Supporting Information

Ruthenium(II)-Catalyzed Regioselective C-H Hydroxymethylation of *N*-Aryl-Azaindoles with Paraformaldehyde

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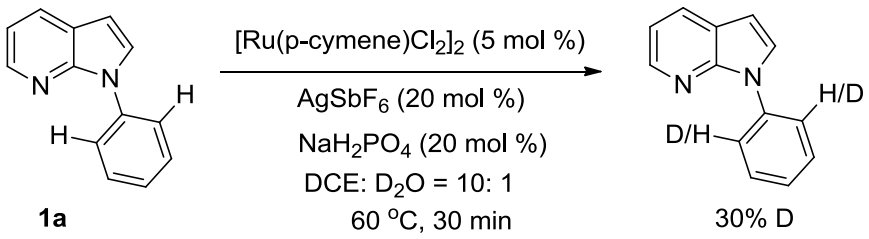
General Information:

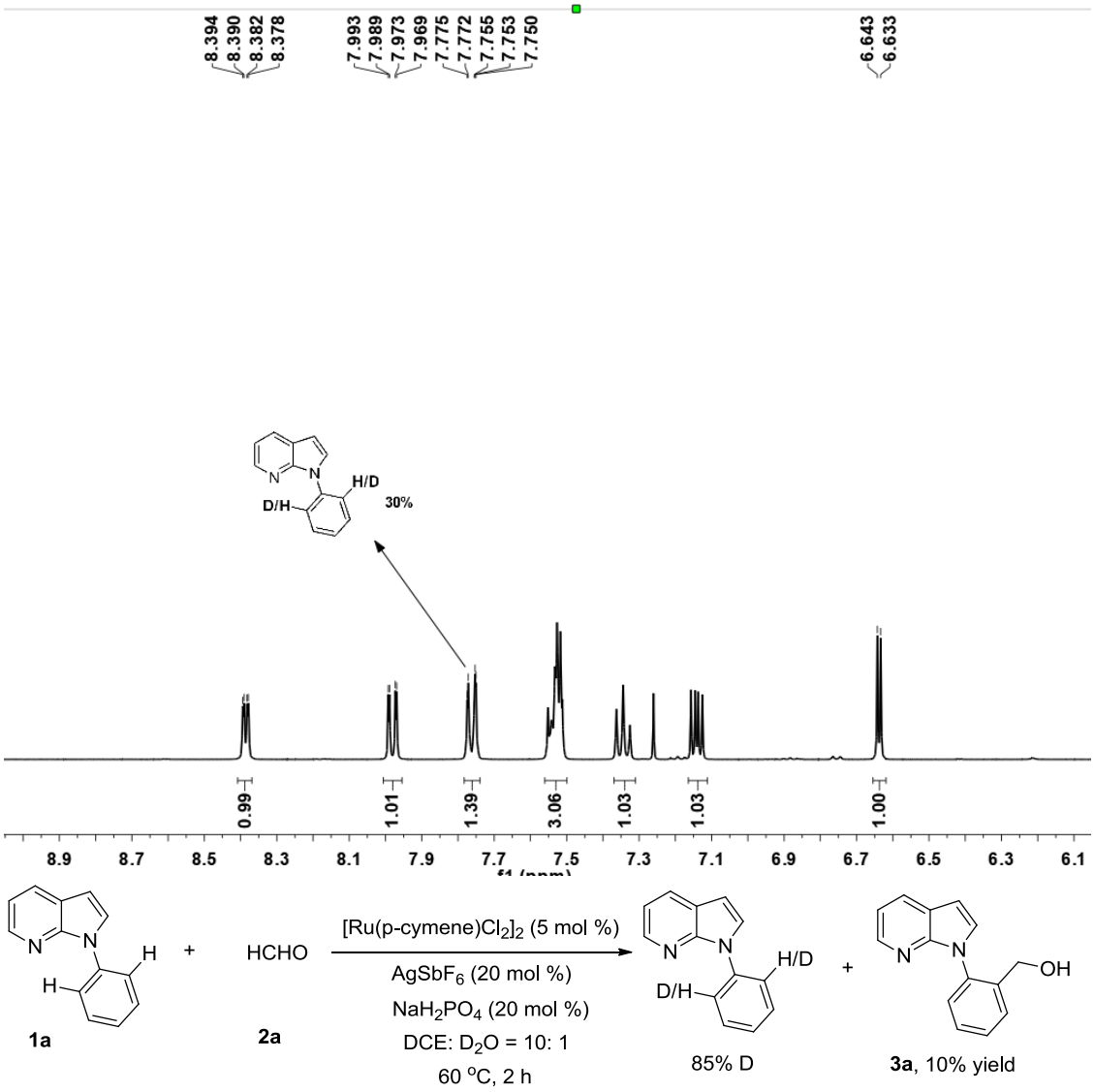
Mass spectra and high-resolution mass spectra were measured on a Finnigan MAT-95 mass spectrometer. ^{1}H and ^{13}C NMR spectra were determined on Bruker AM-300, Bruker AM-400, Bruker AM-500 instruments using tetramethylsilane as internal reference. Data are presented as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, m = multiplet), J = coupling constant in hertz (Hz). Silica gel 60H (200 – 300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography. All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated.

Mechanistic study

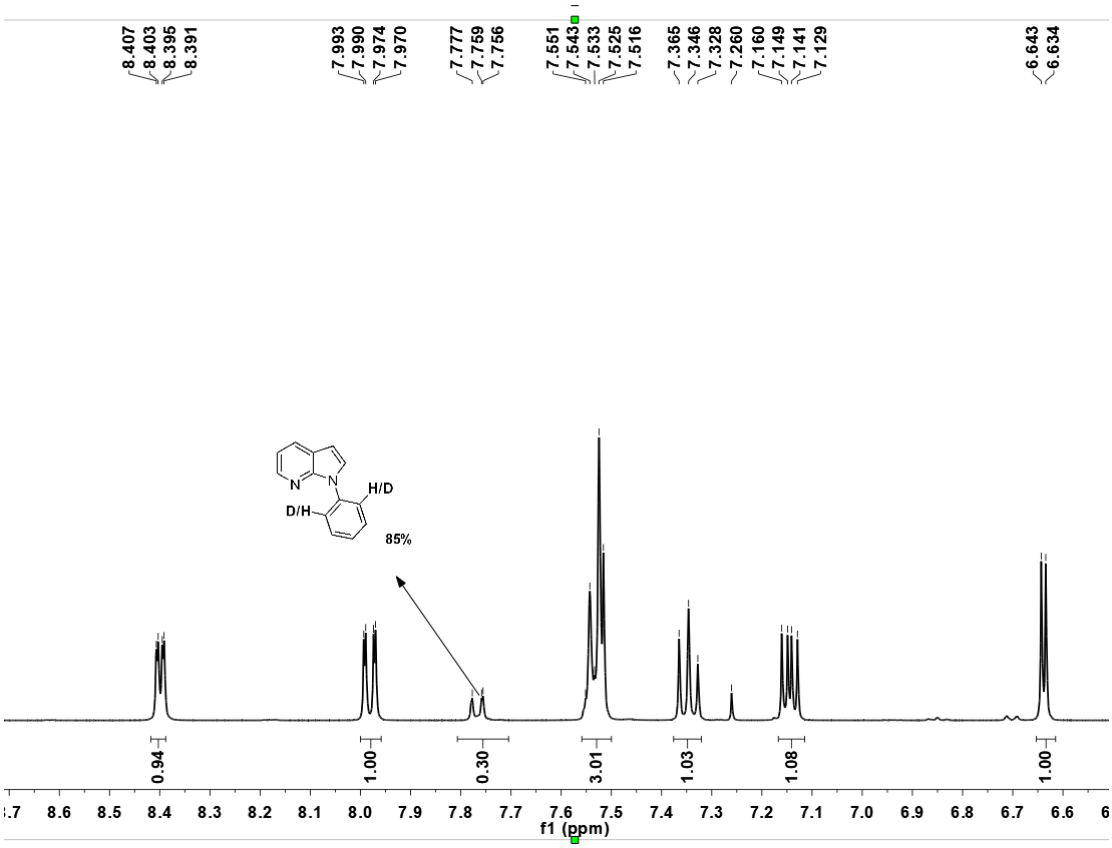
(a) Procedure for H/D exchange experiment:



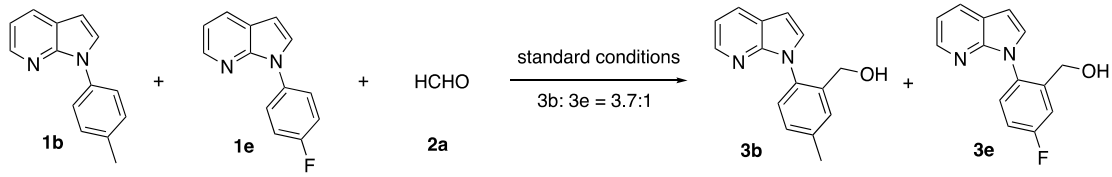
A mixture of **1a** (0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), $AgSbF_6$ (20 mol %), NaH_2PO_4 (20 mol %) were dissolved in DCE: D_2O (10: 1) (2 mL) in sealed tube and the mixture was stirred at 60 ℃ for 30 min. The solvent was removed under reduced pressure and the residue was purified the residue by silica gel chromatograph to recovery **1a**.



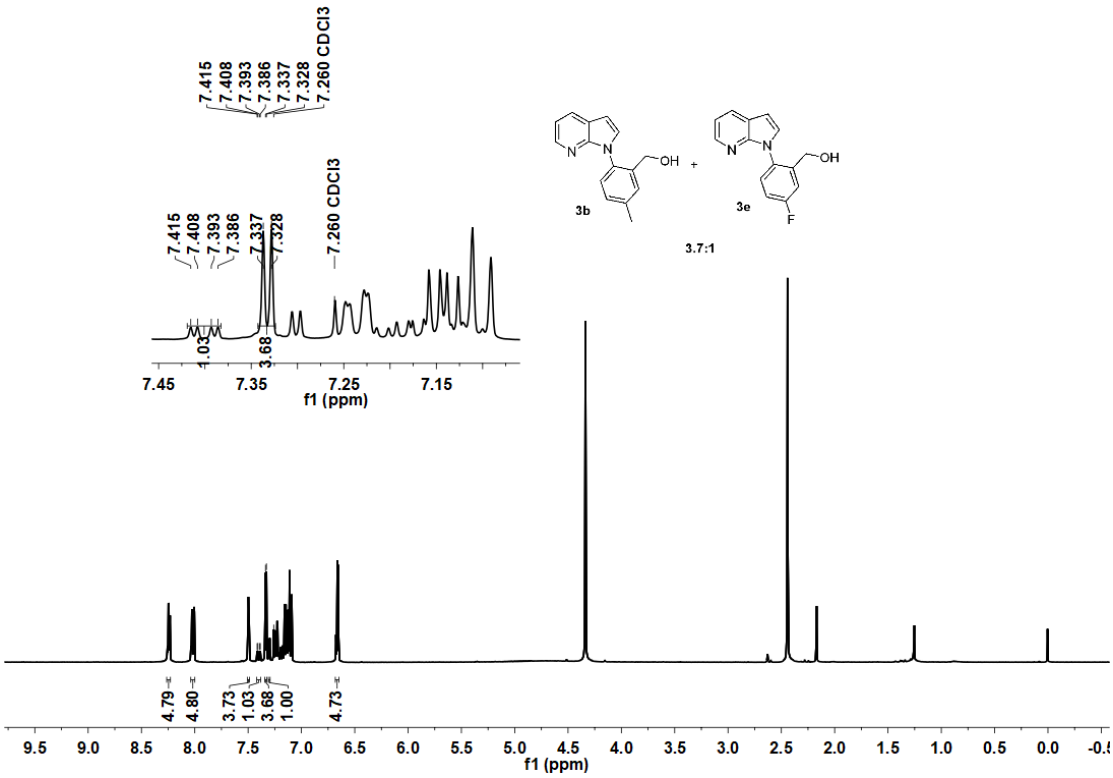
A mixture of **1a** (0.2 mmol), **2a** (0.6 mmol, 3 equiv), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), $AgSbF_6$ (20 mol %), NaH_2PO_4 (20 mol %) were dissolved in DCE: D_2O (10: 1) (2 mL) in sealed tube and the mixture was stirred at 60 ℃ for 2 h. The solvent was removed under reduced pressure to give the residue which was purified the residue by silica gel chromatograph to give **1a-d_n and 3a**.



(b) Competitive experiment:



A mixture of **1b** (0.1 mmol), **1e** (0.1 mmol), **2a** (0.1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), $AgSbF_6$ (20 mol %), NaH_2PO_4 (20 mol %) were dissolved in DCE (1 ml) in sealed tube and the mixture was stirred at 60 ℃ for 36 h. The solvent was removed under reduced pressure and the residue was purified the residue by silica gel chromatograph to give **3b** and **3e** (3.7:1).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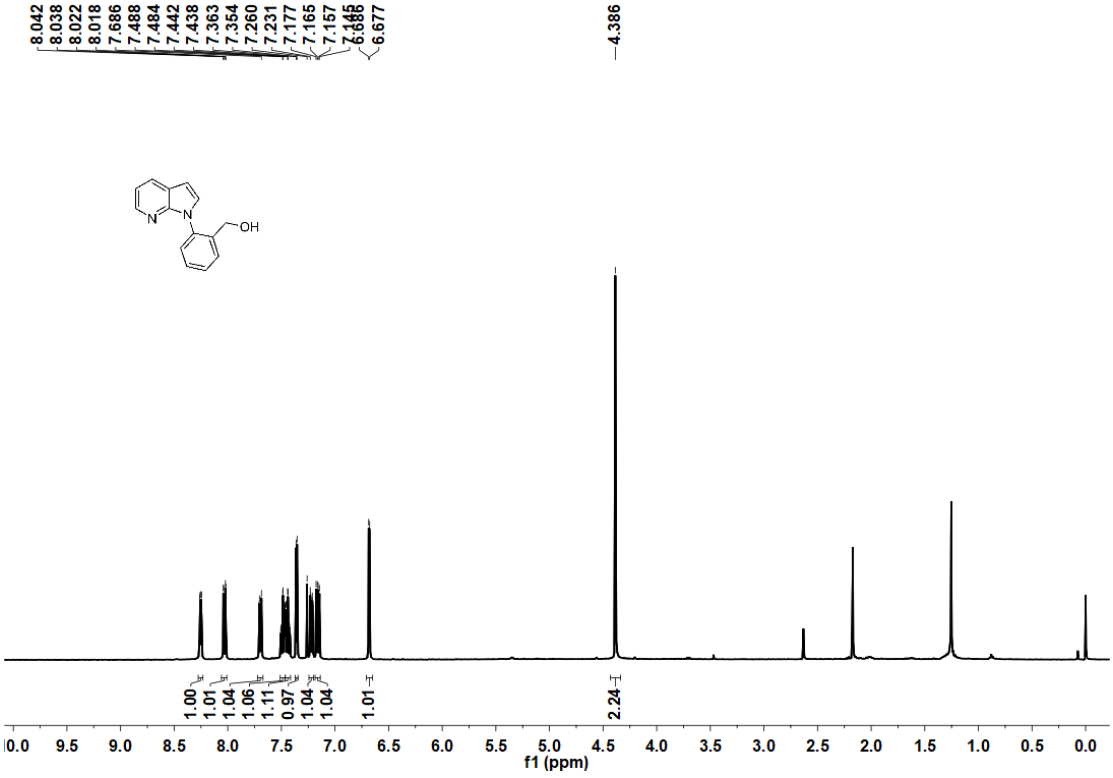
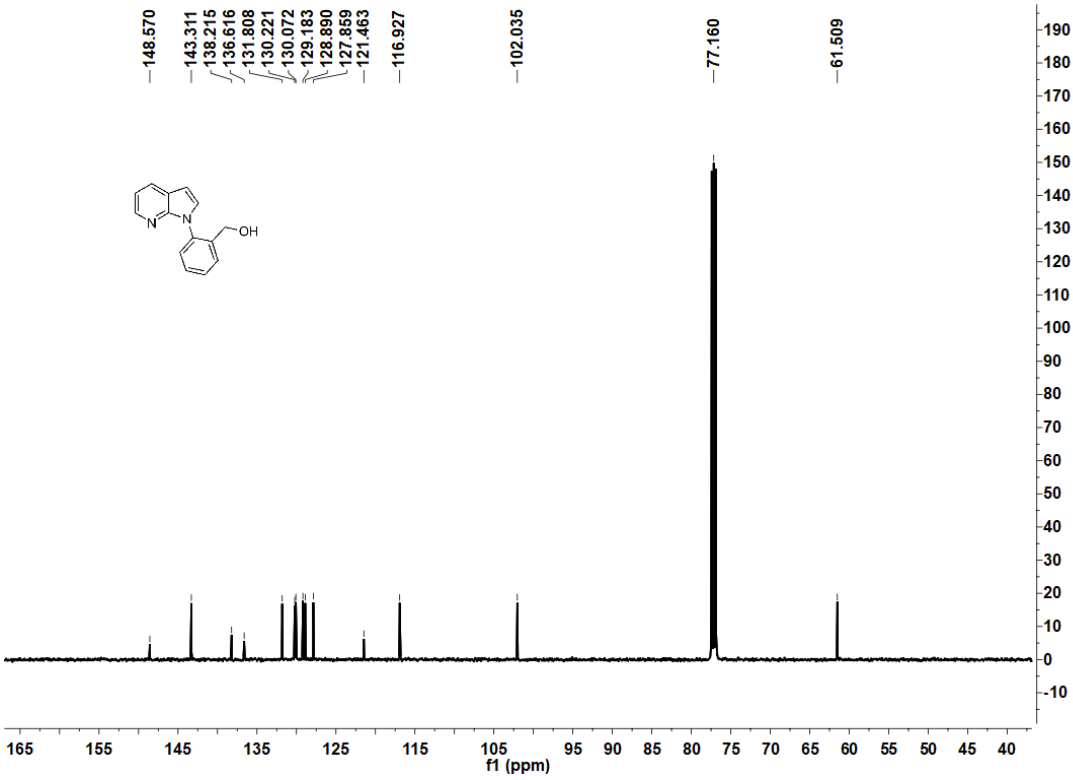
7.408
7.393
7.386
7.337
7.328
7.260 CDCl3
1.03
3.68
7.45
7.35
7.25
7.15
f1 (ppm)
OH
3b
3e
F
3.7:1
4.79
4.80
3.73
1.03
3.68
1.00
4.73
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

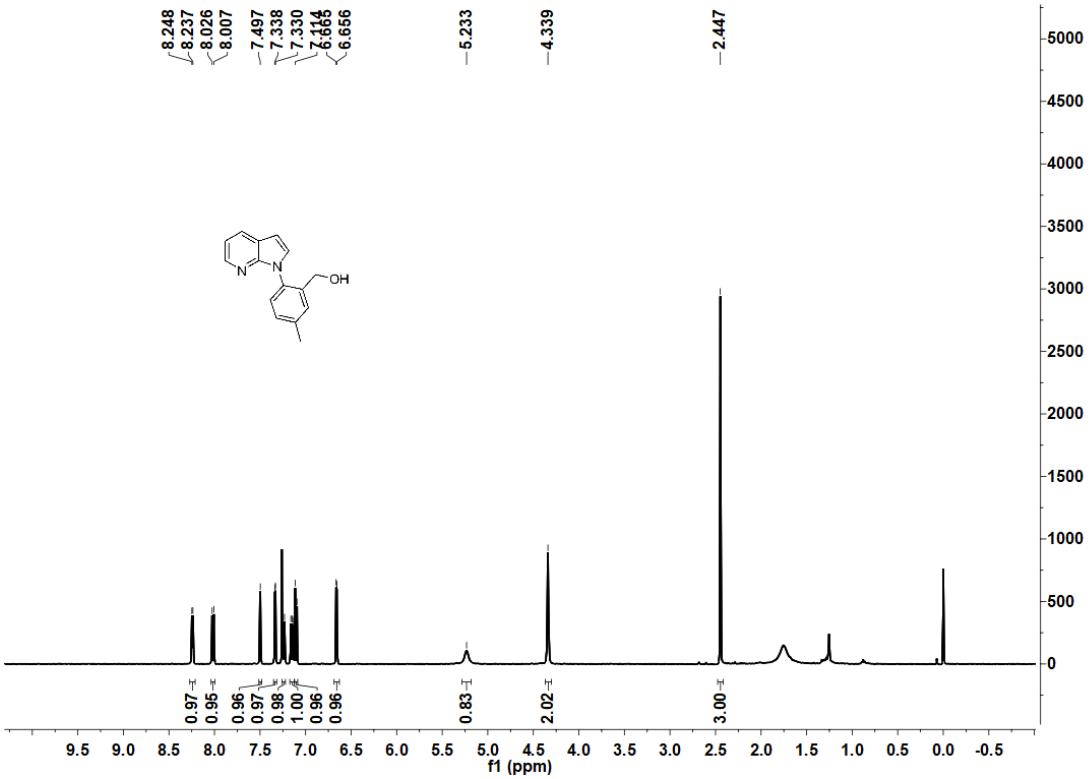
^{1}H and ^{13}C NMR Spectrum of Compounds

Compound 3a





Compound 3b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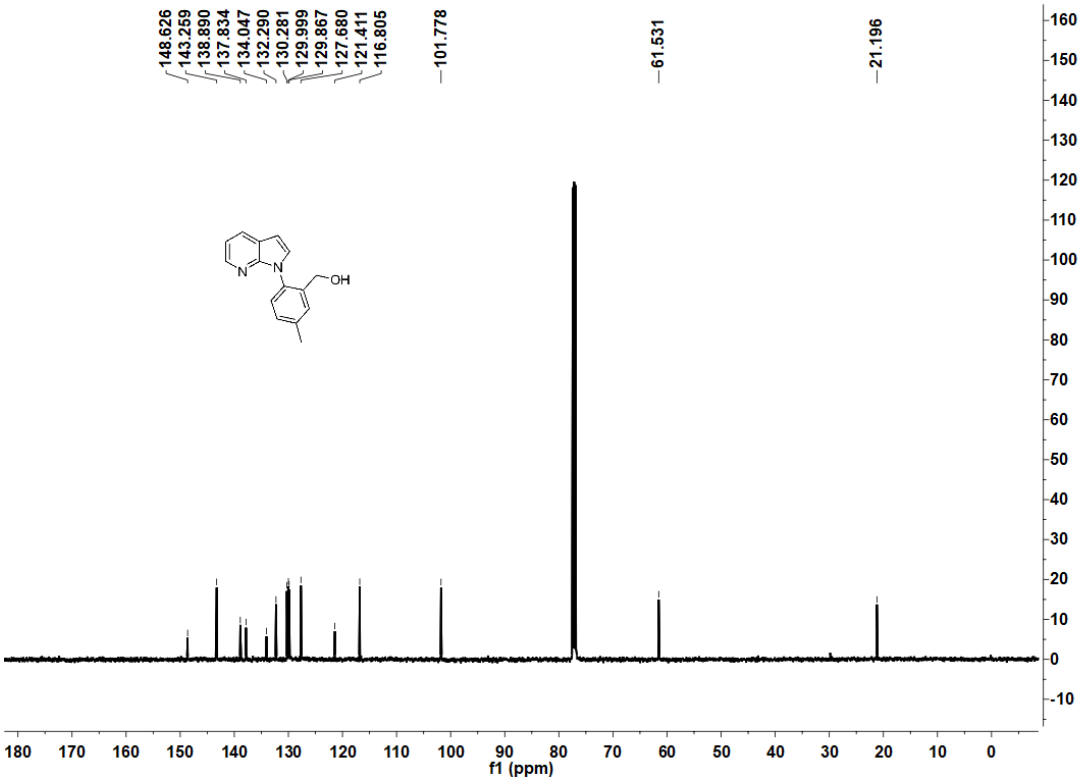
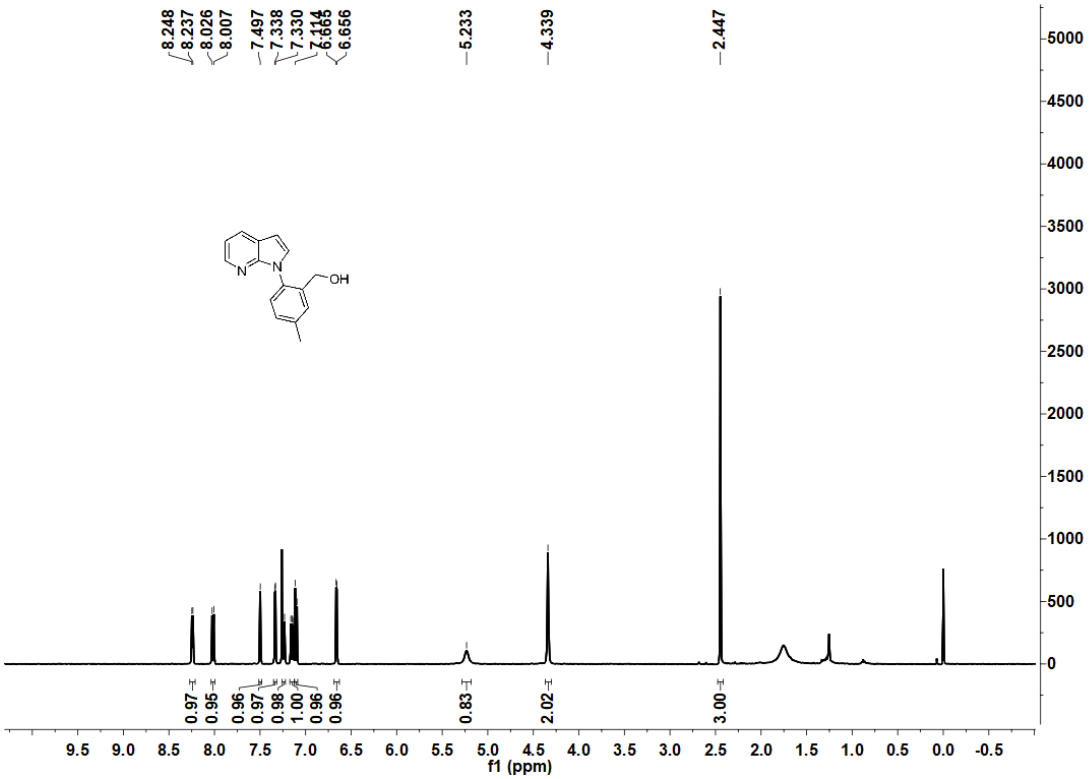
8.237
8.026
8.007
7.497
7.338
7.330
7.114
6.665
6.656
5.233
4.339
2.447
OH
0.97
0.95
0.96
0.97
0.98
1.00
0.96
0.96
0.83
2.02
3.00
f1 (ppm)


148.626
143.259
138.890
137.834
134.047
132.290
130.281
129.999
129.867
127.680
121.411
116.805
101.778
61.531
21.196
OH
f1 (ppm)

Compound 3c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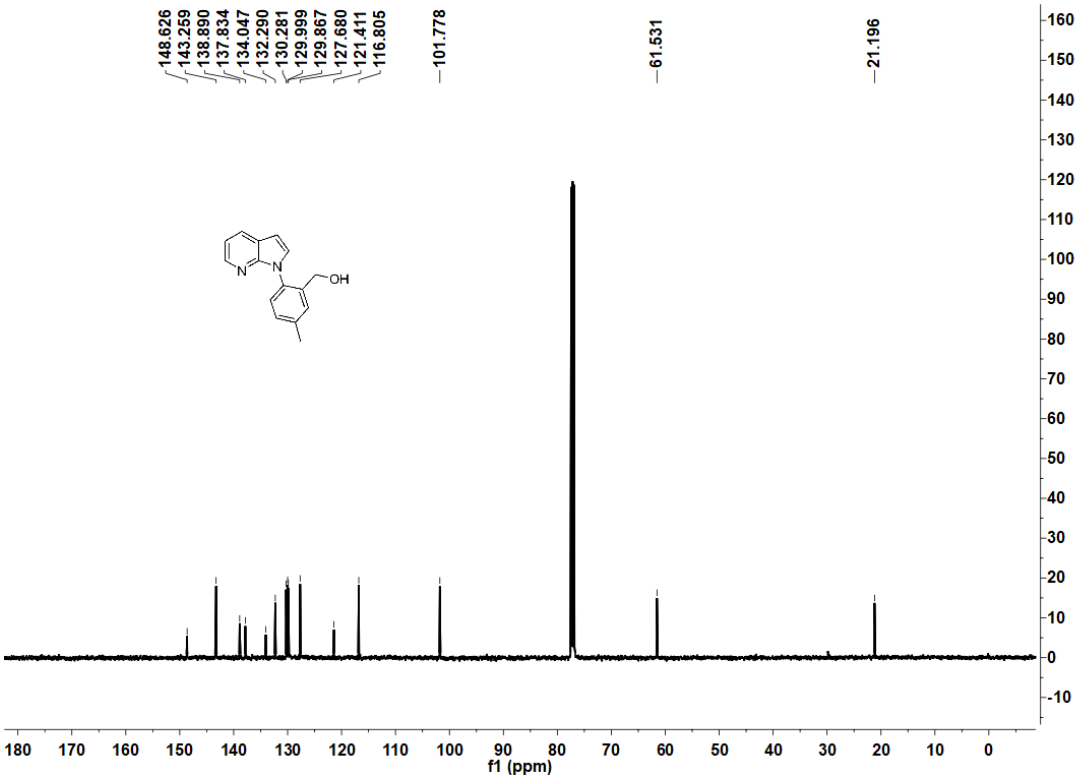
8.237
8.026
8.007
7.497
7.338
7.330
7.114
6.665
6.656
5.233
4.339
2.447
OH
0.97
0.95
0.96
0.97
0.98
1.00
0.96
0.96
0.83
2.02
3.00
f1 (ppm)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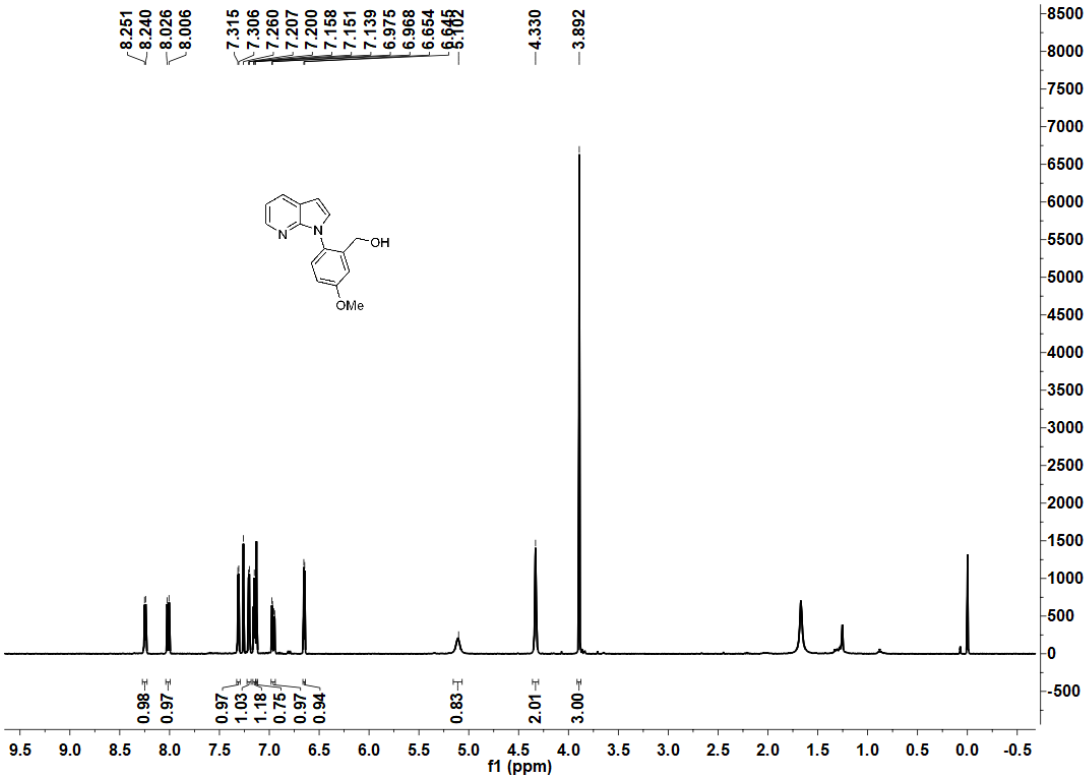
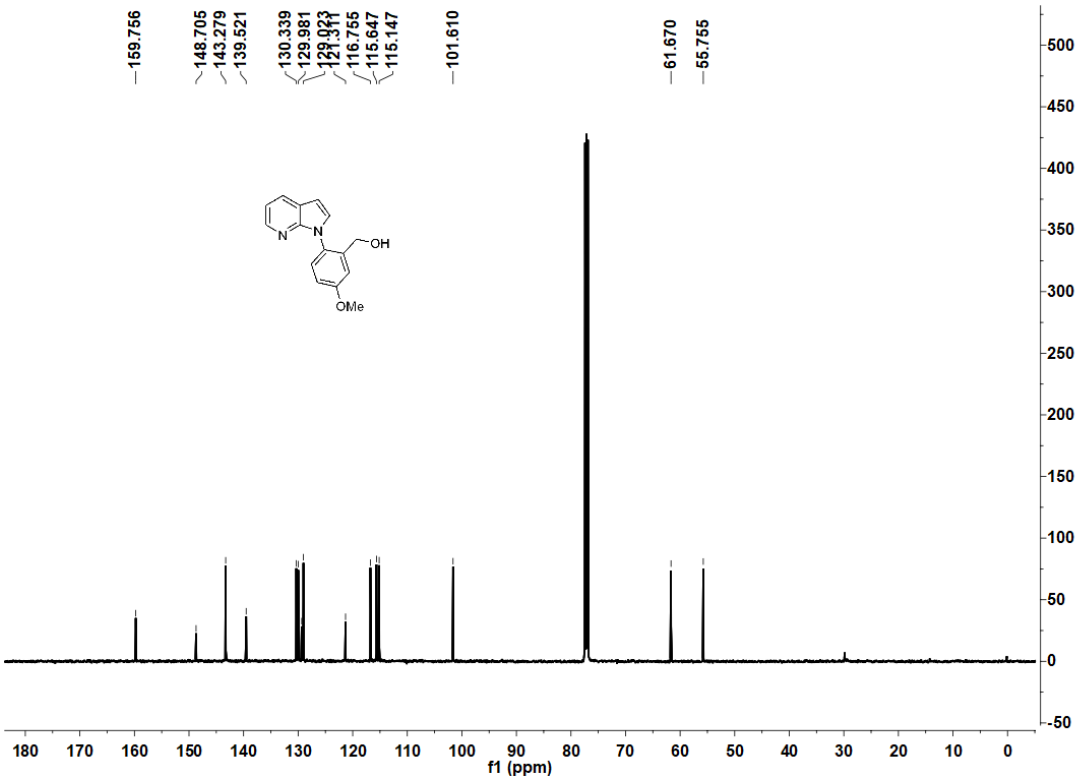
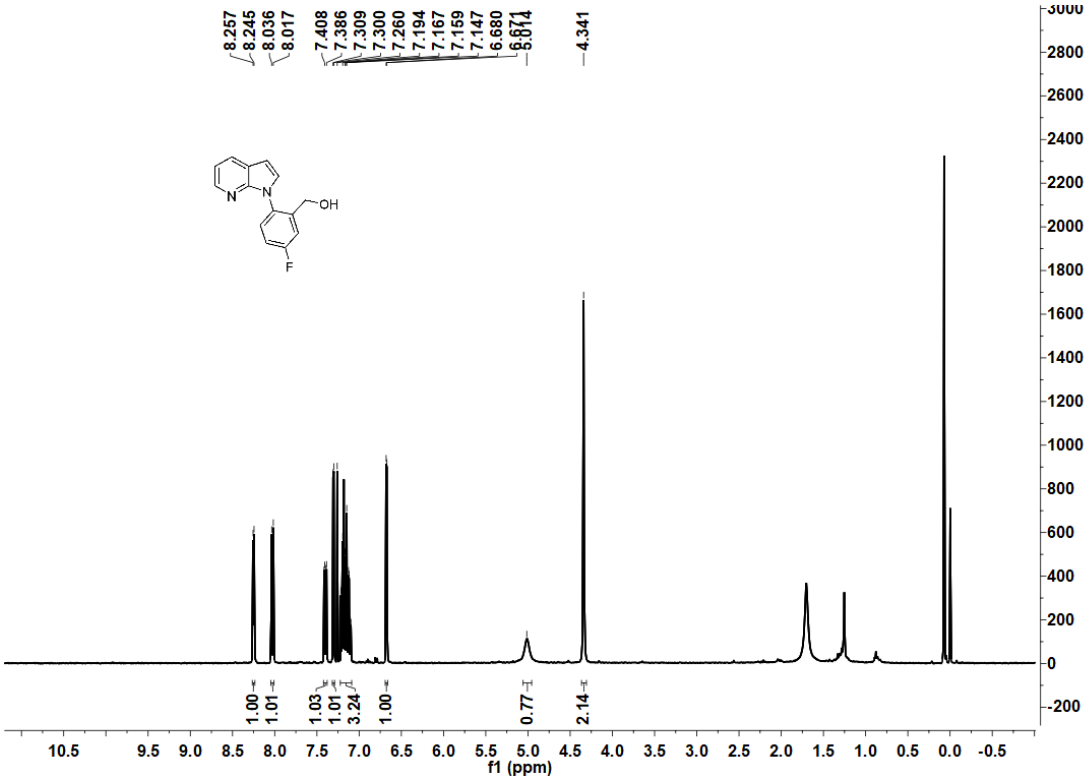
143.259
138.890
137.834
134.047
132.290
130.281
129.999
129.867
127.680
121.411
116.805
101.778
61.531
21.196
OH
f1 (ppm)

Compound 3d


8.251
8.240
8.026
8.006
7.315
7.306
7.260
7.207
7.200
7.158
7.151
7.139
6.975
6.968
6.654
6.645
5.102
4.330
3.892
OH
OMe
0.98
0.97
0.97
1.03
1.18
0.75
0.97
0.94
0.83
2.01
3.00
f1 (ppm)


159.756
148.705
143.279
139.521
130.339
129.981
129.023
121.311
116.755
115.647
115.147
101.610
61.670
55.755
OH
OMe
f1 (ppm)

Compound 3e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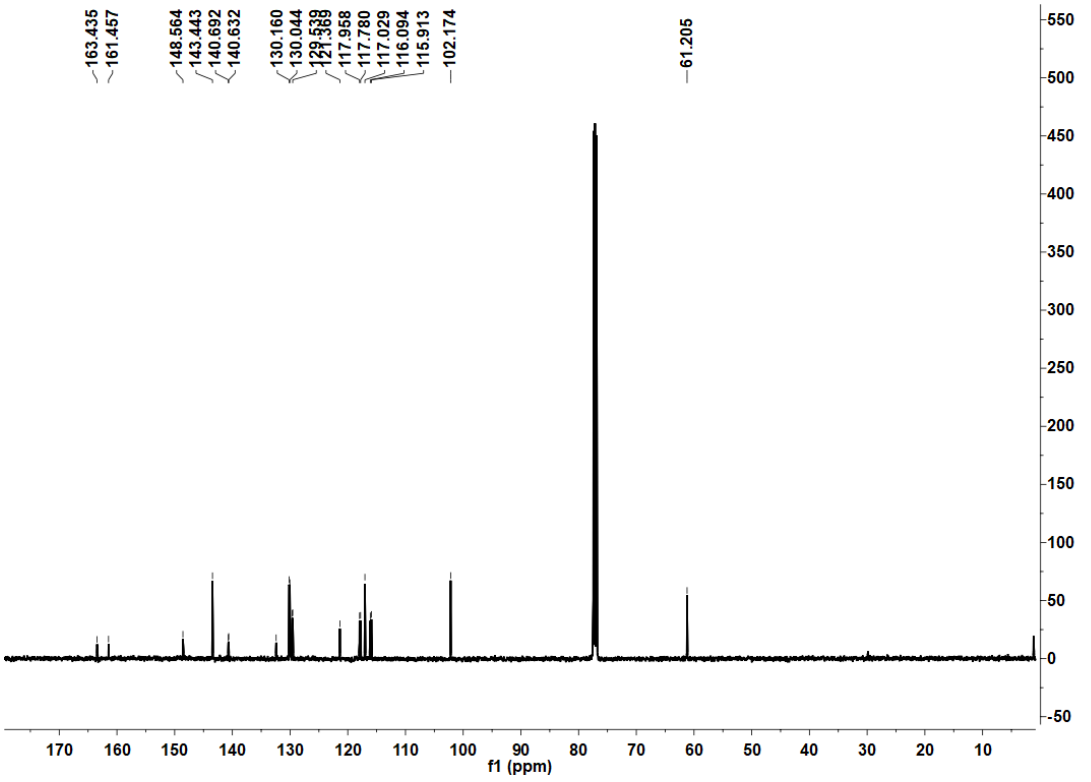
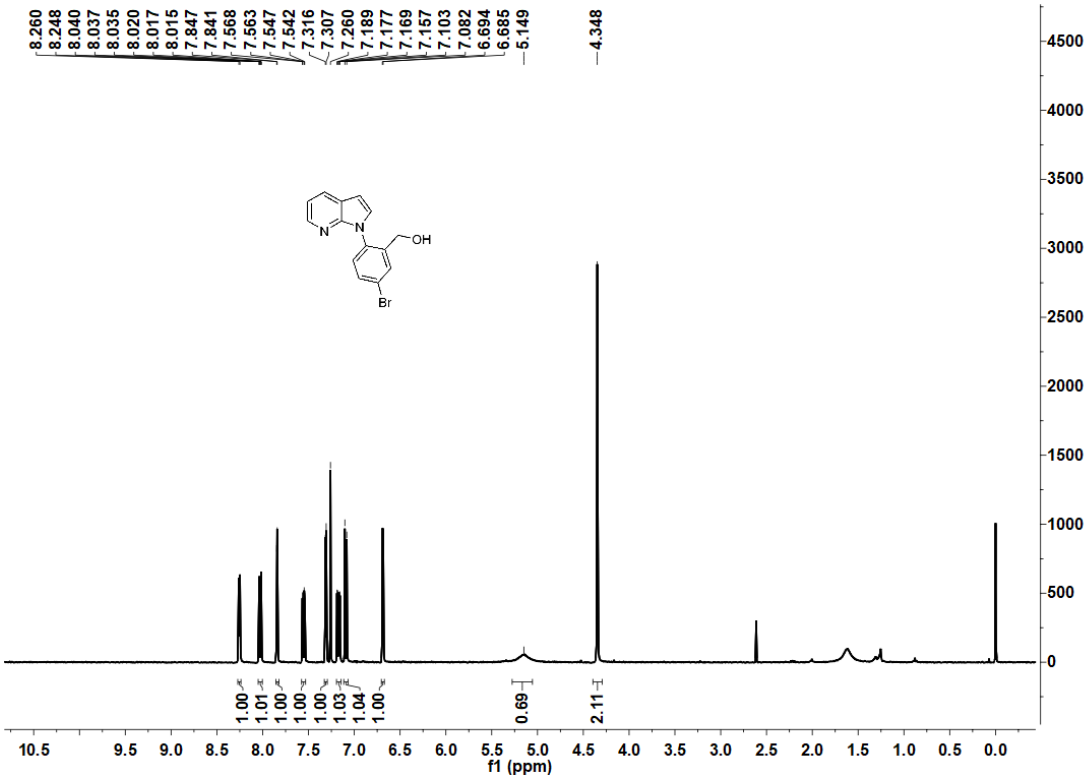
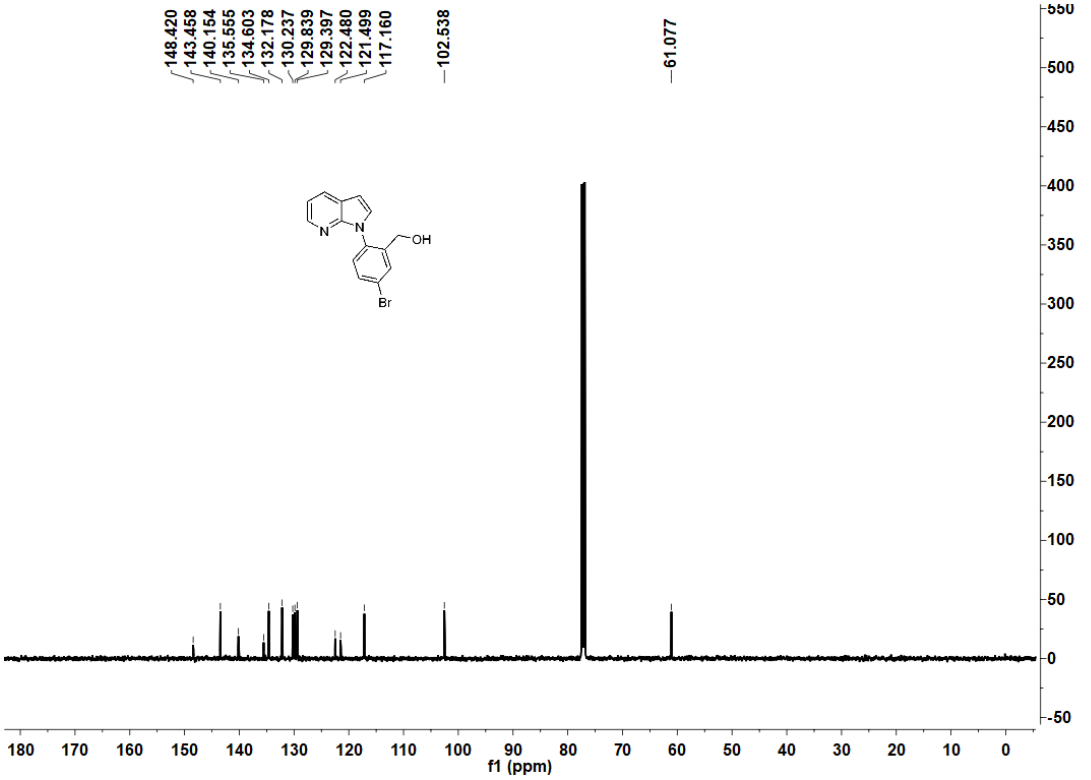
8.245
8.036
8.017
7.408
7.386
7.309
7.300
7.260
7.194
7.167
7.159
7.147
6.680
6.671
6.614
4.341
OH
F
1.00
1.01
1.03
1.01
3.24
1.00
0.77
2.14
f1 (ppm)

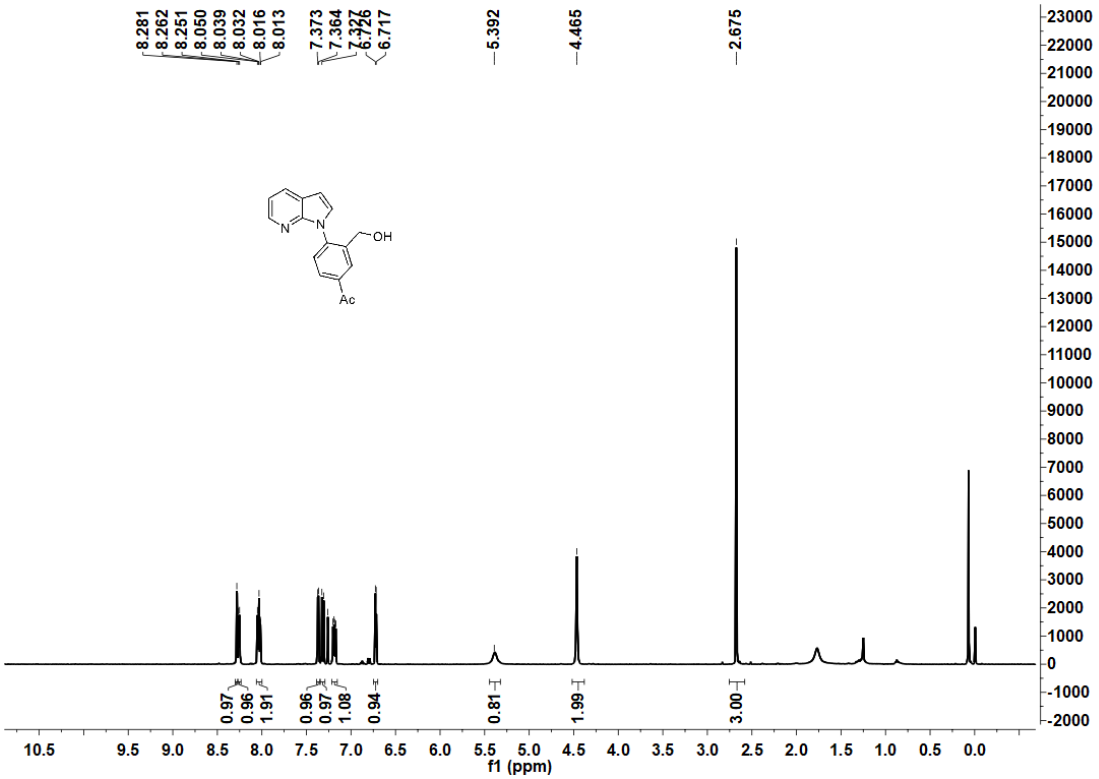

163.435
161.457
148.564
143.443
140.692
140.632
130.160
130.044
129.539
121.389
117.958
117.780
117.029
116.094
115.913
102.174
61.205
f1 (ppm)

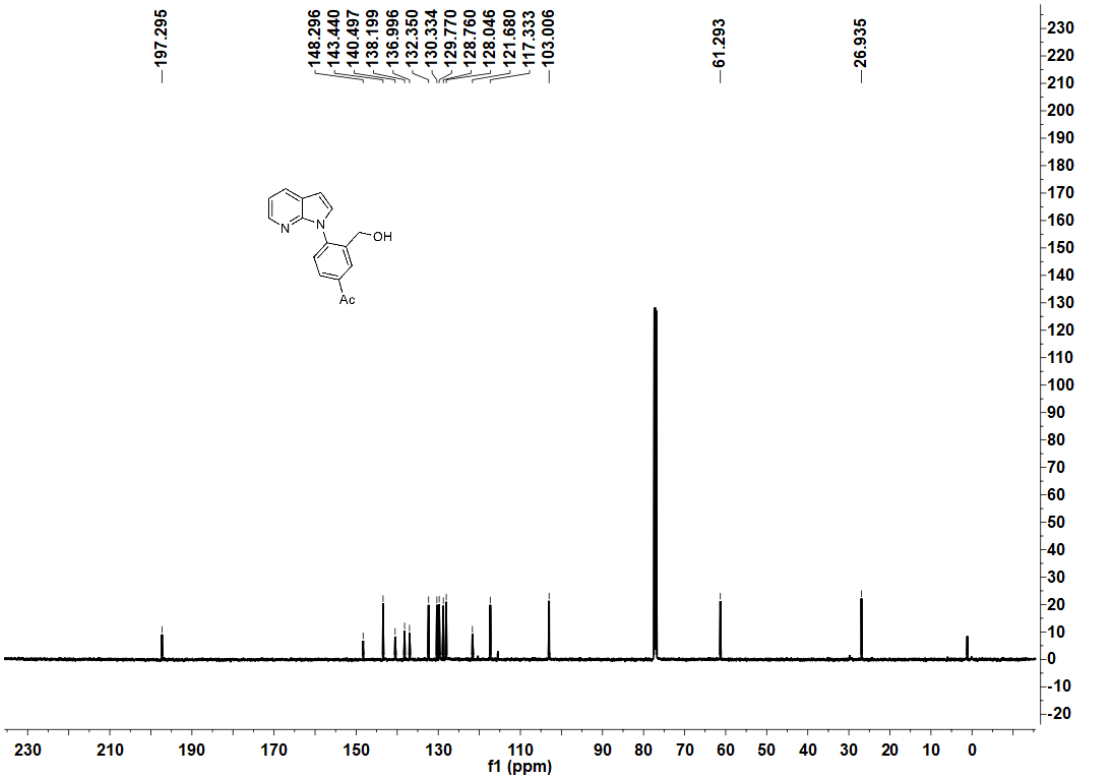
Compound 3f


8.260
8.248
8.040
8.037
8.035
8.020
8.017
8.015
7.847
7.841
7.568
7.563
7.547
7.542
7.316
7.307
7.260
7.189
7.177
7.169
7.157
7.103
7.082
6.694
6.685
5.149
4.348
OH
Br
1.00
1.01
1.00
1.00
1.00
1.03
1.04
1.00
0.69
2.11
f1 (ppm)

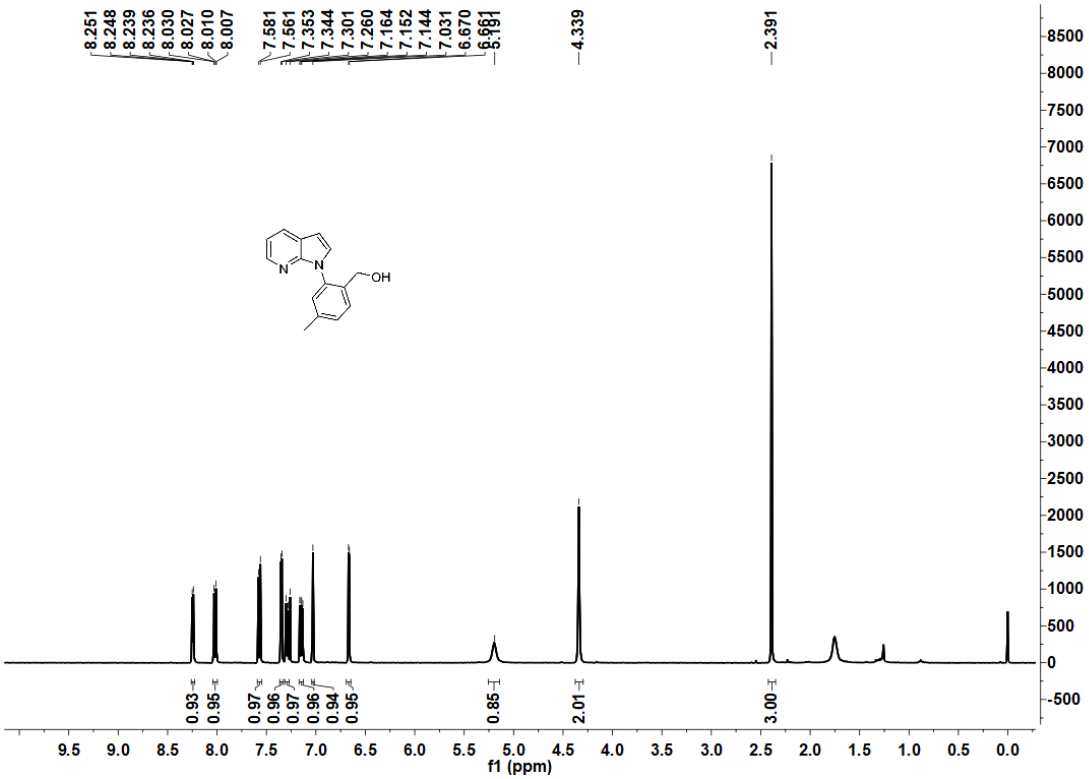

148.420
143.458
140.154
135.555
134.603
132.178
130.237
129.839
129.397
122.480
121.499
117.160
102.538
61.077
OH
Br
f1 (ppm)

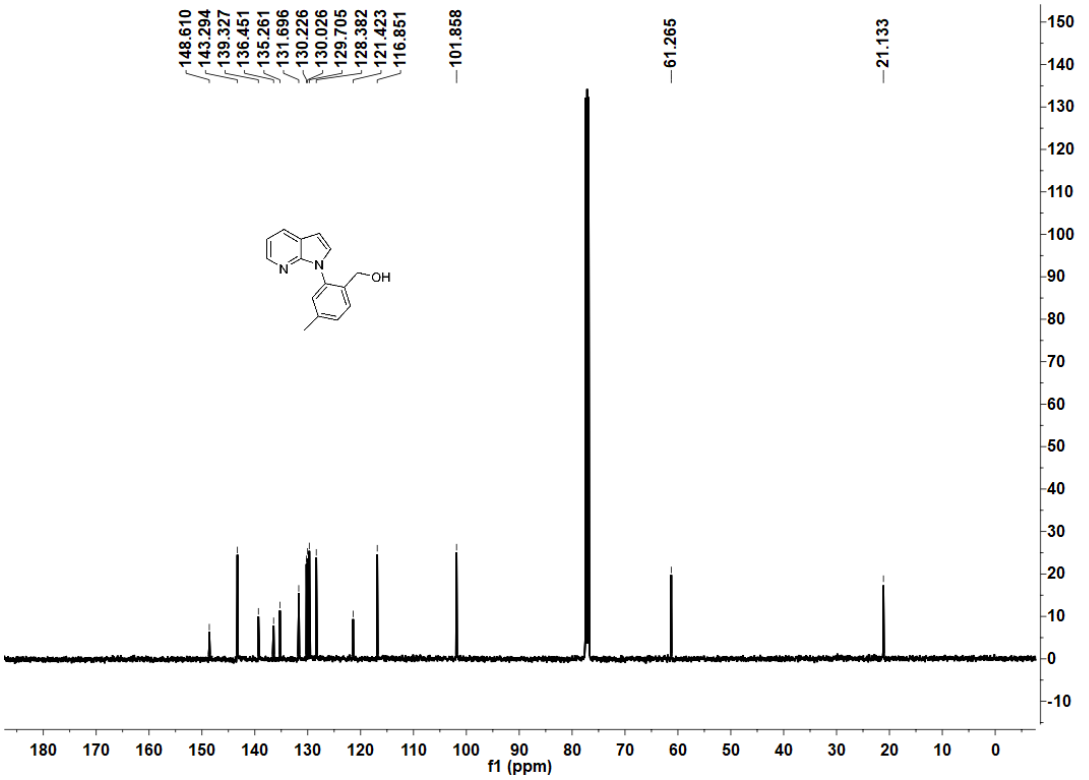
Compound 3g


8.281
8.262
8.251
8.050
8.039
8.032
8.016
8.013
7.373
7.364
6.726
6.717
5.392
4.465
2.675
OH
Ac
0.97
0.96
1.91
0.96
0.97
1.08
0.94
0.81
1.99
3.00
f1 (ppm)

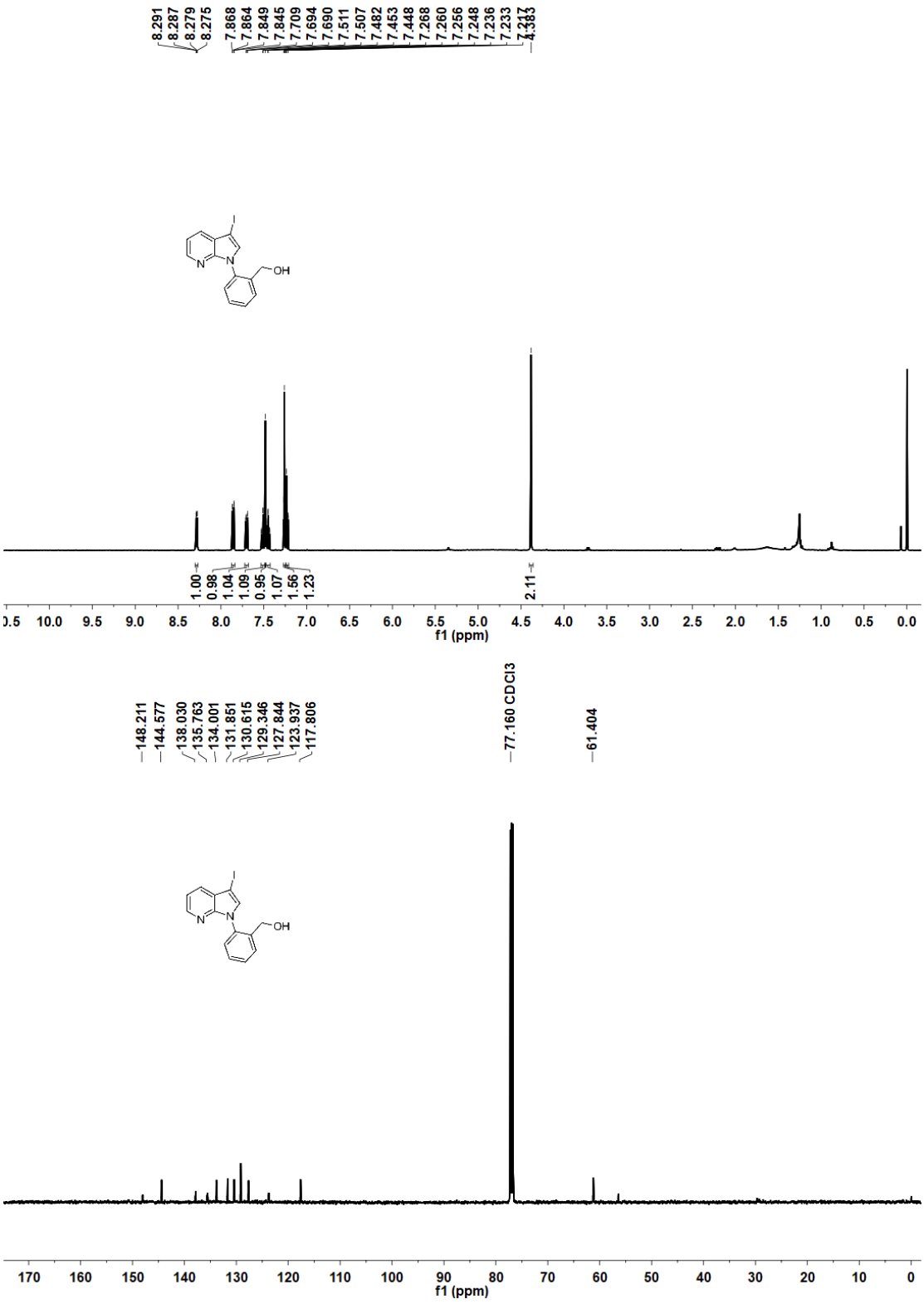

197.295
148.296
143.440
140.497
138.199
136.996
132.350
130.334
129.770
128.760
128.046
121.680
117.333
103.006
61.293
26.935
OH
Ac
f1 (ppm)

Compound 3h

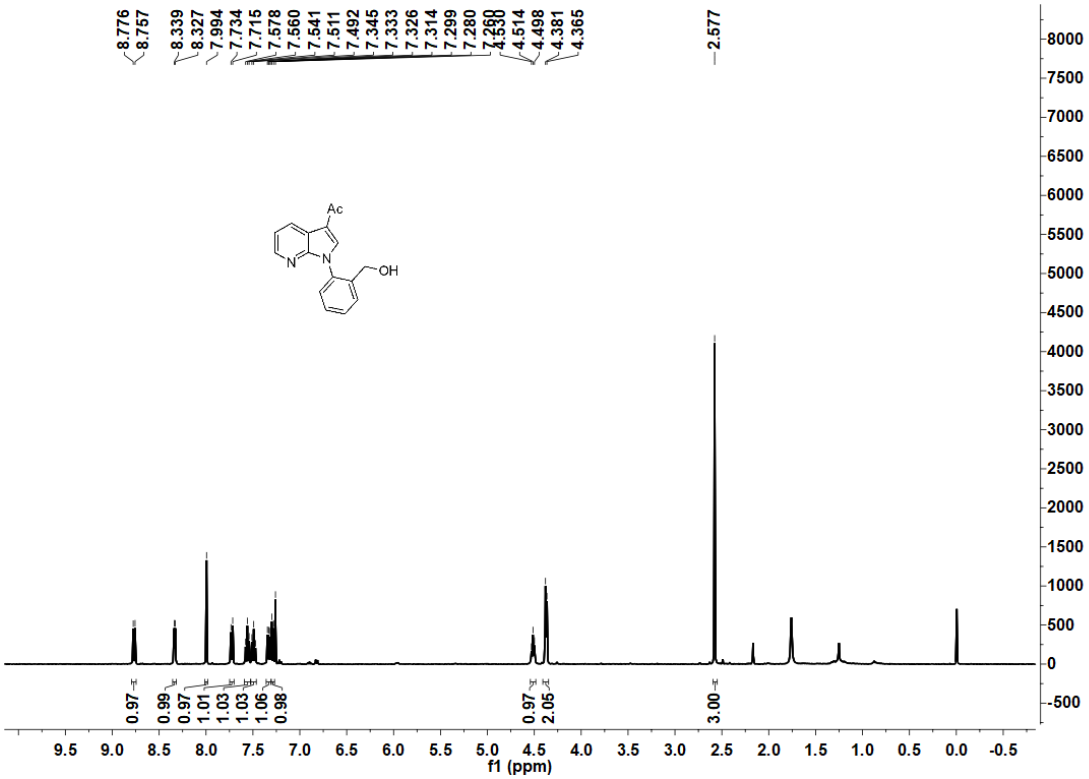

8.251
8.248
8.239
8.236
8.030
8.027
8.010
8.007
7.581
7.561
7.353
7.344
7.301
7.260
7.164
7.152
7.144
7.031
6.670
5.191
4.339
2.391
OH
0.93
0.95
0.97
0.96
0.97
0.96
0.94
0.95
0.85
2.01
3.00
f1 (ppm)

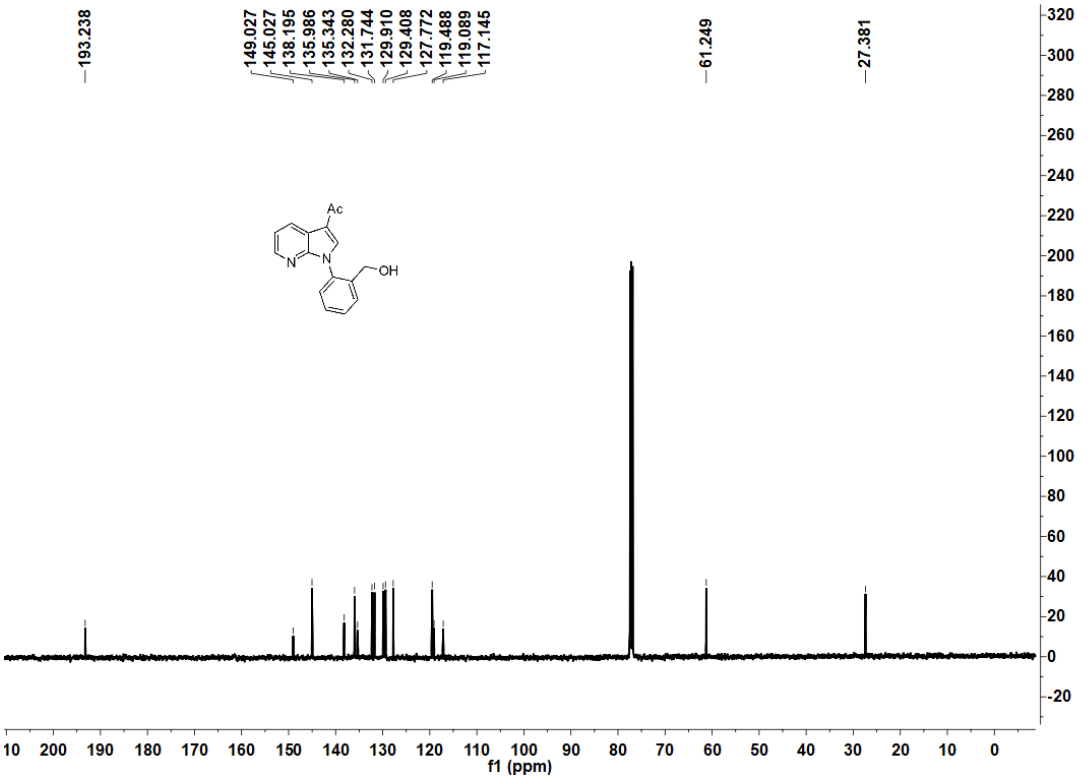

148.610
143.294
139.327
136.451
135.261
131.696
130.226
130.026
129.705
128.382
121.423
116.851
101.858
61.265
21.133
OH
f1 (ppm)

Compound 3i

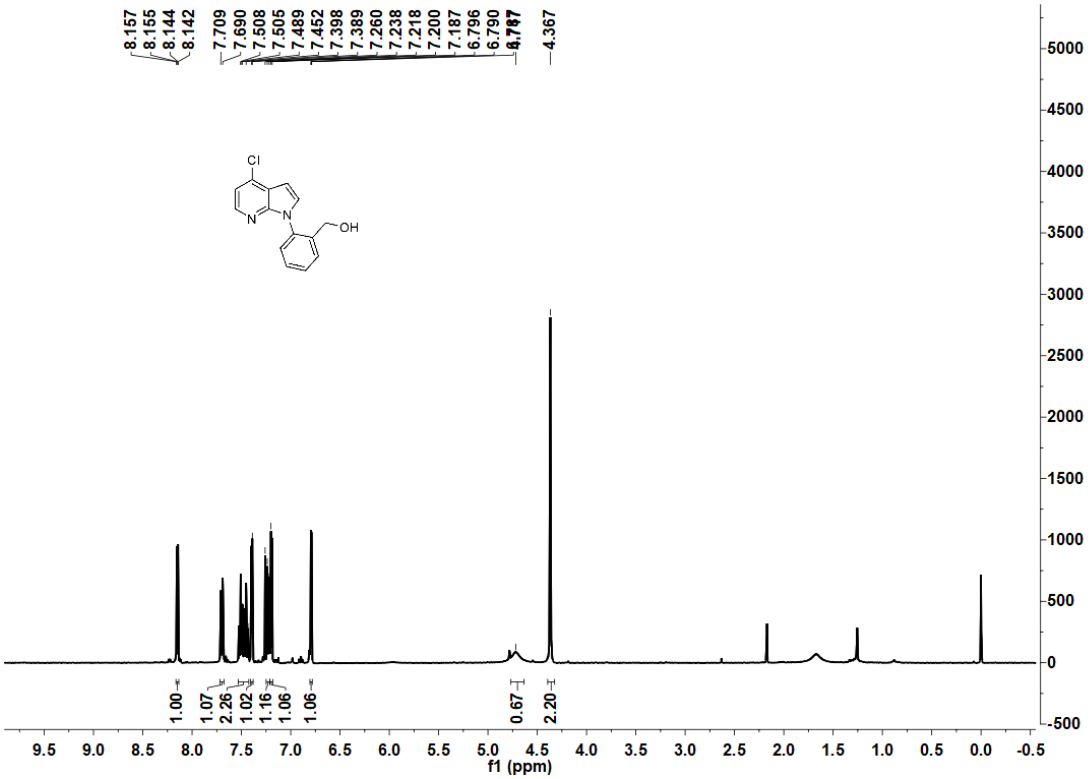

8.291
8.287
8.279
8.275
7.868
7.864
7.849
7.845
7.709
7.694
7.690
7.511
7.507
7.482
7.453
7.448
7.268
7.260
7.256
7.248
7.236
7.233
7.217
4.383
OH
1.00
0.98
1.04
1.09
0.95
1.07
1.56
1.23
2.11
f1 (ppm)
148.211
144.577
138.030
135.763
134.001
131.851
130.615
129.346
127.844
123.937
117.806
77.160 CDCl3
61.404
OH
f1 (ppm)

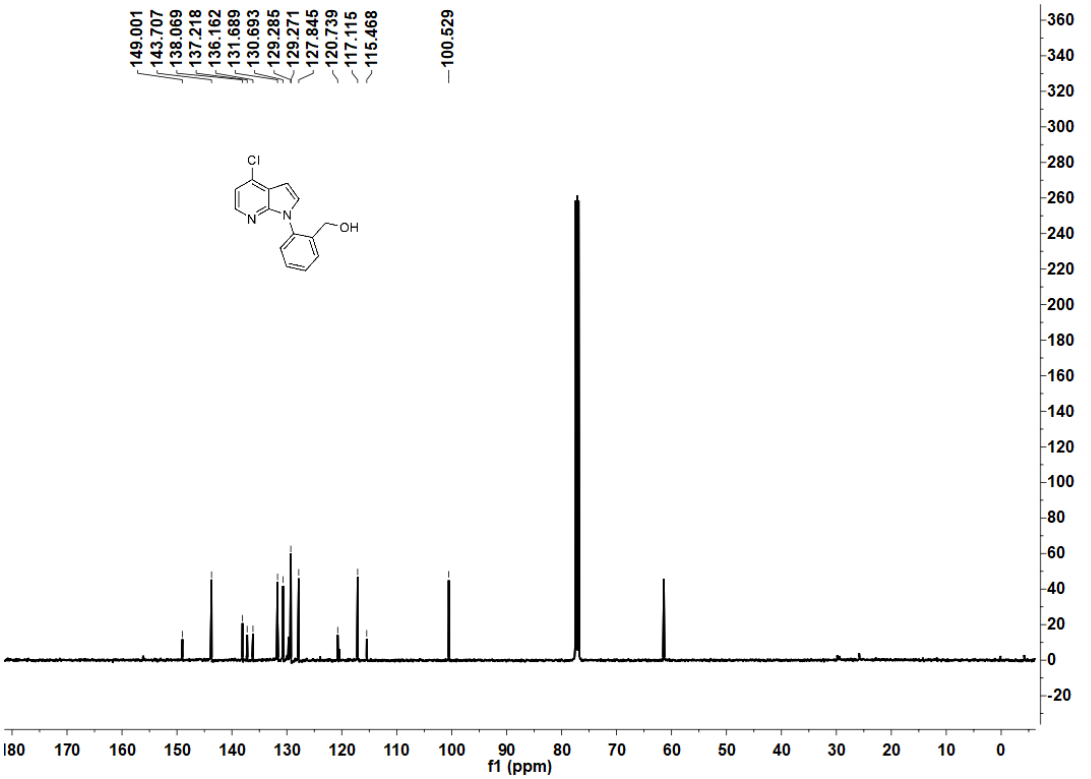
Compound 3j


8.776
8.757
8.339
8.327
7.994
7.734
7.715
7.578
7.560
7.541
7.511
7.492
7.345
7.333
7.326
7.314
7.299
7.280
7.260
4.530
4.514
4.498
4.381
4.365
2.577
Ac
OH
0.97
0.99
0.97
1.01
1.03
1.03
1.06
0.98
0.97
2.05
3.00
f1 (ppm)

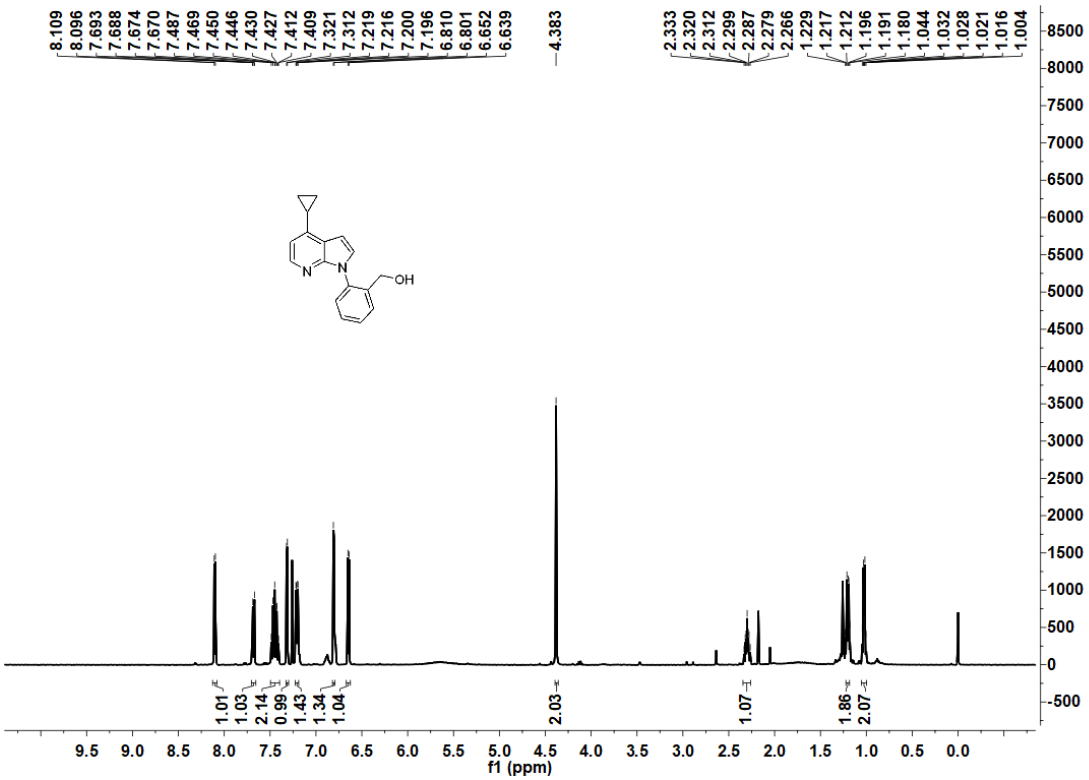

193.238
149.027
145.027
138.195
135.986
135.343
132.280
131.744
129.910
129.408
127.772
119.488
119.089
117.145
61.249
27.381
Ac
OH
f1 (ppm)

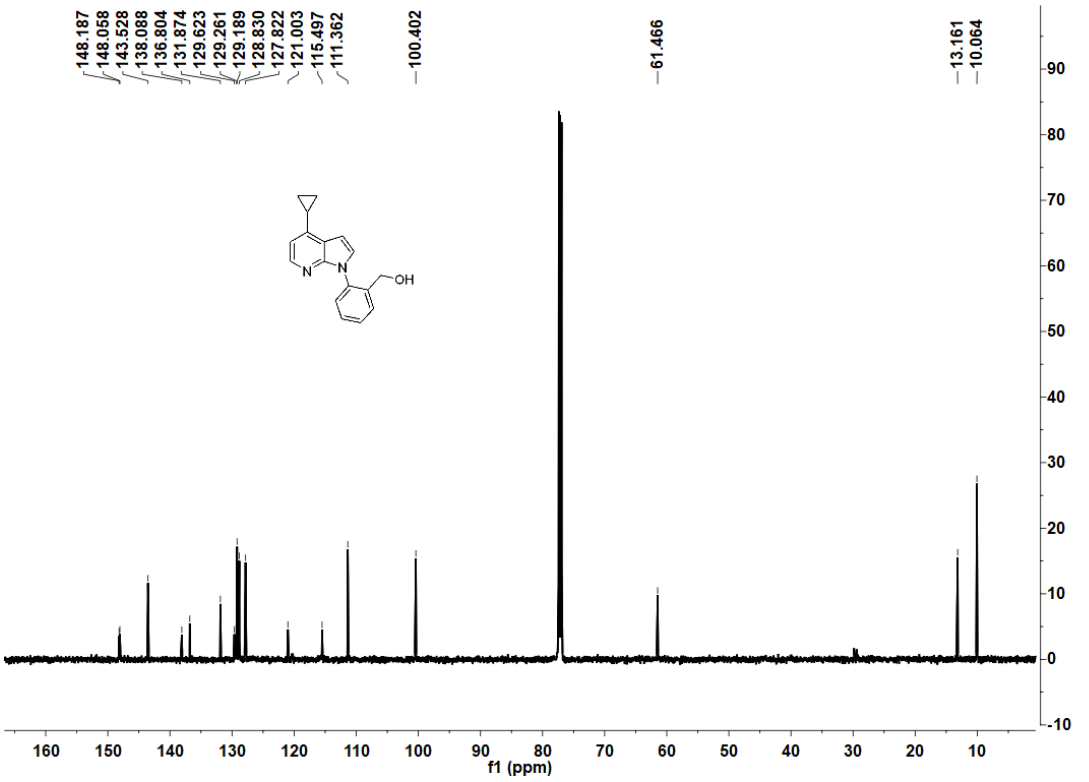
Compound 3k


8.157
8.155
8.144
8.142
7.709
7.690
7.508
7.505
7.489
7.452
7.398
7.389
7.260
7.238
7.218
7.200
7.187
6.796
6.790
4.367
Cl
N
OH
1.00
1.07
2.26
1.02
1.16
1.06
1.06
0.67
2.20
f1 (ppm)

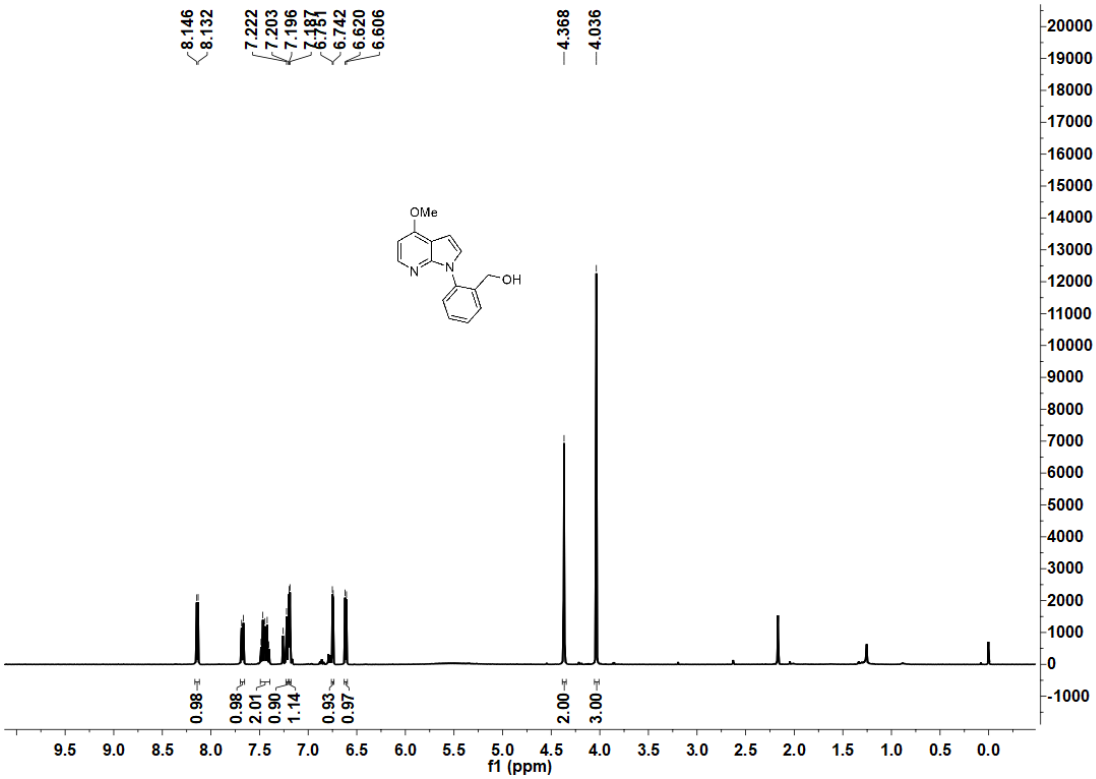

149.001
143.707
138.069
137.218
136.162
131.689
130.693
129.285
129.271
127.845
120.739
117.115
115.468
100.529
Cl
N
OH
f1 (ppm)

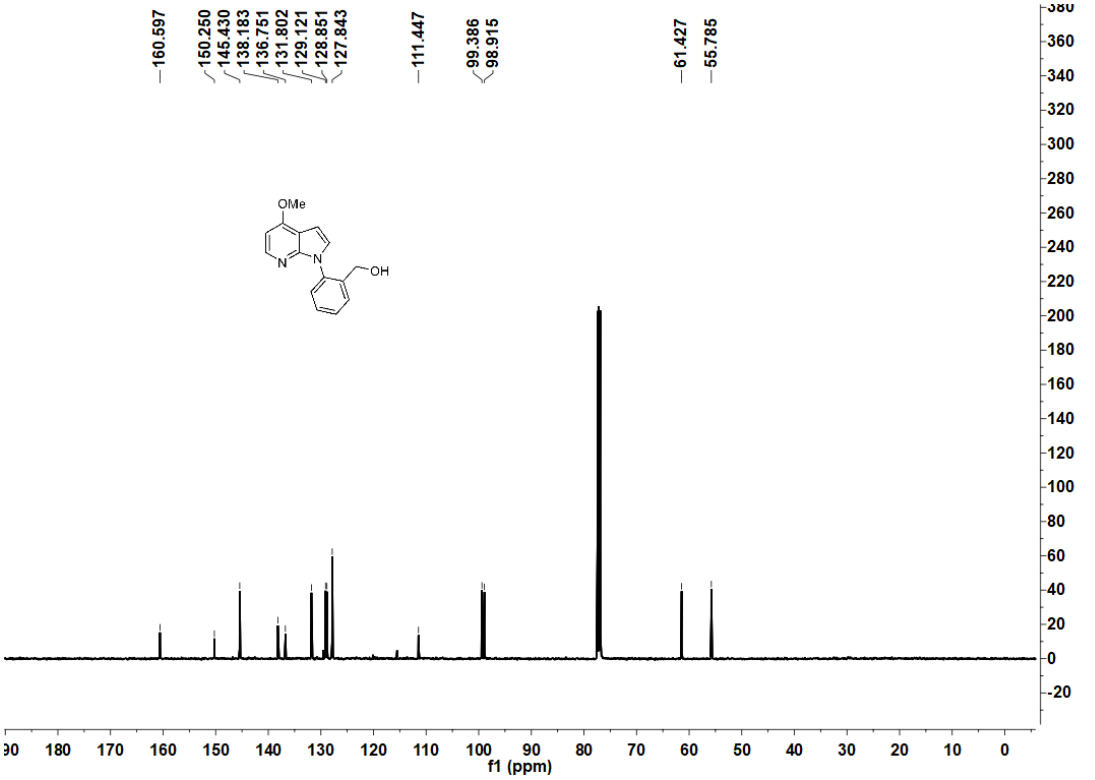
Compound 3l


8.109
8.096
7.693
7.688
7.674
7.670
7.487
7.469
7.450
7.446
7.430
7.427
7.412
7.409
7.321
7.312
7.219
7.216
7.200
7.196
6.810
6.801
6.652
6.639
4.383
2.333
2.320
2.312
2.299
2.287
2.279
2.266
1.229
1.217
1.212
1.196
1.191
1.180
1.044
1.032
1.028
1.021
1.016
1.004
OH
1.01
1.03
2.14
0.99
1.43
1.34
1.04
2.03
1.07
1.86
2.07
f1 (ppm)

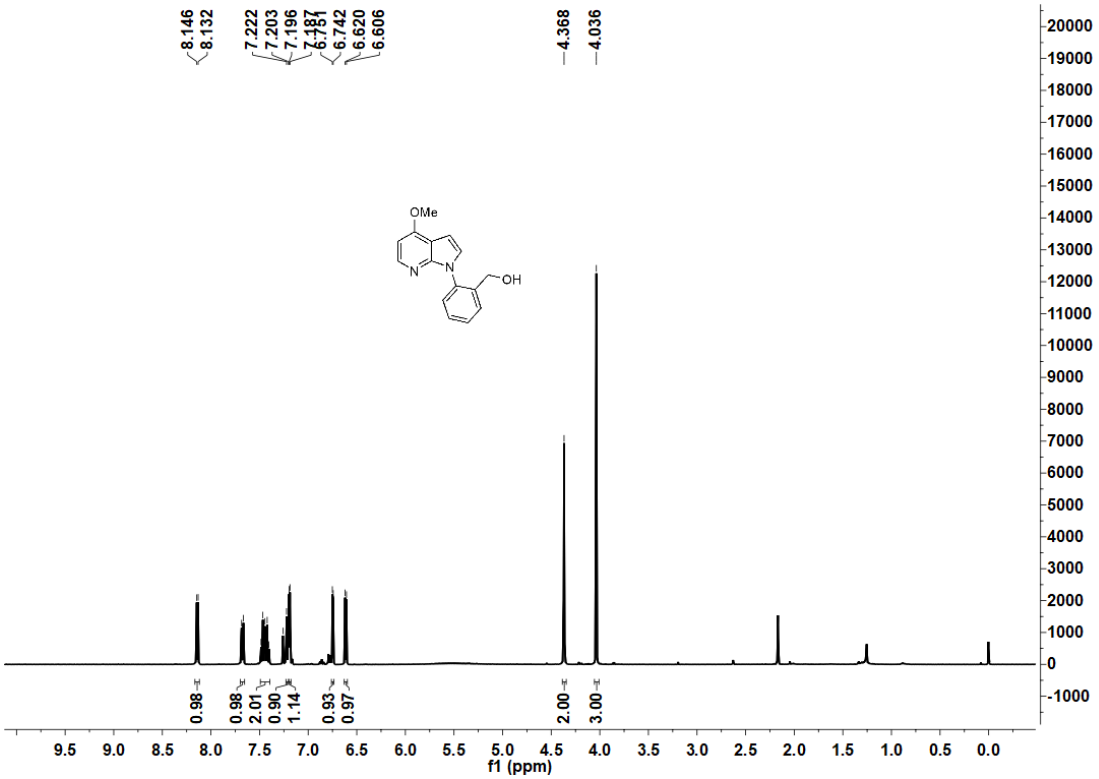

148.187
148.058
143.528
138.088
136.804
131.874
129.623
129.261
129.189
128.830
127.822
121.003
115.497
111.362
100.402
61.466
13.161
10.064
OH
f1 (ppm)

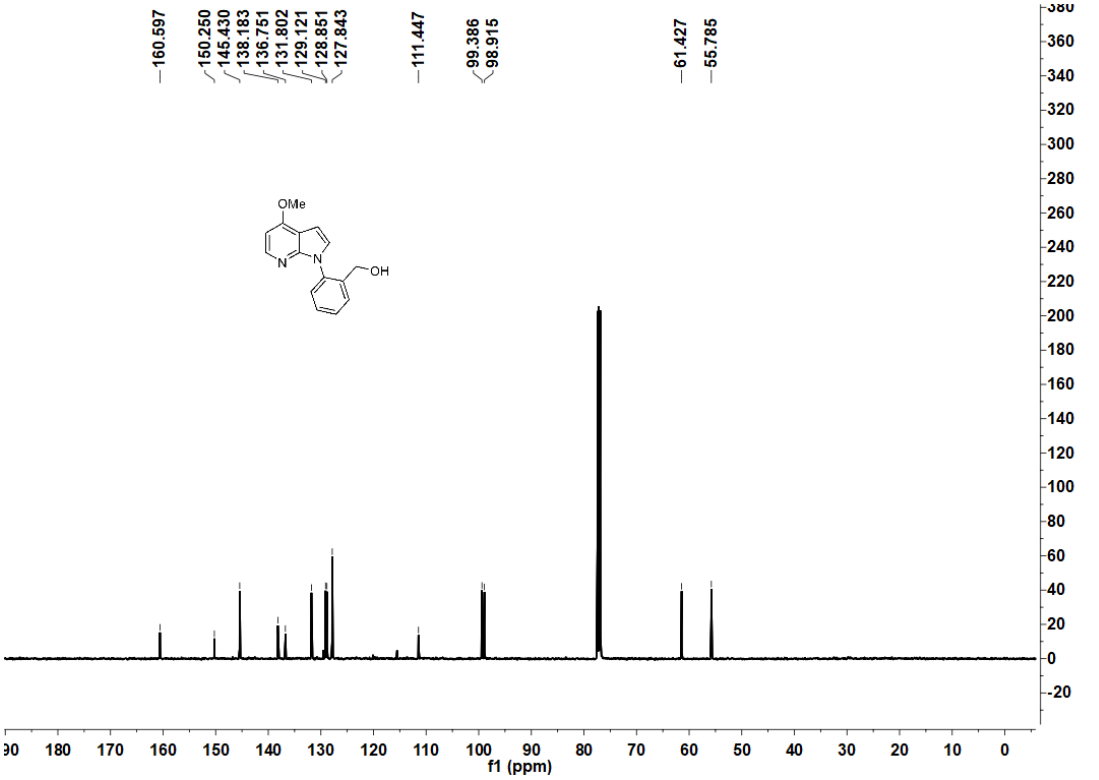
Compound 3m


8.146
8.132
7.222
7.203
7.196
6.742
6.620
6.606
4.368
4.036
OMe
OH
0.98
0.98
2.01
0.90
1.14
0.93
0.97
2.00
3.00
f1 (ppm)

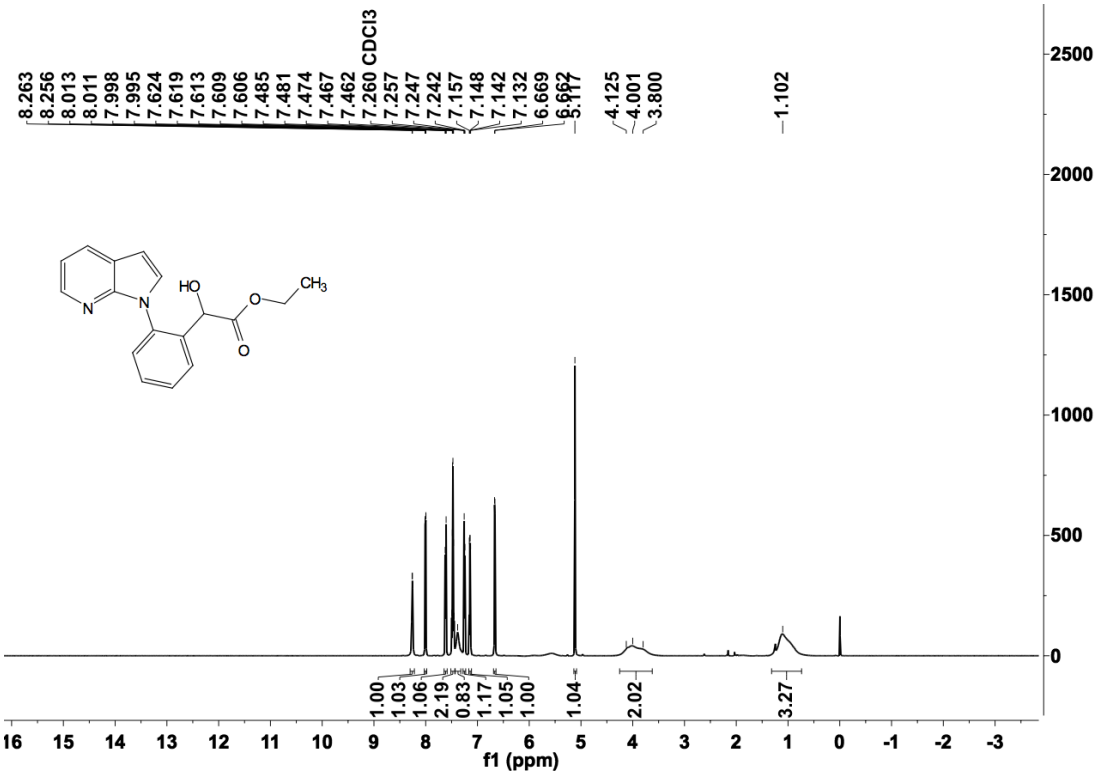

160.597
150.250
145.430
138.183
136.751
131.802
129.121
128.851
127.843
111.447
99.386
98.915
61.427
55.785
OMe
OH
f1 (ppm)

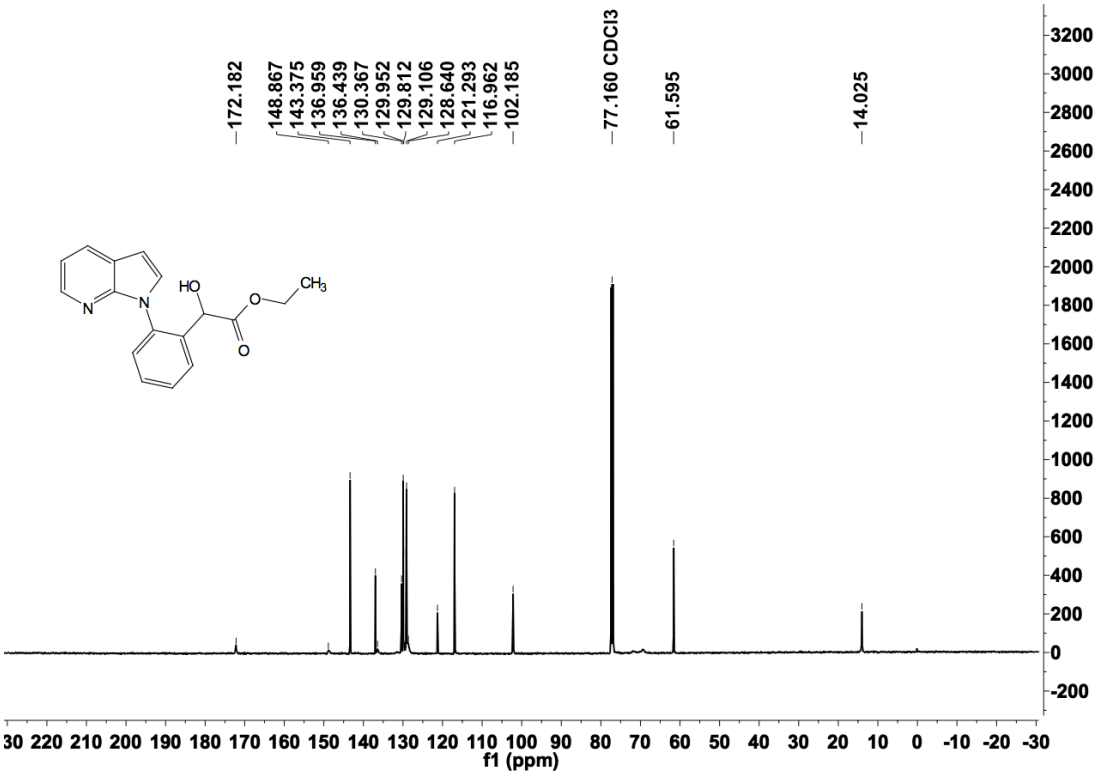
Compound 3n


8.146
8.132
7.222
7.203
7.196
7.181
6.742
6.620
6.606
4.368
4.036
OMe
OH
0.98
0.98
2.01
0.90
1.14
0.93
0.97
2.00
3.00
f1 (ppm)

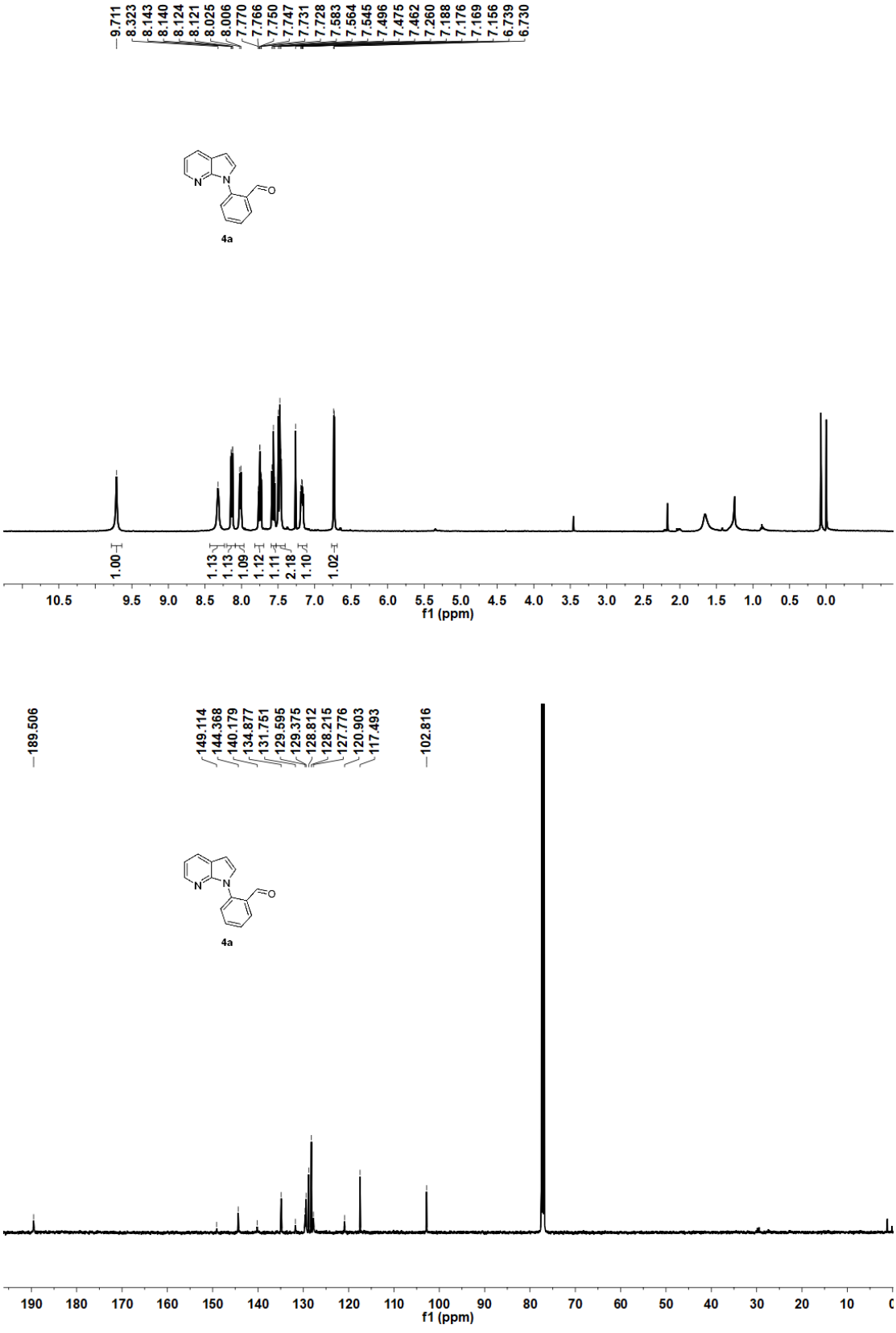

160.597
150.250
145.430
138.183
136.751
131.802
129.121
128.851
127.843
111.447
99.386
98.915
61.427
55.785
OMe
OH
f1 (ppm)

Compound 3q

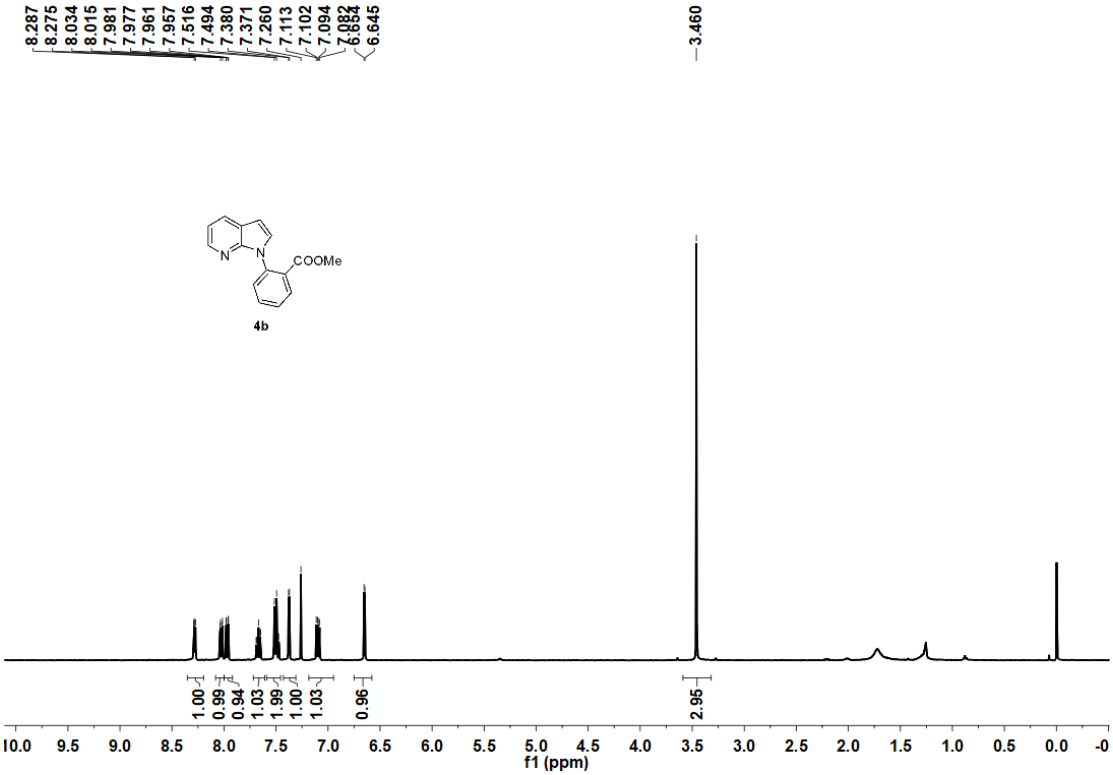

8.263
8.256
8.013
8.011
7.998
7.995
7.624
7.619
7.613
7.609
7.606
7.485
7.481
7.474
7.467
7.462
7.260 CDCl3
7.257
7.247
7.242
7.157
7.148
7.142
7.132
6.669
4.125
4.001
3.800
1.102
HO
O
CH3
O
N
N
1.00
1.03
1.06
2.19
0.83
1.17
1.05
1.00
1.04
2.02
3.27
f1 (ppm)

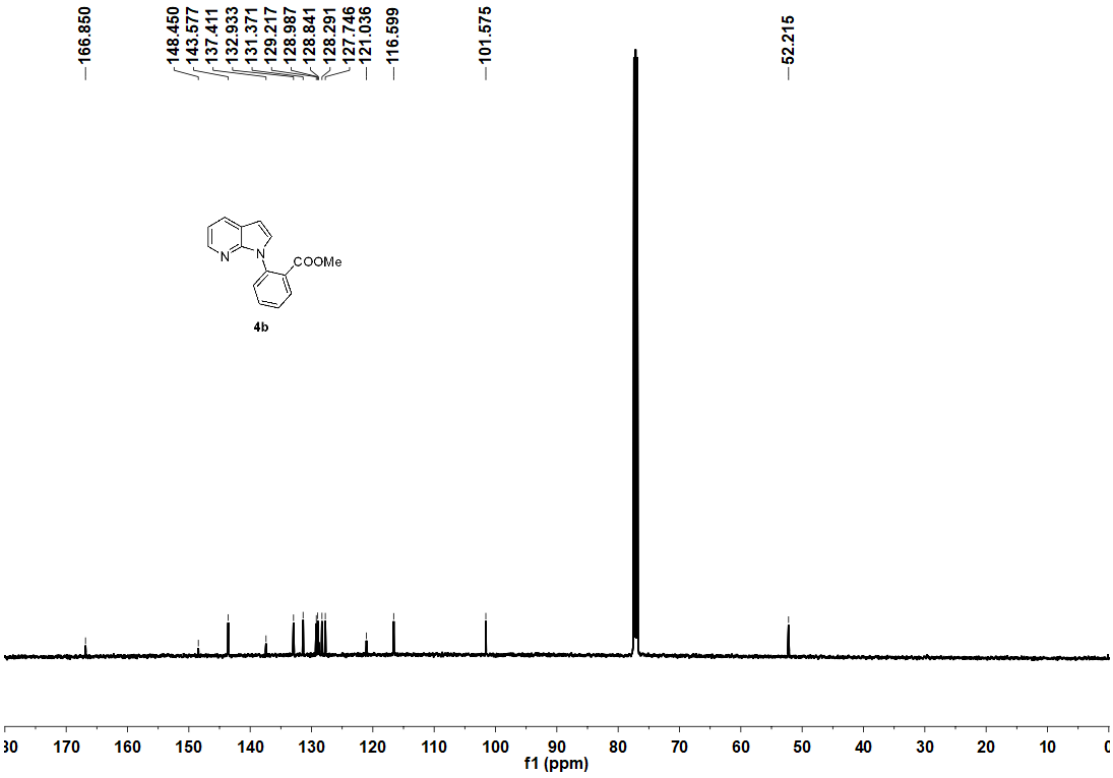

172.182
148.867
143.375
136.959
136.439
130.367
129.952
129.812
129.106
128.640
121.293
116.962
102.185
77.160 CDCl3
61.595
14.025
HO
O
CH3
O
N
N
f1 (ppm)

Compound 4a


9.711
8.323
8.143
8.140
8.124
8.121
8.025
8.006
7.770
7.766
7.750
7.747
7.731
7.728
7.583
7.564
7.545
7.496
7.475
7.462
7.260
7.188
7.176
7.169
7.156
6.739
6.730
4a
1.00
1.13
1.13
1.09
1.12
1.11
2.18
1.10
1.02
f1 (ppm)
189.506
149.114
144.368
140.179
134.877
131.751
129.595
129.375
128.812
128.215
127.776
120.903
117.493
102.816
4a
f1 (ppm)

Compound 4b


8.287
8.275
8.034
8.015
7.981
7.977
7.961
7.957
7.516
7.494
7.380
7.371
7.260
7.113
7.102
7.094
7.082
6.854
6.645
3.460
COOMe
4b
1.00
0.99
0.94
1.03
1.99
1.00
1.03
0.96
2.95
f1 (ppm)


166.850
148.450
143.577
137.411
132.933
131.371
129.217
128.987
128.841
128.291
127.746
121.036
116.599
101.575
52.215
COOMe
4b
f1 (ppm)