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

Denitrative Imino-Diaza-Nazarov Cyclization: Synthesis of Pyrazoles

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SUPPLEMENTARY INFORMATION

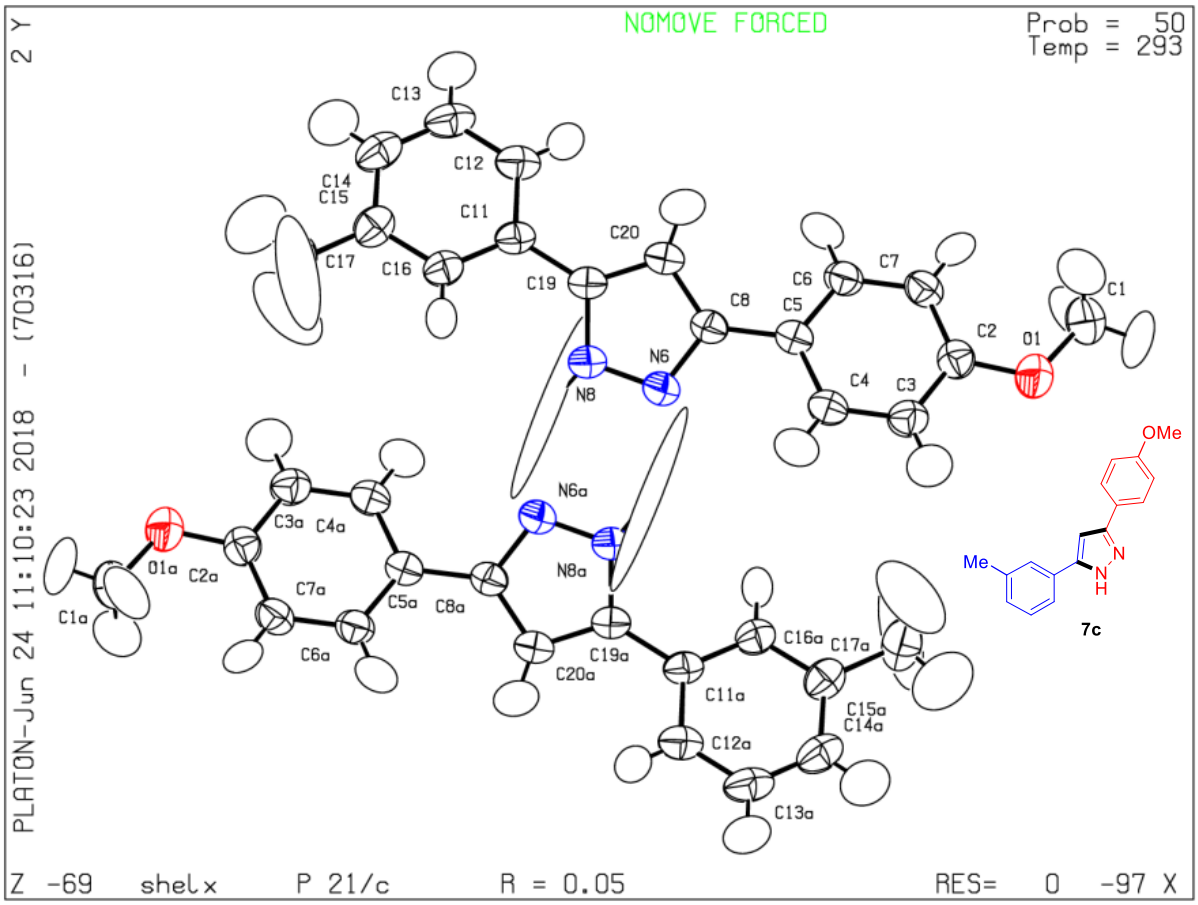


Figure S1. ORTEP plot of crystal structure of **7c** (numbering is arbitrary).

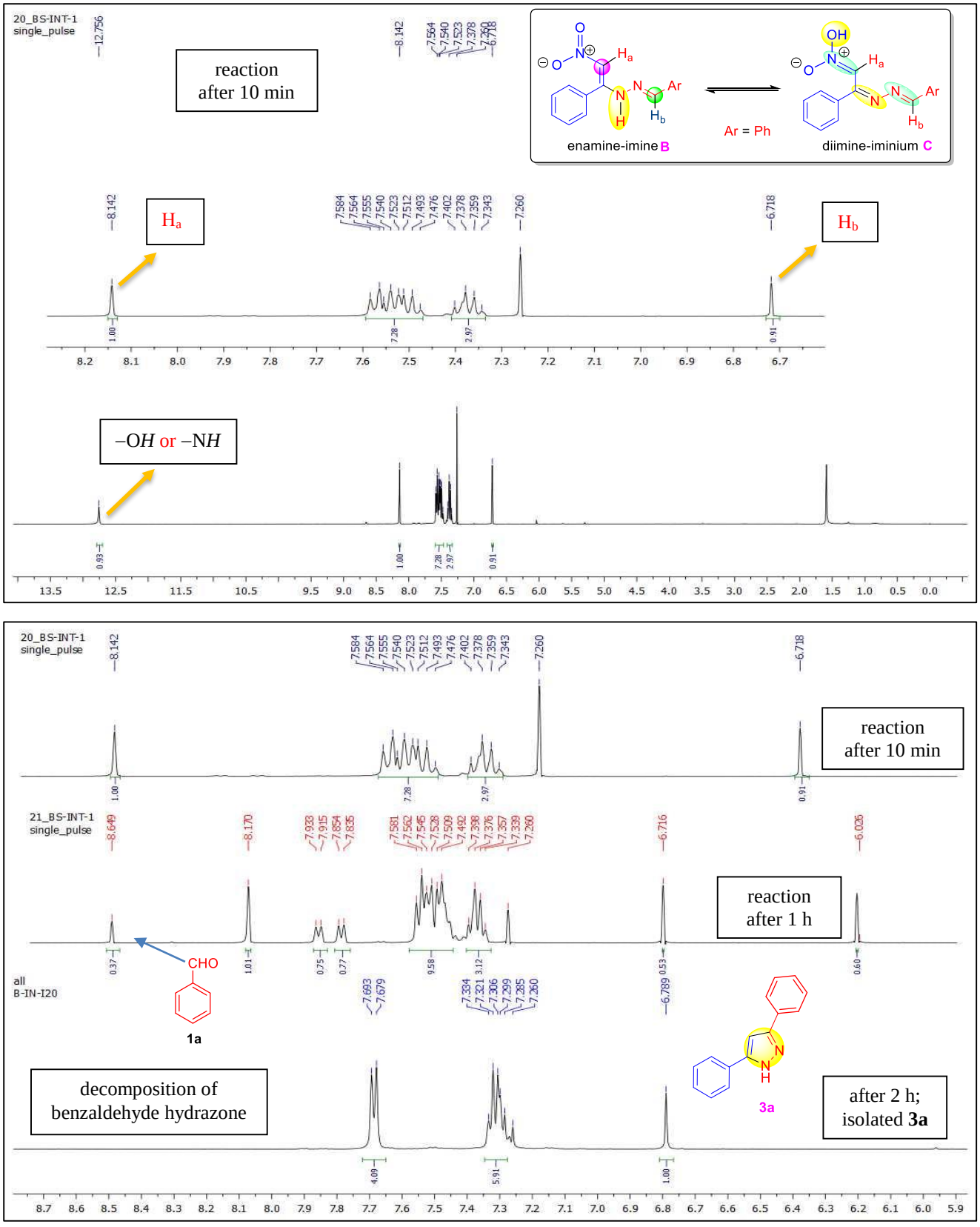
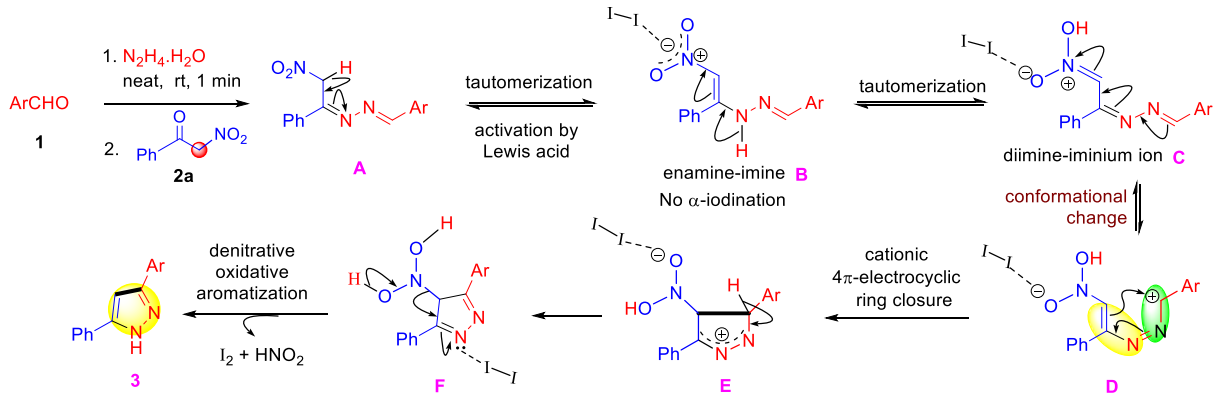


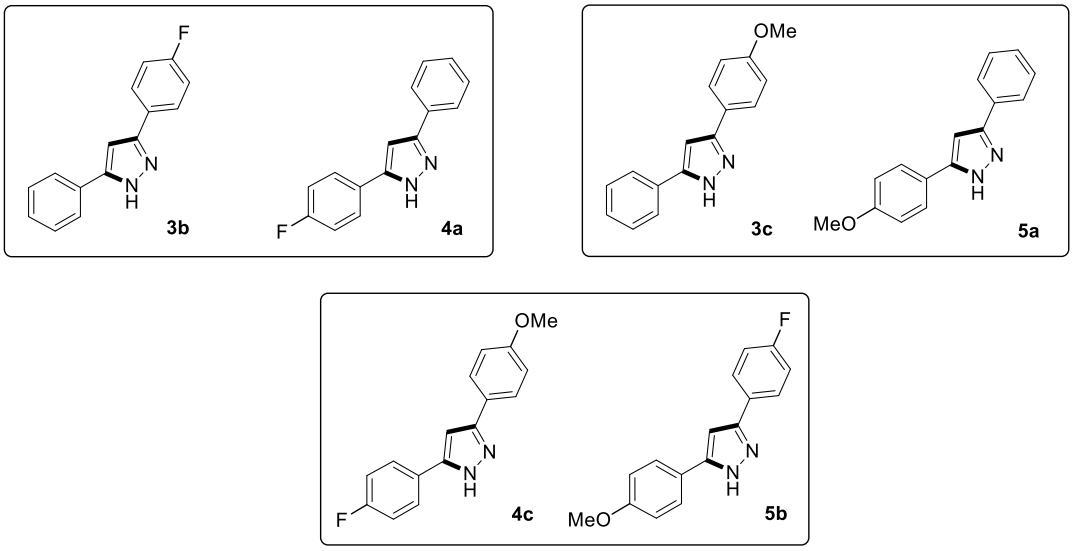
Figure S2. Monitoring reaction of **1a** and **2a** by ^{1}H NMR analysis.

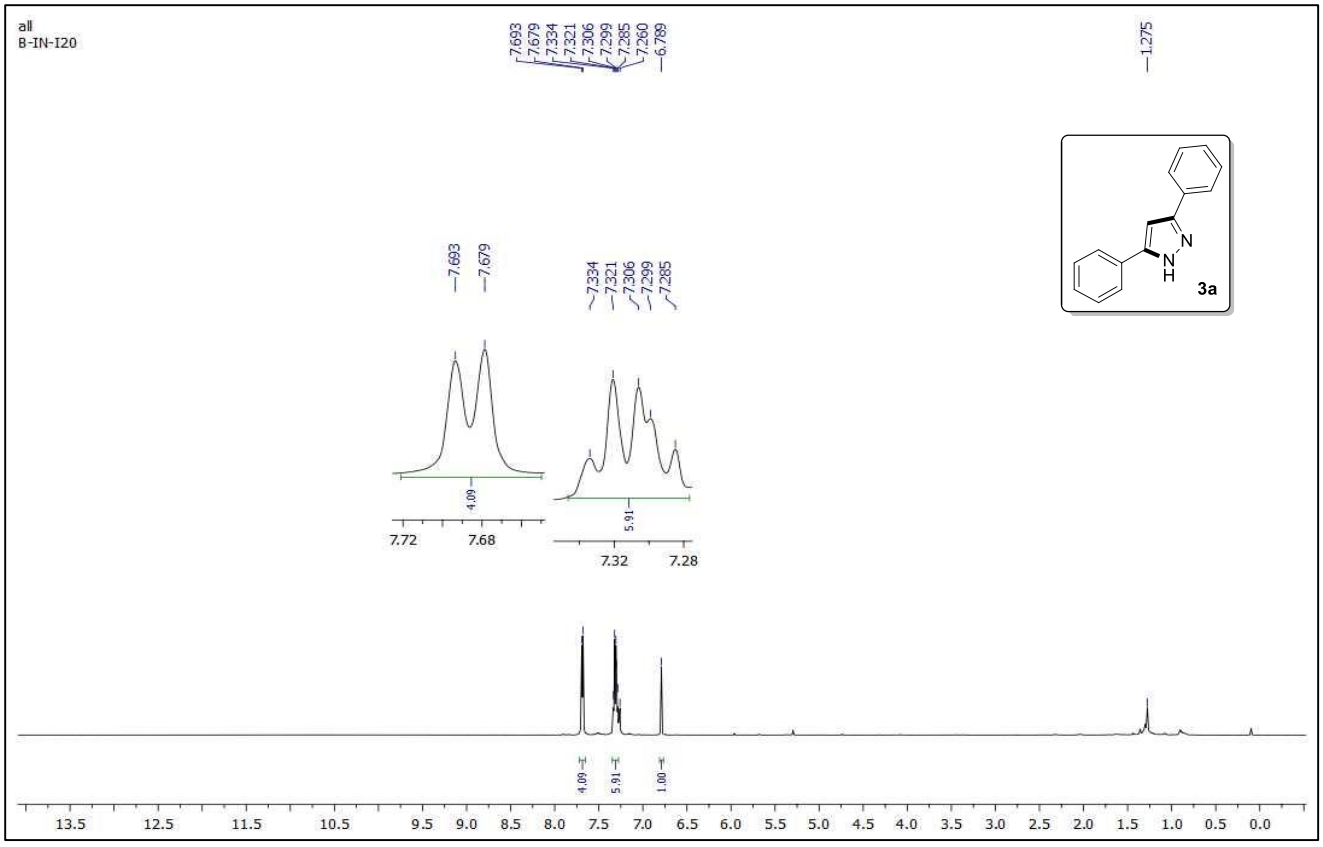


Scheme S1: Plausible reaction mechanism.

Prototropic tautomers:

The NMR spectra of the products **3b** & **4a** are identical. Similarly, each product of the other two sets **3c** & **5a**, **4c** & **5b** have identical spectral data. This indicates that most likely, the proton in the pyrazole ring is delocalized between the two nitrogen atoms of the heterocycle. Though the position of the proton in the pyrazole ring is shown in the structures on one nitrogen atom, in principle, it can be on either of the two nitrogen atoms due to prototropic tautomerism.

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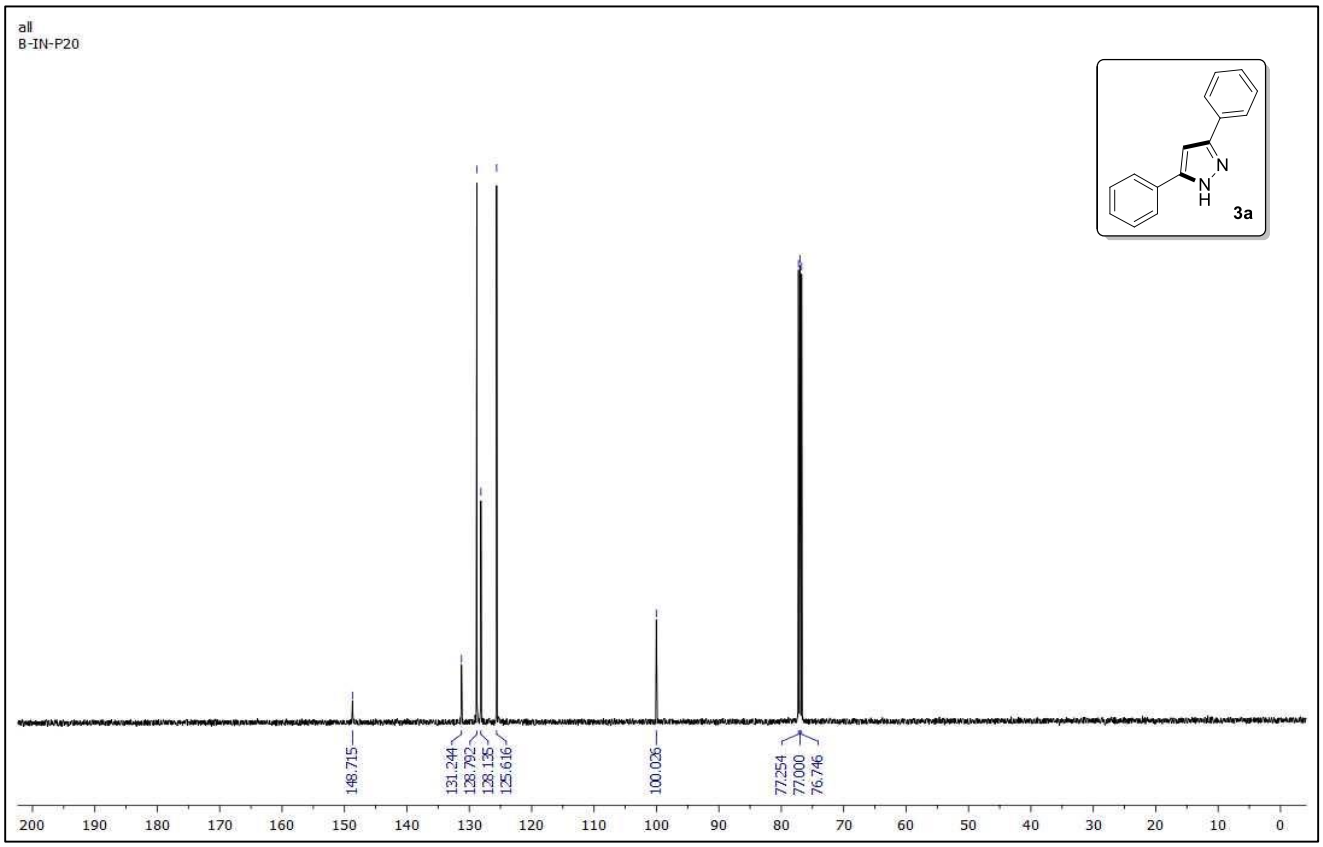
7.693
7.679
7.334
7.321
7.306
7.299
7.285
7.260
6.789
1.275
3a
4.09
5.91
1.00


all
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3a
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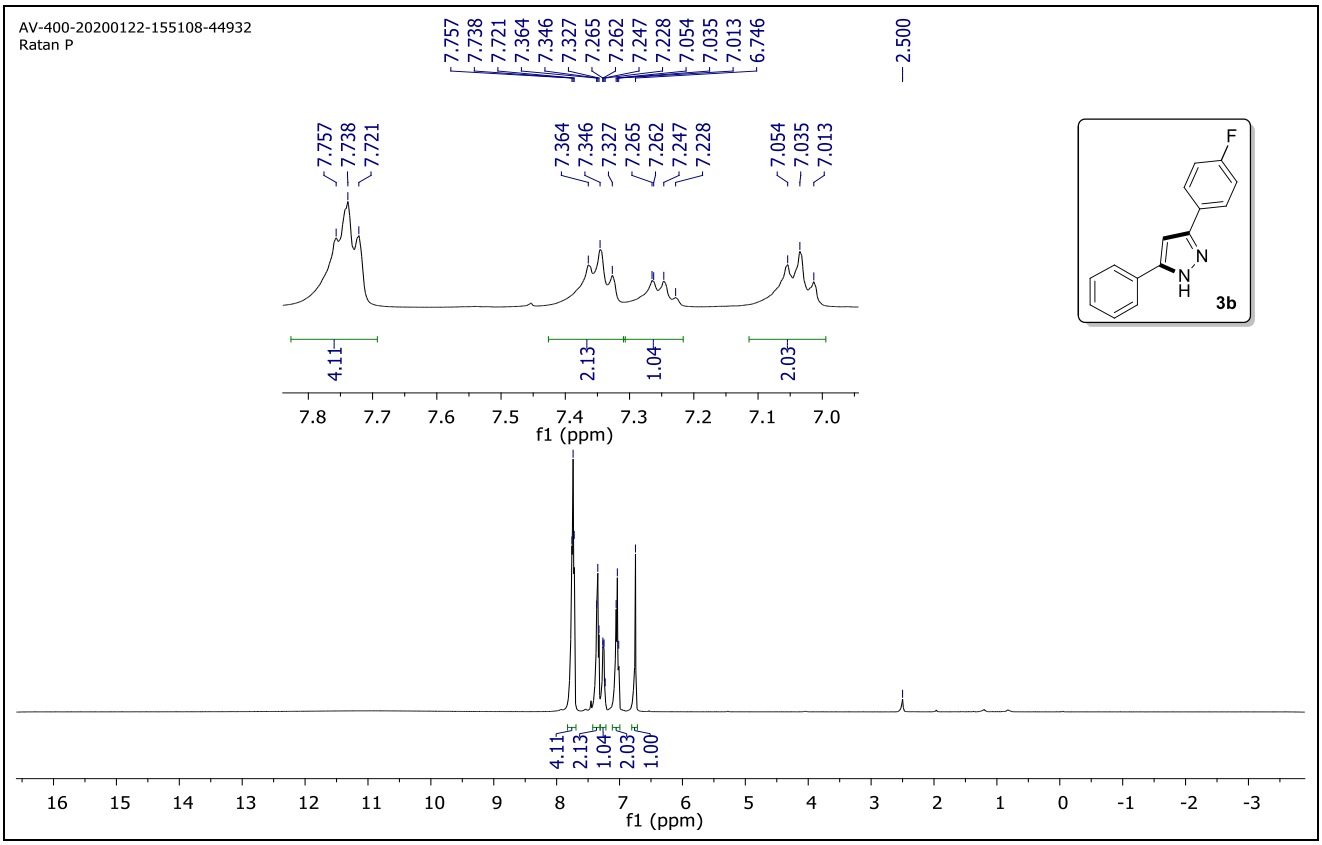
128.792
128.135
125.616
100.026
77.254
77.000
76.746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Ratan P
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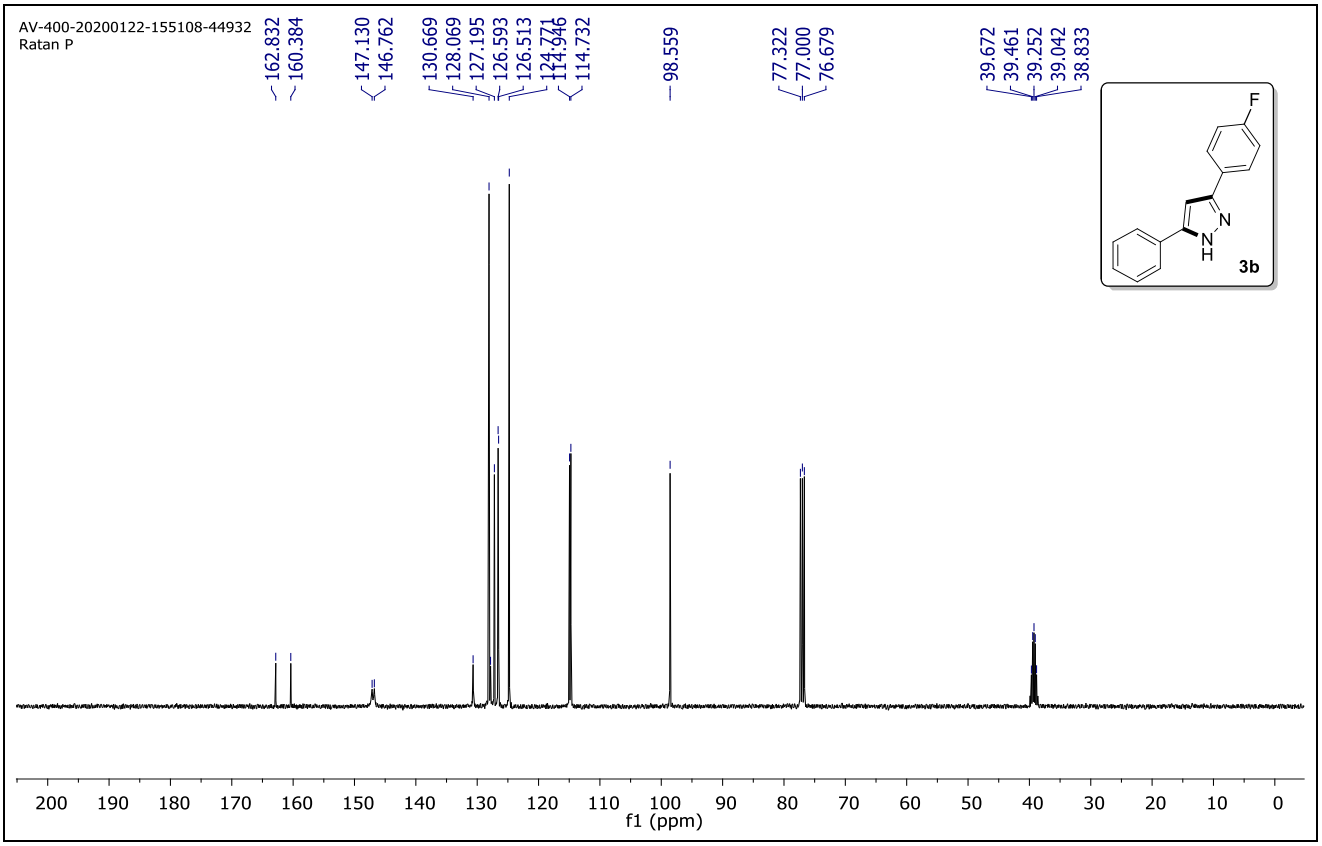
7.738
7.721
7.364
7.346
7.327
7.265
7.262
7.247
7.228
7.054
7.035
7.013
6.746
2.500
4.11
2.13
1.04
2.03
1.00
f1 (ppm)
F
N
N
H
3b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Ratan P
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160.384
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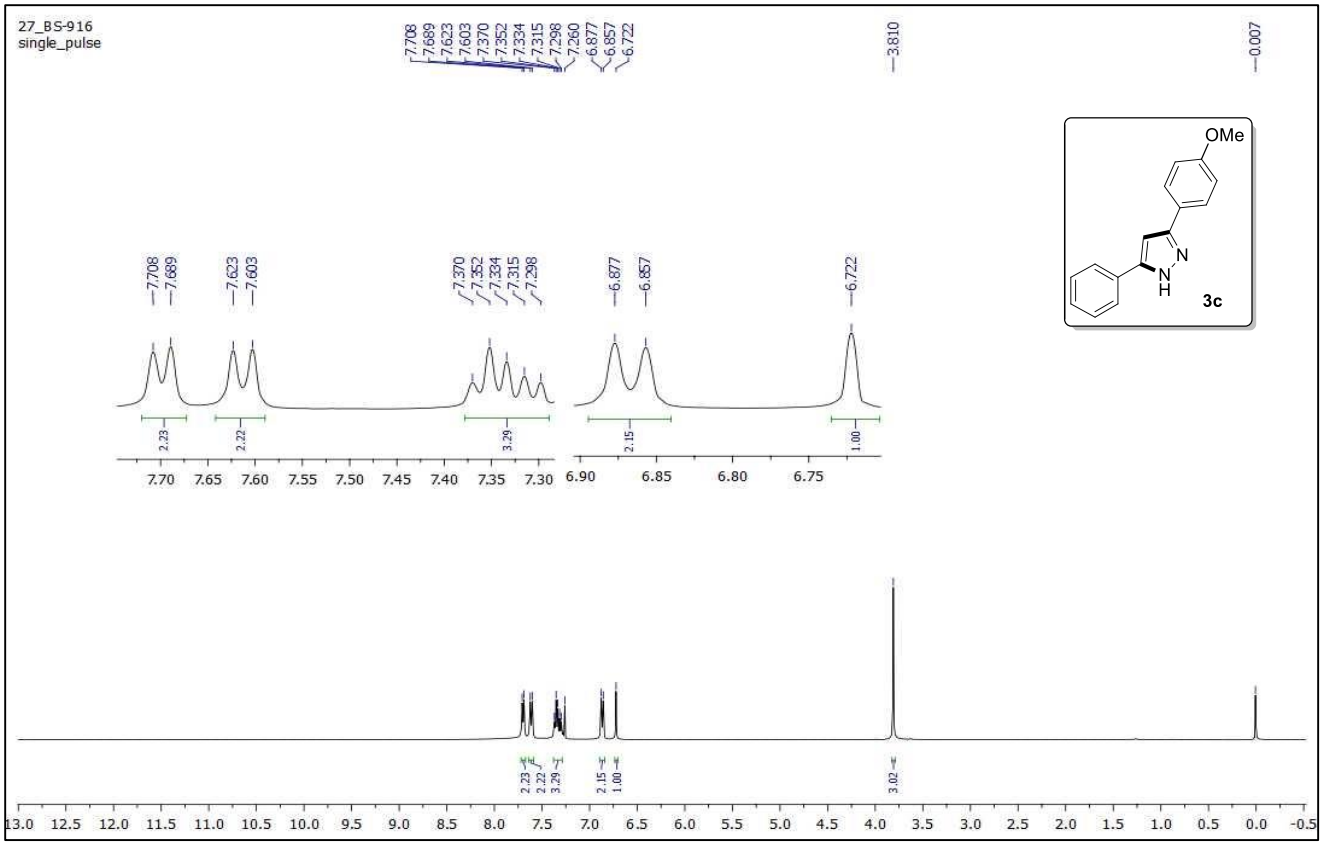
146.762
130.669
128.069
127.195
126.593
126.513
124.771
114.946
114.732
98.559
77.322
77.000
76.679
39.672
39.461
39.252
39.042
38.833
f1 (ppm)
F
N
N
H
3b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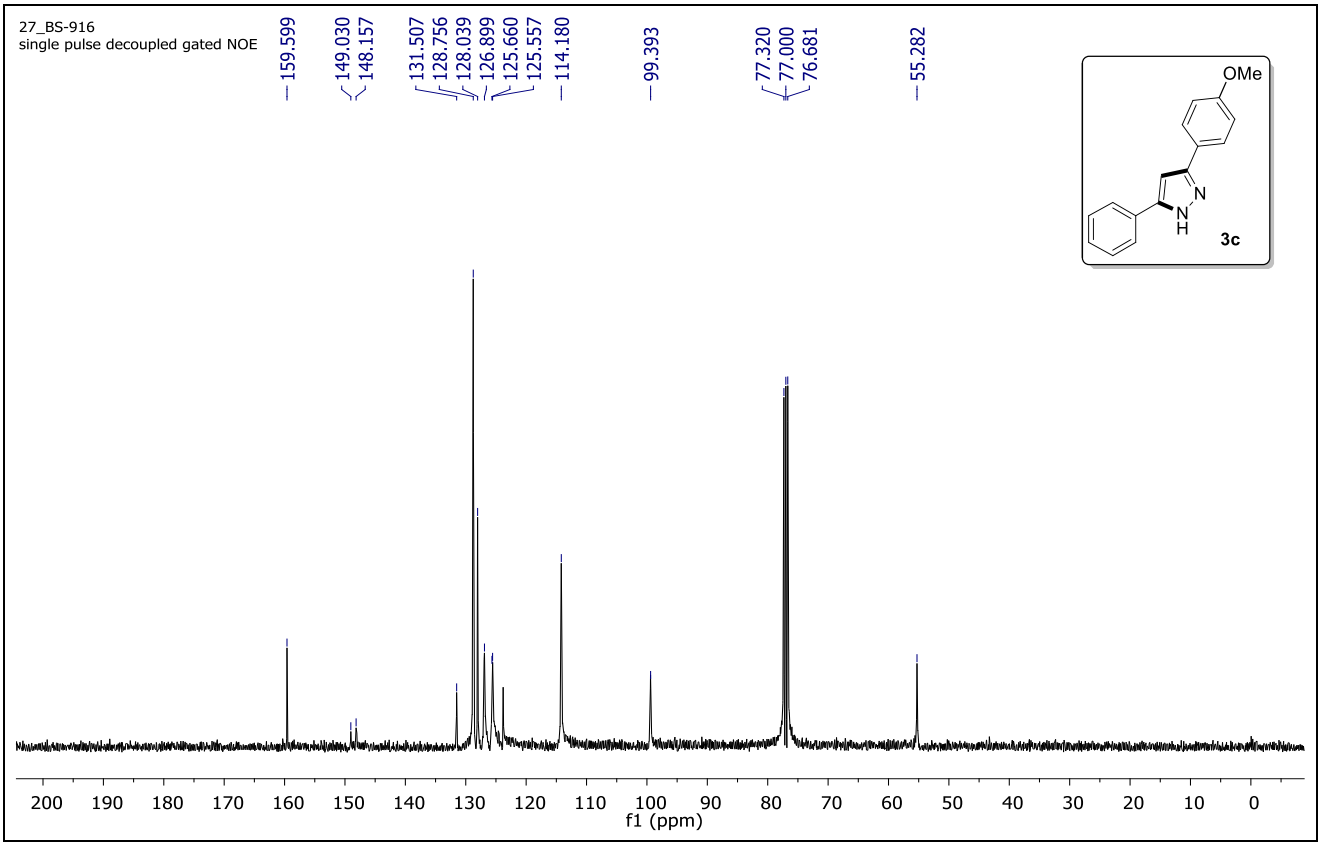
7.689
7.623
7.603
7.370
7.352
7.334
7.315
7.298
7.260
6.877
6.857
6.722
3.810
0.007
OMe
N
N
H
3c
2.23
2.22
3.29
2.15
1.00
3.02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149.030
148.157
131.507
128.756
128.039
126.899
125.660
125.557
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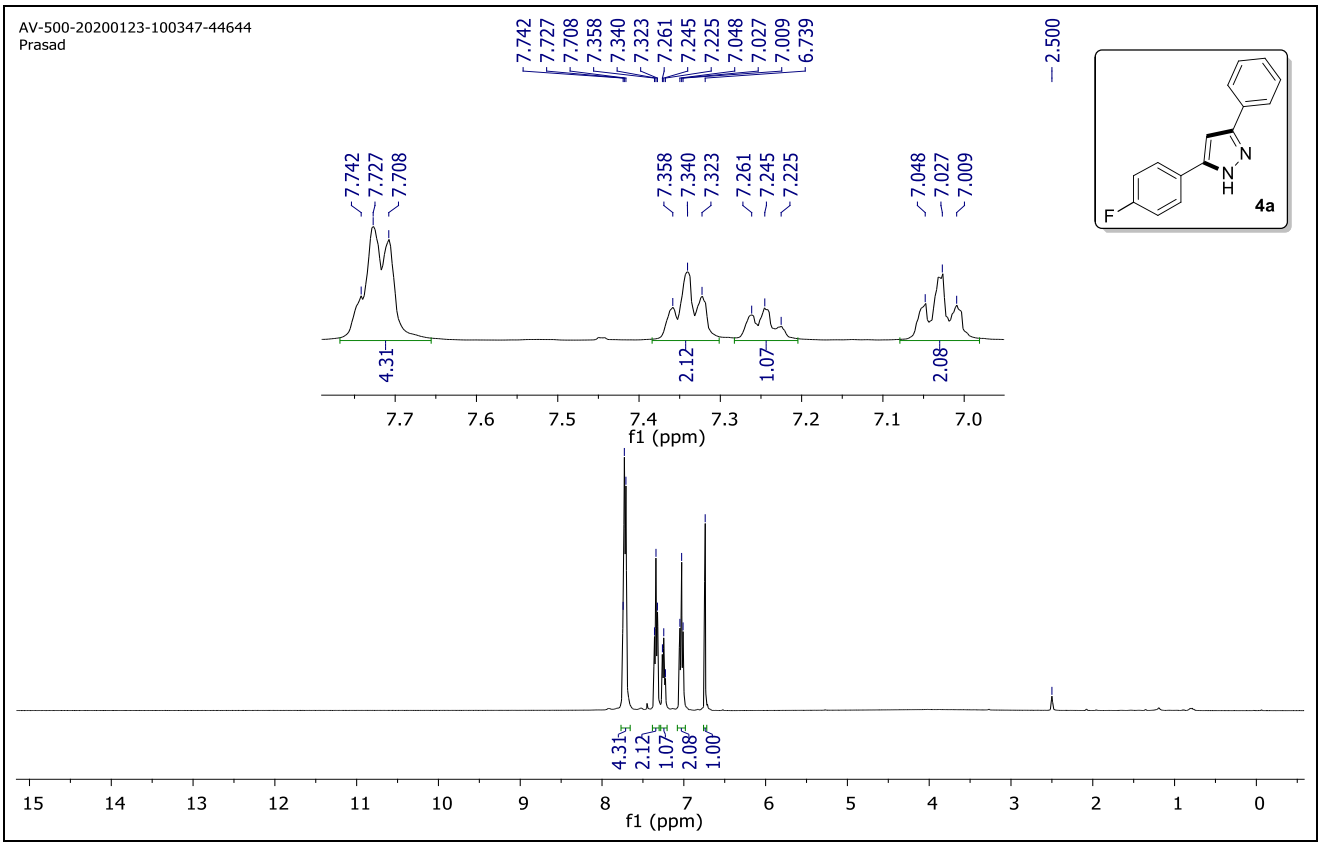
99.393
77.320
77.000
76.681
55.282
OMe
N
N
H
3c
f1 (ppm)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Prasad
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7.727
7.708
7.358
7.340
7.323
7.261
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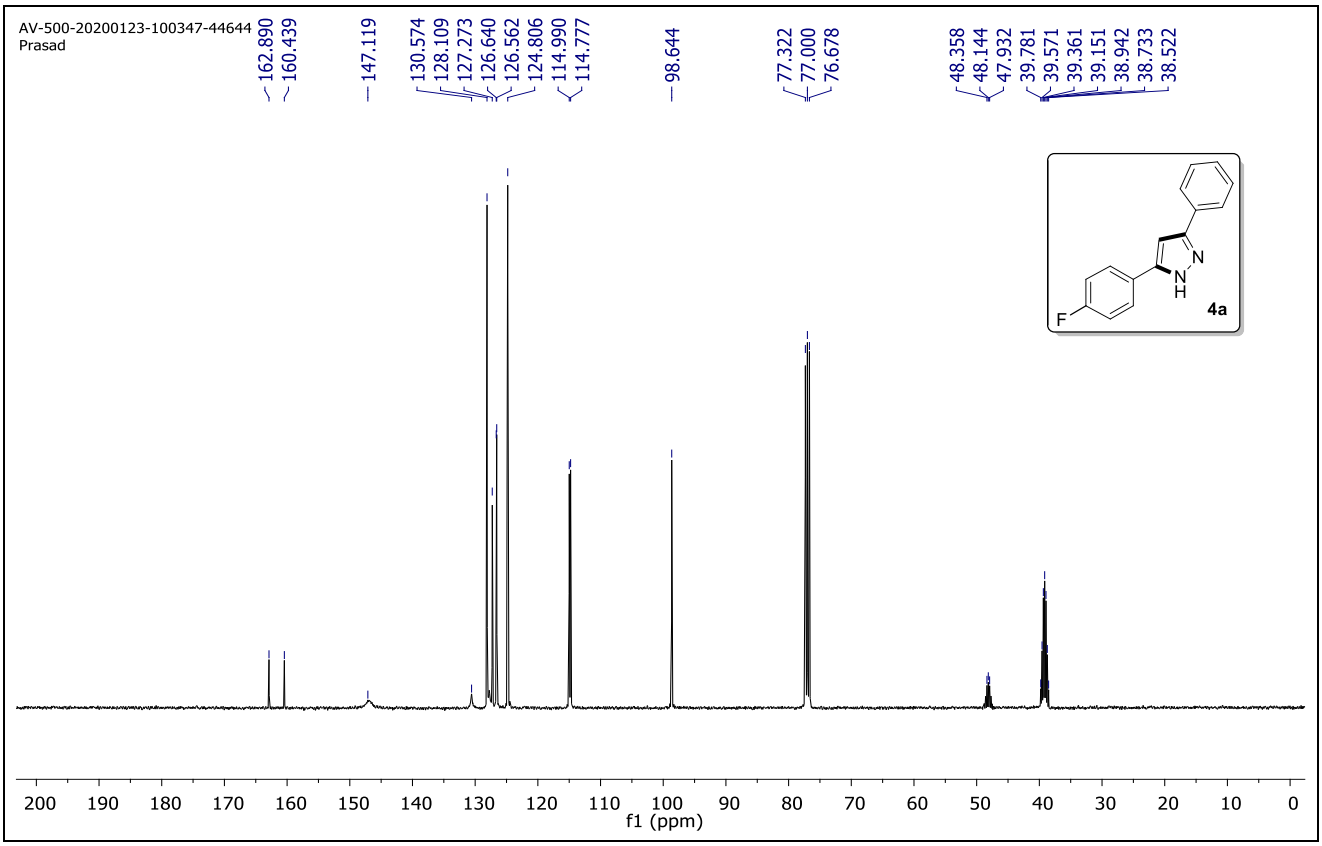
7.225
7.048
7.027
7.009
6.739
2.500
4.31
2.12
1.07
2.08
1.00
f1 (ppm)
4a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Prasad
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130.574
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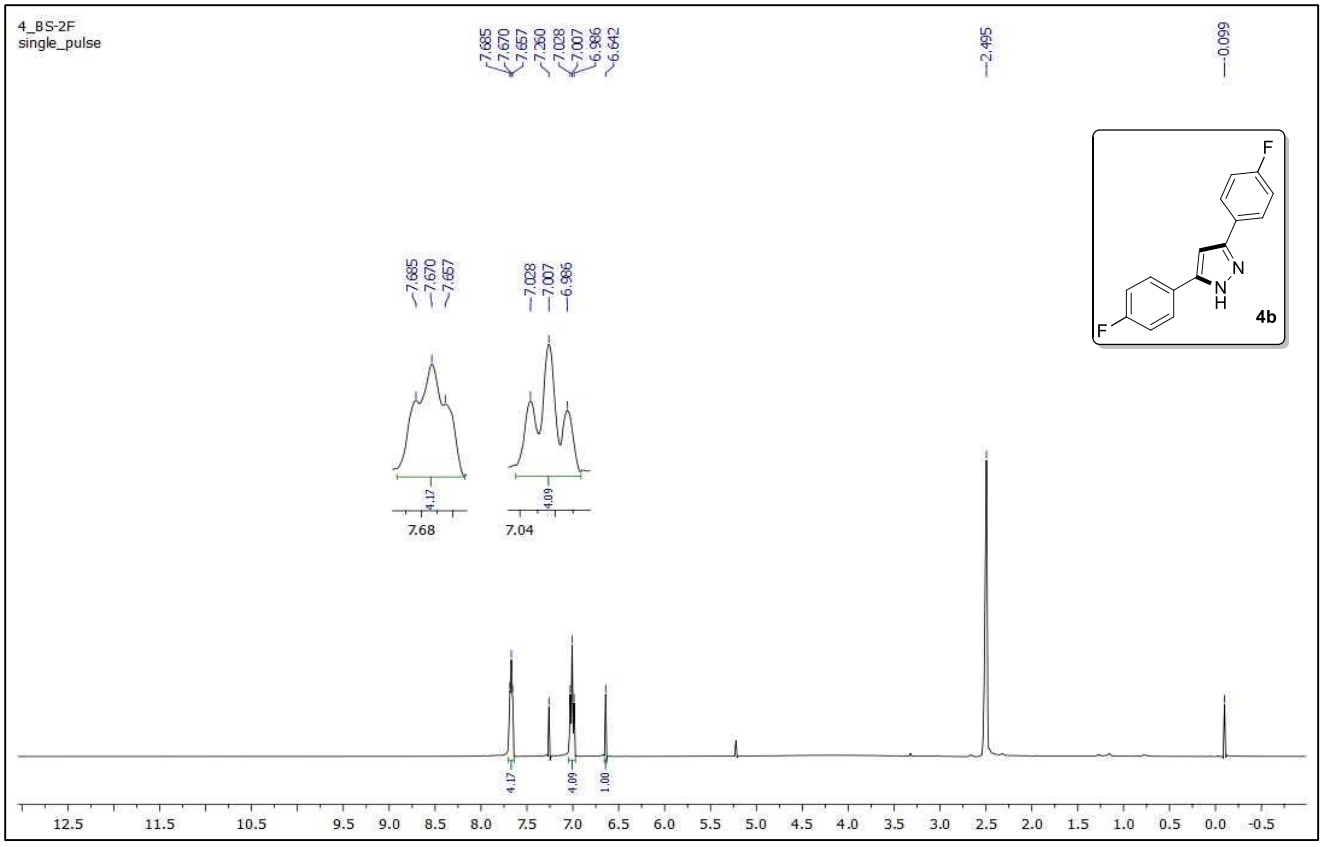
126.640
126.562
124.806
114.990
114.777
98.644
77.322
77.000
76.678
48.358
48.144
47.932
39.781
39.571
39.361
39.151
38.942
38.733
38.522
f1 (ppm)
4a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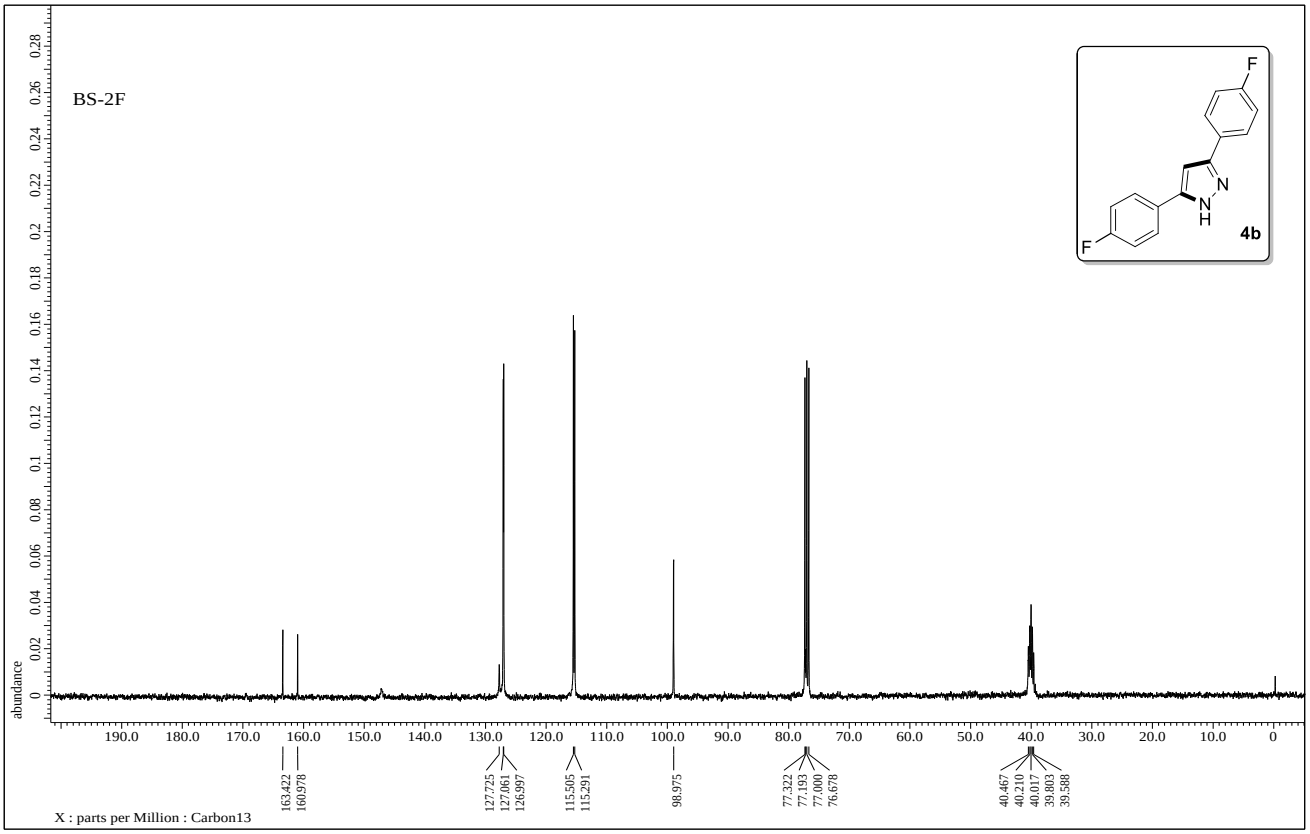
7.670
7.657
7.360
7.028
7.007
6.996
6.642
2.495
0.099
F
N
N
H
F
4b
7.685
7.670
7.657
7.028
7.007
6.996
4.17
4.09
7.68
7.04
4.17
4.09
1.00
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


BS-2F
F
N
N
H
F
4b
abundance
0.28
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
163.422
160.978
127.725
127.061
126.997
115.505
115.291
98.975
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77.193
77.000
76.678
40.467
40.210
40.017
39.803
39.588
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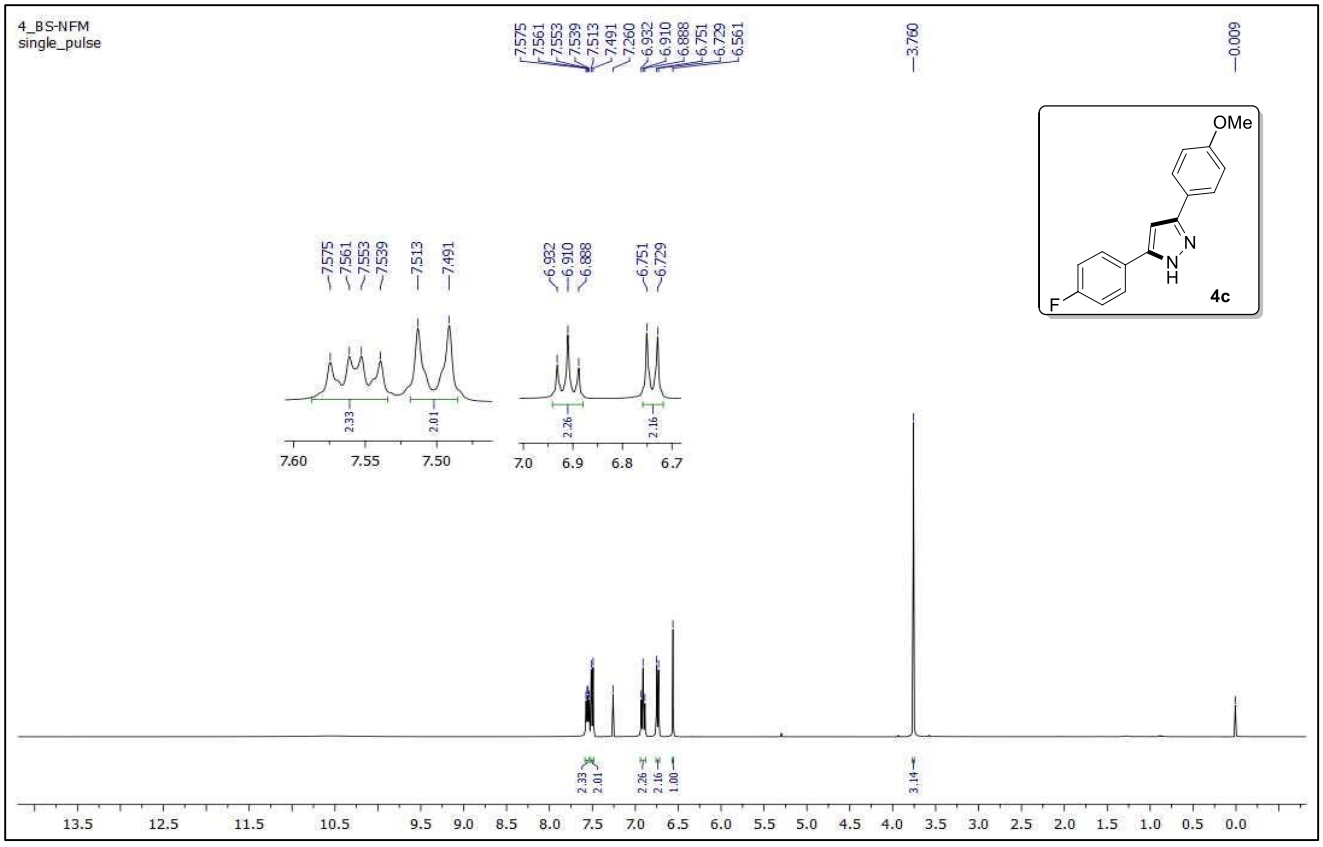
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7.575
7.561
7.553
7.539
7.513
7.491
7.260
6.932
6.910
6.888
6.751
6.729
6.561
3.760
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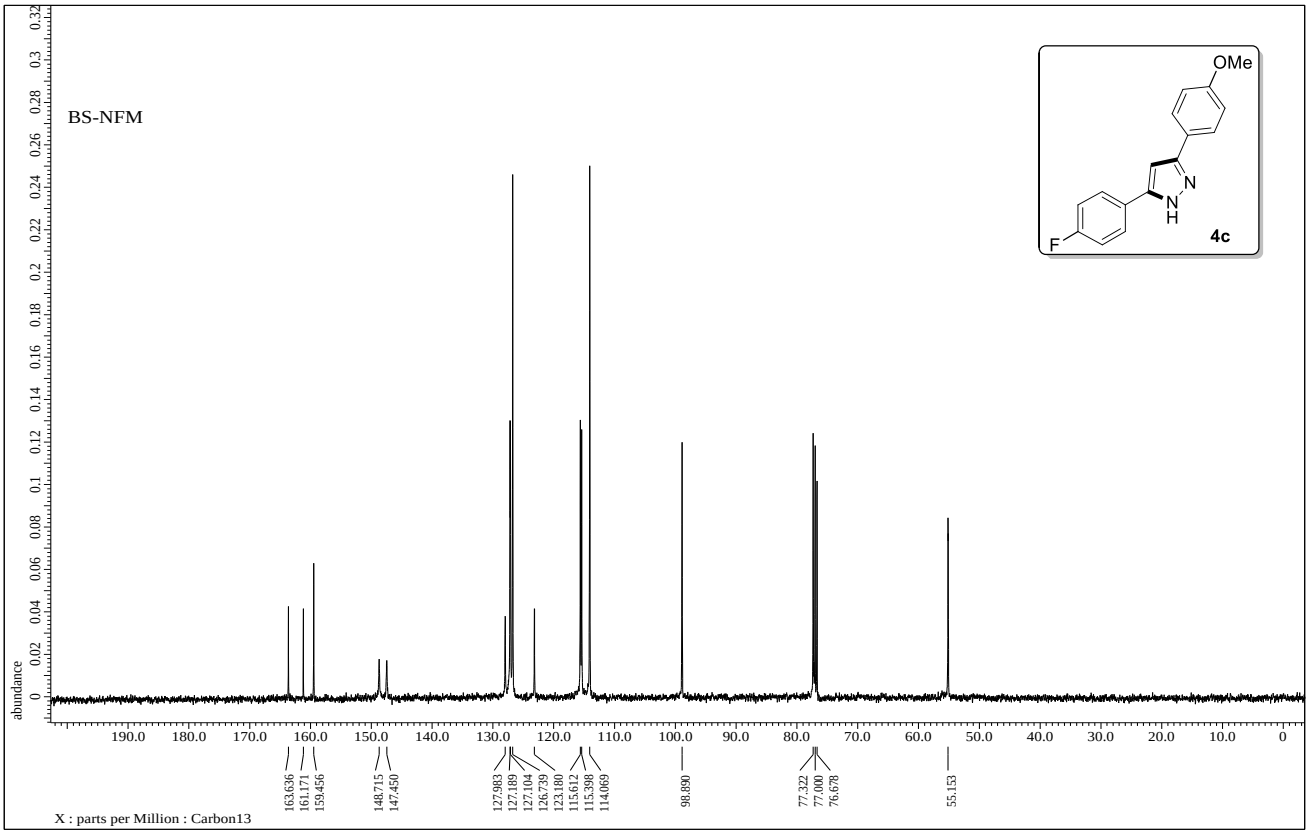
OMe
N
N
H
F
4c
2.33
2.01
2.26
2.16
1.00
3.14


BS-NFM
OMe
N
N
H
F
4c
abundance
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127.189
127.104
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77.000
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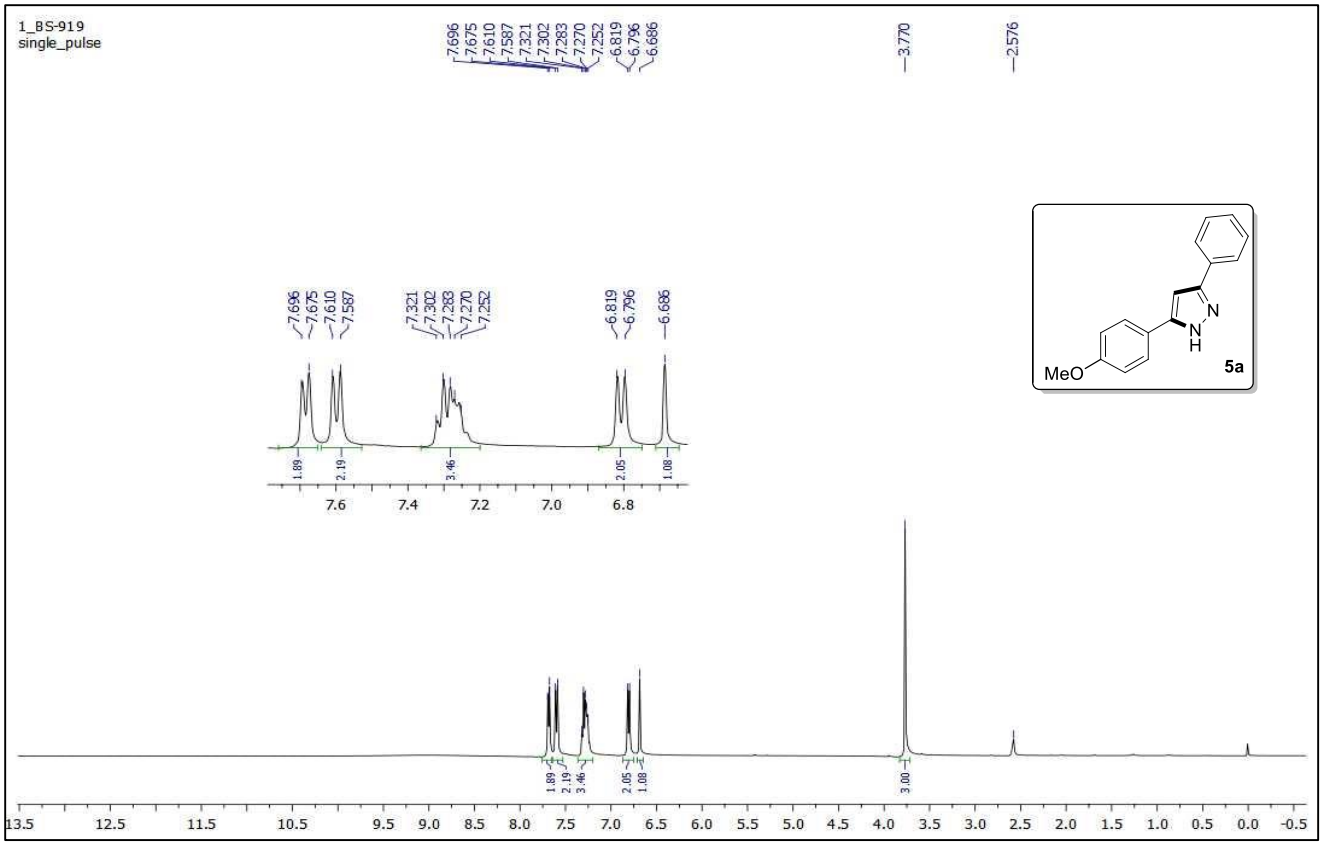
X : parts per Million : Carbon13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7.675
7.610
7.587
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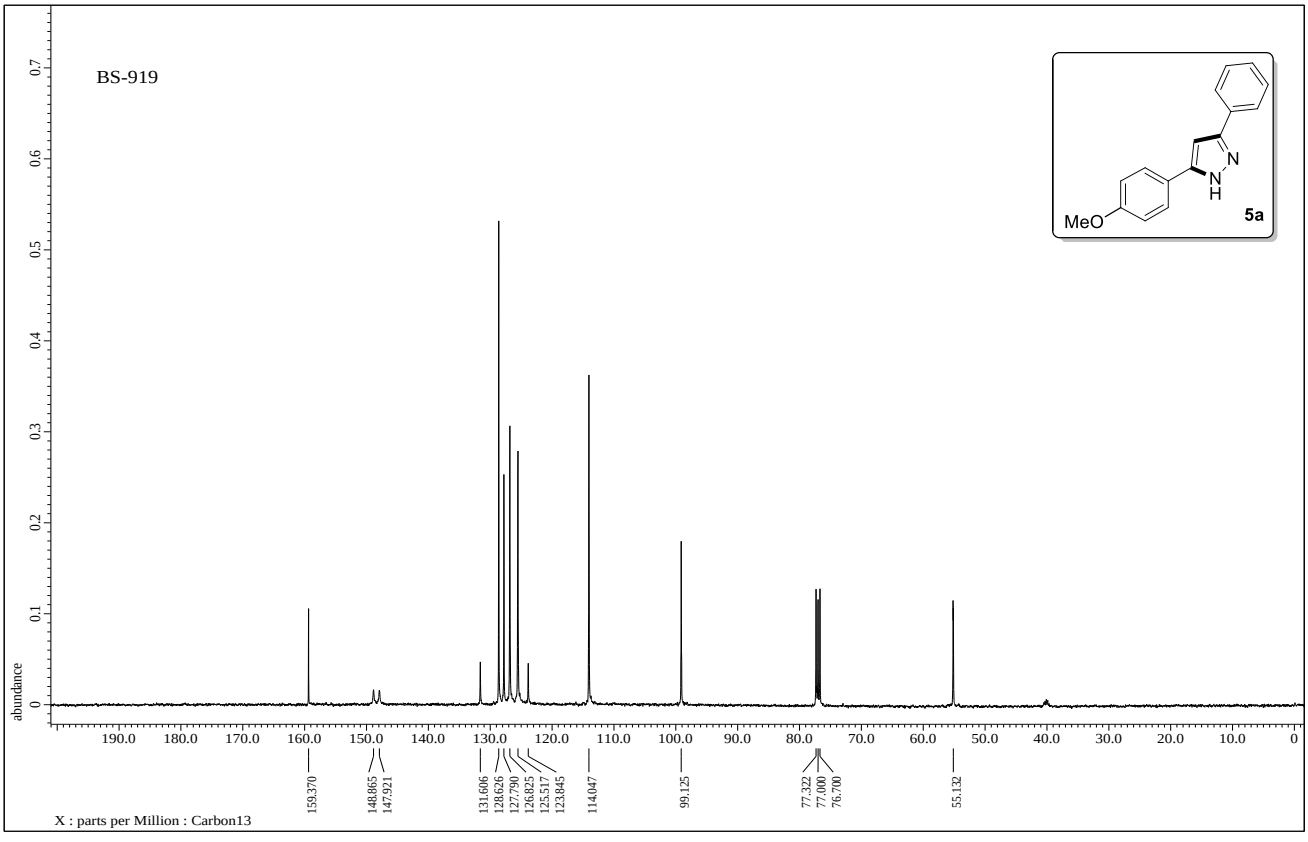
7.270
7.252
6.819
6.796
6.686
3.770
2.576
MeO
5a


BS-919
MeO
5a
abundance
159.370
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147.921
131.606
128.626
127.790
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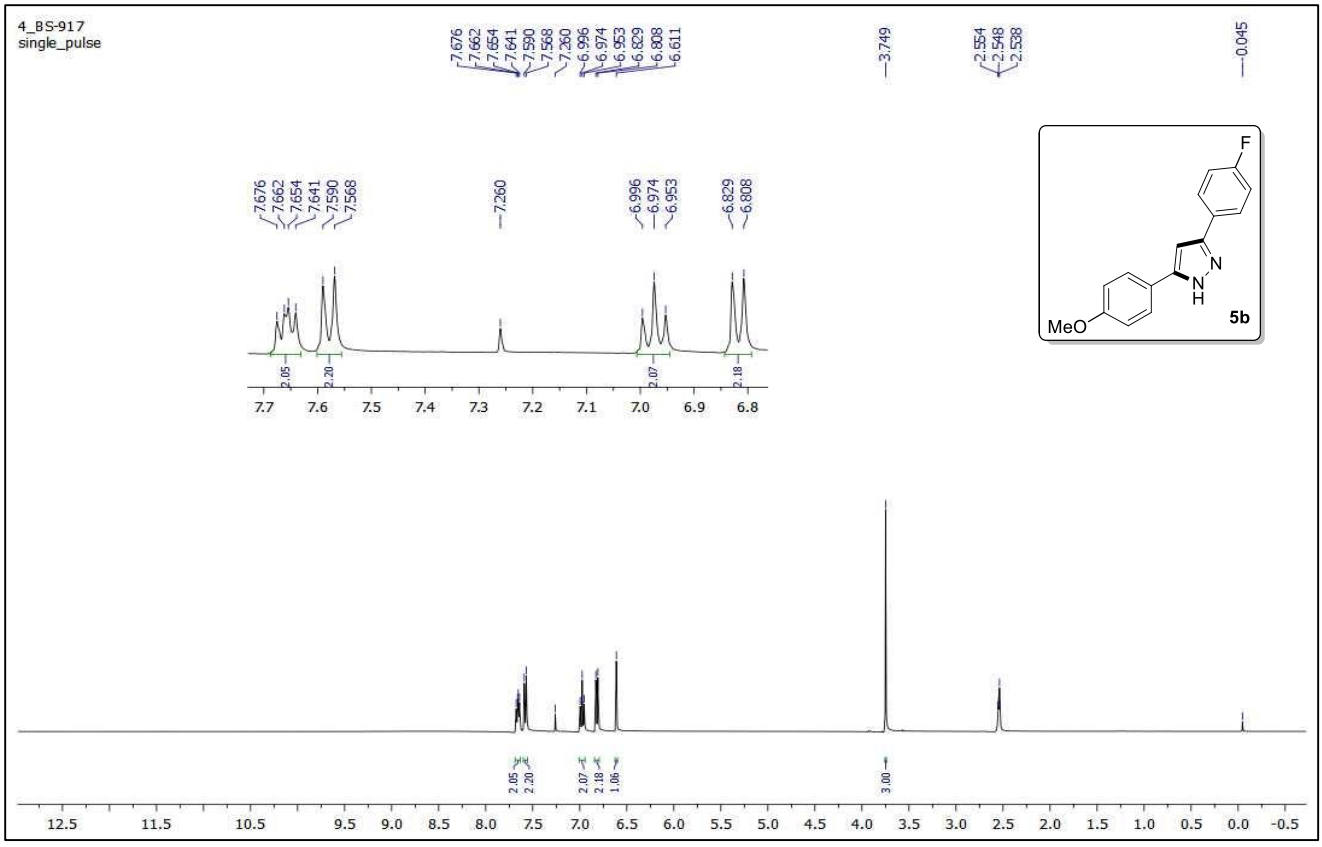
123.845
114.047
99.125
77.322
77.000
76.700
55.132
X : parts per Million : Carbon13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7.662
7.654
7.641
7.590
7.568
7.260
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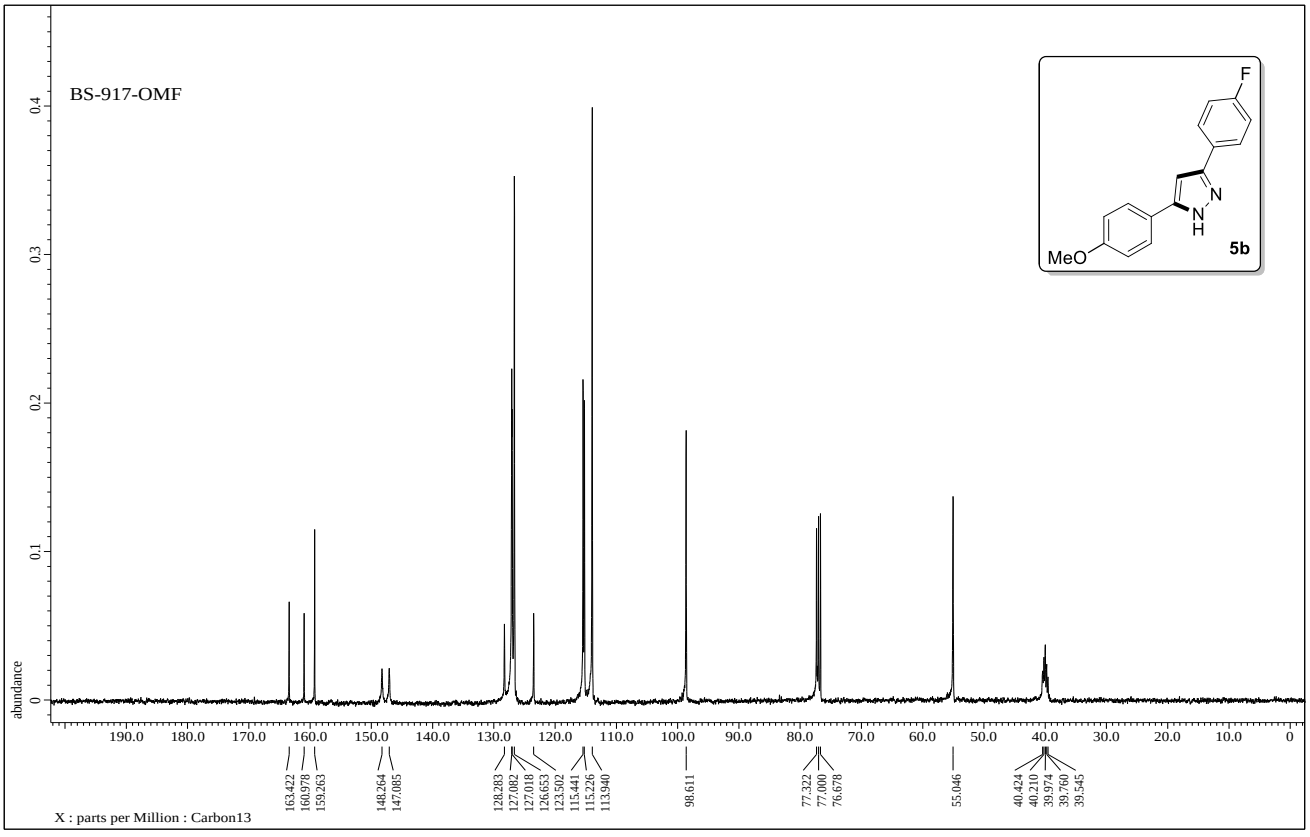
6.974
6.953
6.829
6.808
6.611
3.749
2.554
2.548
2.538
0.045
F
N
N
H
MeO
5b


BS-917-OMF
F
N
N
H
MeO
5b
abundance
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148.264
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128.283
127.082
127.018
126.653
123.502
115.441
115.226
113.940
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40.210
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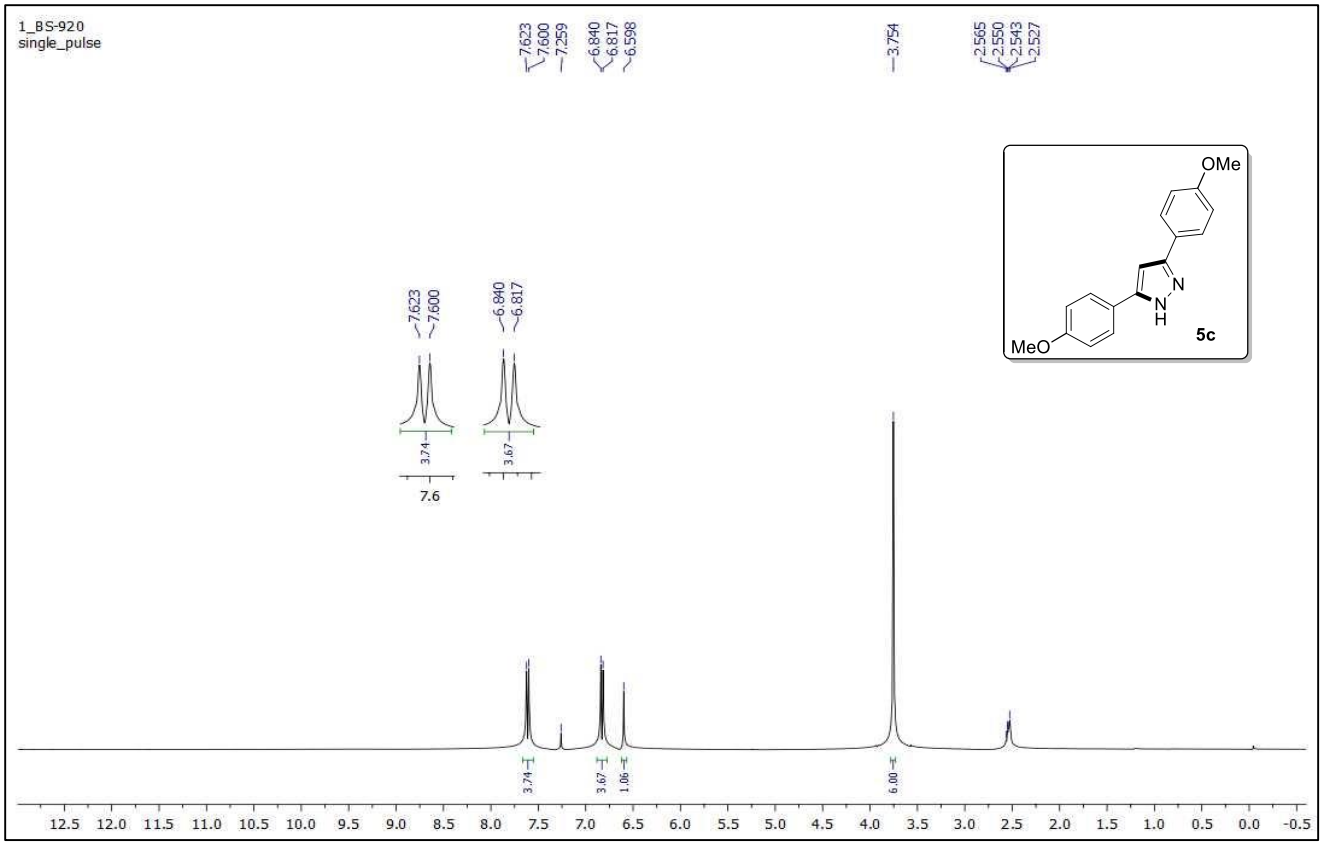
X : parts per Million : Carbon13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7.600
7.259
6.840
6.817
6.598
3.754
2.565
2.550
2.543
2.527
OMe
MeO
5c
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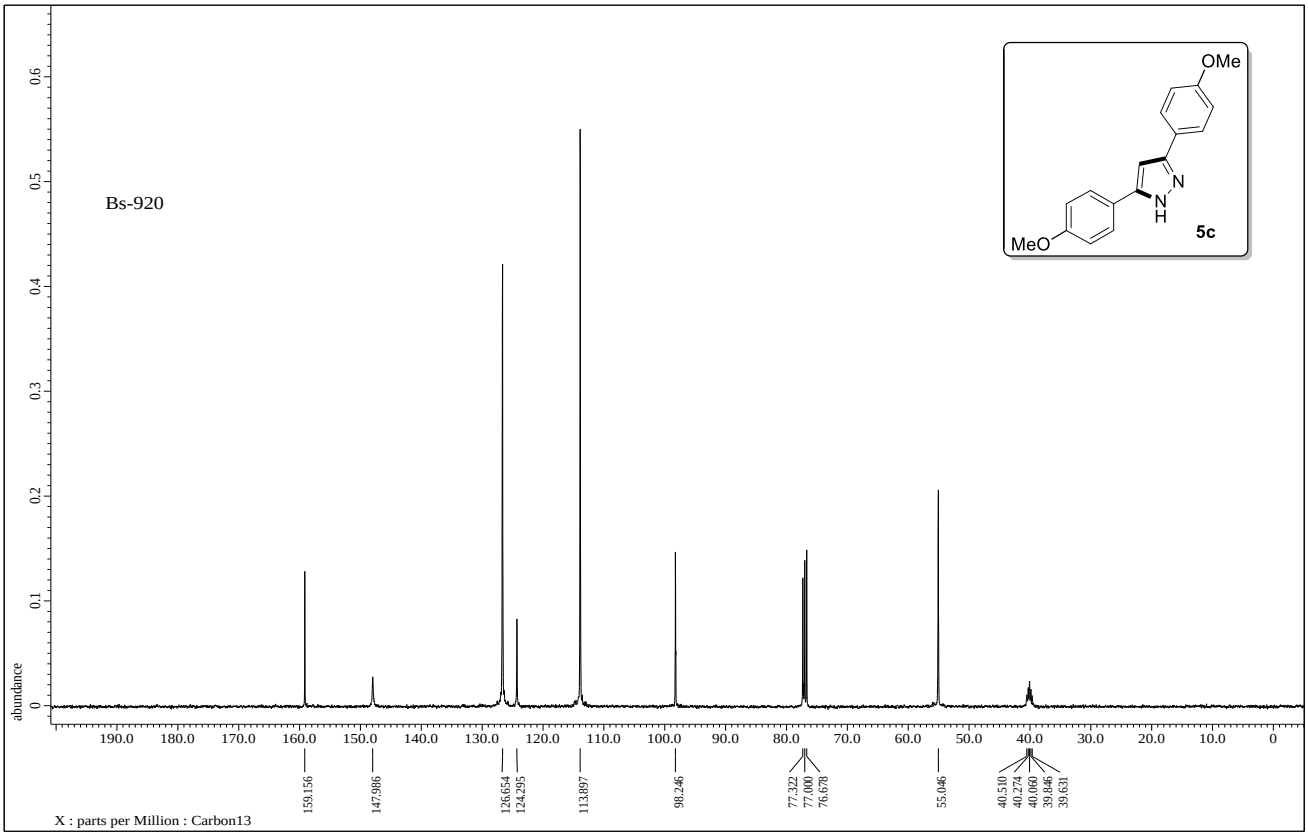
3.67
7.6
3.74
3.67
1.06
6.00


Bs-920
OMe
MeO
5c
abundance
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124.295
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76.678
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40.060
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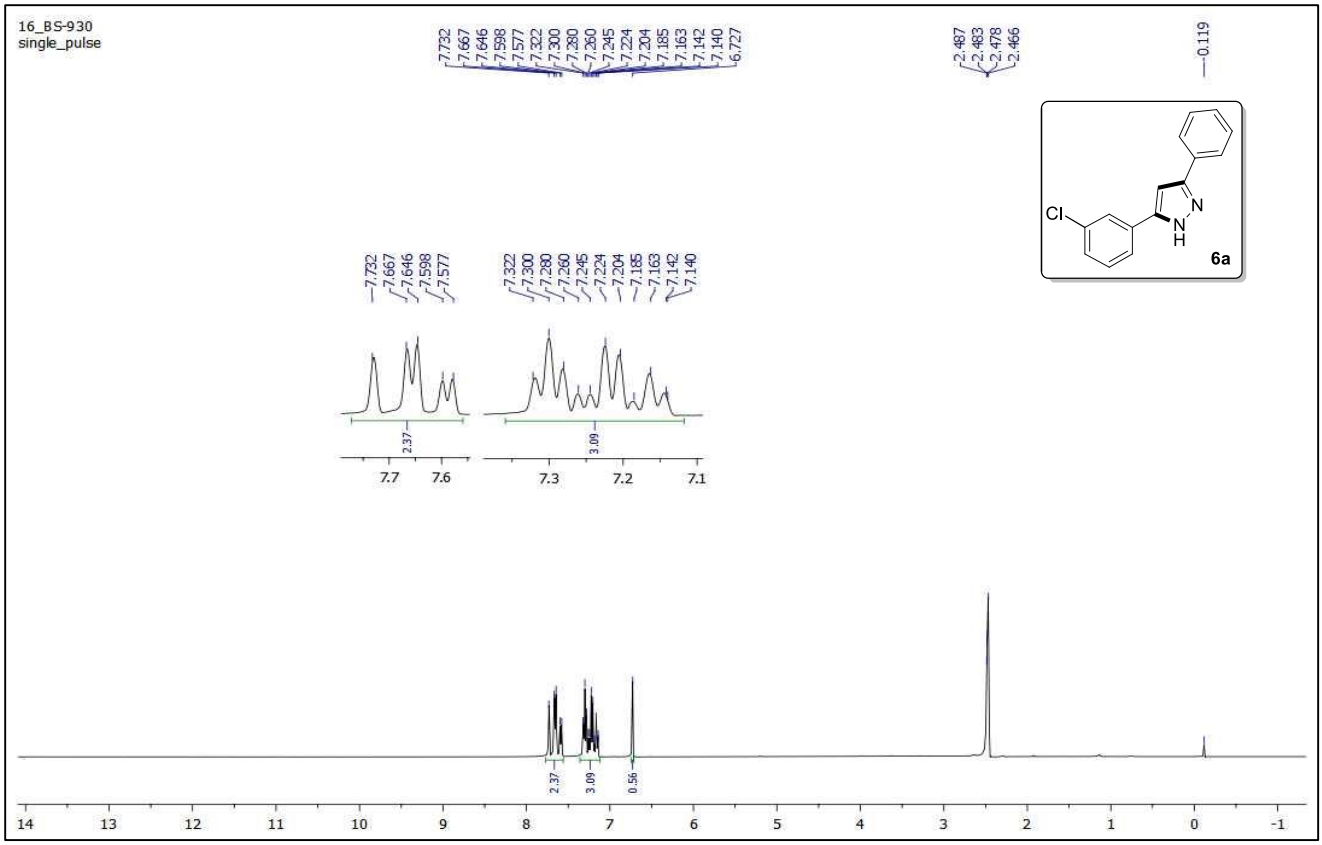
39.631
X : parts per Million : Carbon13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7.646
7.598
7.577
7.322
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7.280
7.260
7.245
7.224
7.204
7.185
7.163
7.142
7.140
6.727
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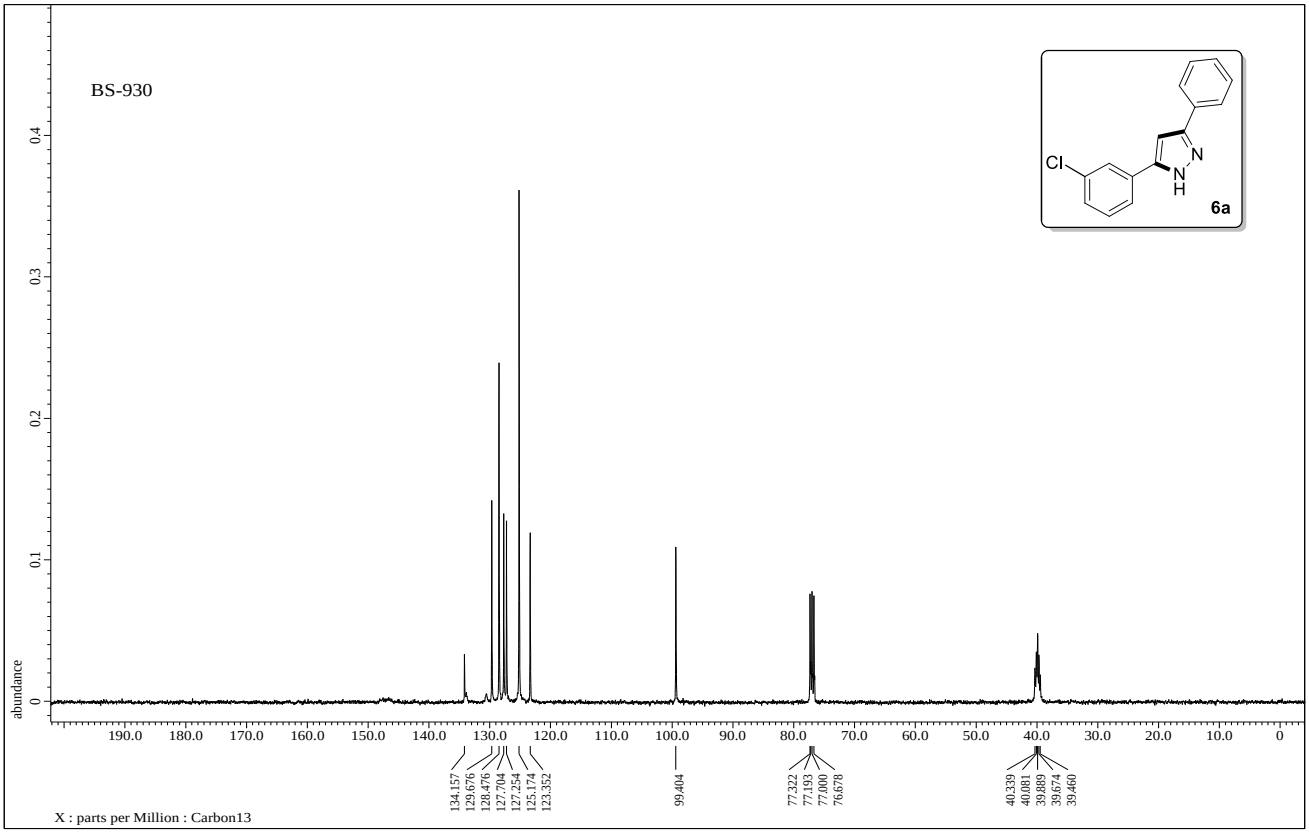
2.478
2.466
0.119
Cl
N
N
H
6a
2.37
3.09
0.56


BS-930
Cl
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N
H
6a
abundance
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127.254
125.174
123.352
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77.000
76.678
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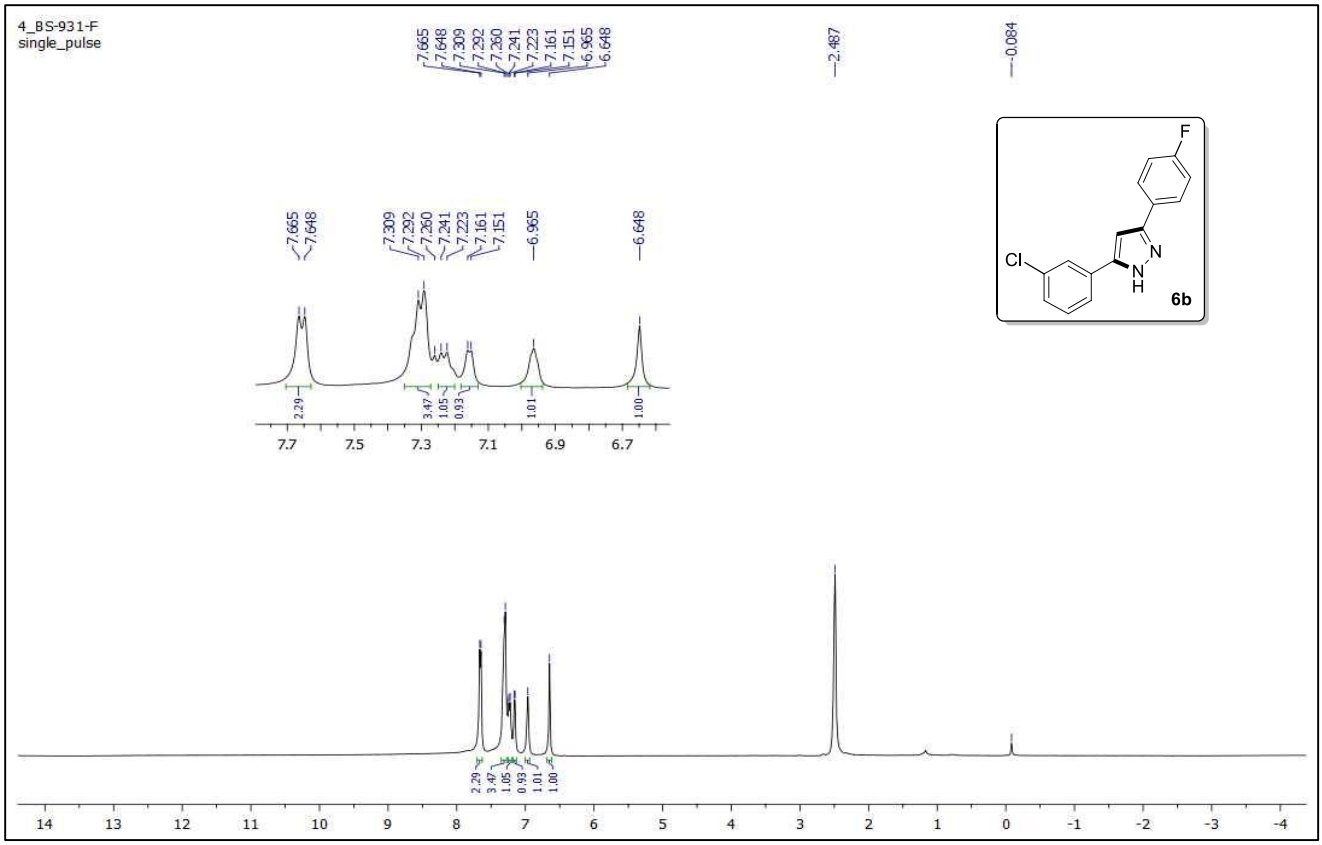
X : parts per Million : Carbon13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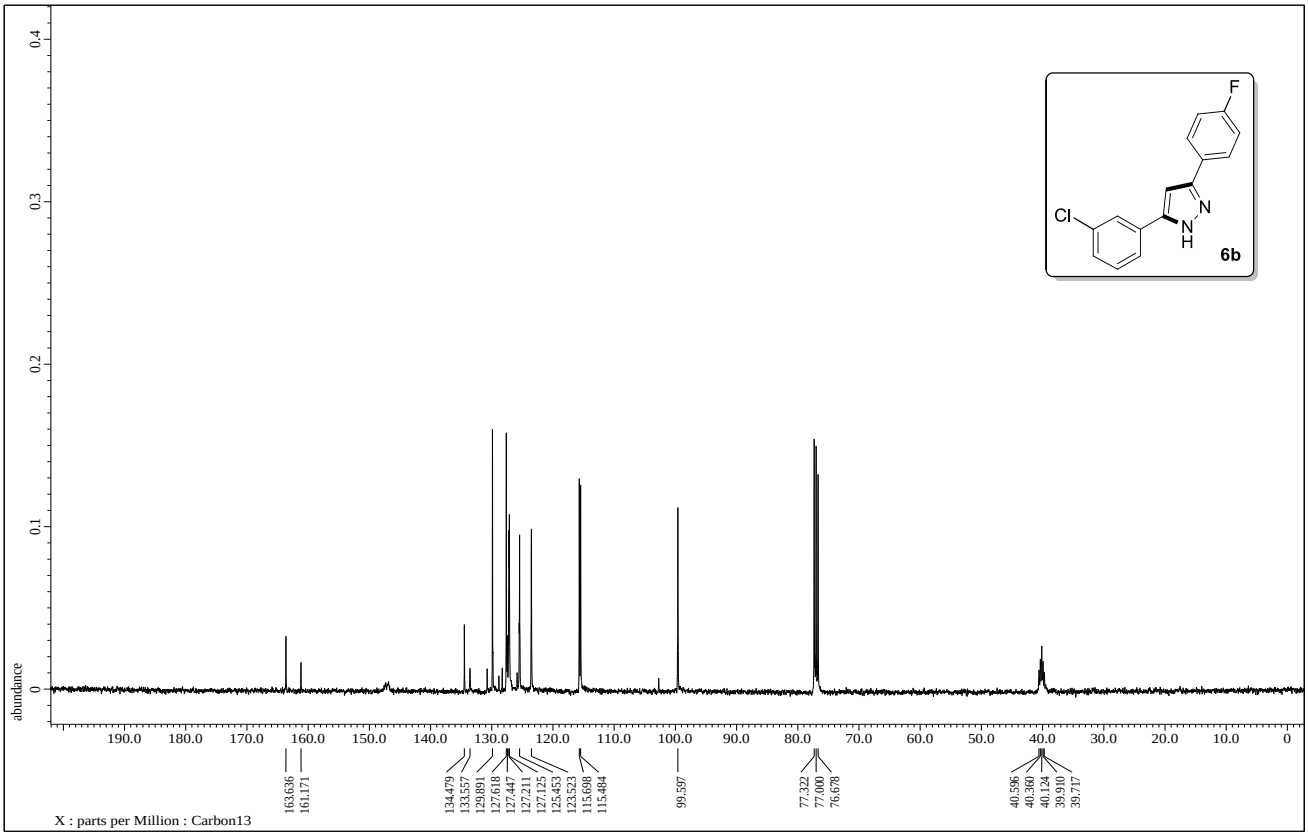
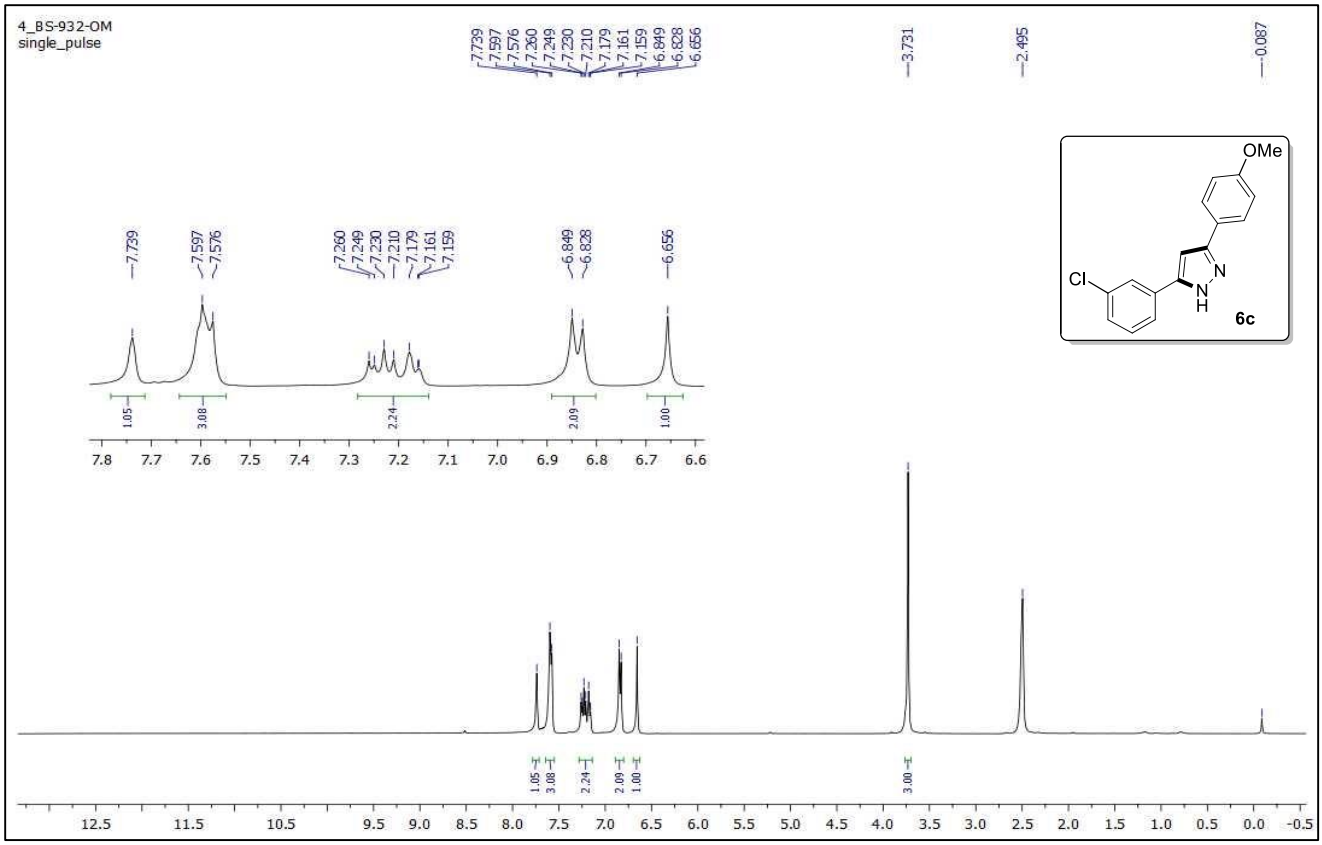
0.084
F
Cl
N
N
H
6b


F
Cl
N
N
H
6b
abundance
X : parts per Million : Carbon13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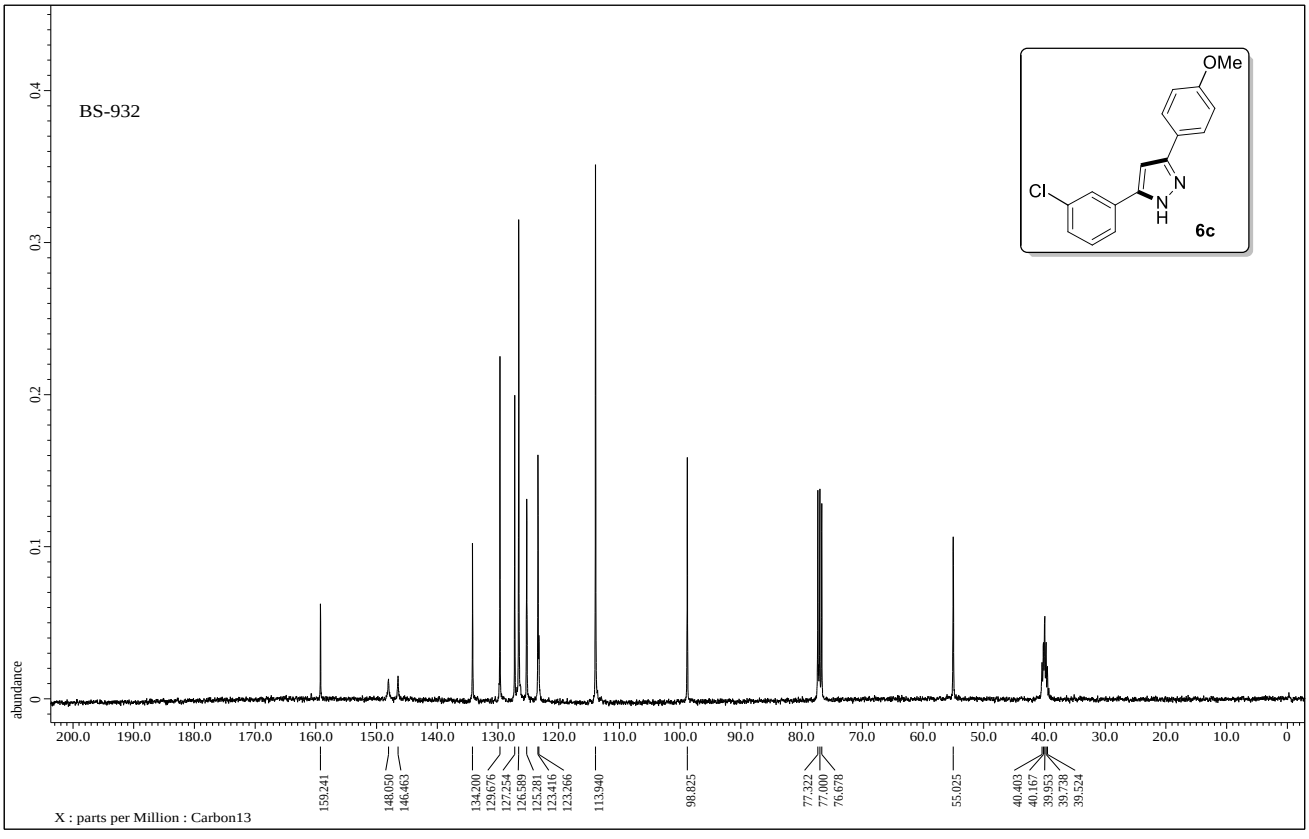
7.739
7.597
7.576
7.260
7.249
7.230
7.210
7.179
7.161
7.159
6.849
6.828
6.656
3.731
2.495
0.087
OMe
Cl
N
N
H
6c


BS-932
OMe
Cl
N
N
H
6c
abundance
159.241
148.050
146.463
134.200
129.676
127.254
126.589
125.281
123.416
123.266
113.940
98.825
77.322
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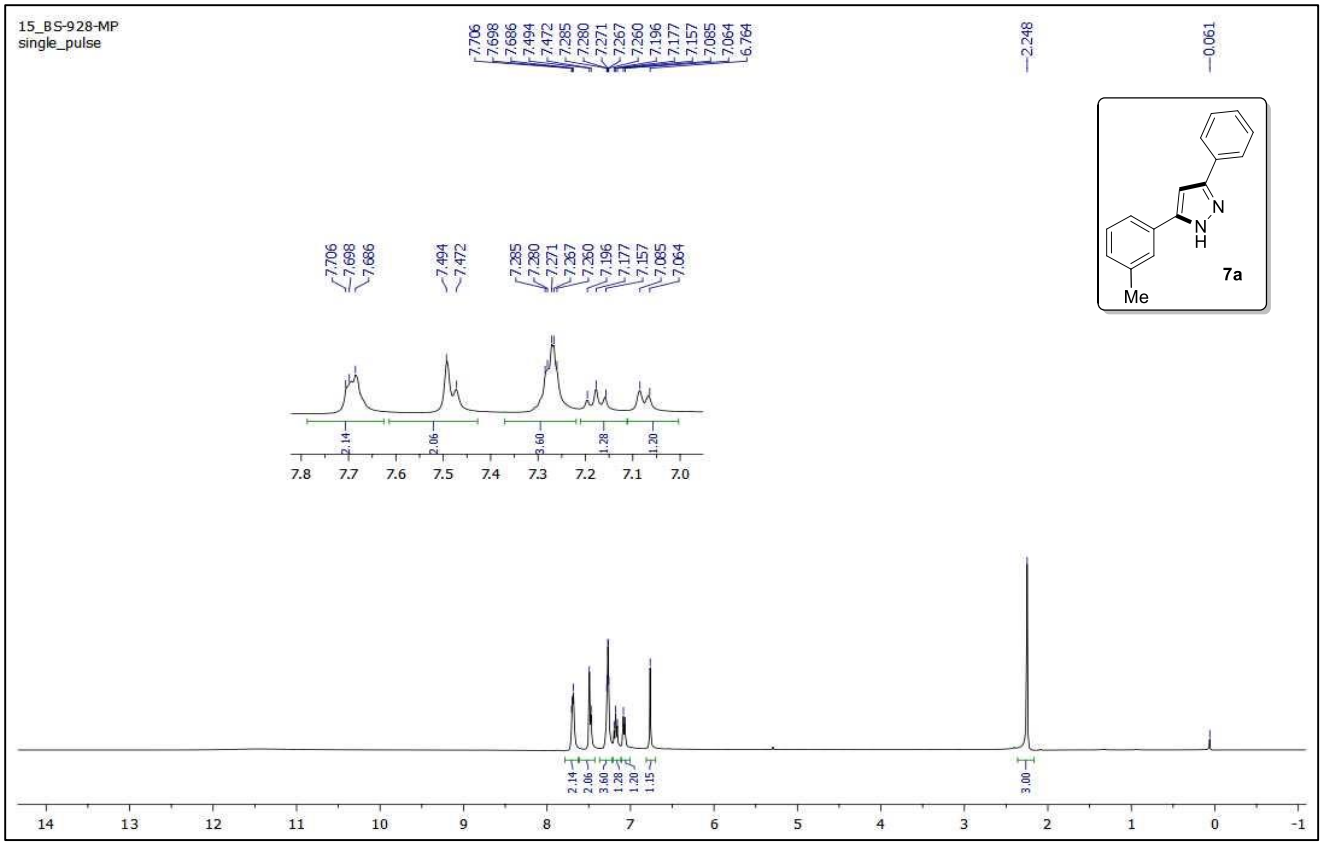
40.403
40.167
39.953
39.738
39.524
X : parts per Million : Carbon13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7.686
7.494
7.472
7.285
7.280
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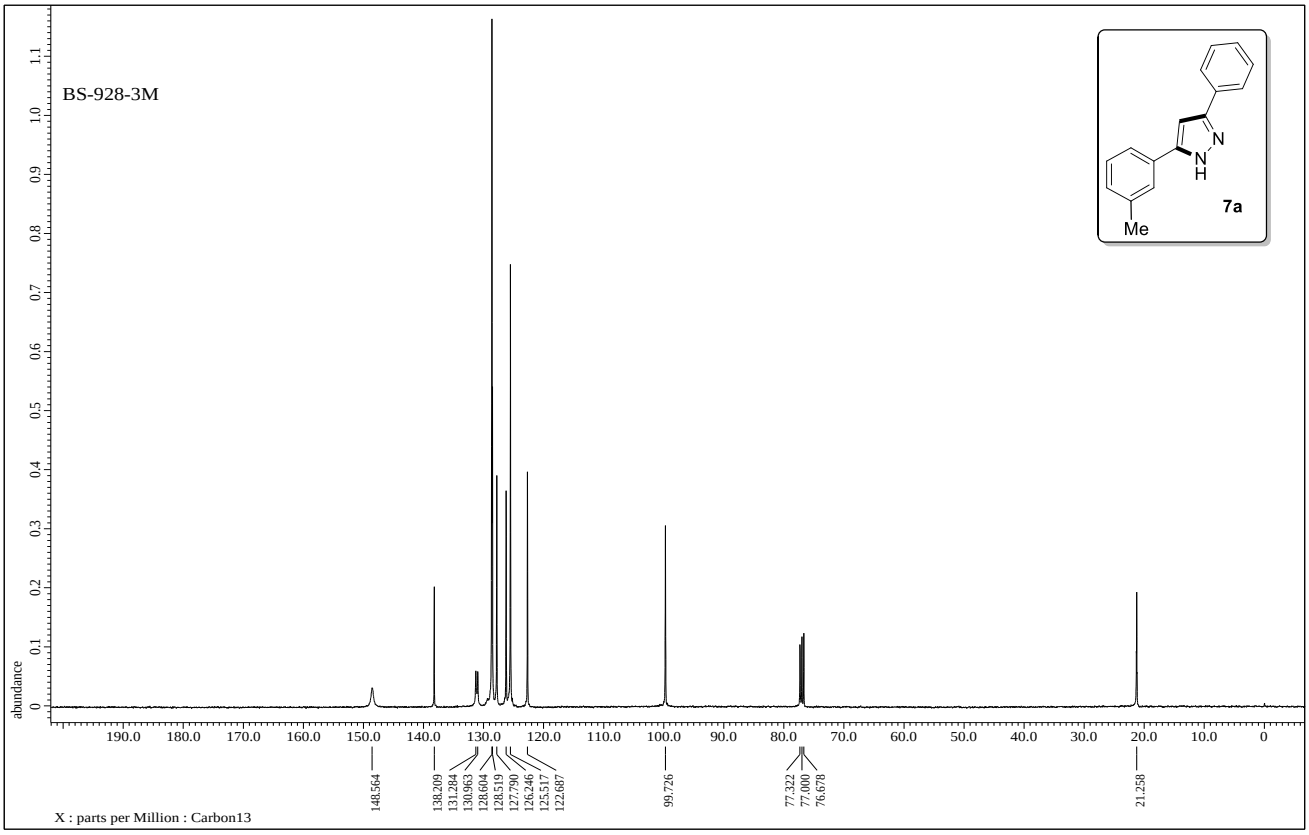
7.177
7.157
7.085
7.064
6.764
2.248
0.061
Me
7a


BS-928-3M
Me
7a
abundance
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130.963
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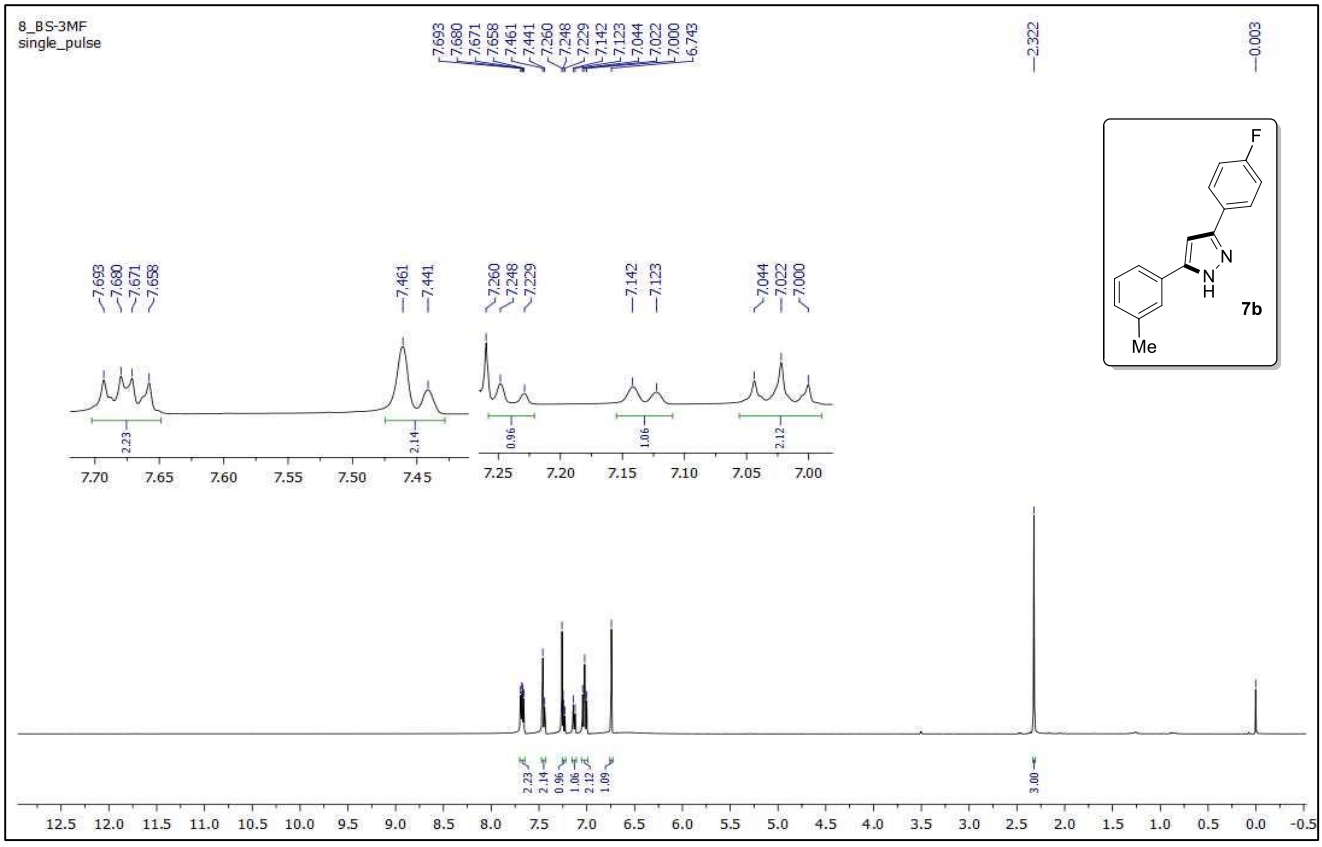
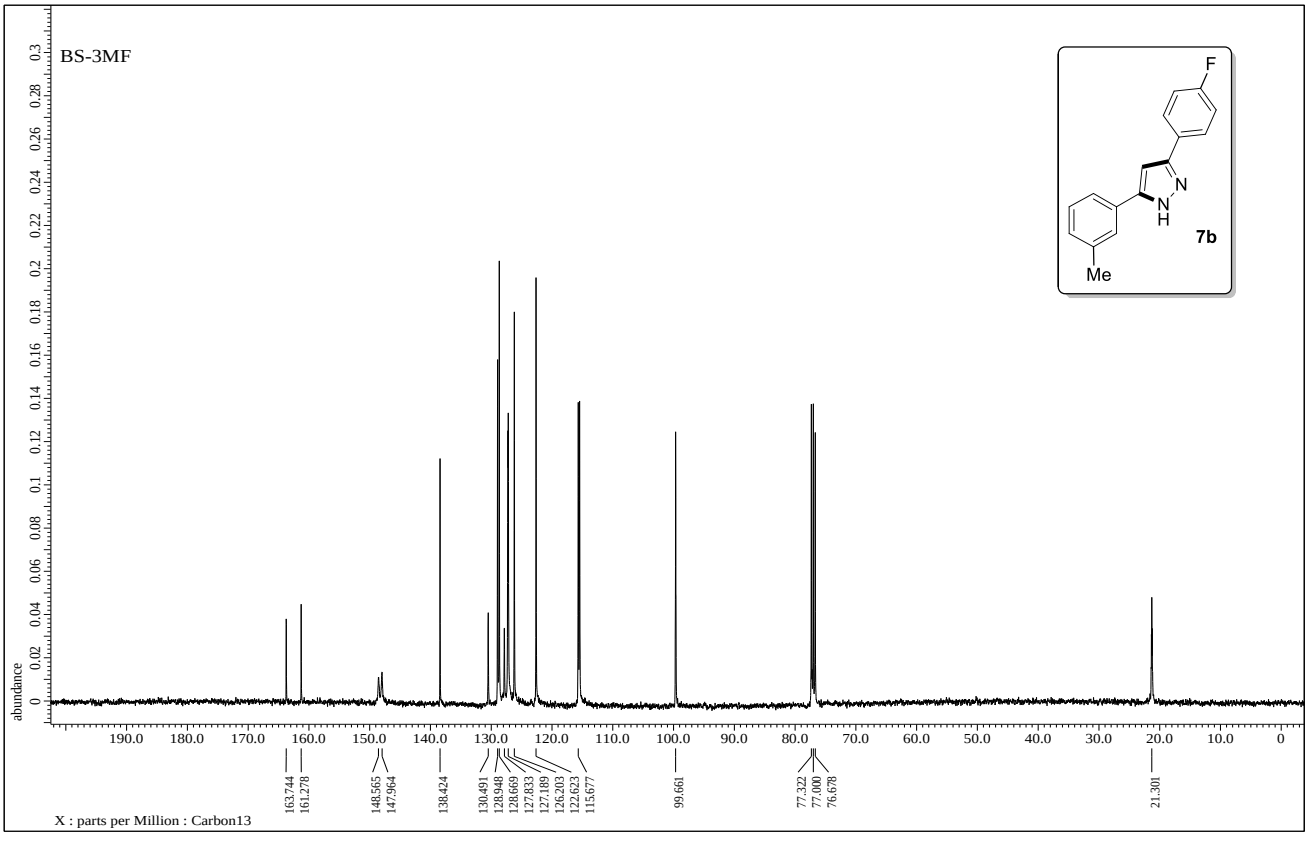
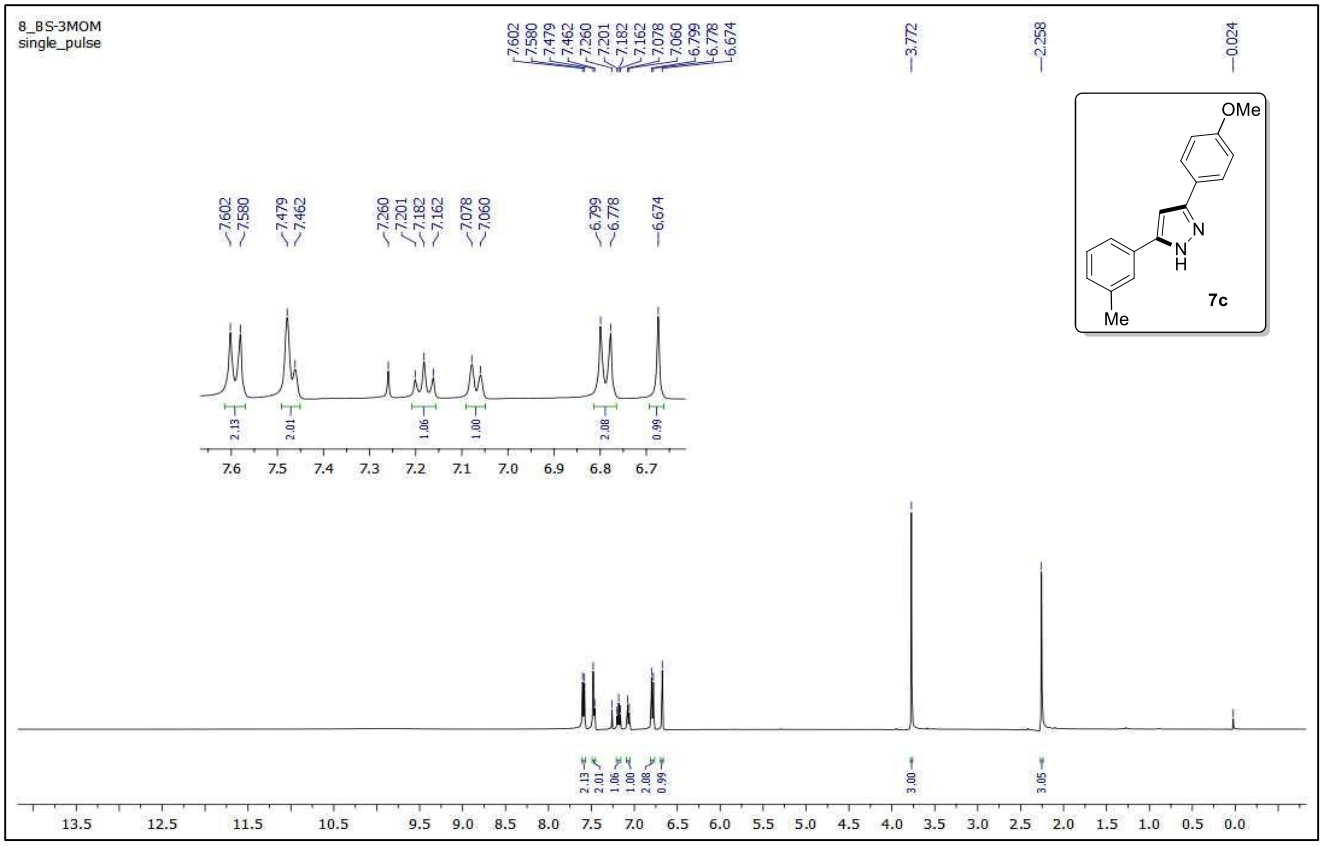
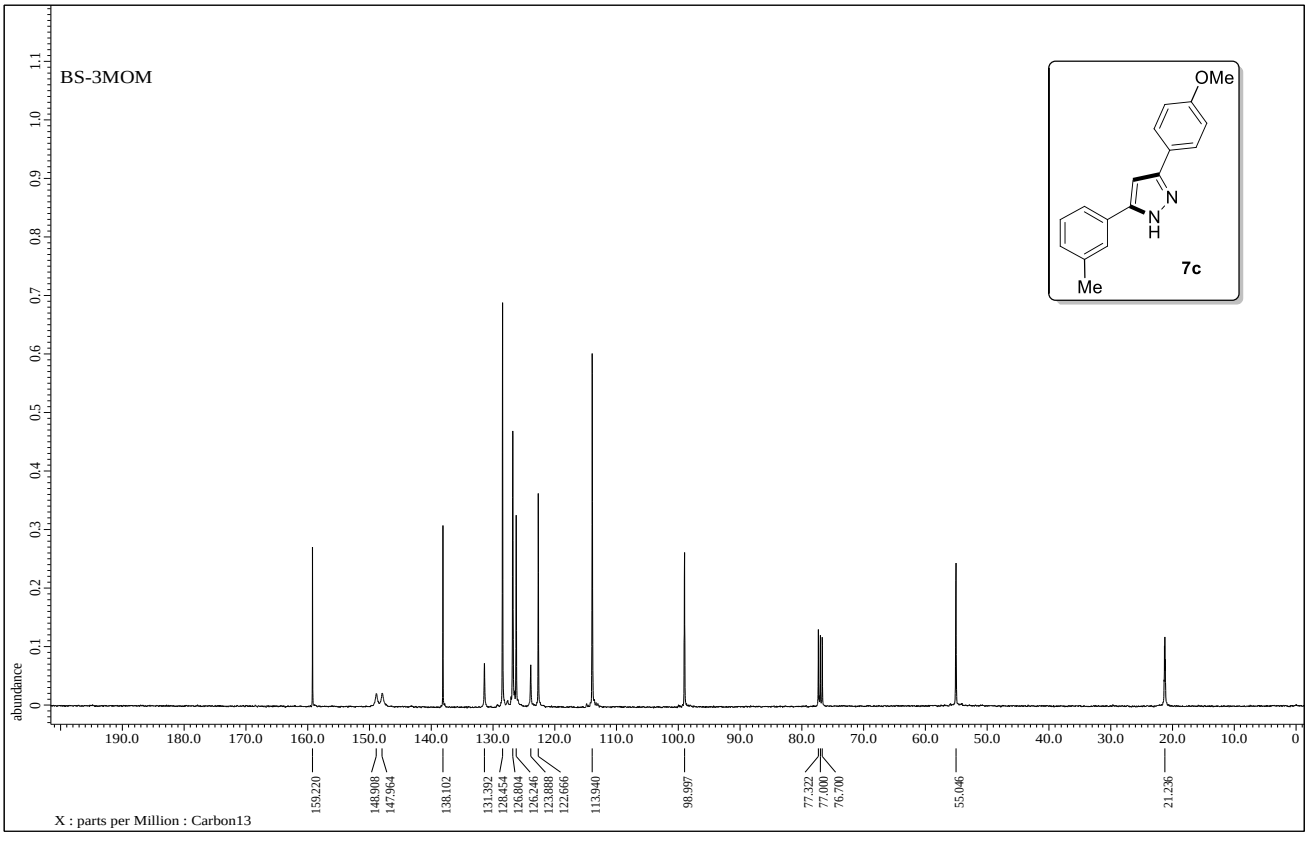
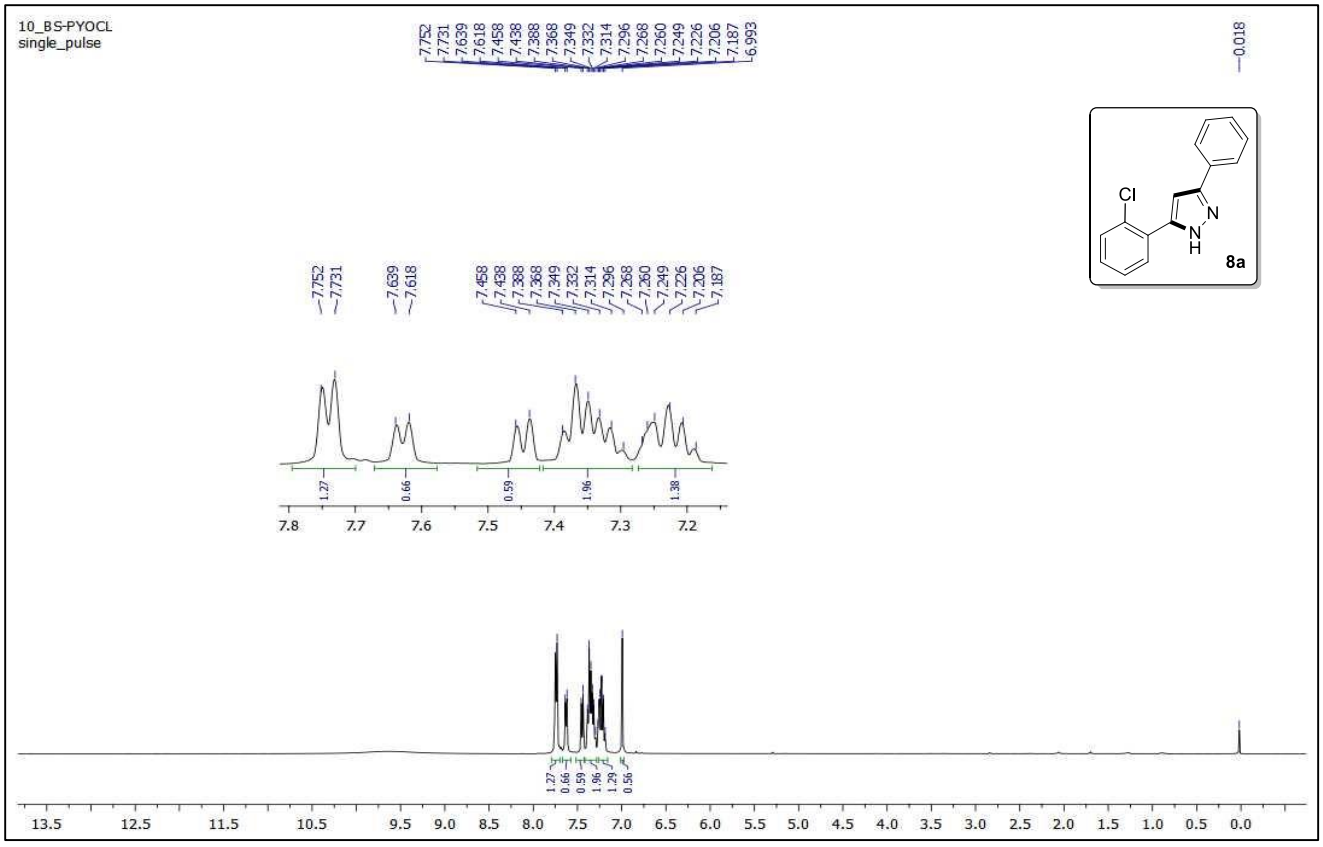
126.246
125.517
122.687
99.726
77.322
77.000
76.678
21.258
X : parts per Million : Carbon13

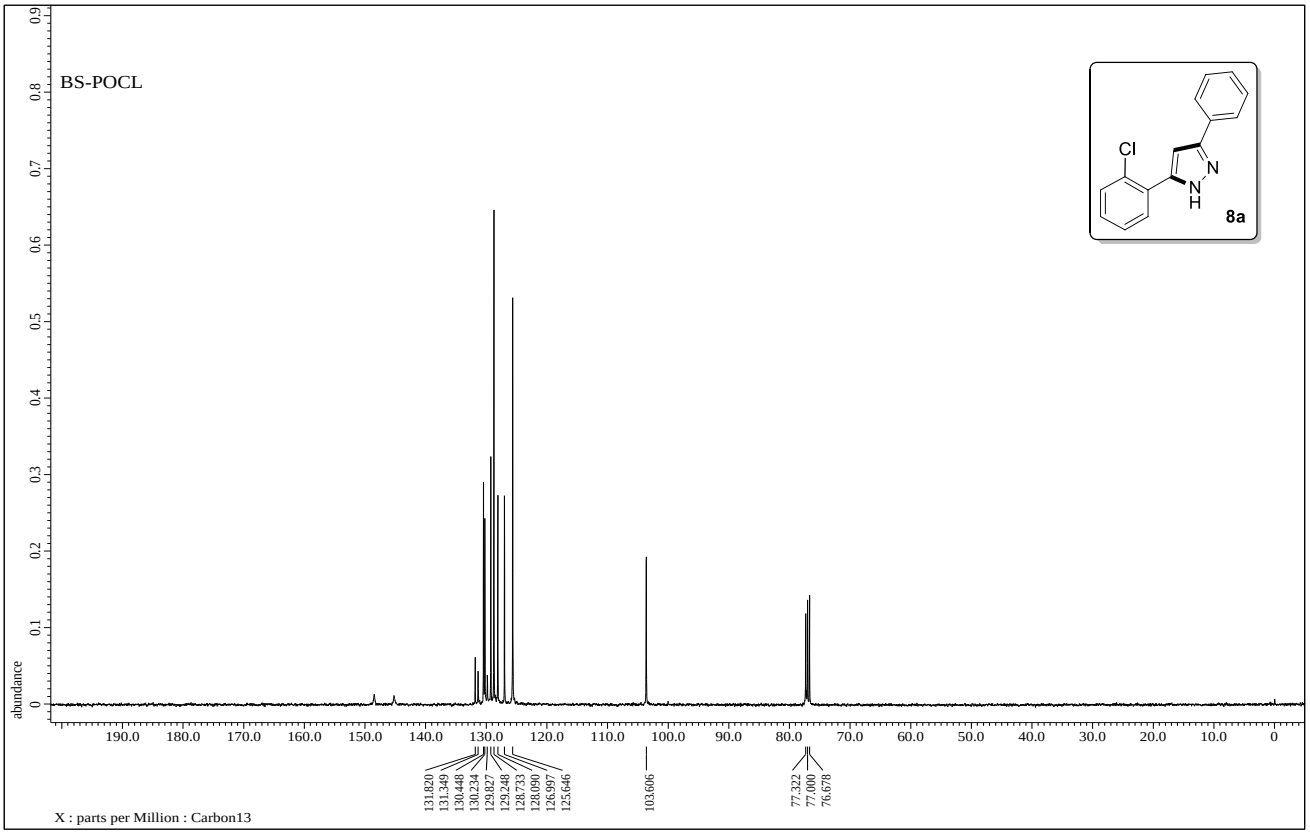

8_BS-3MF
single_pulse
7b
Me
F
N
H

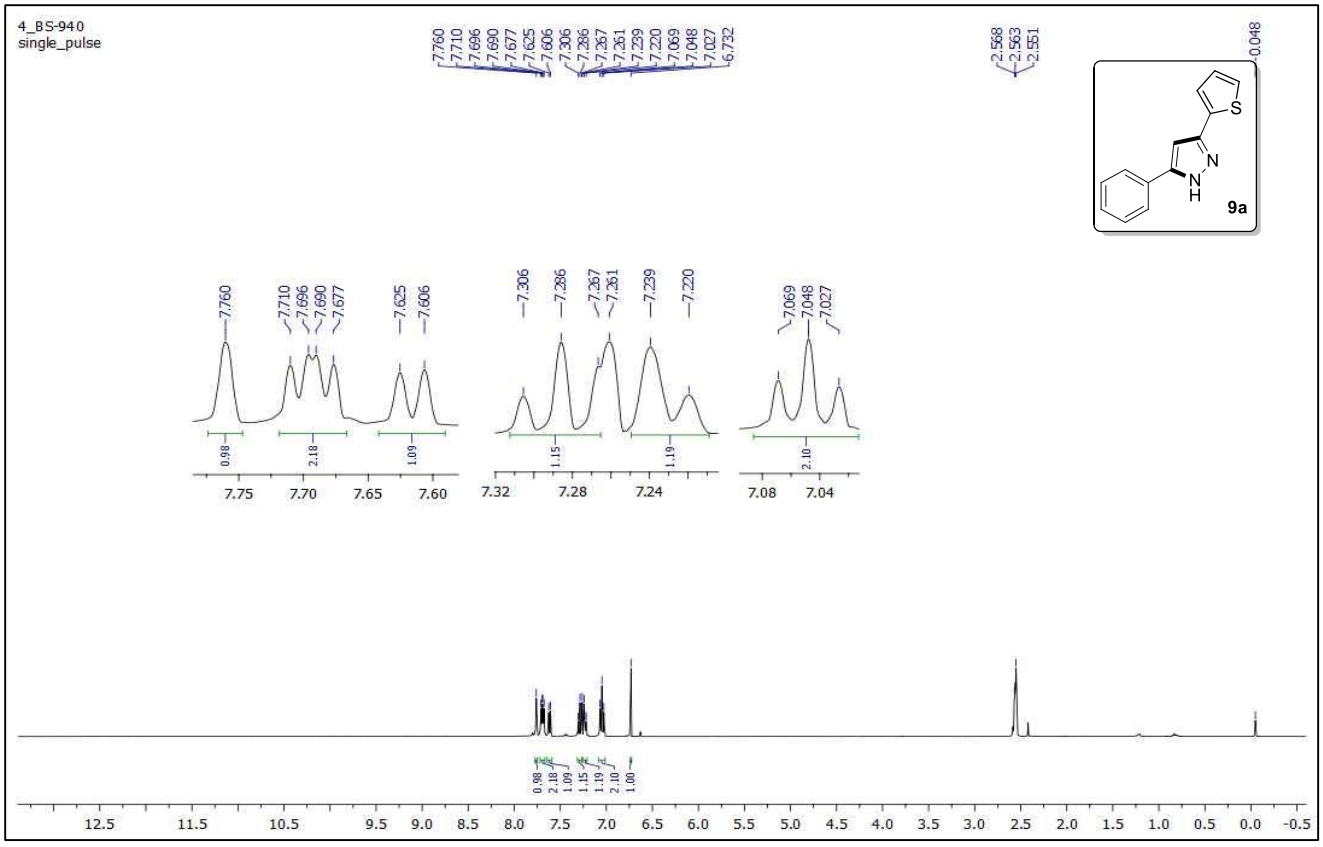

BS-3MF
7b
Me
F
N
H
abundance
X : parts per Million : Carbon13

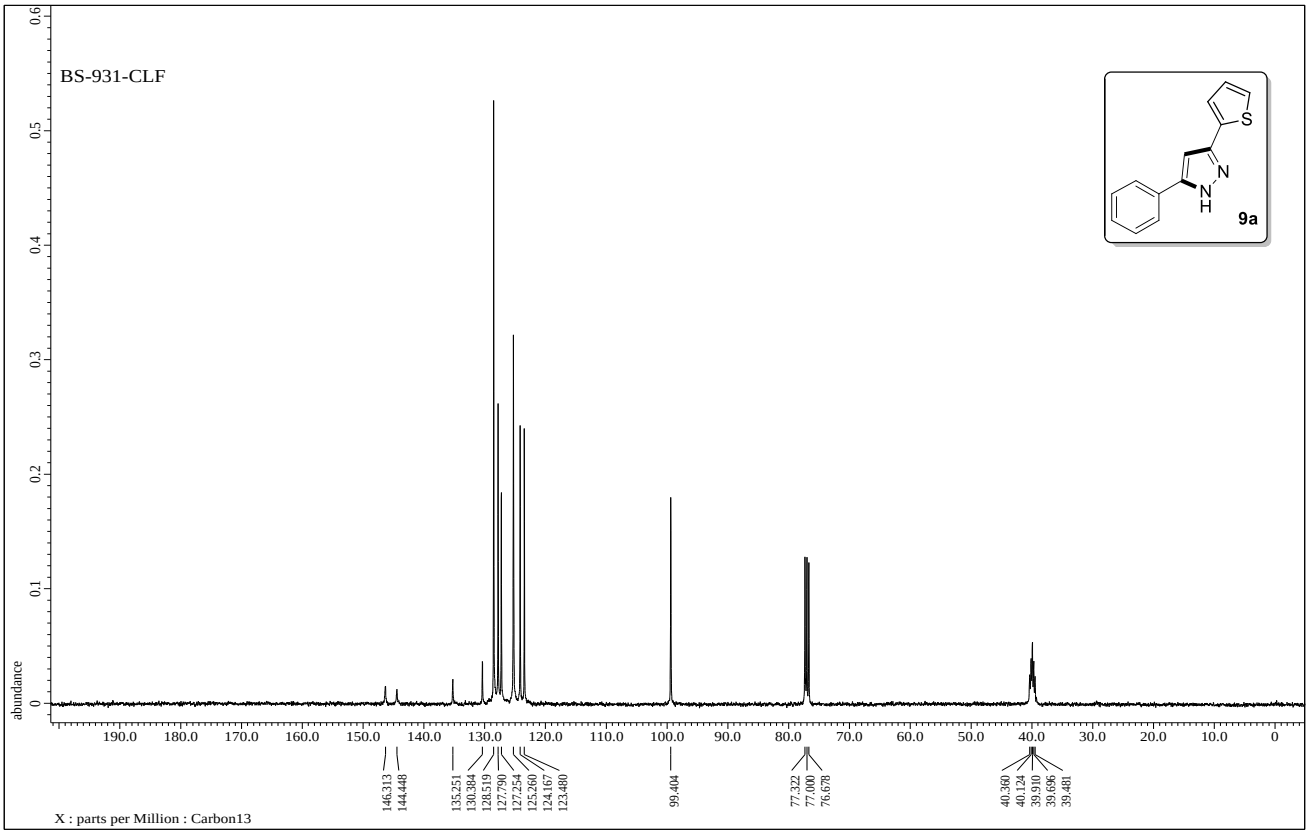

8_BS-3MOM
single_pulse
7.602
7.580
7.479
7.462
7.260
7.201
7.182
7.162
7.078
7.060
6.799
6.778
6.674
3.772
2.258
0.024
OMe
N
N
H
Me
7c
2.13
2.01
1.06
1.00
2.08
0.99
3.00
3.05

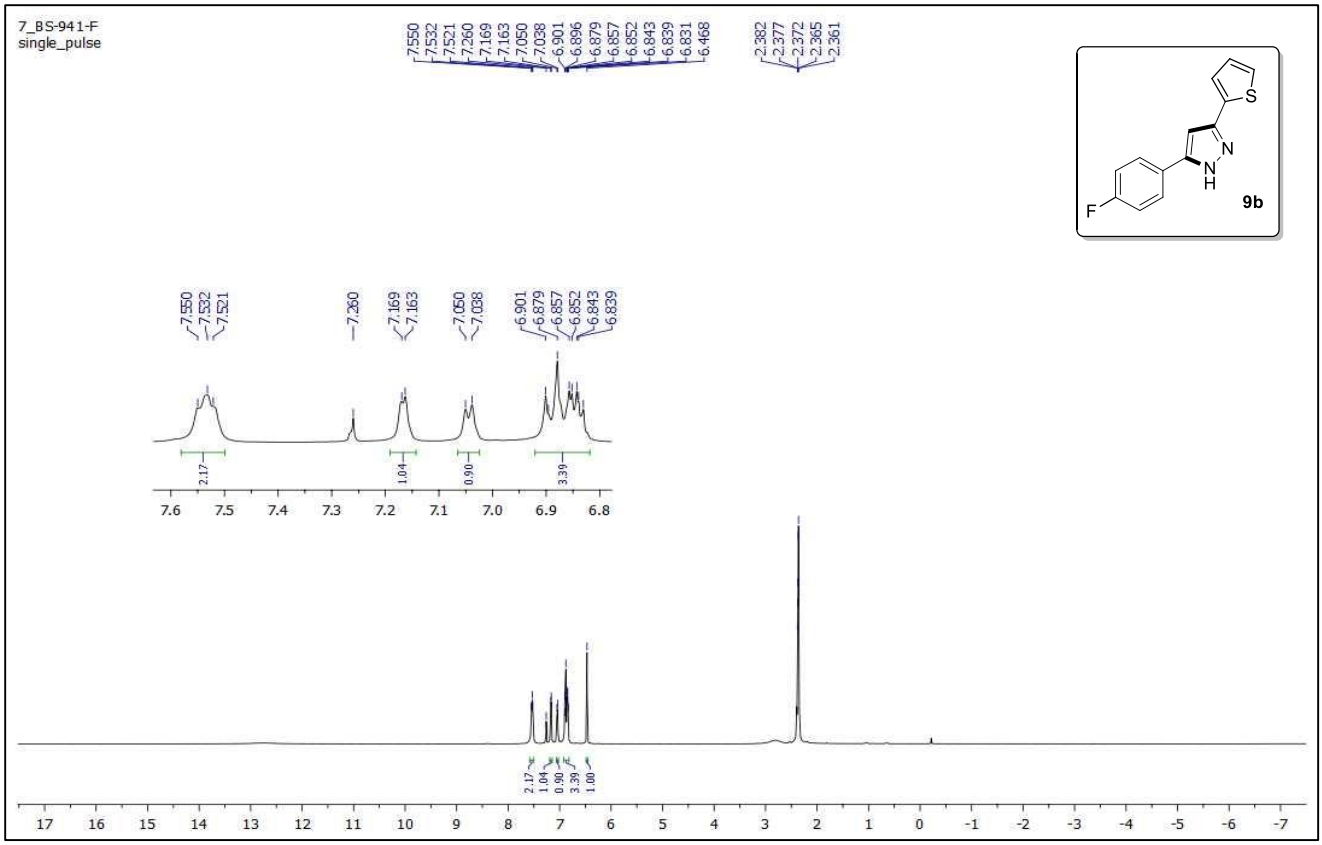

BS-3MOM
OMe
N
N
H
Me
7c
abundance
159.220
148.908
147.964
138.102
131.392
128.454
126.804
126.246
123.888
122.666
113.940
98.997
77.322
77.000
76.700
55.046
21.236
X : parts per Million : Carbon13

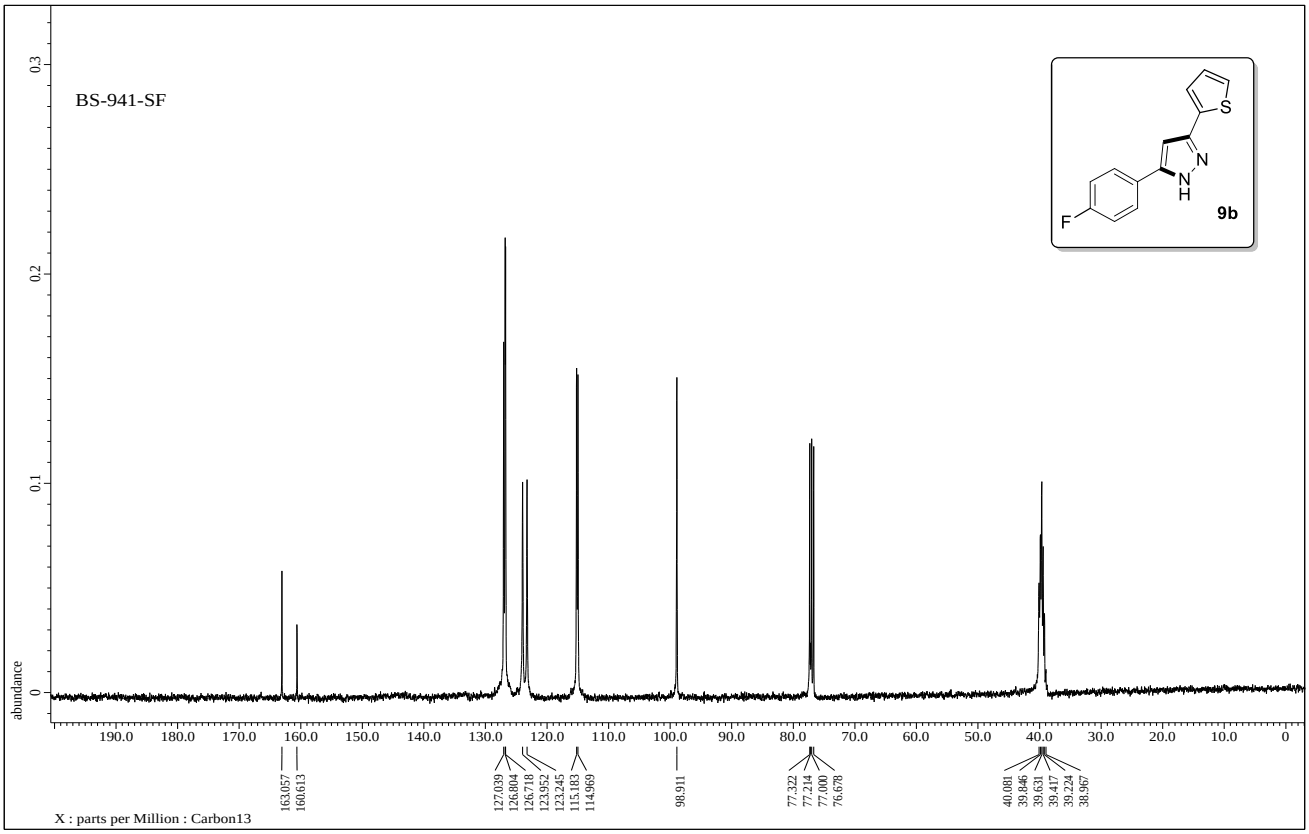

10_BS-PYOCL
single_pulse
7.752
7.731
7.639
7.618
7.458
7.438
7.388
7.368
7.349
7.332
7.314
7.296
7.268
7.260
7.249
7.226
7.206
7.187
6.993
0.018
Cl
N
N
H
8a
1.27
0.66
0.59
1.96
1.38
1.29
0.56

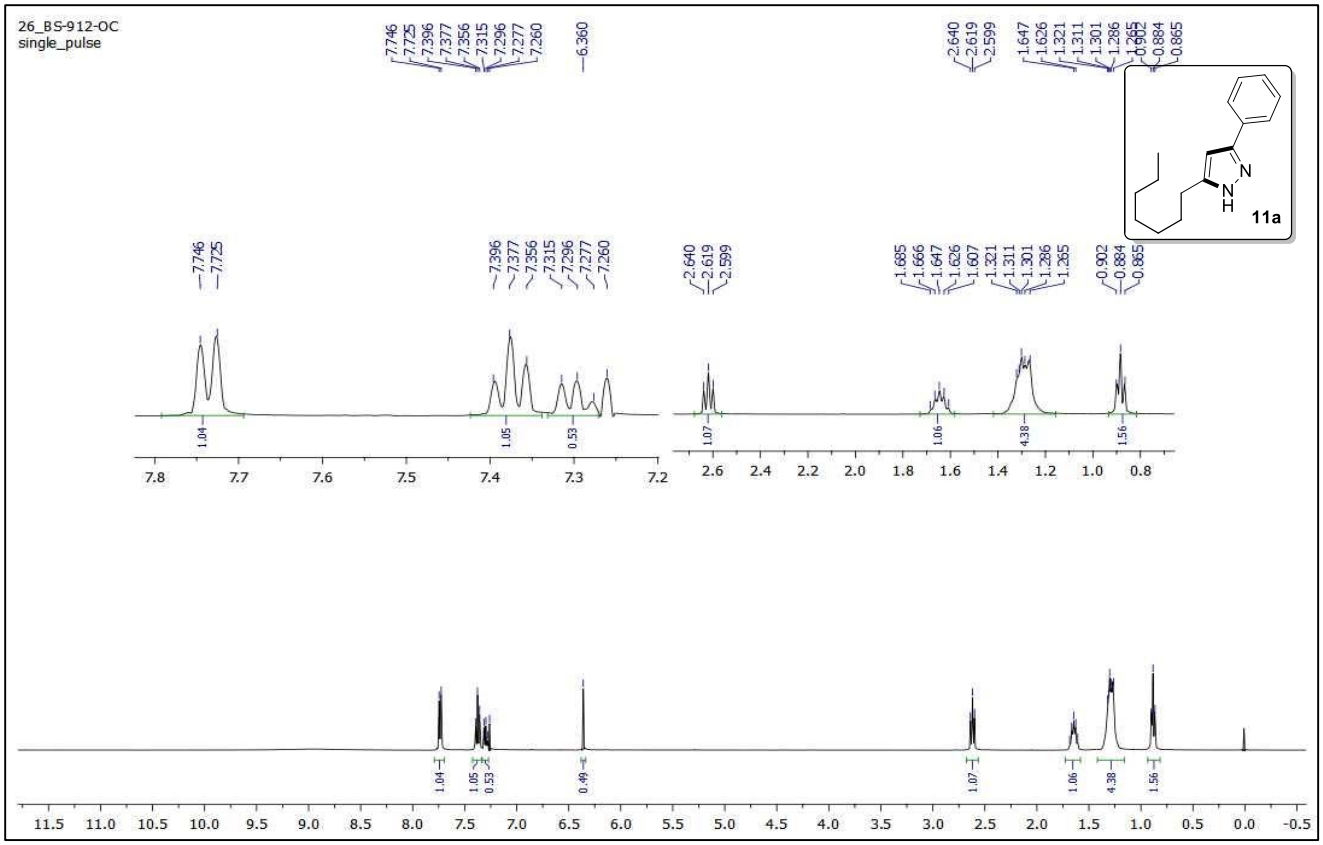

BS-POCL
Cl
N
N
H
8a
abundance
131.820
131.349
130.448
130.234
129.827
129.248
128.733
128.090
126.997
125.646
103.606
77.322
77.000
76.678
X : parts per Million : Carbon13

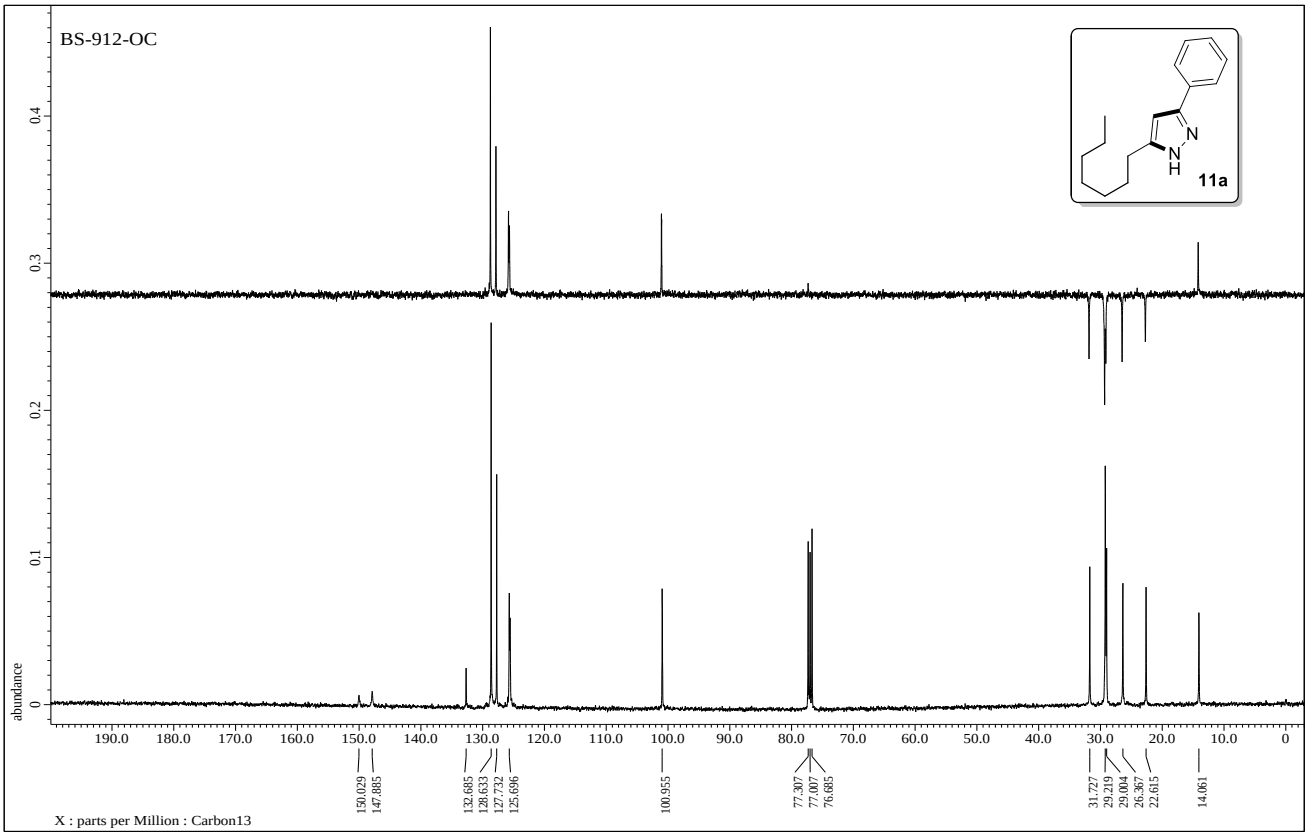

4_BS-940
single_pulse
9a

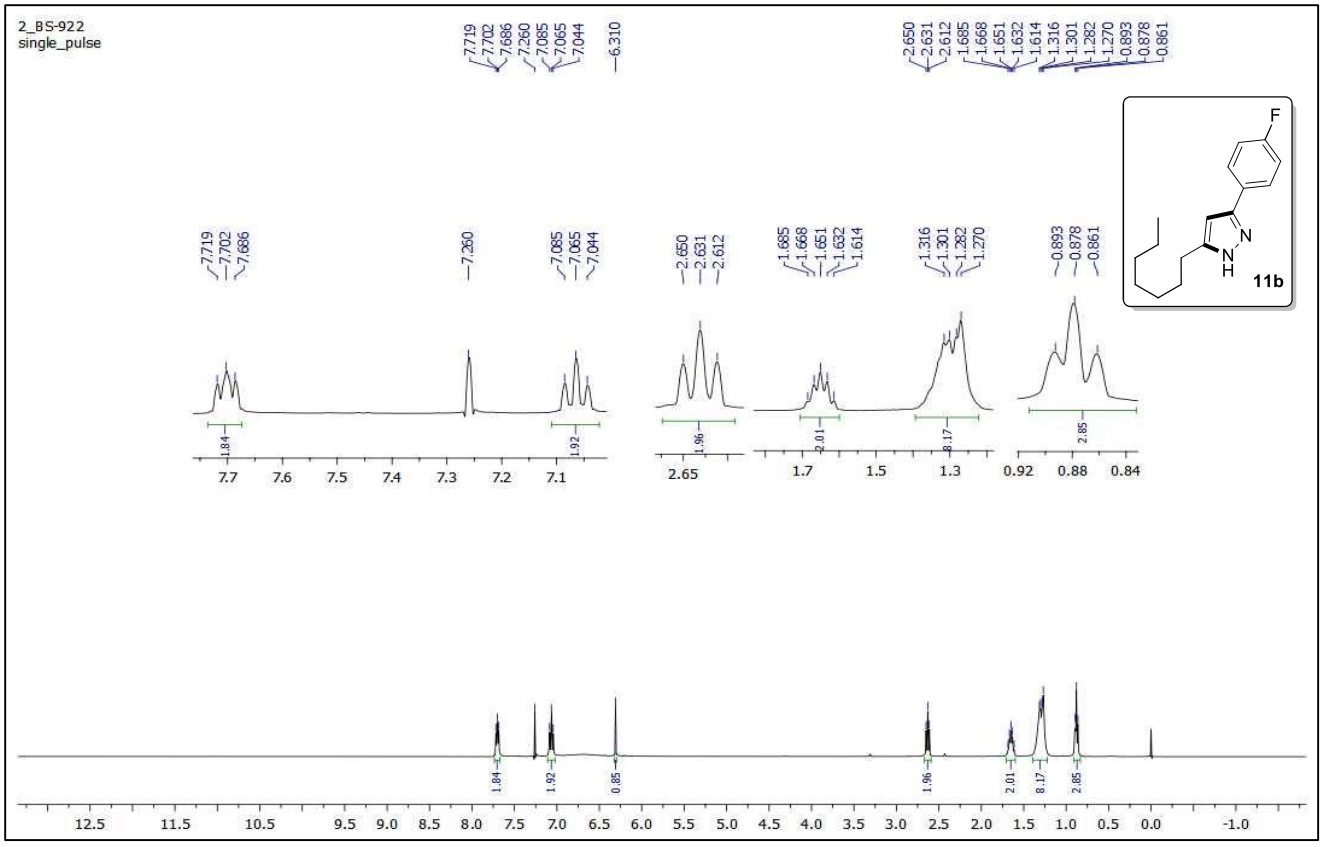

BS-931-CLF
9a
abundance
X : parts per Million : Carbon13

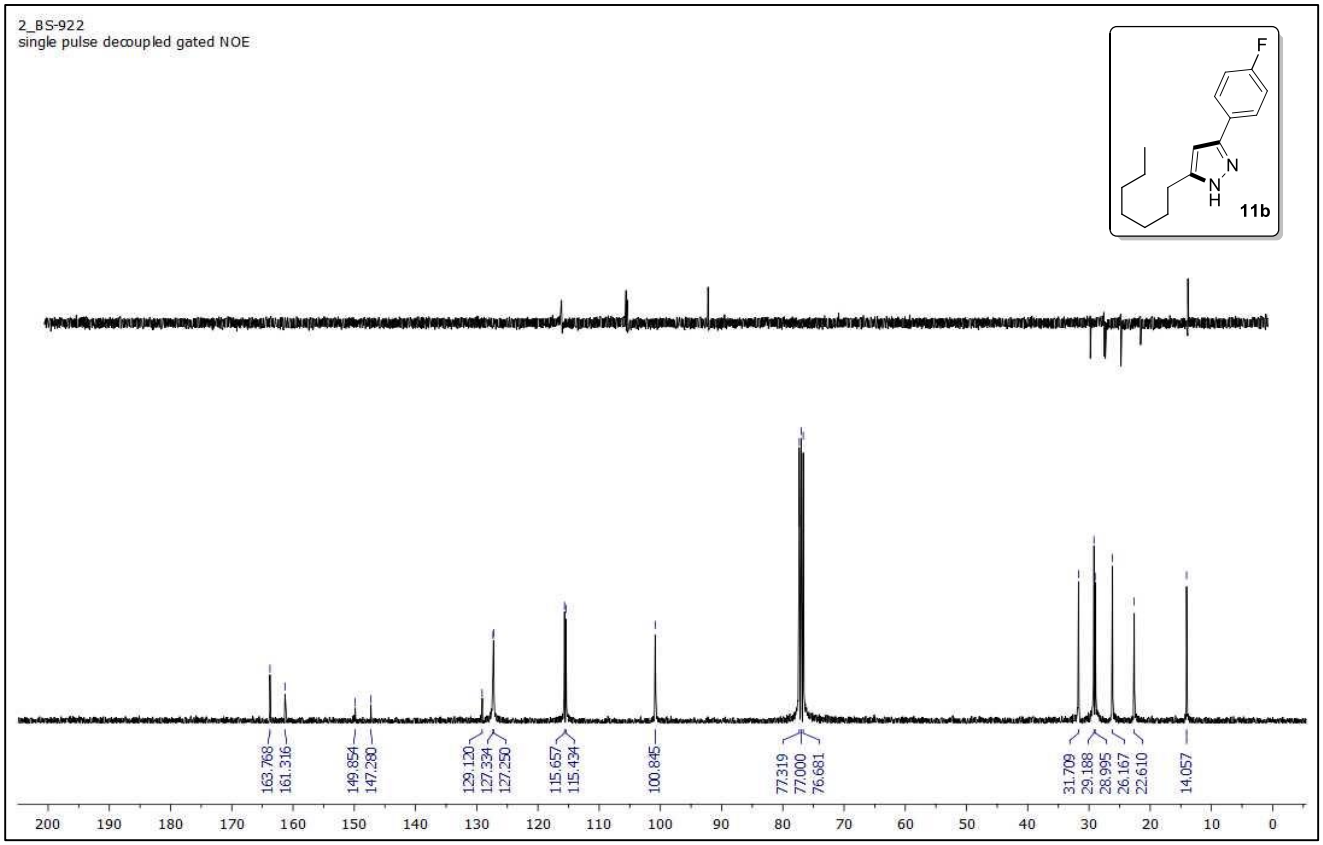

7_BS-941-F
single_pulse
9b

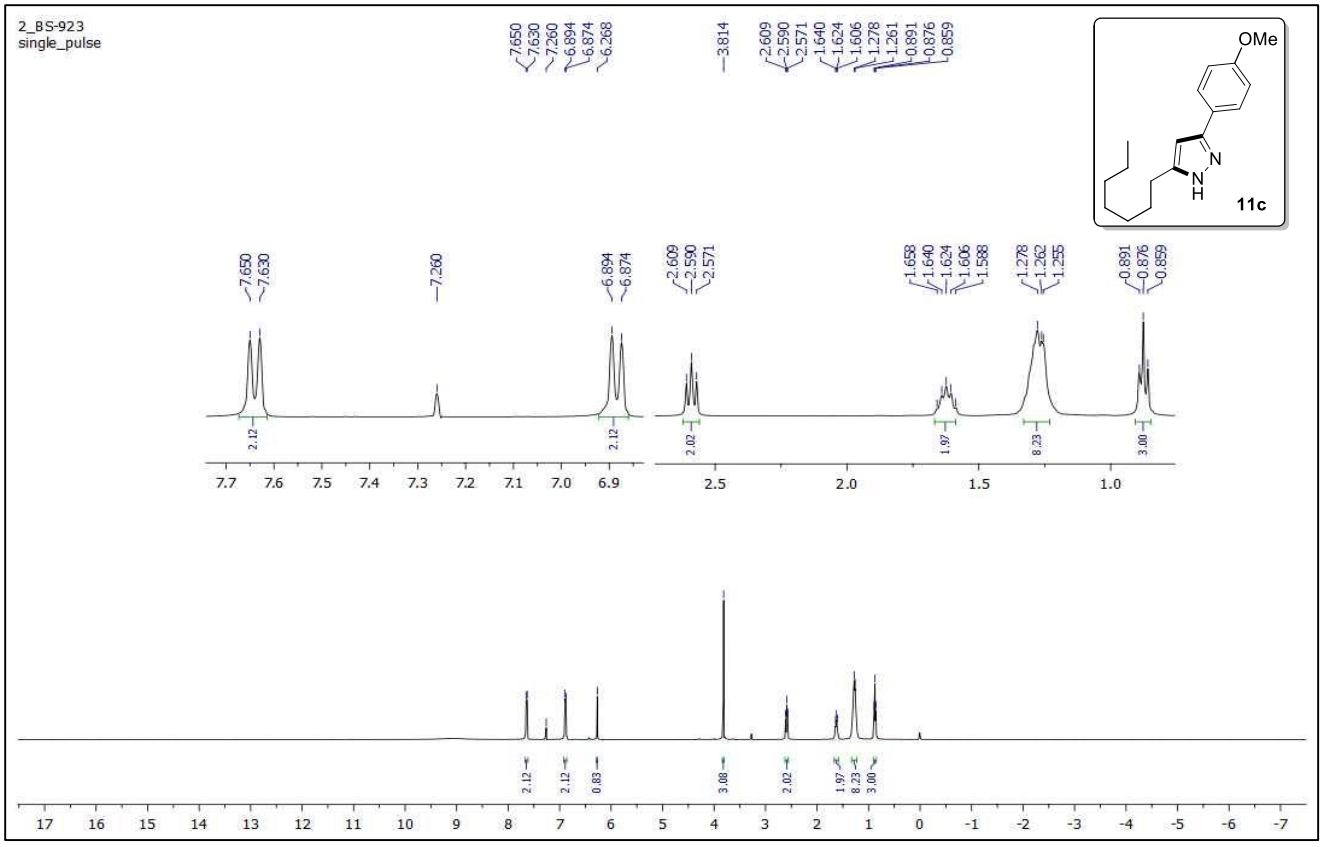

BS-941-SF
9b
abundance
X : parts per Million : Carbon13

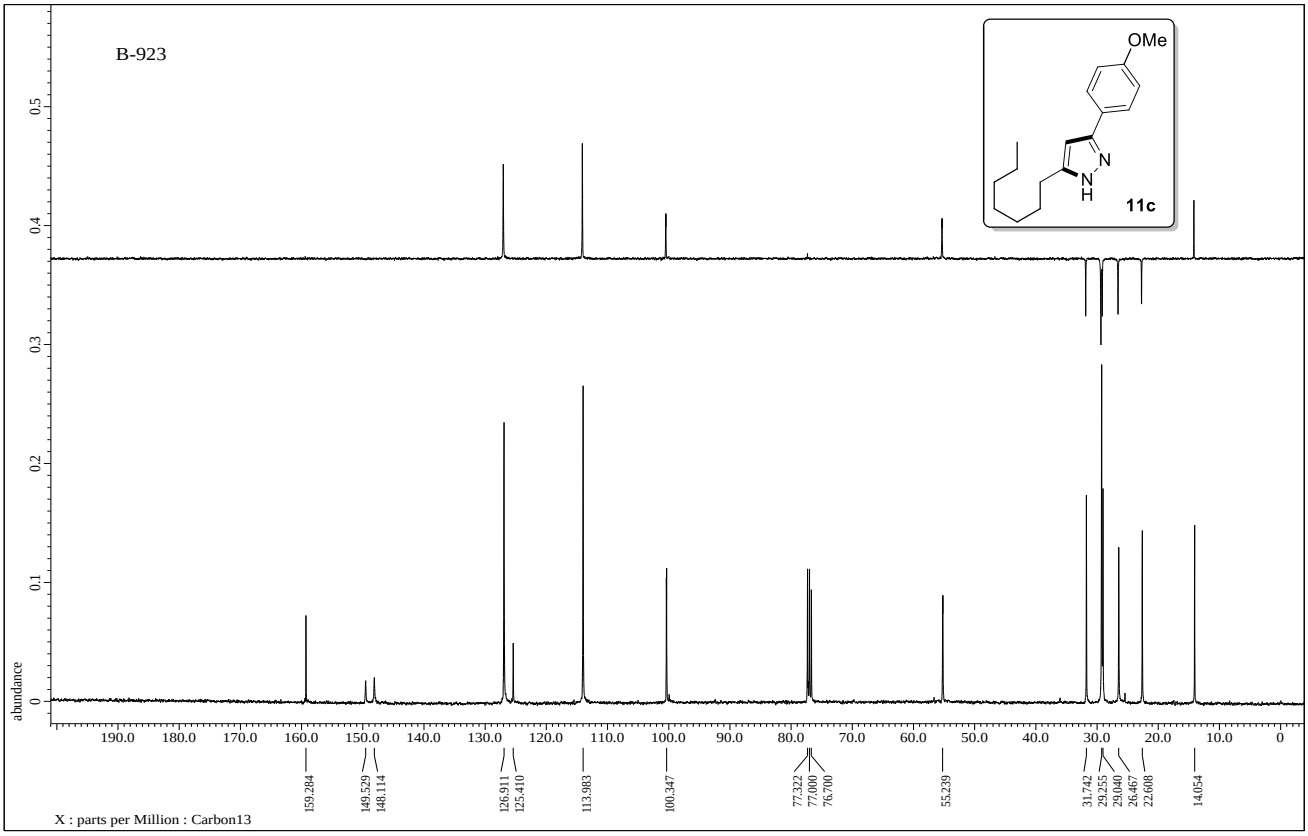

26_BS-912-OC
single_pulse
11a


BS-912-OC
11a
abundance
X : parts per Million : Carbon13


2_BS-922
single_pulse
11b


2_BS-922
single pulse decoupled gated NOE
11b


2_BS-923
single_pulse
OMe
N
N
H
11c


B-923
OMe
N
N
H
11c
abundance
X : parts per Million : Carbon13