Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary data

On-water Facile Synthesis of poly-substituted 6-arylamino pyridines and 2-pyrrolidone derivatives using tetragonal nano-ZrO_2 as reusable catalyst

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Materials: All the chemicals and reagents used in this work have been purchased from Sigma Aldrich without out further purification. The solvents were purchased from Himedia Pvt. Ltd. and distilled before use. Deionised water was used wherever required.

ESI-1. Method for the preparation of nano-catalysts:

(i) Method for the preparation of *t*-ZrO_2 nanoparticles:[1]

t-ZrO_2 nanoparticles (NPs) have been synthesized by dissociation of $ZrO_2Cl_2.8H_2O$ in a basic medium (pH~10) at low temperature without adding any stabilizer. For synthesizing *t*-ZrO_2 NPs, 100 ml 0.05M NaOH solution in deionized water was added in 100 ml 0.005M solution of $ZrO_2Cl_2.8H_2O$ in methanol-water (1:1) drop by drop over 30 minutes at constant temperature (5 ^oC) with continuous stirring. Subsequently, the mixture was stirred for 1 hour and then the sol solution was aged at 100 ^oC for 24 hours with continuous stirring. The white solids formed were separated by centrifugation and washed with dilute solution of NH_4NO_3 for subsequent times until negative test for chloride ion followed by washed with de-ionized water (4x20 ml) and ethanol (2x10 ml). The nanoparticles were dried well and then calcined at 500 ^oC for 4 hours. The formation of nano-sized *t*-ZrO_2 particles was confirmed by powder XRD, HRTEM studies.

(ii) Method for the preparation of monoclinic ZrO_2 nanoparticles:[1]

Monoclinic ZrO_2 nanoparticles were prepared following the above mentioned protocol and calcined the solid sample at 900 ^oC for 4 hrs.

(iii) Method for the preparation of Fe_3O_4 nanoparticles:[2]

The magnetic Fe_3O_4 nanoparticles were synthesized by co-precipitation method. Briefly, co-precipitating aqueous solutions of $(NH_4)_2Fe_2(SO_4)_3$ and $FeCl_3$ mixtures, in alkaline medium. $(NH4)_2Fe_2(SO_4)_3$ and $FeCl_3$ solutions are mixed in their respective stoichiometry (i.e. Ratio Fe : Fe =1:2).The mixture is kept at 80 ^oC. This mixture is added to the boiling solution of NaOH (0.5

mol. is dissolved in 200 ml of distilled water) within 10 second under constant stirring. The solution was maintained at 90-95 ^{o}C for 1.5 h. The Fe_3O_4 nanoparticles were washed several times by distilled water and used for reaction.

(iv) Method for the preparation of SiO_2 nanoparticles:[3]

A mixture of 20 ml of ethanol and 20 ml water was stirred for few minutes then 4 ml of tetraethyl orthosilicate (TEOS) followed by 4 ml of aqueous ammonia solution (NH_4OH) were added with continuous stirring by the mechanical stirrer machine for 5 hours. After that the mixture was kept to settle down and washed thoroughly with water and ethanol, centrifuged and white colloidal part was used for reactions.

(v) Method for the Preparation of CuO nanoparticles:[4]

To prepare CuO NPs NaOH (0.5M) solution added drop by drop to a 0.1 M copper nitrate solution (100 ml) in a 500 ml beaker till the pH of the solution reaches to 12 (checked by pH paper). The blue green gel was formed. It was then filtered and washed several time with distilled water to free nitrate. It was then dried in a hot oven at 100 ^{o}C for 10 hours to decompose $Cu(OH)_2$ to CuO NPs.

(vi) Method for the Preparation of NiO nanoparticles:[5]

To prepare NiO NPs NaOH (0.5M) solution added drop by drop to a 0.1 M nickel nitrate solution (100 ml) in a 500 ml beaker till the pH of the solution reaches to 12 (checked by pH paper). The greenish gel was formed. It was then filtered and washed several time with distilled water to free nitrate. It was then dried in a hot oven at 100 ^{o}C for 10 hours to decompose $Ni(OH)_2$ to NiO NPs.

(vii) Method for the Preparation of ZnO nanoparticles:[6]

ZnO NPs have been synthesized by dissociation of $Zn(OAc)_2.2H_2O$ in a basic medium at temperatures 60-75°C. For synthesizing nanoparticles ZnO NPs, 100 ml 3M NaOH solution in ethanol is slowly added in 50 ml 1M solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ in ethanol kept at 65 °C. The final solution was stirred and heated at 65 °C for 1 h. When the reactions were completed, the

solid and solution phases were separated by centrifugation and the solids were washed free of salts with de-ionized water (3x5 ml) and ethanol (2x5 ml).

ESI-2. Experimental procedure for the synthesis of ethyl 5-cyano-2-methyl-4-phenyl-6-(phenylamino)nicotinate (1a):

A mixture of the benzaldehyde (1 mmol, 106 mg), malononitrile (1 mmol, 66 mg), ethylaceto acetate (1 mmol, 130 mg), aniline (1 mmol, 93mg) and *t*-ZrO_2 catalyst (10 mmol%, 12 mg) was refluxed in 5 mL ethanol-water (1:1) mixture for 2 hours indicated by TLC. After the completion of the reaction, catalyst was separated by simple filtration and the solid product was extracted with ethyl acetate. After evaporation of solvent off-white crystals were obtained which was further purified by recrystallization form hot ethanol to produce pure ethyl 5-cyano-2-methyl-4-phenyl-6-(phenylamino)nicotinate (yield = 92%, 325 mg).

ESI-3. Experimental procedure for the synthesis of ethyl 4-hydroxy-5-oxo-1,2-diphenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (2a):

A mixture of the benzaldehyde (1 mmol, 106 mg), aniline (1 mmol, 93 mg), diethyl acetylenedicarboxylate (1 mmol, 170 mg) and *t*-ZrO_2 catalyst (10 mmol%, 12 mg) was refluxed in 5 mL ethanol-water (1:1) mixture for 8 minutes indicated by TLC. After the completion of the reaction, nanoparticles were separated by simple filtration and the semi solid product was extracted with ethyl acetate. After evaporation of solvent yellowish crystals were obtained which was then further recrystallized from hot ethanol to get pure yellow crystals of ethyl 4-hydroxy-5-oxo-1,2-diphenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (2a) (yield = 92%, 297 mg).

ESI-4. Powder XRD of 8th times reused *t*-ZrO_2 nanoparticles:

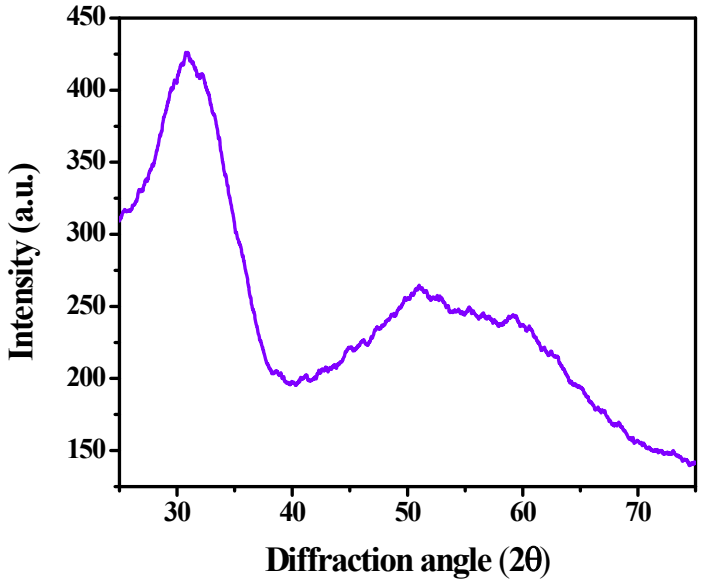


Fig. S1 Powder XRD pattern of t-ZrO_2 nanoparticles after 8th cycle.

ESI-5. IR Based Absorption Experiment to evaluate Lewis acidity/basicity of *t*-ZrO_2 nanoparticles:

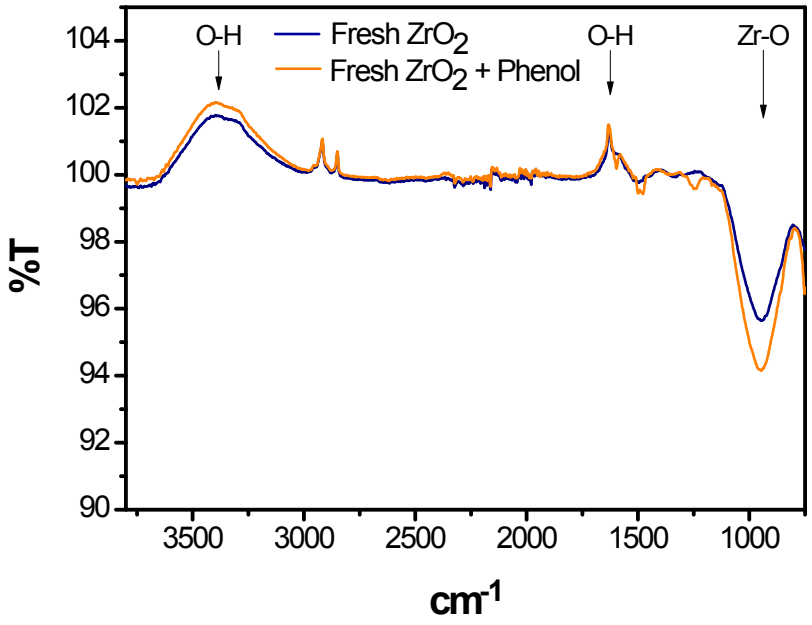


Fig. S2 IR based absorption experiment to evaluate Lewis basicity of *t*-ZrO_2 NPs.

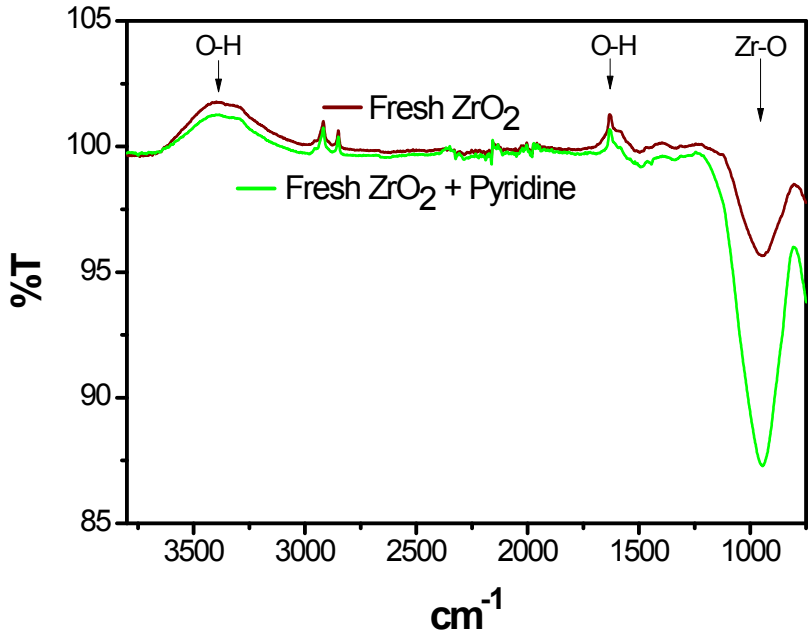
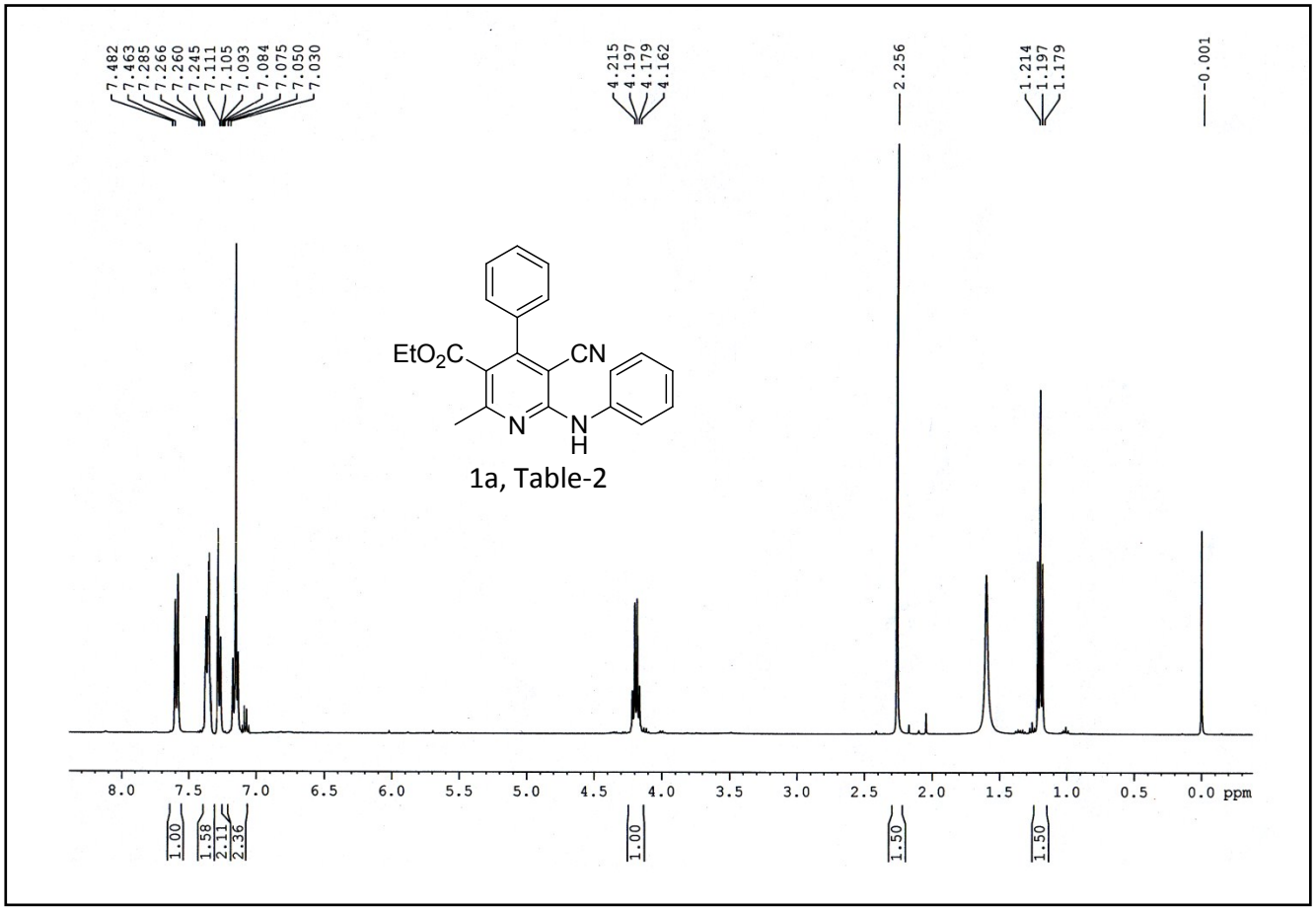
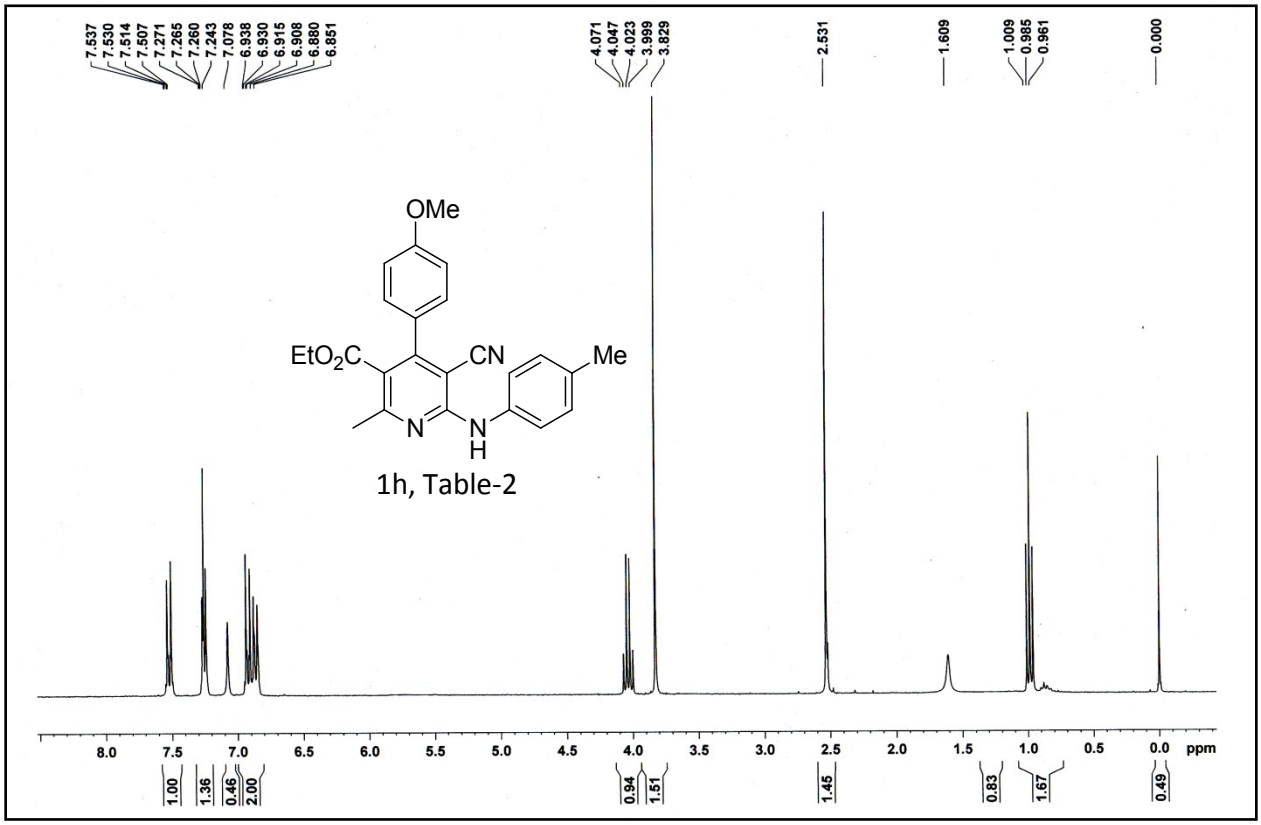


Fig. S3 IR based absorption experiment to evaluate Lewis acidity of *t*-ZrO_2 NPs.

ESI-5. Representative ^{1}HNMR copies of compounds: The NMR spectra were recorded in 300 or 500 MHz Bruker instrument and $CDCl_3$ were used as NMR solvent.

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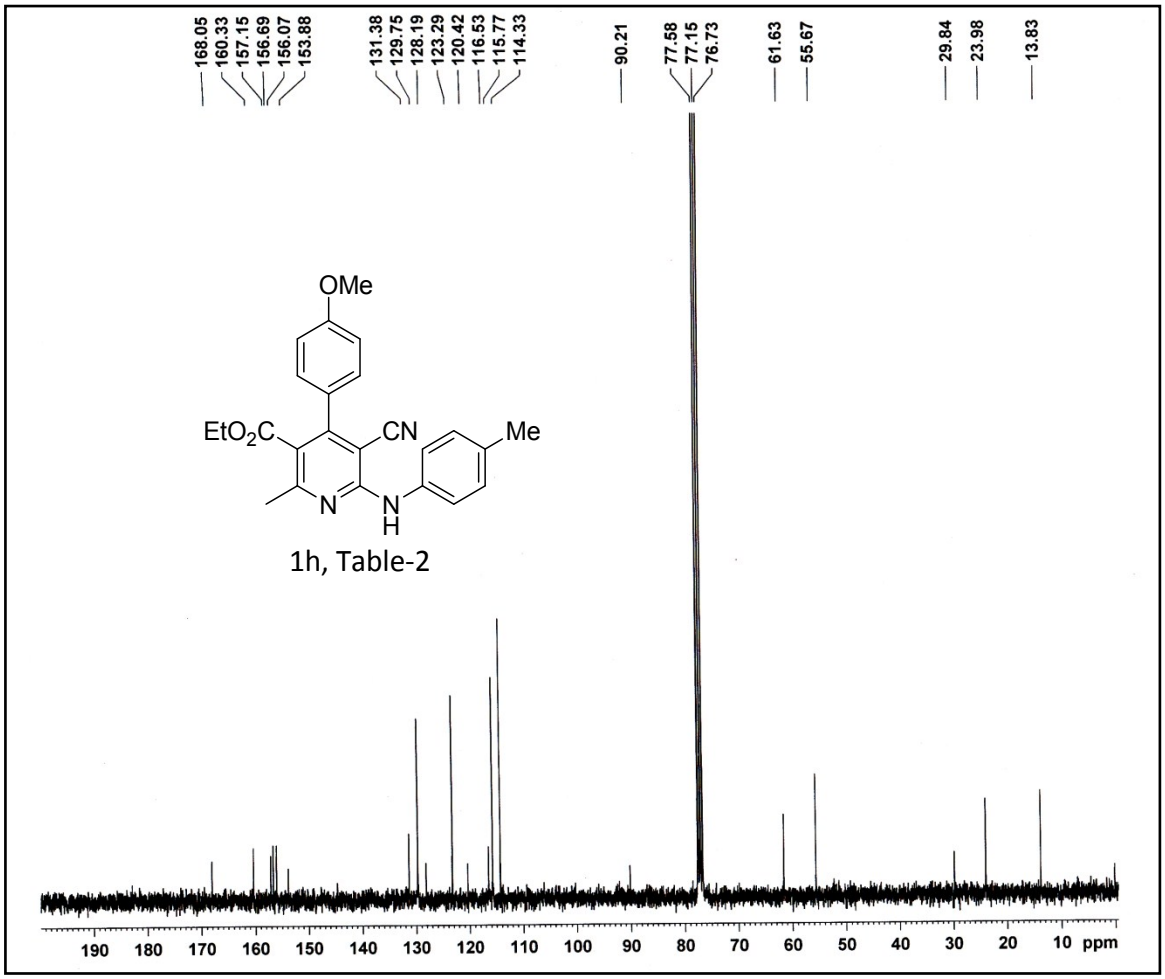
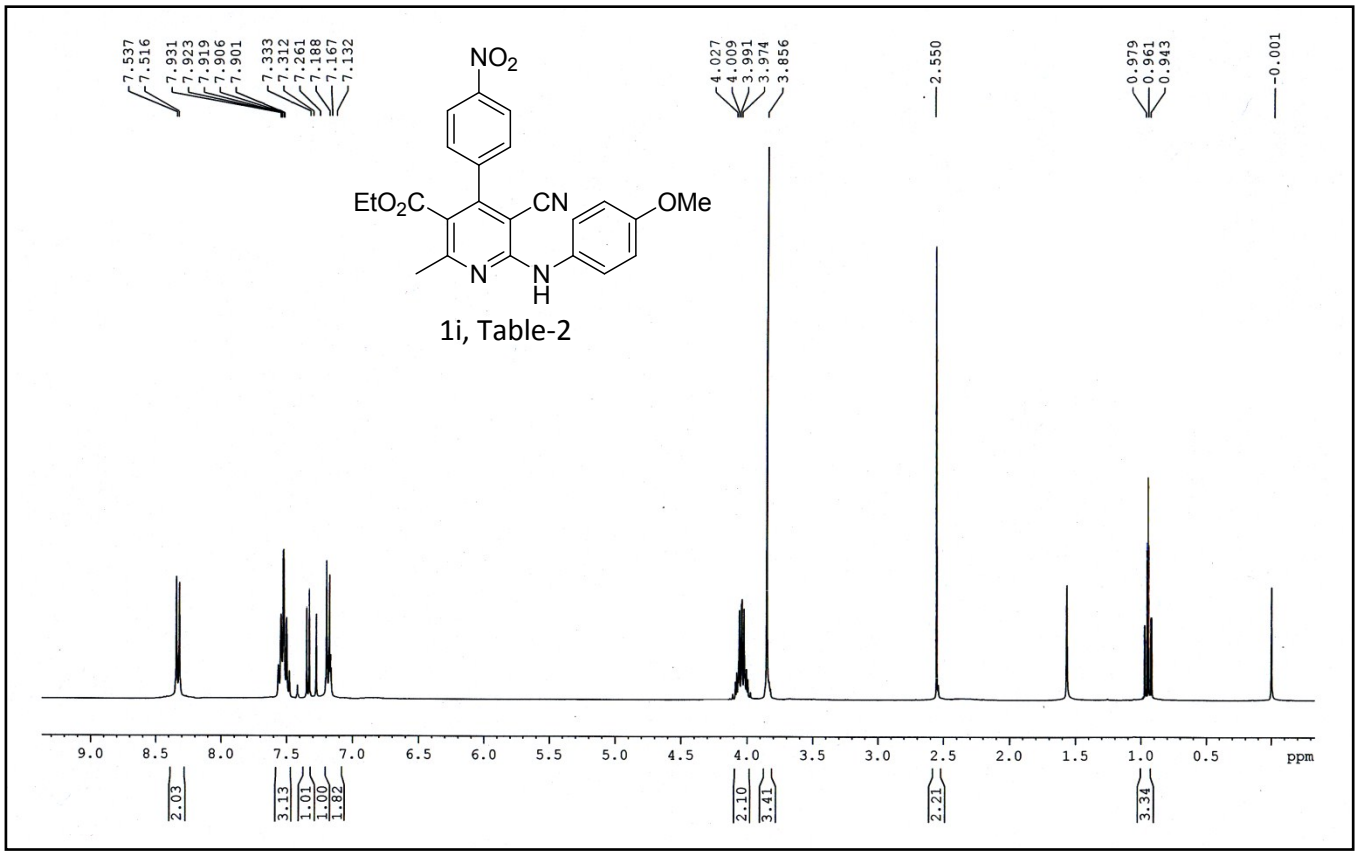
7.530
7.514
7.507
7.271
7.265
7.260
7.243
7.078
6.938
6.930
6.915
6.908
6.880
6.851
4.071
4.047
4.023
3.999
3.829
2.531
1.609
1.009
0.985
0.961
0.000
OMe
EtO2C
CN
Me
N
N
H
1h, Table-2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.36
0.46
2.00
0.94
1.51
1.45
0.83
1.67
0.49


168.05
160.33
157.15
156.69
156.07
153.88
131.38
129.75
128.19
123.29
120.42
116.53
115.77
114.33
90.21
77.58
77.15
76.73
61.63
55.67
29.84
23.98
13.83
OMe
EtO2C
CN
Me
N
N
H
1h, Table-2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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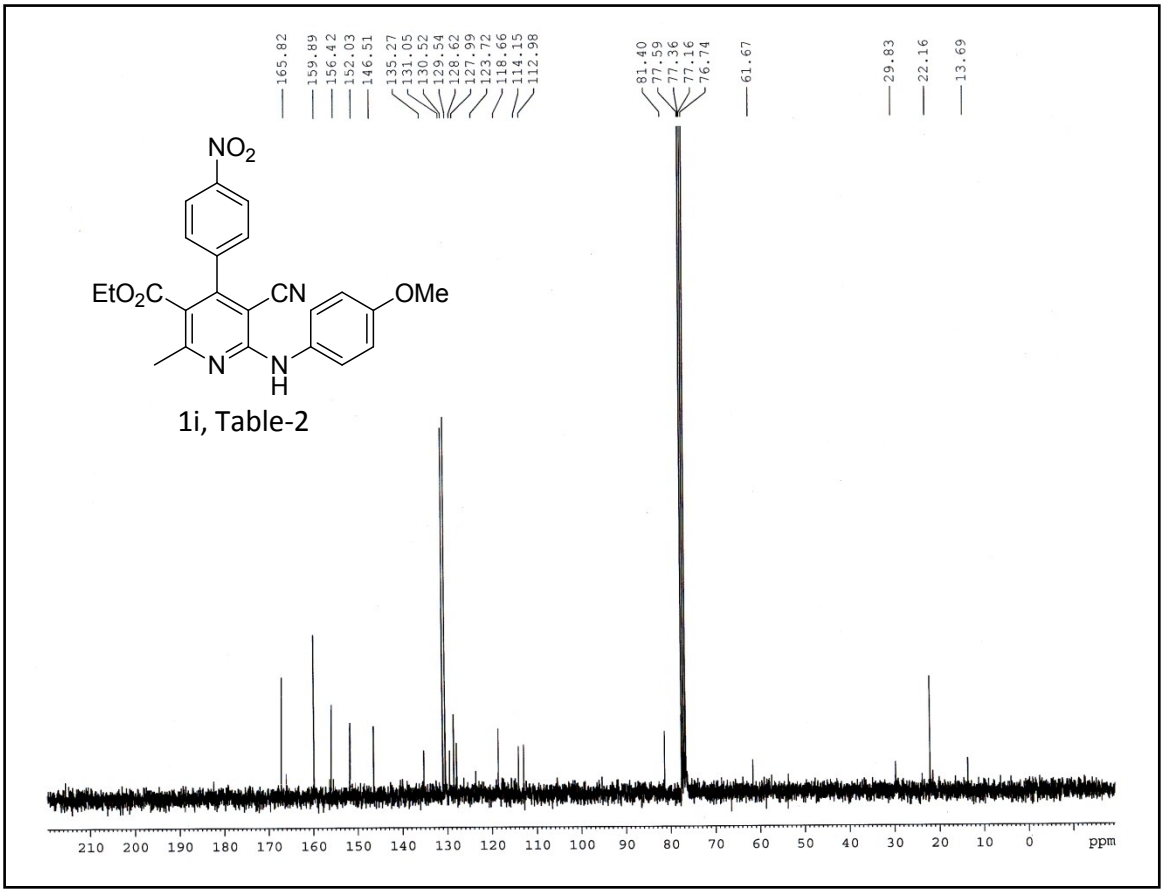
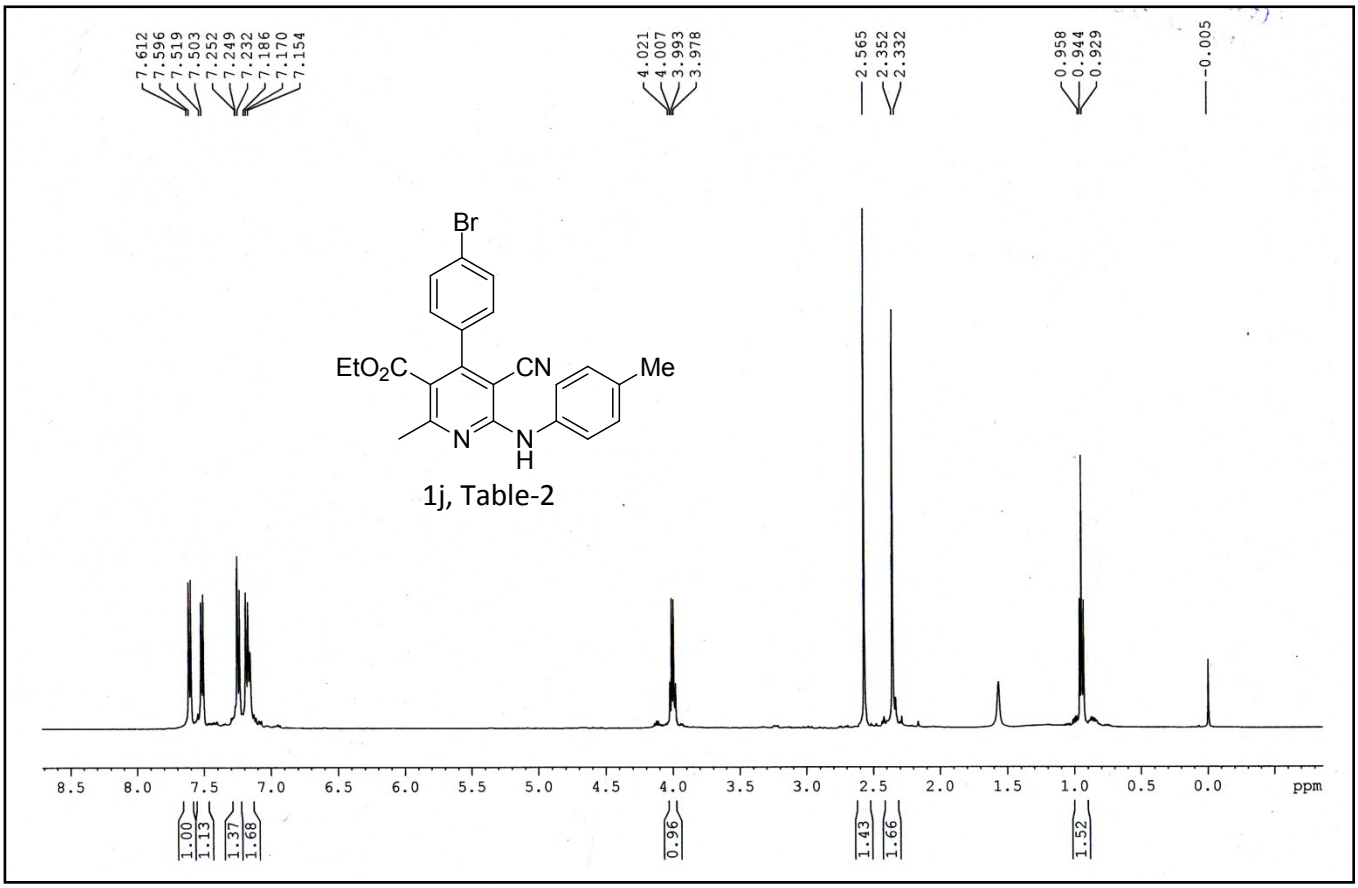
7.516
7.931
7.923
7.919
7.906
7.901
7.333
7.312
7.261
7.188
7.167
7.132
4.027
4.009
3.991
3.974
3.856
2.550
0.979
0.961
0.943
-0.001
NO2
EtO2C
CN
OMe
N
N
H
1i, Table-2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
3.13
1.01
1.00
1.82
2.10
3.41
2.21
3.34


165.82
159.89
156.42
152.03
146.51
135.27
131.05
130.52
129.54
128.62
127.99
123.72
118.66
114.15
112.98
81.40
77.59
77.36
77.16
76.74
61.67
29.83
22.16
13.69
NO2
EtO2C
CN
OMe
N
N
H
1i, Table-2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.519
7.503
7.252
7.249
7.232
7.186
7.170
7.154
4.021
4.007
3.993
3.978
2.565
2.352
2.332
0.958
0.944
0.929
-0.005
Br
EtO2C
CN
Me
N
N
H
1j, Table-2
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
ppm
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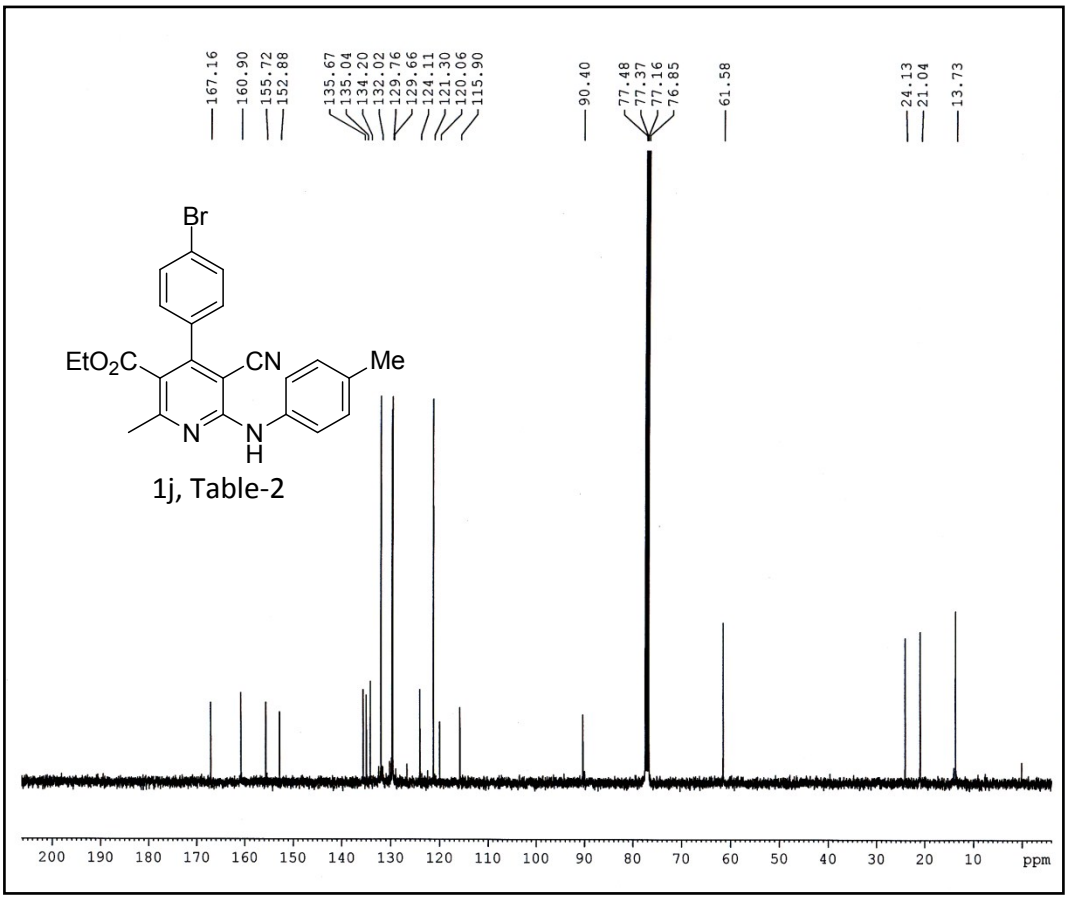
1.37
1.68
0.96
1.43
1.66
1.52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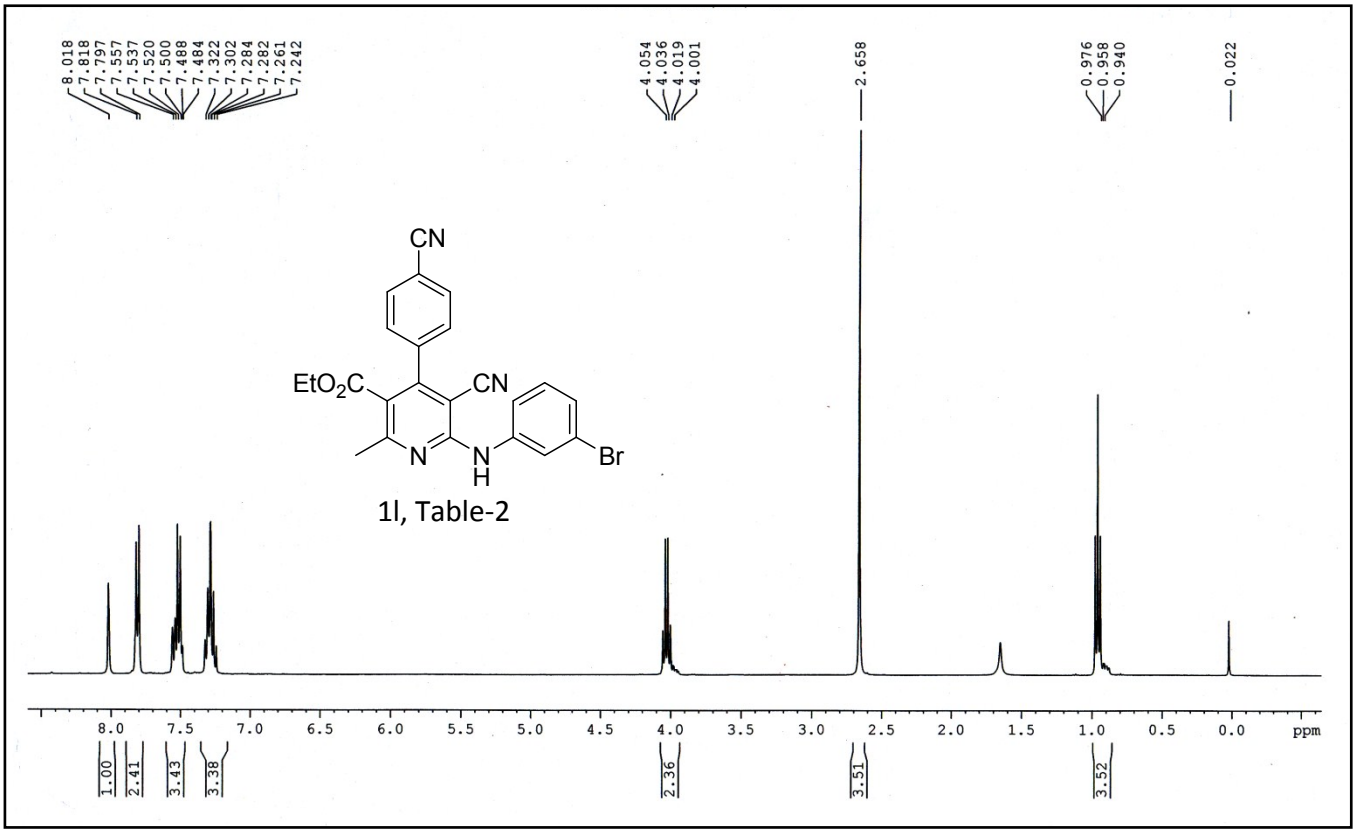
160.90
155.72
152.88
135.67
135.04
134.20
132.02
129.76
129.66
124.11
121.30
120.06
115.90
90.40
77.48
77.37
77.16
76.85
61.58
24.13
21.04
13.73
Br
EtO2C
CN
Me
N
N
H
1j, Table-2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.797
7.557
7.537
7.520
7.500
7.488
7.484
7.322
7.302
7.284
7.282
7.261
7.242
4.054
4.036
4.019
4.001
2.658
0.976
0.958
0.940
0.022
CN
EtO2C
CN
N
N
H
Br
1l, Table-2
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
ppm
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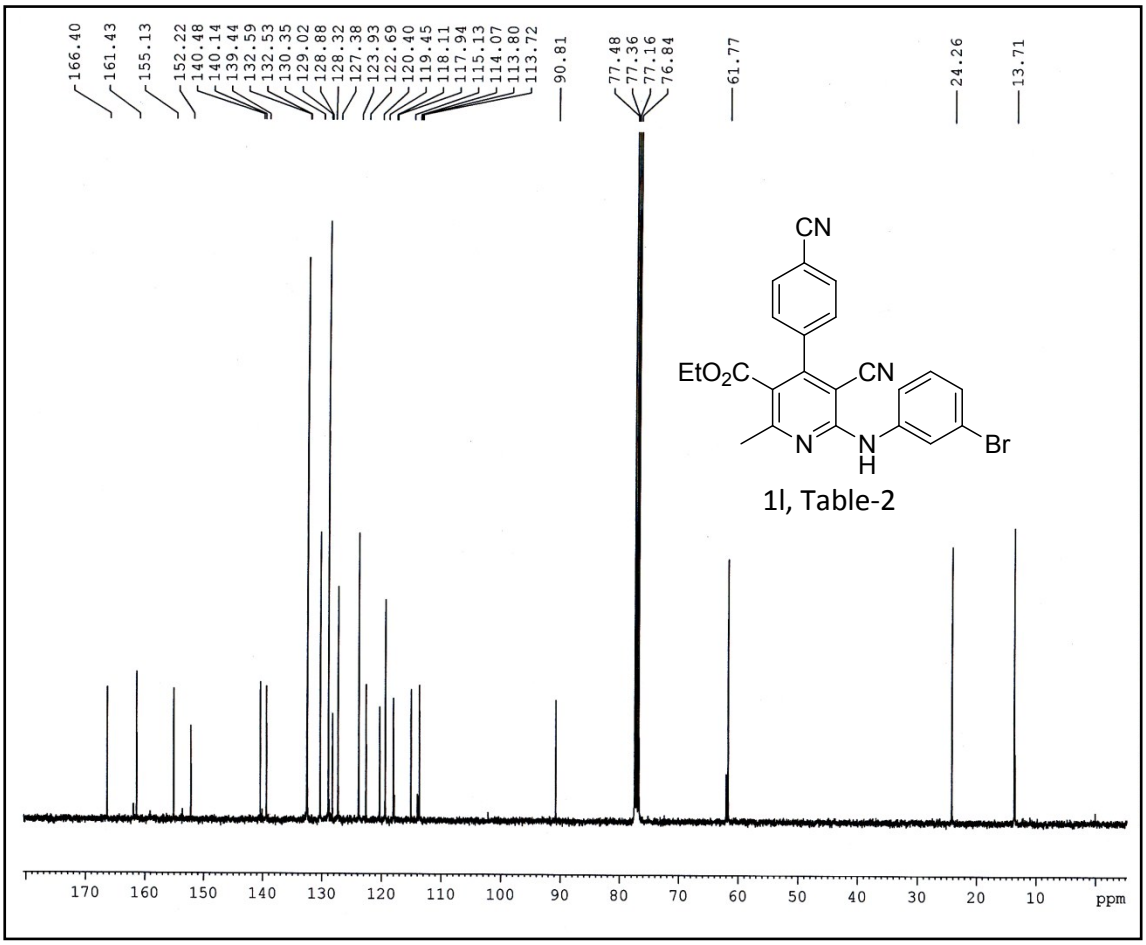
2.41
3.43
3.38
2.36
3.51
3.52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155.13
152.22
140.48
140.14
139.44
132.59
132.53
130.35
129.02
128.88
128.32
127.38
123.93
122.69
120.40
119.45
118.11
117.94
115.13
114.07
113.80
113.72
90.81
77.48
77.36
77.16
76.84
61.77
24.26
13.71
CN
EtO2C
CN
N
N
H
Br
1l, Table-2
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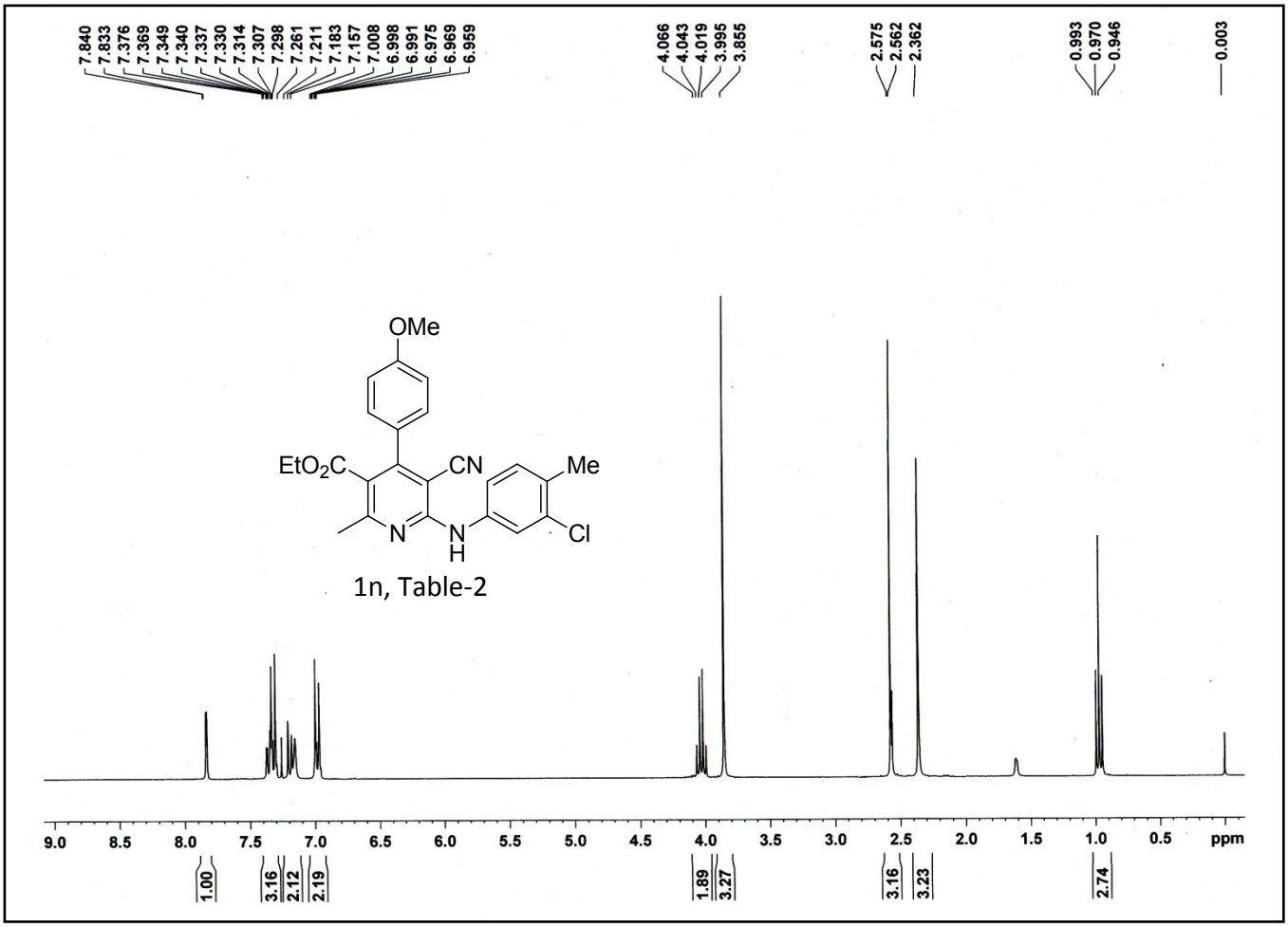
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.833
7.376
7.369
7.349
7.340
7.337
7.330
7.314
7.307
7.298
7.261
7.211
7.183
7.157
7.008
6.998
6.991
6.975
6.969
6.959
4.066
4.043
4.019
3.995
3.855
2.575
2.562
2.362
0.993
0.970
0.946
0.003
OMe
EtO2C
CN
Me
N
N
H
Cl
1n, Table-2
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
ppm
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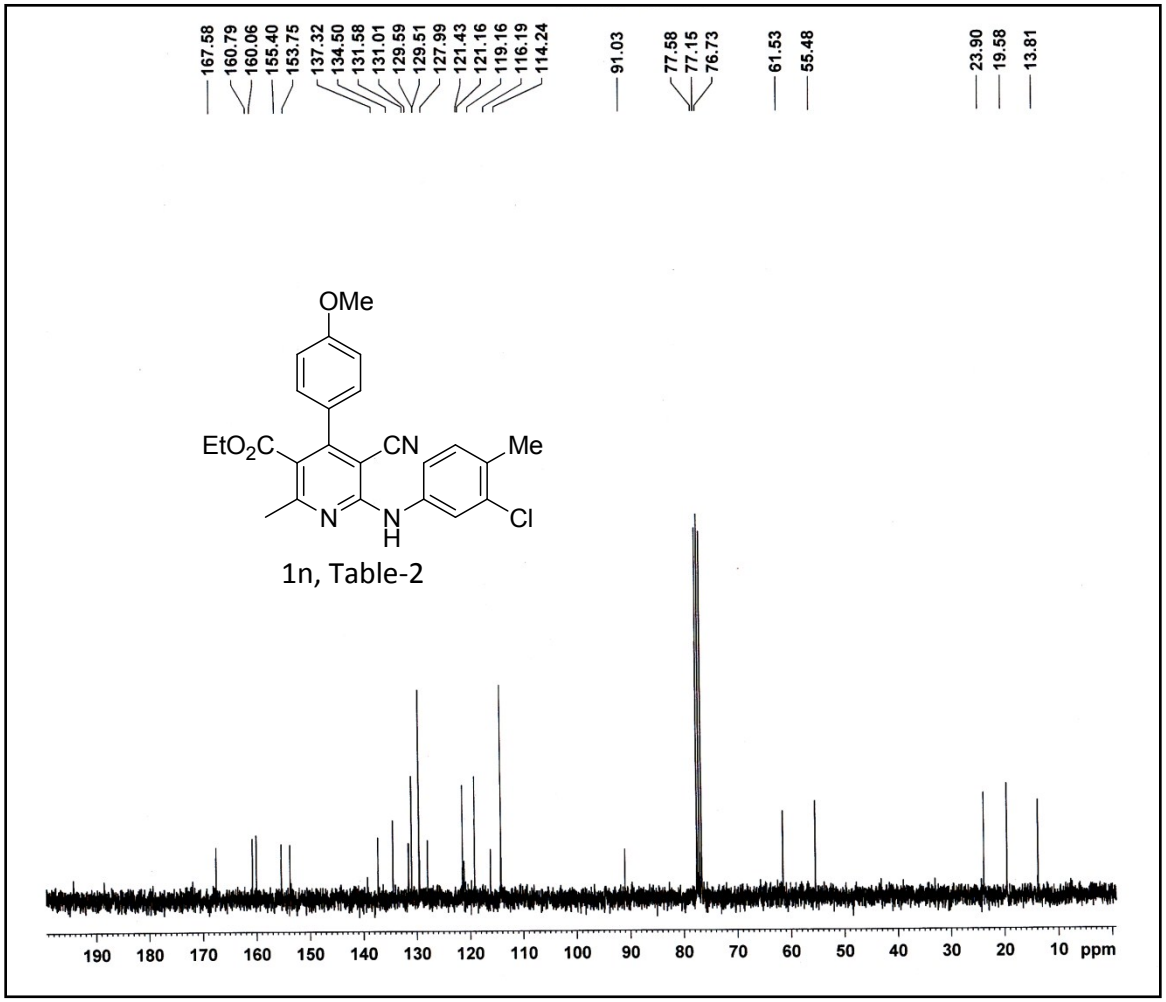
2.12
2.19
1.89
3.27
3.16
3.23
2.74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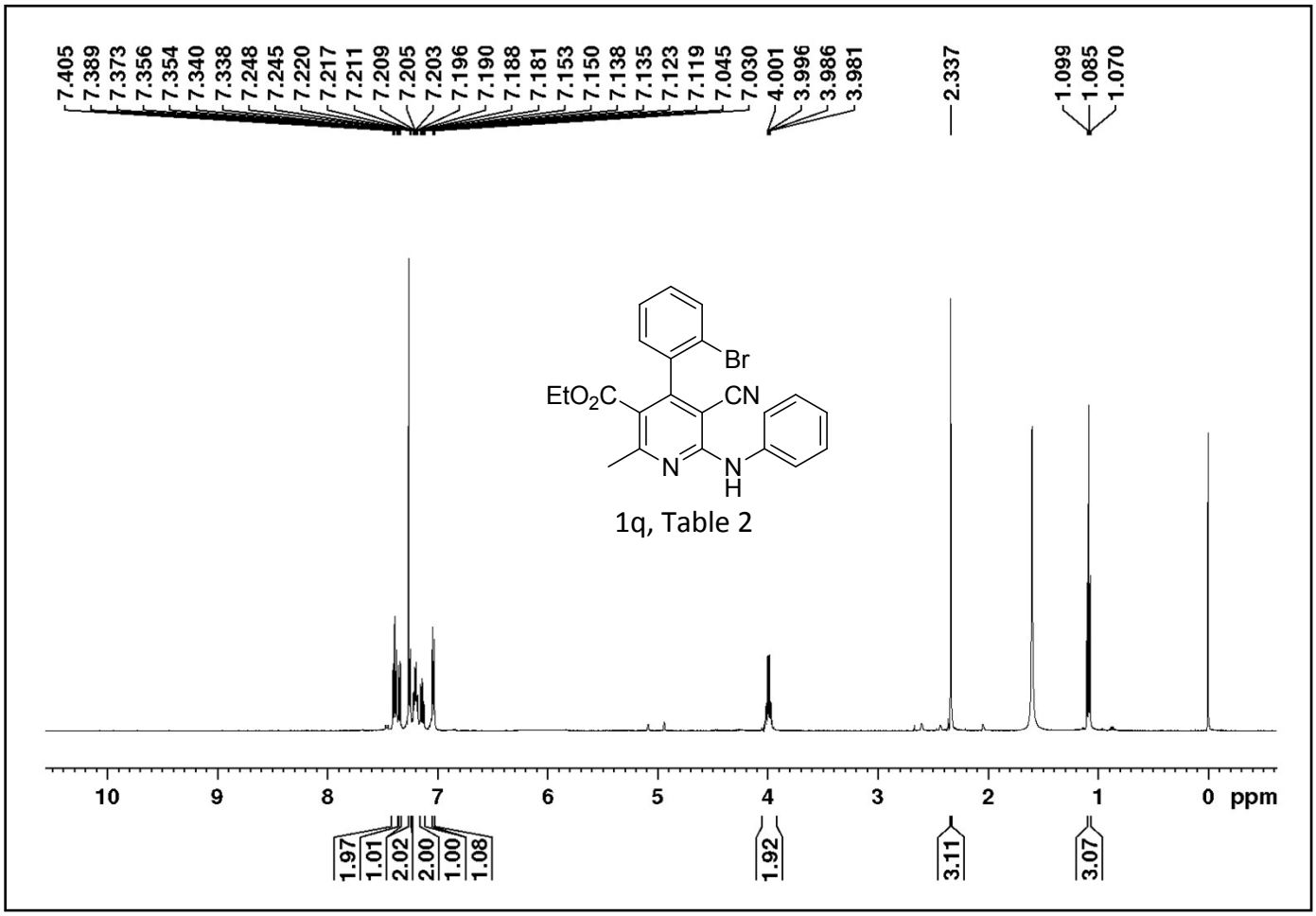
155.40
153.75
137.32
134.50
131.58
131.01
129.59
129.51
127.99
121.43
121.16
119.16
116.19
114.24
91.03
77.58
77.15
76.73
61.53
55.48
23.90
19.58
13.81
OMe
EtO2C
CN
Me
N
N
H
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

1n, Table-2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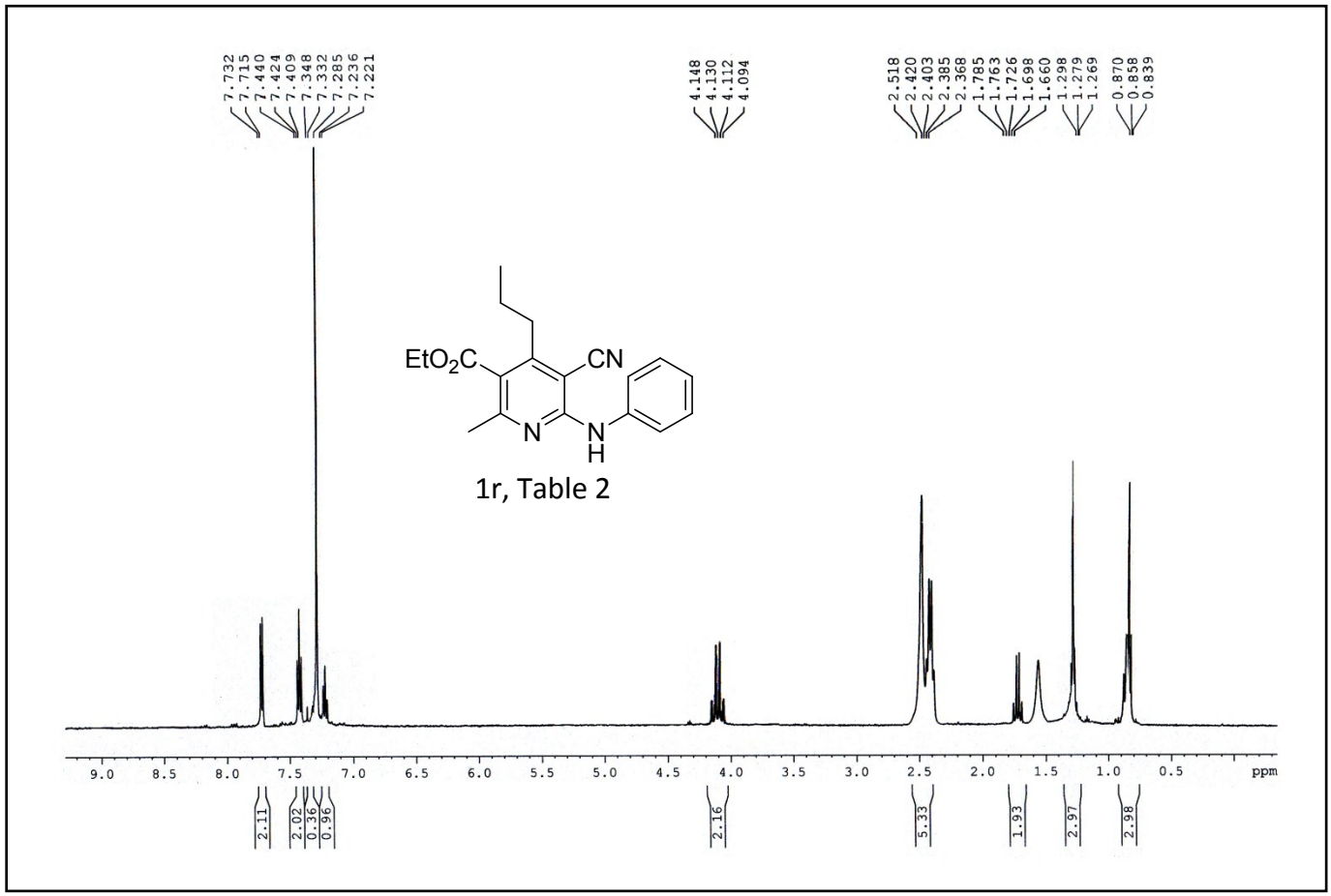
7.248
7.245
7.220
7.217
7.211
7.209
7.205
7.203
7.196
7.190
7.188
7.181
7.153
7.150
7.138
7.135
7.123
7.119
7.045
7.030
4.001
3.996
3.986
3.981
2.337
1.099
1.085
1.070
Br
EtO2C
CN
N
N
H
1q, Table 2
10
9
8
7
6
5
4
3
2
1
0 ppm
1.97
1.01
2.02
2.00
1.00
1.08
1.92
3.11
3.07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7.348
7.332
7.285
7.236
7.221
4.148
4.130
4.112
4.094
2.518
2.420
2.403
2.385
2.368
1.785
1.763
1.726
1.698
1.660
1.298
1.279
1.269
0.870
0.858
0.839
EtO2C
CN
N
N
H
1r, Table 2
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
ppm
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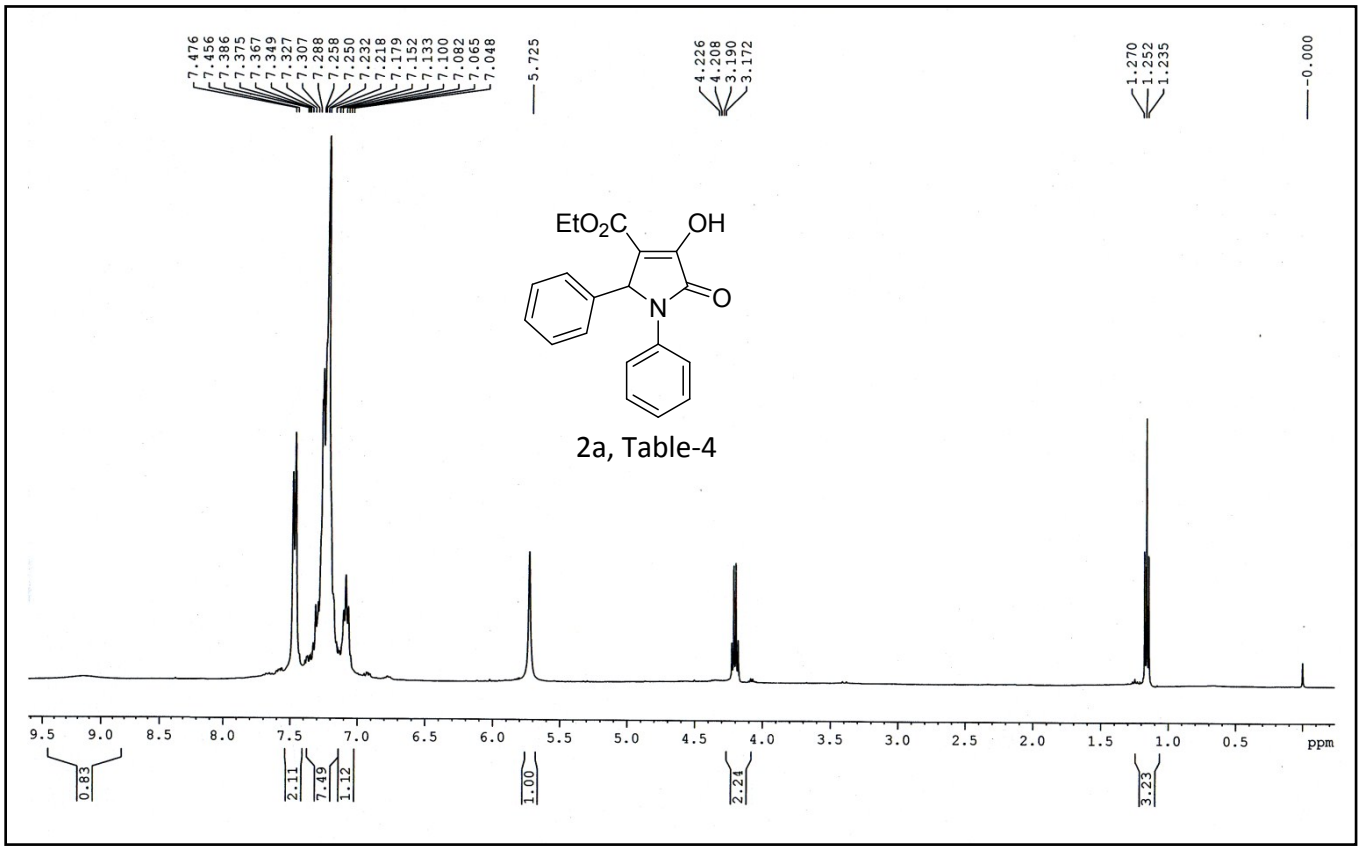
0.96
2.16
5.33
1.93
2.97
2.98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7.375
7.367
7.349
7.327
7.307
7.288
7.258
7.250
7.232
7.218
7.179
7.152
7.133
7.100
7.082
7.065
7.048
5.725
4.226
4.208
3.190
3.172
1.270
1.252
1.235
0.000
EtO2C
OH
O
N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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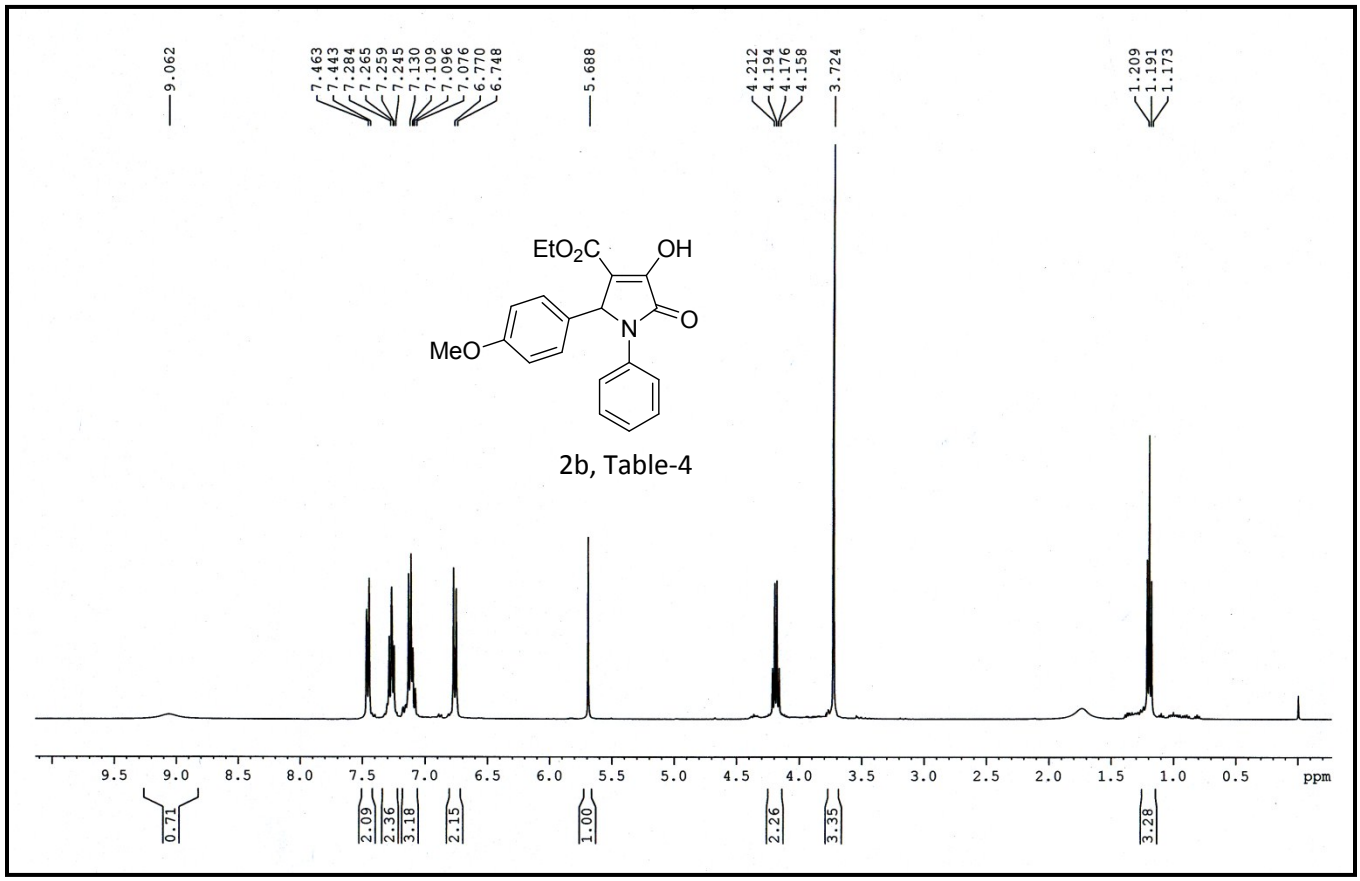
1.12
1.00
2.24
3.23

2a, Table-4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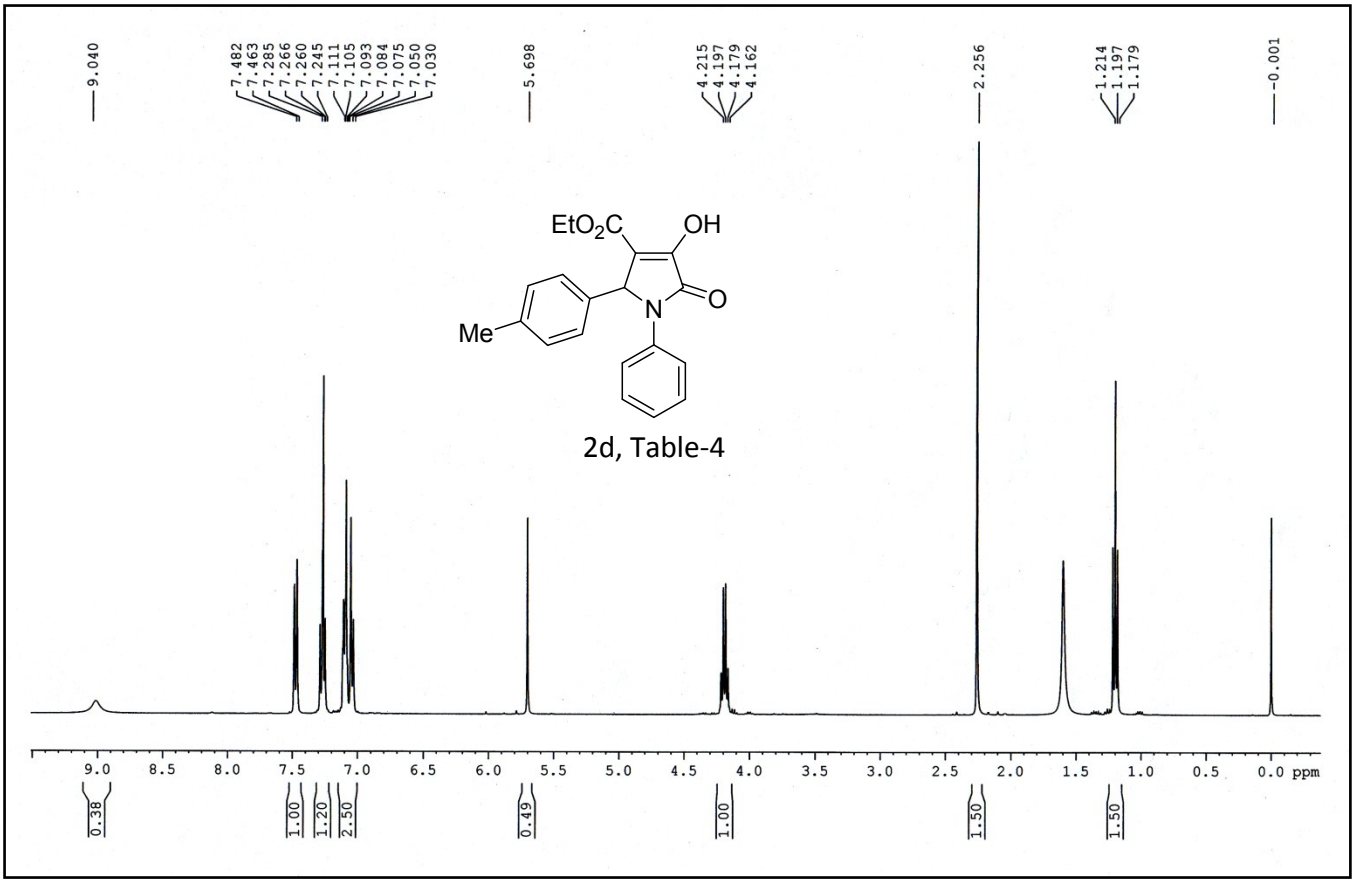
7.443
7.284
7.265
7.259
7.245
7.130
7.109
7.096
7.076
6.770
6.748
5.688
4.212
4.194
4.176
4.158
3.724
1.209
1.191
1.173
EtO2C
OH
O
N
MeO
2b, Table-4
ppm
0.71
2.09
2.36
3.18
2.15
1.00
2.26
3.35
3.28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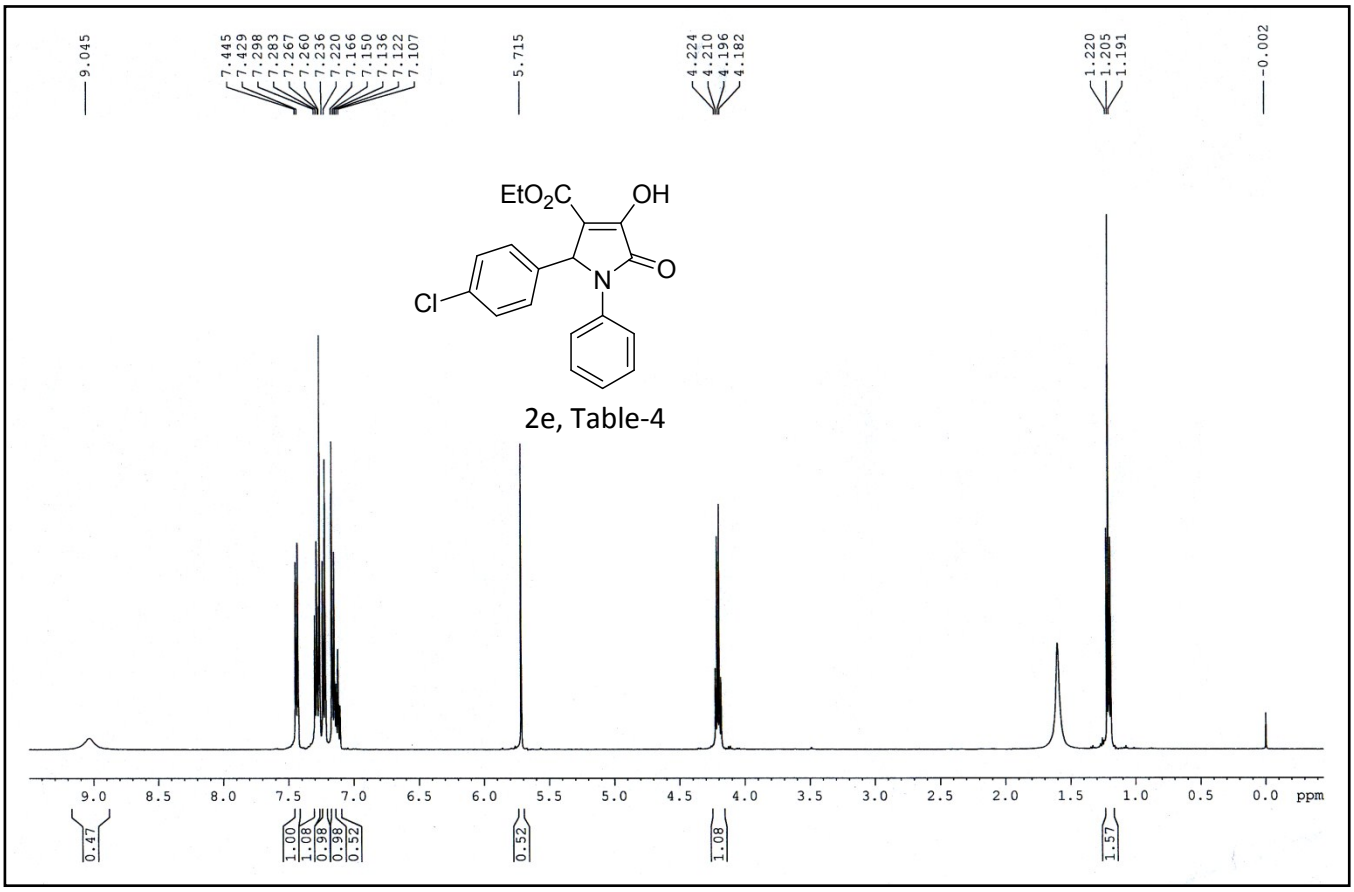
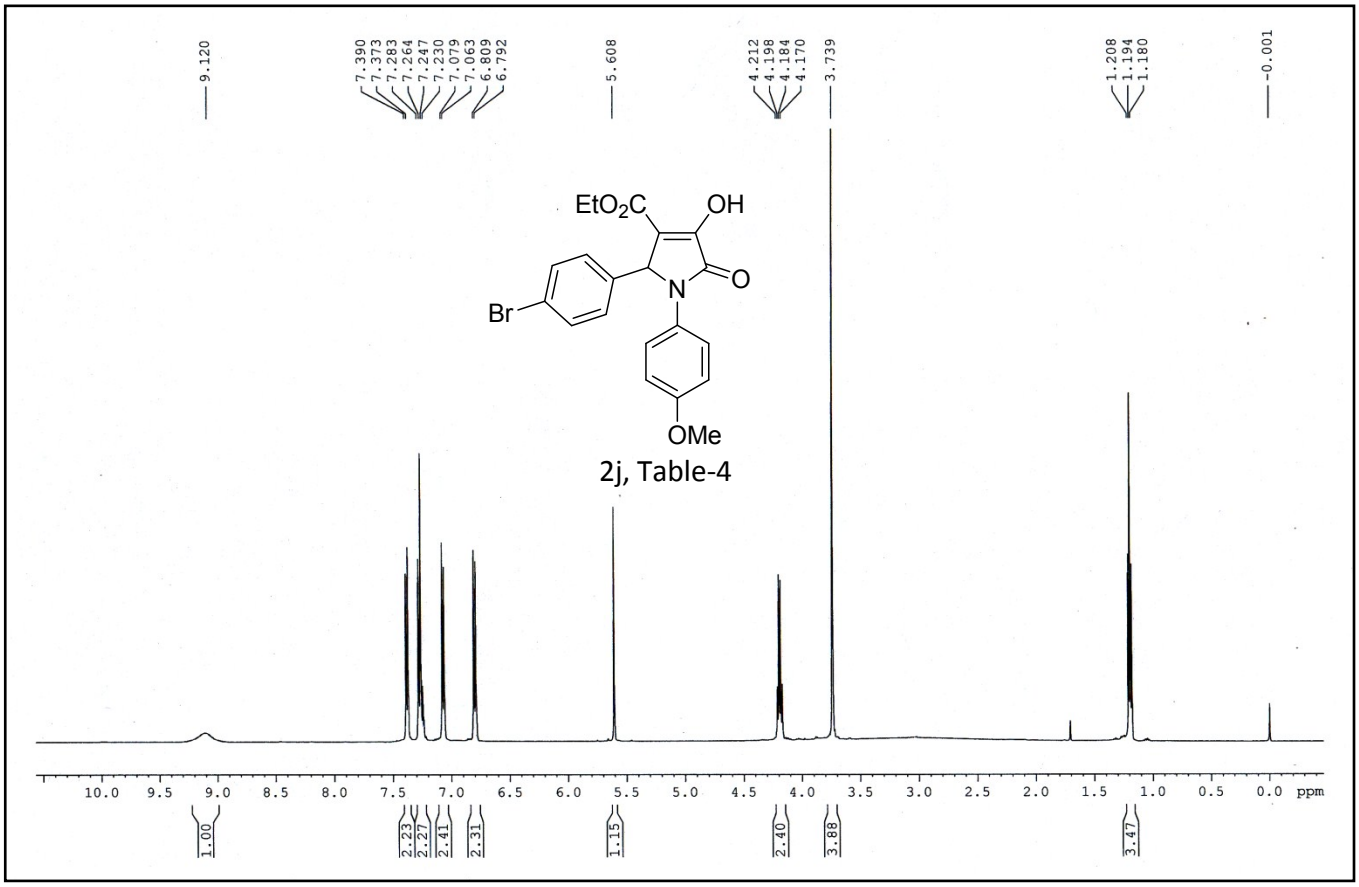
7.463
7.285
7.266
7.260
7.245
7.111
7.105
7.093
7.084
7.075
7.050
7.030
5.698
4.215
4.197
4.179
4.162
2.256
1.214
1.197
1.179
-0.001
EtO2C
OH
N
O
Me
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
0.38
1.00
1.20
2.50
0.49
1.00
1.50
1.50

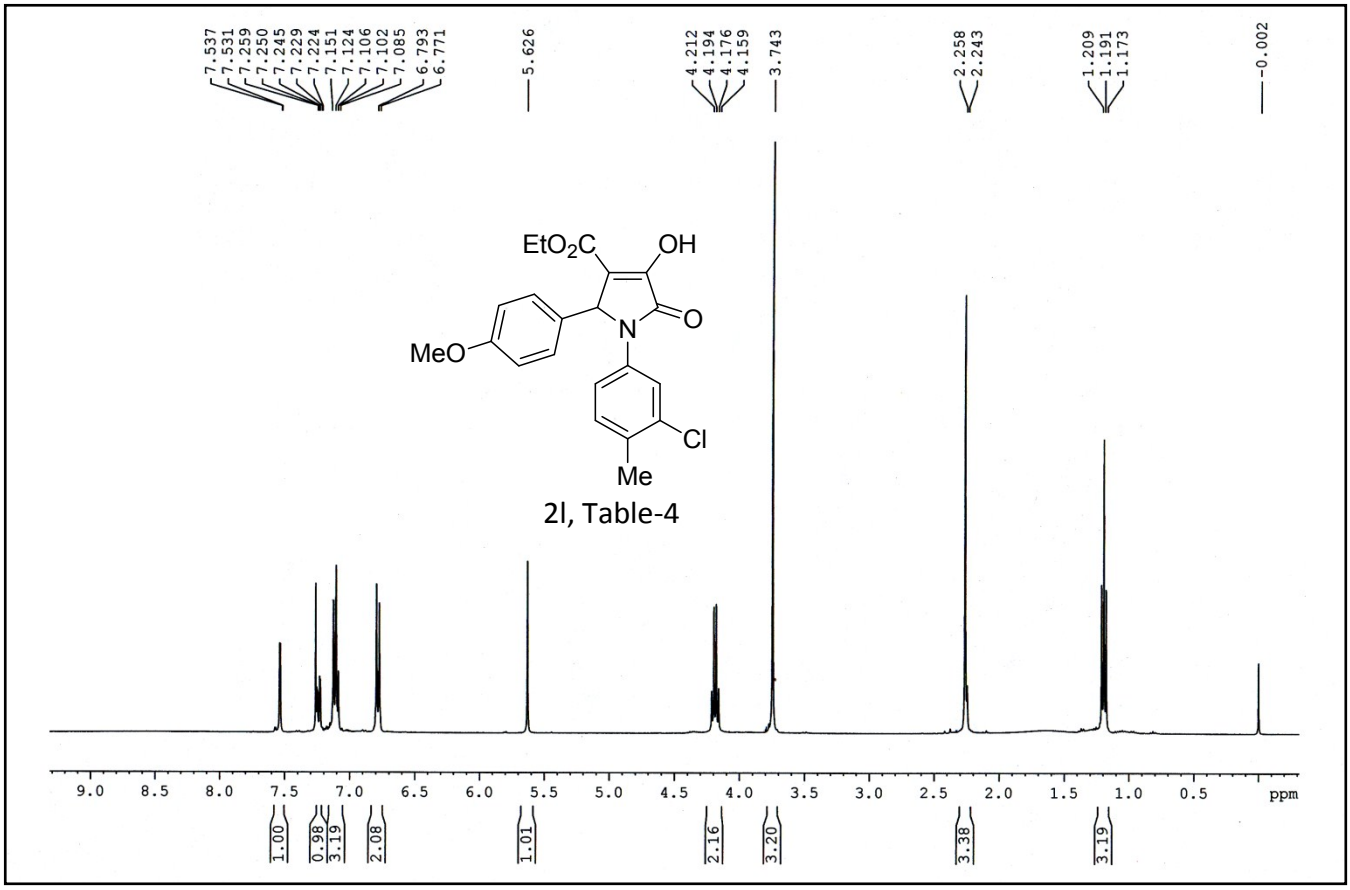
2d, Table-4


9.045
7.445
7.429
7.298
7.283
7.267
7.260
7.236
7.220
7.166
7.150
7.136
7.122
7.107
5.715
4.224
4.210
4.196
4.182
1.220
1.205
1.191
-0.002
EtO2C
OH
O
N
Cl
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
ppm
0.47
1.00
1.08
0.98
0.98
0.52
0.52
1.08
1.57

2e, Table-4


9.120
7.390
7.373
7.283
7.264
7.247
7.230
7.079
7.063
6.809
6.792
5.608
4.212
4.198
4.184
4.170
3.739
1.208
1.194
1.180
-0.001
EtO2C
OH
O
N
Br
OMe
10.0 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 ppm
1.00
2.23
2.27
2.41
2.31
1.15
2.40
3.88
3.47

2j, Table-4


7.537
7.531
7.259
7.250
7.245
7.229
7.224
7.151
7.124
7.106
7.102
7.085
6.793
6.771
5.626
4.212
4.194
4.176
4.159
3.743
2.258
2.243
1.209
1.191
1.173
-0.002
EtO2C
OH
O
N
MeO
Cl
Me
2l, Table-4
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
ppm
1.00
0.98
3.19
2.08
1.01
2.16
3.20
3.38
3.19

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