Supporting Information

Development of Metal-Free, Trifluoromethanesulfonic Acid-Immobilized Nitrogen-Doped Carbon Catalysts for Povarov Reactions

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[#] Equally contributed

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1. Elemental analysis of NCI-Nb-TfOH and NC-TfOH:

Table S1. Elemental analysis

catalyst	C%	H%	N%	S%	F%
NCI-Nb-TfOH	87.04	0.76	1.82	1.17	1.83
NC-TfOH	91.01	0.74	1.12	1.84	2.14

2. Comparison with reported examples

Table S2. Comparison with reported examples of heterogeneous catalysts

The reaction with aniline, benzaldehyde and dihydrofuran

catalyst	cat. loading	scale	conditions	yield (cis/trans)	ref.
NC-TfOH	~1 mol%	0.5 mmol	rt, 0.5 h, toluene	93 (24:1)	This work
Fe^{3+}-K-10 clay	100 mg	1.0 mmol	rt, 3.5 h, MeCN	84 (18:82)	9b
AG®50W-X2	30 mg	0.5 mmol	80 ˚C, 2 h, H_2O	77 (47:53)	9c[a,b]
$SbCl_3$-HAP	1.6 mol%	10 mmol	reflux, 2.5 h, MeCN	85 (0:100)	9d[a]
PANI-$InCl_3$	10 mol%	0.5 mmol	rt, 16 h, H_2O	95 (45:55)	9e
$HClO_4$-SiO_2	5 mol%	5 mmol	rt, 20 min, MeCN	83 (16:84)	9f
TPA/MCM-41	0.5 mol%	1 mmol	rt, 2.15 h, MeCN	88 (42:58)	9g[a]
PANI-PTSA	25 wt%	1 mmol	rt, 20 min, THF	78 (100:0)	9h
Zr_6OTf-BTB	1 mol%	0.5 mmol	rt, 24 h, MeCN	85 (13:1)	10

[a] Dihydropyran was used instead of dihydrofuran. [b] Aldehyde was not used.

3. FTIR spectroscopy

3-1. FTIR of NC-TfOH

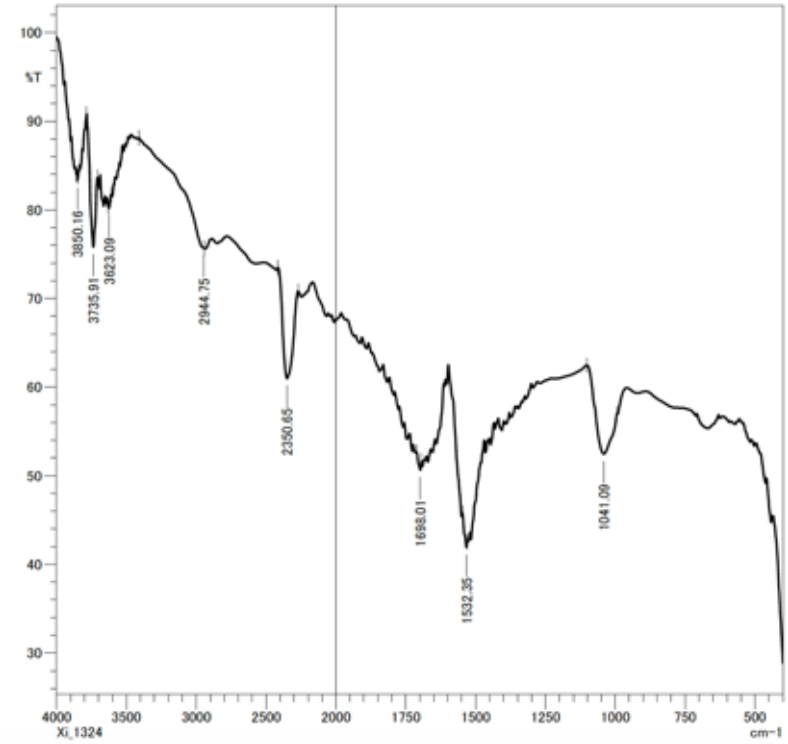


Figure S1. FTIR of NC-TfOH

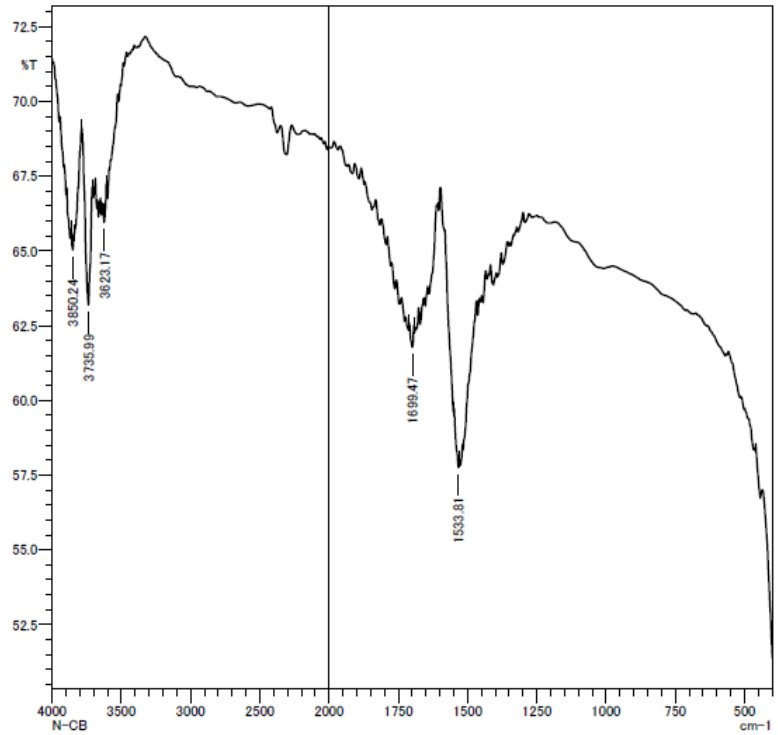


Figure S2. FTIR of N-doped carbon

3-2. FTIR of pyridine absorption on NC-TfOH

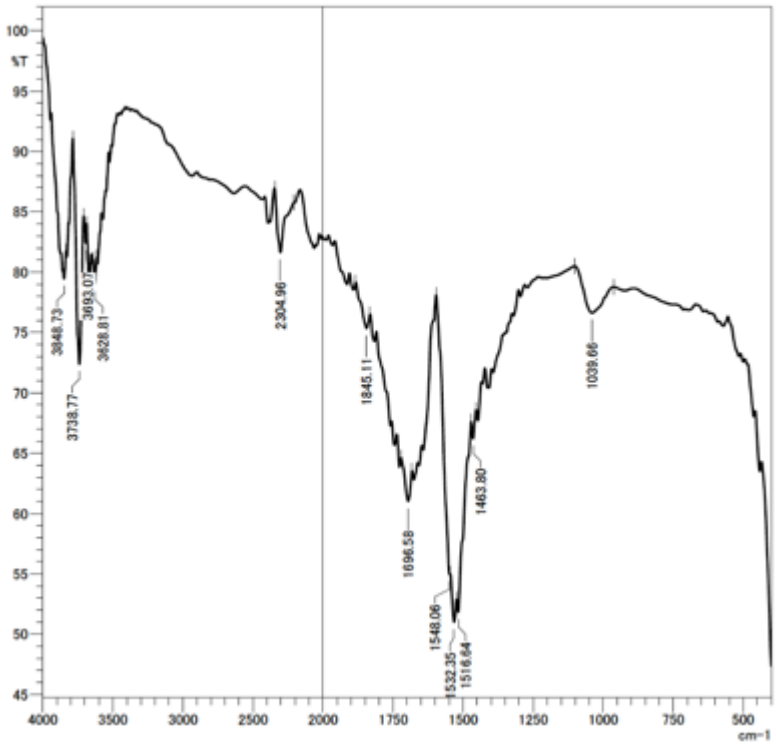


Figure S3. FTIR of pyridine absorption on NC-TfOH

4. STEM and EDS analysis

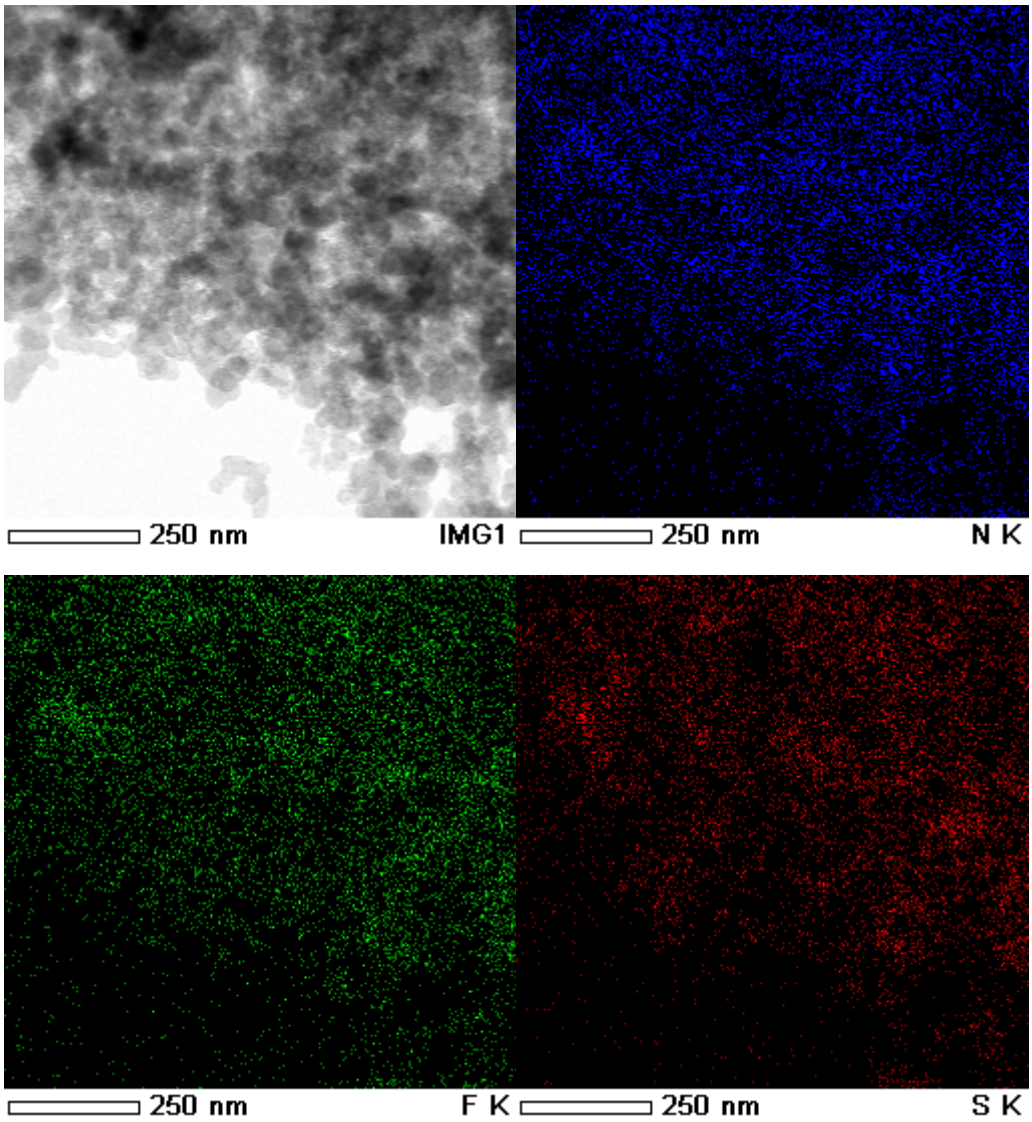
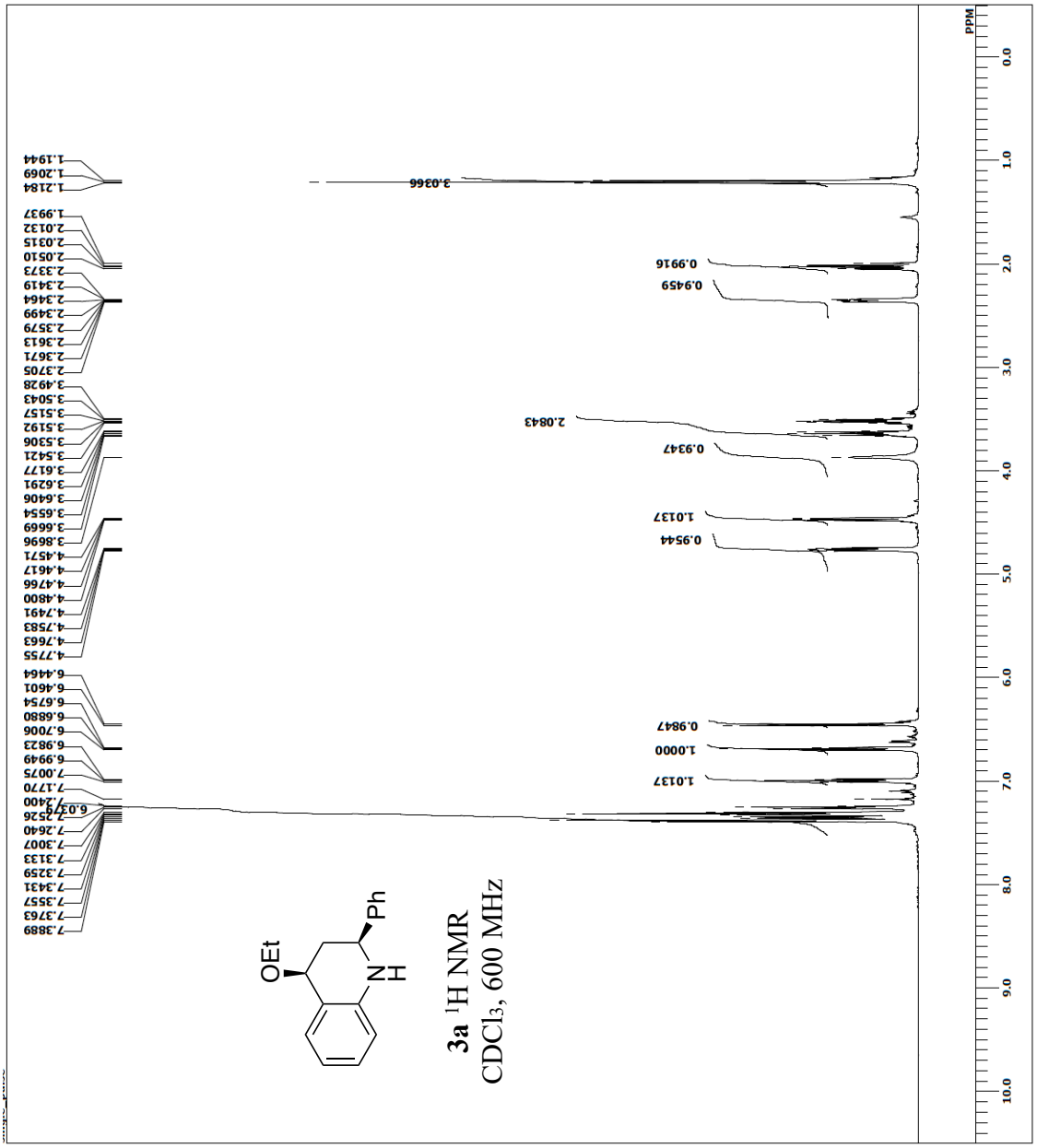
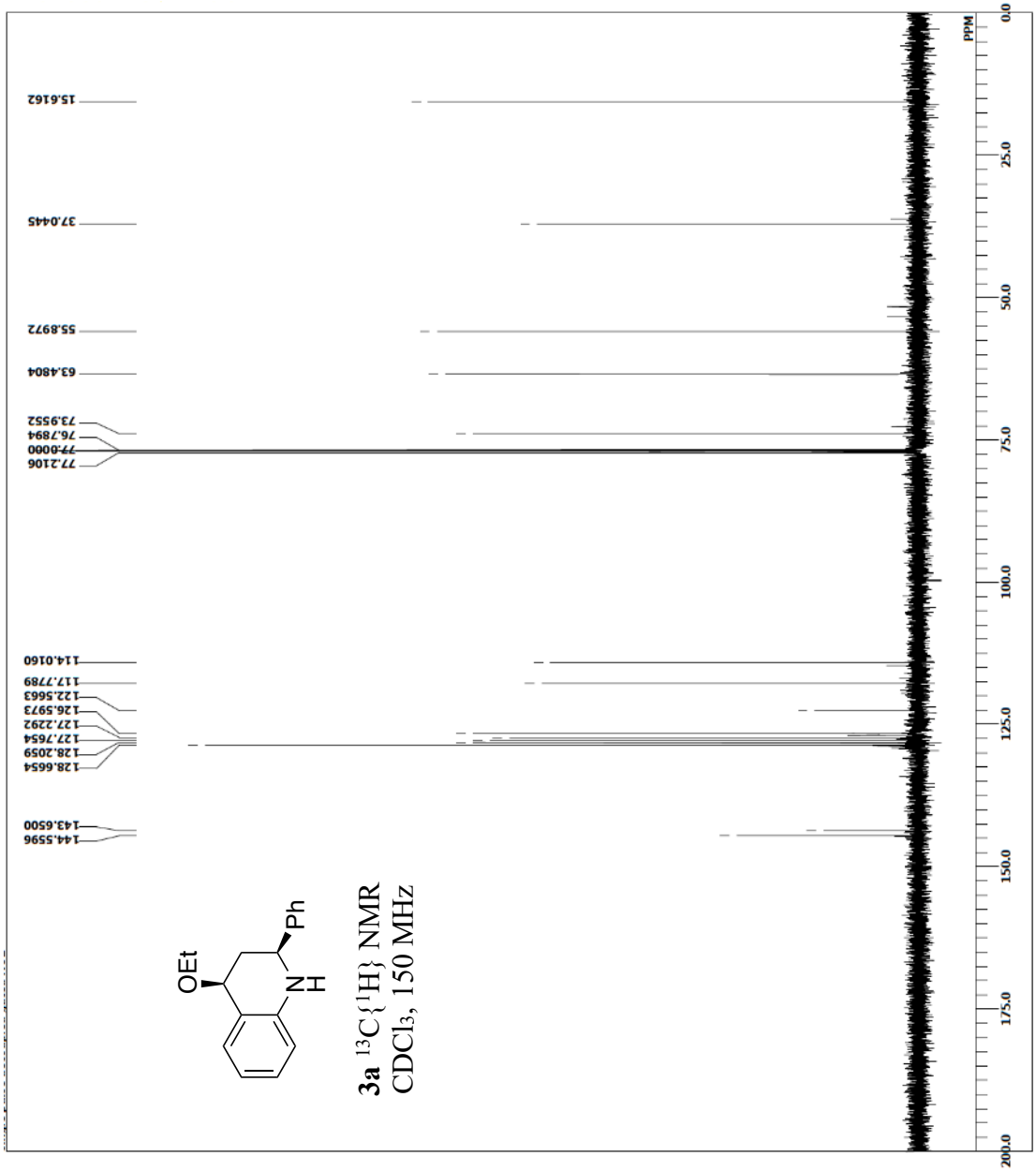


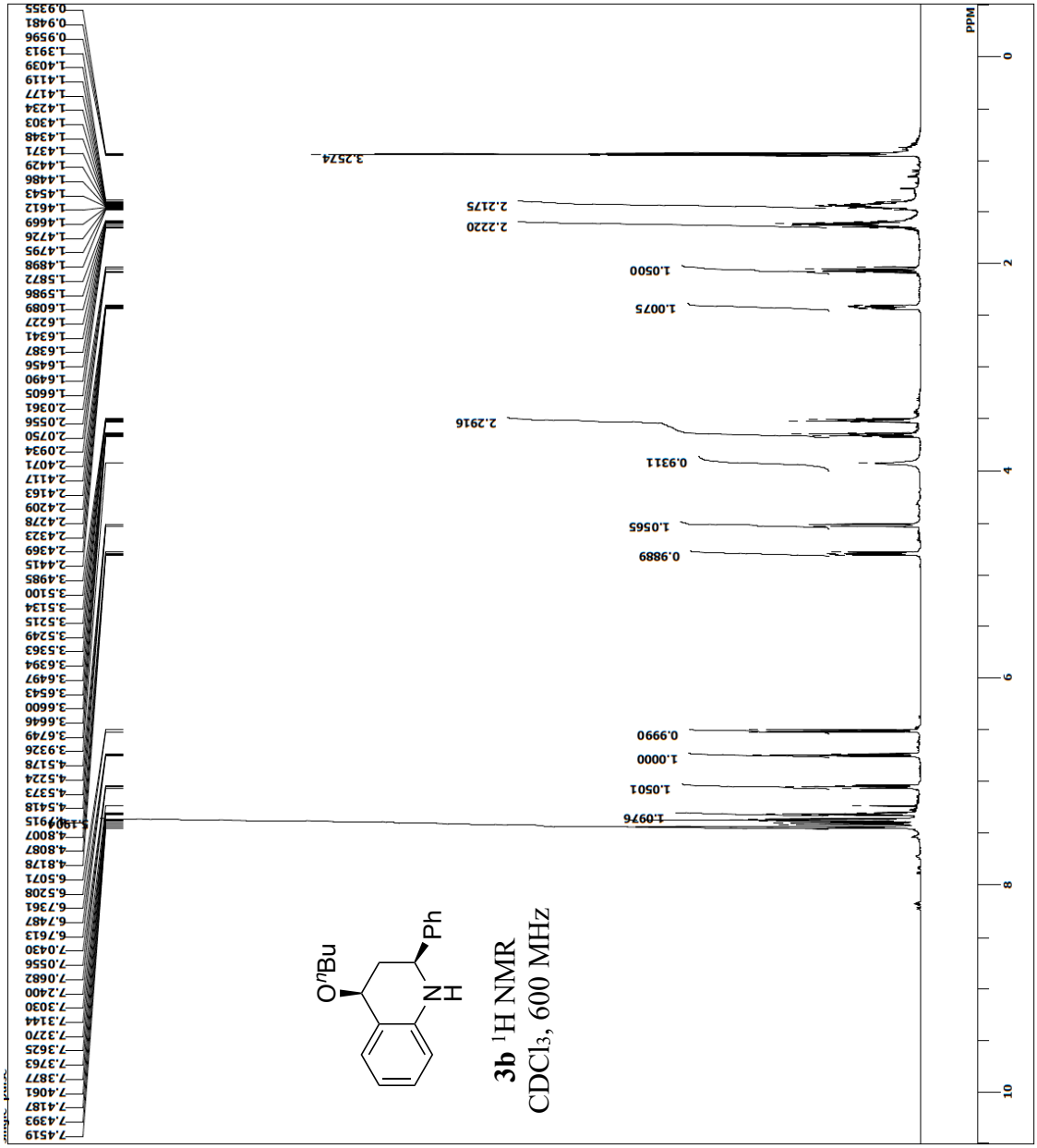
Figure S3 STEM and EDS analysis of NC-TfOH

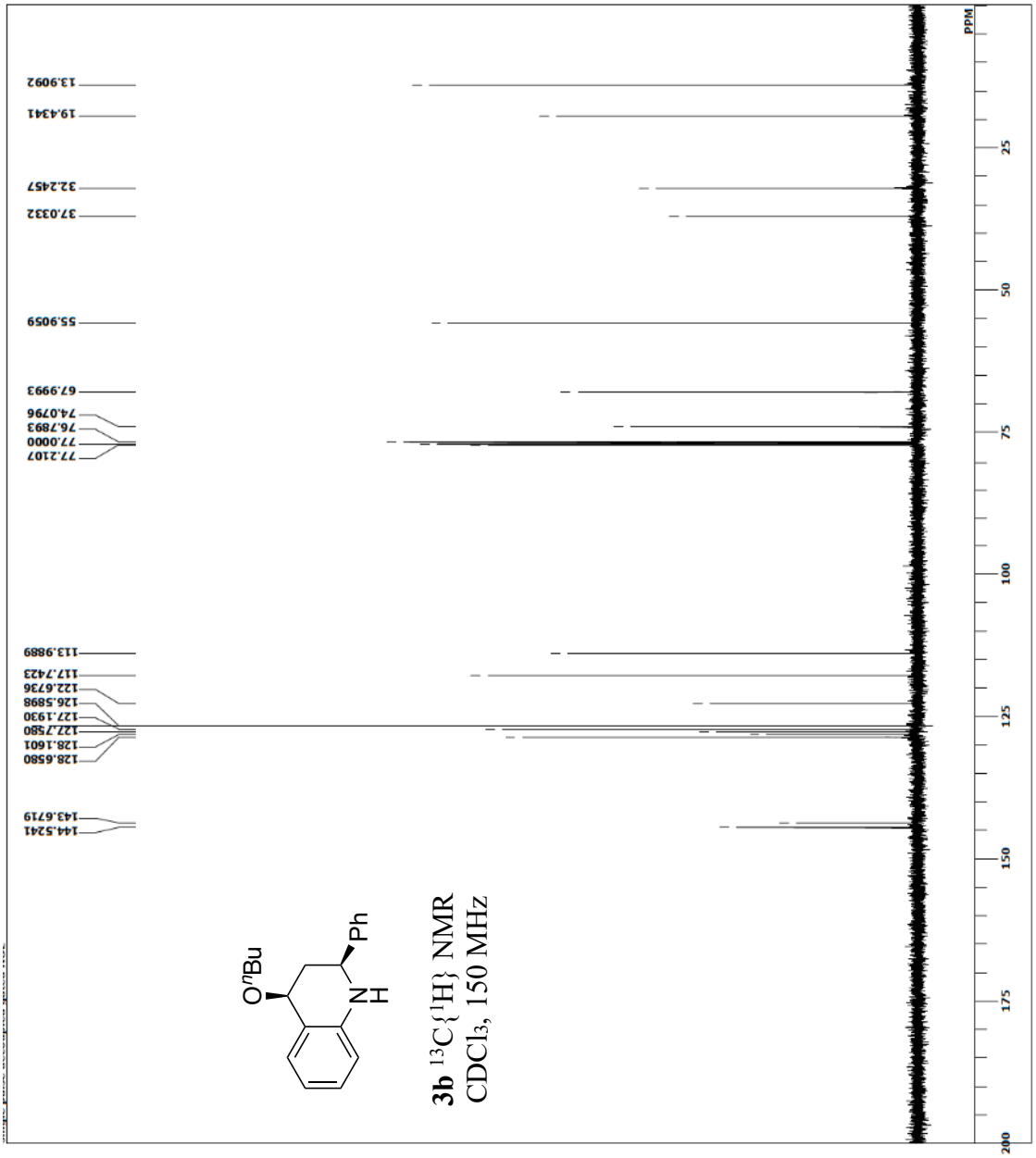
5. NMR charts




OEt
Ph
N
H
3a $^{13}C\{^1H\}$ NMR
$CDCl_3$, 150 MHz
144.5596
143.6500
128.6654
128.2059
127.7654
127.2292
126.5973
122.5663
117.7789
114.0160
77.2106
77.0000
76.7894
73.9552
63.4804
55.8972
37.0445
15.6162
PPM
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0

Small amount of 2-phenylquinoline was contaminated.




O/Bu
Ph
N
H
3b $^{13}C\{^1H\}$ NMR
$CDCl_3$, 150 MHz
144.5241
143.6719
128.6580
128.1601
127.7580
127.1930
126.5898
122.6736
117.7423
113.9889
77.2107
77.0000
76.7893
74.0796
67.9993
55.9059
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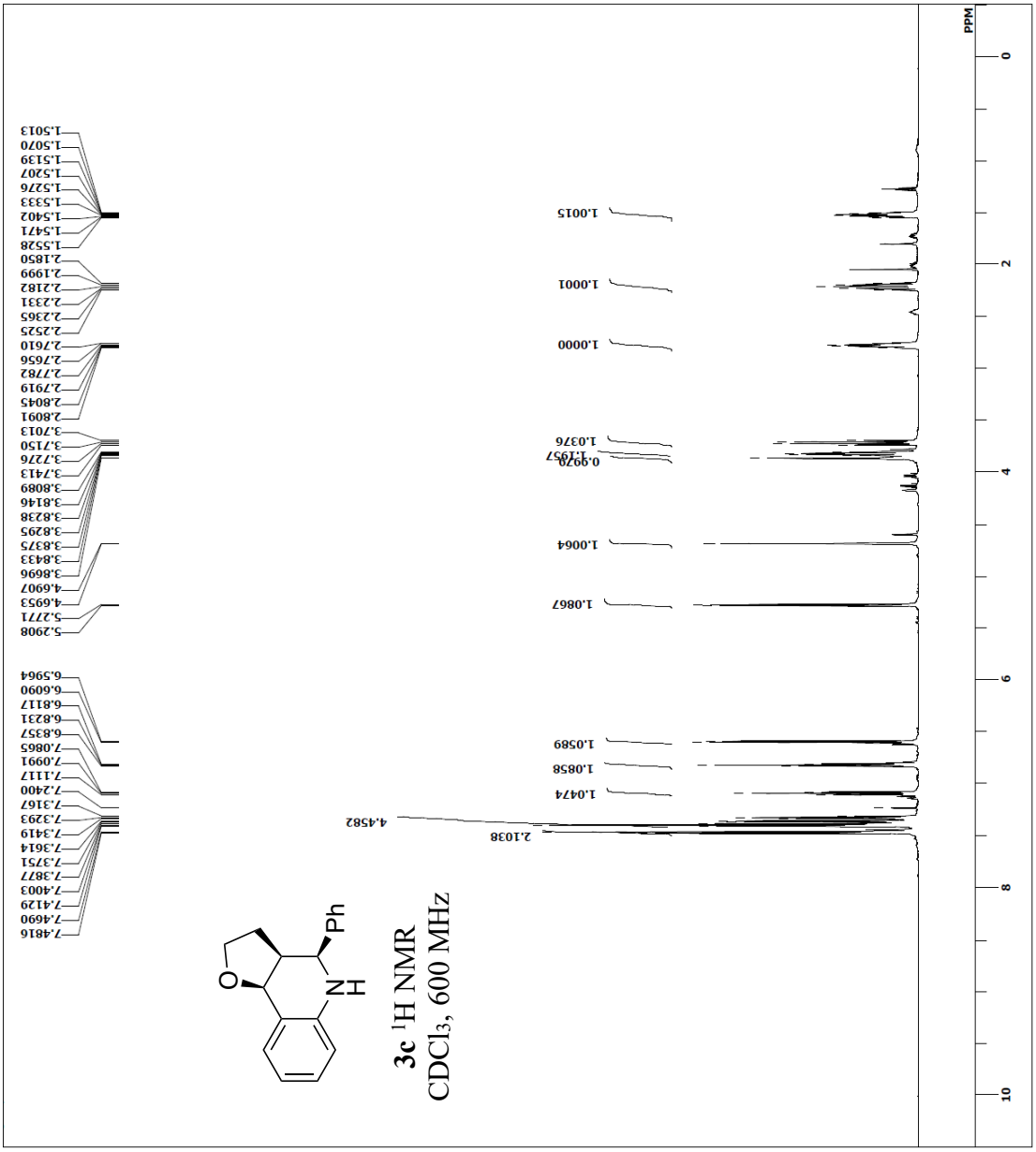
32.2457
19.4341
13.9092
PPM
200
175
150
125
100
75
50
25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4
6
8
10
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1.0000
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1.1957
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1.0867
1.0589
1.0858
1.0474
4.4582
2.1038
5.2908
5.2771
4.6953
4.6907
3.8696
3.8433
3.8375
3.8295
3.8238
3.8146
3.8089
3.7413
3.7276
3.7150
3.7013
2.8091
2.8045
2.7919
2.7782
2.7656
2.7610
2.2525
2.2365
2.2331
2.2182
2.1999
2.1850
1.5528
1.5471
1.5402
1.5333
1.5276
1.5207
1.5139
1.5070
1.5013
6.5964
6.6090
6.8117
6.8231
6.8357
7.0865
7.0991
7.1117
7.2400
7.3167
7.3293
7.3419
7.3614
7.3751
7.3877
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7.4129
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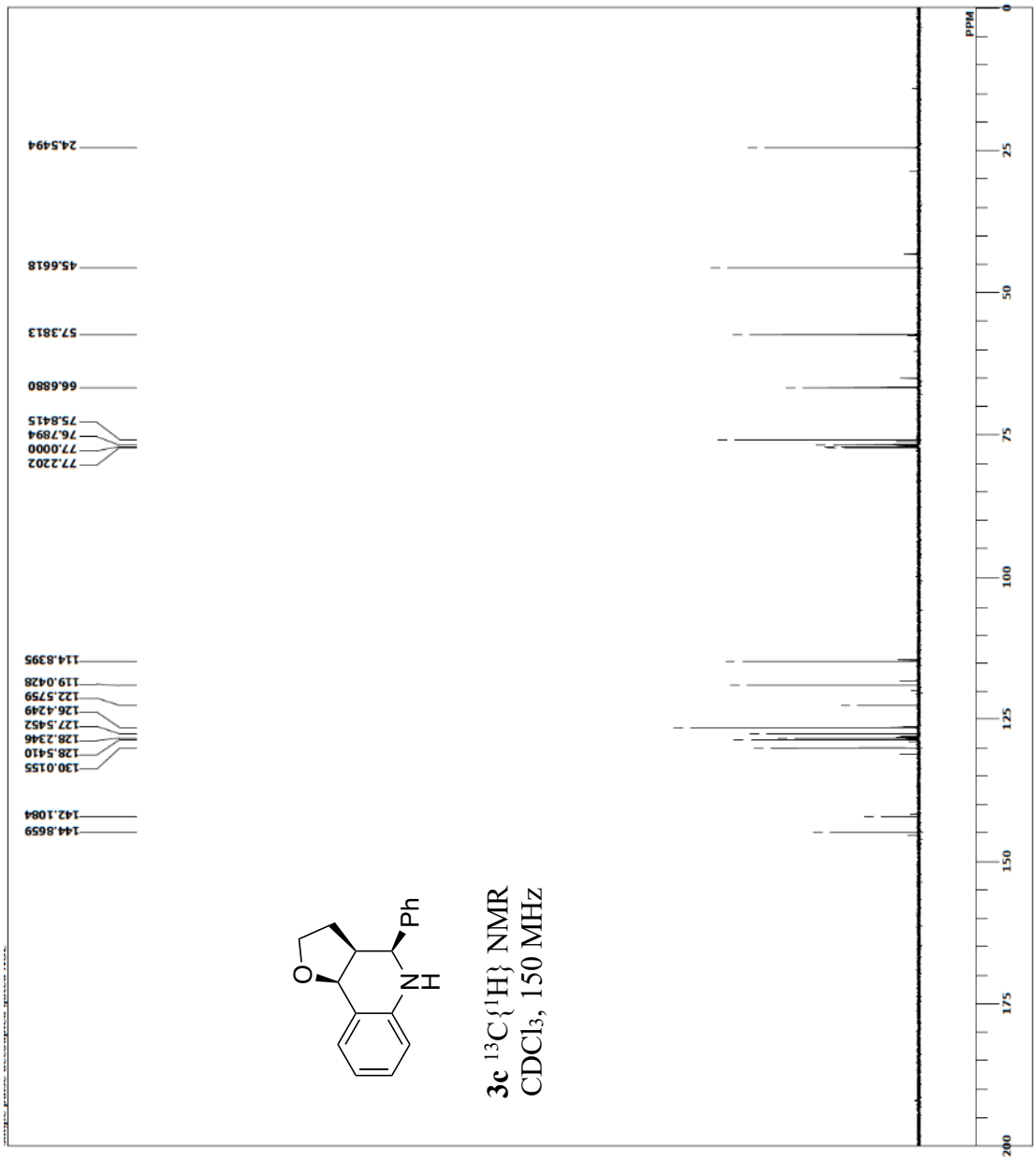
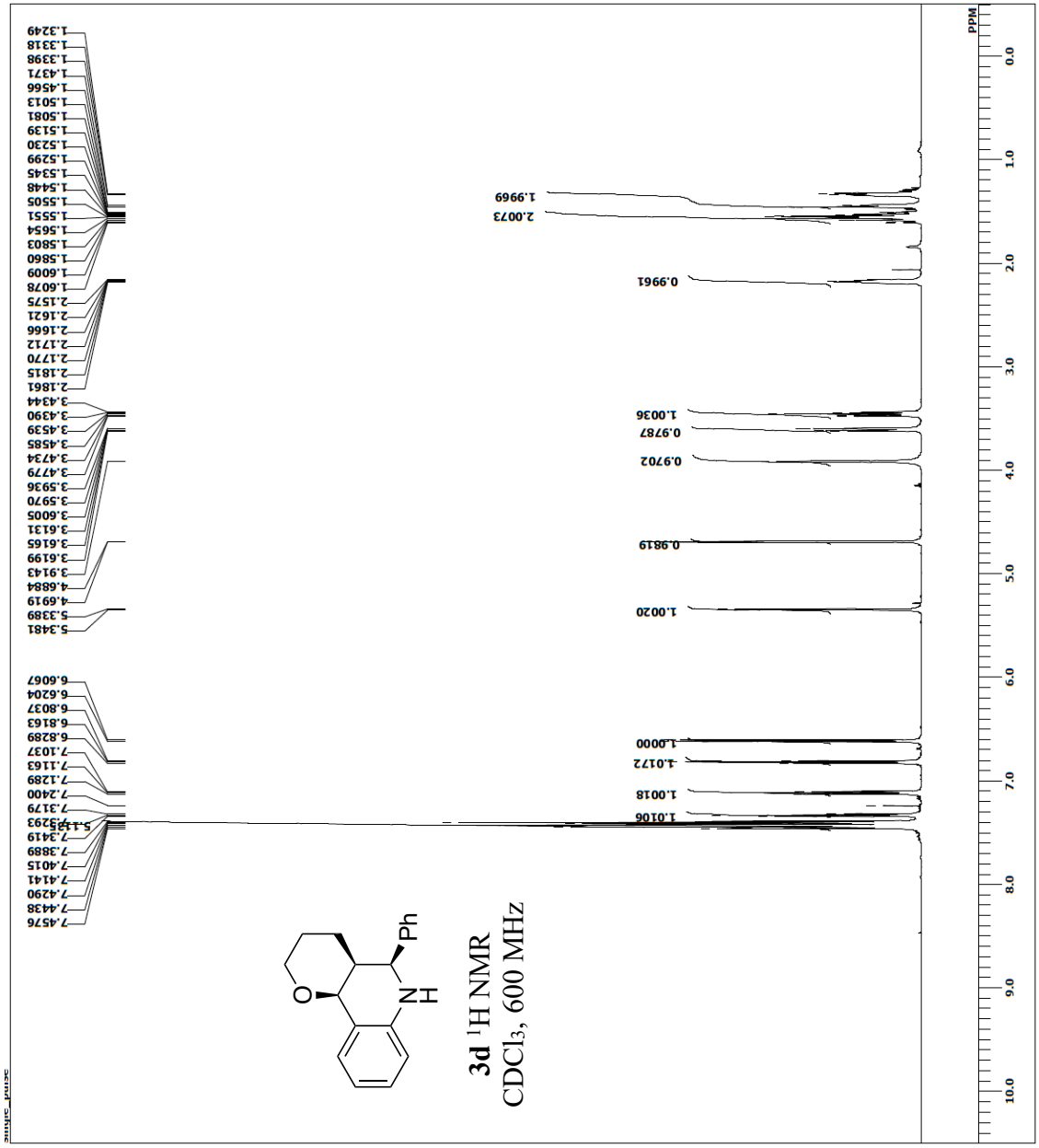
7.4816
O
N
H
Ph
3c ^{1}H NMR
$CDCl_3$, 600 MHz



3c $^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 150 MHz


Ph
H
N
O
3d ^{1}H NMR
$CDCl_3$, 600 MHz
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
1.0106
1.0018
1.0172
1.0000
1.0020
0.9819
0.9702
0.9787
1.0036
0.9961
2.0073
1.9969
7.4576
7.4438
7.4290
7.4141
7.4015
7.3889
7.3419
5.1195
7.3293
7.3179
7.2400
7.1289
7.1163
7.1037
6.8289
6.8163
6.8037
6.6204
6.6067
5.3481
5.3389
4.6819
4.6884
3.9143
3.6199
3.6165
3.6131
3.6005
3.5970
3.5936
3.4779
3.4734
3.4585
3.4539
3.4390
3.4344
2.1861
2.1815
2.1770
2.1712
2.1666
2.1621
2.1575
1.6078
1.6009
1.5860
1.5803
1.5654
1.5551
1.5505
1.5448
1.5345
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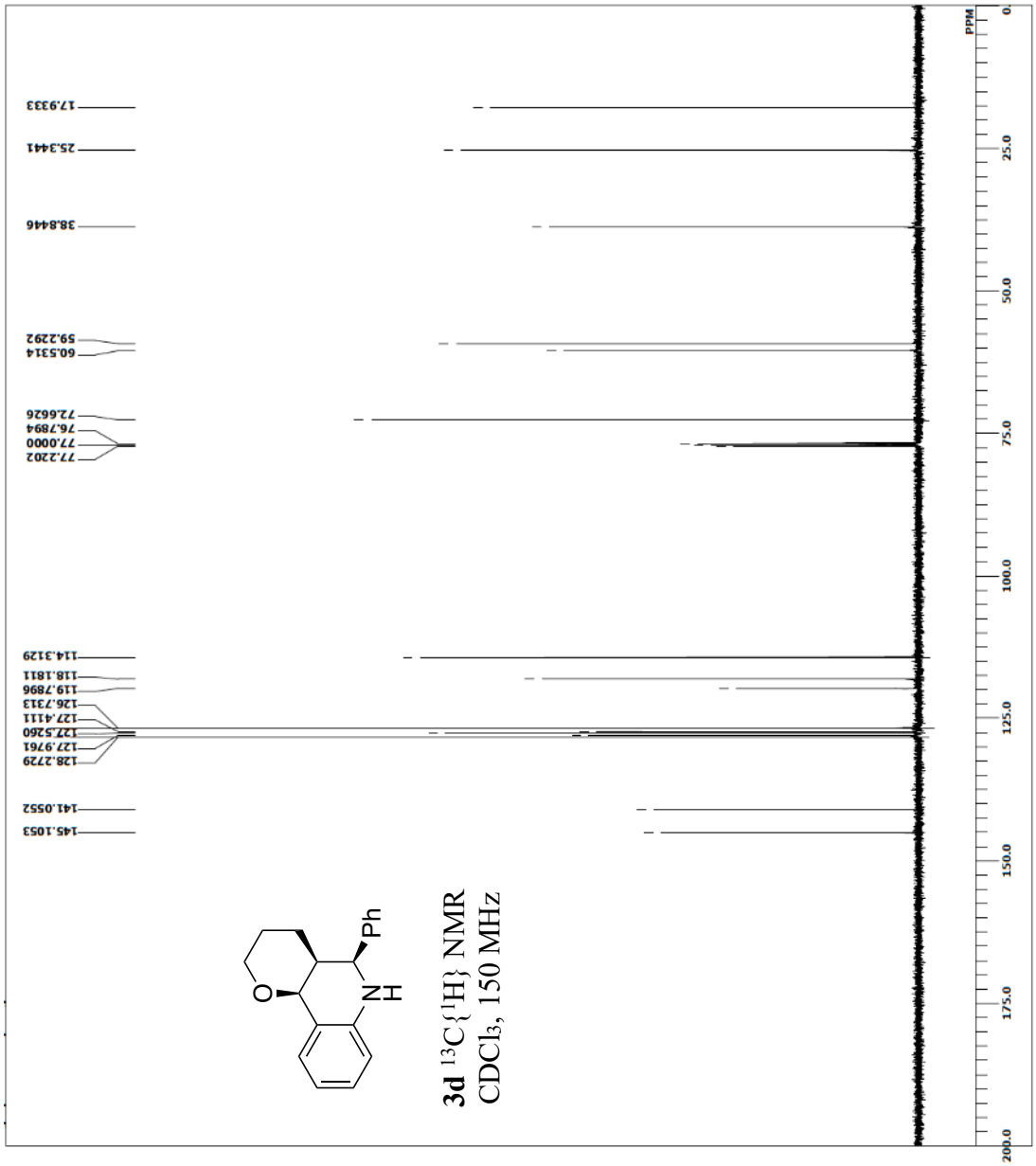
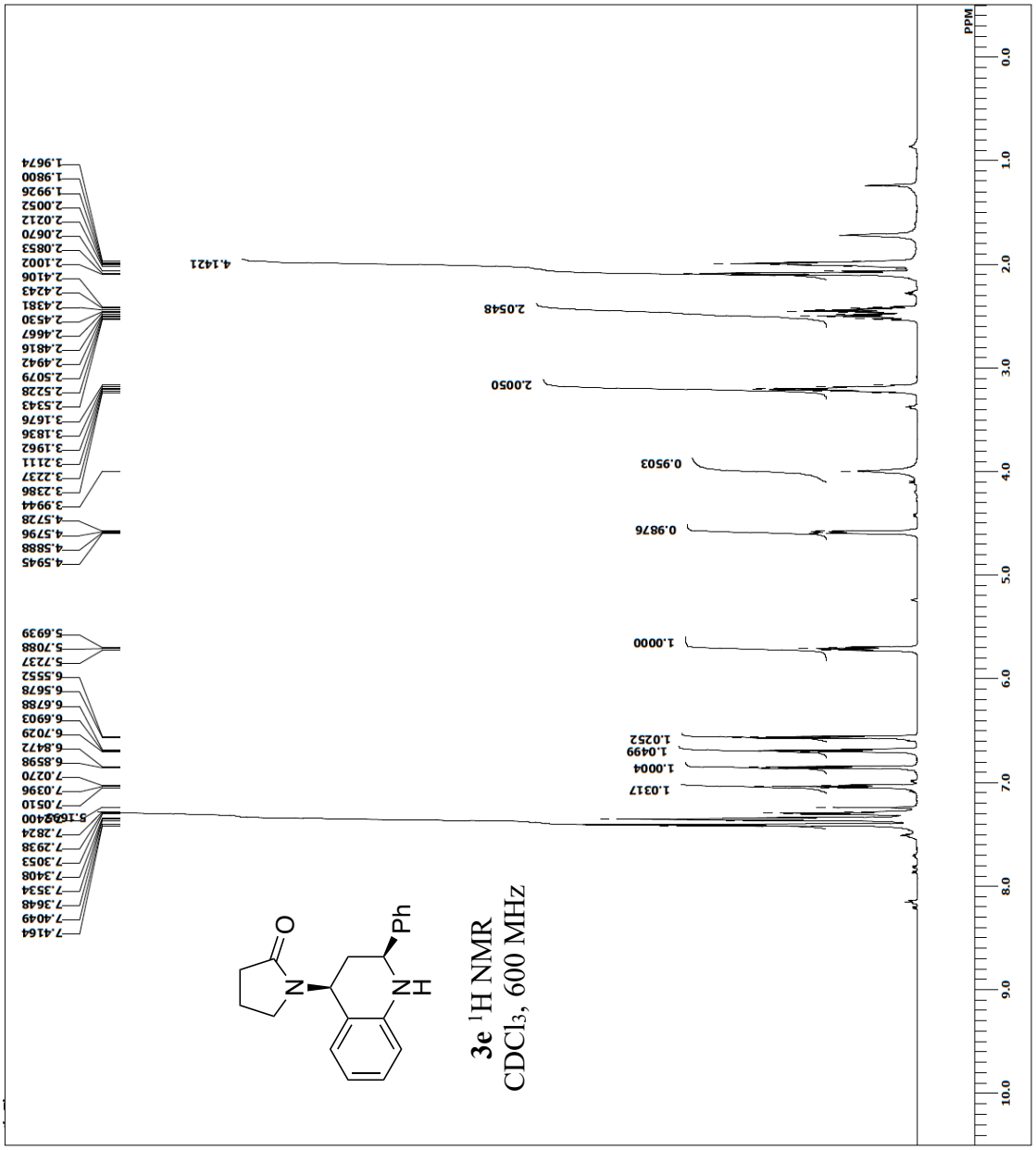
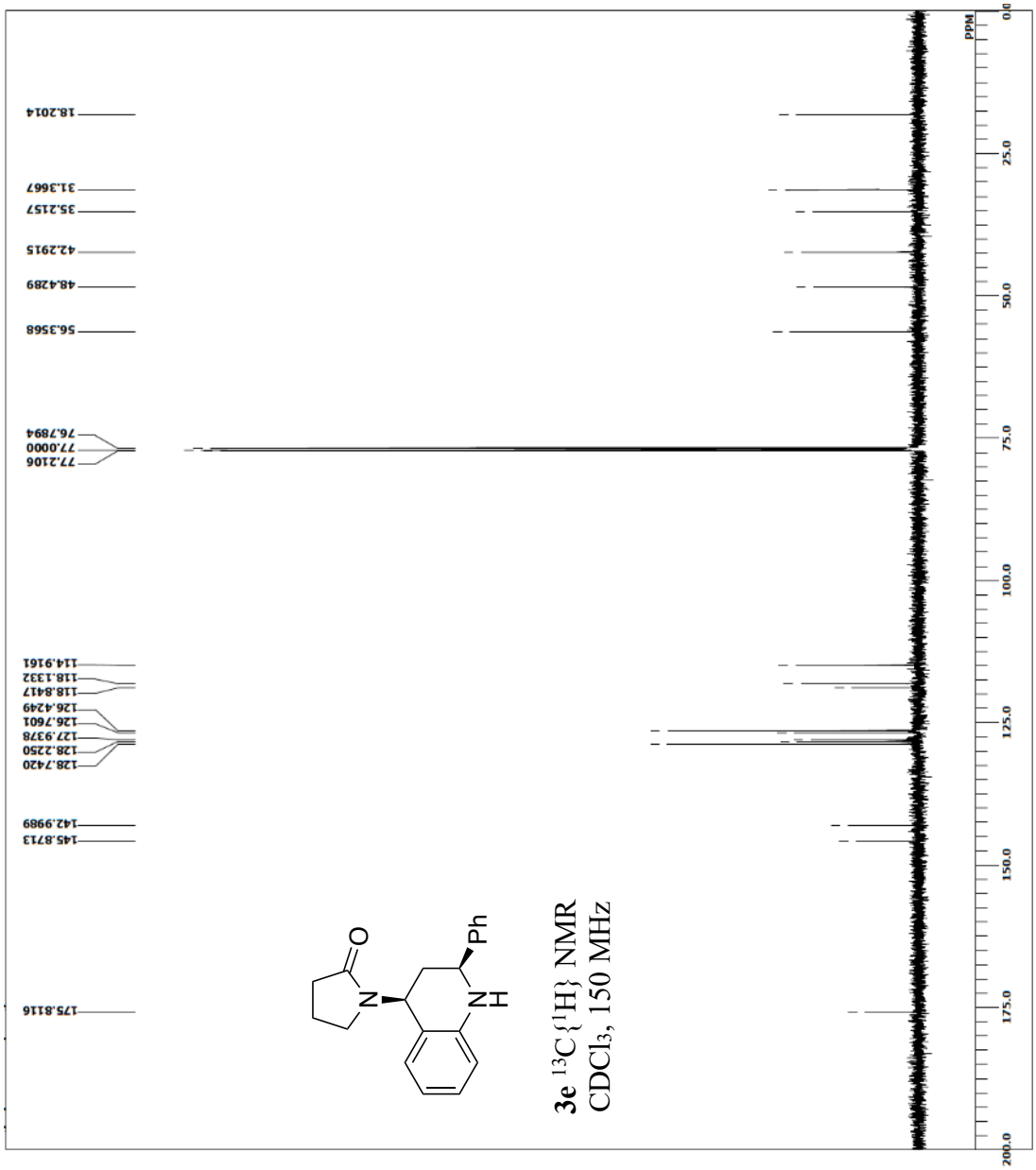
1.3318
1.3249

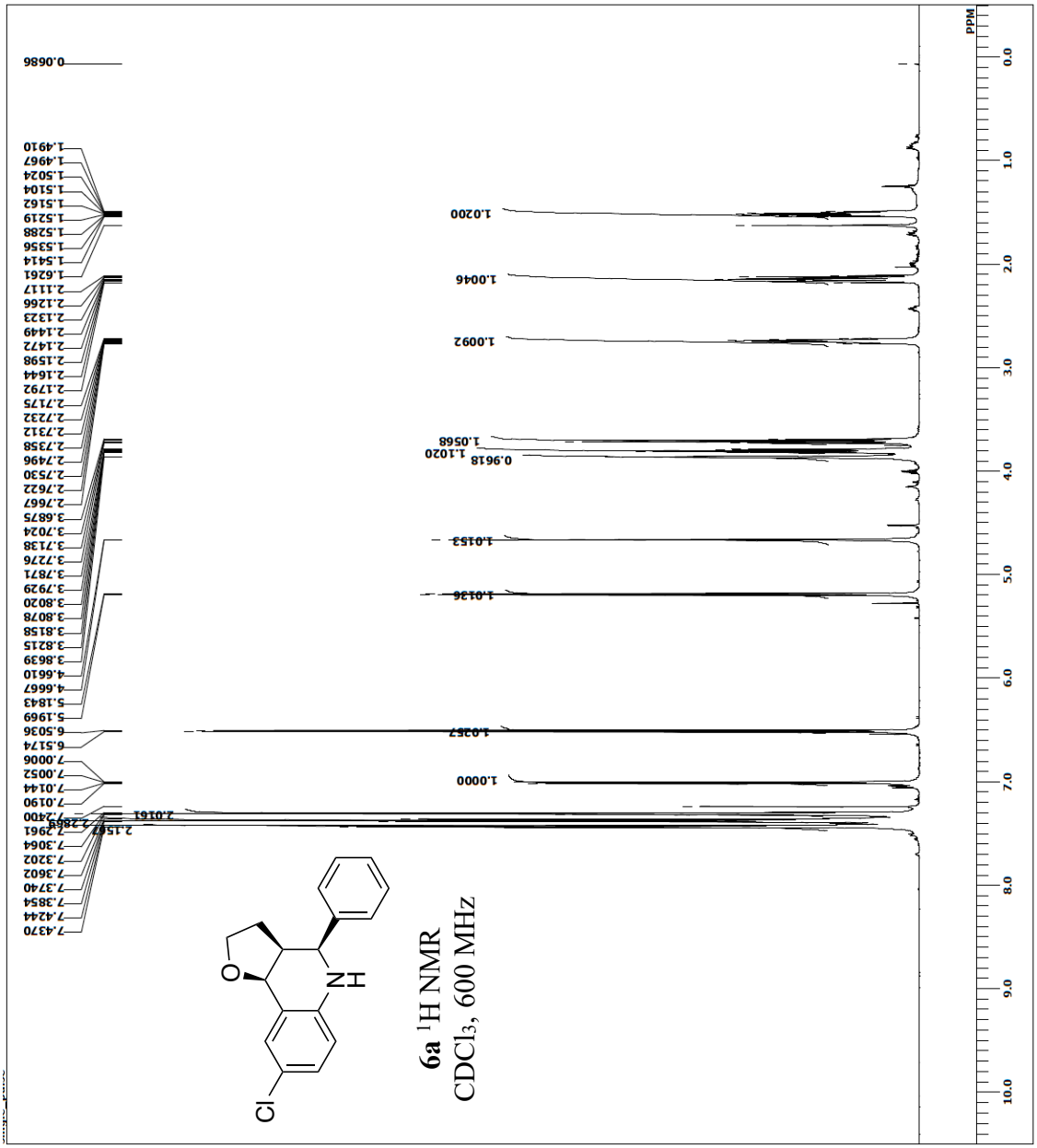

Ph
O
N
H
3d $^{13}C\{^1H\}$ NMR
$CDCl_3$, 150 MHz
145.1053
141.0552
128.2729
127.9761
127.5260
127.4111
126.7313
119.7896
118.1811
114.3129
77.2202
77.0000
76.7894
72.6626
60.5314
59.2292
38.8446
25.3441
17.9333
PPM
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.

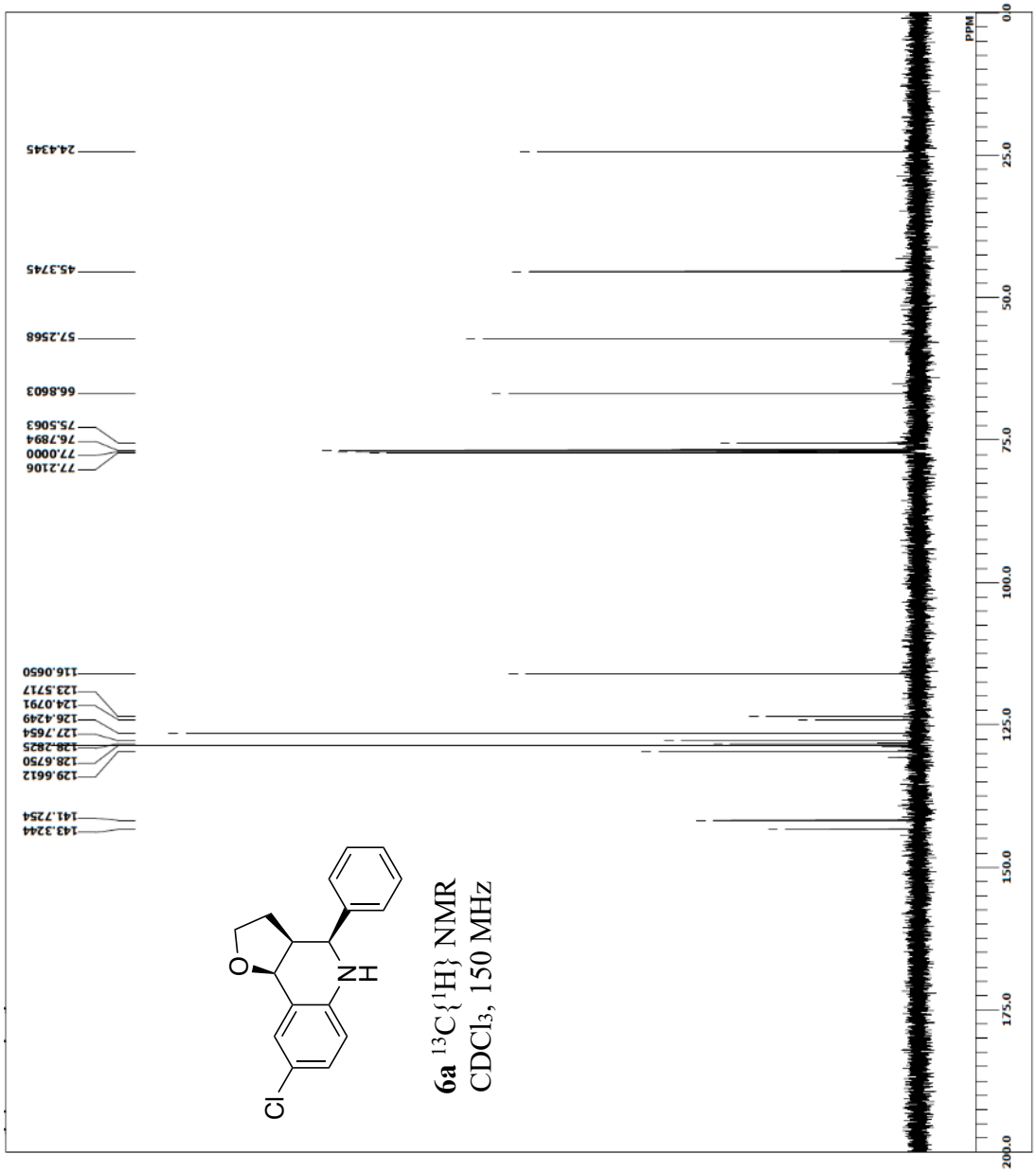
Small amount of 2-phenylquinoline was contaminated.



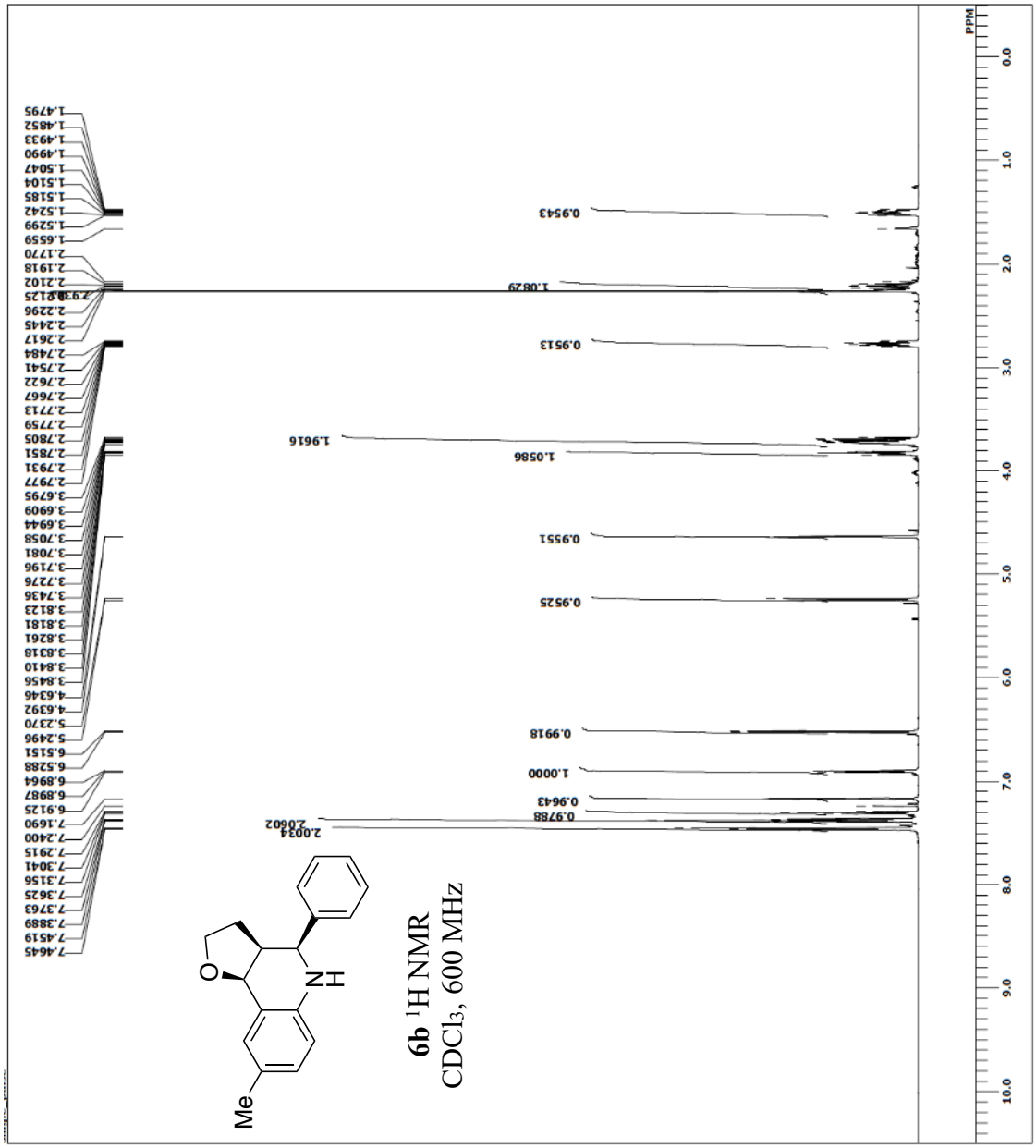


3e $^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 150 MHz


6a ^{1}H NMR
$CDCl_3$, 600 MHz
PPM

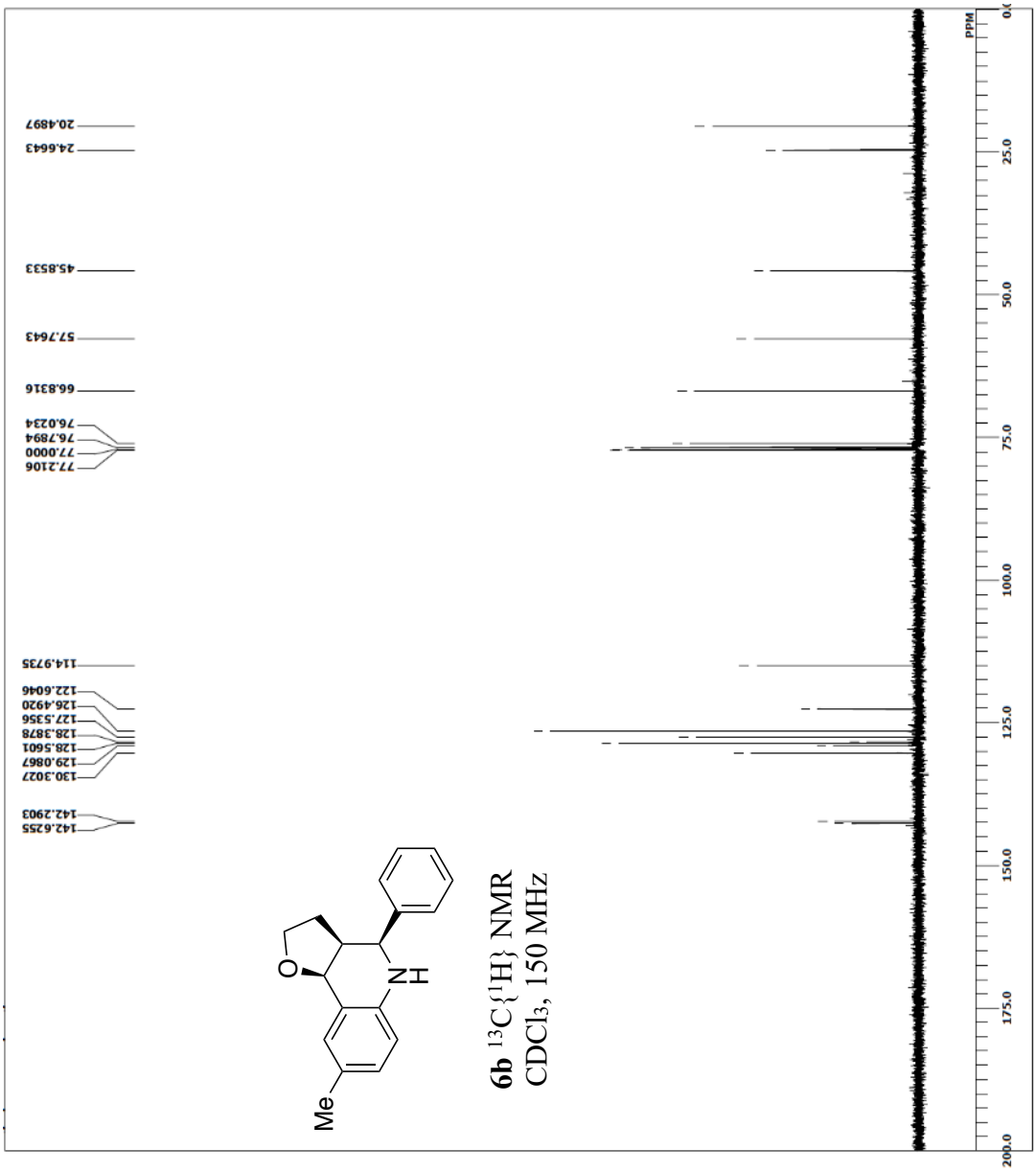


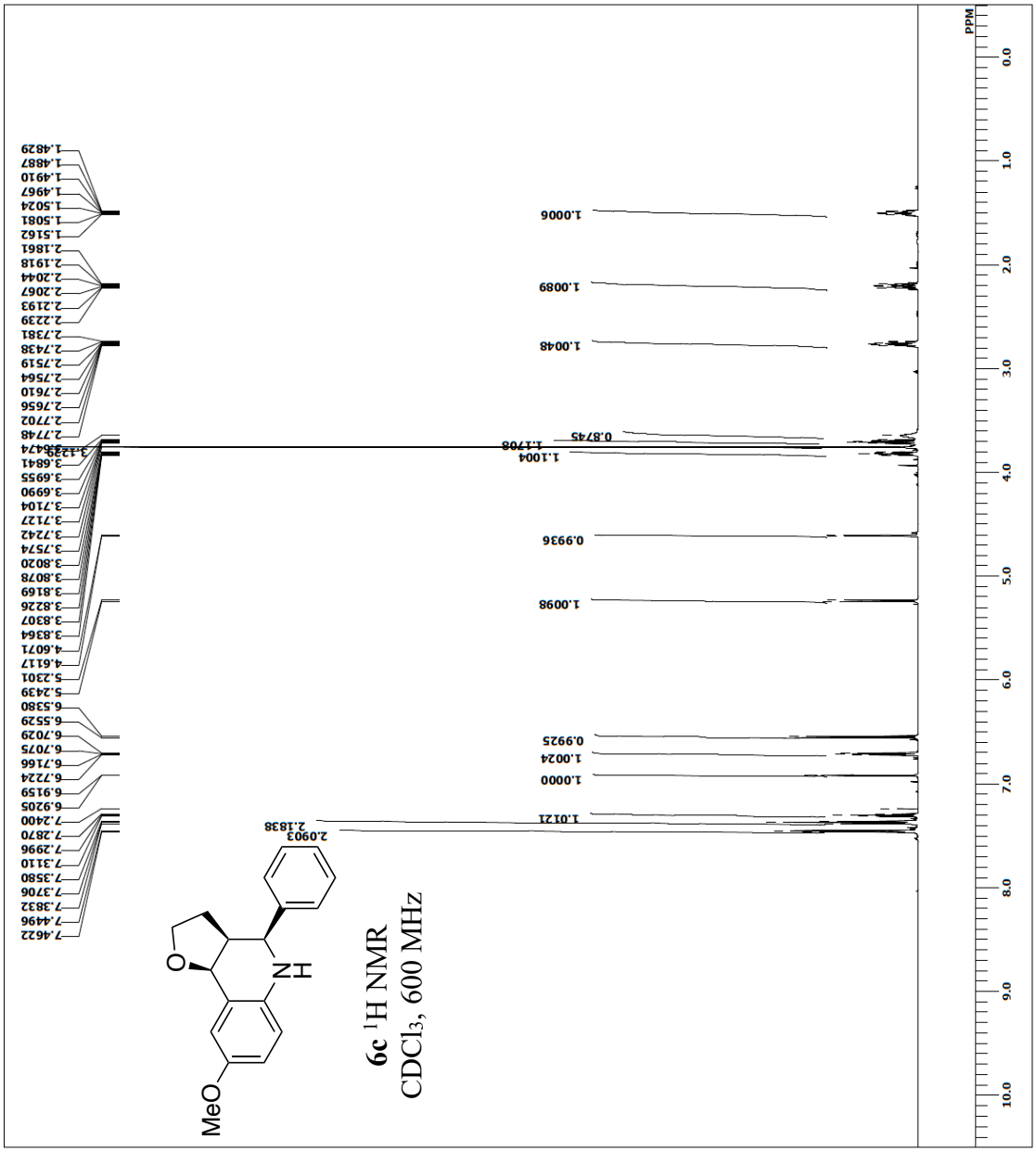
6a $^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 150 MHz



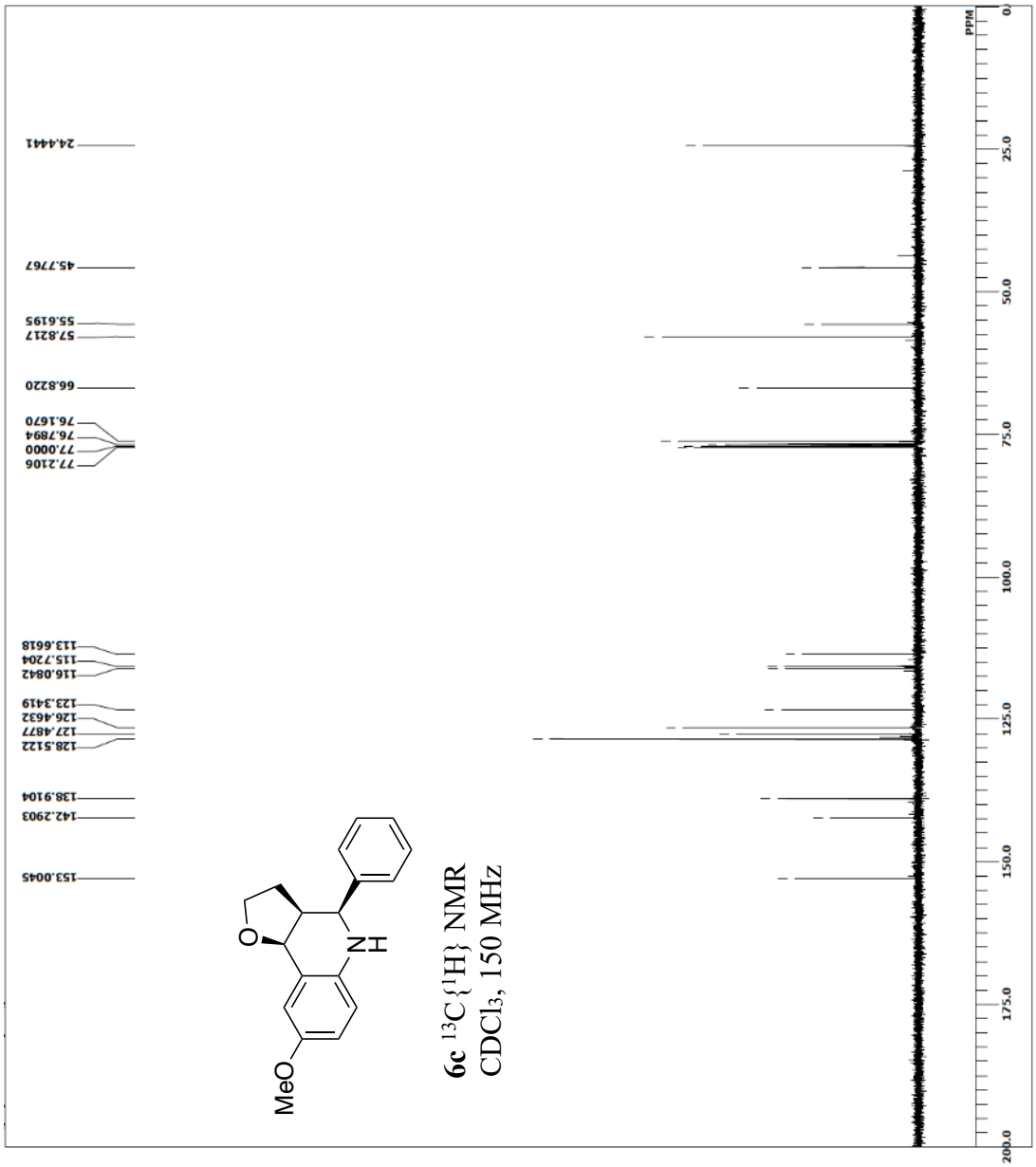
6b ^{1}H NMR
$CDCl_3$, 600 MHz

\

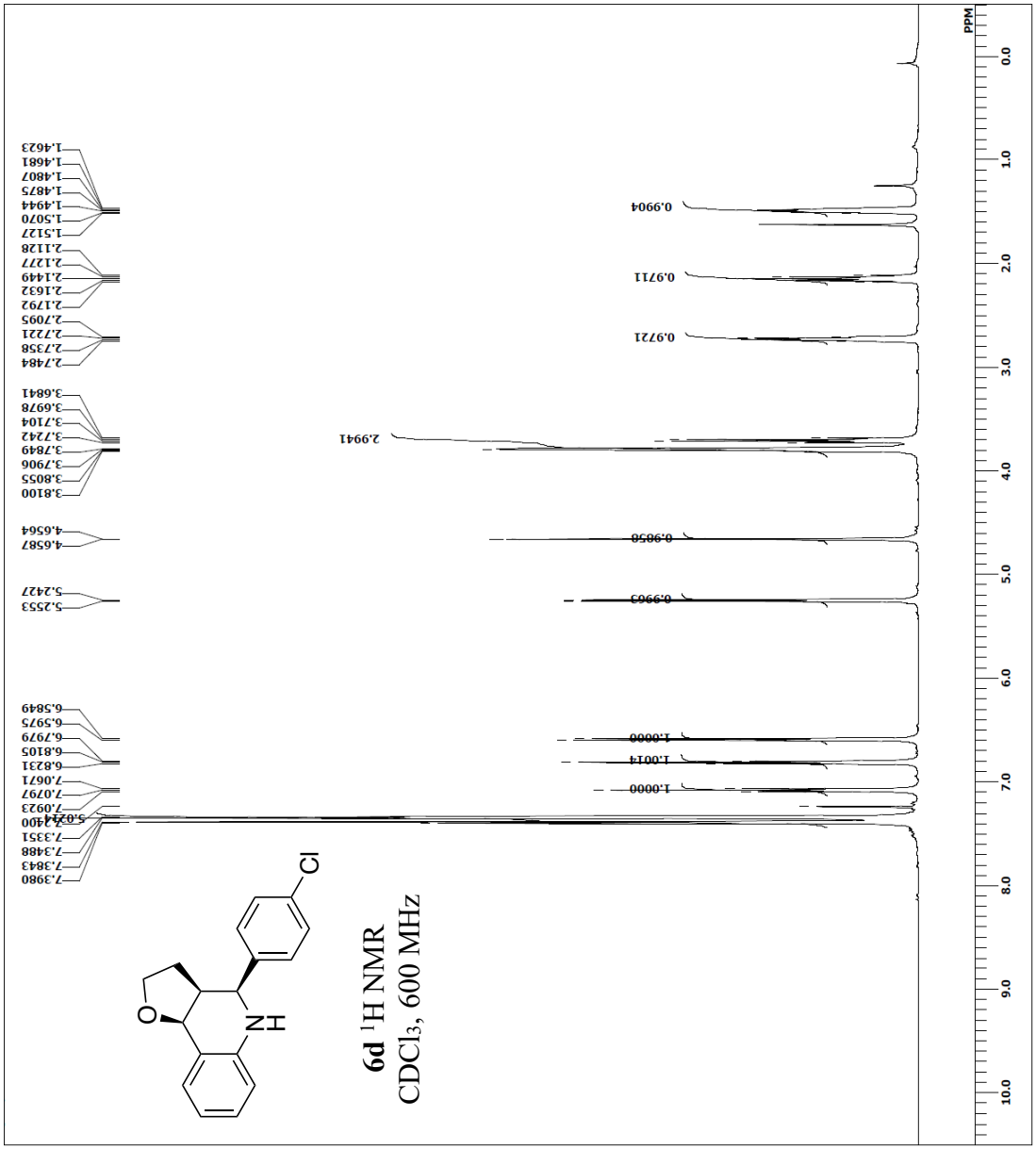

Me
O
N
H
6b $^{13}C\{^1H\}$ NMR
$CDCl_3$, 150 MHz
142.6255
142.2903
130.3027
129.0867
128.5601
128.3878
127.5356
126.4920
122.6046
114.9735
77.2106
77.0000
76.7894
76.0234
66.8316
57.7643
45.8533
24.6643
20.4897
PPM
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0



6c ^{1}H NMR
$CDCl_3$, 600 MHz



6c $^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 150 MHz


6d ^{1}H NMR
$CDCl_3$, 600 MHz
PPM
7.3980
7.3843
7.3488
7.3351
7.2400
7.0923
7.0797
7.0671
6.8231
6.8105
6.7979
6.5975
6.5849
5.2553
5.2427
4.6587
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2.7095
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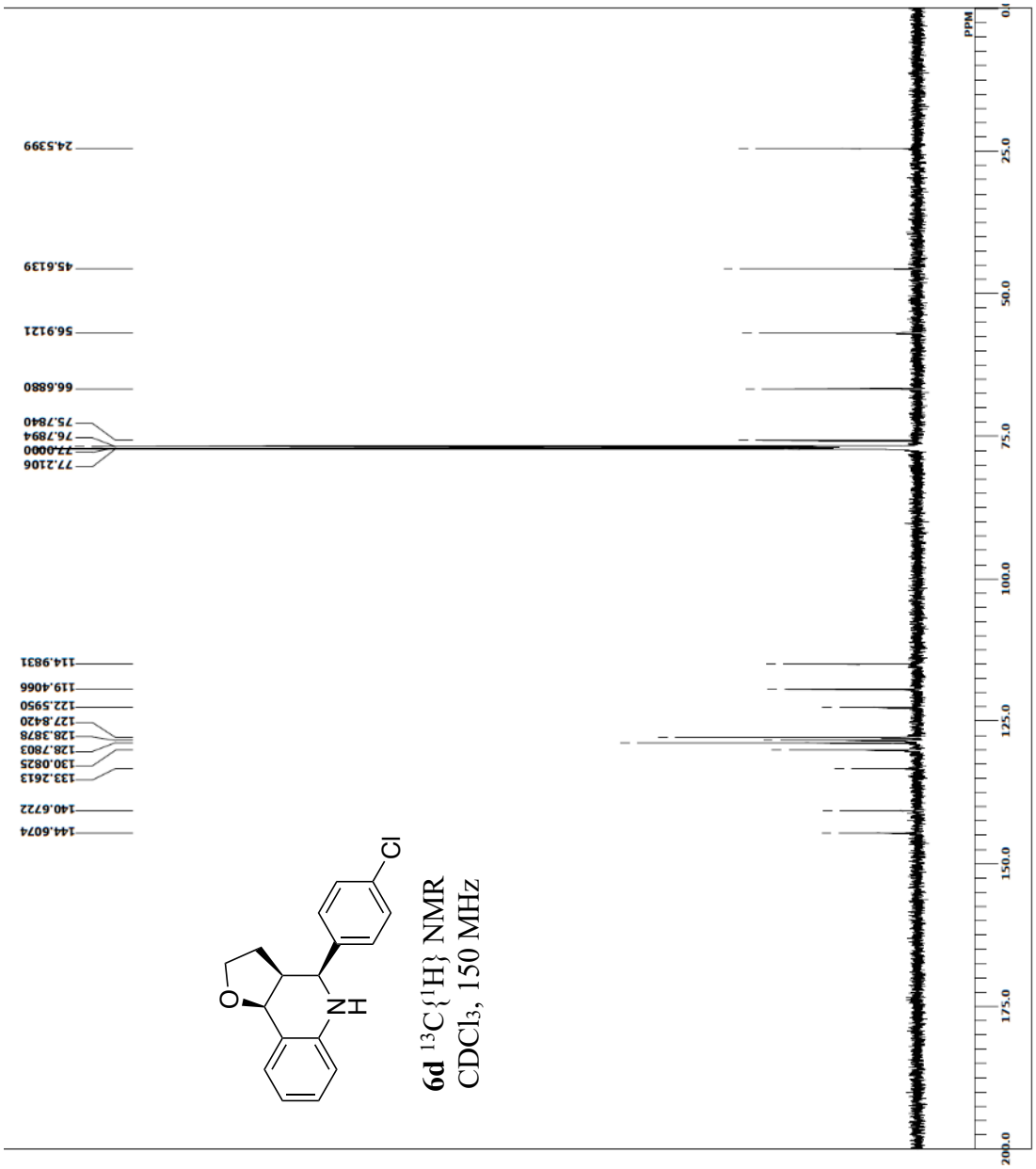
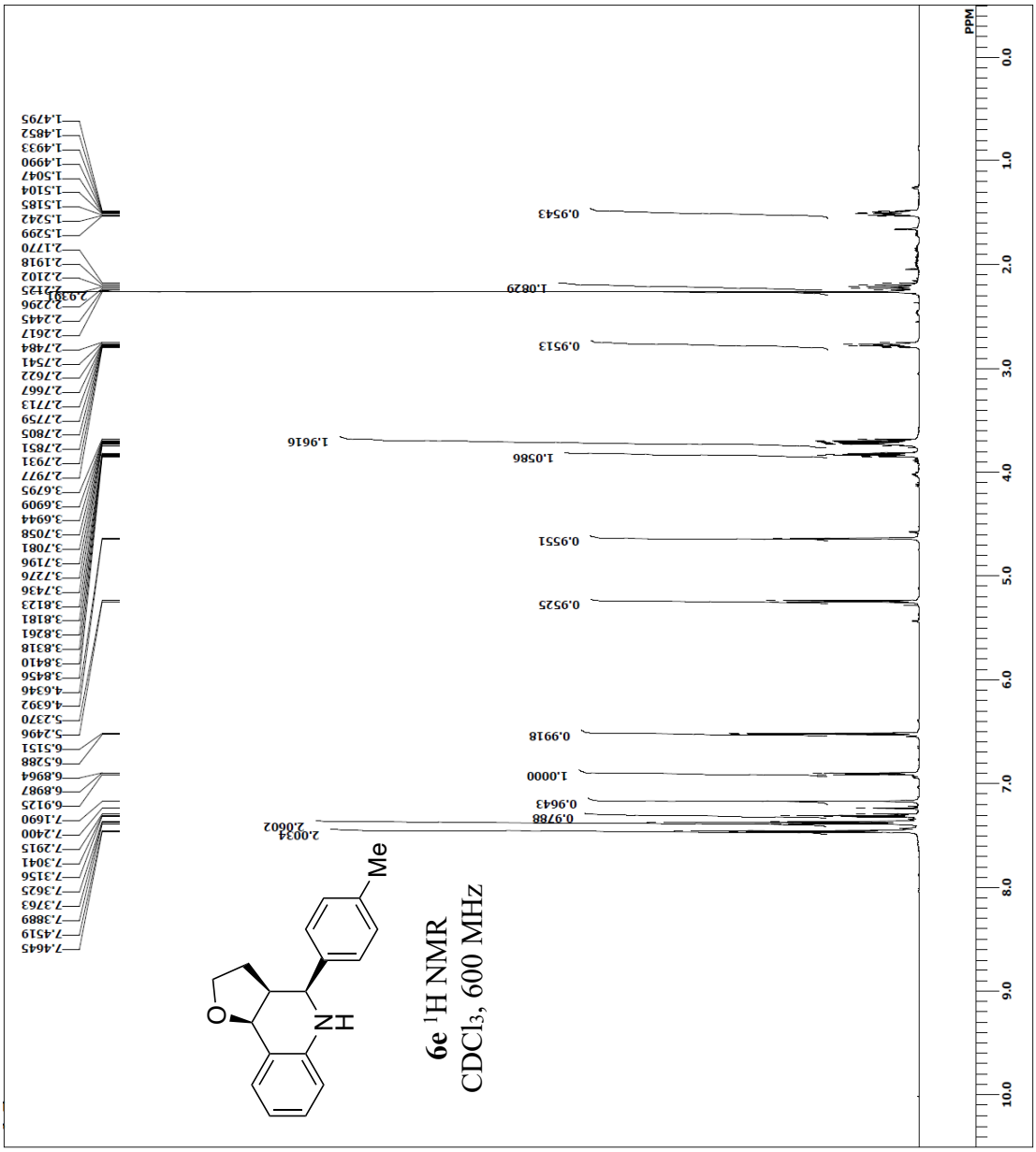
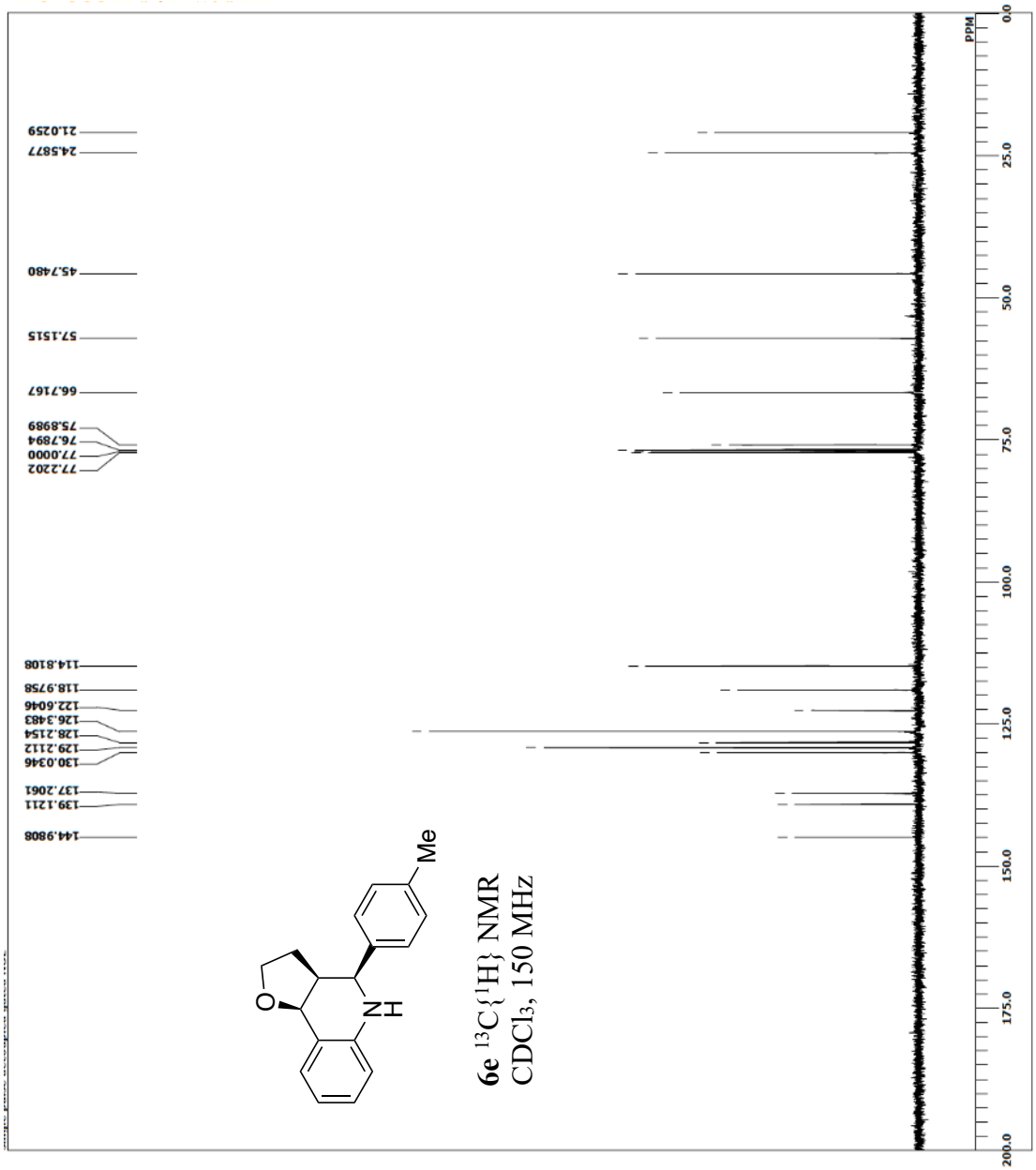
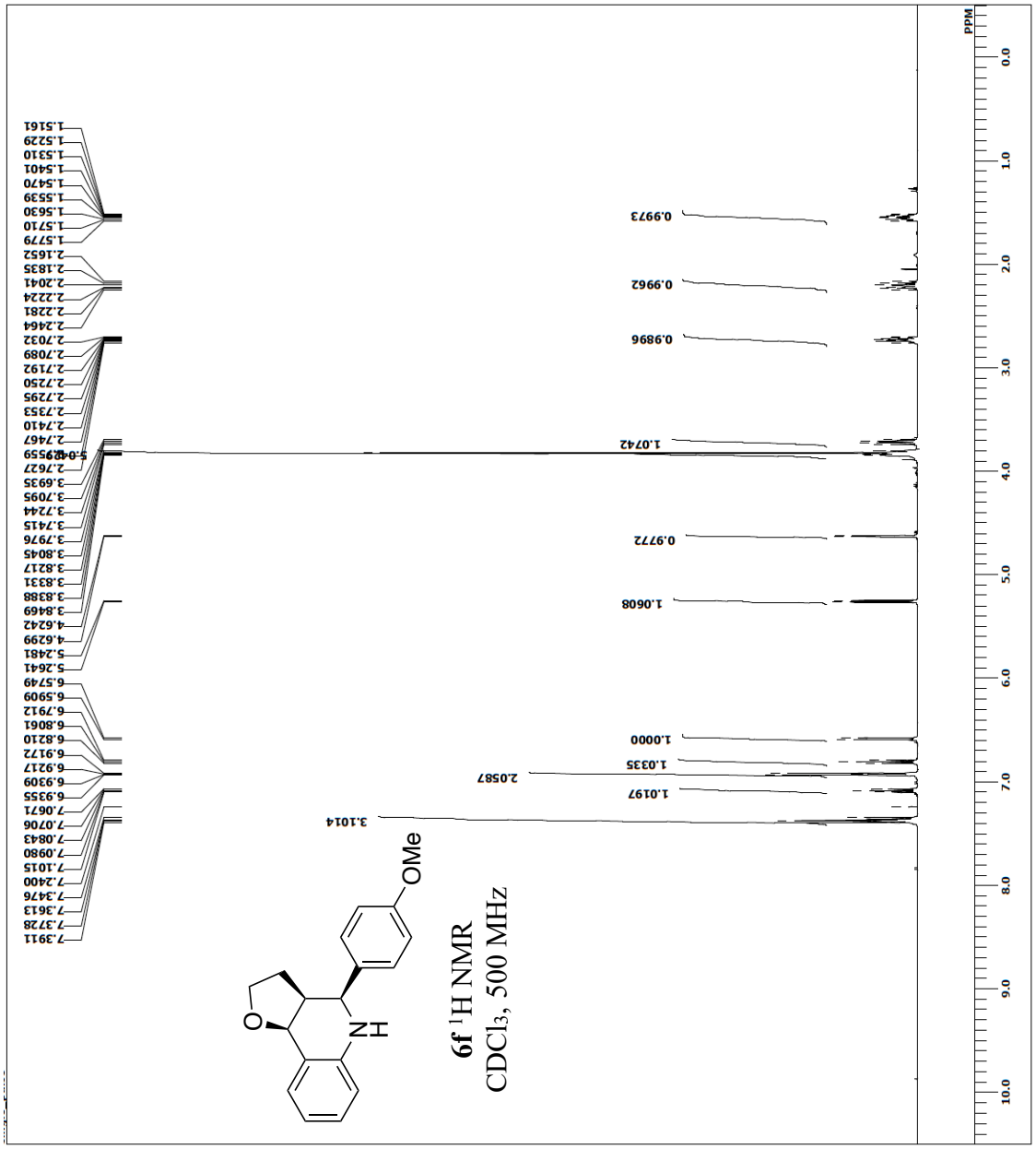


6d $^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 150 MHz


6e ^{1}H NMR
$CDCl_3$, 600 MHz
PPM
Me
H
N
O



6e $^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 150 MHz


6f ^{1}H NMR
$CDCl_3$, 500 MHz
OMe
H
N
O
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1.0197
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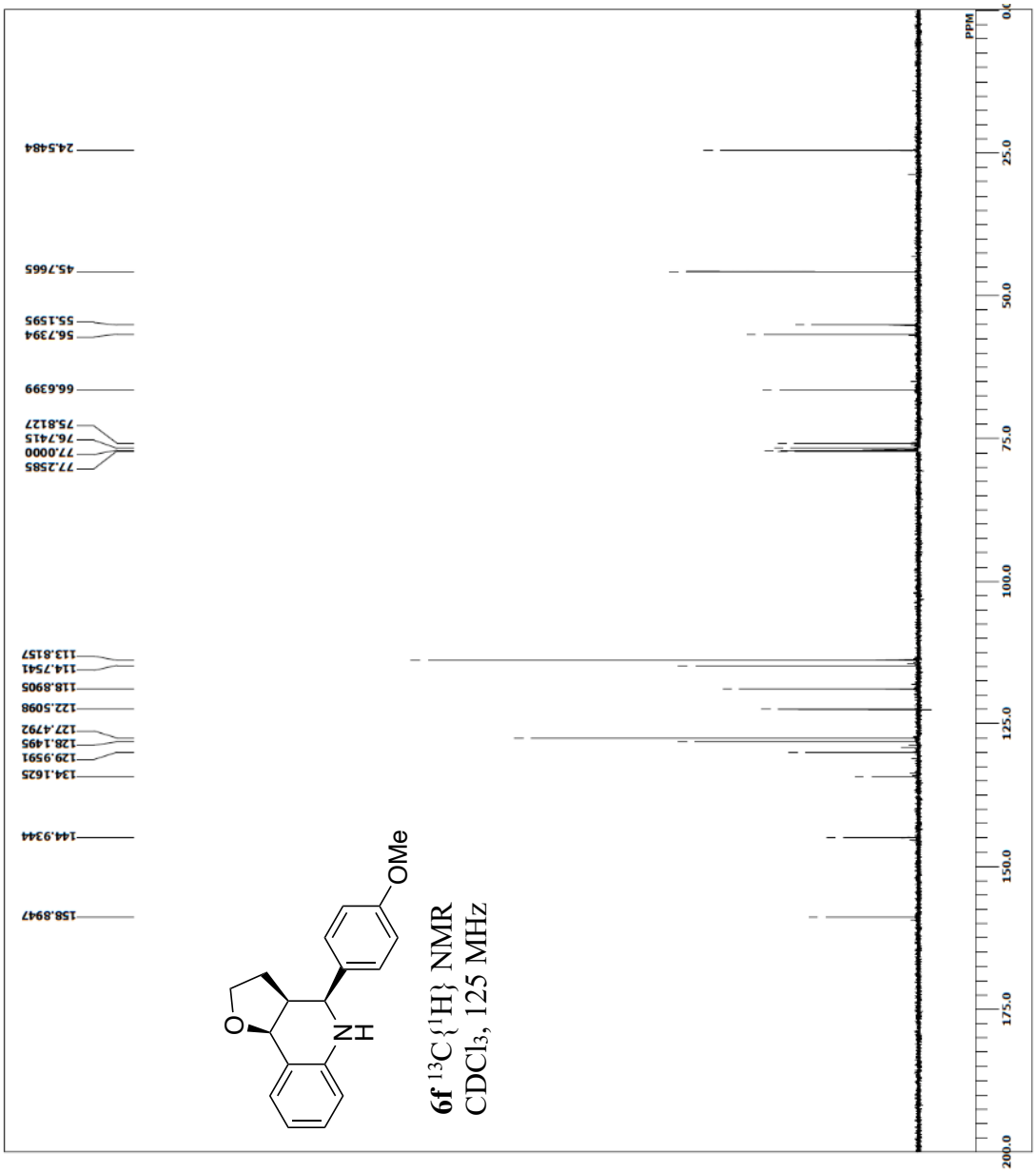
1.0608
0.9772
1.0742
0.9896
0.9962
0.9973
PPM



6f $^{13}C\{^{1}H\}$ NMR
$CDCl_3$, 125 MHz