Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Palladium-Catalyzed Direct C-H Arylation of Ferrocenecarboxamides with Aryl Halides

Huijie Qiao,[a] Suyan Sun,[a] Fan Yang,*[a] Yu Zhu,[a] Weiguo Zhu,[a] Yusheng Wu,*[b,c] and Yangjie Wu*[a]

[a] *The College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, People's Republic of China*

[b] *Tetranov Biopharm, LLC. 75 Daxue Road, Zhengzhou, 450052, People's Republic of China*

[c] *Collaborative Innovation Center of New Drug Research and Safety Evaluation, Henan Province, PR China.*

*E-mail: yangf@zzu.edu.cn; wyj@zzu.edu.cn; yusheng.wu@tetranovglobal.com

Contents

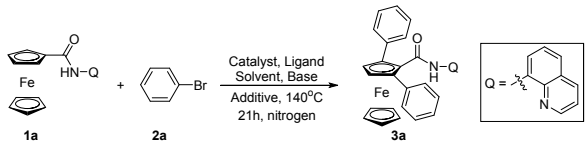
1. Preparation of Substrates

All amides were prepared from the corresponding ferrocenecarboxylic acid and amines according to the reported procedure.[1]

2. Optimization of Reaction Conditions

A 25 mL schlenk tube was equipped with a magnetic stir bar and charged with **1a** (71.2 mg, 0.2 mmol), **2a** (63 uL, 0.6 mmol, 3 equiv), base (0.4 mmol, 2 equiv), catalyst (0.02 mmol, 10 mol %), ligand (0.02 mmol, 10 mol %), PivOH (6.2mg, 0.06 mmol, 30 mol %) in solvent (1.0 mL). The resulting mixture was heated under nitrogen at 140 °C for 21 h, and cooled to room temperature. Upon completion, CH_2Cl_2 (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using hexane-EtOAc as an eluent to afford the pure product **3a**.

Table S1 Screening of Reaction Conditions[a]



Entry	Solvent	Base	Catalyst	Ligand	Additive	Yield(%)[b]
1	toluene	K_2CO_3	$Pd(OAc)_2$	PPh_3	PivOH	8
2	DCE	K_2CO_3	$Pd(OAc)_2$	PPh_3	PivOH	Trace
3	dioxane	K_2CO_3	$Pd(OAc)_2$	PPh_3	PivOH	Trace
4	CH_3CN	K_2CO_3	$Pd(OAc)_2$	PPh_3	PivOH	Trace
5	DMF	K_2CO_3	$Pd(OAc)_2$	PPh_3	PivOH	Trace
6	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	PPh_3	PivOH	30
7	*o*-xylene	Na_2CO_3	$Pd(OAc)_2$	PPh_3	PivOH	20
8	*o*-xylene	Cs_2CO_3	$Pd(OAc)_2$	PPh_3	PivOH	Trace
9	*o*-xylene	K_3PO_4	$Pd(OAc)_2$	PPh_3	PivOH	18
10	*o*-xylene	$KHCO_3$	$Pd(OAc)_2$	PPh_3	PivOH	Trace
11	*o*-xylene	K_2CO_3	-	PPh_3	PivOH	Trace
12	*o*-xylene	K_2CO_3	$PdCl_2$	PPh_3	PivOH	11
13	*o*-xylene	K_2CO_3	Pd_2dba_3	PPh_3	PivOH	17
14	*o*-xylene	K_2CO_3	$Pd(CF_3COO)_2$	PPh_3	PivOH	10
15	*o*-xylene	K_2CO_3	$Ni(OAc)_2$	PPh_3	PivOH	Trace
16	*o*-xylene	K_2CO_3	$[RuCl_2(cymene)]_2$	PPh_3	PivOH	Trace
17	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	PPy_3	PivOH	23
18	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	DPPF	PivOH	49
19	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	RuPhos	PivOH	61

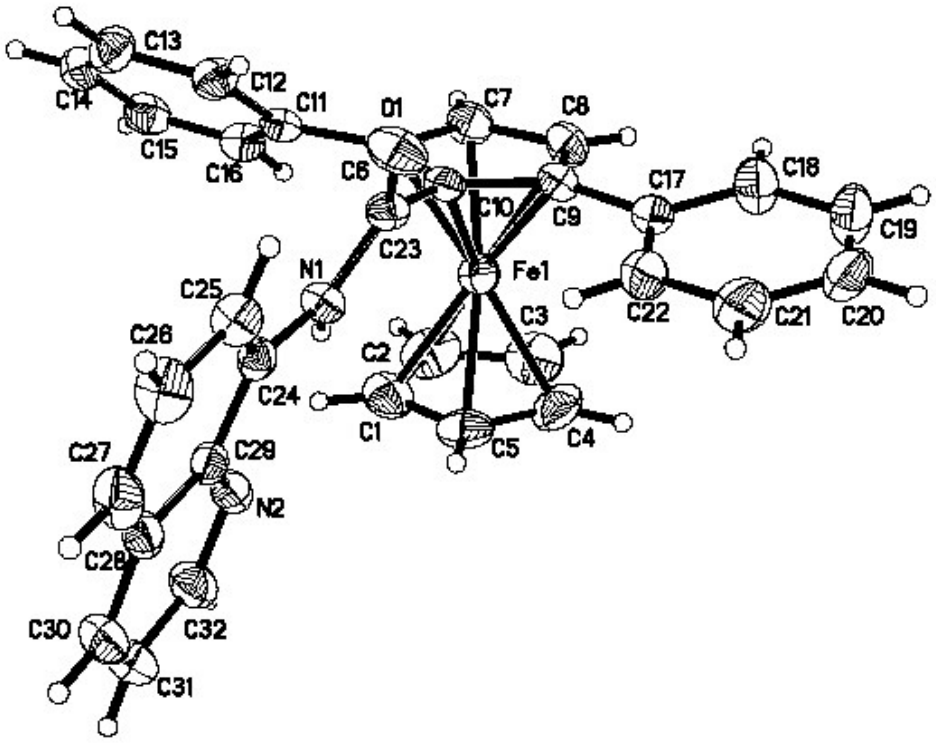
20	***o*-xylene**	**K_2CO_3**	**$Pd(OAc)_2$**	**XPhos**	**PivOH**	**83**
21	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	XantPhos	PivOH	42
22	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	^{t}BuXPhos	PivOH	60
23	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	XPhos	AcOH	61
24	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	XPhos	AcOK	75
25	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	XPhos	PhCOOH	74
26	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	XPhos	-	72
27[c]	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	XPhos	PivOH	82
28[d]	*o*-xylene	K_2CO_3	$Pd(OAc)_2$	XPhos	PivOH	51

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Catalyst (0.02 mmol), Ligand (0.02 mmol), PivOH (0.06 mmol), Base (0.4 mmol) and Solvent (1.0 mL) under nitrogen at 140 °C for 21 h unless otherwise noted. [b] Isolated yield based on **1a**. [c] Without PivOH. [d] At 150 °C. [e] At 130 °C.

3. References

1. (a) L. D.Tran, J.Roane and O. Daugulis, *Angew. Chem., Int. Ed*. 2013, **52**, 6043; (b) T. Truong, K. Klimovica and O. Daugulis, *J. Am. Chem. Soc*. 2013, **135**, 9342.

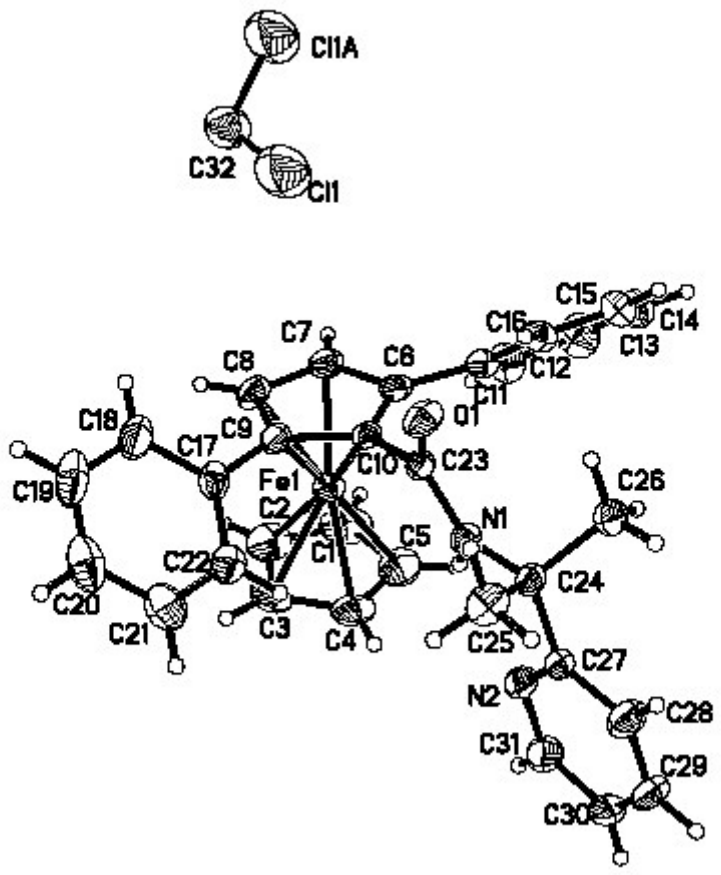
4. The Single Crystal X-ray Diffraction Study of 3a and 5a



CCDC 1446343 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc.cam.ac.uk/data_request/cif.

Table S2 Crystal dData and Structure Refinement for 3a.

Identification code	201506168
Empirical formula	$C_{32}H_{24}FeN_2O$
Formula weight	508.38
Temperature/K	291.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.3423(6)
b/Å	14.2822(4)
c/Å	16.0589(7)
α/°	90
β/°	107.980(5)
γ/°	90
Volume/Å^3	2474.4(2)
Z	4
ρ_{calc}g/cm^3	1.365
μ/mm^{-1}	5.099
F(000)	1056.0
Crystal size/mm^3	0.2 × 0.2 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.196 to 134.122
Index ranges	$-13 \leq h \leq 13$, $-17 \leq k \leq 14$, $-19 \leq l \leq 13$
Reflections collected	9066
Independent reflections	4408 [R_{int} = 0.0267, R_{sigma} = 0.0364]
Data/restraints/parameters	4408/13/325
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.0962
Final R indexes [all data]	R_1 = 0.0531, wR_2 = 0.1034
Largest diff. peak/hole / e Å^{-3}	0.32/-0.21



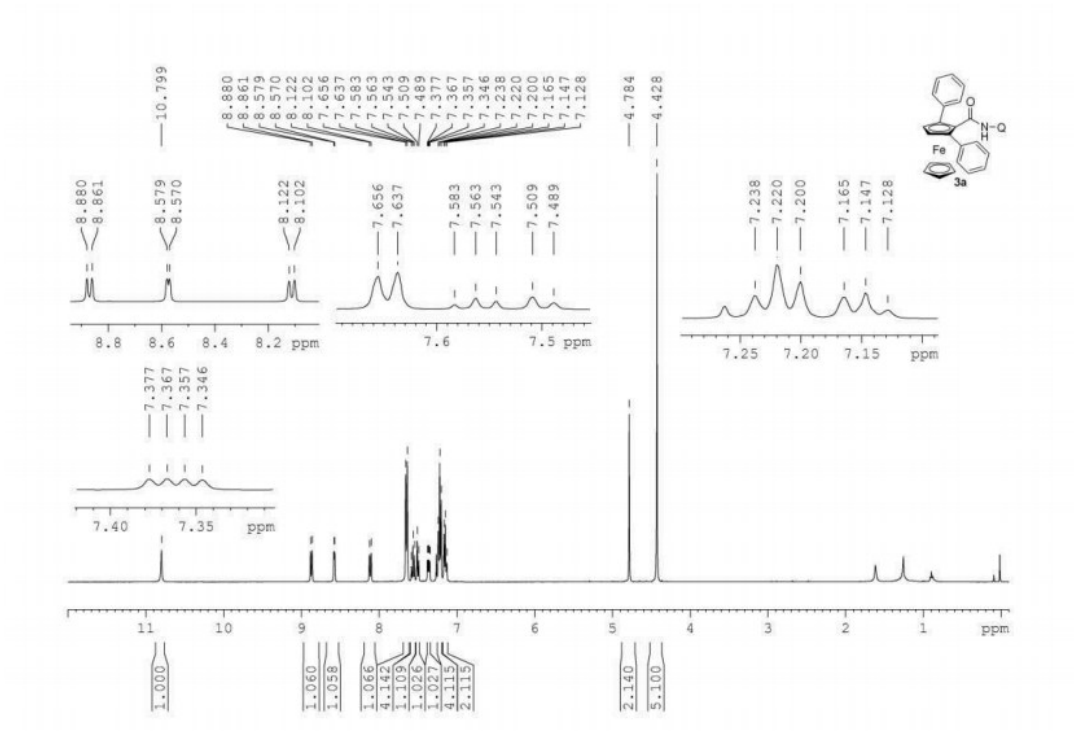
CCDC 1446344 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www. ccdc.cam.ac.uk/data_request/cif.

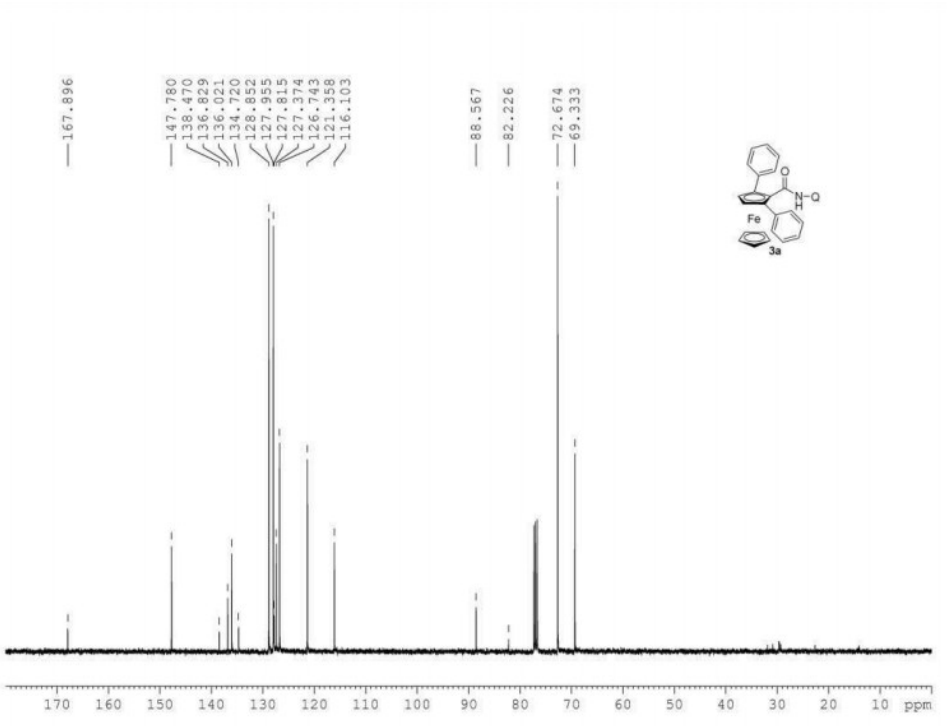
Table S3 Crystal Data and Structure Refinement for 5a.

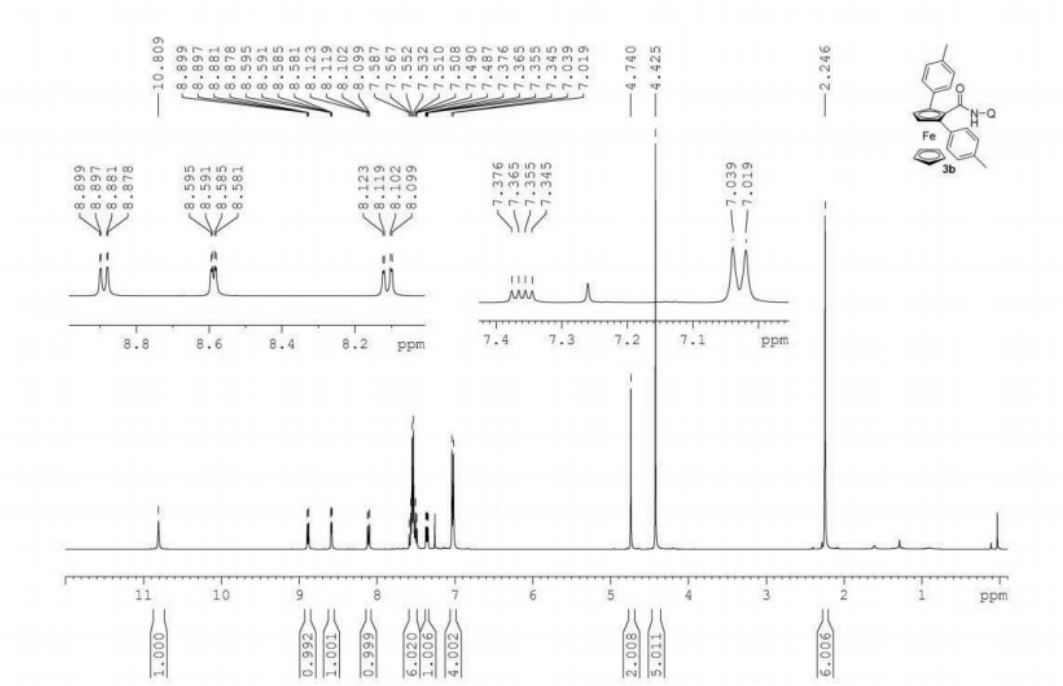
Identification code	201506167
Empirical formula	$C_{63}H_{58}Cl_2Fe_2N_4O_2$
Formula weight	1085.73
Temperature/K	291.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.7314(2)
b/Å	10.30632(19)
c/Å	17.8542(4)
α/°	90
β/°	95.6050(17)
γ/°	90
Volume/Å^3	2697.78(9)
Z	2
ρ_{calc}g/cm^3	1.337

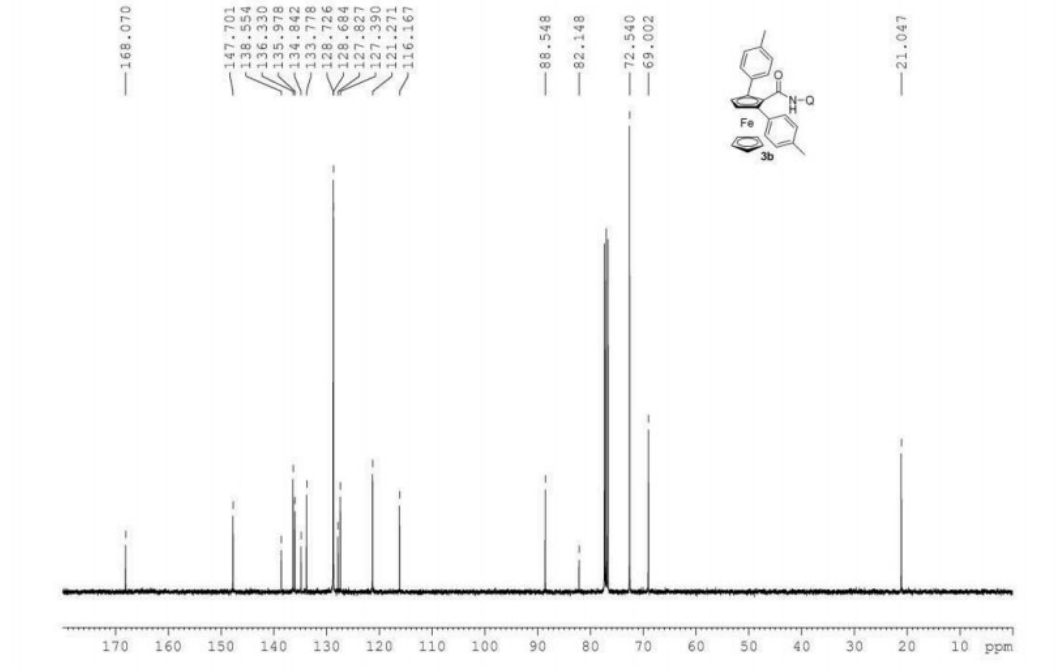
μ/mm^{-1}	5.596
F(000)	1132.0
Crystal size/mm^3	0.22 × 0.2 × 0.17
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.028 to 134.156
Index ranges	$-17 \leq h \leq 17$, $-12 \leq k \leq 6$, $-21 \leq l \leq 21$
Reflections collected	9723
Independent reflections	4818 [R_{int} = 0.0292, R_{sigma} = 0.0363]
Data/restraints/parameters	4818/4/340
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0497, wR_2 = 0.1388
Final R indexes [all data]	R_1 = 0.0625, wR_2 = 0.1497
Largest diff. peak/hole / e $Å^{-3}$	0.68/-0.64

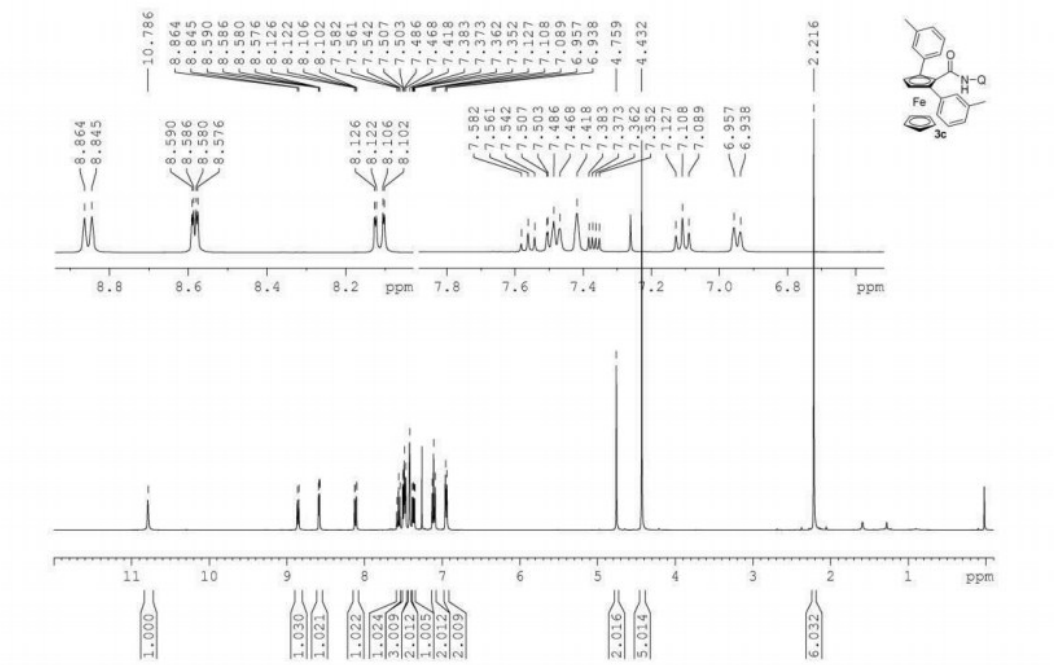
5. Copies of NMR Spectra for the Products

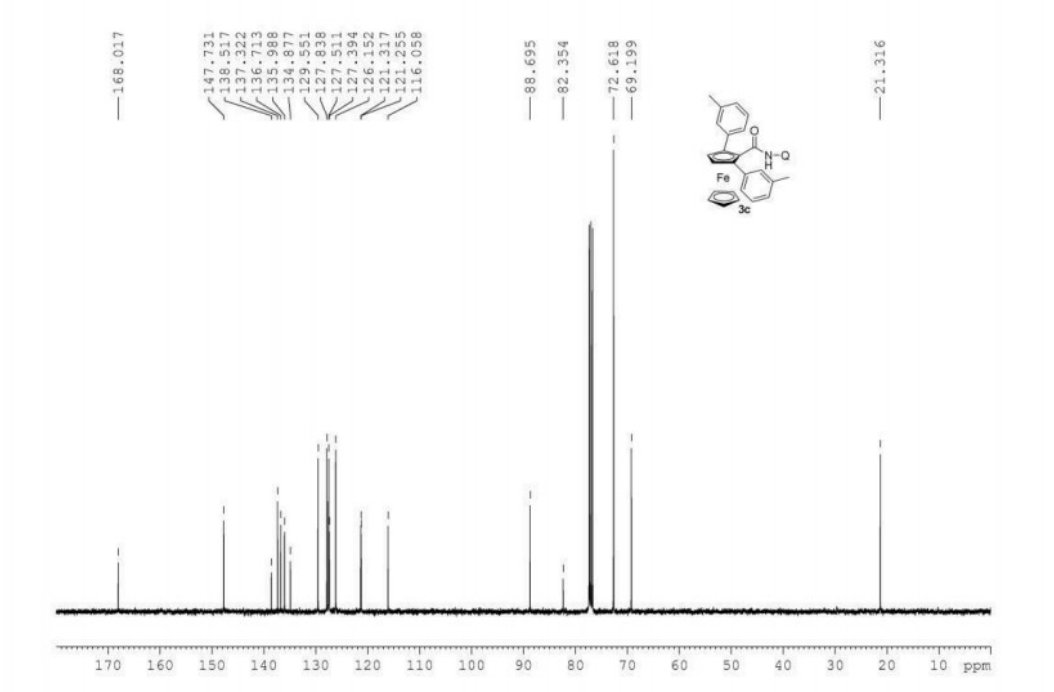


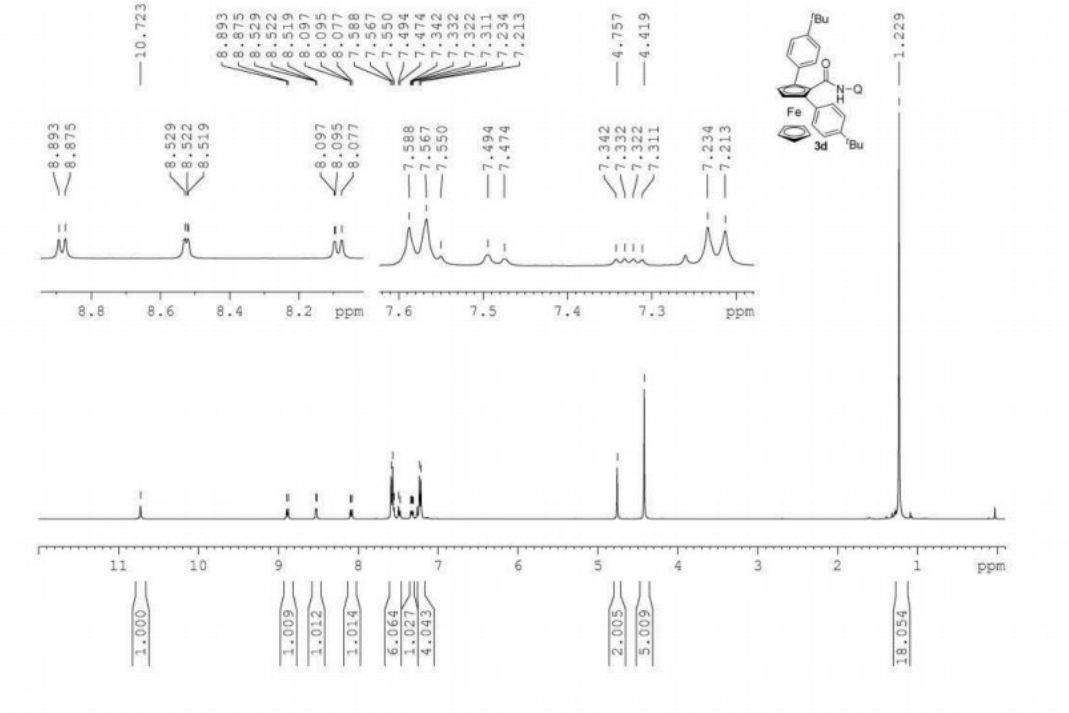


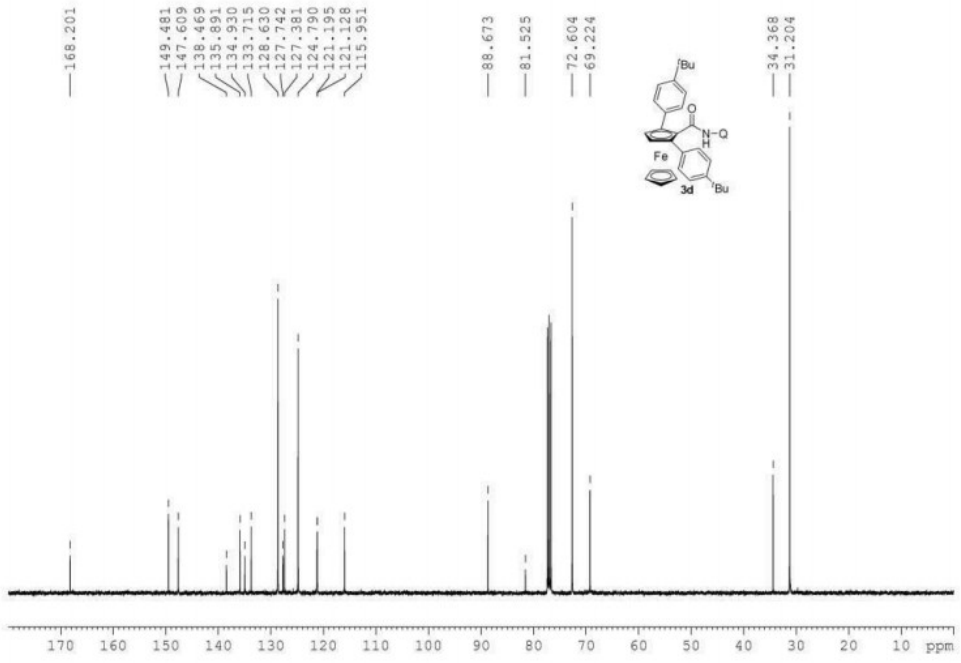

10.809
8.899
8.897
8.881
8.878
8.595
8.591
8.585
8.581
8.123
8.119
8.102
8.099
7.587
7.567
7.552
7.532
7.510
7.508
7.490
7.487
7.376
7.365
7.355
7.345
7.039
7.019
4.740
4.425
2.246
Fe
3b
ppm
1.000
0.992
1.001
0.999
6.020
1.006
4.002
2.008
5.011
6.006

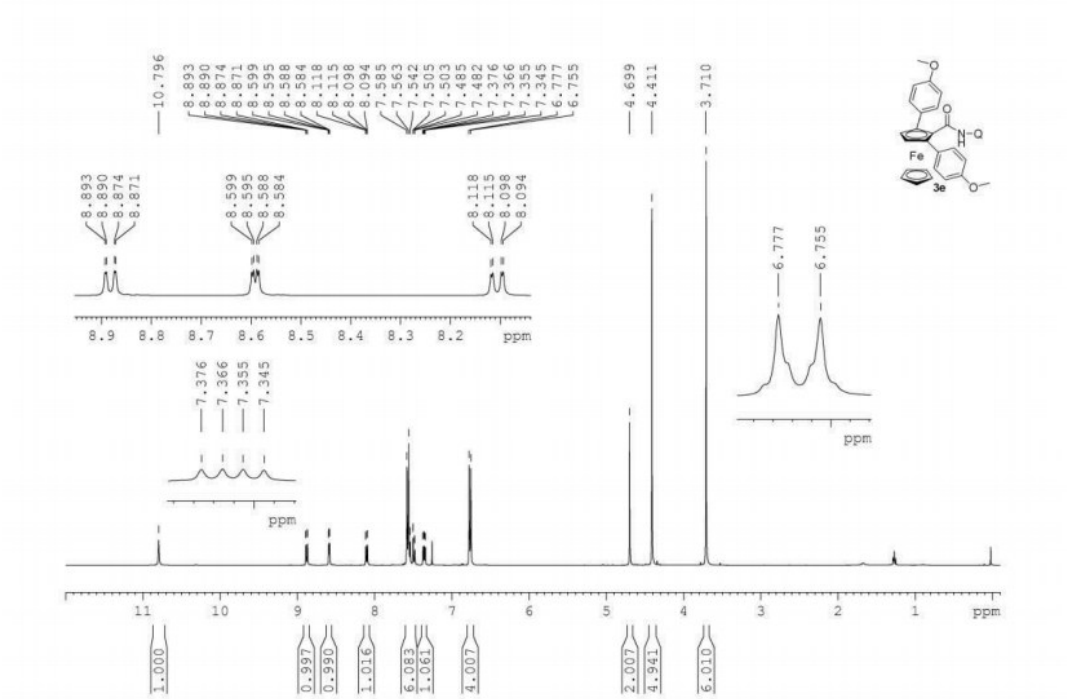

168.070
147.701
138.554
136.330
135.978
134.842
133.778
128.726
128.684
127.827
127.390
121.271
116.167
88.548
82.148
72.540
69.002
21.047
Fe
3b
ppm

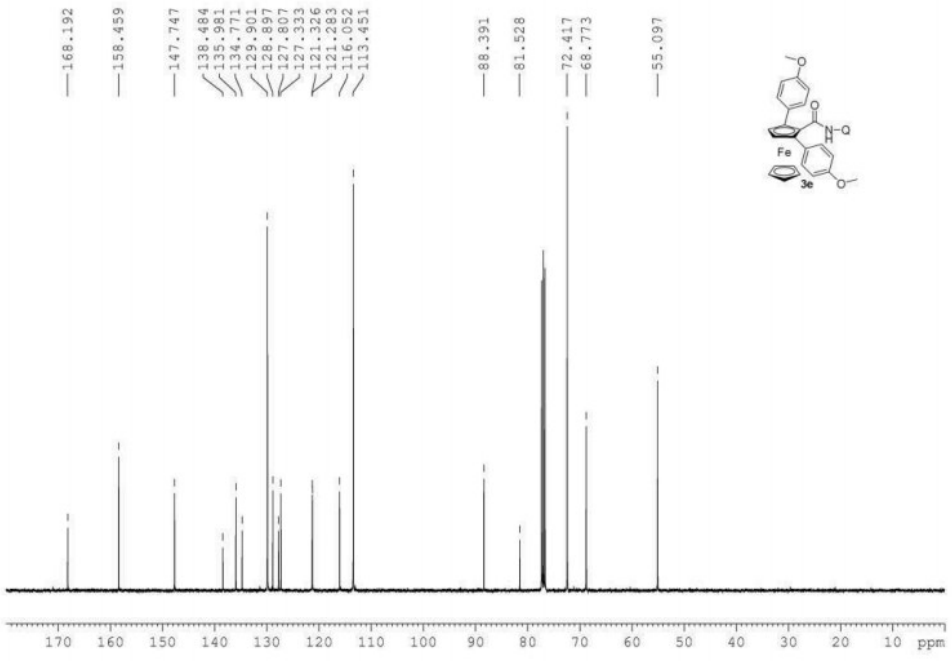

10.786
8.864
8.845
8.590
8.586
8.580
8.576
8.126
8.122
8.106
8.102
7.582
7.561
7.542
7.507
7.503
7.486
7.468
7.418
7.383
7.373
7.362
7.352
7.127
7.108
7.089
6.957
6.938
4.759
4.432
2.216
Fe
3c
ppm
1.000
1.030
1.021
1.022
1.024
3.009
2.012
1.005
2.012
2.009
2.016
5.014
6.032

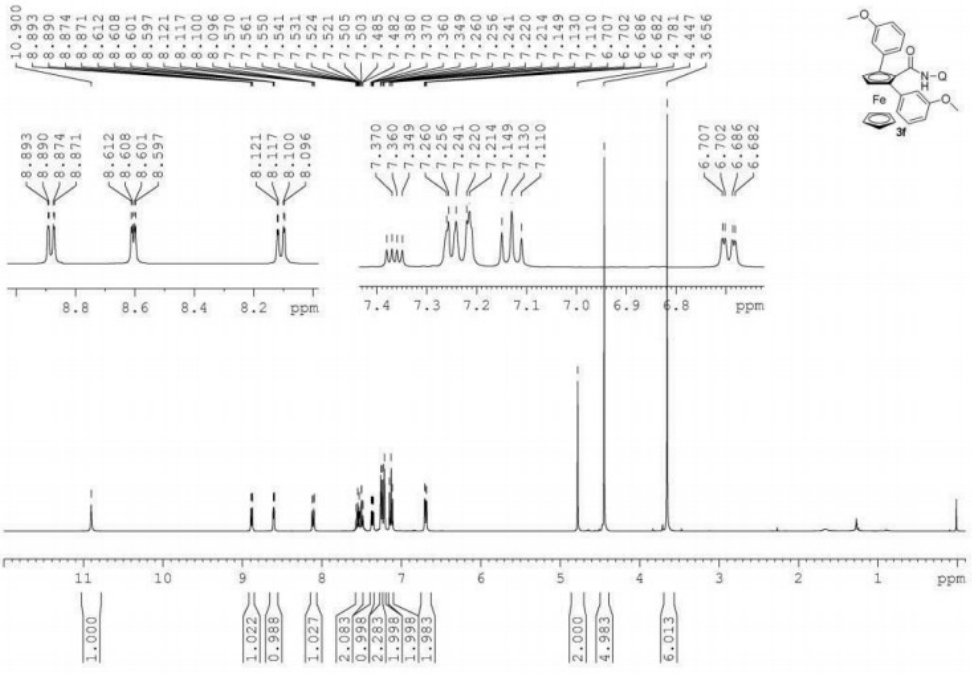

168.017
147.731
138.517
137.322
136.713
135.988
134.877
129.551
127.838
127.511
127.394
126.152
121.317
121.255
116.058
88.695
82.354
72.618
69.199
21.316
Fe
3c
ppm

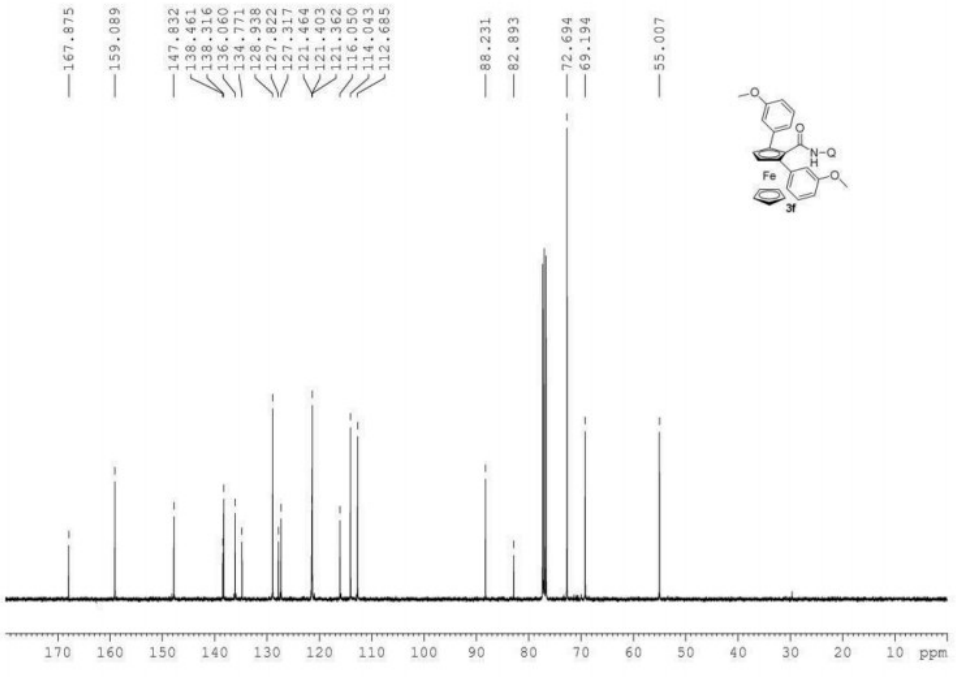

10.723
8.893
8.875
8.529
8.522
8.519
8.097
8.095
8.077
7.588
7.567
7.550
7.494
7.474
7.342
7.332
7.322
7.311
7.234
7.213
4.757
4.419
1.229
3d
Fe
ppm
1.000
1.009
1.012
1.014
6.064
1.027
4.043
2.005
5.009
18.054

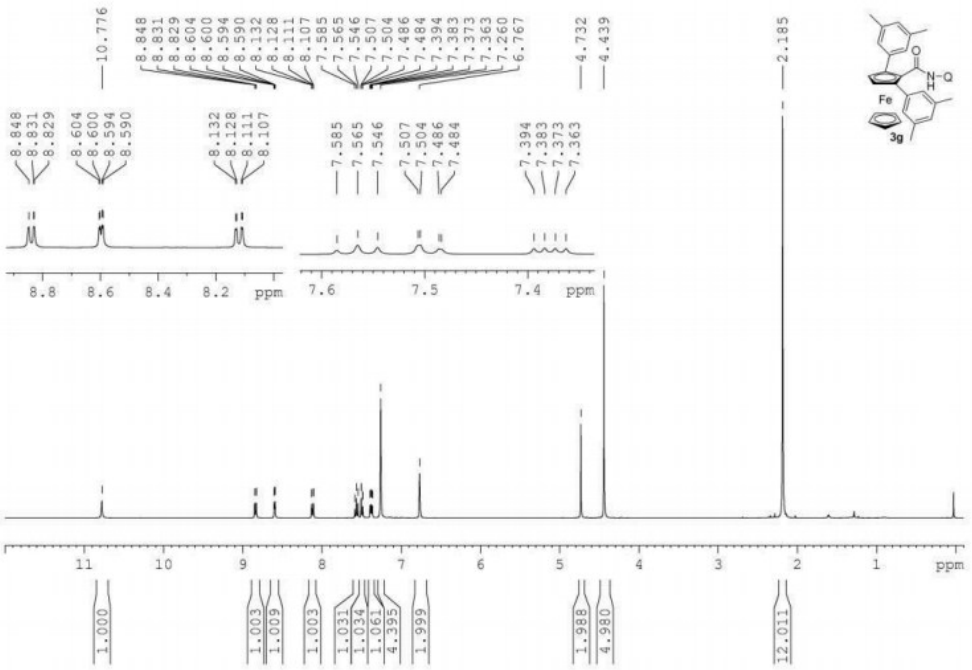

168.201
149.481
147.609
138.469
135.891
134.930
133.715
128.630
127.742
127.381
124.790
121.195
121.128
115.951
88.673
81.525
72.604
69.224
34.368
31.204
3d
Fe
ppm

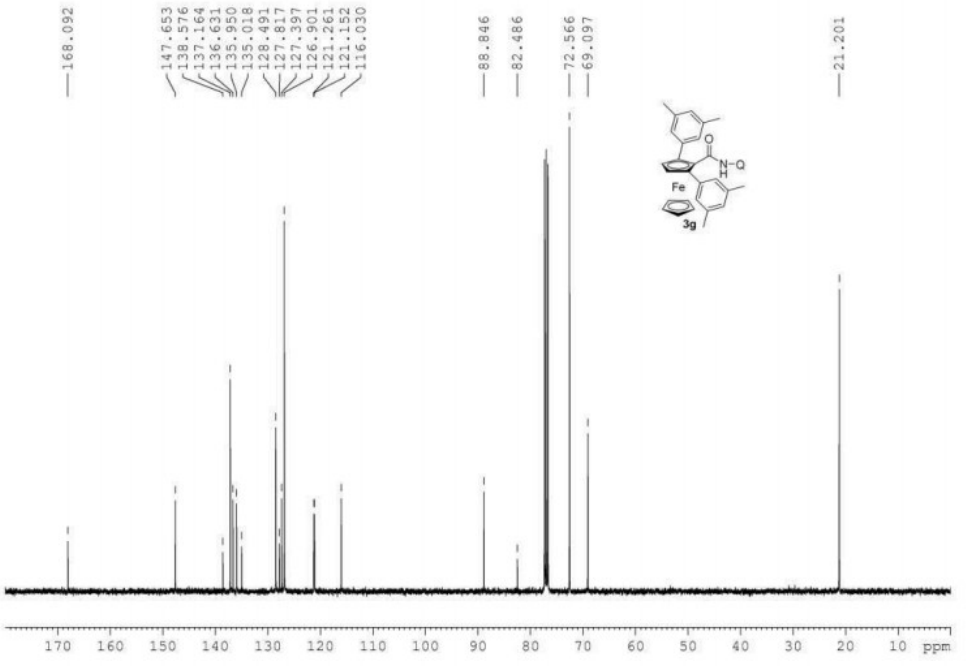

10.796
8.893
8.890
8.874
8.871
8.599
8.595
8.588
8.584
8.118
8.115
8.098
8.094
7.585
7.563
7.542
7.505
7.503
7.485
7.482
7.376
7.366
7.355
7.345
6.777
6.755
4.699
4.411
3.710
Fe
3e
ppm
1.000
0.997
0.990
1.016
6.083
1.061
4.007
2.007
4.941
6.010

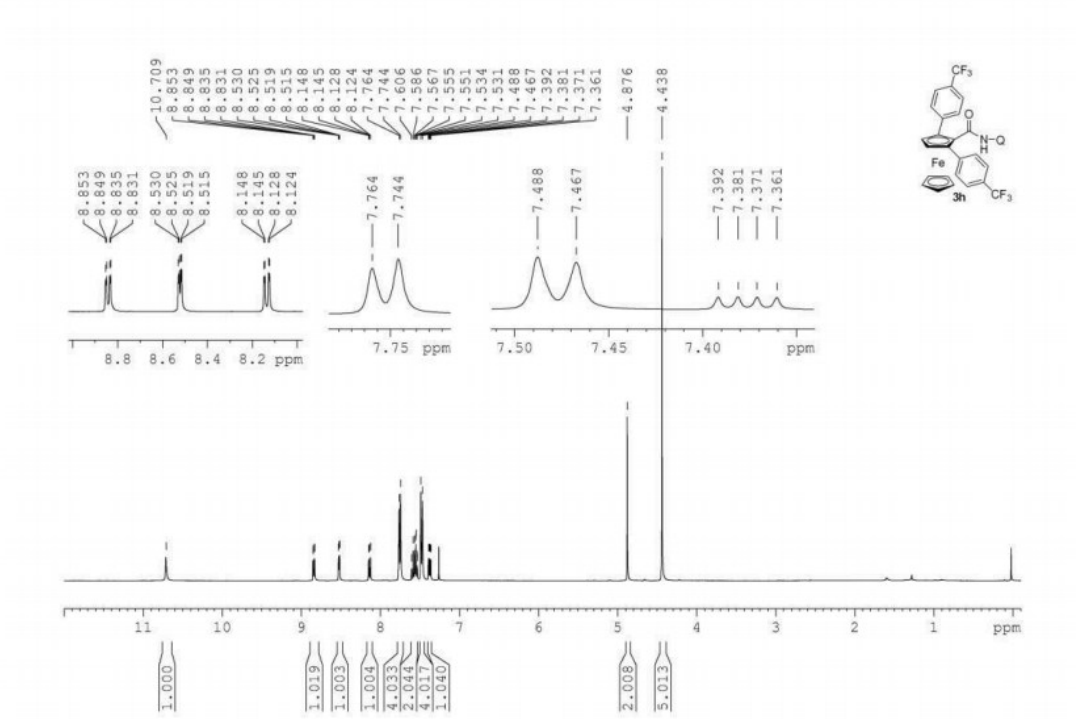

168.192
158.459
147.747
138.484
135.981
134.771
129.901
128.897
127.807
127.333
121.326
121.283
116.052
113.451
88.391
81.528
72.417
68.773
55.097
Fe
3e
ppm

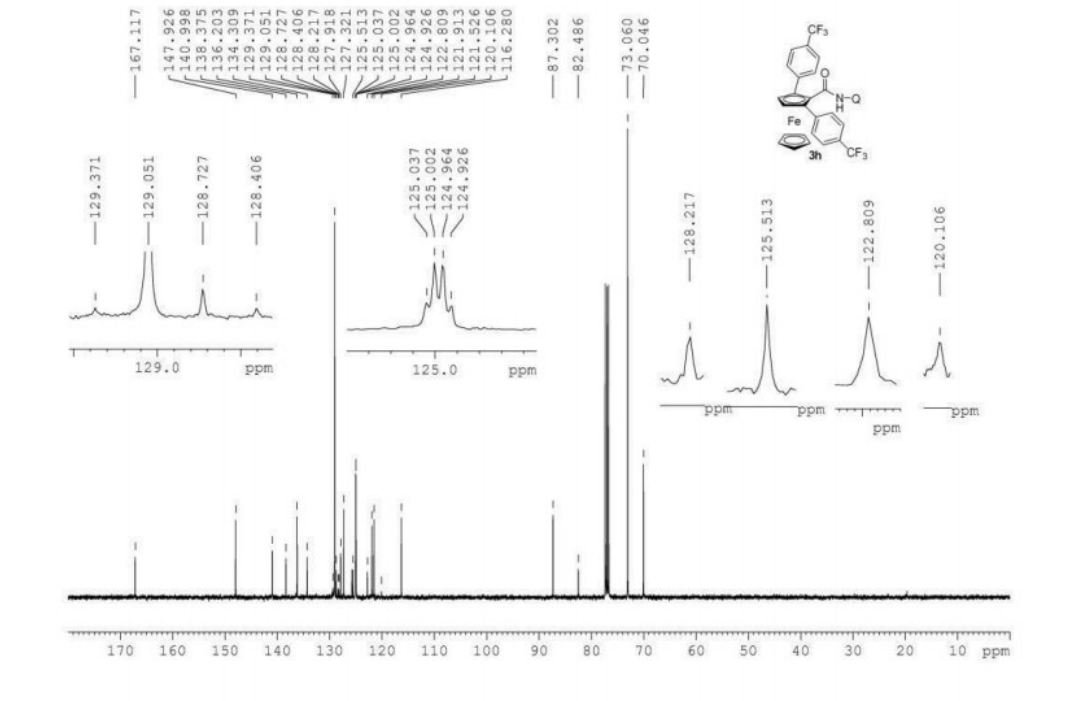

10.900
8.893
8.890
8.874
8.871
8.612
8.608
8.601
8.597
8.121
8.117
8.100
8.096
7.570
7.561
7.550
7.541
7.531
7.524
7.521
7.505
7.503
7.485
7.482
7.380
7.370
7.360
7.349
7.260
7.256
7.241
7.220
7.214
7.149
7.130
7.110
6.707
6.702
6.686
6.682
4.781
4.447
3.656
ppm
1.000
1.022
0.988
1.027
2.083
0.998
2.283
1.998
1.998
1.983
2.000
4.983
6.013
Fe
3f

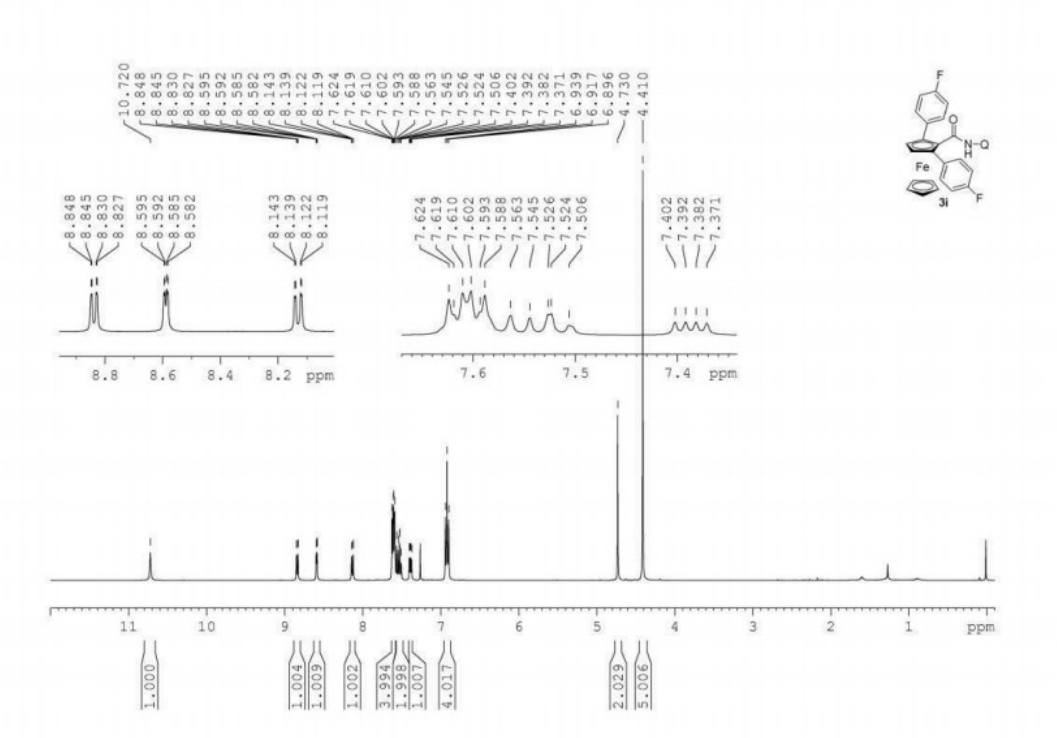

167.875
159.089
147.832
138.461
138.316
136.060
134.771
128.938
127.822
127.317
121.464
121.403
121.362
116.050
114.043
112.685
88.231
82.893
72.694
69.194
55.007
ppm
Fe
3f

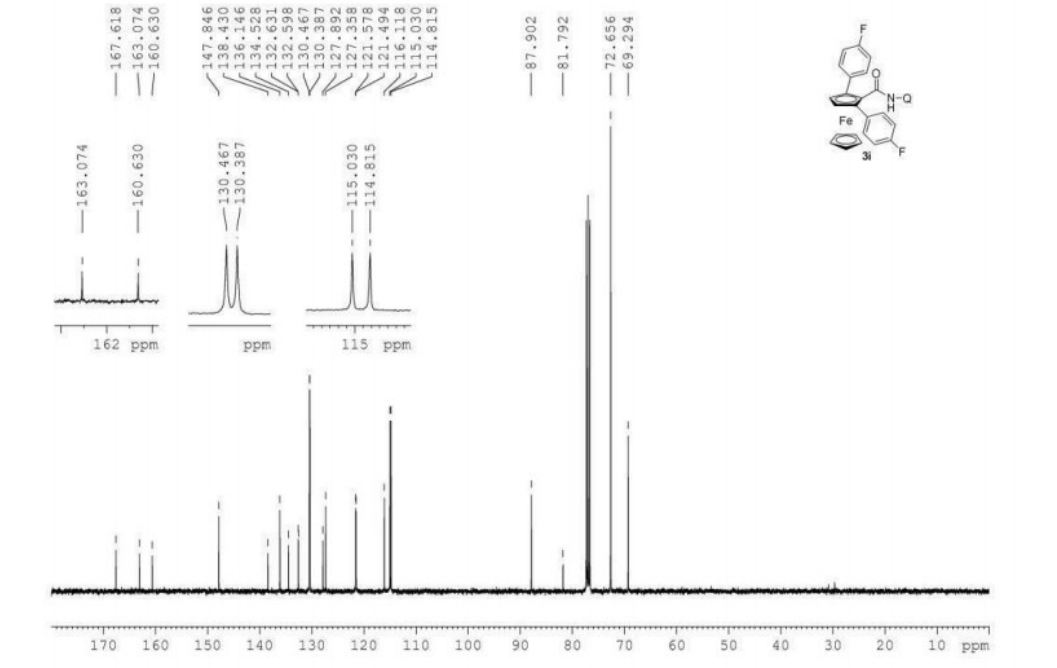

10.776
8.848
8.831
8.829
8.604
8.600
8.594
8.590
8.132
8.128
8.111
8.107
7.585
7.565
7.546
7.507
7.504
7.486
7.484
7.394
7.383
7.373
7.363
7.260
6.767
4.732
4.439
2.185
Fe
3g
ppm
1.000
1.003
1.009
1.003
1.031
1.034
1.061
4.395
1.999
1.988
4.980
12.011

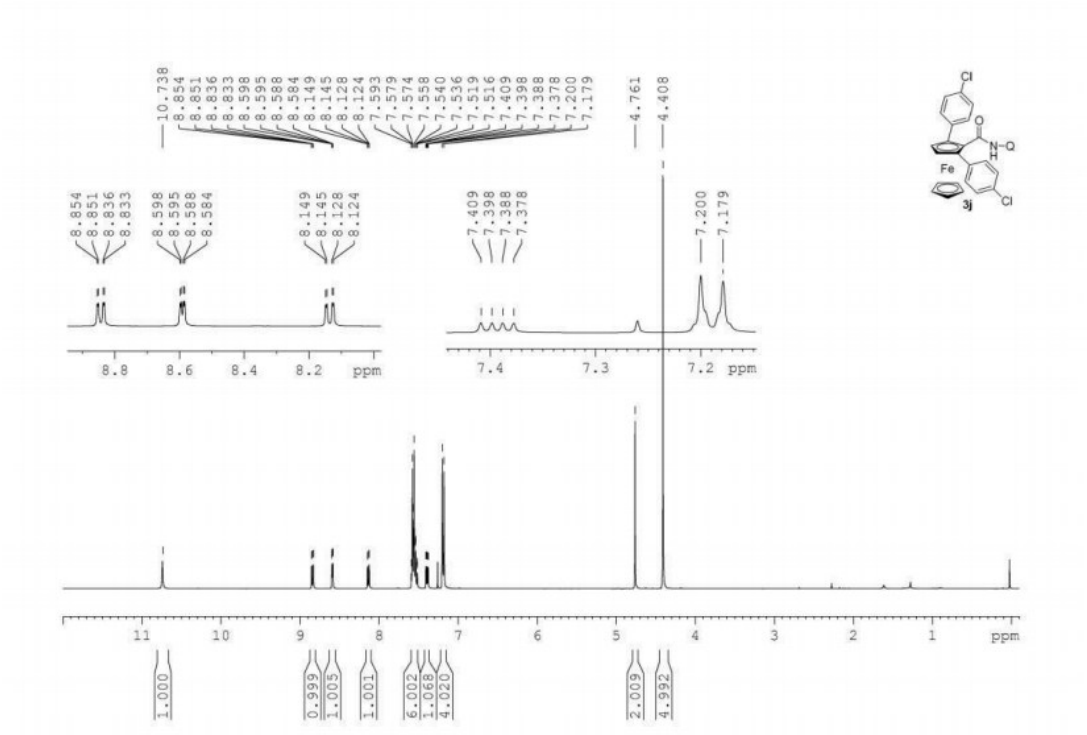

168.092
147.653
138.576
137.164
136.631
135.950
135.018
128.491
127.817
127.397
126.901
121.261
121.152
116.030
88.846
82.486
72.566
69.097
21.201
Fe
3g
ppm

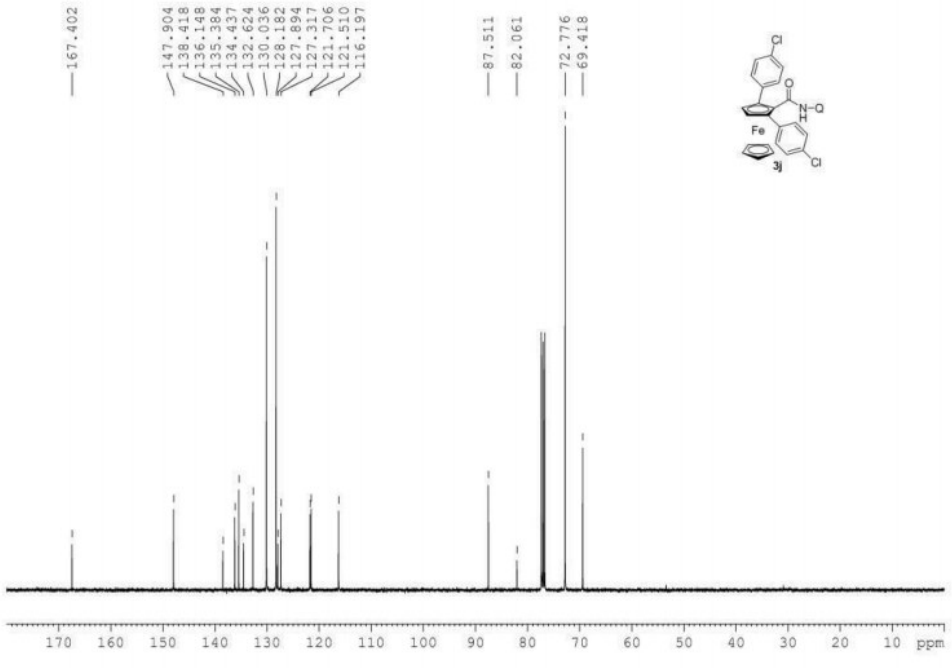

10.709
8.853
8.849
8.835
8.831
8.530
8.525
8.519
8.515
8.148
8.145
8.128
8.124
7.764
7.744
7.606
7.586
7.567
7.555
7.551
7.534
7.531
7.488
7.467
7.392
7.381
7.371
7.361
4.876
4.438
CF3
O
N-O
H
Fe
3h
CF3
8.8 8.6 8.4 8.2 ppm
7.75 ppm
7.50 7.45 7.40 ppm
11 10 9 8 7 6 5 4 3 2 1 ppm
1.000
1.019
1.003
1.004
4.033
2.044
4.017
1.040
2.008
5.013

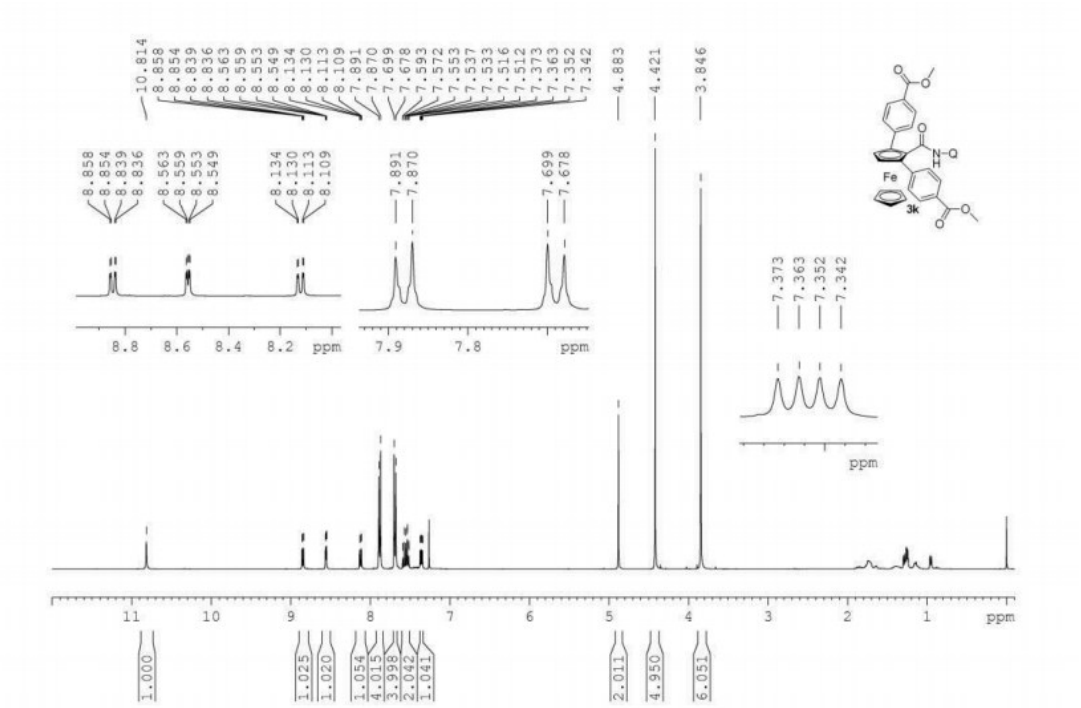

167.117
147.926
140.998
138.375
136.203
134.309
129.371
129.051
128.727
128.406
128.217
127.918
127.321
125.513
125.037
125.002
124.964
124.926
122.809
121.913
121.526
120.106
116.280
87.302
82.486
73.060
70.046
CF3
O
N-O
H
Fe
3h
CF3
129.371
129.051
128.727
128.406
129.0 ppm
125.037
125.002
124.964
124.926
125.0 ppm
128.217
125.513
122.809
120.106
ppm
ppm
ppm
ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

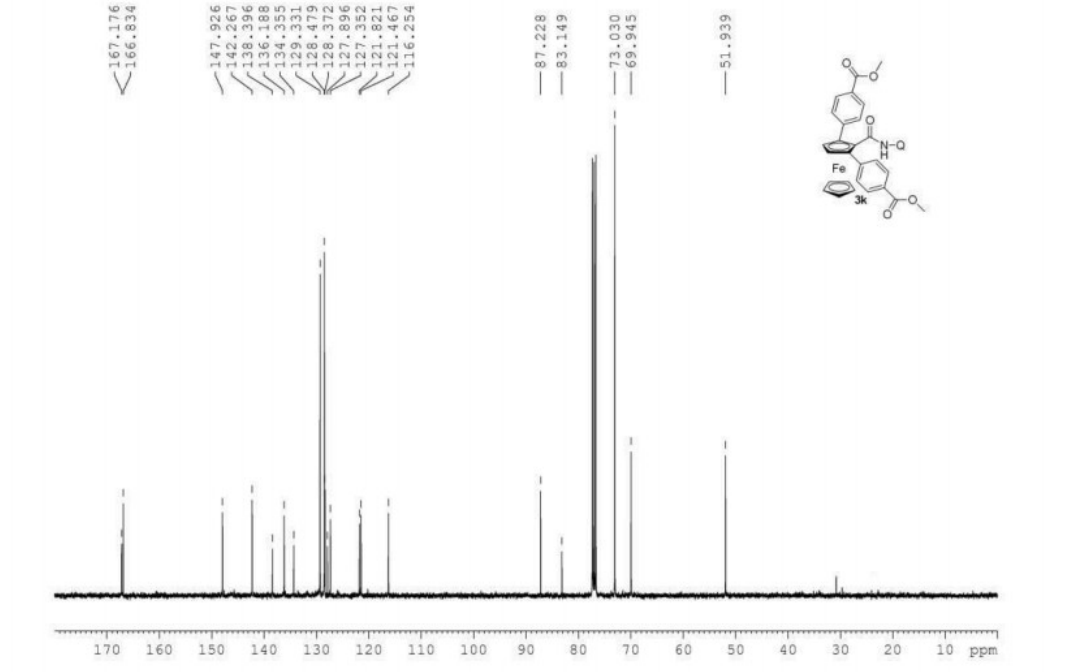

10.720
8.848
8.845
8.830
8.827
8.595
8.592
8.585
8.582
8.143
8.139
8.122
8.119
7.624
7.619
7.610
7.602
7.593
7.588
7.563
7.545
7.526
7.524
7.506
7.402
7.392
7.382
7.371
6.939
6.917
6.896
4.730
4.410
F
O
N-Q
H
Fe
F
3i
8.8
8.6
8.4
8.2 ppm
7.6
7.5
7.4 ppm
11
10
9
8
7
6
5
4
3
2
1
ppm
1.000
1.004
1.009
1.002
3.994
1.998
1.007
4.017
2.029
5.006

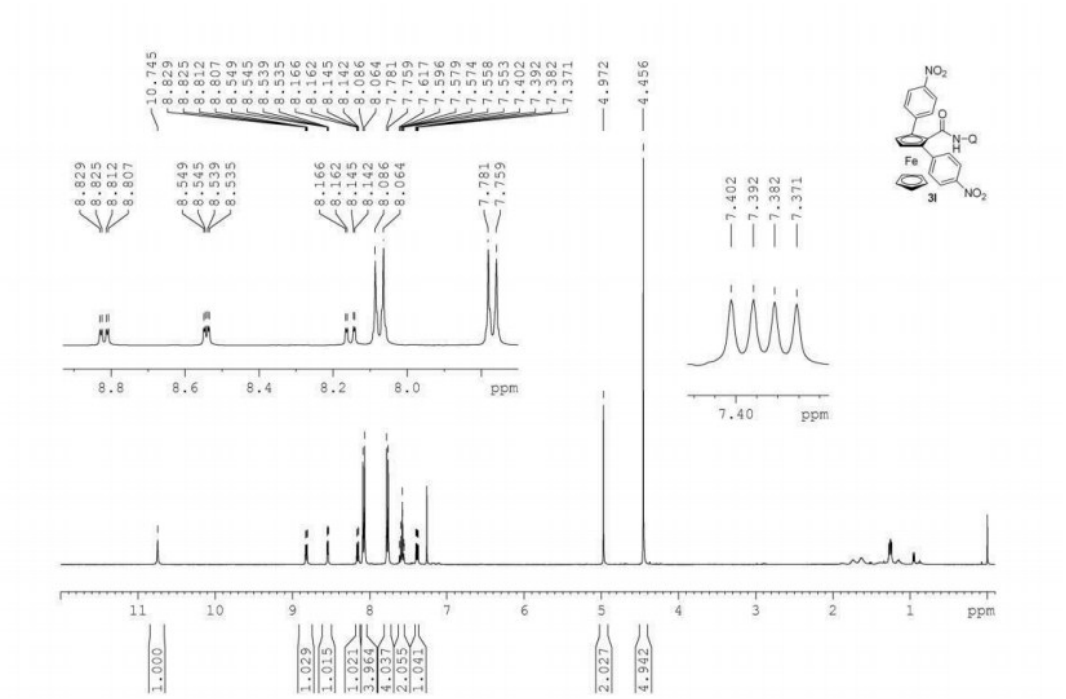

167.618
163.074
160.630
147.846
138.430
136.146
134.528
132.631
132.598
130.467
130.387
127.882
127.358
121.578
121.494
116.118
115.030
114.815
87.902
81.792
72.656
69.294
F
O
N-Q
H
Fe
F
3i
162 ppm
ppm
115 ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

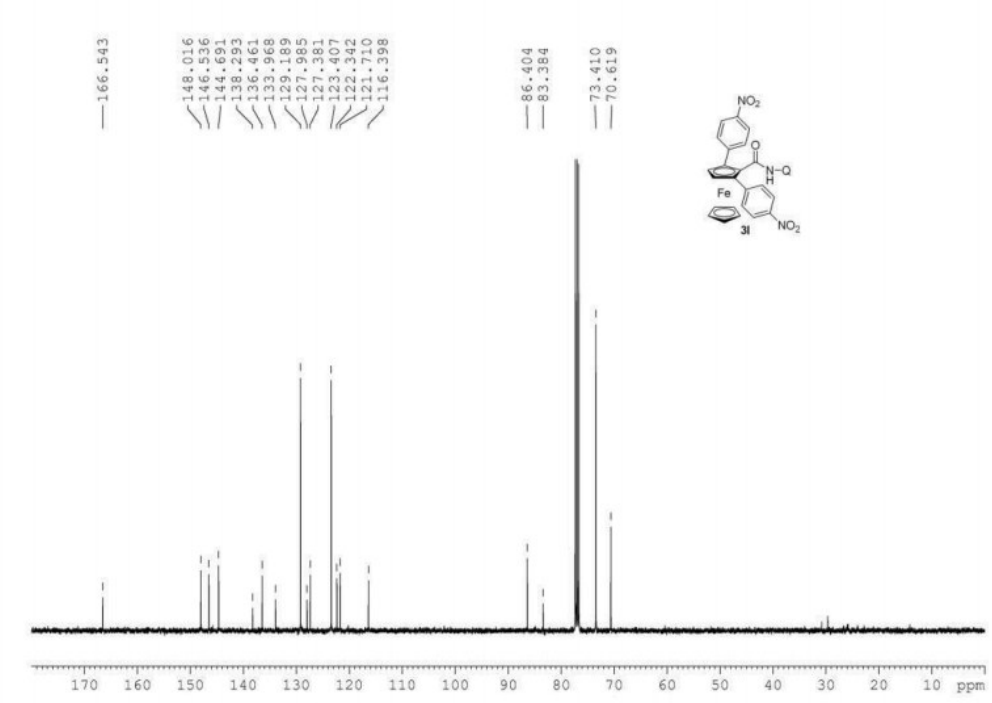

10.738
8.854
8.851
8.836
8.833
8.598
8.595
8.588
8.584
8.149
8.145
8.128
8.124
7.593
7.579
7.574
7.558
7.540
7.536
7.519
7.516
7.409
7.398
7.388
7.378
7.200
7.179
4.761
4.408
Cl
O
N
H
O
Fe
3j
Cl
8.8
8.6
8.4
8.2
ppm
7.4
7.3
7.2
ppm
11
10
9
8
7
6
5
4
3
2
1
ppm
1.000
0.999
1.005
1.001
6.002
1.068
4.020
2.009
4.992

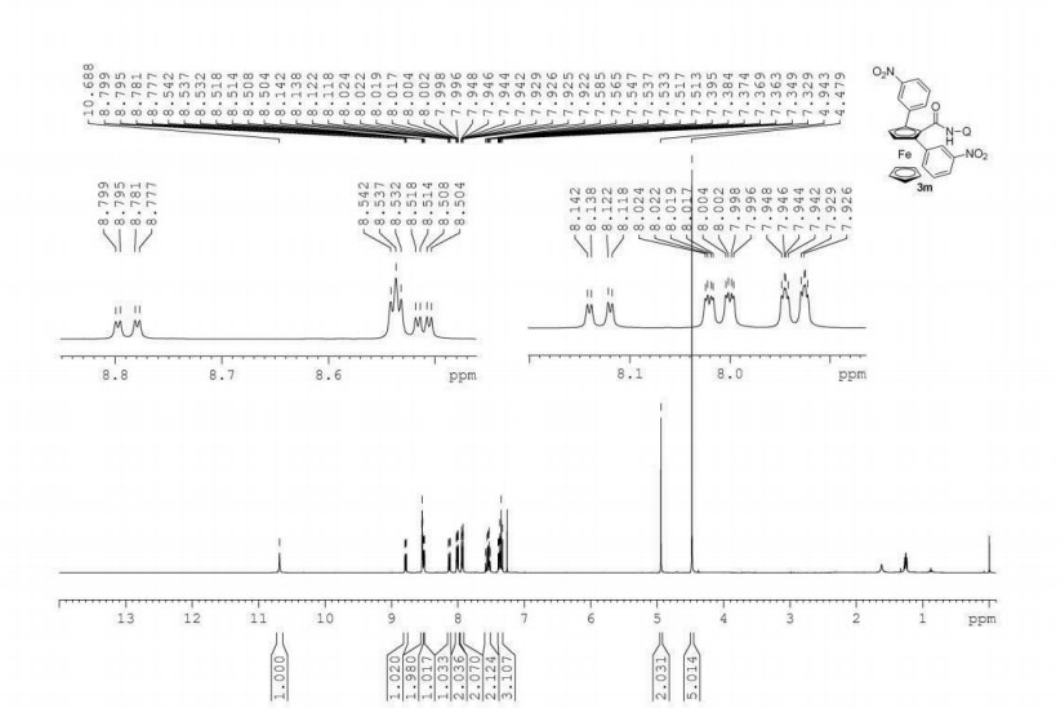

167.402
147.904
138.418
136.148
135.384
134.437
132.624
130.036
128.182
127.894
127.317
121.706
121.510
116.197
87.511
82.061
72.776
69.418
Cl
O
N
H
O
Fe
3j
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

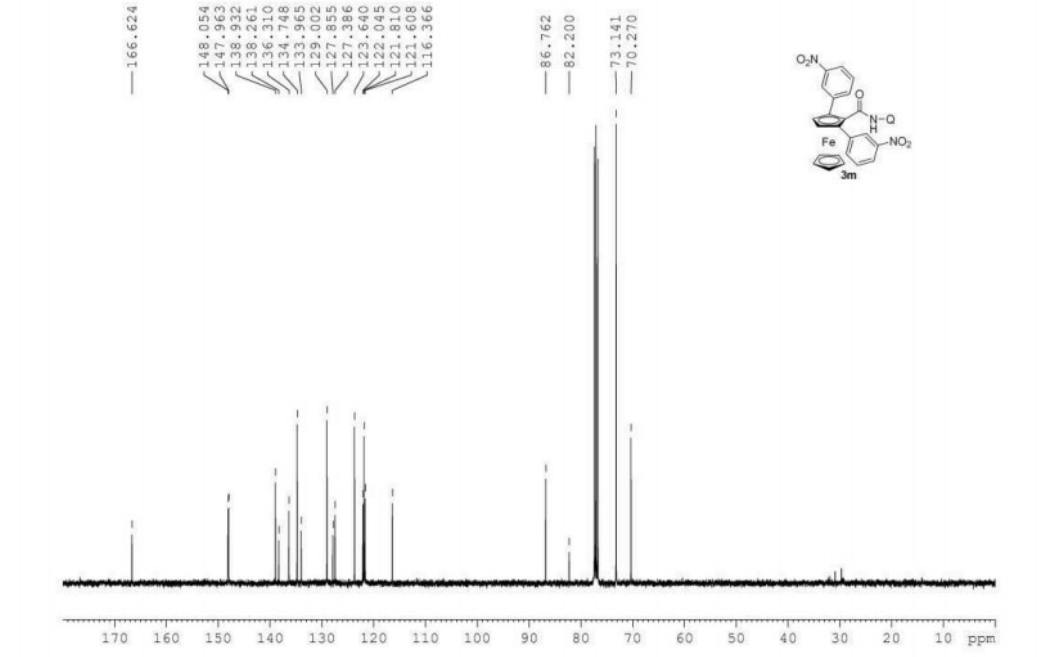

10.814
8.858
8.854
8.839
8.836
8.563
8.559
8.553
8.549
8.134
8.130
8.113
8.109
7.891
7.870
7.699
7.678
7.593
7.572
7.553
7.537
7.533
7.516
7.512
7.373
7.363
7.352
7.342
4.883
4.421
3.846
Fe
3k
ppm
1.000
1.025
1.020
1.054
4.015
3.998
2.042
1.041
2.011
4.950
6.051

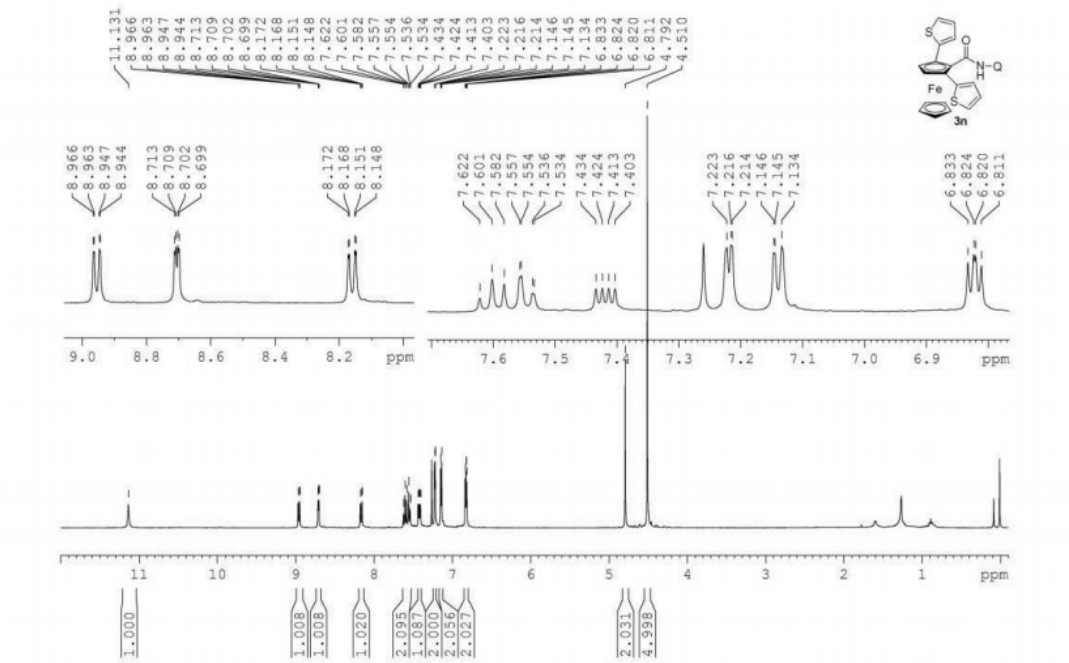

167.176
166.834
147.926
142.267
138.396
136.188
134.355
129.331
128.479
128.372
127.896
127.352
121.821
121.467
116.254
87.228
83.149
73.030
69.945
51.939
Fe
3k
ppm

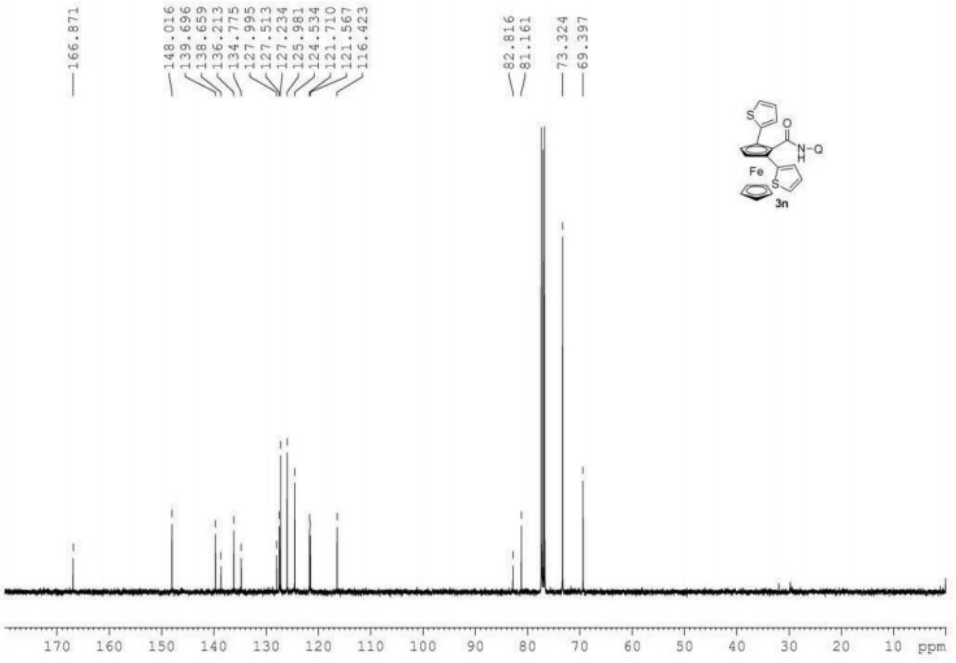

10.745
8.829
8.825
8.812
8.807
8.549
8.545
8.539
8.535
8.166
8.162
8.145
8.142
8.086
8.064
7.781
7.759
7.617
7.596
7.579
7.574
7.558
7.553
7.402
7.392
7.382
7.371
4.972
4.456
NO2
N-Q
H
Fe
NO2
3l
ppm
1.000
1.029
1.015
1.021
3.964
4.037
2.055
1.041
2.027
4.942

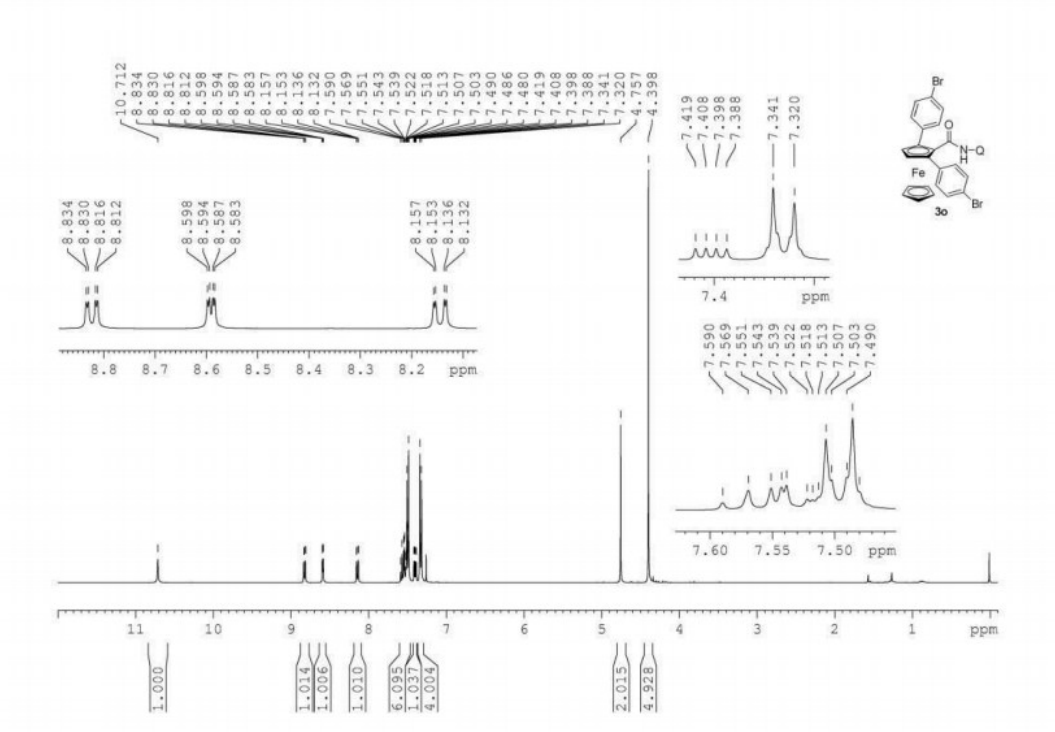

166.543
148.016
146.536
144.691
138.293
136.461
133.968
129.189
127.985
127.381
123.407
122.342
121.710
116.398
86.404
83.384
73.410
70.619
NO2
N-Q
H
Fe
NO2
3l
ppm

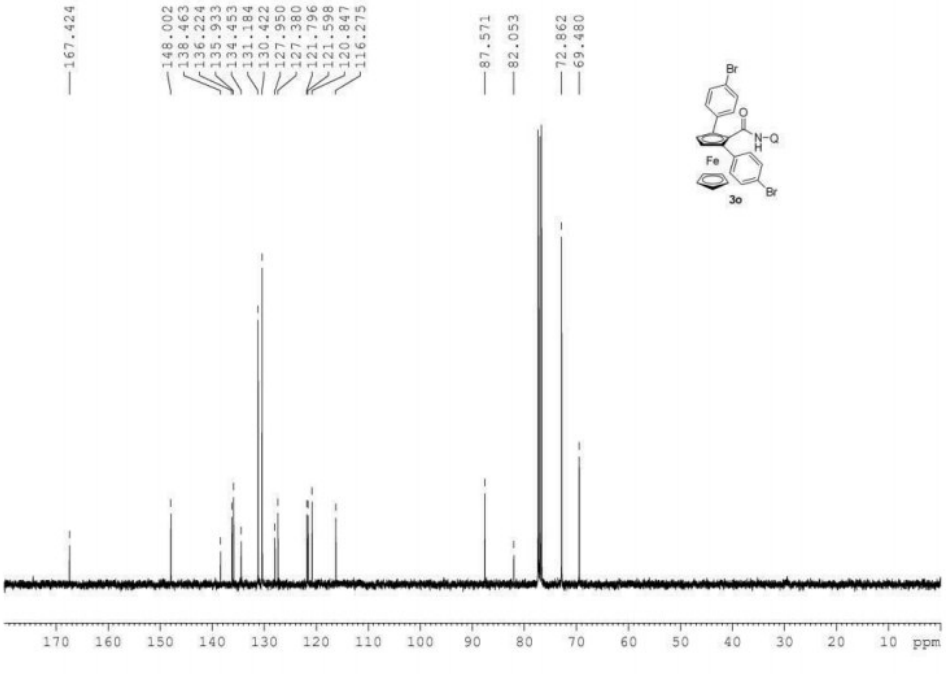

10.688
8.799
8.795
8.781
8.777
8.542
8.537
8.532
8.518
8.514
8.508
8.504
8.142
8.138
8.122
8.118
8.024
8.022
8.019
8.017
8.004
8.002
7.998
7.996
7.948
7.946
7.944
7.942
7.929
7.926
7.925
7.922
7.585
7.565
7.547
7.537
7.533
7.517
7.513
7.395
7.384
7.374
7.369
7.363
7.349
7.329
4.943
4.479
ppm
1.000
1.020
1.980
1.017
1.033
2.036
2.070
2.124
3.107
2.031
5.014
3m

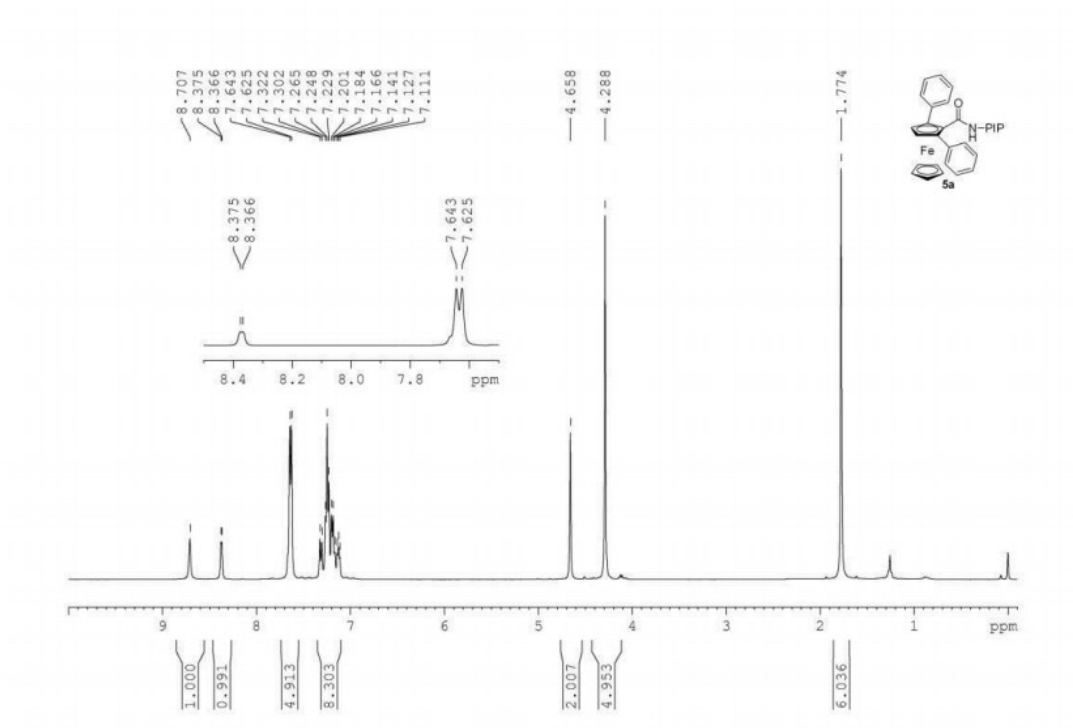

166.624
148.054
147.963
138.932
138.261
136.310
134.748
133.965
129.002
127.855
127.386
123.640
122.045
121.810
121.608
116.366
86.762
82.200
73.141
70.270
ppm
3m

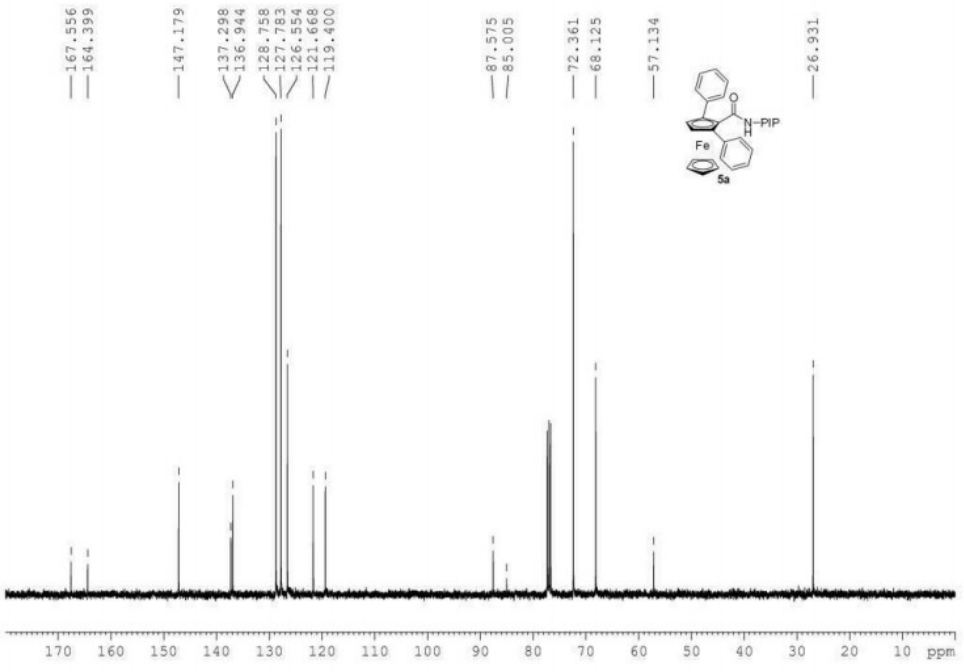

11.131
8.966
8.963
8.947
8.944
8.713
8.709
8.702
8.699
8.172
8.168
8.151
8.148
7.622
7.601
7.582
7.557
7.554
7.536
7.534
7.434
7.424
7.413
7.403
7.223
7.216
7.214
7.146
7.145
7.134
6.833
6.824
6.820
6.811
4.792
4.510
3n
ppm
1.000
1.008
1.008
1.020
2.095
1.087
2.000
2.056
2.027
2.031
4.998

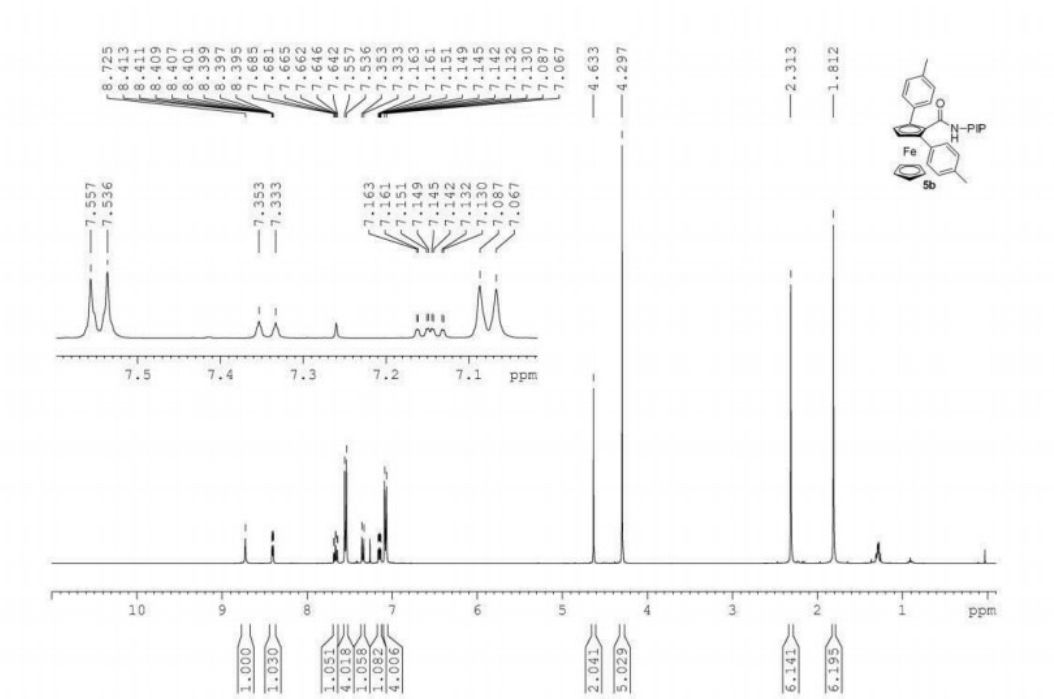

166.871
148.016
139.696
138.659
136.213
134.775
127.995
127.513
127.234
125.981
124.534
121.710
121.567
116.423
82.816
81.161
73.324
69.397
3n
ppm

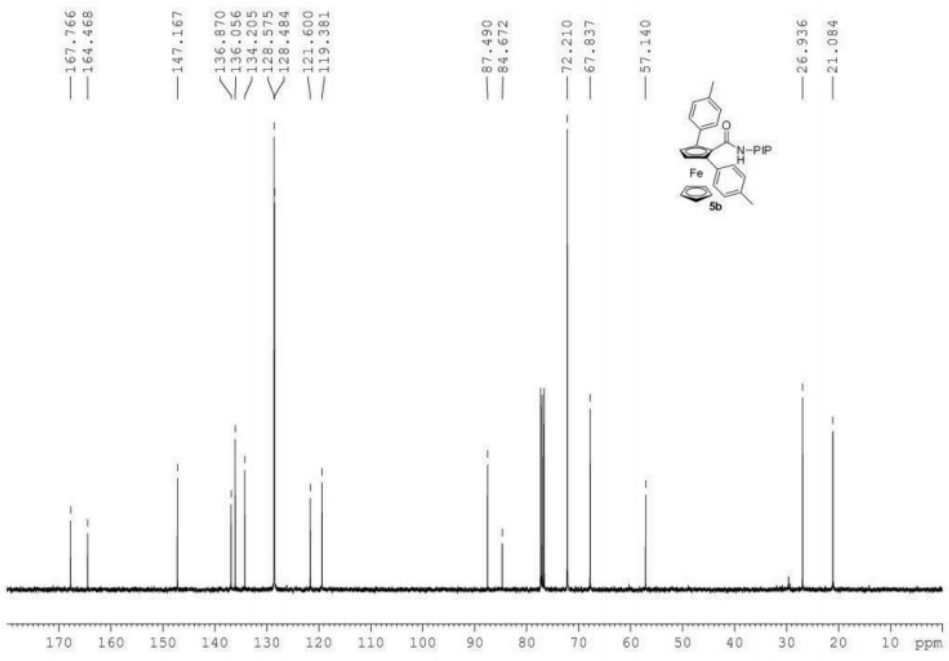

10.712
8.834
8.830
8.816
8.812
8.598
8.594
8.587
8.583
8.157
8.153
8.136
8.132
7.590
7.569
7.551
7.543
7.539
7.522
7.518
7.513
7.507
7.503
7.490
7.486
7.480
7.419
7.408
7.398
7.388
7.341
7.320
4.757
4.398
3o
ppm
1.000
1.014
1.006
1.010
6.005
1.037
4.004
2.015
4.928

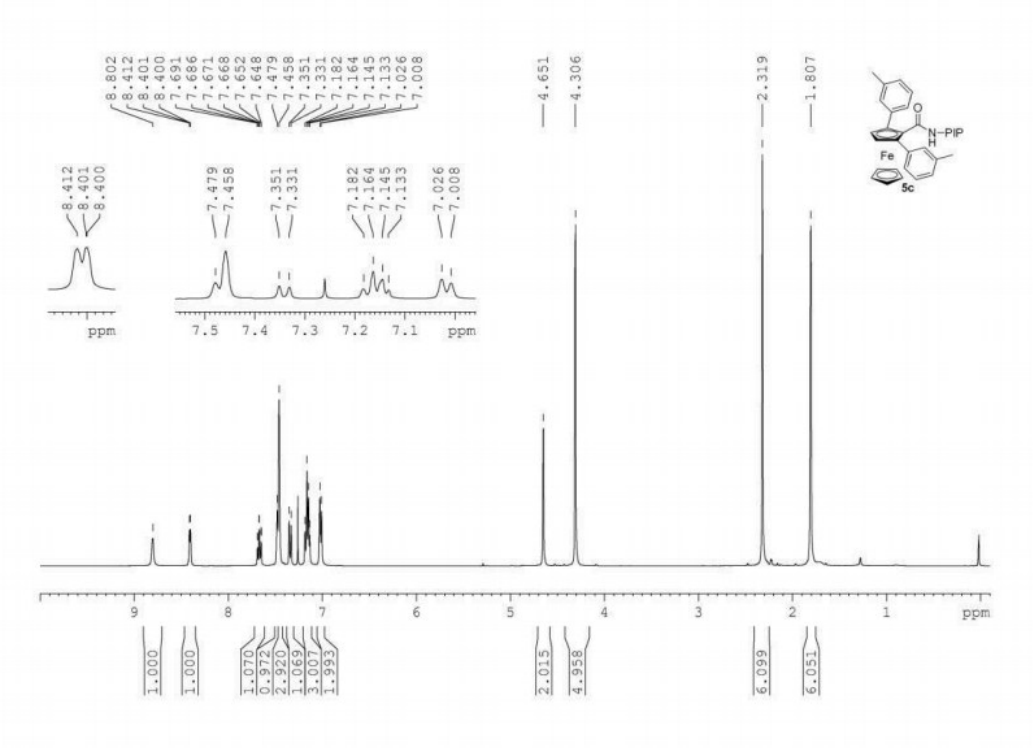

167.424
148.002
138.463
136.224
135.933
134.453
131.184
130.422
127.950
127.380
121.796
121.598
120.847
116.275
87.571
82.053
72.862
69.480
3o
ppm

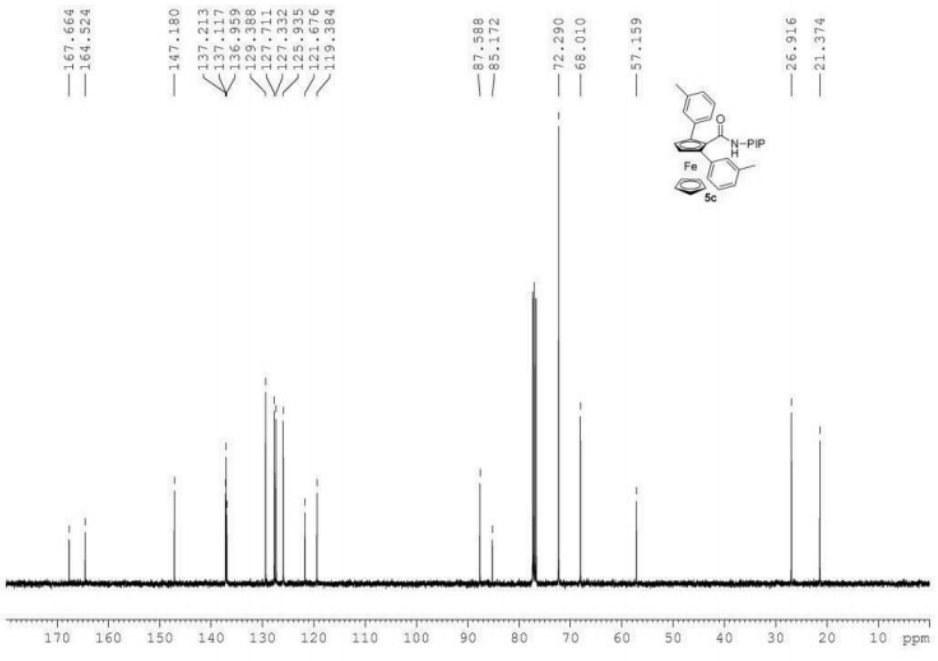

8.707
8.375
8.366
7.643
7.625
7.322
7.302
7.265
7.248
7.229
7.201
7.184
7.166
7.141
7.127
7.111
4.658
4.288
1.774
8.375
8.366
7.643
7.625
8.4
8.2
8.0
7.8
ppm
N-PIP
Fe
5a
9
8
7
6
5
4
3
2
1
ppm
1.000
0.991
4.913
8.303
2.007
4.953
6.036

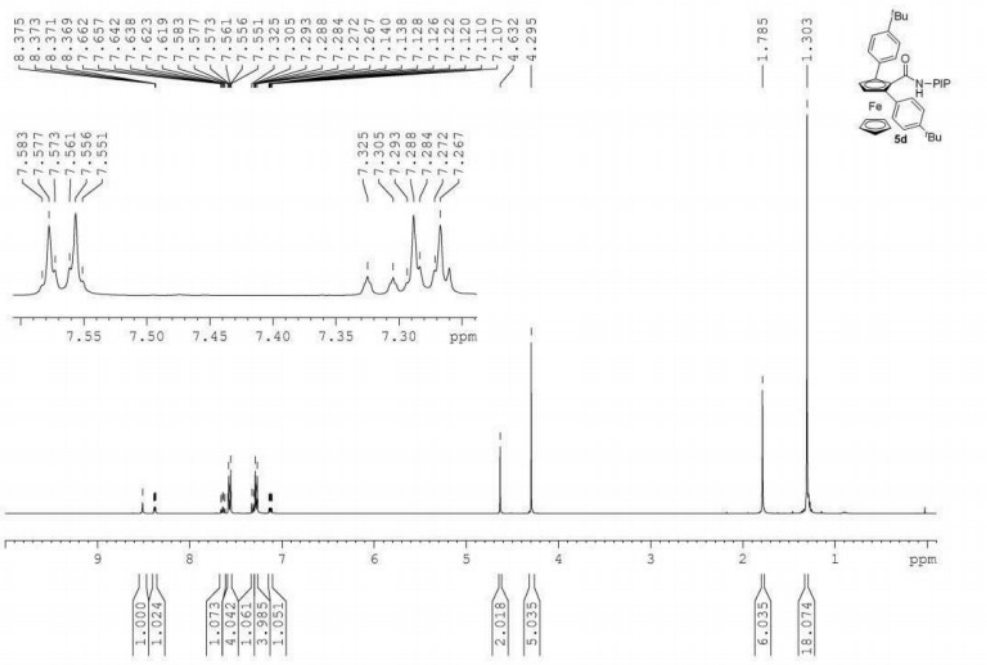

167.556
164.399
147.179
137.298
136.944
128.758
127.783
126.554
121.668
119.400
87.575
85.005
72.361
68.125
57.134
26.931
N-PIP
Fe
5a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

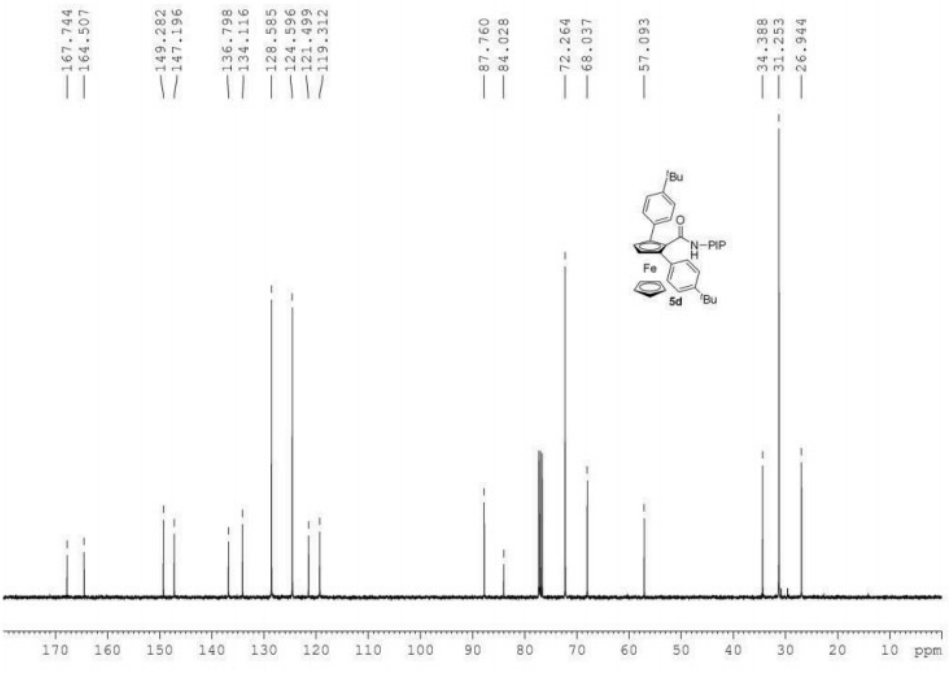

8.725
8.413
8.411
8.409
8.407
8.401
8.399
8.397
8.395
7.685
7.681
7.665
7.662
7.646
7.642
7.557
7.536
7.353
7.333
7.163
7.161
7.151
7.149
7.145
7.142
7.132
7.130
7.087
7.067
4.633
4.297
2.313
1.812
N–PIP
Fe
5b
ppm
1.000
1.030
1.051
4.018
1.038
1.082
4.006
2.041
5.029
6.141
6.195

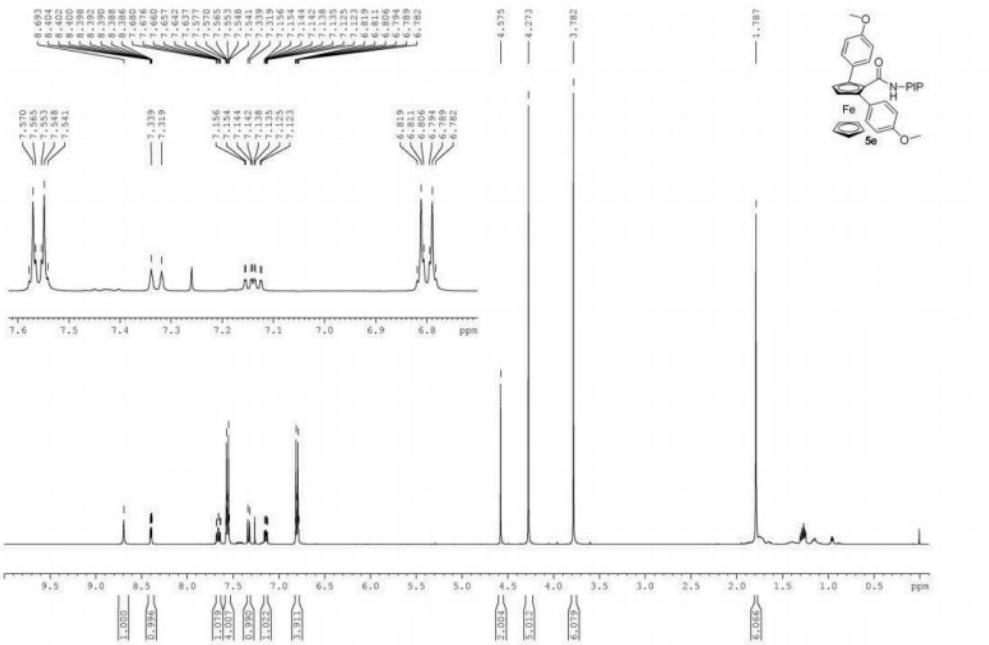

167.766
164.468
147.167
136.870
136.056
134.205
128.575
128.484
121.600
119.381
87.490
84.672
72.210
67.837
57.140
26.936
21.084
N–PIP
Fe
5b
ppm

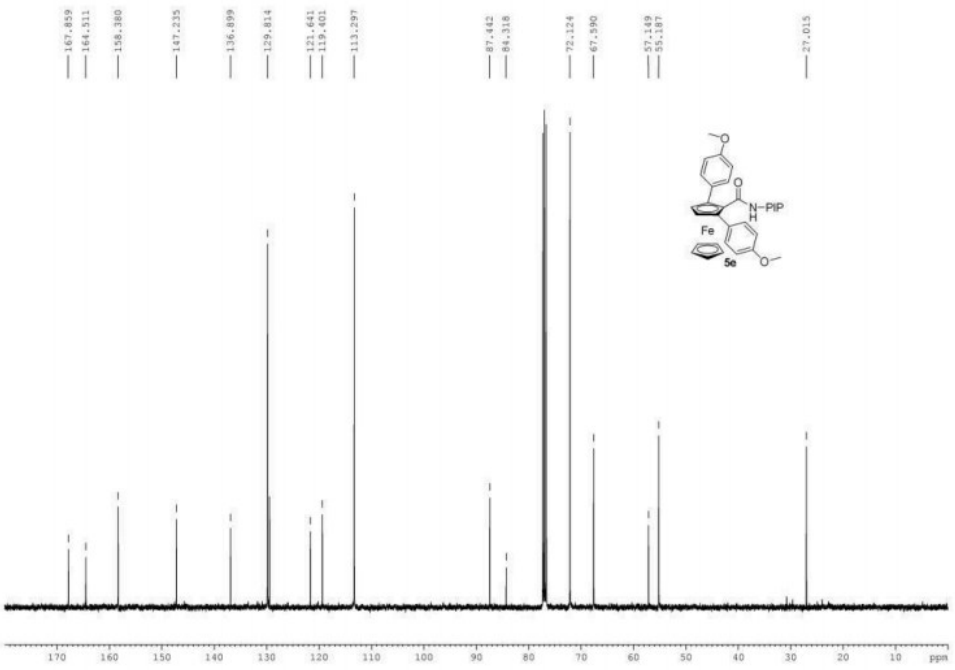

8.802
8.412
8.401
8.400
7.691
7.686
7.671
7.668
7.652
7.648
7.479
7.458
7.351
7.331
7.182
7.164
7.145
7.133
7.026
7.008
4.651
4.306
2.319
1.807
N–PIP
Fe
5c
ppm
1.000
1.000
1.070
0.972
2.920
1.069
3.007
1.993
2.015
4.958
6.099
6.051

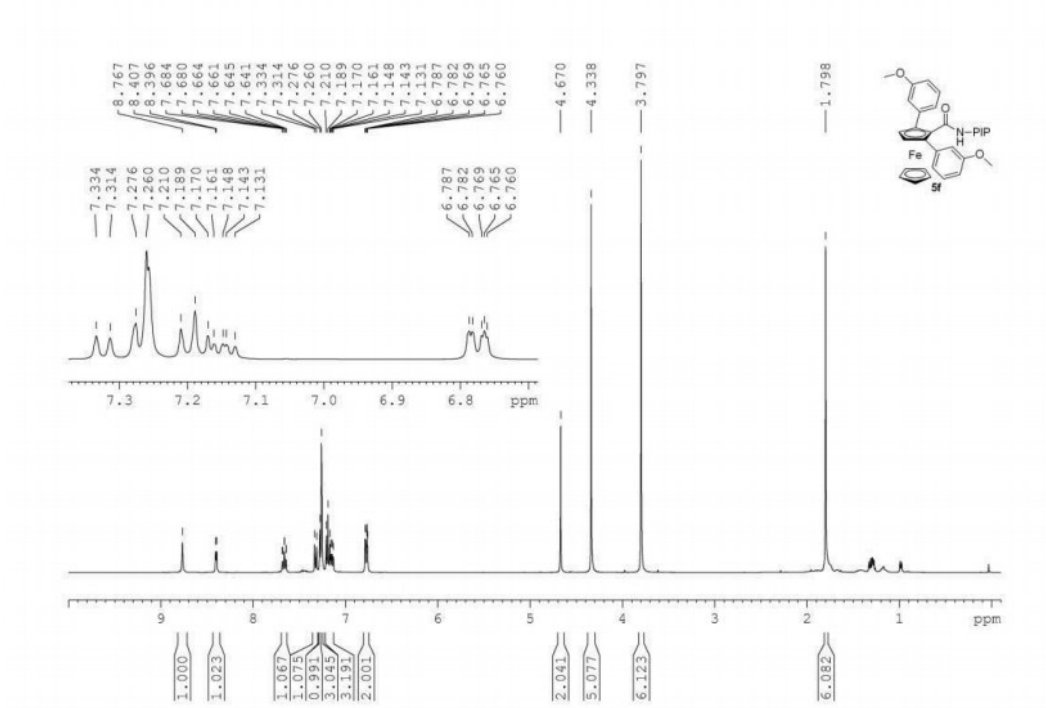

167.664
164.524
147.180
137.213
137.117
136.959
129.388
127.711
127.332
125.935
121.676
119.384
87.588
85.172
72.290
68.010
57.159
26.916
21.374
N–PIP
Fe
5c
ppm

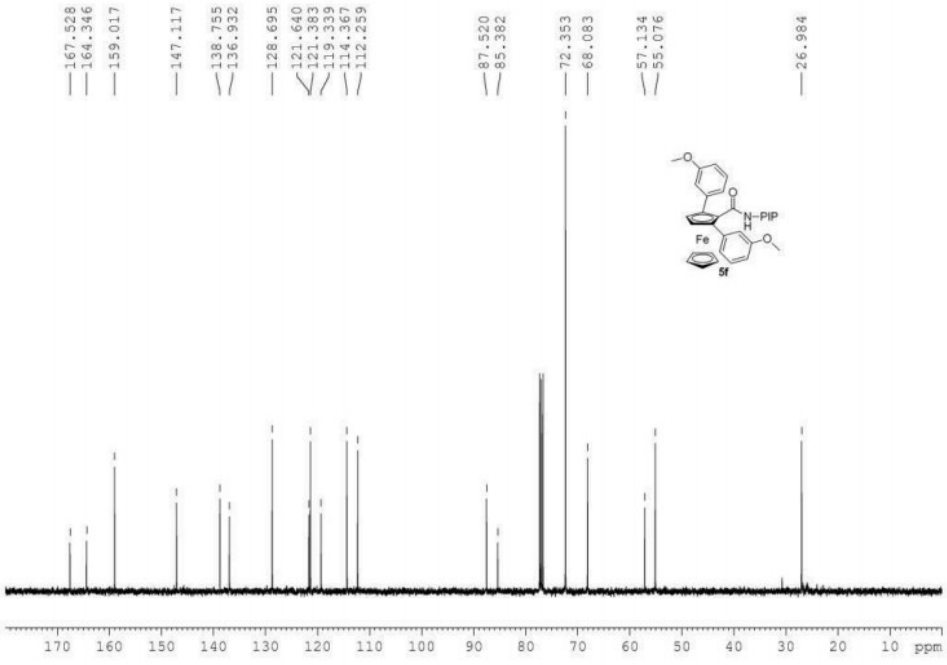

8.375
8.373
8.371
8.369
7.662
7.657
7.642
7.638
7.623
7.619
7.583
7.577
7.573
7.561
7.556
7.551
7.325
7.305
7.293
7.288
7.284
7.272
7.267
7.140
7.138
7.128
7.126
7.122
7.120
7.110
7.107
4.632
4.295
1.785
1.303
7.583
7.577
7.573
7.561
7.556
7.551
7.325
7.305
7.293
7.288
7.284
7.272
7.267
7.55 7.50 7.45 7.40 7.35 7.30 ppm
9 8 7 6 5 4 3 2 1 ppm
1.000
1.024
1.073
4.042
1.061
3.985
1.051
2.018
5.035
6.035
18.074
tBu
N–PIP
H
Fe
5d
tBu

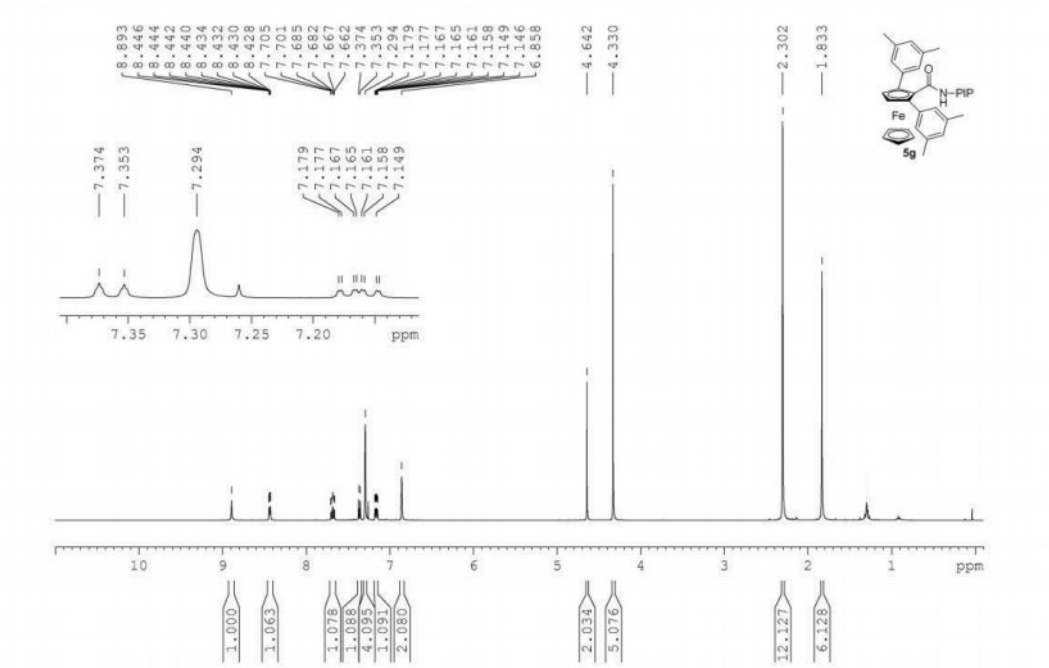

167.744
164.507
149.282
147.196
136.798
134.116
128.585
124.596
121.499
119.312
87.760
84.028
72.264
68.037
57.093
34.388
31.253
26.944
tBu
N–PIP
H
Fe
5d
tBu
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

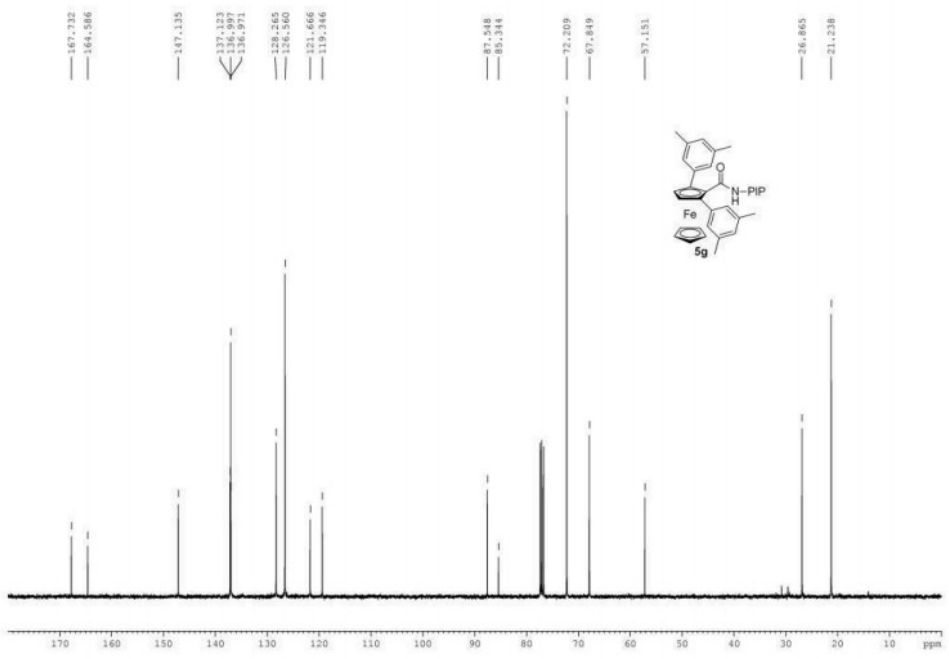

8.693
8.404
8.402
8.400
8.398
8.392
8.390
8.388
8.386
7.680
7.676
7.660
7.657
7.642
7.637
7.577
7.570
7.565
7.553
7.541
7.339
7.319
7.156
7.154
7.144
7.142
7.138
7.135
7.125
7.123
6.819
6.811
6.806
6.794
6.789
6.782
4.575
4.273
3.782
1.787
N–PIP
H
Fe
5e
1.000
0.996
1.019
1.007
0.980
1.002
3.911
2.004
3.012
6.079
6.066
ppm

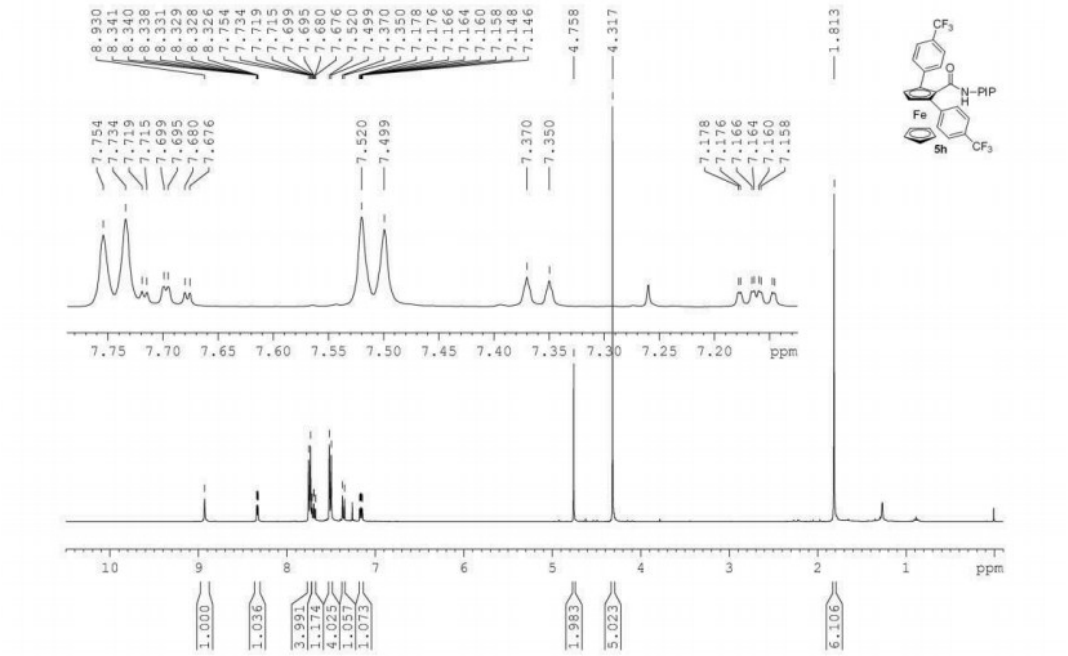

167.859
164.511
158.380
147.235
136.899
129.814
121.641
119.401
113.297
87.442
84.318
72.124
67.590
57.149
55.187
27.015
N–PIP
H
Fe
5e
ppm

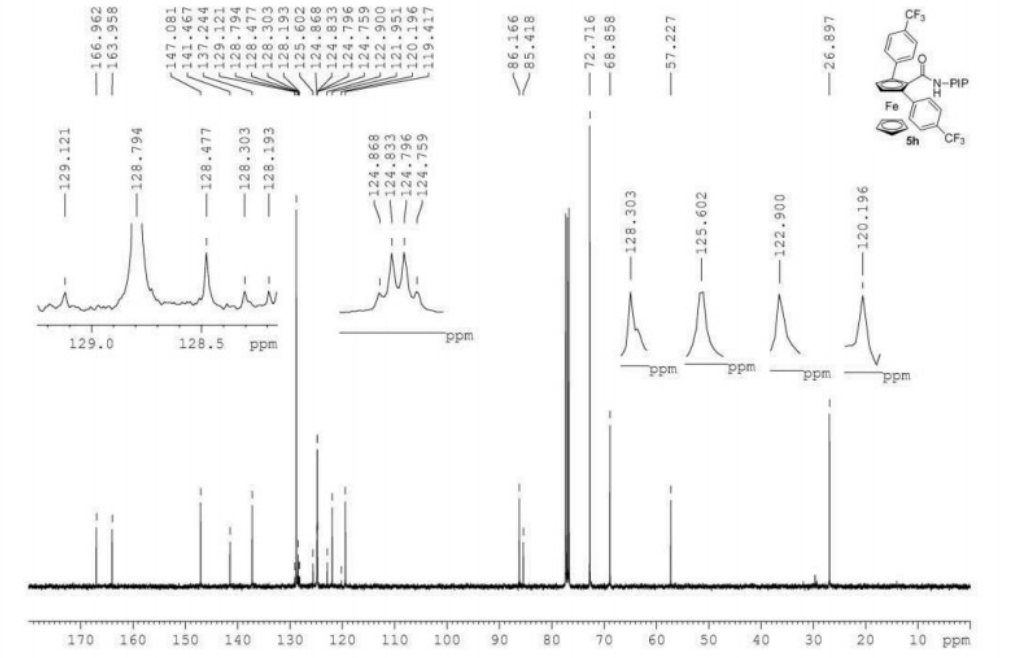

8.767
8.407
8.396
7.684
7.680
7.664
7.661
7.645
7.641
7.334
7.314
7.276
7.260
7.210
7.189
7.170
7.161
7.148
7.143
7.131
6.787
6.782
6.769
6.765
6.760
4.670
4.338
3.797
1.798
N–PIP
H
Fe
5f
ppm
1.000
1.023
1.067
1.075
0.991
3.045
3.191
2.001
2.041
5.077
6.123
6.082

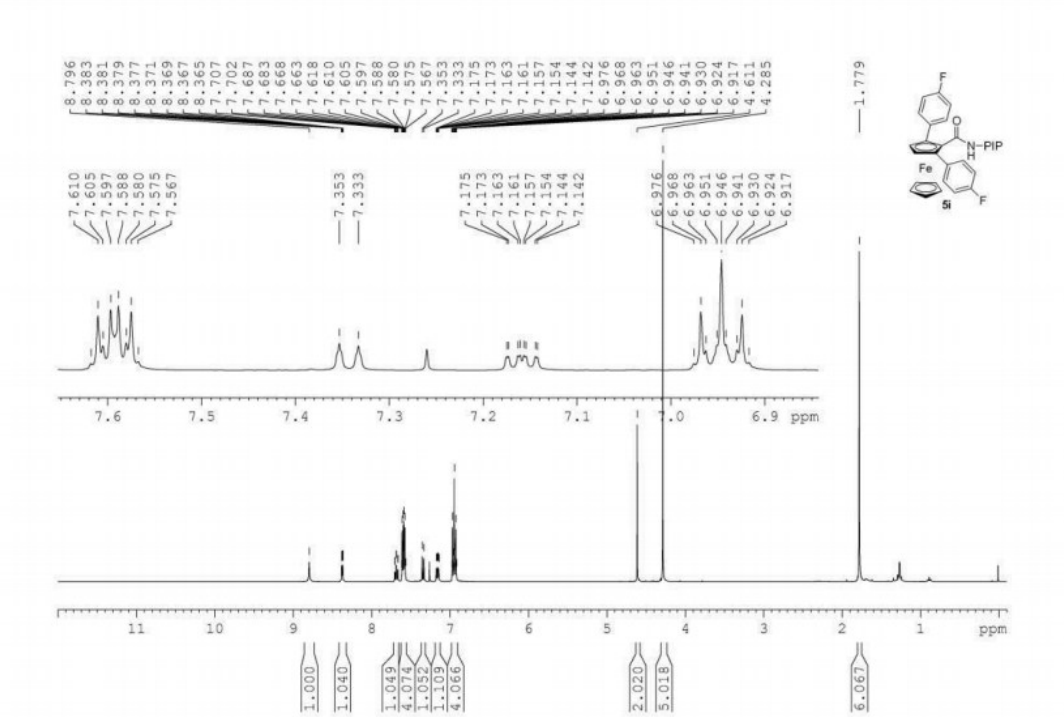

167.528
164.346
159.017
147.117
138.755
136.932
128.695
121.640
121.383
119.339
114.367
112.259
87.520
85.382
72.353
68.083
57.134
55.076
26.984
N–PIP
H
Fe
5f
ppm

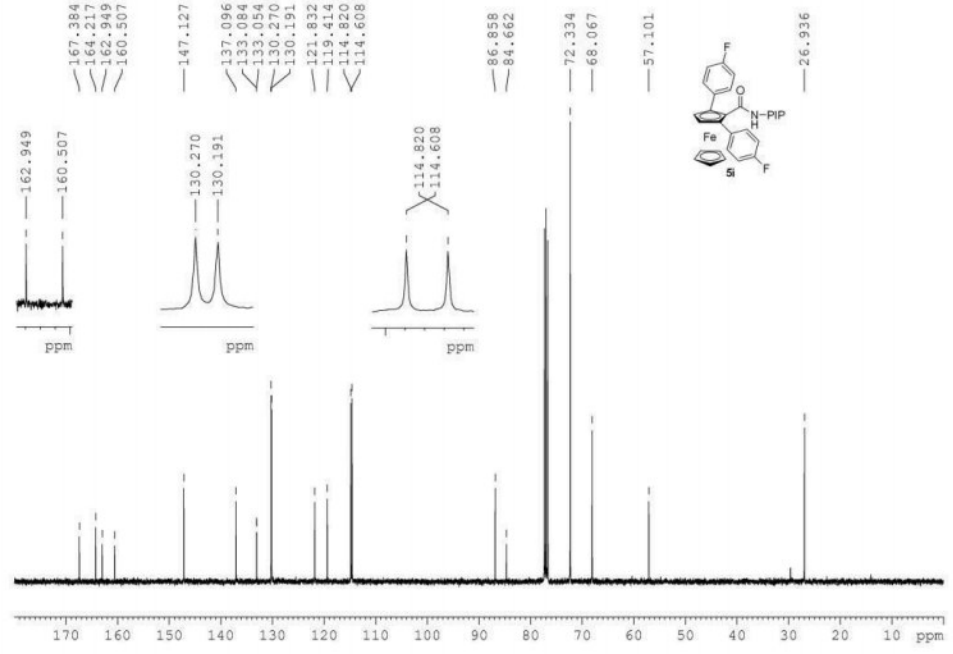

8.893
8.446
8.444
8.442
8.440
8.434
8.432
8.430
8.428
7.705
7.701
7.685
7.682
7.667
7.662
7.374
7.353
7.294
7.179
7.177
7.167
7.165
7.161
7.158
7.149
7.146
6.858
4.642
4.330
2.302
1.833
PIP
Fe
5g
7.35
7.30
7.25
7.20
ppm
10
9
8
7
6
5
4
3
2
1
1.000
1.063
1.078
1.088
4.095
1.091
2.080
2.034
5.076
12.127
6.128

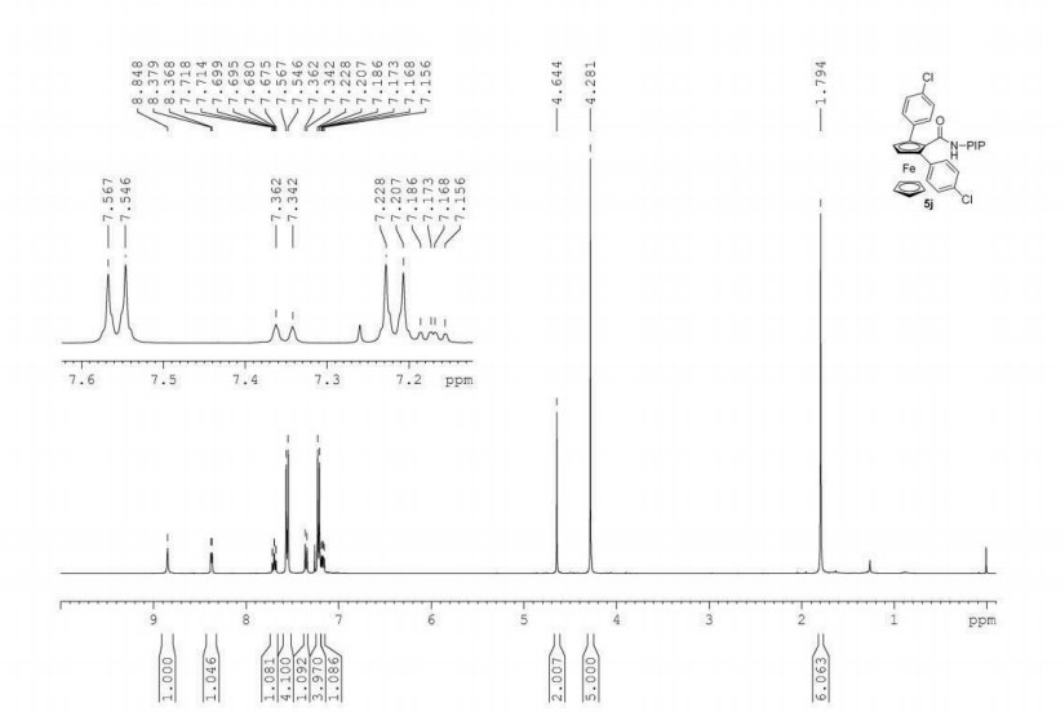

167.732
164.586
147.135
137.123
136.997
136.971
128.265
126.560
121.666
119.346
87.548
85.344
72.809
67.849
57.151
26.865
21.238
PIP
Fe
5g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

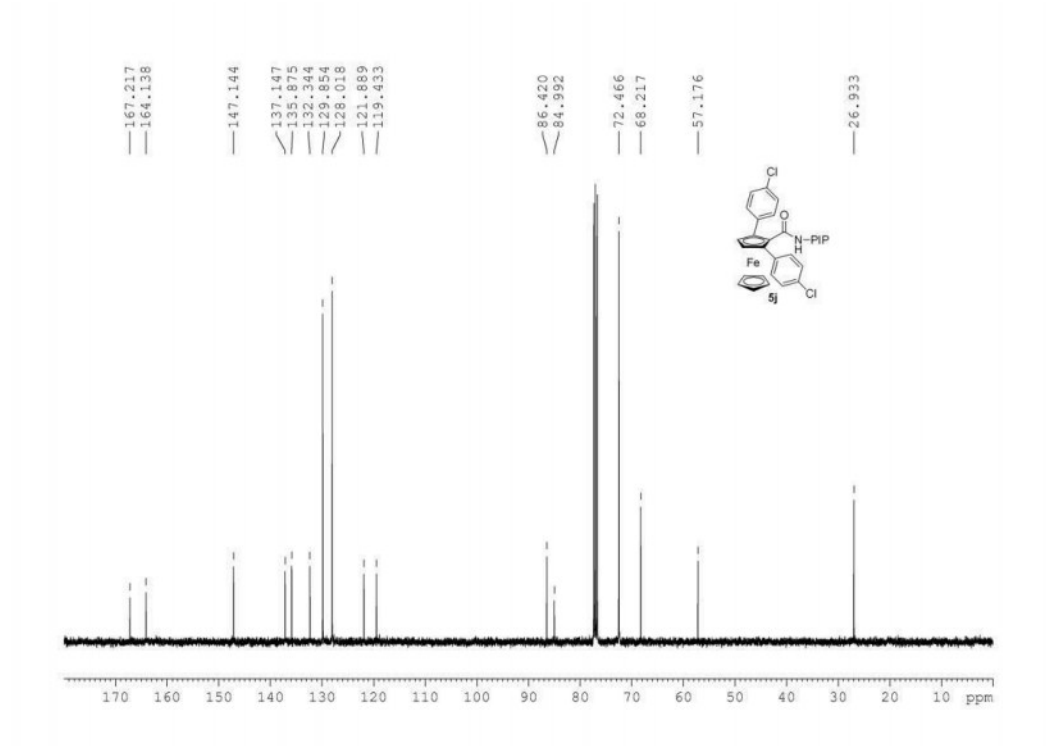

8.930
8.341
8.340
8.338
8.331
8.329
8.328
8.326
7.754
7.734
7.719
7.715
7.699
7.695
7.680
7.676
7.520
7.499
7.370
7.350
7.178
7.176
7.166
7.164
7.160
7.158
4.758
4.317
1.813
CF3
N-PIP
Fe
5h
CF3
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 ppm
10 9 8 7 6 5 4 3 2 1 ppm
1.000
1.036
3.991
1.174
4.025
1.057
1.073
1.983
5.023
6.106

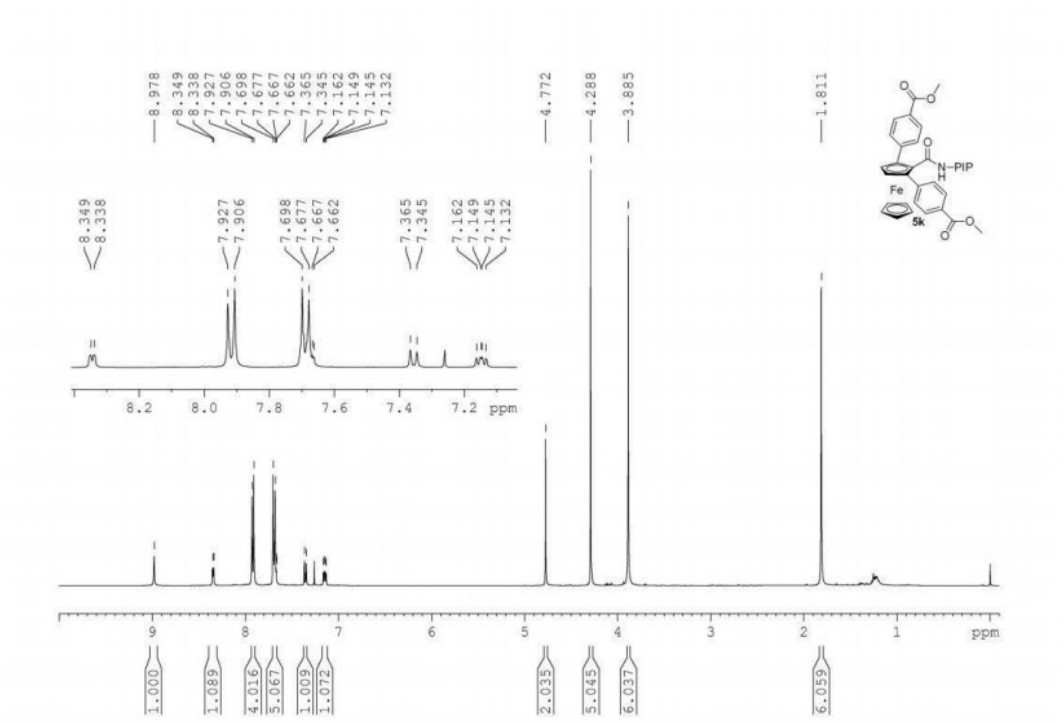

166.962
163.958
147.081
141.467
137.244
129.121
128.794
128.477
128.303
128.193
125.602
124.868
124.833
124.796
124.759
122.900
121.951
120.196
119.417
86.166
85.418
72.716
68.858
57.227
26.897
CF3
N-PIP
Fe
5h
CF3
129.121
128.794
128.477
128.303
128.193
129.0 128.5 ppm
124.868
124.833
124.796
124.759
ppm
128.303
125.602
122.900
120.196
ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

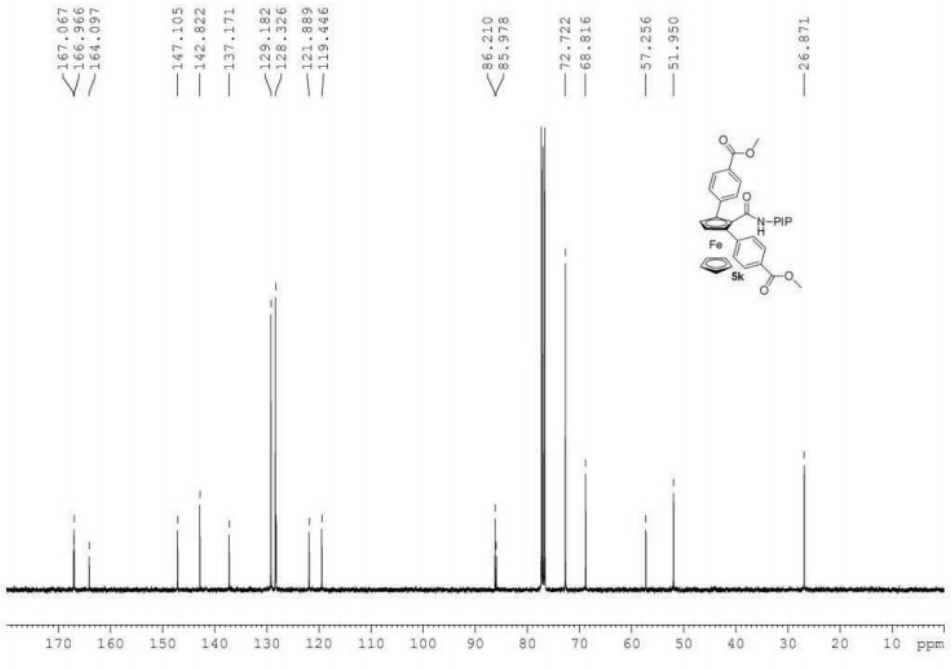

8.796
8.383
8.381
8.379
8.377
8.371
8.369
8.367
8.365
7.707
7.702
7.687
7.683
7.668
7.663
7.618
7.610
7.605
7.597
7.588
7.580
7.575
7.567
7.353
7.333
7.175
7.173
7.163
7.161
7.157
7.154
7.144
7.142
6.976
6.968
6.963
6.951
6.946
6.941
6.930
6.924
6.917
4.611
4.285
1.779
N-PIP
Fe
Si
F
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9 ppm
11
10
9
8
7
6
5
4
3
2
1
ppm
1.000
1.040
1.049
4.074
1.052
1.109
4.066
2.020
5.018
6.067

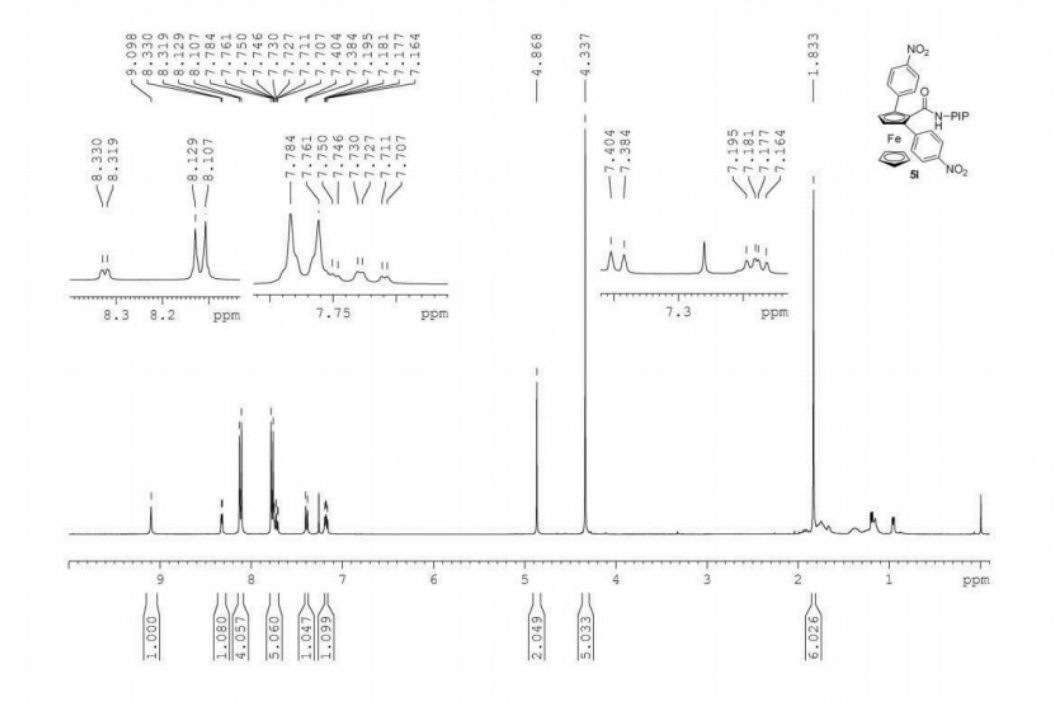

167.384
164.217
162.949
160.507
147.127
137.096
133.084
133.054
130.270
130.191
121.832
119.414
114.820
114.608
86.858
84.662
72.334
68.067
57.101
26.936
N-PIP
Fe
Si
F
162.949
160.507
130.270
130.191
114.820
114.608
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

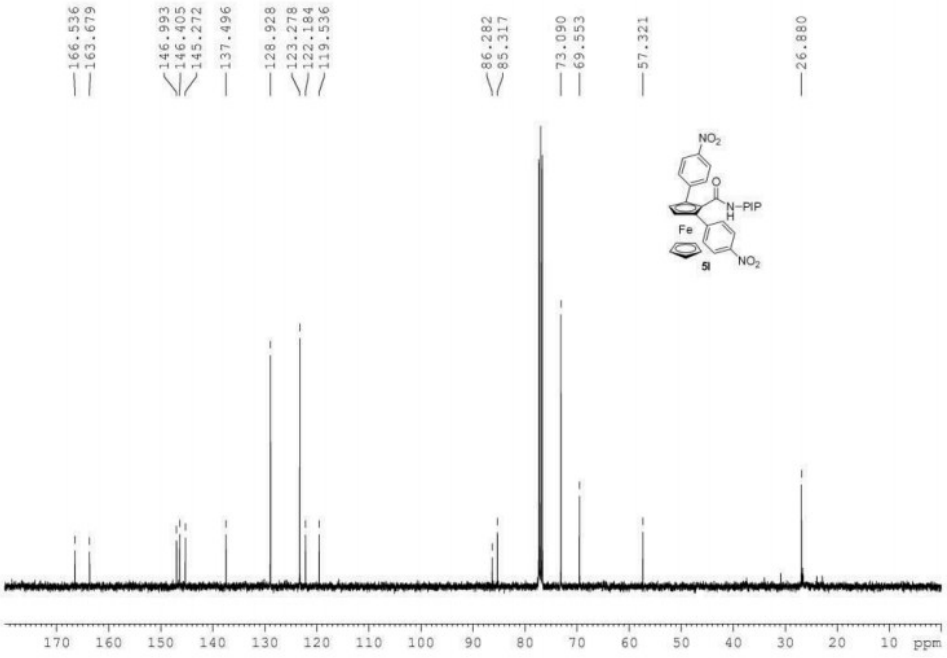

8.848
8.379
8.368
7.718
7.714
7.699
7.695
7.680
7.675
7.567
7.546
7.362
7.342
7.228
7.207
7.186
7.173
7.168
7.156
4.644
4.281
1.794
N-PIP
Fe
5j
Cl
ppm
1.000
1.046
1.081
4.100
1.092
3.970
1.086
2.007
5.000
6.063

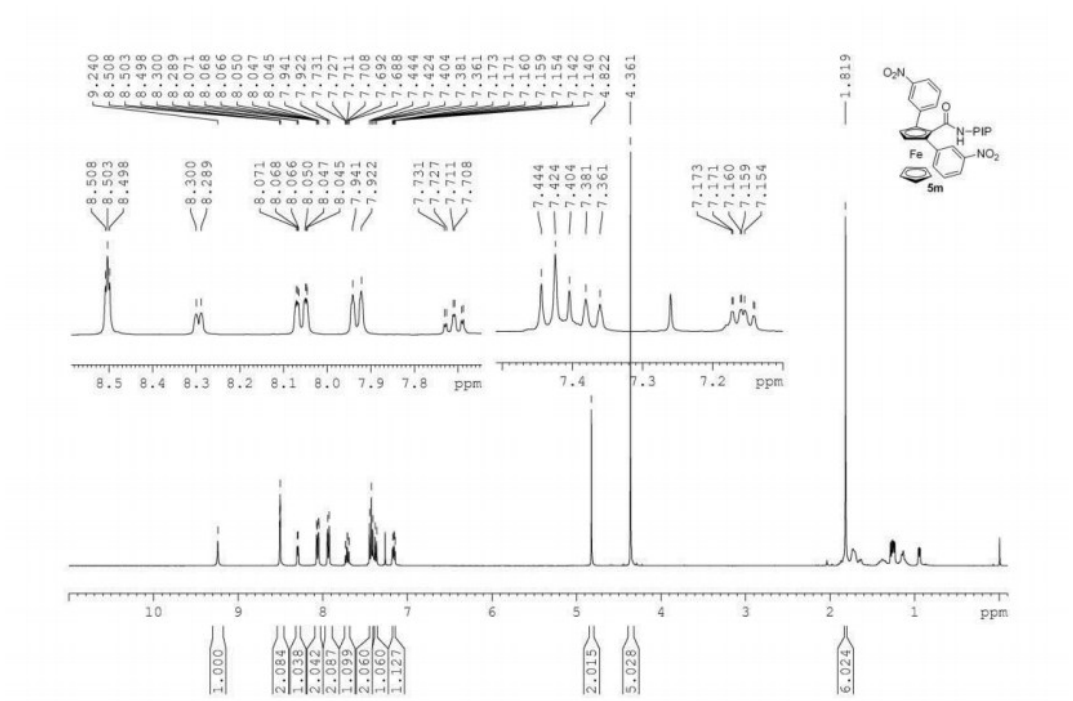

167.217
164.138
147.144
137.147
135.875
132.344
129.854
128.018
121.889
119.433
86.420
84.992
72.466
68.217
57.176
26.933
N-PIP
Fe
5j
Cl
ppm

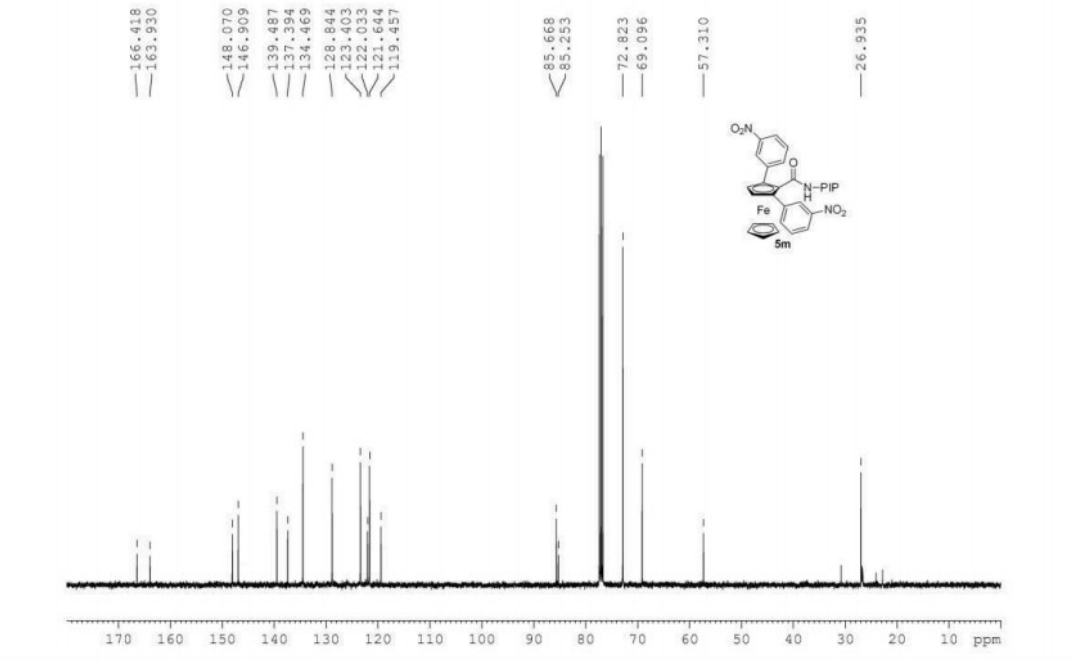

8.978
8.349
8.338
7.927
7.906
7.698
7.677
7.667
7.662
7.365
7.345
7.162
7.149
7.145
7.132
4.772
4.288
3.885
1.811
N-PIP
Fe
5k
8.2
8.0
7.8
7.6
7.4
7.2 ppm
9
8
7
6
5
4
3
2
1
ppm
1.000
1.089
4.016
5.067
1.009
1.072
2.035
5.045
6.037
6.059

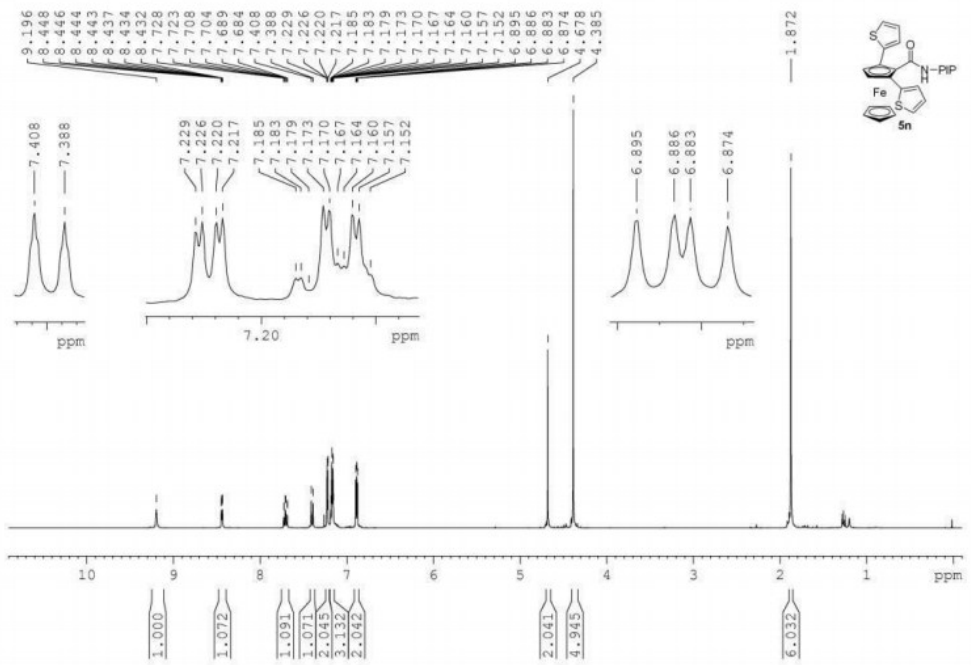

167.067
166.966
164.097
147.105
142.822
137.171
129.182
128.326
121.889
119.446
86.210
85.978
72.722
68.816
57.256
51.950
26.871
N-PIP
Fe
5k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

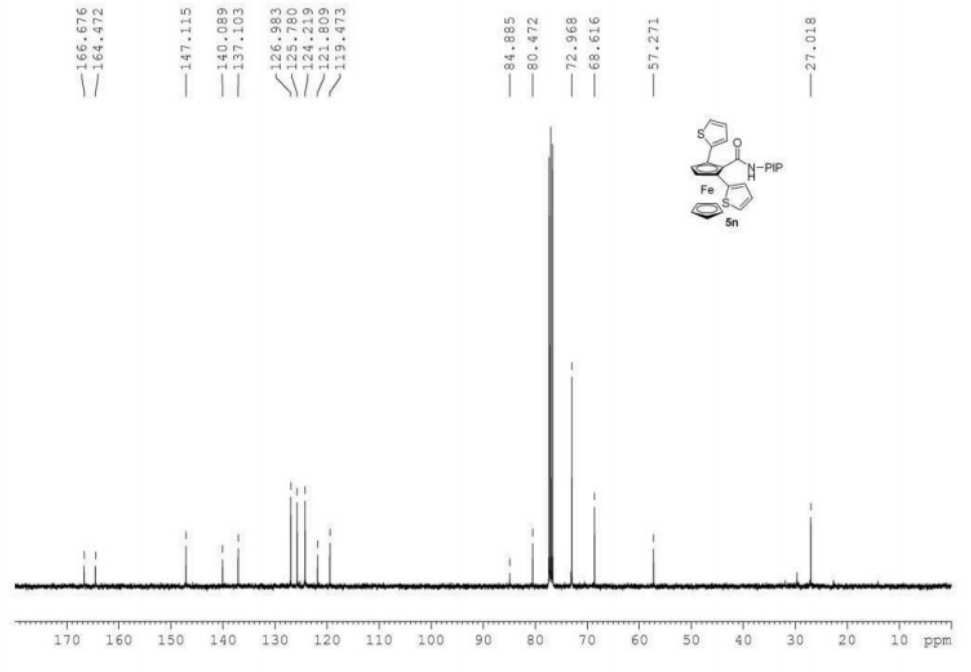

9.098
8.330
8.319
8.129
8.107
7.784
7.761
7.750
7.746
7.730
7.727
7.711
7.707
7.404
7.384
7.195
7.181
7.177
7.164
4.868
4.337
1.833
NO2
N-PIP
H
Fe
Si
NO2
8.3
8.2
ppm
7.75
ppm
7.3
ppm
9
8
7
6
5
4
3
2
1
ppm
1.000
1.080
4.057
5.060
1.047
1.099
2.049
5.033
6.026

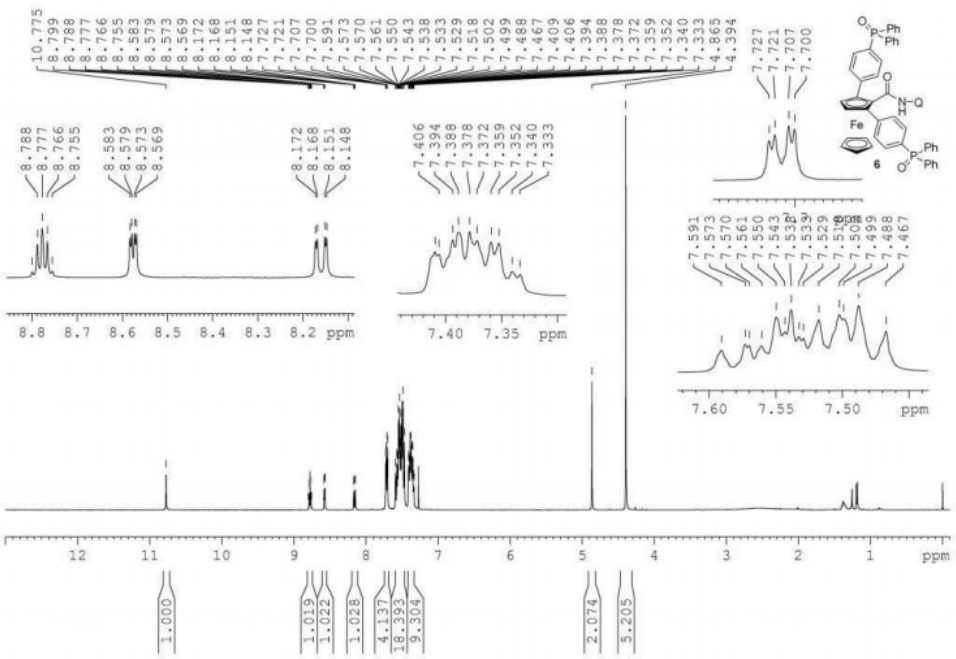

166.536
163.679
146.993
146.405
145.272
137.496
128.928
123.278
122.184
119.536
86.282
85.317
73.090
69.553
57.321
26.880
NO2
N-PIP
H
Fe
Si
NO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

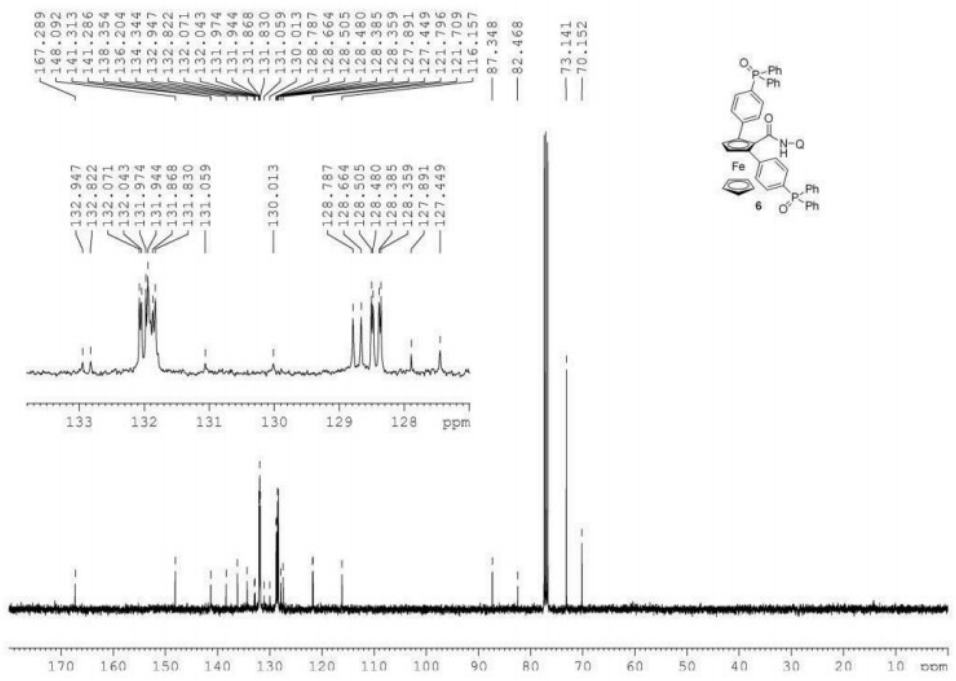

9.240
8.508
8.503
8.498
8.300
8.289
8.071
8.068
8.066
8.050
8.047
8.045
7.941
7.922
7.731
7.727
7.711
7.708
7.692
7.688
7.444
7.424
7.404
7.381
7.361
7.173
7.171
7.160
7.159
7.154
7.142
7.140
4.822
4.361
1.819
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 ppm
7.4 7.3 7.2 ppm
10 9 8 7 6 5 4 3 2 1 ppm
1.000
2.084
1.038
2.042
2.087
1.099
2.060
1.060
1.127
2.015
5.028
6.024
O2N
N–PIP
H
Fe
NO2
5m

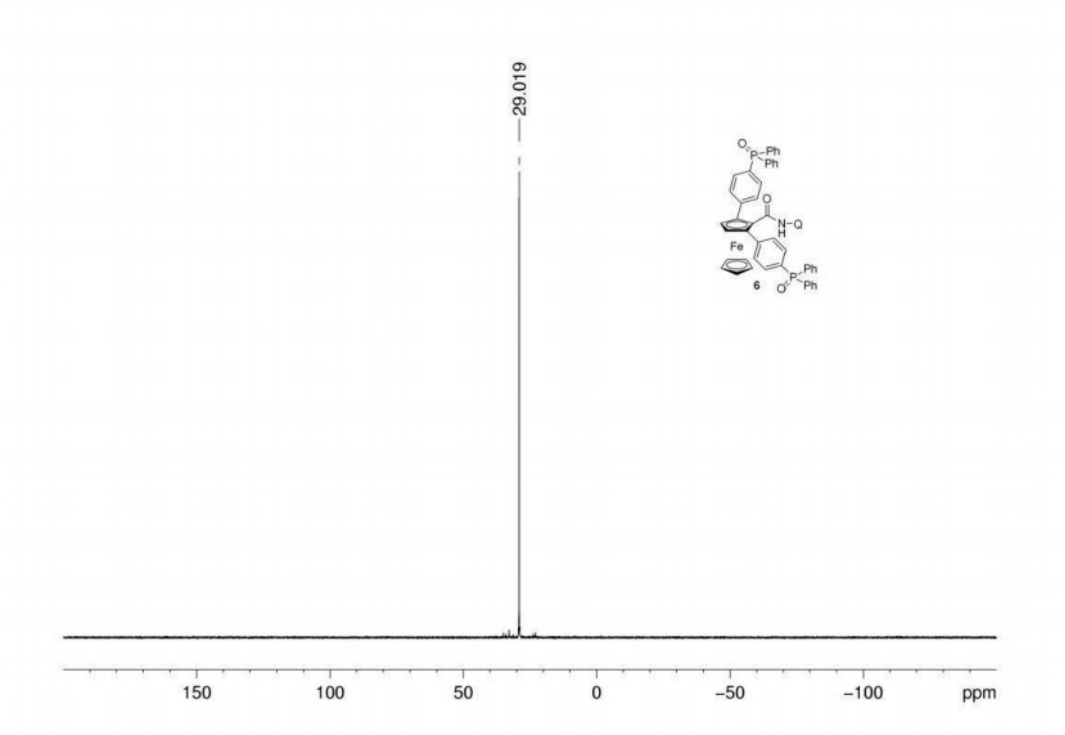

166.418
163.930
148.070
146.909
139.487
137.394
134.469
128.844
123.403
122.033
121.644
119.457
85.668
85.253
72.823
69.096
57.310
26.935
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
O2N
N–PIP
H
Fe
NO2
5m


9.196
8.448
8.446
8.444
8.443
8.437
8.434
8.432
7.728
7.723
7.708
7.704
7.689
7.684
7.408
7.388
7.229
7.226
7.220
7.217
7.185
7.183
7.179
7.173
7.170
7.167
7.164
7.160
7.157
7.152
6.895
6.886
6.883
6.874
4.678
4.385
1.872
Fe
5n
ppm
7.20
ppm
ppm
10
9
8
7
6
5
4
3
2
1
ppm
1.000
1.072
1.091
1.071
2.045
3.132
2.042
2.041
4.945
6.032


166.676
164.472
147.115
140.089
137.103
126.983
125.780
124.219
121.809
119.473
84.885
80.472
72.968
68.616
57.271
27.018
Fe
5n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm






29.019
Ph
Ph
O
P
N
H
Q
Fe
6
Ph
Ph
O
P
150
100
50
0
−50
−100
ppm