Supporting Information

Amide-Directed Cobalt(III)-Catalyzed C–H Amidation of Ferrocenes

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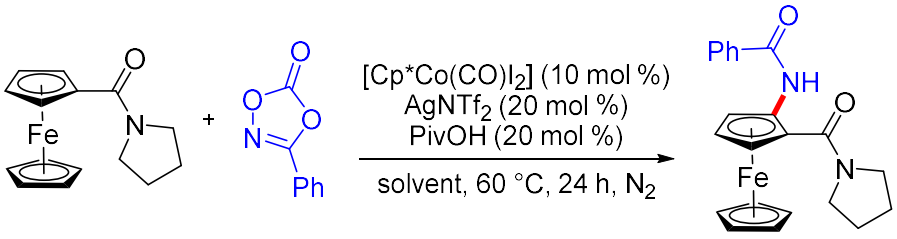
1. General Information

All commercially available chemicals were used as received without further purification, unless otherwise stated. All the reactions were carried out under nitrogen atmosphere under standard conditions. 3-Substituted-1,4,2-dioxazol-5-ones (**2**)[1], [Cp *$Co(CO)I_2$][2], were prepared according to the literature. **2a-2q** are known compounds.[1] NMR spectra were recorded on a Bruke Avance operating for ^1H NMR at 400 MHz, ^{13}C NMR at 101 MHz, ^{19}F NMR at 376 MHz, using TMS as internal standard. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^1H NMR, 77.36 ppm for ^{13}C NMR).The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd =doublet of doublet, m = multiplet. Coupling constants, *J*, were reported in hertz (Hz). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument using EI ionization and ESI ionization.

2 Experimental Section.

2.1 Optimization of the Reaction Conditions.

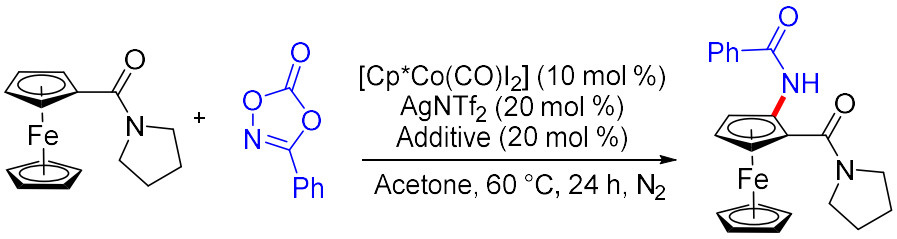


1a **2a** **3a**

Table S1 Screening of Solvent[a]

entry	solvent	yield (%)[b]
1	dioxane	62
2	DCE	55
3	ethyl acetate	64
4	THF	60
5	cyclohexane	51
6	dichloromethane	55
7	methyl acetate	64
8	toluene	54[c]
9	acetone	74 (73 [c])
10	DMF	0
11	DMSO	0
12	CH_3CN	0
13	TFE	0
14	MeOH	0

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), [Cp*Co(CO)I_2] (0.01 mmol, 10 mol %), $AgNTf_2$ (0.02 mmol), PivOH (0.02 mmol), dry solvent (1.0 mL), 60 °C, 24 h. [b]^{1}H NMR yield using mesitylene as the internal standard. [c]Isolated yield.

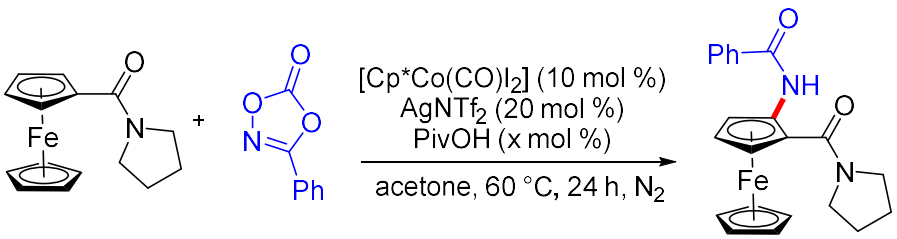


1a **2a** **3a**

Table S2 Optimization of the Reaction Additive[a]

entry	additive	yield (%)[b]
1	PivOH	74
2	PhCOOH	36
3	1-adamantanecarboxylic acid	46
4	CH_3COOH	47
5	PivONa	54
6	CH_3COONa	27
7	$NaHCO_3$	43

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), [Cp*Co(CO)I_2] (0.01 mmol, 10 mol %), $AgNTf_2$ (0.02 mmol), additive (0.02 mmol), dry acetone (1.0 mL), 60 °C, 24 h. [b]^{1}H NMR yield using mesitylene as the internal standard.

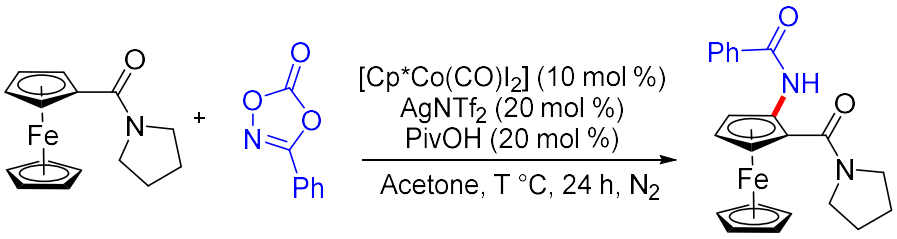


1a **2a** **3a**

Table S3 Optimization of the Equivalent of PivOH.[a]

entry	PivOH(x-mol %)	yield (%)[b]
1	0	14
2	20	74
3	40	41
4	60	30
5	80	28

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), [Cp*Co(CO)I_2] (0.01 mmol, 10 mol %), $AgNTf_2$ (0.02 mmol), PivOH (x - mol %), dry acetone (1.0 mL), 60 °C, 24 h. [b]^{1}H NMR yield using mesitylene as the internal standard.



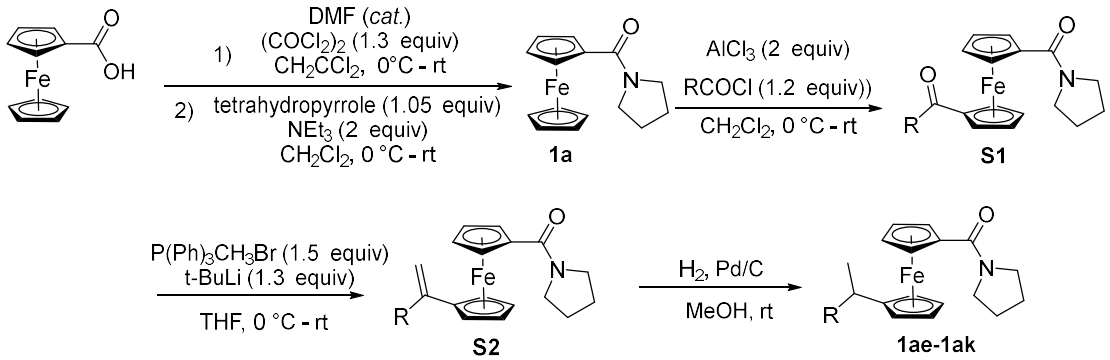
1a **2a** **3a**

Table S4 Optimization of the Temperature.[a]

entry	temp/ ºC	yield (%)[b]
1	25	36
2	40	70
3	60	74
4	60[c]	42
5	80	64

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), [Cp*Co(CO)I_2] (0.01 mmol, 10 mol %), $AgNTf_2$ (0.02 mmol), PivOH (0.02 mmol), dry acetone (1.0 mL), T °C, 24 h. [b]^{1}H NMR yield using mesitylene as the internal standard. [c][Cp*Co(CO)I_2] (5 mol %).

2.2 General Procedure for Synthesis of Ferrocene Carboxamides

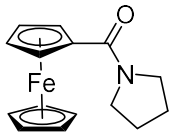


Oxalyl chloride was added to a suspension of ferrocenecarboxylic acid and DMF in CH_2Cl_2 dropwise at 0 ºC and the resulting mixture was stirred at room temperature for additional 1 h and a clear solution was formed. The volatile liquid was removed by evaporation and dried under vacuum to get a crude acid chloride. The above acid chloride solution in CH_2Cl_2 was added to a mixture of tetrahydropyrrole and NEt_3 in CH_2Cl_2 at 0 ºC and stirred for additional 3 h at room temperature. The reaction was quenched by the addition of 1 M HCl and extracted with CH_2Cl_2 twice. The combined organic phase was washed with saturated solution of $NaHCO_3$ and dried by Na_2SO_4. After filtration the solvent was removed by evaporation, the crude ferrocenecarboxamide**(1a**) was obtain.

The acid chloride solution in CH_2Cl_2 was added to a mixture of ferrocenecarboxamide and $AlCl_3$ in CH_2Cl_2 at 0 ºC and stirred for additional 3 h at room temperature. The reaction was quenched by the addition of crushed ice and extracted with CH_2Cl_2 twice. The combined organic phase was washed with water and dried over Na_2SO_4. After filtration the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 2:1) to afford **S1**.

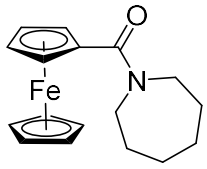
The *t*-BuLi was added to a suspension of methyltriphenyl- phosphonium bromide and dry THF at 0 ºC and then stirred for additional 0.5 h at room temperature until the suspension turn to yellow. And then a solution of **S1** in dry THF was injected into the above suspension 0ºC and then stirred for additional 3 h at room temperature. Inspection by TLC. The reaction was quenched by water, filtered through a pad of celite and then extracted with ethyl acetate three times. The combined organic phase was dried by Na_2SO_4. After filtration the solvent was removed by evaporation, and the resulting mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate = 4:1) to afford **S2.**

A suspension of **S2**, hydrogen, Pd/C and MeOH was stirred over night, the mixture filtered through a pad of celite and then purified by column chromatography on silica gel (hexanes/ethyl acetate = 8:1) to afford **1ae-1ak**.

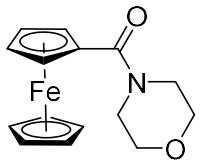


1-(pyrrolidine-1-carbonyl)ferrocene (1a). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 – 4.70 (m, 2H), 4.33 – 4.29 (m, 2H), 4.19 (s, 5H), 3.72 -

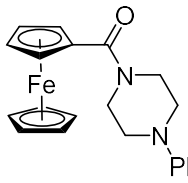
3.54 (m, 4H), 2.01 - 1.82(m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.44, 78.30, 70.58, 70.09, 69.86, 48.34, 47.34, 27.10, 24.27. HRMS (EI) Calculated for $C_{15}H_{17}FeNO$: 283.0660: found, 283.0663.



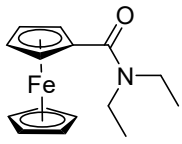
1-(azepane-1-carbonyl)ferrocene (1aa). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.59 (s, 2H), 4.37 - 4.07 (m, 7H), 3.82 -3.43 (m, 4H), 1.74 (s, 2H), 1.57 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.20, 79.17, 70.48, 69.73 , 69.21, 48.68, 47.02, 30.14, 27.91, 27.33 , 26.77 . HRMS (EI) Calculated for $C_{17}H_{21}FeNO$: 311.0973; found, 311.0971.



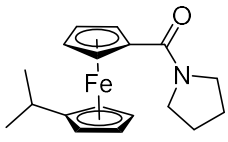
1-(morpholine-4-carbonyl)ferrocene(1ab). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 – 4.52 (m, 2H), 4.33 – 4.29 (m, 2H), 4.23 (s, 5H), 3.75 -3.71 (m, 4H), 3.70 - 3.64 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.95, 78.46, 70.47, 70.09, 69.44, 67.17, 45.47. HRMS (EI) Calculated for $C_{15}H_{17}FeNO_2$: 299.0609; found, 299.0608.



1-(4-phenylpiperazine-1-carbonyl)ferrocene (1ac). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 -7.24 (m, 2H), 6.96 - 6.86 (m, 1H), 4.61 - 4.55 (m, 1H), 4.35 - 4.30 (m, 2H), 4.25 (s, 5H), 3.93 – 3.84 (m, 4H), 3.23 – 3.15 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.95 , 151.24, 129.49, 120.64, 116.76, 78.73, 70.60, 70.15, 69.50, 49.93 . HRMS (EI) Calculated for $C_{21}H_{22}FeN_2O$: 374.1082; found 374.1083.

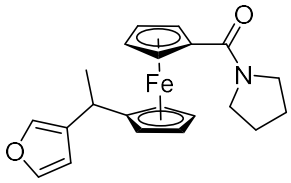


***N,N*-diethylferrocenecarboxamide (1ad),** Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 – 4.57 (m, 2H), 4.29 – 4.26 (m, 2H), 4.20 (s, 5H), 3.60 -3.40 (m, 4H), 1.19 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.87, 79.16, 70.56 , 70.02 , 69.56, 42.87, 41.16, 15.09 , 13.14. HRMS (EI) Calculated for $C_{15}H_{19}FeNO$: 285.0816; found, 285.0815.

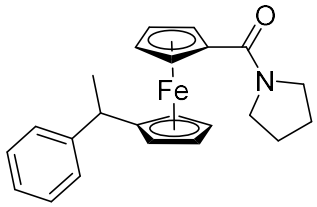


1-(pyrrolidine-1-carbonyl)-1'-isopropyl-ferrocene (1ae). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (s, 2H), 4.26 (s, 2H), 4.08

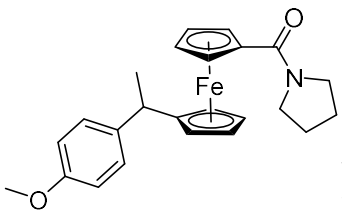
(d, J = 3.6 Hz, 4H), 3.72 - 3.47 (m, 4H), 2.70 – 2.50 (m, 1H), 2.05 - 1.76 (m, 4H), 1.15 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.44 , 98.39, 78.21, 70.92, 70.63, 69.05, 67.89, 48.38, 47.32, 27.50, 27.08, 24.29, 23.79. HRMS (EI) Calculated for $C_{18}H_{23}FeNO$: 325.1129; found, 325.1125.



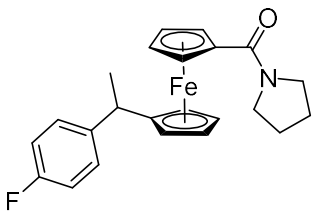
1-(pyrrolidine-1-carbonyl)-1'-(1-(furan-2-yl)ethyl)-ferrocene (1af). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{11}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.28 (dd, J = 2.8, 1.9 Hz, 1H), 5.96 (d, J = 3.2 Hz, 1H), 4.69 -4.66 (m, 1H), 4.66 - 4.65(m, 1H) 4.27 -4.22 (m, 2H), 4.17 -4.15(m, 1H), 4.15 - 4.10(m, 3H), 3.88 (q, J = 7.2 Hz, 1H), 3.69 – 3.55 (m, 4H), 2.99 – 1.85 (m, 4H), 1.55 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.29, 159.50, 140.88, 110.19, 104.27, 93.62, 78.49, 71.24, 71.02, 70.92, 70.88, 69.53, 69.32, 69.26, 68.23, 48.37, 47.28, 32.82, 27.02, 24.26, 20.11. HRMS (EI) Calculated for $C_{21}H_{23}FeNO_2$: 377.1078; found, 377.1080.



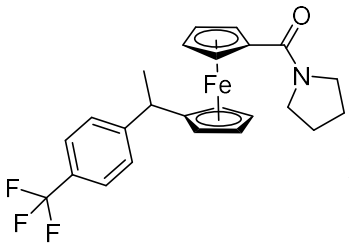
1-(pyrrolidine-1-carbonyl)-1'-(1-phenylethyl)-ferrocene (1ag). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.20 (m, 2H), 7.18 - 7.09 m, 3H), 4.70 (s, 1H), 6.67(s, 1H), 4.30 - 4.21 (m, 3H), 4.15 (s, 1H), 4.112(s, 1H), 3.98 (s, 1H), 3.86 (q, J = 7.1 Hz, 1H), 3.72 – 3.56 (m, 4H), 2.02 – 1.82 (m, 4H), 1.56 (d, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.37, 147.64, 128.56, 127.43, 126.31, 95.80, 78.44, 71.23, 71.14, 70.93, 69.83, 69.76, 69.10, 68.07, 48.44, 47.39, 39.55, 27.11, 24.31, 22.76. HRMS (EI) Calculated for $C_{23}H_{25}FeNO$: 387.1286; found, 387.1285.



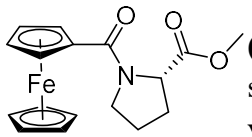
1-(pyrrolidine-1-carbonyl)-1'-(1-(4-methoxyphenyl)ethyl)-ferrocene (1ah). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 7.2 Hz, 2H), 6.79 (d, J = 7.2 Hz, 2H), 4.76 - 4.62 (m, 2H), 4.32 - 4.18 (m, 3H), 4.17 - 4.05 (m, 12H), 3.97 (s, 1H), 3.88 – 3.70 (m, 4H), 3.68 - 3.54 (m, 4H), 2.03 - 1.81 (m, 4H), 1.54 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.25, 158.01, 139.76, 128.21, 113.83, 96.16, 78.30, 71.12, 71.02, 70.82, 69.65, 69.57, 68.96, 67.87, 55.43, 48.30, 47.28, 38.55, 27.00, 24.20 , 22.77. HRMS (EI) Calculated for $C_{24}H_{27}FeNO_2$: 417.1391; found 417.1388.



1-(pyrrolidine-1-carbonyl)-1'-(1-(4-fluorophenyl)ethyl)-ferrocene (1ai). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 -7.01 (m, 2H), 6.99 - 6.85(m, 2H), 4.75 - 4.63 (m, 2H), 4.33 - 4.21(m, 3H), 4.18 - 4.09 (m, 2H), 3.95 (s, 1H), 3.87 (t, *J* = 6.4 Hz, 1H), 3.73 – 3.52 (m, 4H), 2.02 - 1.82 (m, 4H), 1.53 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.27, 162.65,160.27, 160.21, 143.36, 128.77, 128.69, 115.30, 115.09, 95.61, 78.50, 71.20, 71.14, 70.84 , 69.82, 69.68, 69.07, 67.89, 47.90, 38.73, 27.05, 24.28, 22.79. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.50 (s, 1H). HRMS (EI) Calculated for $C_{23}H_{24}FFeNO$: 405.1191; found, 405.1191.

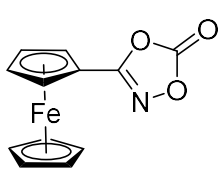


1-(pyrrolidine-1-carbonyl)-1'-(1-(4-(trifluoromethyl)phenyl)ethyl)-ferrocene (1aj), Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz,2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.71 (d, *J* = 9.2 Hz, 2H), 4.33 – 4.21 (m, 3H), 4.18 (s, 1H), 4.16 (s, 1H), 4.01 – 3.91 (m, 2H), 3.67 - 3.57 (m, 2H), 2.01 – 1.85 (m, 4H), 1.58 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.22, 151.68, 129.15 , 128.96, 128.63, 128.31, 127.99, 127.69, 127.21, 125.90 , 125.46, 125.42, 123.20, 120.50, 94.72, 78.57, 71.20, 70.82, 70.79, 69.92, 69.75, 69.13 , 67.85, 48.43 , 47.34, 39.30, 26.96, 24.21, 22.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ-62.31. HRMS (EI) Calculated for $C_{24}H_{24}F_3FeNO$: 455.1159; found 455.1161.



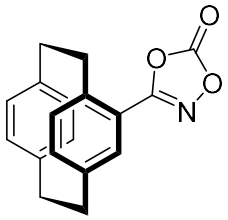
(1-((S)-2-(methoxycarbonyl)pyrrolidin-1-yl)ethyl)ferrocene (1ak), Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (s, 1H), 4.71 (s, 1H), 4.61 (dd, *J* = 7.6, 4.4 Hz, 1H), 4.39 - 4.33 (m, 2H), 4.26 (s, 5H), 4.01 - 3.92(m, 1H), 3.83 – 3.74 (m, 4H), 2.29 – 2.09 (m, 2H), 2.07 - 1.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.29, 169.92, 76.29, 71.55, 70.80, 70.57, 69.98, 60.44, 52.44, 48.59, 28.98, 25.88. HRMS (EI) Calculated for $C_{17}H_{19}FeNO_3$: 341.0714; found, 341.0713.

Dioxazolones **2r** and **2s** are prepared according to the literature.[1]



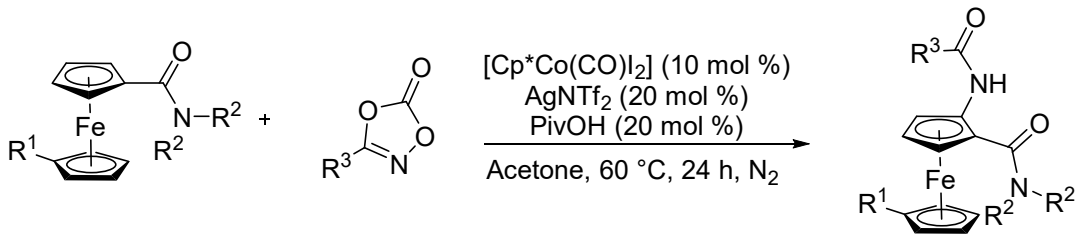
3-ferrocene-1,4,2-dioxazol-5-one (2r). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=4:1) afforded the title product as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (s, 2H), 4.56 (s, 2H), 4.29 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.56, 154.57, 72.29, 70.71, 68.16,

62.21. ESI-HRMS (m/z) calculated for $C_{12}H_9FeNO_3[M\text{-}CO+H]^+$: 228.0106; found, 228.0097.



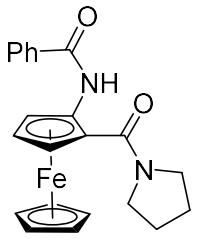
3-(1,4(1,4)-dibenzenacyclohexaphane-1^2-yl)-1,4,2-dioxazol-5-one (2s). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=4:1) afforded the title product as while solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 – 6.88 (d, *J* =1.2, 1H), 6.78 (*J* = 7.8 Hz, 1.6H, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.61 – 6.51 (m, 3H), 6.48 - 6.42 (d, *J* = 8.0 Hz, 1H), 3.94 - 3.80 (m, 1H), 3.26 – 2.95 (m, 7H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.24, 154.27, 141.38, 141.22, 139.88, 139.71, 137.77, 136.95, 133.61, 133.56, 132.97, 132.57, 130.90, 120.92, 35.66, 35.51, 35.39, 34.48. ESI-HRMS (m/z) calculated for $C_{18}H_{15}NO_3[M\text{-}CO+H]^+$, 250.1226; found, 250.1239.

2.3 General Procedure for Co(III)-Catalyzed C-H Amidation of Ferrocenes

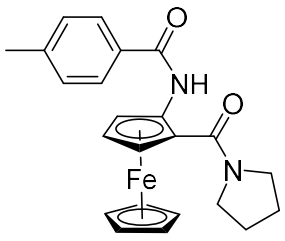


1 **2** **3**

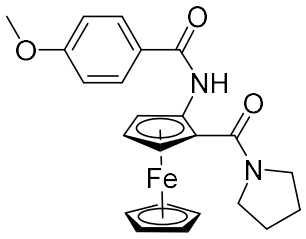
A mixture of ferrocene amide (1, 0.1 mmol), 3-substituted-1,4,2-dioxazol-5-ones (1.5, 0.15 mmol), [Cp*Co(CO)I_2] (10 mol %), $AgNTf_2$ (20 mol %), PivOH (20 mol %), and dry acetone (1 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 60 ºC for 24 h. The solvent was filtered through a pad of celite and then washed with CH_2Cl_2 after the reaction was cooled to room temperature, and then removed the solvent under reduced pressure, the residue was purified by silica gel chromatography using hexanes/ethyl acetate (2:1) to afford the product 3.



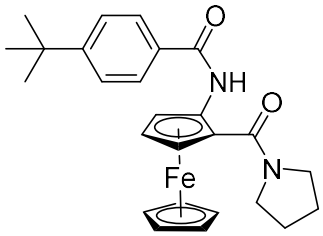
2-benzamido-(pyrrolidine-1-carbonyl)ferrocene (3a). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (29.4 mg, 73%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 8.03 – 7.95 (m, 2H), 7.54 – 7.43 (m, 3H), 5.80 (dd, *J* = 2.8, 1.2 Hz, 1H), 4.42 (dd, *J* = 2.8, 1.2 Hz, 1H), 4.27 (t, *J* = 2.8 Hz, 1H), 4.24 – 4.15 (m, 5H), 4.07 – 3.90 (m, 1H), 3.80 – 3.55 (m, 3H), 2.12 – 1.87 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.64, 165.52, 134.80, 131.76, 128.96, 127.43, 99.62, 70.95, 66.85, 65.28, 64.09, 63.89, 48.76 , 47.72, 27.19, 24.09. HRMS (EI) Calculated for $C_{22}H_{22}FeN_2O_2$: 402.1031; found, 402.1033.



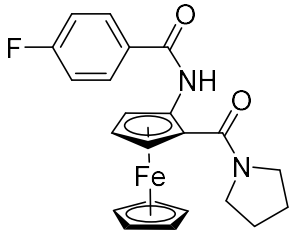
2-(4-methylbenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3b). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (30.4 mg, 73%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 5.80 (d, *J* = 1.2 Hz, 1H), 4.41 (d, *J* = 1.6Hz, 1H), 4.26 (t, *J* = 2.8 Hz, 1H), 4.176 (s, 5H), 4.06 – 3.90 (m, 1H), 3.80-3.50(m, 3H), 2.41(s, 3H), 2.10-1.85(m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69, 165.57, 142.19, 132.07, 129.63, 127.48, 99.84, 70.96, 66.81, 65.20, 64.11, 63.90, 48.80, 47.71, 27.21, 24.13, 21.79. HRMS (EI) Calculated for $C_{23}H_{24}FeN_2O_2$: 416.1187; found, 416.1187.



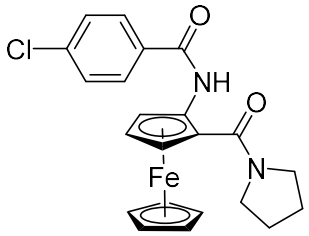
2-(4-methoxybenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3c). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (23.3 mg, 54%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.78 (d, *J* = 1.2 Hz, 1H), 4.40 (d, *J* = 1.5 Hz, 1H), 4.25 (t, *J* = 2.8, 1H), 4.17 (s, 5H), 4.06 - 3.92(m, 1H), 3.85 (s, 3H), 3.75-3.55 (m, 3H), 2.10 – 1.87 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.77, 165.20, 162.58, 129.33, 127.36, 114.19, 100.04, 70.95, 66.79, 65.16, 64.01, 63.80, 55.74, 48.80, 47.74, 27.23, 24,16. HRMS (EI) Calculated for $C_{23}H_{24}FeN_2O_3$: 432.1136; found, 432.1135.



2-(4-(tert-butyl)benzamido)-(pyrrolidine-1-carbonyl)ferrocene (3d). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (11.4mg, 25%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.00 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 5.80 (s, 1H), 4.41 (s, 1H), 4.26 (s, 1H), 4.17 (s, 5H), 4.06 - 4.95 (m, 1H), 3.76 - 3.56(m, 3H), 2.10 – 1.90 (m, 4H), 1.34 (s, 11H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69, 165.66, 155.24, 132.09, 127.32, 125.96, 99.82, 70.99, 66.85, 65.23, 64.10, 63.90, 48.80, 47.69, 35.27, 31.52, 27.16, 24.17. ESI-HRMS (m/z) calculated for $C_{26}H_{30}FeN_2O_2[M+H]^+$:459.1729; found, 459.1725.

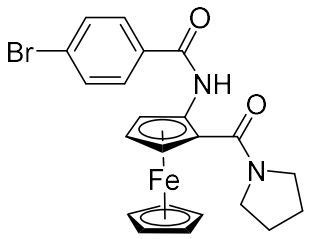


2-(4-fluorobenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3e). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (34.4 mg, 82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 7.99(dd, *J* = 5.6, 3.2 Hz, 2H), 7.14 (t, *J* = 8.8 Hz, 2H), 5.76 (d, *J* = 1.2 Hz, 1H), 4.42 (d, *J* = 1.6 Hz, 1H), 4.26 (t, *J* = 2.8 Hz, 1H), 4.17 (s,5H), 4.05-3.9 (m, 1H), 3.75-3.55 (m, 3H), 2.10 – 1.89 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.74, 166.37, 164.44, 163.87, 131.07, 129.85, 129.76, 116.08, 115.86, 99.58, 70.97, 66.92, 65.34, 64.05, 63.79, 48.79, 47.77, 27.20, 24.10. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.44. HRMS (EI) Calculated for $C_{22}H_{21}FFeN_2O_2$: 420.0936; found 420.0932.

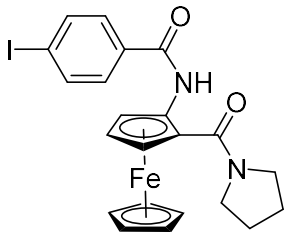


2-(4-chlorobenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3f). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (39.3 mg, 90%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.76 (s, 1H), 4.42 (d, *J* = 1.6 Hz, 1H), 4.26 (t, *J* = 2.4 Hz, 1H), 4.17 (s, 5H), 4.04 - 3.90(m, 1H), 3.77

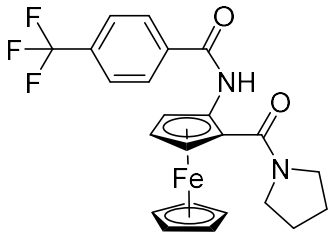
- 3.53 (m, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69, 164.37, 138.01, 133.18, 129.20, 128.89, 99.34, 70.98, 66.96, 65.39, 64.08, 63.79, 48.79, 47.76, 27.20, 24.09. HRMS (EI) Calculated for $C_{22}H_{21}ClFeN_2O_2$:436.0641; found, 436.0644.



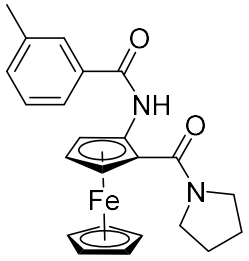
2-(4-bromobenzsamido)-(pyrrolidine-1-carbonyl)ferrocene (3g). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (40.3 mg, 84%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 5.76 (d, *J* = 1.2 Hz, 1H), 4.42 (d, *J* = 1.2 Hz, 1H), 4.26 (t, *J* = 2.8 Hz, 1H), 4.17 (s, 5H), 4.05 -3.85(m, 1H), 3.75-3.50 (m, 3H), 2.11 – 1.88 (m, 4H). **^{13}C** NMR (101 MHz, $CDCl_3$) δ 172.69, 164.47, 133.68, 132.18, 129.09, 126.53, 99.40, 70.99, 66.96 , 65.39, 64.11, 63.83, 48.77, 47.77, 27.21, 24.10. HRMS (EI) Calculated for $C_{22}H_{21}BrFeN_2O_2$: 480.0136; found, 480.0135.



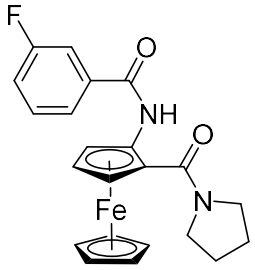
2-(4-iodobenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3h). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (43.3 mg, 82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 5.75 (d, *J* = 1.2 Hz, 1H), 4.42 (d, *J* = 1.2 Hz, 1H), 4.26 (t, *J* = 2.4 Hz, 1H), 4.16 (s, 5H), 4.05 - 3.90(m, 1H), 3.75 - 3.55 (m, 3H), 2.12 – 1.90 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.65 , 164.65, 138.16, 134.22, 129.06 , 99.33, 98.91, 70.98 , 66.96 , 65.39, 64.09, 63.81, 48.78, 47.75, 27.20, 24.09. HRMS (EI) Calculated for $C_{22}H_{21}IFeN_2O_2$: 527.9997; found, 528.0000.



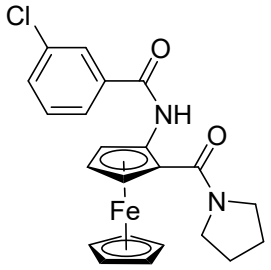
2-(4-(trifluoromethyl)benzamido)-(pyrrolidine-1-carbonyl)ferrocene (3i). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (38.6 mg, 82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 5.77 (d, *J* = 1.2 Hz, 1H), 4.44 (d, *J* = 1.6 Hz, 1H), 4.28 (t, *J* = 2.8 Hz, 1H), 4.18 (s, 5H), 4.05 - 3.90 (m, 1H), 3.76 – 3.57 (m, 3H), 2.10- 1-88(m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.66, 164.06, 138.06, 133.85, 133.52, 133.20, 132.90 ,132.84, 127.89, 126.07, 126.04, 126.00, 125.96, 125.46, 122.75, 99.14, 71.02, 67.06, 65.52, 64.17, 63.88, 48.77, 47.79, 27.20, 24.09. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.86. HRMS (EI) Calculated for $C_{23}H_{21}F_3FeN_2O_2$: 470.0905; found, 470.0906.



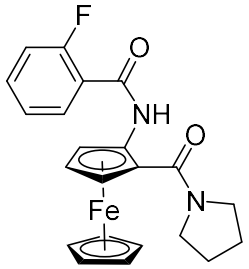
2-(3-methylbenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3j). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (19.1 mg, 46%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.96 (s, 1H), 7.81 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.38 - 7.29 (m, 2H), 5.79 (dd, *J* = 2.8, 1.2 Hz, 1H), 4.41 (dd, *J* = 2.8, 1.2 Hz, 1H), 4.26 (t, *J* = 2.8 Hz, 1H), 4.18 (s, 5H), 4.04 – 3.92 (m, 1H), 3.76 - 3.55 (m, 3H), 2.44 (s, 3H), 2.09 -1.88 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 172.64, 165.83, 138.77, 134.79, 132.58, 128.85, 128.30, 124.33, 99.66, 70.98 , 66.85 , 65.25, 64.19, 63.99, 48.81, 47.71, 27.22 (s, 6H), 24.14 (s, 6H), 21.79 (s, 5H). HRMS (EI) Calculated for $C_{23}H_{24}FeN_2O_2$: 416.1187; found, 416.1187.



2-(3-fluorobenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3k). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (27.7 mg, 66%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 7.75 -7.67 (m, 2H), 7.45 (dd, *J* = 14.0, 7.2 Hz, 1H), 7.20 (t, *J* = 8.2 Hz, 1H), 5.76 (s, 1H), 4.43 (s, 1H), 4.27 (s, 1H), 4.18 (s, 5H), 4.04 - 3.91(m, 1H), 3.78 - 3.56 (m, 3H), 2.12 - 1.86(m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 164.23, 163.96 , 161.77, 137.05, 136.97, 130.37, 130.29, 122.55, 122.52, 118.59, 118.37, 114.74, 114.51, 99.09, 70.74 , 66.69, 65.13, 63.92, 63.66, 48.49, 47.49, 26.93, 23.83. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.90. HRMS (EI) Calculated for $C_{22}H_{21}FFeN_2O_2$: 420.0936; found, 420.0936.

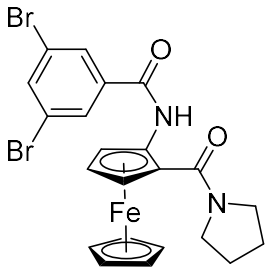


2-(3-chlorobenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3l). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (36.6 mg, 84%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 7.99 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 5.75 (s, 1H), 4.42 (s, 1H), 4.27 (s, 1H), 4.17 (s, 5H), 4.05 – 3.90 (m, 1H), 3.75 - 3.53 (m, 3H), 1.98 (dd, *J* = 19.1, 13.5 Hz, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.63, 164.15, 136.68, 135.25, 131.82, 130.26, 128.08, 125.19, 99.28, 71.01, 66.98, 65.43, 64.19, 63.93, 48.78, 47.76, 27.21, 24.11. HRMS (EI) Calculated for $C_{22}H_{21}ClFeN_2O_2$: 436.0641; found, 436.0641.

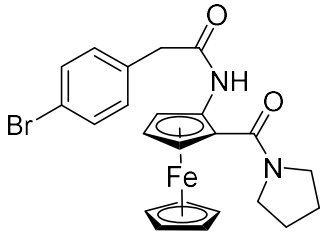


2-(2-fluorobenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3m). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (15.6 mg, 37%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (d, *J* = 8.8 Hz, 1H), 8.08 (t, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 13.6, 6.8 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.17 (dd, *J* = 11.2, 8.8 Hz, 1H), 5.80 (s, 1H), 4.42 (s, 1H), 4.27 (s, 1H), 4.20 (s,

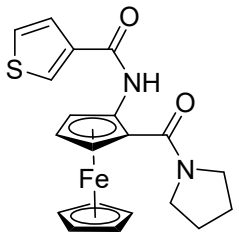
5H), 4.04 - 3.92 (m, 1H), 3.77 – 3.56 (m, 3H), 2.12 -1.83(m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.68, 161.81, 161.76, 159.33, 133.12, 133.03, 131.41, 131.39, 124.58, 124.54, 122.33, 122.21, 116.54, 116.30, 98.49, 70.81, 66.58, 65.06, 64.57, 64.39, 48.52, 47.35, 26.93, 23.84. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.52. HRMS (EI) Calculated for $C_{22}H_{21}FFeN_2O_2$: 420.0936; found, 420.0933.



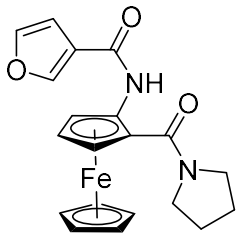
2-(3,5-dibromobenzamido)-(pyrrolidine-1-carbonyl)ferrocene (3n). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (43.0 mg, 77%)**,** ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.12 (s, 1H), 8.00 (d, *J* = 1.6 Hz, 2H), 7.83 -7-75 (m, 1H), 5.71 (d, *J* = 1.2 Hz, 1H), 4.43 (d, *J* = 1.6 Hz, 1H), 4.27 (t, *J* = 2.8 Hz, 1H), 4.17 (s, 5H), 4.02 - 3.90 (m, 1H), 3.77 – 3.54 (m, 3H), 2.12 - 1.88 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.51, 162.68, 138.33, 137.13, 129.37, 123.64, 98.92 , 71.04 , 67.04, 65.54, 64.29, 64.03, 48.74, 47.78, 27.23, 24.09. ESI-HRMS (m/z) calculated for $C_{22}H_{20}Br_2FeN_2O_2[M+H]^+$: 558.9314; found, 558.9308.



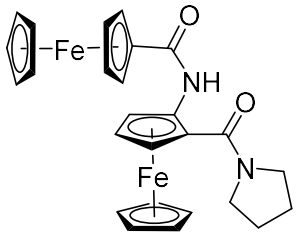
2-(2-(4-bromophenyl)acetamido)-(pyrrolidine-1-carbonyl)ferrocene (3o), Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (21.3 mg, 43%)**,** ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.58 (s, 1H), 4.33 (s, 1H), 4.20 - 4.16 (m, 1H), 4.08 (s, 5H), 3.98 - 3.85 (m, 1H), 3.70 - 3.51 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.32, 169.11, 134.53, 132.10, 131.25, 121.35, 99.18, 70.89, 66.71, 65.03, 64.05, 63.84, 48.71, 47.63, 44.56, 27.19, 24.11. HRMS (EI) Calculated for $C_{23}H_{23}BrFeN_2O_2$: 494.0292; found, 494.0290.



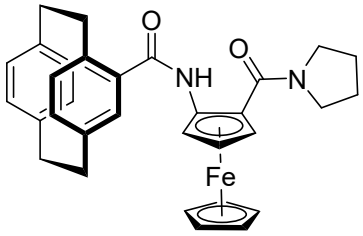
2-(thiophene-2-carboxamido)-(pyrrolidine-1-carbonyl)ferrocene (3p). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (31.0 mg, 76%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.97 (s, 1H), 7.68 – 7.64 (m, 1H), 7.51 – 7.47 (m, 1H), 7.09 (dd, *J* = 4.8, 4.0 Hz, 1H), 5.70 (d, *J* = 1.2 Hz, 1H), 4.42 – 4.38 (m, 1H), 4.24 (t, *J* = 2.8 Hz, 1H), 4.18 (s, 5H), 4.06 - 3.90 (m,1H), 3.73 – 3.56 (m, 3H), 2.10 -1.85(m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.61, 160.40, 140.46, 130.58, 128.41, 128.10, 99.44, 70.96, 66.87, 65.27, 63.86, 63.66, 48.73, 47.74, 27.19, 24.09. ESI-HRMS (m/z) calculated for $C_{20}H_{20}FeN_2O_2S$ $[M+H]^+$: 409.0668; found, 409.0672.



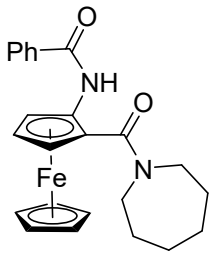
2-(furan-2-carboxamido)-(pyrrolidine-1-carbonyl)ferrocene (3q). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (32.2 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 7.53 (d, *J* = 0.8 Hz, 1H), 7.15 (d, *J* = 3.2 Hz, 1H), 6.49 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.71 (d, *J* = 1.2 Hz, 1H), 4.42 – 4.38 (m, 1H), 4.24 (t, *J* = 2.8 Hz, 1H), 4.17 (s, 5H), 4.06- 3.88(m, 1H), 3.78 - 3.50(m, 3H), 2.06 - 1.86(m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69 , 164.47, 133.68, 132.18 , 129.08, 126.53, 99.40, 71.05, 66.96, 65.39, 64.11, 63.83, 48.77, 47.75, 27.21, 24.10. HRMS (EI) Calculated for $C_{20}H_{20}FeN_2O_3$: 392.0823; found, 392.0822.



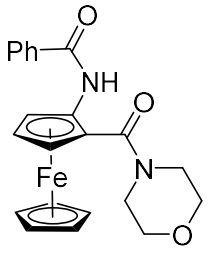
***N*-(2-(pyrrolidine-1-carbonyl)ferrocene)ferrocenecarboxamide (3r).** Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (35.2 mg, 69%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 5.68 (s, 1H), 4.84 (d, *J* = 6.8 Hz, 2H), 4.40 - 4.34 (m, 3H), 4.28- 4.21 (m, 6H), 4.18 (s, 5H), 4.07 - 3.91 (s, 1H), 3.78 - 3.54 (m, 3H), 2.00 (d, *J* = 17.6 Hz, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 172.54, 169.18, 100.09, 70.92, 70.19, 68.76, 68.73, 66.68, 64.93, 63.72, 63.51, 48.76, 47.72, 27.22, 24.13. ESI-HRMS (m/z) calculated for $C_{26}H_{26}Fe_2N_2O_2[M+H]^+$: 511.0766; found, 511.0759 .



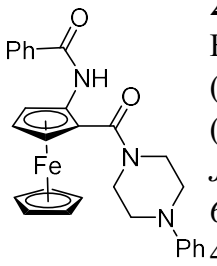
2-(1,4(1,4)-dibenzenacyclohexaphane-1^2-carboxamido)-(pyrrolidine-1-carbonyl)ferrocene (3s). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (28.2 mg, 53%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28(s, 0.5H), 10.23(s, 0.5H), 6.89 (d, *J* = 1.1 Hz, 1H), 6.86 - 6.80 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 0.5H), 6.66 (d, *J* = 8.0 Hz, 0.5H), 6.61 - 6.51 (m, 4.5H), 5.82 (s, 1H), 4.40 (s, 1H), 4.30 - 4.26 (m, 1H), 4.24 (s, 2.5H), 4.22(s, 2.5H), 4.09 – 3.79 (m, 2H), 3.72 - 3.54 (m, 3H), 3.26 – 2.91 (m, 7H), 2.08 - 1.84 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 172.19, 172.15, 167.53, 167.51, 140.45, 140.36, 140.14, 139.73, 139.70, 139.57, 136.65, 136.60, 136.56, 136.45, 135.33, 135.29, 133.02, 132.97, 132.94, 132.37, 132.11, 132.09, 132.00, 99.87, 99.77, 70.88, 70.86, 66.71, 66.64, 65.29, 64.95, 64.41, 64.36, 64.22, 63.83, 48.77, 47.61, 35.80, 35.77, 35.70, 35.68, 35.57, 35.43, 35.26, 27.21, 24.06. ESI-HRMS (m/z) calculated for $C_{32}H_{32}FeN_2O_2[M+H]^+$, 533.1886; found, 533.1874.



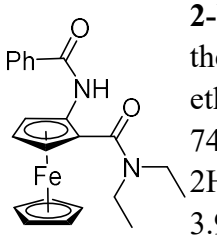
2-benzamido-(azepane-1-carbonyl)ferrocene (3aa). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (28.0 mg, 65%), **^{1}H NMR (400 MHz, CDCl$_3$)** δ 10.73 (s, 1H), 7.97 (d, *J* = 6.8 Hz, 2H), 7.56 – 7.43 (m, 3H), 5.76 (s, 1H), 4.33 – 4.25 (m, 2H), 4.20 (s, 5H), 3.98 - 3.82 (m, 2H), 3.78 - 3.58 (m, 2H), 1.95- 1.79 (m, 4H), 1.72 - 1.60 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.46, 165.47, 134.85, 131.80, 128.99, 127.43, 99.52, 71.19, 66.71, 65.47, 64.64, 64.26, 49.21, 47.68, 30.56, 28.28, 27.10. HRMS (EI) Calculated for $C_{24}H_{26}FeN_2O_2$: 430.1344; found, 430.1344.



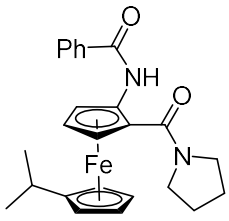
2-benzamido-(morpholine-4-carbonyl)ferrocene (3ab). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (17.2 mg, 41%), ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.18 (s, 1H), 7.94 (d, *J* = 7.2 Hz, 2H), 7.55 - 7.43 (m, 3H), 5.73 (s, 1H), 4.28 (t, *J* = 2.4 Hz, 1H), 4.21- 4.16 (m, 6H), 4.00- 3.88 (m, 2H), 3.87 – 3.69 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.85, 165.45, 134.65, 131.91, 129.00, 127.35 , 99.03, 71.27, 67.28, 66.75, 65.34, 64.32, 64.19, 45.87. ESI-HRMS (m/z) calculated for $C_{22}H_{22}FeN_2O_3$ $[M+H]^+$: 419.1053; found, 419.1052.



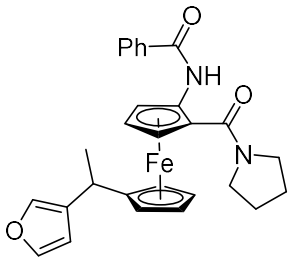
2-benzamido-(4-phenylpiperazine-1-carbonyl)ferrocene (3ac). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (31.1 mg, 41%), ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.25 (s, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.46 (m, 3H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.02 – 6.89 (m, 3H), 5.76 (s, 1H), 4.32 (m, 1H), 4.27 (s, 1H), 4.24 (s, 5H), 4.15 - 3.93 (m, 4H), 3.29 (t, *J* = 4.8 Hz, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.90, 165.51, 151.12, 134.69, 131.95, 129.63, 129.05, 127.41, 120.92, 116.86, 99.09, 71.32, 66.82, 65.56, 64.35, 50.08. ESI-HRMS (m/z) calculated for $C_{28}H_{27}FeN_3O_2$$[M+H]^+$: 494.1525; found, 494.1536.



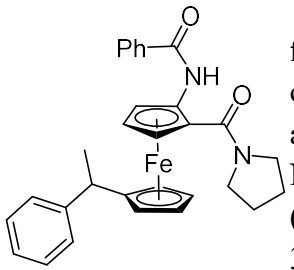
2-benzamido-*N*,*N*-diethylferrocenecarboxamide (3ad). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (31.1 mg, 74%), ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.75 (s, 1H), 7.97 (d, *J* = 6.8 Hz, 2H), 7.56 – 7.45 (m, 3H), 5.77 (s, 1H), 4.31 – 4.25 (m, 2H), 4.18 (s, 5H), 3.92 – 3.40 (m, 4H), 1.38 - 1.26 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.60, 165.19, 134.56, 131.50, 128.69, 127.14, 99.29, 70.92, 66.43, 64.72, 64.10, 63.95, 41.85, 14.17. ESI-HRMS (m/z) calculated for $C_{22}H_{24}FeN_2O_2$ $[M+H]^+$, 405.1060; found, 405.1265.



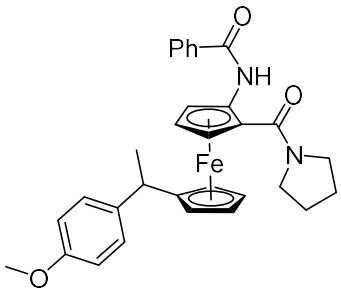
2-benzamido-1-(pyrrolidine-1-carbonyl)-1'-isopropyl-ferrocene (3ae). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (29.4 mg, 66%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.56 – 7.41 (m, 3H), 5.78 (s, 1H), 4.40 (s, 1H), 4.27- 4.21 (m, 1H), 4.07 (s, 5H), 3.96 - 3.80 (m, 1H), 3.76 - 3.55(m, 3H), 2.68 -2.52 (m, 1H), 2.11 -1.88 (m, 4H), 1.11 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.70, 165.53, 134.94, 131.72, 128.99, 127.41, 99.79, 98.82, 70.46 , 69.87, 69.29, 68.56, 67.40, 65.20, 64.90, 63.88, 48.86, 47.73, 27.24, 26.98, 24.17, 23.77. HRMS (EI) Calculated for $C_{25}H_{28}FeN_2O_2$: 444.1495; found, 444.1500.



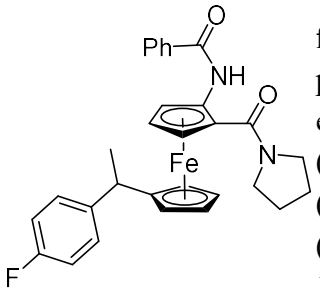
2-benzamido-1-(pyrrolidine-1-carbonyl)-1'-(1-(furan-2-yl)ethyl)-ferrocene (3af). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (11 mg, 22%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.05 - 10.95 (m, 1H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.49(m, 3H), 7.28 -7.25 (m, 1H), 6.25 -6.20 (s, 1H), 5.96 5.88 (m, 1H), 5.82 - 5.74 (m, 1H), 4.41 - 4.31 m, 1H), 4.22 - 4.14 m, 2H), 4.14 -4.05 (m, 3H), 3.96 – 3.81 (m, 2H), 3.74 -3.54 (m, 3H), 2.09 - 1.88(m, 4H), 1.53 - 1.44(m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.50, 165.58, 159.51, 159.40, 141.02, 134.91, 131.77, 129.00, 127.45, 127.43 110.25, 104.39, 104.30, 99.91, 99.87, 93.98, 93.95 (s, 1H), 71.15, 71.03, 70.79, 70.66, 70.31, 70.08, 69.27, 68.73, 67.89, 67.72, 65.63, 65.54, 65.21, 65.03, 64.22, 64.16, 48.86, 47.75, 32.48, 32.28, 27.17, 24.15, 20.06, 19.61. ESI-HRMS (m/z) calculated for $C_{28}H_{28}FeN_2O_3[M+H]^+$: 497.1522; found, 497.1527.



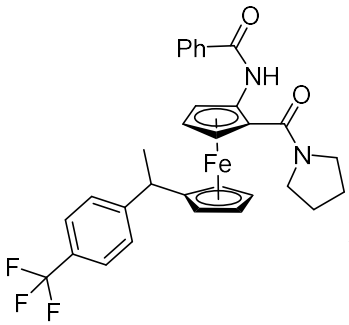
2-benzamido-1-(pyrrolidine-1-carbonyl)-1'-(1-phenylethyl)-ferrocene (3ag). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (42.0 mg, 83%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 - 11.02 (m, 1H), 8.05 - 7.97 (m, 2H), 7.55 - 7.45 (m, 3H), 7.23 - 715(m, 2H), 7.15 – 7.01 (m, 3H), 5.89-5.75 (m, 1H), 4.42 - 4.34 (m, 1H), 4.29 - 4.18(m, 2H), 4.14 (s, 1H), 4.07 (s, 1H), 4.01 – 3.75 (m, 3H), 4.75 - 3.52 (m, 3H), 2.10 - 1.85 (m, 4H), 1.55 – 1.43 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.56, 172.48, 165.56 , 147.77 , 147.54, 134.86, 131.77, 129.00 , 128.52, 127.44, 127.40,127.37, 126.26, 126.24, 99.90, 96.21, 92.06, 71.69, 71.18, 70.53, 70.34, 69.53, 69.09, 68.41, 67.63, 67.60, 65.51, 65.43, 65.12, 64.91, 64.03, 63.96, 48.82, 47.79, 38.82, 38.76, 27.19, 24.11, 22.60, 22.18. ESI-HRMS (m/z) calculated for $C_{30}H_{30}FeN_2O_2$ $[M+Na]^+$: 529.1540; found, 529.1555.



2-benzamido-1-(pyrrolidine-1-carbonyl)-1'-(1-(4-methoxyphenyl)ethyl)-ferrocene (3ah). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (28.5 mg, 53%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.14 - 10.98(m, 1H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.57 - 7.42 (m, 3H), 7.04- 6.92 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.85 - 5.76 (m, 1H), 4.43 - 4.34(m, 1H), 4.28 - 4.19 (m, 2H), 4.13 (s, 1H), 4.06 (s, 1H), 3.98 – 3.55 (m, 9H), 2.08 - 1.88 m, 4H), 1.51 - 1.39 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.61, 172.52, 165.57, 158.08, 140.03, 139.78 , 134.87, 131.78 , 129.01, 128.35, 128.26, 127.41, 127.39, 113.91, 99.86 , 96.66, 96.56, 71.63, 71.20, 70.49, 70.45, 70.35, 69.54, 69.05, 68.32, 67.63, 65.51, 65.42, 65.18, 64.94, 64.01, 63.94, 55.51, 48.83, 47.77, 37.96, 37.90, 27.17, 24.15, 22.77, 22.30. ESI-HRMS (m/z) Calculated for $C_{24}H_{27}FeNO_2[M+H]^+$: 537.1835, found 537.1835.

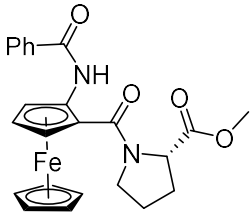


2-benzamido-1-(pyrrolidine-1-carbonyl)-1'-(1-(4-fluorophenyl)ethyl)-ferrocene (3ai). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (21.1 mg, 40%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.15 -10.96 (m, 1H), 8.04 - 7.96(m, 2H), 7.56 - 7.45 (m, 3H), 7.05 – 6.96 (m, 2H), 6.92 - 8.82 (m, 2H), 5.87 - 5.73 (m, 1H), 4.44 - 4.36(m, 1H), 4.28 – 4.19 (m, 2H), 4.14 (s, 1H), 4.08 (s, 1H), 3.96 - 3.74(m, 3H), 3.74 - 3.55 (m, 3H), 2.09 - 1.90(m, 5H), 1.50 - 1.40(m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.54, 172.43, 165.59, 162.69, 160.25, 144.17, 143.54, 143.50, 143.31, 143.27, 134.83, 131.83, 129.03, 128.84, 128.77, 128.69, 127.39, 117.55, 115.32, 115.11, 99.98, 96.07, 95.95, 71.87, 71.30, 70.40, 70.35, 69.46, 69.12, 68.14, 67.57, 65.40, 65.35, 65.25, 64.94, 64.11, 63.97, 48.91, 47.86, 38.05, 27.20, 24.11, 22.70, 22.27.^{19}F NMR (376 MHz, $CDCl_3$) δ -117.42, -117.49. ESI-HRMS (m/z) Calculated for $C_{30}H_{29}FFeN_2O_2[M+H]^+$: 525.1635; found, 525.1638.



2-benzamido-1-(pyrrolidine-1-carbonyl)-1'-(1-(4-(trifluoromethyl)phenyl)ethyl)-ferrocene (3aj), Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (21.3 mg, 37%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.12 -11.02 (m, 1H), 8.01 (d, *J* = 6.8 Hz, 1H), 7.57 – 7.46 (m, 3H), 7.43 (d, *J* = 8.0Hz, 1H), 7.17 - 7.11(m, 1H), 5.85-5.79 (m, 1H), 4.44 - 4.37 (m, 1H), 4.31 – 4.25 (m, 2H), 4.15 (s, 1H), 4.12 - 4.07 (m, 1H), 4.03 - 3.77 (m, 3H), 3.74 - 3.59 (m, 3H), 2.10 - 1.88 (m, 4H), 1.54 -1.42 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.44, 172.34 , 165.62, 165.58, 151.86, 151.62, 134.75, 134.71, 131.89, 129.21, 129.05, 128.69, 128.65, 128.61, 128.37,

128.33， 127.77, 127.72, 127.38, 127.35, 125.91, 125.56, 125.52, 125.48, 125.45, 123.21, 120.50, 100.06, 100.03, 95.21, 95.04, 72.09, 71.39, 70.39, 70.36, 69.41, 69.18, 68.03, 67.56 , 65.40, 65.32, 65.27, 64.90, 64.16, 64.03, 48.85, 47.80, 38.65, 38.61, 27.17, 24.11, 22.25, 21.92. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.33. HRMS (EI) Calculated for $C_{31}H_{29}F_3FeN_2O_2$: 574.1531, found 574.1531.



2-benzamido-(1-((S)-2-(methoxycarbonyl)pyrrolidin-1-yl)ethyl)ferrocene (3ak). Following the general procedure, column chromatography on silica gel (hexanes : ethyl acetate=2:1) afforded the title product as yellow solid (12.5 mg, 27%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.86 (s, 0.6H), 10.69 (s, 0.3H), 8.00 - 7.89 (m, 2H), 7.55 – 7.42 (m, 3H), 5.87 - 5.77 (m, 1H), 4.78 - 4.66 (m, 1H), 4.53 - 4.41 (m, 1H), 4.32 – 4.25 (m, 4H), 4.21 - 4.12(m, 3H), 3.83(m, 2H), 3.80 – 3.70 (m, 2H), 2.40 – 2.14 (m, 2H), 2.13 - 1.95 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.30, 173.01, 172.96, 165.73, 165.69, 134.87, 134.82, 131.83, 128.97, 127.56, 127.52, 99.92, 71.24, 71.01, 67.21, 65.33, 64.65, 62.65, 60.60, 60.49, 52.67, 49.16, 28.91, 25.84. HRMS (EI) Calculated for $C_{24}H_{24}FeN_2O_4$: 460.1085; found, 460.1088.

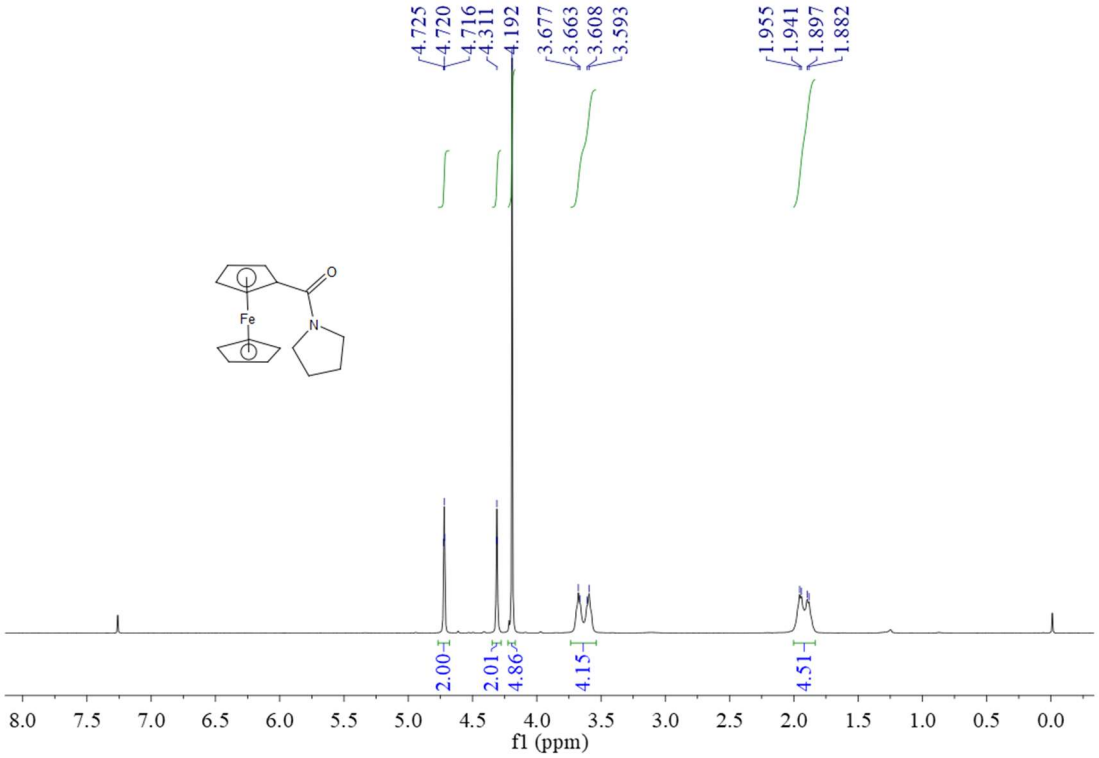
3 REFERENCES

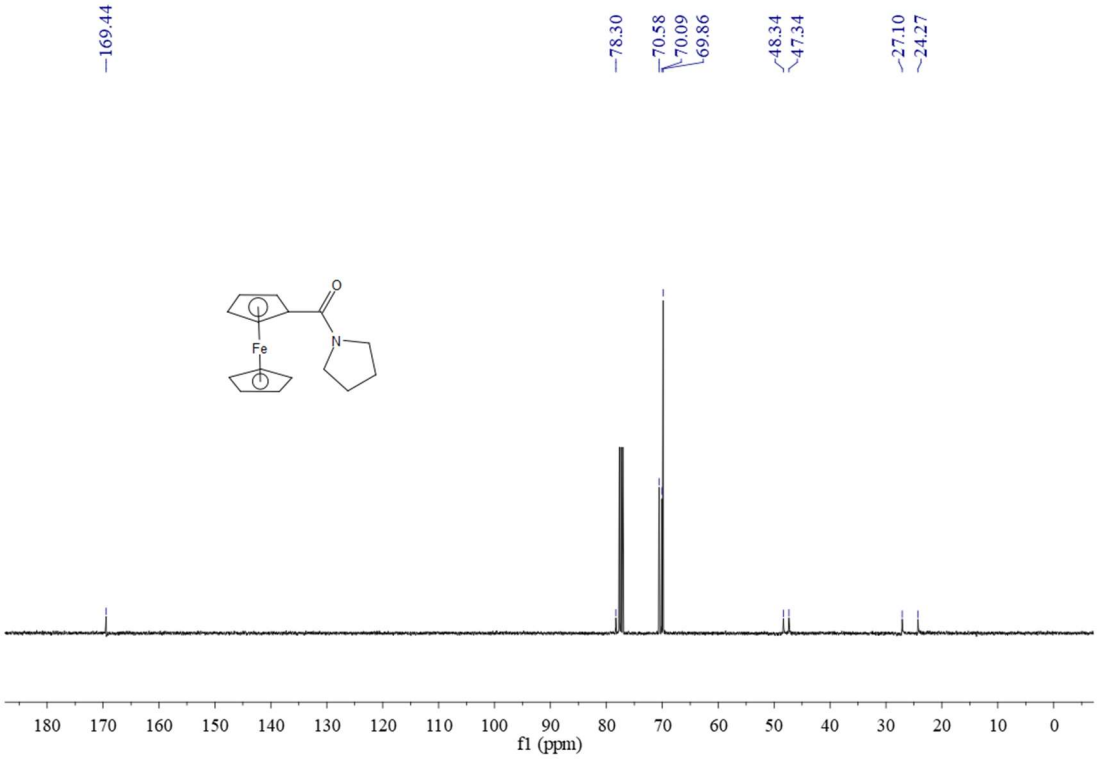
(1) (a) Park, P.; Park, K. T.; Kim, J. G.; Chang, S. *J. Am. Chem. Soc*. **2015**, *137*, 4534–4542. (b) Lam, H-W.; Man, K.-Y.; Chan, W-.W.; Zhou, Z.; Yu, W.-Y. *Org. Biomol. Chem.* **2014**, *12*, 4112-4116.

(2) (a) Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Adv. Synth. Catal*. **2014**, 356, 1491. (b) Frith, S. A.; Spencer, J. *Inorganic Syntheses.* **1990**, 28, 273. (c) Li, W.; Weng, L.; G. Jin, Inorg. *Chem. Commun*. **2004**, 7, 1174.

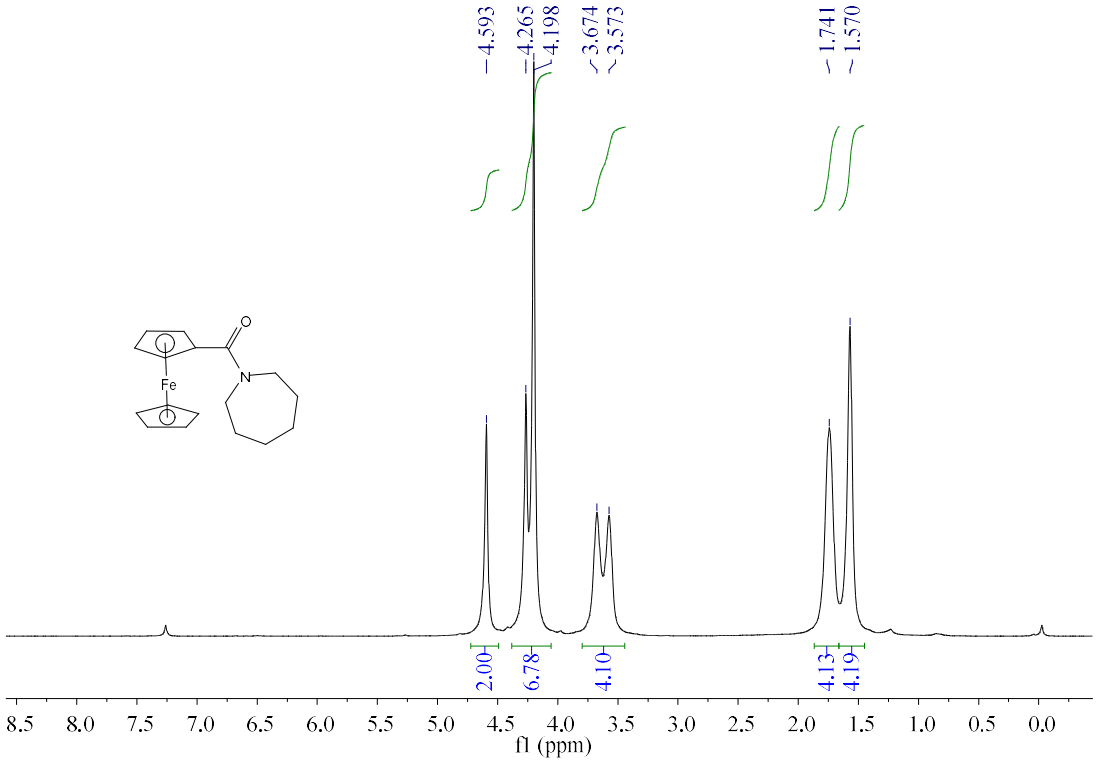
4. Spectra

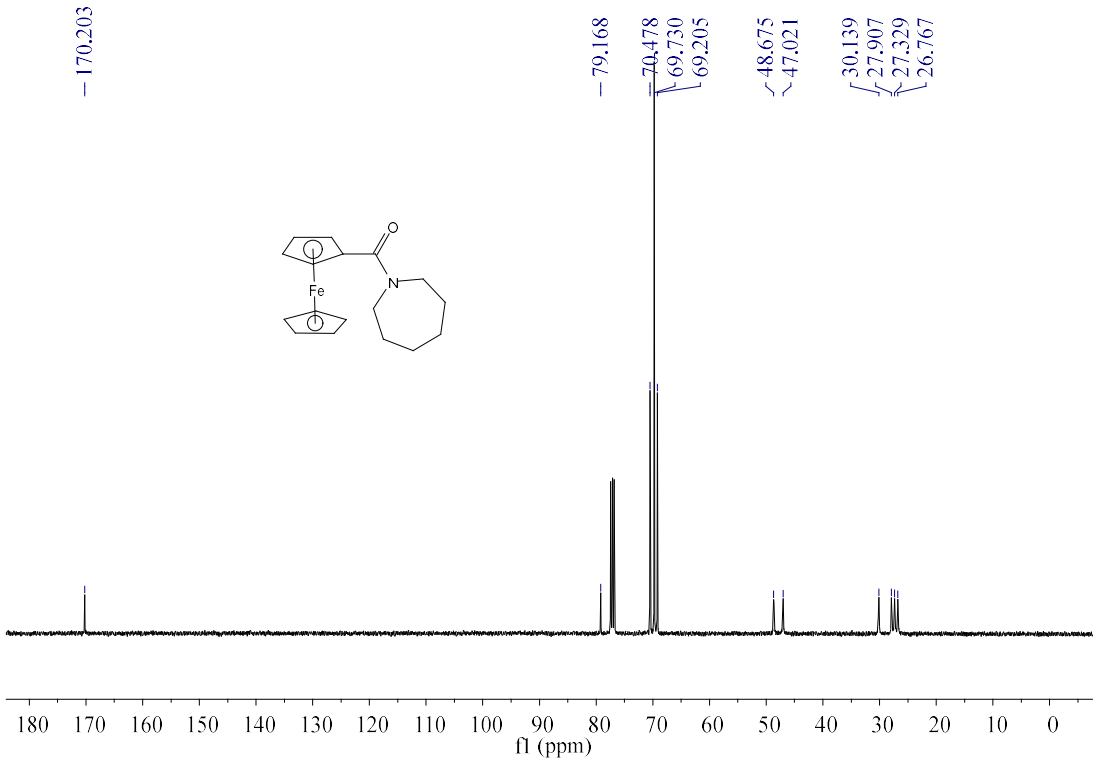
1a（^{1}H NMR and ^{13}C NMR).



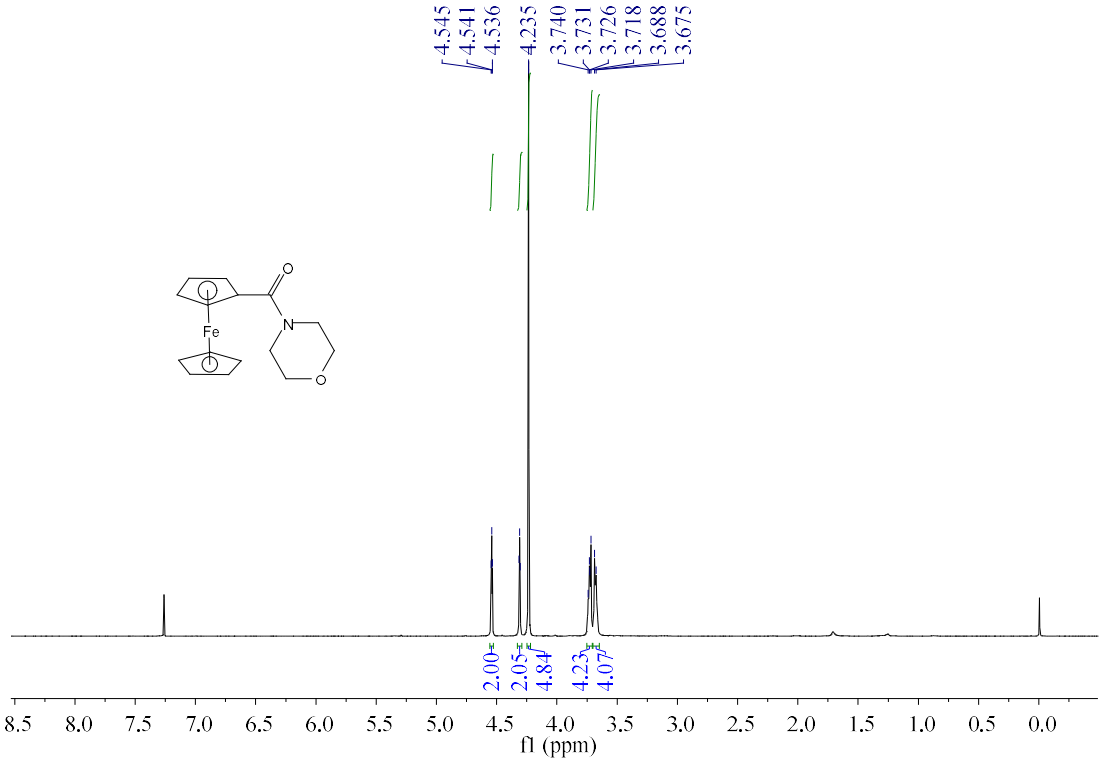


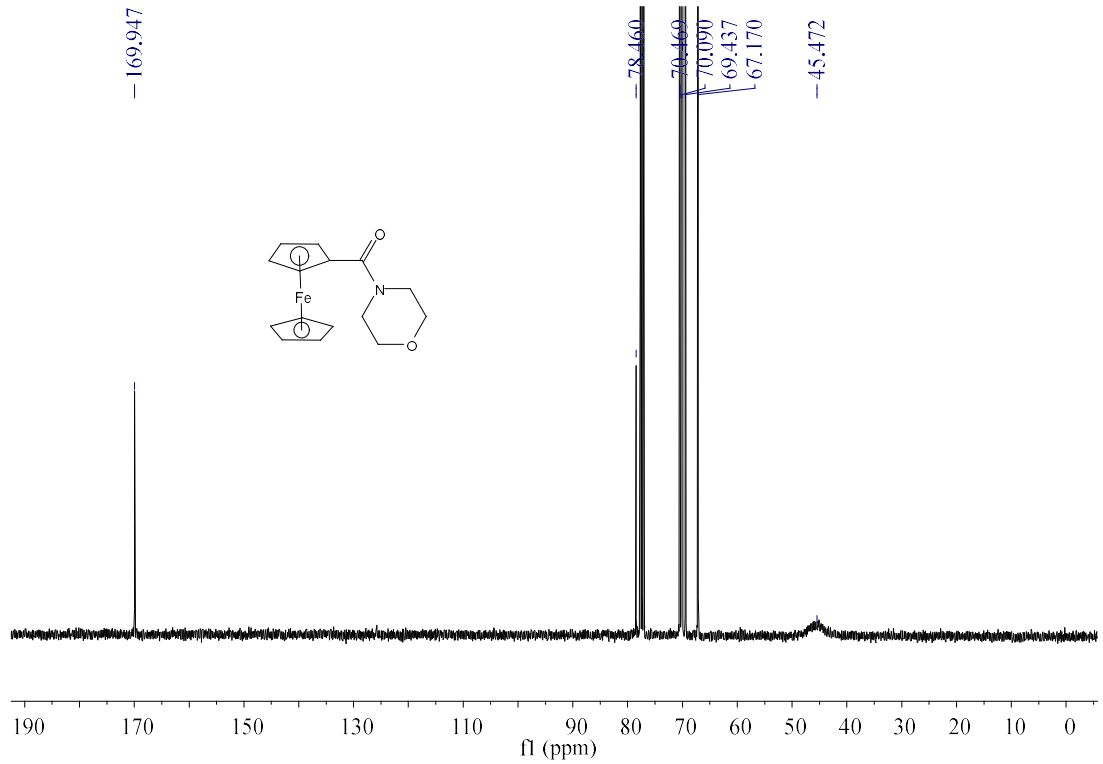
1aa（^{1}H NMR and ^{13}C NMR）



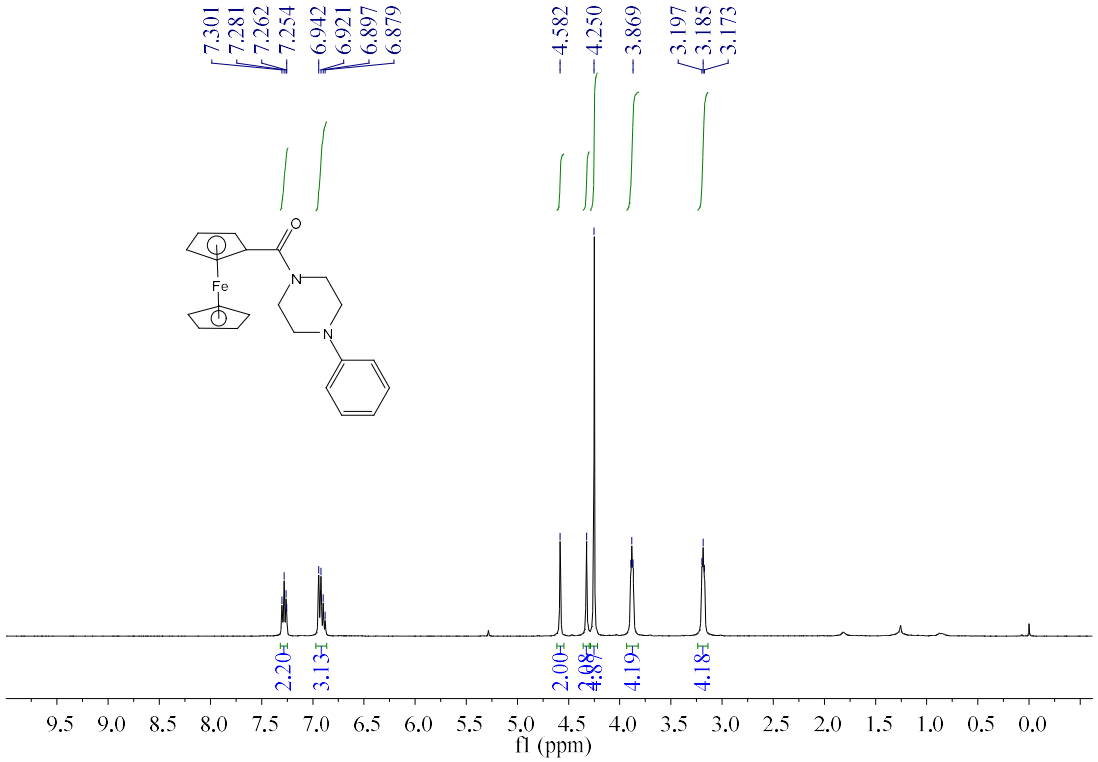


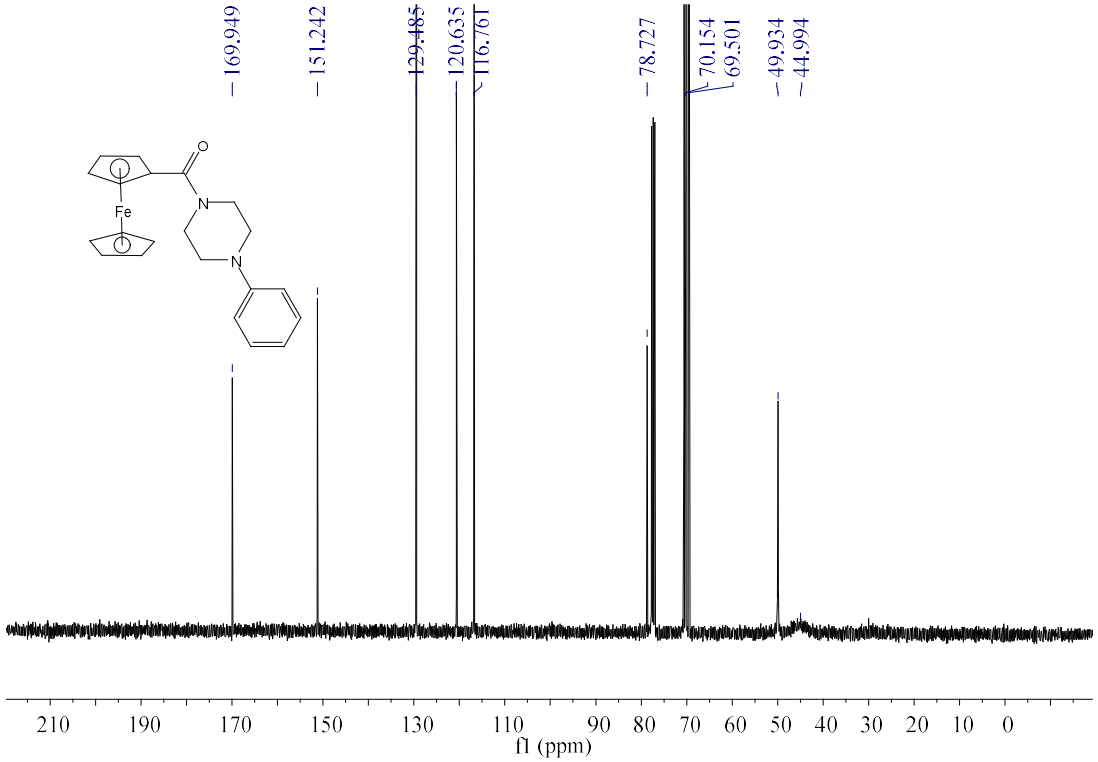
1ab（^{1}H NMR and ^{13}C NMR）



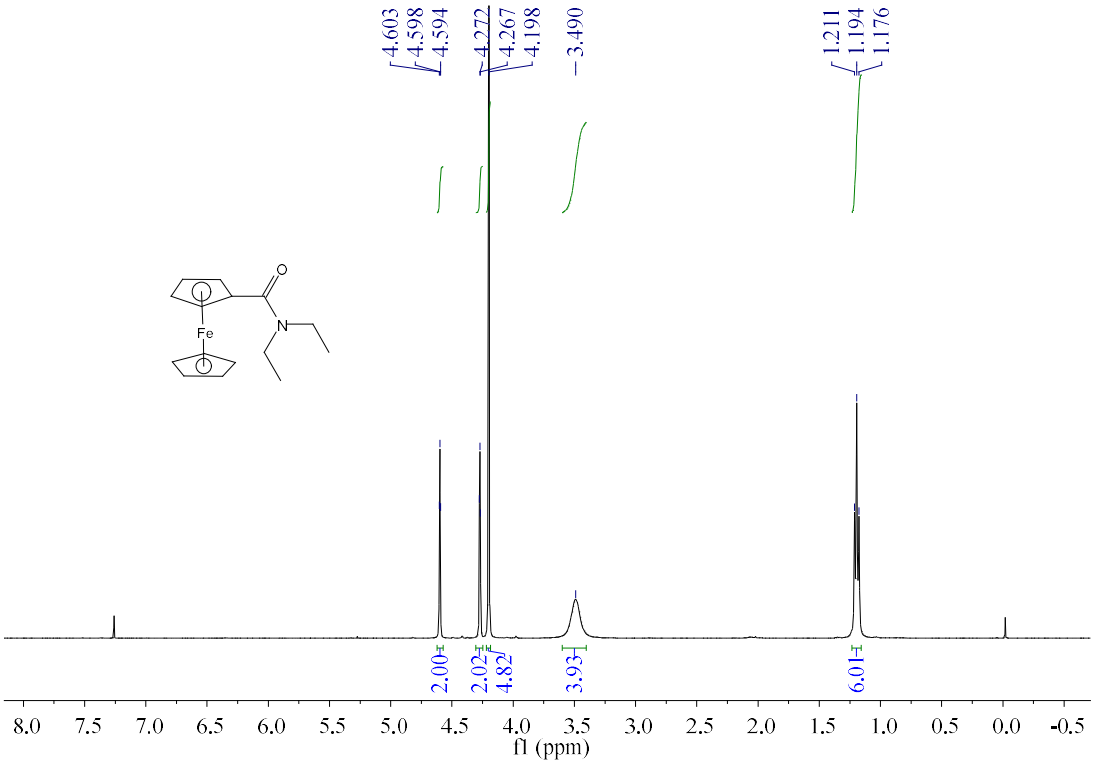


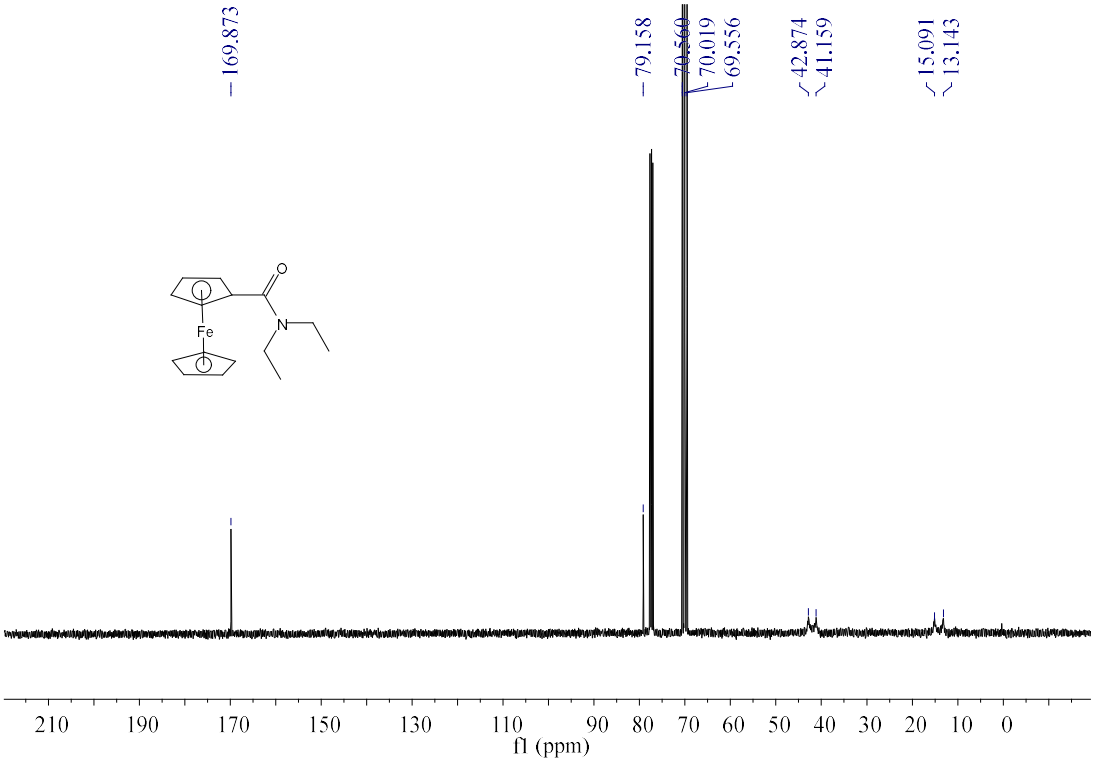
1ac（^{1}H NMR and ^{13}C NMR）



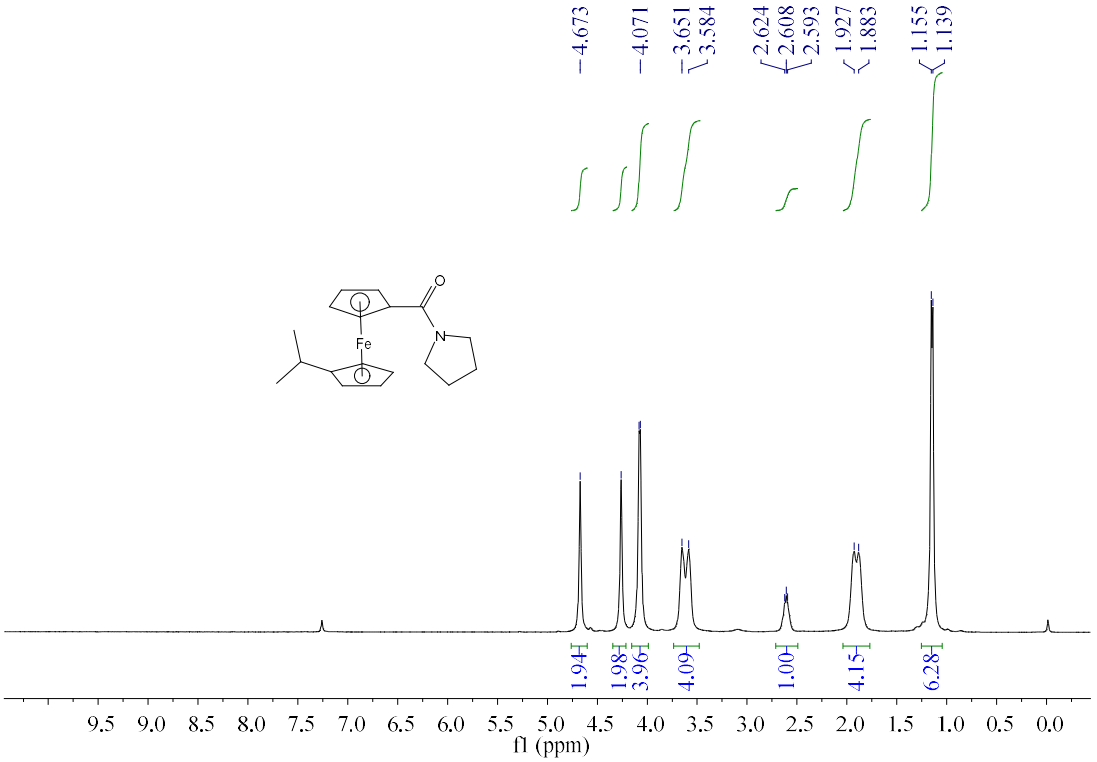


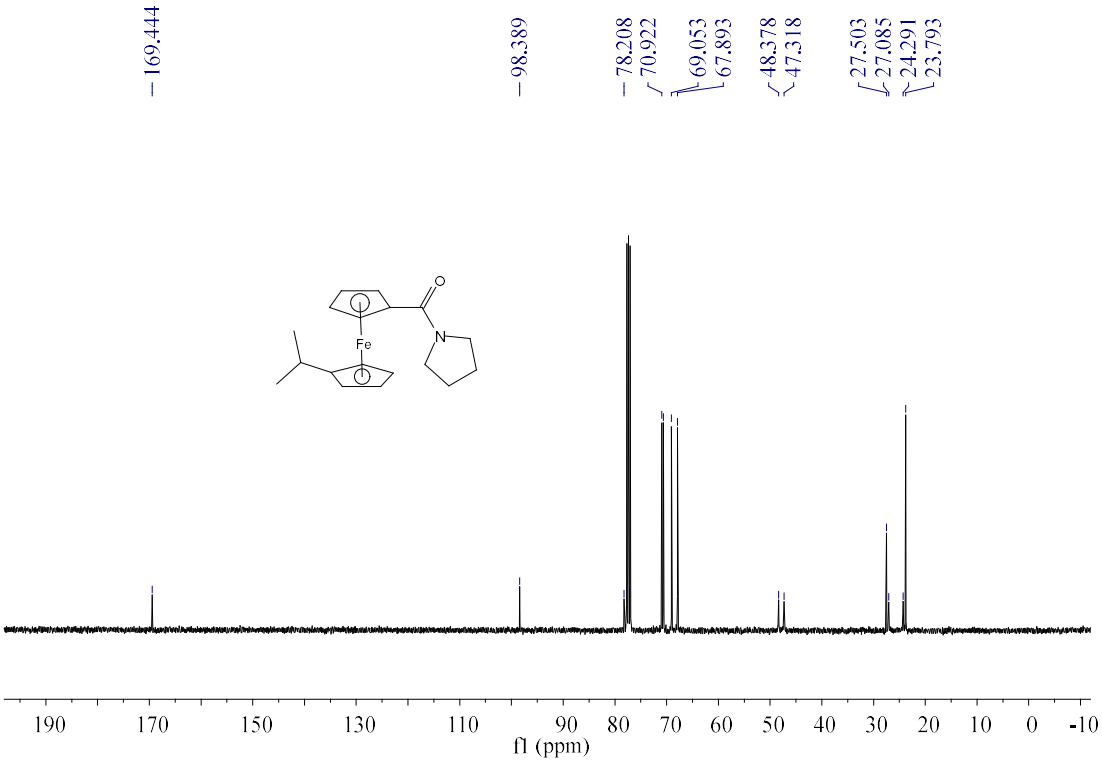
1ad（^{1}H NMR and ^{13}C NMR）



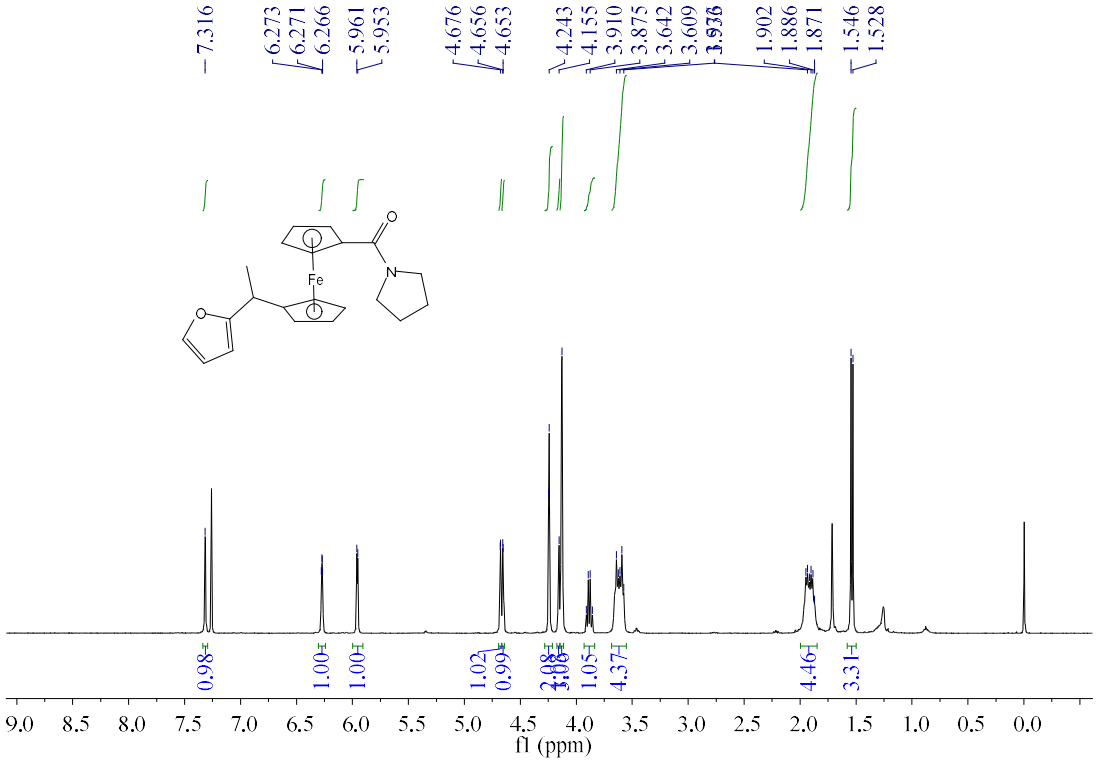


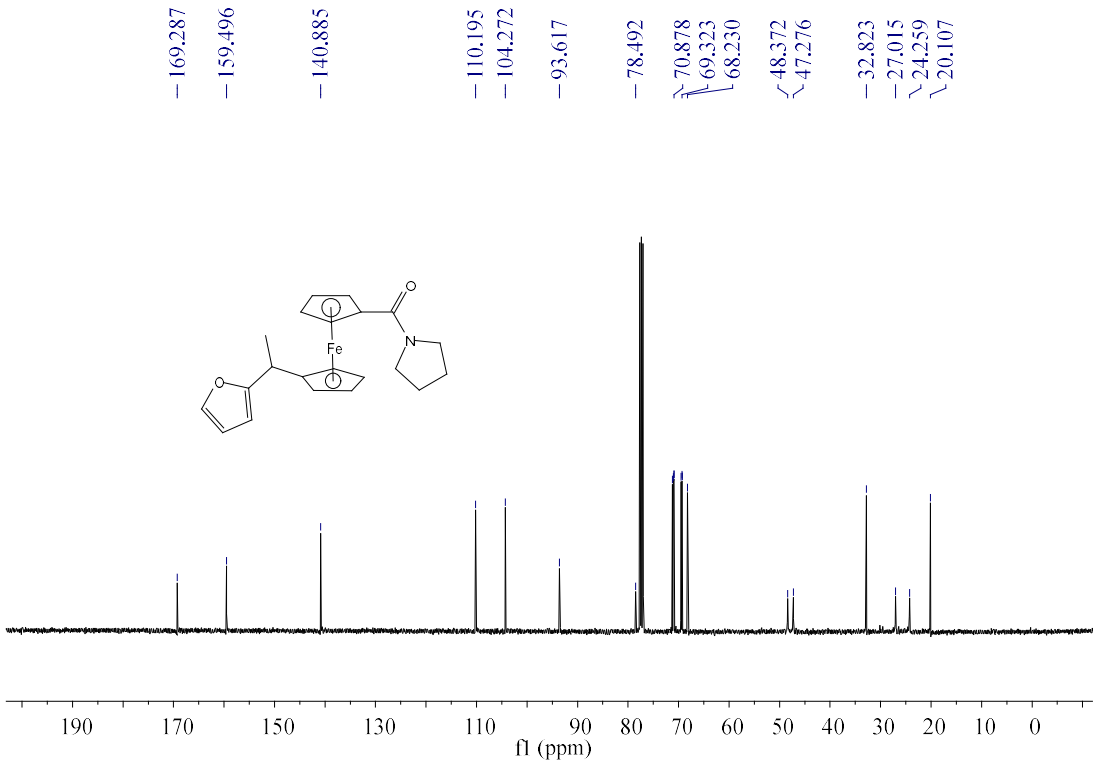
1ae（^{1}H NMR and ^{13}C NMR）



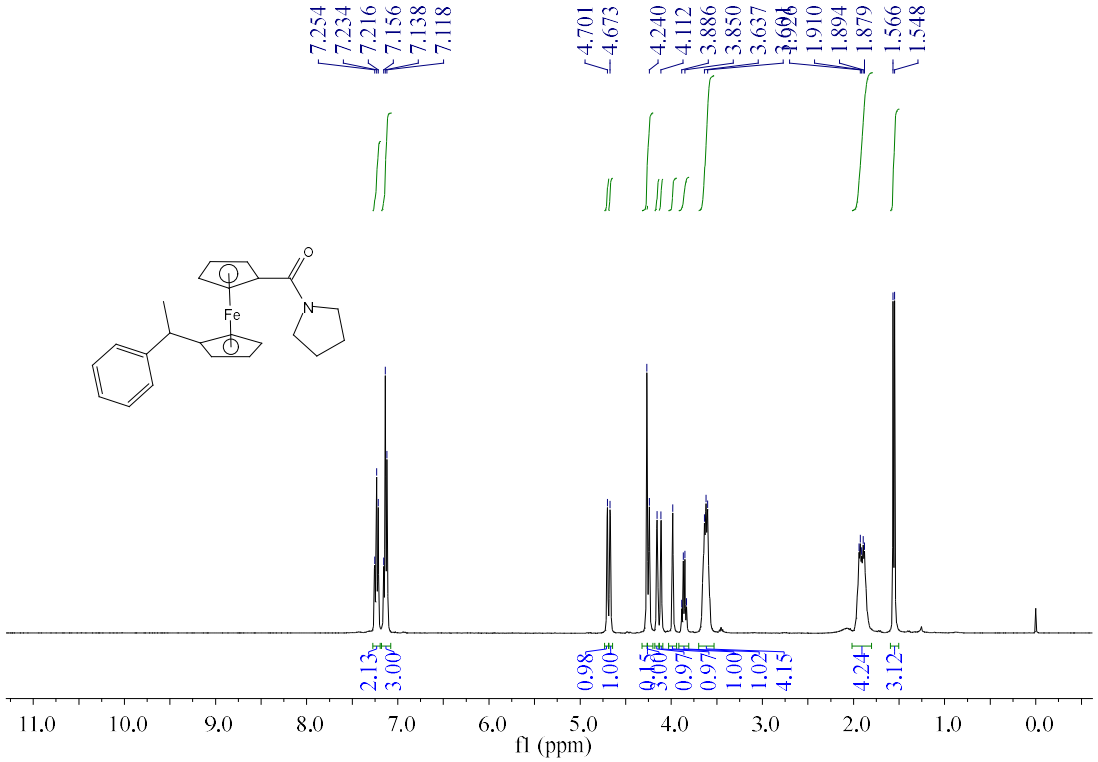


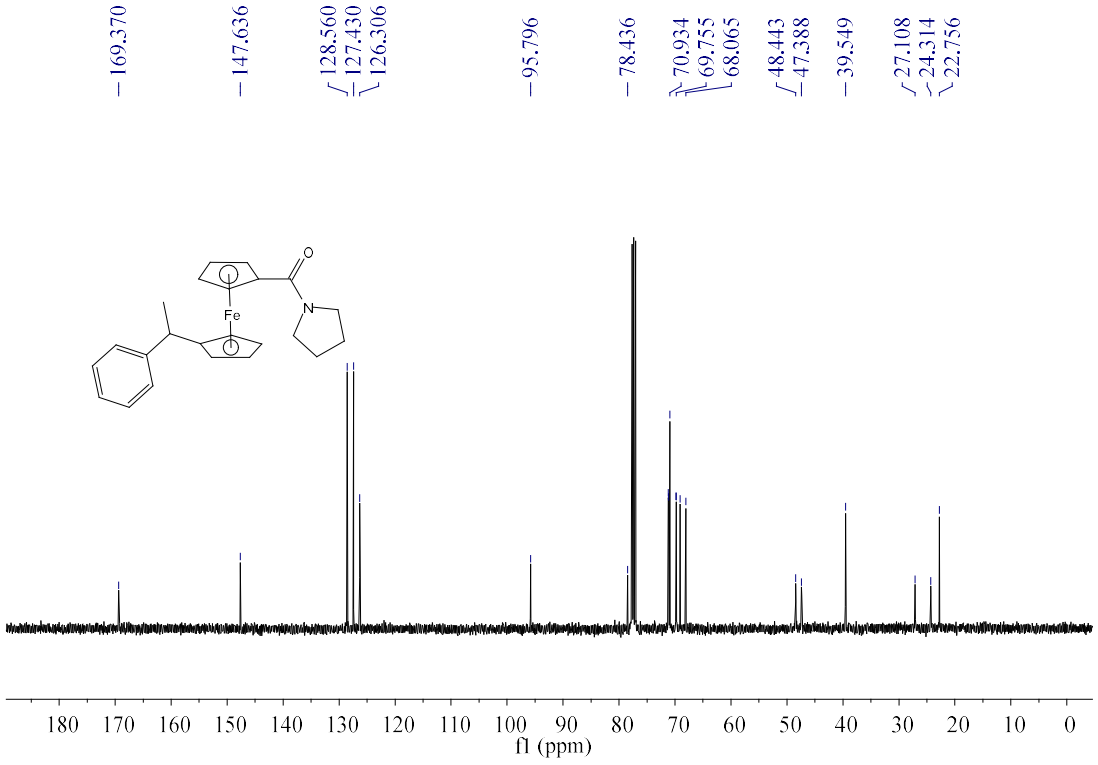
1af（^{1}H NMR and ^{13}C NMR）



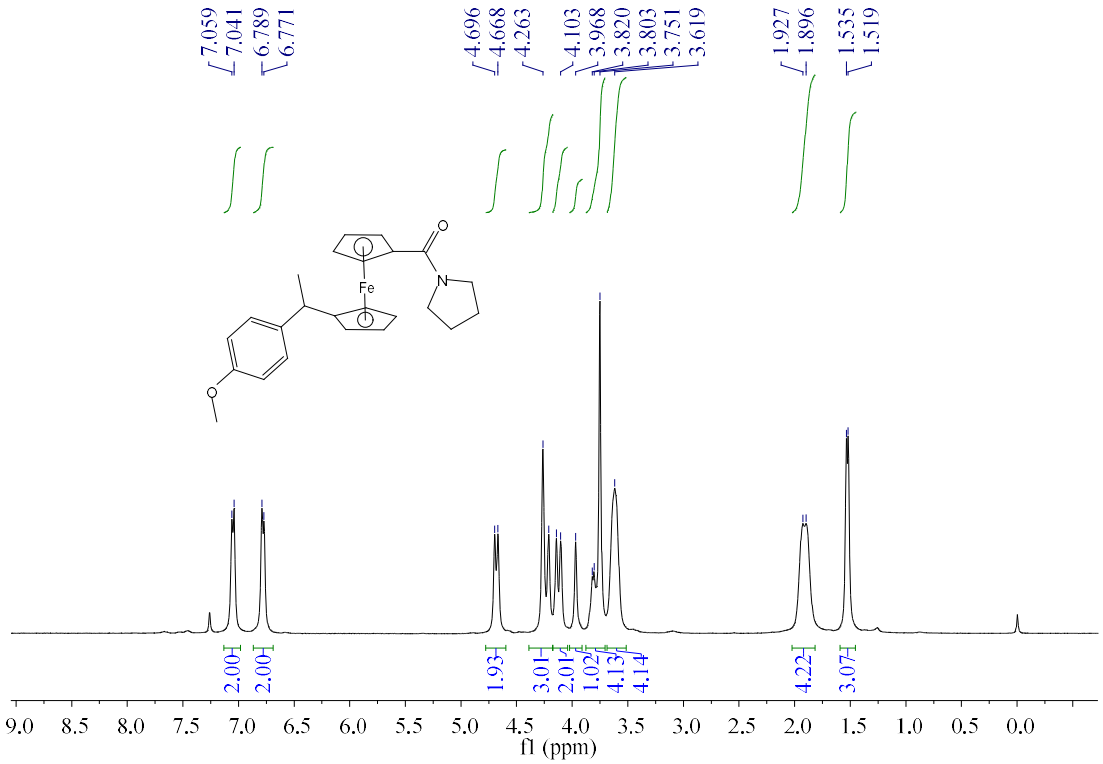


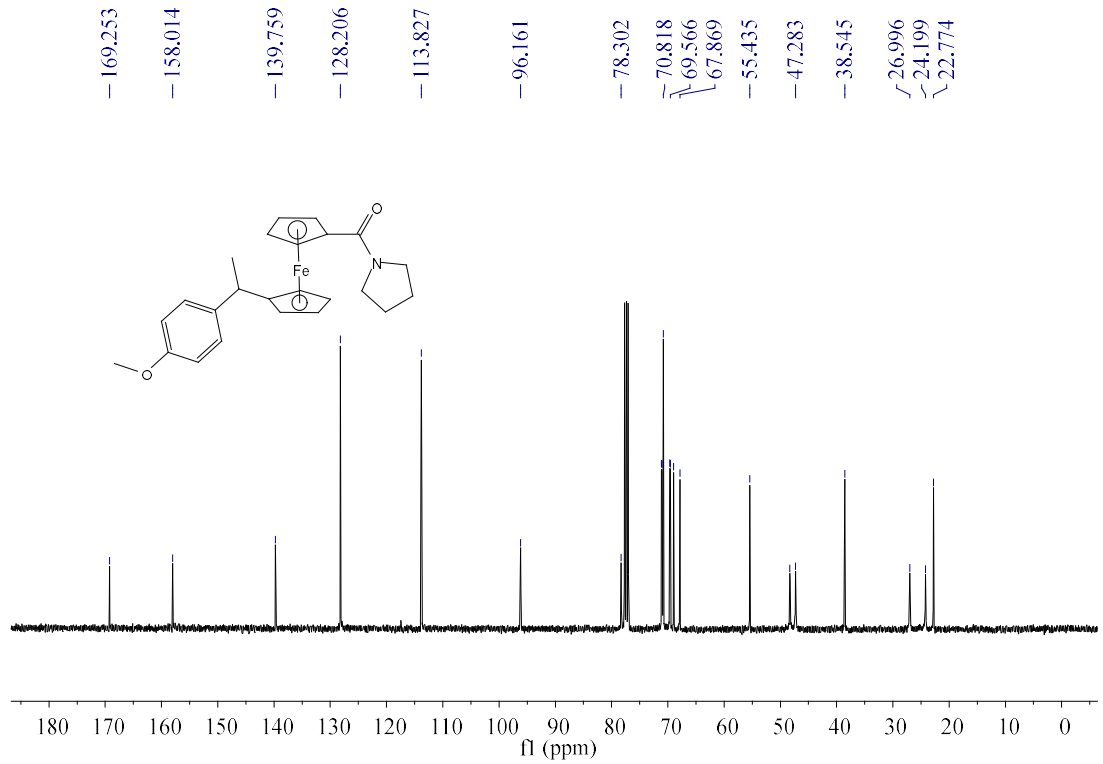
1ag（^{1}H NMR and ^{13}C NMR）



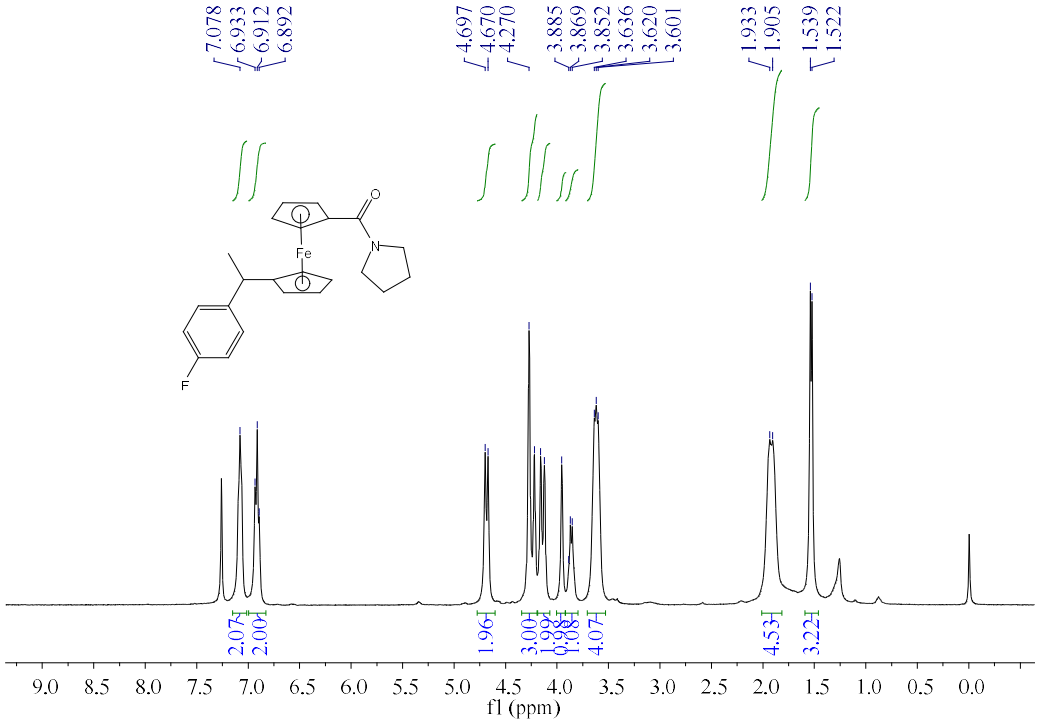


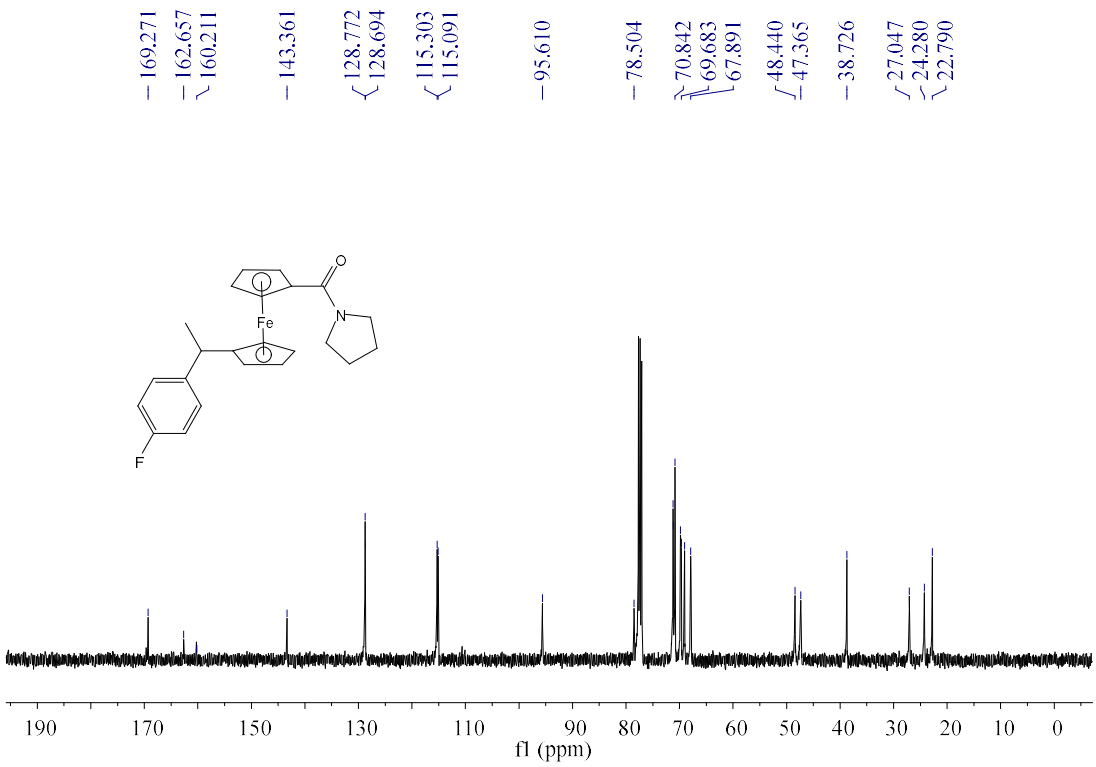
1ah（^{1}H NMR and ^{13}C NMR）

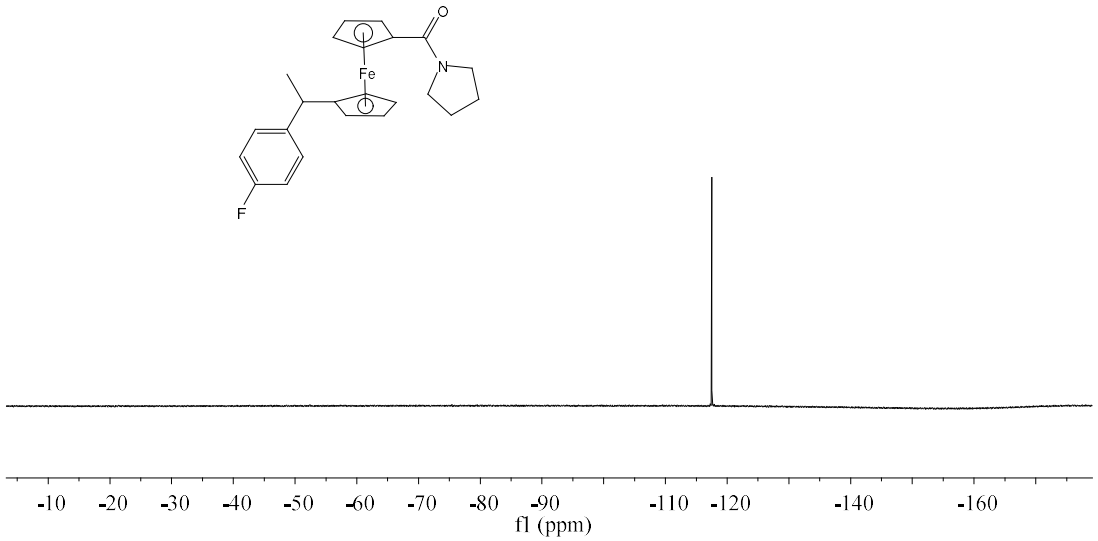




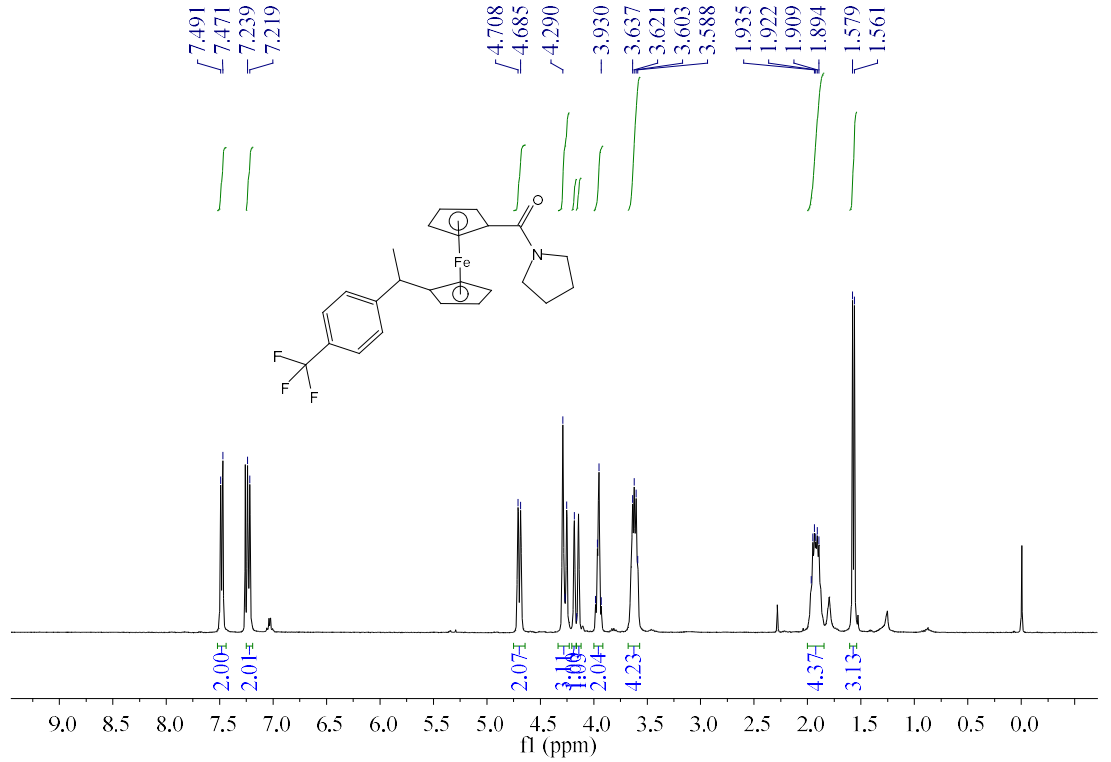
1ai（^{1}H NMR ,^{13}C NMR and ^{19}F NMR）

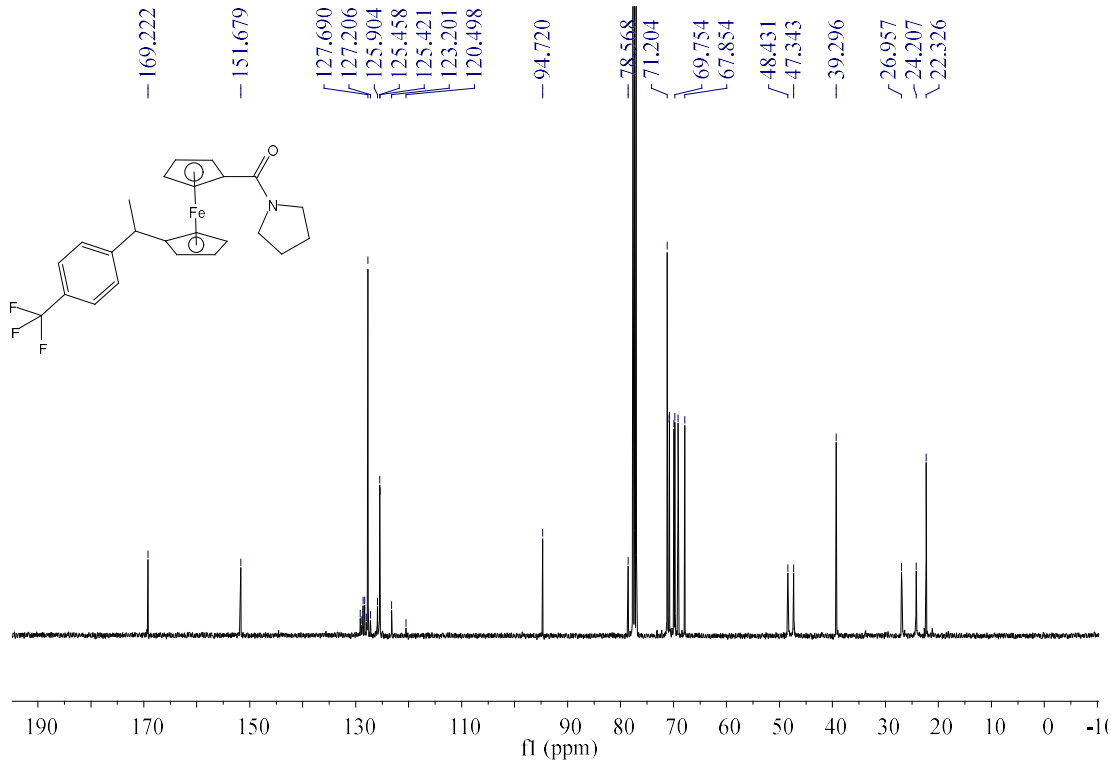


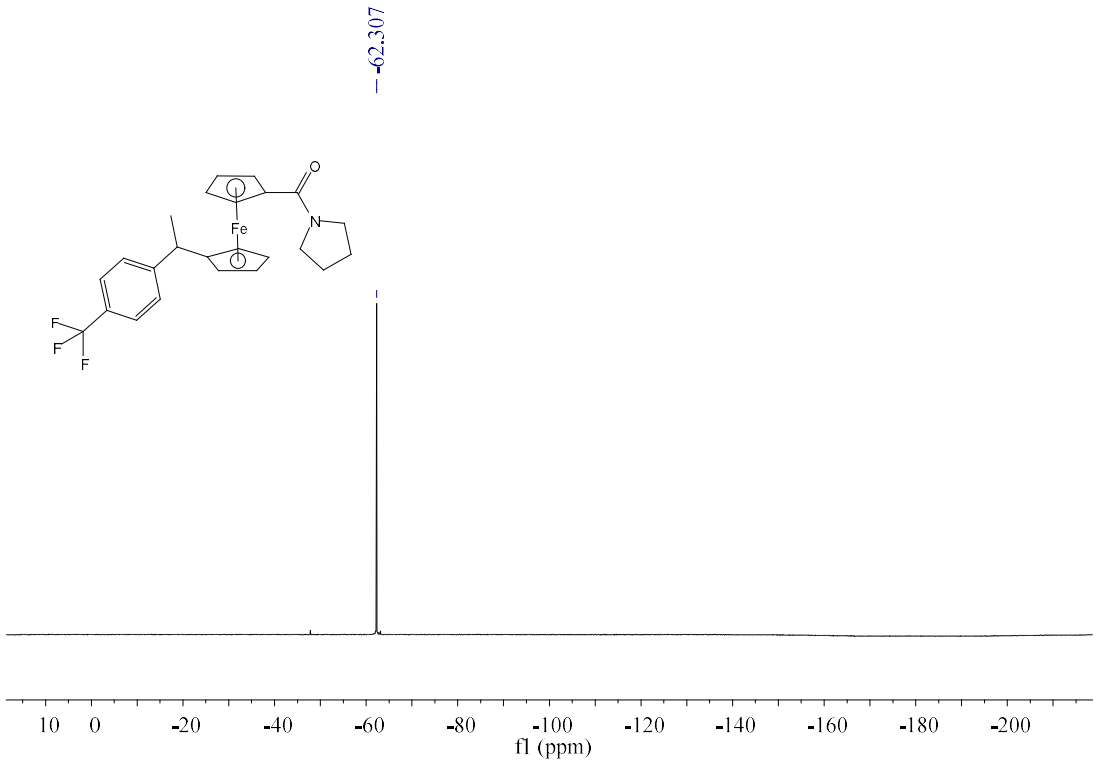



O
N
Fe
F
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-120
-140
-160
f1 (ppm)

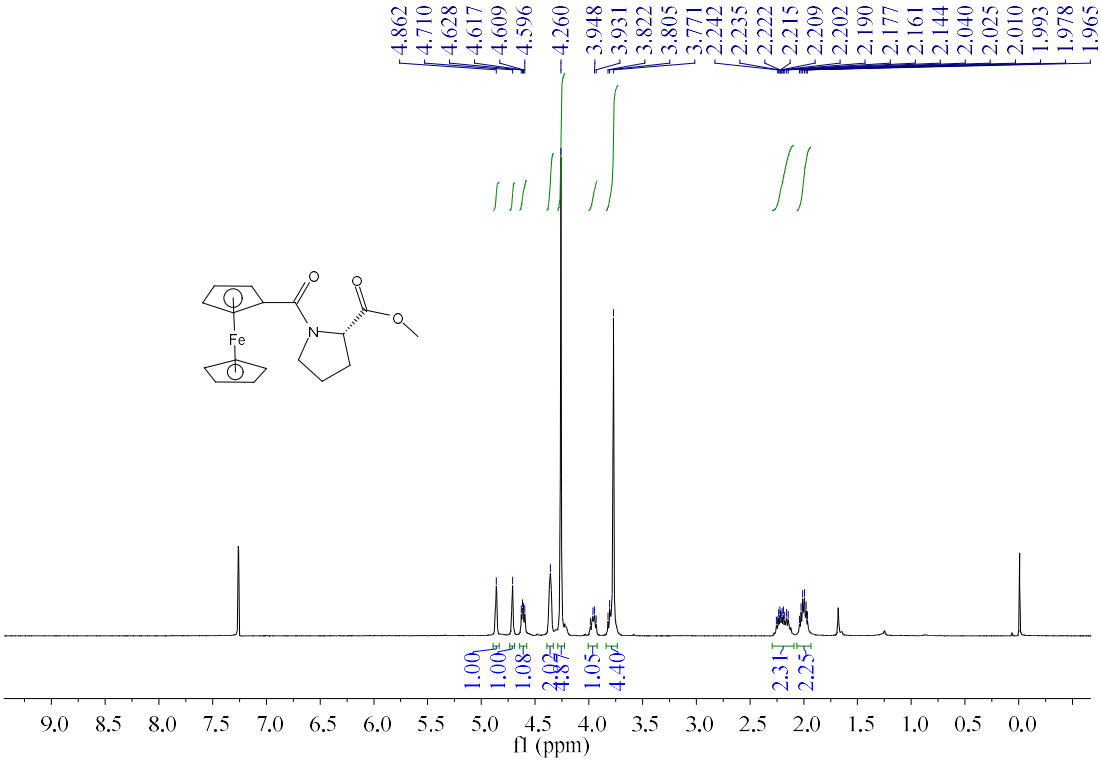
1aj（^{1}H NMR ,^{13}C NMR and ^{19}F NMR）

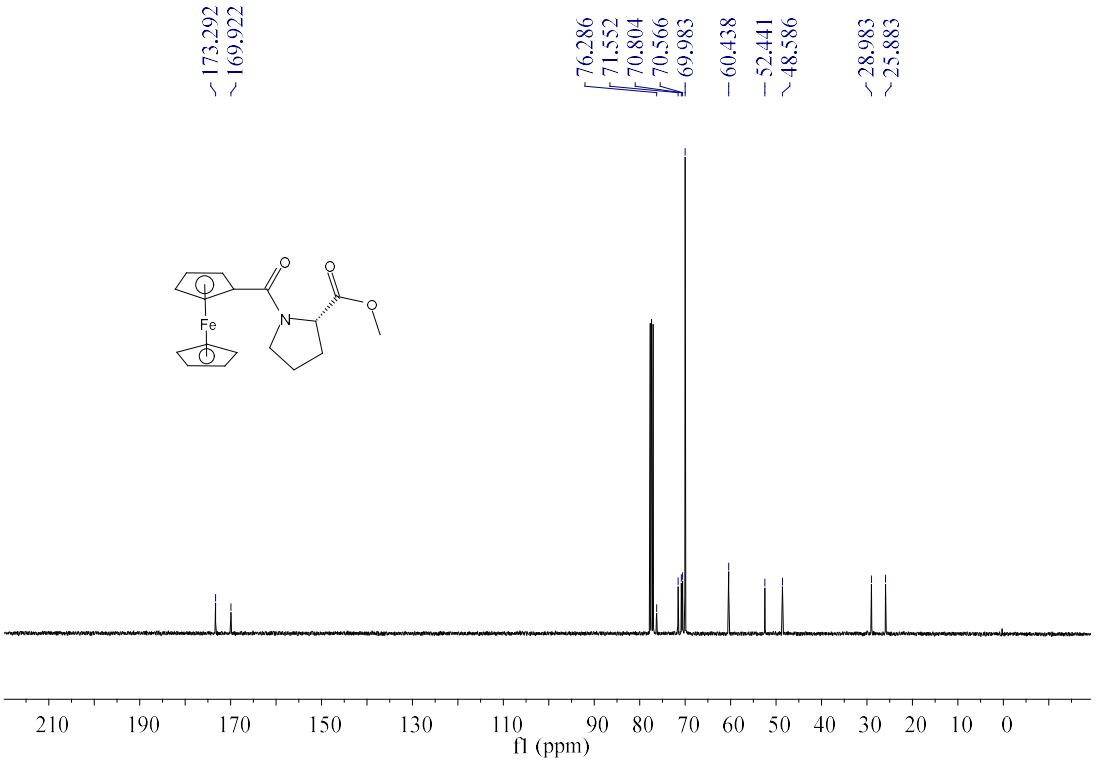




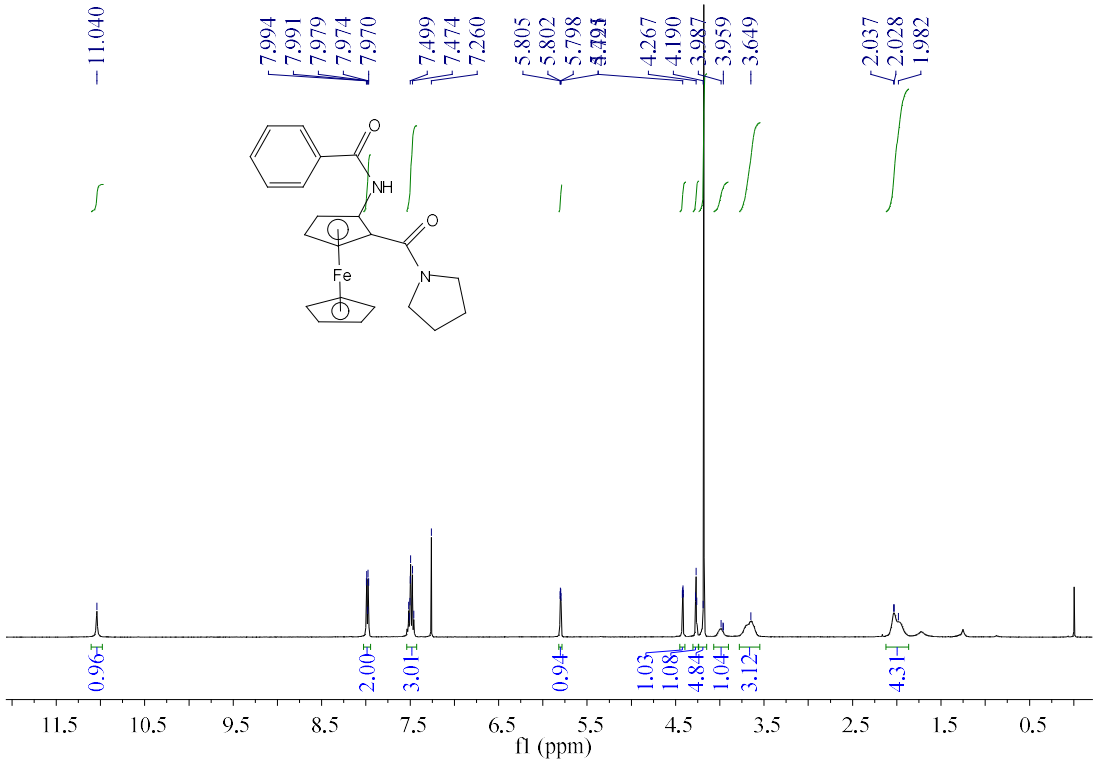

-62.307
O
N
Fe
F
F
F
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

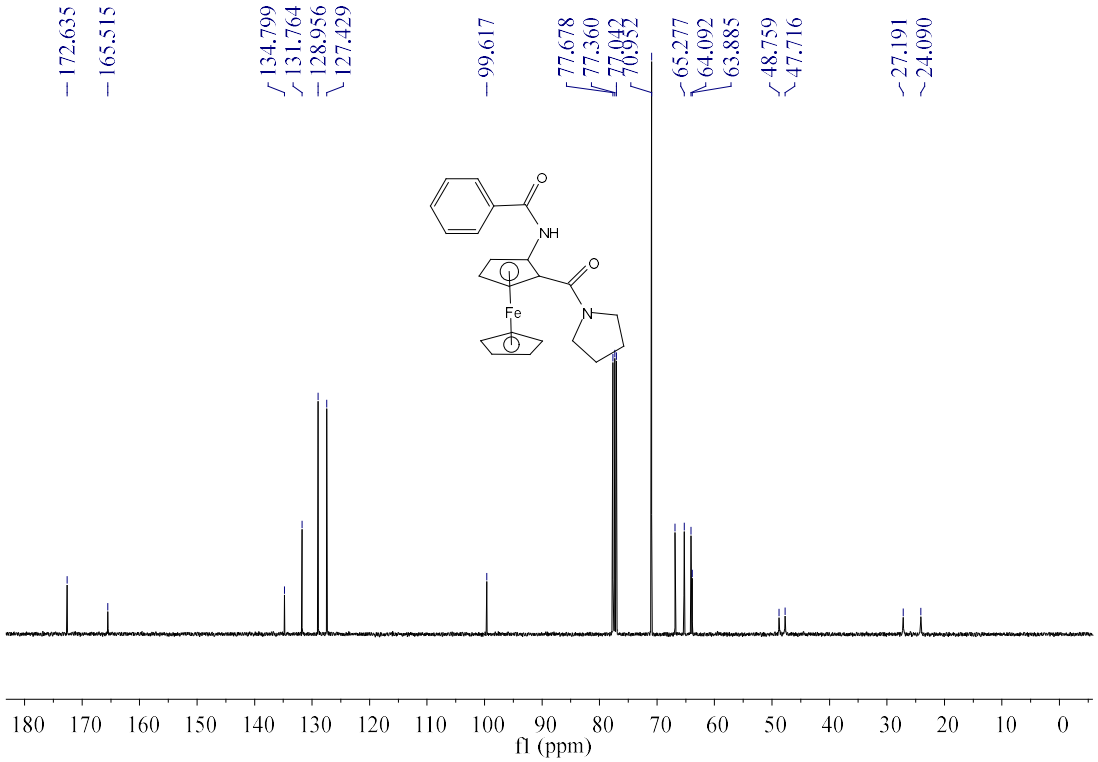
1ak（^{1}H NMR and ^{13}C NMR）



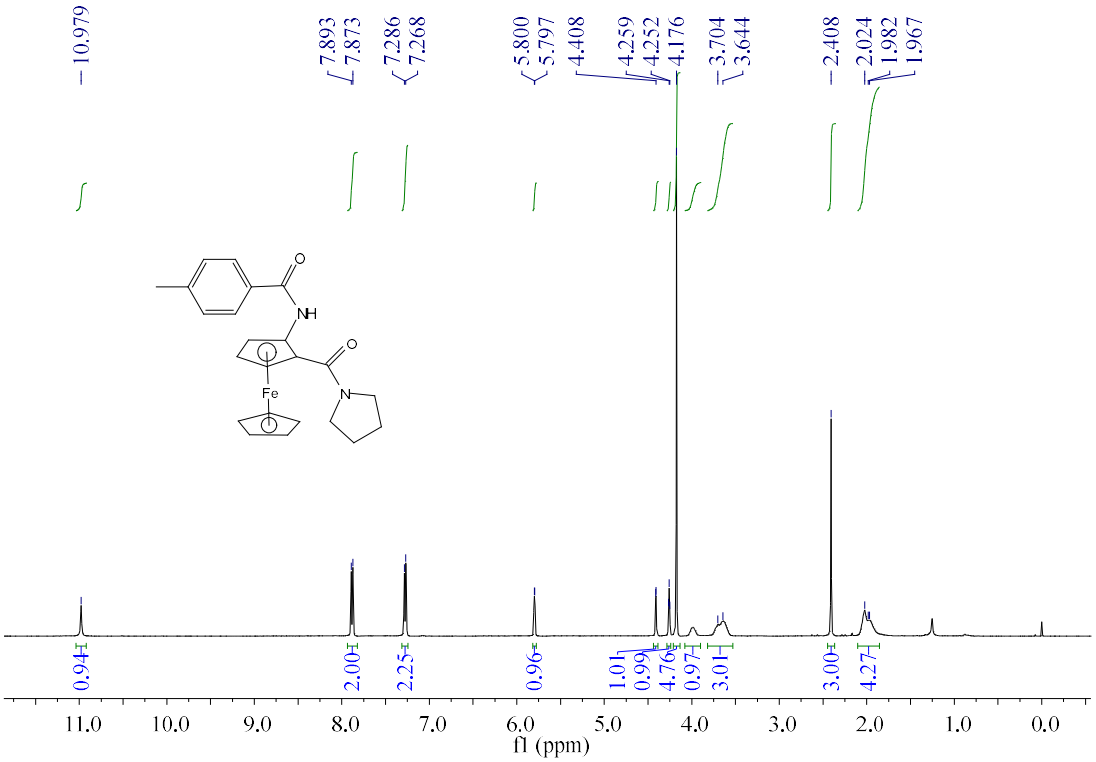


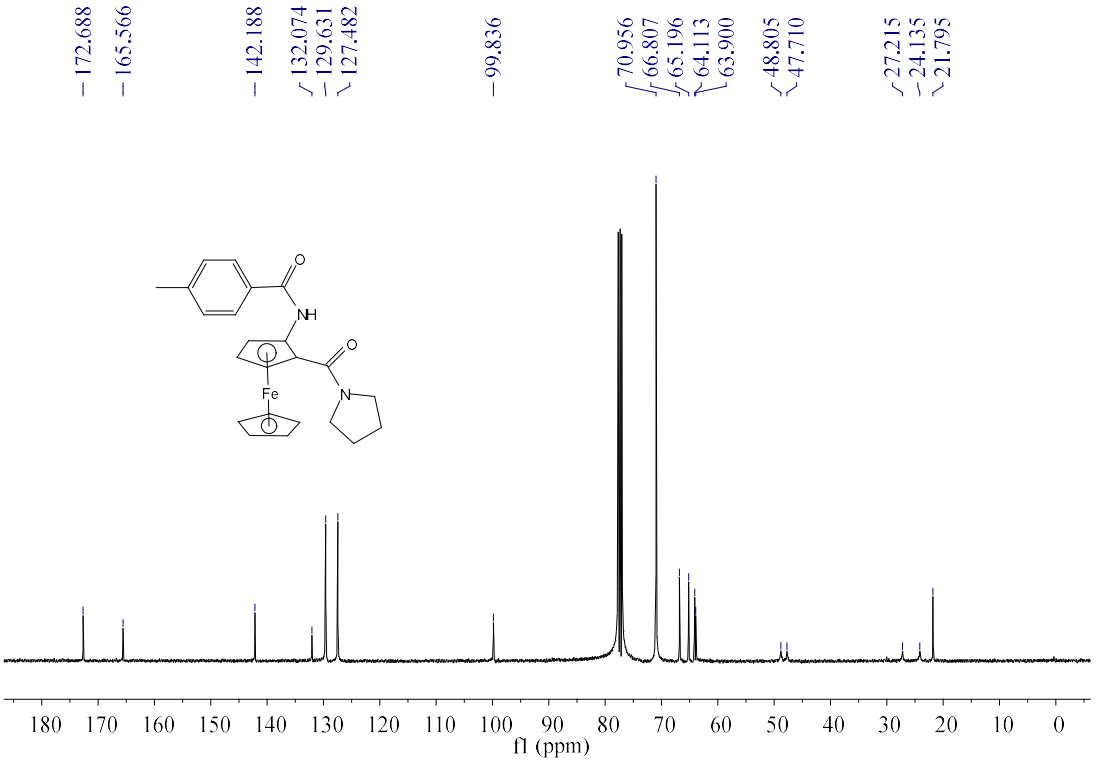
3a（^{1}H NMR and ^{13}C NMR).



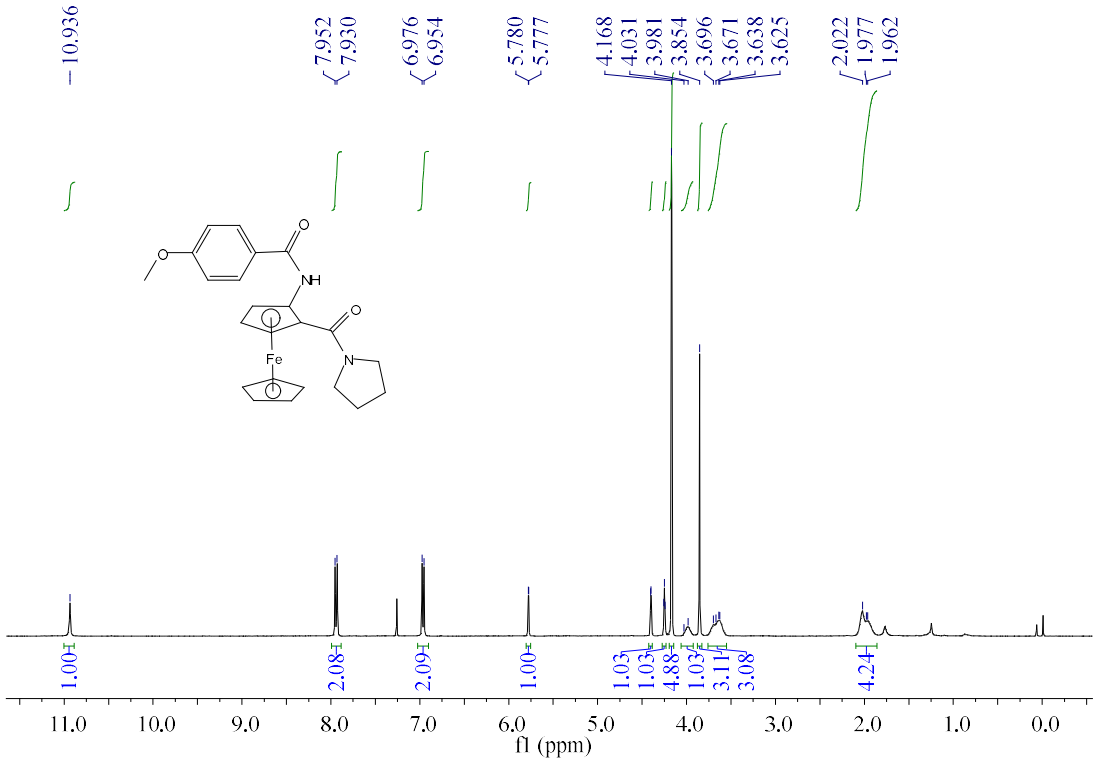


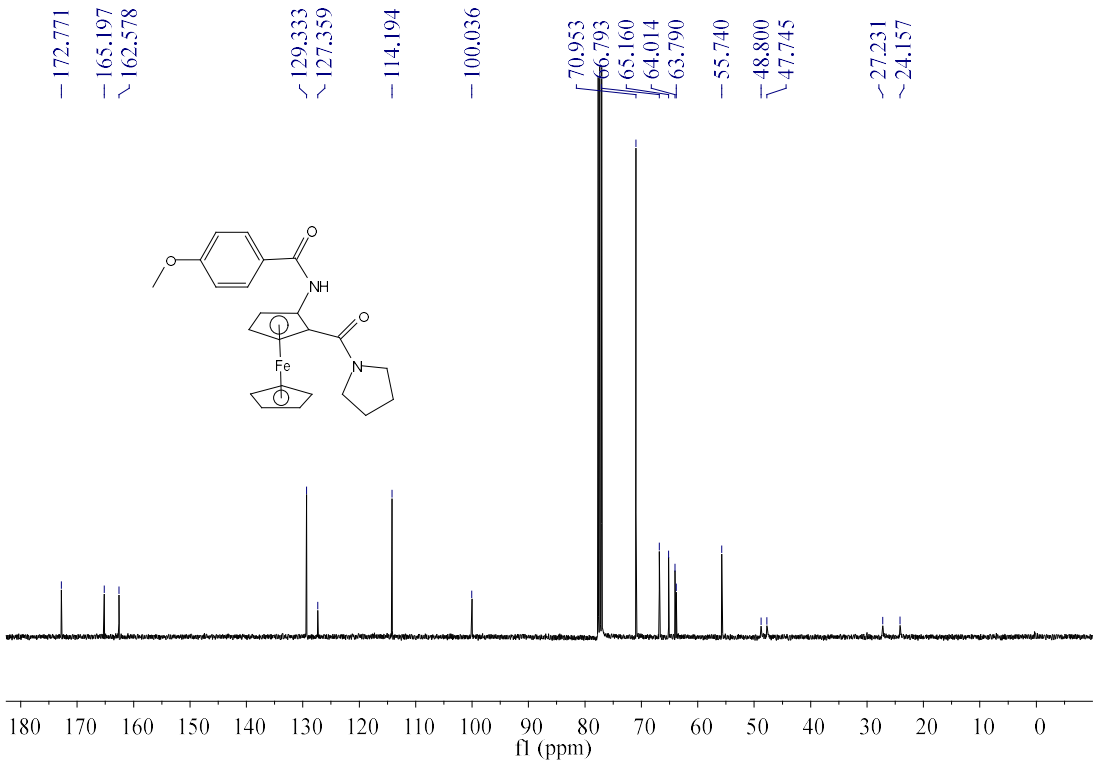
3b（^{1}H NMR and ^{13}C NMR).



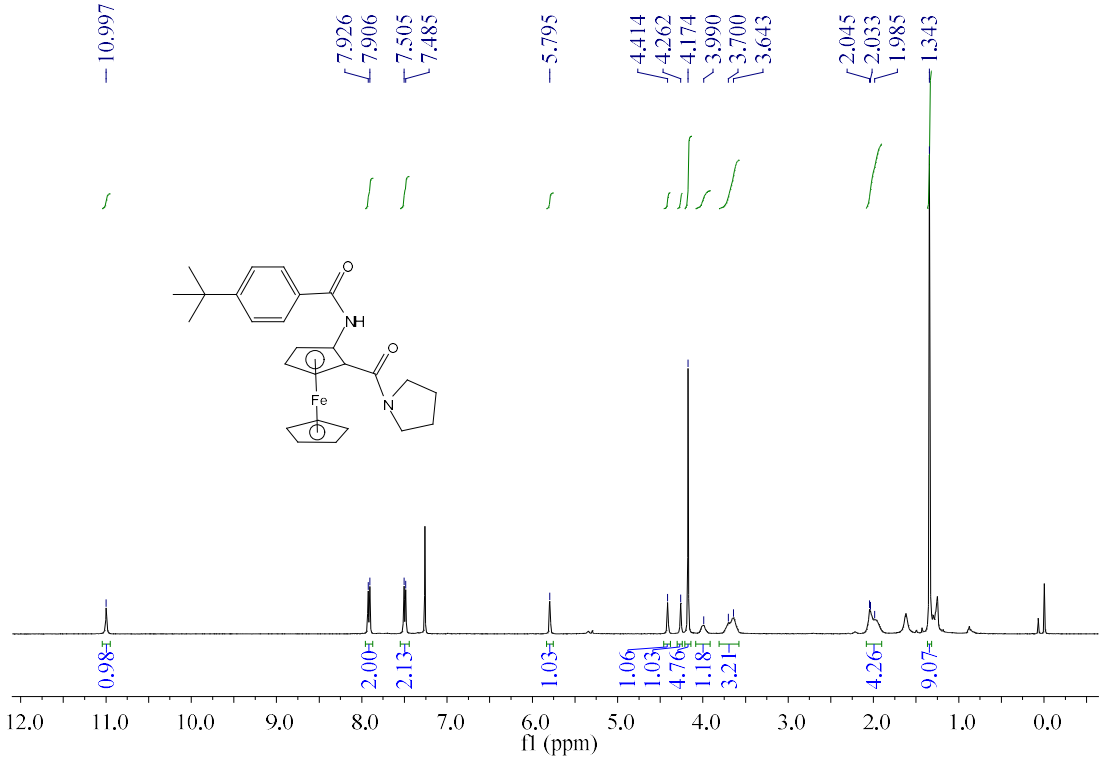


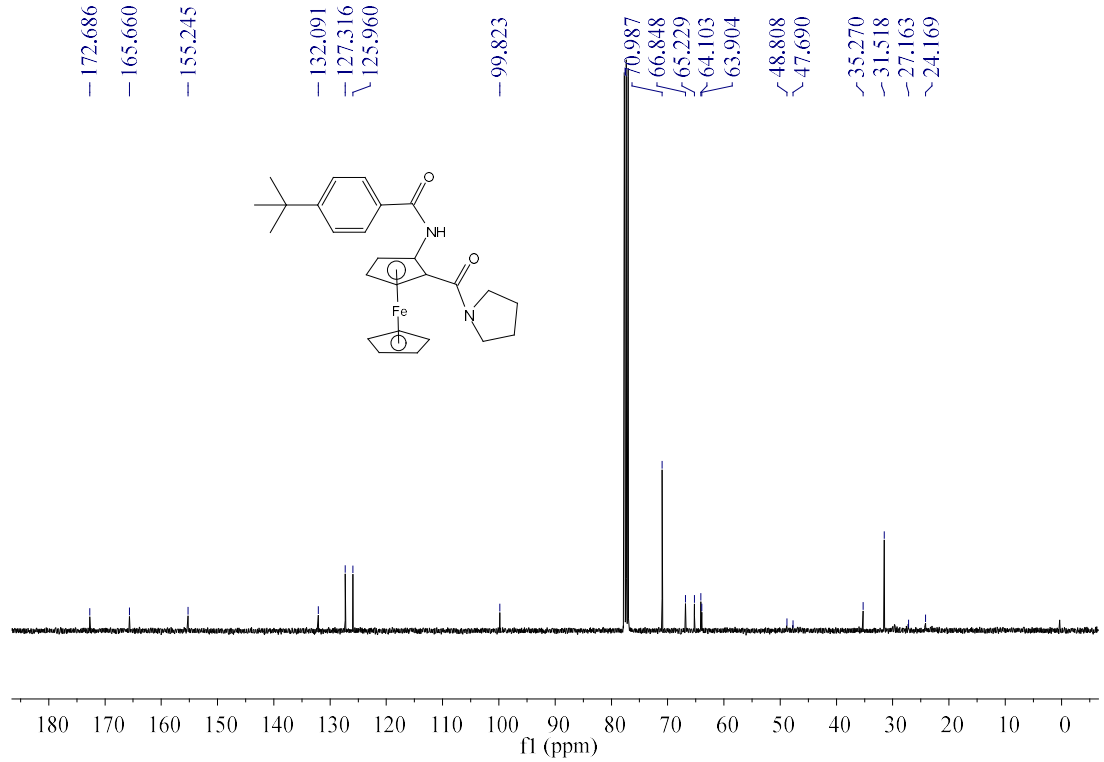
3c（^{1}H NMR and ^{13}C NMR）.



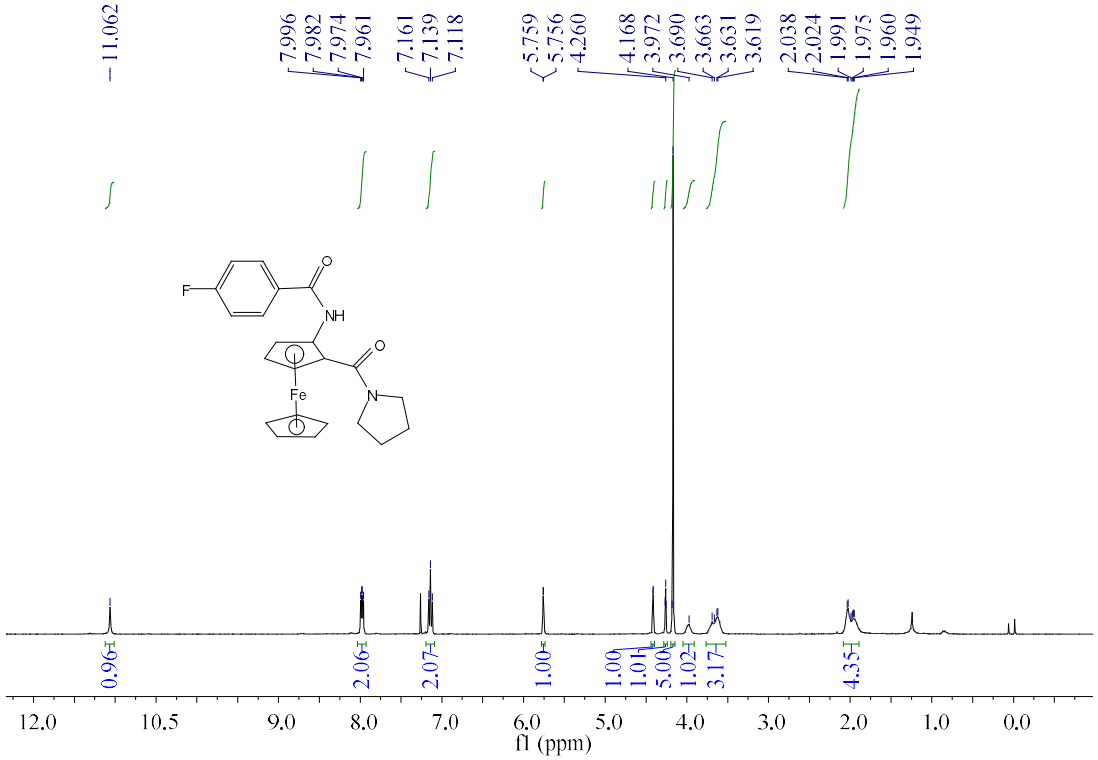


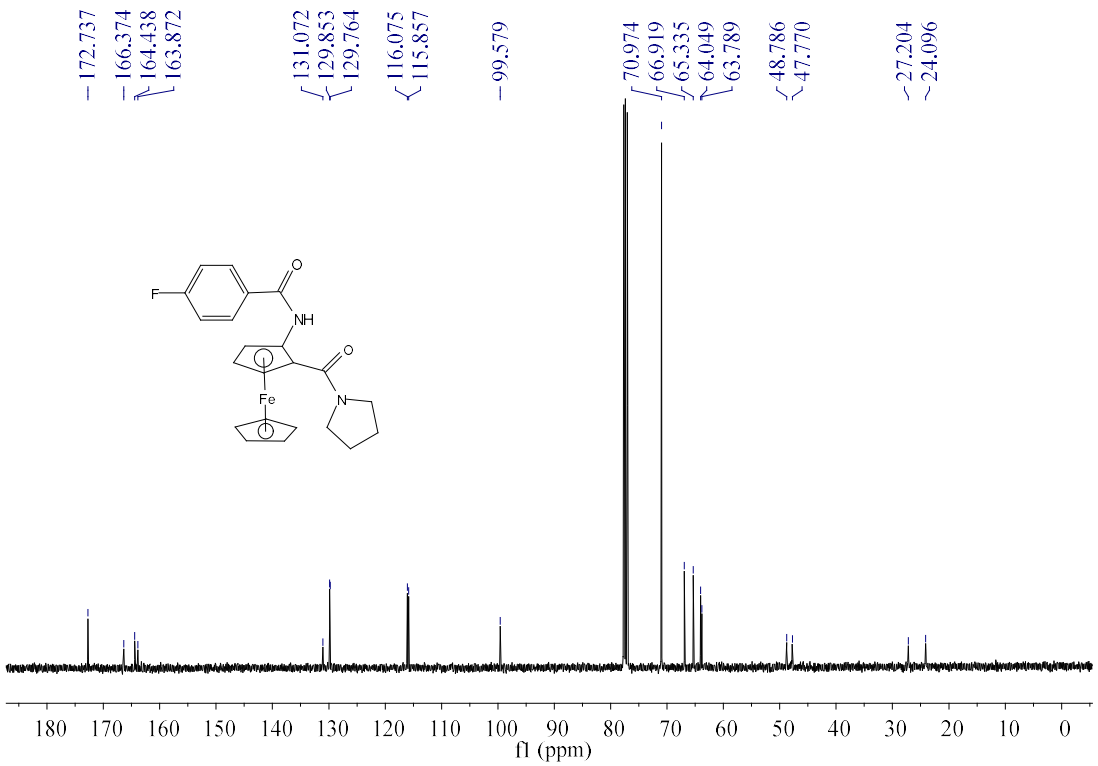
3d（^{1}H NMR and ^{13}C NMR)

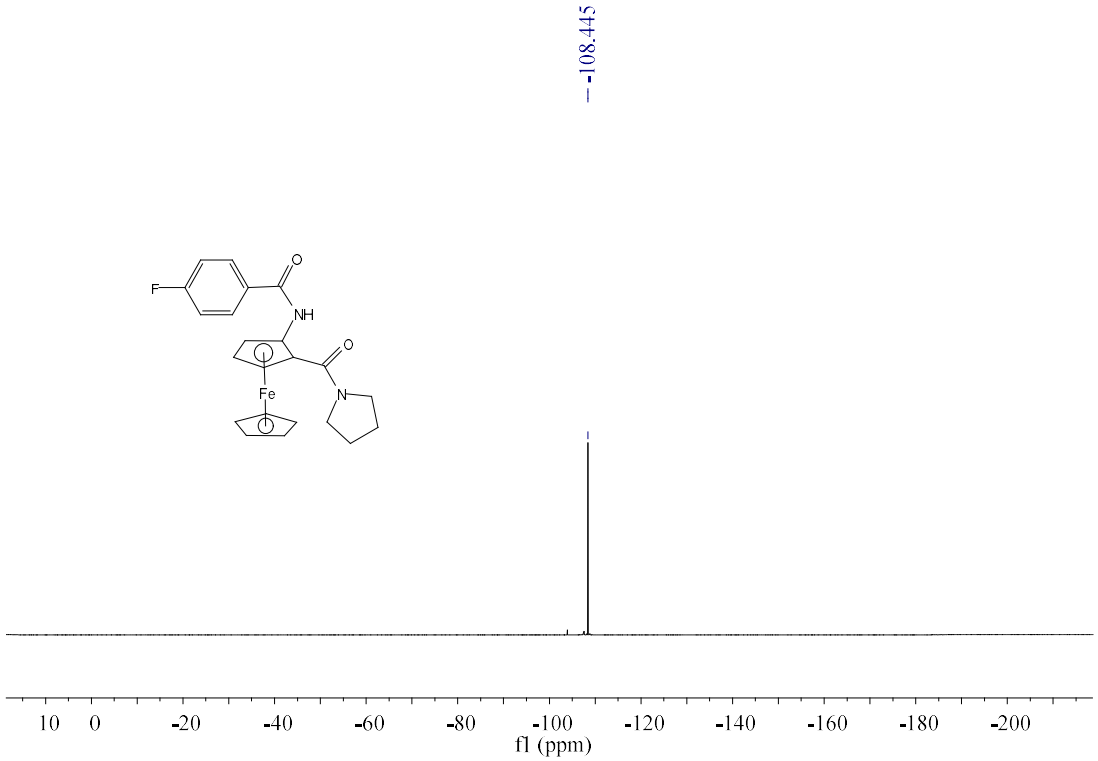




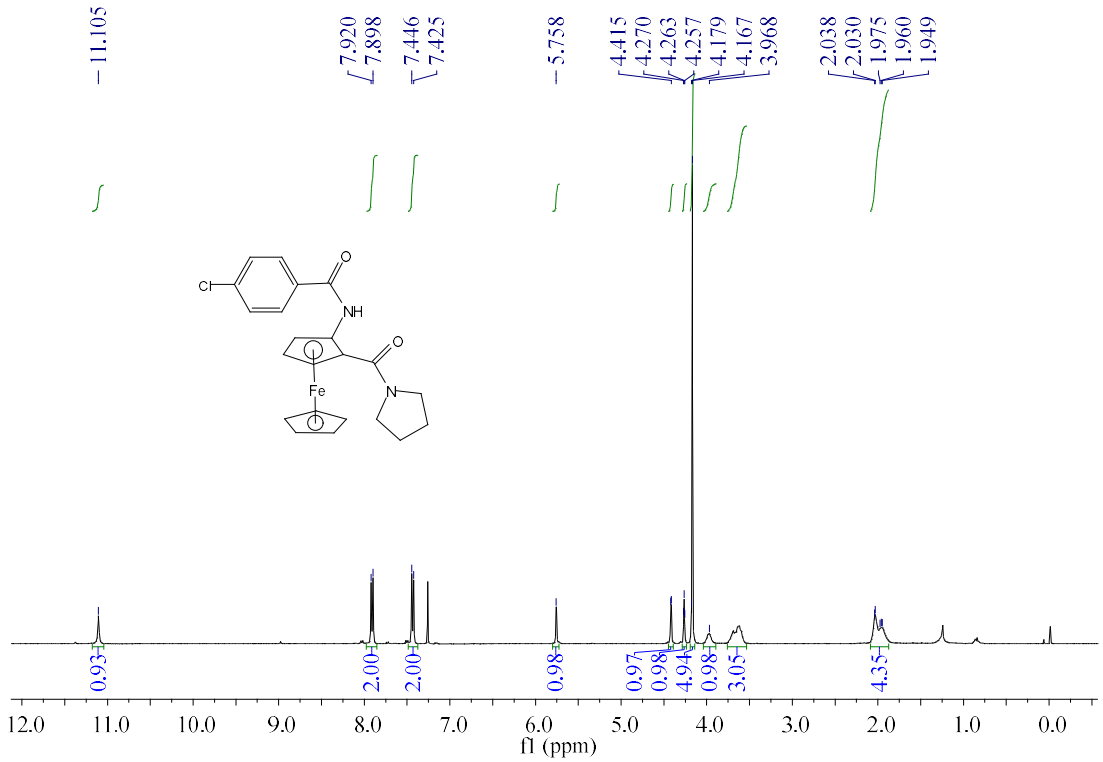
3e（^{1}H NMR , ^{13}C NMR and ^{19}F NMR)

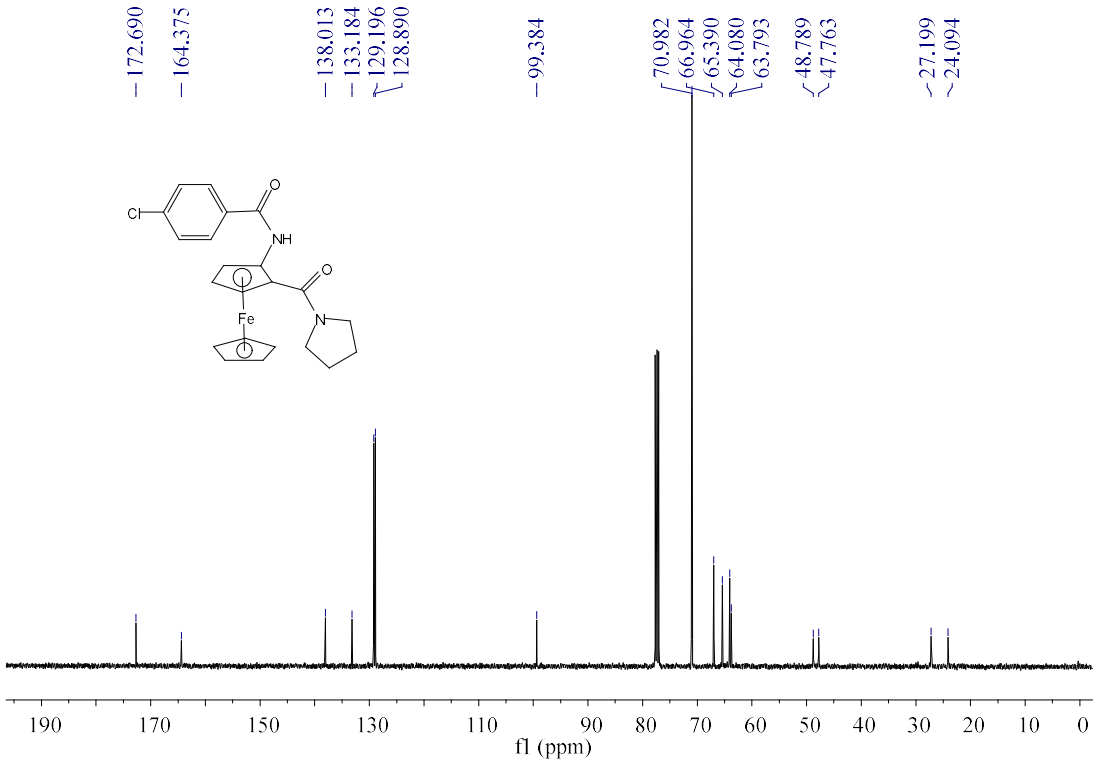






3f（^{1}H NMR and ^{13}C NMR)

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129.196
128.890
99.384
70.982
66.964
65.390
64.080
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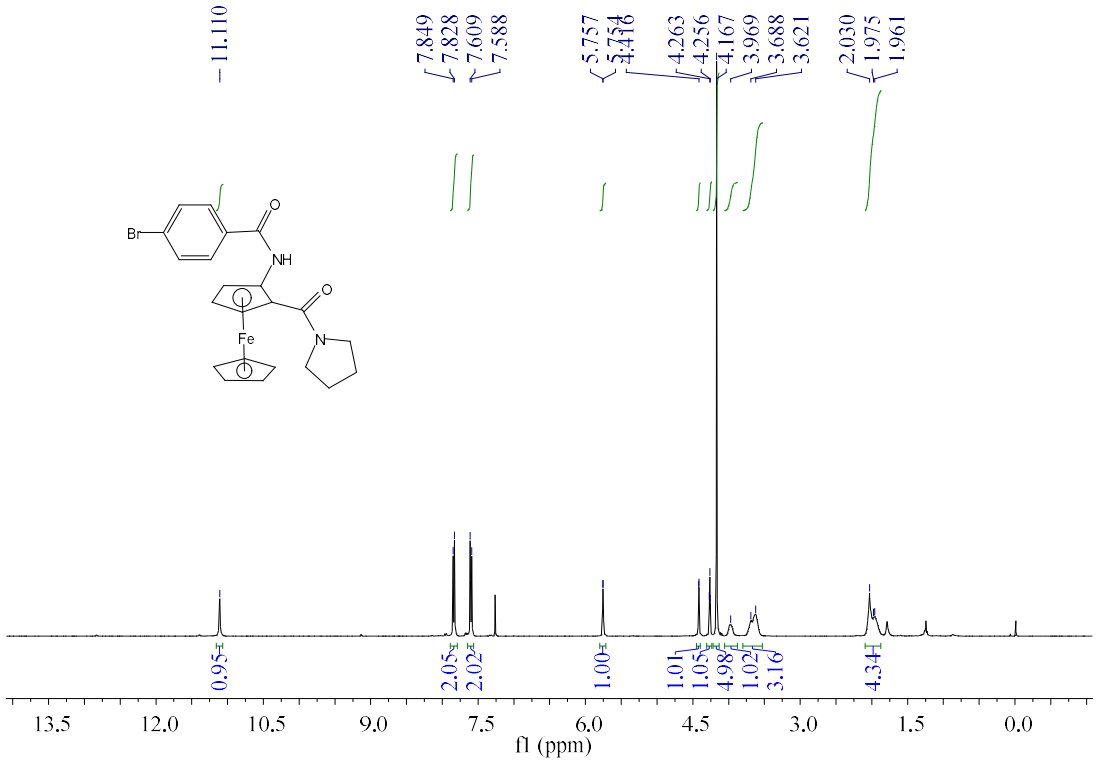
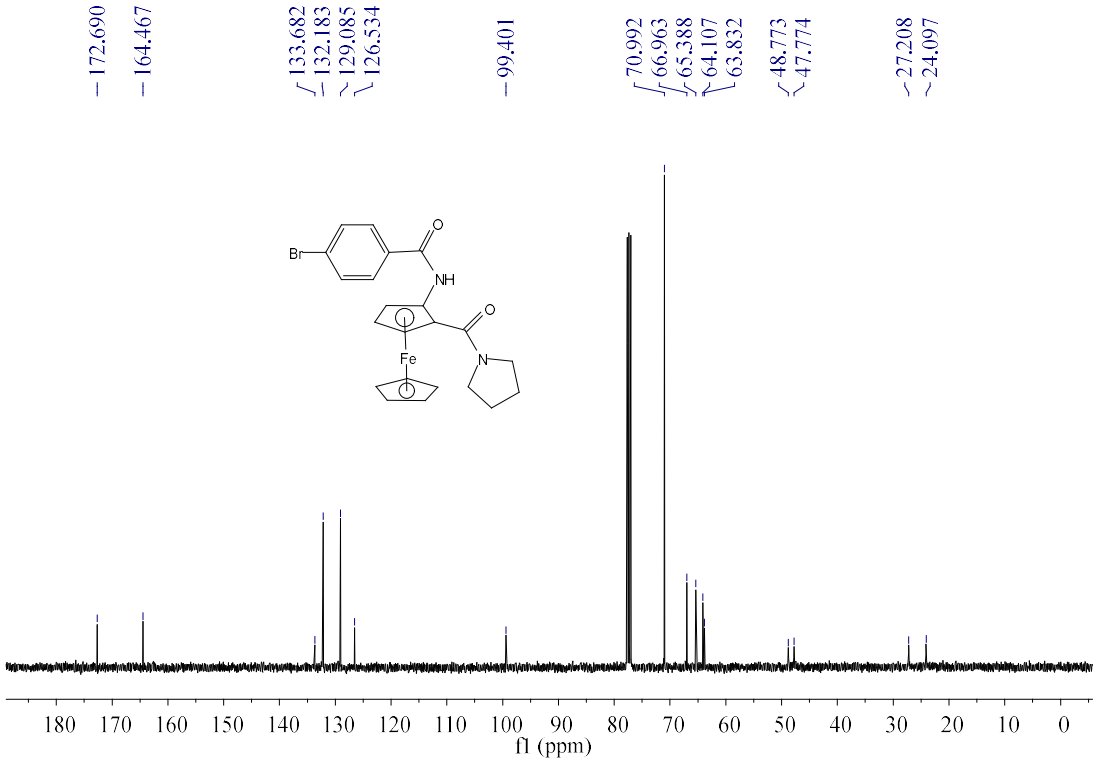
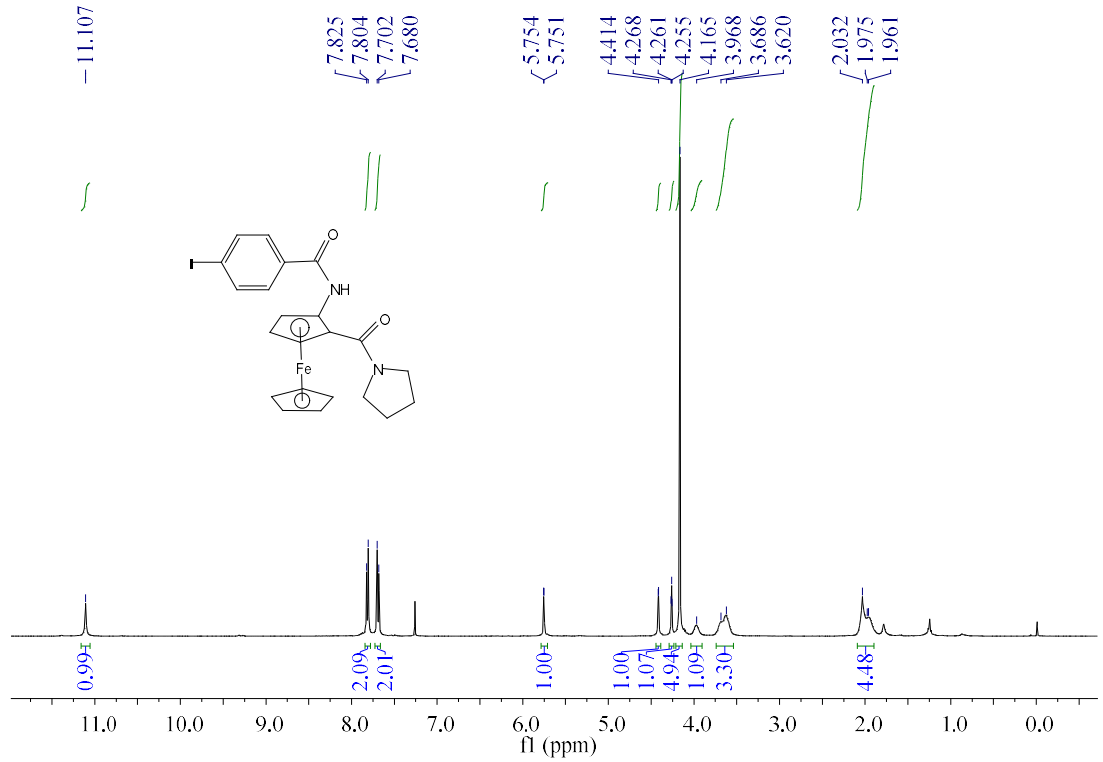
48.789
47.763
27.199
24.094
Cl
O
NH
O
Fe
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

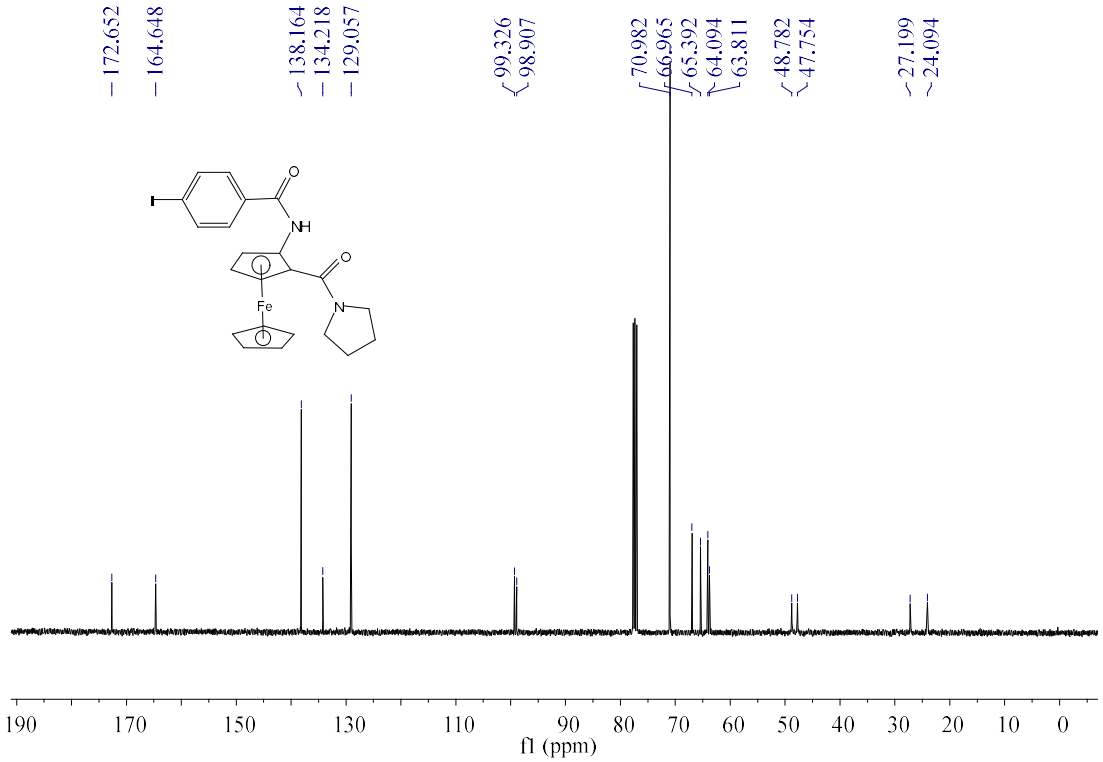
3g（^{1}H NMR and ^{13}C NMR)



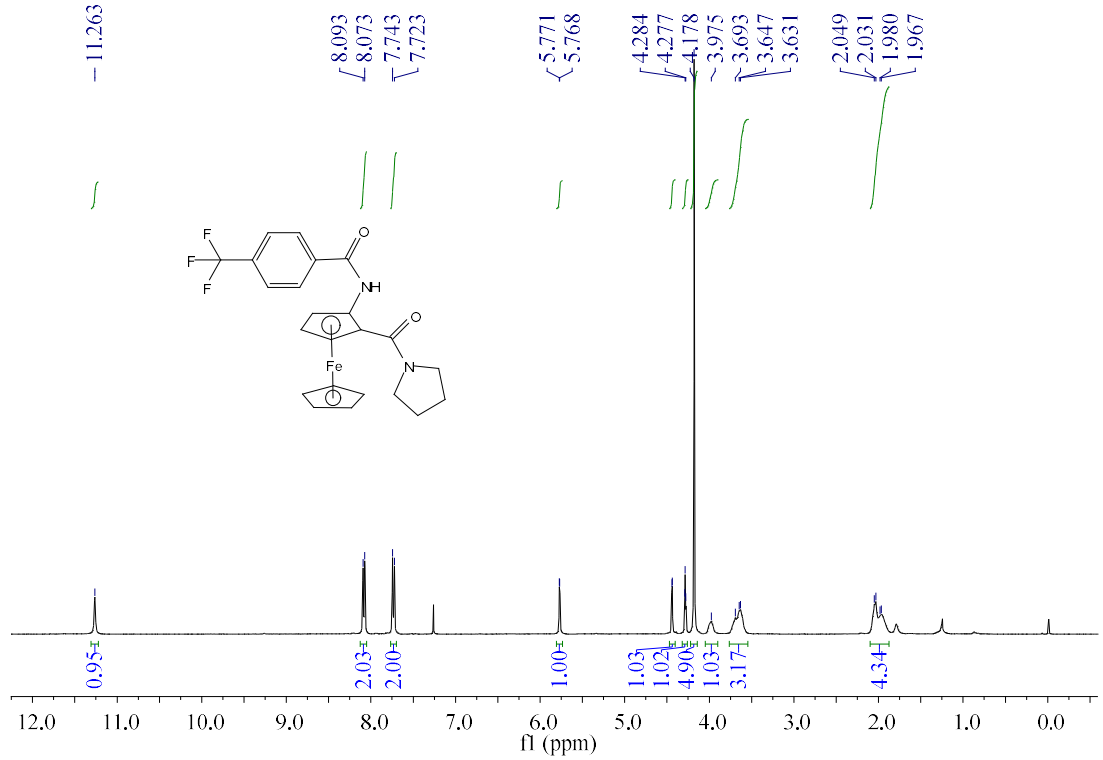


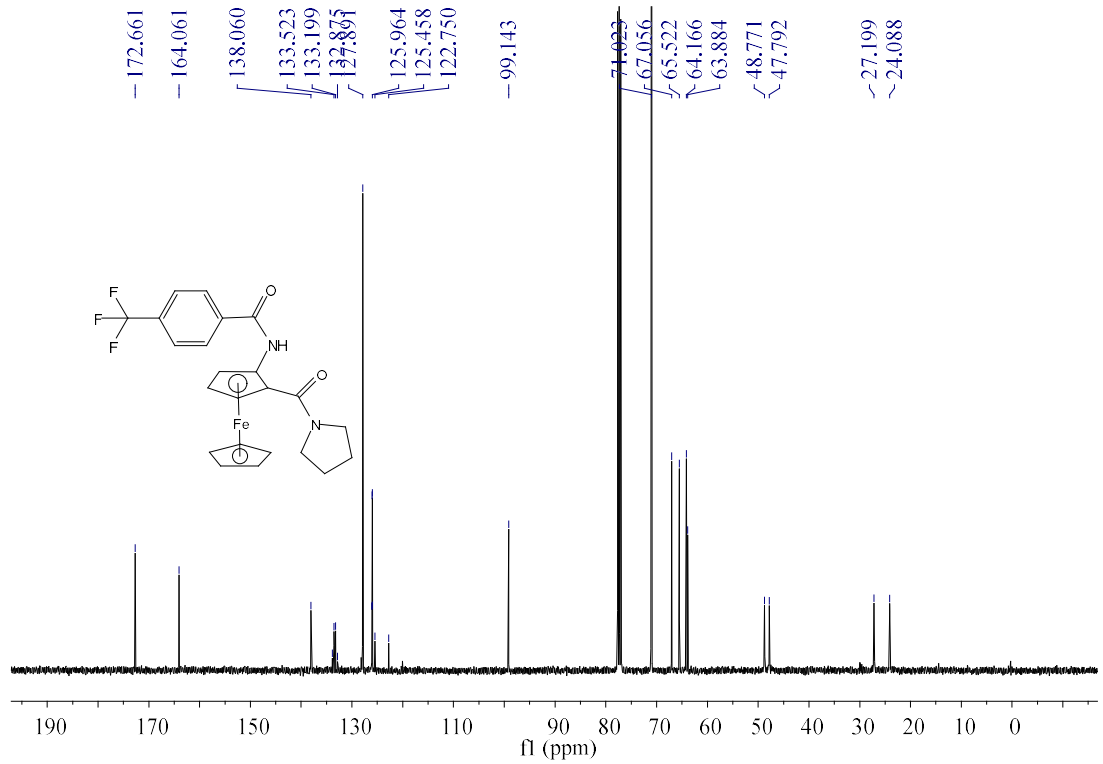
3h（^{1}H NMR and ^{13}C NMR)

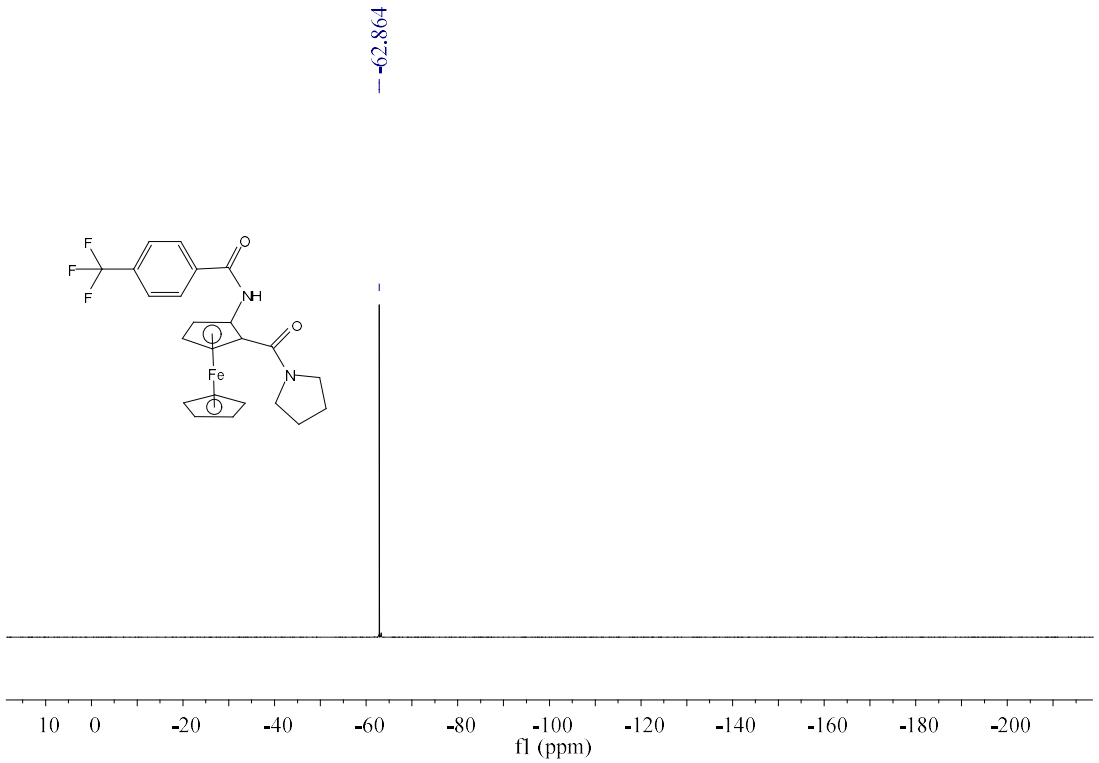




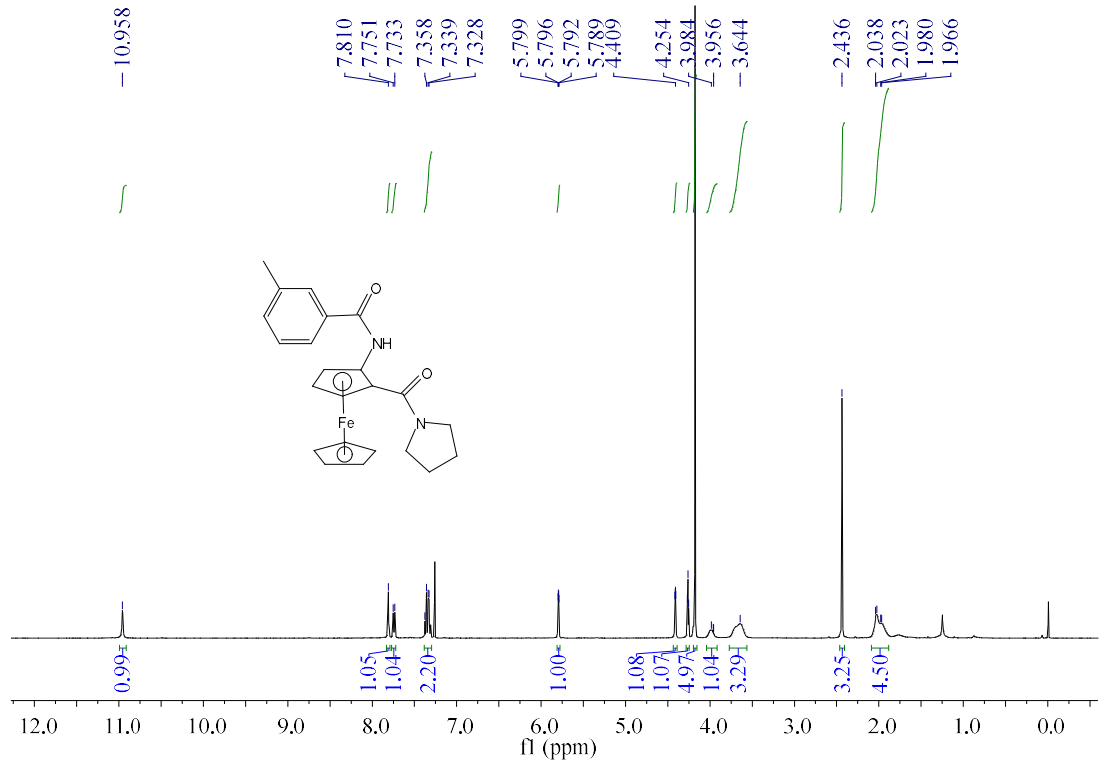
3i（^{1}H NMR, ^{13}C NMR and ^{19}F NMR)

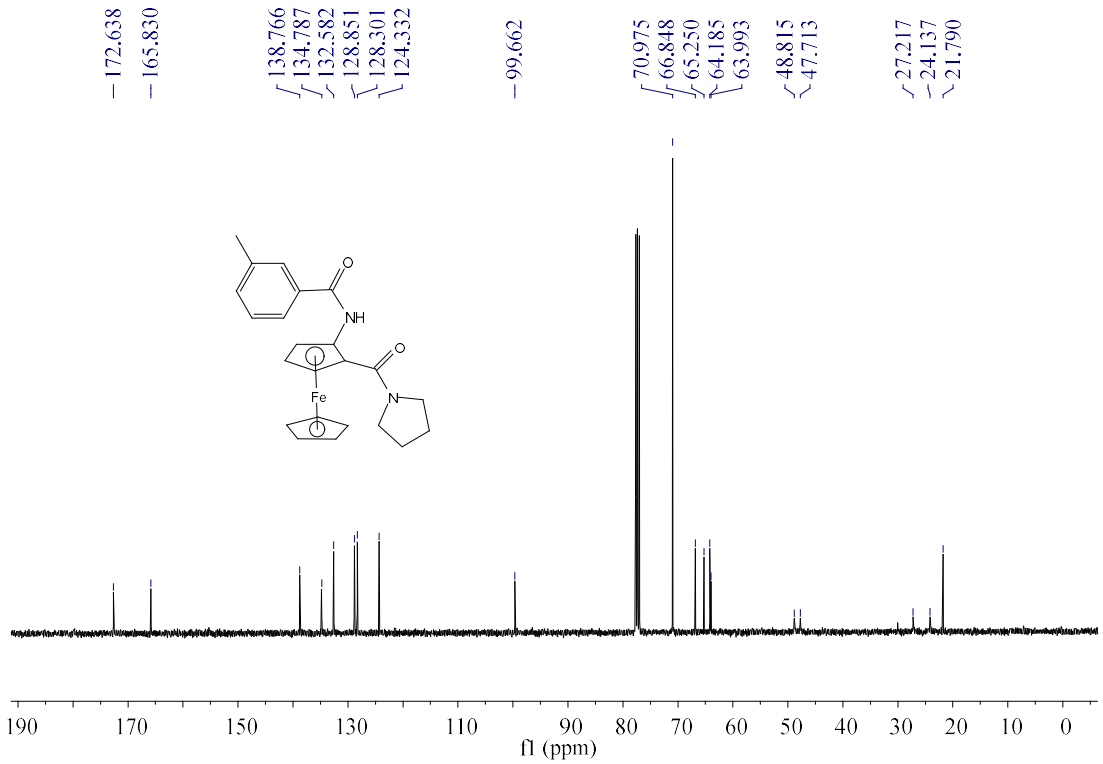




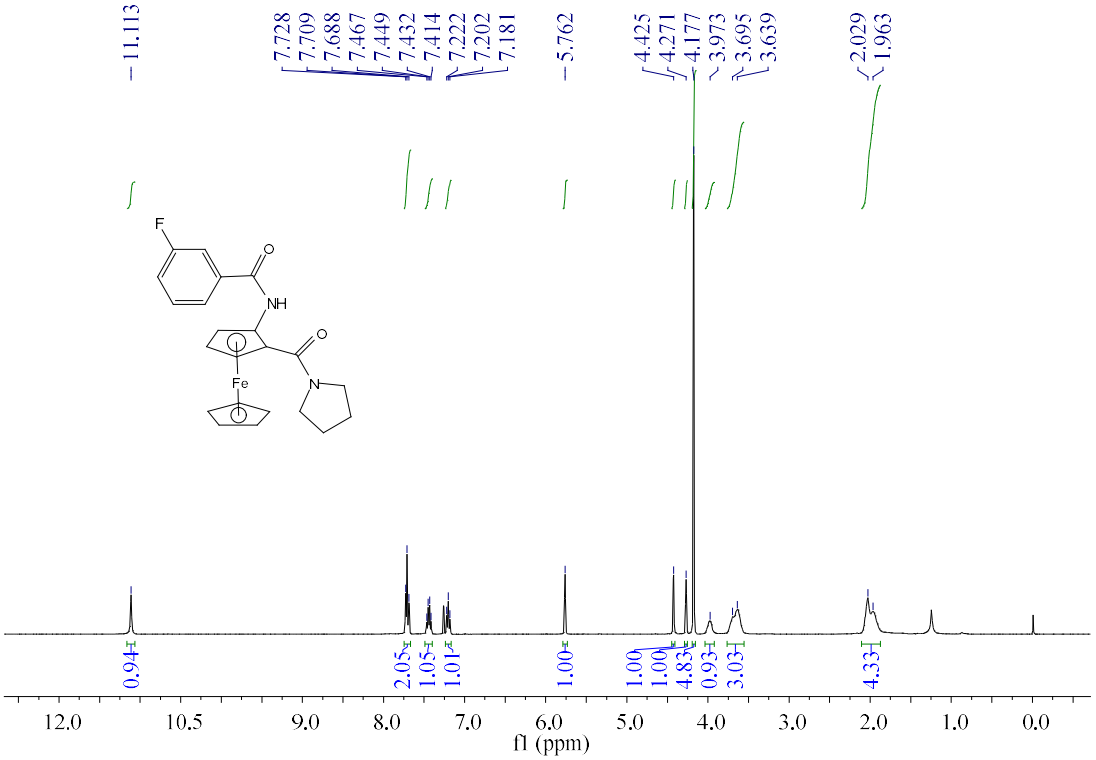

-62.864
F
F
F
O
NH
O
Fe
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

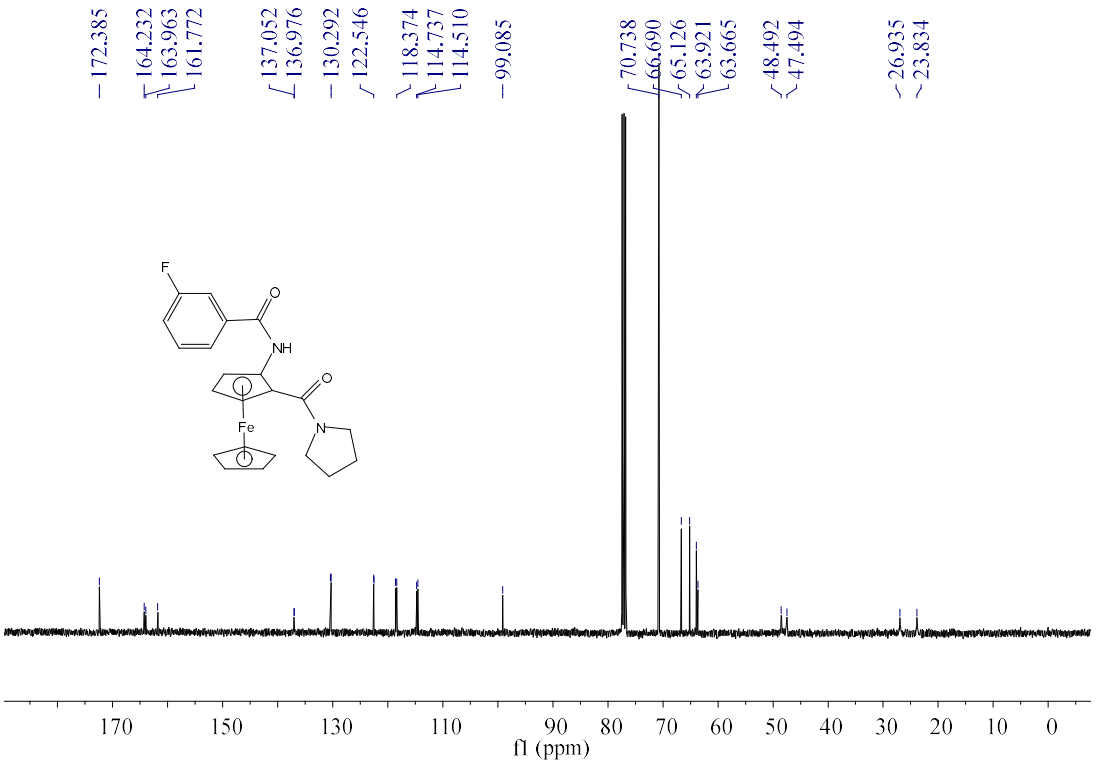
3j（^{1}H NMR and ^{13}C NMR)

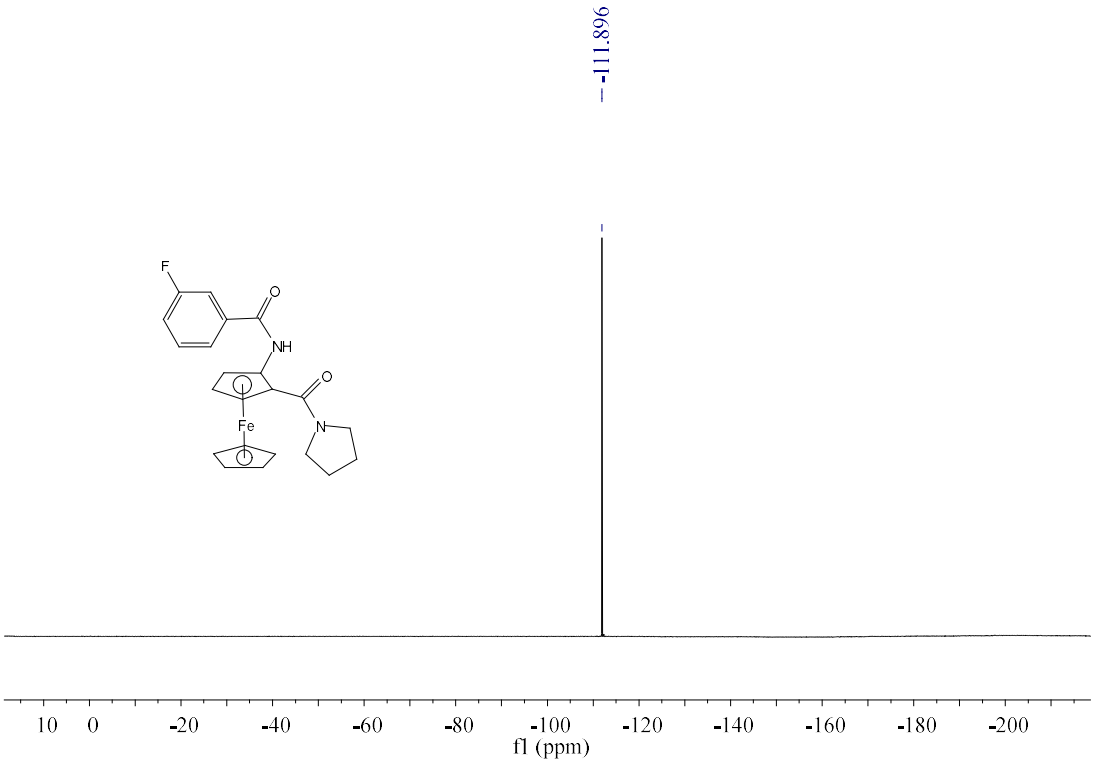




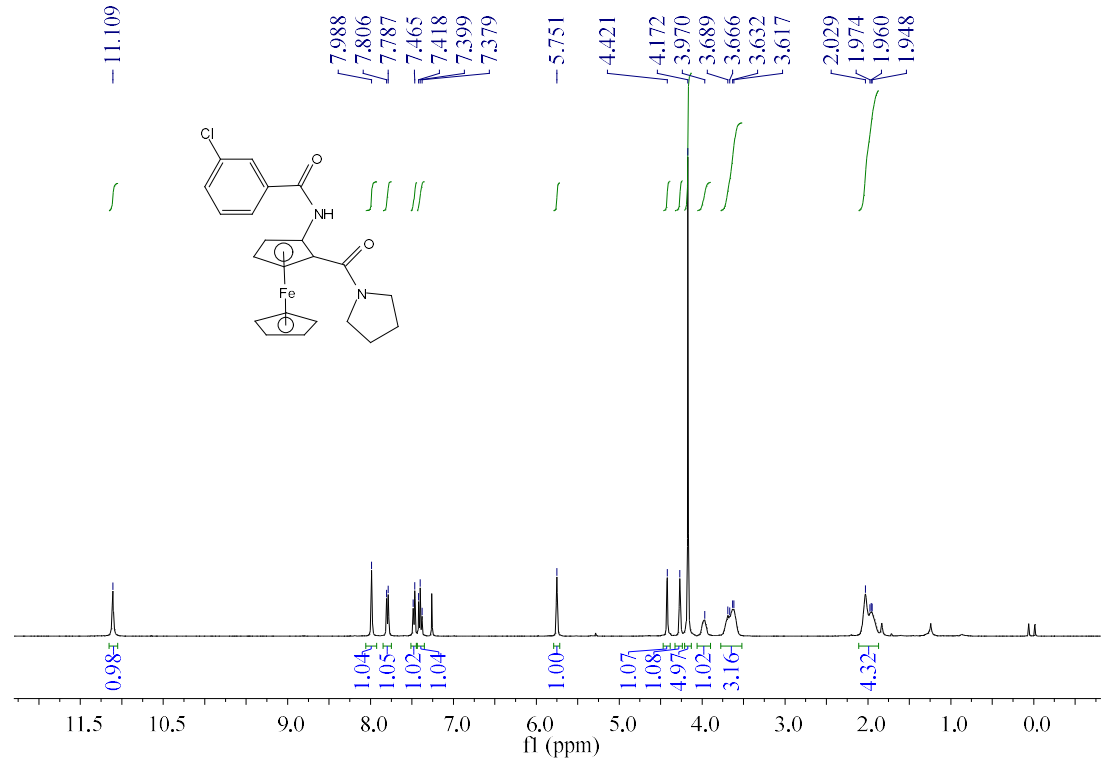
3k（^{1}H NMR, ^{13}C NMR and ^{19F} NMR)

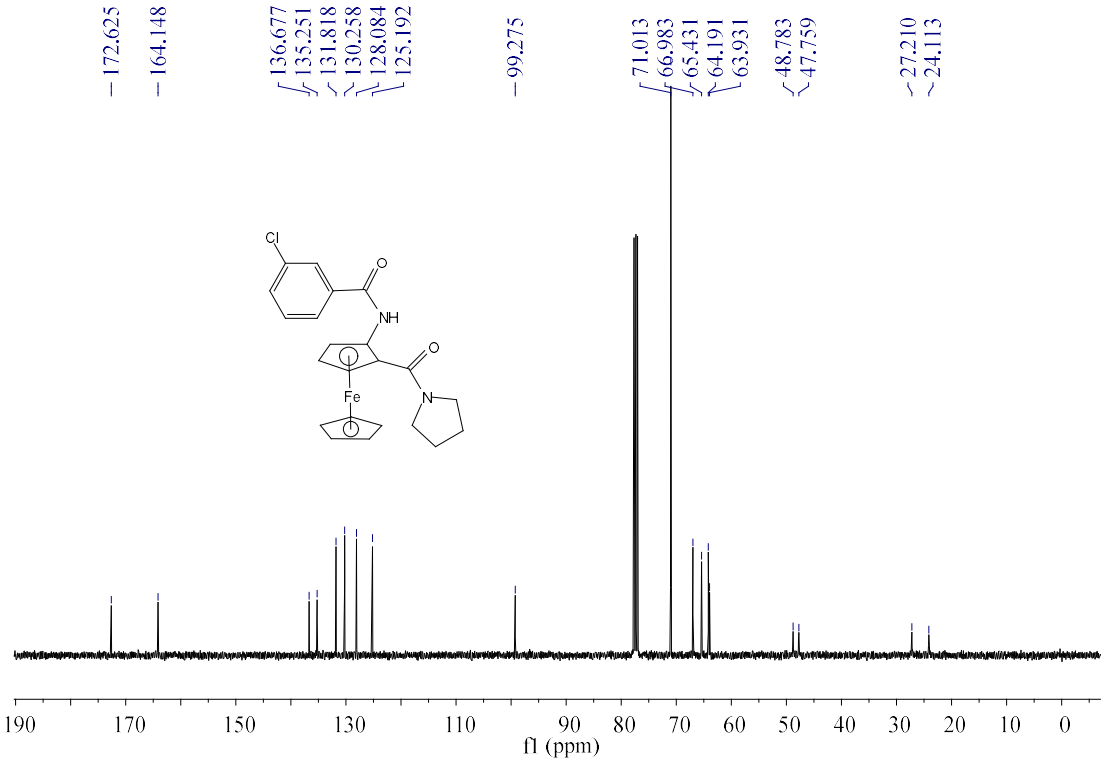




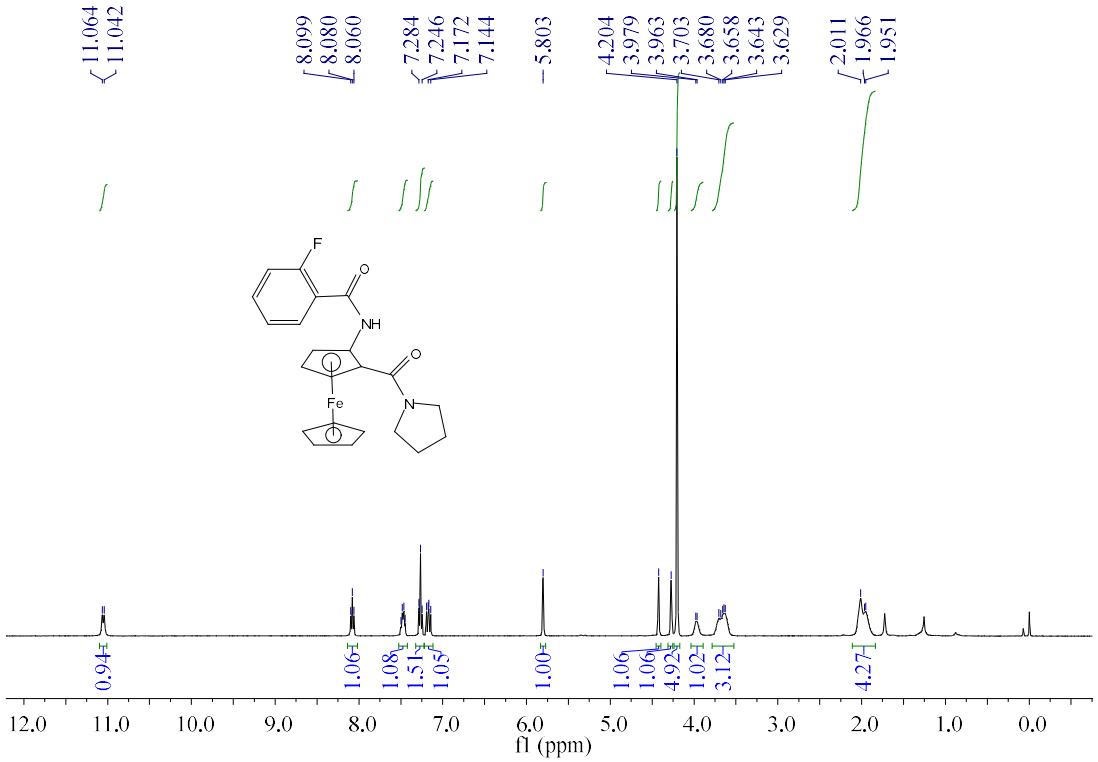

-111.896
F
O
NH
O
Fe
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

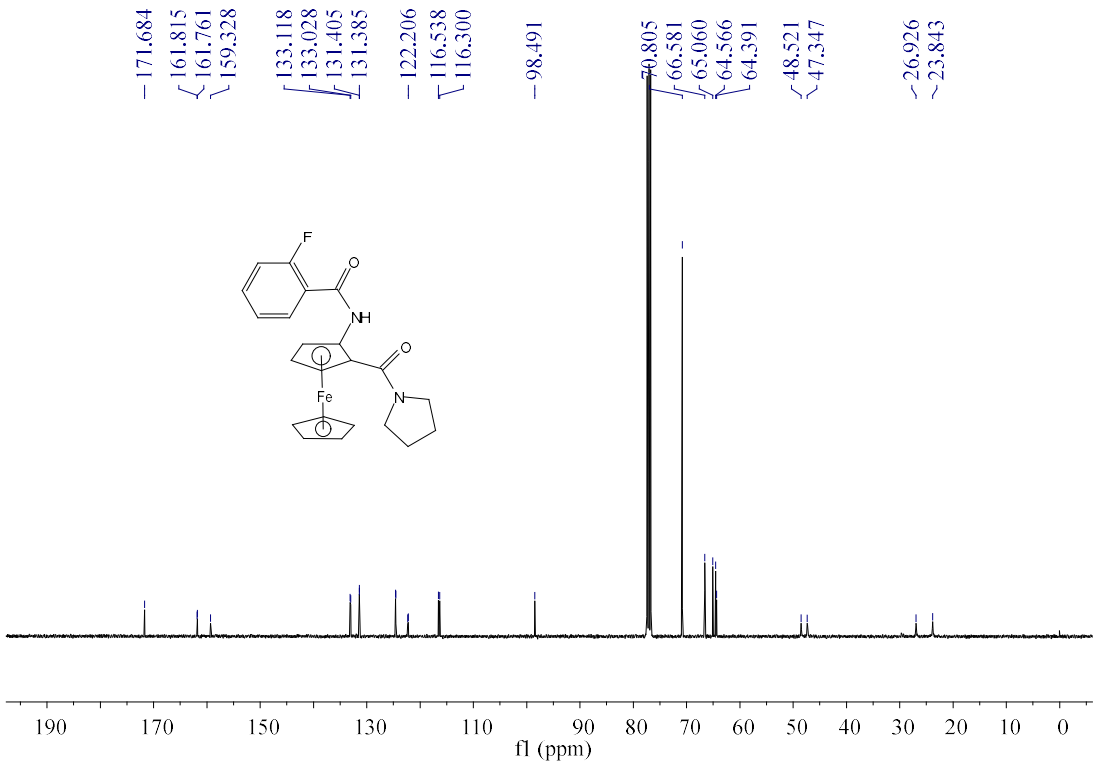
3l（^{1}H NMR and ^{13}C NMR）

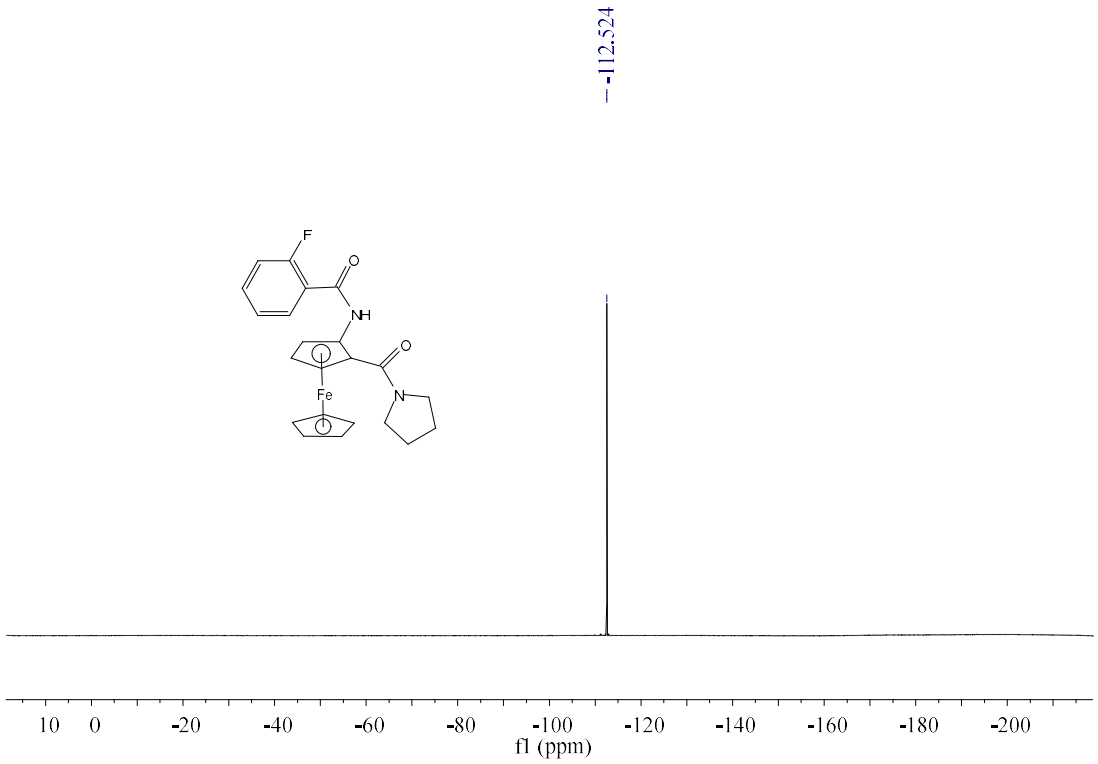




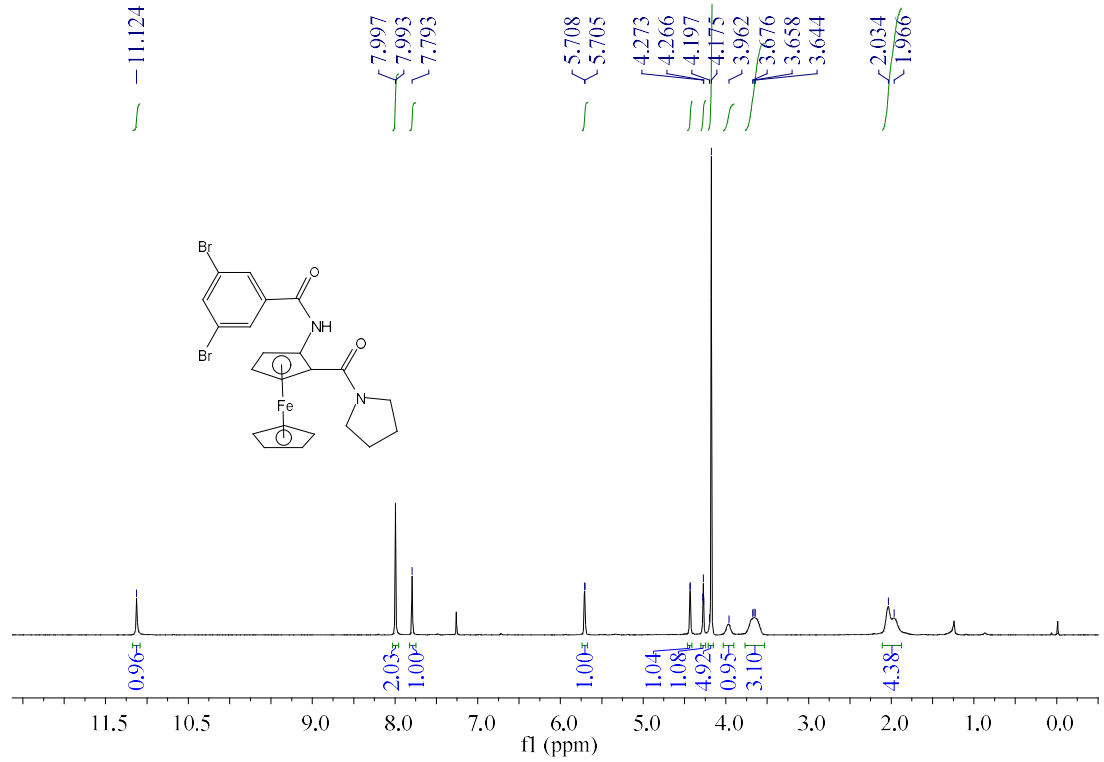
3m（^{1}H NMR, ^{13}C NMR and ^{19}F NMR）

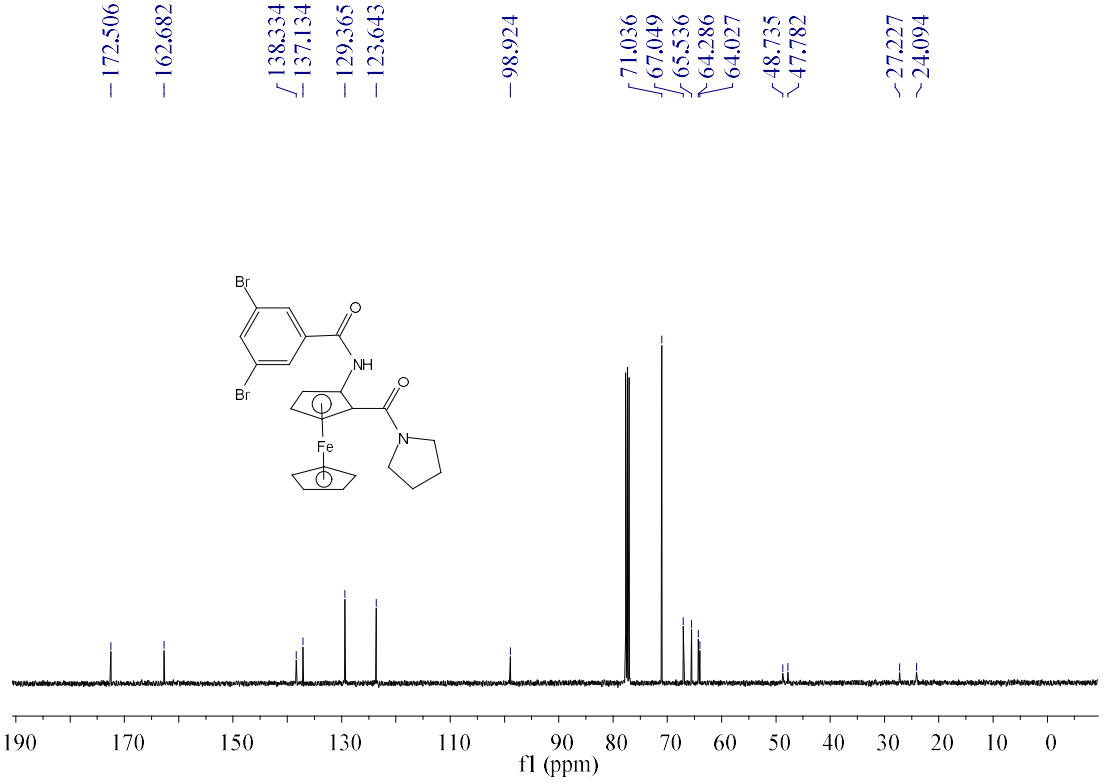



171.684
161.815
161.761
159.328
133.118
133.028
131.405
131.385
122.206
116.538
116.300
98.491
70.805
66.581
65.060
64.566
64.391
48.521
47.347
26.926
23.843
F
O
NH
O
Fe
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

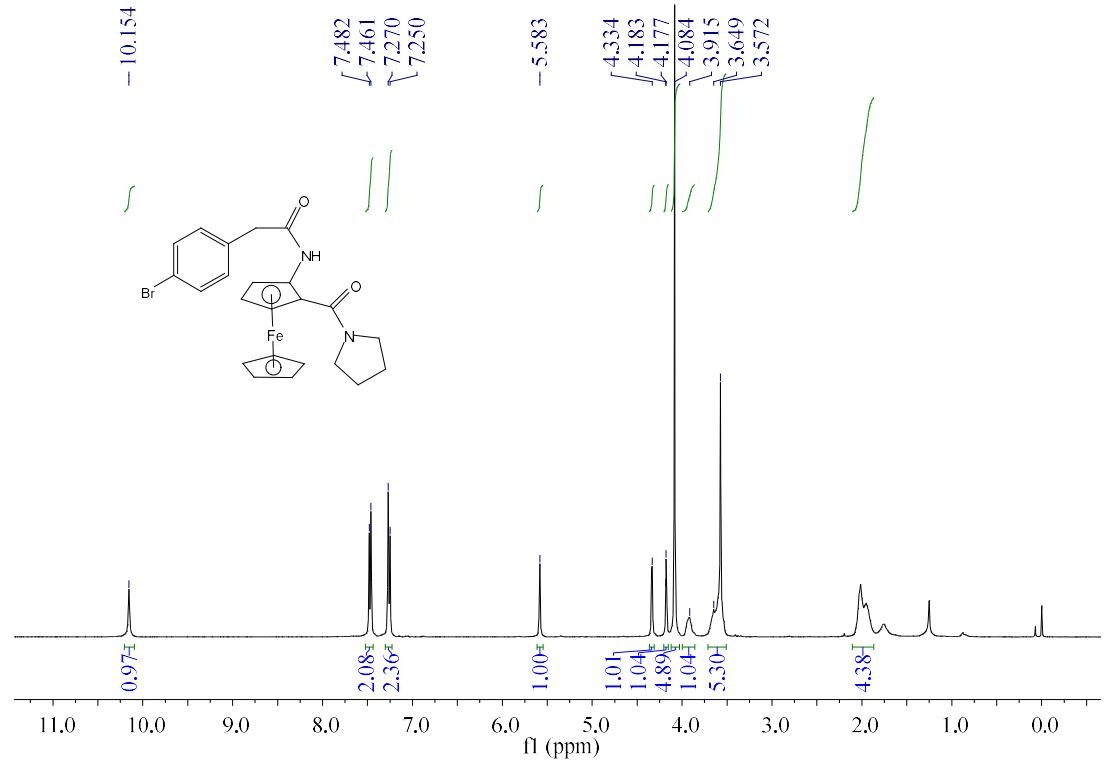

-112.524
F
O
NH
O
Fe
N
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

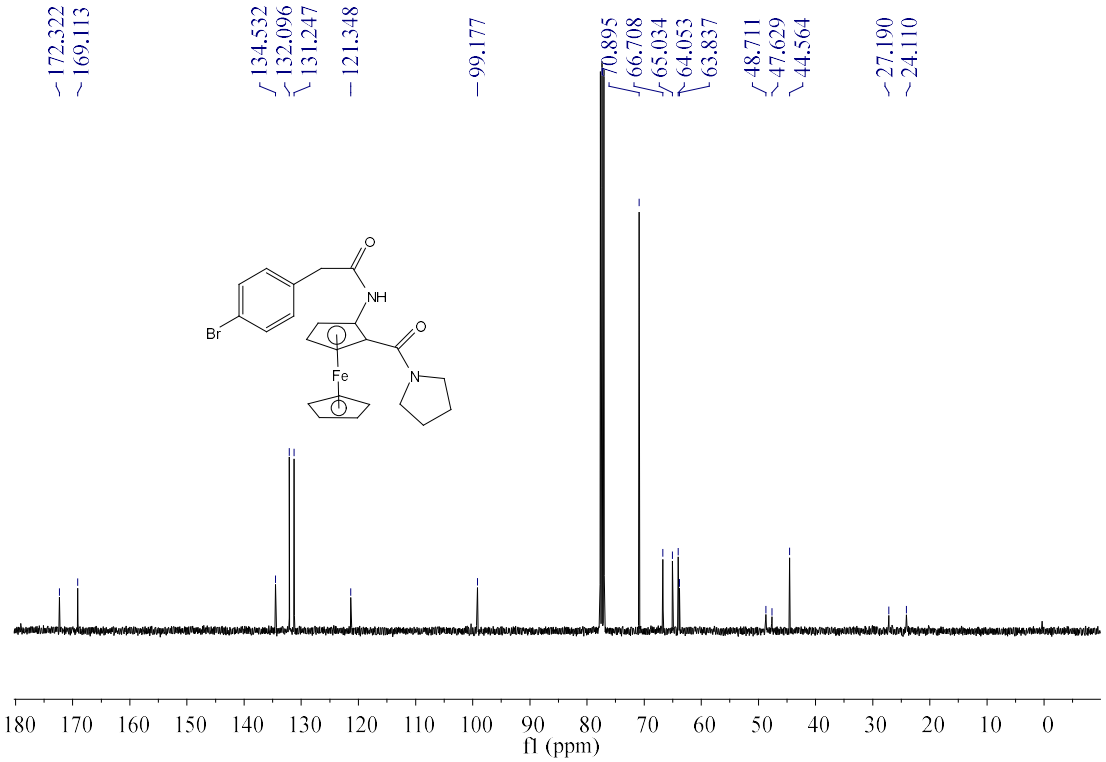
3n（1H NMR and ^{13}C NMR）



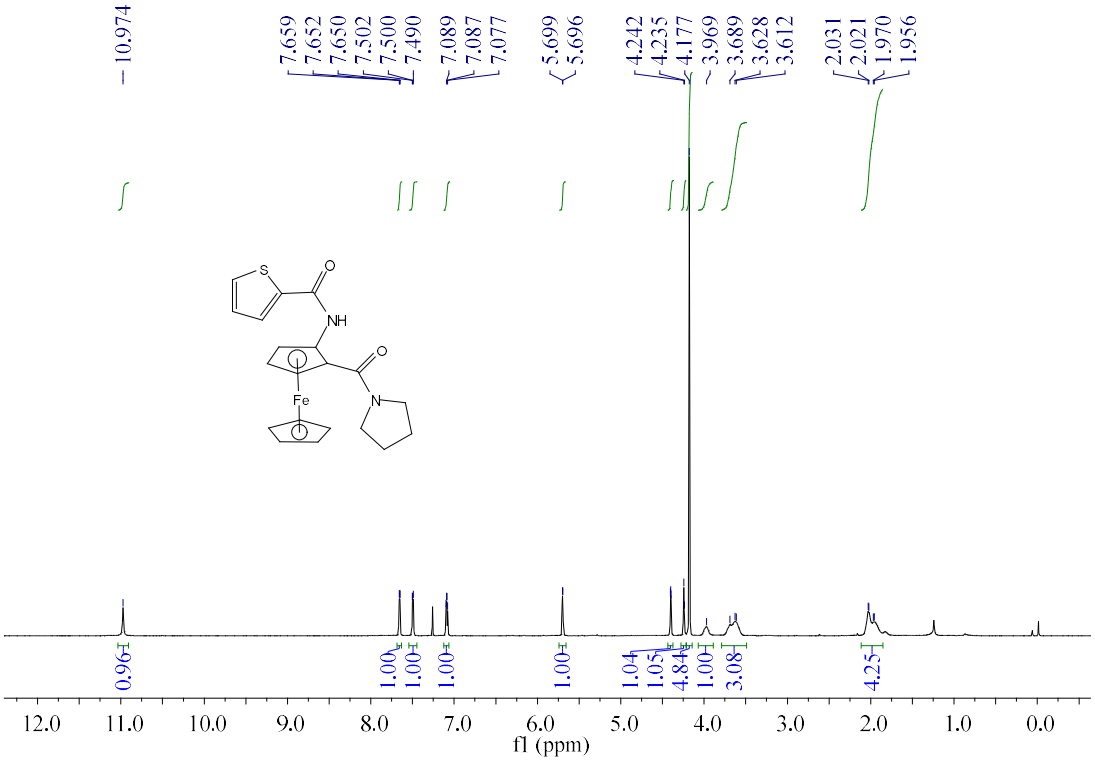


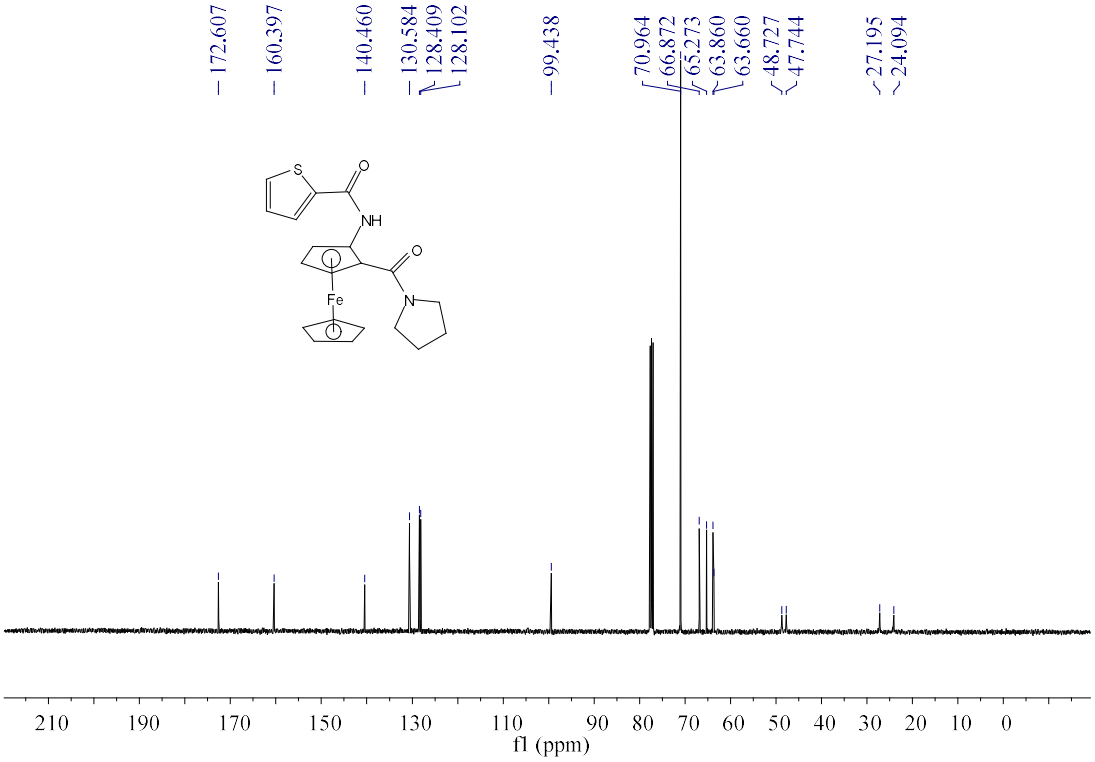
3o（^{1}H NMR and ^{13}C NMR）



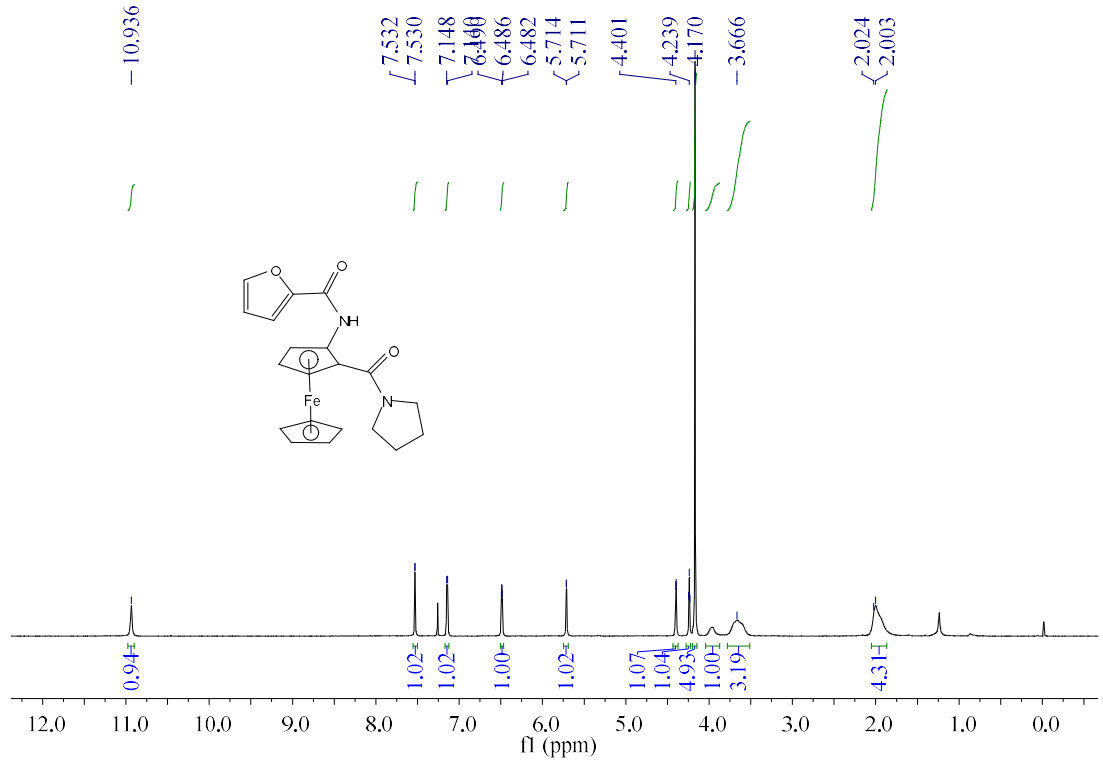


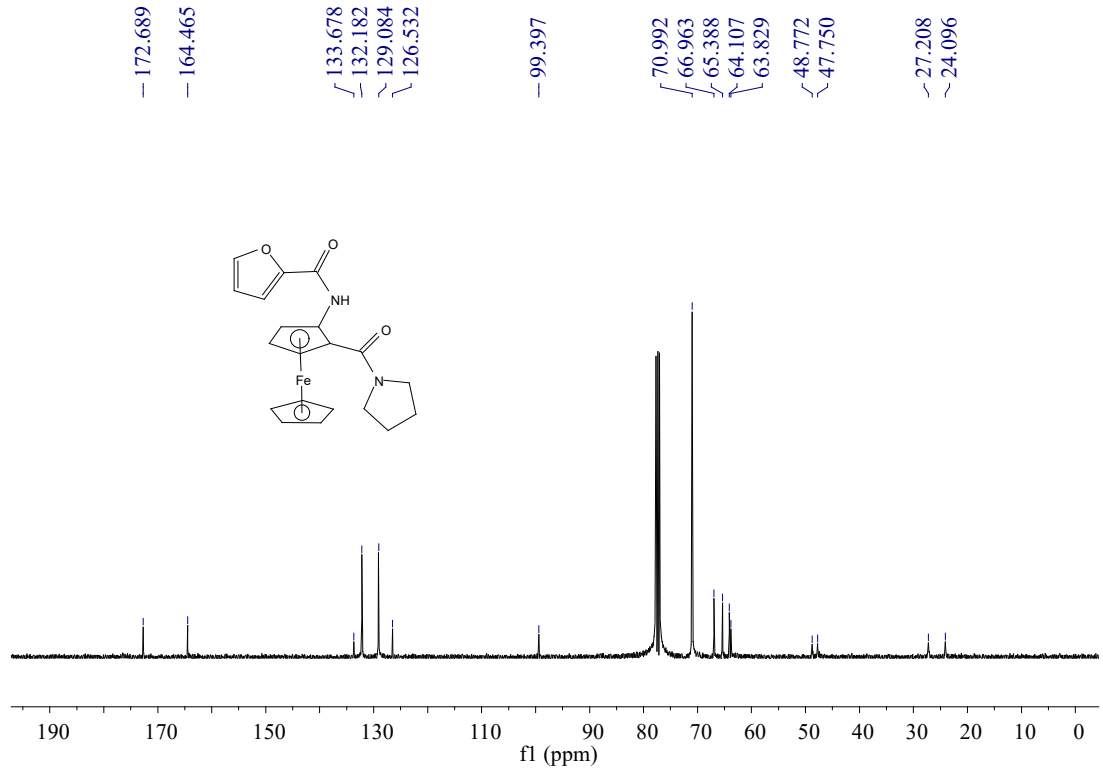
3p（^{1}H NMR and ^{13}C NMR）



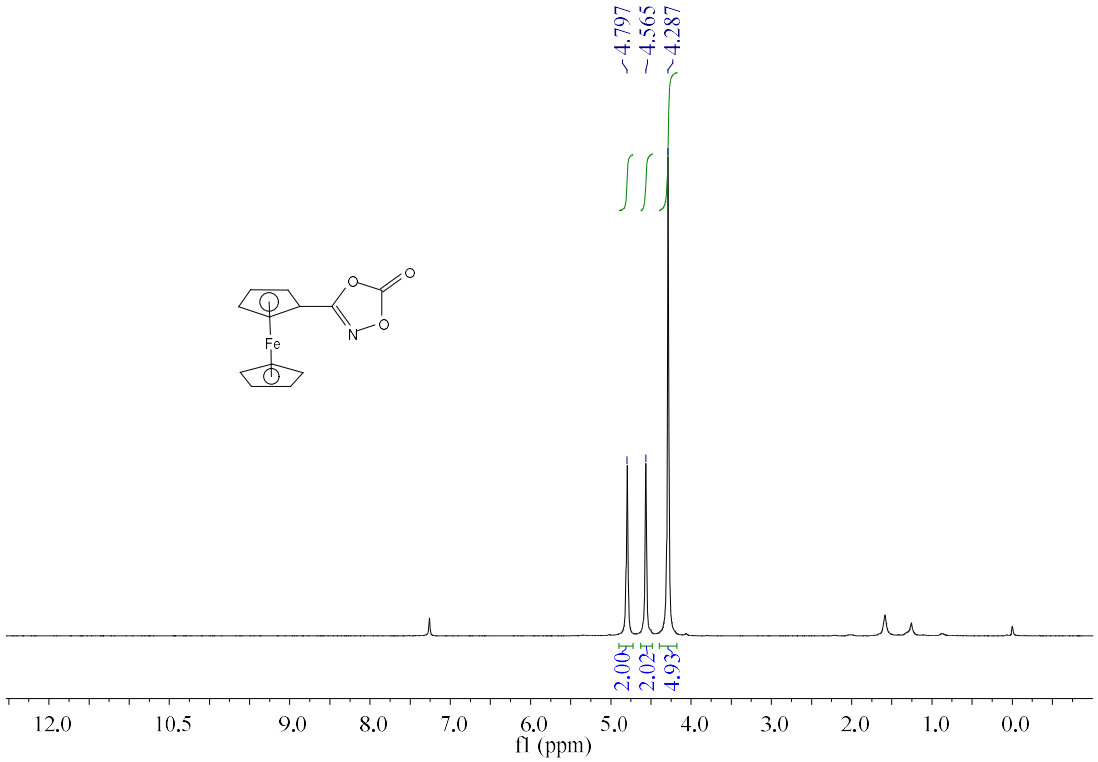


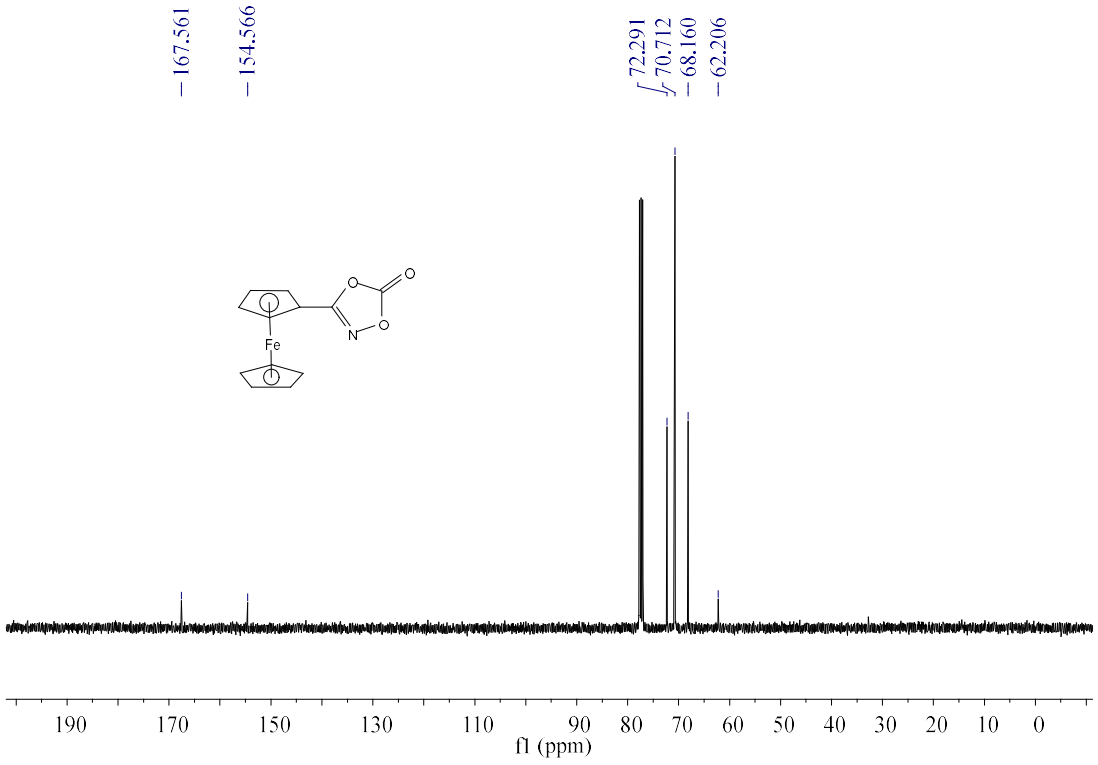
3q（^{1}H NMR and ^{13}C NMR）



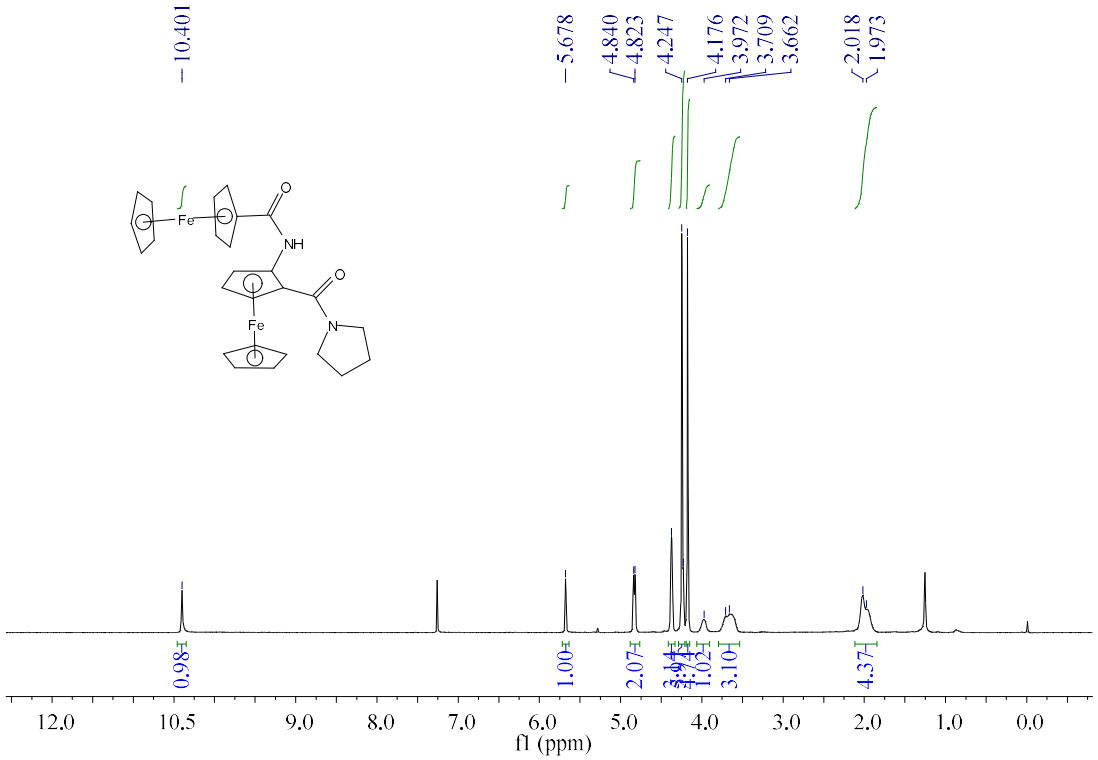


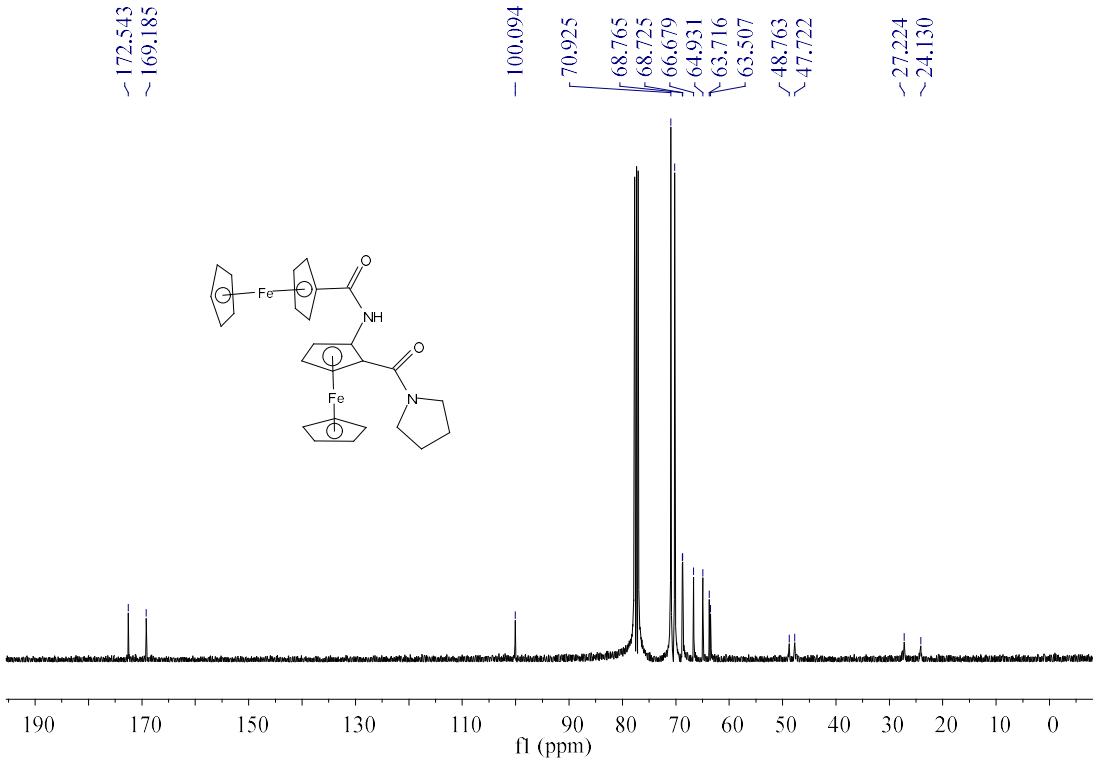
2r（^{1}H NMR and ^{13}C NMR）



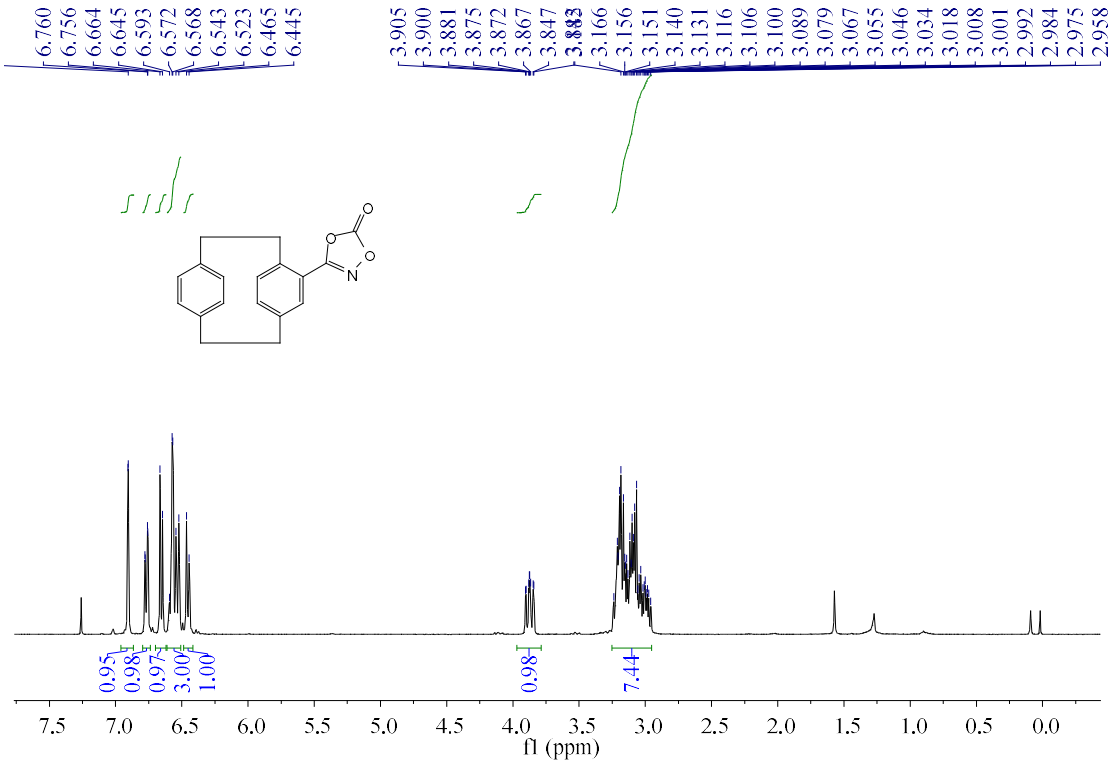


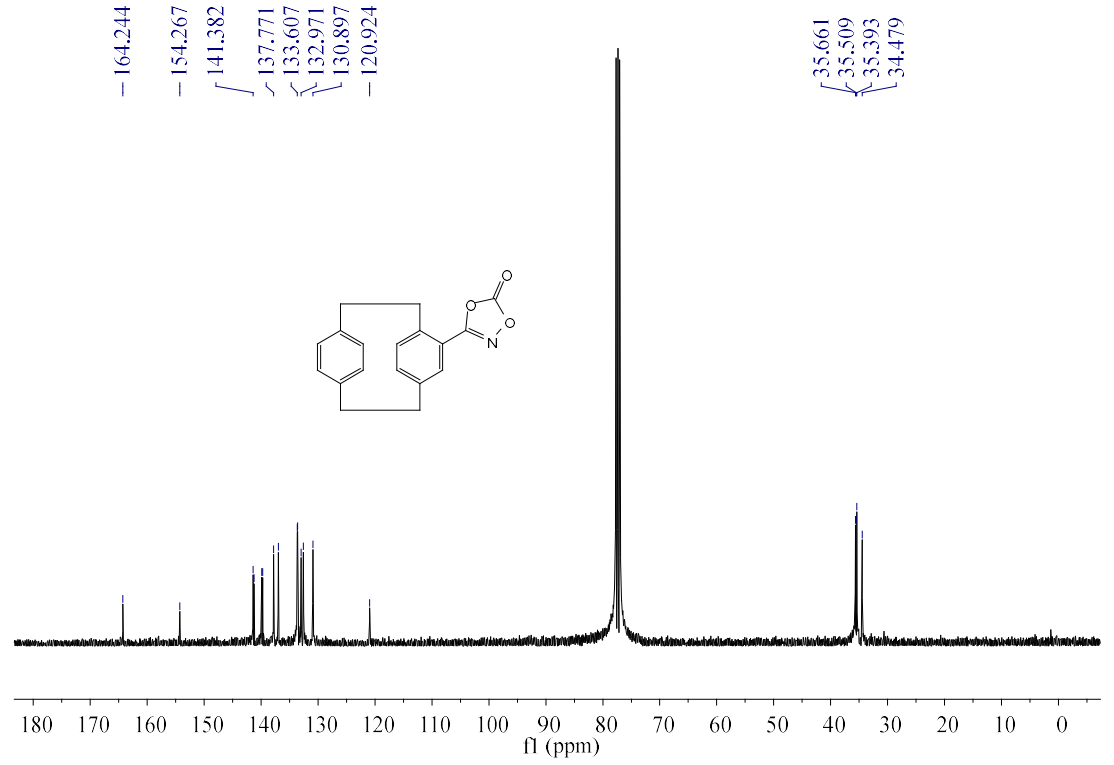
3r（^{1}H NMR and ^{13}C NMR）



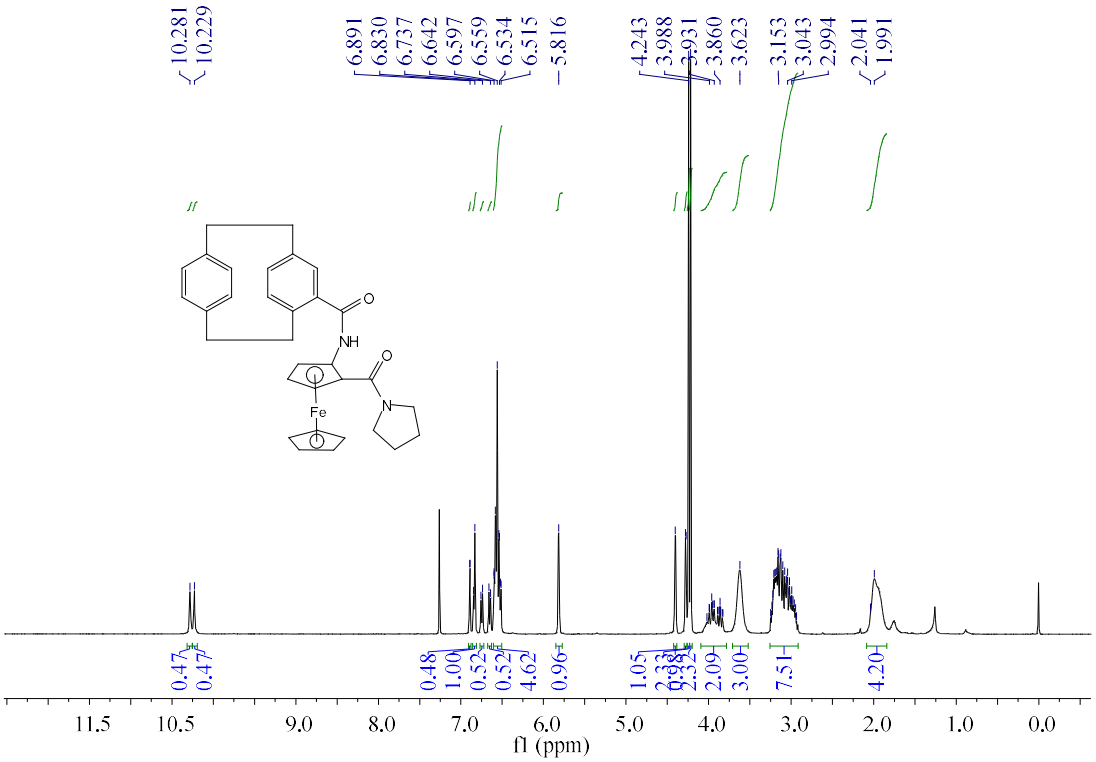


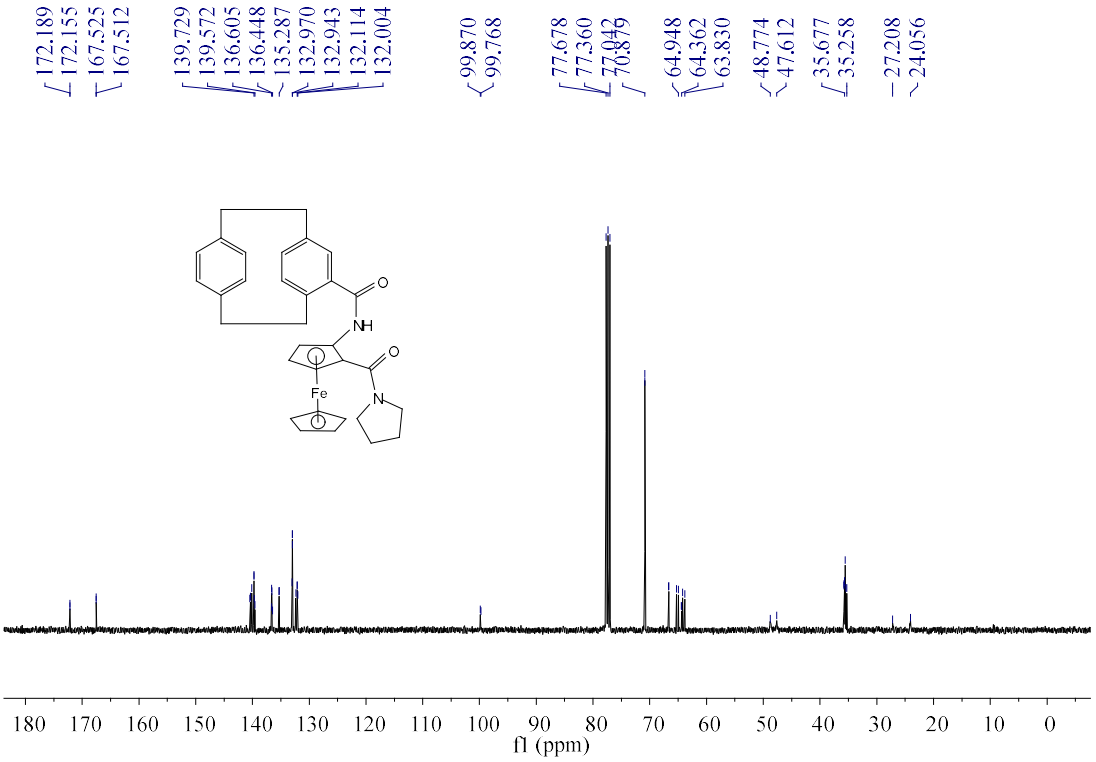
2s（^{1}H NMR and ^{13}C NMR）



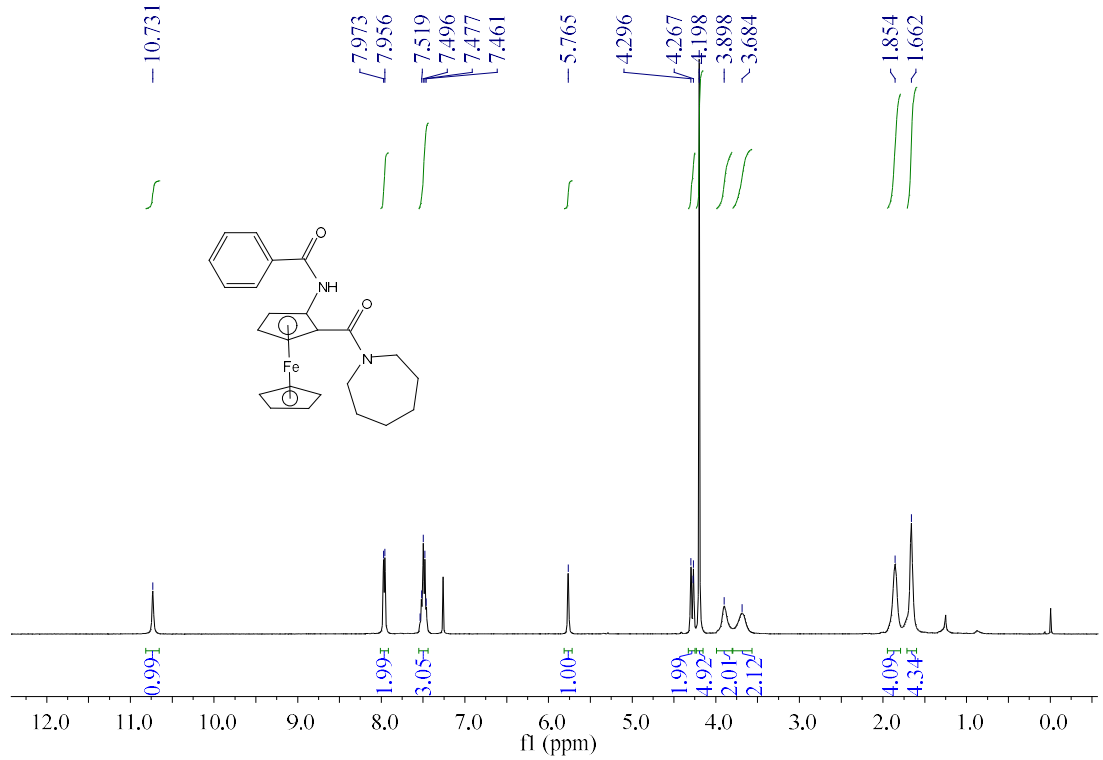


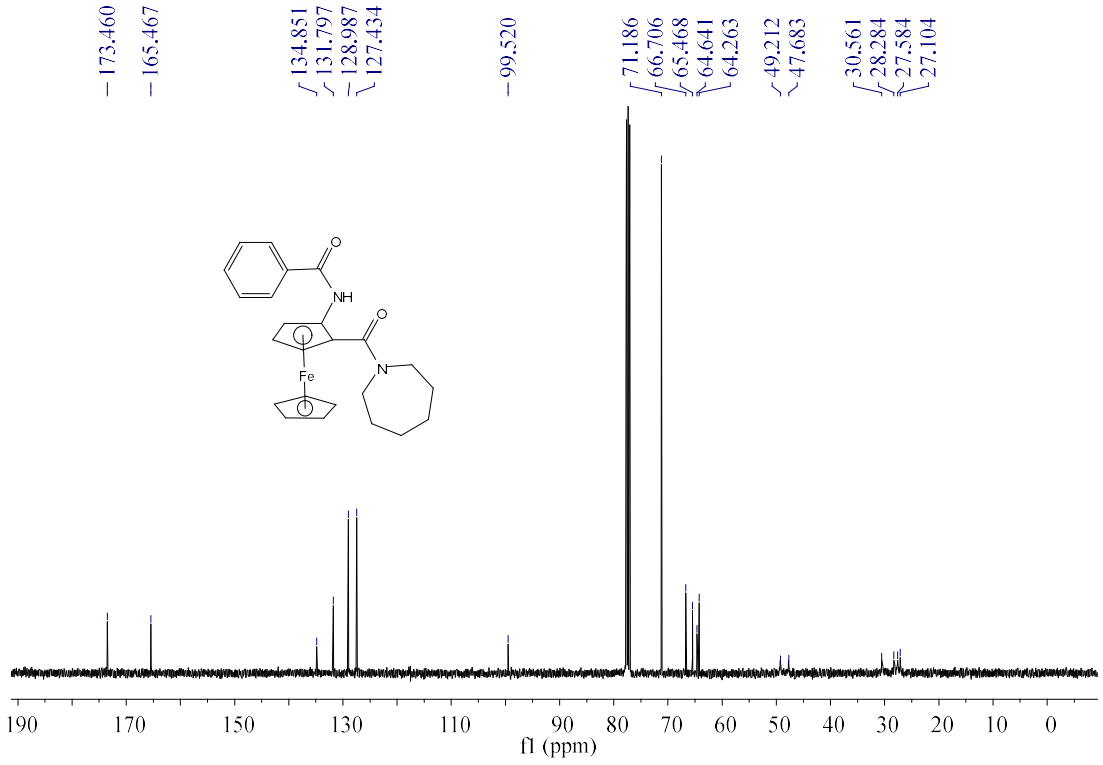
3s（^{1}H NMR and ^{13}C NMR）



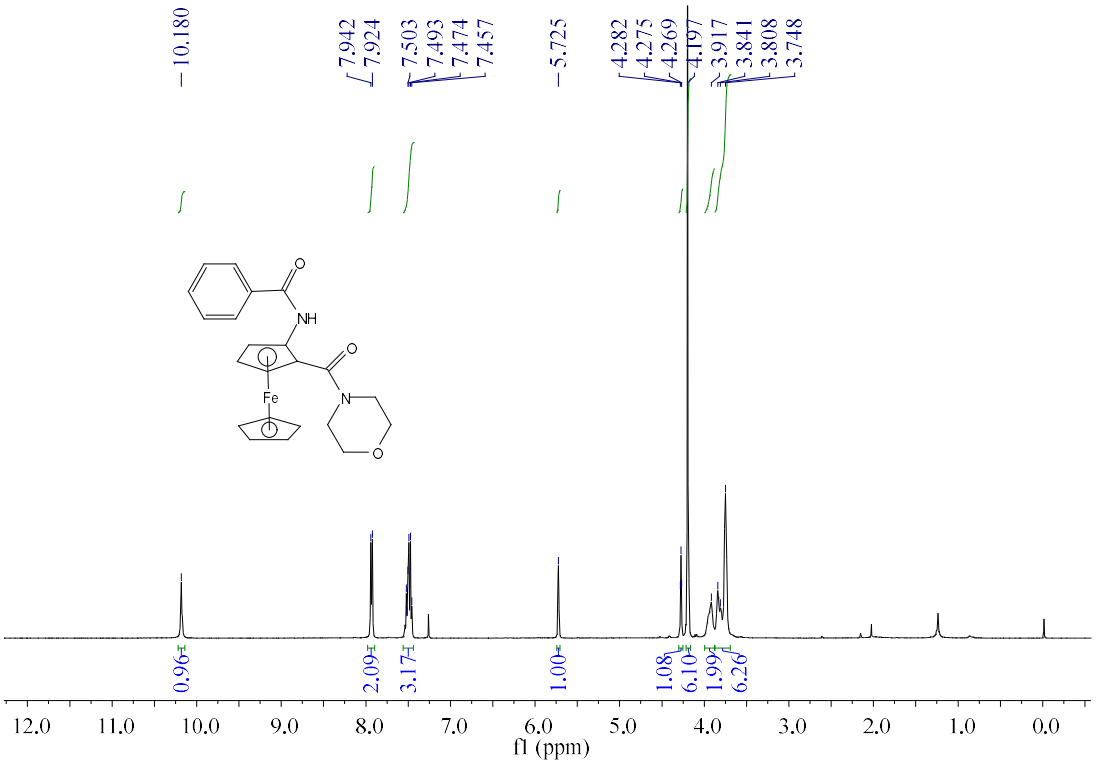


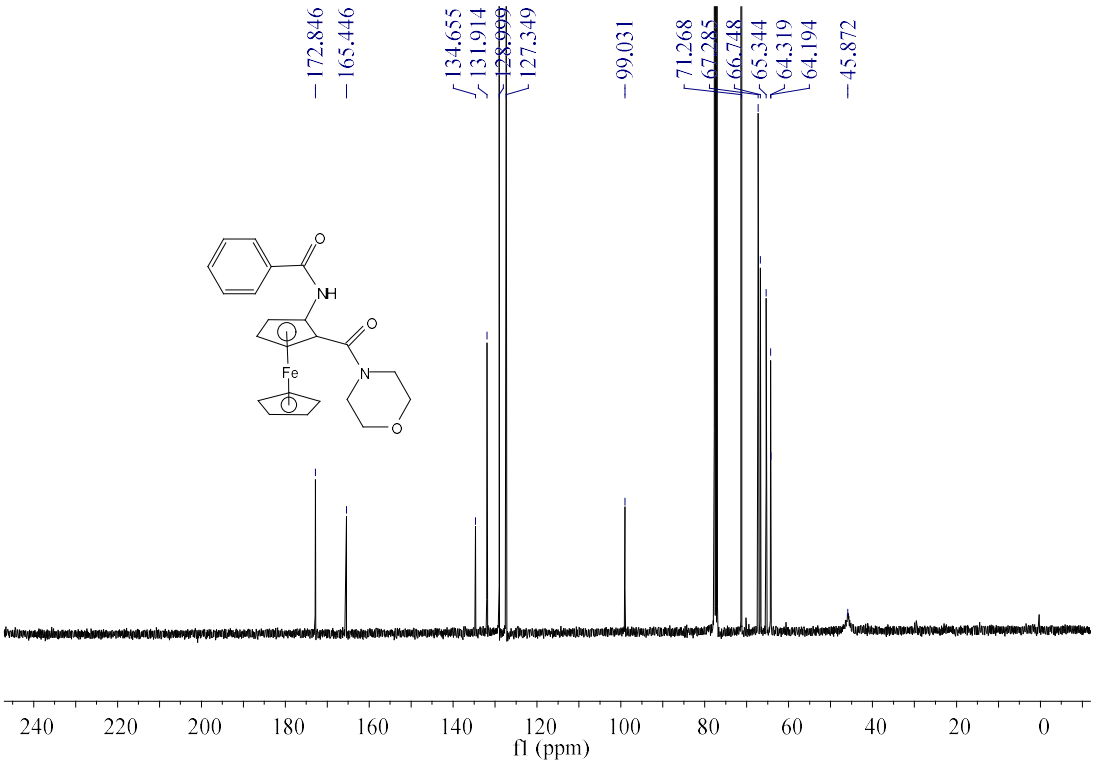
3aa（^{1}H NMR and ^{13}C NMR）



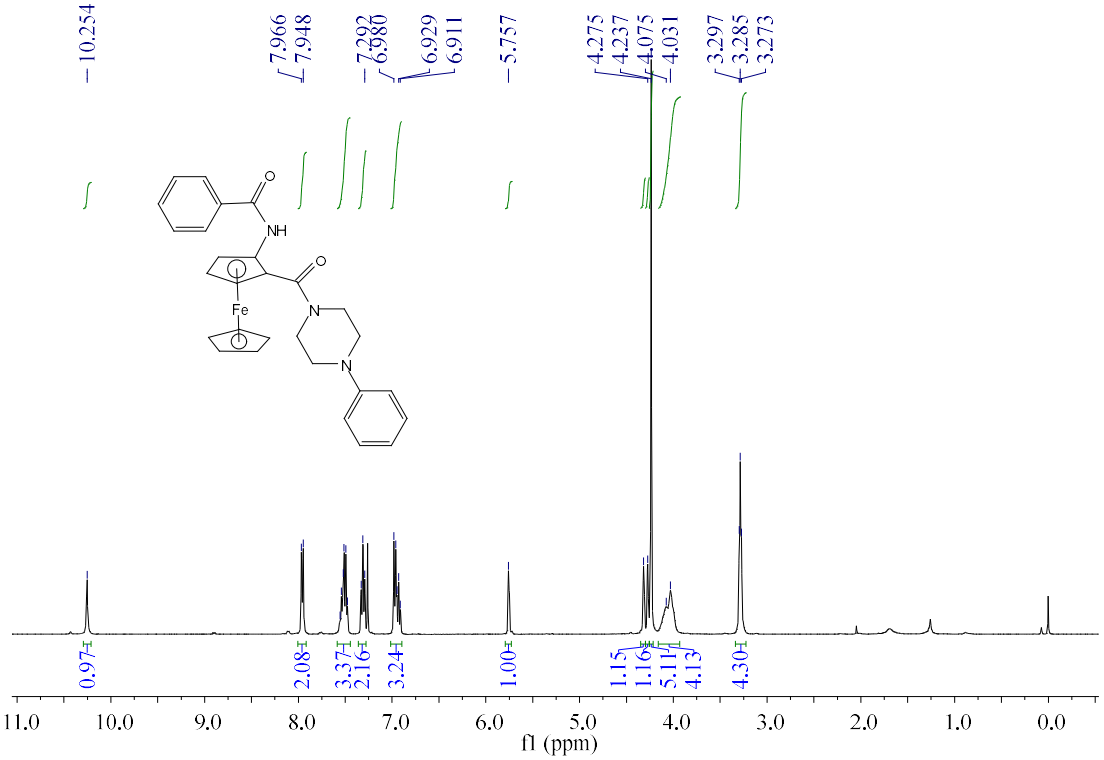


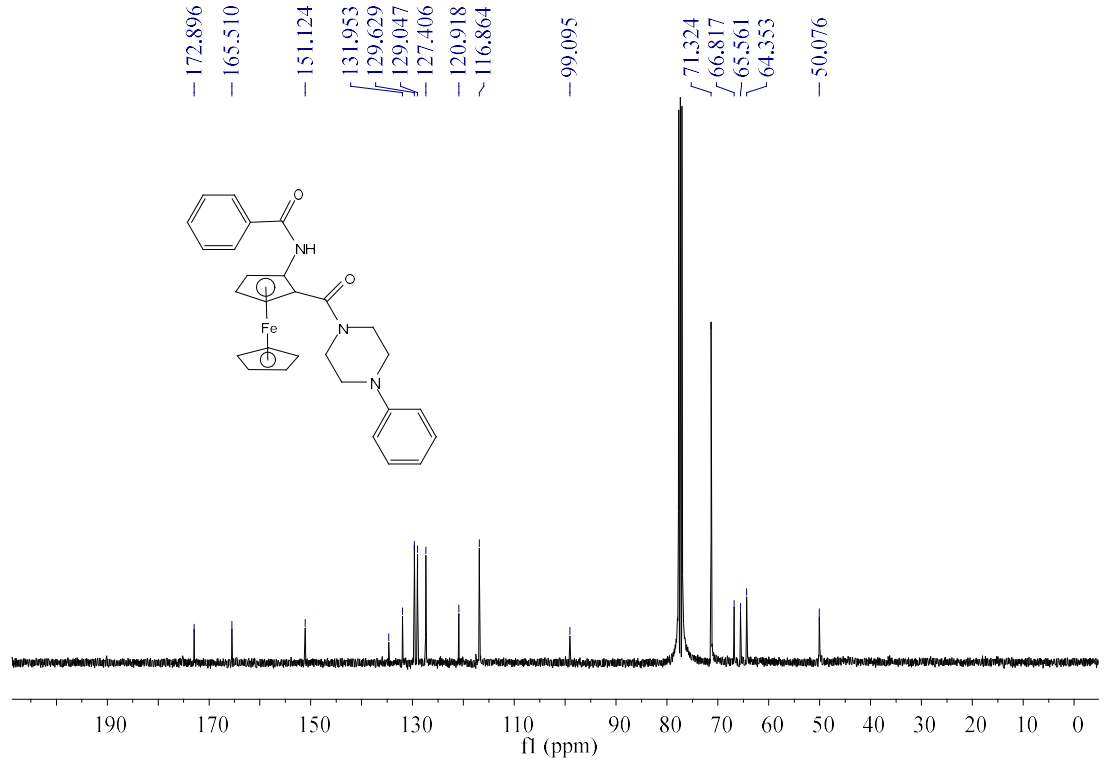
3ab（^{1}H NMR and ^{13}C NMR）



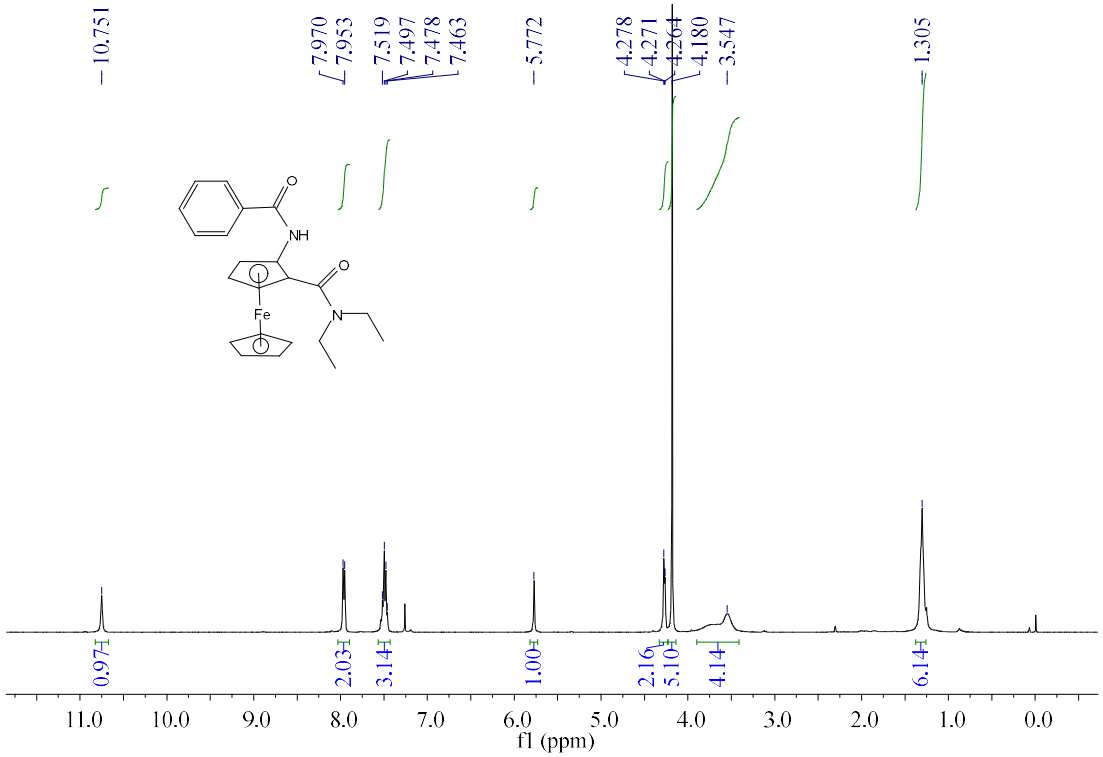


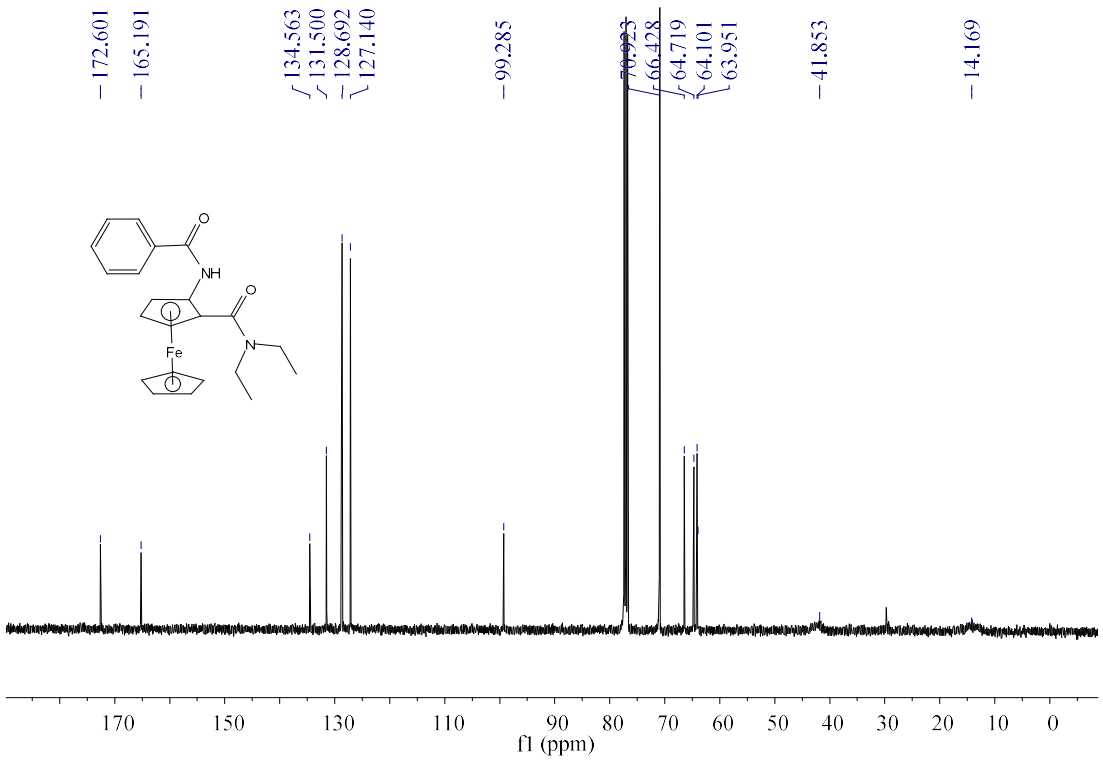
3ac（^{1}H NMR and ^{13}C NMR）



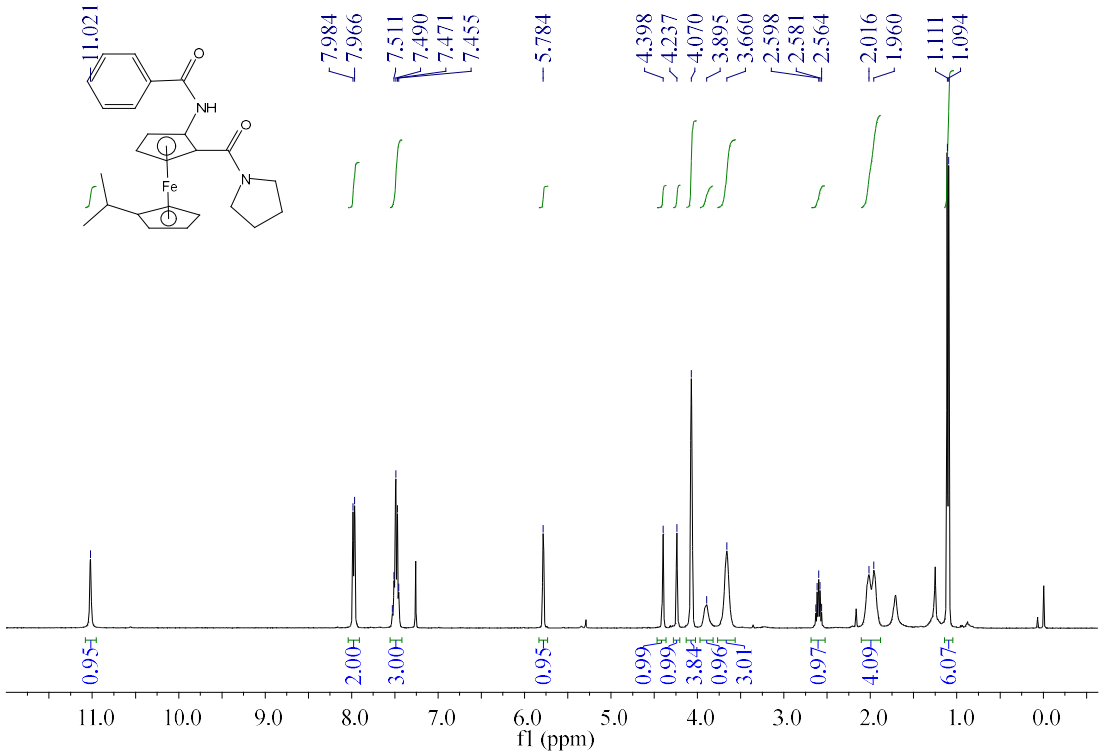


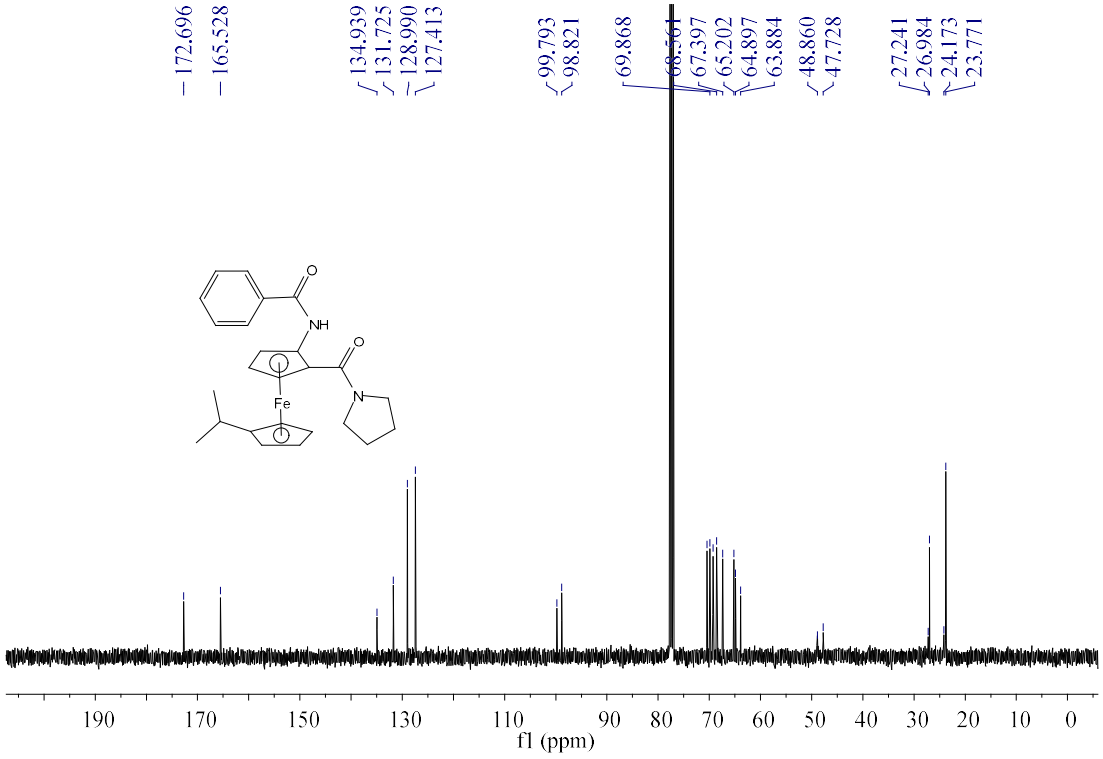
3ad（^{1}H NMR and ^{13}C NMR）



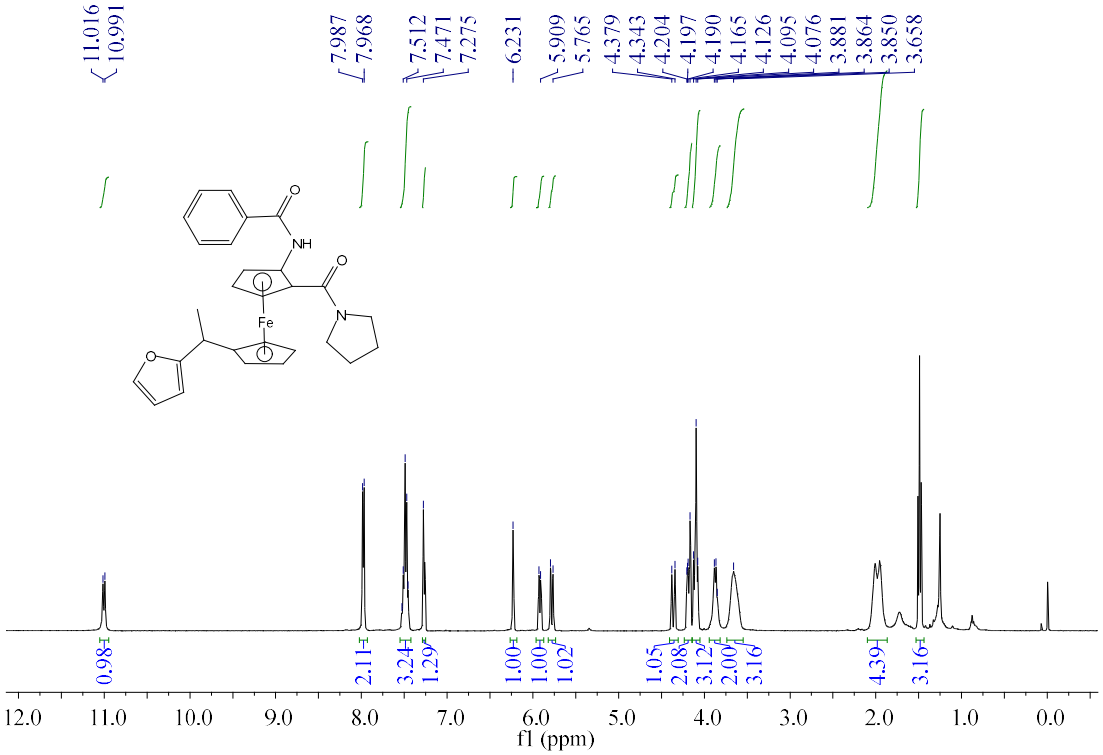


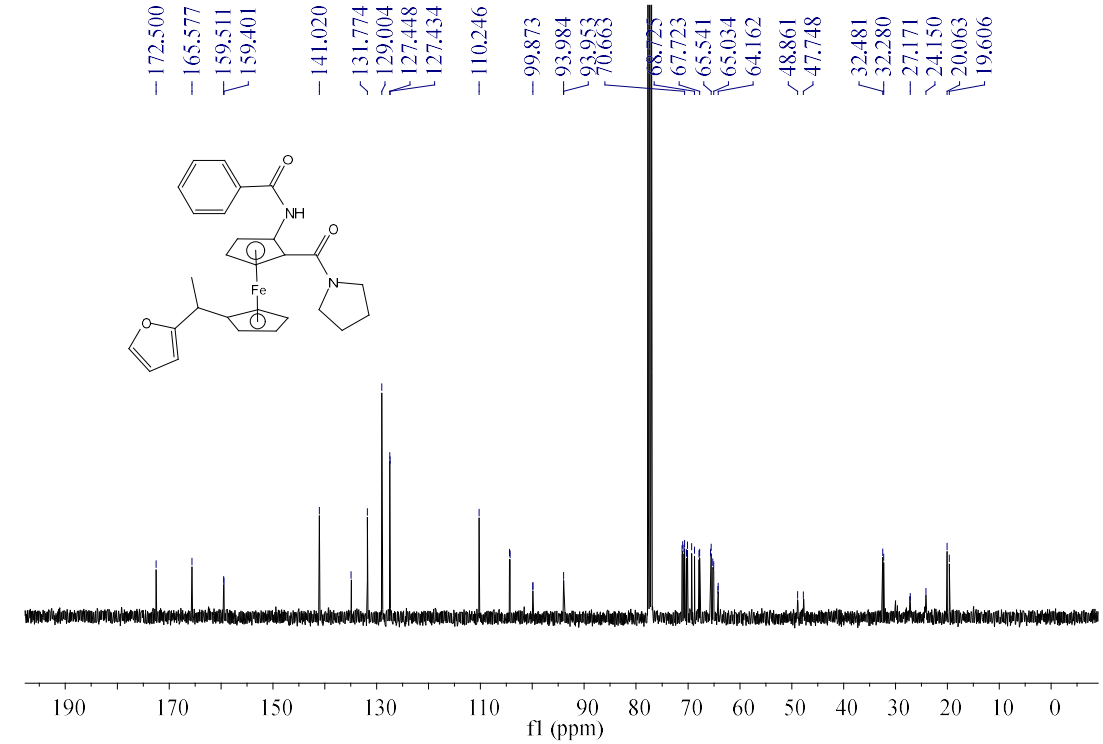
3ae（^{1}H NMR and ^{13}C NMR）



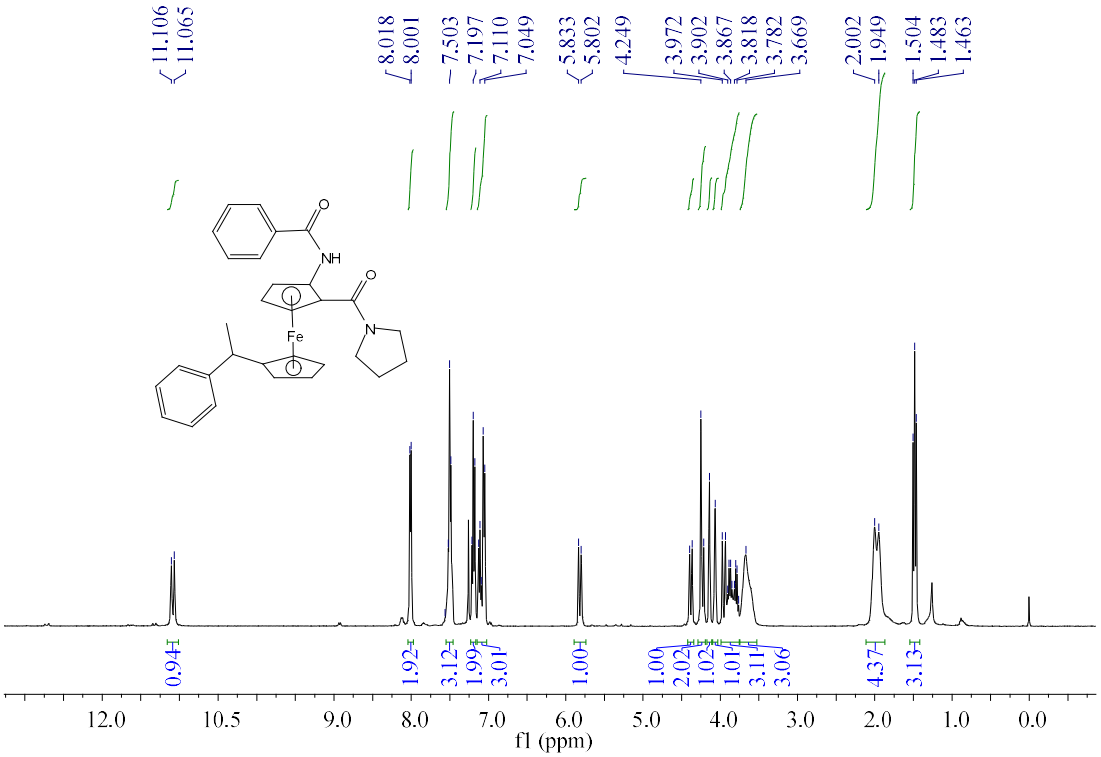


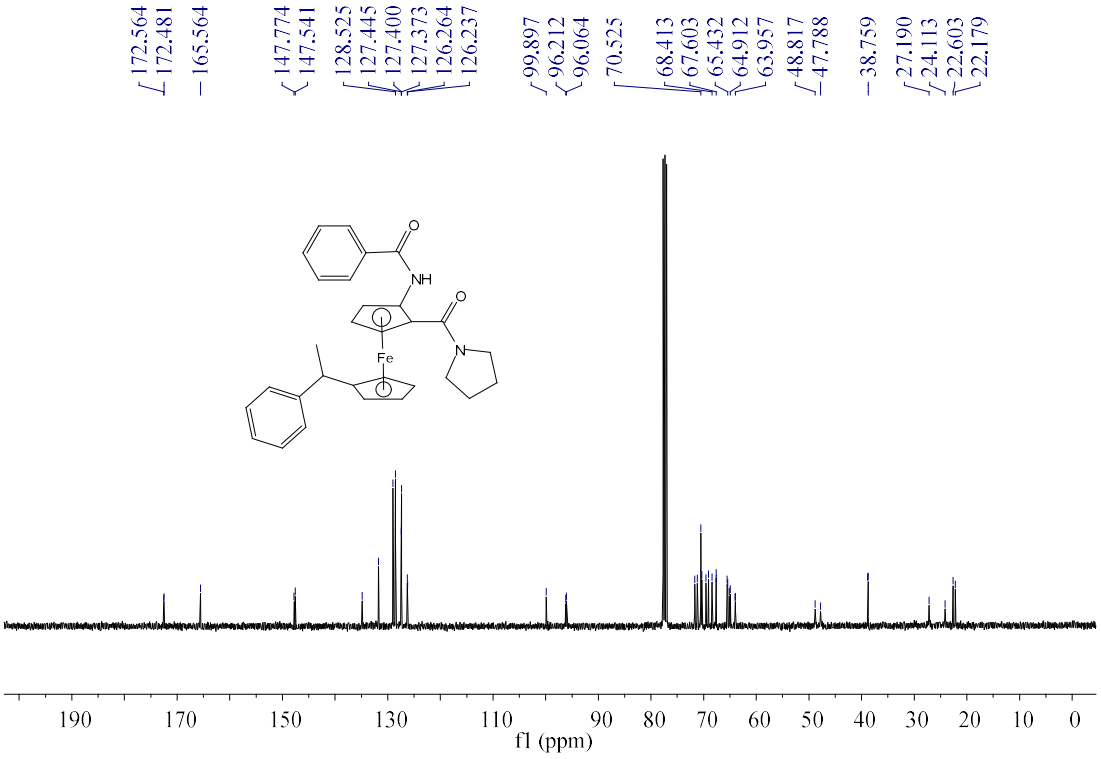
3af（^{1}H NMR and ^{13}C NMR）



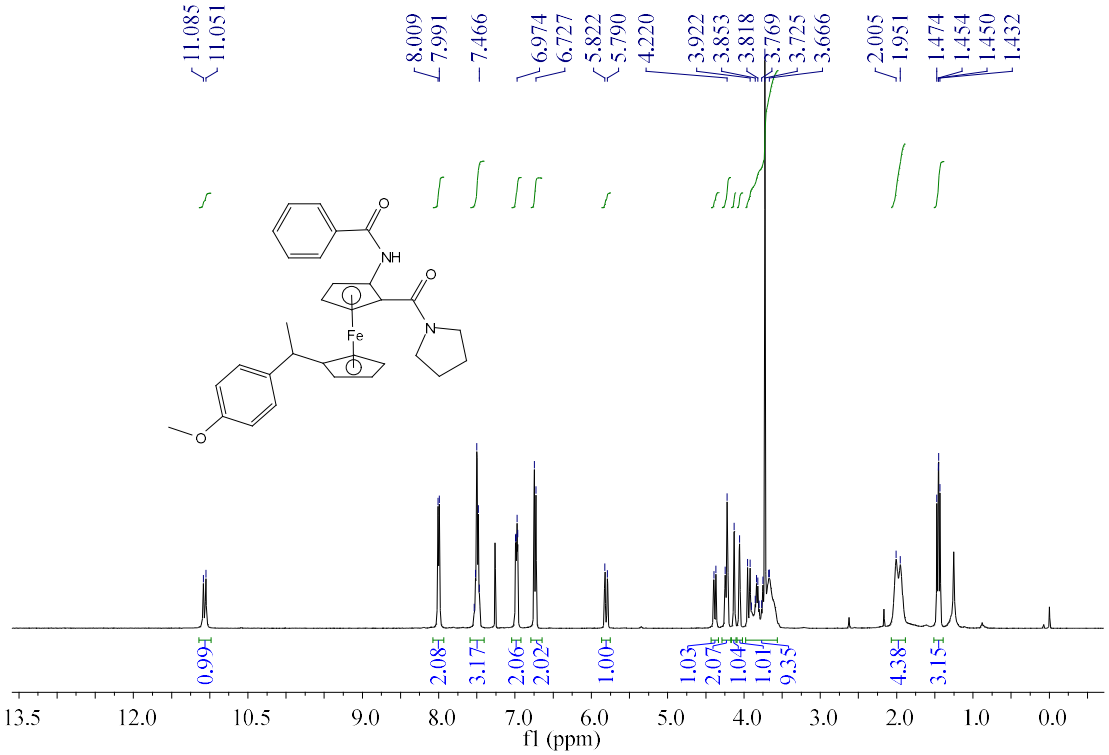


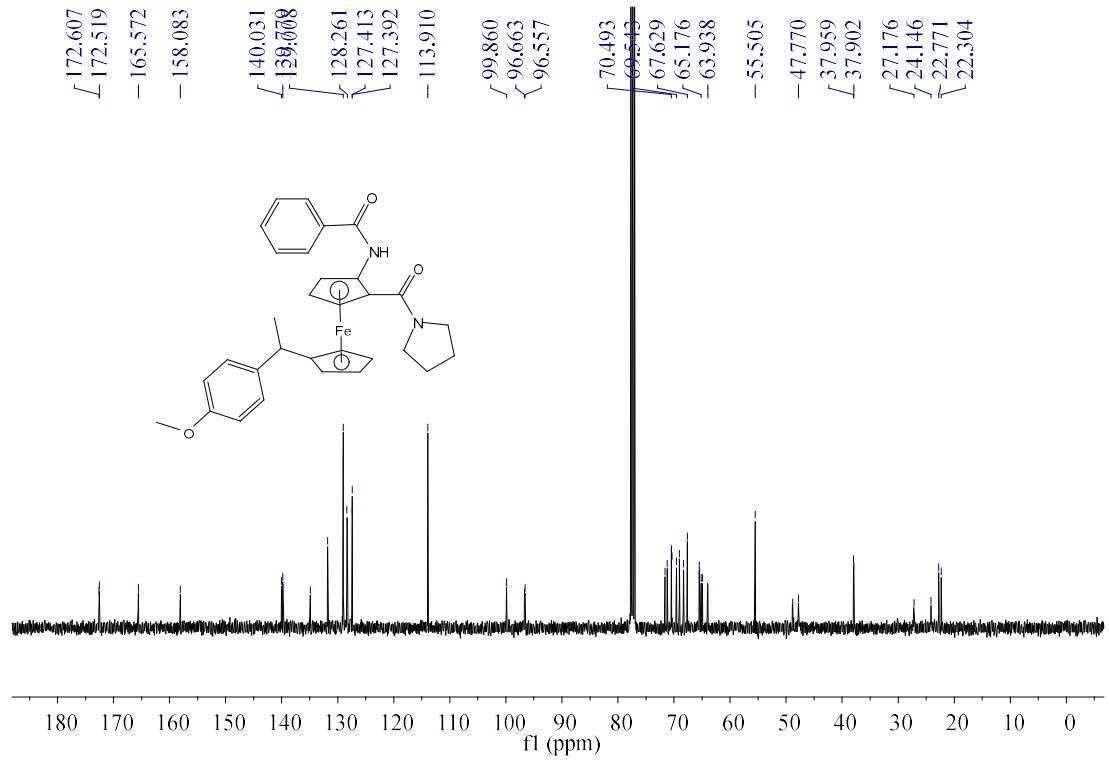
3ag（^{1}H NMR and ^{13}C NMR）



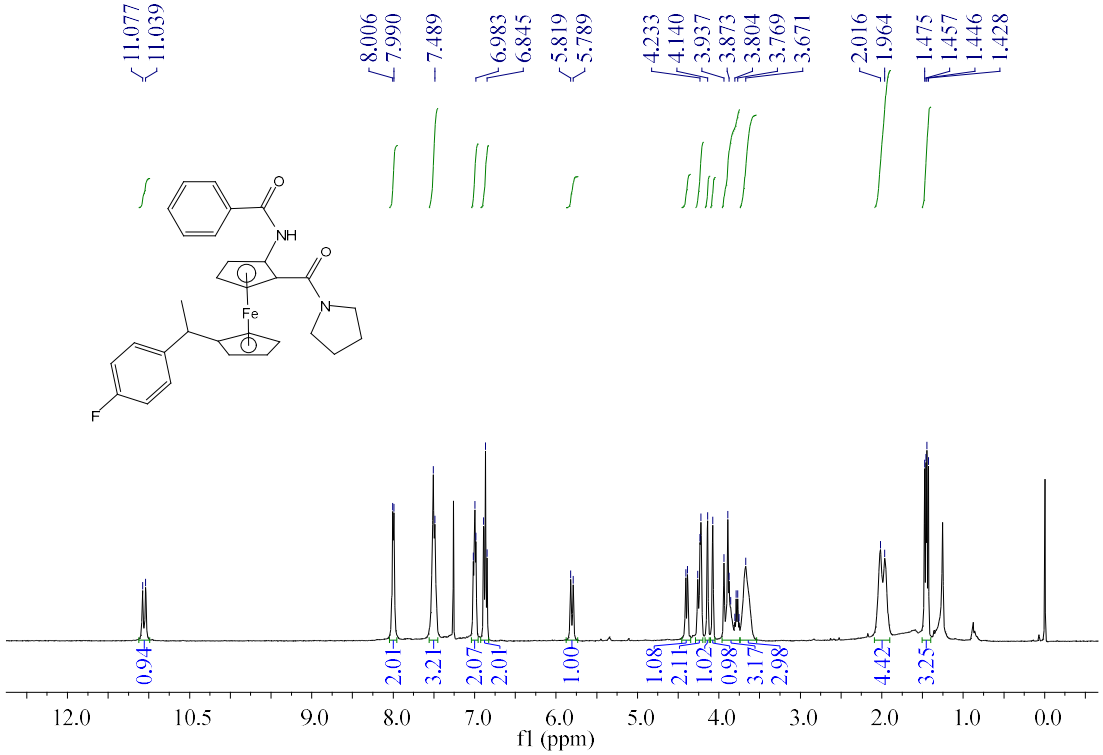


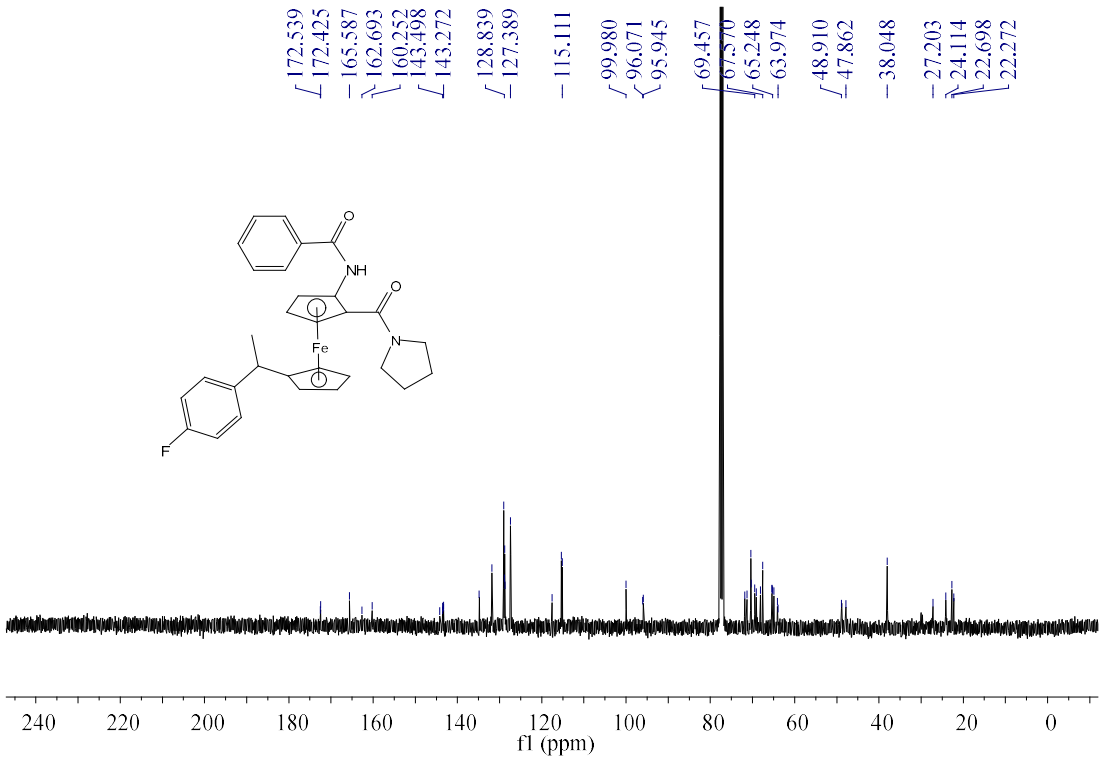
3ah（^{1}H NMR and ^{13}C NMR）

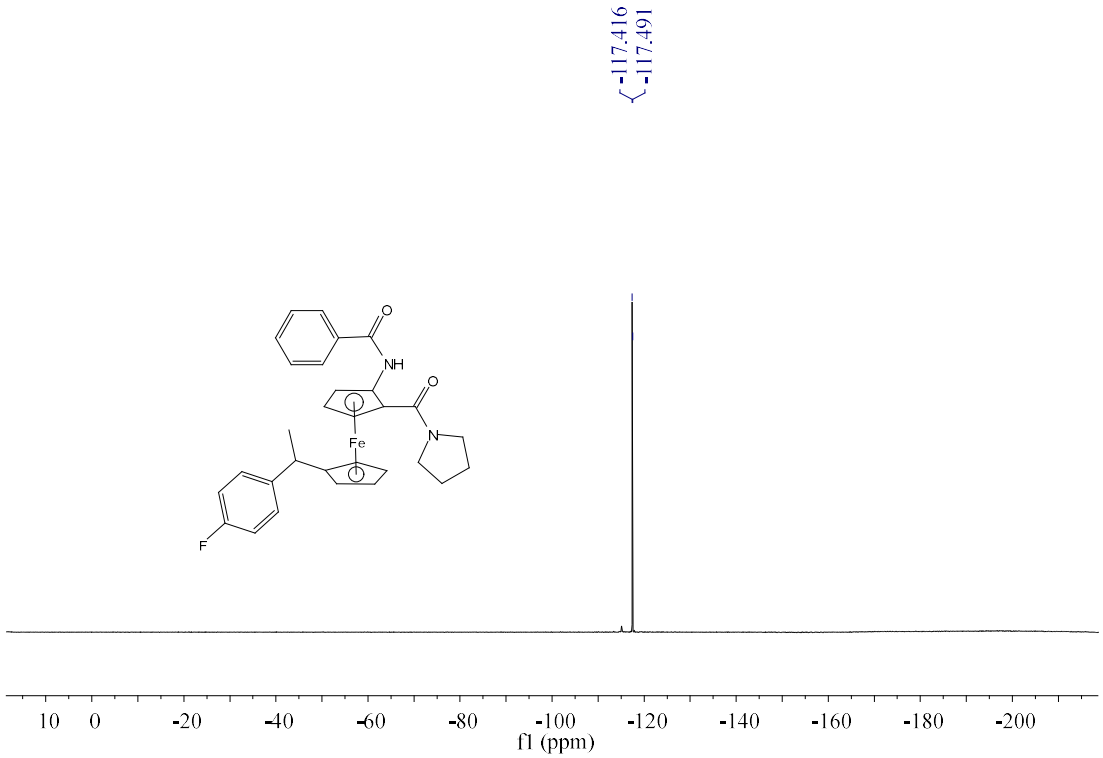




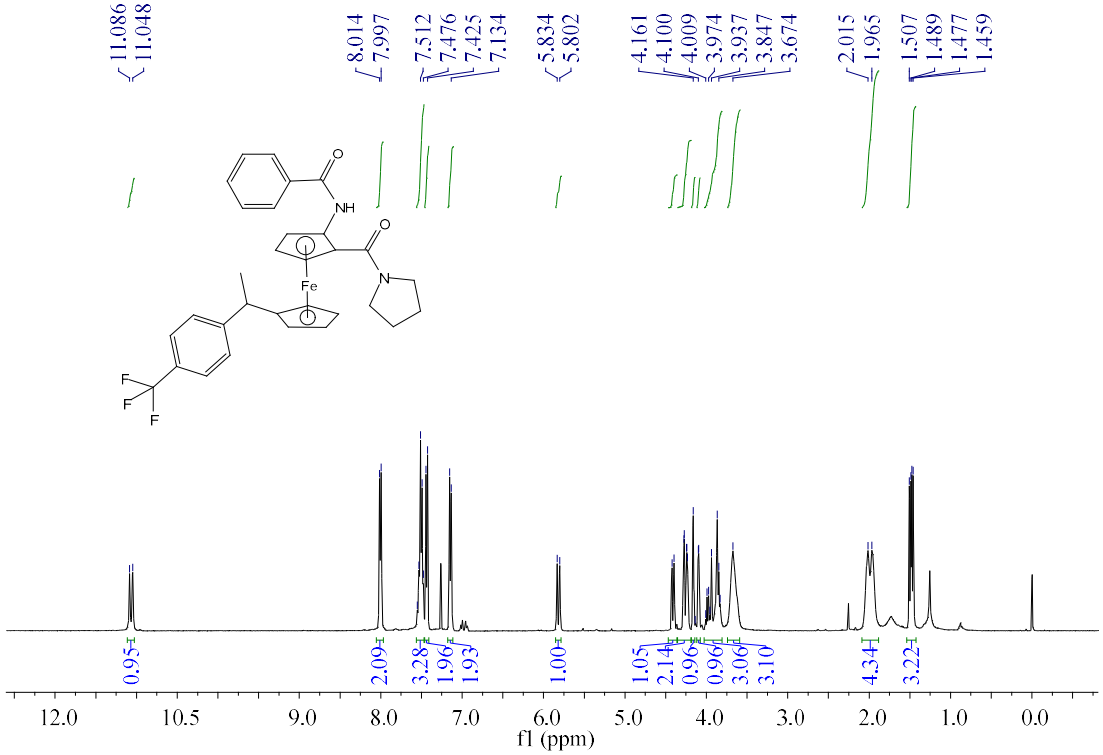
3ai（^{1}H NMR ,^{13}C NMR and ^{19}F NMR）

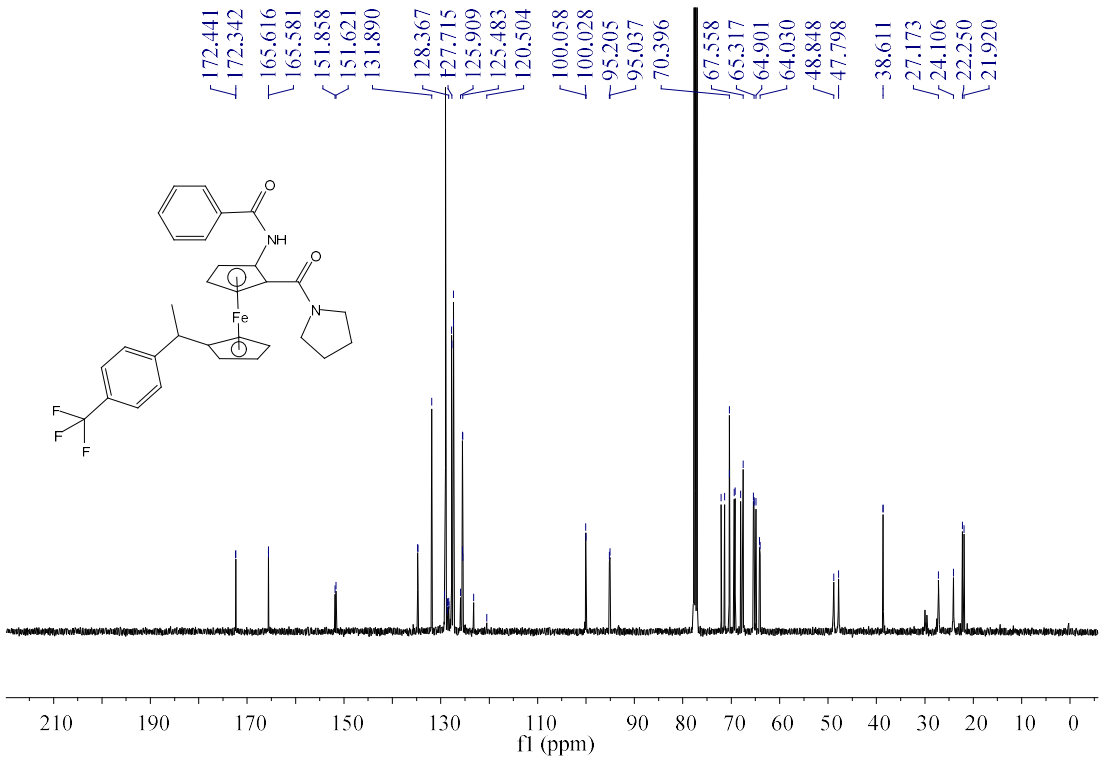


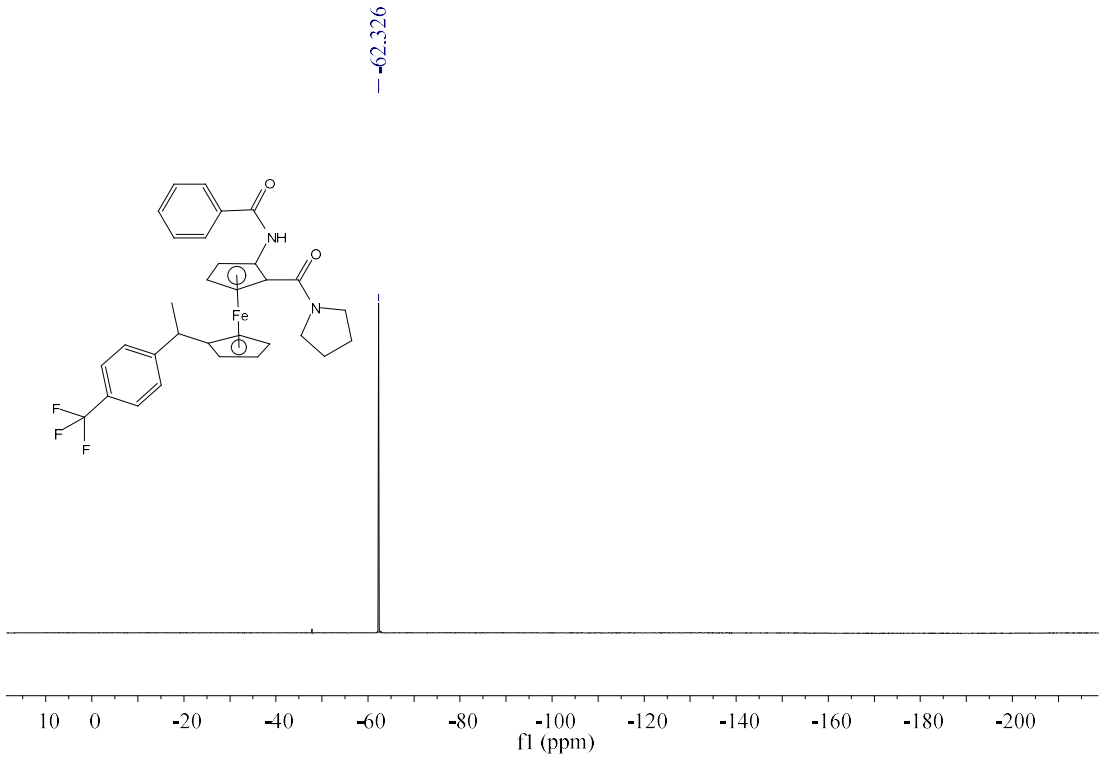



-117.416
-117.491
O
NH
O
N
Fe
F
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

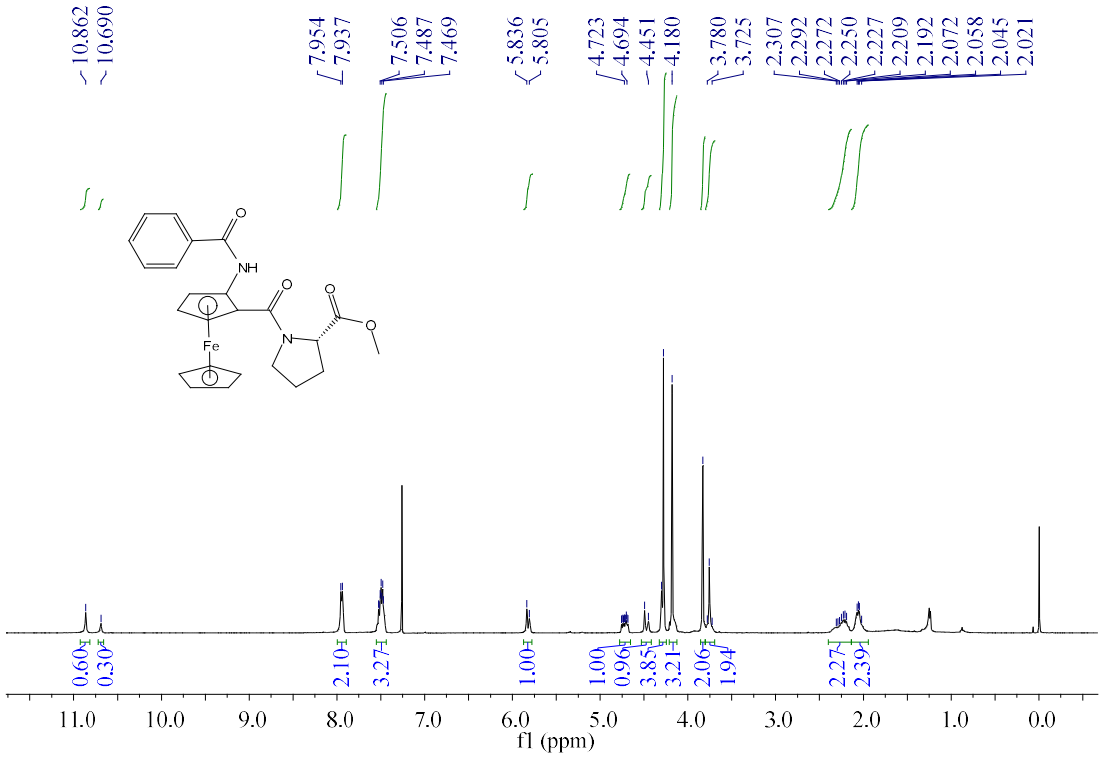
3aj（^{1}H NMR ,^{13}C NMR and ^{19}F NMR）

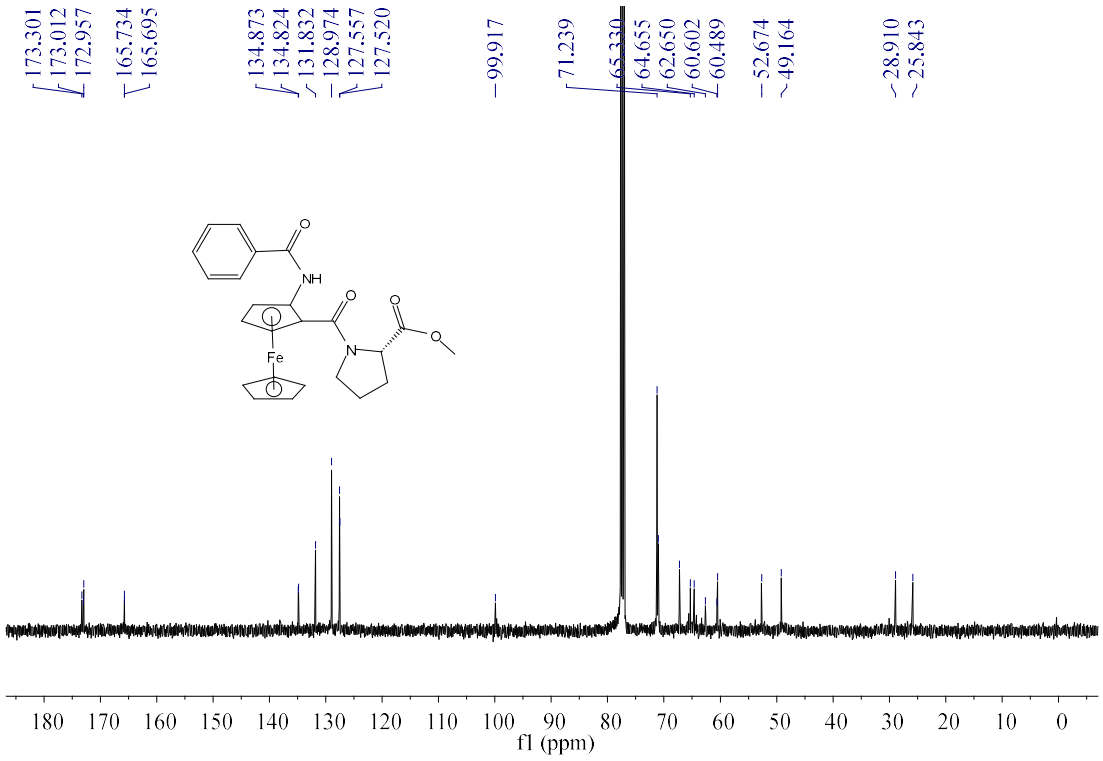





-62.326
O
NH
O
N
Fe
F
F
F
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

3ak（^{1}H NMR and ^{13}C NMR）





5. X-ray Crystallographic Analysis of 3a.

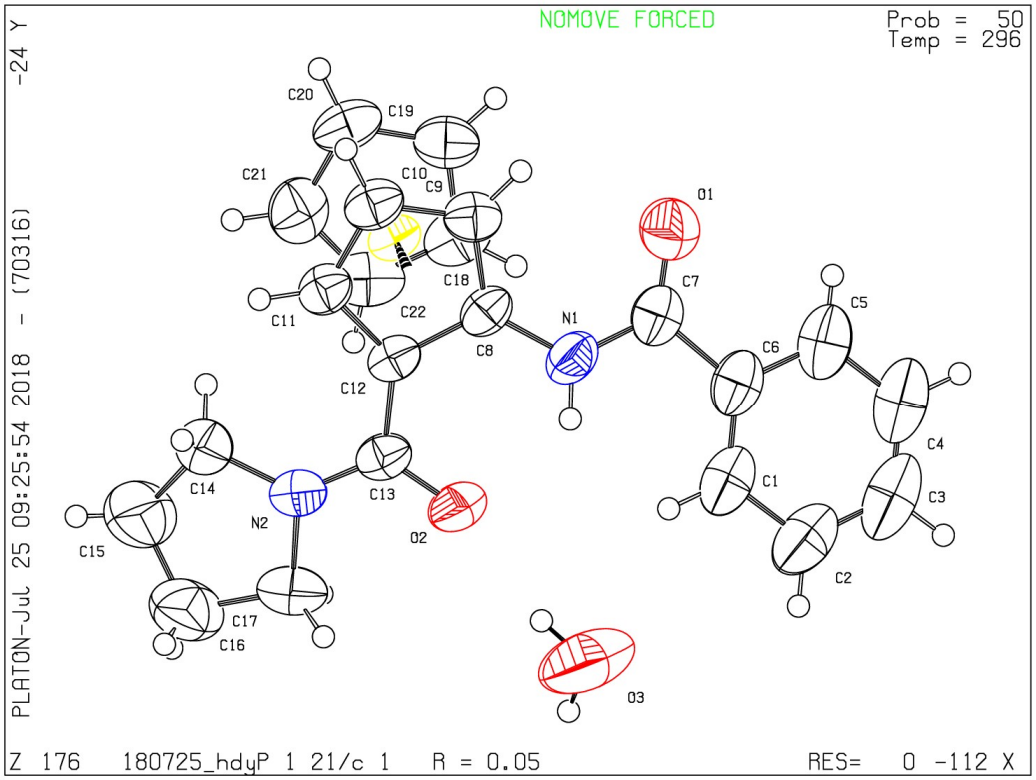


Figure 1. X-ray Crystallographic Analysis of **3a**