Supplementary Material

Aromatic N-arylations catalyzed by heterometallic (Cu^{II}-Ba^{II}) metal–organic framework under heterogeneous base-free conditions in ethanol

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Table S1. Crystallographic Data and Structure Refinement Parameters of compound **1**

Parameters	Compound **1**
Chemical formula sum	$C_{14}H_{18}BaCuN_2O_{14}$
Chemical formula weight	639.18
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	7.945(5)
b (Å)	10.896(5)
c (Å)	21.504(5)
α(º)	90.00
β(º)	92.786(5)
γ(º)	90.00
V (Å^3)	1859.4(15)
Z	4
Temperature (K)	100(2)
D_c (g cm^{-3})	2.283
μ (mm^{-1})	3.334
F(000)	1252
ϑ range (º)	1.90-25.00
Intervals of reflection indices	-9≤h≥9, -12≤k≥12, -25≤l≥25
Measured reflections	21560
Reflections with [I > *2σ* (I)]	3059
Independent reflections	3269
Final *R* indices[*I>2σ (I)*]	*R1*=0.0431, *wR2*=0.1508
R indices (all data)	*R1*=0.0463, *wR2*=0.1609
R_{int}	0.0246
$\Delta\rho_{max}$ (e Å^{-3})	2.244
$\Delta\rho_{min}$ (e Å^{-3})	-2.078
Goodness-of-fit on F^2	1.186

Table S2. Selected Bond Lengths (Å) and Angles (°) for compound **1**

Bond	Lengths (Å)	Bond	Angles (°)
Ba1-O9	2.829(6)	[a]O7-Ba1-O9	80.96(17)
Ba1-[a]O7	2.772(5)	O9-Ba1-[b]O14	134.5(2)
Ba1-[b]O14	2.830(7)	[c]O3-Ba1-O9	135.58(17)
Ba1-[c]O3	2.804(5)	[d]O6-Ba1-O9	73.32(17)
Ba1-[d]O6	2.734(5)	O9-Ba1-[d]O10	137.45(19)
Ba1-[d]O10	2.827(7)	O9-Ba1-[d]O11	66.39(18)
Ba1-[d]O11	2.830(8)	[e]O4-Ba1-O9	89.61(17)
Ba1-[e]O4	2.763(5)	O9 -Ba1-[e]O12	62.28(19)
Ba1-[e]O12	2.945(7)	[a]O7-Ba1-[b]O14	140.88(18)
Cu1-O1	1.978(5)	[c]O3-Ba1-[b]O7	79.41(14)
Cu1-O2	1.956(5)	[d]O6-Ba1-[a]O7	77.24(14)
Cu1-N1	2.004(5)	[a]O7-Ba1-[d]O10	75.31(19)
Cu1-N2	1.996(5)	[a]O7-Ba1-[d]O11	141.36(16)
Cu1-[s]O5	2.348(6)	[e]O4-Ba1-[a]O7	132.21(14)
		[a]O7-Ba1-[e]O12	71.06(17)
		[c]O3-Ba1-[b]O14	81.36(19)
		[d]O6-Ba1-[b]O14	95.78(18)
		[d]O10-Ba1-[b]O14	66.7(2)
		[d]O11-Ba1-[b]O14	68.1(2)
		[e]O4-Ba1-[b]O14	73.54(17)
		[e]O12-Ba1-[b]O14	134.11(18)
		[c]O3-Ba1-[e]O6	138.33(15)
		[c]O3-Ba1-[d]O10	73.63(18)
		[c]O3-Ba1-[d]O11	138.70(17)
		[c]O3-Ba1-[e]O4	75.29(13)
		[c]O3-Ba1-[e]O12	73.73(18)
		[d]O6-Ba1-[d]O10	67.33(19)
		[d]O6-Ba1-[d]O11	74.10(17)
		[e]O4-Ba1-[d]O6	143.93(14)
		[d]O6-Ba1-[e]O12	128.25(18)
		[d]O10-Ba1-[d]O11	115.4(2)
		[e]O4-Ba1-[d]O10	132.23(18)
		[d]O10-Ba1-[e]O12	136.5(2)
		[e]O4-Ba1-[d]O11	69.94(16)
		[d]O11-Ba1-[e]O12	108.2(2)
		[e]O4-Ba1-[e]O12	63.25(17)
		O1-Cu1-O2	170.1(2)
		O1-Cu1-N1	83.01(18)

	O1-Cu1-N2	95.53(18)
	O1-Cu1-^{d}O5	91.2(2)
	O2-Cu1-N1	96.2(2)
	O2-Cu1-N2	83.6(2)
	O2-Cu1-^{s}O5	98.7(2)
	N1-Cu1-N2	170.35(19)
	^{s}O5-Cu1-N1	91.96(19)
	^{s}O5-Cu1-N2	97.61(19)

Symmetry Code: [a] 1+x, y, z; [b] -1/2-x, -1/2+y, 3/2-z; [c] 1/2-x, 1/2+y, 3/2-z; [d] 1-x, -y, 2-z; [e] 1/2+x, 1/2-y, -1/2+z.

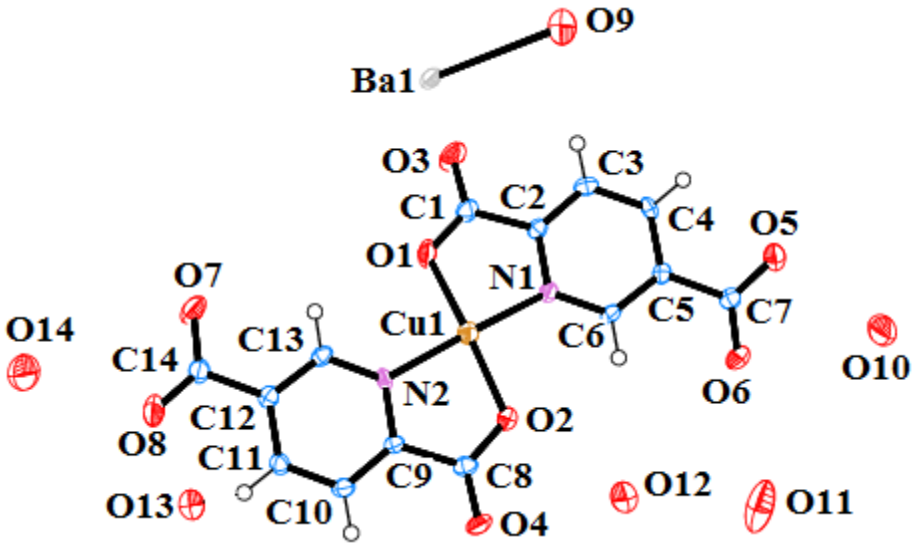
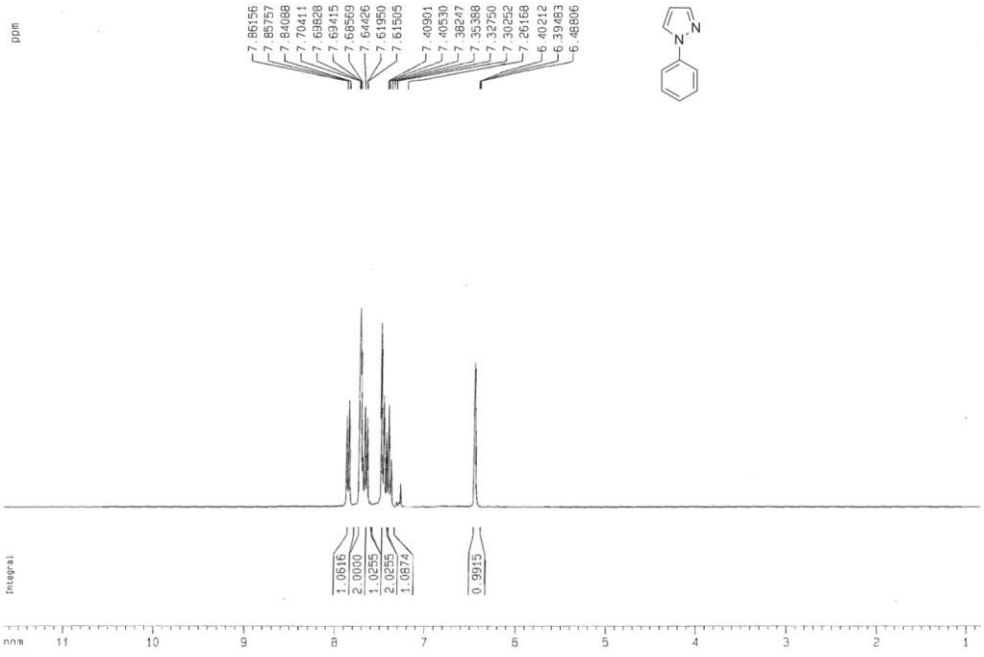
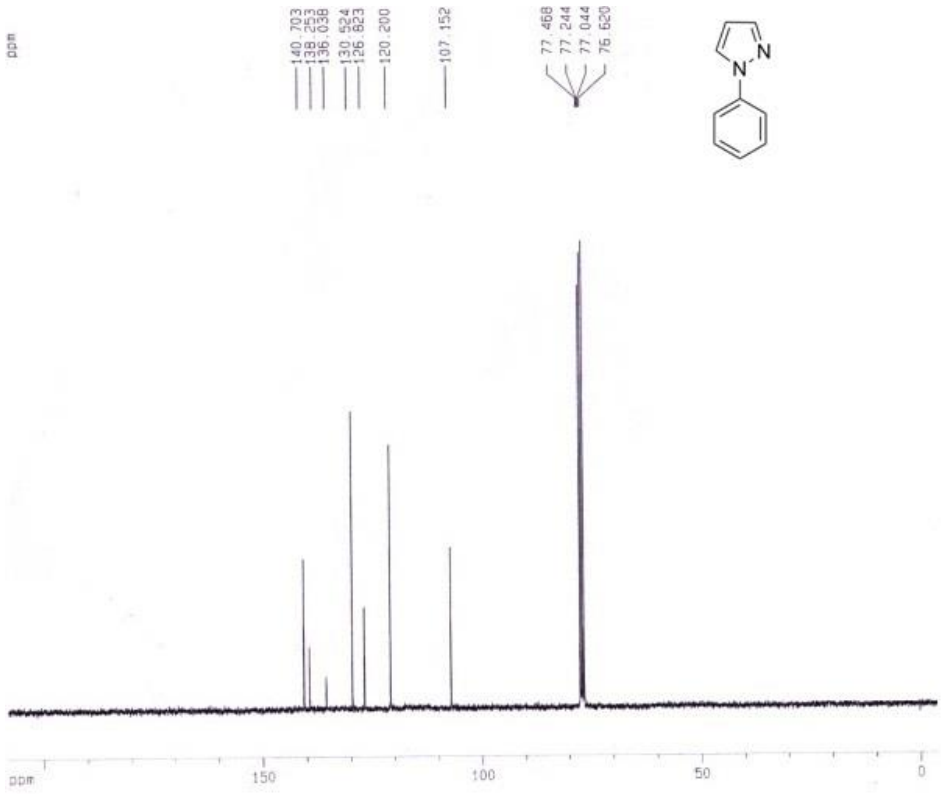
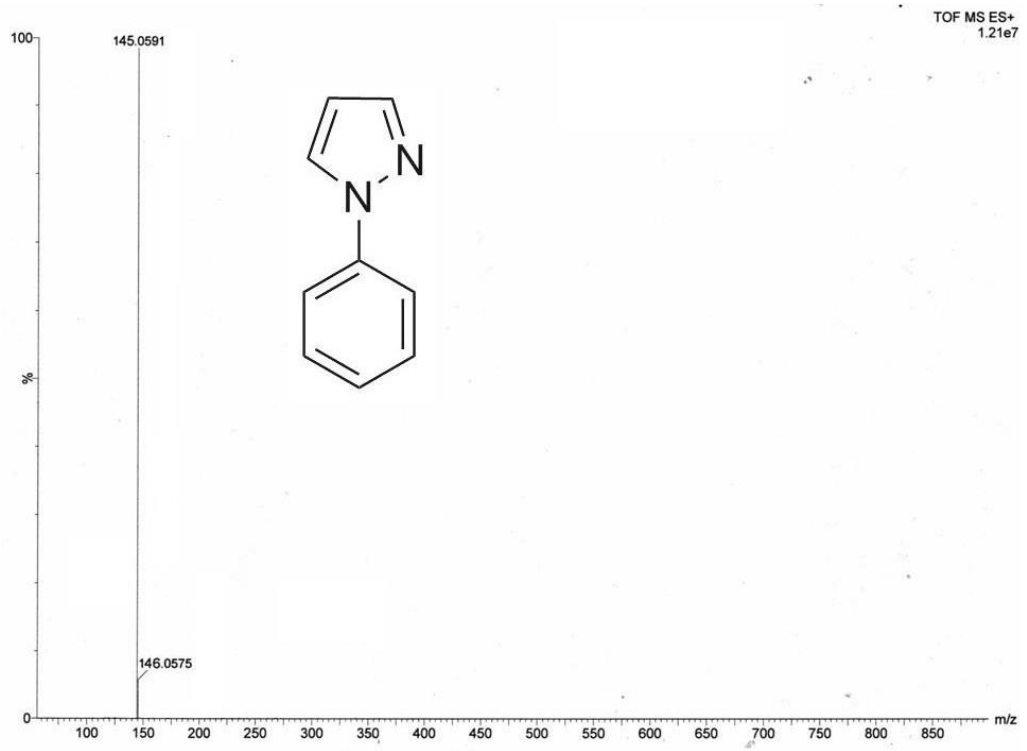


Figure S1. ORTEP diagram of compound **1** with 40% ellipsoid probability

^{1}H NMR, ^{13}C NMR and HRMS of the Products







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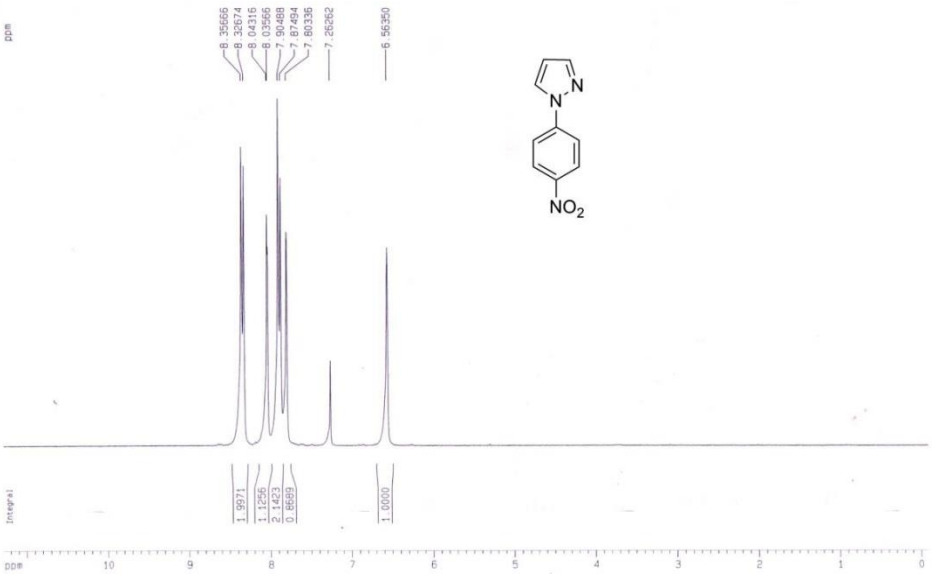
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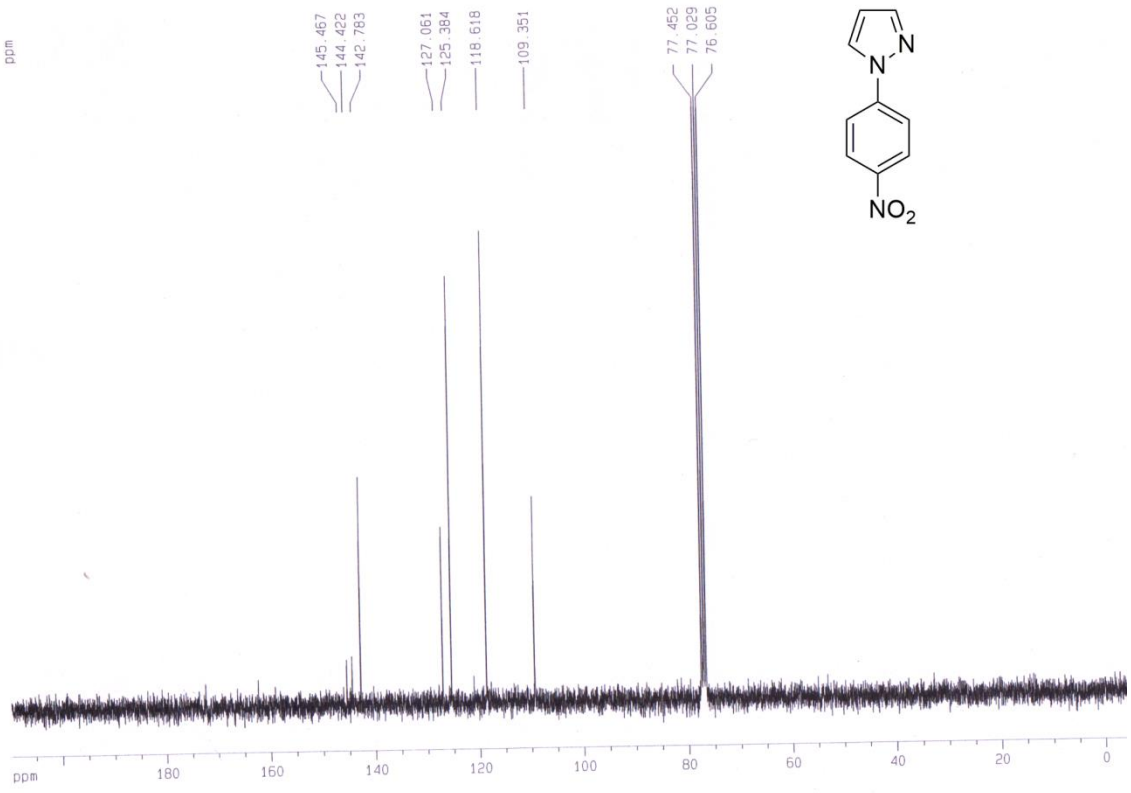
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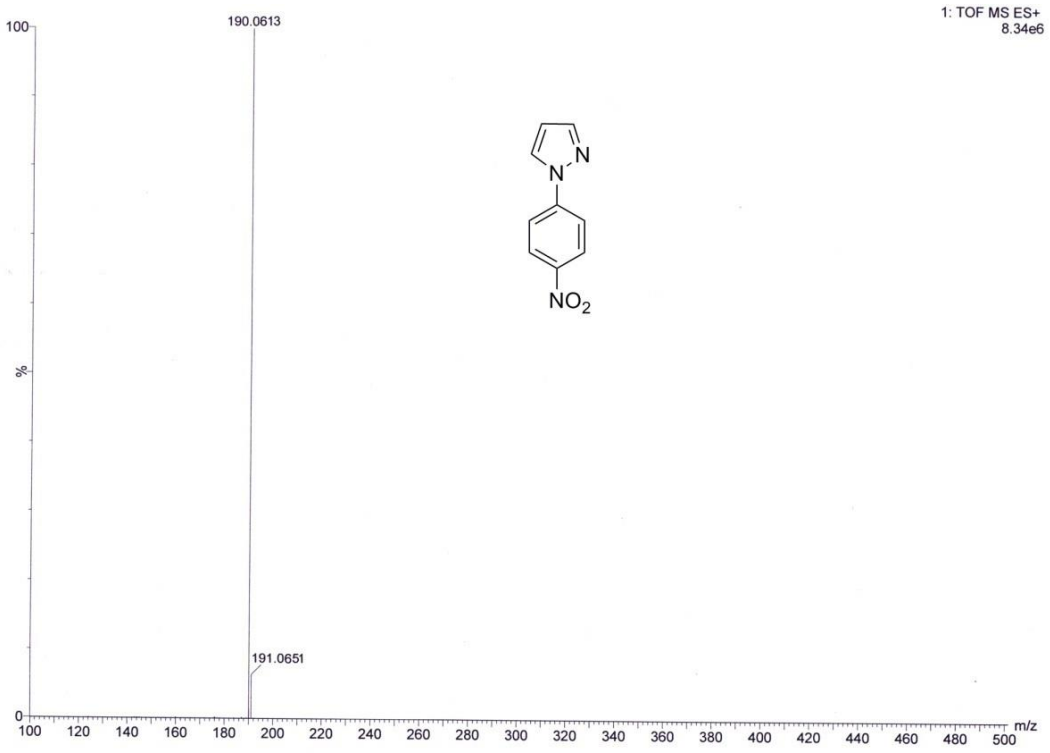

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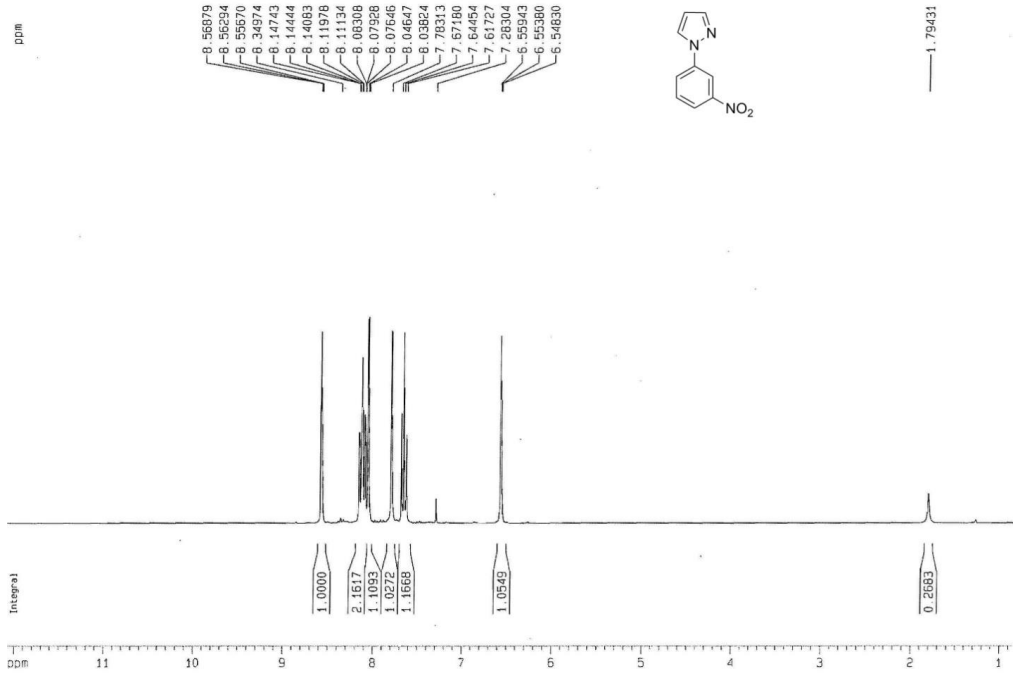

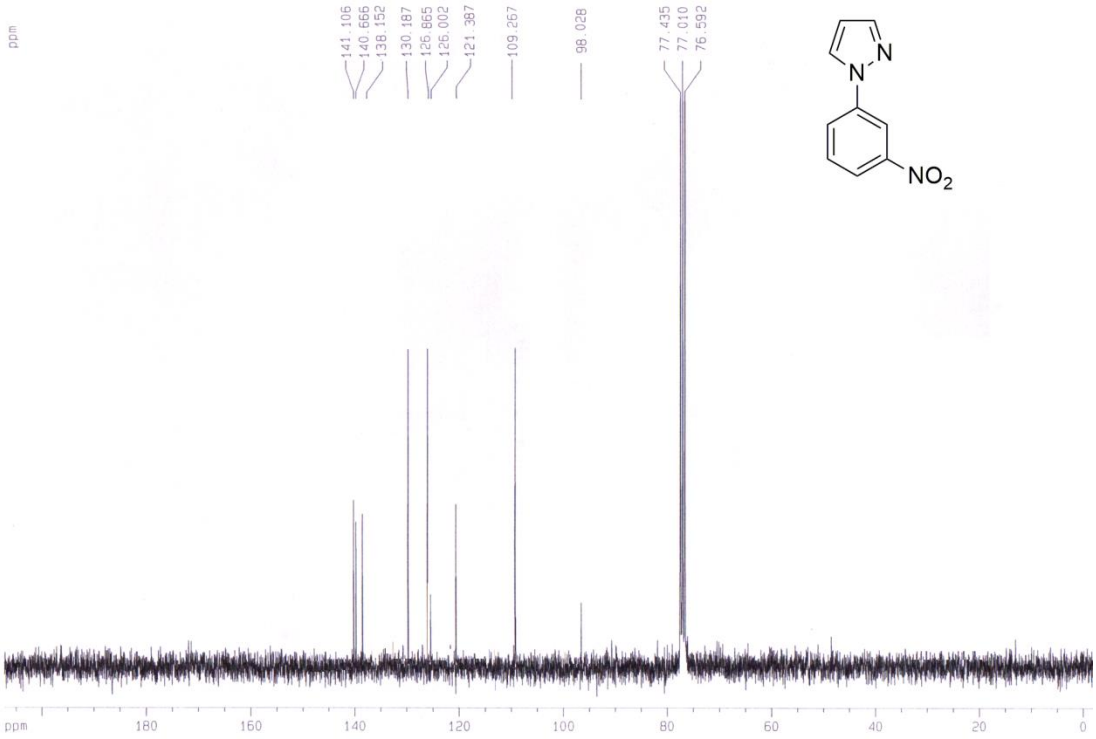

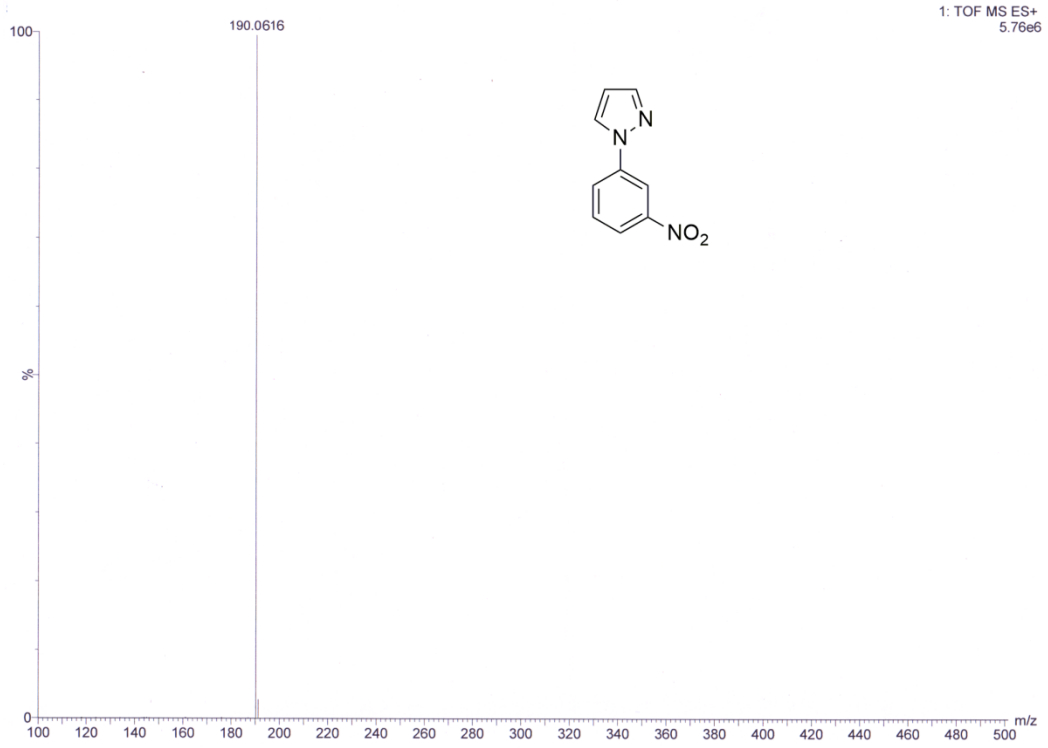

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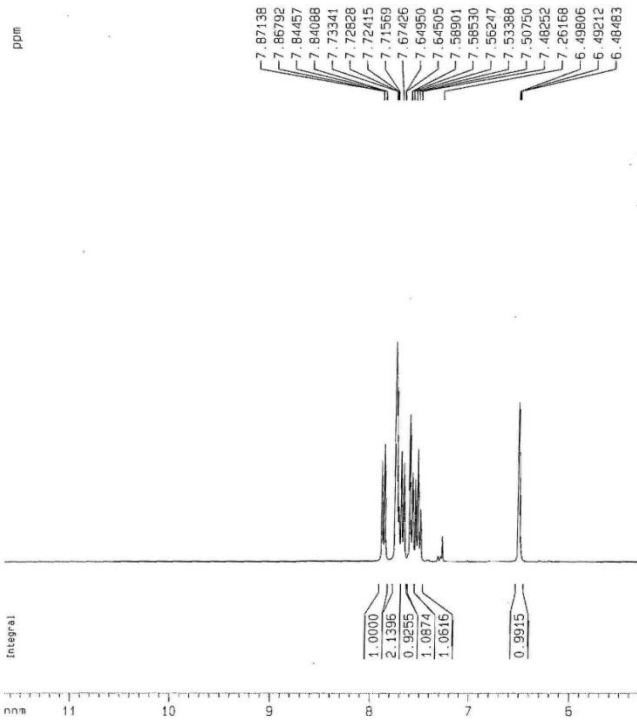
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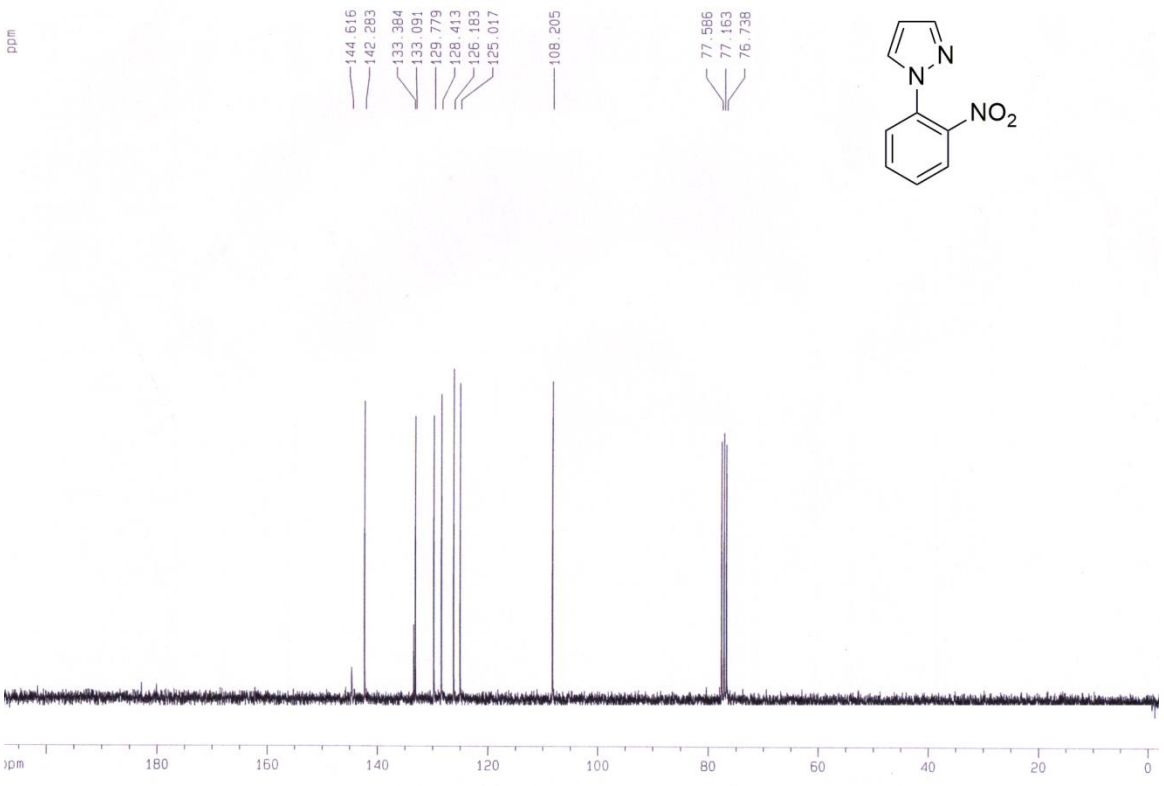
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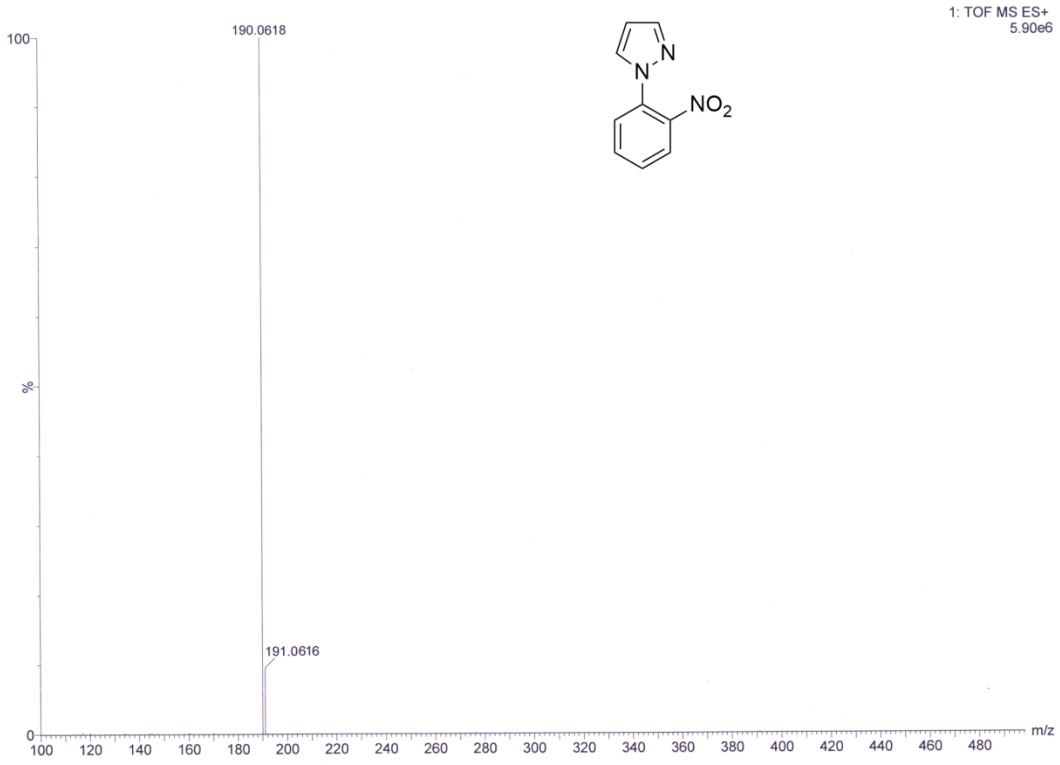

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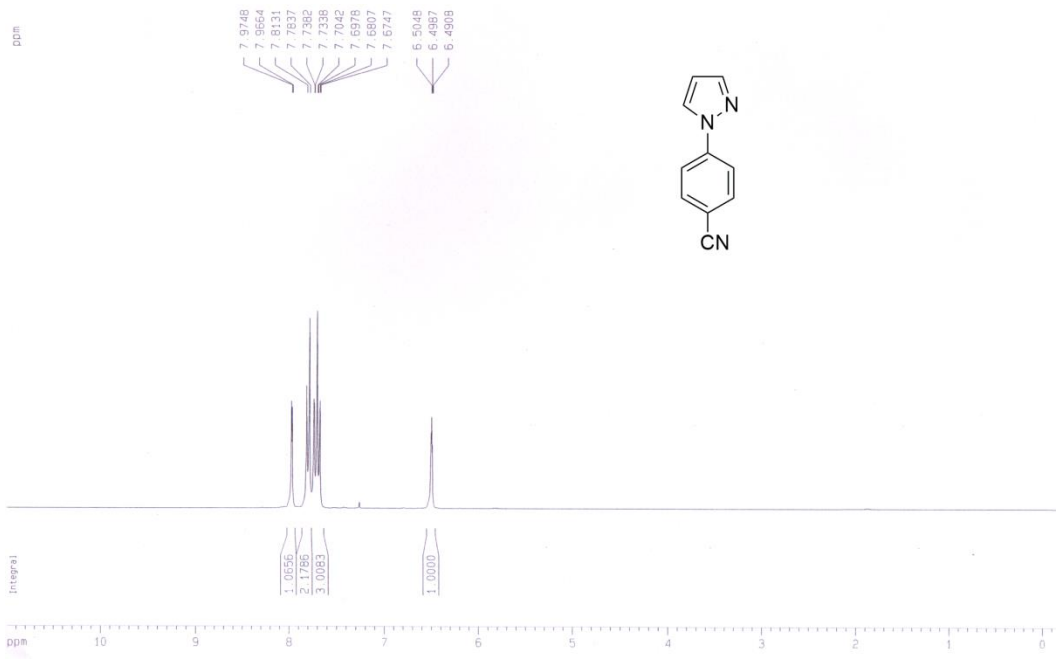

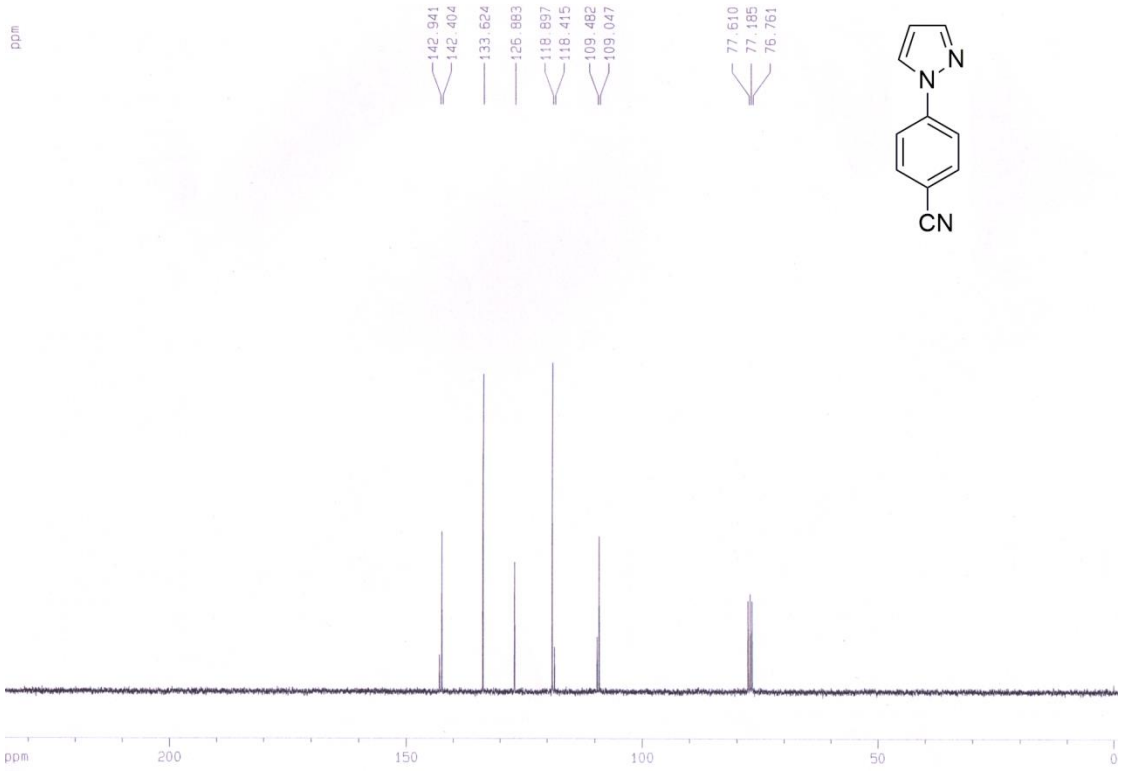

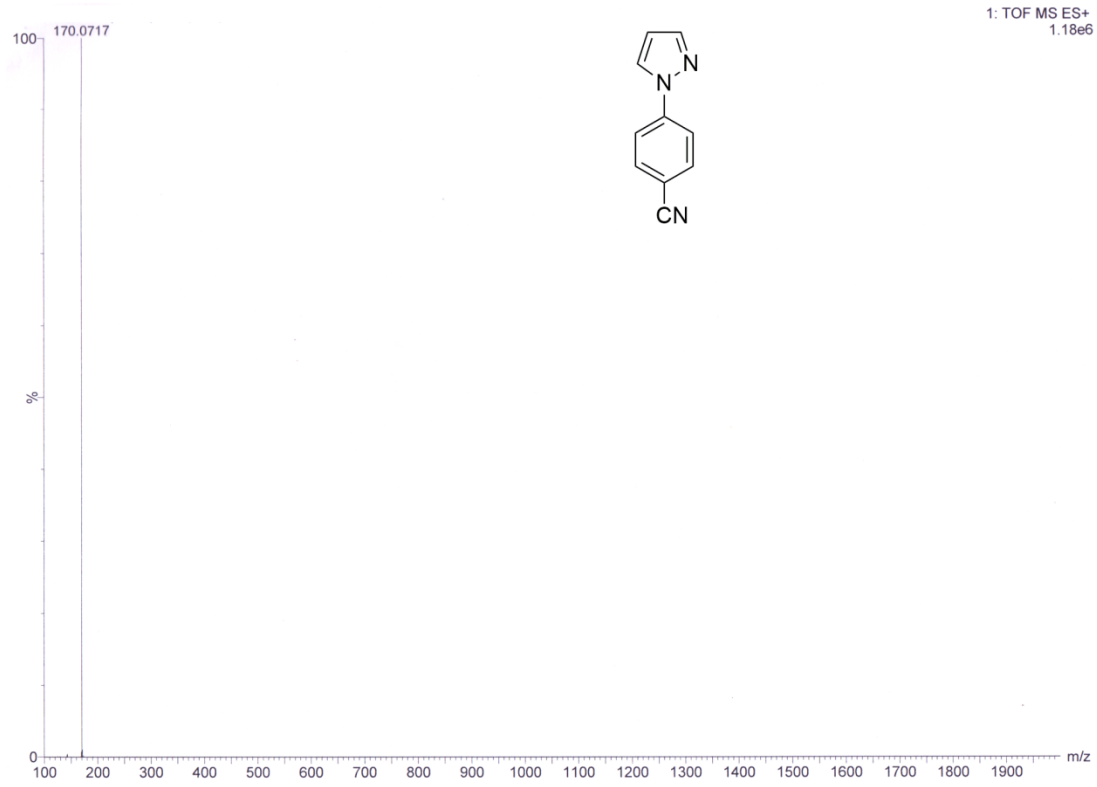

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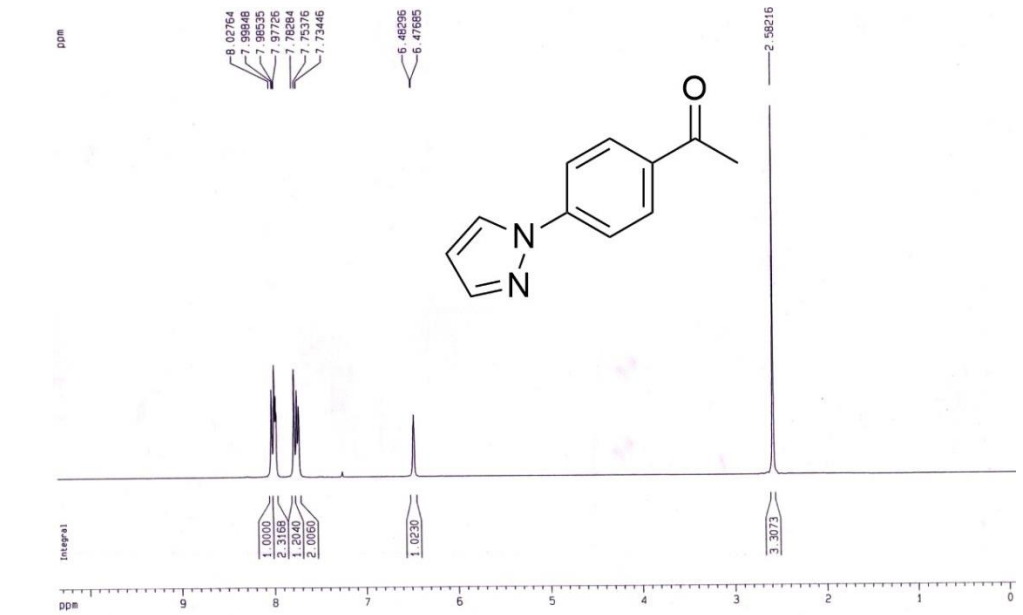
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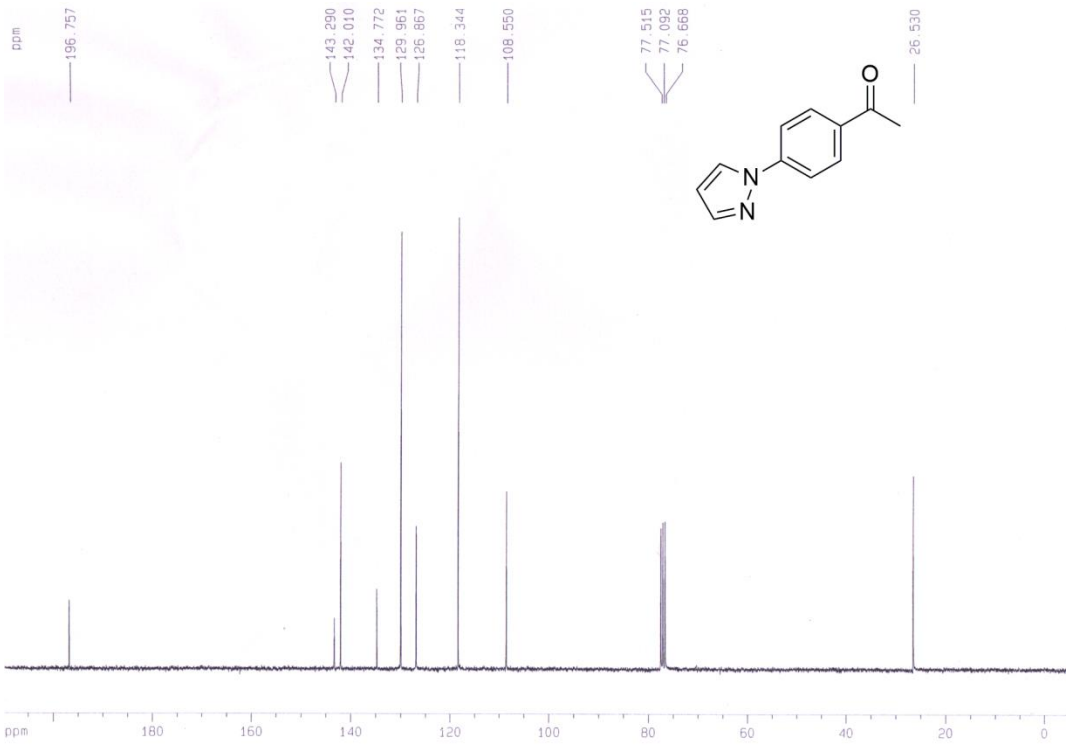
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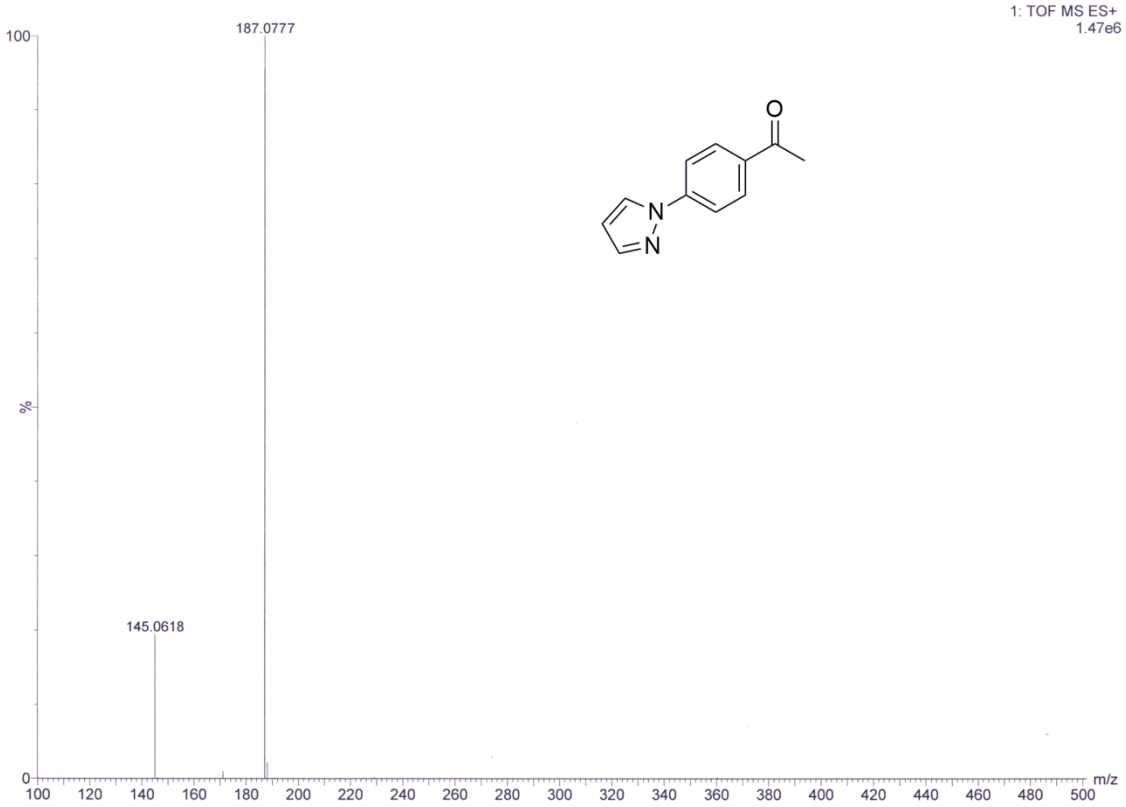

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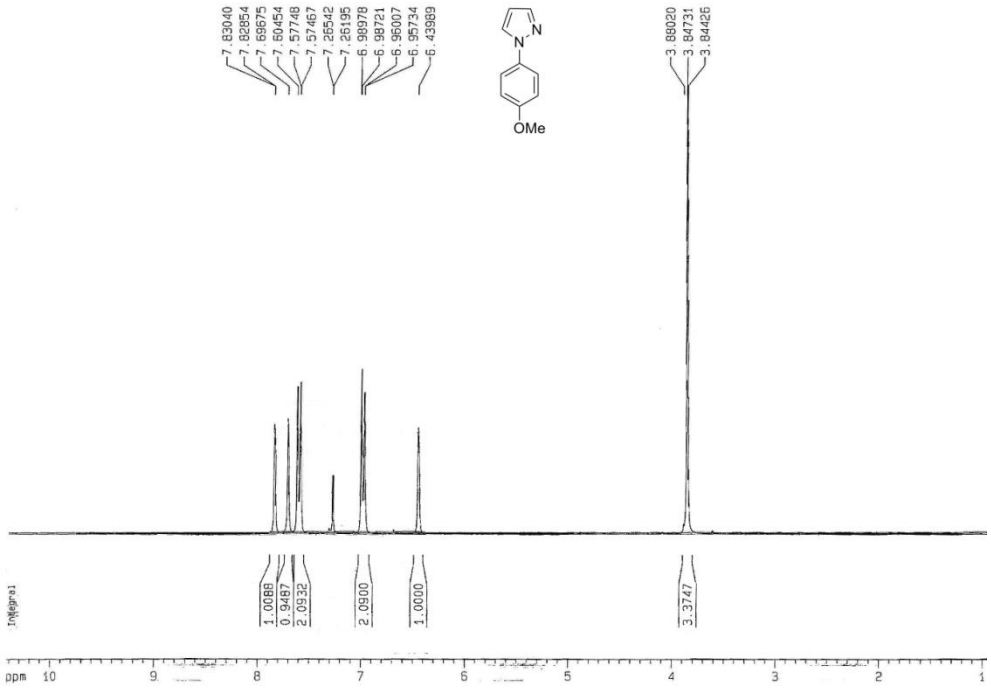

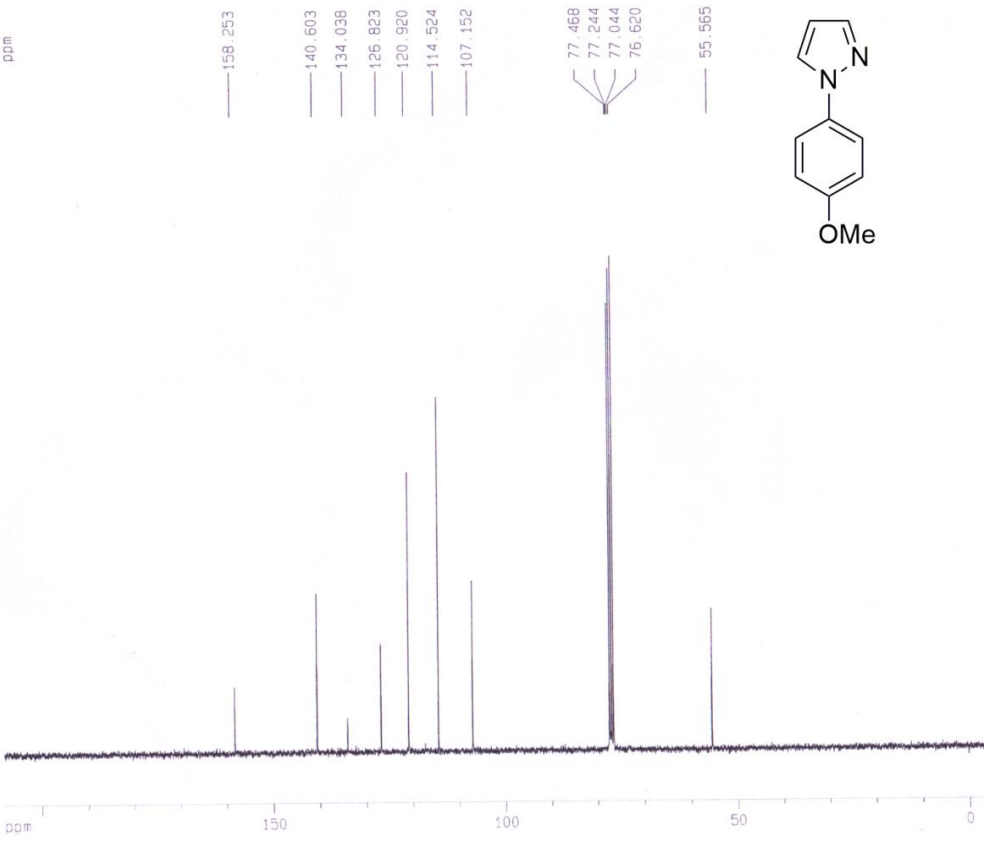

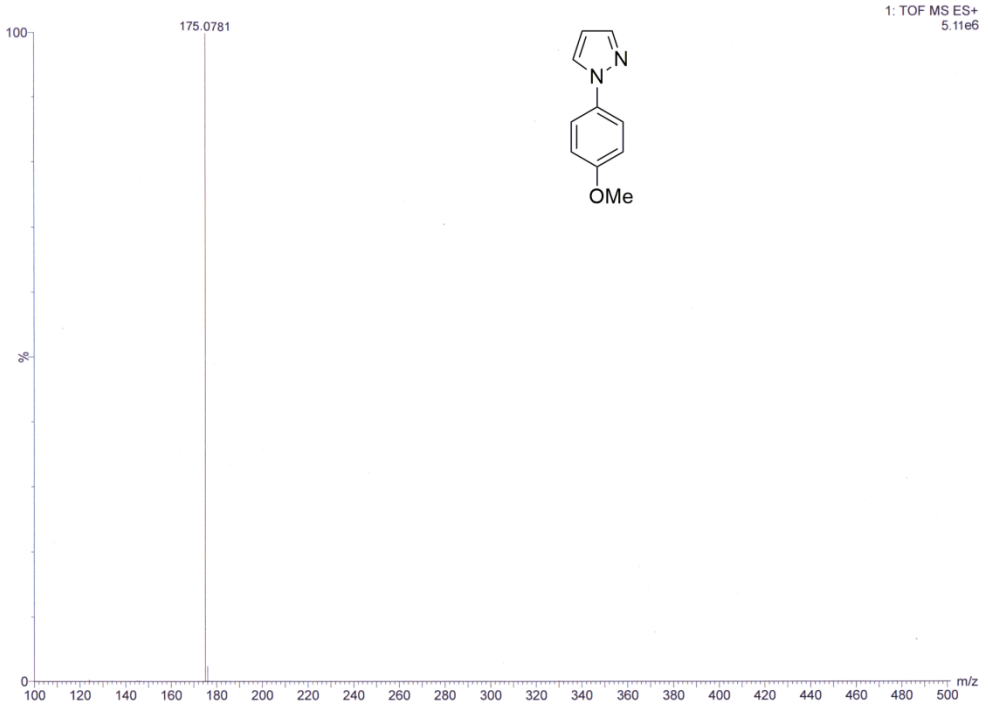

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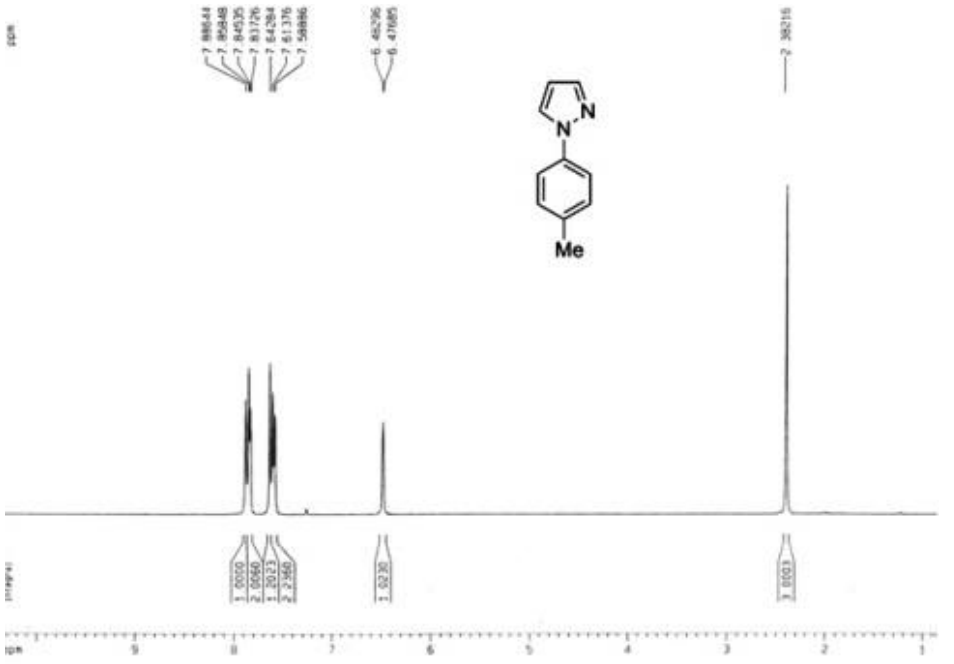
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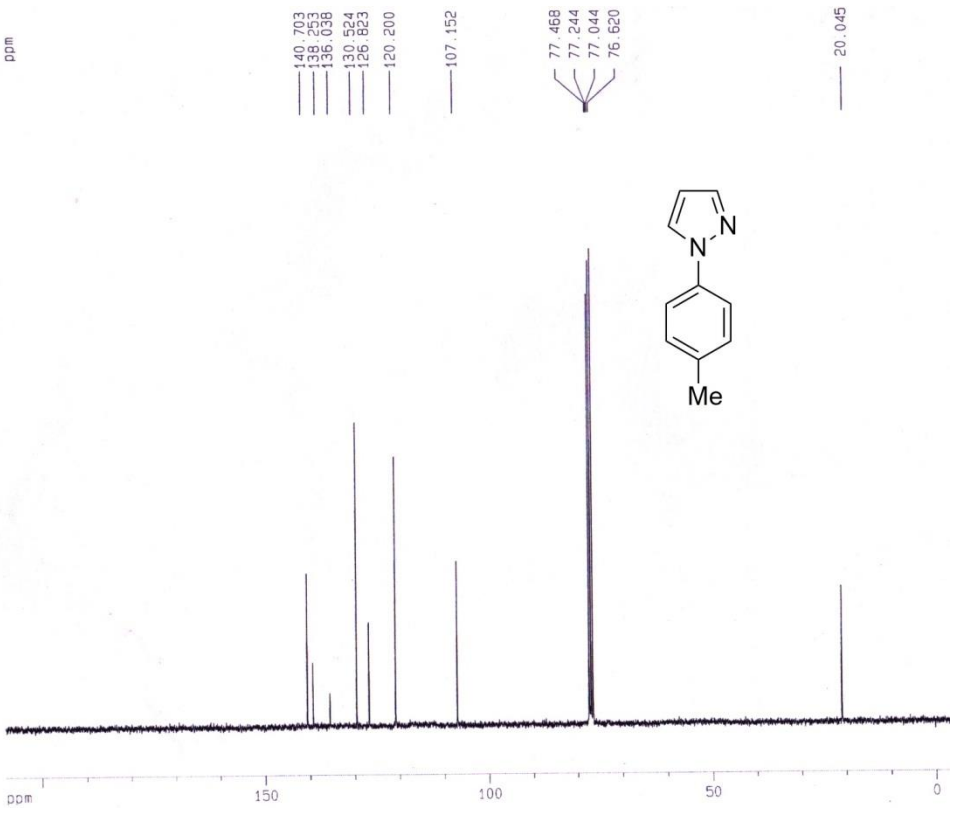
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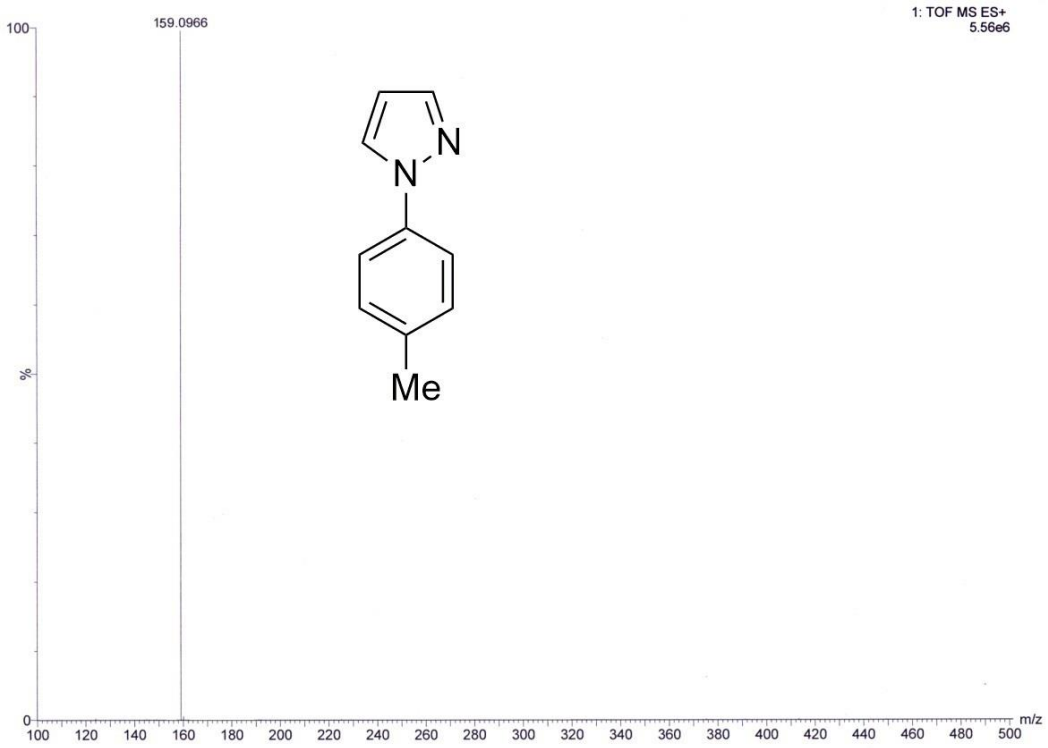

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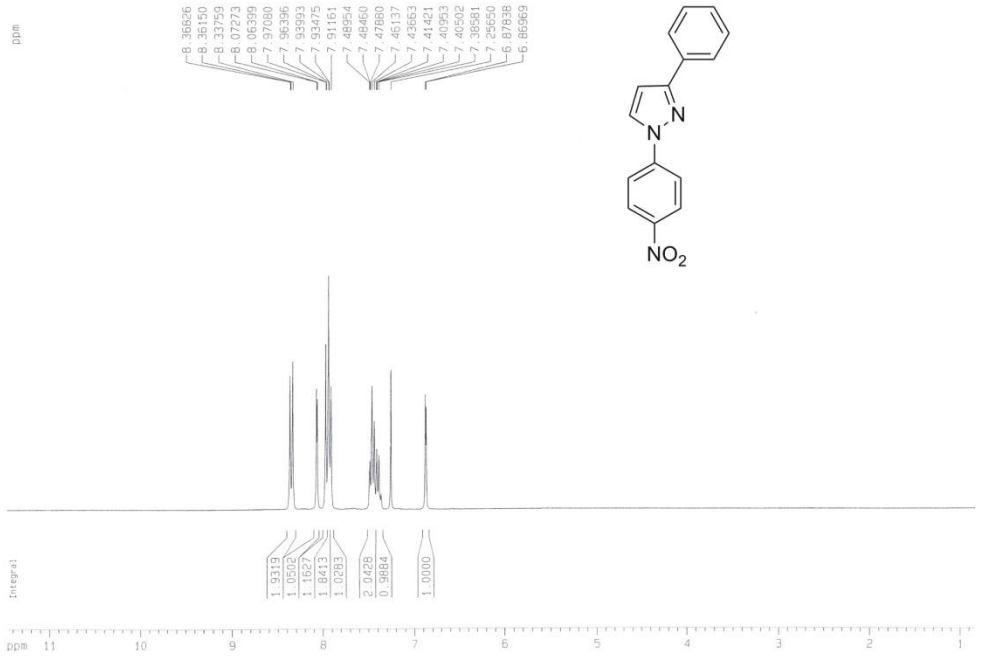

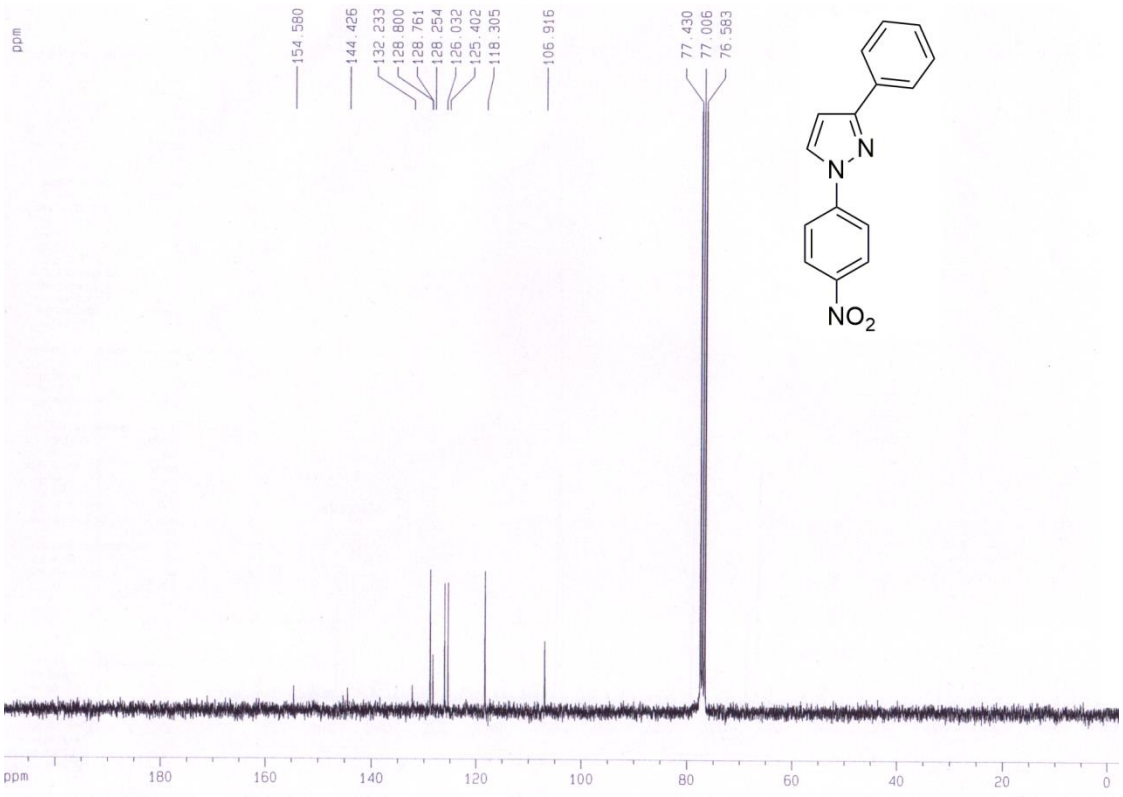

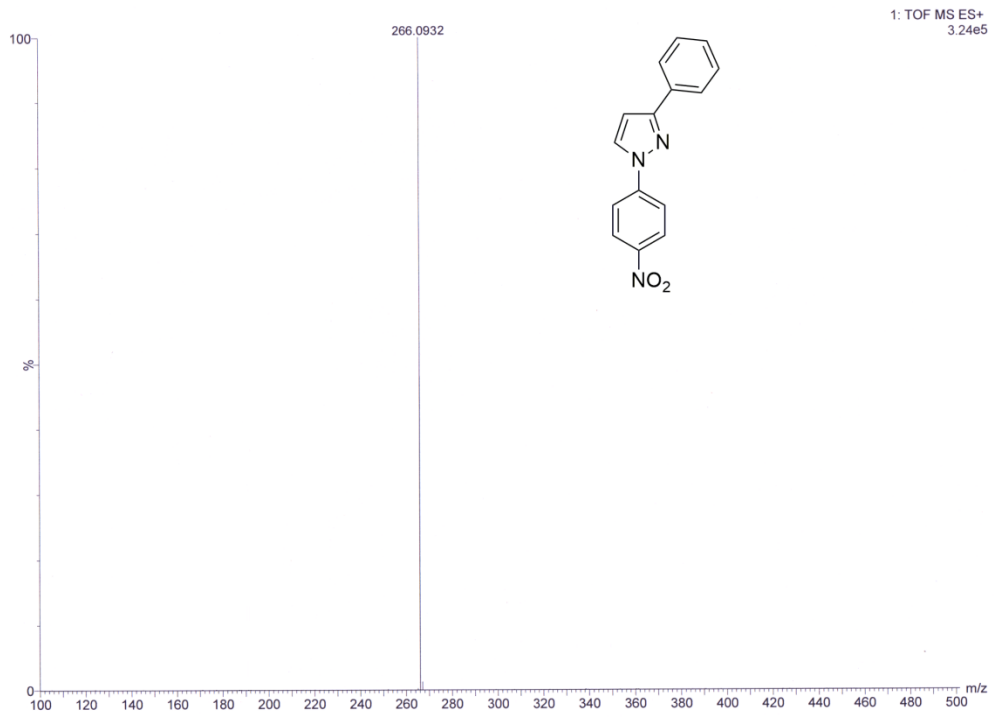

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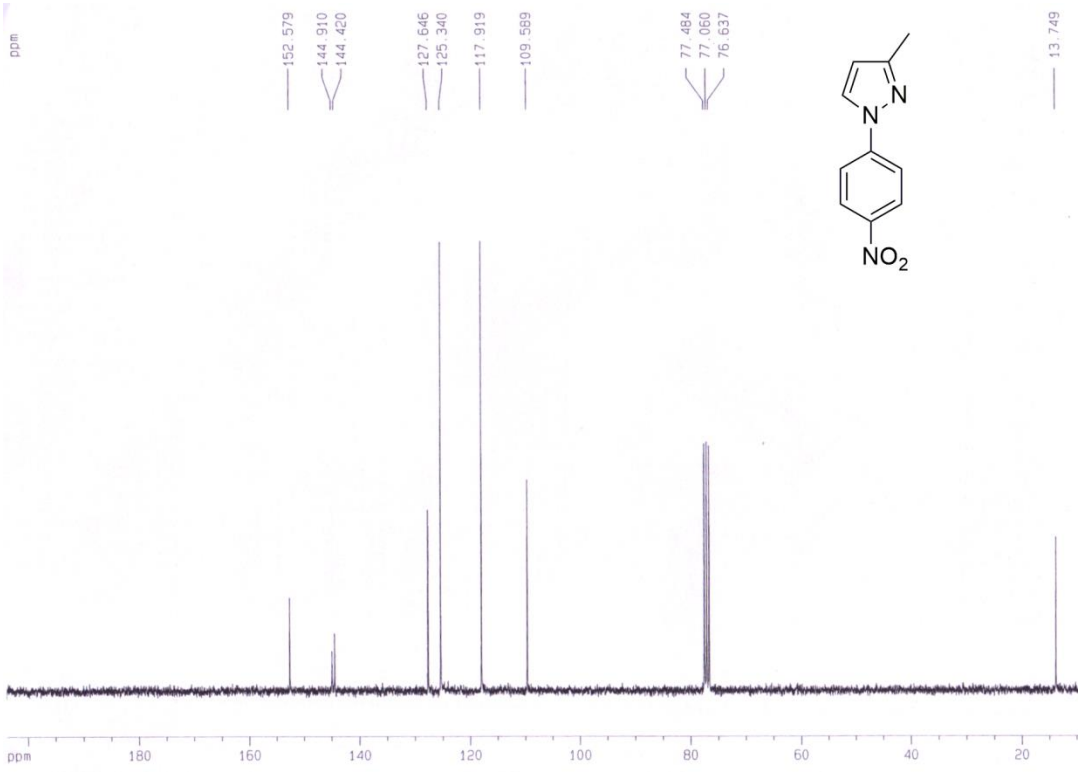
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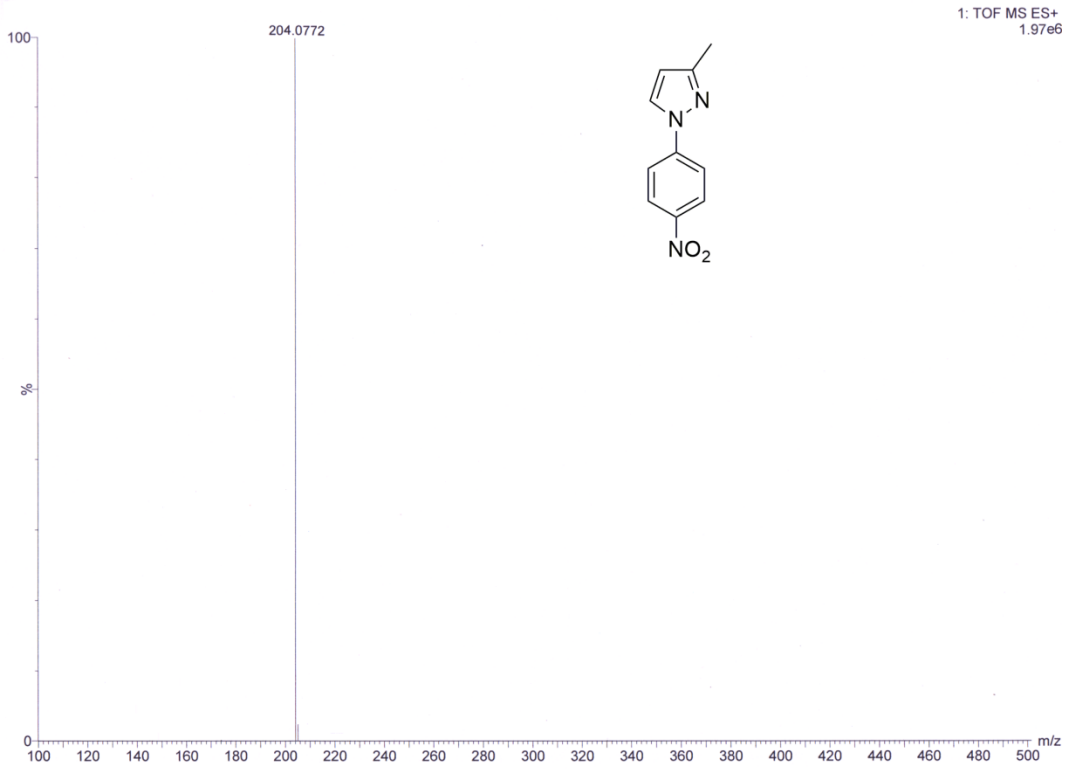

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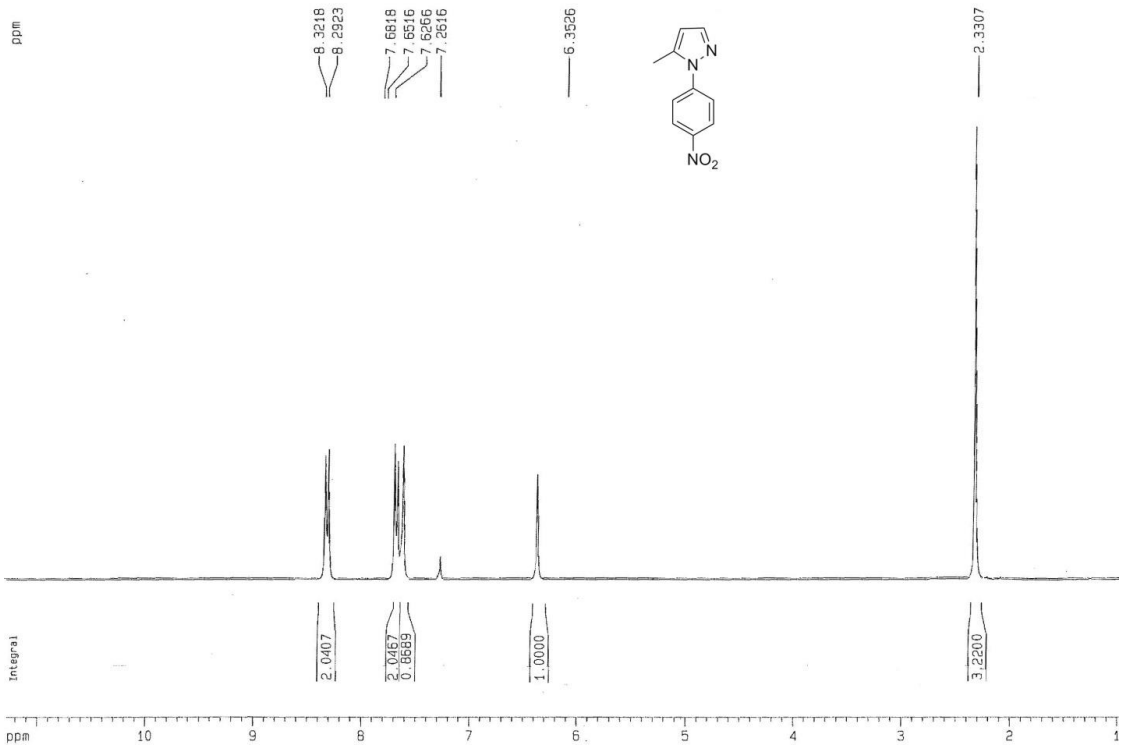

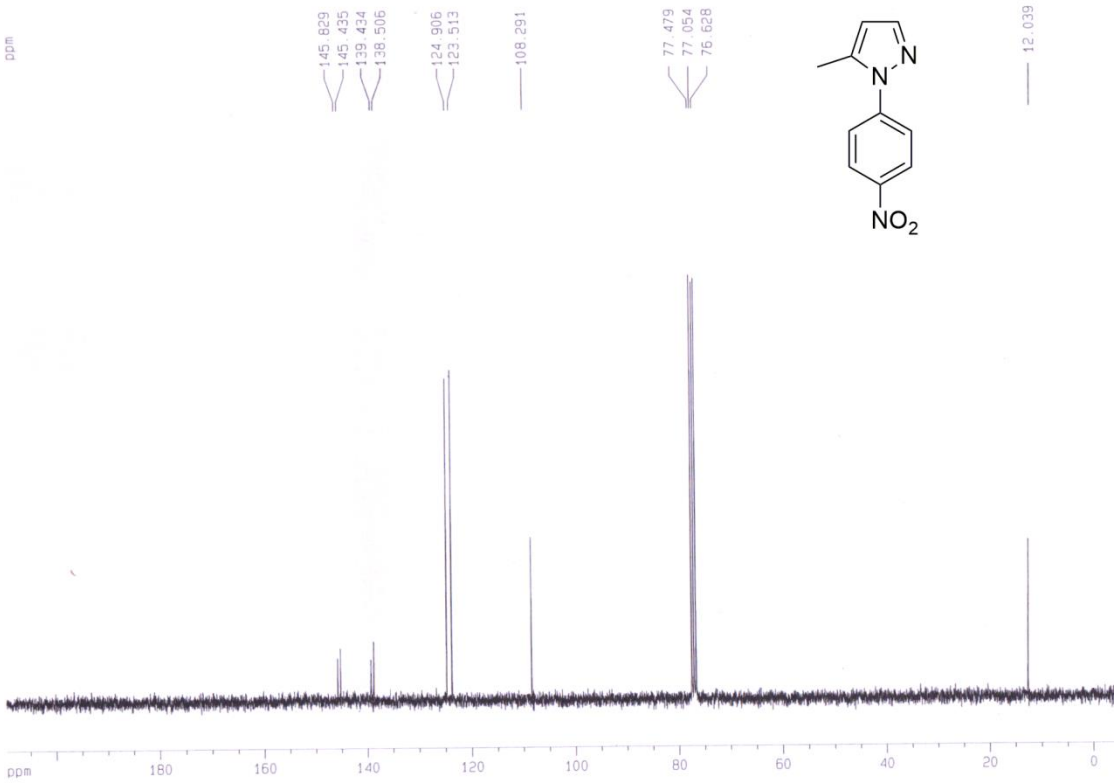

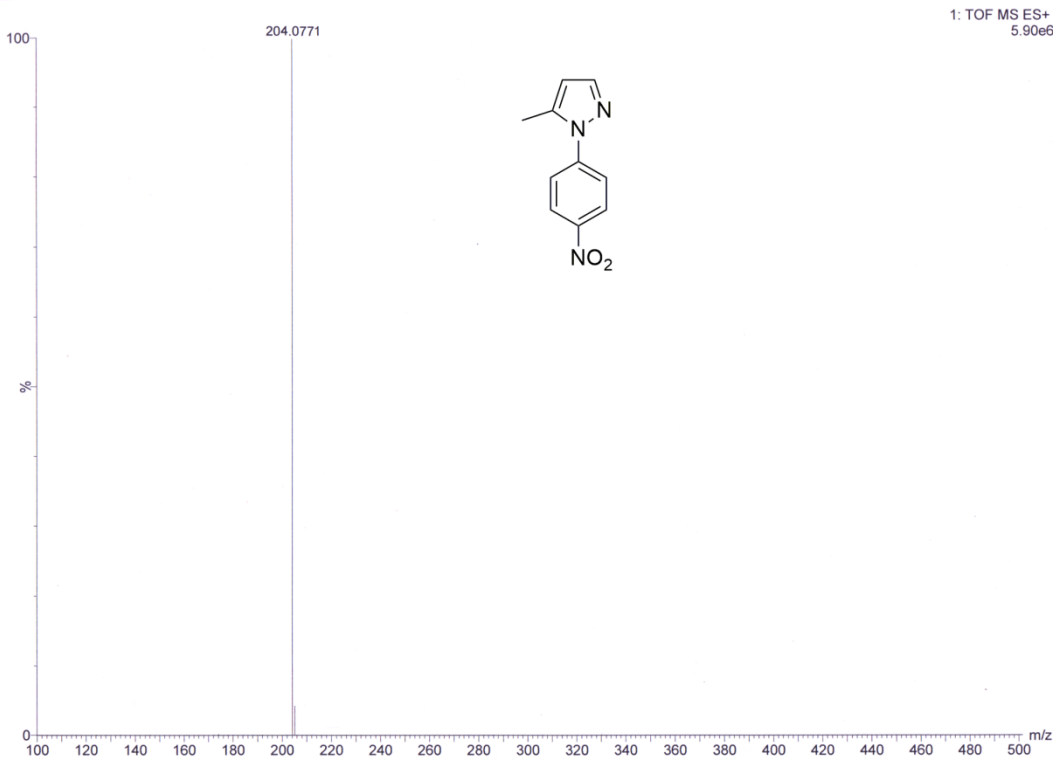

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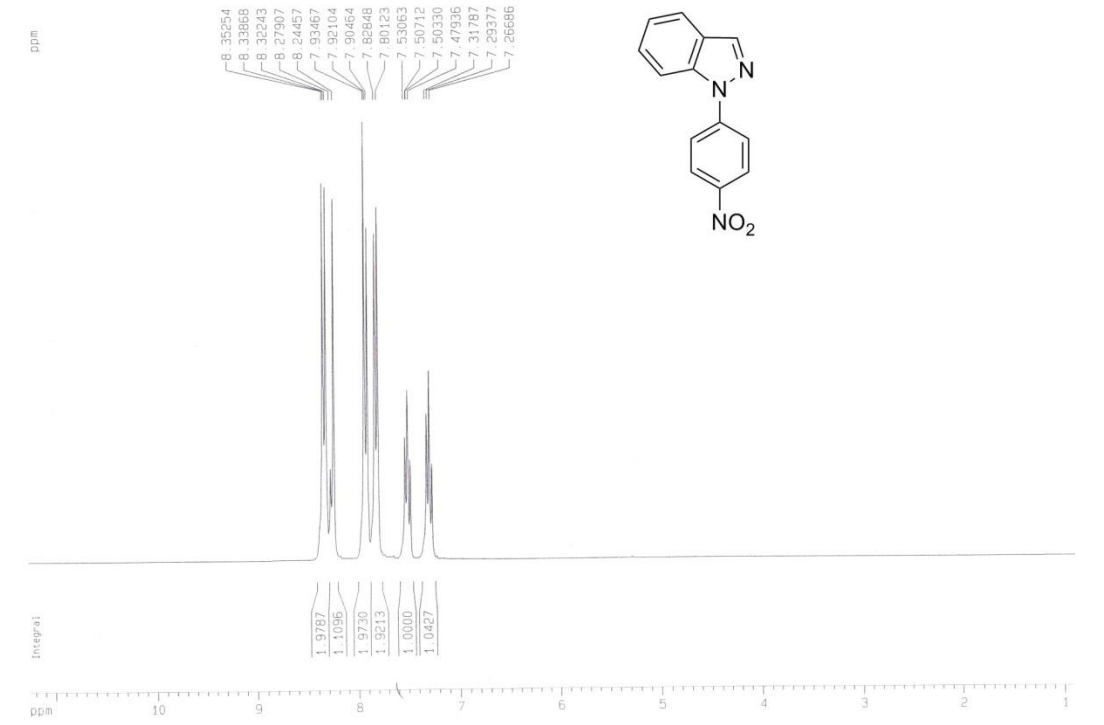
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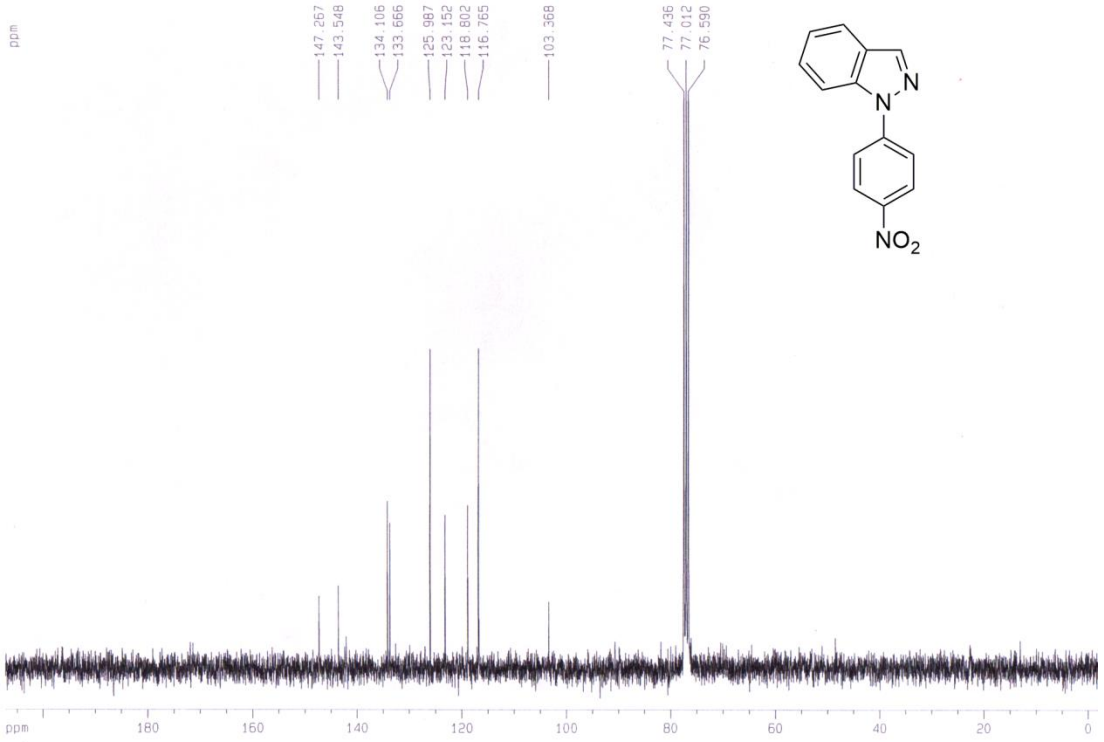
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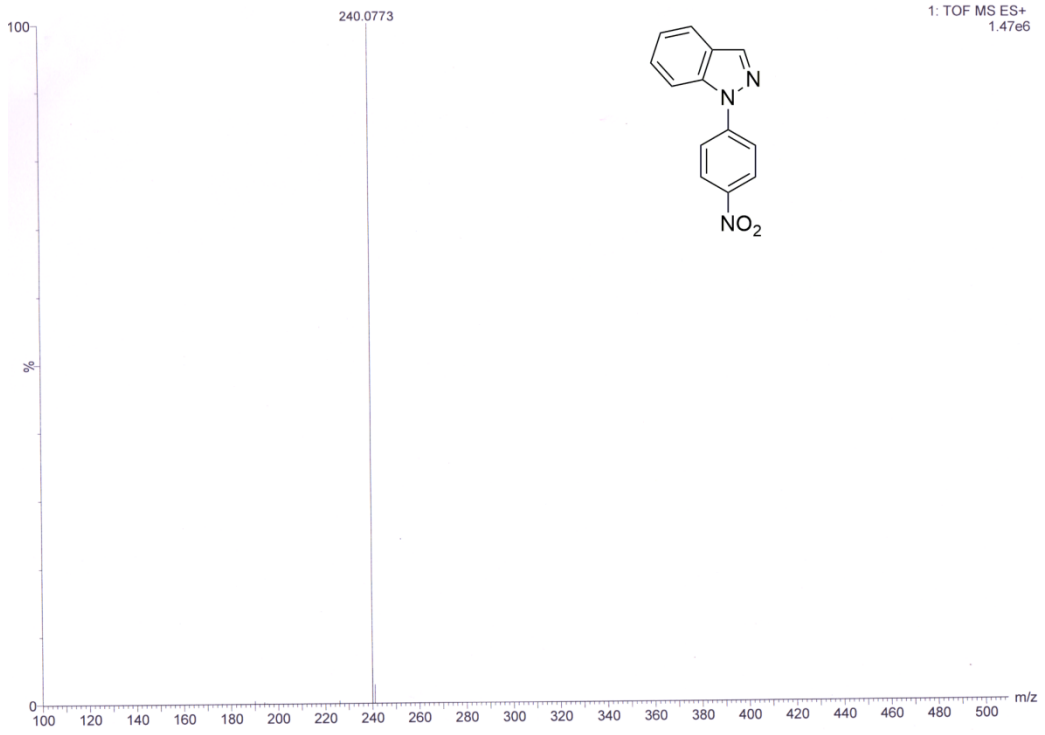
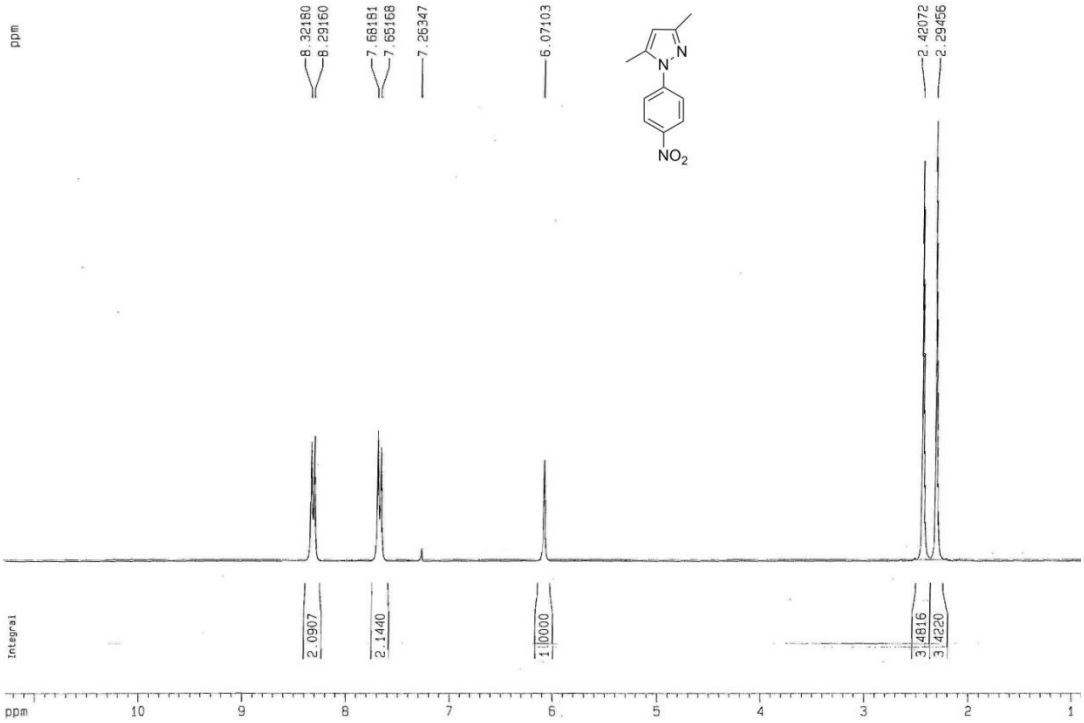
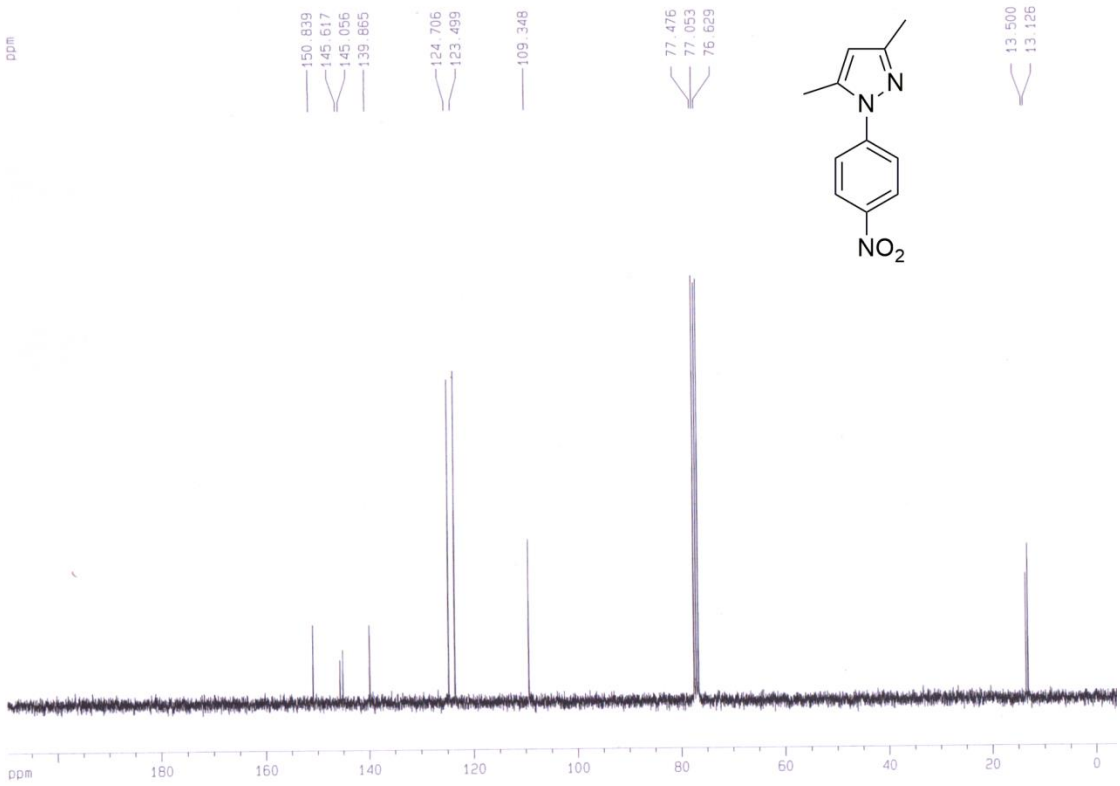
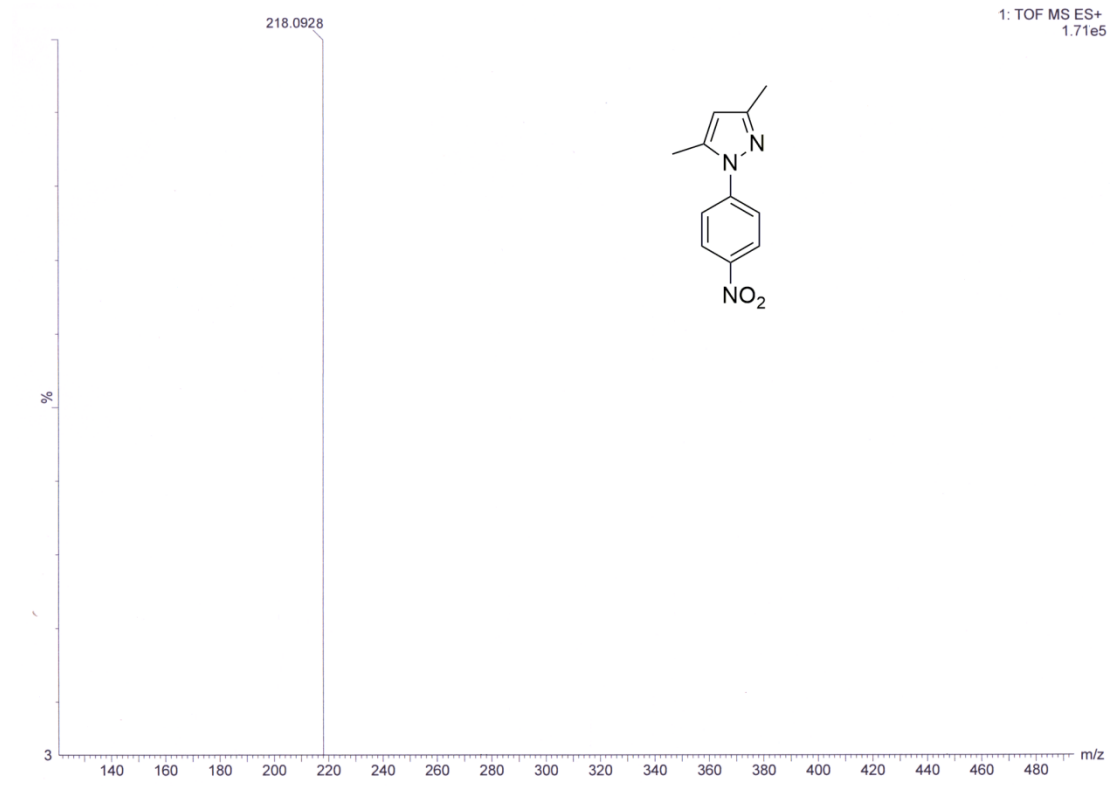


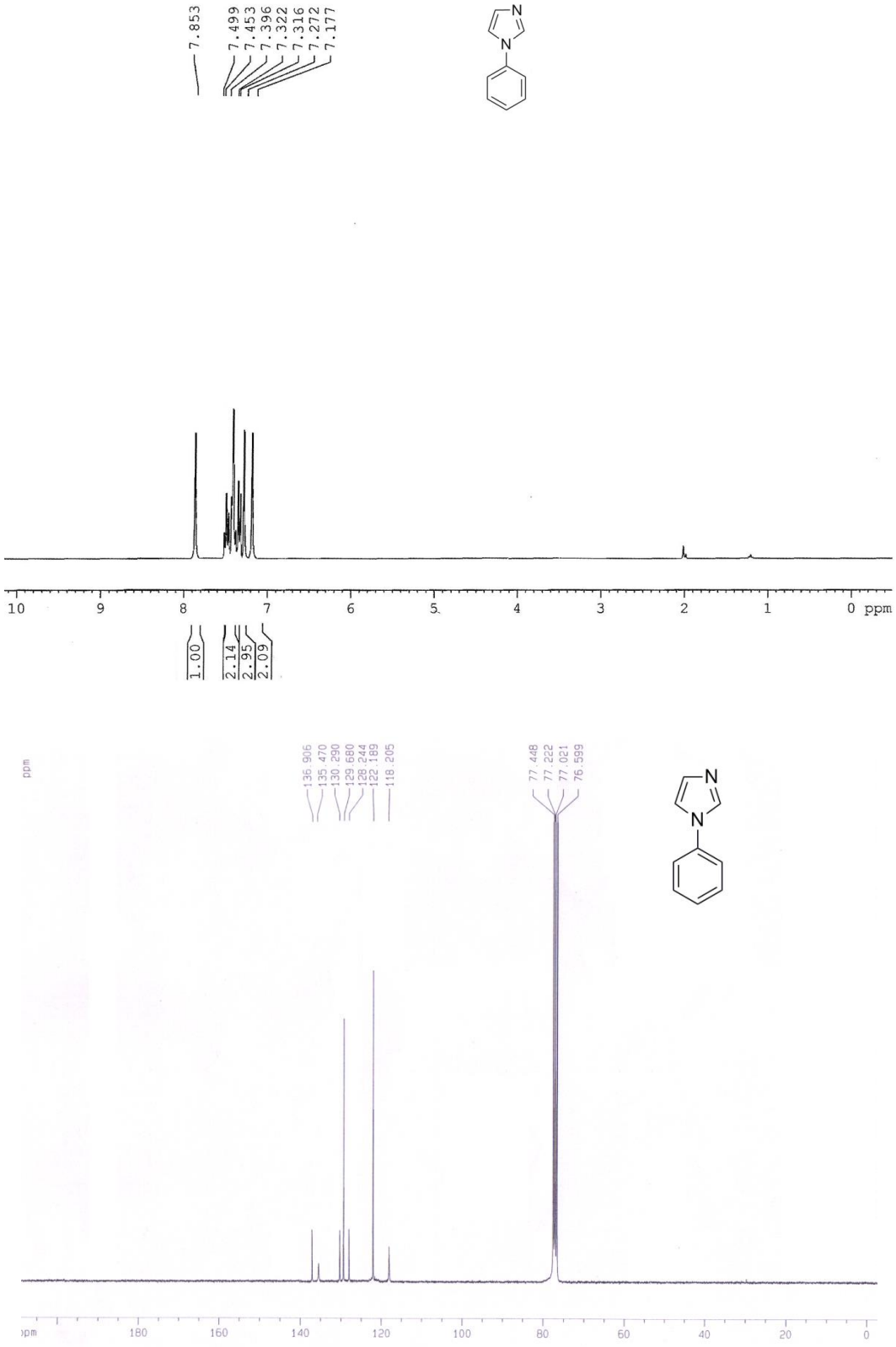
Entry 12

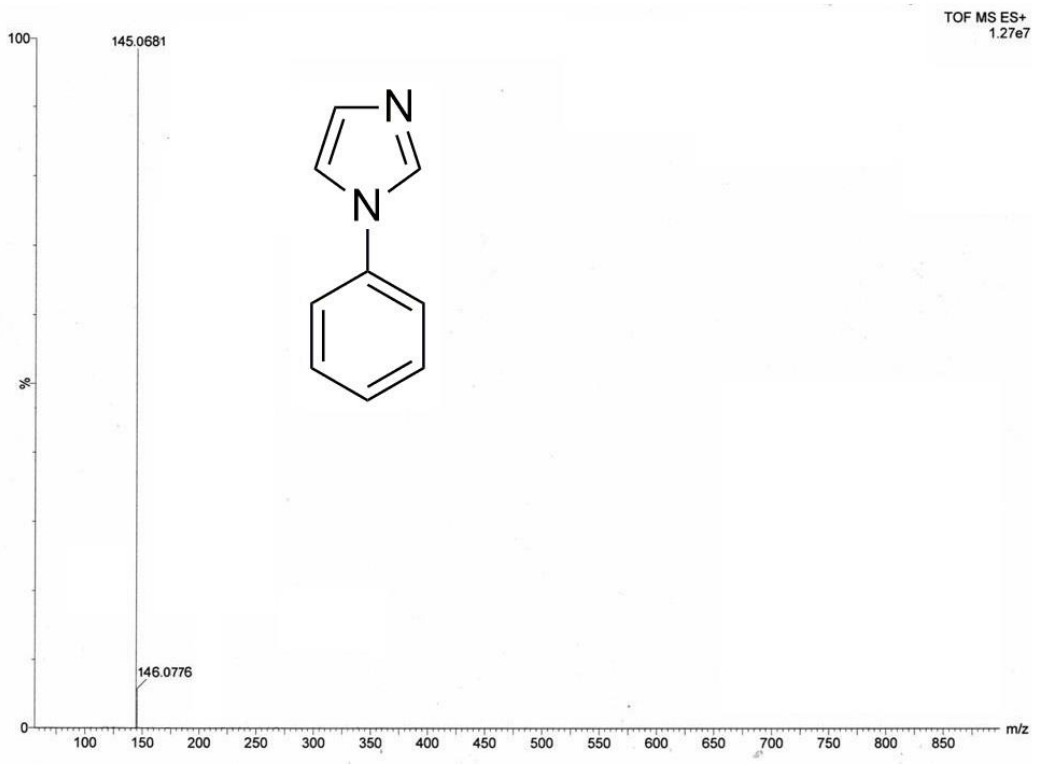



ppm
150.839
145.617
145.056
139.865
124.706
123.499
109.348
77.476
77.053
76.629
13.500
13.126
N
N
NO2
ppm
180
160
140
120
100
80
60
40
20
0

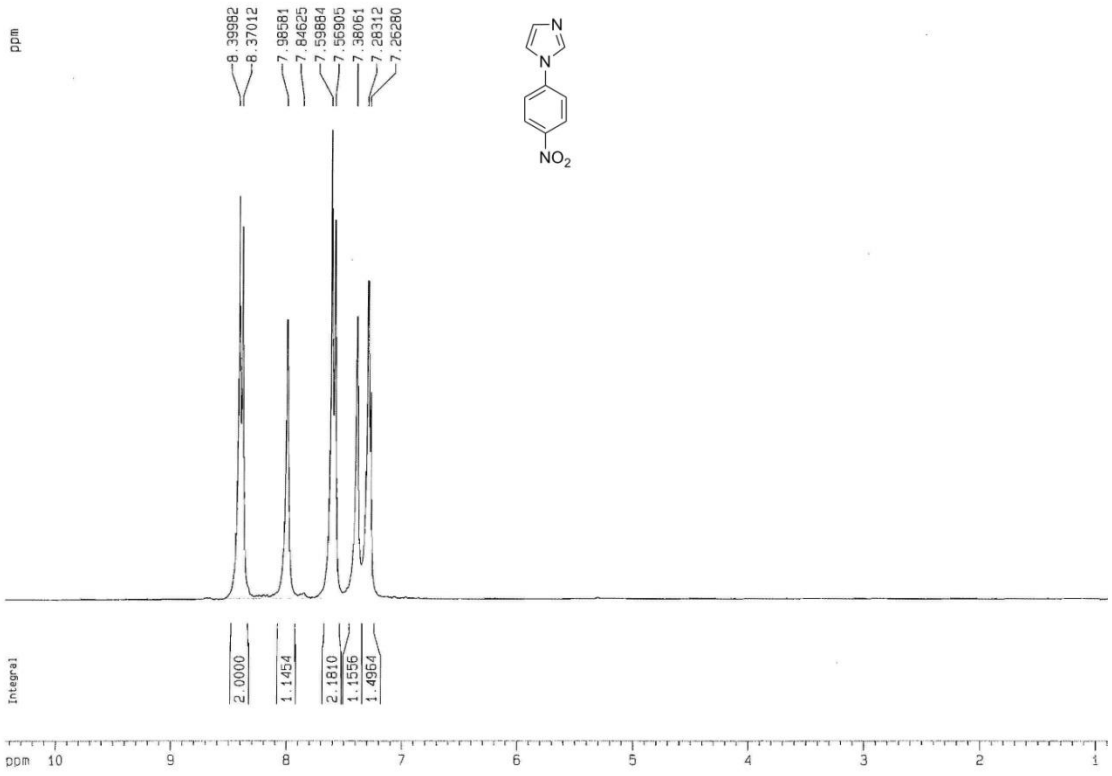

218.0928
1: TOF MS ES+
1.71e5
N
N
NO2
%
3
m/z
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480

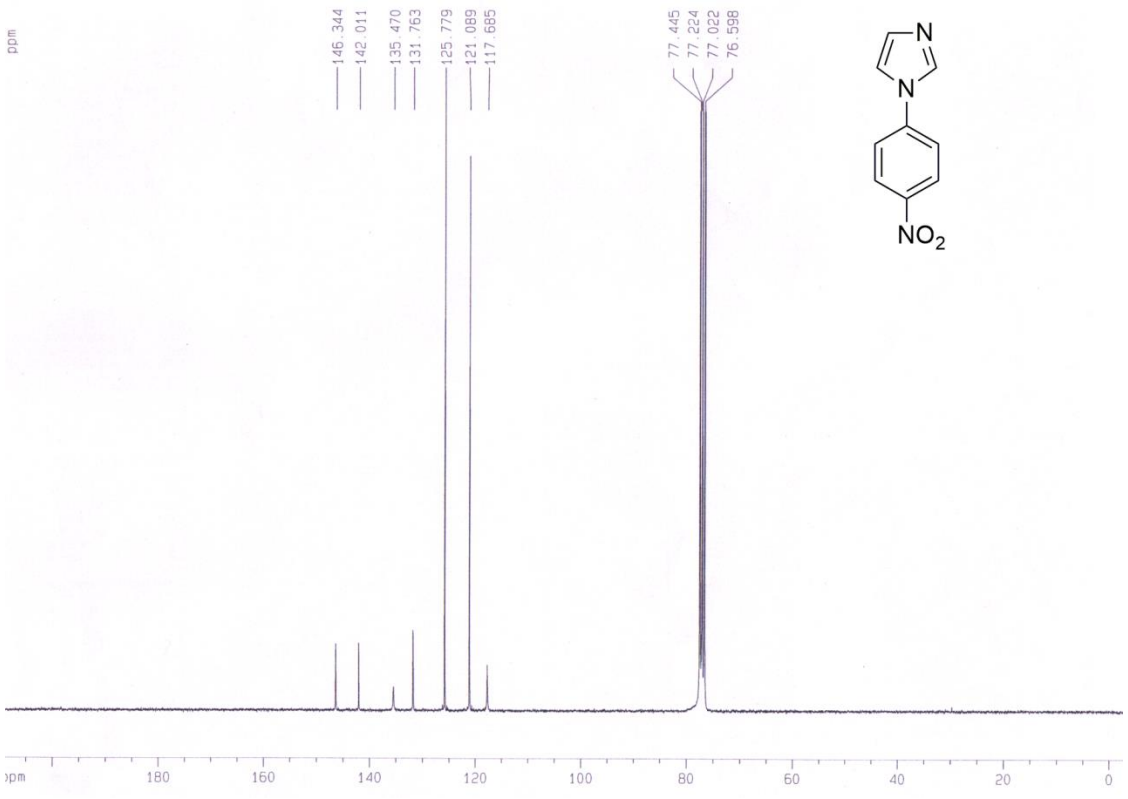
Entry 13

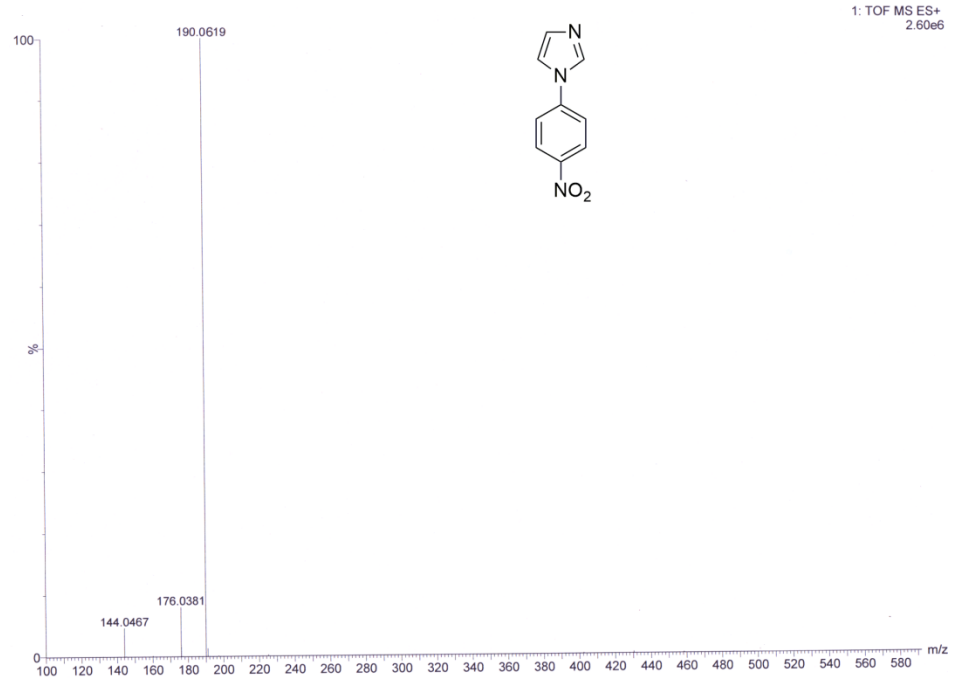




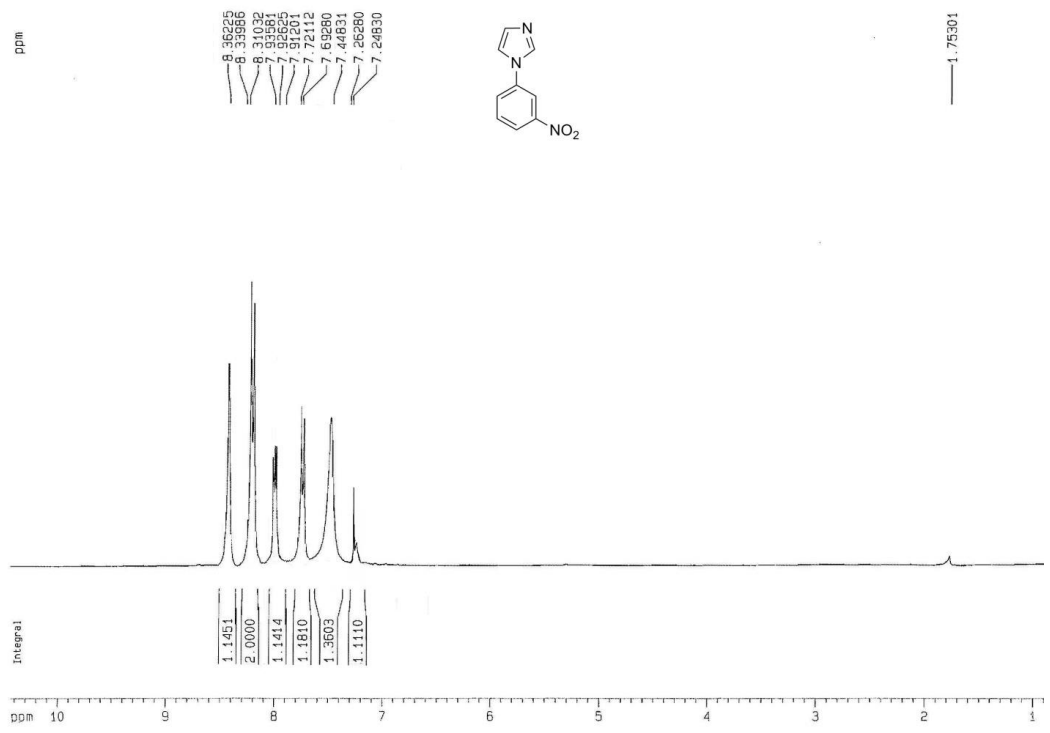
Entry 14

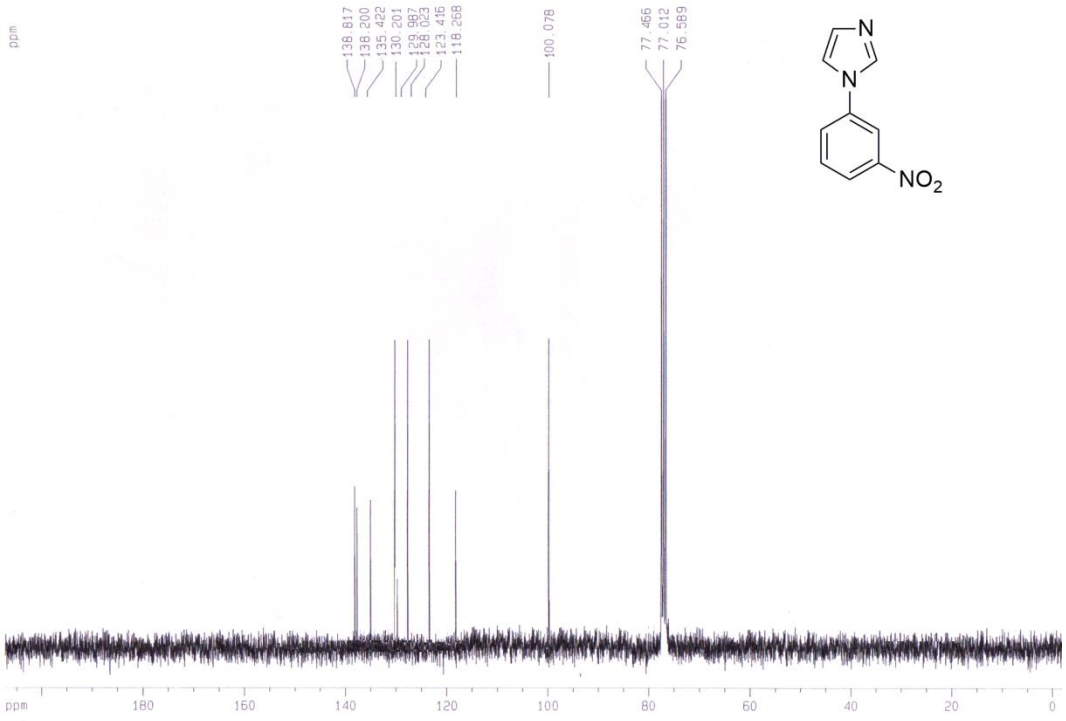


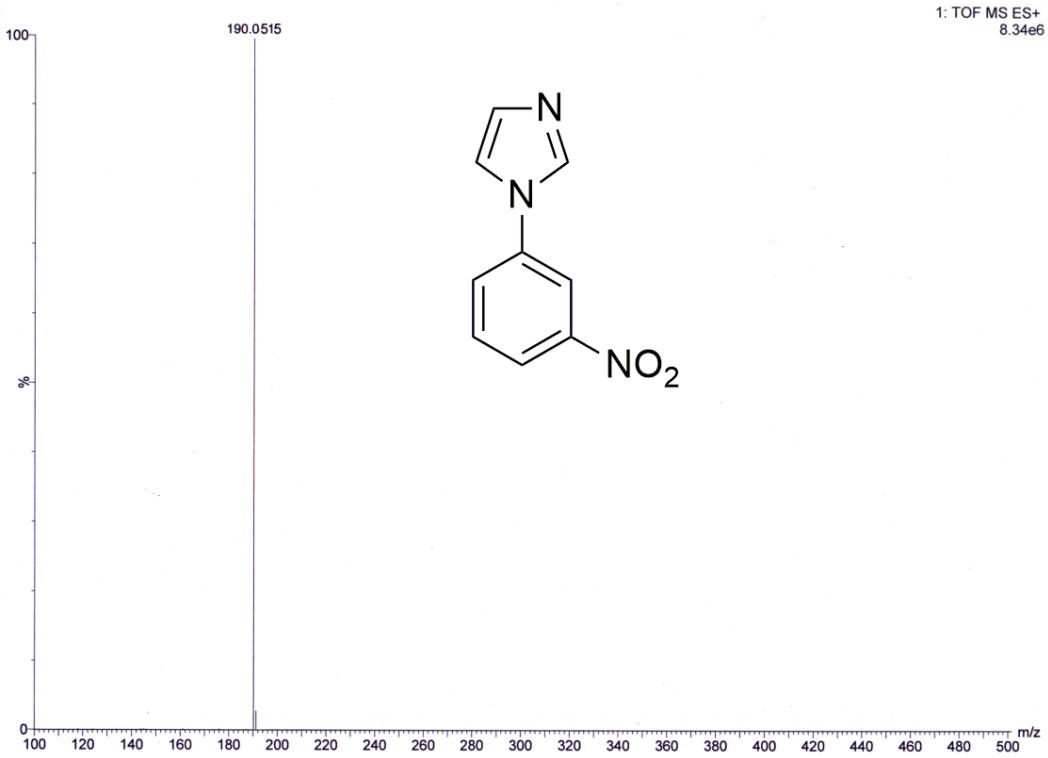




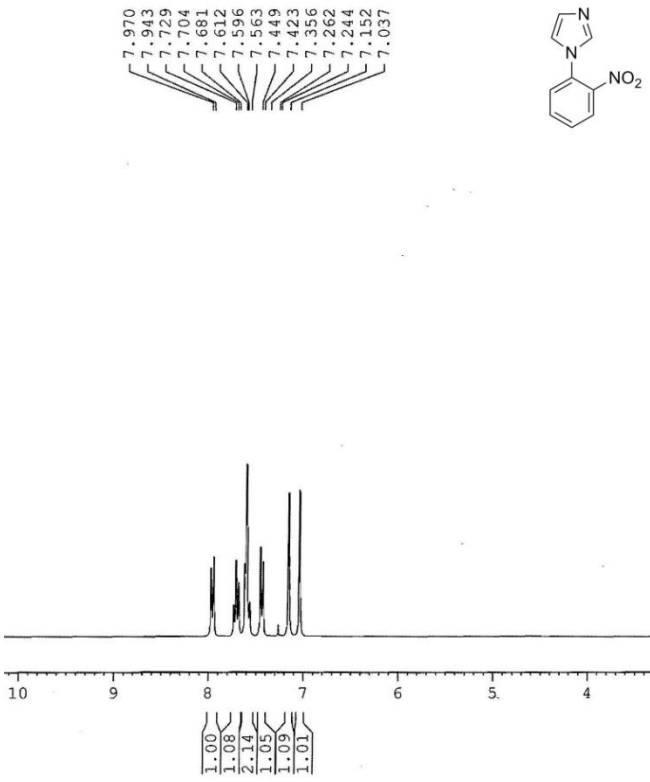
Entry 15

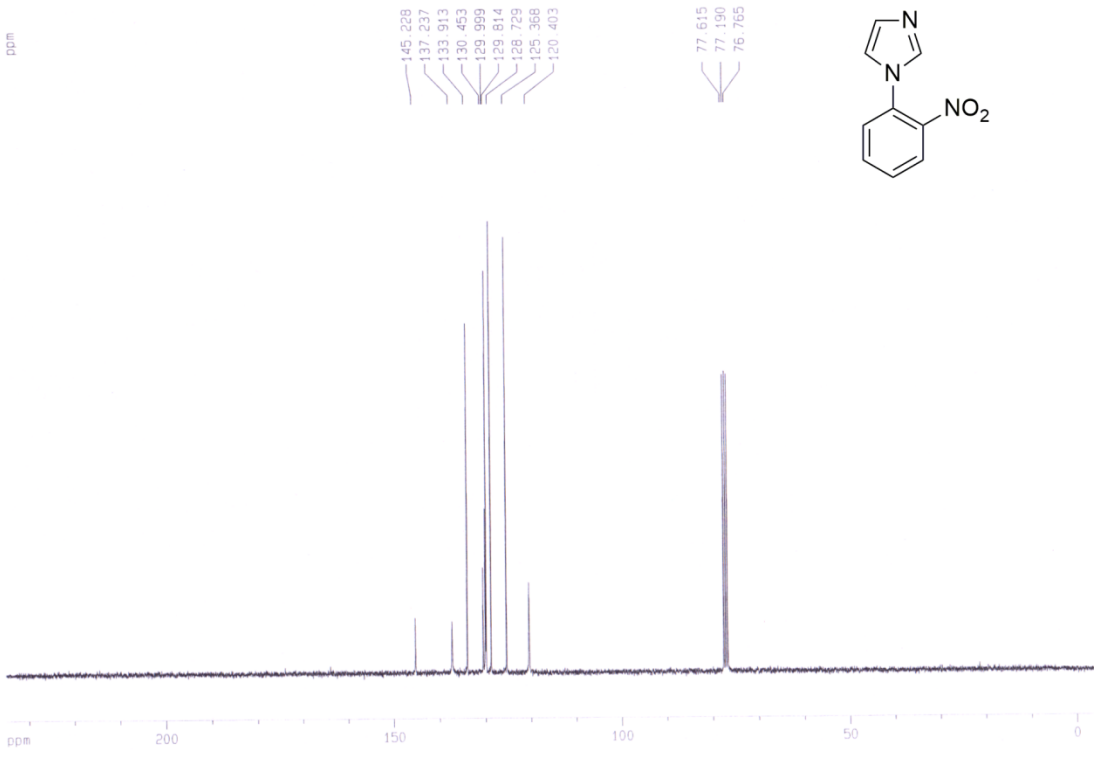

ppm
8.36225
8.33986
8.31032
7.93581
7.92625
7.91201
7.72112
7.69280
7.44831
7.26280
7.24830
1.75301
Integral
1.1451
2.0000
1.1414
1.1810
1.3603
1.1110
ppm 10 9 8 7 6 5 4 3 2 1

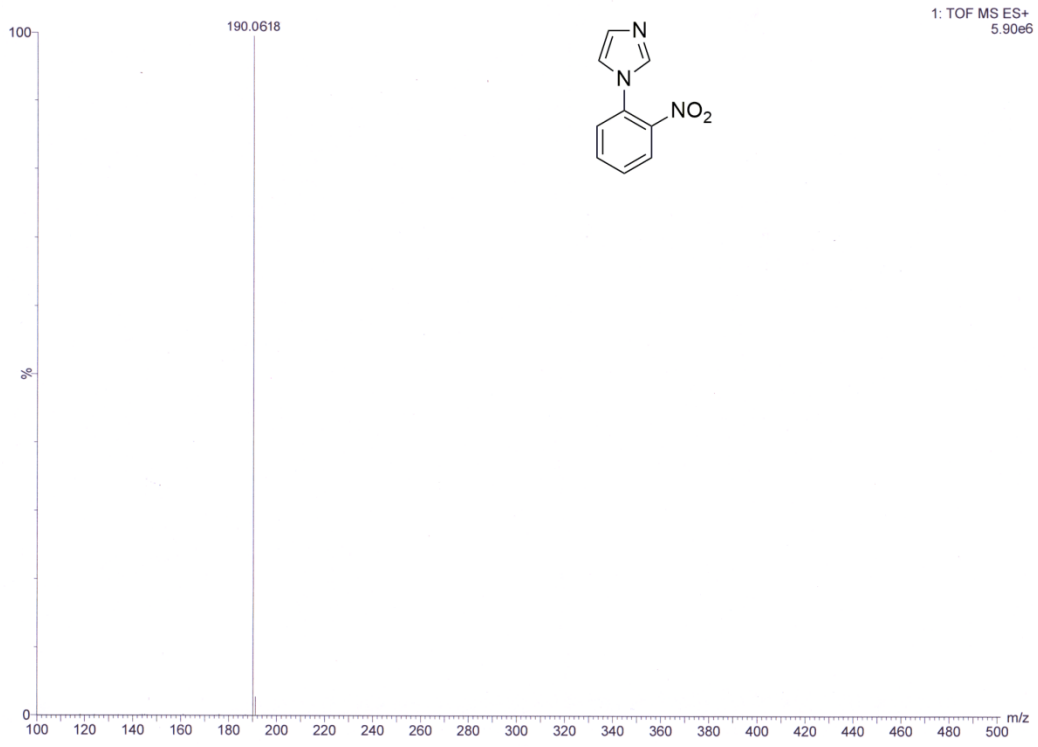

ppm
138.817
138.200
135.422
130.201
129.987
128.023
123.416
118.268
100.078
77.466
77.012
76.589
ppm 180 160 140 120 100 80 60 40 20 0



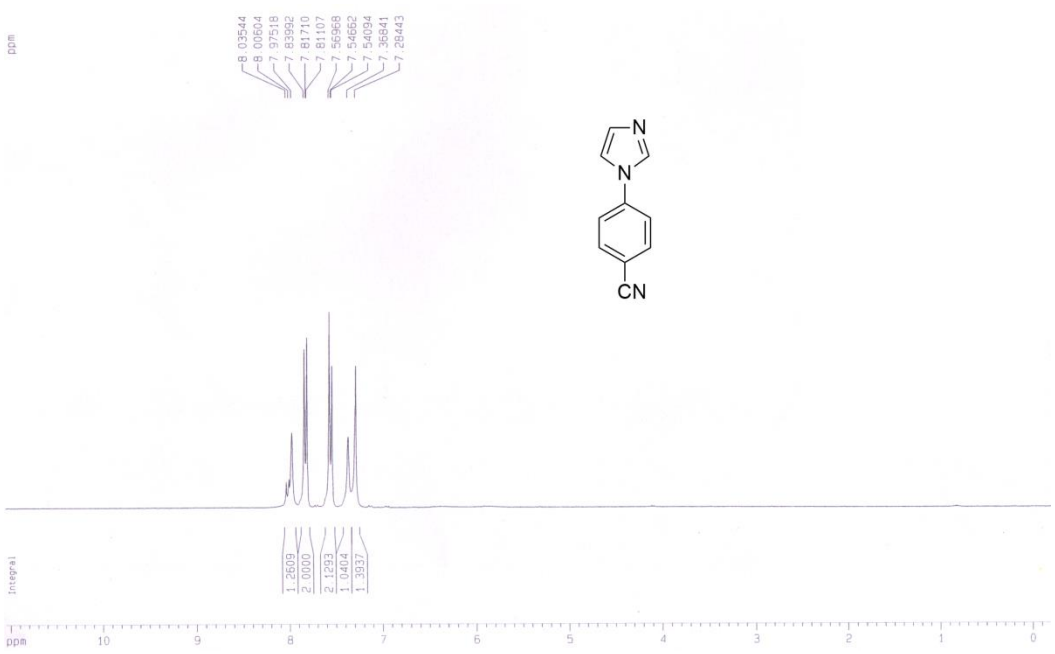
Entry 16

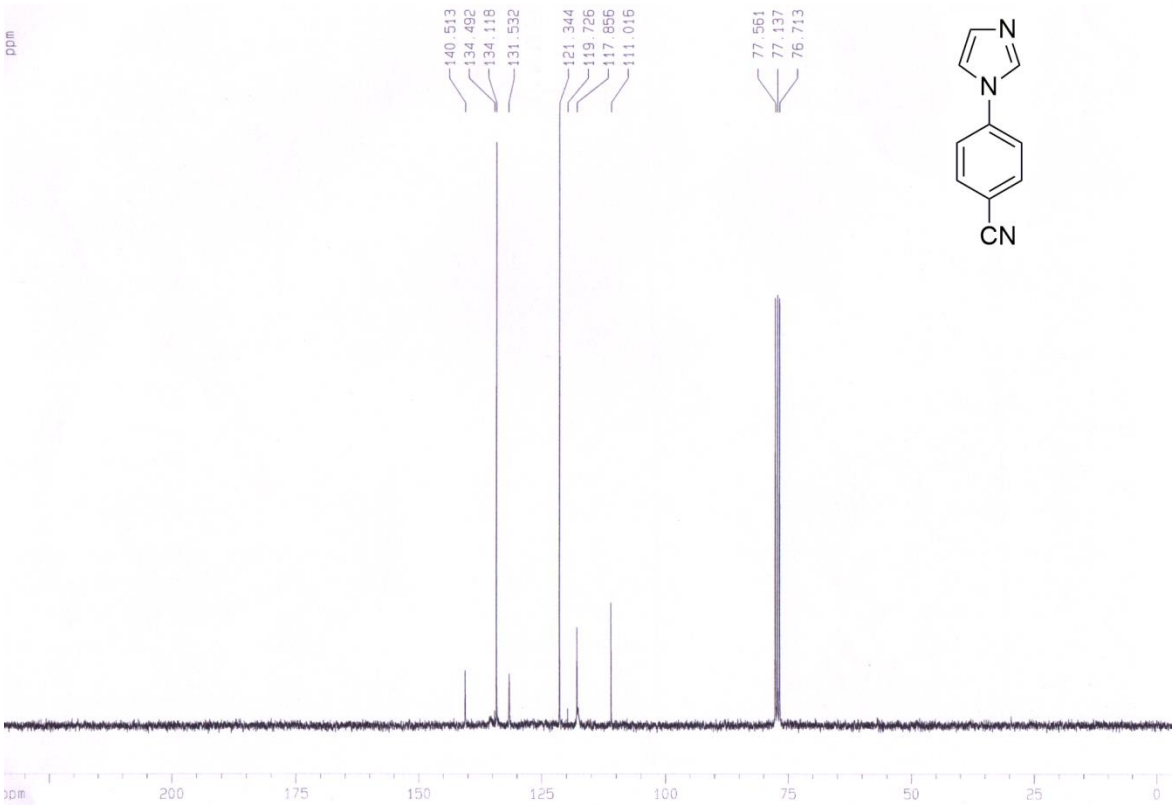


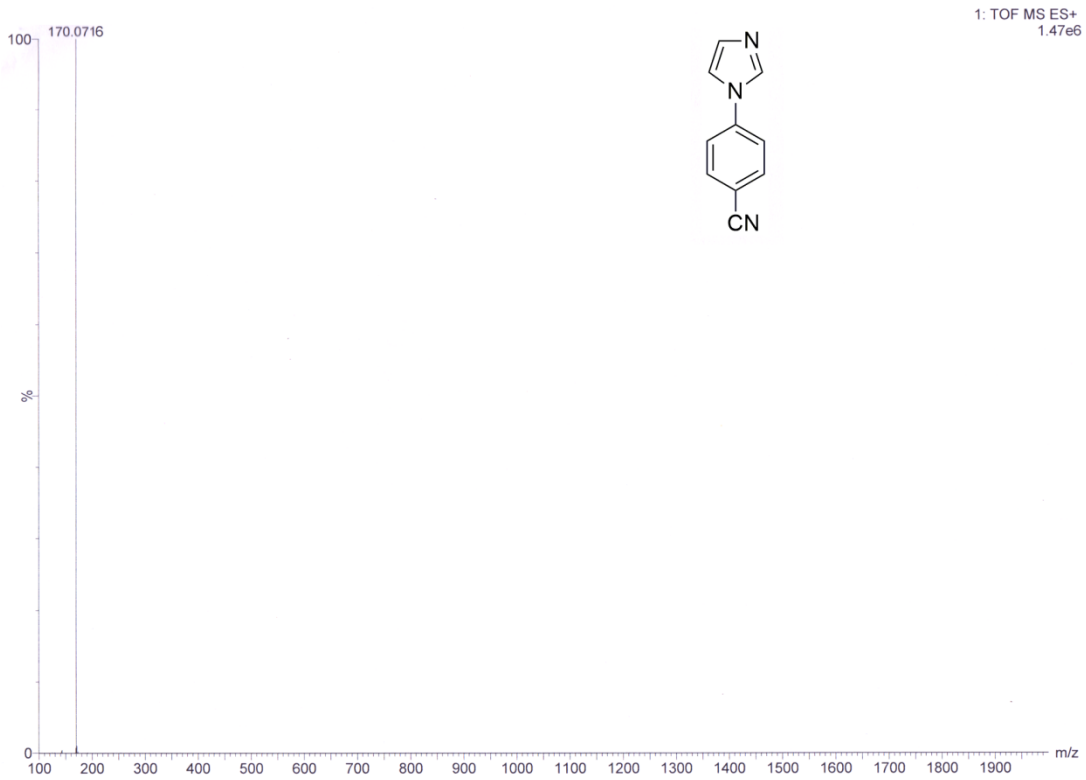




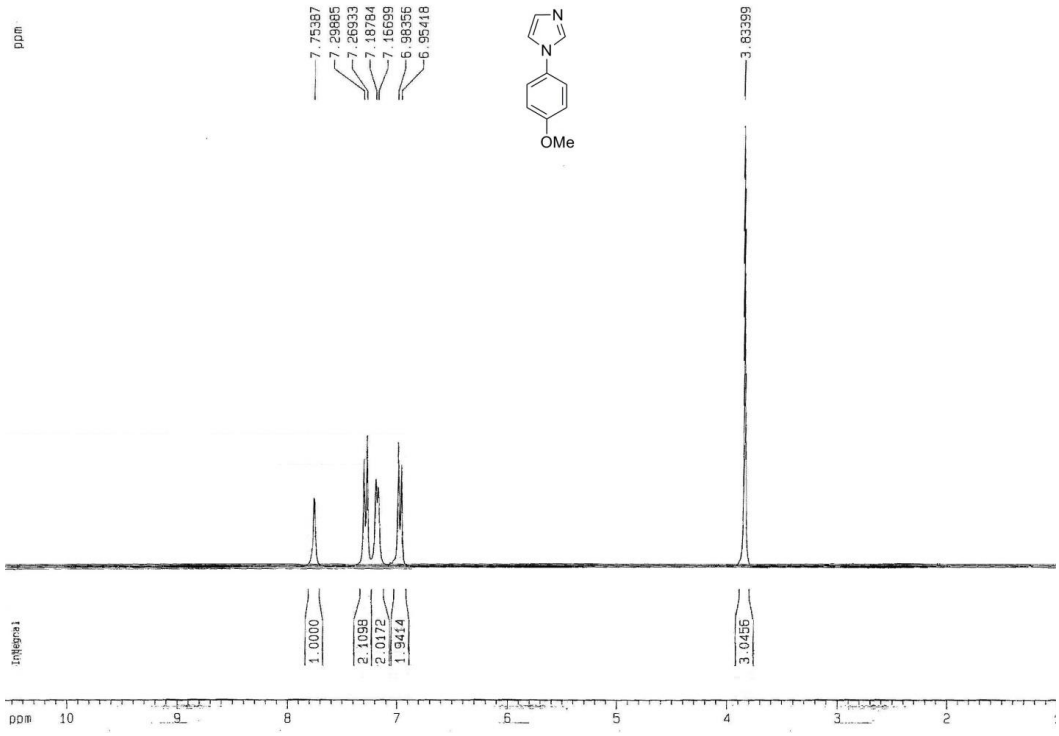
Entry 17

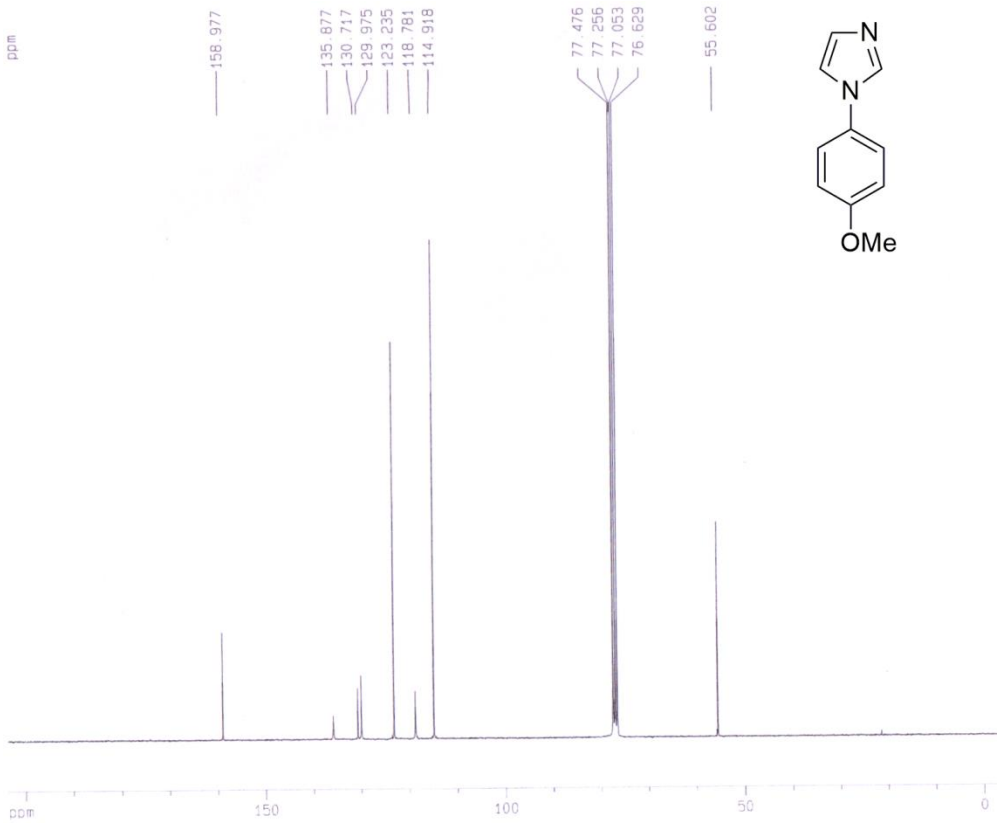

8.03544
8.00604
7.97518
7.83992
7.81710
7.81107
7.56968
7.54662
7.54094
7.36841
7.28443
N
N
CN
1.2609
2.0000
2.1293
1.0404
1.3937
ppm
10
9
8
7
6
5
4
3
2
1
0

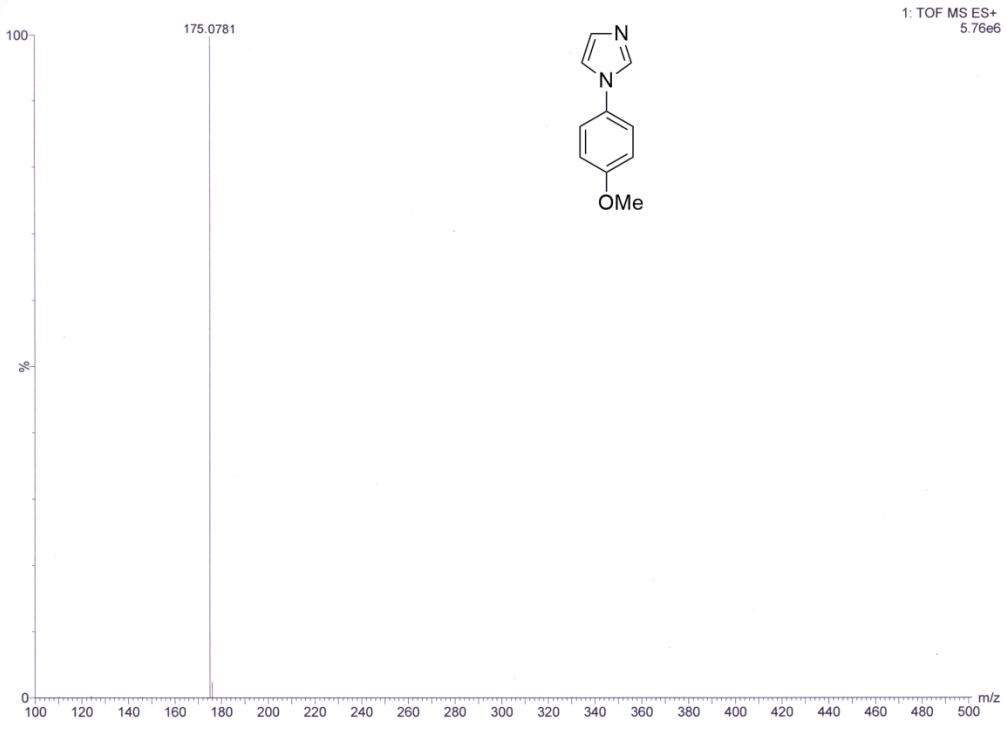

140.513
134.492
134.118
131.532
121.344
119.726
117.856
111.016
77.561
77.137
76.713
N
N
CN
200
175
150
125
100
75
50
25
0



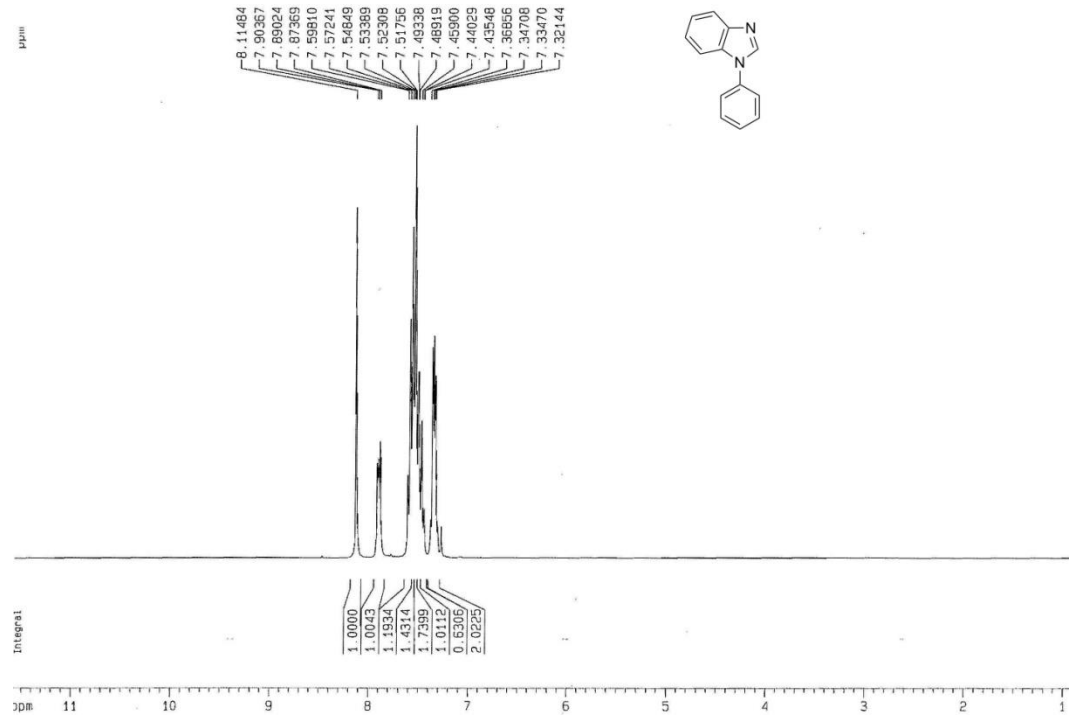
Entry 18







Entry 19


8.11484
7.90367
7.89024
7.87369
7.59810
7.57241
7.54849
7.53389
7.52308
7.51756
7.49338
7.48919
7.45900
7.44029
7.43548
7.36656
7.34708
7.33470
7.32144
Integral
1.0000
1.0043
1.1934
1.4314
1.7399
1.0112
0.6306
2.0225
ppm
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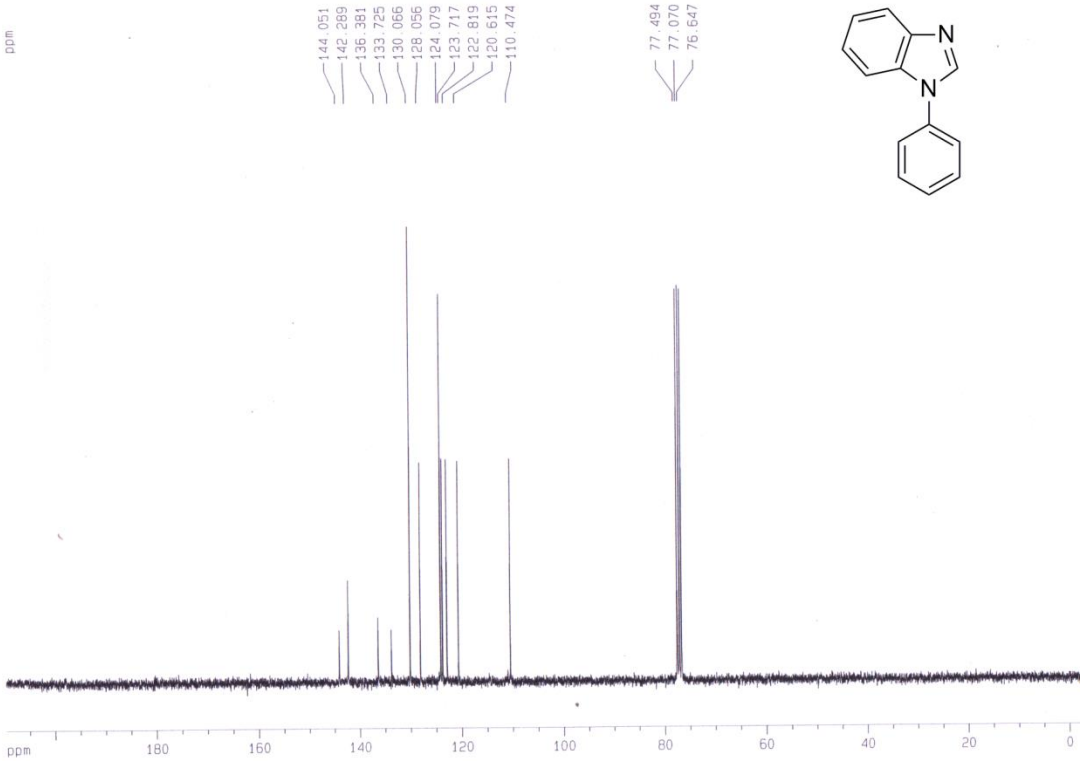
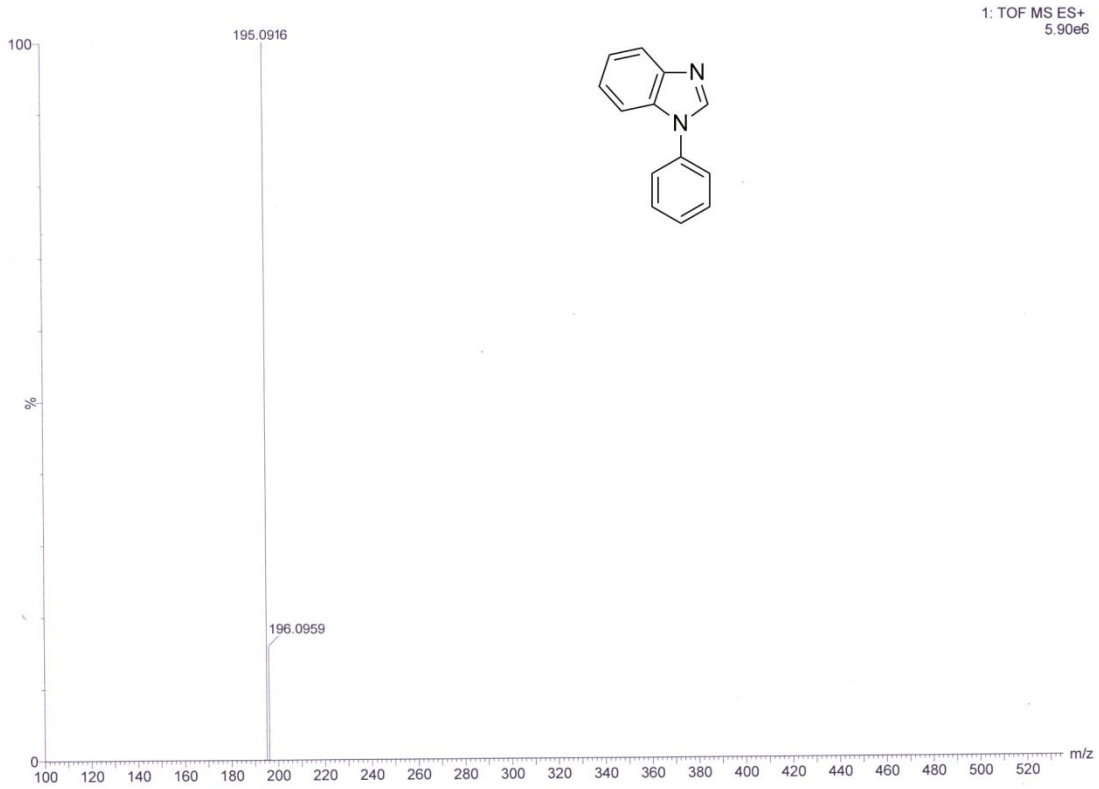
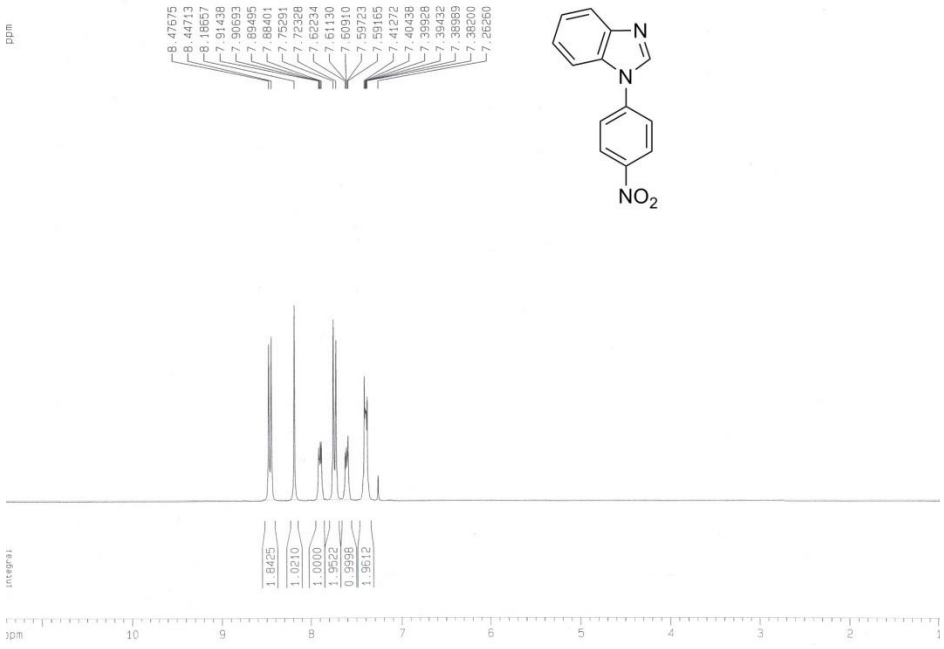
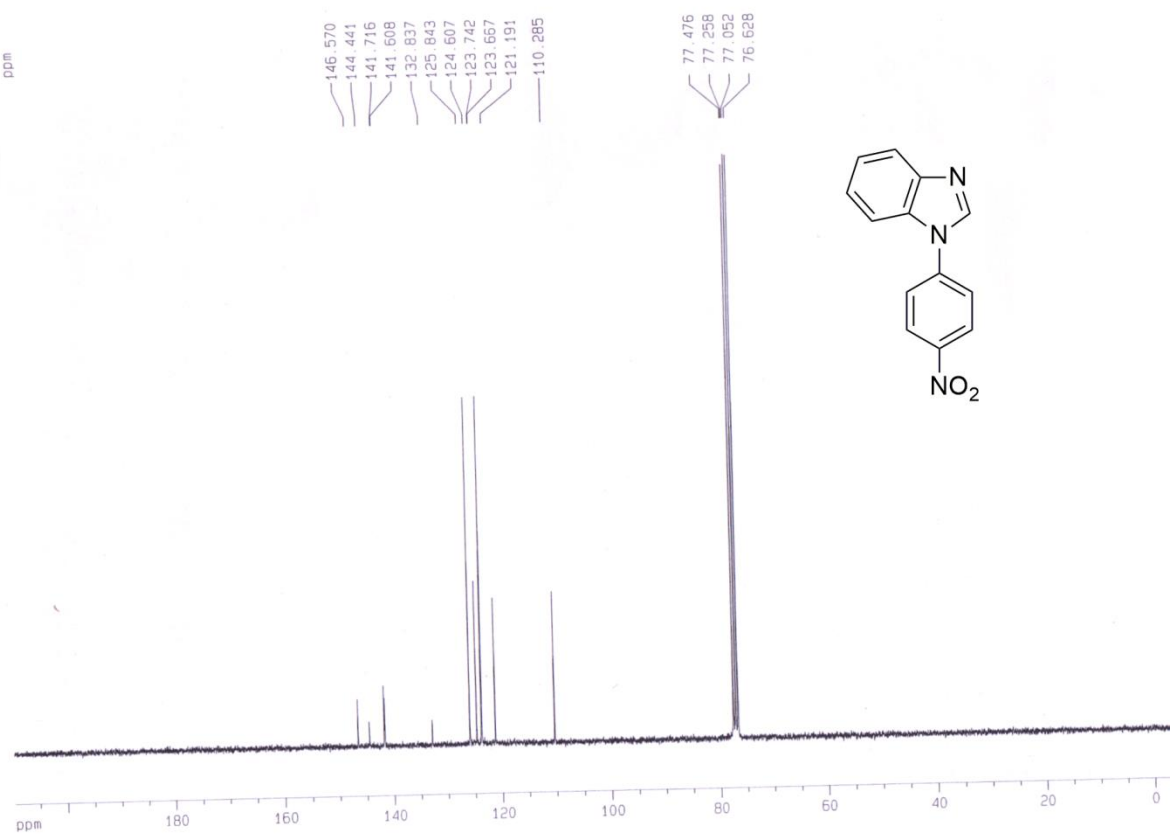
10
9
8
7
6
5
4
3
2
1

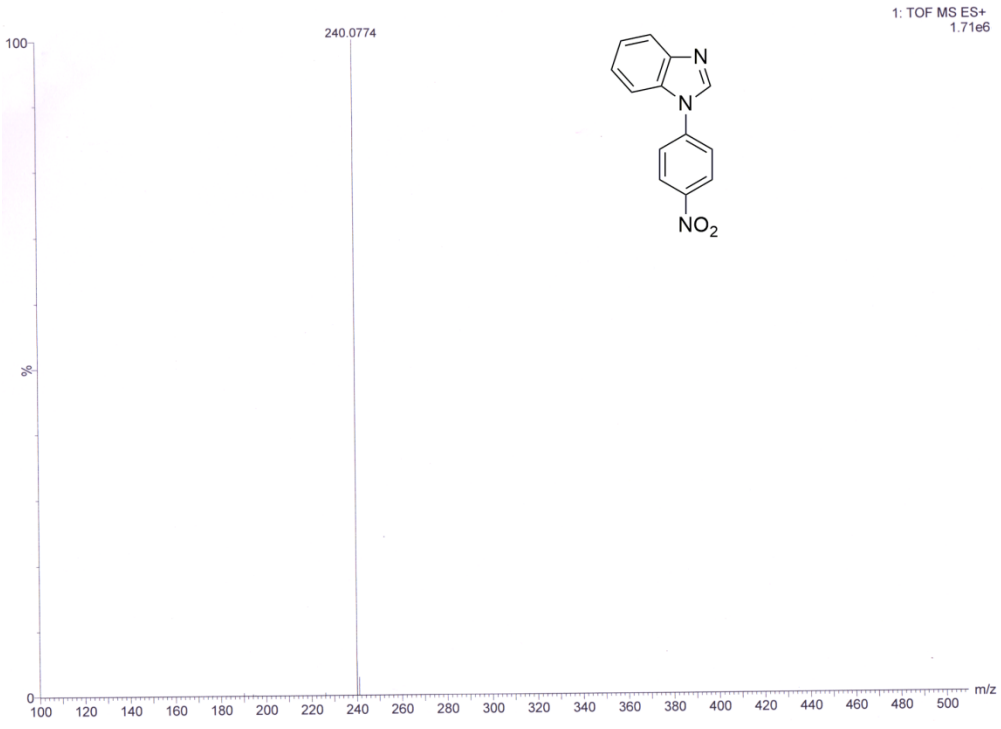

144.051
142.289
136.381
133.725
130.066
128.056
124.079
123.717
122.819
120.615
110.474
77.494
77.070
76.647
ppm
180
160
140
120
100
80
60
40
20
0



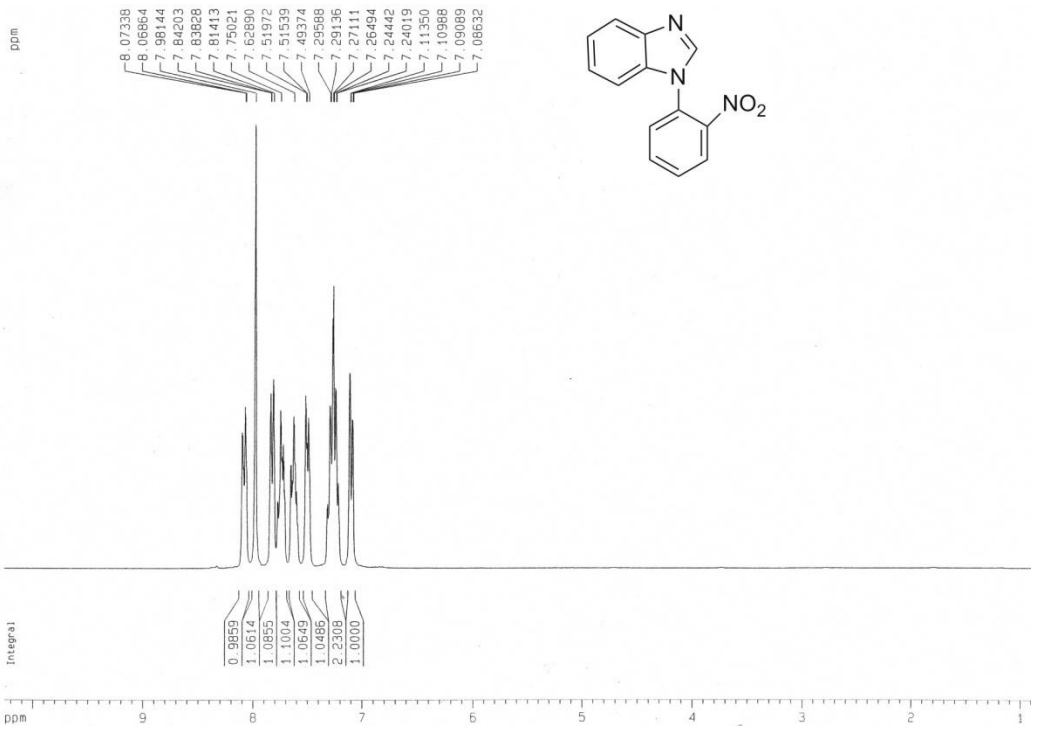
Entry 20

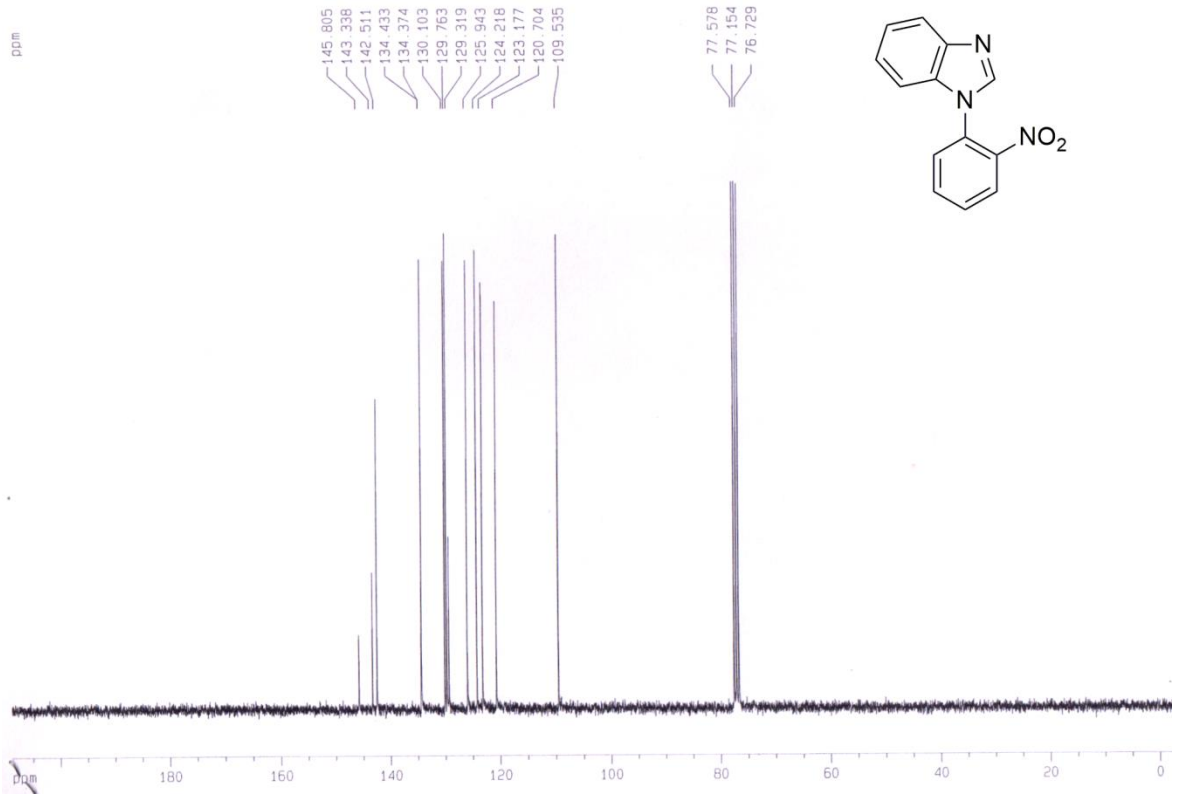


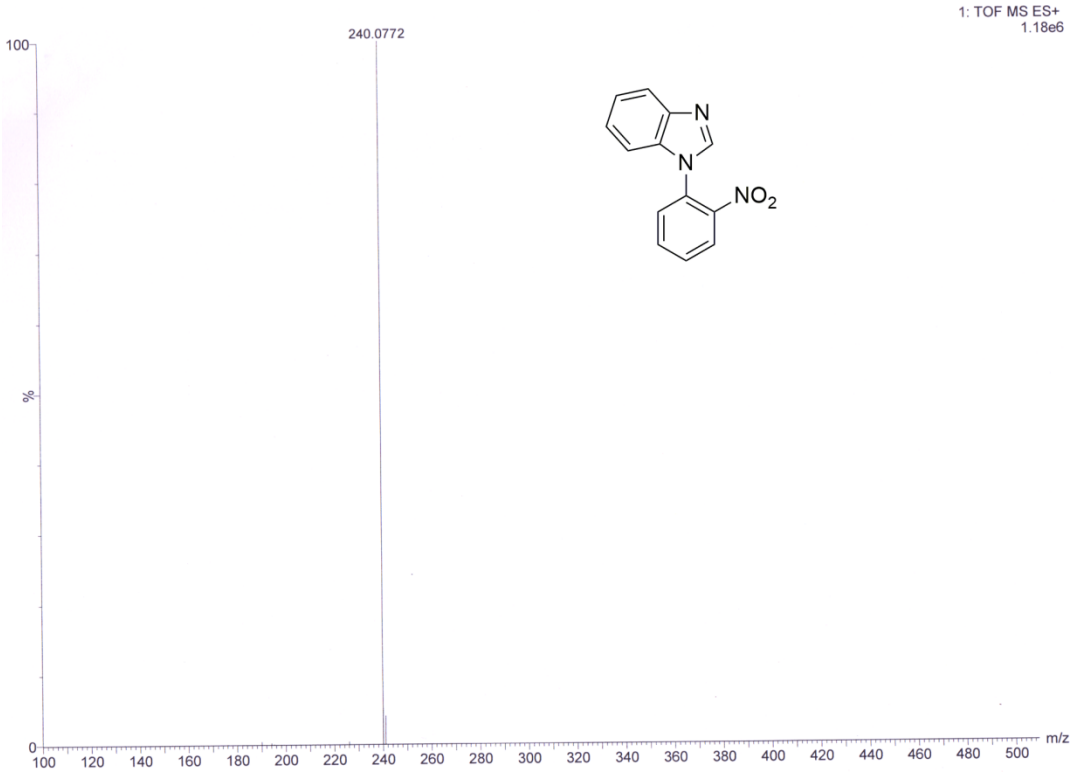




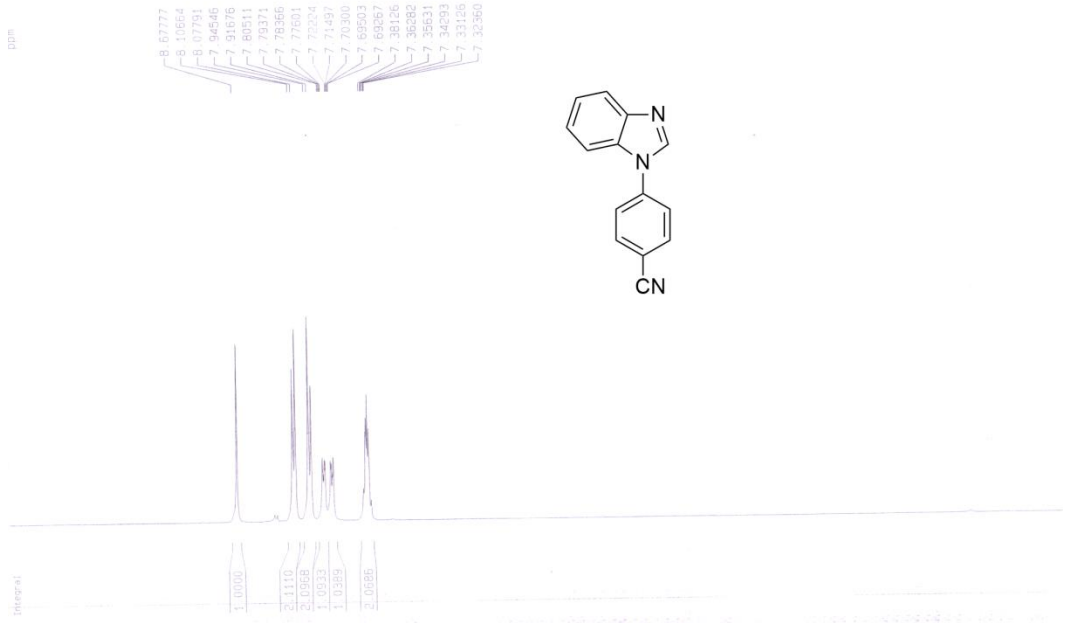
Entry 21

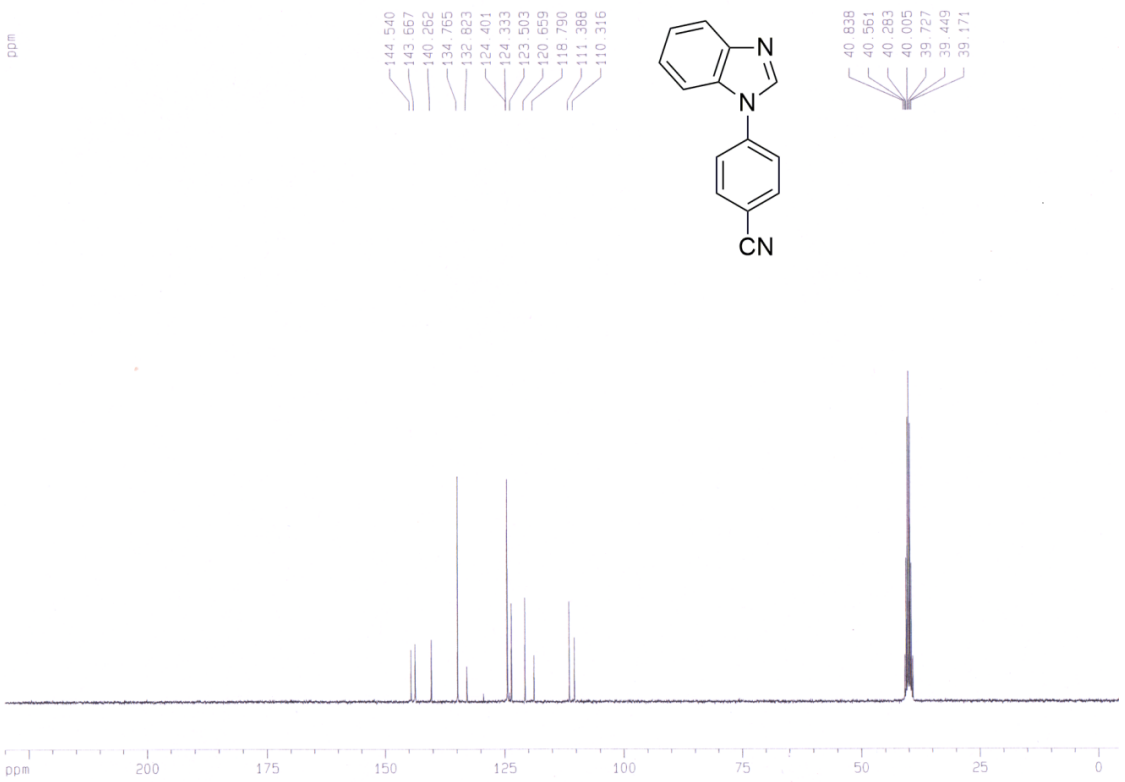

ppm
8.07338
8.06864
7.98144
7.84203
7.83828
7.81413
7.75021
7.62890
7.51972
7.51539
7.49374
7.29588
7.29136
7.27111
7.26494
7.24442
7.24019
7.11350
7.10988
7.09089
7.08632
N
N
NO2
Integral
0.9859
1.0614
1.0855
1.1004
1.0649
1.0486
2.2308
1.0000
ppm
9
8
7
6
5
4
3
2
1

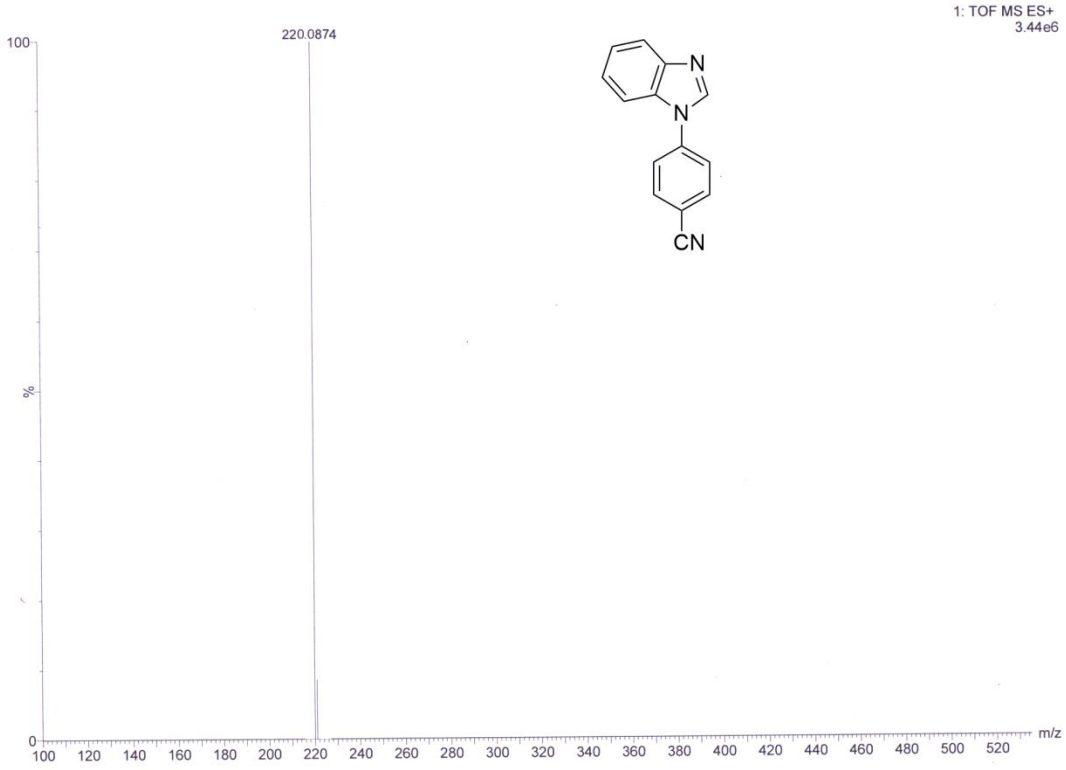

ppm
145.805
143.338
142.511
134.433
134.374
130.103
129.763
129.319
125.943
124.218
123.177
120.704
109.535
77.578
77.154
76.729
N
N
NO2
ppm
180
160
140
120
100
80
60
40
20
0



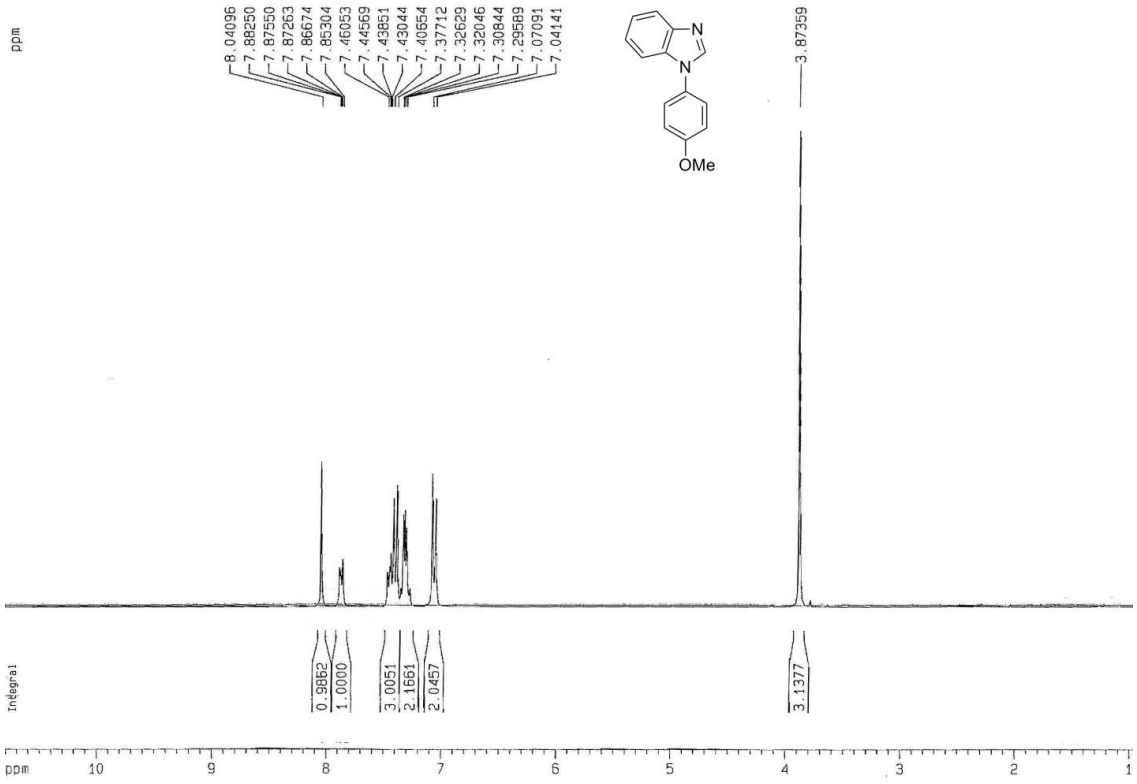
Entry 22

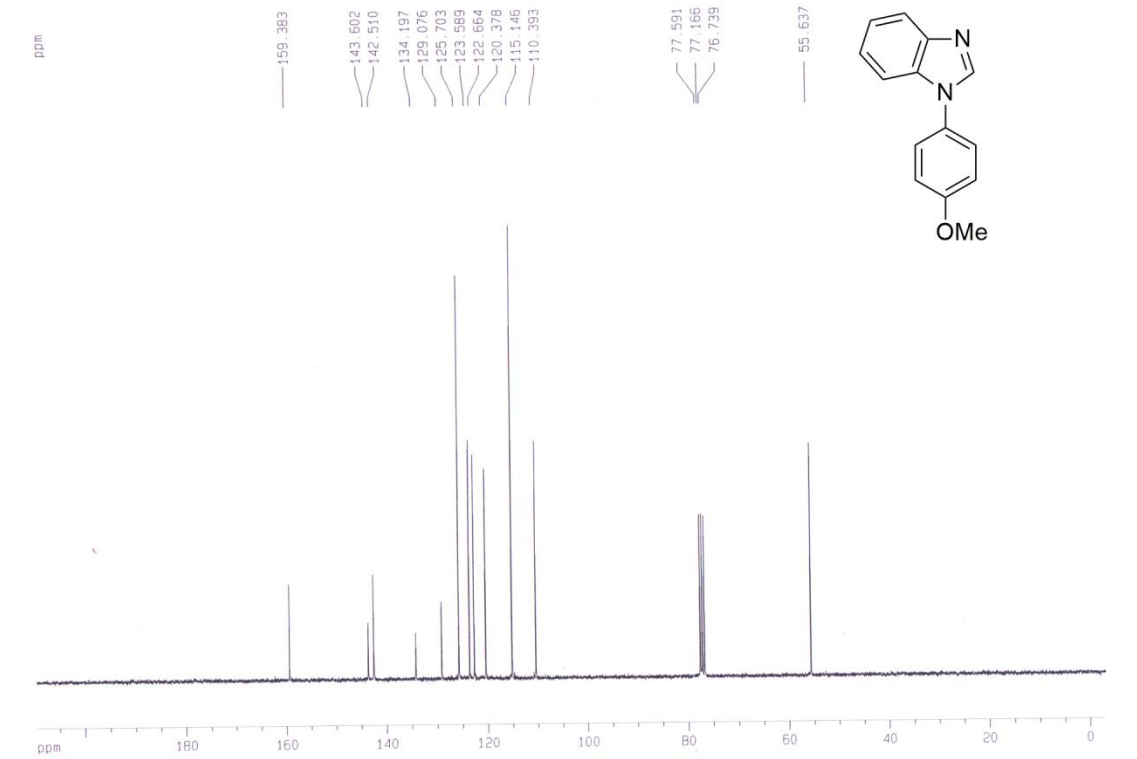


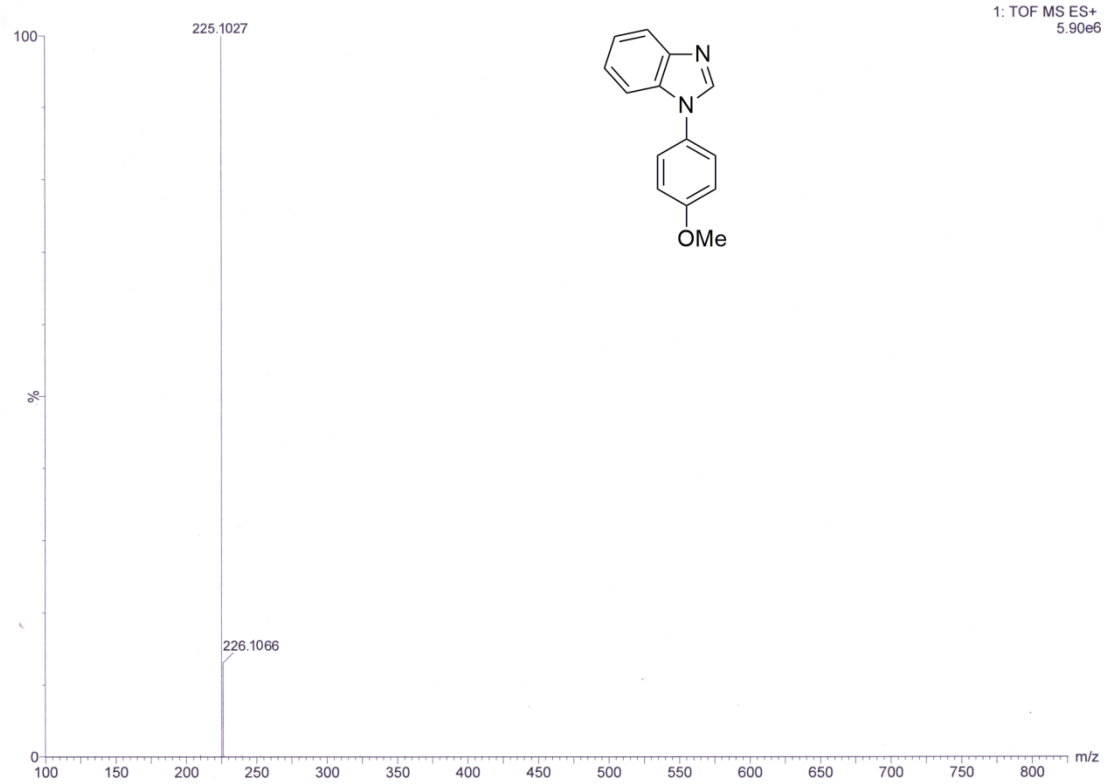




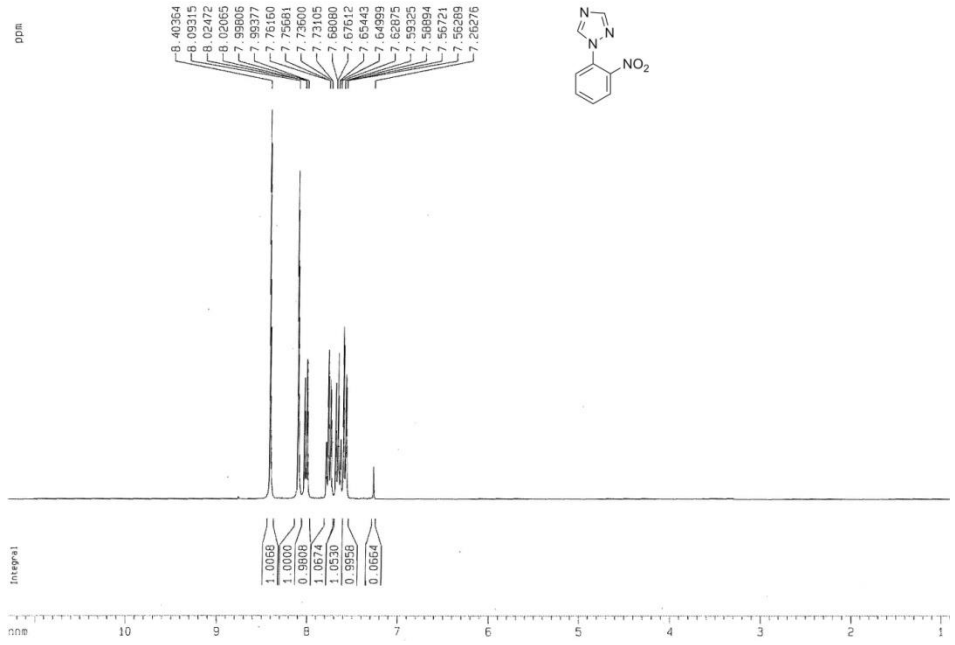
Entry 23

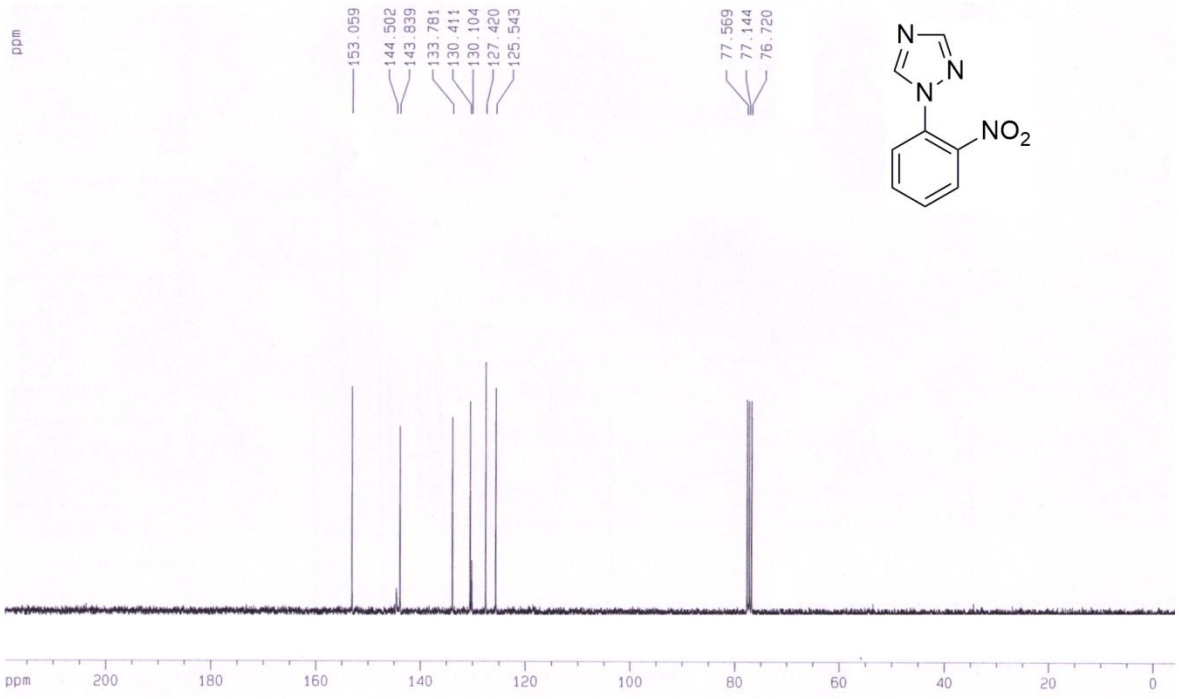

ppm
8.04096
7.88250
7.87550
7.87263
7.86674
7.85304
7.46053
7.44569
7.43851
7.43044
7.40654
7.37712
7.32629
7.32046
7.30844
7.29589
7.07091
7.04141
3.87359
N
N
OMe
Integral
0.9862
1.0000
3.0051
2.1661
2.0457
3.1377
ppm
10
9
8
7
6
5
4
3
2
1

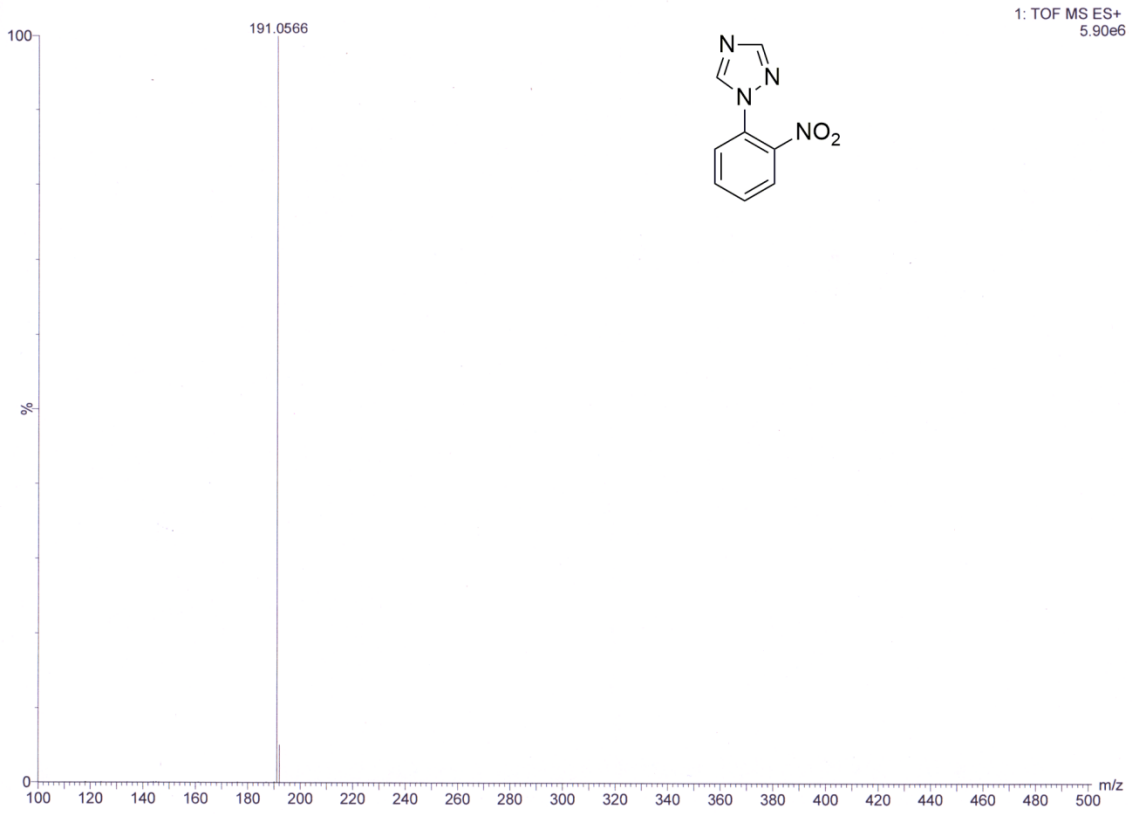

ppm
159.383
143.602
142.510
134.197
129.076
125.703
123.589
122.664
120.378
115.146
110.393
77.591
77.166
76.739
55.637
N
N
OMe
ppm
180
160
140
120
100
80
60
40
20
0



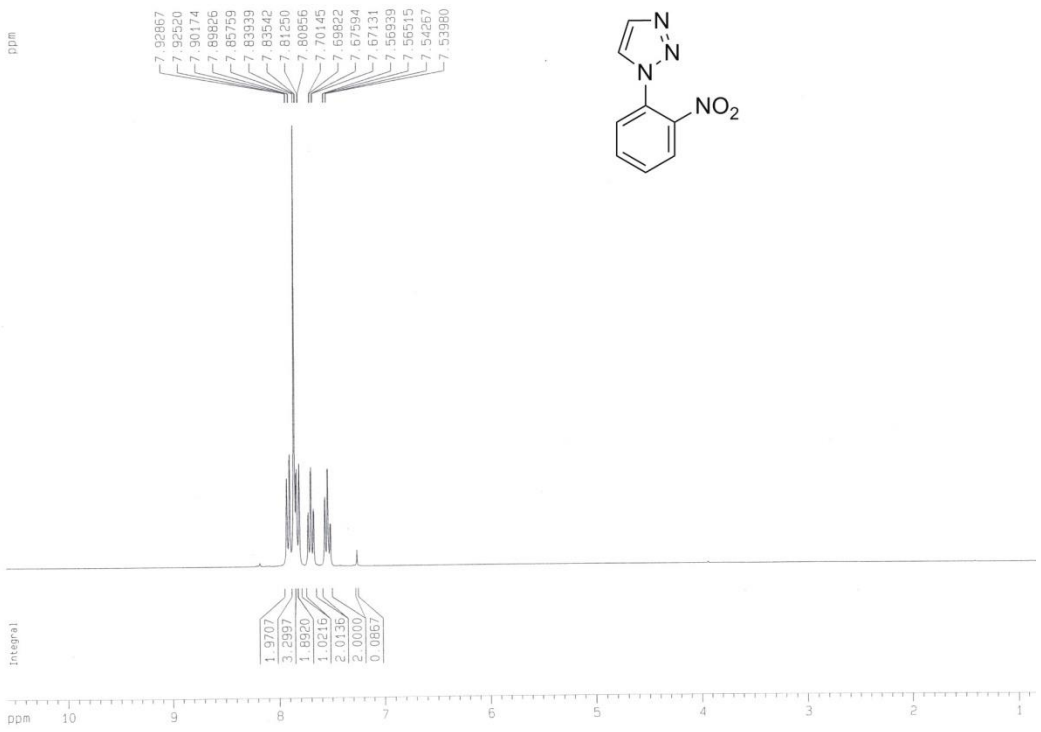
Entry 24

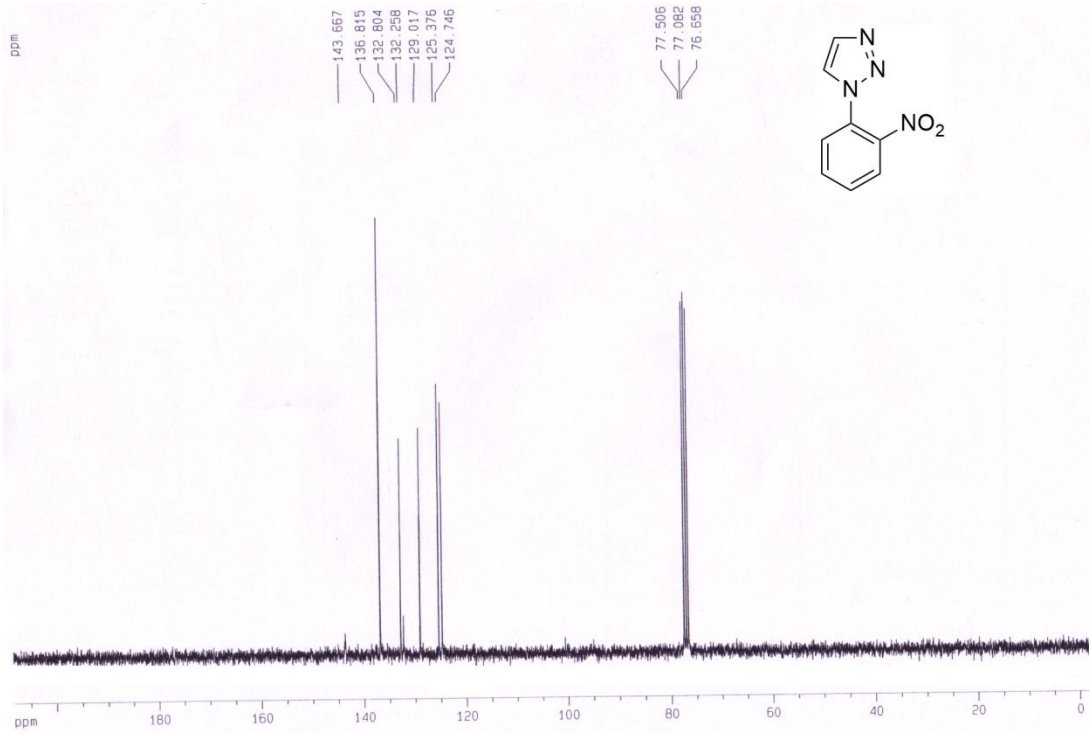


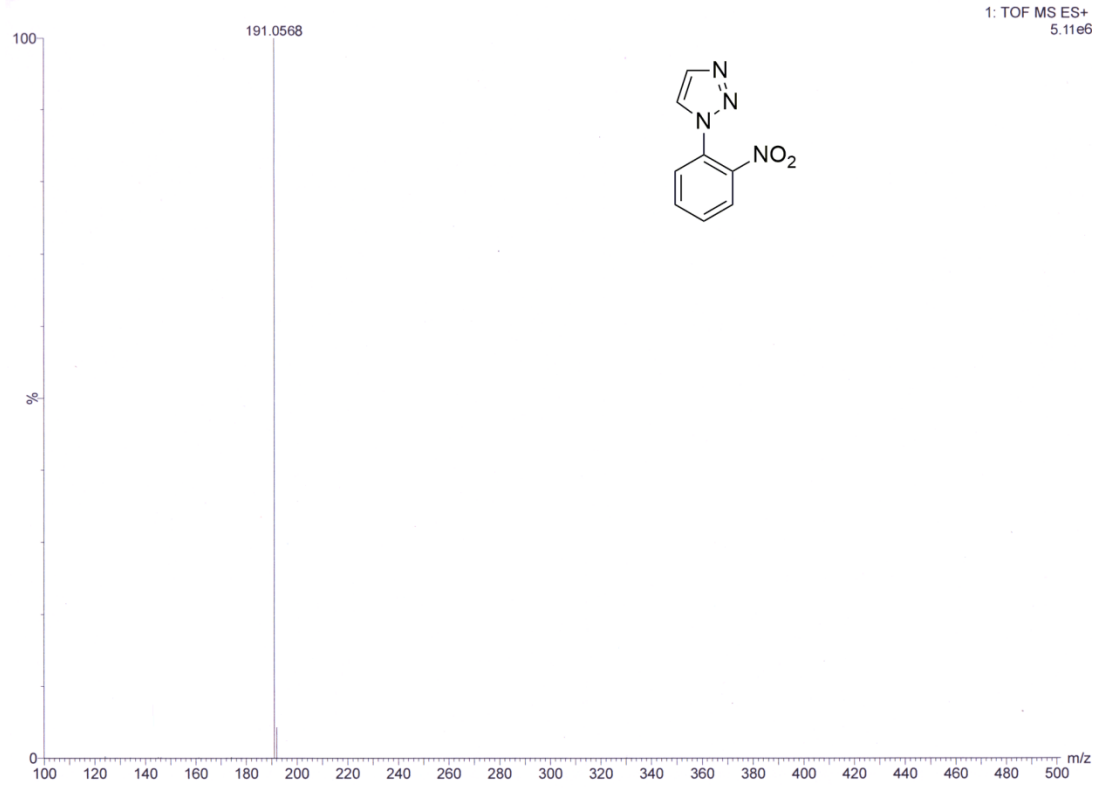




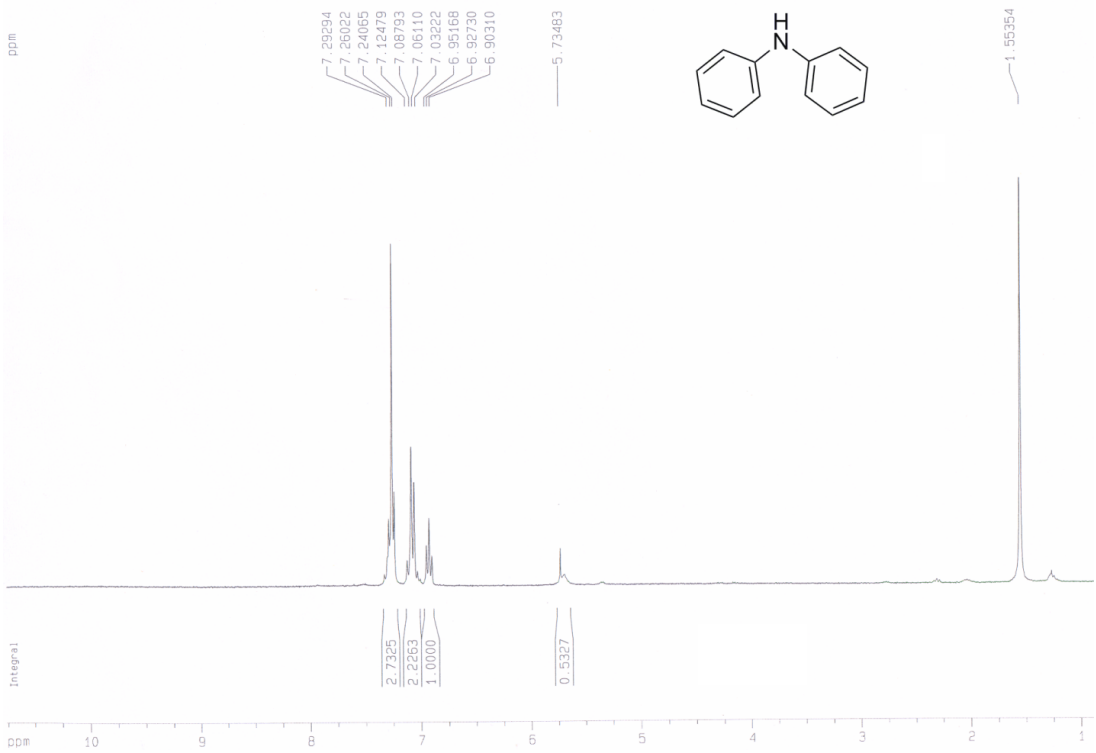
Entry 25

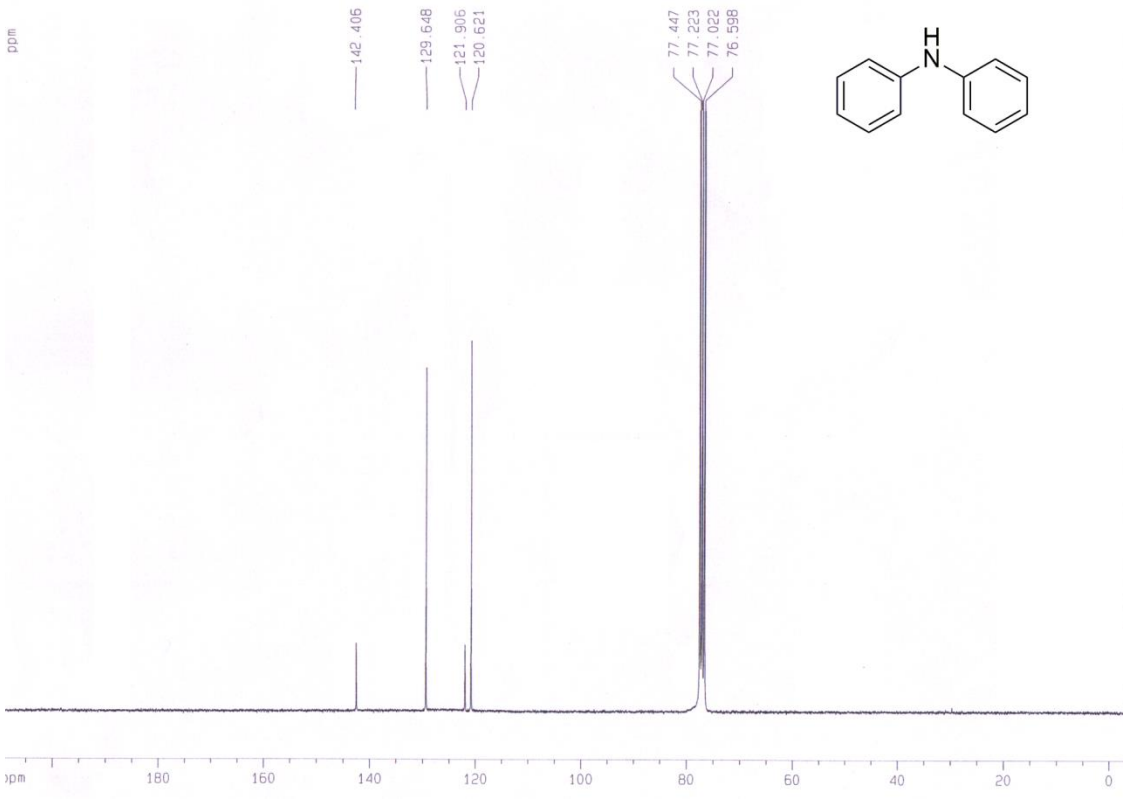

ppm
7.92867
7.92520
7.90174
7.89826
7.85759
7.83939
7.83542
7.81250
7.80856
7.70145
7.69822
7.67594
7.67131
7.56939
7.56515
7.54267
7.53980
N
N
N
NO2
Integral
1.9707
3.2997
1.8920
1.0215
2.0135
2.0000
0.0867
ppm 10 9 8 7 6 5 4 3 2 1

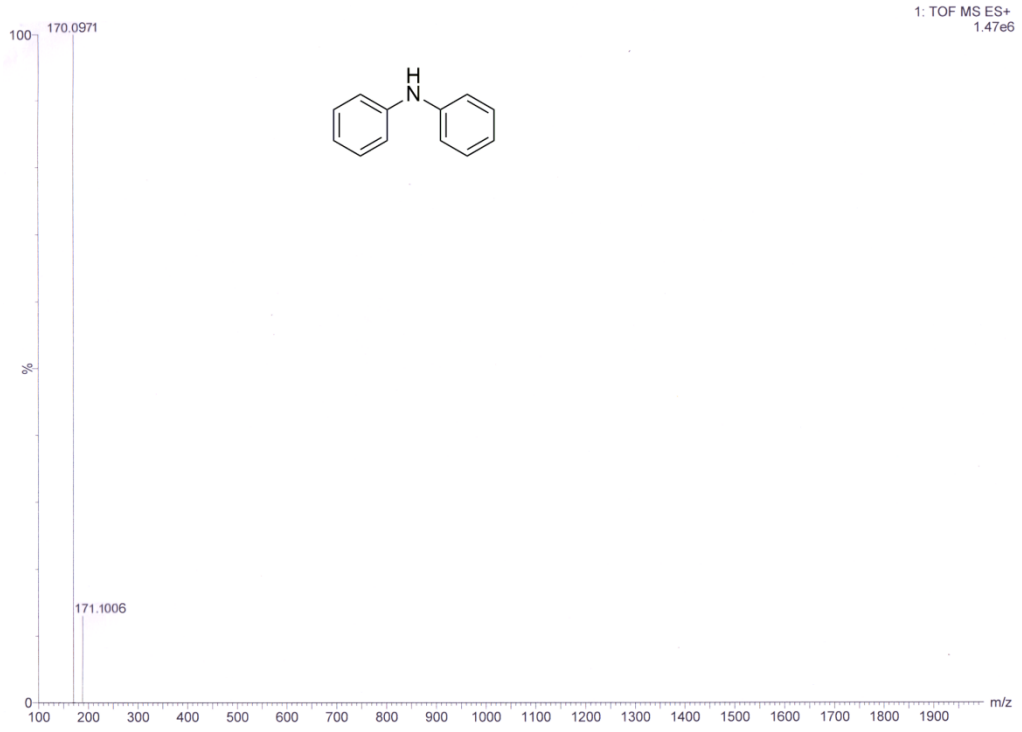

ppm
143.667
136.815
132.804
132.258
129.017
125.376
124.746
77.506
77.082
76.658
N
N
N
NO2
ppm 180 160 140 120 100 80 60 40 20 0



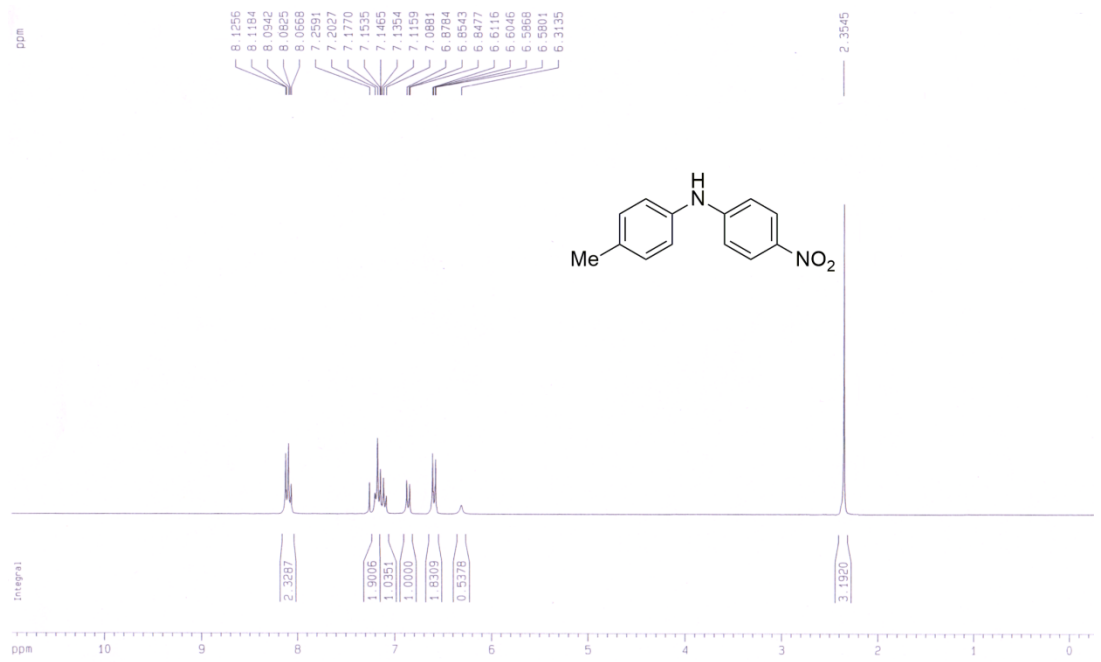
Entry 26







Entry 27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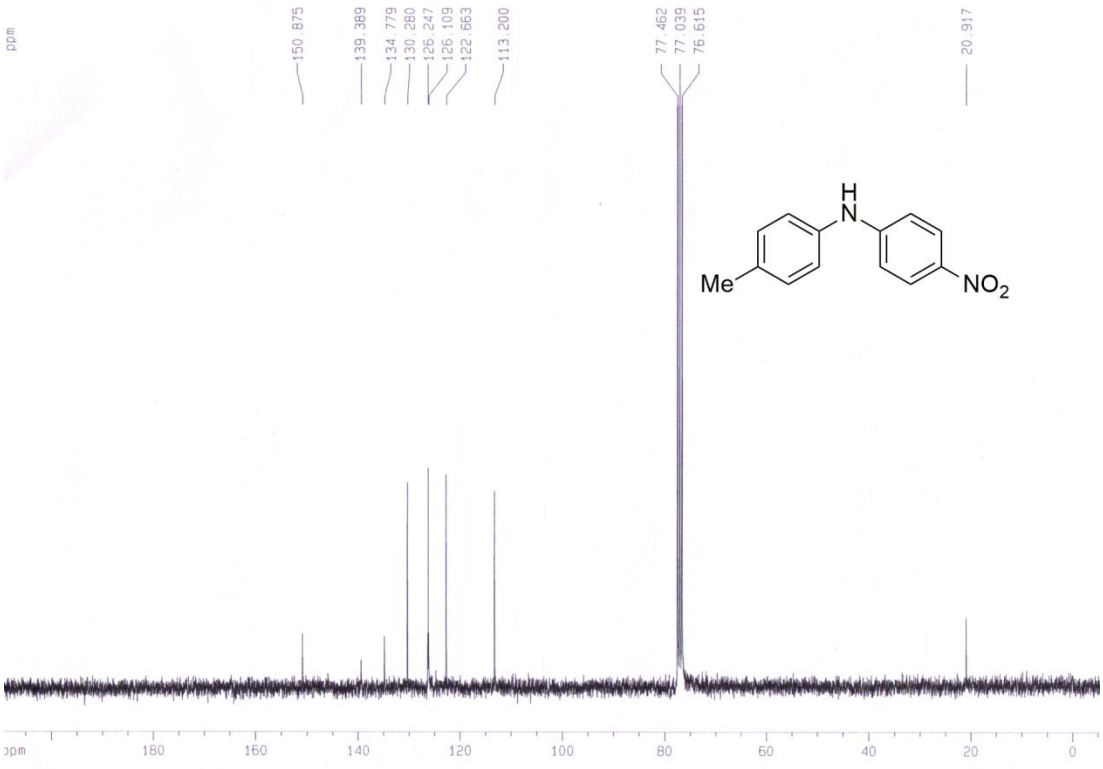
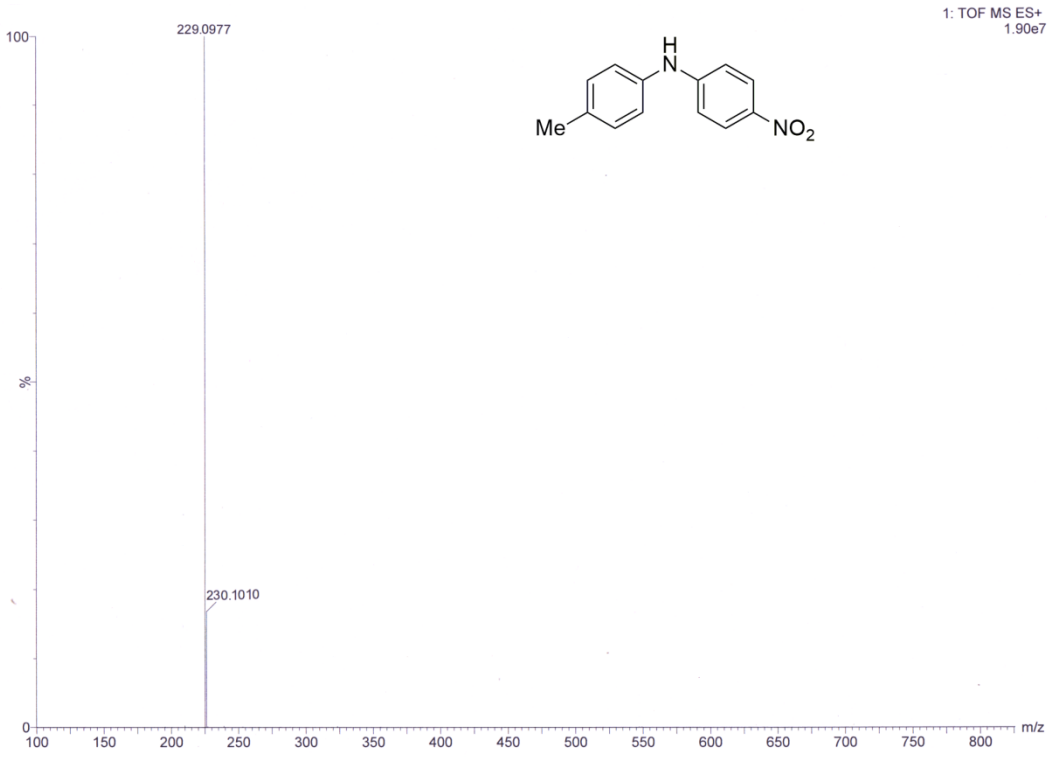
8.1184
8.0942
8.0825
8.0668
7.2591
7.2027
7.1770
7.1535
7.1465
7.1354
7.1159
7.0881
6.8784
6.8543
6.8477
6.6116
6.6046
6.5868
6.5801
6.3135
2.3545
Me
NO2
2.3287
1.9006
1.0351
1.0000
1.8309
0.5378
3.1920


150.875
139.389
134.779
130.280
126.247
126.109
122.663
113.200
77.462
77.039
76.615
20.917
Me
NO2



Entry 28

