"One-Pot" Access to Dihydrofurans *via* Tandem Oxidative Difunctionalization and Ring Contraction of Aminopyrans

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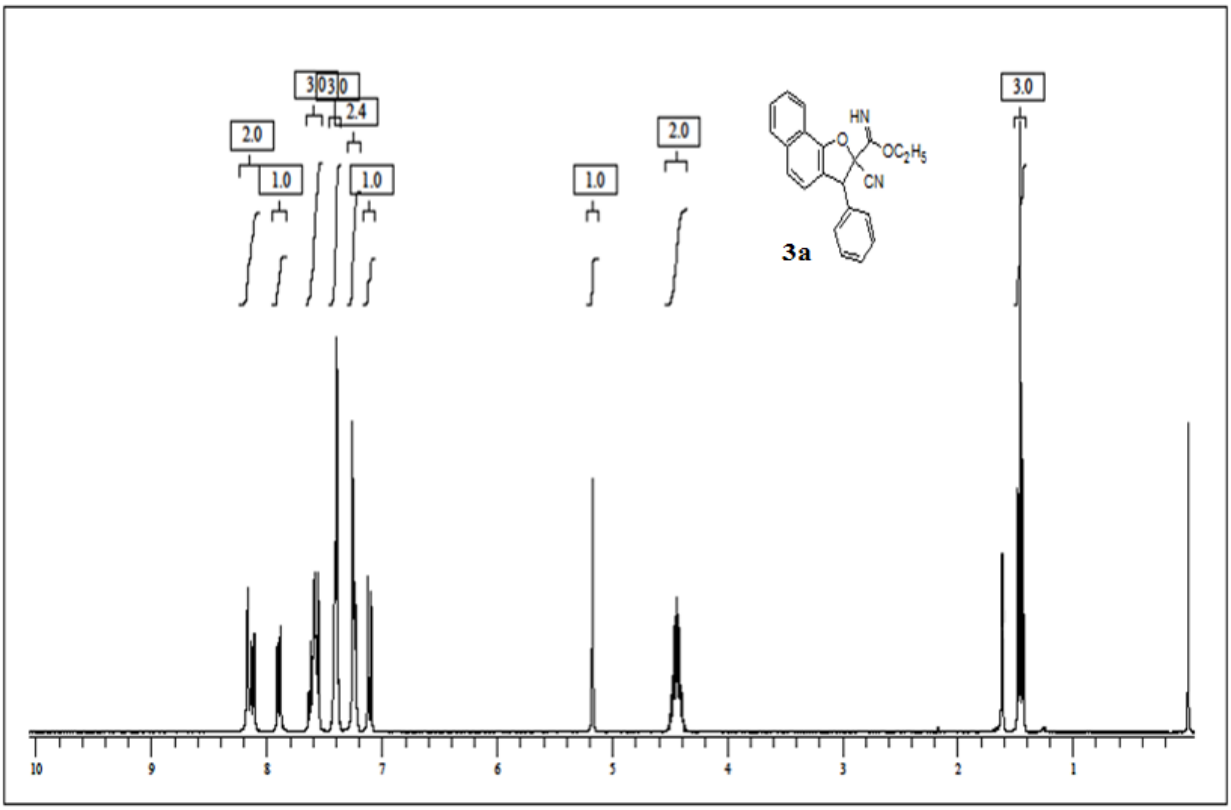
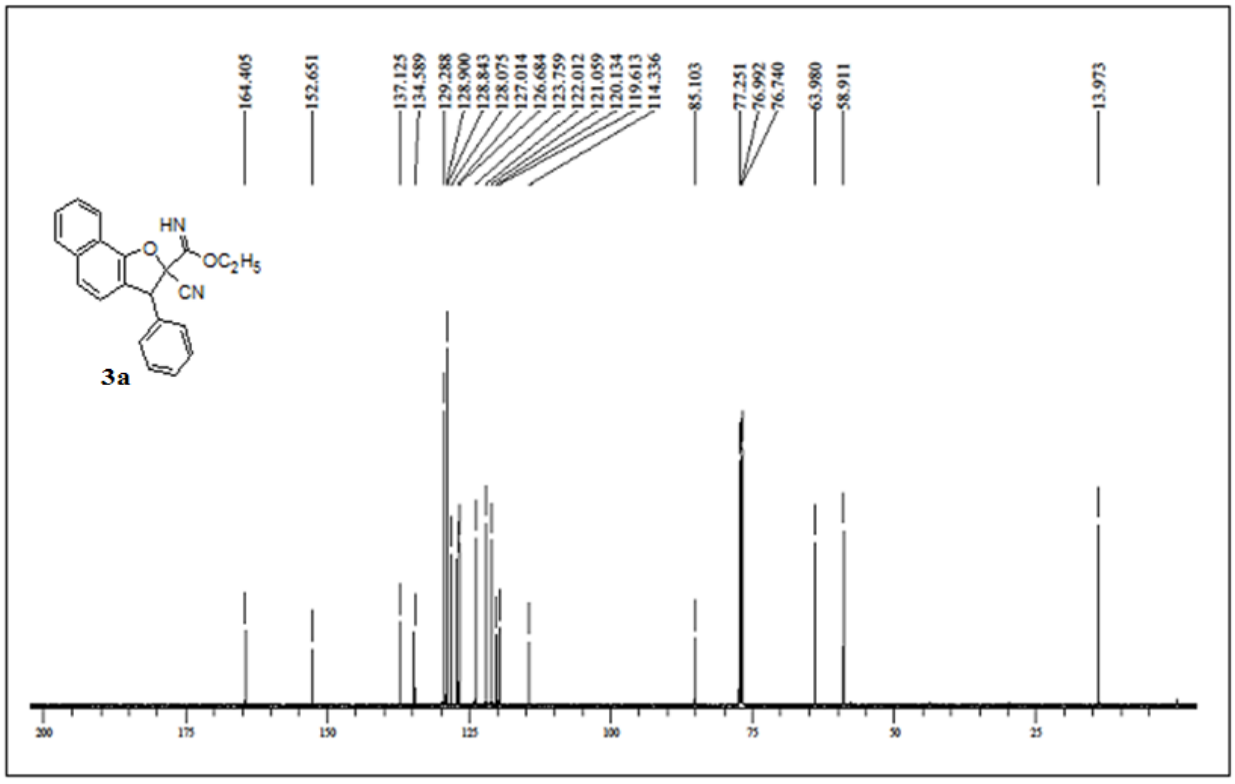
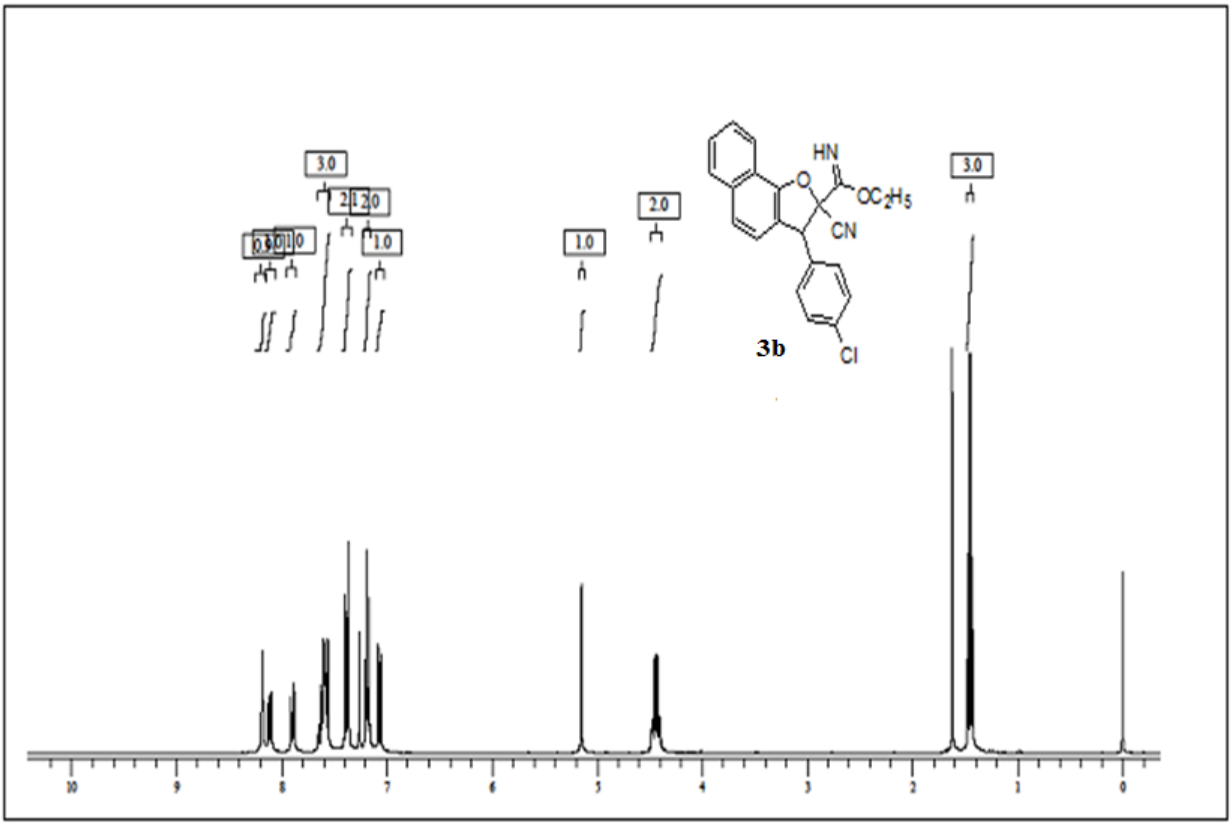
Supporting information

1. ^{1}H & ^{13}C NMR spectral copies [S-2 to S-28]
2. Deuterium exchange PMR spectra of **'3e'** [S-29]
3. X-ray crystallography data for **'3h'** and **'6'** [S-30 to S-32]
4. References [S-33]

^{1}H & ^{13}C NMR Spectral copies



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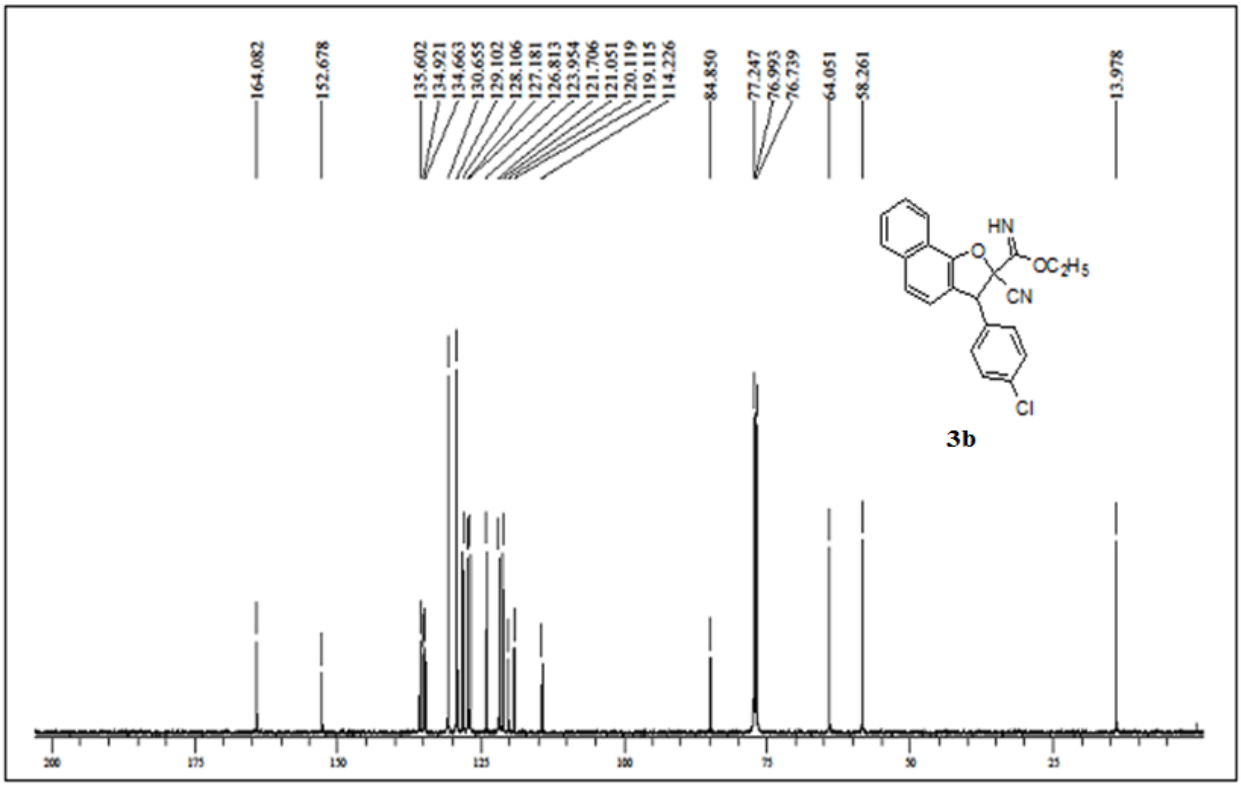
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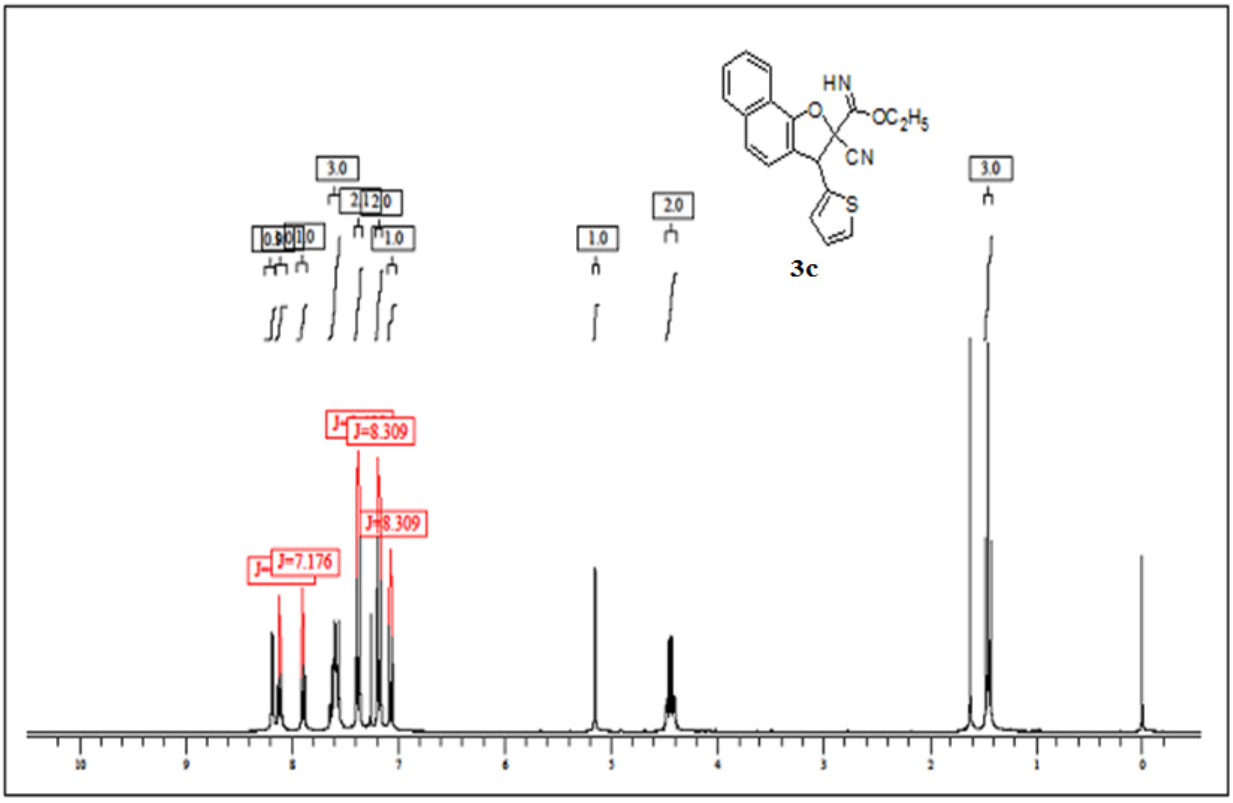
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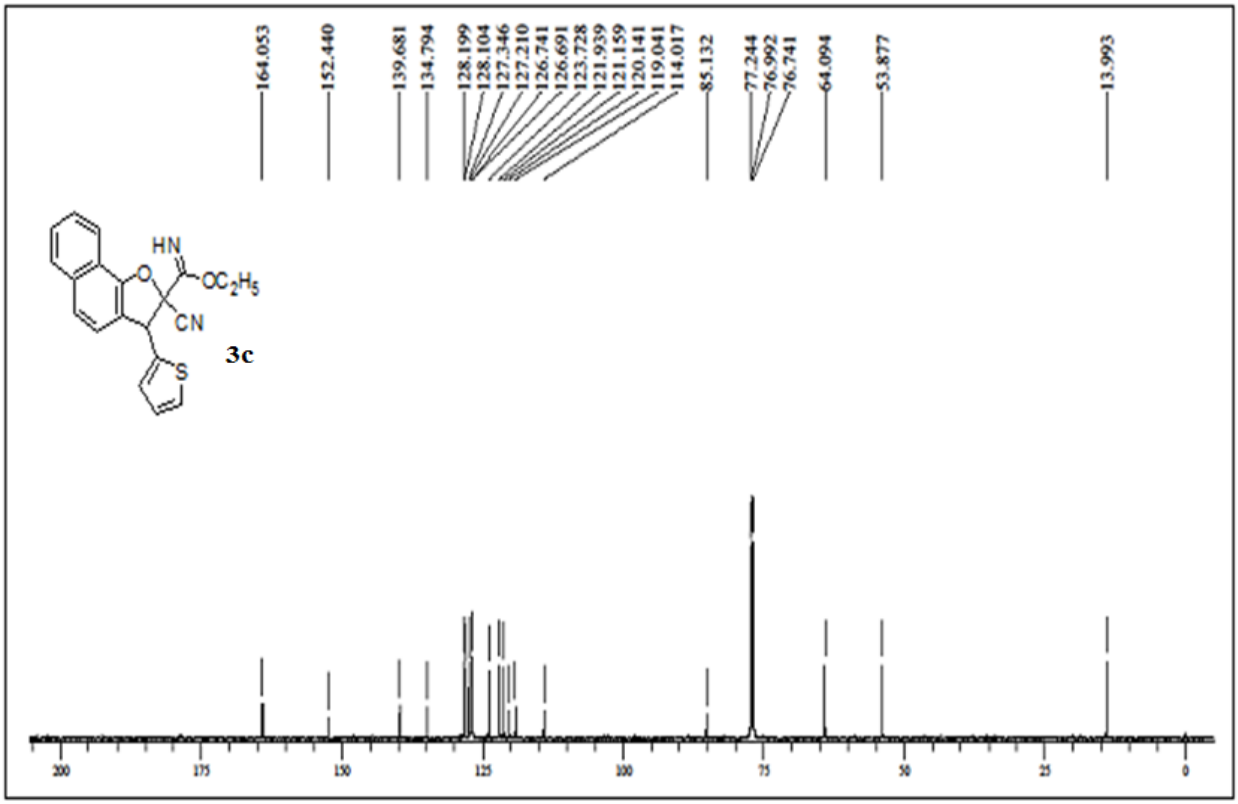
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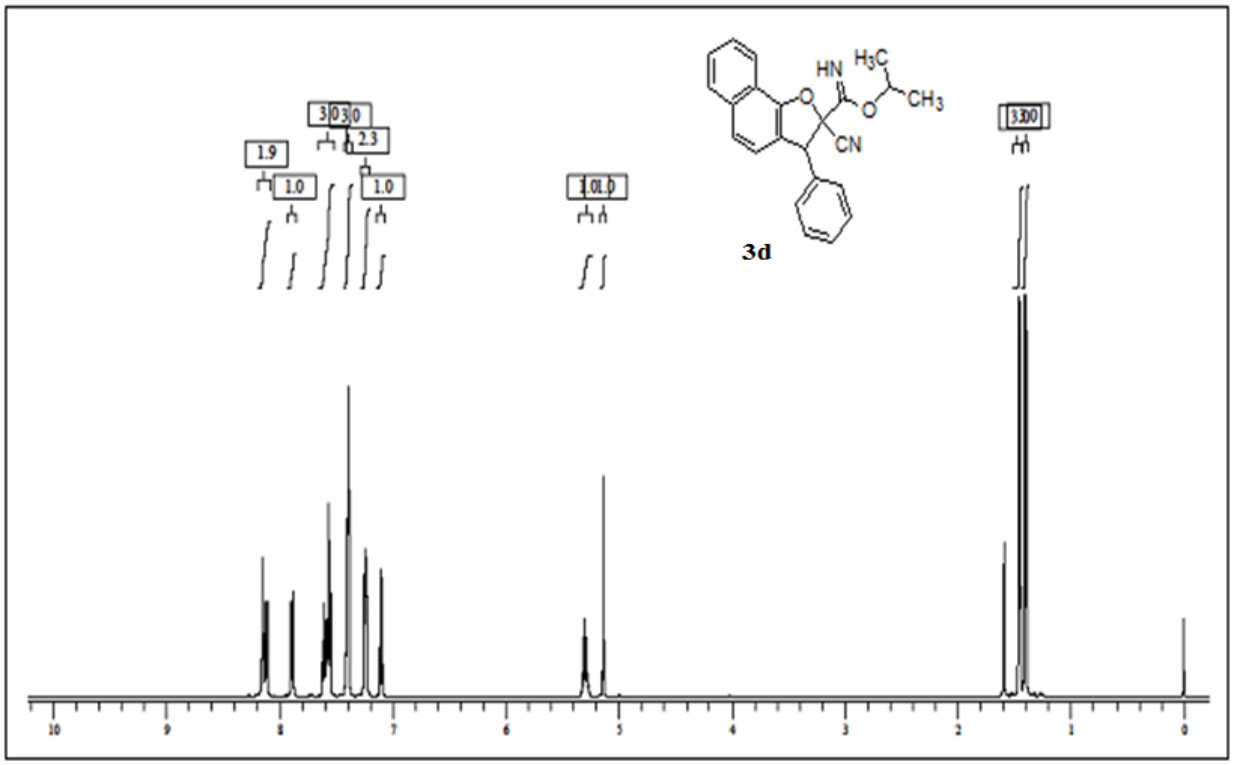
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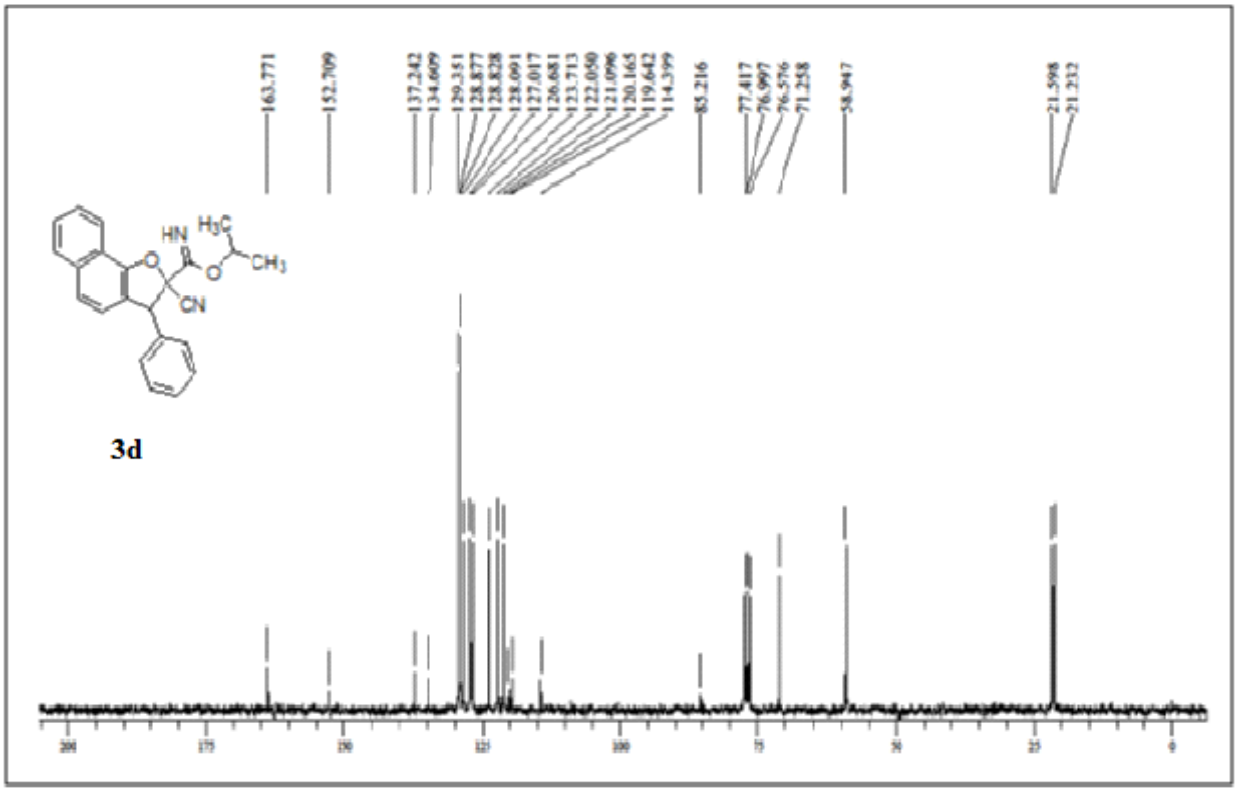
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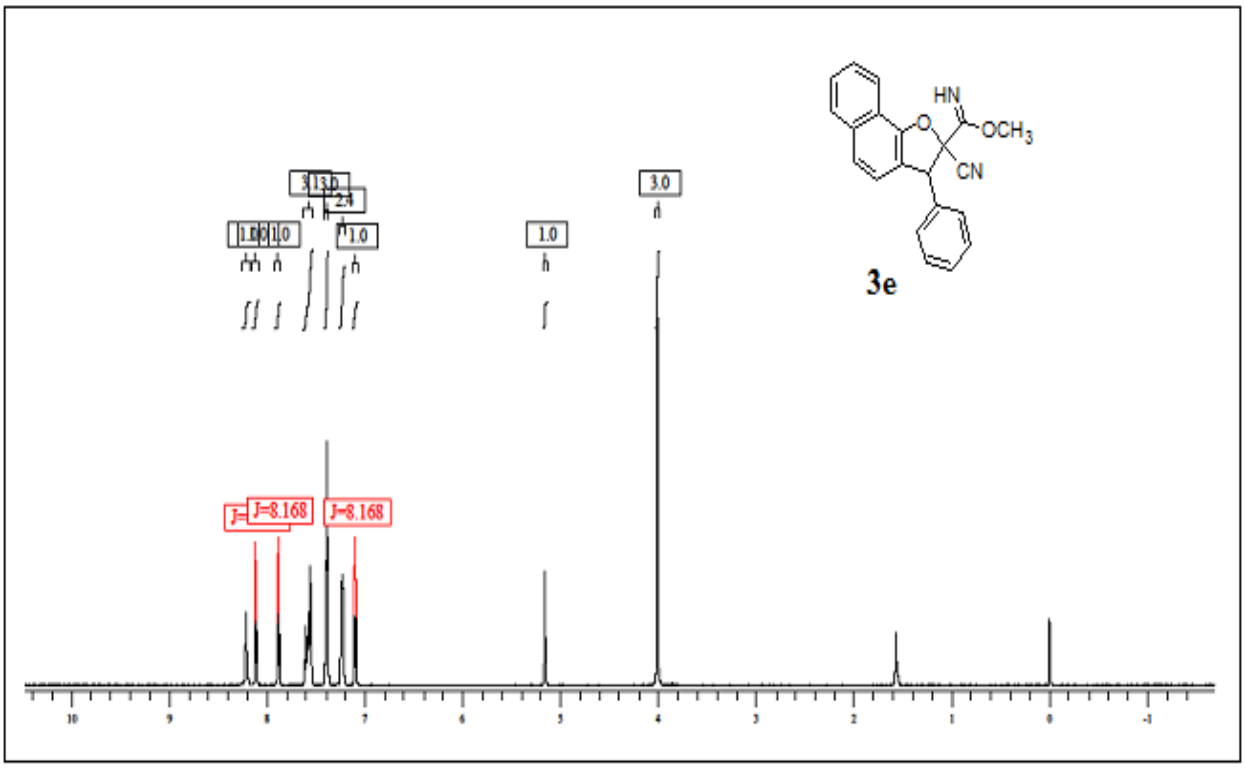
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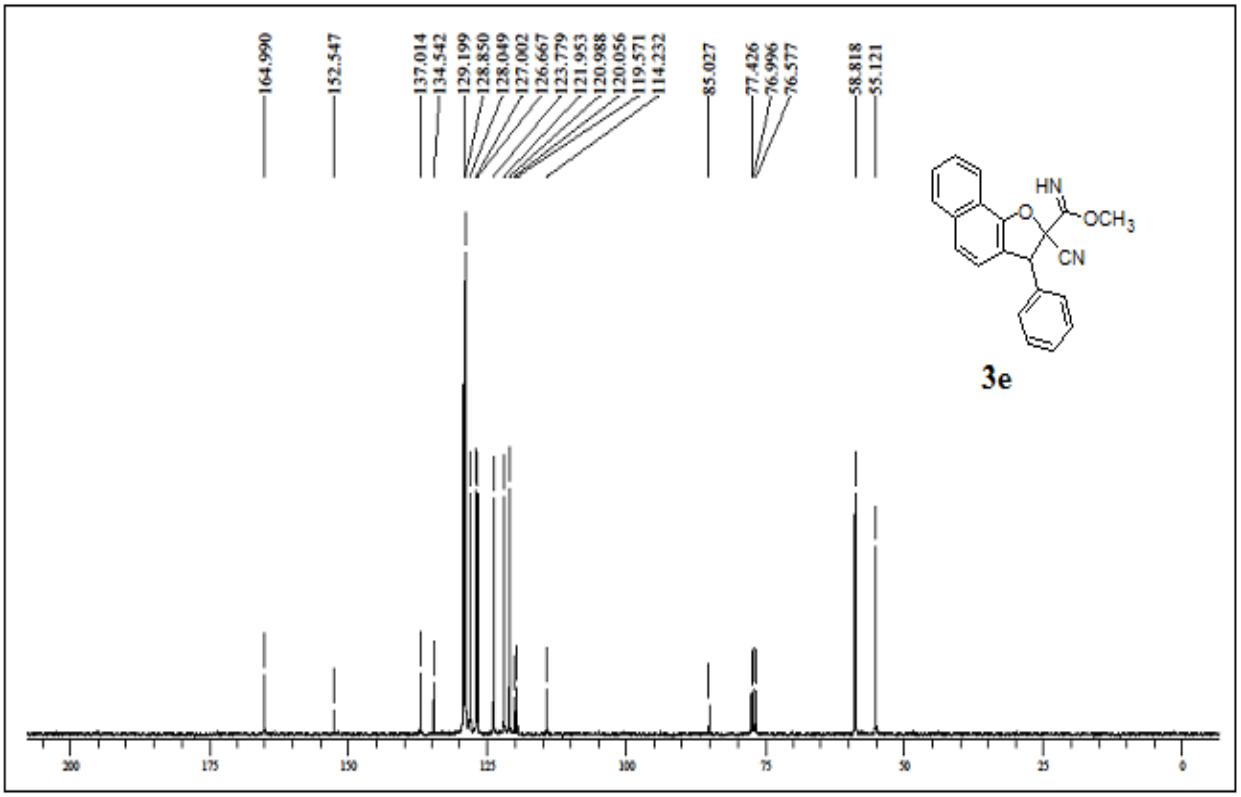
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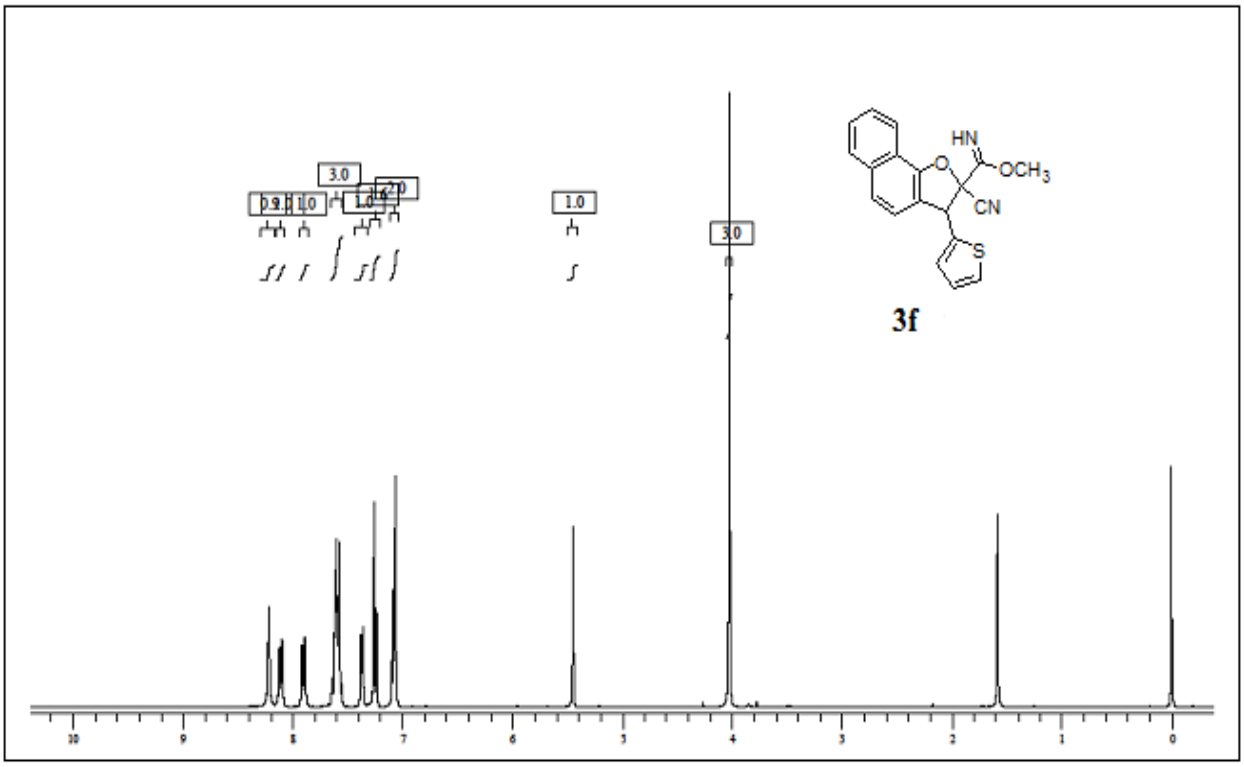
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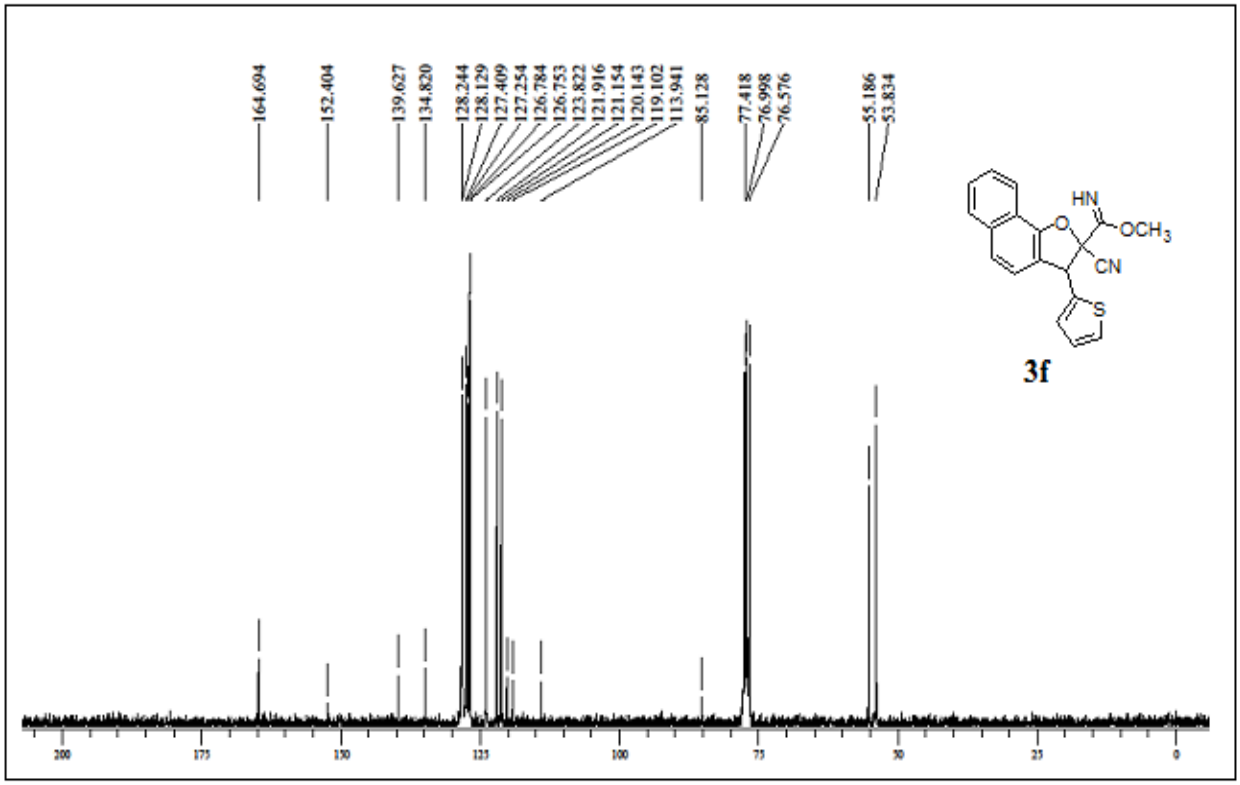
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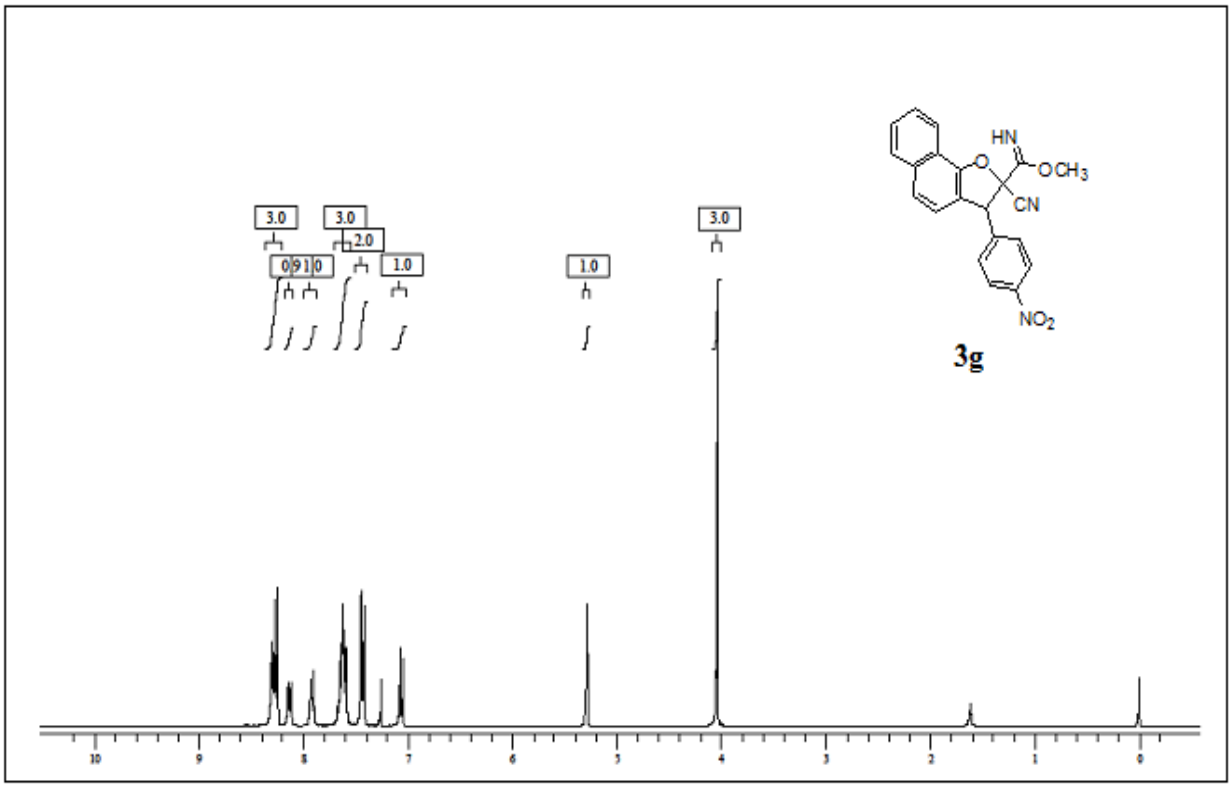
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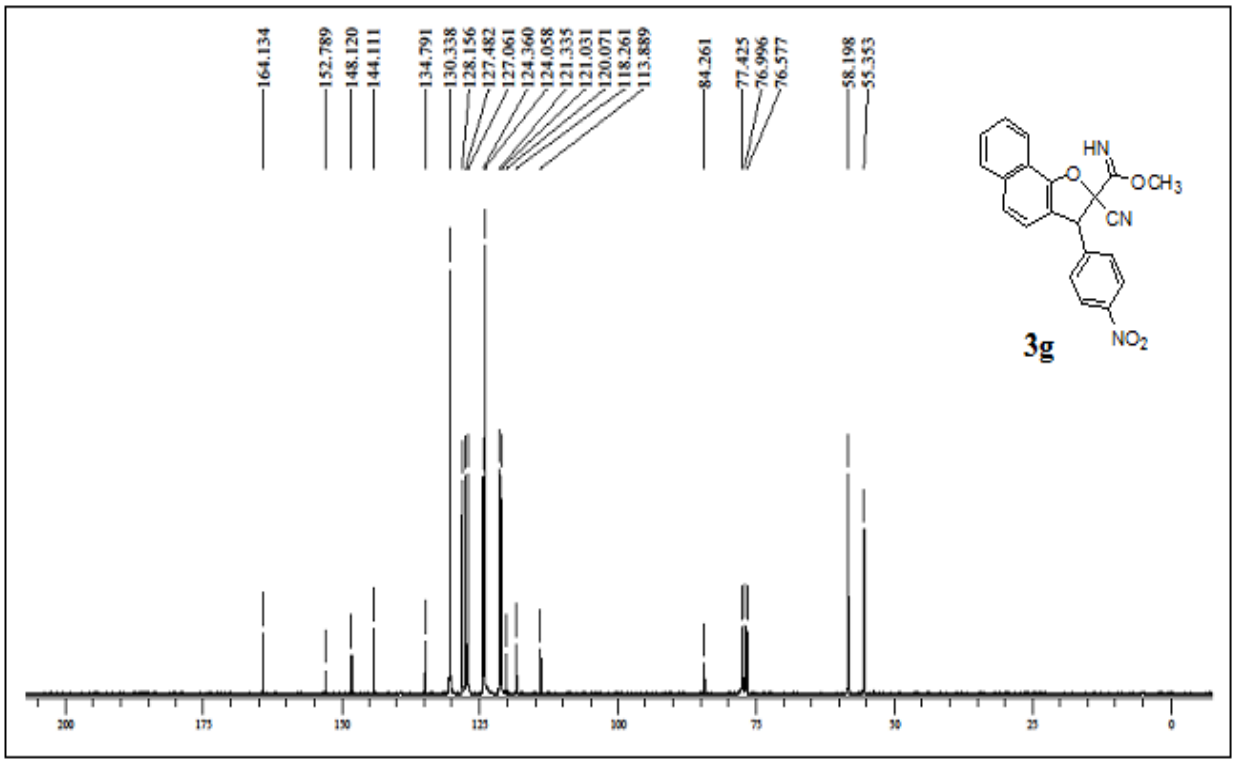
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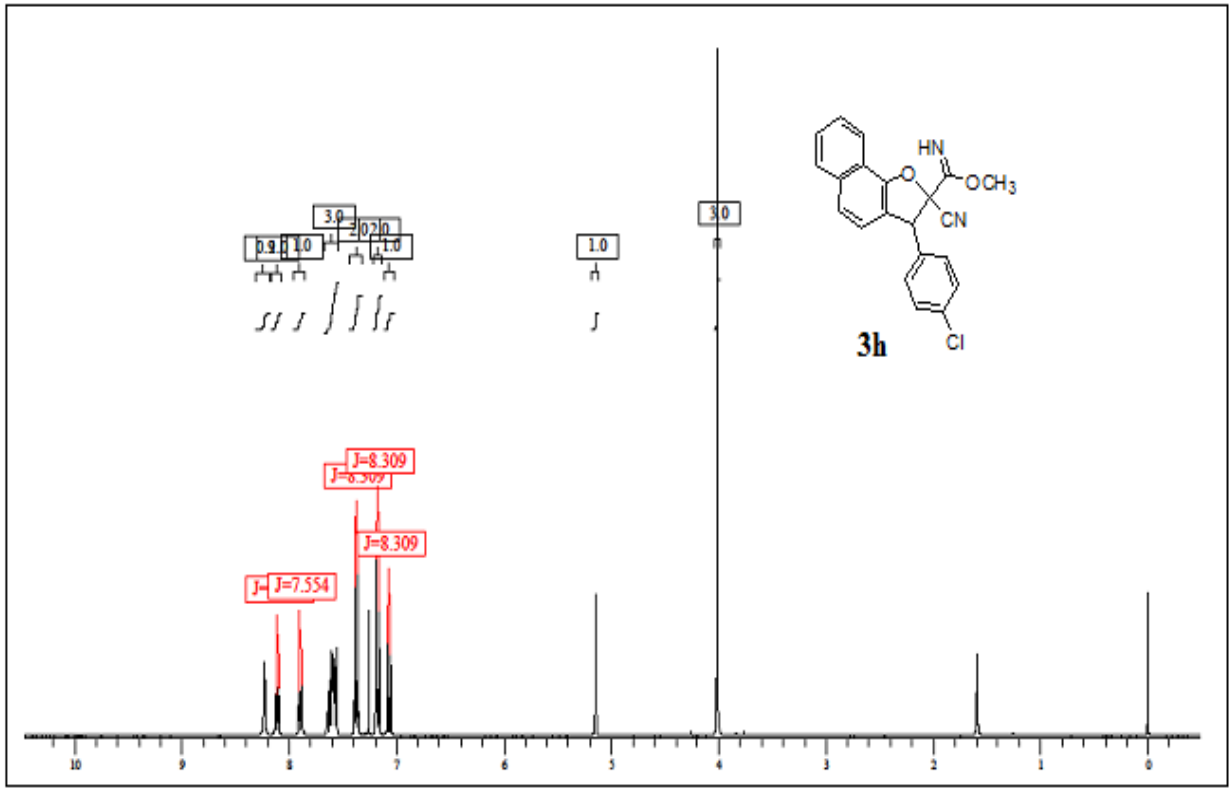
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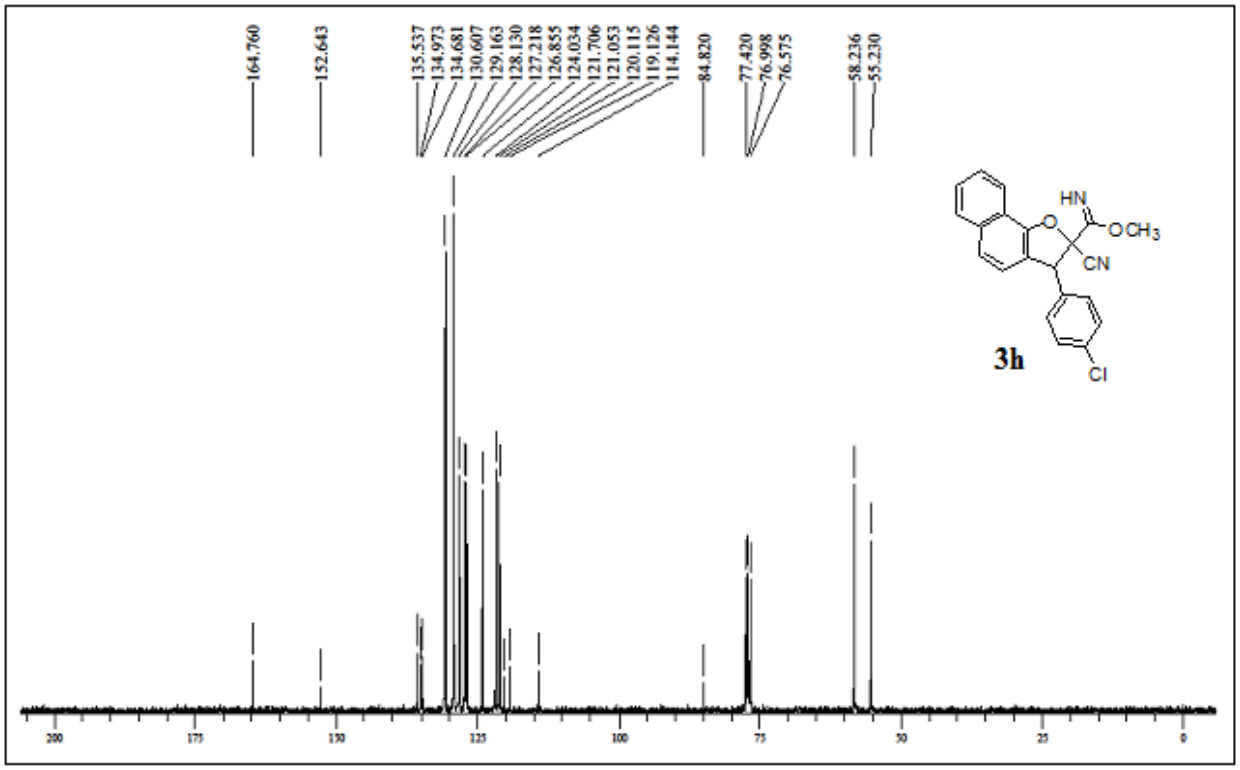
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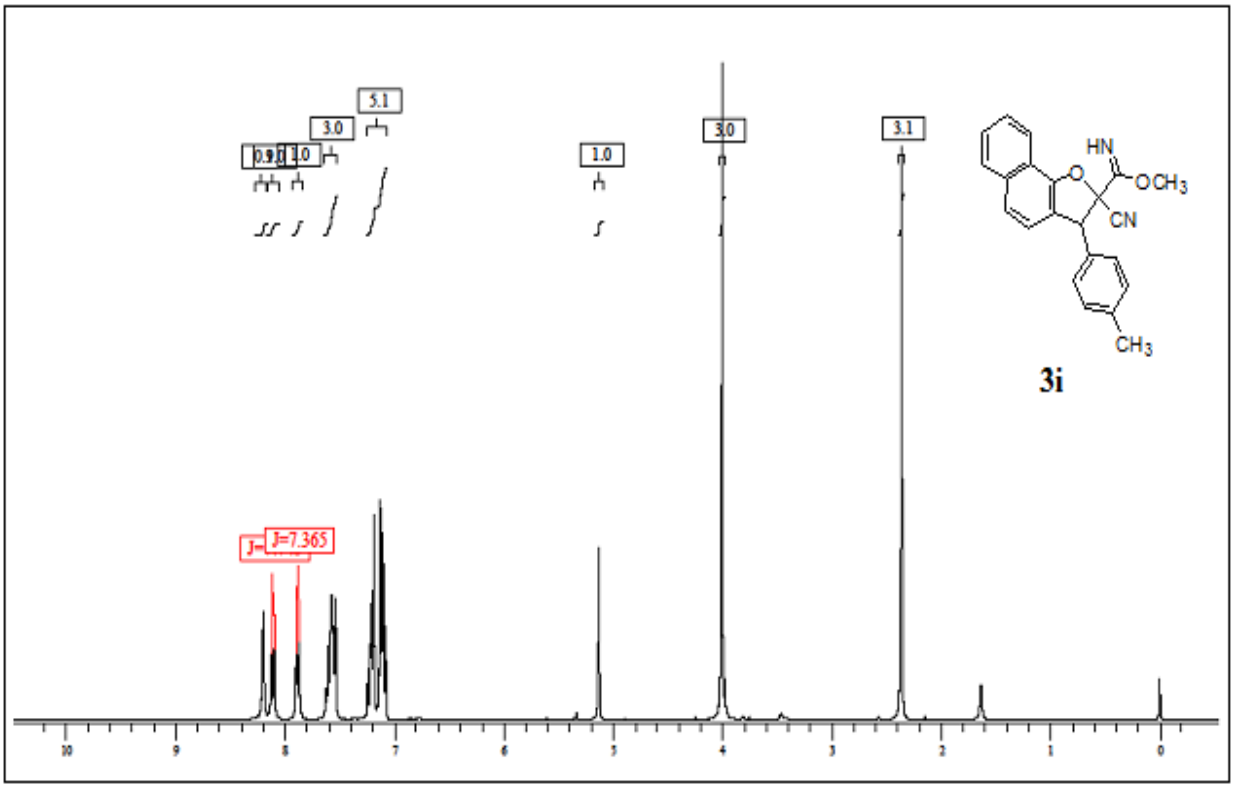
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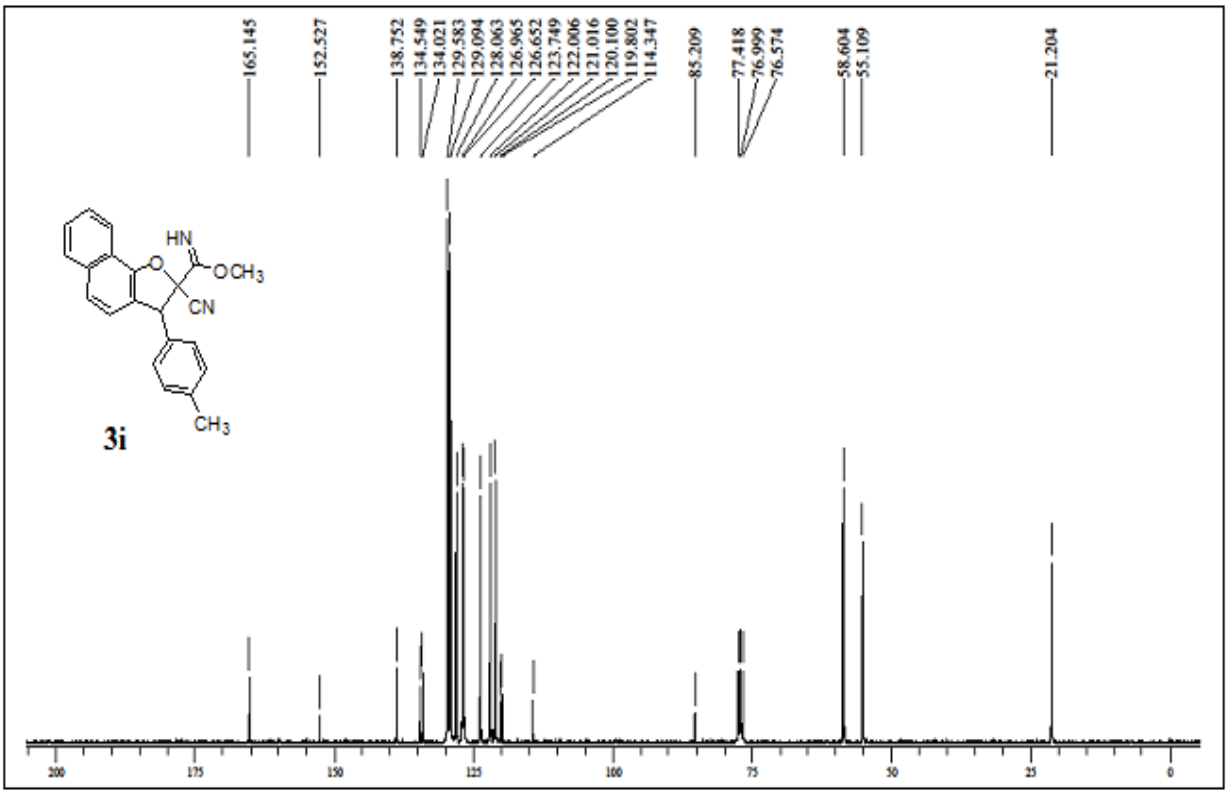
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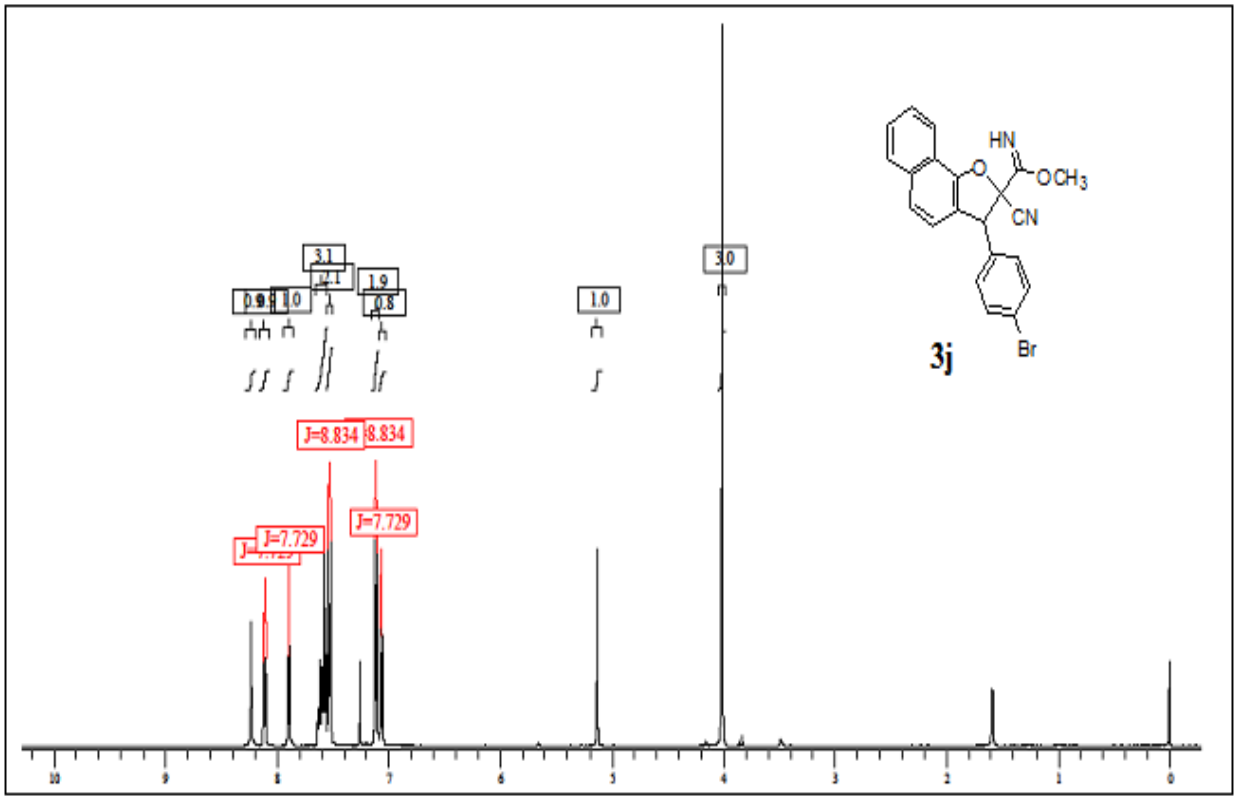
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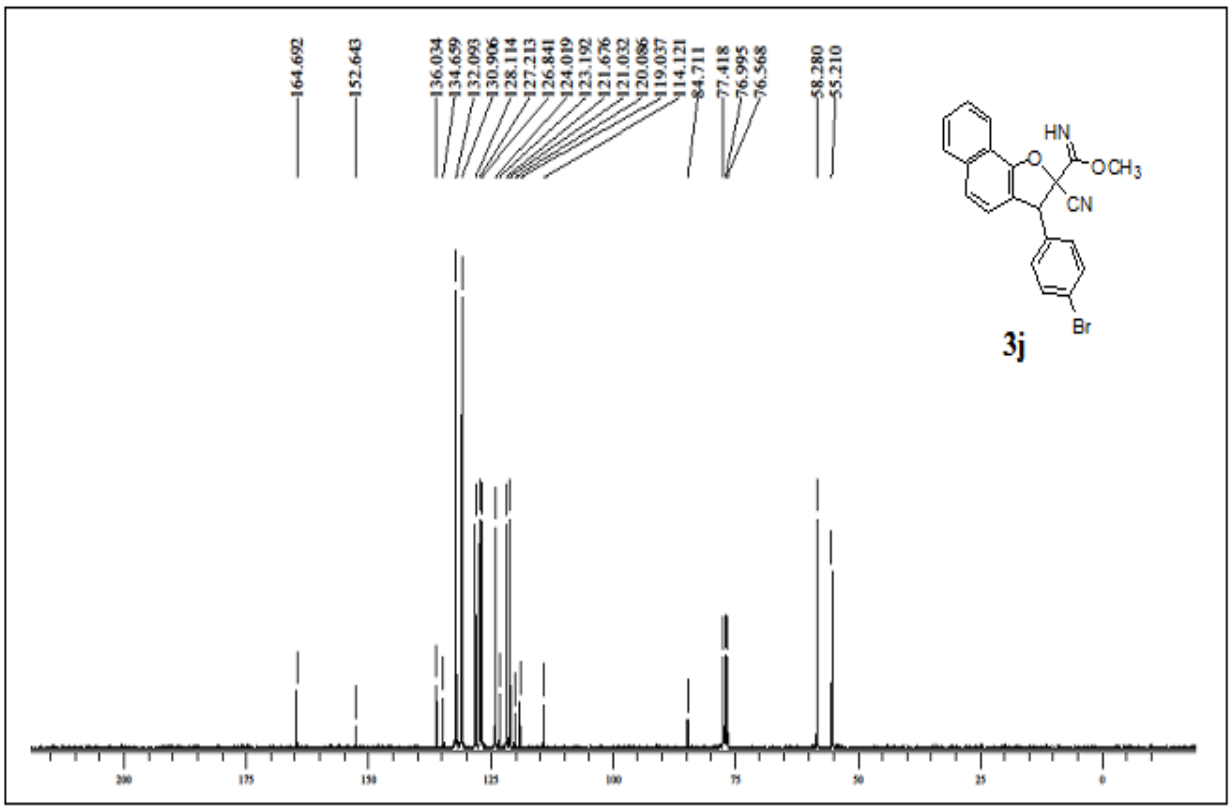
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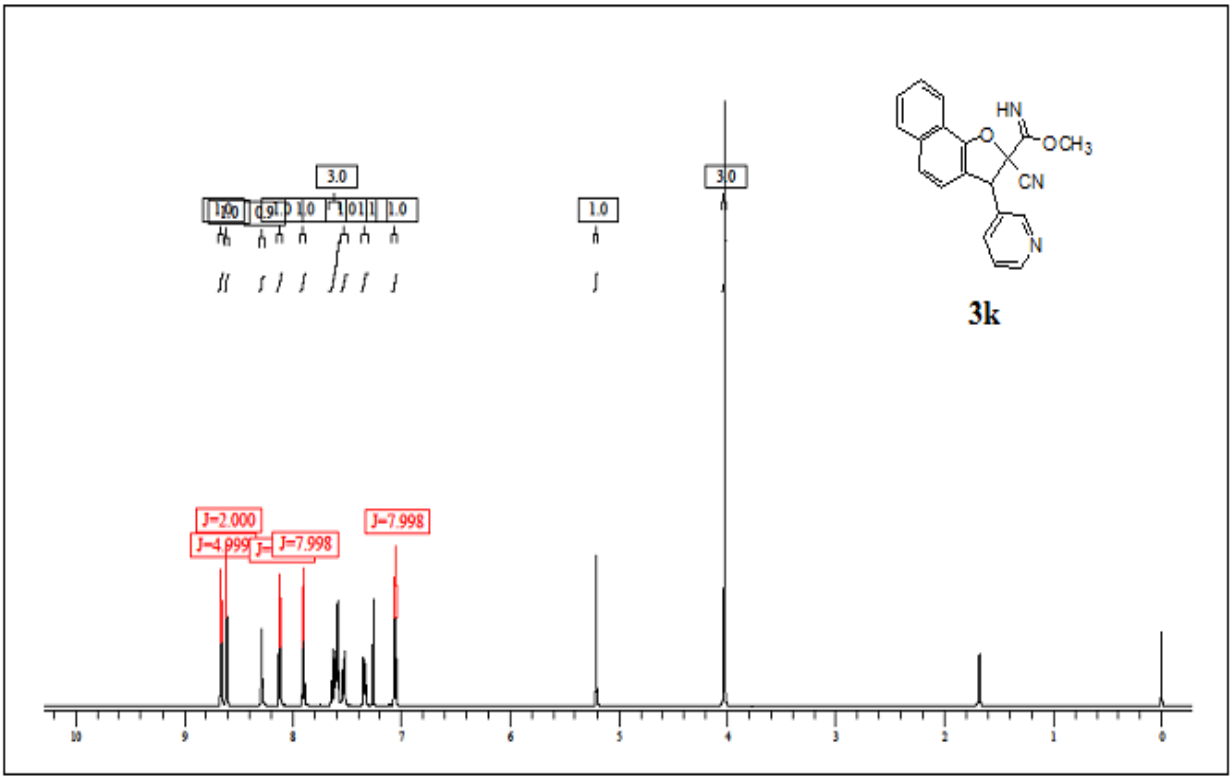
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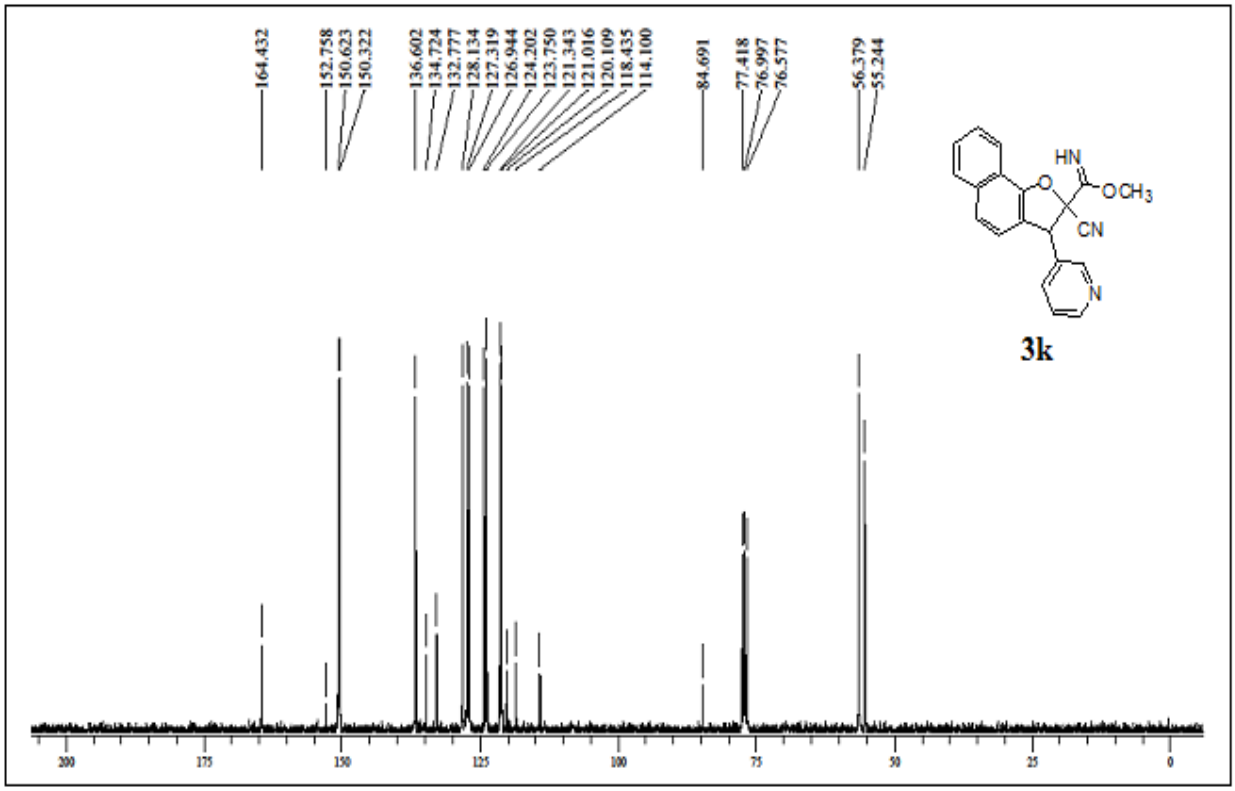
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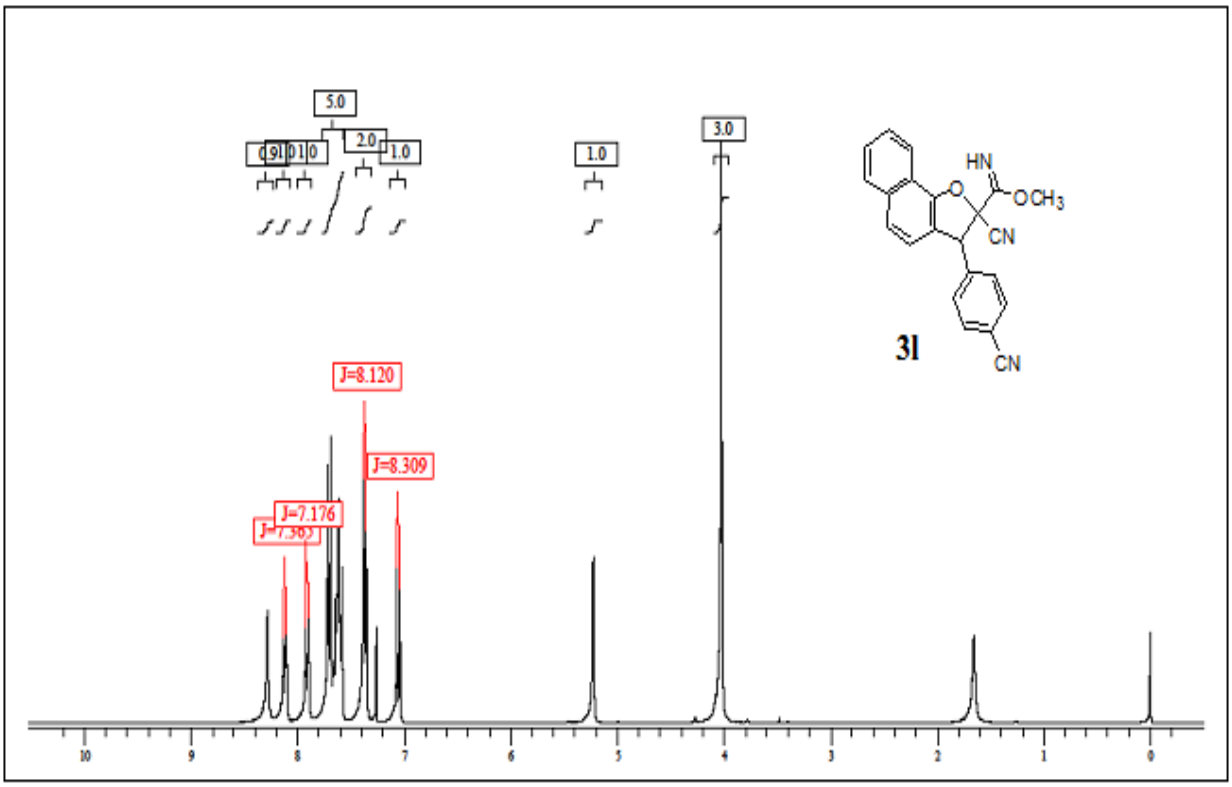
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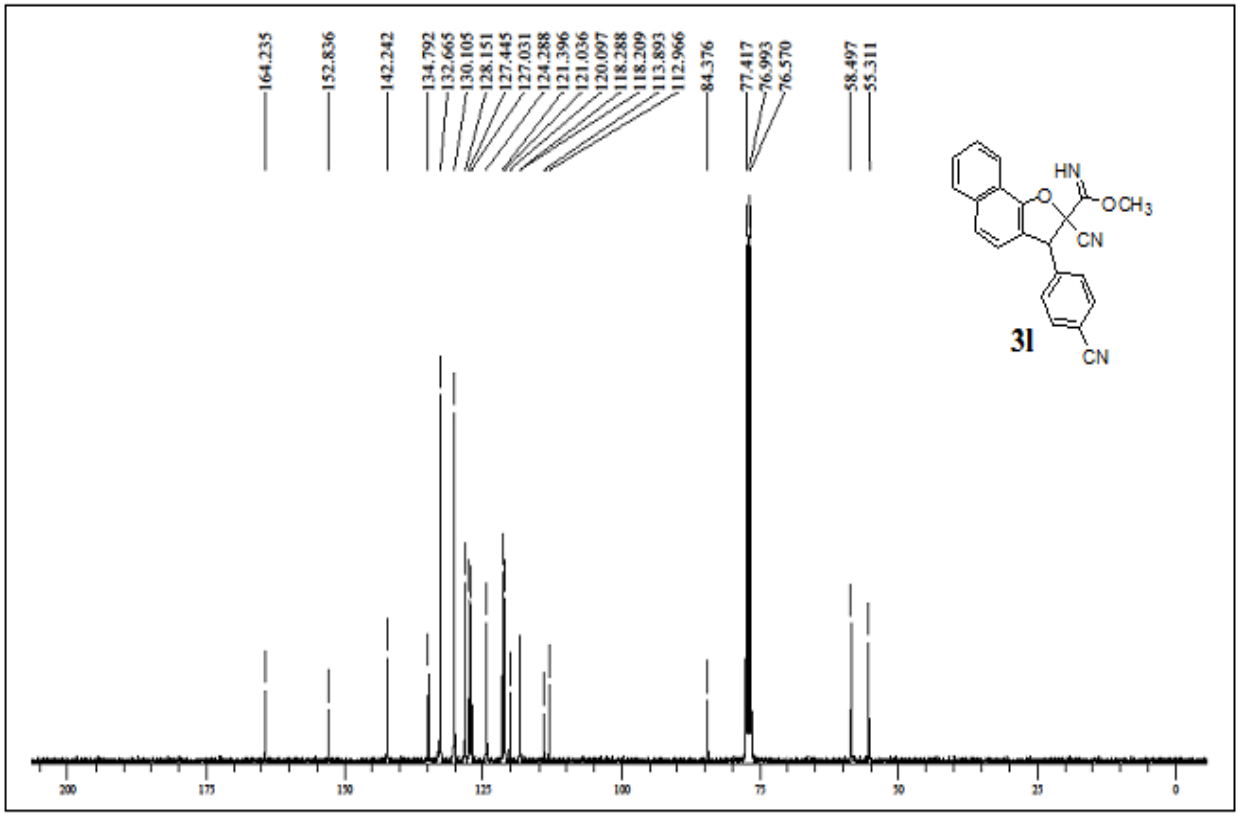
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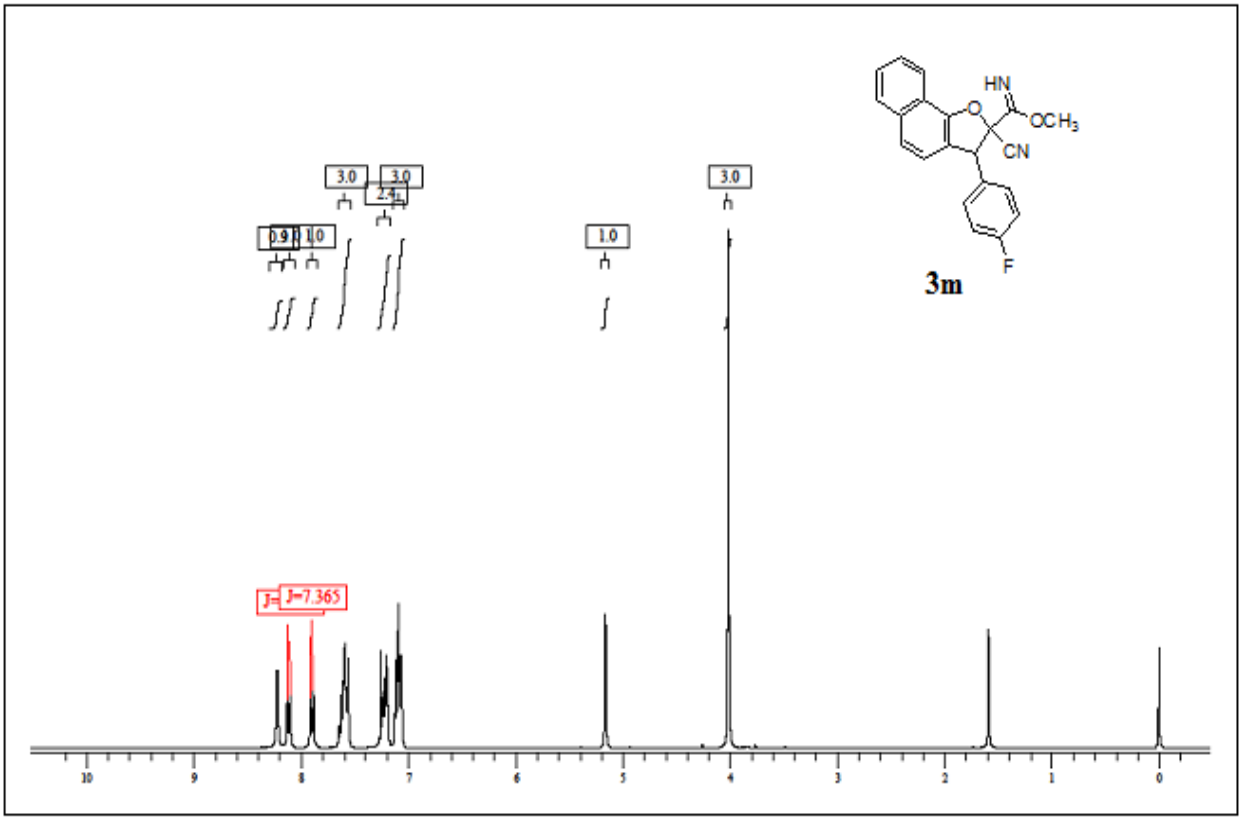
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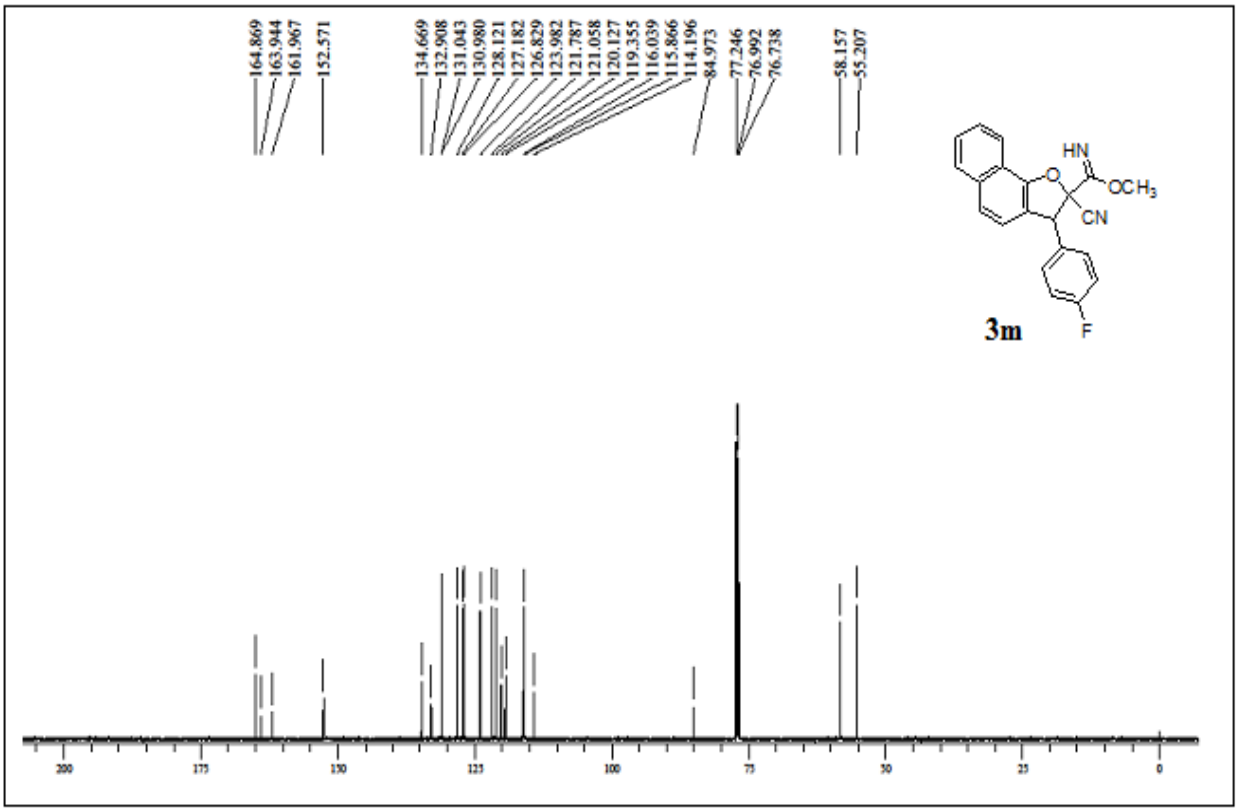
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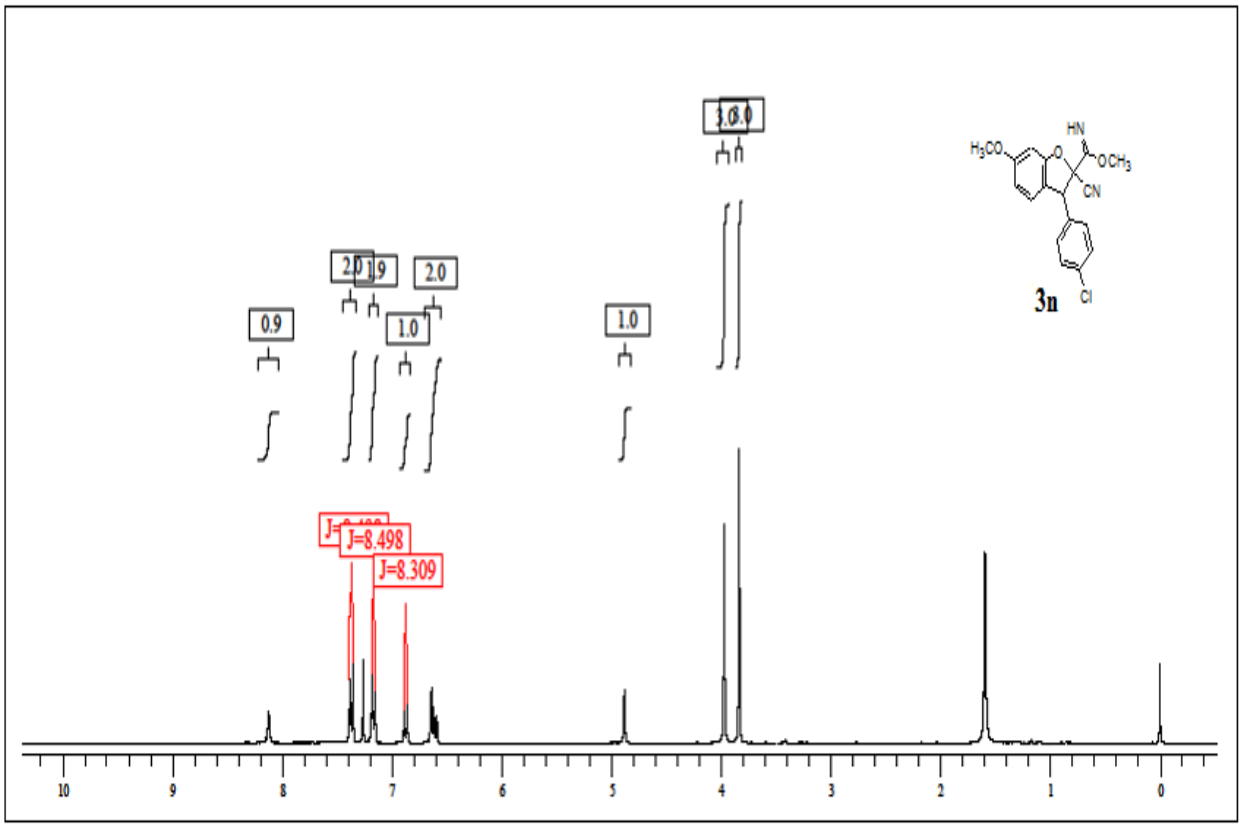
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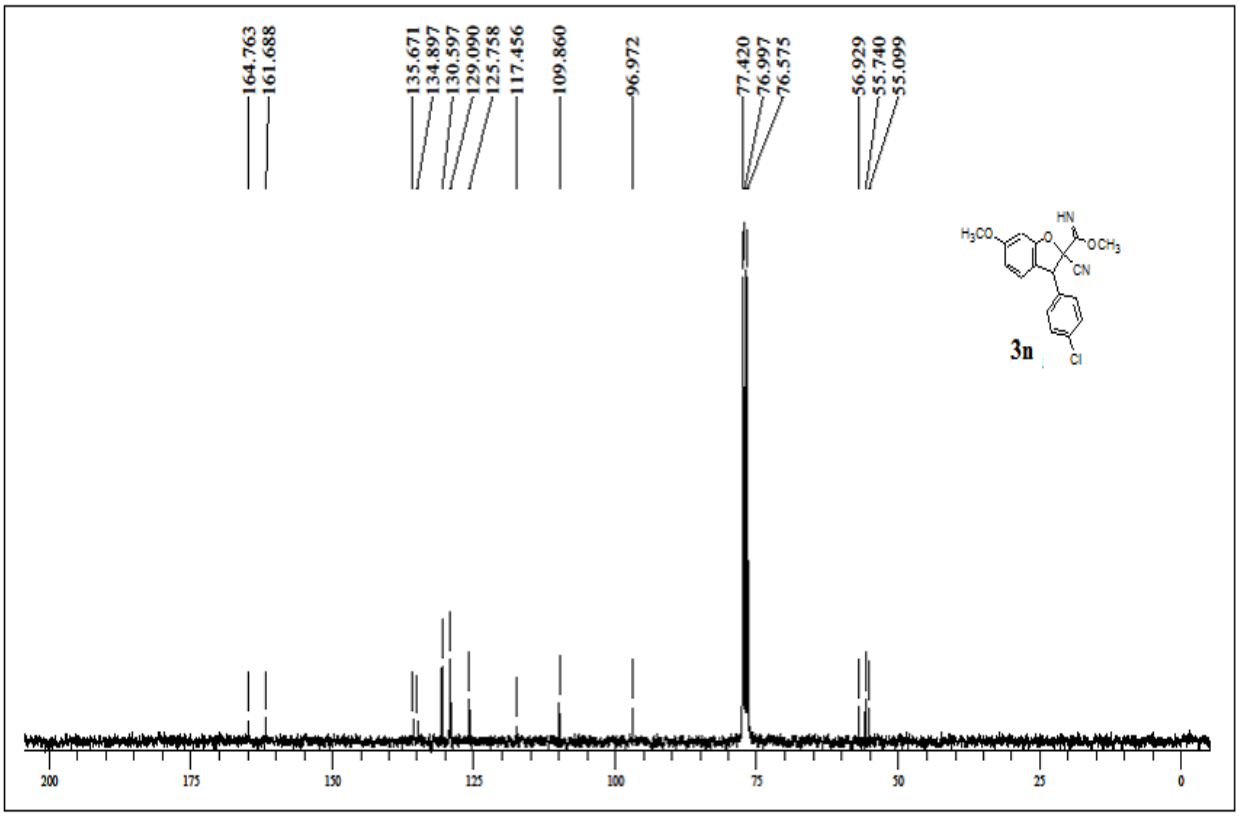
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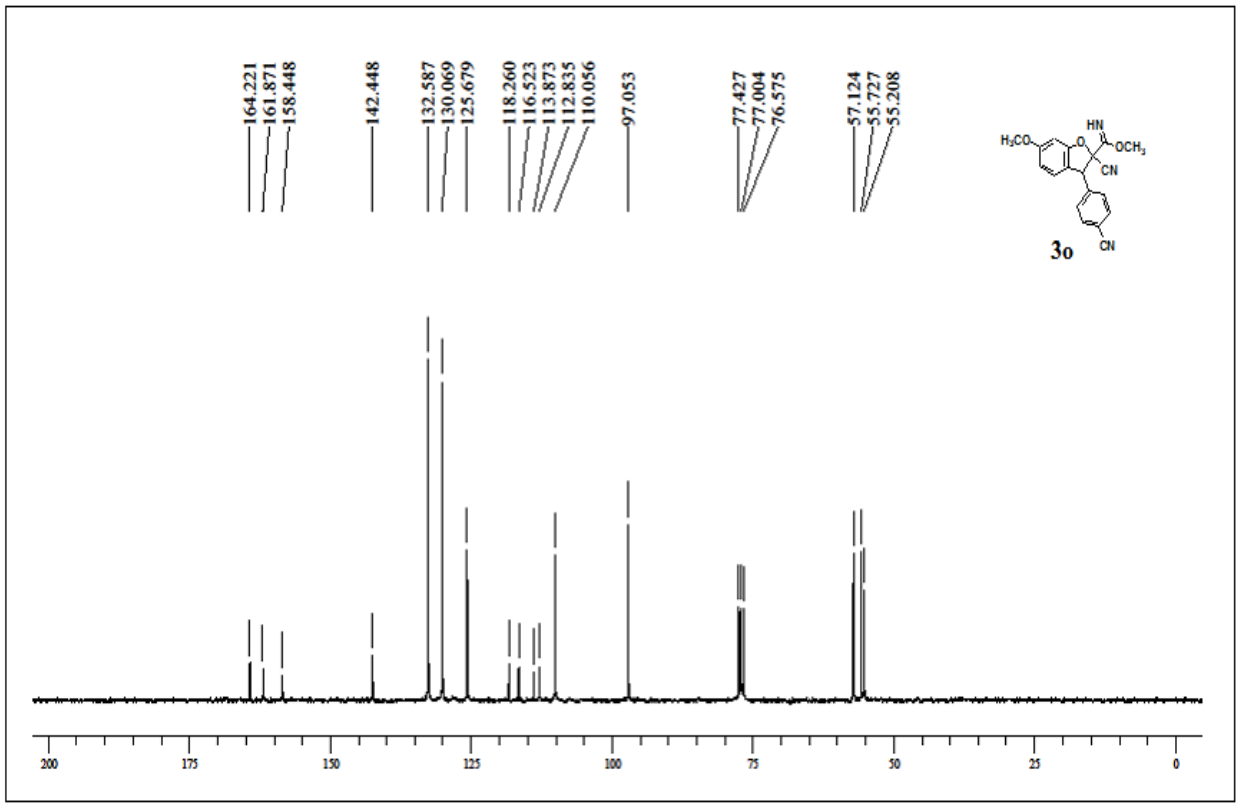
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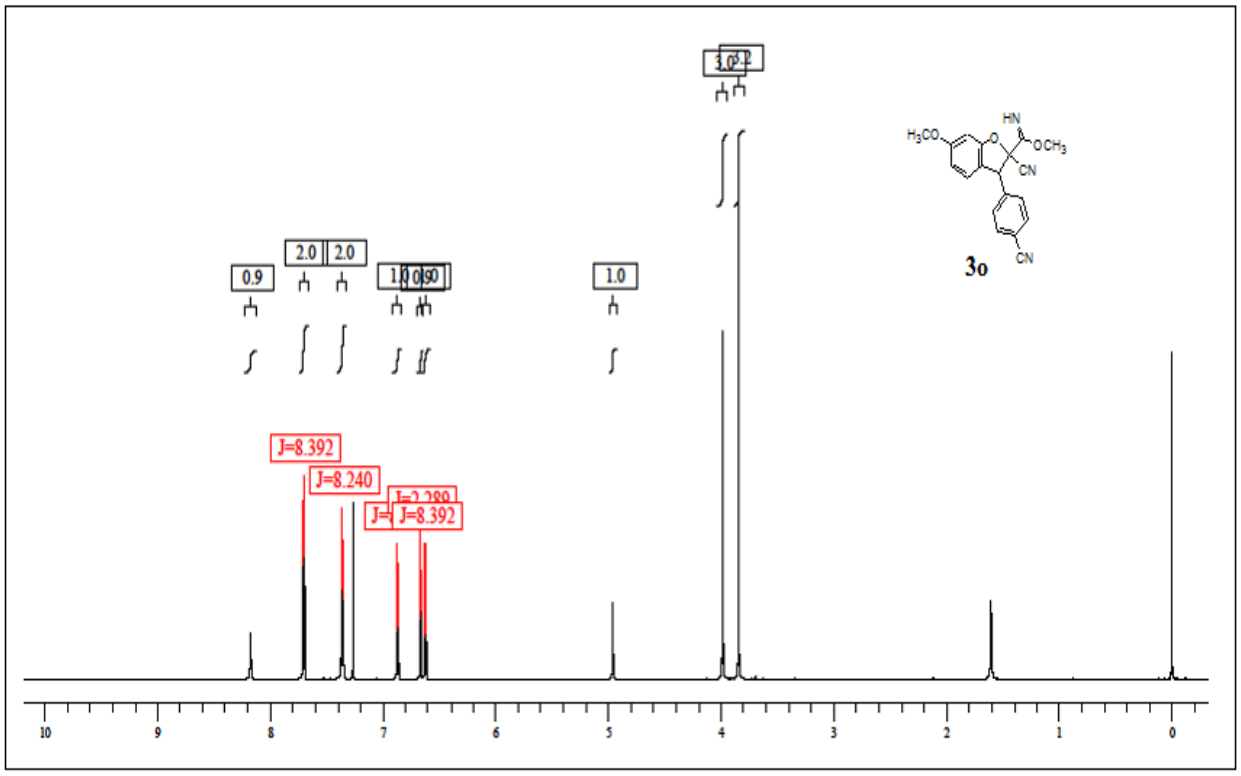
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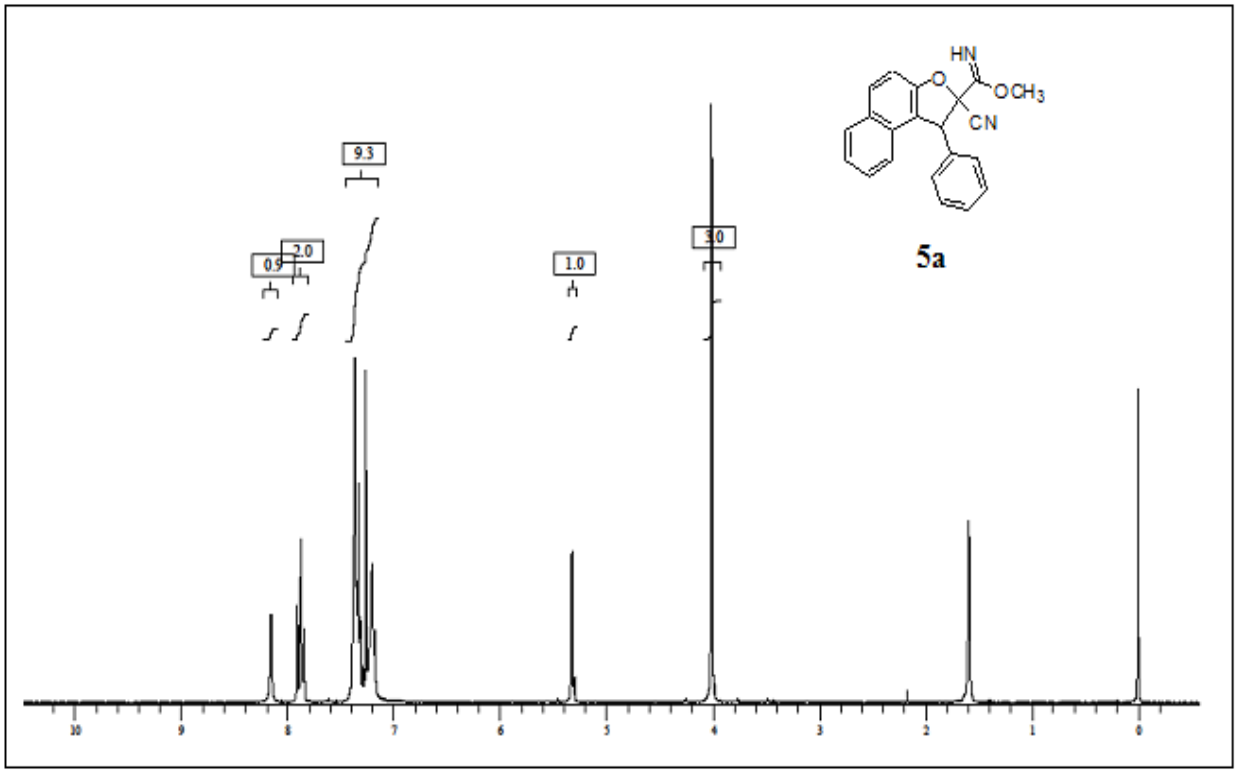
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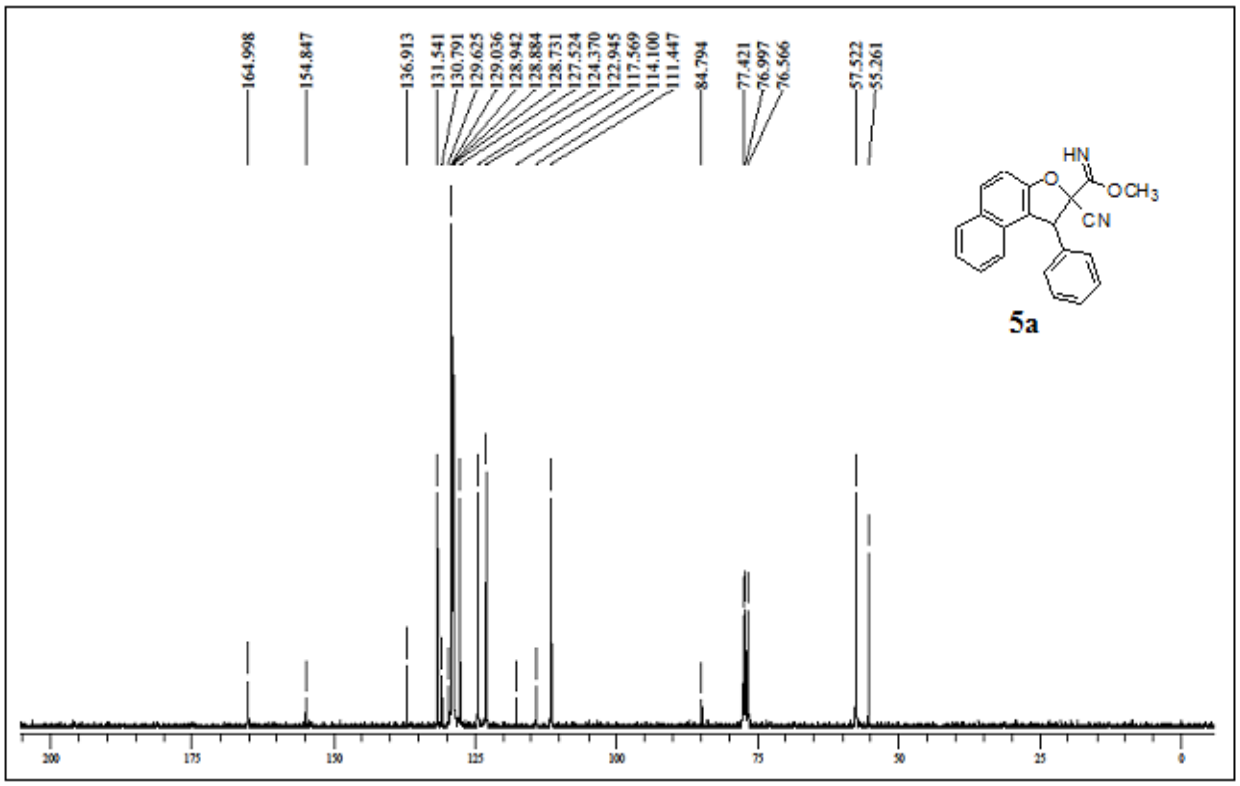
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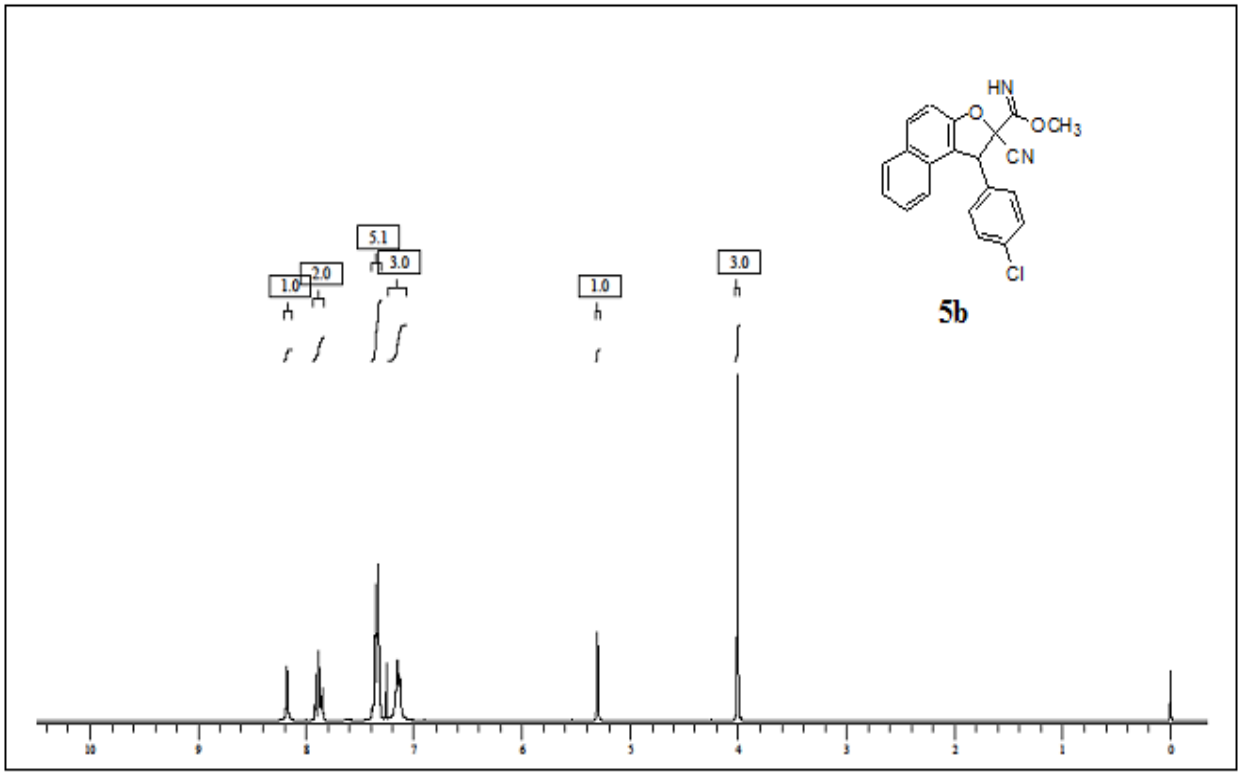
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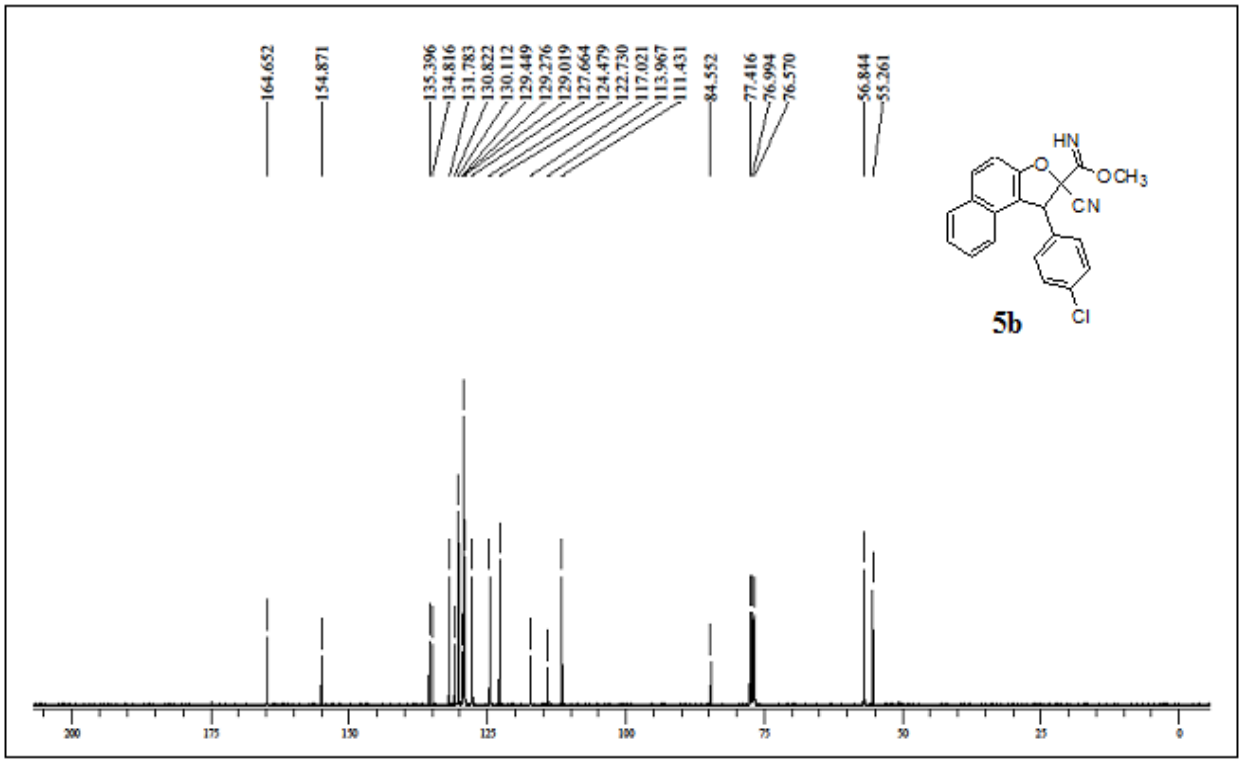
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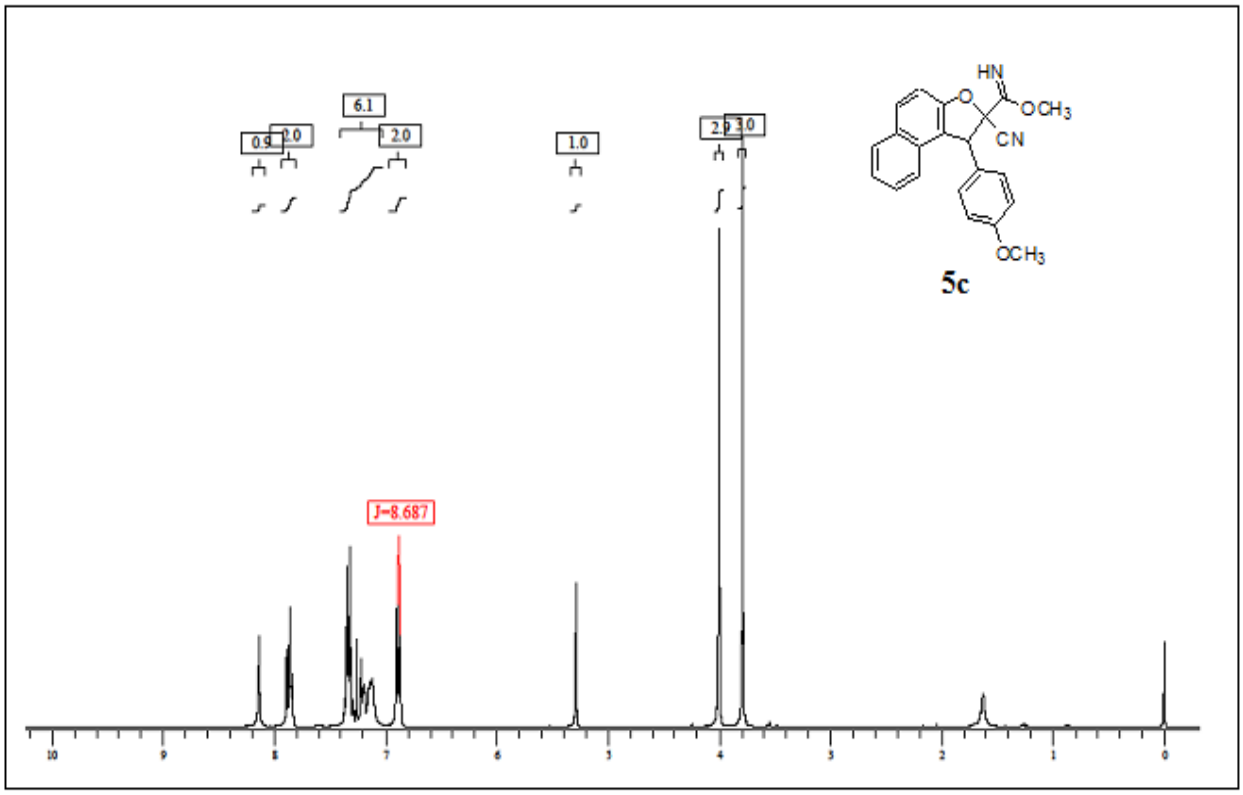
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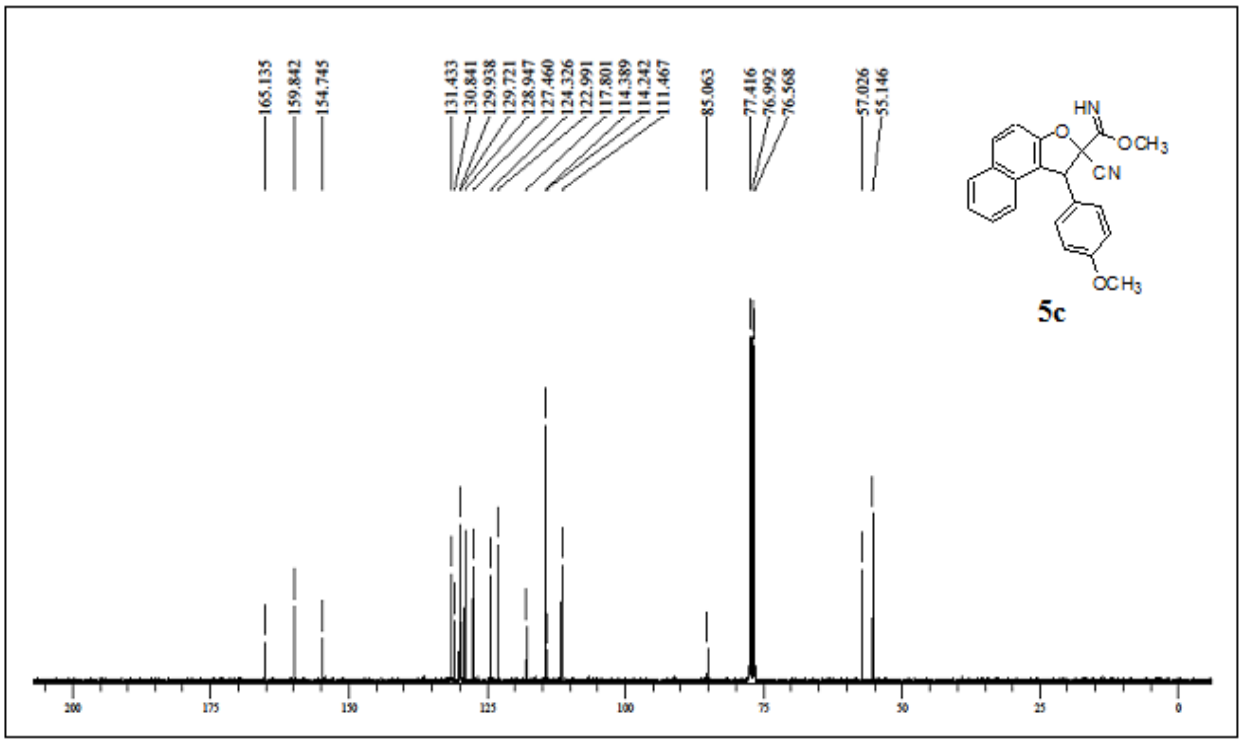
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129.721
128.947
127.460
124.326
122.991
117.801
114.389
114.242
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77.416
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76.568
57.026
55.146
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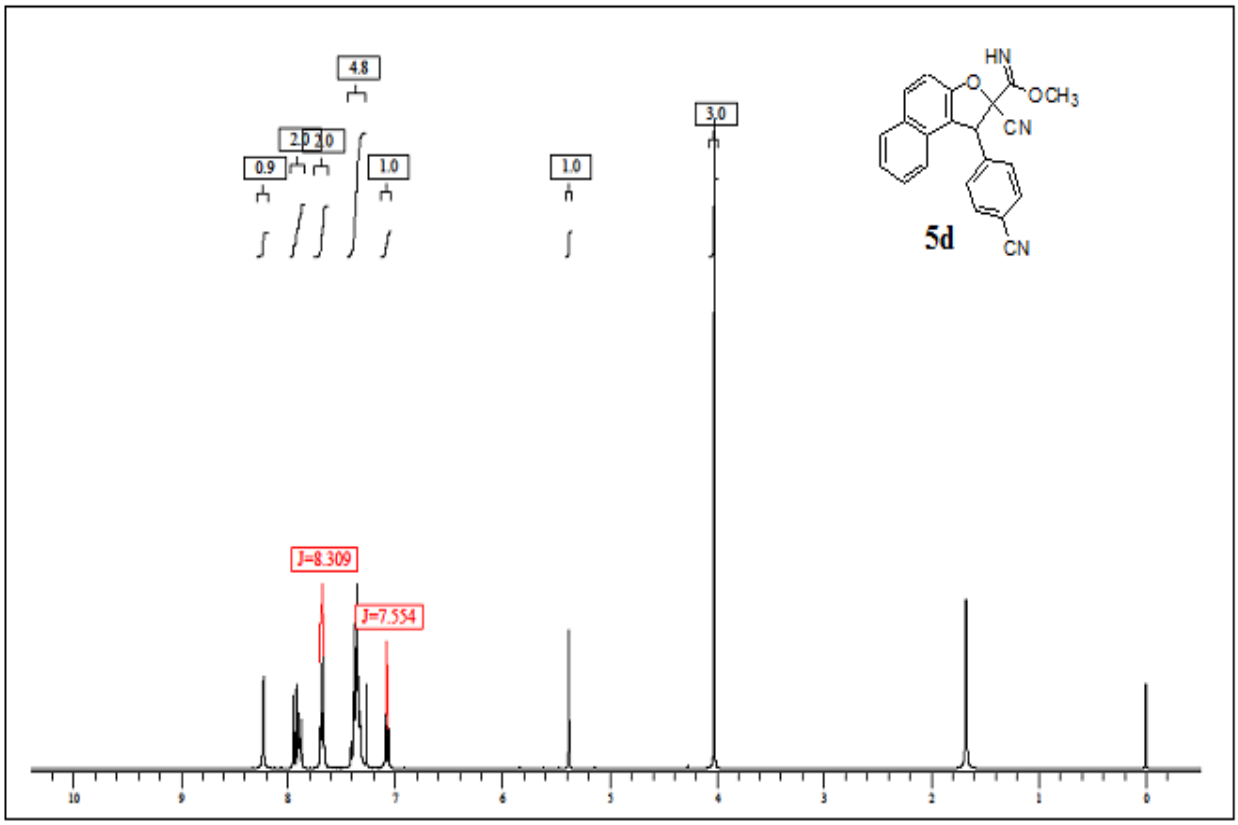
OCH3
CN
OCH3
5c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HN
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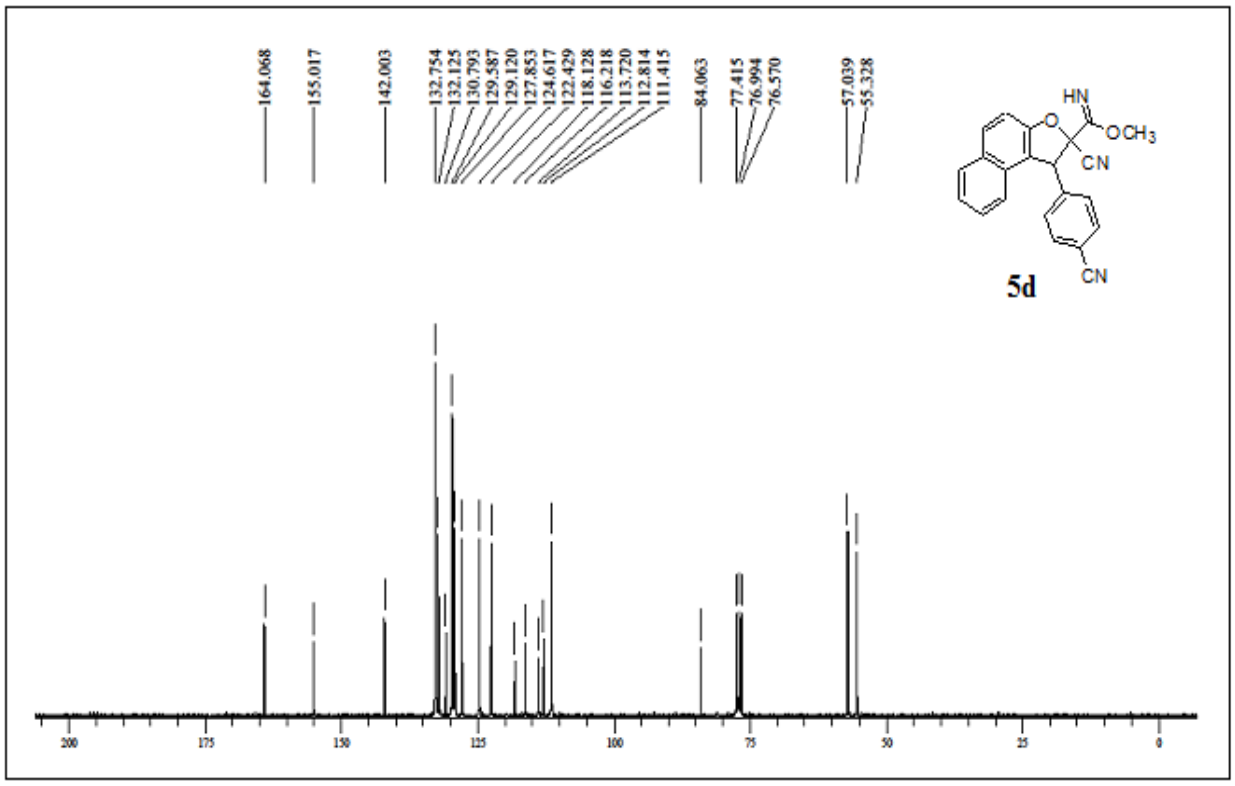
CN
CN
5d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129.120
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116.218
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55.328
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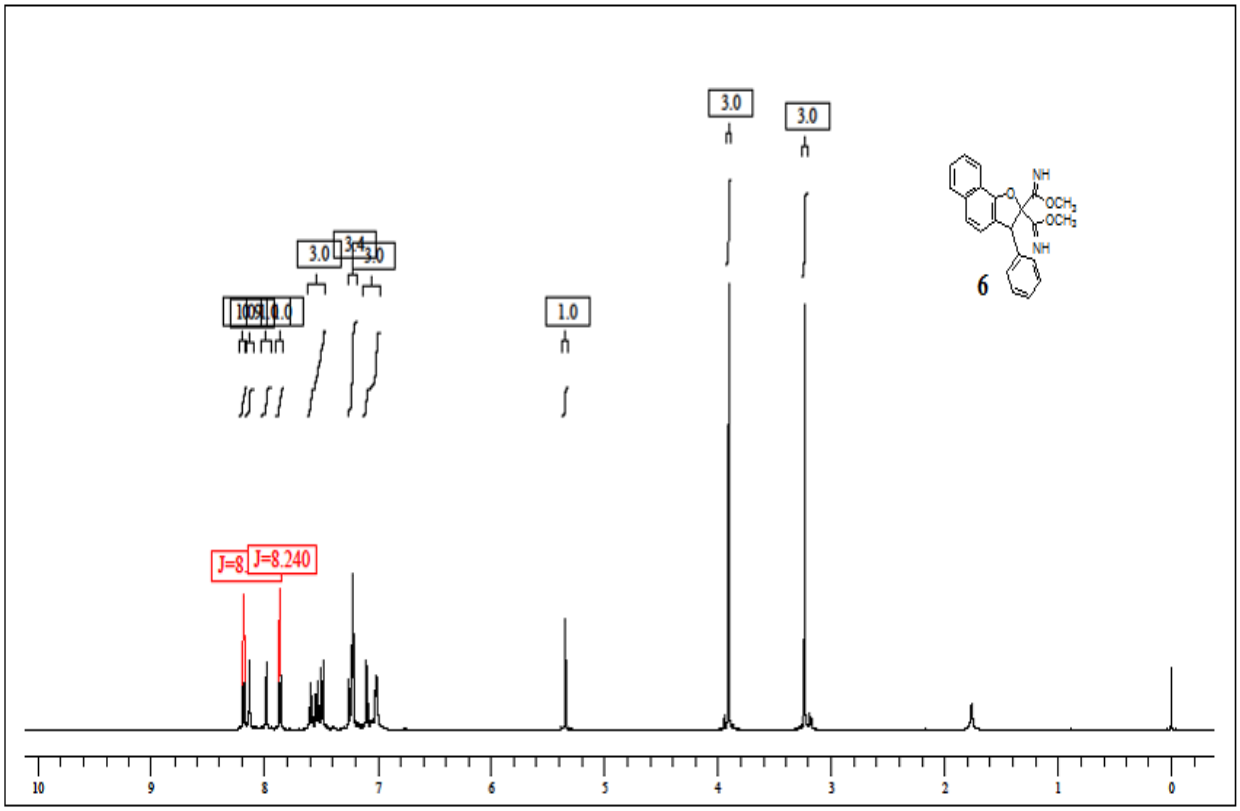
OCH3
CN
CN
5d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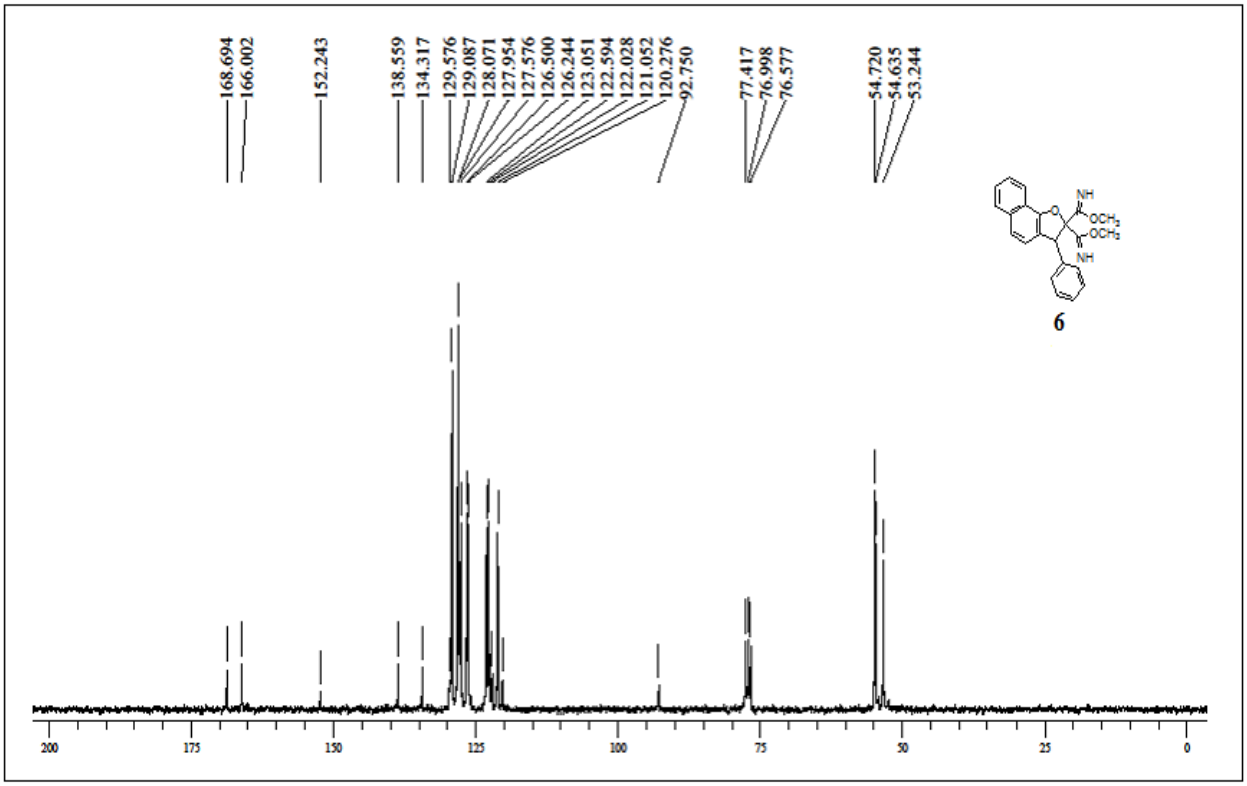
OCH3
NH
6
10
9
8
7
6
5
4
3
2
1
0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129.087
128.071
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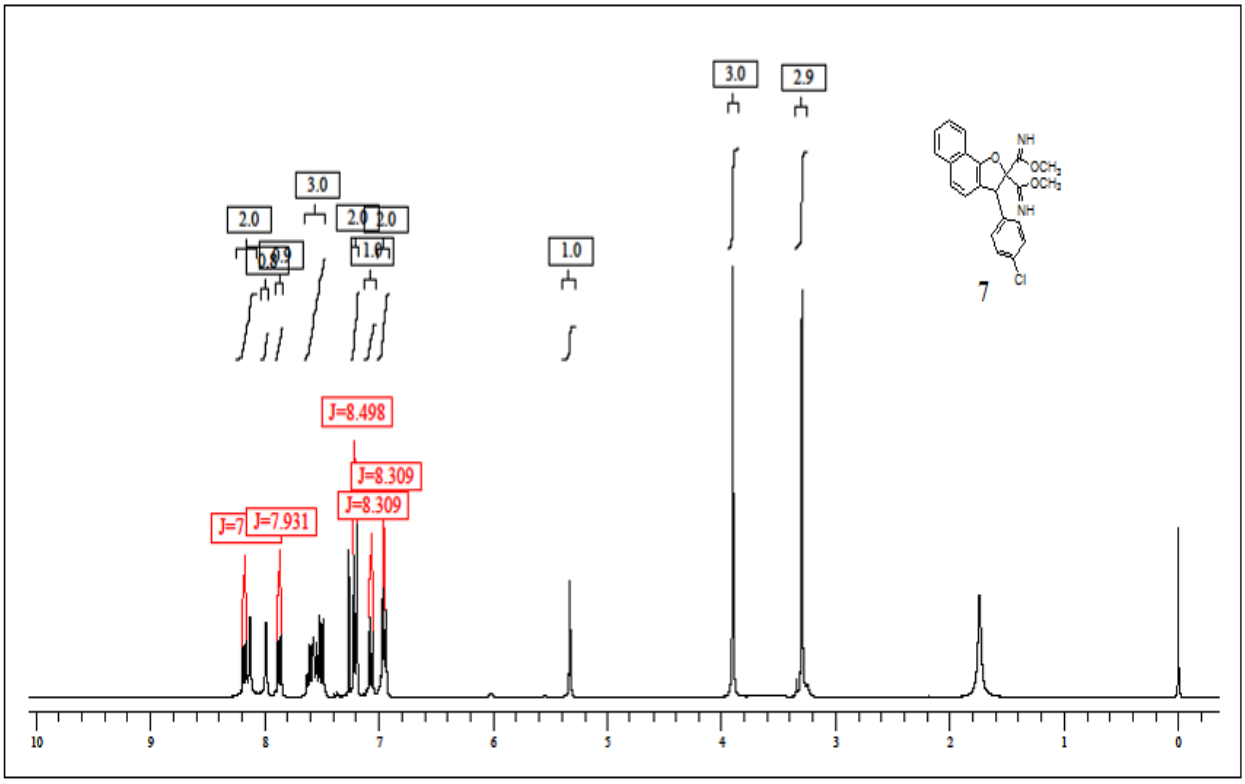
126.500
126.244
123.051
122.594
122.028
121.052
120.276
92.750
77.417
76.998
76.577
54.720
54.635
53.244
NH
OCH3
OCH3
NH
6
200
175
150
125
100
75
50
25
0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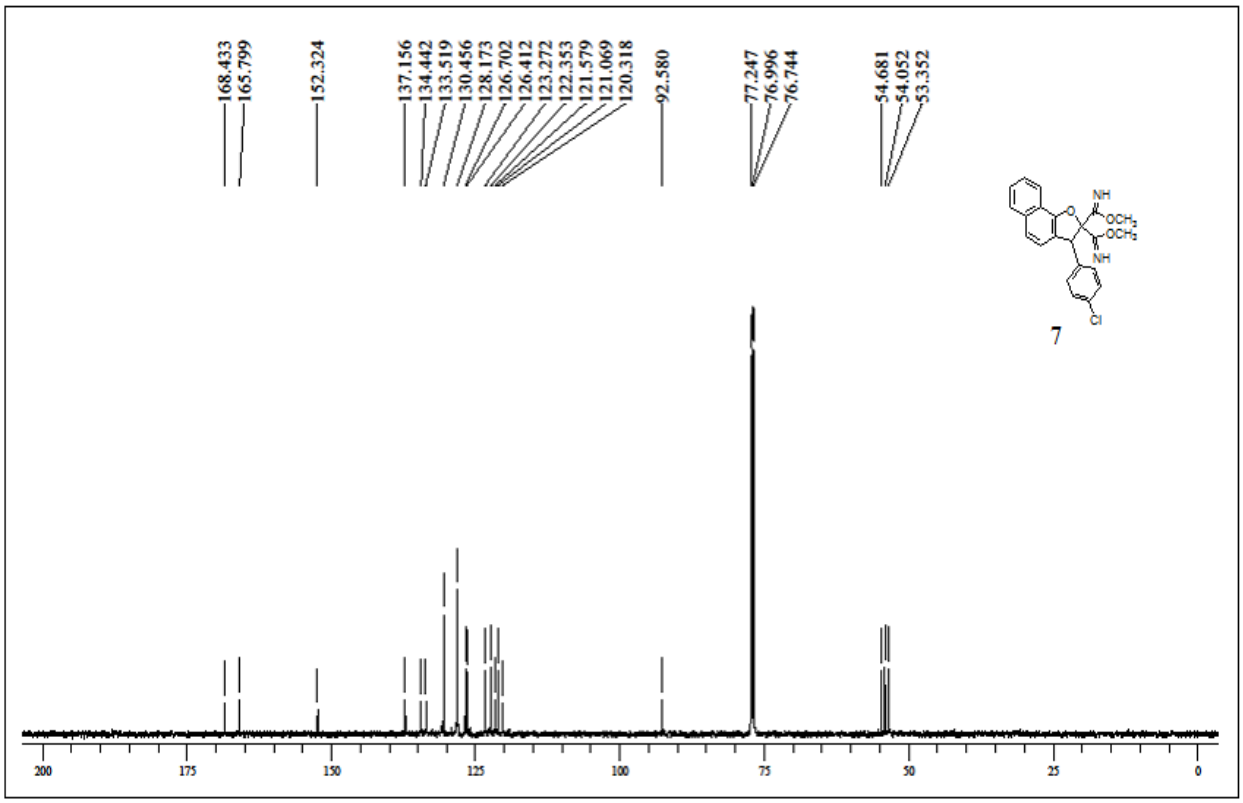
J=8.309
J=7.931
7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134.442
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130.456
128.173
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126.412
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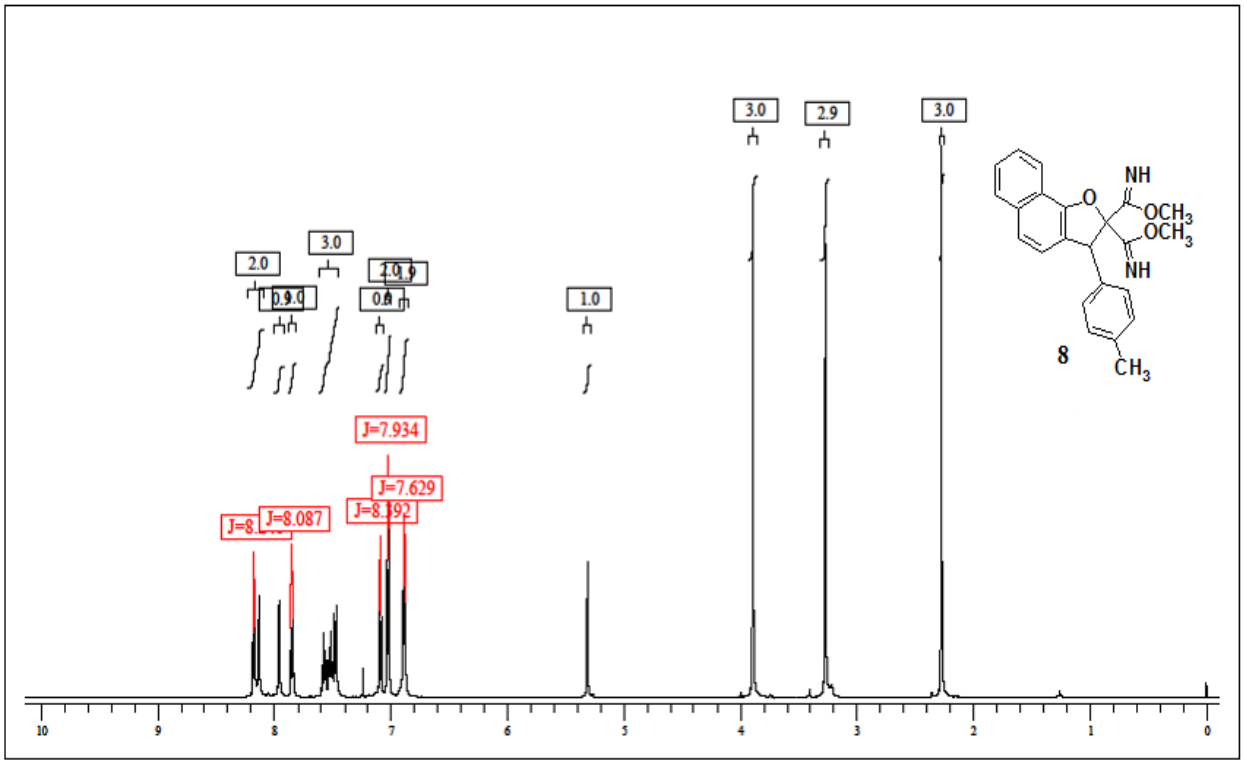
122.353
121.579
121.069
120.318
92.580
77.247
76.996
76.744
54.681
54.052
53.352
7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3.0
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J=8.087
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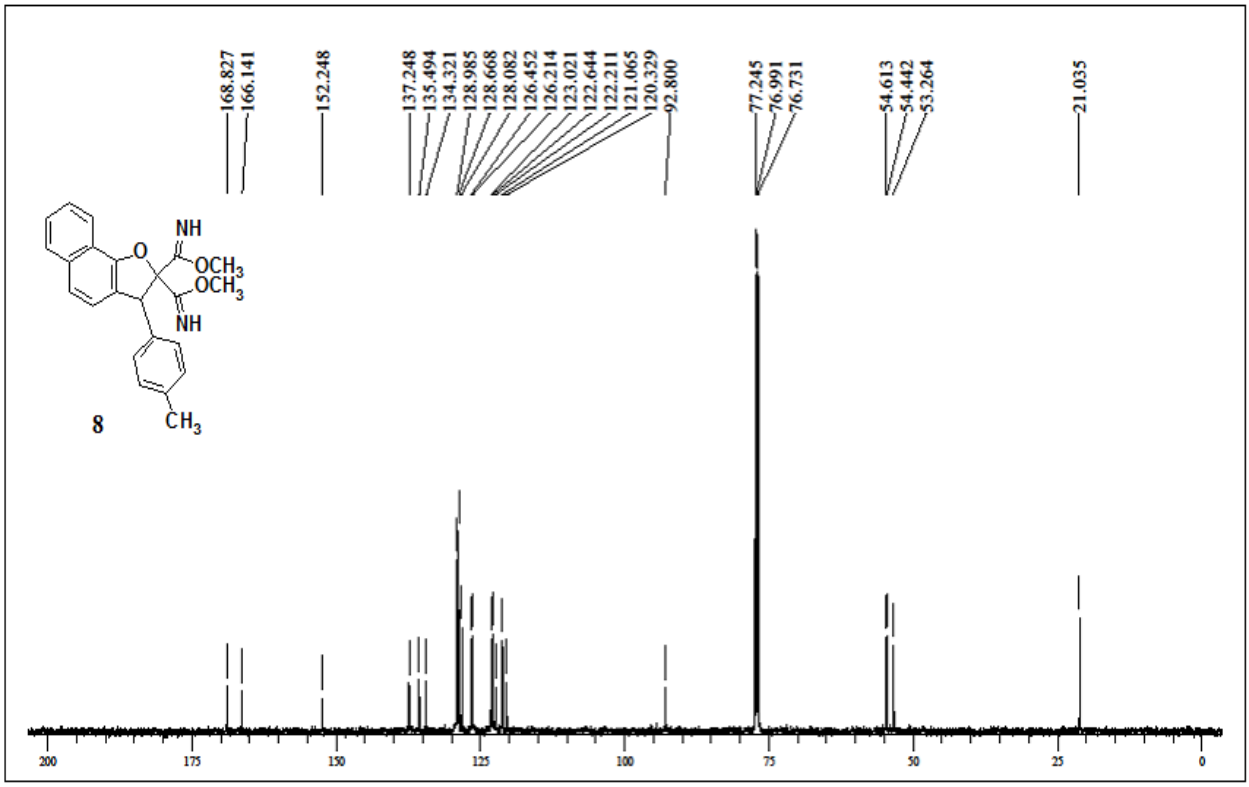
OCH3
NH
O
8
CH3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137.248
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134.321
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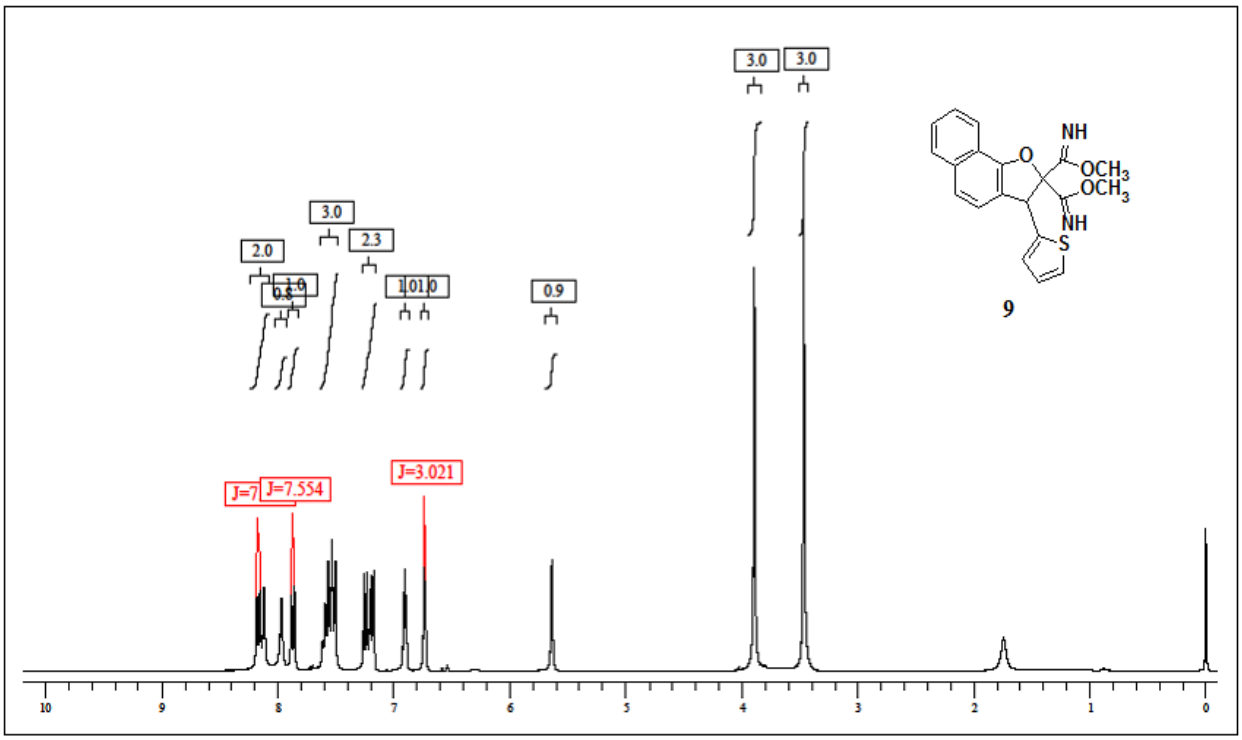
128.668
128.082
126.452
126.214
123.021
122.644
122.211
121.065
120.329
92.800
77.245
76.991
76.731
54.613
54.442
53.264
21.035
NH
OCH3
OCH3
NH
O
8
CH3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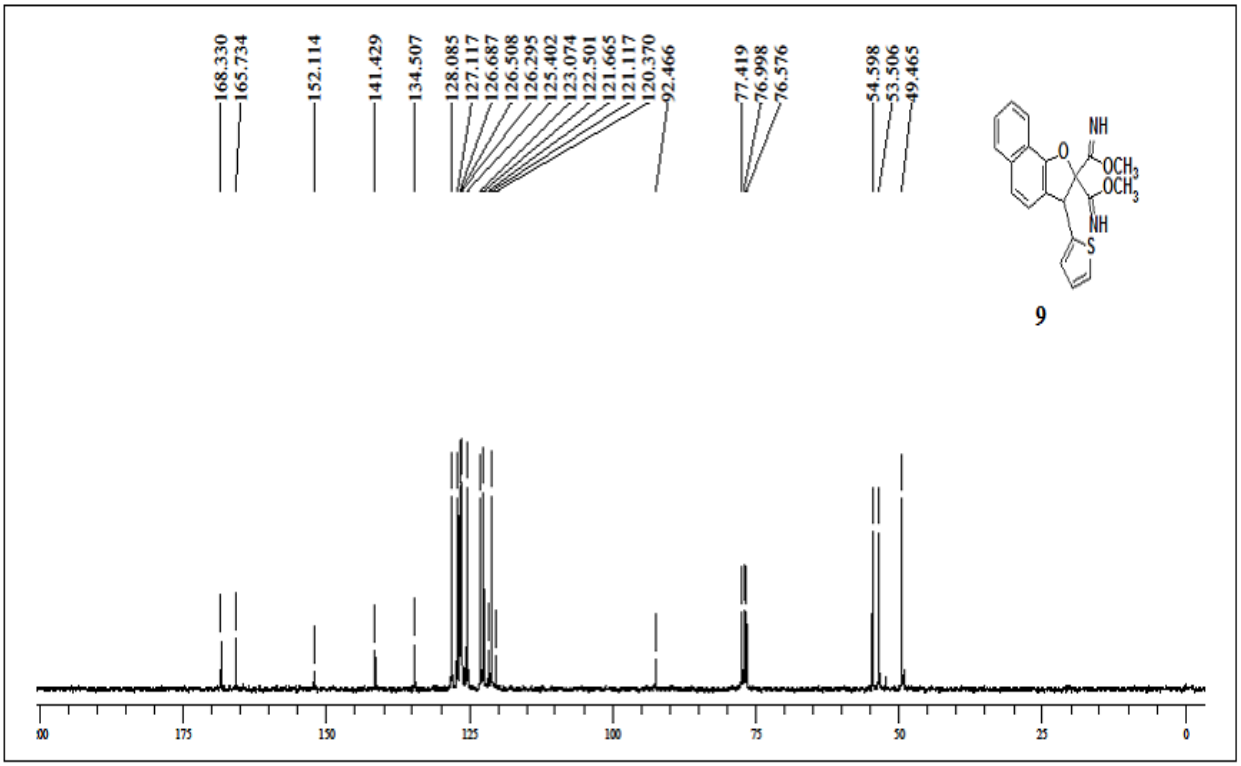
2.0
3.0
2.3
1.01.0
0.9
J=7
J=7.554
J=3.021
NH
O
OCH3
OCH3
NH
S
9
10
9
8
7
6
5
4
3
2
1
0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126.687
126.508
126.295
125.402
123.074
122.501
121.665
121.117
120.370
92.466
77.419
76.998
76.576
54.598
53.506
49.465
NH
O
OCH3
OCH3
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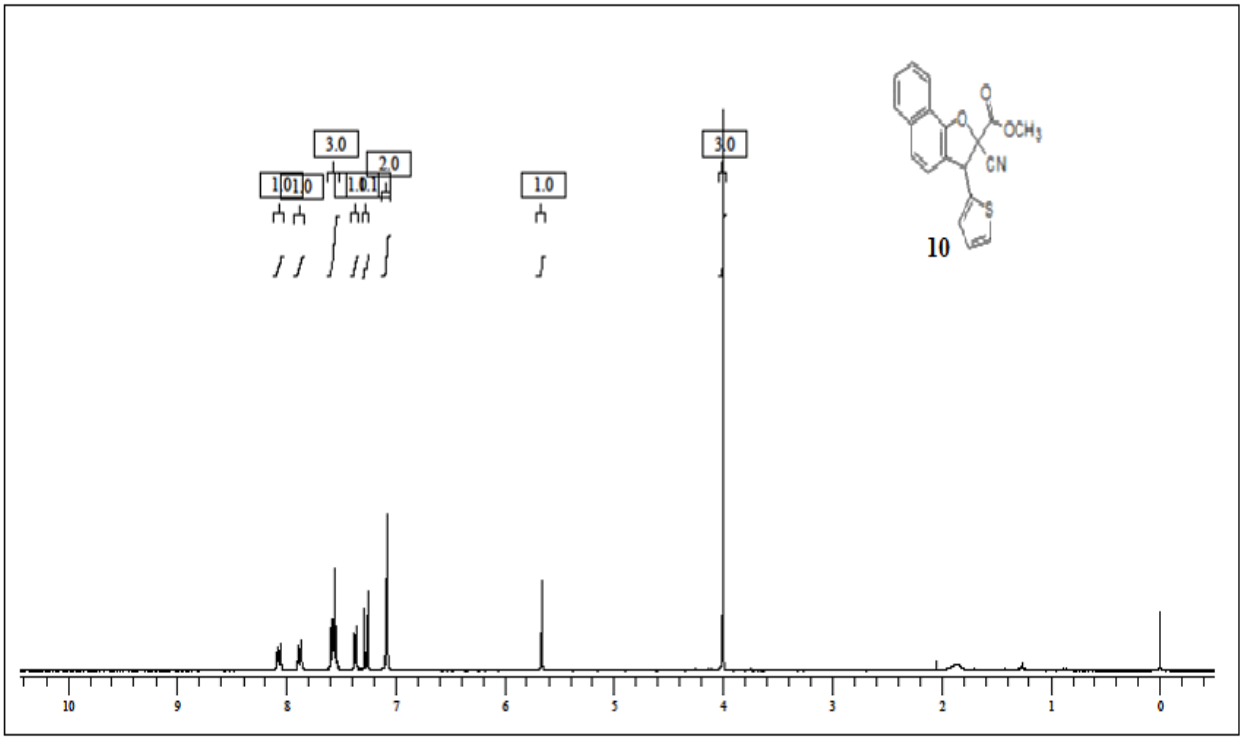
S
9
175
150
125
100
75
50
25
0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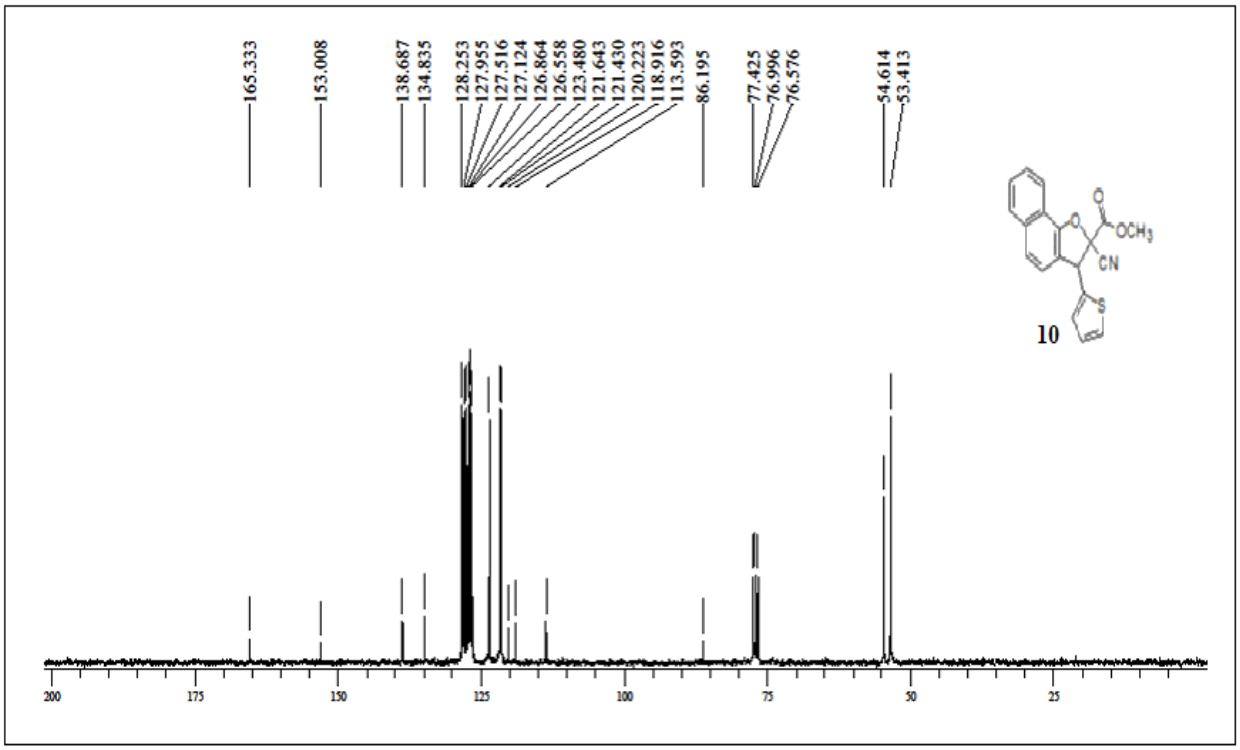
1.0
1.0
3.0
10
10
9
8
7
6
5
4
3
2
1
0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121.430
120.223
118.916
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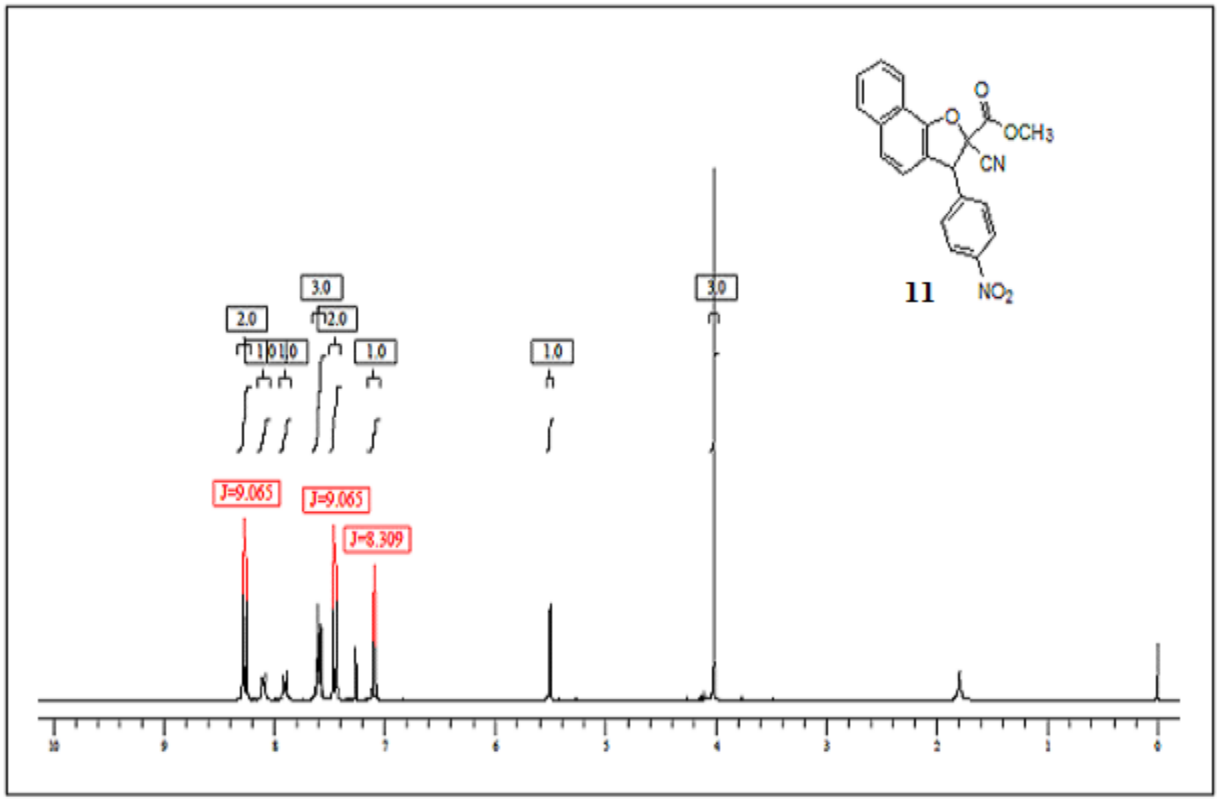
76.996
76.576
54.614
53.413
10
200
175
150
125
100
75
50
25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OCH3
CN
NO2
11
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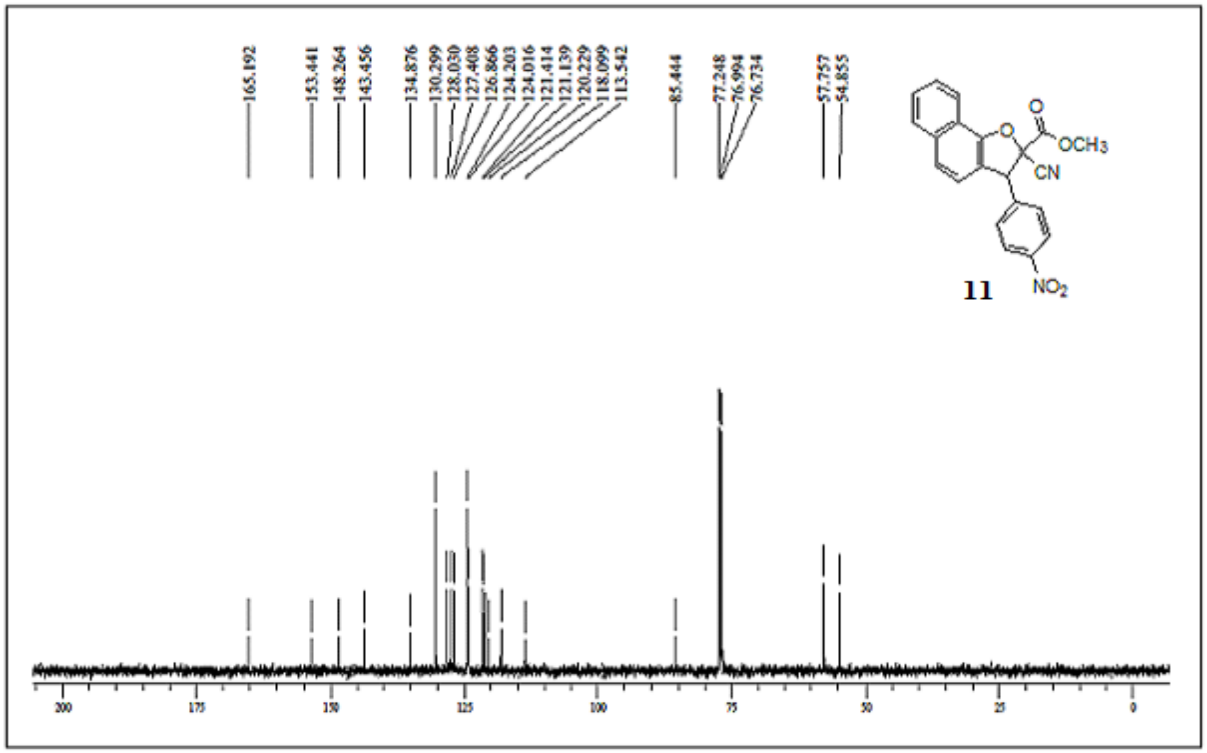
1.0
2.0
1.0
1.0
3.0
J=9.065
J=9.065
J=8.309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153.441
148.264
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134.876
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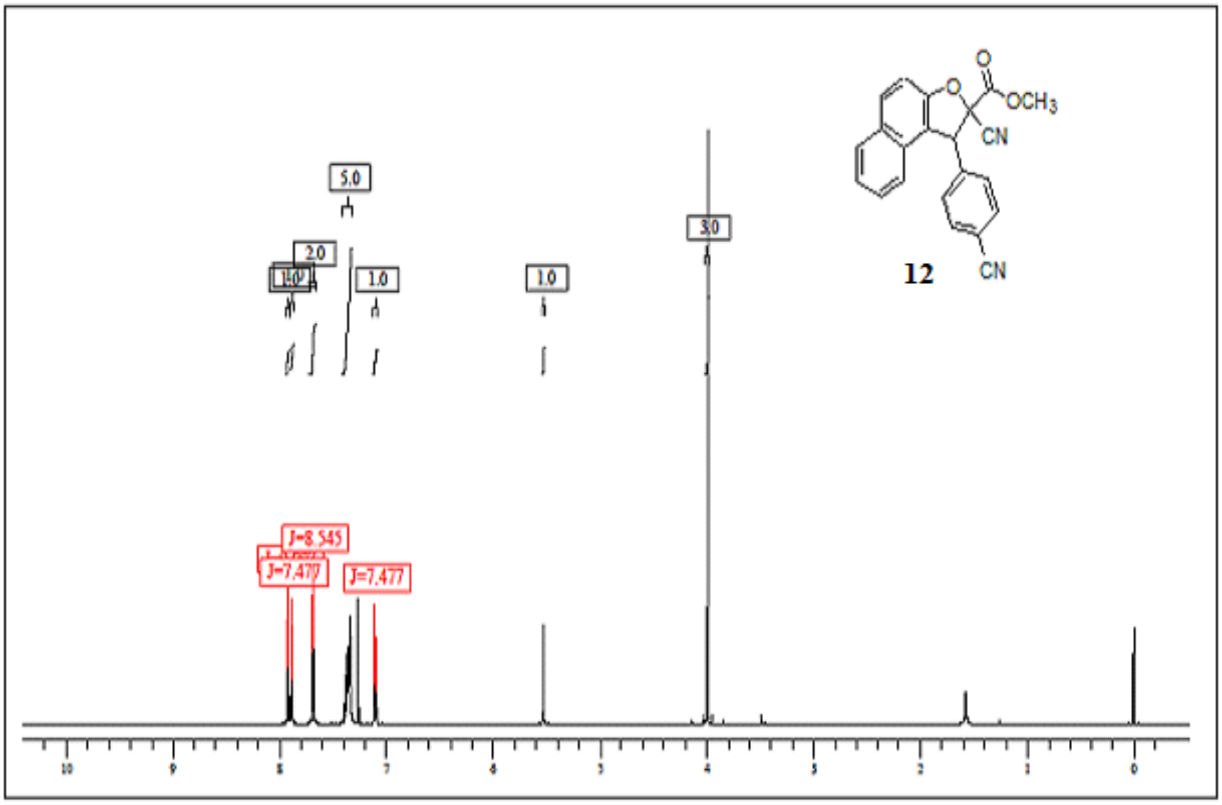
128.030
127.408
126.866
124.203
124.016
121.414
121.139
120.229
118.099
113.542
85.444
77.248
76.994
76.734
57.757
54.855
O
OCH3
CN
NO2
11


O
OCH3
CN
CN
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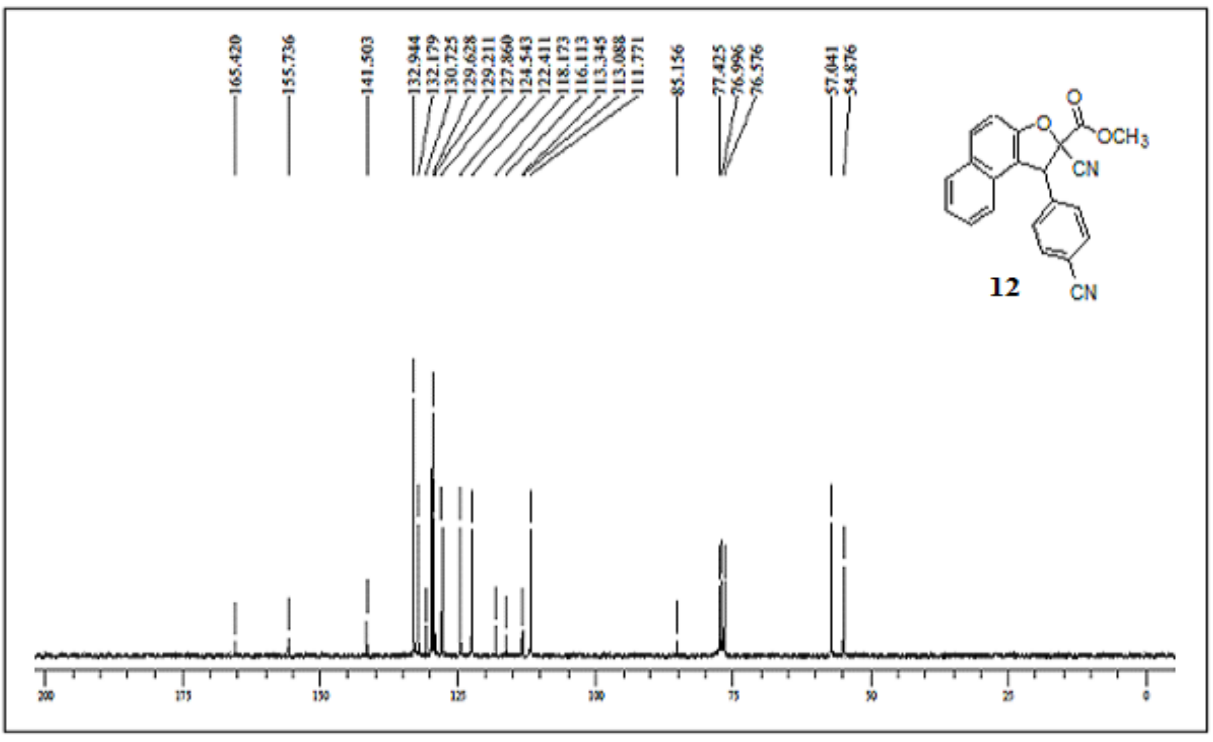
1.0
1.0
1.0
3.0
J=8.545
J=7.477
J=7.477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122.411
118.173
116.113
113.345
113.088
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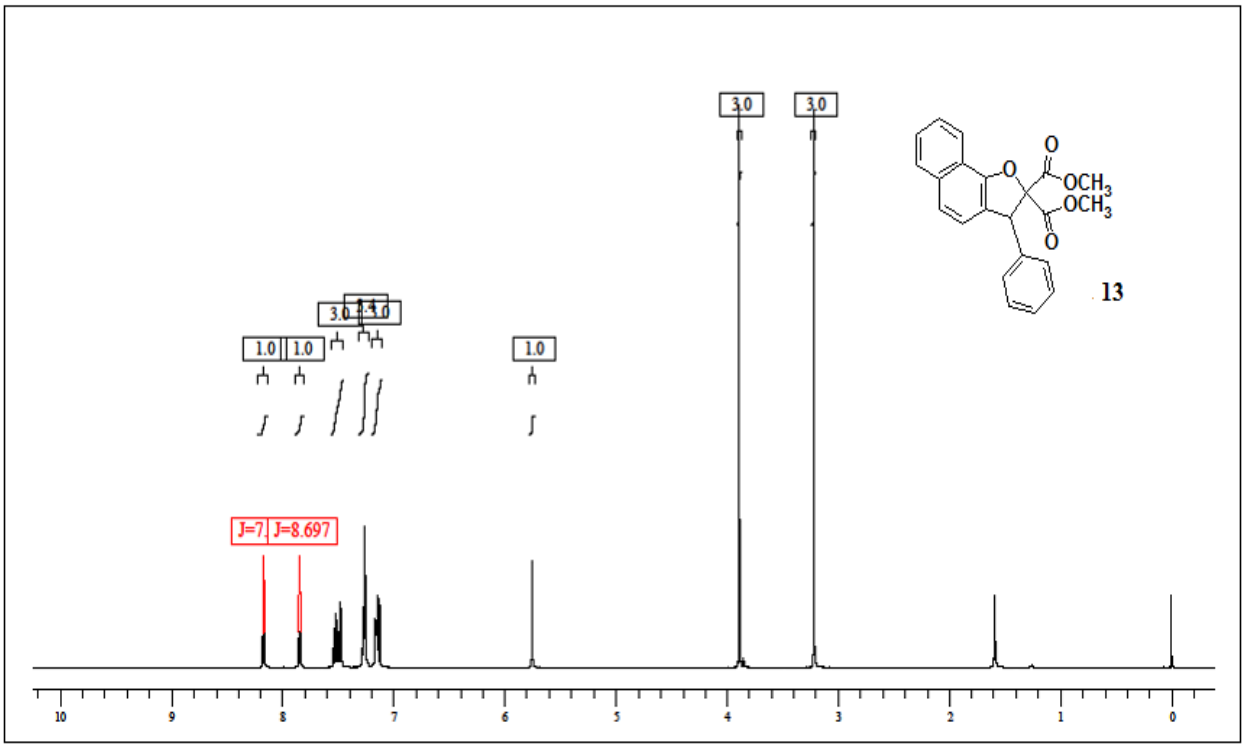
85.156
77.425
76.996
76.576
57.041
54.876
O
OCH3
CN
CN
12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3.0
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1.0
1.0
J=7
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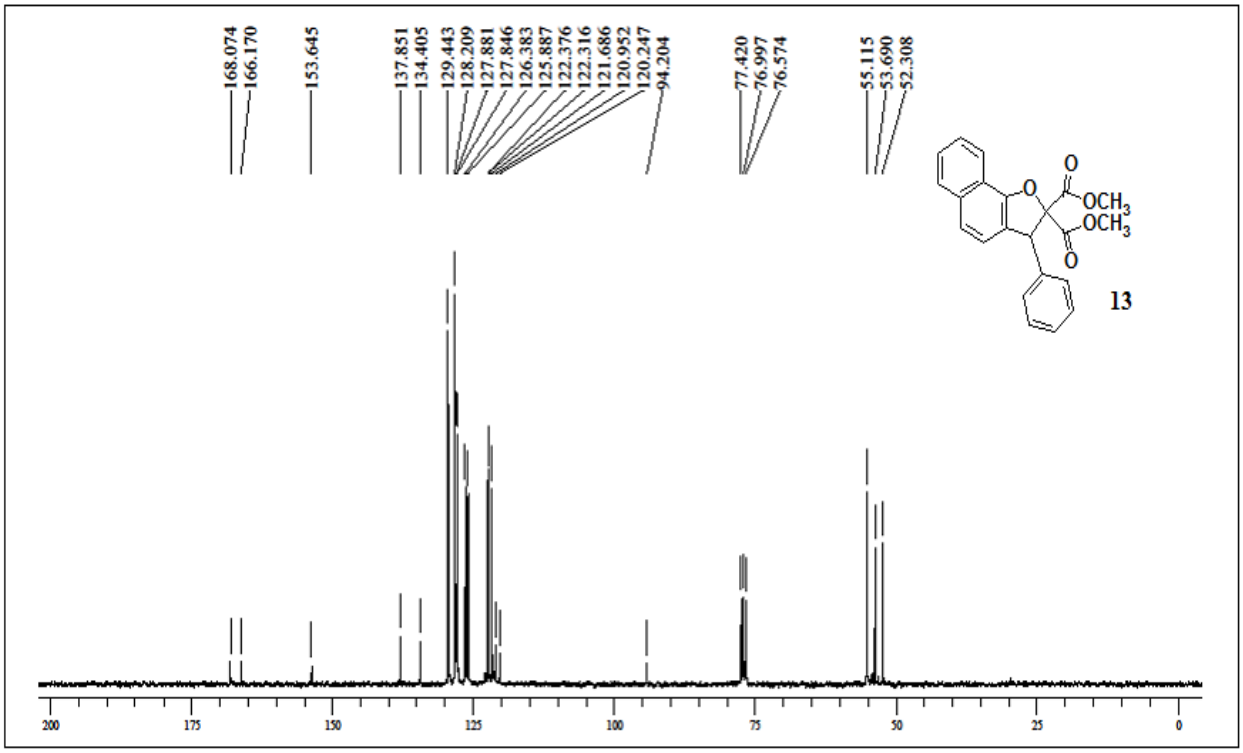
13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127.881
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126.383
125.887
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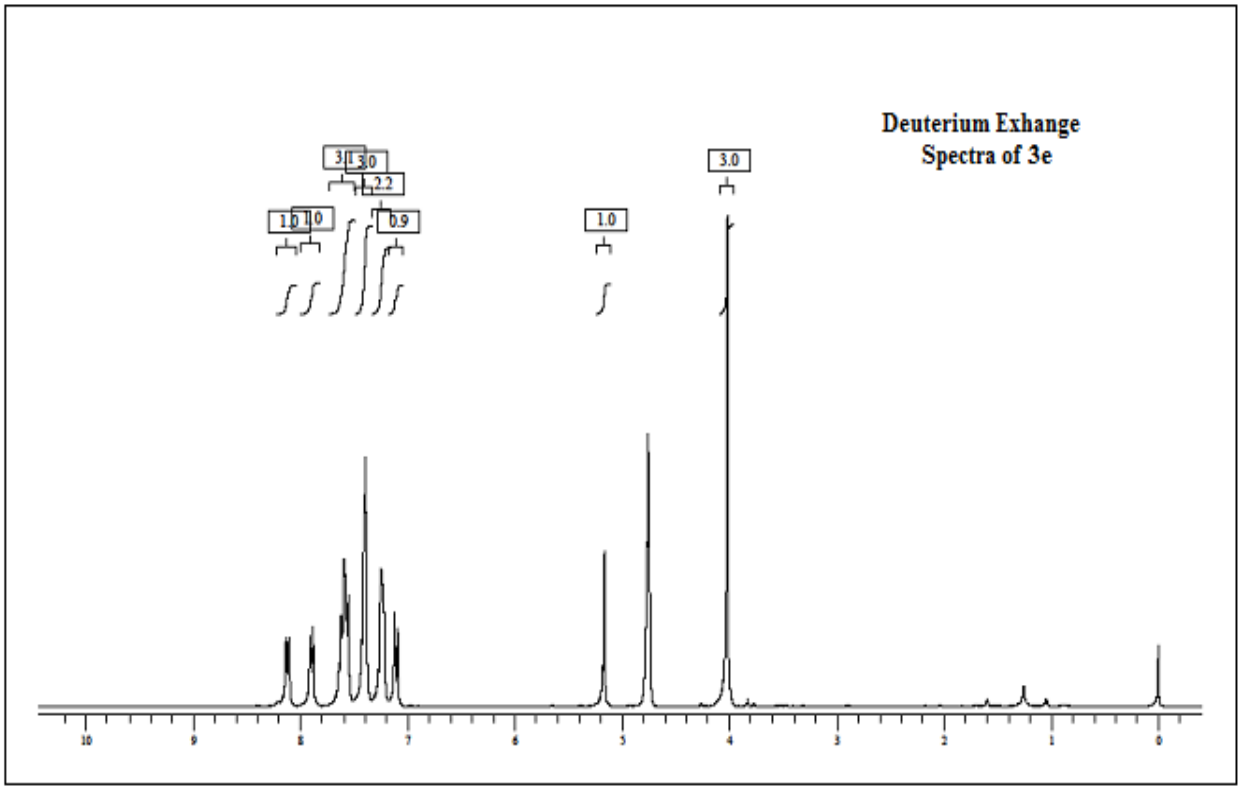
76.997
76.574
55.115
53.690
52.308
13

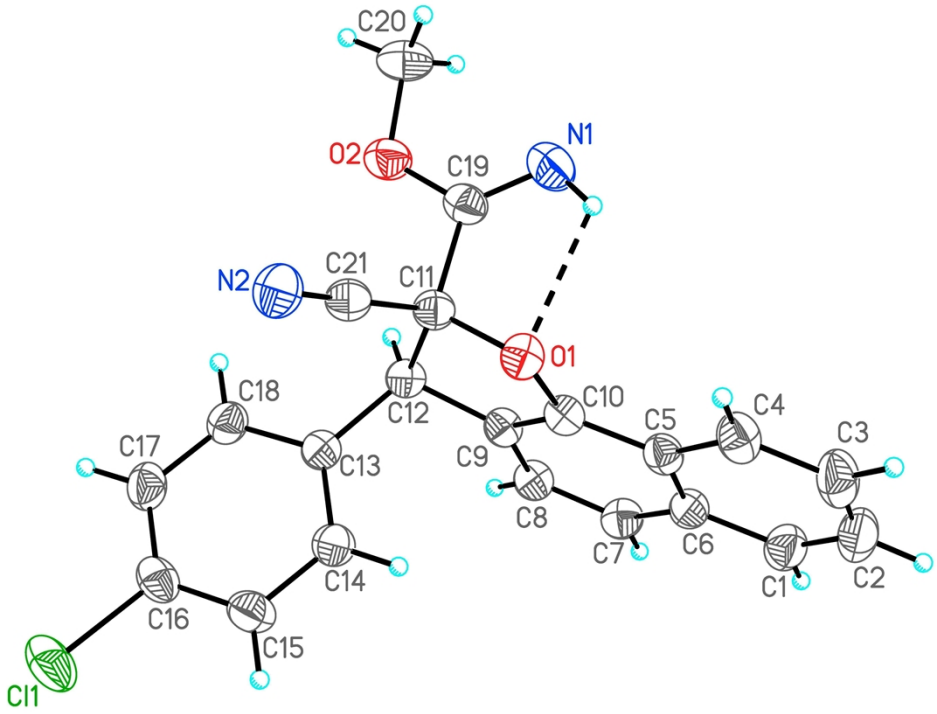

Deuterium Exhange
Spectra of 3e
3.1
3.0
2.2
1.0
1.0
0.9
1.0
3.0
10
9
8
7
6
5
4
3
2
1
0

X-ray crystallographic data

X-ray data for the compounds **3h** and **6** were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 5195 reflections for **3h** data and 6764 reflections for **6** data. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL97.[2] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$ for methyl atoms.

Crystal data for 3h (CCDC 938721):

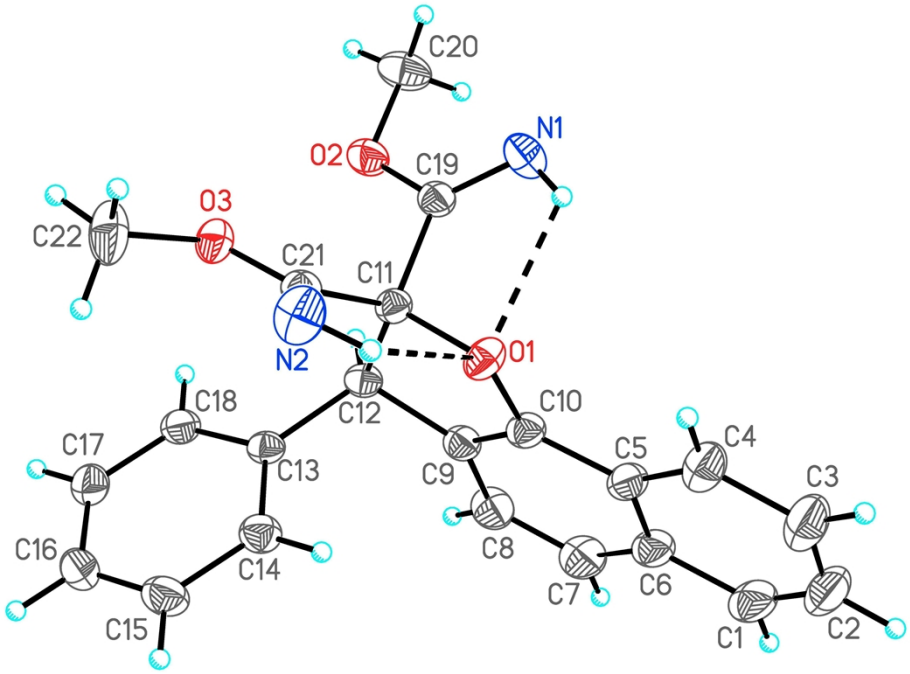
$C_{21}H_{15}N_2O_2Cl$, M = 362.80, colorless block, 0.38 × 0.22 × 0.18 mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 8.8826(8), b = 9.7822(8), c = 20.8708(18) Å, V = 1813.5(3) Å^3, Z = 4, D_c = 1.329 g/cm^3, F_{000} = 752, CCD area detector, Mo-Kα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 52.0º, 18905 reflections collected, 3547 unique (R_{int} = 0.0208). Final *GooF* = 0.986, R_1 = 0.0324, wR_2 = 0.0858, R indices based on 3369 reflections with I >2σ(I) (refinement on F^2), 240 parameters, μ = 0.228 mm^{-1}, absolute structure parameter = 0.00(6).[3]



The ORTEP diagram of **3h** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. An intramolecular N-H···O hydrogen bond is indicated by dotted lines [bond distances N1-H1, H1N···O1, N1···O1 and angle ∠N1-H1N···O1 parameters are 0.90 Å, 2.22 Å, 2.720(2)Å and 114˚, respectively].

Crystal data for 6 (CCDC 938722):

$C_{22}H_{20}N_2O_3$, M = 360.40, colorless needle, 0.43 × 0.21 × 0.14 mm^3, orthorhombic, space group *Pbca* (No. 61), a = 15.9828(14), b = 6.8208(6), c = 34.232(3) Å, V = 3731.9(6) Å^3, Z = 8, D_c = 1.283 g/cm^3, F_{000} = 1520, CCD area detector, Mo-Kα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 50.0º, 32809 reflections collected, 3277 unique (R_{int} = 0.0386). Final *GooF* = 1.049, R_1 = 0.0383, wR_2 = 0.0986, R indices based on 2964 reflections with I>2σ(I) (refinement on F^2), 254 parameters, μ = 0.086 mm^{-1}.



The ORTEP diagram of **6** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. The two intramolecular N-H···O hydrogen bonds are indicated by dotted lines [bond distances N-H, H···O, N···O and angle ∠N-H···O parameters are 0.87 Å, 2.26 Å, 2.722(2)Å, 116˚ for N1-H1N···O1 and 0.91 Å, 2.21 Å, 2.707(2)Å, 114˚ for N2-H2N···O1, respectively].

Hydrogen bondings are shown by using PLATON[4]. Crystallographic data for these compounds (**3h** and **6**) can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

References

1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. G. M. Sheldrick, SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.
3. H. D. Flack, *Acta Cryst*., 1983, *A39*, 876-881.
4. A. L. Spek, Single crystal structure validation with the program PLATON, *J. Appl. Cryst.,* 2003, **36**, 7-13