Electronic Supplementary Material (ESI) for Green Chemistry.

Copper-nicotinamide complex: sustainable applications in coupling and cycloaddition reactions

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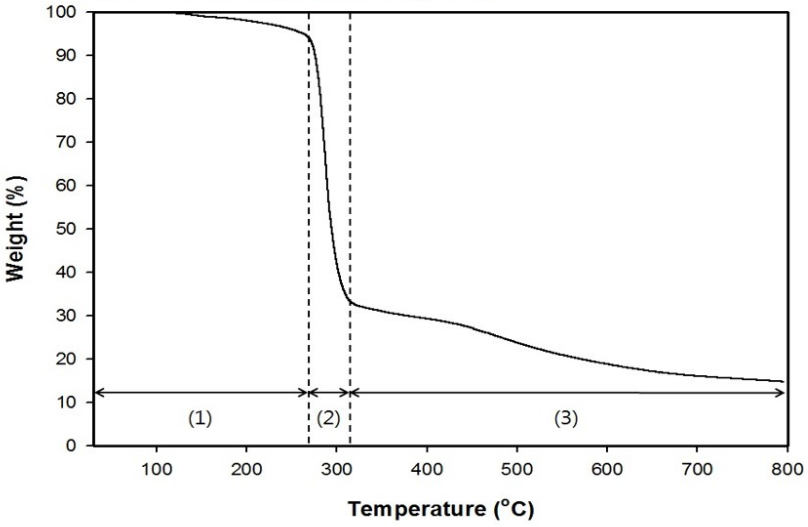
Synthesis of Copper (II)-nicotinamide complex

Copper chloride (0.1N) and nicotinamide (0.1N) solutions were mixed in a 2:5 ratio. The crystals of copper(II)-nicotinamide complex, Cu(nicotinamide)$_2$Cl$_2$, start growing immediately after mixing. The supernatant liquid was filtered off and dried under vacuum at 40 ^{o}C, characterized using CHN (C, 36.32%; H, 3.54%; and N, 14.13%) and TGA (ESI, Figure S1) analysis and stored at ambient conditions.

Figure S1 TGA of Cu-(Nicotinamide)$_2$·2Cl·H$_2$O



At the first stage (30-260 ^{o}C), about 5% of weight loss was observed due to the evaporation of water, which indicates the presence of one water molecule in the sample. At the second stage (260-310 ^{o}C), mostly organics (i.e., nicotinamide) in the sample were removed. After the second stage, 34% weight, which corresponds to $CuCl_2$, remained in the sample.

Synthesis of diaryl sulfides

Aryl iodide (1.0 mmol), thiophenol (1.2 mmol), Cs_2CO_3 (1.0 mmol), 10 mg (0.025 mol %) of Copper (II)-nicotinamide complex and PEG-400 (2 mL) were added to a crimp-sealed thick-walled glass tube. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system equipped with a pressure sensor and a magnetic stirrer. The reaction conditions

were set at 150 ^{o}C, 100 Watts for 15 min. After completion of the reaction, the products were extracted using ethyl acetate, washed with water and dried over sodium sulfate followed by concentration under vacuum and purification using column chromatography.

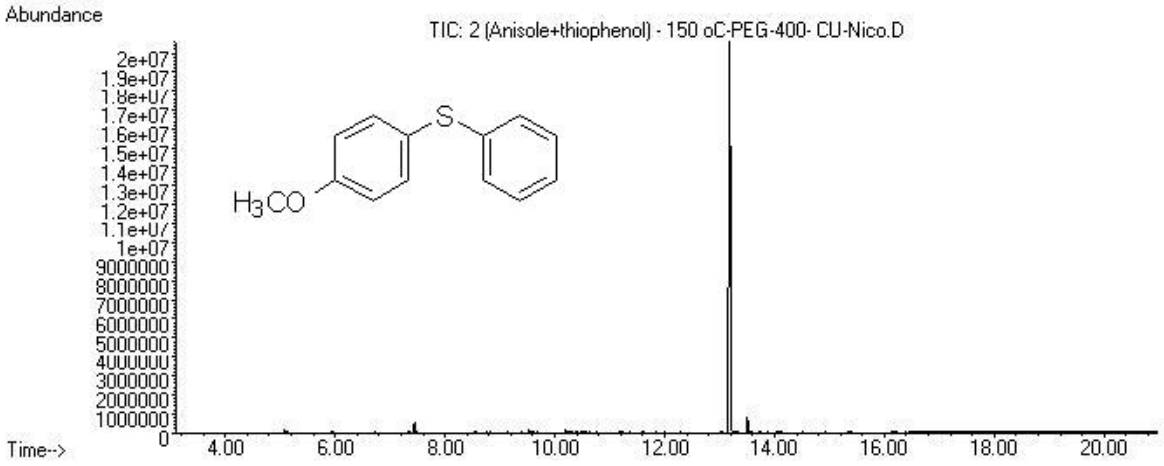
Synthesis of 1,2,3-triazoles

1.2 mmol of alkyl halide, 1.5 mmol of NaN_3, 1.0 mmol of alkyne, and 10 mn (0.025 mol %) of catalyst were placed in a crimp-sealed thick-walled glass tube. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system equipped with a pressure sensor and a magnetic stirrer. The reaction temperature was set at 100 ^{o}C (temperature monitored by a built-in infrared sensor), a power level of 100 W, and pressure 10–60 psi for a duration of 8-30 min (Table 1). After completion of the reaction, the crude product was extracted with ethyl acetate followed by recrystallization or purification by column chromatography.

Amination of 4-bromonitrobenzene

4-Bromonitrobenzene (1.0 mmol), aliphatic amine (1.2 mmol), and 10 mg (0.025 mol %) of copper(II)-nicotinamide complex were placed in a crimp-sealed thick-walled glass tube. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system equipped with a pressure sensor and a magnetic stirrer, operated at 100 ^{o}C (temperature monitored by a built-in infrared sensor) and a power level of 100 W for 60 min. After completion of the reaction, the products were extracted using ethyl acetate, dried over sodium sulfate, concentrated under reduced pressure and purified by column chromatography.

Gas Chromatography-Mass Spectrometry profiles of the representative crude reaction mixtures: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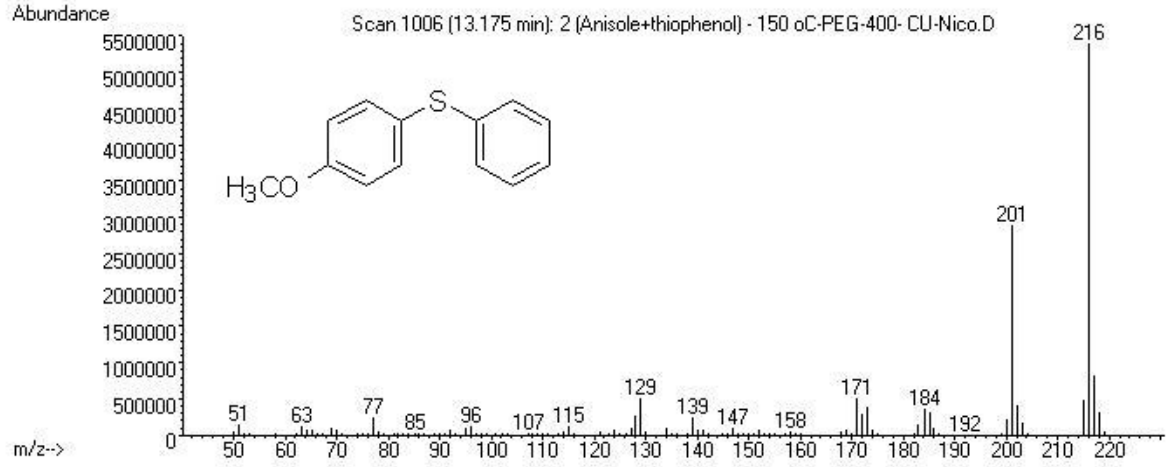
TIC: 2 (Anisole+thiophenol) - 150 oC-PEG-400- CU-Nico.D
Time-->


Abundance
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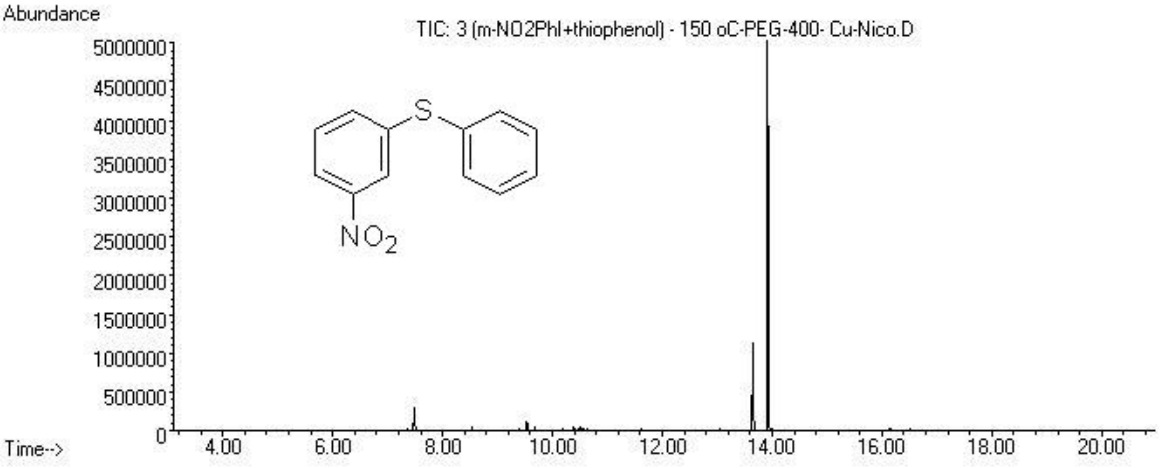
m/z-->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4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
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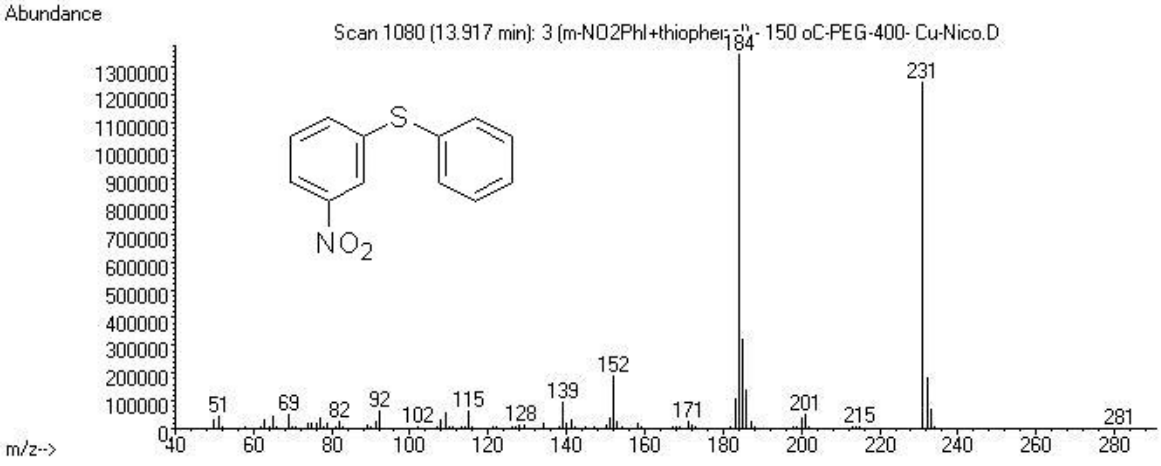
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
S
NO2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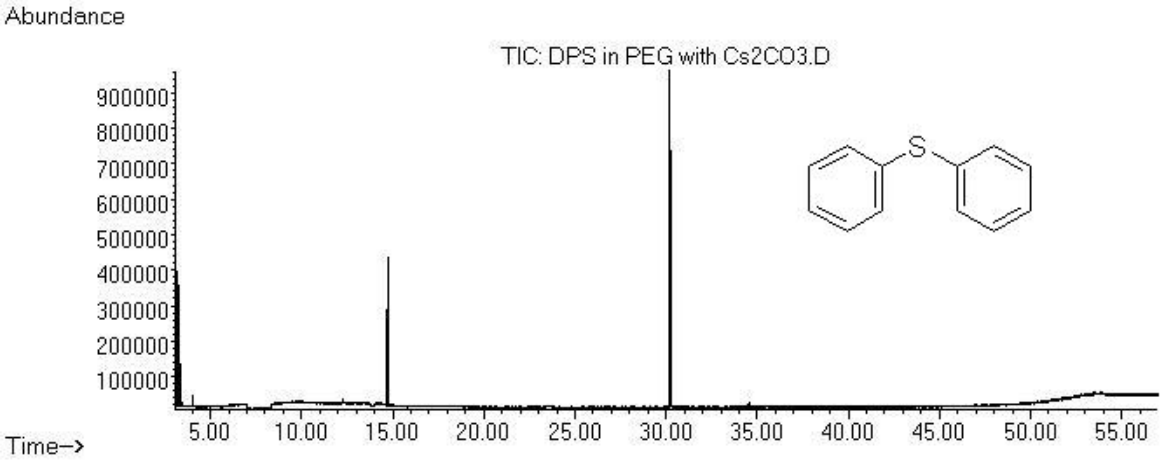
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
280
184
231
152
139
115
92
82
69
51
102
128
171
201
215
281
S
NO2


Abundance
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800000
700000
600000
500000
400000
300000
200000
100000
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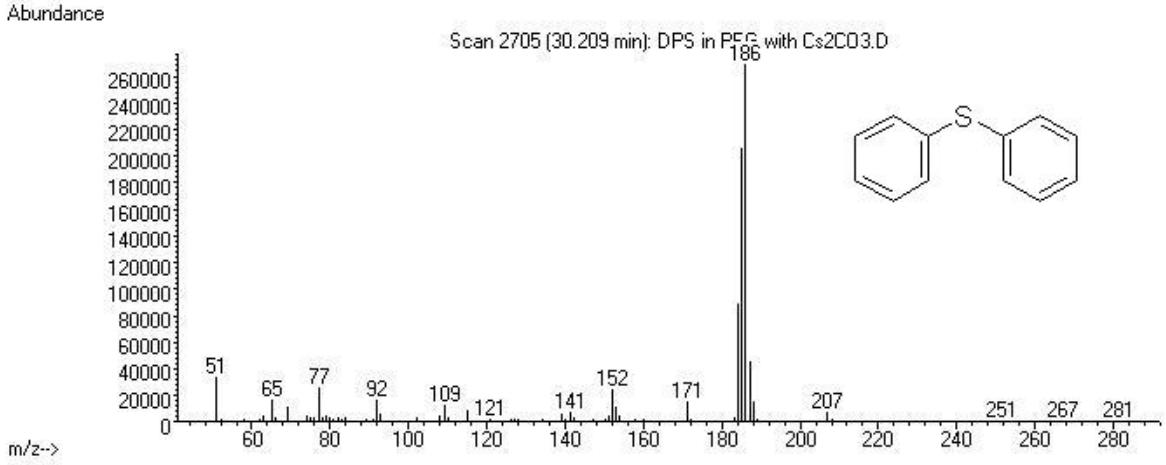
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
Time-->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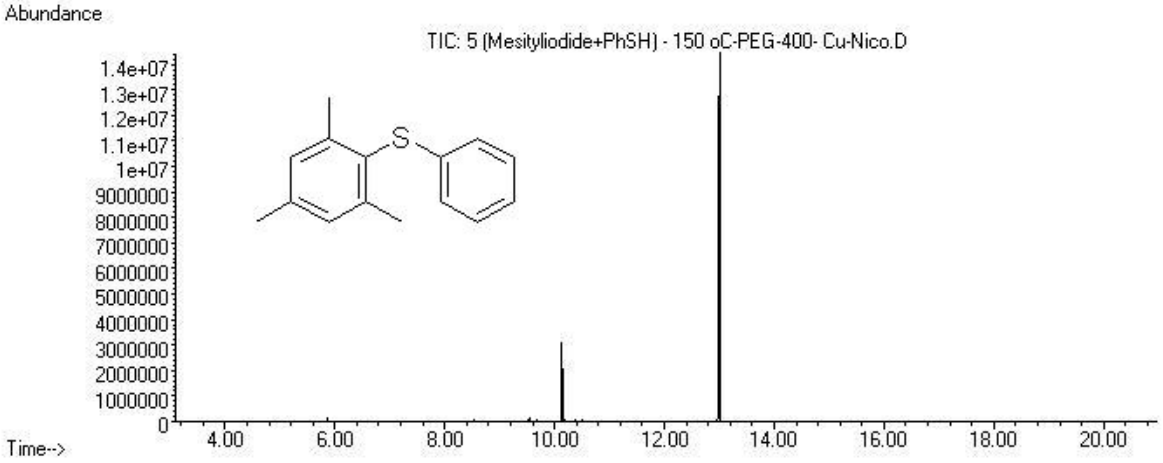
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
51
65
77
92
109
121
141
152
171
207
251
267
281
60
80
100
120
140
160
180
200
220
240
260
280
m/z-->


Abundance
TIC: 5 (Mesityliodide+PhSH) - 150 oC-PEG-400- Cu-Nico.D
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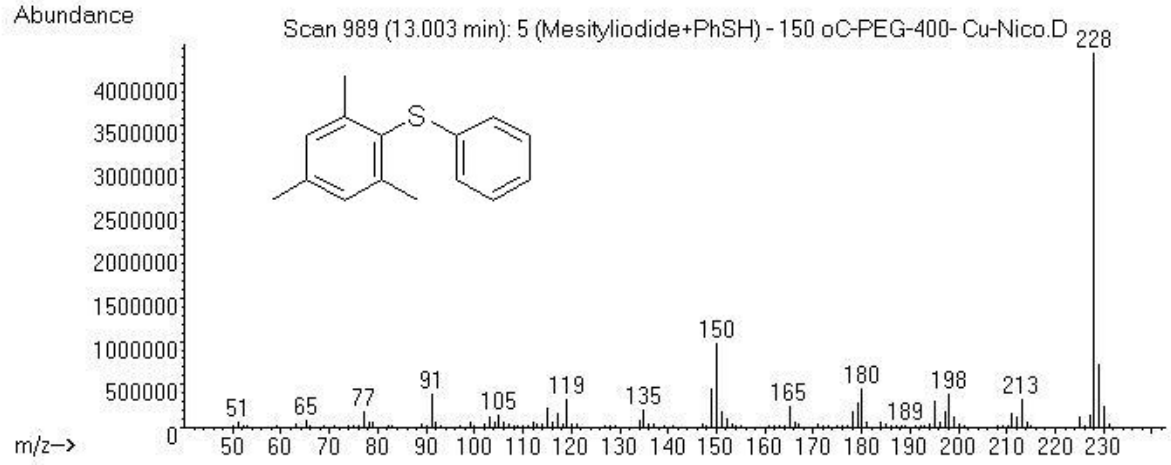
1.3e+07
1.2e+07
1.1e+07
1e+07
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
S
Time-->
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00


Abundance
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4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
S
150
180
198
213
91
119
77
105
135
165
189
51
65
m/z-->
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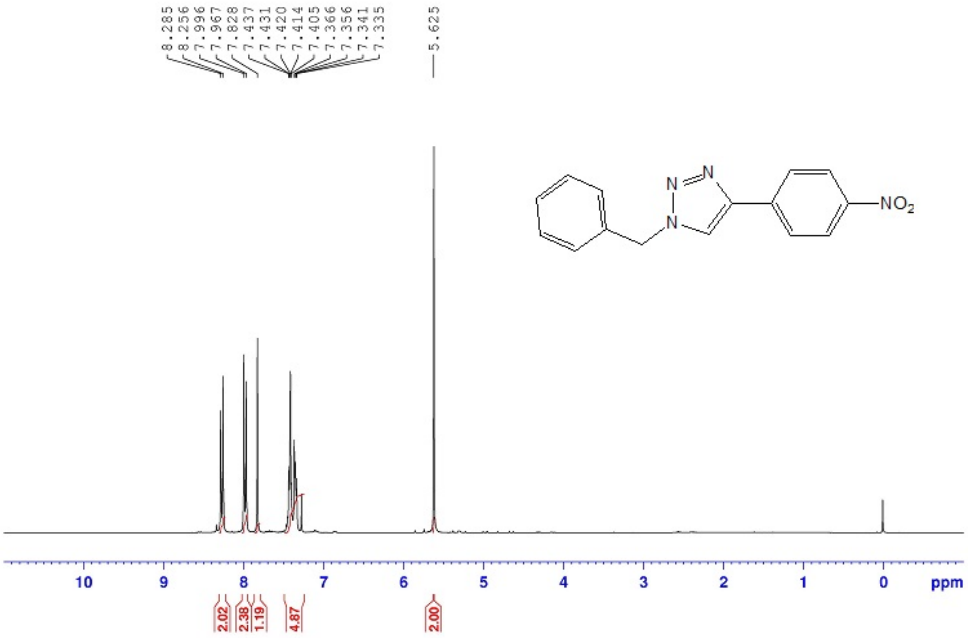
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7.967
7.828
7.437
7.431
7.420
7.414
7.405
7.366
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7.341
7.335
5.625
N
N
N
NO2
10
9
8
7
6
5
4
3
2
1
0
ppm
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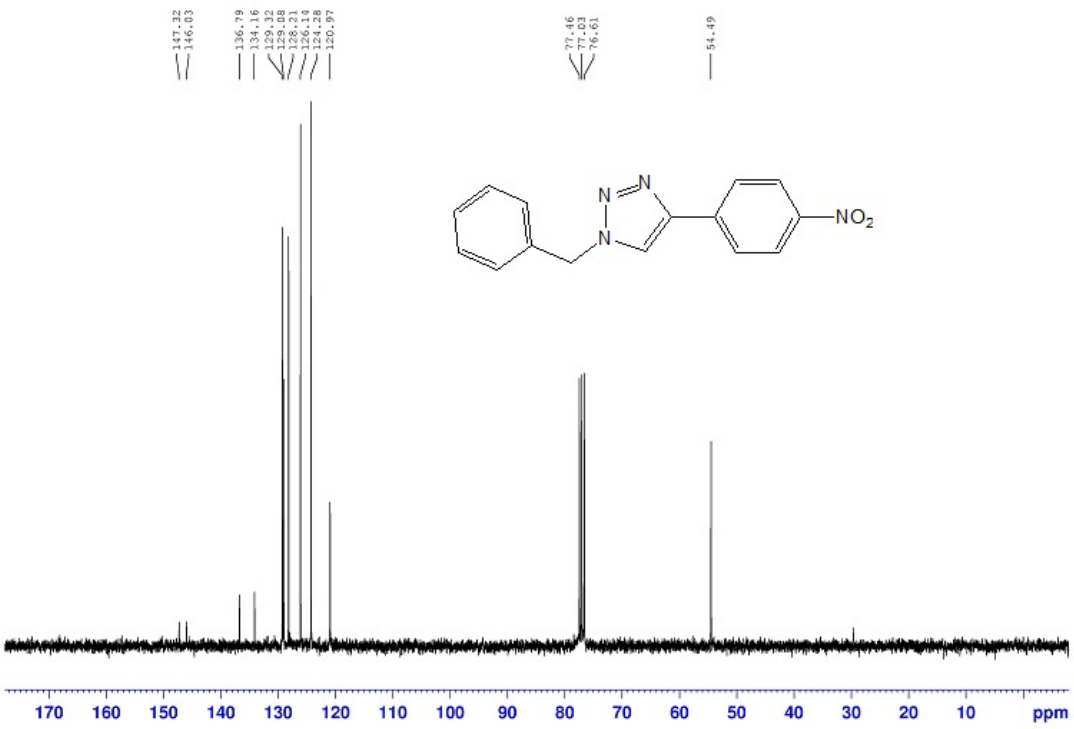
1.19
4.87
2.00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134.16
129.32
129.08
128.21
126.14
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77.46
77.03
76.61
54.49
N
N
N
NO2
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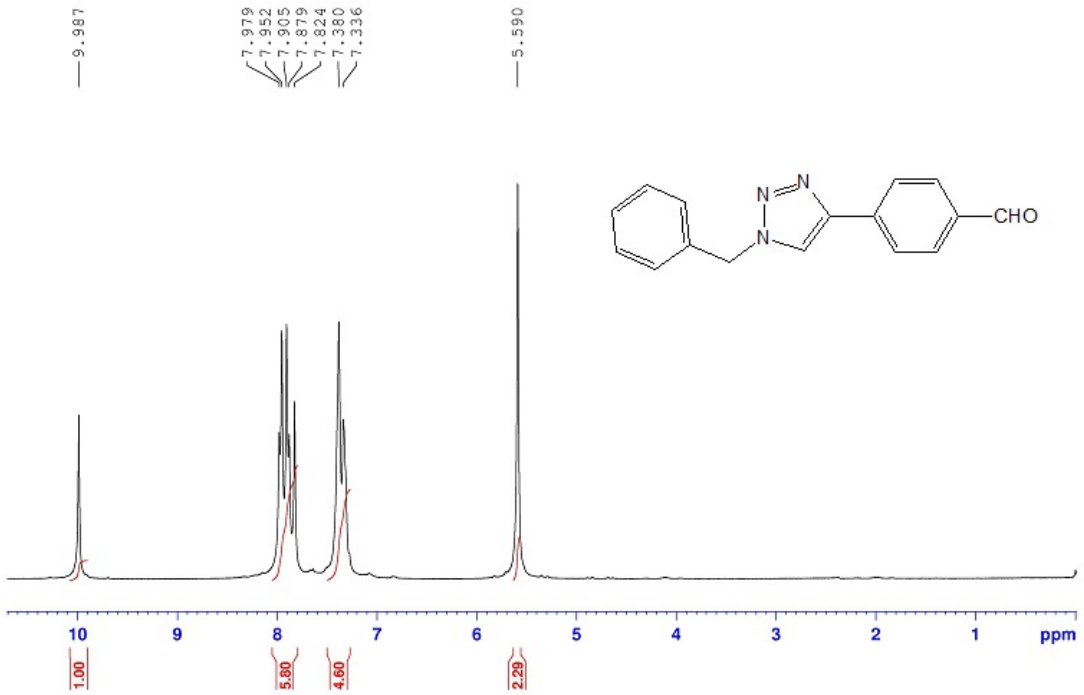
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.979
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7.824
7.380
7.336
5.590
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N
N
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9
8
7
6
5
4
3
2
1
ppm
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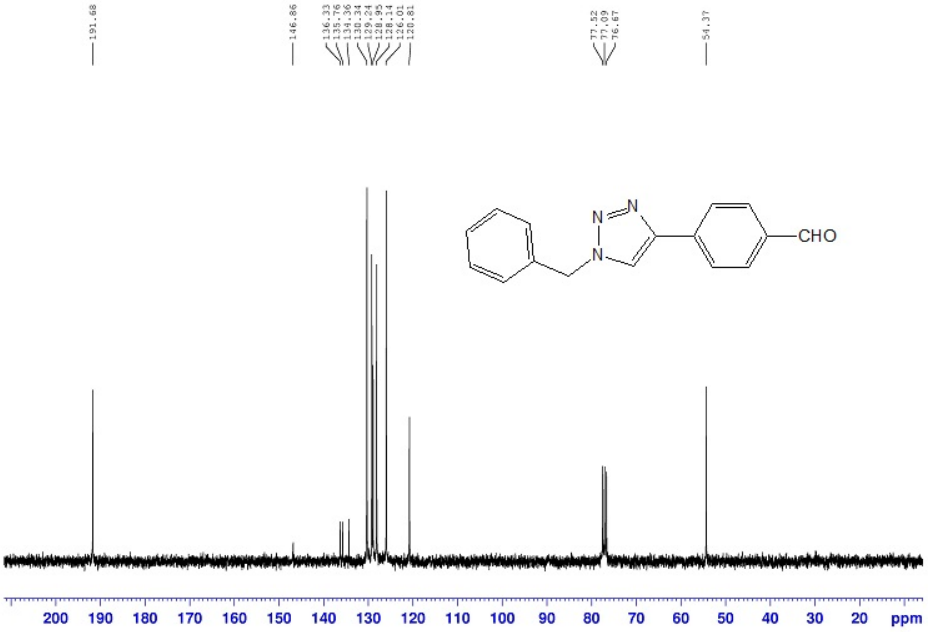
2.29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130.34
129.24
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N
CHO
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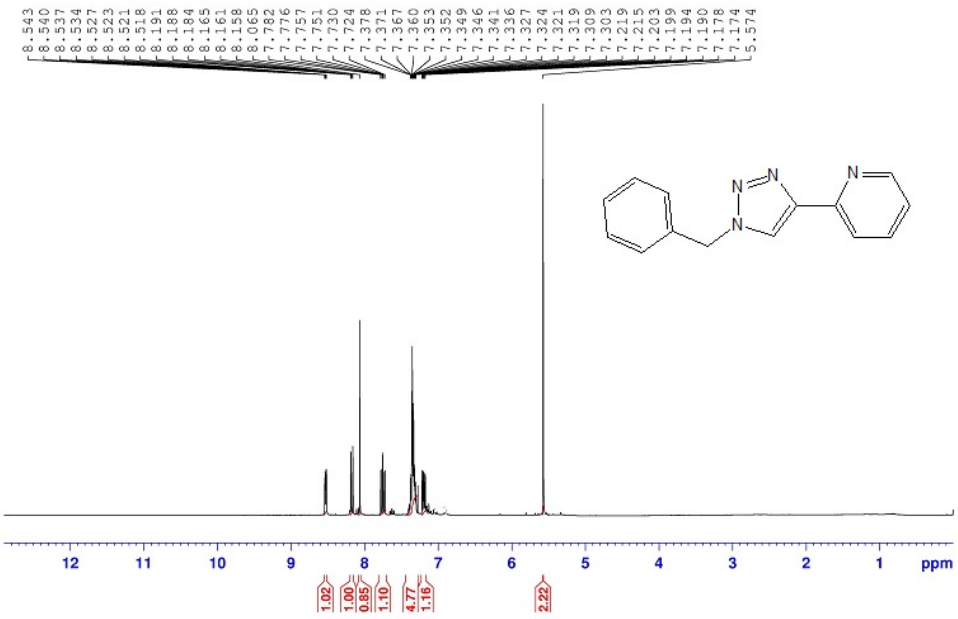
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8.534
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8.518
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8.161
8.158
8.065
7.782
7.776
7.757
7.751
7.730
7.724
7.378
7.371
7.367
7.360
7.353
7.352
7.349
7.346
7.341
7.336
7.327
7.324
7.321
7.319
7.309
7.303
7.219
7.215
7.203
7.199
7.194
7.190
7.178
7.174
5.574
N
N
N
12
11
10
9
8
7
6
5
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3
2
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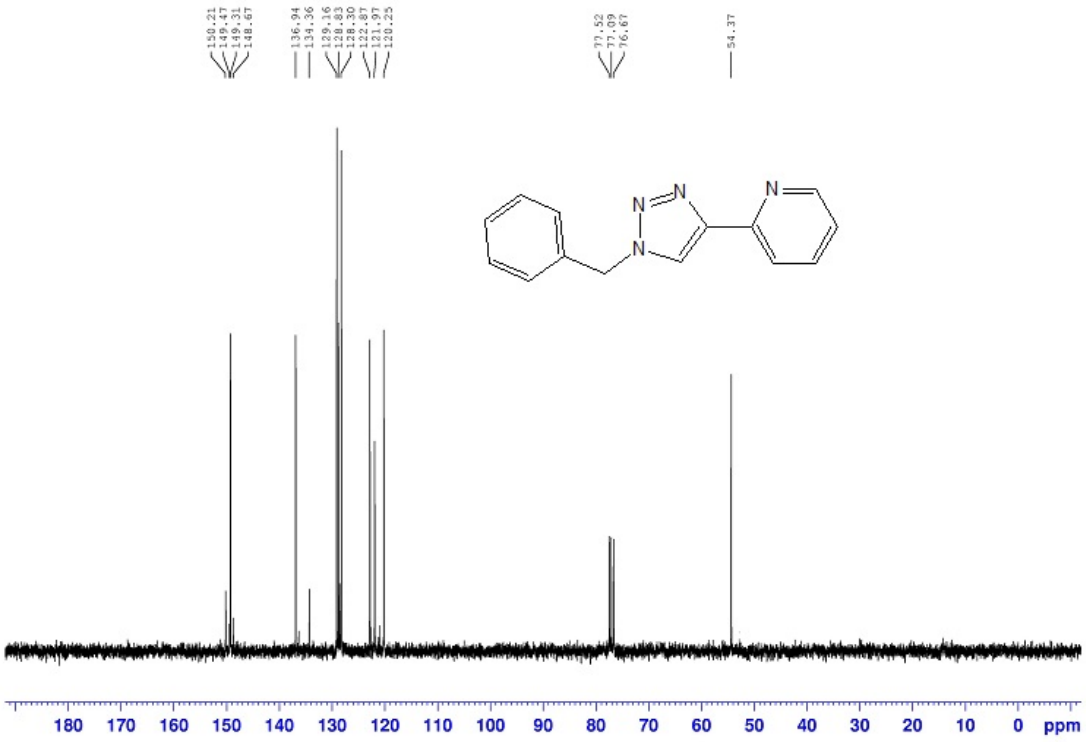
4.77
1.16
2.22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128.83
128.30
122.87
121.97
120.25
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77.09
76.67
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N
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N
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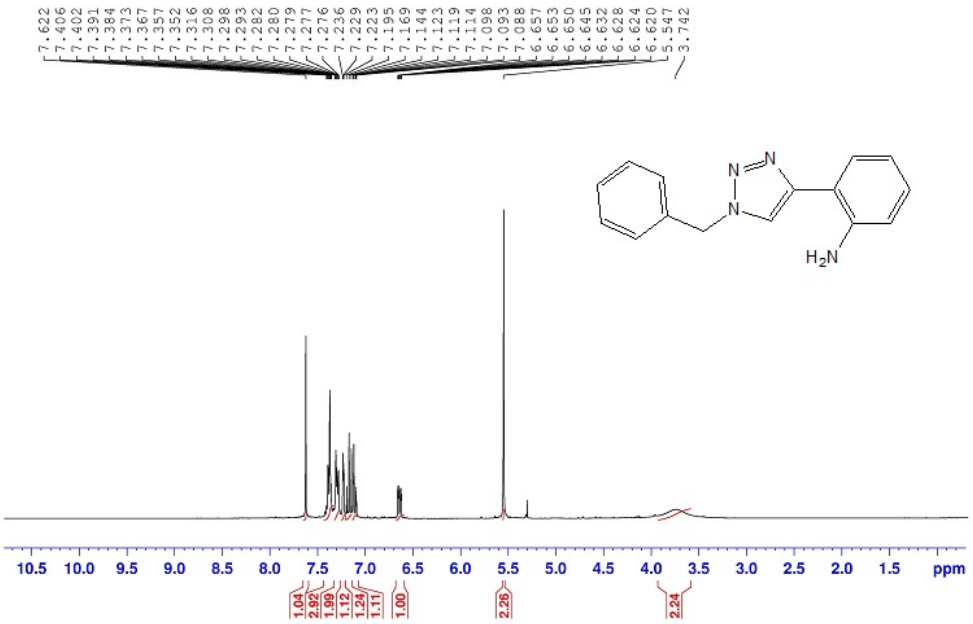
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7.293
7.282
7.280
7.279
7.277
7.276
7.236
7.229
7.223
7.195
7.169
7.144
7.123
7.119
7.114
7.098
7.093
7.088
6.657
6.653
6.650
6.645
6.632
6.628
6.624
6.620
5.547
3.742
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N
N
H2N
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
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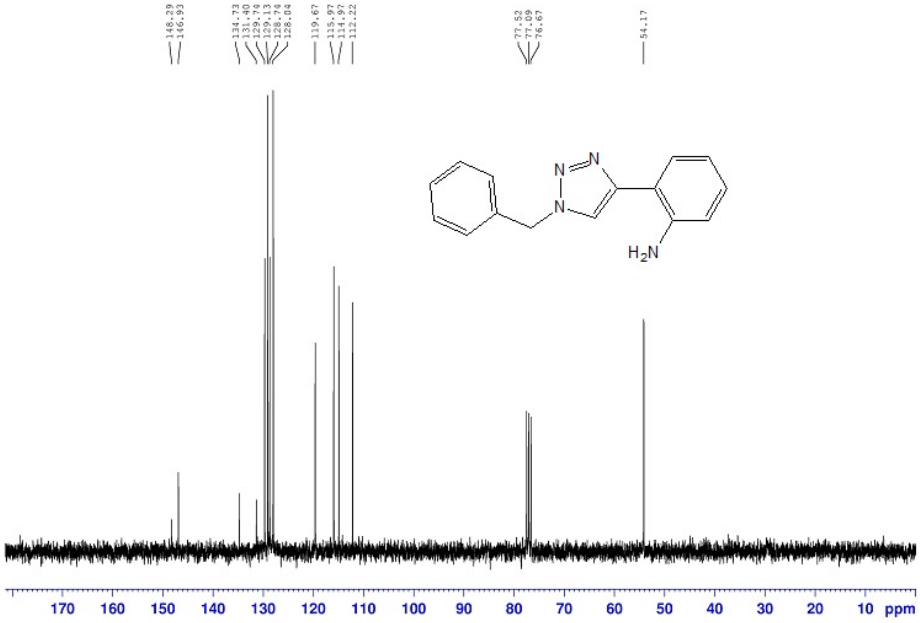
1.12
1.24
1.11
1.00
2.26
2.24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129.13
128.78
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119.67
115.97
114.97
112.22
77.53
77.09
76.67
54.17
N
N
N
H2N
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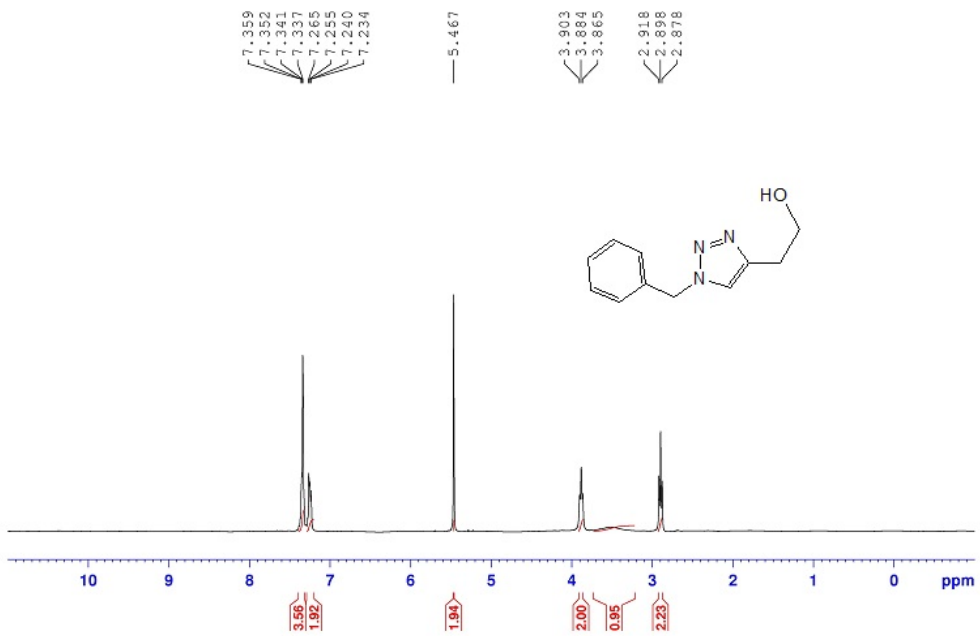
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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2.918
2.898
2.878
HO
N
N
N
10
9
8
7
6
5
4
3
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ppm
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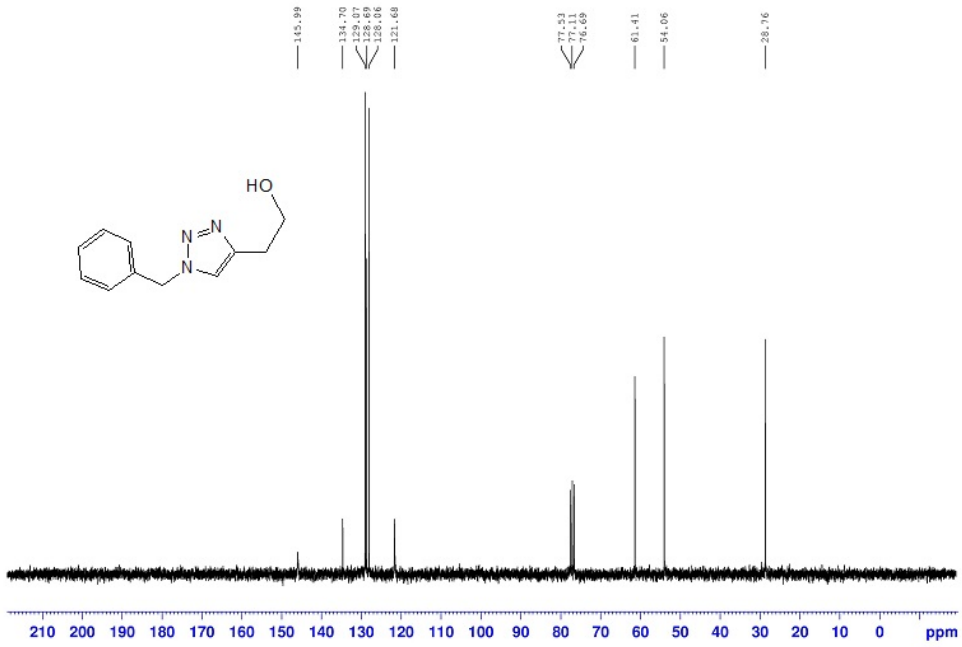
1.94
2.00
0.95
2.23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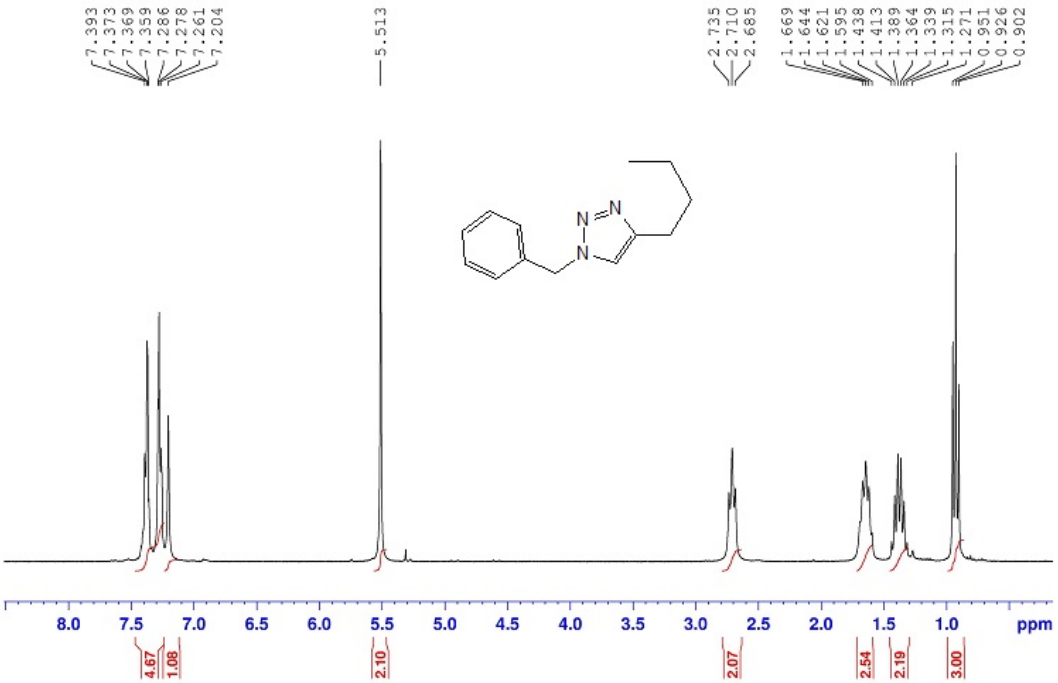
128.69
128.06
121.68
77.53
77.11
76.69
61.41
54.06
28.76
HO
N
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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1.644
1.621
1.595
1.438
1.413
1.389
1.364
1.339
1.315
1.271
0.951
0.926
0.902
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N
N
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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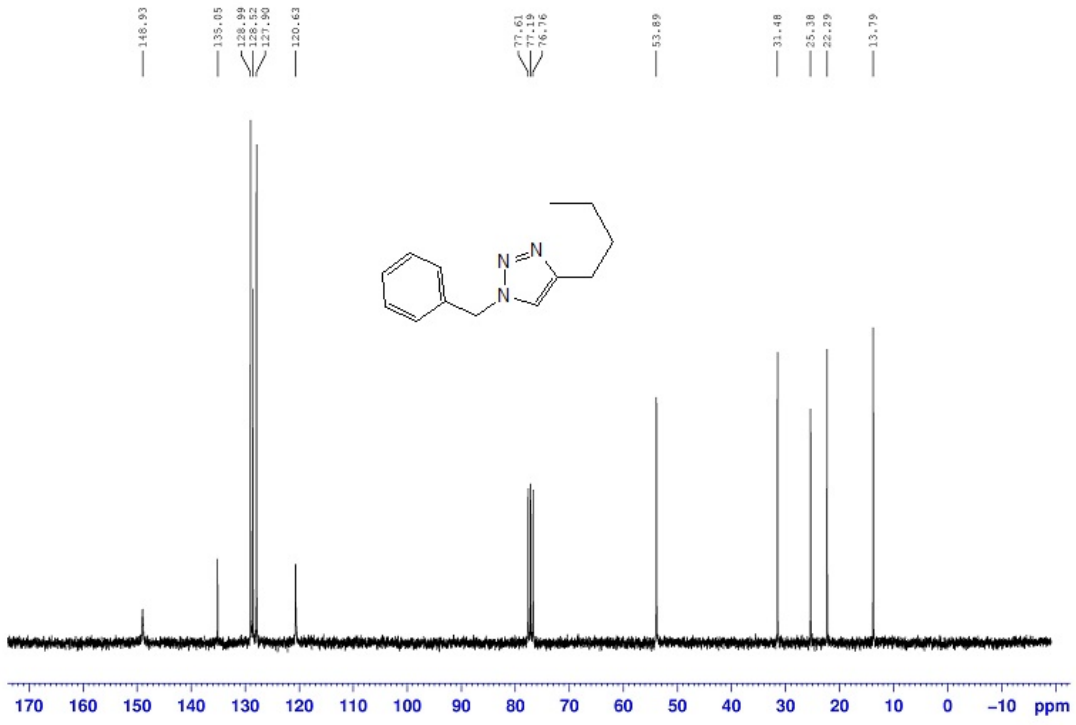
3.00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128.52
127.90
120.63
77.61
77.19
76.76
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N
N
N
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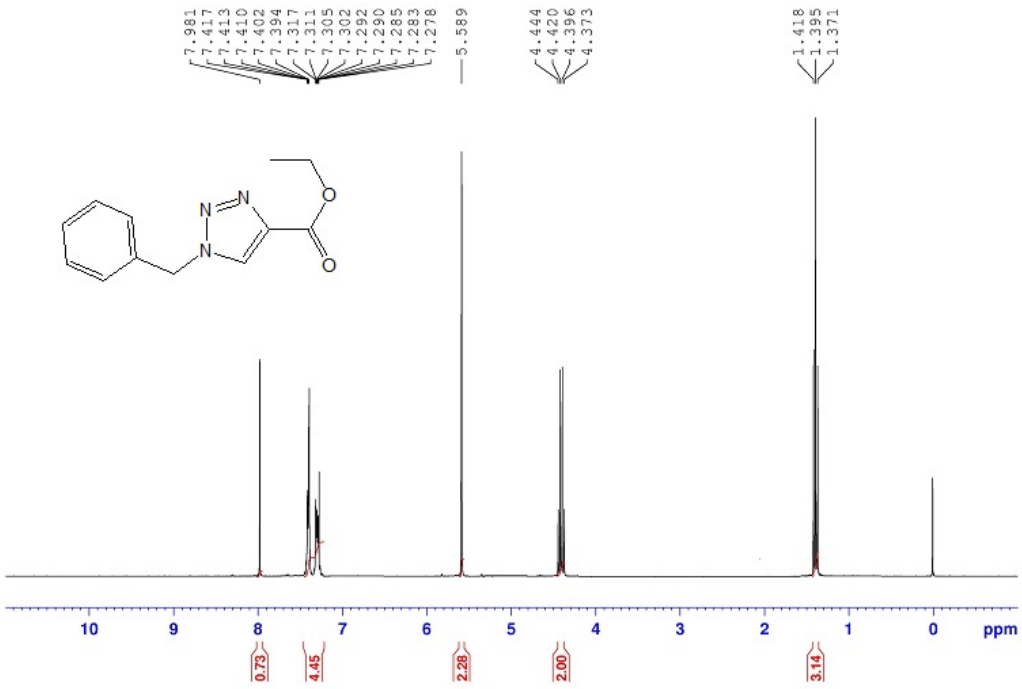
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7.402
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7.317
7.311
7.305
7.302
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7.290
7.285
7.283
7.278
5.589
4.444
4.420
4.396
4.373
1.418
1.395
1.371
N
N
N
O
O
10
9
8
7
6
5
4
3
2
1
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ppm
0.73
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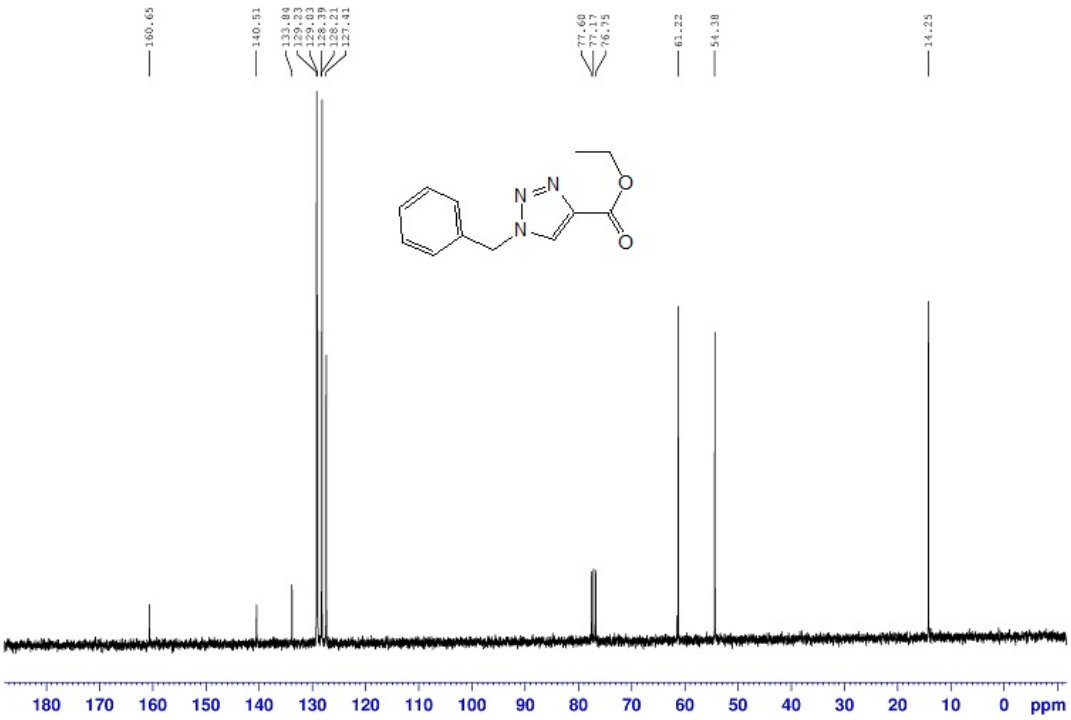
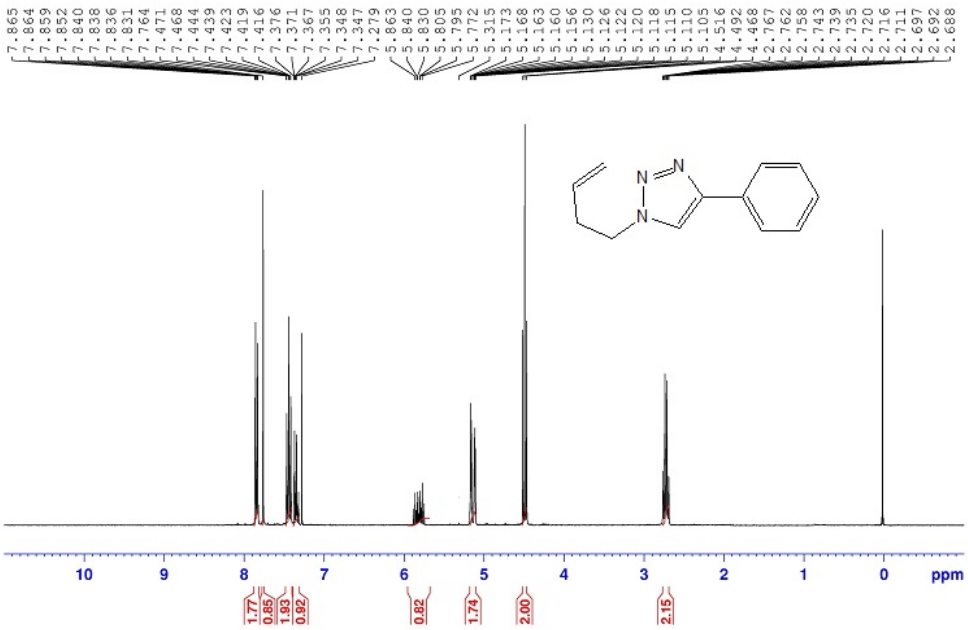
2.28
2.00
3.14


160.65
140.51
133.84
129.73
129.03
128.39
128.21
127.41
77.60
77.17
76.75
61.22
54.38
14.25
N
N
N
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.831
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7.468
7.444
7.439
7.423
7.419
7.416
7.376
7.371
7.367
7.355
7.348
7.347
7.279
5.863
5.840
5.830
5.805
5.795
5.772
5.315
5.173
5.168
5.163
5.160
5.156
5.130
5.126
5.122
5.120
5.118
5.115
5.110
5.105
4.516
4.492
4.468
2.767
2.762
2.758
2.743
2.739
2.735
2.720
2.716
2.711
2.697
2.692
2.688
N
N
N
10
9
8
7
6
5
4
3
2
1
0
ppm
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0.92
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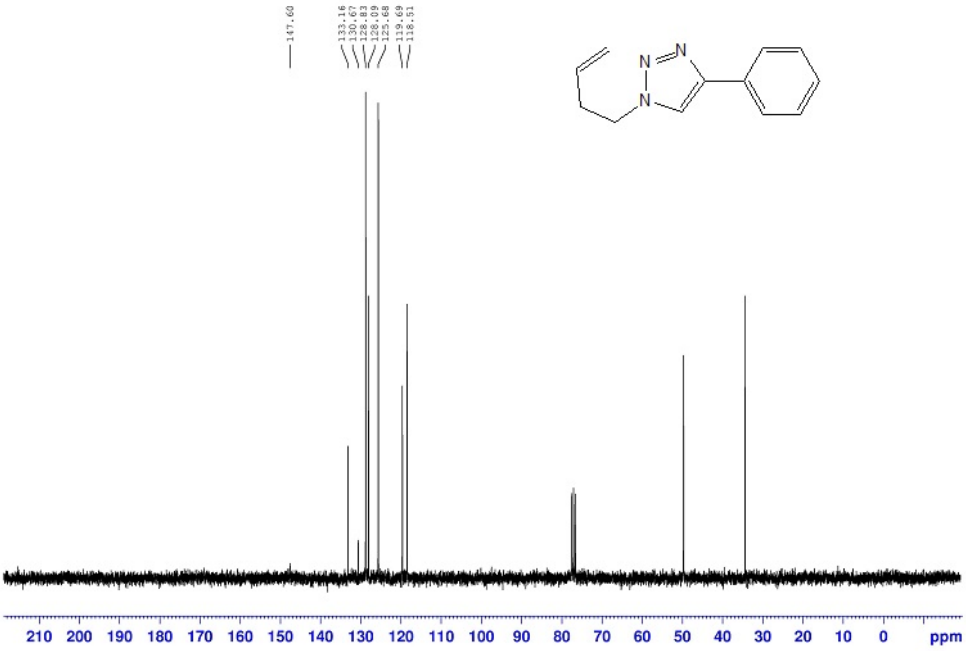
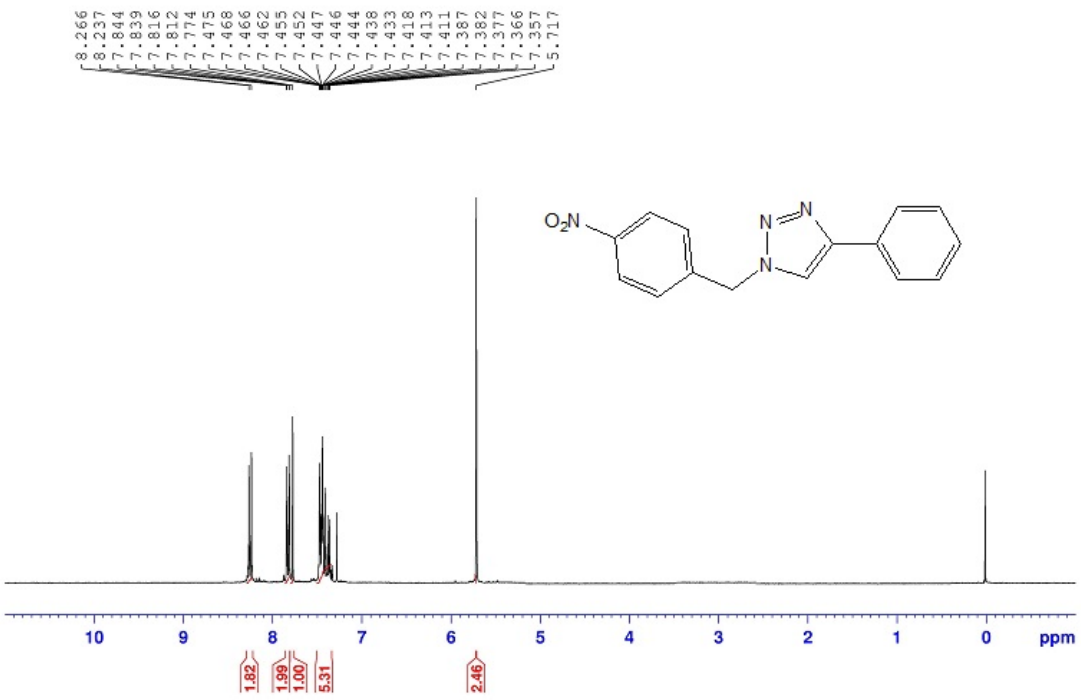
1.74
2.00
2.15


147.60
133.16
130.67
128.83
126.09
125.68
119.69
118.51
N
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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8.237
7.844
7.839
7.816
7.812
7.774
7.475
7.468
7.466
7.462
7.455
7.452
7.447
7.446
7.444
7.438
7.433
7.418
7.413
7.411
7.387
7.382
7.377
7.366
7.357
5.717
O2N
N
N
N
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6
5
4
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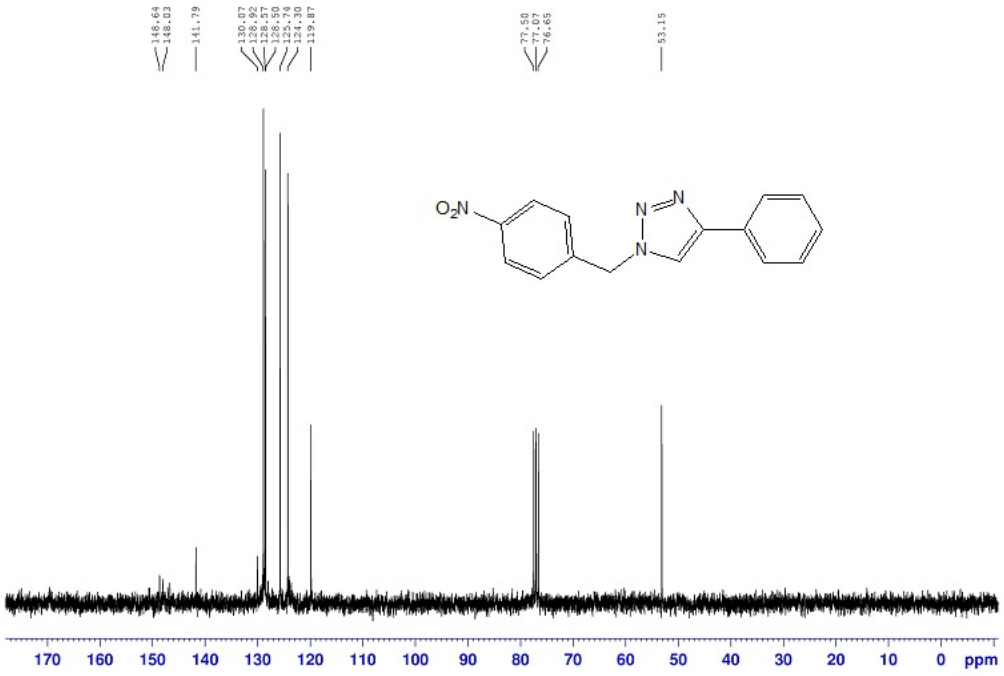
1.00
5.31
2.46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141.79
130.07
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128.57
126.50
125.78
124.30
119.87
77.50
77.07
76.65
53.15
O2N
N
N
N
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140
130
120
110
100
90
80
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60
50
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30
20
10
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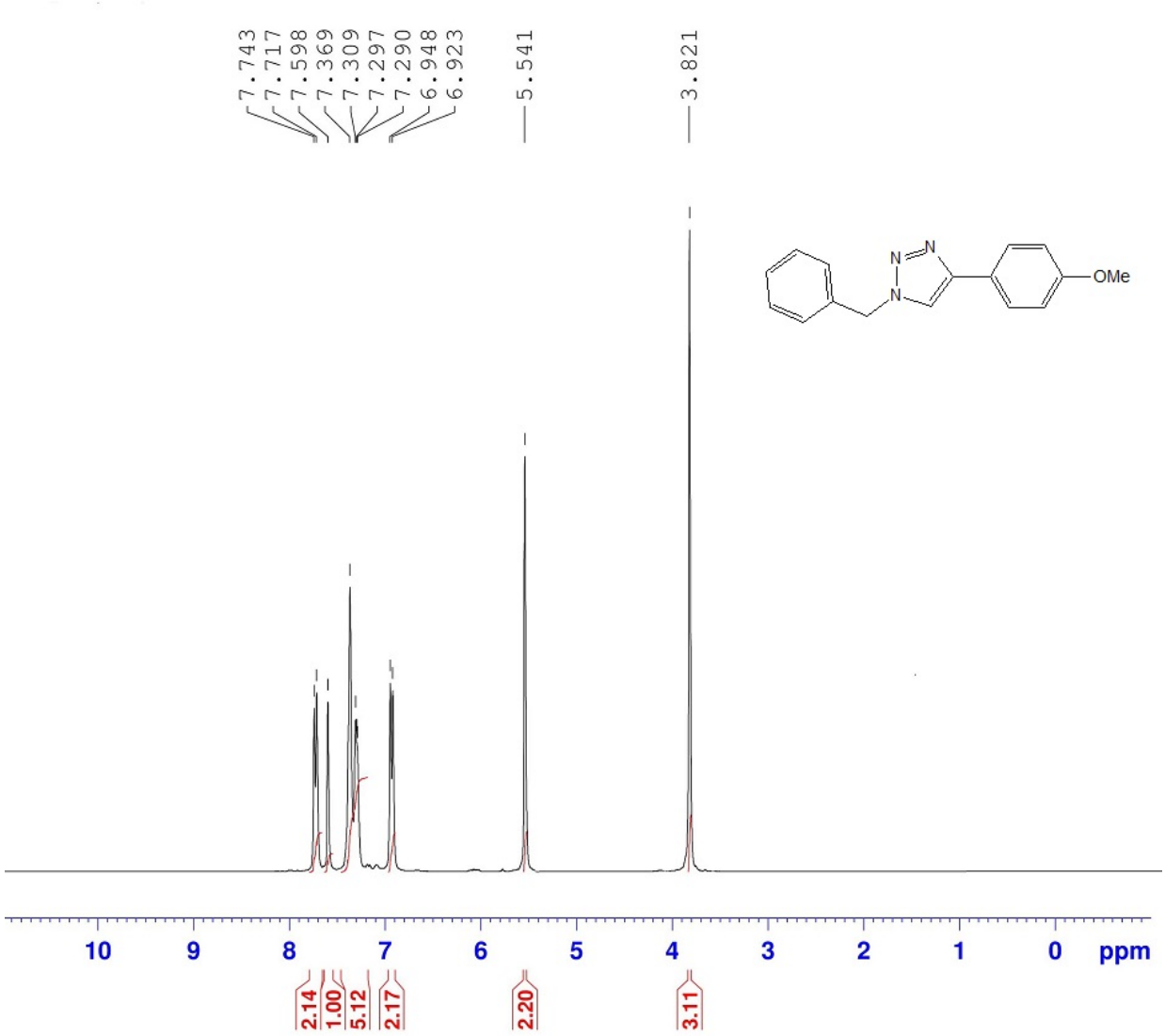
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7.717
7.598
7.369
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7.297
7.290
6.948
6.923
5.541
3.821
N
N
N
OMe
10
9
8
7
6
5
4
3
2
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ppm
2.14
1.00
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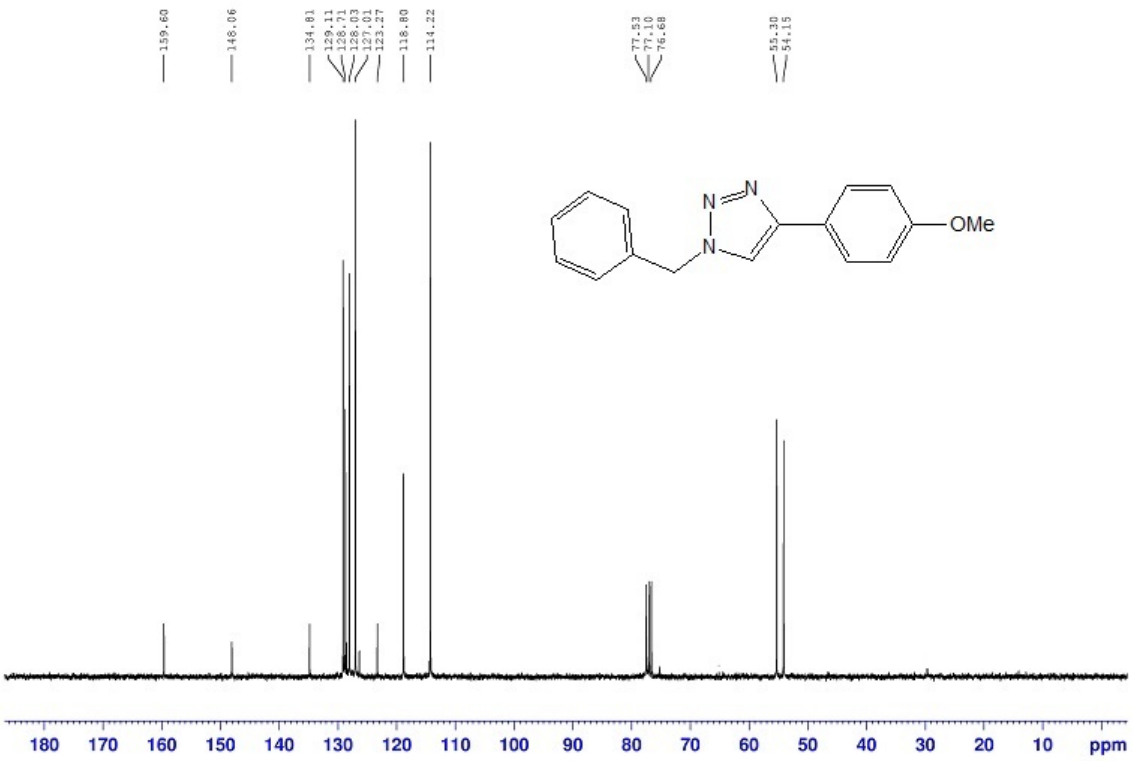
2.17
2.20
3.11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127.01
123.27
118.80
114.22
77.53
77.10
76.68
55.30
54.15
N
N
N
OMe
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150
140
130
120
110
100
90
80
70
60
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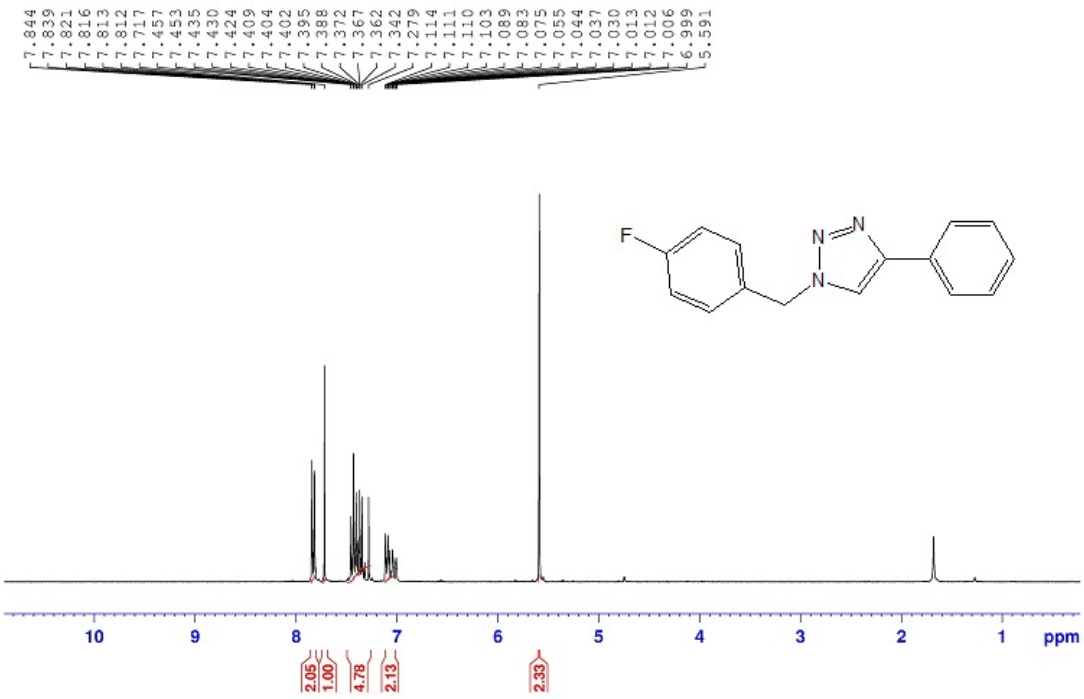
40
30
20
10
ppm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7.839
7.821
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7.424
7.409
7.404
7.402
7.395
7.388
7.372
7.367
7.362
7.342
7.279
7.114
7.111
7.110
7.103
7.089
7.083
7.075
7.055
7.044
7.037
7.030
7.013
7.012
7.006
6.999
5.591
F
N
N
N
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9
8
7
6
5
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ppm
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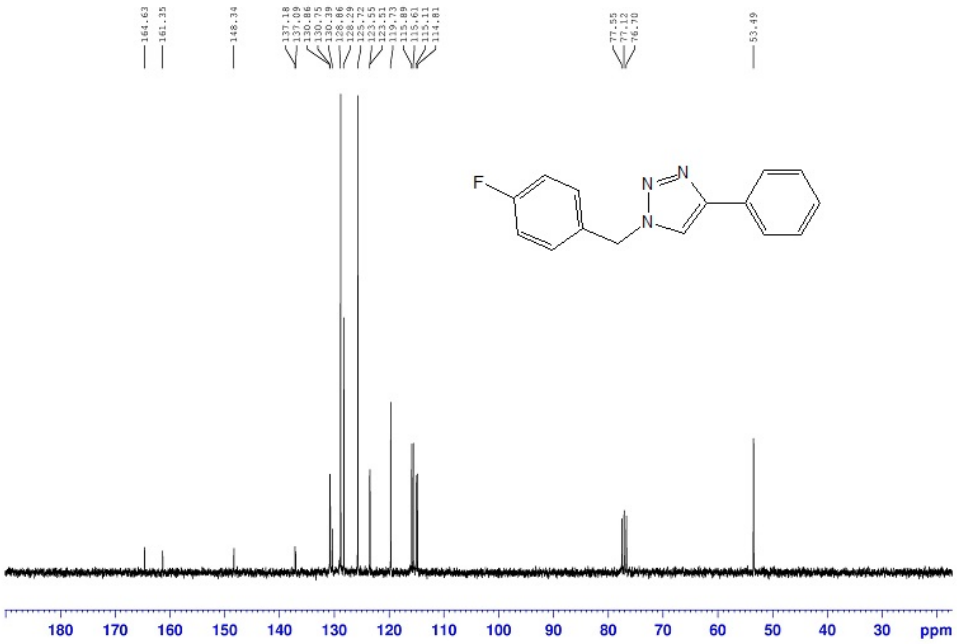
2.33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148.34
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130.86
130.75
130.39
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128.29
125.72
123.55
123.51
119.73
115.89
115.61
115.11
114.81
77.55
77.12
76.70
53.49
F
N
N
N
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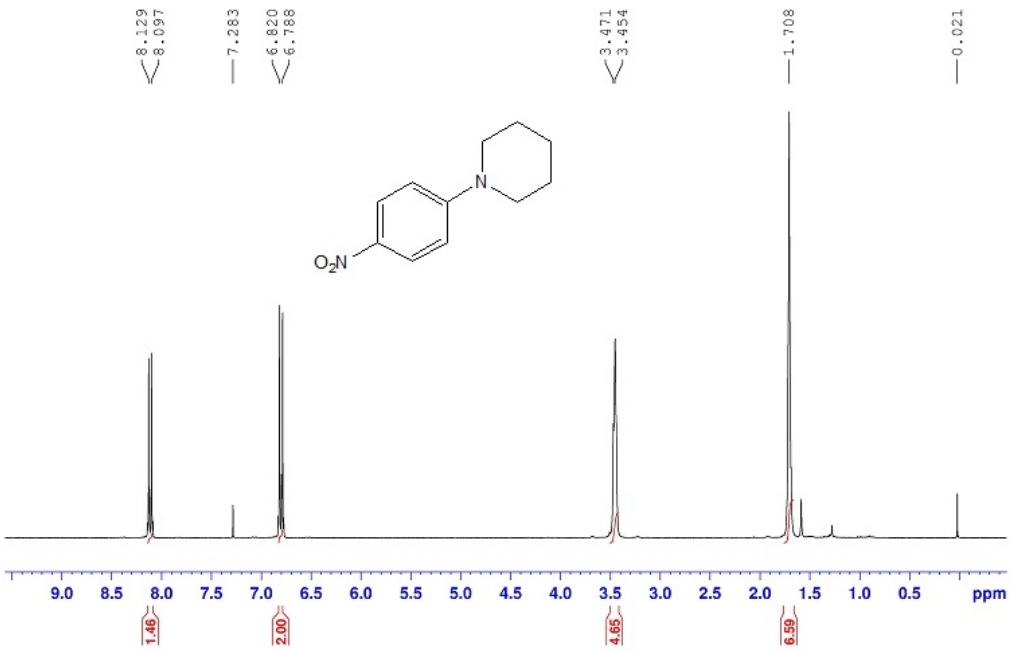
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


8.129
8.097
7.283
6.820
6.788
3.471
3.454
1.708
0.021
N
O2N
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
2.0
1.5
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ppm
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2.00
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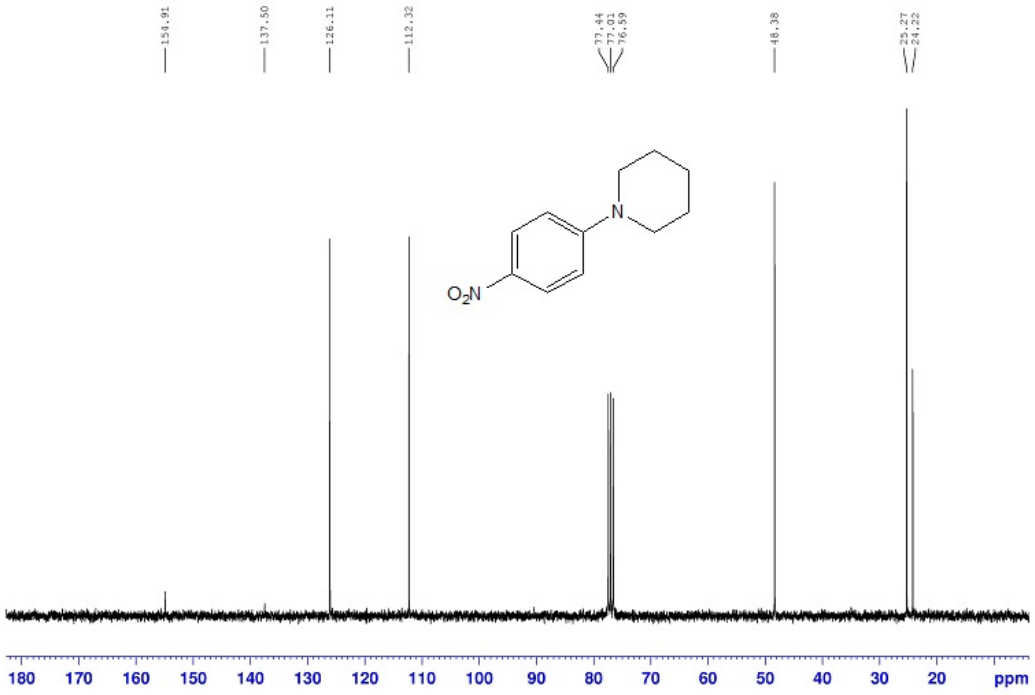
6.59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137.50
126.11
112.32
77.44
77.03
76.59
48.38
25.27
24.22
N
O2N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.124
8.093
6.484
6.453
3.431
3.417
3.409
3.401
3.386
2.109
2.098
2.087
2.077
2.075
2.065
0.092
N
O2N
9
8
7
6
5
4
3
2
1
0
ppm
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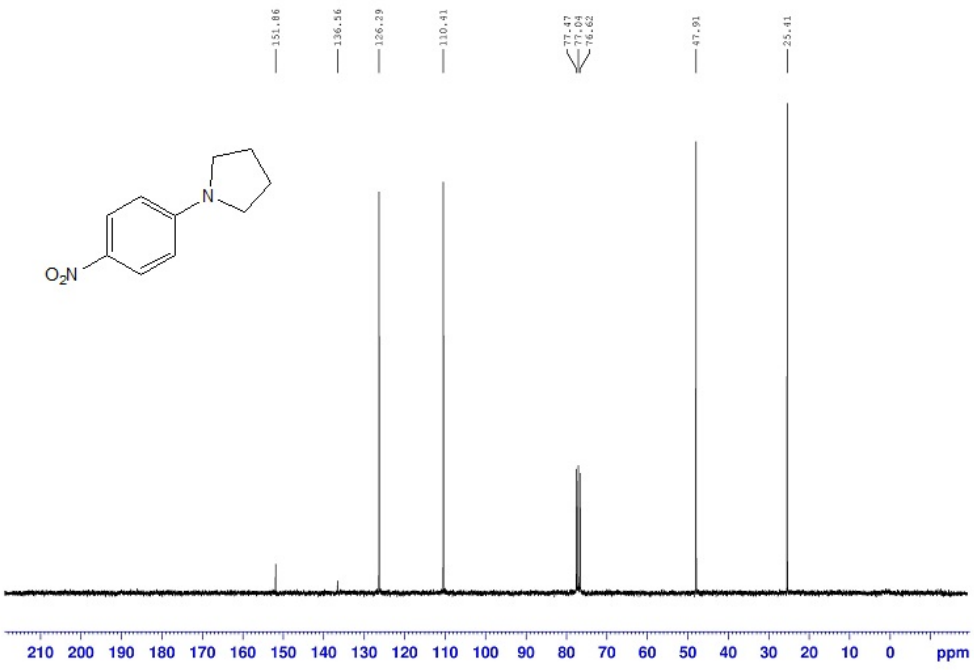
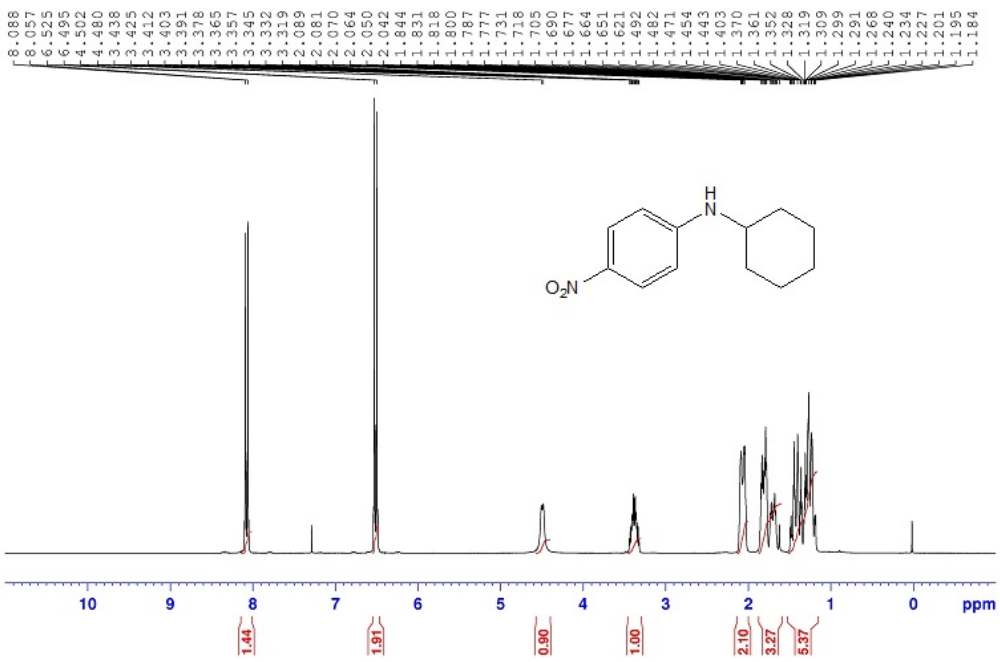
2.00
4.60
4.30


151.86
136.56
126.29
110.41
77.47
77.04
76.62
47.91
25.41
N
O2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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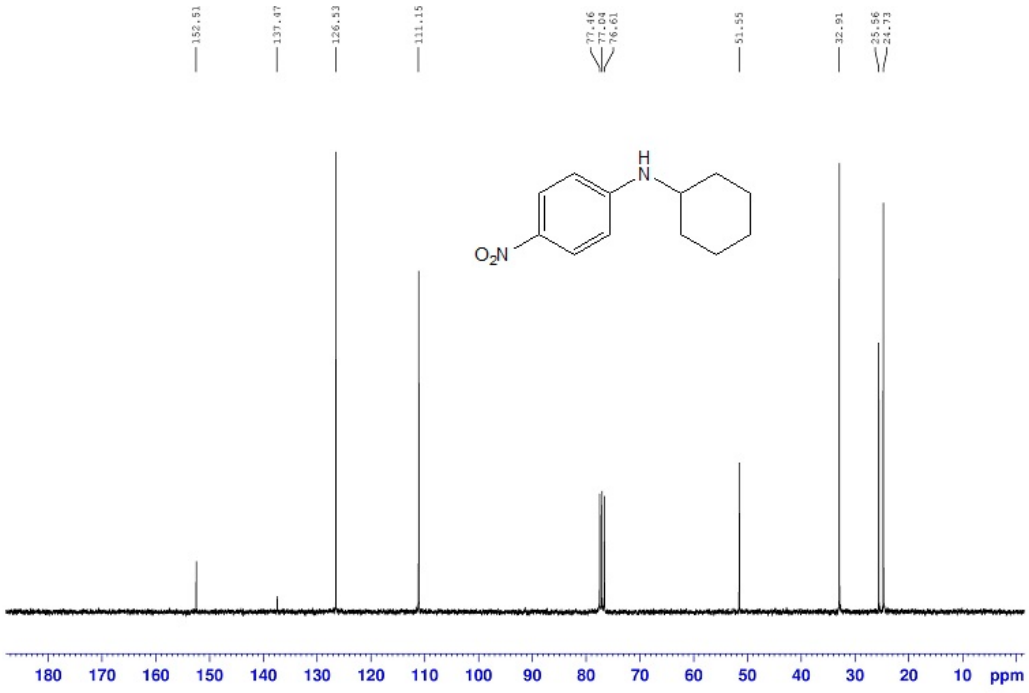
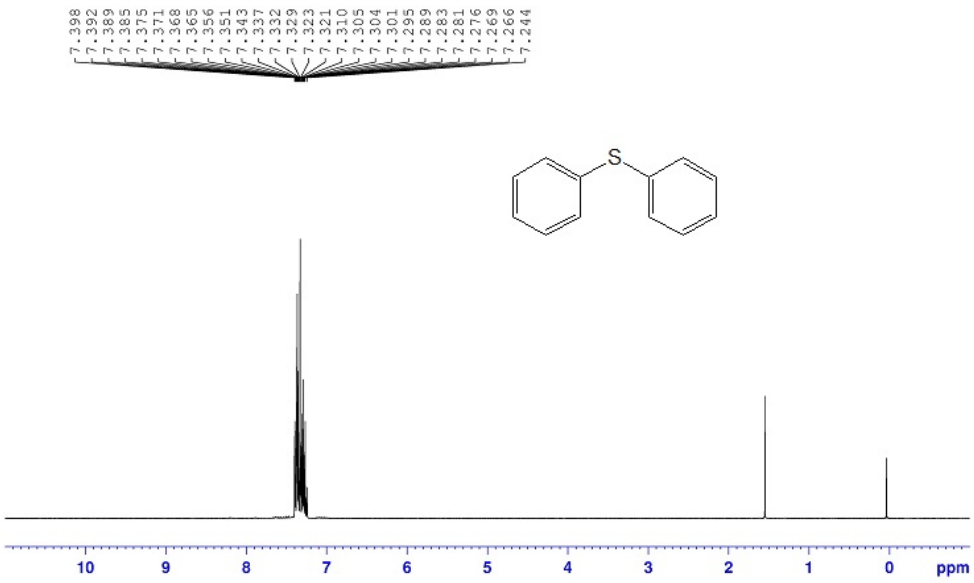
8.057
6.525
6.495
4.502
4.480
3.438
3.425
3.412
3.403
3.391
3.378
3.365
3.357
3.345
3.332
3.319
2.089
2.081
2.070
2.064
2.050
2.042
1.844
1.831
1.818
1.800
1.787
1.777
1.731
1.718
1.705
1.690
1.677
1.664
1.651
1.621
1.492
1.482
1.471
1.454
1.443
1.403
1.370
1.361
1.352
1.328
1.319
1.309
1.299
1.291
1.268
1.240
1.234
1.227
1.201
1.195
1.184
H
N
O2N
10
9
8
7
6
5
4
3
2
1
0
ppm
1.44
1.91
0.90
1.00
2.10
3.27
5.37


152.51
137.47
126.53
111.15
77.46
77.04
76.61
51.55
32.91
25.56
24.73
H
N
O2N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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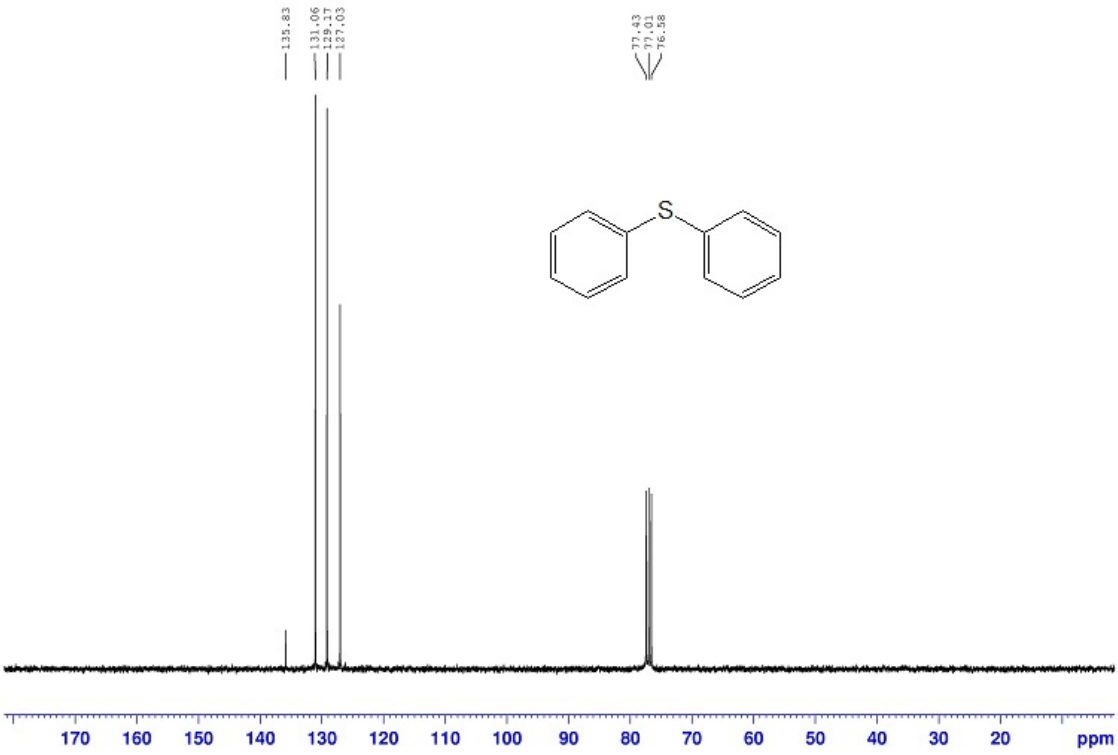
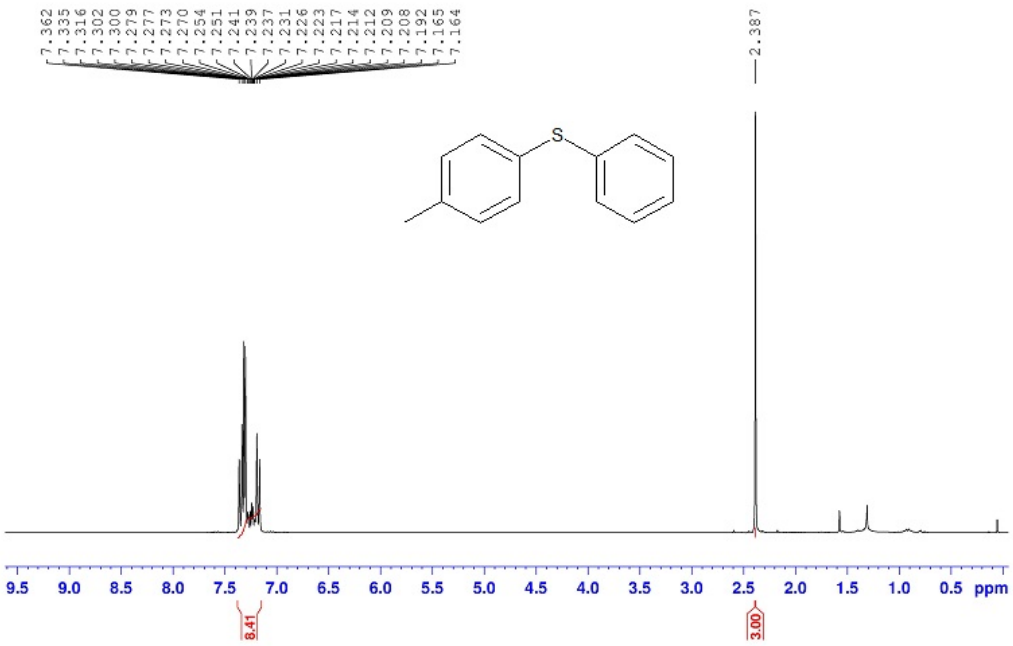
7.389
7.385
7.375
7.371
7.368
7.365
7.356
7.351
7.343
7.337
7.332
7.329
7.323
7.321
7.310
7.305
7.304
7.301
7.295
7.289
7.283
7.281
7.276
7.269
7.266
7.244
S
10
9
8
7
6
5
4
3
2
1
0
ppm


135.83
131.06
129.17
127.03
77.43
77.01
76.58
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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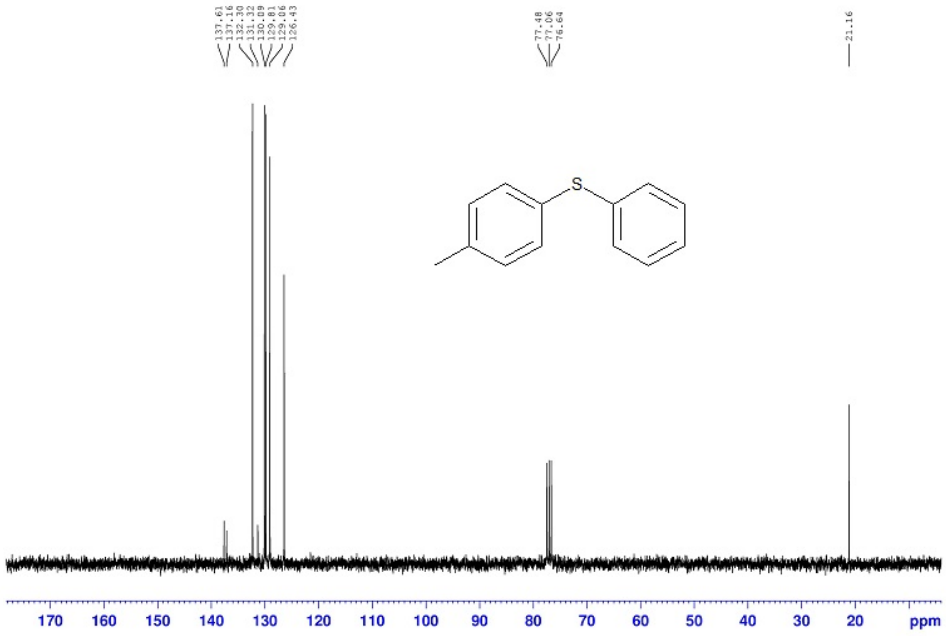
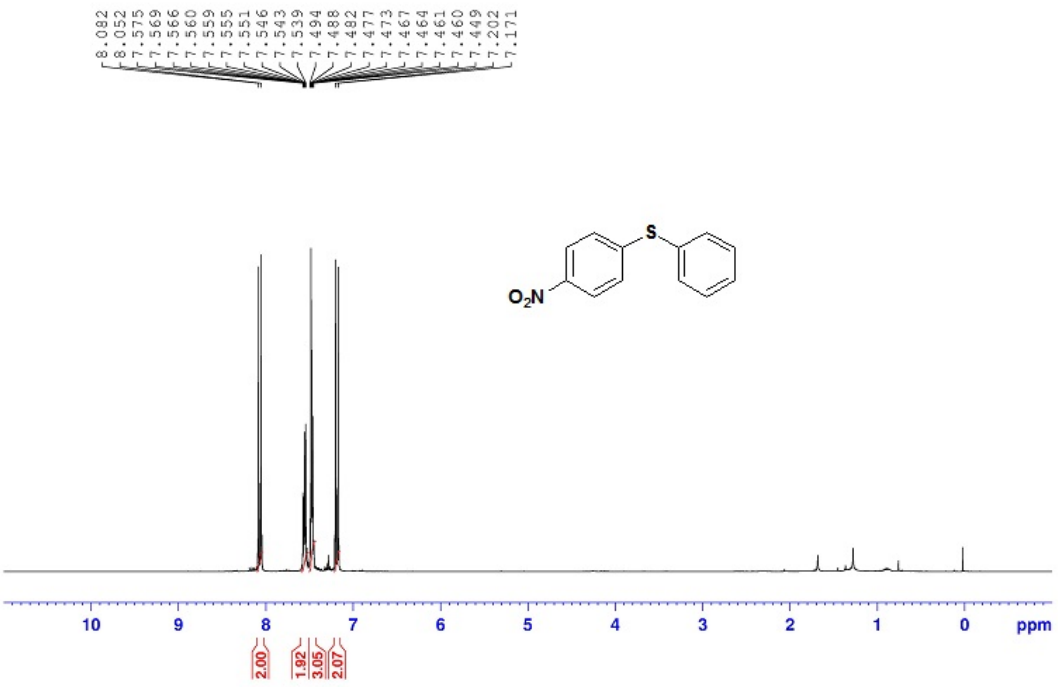
7.335
7.316
7.302
7.300
7.279
7.277
7.273
7.270
7.254
7.251
7.241
7.239
7.237
7.231
7.226
7.223
7.217
7.214
7.212
7.209
7.208
7.192
7.165
7.164
2.387
S
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
8.41
3.00


137.61
137.16
132.30
131.12
130.89
129.81
129.06
126.43
77.48
77.06
76.64
21.16
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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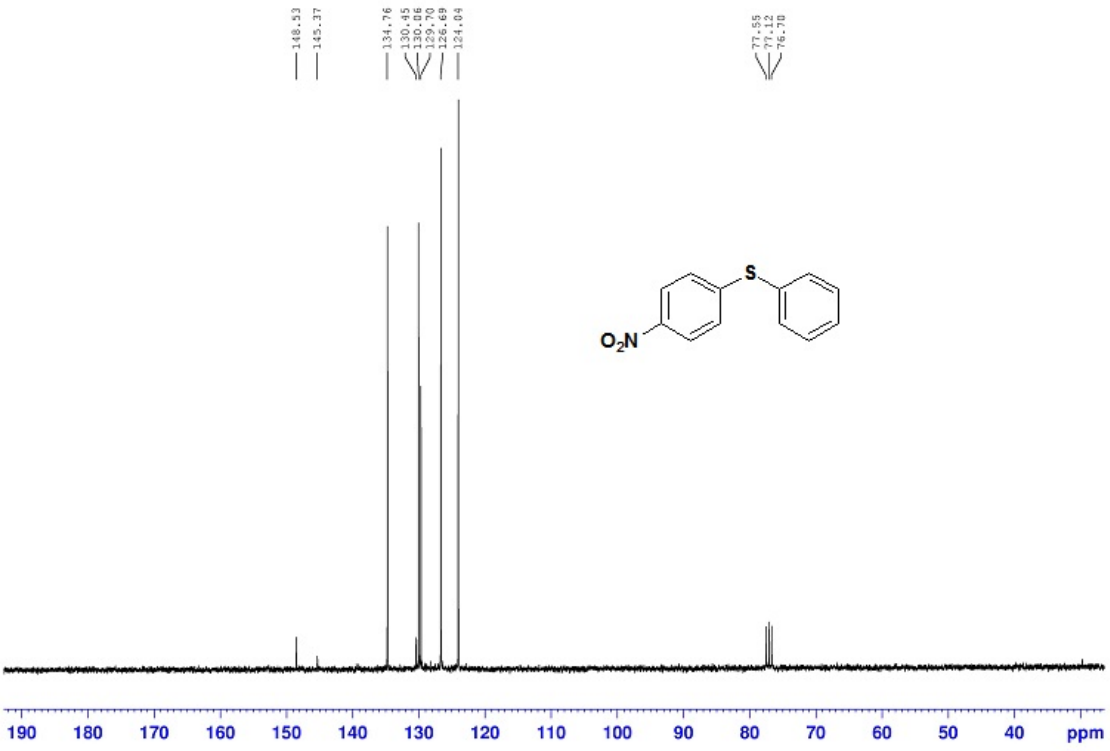
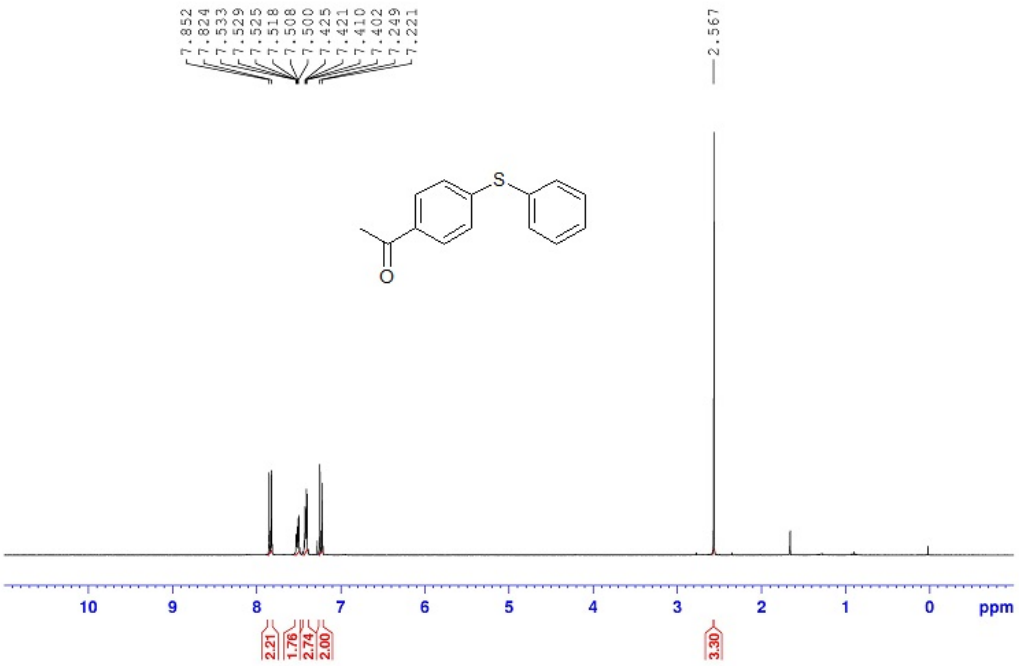
8.052
7.575
7.569
7.566
7.560
7.559
7.555
7.551
7.546
7.543
7.539
7.494
7.488
7.482
7.477
7.473
7.467
7.464
7.461
7.460
7.449
7.202
7.171
S
O2N
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.92
3.05
2.07


148.53
145.37
134.76
130.45
130.06
129.70
126.69
124.04
77.55
77.12
76.70
S
O2N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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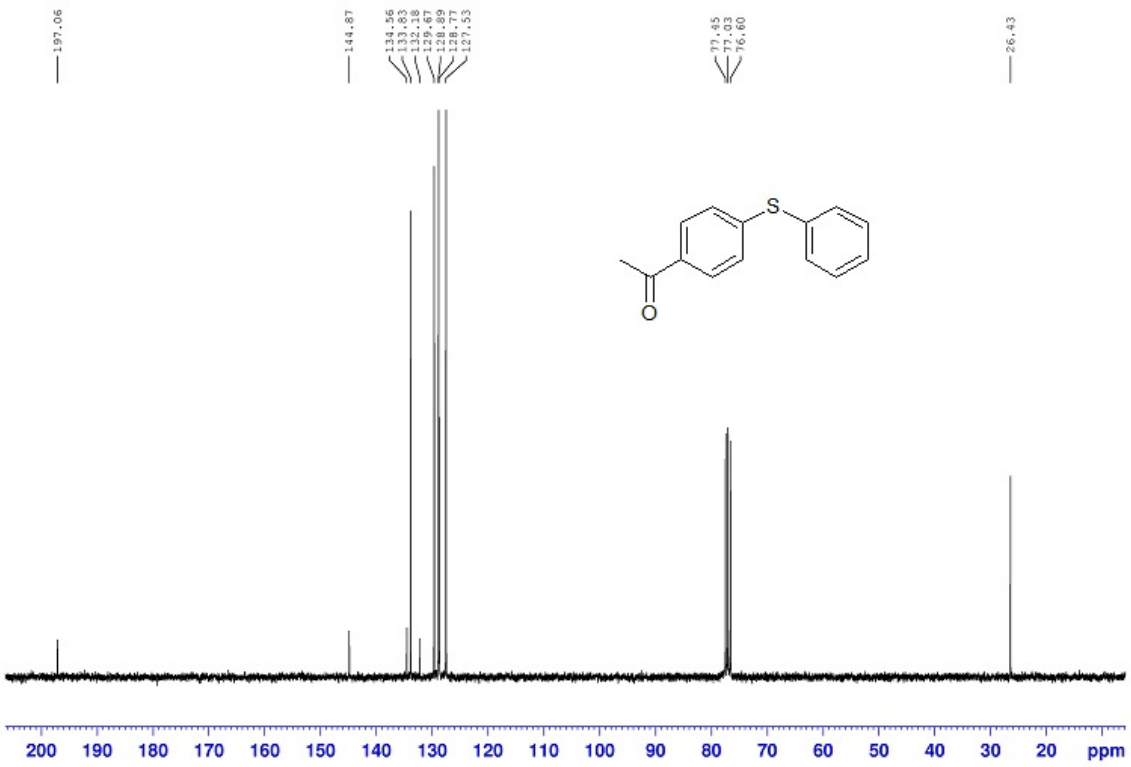
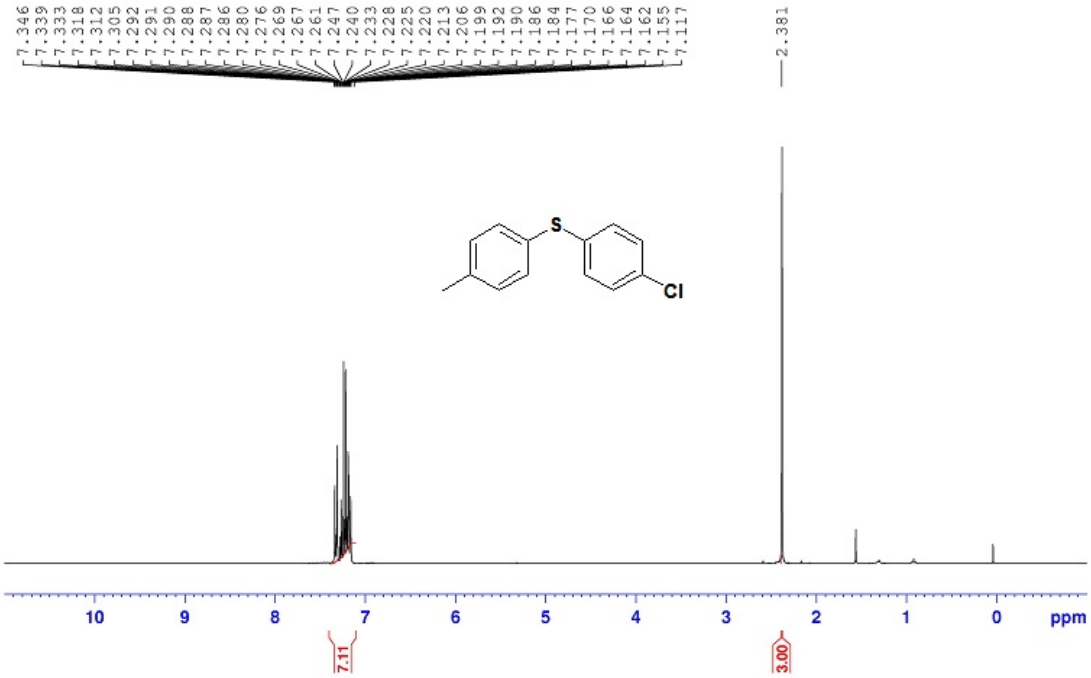
7.529
7.525
7.518
7.508
7.500
7.425
7.421
7.410
7.402
7.249
7.221
2.567
S
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.21
1.76
2.74
2.00
3.30


197.06
144.87
134.56
133.83
132.18
129.67
128.89
128.77
127.53
77.45
77.03
76.60
26.43
S
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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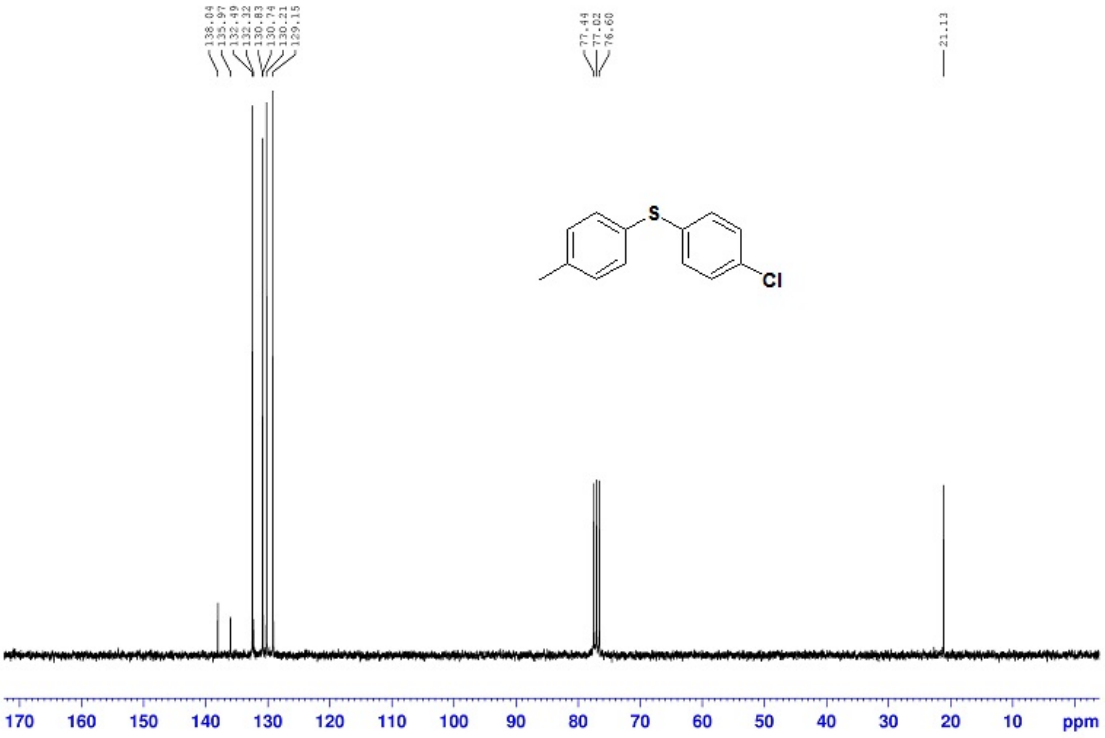
7.291
7.290
7.288
7.287
7.286
7.280
7.276
7.269
7.267
7.261
7.247
7.240
7.233
7.228
7.225
7.220
7.213
7.206
7.199
7.192
7.190
7.186
7.184
7.177
7.170
7.166
7.164
7.162
7.155
7.117
2.381
S
Cl
10
9
8
7
6
5
4
3
2
1
0
ppm
7.11
3.00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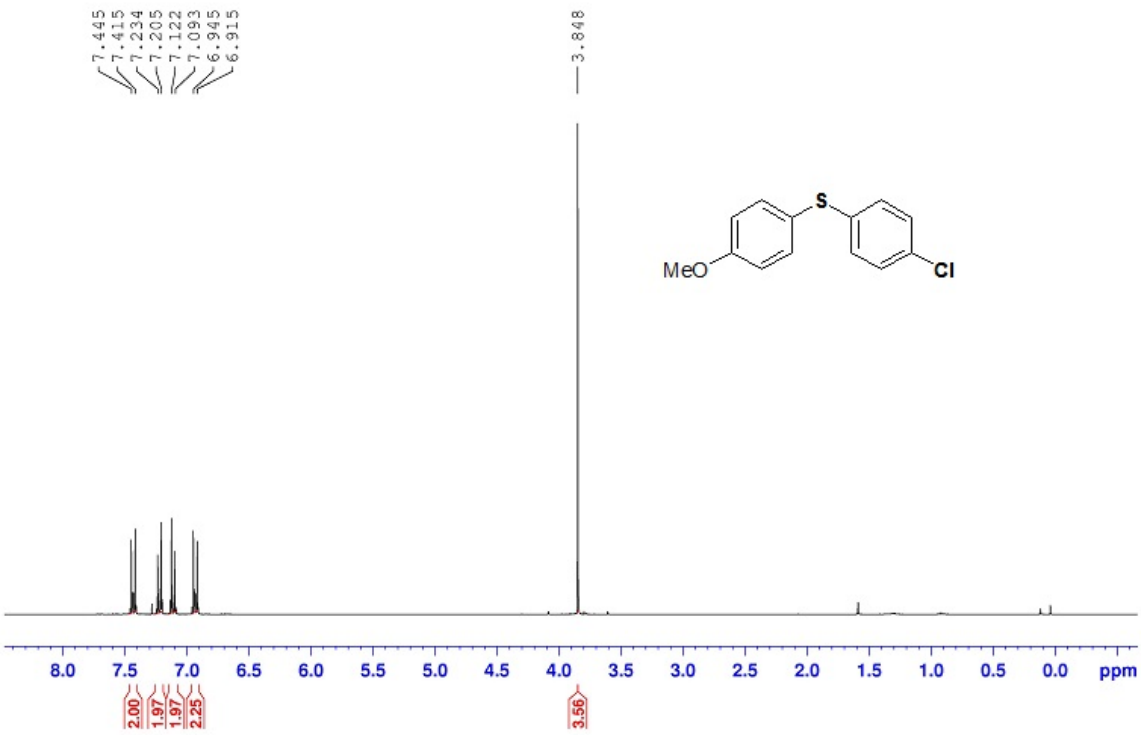
132.32
130.83
130.74
130.21
129.15
77.44
77.02
76.60
21.13
S
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.234
7.205
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7.093
6.945
6.915
3.848
S
MeO
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
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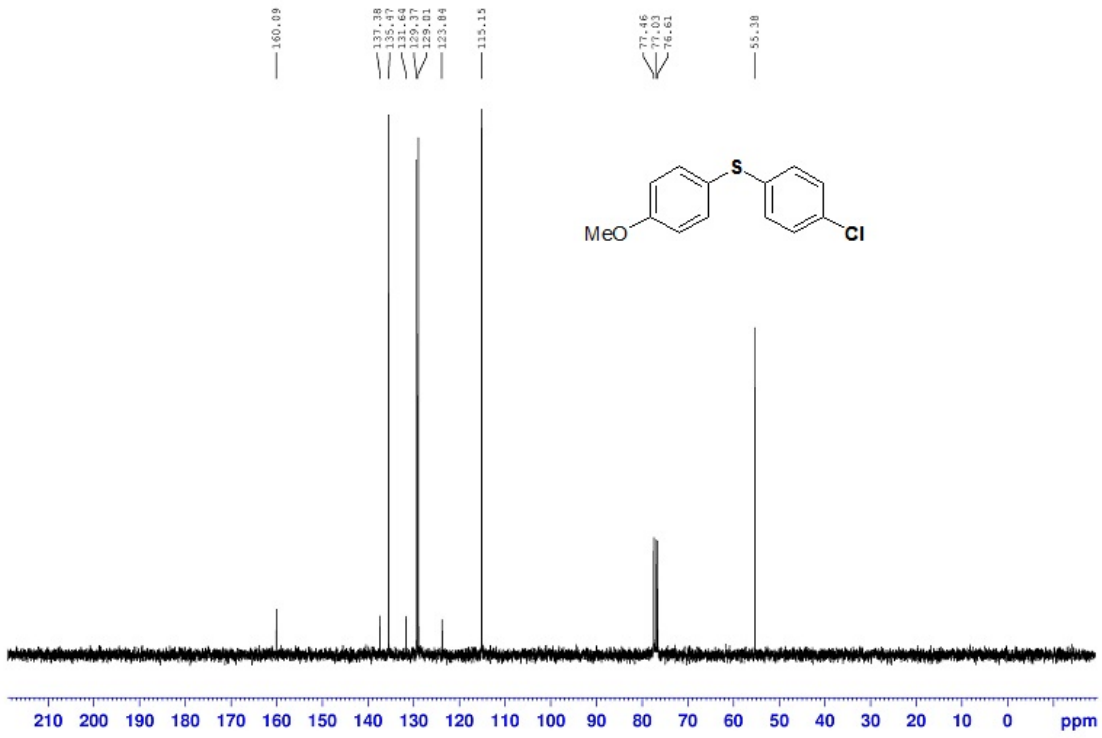
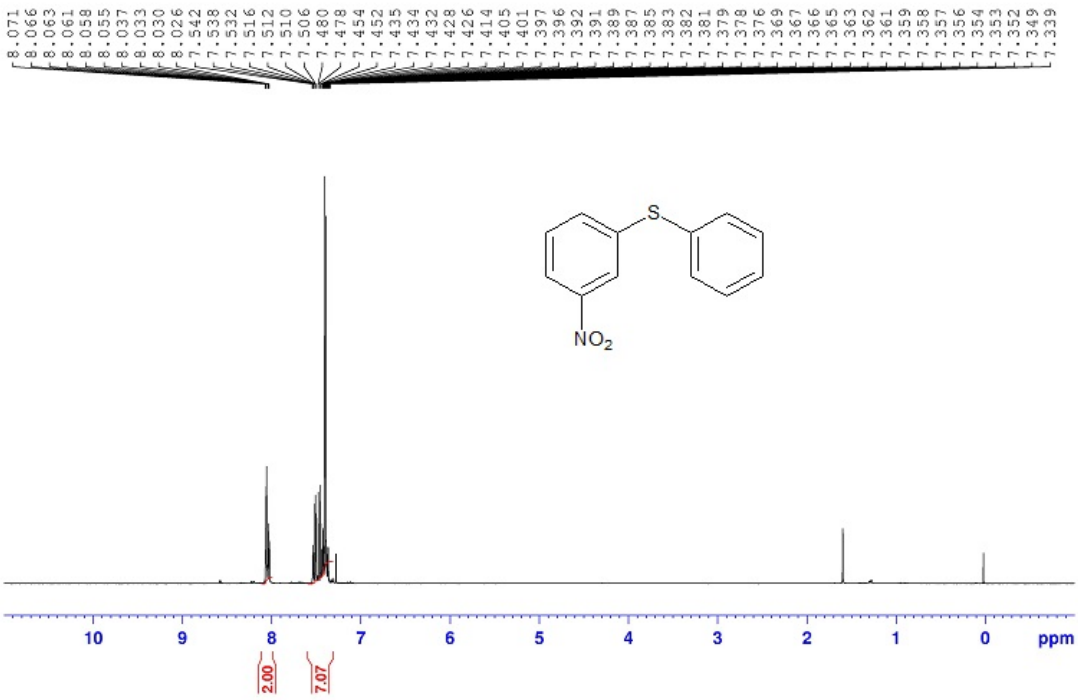
1.97
2.25
3.56


160.09
137.38
135.47
131.64
129.37
129.01
123.04
115.15
77.46
77.03
76.61
55.38
S
MeO
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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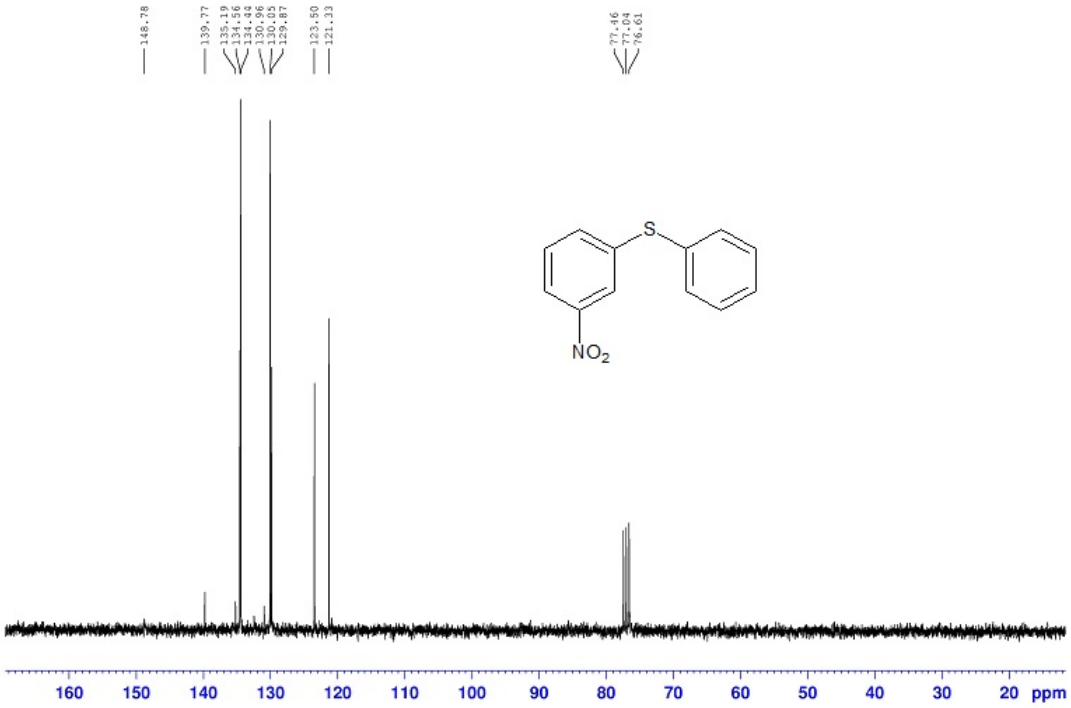
7.532
7.516
7.512
7.510
7.506
7.480
7.478
7.454
7.452
7.435
7.434
7.432
7.428
7.426
7.414
7.405
7.401
7.397
7.396
7.392
7.391
7.389
7.387
7.385
7.383
7.382
7.381
7.379
7.378
7.376
7.369
7.367
7.366
7.365
7.363
7.362
7.361
7.359
7.358
7.357
7.356
7.354
7.353
7.352
7.349
7.339
S
NO2
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
7.07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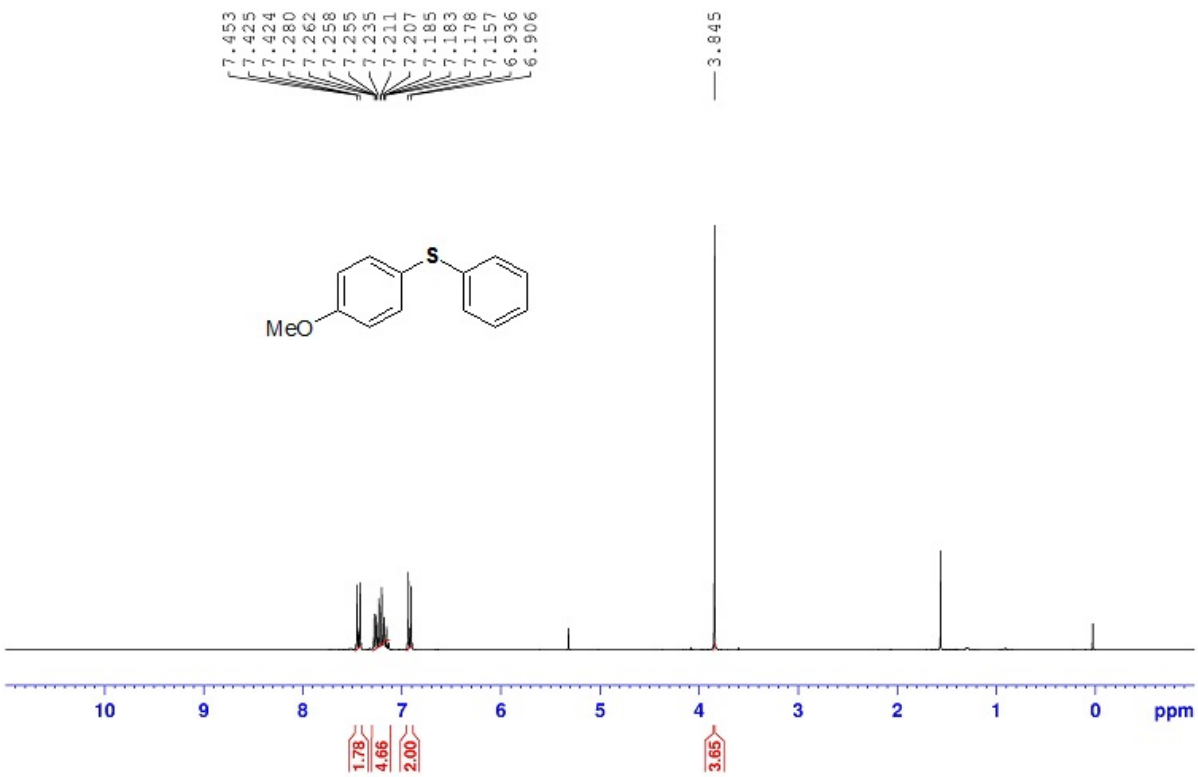
139.77
135.19
134.56
134.44
130.96
130.65
129.87
123.50
121.33
77.46
77.04
76.61
S
NO2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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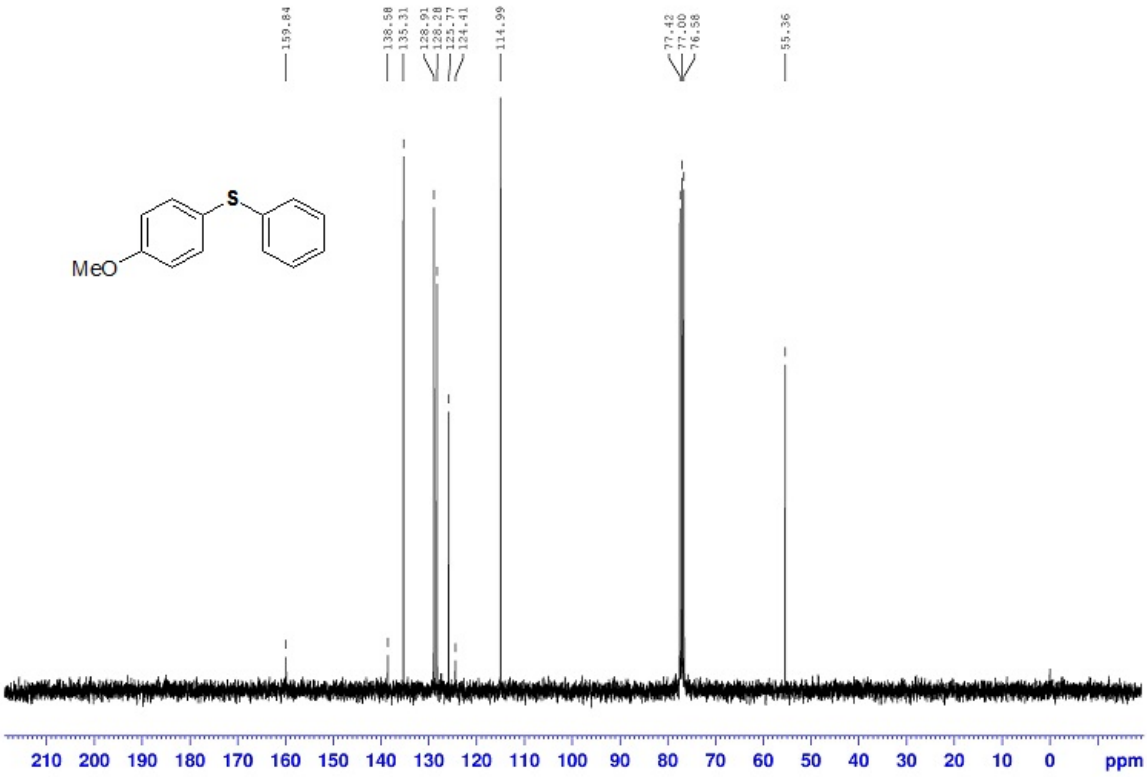
7.280
7.262
7.258
7.255
7.235
7.211
7.207
7.185
7.183
7.178
7.157
6.936
6.906
3.845
S
MeO
10
9
8
7
6
5
4
3
2
1
0
ppm
1.78
4.66
2.00
3.65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128.91
128.28
125.77
124.41
114.99
77.42
77.00
76.58
55.36
S
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm