Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Decarboxylative/Decarbonylative C3-acylation of indoles via photocatalysis: a simple and efficient route to 3-acylindoles

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Table of Contents for Supporting Information

1. Reaction mechanism study

1.1 Determination of singlet oxygen

In order to determine the active species of oxygen involved in the present reaction, 2,2,6,6-tetramethylpiperidine (TEMP) and 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) were employed to capture $^1O_2$ and $O^{2\bullet-}$, respectively. Irradiation of the ethanol solution of TEMP and rose bengal (RB) in air by green LED resulted in the formation of a strong characteristic signal of $^1O_2$ adduct with TEMP (Figure S1b *vs* S1a), and this signal decreased obviously as addition of phenylglyoxylic acid (**2a**) into the solution (Figure S1c). It is indicated that **2a** reacted with $^1O_2$ efficiently to consume it rapidly. However, there is no signal of $O^{2\bullet-}$ adduct with DMPO, excluding the formation of $O^{2\bullet-}$ in the reaction system.

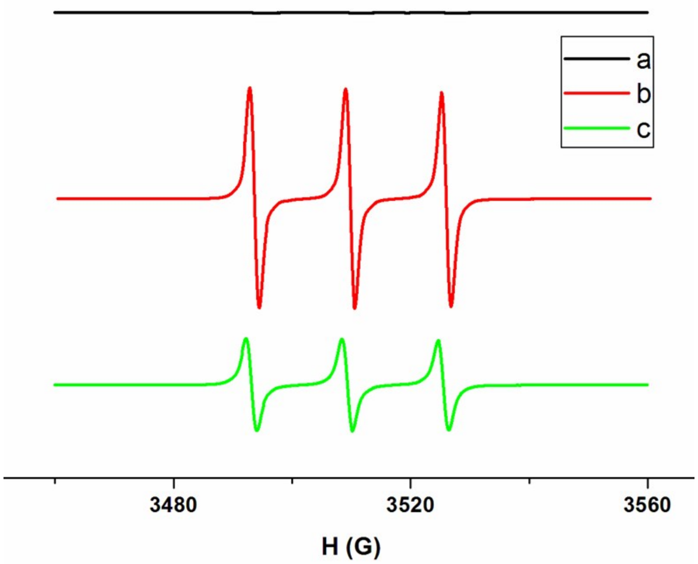
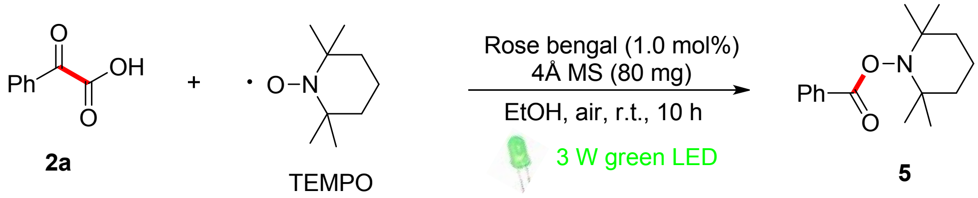


Figure S1. Electron spin resonance (ESR) spectra: (a) a solution of TEMP (0.12 mol/L), rose bengal (1.0 mol%) in air-saturated C_2H_5OH without green LED irradiation; (b) a solution of TEMP (0.12 M), rose bengal (1.0 mol%) in air-saturated C_2H_5OH with green LED irradiation for 30 s; (c) a solution of TEMP (0.12 mol/L), rose bengal (1.0 mol%) in air-saturated C_2H_5OH with green LED irradiation for 30 s, then with addition of **2a** (1.5×10^{-2} mol/L).

1.2 Benzoyl radical-trapping experiment



Phenylglyoxylic acid (**2a**, 0.30 mmol), 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 1.0 mmol), rose bengal (RB, 0.003 mmol), 4Å molecular sieve (80 mg) were dissolved in ethanol (2.0 mL) in an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated using green LED at room temperature under air atmosphere for 10 h. After the reaction was carried out, concentrated under reduced pressure to yield the crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1 to 10:1), affording the adduct **5** as a colorless solid in 52% yield. 2,2,6,6-Tetramethylpiperidin-1-yl benzoate (**5**) (See: H. Tan, H. Li, W. Ji, L. Wang, *Angew. Chem., Int. Ed.*, 2015, **54**, 8374): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 7.6 Hz, 2H), 7.58–7.55 (m, 1H), 7.47–7.44 (m, 2H), 1.81–1.75 (m, 2H), 1.70–1.67 (m, 1H), 1.63–1.57 (m, 2H), 1.47–1.44 (m, 1H), 1.28 (s, 6H), 1.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.15, 132.64, 129.61, 129.36, 128.26, 60.21, 38.92, 31.80, 20.68, 16.84. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{16}H_{24}NO_2$: 262.1802, Found: 262.1805. The following Figure S2 is the HRMS analysis of reaction mixture.

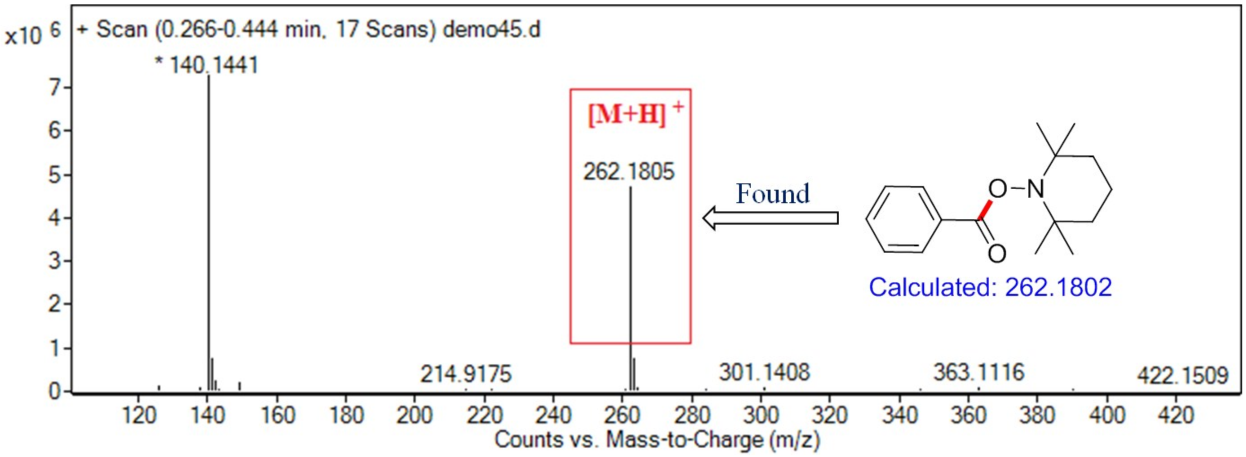
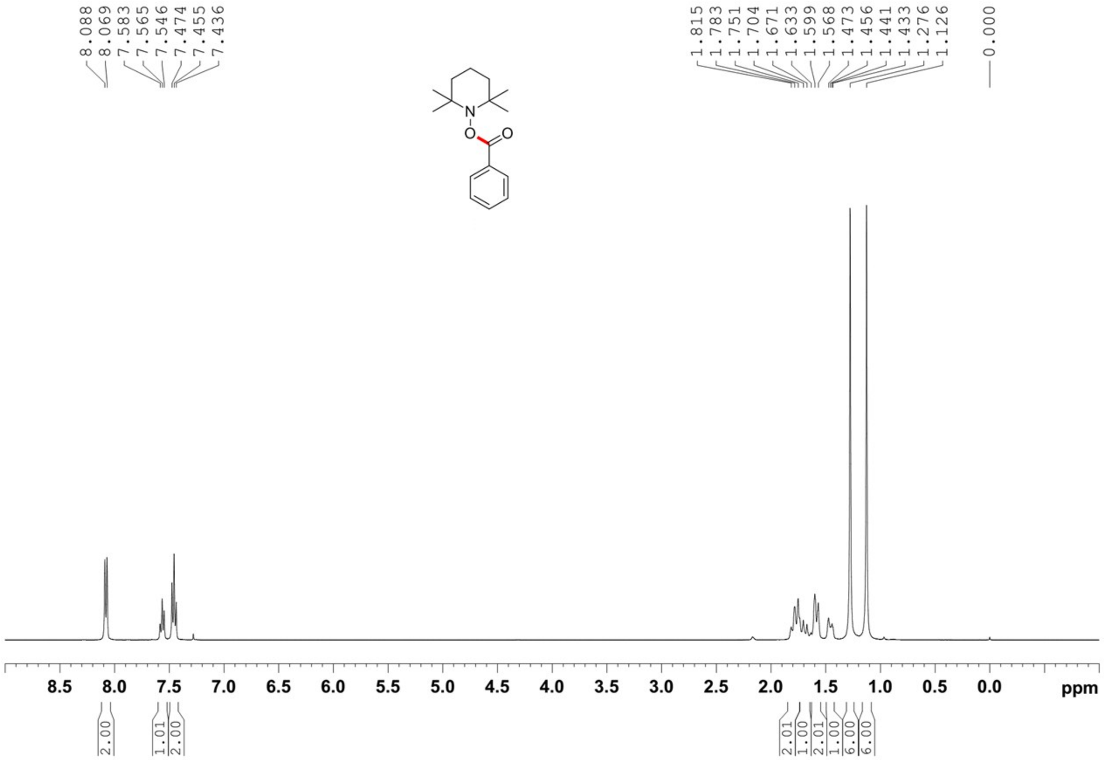


Figure S2. Analysis of reaction mixture by HRMS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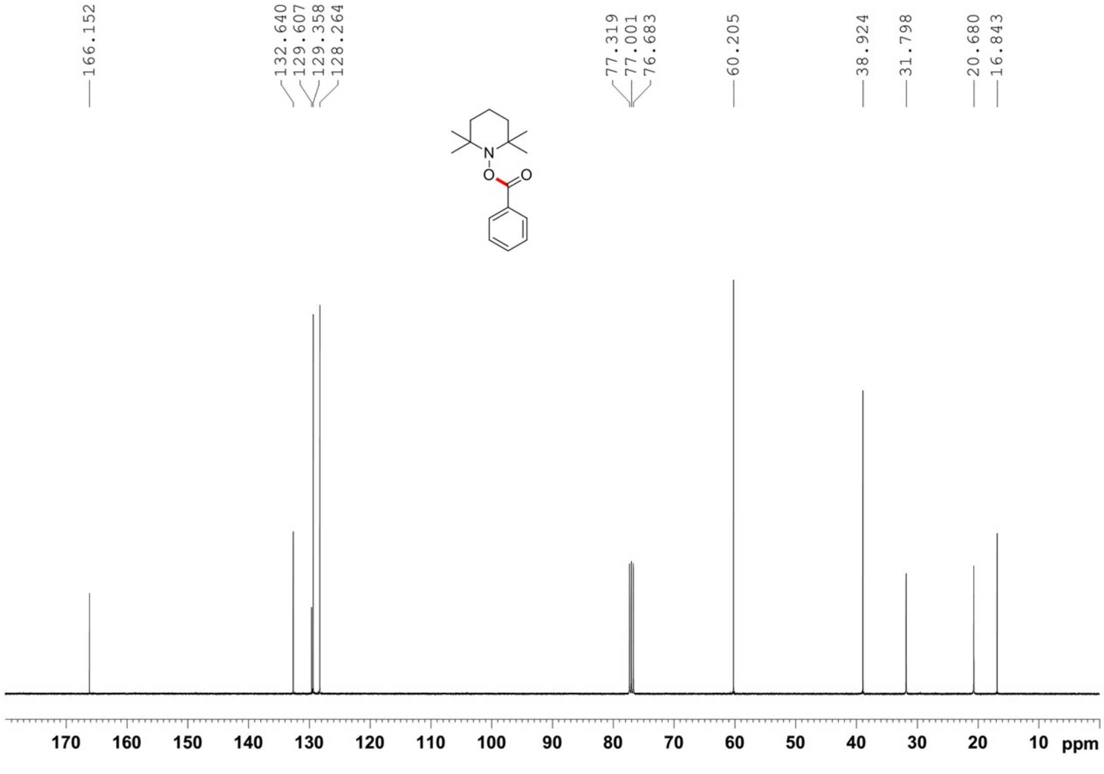
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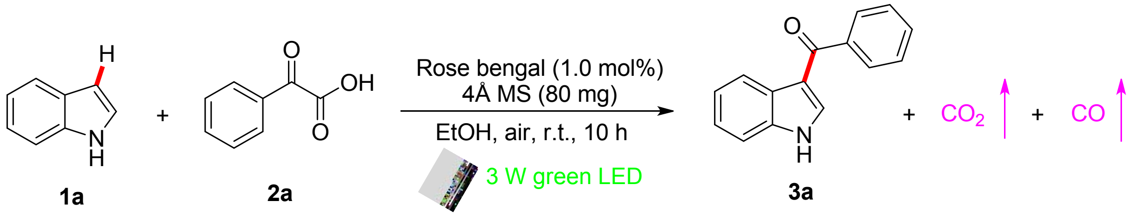
1.3 Determination of CO_2 and CO during the reaction by FT-IR



An Schlenk tube equipped with a magnetic stirrer bar was charged with indole (**1a**, 0.30 mmol), phenylglyoxylic acid (**2a**, 0.6 mmol), rose bengal (1.0 mol%), 4Å molecular sieve (80 mg) and ethanol (2.0 mL). The reaction vessel was exposed to green LED at room temperature for 10 h. After completion of the reaction, the resulting gas from the reaction system was directly determined by a Bruker Tensor 27 FT-IR, and the concentration of CO_2 and CO was found to be 2839.70, and 94.27 ppm (Figure S3 and Figure S4), respectively.

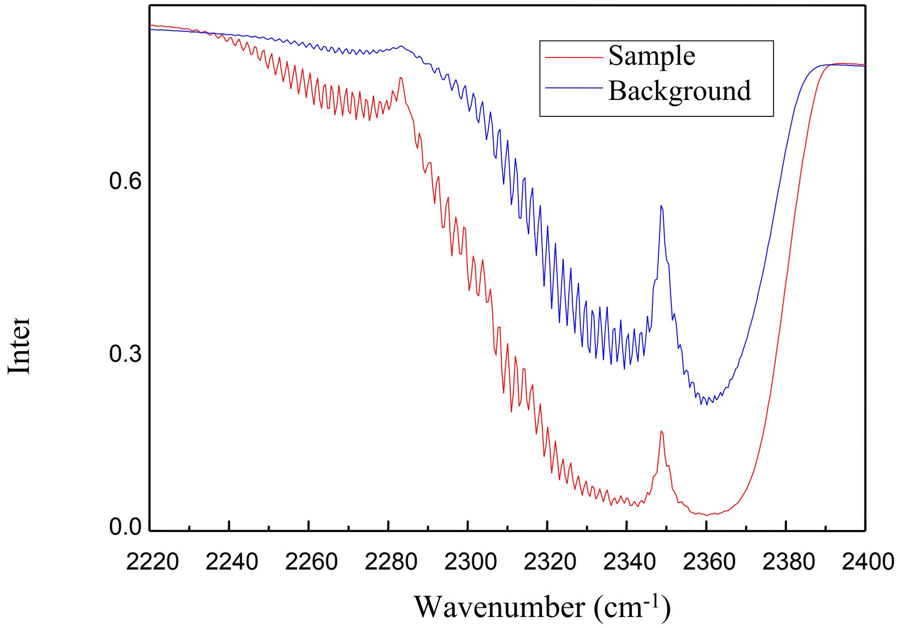


Figure S3. FT-IR analysis of the formation of CO_2 in the reaction

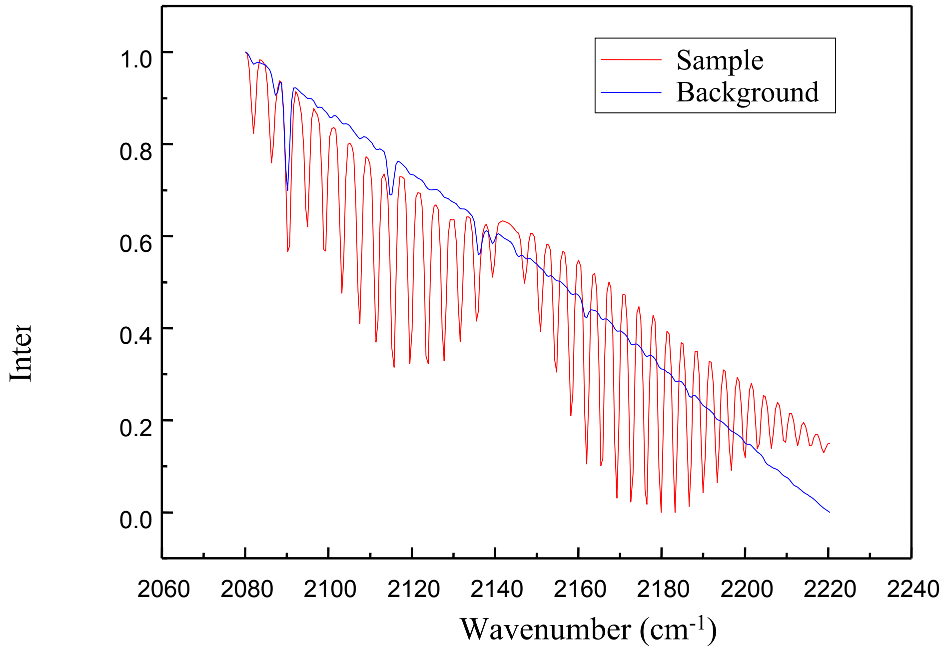
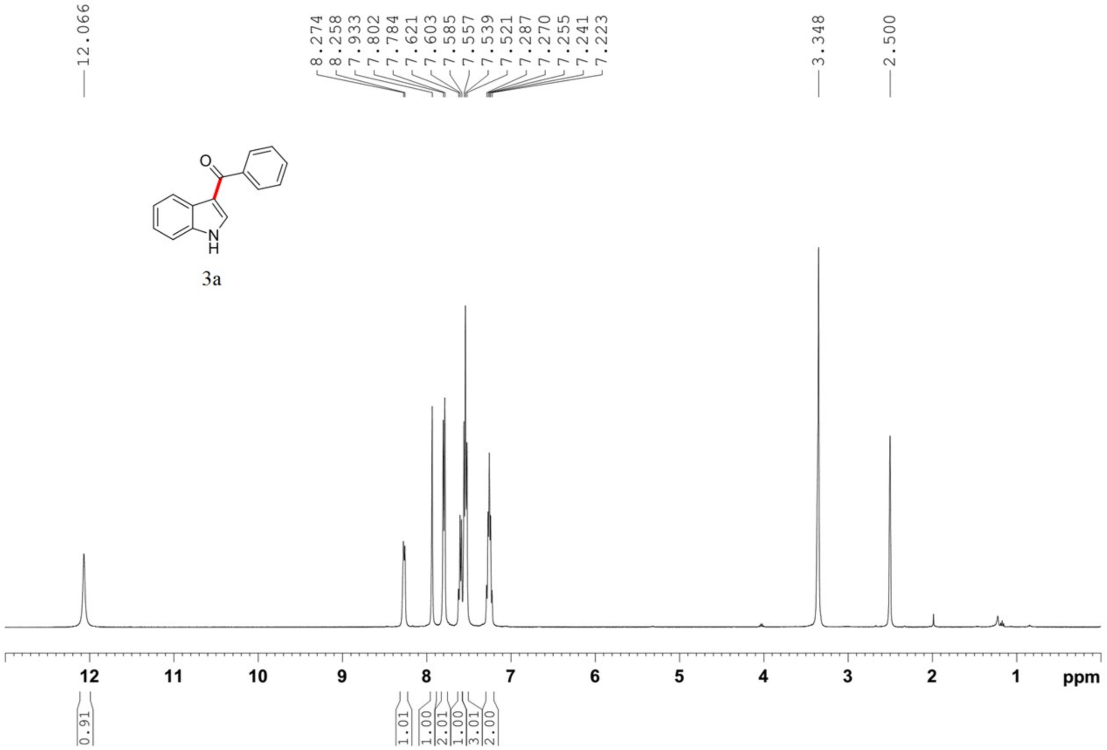
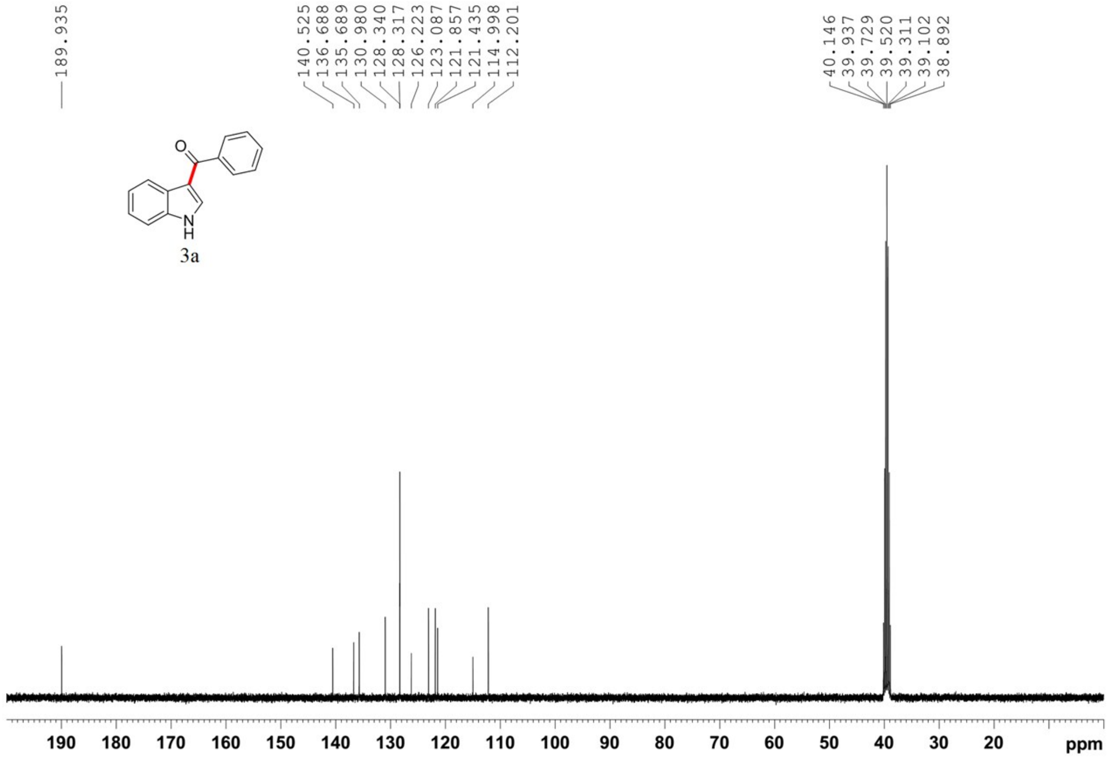
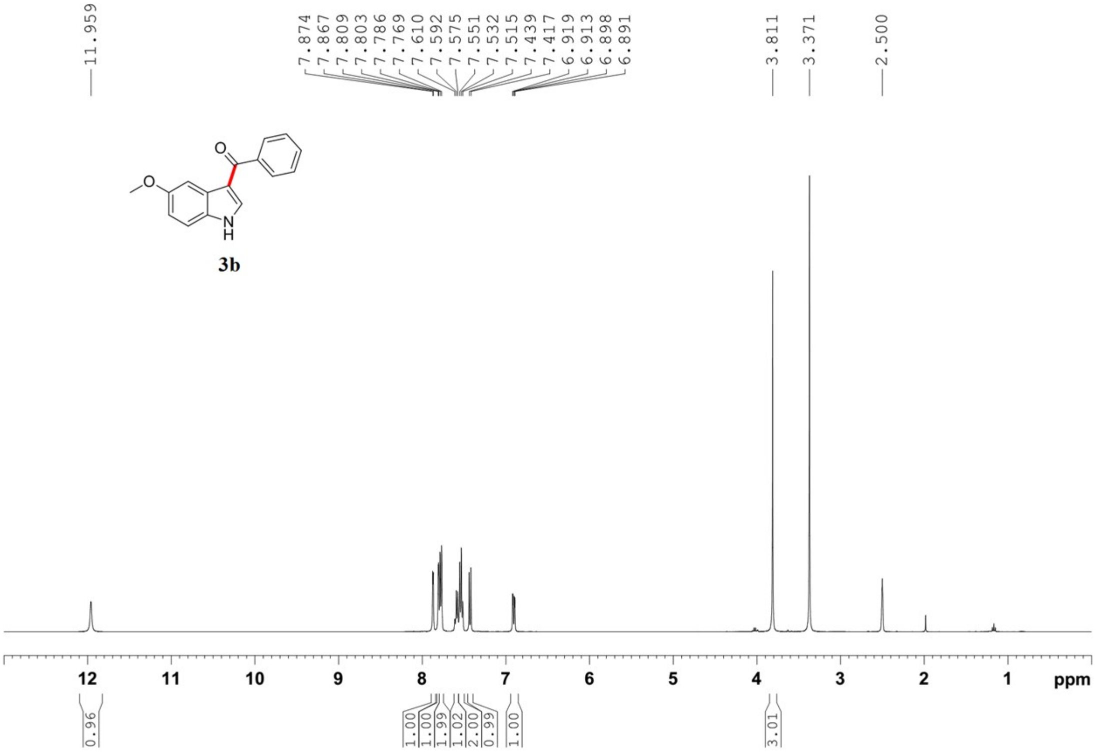


Figure S4. FT-IR analysis of the formation of CO in the reaction

2. ^{1}H and ^{13}C NMR spectra of the products



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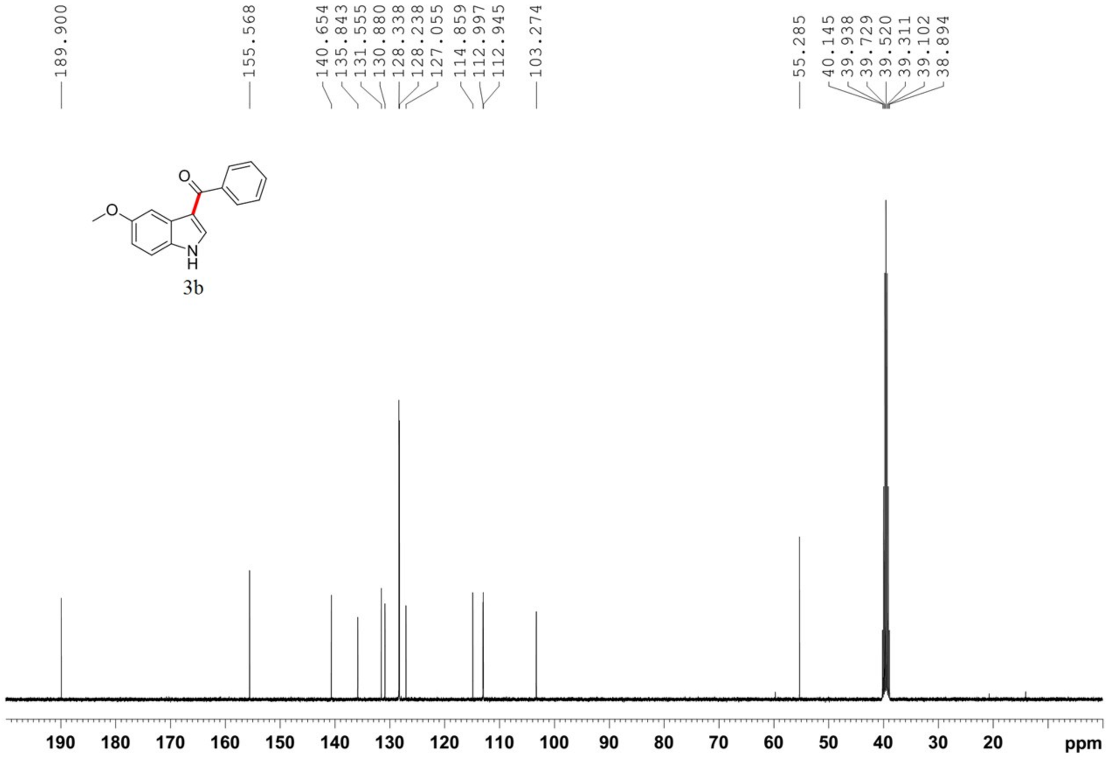
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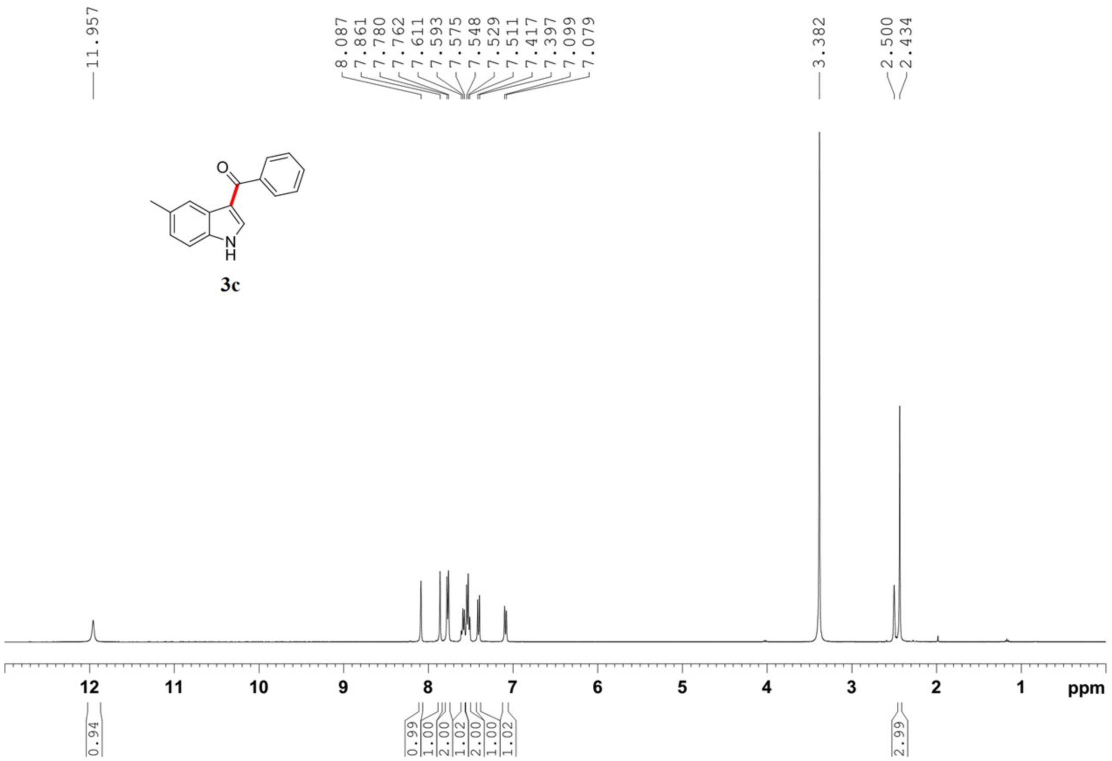
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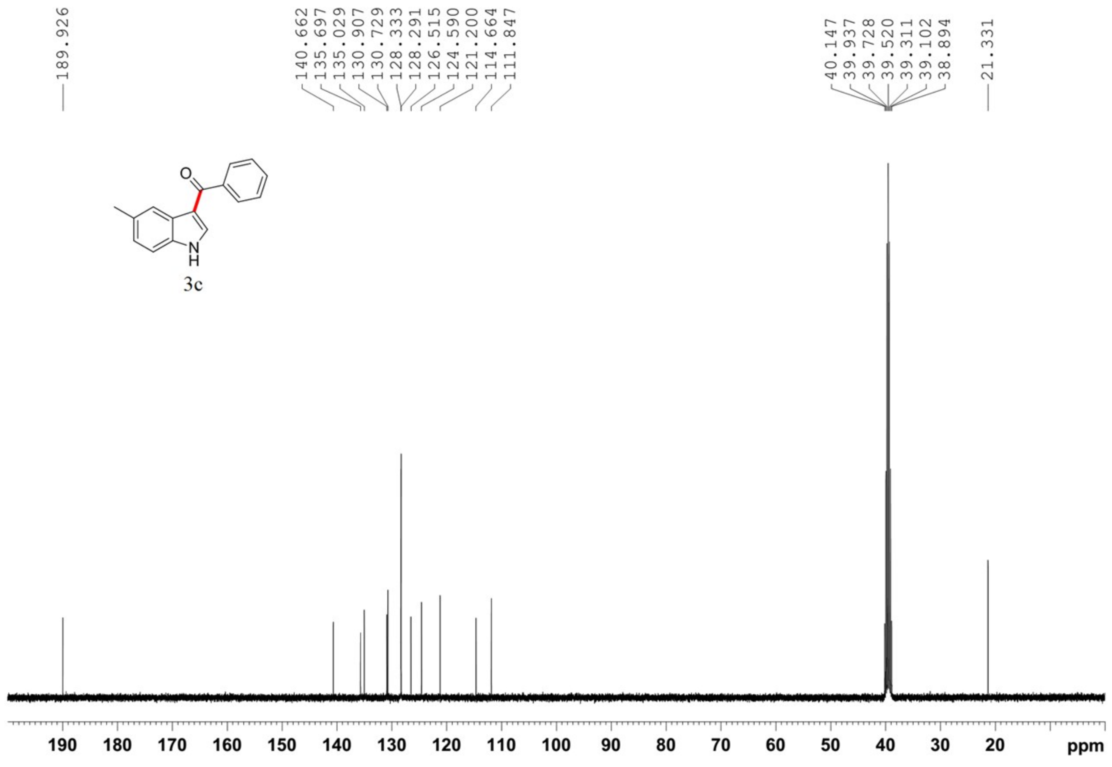
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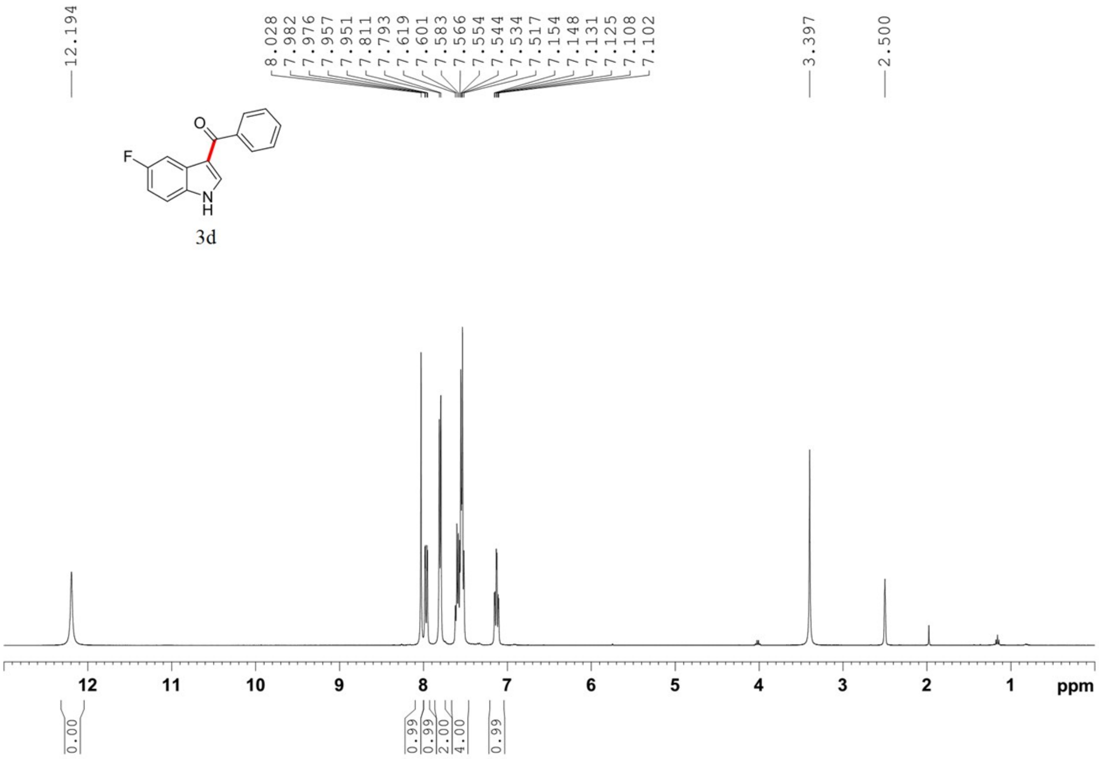
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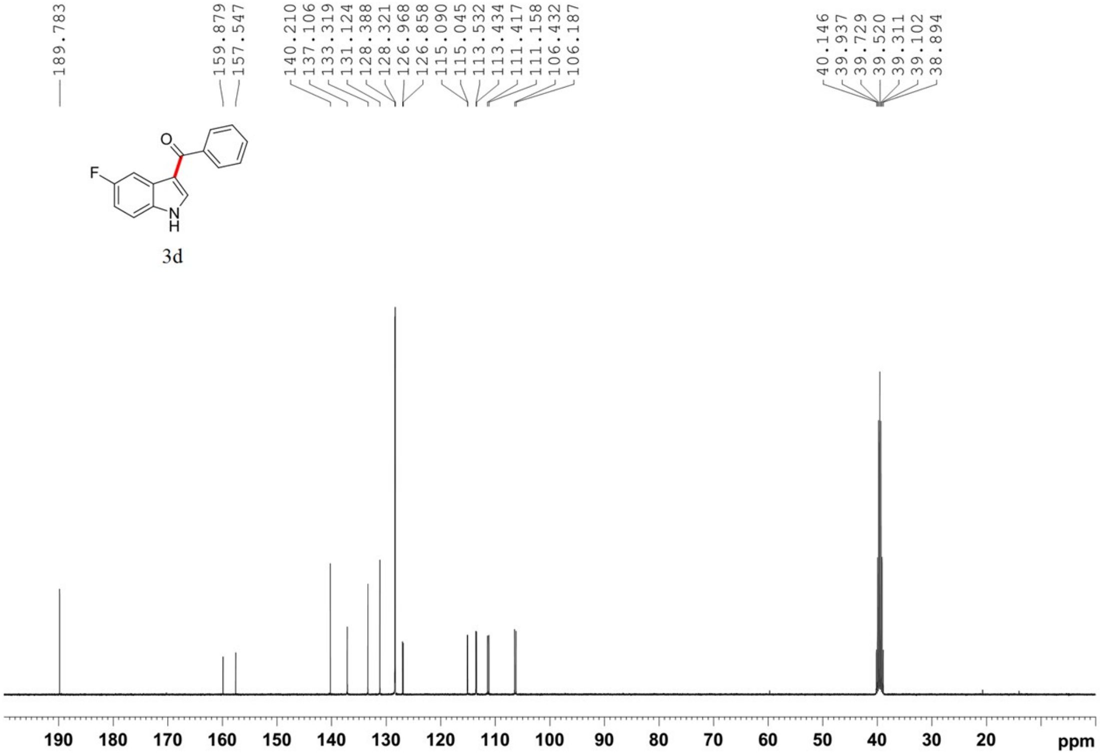
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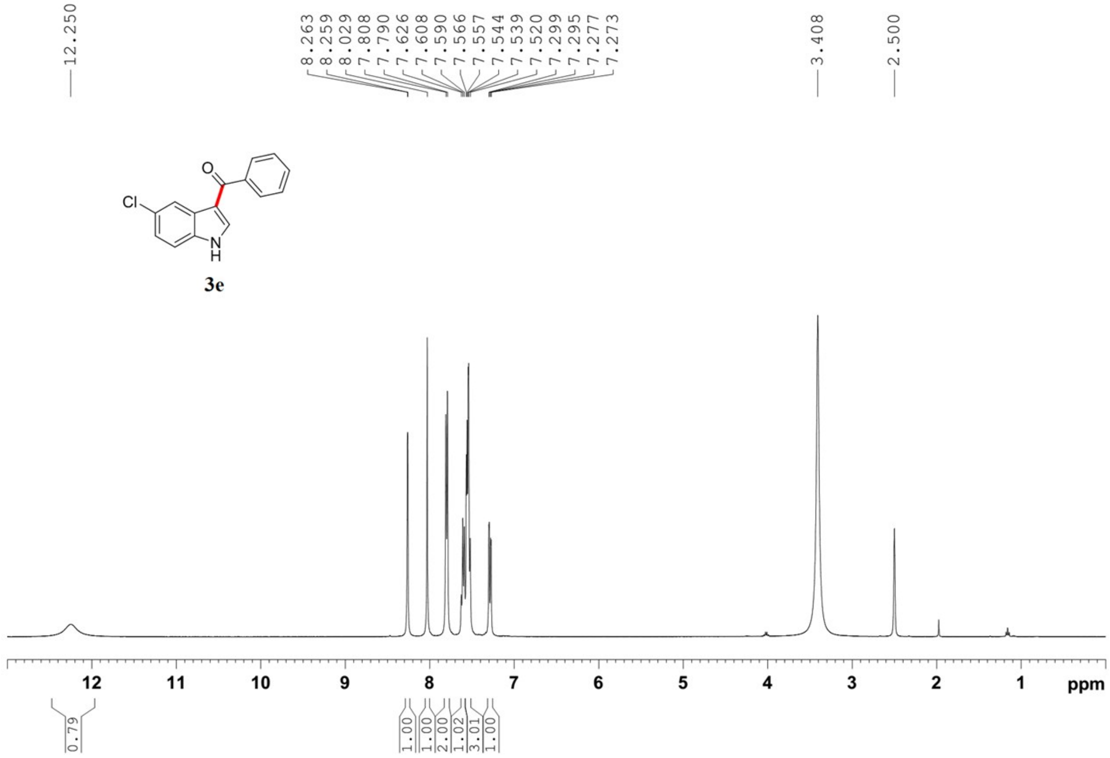
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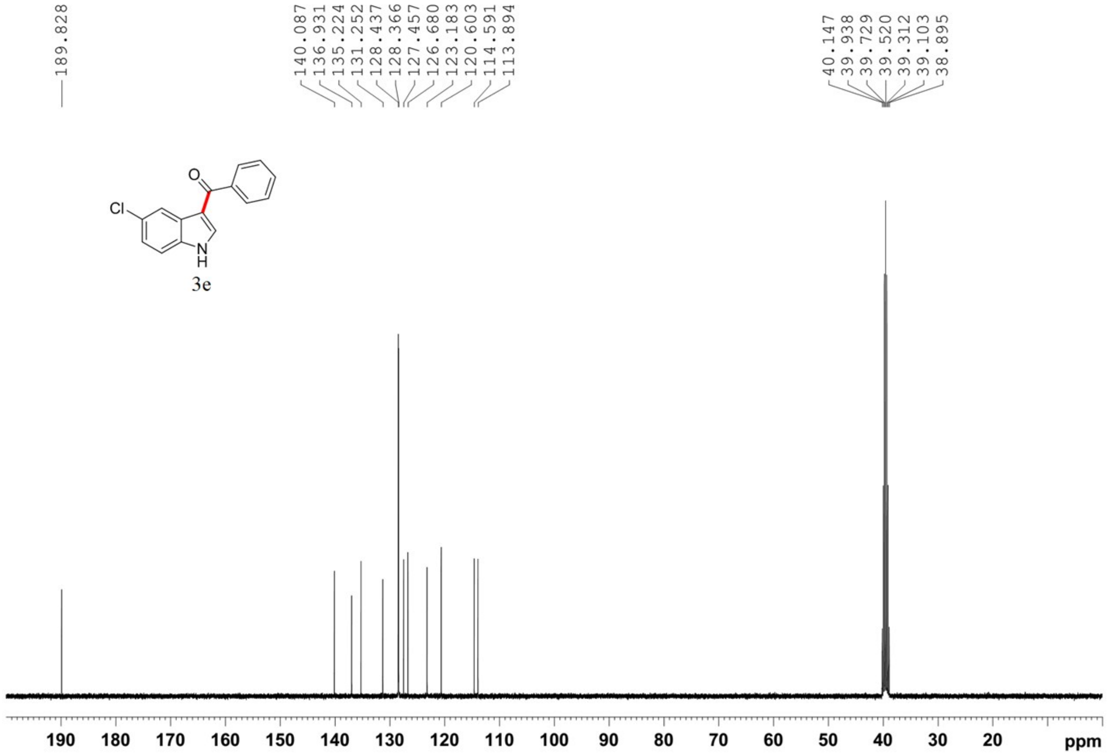
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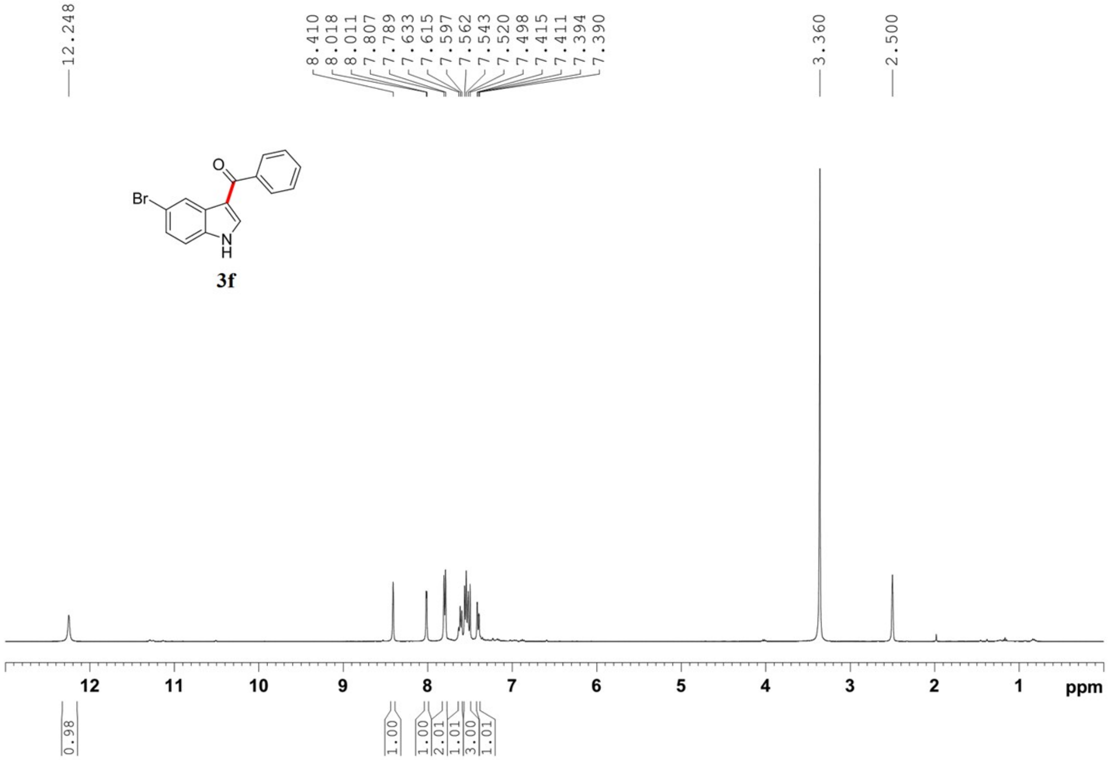
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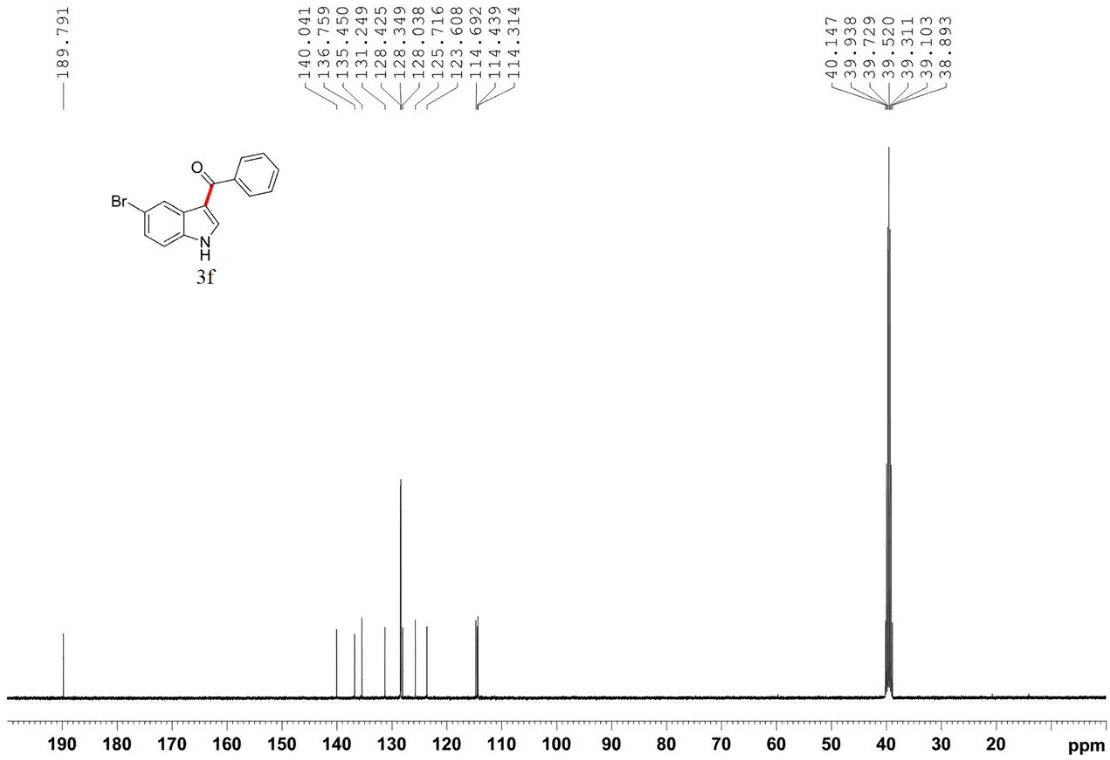
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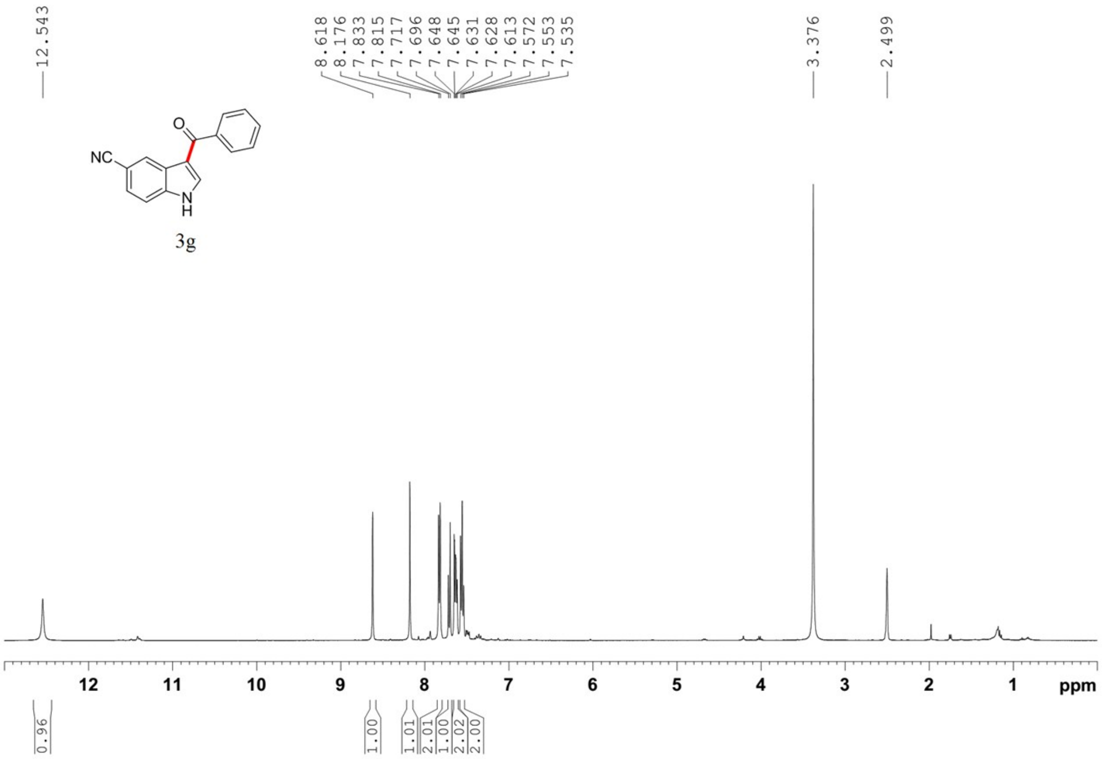
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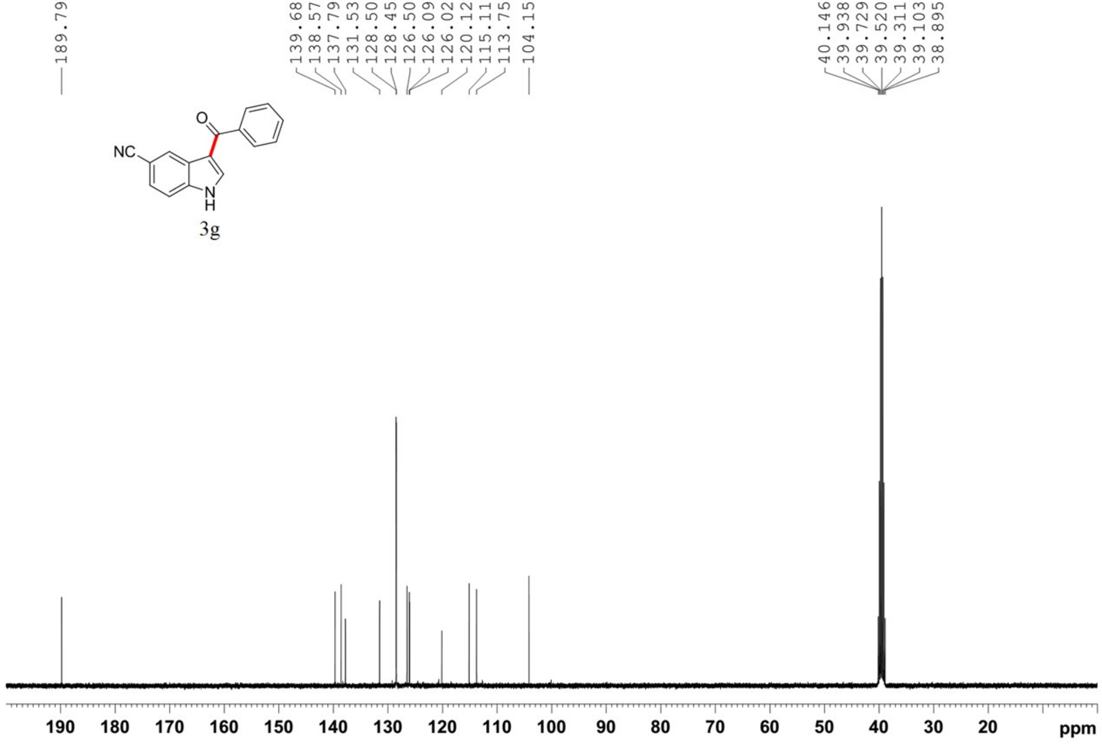
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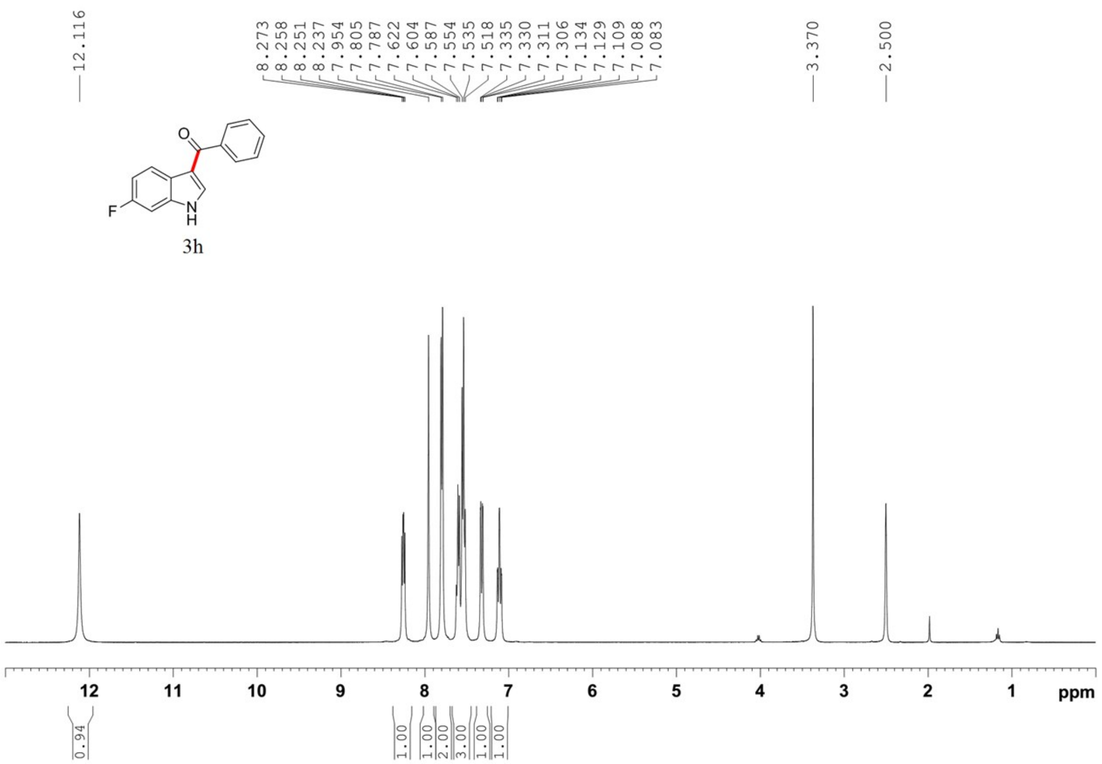
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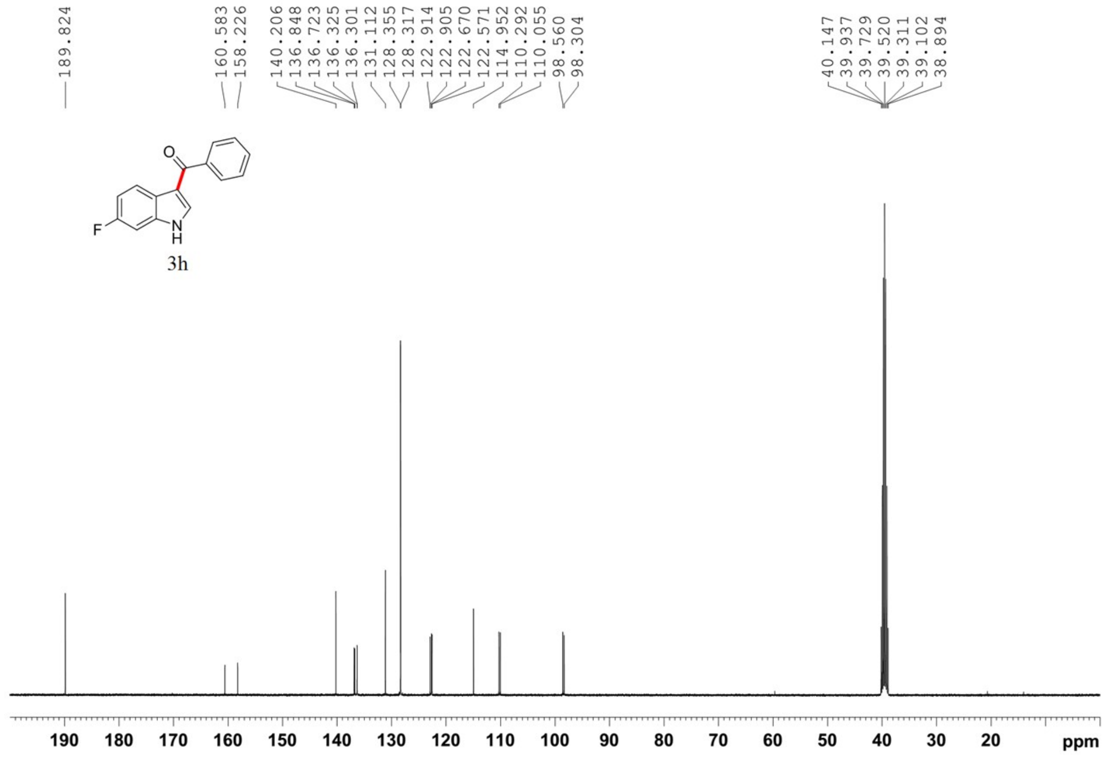
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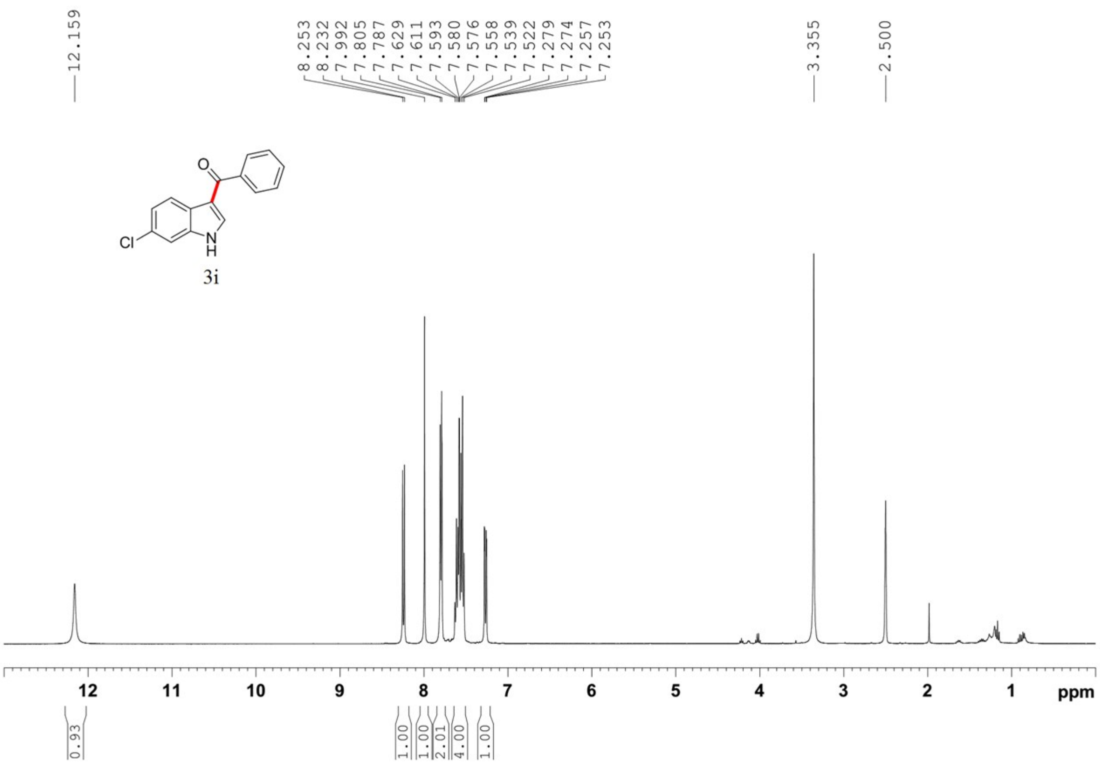
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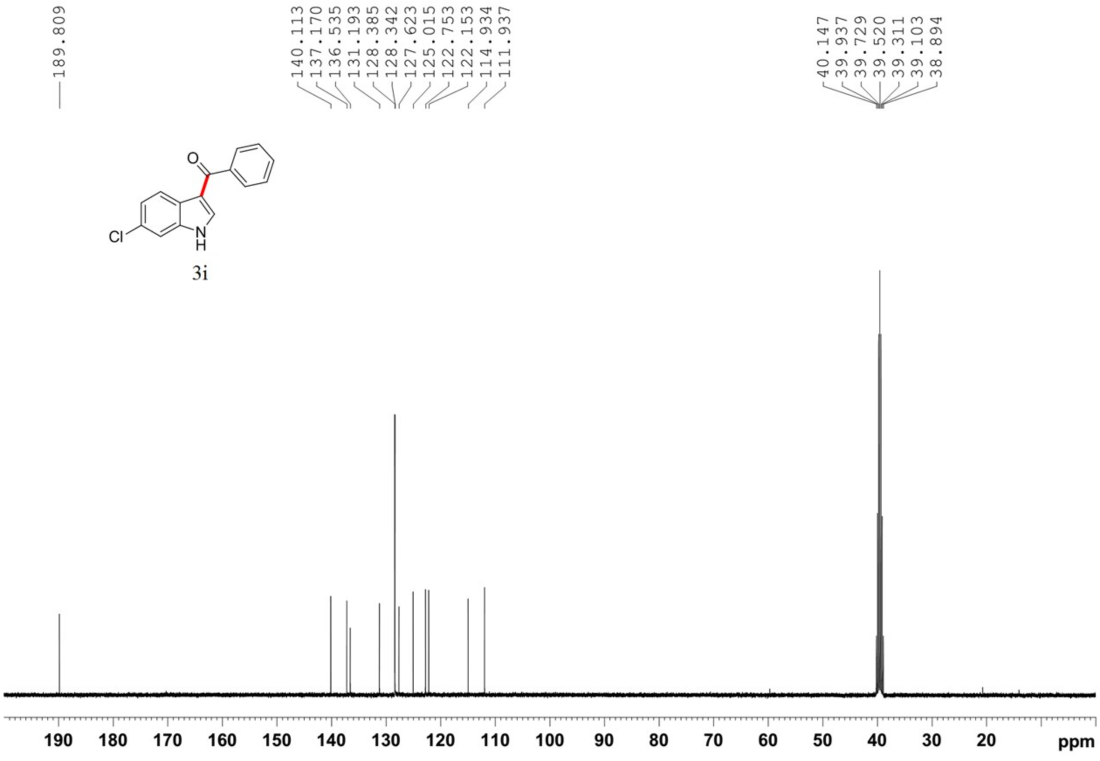
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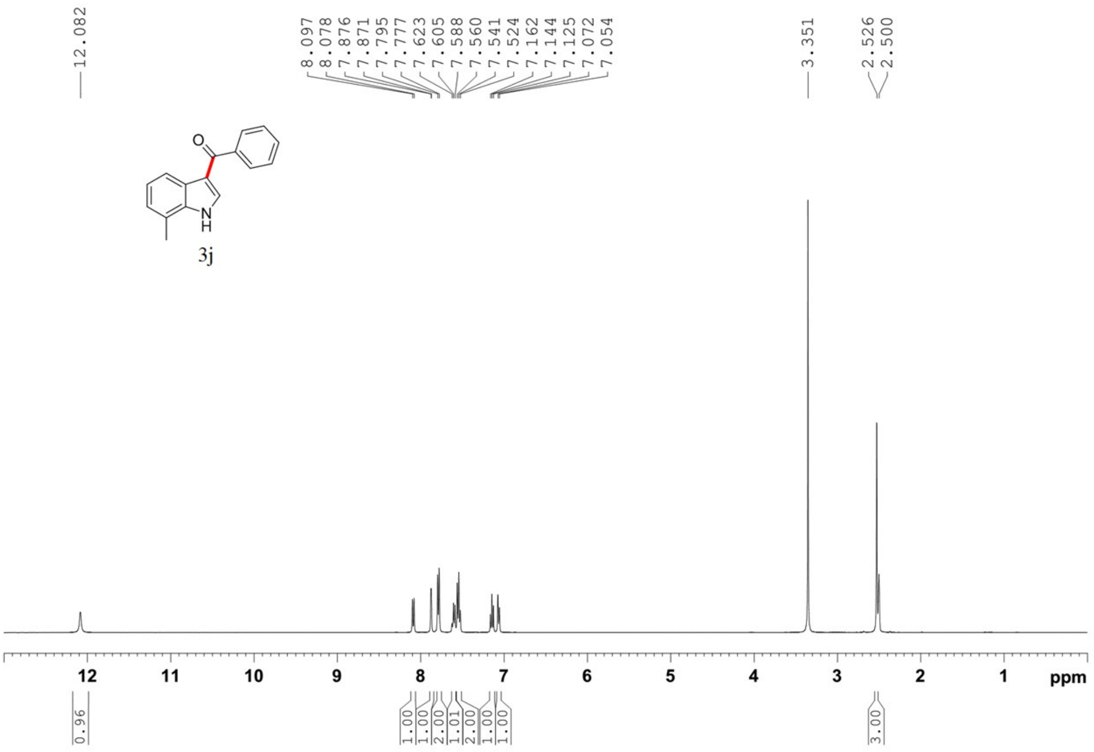
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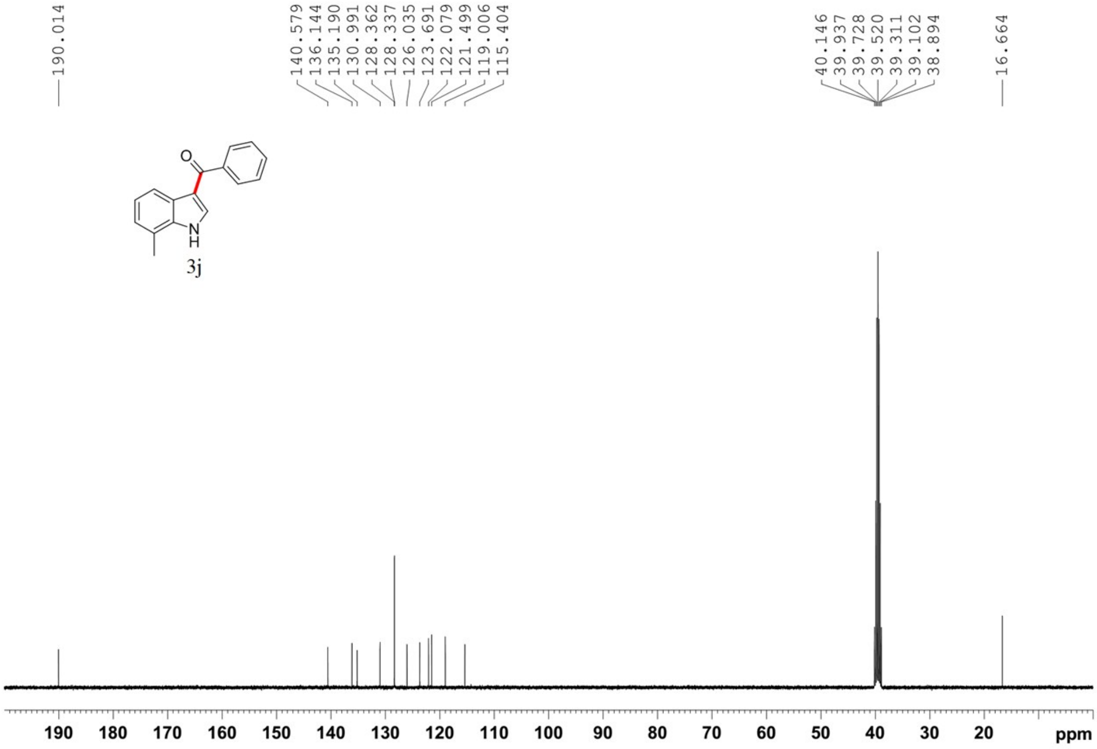
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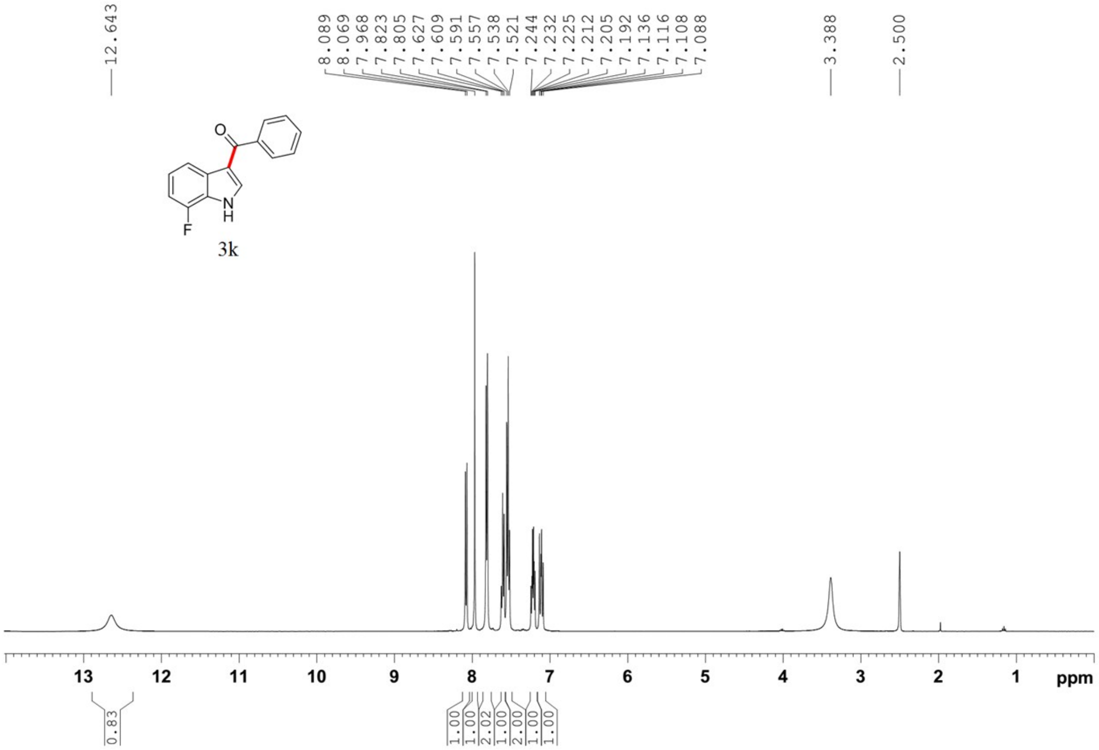
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7.232
7.225
7.212
7.205
7.192
7.136
7.116
7.108
7.088
3.388
2.500
O
F
N
H
3k
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8
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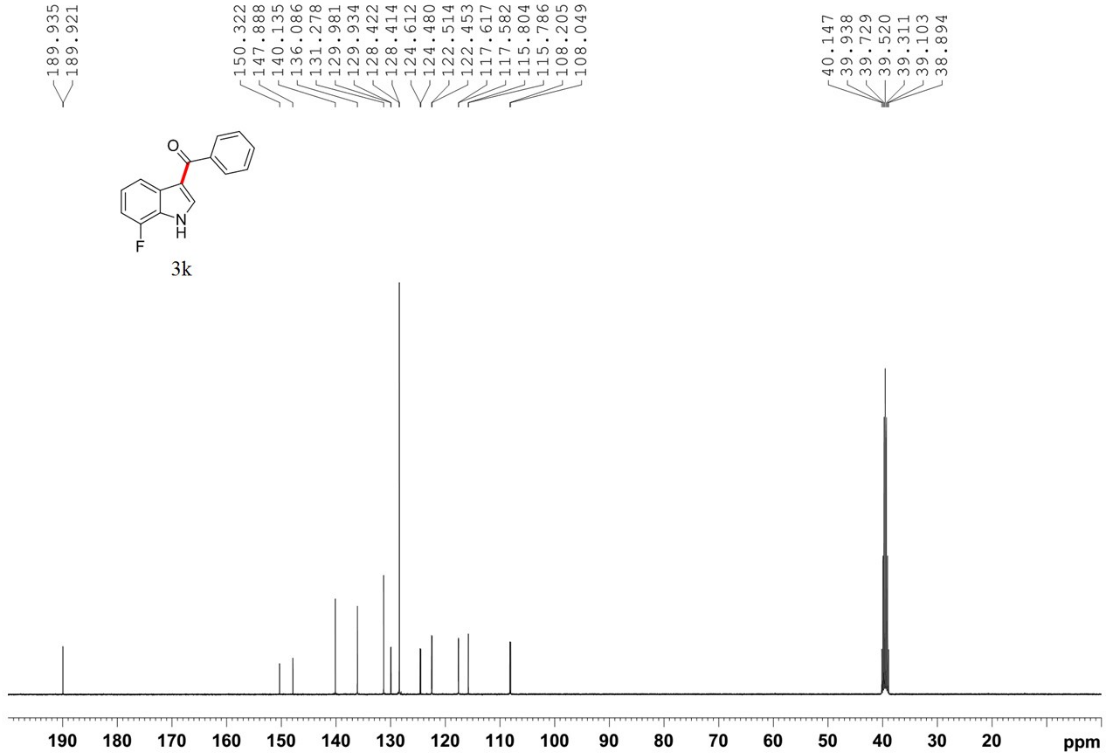
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117.582
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115.786
108.205
108.049
40.147
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39.729
39.520
39.311
39.103
38.894
O
F
N
H
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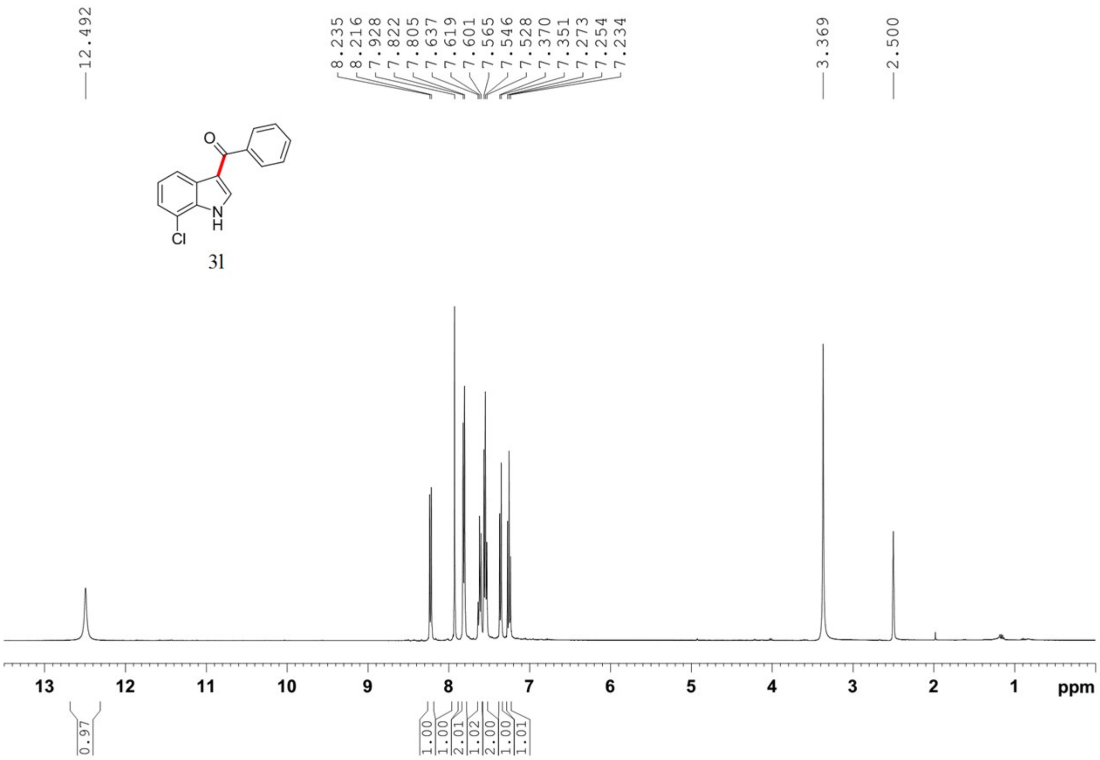
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7.273
7.254
7.234
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NH
Cl
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8
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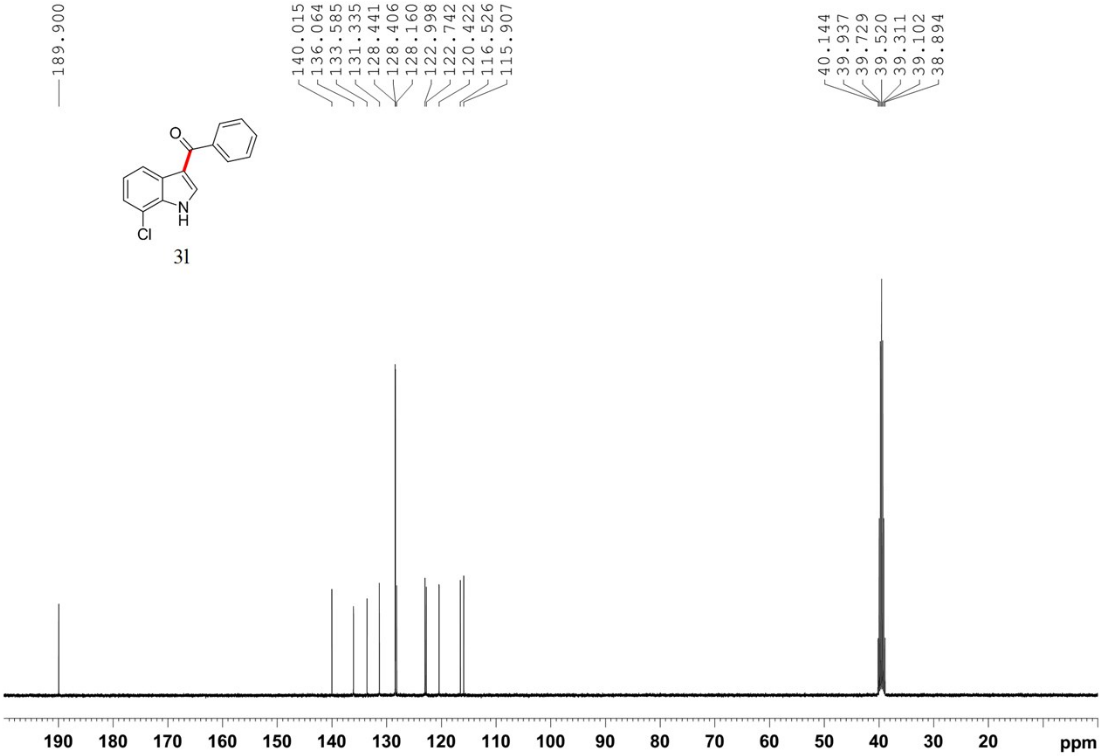
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39.311
39.102
38.894
O
NH
Cl
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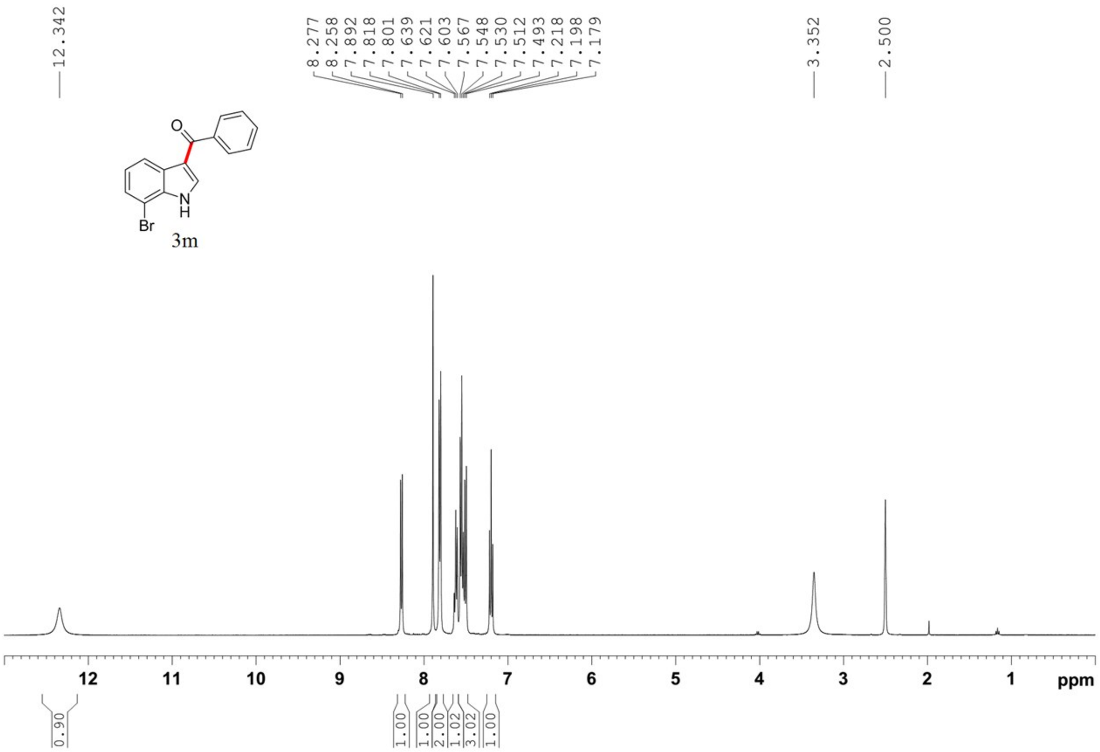
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7.493
7.218
7.198
7.179
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2.500
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Br
N
H
3m
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11
10
9
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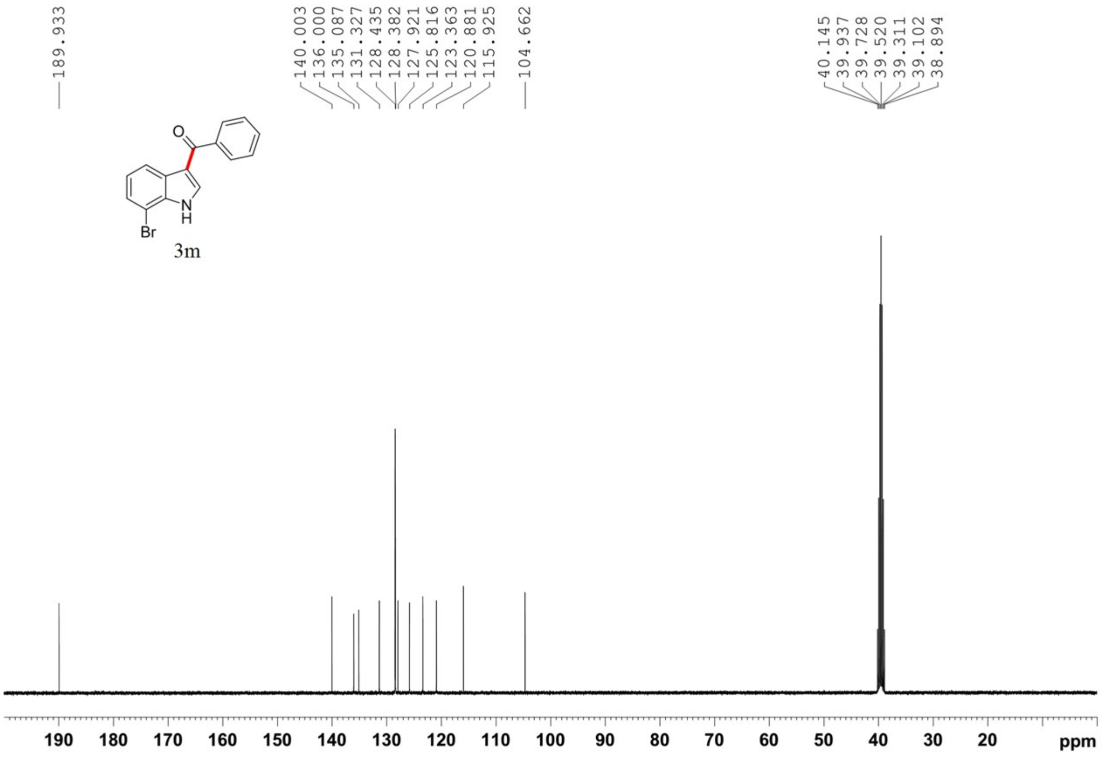
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39.728
39.520
39.311
39.102
38.894
O
Br
N
H
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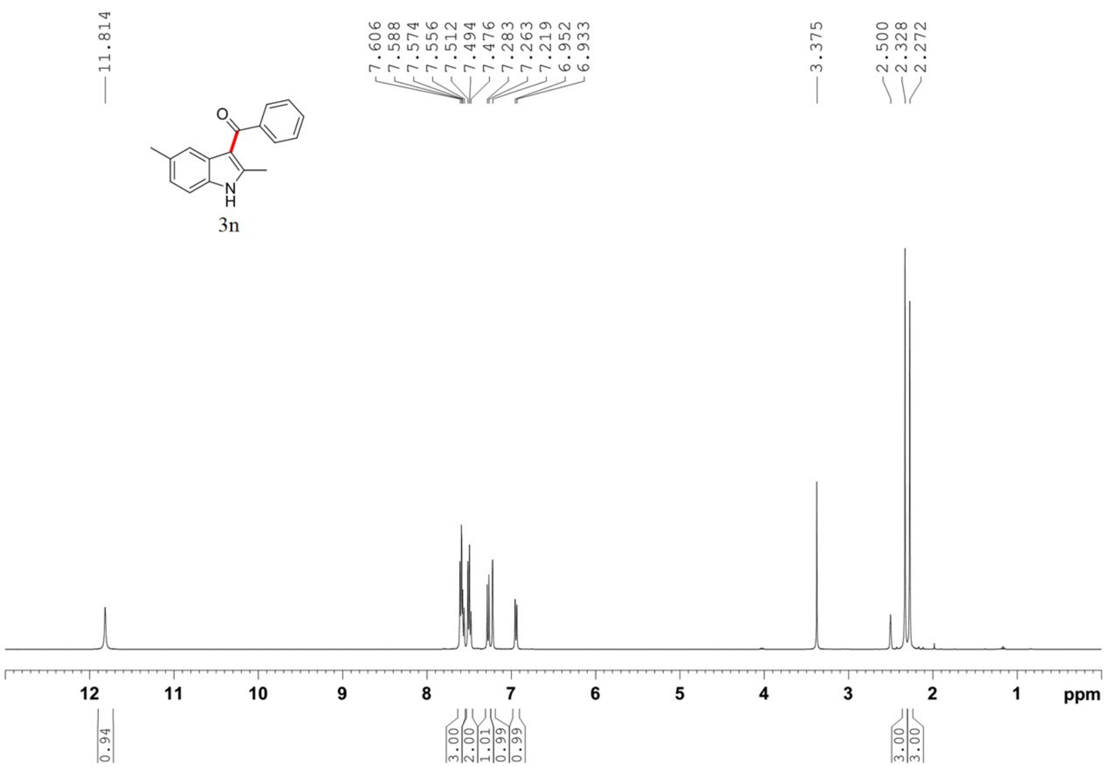
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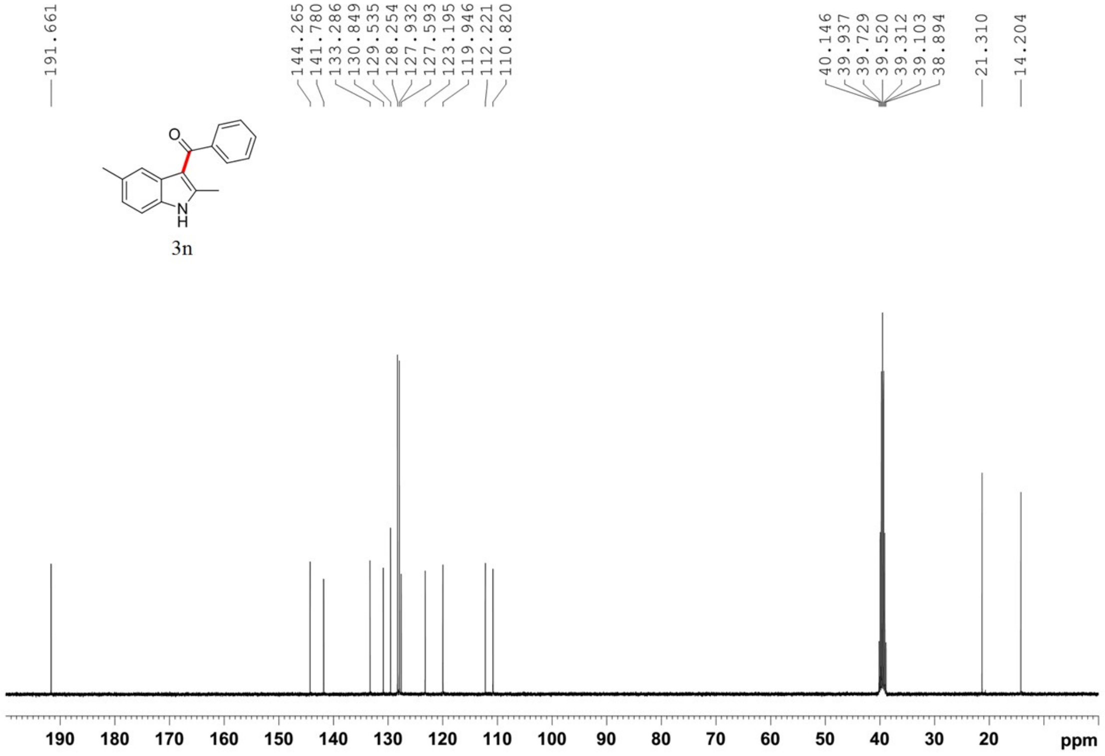
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39.312
39.103
38.894
21.310
14.204
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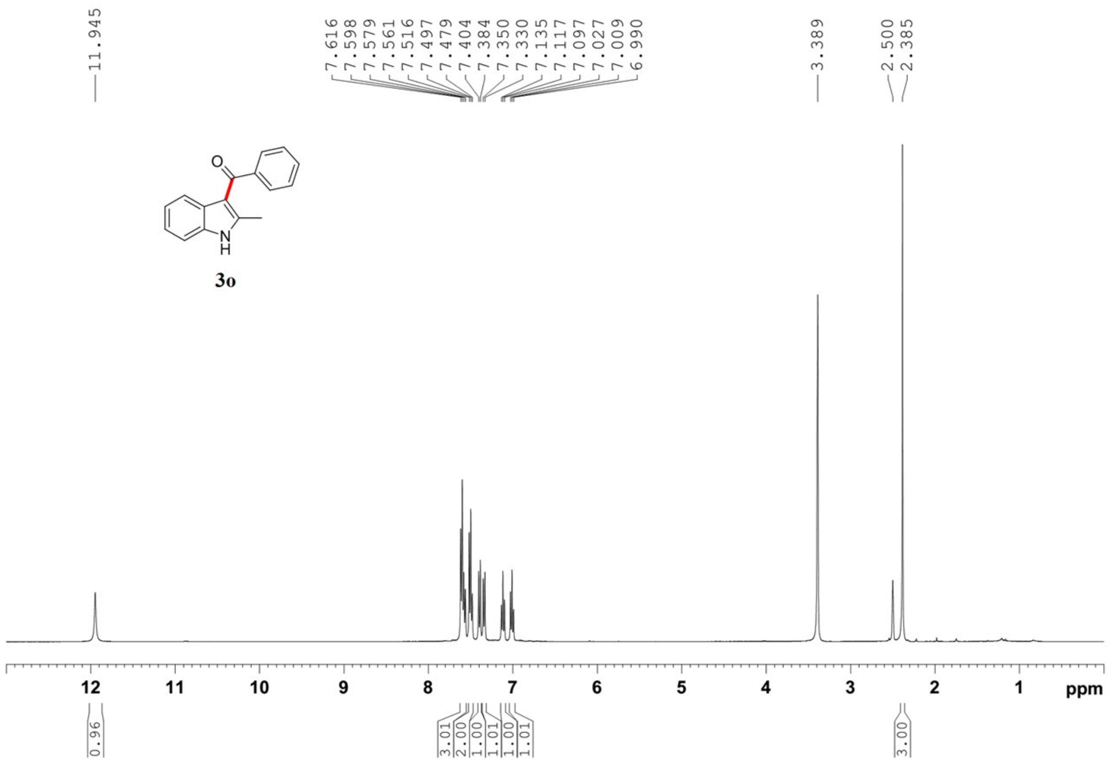
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7.516
7.497
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7.404
7.384
7.350
7.330
7.135
7.117
7.097
7.027
7.009
6.990
3.389
2.500
2.385
O
N
H
12
11
10
9
8
7
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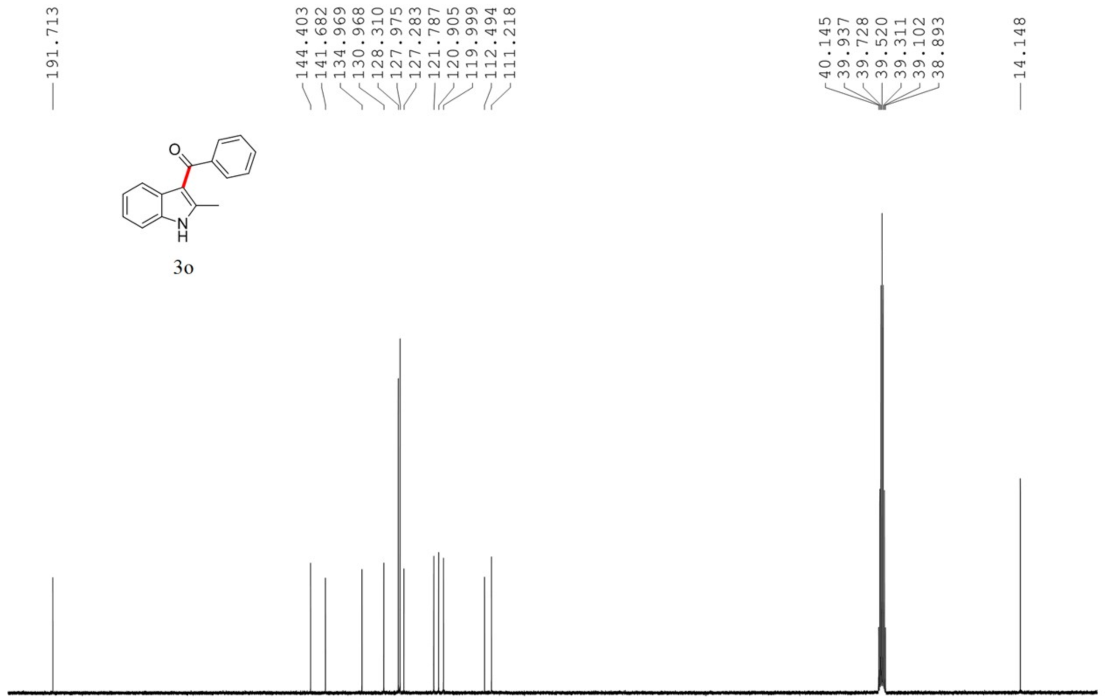
1.00
1.01
3.00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112.494
111.218
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39.728
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39.311
39.102
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14.148
O
N
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160
150
140
130
120
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100
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30
20
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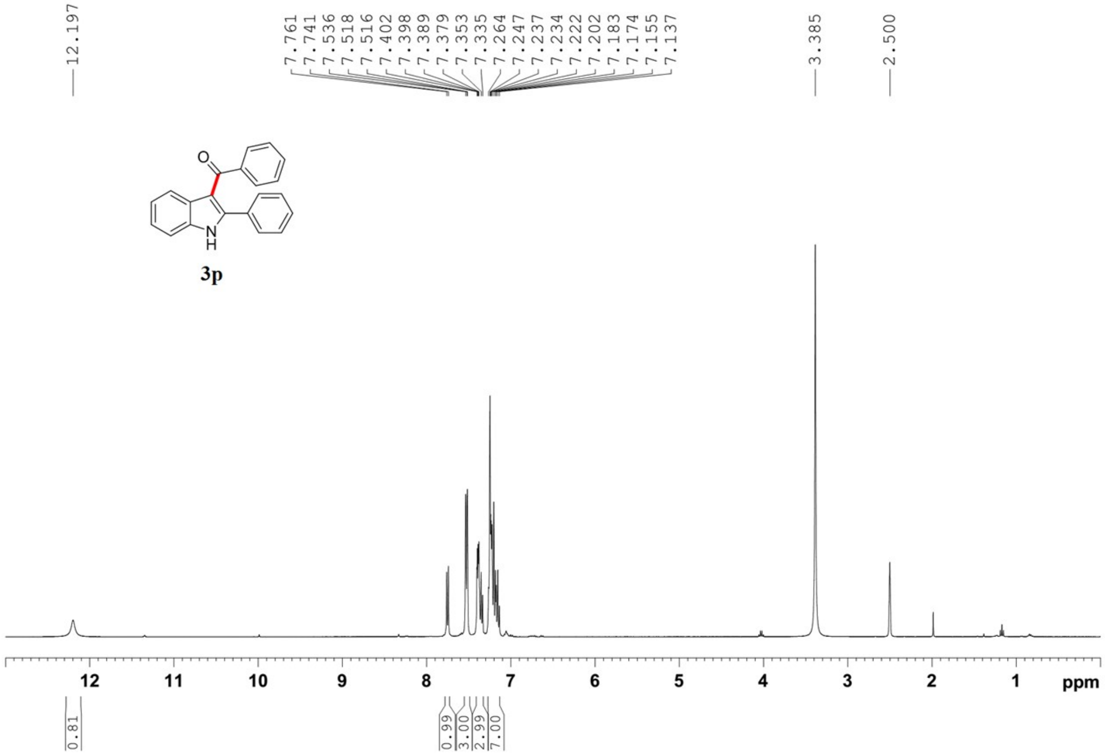
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7.402
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7.389
7.379
7.353
7.335
7.264
7.247
7.237
7.234
7.222
7.202
7.183
7.174
7.155
7.137
3.385
2.500
O
N
H
12
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6
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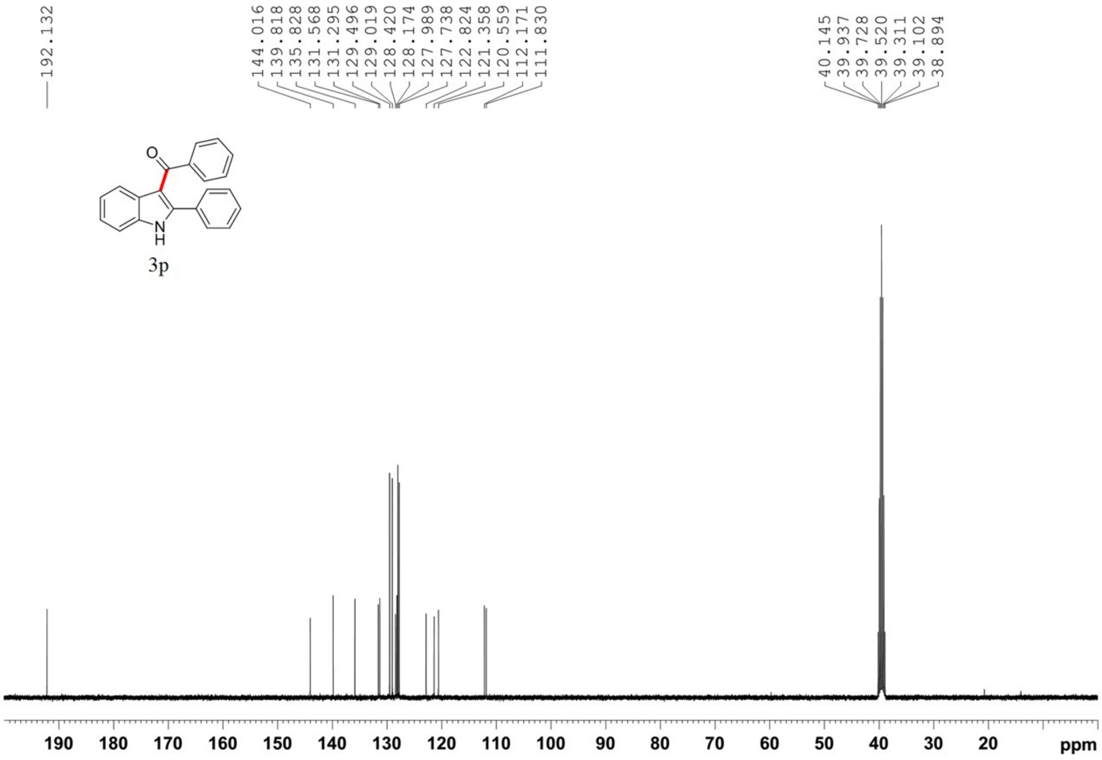
2.99
7.00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127.738
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121.358
120.559
112.171
111.830
40.145
39.937
39.728
39.520
39.311
39.102
38.894
O
N
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150
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120
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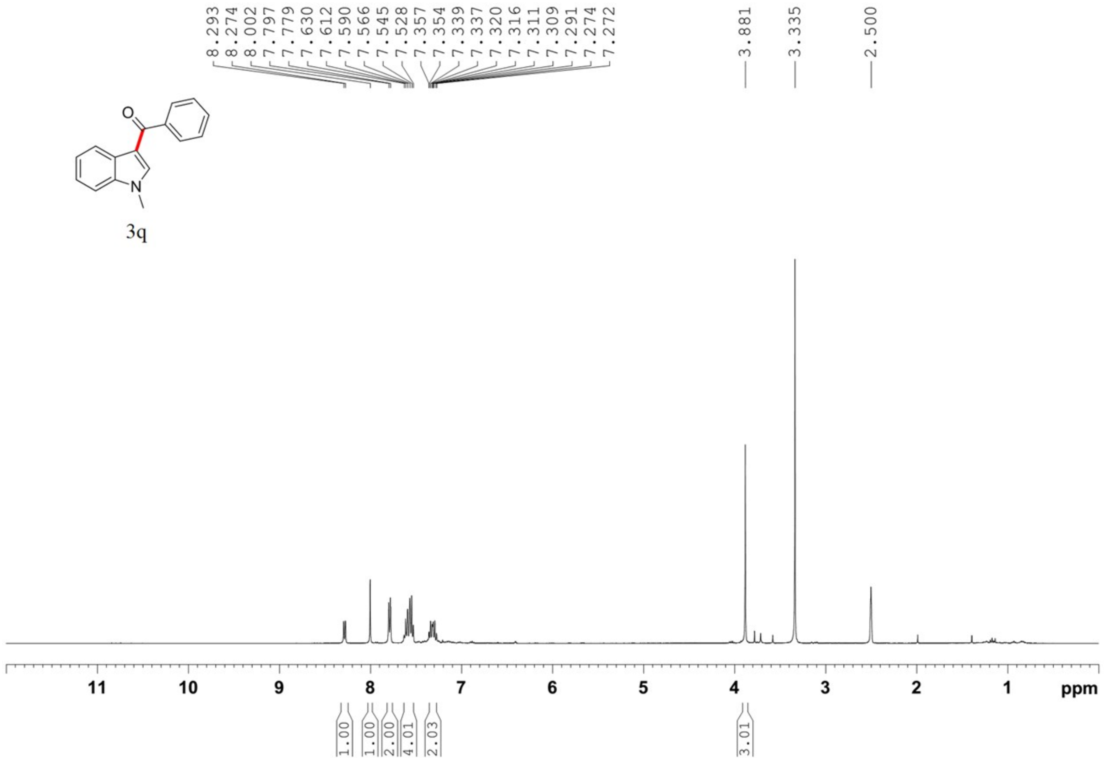
20
ppm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7.545
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7.354
7.339
7.337
7.320
7.316
7.311
7.309
7.291
7.274
7.272
3.881
3.335
2.500
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N
3q
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1.00
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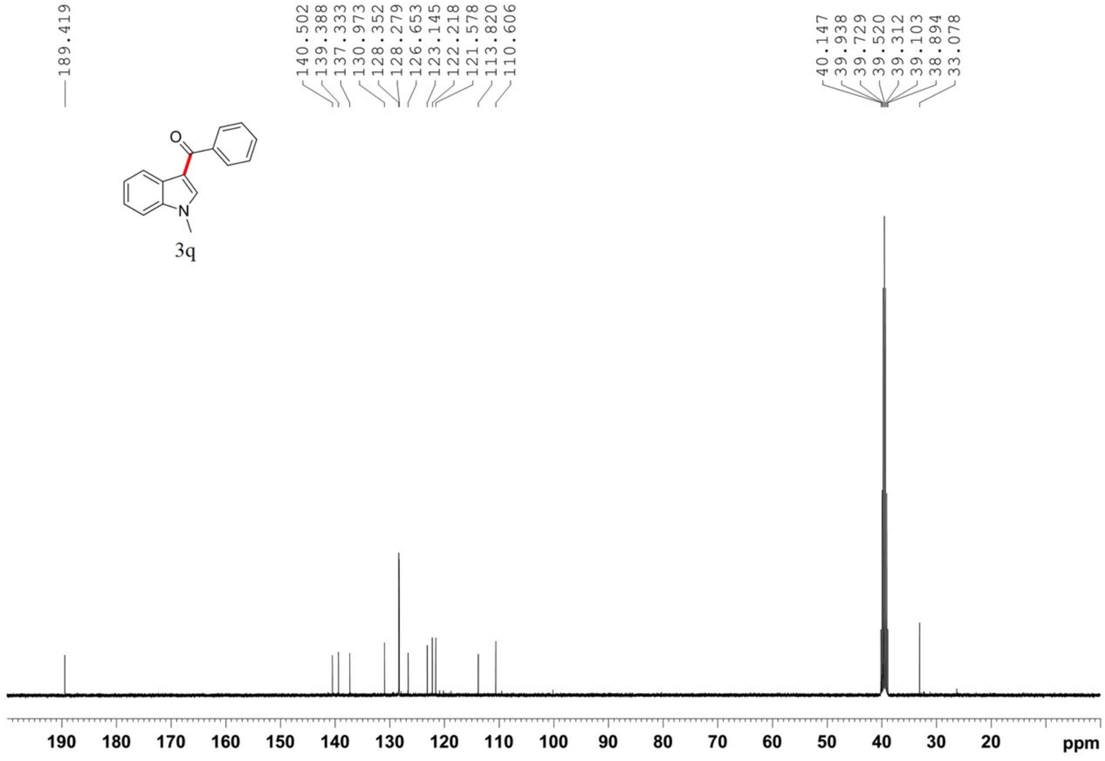
3.01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126.653
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121.578
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110.606
40.147
39.938
39.729
39.520
39.312
39.103
38.894
33.078
O
N
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120
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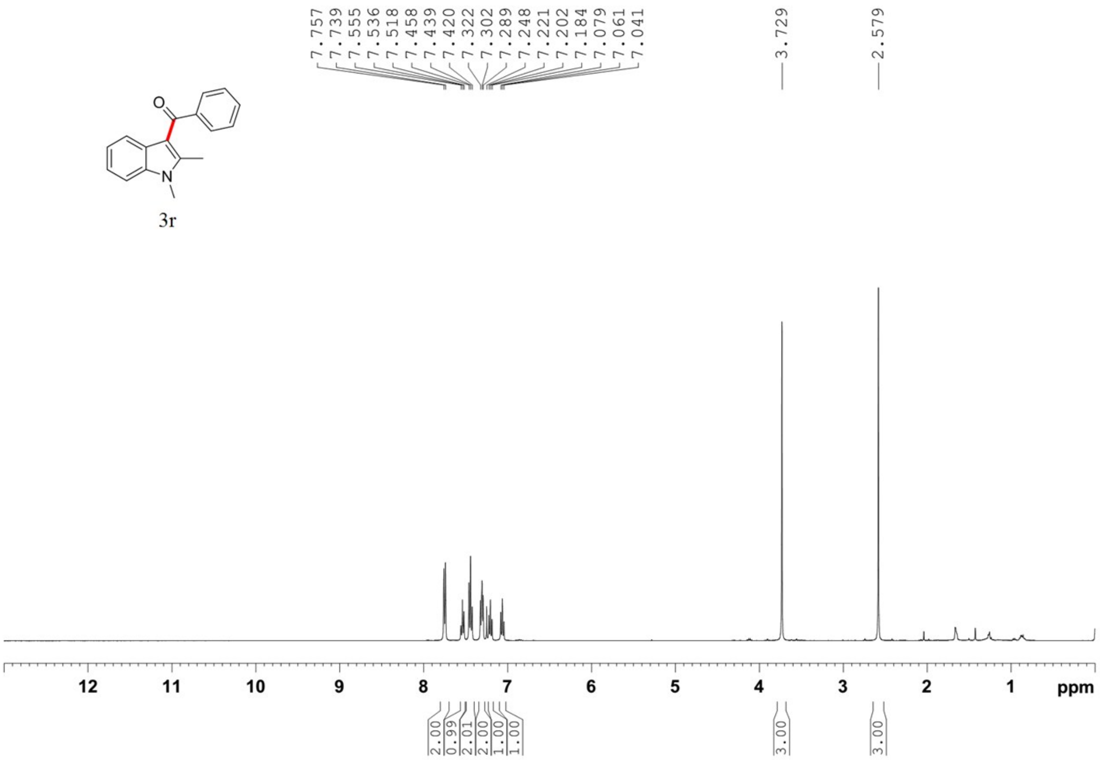
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7.221
7.202
7.184
7.079
7.061
7.041
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N
3r
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9
8
7
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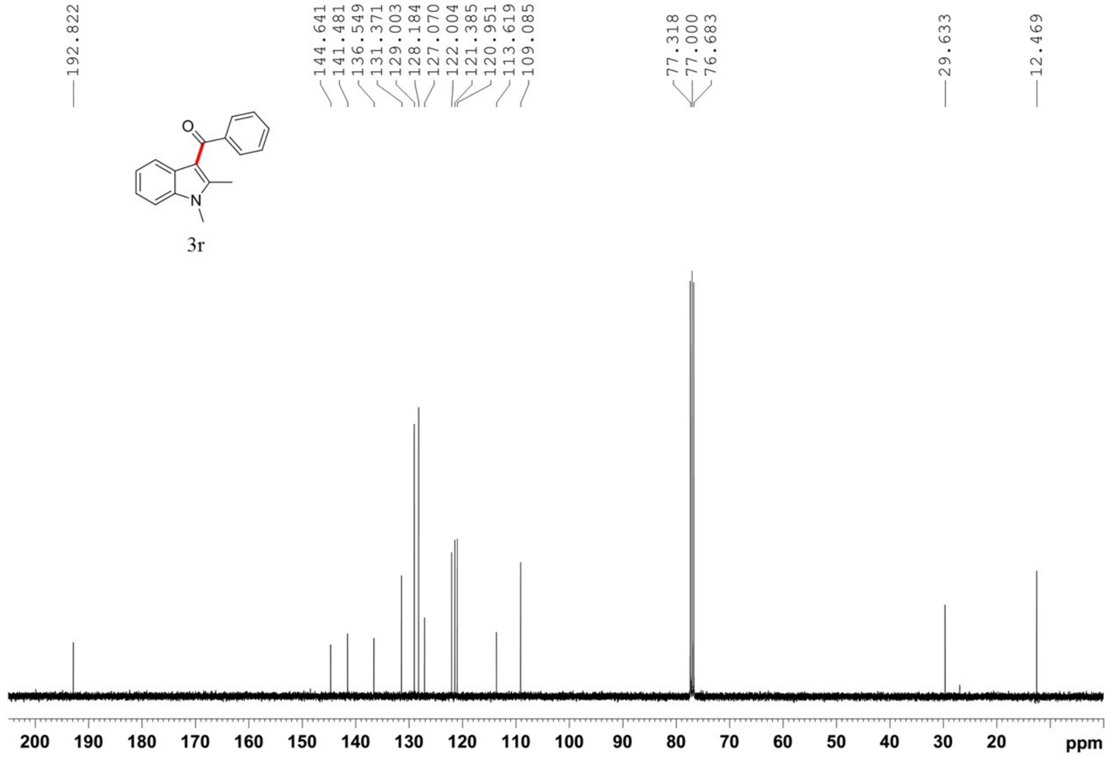
3.00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77.000
76.683
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N
3r
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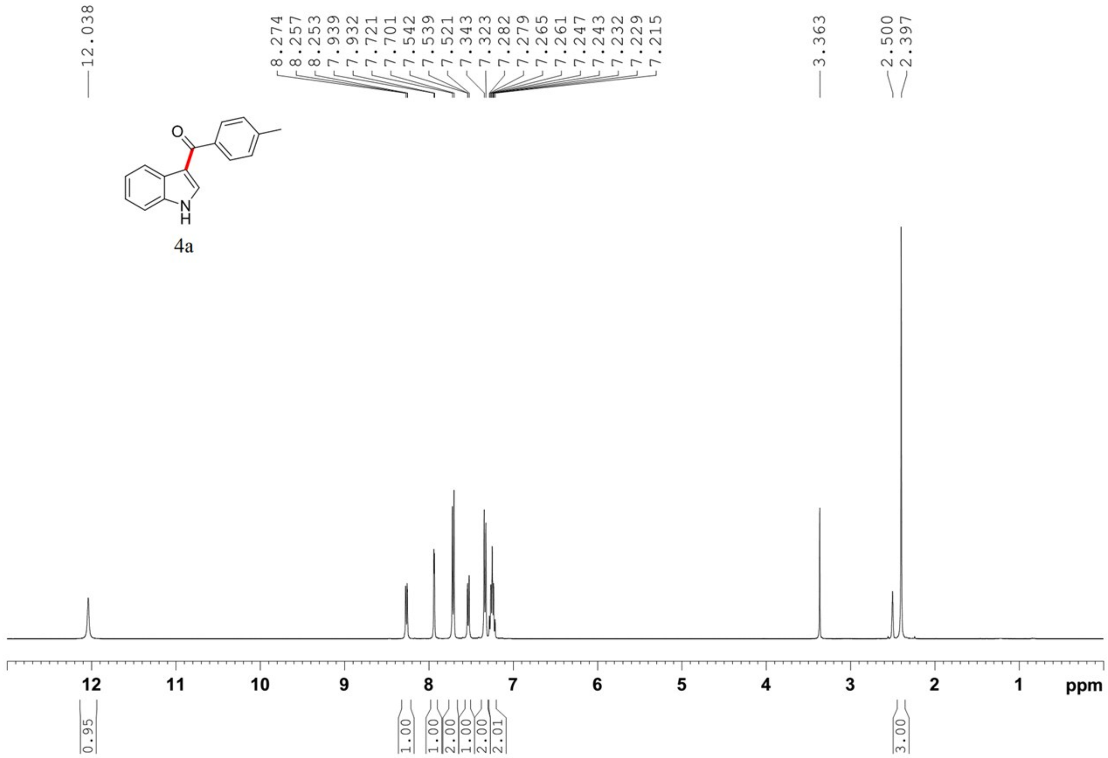
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7.343
7.323
7.282
7.279
7.265
7.261
7.247
7.243
7.232
7.229
7.215
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2.397
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N
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11
10
9
8
7
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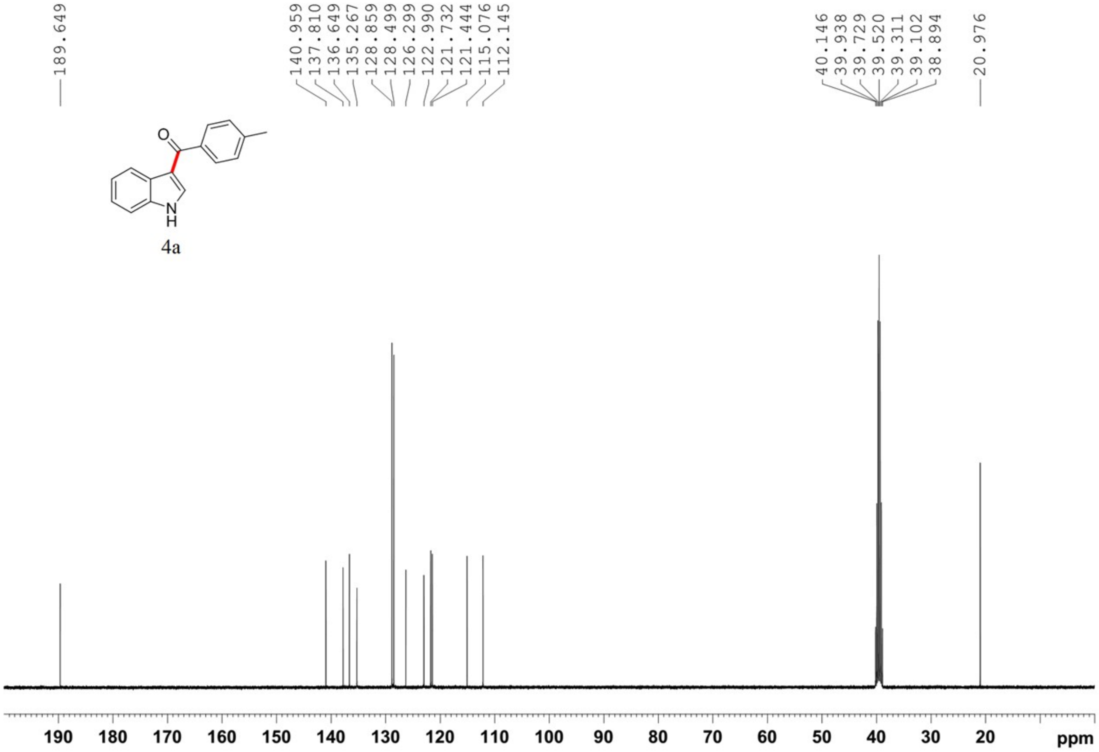
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39.102
38.894
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N
H
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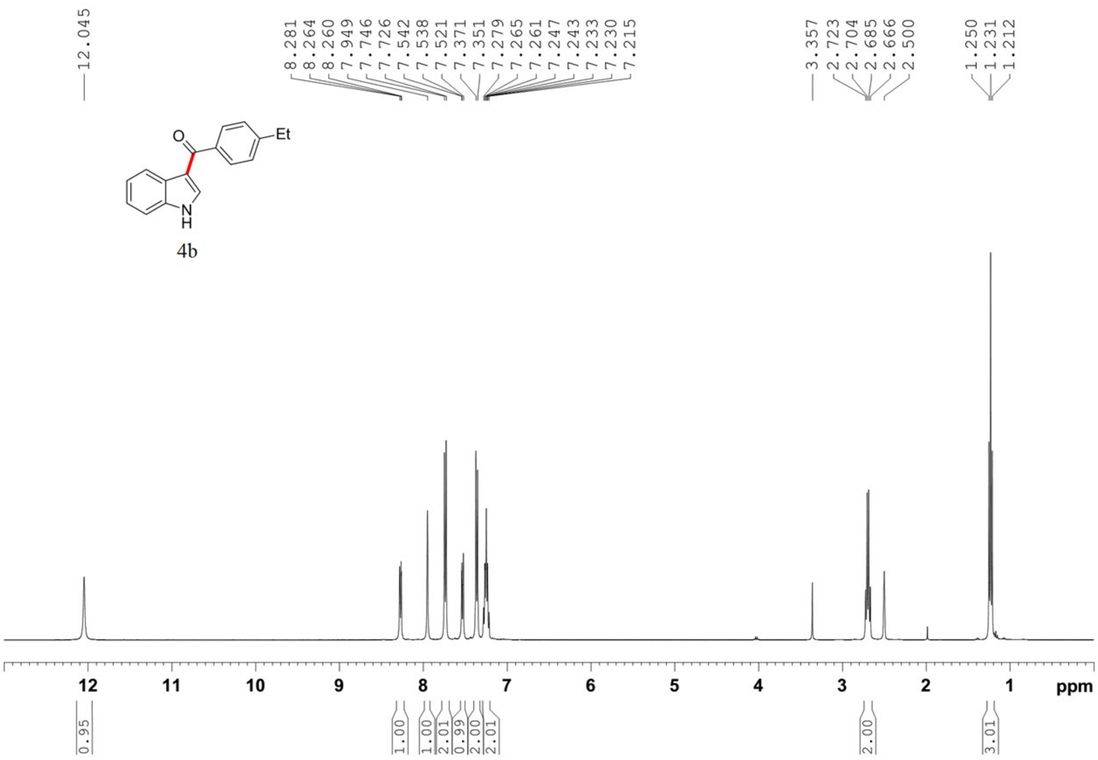
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7.265
7.261
7.247
7.243
7.233
7.230
7.215
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2.685
2.666
2.500
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1.231
1.212
O
Et
N
H
12
11
10
9
8
7
6
5
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ppm
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1.00
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0.99
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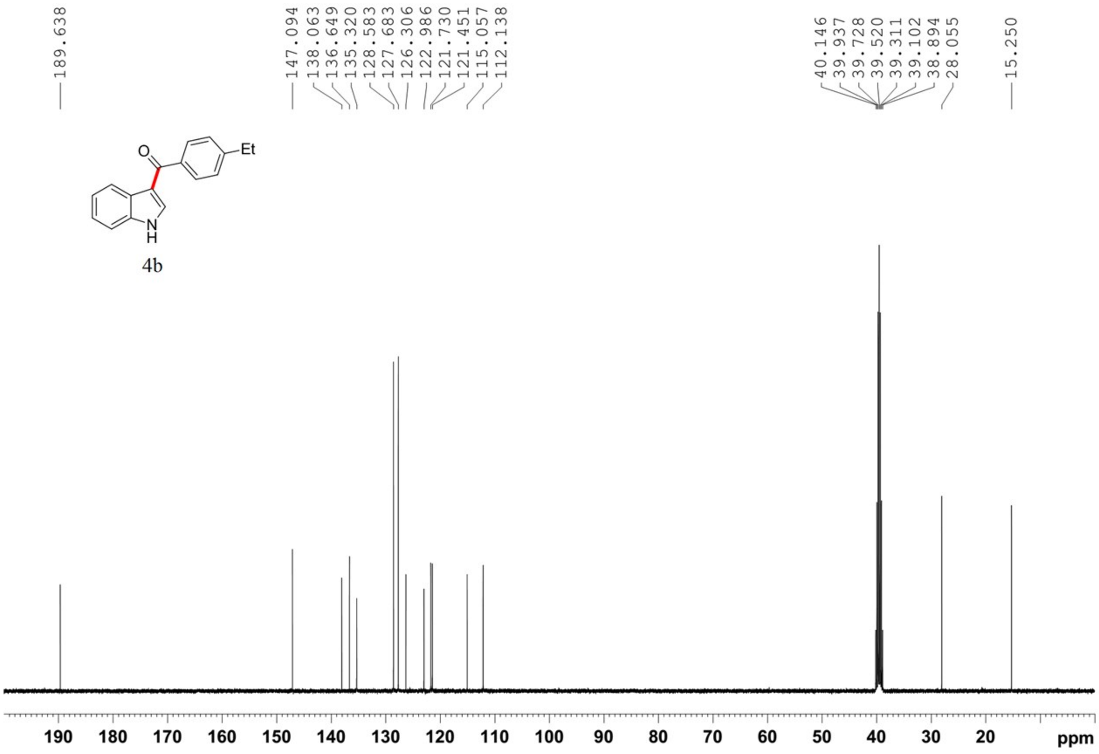
2.01
2.00
3.01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121.730
121.451
115.057
112.138
40.146
39.937
39.728
39.520
39.311
39.102
38.894
28.055
15.250
O
Et
N
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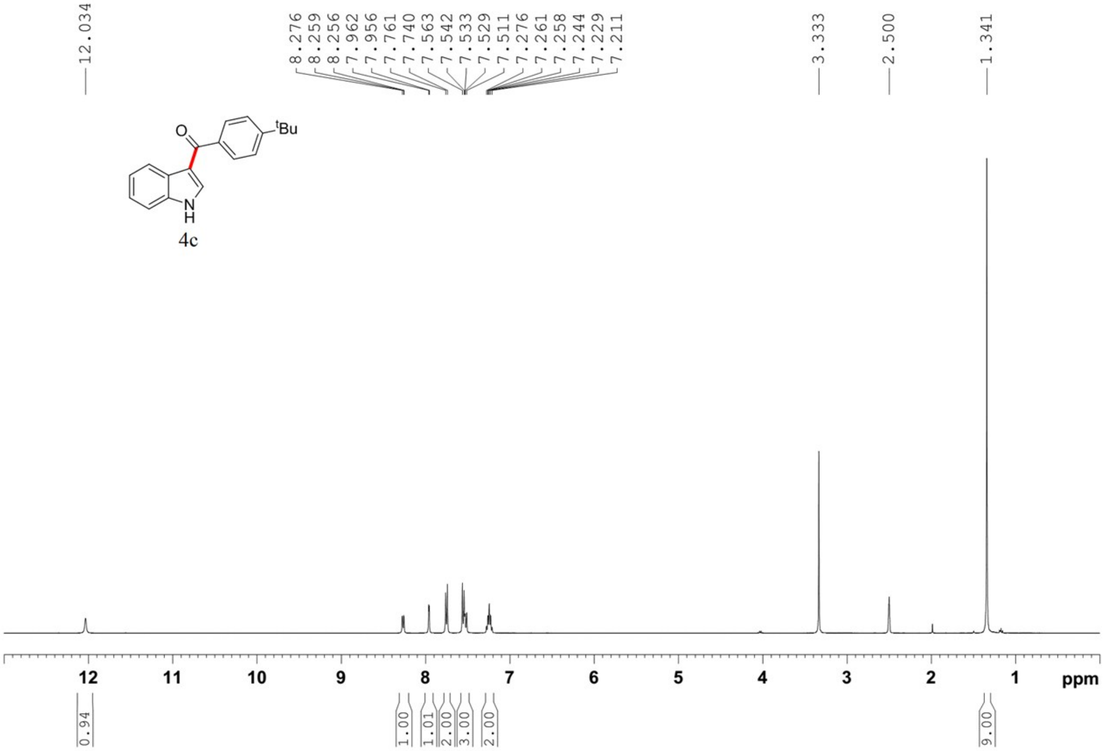
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7.533
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7.511
7.276
7.261
7.258
7.244
7.229
7.211
3.333
2.500
1.341
O
ᵗBu
N
H
4c
12
11
10
9
8
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3
2
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ppm
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1.01
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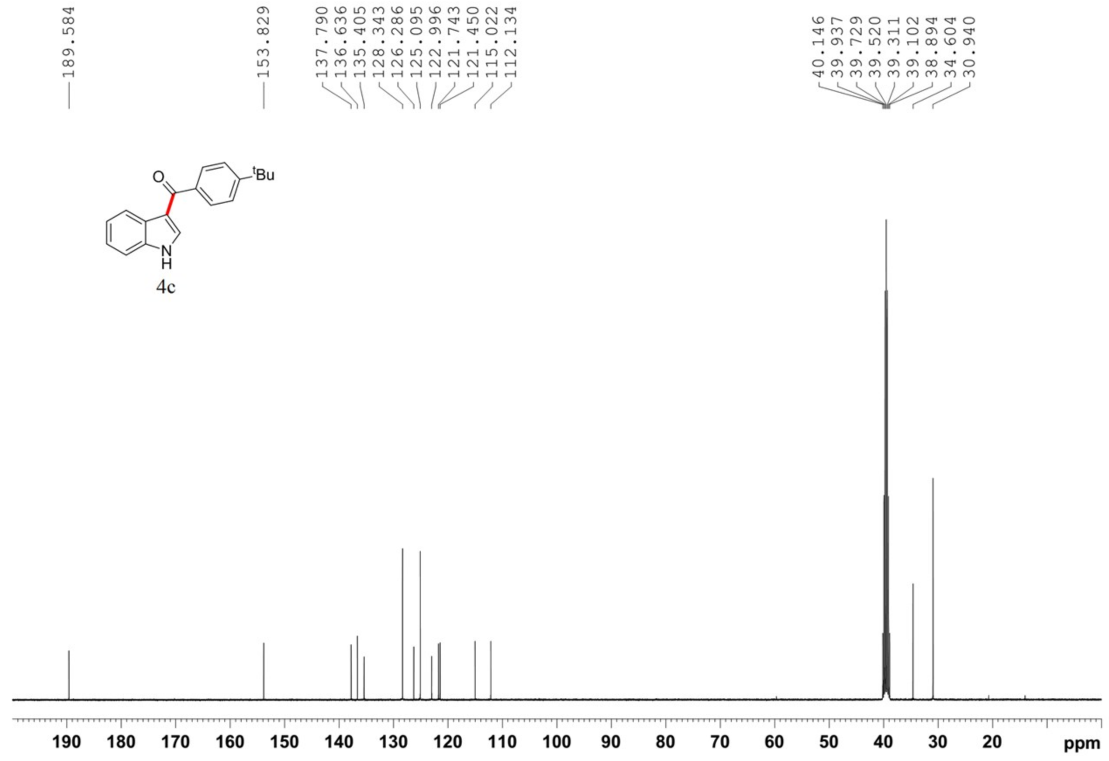
9.00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121.743
121.450
115.022
112.134
40.146
39.937
39.729
39.520
39.311
39.102
38.894
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ᵗBu
N
H
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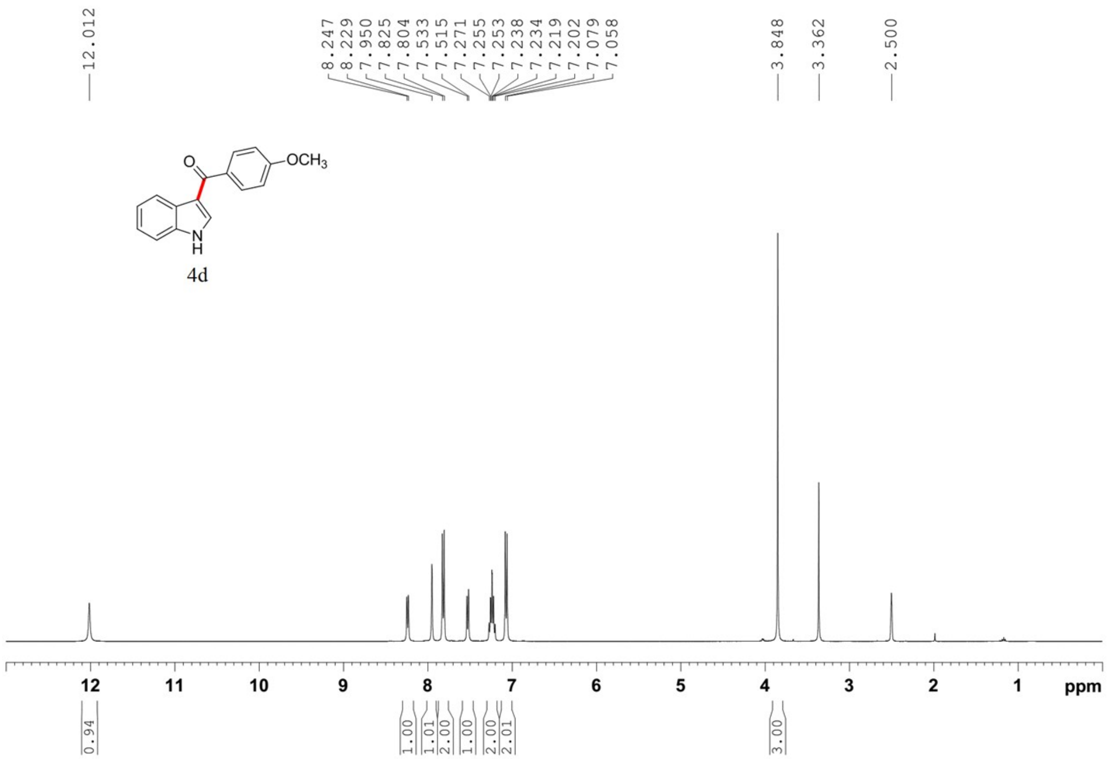
4d

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7.219
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7.058
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O
N
H
12
11
10
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8
7
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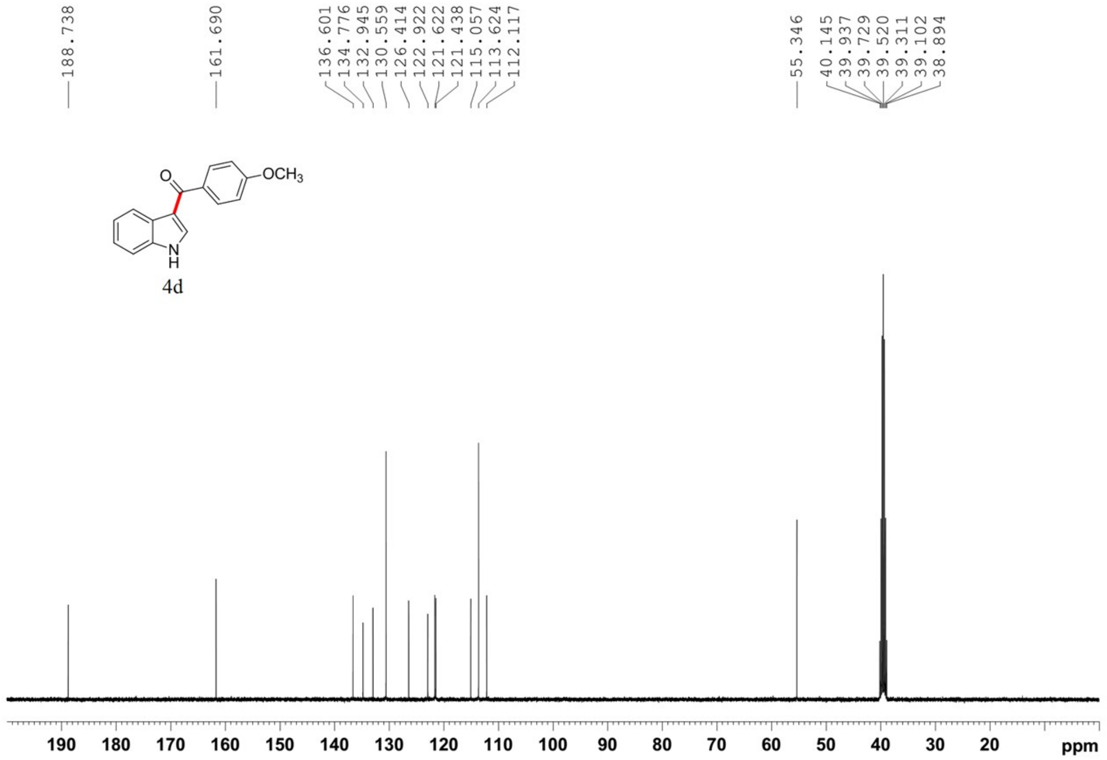
3.00


4d

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113.624
112.117
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40.145
39.937
39.729
39.520
39.311
39.102
38.894
OCH3
O
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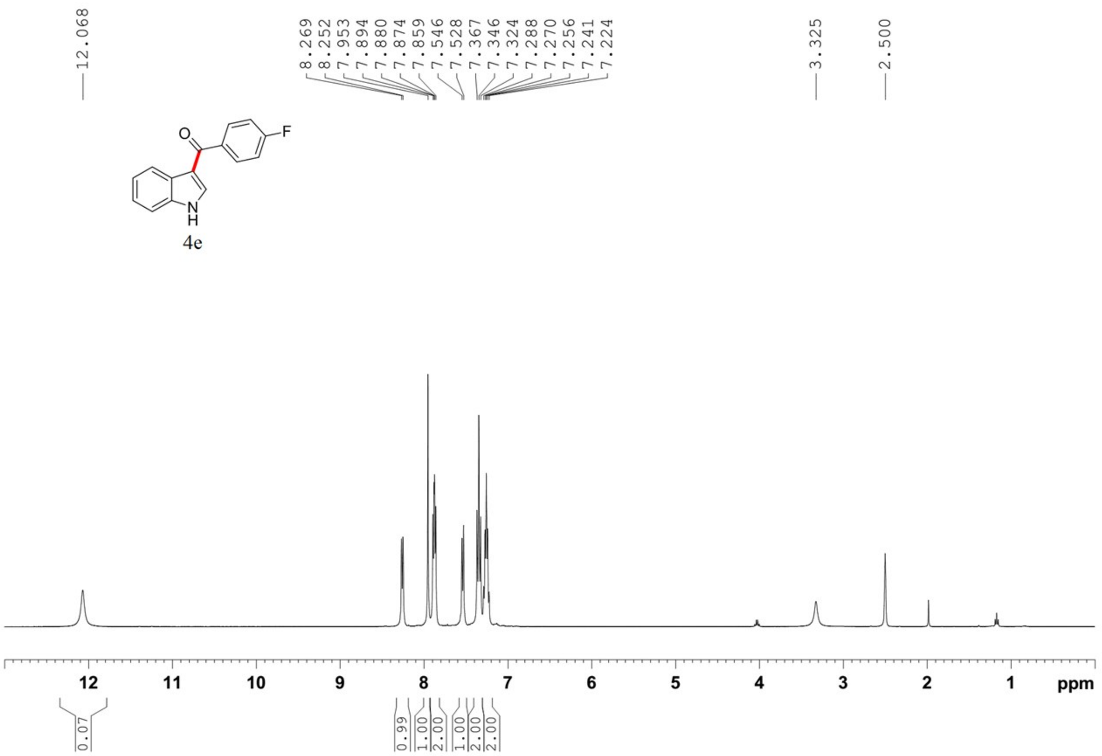
20
ppm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7.367
7.346
7.324
7.288
7.270
7.256
7.241
7.224
3.325
2.500
O
F
N
H
4e
12
11
10
9
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2
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ppm
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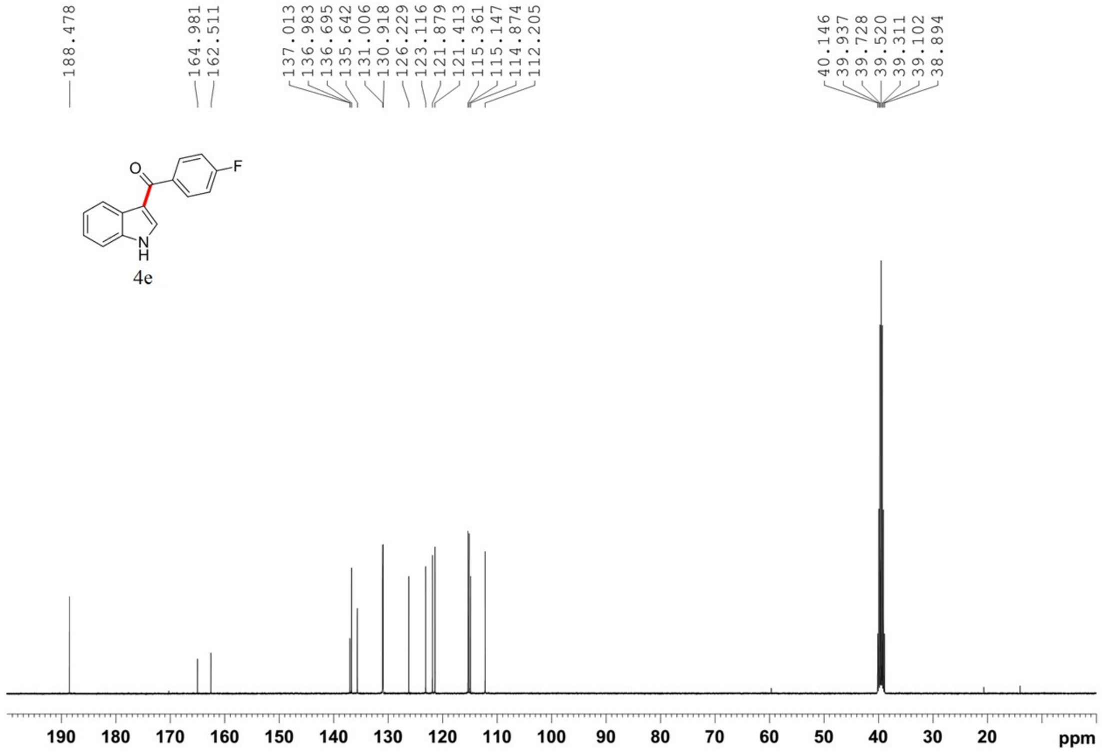
2.00
2.00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121.879
121.413
115.361
115.147
114.874
112.205
40.146
39.937
39.728
39.520
39.311
39.102
38.894
O
F
N
H
4e
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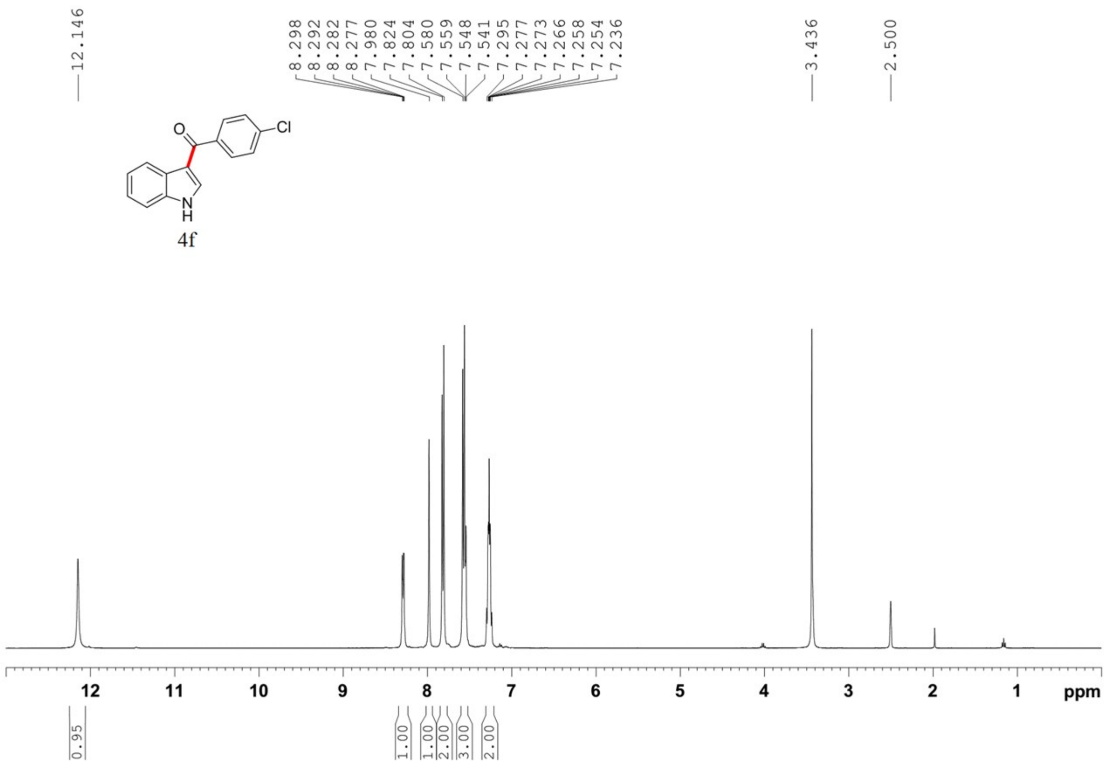
4f
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7.824
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7.580
7.559
7.548
7.541
7.295
7.277
7.273
7.266
7.258
7.254
7.236
3.436
2.500
O
Cl
N
H
12
11
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5
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3
2
1
ppm
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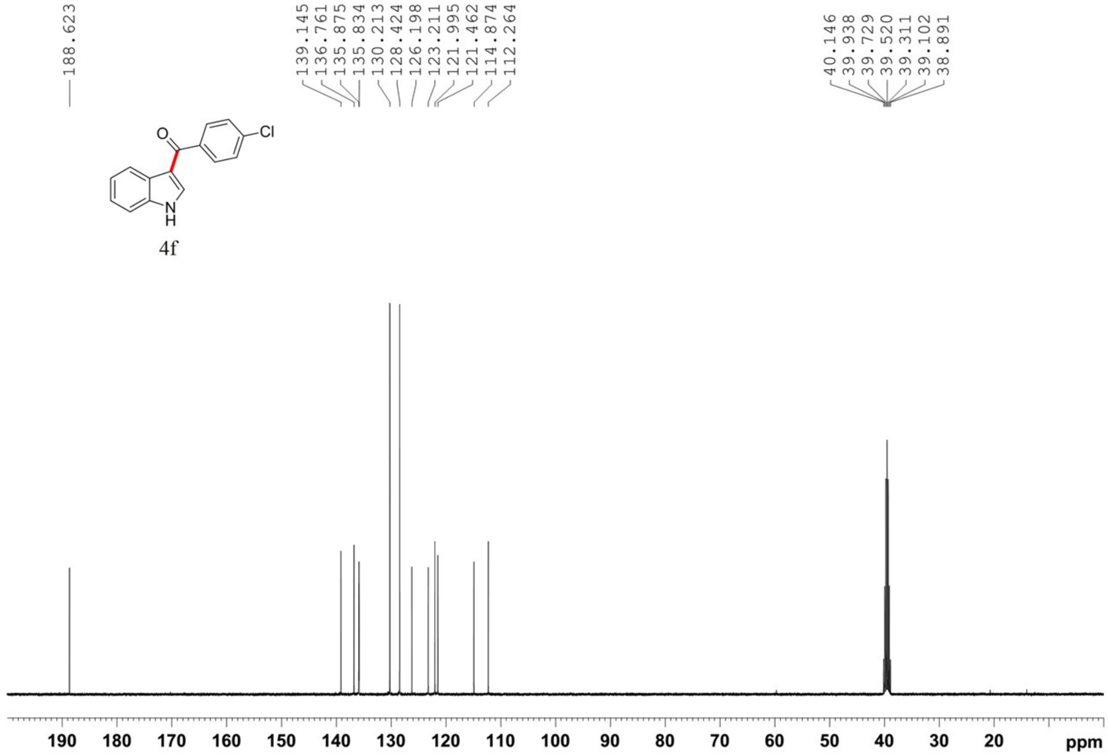
3.00
2.00


4f
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135.875
135.834
130.213
128.424
126.198
123.211
121.995
121.462
114.874
112.264
40.146
39.938
39.729
39.520
39.311
39.102
38.891
O
Cl
N
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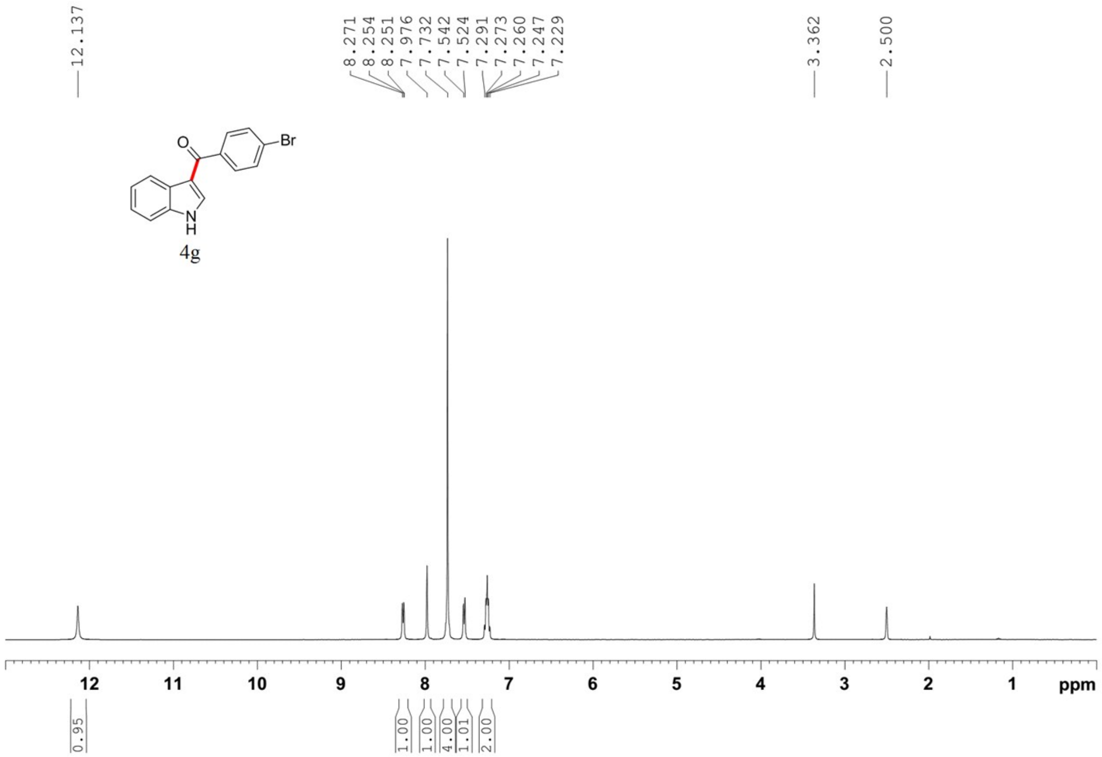
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7.273
7.260
7.247
7.229
3.362
2.500
O
Br
N
H
12
11
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5
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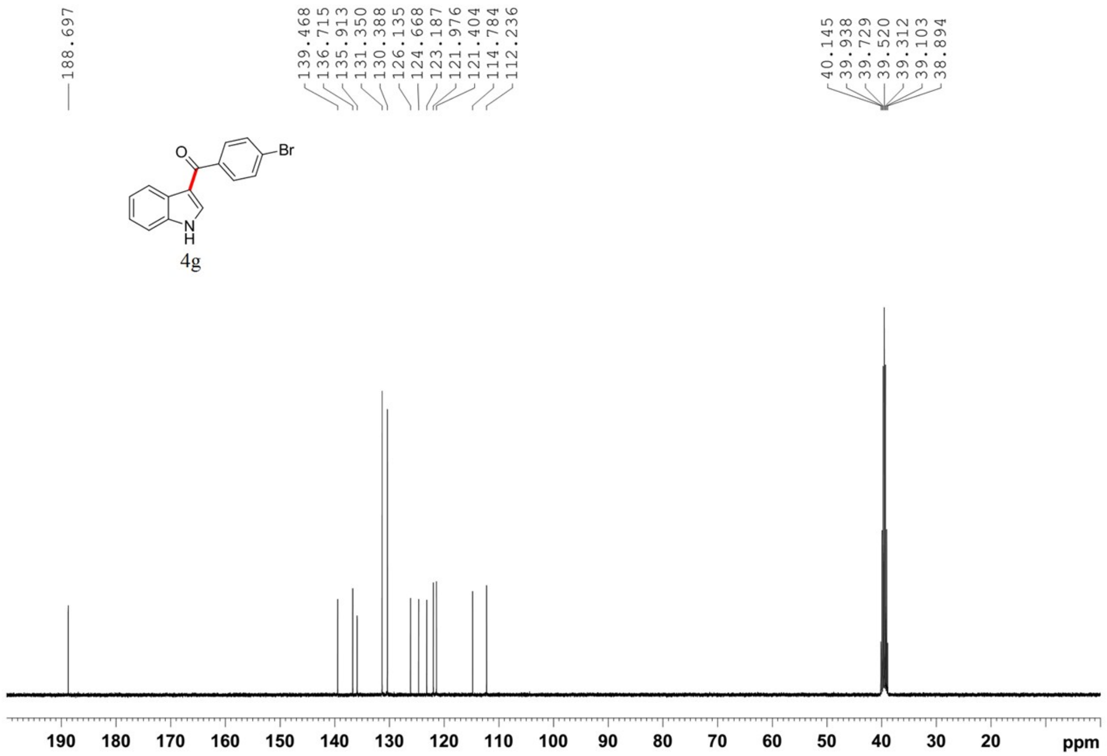
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121.404
114.784
112.236
40.145
39.938
39.729
39.520
39.312
39.103
38.894
O
Br
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H
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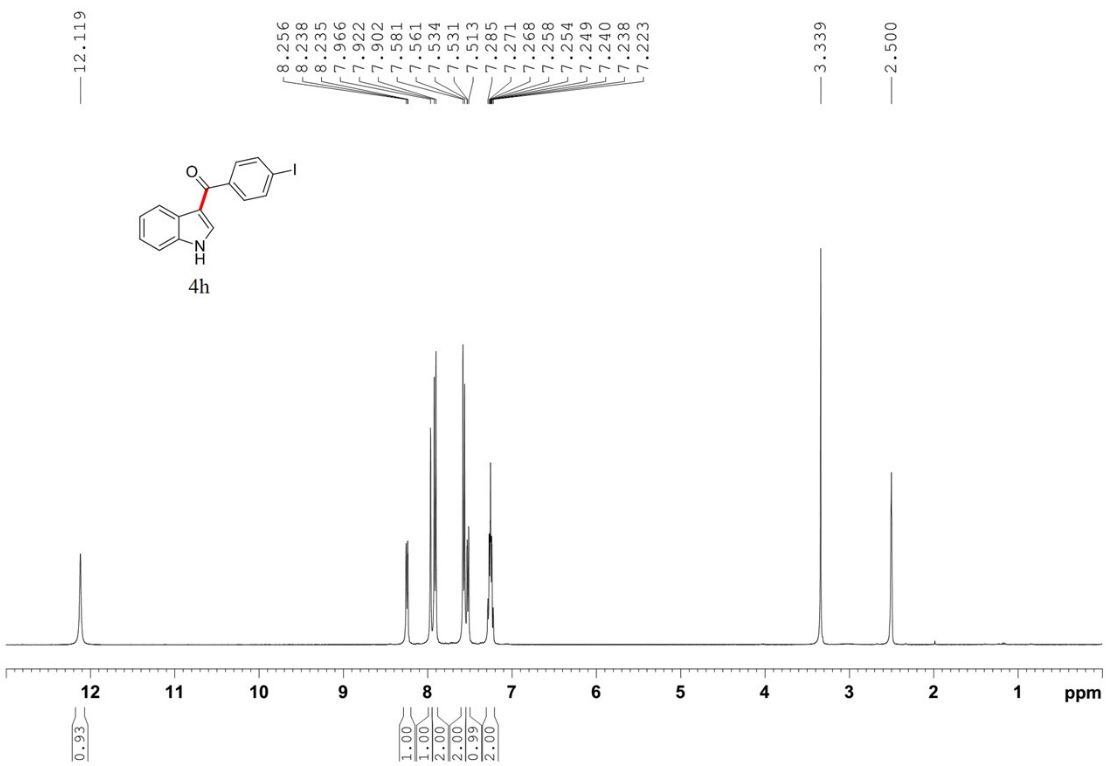
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7.902
7.581
7.561
7.534
7.531
7.513
7.285
7.271
7.268
7.258
7.254
7.249
7.240
7.238
7.223
3.339
2.500
O
I
N
H
4h
12
11
10
9
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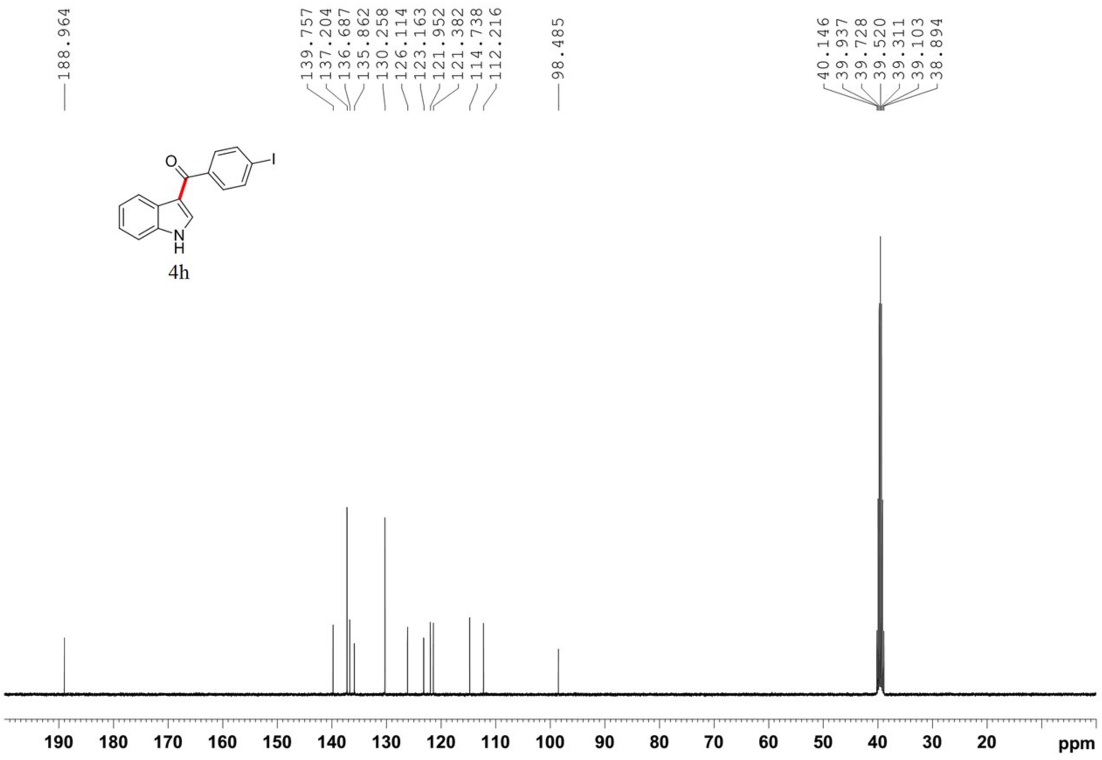
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137.204
136.687
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126.114
123.163
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121.382
114.738
112.216
98.485
40.146
39.937
39.728
39.520
39.311
39.103
38.894
O
I
N
H
4h
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160
150
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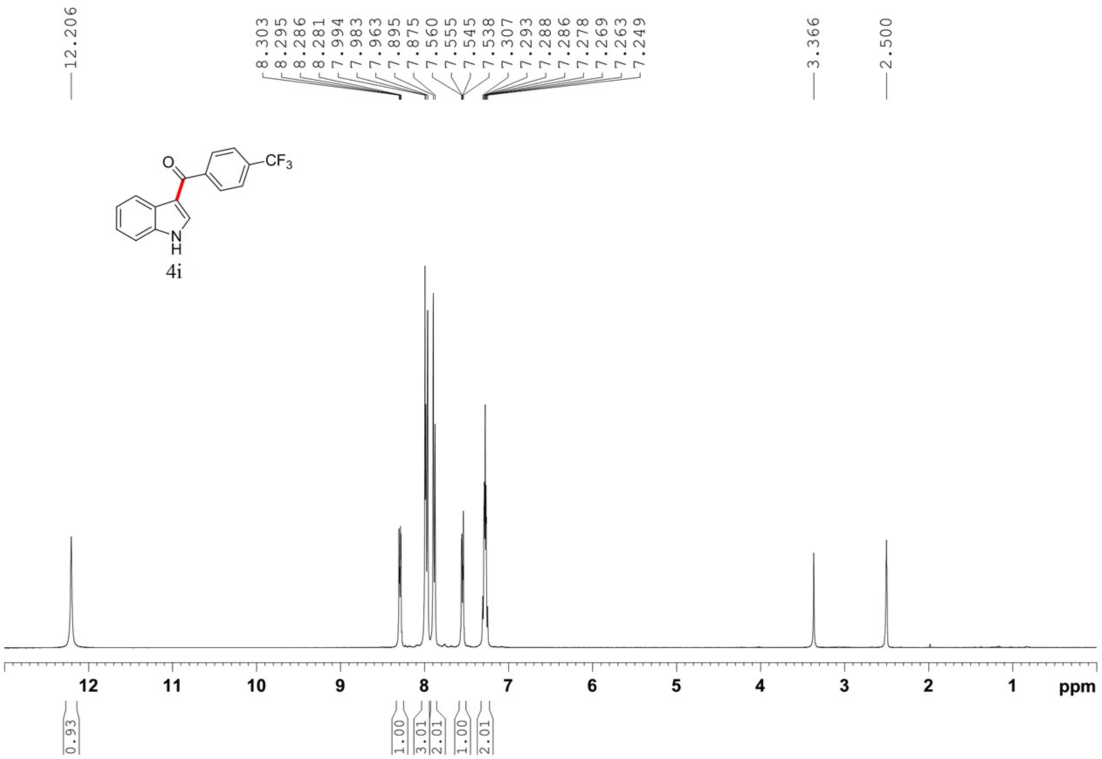
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7.963
7.895
7.875
7.560
7.555
7.545
7.538
7.307
7.293
7.288
7.286
7.278
7.269
7.263
7.249
3.366
2.500
O
CF3
N
H
12
11
10
9
8
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4
3
2
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ppm
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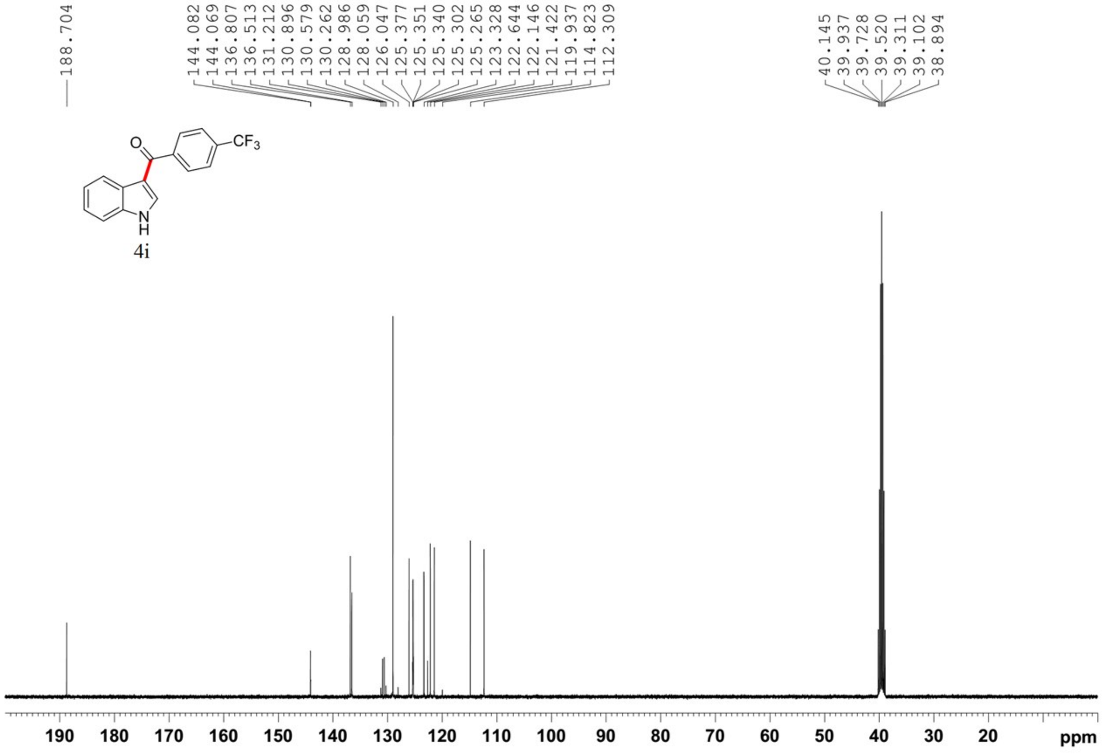
3.01
2.01
1.00
2.01

4i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125.377
125.351
125.340
125.302
125.265
123.328
122.644
122.146
121.422
119.937
114.823
112.309
40.145
39.937
39.728
39.520
39.311
39.102
38.894
O
CF3
N
H
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30
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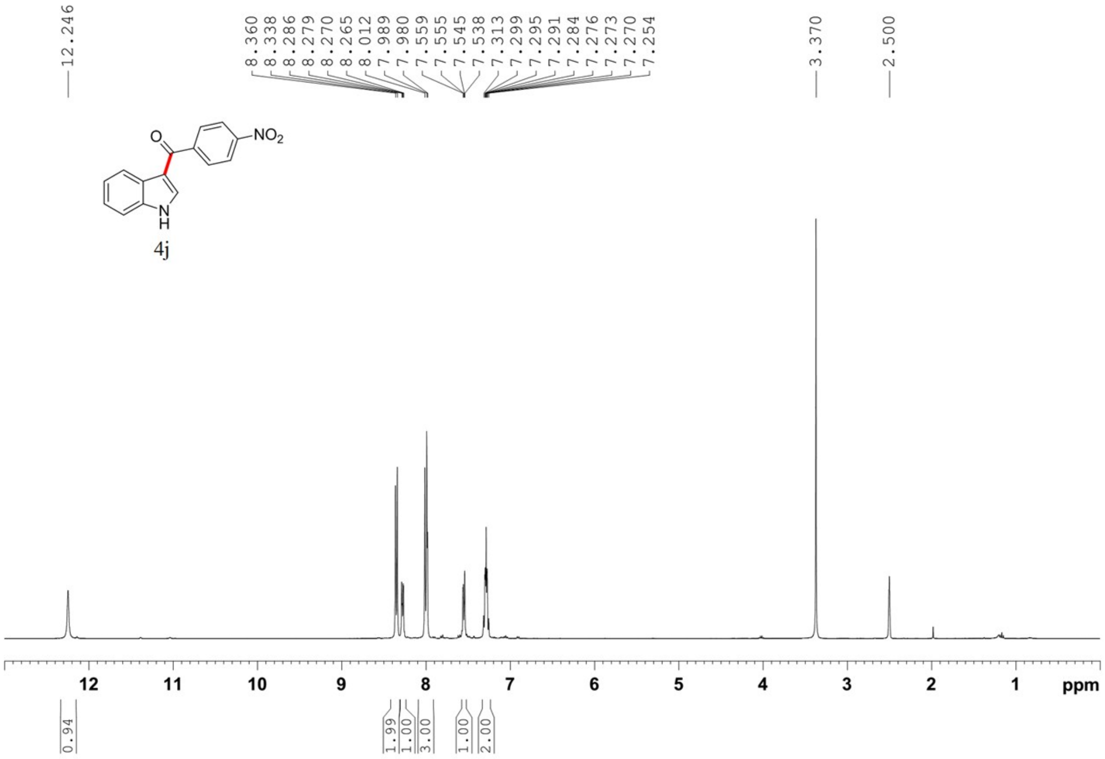
ppm

4i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7.980
7.559
7.555
7.545
7.538
7.313
7.299
7.295
7.291
7.284
7.276
7.273
7.270
7.254
3.370
2.500
O
NO2
N
H
4j
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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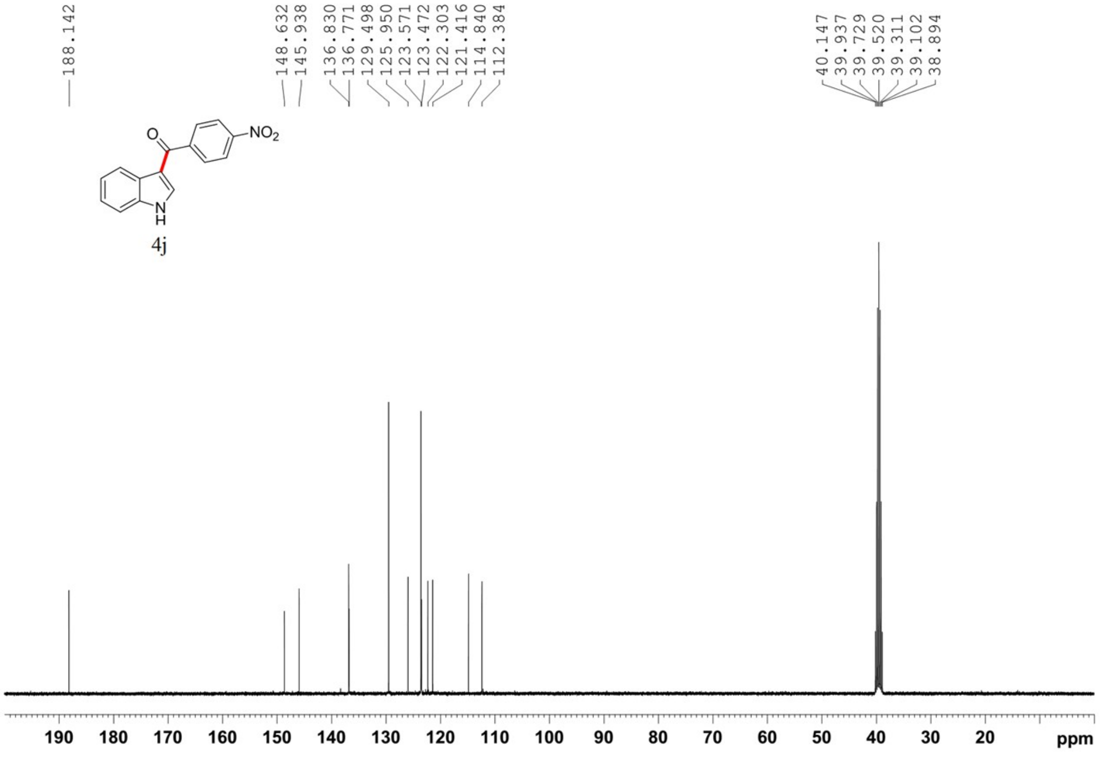
1.99
1.00
3.00
1.00
2.00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136.771
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123.571
123.472
122.303
121.416
114.840
112.384
40.147
39.937
39.729
39.520
39.311
39.102
38.894
O
NO2
N
H
4j
190
180
170
160
150
140
130
120
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100
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80
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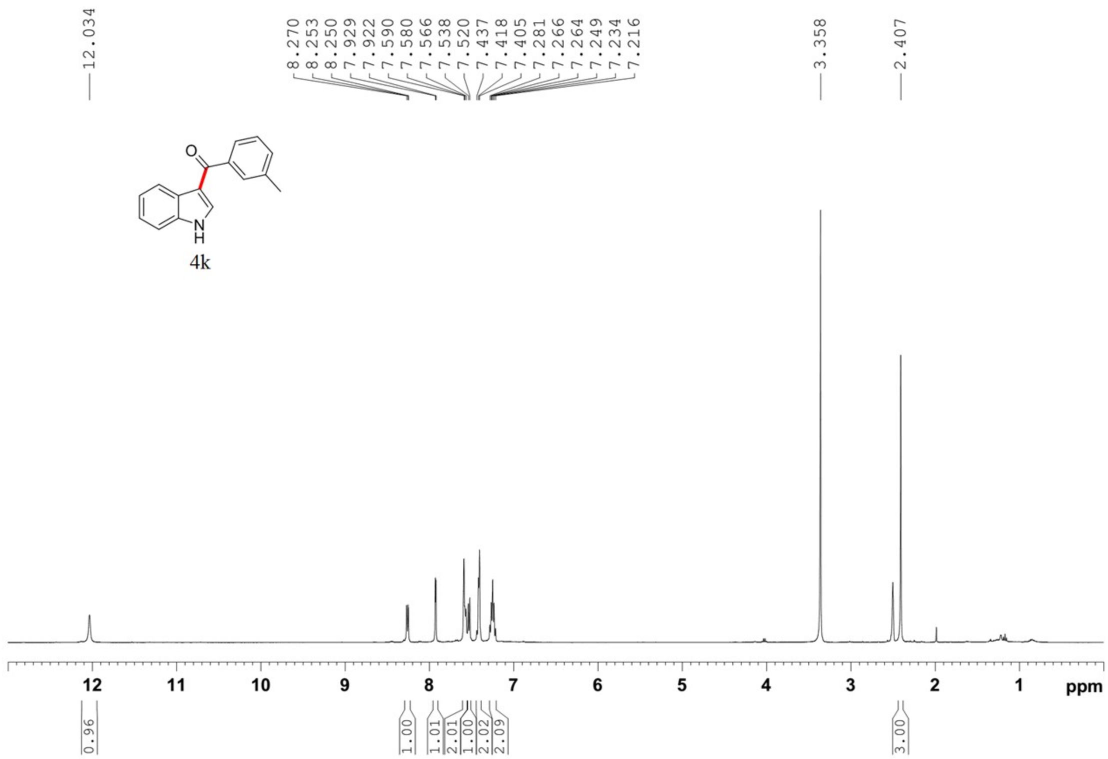
40
30
20
ppm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7.590
7.580
7.566
7.538
7.520
7.437
7.418
7.405
7.281
7.266
7.264
7.249
7.234
7.216
3.358
2.407
O
N
H
4k
12
11
10
9
8
7
6
5
4
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2
1
ppm
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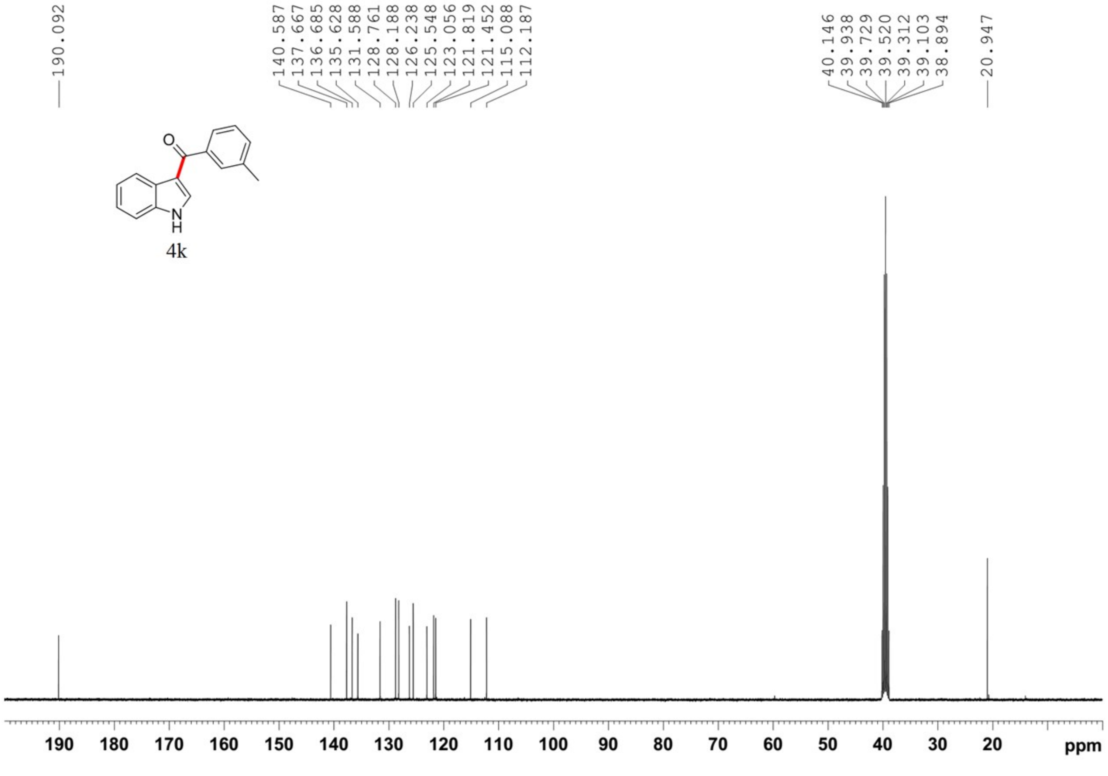
2.01
1.00
2.02
2.09
3.00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128.188
126.238
125.548
123.056
121.819
121.452
115.088
112.187
40.146
39.938
39.729
39.520
39.312
39.103
38.894
20.947
O
N
H
4k
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180
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160
150
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100
90
80
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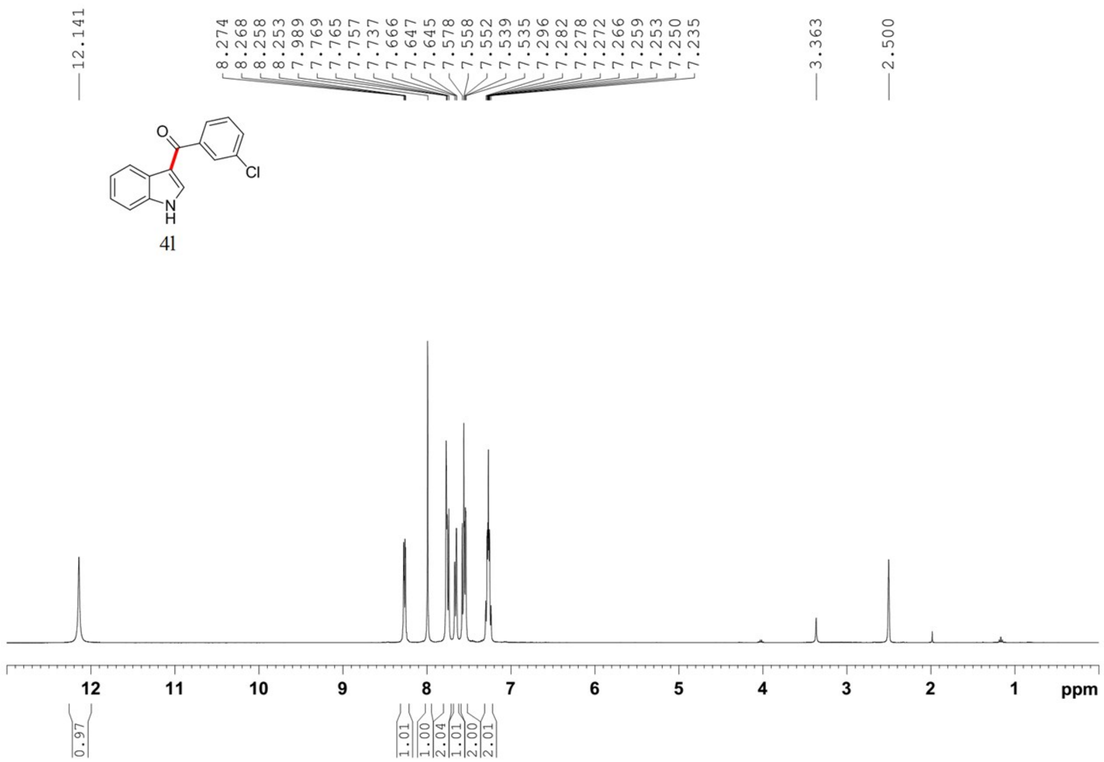
60
50
40
30
20
ppm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8.253
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7.769
7.765
7.757
7.737
7.666
7.647
7.645
7.578
7.558
7.552
7.539
7.535
7.296
7.282
7.278
7.272
7.266
7.259
7.253
7.250
7.235
3.363
2.500
O
Cl
N
H
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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2.04
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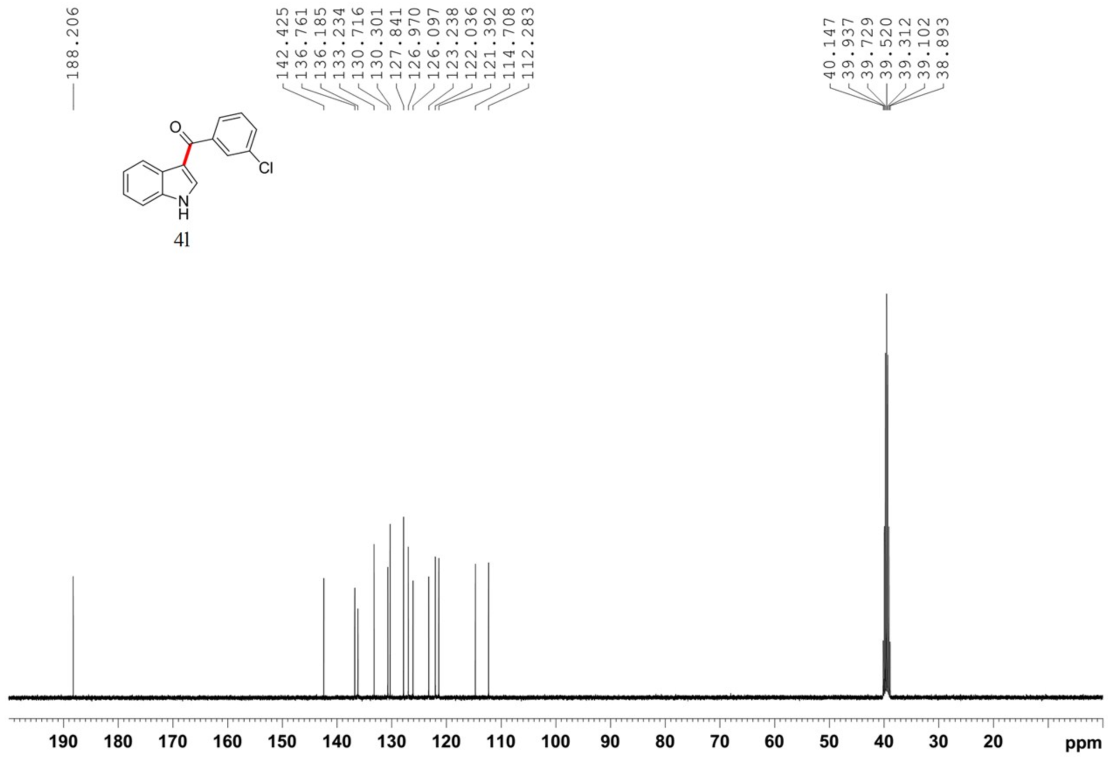
2.00
2.01

4l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130.716
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126.970
126.097
123.238
122.036
121.392
114.708
112.283
40.147
39.937
39.729
39.520
39.312
39.102
38.893
O
Cl
N
H
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150
140
130
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110
100
90
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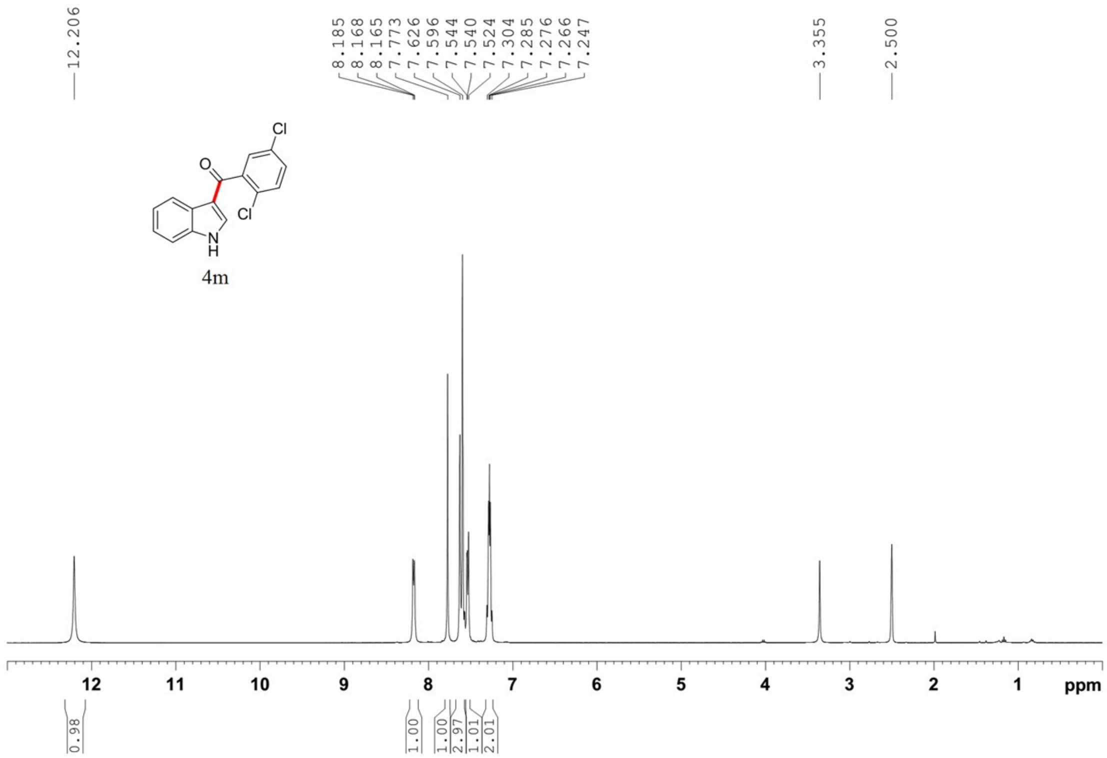
30
20
ppm

4l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7.544
7.540
7.524
7.304
7.285
7.276
7.266
7.247
3.355
2.500
O
Cl
Cl
N
H
4m
12
11
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4
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ppm
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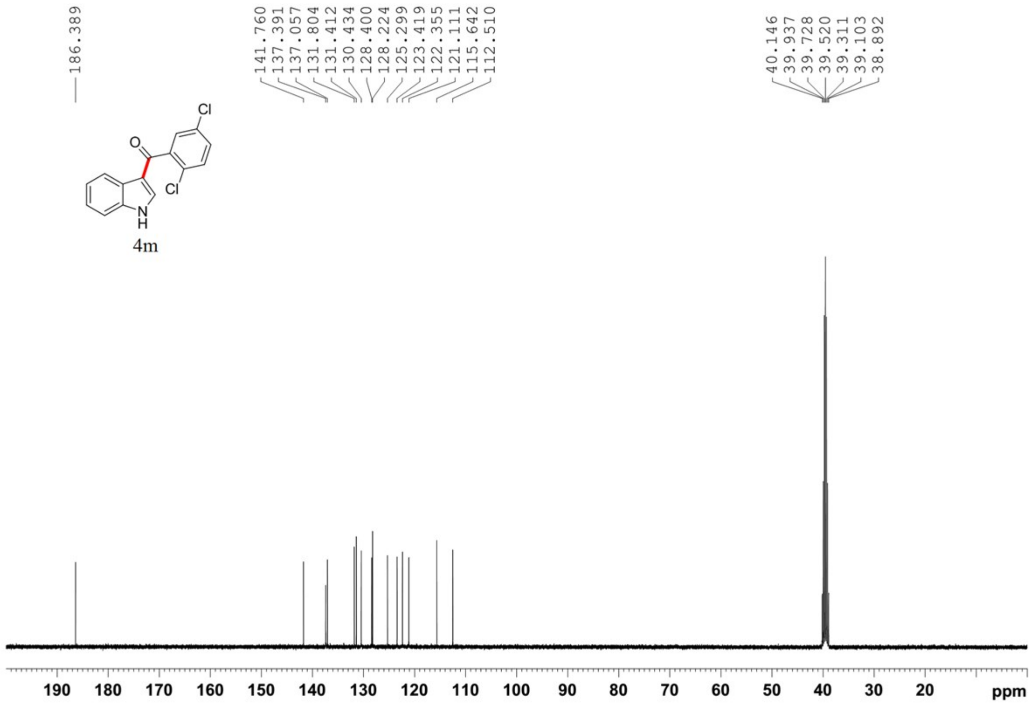
2.01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123.419
122.355
121.111
115.642
112.510
40.146
39.937
39.728
39.520
39.311
39.103
38.892
O
Cl
Cl
N
H
4m
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150
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80
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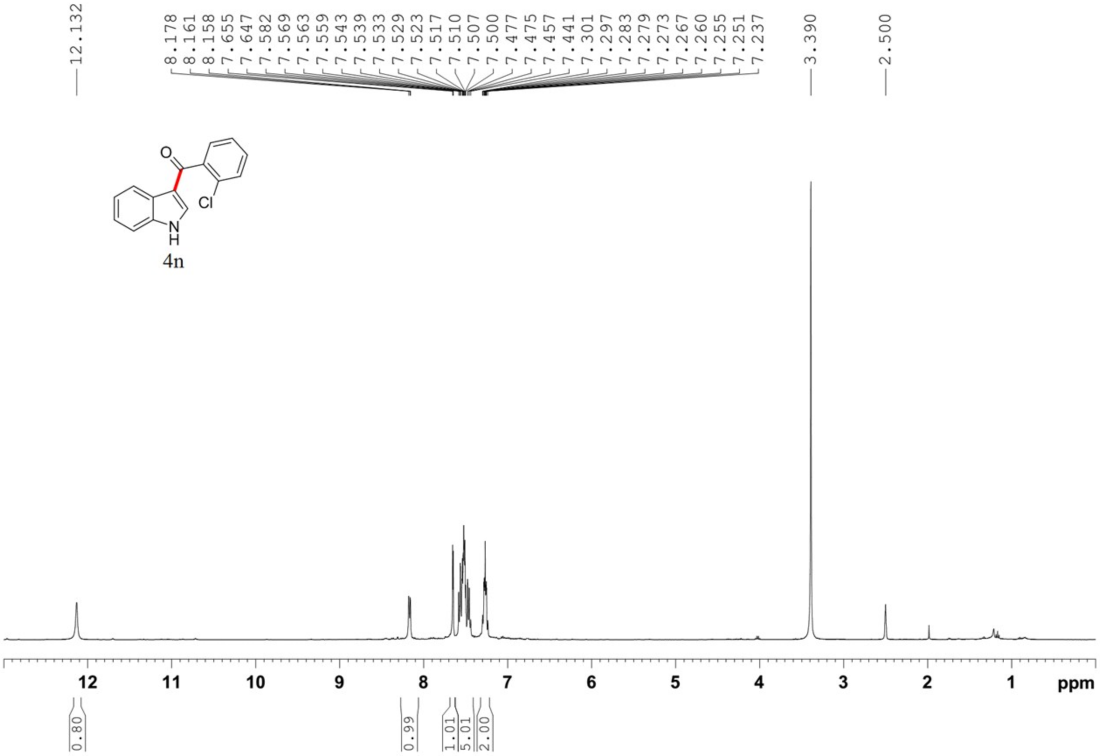
40
30
20
ppm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7.569
7.563
7.559
7.543
7.539
7.533
7.529
7.523
7.517
7.510
7.507
7.500
7.477
7.475
7.457
7.441
7.301
7.297
7.283
7.279
7.273
7.267
7.260
7.255
7.251
7.237
3.390
2.500
O
Cl
H
N
4n
12
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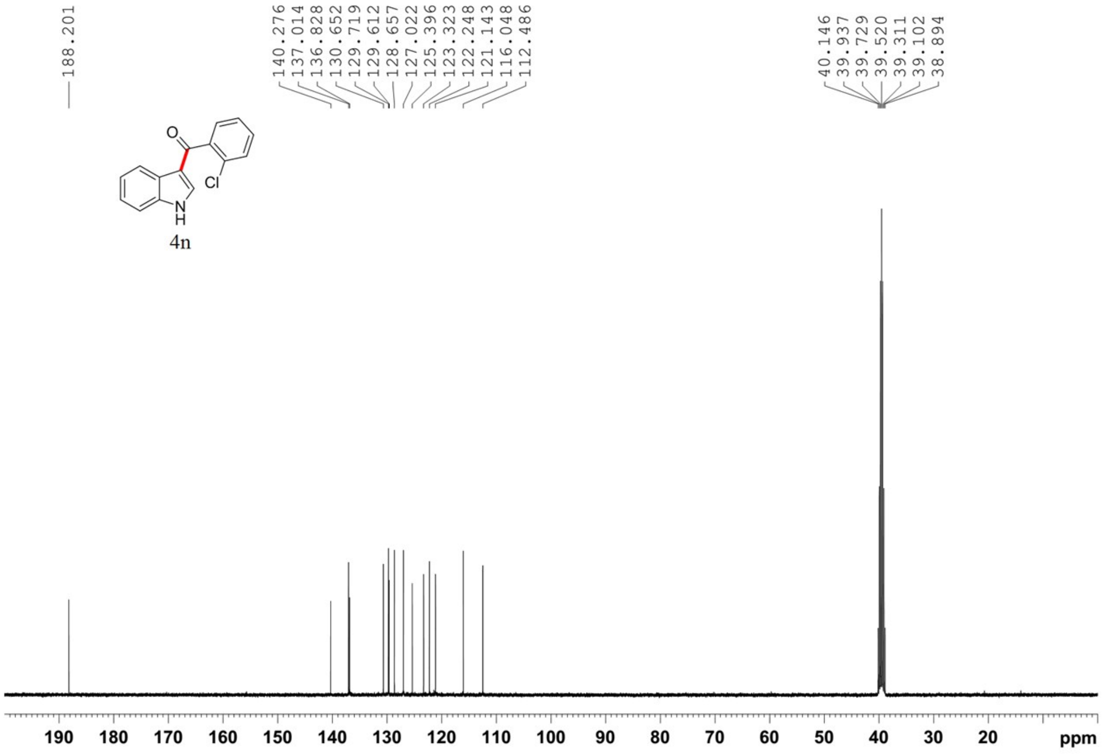
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125.396
123.323
122.248
121.143
116.048
112.486
40.146
39.937
39.729
39.520
39.311
39.102
38.894
O
Cl
H
N
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40
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20
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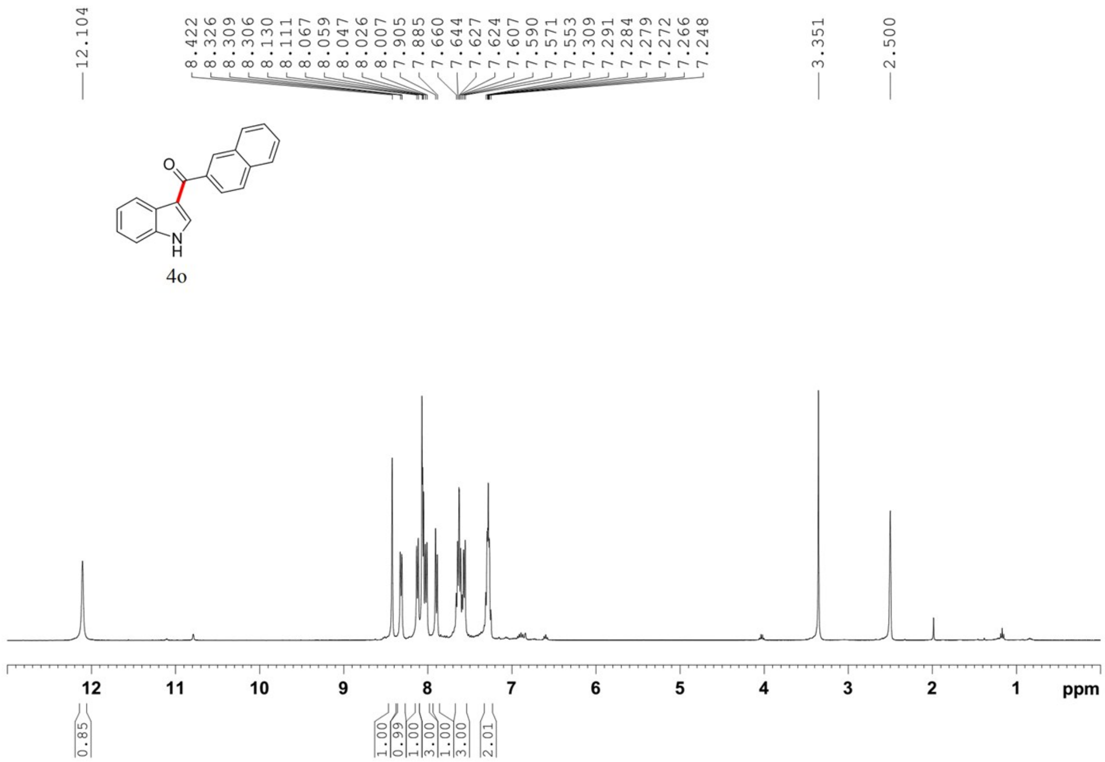
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7.885
7.660
7.644
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7.624
7.607
7.590
7.571
7.553
7.309
7.291
7.284
7.279
7.272
7.266
7.248
3.351
2.500
O
NH
4o
12
11
10
9
8
7
6
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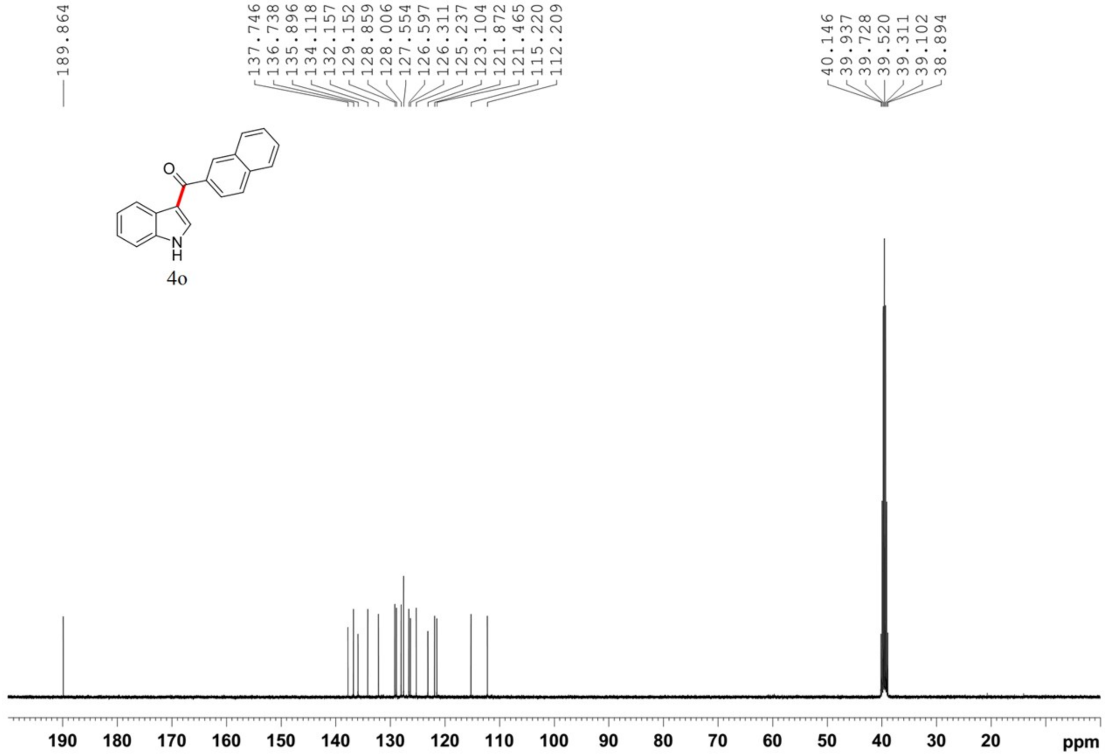
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126.311
125.237
123.104
121.872
121.465
115.220
112.209
40.146
39.937
39.728
39.520
39.311
39.102
38.894
O
NH
4o
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160
150
140
130
120
110
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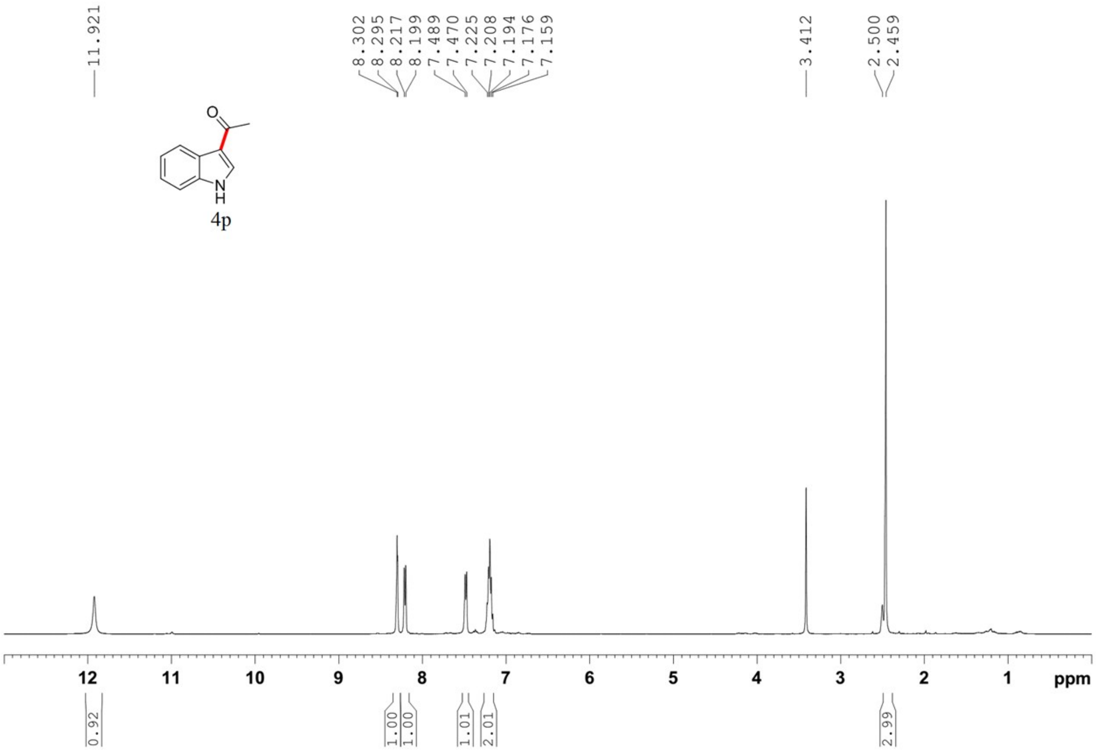
90
80
70
60
50
40
30
20
ppm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7.225
7.208
7.194
7.176
7.159
3.412
2.500
2.459
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H
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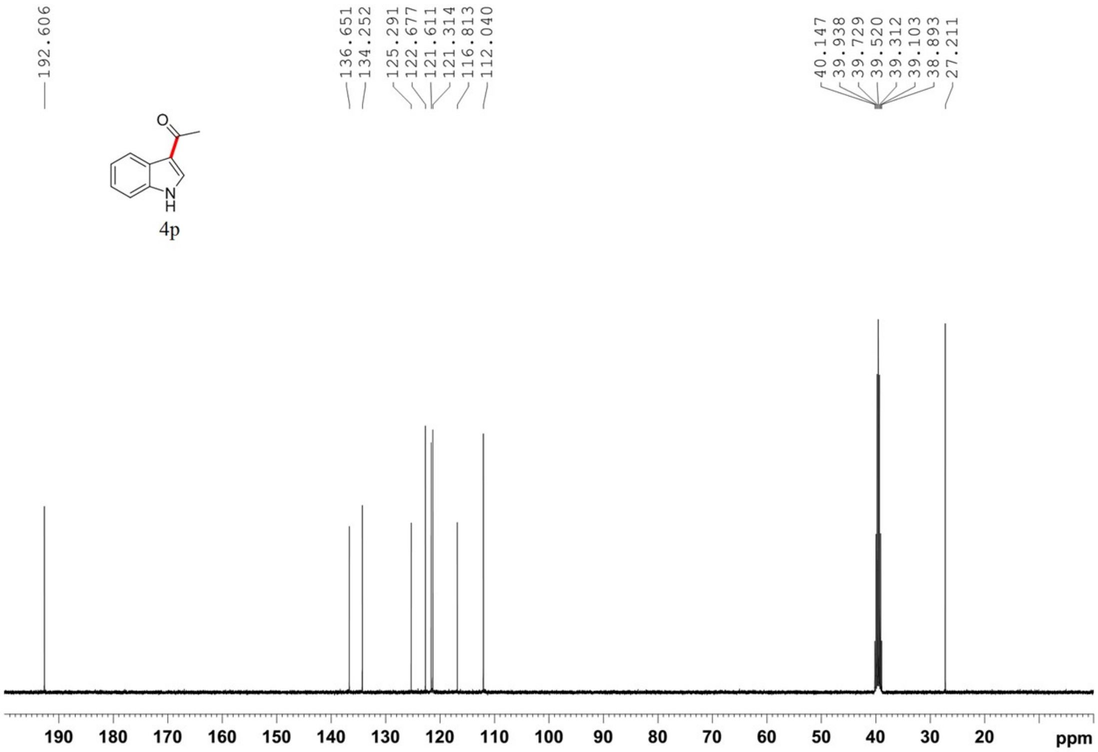
2.01
2.99


4p
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121.314
116.813
112.040
40.147
39.938
39.729
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39.103
38.893
27.211
O
N
H
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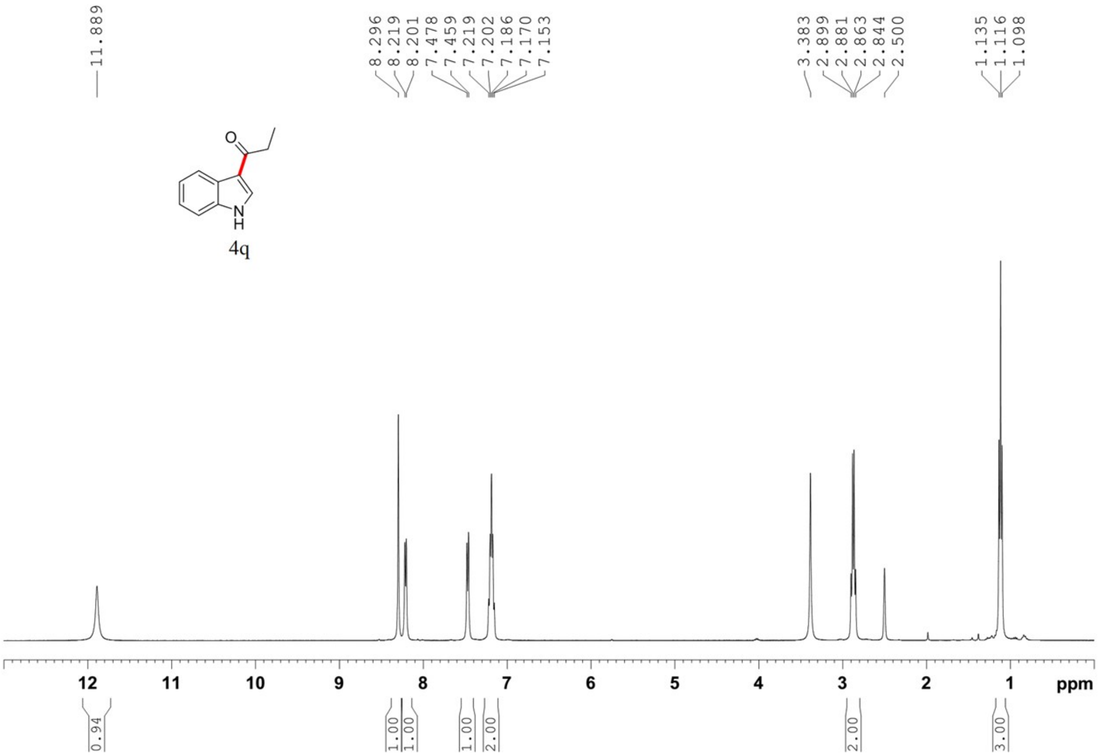
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7.459
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7.202
7.186
7.170
7.153
3.383
2.899
2.881
2.863
2.844
2.500
1.135
1.116
1.098
O
H
N
12
11
10
9
8
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6
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4
3
2
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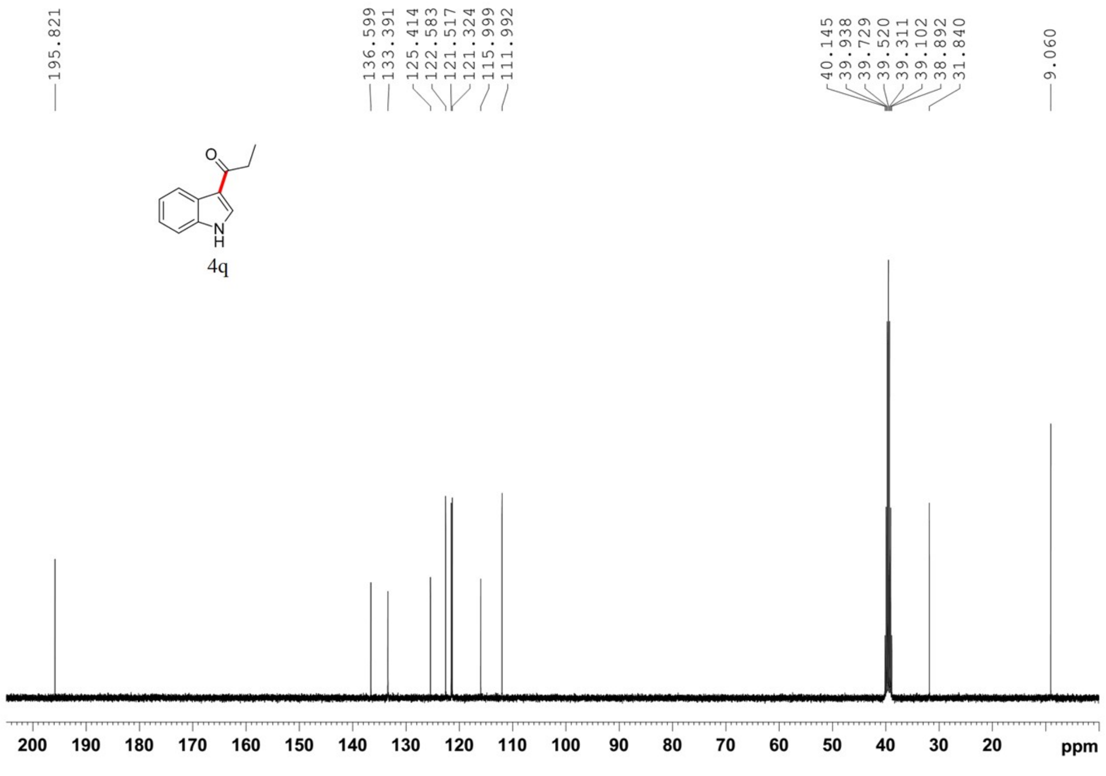
2.00
3.00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122.583
121.517
121.324
115.999
111.992
40.145
39.938
39.729
39.520
39.311
39.102
38.892
31.840
9.060
O
H
N
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150
140
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100
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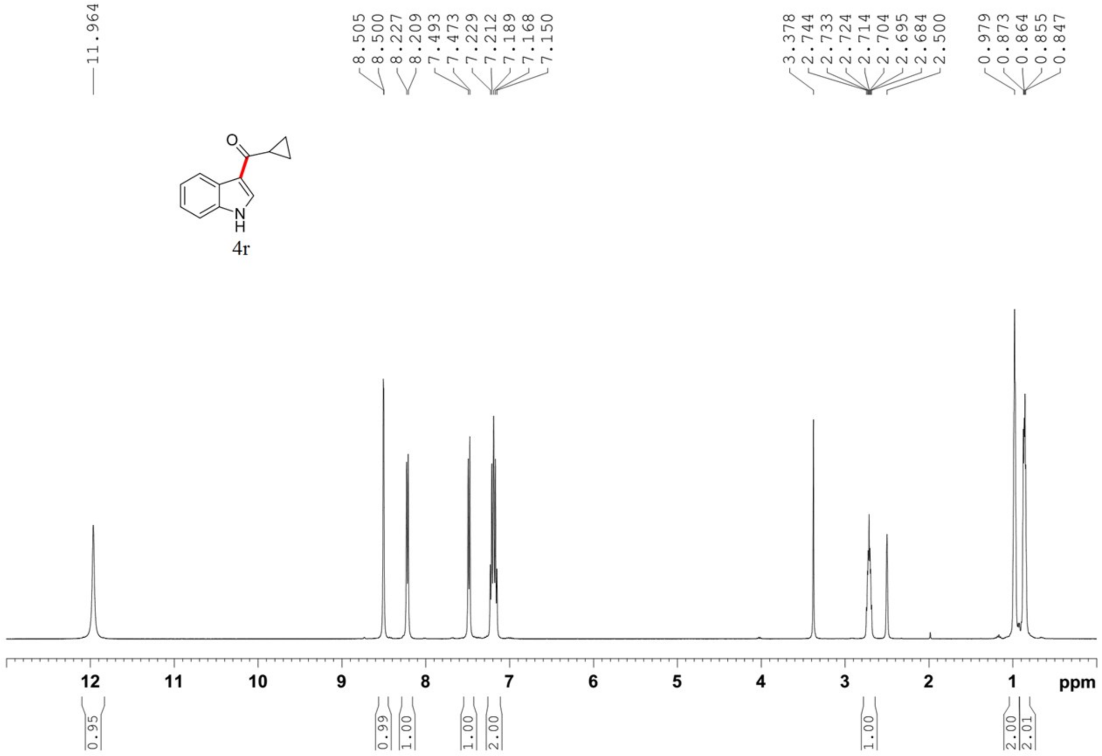
30
20
ppm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8.500
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7.473
7.229
7.212
7.189
7.168
7.150
3.378
2.744
2.733
2.724
2.714
2.704
2.695
2.684
2.500
0.979
0.873
0.864
0.855
0.847
O
N
H
4r
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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1.00
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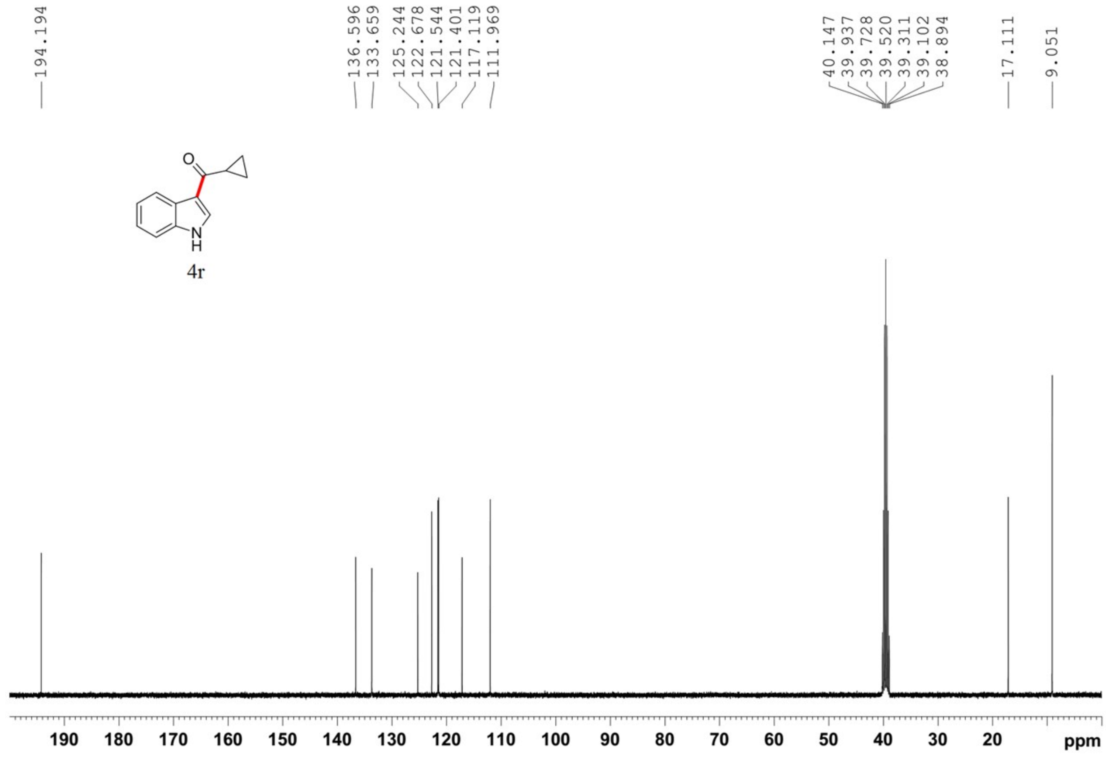
1.00
2.00
2.01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121.544
121.401
117.119
111.969
40.147
39.937
39.728
39.520
39.311
39.102
38.894
17.111
9.051
O
N
H
4r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm