# Synthesis of Novel Ferrocenyl N/O-Heterocycles, Chiral P, N Ligand and α-dehydro-β-aminoacid Derived Short Peptides from Morita-Baylis-Hillman Adducts of Ferrocenealdehyde

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## Contents



## 1. General remarks

All the reactions were carried out in oven-dried glassware. Progress of reactions was monitored by Thin Layer Chromatography (TLC) while purification of crude compounds was done by column chromatography using silica gel (100-200 mesh). NMR spectra were recorded on Bruker Avance DPX-500 MHz, Bruker Avance 400 and Bruker Avance DPX-300 MHz (based on availability of instruments). Chemical shifts are reported in δ (ppm) relative to TMS ($^{1}H$) or $CDCl_3$ ($^{13}C$) as internal standards. Integrals are in accordance with assignments; coupling constants are given in Hz. All $^{13}C$ spectra are proton-decoupled. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), ddd (doublet of doublet of doublet), brs (broad singlet). For detailed peak assignments 2D spectra were measured (COSY and HMQC if necessary). HRMS analyses were recorded using JEOL JMS 600H, Q-Tof Micro and thermoscienific Exactive mass spectrometers. IR spectra were recorded on Bruker Alpha FT-IR and AT-IR spectrometers; absorbences are reported in $cm^{-1}$. Yields refer to quantities obtained after chromatography.

## 2. General experimental procedure:

### (a) Synthesis of N-allylated products 8-10, 15:

To ferrocenyl aza/classical MBH adduct **2-7** (1 equiv.) in dry acetone anhydrous $K_2CO_3$ (2 equiv.) was added and stirred at 60 $^{o}C$ for 5 minutes. Then allyl bromide (1.5

equiv.) was added and the reaction mixture was refluxed for 12 hours. The *N*-allylated products **8-10/15** was obtained without workup after purification by silica gel column chromatography using EtOAc: hexane as eluent in good yields (82-95%).

**(b) Synthesis of N/O heterocycles 11-13, 16:**

To the *N/O*-allylated adduct **8-10/15** (1 equiv.) in dry toluene Grubbs II generation catalyst (10 mol%) was added and stirred at 110 $^{o}$C for 6 hours to yield the five membered nitrogen ferrocenyl derivatives **11-13** and dihydro furan derivative **16** after purification by silica gel column chromatography using EtOAc: hexane in moderate yields (40-52%).

**(c) Synthesis of ferrocenyl piperidine derivative 14**

To ferrocenyl ethyl aza-MBH adduct **4** (1 equiv.) in dry THF, methyl vinyl ketone (MVK) (1.1 equiv.) and DBU (0.5 equiv.) was added and stirred at room temperature for 12 hours. The reaction afforded the ferrocenyl piperidine derivative **14** after purification by silica gel column chromatography using EtOAc: hexane as eluent in 78%.

**(d) Synthesis of ferrocenyl ligands 19/21/22:**

To the cooled solution (-78 $^{o}$C) of ferrocenyl MBH adduct/heterocycle **17/10/4/6/13** (1 equiv.) and TMEDA (1.3 equiv.) in dry THF under argon atmosphere, pre-cooled n-BuLi (2.5 equiv.) in hexane was added in drop wise and stirred for 1 hour at -78 $^{o}$C. Then $PPh_2Cl$ (1.3 equiv.) was added to the reaction mixture and stirred for another 2 hour at -78 $^{o}$C. The orange red reaction mixture was allowed to warm to room temperature and stirred over a period of 12 hours. The reaction mixture was treated with aqueous $NaHCO_3$ solution and the mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over sodium sulphate, filtered, concentrated under vacuum. Purification by silica gel column chromatography gave compounds **19/21/22** in good yields (40-95%).

**(e) Synthesis of ferrocenyl α-dehydro-β-aminoacids 23/24:**

Ferrocenyl ethyl ester aza-MBH adduct/rearranged adduct **4**/**5** (1 equiv.) was dissolved in ethanol: water mixture (8:2). Then NaOH (2.5 equiv.) was dissolved in 10 ml ethanol: water mixture (8:2) was added and the reaction mixture was heated at 80 $^{o}$C for 12 h. After the completion of the reaction (monitored by TLC), solvent was removed by applying vacuum and without workup the reaction mixture was purified by silica gel column chromatography gave corresponding acid **23/24** and protected amine **25** in good yield.

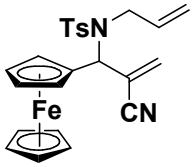
(f) **Synthesis of dipeptides 26-29 by solution phase peptide coupling reaction**:

Ferrocenyl acid **24/23** (1 equiv.**)** was taken in 1:1 mixture of dry DCM and DMF under argon atmosphere and cooled to 0 $^{o}$C. EDC.HCl (3 equiv.) was added to it and the mixture was stirred for 5 minutes. Then HOBt.$H_2O$ (3.5 equiv.) was added followed by acid protected amine hydrochloride (1.1 equiv.), DIPEA (5 equiv.). The mixture was stirred at 0 $^{o}$C for 3 hours and then at room temperature for 12 h. After completion of the reaction (monitored by TLC), few pieces of ice was added and stirred for 5 minutes and ethyl acetate was added and extracted. The organic layer was washed with water and dried over sodium sulphate, solvent was removed under reduced pressure. The reaction mixture after purification by silica gel column chromatography afforded dipeptides **26-29** in good yields (83-88 %).

**(g) Synthesis of ferrocenyl-β-lactam 30:**

To the solution of ferrocenyl aminoacid **23** (1equiv.) in THF, DIPEA (0.7 equiv.) was added followed by coupling reagent BOPCl (1.3 equiv.) and stirred at room temperature for 12 hours. Without any aqueous workup the reaction mixture was subjected silica gel column chromatography (in 2% MeOH:$CHCl_3$) to yield the ferrocenyl β-lactam **30** in 70% yield.

## 3. Characterization data for Compounds




**8**

**IR** (neat) $\nu_{max}$: 2919, 2852, 2226, 1159, 737 cm$^{-1}$;

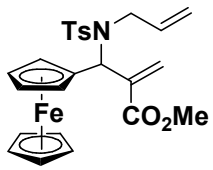
**$^{1}$H NMR** ($CDCl_3$/TMS, 500 MHz): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.18 (s, 1H), 6.14 (s, 1H), 5.69 (s, 1H), 5.42-5.41 (m, 1H), 4.90-4.86 (m, 2H), 4.43-3.87 (m, 9H), 3.70 (dd, *J* = 7.0, 16.0 Hz, 1H), 3.65 (dd, *J* = 7.0, 16.5 Hz, 1H), 2.45 (s, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 146.8, 143.8, 136.6, 132.0, 129.9, 129.8, 127.3, 120.2, 119.1, 89.9, 71.3, 70.7, 70.1, 69.8, 69.7, 69.4, 68.8, 68.7, 54.5, 49.5, 21.5;

**HRMS** (ESI): Calcd. for $C_{24}H_{24}FeN_2O_2S$ is 460.0907; Found: 460.0905 ($M^+$).

**IR** (neat) $\nu_{max}$: 2951, 1721, 1339, 1160, 817 cm$^{-1}$;

**$^{1}$H NMR** ($CDCl_3$/TMS, 500 MHz): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.36 (s, 1H), 6.09 (s, 1H), 5.93 (s, 1H), 5.51-5.46

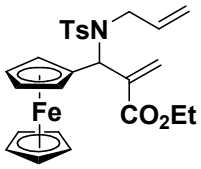



**9**

(m, 1H), 4.89-4.84 (m, 2H), 4.13-4.12 (m, 2H), 4.12-4.08 (m, 5H), 3.98-3.97 (m, 1H), 3.89-3.88 (m, 1H), 3.81 (m, 3H), 3.79-3.77 (m, 1H), 3.59 (dd, *J* = 6.5, 16.5 Hz, 1H), 2.43 (s, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 166.9, 143.0, 140.4, 137.7, 135.5, 129.2, 128.1, 127.7, 116.9, 84.0, 69.6, 69.2, 68.6, 68.4, 68.0, 56.7, 52.1, 48.0, 21.5;

**HRMS** (ESI): Calcd. for $C_{25}H_{27}FeNO_4S$ is 493.1010; Found: 516.1019 $(M+Na)^+$



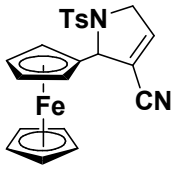

**10**

**IR** (neat) $\nu_{max}$: 2981, 2926, 1725, 1160, 817 $cm^{-1}$;

**$^{1}$H NMR** ($CDCl_3$/TMS, 300 MHz): δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.35 (s, 1H), 6.09 (s, 1H), 5.91 (s, 1H), 5.54-5.41 (m, 1H), 4.87-4.82 (m, 2H), 4.24 (q, *J* = 7.2, 14.4, 2H), 4.11 (s, 2H), 4.07 (s, 5H), 3.97 (s, 1H), 3.86 (s, 1H), 3.79 (dd, *J* = 5.7, 16.5, 1H), 3.58 (dd, *J* = 6.3, 16.2 Hz, 1H), 2.40 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3 H);

**$^{13}$C NMR** ($CDCl_3$/ TMS, 125 MHz): δ 166.4, 142.9, 140.6, 137.7, 135.5, 129.5, 127.9, 127.8, 127.7, 116.9, 84.0, 71.0, 70.4, 70.1, 70.0, 69.6, 69.2, 68.6, 68.5, 68.0, 61.1, 56.6, 48.0, 21.5, 14.2 ;

**HRMS** (ESI): Calcd. for $C_{26}H_{29}FeNO_4S$ is 507.1166; Found: 530.1152 $(M+Na)^+$




**11**

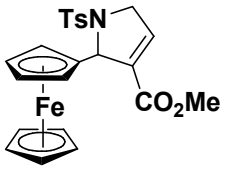
**IR** (neat) $\nu_{max}$: 2920, 2854, 2128, 1594, 1164 $cm^{-1}$;

**$^{1}$H NMR** ($CDCl_3$/TMS, 500 MHz): δ 7.16 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 5.91 (s, 1H), 5.16 (t, *J* = 1.5 Hz, 1H), 4.76-4.52 (m, 11H), 2.37 (s, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS,125 MHz): δ 143.5, 140.9, 138.2, 136.5, 129.7, 128.7, 128.2, 117.4, 84.5, 70.1, 69.7, 69.1, 69.0, 68.5, 57.2, 22.0;

**HRMS** (ESI): Calcd. for $C_{22}H_{20}FeN_2O_2S$ is 432.0594; Found: 432.0596 $(M^+)$.

**IR** (neat) $\nu_{max}$: 2921, 1723, 1348, 1162, 817 $cm^{-1}$;

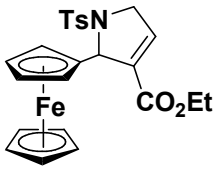



**12**

**$^1$H NMR** ($CDCl_3$/TMS, 500 MHz): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.44 (s, 1H), 5.70 (t, *J* = 1.5 Hz, 1H), 4.27-4.12 (m, 11H), 3.75 (s, 3H), 2.41 (s, 3H) ;

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 162.9, 143.7, 136.5, 135.2, 134.5, 129.8, 129.4, 127.9, 127.4, 89.1, 69.4, 69.0, 68.8, 67.9, 67.4, 67.1, 66.6, 64.6, 54.6, 51.9, 21.5;

**HRMS** (ESI): Calcd. for $C_{23}H_{23}FeNO_4S$ is 465.0697; Found: 488.0679 $(M+Na)^+$



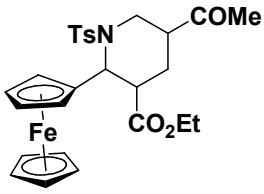

**13**

**IR** (neat) $\nu_{max}$: 2920, 1727, 1341, 1166, 819 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 500 MHz): δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.42 (s, 1H), 5.69 (s, 1H), 4.30-4.12 (m, 13H), 2.40 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 162.5, 143.7, 137.0, 134.9, 129.8, 129.4, 127.9, 127.4, 89.2, 69.6, 69.4, 69.0, 68.8, 67.9, 67.6, 67.3, 67.2, 66.6, 64.6, 61.1, 54.7, 21.5, 14.2;

**HRMS** (ESI): Calcd. for $C_{24}H_{25}FeNO_4S$ is 479.0853; Found: 502.0805 $(M+Na)^+$.




**14**

**IR** (neat) $\nu_{max}$: 2980, 2925, 1731, 1710, 1158, 817, 733 $cm^{-1}$;

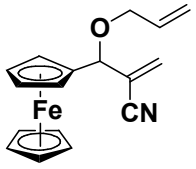
**$^1$H NMR** ($CDCl_3$/TMS, 500 MHz): δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.82 (s, 1H), 4.26-3.94 (m, 11H), 3.52 (d, *J* = 10 Hz, 1H), 3.23 (s, 1H), 2.85 (tt, *J* = 4.0, 12 Hz, 1H), 2.75-2.73 (m, 1H), 2.43 (s, 3H), 2.38-2.35 (m, 1H), 2.11 (s, 3 H), 1.79 (td, *J* = 5.0, 13.5 Hz, 1H), 1.41-1.37 (m, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 208.2, 172.1, 143.5, 138.1, 129.9, 127.2, 70.4, 69.5, 68.9, 68.7, 68.1, 67.5, 61.3, 53.5, 47.7, 45.2, 41.5, 28.3, 24.3, 21.5, 14.2;

**HRMS** (ESI): Calcd. for $C_{27}H_{31}FeNO_5S$ is 537.1272; Found: 560.1261 $(M+Na)^+$.

**IR** (neat) $\nu_{max}$: 2924, 2859, 2225, 1412, 1050, 819 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 500 MHz): δ 6.01 (s, 1H), 5.93 (s, 1H),

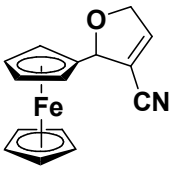



**15**

5.90-5.83 (m, 1H), 5.27 (d, $J$ = 10.5 Hz, 1H), 5.18 (d, $J$ = 10.5, 1H), 4.63 (s, 1H), 4.20-4.12 (m, 9H), 4.06 (dd, $J$ = 6.0, 13.0 Hz, 1H), 3.88 (dd, $J$ = 6.5, 13.0 Hz, 1H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 133.9, 131.0, 124.5, 117.7, 117.4, 85.9, 77.7, 70.0, 69.2, 68.4, 68.3, 67.4, 66.6 ;

**HRMS** (ESI): Calcd. for $C_{17}H_{17}FeNO$ is 307.0660; Found: 330.0647 $(M+Na)^+$



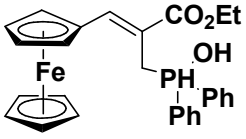

**16**

**IR** (neat) $\nu_{max}$: 2924, 2211, 1592, 1462, 1054 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 500 MHz): δ 6.88 (s, 1H), 5.79 (t, $J$ = 5.0 Hz, 1H), 4.82-4.79 (m, 2H), 4.26-4.17 (m, 9H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 143.4, 118.0, 89.7, 83.0, 71.0, 70.6, 70.2, 70.0, 69.6, 69.2, 68.8, 68.5, 68.0, 49.9;

**HRMS** (ESI): Calcd. for $C_{15}H_{13}FeNO$ is 279.0347; Found: 279.0342 $(M^+)$.




**19**

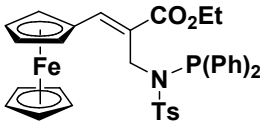
**IR** (neat) $\nu_{max}$: 2693, 1689, 1623, 889, 815 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 300 MHz): δ 7.87-7.81 (m, 5H), 7.58-7.46 (m, 8H), 4.90 (s, 2H), 4.42 (s, 2H), 4.24 (s, 5H), 3.83 (q, $J$ = 7.2, 14.0 Hz, 2H), 3.70 (d, $^2J_{H,P}$ = 14.7 Hz, 2H), 1.08 (t, $J$ = 7.2 Hz, 3 H);

**$^{13}$C {$^1$H} NMR** ($CDCl_3$/TMS, 125 MHz): δ 167.5 (d, $J_{P,C}$ = 2.5 Hz), 142.9 (d, $^3J_{P,C}$ = 8.7 Hz), 133.0, 132.2, 131.7 (d, $J_{P,C}$ = 2.5 Hz), 131.4 (d, $J_{P,C}$ = 8.7 Hz) (2C), 118.9 (d, $^2J_{P,C}$ = 8.7 Hz), 78.1 (d, $^2J_{P,C}$ = 2.5 Hz), 71.1, 69.4, 60.7, 31.8 (d, $^1J_{P,C}$ = 67.8 Hz), 14.1;

**$^{31}$P {$^1$H} NMR**: δ 29.73;

**HRMS** (ESI): Calcd. for $C_{28}H_{29}FeO_3P$ is 500.1204; Found: 500.1211 $(M^+)$.




**21**

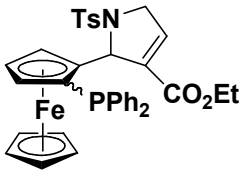
**IR** (neat) $\nu_{max}$: 1692, 1623, 1438, 1272 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 300 MHz): δ 7.74-7.61 (m, 4H), 7.54-7.44 (m, 5H), 7.39-7.34 (m, 4H), 7.14-7.04 (m, 2H), 4.58 (s, 2H), 4.34 (s, 2H), 4.15 (s, 5H), 4.04 (d, $J$ = 16.3 Hz, 2H), 3.84 (q, $J$ = 7.2, 14.4 Hz, 2H), 2.33 (s, 3H), 1.37 (t, $J$ = 7.8 Hz, 3H);

**$^{13}$C {$^{1}$H} NMR** ($CDCl_3$/TMS, 75 MHz): δ 167.2 (d, $J_{P,C}$ = 2.0 Hz), 144.2 (d, $J_{P,C}$ = 10.1 Hz), 143.3 (d, $J_{P,C}$ = 3.0 Hz), 140.50, 132.8 (d, $J_{P,C}$ = 10.1 Hz), 132.5 (d, $J_{P,C}$ = 2.2 Hz), 128.6, 128.2 (d, $J_{P,C}$ = 12.6 Hz), 127.1, 125.8 (d, $^{2}J_{P,C}$ = 3.7 Hz), 117.9 (d, $J_{P,C}$ = 9.1 Hz), 77.3 (d, $J_{P,C}$ = 13.5 Hz), 70.5 (d, $J_{P,C}$ = 13.6 Hz), 69.5, 60.6 (d, $J_{P,C}$ = 43.5 Hz), 29.8 (d, $^{2}J_{P,C}$ = 68.5 Hz), 21.1 (d, $J_{P,C}$ = 23.0 Hz), 14.1 (d, $J_{P,C}$ = 8.9 Hz);

**$^{31}$P {$^{1}$H} NMR**: δ 19.00 ;

**HRMS** (ESI): Calcd. for $C_{35}H_{34}FeNO_4PS$ is 651.1296; Found: 674.1234 $(M+Na)^+$.




**22**

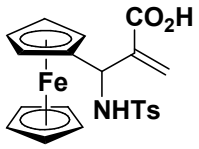
**IR** (neat) $\nu_{max}$: 2976, 1720, 1641, 1115 $cm^{-1}$;

**$^{1}$H NMR** ($CDCl_3$/ TMS, 300 MHz): δ 7.74-7.70 (m, 4H), 7.58-7.52 (m, 7H), 7.36-7.25 (m, 3H), 5.15 (d, $J$ = 4.69 Hz, 1H), 4.67 (s, 1H), 4.20 (s, 5H), 4.17-4.11 (m, 1H), 3.96-3.80 (m, 2H), 3.70-3.48 (m, 3H), 3.28-3.19 (m, 1H), 2.46 (s, 3H), 1.02 (t, $J$ = 7.2 Hz, 3H);

**$^{13}$C NMR** ($CDCl_3$/ TMS, 125 MHz): δ 172.4, 136.1, 132.0, 130.8, 130.7, 130.5, 129.4, 129.0, 128.8, 128.6, 128.4, 88.4, 69.0, 68.8, 68.6, 68.1, 66.4, 61.5, 47.7, 29.6, 13.7;

**$^{31}$P {$^{1}$H} NMR**: δ -16.17;

**HRMS** (ESI): Calcd. for $C_{36}H_{34}FeNO_4PS$ is 663.1296; Found: 663.1288 $(M^+)$.



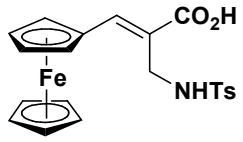

**23**

**IR** (neat): 3361, 3263, 1689, 1627, 1404, 1160, 817 $cm^{-1}$

**$^{1}$H NMR** ($CDCl_3$/ TMS,500 MHz): δ 7.72 (d, $J$ = 8.0 Hz, 2H), 7.26 (d, $J$ = 8.0 Hz, 2H), 6.18 (s, 1H), 5.82 (s, 1H), 5.80 (s, 1H), 5.06 (d, $J$ = 7.5 Hz, 1H), 4.15 (s, 5H), 4.10-4.08 (m, 3H), 3.96 (s, 1H), 2.40 (s, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 169.8, 143.4, 139.0, 137.9, 129.6, 129.5, 128.4, 127.2, 127.1, 88.9, 69.8, 69.0, 68.9, 68.0, 67.9, 67.0(2C), 54.5, 21.3;

**HRMS** (ESI): Calcd. for $C_{21}H_{21}FeNO_4S$ is 439.0541; Found: 462.0512 $(M+Na)^+$.



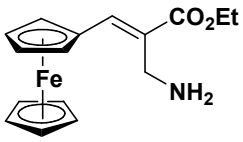

**24**

**IR** (neat) $\nu_{max}$: 3266, 1686, 1620, 1410, 1330, 1160, 816 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 400 MHz): δ 7.74-7.62 (m, 3H), 7.27 (d, *J* = 8 Hz, 2H), 5.71 (s, 1H), 5.05 (s, 1H), 4.19-4.07 (m, 11H), 2.42 (s, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 169.7, 147.6, 143.3, 137.8, 129.7, 127.2, 126.4, 72.1, 71.2, 69.8, 64.2, 21.5;

**HRMS** (ESI): Calcd. for $C_{21}H_{21}FeNO_4S$ is 439.0541; Found: 439.0509 ($M^+$).



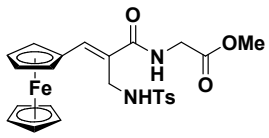

**25**

**IR** (neat) $\nu_{max}$: 3405, 2920, 1656, 1611, 1418, 1262, 1088 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 500 MHz): δ 7.88 (s, 1H), 4.66 (s, 2H) , 4.48 (s, 2H), 4.33 (s, 2H), 4.19 (s, 5H), 3.62 (q, *J* = 10.0, 15.0 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 75 MHz): δ 173.2, 147.8, 122.9, 71.7, 71.3, 69.7, 65.6, 64.4, 15.4;

**HRMS** (ESI): Calcd. for $C_{16}H_{19}FeNO_2$ is 313.0765; Found: 313.0734 ($M^+$).




**26**

**IR** (neat) $\nu_{max}$: 1692, 1623, 1438, 1272 $cm^{-1}$;

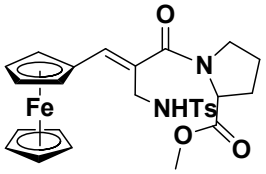
**$^1$H NMR** ($CDCl_3$/TMS, 400 MHz): δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 1H) , 7.58 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.08 (s, 2H), 4.45-4.37 (m, 5H), 4.16-4.14 (m, 6H), 3.77 (s, 3H), 2.42 (s, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 170.1, 167.3, 143.3, 142.2, 137.5, 129.4, 127.3, 120.2, 70.3, 69.0, 68.1, 56.4, 52.5, 41.1, 21.5;

**HRMS** (ESI): Calcd. for $C_{24}H_{26}FeN_2O_5S$ is 510.0912; Found: 533.0916 $(M+Na)^+$.

**IR** (neat): 3269, 2917, 1681, 1614 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 400 MHz): δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.97 (s, 1H), 4.89 (s, 1H), 4.32 (s, 2H), 4.24 (s, 2H), 4.20 (s, 5H), 4.14-4.03 (m, 2H), 3.72 (s, 3H), 3.29-3.26 (m, 1H),

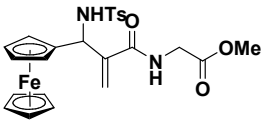



**27**

2.40 (s, 3H), 2.11-2.02 (m, 1H), 1.78-1.65(m, 3H), 1.51-1.49 (m, 1H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 100 MHz): δ 172.4, 168.8, 143.0, 142.0, 141.6, 138.1, 129.4, 129.3, 127.4, 117.3, 69.4, 67.8, 67.7, 66.4, 65.7, 58.7, 58.1, 52.3, 49.3, 45.2, 29.2, 21.5;

**HRMS** (ESI): Calcd for $C_{27}H_{30}FeN_2O_5S$ is 550.1225; Found: 550.1219 ($M^+$).



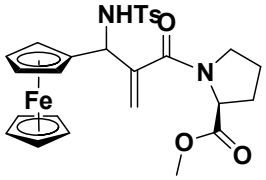

**28**

**IR** (neat): 3040, 1691, 1610, 1580 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 300 MHz): δ 7.76 (d, *J* = 8.0Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.30 (s, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 5.44 (s, 1H), 5.35 (s, 1H), 4.97 (d, *J* = 8.0 Hz, 1H), 4.16 (s, 6H), 4.12 (s, 1H), 4.09-4.08 (m, 1H), 3.99 (s, 1H), 3.95-3.93 (m, 2H), 3.75 (s, 3H), 2.40 (s, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 170.0, 167.3, 143.3, 142.4, 137.6, 129.7, 129,4, 127.3, 127.1, 120.1, 88.5, 69.0, 68.1, 68.0, 66.9, 66.8, 56.5, 52.4, 41.1, 21.5;

**HRMS** (ESI): Calcd. for $C_{24}H_{26}FeN_2O_5S$ is 510.0912; Found: 533.0936 $(M+Na)^+$.




**29**

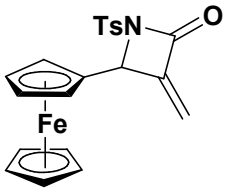
**IR** (neat): 3211, 2917, 1647, 1609 $cm^{-1}$;

**$^1$H NMR** ($CDCl_3$/TMS, 400 MHz): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 1H), 5.52 (s, 1H), 4.50 (s, 2H), 4.46 (s, 1H), 4.37 (s, 2H), 4.25 (s, 1H), 4.17 (s, 5H), 3.76 (s, 3H), 3.65-3.62 (m, 2H), 2.41 (s, 3H), 2.37-2.28 (m, 1H), 2.04-1.98 (m, 2H), 0.90-0.83 (m, 2H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 100 MHz): δ 168.4, 164.2, 145.1, 143.2, 141.2, 135.2, 129.6, 129.4, 128.4, 127.2, 122.7, 70.6, 70.4, 69.6, 69.4, 58.1, 52.4, 48.4, 42.0, 29.6, 21.5;

**HRMS** (ESI): Calcd. for $C_{27}H_{30}FeN_2O_5S$ is 550.1225; Found: 550.1221 $(M)^+$.

**IR** (neat): 3271, 2922, 1700, 1621, 1600, 1336, 1261, 1161, 812




**30**

$cm^{-1}$;

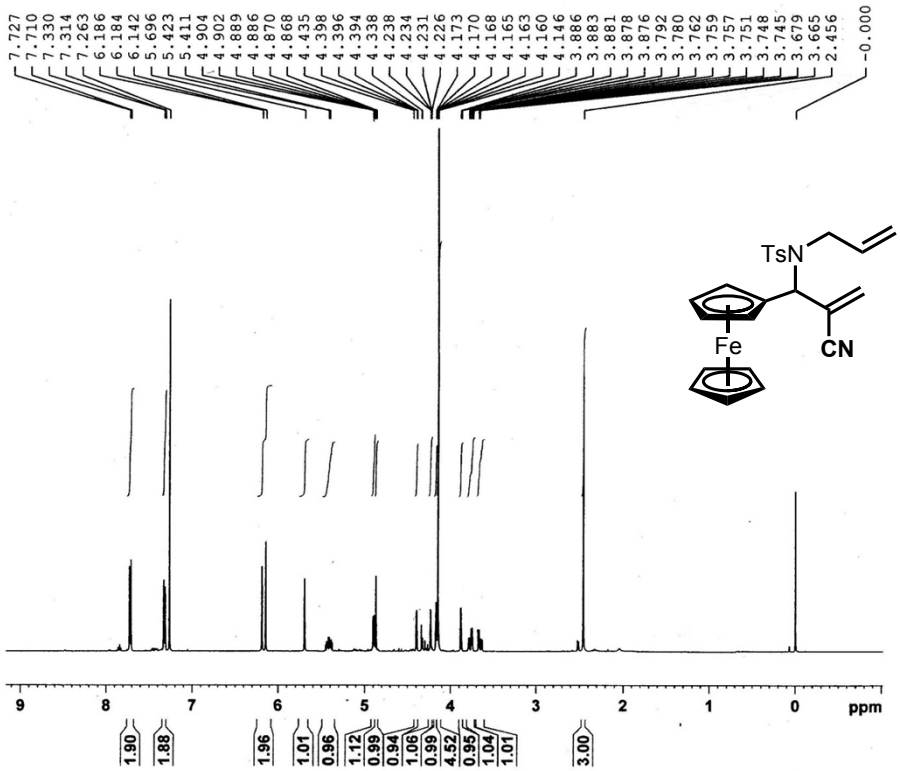
**$^{1}$H NMR** ($CDCl_3$/TMS, 300 MHz): δ 7.81 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 9.0 Hz, 2H), 5.30 (s, 1H), 4.77 (s, 2H), 4.45-4.16 (m, 9H), 2.44 (s, 3H);

**$^{13}$C NMR** ($CDCl_3$/TMS, 125 MHz): δ 161.2, 142.6, 138.1, 128.8, 128.7, 126.5, 126.3, 125.4, 98.9, 69.1, 68.7, 67.9, 66.9, 54.7, 20.5;

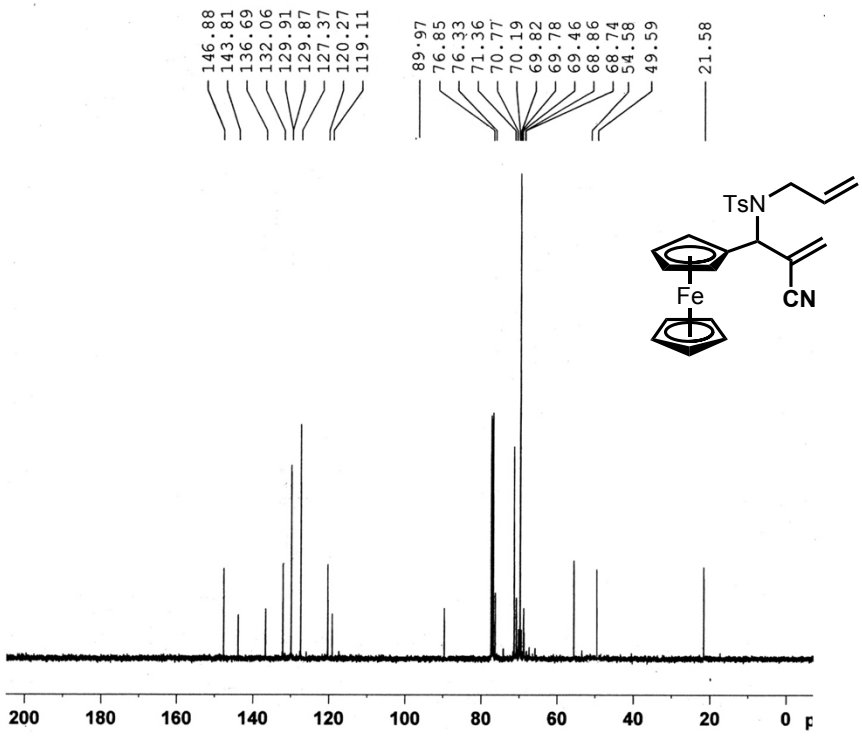
**HRMS** (ESI): Calcd. for $C_{21}H_{19}FeNO_3S$ is 421.0435; Found: 422.0413 $(M+H)^+$.

## 4. Scanned copies of $^{1}H$, $^{13}C$, $^{31}P$, and 2D COSY NMR spectra

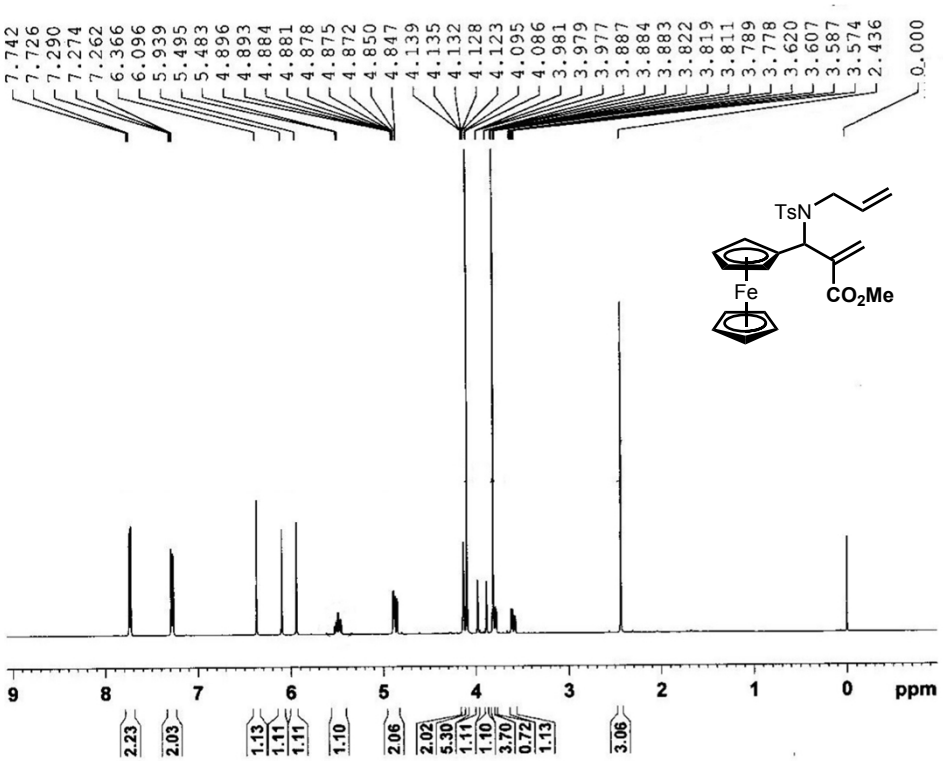
### $^{1}H$ NMR spectrum of Compound 8



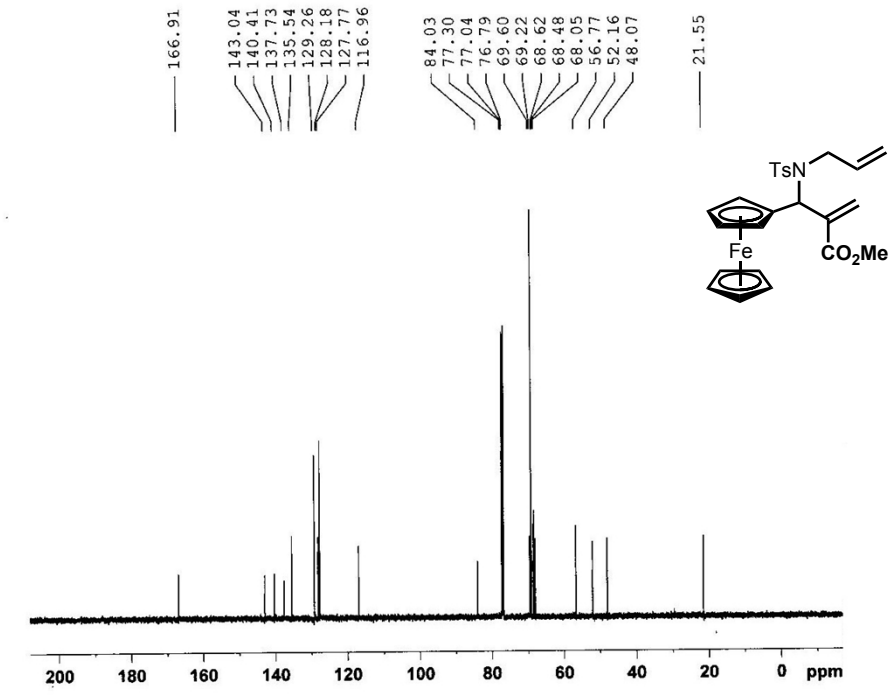

### $^{13}C$ NMR spectrum of Compound 8



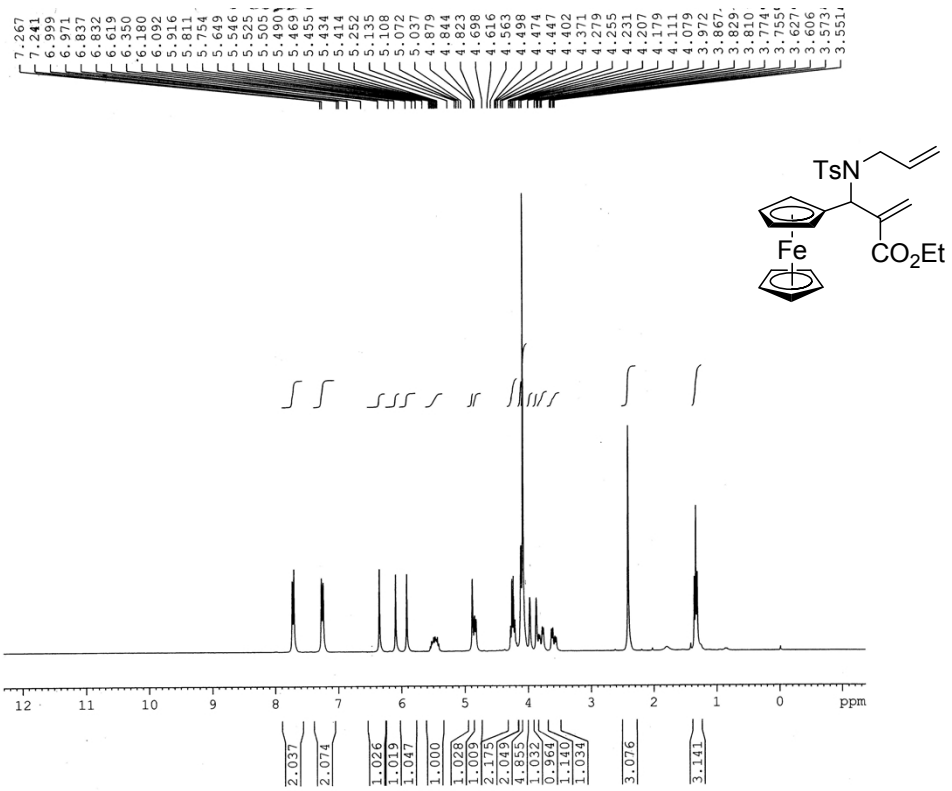
**$^{1}$H NMR spectrum of Compound 9**



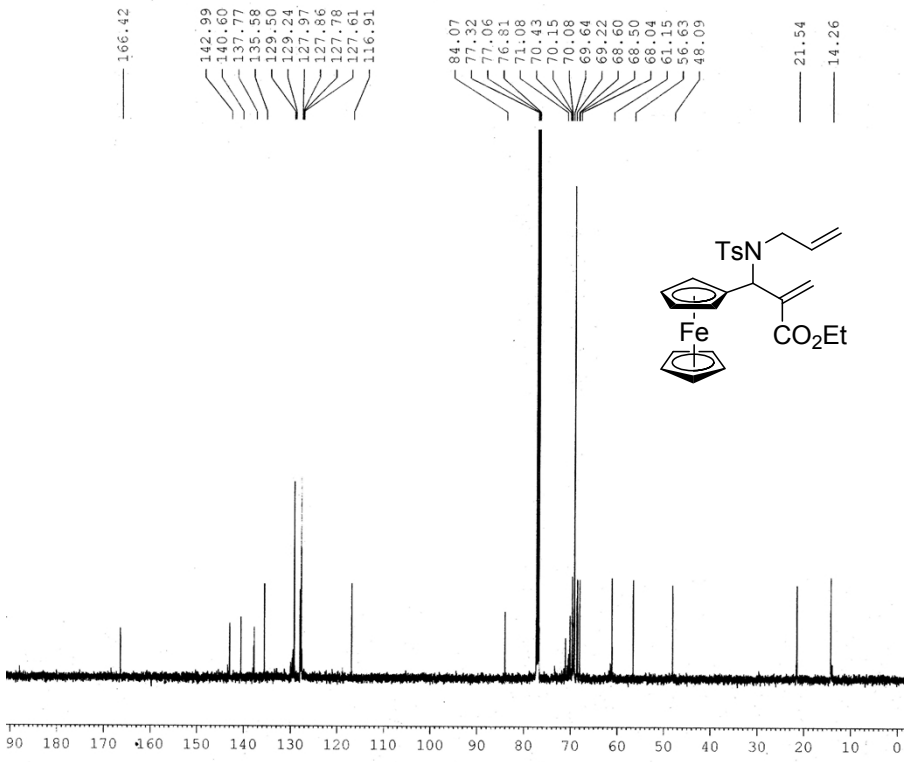

**$^{13}$C NMR spectrum of Compound 9**



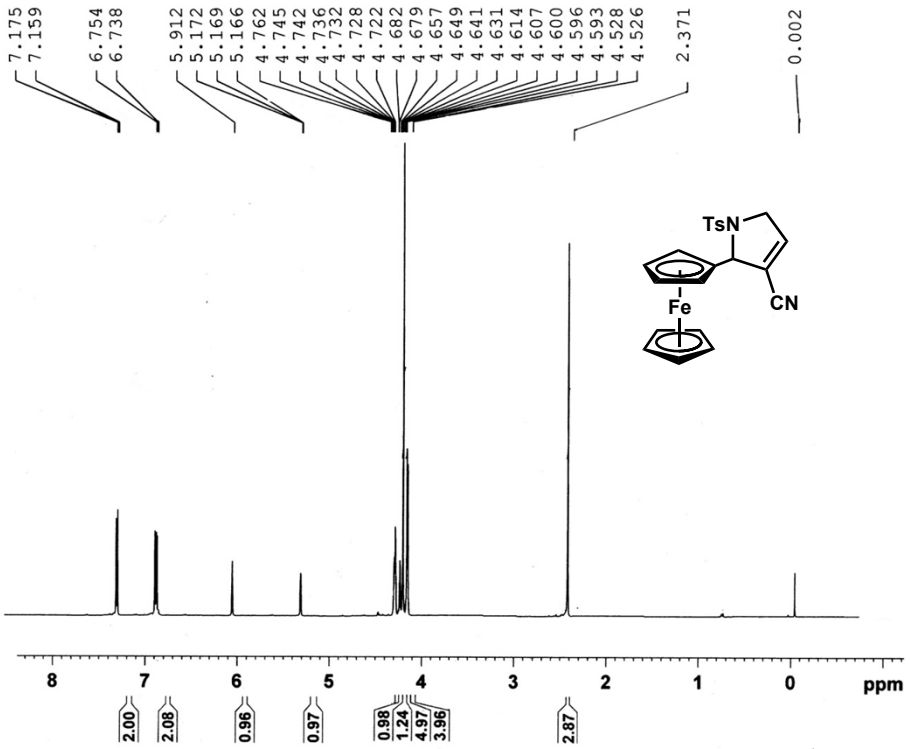
**$^{1}$ H NMR spectrum of Compound 10**



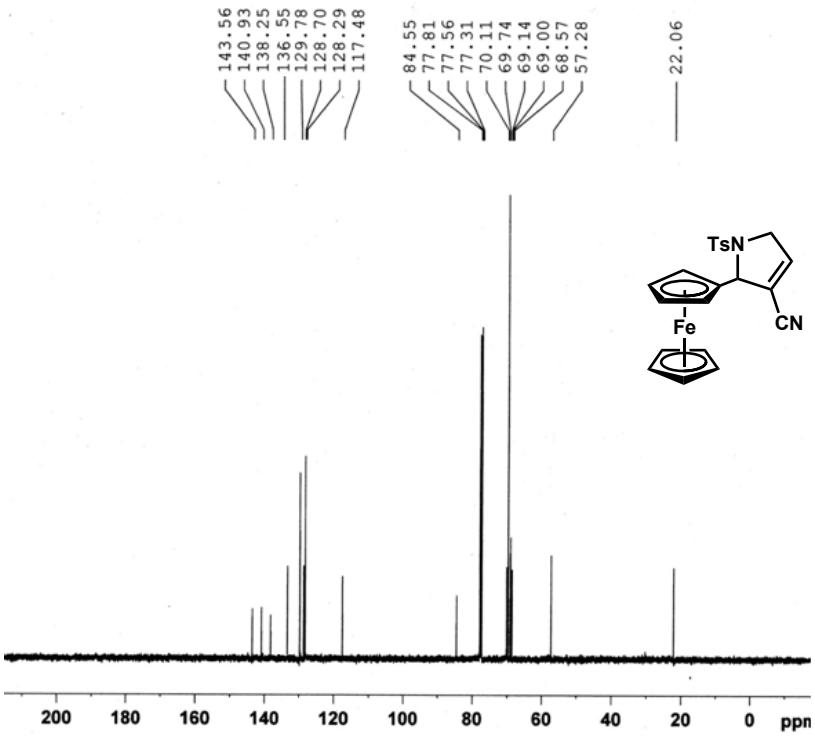

**$^{13}$C NMR spectrum of Compound 10**



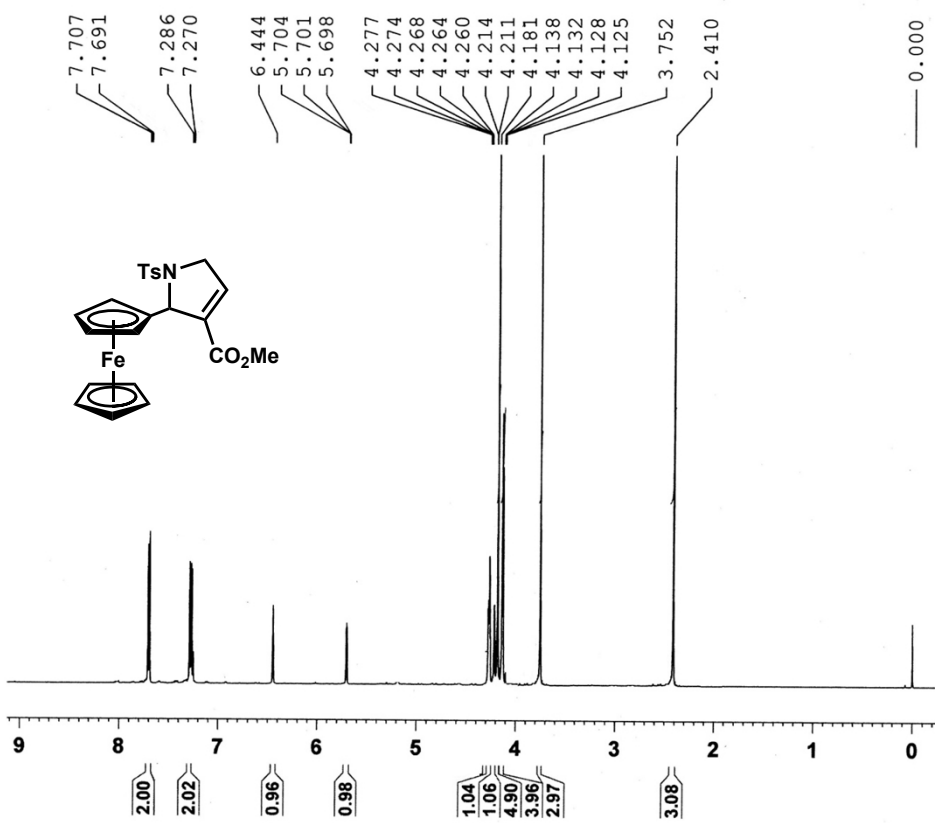
**$^{1}$ H NMR spectrum of Compound 11**



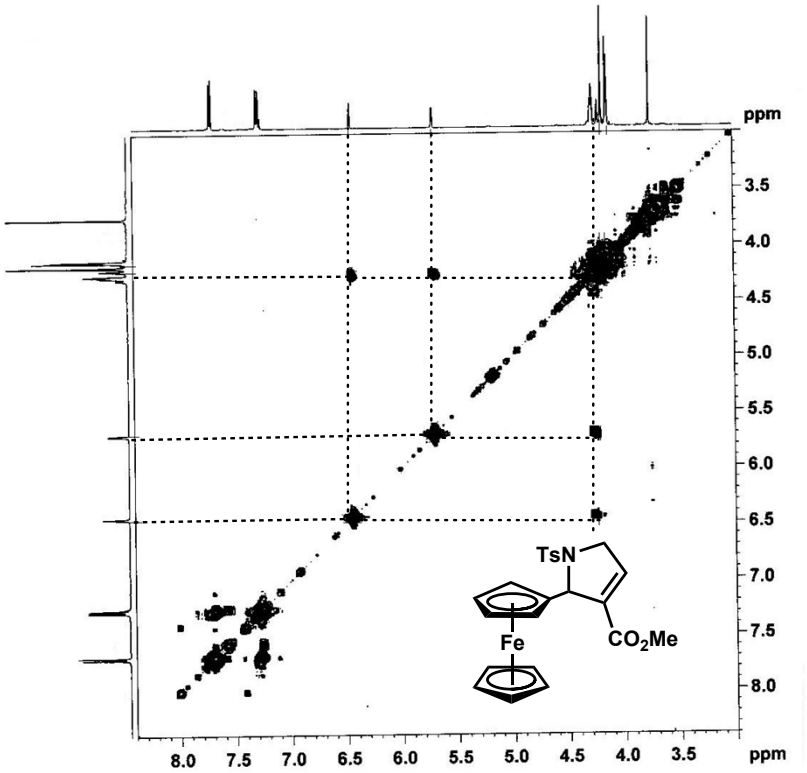

**$^{13}$ C NMR spectrum of Compound 11**



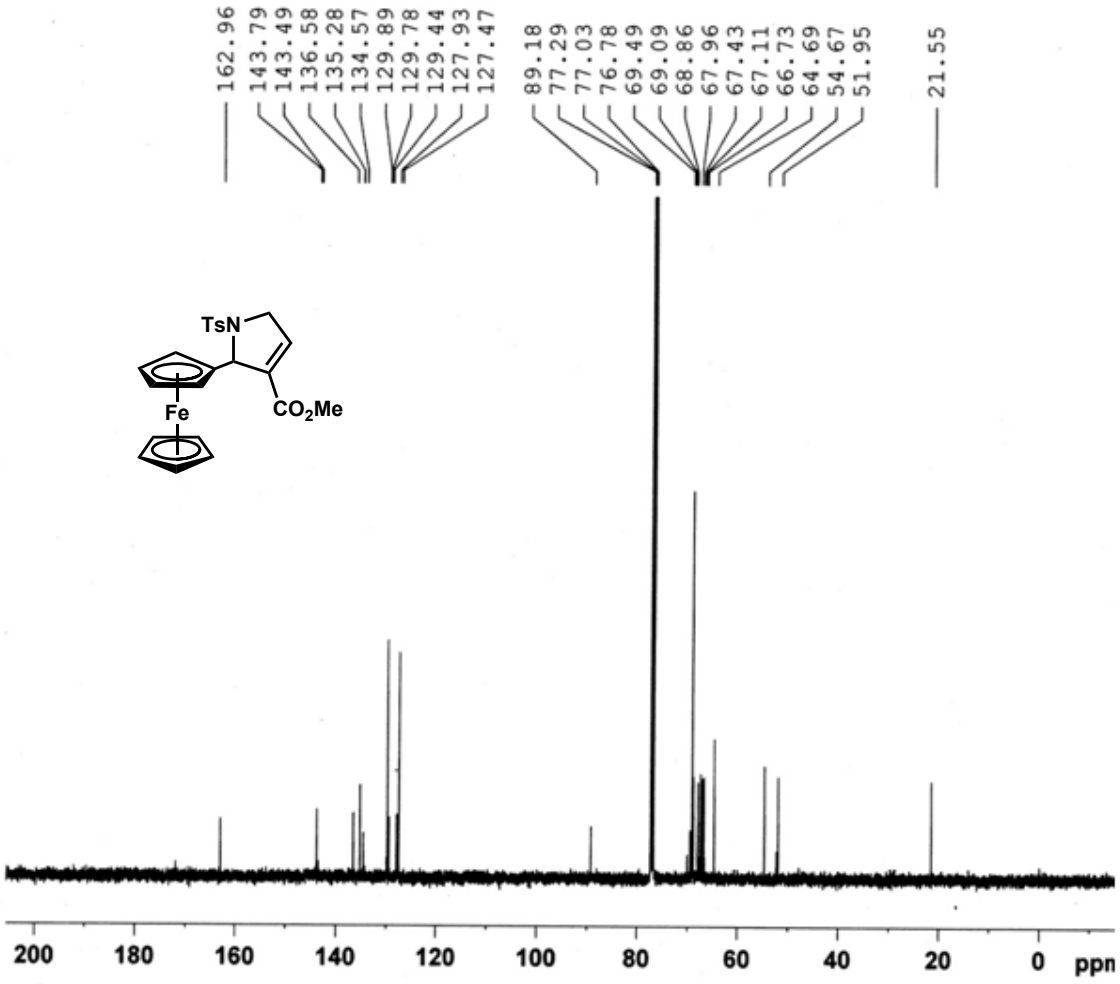
**$^{1}$H NMR spectrum of Compound 12**



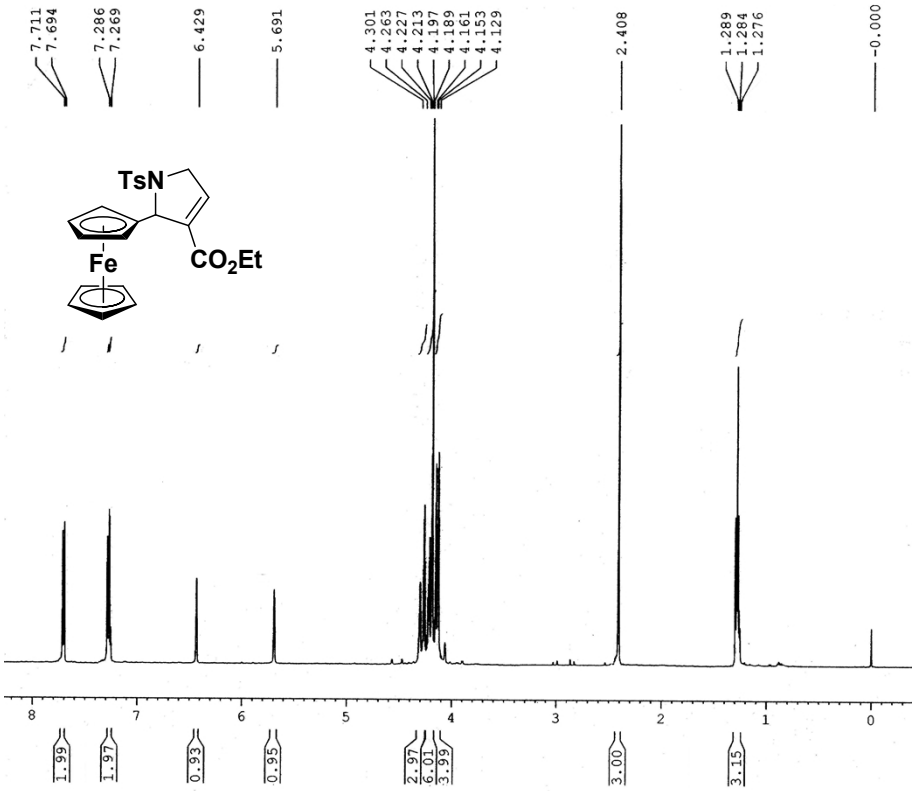

**$^{1}$H- $^{1}$H -COSY spectrum of Compound 12**



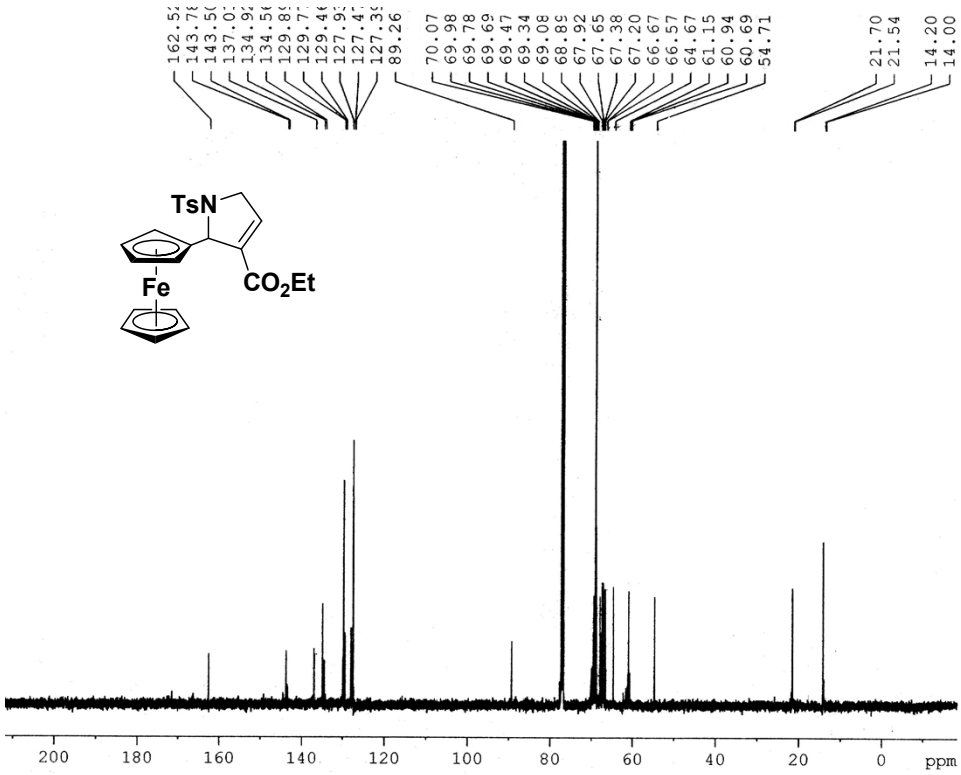
**$^{13}$C NMR spectrum of Compound 12**



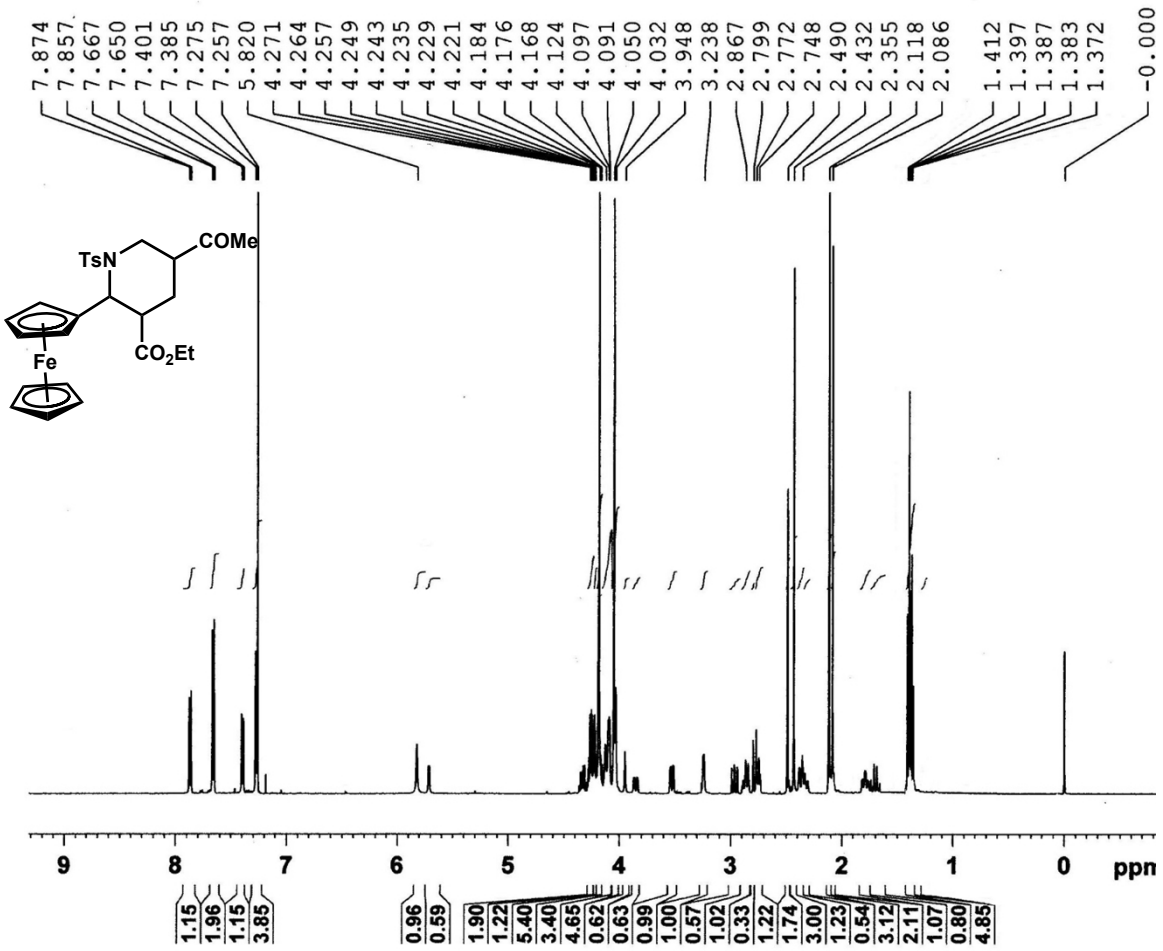
**$^{1}$H NMR spectrum of Compound 13**



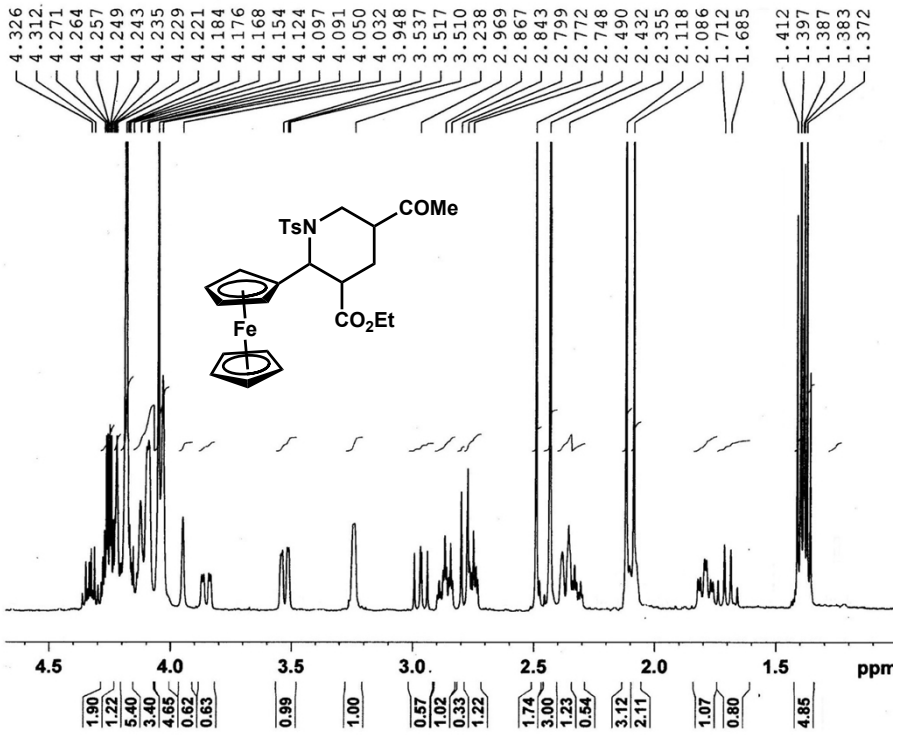

**$^{13}$C NMR spectrum of Compound 13**



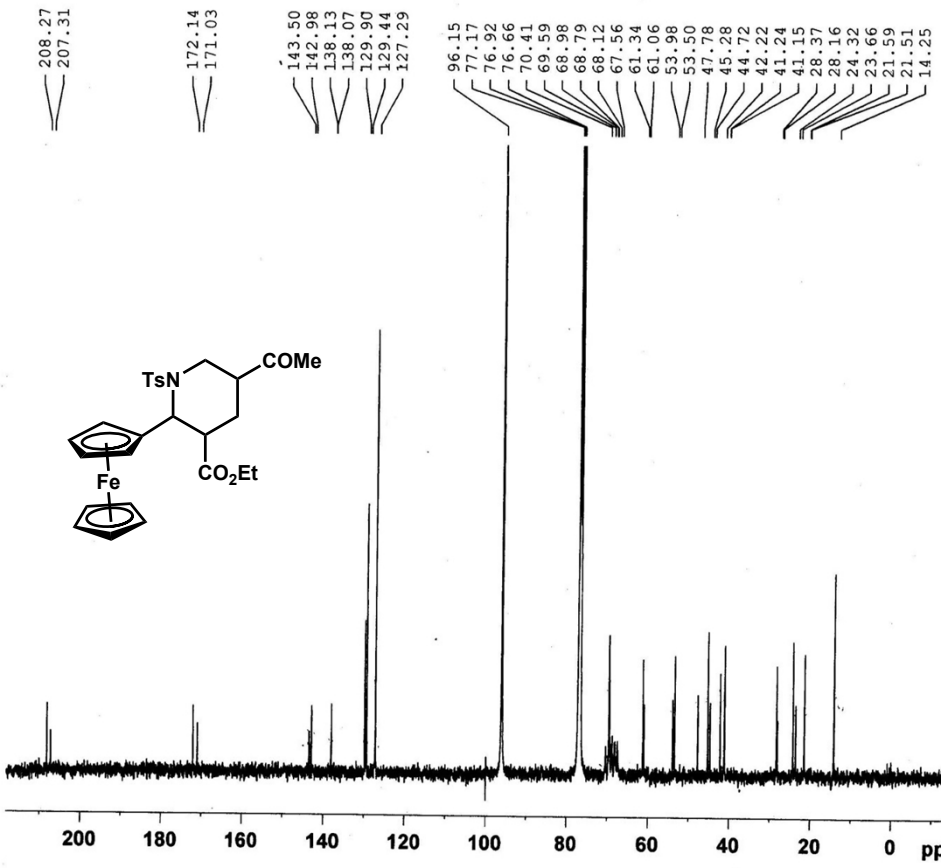
**$^{1}$ H NMR spectrum of Compound 14**



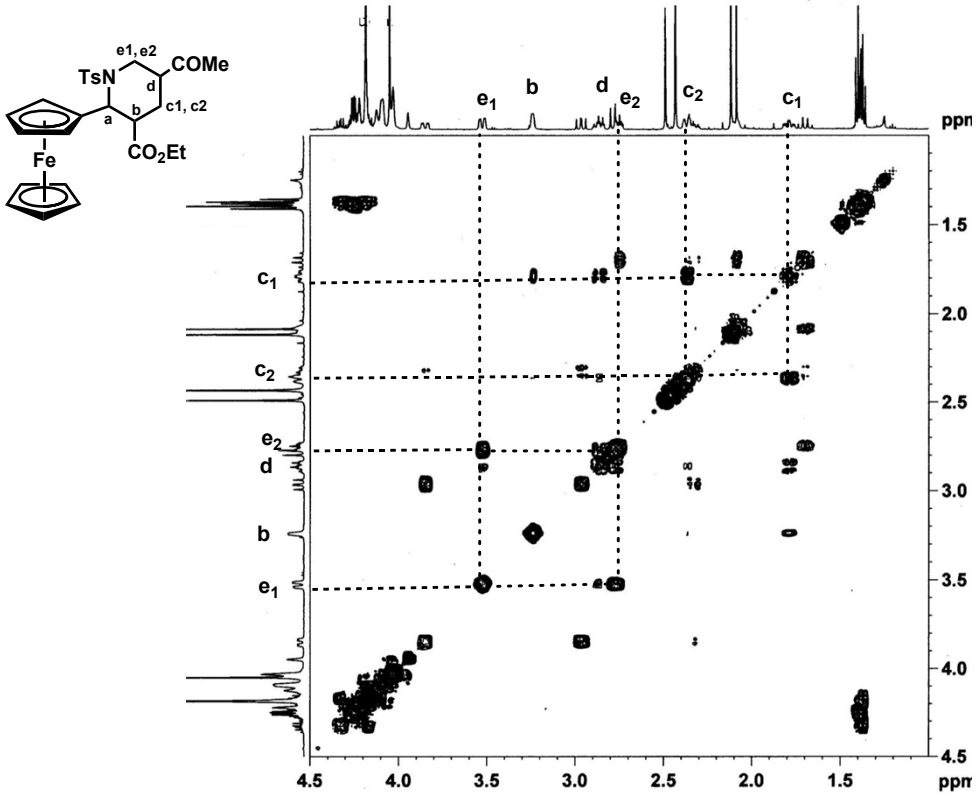
**[1]HNMR spectrum (expansion) of Compound 14**



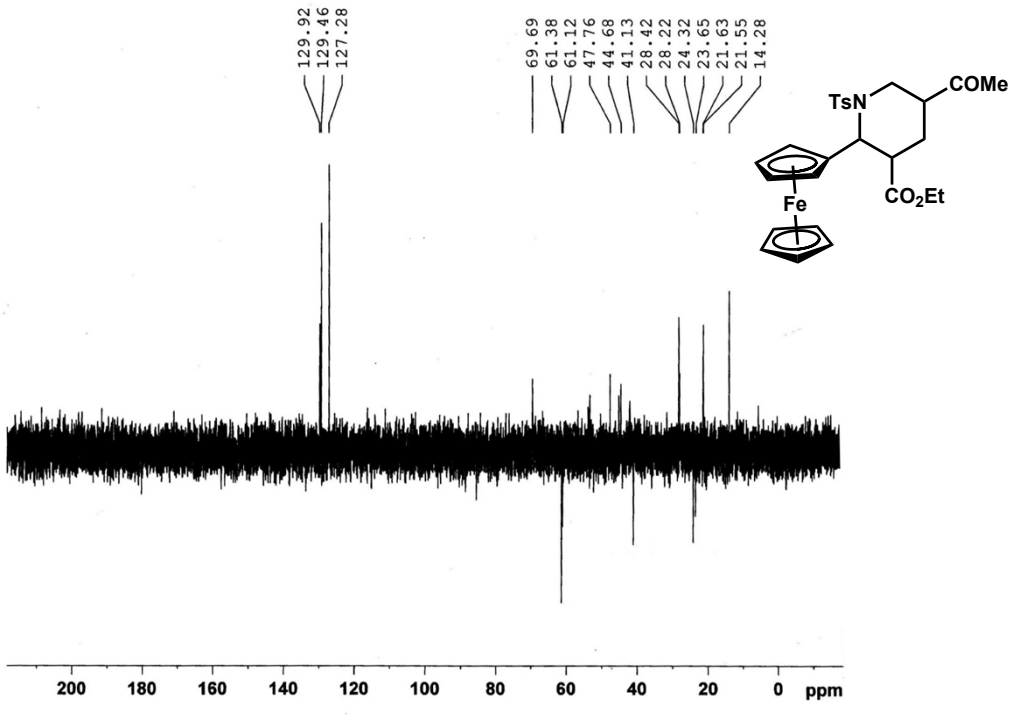

**[13]C NMR spectrum of Compound 14**



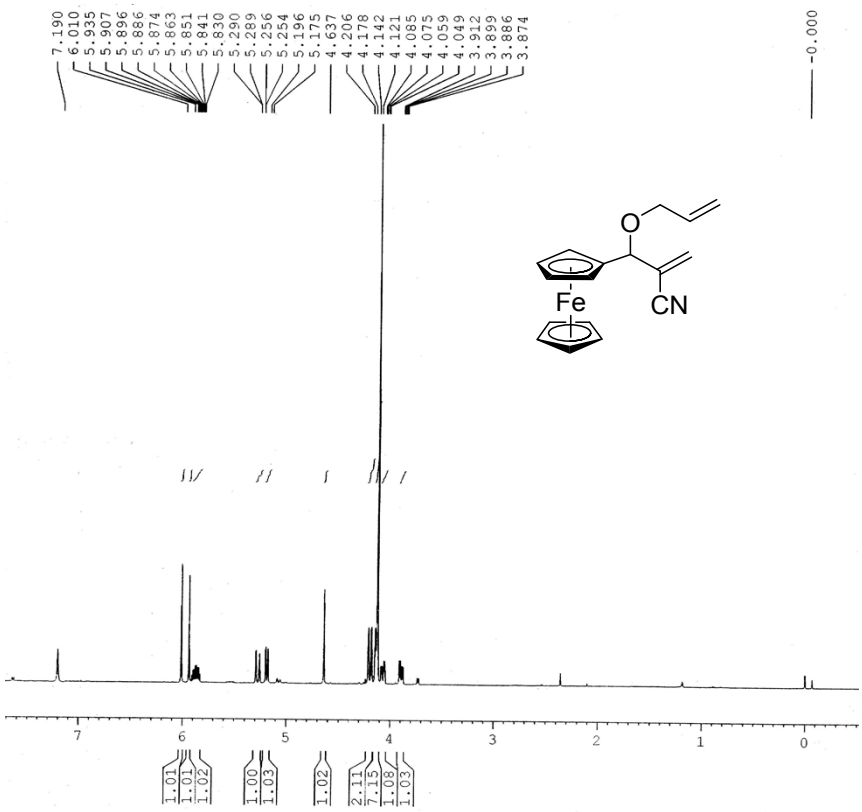
**$^{1}$H-$^{1}$H COSY spectrum (expansion) of Compound 14**



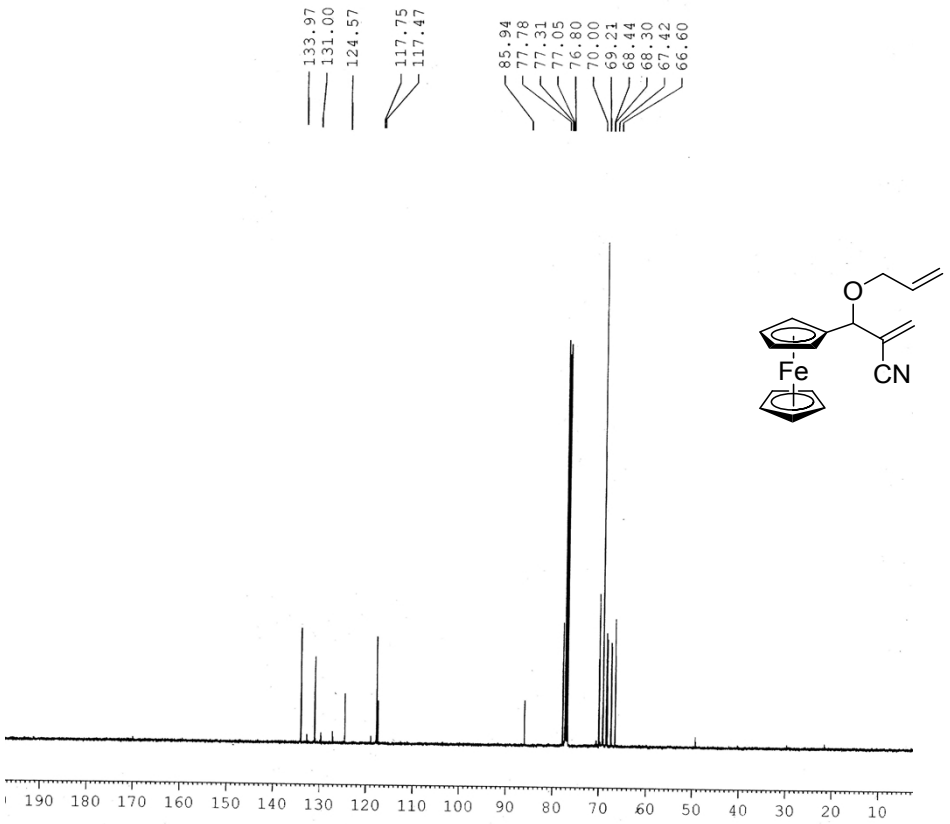

**DEPT- 135 spectrum (expansion) of Compound 14**



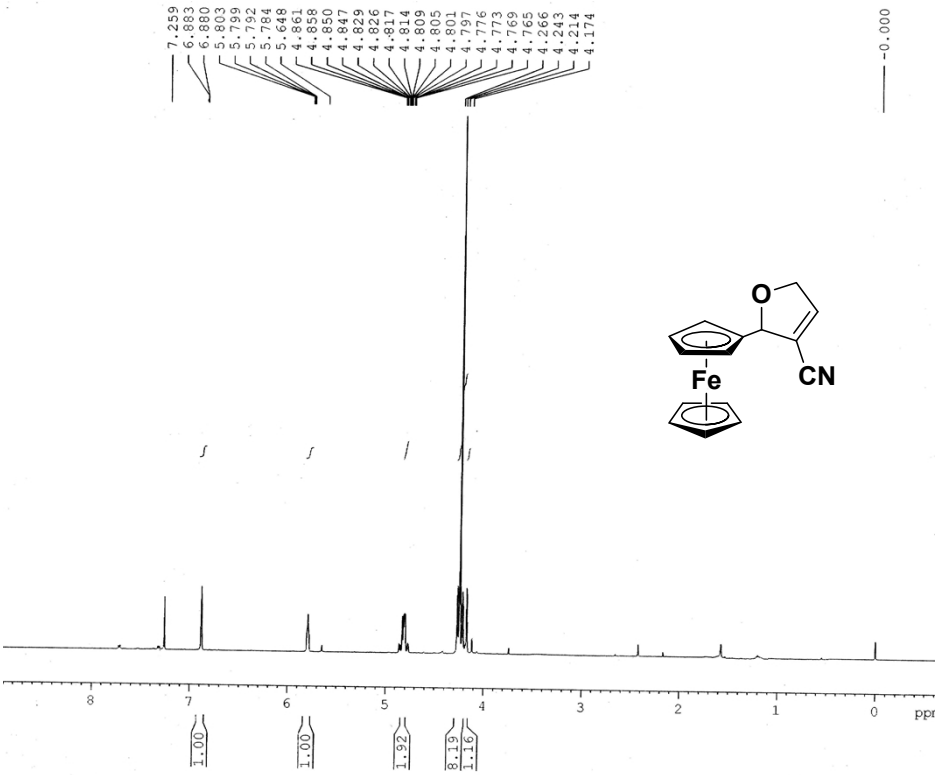
**$^{1}$H NMR spectrum of Compound 15**



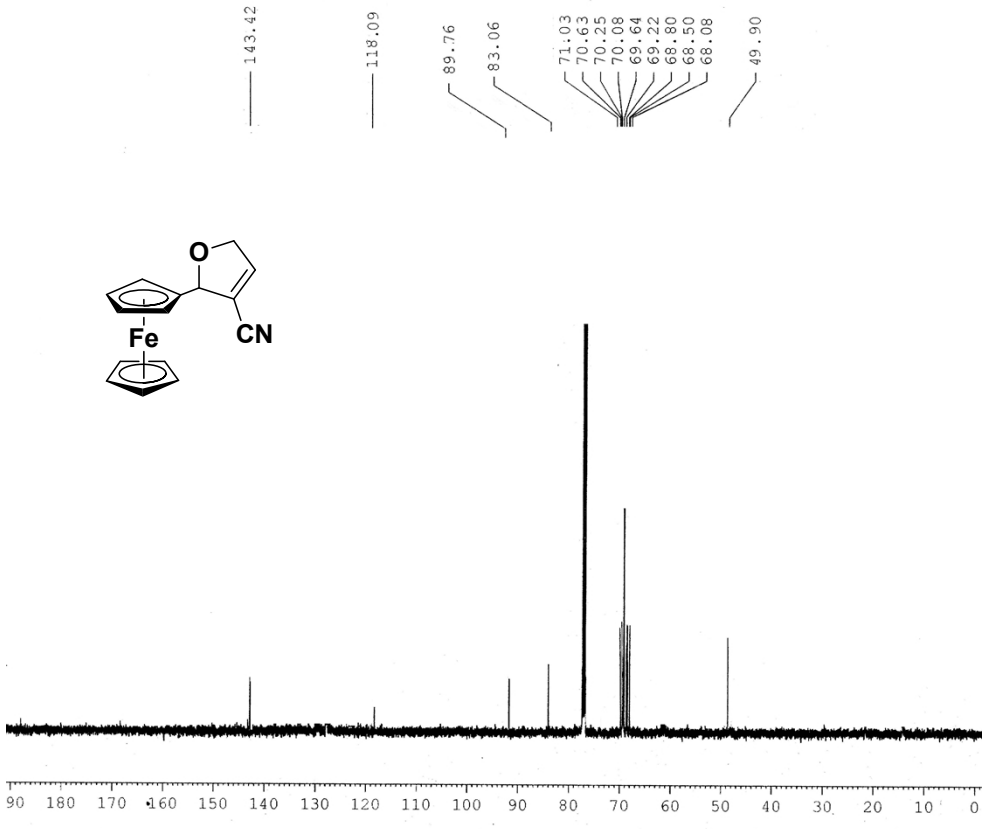

**$^{13}$C NMR spectrum of Compound 15**



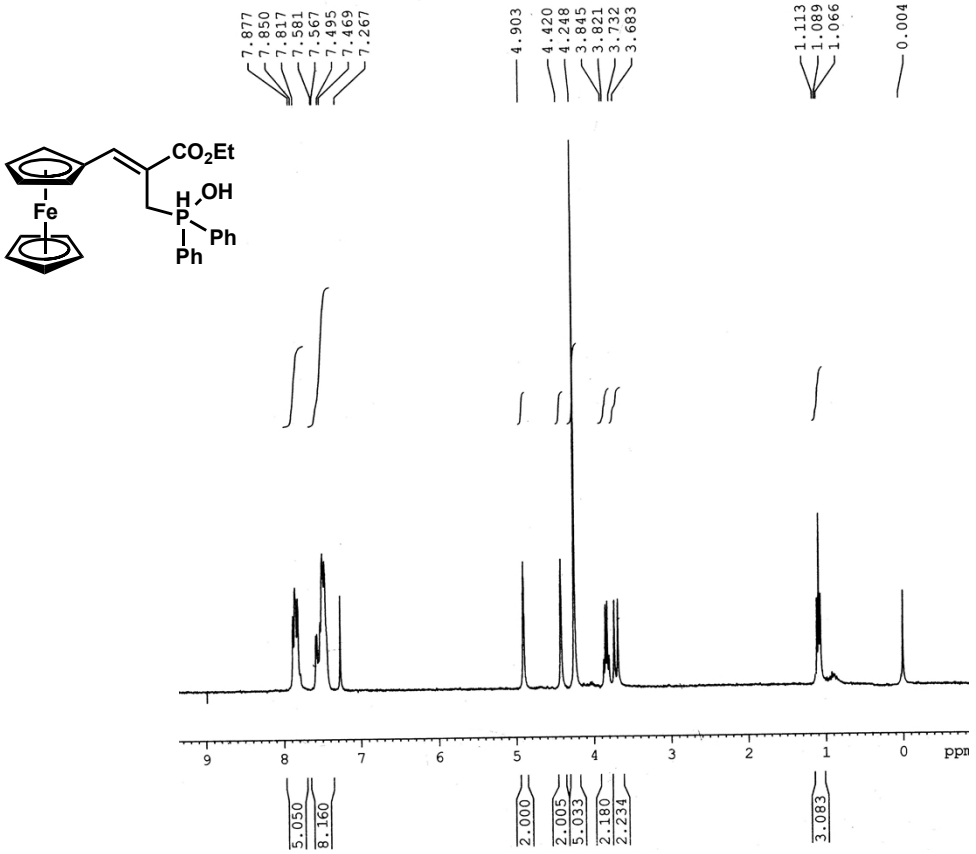
**$^{1}$ H NMR spectrum of Compound 16**



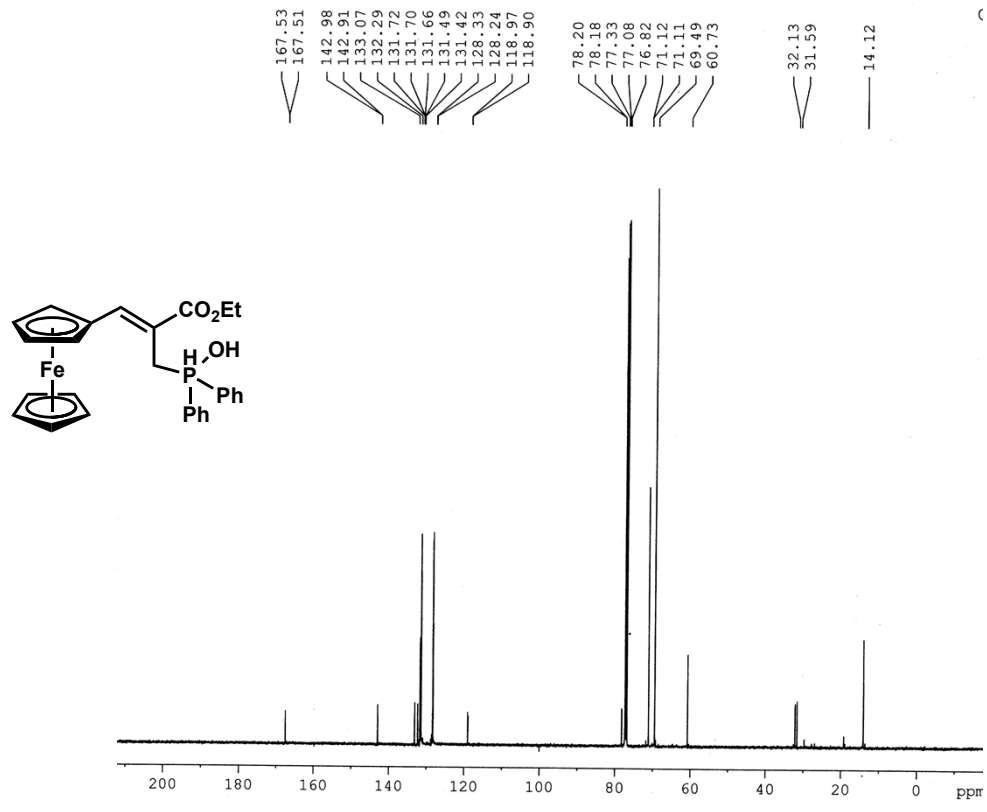

**$^{13}$ C NMR spectrum of Compound 16**



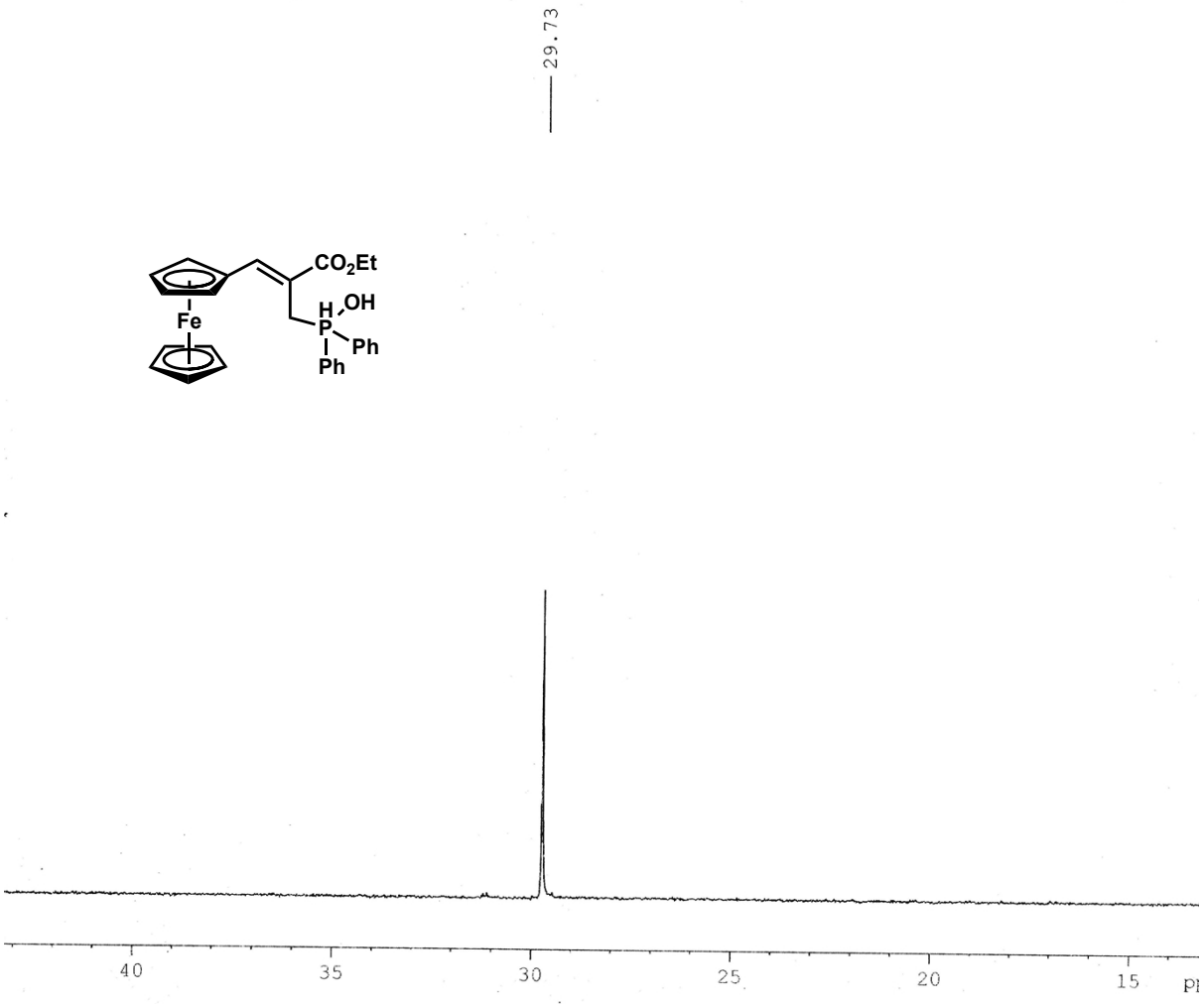
**$^{1}$ H NMR spectrum of Compound 19**



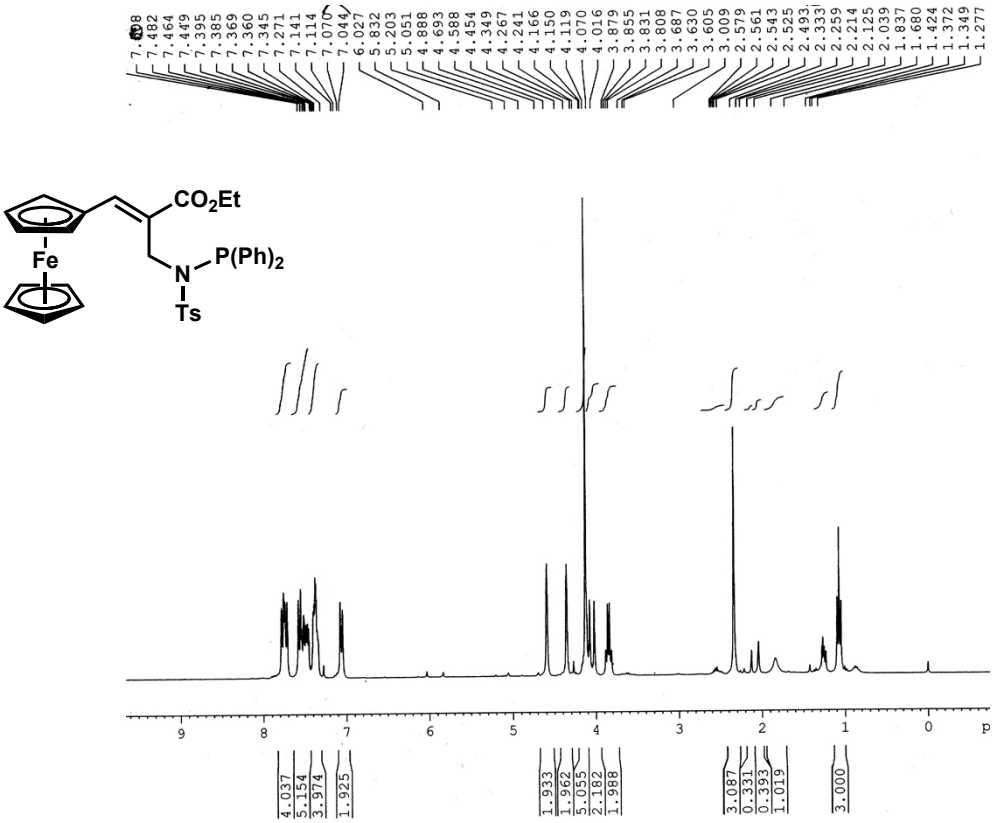

**$^{13}$ C NMR spectrum of Compound 19**



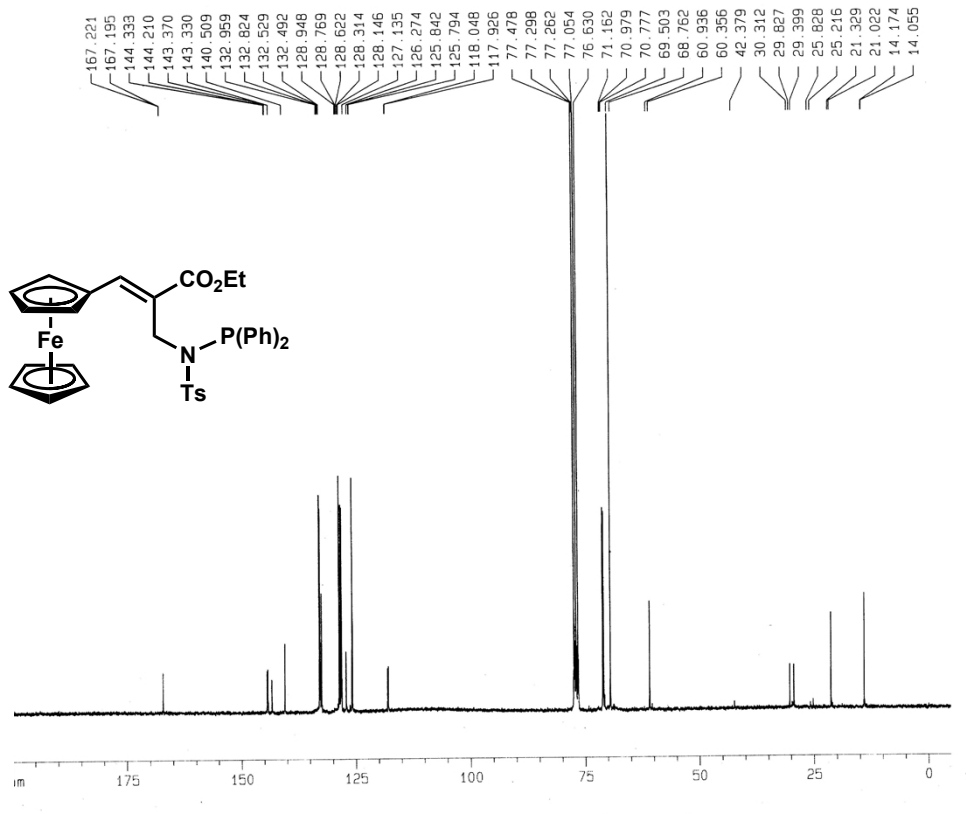
**$^{31}$ P NMR spectrum of Compound 19**



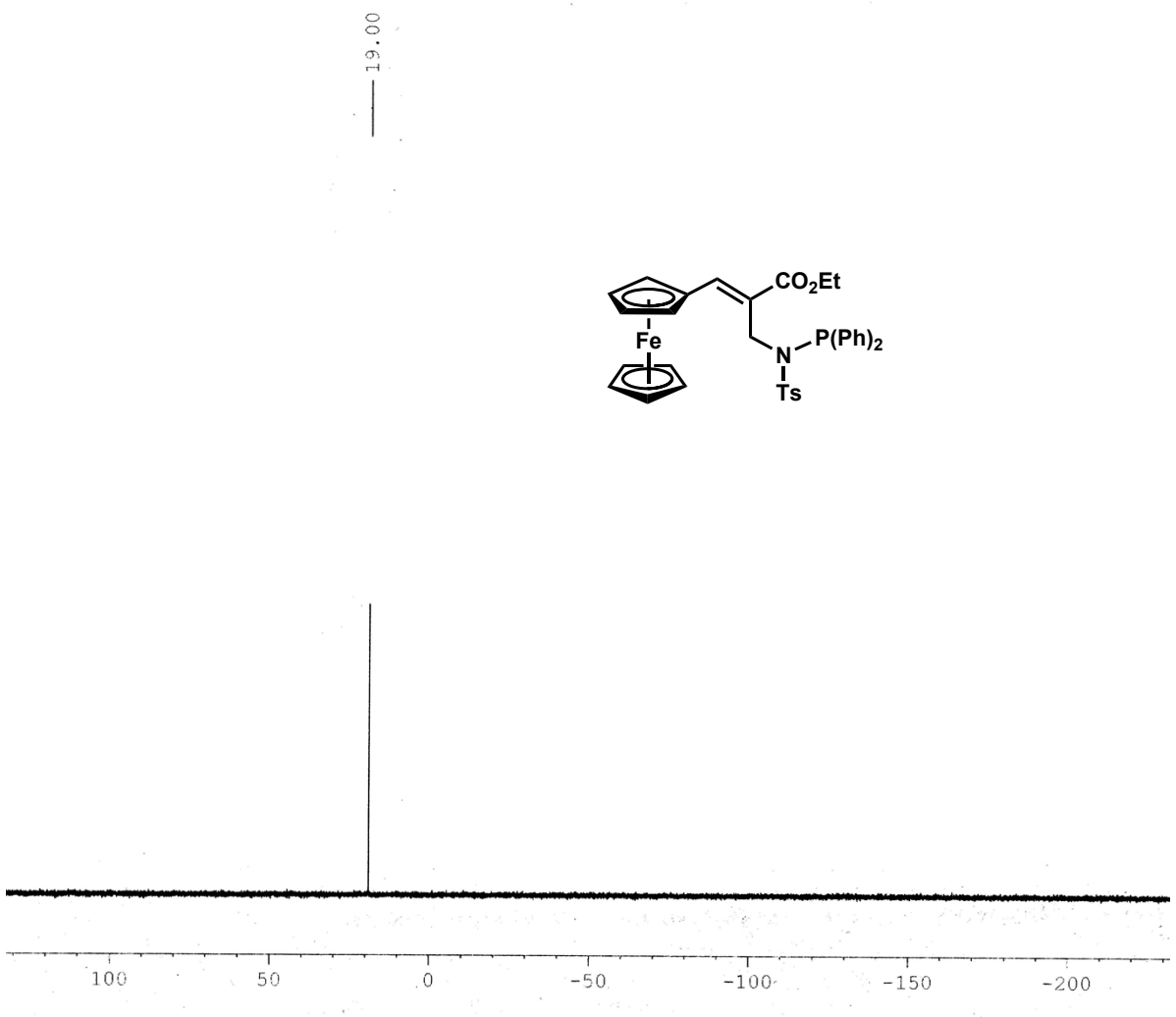
**$^{1}$ H NMR spectrum of Compound 21**



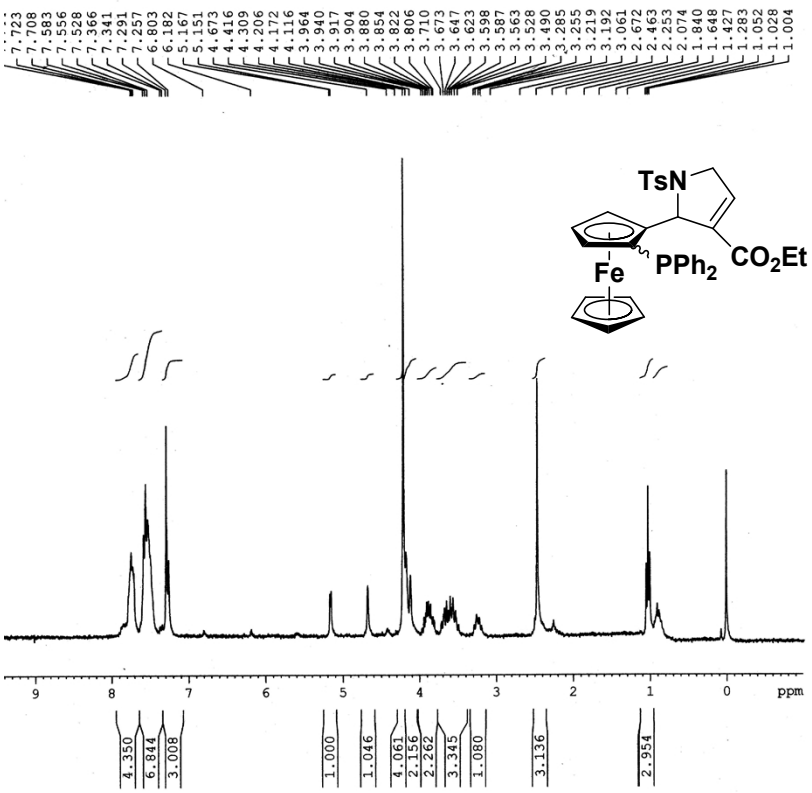

**$^{13}$ C NMR spectrum of Compound 21**



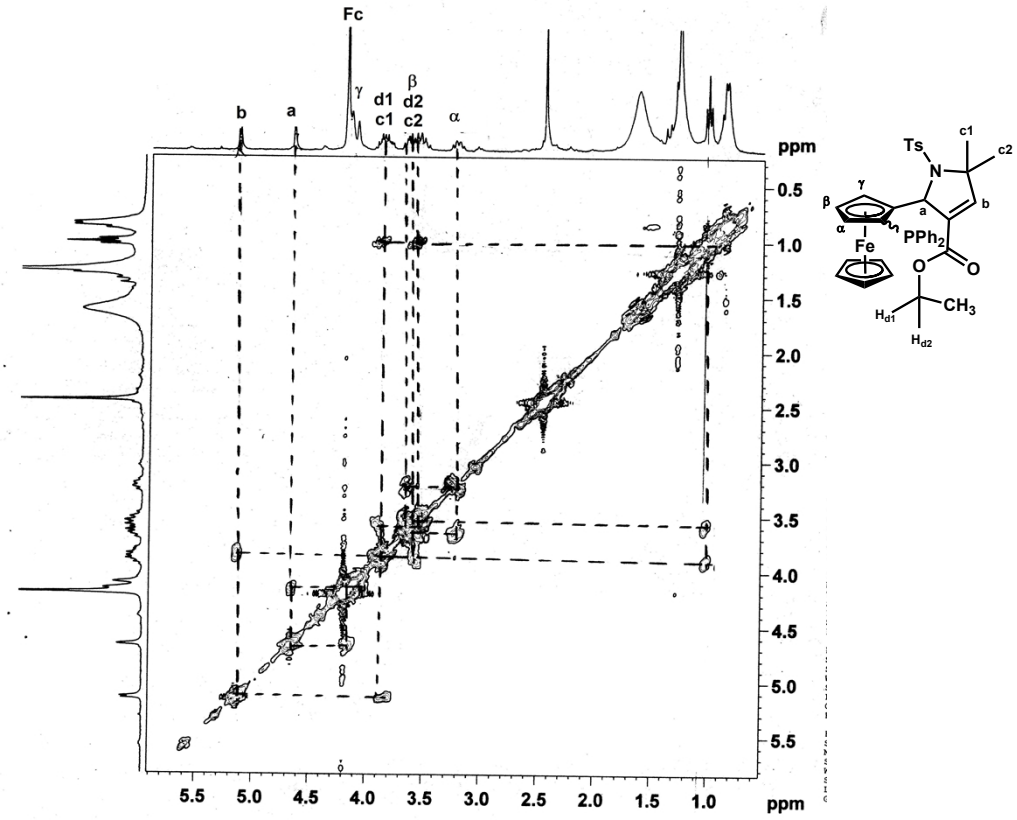
**$^{31}$ P NMR spectrum of Compound 21**



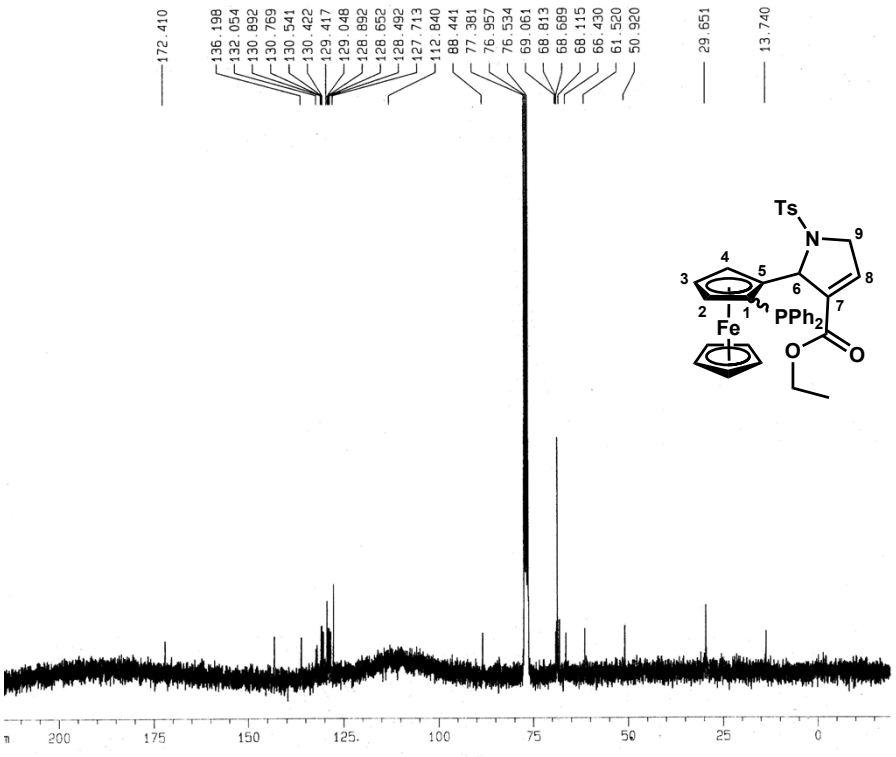
**$^{1}$ H NMR spectrum of Compound 22**



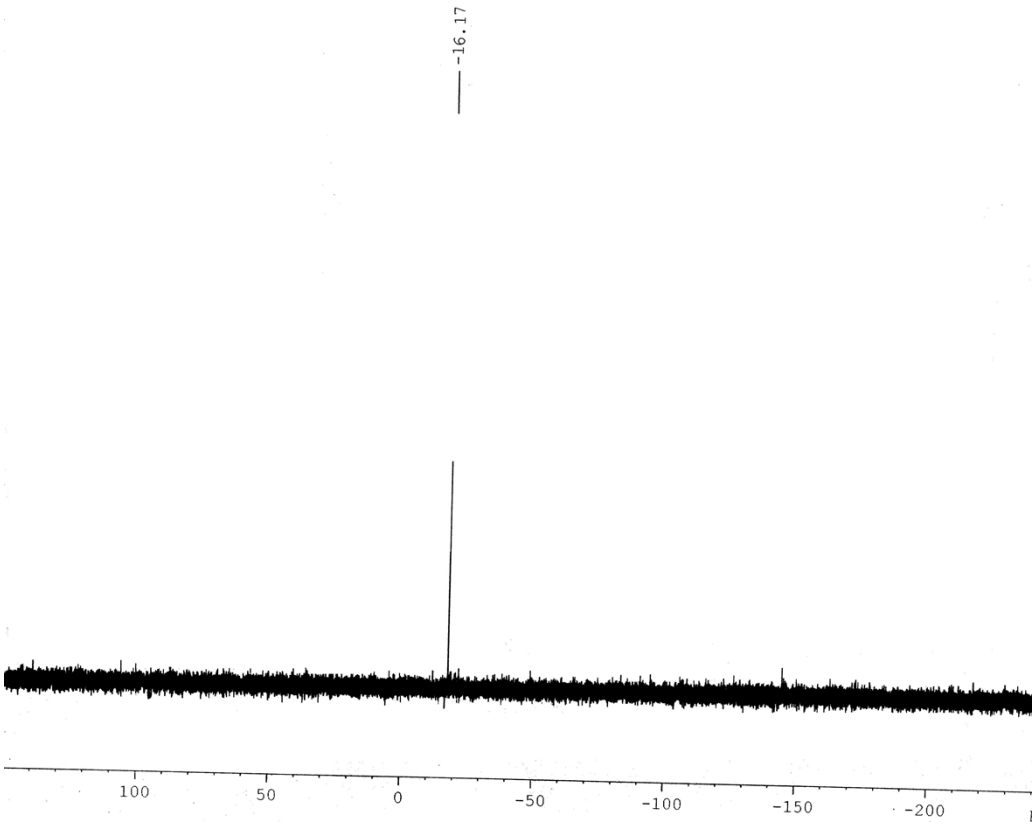

**$^{1}$H-$^{1}$H COSY spectrum (expansion) of Compound 22**



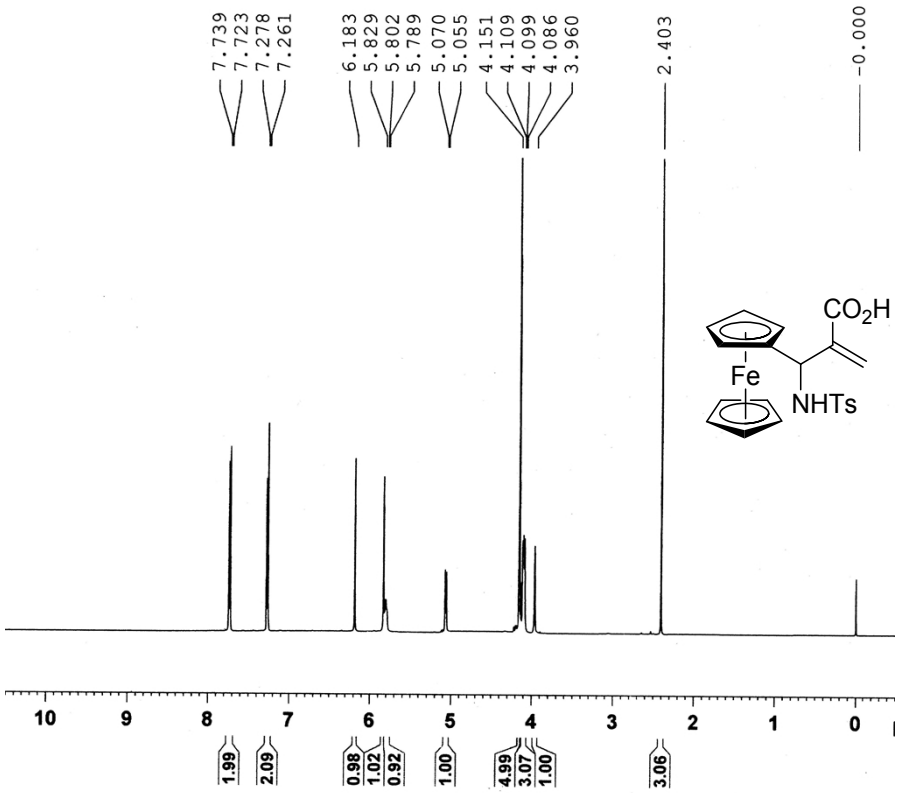
**$^{13}$ C NMR spectrum of Compound 22**



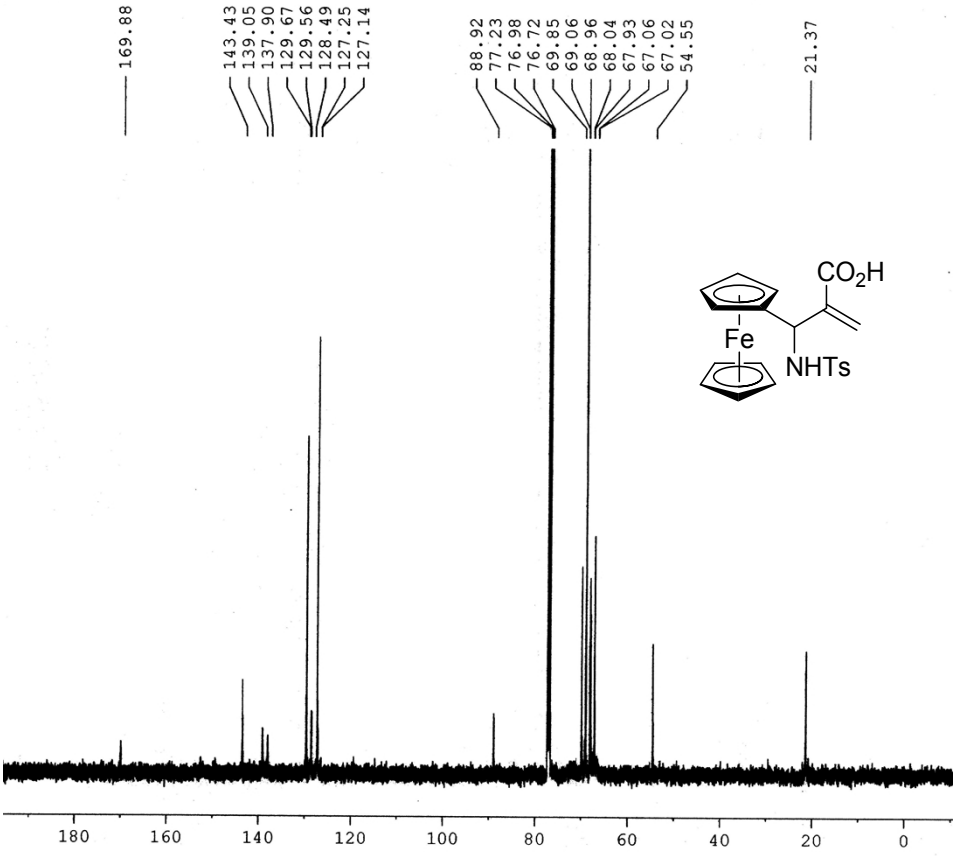

**$^{31}$ P NMR spectrum of Compound 22**



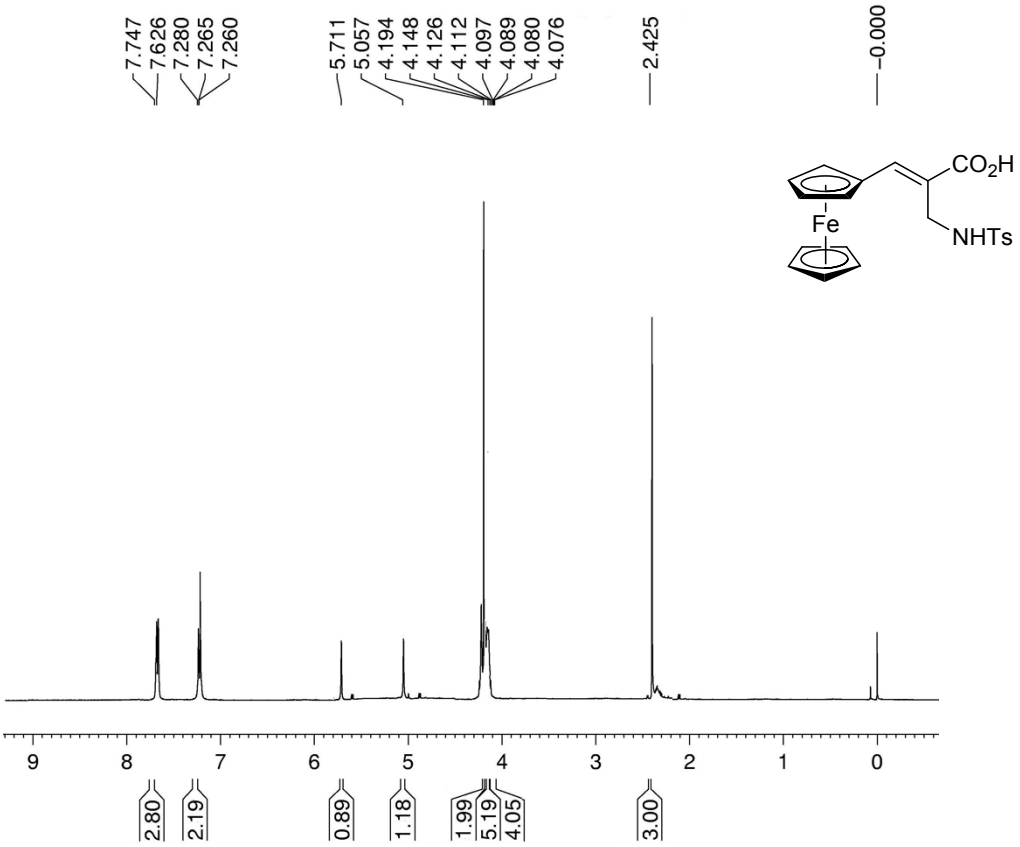
**$^{1}$H NMR spectrum of Compound 23**



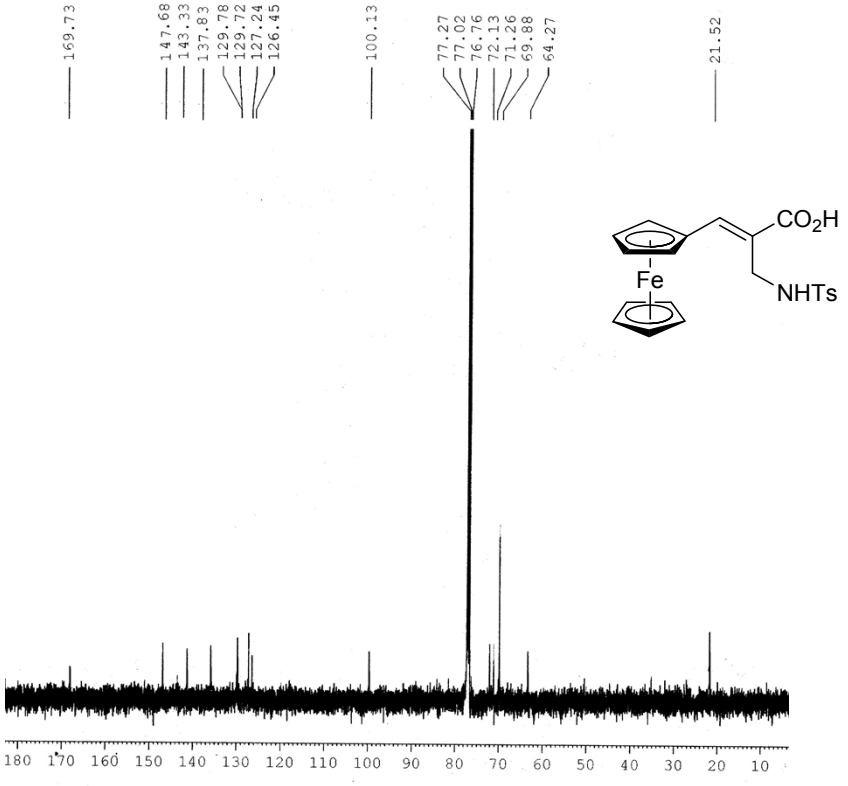

**$^{13}$C NMR spectrum of Compound 23**



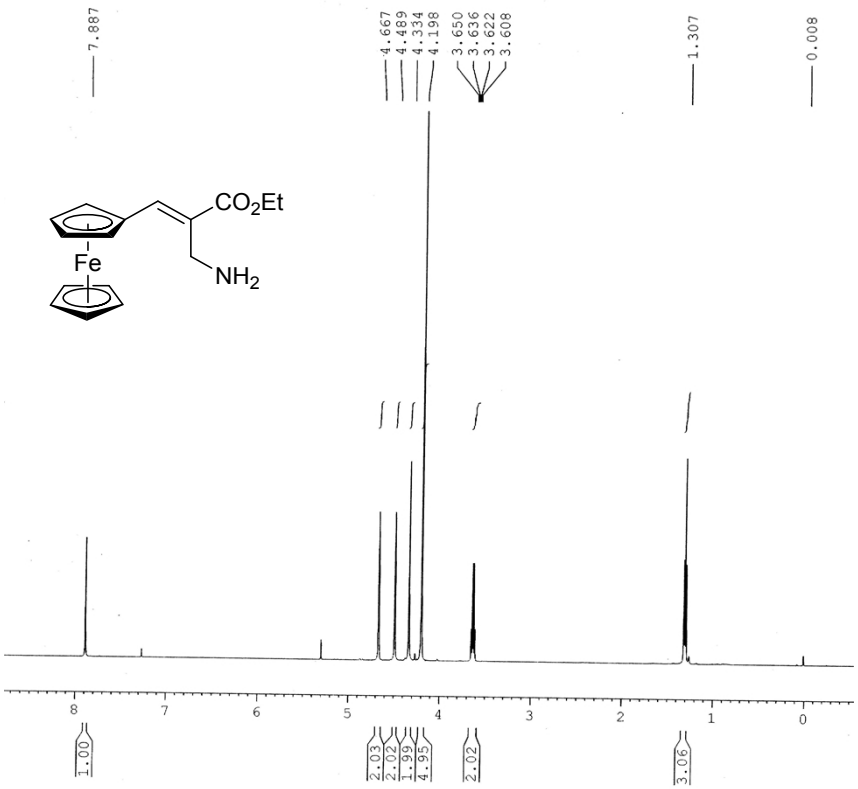
**$^{1}$ H NMR spectrum of Compound 24**



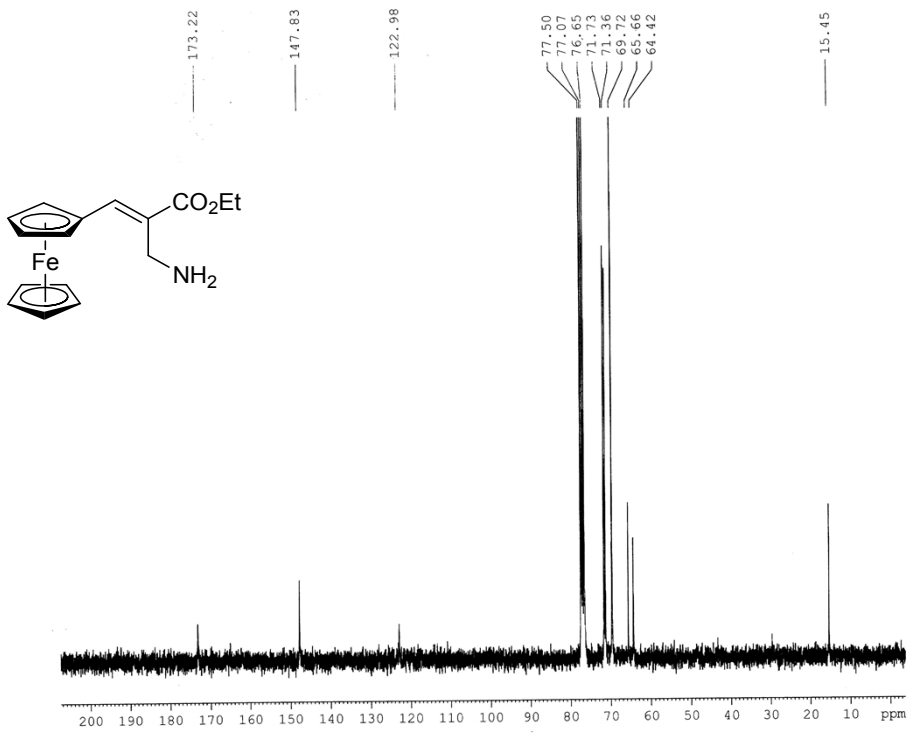

**$^{13}$ C NMR spectrum of Compound 24**



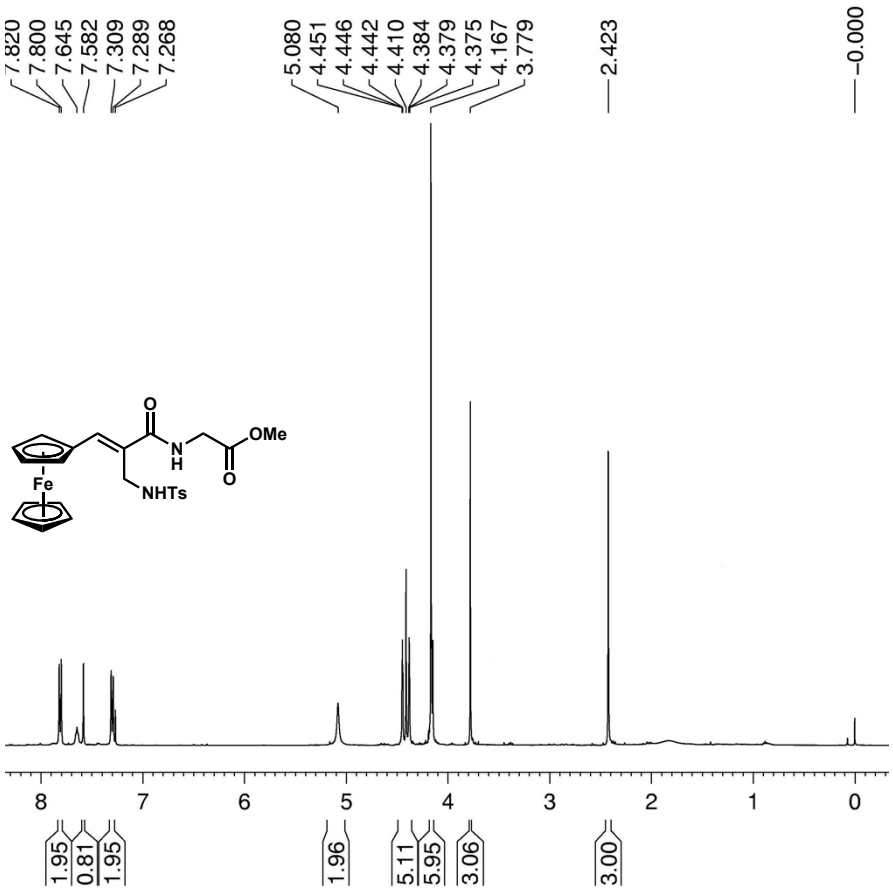
**$^{1}$ H NMR spectrum of Compound 25**



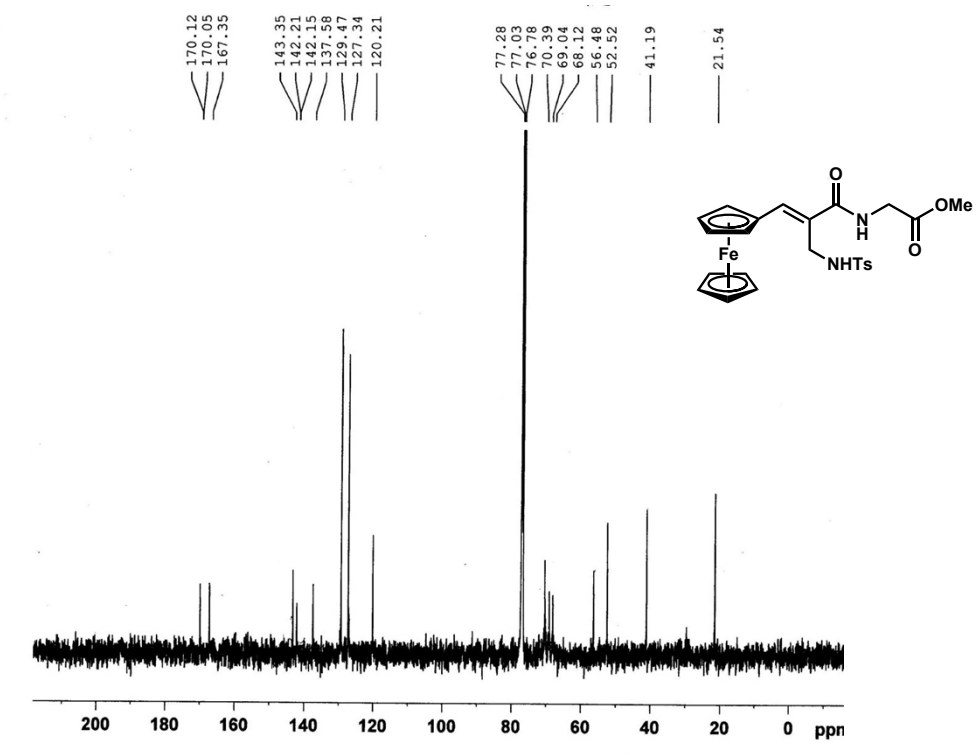

**$^{13}$ C NMR spectrum of Compound 25**



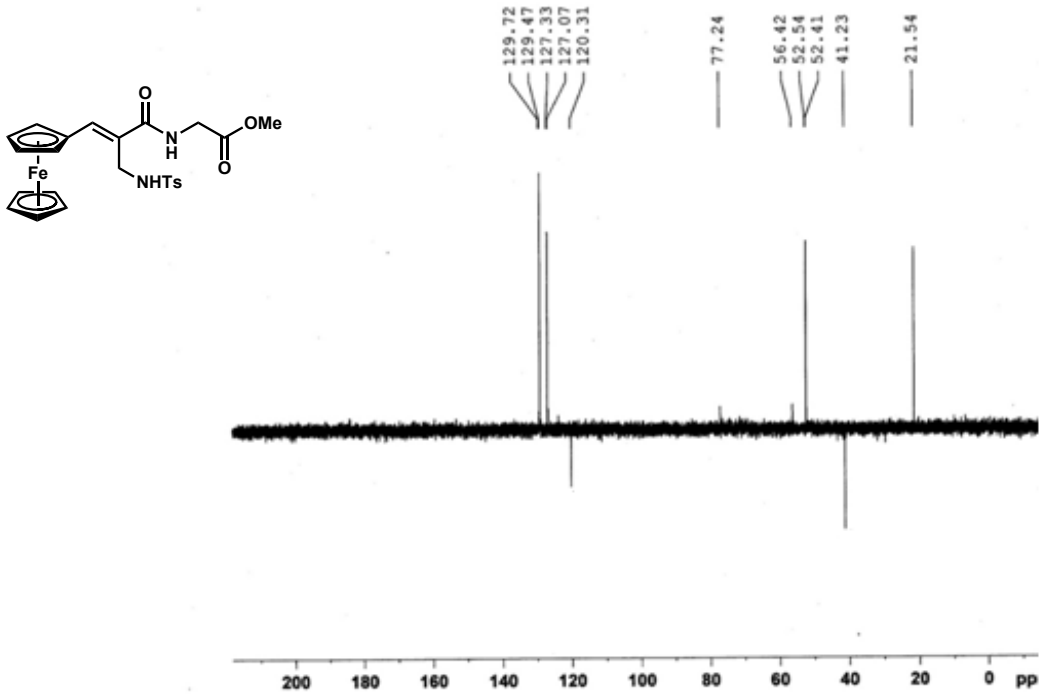
**$^{1}$ H NMR spectrum of Compound 26**



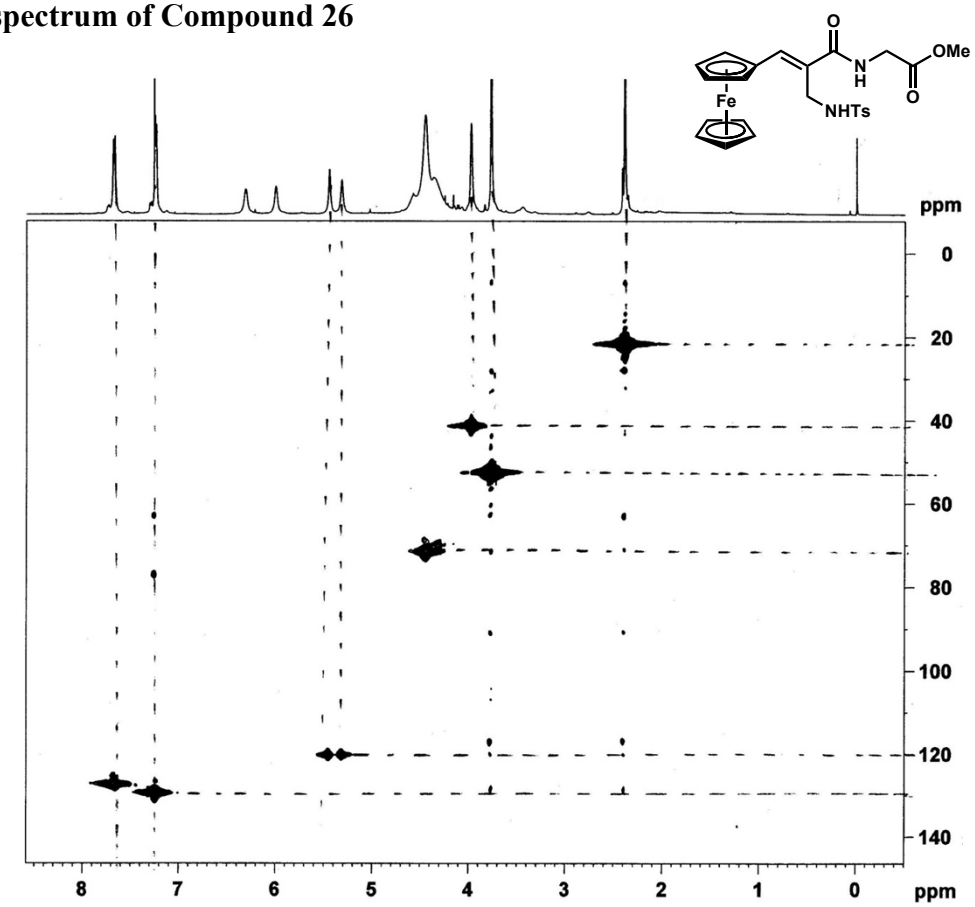

**$^{13}$ C NMR spectrum of Compound 26**



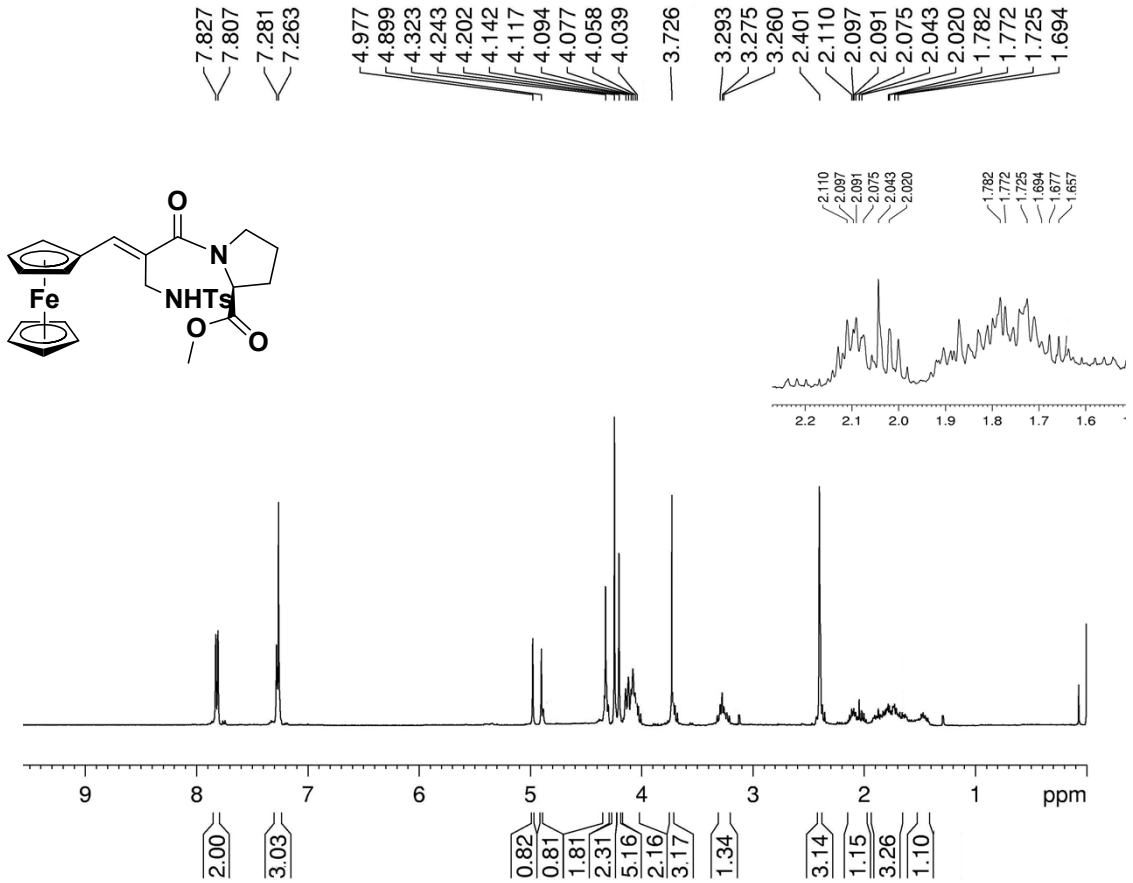
**DEPT-135 NMR spectrum of Compound 26**



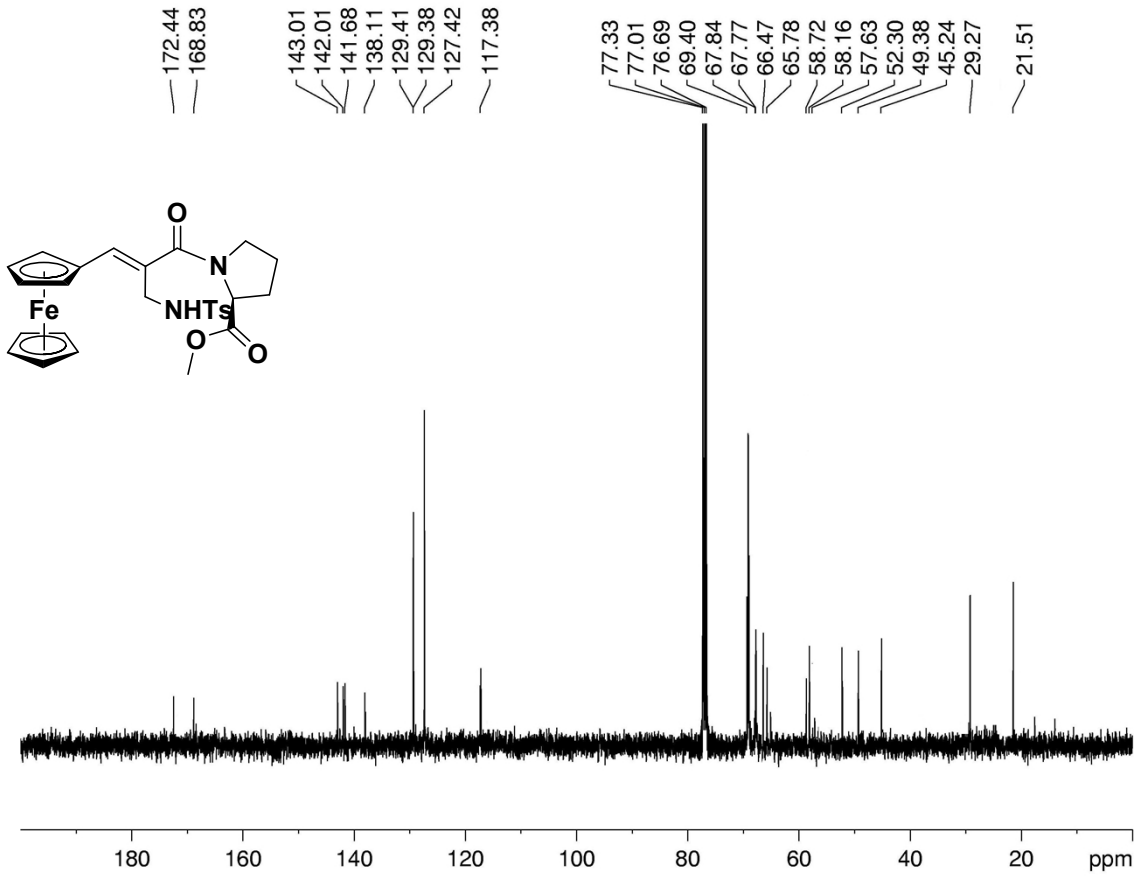

**HMQC spectrum of Compound 26**



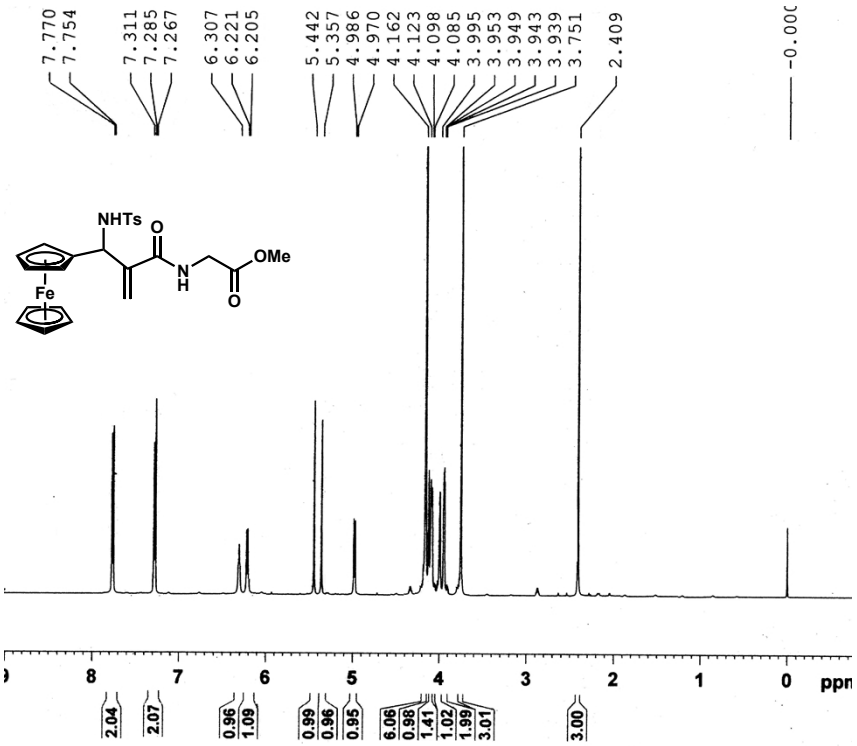
**[1]HNMR spectrum of Compound 27**



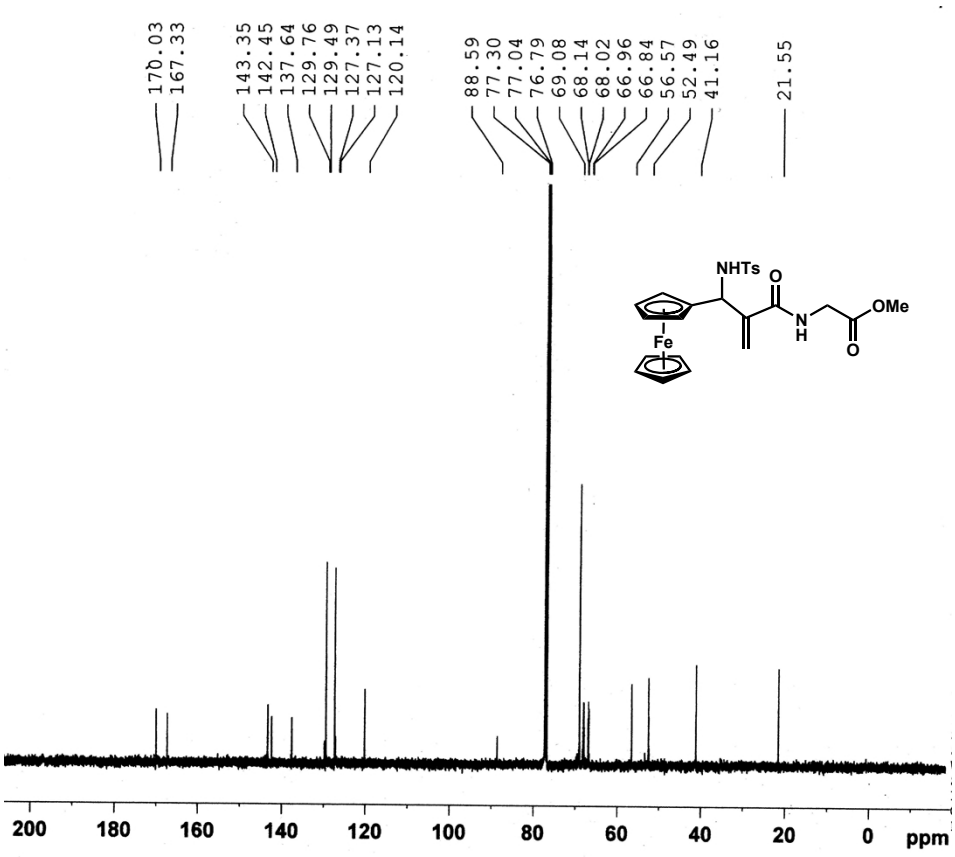

**[13]C NMR spectrum of Compound 27**



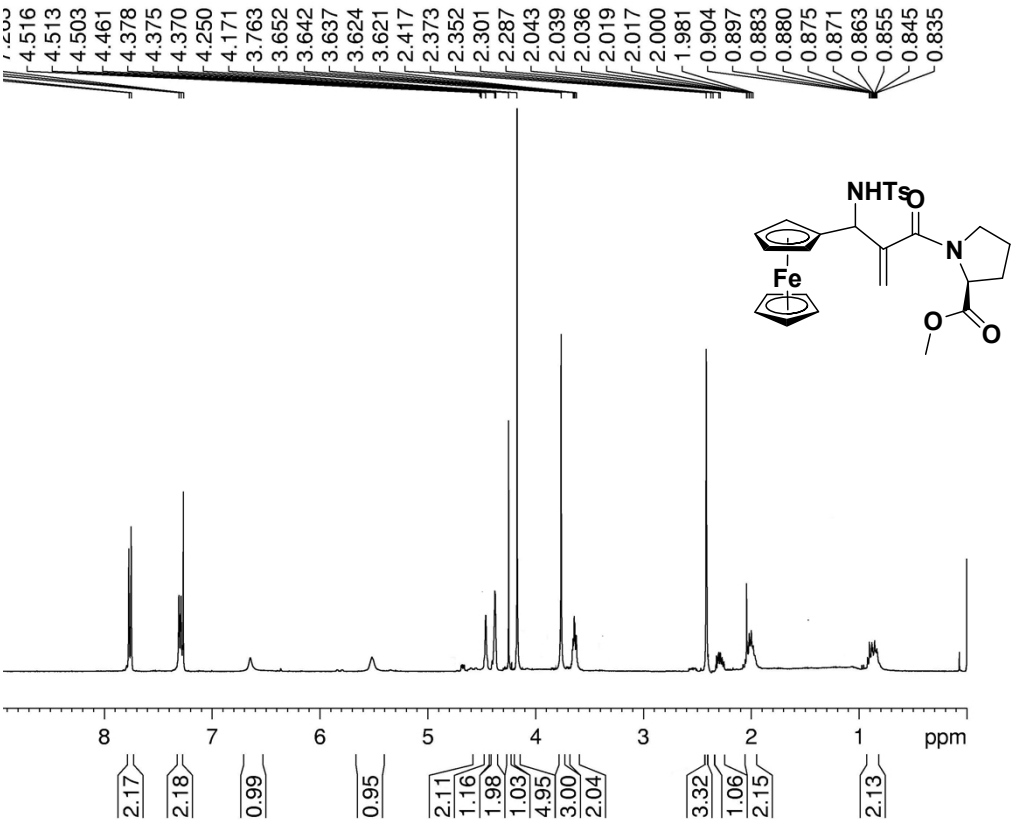
**[1]HNMR spectrum of Compound 28**



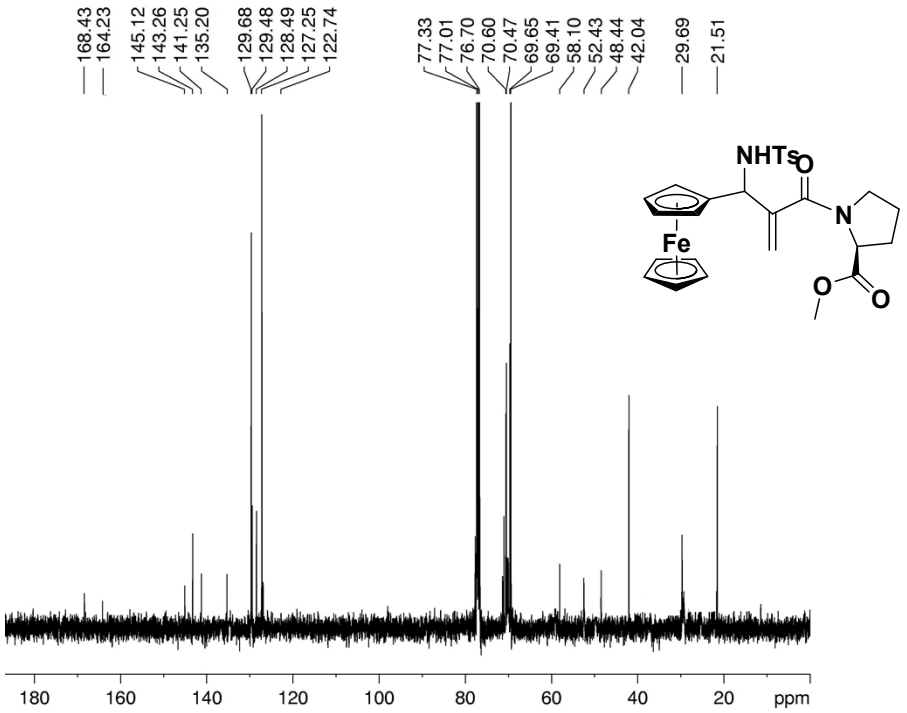

**[13]C NMR spectrum of Compound 28**



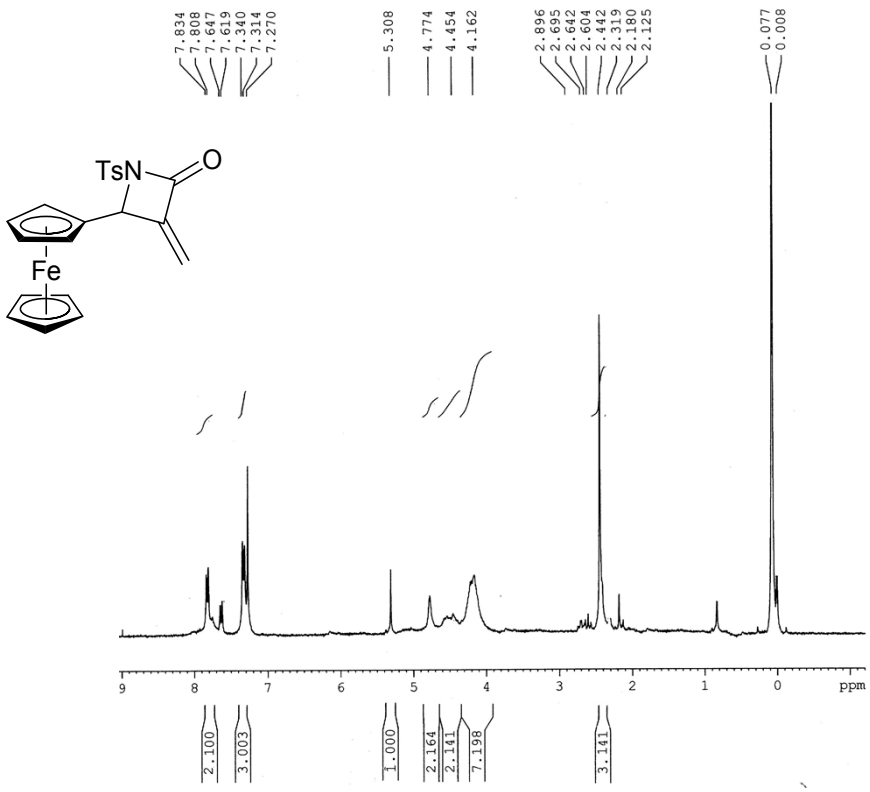
**[1]HNMR spectrum of Compound 29**




**[13]C NMR spectrum of Compound 29**



**$^{1}$H NMR spectrum of Compound 30**




**$^{13}$C NMR spectrum of Compound 30**