Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supporting Information

Visible-light-induced and iron-catalyzed methylation of *N*-arylacrylamides with dimethyl sulphoxide： A convenient access to 3-ethyl-3-methyl oxindoles

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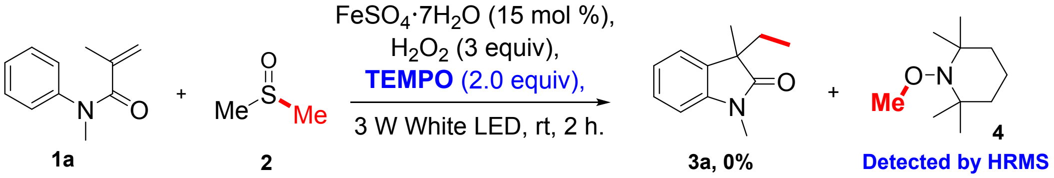
1. General considerations

All ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

N-Arylacrylamides were prepared according to the reported methods.[1] The chemicals and solvents were purchased from commercial suppliers either from Aldrich (USA) or Shanghai Chemical Company (China) without further purification. All the solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2.

2. The control experiments

2.1 Free radical-trapping experiment



N-Arylacrylamide (**1a**, 0.20 mmol), DMSO (**2**, 1.0 mL), $FeSO_4 \cdot 7H_2O$ (0.03 mmol), H_2O_2 (0.60 mmol) and 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 0.40 mmol), were added in an oven-dried reaction vessel equipped with magnetic stirring bar. Then the reaction vessel was irradiated using 3 W White LED under air atmosphere at room temperature for 2 h. After the reaction was stopped, no desired product **3a** was detected by TLC and HPLC-HRMS, indicating that the reaction was completely inhibited. Meanwhile, a methyl radical ($Me^{\cdot}$) trapping product **4** was observed through HPLC-HRMS analysis of the reaction solution, which was shown in Figure S1.

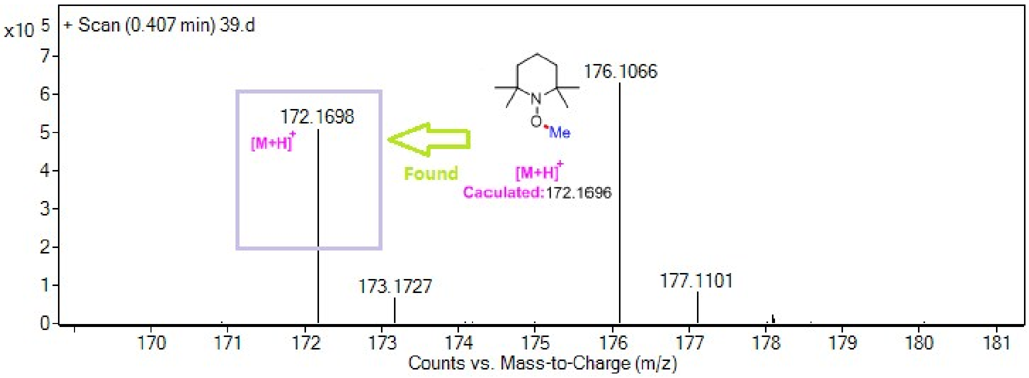
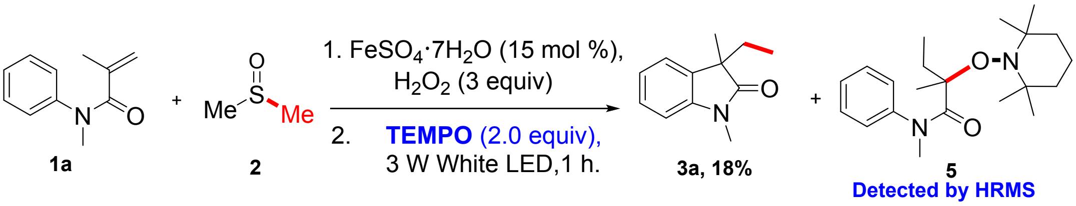


Figure S1 HRMS analysis of TEMPO with a methyl radical (Me˙) trapping product **4**

2.2 Free radical-trapping experiment



N-Arylacrylamide (**1a**, 0.20 mmol), DMSO (**2**, 1.0 mL), $FeSO_4 \cdot 7H_2O$ (0.03 mmol), H_2O_2 (0.60 mmol), were added in an oven-dried reaction vessel equipped with magnetic stirring bar. The reaction vessel was irradiated using 3 W White LED for 20 minutes, then 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 0.40 mmol) was added, under air atmosphere at room temperature the reaction continues for 1 h. After the reaction was stopped, the desired product **3a** was obtained in 18% yields. Meanwhile, a radical trapping product **5** was observed through HPLC-HRMS analysis of the reaction solution, which was shown in Figure S2.

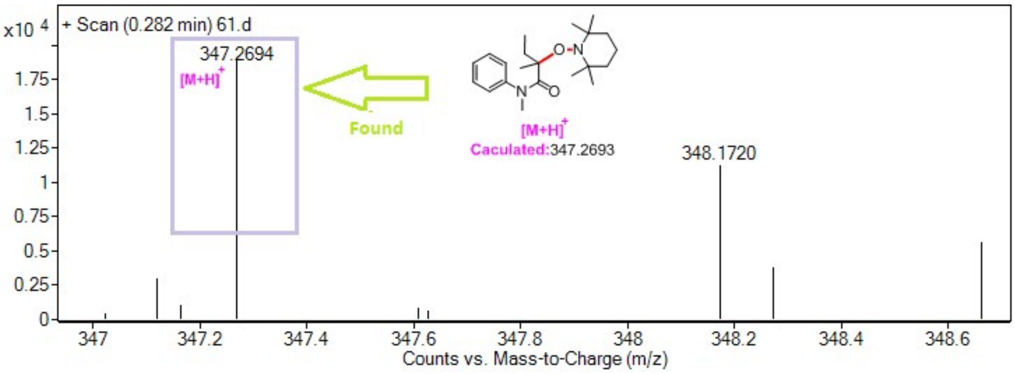
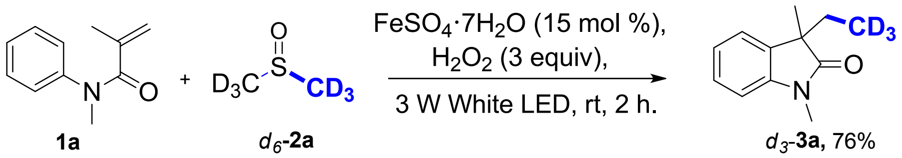


Figure S2 HRMS analysis of TEMPO with a methyl radical trapping product **5**

2.3 The isotopic labeling experiments



N-Arylacrylamide (**1a**, 0.20 mmol), DMSO-*d*$_6$ (1.0 mL), $FeSO_4\cdot 7H_2O$ (0.03 mmol) and H_2O_2 (0.60 mmol) was added to an oven-dried reaction vessel equipped with magnetic stirring bar. Then the reaction vessel was irradiated using 3 W White LED under air atmosphere at room temperature for 2 h. After the reaction was completed, the reaction solution was extracted with EtOAc (2×5.0 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to yield crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give the product *d*$_6$-**3a** as a colorless liquid in 76% yield. The ^{1}H NMR analysis of *d*$_6$-**3a** was shown in Figure S3 .

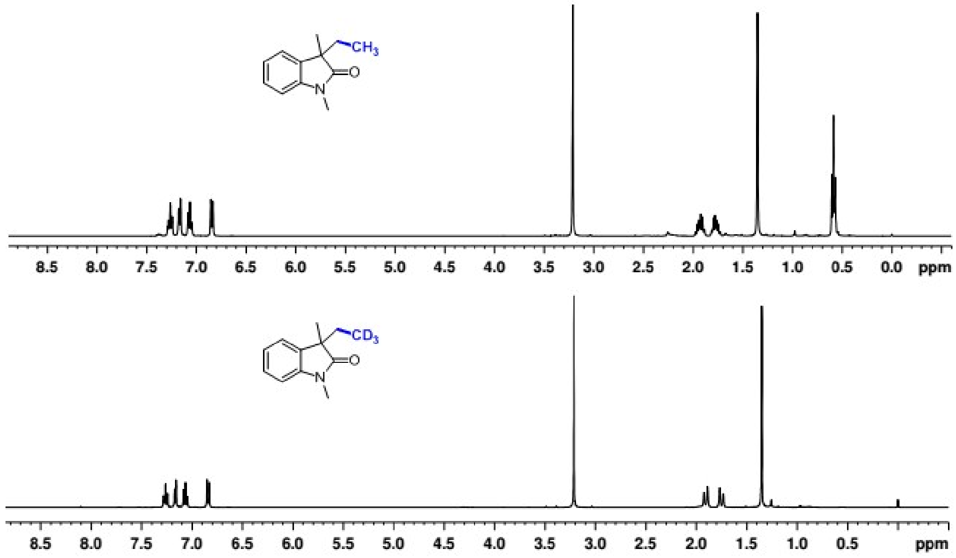
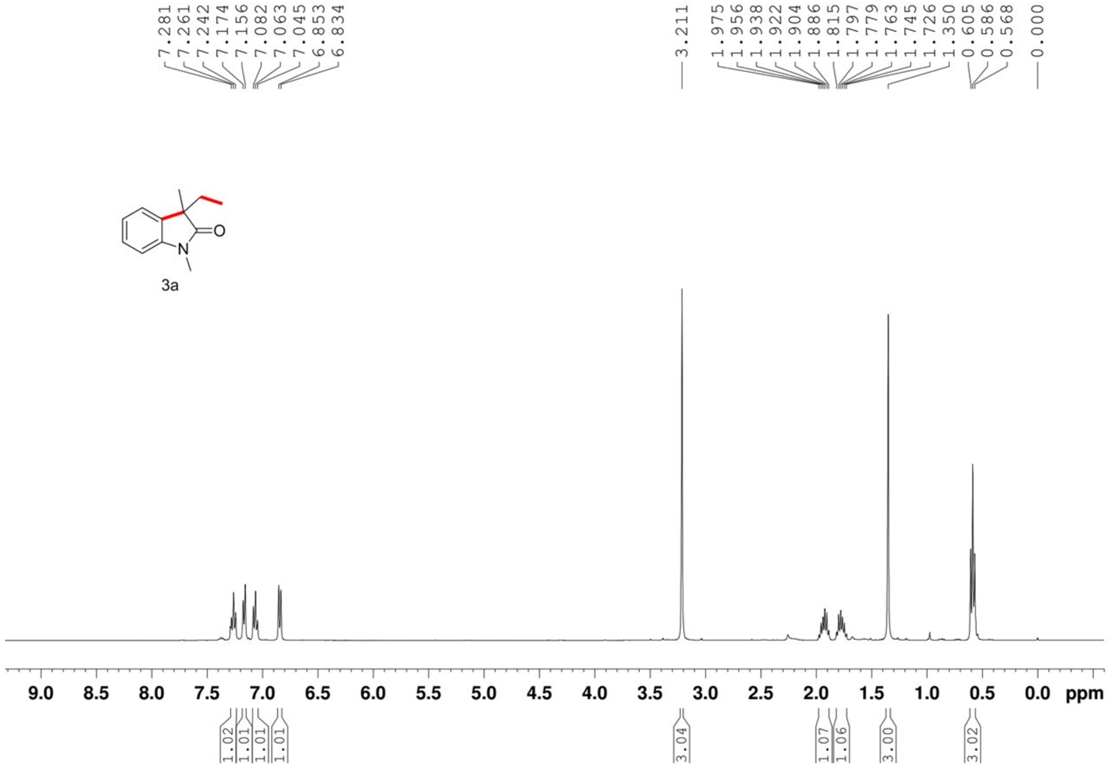
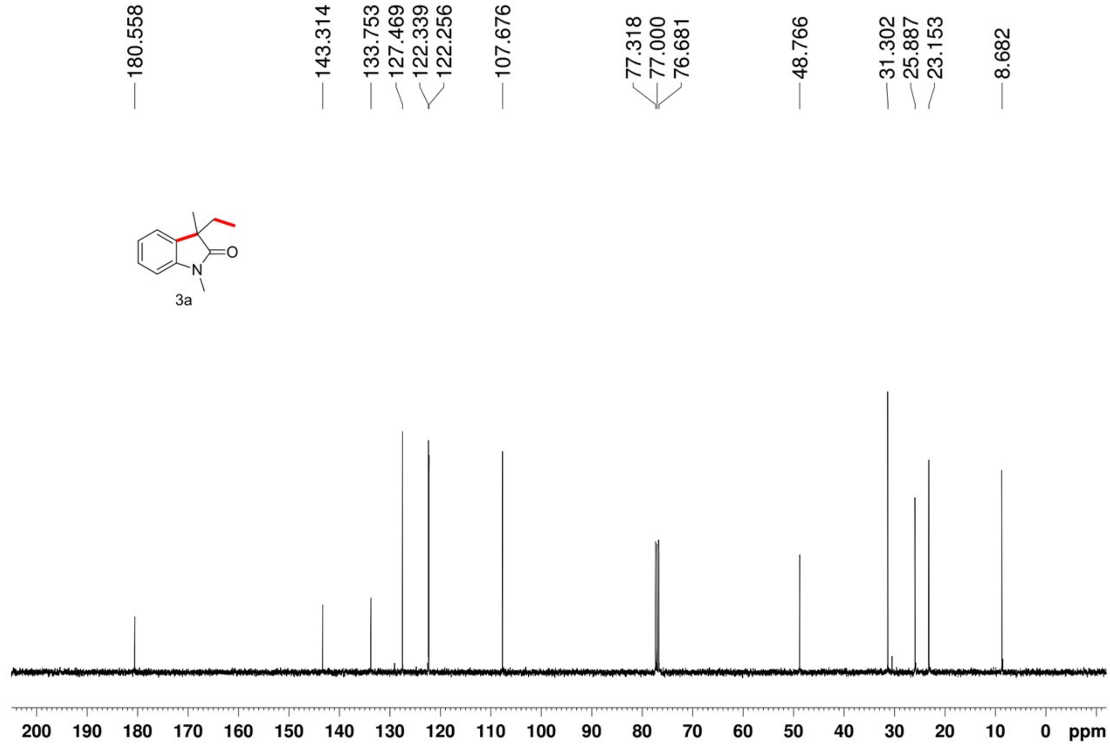
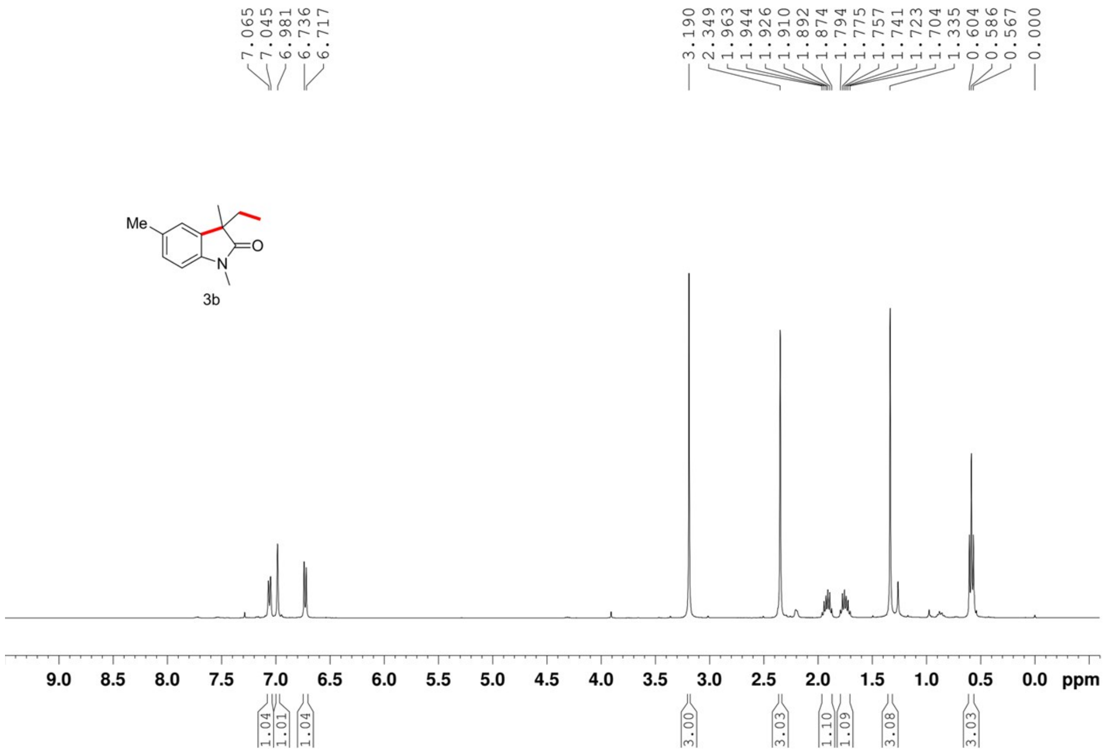


Figure S3 ^{1}H NMR analysis of **3a** and *d*$_3$-**3a**

3. ^{1}H and ^{13}C NMR spectra of the products



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N
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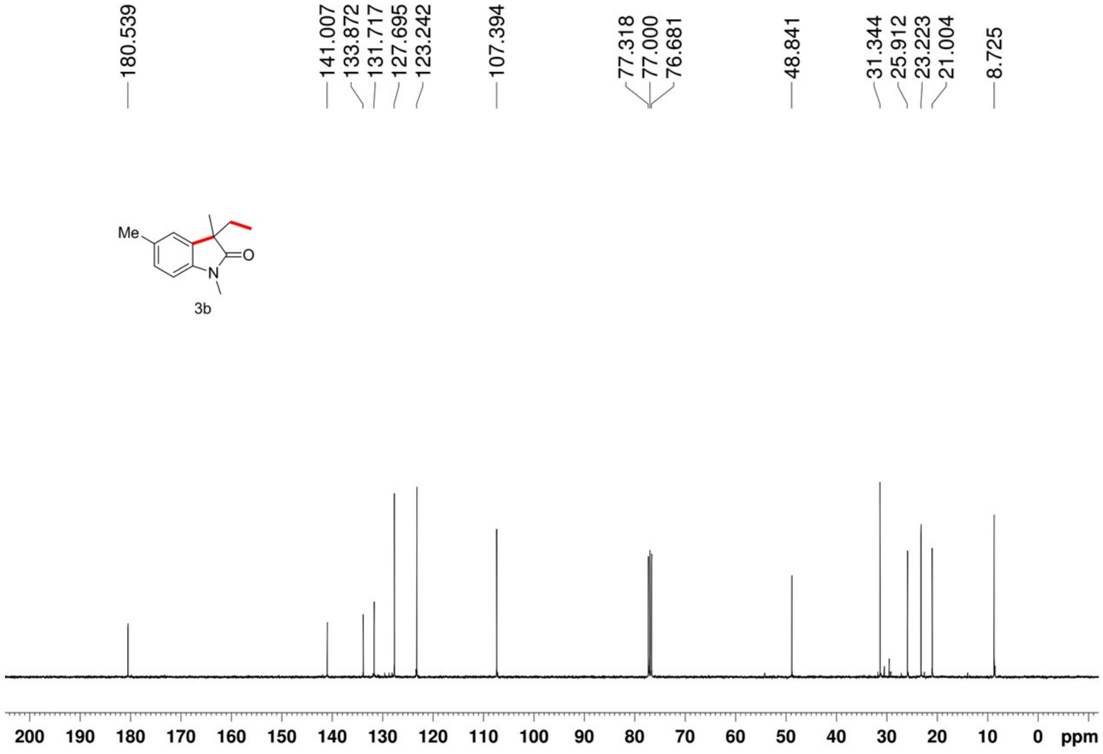
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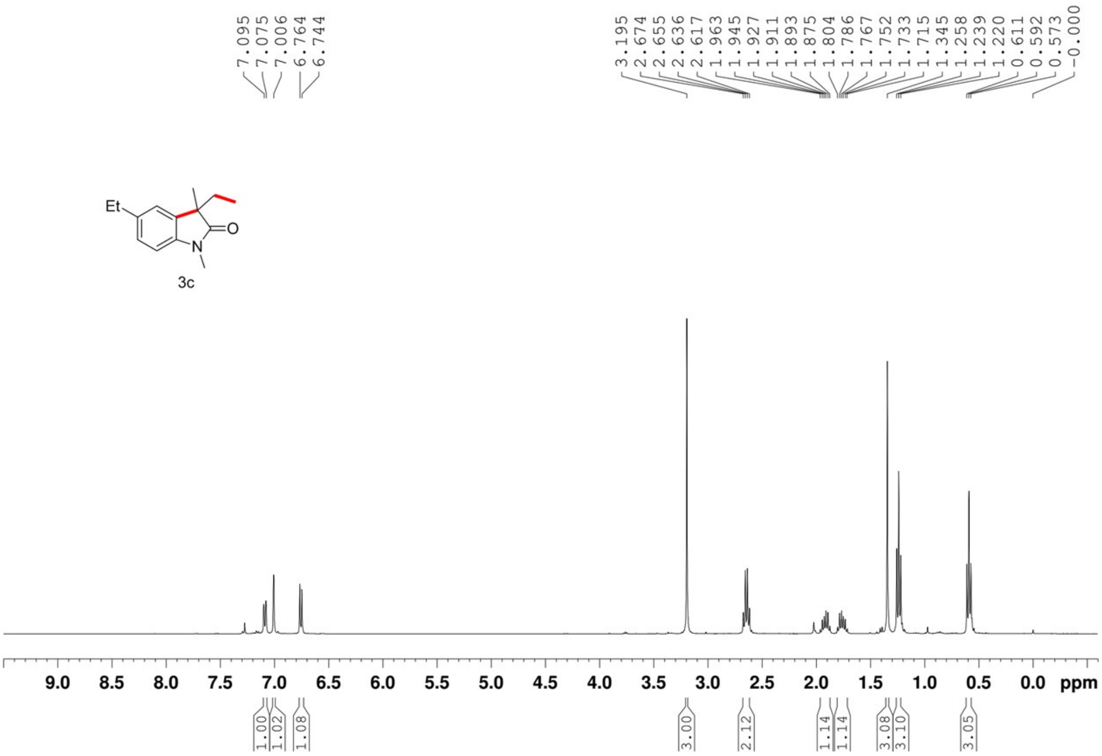
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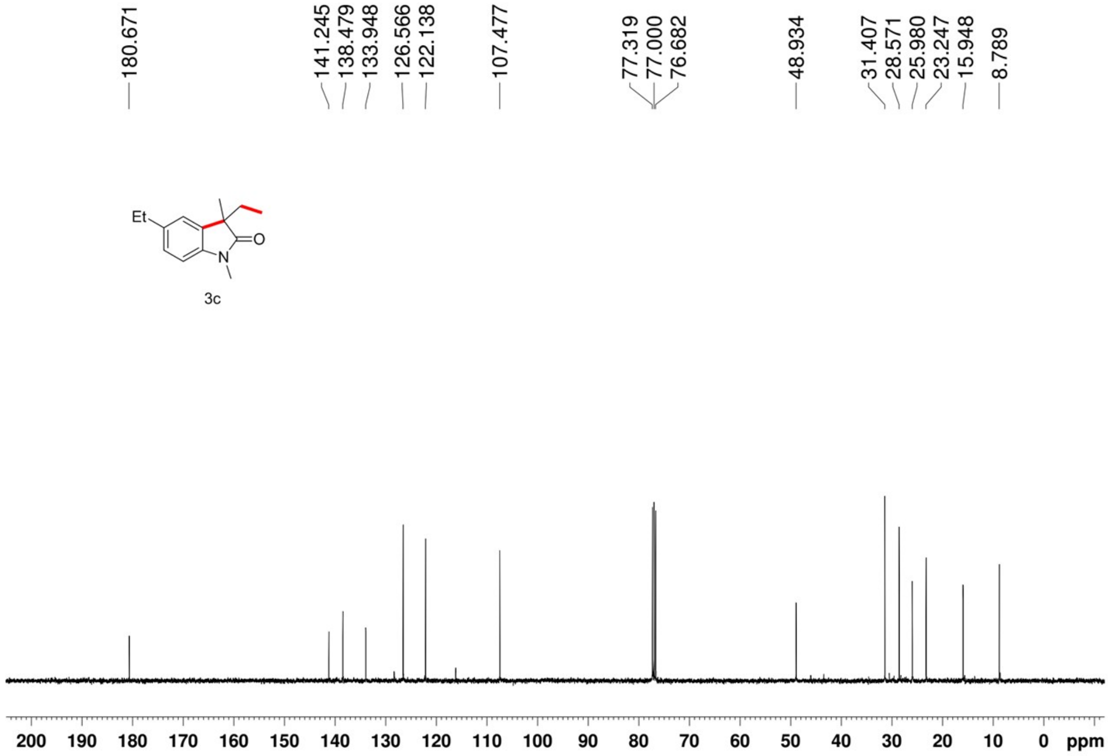
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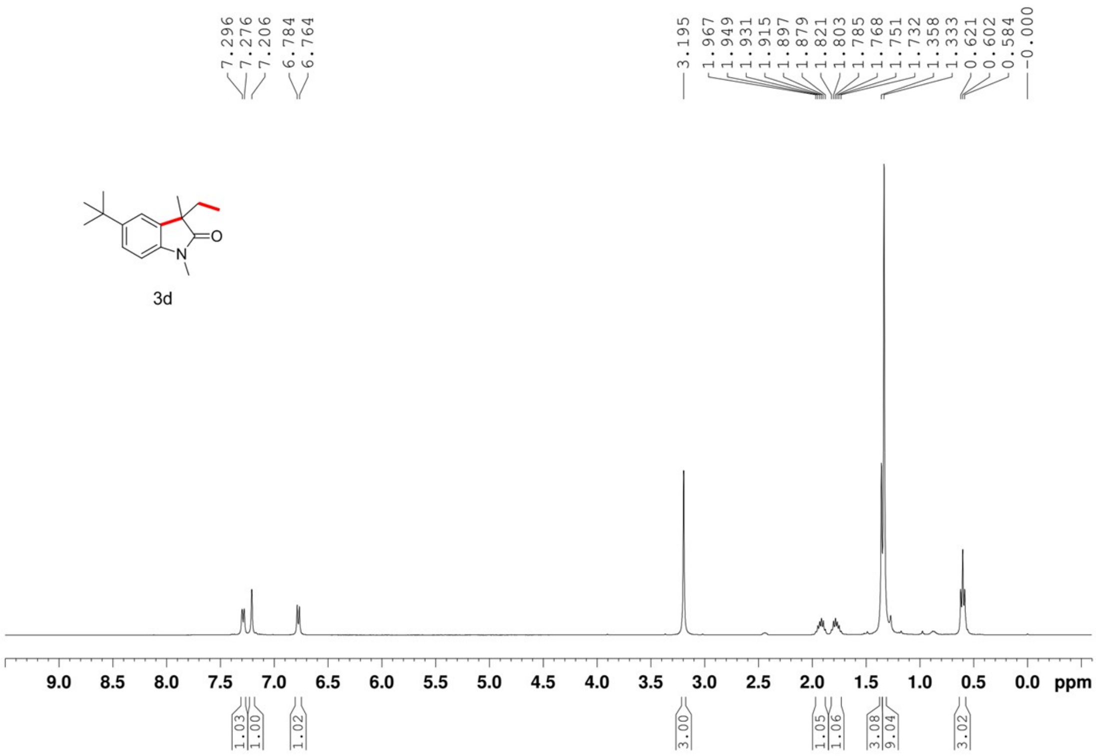
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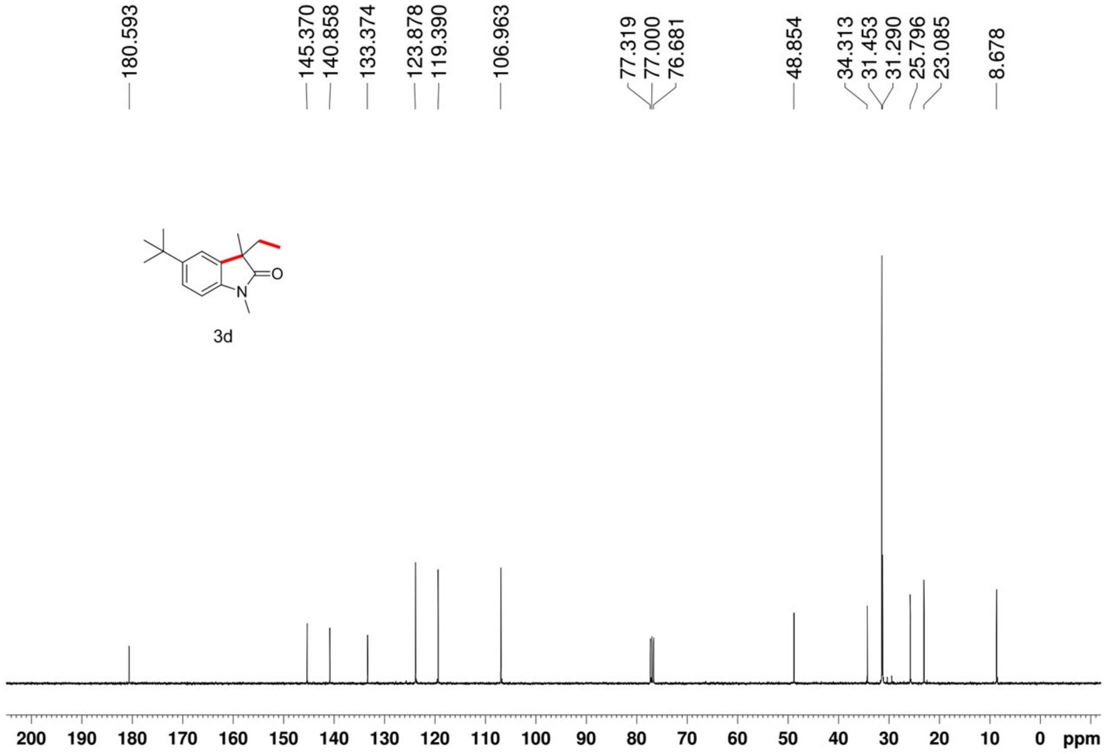
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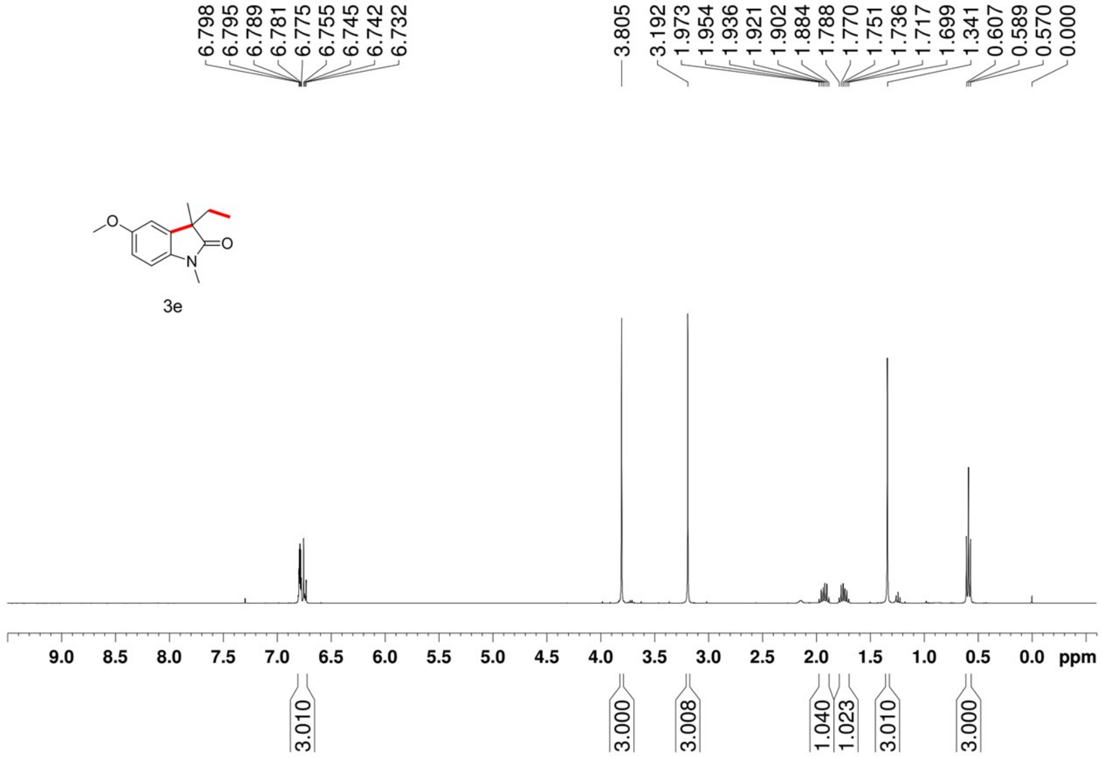
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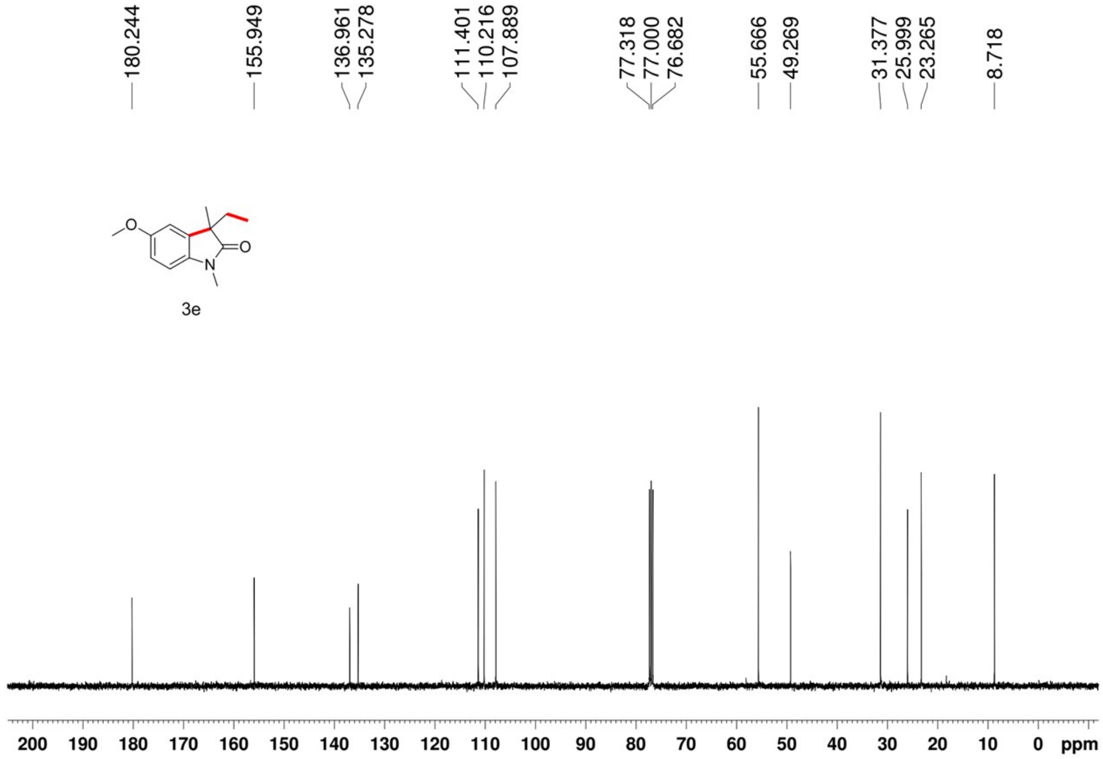
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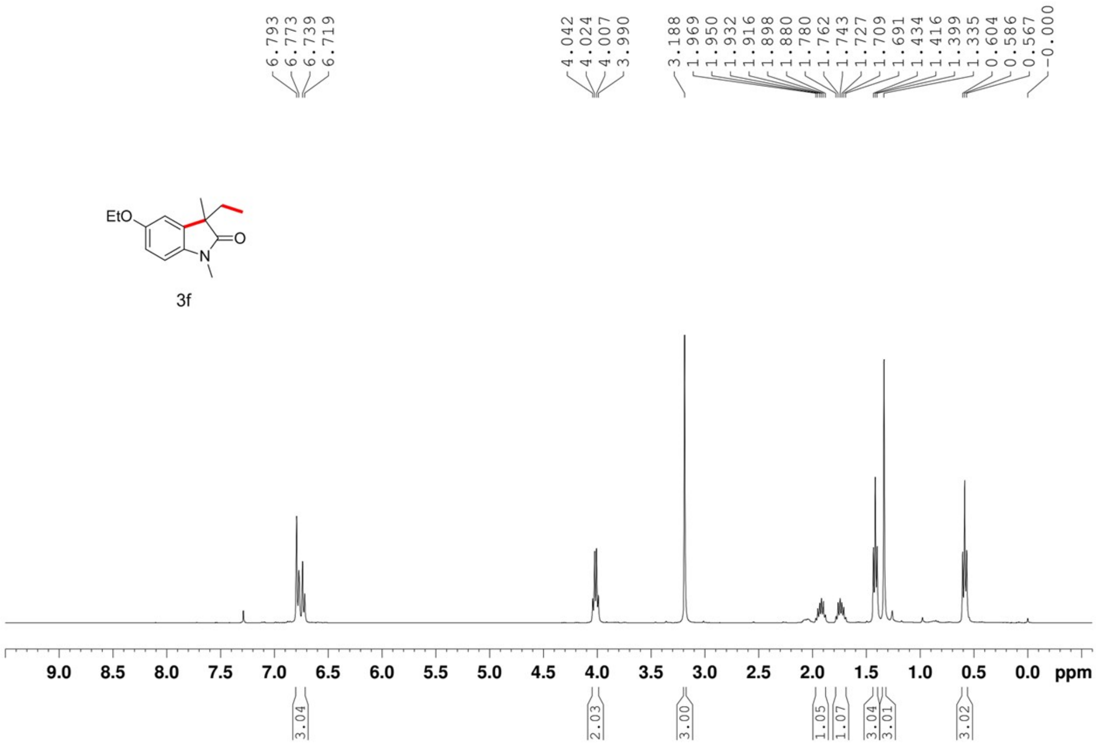
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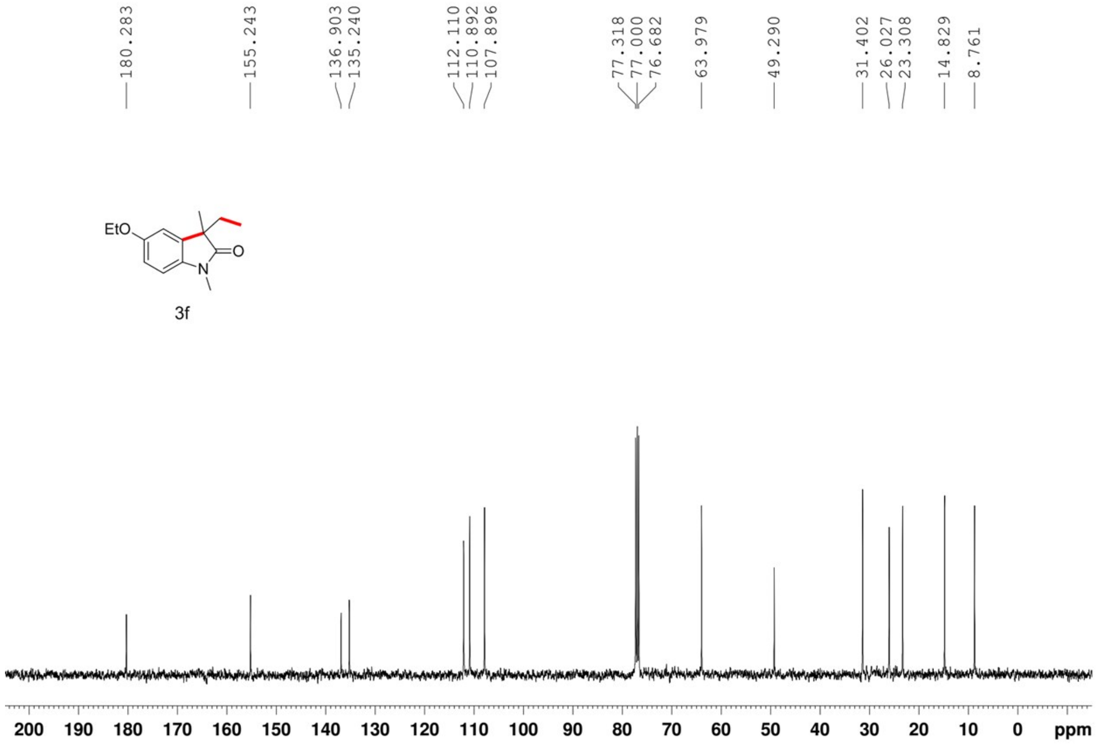
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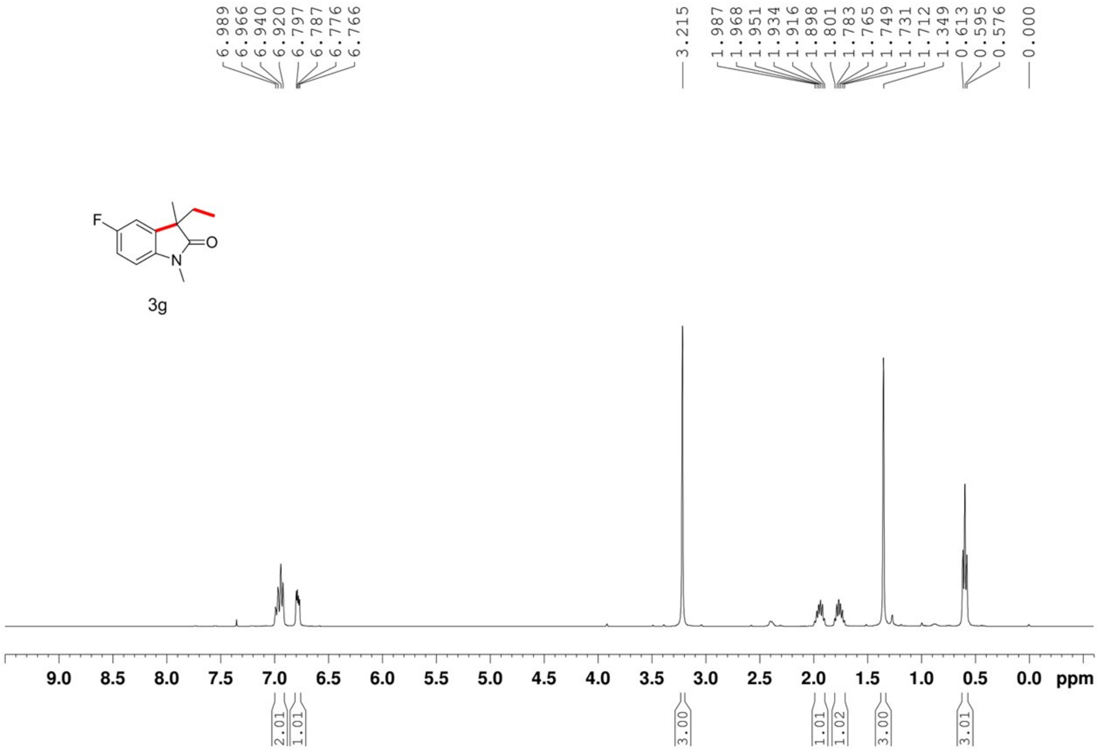
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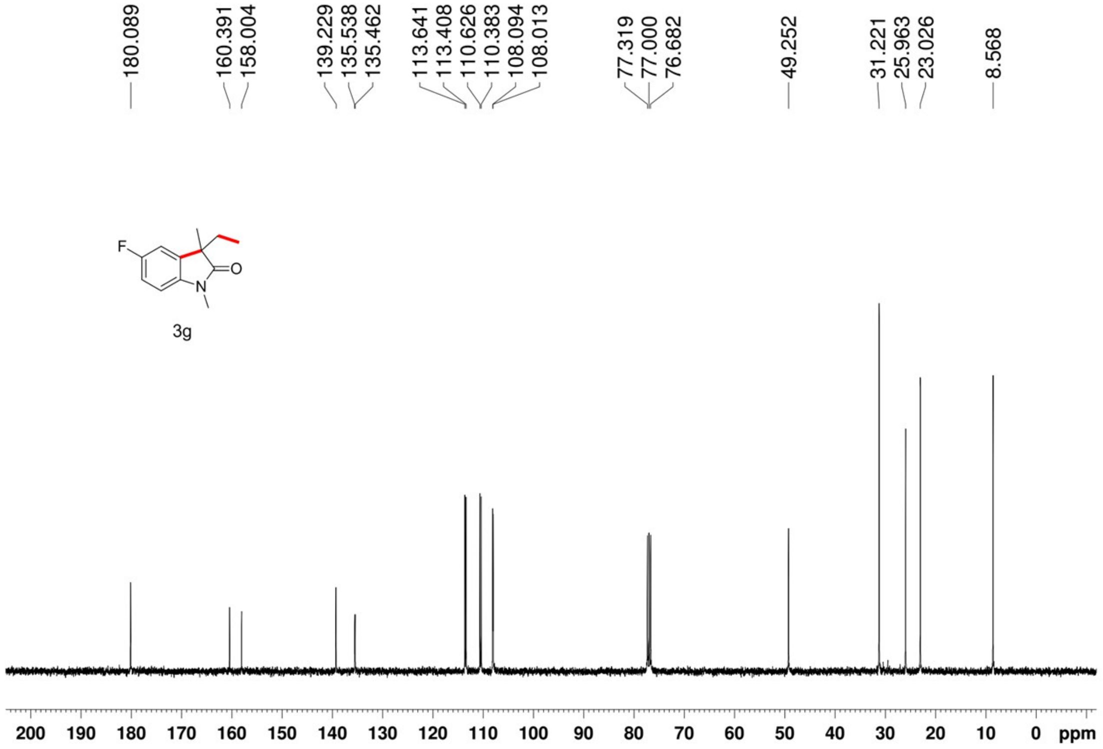
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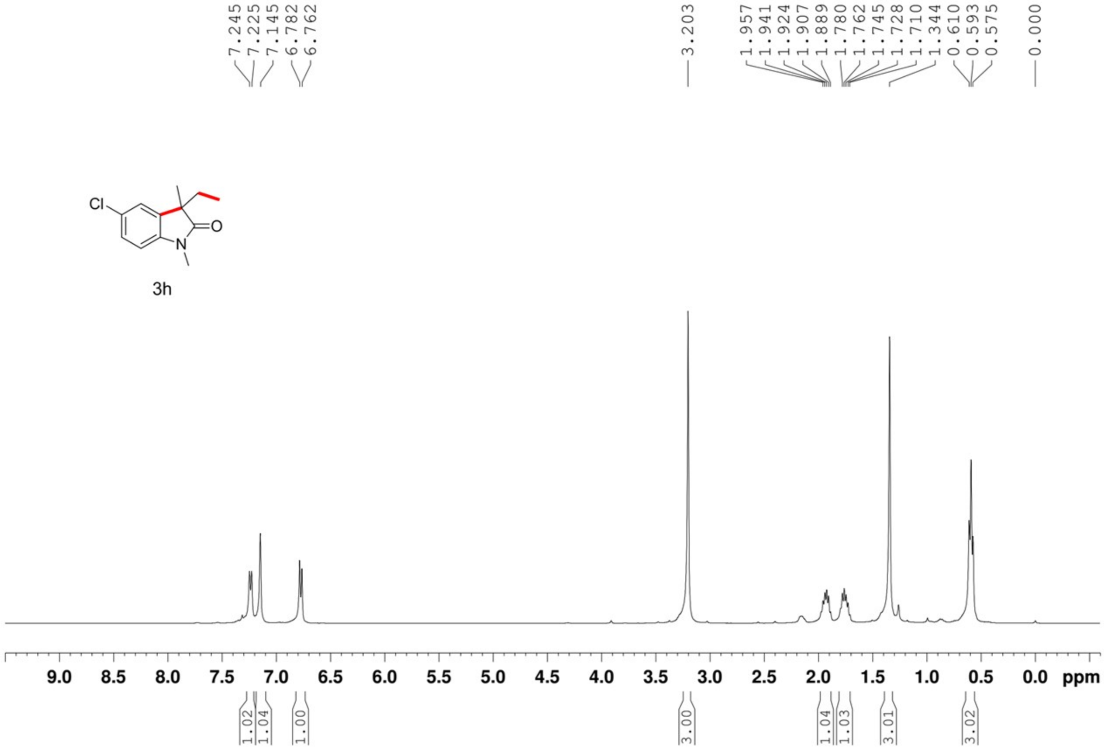
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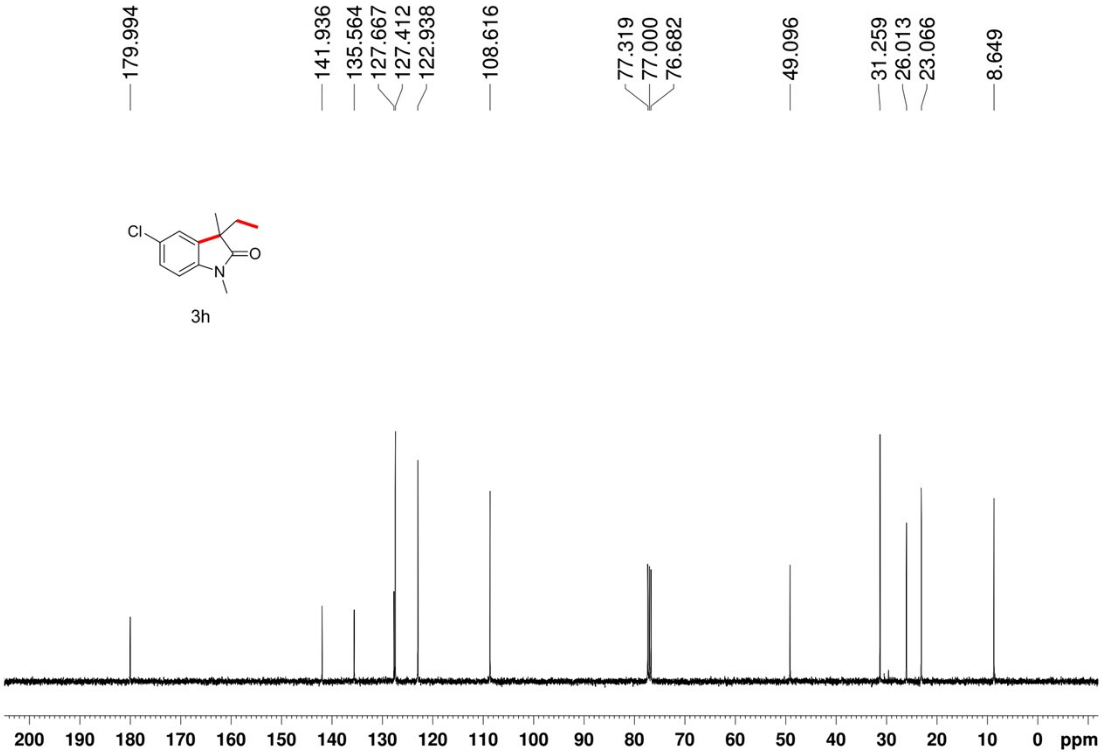
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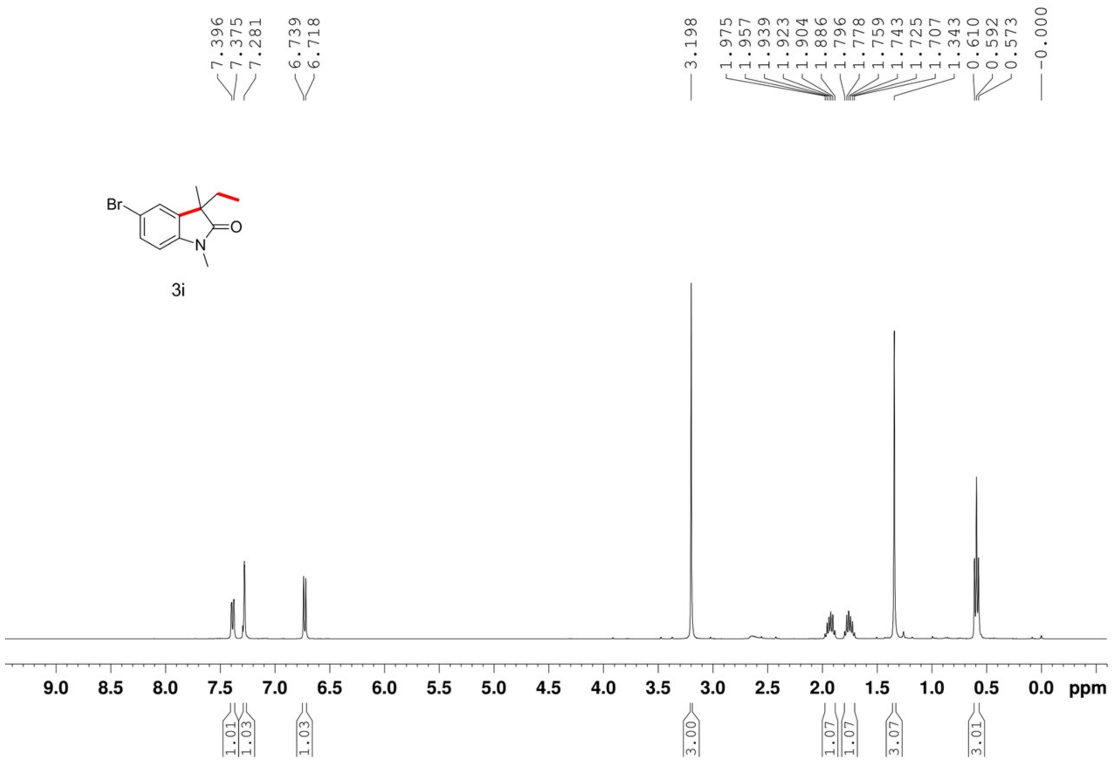
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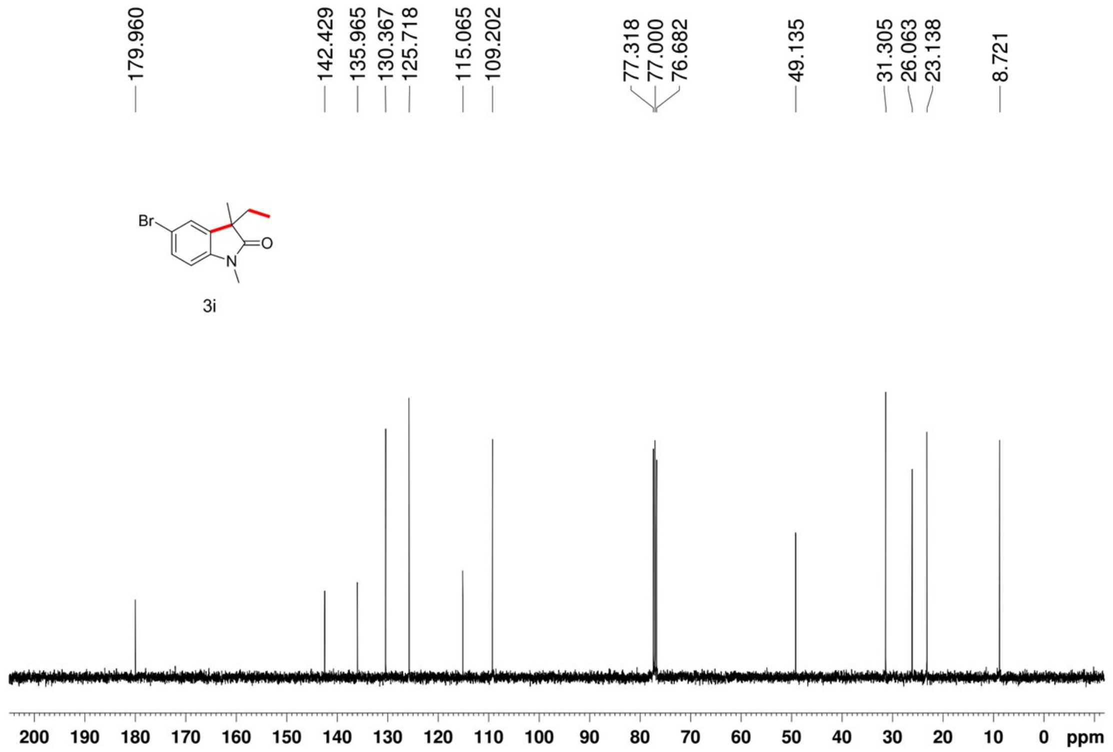
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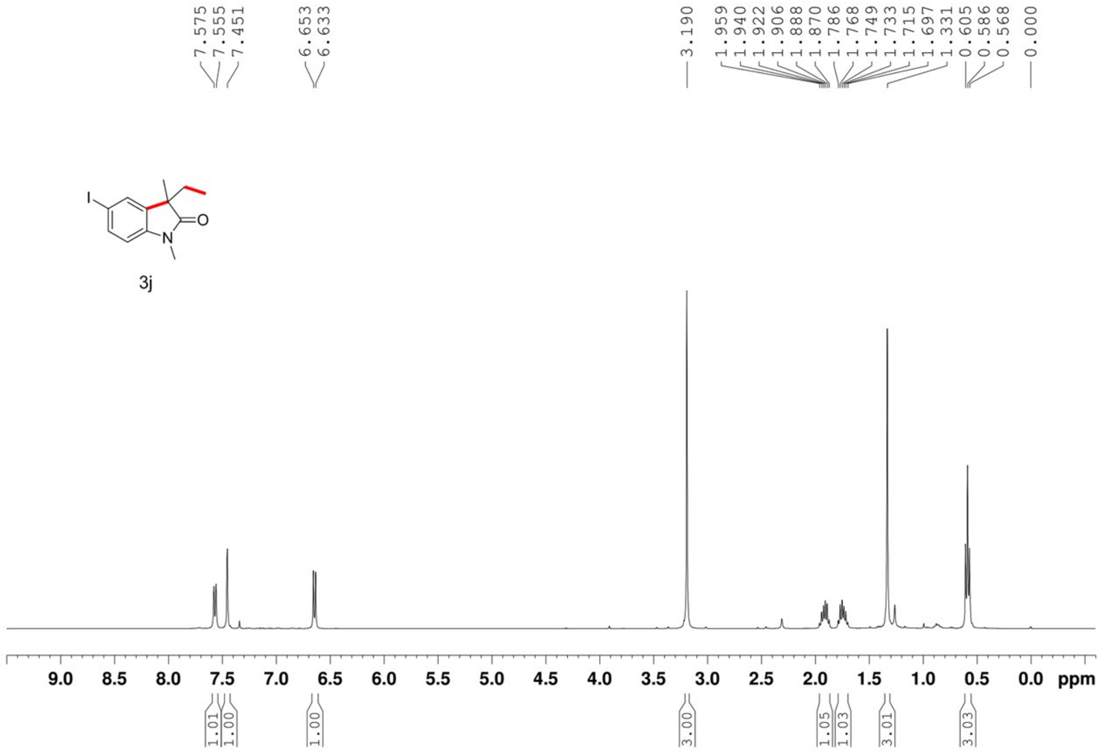
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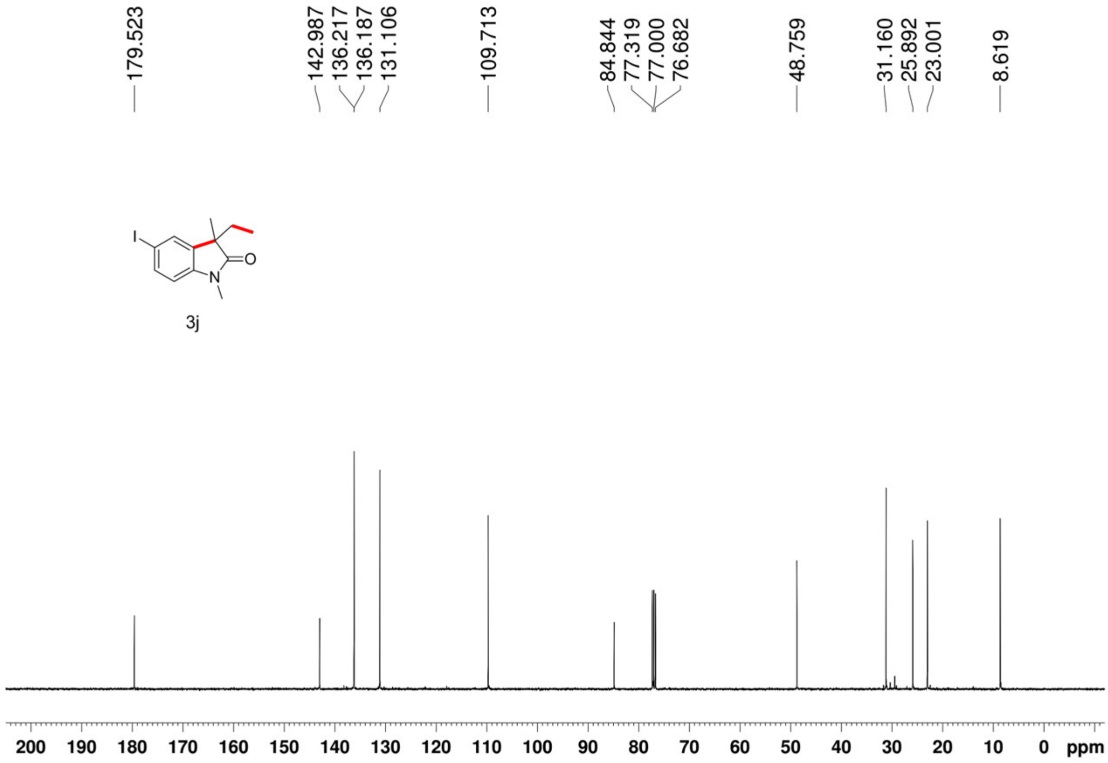
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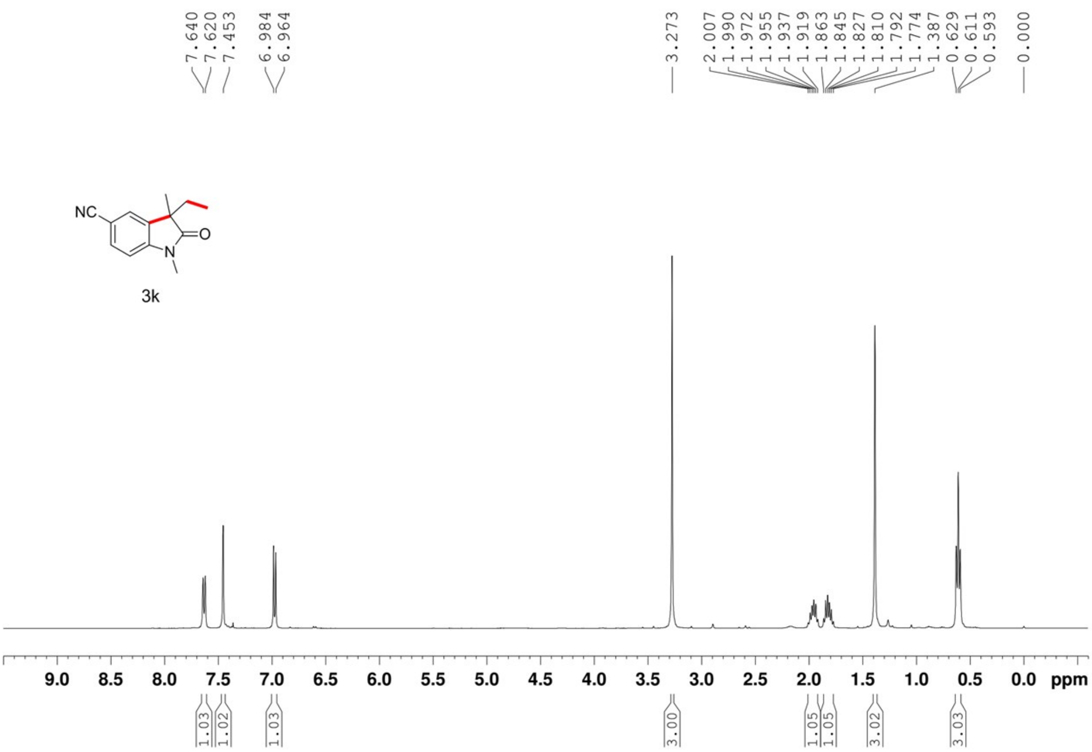
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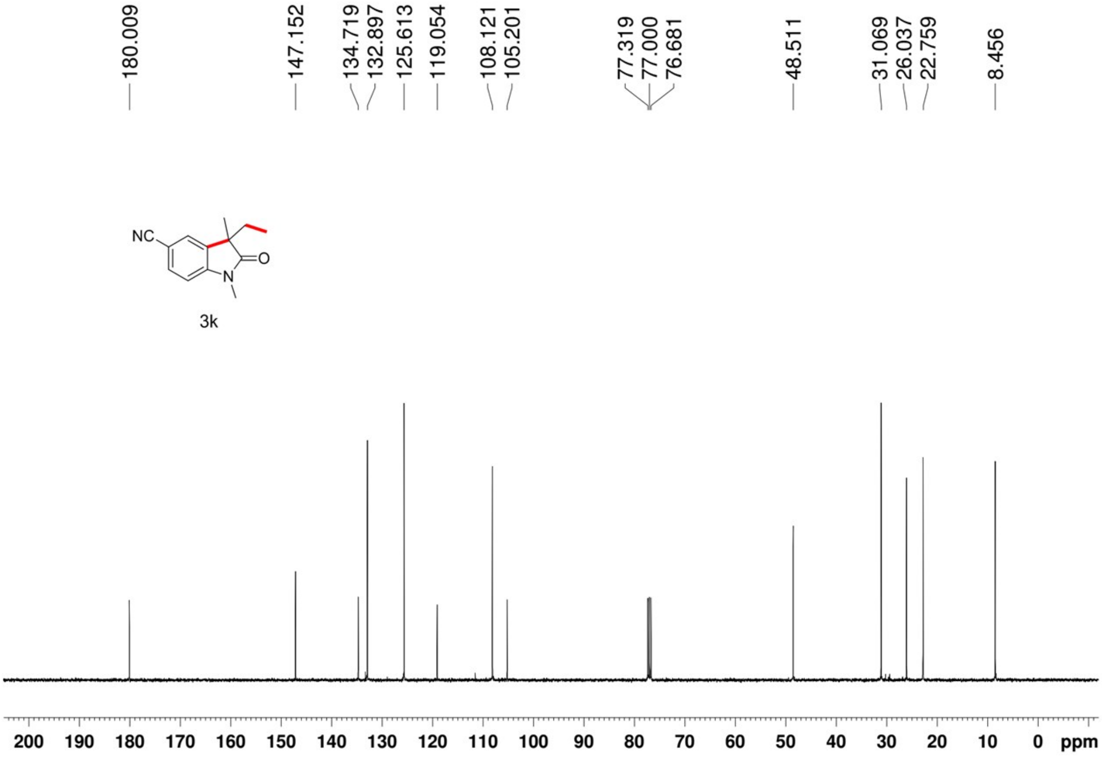
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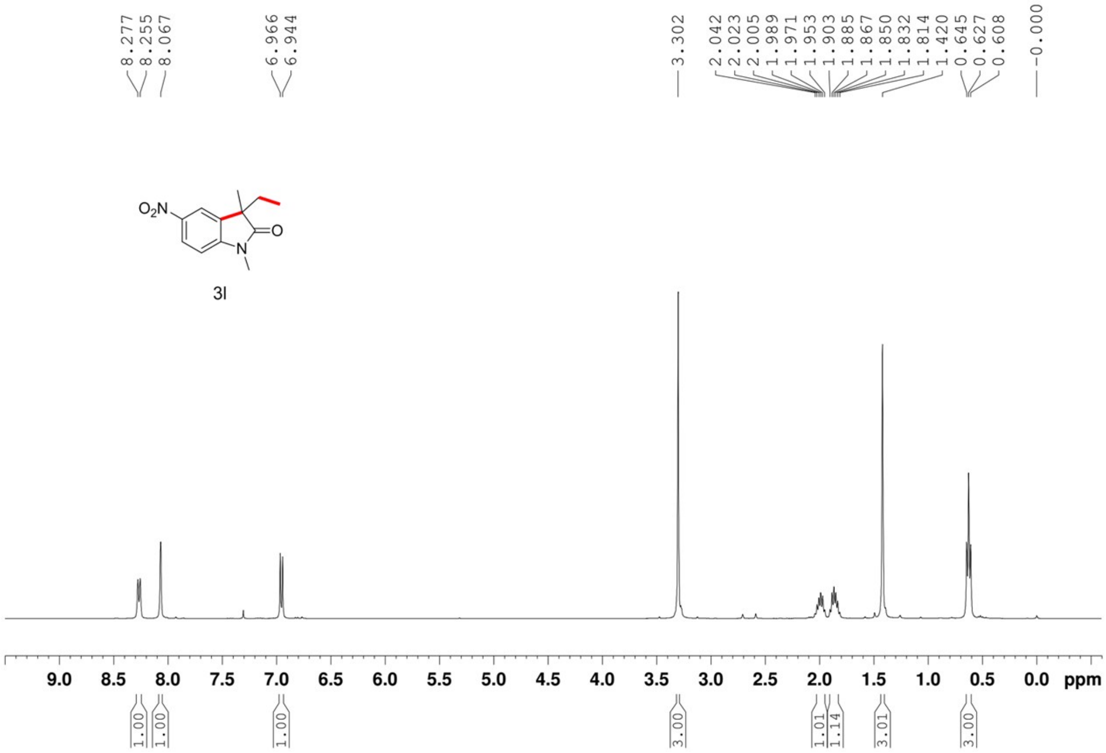
147.152
134.719
132.897
125.613
119.054
108.121
105.201
77.319
77.000
76.681
48.511
31.069
26.037
22.759
8.456
NC
O
N
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.255
8.067
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6.944
3.302
2.042
2.023
2.005
1.989
1.971
1.953
1.903
1.885
1.867
1.850
1.832
1.814
1.420
0.645
0.627
0.608
-0.000
O_2N
N
O
3l
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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1.00
3.00
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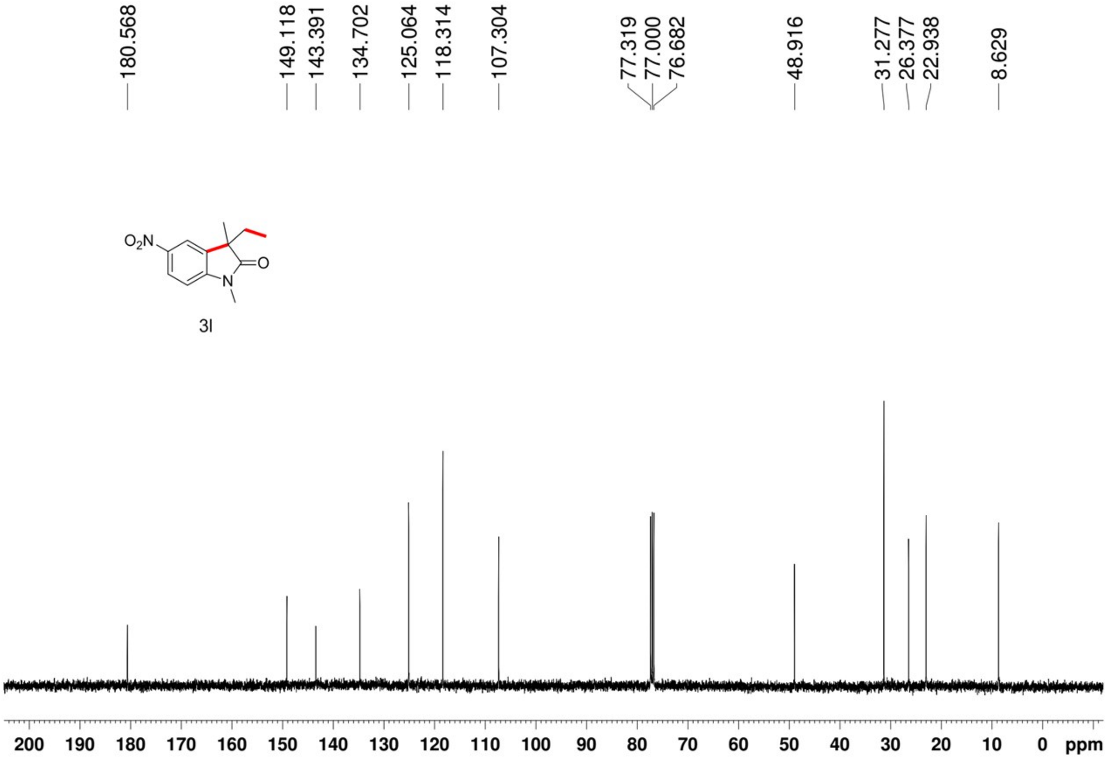
1.14
3.01
3.00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149.118
143.391
134.702
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107.304
77.319
77.000
76.682
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31.277
26.377
22.938
8.629
O_2N
N
O
3l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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20
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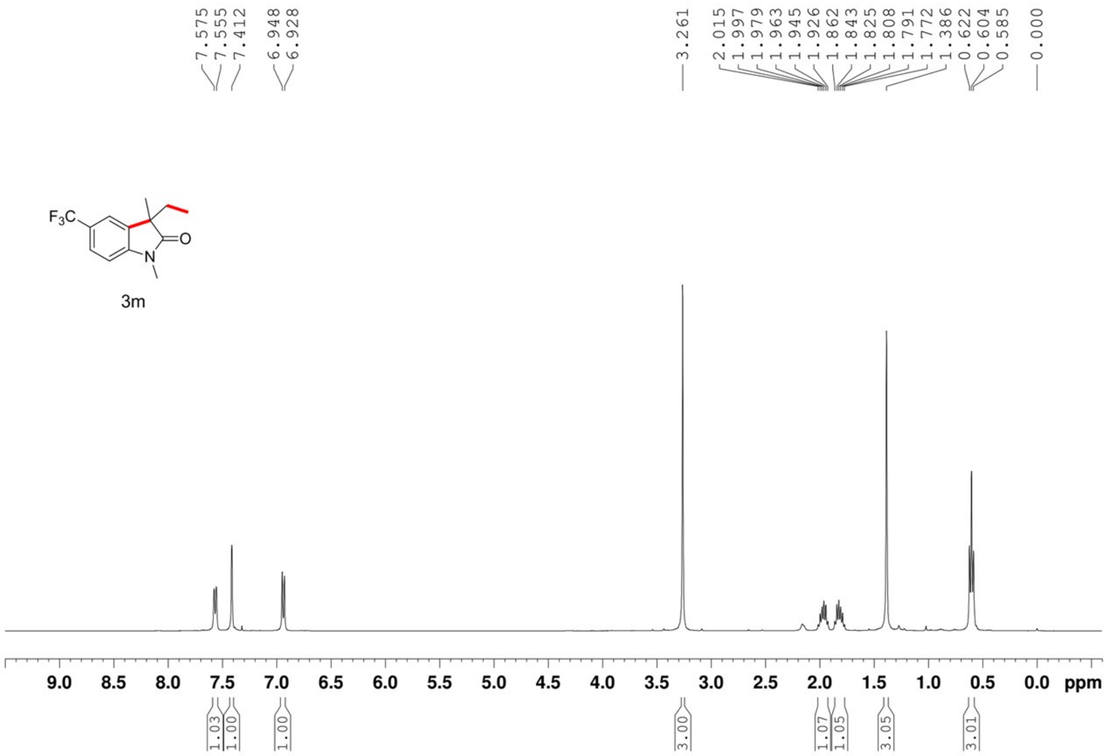
ppm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7.412
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6.928
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2.015
1.997
1.979
1.963
1.945
1.926
1.862
1.843
1.825
1.808
1.791
1.772
1.386
0.622
0.604
0.585
0.000
F_3C
N
O
3m
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.5
0.0
ppm
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1.00
3.00
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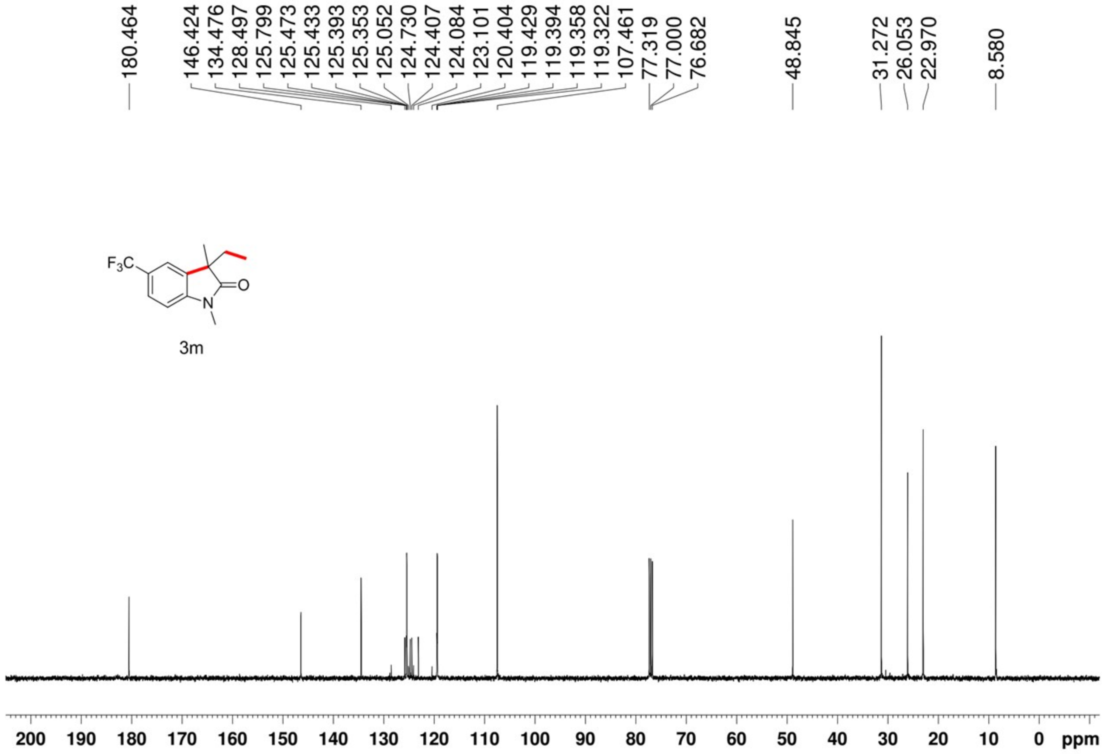
1.05
3.05
3.01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146.424
134.476
128.497
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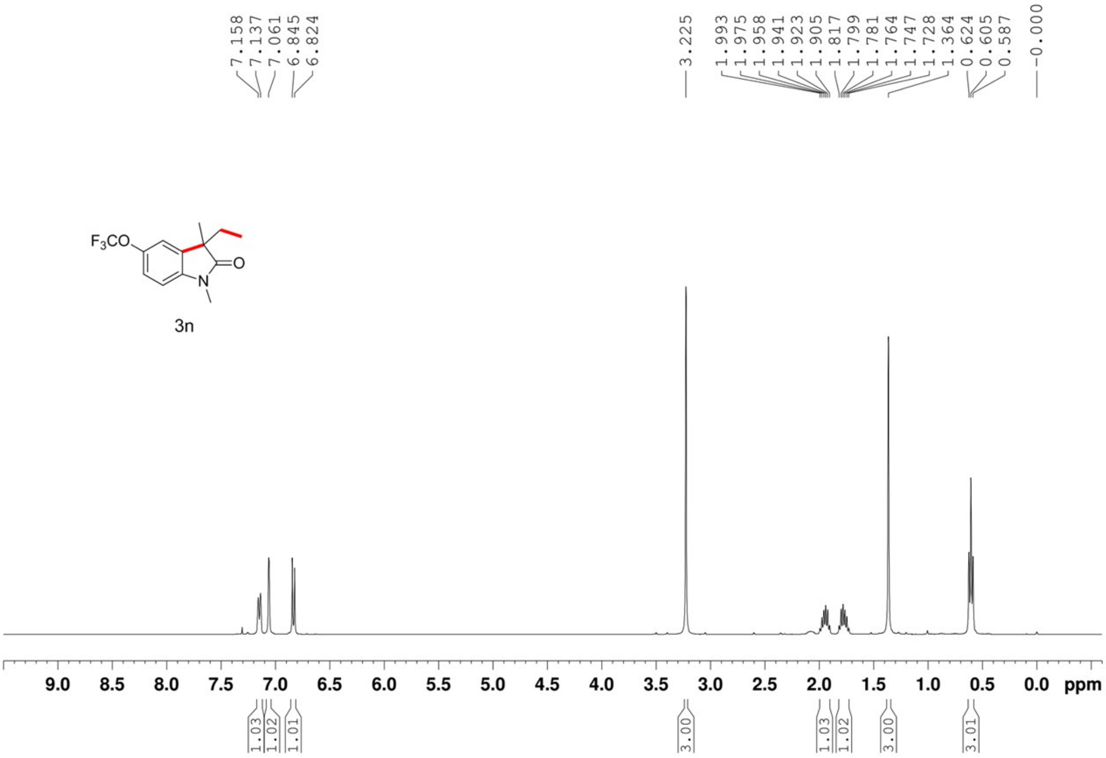
125.433
125.393
125.353
125.052
124.730
124.407
124.084
123.101
120.404
119.429
119.394
119.358
119.322
107.461
77.319
77.000
76.682
48.845
31.272
26.053
22.970
8.580
F_3C
N
O
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



3n

F3CO
N
O
7.158
7.137
7.061
6.845
6.824
3.225
1.993
1.975
1.958
1.941
1.923
1.905
1.817
1.799
1.781
1.764
1.747
1.728
1.364
0.624
0.605
0.587
-0.000
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
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0.5
0.0
ppm
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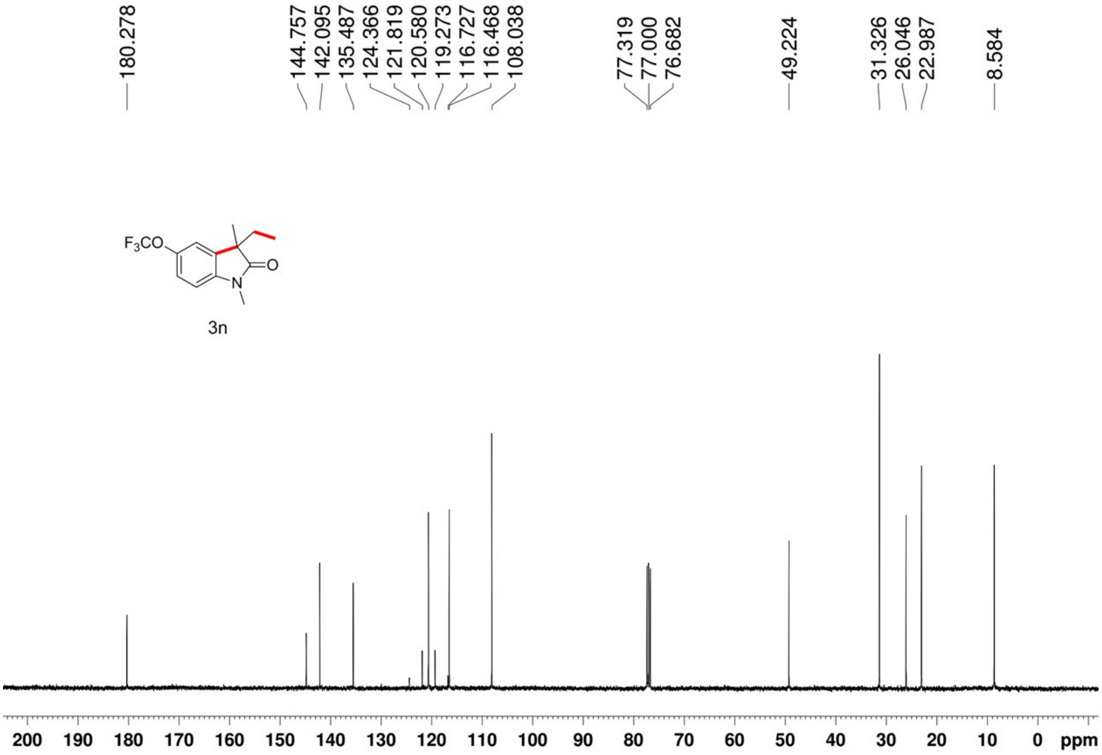
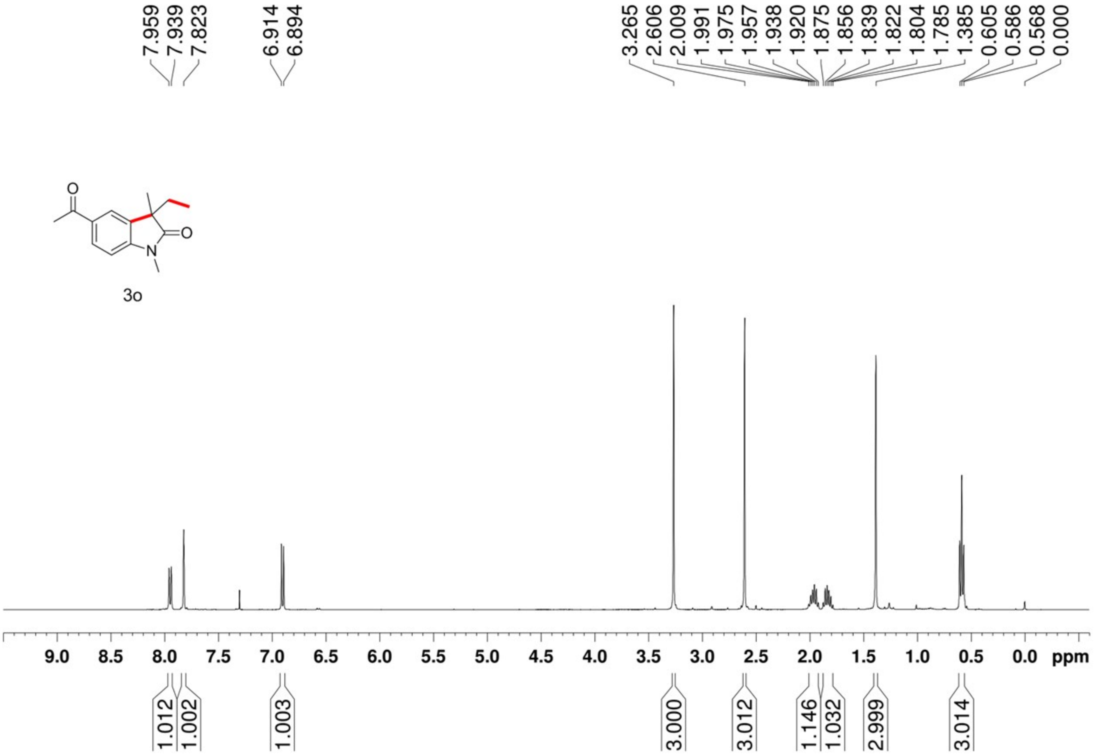
1.02
1.01
3.00
1.03
1.02
3.00
3.01



3n

F3CO
N
O
180.278
144.757
142.095
135.487
124.366
121.819
120.580
119.273
116.727
116.468
108.038
77.319
77.000
76.682
49.224
31.326
26.046
22.987
8.584
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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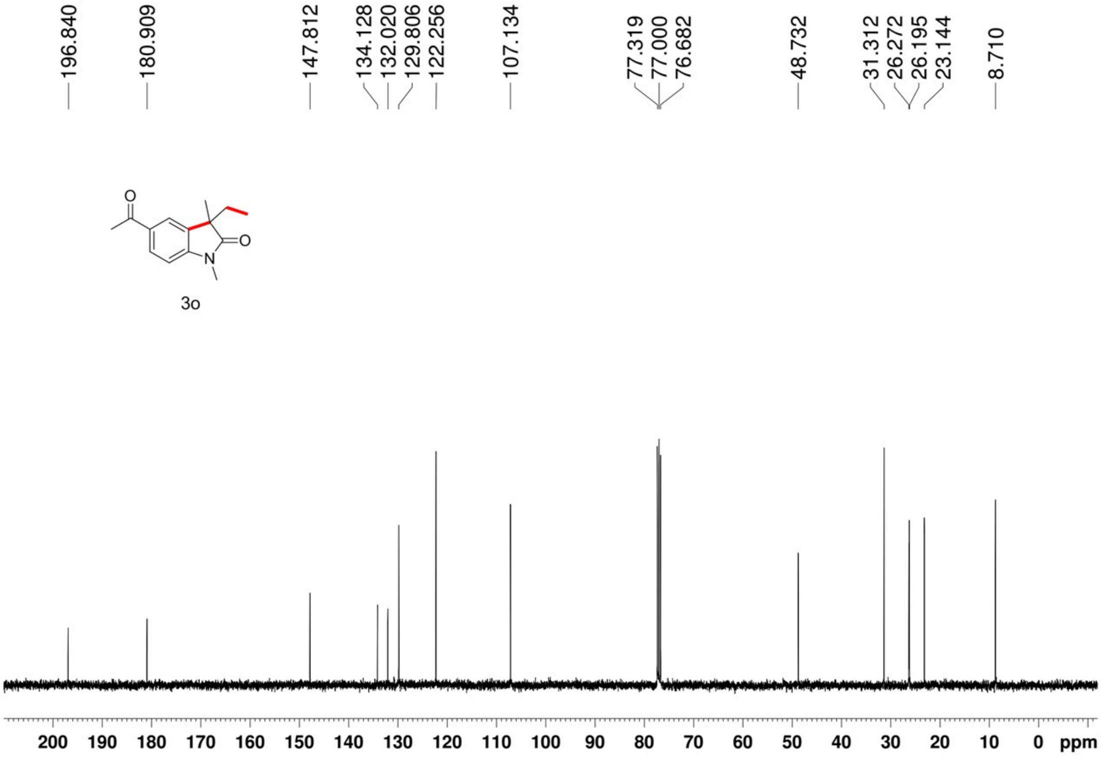
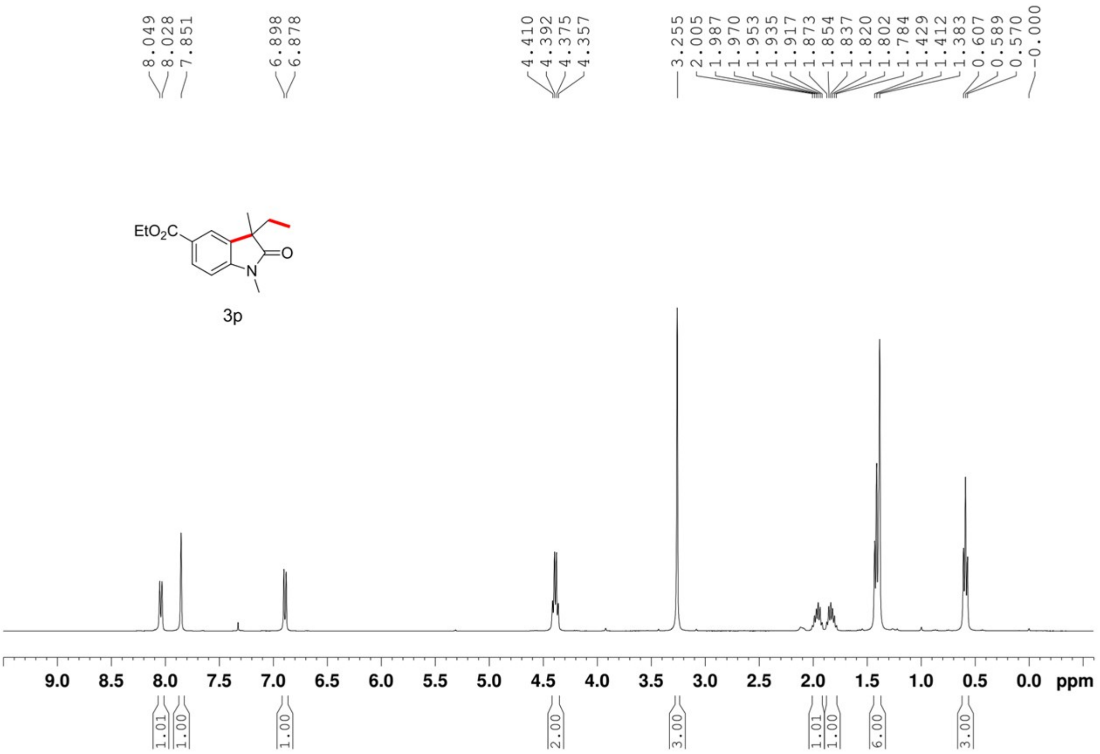
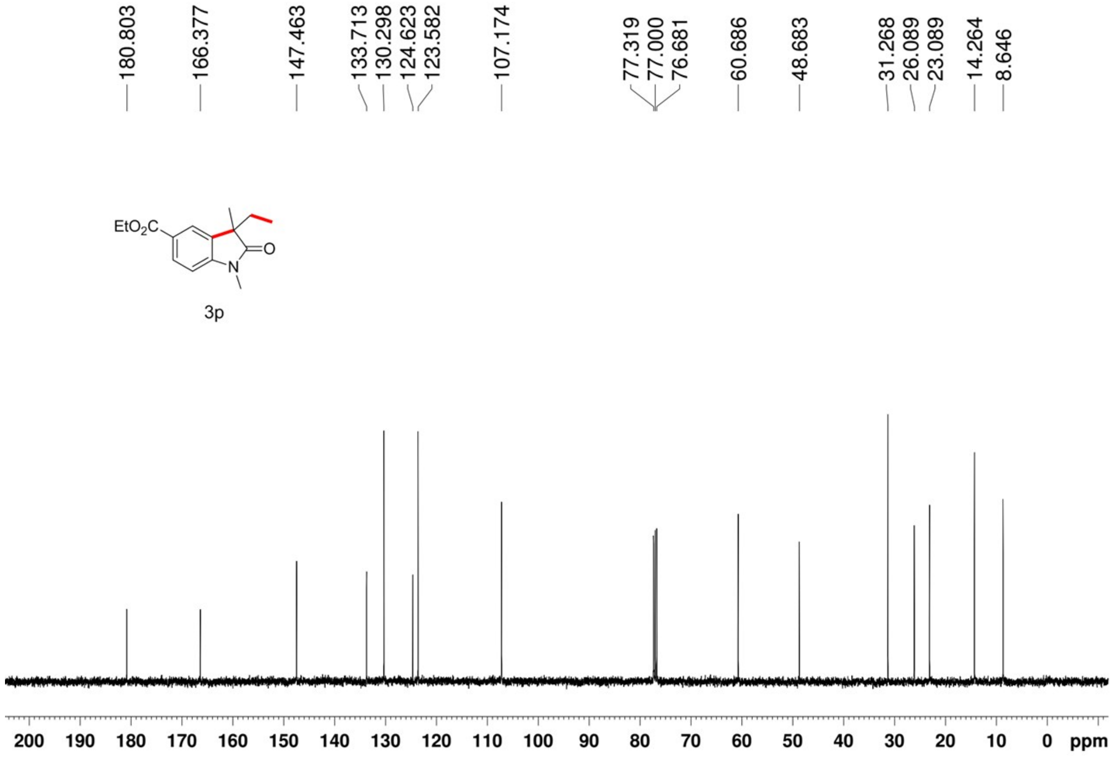
7.939
7.823
6.914
6.894
3.265
2.606
2.009
1.991
1.975
1.957
1.938
1.920
1.875
1.856
1.839
1.822
1.804
1.785
1.385
0.605
0.586
0.568
0.000
O
N
O
3o
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.012
1.002
1.003
3.000
3.012
1.146
1.032
2.999
3.014


196.840
180.909
147.812
134.128
132.020
129.806
122.256
107.134
77.319
77.000
76.682
48.732
31.312
26.272
26.195
23.144
8.710
O
N
O
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.049
8.028
7.851
6.898
6.878
4.410
4.392
4.375
4.357
3.255
2.005
1.987
1.970
1.953
1.935
1.917
1.873
1.854
1.837
1.820
1.802
1.784
1.429
1.412
1.383
0.607
0.589
0.570
-0.000
EtO2C
N
O
3p
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
1.00
1.00
2.00
3.00
1.01
1.00
6.00
3.00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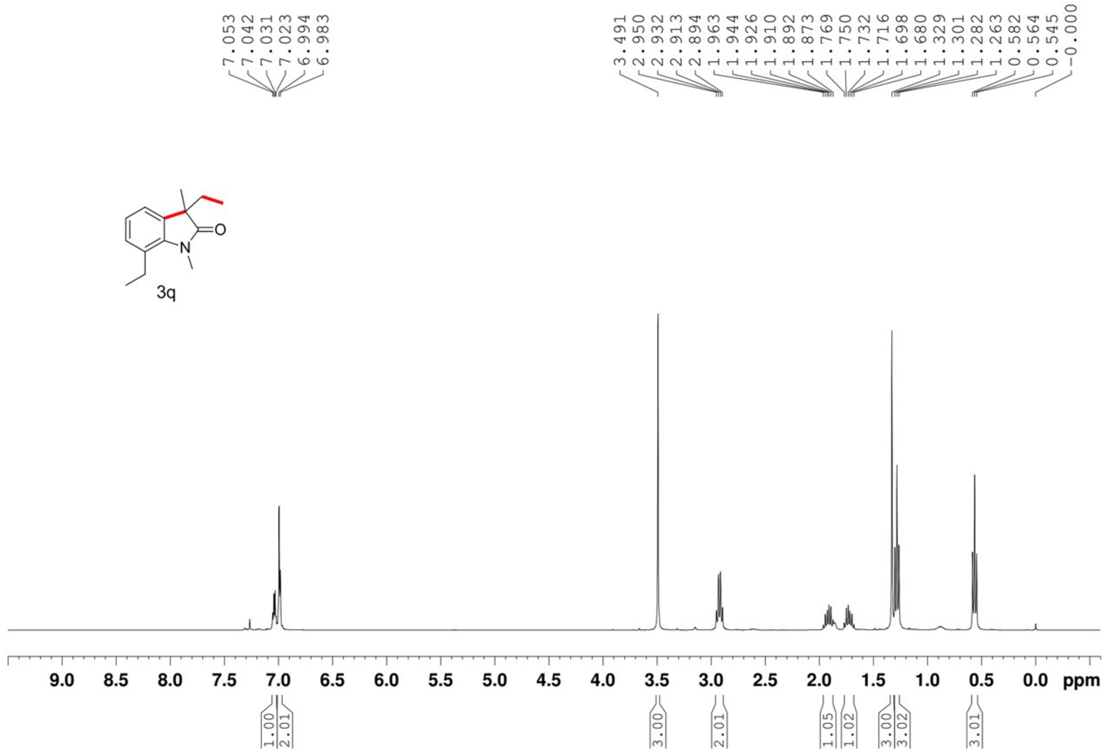
166.377
147.463
133.713
130.298
124.623
123.582
107.174
77.319
77.000
76.681
60.686
48.683
31.268
26.089
23.089
14.264
8.646
EtO2C
N
O
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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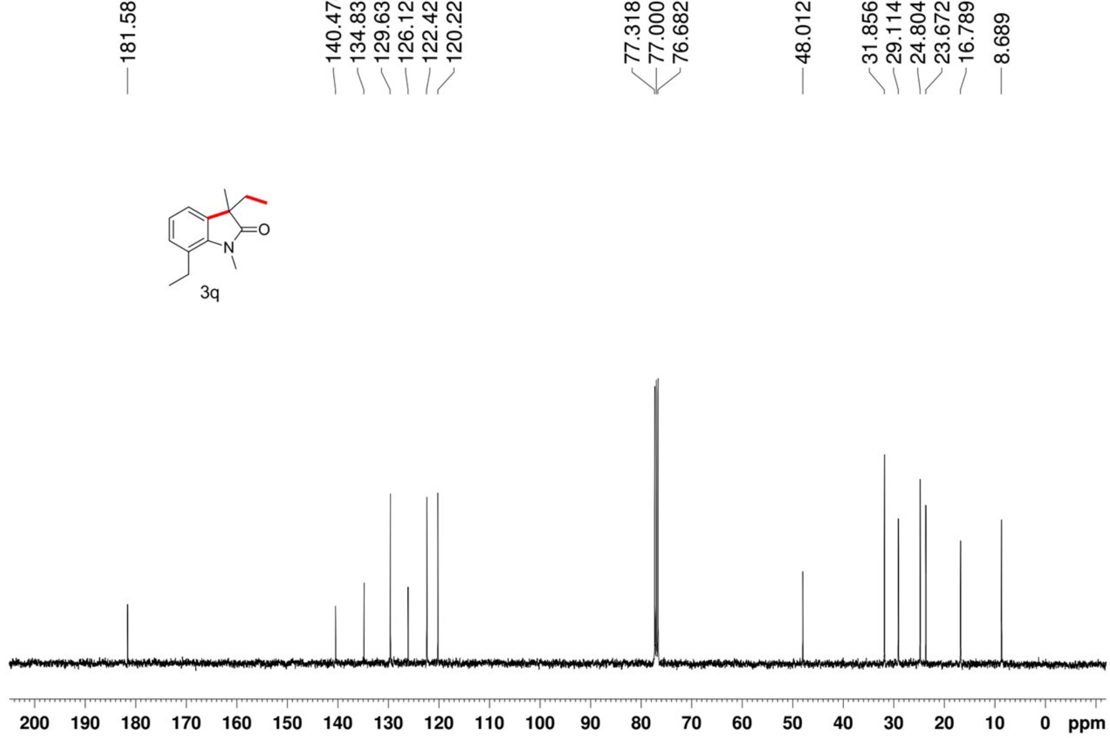
7.042
7.031
7.023
6.994
6.983
3.491
2.950
2.932
2.913
2.894
1.963
1.944
1.926
1.910
1.892
1.873
1.769
1.750
1.732
1.716
1.698
1.680
1.329
1.301
1.282
1.263
0.582
0.564
0.545
-0.000
N
O
3q
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.01
3.00
2.01
1.05
1.02
3.00
3.02
3.01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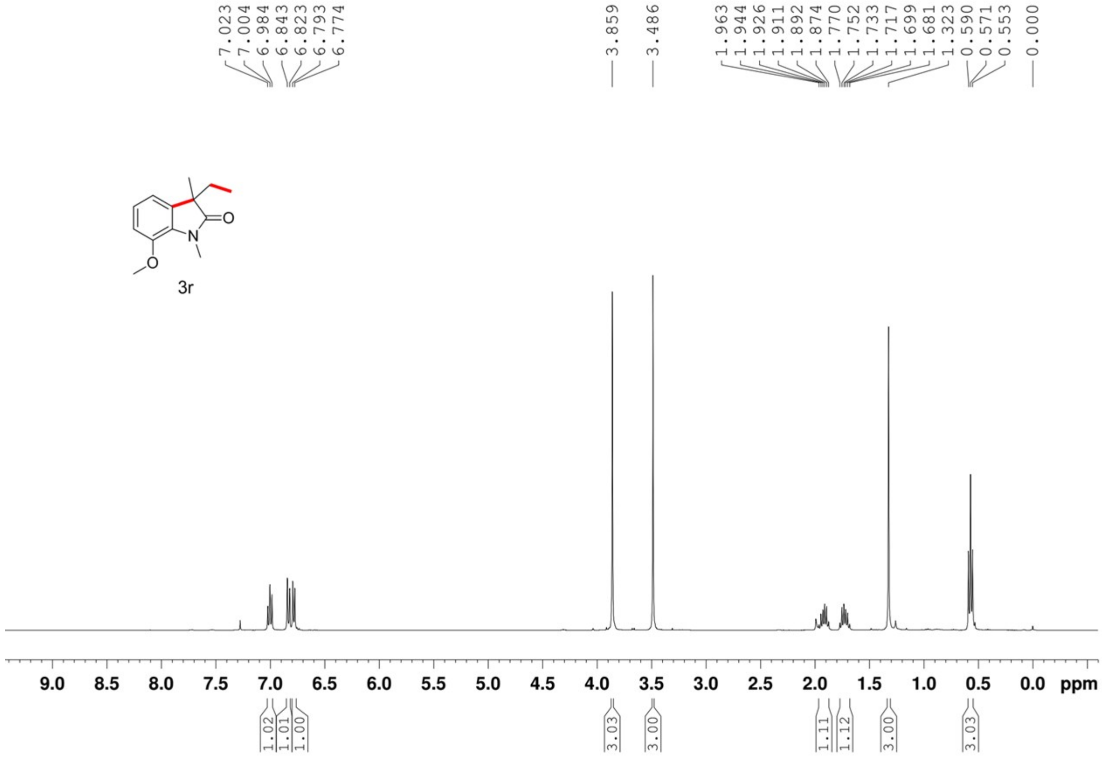
140.474
134.836
129.630
126.124
122.421
120.227
77.318
77.000
76.682
48.012
31.856
29.114
24.804
23.672
16.789
8.689
N
O
3q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


3r

7.023
7.004
6.984
6.843
6.823
6.793
6.774
3.859
3.486
1.963
1.944
1.926
1.911
1.892
1.874
1.770
1.752
1.733
1.717
1.699
1.681
1.323
0.590
0.571
0.553
0.000
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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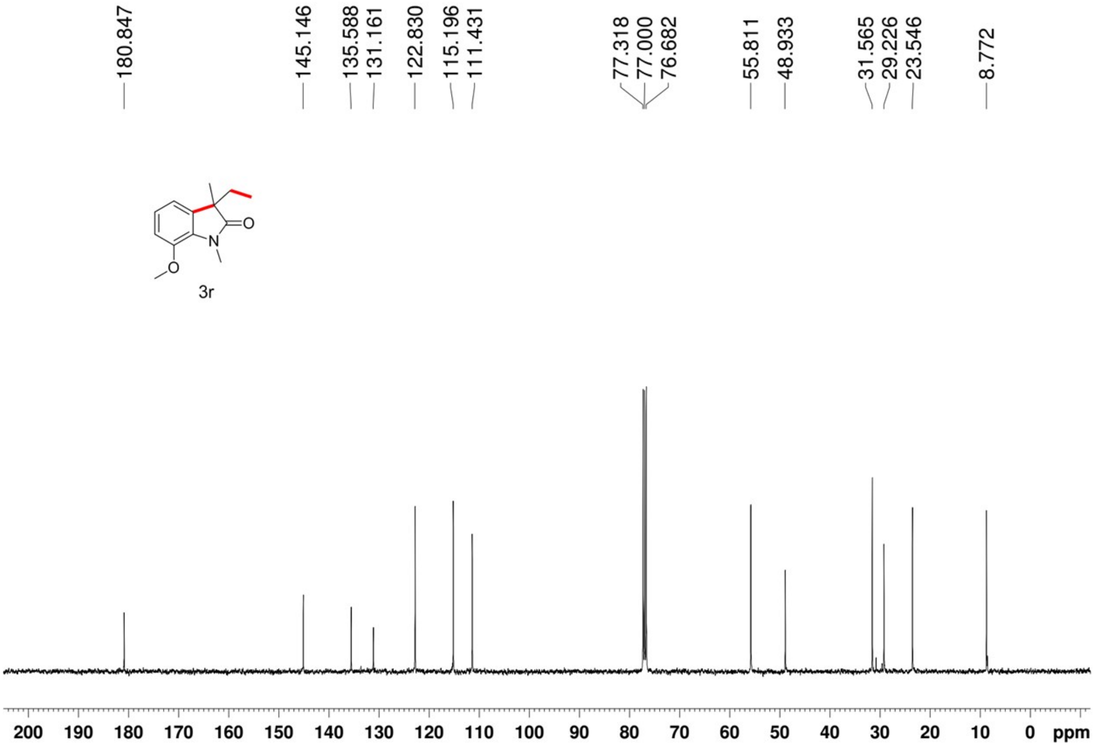
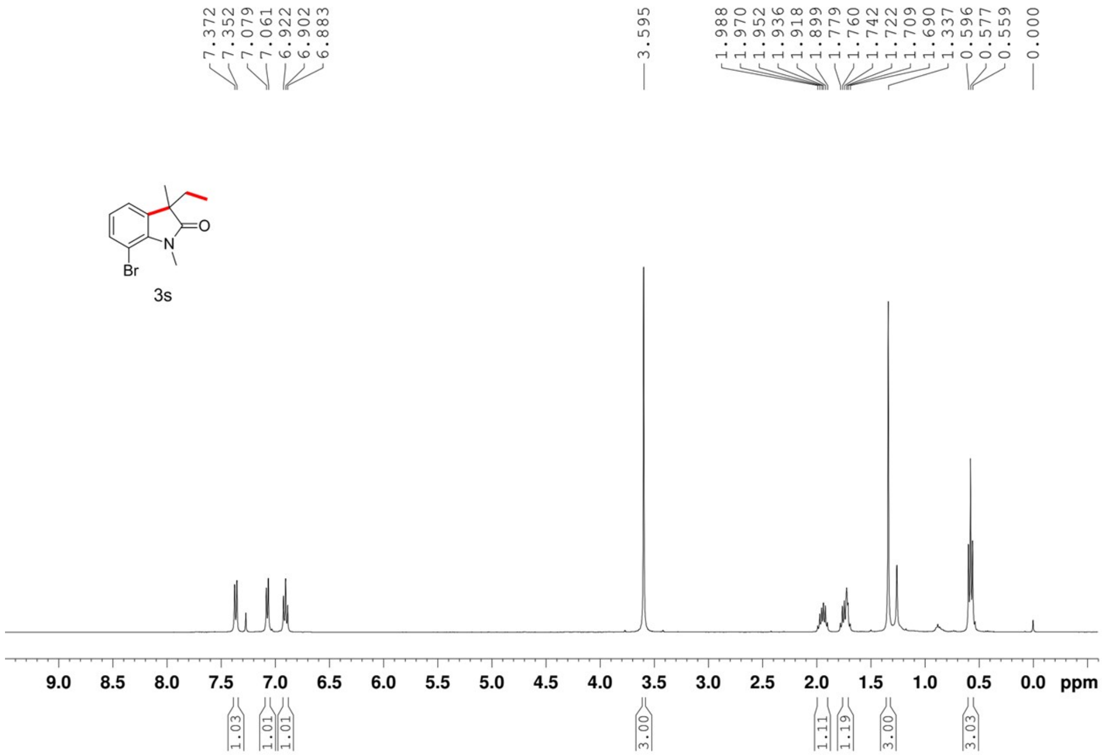
1.01
1.00
3.03
3.00
1.11
1.12
3.00
3.03
N
O


3r

180.847
145.146
135.588
131.161
122.830
115.196
111.431
77.318
77.000
76.682
55.811
48.933
31.565
29.226
23.546
8.772
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
N
O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6.902
6.883
3.595
1.988
1.970
1.952
1.936
1.918
1.899
1.779
1.760
1.742
1.722
1.709
1.690
1.337
0.596
0.577
0.559
0.000
Br
N
O
3s
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
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0.0
ppm
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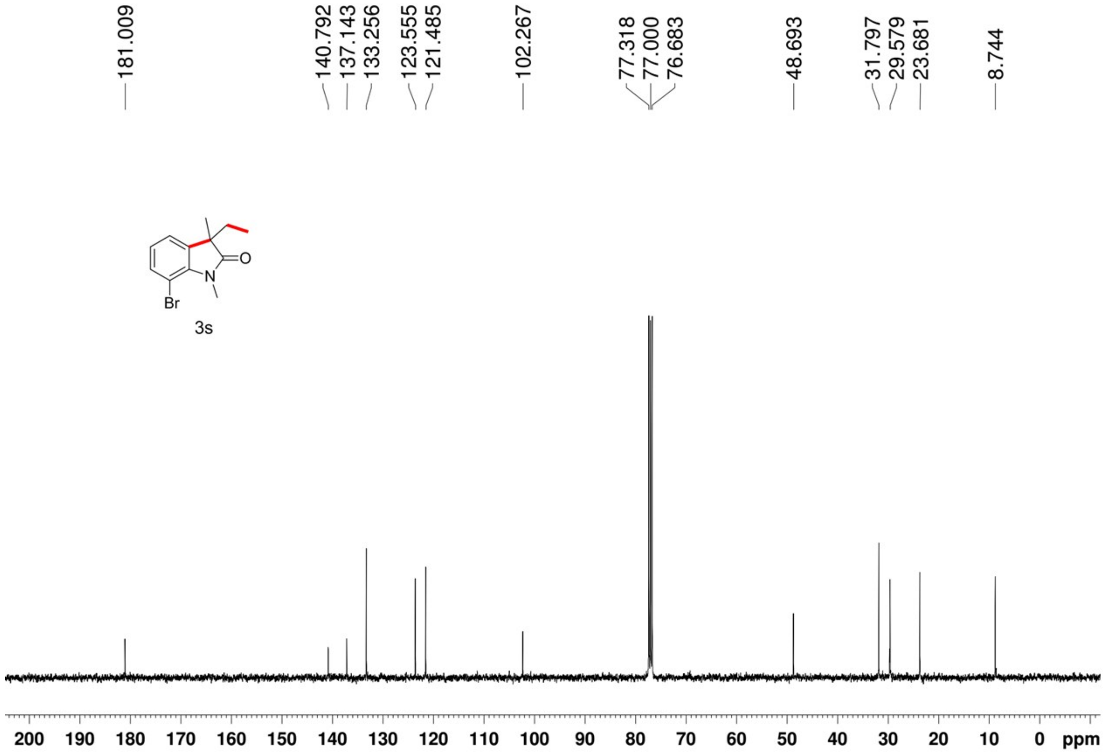
1.01
1.01
3.00
1.11
1.19
3.00
3.03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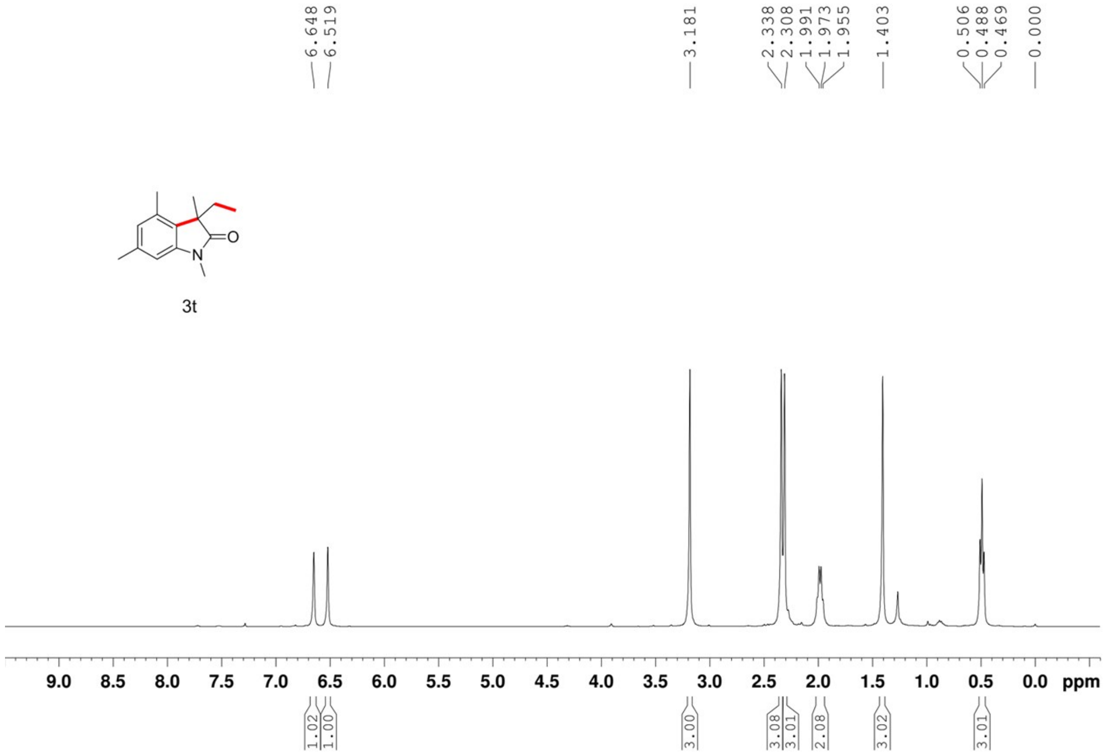
121.485
102.267
77.318
77.000
76.683
48.693
31.797
29.579
23.681
8.744
Br
N
O
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


3t
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6.519
3.181
2.338
2.308
1.991
1.973
1.955
1.403
0.506
0.488
0.469
0.000
N
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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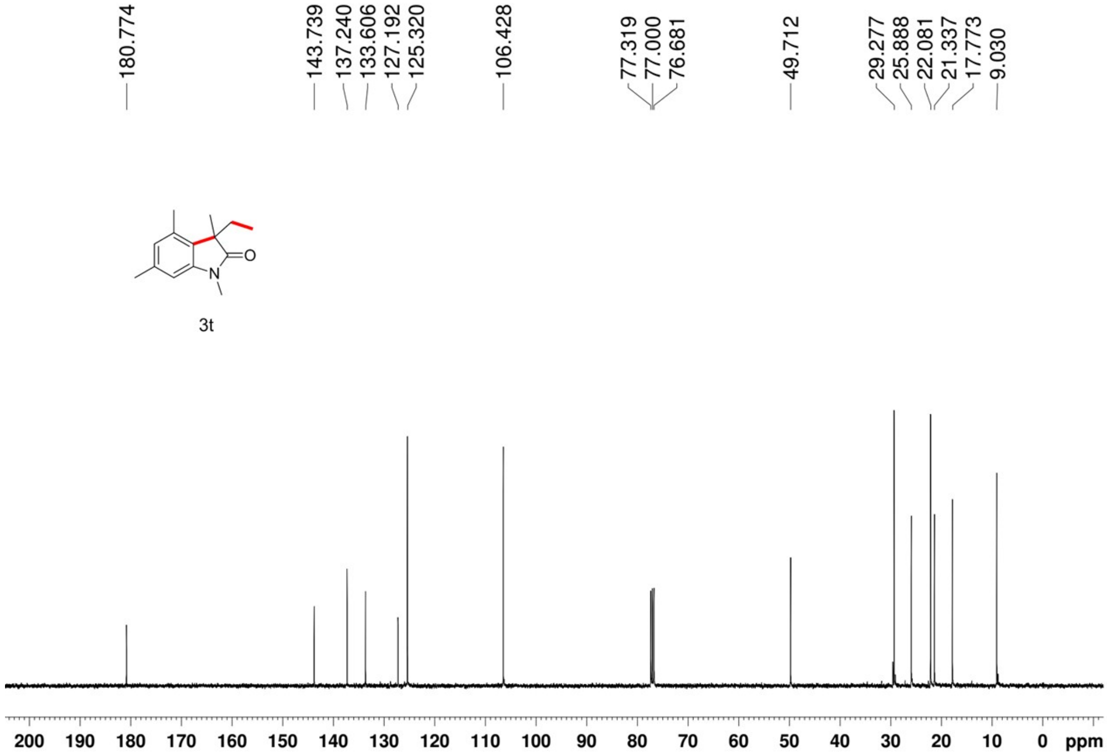
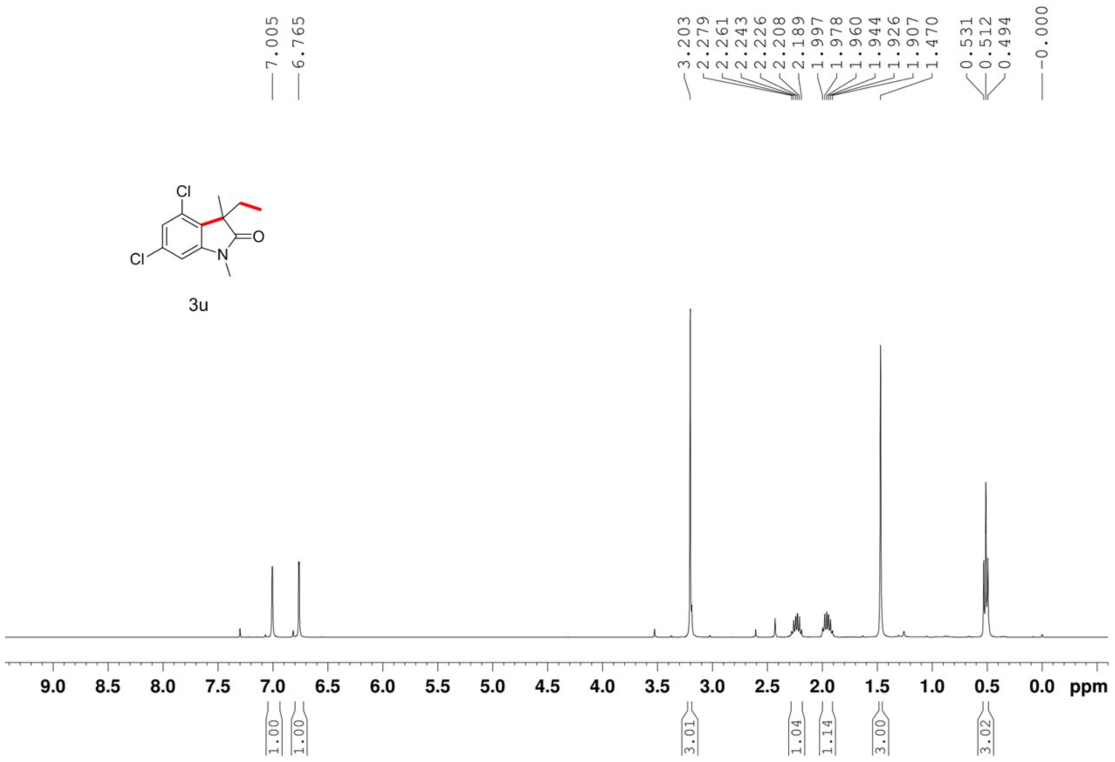
1.00
3.00
3.08
3.01
2.08
3.02
3.01


3t
180.774
143.739
137.240
133.606
127.192
125.320
106.428
77.319
77.000
76.681
49.712
29.277
25.888
22.081
21.337
17.773
9.030
N
O
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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6.765
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2.243
2.226
2.208
2.189
1.997
1.978
1.960
1.944
1.926
1.907
1.470
0.531
0.512
0.494
-0.000
Cl
Cl
N
O
3u
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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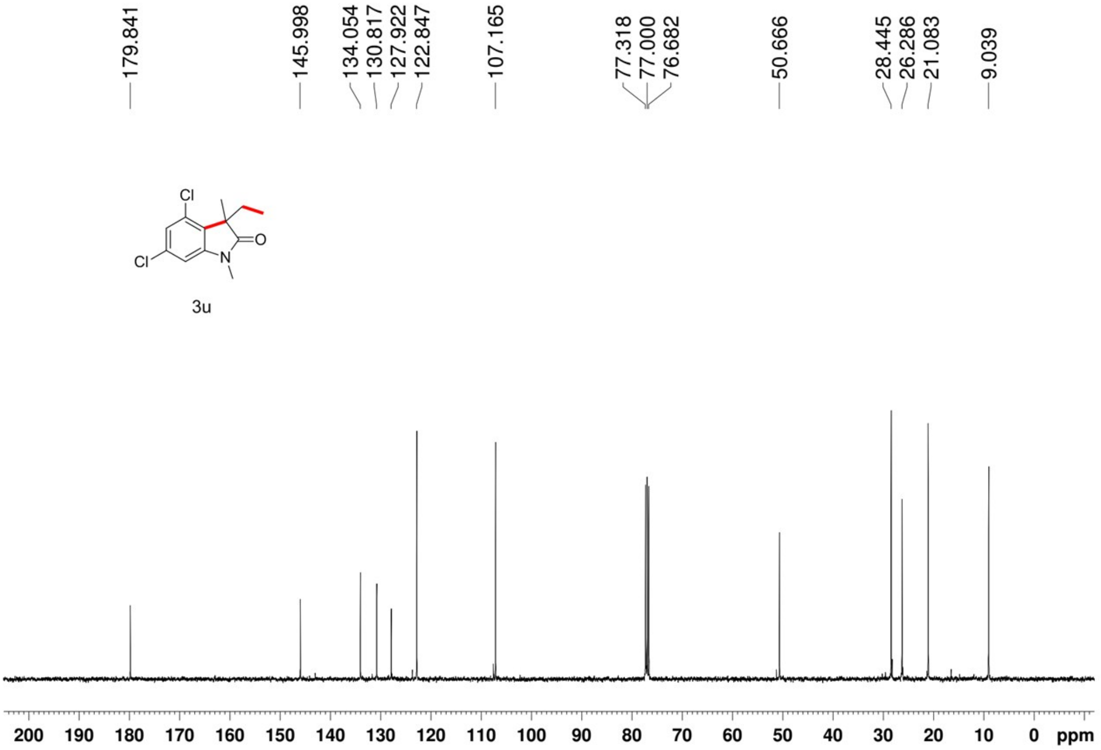
1.00
3.01
1.04
1.14
3.00
3.02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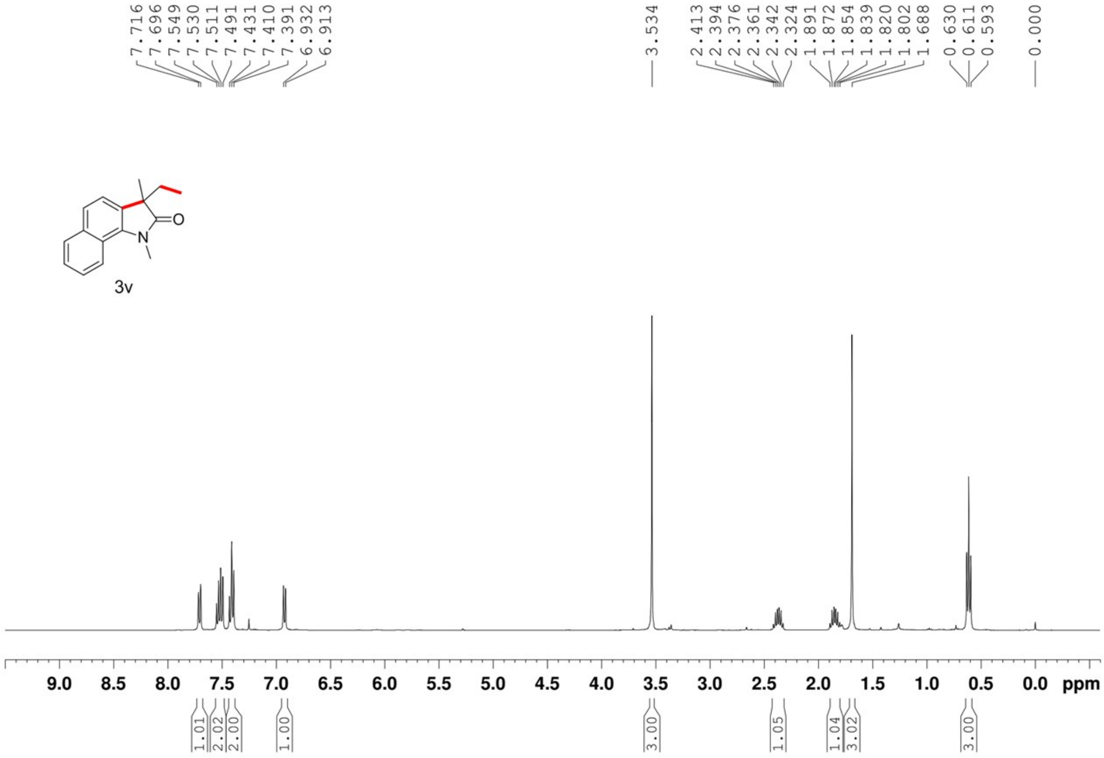
145.998
134.054
130.817
127.922
122.847
107.165
77.318
77.000
76.682
50.666
28.445
26.286
21.083
9.039
Cl
Cl
N
O
3u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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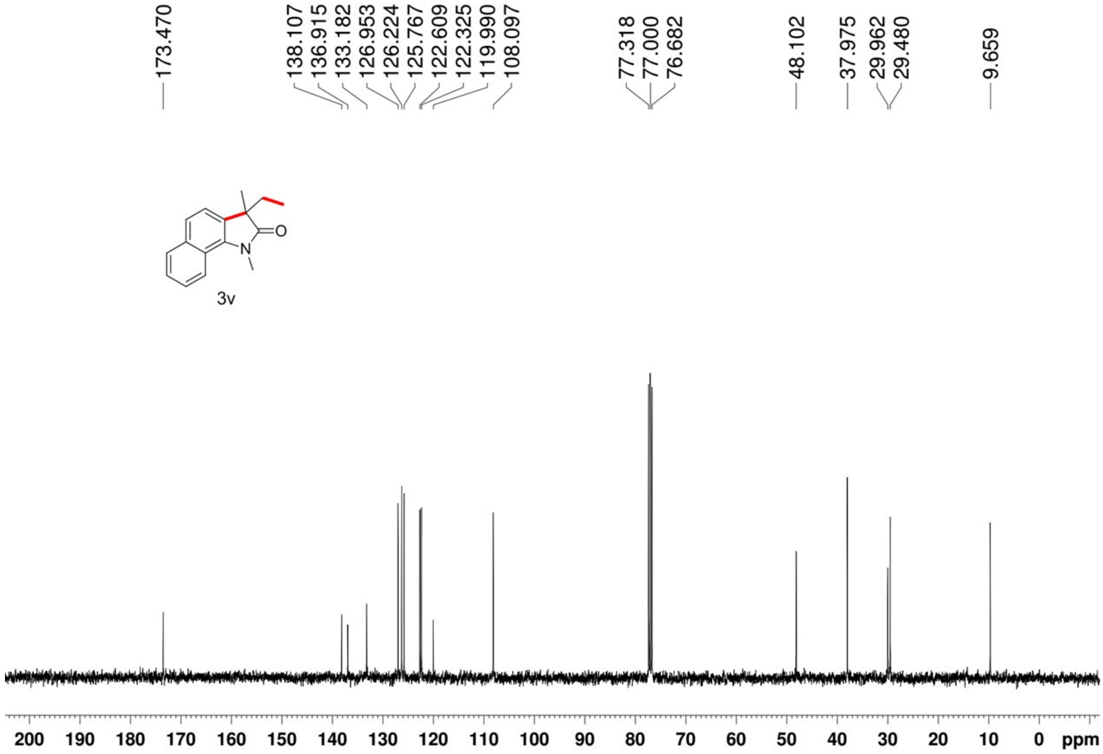
7.511
7.491
7.431
7.410
7.391
6.932
6.913
3.534
2.413
2.394
2.376
2.361
2.342
2.324
1.891
1.872
1.854
1.839
1.820
1.802
1.688
0.630
0.611
0.593
0.000
N
O
3v
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
2.02
2.00
1.00
3.00
1.05
1.04
3.02
3.00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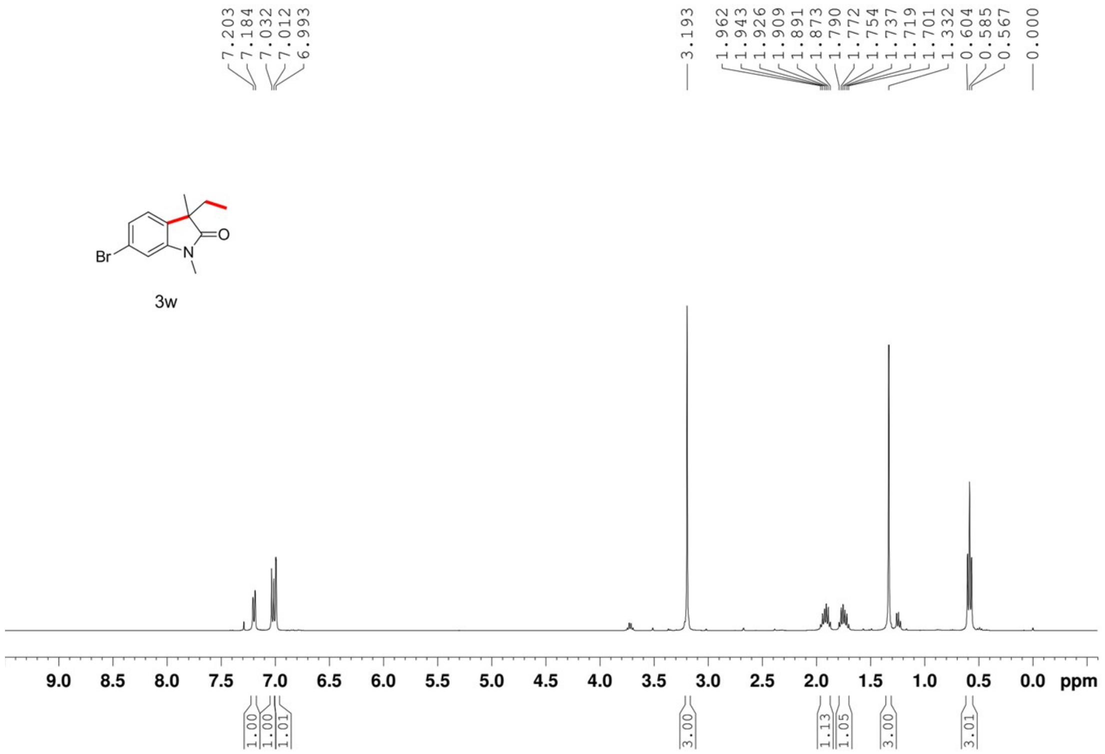
138.107
136.915
133.182
126.953
126.224
125.767
122.609
122.325
119.990
108.097
77.318
77.000
76.682
48.102
37.975
29.962
29.480
9.659
N
O
3v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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3.193
1.962
1.943
1.926
1.909
1.891
1.873
1.790
1.772
1.754
1.737
1.719
1.701
1.332
0.604
0.585
0.567
0.000
Br
N
O
3w
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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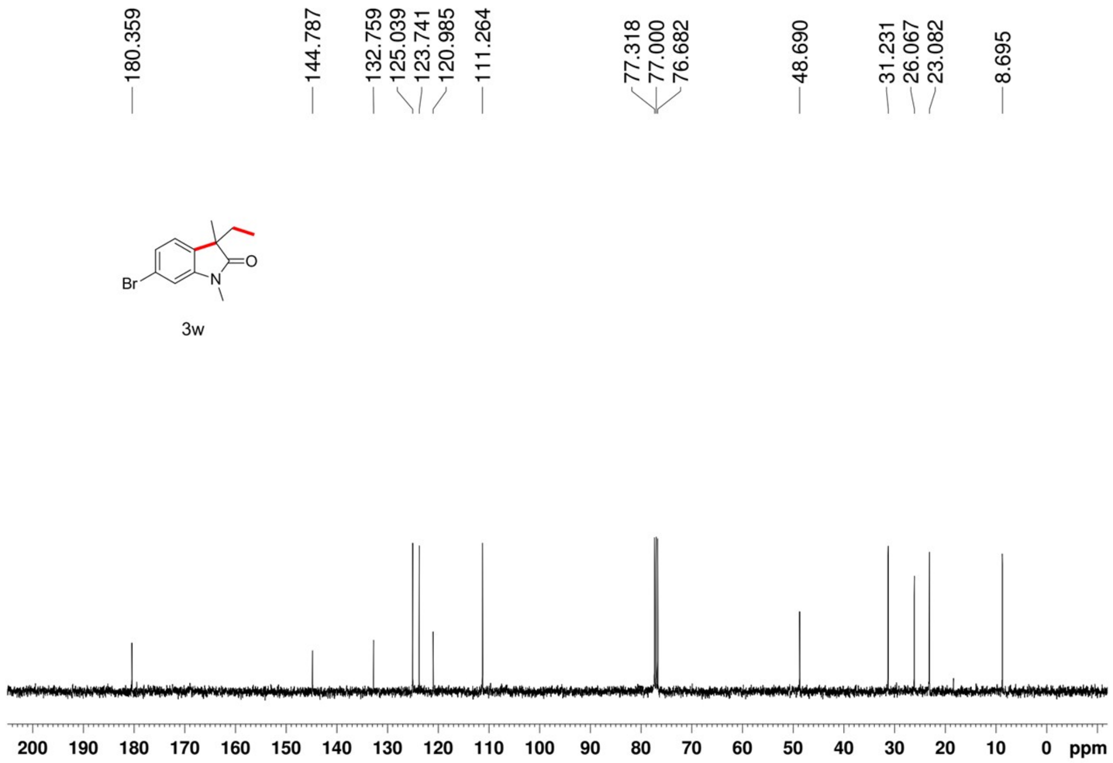
1.00
1.01
3.00
1.13
1.05
3.00
3.01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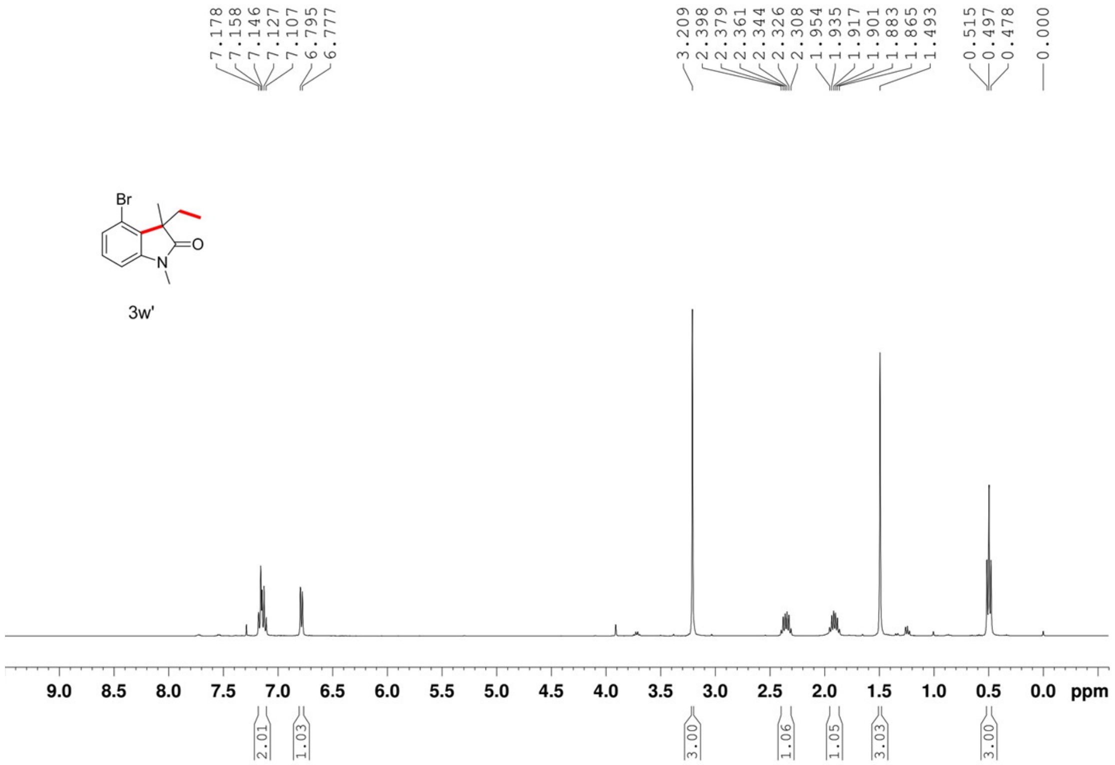
125.039
123.741
120.985
111.264
77.318
77.000
76.682
48.690
31.231
26.067
23.082
8.695
Br
N
O
3w
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.107
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6.777
3.209
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2.379
2.361
2.344
2.326
2.308
1.954
1.935
1.917
1.901
1.883
1.865
1.493
0.515
0.497
0.478
0.000
Br
O
N
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
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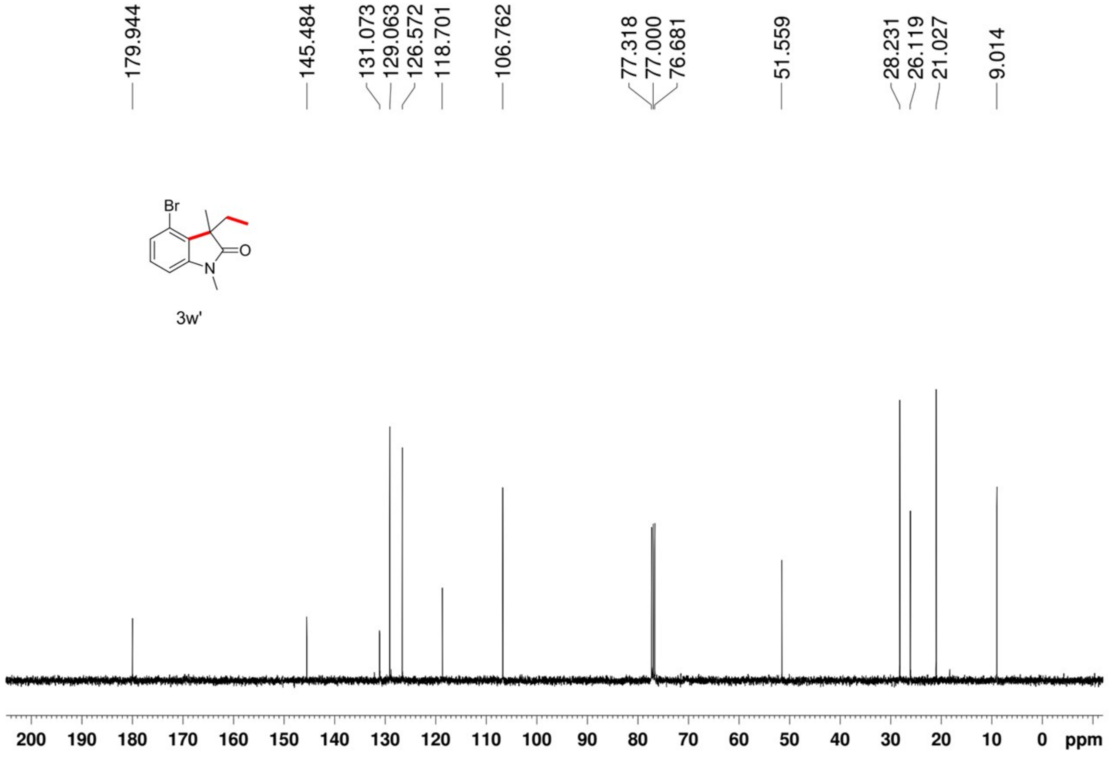
1.03
3.00
1.06
1.05
3.03
3.00

3w'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131.073
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118.701
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76.681
51.559
28.231
26.119
21.027
9.014
Br
O
N
200
190
180
170
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150
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130
120
110
100
90
80
70
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40
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20
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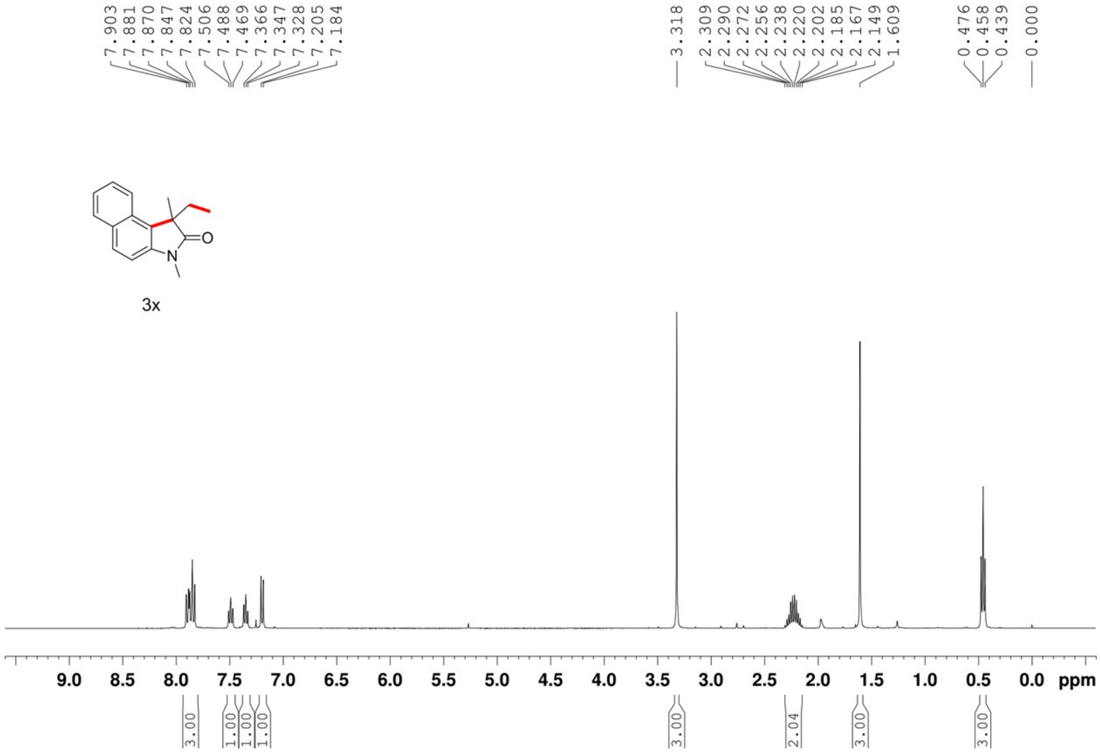
0
ppm

3w'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7.870
7.847
7.824
7.506
7.488
7.469
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7.347
7.328
7.205
7.184
3.318
2.309
2.290
2.272
2.256
2.238
2.220
2.202
2.185
2.167
2.149
1.609
0.476
0.458
0.439
0.000
N
O
3x
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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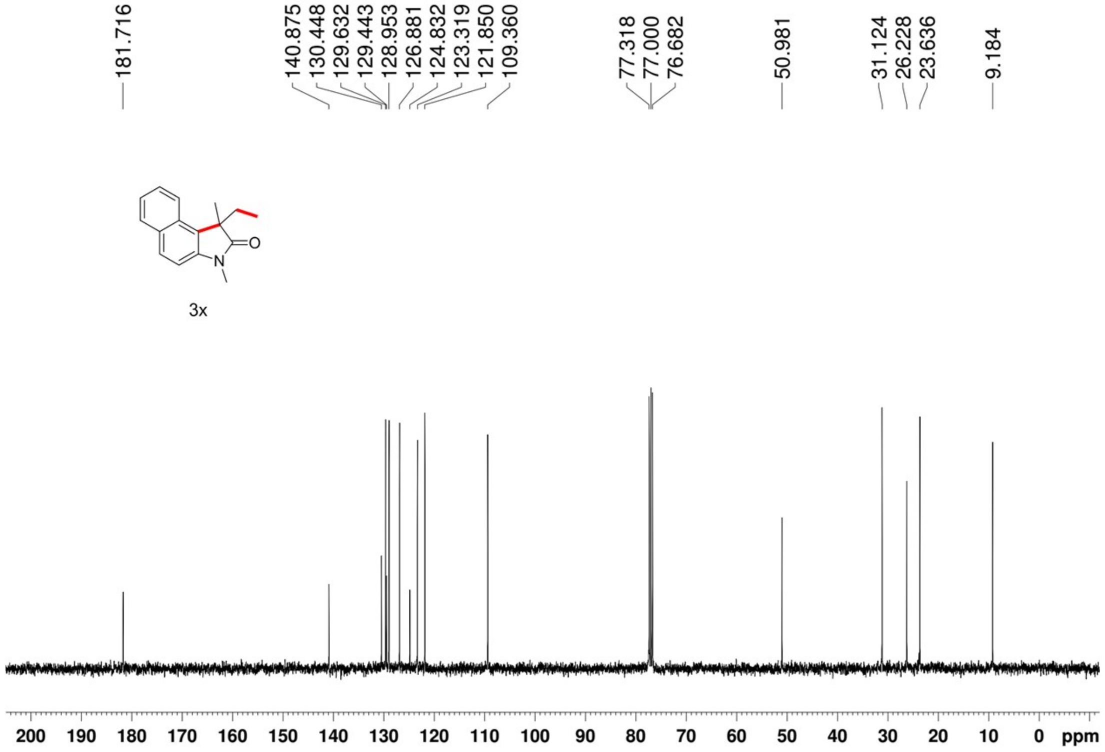
1.00
1.00
3.00
2.04
3.00
3.00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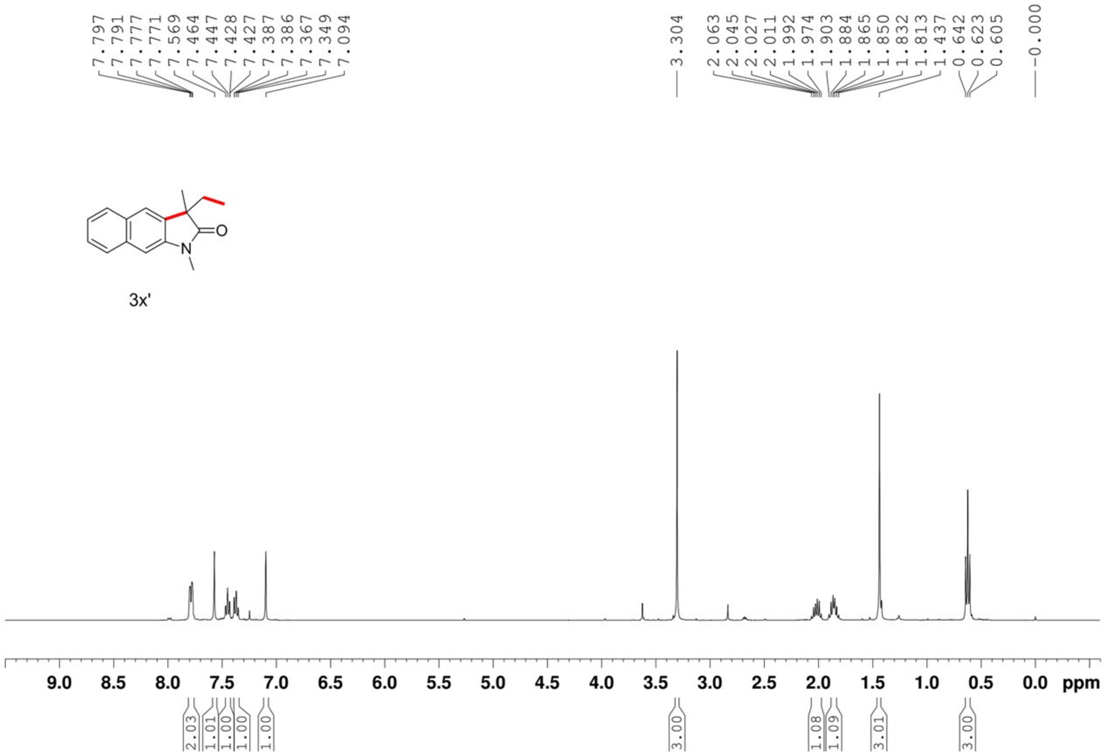
140.875
130.448
129.632
129.443
128.953
126.881
124.832
123.319
121.850
109.360
77.318
77.000
76.682
50.981
31.124
26.228
23.636
9.184
N
O
3x
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.791
7.777
7.771
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7.447
7.428
7.427
7.387
7.386
7.367
7.349
7.094
3.304
2.063
2.045
2.027
2.011
1.992
1.974
1.903
1.884
1.865
1.850
1.832
1.813
1.437
0.642
0.623
0.605
-0.000
O
N
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
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ppm
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1.00
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3.00
1.08
1.09
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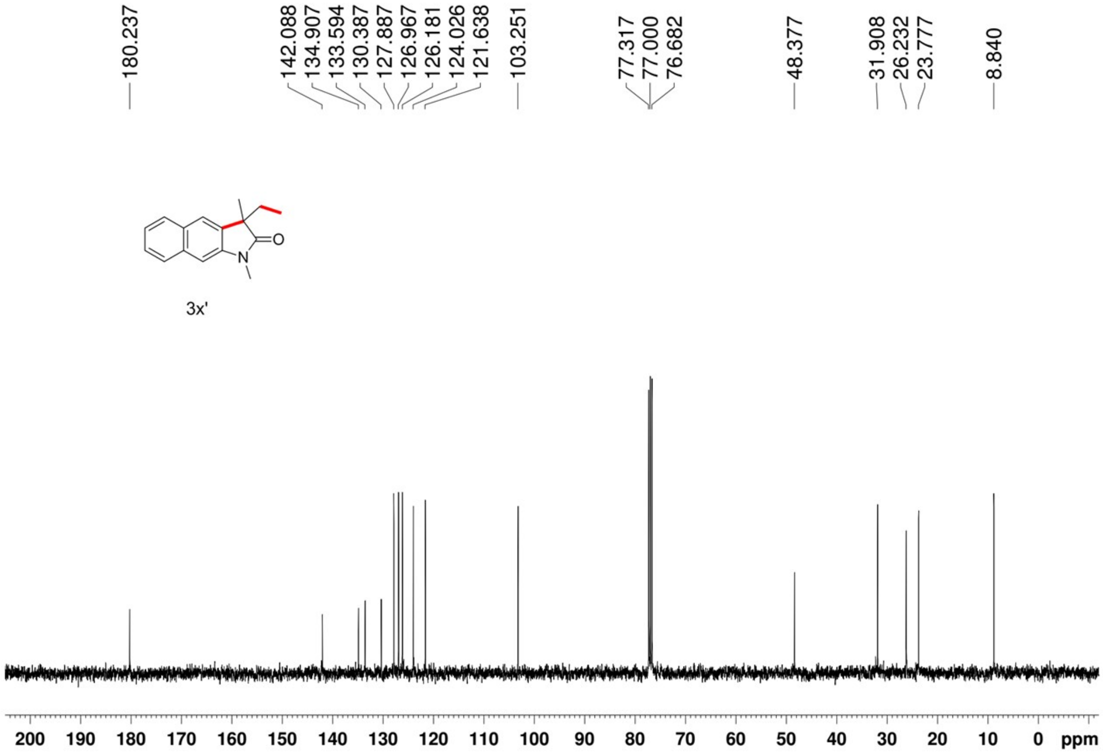
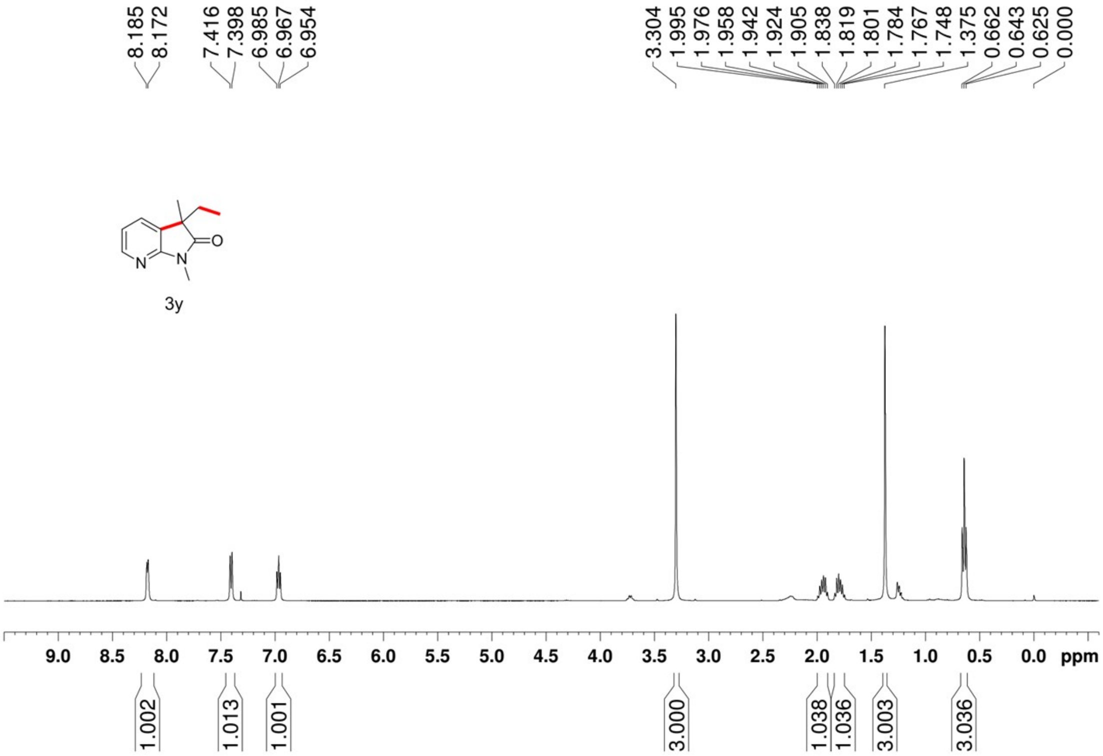
3.00

3x'


180.237
142.088
134.907
133.594
130.387
127.887
126.967
126.181
124.026
121.638
103.251
77.317
77.000
76.682
48.377
31.908
26.232
23.777
8.840
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3x'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8.172
7.416
7.398
6.985
6.967
6.954
3.304
1.995
1.976
1.958
1.942
1.924
1.905
1.838
1.819
1.801
1.784
1.767
1.748
1.375
0.662
0.643
0.625
0.000
N
N
O
3y
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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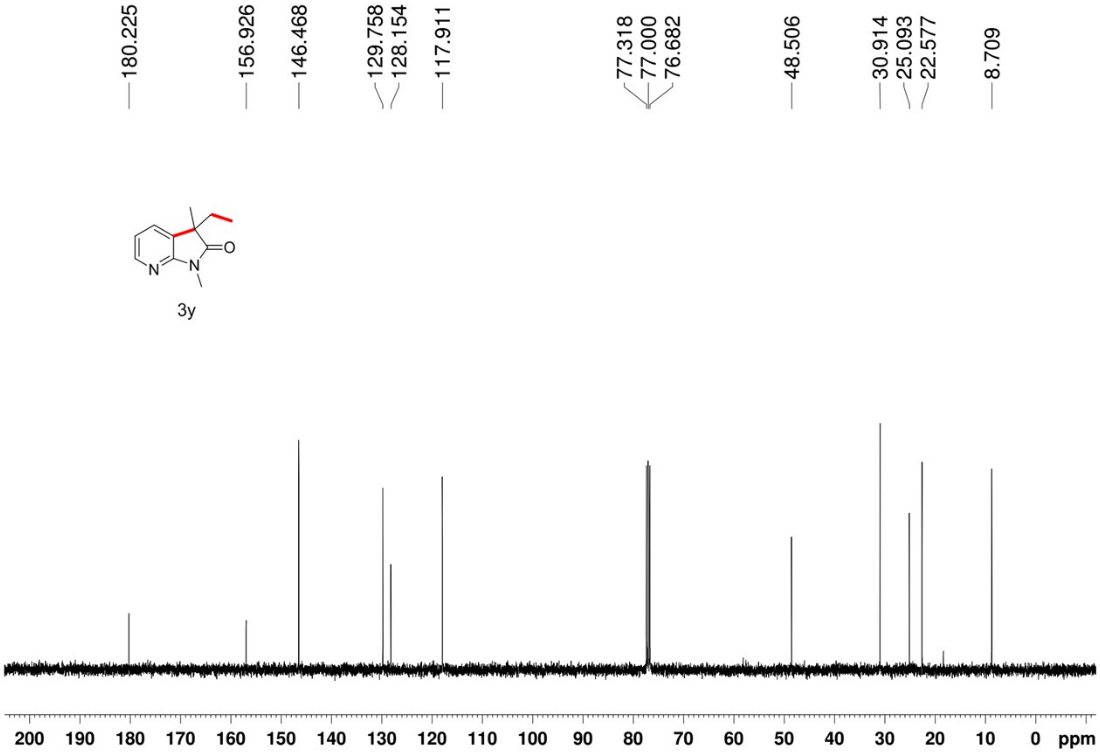
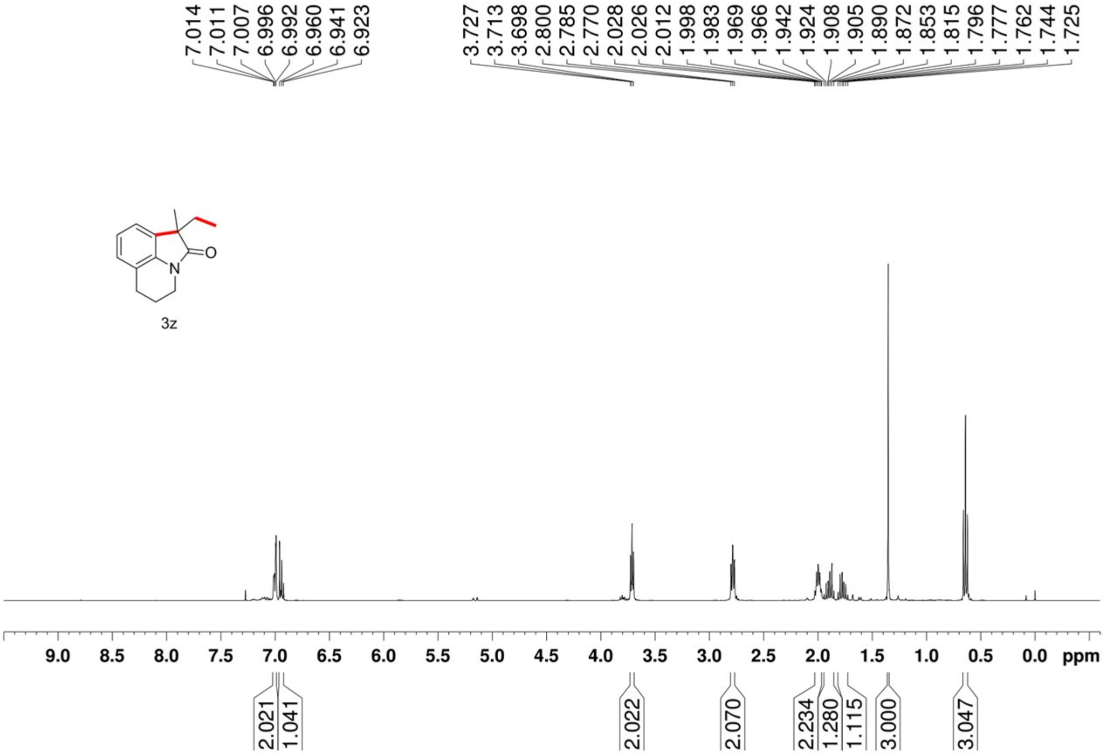
1.013
1.001
3.000
1.038
1.036
3.003
3.036


180.225
156.926
146.468
129.758
128.154
117.911
77.318
77.000
76.682
48.506
30.914
25.093
22.577
8.709
N
N
O
3y
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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7.011
7.007
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6.992
6.960
6.941
6.923
3.727
3.713
3.698
2.800
2.785
2.770
2.028
2.026
2.012
1.998
1.983
1.969
1.966
1.942
1.924
1.908
1.905
1.890
1.872
1.853
1.815
1.796
1.777
1.762
1.744
1.725
N
O
3z
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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2.022
2.070
2.234
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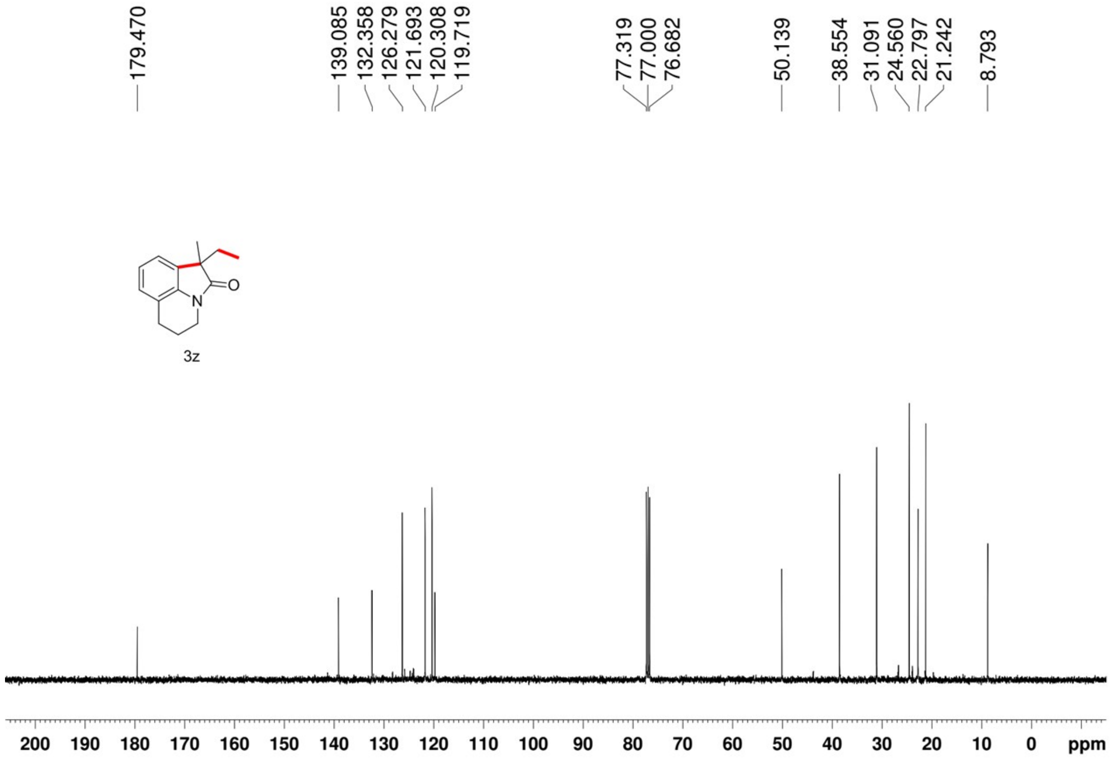
1.115
3.000
3.047


179.470
139.085
132.358
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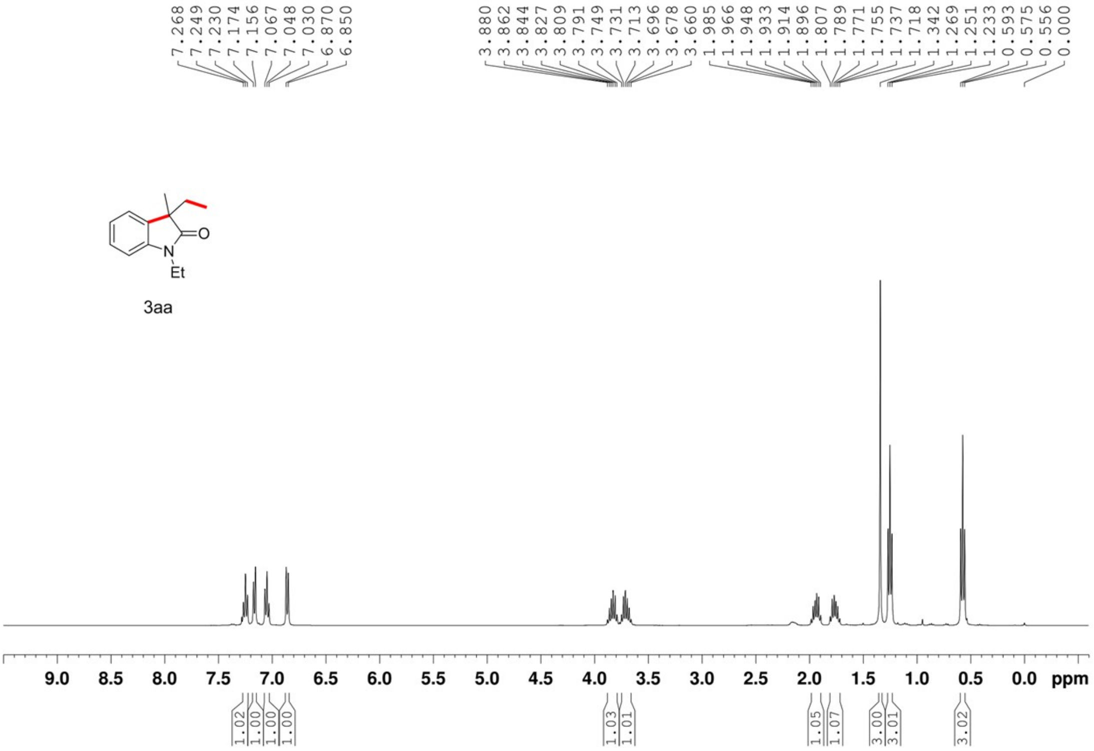
121.693
120.308
119.719
77.319
77.000
76.682
50.139
38.554
31.091
24.560
22.797
21.242
8.793
N
O
3z
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.268
7.249
7.230
7.174
7.156
7.067
7.048
7.030
6.870
6.850
3.880
3.862
3.844
3.827
3.809
3.791
3.749
3.731
3.713
3.696
3.678
3.660
1.985
1.966
1.948
1.933
1.914
1.896
1.807
1.789
1.771
1.755
1.737
1.718
1.342
1.269
1.251
1.233
0.593
0.575
0.556
0.000
O
N
Et
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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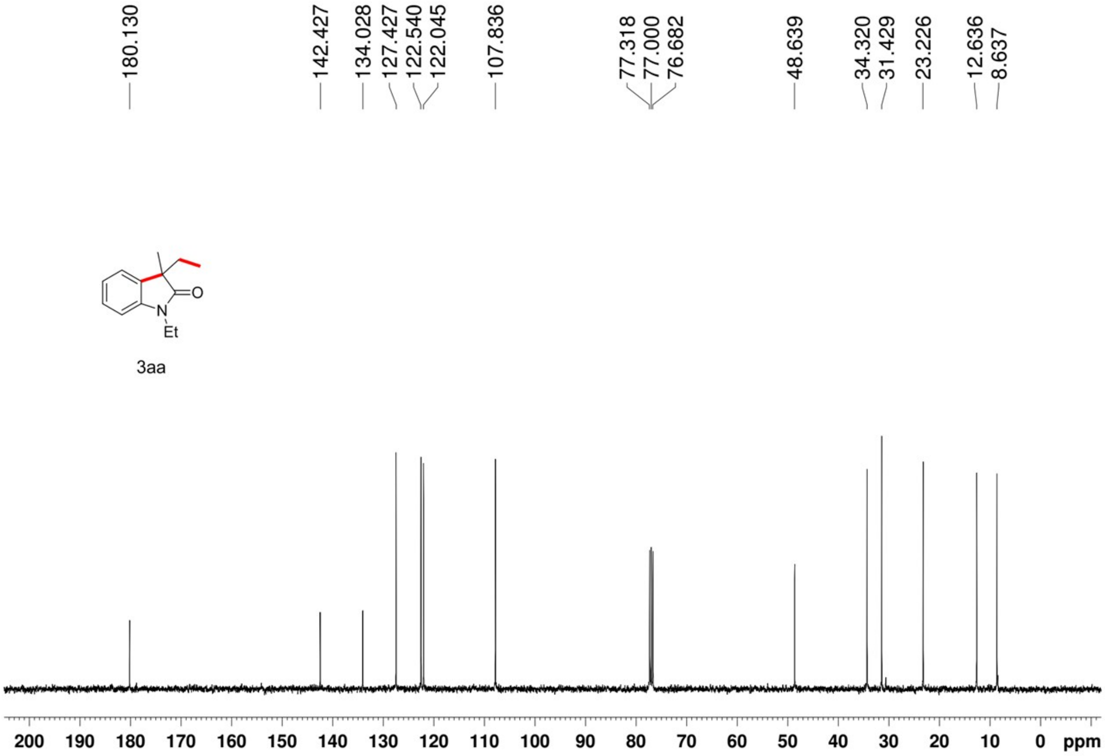
1.00
1.00
1.00
1.03
1.01
1.05
1.07
3.00
3.01
3.02

3aa


180.130
142.427
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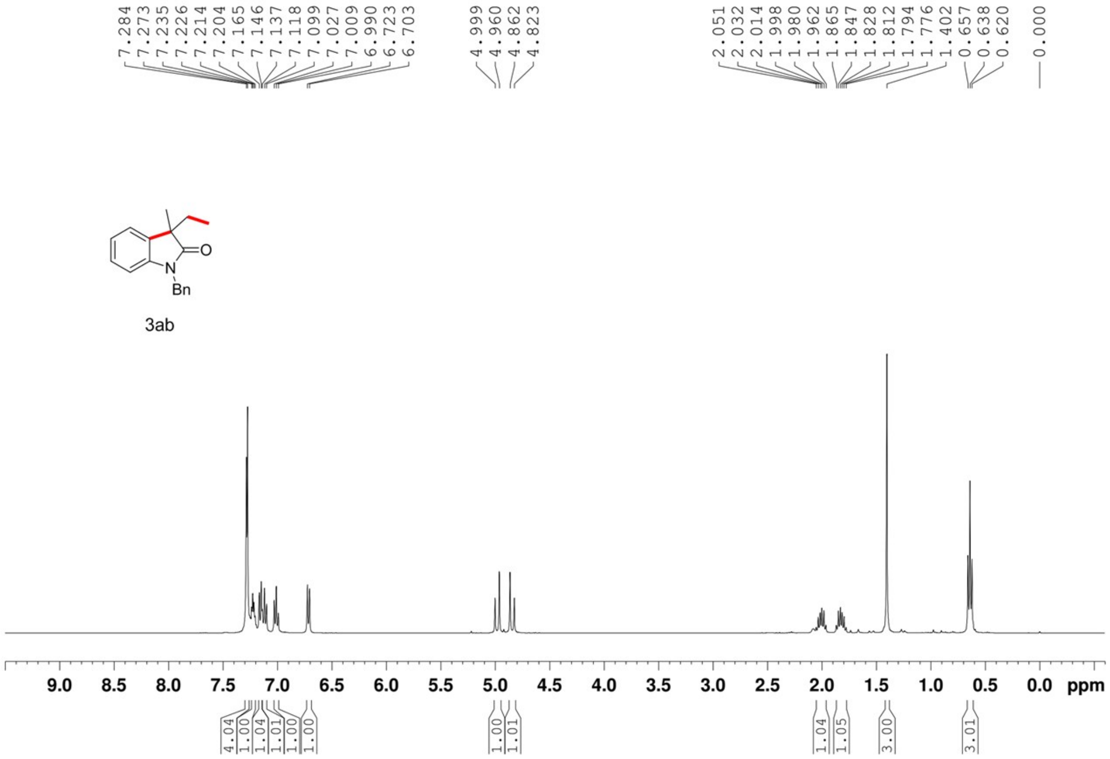
122.540
122.045
107.836
77.318
77.000
76.682
48.639
34.320
31.429
23.226
12.636
8.637
O
N
Et
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3aa


3ab

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7.235
7.226
7.214
7.204
7.165
7.146
7.137
7.118
7.099
7.027
7.009
6.990
6.723
6.703
4.999
4.960
4.862
4.823
2.051
2.032
2.014
1.998
1.980
1.962
1.865
1.847
1.828
1.812
1.794
1.776
1.402
0.657
0.638
0.620
0.000
N
O
Bn
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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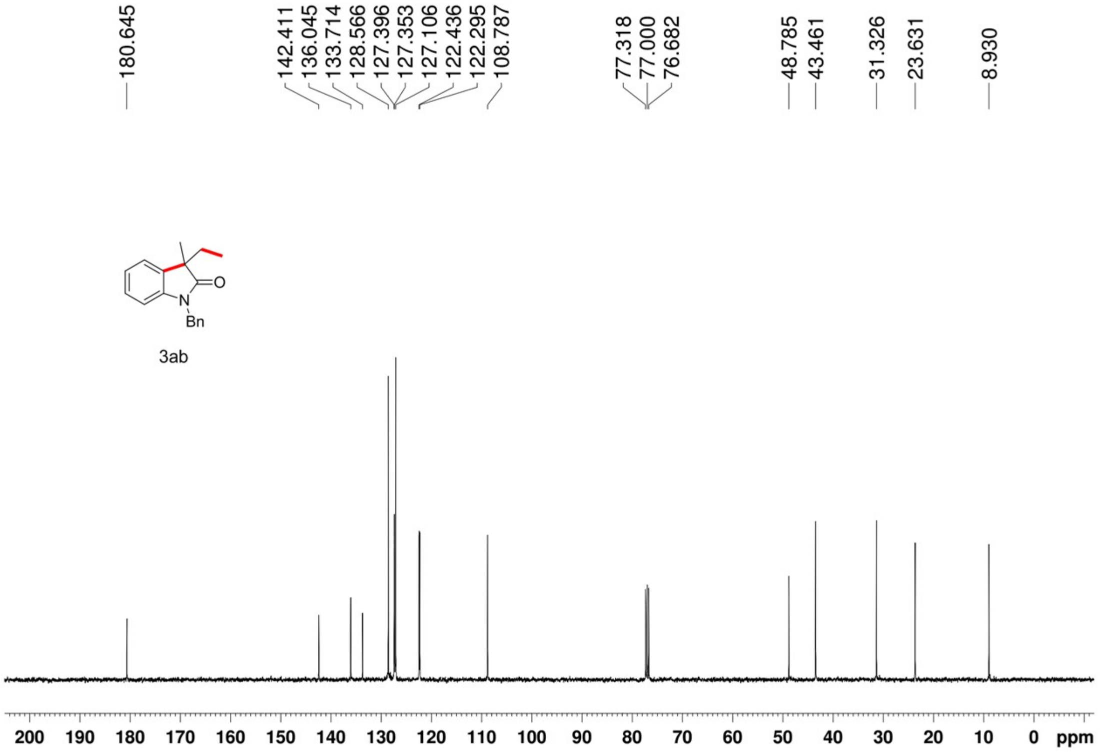
1.04
1.01
1.00
1.00
1.00
1.01
1.04
1.05
3.00
3.01


3ab

180.645
142.411
136.045
133.714
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127.396
127.353
127.106
122.436
122.295
108.787
77.318
77.000
76.682
48.785
43.461
31.326
23.631
8.930
N
O
Bn
200
190
180
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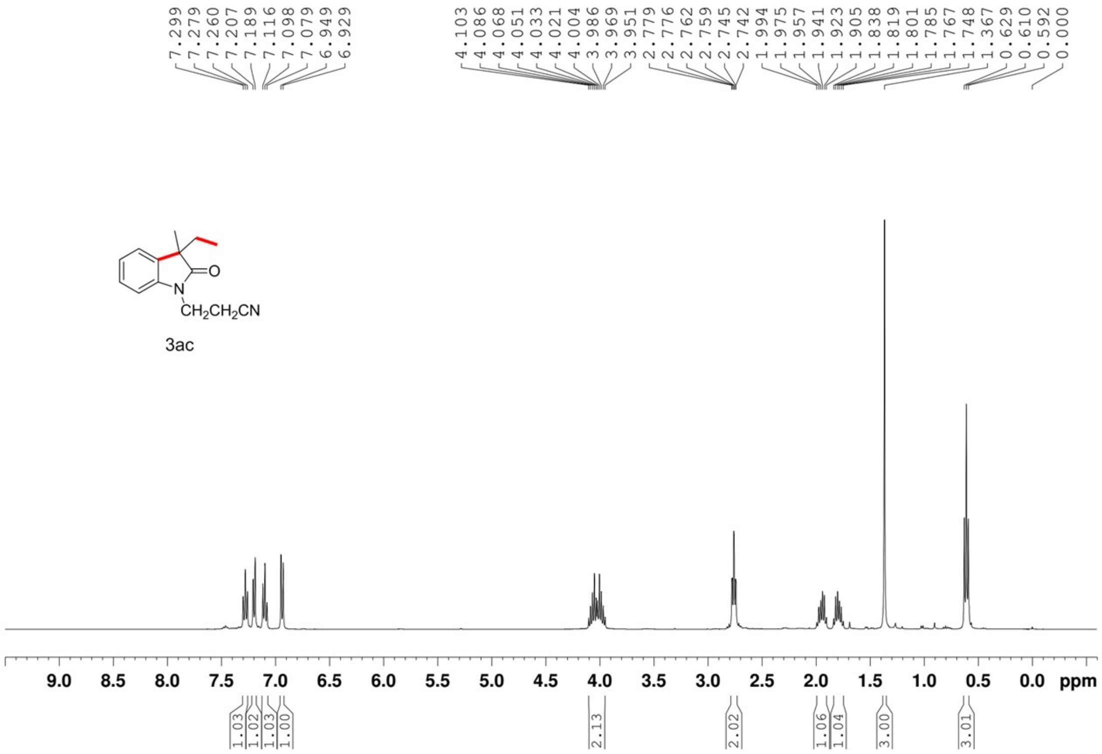
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.189
7.116
7.098
7.079
6.949
6.929
4.103
4.086
4.068
4.051
4.033
4.021
4.004
3.986
3.969
3.951
2.779
2.776
2.762
2.759
2.745
2.742
1.994
1.975
1.957
1.941
1.923
1.905
1.838
1.819
1.801
1.785
1.767
1.748
1.367
0.629
0.610
0.592
0.000
O
N
CH_2CH_2CN
3ac
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
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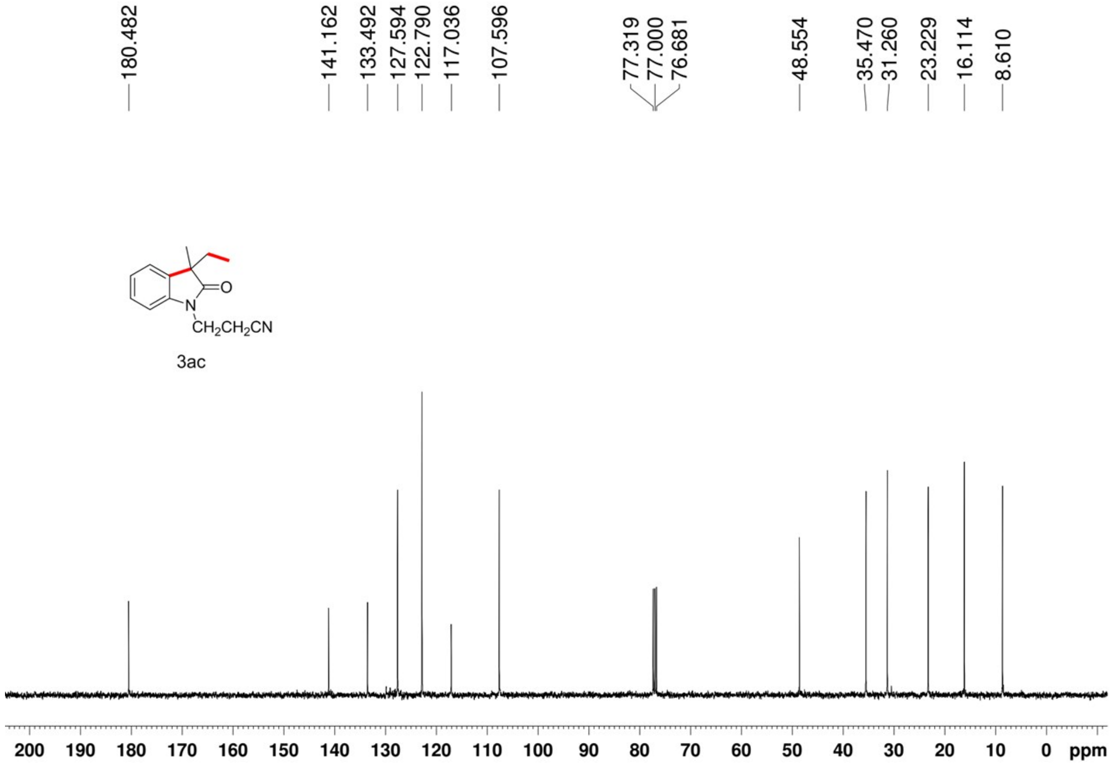
ppm
1.03
1.02
1.03
1.00
2.13
2.02
1.06
1.04
3.00
3.01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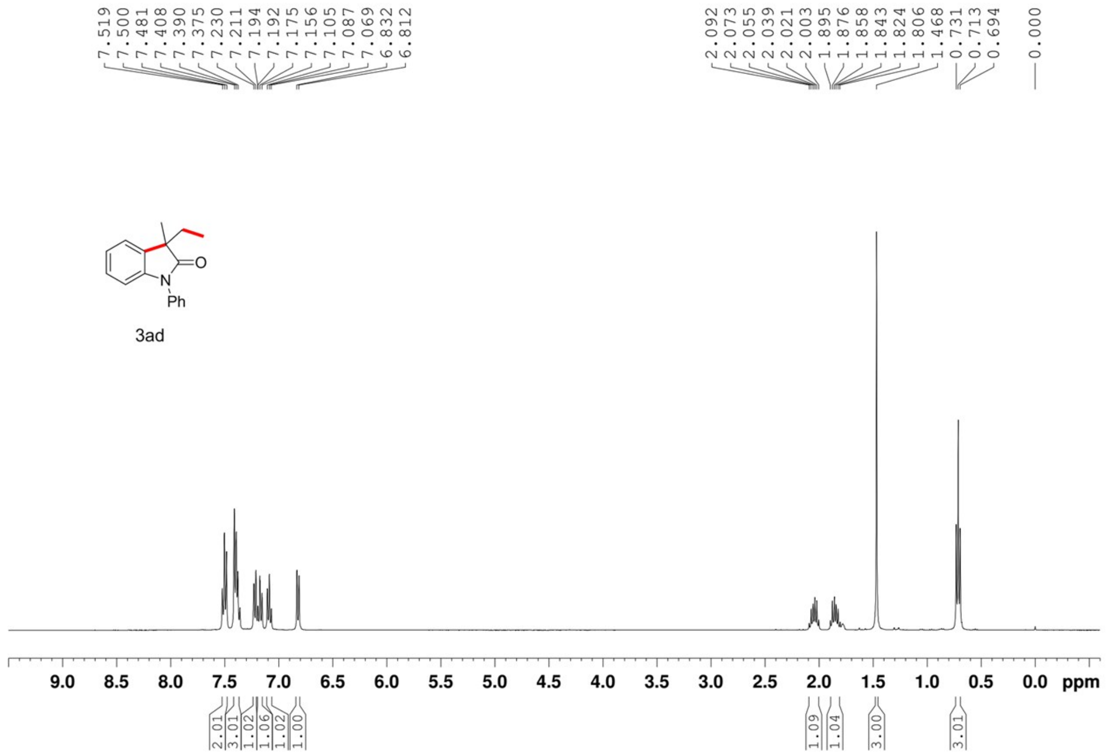
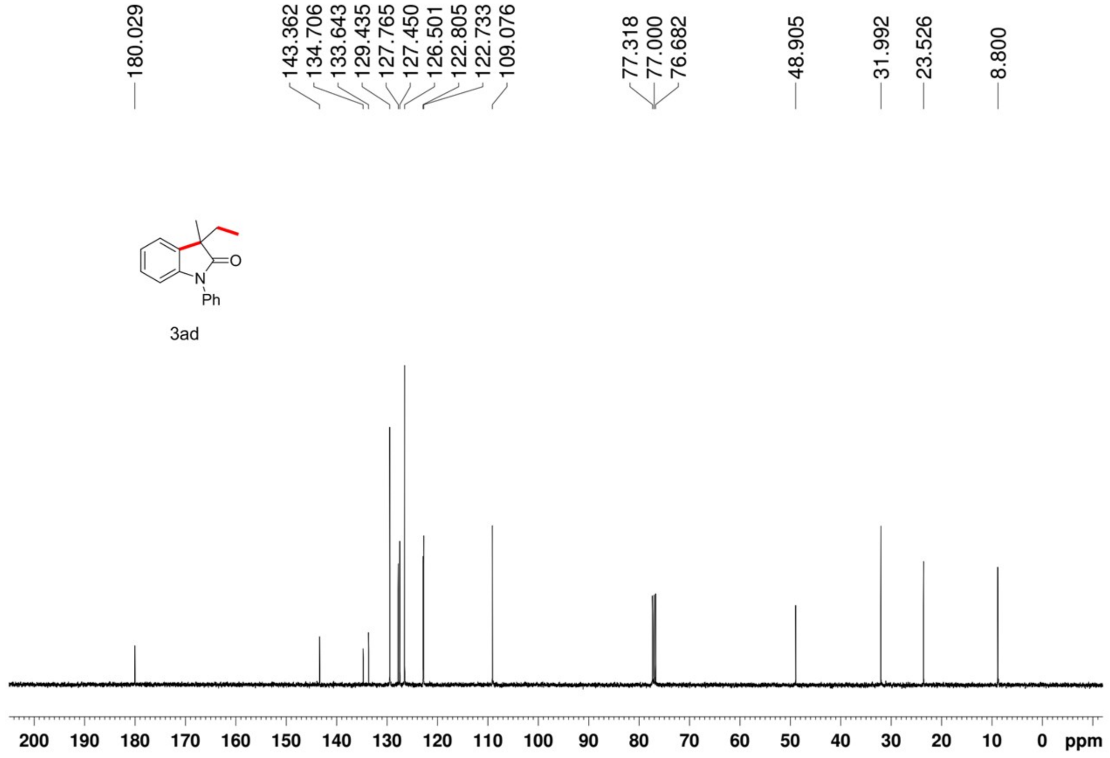
117.036
107.596
77.319
77.000
76.681
48.554
35.470
31.260
23.229
16.114
8.610
O
N
CH_2CH_2CN
3ac
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm





4. References

1. (*a*) X. Mu, T. Wu, H. Wang, Y. Guo and G. Liu, *J. Am. Chem.Soc.* 2012, **134**, 878. (*b*) A. Pinto, Y. Jia, L. Neuville and J. Zhu, *Chem. Eur. J.* 2007, **13**, 961. (*c*) T. Wu, X. Mu and G. Liu, *Angew. Chem., Int. Ed.* 2011, **50**, 12578.