# Thioamide Directed Iridium(I)-Catalyzed C-H Arylation of Ferrocenes with Aryl Boronic Acids

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## Supporting Imformation

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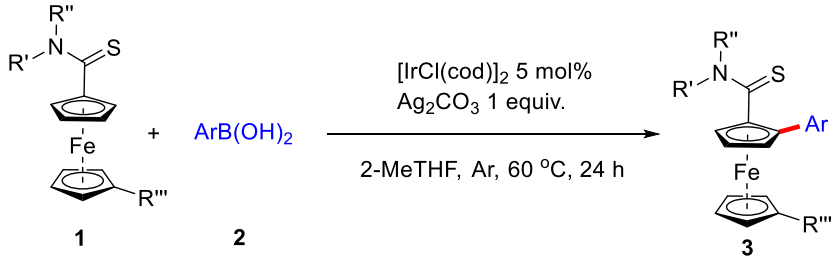
## 1. General methods

The $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer with $CDCl_3$ at room temperature. The chemical shifts in $^{1}H$ NMR and $^{13}C$ NMR spectra were determined with $Si(CH_3)_4$ as the internal standard (δ = 0.00, 77.00 ppm). Data for $^{1}H$ NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for $^{13}C$ NMR, and $^{19}F$ NMR are reported in terms of chemical shift and multiplicity where appropriate (δ, ppm). The high resolution mass spectra (HRMS) were measured on a Bruker micrOTOF QII by ESI. The EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. Melting points were measured on an SGW® X-4 melting point apparatus and were uncorrected. Flash column chromatography was carried out on silica gel (300-400 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. $[IrCl(cod)]_2$ was purchased from J&K Scientific. All Boronic Acids were purchased from Beijing Innochem science & technology Co Ltd and J&K Scientific. Catalytic reactions were carried out in Schlenk flasks under Ar atmosphere using pre-dried glassware, unless otherwise stated. All commercially available chemicals were used as received without further purification. Ferrocene carboxthioamide derivatives **1a**, **1c**, **1e-1g** were known compounds and new compounds **1b**, **1d** and **1h-1m** were prepared according to the literature [1, 2].

## 2. General Procedure of Thioamide-Directed Ir(I)-Catalyzed C–H Arylation of Ferrocenes

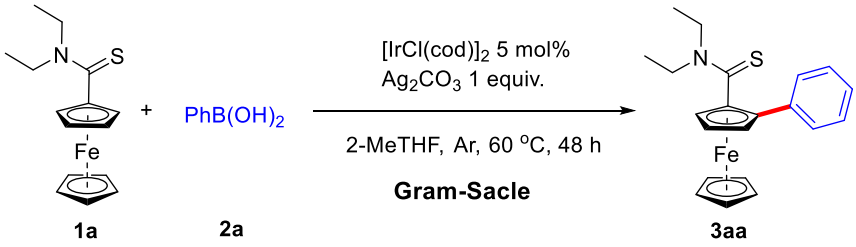



To a 50 mL Schlenk tube was added **1** (0.1 mmol, 1 equiv.), aryl boronic acids **2** (0.3

mmol, 3equiv.), $[IrCl(cod)]_2$ (3.3 mg, 0.005 mmol, 5 mol%), $Ag_2CO_3$ (27.6 mg, 0.1 mmol, 1 equiv.), 2-MeTHF (1 mL). The air was evacuated and refilled three times with argon. Then the tube was capped. The reaction was kept stirring at 60 ℃ (aluminum heat transfer block) for 24 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (petroleum ether : ethyl acetate = 500:1 to 5:1) affording the desired products **3**.

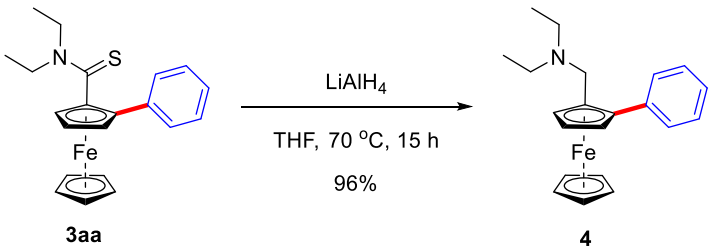
## 3. General Procedure of Gram-Scale Synthesis and Transformation.

### 3.1 Gram-Scale Synthesis




To a 250 mL Schlenk tube was added **1a** (5.3 mmol, 1 equiv.), phenylboronic acid **2a** (1.94 g , 15.9 mmol, 3 equiv.), $[IrCl(cod)]_2$ (178 mg, 0.265 mmol, 5 mol%), $Ag_2CO_3$ (1.46 g, 5.3 mmol, 1 equiv.), 2-MeTHF (25 mL). The air was evacuated and refilled three times with argon. Then the tube was capped. The reaction was kept stirring at 60 ℃ (aluminum heat transfer block) for 48 h. The reaction mixture was diluted with 60 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (hexanes/ethyl acetate = 500:1 to 10:1) affording the desired product **3aa** as orange solid, 1.36 g, 68% yield.

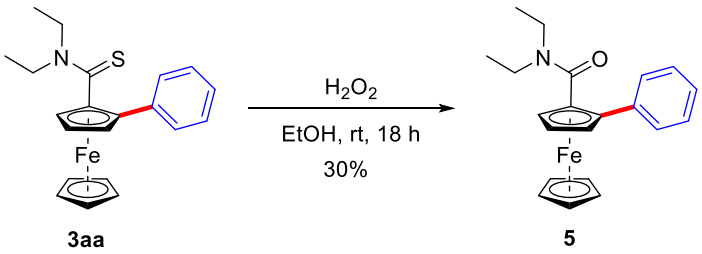
### 3.2 Derivations-Synthesis of 4[3, 4]:




**3aa** (75.4 mg, 0.2 mmol, 1 equiv.) and THF (2 mL) were added to a 50 mL Schlenk tube, the mixture was cooled to 0 ℃. $LiAlH_4$ (22.8 mg, 0.6 mmol, 3.0 equiv.) was

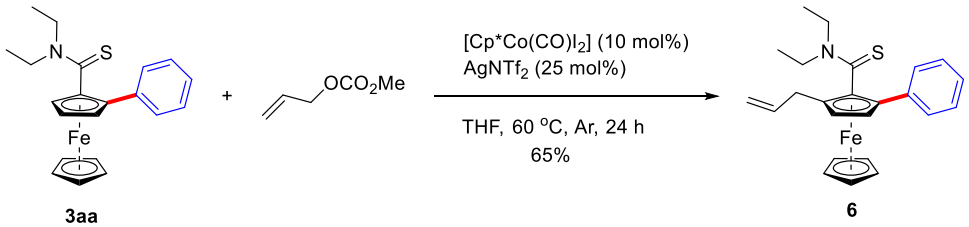
added slowly under the atmosphere of argon. then the tube was capped. The reaction mixture was then stirred at 70 ℃ for 15 h. Afterwards saturated $NH_4Cl$ solution was slowly added to the reaction solution, followed by extraction with DCM (3*10 ml), the solvents were removed in vacuo. The crude mixture was purified by flash chromatography (petroleum ether : ethyl acetate = 2:1) affording **4** as yellow oil, $R_f$ = 0.19, 66.5 mg, 96% yield.

**3.3 Derivations-Synthesis of 5** [5]**:**




**3aa** (75.4 mg, 0.2 mmol, 1 equiv.), $H_2O_2$ (51μL, 0.5 mmol, 2.5 equiv.) and EtOH (2 mL) were added to a 50 mL round-bottom flask, The reaction mixture was then stirred at 25 ℃ for 18 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (petroleum ether : ethyl acetate = 50:1) affording the desired product **5** as yellow solid, 22.0 mg 30% yield.

**3.4 Derivations-Synthesis of 6:**

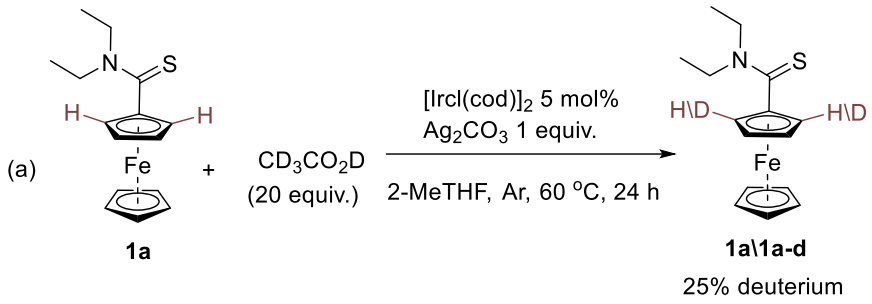



To a 50 mL Schlenk tube was added **3aa** (0.3 mmol, 113.1 mg, 1 eqiv.), allyl methyl carbonate (104.5 mg, 0.9 mmol, 3 equiv.), [Cp*Co(CO)$I_2$] (14.4 mg, 0.03 mmol, 10 mol%), $AgNTf_2$ (29.1 mg, 0.075 mmol, 25 mol%), THF (2 mL), the tube was sealed up with a cap and evacuated then refilled with Ar for three times. The reaction was kept stirring at 60 ℃ (aluminum heat transfer block) for 24 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silica gel (petroleum ether :

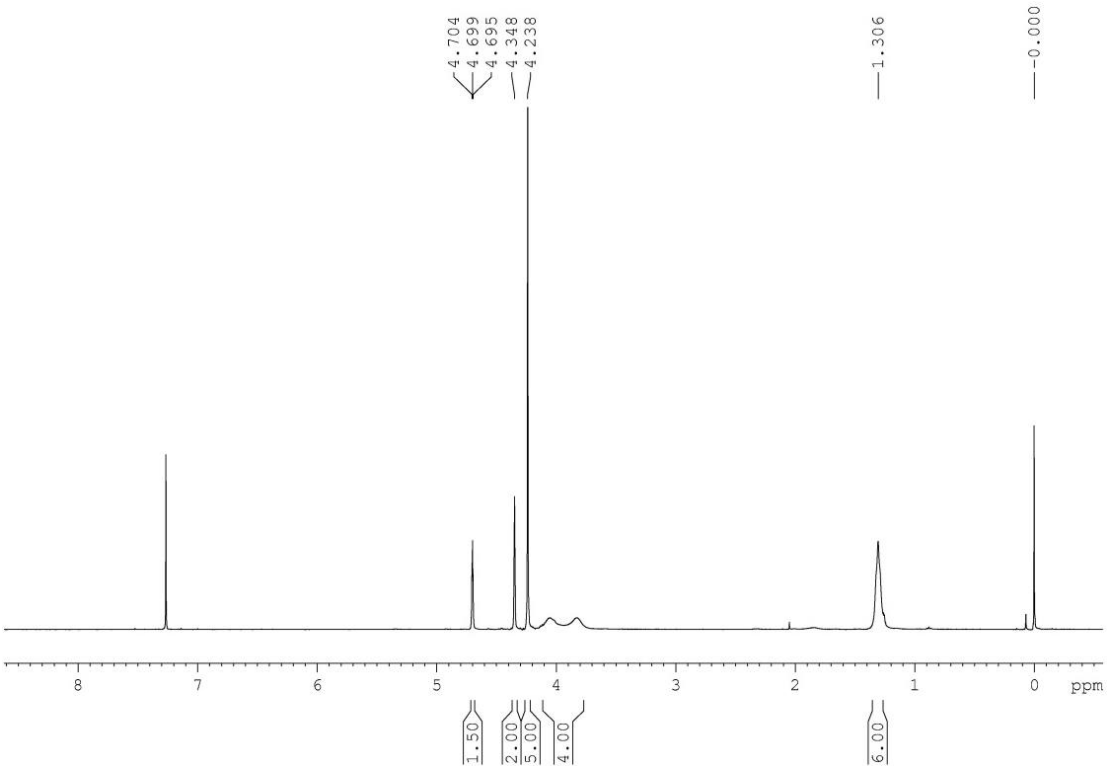
ethyl acetate = 50:1) affording the desired product **6** as yellow oil, $R_f$ = 0.62, 81.8 mg 65% yield.

## 4. Mechanistic Experiments.

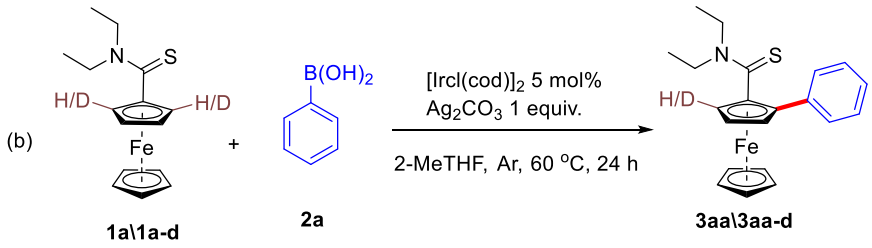
### 4.1 The procedure of synthesis of 1a/1a-d



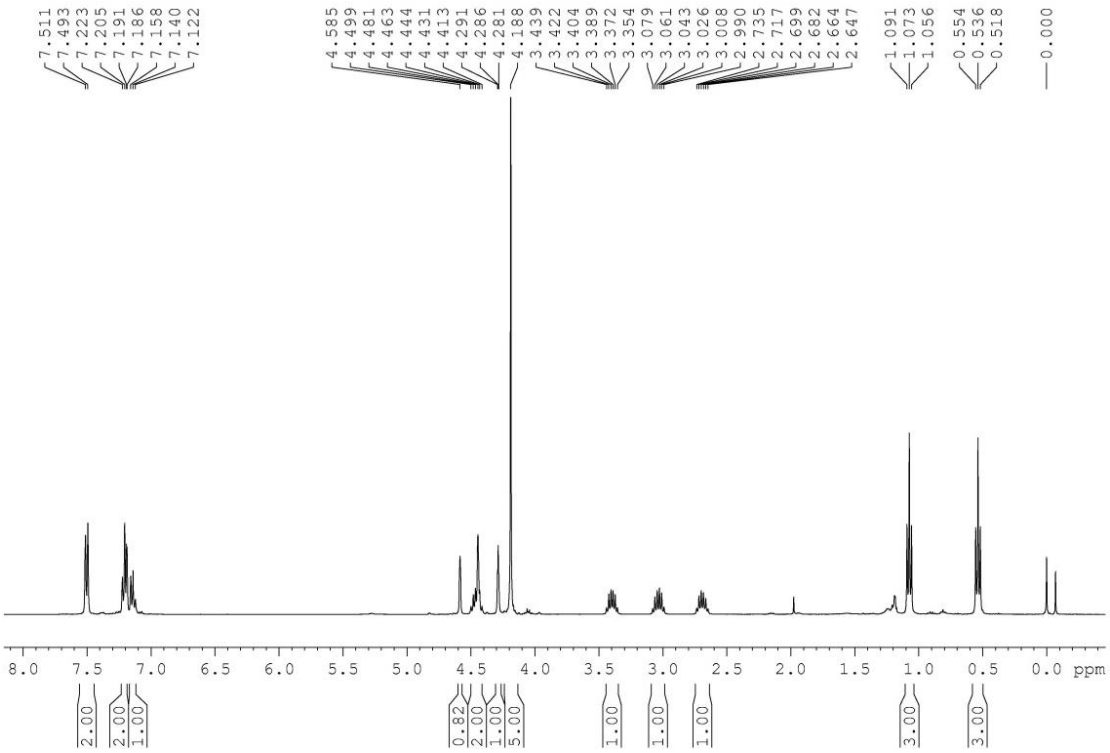

To a 50 mL Schlenk tube was added **1a** (0.1 mmol, 1 equiv.), $CD_3CO_2D$ (114μL, 2 mmol, 20 equiv.), $[IrCl(cod)]_2$ (3.3 mg, 0.005 mmol, 5 mol%), $Ag_2CO_3$ (27.6 mg, 0.1 mmol, 1 equiv.), 2-MeTHF (0.9 mL). The air was evacuated and refilled three times with argon. Then the tube was capped. The reaction was kept stirring at 60 ℃ (aluminum heat transfer block) for 24 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (petroleum ether : ethyl acetate = 10:1) affording the desired product **1a/1a-d**.



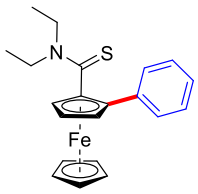
**4.2 The H/D exchange experiment of 3aa**




**General Procedure D:** To a 50 mL Schlenk tube was added **1a** (0.1 mmol), **1a-d** (0.1 mmol), phenylboronic acid **2a** (72 mg, 0.6 mmol, 3 equiv.), $[IrCl(cod)]_2$ (6.6 mg, 0.01 mmol, 5 mol%), $Ag_2CO_3$ (52.2 mg, 0.2 mmol, 1 equiv.), 2-MeTHF (2 mL). The air was evacuated and refilled three times with argon. Then the tube was capped. The reaction was kept stirring at 60 ℃ (aluminum heat transfer block) for 2 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (petroleum ether : ethyl acetate = 100:1) affording the desired product **3aa**/**3aa-d**. The ratio of **3aa** and **3aa-d** was determined by $^1$HNMR to be 4.5:1.

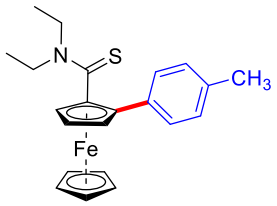


## 5. Spectroscopic data



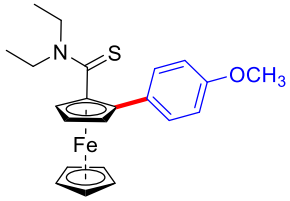

**(2-phenylferrocenyl)(N,N-diethyl)methanethione (3aa)**

Orange solid, 34.5 mg, 92% yield, mp: 165 ~ 166 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 4.6 (s, 1H), 4.55-4.47 (m, 2H), 4.35 (s, 1H), 4.24 (s, 5H), 3.50-3.41 (m, 1H), 3.14-3.05 (m, 1H), 2.80-2.71 (m, 1H), 1.14 (t, *J* = 7.0 Hz, 3H), 0.59 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.3, 138.1, 128.1, 127.7, 126.5, 95.7, 82.7, 73.7, 72.7, 67.1, 64.5, 47.1, 47.0, 12.6, 10.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{23}FeNS$ 378.0973, found: 378.0971.




**(2-(4-methylphenyl)ferrocenyl)(N,N-diethyl)methanethione (3ba)**

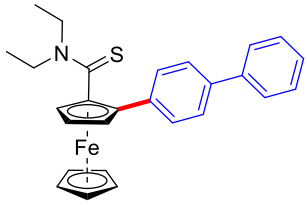
Orange solid, 36.7 mg, 94% yield, mp: 74 ~ 77 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 4.55 (s, 1H), 4.48-4.42 (m, 2H), 4.25 (s, 1H), 4.17 (s, 5H), 3.45-3.36 (m, 1H), 3.09-3.00 (m, 1H), 2.72-2.66 (m, 1H), 2.25 (s, 3H), 1.08 (t, *J* = 7.0 Hz, 3H), 0.55 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.6, 136.2, 135.1, 129.0, 127.7, 95.5, 83.1, 73.7, 72.8, 67.0, 64.6, 47.3, 47.1, 21.3, 12.7, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{25}FeNS$ 292.1130, found: 292.1127.




**(2-(4-methoxyphenyl)ferrocenyl)(N,N-diethyl)methanethione (3ca)**

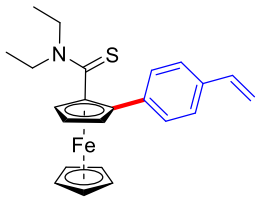
Orange solid, 33.2 mg, 82% yield, mp: 137 ~ 140 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.50 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.61 (s, 1H), 4.55-4.46 (m, 2H), 4.31 (s, 1H), 4.25 (s, 5H), 3.82 (s, 3H), 3.52-3.44 (m, 1H), 3.16-3.06 (m, 1H), 2.82-3.73 (m, 1H), 1.15 (t, *J* = 4.8 Hz, 3H), 0.63 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR**

**($CDCl_3$, 101 MHz)** δ 179.6, 158.4, 130.3, 128.9, 113.7, 95.2, 83.1, 73.4, 72.7, 66.9, 64.6, 55.3, 47.2, 47.1, 12.7, 10.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{25}FeNOS$ 408.1079, found: 408.1076.



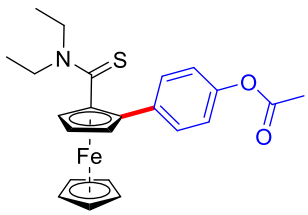

**(2-(1,1'-biphenyl)ferrocenyl)(N,N-diethyl)methanethione (3da)**

Orange solid, 39.2 mg, 87% yield, mp: 166 ~ 168 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.63 (t, *J* = 8.0 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 4.67 (s, 1H), 4.58-4.49 (m, 2H), 4.38 (t, *J* = 2.2 Hz, 1H), 4.28 (s, 5H), 3.54-3.45 (m, 1H), 3.19-3.10 (m, 1H), 2.85-2.76 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H), 0.65 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.4, 140.7, 139.1, 137.4, 128.9, 128.1, 127.3, 126.8, 95.9, 82.3, 73.9, 72.9, 67.3, 64.5, 47.3, 47.2, 12.7, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{27}H_{27}FeNS$ 454.1286, found: 454.1284.




**(2-(4-vinylphenyl)ferrocenyl)(N,N-diethyl)methanethione (3ea)**

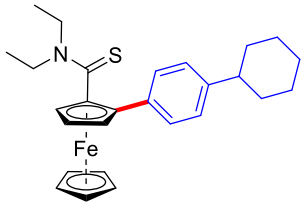
Orange solid, 19.1 mg, 44% yield, mp: 136 ~ 139 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.69 (dd, *J* = 17.6, 6.8 Hz, 1H), 5.75 (d, *J* = 17.6 Hz 1H), 5.25 (d, *J* = 10.8 Hz 1H), 4.65 (t, *J* = 1.6 Hz 1H), 4.55-4.46 (m, 2H), 4.36 (t, *J* = 2.4 Hz 1H), 4.25 (s, 5H), 3.54-3.45 (m, 1H), 3.16-3.07 (m, 1H), 2.82-2.73 (m, 1H), 1.17 (t, *J* = 7.0 Hz 3H), 0.63 (t, *J* = 7.0 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.4, 138.1, 136.6, 135.7, 127.8, 126.1, 113.4, 95.9, 82.3, 74.0, 72.8, 67.3, 64.5, 47.3, 47.1, 12.7, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{23}H_{25}FeNS$ 404.1130, found: 404.1122.




**(2-(4-acetoxyphenyl)ferrocenyl)(N,N-diethyl)methanethione (3fa)**

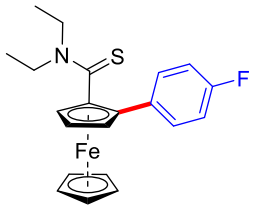
Orange solid, 28.0 mg, 64% yield, mp: 150 ~ 152 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ

7.58 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 4.64 (d, *J* = 1.6 Hz, 1H), 4.55-4.46 (m, 2H), 4.35 (t, *J* = 2.4 Hz 1H), 4.26 (s, 5H), 3.51-3.42 (m, 1H), 3.13-3.04 (m, 1H), 2.82-2.72 (m, 1H), 2.30 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 3H), 0.64 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.2, 169.4, 149.3, 135.9, 128.7, 121.3, 95.9, 82.2, 73.7, 72.8, 67.2, 64.6, 47.2, 47.1, 21.3, 12.7, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{23}H_{25}FeNO_2S$ 436.1028, found: 436.1025.



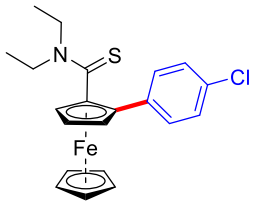

**(2-(4-cyclohexylphenyl)ferrocenyl)(N,N-diethyl)methanethione (3ga)**

Orange oil, 32.9 mg, 72% yield, $R_f$ = 0.45. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.62 (s, 1H), 4.57-4.48 (m, 2H), 4.32 (t, *J* = 2.4 Hz, 1H), 4.25 (s, 5H), 3.48-3.40 (m, 1H), 3.12-3.03 (m, 1H), 2.79-2.70 (m, 1H), 2.47 (s, 1H), 1.86-1.73 (m, 5H), 1.46-1.24 (m, 5H), 1.12 (t, *J* = 7.0 Hz, 3H), 0.58 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.6, 146.6, 135.3, 127.9, 126.6, 95.5, 83.3, 73.6, 72.8, 67.0, 64.6, 47.1, 47.0, 44.3, 34.6, 34.4, 27.0, 26.3, 12.5, 10.7, 1.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{27}H_{33}FeNS$ 460.1756, found: 460.1752.



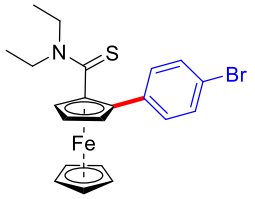

**(2-(4-fluorophenyl)ferrocenyl)(N,N-diethyl)methanethione (3ha)**

Orange solid, 33.6 mg, 85% yield, mp: 167 ~ 170 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.49 (dd, *J* = 8.2, 2.6 Hz, 2H), 6.90 (t, *J* = 8.6 Hz, 2H), 4.55 (s, 1H)，4.47-4.40 (m, 2H), 4.27 (s, 1H), 4.18 (s, 5H), 3.45-3.37 (m, 1H), 3.05-2.96 (m, 1H), 2.75-2.66 (m, 1H), 1.07 (t, *J* = 5.2 Hz, 3H), 0.57 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.3, 162.9, 160.5, 134.2 (d, *J* = 3.3 Hz), 129.4 (d, J = 7.8 Hz), 115.2 (d, *J* = 21.4 Hz), 95.9, 82.2, 73.5, 72.8, 67.2, 64.7, 47.2, 47.1, 12.8, 10.8. **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -115.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{22}FFeNS$ 396.0879, found: 396.0877.



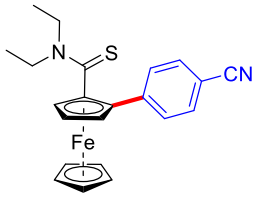

**(2-(4-chlorophenyl)ferrocenyl)(N, N-diethyl)methanethione (3ia)**

Orange solid, 32.1 mg, 78% yield, mp: 167 ~ 169 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 4.57 (s, 1H), 4.45-4.37 (m, 2H), 4.29 (s, 1H), 4.18 (s, 5H), 3.48-3.39 (m, 1H), 3.06-2.97 (m, 1H), 2.75-2.67 (m, 1H), 1.09 (t, *J* = 7.0 Hz, 3H), 0.58 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.1, 137.1, 132.2, 128.9, 128.5, 96.1, 81.6, 73.8, 72.9, 67.3, 64.5, 47.3, 47.1, 12.8, 10.8.**HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{22}ClFeNS$ 412.0584, found: 412.0583.



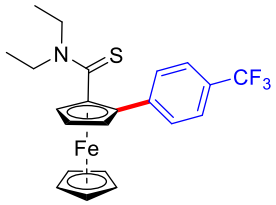

**(2-(4-bromophenyl)ferrocenyl)(N,N-diethyl)methanethione (3ja)**

Orange solid, 34.0 mg, 75% yield, mp: 137 ~ 140 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.64 (t, *J* = 1.8 Hz, 1H), 4.52-4.44 (m, 2H), 4.36 (t, *J* = 2.4 Hz, 1H), 4.25 (s, 5H), 3.55-3.46 (m, 1H), 3.13-3.04 (m, 1H), 2.83-2.74 (m, 1H), 1.16 (t, *J* = 7.0 Hz, 3H), 0.65 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.1, 137.6, 131.4, 129.3, 120.2, 96.1, 81.5, 73.9, 72.9, 67.4, 64.4, 47.3, 47.1, 12.8, 10.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{22}BrFeNS$ 456.0079, found: 456.0079.



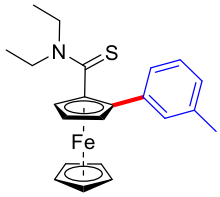

**(2-(4-cyanophenyl)ferrocenyl)(N,N-diethyl)methanethione (3ka)**

Orange solid, 14.8 mg, 37% yield, mp: 171 ~ 173 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 1H), 4.53-4.43 (m, 3H), 4.26 (s, 5H), 3.58-3.49 (m, 1H), 3.11-3.01 (m, 1H), 2.84-2.75 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H), 0.66 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 196.6, 144.6, 132.1, 127.9, 119.2, 109.5, 97.2, 80.1, 74.3, 73.1, 68.1, 64.4, 47.3, 47.1, 12.8, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{22}FeN_2S$ 403.0926, found: 403.0924.



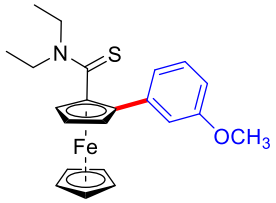

**(2-(4-(trifluoromethyl)phenyl)ferrocenyl)(N,N-diethyl)methanethione (3la)**

Orange solid, 14.6 mg, 33% yield, mp: 131 ~ 134 °C. **$^{1}$H NMR ($CDCl_3$, 400 MHz)** δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 4.69 (s, 1H), 4.54-4.41 (m, 3H), 4.27 (s, 5H), 3.56-3.47 (m, 1H), 3.13-3.04 (m, 1H), 2.82-2.73 (m, 1H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.65 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ196.9, 142.9, 128.9, 128.5, 128.2, 127.8, 125.8, 125.2 (q, *J* = 3.8 Hz), 123.1, 96.8, 80.8, 74.2, 73.1, 67.8, 64.6, 47.3, 47.2, 12.8, 10.7. **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -62.4. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{22}F_3FeNS$ 446.0847, found: 446.0843.




**(2-(3-methylphenyl)ferrocenyl)(N,N-diethyl)methanethione (3ma)**

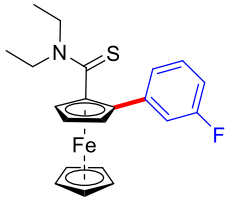
Orange solid, 27.8 mg, 71% yield, mp: 154 ~ 157 °C. **$^{1}$H NMR ($CDCl_3$, 400 MHz)** δ 7.37 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 4.65-4.57 (m, 2H), 4.51 (s, 1H), 4.34 (t, *J* = 2.2 Hz, 1H), 4.26 (s, 5H), 3.42-3.33 (m, 1H), 3.16-3.07 (m, 1H), 2.79-2.70 (m, 1H), 2.35 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.62 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.5, 138.2, 137.7, 128.4, 128.2, 127.4, 125.2, 95.7, 73.9, 72.9, 67.2, 64.6, 47.3, 47.2, 21.6, 12.7, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{25}FeNS$ 392.1130, found: 392.1127.




**(2-(3-methoxyphenyl)ferrocenyl)(N,N-diethyl)methanethione (3na)**

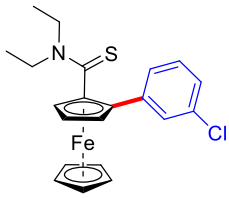
Orange solid, 30.1 mg, 74% yield, mp: 119 ~ 121 °C. **$^{1}$H NMR ($CDCl_3$, 400 MHz)** δ 7.21-7.13 (m, 3H), 6.77-6.75 (m, 1H), 4.62 (t, *J* = 1.4 Hz, 1H), 4.51-4.42 (m, 2H), 4.34 (t, *J* = 2.4 Hz, 1H), 4.27 (s, 5H), 3.83 (s, 3H), 3.57-3.48 (m, 1H), 3.15-3.06 (m, 1H), 2.83-2.74 (m, 1H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.63 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.5, 159.5, 139.8, 129.2, 120.4, 113.3, 112.4, 96.3, 83.0, 73.6, 72.9, 67.2, 64.6, 55.4, 47.3, 47.1, 12.7, 10.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for

$C_{22}H_{25}FeNOS$ 408.1079, found: 408.1077.



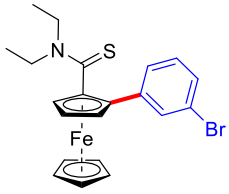

**(2-(3-fluorophenyl)ferrocenyl)(N,N-diethyl)methanethione (3oa)**

Orange solid, 28.1 mg, 71% yield, mp: 95 ~ 97 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.30 (d, *J* = 7.8 Hz, 1H), 7.22-7.14 (m, 2H), 6.86-6.81 (m, 1H), 4.59 (t, *J* = 2.2 Hz, 1H), 4.52-4.42 (m, 2H), 4.31 (t, *J* = 2.4 Hz, 1H), 4.19 (s, 5H), 3.44-3.35 (m, 1H), 3.08-2.99 (m, 1H), 2.76-2.67 (m, 1H), 1.10 (t, *J* = 7.0 Hz, 3H), 0.58 (t, *J* =7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ197.1, 164.0, 161.6, 141.1 (d, *J* = 8.1 Hz), 129.8 (d, *J* = 8.4 Hz), 123.5 (d, *J* = 2.7 Hz), 114.4 (d, *J* = 22.0 Hz), 113.4 (d, *J* = 21.1 Hz), 96.3, 81.4 (d, J = 2.2 Hz), 74.0, 73.0, 67.5, 64.6, 47.3, 47.1, 12.8, 10.6. **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -113.5. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{22}FFeNS$ 396.0879, found: 396.0877.




**(2-(3-chlorophenyl)ferrocenyl)(N,N-diethyl)methanethione (3pa)**

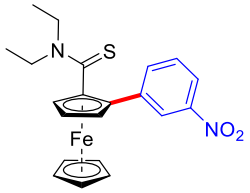
Orange solid, 25.0 mg, 61% yield, mp: 159 ~ 161 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.45-7.43 (m, 2H), 7.16-7.10 (m, 2H), 4.60 (t, *J* = 1.6 Hz, 1H), 4.57-4.48 (m, 1H), 4.43 (t, *J* = 1.6 Hz, 1H), 4.31 (t, *J* = 2.4 Hz, 1H), 4.19 (s, 5H), 3.39-3.30 (m, 1H), 3.08-2.99 (m, 1H), 2.75-2.66 (m, 1H), 1.10 (t, *J* = 7.2 Hz, 3H), 0.59 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.0, 140.7, 134.2, 129.6, 127.3, 126.6, 126.1, 96.2, 81.2, 74.1, 73.0, 67.5, 64.5, 47.3, 47.2, 12.8, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{22}ClFeNS$ 412.0584; found: 412.0582.




**(2-(3-bromophenyl)ferrocenyl)(N,N-diethyl)methanethione (3qa)**

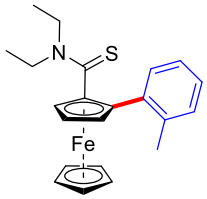
Orange solid, 28.5 mg, 63% yield, mp: 163 ~ 166 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.66 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.34 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 4.67 (t, *J* = 1.6 Hz, 1H), 4.64-4.57 (m, 1H), 4.49 (q, *J* = 2.2, 0.6 Hz, 1H),

4.38 (t, *J* = 2.6 Hz, 1H), 4.26 (s, 5H), 3.45-3.37 (m, 1H), 3.14-3.05 (m, 1H), 2.82-2.73 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H), 0.66 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 196.9, 140.9, 130.1, 129.9, 129.5, 126.5, 122.4, 96.2, 81.1, 74.1, 73.0, 67.5, 64.5, 47.3, 47.2, 12.8, 10.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{22}BrFeNS$ 456.0079, found: 456.0079.



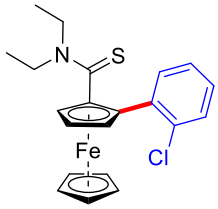

**(2-(3-nitrophenyl)ferrocenyl)(N,N-diethyl)methanethione (3ra)**

Brick red solid, 24.5 mg, 58% yield, mp: 95 ~ 98 °C. **$^{1}$H NMR ($CDCl_3$, 400 MHz)** δ 8.24,(s, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 4.63 (s, 1H), 4.53-4.38 (m, 3H), 4.21 (s, 5H), 3.45-3.39 (m, 1H), 3.08-3.01 (m, 1H), 2.79-2.70 (m, 1H), 1.08 (t, *J* = 6.8 Hz, 3H), 0.63 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 196.3, 148.2, 140.9, 133.8, 129.1, 121.5, 121.1, 96.7, 80.1, 73.6, 72.9, 67.7, 64.8, 47.1, 12.8, 10.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{22}FeN_2O_2S$ 423.0824, found: 423.0821.



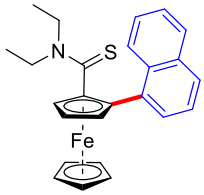

**(2-(2-methylphenyl)ferrocenyl)(N,N-diethyl)methanethione (3sa)**

Orange solid, 9.4 mg, 24% yield, mp: 107 ~ 110 °C. **$^{1}$H NMR ($CDCl_3$, 400 MHz)** δ 7.96 (d, *J* = 7.2 Hz 1H), 7.12-7.04 (m, 3H), 4.62 (s, 1H), 4.40-4.31 (m, 3H), 4.23 (s, 5H), 3.35-3.26 (m, 1H), 3.01-2.93 (m, 1H), 2.69-2.60 (m, 1H), 2.22 (s, 3H), 0.91 (t, *J* = 7.0 Hz 3H), 0.51 (t, *J* = 7.0 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.4, 135.9, 135.5, 132.6, 130.2, 126.7, 125.6, 97.3, 83.9, 73.0, 72.9, 67.9, 66.6, 46.9, 46.8, 21.1, 12.7, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{25}FeNS$ 392.1130, found: 392.1126.



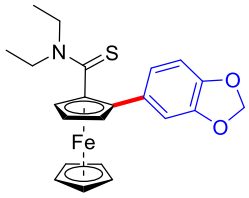

**(2-(2-chlorophenyl)ferrocenyl)(N,N-diethyl)methanethione (3ta)**

Orange solid, 7.6 mg, 18% yield, mp: 120 ~ 122 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 8.15 (d, *J* = 7.8 Hz 1H), 7.31 (d, *J* = 8.0 Hz 1H), 7.25 (t, *J* = 7.6 Hz 1H), 7.16 (t, *J* = 7.6 Hz 1H), 4.75 (s, 1H), 4.68 (s, 1H), 4.48-4.41 (m, 2H), 4.31 (s, 5H), 3.42-3.34 (m, 1H), 3.18-3.10 (m, 1H), 2.82-2.73 (m, 1H), 0.97 (t, *J* = 7.0 Hz 3H), 0.67 (t, *J* = 7.0 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 196.8, 135.7, 134.1, 133.0, 129.6, 127.9, 126.4, 97.8, 81.7, 73.0, 72.4, 68.8, 66.7, 46.9, 46.7, 12.9, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{22}ClFeNS$ 412.0584, found: 412.0582.



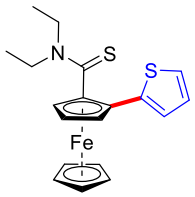

**(2-(naphthalen-1-yl) ferrocenyl)(N,N-diethyl)methanethione (3ua)**

Orange solid, 10.5 mg, 25% yield, mp: 195 ~ 197 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 8.27 (d, *J* = 7.0 Hz 2H), 7.85, (t, *J* = 4.0 Hz 1H), 7.76 (d, *J* = 8.0 Hz 1H), 7.50-7.42 (m, 3H), 4.79 (s, 1H), 4.70 (s, 1H), 4.50 (s, 1H), 4.41-4.33 (m, 6H), 3.33-3.25 (m, 1H), 3.09-3.00 (m, 1H), 2.56-2.50 (m, 1H), 0.84 (t, *J* = 7.0 Hz 3H), 0.38 (t, *J* = 7.0 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.1, 134.1, 133.7, 132.0, 130.1, 128.7, 127.3, 125.9, 125.4, 125.3, 97.9, 83.3, 73.1, 68.3, 68.8, 46.9, 46.8, 12.7, 10.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{25}H_{25}FeNS$ 428.1130, found: 428.1128.



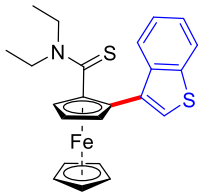

**(2-(benzo[*d*][1,3]dioxol-5-yl)ferrocenyl)(N,N-diethyl)methanethione (3va)**

Brownish yellow solid, 29.8 mg, 71% yield, mp: 153 ~ 155 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.12 (s, 1H), 7.04 (d, *J* = 8.0 Hz 1H), 6.73 (d, *J* = 8.0 Hz 1H), 5.96 (d, *J* = 3.2 Hz 2H), 4.61-4.51 (m, 2H), 4.45 (s, 1H), 4.31 (s, 1H), 4.26 (s, 5H), 3.51-3.42 (m, 1H), 3.17-3.08 (m, 1H), 2.84-2.75 (m, 1H), 1.17 (t, *J* = 7.0 Hz 3H), 0.67 (t, *J* = 7.0 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.3, 147.4, 146.3, 132.0, 121.1, 108.4, 108.1, 100.1, 95.3, 83.1, 73.4, 72.7, 66.8, 64.6, 47.1, 47.0, 12.7, 10.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{23}FeNO_2S$ 422.0872, found: 422.0866.



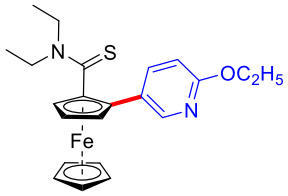
**(2-(thiophen-2-yl)ferrocenyl)(N,N-diethyl)methanethione (3wa)**

Orange solid, 22.1 mg, 58% yield, mp: 172 ~ 175 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.15 (dd, *J* = 8.4, 3.0 Hz 2H), 6.93 (t, *J* = 4.2 Hz 1H), 4.57 (s, 1H), 4.53 (s, 1H), 4.48-4.40 (m, 1H), 4.31 (s, 1H), 4.30 (s, 5H), 3.67-3.60 (m, 1H), 3.21-3.12 (m, 1H), 2.97-2.88 (m, 1H), 1.23 (t, *J* = 7.2 Hz 3H), 0.74 (t, *J* = 7.2 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 196.5, 141.0, 127.3, 124.3, 123.8, 95.3, 77.0, 73.1, 72.3, 66.9, 65.9, 47.3, 47.1, 12.8, 10.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{19}H_{21}FeNS_2$ 384.0538, found:384.0534.



**(2-(benzo[*b*]thiophen-3-yl)ferrocenyl)(N,N-diethyl)methanethione (3xa)**

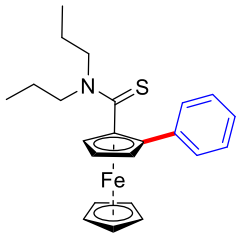
Brown solid, 24.4 mg, 56% yield, mp: 178 ~ 181 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 8.01 (d, *J* = 7.8 Hz 1H), 7.86 (d, *J* = 7.8 Hz 1H), 7.80 (s, 1H), 7.41-7.33 (m, 2H), 4.70 (s, 1H), 4.68 (s, 1H), 4.45-4.36 (m, 2H), 4.33 (s, 5H), 3.44-3.35 (m, 1H), 3.09-3.00 (m, 1H), 2.72-2.63 (m, 1H), 0.96 (t, *J* = 7.0 Hz 3H), 0.52 (t, *J* = 8.8 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.2, 140.3, 138.4, 132.8, 125.1, 124.3, 124.2, 123.1, 123.0, 96.6, 77.9, 72.9, 72.8, 67.1, 66.3, 47.1, 47.0, 12.8, 10.9. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{23}H_{23}FeNS_2$ 434.0694, found: 434.0692.



**(2-(6-ethoxypyridin-3-yl)ferrocenyl)(N,N-diethyl)methanethione (3ya)**

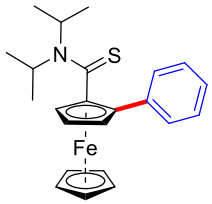
Orange solid, 25.1 mg, 60% yield, mp: 116 ~ 118 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 8.16 (d, *J* = 2.0 Hz 1H), 7.86 (dd, *J* = 8.6, 6.6 Hz 1H), 6.61 (*J* = 8.6 Hz 1H), 4.55 (s, 1H), 4.46-4.37 (m, 2H), 4.32-4.24 (m, 3H), 4.19 (s, 5H), 3.46-3.37 (m, 1H), 3.09-3.00 (m, 1H), 2.78-2.69 (m, 1H), 1.34 (t, *J* = 7.0 Hz 3H), 1.07 (t, *J* = 7.0 Hz 3H), 0.63 (t, *J* = 7.0 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 196.9, 162.7, 144.7, 138.6, 126.8, 110.4, 95.4, 80.0, 73.1, 72.6, 67.1, 64.4, 61.8, 47.1, 47.0, 14.7, 12.8, 10.8. **HRMS**

**(ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{26}FeN_2OS$ 423.1188, found: 423.1182.



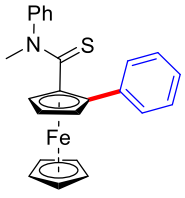

**(2-phenylferrocenyl)(N,N-dipropyl)methanethione (3ab)**

Orange solid, 29.3 mg, 72% yield, mp: 120 ~ 123 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.49 (d, *J* = 7.2 Hz 2H), 7.22-7.12 (m, 3H), 4.59 (s, 1H), 4.49-4.43 (m, 2H), 4.28 (s, 1H), 4.18 (s, 5H), 3.15-3.07 (m, 1H), 3.02-2.95 (m, 1H), 2.53-2.46 (m, 1H), 1.73-1.68 (m, 1H), 1.42-1.31 (m, 1H), 1.15-1.07 (m, 1H), 0.88-0.81 (m, 1H), 0.76 (t, *J* = 7.2 Hz 3H), 0.42 (t, *J* = 7.2 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 198.1, 138.3, 128.3, 127.9, 126.6, 96.0, 83.0, 74.4, 72.9, 67.2, 64.6, 54.7, 54.5, 20.9, 18.7, 11.6, 11.8. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{23}H_{27}FeNS$ 406.1286, found: 406.1283.




**(2-phenylferrocenyl)(N,N-diisopropyl)methanethione (3ac)**

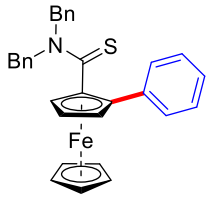
Red-brown solid, 24.1 mg, 60% yield, mp: 137 ~ 139 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.67 (d, *J* = 7.2 Hz 2H), 7.28 (t, *J* = 7.2 Hz 2H), 7.20 (t, *J* = 7.4 Hz 1H), 4.53 (s, 1H), 4.46 (t, *J* = 2.2 Hz 1H), 4.32 (t, *J* = 2.4 Hz 1H), 4.28 (s, 5H), 3.75 (s, 1H), 3.62 (s, 1H), 1.77 (s 3H), 1.62 (s, 3H), 0.83 (d, *J* = 6.8 Hz 3H), 0.22 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 196.4, 138.3, 128.1, 128.1, 126.5, 100.6, 82.8, 72.6, 66.7, 63.6, 56.2, 50.6, 20.5, 20.3, 18.6, 17.5. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{23}H_{27}FeNS$ 406.1286, found: 406.1284.




**(2-phenylferrocenyl)(N-methyl-N-phenyl)methanethione (3ad)**

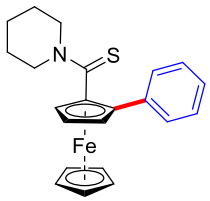
Orange solid, 36.4 mg, 88% yield, mp: 152 ~ 155 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.17 (t, *J* = 1.6 Hz 3H), 7.05 (t, *J* = 3.6 Hz 2H), 6.87 (t, *J* = 7.4 Hz 1H), 6.77 (t, *J* = 7.8 Hz 2H), 6.14 (d, *J* = 7.0 Hz 2H), 4.89 (d, *J* = 1.4 Hz 1H), 4.26 (d, *J* = 2.2 Hz 1H), 4.17 (s, 1H), 4.15 (s, 5H), 3.70 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 200.4, 145.8,

138.5, 127.9, 127.8, 126.2, 125.8, 125.4, 94.9, 83.2, 77.0, 72.9, 67.8, 65.5, 46.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{24}H_{21}FeNS$ 412.0817, found: 412.0814.



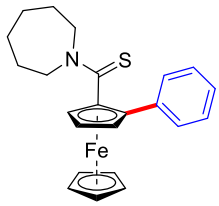

**(2-phenylferrocenyl)(N,N-dibenzyl)methanethione (3ae)**

Yellow solid, 30.0 mg, 60% yield, mp: 75 ~ 78 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.53 (dd, *J* = 6.6, 3.5 Hz 2H), 7.18-7.08 (m, 9H), 6.95 (dd, *J* = 5.6 2.1 Hz 2H), 6.67 (dd, *J* = 5.4, 3.8 Hz 2H), 6.19 (d, *J* = 14.6 Hz 1H), 4.66 (t, *J* = 1.6 Hz 1H), 4.46-4.41 (m, 2H), 4.26 (t, *J* = 2.4 Hz 1H), 4.24 (s, 5H), 4.05 (d, *J* = 14.6 Hz 1H), 3.48 (d, *J* = 15.4 Hz 1H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 201.1, 137.9, 135.5, 135.4, 128.7, 128.6, 128.5, 128.5, 128.5, 127.7, 127.6, 127.5, 126.8, 95.8, 84.1, 74.5, 72.9, 67.6, 65.4, 54.5, 54.4. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{31}H_{27}FeNS$ 502.1286, found: 502.1281.




**(2-phenylferrocenyl)(piperidin-1-yl)methanethione (3af)**

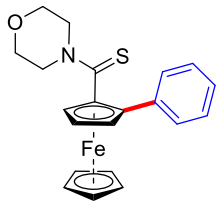
Yellow solid, 23.9 mg, 61% yield, mp: 164 ~ 167 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.46 (d, *J* = 7.4 Hz 2H), 7.22 (t, *J* = 7.2 Hz 2H), 7.15 (t, *J* = 7.2 Hz 1H), 4.66 (s, 1H), 4.44 (s, 1H), 3.33 (s, 1H), 4.18 (s, 5H), 4.13-3.96 (m, 2H), 2.94-2.79 (m, 2H), 1.57-1.22 (m, 4H), 0.99-0.95 (m, 1H), 0.40 (s, 1H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.6, 138.3, 128.3, 126.7, 94.5, 83.1, 75.4, 73.0, 67.8, 64.9, 52.3, 51.7, 25.5, 25.1, 24.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{23}FeNS$ 390.0973, found: 390.0967.




**(2-phenylferrocenyl)(azepan-1-yl)methanethione (3ag)**

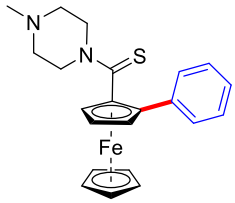
Yellow solid, 26.3 mg, 65% yield, mp: 122 ~ 124 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.58 (d, *J* = 7.4 Hz 2H), 7.28 (t, *J* = 7.2 Hz 2H), 7.21 (t, *J* = 7.0 Hz 1H), 4.60 (s, 1H), 4.52 (s, 1H), 4.39-4.33 (m, 2H), 4.26 (s, 5H), 3.73-3.67 (m, 1H), 3.26-3.19 (m, 1H), 2.74-2.71 (m, 1H), 2.05-1.96 (m, 1H), 1.67-1.60 (m, 1H), 1.49-1.33 (m, 2H),1.22-1.12 (m, 4H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 200.0, 138.5, 128.3, 127.7, 126.5, 96.3, 83.1,

73.7, 72.7, 67.2, 64.6, 54.1, 53.4, 27.9, 27.6, 25.9, 25.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{23}H_{25}FeNS$ 404.1130, found: 404.1126.



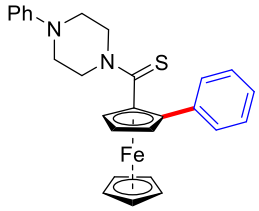

**(2-phenylferrocenyl)(morpholine-4-yl)methanethione (3ah)**

Yellow solid, 7.2 mg, 18% yield, mp: 188 ~ 191 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.52 (d, *J* = 7.2 Hz 2H), 7.32 (t, *J* = 7.0 Hz 2H), 7.26 (t, *J* = 5.8 Hz 1H), 4.77 (s, 1H), 4.52 (s, 1H), 4.45-4.40 (m, 2H), 4.25 (s, 5H), 3.98-3.92 (m, 1H), 3.73-3.65 (m, 1H), 3.41-3.36 (m, 1H), 3.14-2.99 (m, 3H), 2.27 (s, 1H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 199.2, 140.0, 128.5, 128.4, 127.1, 93.3, 83.2, 76.0, 73.1, 68.2, 65.8, 65.6, 65.3, 51.7, 50.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{21}FeNOS$ 392.0772, found: 392.0760.




**(2-phenylferrocenyl)(4-methylpiperazin-1-yl)methanethione (3ai)**

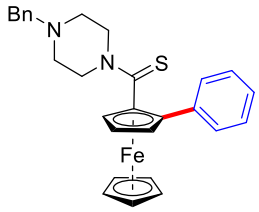
Yellow oil, 24.3 mg, 60% yield, $R_f$ = 0.24. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.51 (d, *J* = 7.2 Hz 2H), 7.30 (t, *J* = 7.0 Hz 2H), 7.23 (t, *J* = 7.2 Hz 1H), 4.76 (s, 1H), 4.52 (s, 1H), 4.42-4.38 (m, 2H), 4.25 (s, 5H), 4.05-4.00 (m, 1H), 3.00 (s, 2H), 2.48-2.43 (m, 1H), 2.15-2.11 (m, 1H), 2.04 (s 3H), 1.94-1.87 (m, 1H), 1.05 (s, 1H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 198.7, 138.1, 128.4, 126.8, 93.8, 83.2, 75.7, 73.0, 68.0, 65.1, 53.7, 50.9, 50.1, 45.4. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{22}H_{24}FeN_2S$ 405.1082, found: 405.1080.




**(2-phenylferrocenyl)(4-phenylpiperazin-1-yl)methanethione (3aj)**

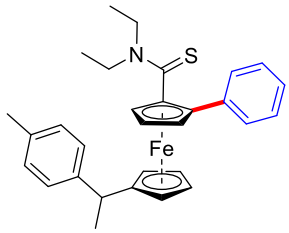
Yellow solid, 9.4 mg, 20% yield, mp: 87 ~ 90 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.53 (d, *J* = 7.4 Hz 2H), 7.28 (t, *J* = 7.4 Hz 2H), 7.21-7.16 (m, 3H), 6.83 (t, *J* = 7.2 Hz 1H), 6.68 (d, *J* = 8.0 Hz 2H), 4.78 (s, 1H), 4.55-4.49 (m, 2H), 4.43 (d, *J* = 2.2 Hz 1H), 4.25 (s, 5H), 4.17-4.11 (m, 1H), 3.27-3.13 (m, 3H), 2.92-2.87 (m, 1H), 2.68-2.63 (m, 1H),

1.87-1.84 (m, 1H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 200.0, 150.3, 138.0, 129.2, 128.4, 128.3, 127.0, 120.4, 116.4, 93.6, 83.2, 76.0, 73.1, 68.1, 65.3, 50.8, 50.1, 48.5, 48.1. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{27}H_{26}FeN_2S$ 467.1239; found: 467.1237.



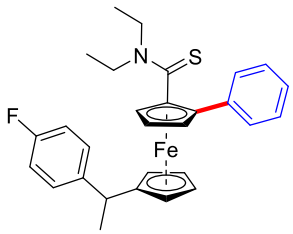

**(2-phenylferrocenyl)(4-benzylpiperazin-1-yl)methanethione (3ak)**

Yellow solid, 22.8 mg, 47% yield, mp: 170 ~ 173 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.49 (d, *J* = 7.2 Hz 2H), 7.31-7.20 (m, 6H), 7.15 (d, *J* = 7.0 Hz 2H), 4.75 (s, 1H), 4.50 (s, 1H), 4.40 (d, *J* = 2.2 Hz 1H), 4.28-4.16 (m, 7H), 3.25 (s, 2H), 3.11-2.85 (m, 2H), 2.52-2.43 (m, 1H), 2.28-2.20 (m, 1H), 1.94-1.86 (m, 1H), 1.25-1.08 (m, 1H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 198.4, 138.1, 137.4, 129.2, 128.4, 127.4, 126.8, 93.8, 83.2, 75.8, 73.1, 68.0, 65.1, 62.4, 51.9, 51.8, 51.1, 50.2. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{28}H_{28}FeN_2S$ 481.1395, found: 481.1390.



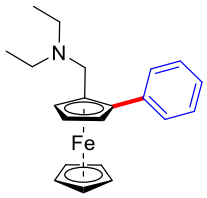

**3al**

Yellow oil, 31.4 mg, 63% yield, $R_f$ = 0.35. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.51-7.48 (m, 2H), 7.22-7.18 (m, 2H), 7.16-7.11 (m, 1H), 6.96-6.90 (m, 3H), 6.85 (d, *J* = 8.0 Hz 1H), 4.56-4.49 (m, 1H), 4.48-4.41 (m, 1H), 4.38-4.36 (m, 1.5H), 4.27 (dd, *J* = 3.6, 2.4 Hz 0.5H), 4.22-4.17 (m, 1.5H), 4.14-4.13 (m, 0.5H), 4.10-4.08 (m, 1H), 4.02-4.00 (m, 0.5H), 3.89 (q, *J* = 7.2 Hz 0.5H), 3.83-3.83 (m, 0.5H), 3.51 (q, *J* = 7.2 Hz 0.5H), 3.45-3.36 (m, 1H), 3.09-2.99 (m, 1H), 2.74-2.64 (m, 1H), 2.19 (d, *J* = 6.0 Hz 3H), 1.34 (t, *J* = 7.0 Hz 3H), 1.08 (td, *J* = 7.0, 3.3 Hz 3H), 0.54 (td, *J* = 7.2, 3.6 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.7, 144.8, 144.7, 138.2, 137.9, 135.3, 129.0, 128.3, 127.9, 127.8, 127.1, 127.0, 126.6, 96.0, 95.9, 95.9, 95.8, 82.7, 75.2, 75.1, 74.9, 74,5, 73.5, 73.2, 72.7, 69.5, 68.3, 68.2, 65.5, 47.2, 47.1, 38.5, 38.4, 22.5, 21.1, 12.7, 10.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{30}H_{33}FeNS$ 496.1756, found: 496.1753.



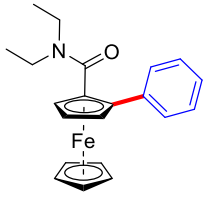

**3am**

Yellow oil, 26.9 mg, 54% yield, $R_f$ = 0.45. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.49 (d, *J* = 7.4 Hz 2H), 7.22-7.18 (m, 2H), 7.16-7.11 (m, 1H), 6.98-6.88 (m, 2H), 6.83-6.76 (m, 2H), 4.55 (s, 0.5H), 4.49-4.41(m, 1.5H), 4.36 (s, 1.5H), 4.25-4.14 (m, 3H), 4.03-3.94 (m, 1.5H), 3.81 (s, 0.5H), 3.53 (q, *J* = 14.2, 7.0 Hz 0.5H), 3.44-3.35 (m, 1H), 3.08-2.98 (m, 1H), 2.73-2.63 (m, 1H), 1.36-1.21 (m, 3H), 1.10-1.05 (m, 3H), 0.55-0.51 (m, 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 197.5, 162.4, 159.9, 143.5 (d, *J* = 3.1 Hz), 143.3 (d, *J* = 3.1 Hz), 138.0, 137.7, 128.5 (t, *J* = 8.0 Hz), 128.3 (d, *J* = 3.2 Hz), 127.8 (d, *J* = 11.6 Hz), 126.6, 114.9 (d, *J* = 21.0 Hz), 96.0 (d, *J* = 16.5 Hz), 95.5 (d, *J* = 8.9 Hz), 82.7 (d, *J* = 1.9 Hz), 75.2, 74.9, 74.5, 73.6, 73.4, 72.9, 72.8, 69.5, 69.3, 68.3, 68.1, 65.4, 47.2, 47.1, 38.1, 37.9, 22.6, 22.5, 12.7, 10.7. **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -117.7. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{29}H_{30}FFeNS$ 500.1500, found: 500.1505.




**1-(2-phenylferrocenyl)(N, N- diethyl)amine (4)**

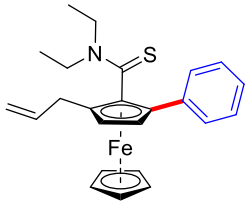
Yellow oil, $R_f$ = 0.19. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.69 (d, J = 7.4 Hz 2H), 7.22 (t, J = 7.4 Hz 2H), 7.14 (t, J = 7.2 Hz 1H), 4.36 (s, 1H), 4.23 (s, 1H), 4.13 (t, J = 2.4 Hz 1H), 3.97 (s, 5H), 3.64 (d, J = 12.8 Hz 1H), 3.33 (d, J = 13.0 Hz 1H), 2.50-2.42 (m, 2H), 2.37-2.28 (m, 2H), 0.86 (t, *J* = 7.1 Hz 6H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 139.0, 129.7, 127.9, 126.2, 88.5, 83.0, 71.7, 70.1, 69.8, 67.0, 51.5, 46.1, 11.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{25}FeN$ 348.1409, found: 348.1404.




**(2-phenylferrocenyl)(N,N-diethyl) amide (5)**

Yellow solid, mp: 70 ~ 72 °C. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.44 (d, J = 7.4 Hz 2H), 7.17 (t, J = 6.8 Hz 2H), 7.13 (t, J = 7.0 Hz 1H), 4.47 (s, 1H), 4.44 (s, 1H), 4.23 (s, 1H), 4.20 (s, 5H), 4.65-4.57 (m, 1H), 3.13-3.04 (m, 1H), 2.89-2.81 (m, 1H), 2.71-2.62 (m, 1H), 1.02 (t, J = 7.0 Hz 3H), 0.57 (t, J = 7.0 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ

168.7, 138.1, 128.2, 127.8, 126.6, 87.2, 85.0, 71.4, 70.3, 67.2, 67.1, 65.4, 42.8, 39.5, 13.5, 12.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{21}H_{23}FeNO$ 362.1202, found: 362.1200.




**(2-allyl-5-phenylferrocenyl)(N,N-diethyl)methanethione (6)**

Yellow oil, $R_f$ = 0.62. **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.55 (d, *J* = 7.4 Hz 2H), 7.18 (t, *J* = 7.2 Hz 2H), 7.11 (t, *J* = 7.2 Hz 1H), 5.87-5.77 (m, 1H), 5.00-4.89 (m, 2H), 4.36 (d, *J* = 2.0 Hz 1H), 4.21 (d, J = 2.0 Hz 1H), 4.18-4.11 (m, 6H), 3.66-3.58 (m, 1H), 3.35-3.22 (m, 2H), 2.95-2.86 (m, 1H), 2.74-2.66 (m, 1H), 1.05 (t, J = 7.0 Hz 3H), 0.43 (t, J = 7.2 Hz 3H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)** δ 196.3, 138.5, 137.2, 128.2, 127.8, 126.4, 115.5, 96.0, 89.2, 82.9, 73.1, 67.4, 67.4, 62.5, 47.0, 46.5, 31.8, 12.6, 10.6. **HRMS (ESI)** m/z: $[M+H]^+$ calc. for $C_{24}H_{27}FeNS$ 418.1286, found: 418.1284.

## 6. References.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2. Z. Z. Zhang, G. Liao, H. M. Chen, B. F. Shi, *Org. Lett.*, 2021, **23**, 2626-2631.
3. P. Nareddy, F. Jordan, M. Szostak, *Chem. Sci.* 2017, **8**, 3204-3210.
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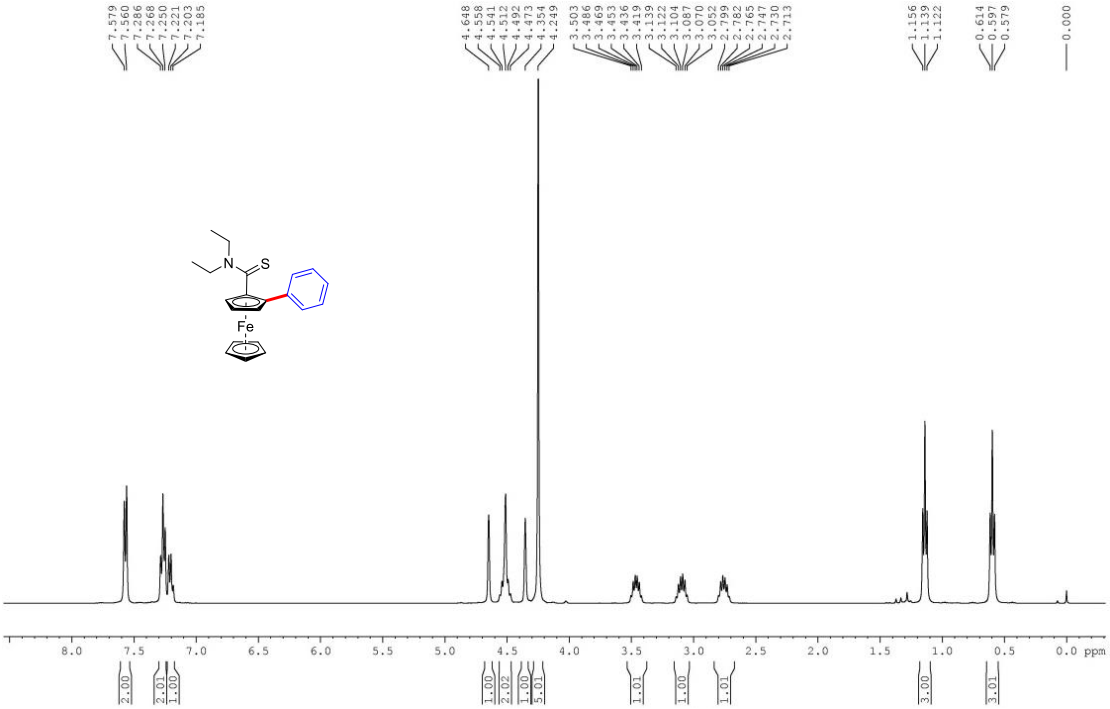
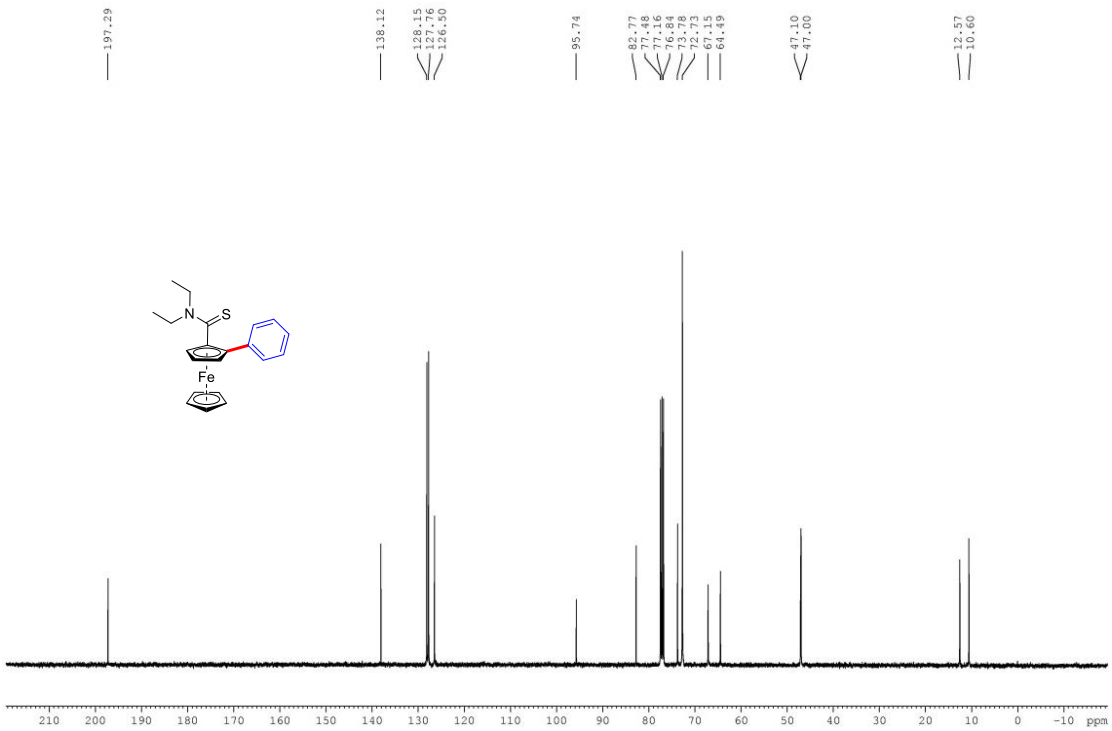
# 7. Spectra.

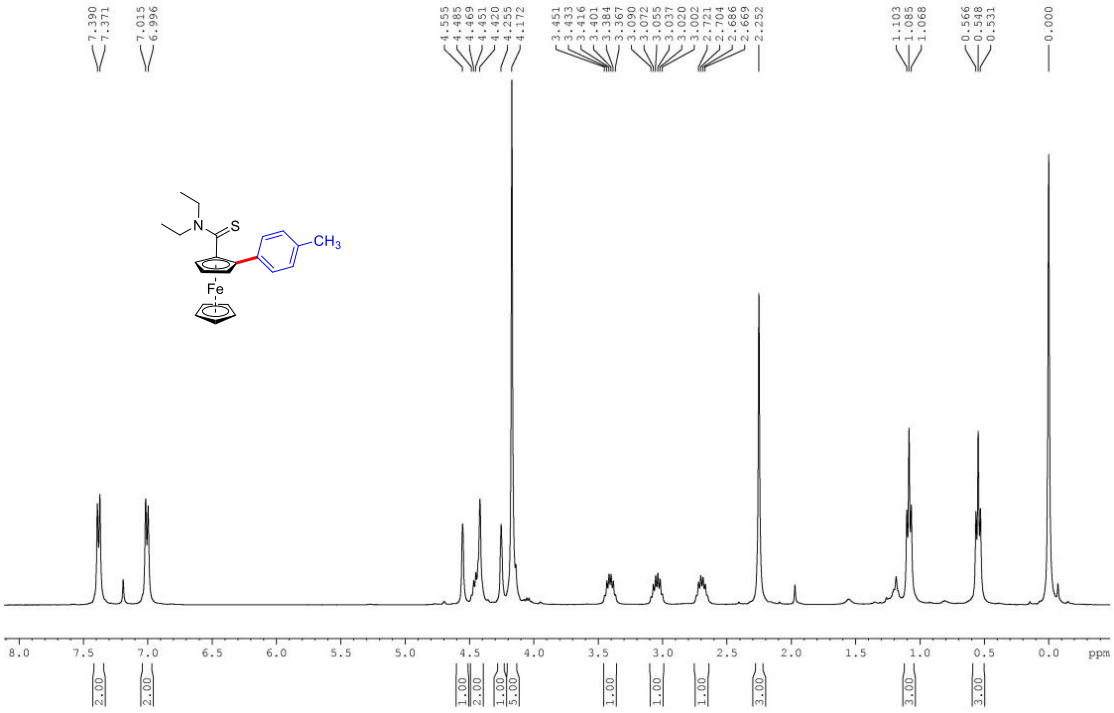
**3aa, $^{1}$H NMR, 400 MHz, $CDCl_3$**



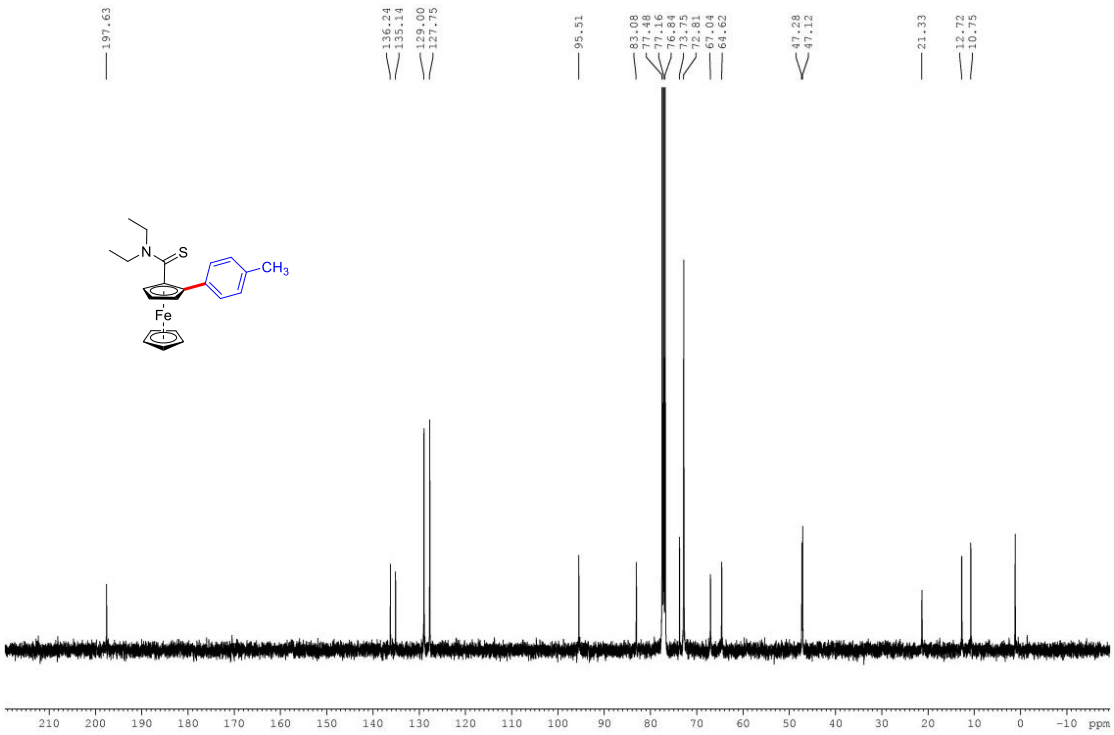

**3aa, $^{13}$C NMR, 101 MHz, $CDCl_3$**



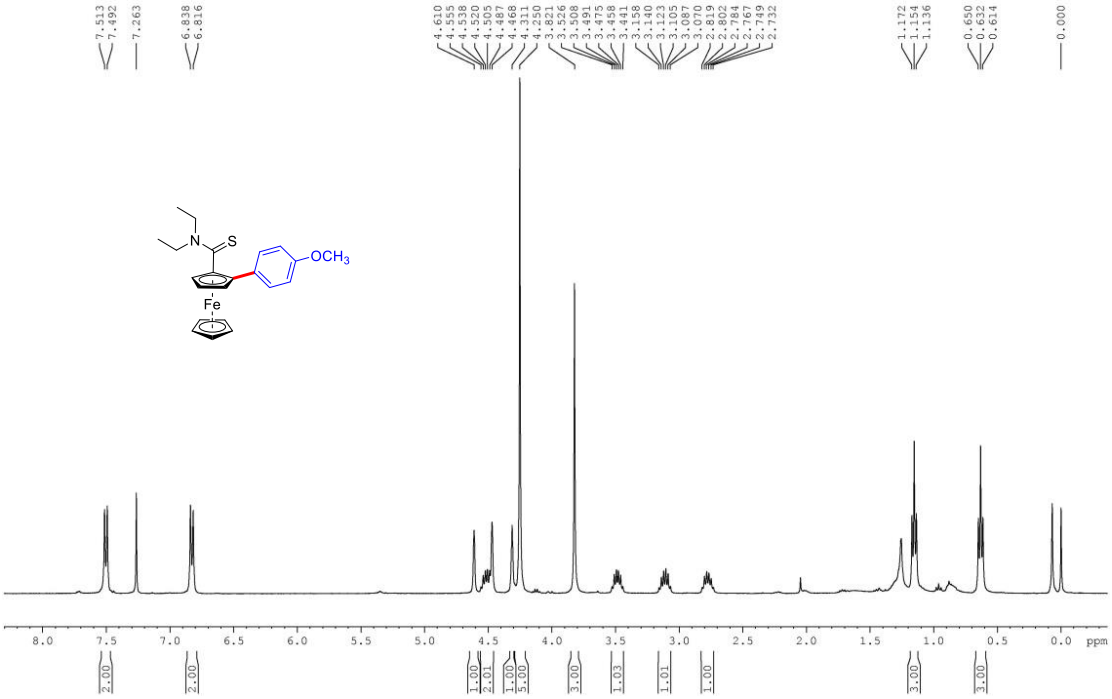
**3ba, $^{1}$H NMR, 400 MHz, $CDCl_3$**



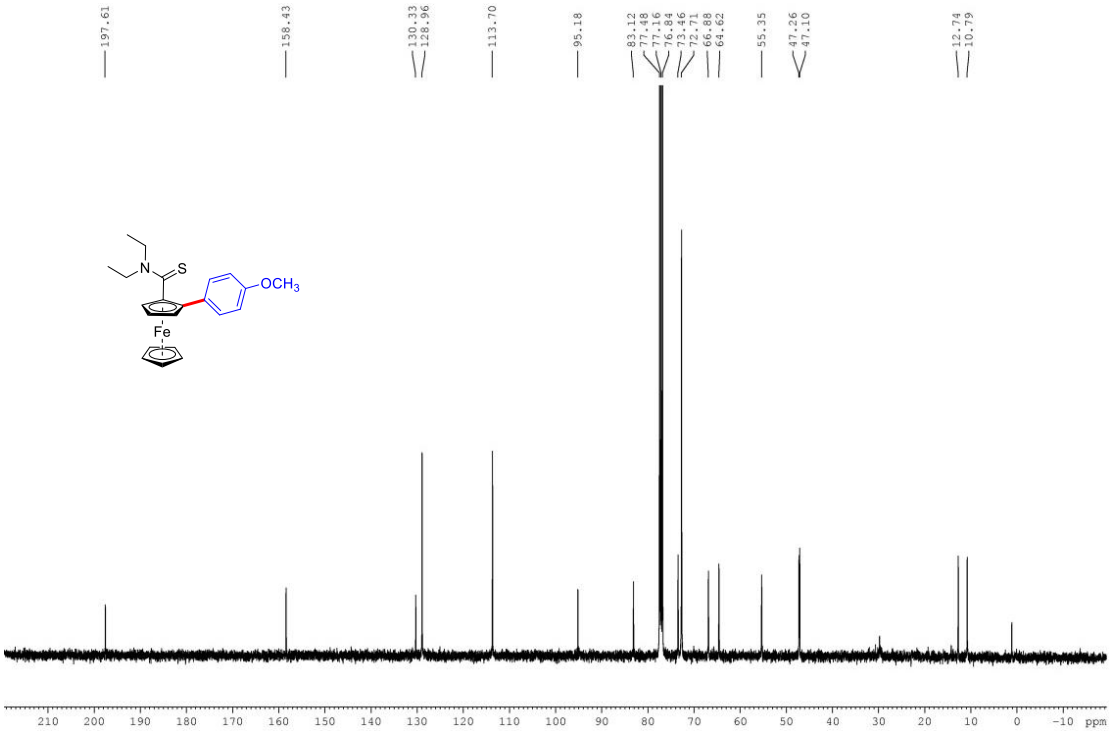

**3ba, $^{13}$C NMR, 101 MHz, $CDCl_3$**



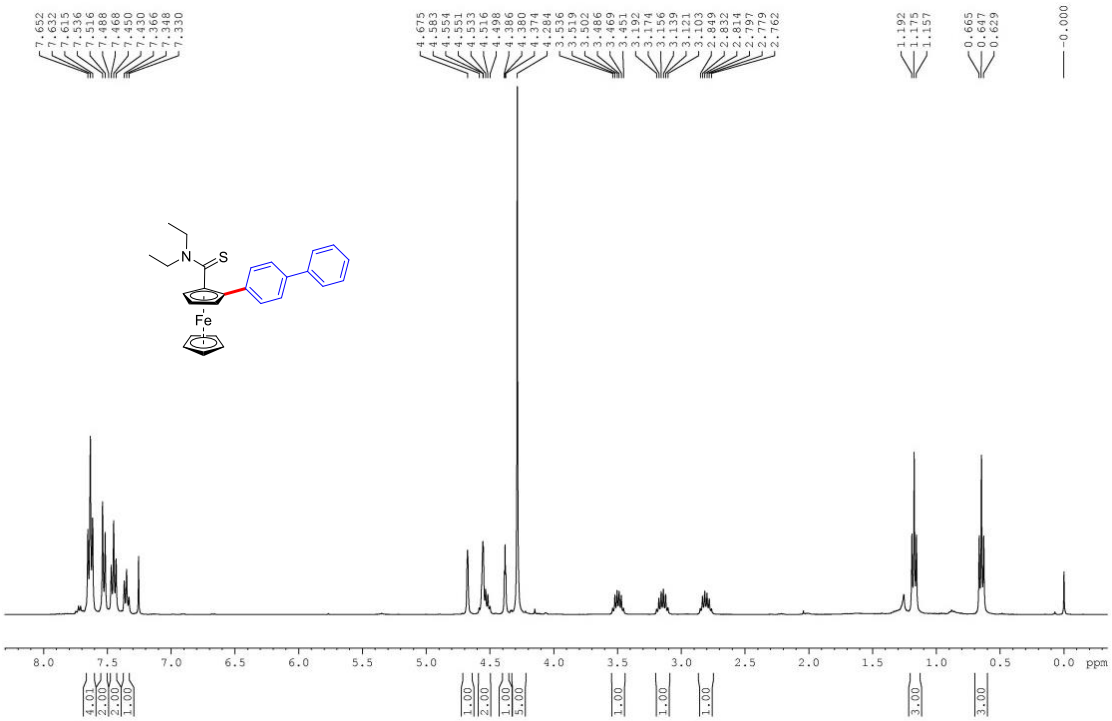
**3ca, $^{1}$H NMR, 400 MHz, $CDCl_3$**



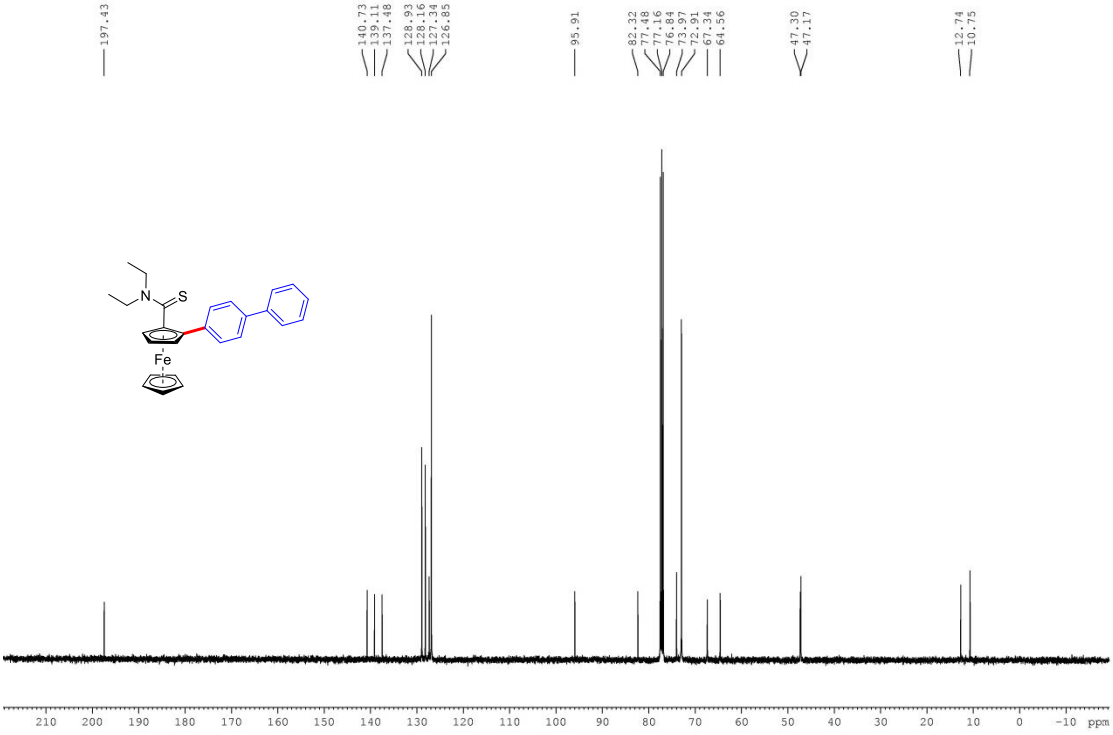

**3ca, $^{13}$C NMR, 101 MHz, $CDCl_3$**



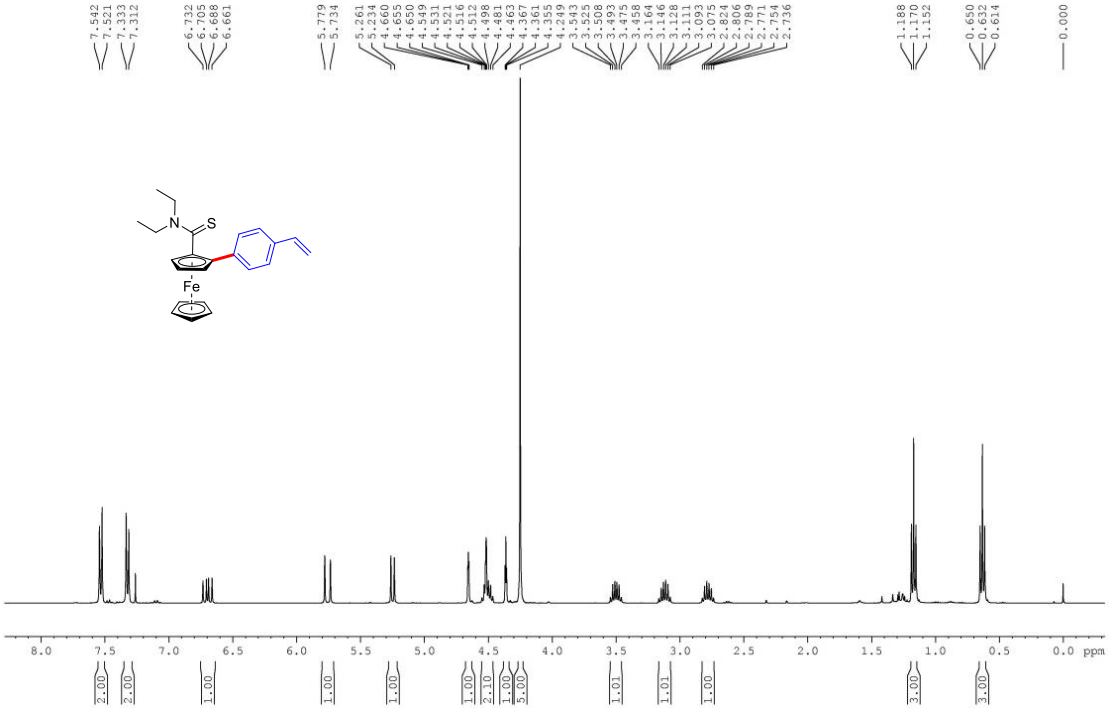
**3da, $^{1}$H NMR, 400 MHz, $CDCl_3$**



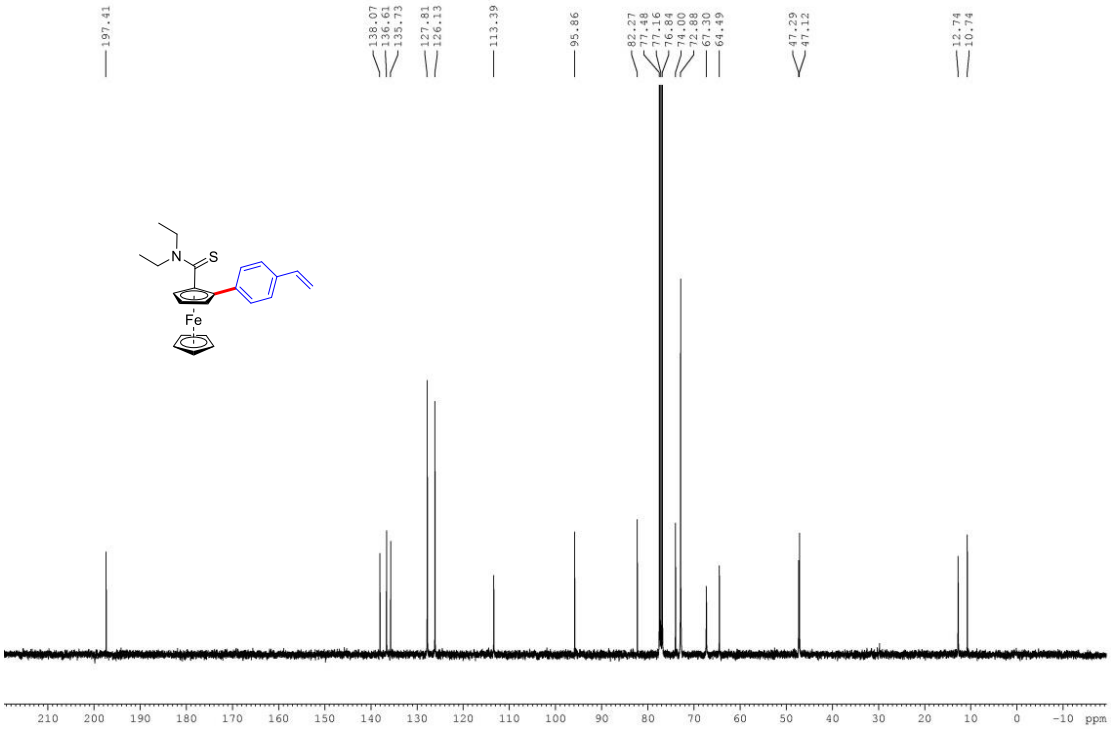

**3da, $^{13}$C NMR, 101 MHz, $CDCl_3$**



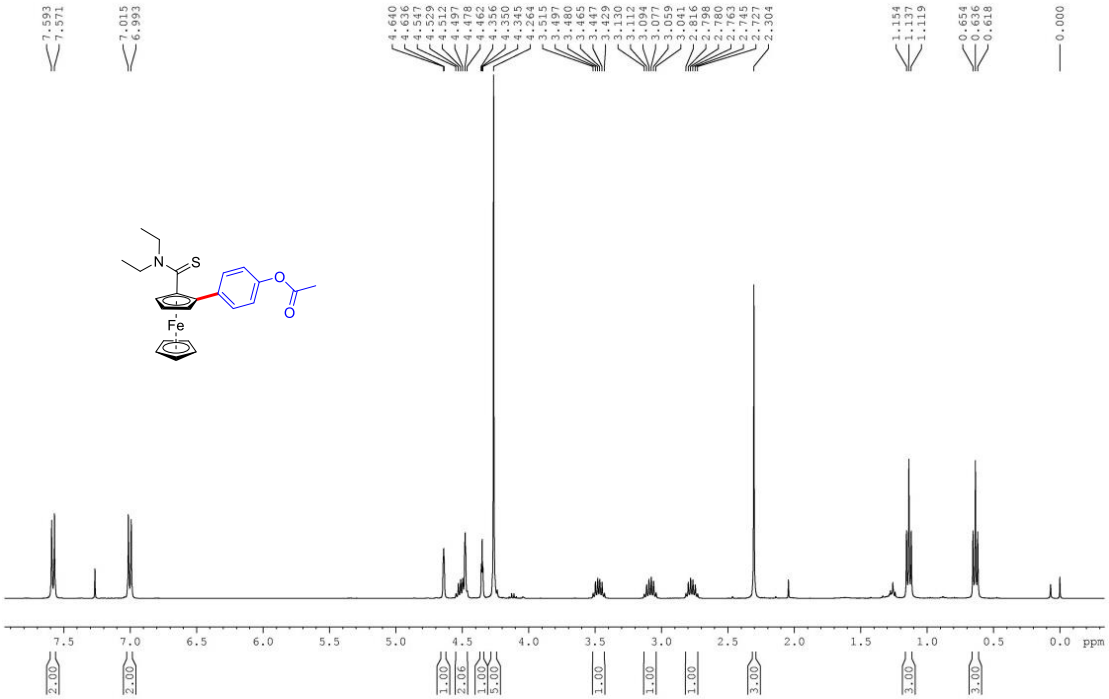
**3ea, $^{1}$H NMR, 400 MHz, $CDCl_3$**



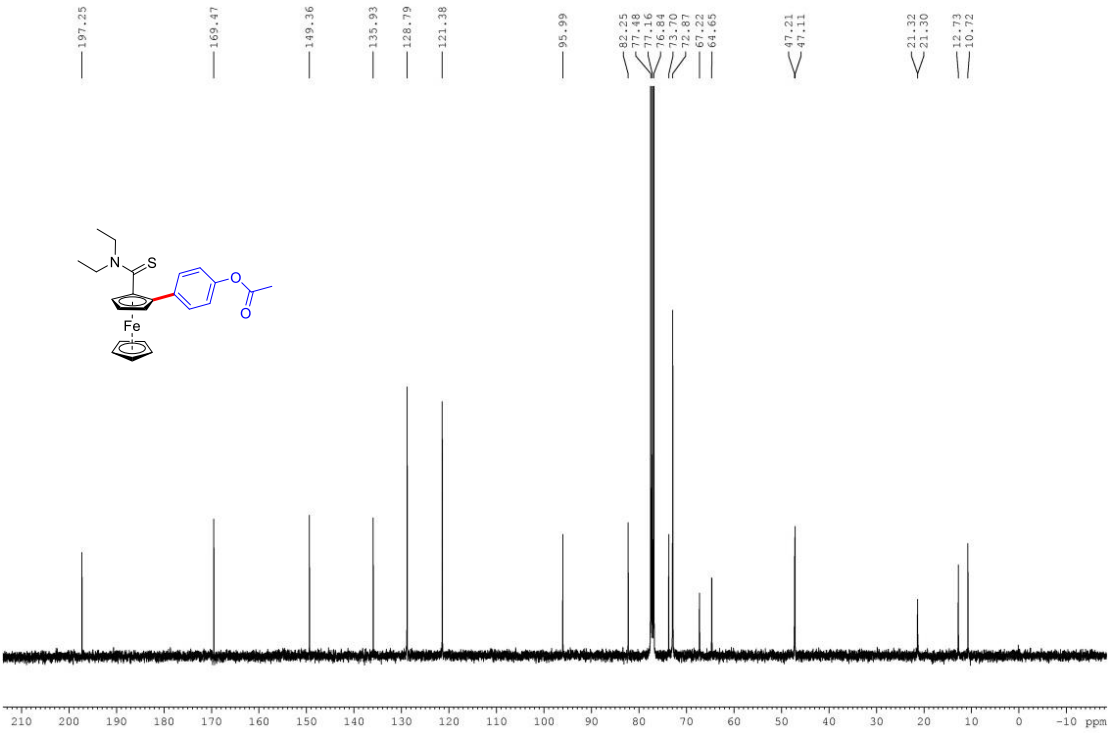

**3ea, $^{13}$C NMR, 101 MHz, $CDCl_3$**



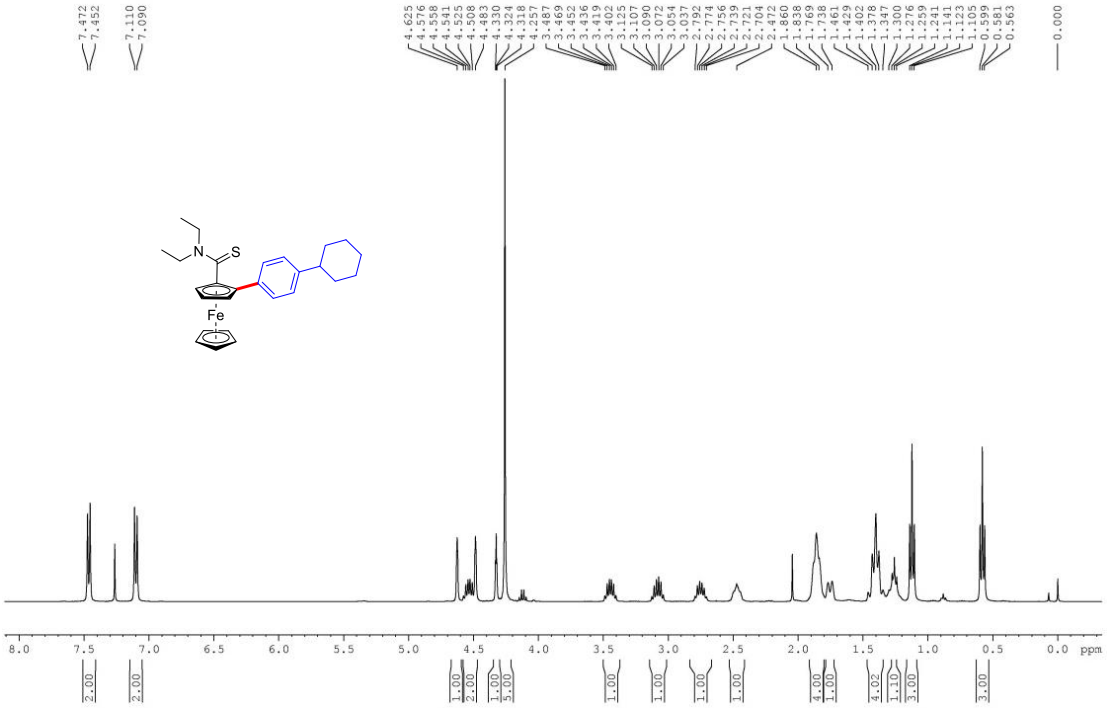
**3fa, $^{1}$H NMR, 400 MHz, $CDCl_3$**



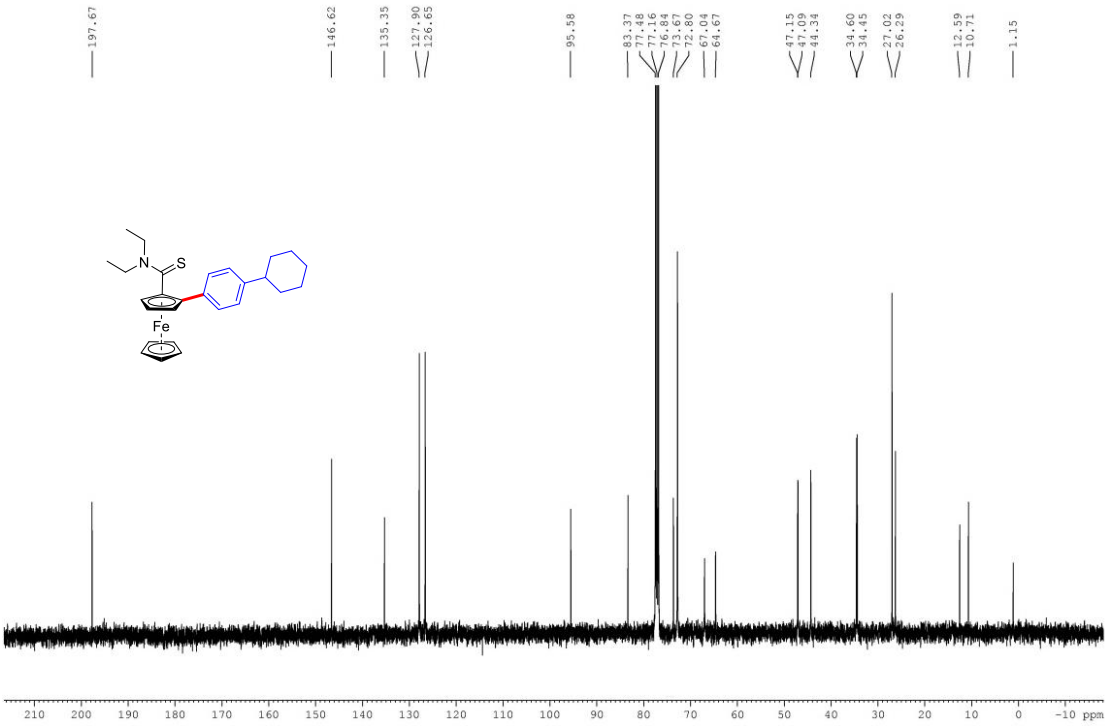
**3fa, $^{13}$C NMR, 101 MHz, $CDCl_3$**



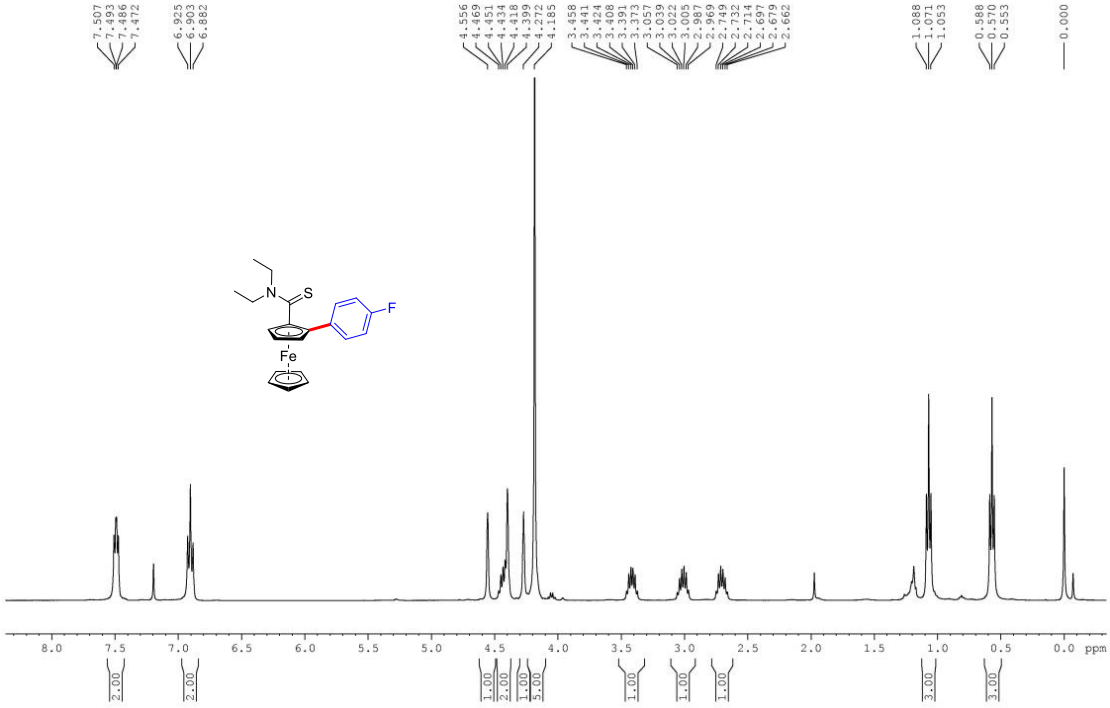
**3ga, $^{1}$H NMR, 400 MHz, $CDCl_3$**



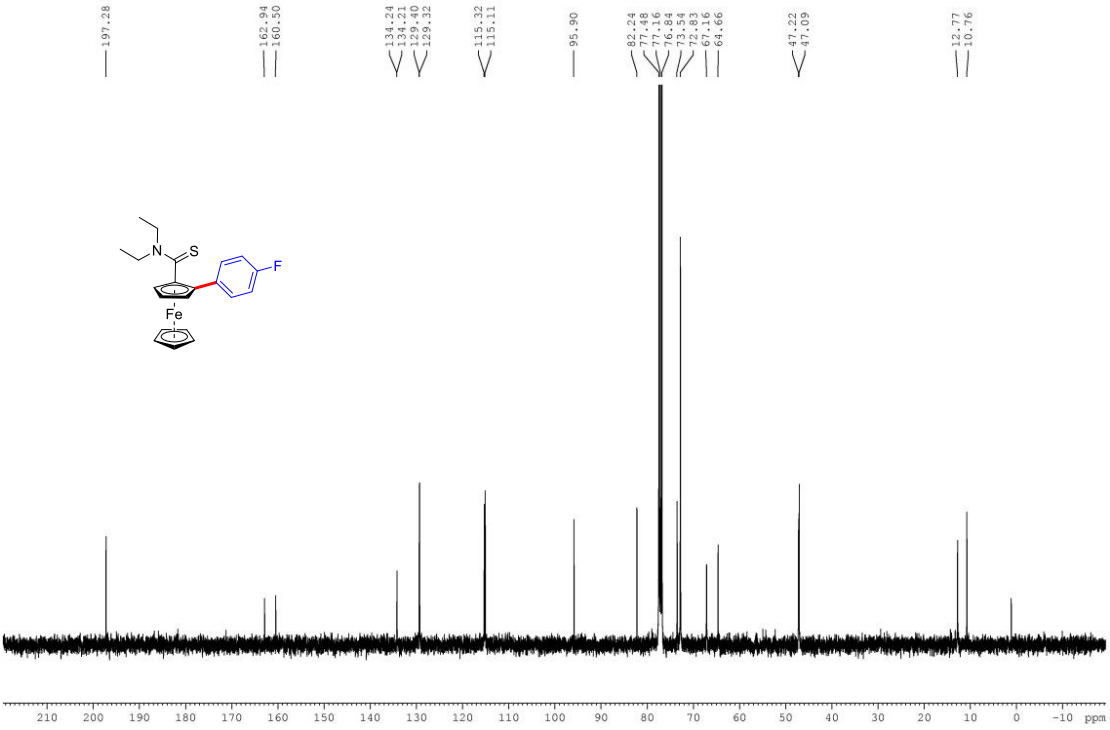
**3ga, $^{13}$C NMR, 101 MHz, $CDCl_3$**



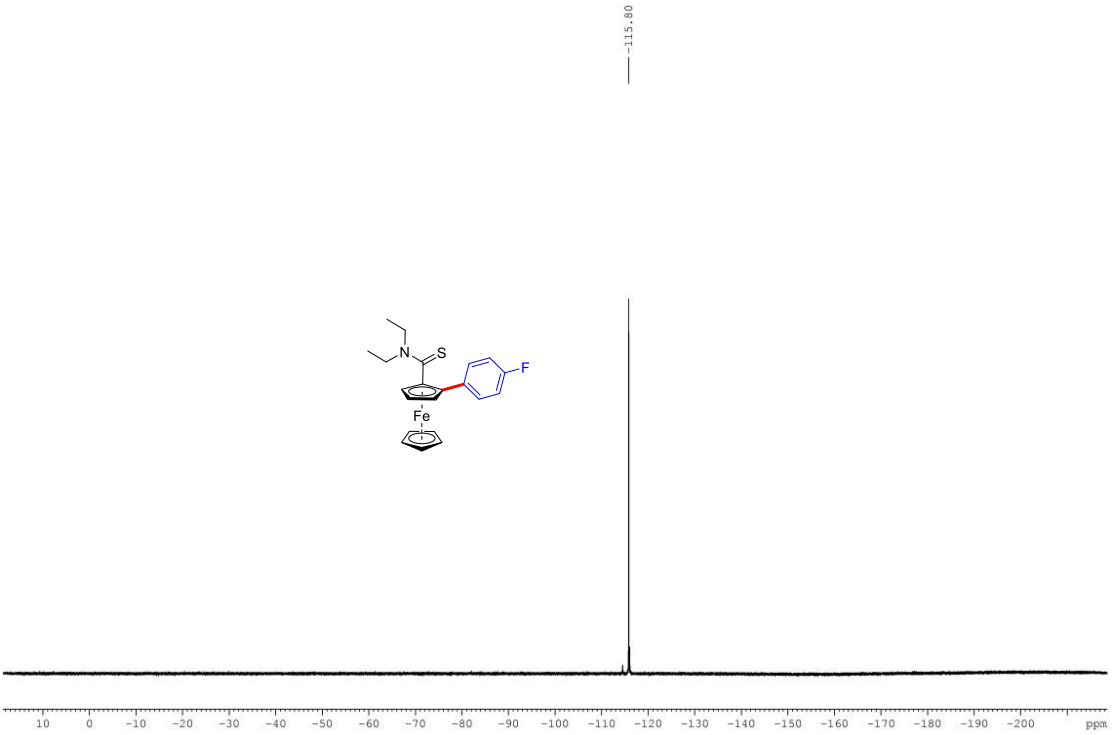
**3ha, $^{1}$H NMR, 400 MHz, $CDCl_3$**



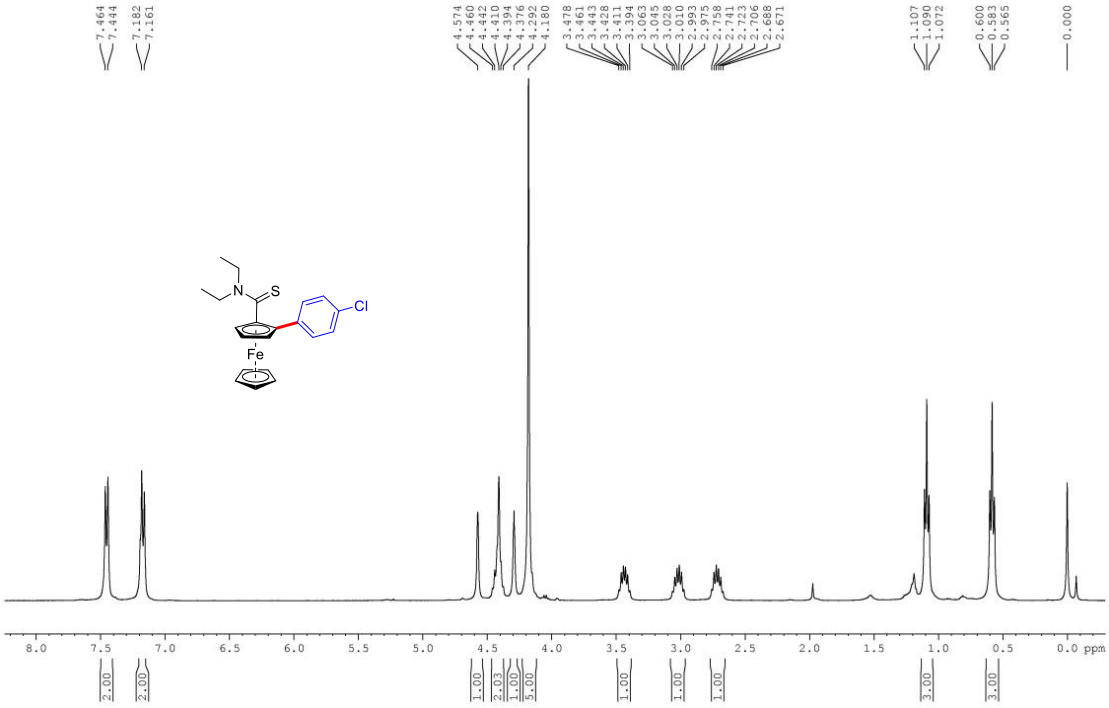

**3ha, $^{13}$C NMR, 101 MHz, $CDCl_3$**



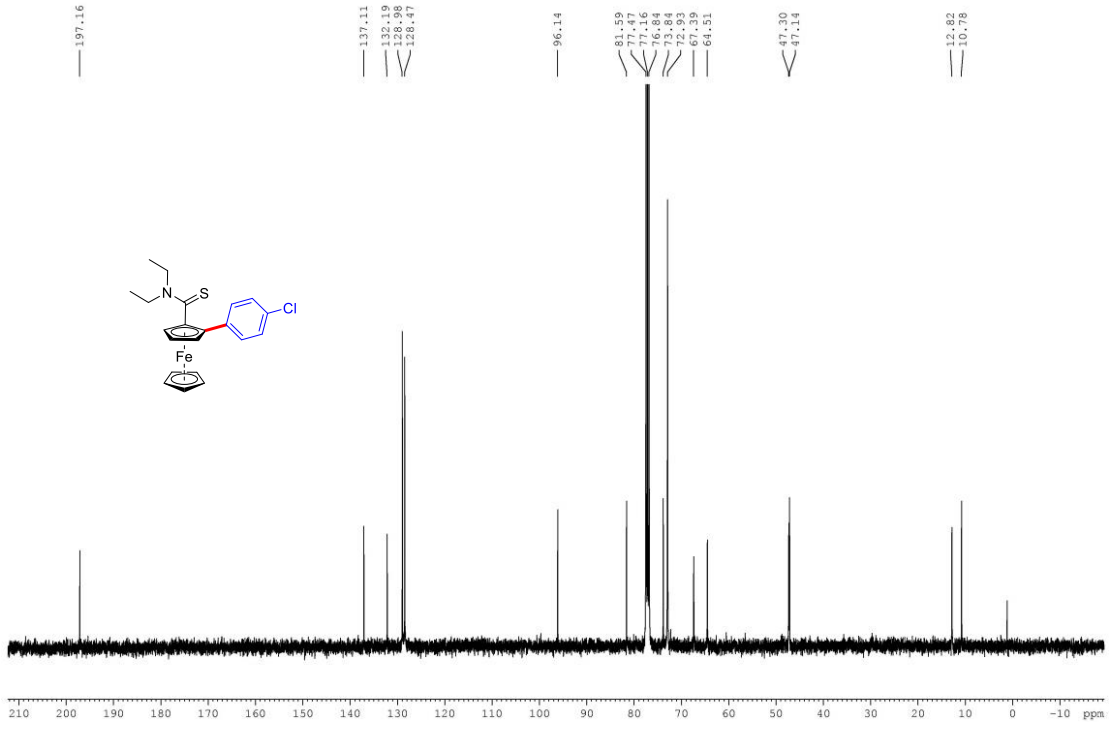
**3ha, $^{19}$F NMR, 376 MHz, $CDCl_3$**



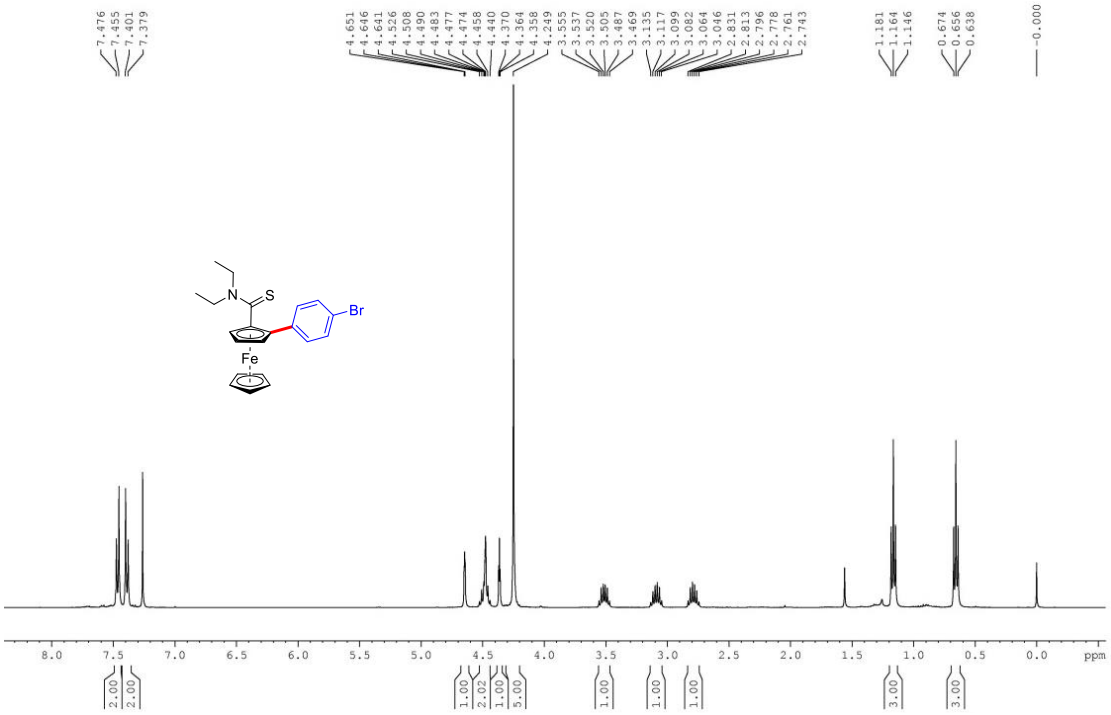
**3ia, $^{1}$H NMR, 400 MHz, $CDCl_3$**



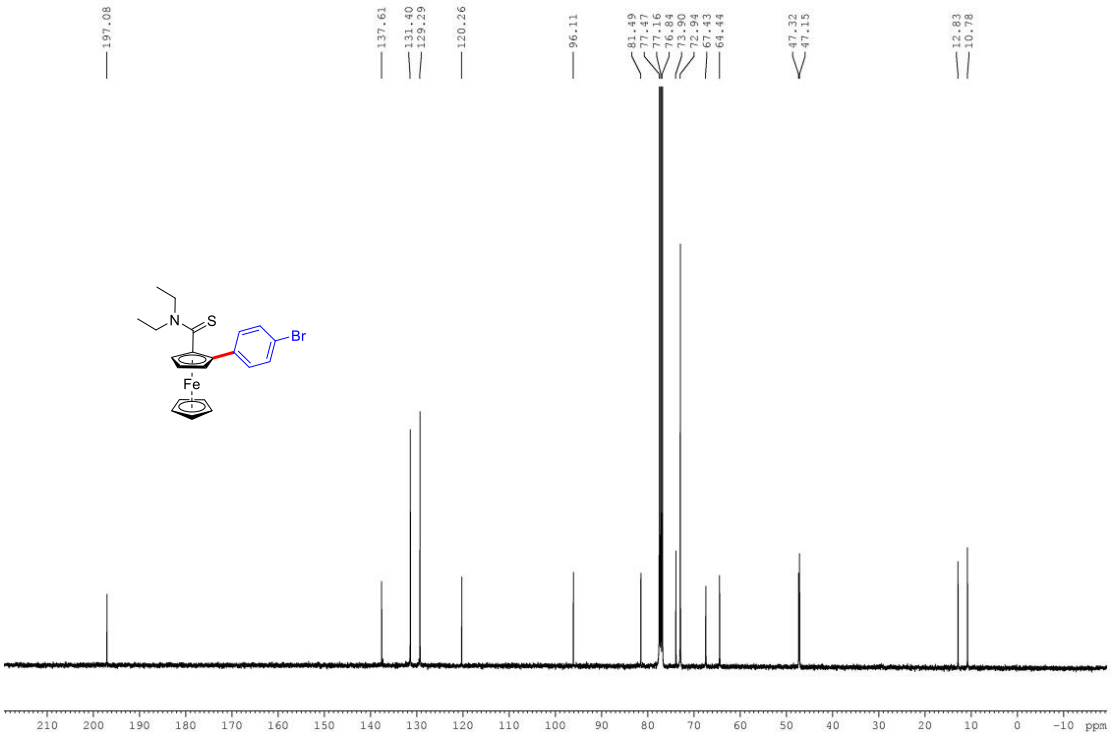

**3ia, $^{13}$C NMR, 101 MHz, $CDCl_3$**



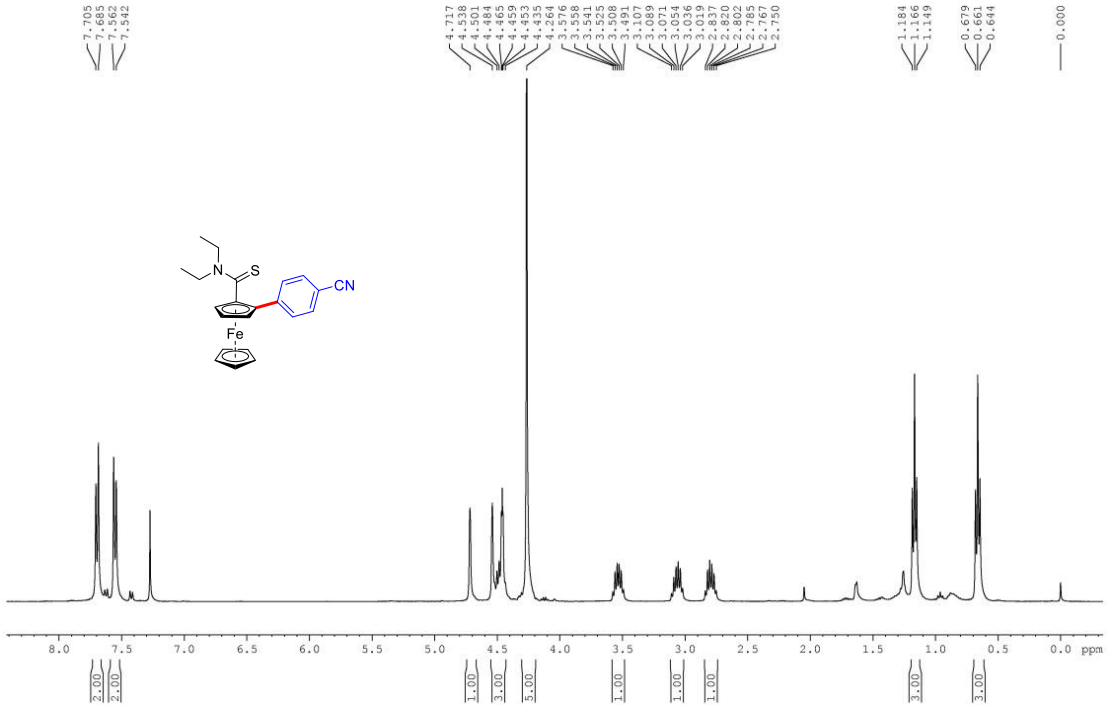
**3ja, $^{1}$H NMR, 400 MHz, $CDCl_3$**



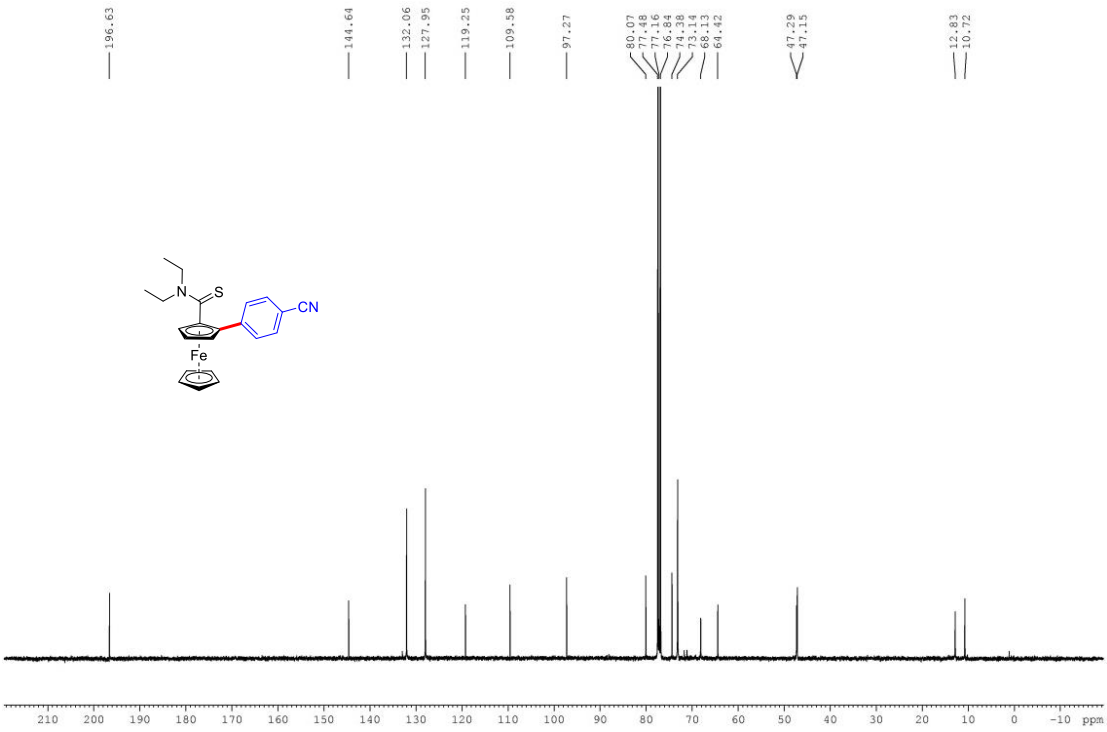

**3ja, $^{13}$C NMR, 101 MHz, $CDCl_3$**



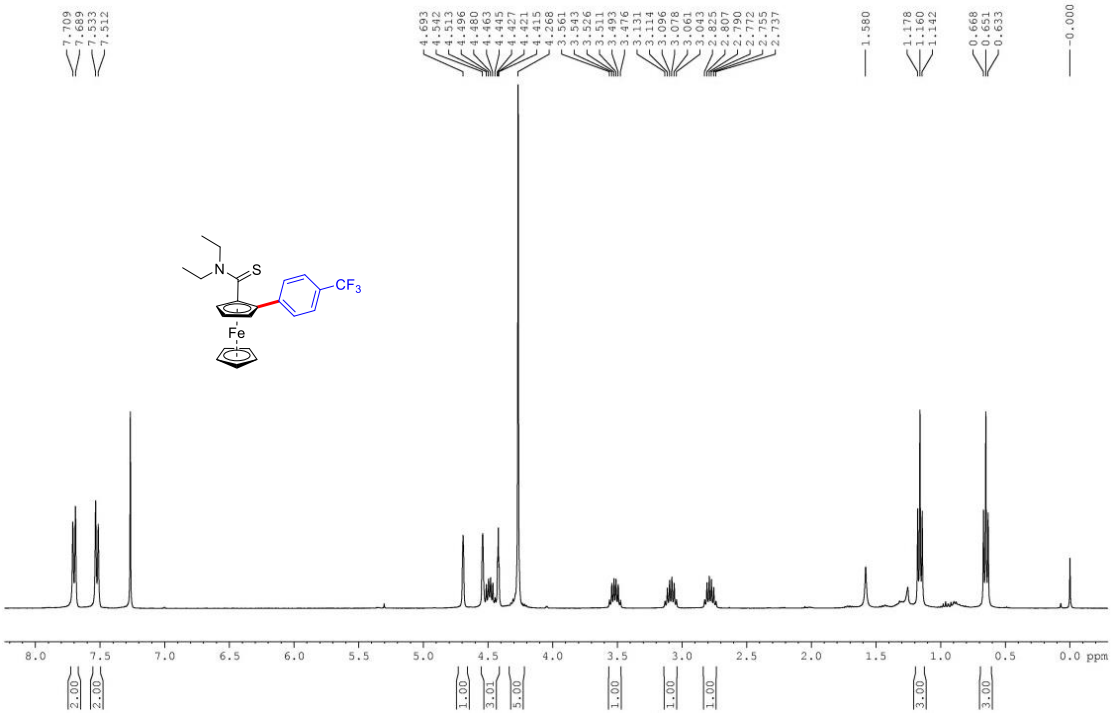
**3ka, $^{1}$H NMR, 400 MHz, $CDCl_3$**



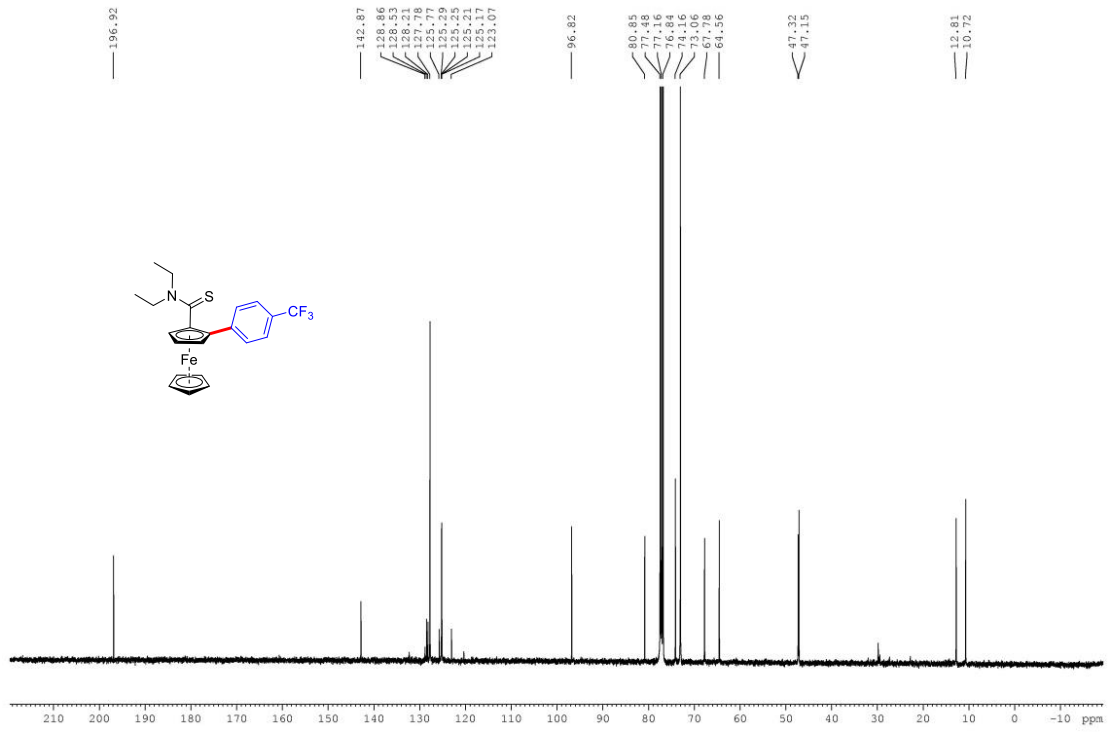

**3ka, $^{13}$C NMR, 101 MHz, $CDCl_3$**



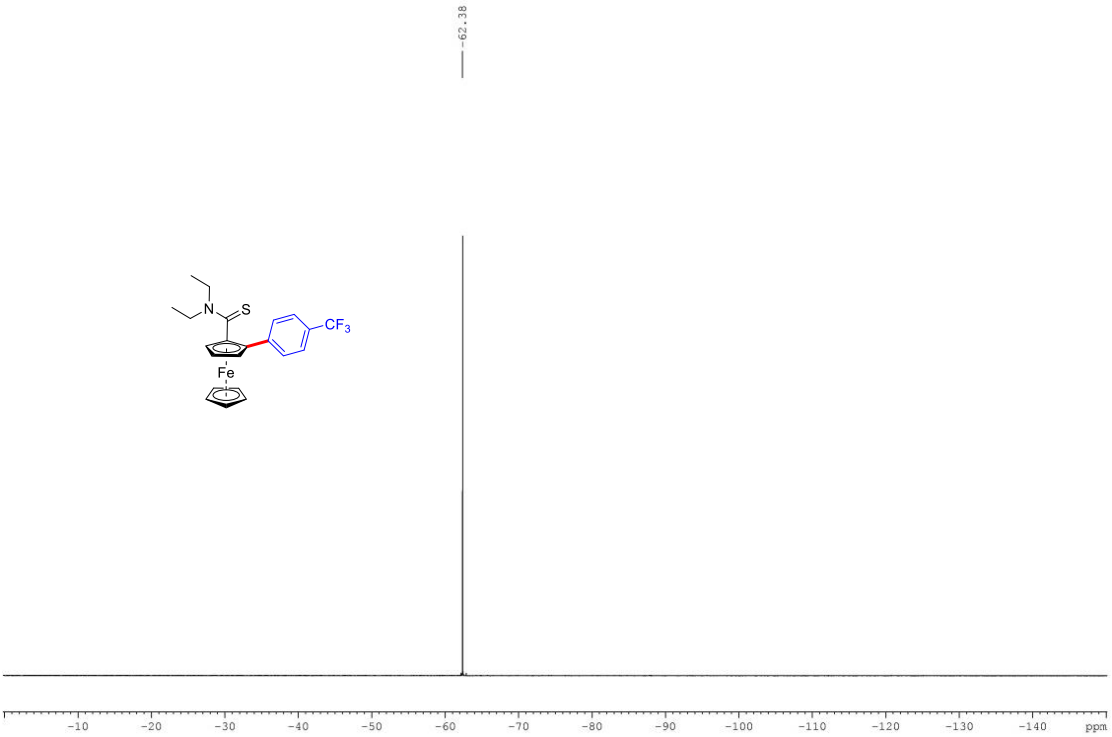
**3la, $^{1}$H NMR, 400 MHz, $CDCl_3$**



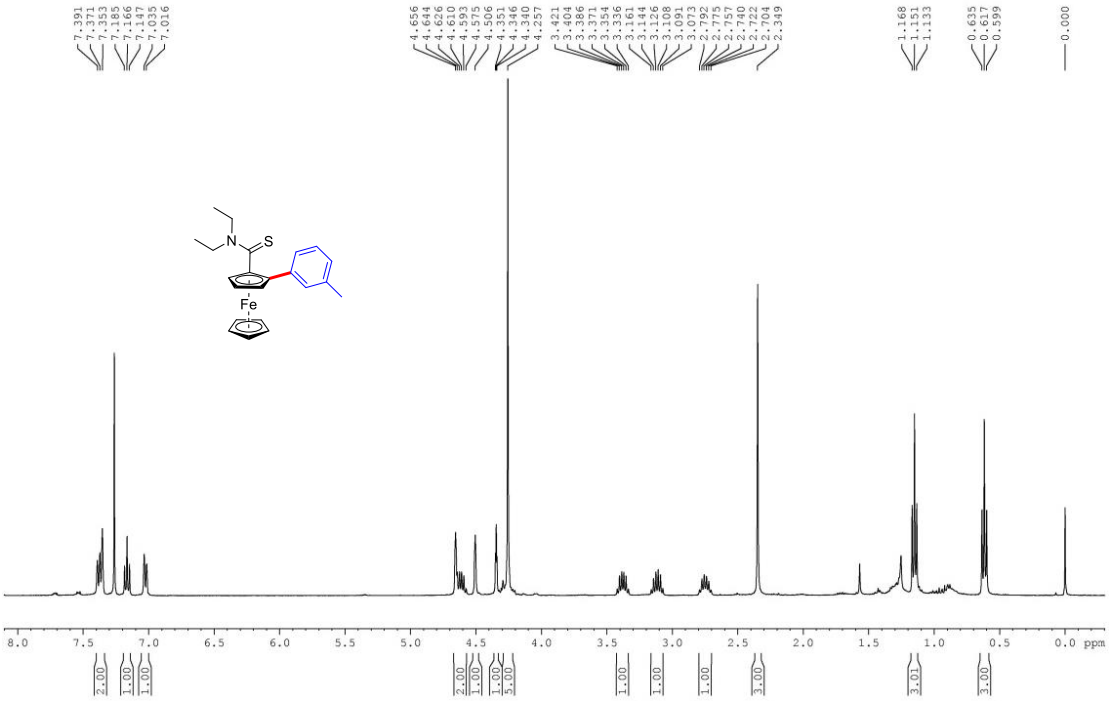

**3la, $^{13}$C NMR, 101 MHz, $CDCl_3$**



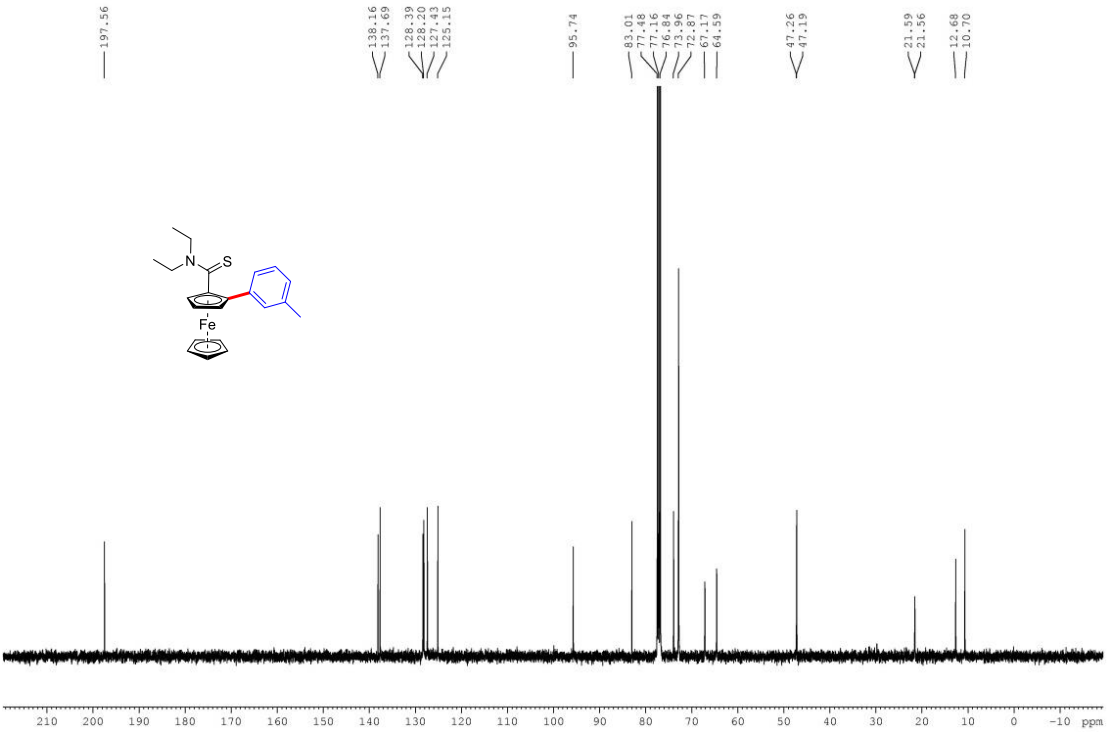
**3la, $^{19}$F NMR, 376 MHz, $CDCl_3$**



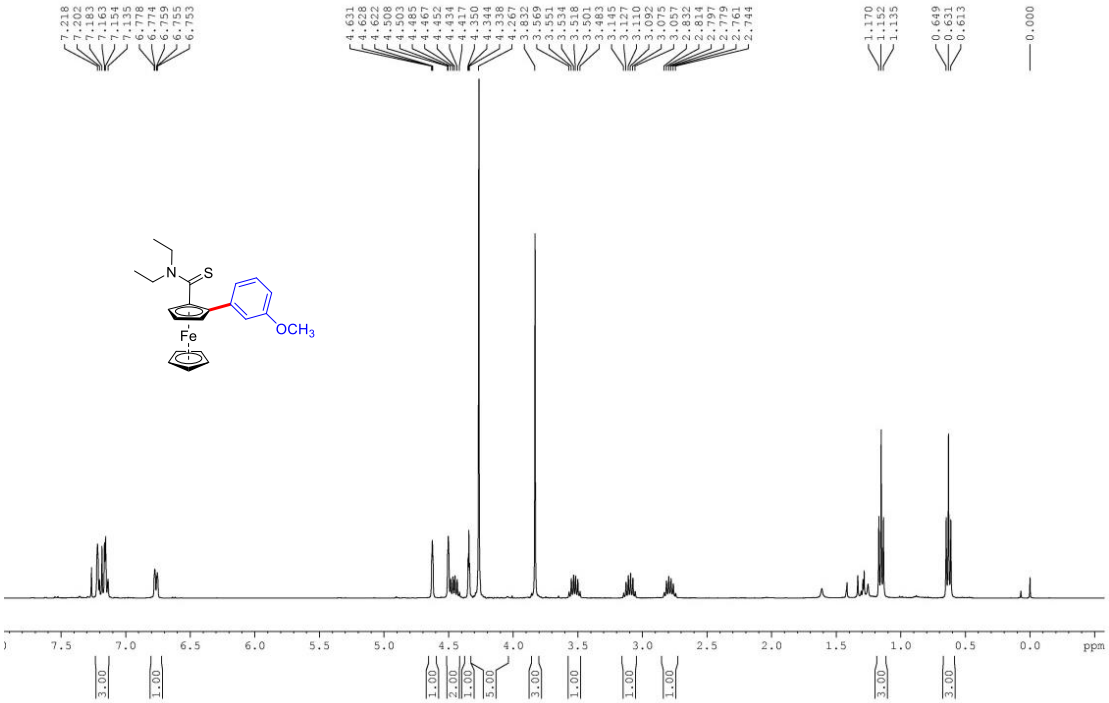
**3ma, $^{1}$H NMR, 400 MHz, $CDCl_3$**



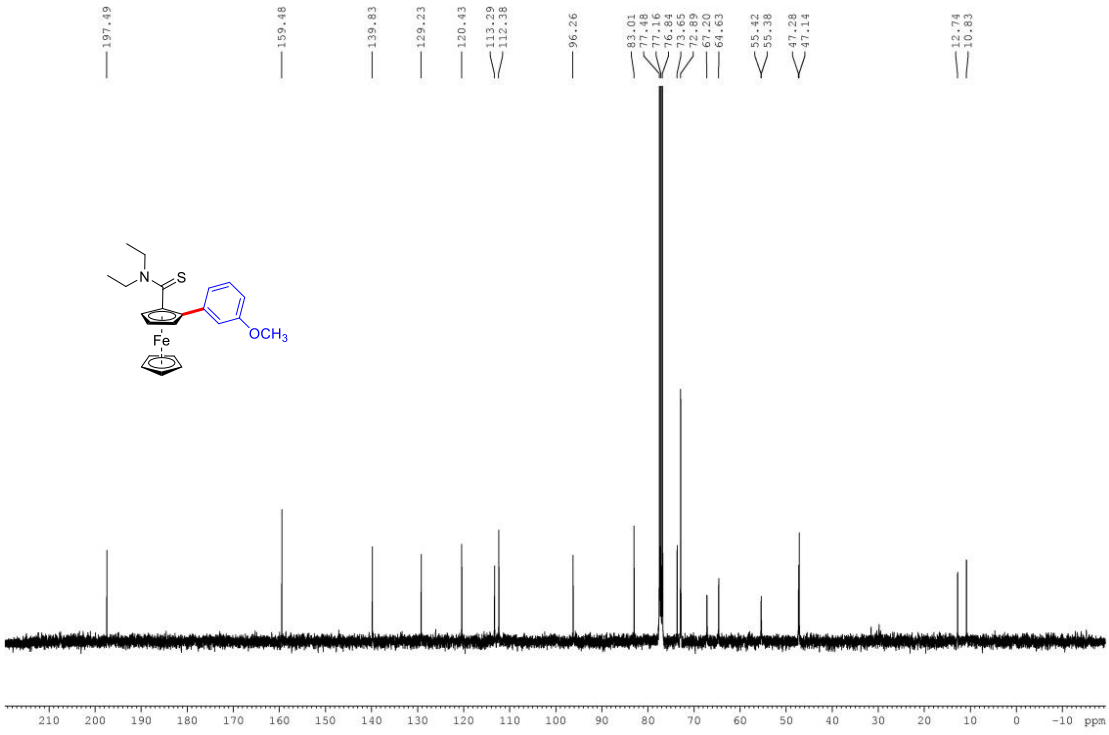

**3ma, $^{13}$C NMR, 101 MHz, $CDCl_3$**



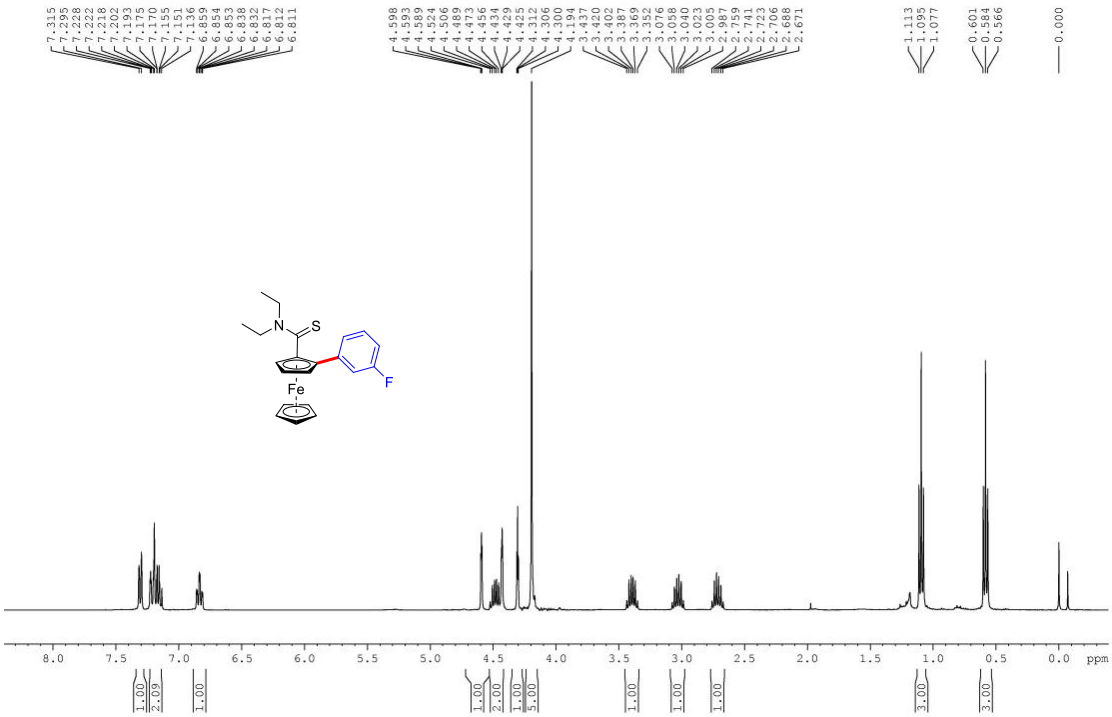
**3na, $^{1}$H NMR, 400 MHz, $CDCl_3$**




**3na, $^{13}$C NMR, 101 MHz, $CDCl_3$**



**3oa, $^{1}$H NMR, 400 MHz, $CDCl_3$**

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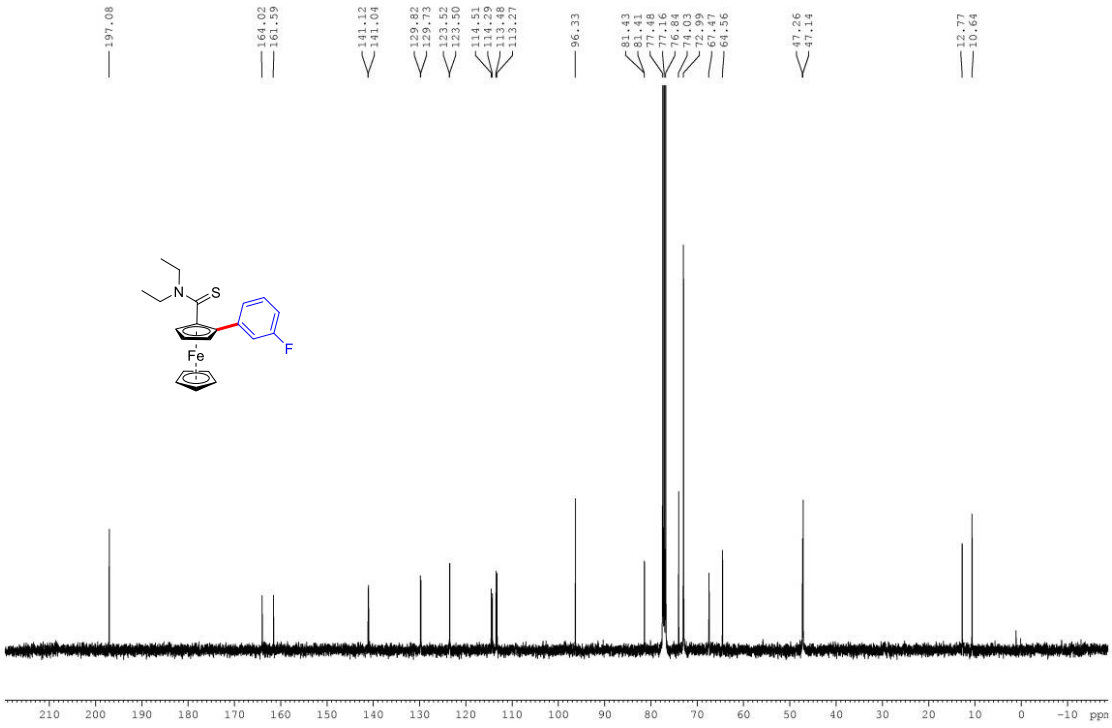
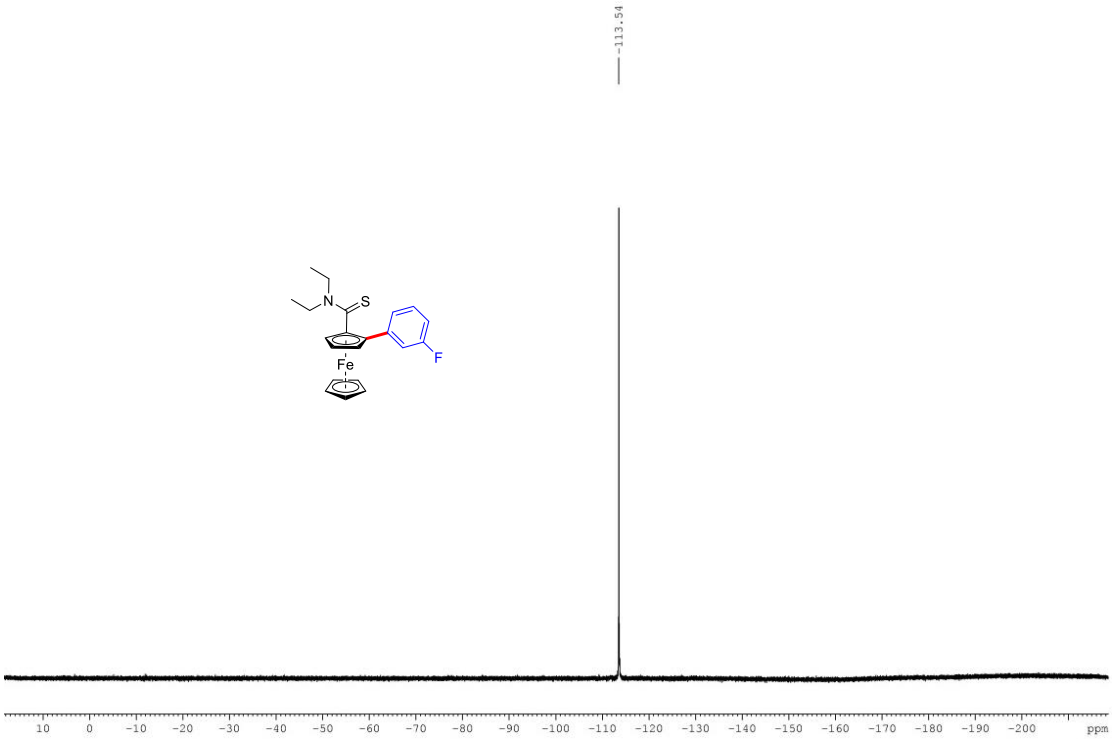
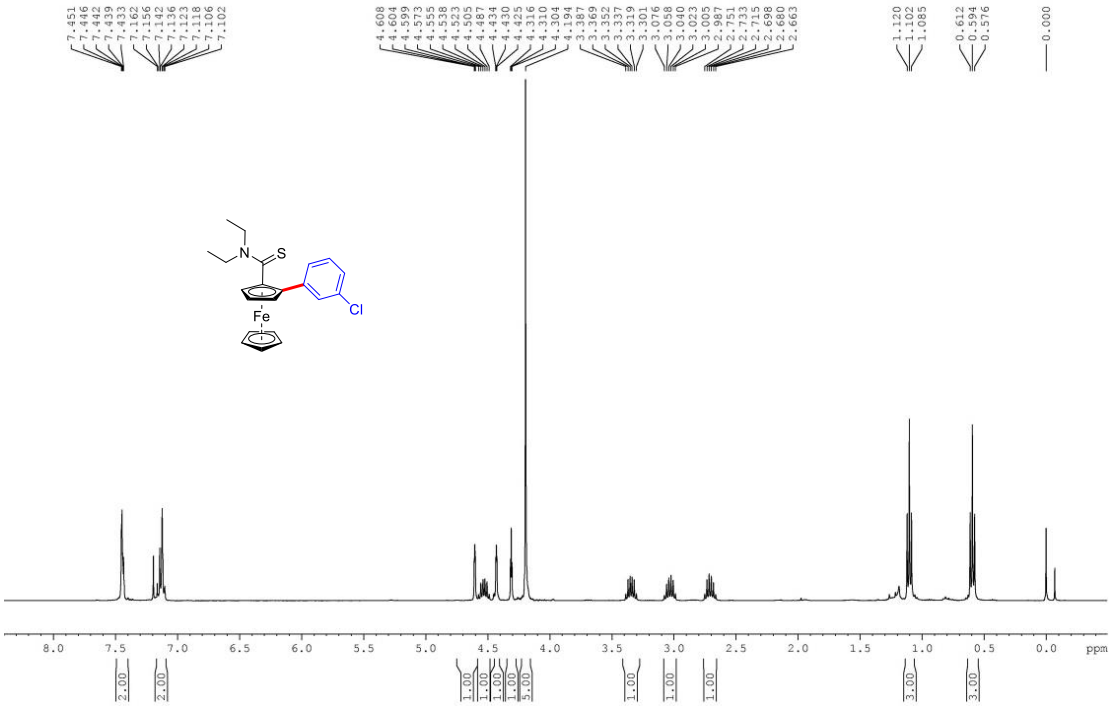


**3oa, $^{19}$F NMR, 376 MHz, $CDCl_3$**



**3pa, $^{1}$H NMR, 400 MHz, $CDCl_3$**

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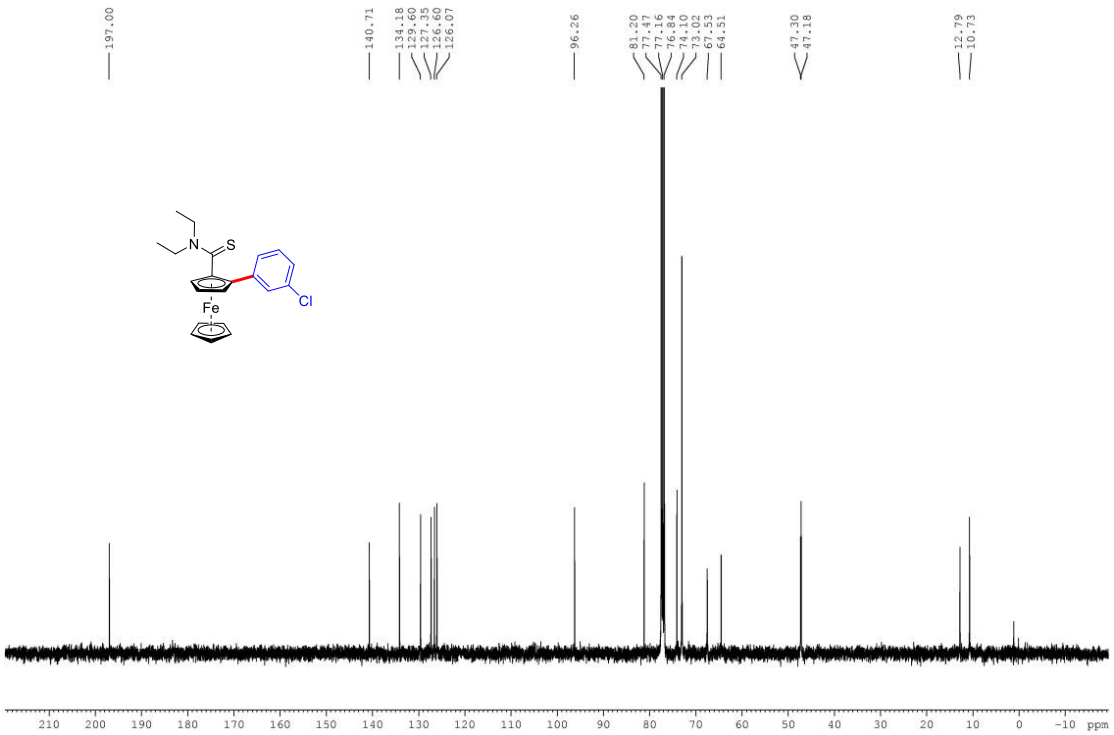
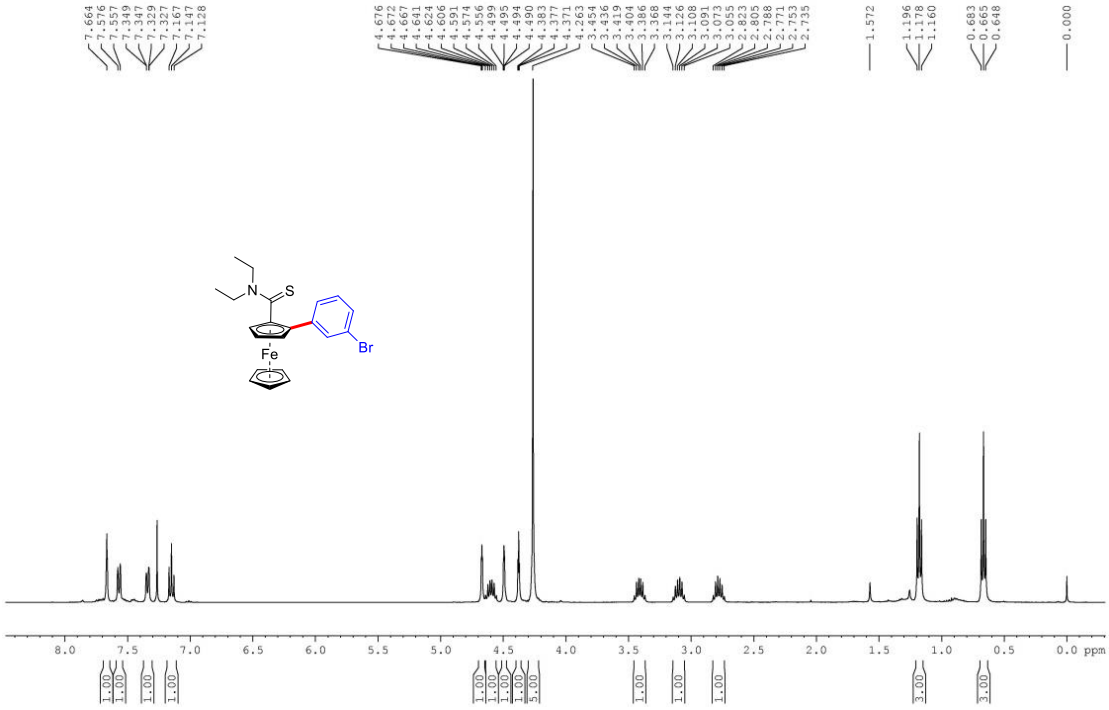
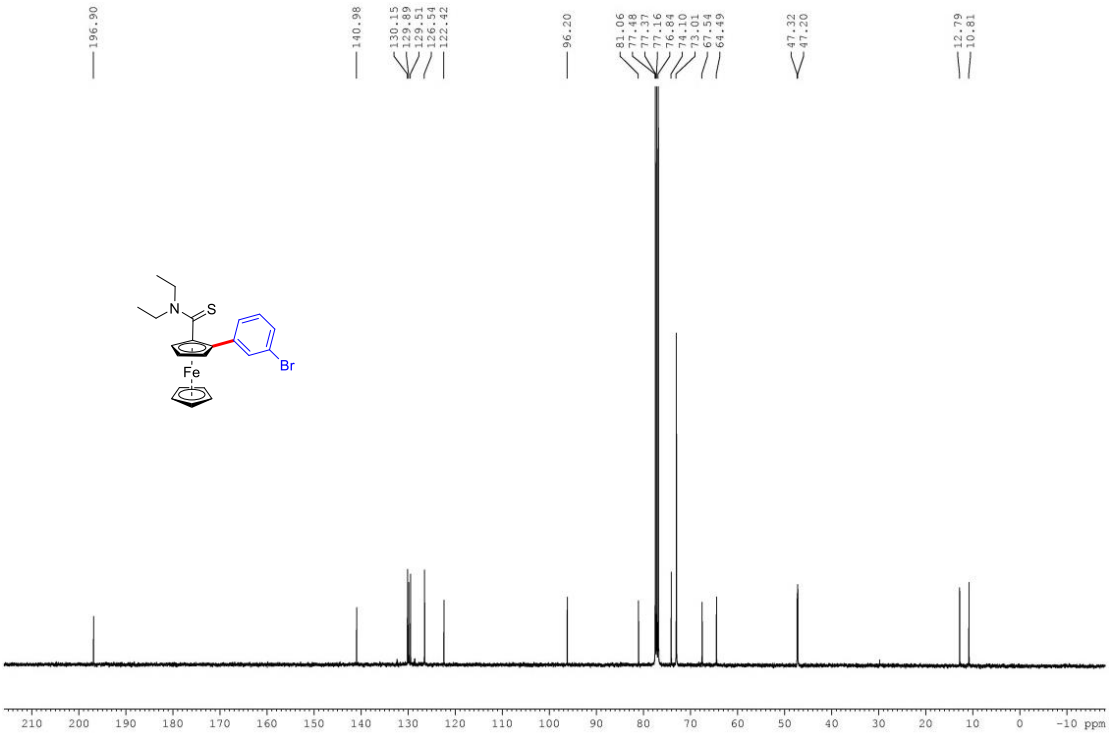


**3qa, $^{1}$H NMR, 400 MHz, $CDCl_3$**




**3qa, $^{13}$C NMR, 101 MHz, $CDCl_3$**



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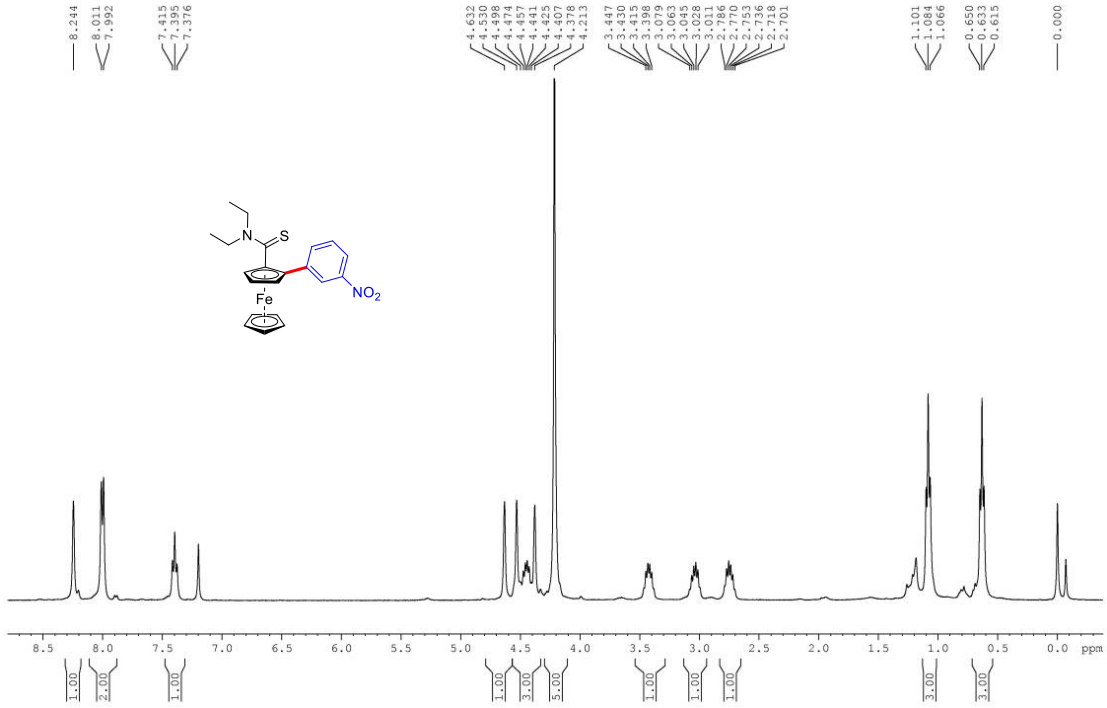


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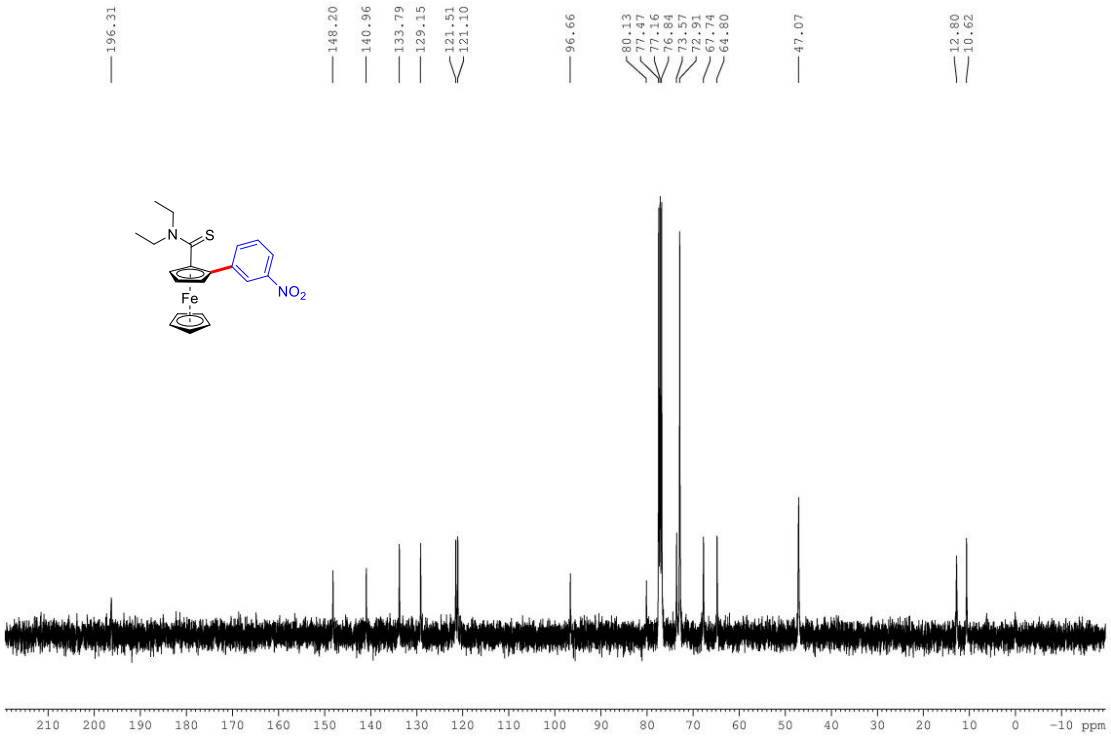

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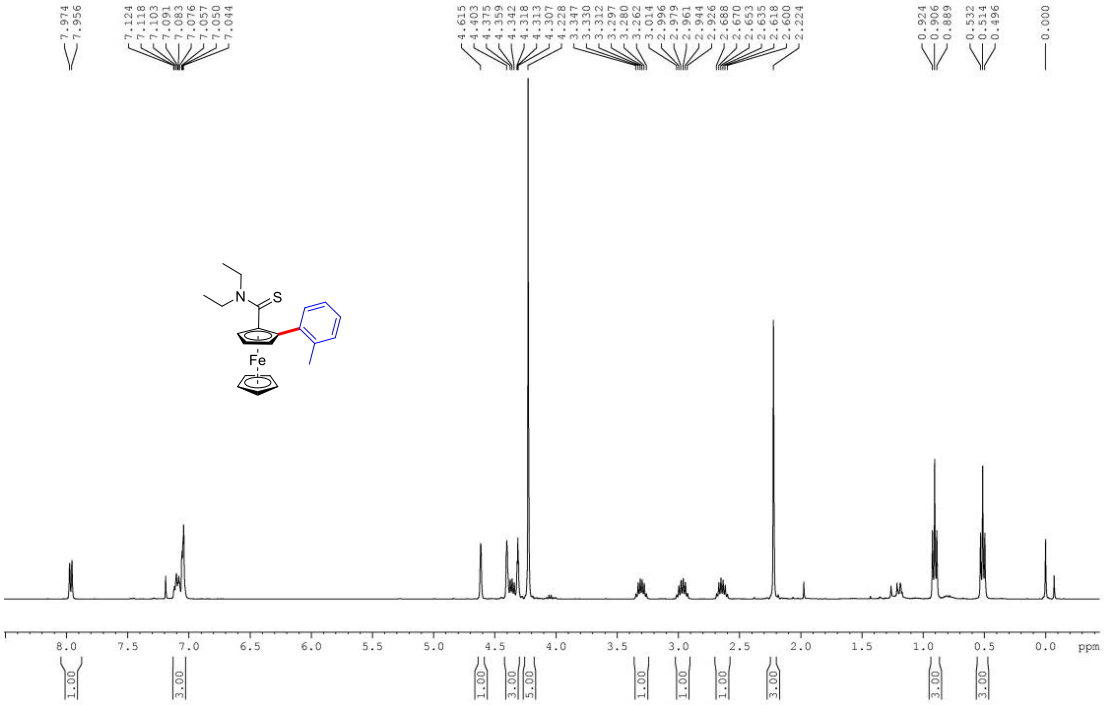
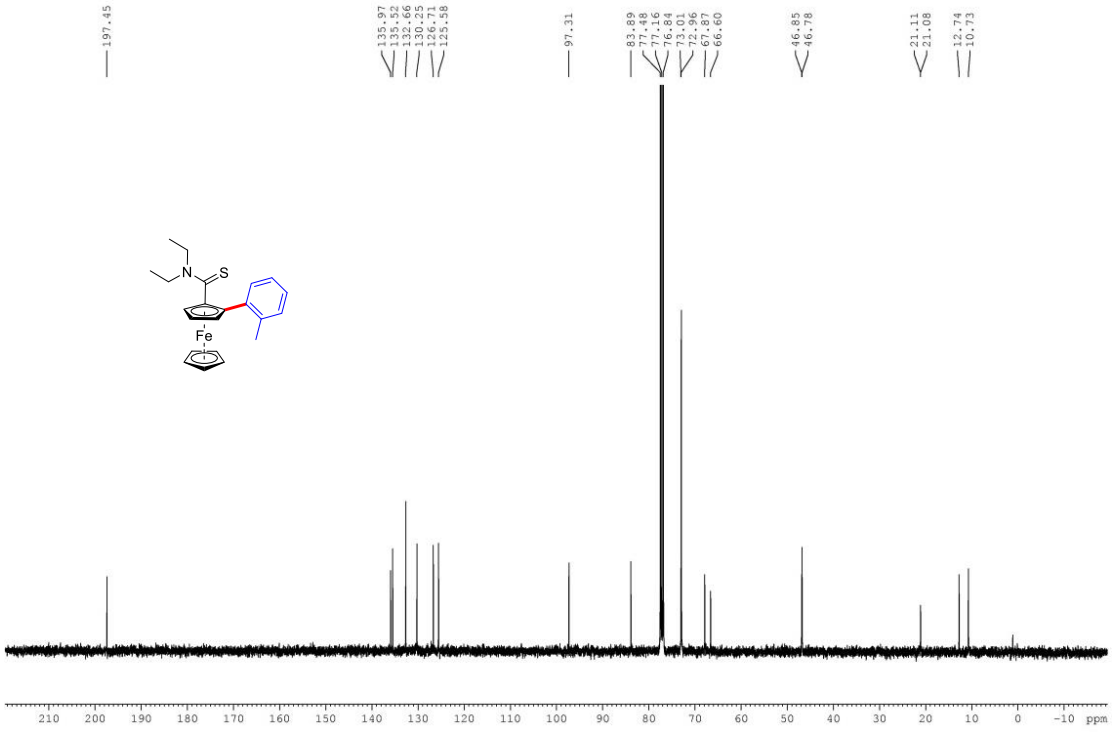
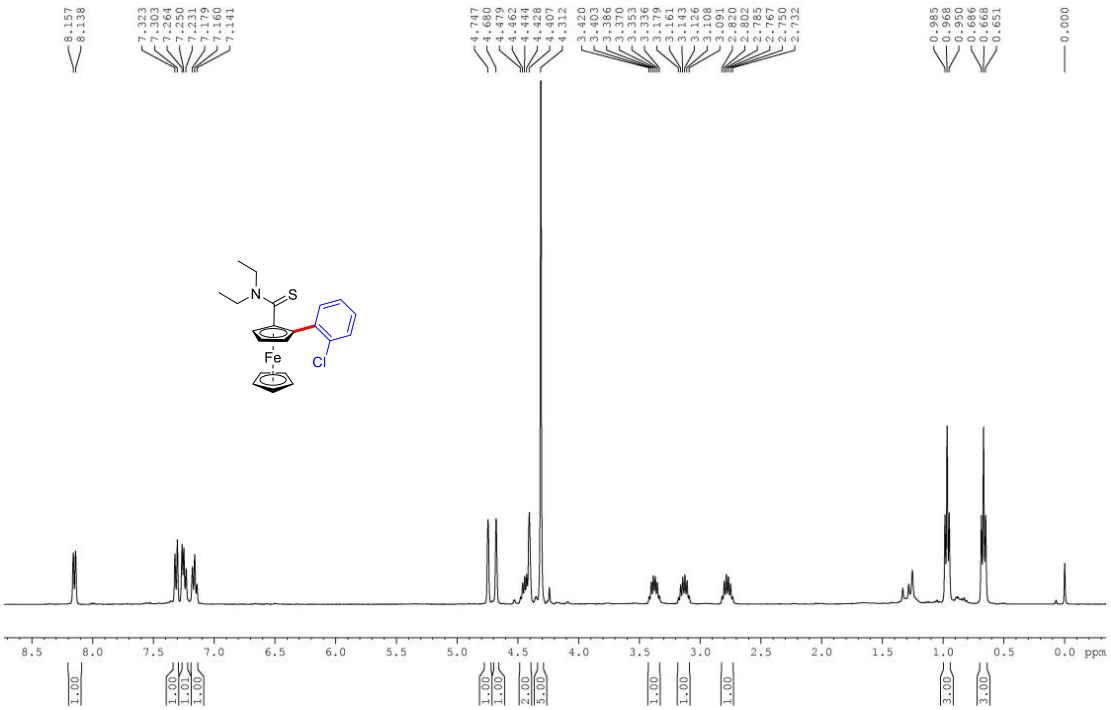



**3sa, $^{13}$C NMR, 101 MHz, $CDCl_3$**



**3ta, $^{1}$H NMR, 400 MHz, $CDCl_3$**

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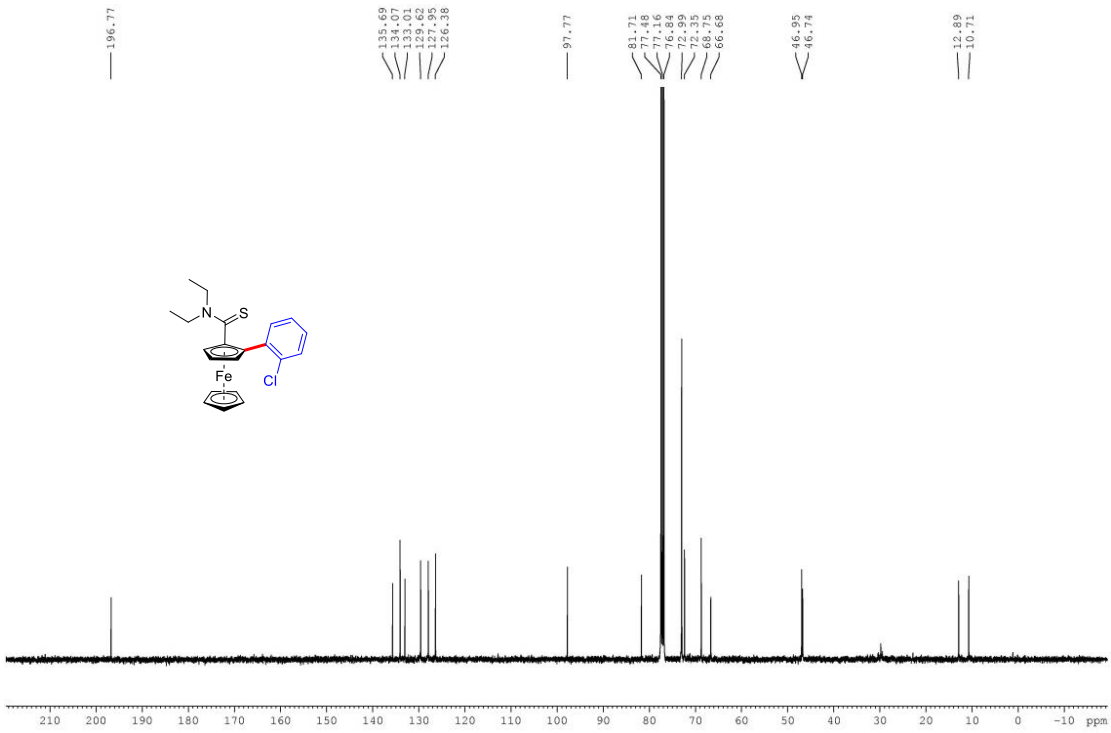

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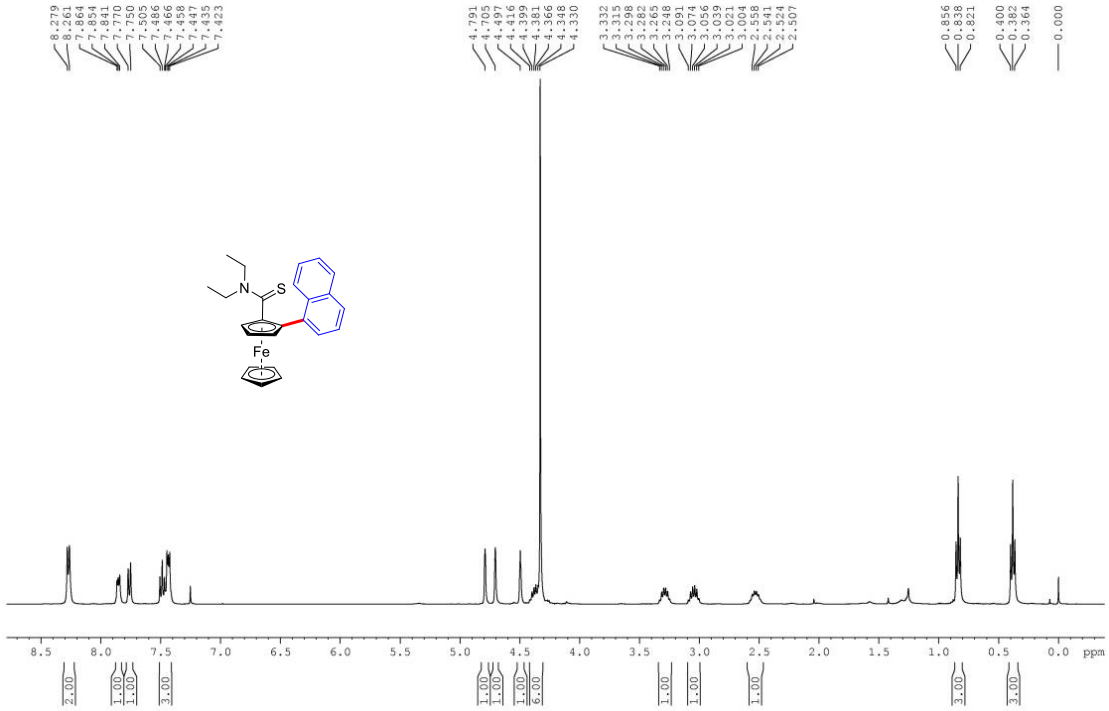


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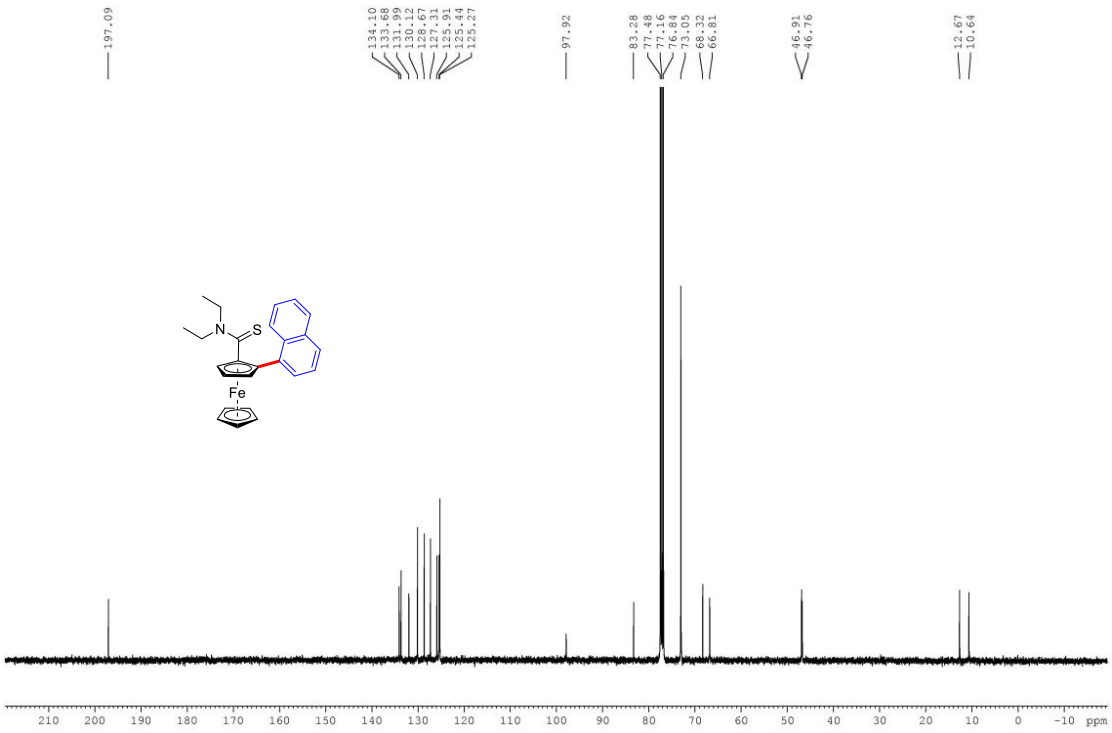

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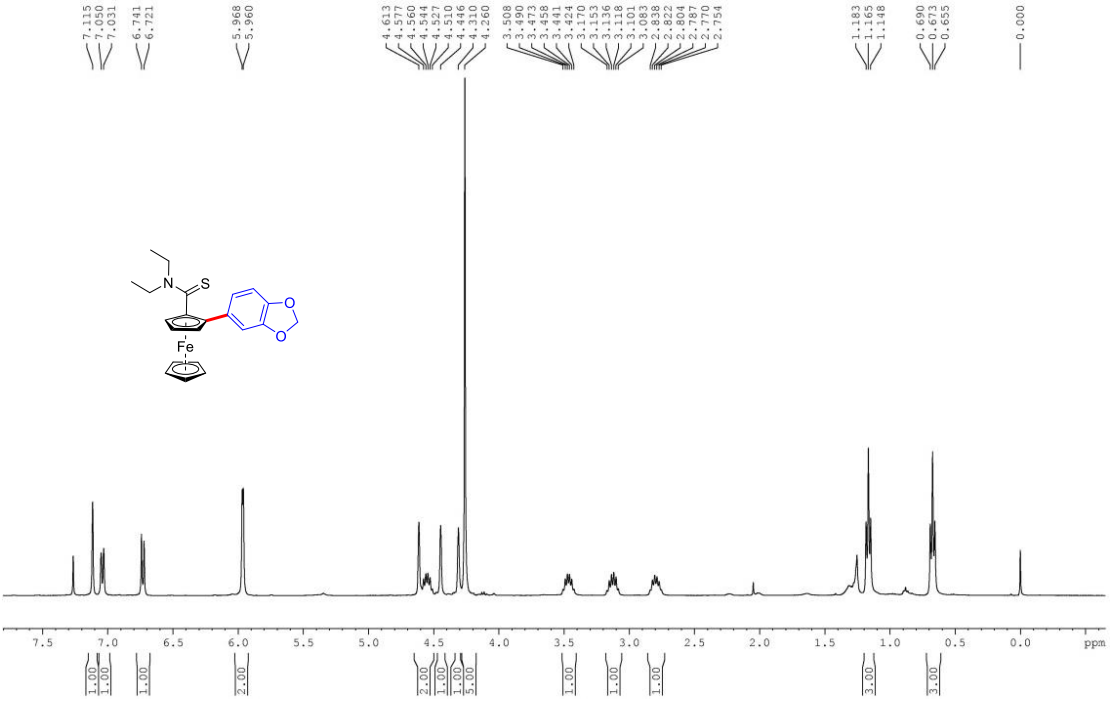
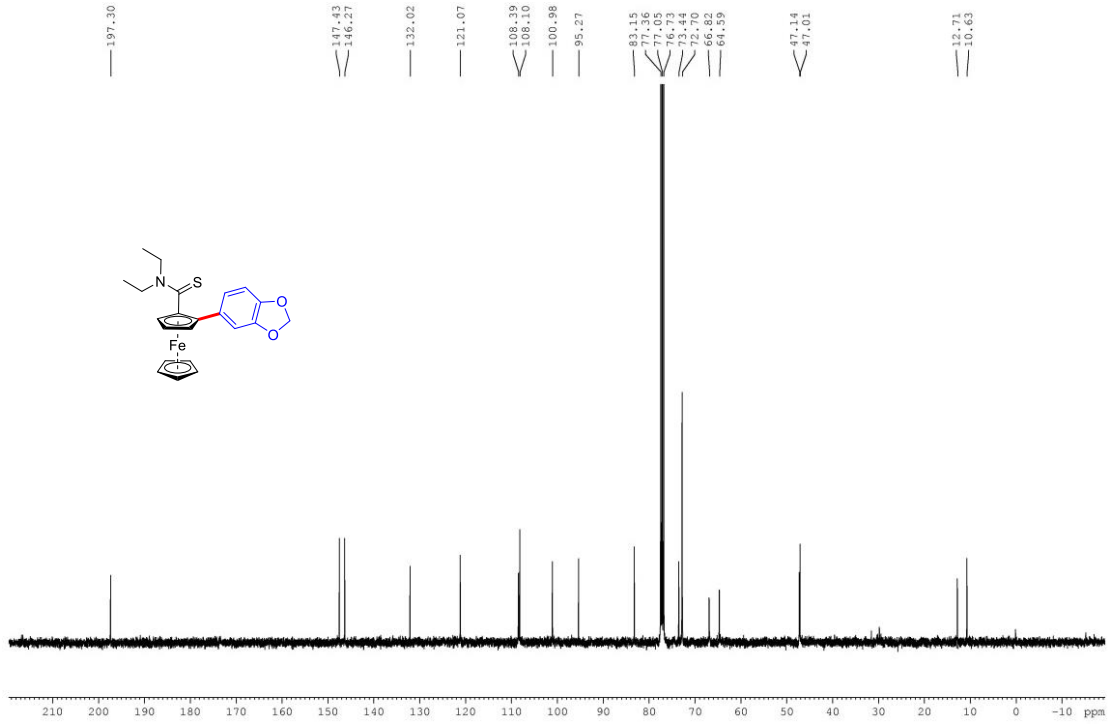



**3va, $^{13}$C NMR, 101 MHz, $CDCl_3$**



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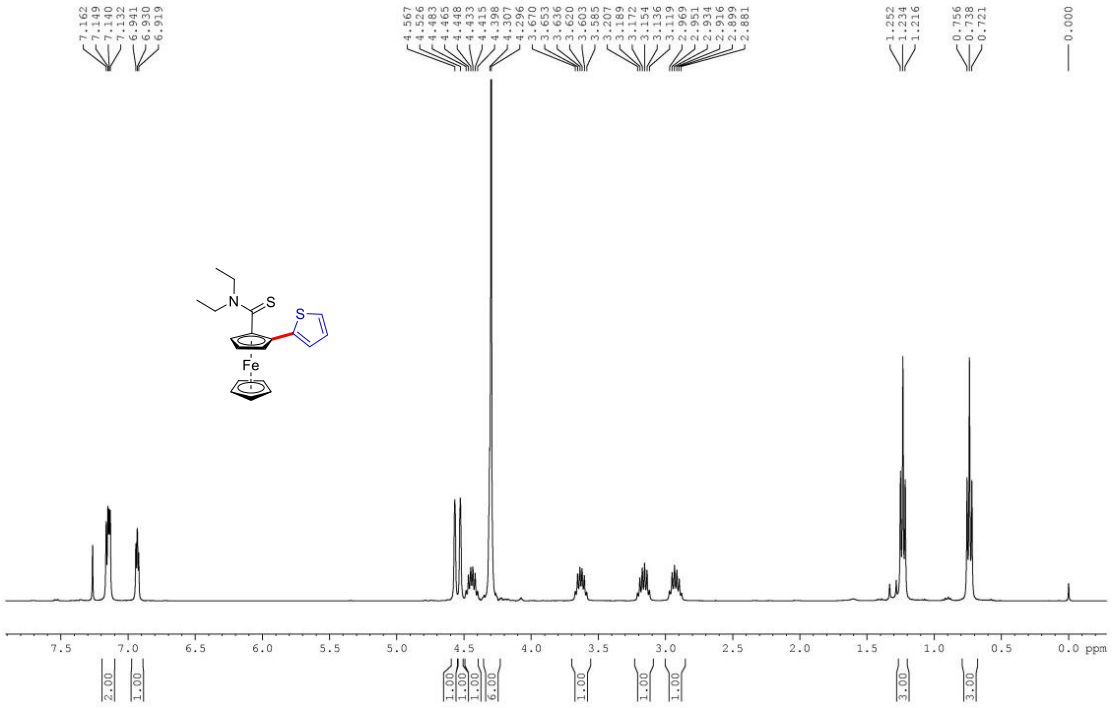
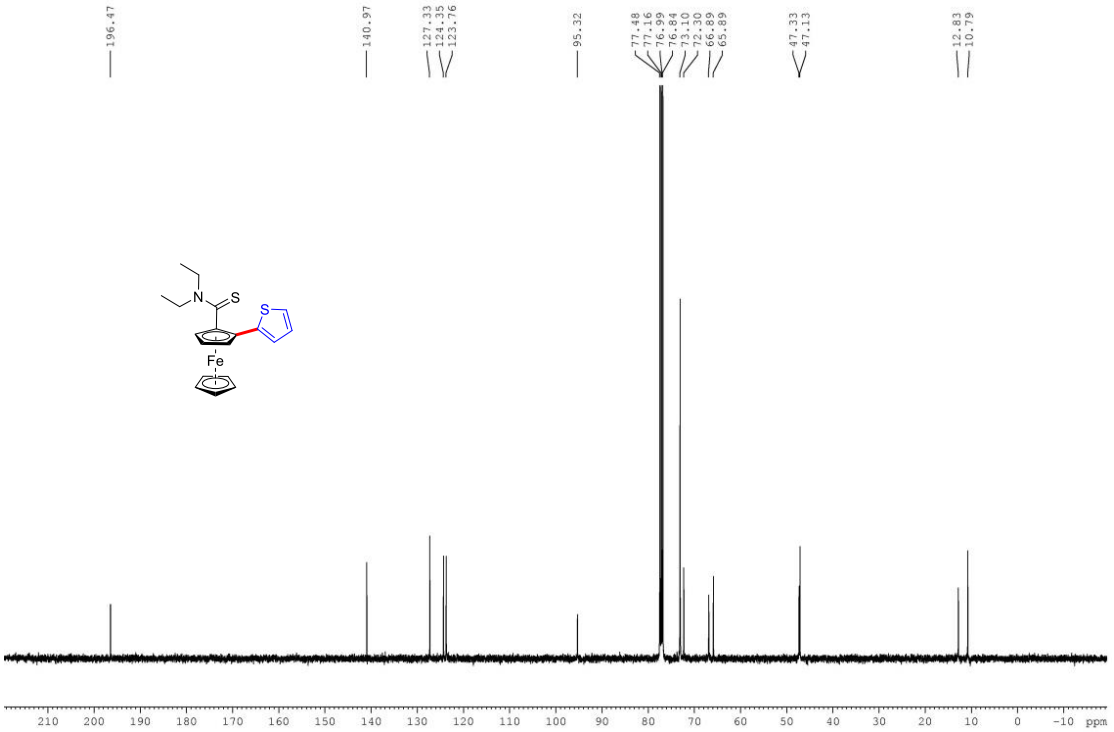
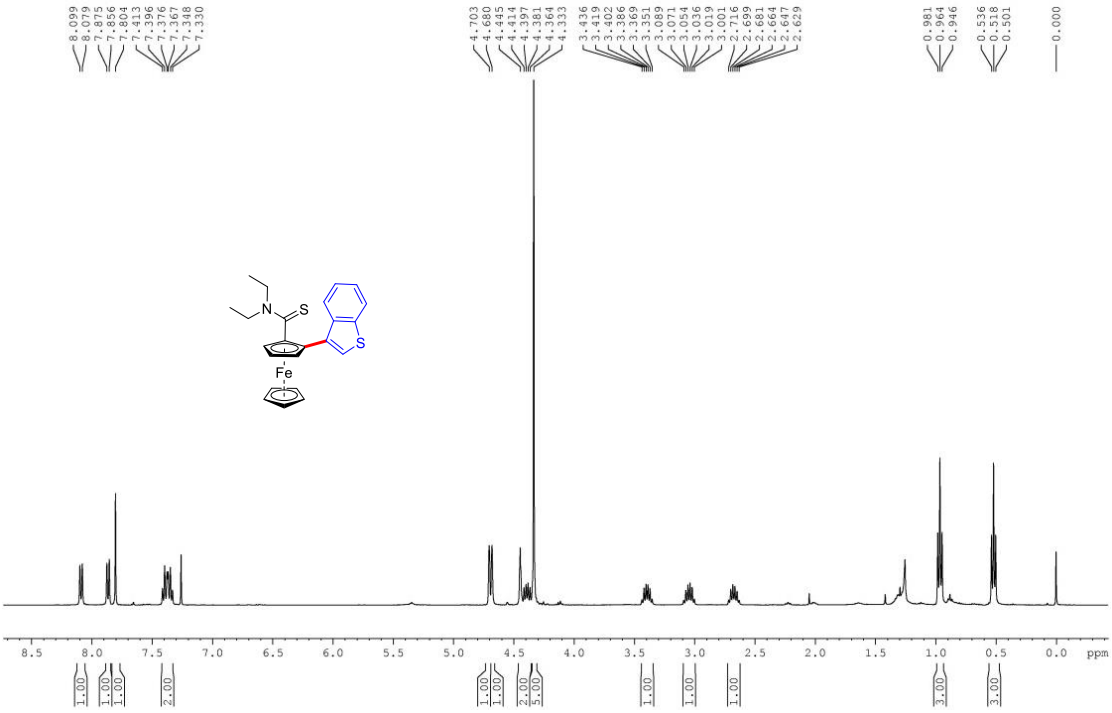


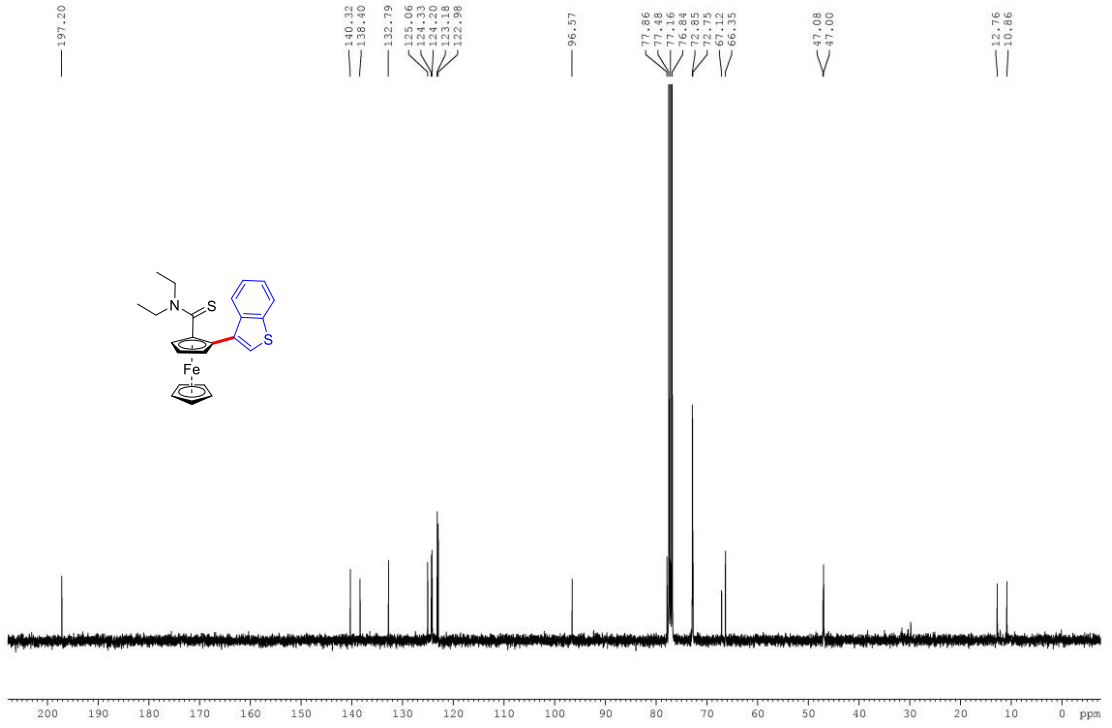

**3wa, $^{13}$C NMR, 101 MHz, $CDCl_3$**



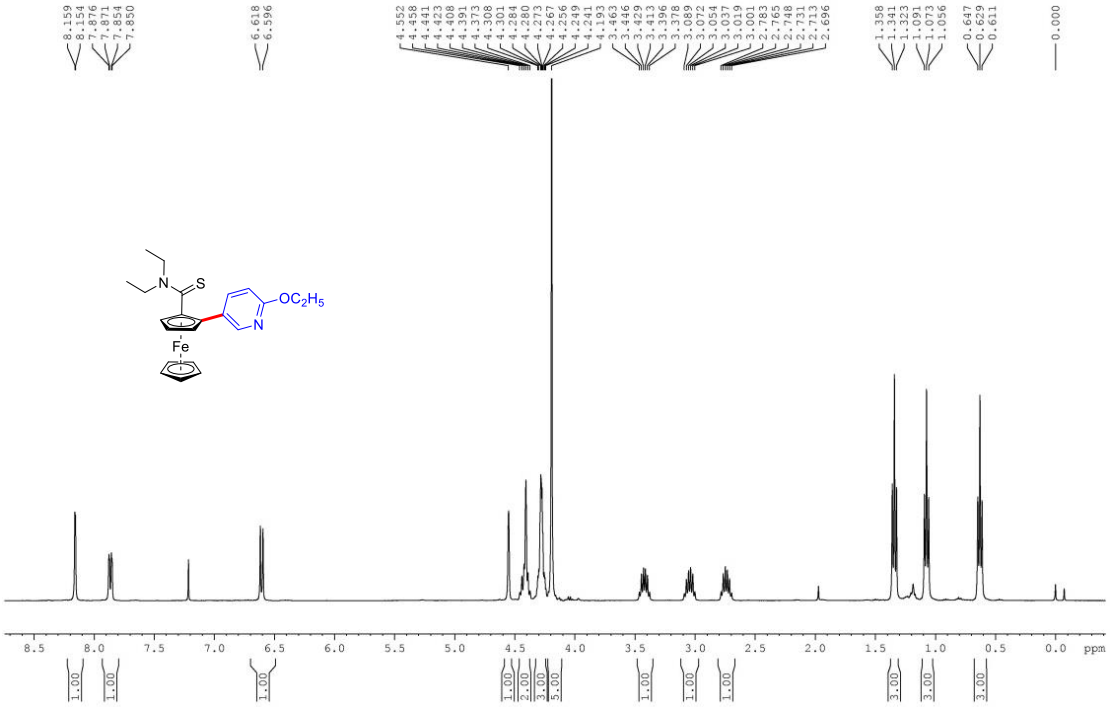
**3xa, $^{1}$H NMR, 400 MHz, $CDCl_3$**



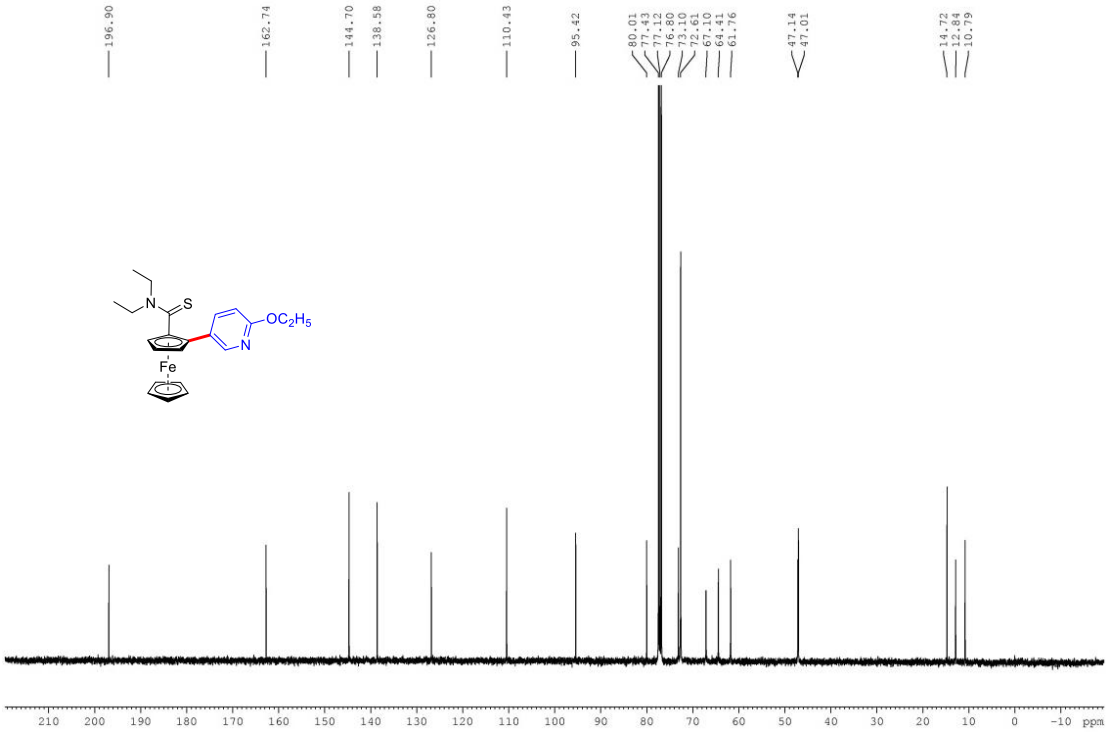

**3xa, $^{13}$C NMR, 101 MHz, $CDCl_3$**



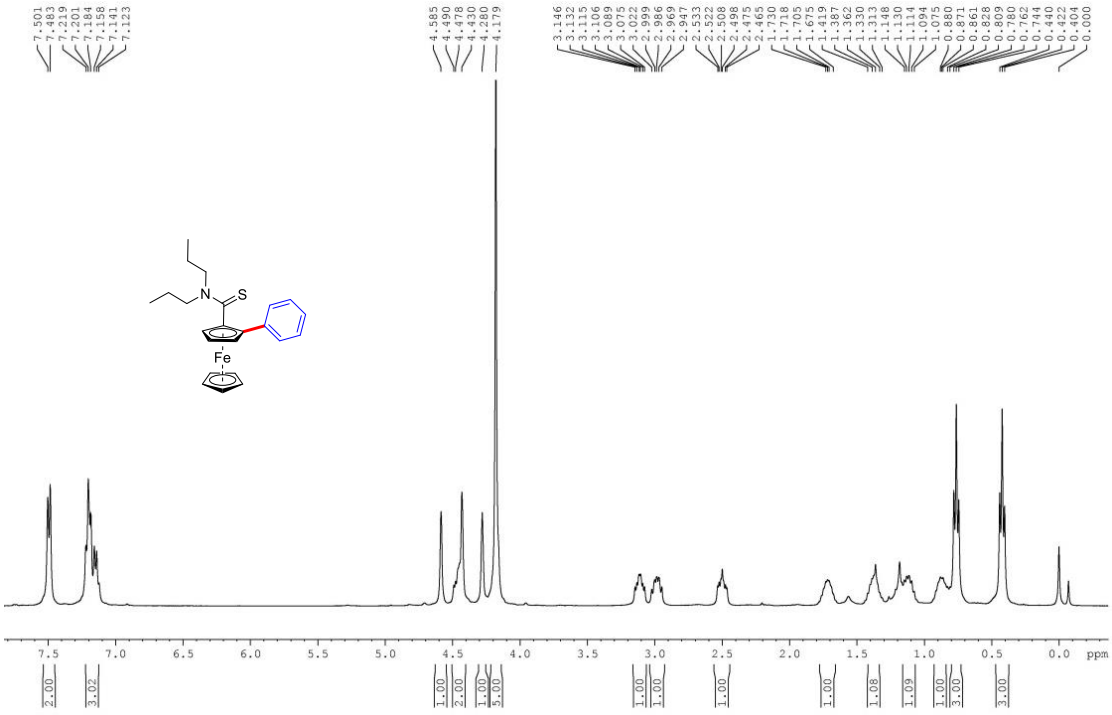
**3ya, $^{1}$H NMR, 400 MHz, $CDCl_3$**



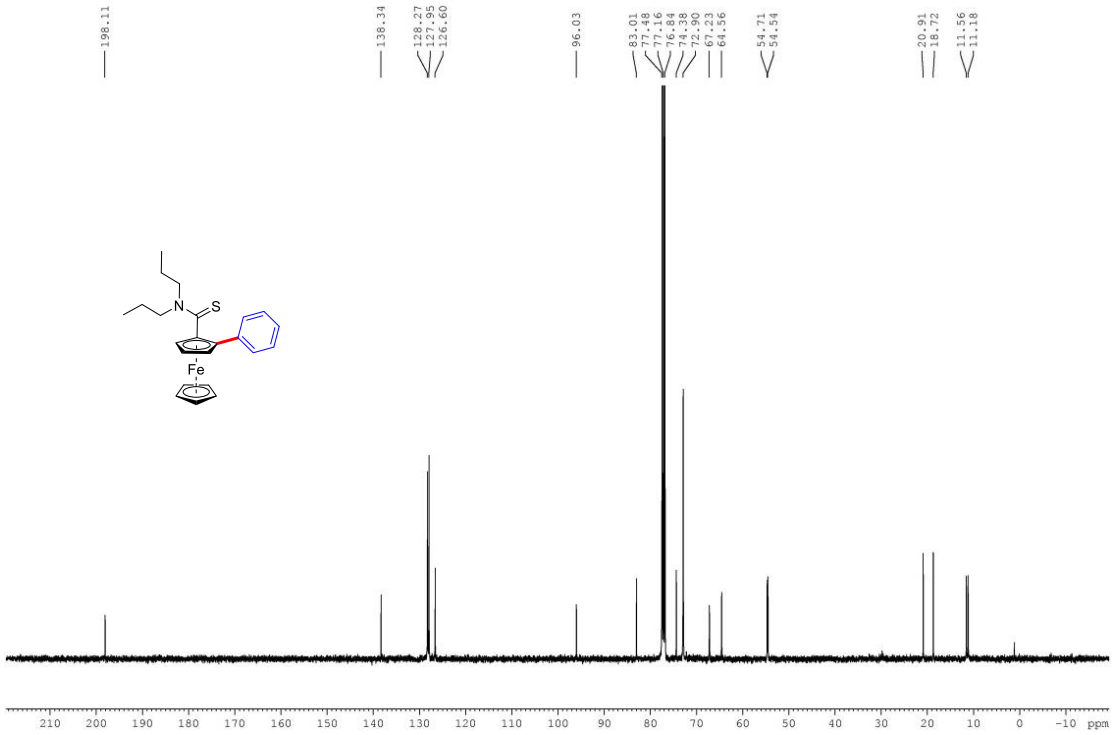

**3ya, $^{13}$C NMR, 101 MHz, $CDCl_3$**



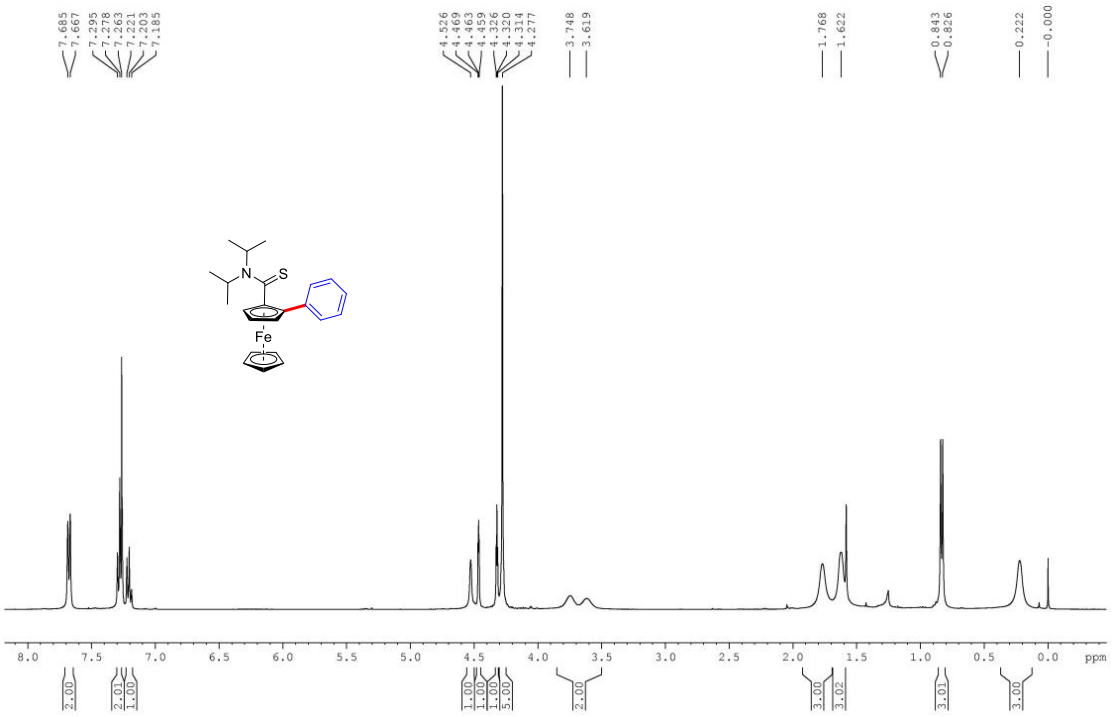
**3ab, $^{1}$H NMR, 400 MHz, $CDCl_3$**



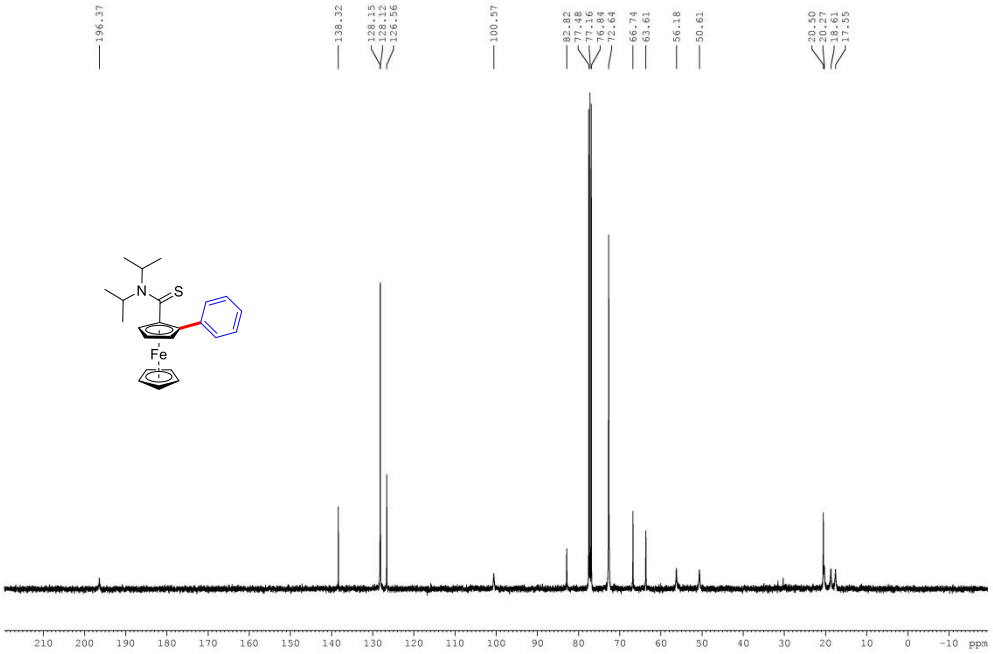

**3ab, $^{13}$C NMR, 101 MHz, $CDCl_3$**



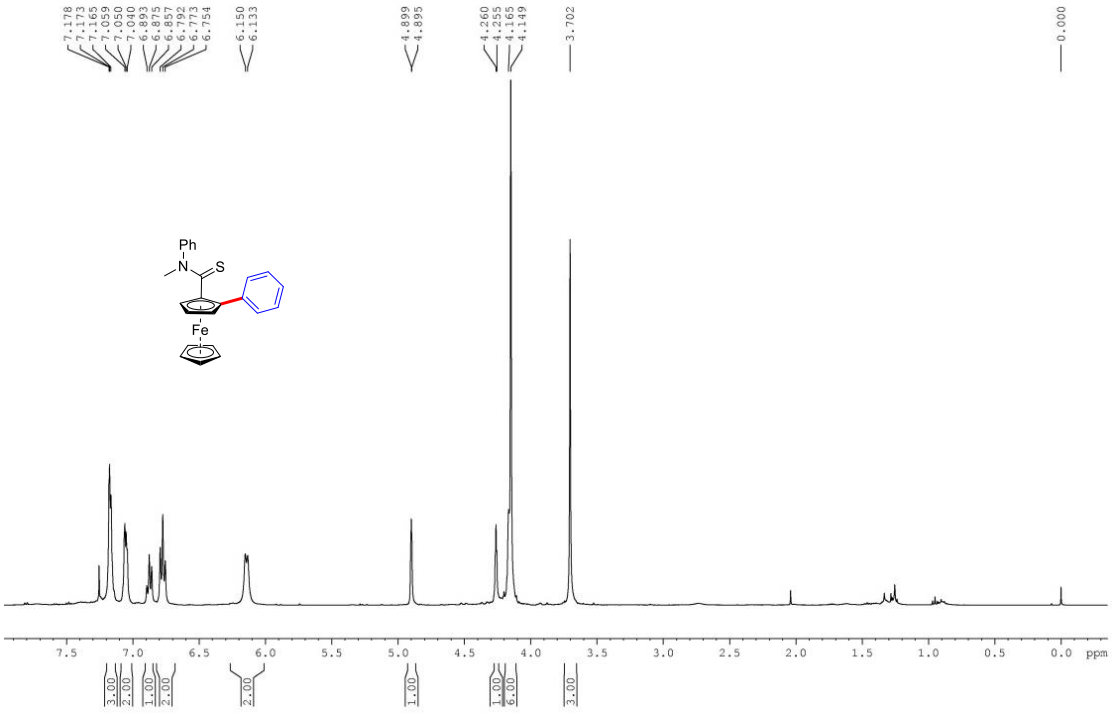
**3ac, $^{1}$H NMR, 400 MHz, $CDCl_3$**



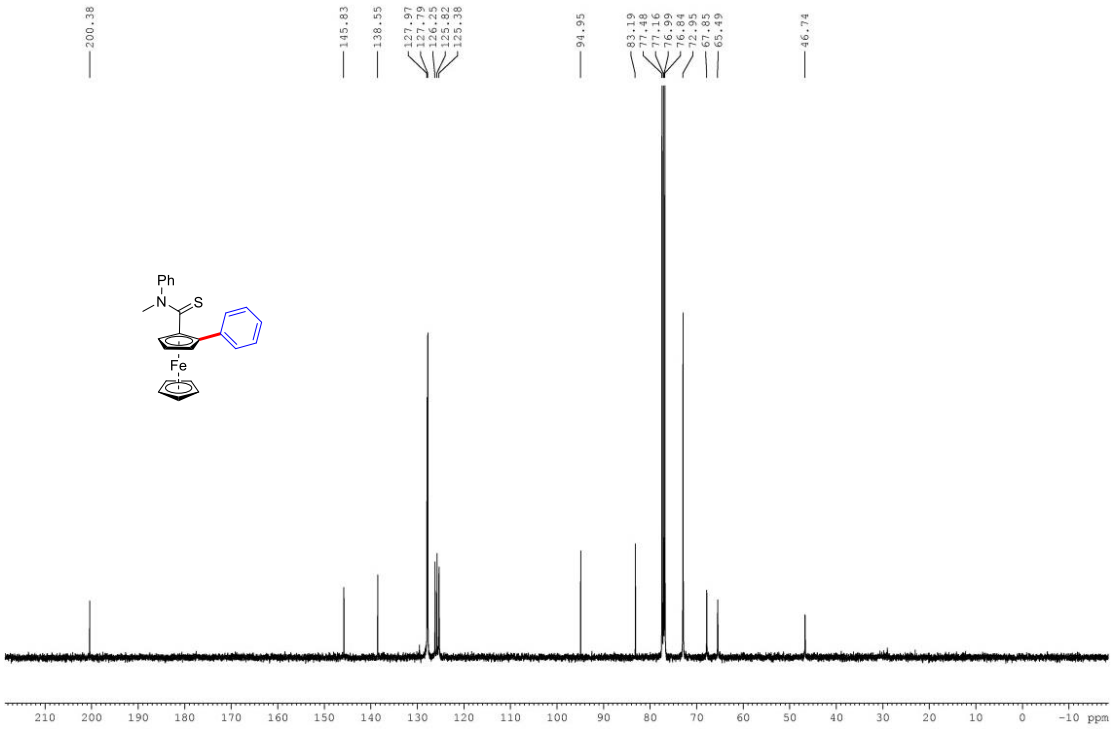

**3ac, $^{13}$C NMR, 101 MHz, $CDCl_3$**



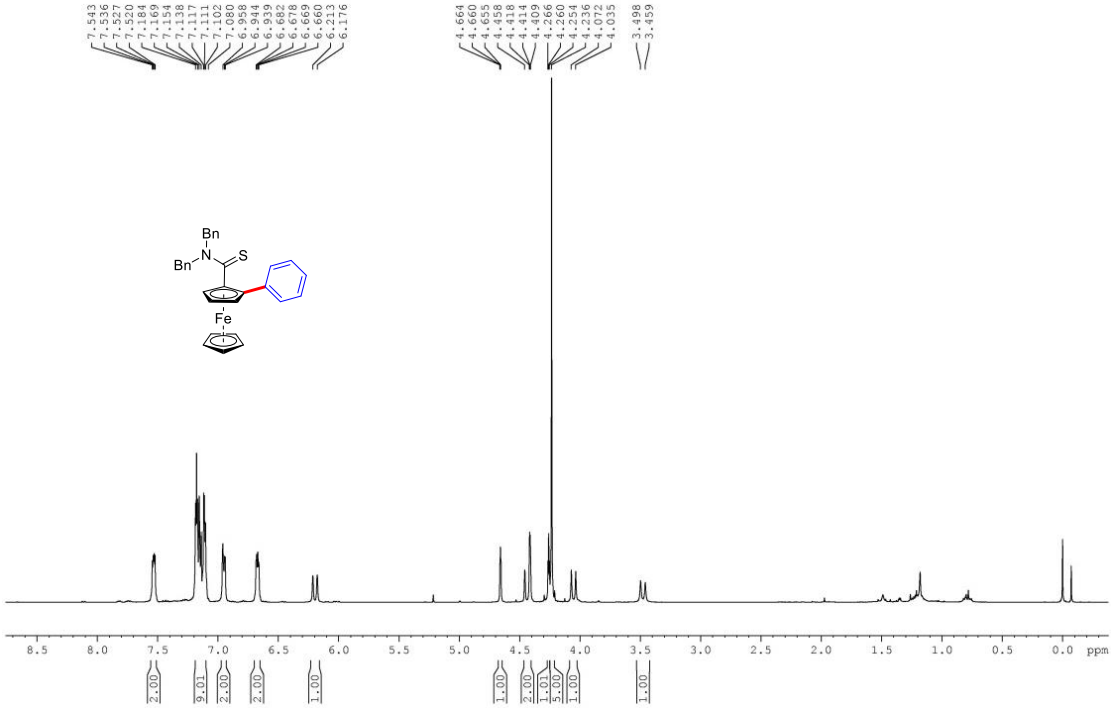
**3ad, $^{1}$H NMR, 400 MHz, $CDCl_3$**



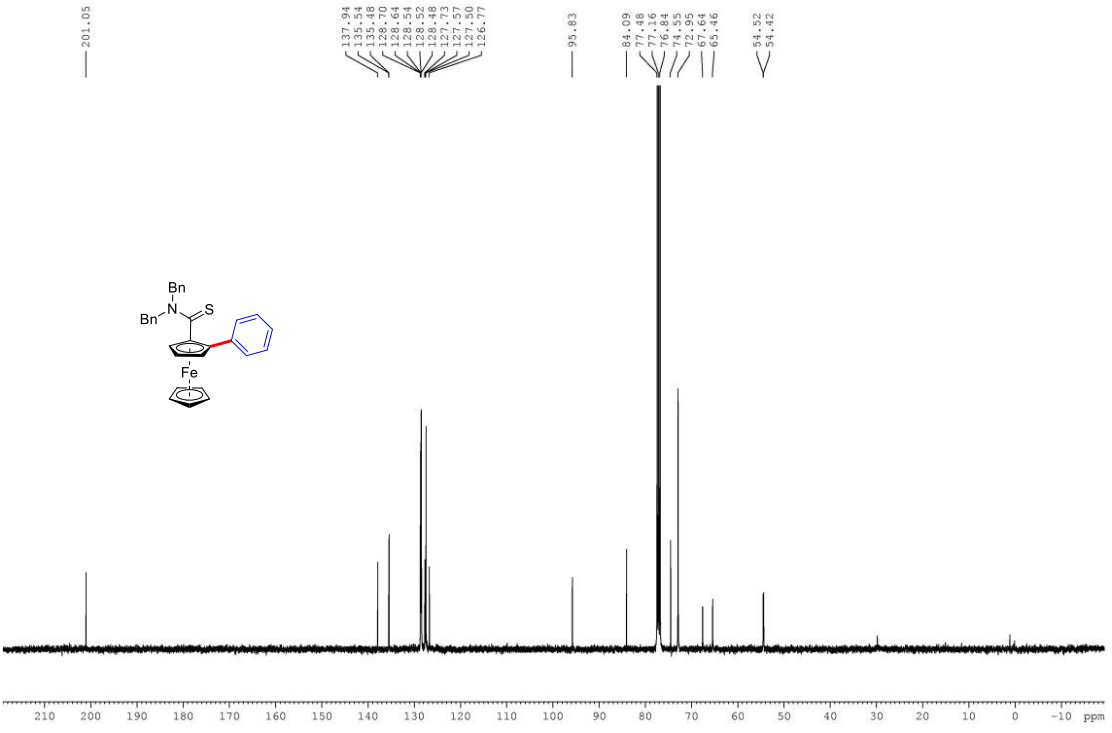

**3ad, $^{13}$C NMR, 101 MHz, $CDCl_3$**



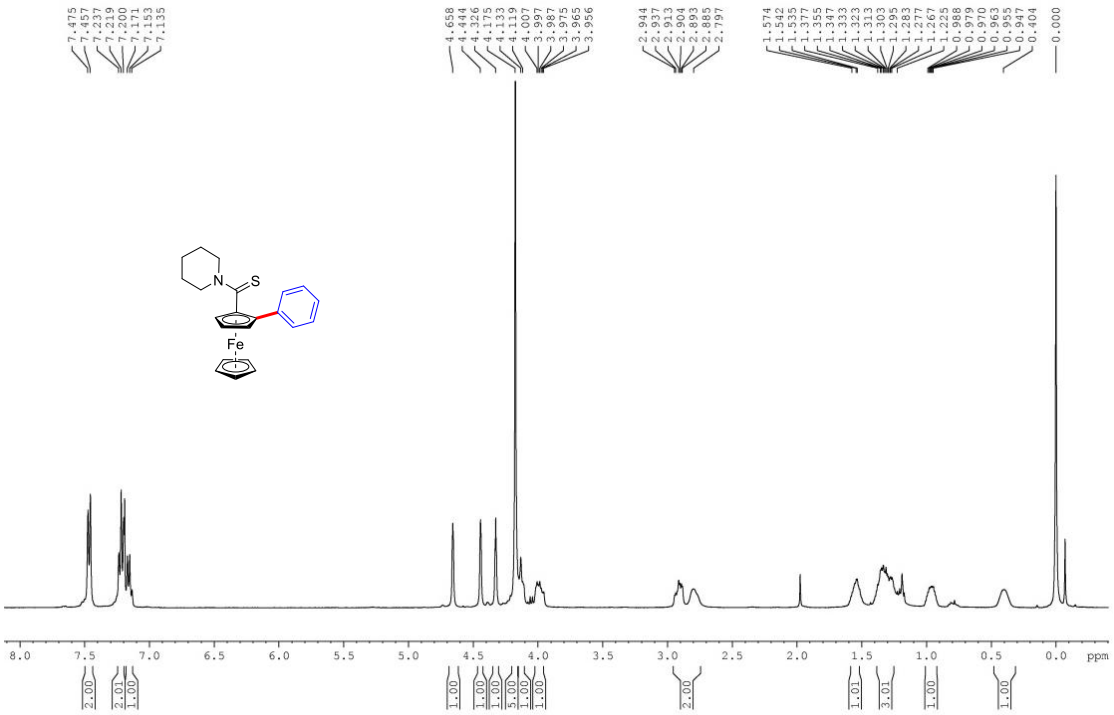
**3ae, $^{1}$H NMR, 400 MHz, $CDCl_3$**



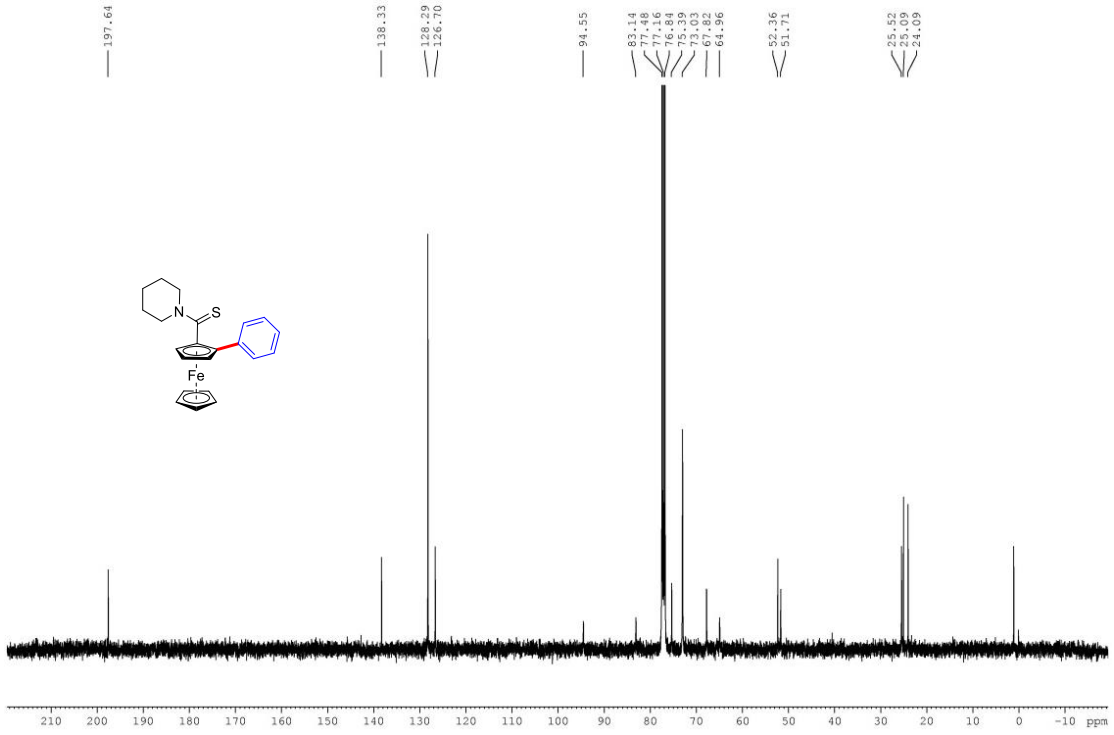

**3ae, $^{13}$C NMR, 101 MHz, $CDCl_3$**



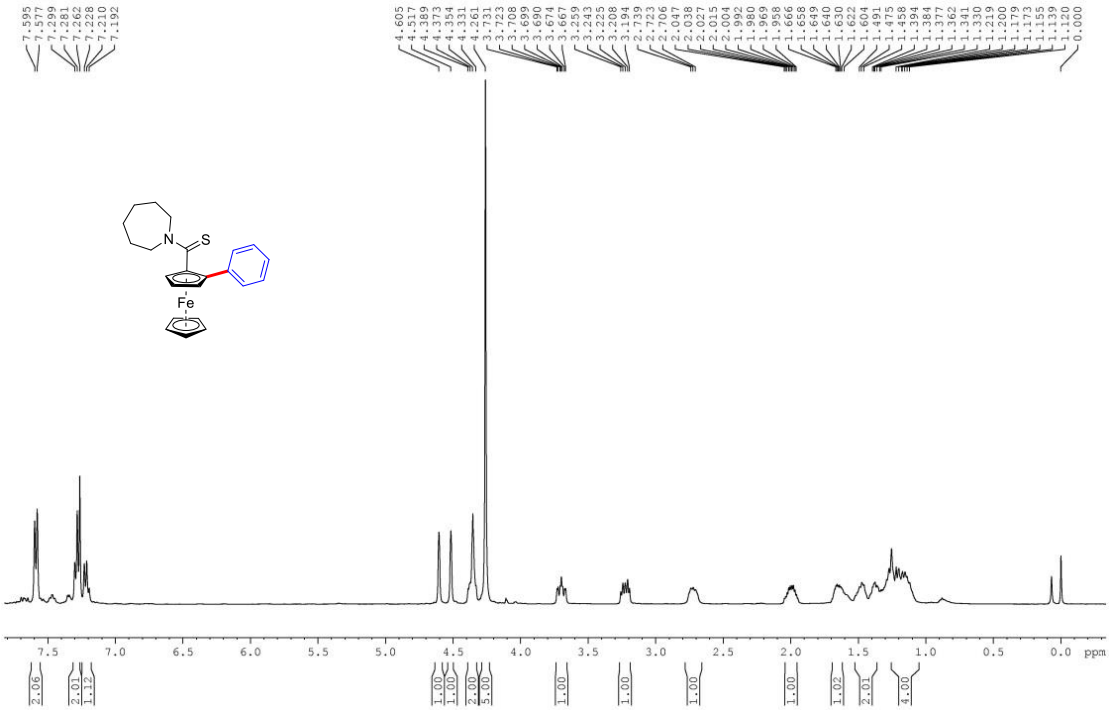
**3af, $^{1}$H NMR, 400 MHz, $CDCl_3$**



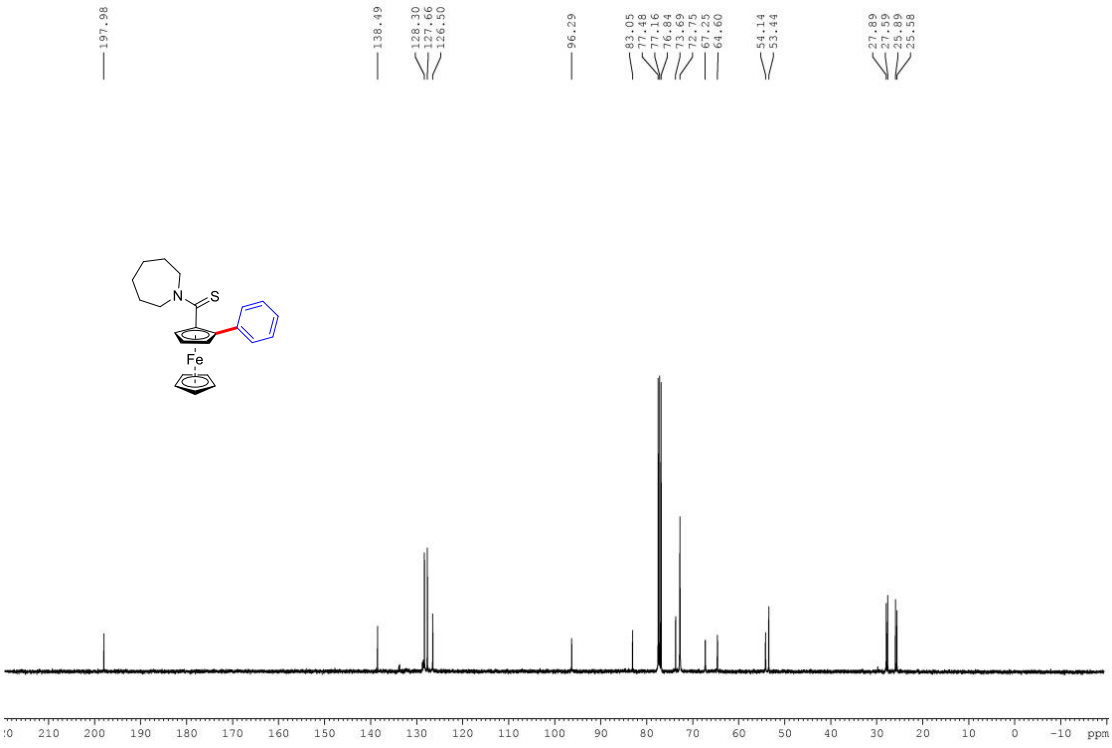

**3af, $^{13}$C NMR, 101 MHz, $CDCl_3$**



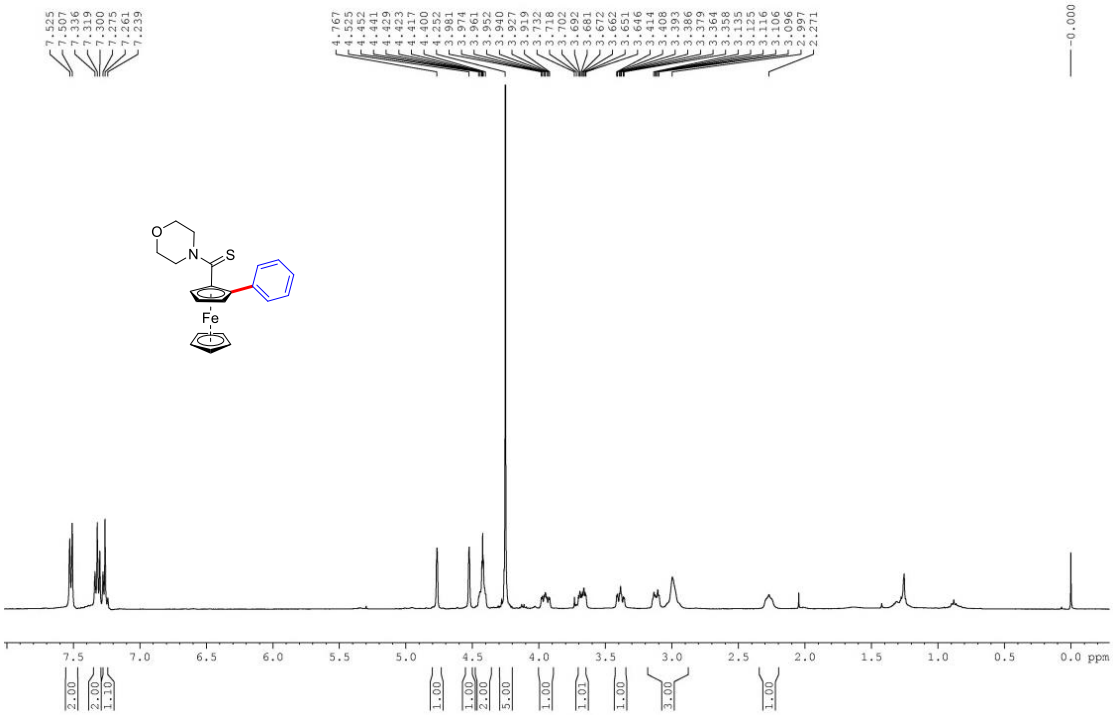
**3ag, $^{1}$H NMR, 400 MHz, $CDCl_3$**



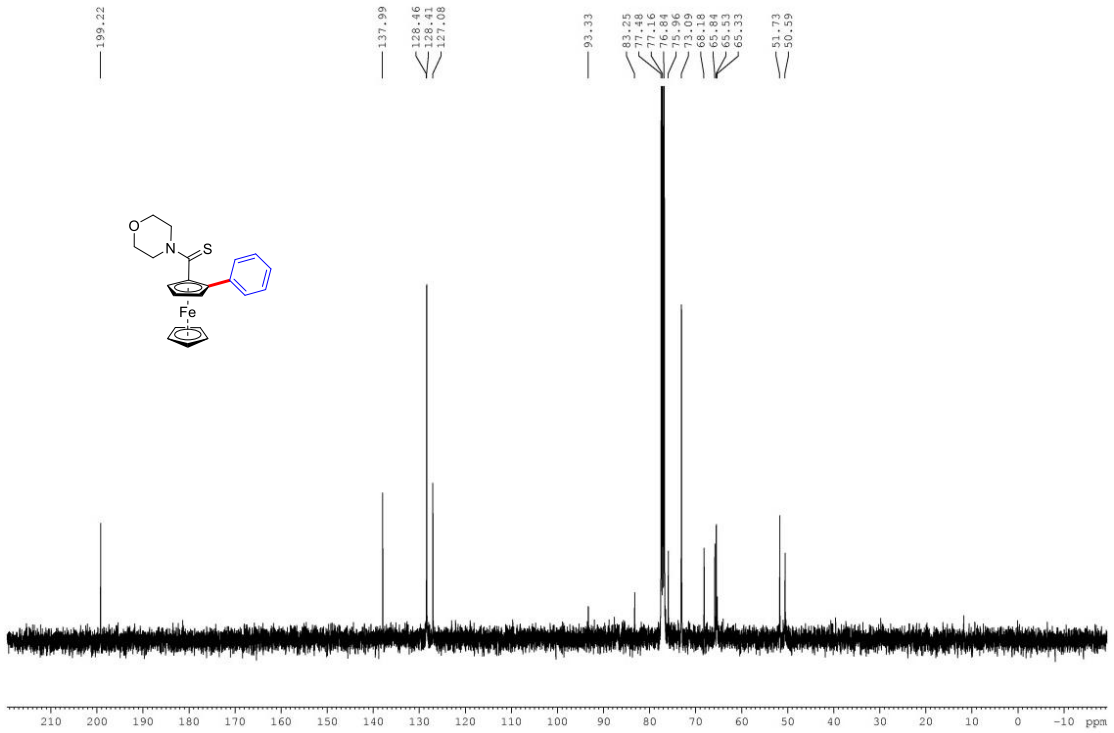

**3ag, $^{13}$C NMR, 101 MHz, $CDCl_3$**



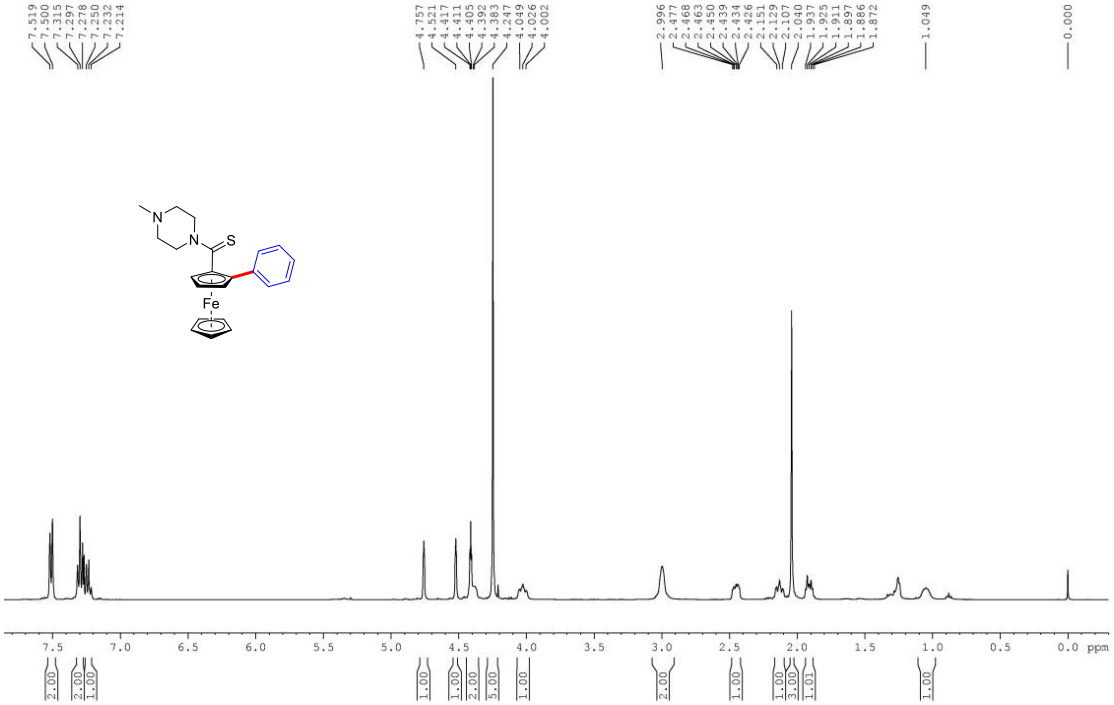
**3ah, $^{1}$H NMR, 400 MHz, $CDCl_3$**



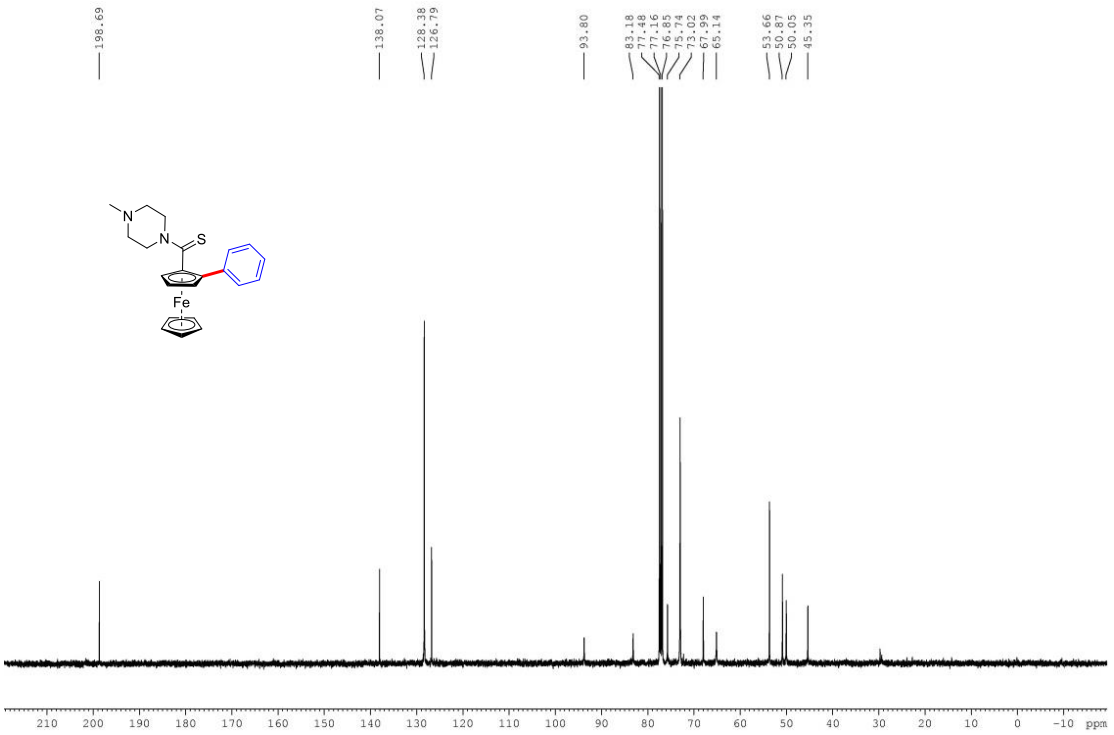

**3ah, $^{13}$C NMR, 101 MHz, $CDCl_3$**



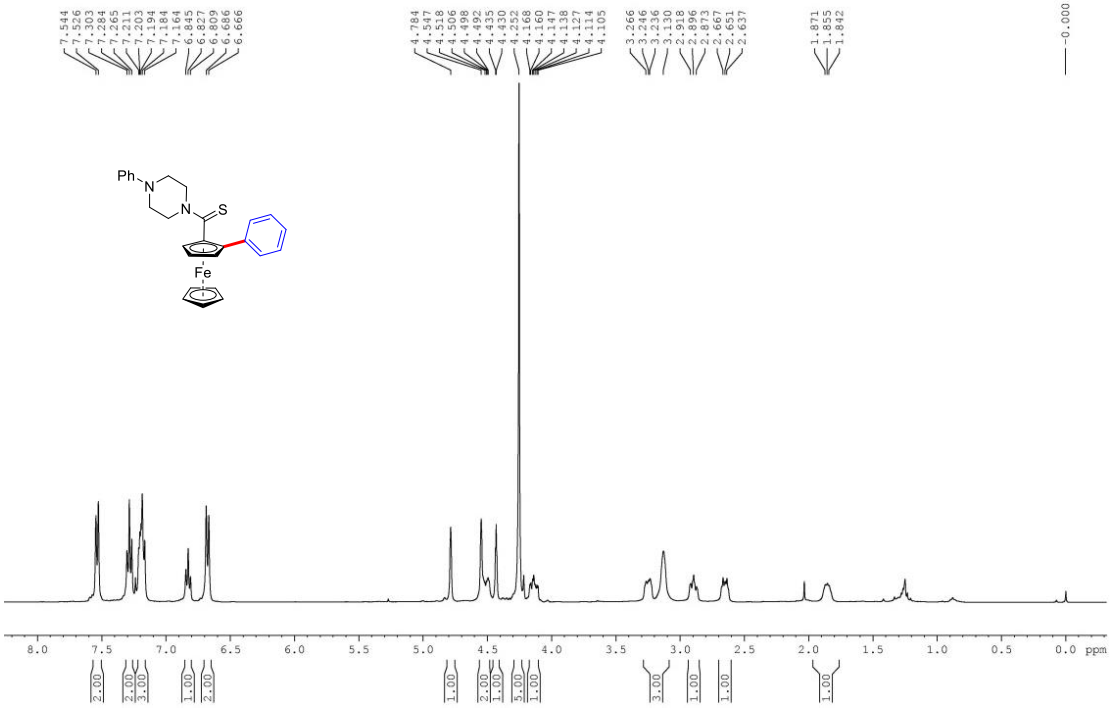
**3ai, $^{1}$H NMR, 400 MHz, $CDCl_3$**



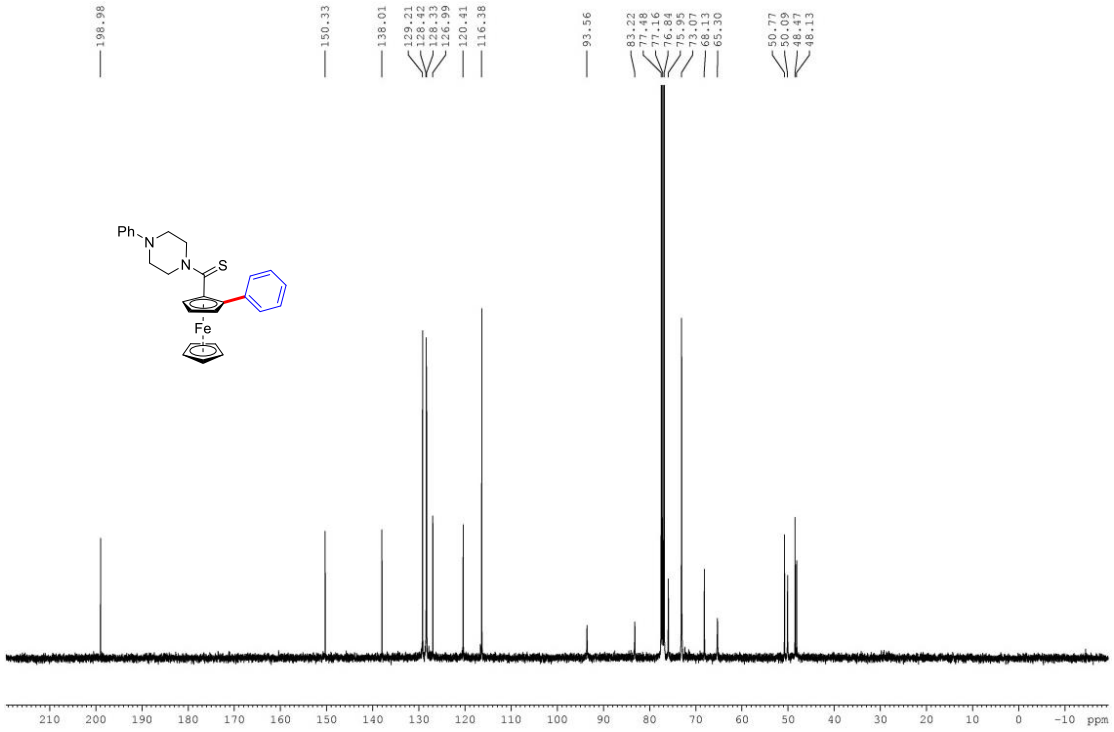

**3ai, $^{13}$C NMR, 101 MHz, $CDCl_3$**



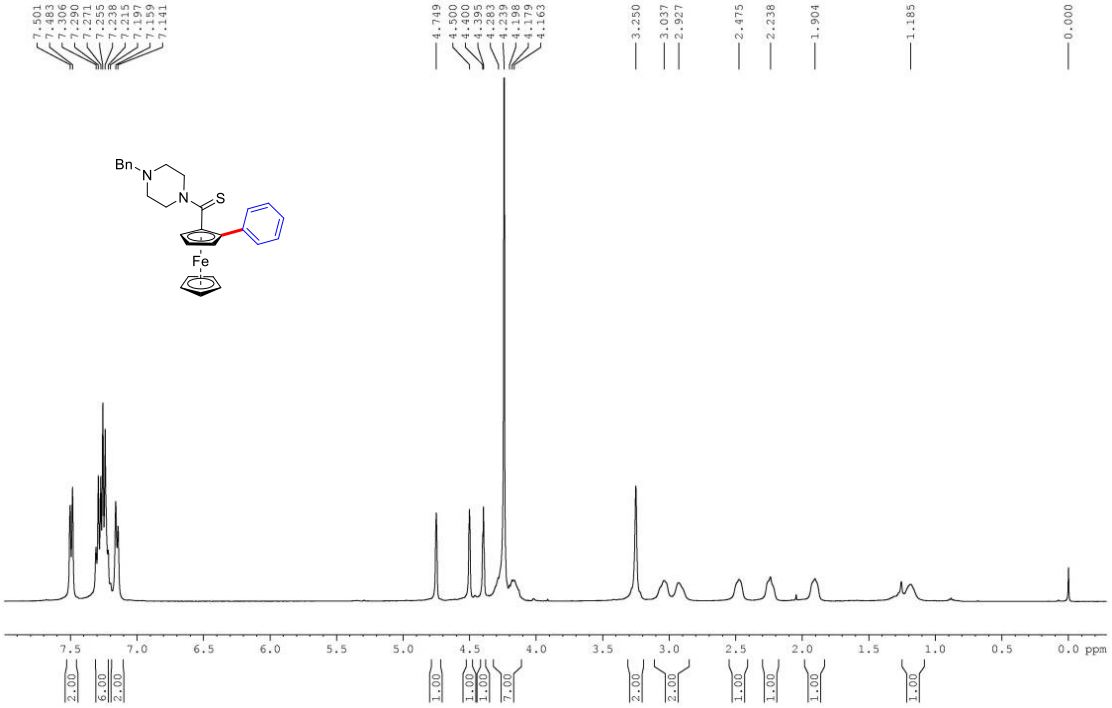
**3aj, $^{1}$H NMR, 400 MHz, $CDCl_3$**



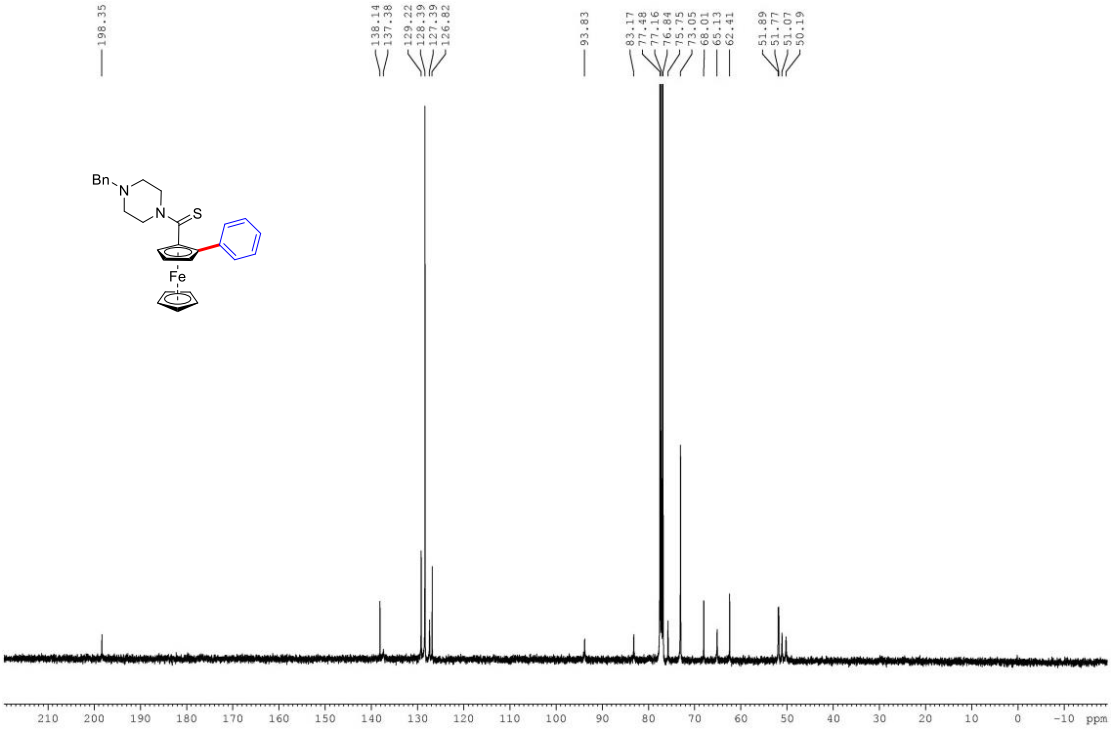

**3aj, $^{13}$C NMR, 101 MHz, $CDCl_3$**



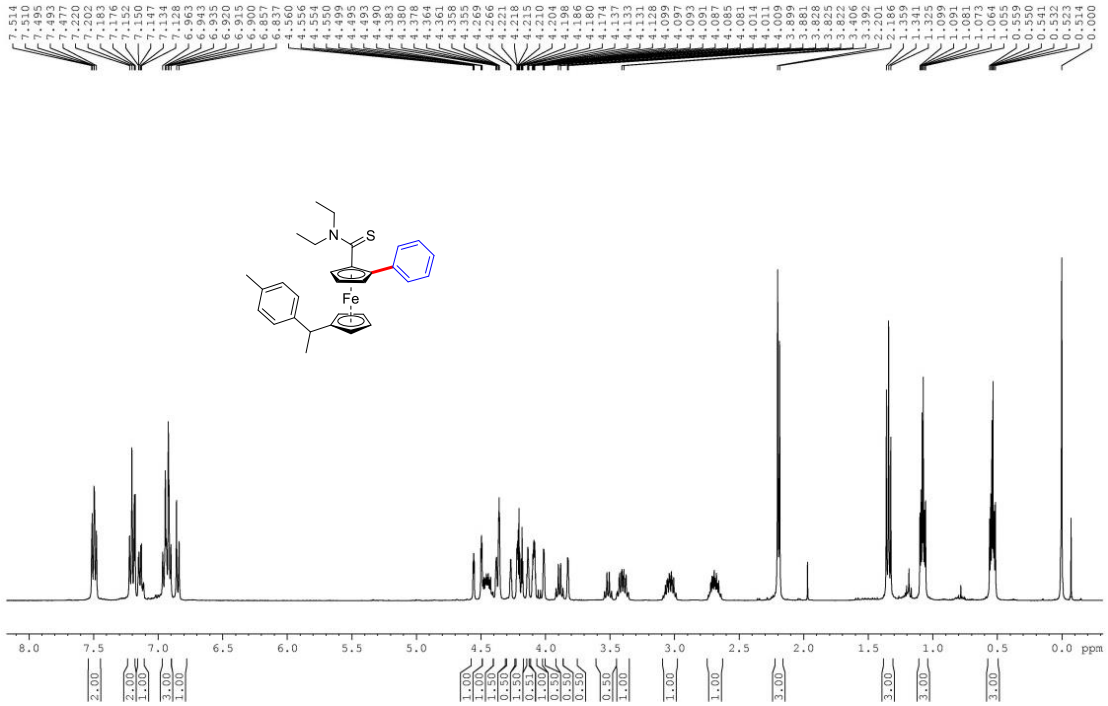
**3ak, $^{1}$H NMR, 400 MHz, $CDCl_3$**



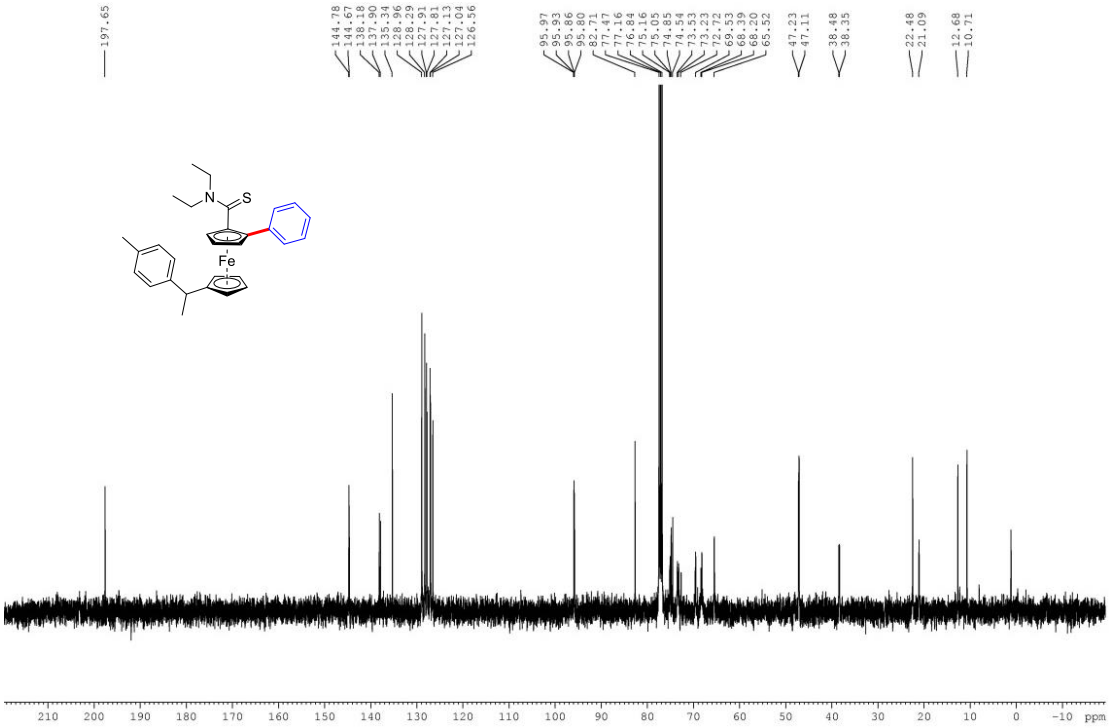

**3ak, $^{13}$C NMR, 101 MHz, $CDCl_3$**



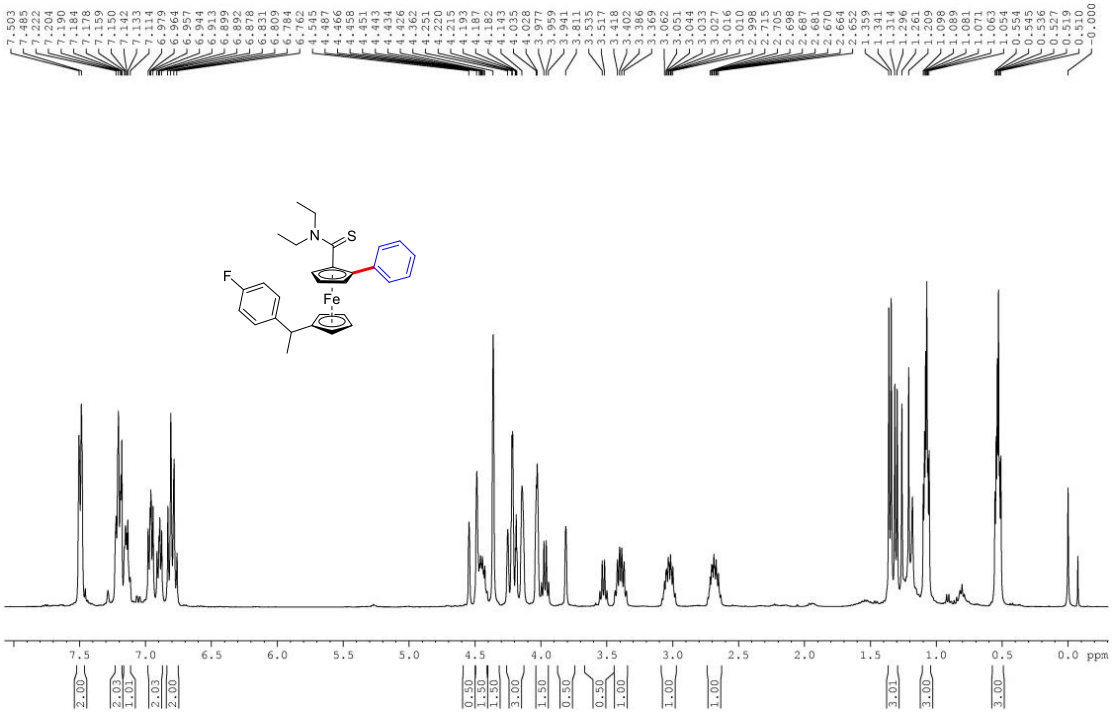
**3al, $^{1}$H NMR, 400 MHz, $CDCl_3$**



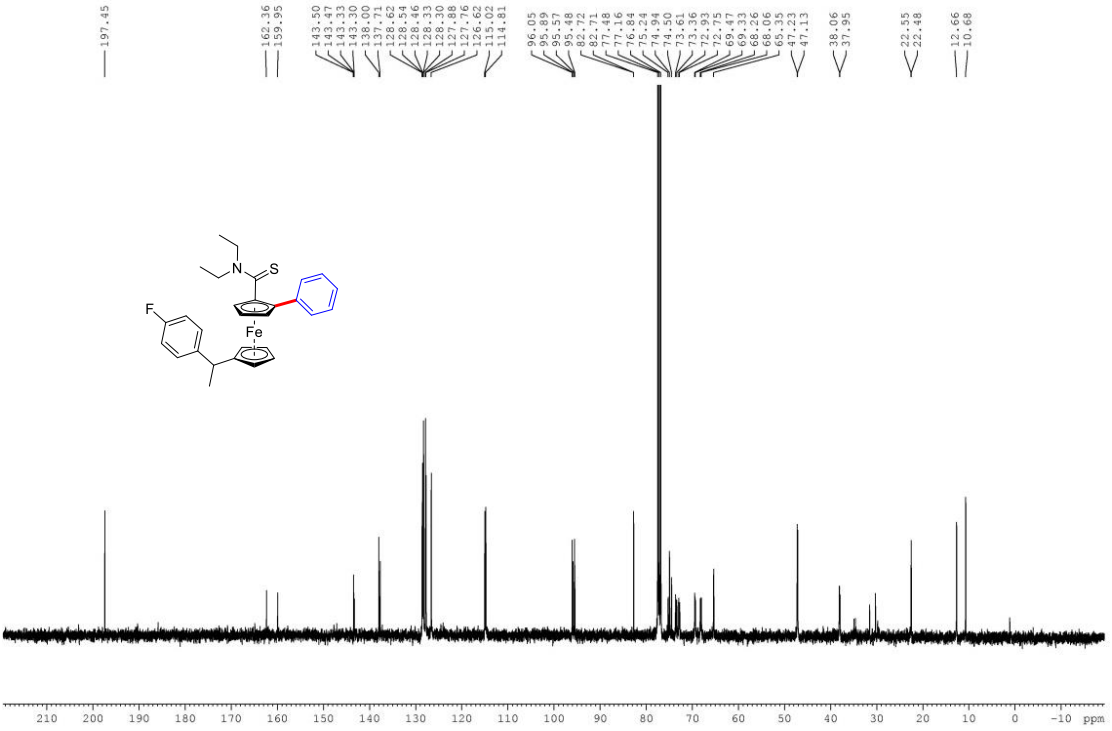

**3al, $^{13}$C NMR, 101 MHz, $CDCl_3$**



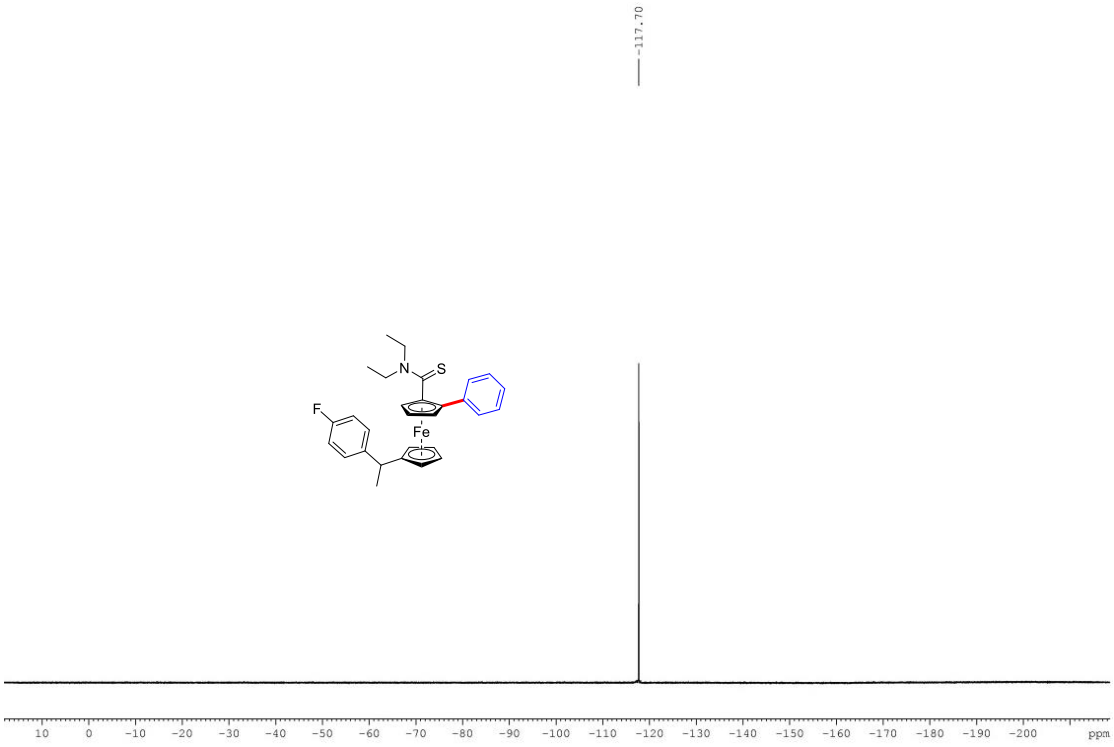
**3am, $^{1}$H NMR, 400 MHz, $CDCl_3$**



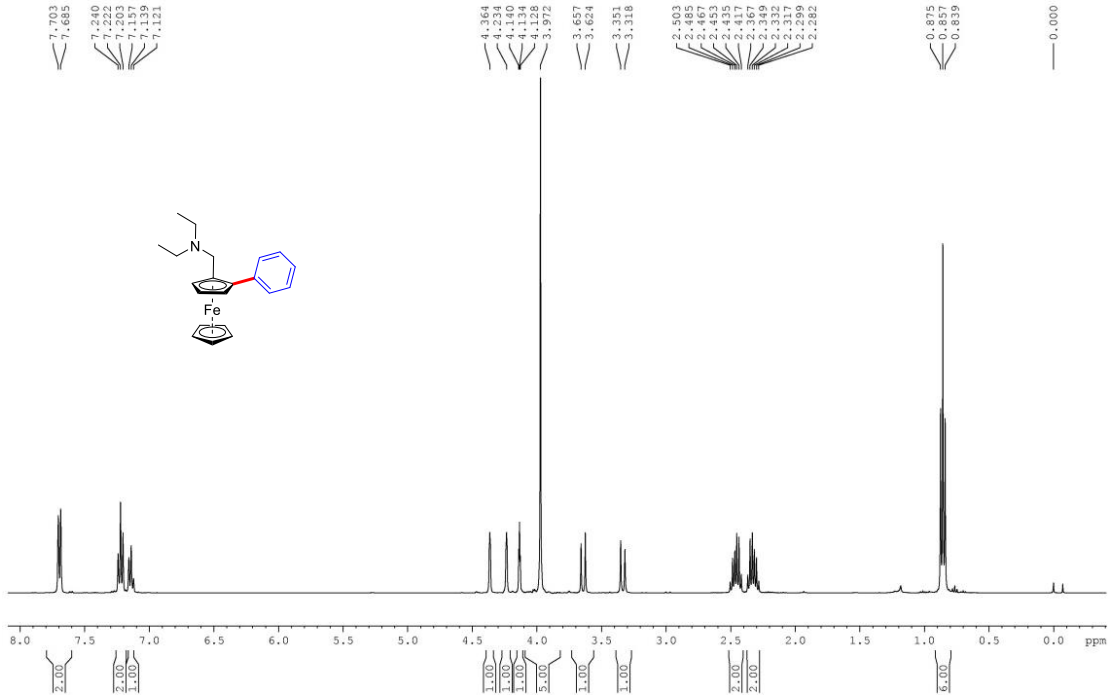
**3am, $^{13}$C NMR, 101 MHz, $CDCl_3$**



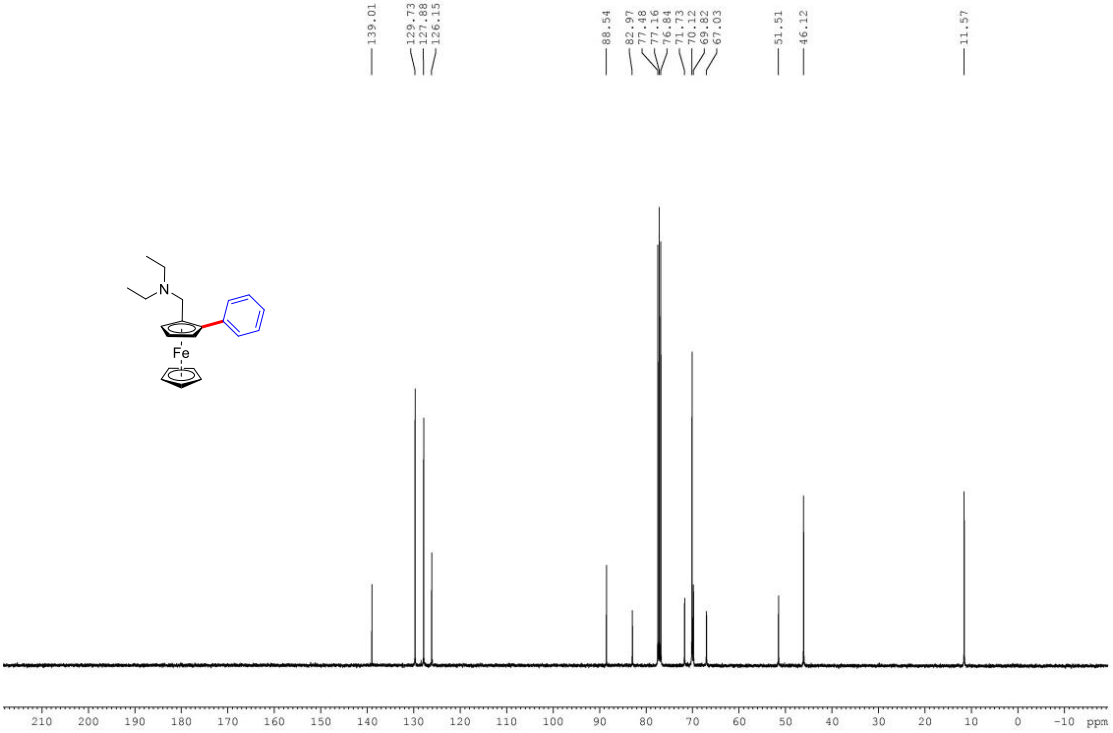
**3am, $^{19}$F NMR, 376 MHz, $CDCl_3$**



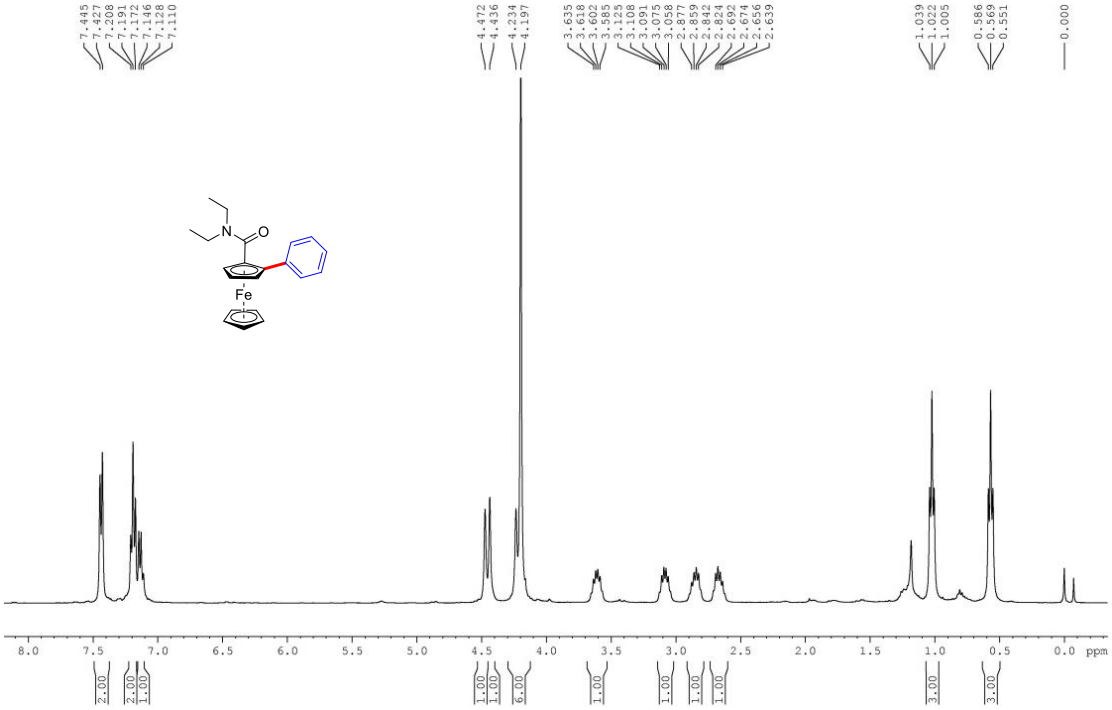
**4, $^{1}$H NMR, 400 MHz, $CDCl_3$**



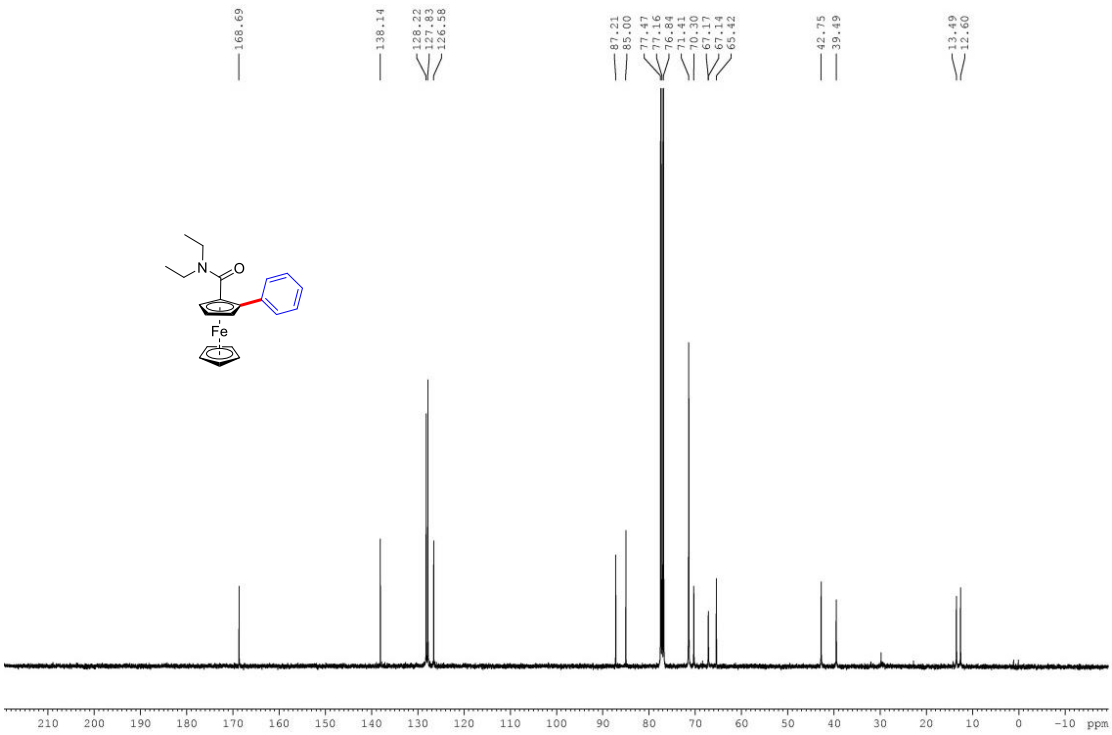

**4, $^{13}$C NMR, 101 MHz, $CDCl_3$**



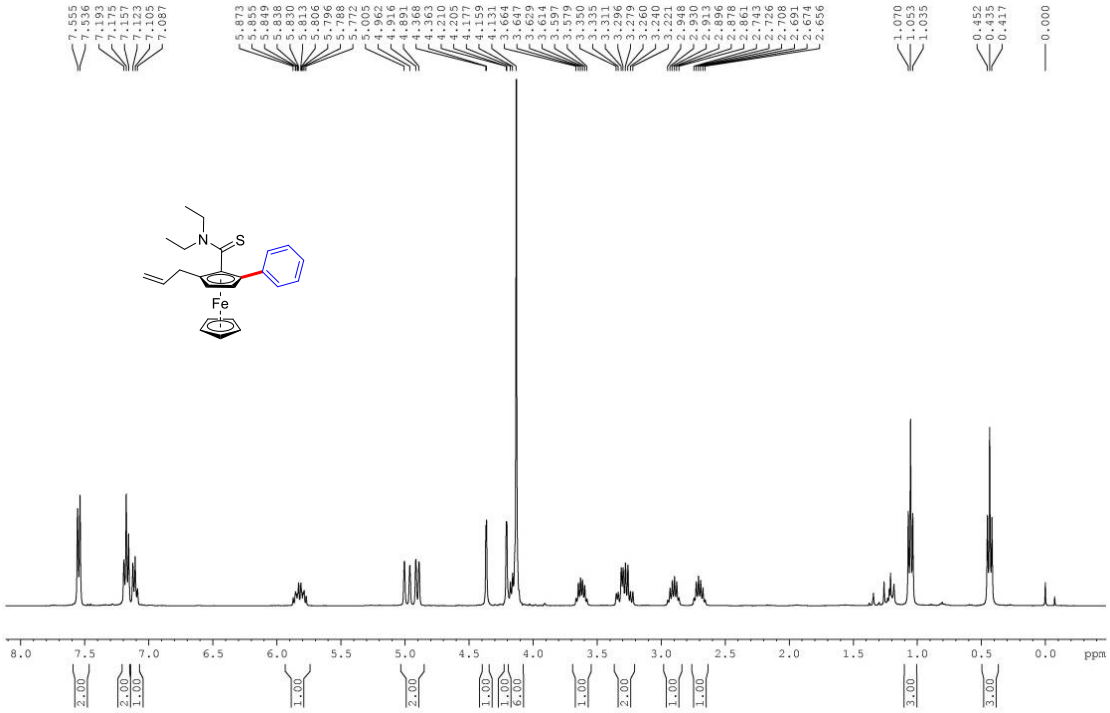
**5, $^{1}$H NMR, 400 MHz, $CDCl_3$**




**5, $^{13}$C NMR, 101 MHz, $CDCl_3$**



**6, $^{1}$H NMR, 400 MHz, $CDCl_3$**



**6,$^{13}$C NMR, 101 MHz, $CDCl_3$**