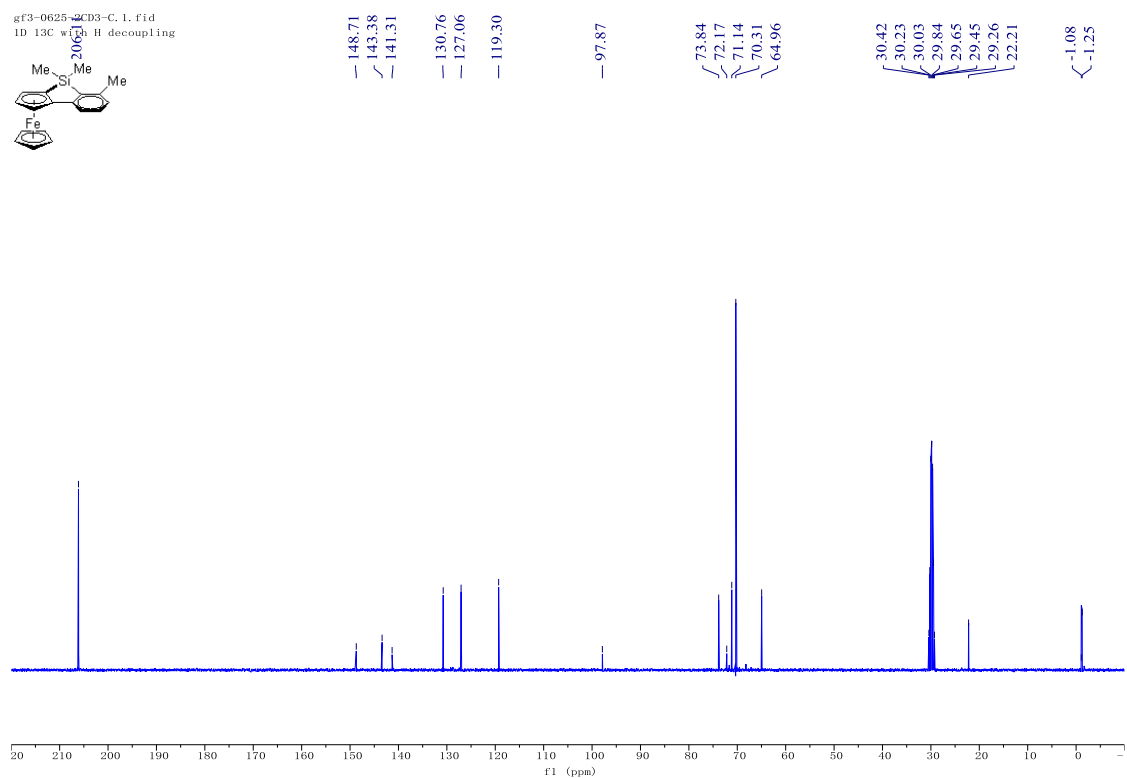
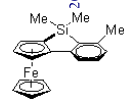


Compound 2m

gF3-0625-2CD3. 1. fid
H1

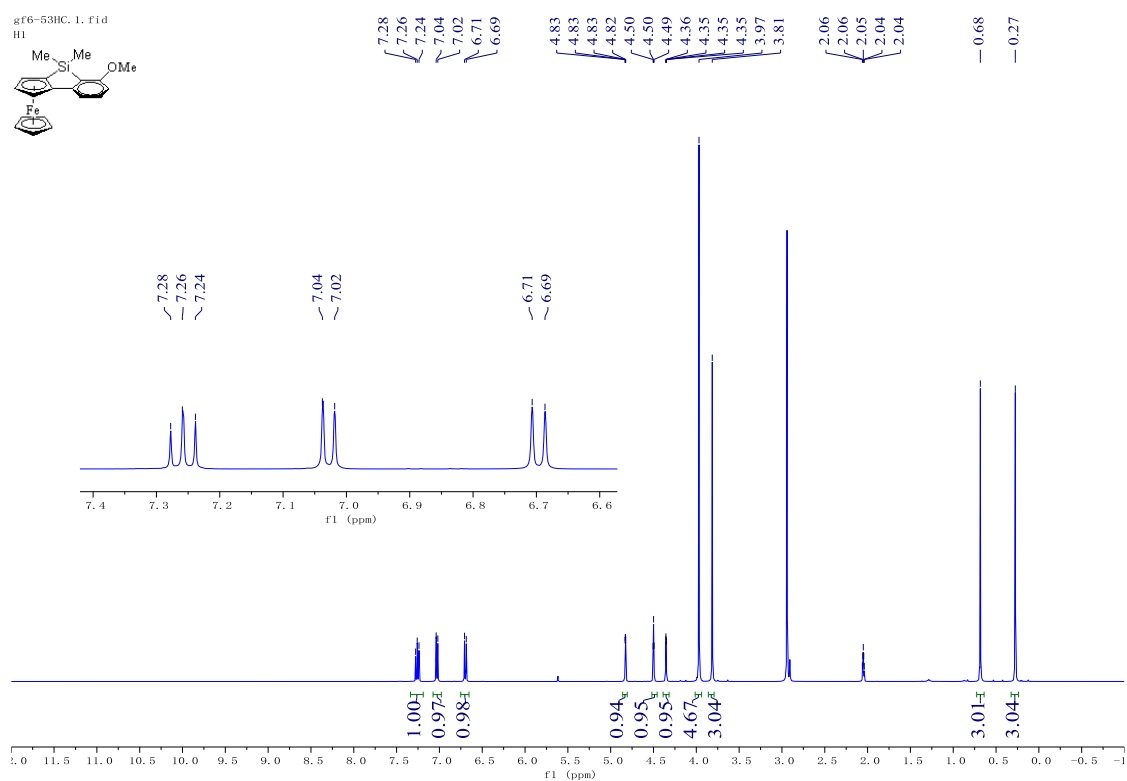
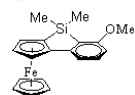


gF3-0625-2CD3-C. 1. fid
ID 13C w/13H H decoupling

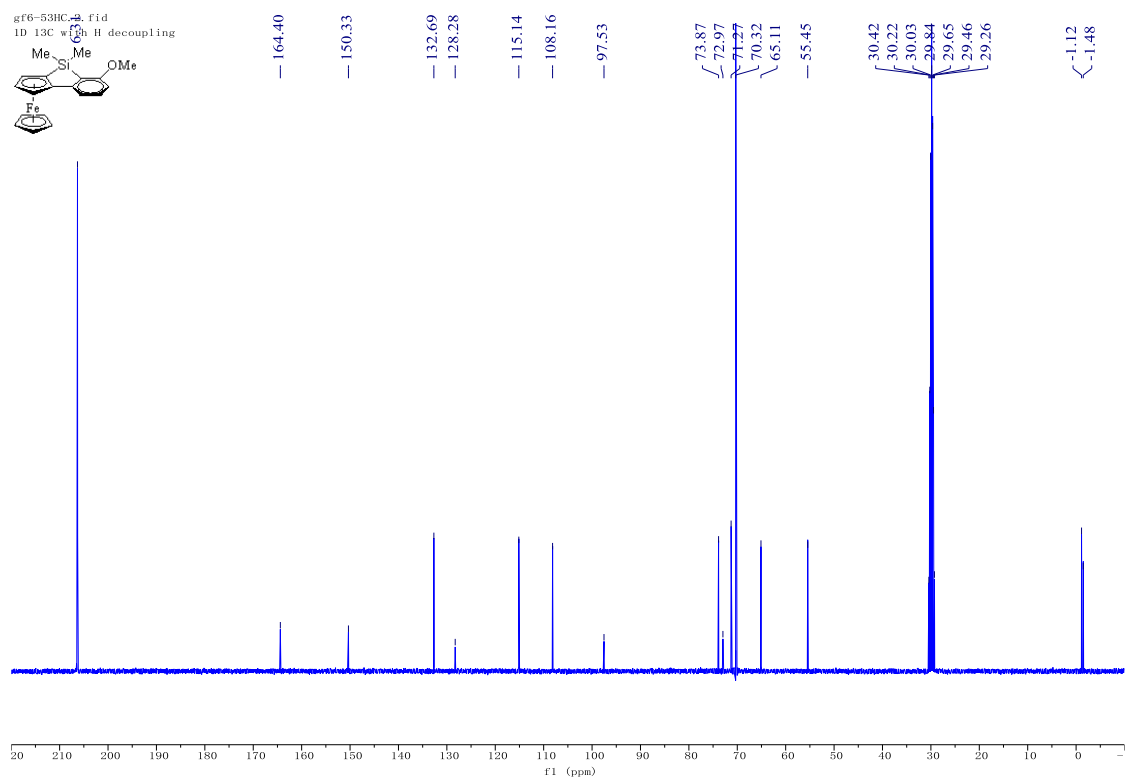
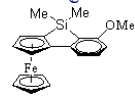


Compound 2n

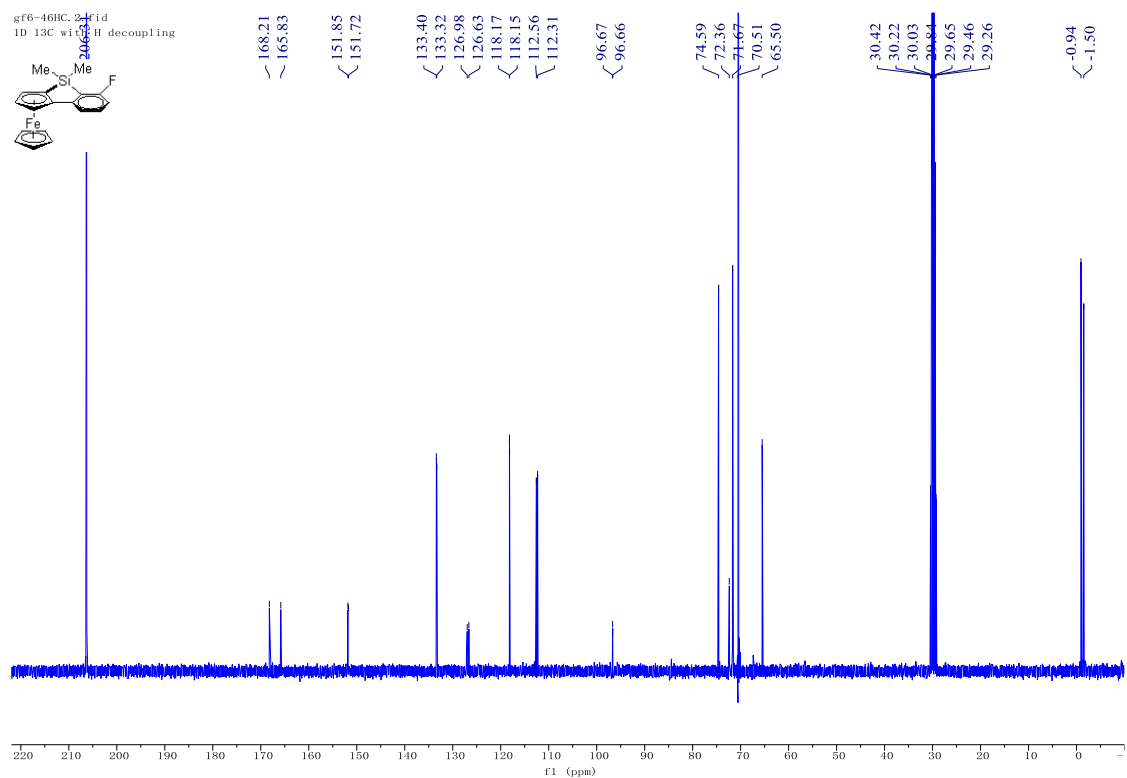
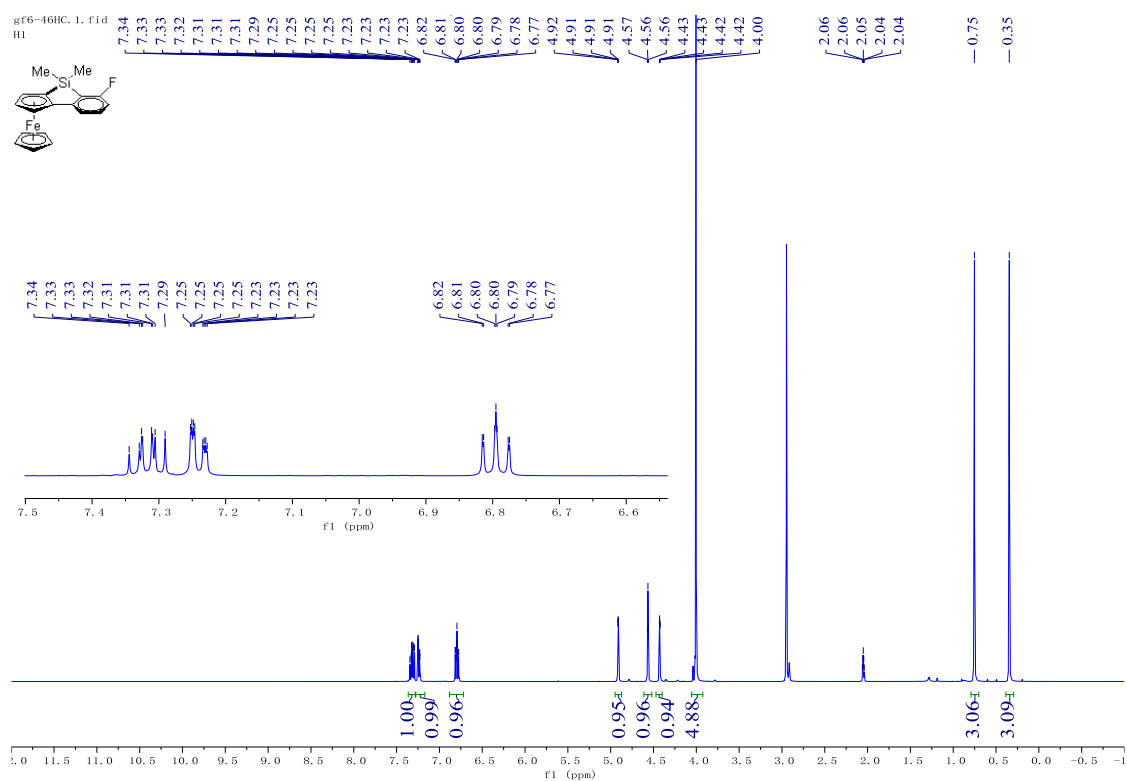
gf6-53HC.1.fid
H1



gf6-53HC.2.fid
ID 13C w/63H H decoupling

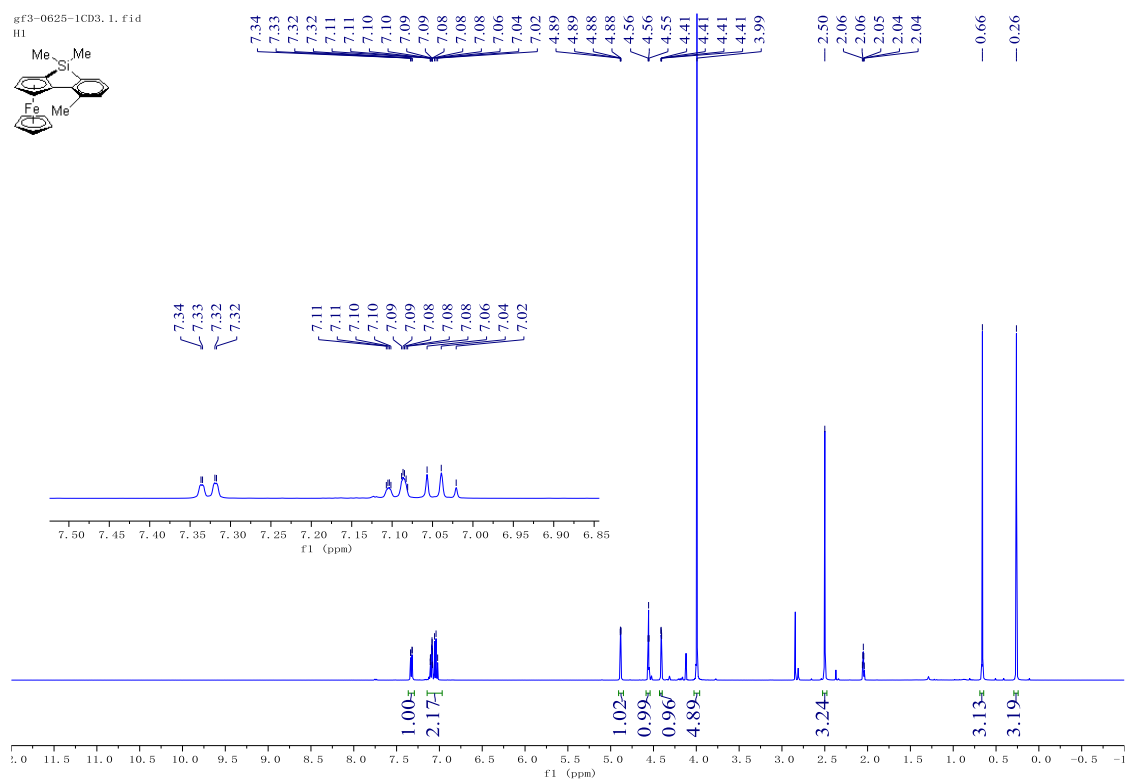
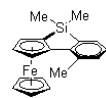


Compound 2o

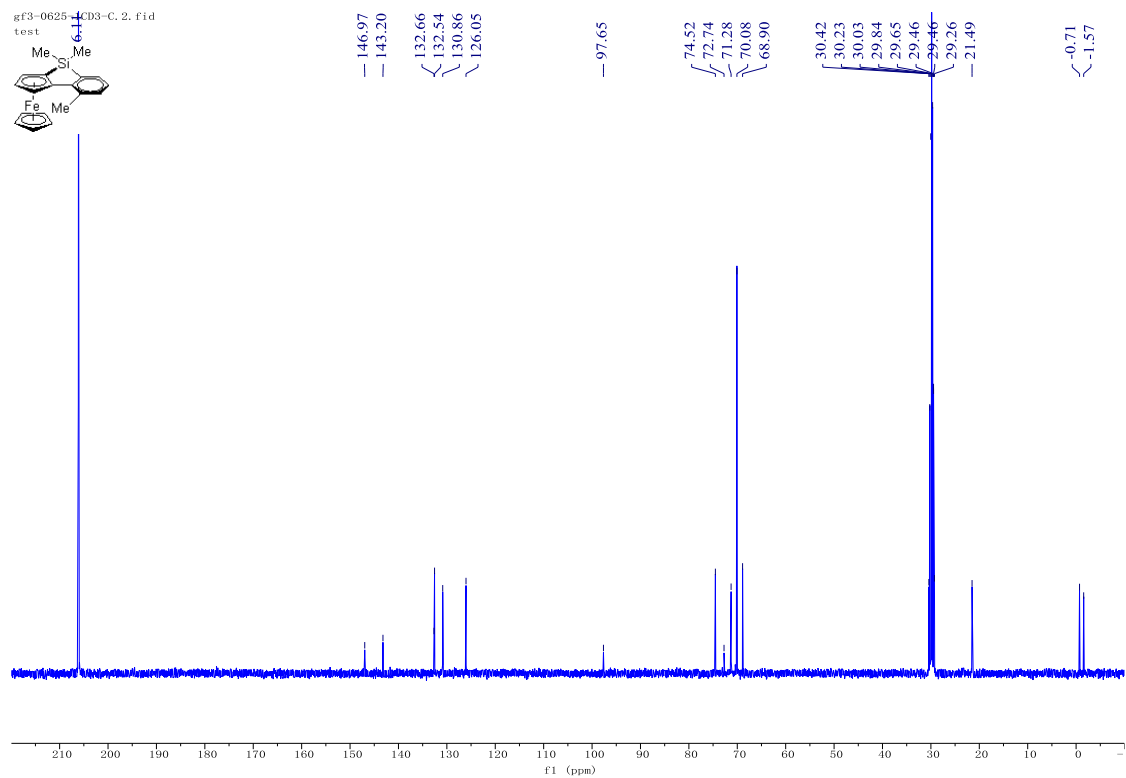
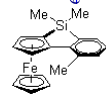


Compound 2p

gF3-0625-1CD3.1.f1d
H1

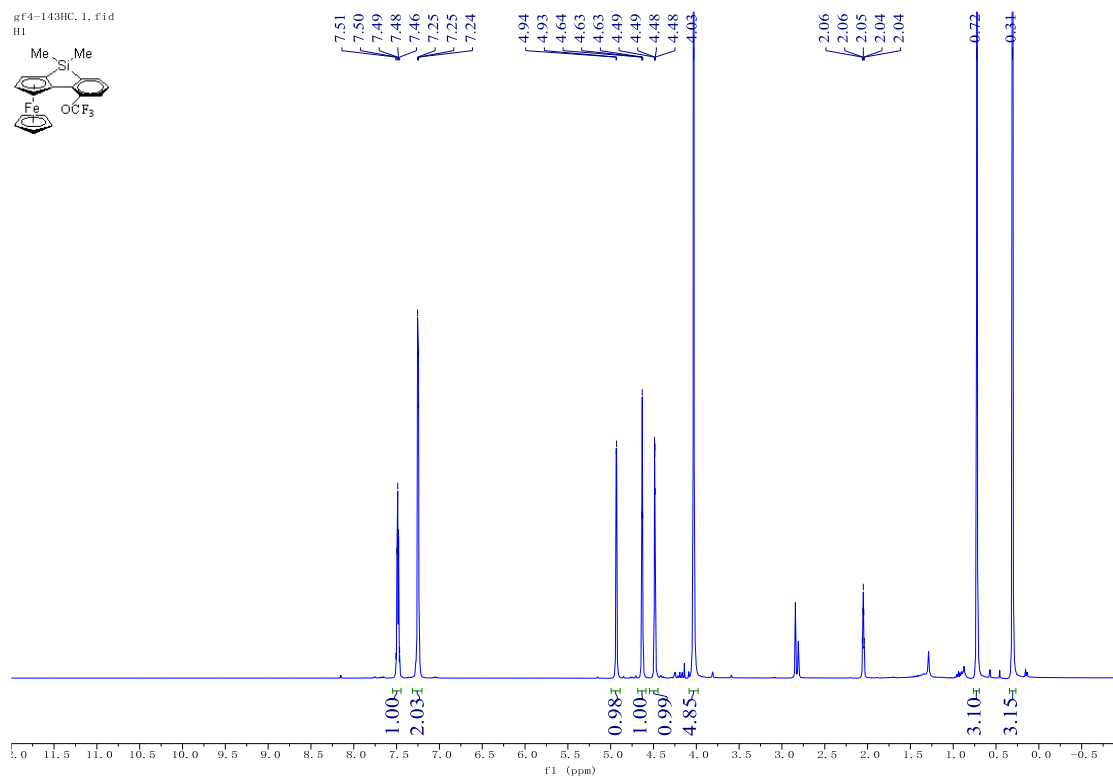
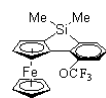


gF3-0625-1CD3-C.2.f1d
test

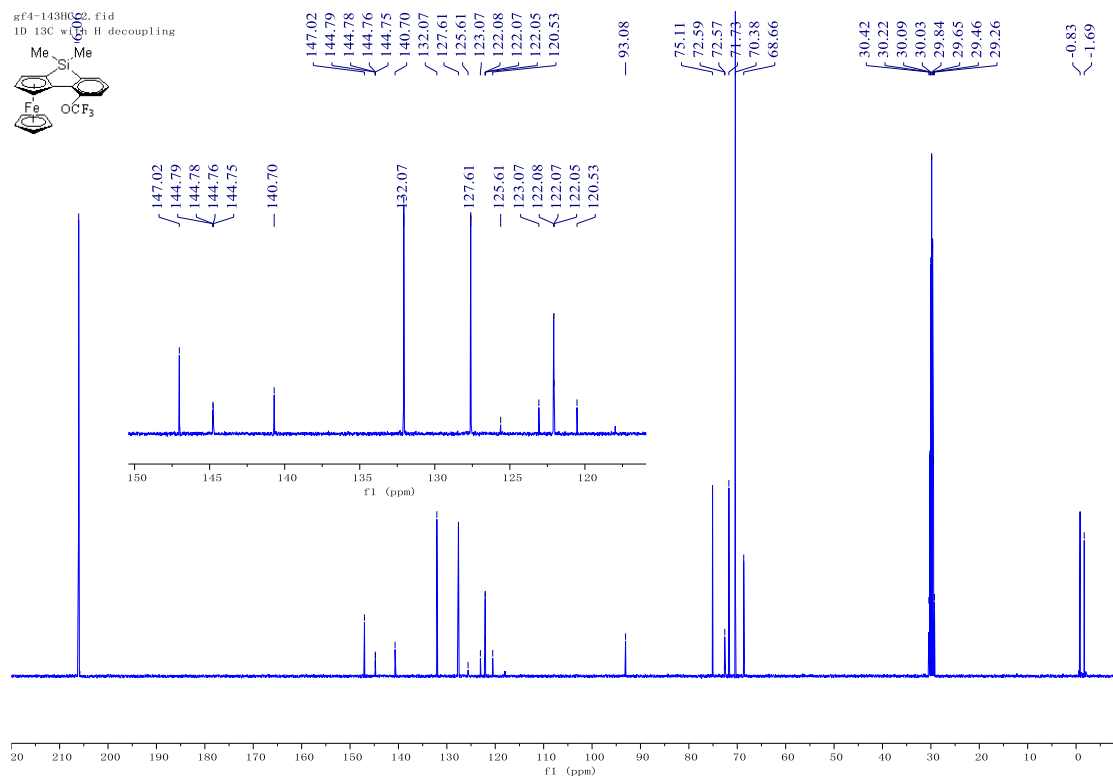
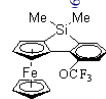


Compound 2q

gF4-143HC. 1. f1d
H1

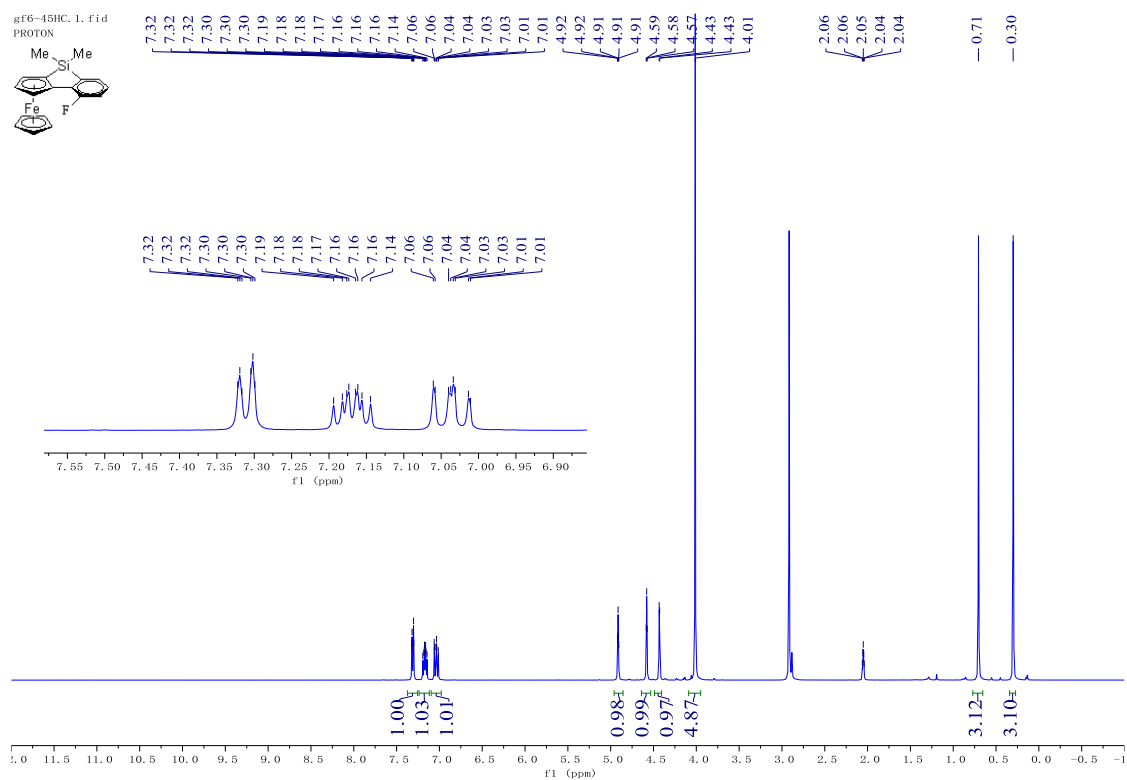
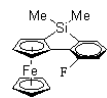


gF4-143HC2. f1d
ID 13C w/1H H decoupling

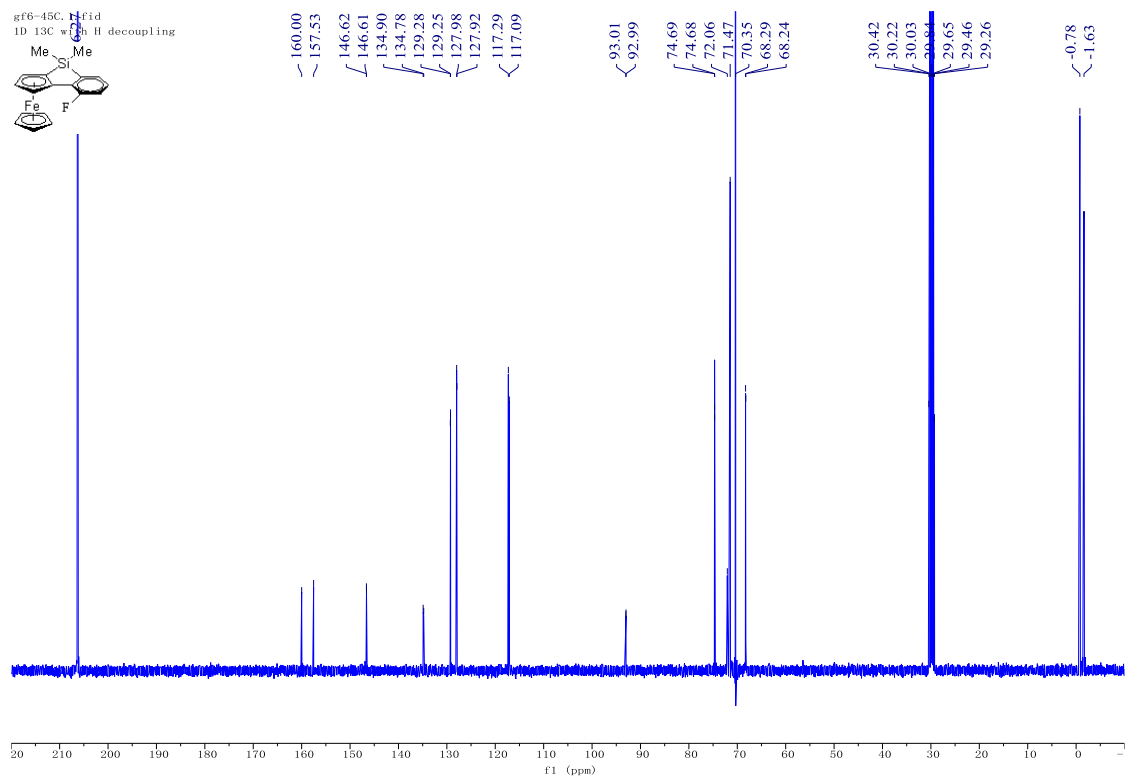
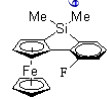


Compound 2r

gF6-45HC. 1. F1d
PROTON

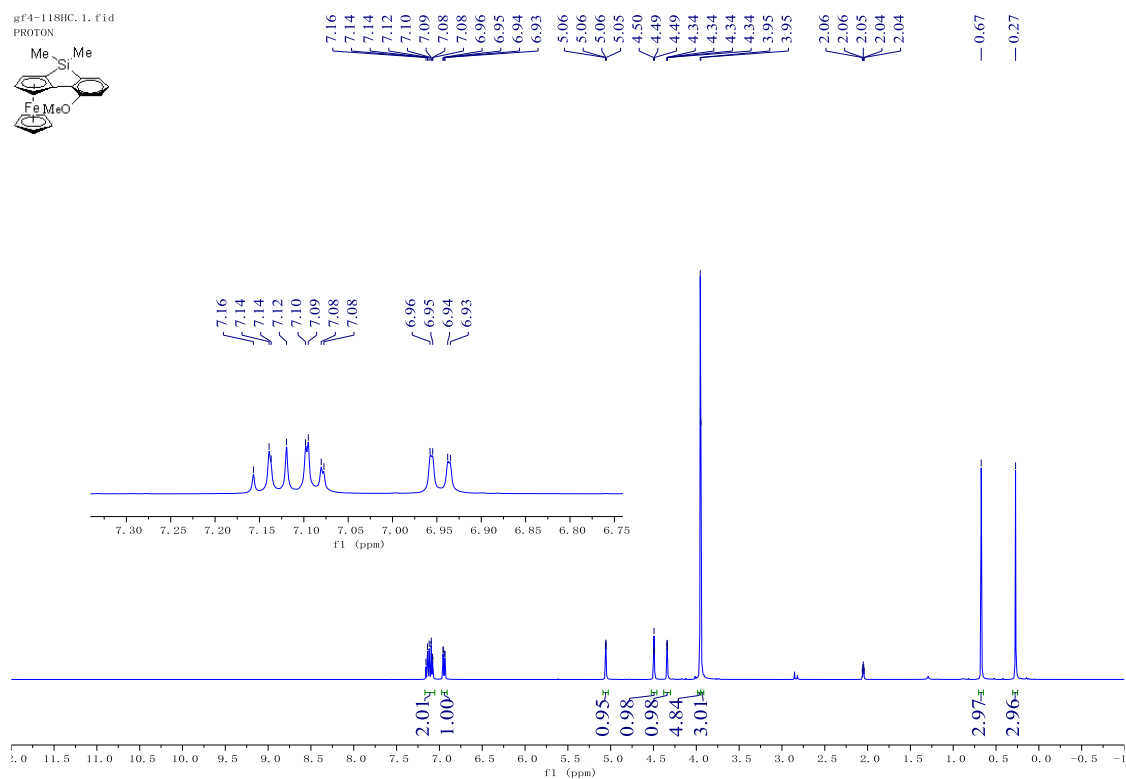
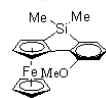


gF6-45C. H.fid
ID 13C with H decoupling

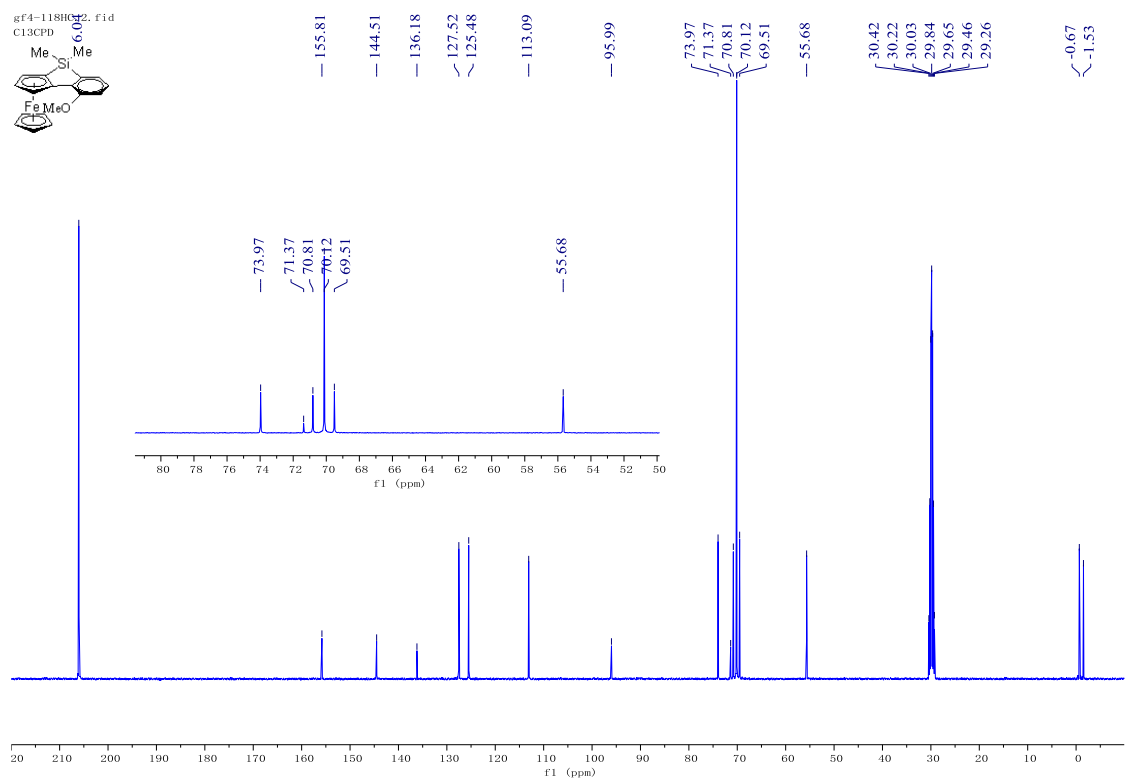
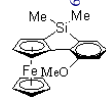


Compound 2s

gF4-118HC.1.fid
PROTON

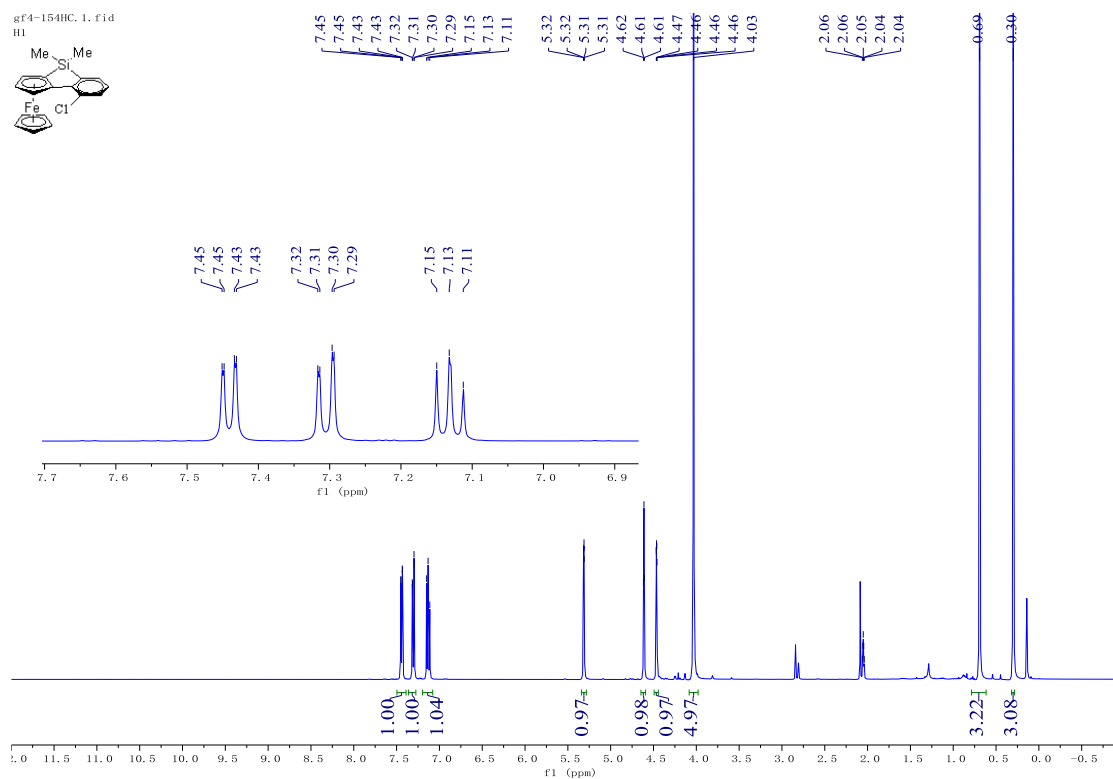
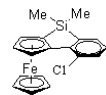


gF4-118HC.2.fid
C13CPD

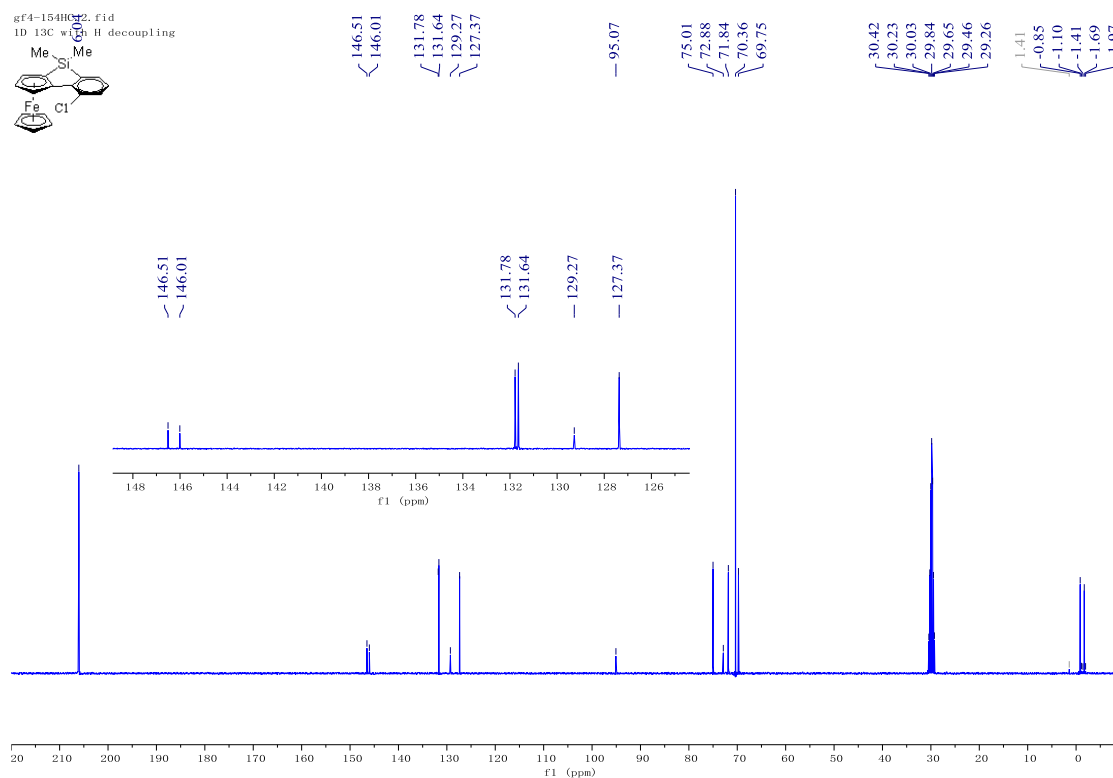
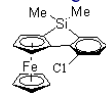


Compound 2t

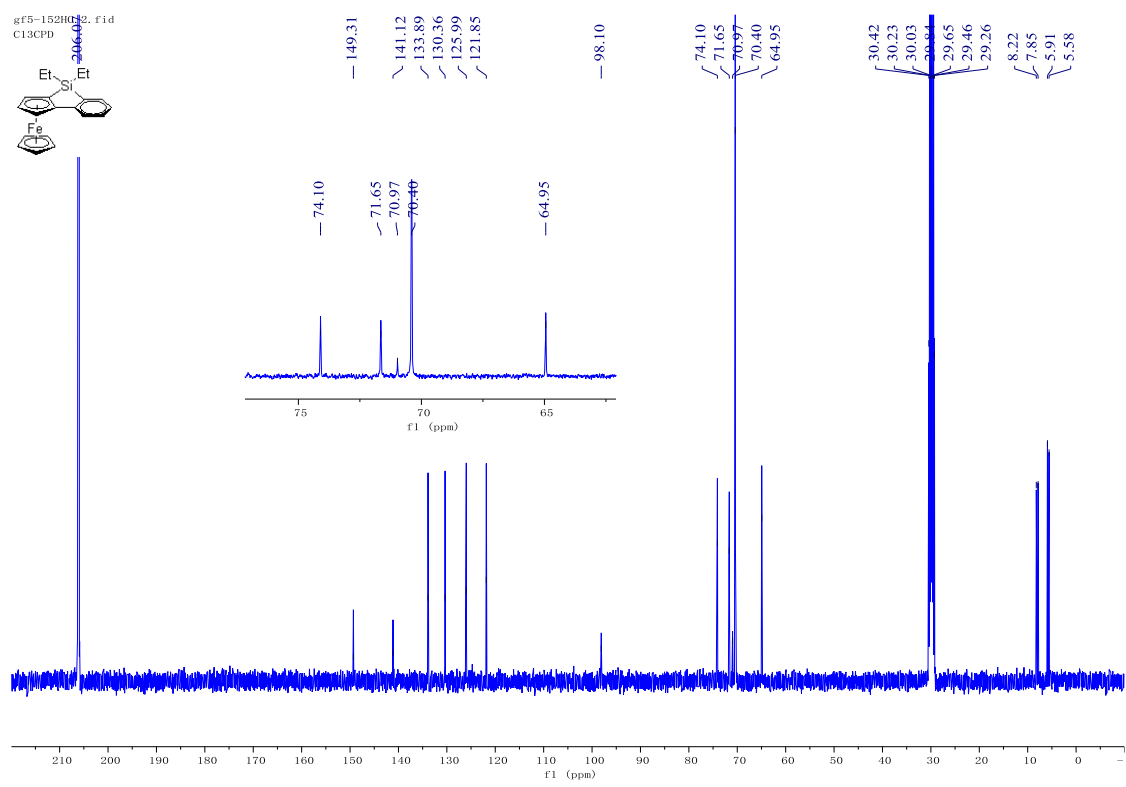
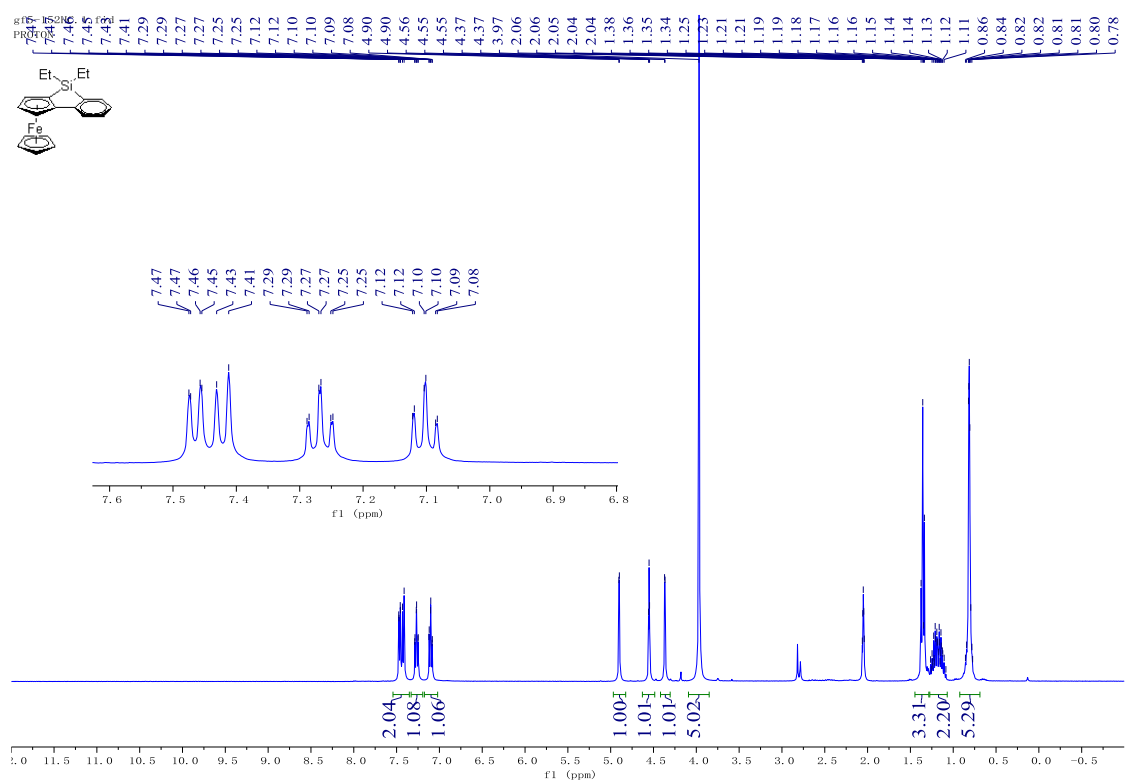
gF4-154HC.1.fid
H1



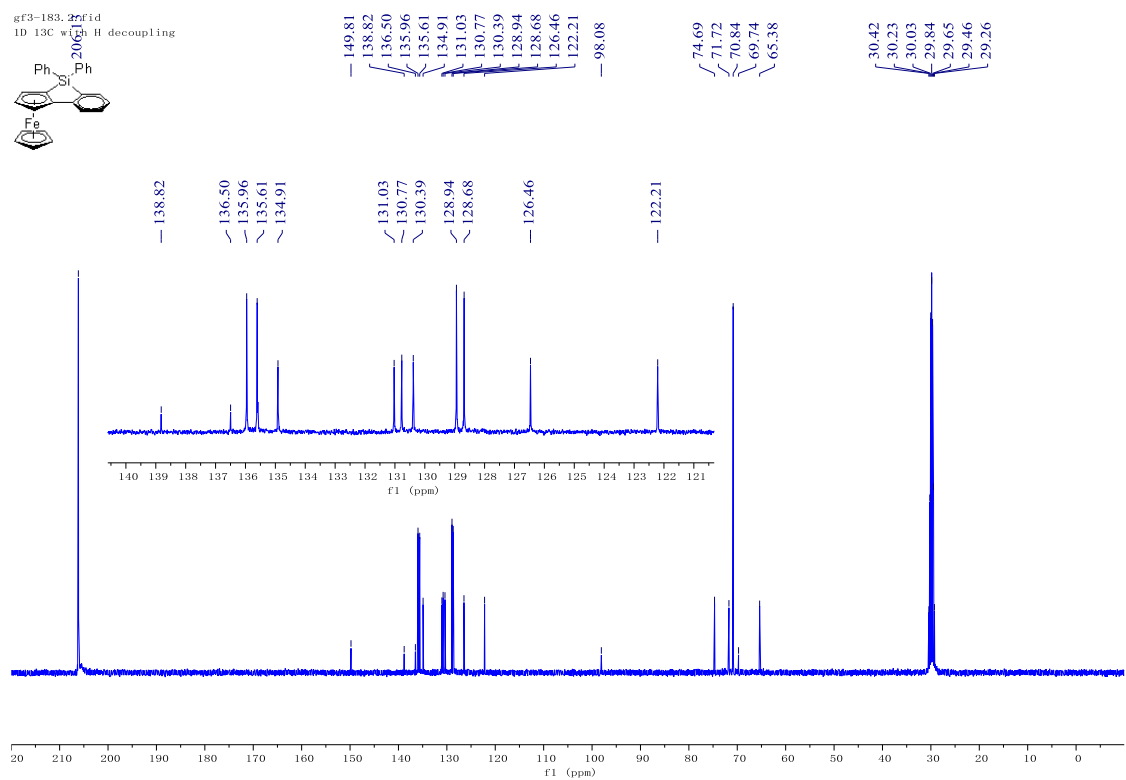
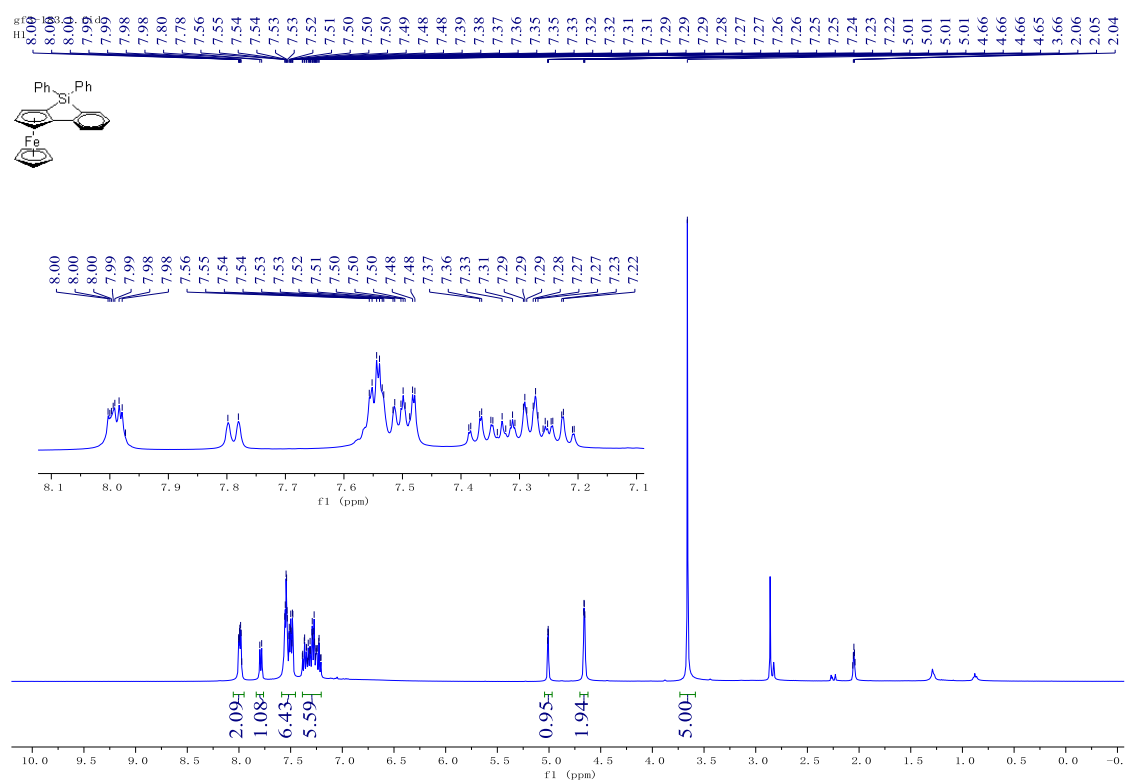
gF4-154HC.1.fid
ID 13C w/CH H decoupling



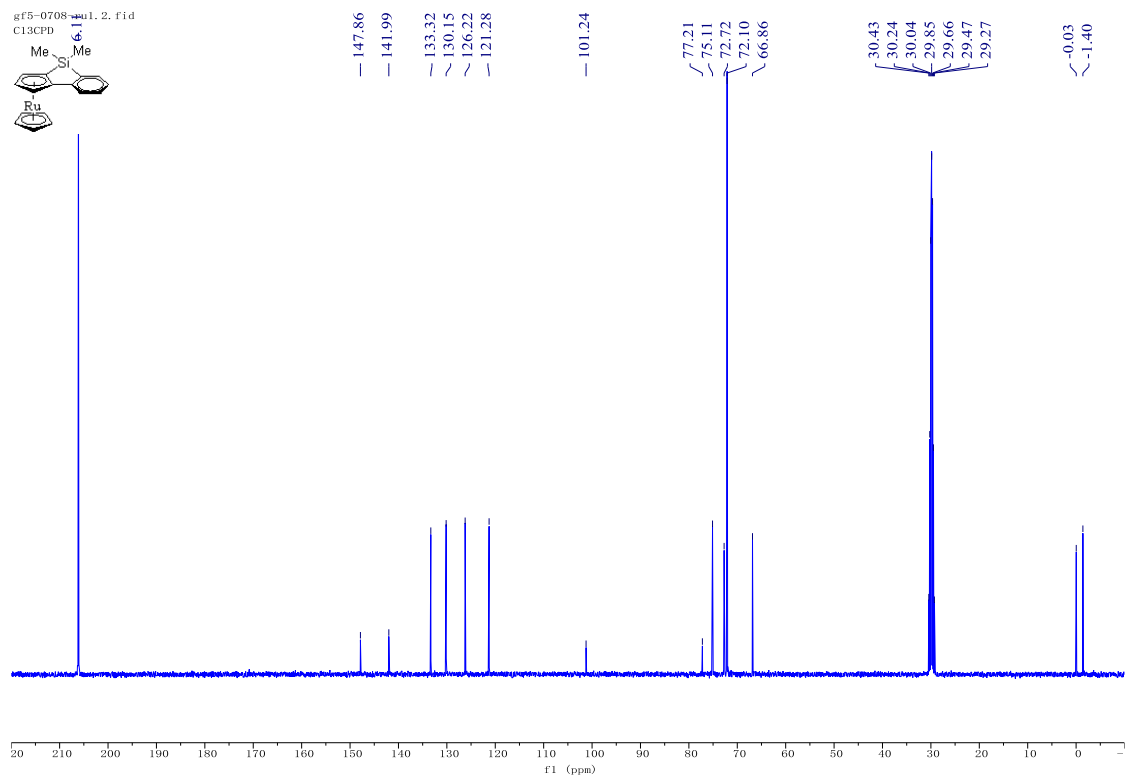
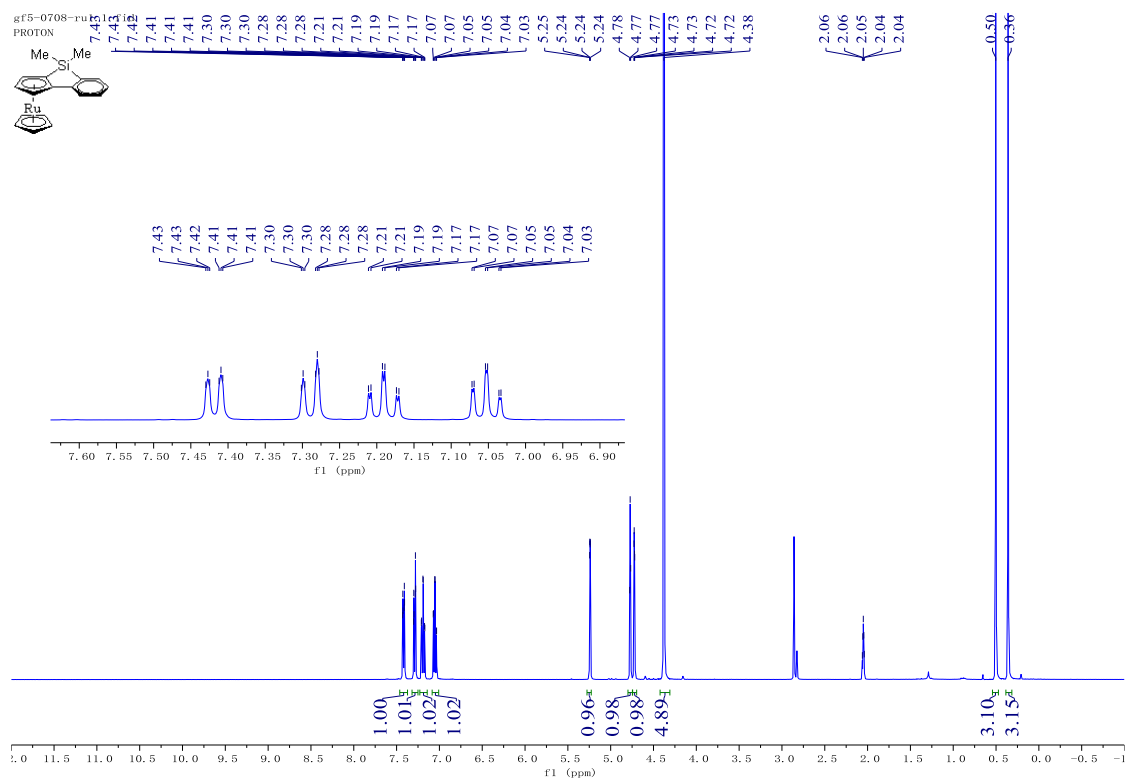
Compound 2u



Compound 2v

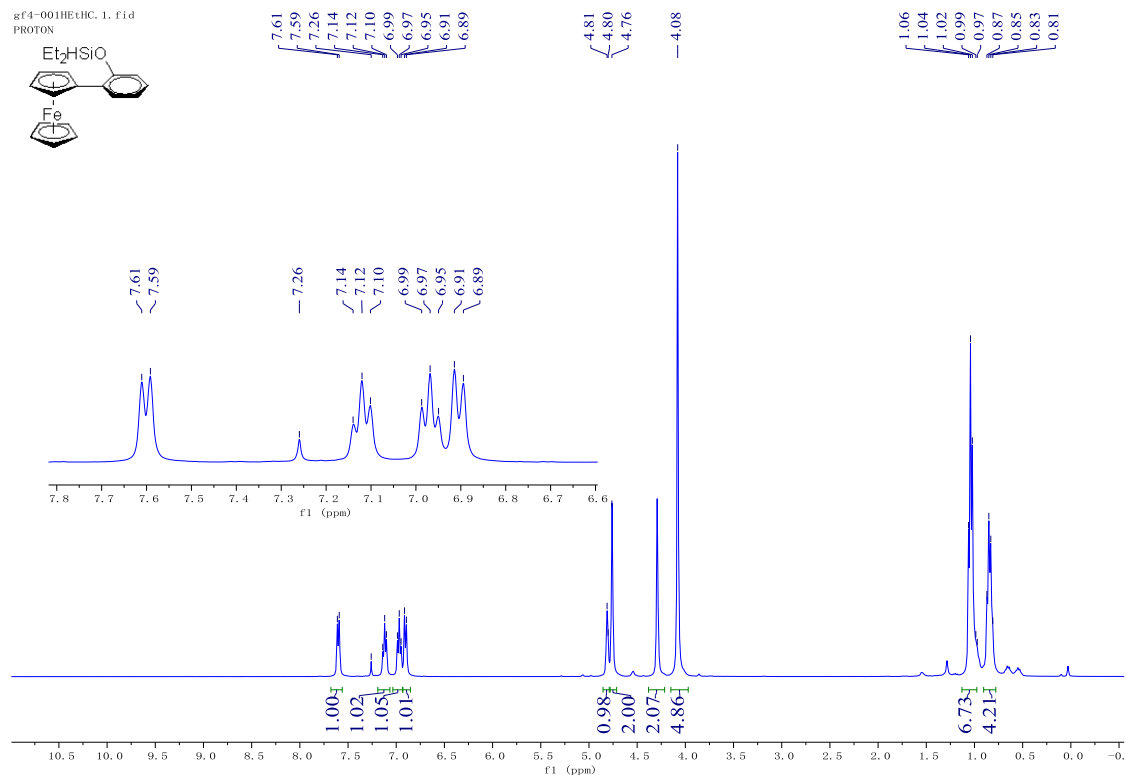
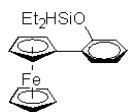


Compound 2w

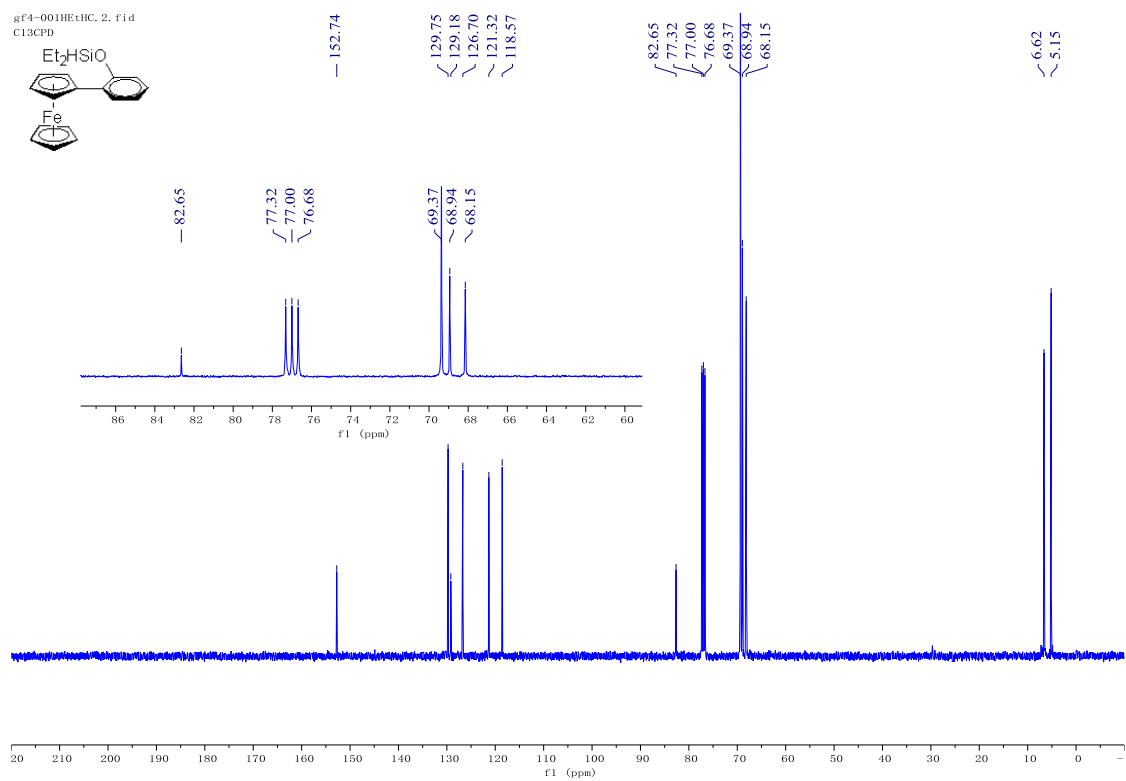
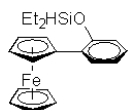


Compound 3a

gf4-001HEtHC. 1. f1d
PROTON

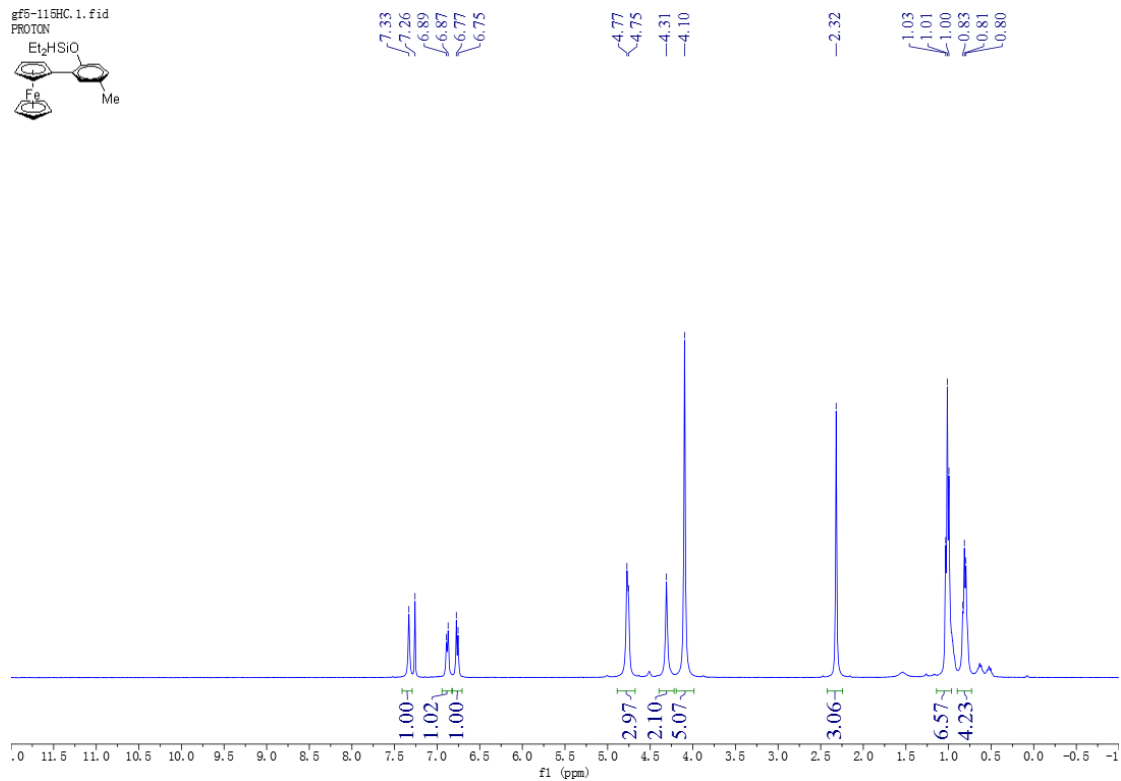
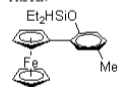


gf4-001HEtHC. 2. f1d
C13CPD

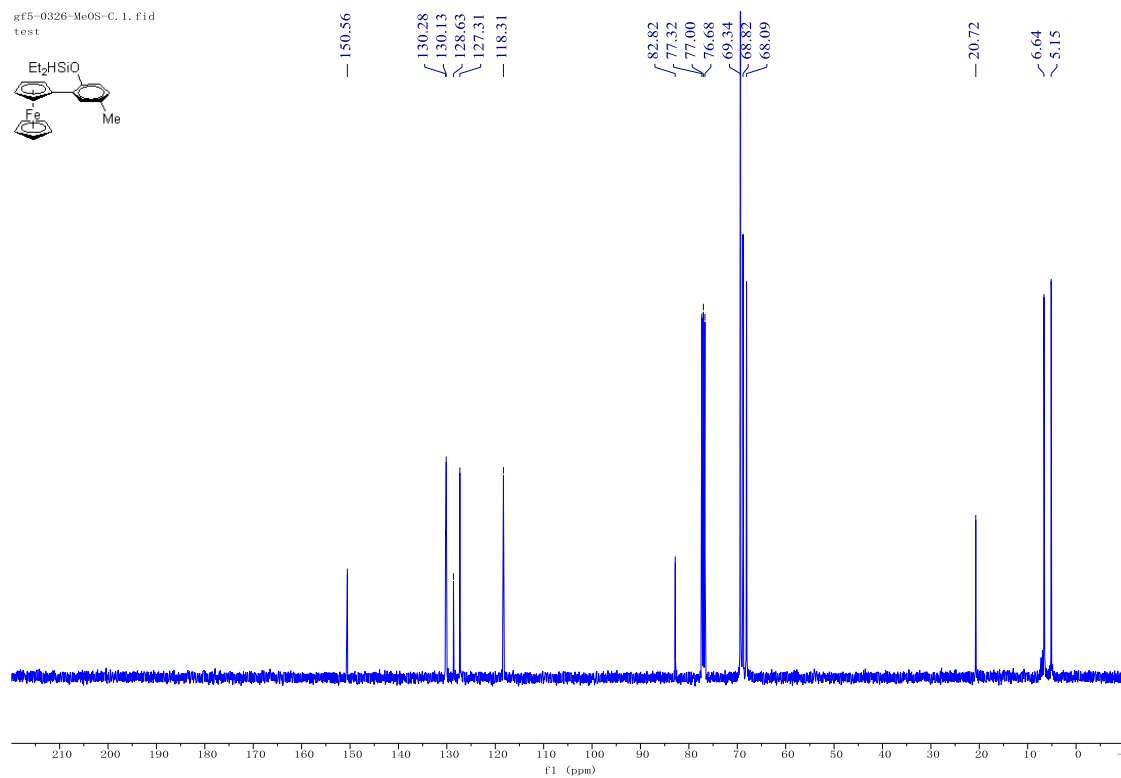
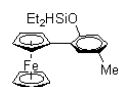


Compound 3b

gf5-116HC.1.fid
PROTON

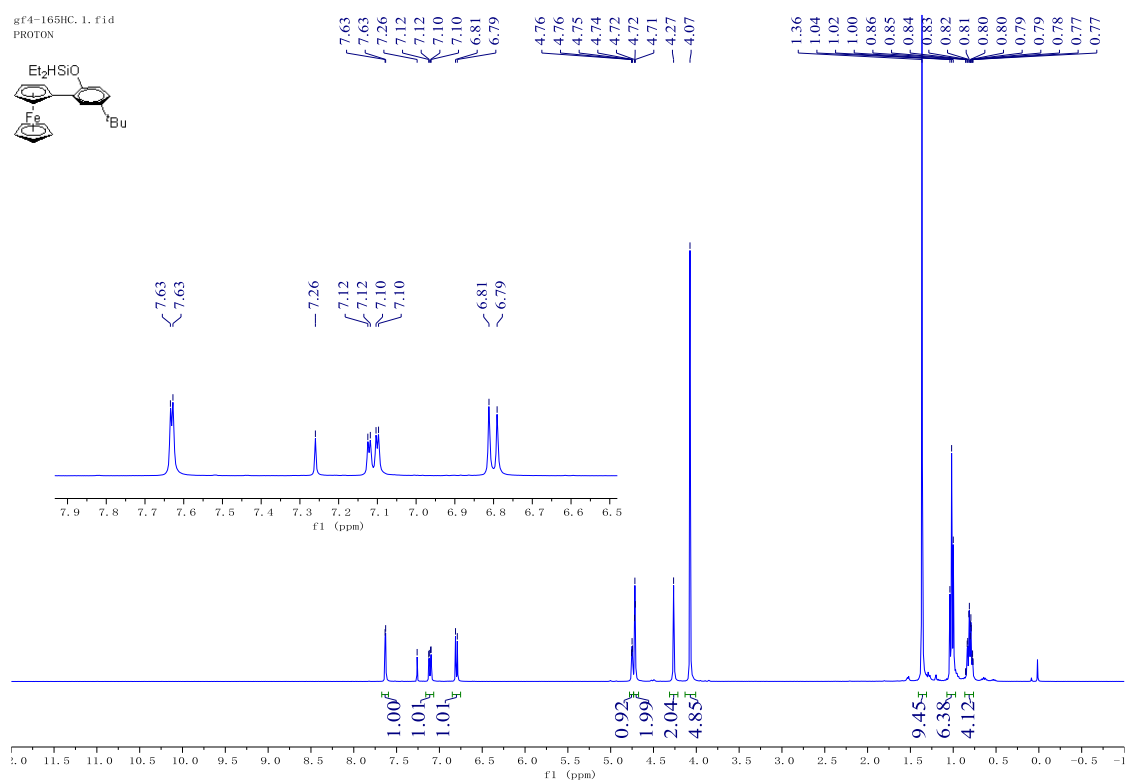
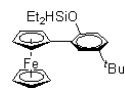


gf5-0326-MeOS-C.1.fid
test

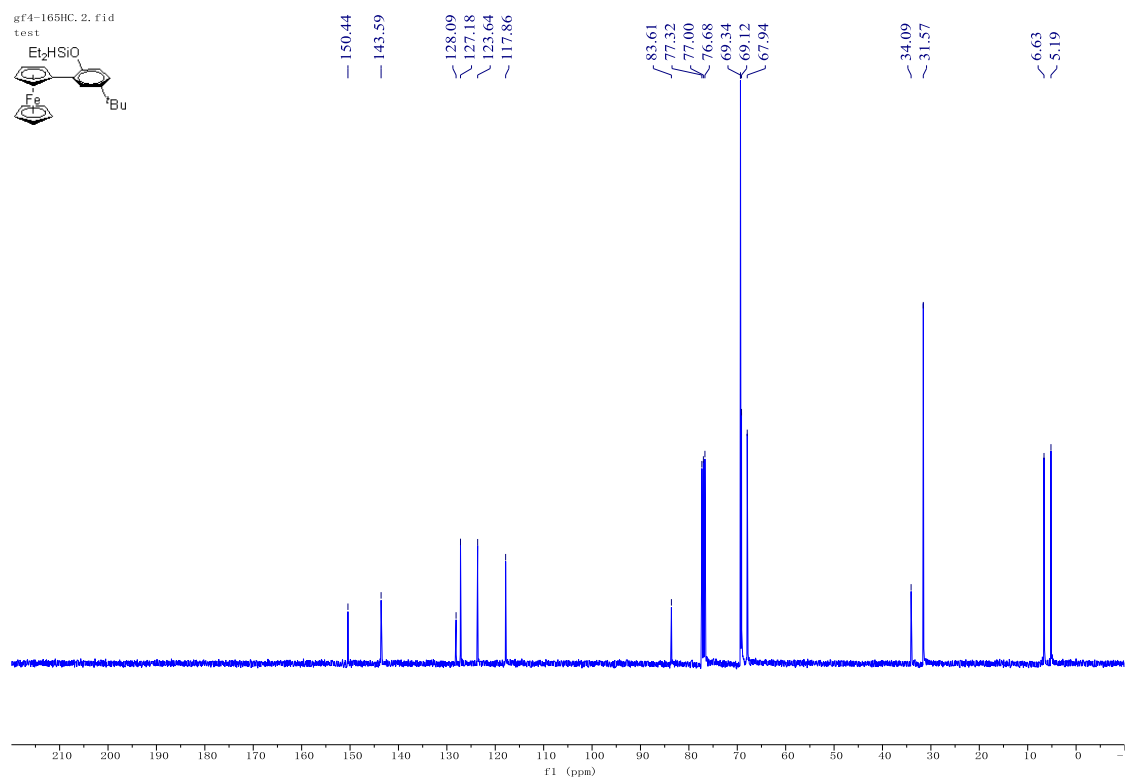
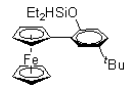


Compound 3c

gF4-165HC. 1. f1d
PROTON

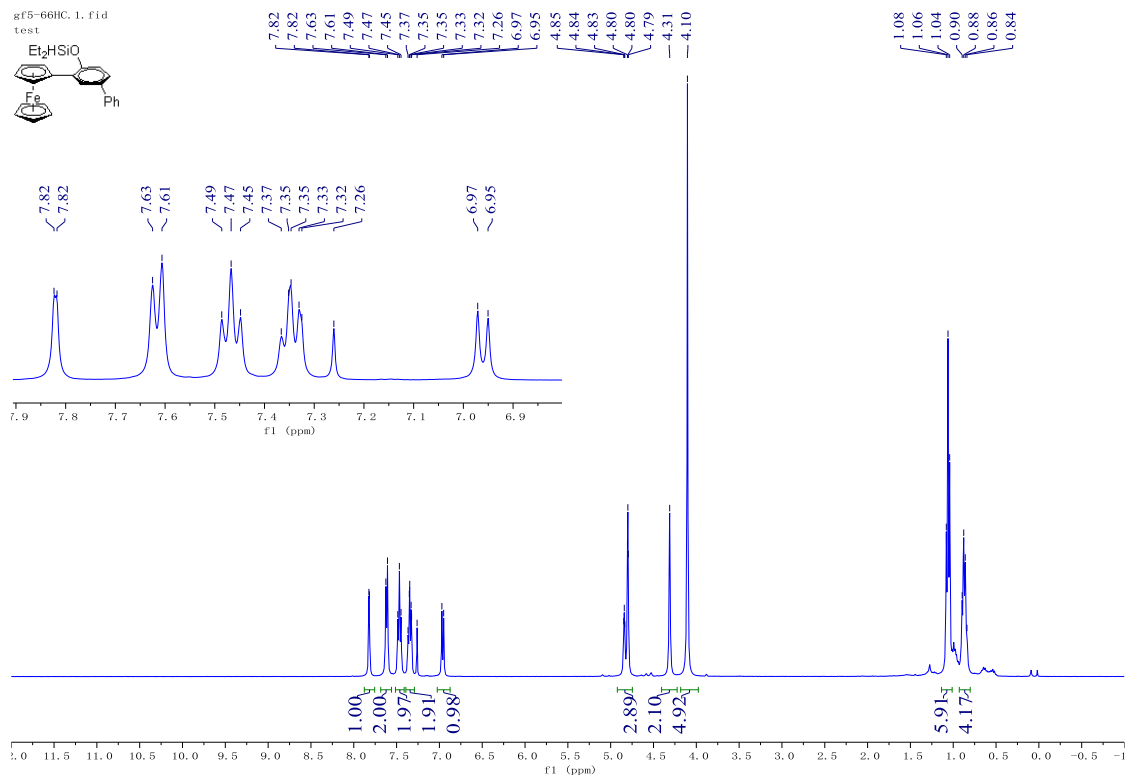
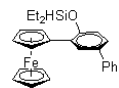


gF4-165HC. 2. f1d
test

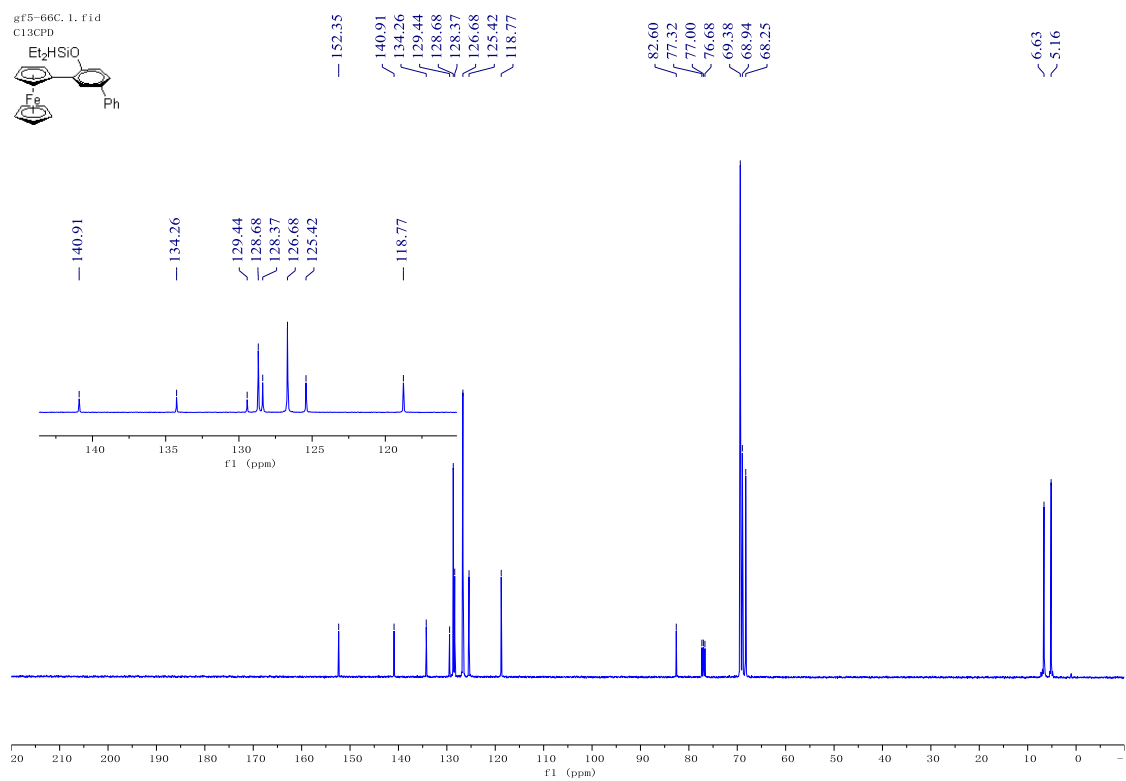
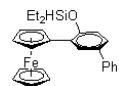


Compound 3d

gF5-666C.1.fid
test

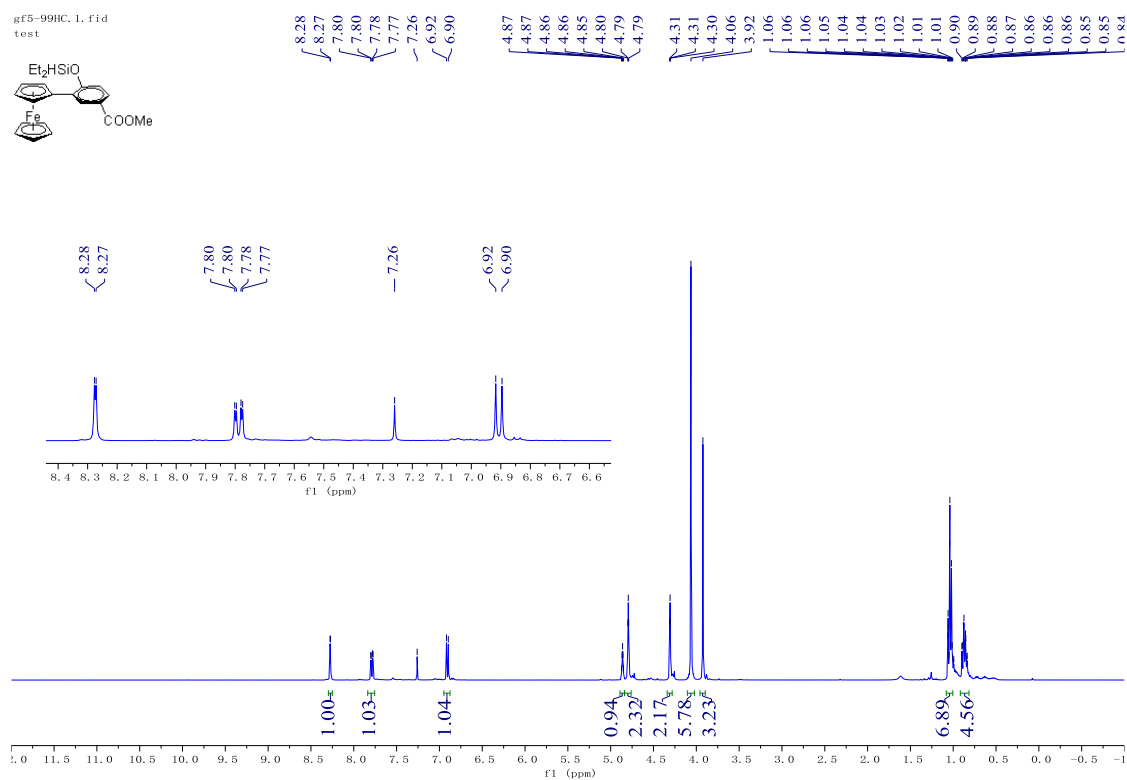
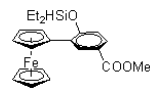


gF5-66C.1.fid
C13CPD

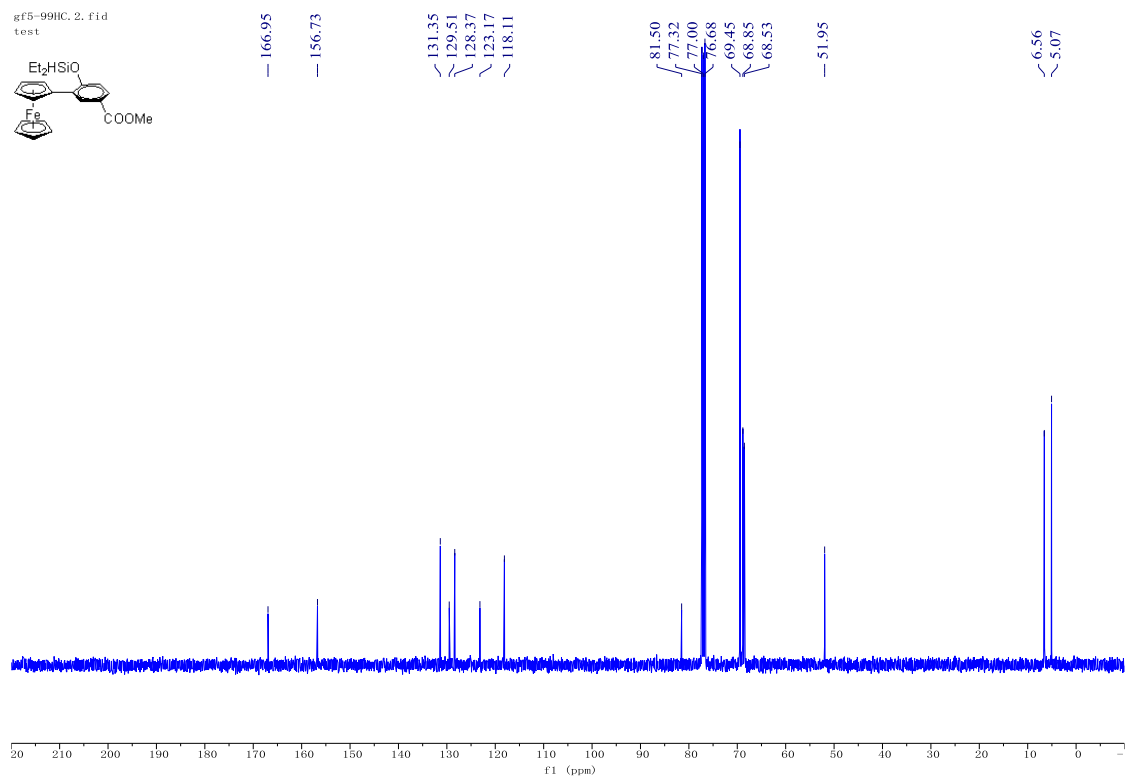
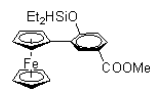


Compound 3c

gF5-9911C.1.fid
test

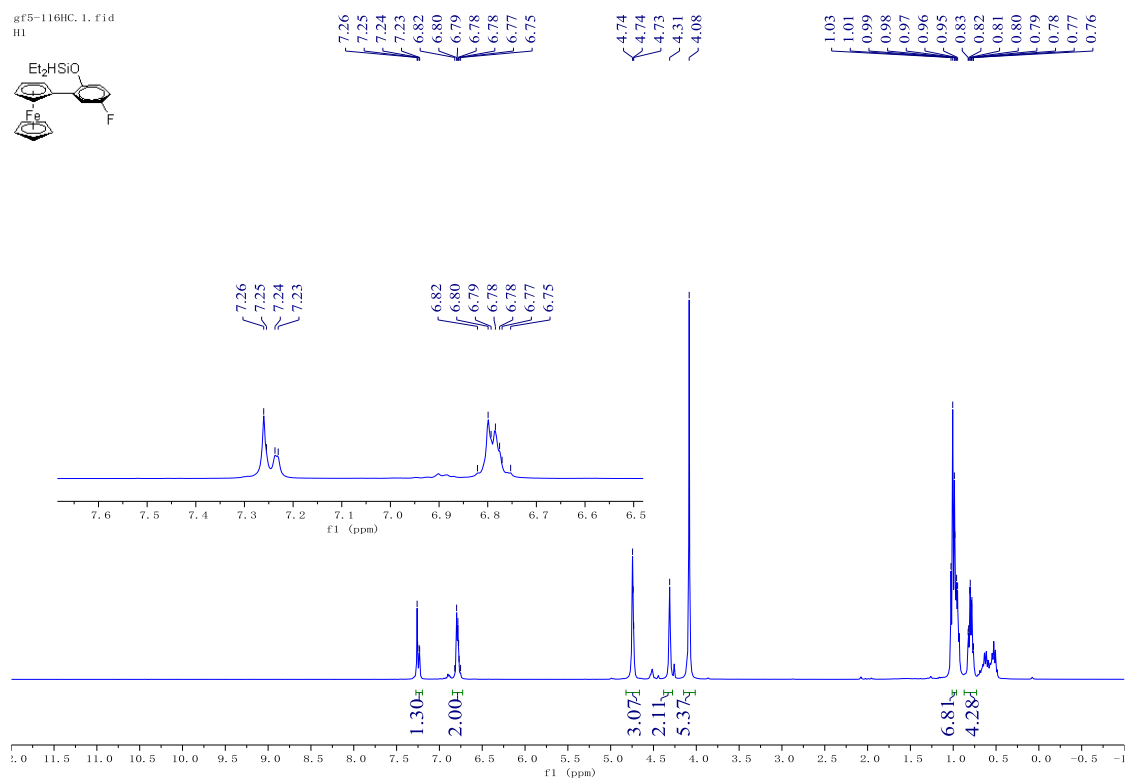
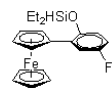


gF5-9911C.2.fid
test

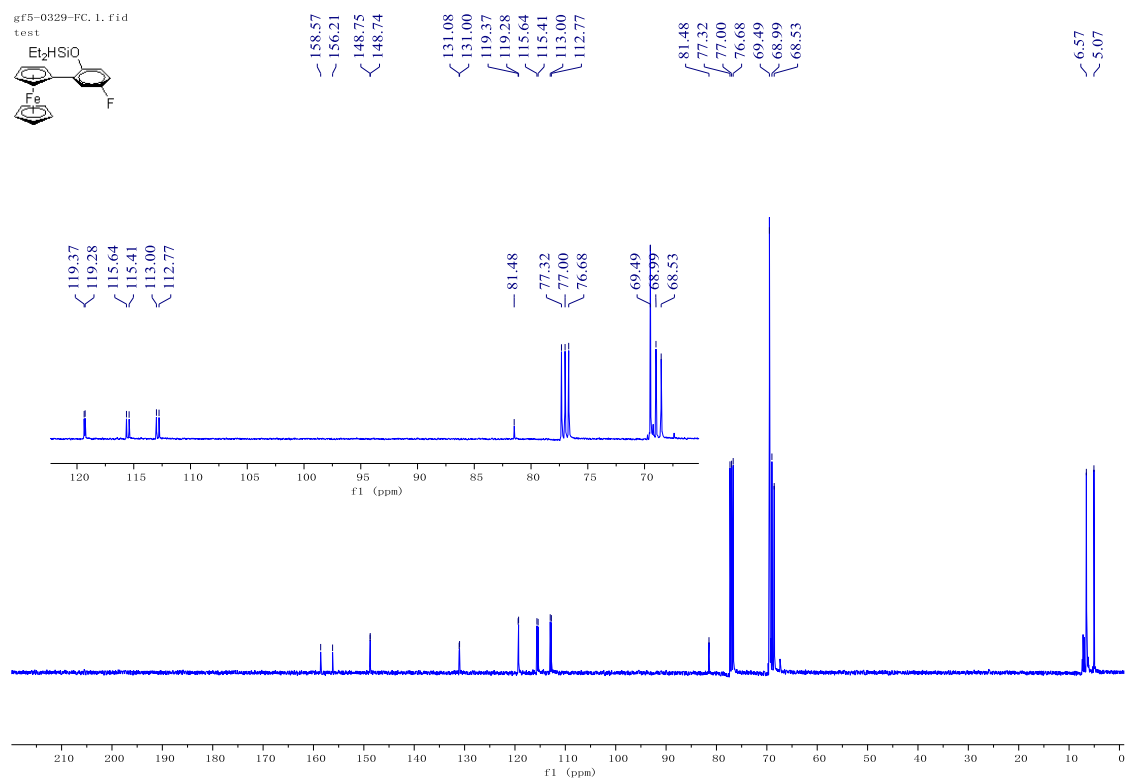
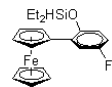


Compound 3f

gF5-116HC. 1. f1d
H1

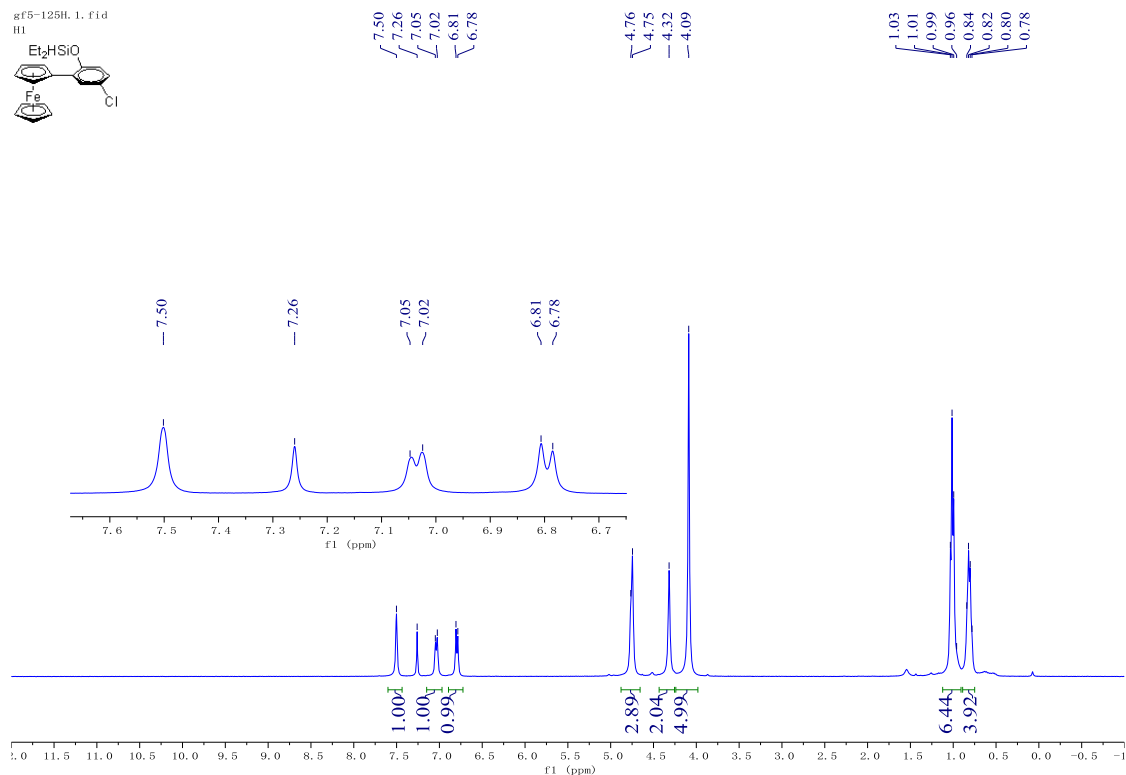
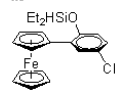


gF5-0329-FC. 1. f1d
test

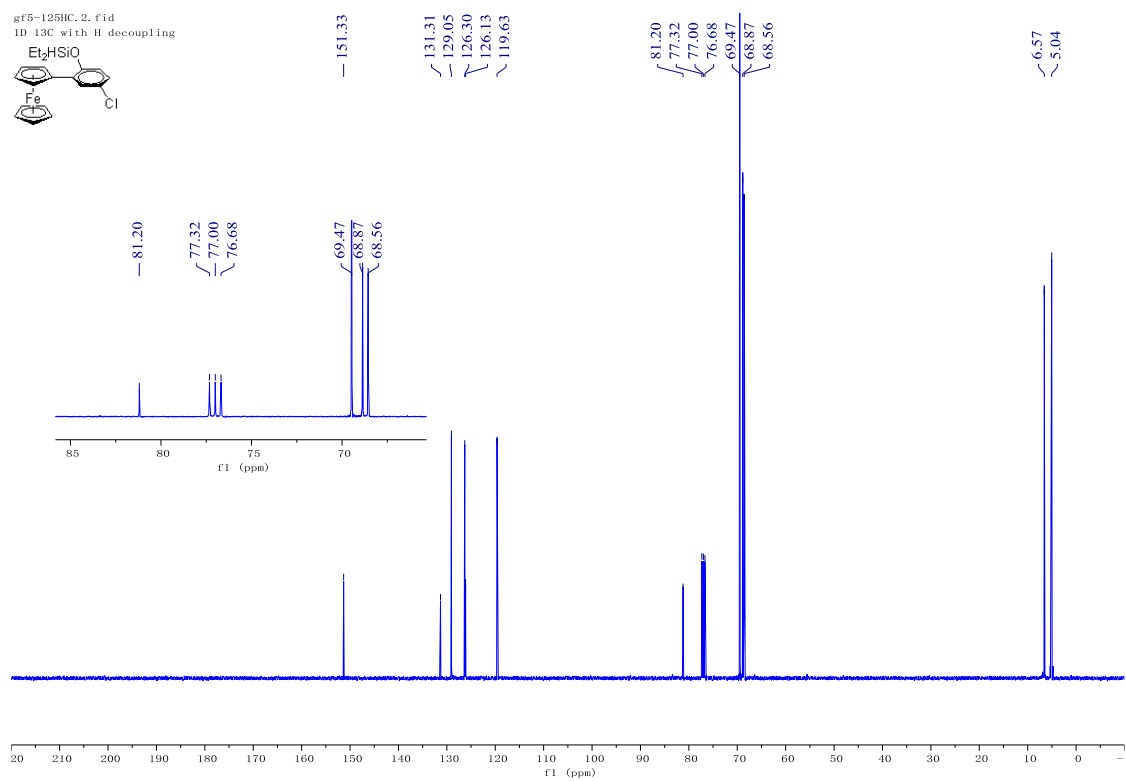
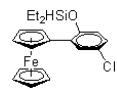


Compound 3g

gF5-125H.1.fid
H1

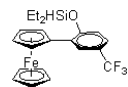


gF5-125HC.2.fid
1D 13C with H decoupling



Compound 3h

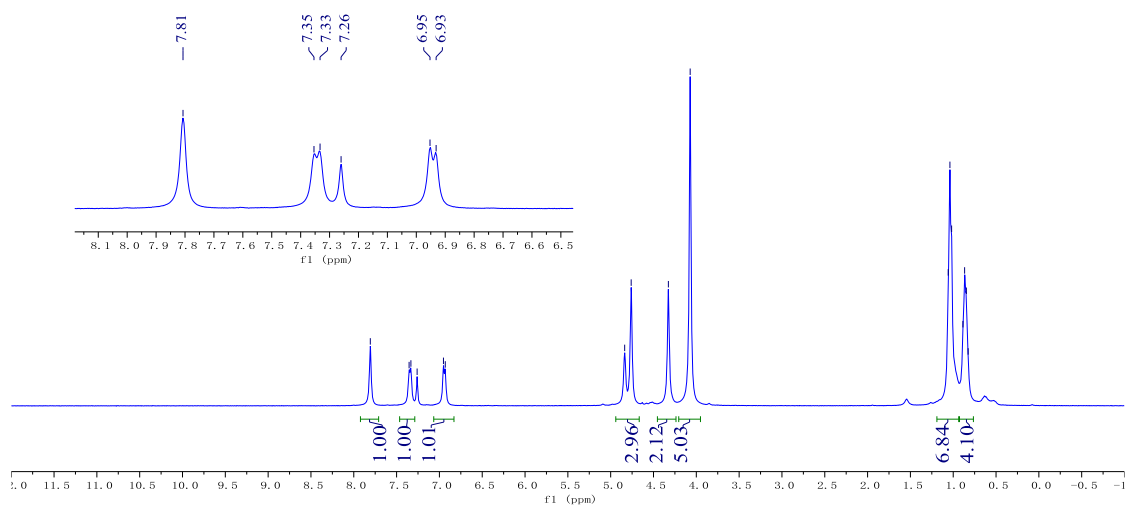
gF5-124H.1.fid
H1



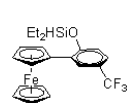
7.81
7.35
7.33
7.26
6.95
6.93

4.84
4.76
4.33
4.07

1.06
1.04
1.02
0.87
0.85
0.83



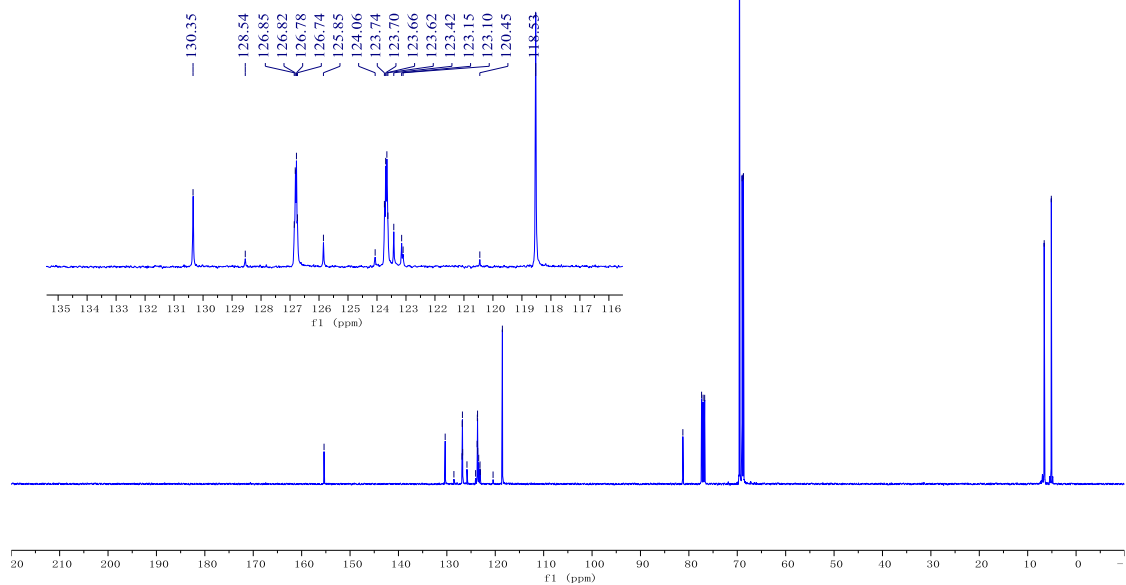
gF5-124HC.4.fid
C13CPD



155.37

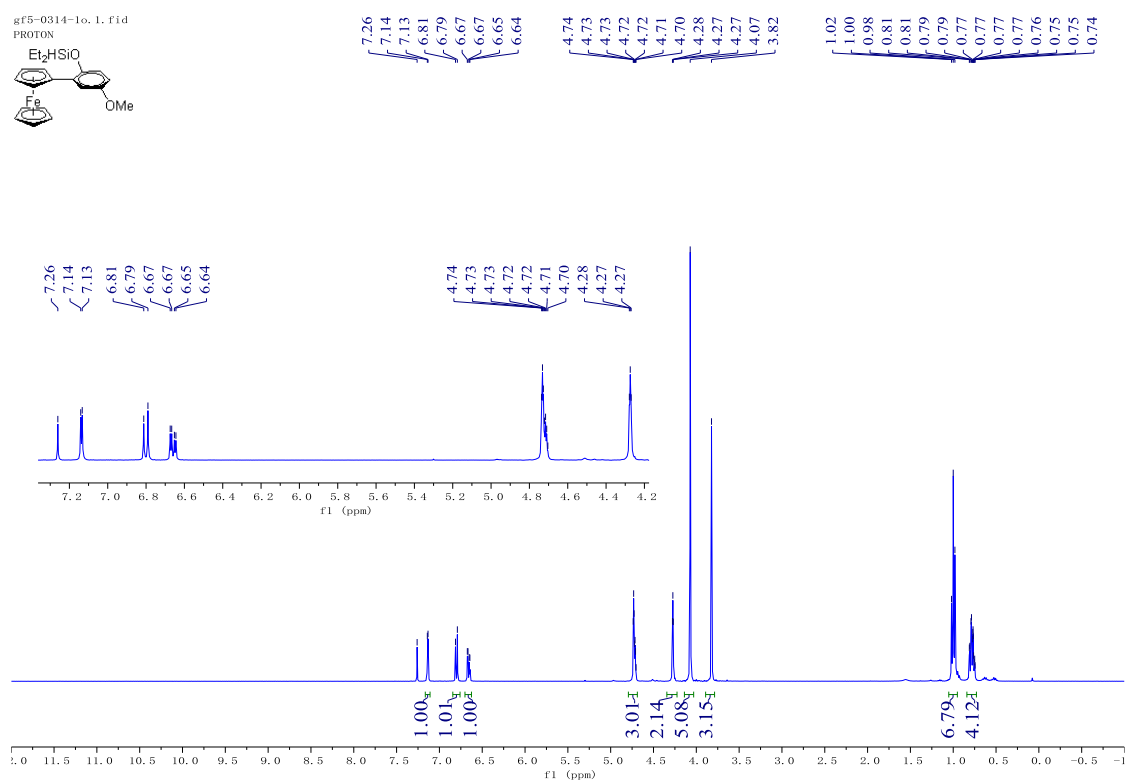
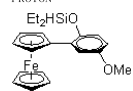
130.35
128.54
126.85
126.82
126.78
126.74
125.85
124.06
123.74
123.70
123.66
123.62
123.42
123.15
123.10
120.45
118.53
81.24
77.37
77.06
76.74
69.55
68.99
68.73

6.59
5.12

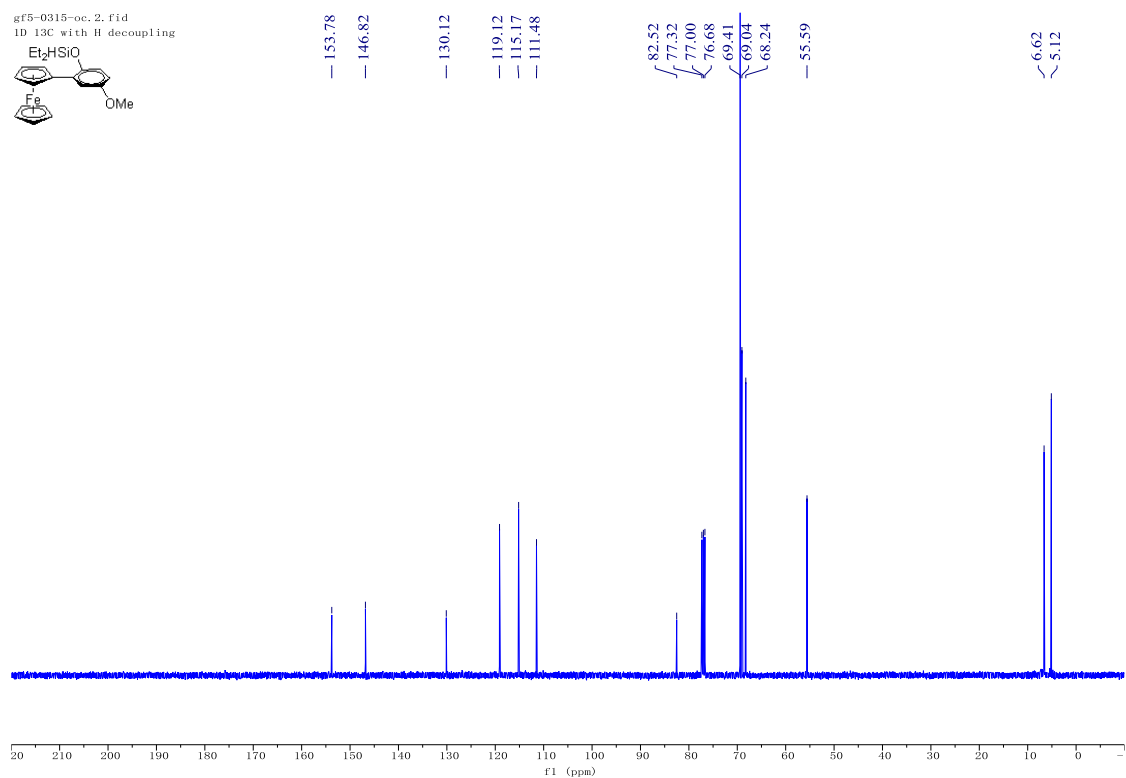
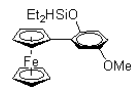


Compound 3i

gF5-0314-1o. 1. fid
PROTON

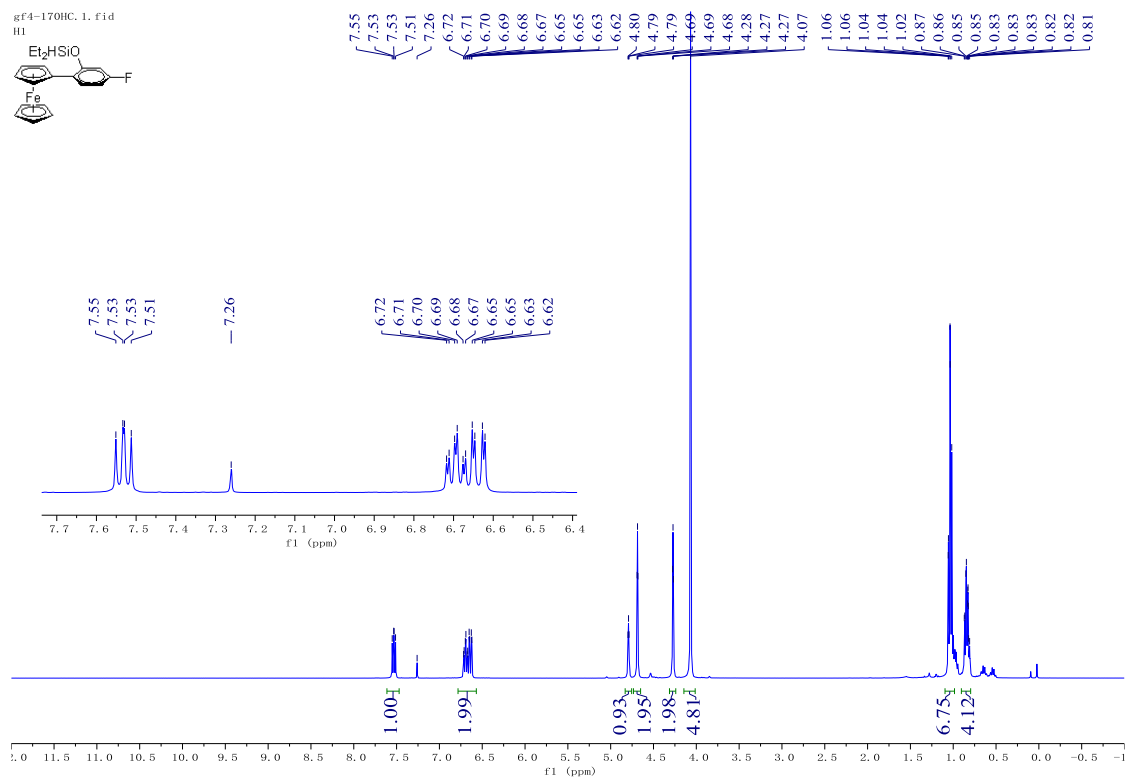
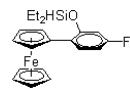


gF5-0315-oc. 2. fid
1D 13C with H decoupling

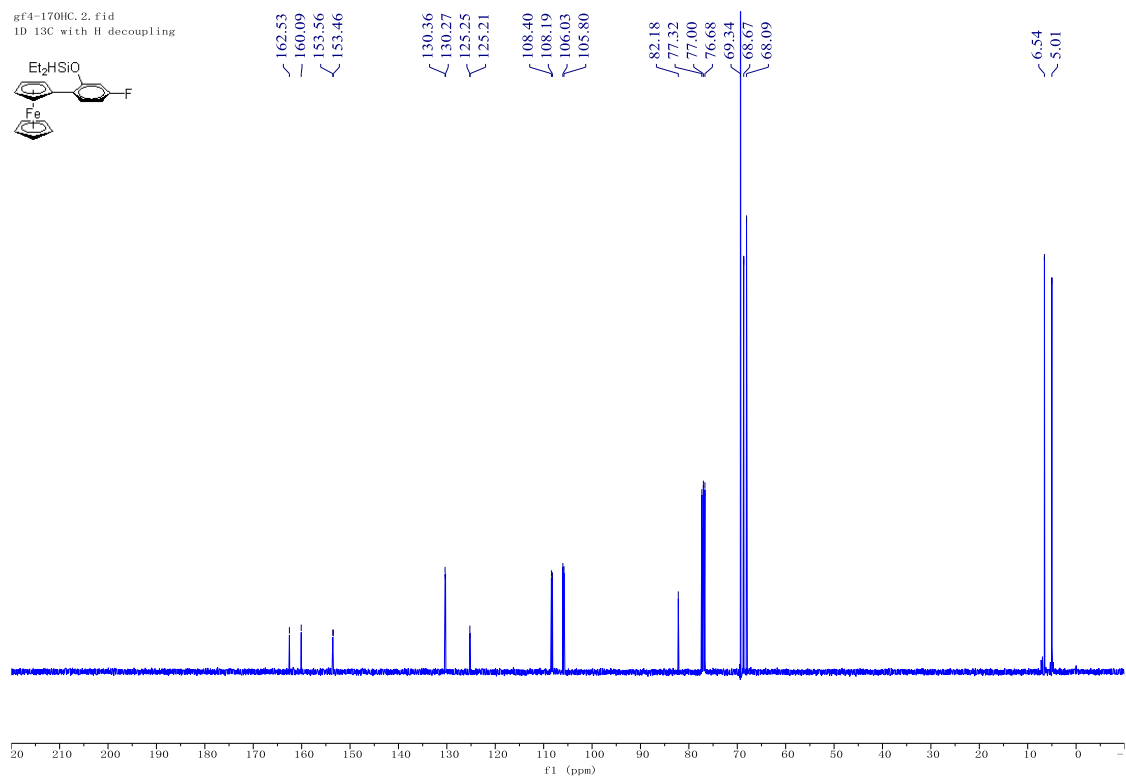
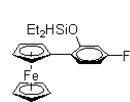


Compound 3j

gF4-170HC. 1. f1d
H1

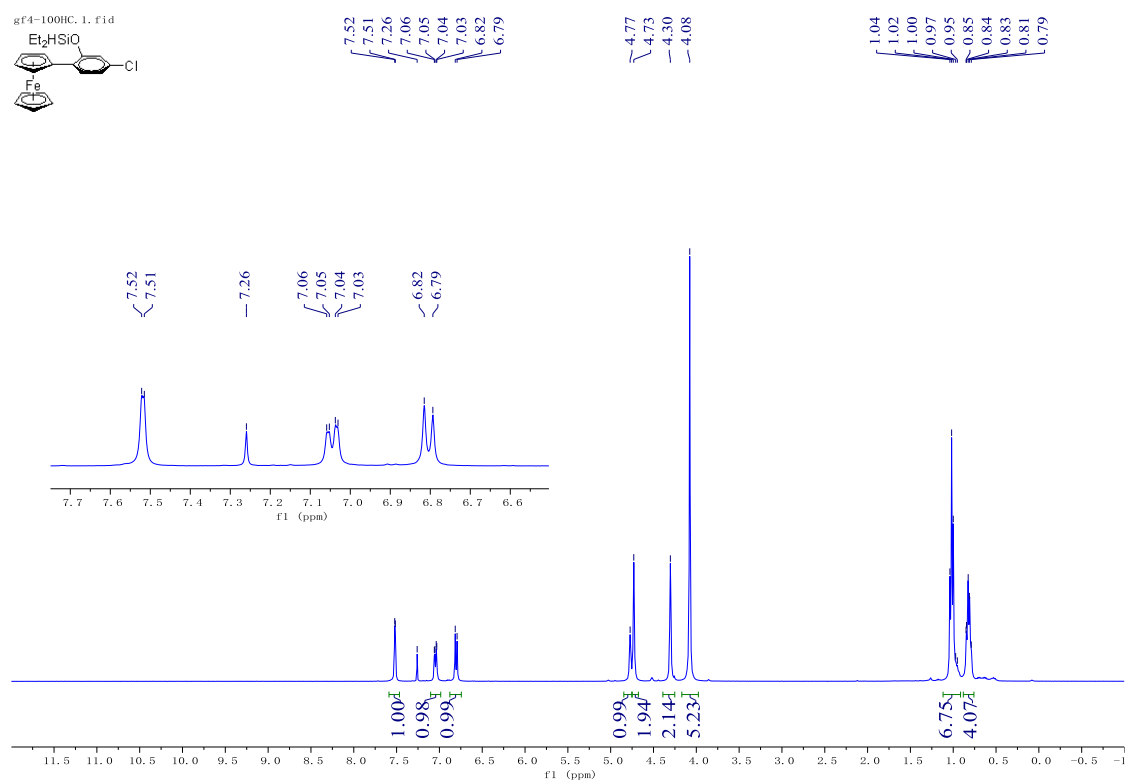
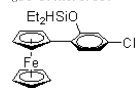


gF4-170HC. 2. f1d
1D 13C with H decoupling



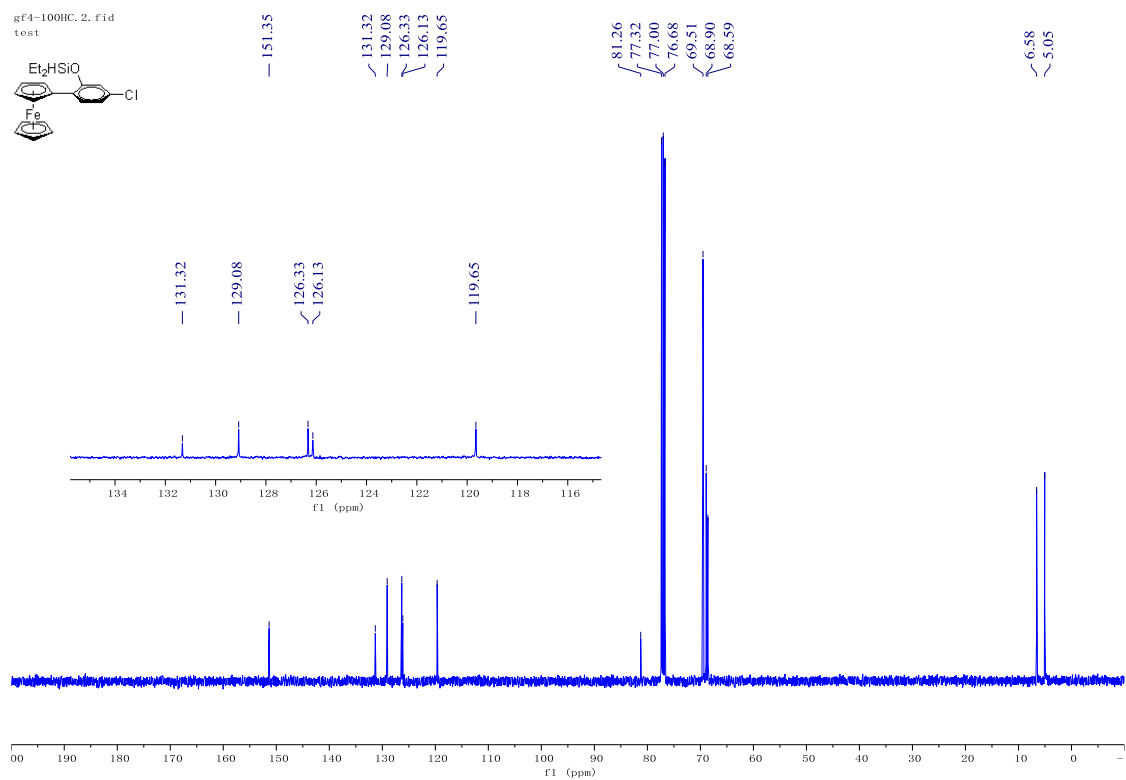
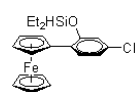
Compound 3k

gF4-100HC. 1. fid



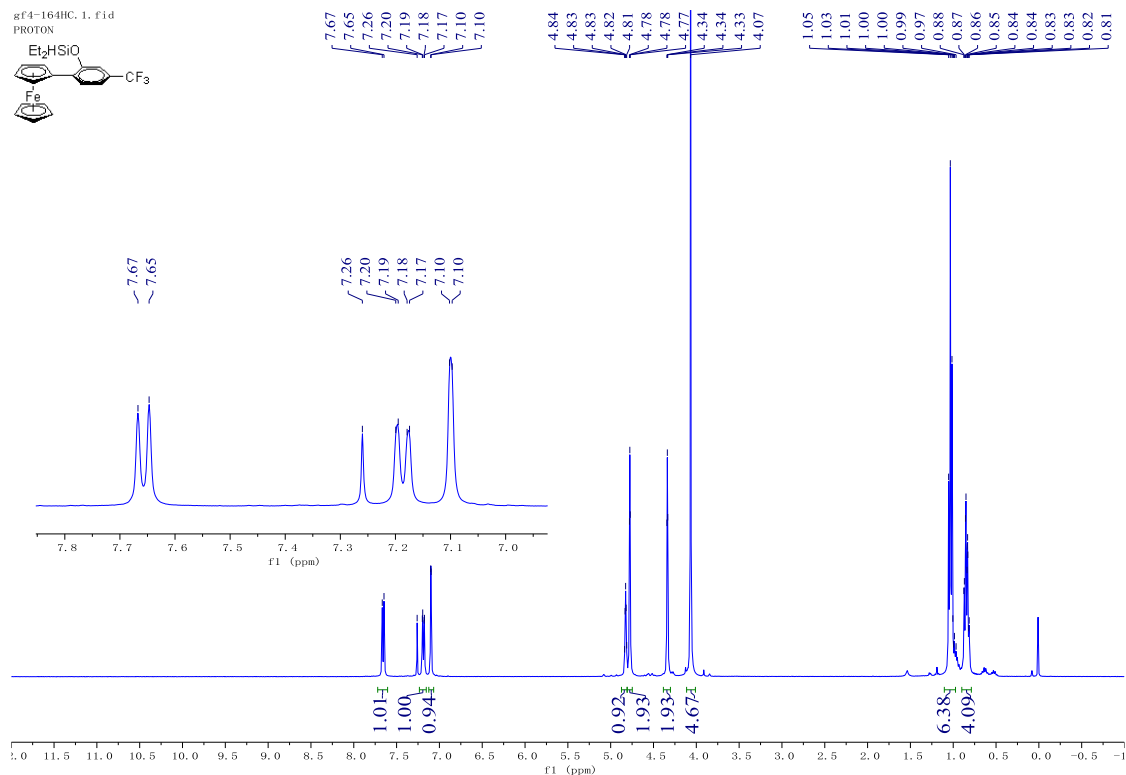
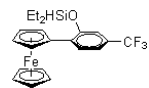
gF4-100HC. 2. fid

test

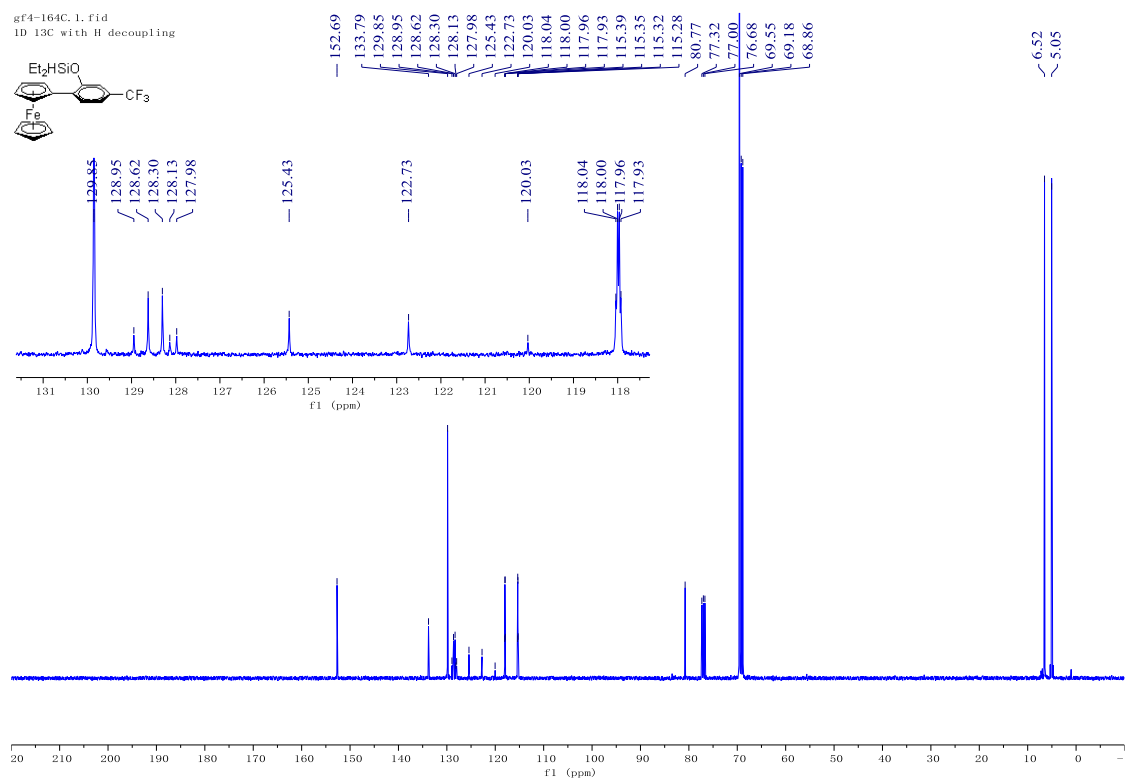
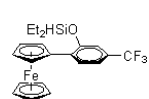


Compound 31

gf4-164HC, 1. fid
PROTON

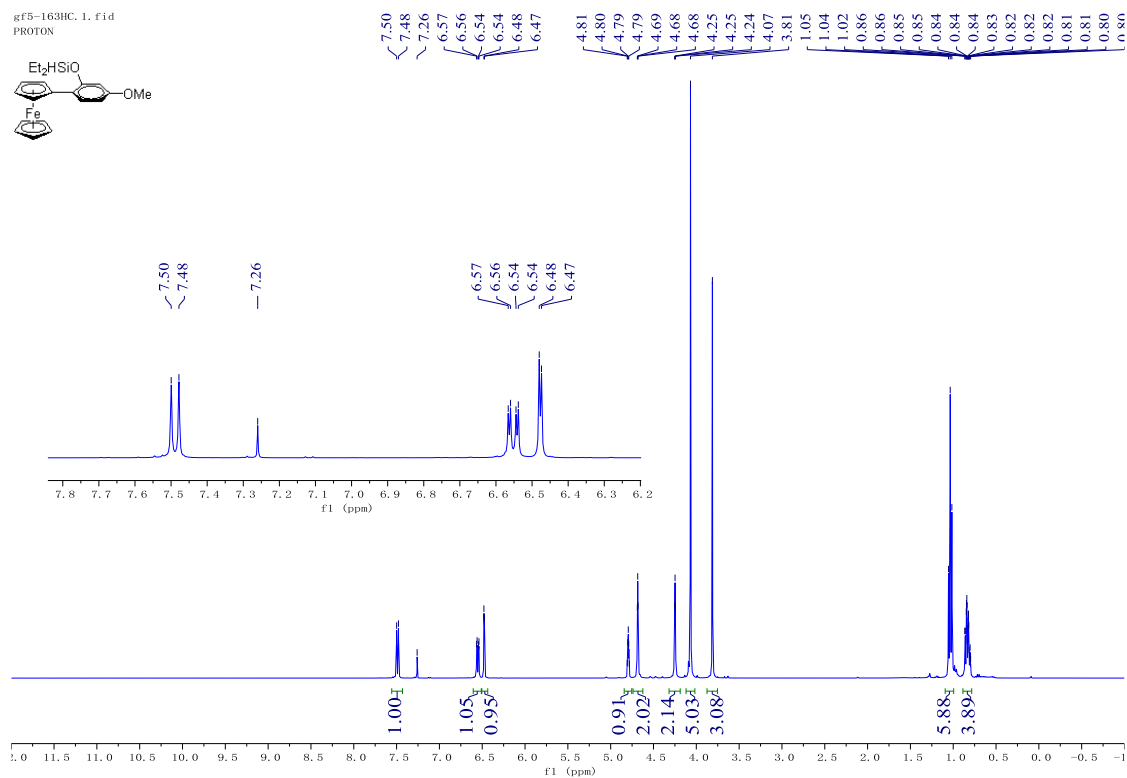
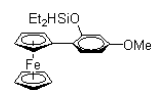


gf4-164C, 1. fid
1D 13C with H decoupling

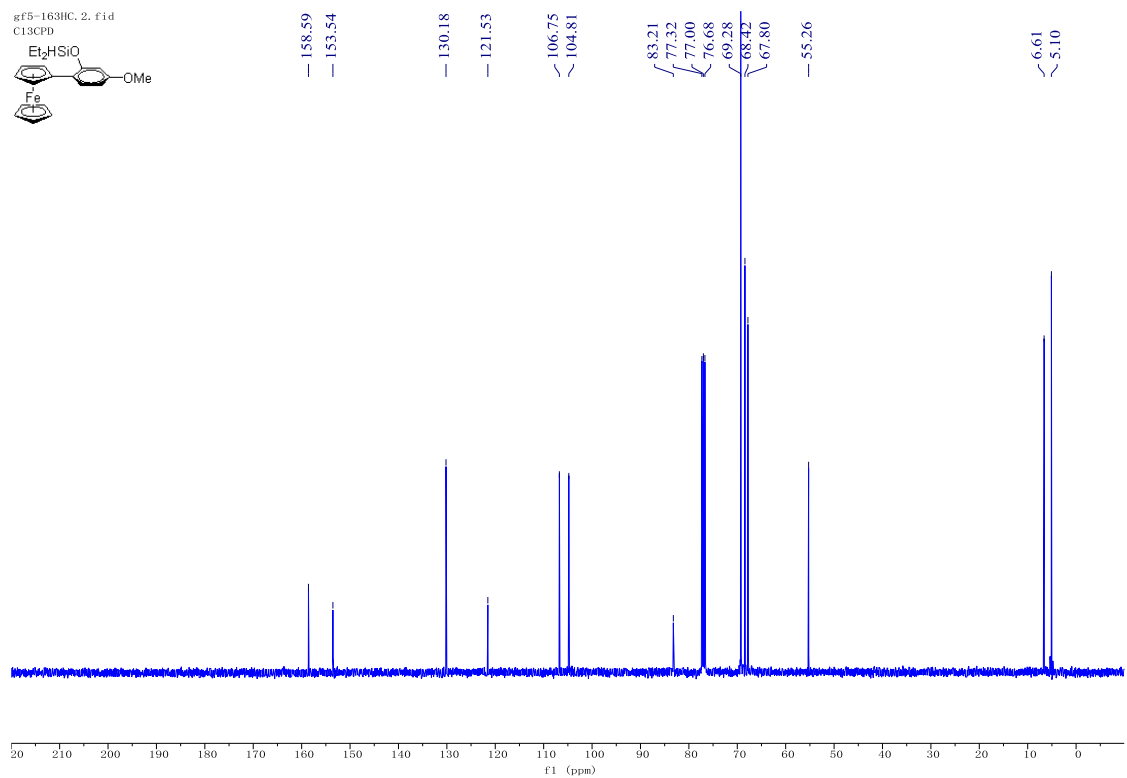
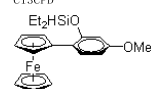


Compound 3m

gF5-163HC. 1. f1d
PROTON

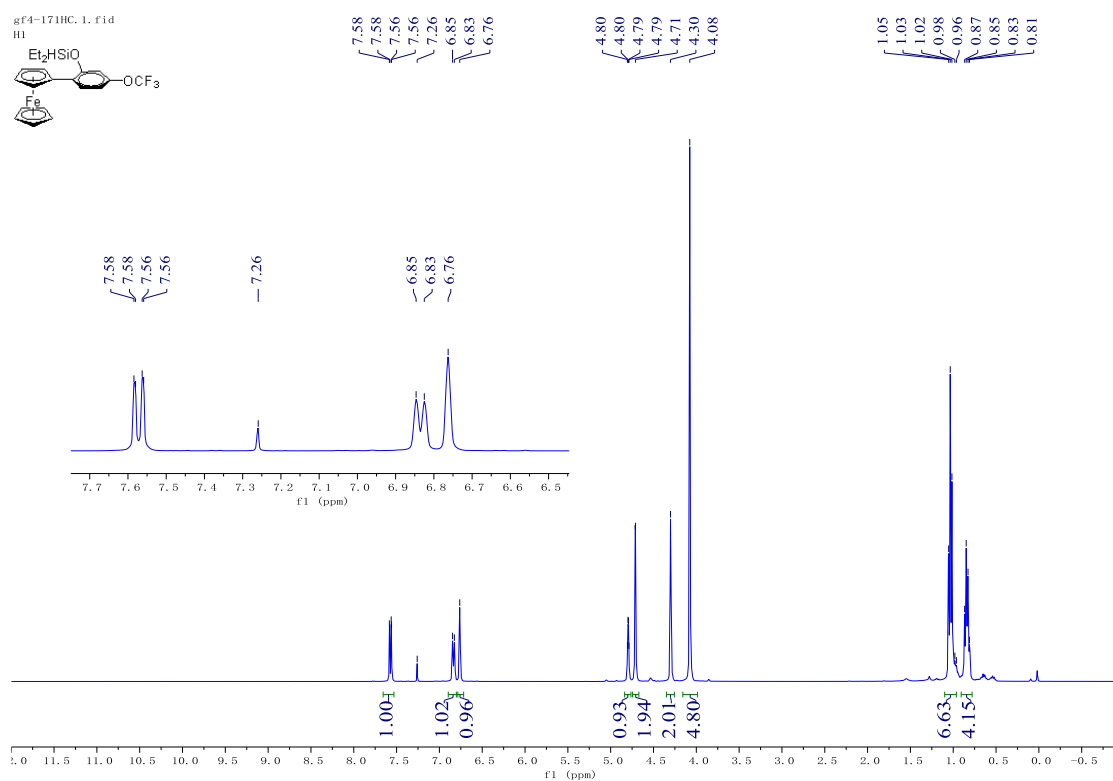
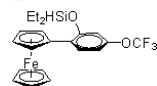


gF5-163HC. 2. f1d
C13CPD

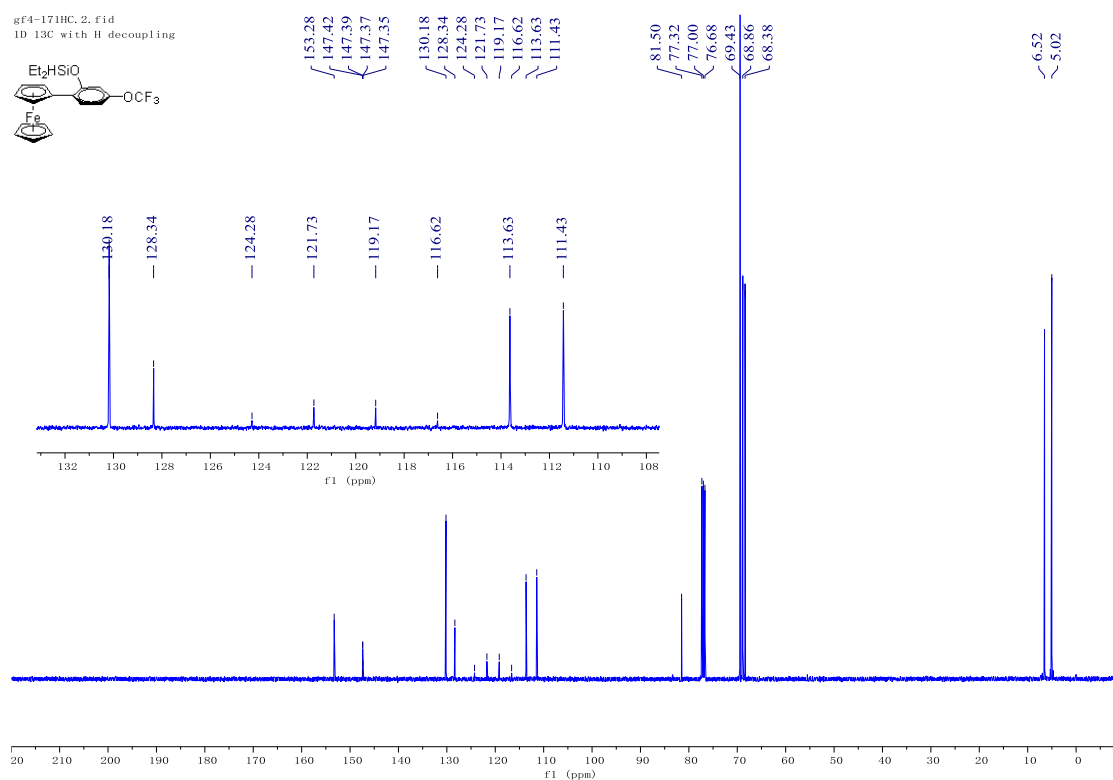
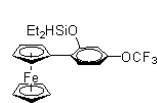


Compound 3n

gF4-171HC. 1. f1d
H1

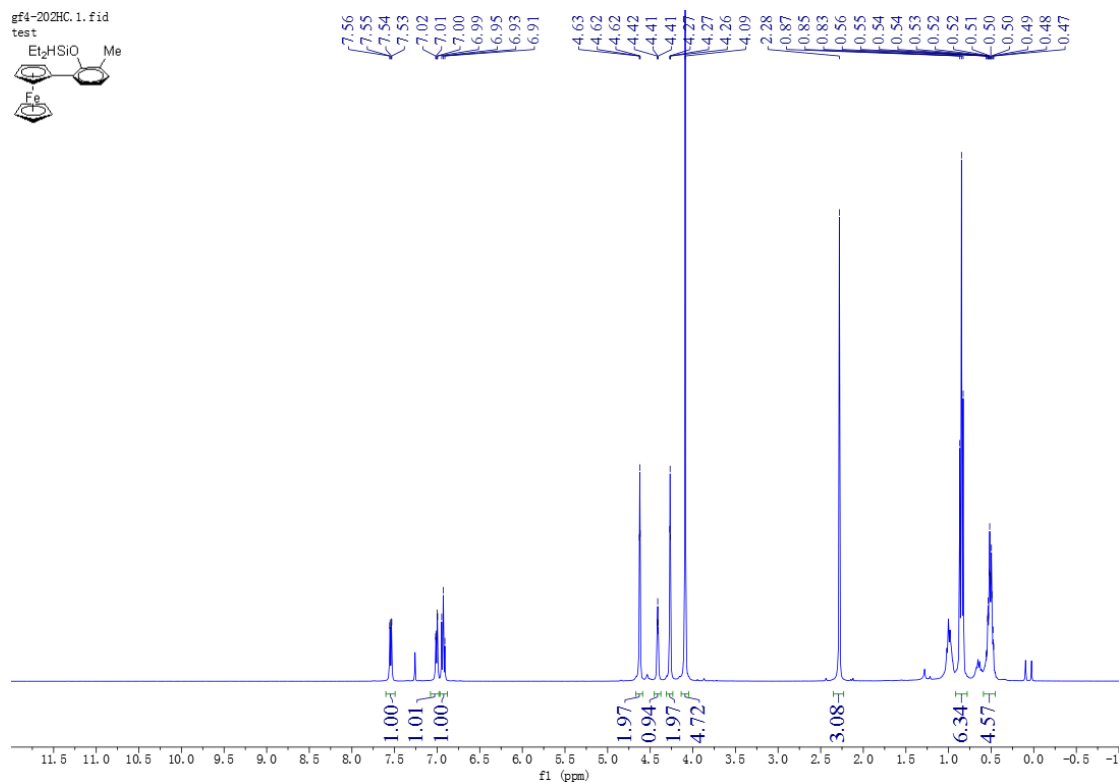
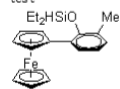


gF4-171HC. 2. f1d
ID 13C with H decoupling

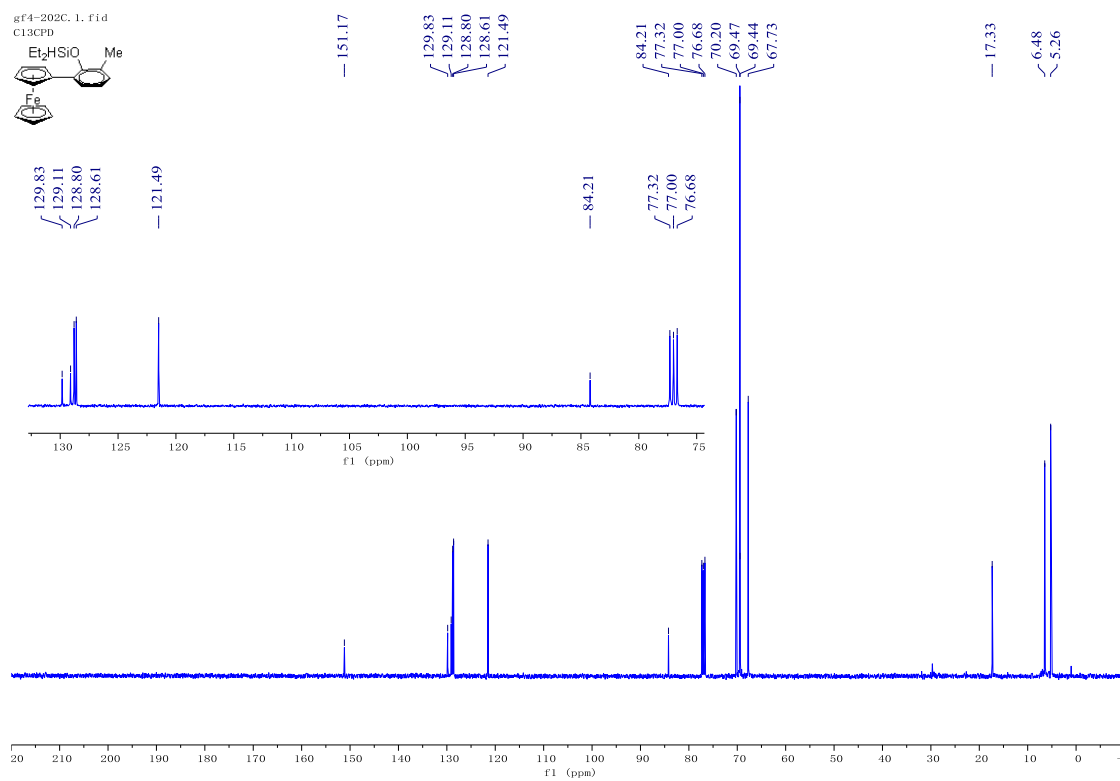
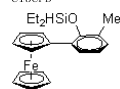


Compound 3o

gf4-202HC.1.fid
test

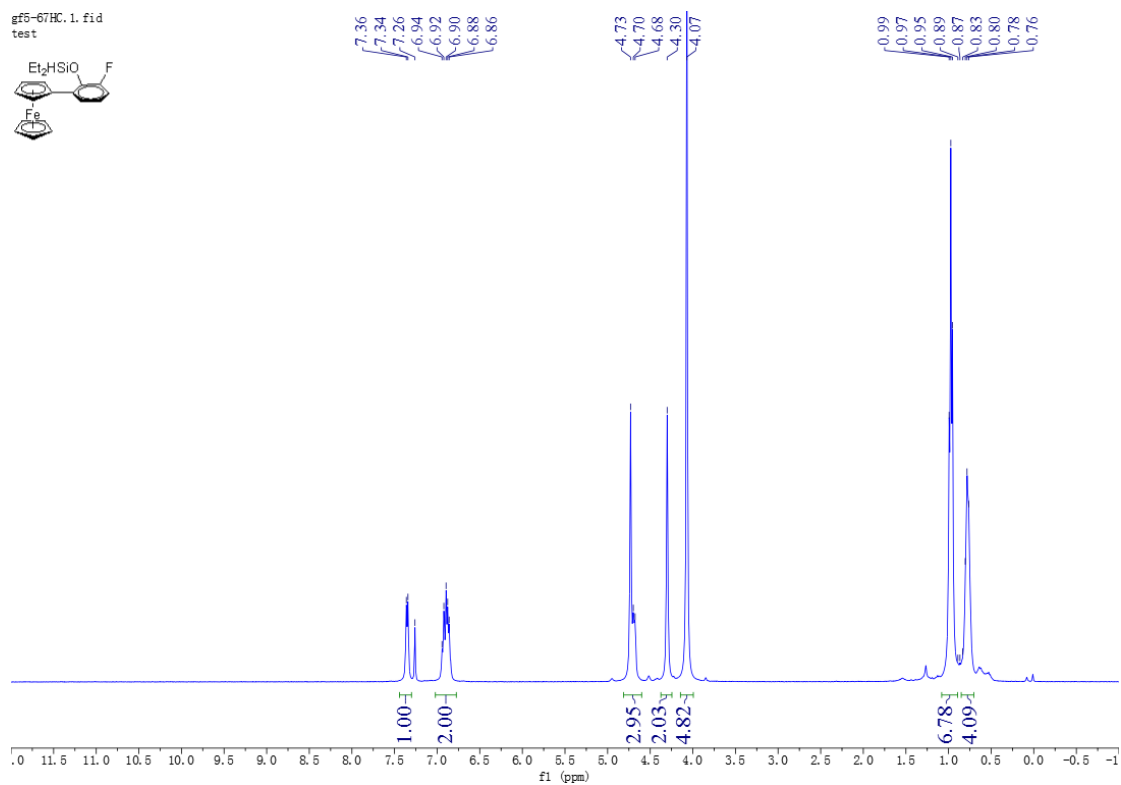


gf4-202C.1.fid
C13CPD

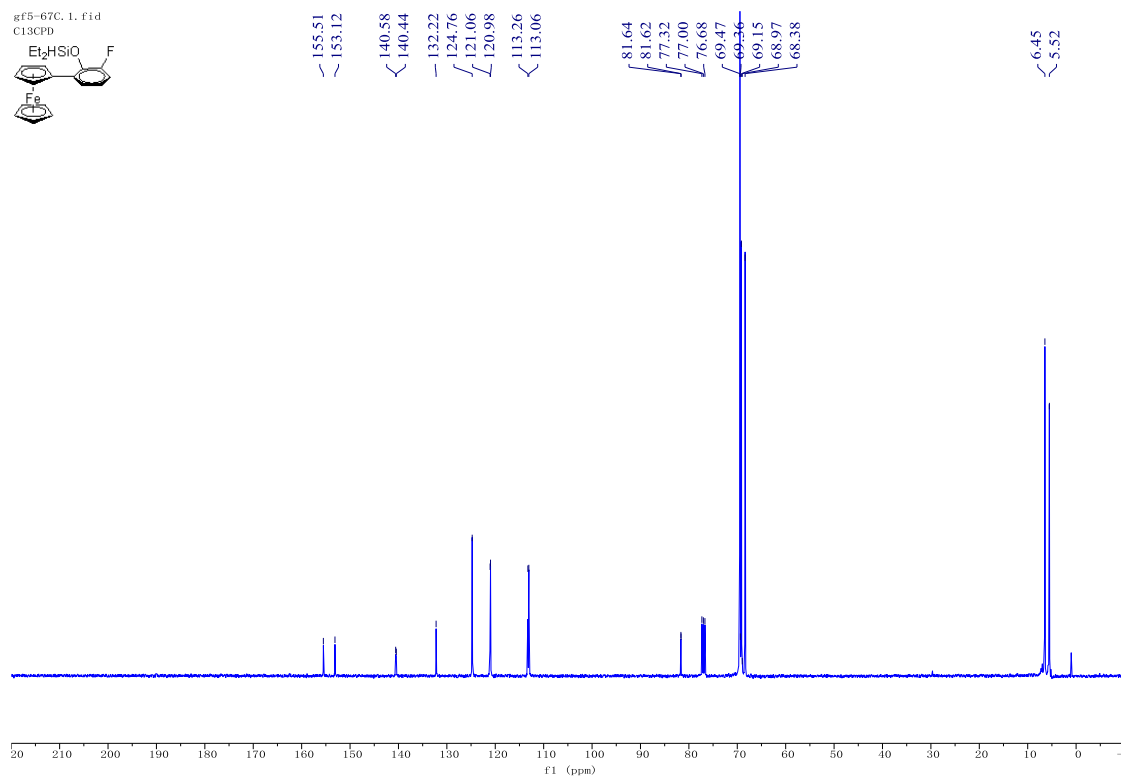
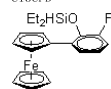


Compound 3p

gf5-67HC. 1. fid
test

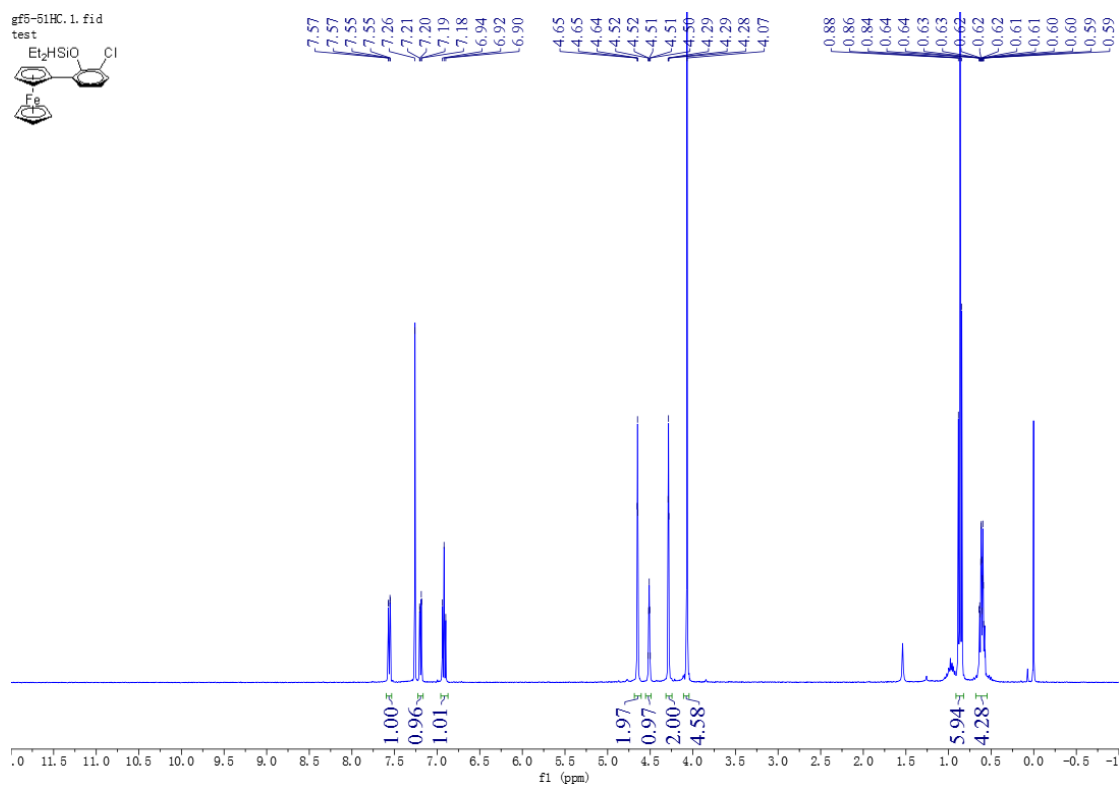
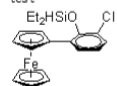


gf5-67C. 1. fid
C13CPD

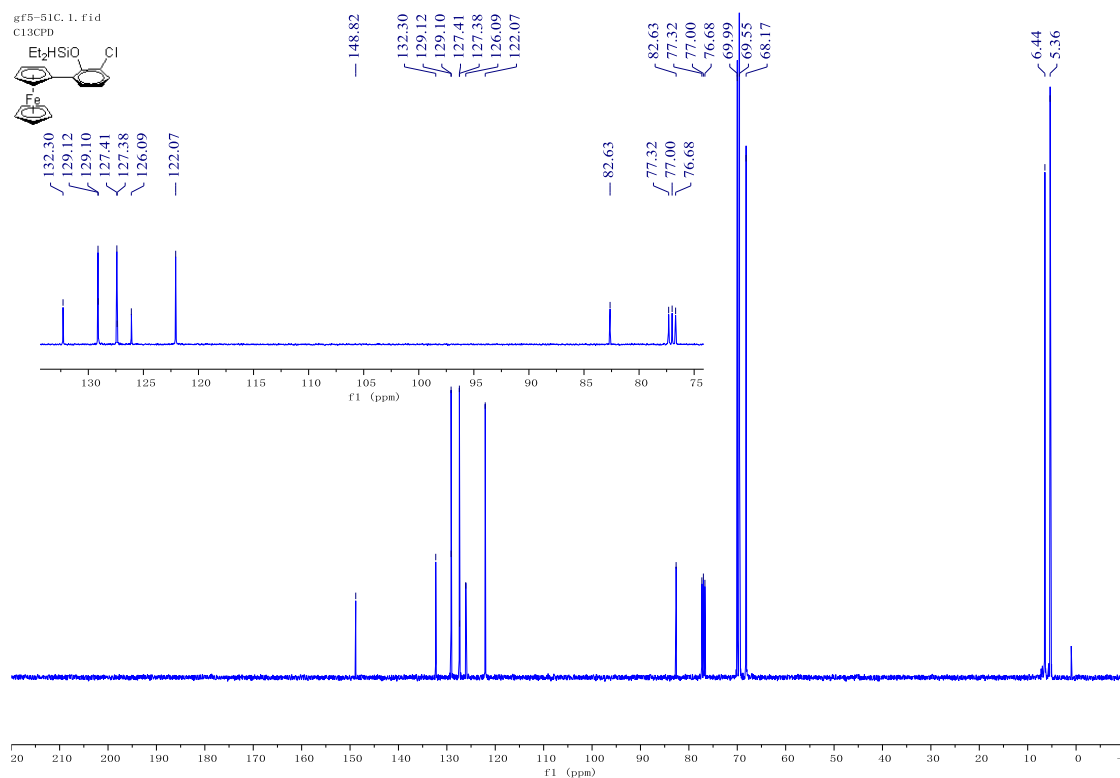
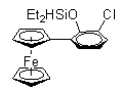


Compound 3q

gF5-51HC. 1. fid
test

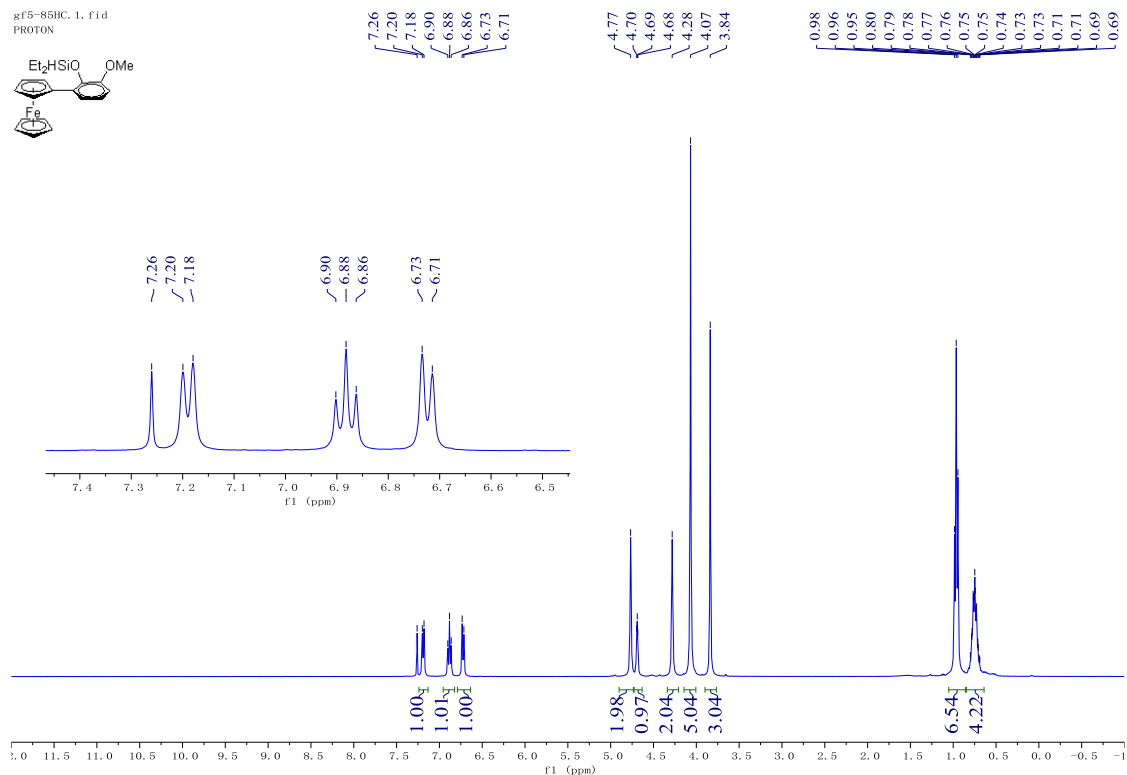
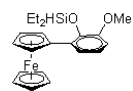


gF5-51C. 1. fid
C13CPD

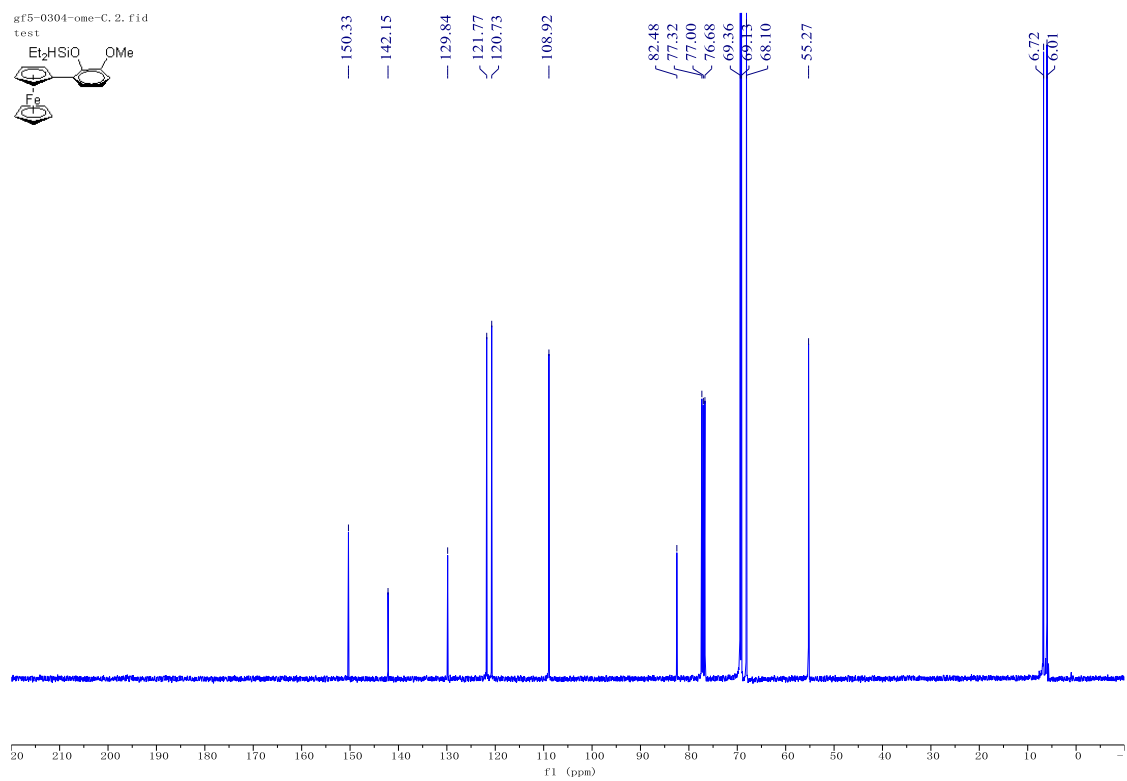
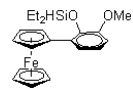


Compound 3r

gF5-85HC.1.fid
PROTON

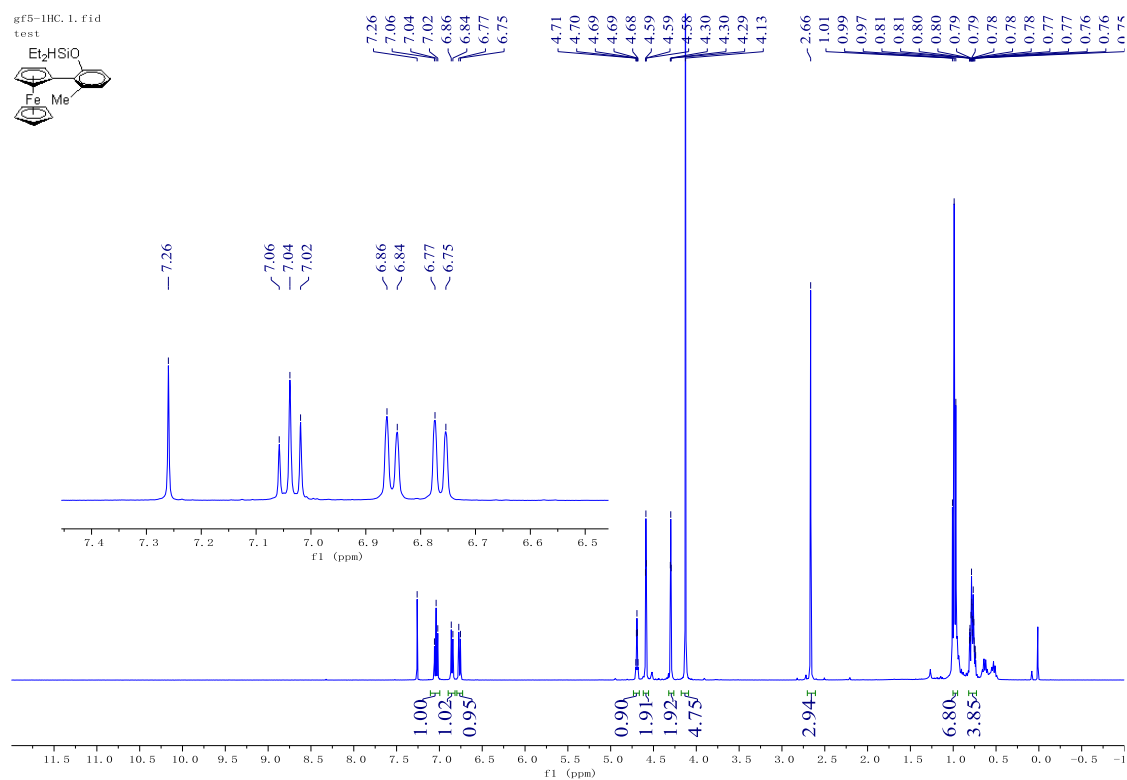
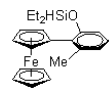


gF5-0304-ome-C.2.fid
test

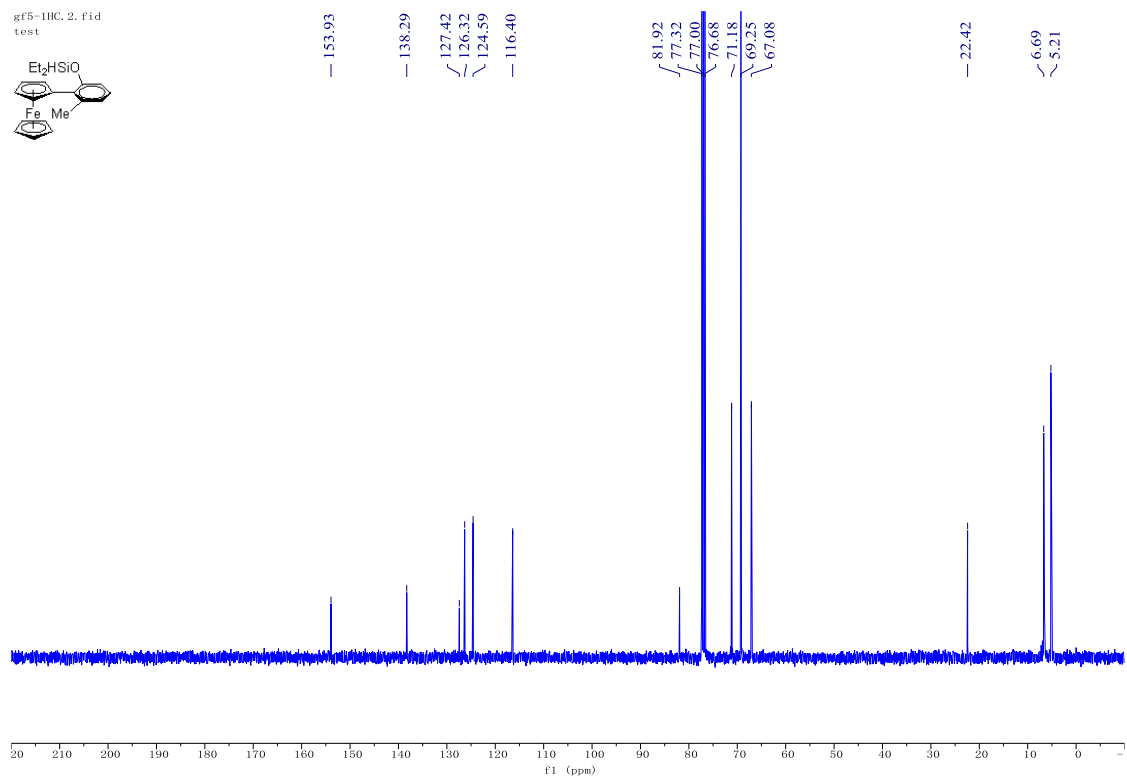
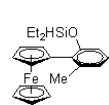


Compound 3s

gf5-1HC. 1. fid
test

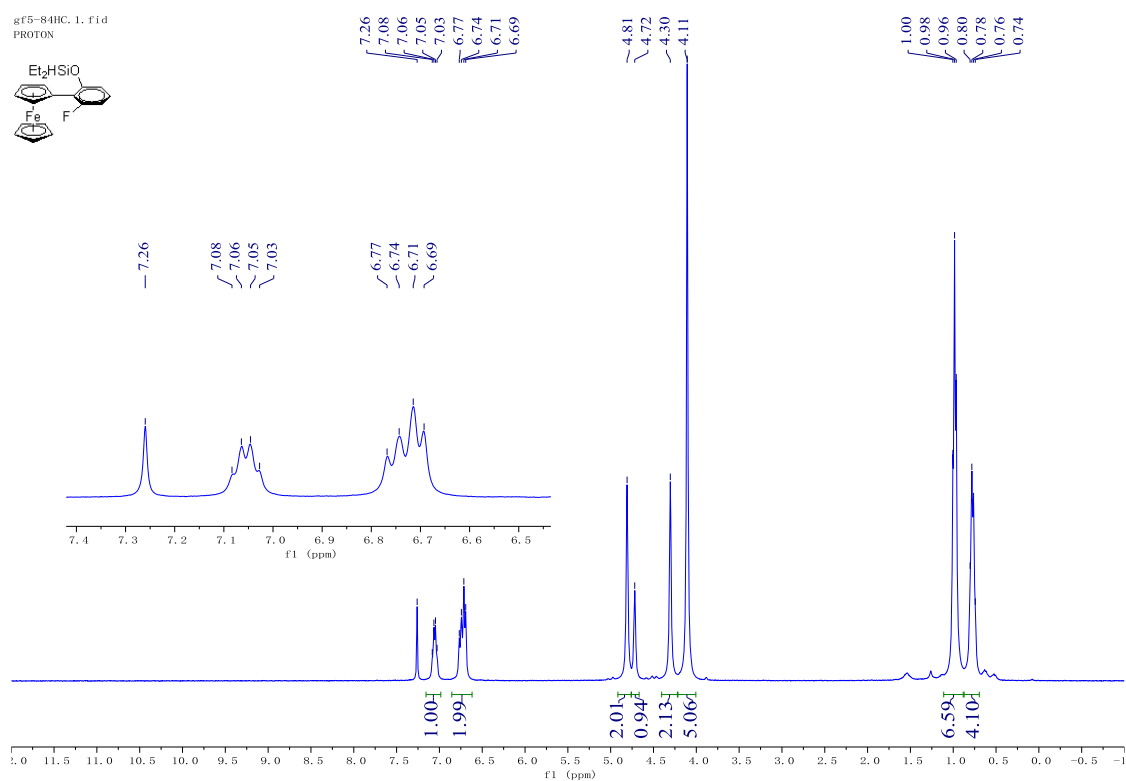


gf5-1HC. 2. fid
test

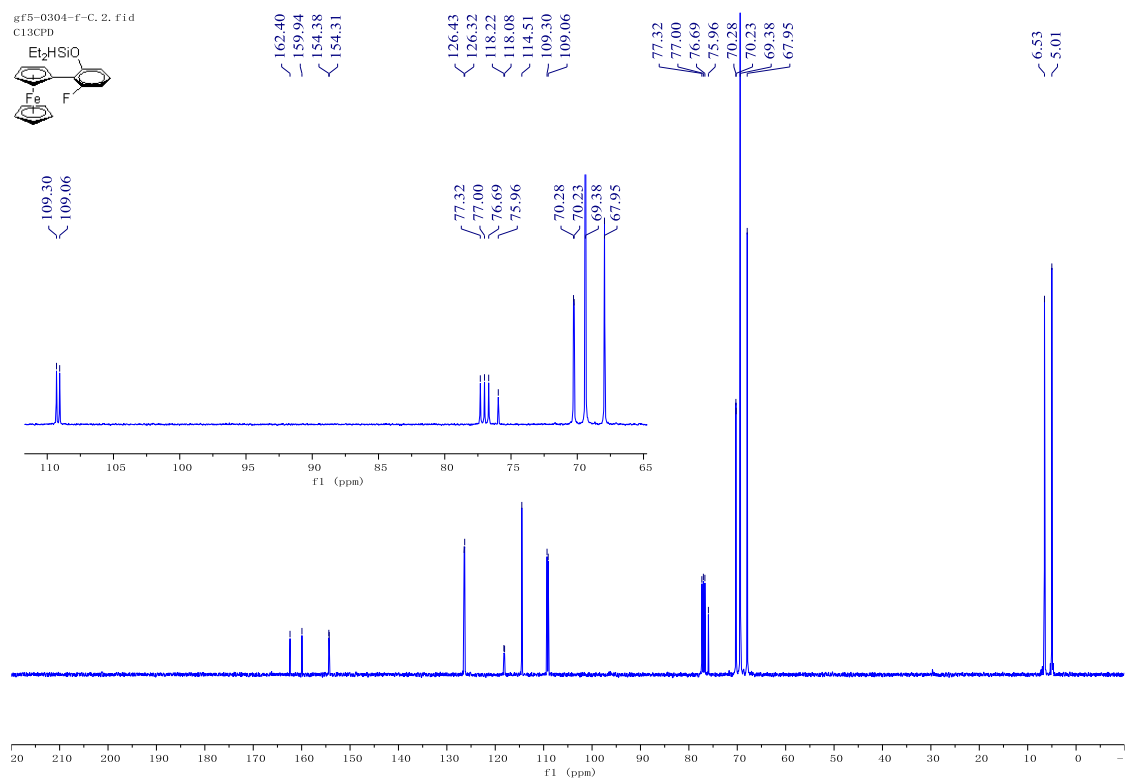
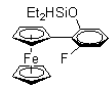


Compound 3t

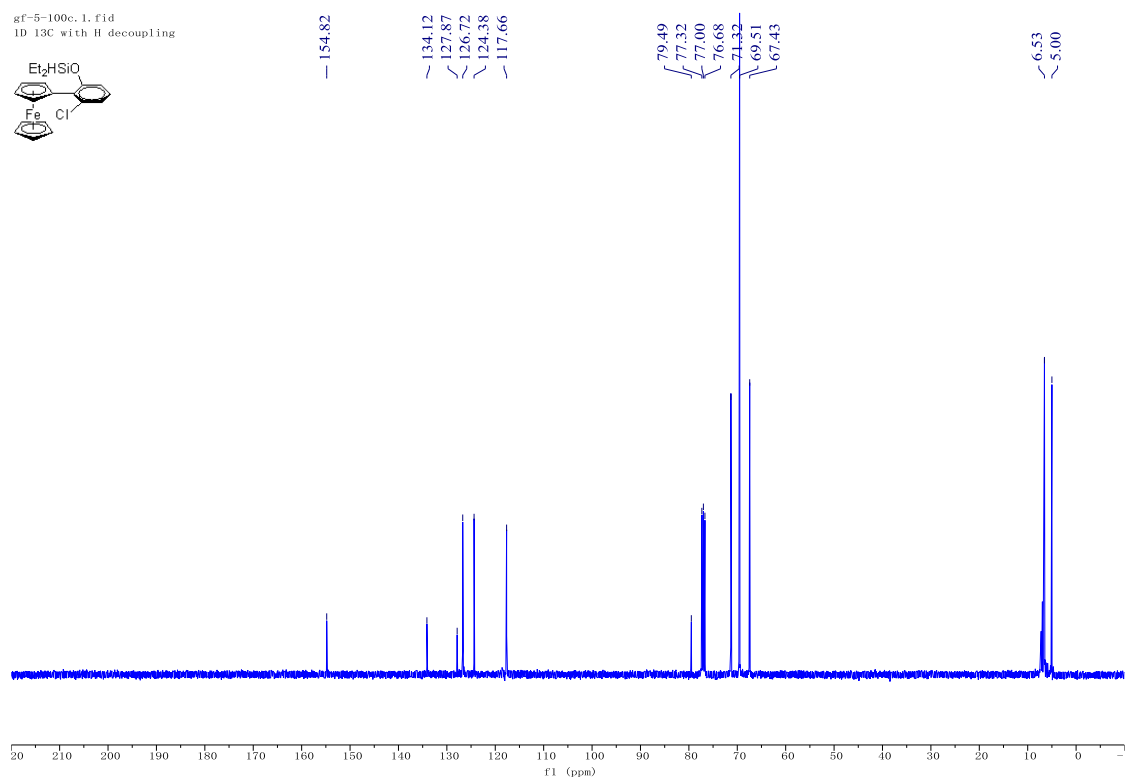
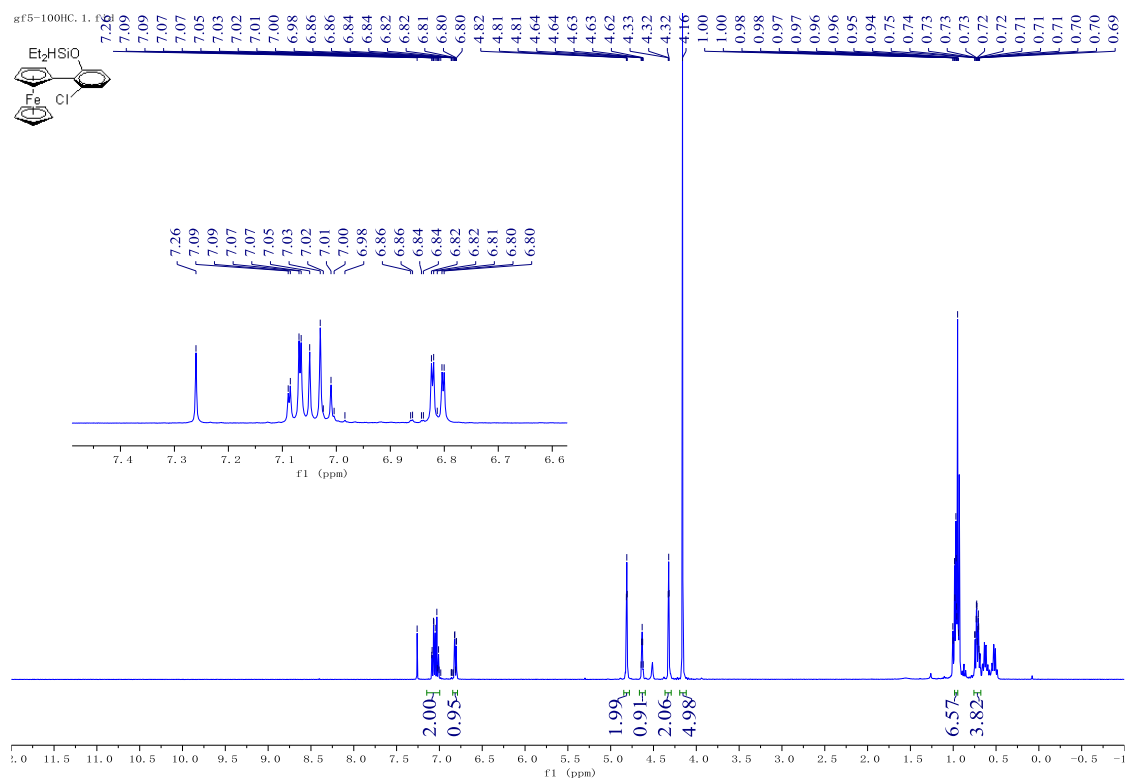
gF5-84HC. 1. F1d
PROTON



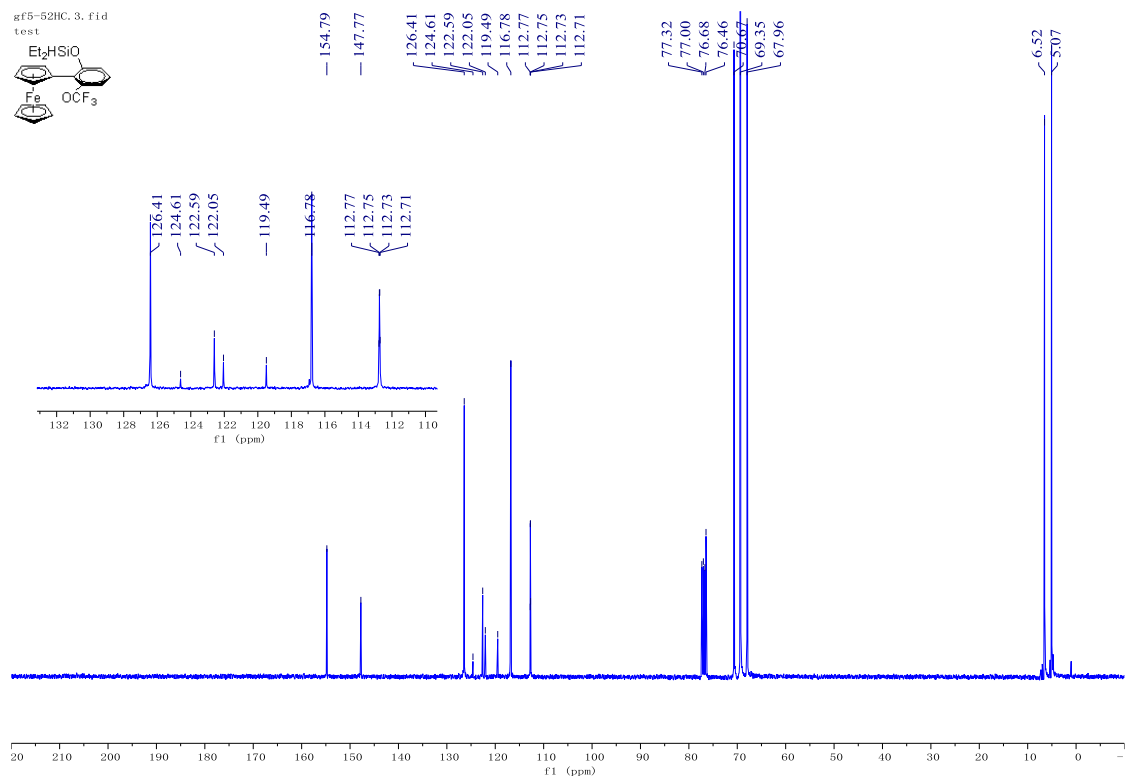
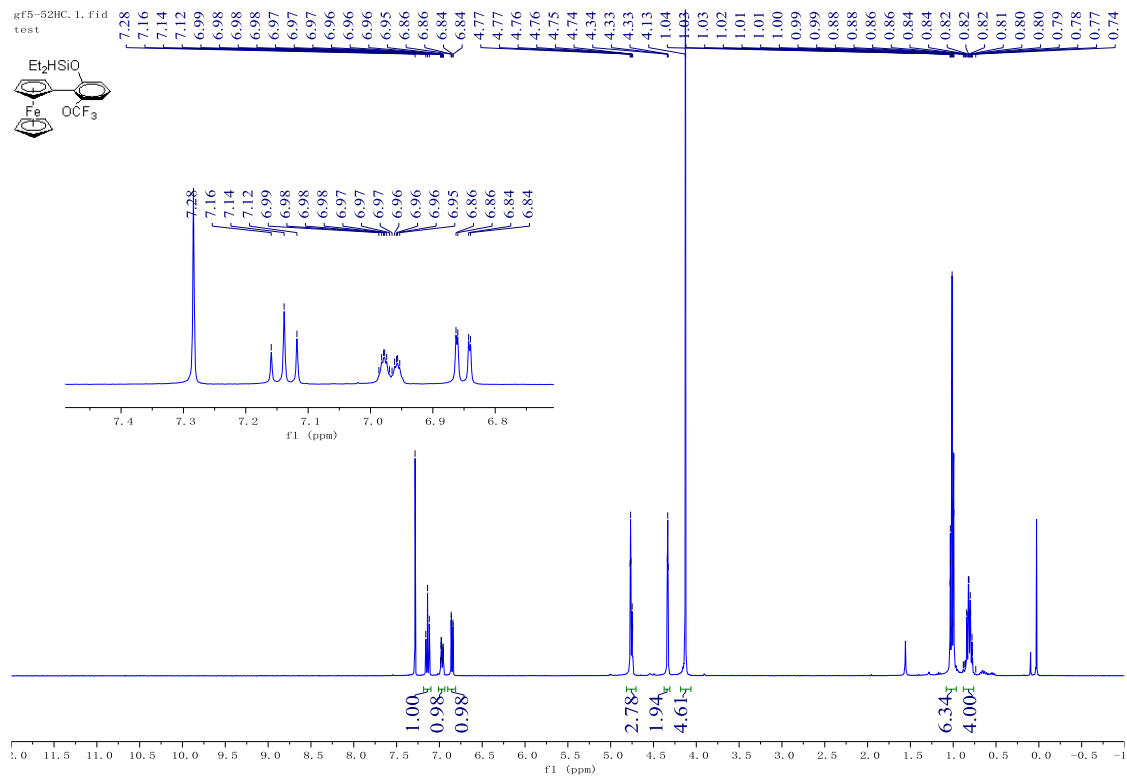
gF5-0304-f-C. 2. F1d
C13CPD



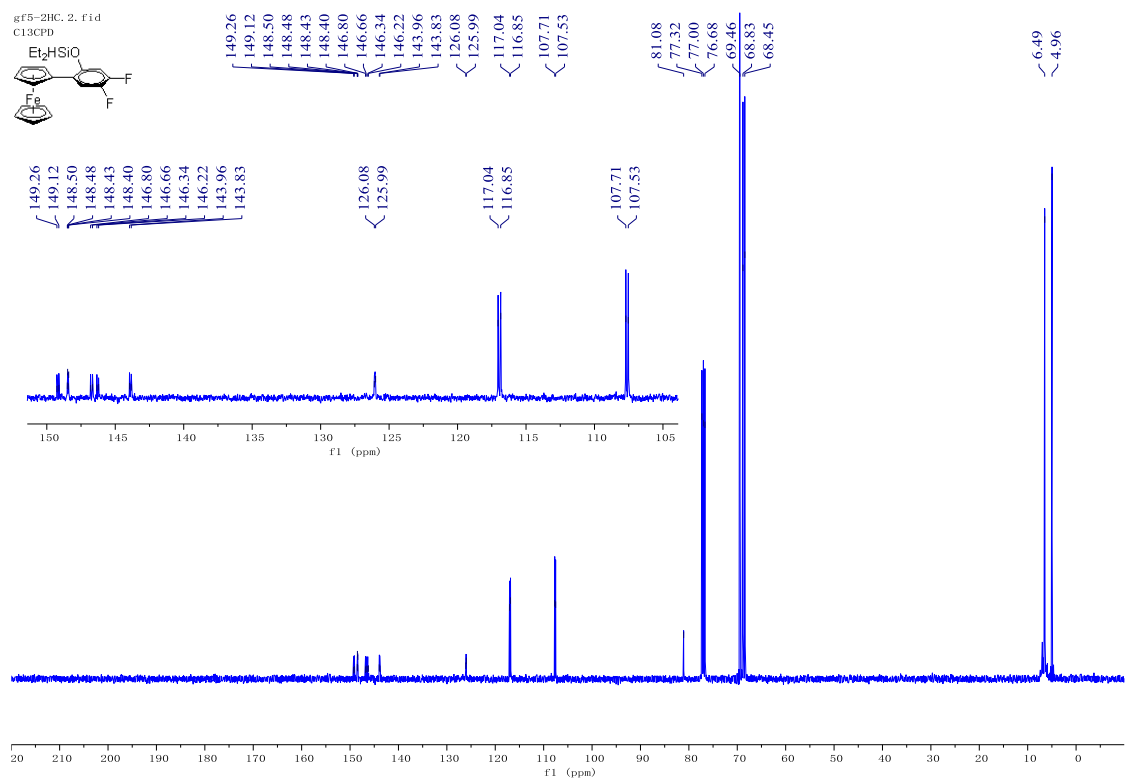
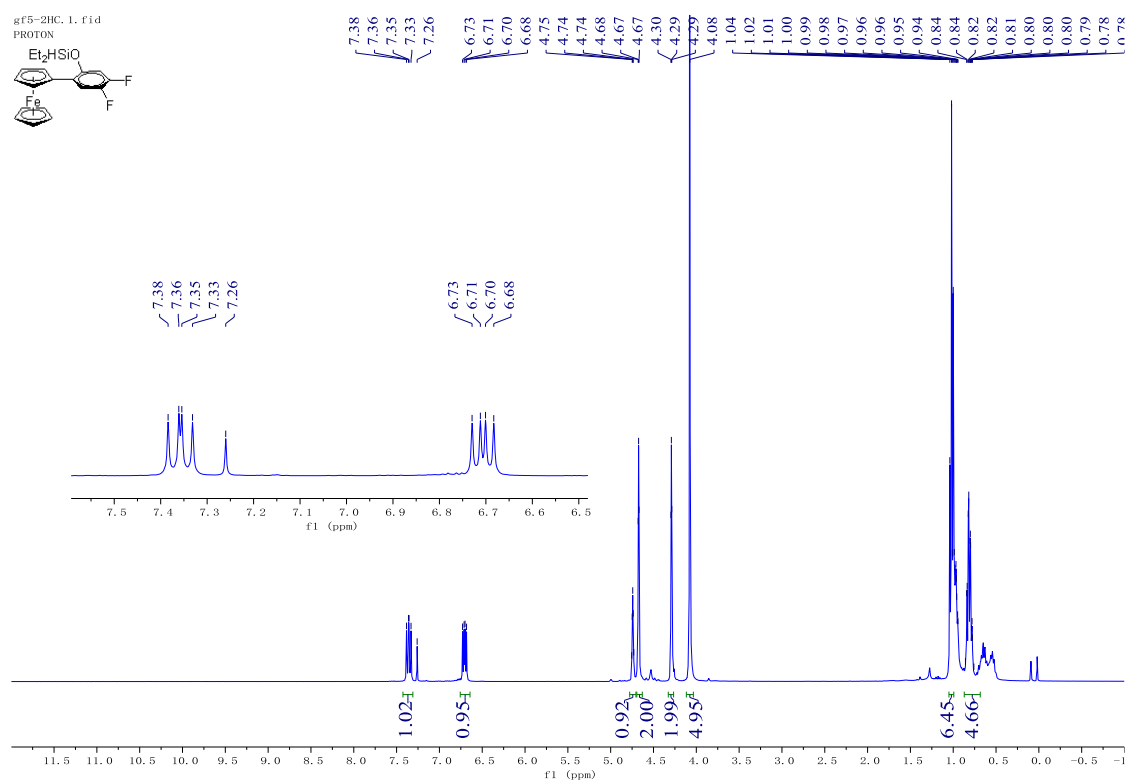
Compound 3u



Compound 3v

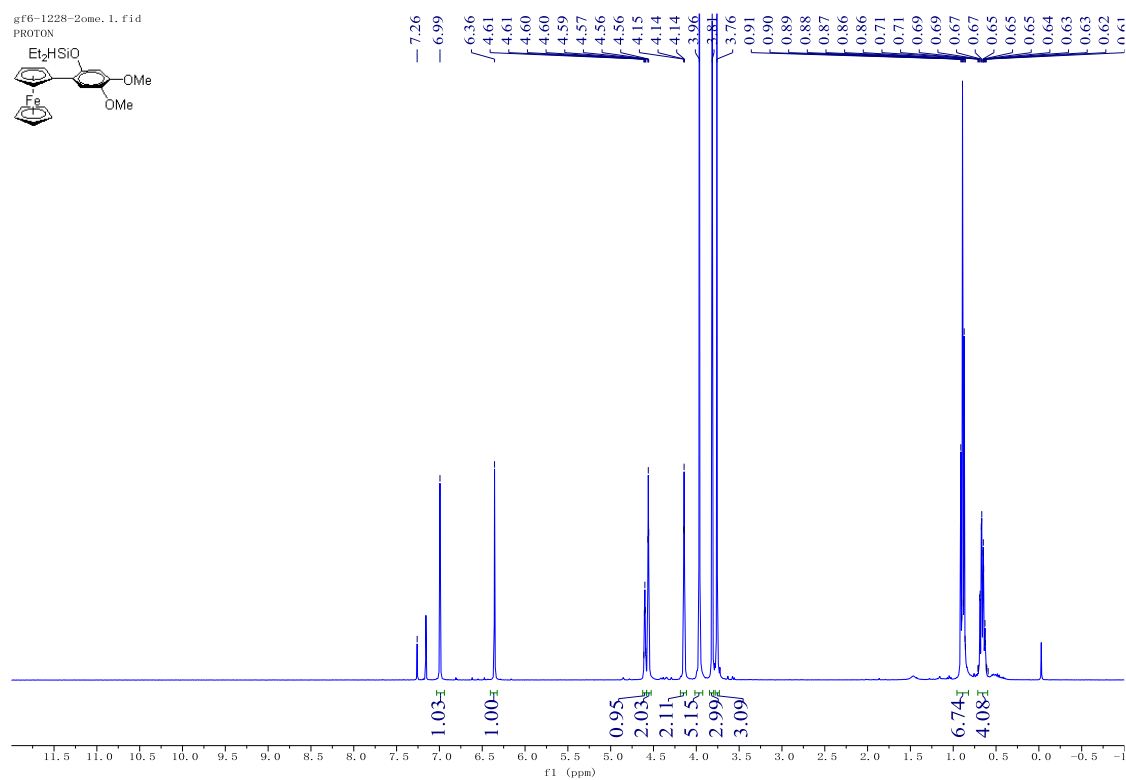
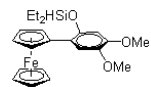


Compound 3w

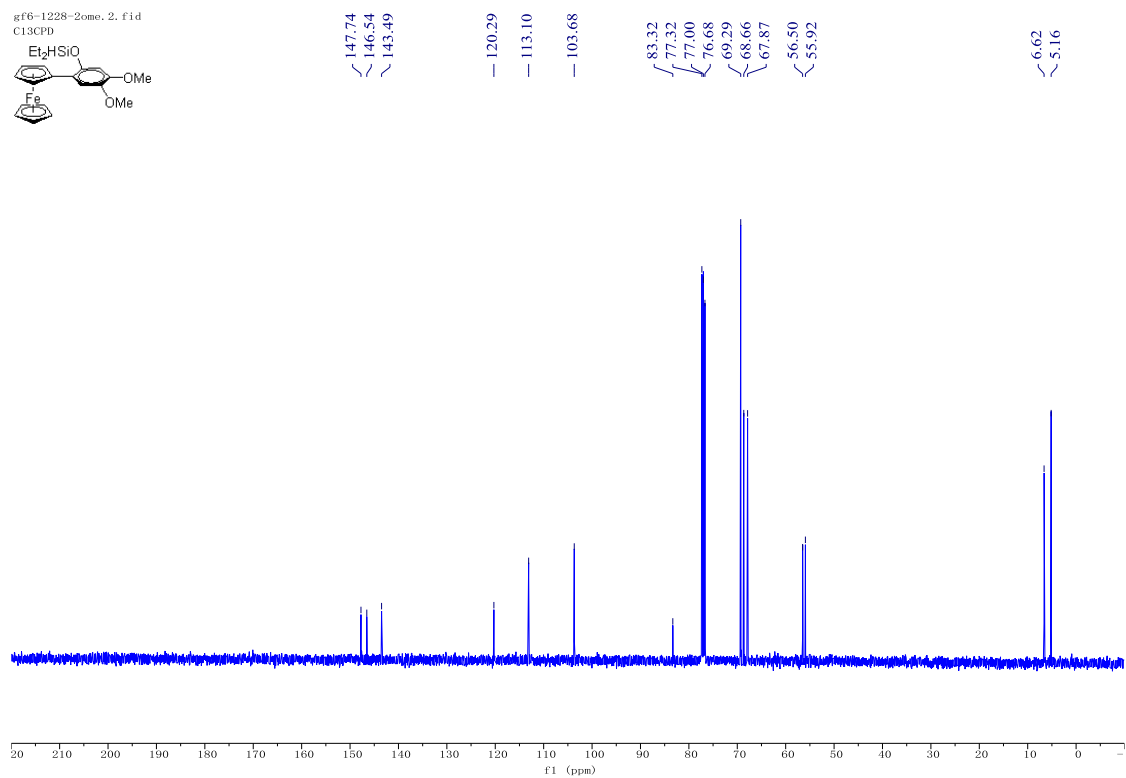
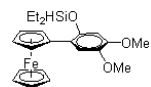


Compound 3x

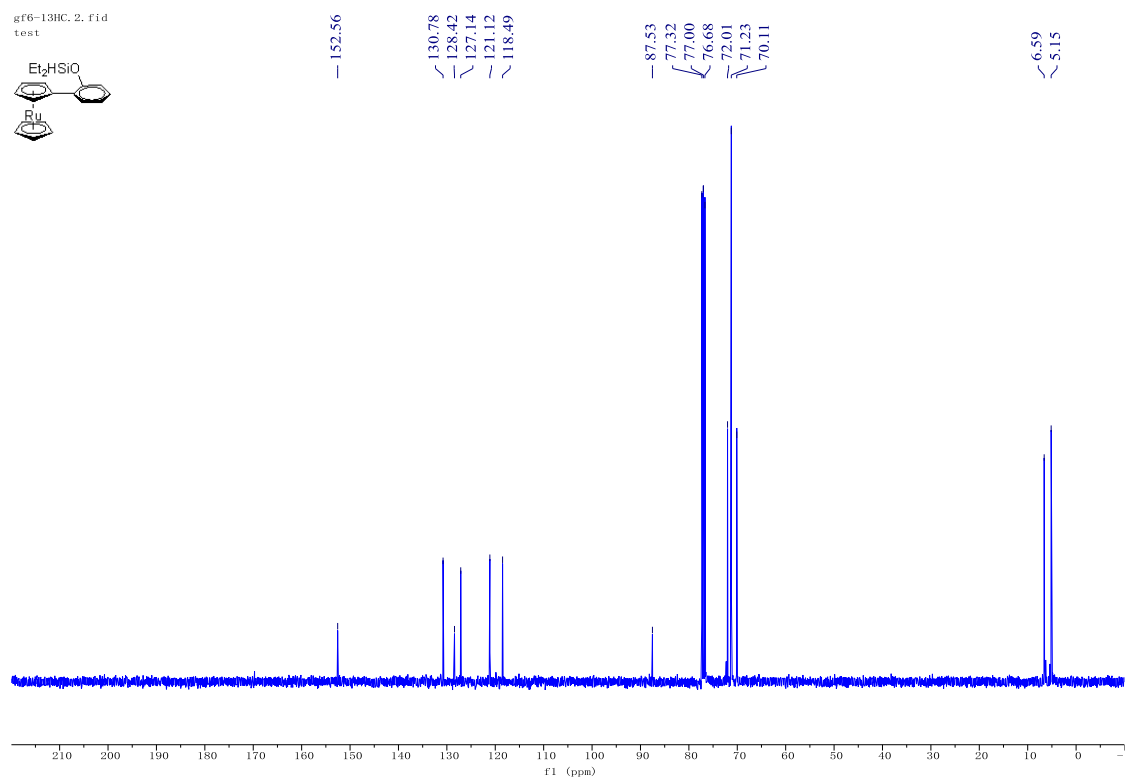
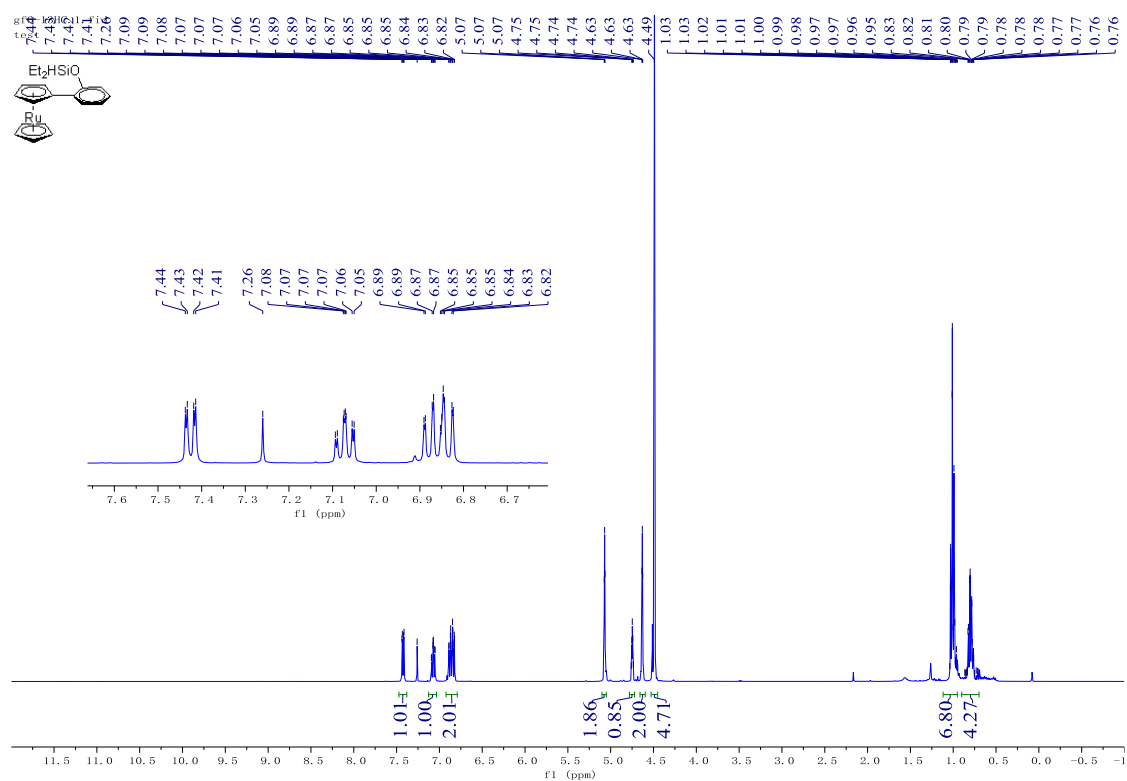
gF6-1228-2ome. 1. fid
PROTON



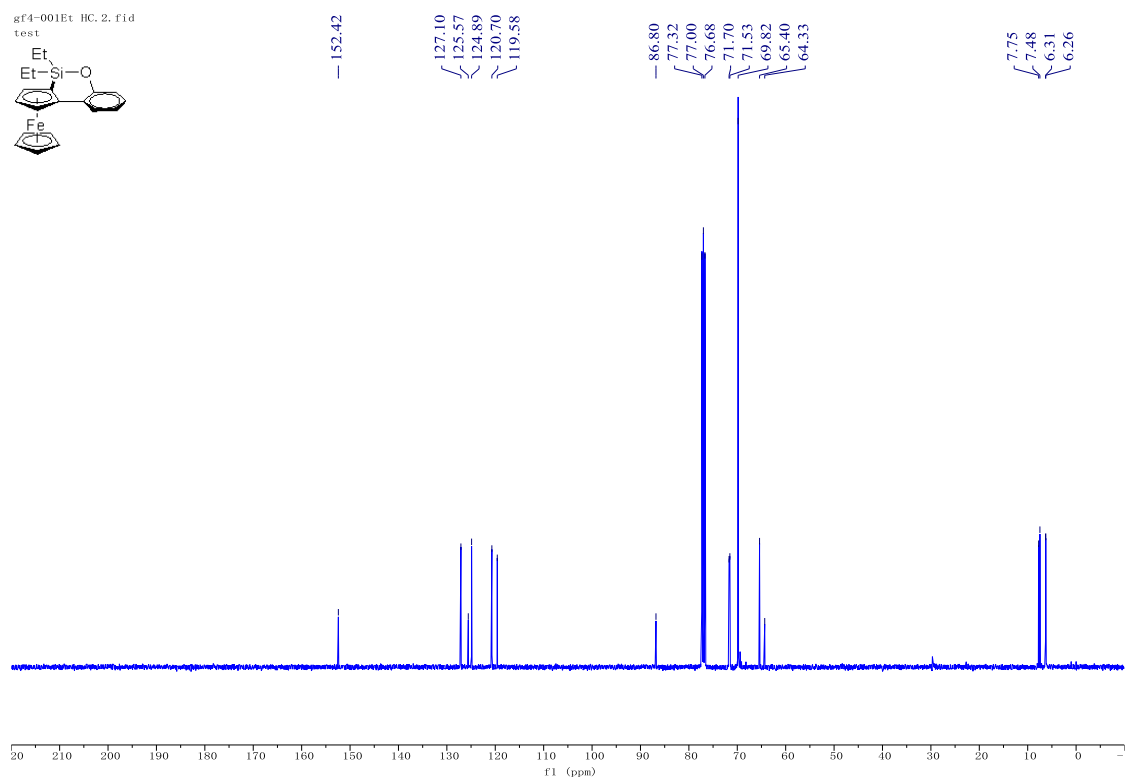
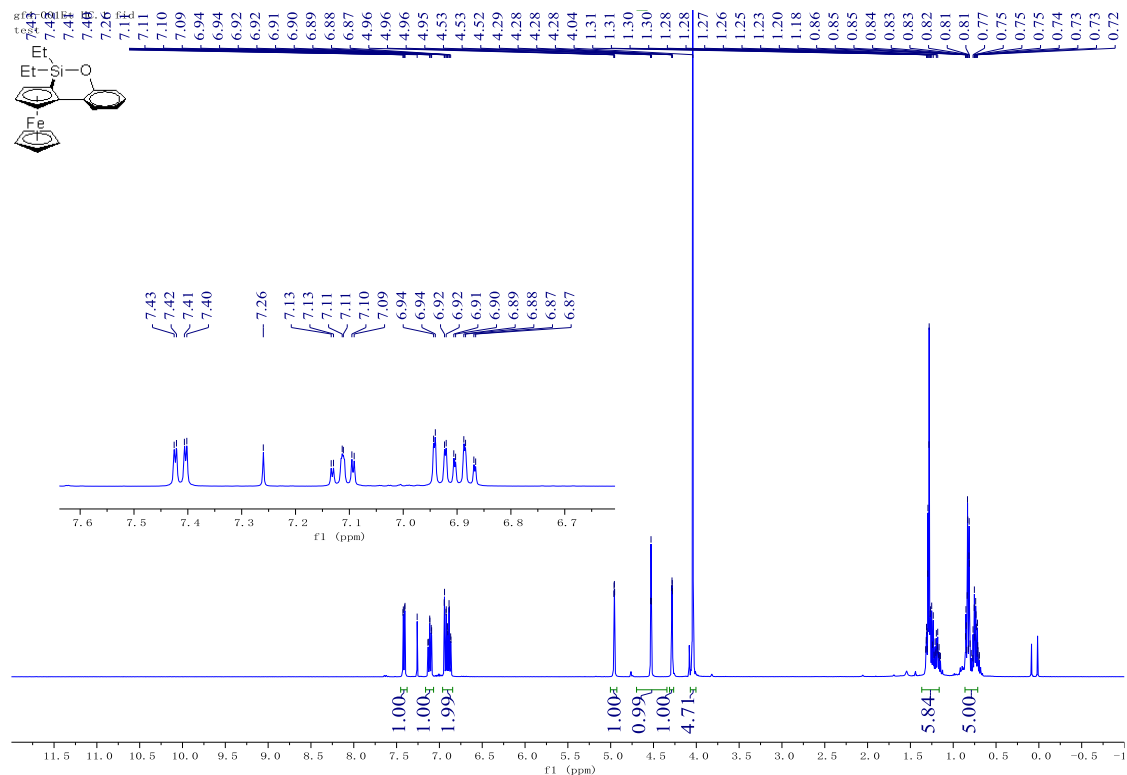
gF6-1228-2ome. 2. fid
C13CPD



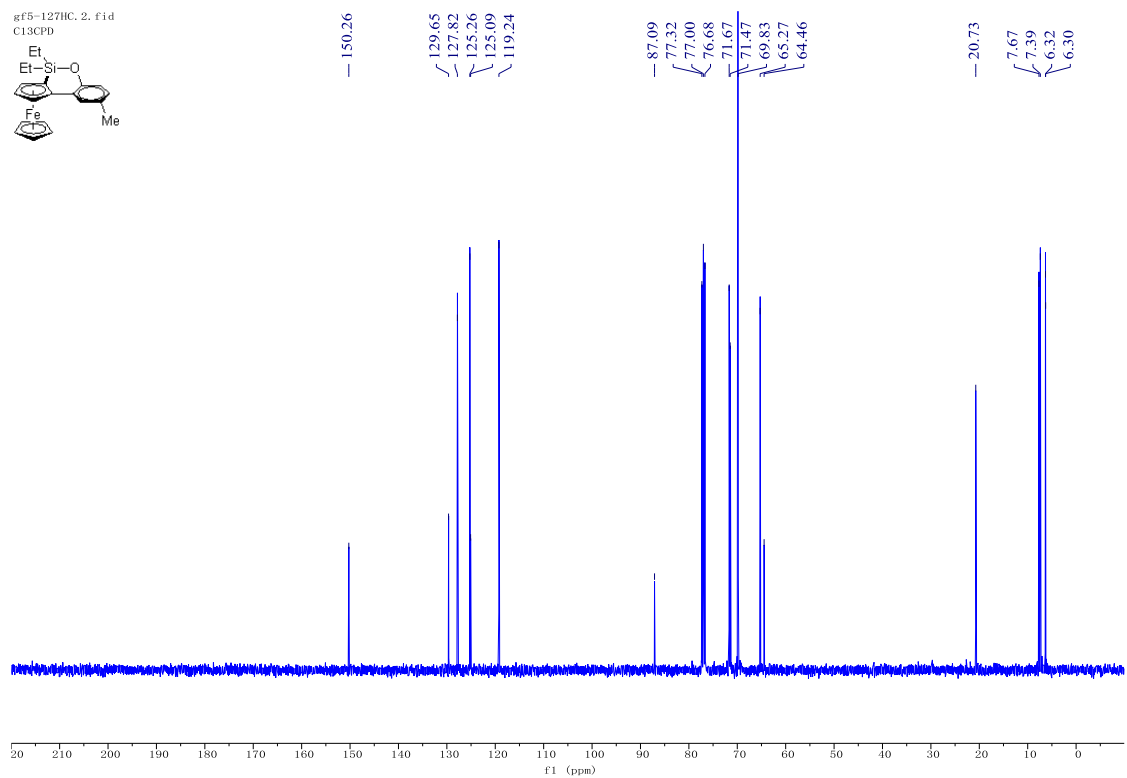
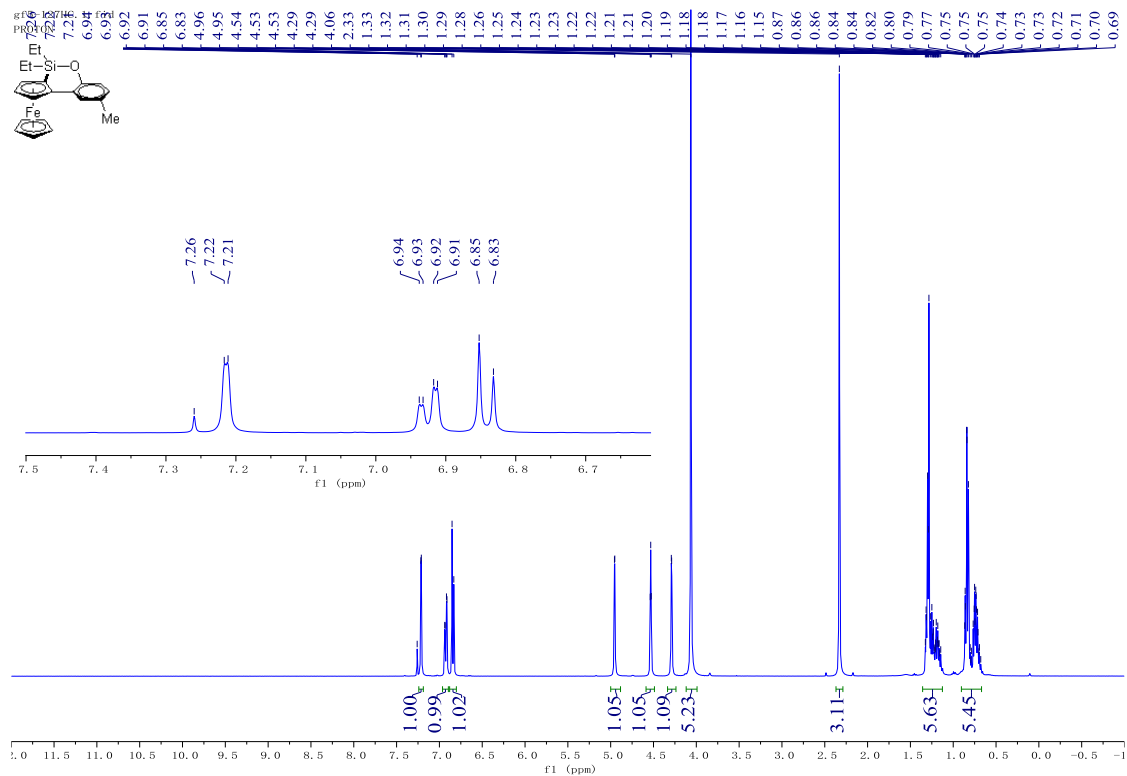
Compound 3y



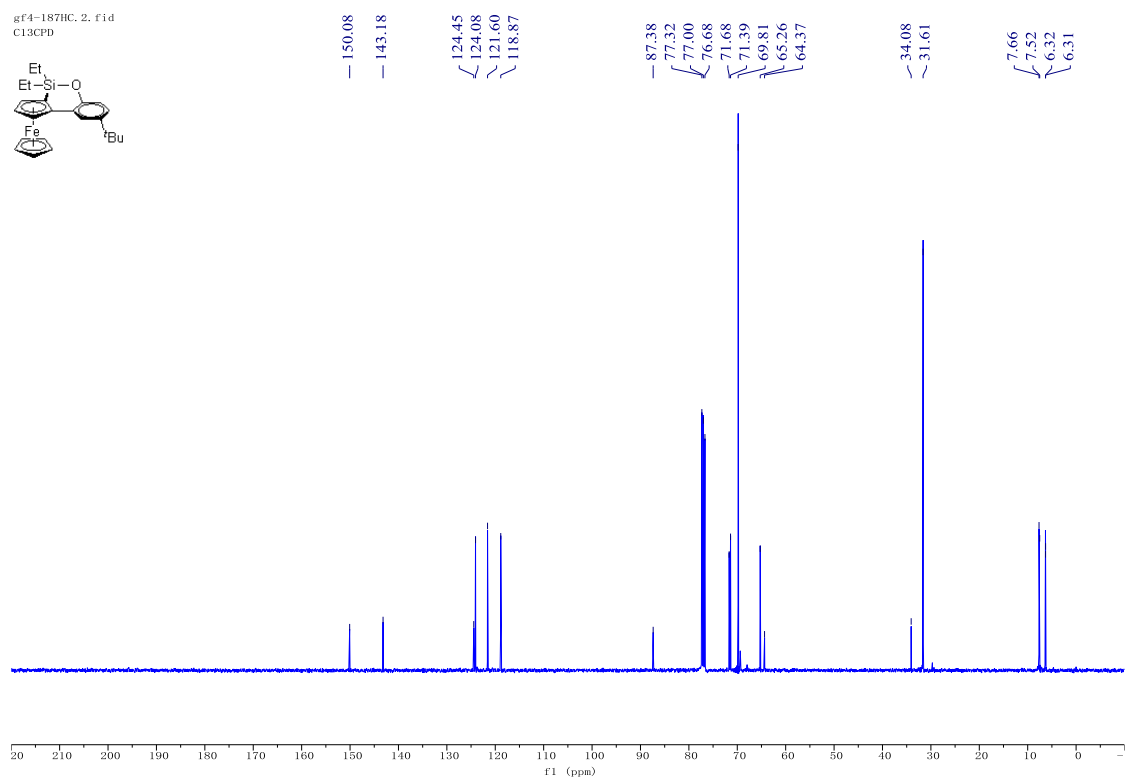
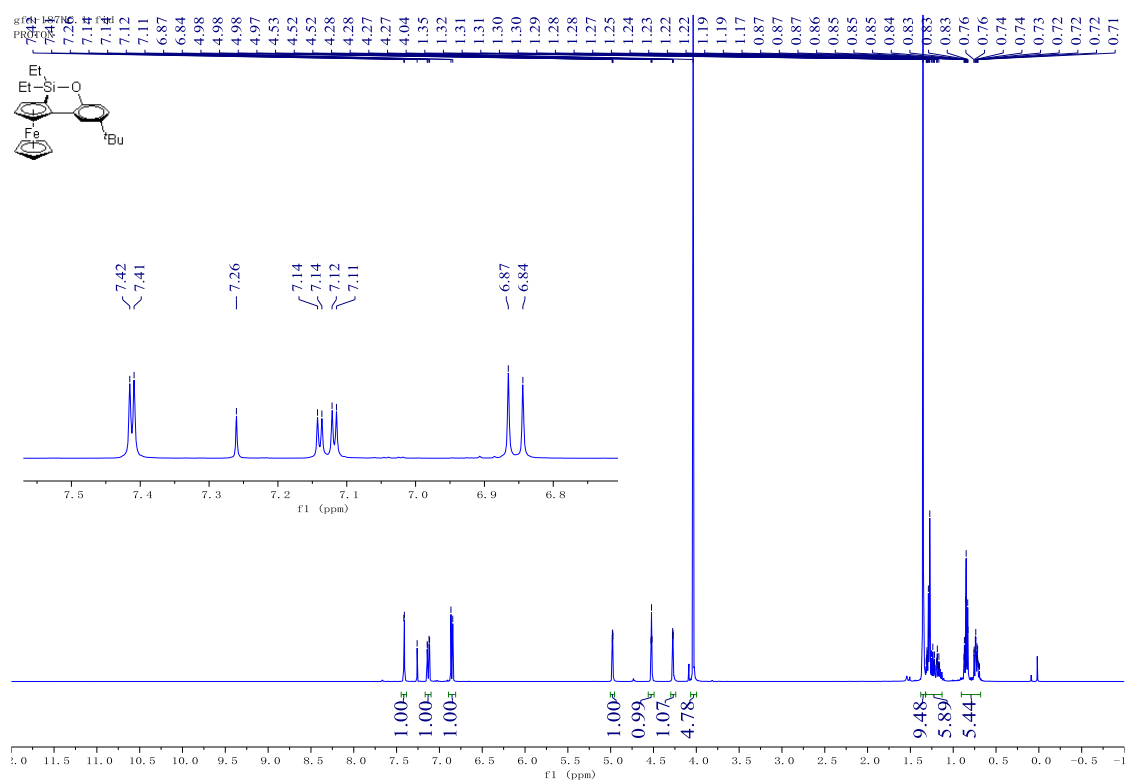
Compound 4a



Compound 4b

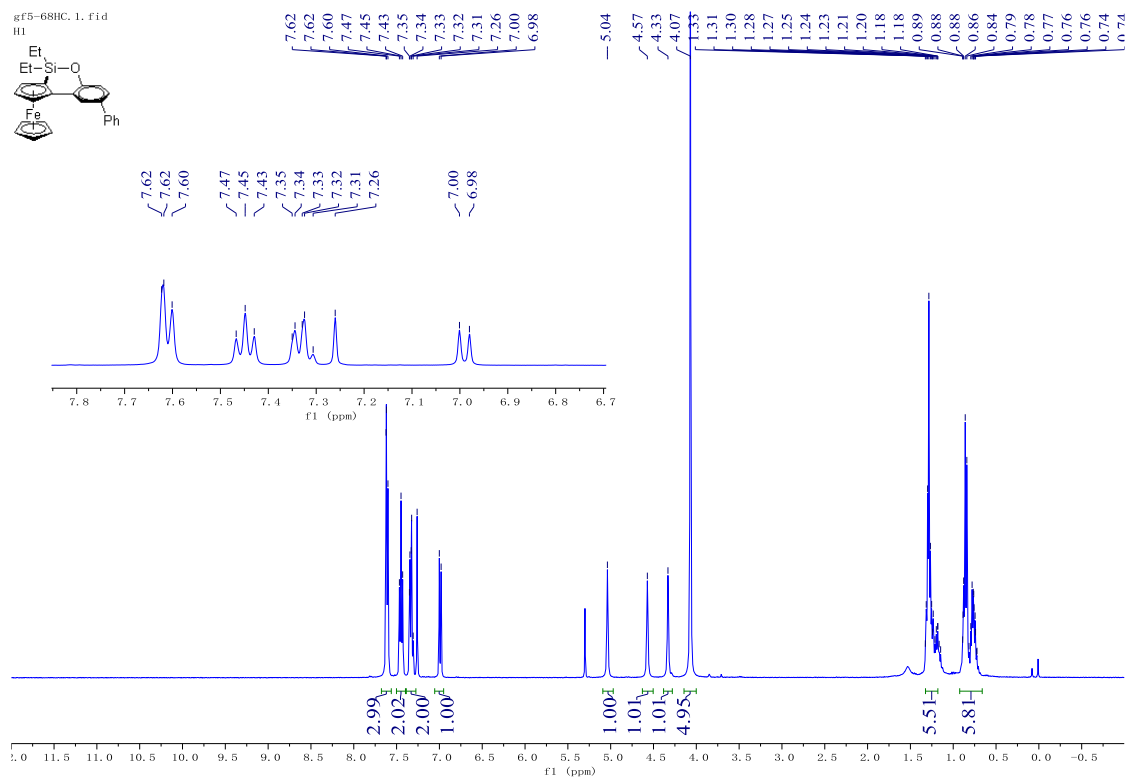
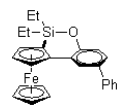


Compound 4c

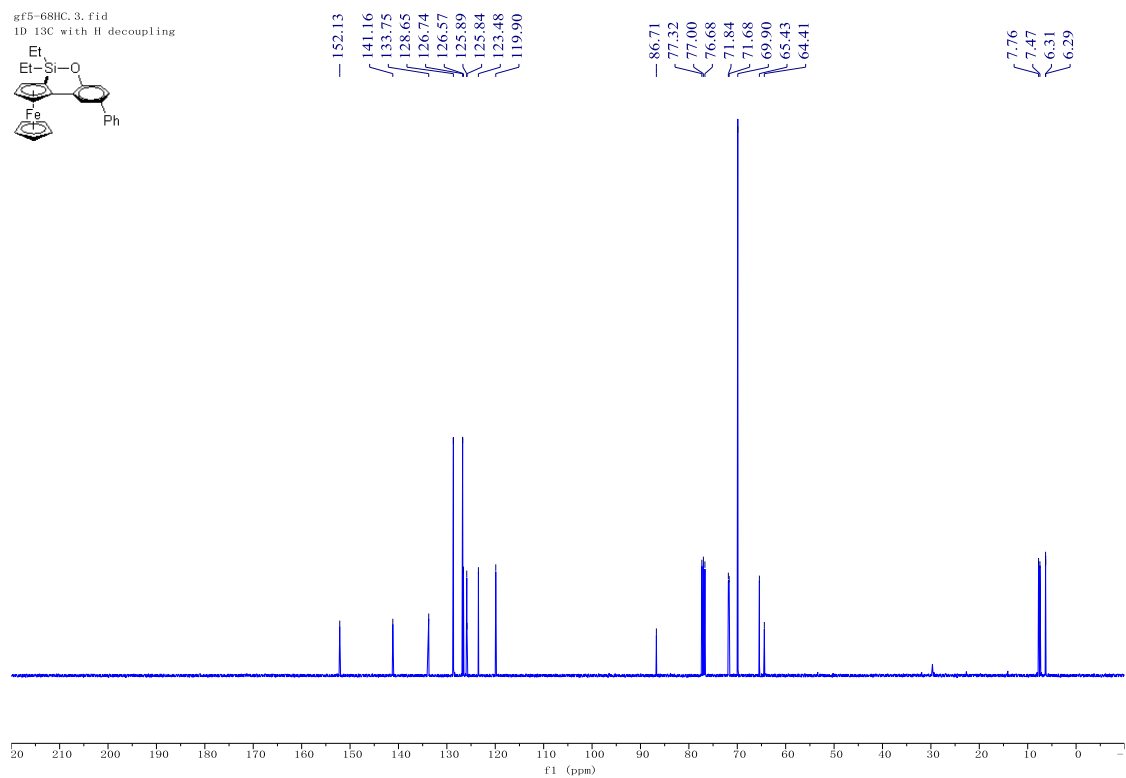
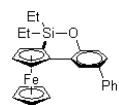


Compound 4d

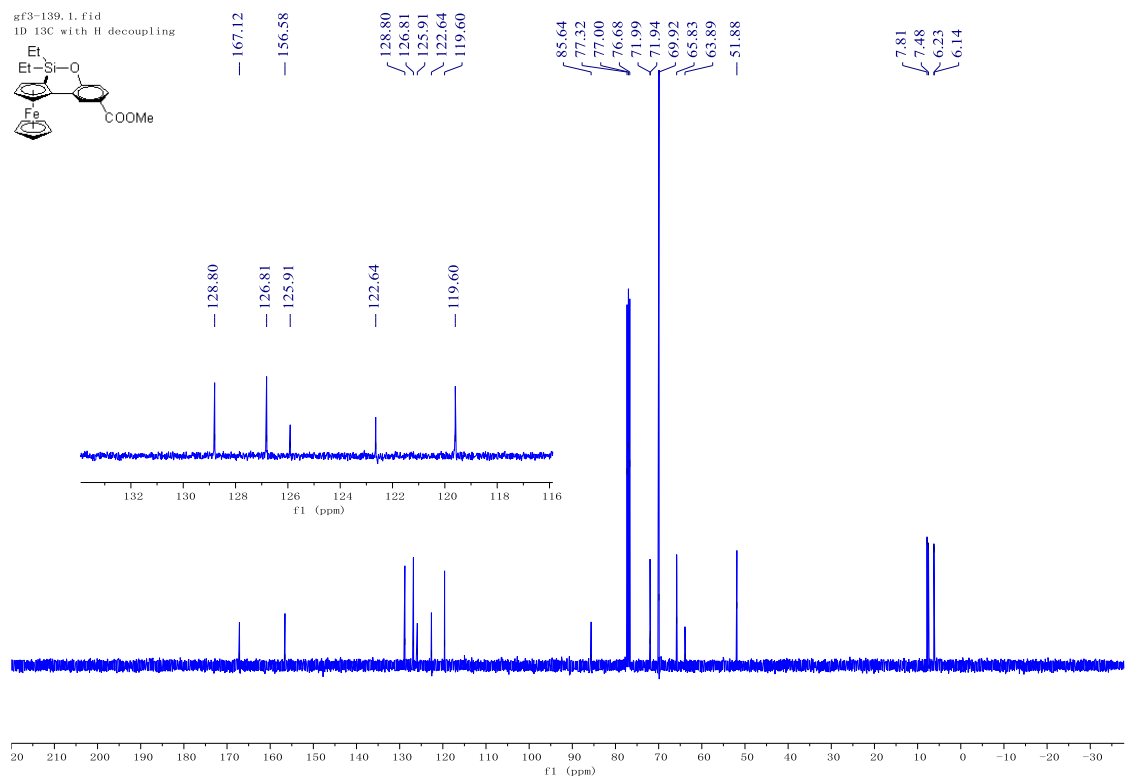
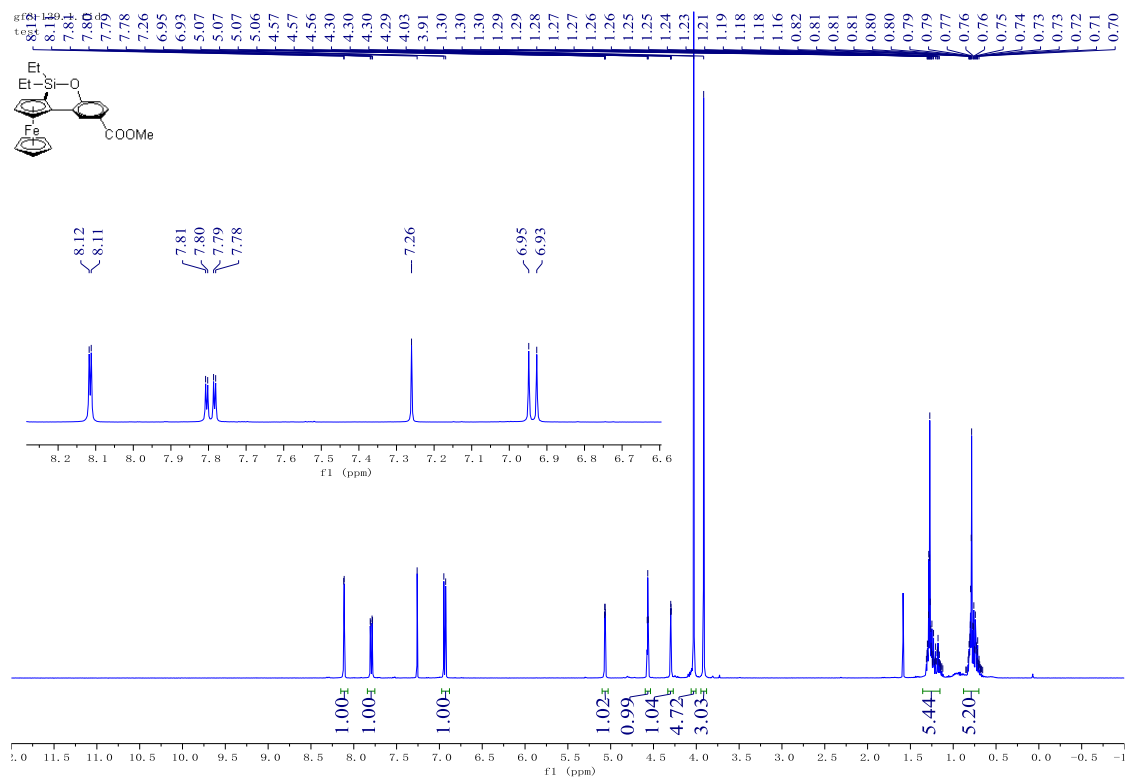
gF5-68HC.1.fid
H1



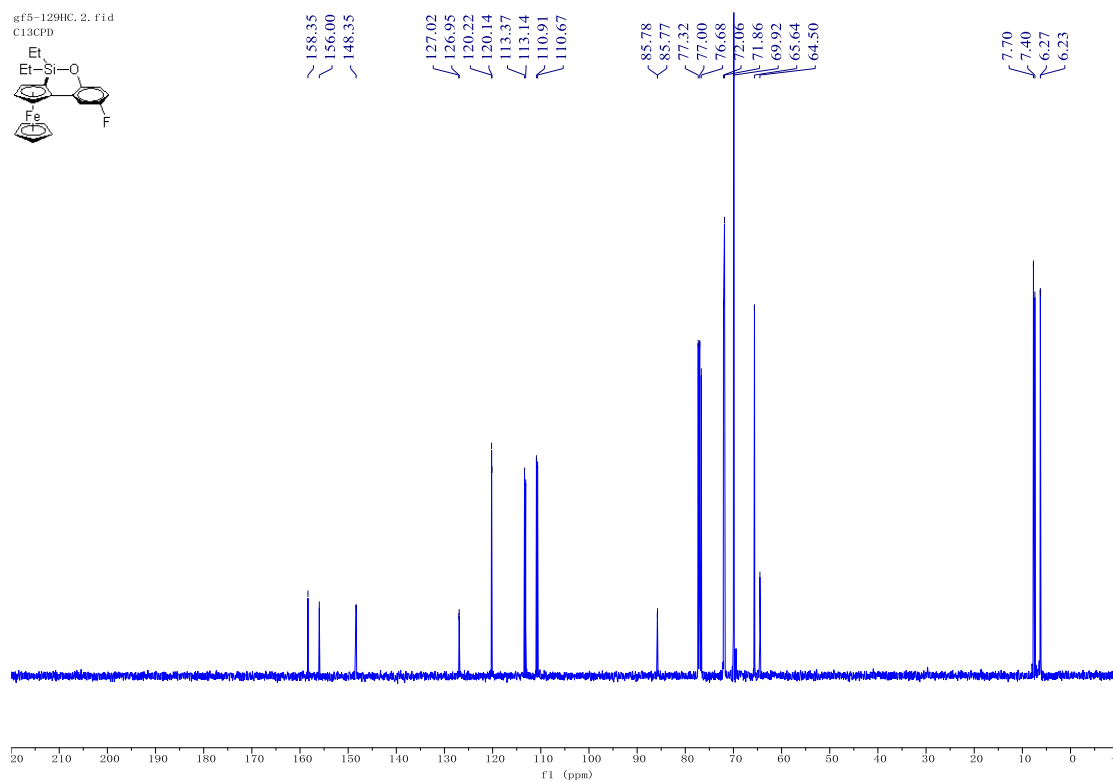
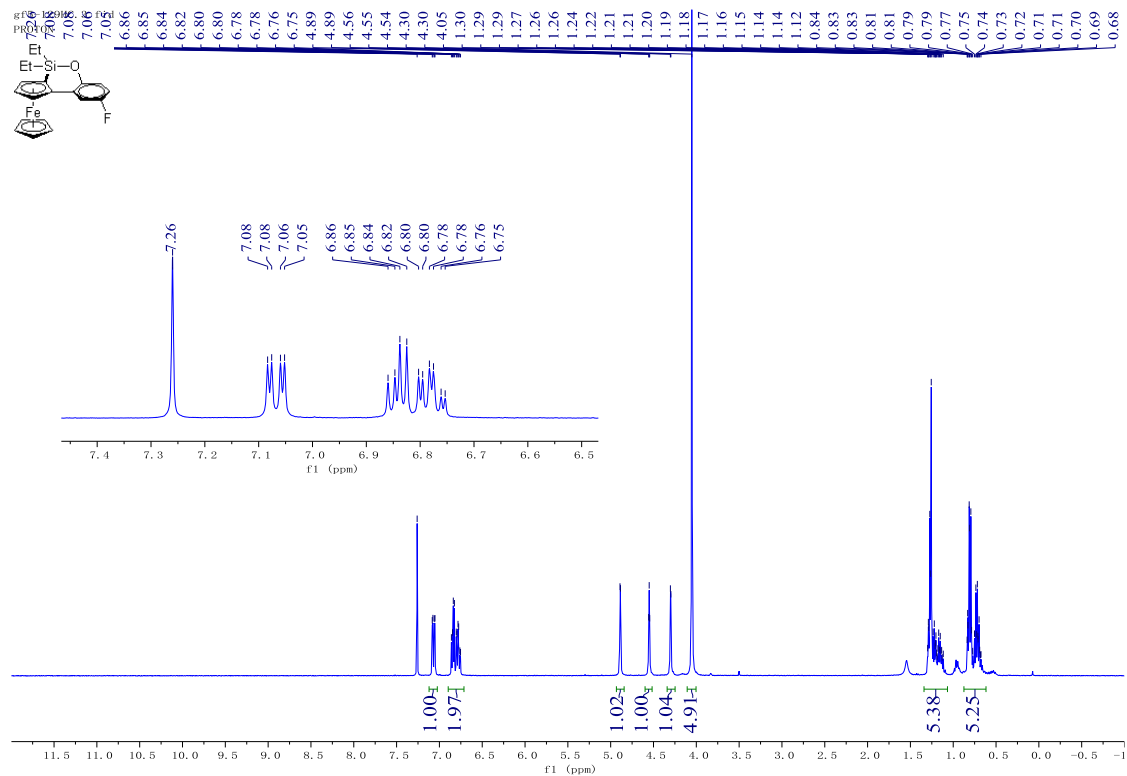
gF5-68HC.3.fid
ID 13C with H decoupling



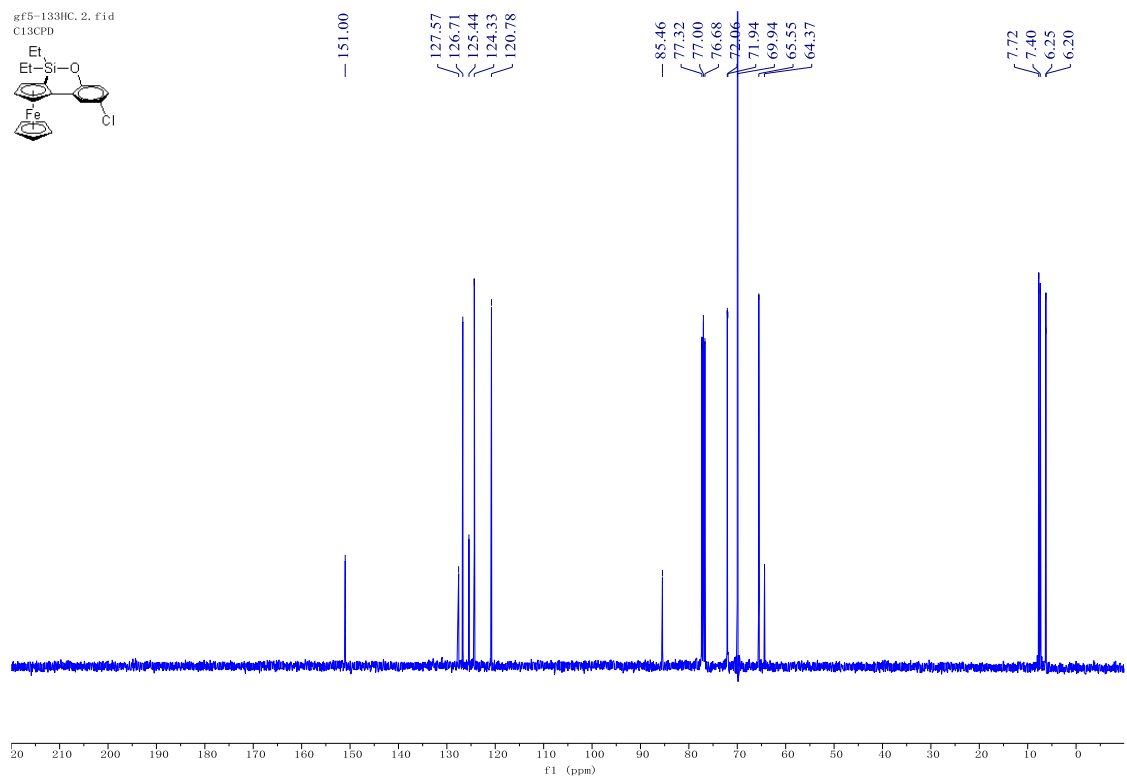
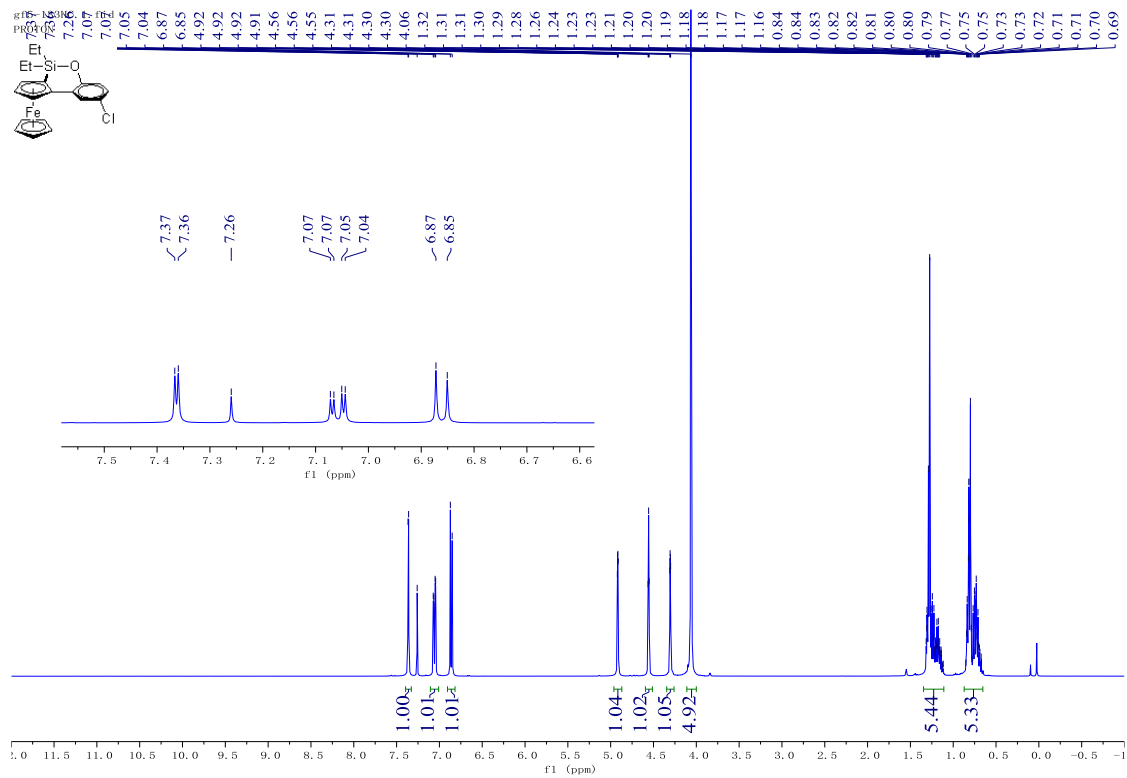
Compound 4e



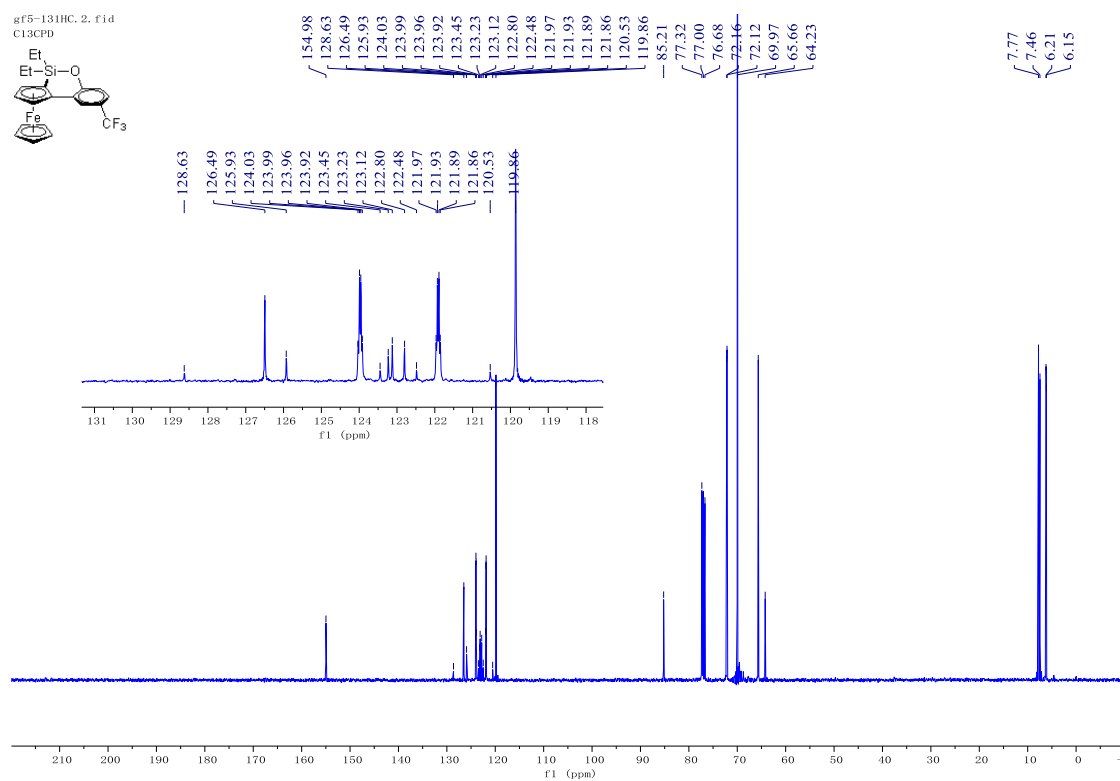
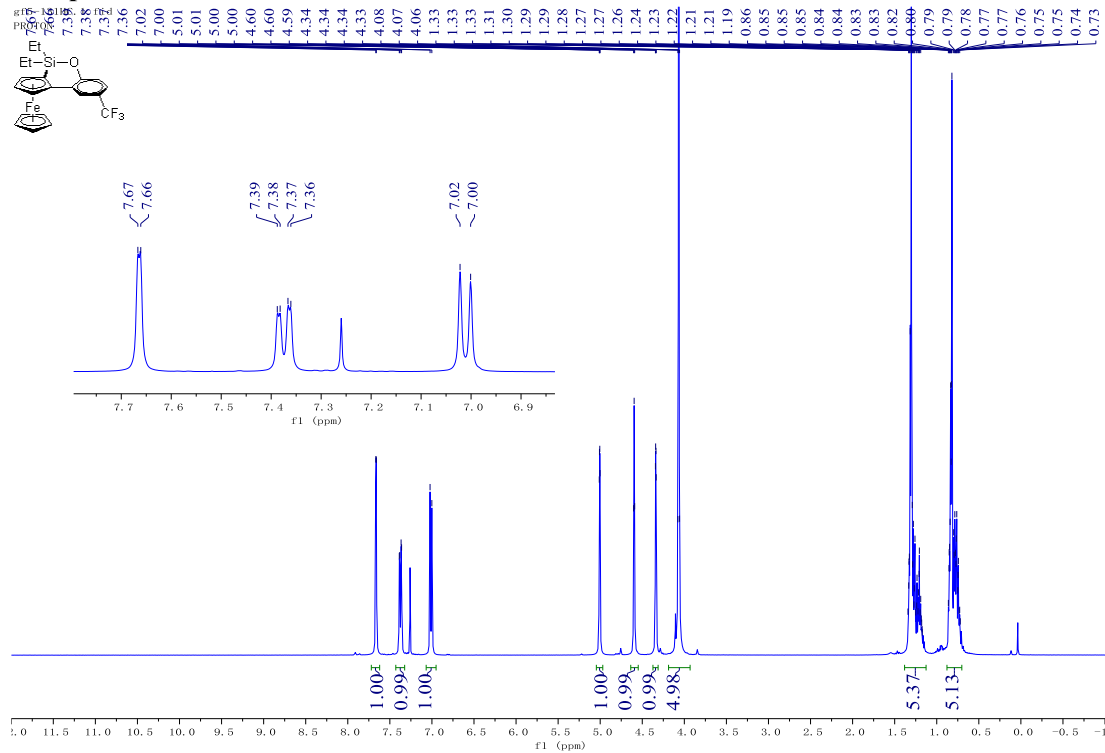
Compound 4f



Compound 4g

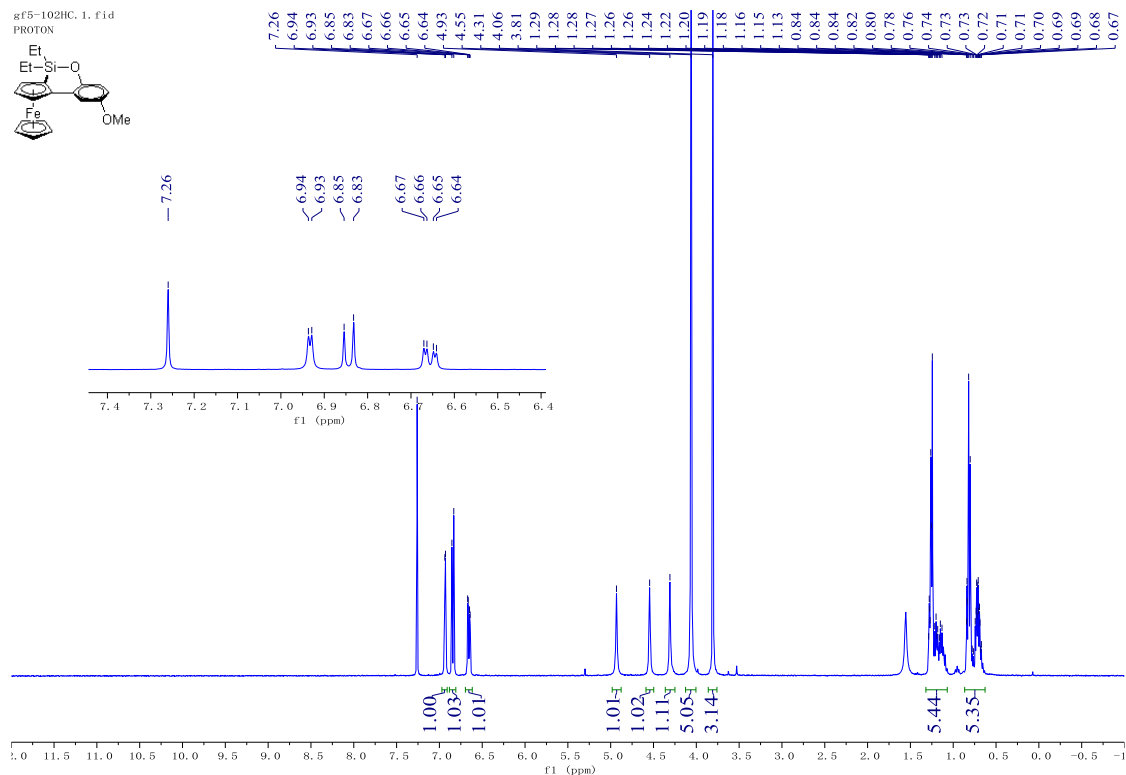
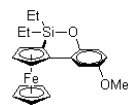


Compound 4h

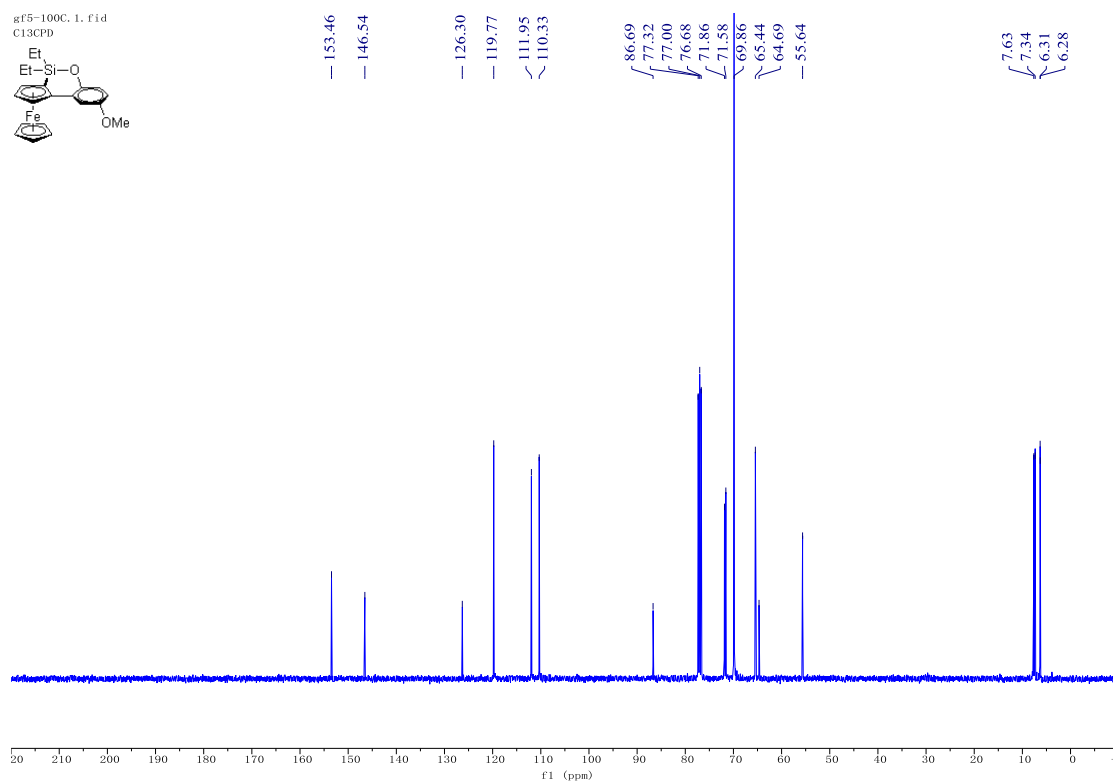
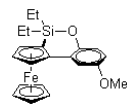


Compound 4i

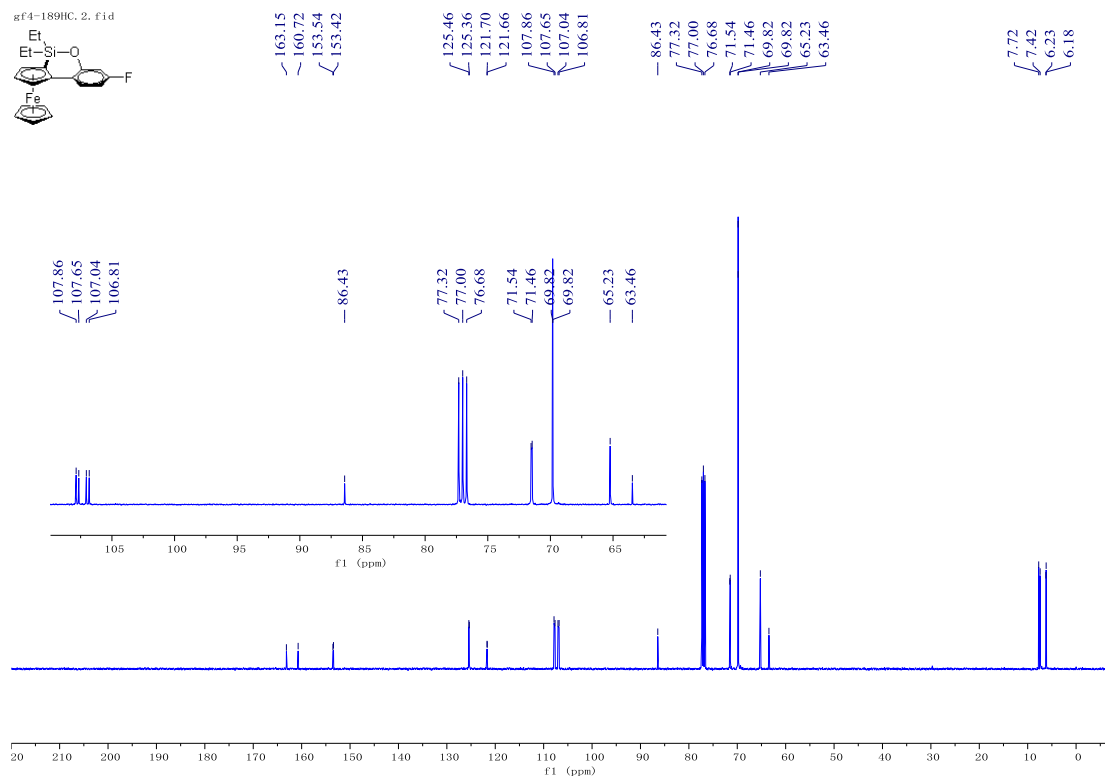
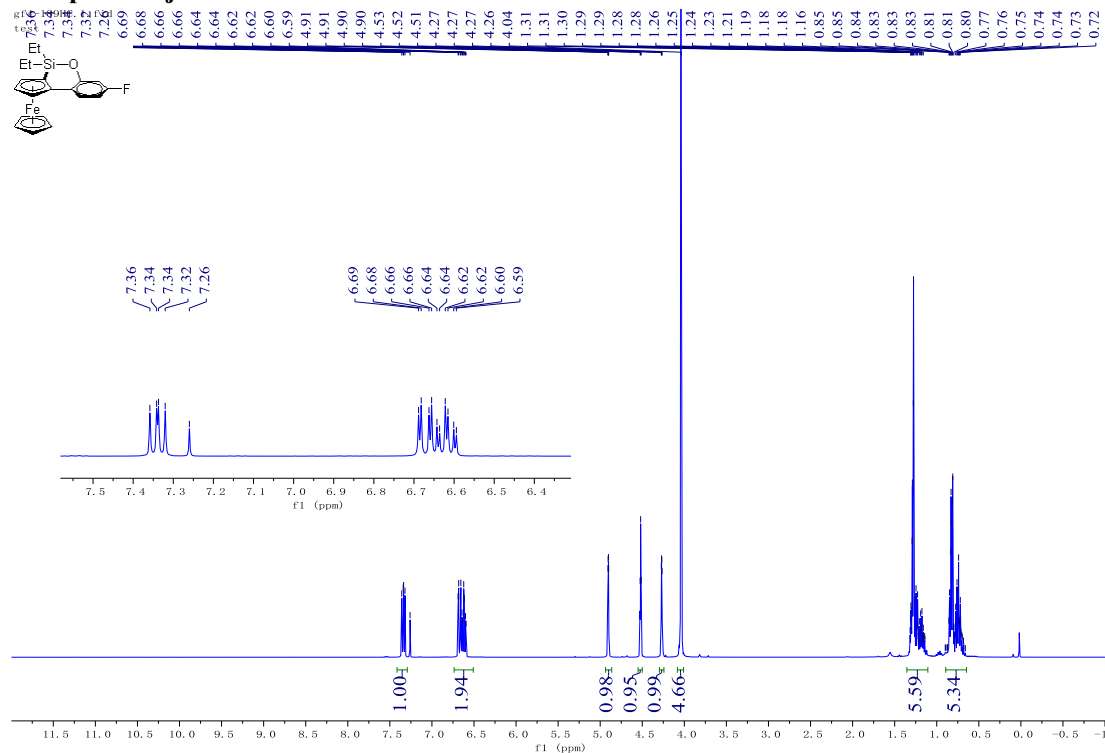
gF5-102HC. 1. f1d
PROTON



gF5-100C. 1. f1d
C13CPD

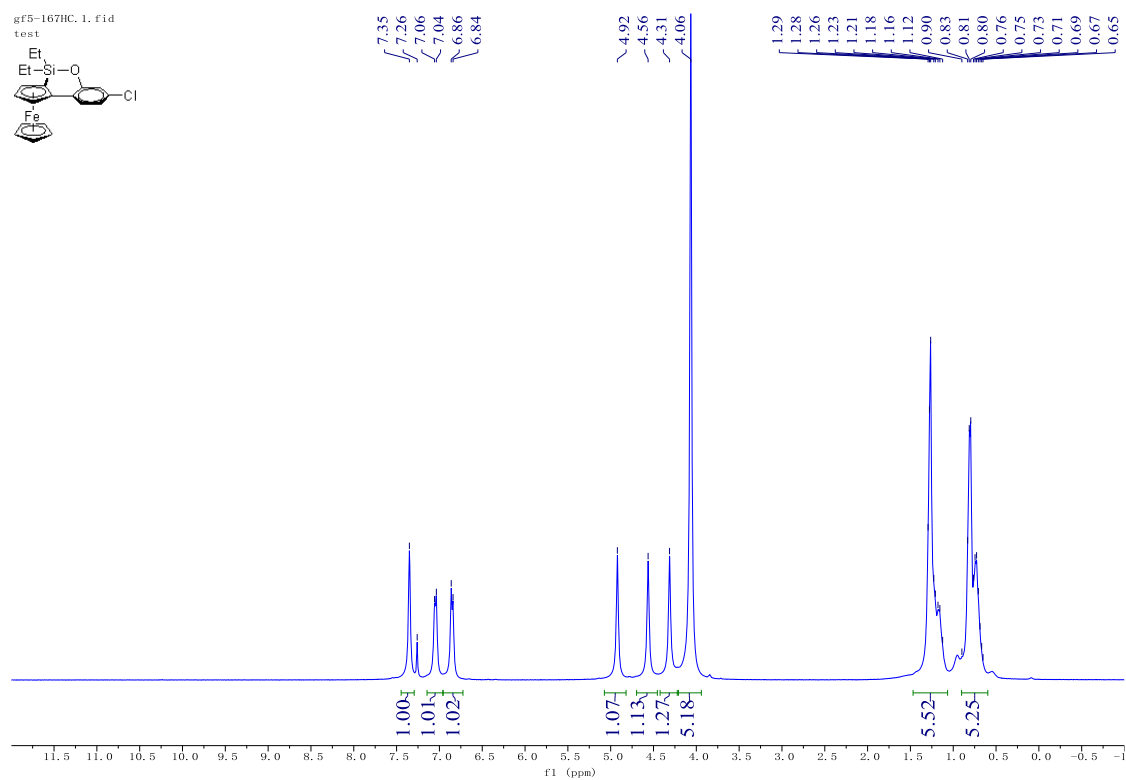
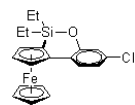


Compound 4j

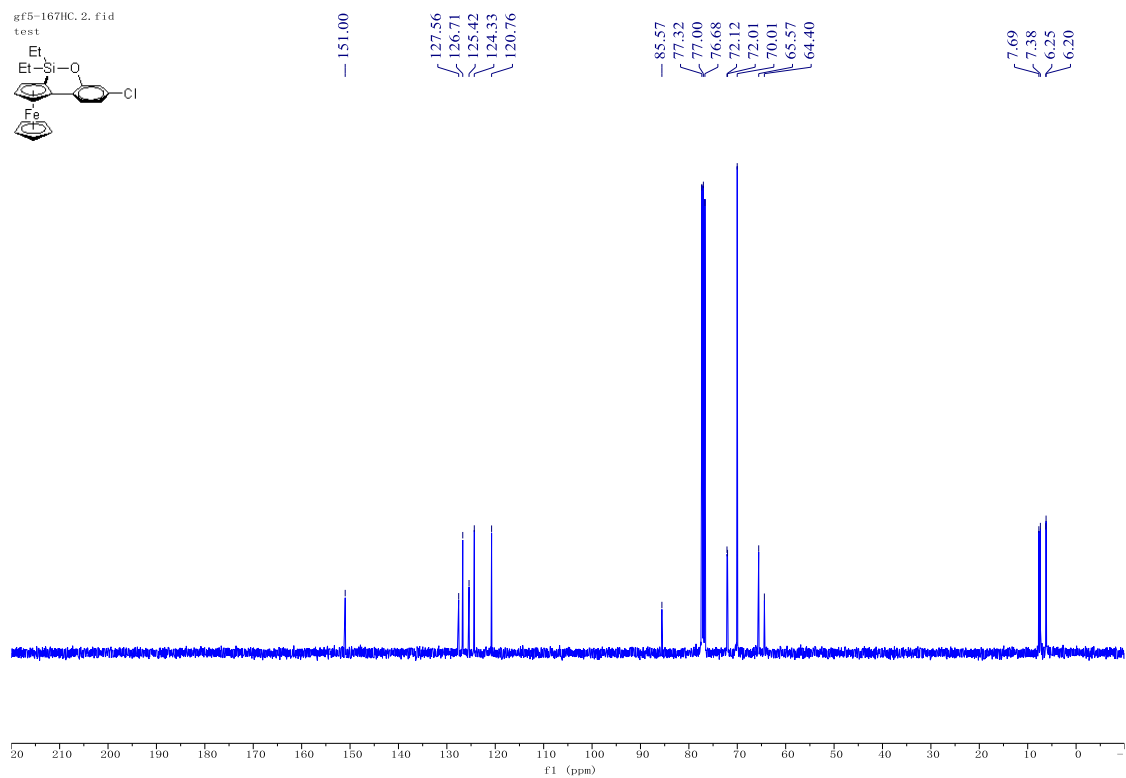
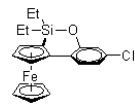


Compound 4k

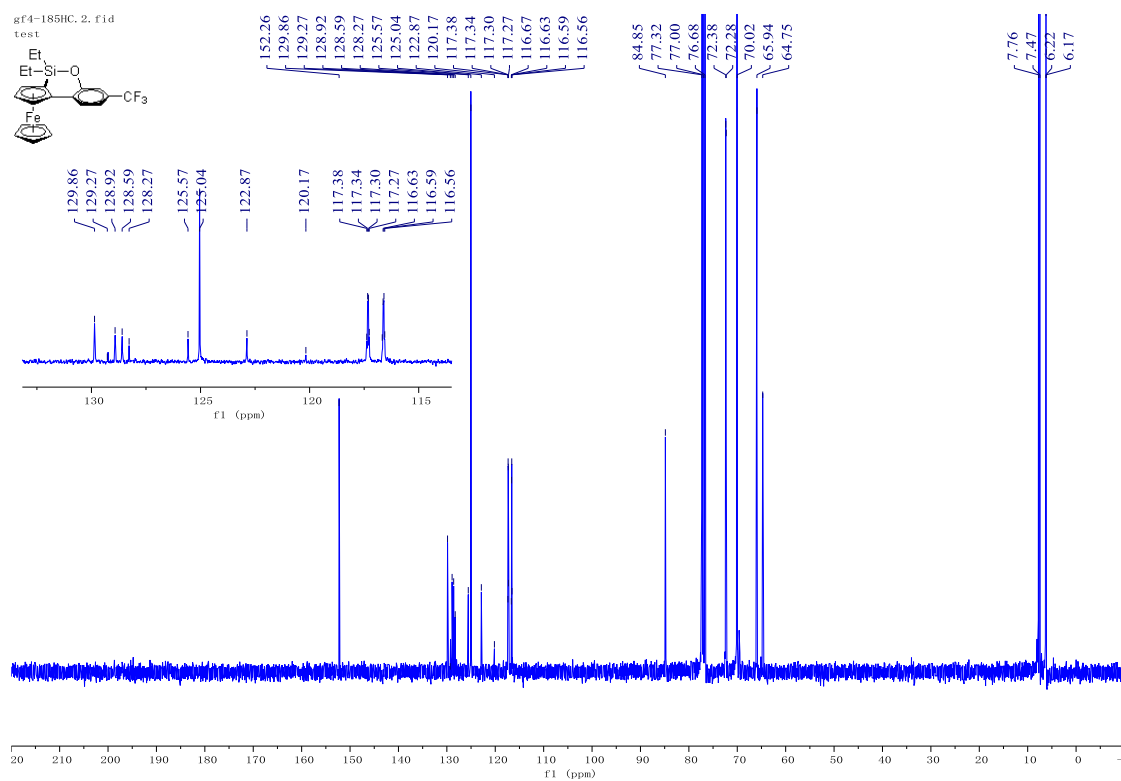
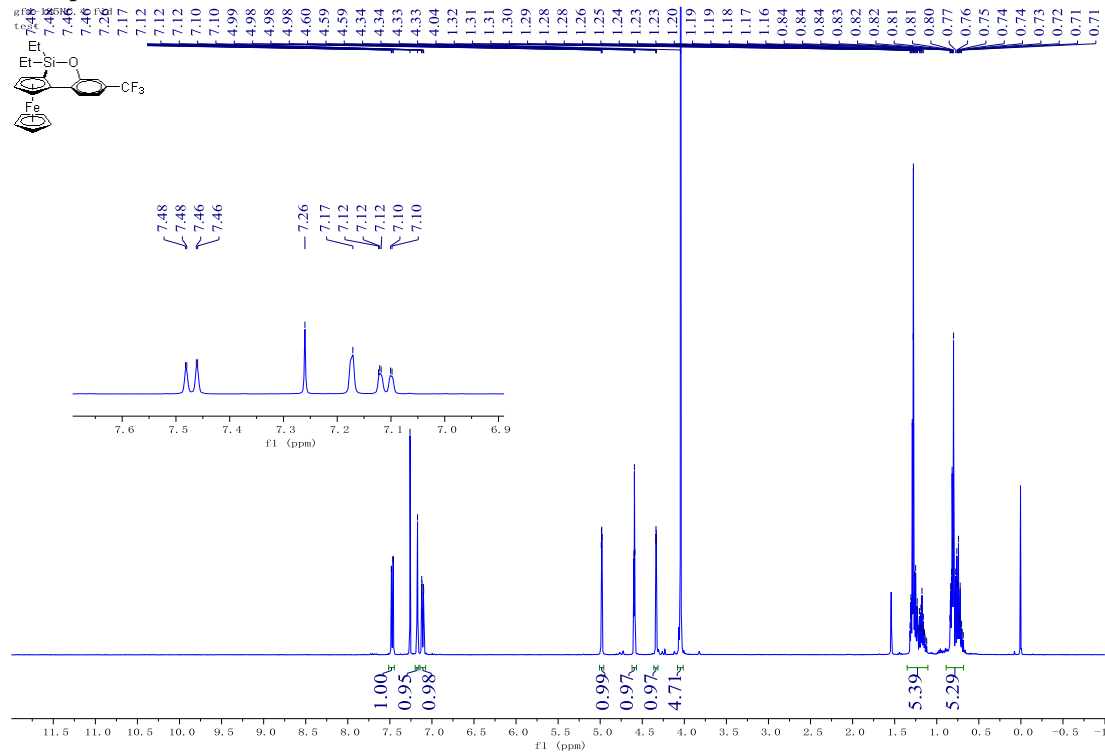
gf5-167HC. 1. fid
test



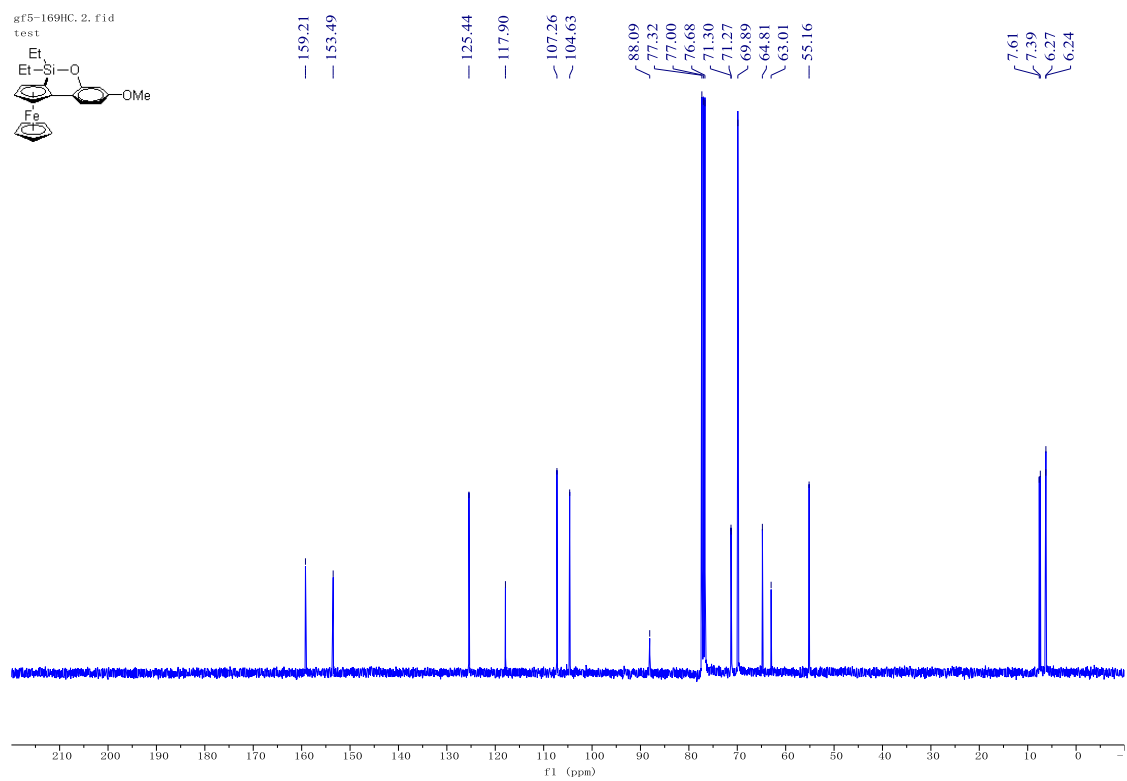
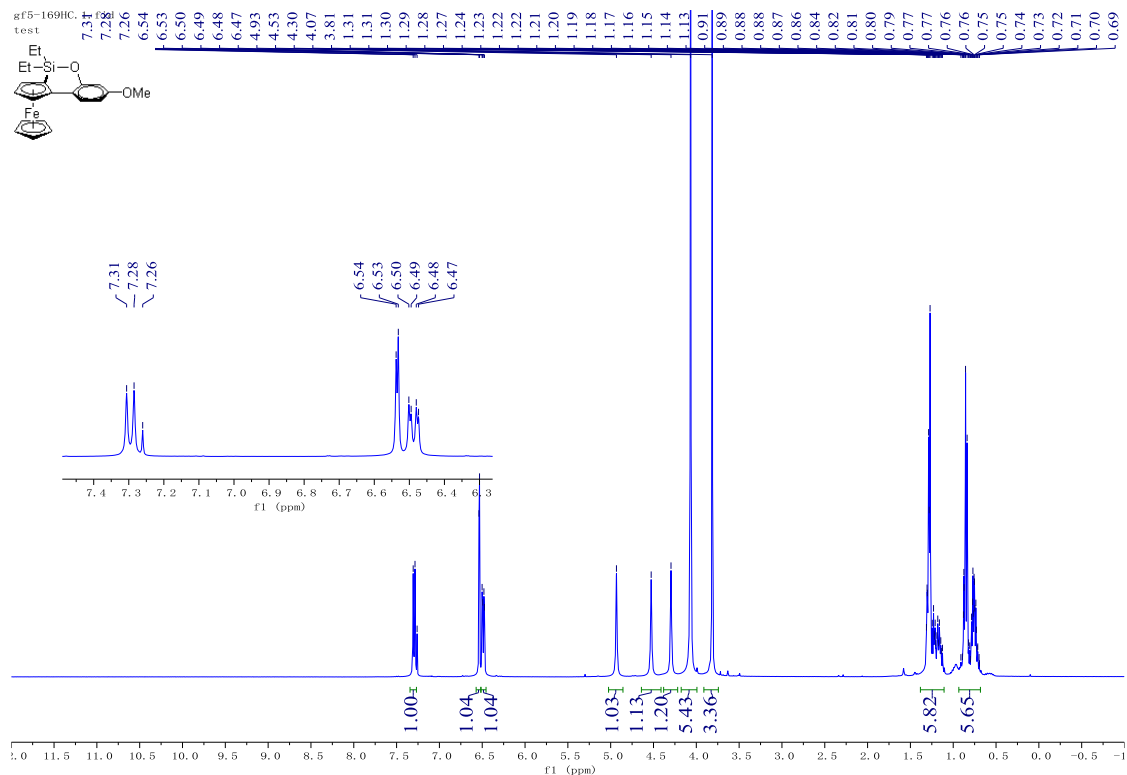
gf5-167HC. 2. fid
test



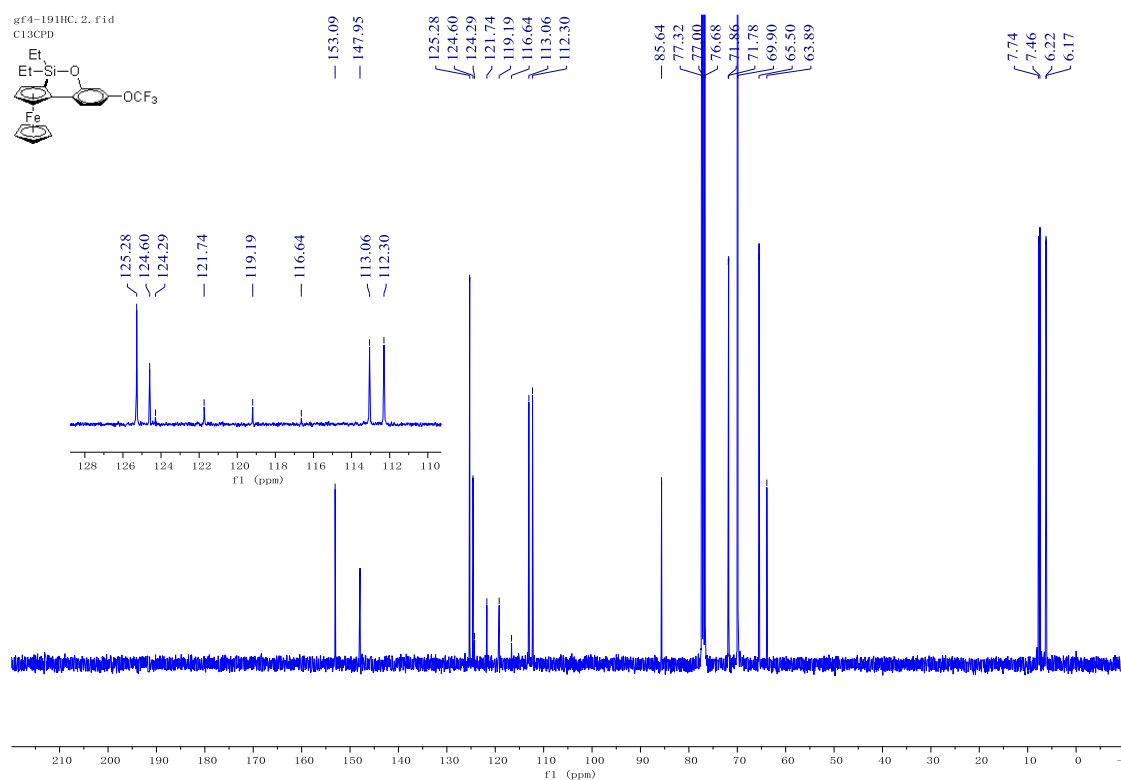
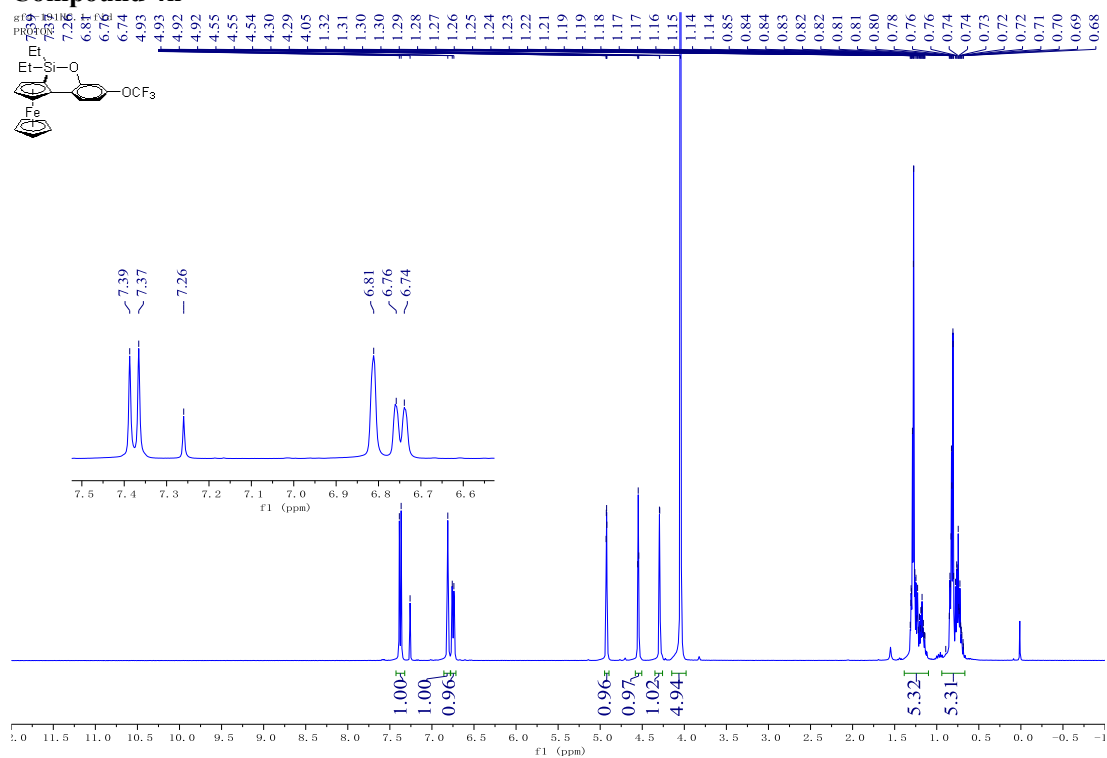
Compound 41



Compound 4m

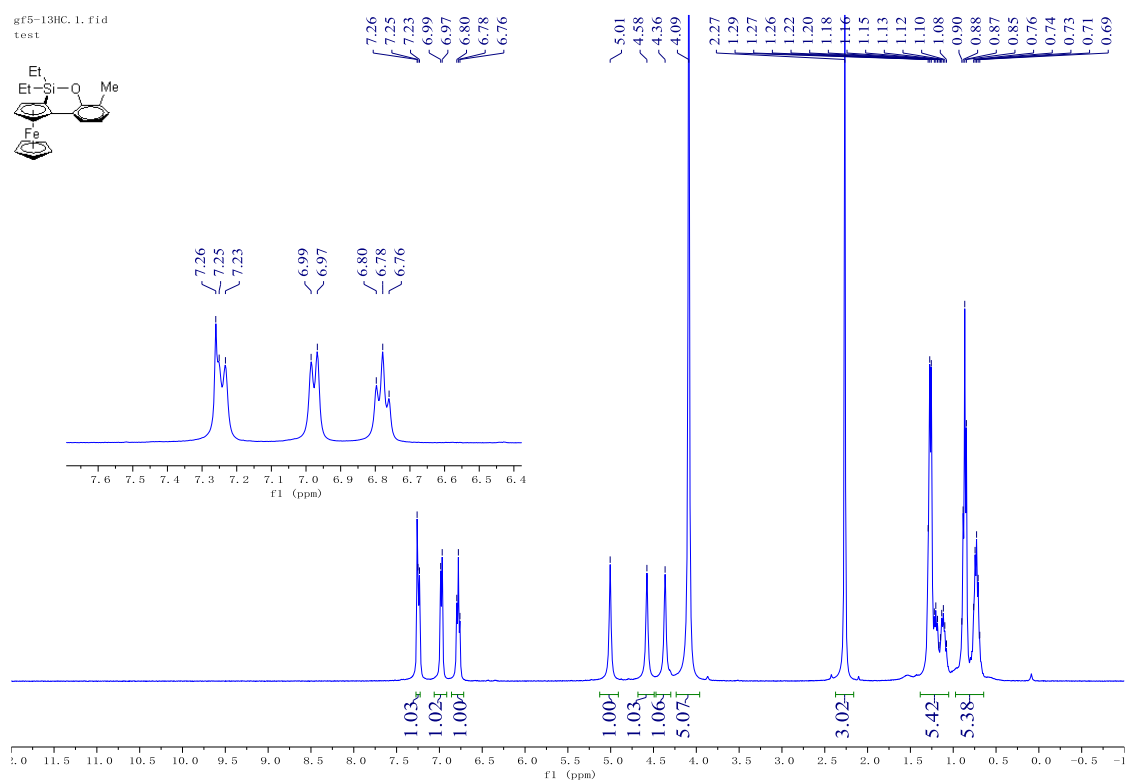
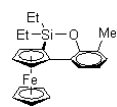


Compound 4n

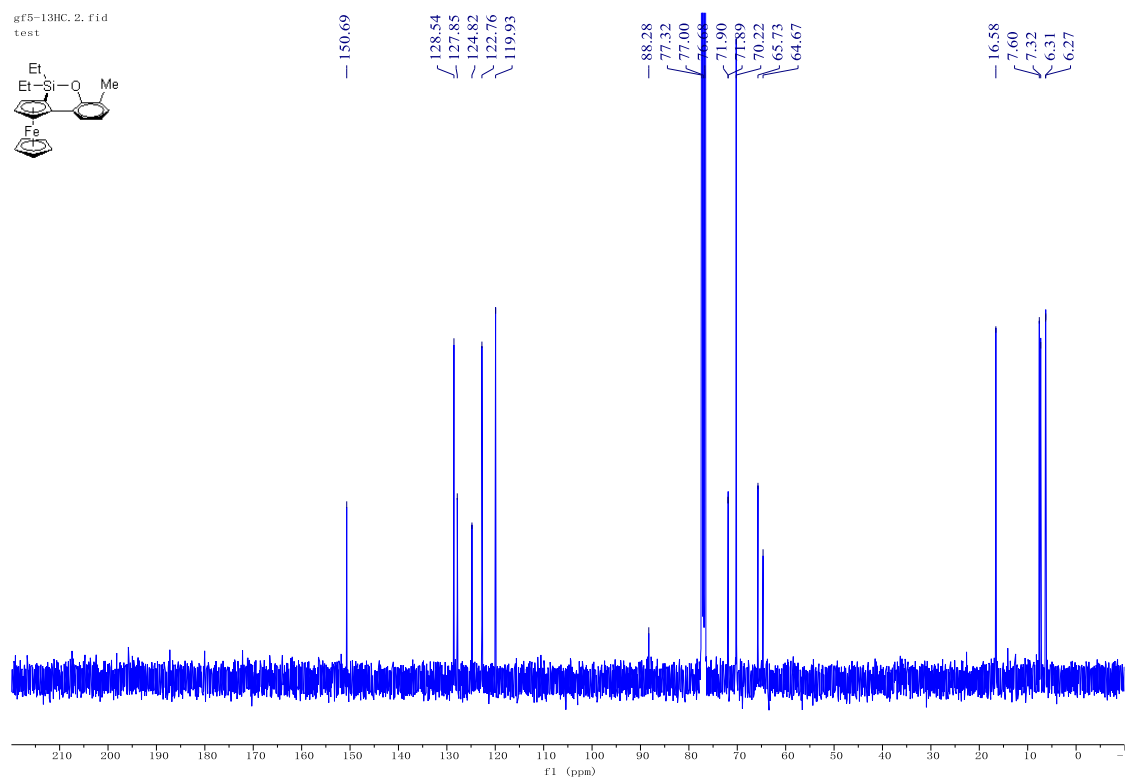
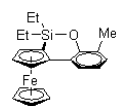


Compound 4o

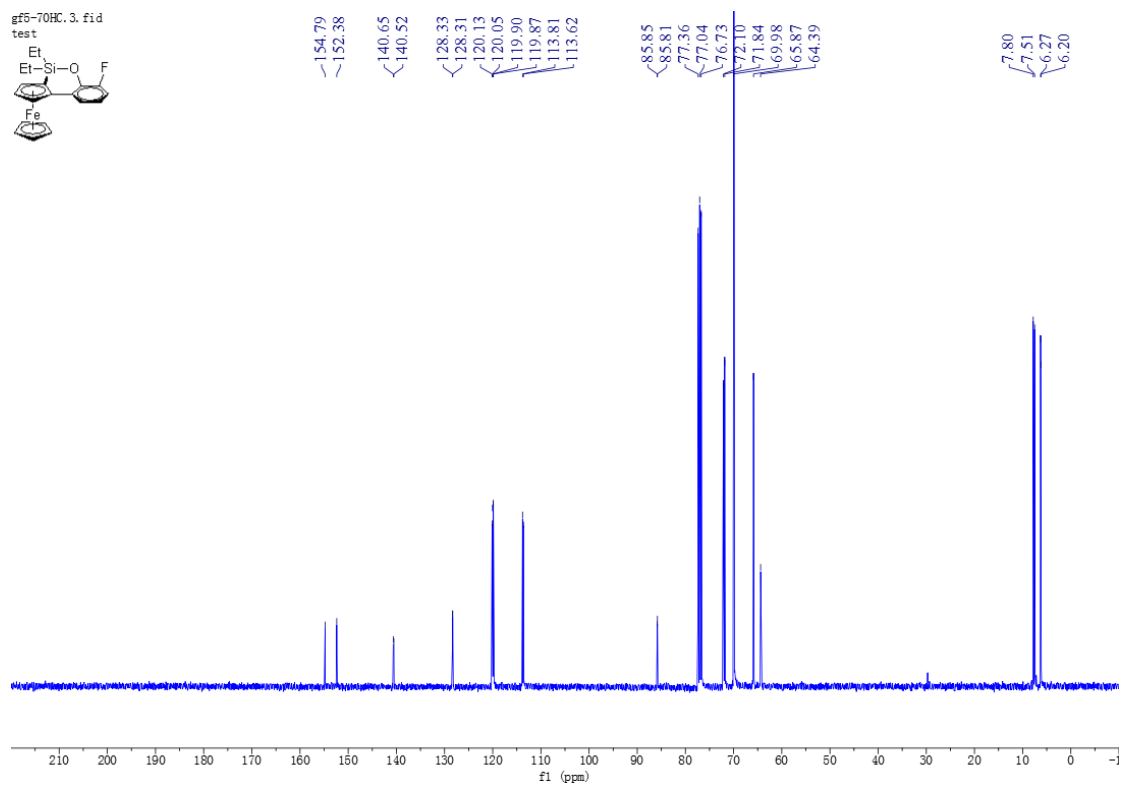
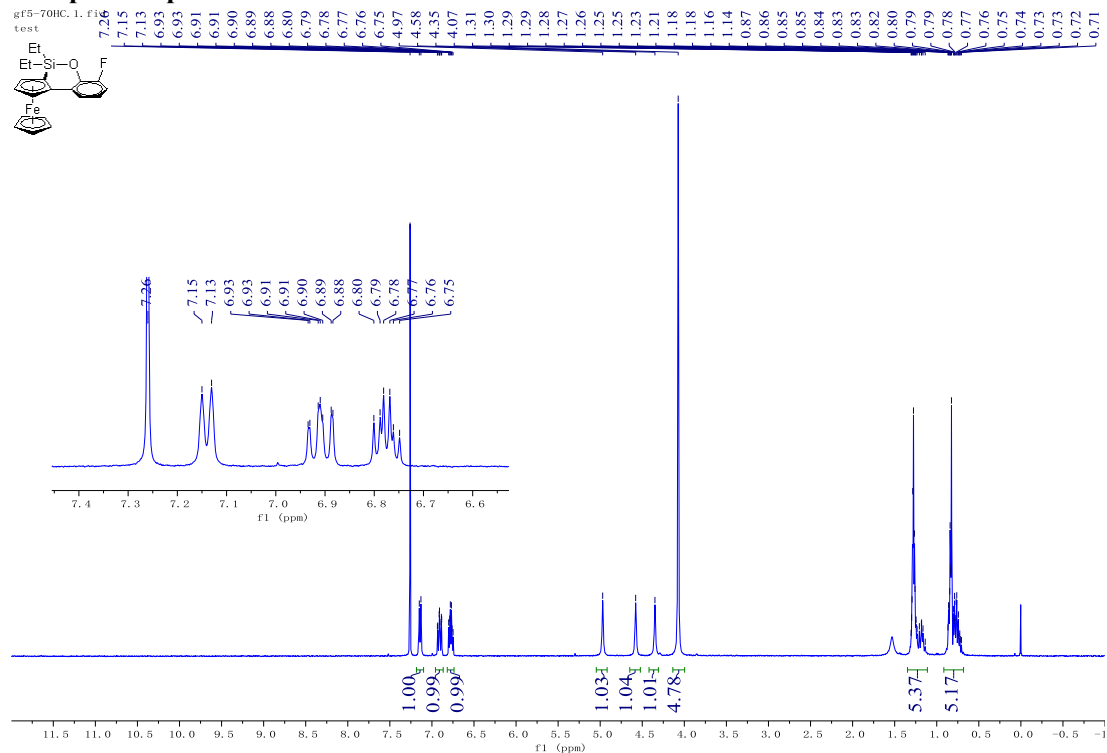
gF5-13HC. 1. fid
test



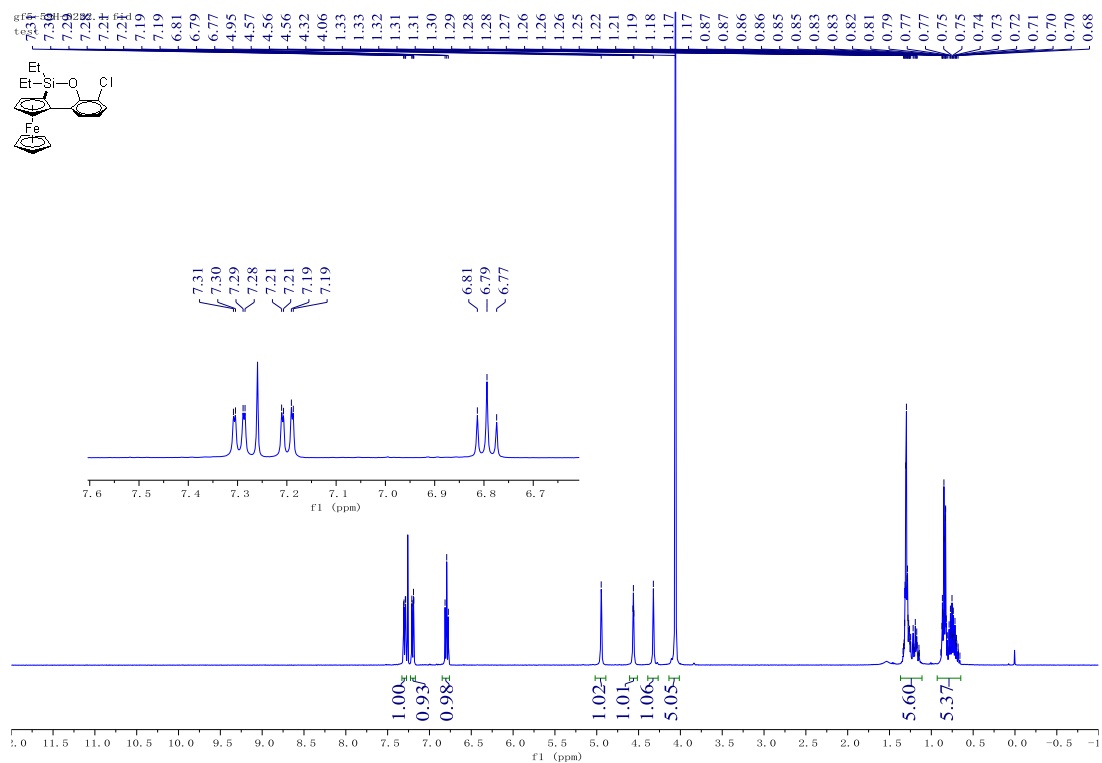
gF5-13HC. 2. fid
test



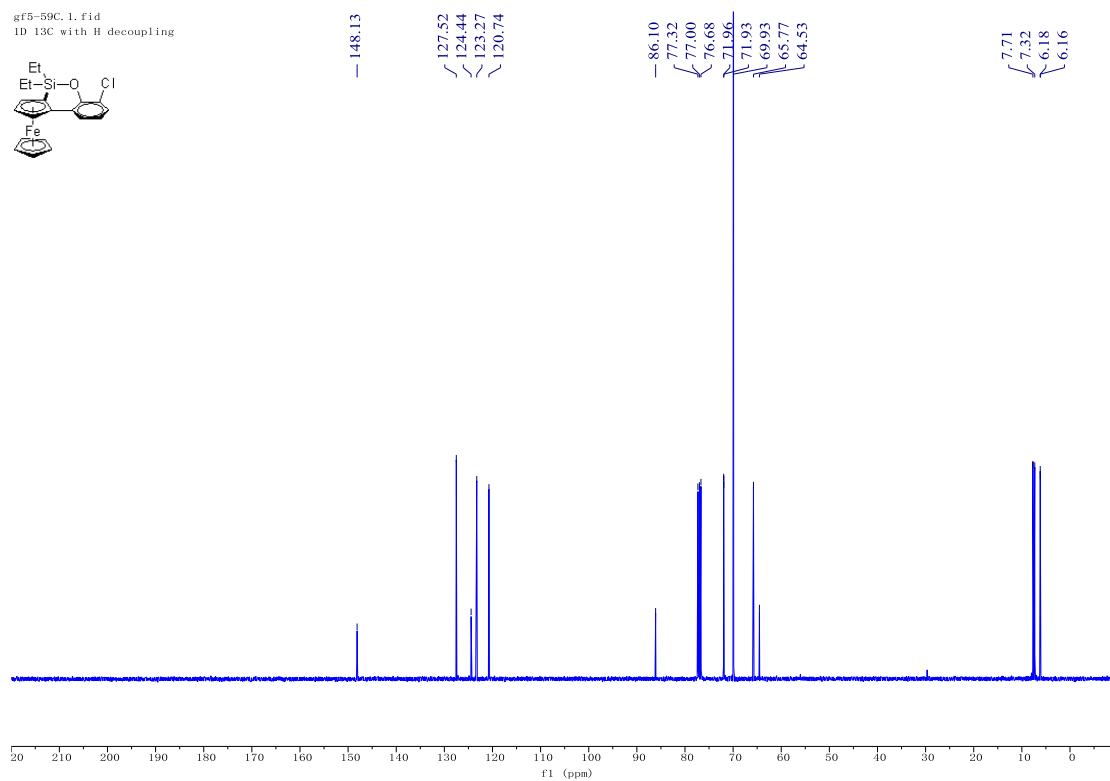
Compound 4p



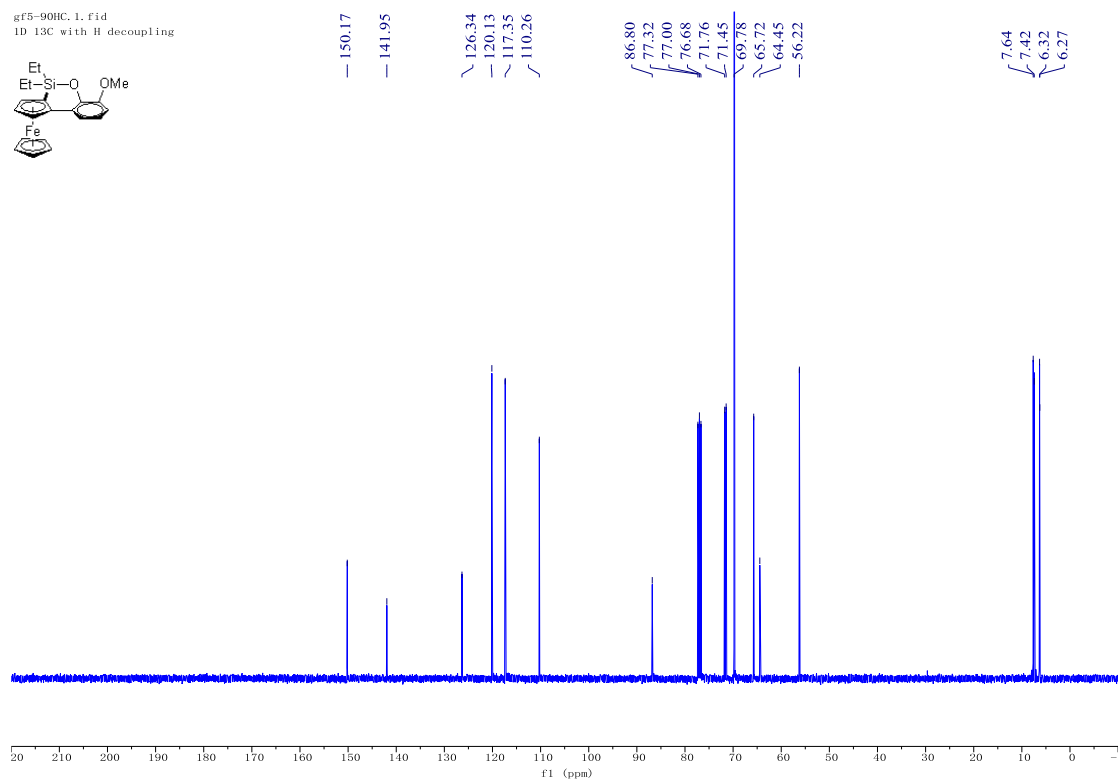
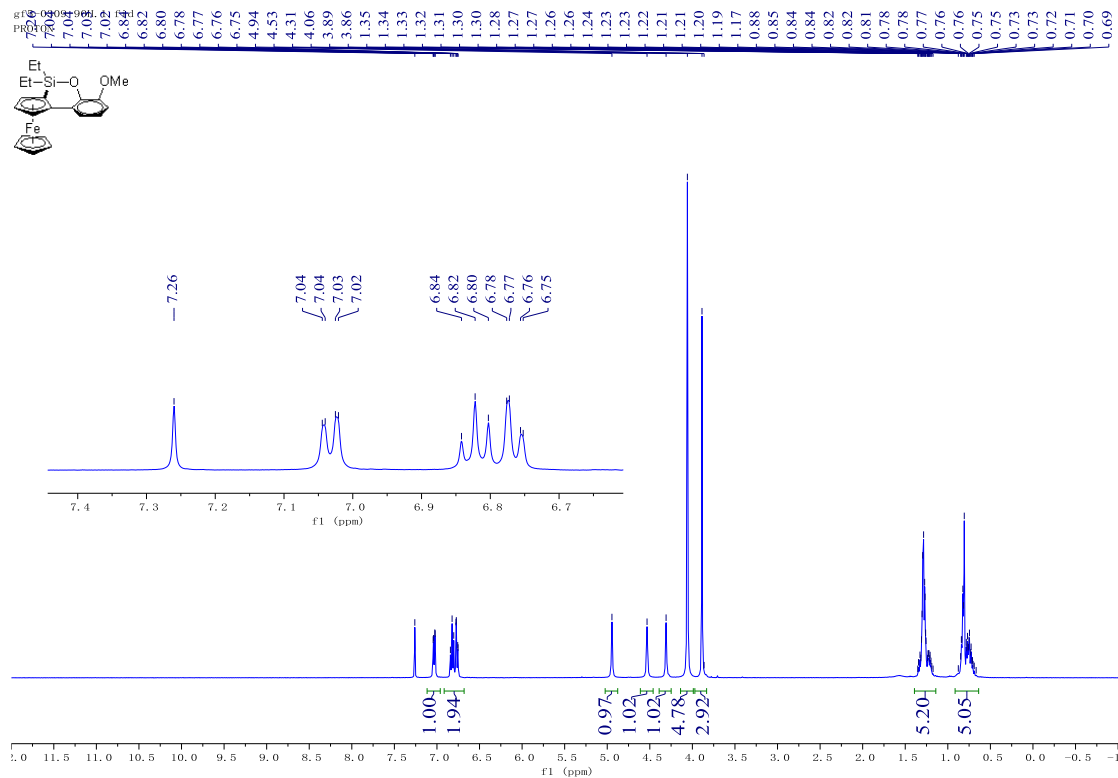
Compound 4q



gf5-59C.1.fid
ID 13C with H decoupling

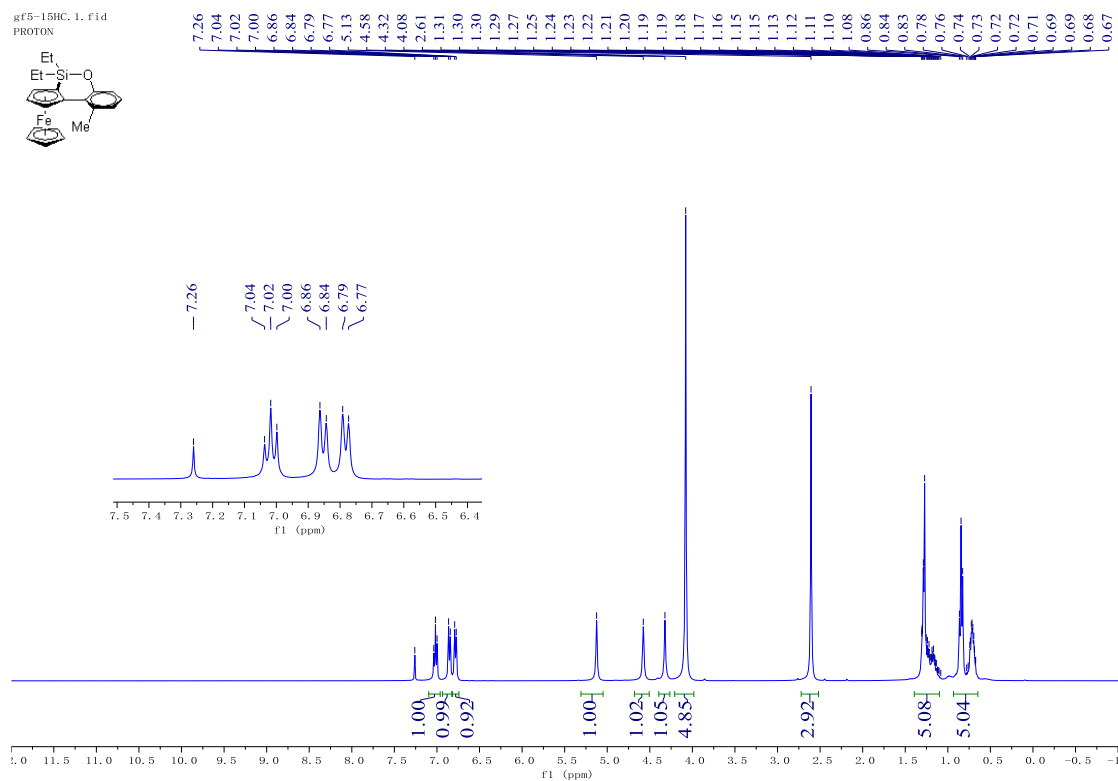
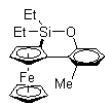


Compound 4r

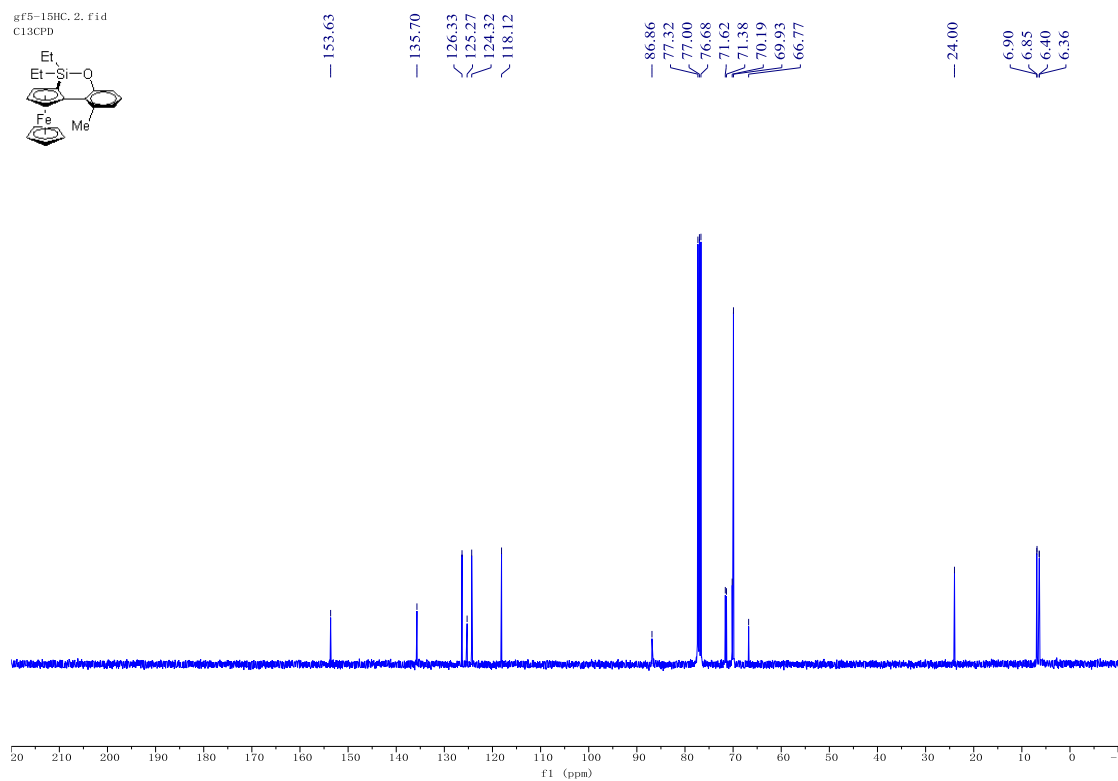
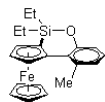


Compound 4s

gF5-15HC. 1. f1d
PROTON

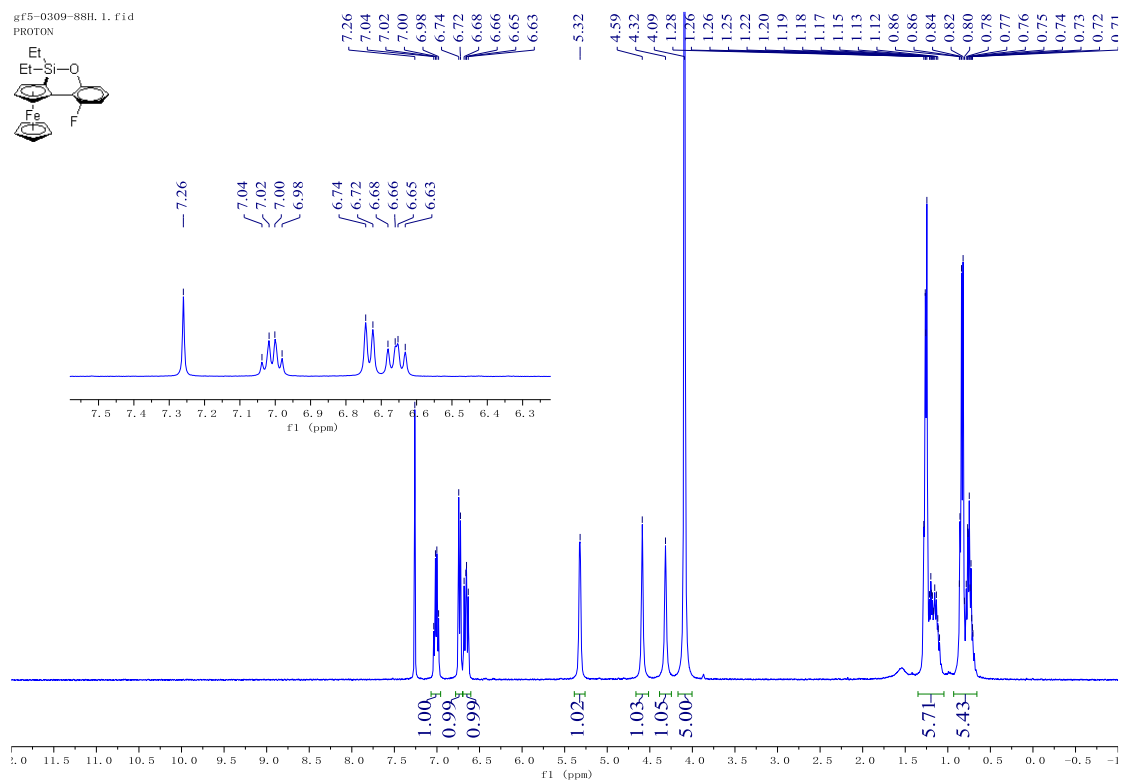
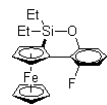


gF5-15HC. 2. f1d
C13CPD

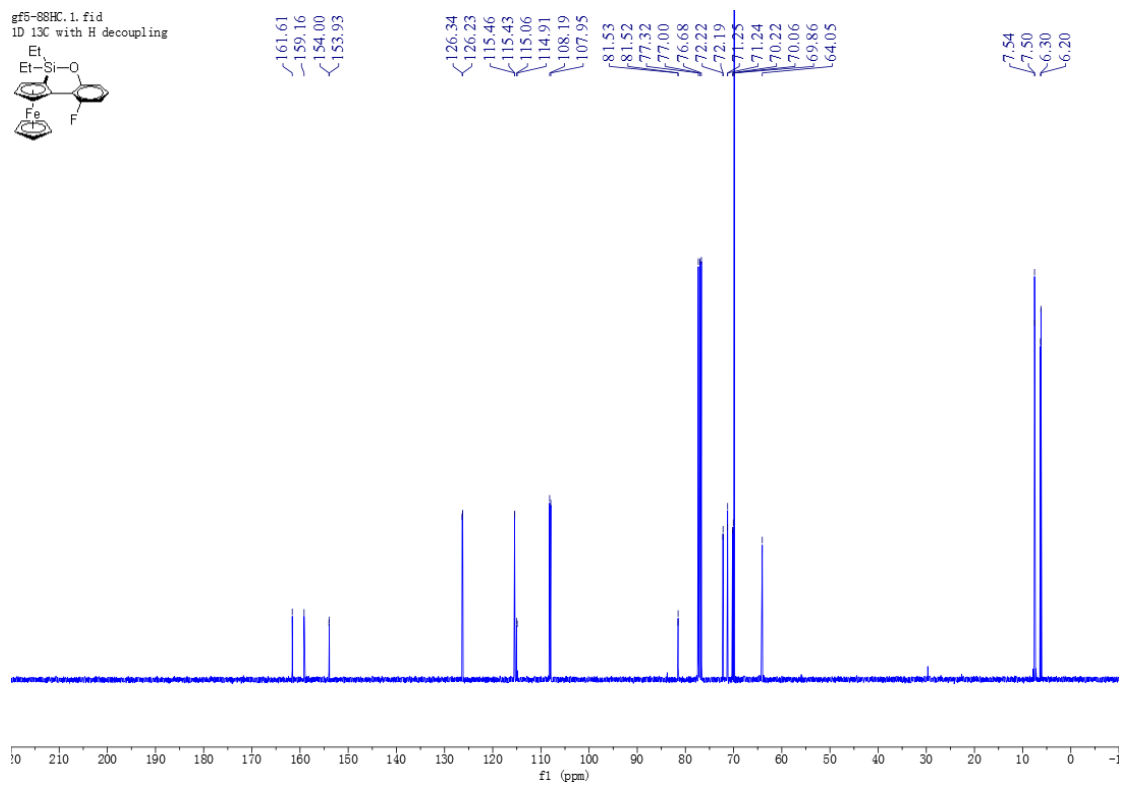
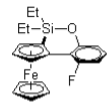


Compound 4t

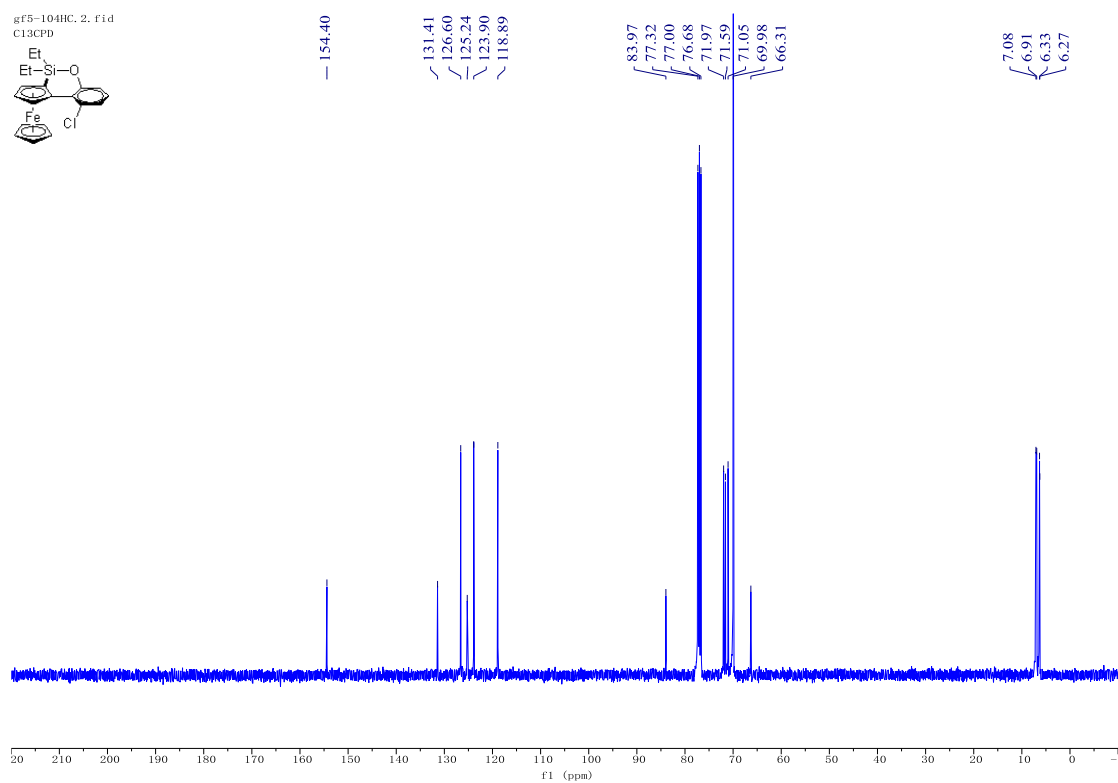
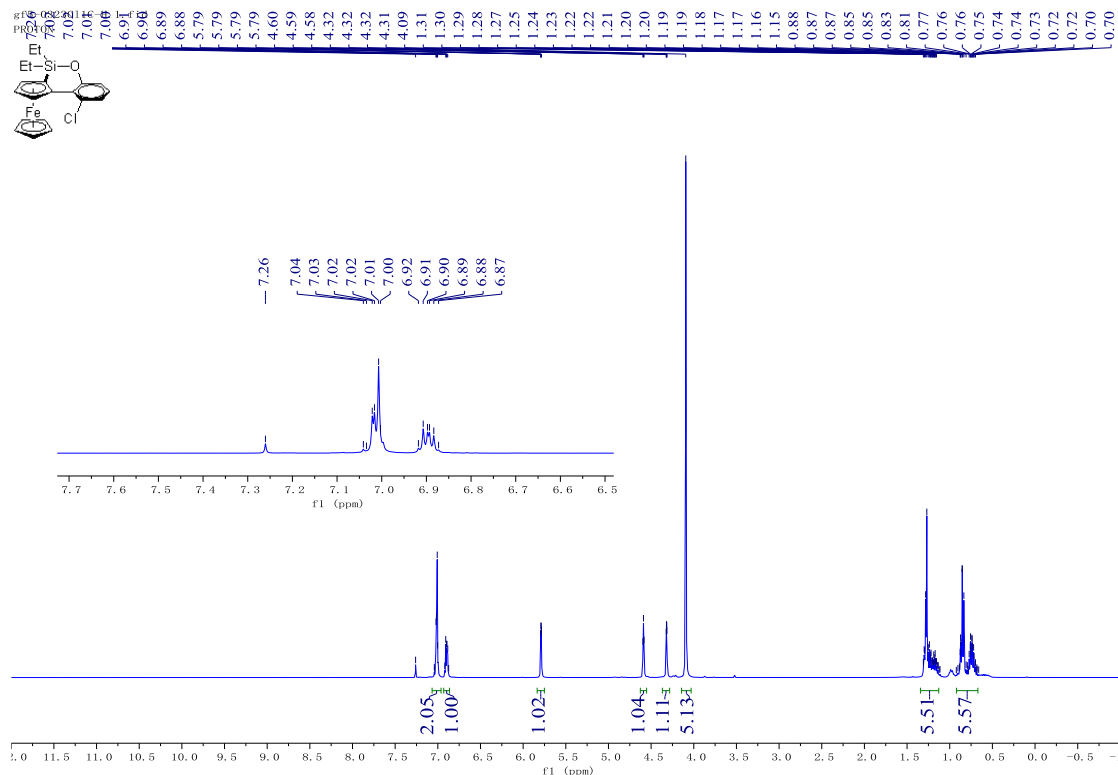
gf5-0309-88H.1.fid
PROTON



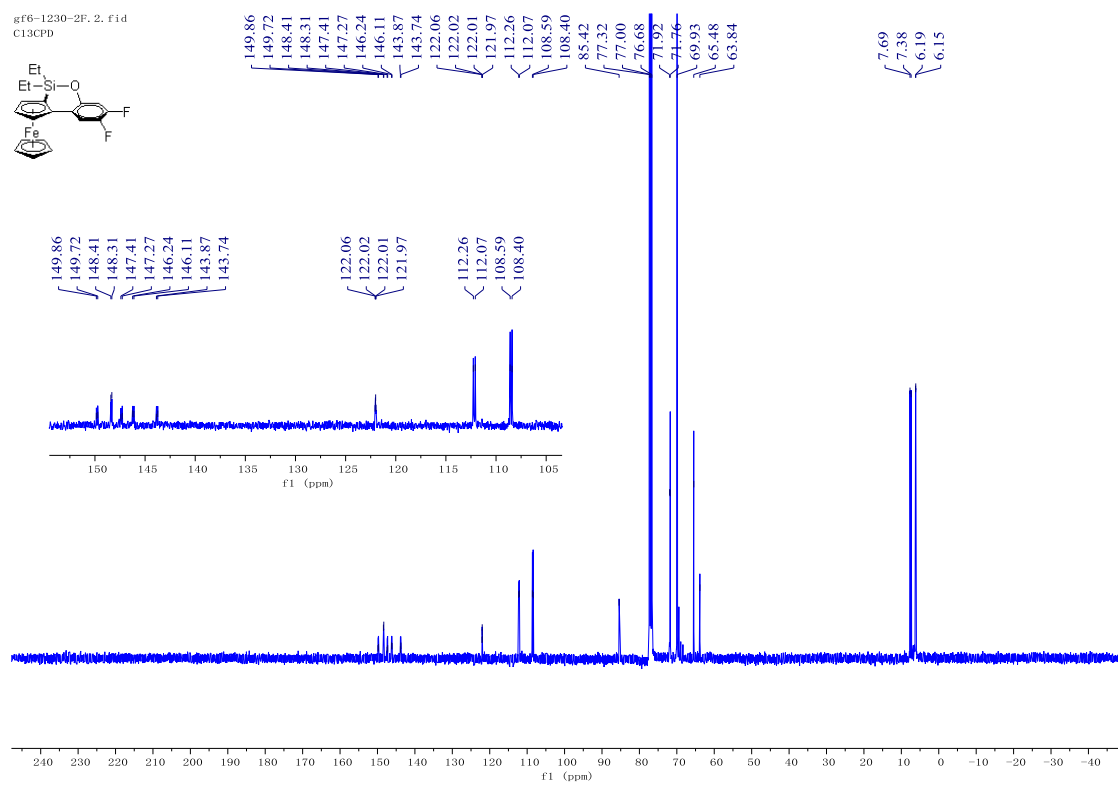
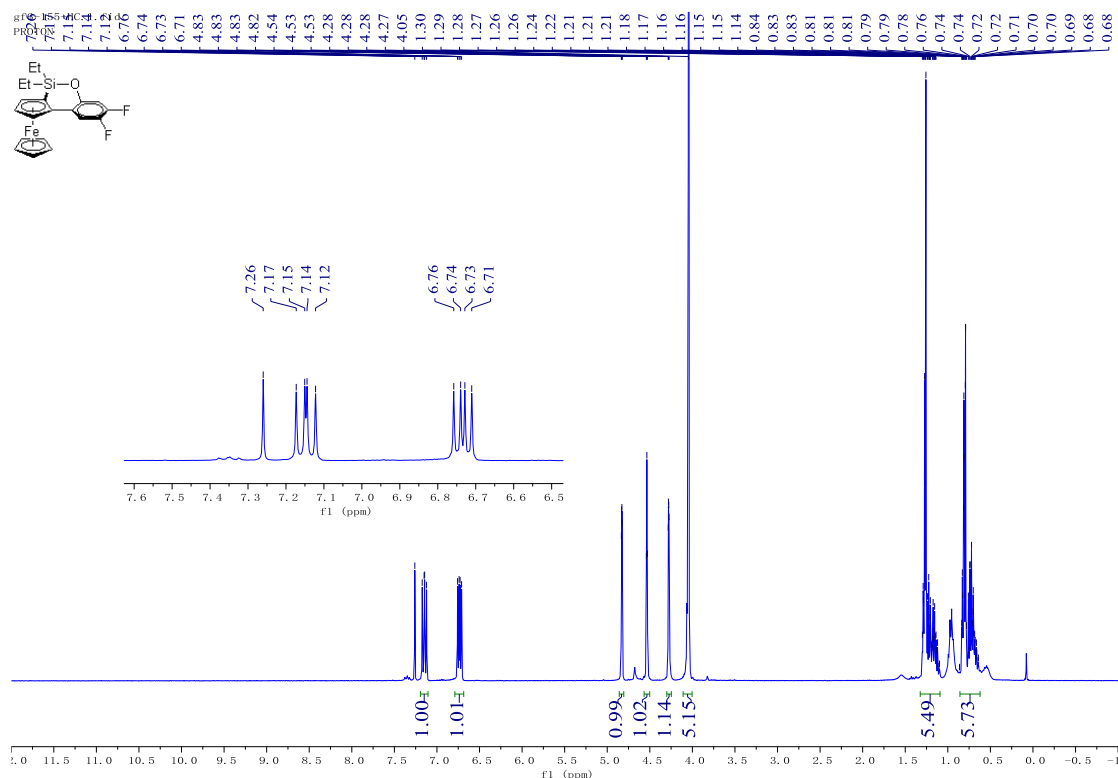
gf5-88HC.1.fid
ID 13C with H decoupling



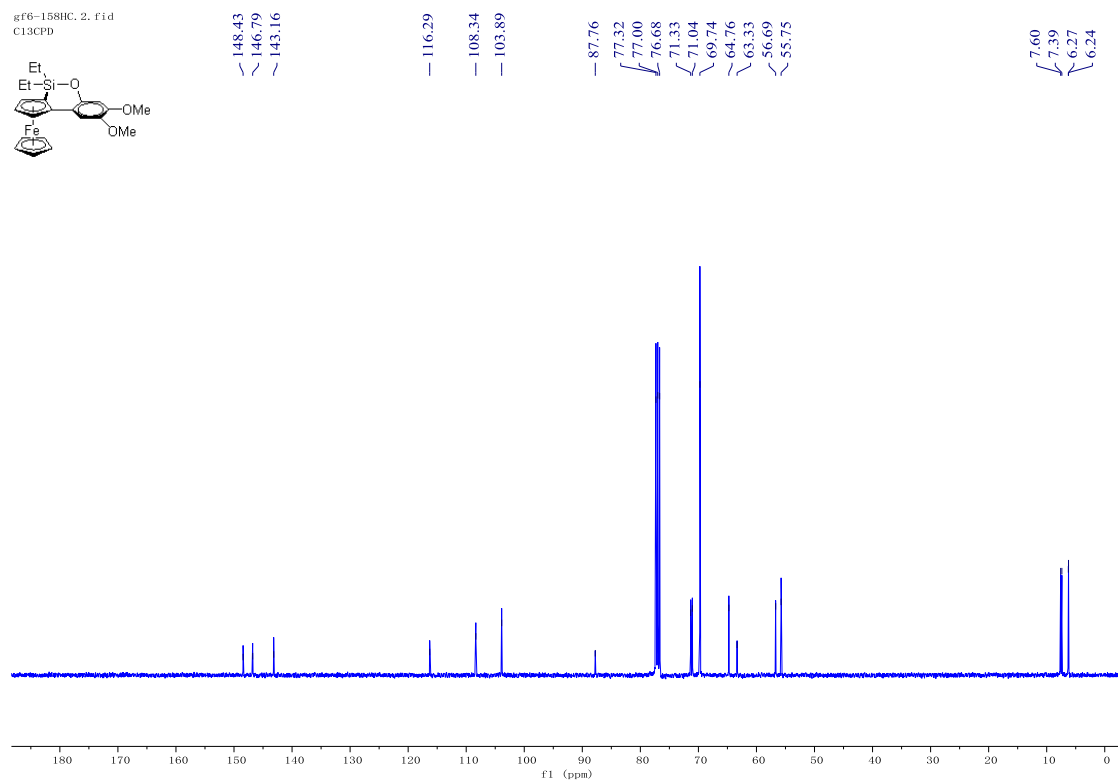
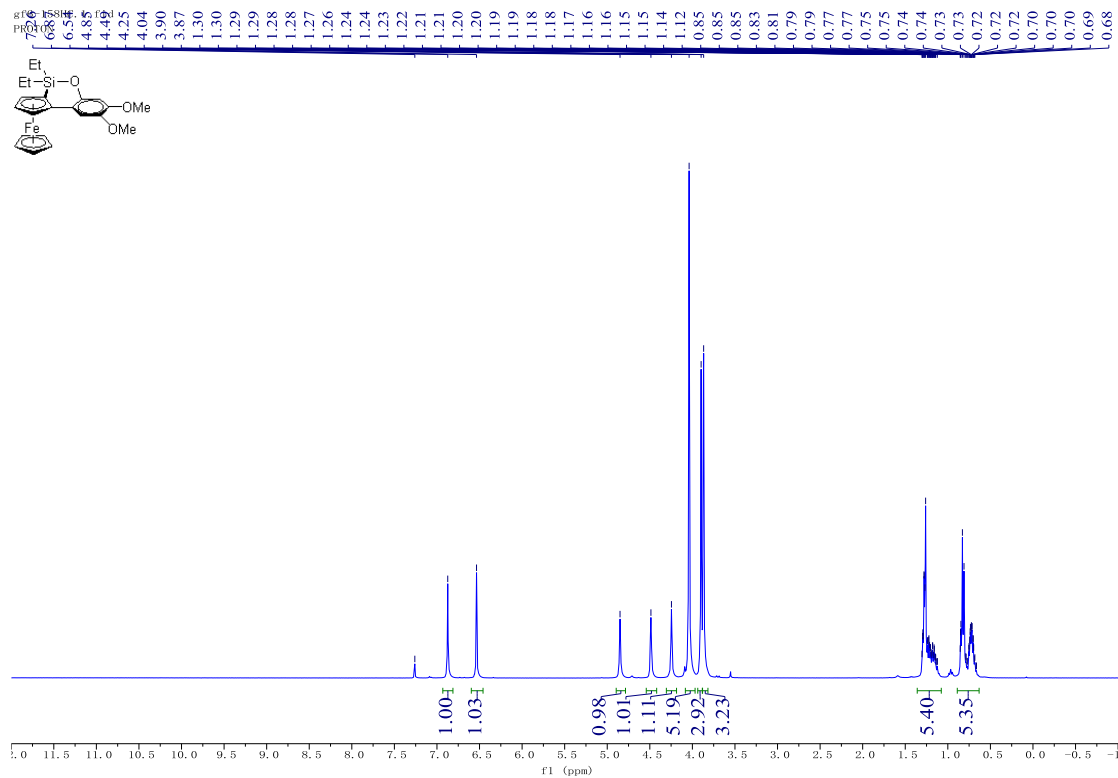
Compound 4u



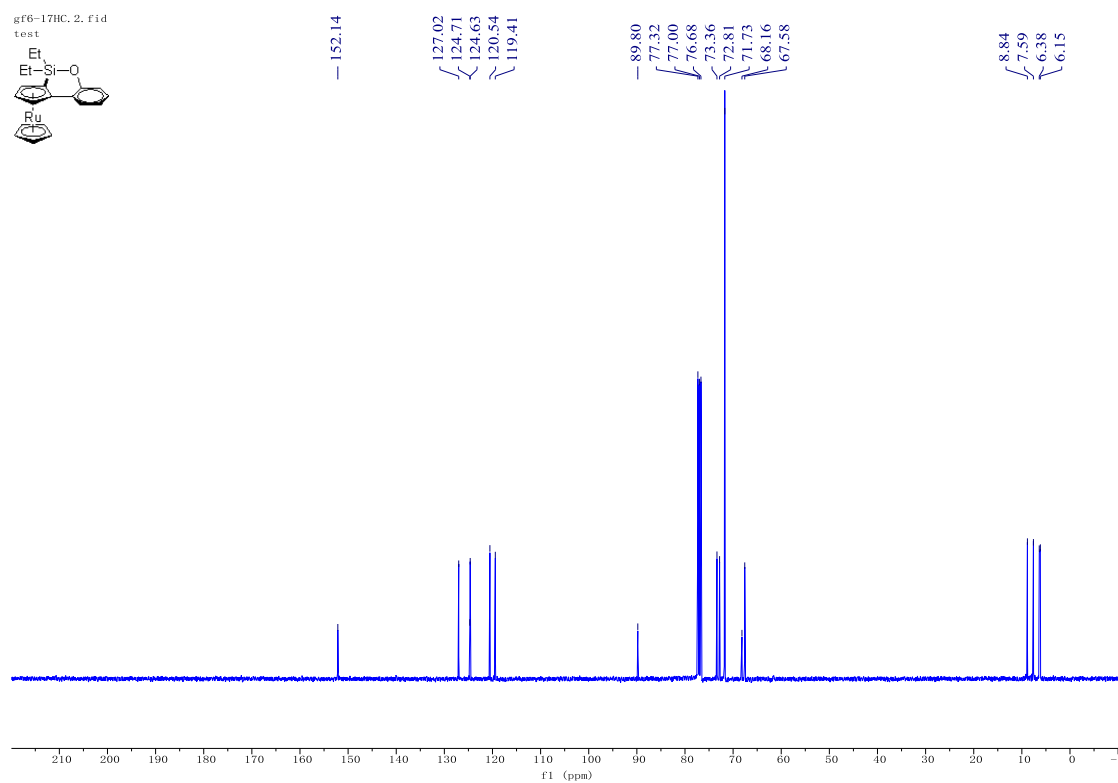
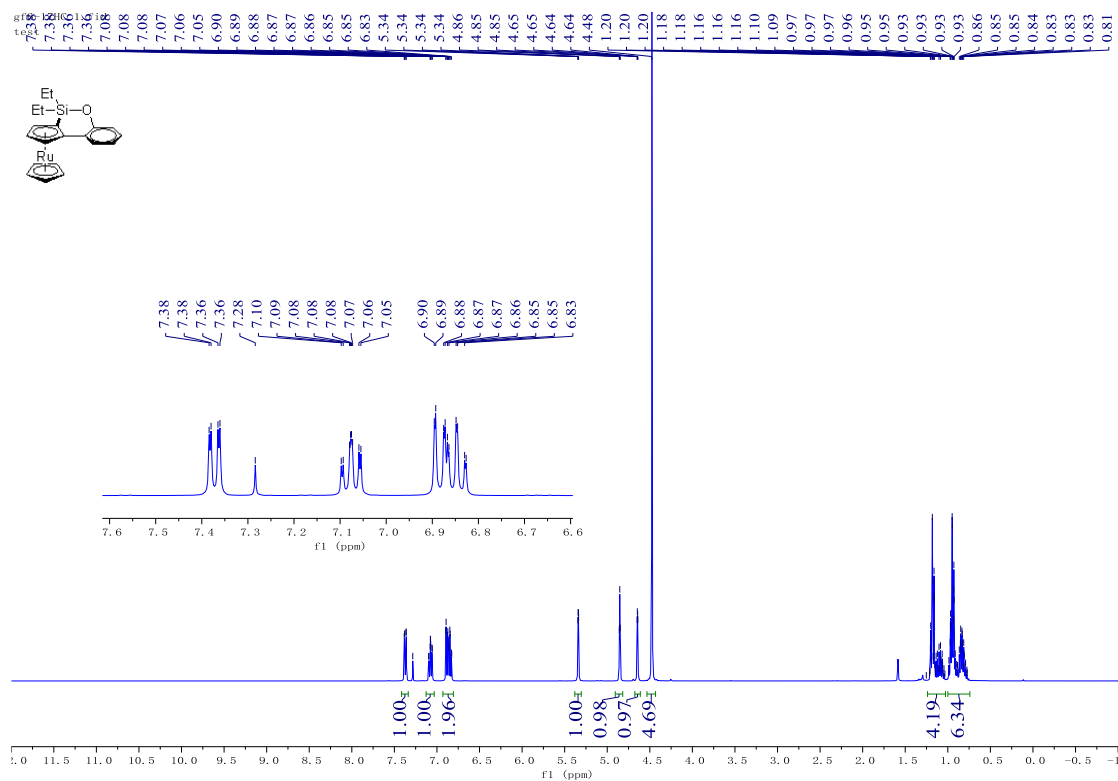
Compound 4w



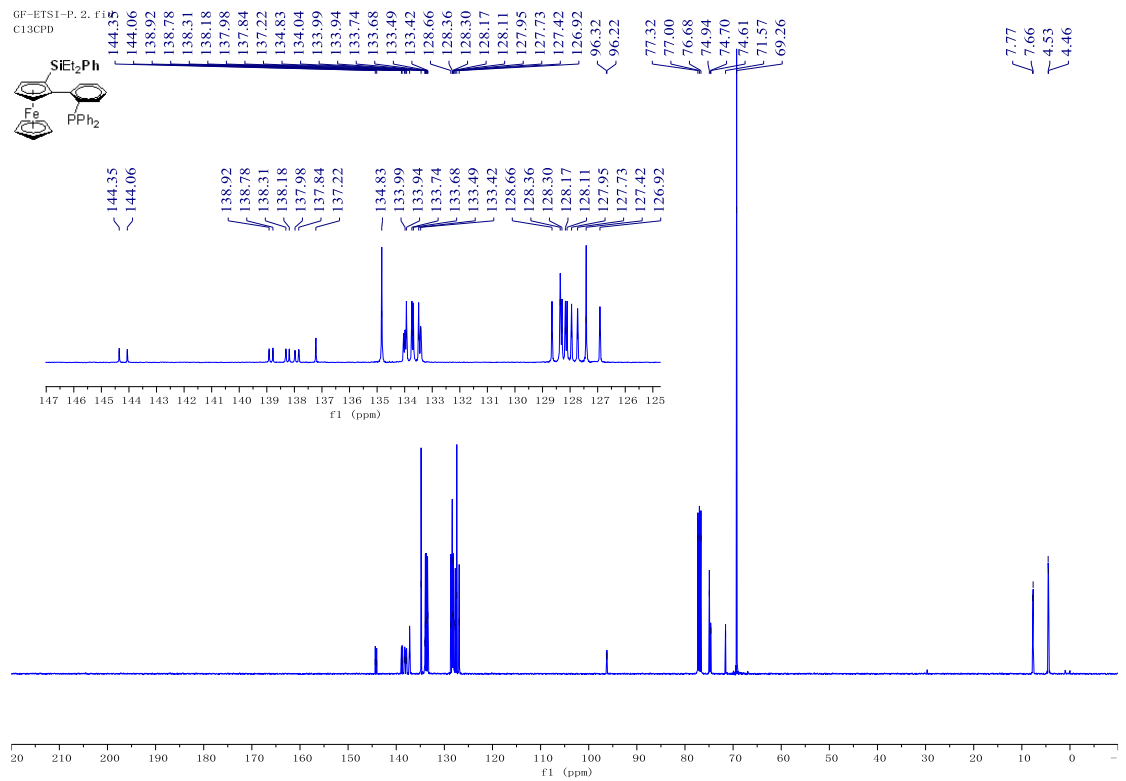
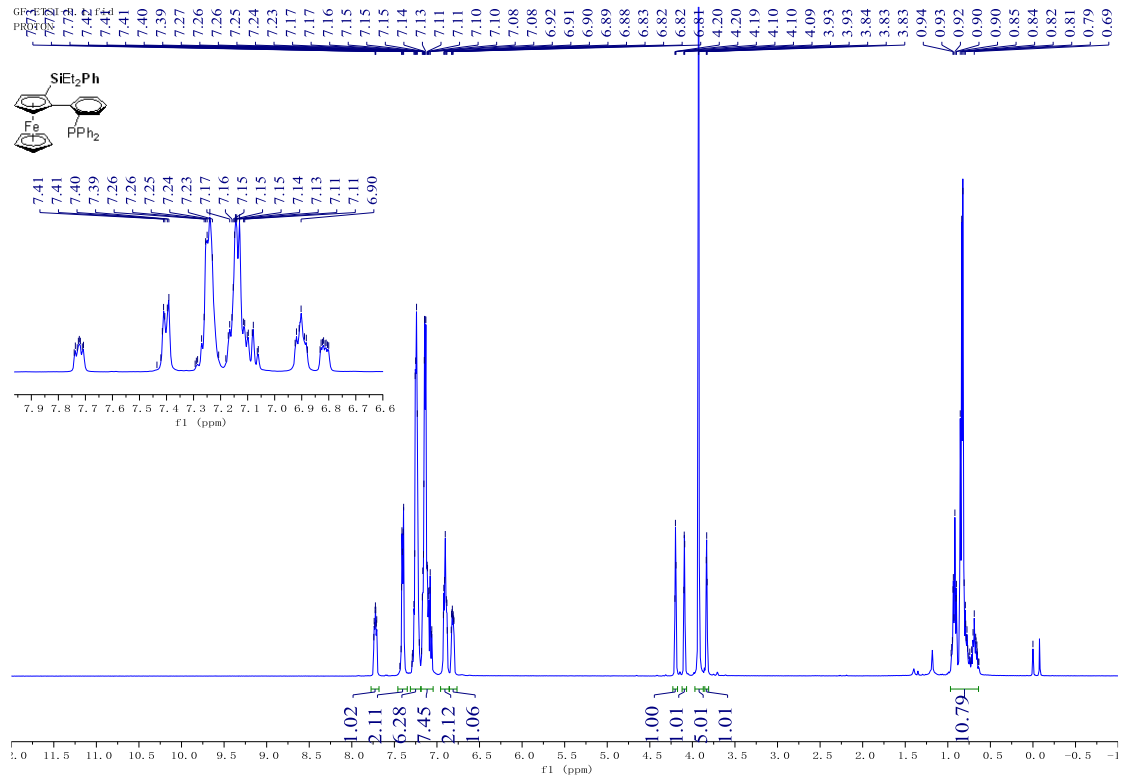
Compound 4x



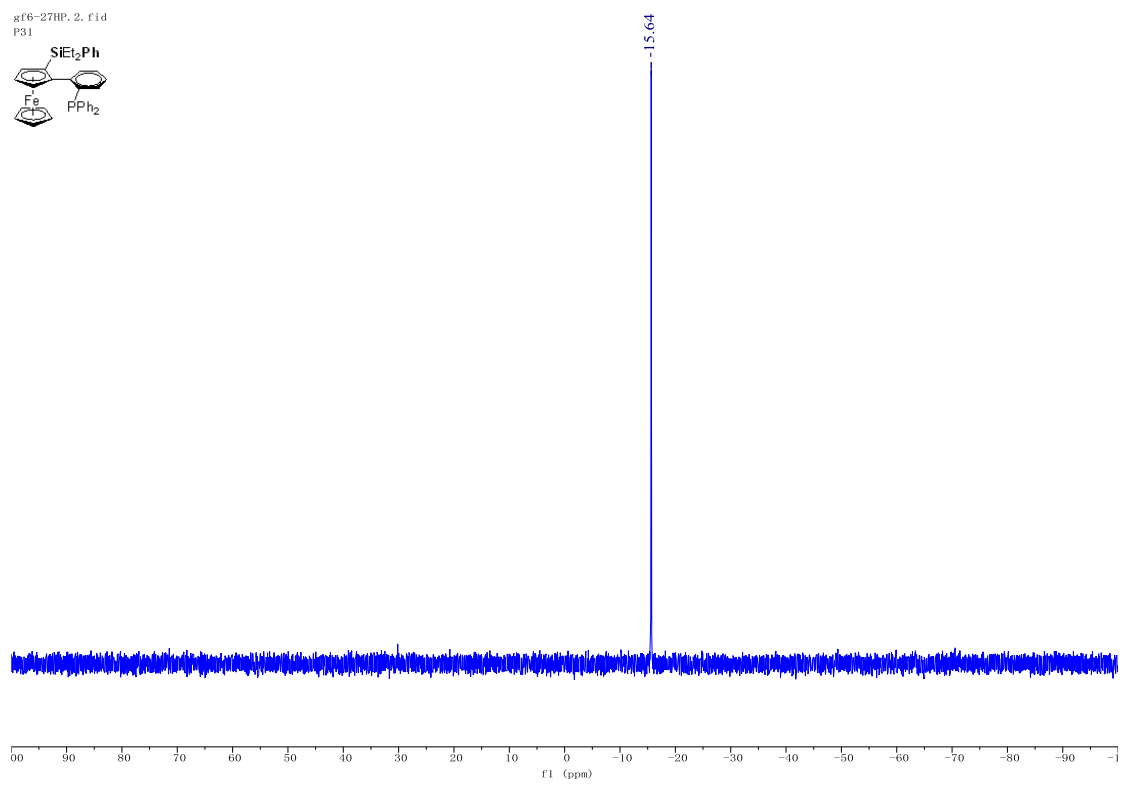
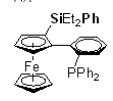
Compound 4y



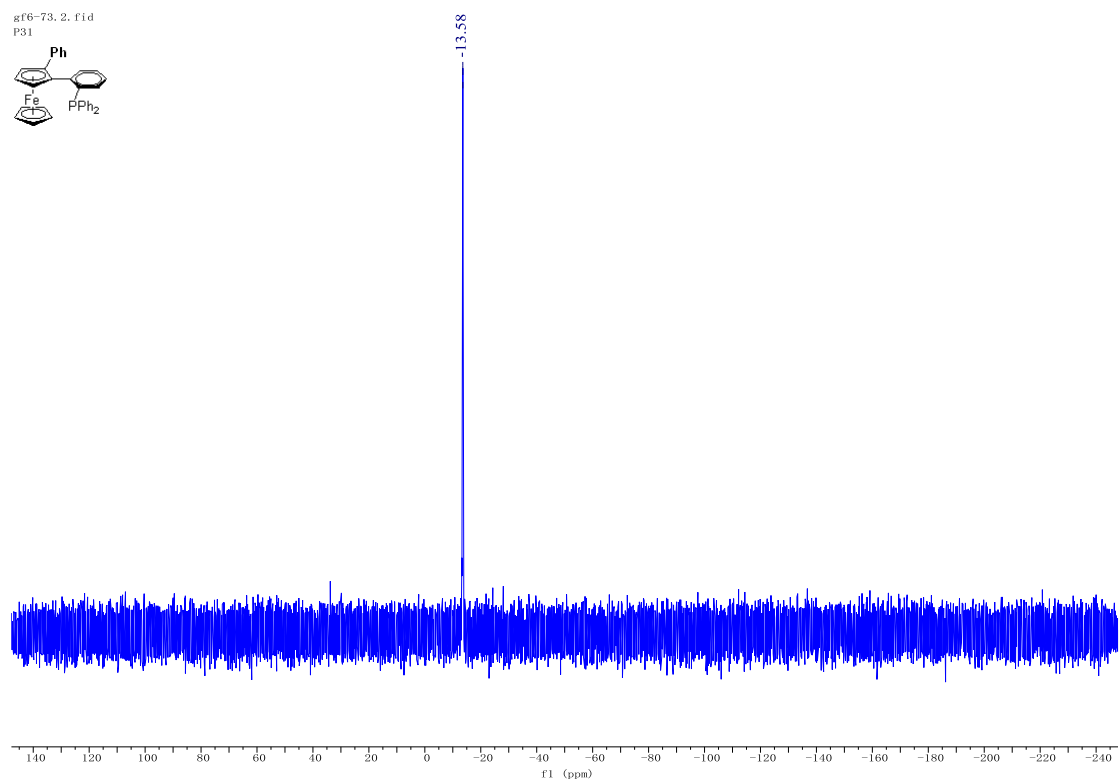
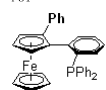
Compound FcL1



gF6-27HP. 2. f1d
P31

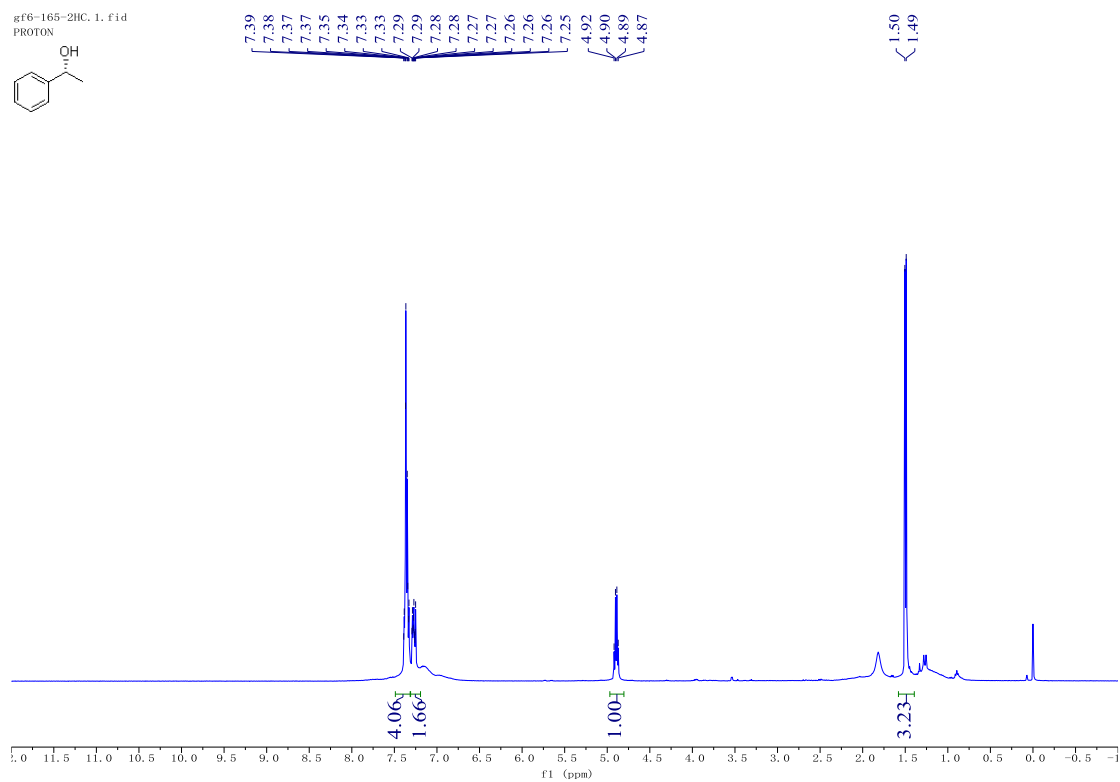


gf6-73.2.fid
P31

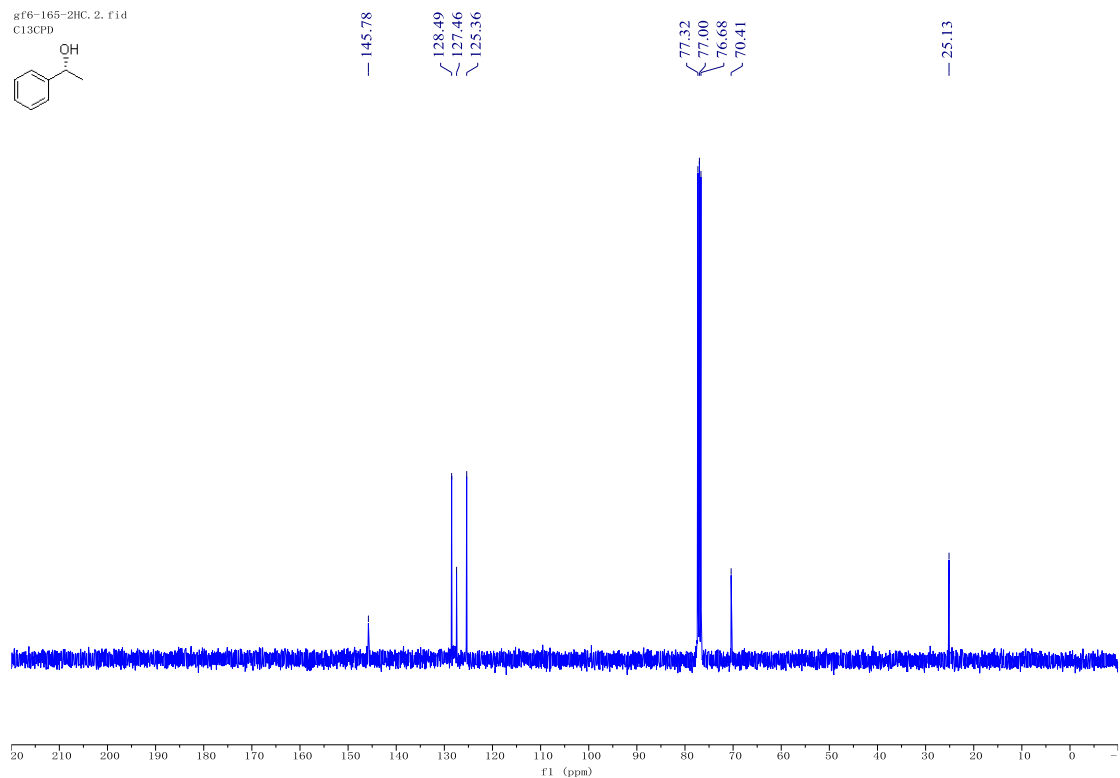


Compound 6-1

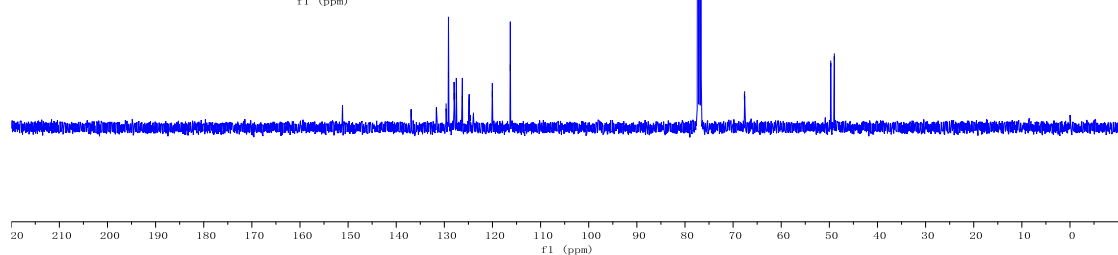
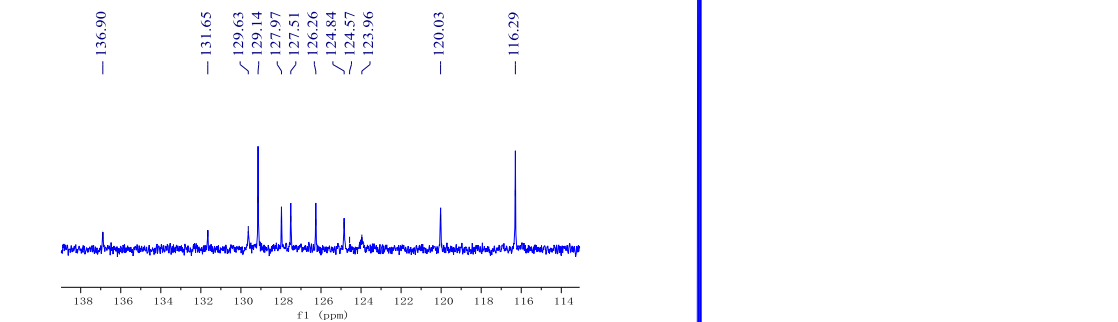
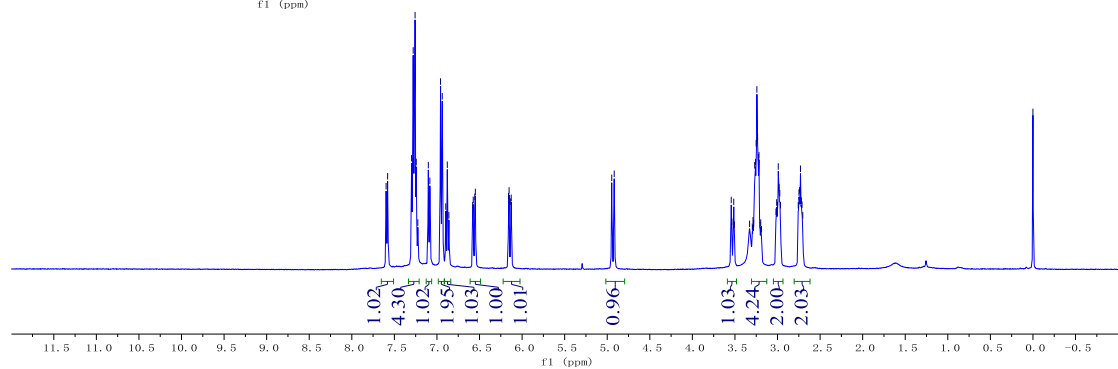
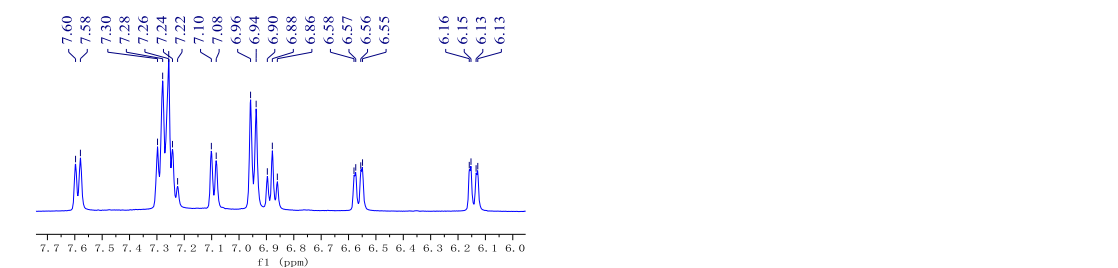
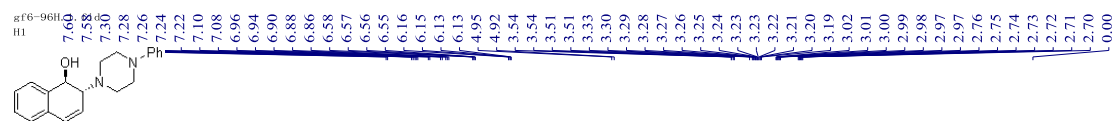
gF6-165-2HC, 1. fid
PROTON



gF6-165-2HC, 2. fid
C13CPD

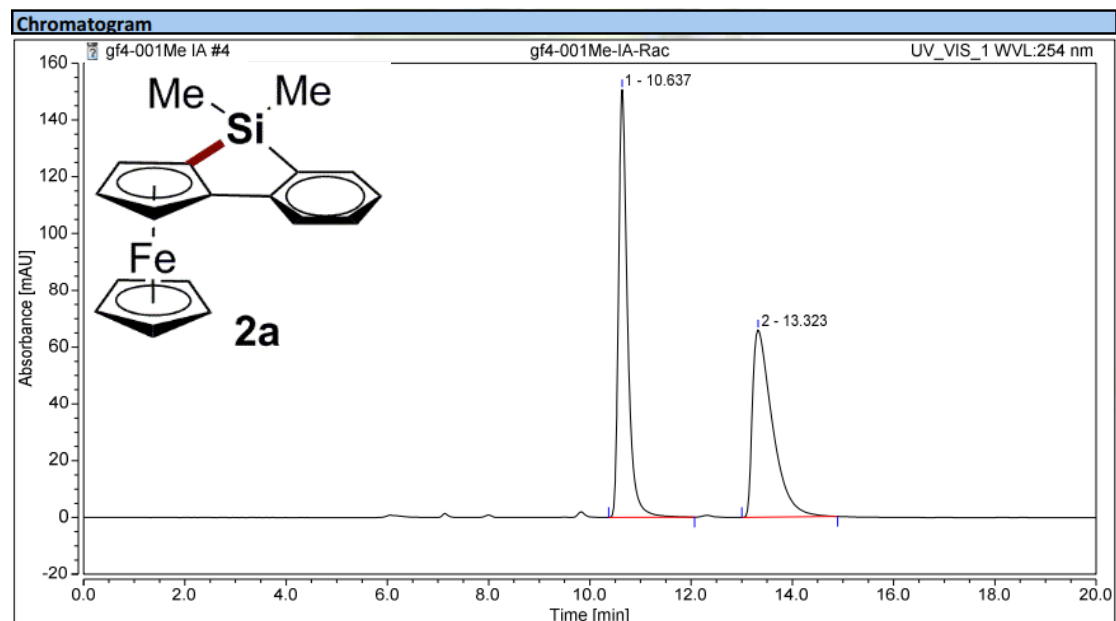


Compound 7



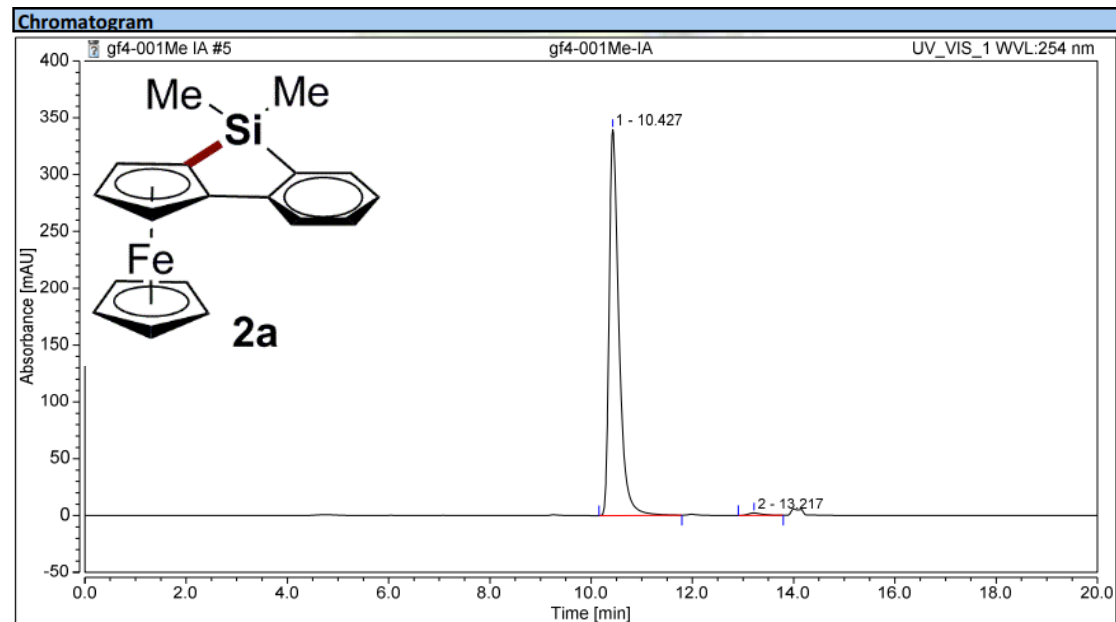
7. HPLC Traces

Compound 2a



Result

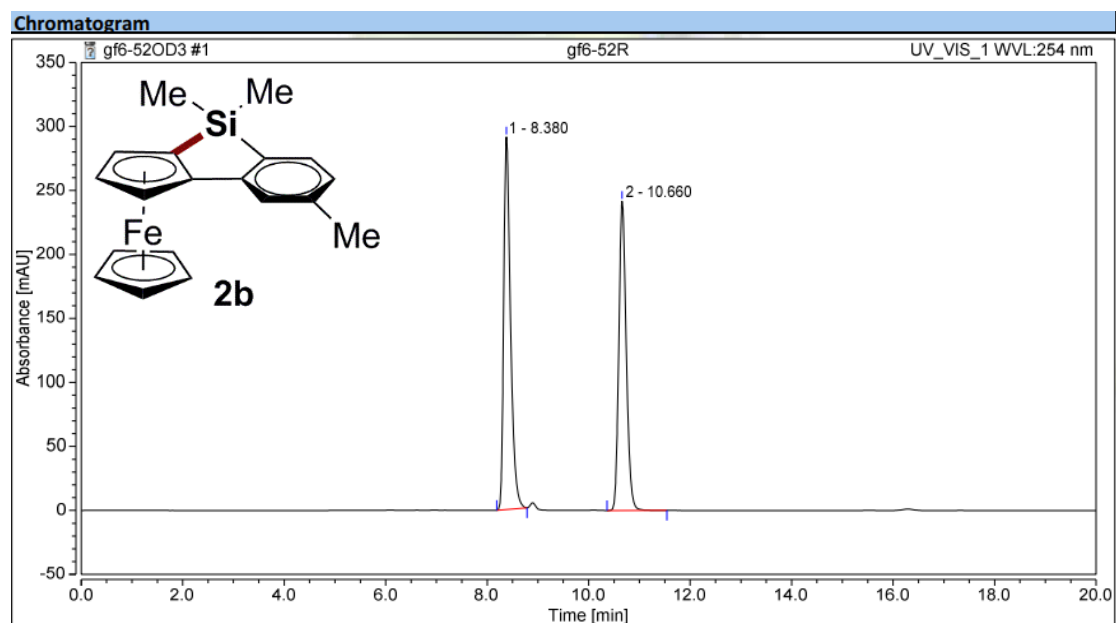
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.637	31.391	150.698	50.97	69.55
2	13.323	30.202	65.992	49.03	30.45
Totals:		61.593	216.690	100.00	100.00



Result

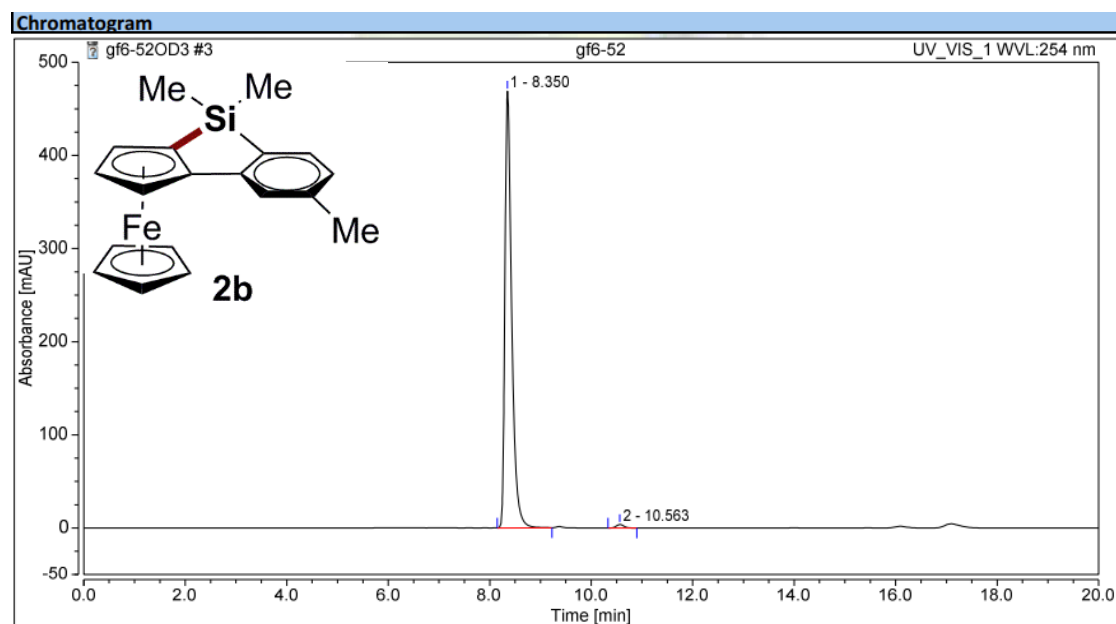
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.427	75.550	339.730	99.06	99.37
2	13.217	0.715	2.167	0.94	0.63
Totals:		76.265	341.897	100.00	100.00

Compound 2b



Result

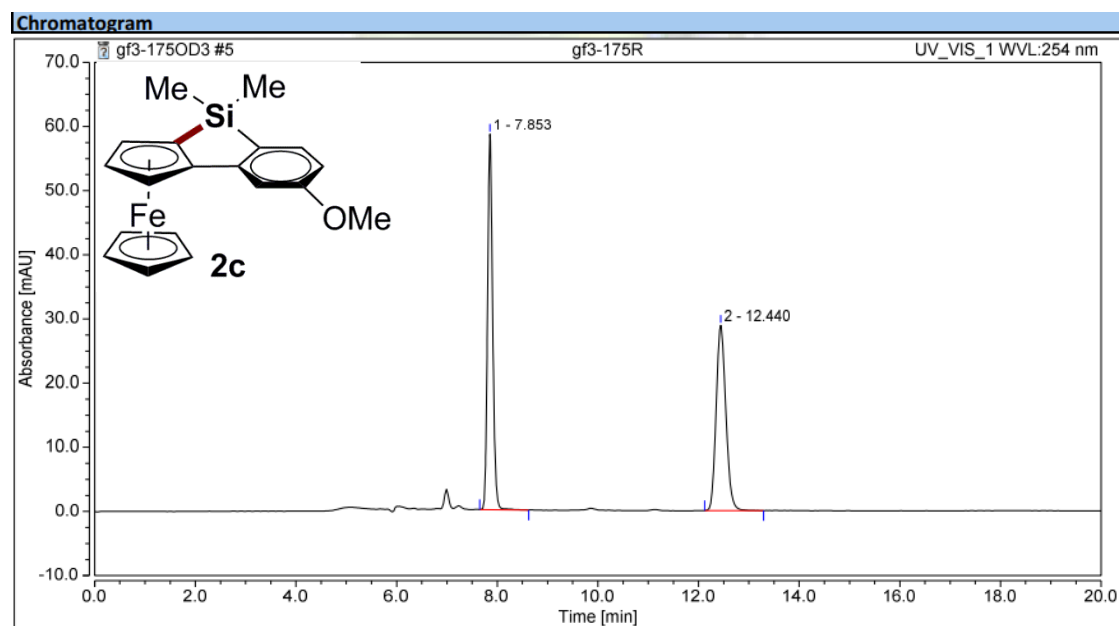
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.380	45.265	291.110	52.15	54.65
2	10.660	41.537	241.542	47.85	45.35
Totals:		86.802	532.652	100.00	100.00



Result

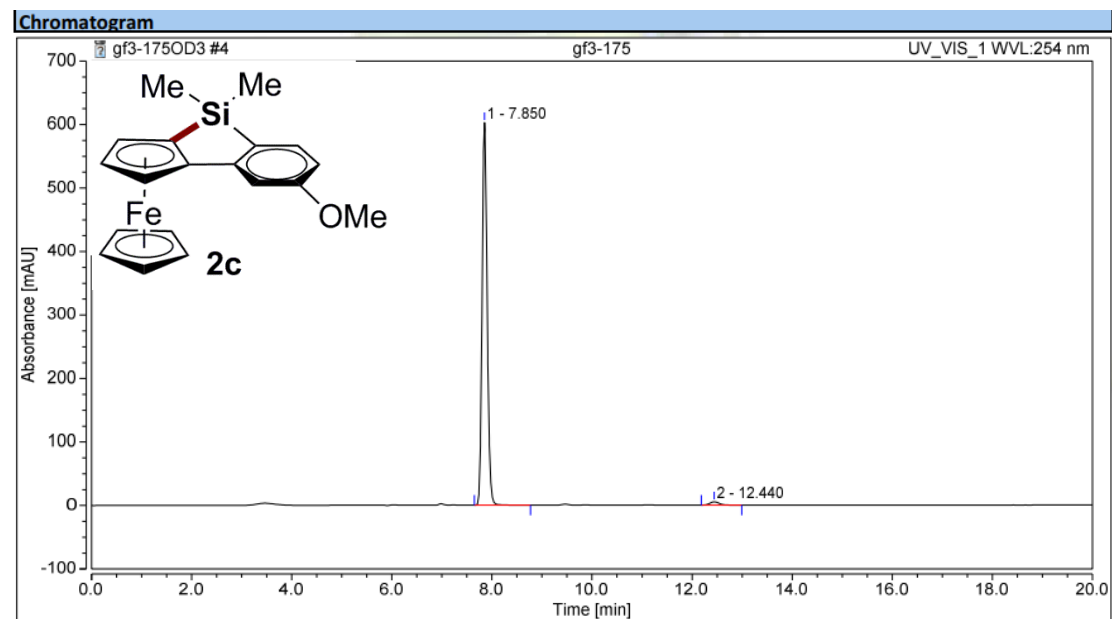
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.350	72.810	468.889	99.12	99.19
2	10.563	0.644	3.832	0.88	0.81
Totals:		73.454	472.721	100.00	100.00

Compound 2c



Result

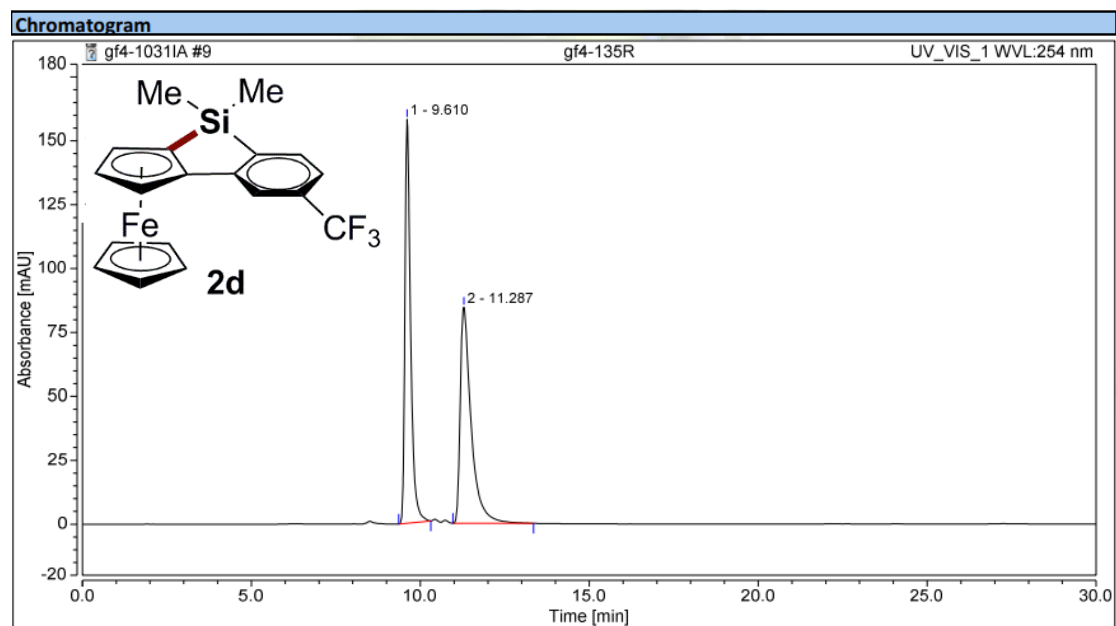
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	7.853	6.889	58.510	51.89	66.96
2	12.440	6.387	28.869	48.11	33.04
Totals:		13.276	87.379	100.00	100.00



Result

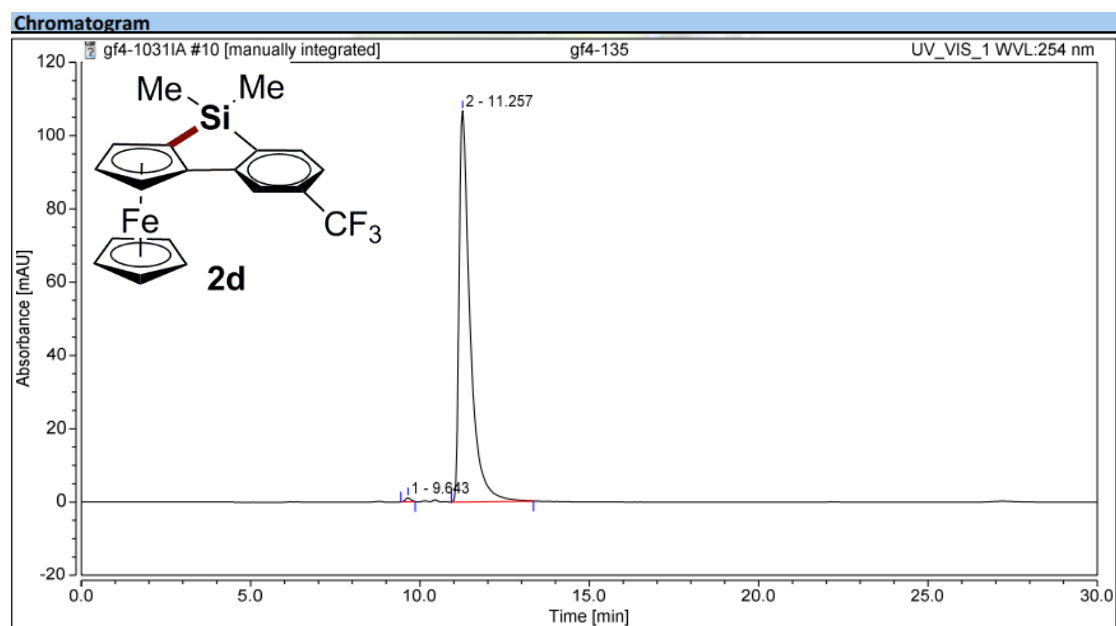
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	7.850	70.294	602.668	98.36	99.13
2	12.440	1.175	5.313	1.64	0.87
Totals:		71.469	607.981	100.00	100.00

Compound 2d



Result

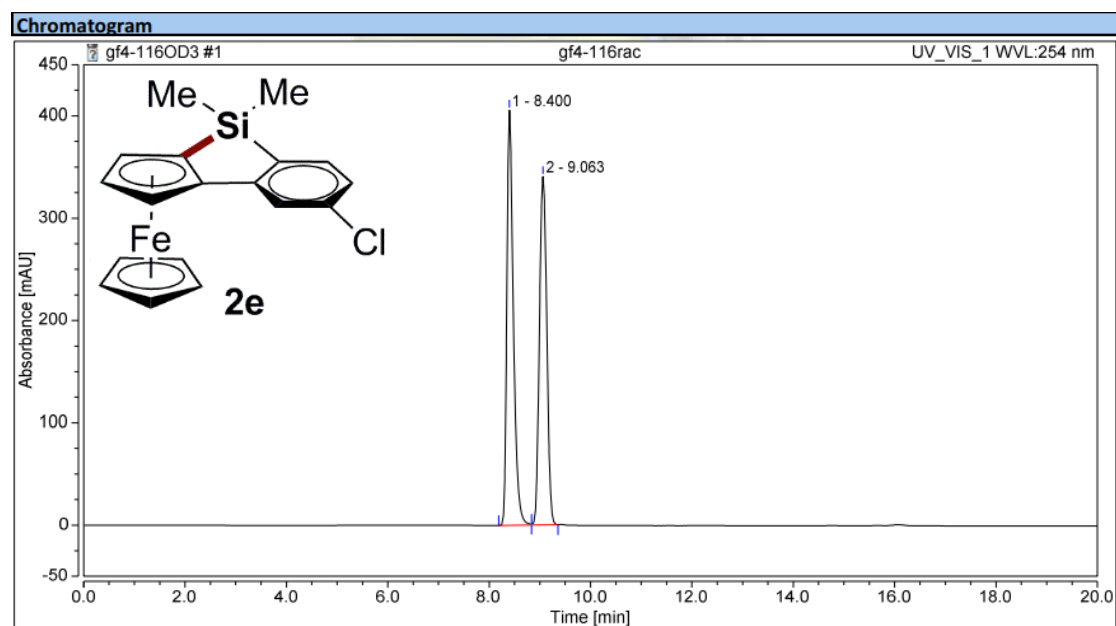
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.610	30.783	158.048	49.28	65.16
2	11.287	31.685	84.514	50.72	34.84
Totals:		62.468	242.562	100.00	100.00



Result

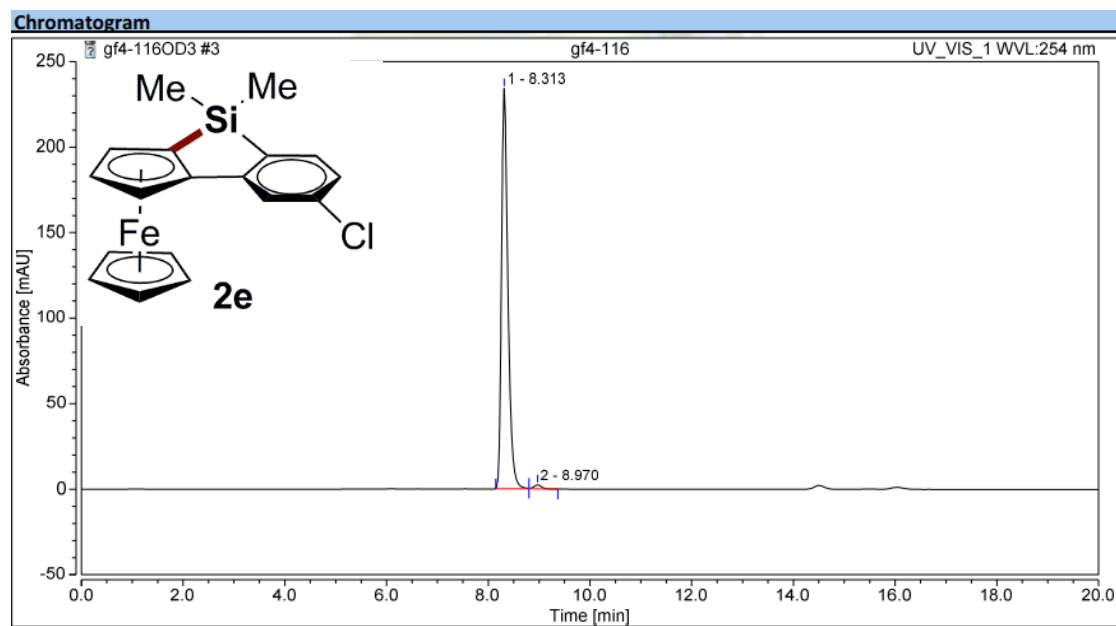
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.643	0.185	1.062	0.46	0.98
2	11.257	40.229	106.729	99.54	99.02
Totals:		40.414	107.791	100.00	100.00

Compound 2e



Result

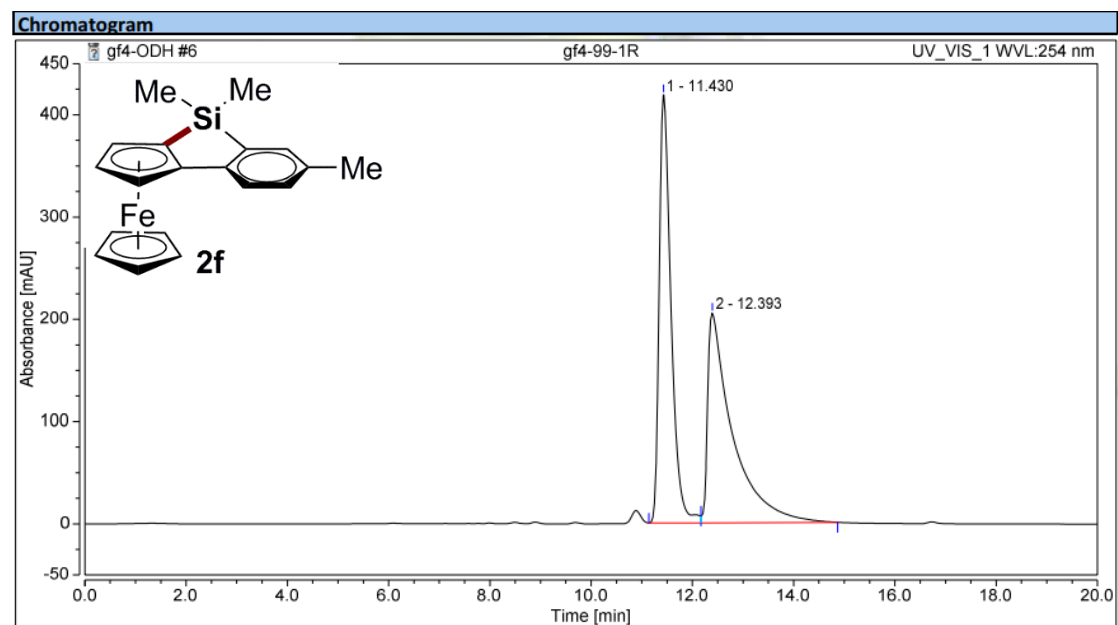
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.400	60.620	405.758	51.69	54.38
2	9.063	56.662	340.381	48.31	45.62
Totals:		117.282	746.139	100.00	100.00



Result

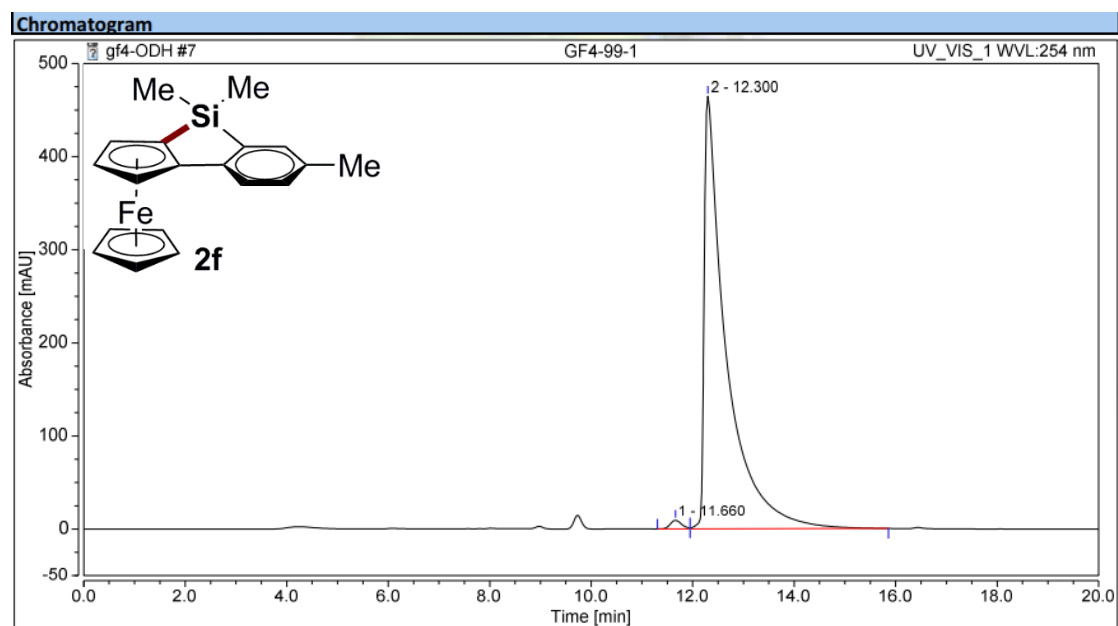
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.313	34.412	233.925	98.81	99.01
2	8.970	0.415	2.342	1.19	0.99
Totals:		34.828	236.266	100.00	100.00

Compound 2f



Result

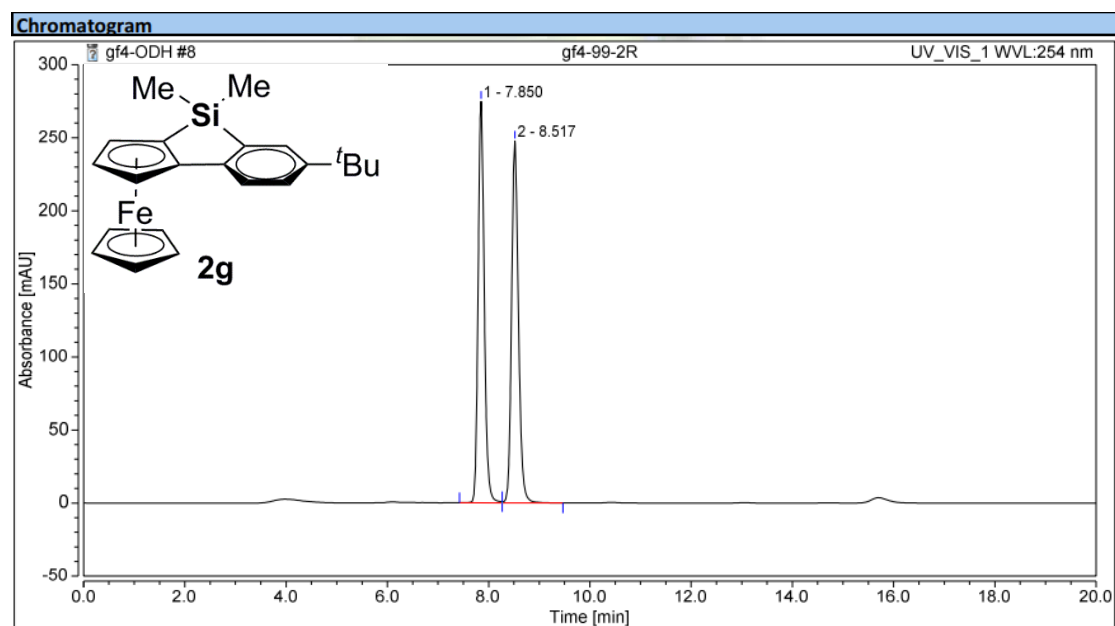
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.430	112.981	418.718	49.37	67.13
2	12.393	115.858	205.048	50.63	32.87
Totals:		228.839	623.765	100.00	100.00



Result

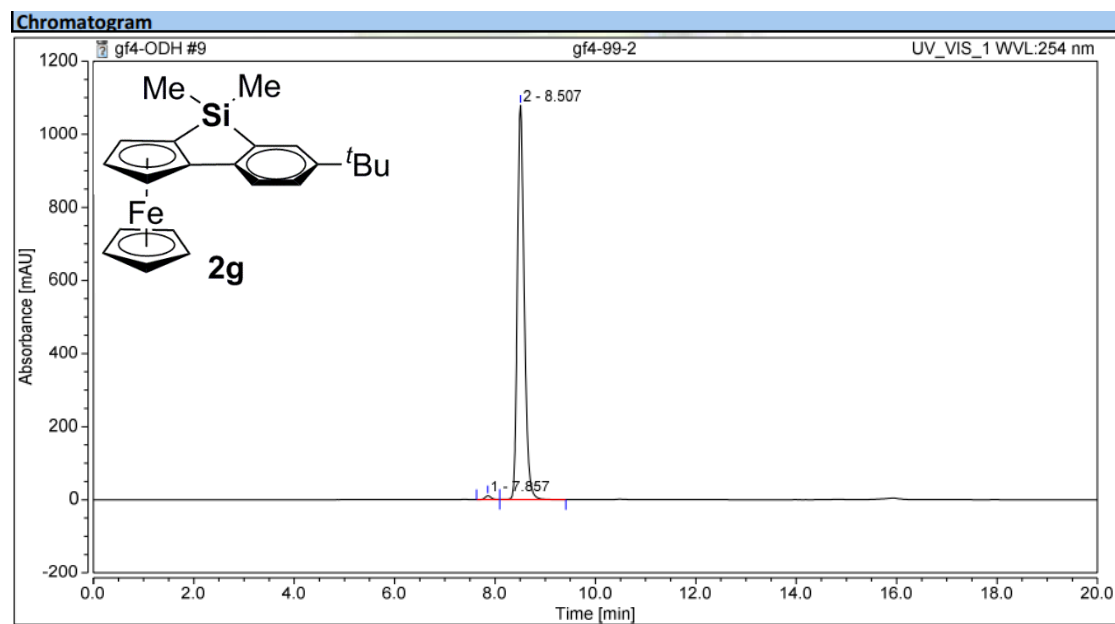
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.660	2.425	9.317	1.04	1.97
2	12.300	231.627	464.629	98.96	98.03
Totals:		234.052	473.945	100.00	100.00

Compound 2g



Result

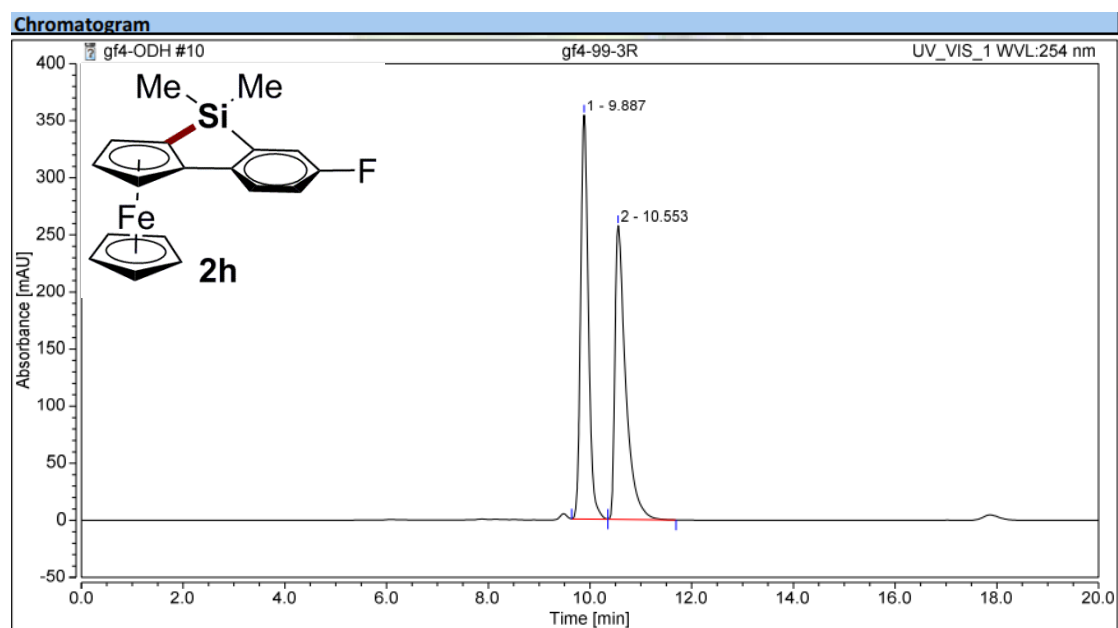
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	7.850	38.290	274.719	49.47	52.59
2	8.517	39.110	247.651	50.53	47.41
Totals:		77.400	522.370	100.00	100.00



Result

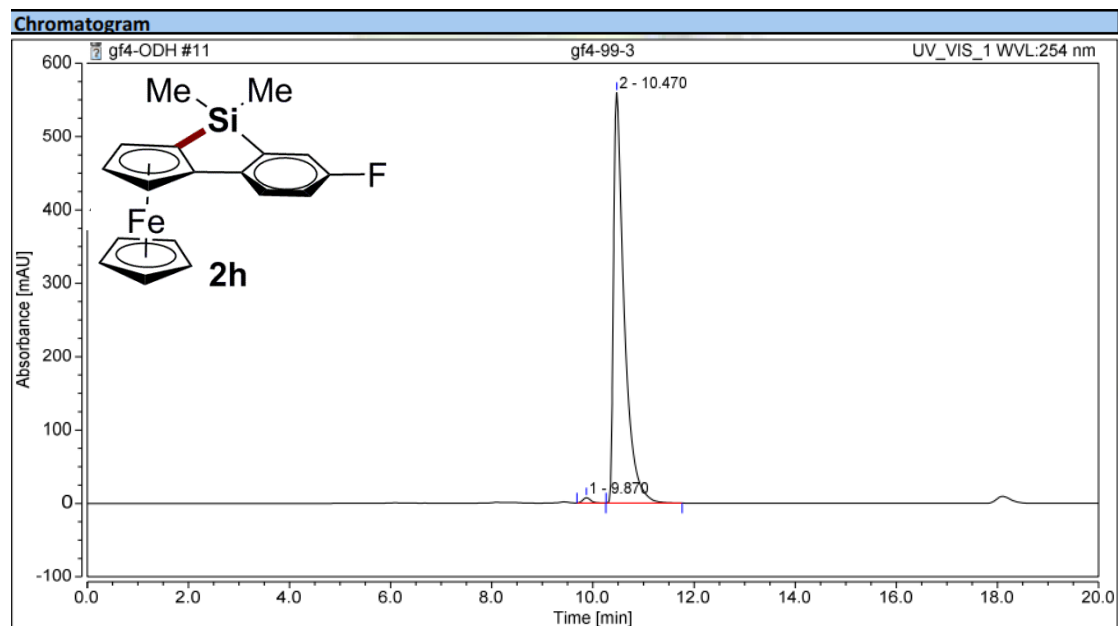
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	7.857	1.584	10.860	0.92	1.00
2	8.507	170.952	1078.877	99.08	99.00
Totals:		172.536	1089.737	100.00	100.00

Compound 2h



Result

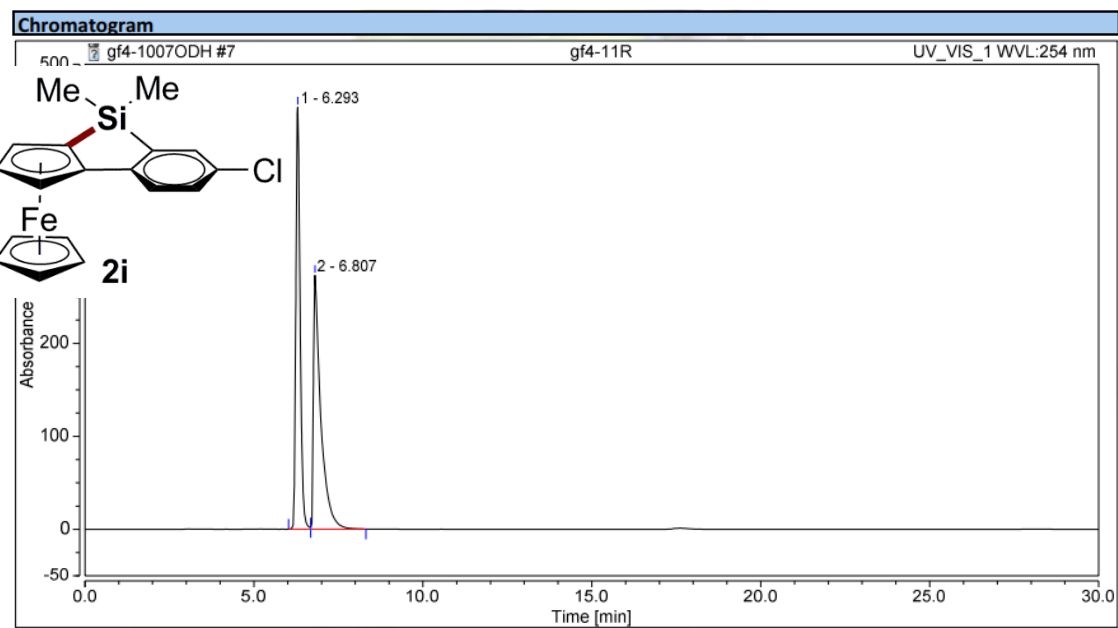
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.887	62.287	353.820	49.55	57.89
2	10.553	63.422	257.361	50.45	42.11
Totals:		125.709	611.182	100.00	100.00



Result

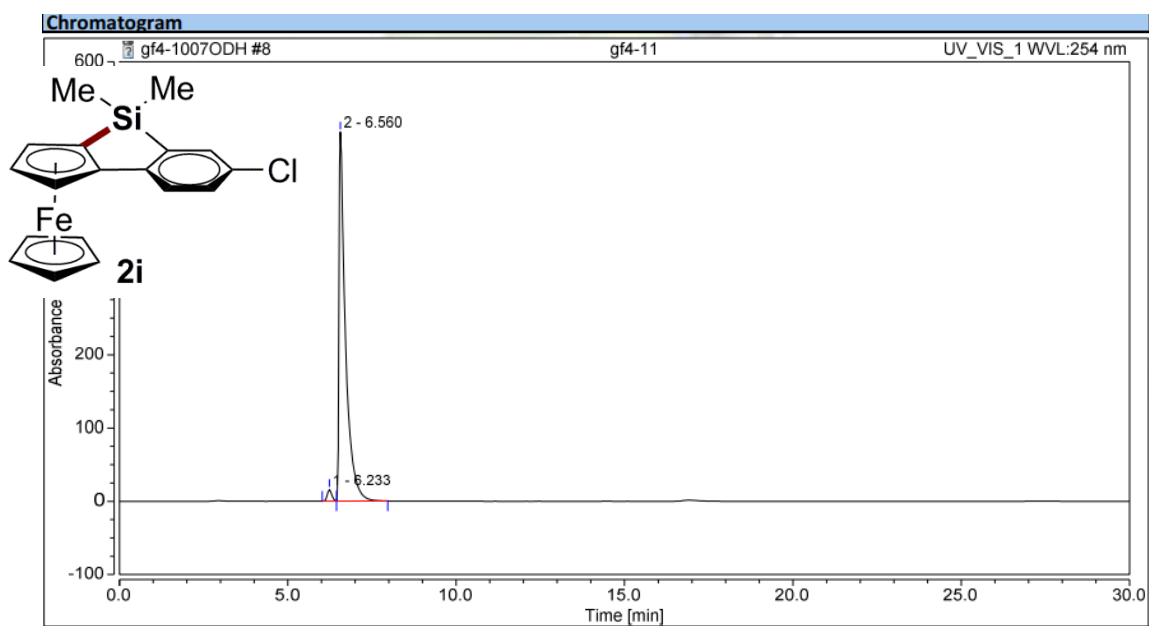
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.870	1.309	7.126	0.94	1.26
2	10.470	137.692	559.538	99.06	98.74
Totals:		139.001	566.664	100.00	100.00

Compound 2i



Result

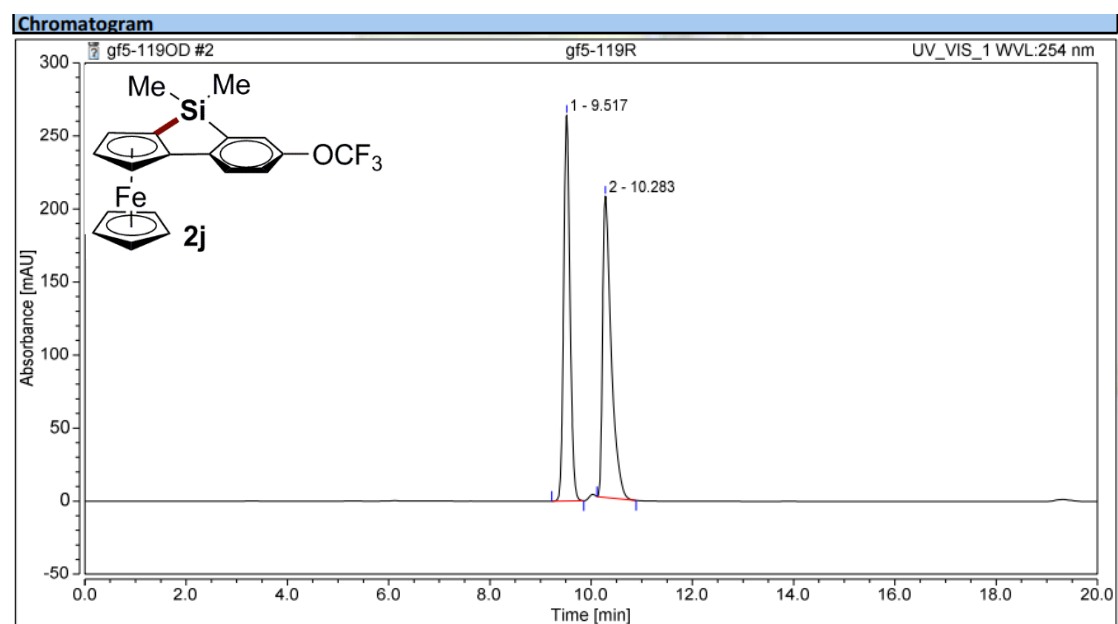
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	6.293	66.252	453.828	49.09	62.45
2	6.807	68.707	272.919	50.91	37.55
Totals:		134.959	726.747	100.00	100.00



Result

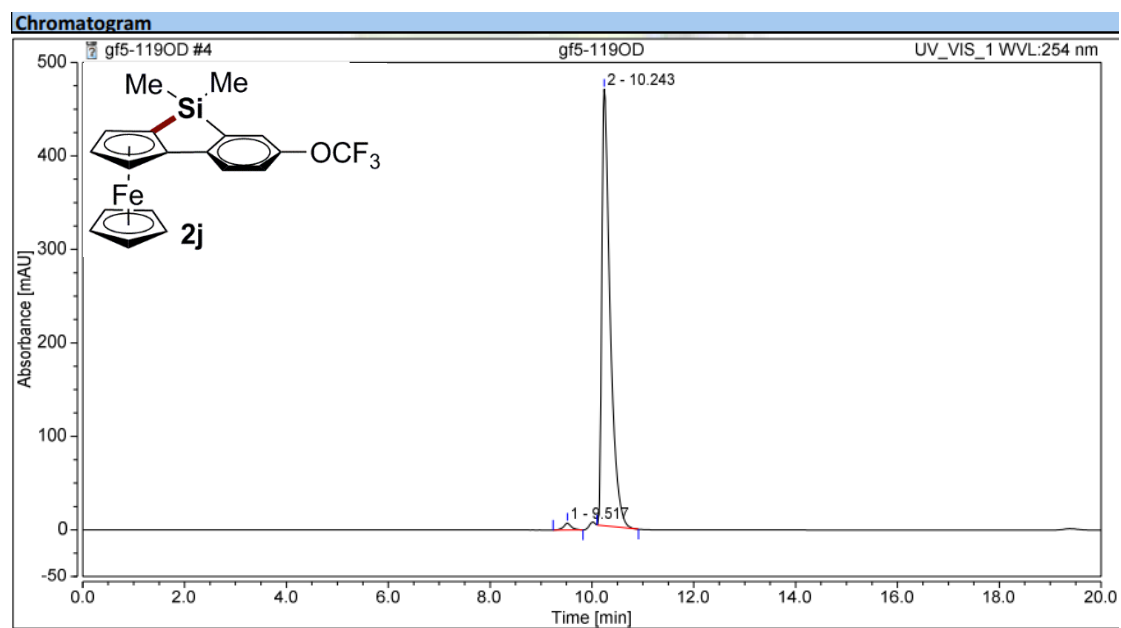
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	6.233	2.433	15.889	2.13	3.06
2	6.560	111.621	503.825	97.87	96.94
Totals:		114.055	519.715	100.00	100.00

Compound 2j



Result

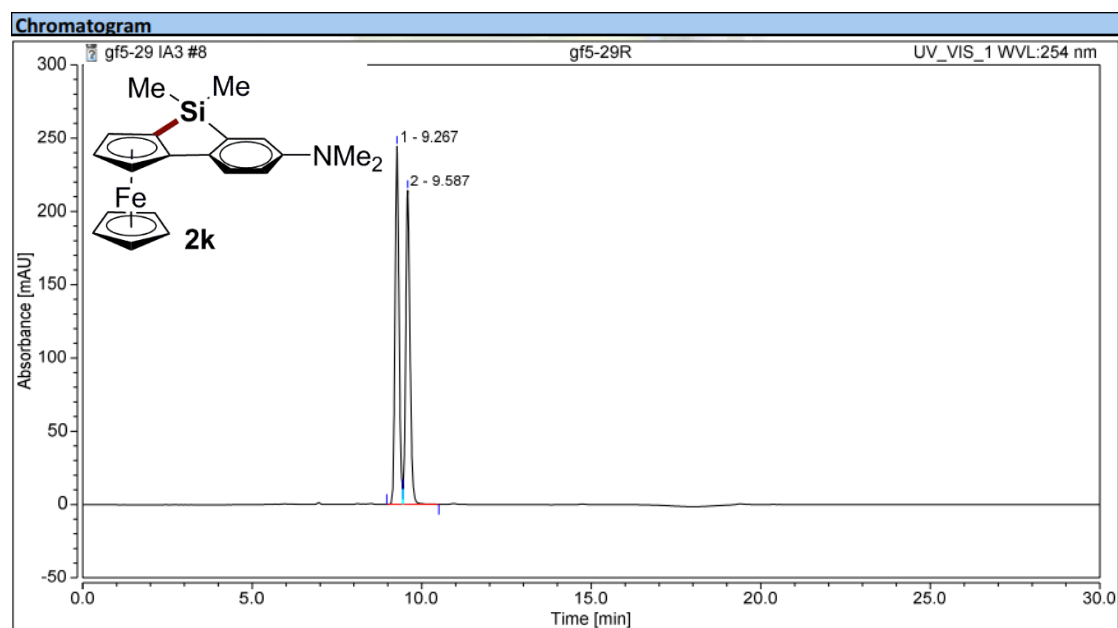
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.517	38.016	264.060	48.52	56.15
2	10.283	40.332	206.206	51.48	43.85
Totals:		78.348	470.265	100.00	100.00



Result

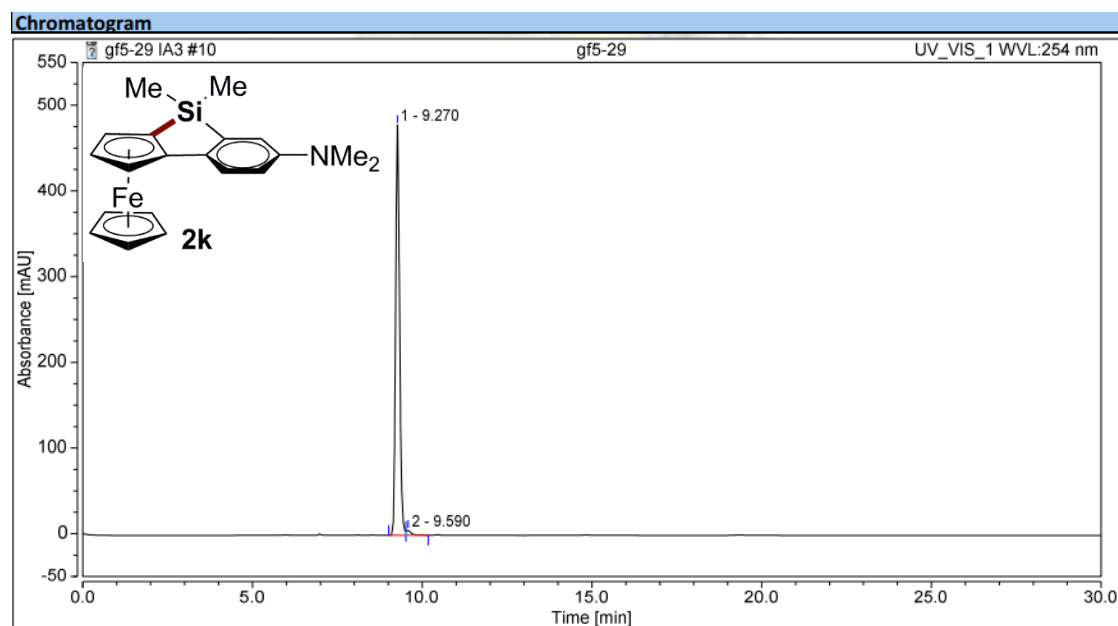
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.517	1.253	7.179	1.40	1.51
2	10.243	88.041	466.918	98.60	98.49
Totals:		89.293	474.096	100.00	100.00

Compound 2k



Result

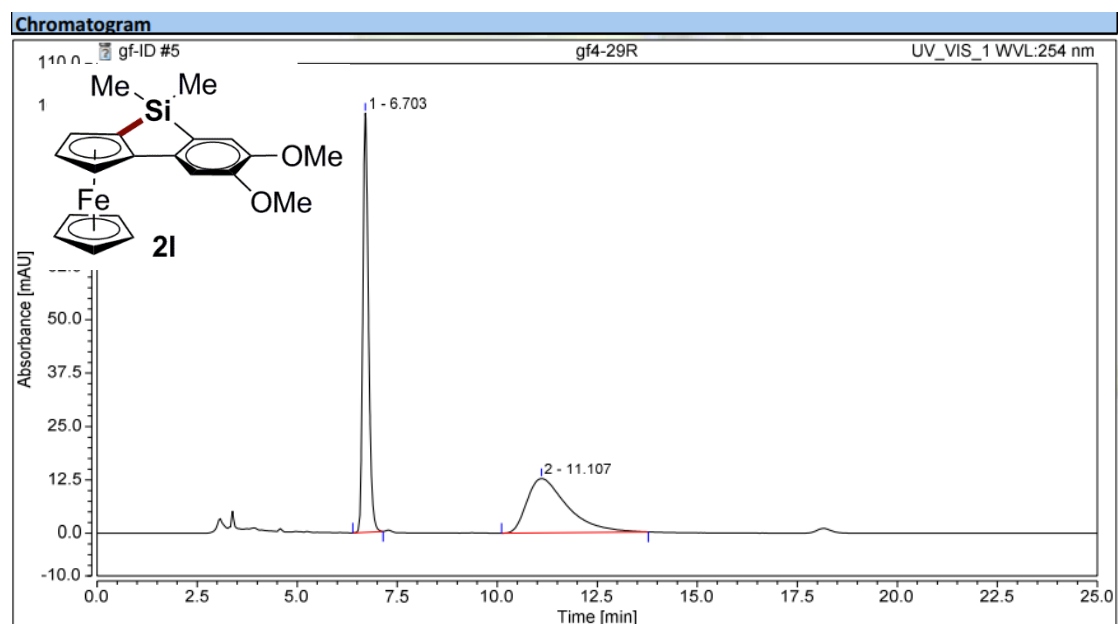
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.267	32.463	244.337	50.90	53.29
2	9.587	31.309	214.173	49.10	46.71
Totals:		63.772	458.510	100.00	100.00



Result

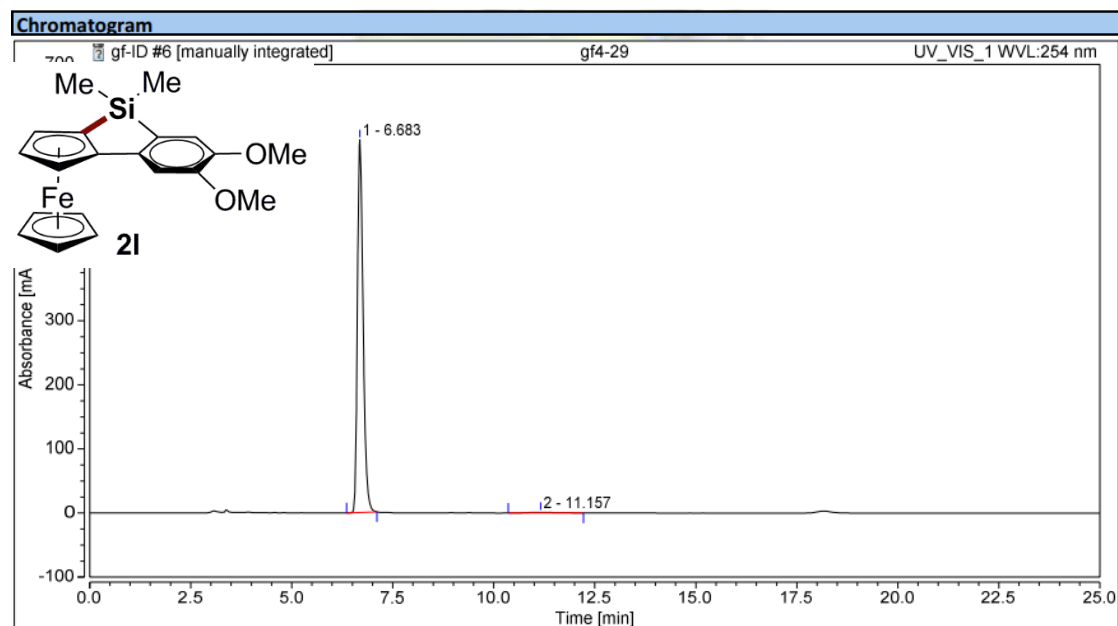
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.270	64.108	478.248	98.60	98.83
2	9.590	0.913	5.684	1.40	1.17
Totals:		65.021	483.932	100.00	100.00

Compound 2l



Result

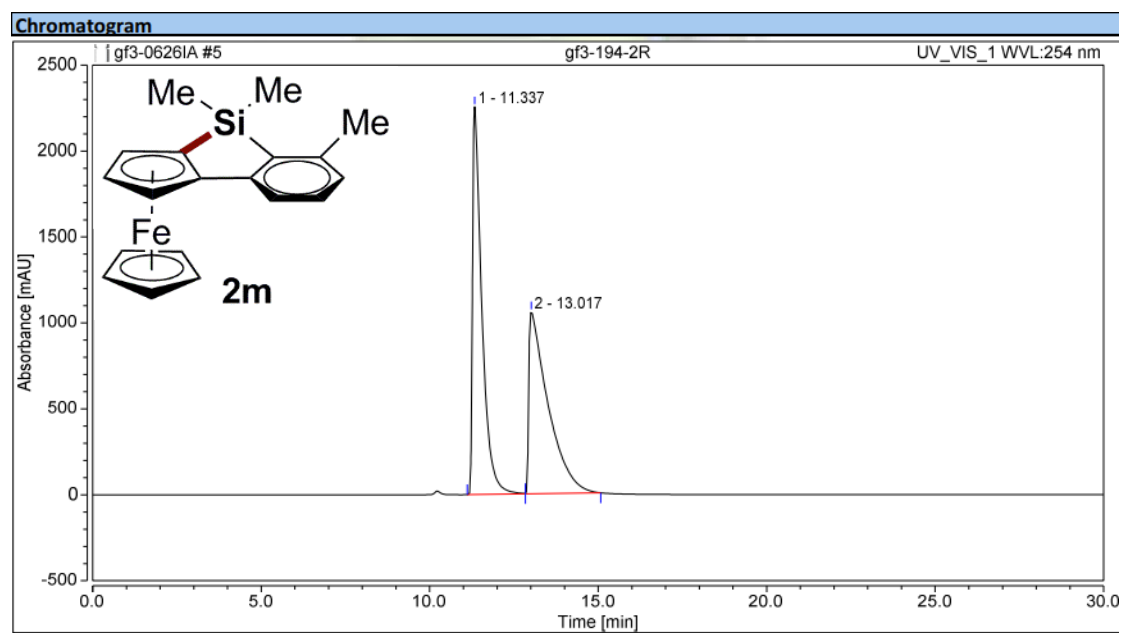
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	6.703	15.983	98.136	51.81	88.54
2	11.107	14.867	12.707	48.19	11.46
Totals:		30.850	110.843	100.00	100.00



Result

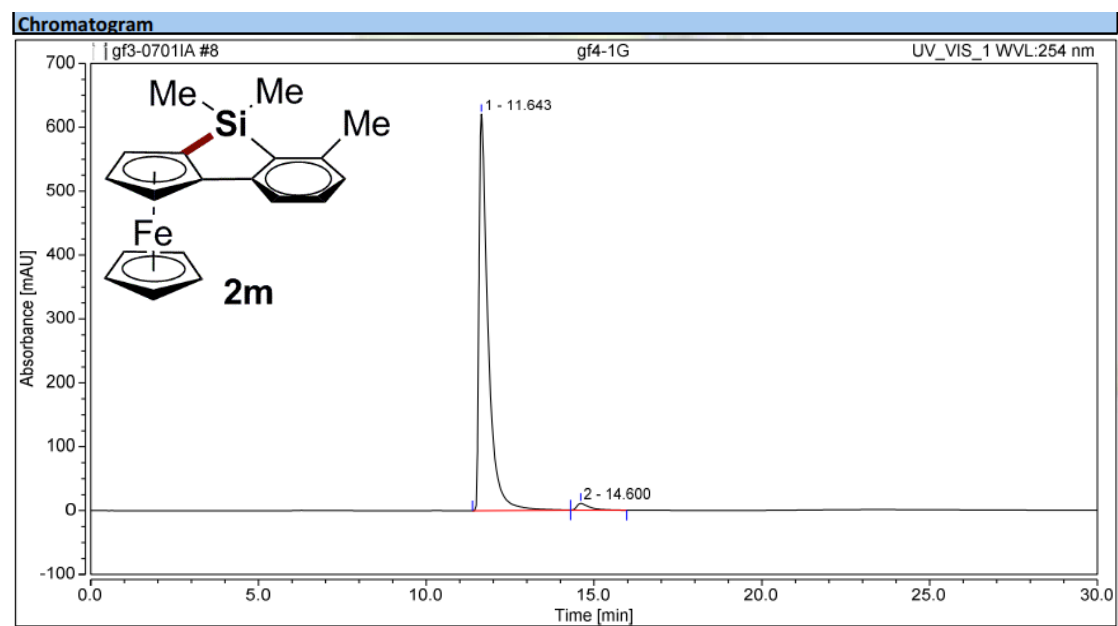
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	6.683	94.114	581.349	99.06	99.84
2	11.157	0.897	0.912	0.94	0.16
Totals:		95.011	582.261	100.00	100.00

Compound 2m



Result

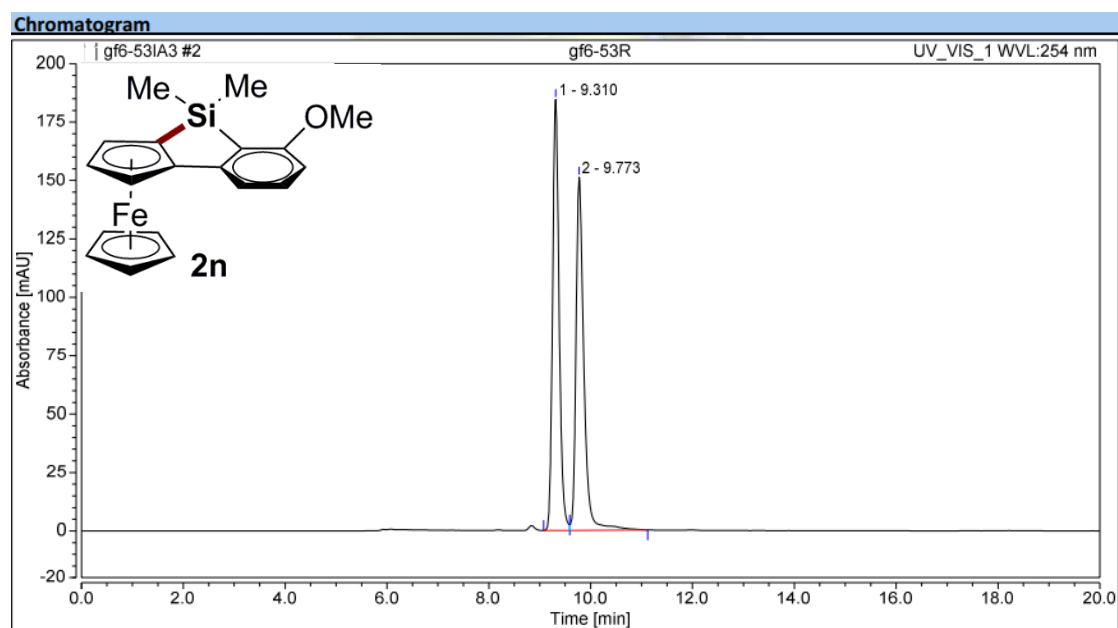
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.337	725.427	2256.142	50.93	68.07
2	13.017	698.865	1058.354	49.07	31.93
Totals:		1424.292	3314.497	100.00	100.00



Result

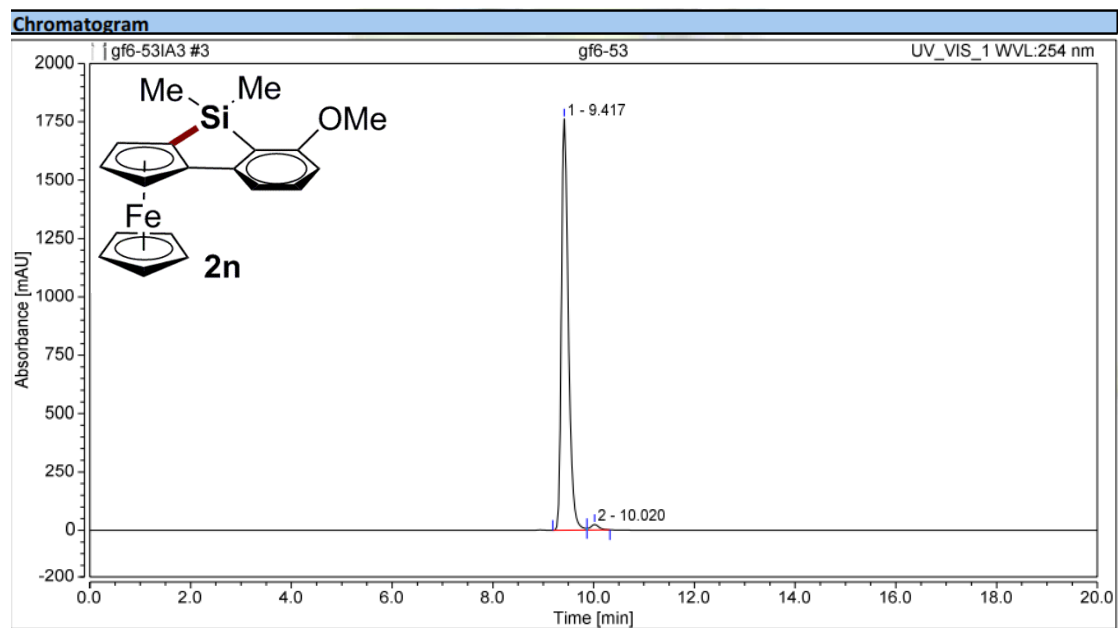
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.643	196.111	620.169	97.55	98.30
2	14.600	4.925	10.757	2.45	1.70
Totals:		201.035	630.926	100.00	100.00

Compound 2n



Result

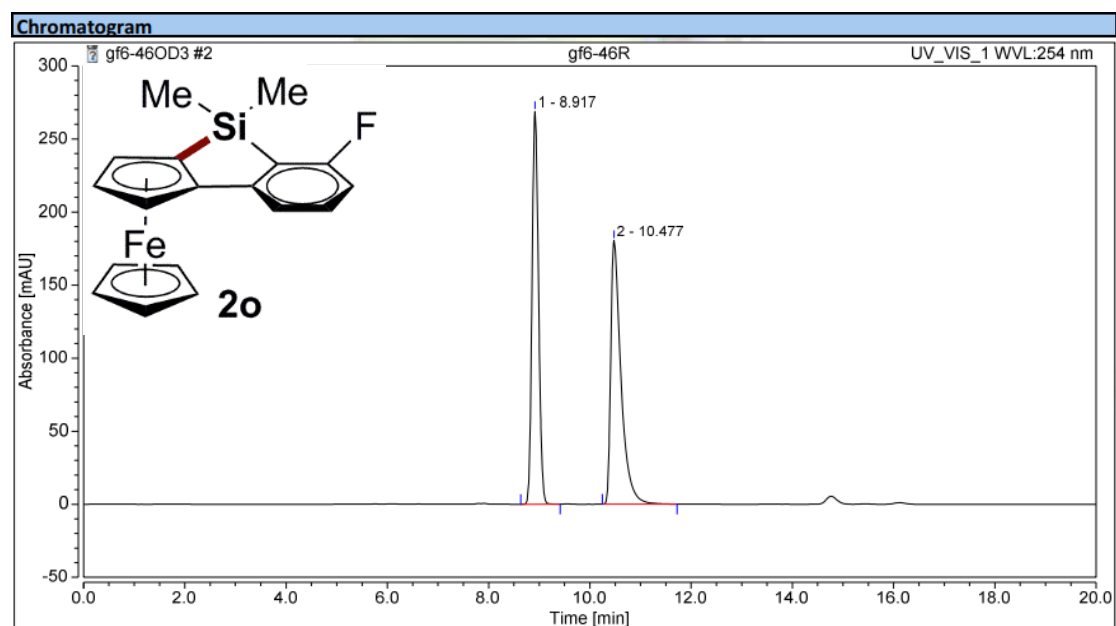
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.310	27.481	184.483	50.34	54.95
2	9.773	27.107	151.231	49.66	45.05
Totals:		54.588	335.714	100.00	100.00



Result

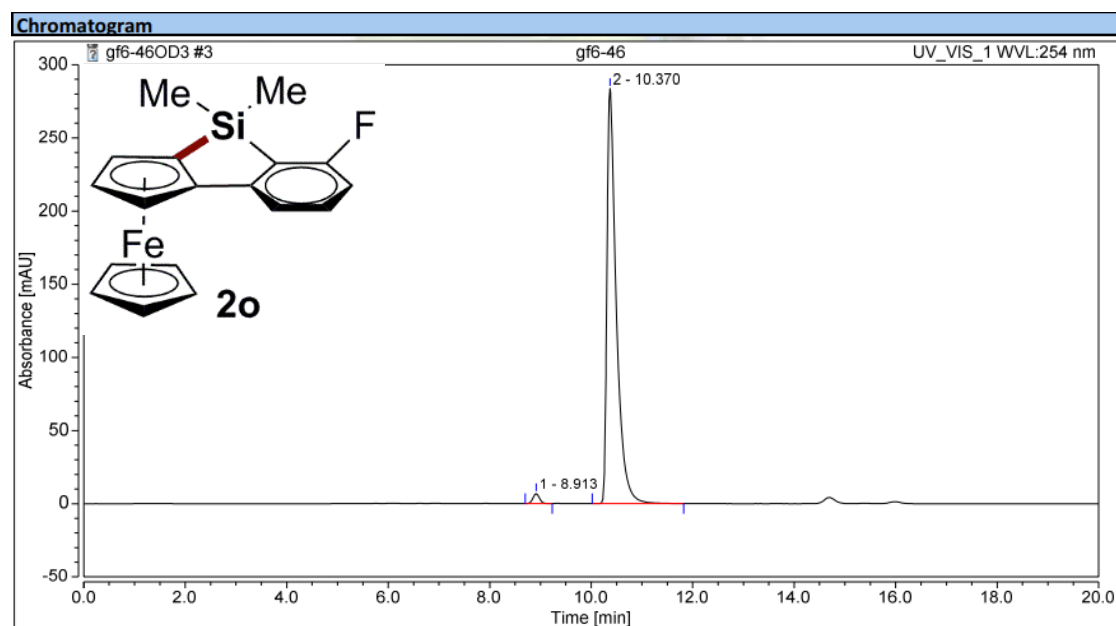
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.417	282.290	1761.602	98.45	98.68
2	10.020	4.446	23.600	1.55	1.32
Totals:		286.736	1785.202	100.00	100.00

Compound 2o



Result

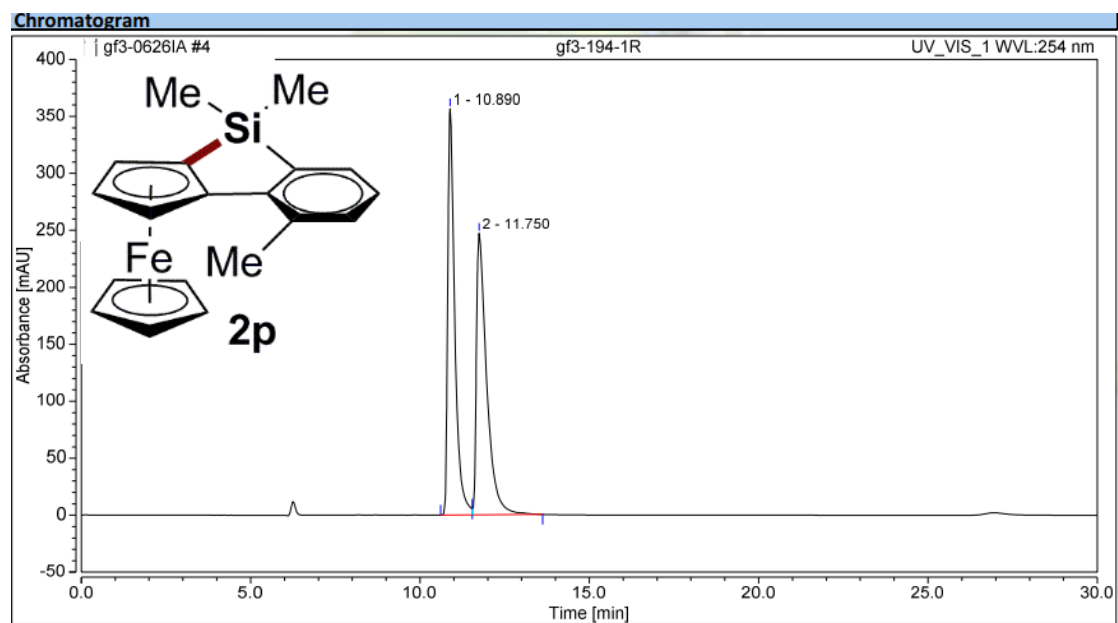
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.917	39.874	268.835	48.59	59.84
2	10.477	42.182	180.418	51.41	40.16
Totals:		82.057	449.253	100.00	100.00



Result

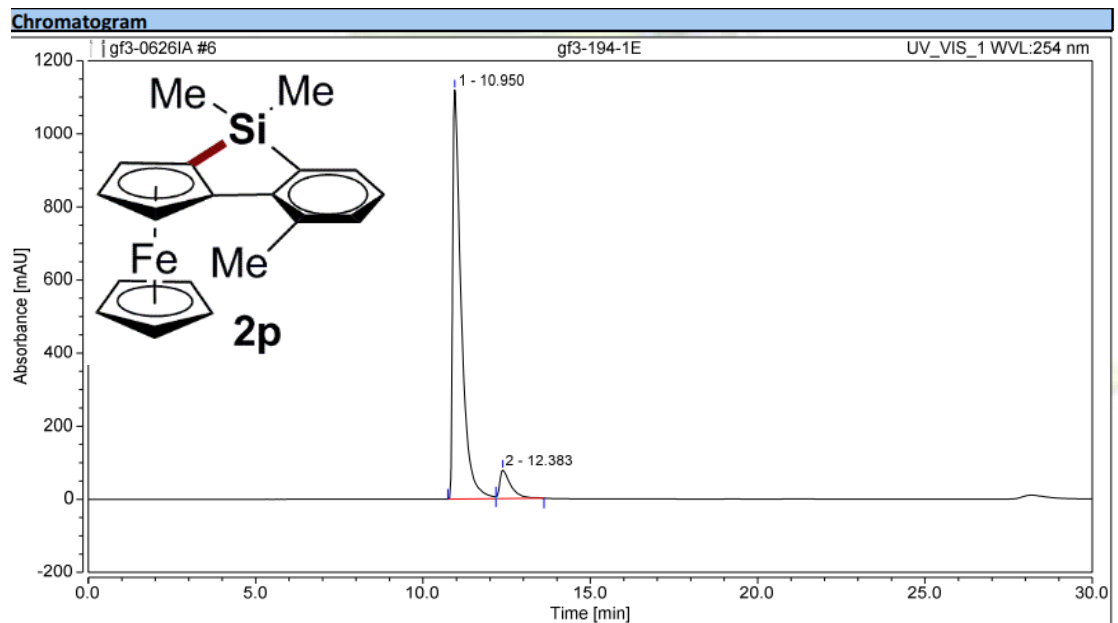
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.913	1.020	6.853	1.68	2.36
2	10.370	59.781	283.776	98.32	97.64
Totals:		60.801	290.629	100.00	100.00

Compound 2p



Result

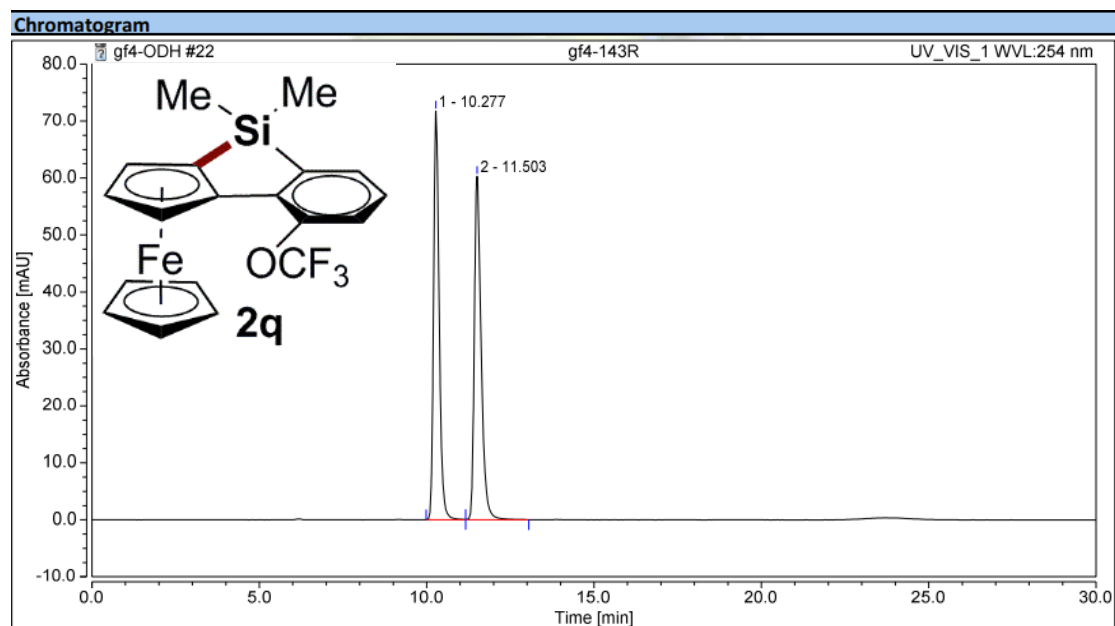
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.890	85.956	356.661	49.80	59.06
2	11.750	86.646	247.202	50.20	40.94
Totals:		172.601	603.862	100.00	100.00



Result

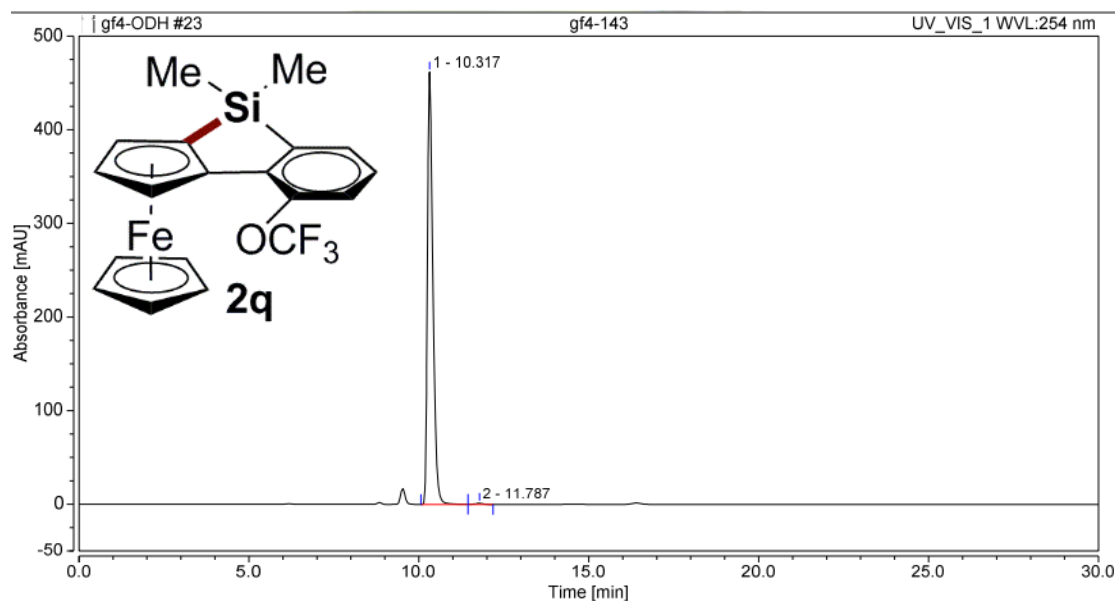
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.950	332.174	1119.197	91.81	93.48
2	12.383	29.625	78.071	8.19	6.52
Totals:		361.799	1197.268	100.00	100.00

Compound 2q



Result

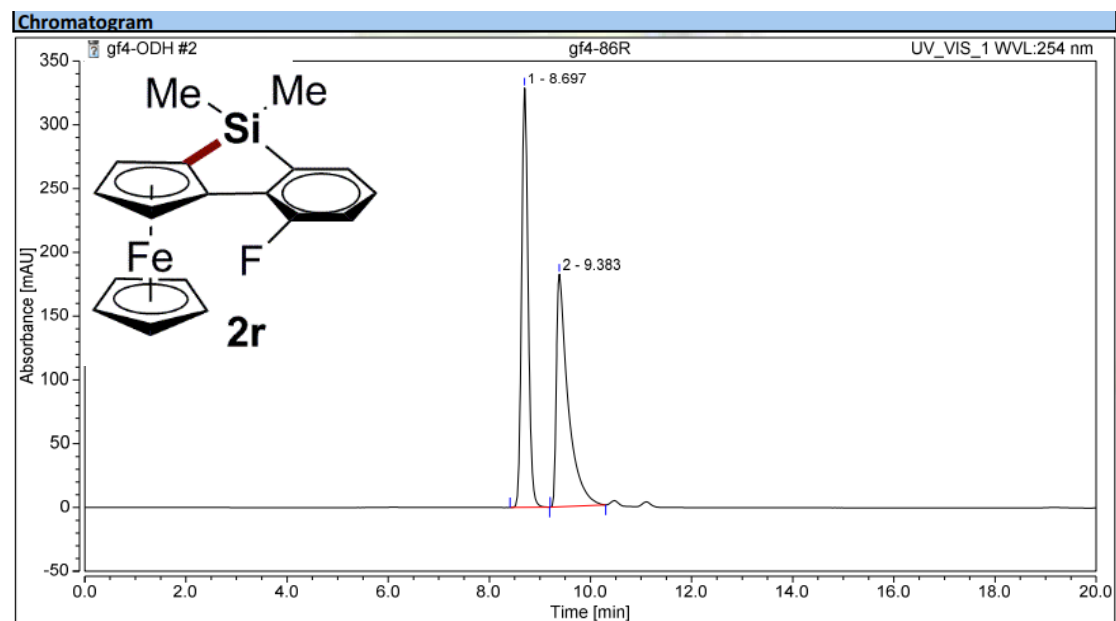
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.277	13.874	71.718	49.38	54.34
2	11.503	14.220	60.274	50.62	45.66
Totals:		28.094	131.991	100.00	100.00



Result

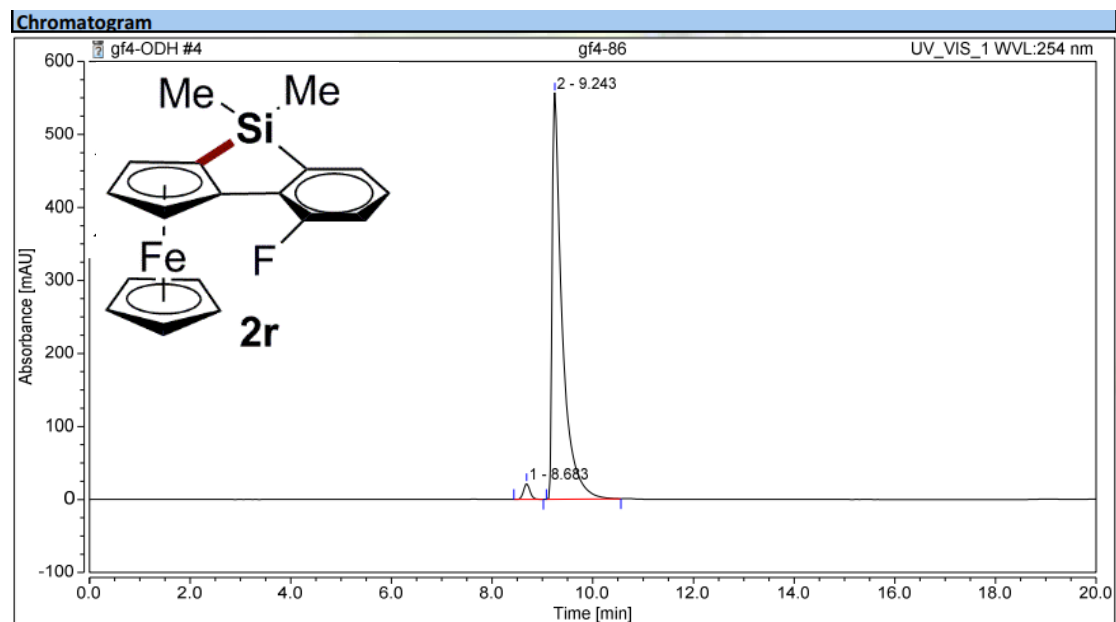
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.317	85.854	461.930	99.63	99.72
2	11.787	0.316	1.297	0.37	0.28
Totals:		86.170	463.227	100.00	100.00

Compound 2r



Result

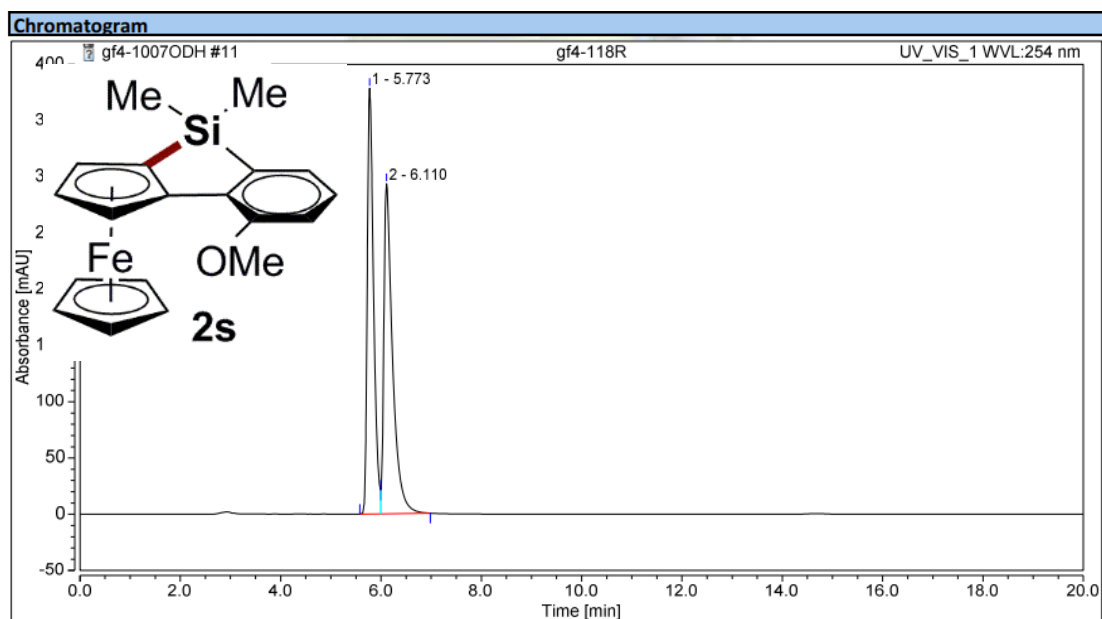
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.697	49.267	328.724	50.09	64.31
2	9.383	49.087	182.444	49.91	35.69
Totals:		98.354	511.168	100.00	100.00



Result

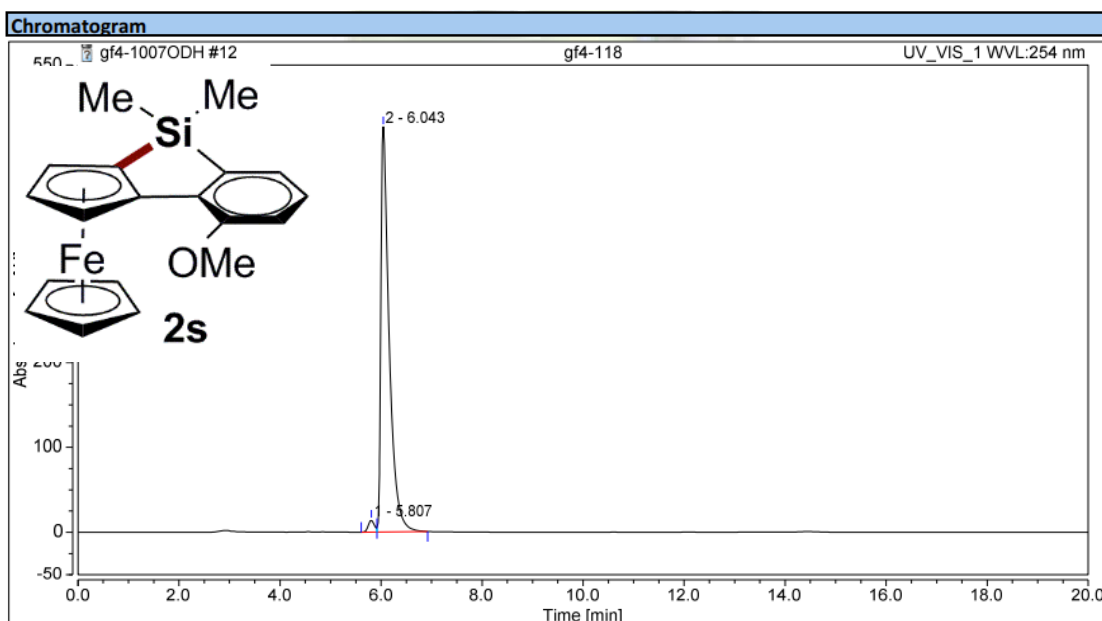
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.683	3.179	21.564	2.42	3.73
2	9.243	127.932	556.614	97.58	96.27
Totals:		131.111	578.178	100.00	100.00

Compound 2s



Result

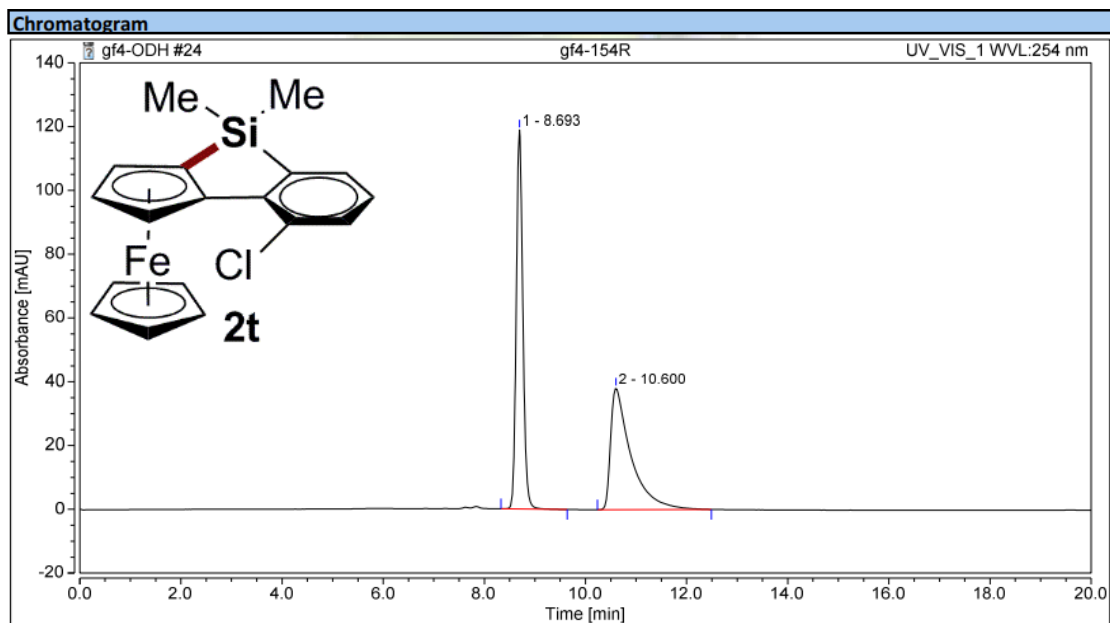
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	5.773	55.188	378.402	48.44	56.32
2	6.110	58.738	293.515	51.56	43.68
Totals:		113.926	671.917	100.00	100.00



Result

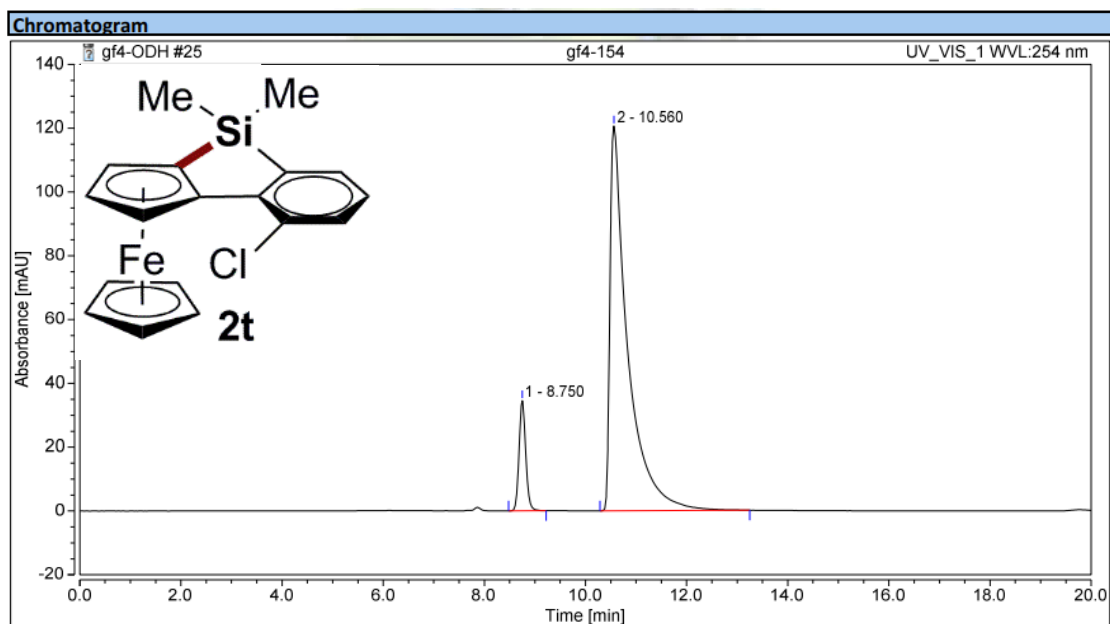
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	5.807	1.941	14.014	2.09	2.85
2	6.043	90.762	476.902	97.91	97.15
Totals:		92.703	490.916	100.00	100.00

Compound 2t



Result

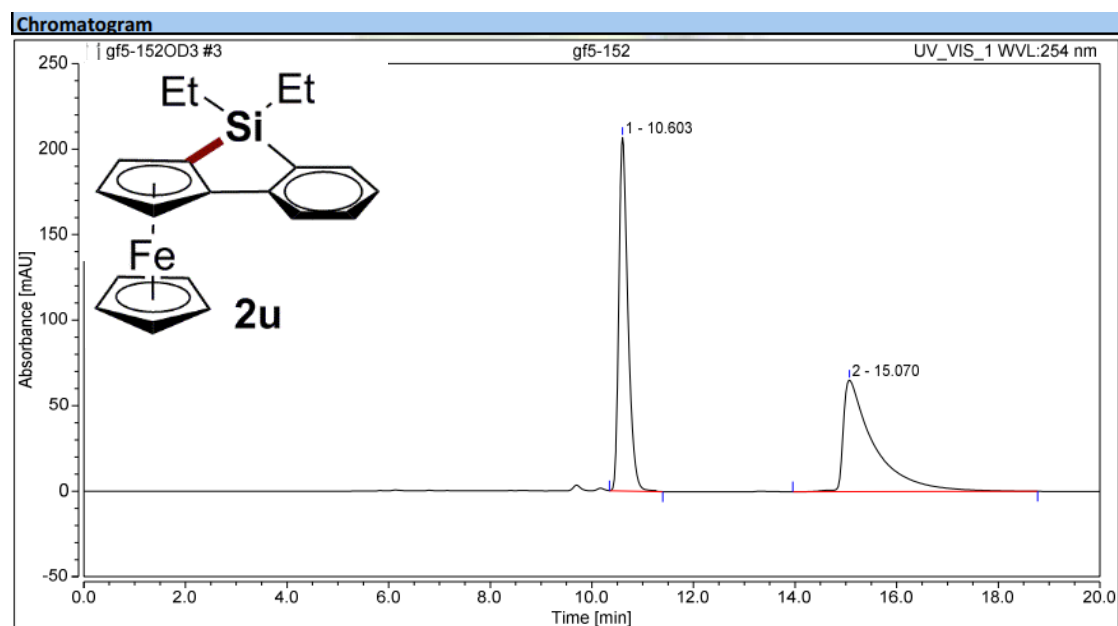
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.693	17.845	118.870	50.03	75.72
2	10.600	17.825	38.110	49.97	24.28
Totals:		35.670	156.980	100.00	100.00



Result

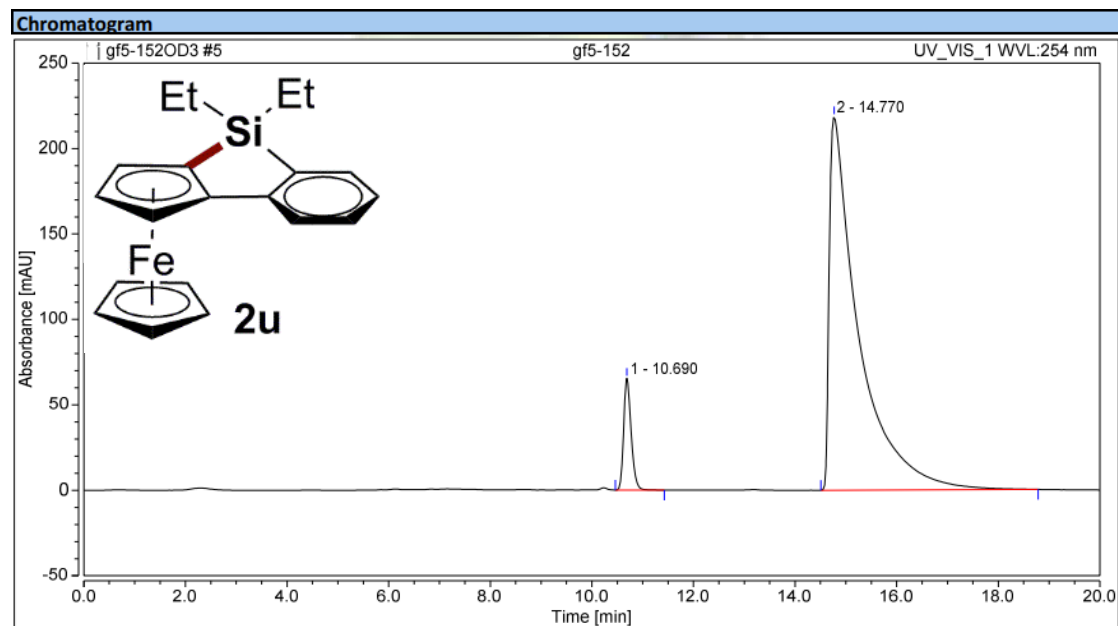
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.750	5.251	34.532	9.72	22.25
2	10.560	48.754	120.637	90.28	77.75
Totals:		54.005	155.169	100.00	100.00

Compound 2u



Result

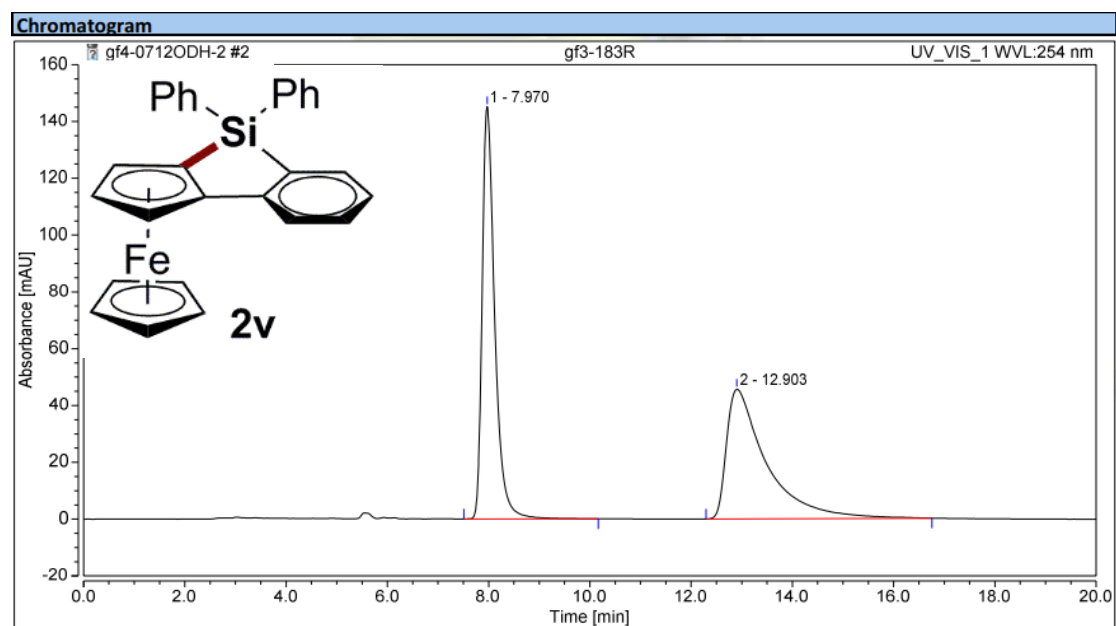
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.603	43.402	206.657	48.83	76.00
2	15.070	45.477	65.259	51.17	24.00
Totals:		88.879	271.916	100.00	100.00



Result

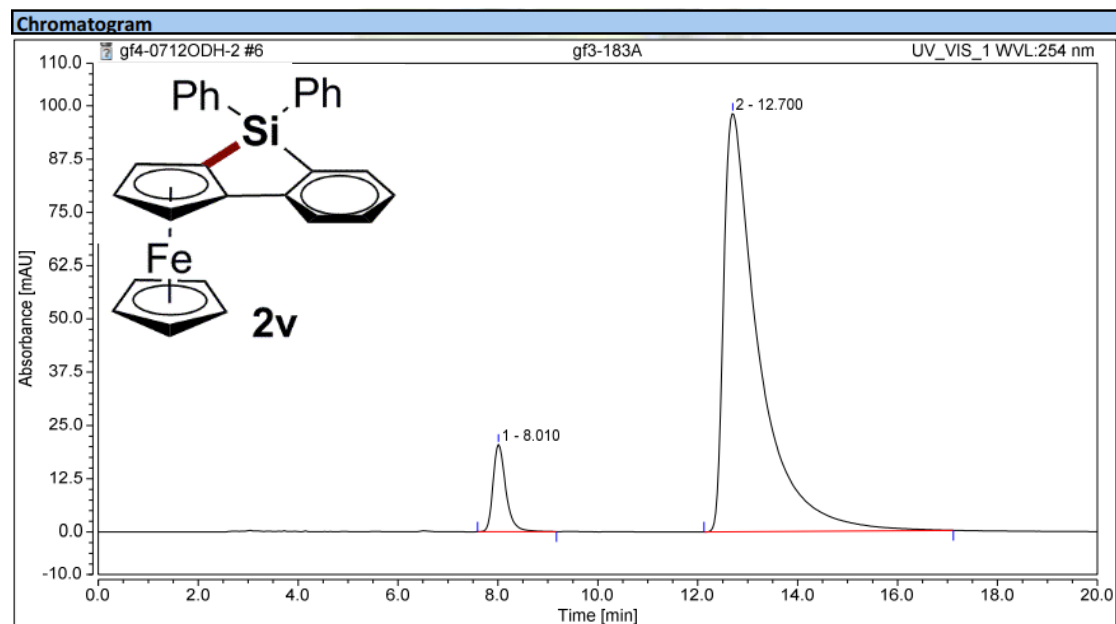
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.690	11.324	65.423	7.24	23.04
2	14.770	145.076	218.513	92.76	76.96
Totals:		156.401	283.936	100.00	100.00

Compound 2v



Result

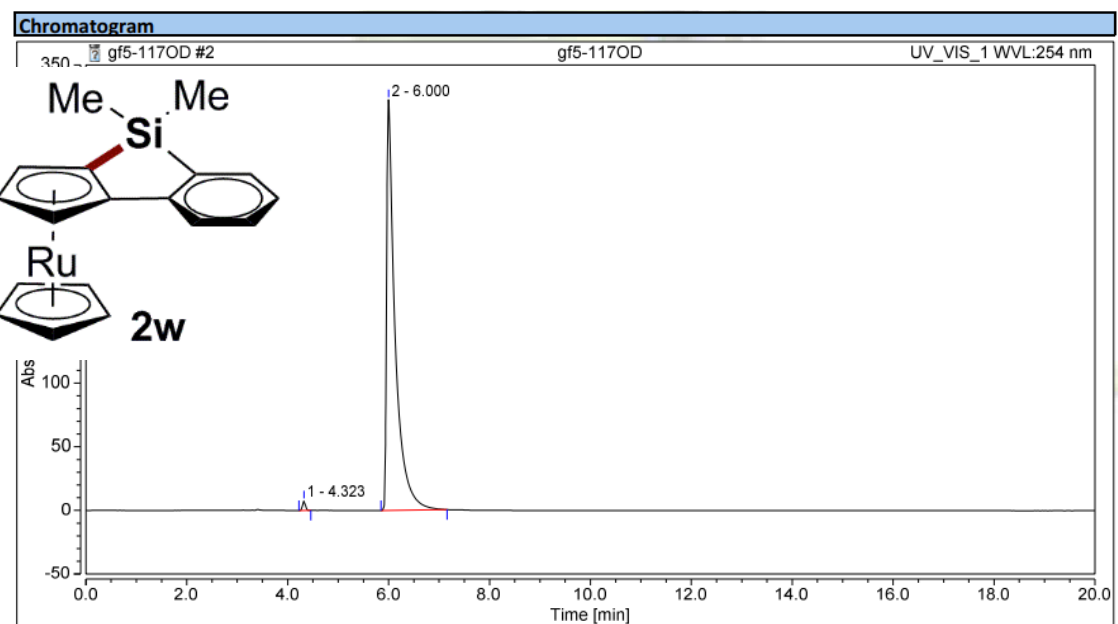
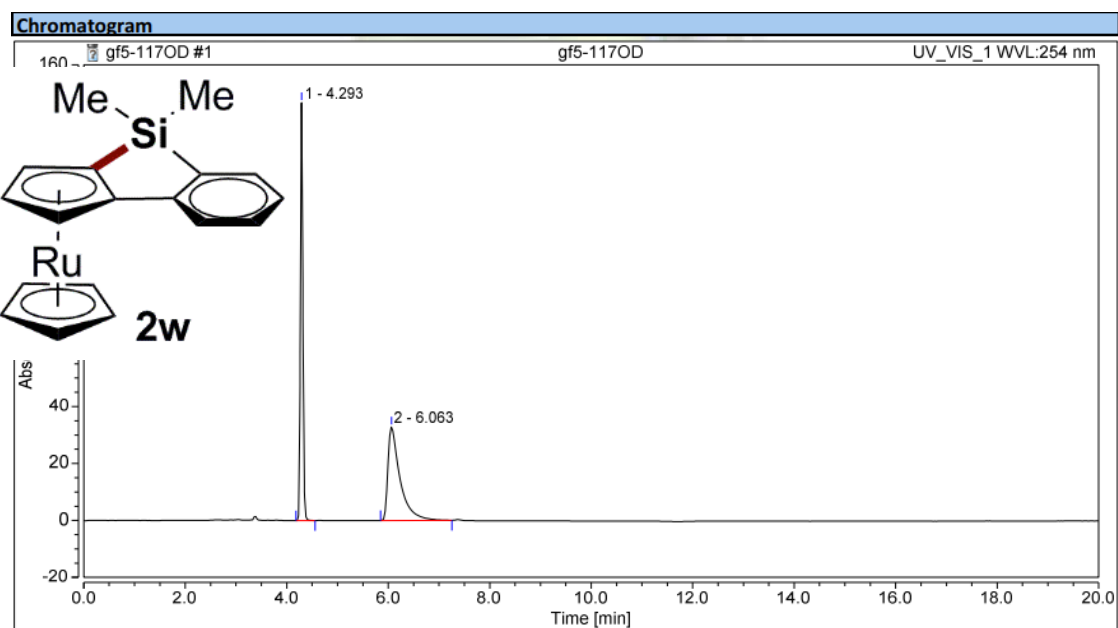
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	7.970	41.864	145.113	50.22	76.06
2	12.903	41.497	45.674	49.78	23.94
Totals:		83.361	190.787	100.00	100.00



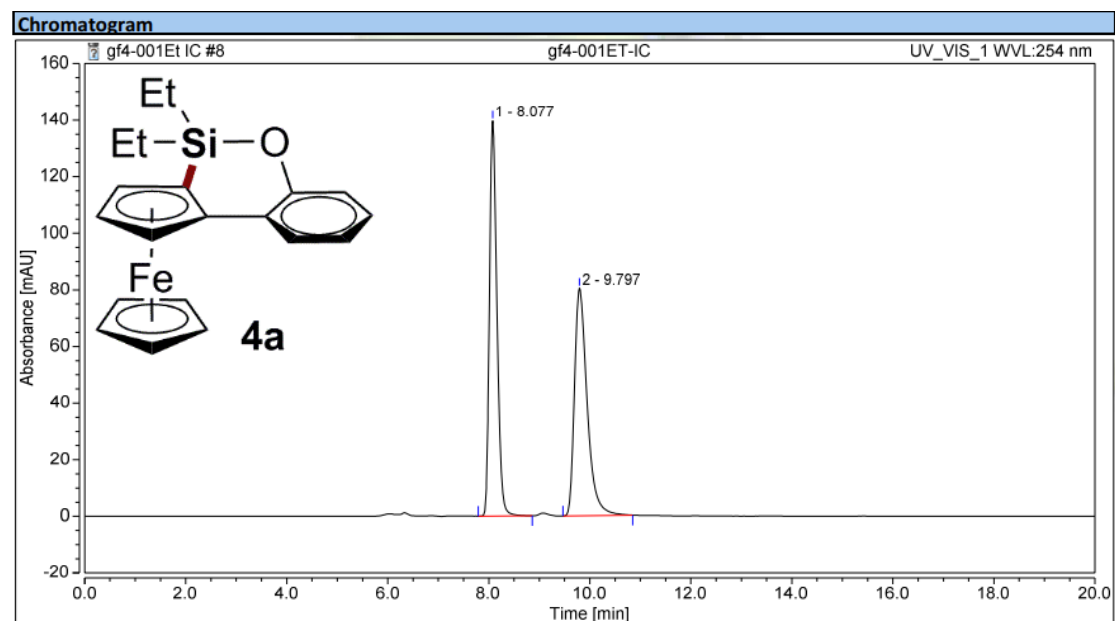
Result

Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.010	6.085	20.502	7.10	17.27
2	12.700	79.594	98.210	92.90	82.73
Totals:		85.679	118.712	100.00	100.00

Compound 2w

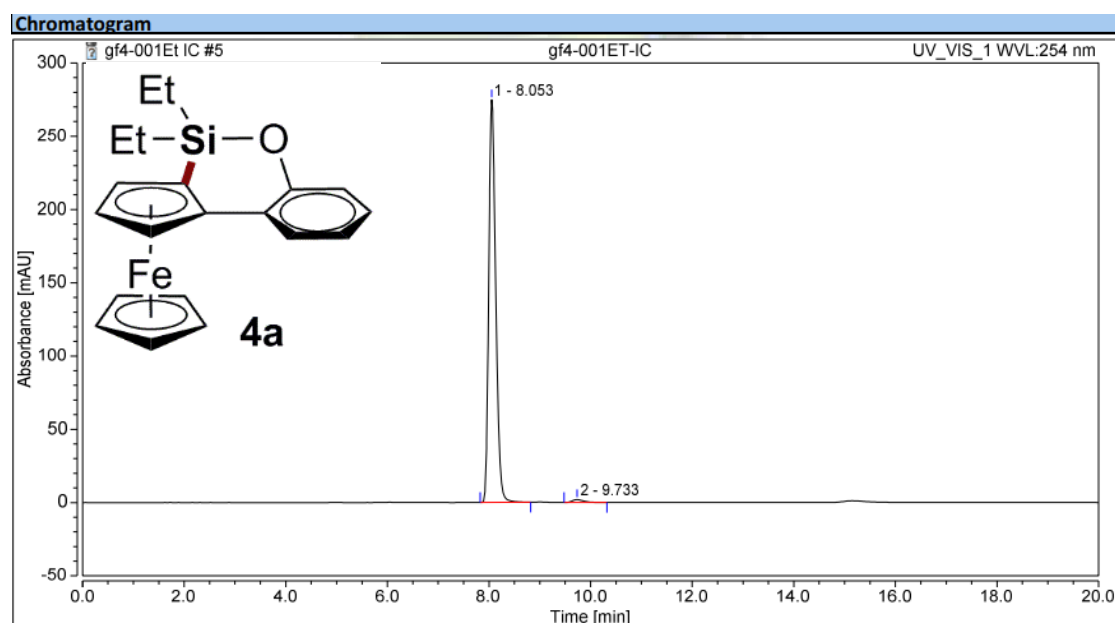


Compound 4a



Result

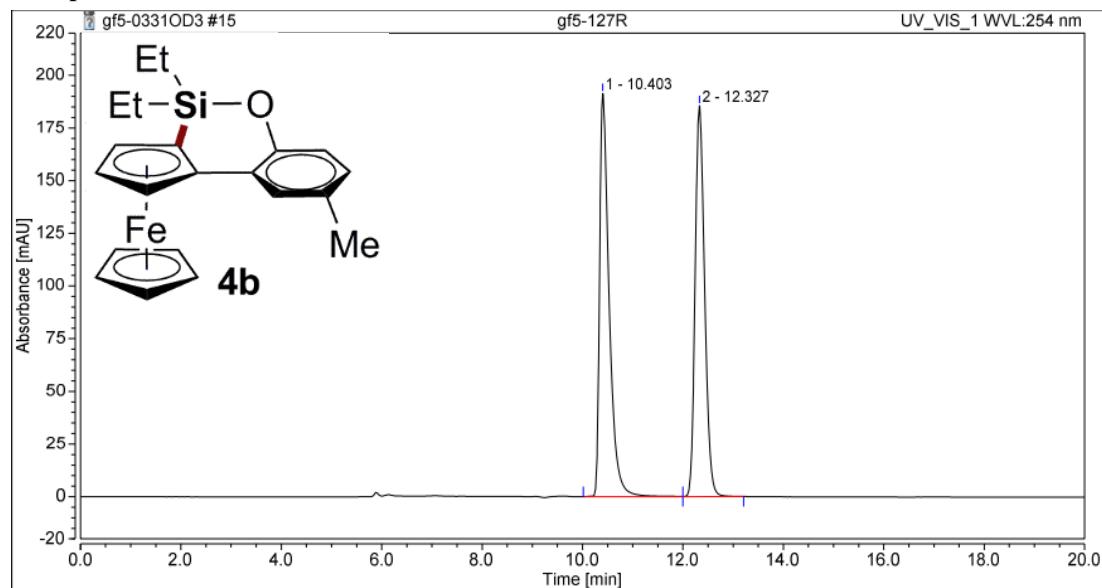
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.077	24.282	139.624	51.06	63.46
2	9.797	23.275	80.385	48.94	36.54
Totals:		47.556	220.008	100.00	100.00



Result

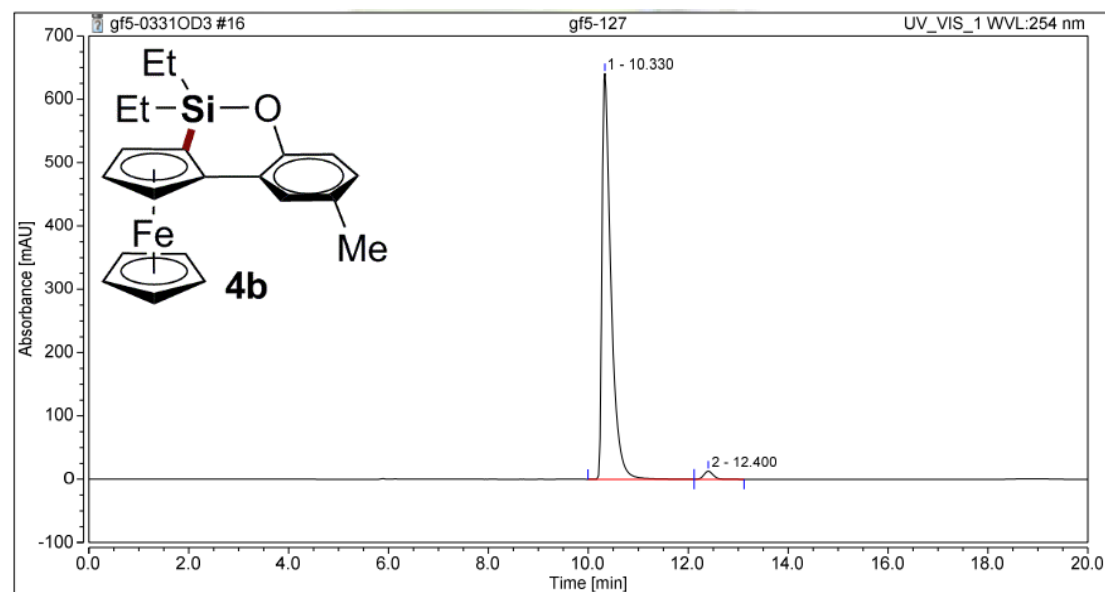
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.053	44.258	274.833	98.90	99.29
2	9.733	0.493	1.971	1.10	0.71
Totals:		44.751	276.805	100.00	100.00

Compound 4b



Result

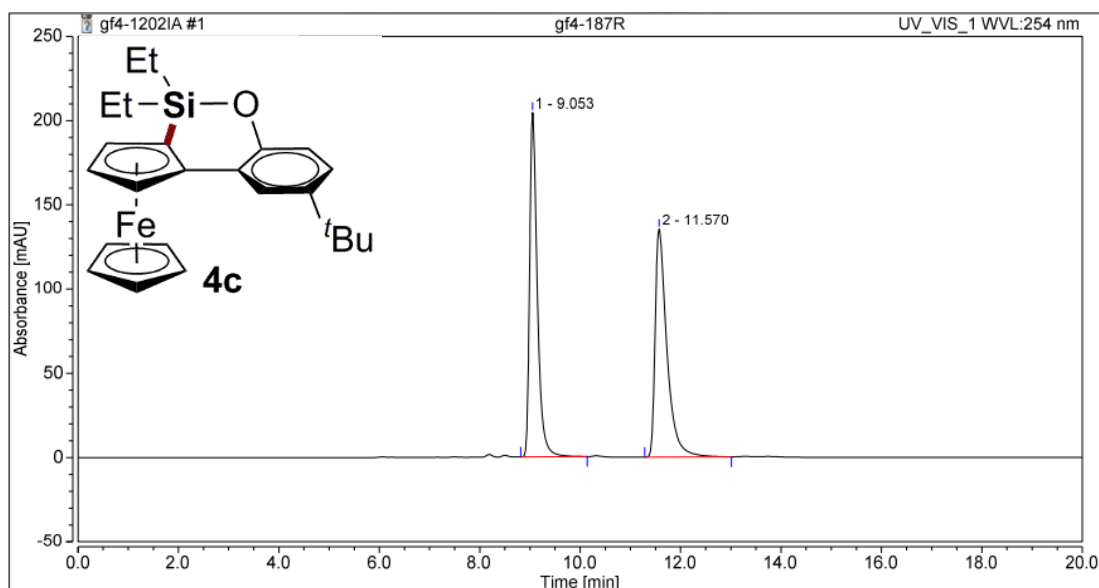
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.403	41.802	191.318	50.67	50.77
2	12.327	40.697	185.531	49.33	49.23
Totals:		82.499	376.850	100.00	100.00



Result

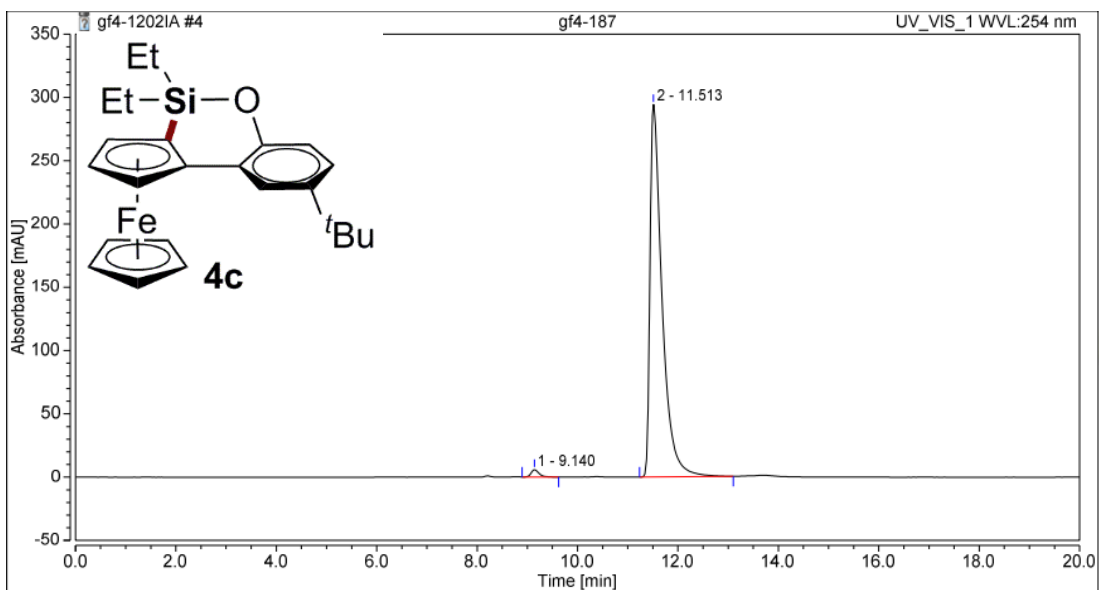
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.330	132.968	640.831	97.99	98.04
2	12.400	2.722	12.798	2.01	1.96
Totals:		135.690	653.629	100.00	100.00

Compound 4c



Result

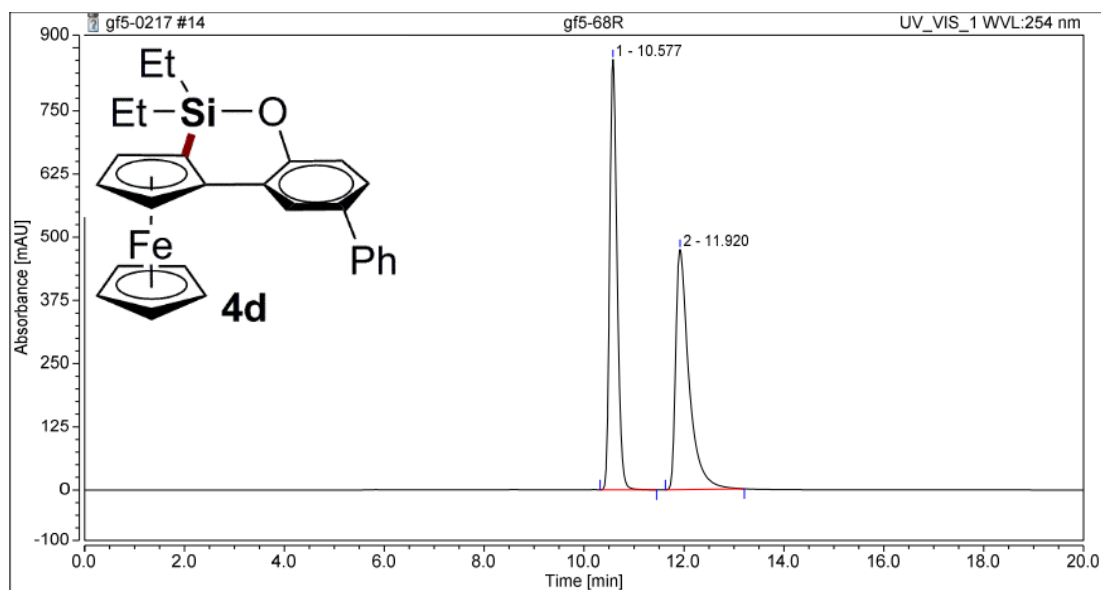
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.053	35.756	204.501	49.48	60.17
2	11.570	36.509	135.353	50.52	39.83
Totals:		72.266	339.854	100.00	100.00



Result

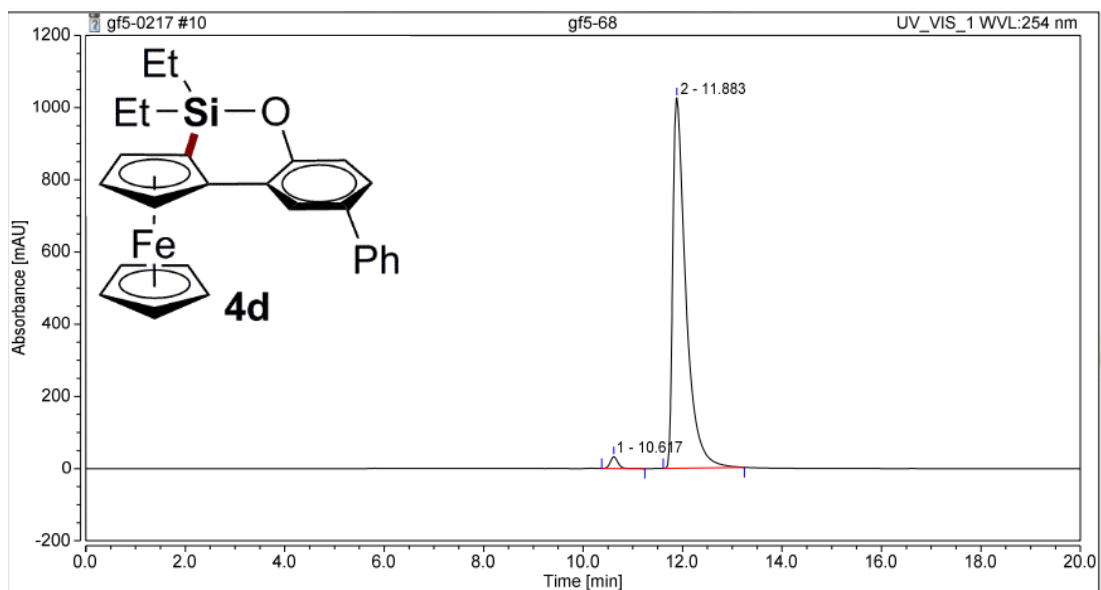
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.140	1.043	5.844	1.26	1.95
2	11.513	81.816	294.328	98.74	98.05
Totals:		82.858	300.172	100.00	100.00

Compound 4d



Result

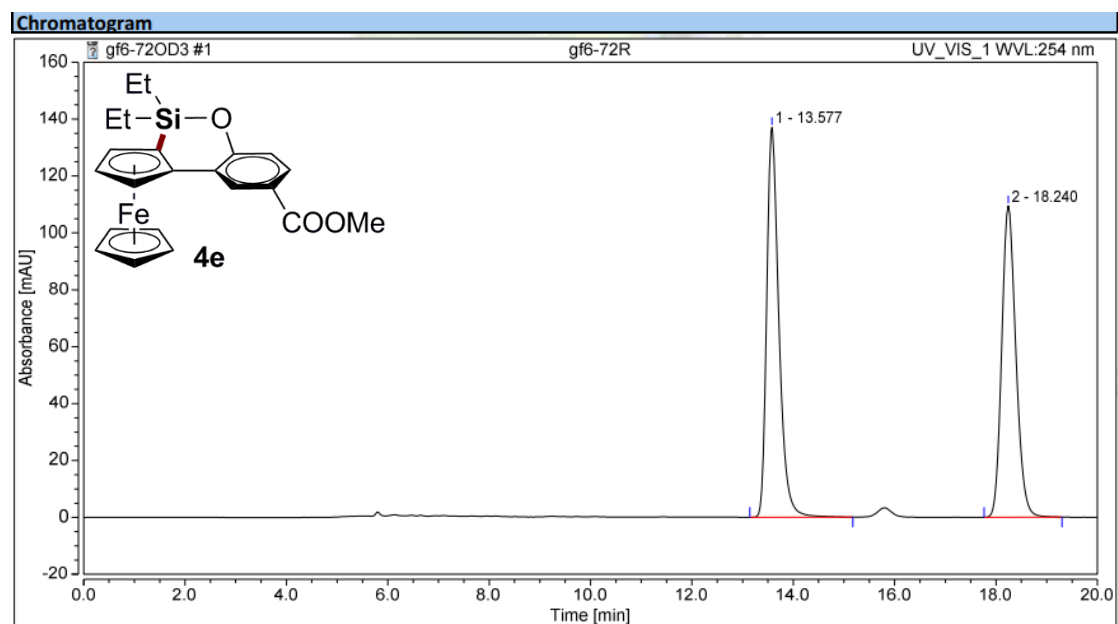
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.577	145.660	851.121	49.94	64.17
2	11.920	145.995	475.281	50.06	35.83
Totals:		291.655	1326.402	100.00	100.00



Result

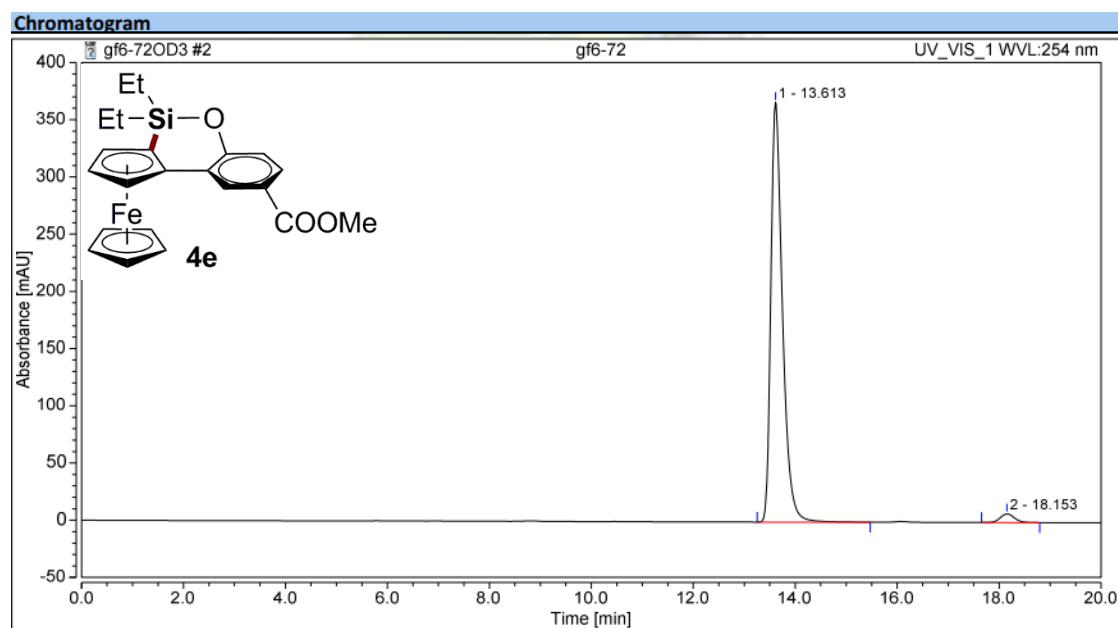
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.617	5.866	32.861	1.84	3.10
2	11.883	312.288	1026.186	98.16	96.90
Totals:		318.154	1059.047	100.00	100.00

Compound 4e



Result

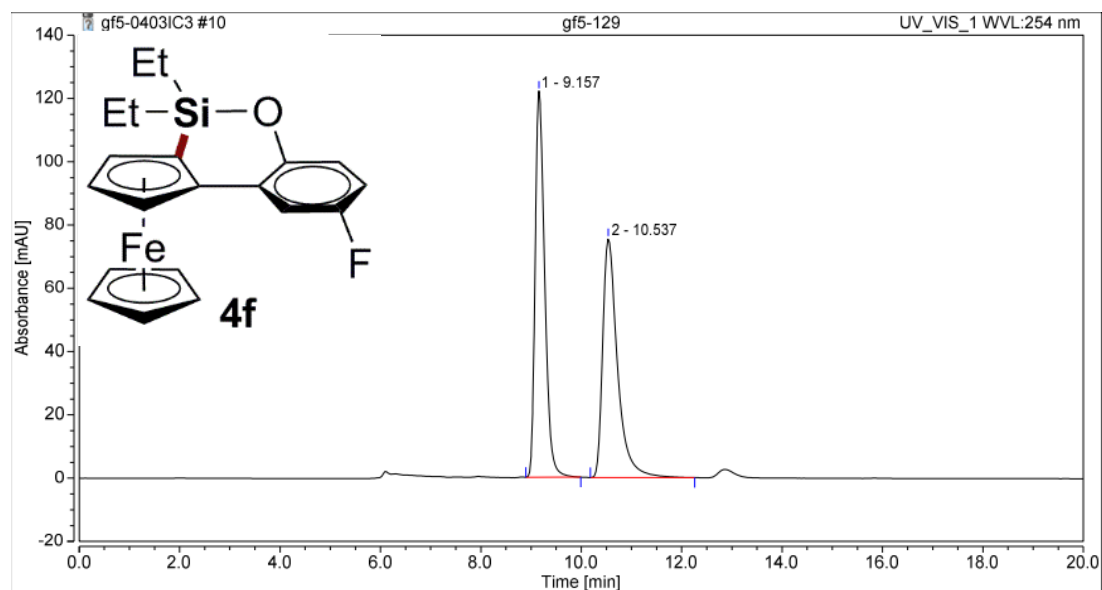
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	13.577	37.990	136.990	51.52	55.57
2	18.240	35.746	109.521	48.48	44.43
Totals:		73.735	246.510	100.00	100.00



Result

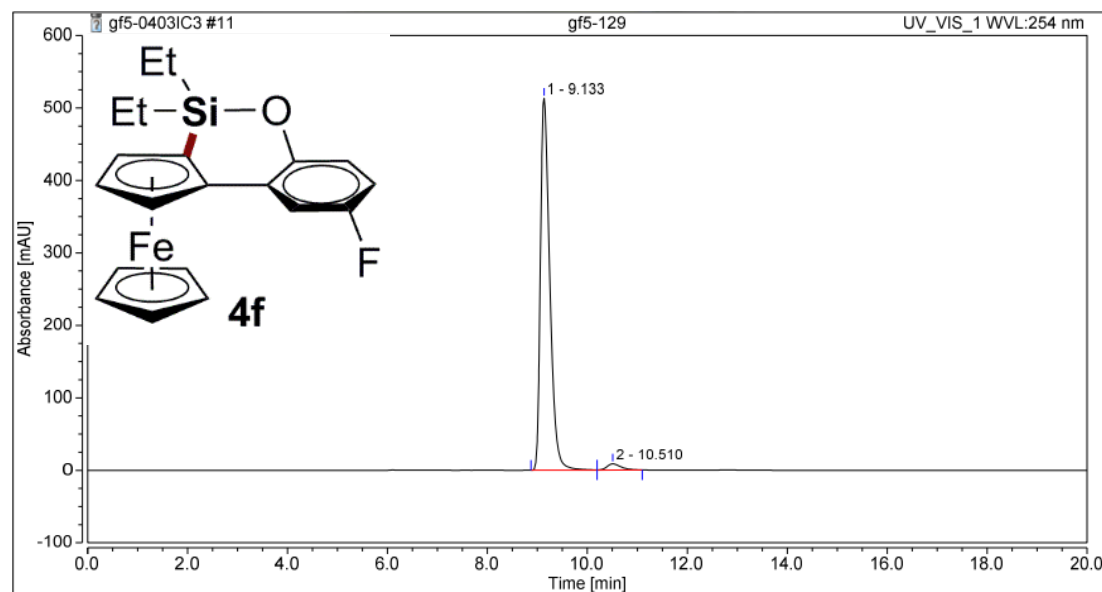
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	13.613	96.751	366.601	97.52	97.98
2	18.153	2.463	7.546	2.48	2.02
Totals:		99.214	374.148	100.00	100.00

Compound 4f



Result

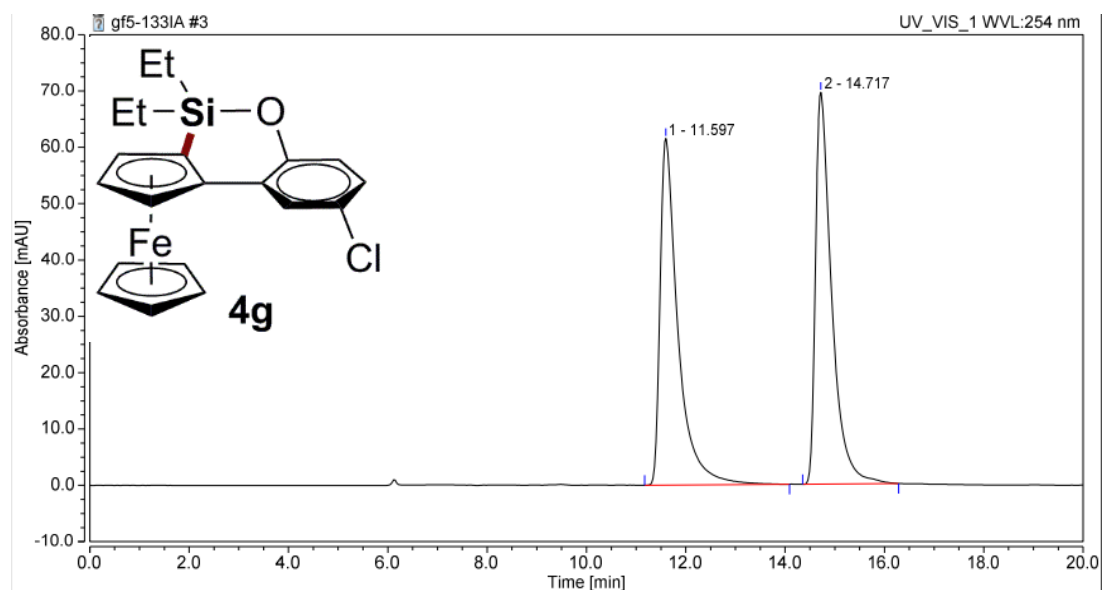
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.157	26.718	122.051	50.77	61.79
2	10.537	25.909	75.481	49.23	38.21
Totals:		52.627	197.532	100.00	100.00



Result

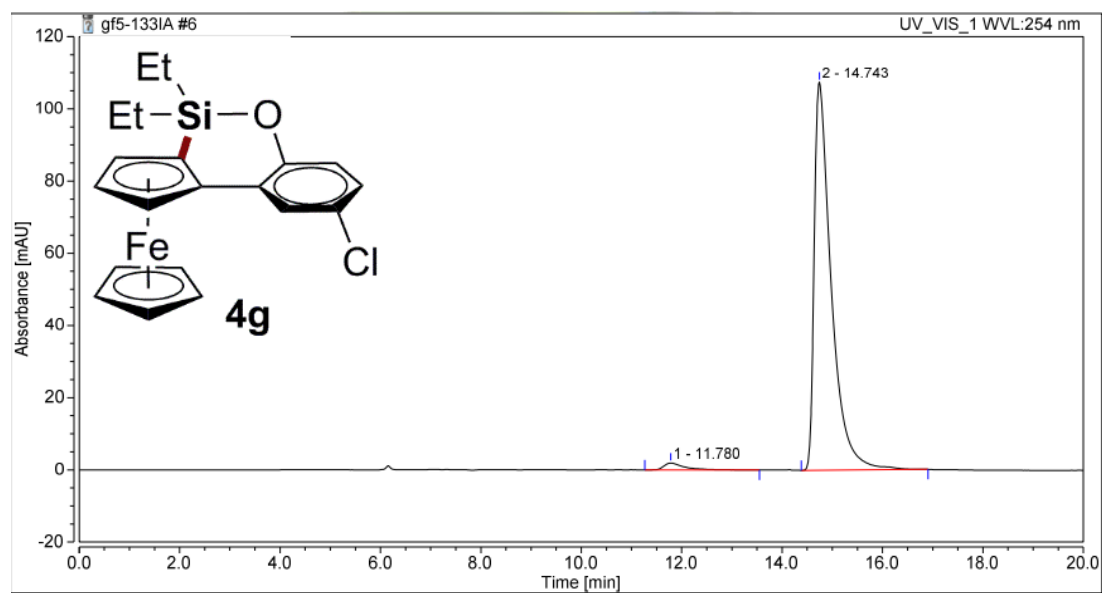
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.133	110.906	513.400	97.56	98.36
2	10.510	2.779	8.567	2.44	1.64
Totals:		113.684	521.967	100.00	100.00

Compound 4g



Result

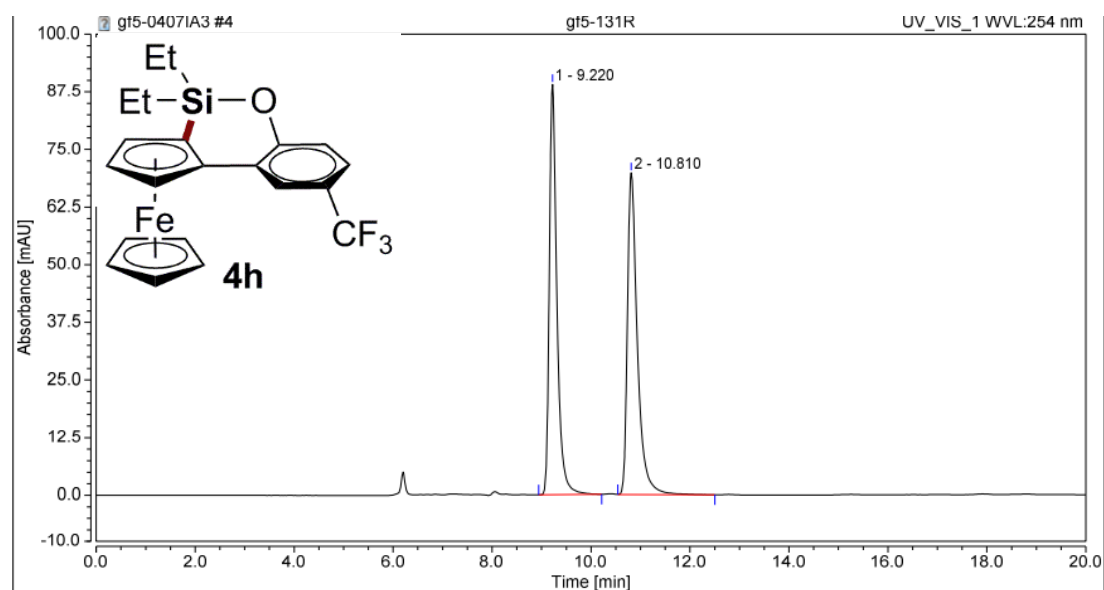
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.597	25.692	61.535	49.40	46.94
2	14.717	26.317	69.570	50.60	53.06
Totals:		52.009	131.104	100.00	100.00



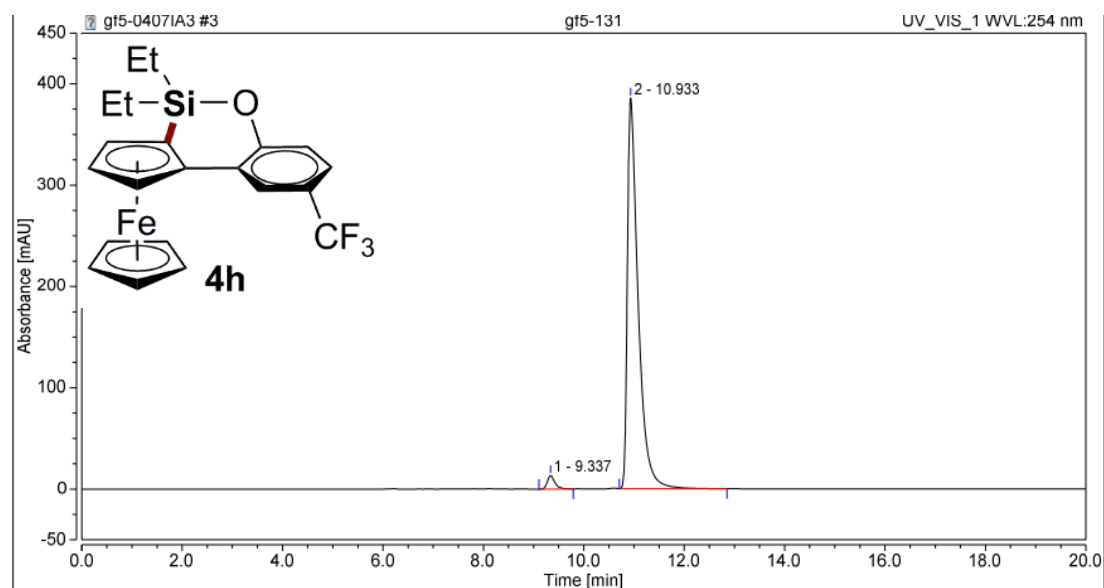
Result

Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.780	0.924	1.914	2.15	1.75
2	14.743	42.153	107.454	97.85	98.25
Totals:		43.077	109.368	100.00	100.00

Compound 4h

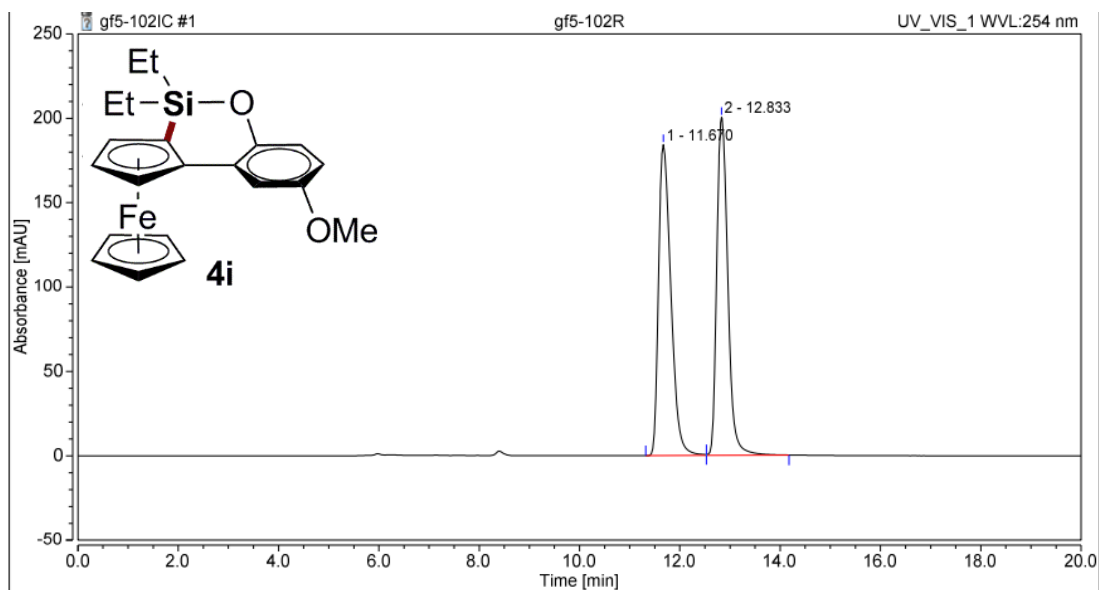


Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.220	15.906	89.002	49.47	56.06
2	10.810	16.244	69.761	50.53	43.94
Totals:		32.150	158.763	100.00	100.00



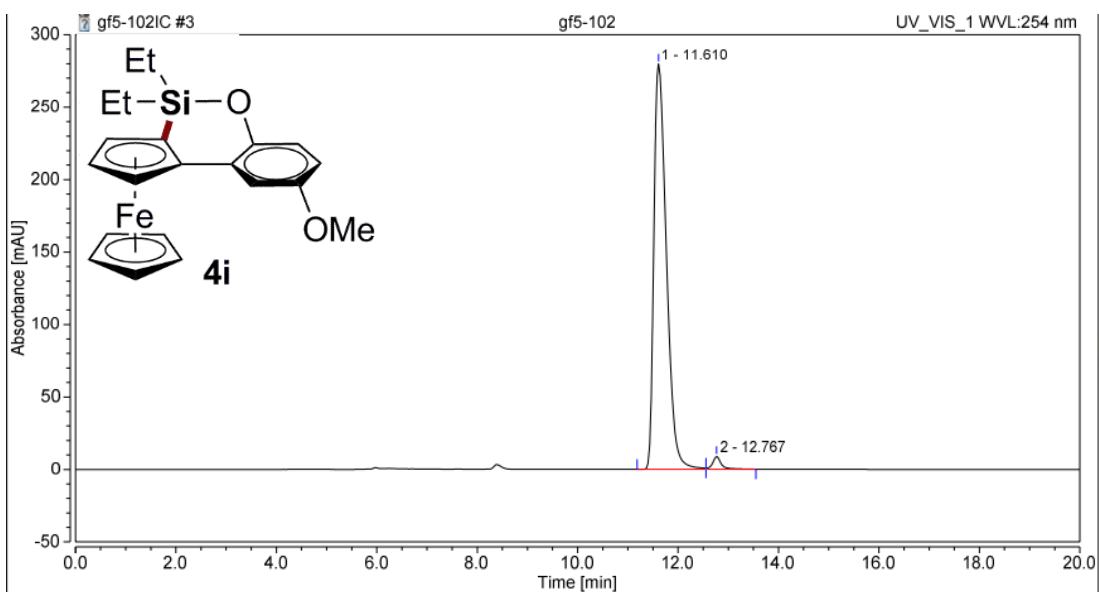
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.337	2.328	13.225	2.37	3.32
2	10.933	95.782	385.452	97.63	96.68
Totals:		98.110	398.677	100.00	100.00

Compound 4i



Result

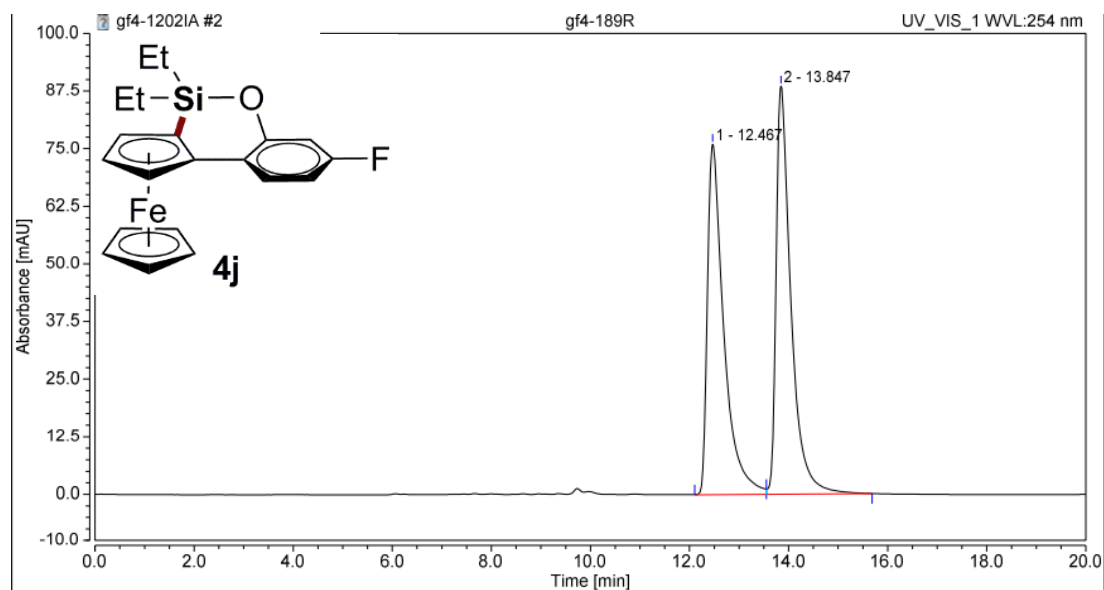
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.670	52.256	184.295	50.69	47.92
2	12.833	50.828	200.255	49.31	52.08
Totals:		103.084	384.550	100.00	100.00



Result

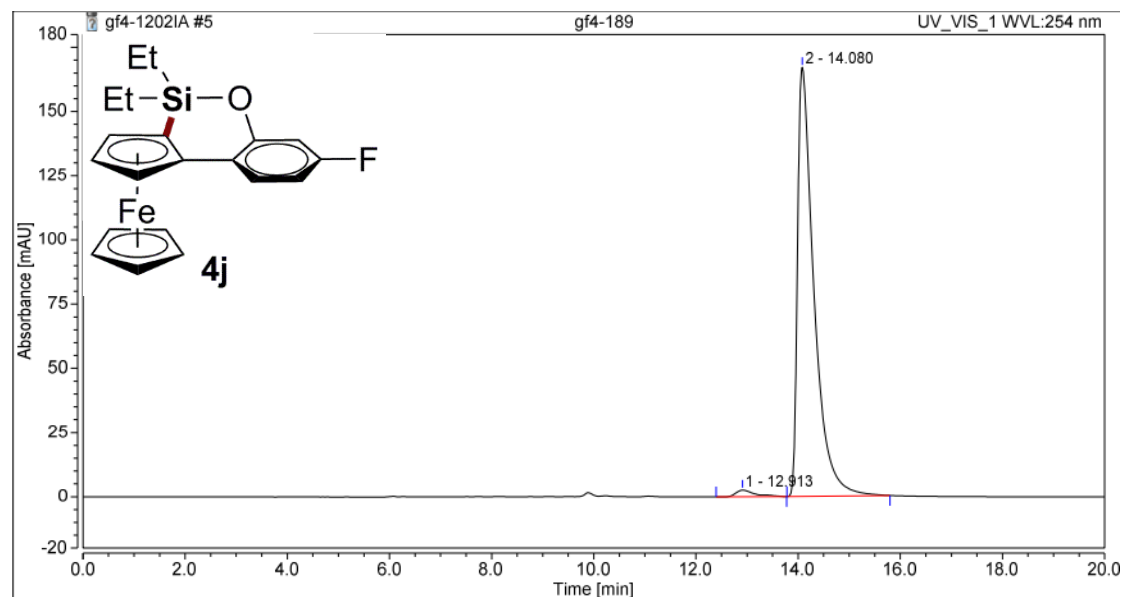
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.610	80.432	279.776	97.84	96.93
2	12.767	1.778	8.857	2.16	3.07
Totals:		82.210	288.634	100.00	100.00

Compound 4j



Result

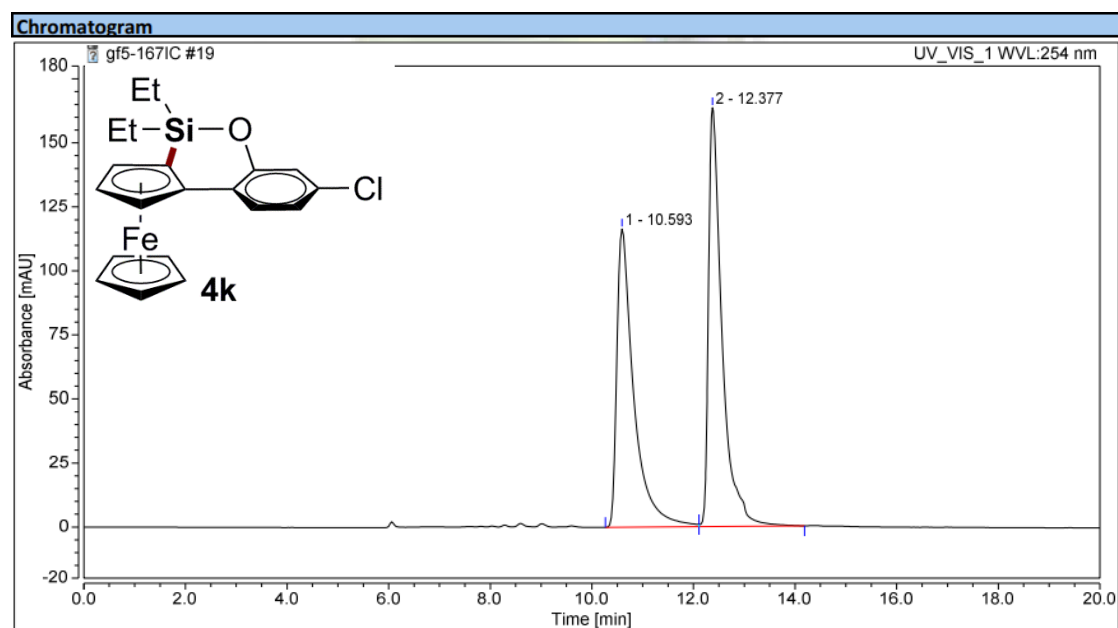
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	12.467	29.112	76.005	48.76	46.18
2	13.847	30.597	88.569	51.24	53.82
Totals:		59.709	164.575	100.00	100.00



Result

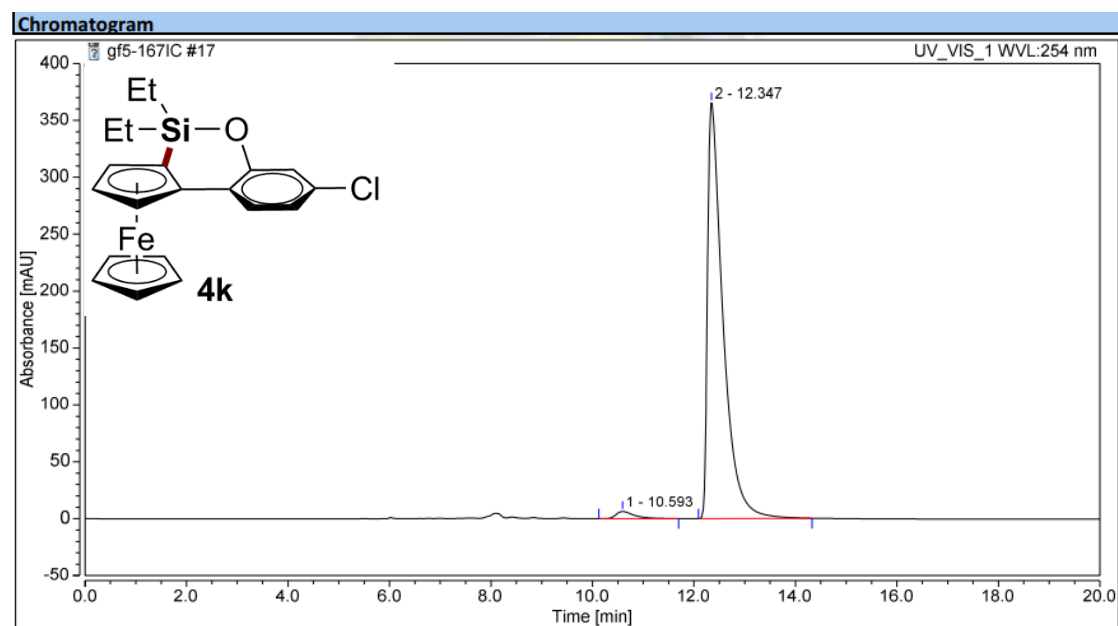
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	12.913	1.143	2.576	1.81	1.52
2	14.080	61.929	167.063	98.19	98.48
Totals:		63.071	169.639	100.00	100.00

Compound 4k



Result

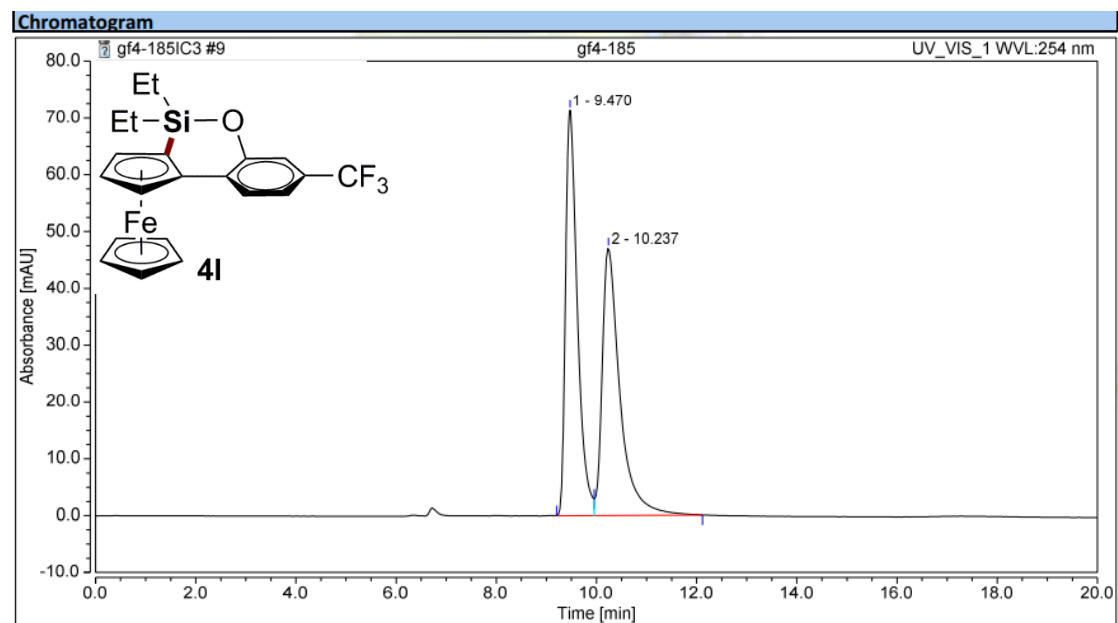
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.593	45.370	116.474	47.27	41.59
2	12.377	50.607	163.551	52.73	58.41
Totals:		95.977	280.025	100.00	100.00



Result

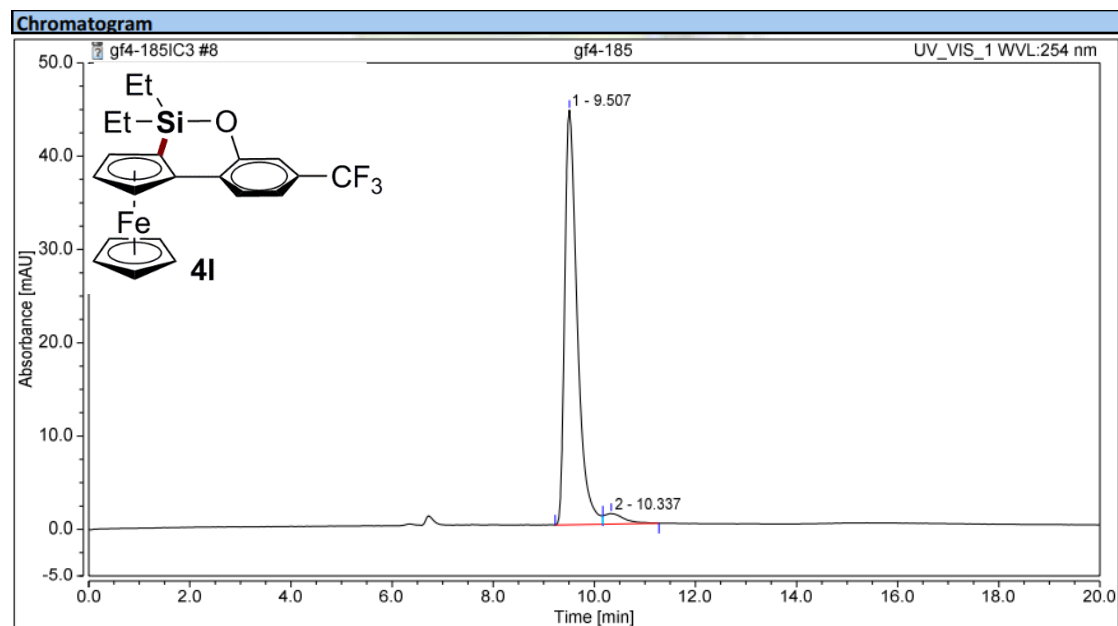
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.593	2.735	6.440	2.08	1.73
2	12.347	128.739	365.562	97.92	98.27
Totals:		131.474	372.002	100.00	100.00

Compound 4l



Result

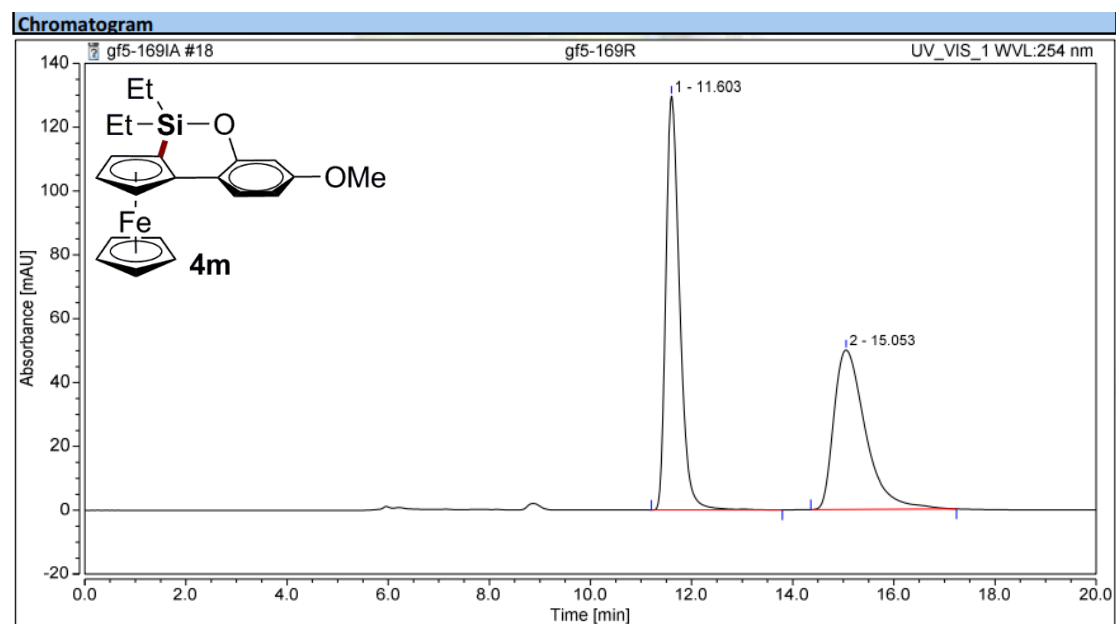
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.470	19.593	71.389	50.44	60.27
2	10.237	19.252	47.056	49.56	39.73
Totals:		38.845	118.445	100.00	100.00



Result

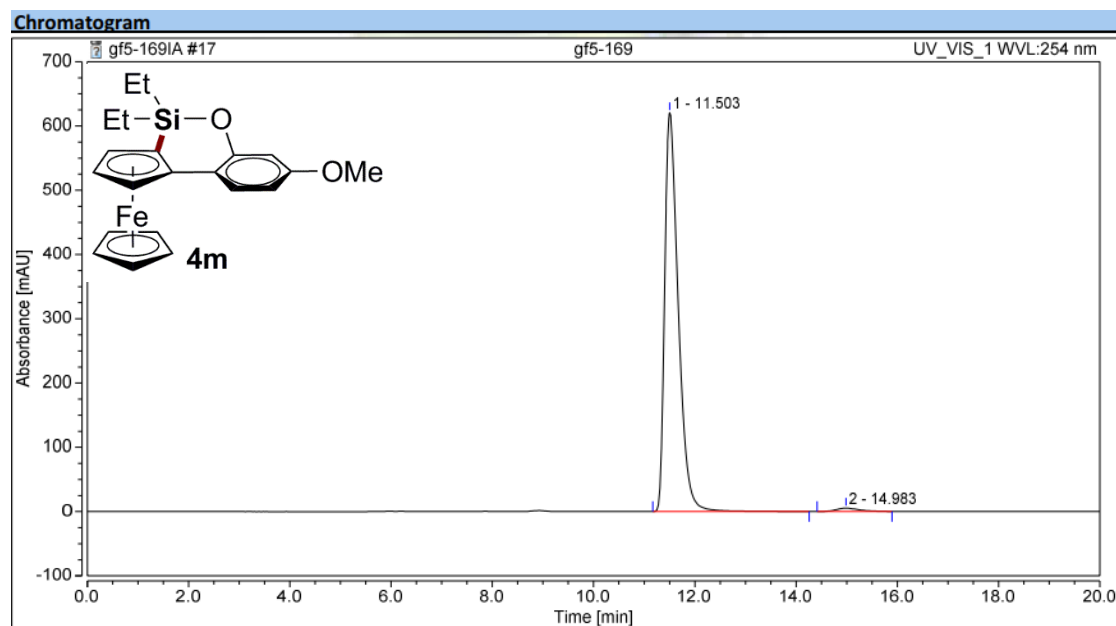
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.507	12.752	44.424	96.13	97.56
2	10.337	0.513	1.113	3.87	2.44
Totals:		13.265	45.537	100.00	100.00

Compound 4m



Result

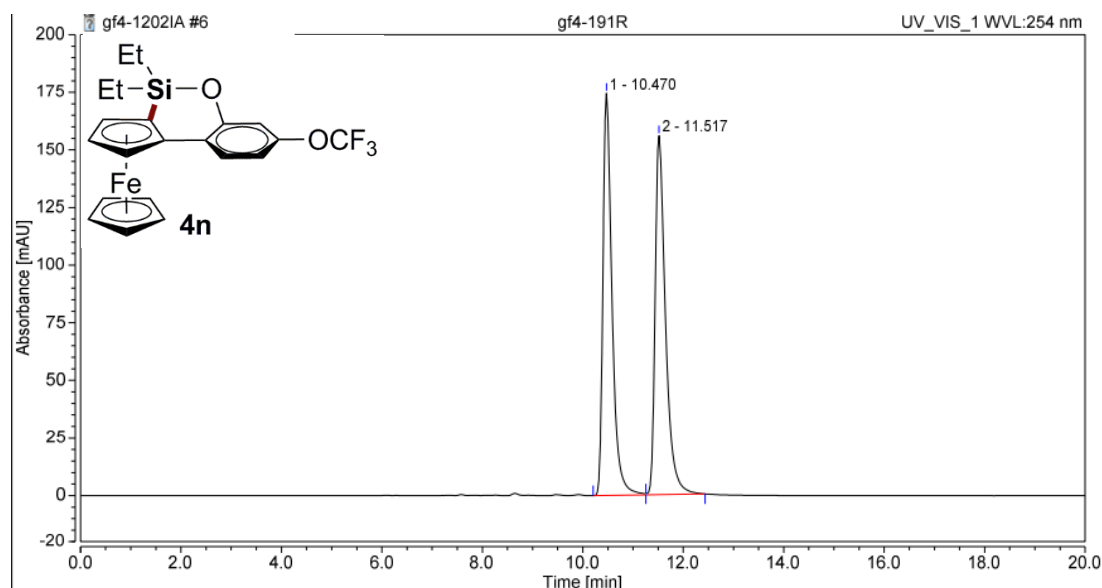
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.603	40.762	129.617	53.06	72.18
2	15.053	36.056	49.957	46.94	27.82
Totals:		76.819	179.574	100.00	100.00



Result

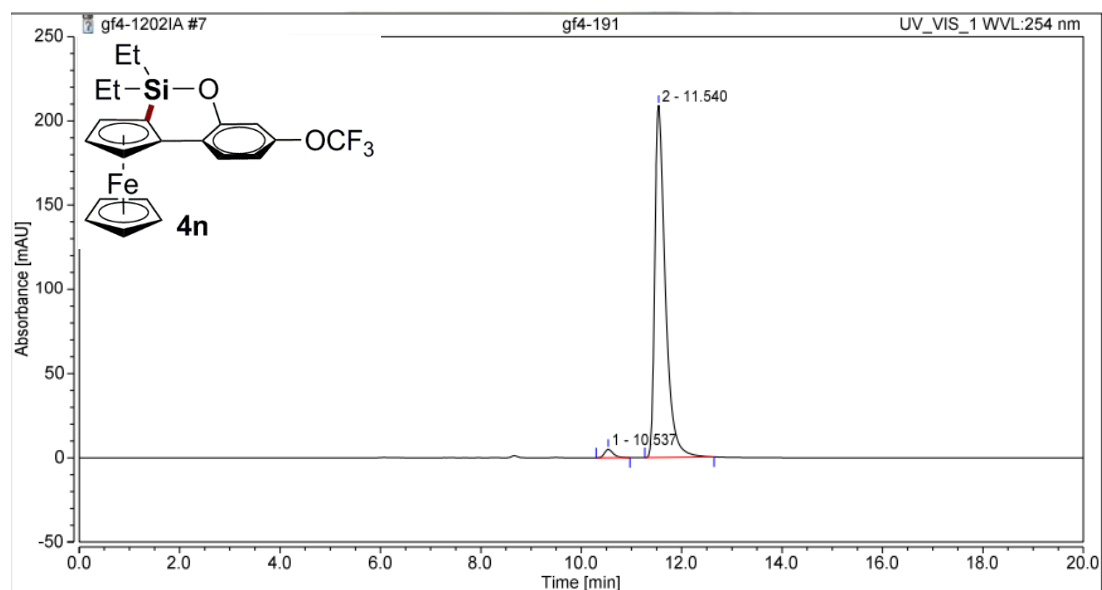
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.503	193.038	620.397	98.67	99.19
2	14.983	2.611	5.081	1.33	0.81
Totals:		195.649	625.478	100.00	100.00

Compound 4n



Result

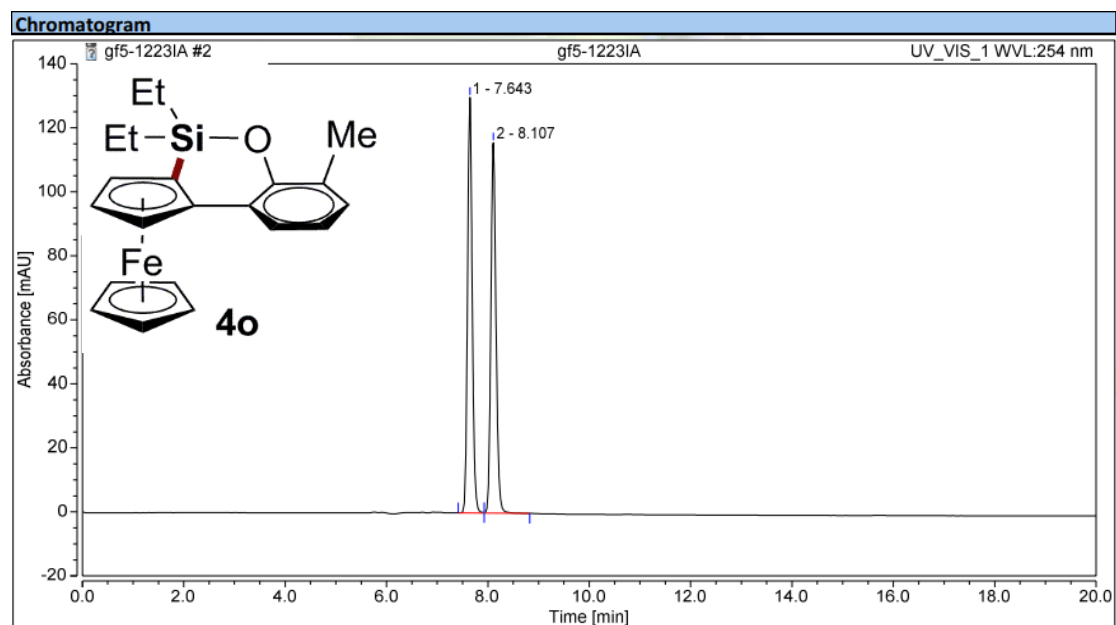
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.470	36.316	174.508	49.52	52.83
2	11.517	37.019	155.813	50.48	47.17
Totals:		73.335	330.322	100.00	100.00



Result

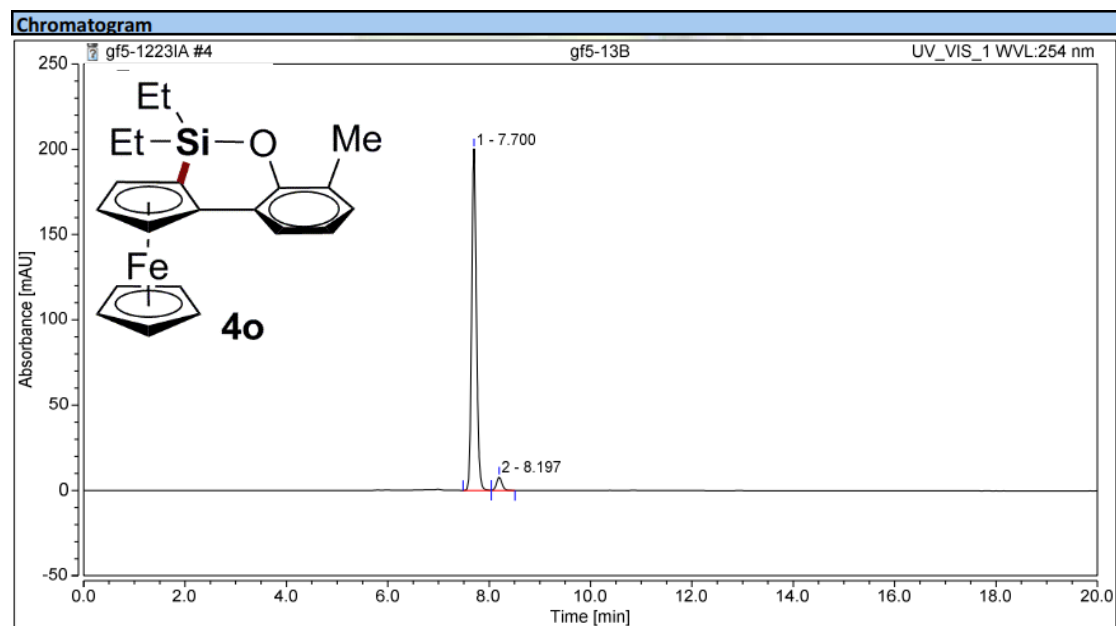
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.537	1.031	5.005	2.00	2.34
2	11.540	50.509	209.091	98.00	97.66
Totals:		51.540	214.096	100.00	100.00

Compound 4o



Result

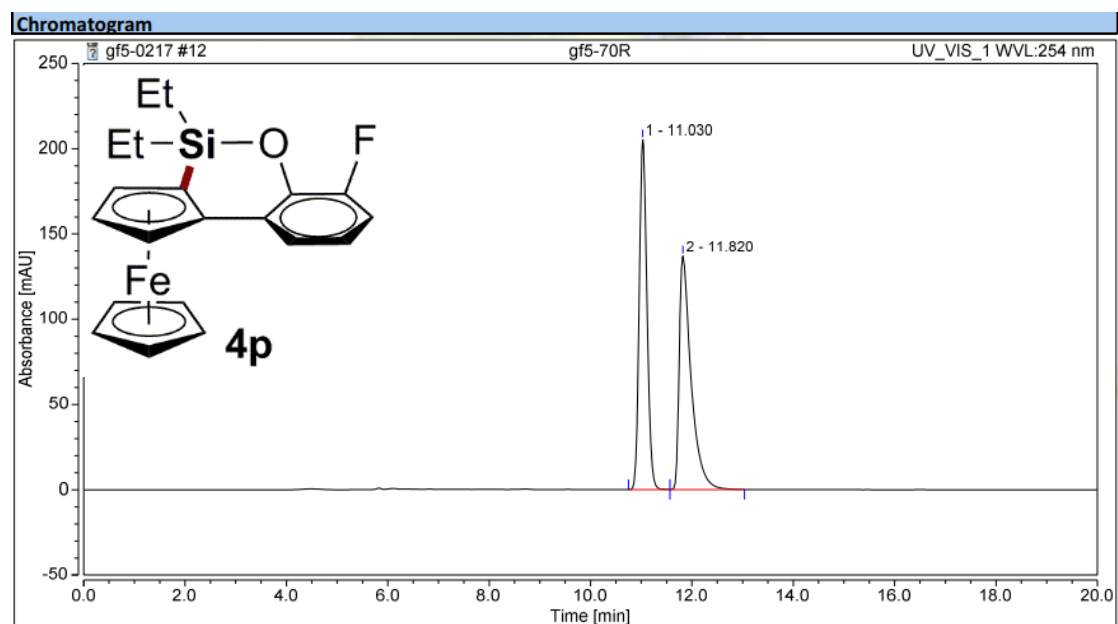
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	7.643	13.978	129.788	50.56	52.87
2	8.107	13.666	115.677	49.44	47.13
Totals:		27.644	245.465	100.00	100.00



Result

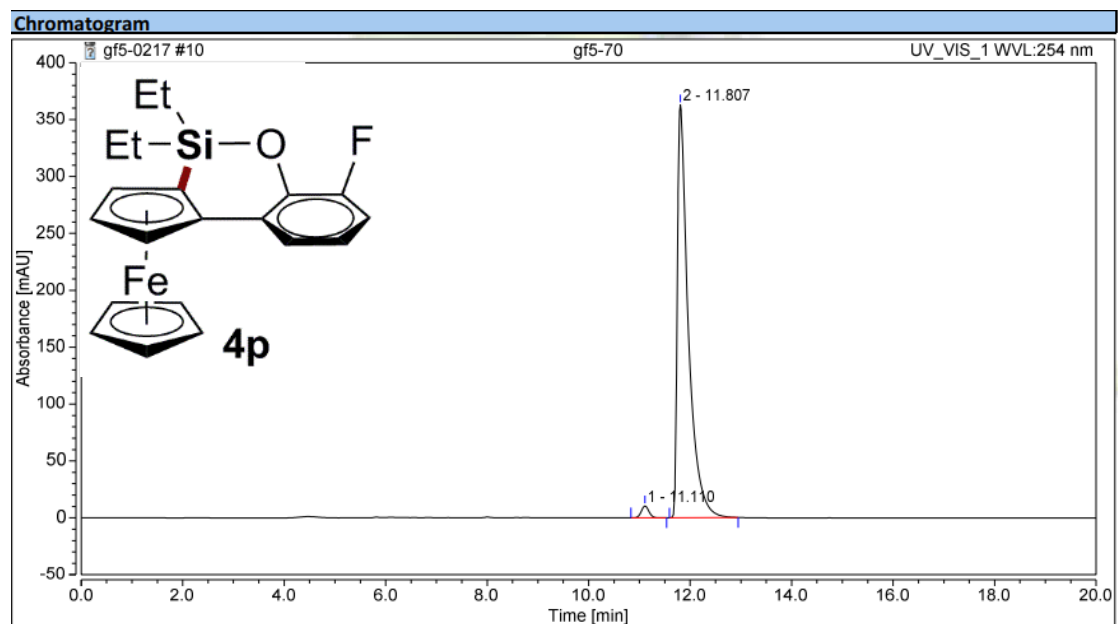
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	7.700	21.907	200.297	95.77	96.21
2	8.197	0.967	7.896	4.23	3.79
Totals:		22.874	208.193	100.00	100.00

Compound 4p



Result

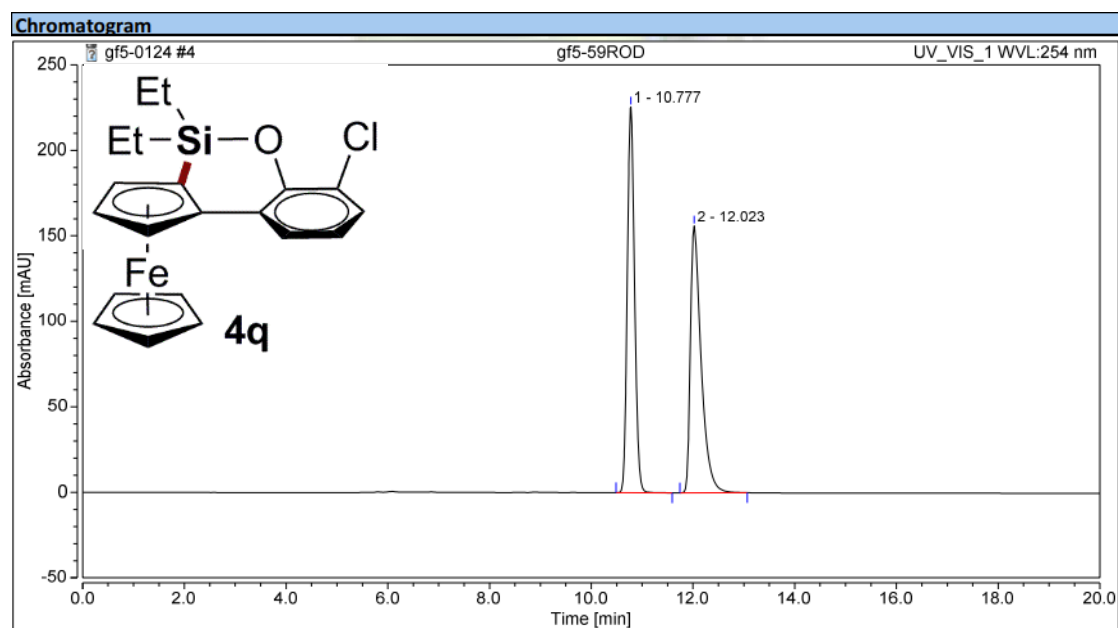
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.030	36.217	205.127	49.38	59.97
2	11.820	37.120	136.897	50.62	40.03
Totals:		73.336	342.023	100.00	100.00



Result

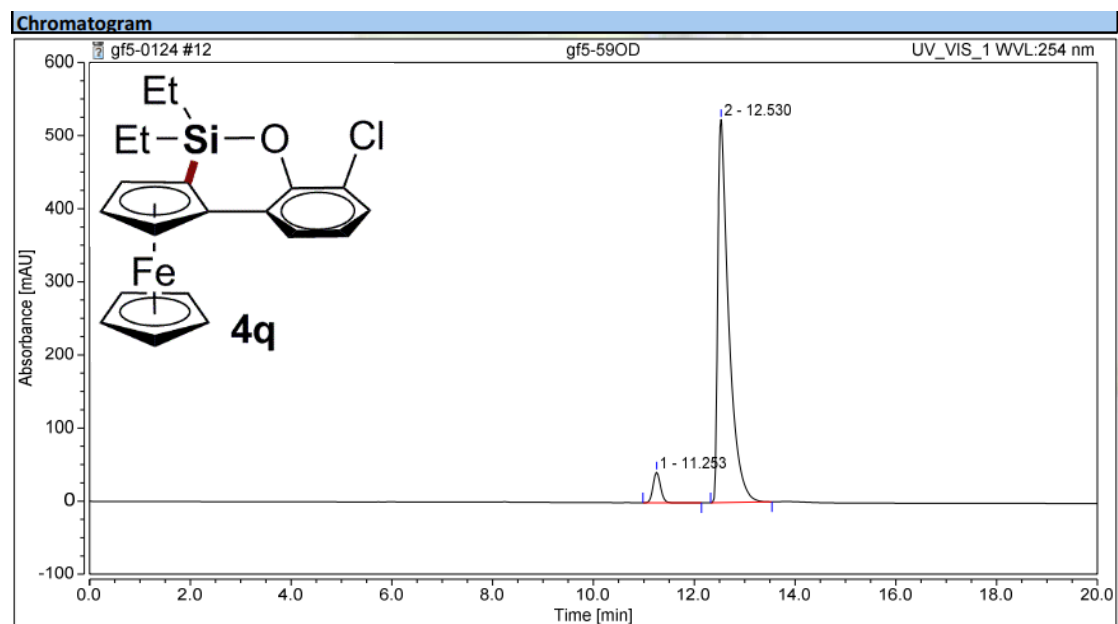
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.110	1.806	10.529	1.95	2.82
2	11.807	90.876	362.907	98.05	97.18
Totals:		92.682	373.436	100.00	100.00

Compound 4q



Result

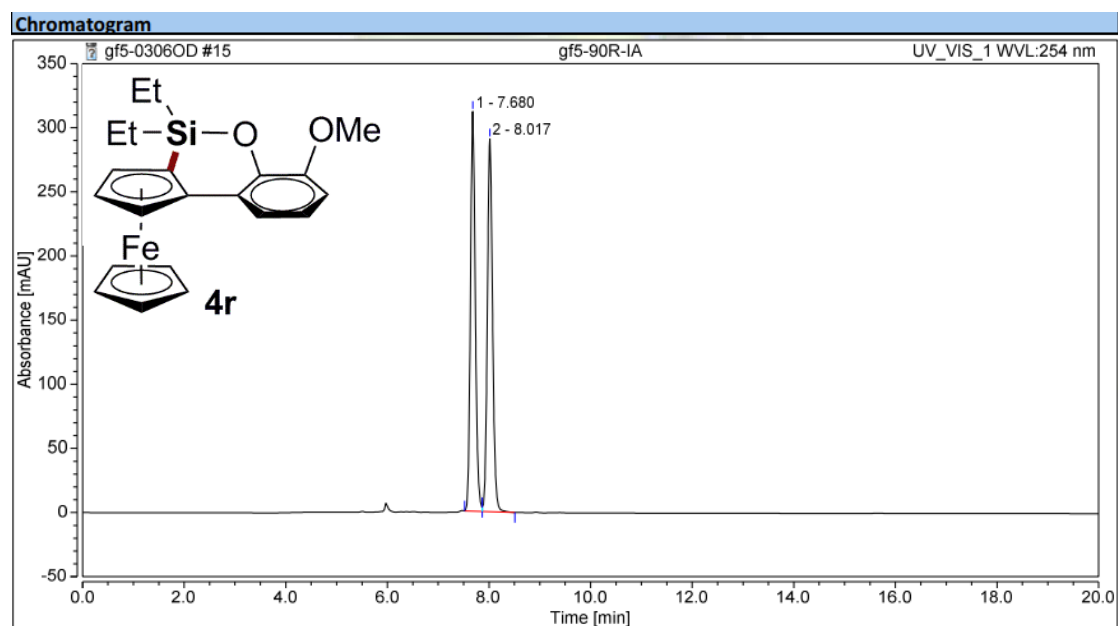
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.777	37.353	225.551	49.41	59.10
2	12.023	38.249	156.099	50.59	40.90
Totals:		75.603	381.650	100.00	100.00



Result

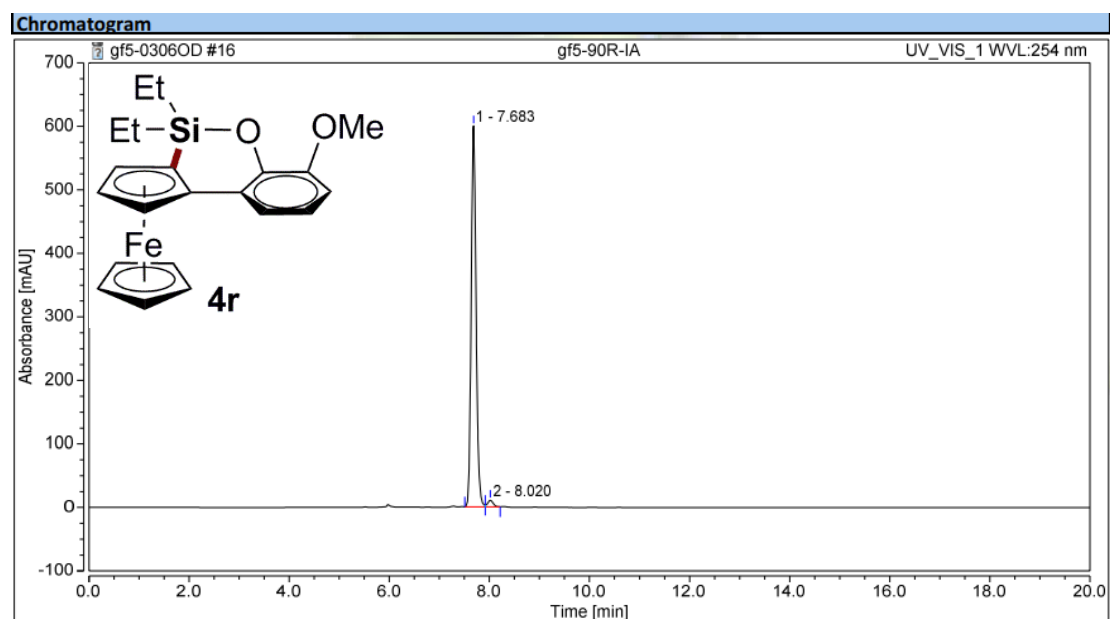
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.253	7.087	42.014	5.07	7.42
2	12.530	132.628	524.036	94.93	92.58
Totals:		139.715	566.050	100.00	100.00

Compound 4r



Result

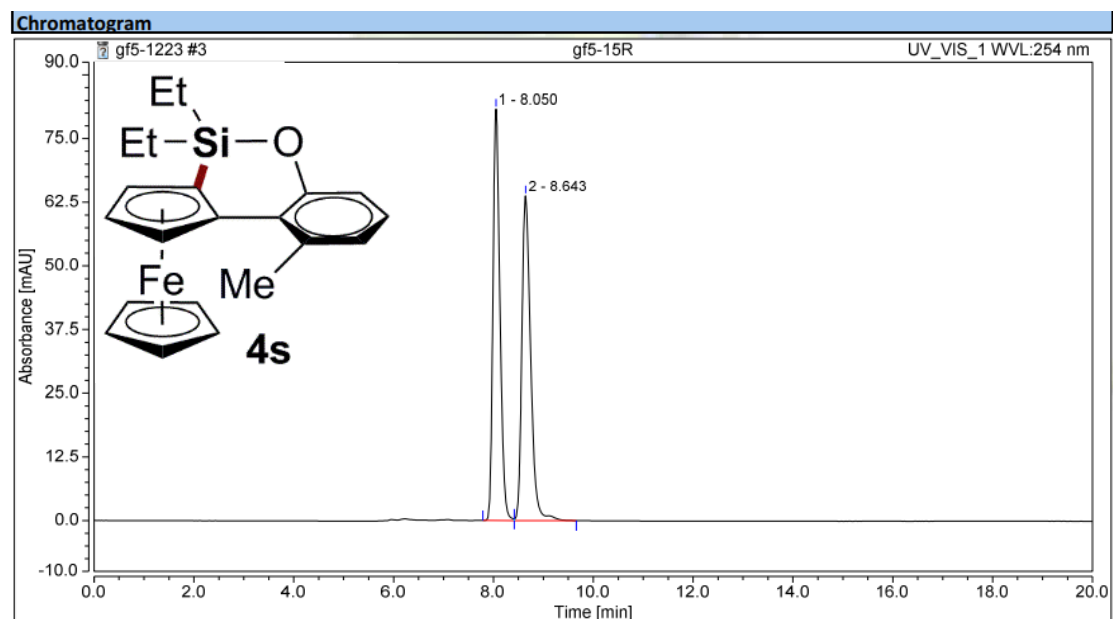
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	7.680	34.955	311.690	50.27	51.76
2	8.017	34.574	290.548	49.73	48.24
Totals:		69.530	602.238	100.00	100.00



Result

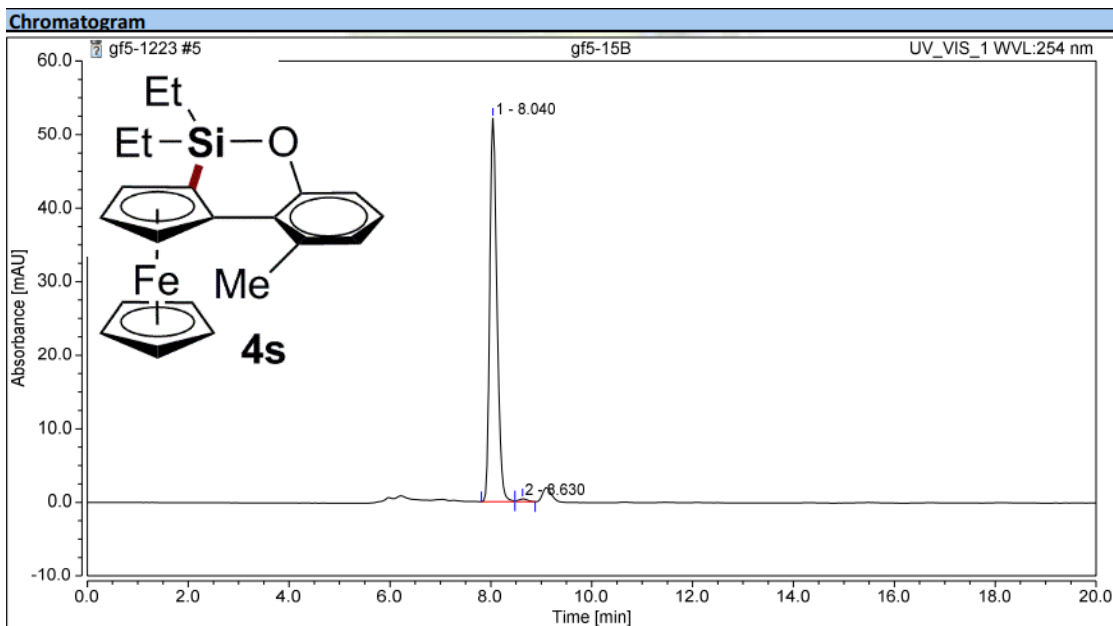
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	7.683	67.879	599.923	98.17	98.29
2	8.020	1.265	10.439	1.83	1.71
Totals:		69.144	610.362	100.00	100.00

Compound 4s



Result

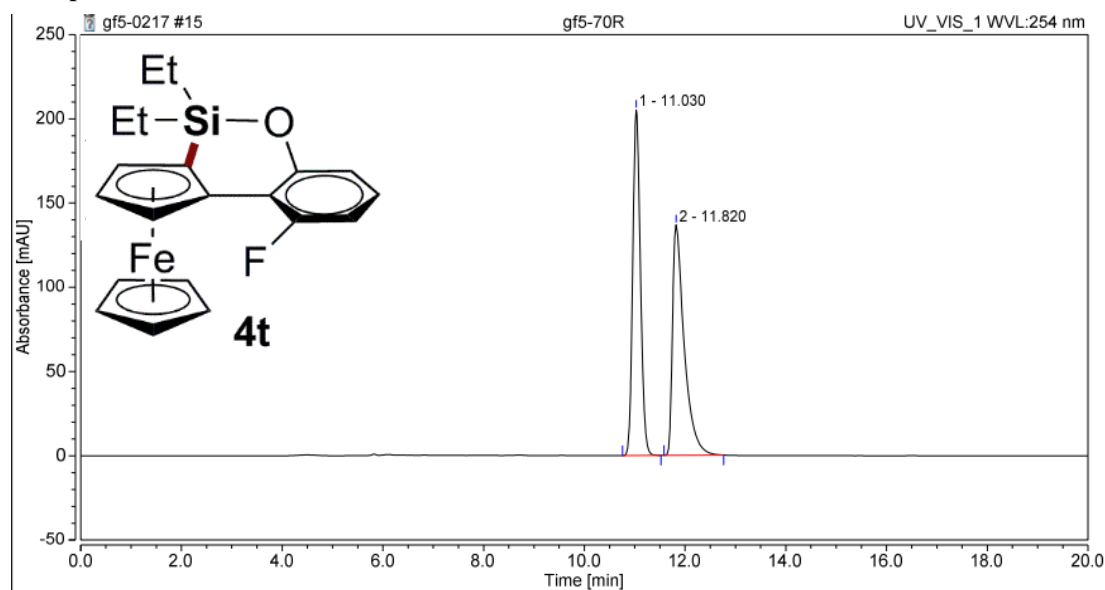
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.050	13.126	80.771	50.35	55.88
2	8.643	12.942	63.772	49.65	44.12
Totals:		26.069	144.542	100.00	100.00



Result

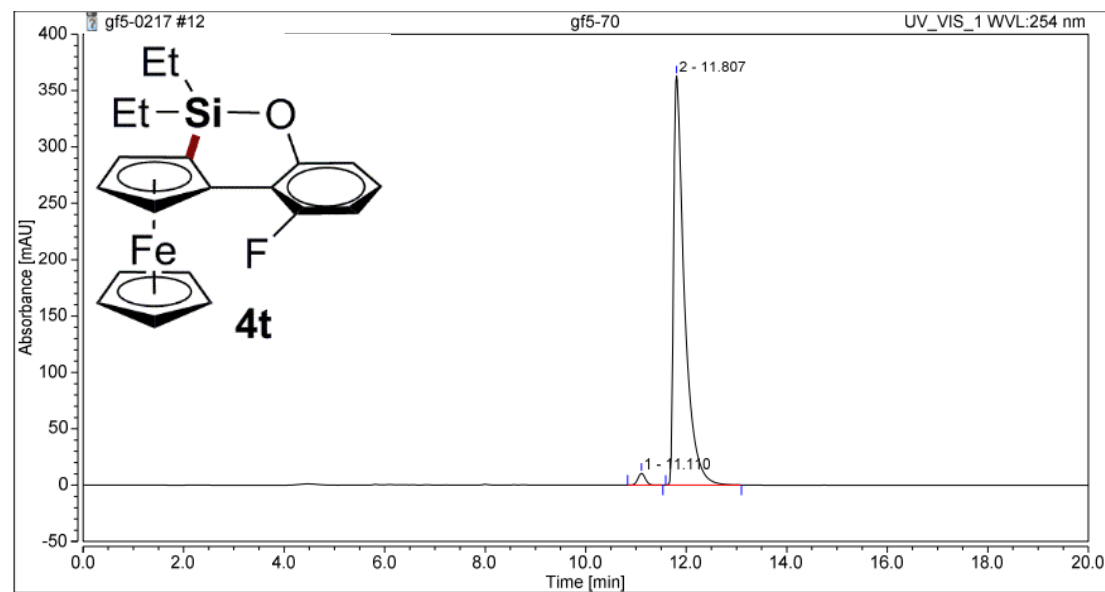
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	8.040	8.674	52.142	99.12	99.27
2	8.630	0.077	0.386	0.88	0.73
Totals:		8.751	52.528	100.00	100.00

Compound 4t



Result

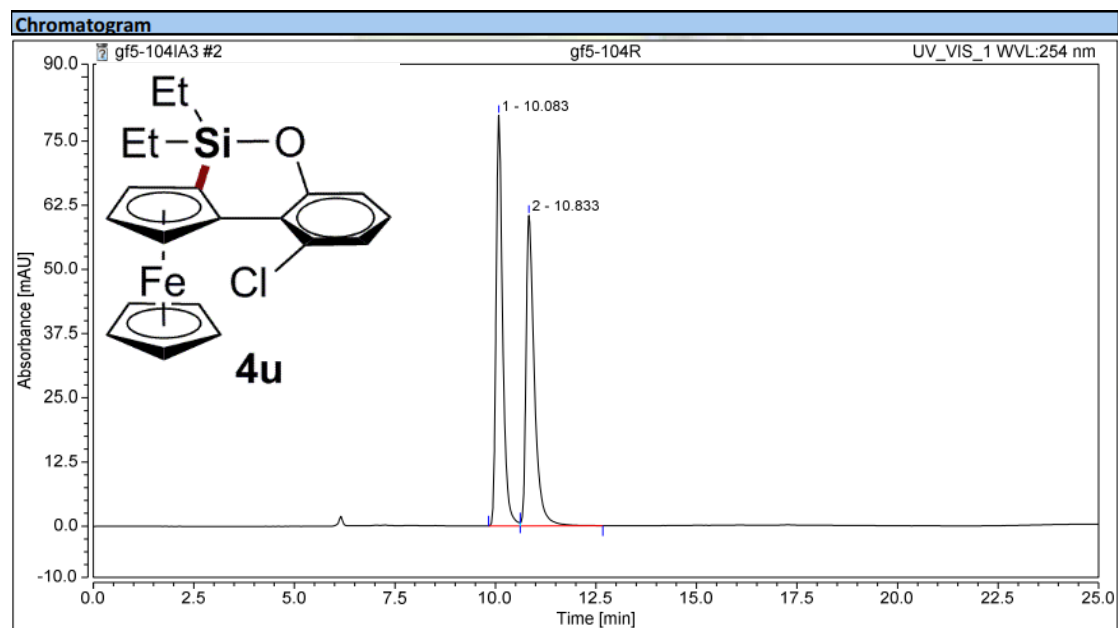
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.030	36.170	205.086	49.51	59.99
2	11.820	36.888	136.780	50.49	40.01
Totals:		73.058	341.866	100.00	100.00



Result

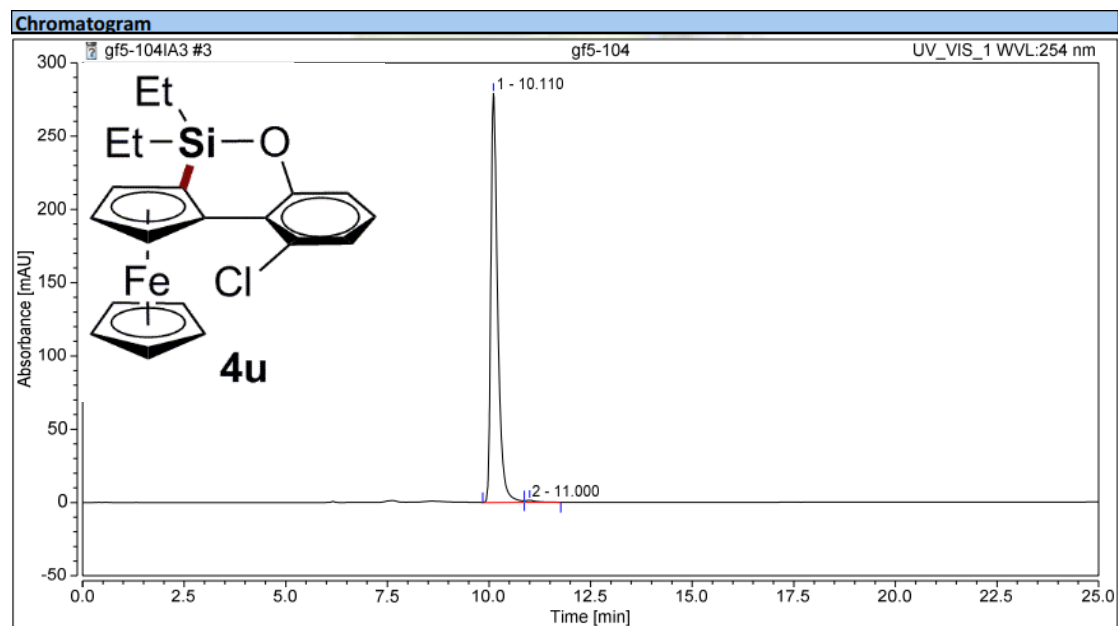
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.110	1.806	10.529	1.95	2.82
2	11.807	91.013	362.936	98.05	97.18
Totals:		92.819	373.465	100.00	100.00

Compound 4u



Result

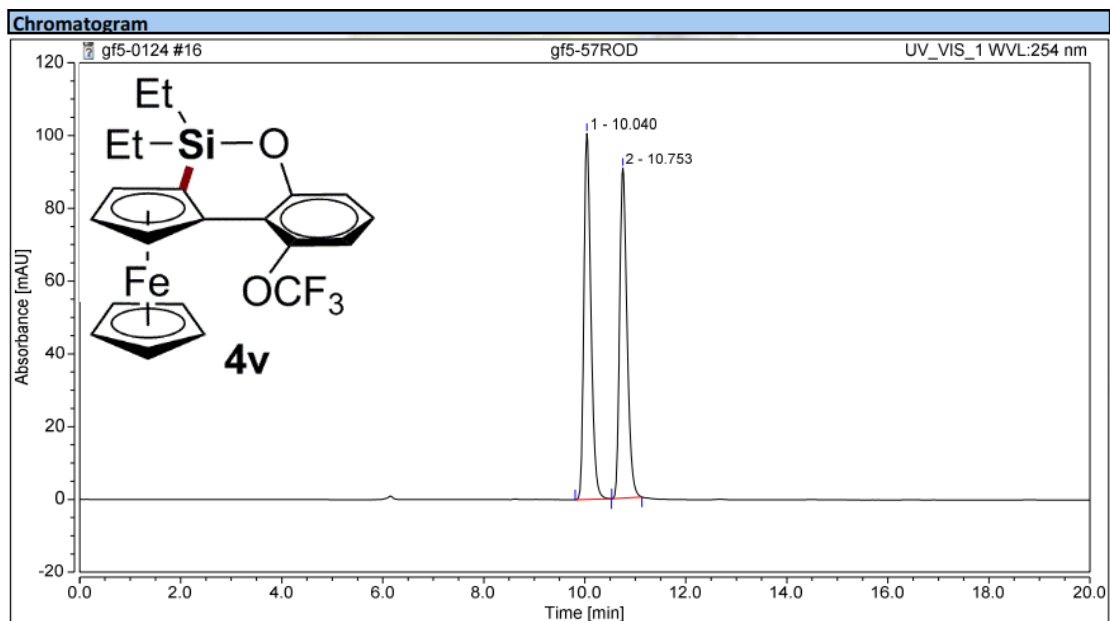
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.083	15.249	79.991	51.08	56.94
2	10.833	14.603	60.494	48.92	43.06
Totals:		29.851	140.485	100.00	100.00



Result

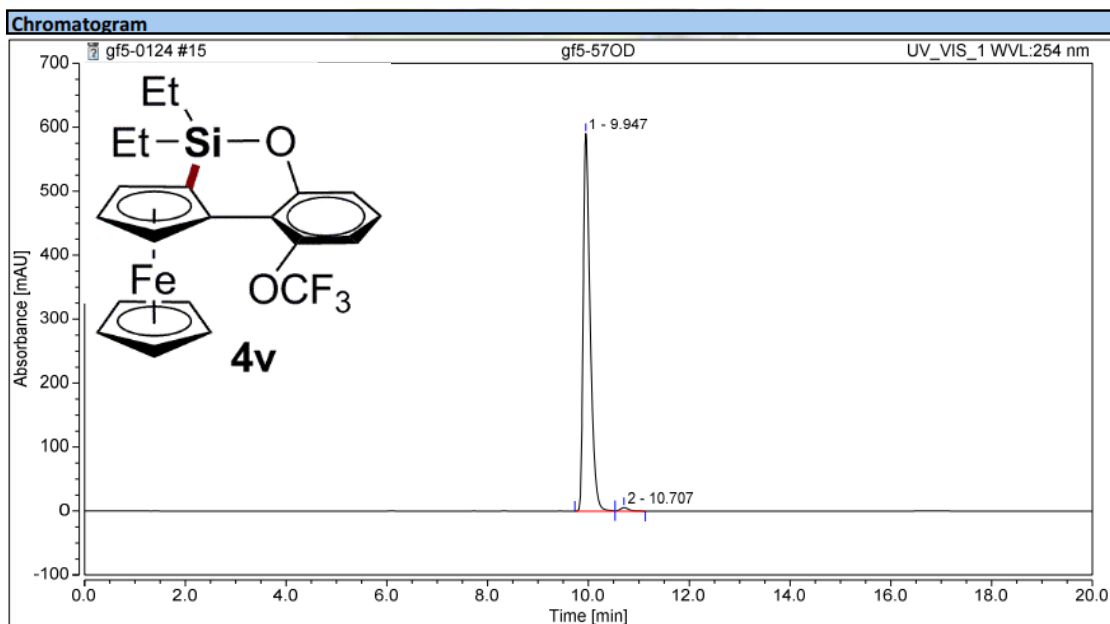
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.110	54.705	279.003	99.19	99.50
2	11.000	0.446	1.398	0.81	0.50
Totals:		55.151	280.400	100.00	100.00

Compound 4v



Result

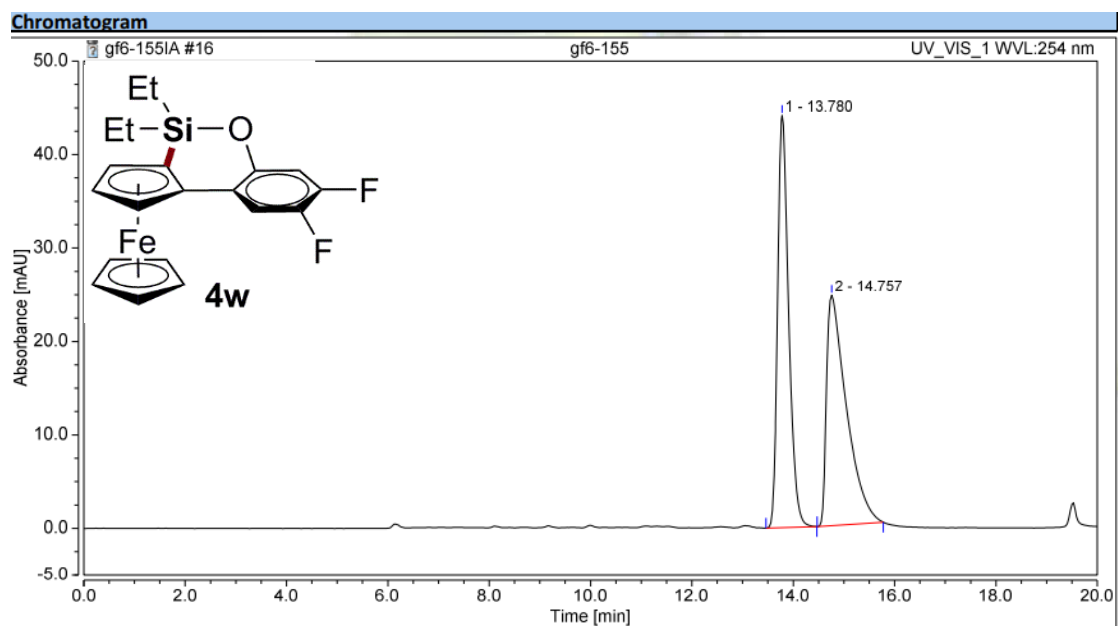
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	10.040	16.141	100.539	51.07	52.59
2	10.753	15.465	90.650	48.93	47.41
Totals:		31.606	191.188	100.00	100.00



Result

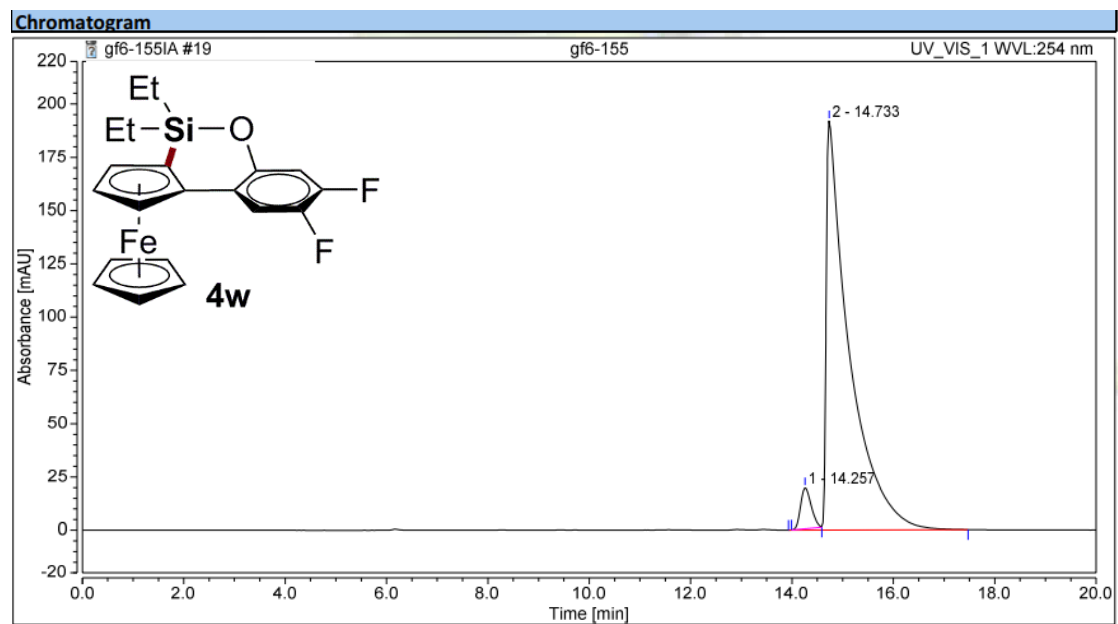
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	9.947	94.330	590.143	98.92	99.08
2	10.707	1.027	5.492	1.08	0.92
Totals:		95.357	595.636	100.00	100.00

Compound 4w



Result

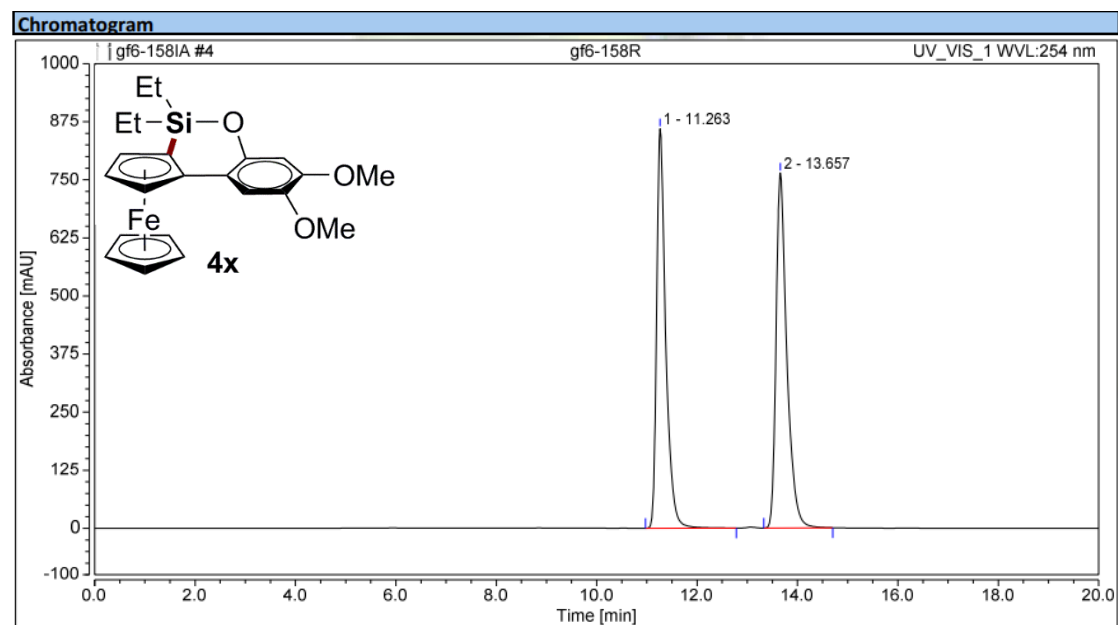
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	13.780	11.055	44.111	49.68	64.16
2	14.757	11.199	24.642	50.32	35.84
Totals:		22.254	68.753	100.00	100.00



Result

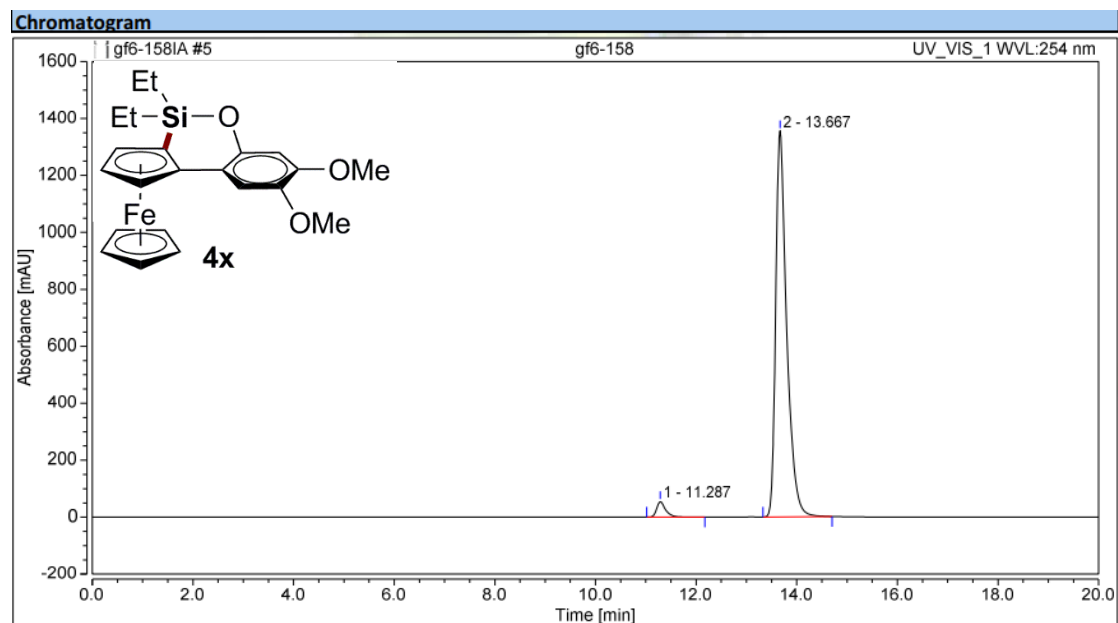
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	14.257	4.657	19.272	4.44	9.12
2	14.733	100.252	192.093	95.56	90.88
Totals:		104.908	211.365	100.00	100.00

Compound 4x



Result

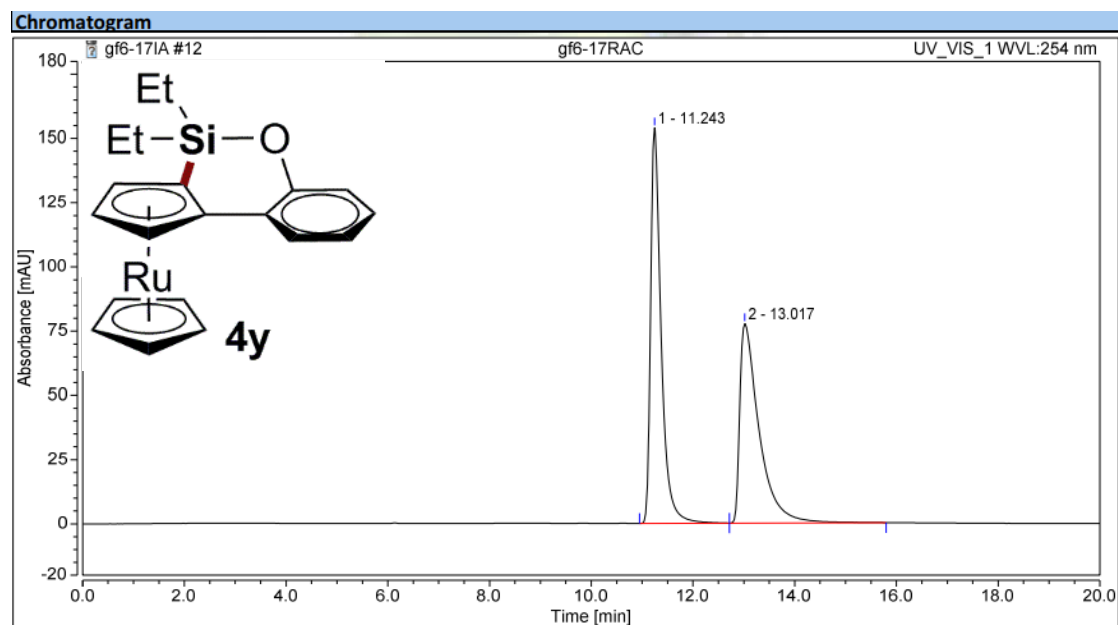
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.263	179.740	859.643	48.63	52.96
2	13.657	189.904	763.634	51.37	47.04
Totals:		369.644	1623.277	100.00	100.00



Result

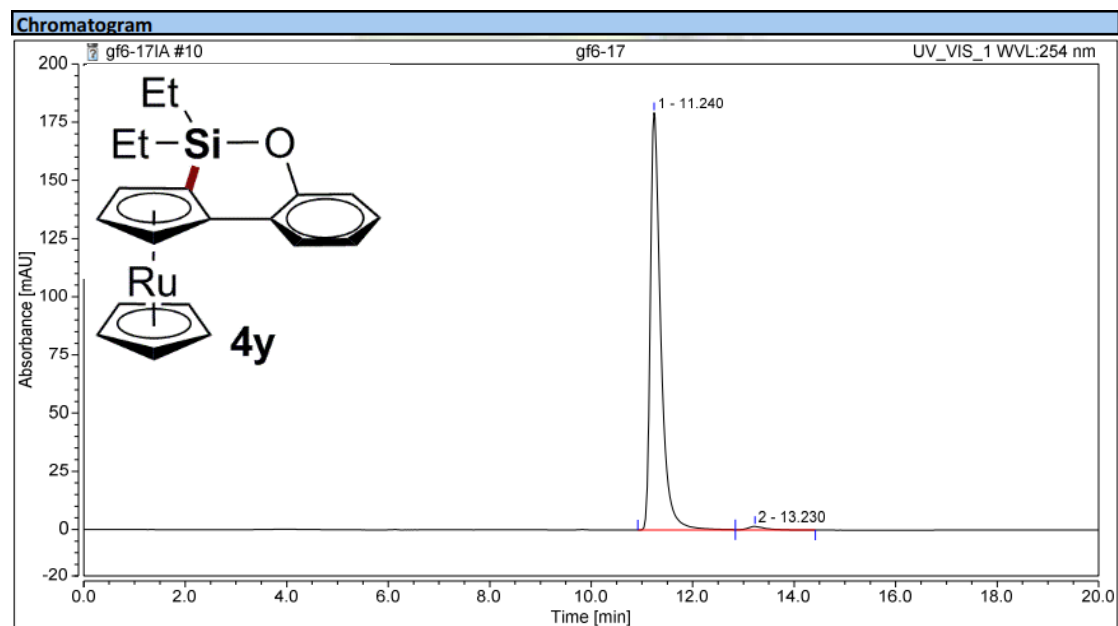
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.287	11.325	54.735	3.20	3.88
2	13.667	342.102	1356.062	96.80	96.12
Totals:		353.427	1410.797	100.00	100.00

Compound 4y



Result

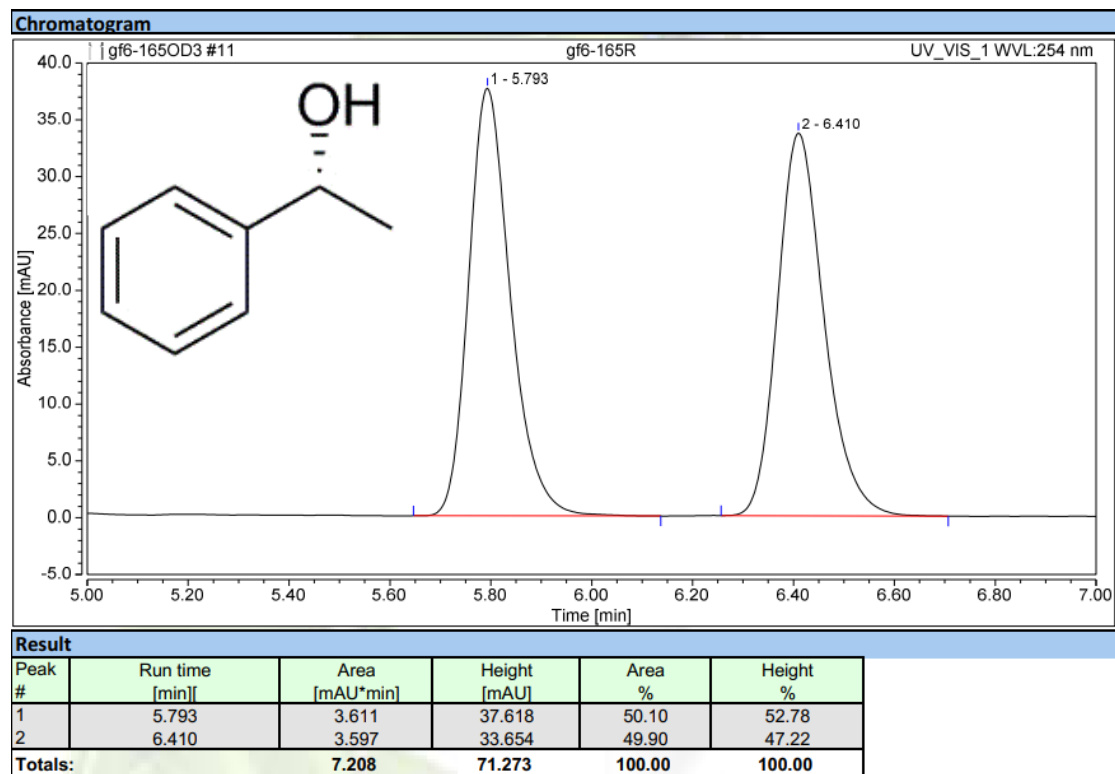
Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.243	36.828	153.965	51.75	66.46
2	13.017	34.340	77.698	48.25	33.54
Totals:		71.168	231.663	100.00	100.00



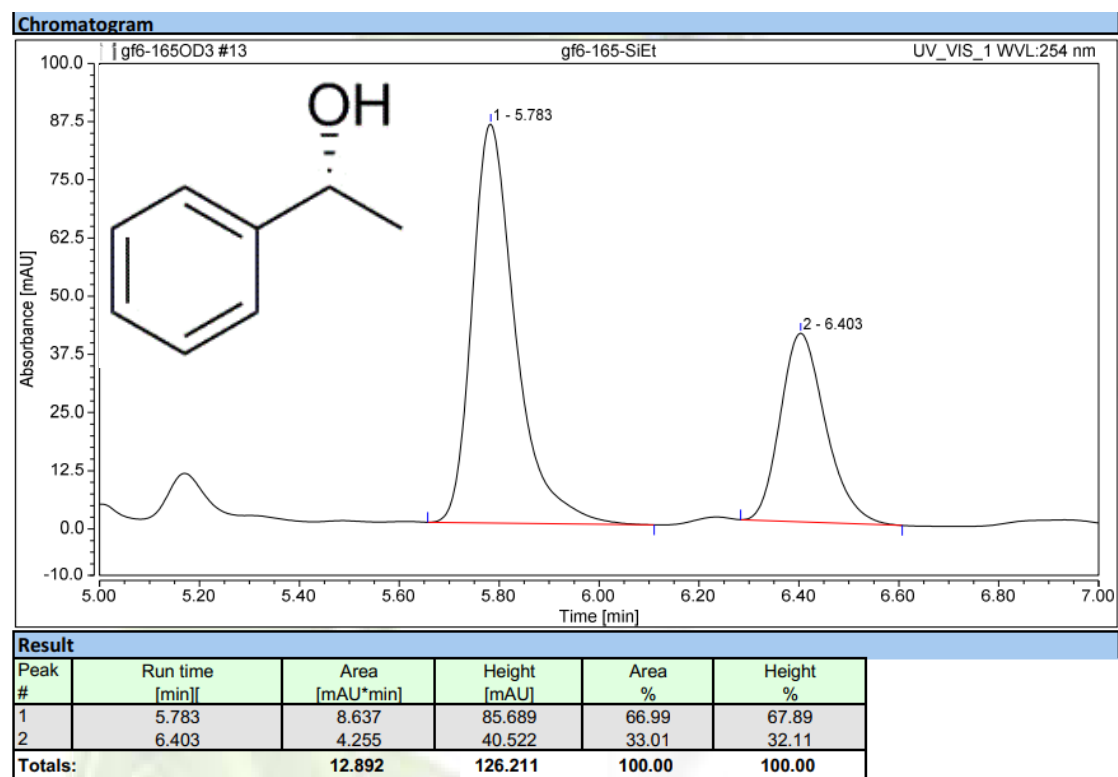
Result

Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.240	42.687	179.316	98.45	99.16
2	13.230	0.671	1.527	1.55	0.84
Totals:		43.357	180.842	100.00	100.00

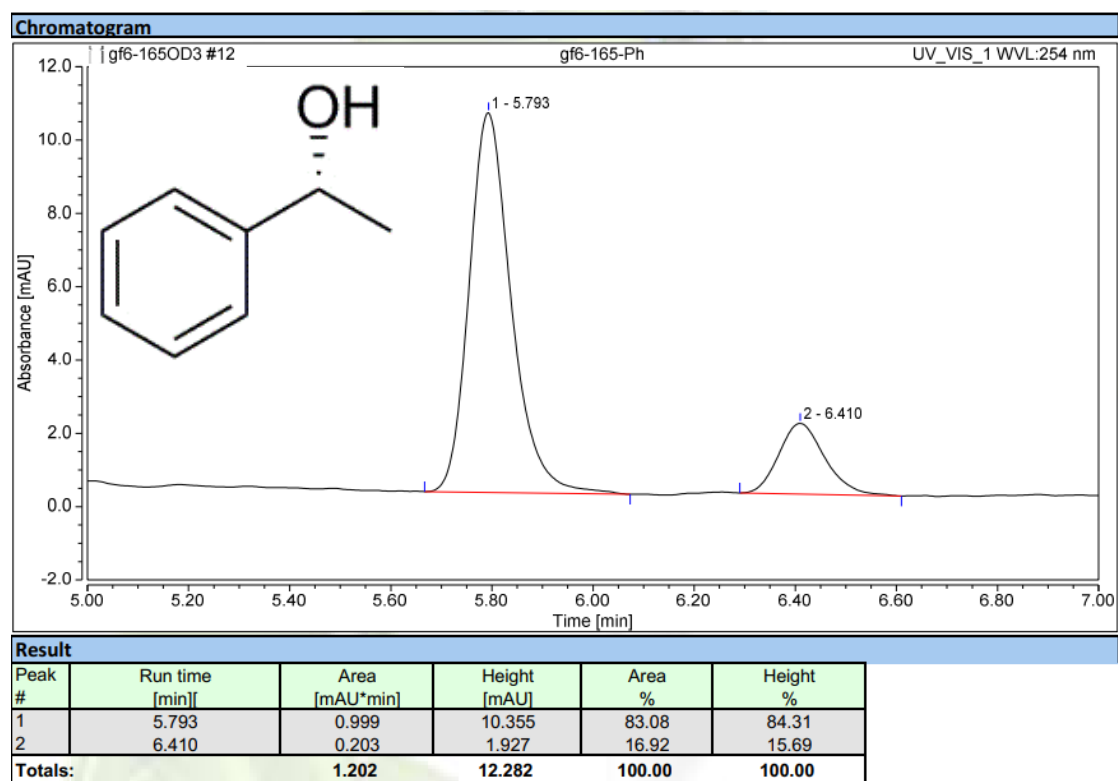
Compound 6-1



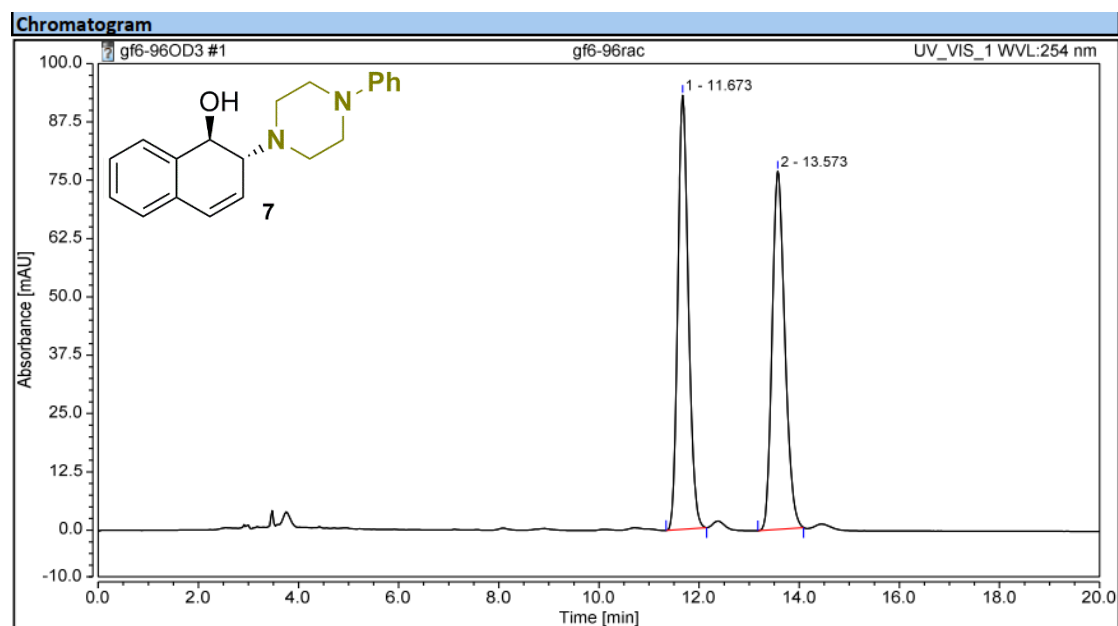
Using FcL1 as ligand



Using FcL2 as ligand



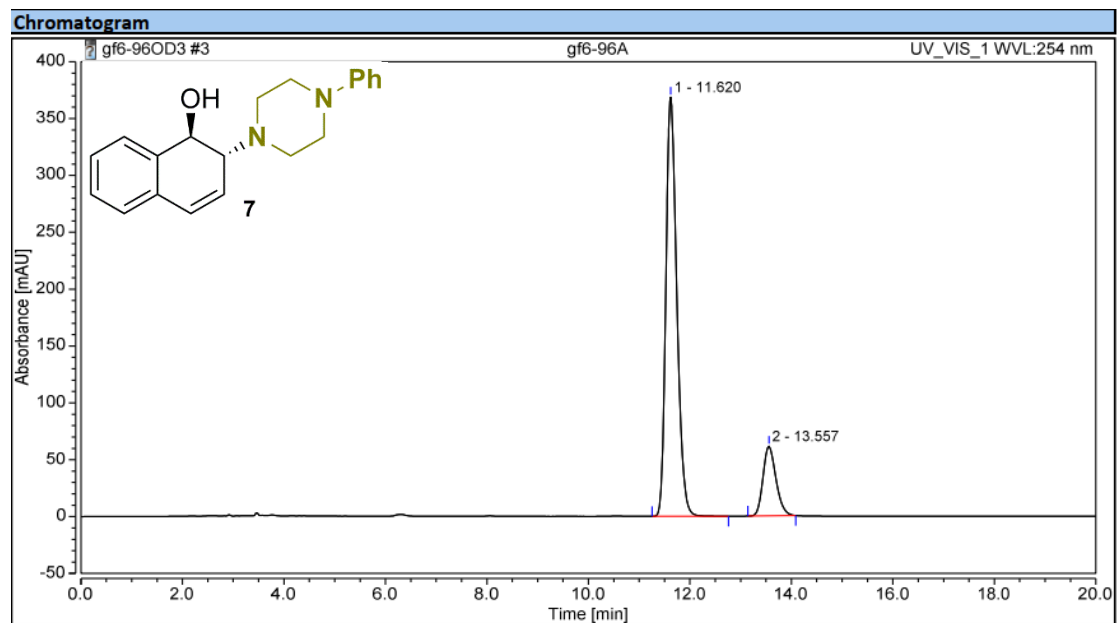
Compound 7



Result

Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.673	22.699	92.989	50.12	54.78
2	13.573	22.592	76.756	49.88	45.22
Totals:		45.292	169.745	100.00	100.00

Using FcL1 as ligand



Result

Peak #	Run time [min]	Area [mAU*min]	Height [mAU]	Area %	Height %
1	11.620	91.171	368.583	83.47	85.76
2	13.557	18.055	61.186	16.53	14.24
Totals:		109.226	429.768	100.00	100.00

Using FcL2 as ligand

