Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Selective Synthesis of Pyrrolidin-2-ones and 3-Iodopyrroles *via* the Ring Contraction and Deformylative Functionalization of Piperidine Derivatives

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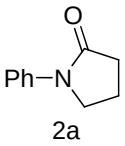
I. General Experimental Information

Commercial reagents were used without further purification. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet), br s (broad singlet), etc. The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI and APCI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Copies of the NMR spectra of 2a-2m



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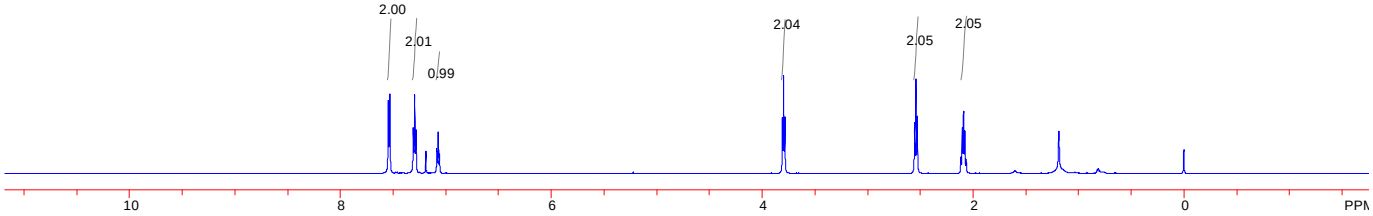

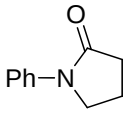

2a


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7.501
7.497
7.493
7.490
7.485
7.482
7.193
6.995
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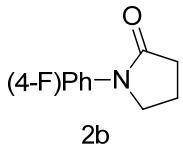
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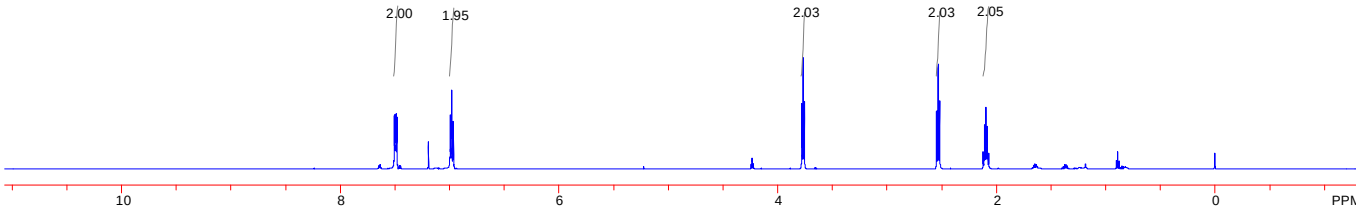
(4-F)Ph−N

2b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2.03
2.05
10
8
6
4
2
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PPM


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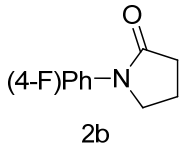
115.577
115.431
77.258
77.047
76.836
49.032
32.516
17.969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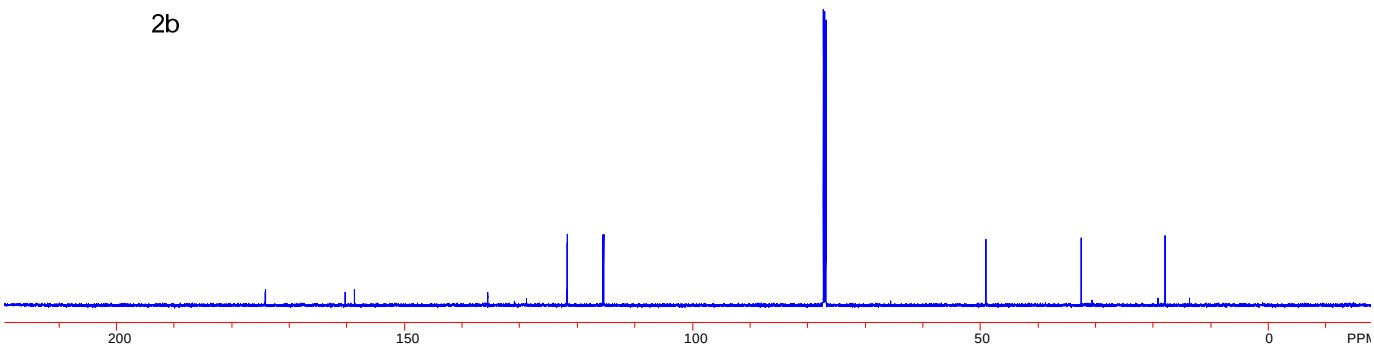
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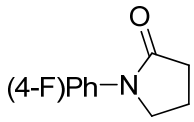

2b


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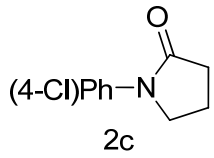
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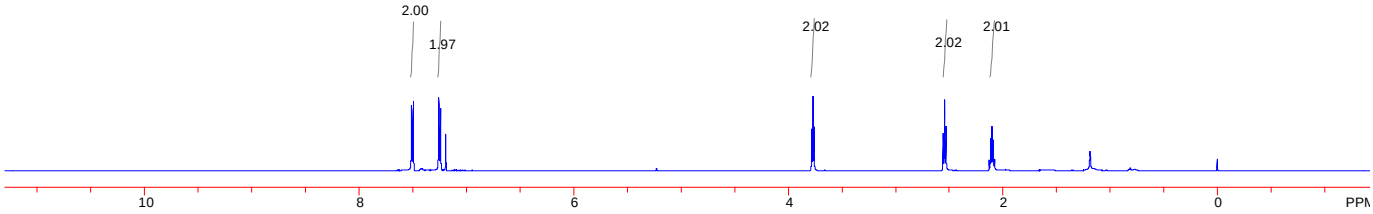
(4-Cl)Ph−N

2c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8
6
4
2
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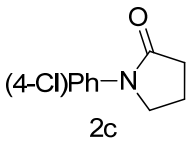
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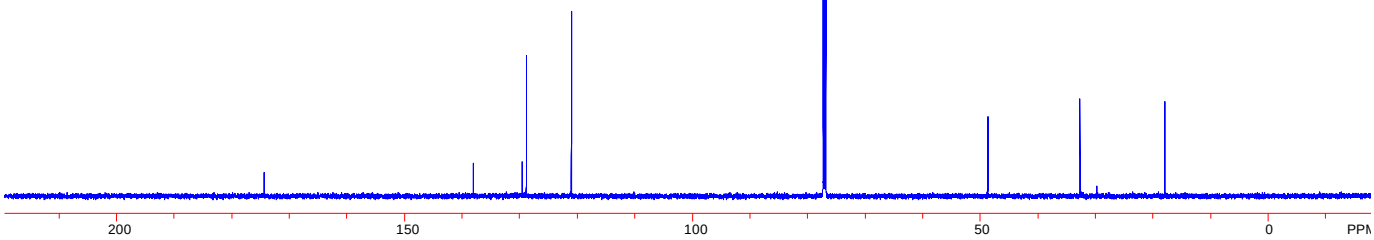
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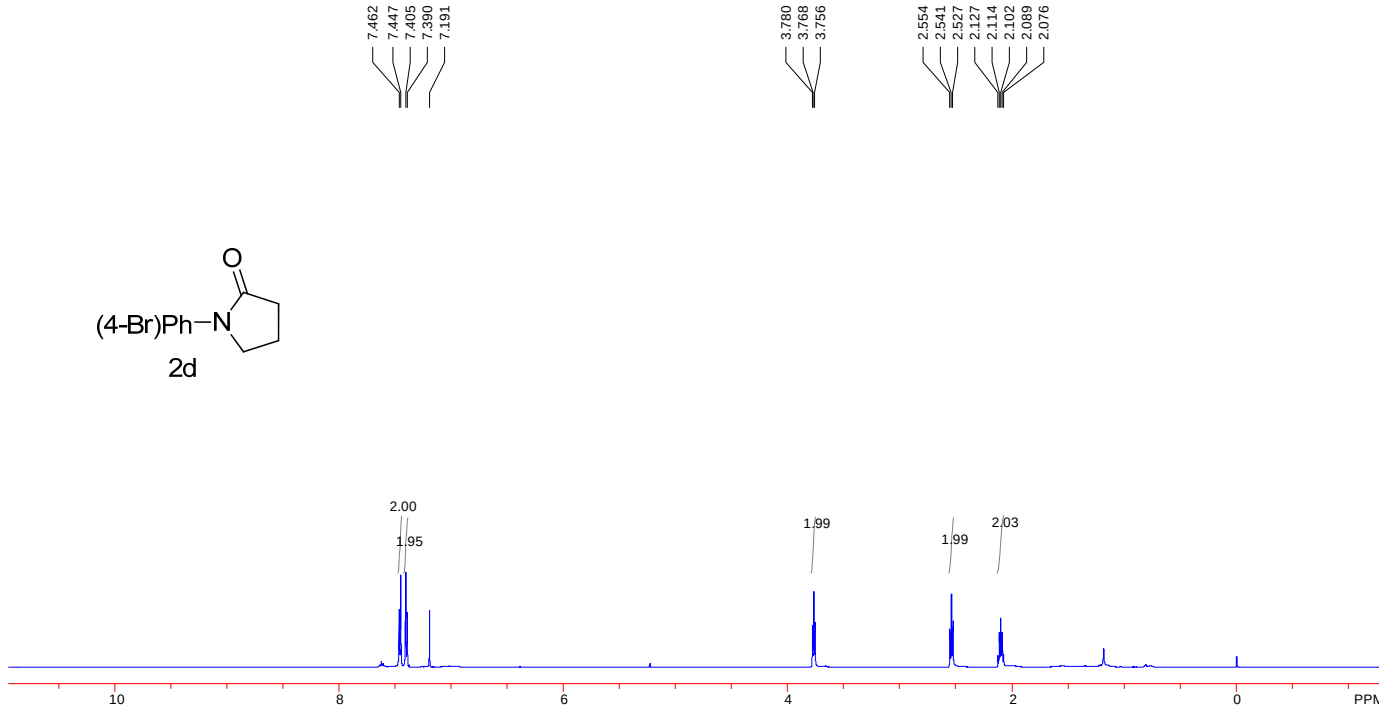
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2.102
2.089
2.076
O
(4-Br)Ph−N
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1.99
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10
8
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4
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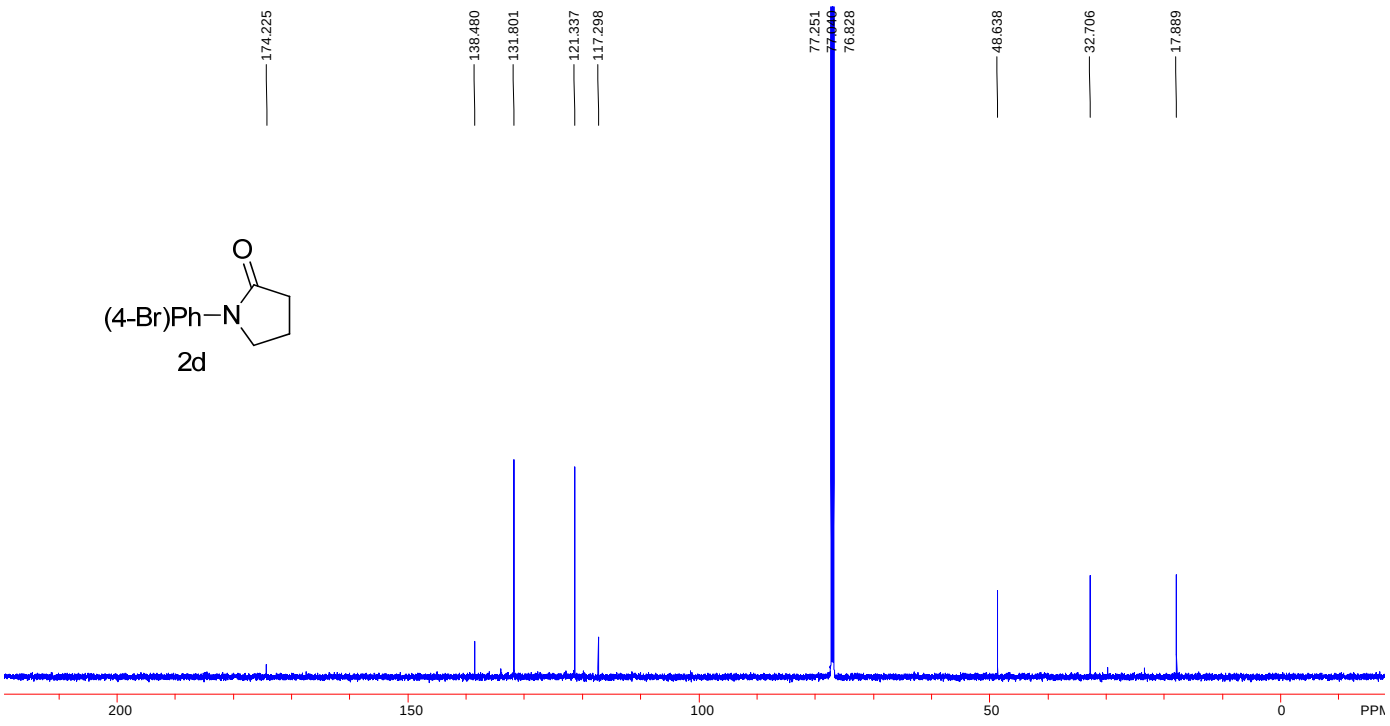
0
PPM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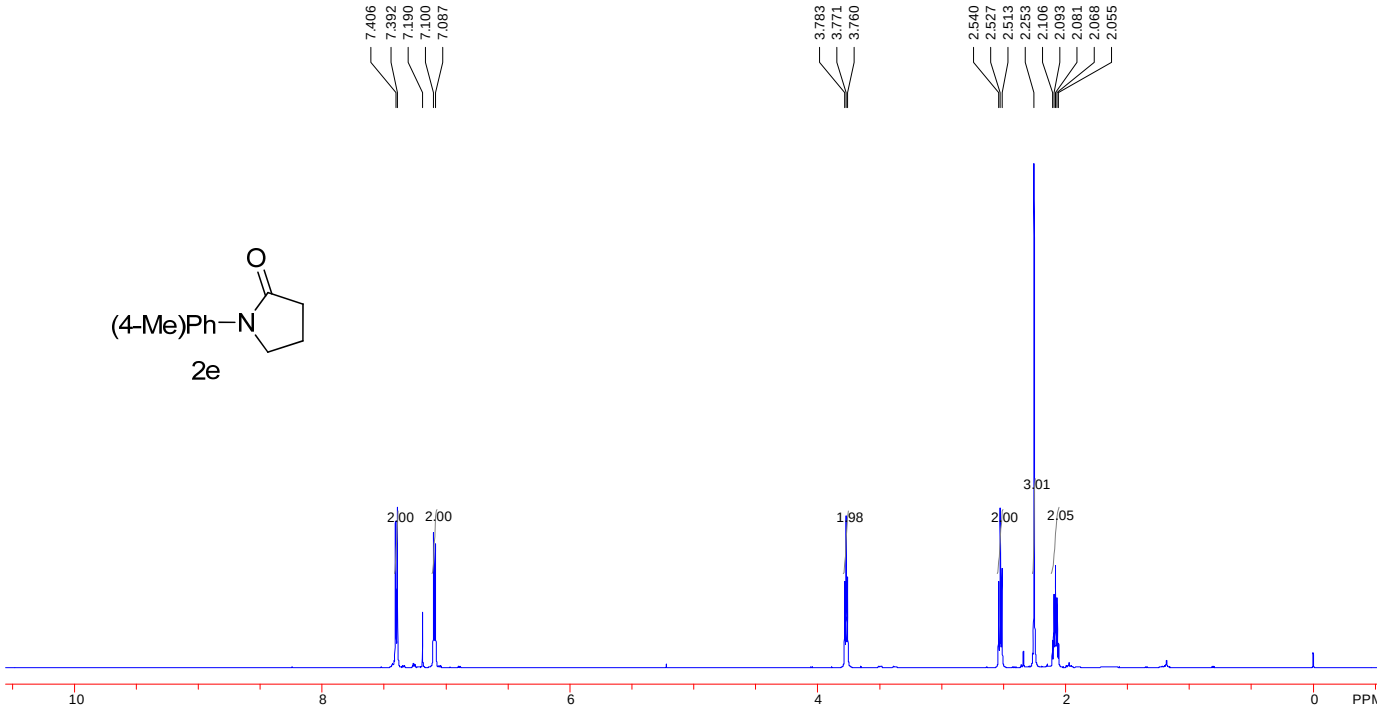
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O
(4-Me)Ph−N
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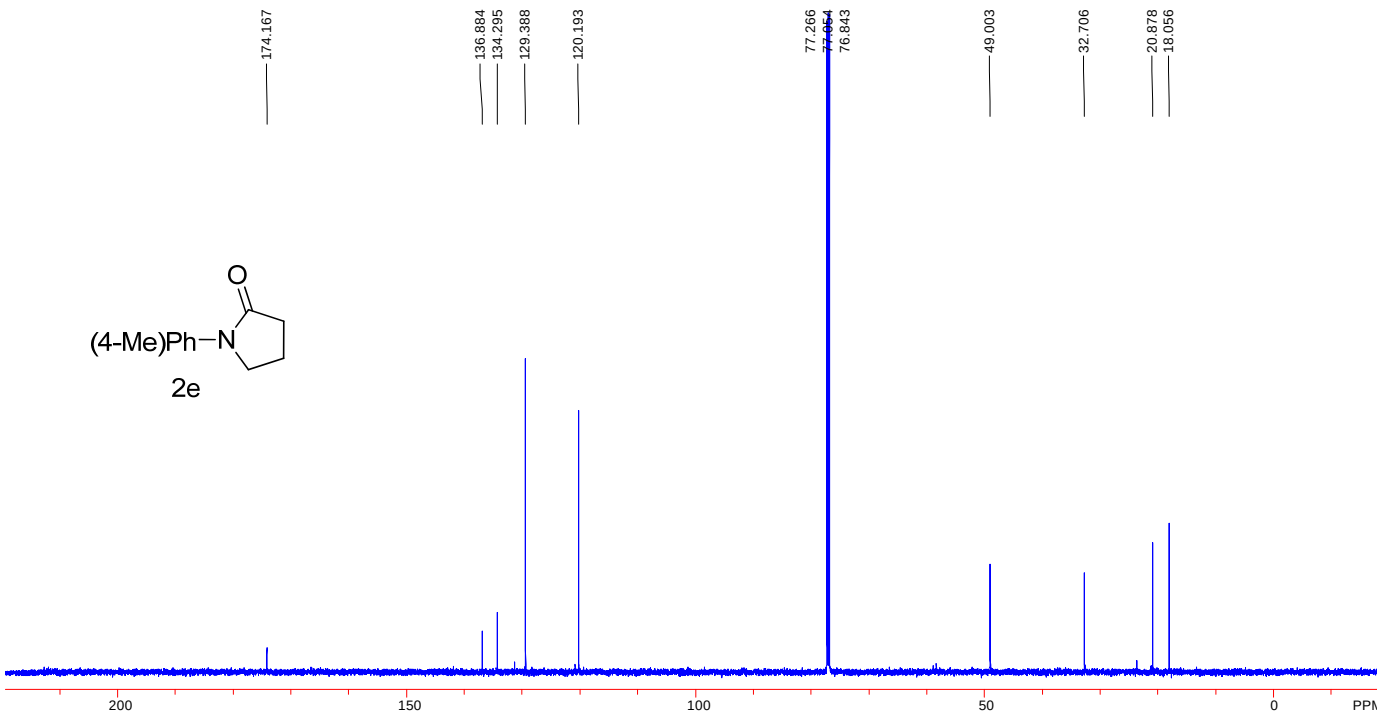
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50
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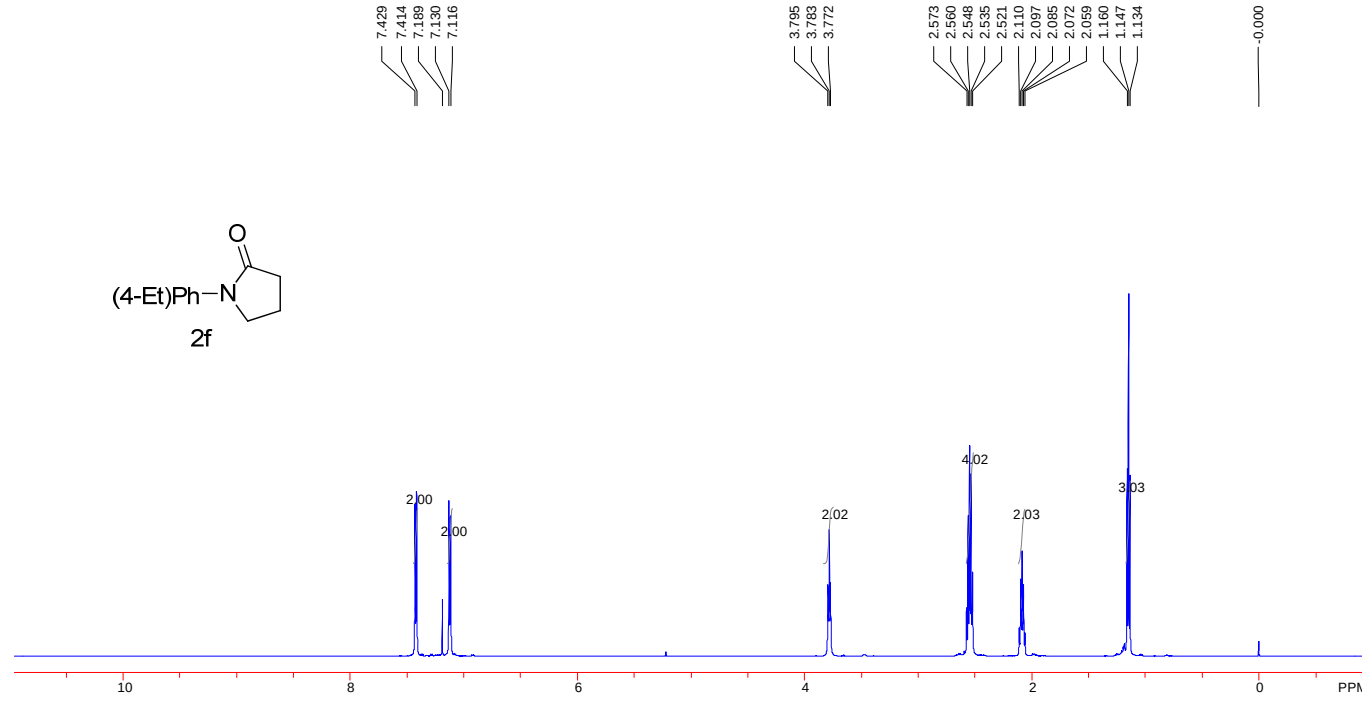
PPM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2.521
2.110
2.097
2.085
2.072
2.059
1.160
1.147
1.134
-0.000
(4-Et)Ph−N
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6
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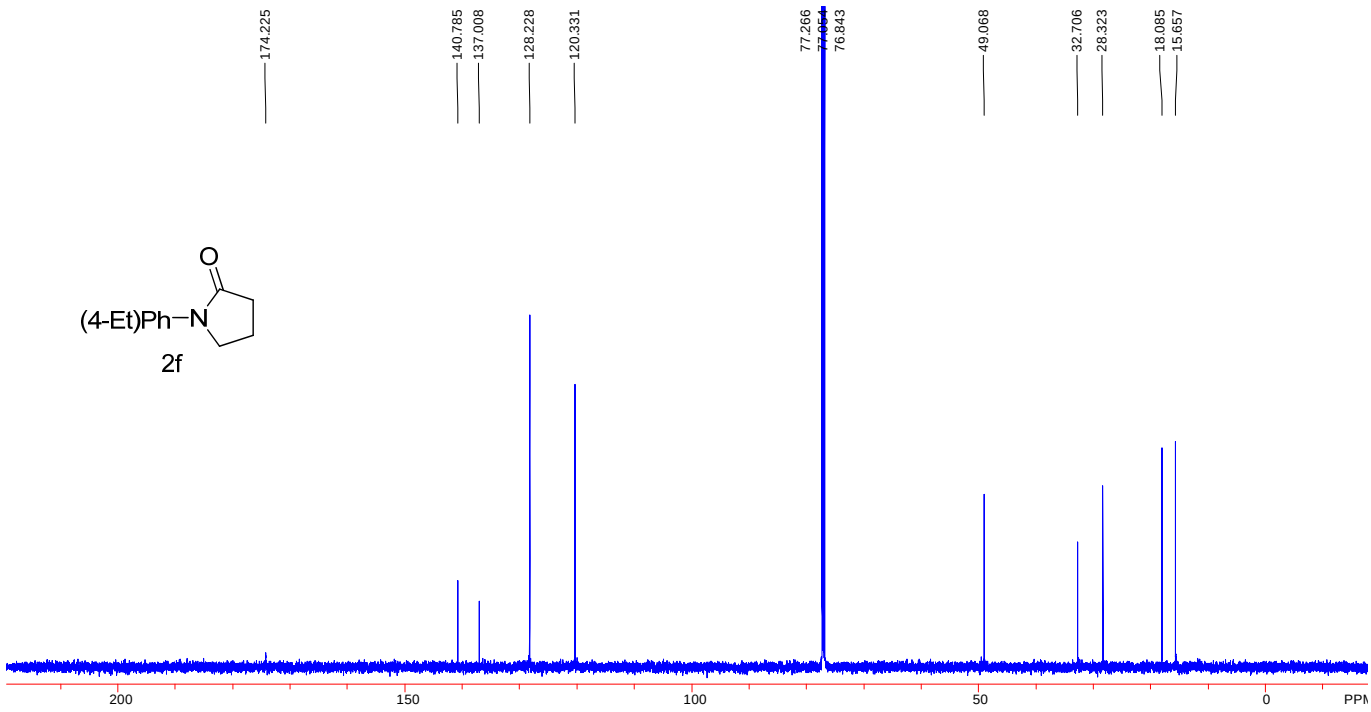
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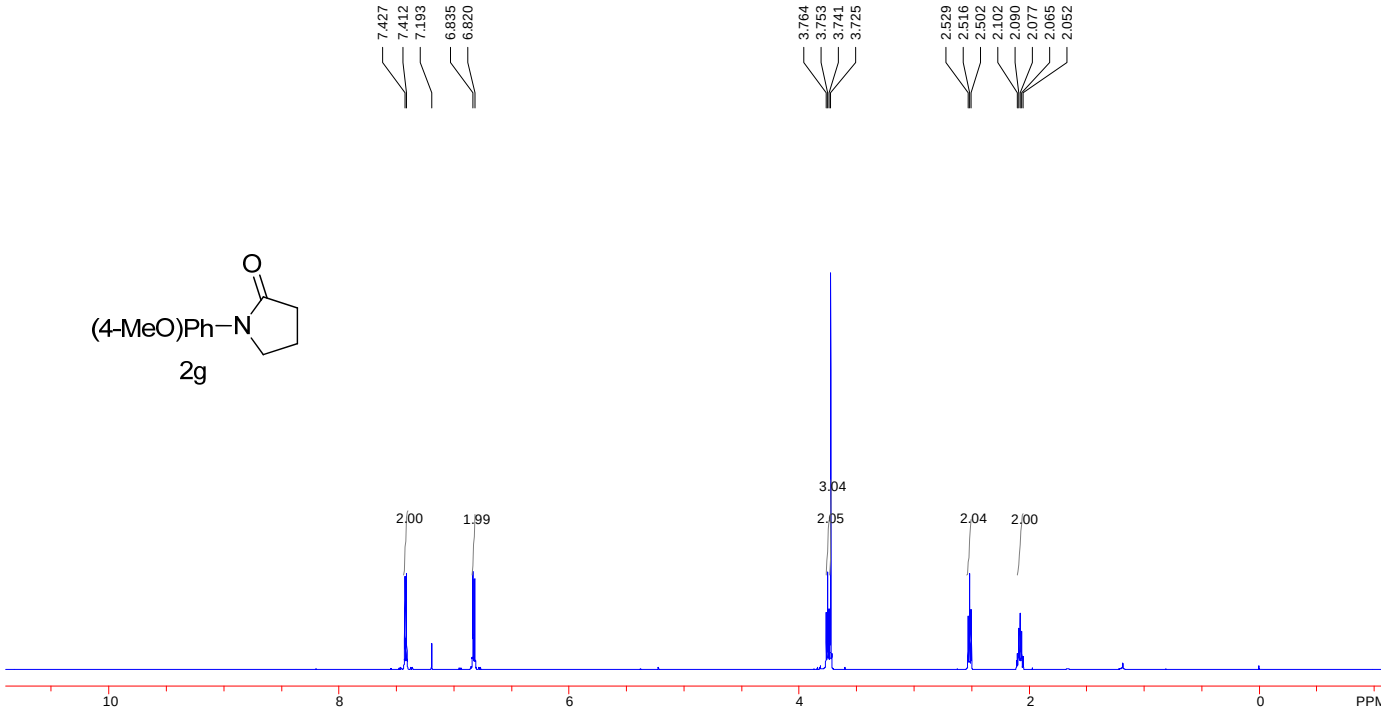
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2.102
2.090
2.077
2.065
2.052
O
(4-MeO)Ph–N
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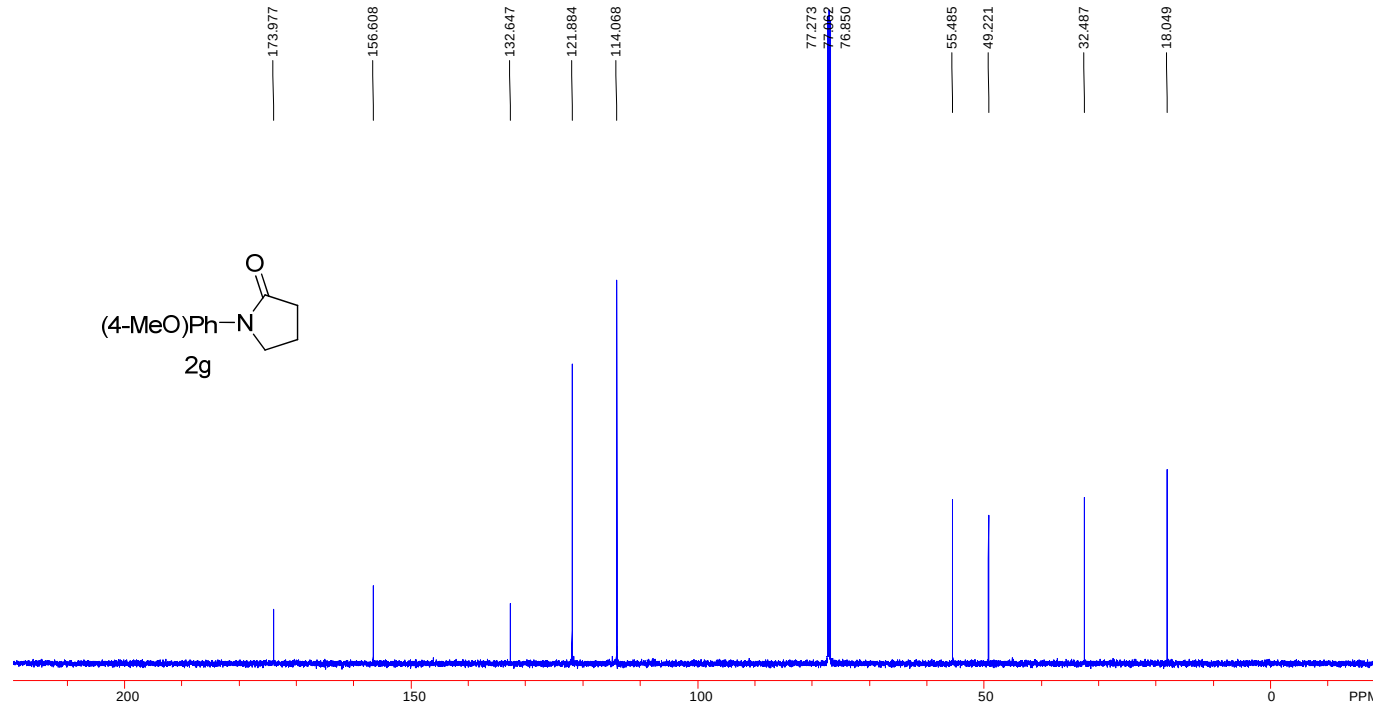
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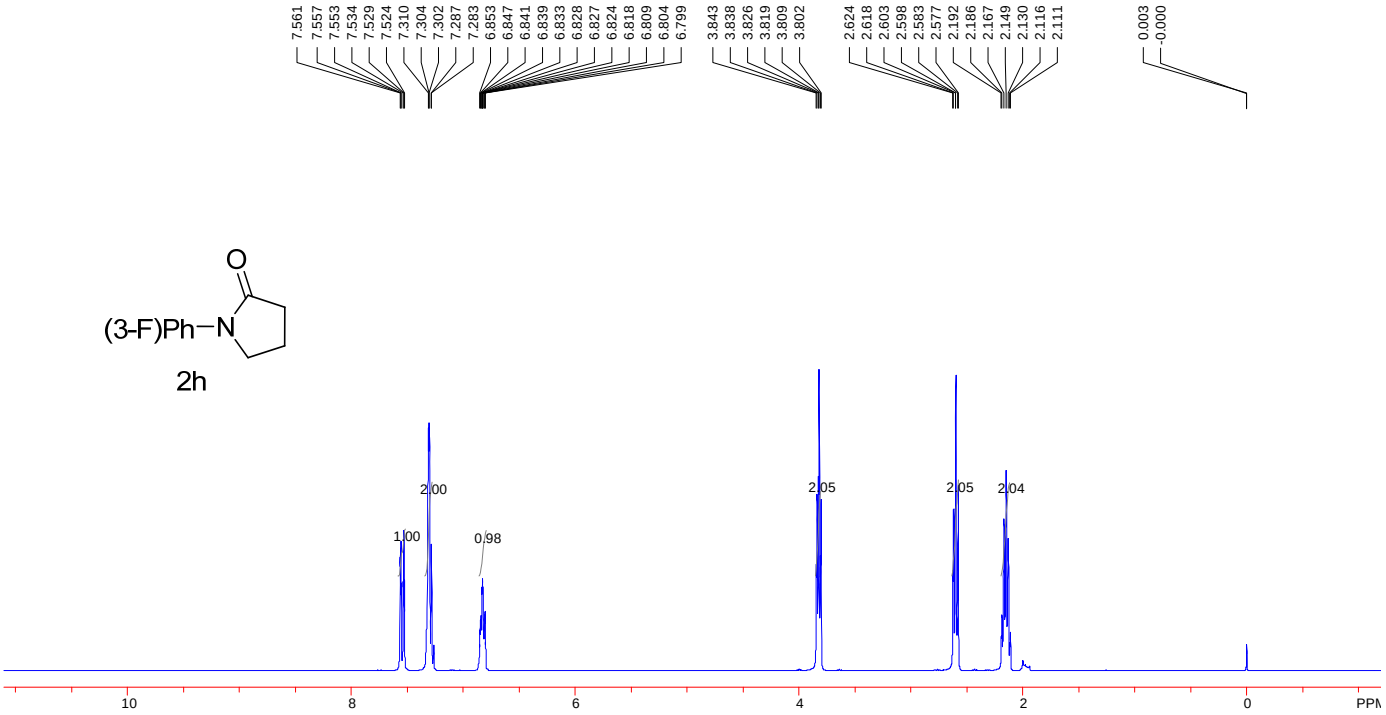
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-0.000
O
(3-F)Ph−N
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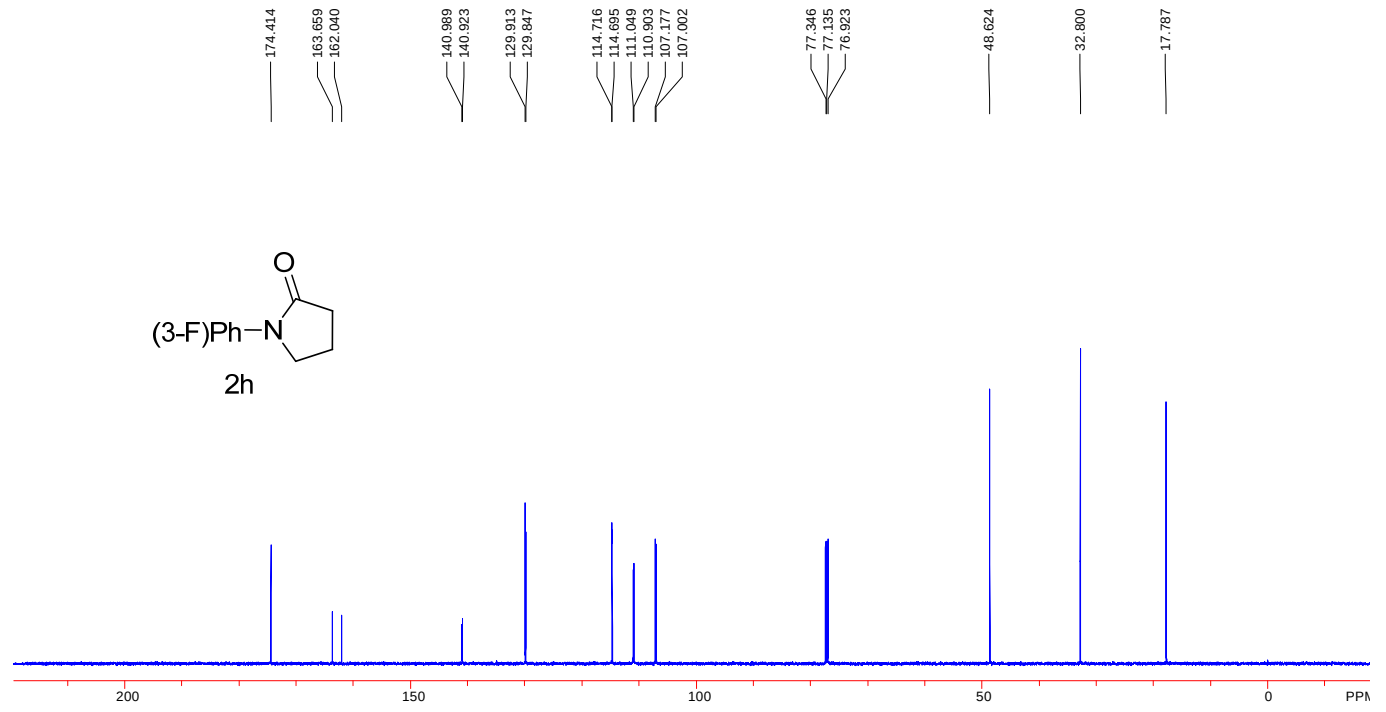
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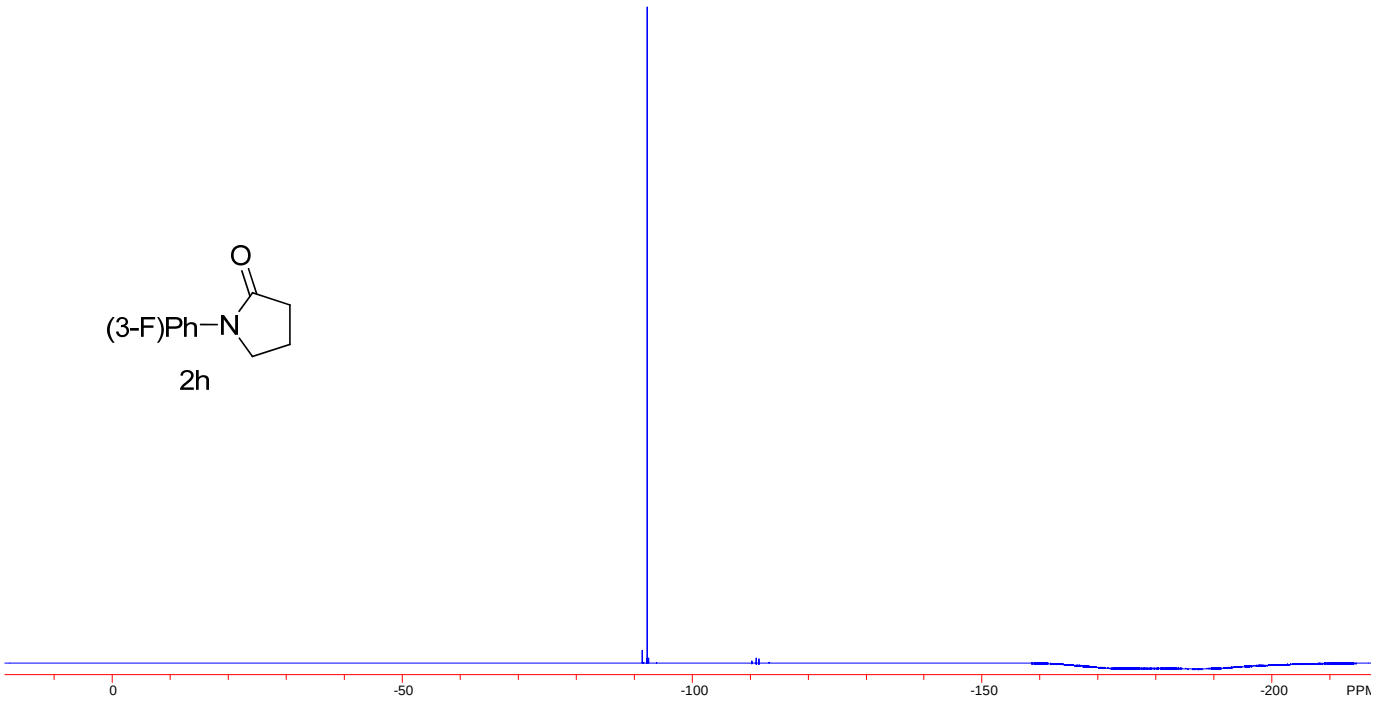
PPM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2h
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-50
-100
-150
-200
PPM


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7.158
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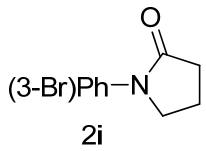
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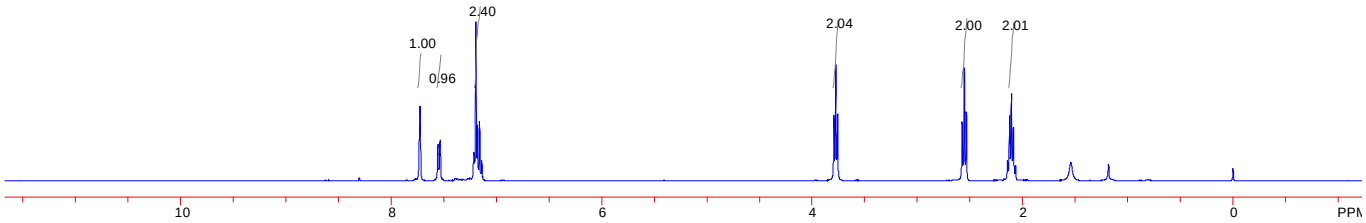
2i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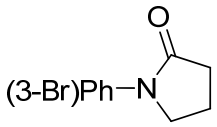
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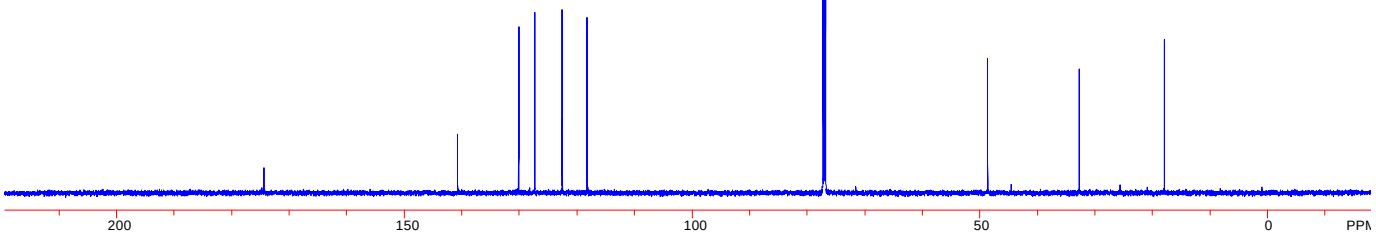
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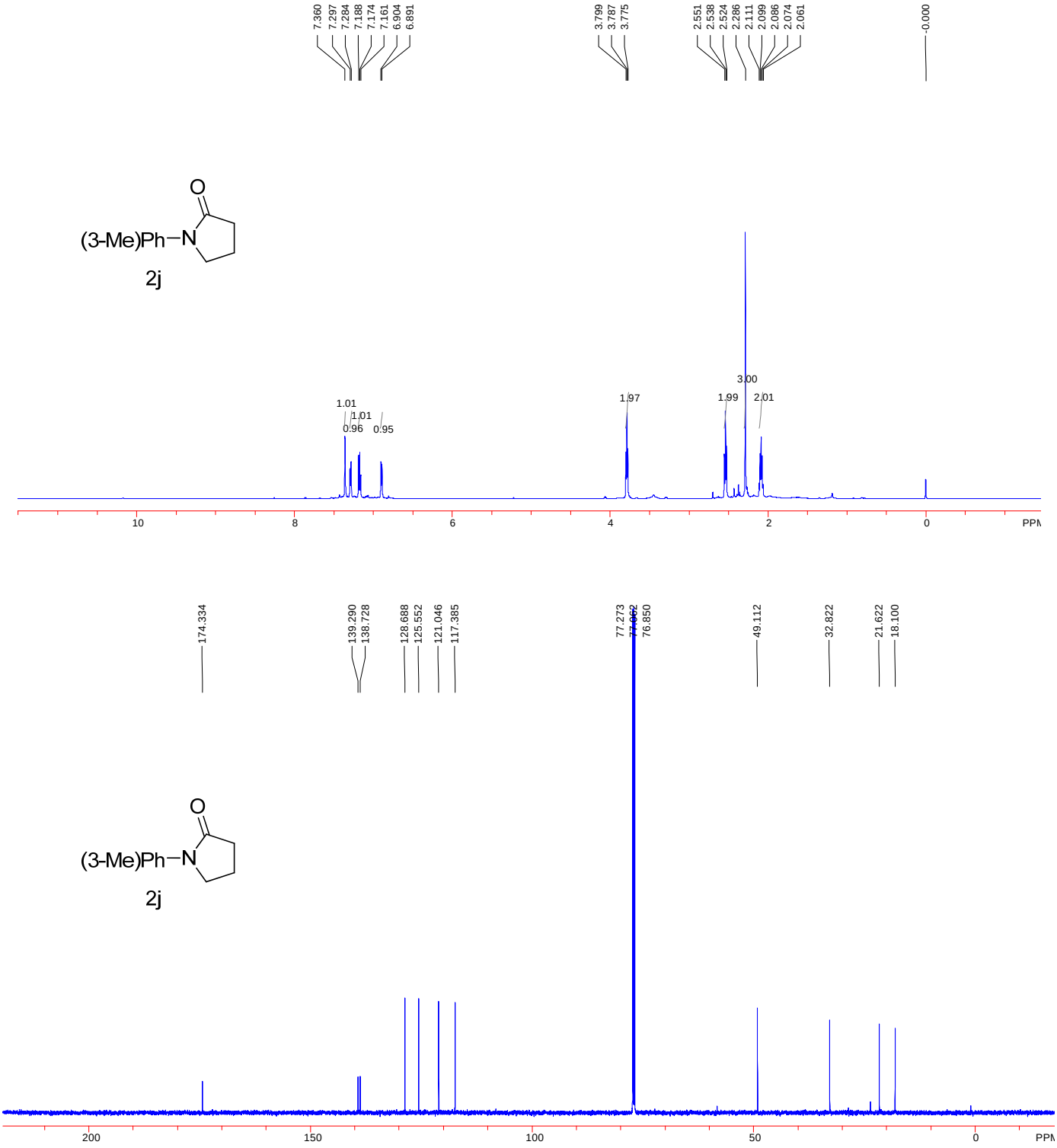
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2.538
2.524
2.286
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2.099
2.086
2.074
2.061
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(3-Me)Ph−N
O
2j
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1.99
2.01
10
8
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4
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139.290
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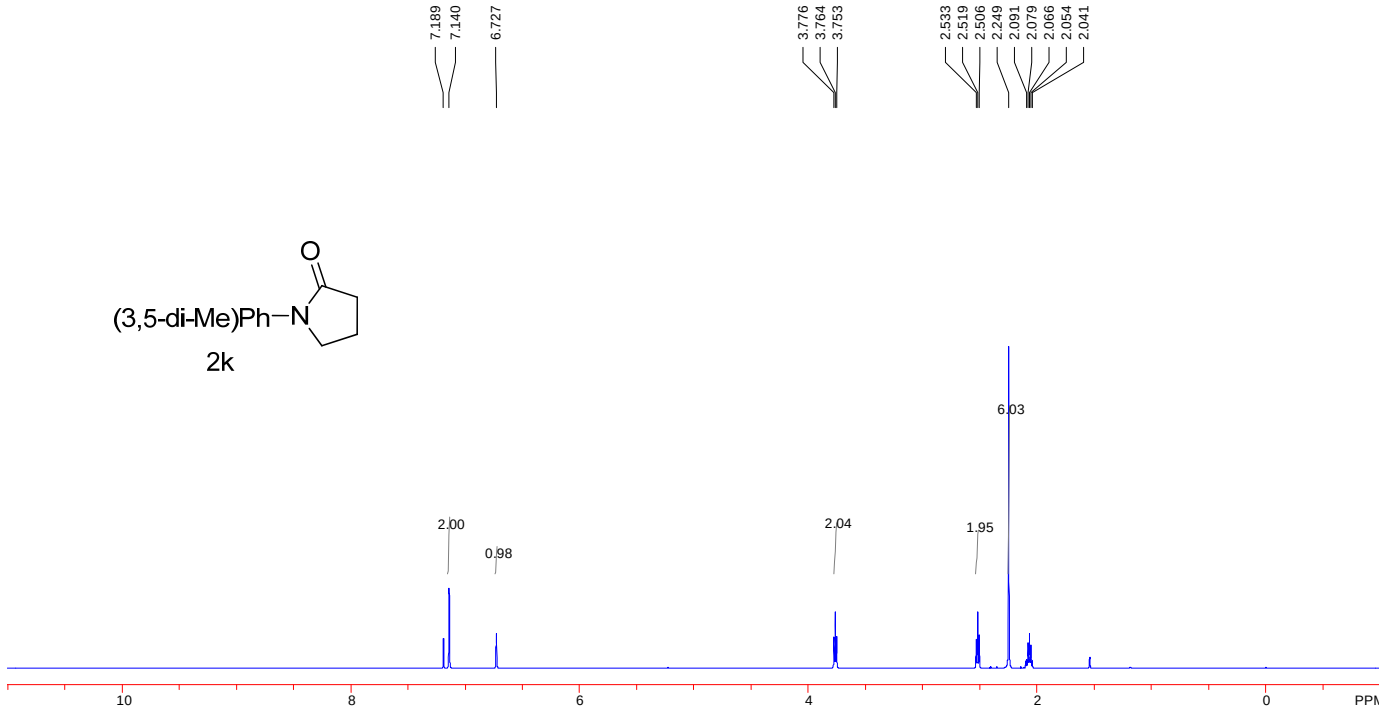
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2.091
2.079
2.066
2.054
2.041
O
(3,5-di-Me)Ph–N
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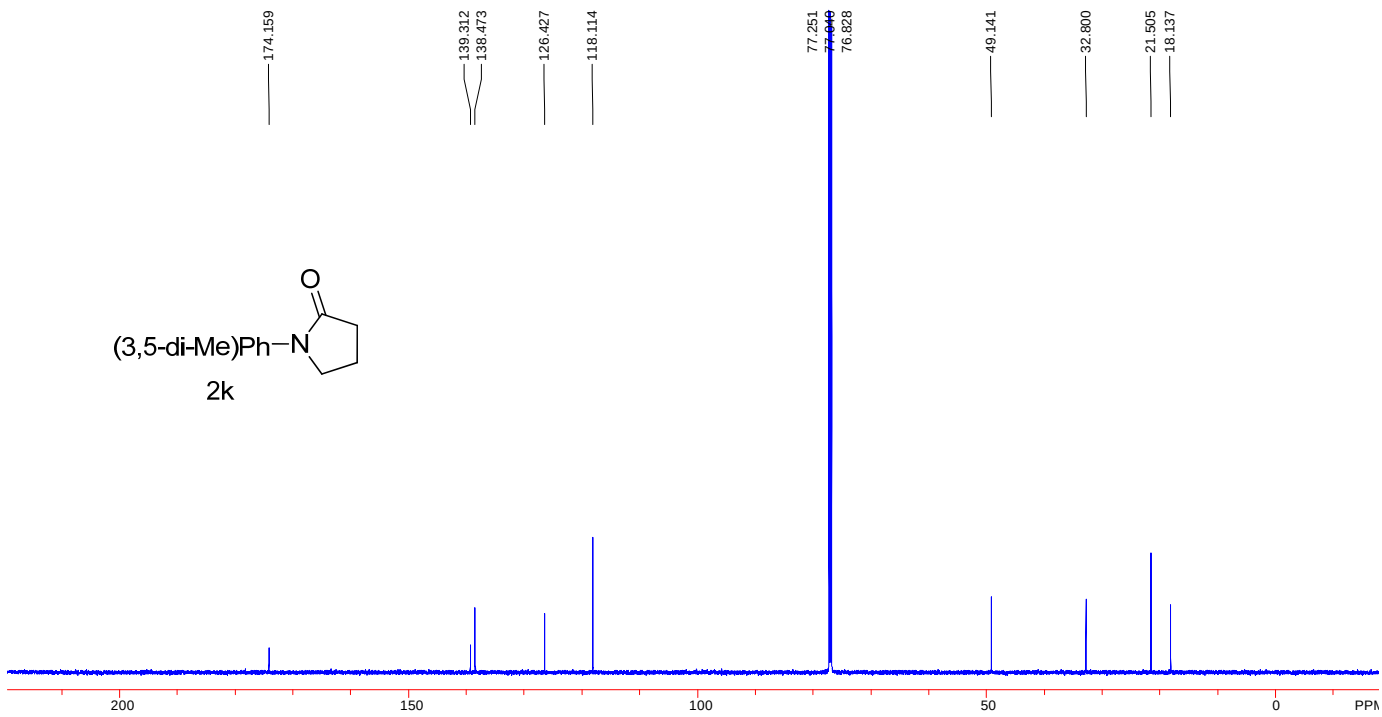
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O
(3,5-di-Me)Ph–N
2k
200
150
100
50
0
PPM


7.449
7.443
7.211
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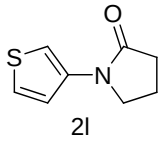
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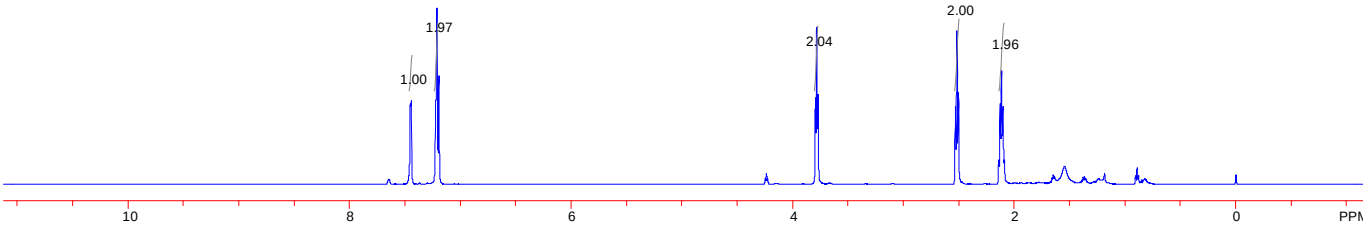
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2
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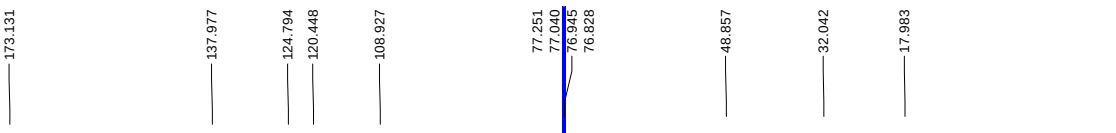
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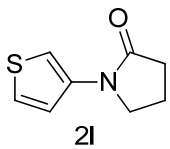
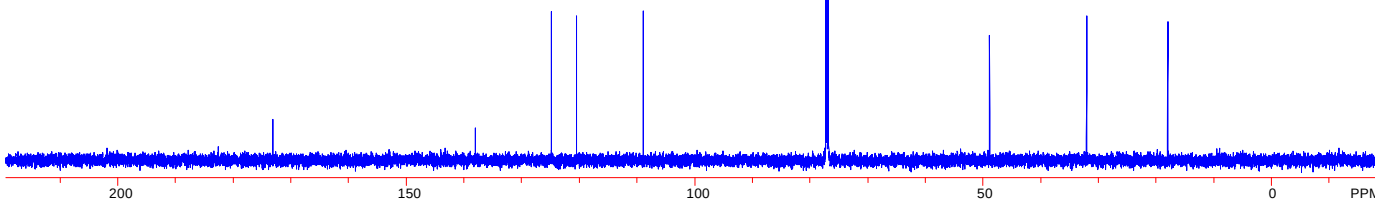

O
S
N

2l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100
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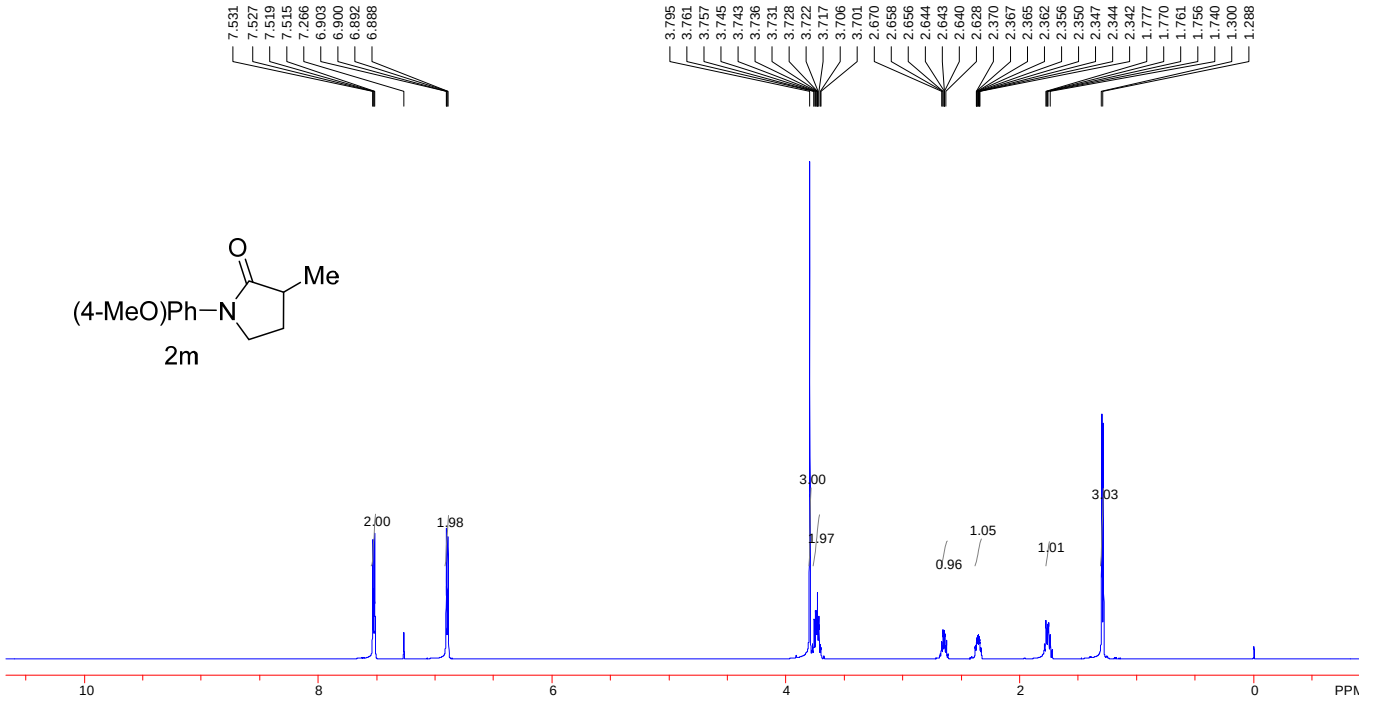
0
PPM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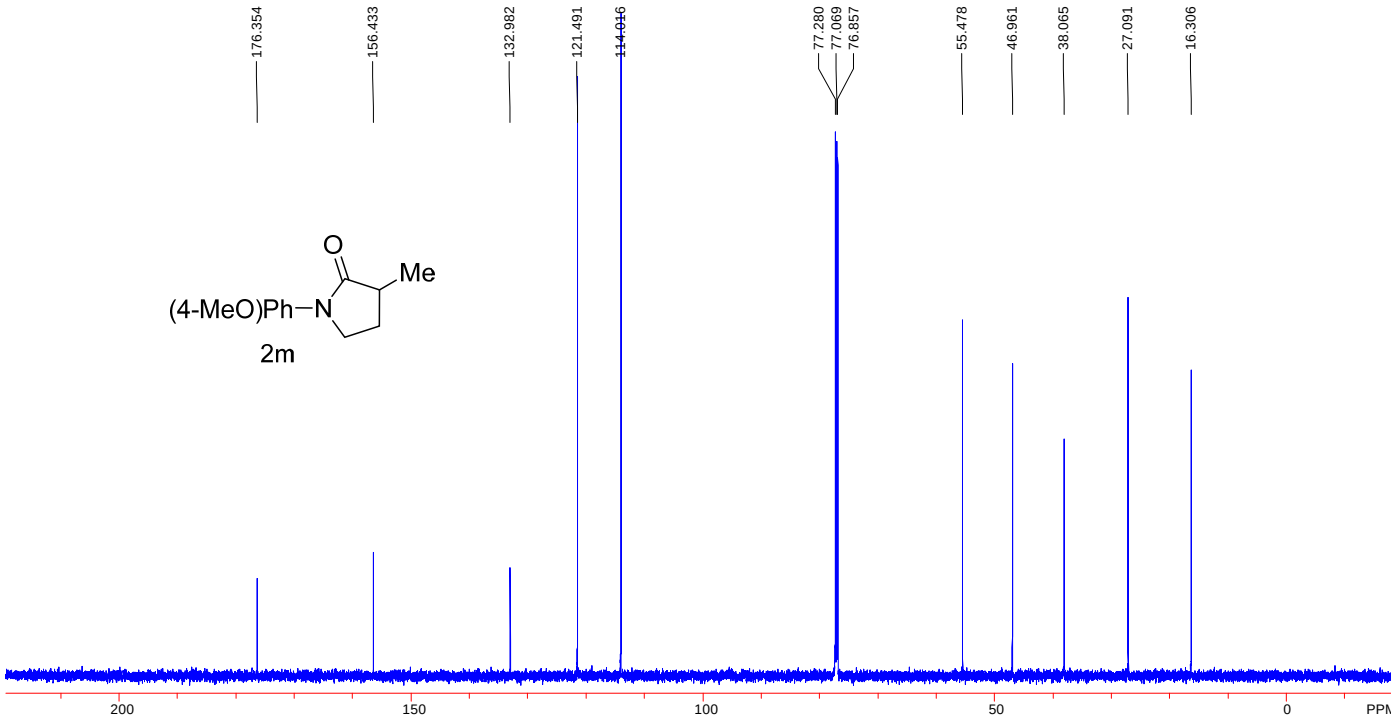
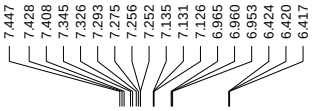
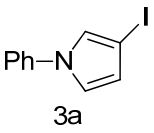
7.527
7.519
7.515
7.266
6.903
6.900
6.892
6.888
3.795
3.761
3.757
3.745
3.743
3.736
3.731
3.728
3.722
3.717
3.706
3.701
2.670
2.658
2.656
2.644
2.643
2.640
2.628
2.370
2.367
2.365
2.362
2.356
2.350
2.347
2.344
2.342
1.777
1.770
1.761
1.756
1.740
1.300
1.288
O
Me
(4-MeO)Ph—N
2m
2.00
1.98
3.00
1.97
0.96
1.05
1.01
3.03
10
8
6
4
2
0
PPM

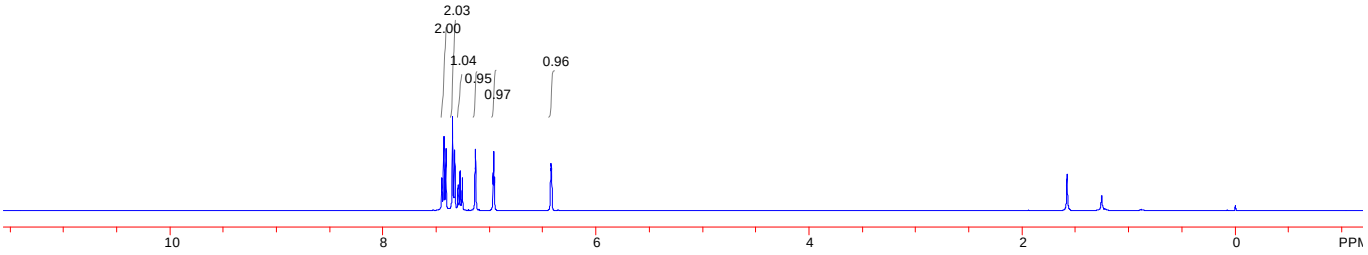

176.354
156.433
132.982
121.491
114.016
77.280
77.069
76.857
55.478
46.961
38.065
27.091
16.306
O
Me
(4-MeO)Ph—N
2m
200
150
100
50
0
PPM

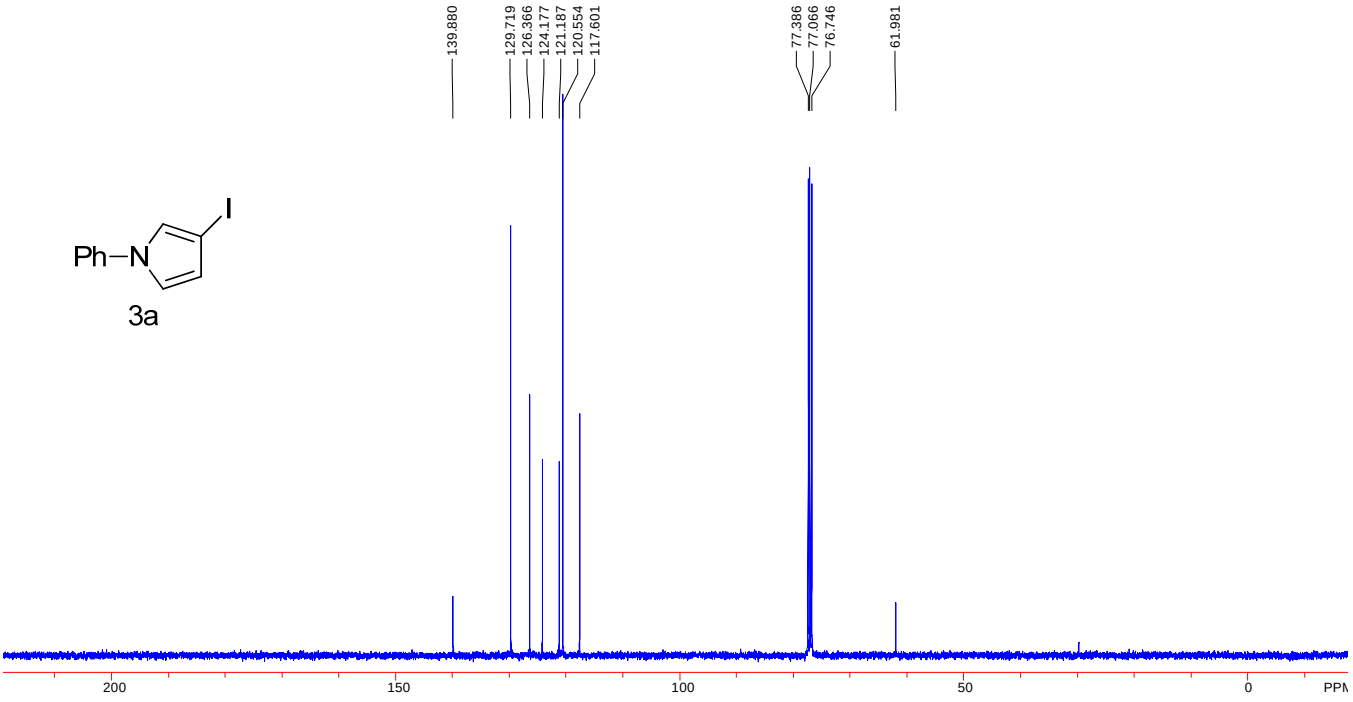
III. Copies of the NMR spectra of 3a-3n



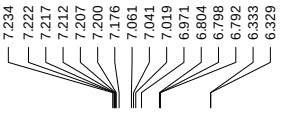


3a





3a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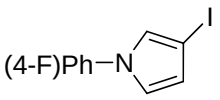
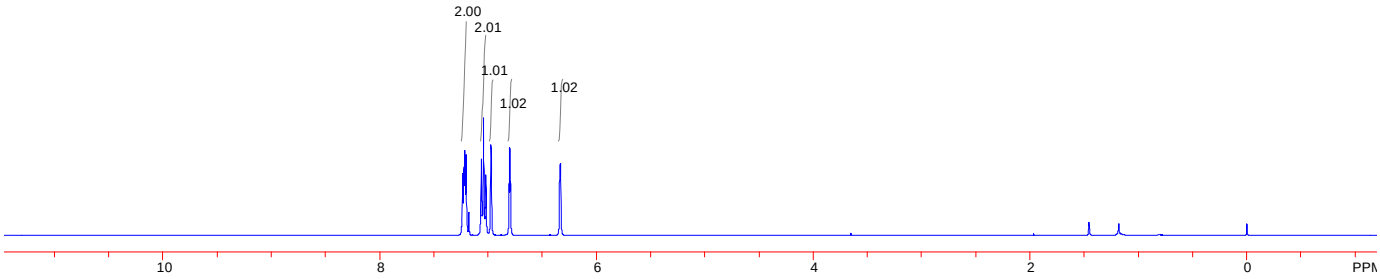
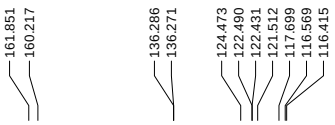
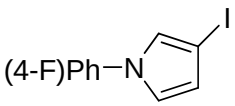
7.222
7.217
7.212
7.207
7.200
7.176
7.061
7.041
7.019
6.971
6.804
6.798
6.792
6.333
6.329


(4-F)Ph−N
I

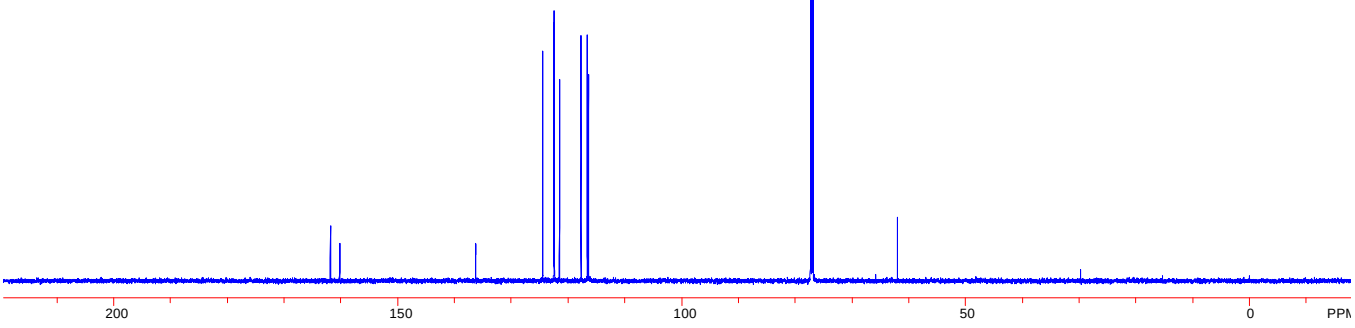
3b

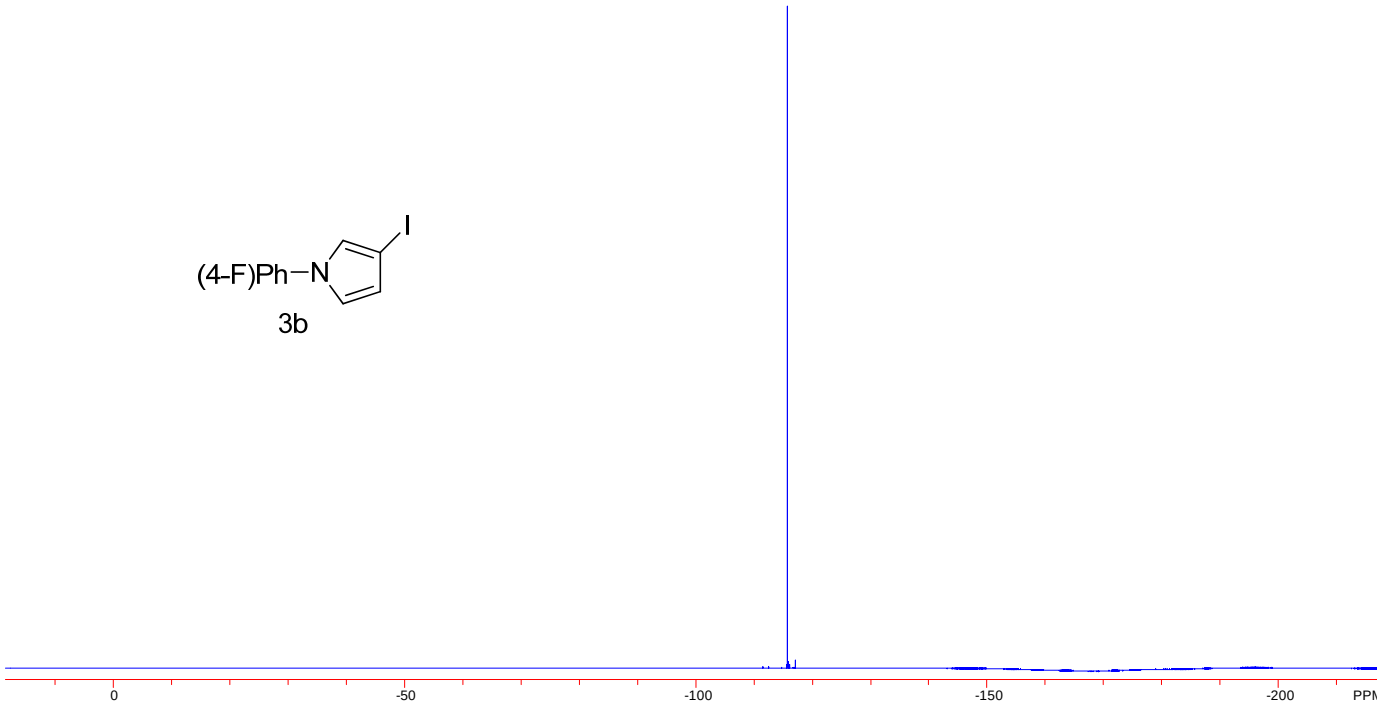

2.00
2.01
1.01
1.02
1.02
10
8
6
4
2
0
PPM

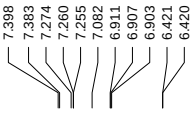

161.851
160.217
136.286
136.271
124.473
122.490
122.431
121.512
117.699
116.569
116.415
77.258
77.047
76.836
61.968

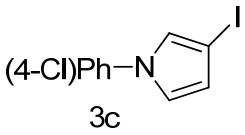

(4-F)Ph−N
I

3b

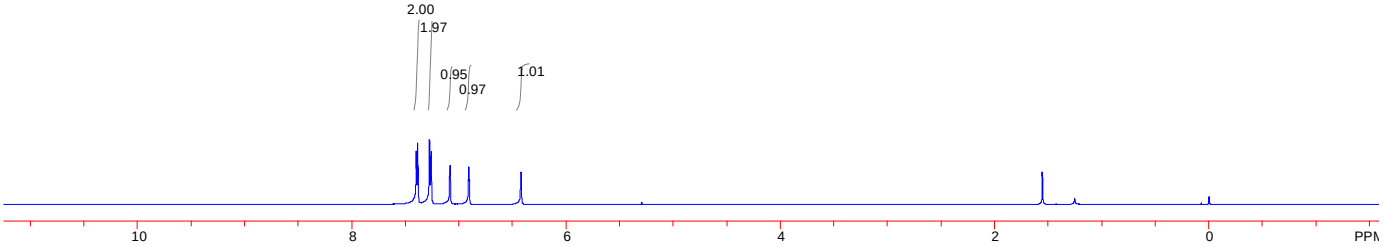

200
150
100
50
0
PPM

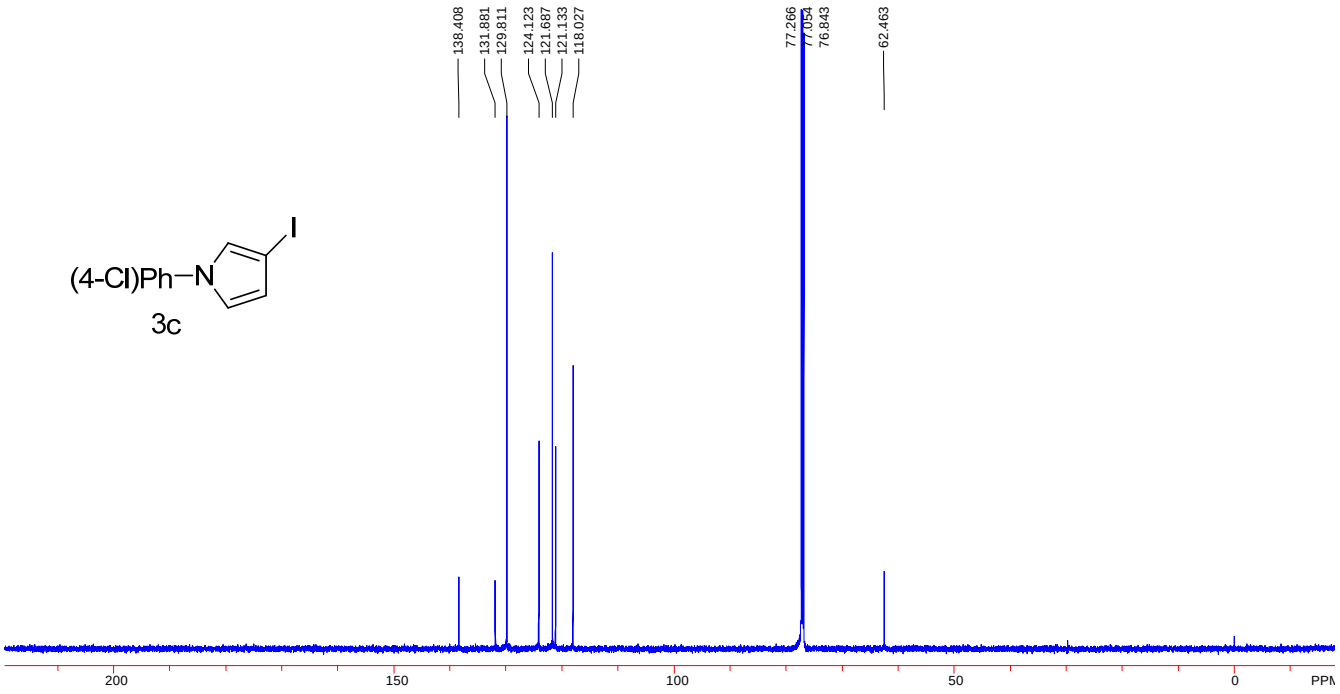

I
(4-F)Ph−N
3b
0
-50
-100
-150
-200
PPM


7.398
7.383
7.274
7.260
7.255
7.082
6.911
6.907
6.903
6.421
6.420


(4-Cl)Ph–N
I

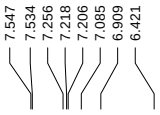
3c

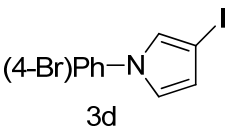

2.00
1.97
0.95
0.97
1.01
10
8
6
4
2
0
PPM


138.408
131.881
129.811
124.123
121.687
121.133
118.027
77.266
77.054
76.843
62.463
200
150
100
50
0
PPM

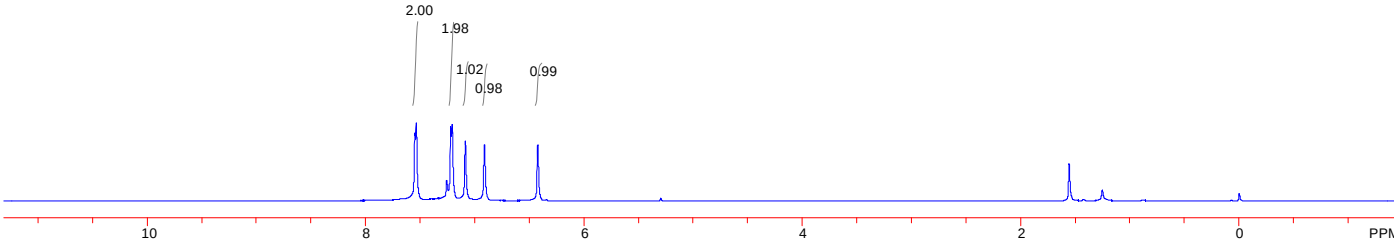
(4-Cl)Ph–N
I

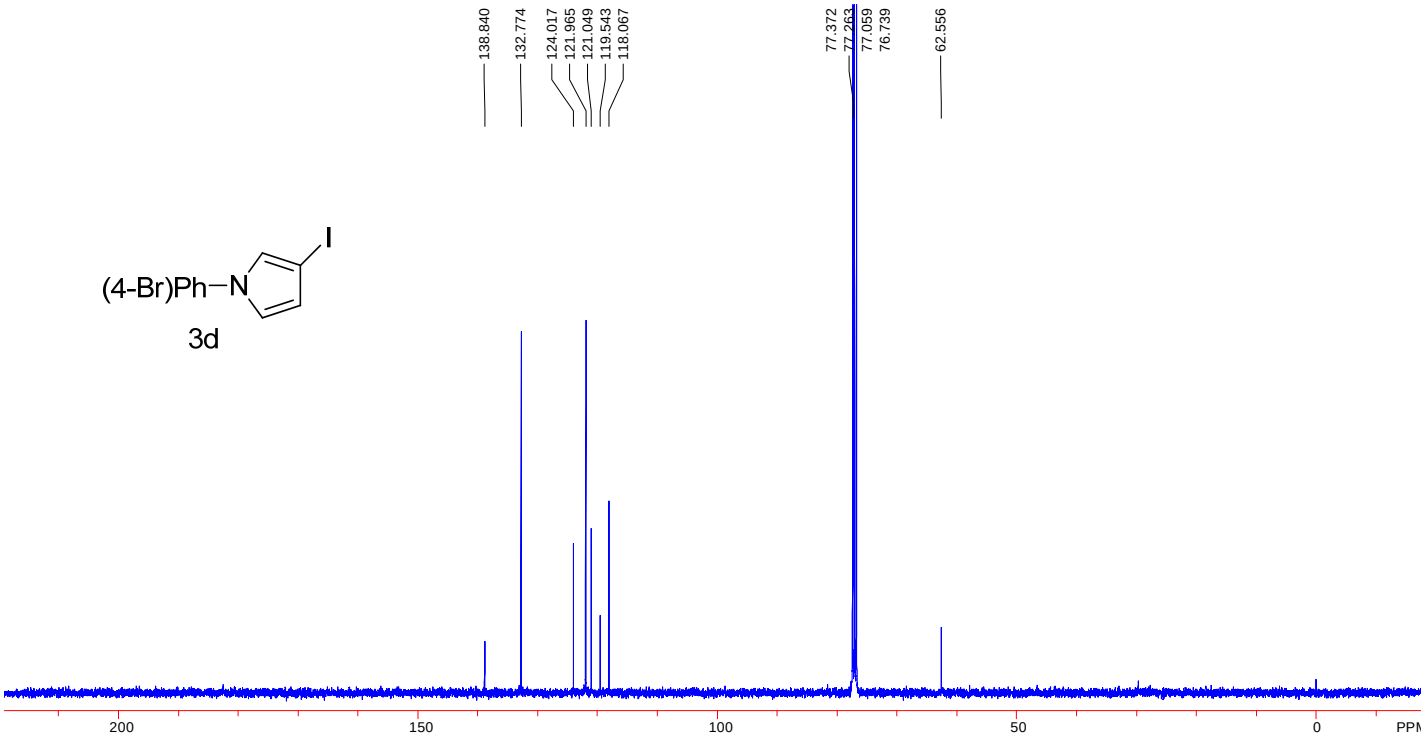
3c


7.547
7.534
7.256
7.218
7.206
7.085
6.909
6.421


(4-Br)Ph–N
I

3d

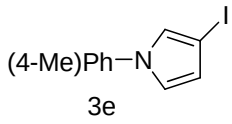

2.00
1.98
1.02
0.98
0.99
10
8
6
4
2
0
PPM


138.840
132.774
124.017
121.965
121.049
119.543
118.067
77.372
77.263
77.059
76.739
62.556
200
150
100
50
0
PPM

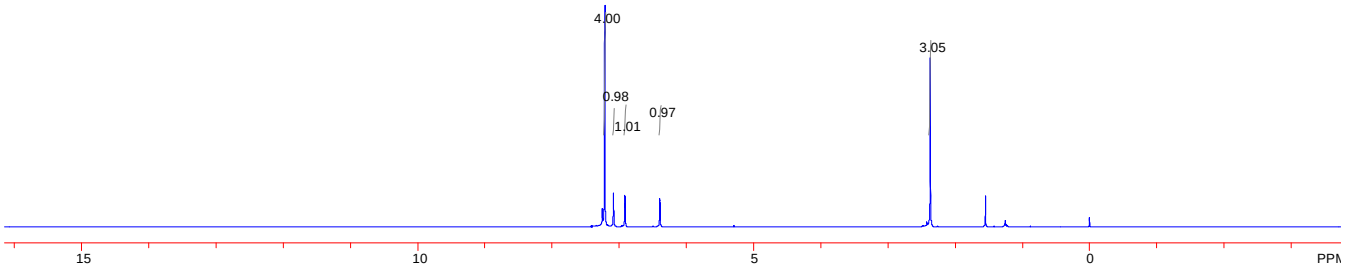
(4-Br)Ph–N
I

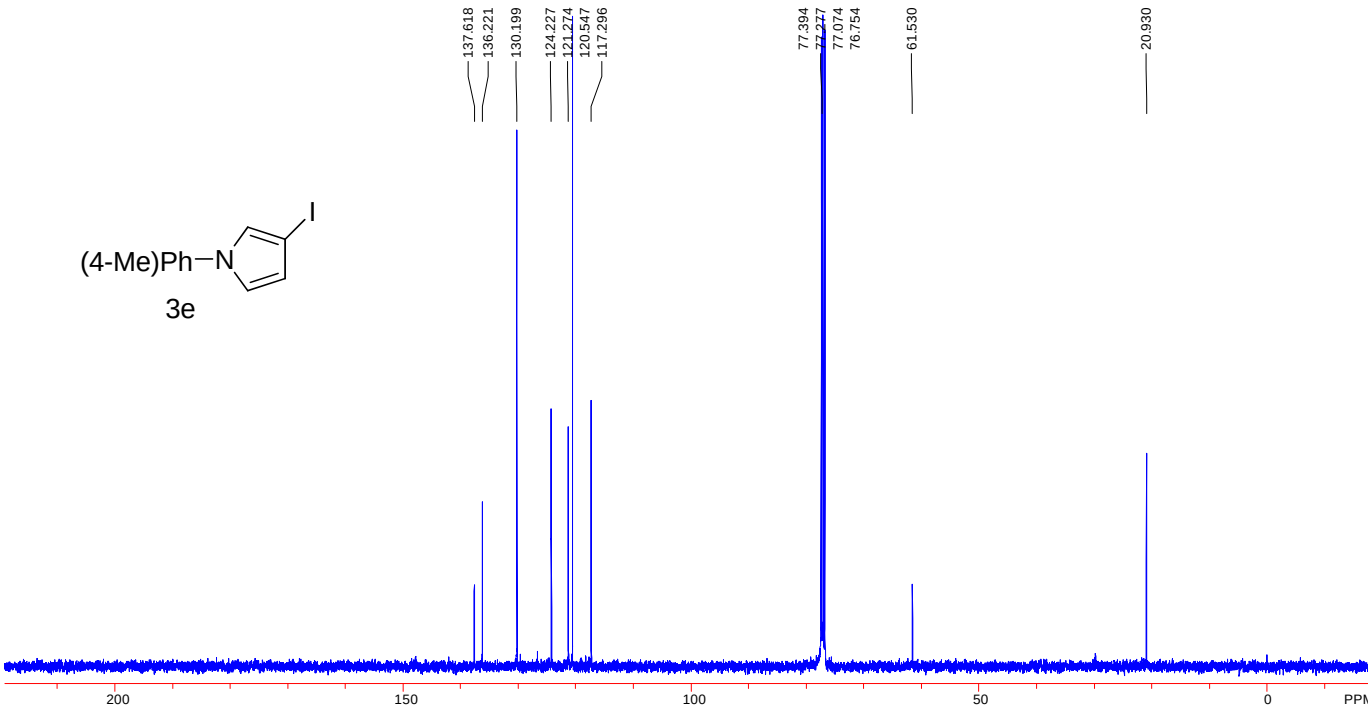
3d


7.250
7.215
7.085
7.082
6.918
6.914
6.910
6.397
6.395
6.393
6.390
2.370


I
(4-Me)Ph−N

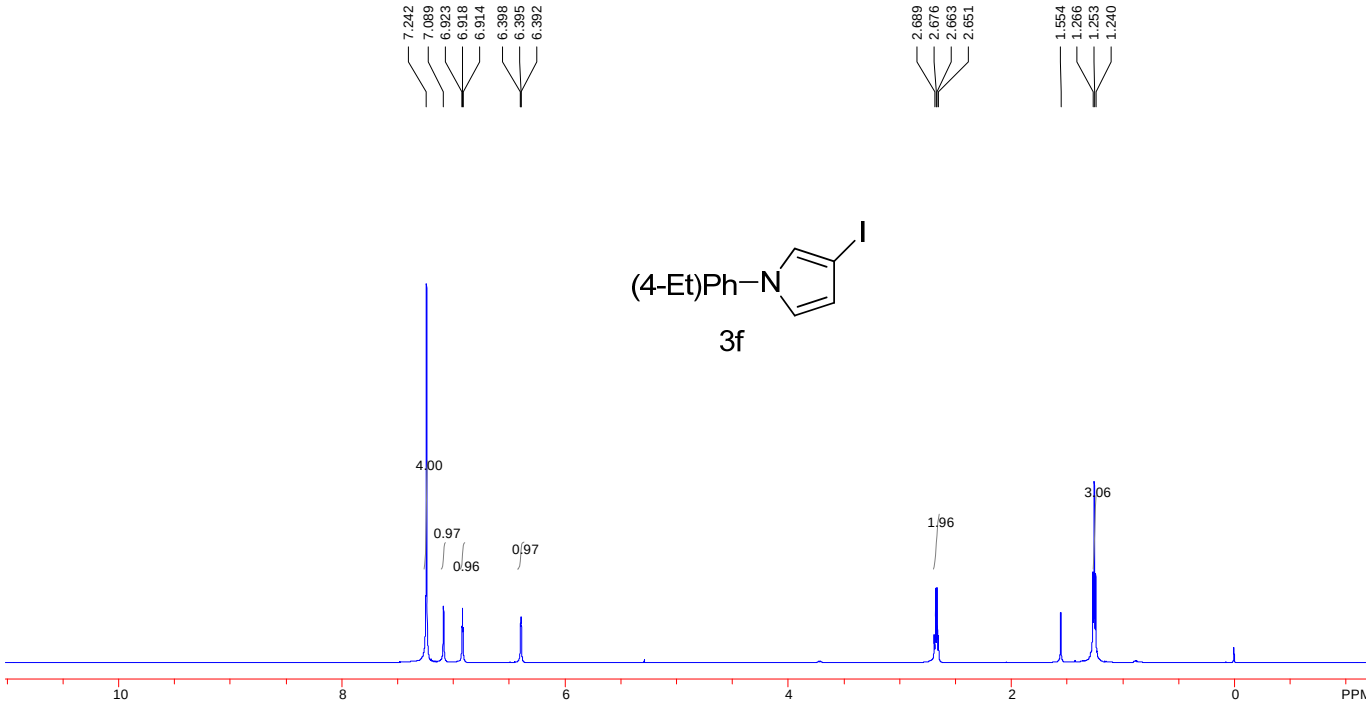
3e

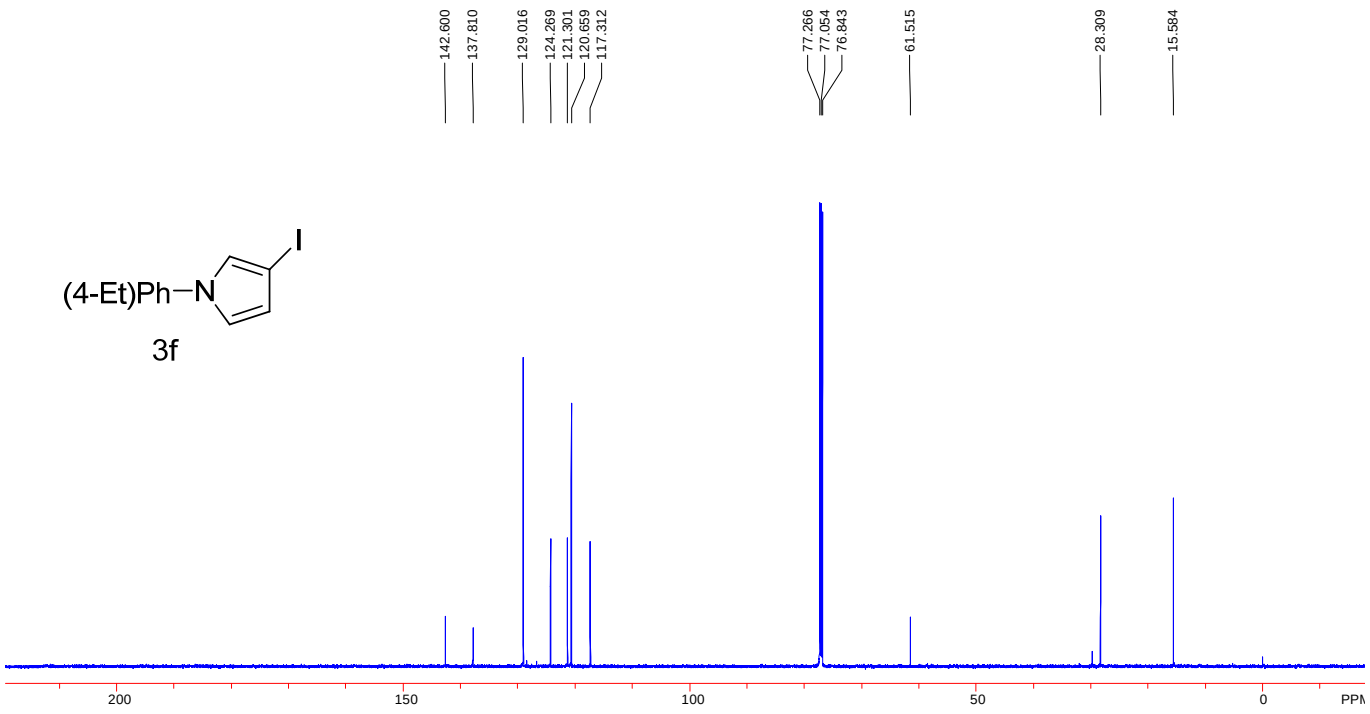

4.00
3.05
0.98
1.01
0.97
15
10
5
0
PPM

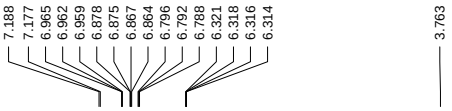

137.618
136.221
130.199
124.227
121.274
120.547
117.296
77.394
77.227
77.074
76.754
61.530
20.930
200
150
100
50
0
PPM

I
(4-Me)Ph−N

3e


7.242
7.089
6.923
6.918
6.914
6.398
6.395
6.392
2.689
2.676
2.663
2.651
1.554
1.266
1.253
1.240
(4-Et)Ph−N
I
3f
4.00
0.97
0.96
0.97
1.96
3.06
10
8
6
4
2
0
PPM


142.600
137.810
129.016
124.269
121.301
120.659
117.312
77.266
77.054
76.843
61.515
28.309
15.584
(4-Et)Ph−N
I
3f
200
150
100
50
0
PPM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7.177
6.965
6.962
6.959
6.878
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6.792
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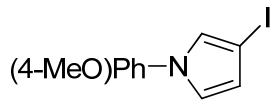
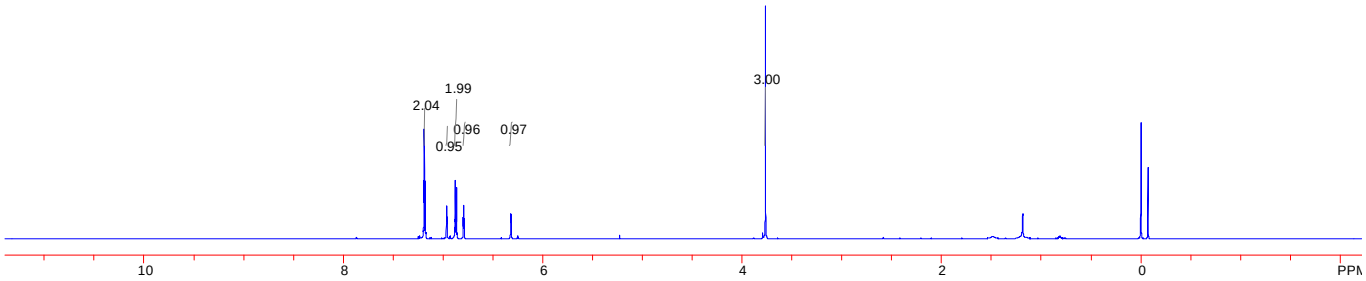
6.321
6.318
6.316
6.314
3.763


(4-MeO)Ph–N
I

3g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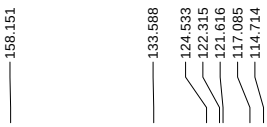
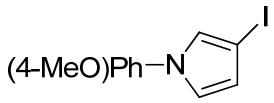
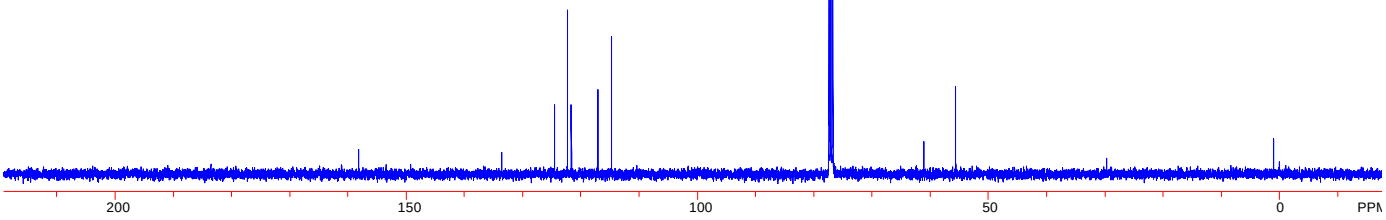
1.99
2.04
0.96
0.97
0.95
10
8
6
4
2
0
PPM


158.151
133.588
124.533
122.315
121.616
117.085
114.714
77.357
77.241
77.037
76.884
76.724
61.137
55.602


(4-MeO)Ph–N
I

3g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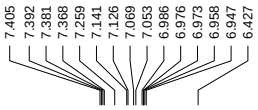
150
100
50
0
PPM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7.381
7.368
7.259
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7.126
7.069
7.053
6.986
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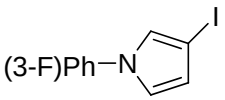
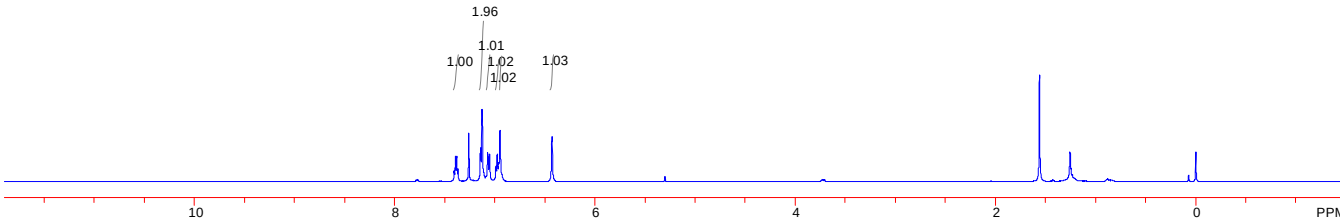
6.973
6.958
6.947
6.427


(3-F)Ph−N
I

3h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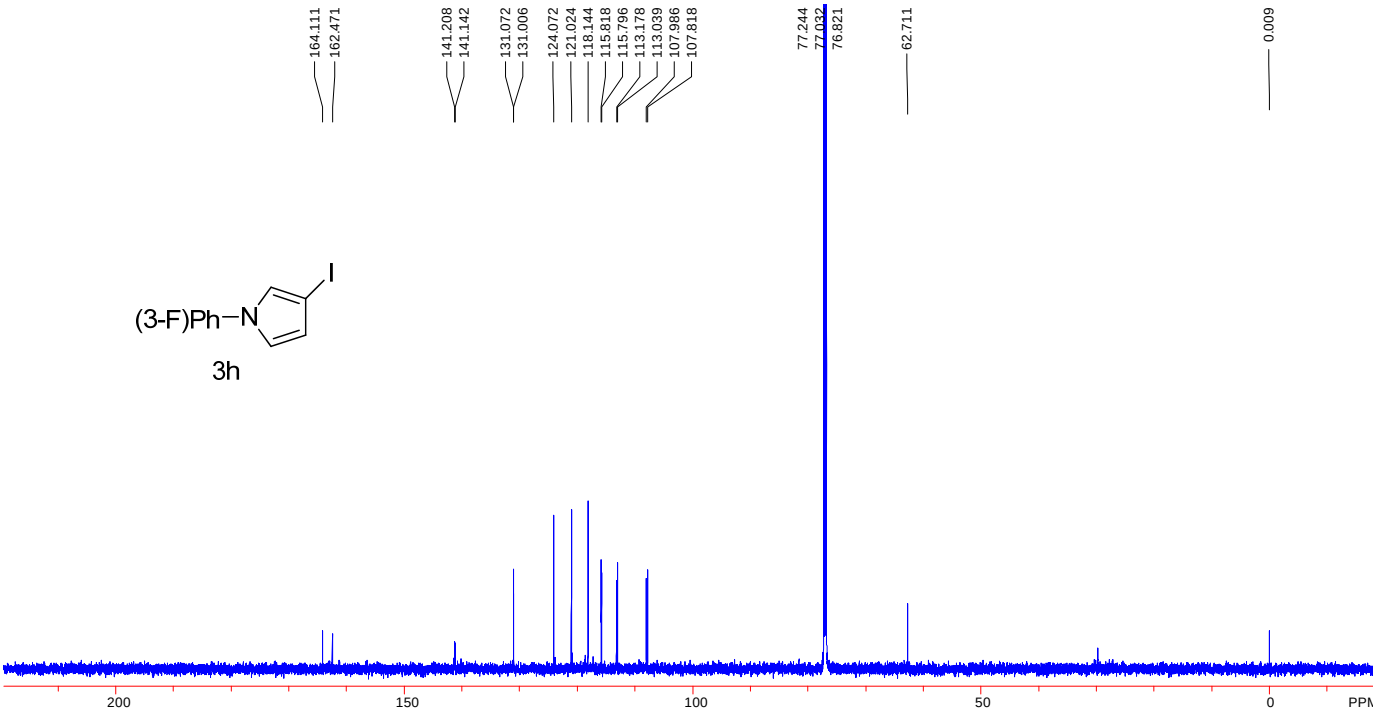
1.01
1.00
1.02
1.02
1.03
10
8
6
4
2
0
PPM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131.006
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121.024
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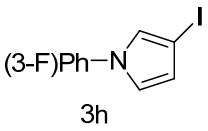
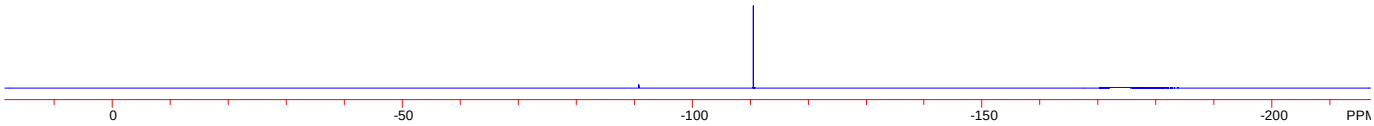
115.818
115.796
113.178
113.039
107.986
107.818
77.244
77.032
76.821
62.711
0.009
200
150
100
50
0
PPM

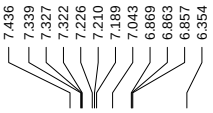
(3-F)Ph−N
I

3h



3h

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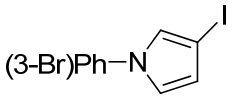
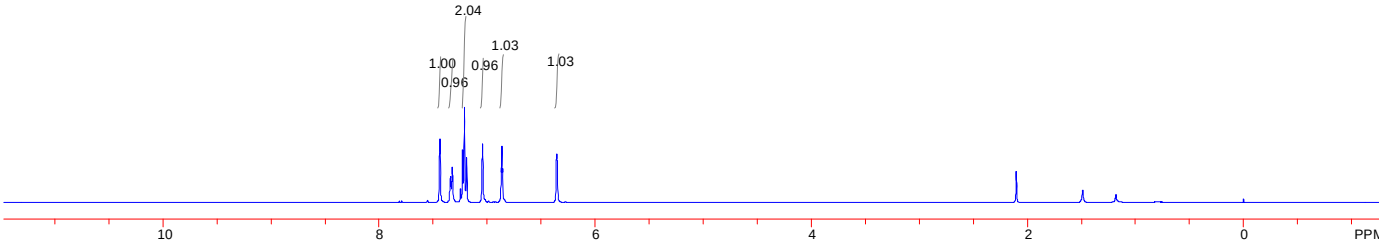
7.339
7.327
7.322
7.226
7.210
7.189
7.043
6.869
6.863
6.857
6.354


(3-Br)Ph–N
I

3i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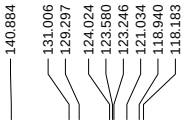
1.03
1.00
0.96
0.96
1.03
10
8
6
4
2
0
PPM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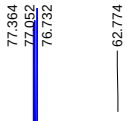
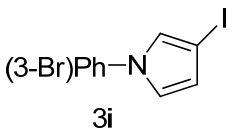
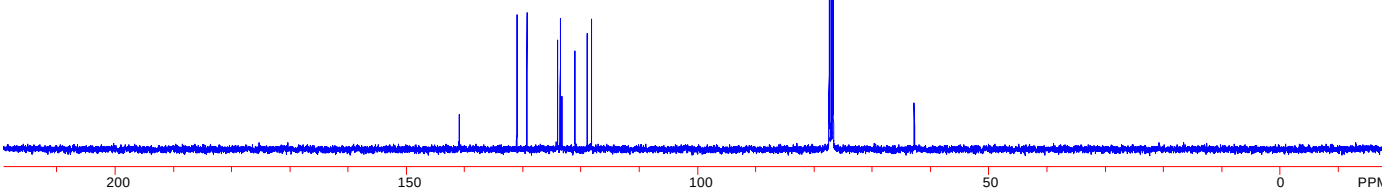
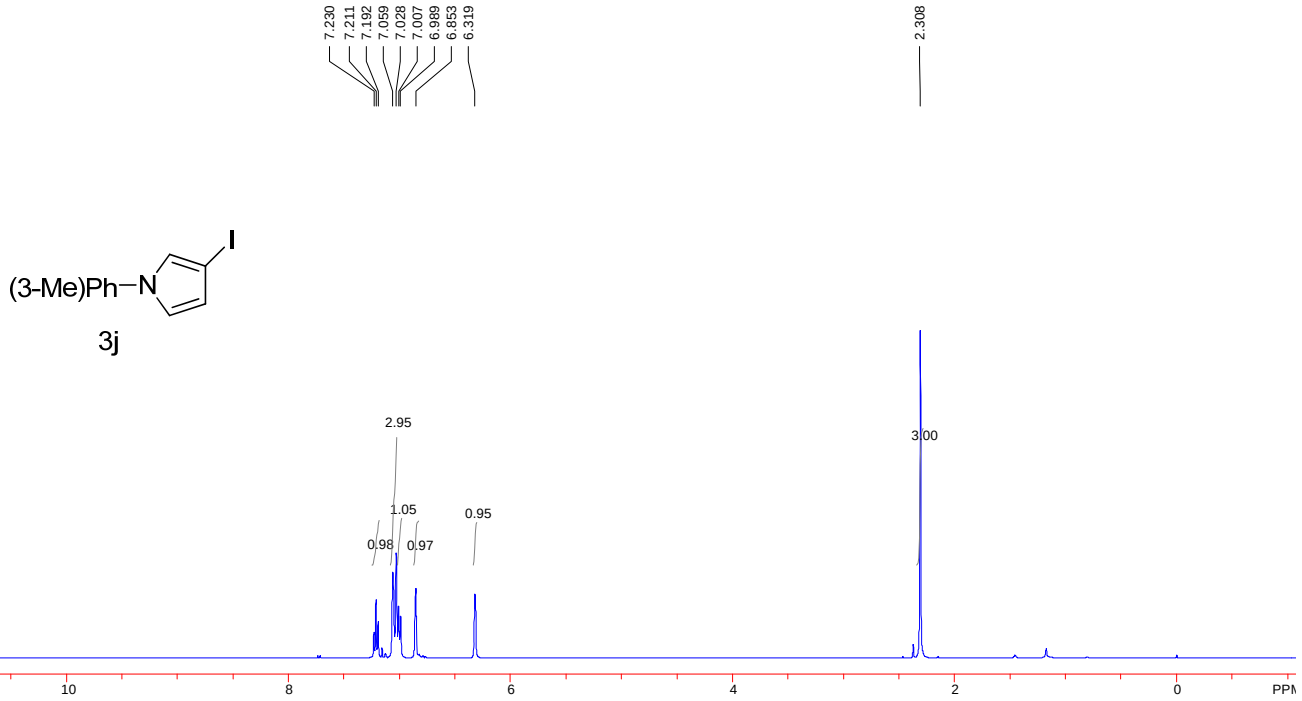
129.297
124.024
123.580
123.246
121.034
118.940
118.183

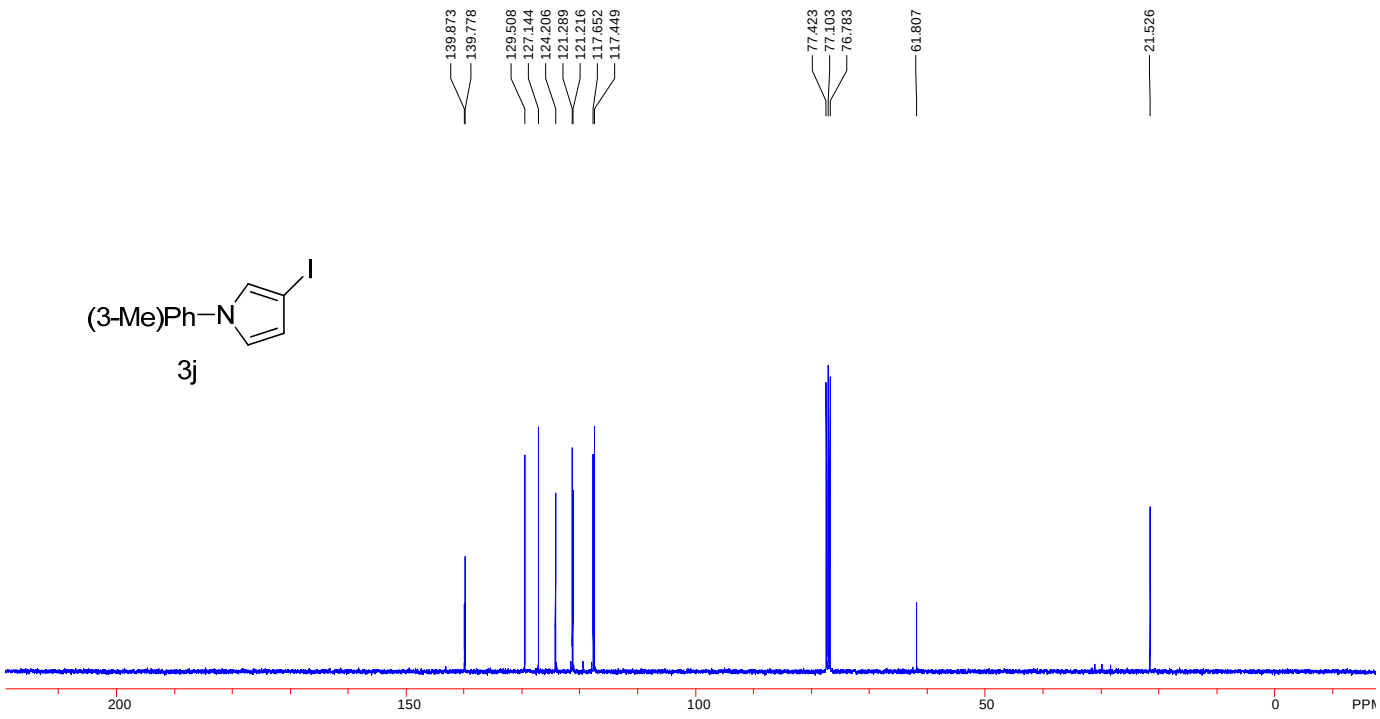

77.364
77.052
76.732
62.774

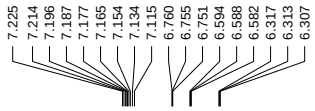

(3-Br)Ph–N
I

3i

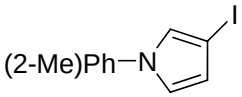

200
150
100
50
0
PPM


7.230
7.211
7.192
7.059
7.028
7.007
6.989
6.853
6.319
2.308
(3-Me)Ph−N
I
3j
2.95
1.05
0.98
0.97
0.95
3.00
10
8
6
4
2
0
PPM

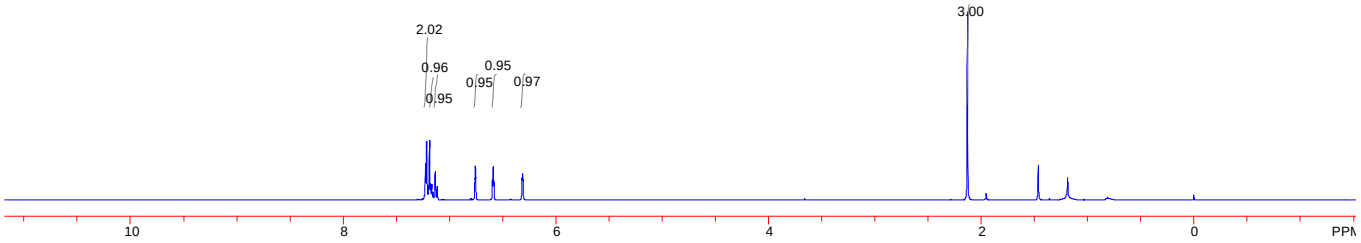

139.873
139.778
129.508
127.144
124.206
121.289
121.216
117.652
117.449
77.423
77.103
76.783
61.807
21.526
(3-Me)Ph−N
I
3j
200
150
100
50
0
PPM

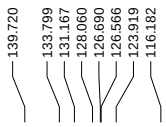

7.225
7.214
7.196
7.187
7.177
7.165
7.154
7.134
7.115
6.760
6.755
6.751
6.594
6.588
6.582
6.317
6.313
6.307


2.128

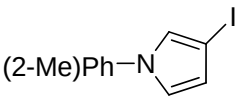

(2-Me)Ph
N
I

3k

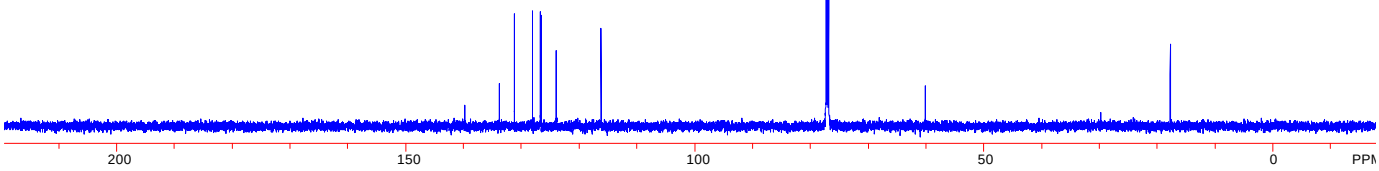

2.02
0.96
0.95
0.95
0.95
0.97
3.00
10
8
6
4
2
0
PPM


139.720
133.799
131.167
128.060
126.690
126.566
123.919
116.182


77.237
77.025
76.814
60.108
17.735


(2-Me)Ph
N
I

3k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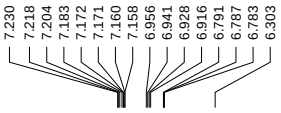
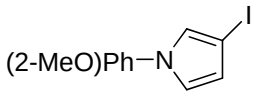
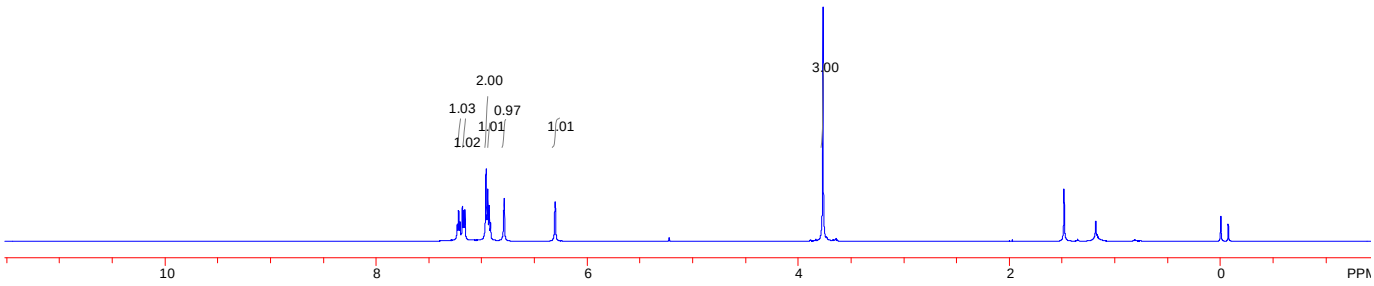
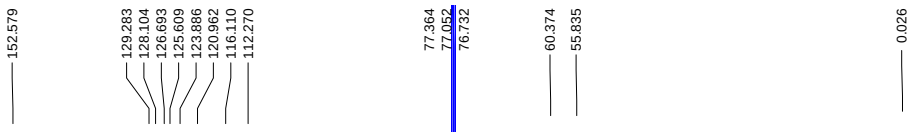
150
100
50
0
PPM

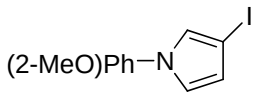

7.230
7.218
7.204
7.183
7.172
7.171
7.160
7.158
6.956
6.941
6.928
6.916
6.791
6.787
6.783
6.303
3.766


(2-MeO)Ph–N
I

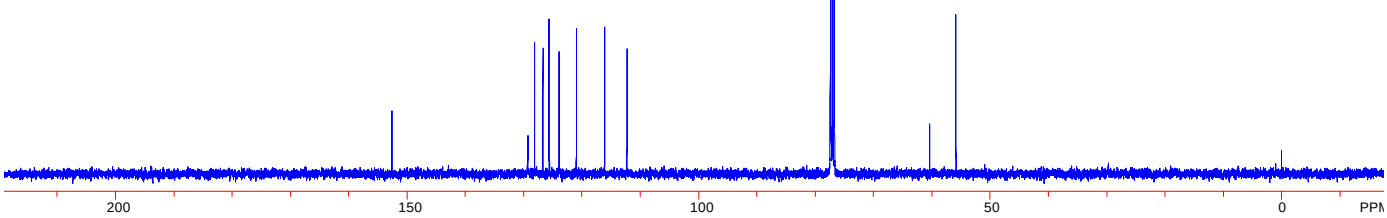
3l

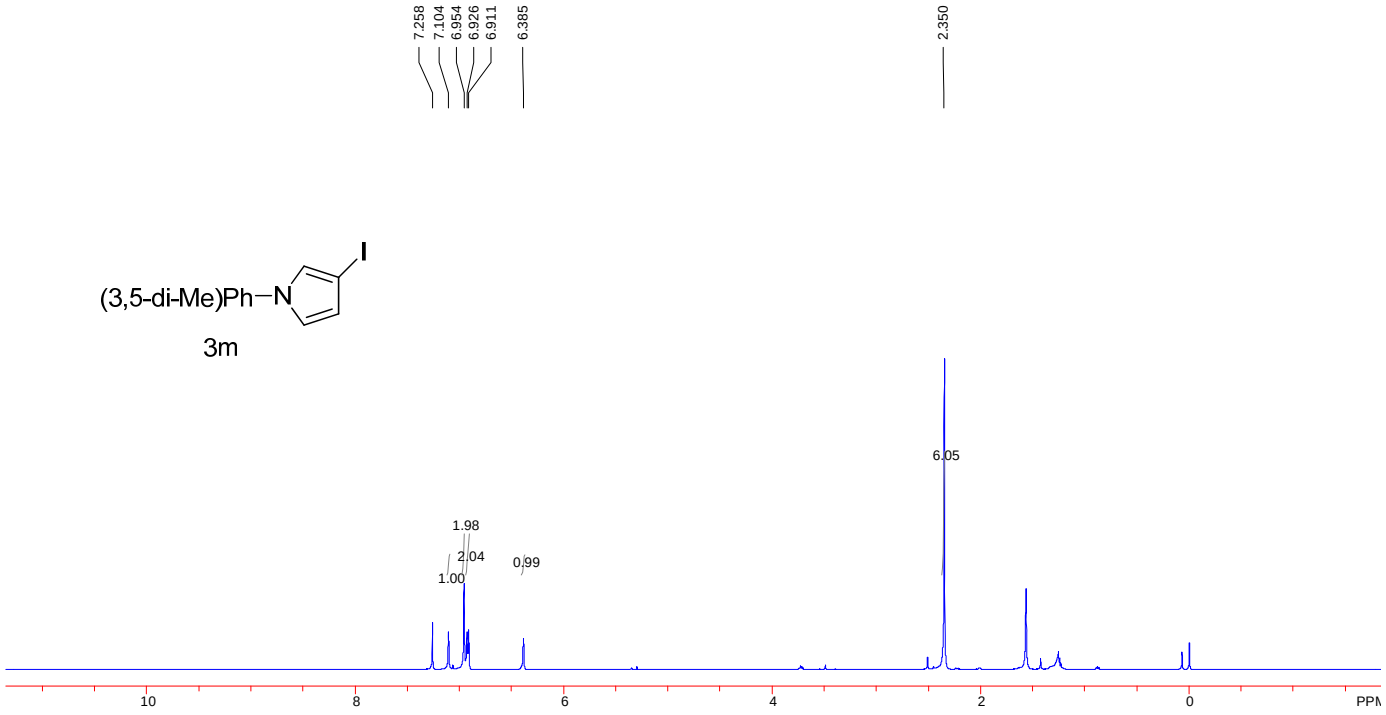

2.00
1.03
0.97
1.01
1.02
1.01
3.00
10
8
6
4
2
0
PPM

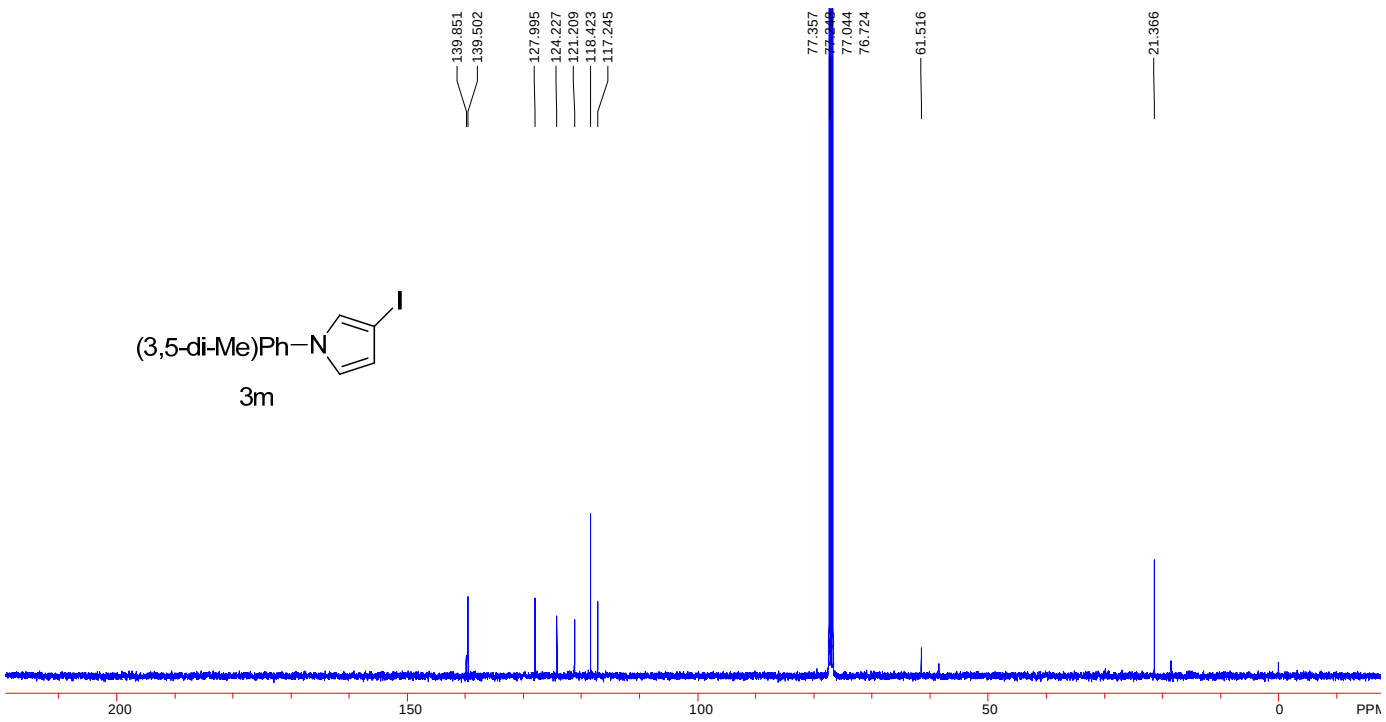

152.579
129.283
128.104
126.693
125.609
123.886
120.962
116.110
112.270
77.364
77.052
76.732
60.374
55.835
0.026

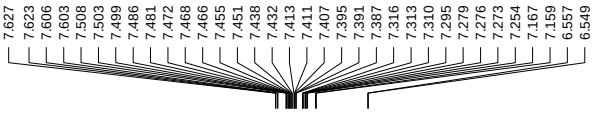

(2-MeO)Ph–N
I

3l


200
150
100
50
0
PPM


7.258
7.104
6.954
6.926
6.911
6.385
2.350
(3,5-di-Me)Ph–N
I
3m
6.05
1.98
2.04
1.00
0.99
10
8
6
4
2
0
PPM


139.851
139.502
127.995
124.227
121.209
118.423
117.245
77.357
77.044
76.724
61.516
21.366
(3,5-di-Me)Ph–N
I
3m
200
150
100
50
0
PPM


7.627
7.623
7.606
7.603
7.508
7.503
7.499
7.486
7.481
7.472
7.468
7.466
7.455
7.451
7.438
7.432
7.413
7.411
7.407
7.395
7.391
7.387
7.316
7.313
7.310
7.295
7.279
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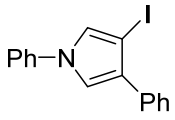
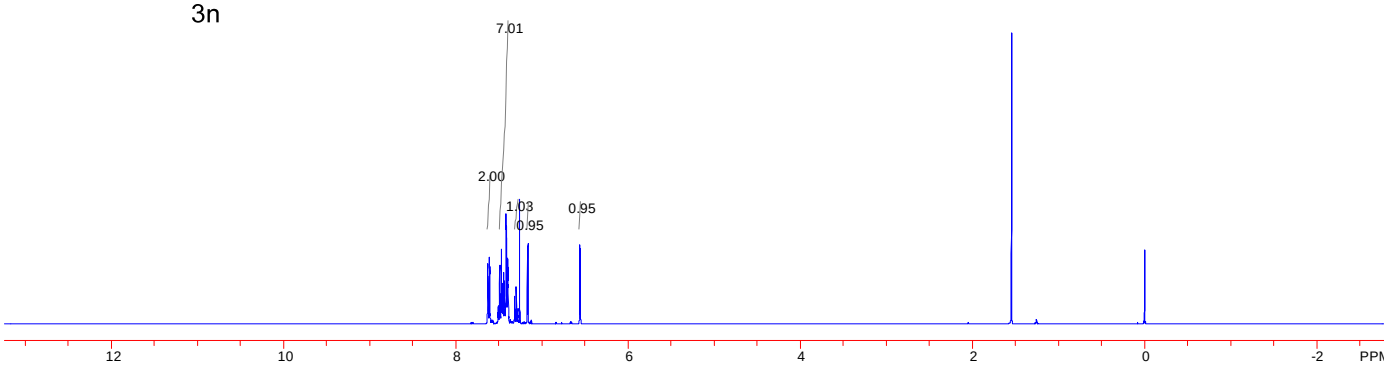
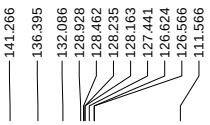
7.273
7.254
7.167
7.159
6.557
6.549

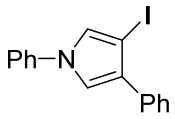

I
Ph—N
Ph

3n


7.01
2.00
1.03
0.95
0.95
12
10
8
6
4
2
0
-2
PPM


141.266
136.395
132.086
128.928
128.462
128.235
128.163
127.441
126.624
126.566
111.566

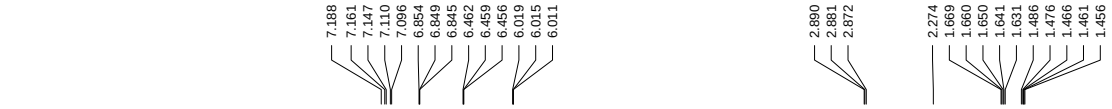

77.244
77.032
76.821
70.944

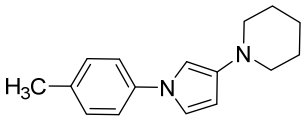

I
Ph—N
Ph

3n

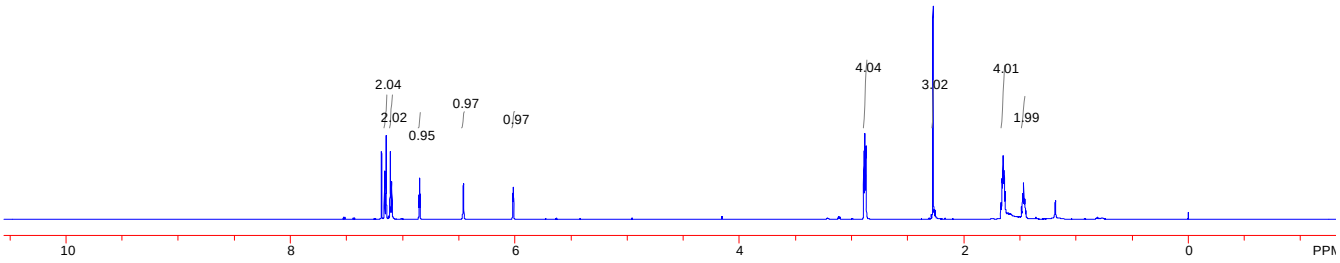
200
150
100
50
0
PPM

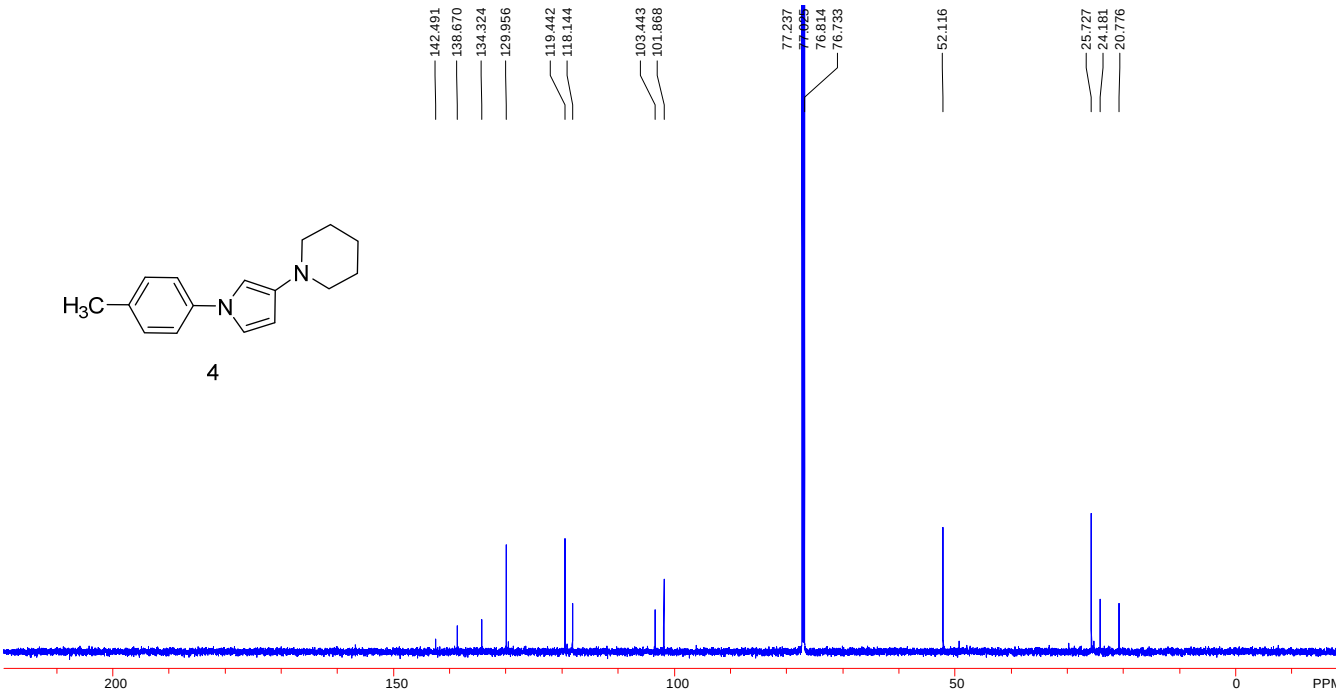
IV. Copies of the NMR spectra of 4-7



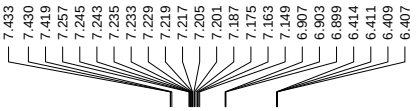


4

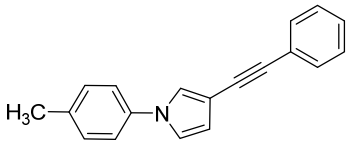




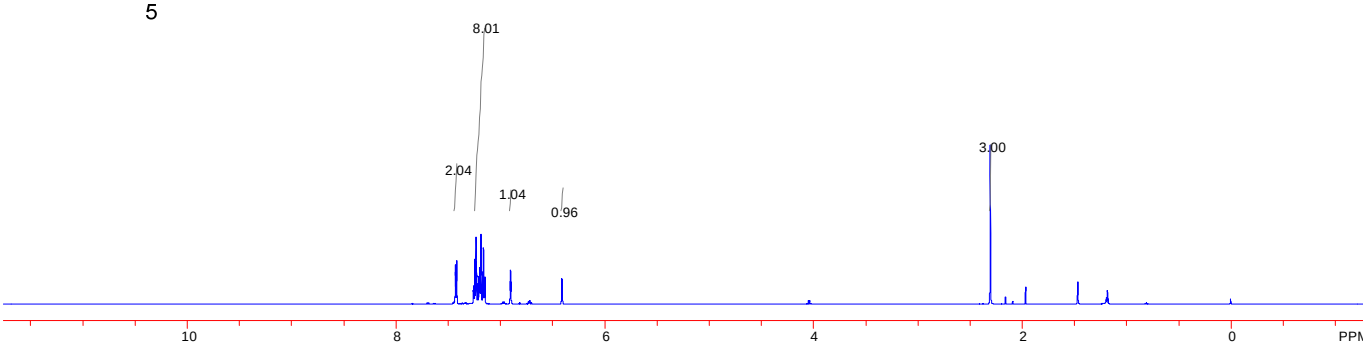
4

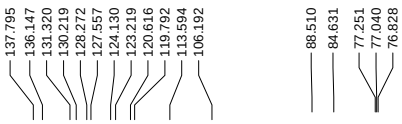

7.433
7.430
7.419
7.257
7.245
7.243
7.235
7.233
7.229
7.219
7.217
7.205
7.201
7.187
7.175
7.163
7.149
6.907
6.903
6.899
6.414
6.411
6.409
6.407


2.305


H3C
N

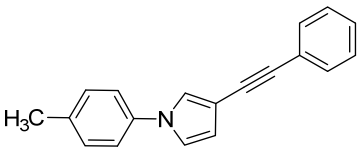
5


8.01
2.04
1.04
0.96
3.00
10
8
6
4
2
0
PPM

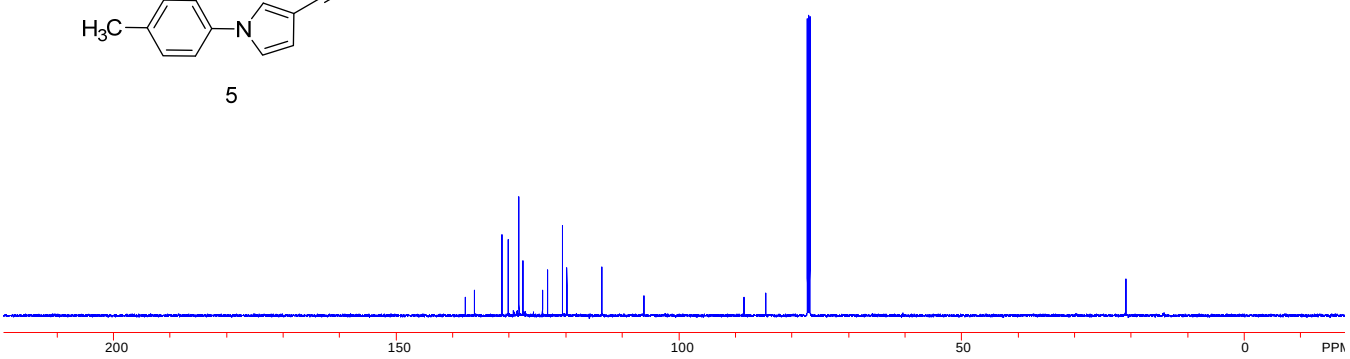

137.795
136.147
131.320
130.219
128.272
127.557
124.130
123.219
120.616
119.792
113.594
106.192

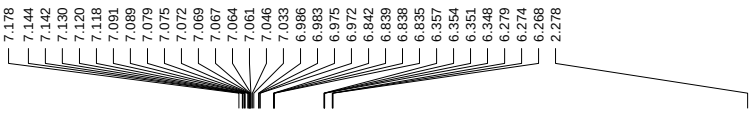
88.510
84.631
77.251
77.040
76.828


20.900


H3C
N

5


200
150
100
50
0
PPM


7.178
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7.142
7.130
7.120
7.118
7.091
7.089
7.079
7.075
7.072
7.069
7.067
7.064
7.061
7.046
7.033
6.986
6.983
6.975
6.972
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6.835
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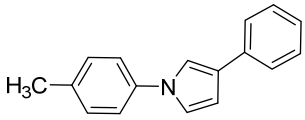
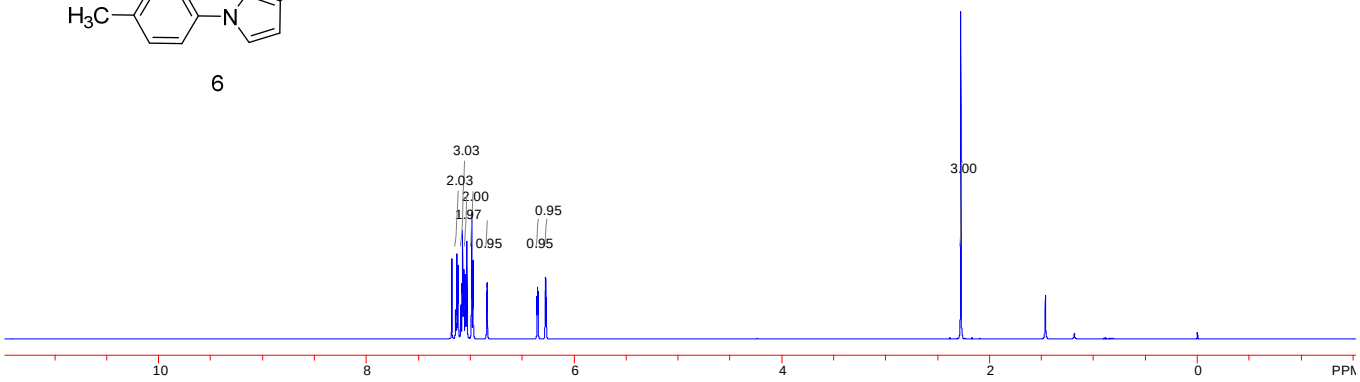
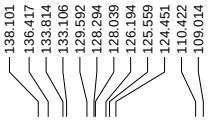
6.354
6.351
6.348
6.279
6.274
6.268
2.278


H3C
N

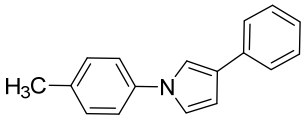
6


3.03
2.03
2.00
1.97
0.95
0.95
0.95
3.00
10
8
6
4
2
0
PPM

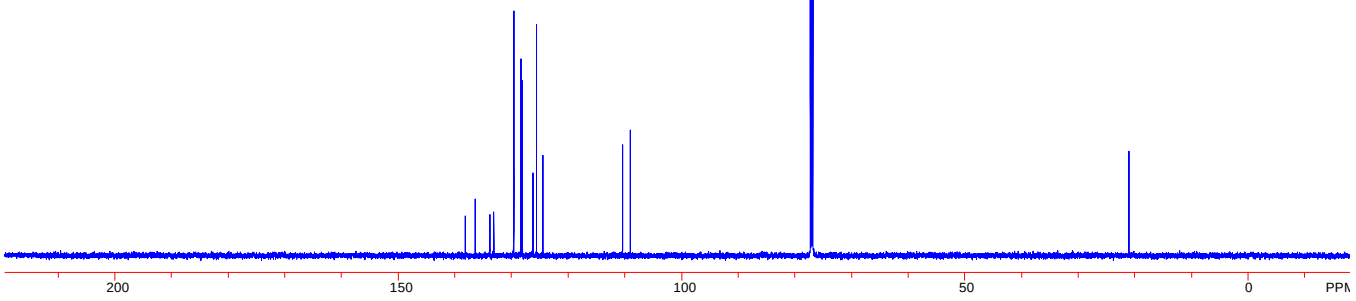

138.101
136.417
133.814
133.106
129.592
128.294
128.039
126.194
125.559
124.451
110.422
109.014

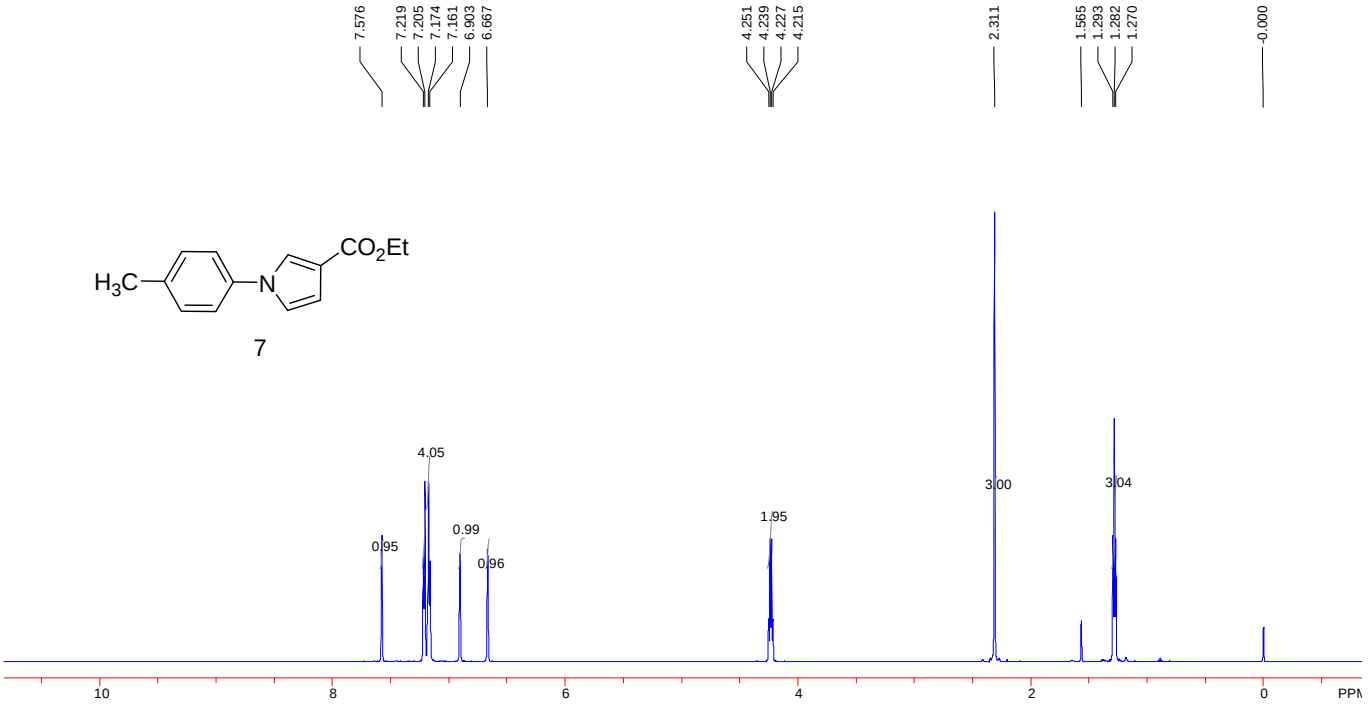

77.244
77.032
76.821

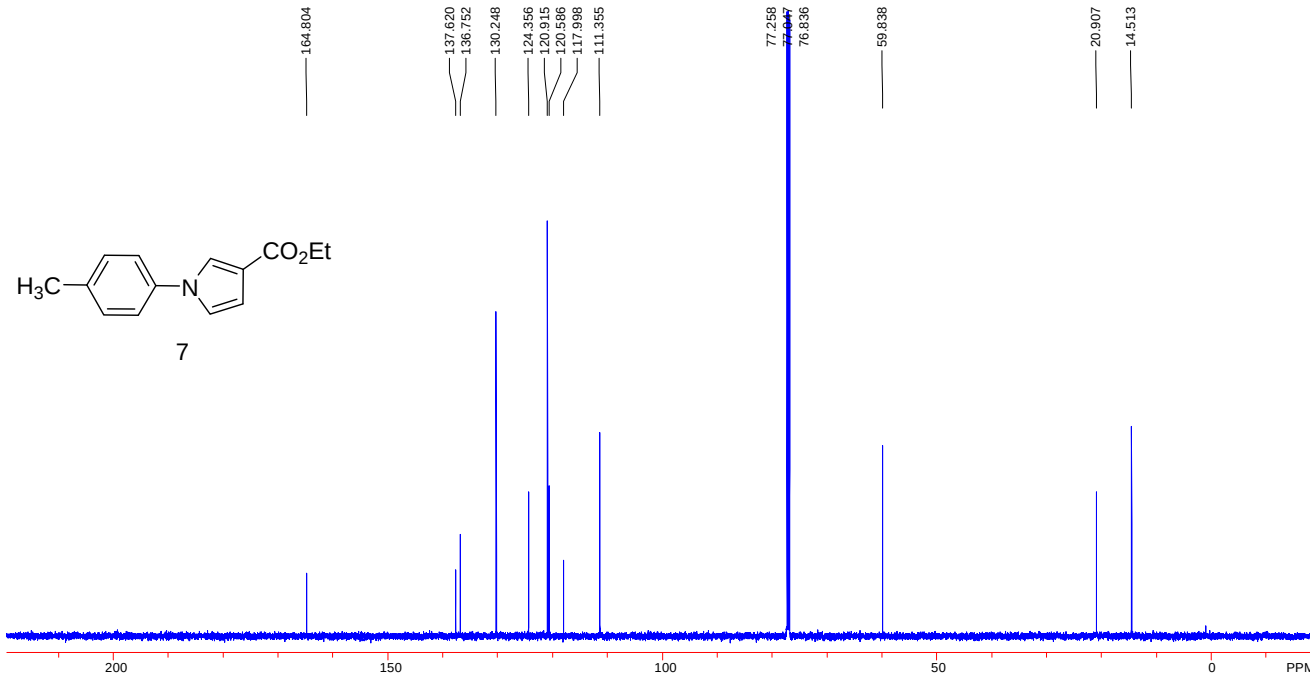

21.017


H3C
N

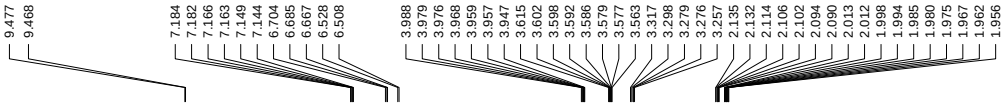
6

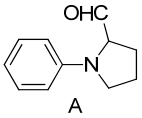

200
150
100
50
0
PPM

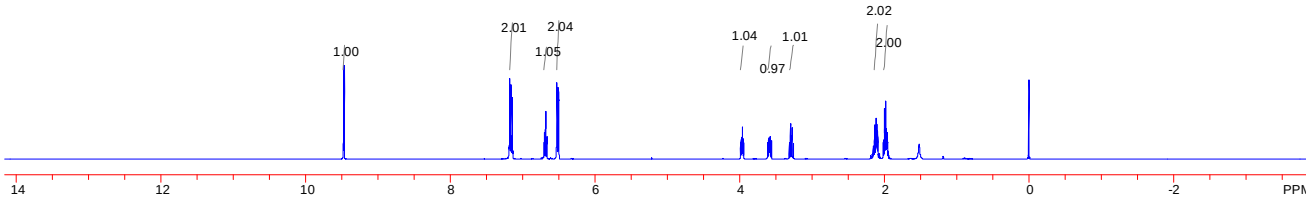

7.576
7.219
7.205
7.174
7.161
6.903
6.667
4.251
4.239
4.227
4.215
2.311
1.565
1.293
1.282
1.270
-0.000
CO2Et
H3C
N
7
4.05
0.95
0.99
0.96
1.95
3.00
3.04
10
8
6
4
2
0
PPM

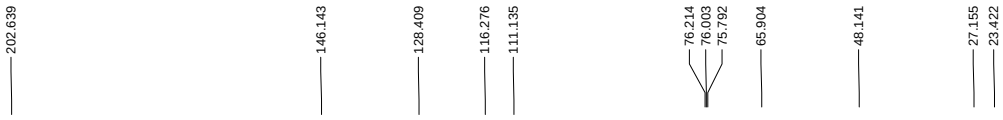

164.804
137.620
136.752
130.248
124.356
120.915
120.586
117.998
111.355
77.258
77.047
76.836
59.838
20.907
14.513
CO2Et
H3C
N
7
200
150
100
50
0
PPM

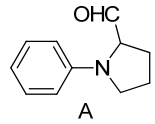
V. Copies of the NMR spectra of A

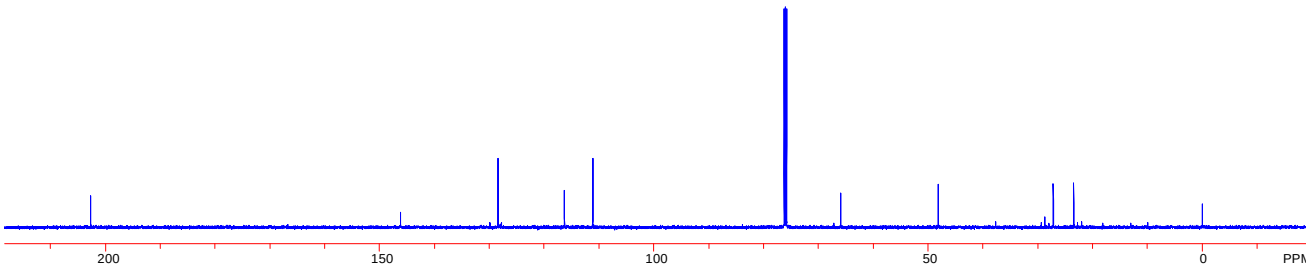












VI. X-ray crystal structure and data of 3d

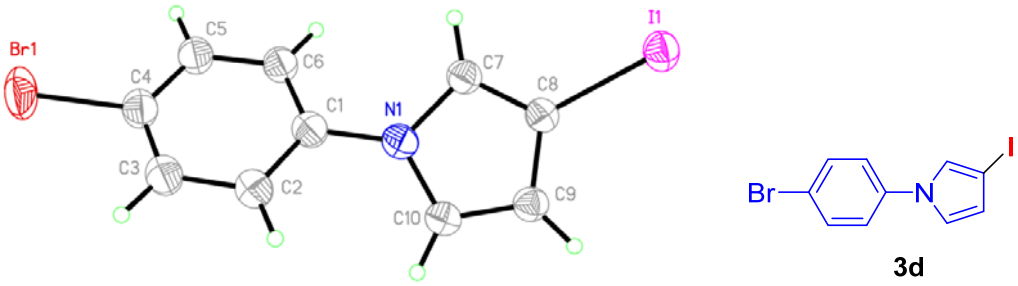


Fig. S1 X-ray structure of **3d** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a cyclohexane solution of **3d**. Crystal data collection and refinement parameters of **3d** are summarized in Table S1. Intensity data were collected at 295 K on a SuperNova Dual diffractometer using mirror-monochromated Mo Kα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table S1 Crystallographic data and structure refinement results of **3d**

Empirical formula	$C_{10}H_7BrIN$
Formula weight	347.98
Temp, K	294.63(10)
Crystal system	orthorhombic
Space group	Pbca
a, Å	10.5281(10)
b, Å	7.7940(9)
c, Å	25.907(2)
α (°)	90
β (°)	90
γ (°)	90
Volume, Å^3	2125.8(4)
Z	8
d_{calc}, g cm^{-3}	2.174
λ, Å	0.71073
μ, mm^{-1}	6.724
No. of data collected	7533

No. of unique data	1871
R_{int}	0.1758
Goodness-of-fit on F^2	1.043
R_1, wR_2 ($I > 2\sigma(I)$)	0.1155, 0.2883
R_1, wR_2 (all data)	0.1534, 0.3252