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SUPPLEMENTARY MATERIAL

Palladium catalyzed Suzuki cross-coupling of 2-halo-deazapurines with potassium organotrifluoroborate salts in the regioselective synthesis of imidazo[4,5-b]pyridine analogues

Savitha Bhaskaran[b¥], Ayyiliath. M. Sajith[a¥*], M. Nibin Joy[c], K.K. Abdul Khader[b], A. Muralidharan[a], M. Syed Ali Padusha[b]*, Yadav D. Bodke

[a]Post graduate and Research Department of Chemistry, Kasargod Govt. College, Kannur University, Kasargod.

[b]Post Graduate and Research Department of Chemistry, Jamal Mohamed College, Bharathidasan University, Tiruchirapalli

[c]Department of P.G studies and Research in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta, Shimoga, Karnataka, India- 577451.

[¥]Both are equal contributors to the work

*Email id: sajithmeleveetil@gmail.com, Tel. No. +91 9901088933, Fax. No. +91 467 2280335, m.padusha@gmail.com

CONTENTS

1) Procedure for the coupling of 2-halo imidazo[4,5-b]pyridine with different potassium organotrifluoroborates

Method A

To a degassed solution of 3-substituted-2-halo imidazo[4,5-b]pyridine derivative, **3** (1 equiv.) in acetonitrile/water (1:2), was added Palladium catalyst (4 mol %), and phosphine ligand (8 mol %). The solution was again purged with nitrogen and stirred at room temperature for 15 min, at this time the potassium organotrifluoroborate salts (1.3 equiv.), cesium acetate (3 equiv.) and tetrabutylammonium acetate (1 equiv.) were added. The reaction solution was purged again with nitrogen and then placed in the microwave and heated for 20 to 50 min at 150 °C. When TLC and LC-MS showed full consumption of starting materials, the reaction mixture was diluted with ethyl acetate, separated the ethyl acetate layer, washed with water, followed by brine wash and was dried over anhydrous sodium sulfate and concentrated to get the crude material. The crude product was directly purified by column chromatography (0–20% hexane/EtOAc) to isolate the 3-substituted-2-aryl/heteroaryl imidazo[4,5-b]pyridine derivatives.

Method B

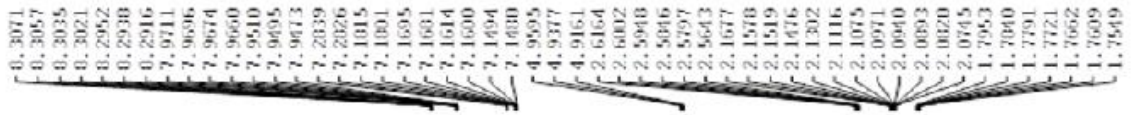
To a degassed solution of 3-substituted-2-halo imidazo[4,5-b]pyridine derivative (1 equiv.) in acetonitrile/water (1:2) in a sealed vial, was added palladium catalyst (4 mol%), and phosphine ligand (8 mol%). The solution was again purged with nitrogen, stirred at room temperature for 15 min. and potassium organotrifluoroborate salts (1.3 equiv.) and cesium acetate (3 equiv.) were added. The reaction contents were then heated to 90 °C for 15 h. When TLC and LC-MS showed complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate, separated the ethyl acetate layer, washed with water, followed by brine wash and dried over anhydrous sodium sulfate and concentrated to get the crude material. The crude product was directly purified by column chromatography (0–20% hexane/EtOAc) to isolate the 3-substituted-2-aryl/heteroaryl imidazo[4,5-b]pyridine derivatives.

Method C

To a degassed solution of 3-substituted-2-halo imidazo[4,5-b]pyridine derivative (1 equiv.) in acetonitrile/ water (1:2) in a sealed vial, was added palladium catalyst (4 mol%), and phosphine ligand (8 mol%). The solution was again purged with nitrogen, stirred at room temperature for 15 min. and potassium organotrifluoroborate salts (1.3 equiv.) and cesium

acetate (3 equiv.) were added. The reaction contents were then heated to 90 °C for 3 h. When TLC and LC-MS showed full consumption of starting materials, the reaction mixture was diluted with ethyl acetate, separated the ethyl acetate layer, washed with water, followed by brine wash and dried over anhydrous sodium sulfate and concentrated to get the crude material. The crude product was directly purified by column chromatography (0–20% hexane/EtOAc) to isolate the 3-substituted-2-aryl/heteroaryl imidazo[4,5-b]pyridine derivatives.

The synthesis of the halo intermediates **3** (**3a, 3b, and 3c**) was done according to the procedures mentioned in reference 21. The intermediates were found to be very labile and was found to degrade over a period of time (stored at −20 °C and used immediately for the coupling step)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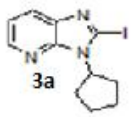
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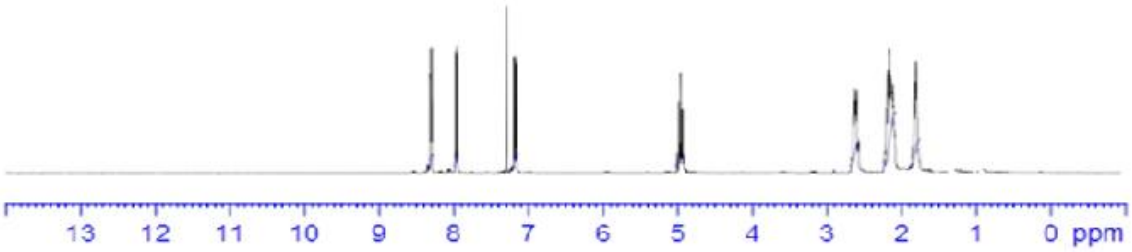
I
N
N

3a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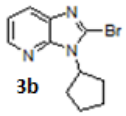
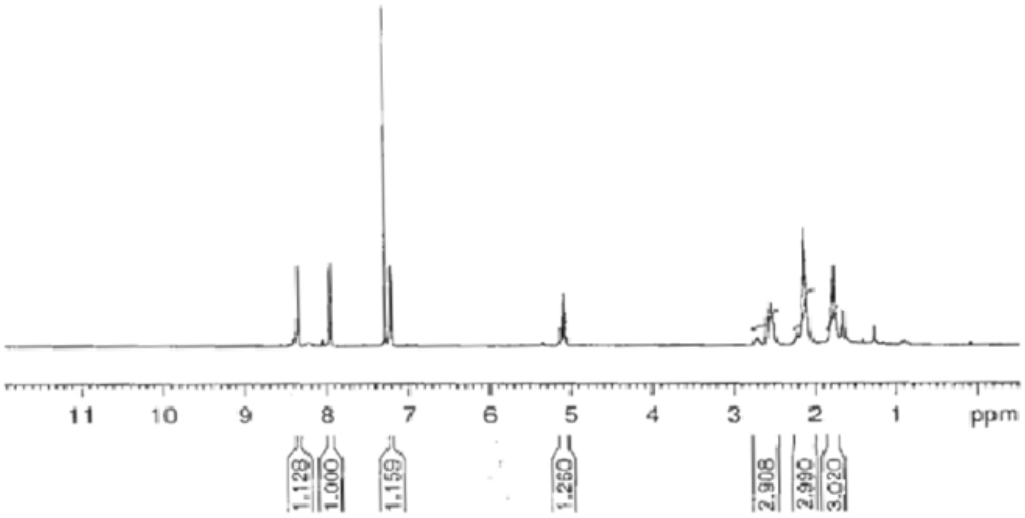
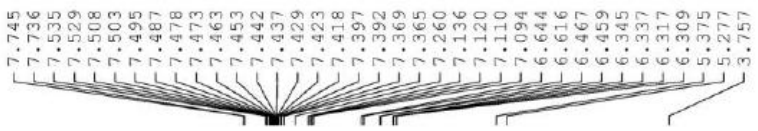


3b

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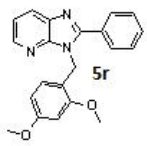
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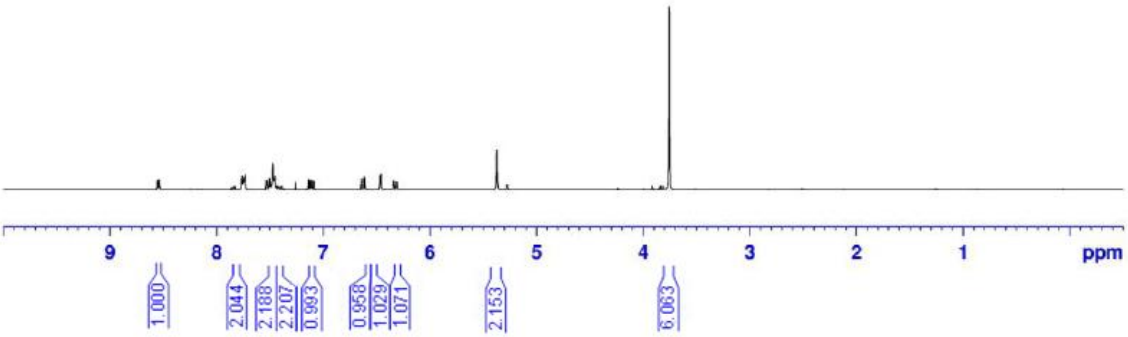
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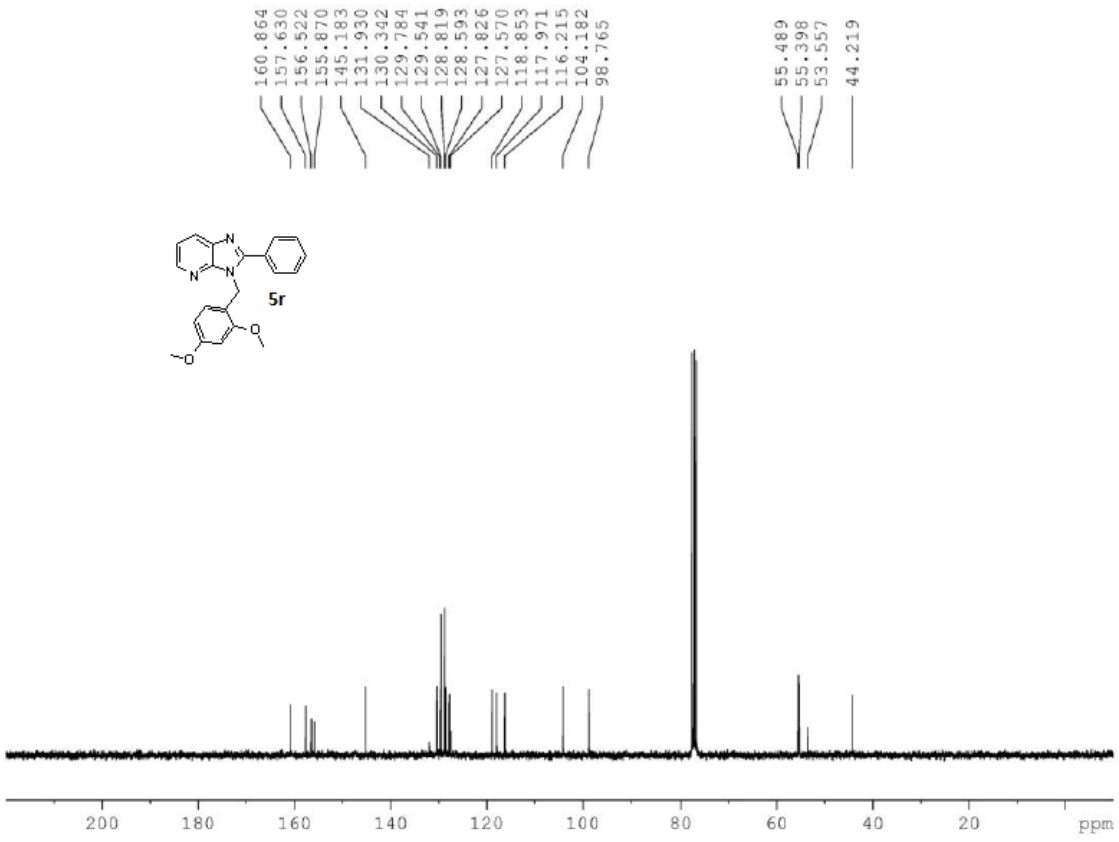
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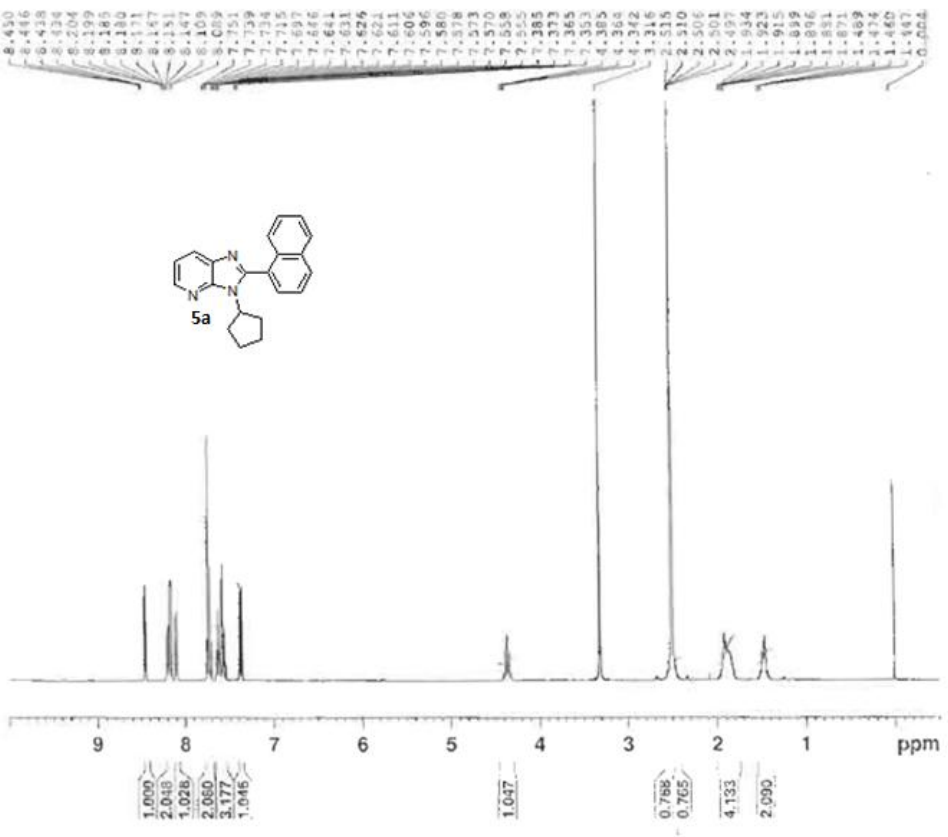
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1.047
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0.765
4.133
2.090

Method Info. : Solvent A: 0.1% TFA
Solvent B:Acetonitrile
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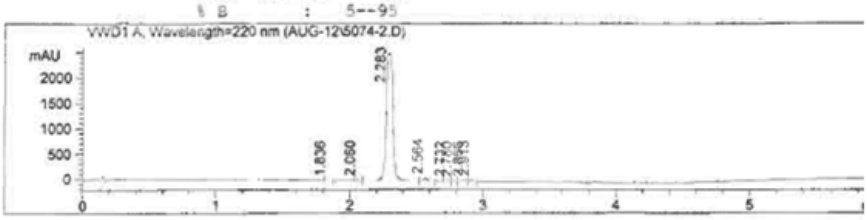
Temp : 45° C
Column: XBridge C18 (4.6X50)mm,5µm
Time (min.): 0--4.0
% B : 5--95



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4	2.564	8.375e+001	0.959
5	2.732	8.435e+000	0.097
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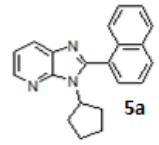

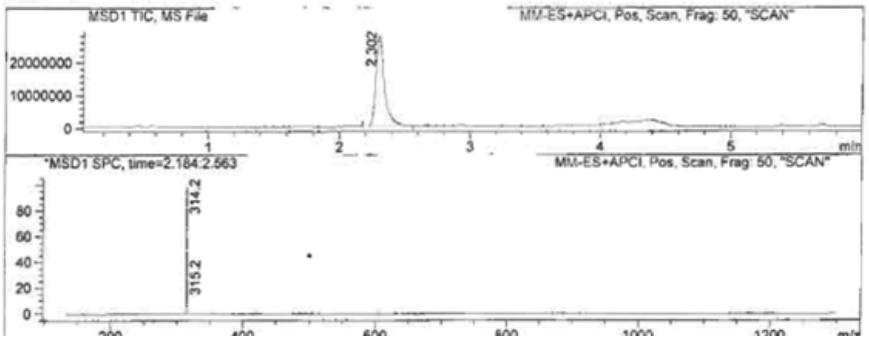

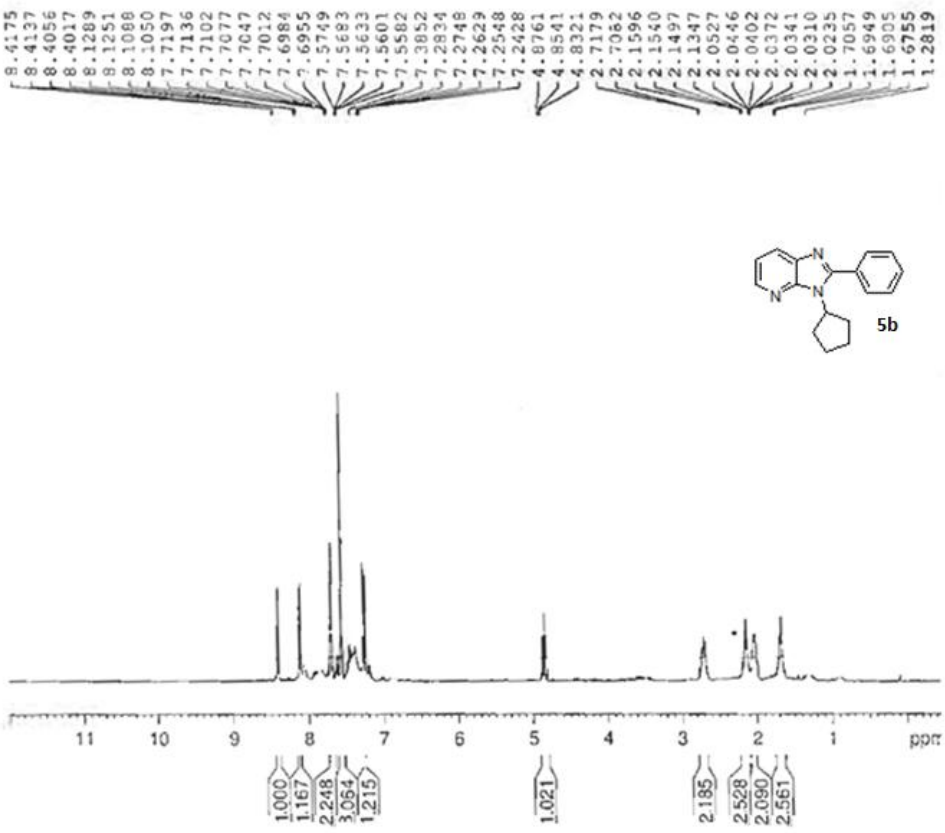
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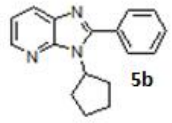
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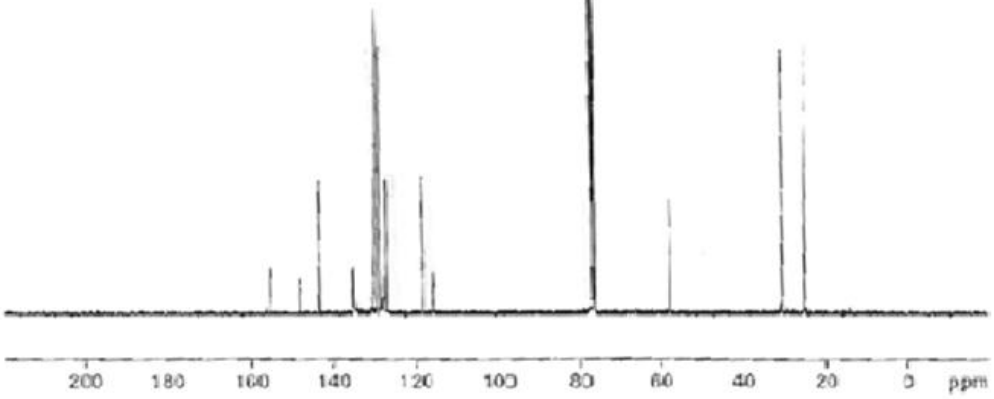
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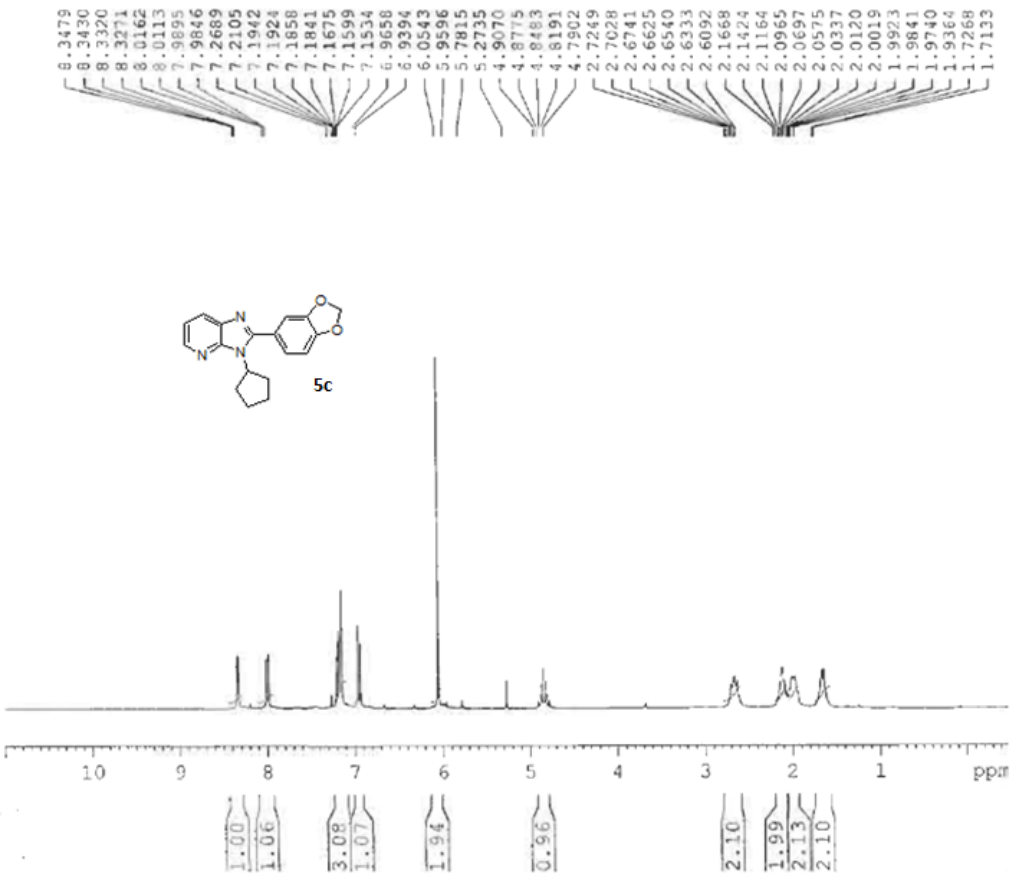
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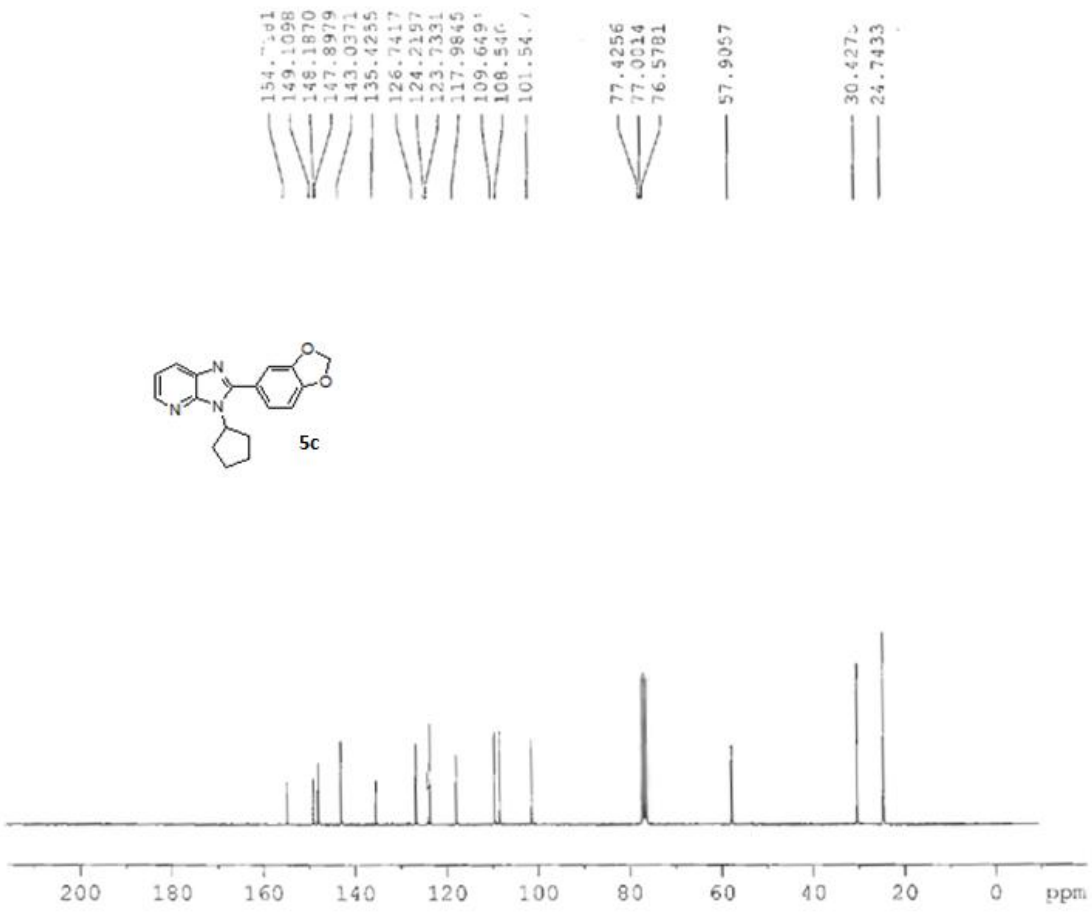
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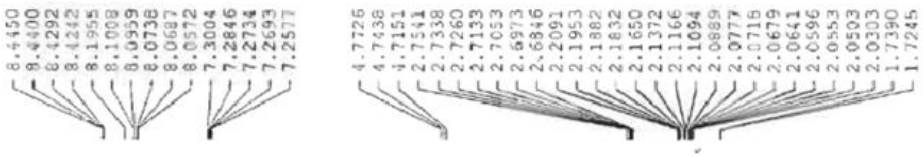
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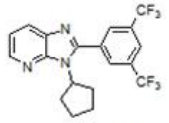
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CF3

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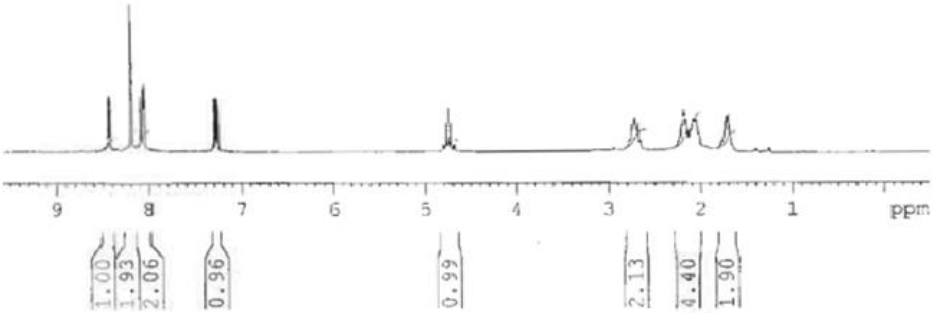
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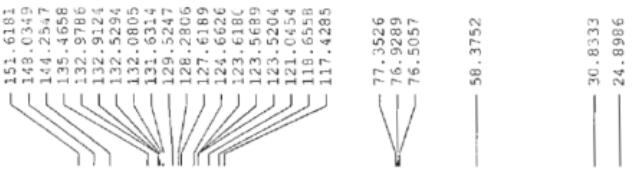
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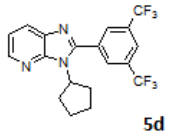
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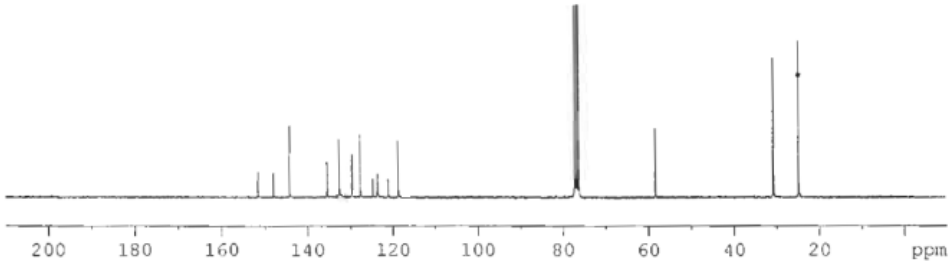
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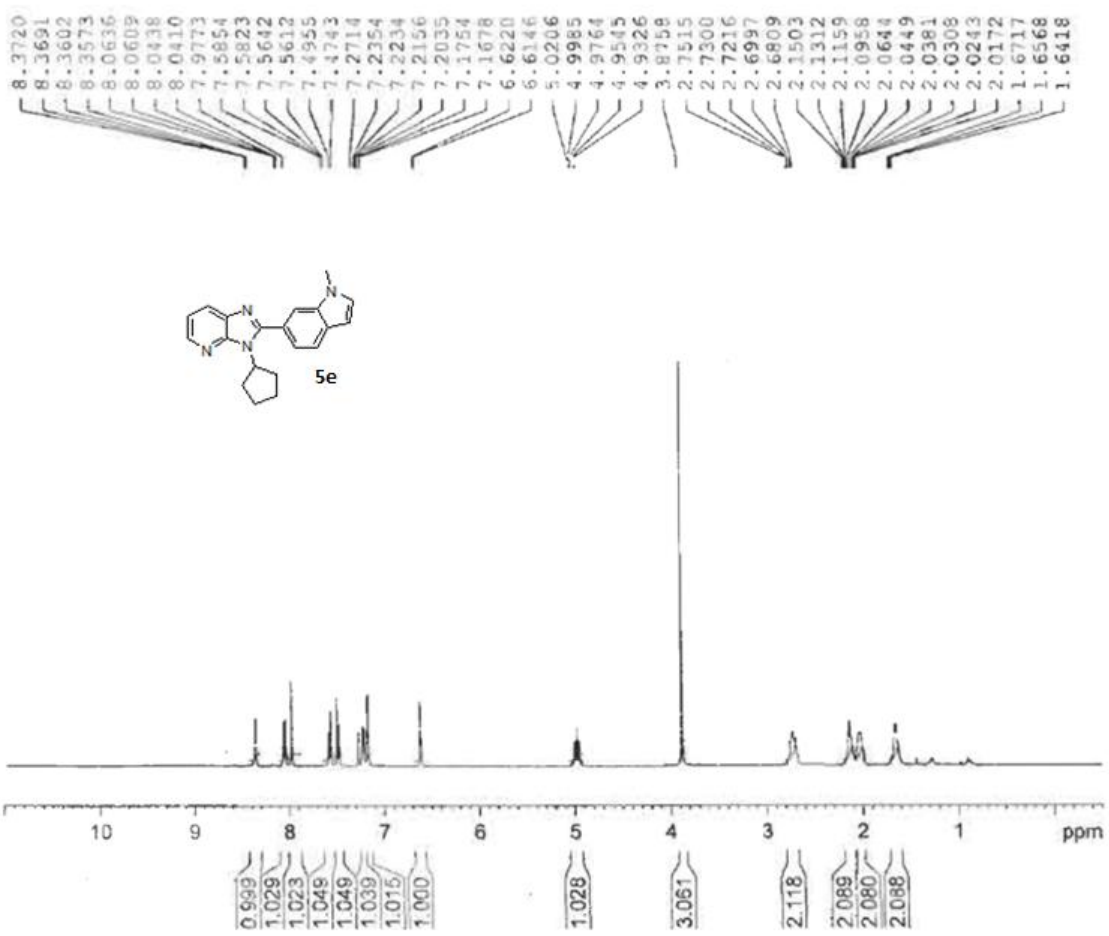
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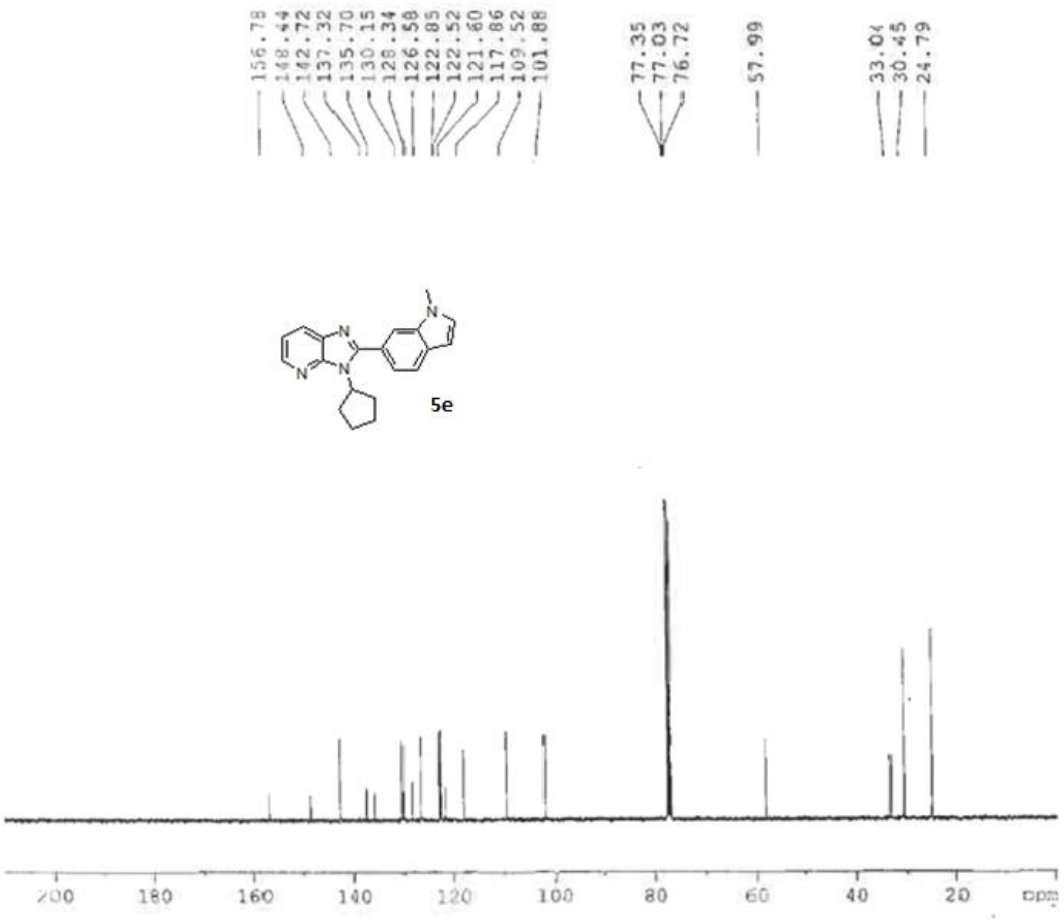
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77.03
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180
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140
120
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80
60
40
20
ppm


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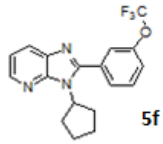
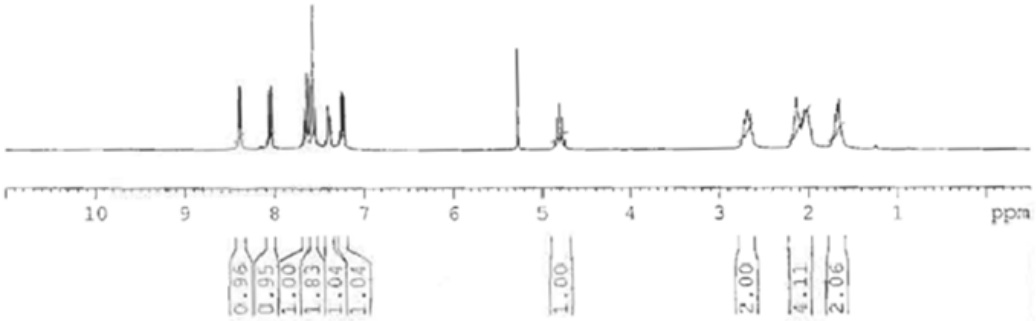

F3C
O
N
N
N

5f


10
9
8
7
6
5
4
3
2
1
ppm
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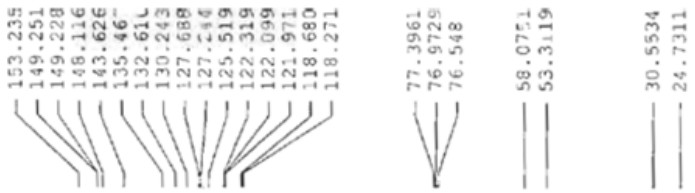
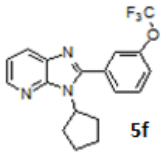
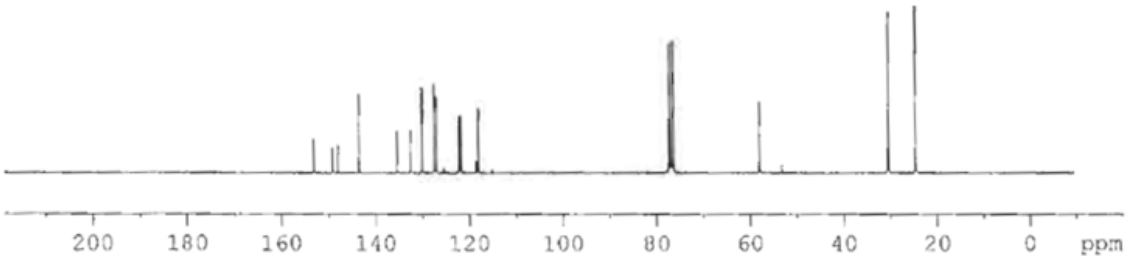
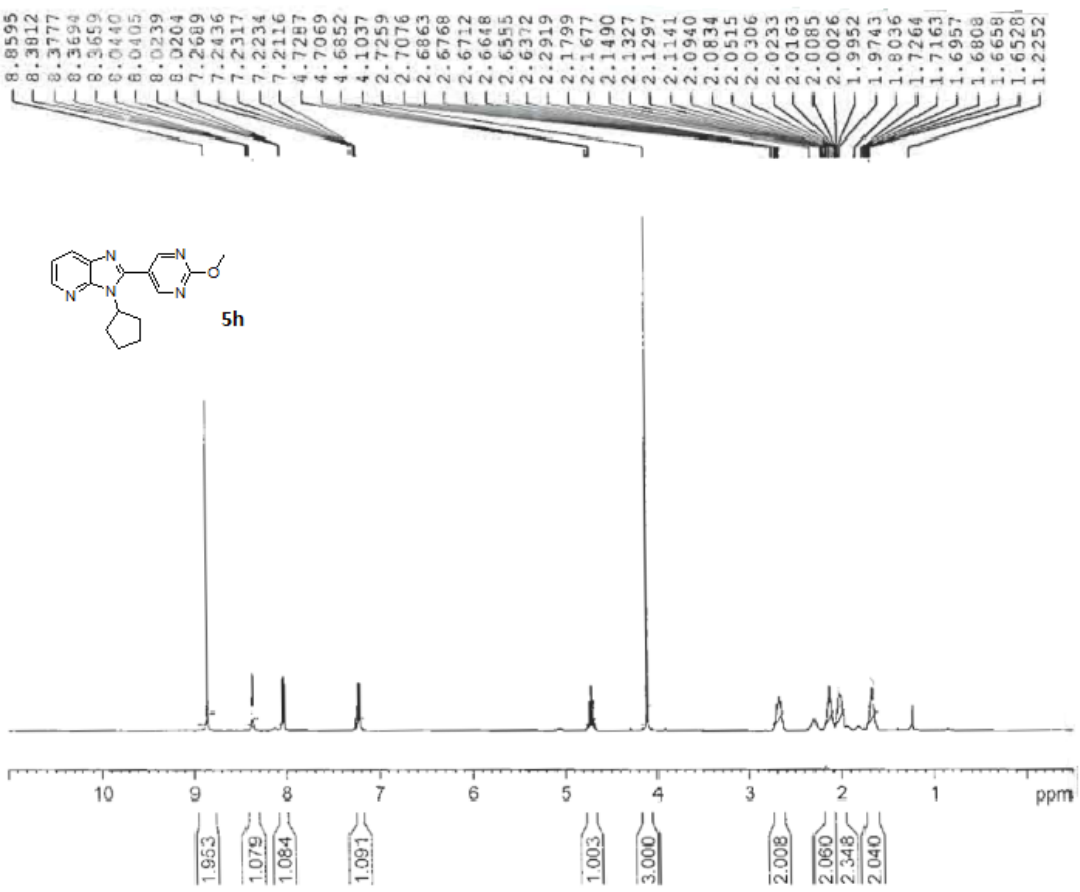
0.95
1.00
1.83
1.04
1.04
1.00
2.00
4.11
2.06


153.235
149.251
149.228
148.116
143.626
135.46
132.61
130.243
127.688
127.
125.519
122.319
122.099
121.971
118.680
118.271
77.3961
76.9729
76.548
58.075
53.3119
30.5534
24.7311


F3C
O
N
N
5f


200
180
160
140
120
100
80
60
40
20
0
ppm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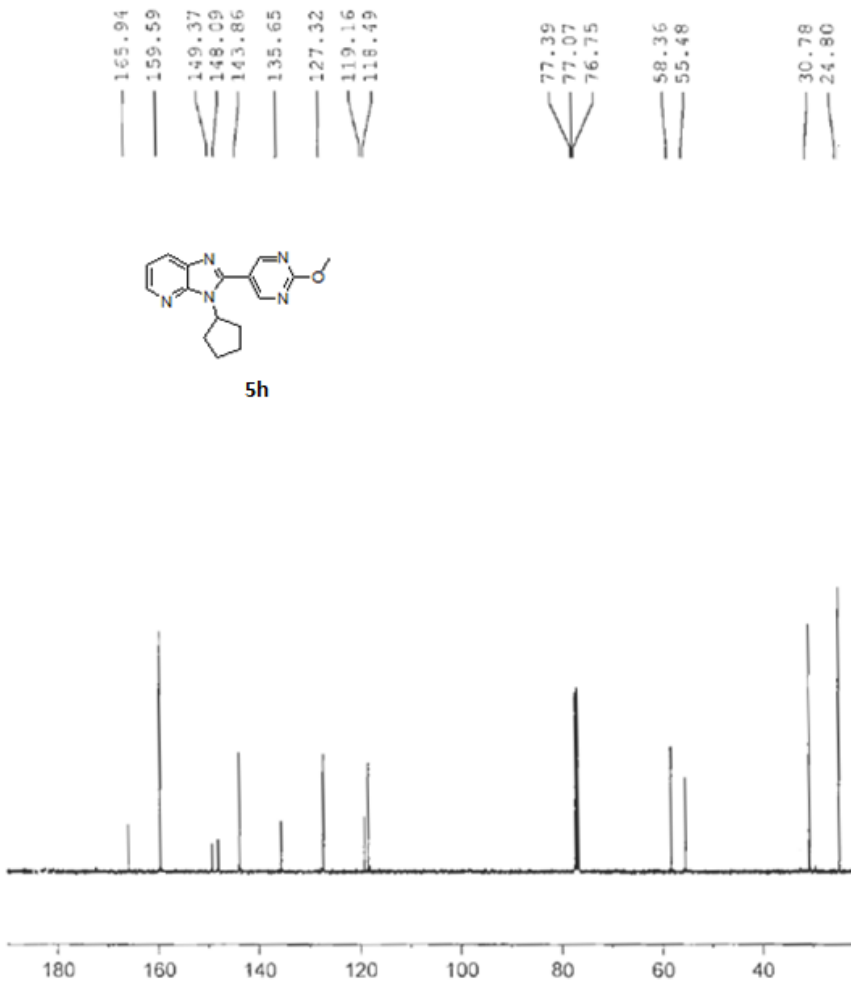
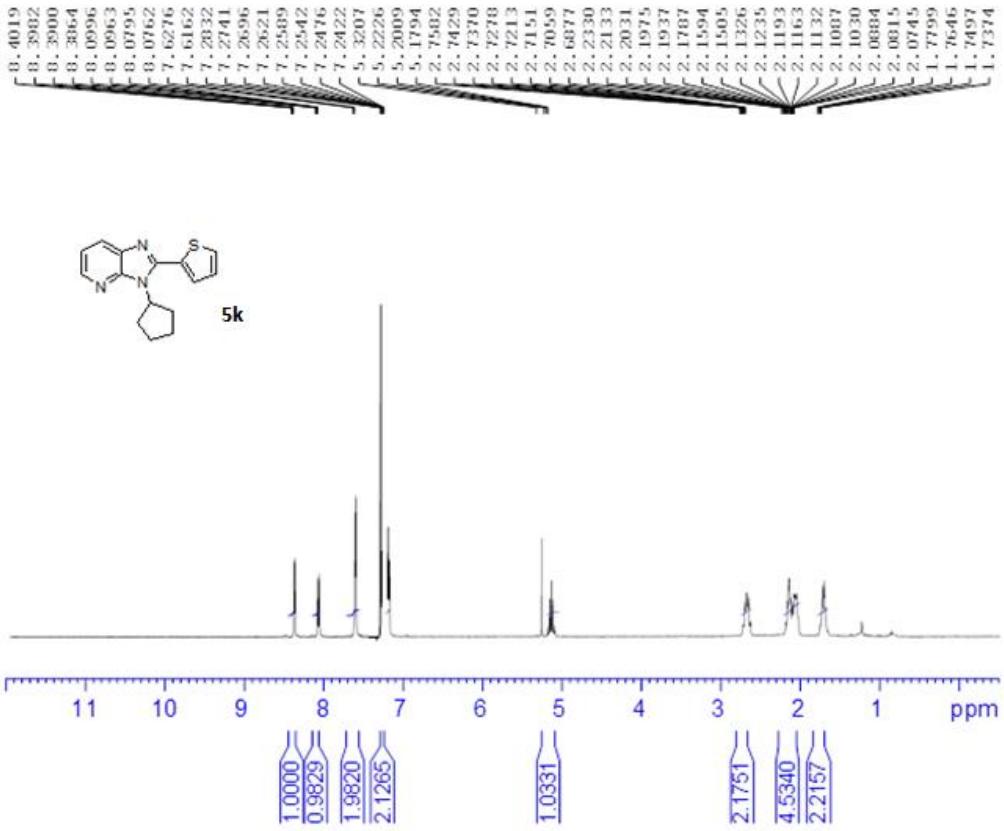
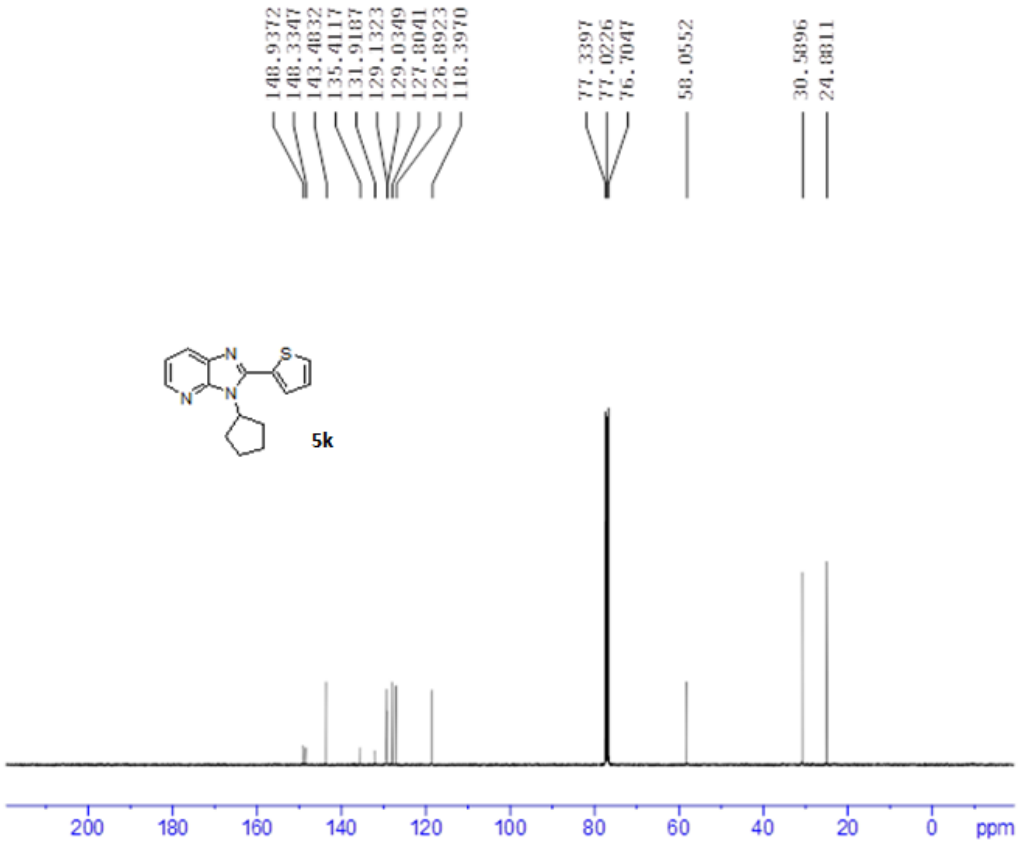
8.3812
8.3777
8.3694
8.3659
8.0440
8.0405
8.0239
8.0204
7.2689
7.2436
7.2317
7.2234
7.2116
4.7287
4.7069
4.6852
4.1037
2.7259
2.7076
2.6863
2.6768
2.6712
2.6648
2.6555
2.6372
2.2919
2.1799
2.1677
2.1490
2.1327
2.1297
2.1141
2.0940
2.0834
2.0515
2.0306
2.0233
2.0163
2.0085
2.0026
1.9952
1.9743
1.8036
1.7264
1.7163
1.6957
1.6808
1.6658
1.6528
1.2252
5h
10
9
8
7
6
5
4
3
2
1
ppm
1.953
1.079
1.084
1.091
1.003
3.000
2.008
2.060
2.348
2.040


165.94
159.59
149.37
148.09
143.86
135.65
127.32
119.16
118.49
77.39
77.07
76.75
58.36
55.48
30.78
24.80
180
160
140
120
100
80
60
40
20
ppm

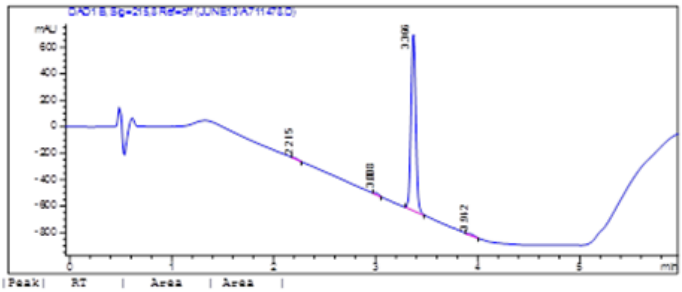
5h


8.4019
8.3982
8.3900
8.3864
8.0996
8.0963
8.0795
8.0762
7.6276
7.6162
7.2832
7.2741
7.2696
7.2621
7.2589
7.2542
7.2476
7.2422
5.3207
5.2226
5.2009
5.1794
2.7582
2.7429
2.7370
2.7278
2.7213
2.7151
2.7059
2.6877
2.2330
2.2133
2.2031
2.1975
2.1937
2.1787
2.1594
2.1505
2.1326
2.1235
2.1193
2.1163
2.1132
2.1087
2.1030
2.0884
2.0815
2.0745
1.7799
1.7646
1.7497
1.7374
5k
11
10
9
8
7
6
5
4
3
2
1
ppm
1.0000
0.9829
1.9820
2.1265
1.0331
2.1751
4.5340
2.2157

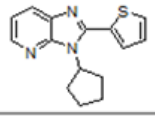

148.9372
148.3347
143.4832
135.4117
131.9187
129.1323
129.0349
127.8041
126.8923
118.3970
77.3397
77.0226
76.7047
58.0552
30.5896
24.8811
5k
200
180
160
140
120
100
80
60
40
20
0
ppm

Injection Date : 11- Jun- 2013 3:39:23 PM
Injection vol : 2.0uL
Acq Method : METHODS\AT_595FAD.M

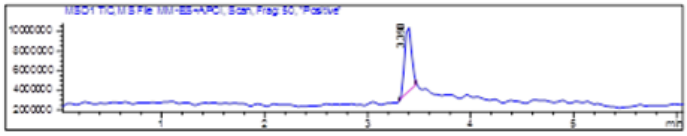
Method info :A-0.1%HCOOH;B-ACN Flow: 1.5ml/min,
Column-ATLANTIS dC18 (50X4.6mm-5um,) DUAL MODE
TIME (MIN) : 0--3 3--4 4--4.5 4.5-6
%B 5-95 95 95-5 5

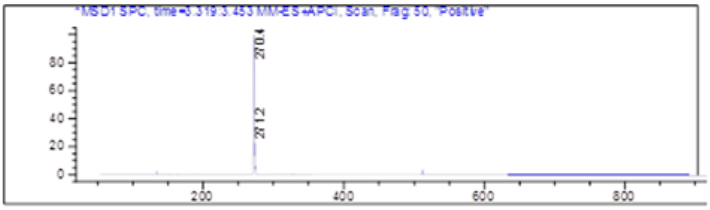


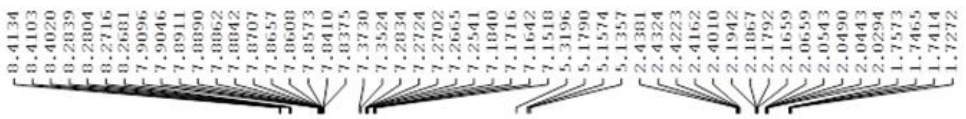
Peak No	RT min	Area	Area %
1	2.215	2.631e+001	0.586
2	3.008	6.315e+001	1.405
3	3.366	4.350e+003	96.809
4	3.942	5.392e+001	1.200

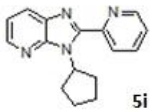


5k

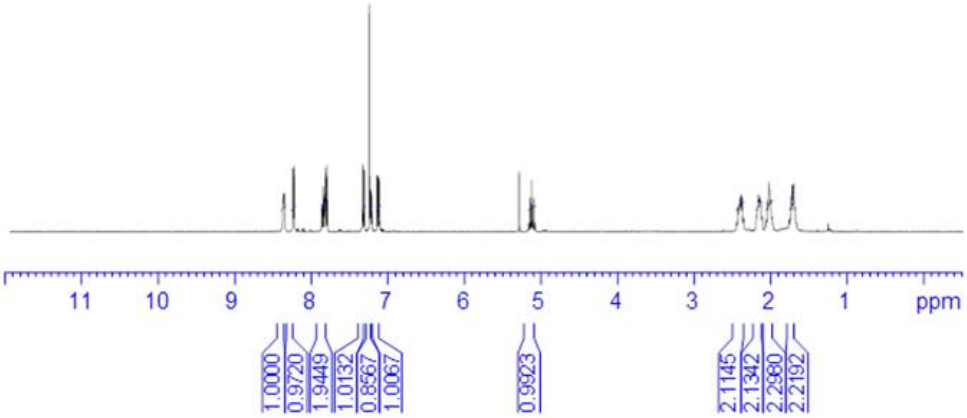


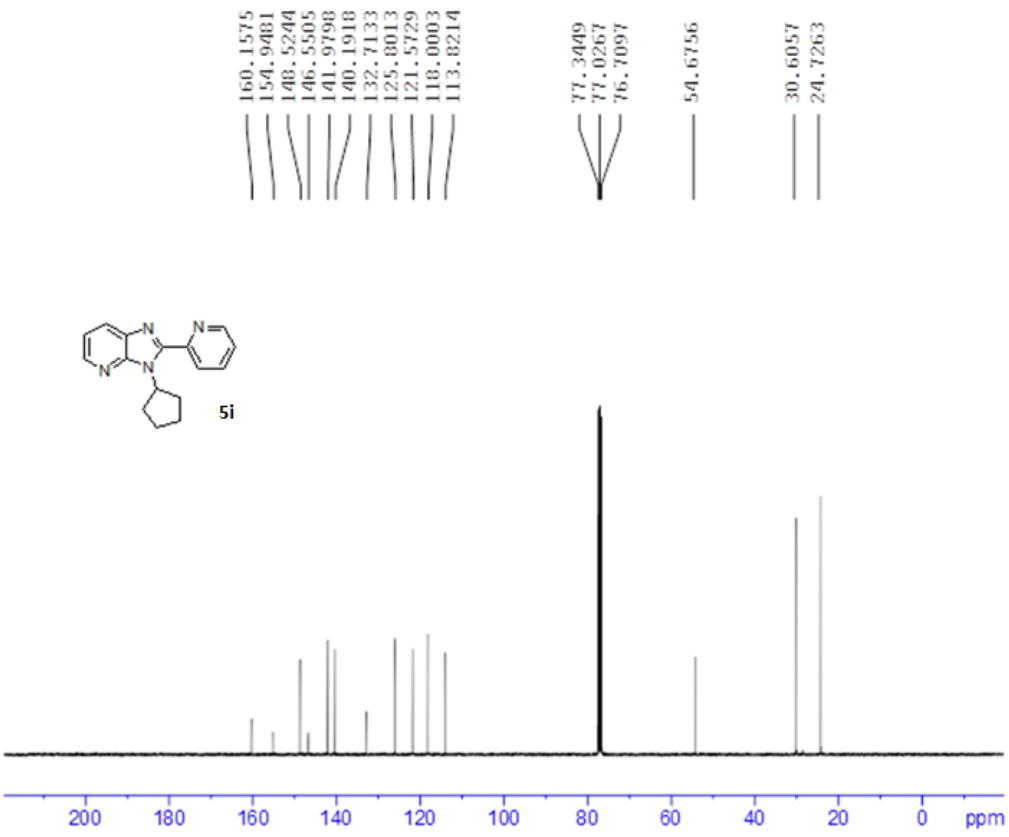



8.4134
8.4103
8.4020
8.2839
8.2804
8.2716
8.2681
7.9096
7.9046
7.8911
7.8890
7.8862
7.8842
7.8707
7.8657
7.8608
7.8573
7.8410
7.8375
7.3730
7.3524
7.2834
7.2724
7.2702
7.2665
7.2541
7.1840
7.1716
7.1642
7.1518
5.3196
5.1790
5.1574
5.1357
2.4381
2.4324
2.4223
2.4162
2.4010
2.1942
2.1867
2.1792
2.1659
2.0659
2.0543
2.0490
2.0443
2.0294
1.7573
1.7465
1.7414
1.7272

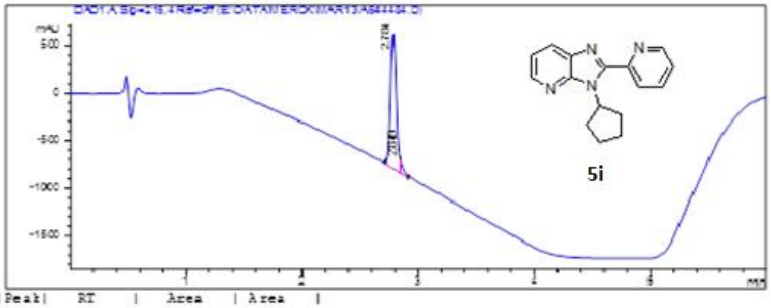


5i


11
10
9
8
7
6
5
4
3
2
1
ppm
1.0000
0.9720
1.9449
1.0132
0.8567
1.0067
0.9923
2.1145
2.1342
2.2980
2.2192

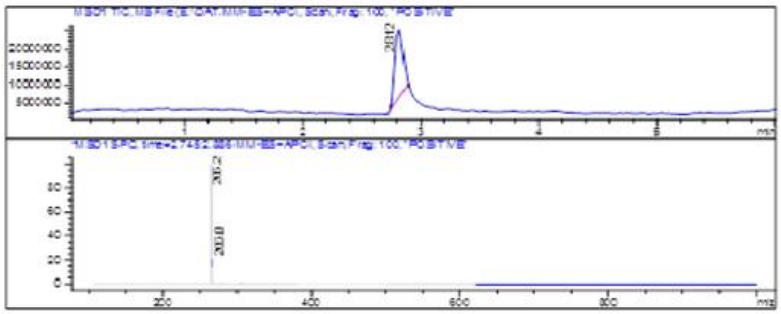

160.1575
154.9481
148.5244
146.5505
141.9798
140.1918
132.7133
125.8013
121.5729
118.0003
113.8214
77.3449
77.0267
76.7097
54.6756
30.6057
24.7263
5i
200
180
160
140
120
100
80
60
40
20
0
ppm

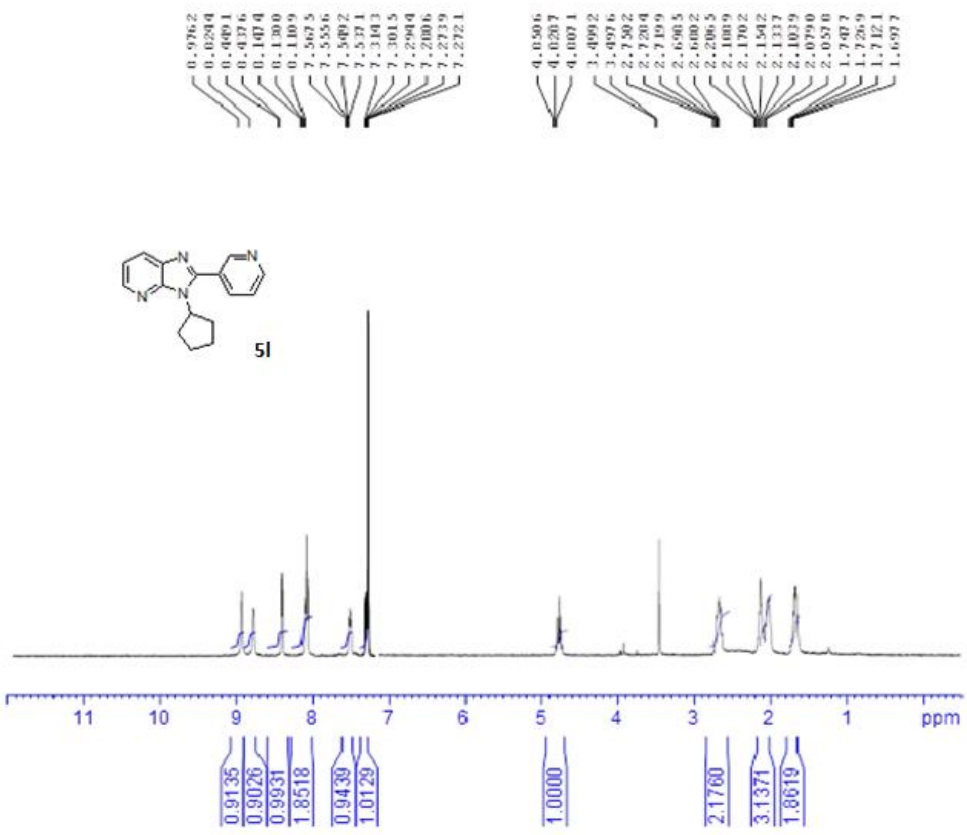
```
Vial No.          :  P1-D-07
Injection Date    :  15- Mar- 2018
Injection vol     :  2.0uL
Acq Method        :  METHODS\AT_595FAD.M
Method info  :A-0.1%HCOOH;B-ACN  Flow: 1.5ml/min,
              Column-Atlantis dC18  (50X4.6mm-5µm, )   postive mode & Negative mode
              TIME (MIN)  :  0--3.0      3.0--4.0      4.0--4.5      4.5-6.0
                   %B          5-95          95          95-5            5
```

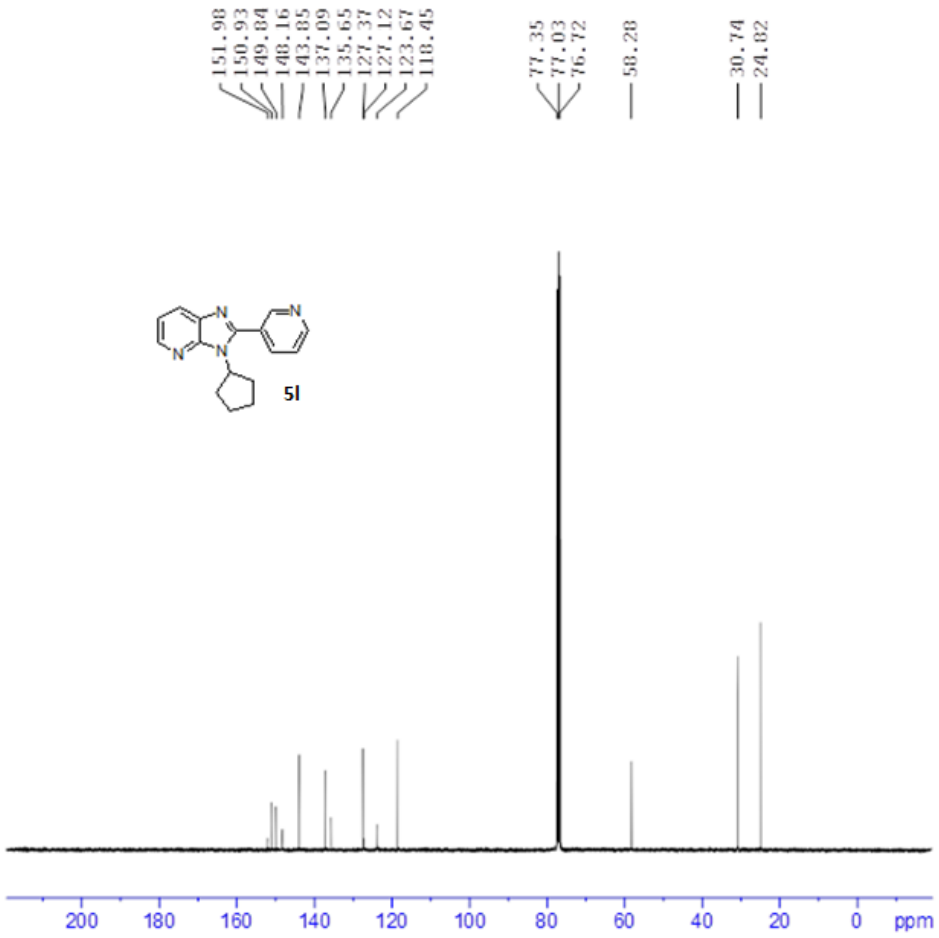


5i

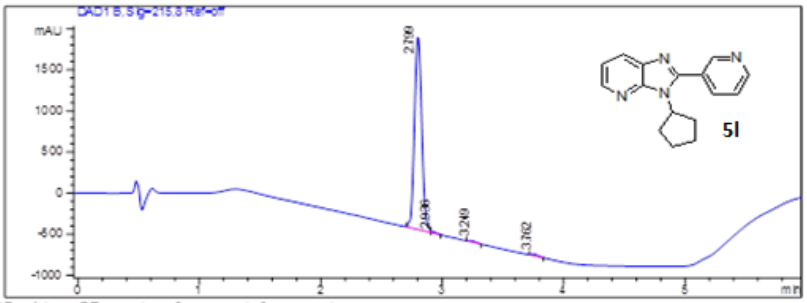
Peak No	RT min	Area	Area %
1	2.784	4.824e+003	95.908
2	2.849	2.058e+002	4.092



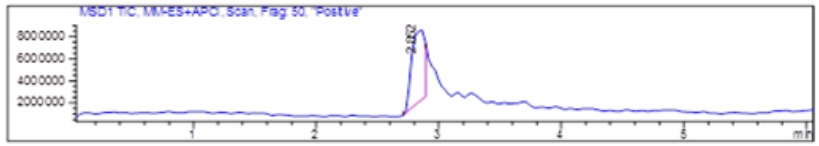

5l
11
10
9
8
7
6
5
4
3
2
1
ppm
0.9135
0.9026
0.9931
1.8518
0.9439
1.0129
1.0000
2.1760
3.1371
1.8619

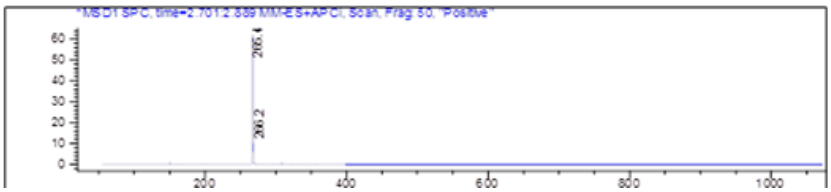

151.98
150.93
149.84
148.16
143.85
137.09
135.65
127.37
127.12
123.67
118.45
77.35
77.03
76.72
58.28
30.74
24.82
5l
200
180
160
140
120
100
80
60
40
20
0
ppm

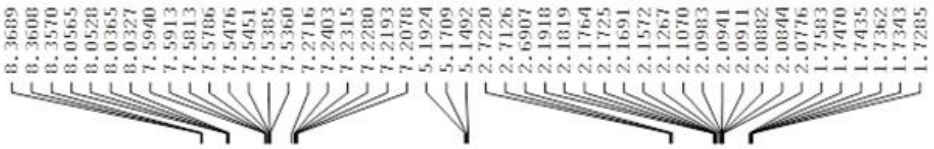
```
Injection vol    :  2.0uL
Acq Method       :  METHODS\AT_595FAD.M
Method info  :A-0.1%HCOOH;B-ACN  Flow: 1.5ml/min,
              Column-ATLANTIS dC18 (50X4.6mm-5µm, )   DUAL MODE
              TIME (MIN)   :  0--3     3--4     4--4.5   4.5-6
                    %B         5-95       95     95-5      5
```



Peak No	RT min	Area	Area %
1	2.799	9.717e+003	97.833
2	2.936	6.508e+001	0.655
3	3.249	7.286e+001	0.734
4	3.762	7.725e+001	0.778






8.3689
8.3608
8.3570
8.0565
8.0528
8.0365
8.0327
7.5940
7.5913
7.5813
7.5786
7.5476
7.5451
7.5385
7.5360
7.2716
7.2403
7.2315
7.2280
7.2193
7.2078
5.1924
5.1709
5.1492
2.7220
2.7126
2.6907
2.1918
2.1819
2.1764
2.1725
2.1691
2.1572
2.1267
2.1070
2.0983
2.0941
2.0911
2.0882
2.0844
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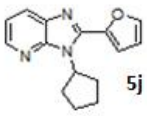
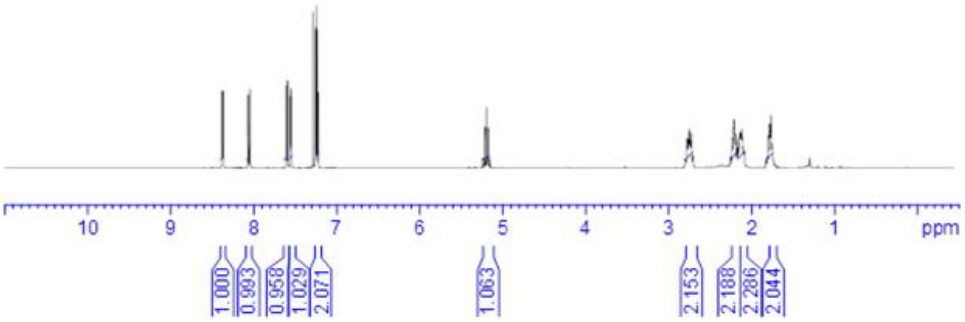
1.7583
1.7470
1.7435
1.7362
1.7343
1.7285



5j


10
9
8
7
6
5
4
3
2
1
ppm
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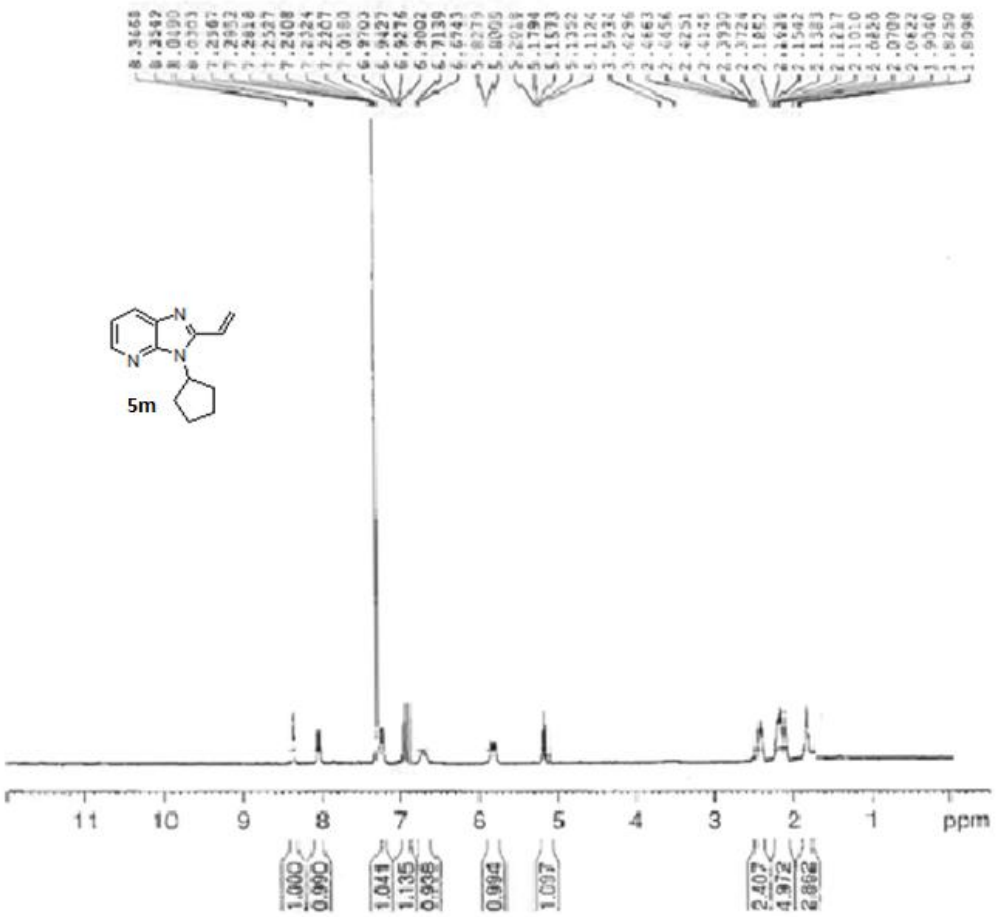
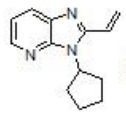
0.993
0.958
1.029
2.071
1.063
2.153
2.188
2.286
2.044

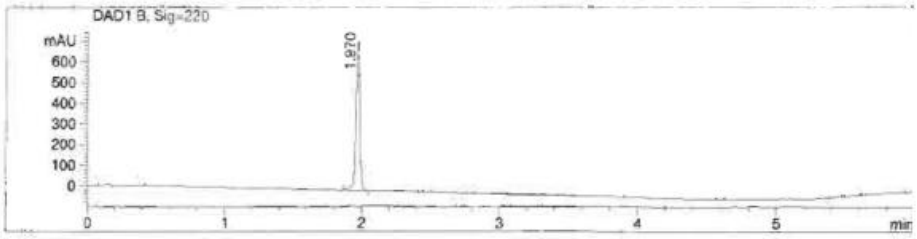

5m
11
10
9
8
7
6
5
4
3
2
1
ppm
1.000
0.990
1.041
1.135
0.938
0.994
1.097
2.407
4.972
2.862

Method info :

A: 10mM NH4OAC in Water
B: :Methanol
Flow: 4 ml/min
Temp :45°C
Column: Xbridge C18 (50x4.6) ,5µm
Time (min) : 0---4
%B : 5---95

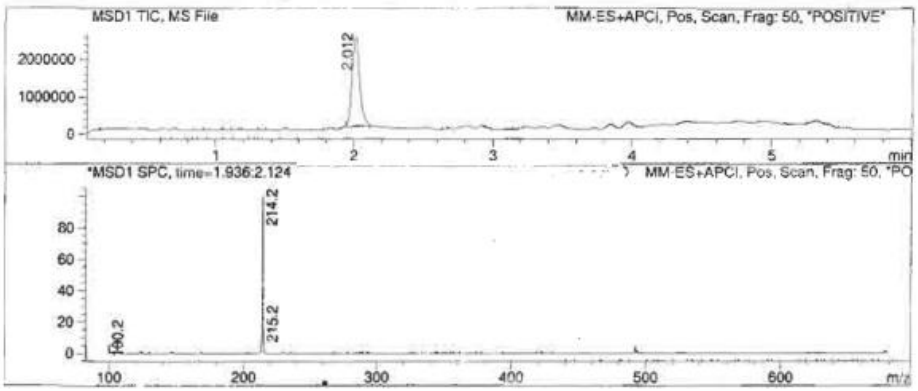


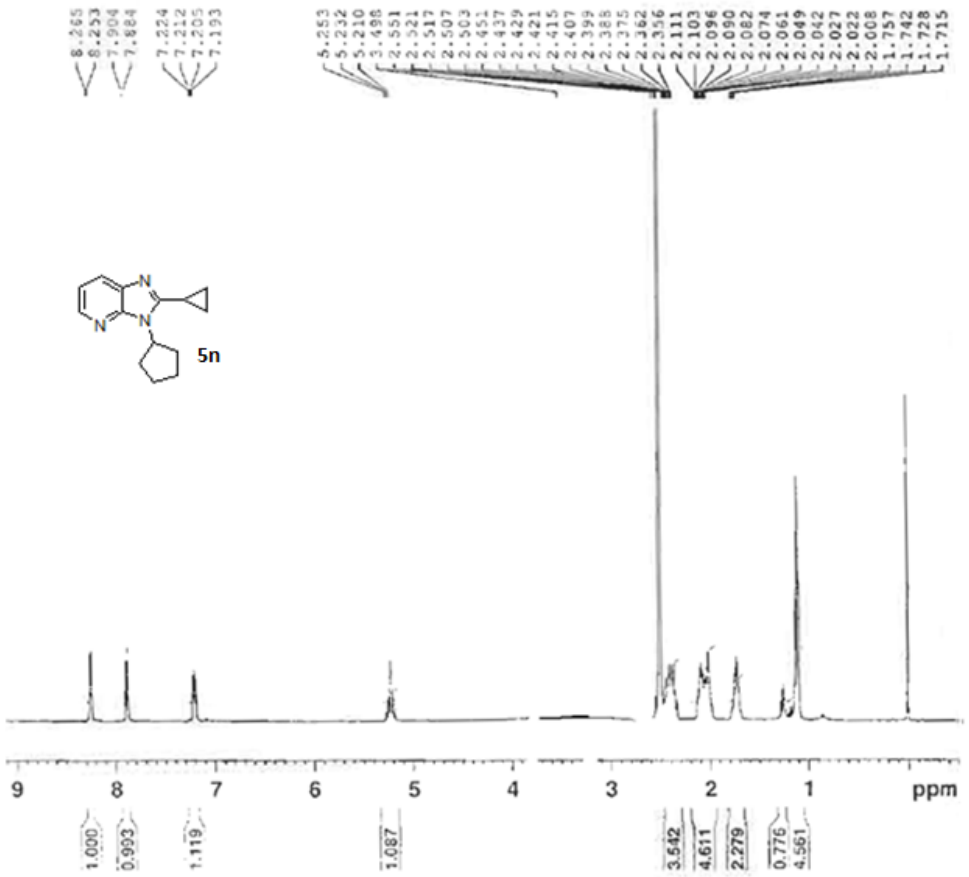
5m



DAD1 B, Sig=220,4 Ref=off

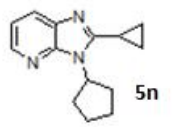
#	Meas. R	Area	Area %
1	1.970	1.422e3	100.000



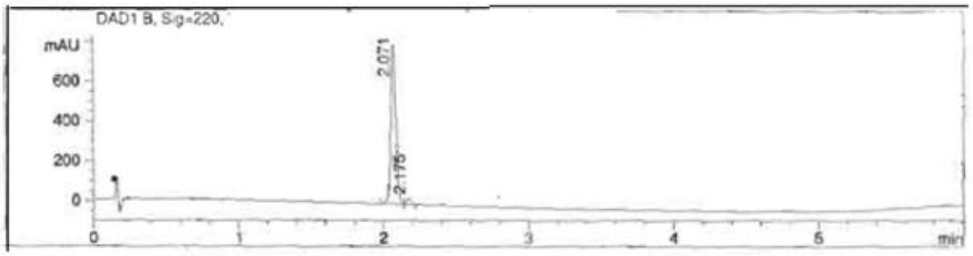

8.265
8.253
7.904
7.884
7.224
7.212
7.205
7.193
5.253
5.232
5.210
3.498
2.551
2.521
2.517
2.507
2.503
2.451
2.437
2.429
2.421
2.415
2.407
2.399
2.388
2.375
2.362
2.356
2.111
2.103
2.096
2.090
2.082
2.074
2.061
2.049
2.042
2.027
2.022
2.008
1.757
1.742
1.728
1.715
N
N
5n
9
8
7
6
5
4
3
2
1
ppm
1.000
0.993
1.119
1.087
3.542
4.611
2.279
0.776
4.561

Method info :

A: 10mM NH4OAC in Water
B: :Methanol
Flow: 4 ml/min
Temp :45°C
Column: Xbridge C18 (50x4.6) ,5um
Time (min) : 0---4
%B : 5---95

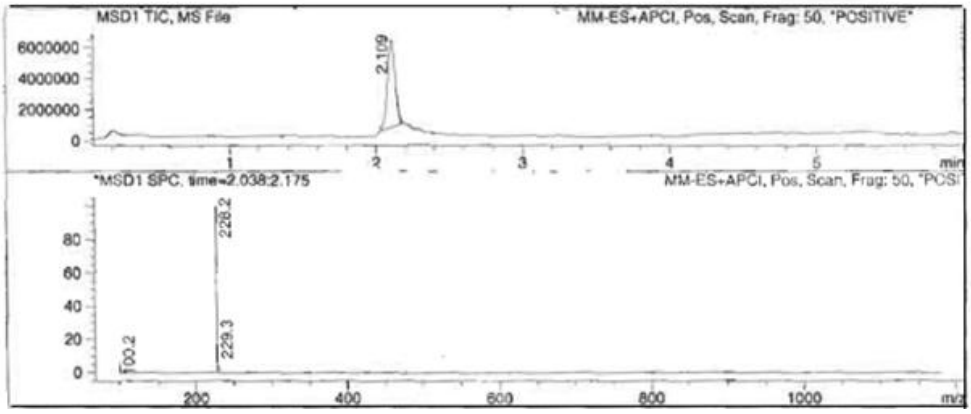


5n



DAD1 B, Sig=220,4 Ref=off

#	Meas. R	Area	Area %
1	2.071	1.937e3	96.614
2	2.175	67.894	3.386



Vial No. : P1-D-04 1:37:32 PM

Injection Date : 12th Jun 2013

Injection vol : 2.0uL

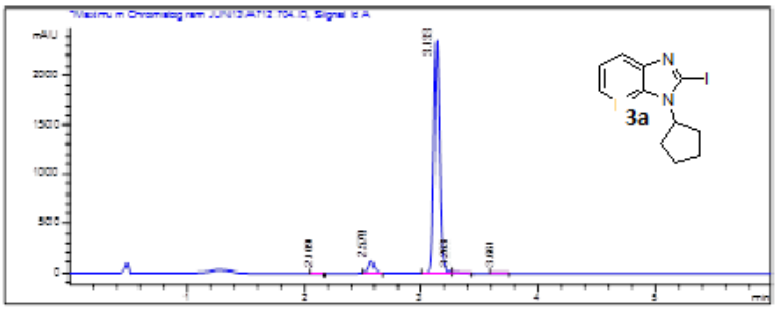
Acq Method : [illegible]

Method info :A-0.1%HCOOH;B-ACN Flow: 1.0ml/min,

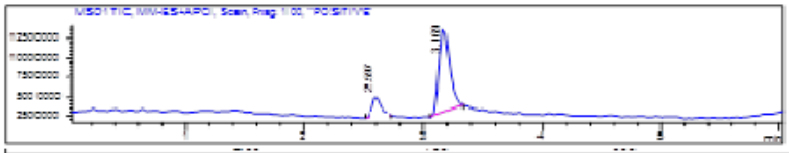
Column-Atlantis dC18 (50X4.6mm-5um,) positive mode & Negative mode

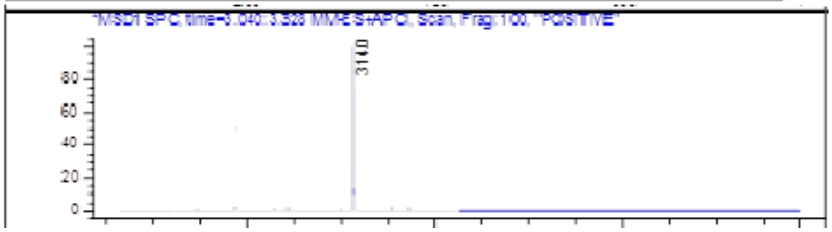
TIME (MIN) = 0--3.0 3.0--4.0 4.0--4.5 4.5-6.0

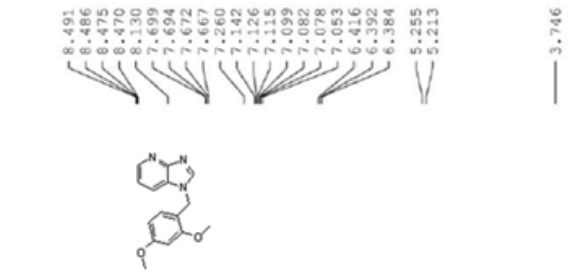
%B 5-95 95 95-5 5



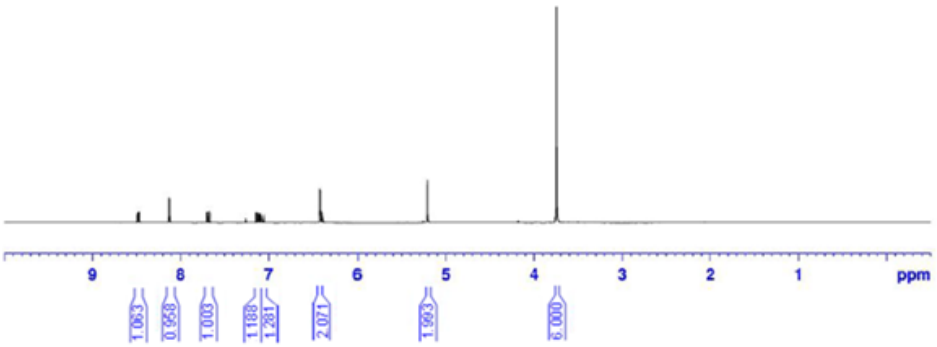
Peak No	RT min	Area	Area %
1	2.109	2.775e4002	0.0393
2	2.570	3.659e4002	4.3394
3	3.133	8.002e4003	95.3917
4	3.263	1.915e4002	0.2285
5	3.661	3.586e4002	0.0010

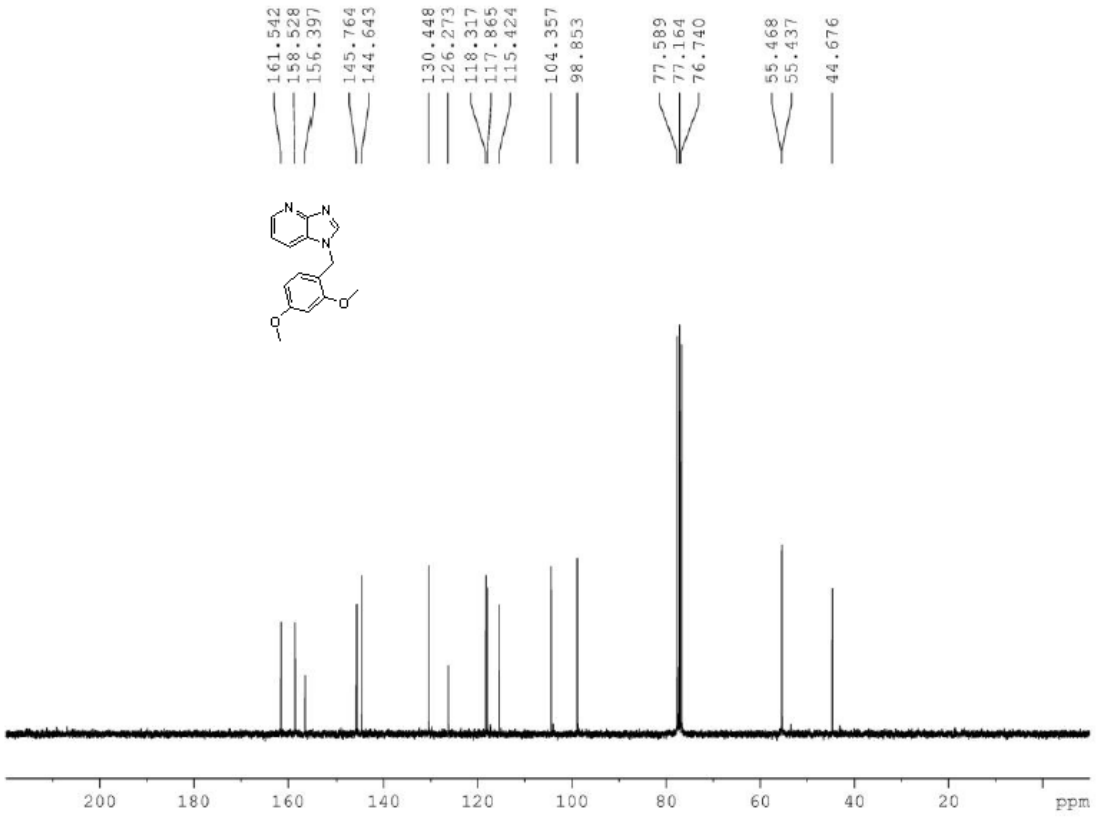


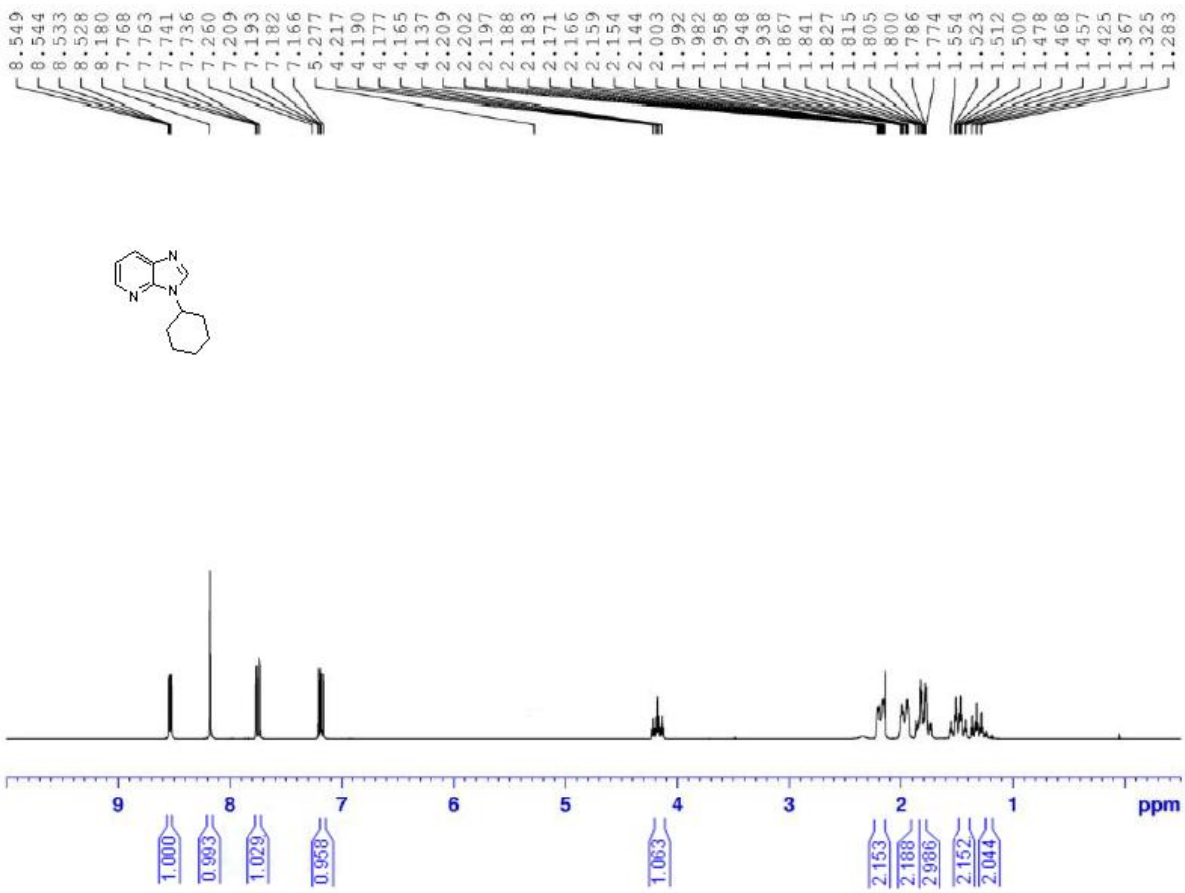


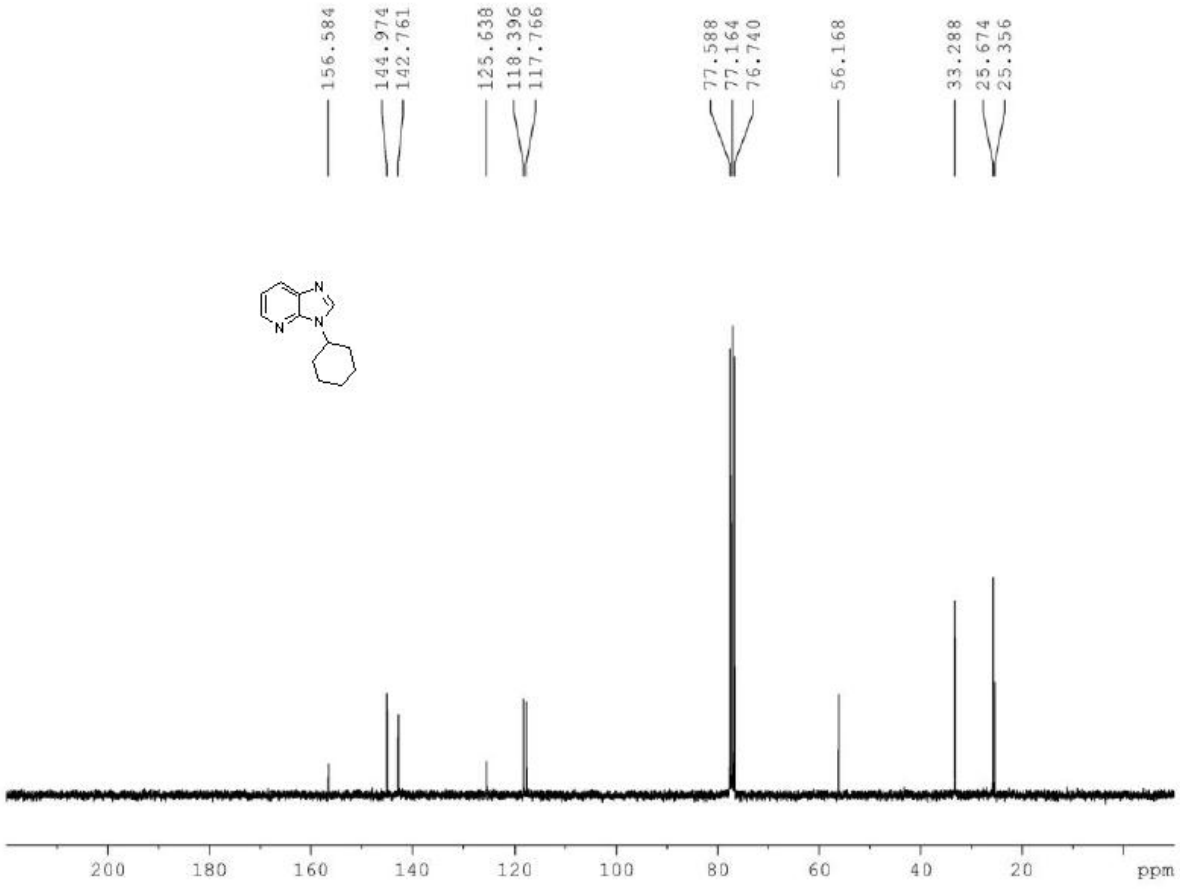


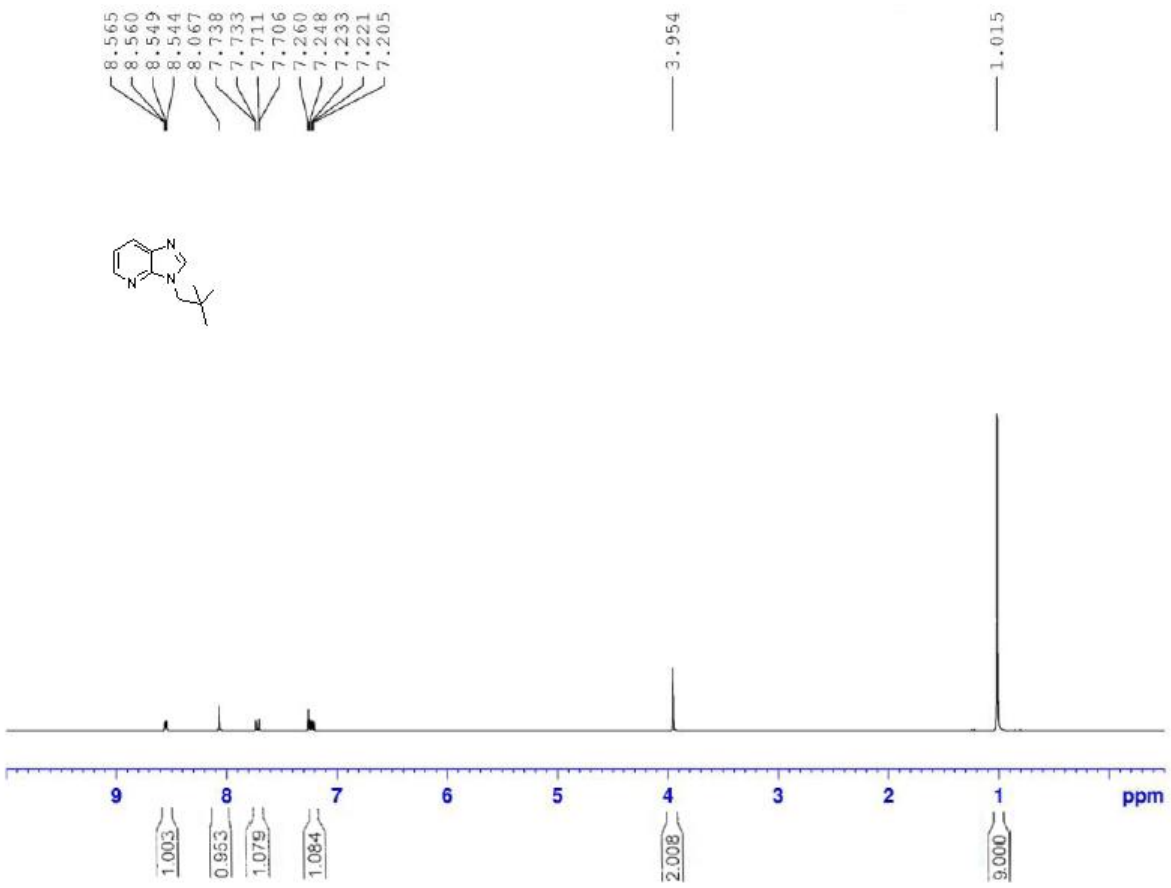
1-(2,4-dimethoxybenzyl)-1H-imidazo[4,5-b]pyridine

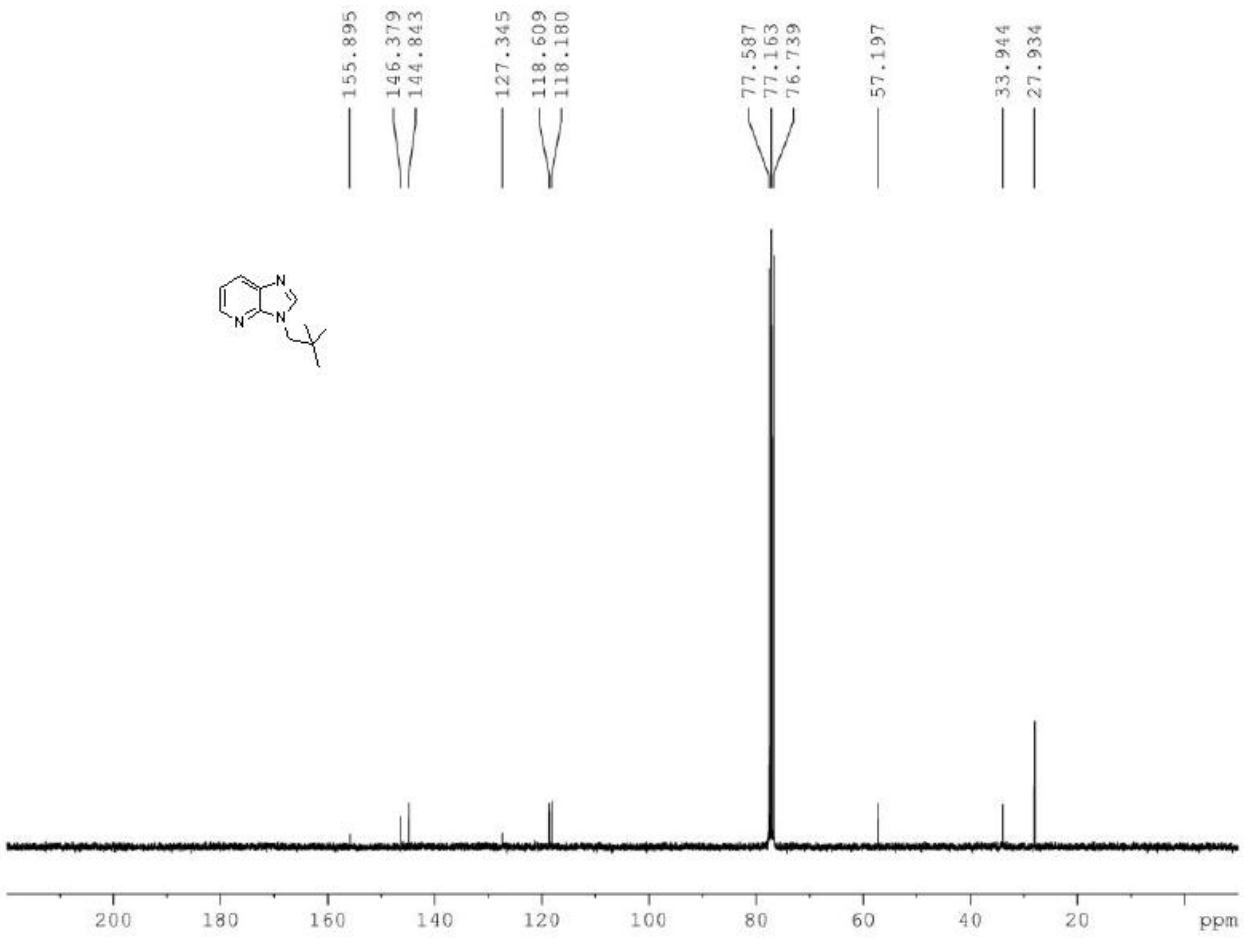


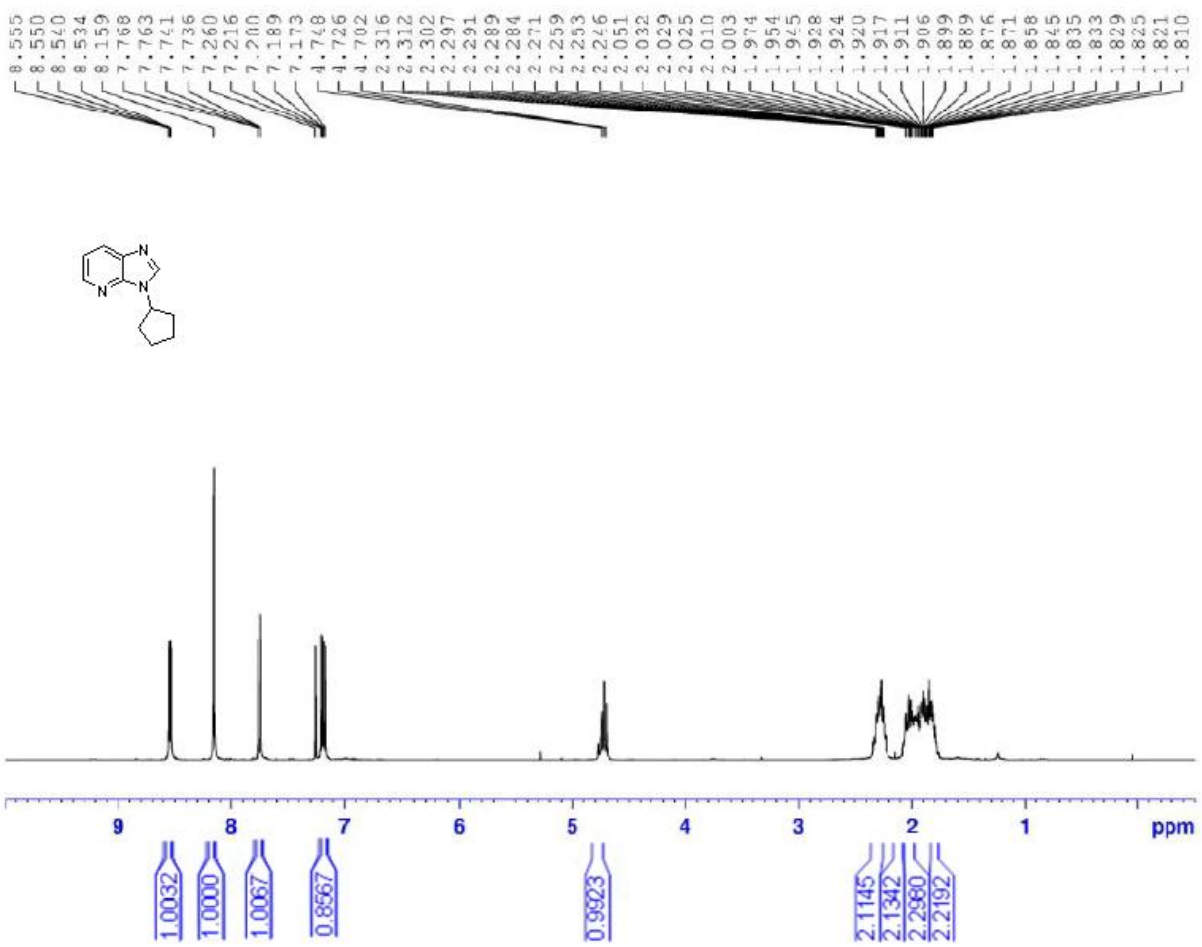

161.542
158.528
156.397
145.764
144.643
130.448
126.273
118.317
117.865
115.424
104.357
98.853
77.589
77.164
76.740
55.468
55.437
44.676
200
180
160
140
120
100
80
60
40
20
ppm


8.549
8.544
8.533
8.528
8.180
7.768
7.763
7.741
7.736
7.260
7.209
7.193
7.182
7.166
5.277
4.217
4.190
4.177
4.165
4.137
2.209
2.202
2.197
2.188
2.183
2.171
2.166
2.159
2.154
2.144
2.003
1.992
1.982
1.958
1.948
1.938
1.867
1.841
1.827
1.815
1.805
1.800
1.786
1.774
1.554
1.523
1.512
1.500
1.478
1.468
1.457
1.425
1.367
1.325
1.283
N
N
N
9
8
7
6
5
4
3
2
1
ppm
1.000
0.993
1.029
0.958
1.063
2.153
2.188
2.986
2.152
2.044


156.584
144.974
142.761
125.638
118.396
117.766
77.588
77.164
76.740
56.168
33.288
25.674
25.356
N
N
N
200
180
160
140
120
100
80
60
40
20
ppm


8.565
8.560
8.549
8.544
8.067
7.738
7.733
7.711
7.706
7.260
7.248
7.233
7.221
7.205
3.954
1.015
9
8
7
6
5
4
3
2
1
ppm
1.003
0.953
1.079
1.084
2.008
9.000


155.895
146.379
144.843
127.345
118.609
118.180
77.587
77.163
76.739
57.197
33.944
27.934
N
N
200
180
160
140
120
100
80
60
40
20
ppm


8.555
8.550
8.540
8.534
8.159
7.768
7.763
7.741
7.736
7.260
7.216
7.200
7.189
7.173
4.748
4.726
4.702
2.316
2.312
2.302
2.297
2.291
2.289
2.284
2.271
2.259
2.253
2.246
2.051
2.032
2.029
2.025
2.010
2.003
1.974
1.954
1.945
1.928
1.924
1.920
1.917
1.911
1.906
1.899
1.889
1.876
1.871
1.858
1.845
1.835
1.833
1.829
1.825
1.821
1.810
N
N
9
8
7
6
5
4
3
2
1
ppm
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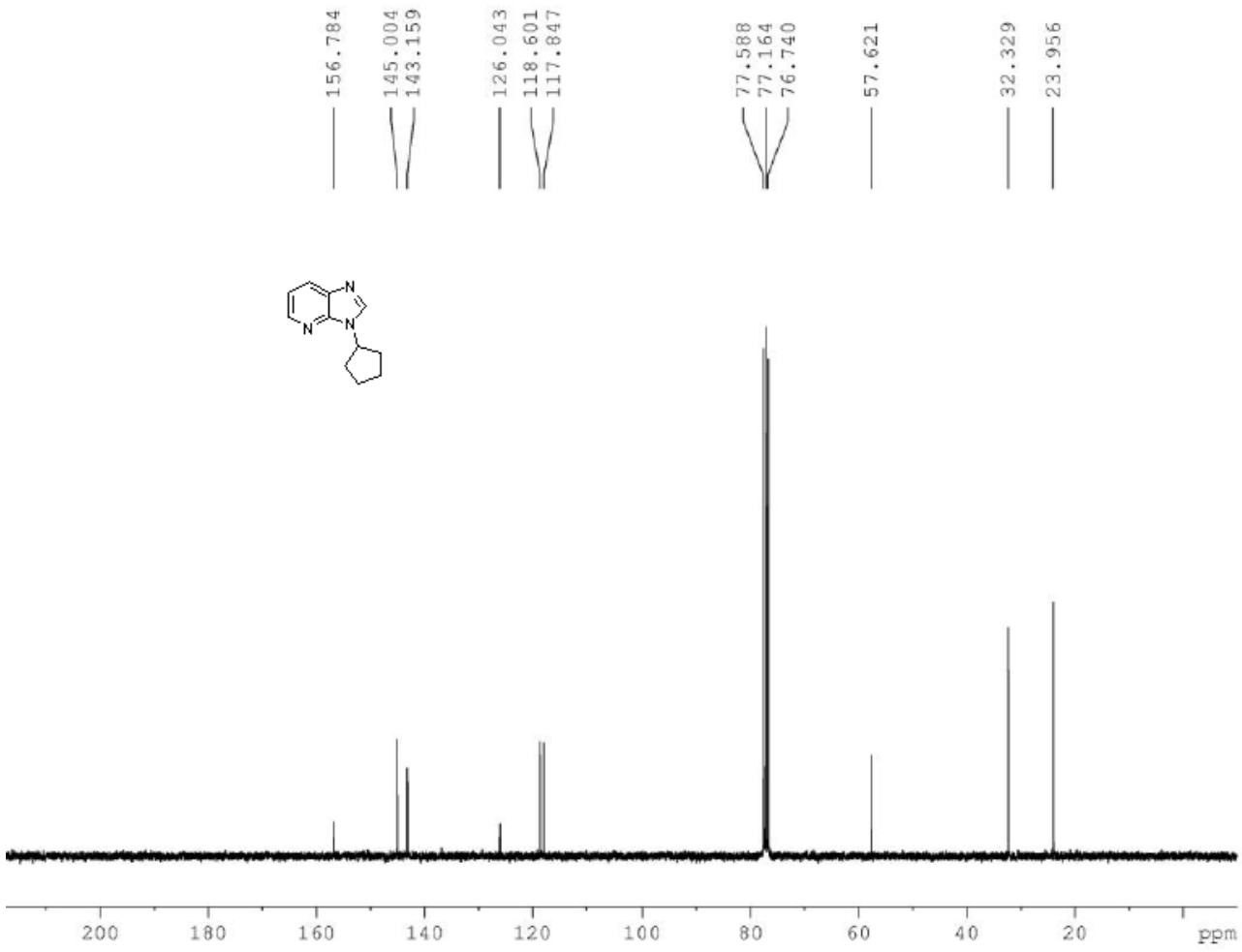
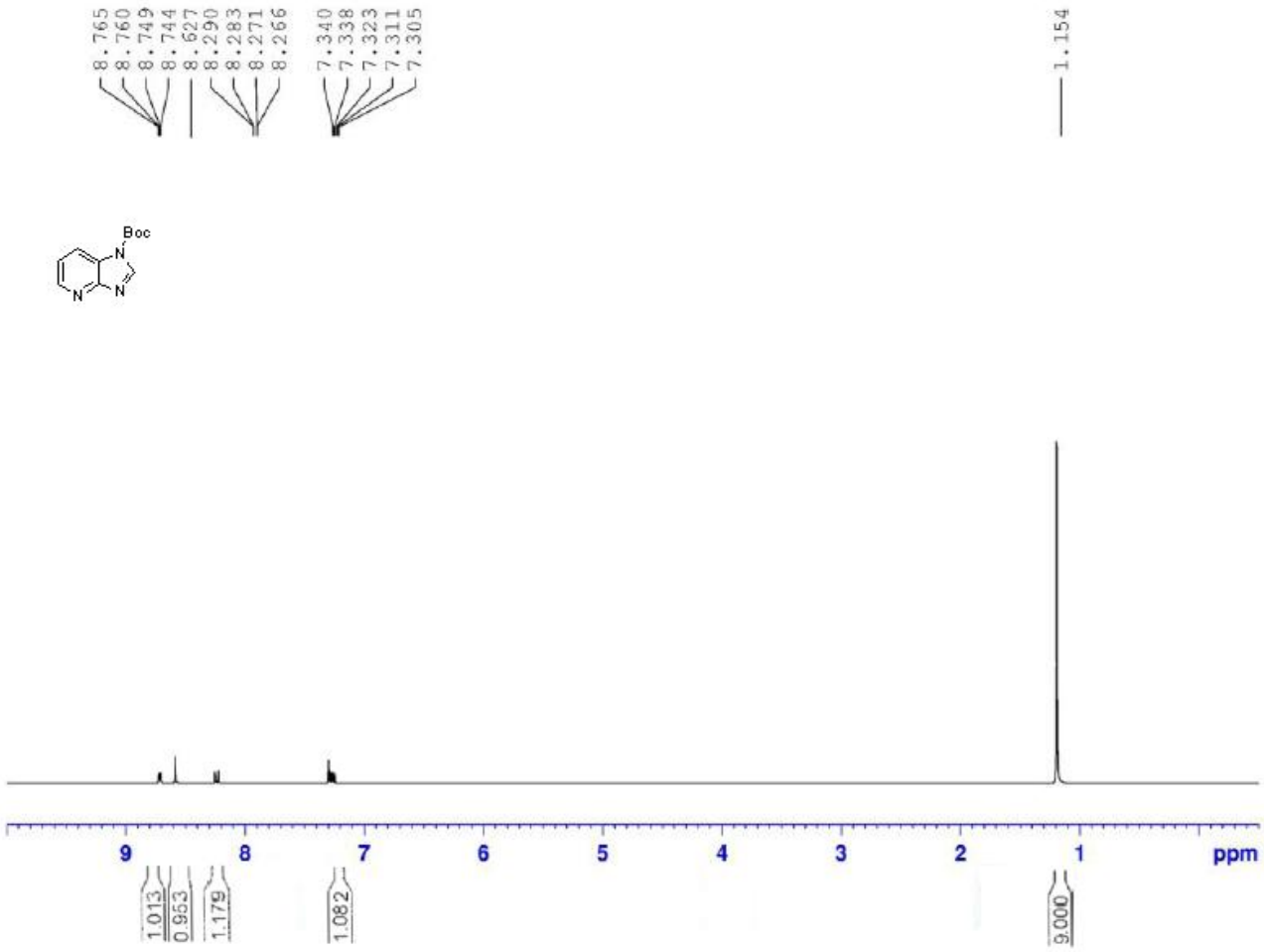
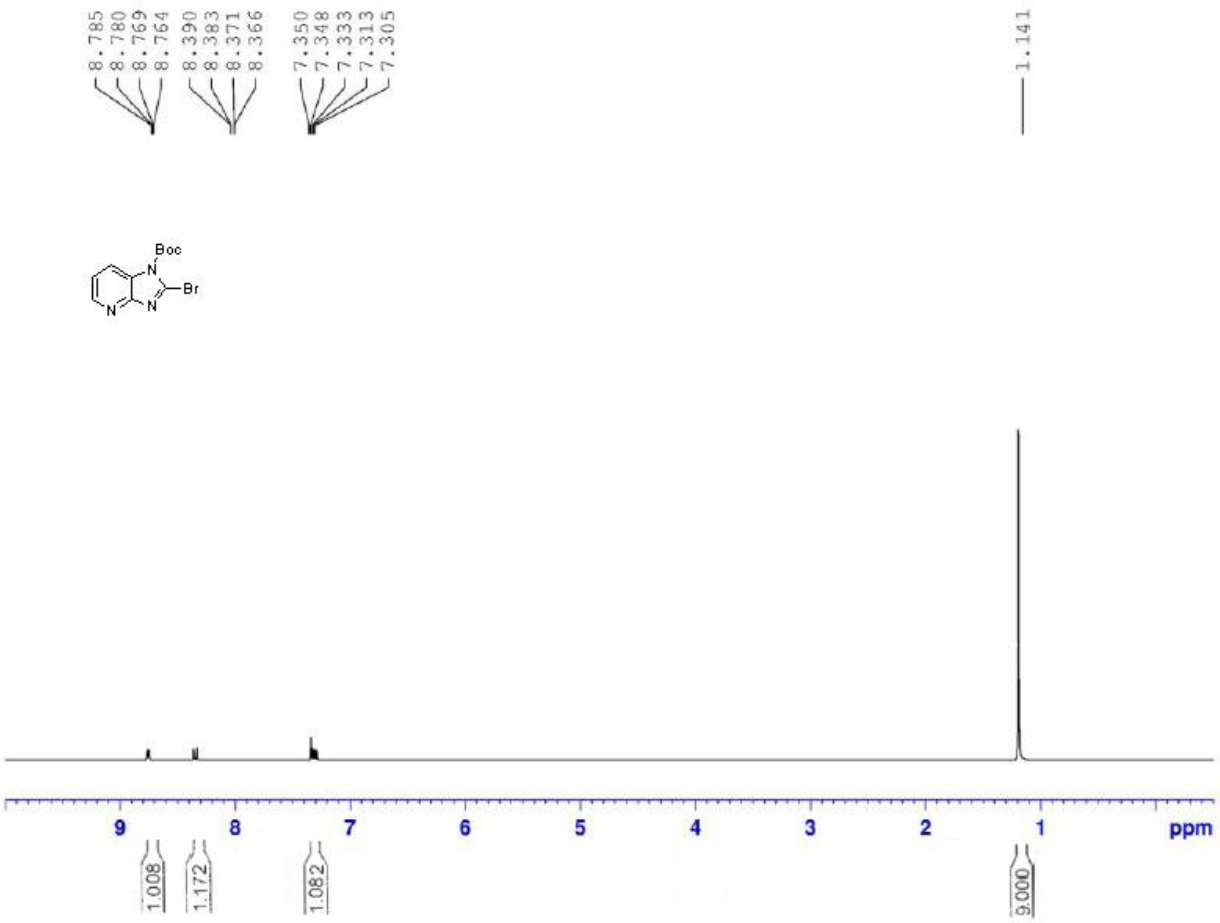
1.0000
1.0067
0.8667
0.9923
2.1145
2.1342
2.2960
2.2192


156.784
145.004
143.159
126.043
118.601
117.847
77.588
77.164
76.740
57.621
32.329
23.956
N
N
N
200
180
160
140
120
100
80
60
40
20
ppm


8.765
8.760
8.749
8.744
8.627
8.290
8.283
8.271
8.266
7.340
7.338
7.323
7.311
7.305
1.154
Boc
N
N
N
9
8
7
6
5
4
3
2
1
ppm
1.013
0.953
1.179
1.082
9.000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8.780
8.769
8.764
8.390
8.383
8.371
8.366
7.350
7.348
7.333
7.313
7.305
1.141
Boc
N
Br
N
N
9
8
7
6
5
4
3
2
1
ppm
1.008
1.172
1.082
9.000