Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPORTING INFORMATION

Synthesis of Benzimidazolones and N-phenyl formamides by CO2 fixation Under Mild Reaction Conditions Using Polymer Supported Zinc Complex as Catalyst

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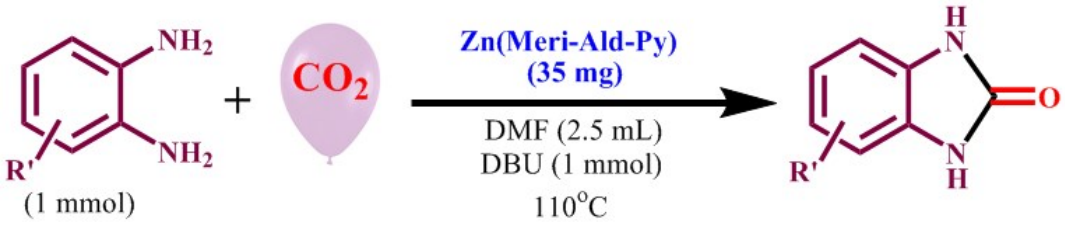
1. Physical and spectroscopic instruments:

A lot of different types of spectroscopic and physical instrumentation were done for specification and characterization of newly prepared catalyst [Zn(Meri-Ald-Py)]. The ligand (Meri-Ald-Py) and its corresponding complex catalyst [Zn(Meri-Ald-Py)] was undergo a TGA-DTA study facilitate with a Mettler Toledo TGA/DSC 2 STARe instrument. The surface morphology and the elements present in the ligand [Meri-Ald-Py] and the catalyst [Zn(Meri-Ald-Py)] was detected by a scanning electron microscope (SEM) instrument ZEISS EVO40, England. The percentage of loading zinc in the Meri-Ald-Py ligand was confirmed by using AAS instrument, Varian AA240. N_2 adsorption desorption study (BET) was carried out through Quantachrome (Model- NOVA 1000e). The FTIR spectra of ligand and the catalyst were detected in Perkin Elmer FTIR 783 spectrophotometer by making a disc of KBr and sample mixture. Exeter Analytical Inc. model: CE 440 instrument help to recognize the composition (elementaly) of ligand and also catalyst. PXRD (powder X-ray diffraction) data of catalyst was recorded by using Bruker D8 Advance X-ray diffractometer with Cu-K_α radiation (λ = 1.5418 Å) which operat at 40 kV and 40 mA. Bruker AMX- 400 instrument was operates for ^{1}HNMR spectra.

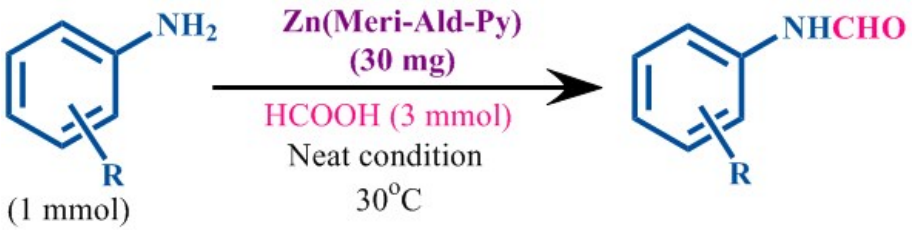
2. General procedure for the synthesis of benzimidazolone derivatives using Zn(Meri-Ald-Py) catalyst



The catalytic synthesis of benzimidazolone derivatives was obtained when derivatives of *o*-phenylendiamine (1 mmol) was stirred with 1 mmol amount of DBU in 2.5 mL DMF

medium and in the presence of 35 mg of Zn(Meri-Ald-Py) catalyst under atmospheric CO_2 pressure. The reaction mixture was continuously swirled under 110 ˚C temperature and 8 h reaction time. After completion of reaction time the reaction mixture was worked-up with ethyl acetate-water mixture. The pure product was isolated with column chromatography and indentified with ^{1}HNMR spectroscopy.

General procedure for the synthesis of N-phenyl formamides, using Zn(Meri-Ald-Py) catalyst



For the synthesis of N-phenyl formamide derivatives, 1 mmol of aromatic amine swirled with 30 mg of Zn(Meri-Ald-Py) catalyst in the presence of 3 mmol of formic acid in a 25 mL round bottom flask. Under solvent free condition the reaction was continued for several minute depending upon the type of aniline derivatives used in the reaction mixture. After that the product was separated out by work up with ethyl acetate-water mixture up-to three times. Then pure product was isolated, purified, and identified by ^{1}HNMR spectroscopy.

3. Kinetic study (conversion vs. time) for benzimidazolone and N-phenyl formamide synthesis

We have studied the conversion and selectivity vs. time plot for both of the catalytic reactions which are represented in Figure S1 and Figure S2. In Figure S1, a study of conversion and selectivity vs. time is performed for benzimidazolone synthesis in the presence of Zn(Meri-Ald-Py) catalyst. For N-phenyl formamide synthesis, the study of conversion and selectivity with time in the presence and absence of Zn(Meri-Ald-Py) catalyst is represented in Figure S2. For both of the said figures, the kinetic plot reveals that the conversion rate of substrate gradually increased and after achieving maximum substrate conversion the curve get flattened.

For N-phenyl formamide synthesis, some conversion of the substrate was also observed in absent of catalyst. This result agrees with another research group experimental result, they also performed the same type of reaction without any catalyst under similar reaction conditions.[1]

The selectivity curve for benzimidazolone synthesis is parallel to the time axis as no side product was identified during the course of the reaction. But for N-phenyl formamide synthesis, the product was obtained with major selectivity and after achieving maximum selectivity, the selectivity of the desired product decreased slightly with an increase in reaction time.

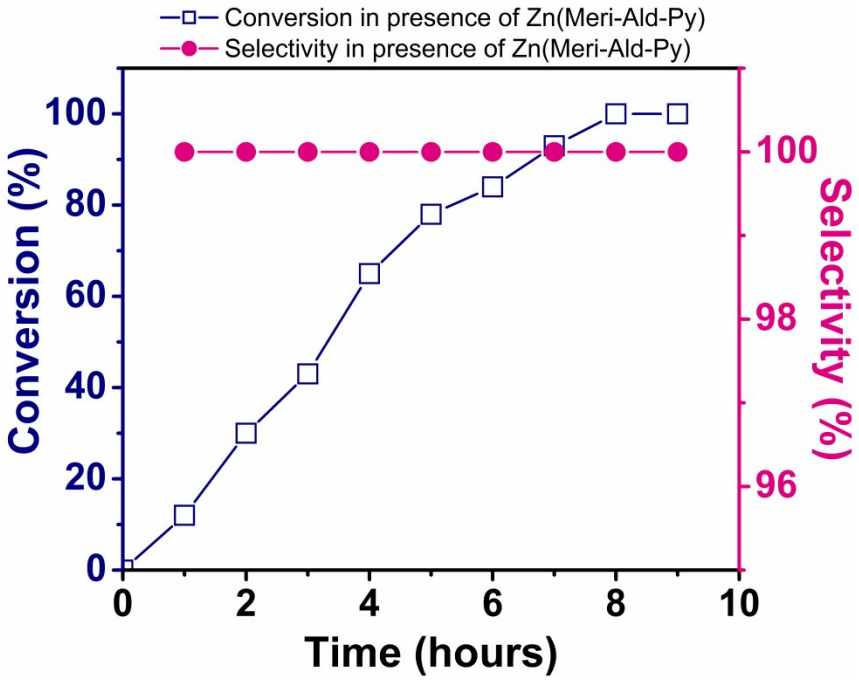


Figure S1: Kinetic curve of benzimidazolone synthesis.

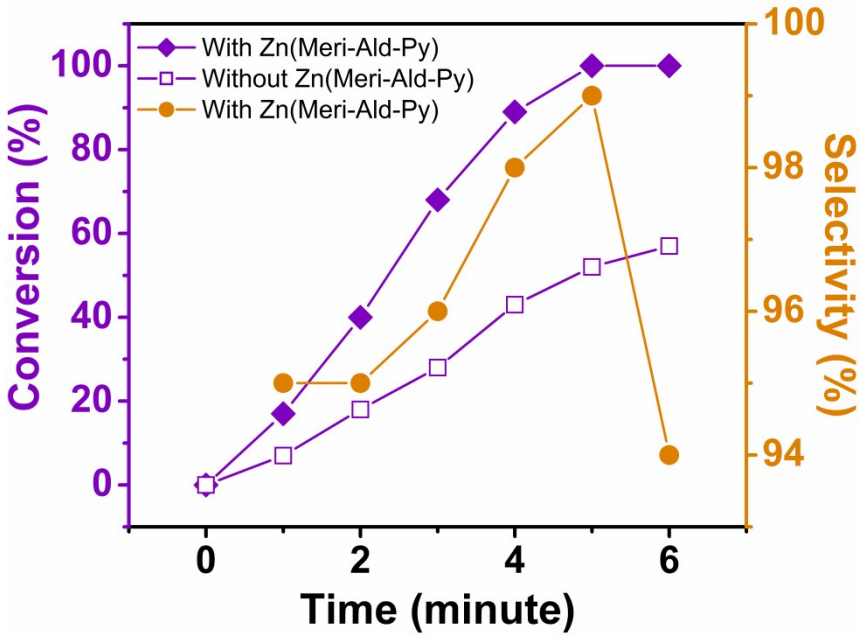


Figure S2: Kinetic curve of N-phenyl formamide synthesis.

The conversion percentage at different reaction cycle with time is described in Figure S3 and Figure S4 for benzimidazolone and N-phenyl formamide reactions respectively. The figures represent that there was very minimal change in the conversion from the first reaction cycle to the next reaction cycle with an increase of time. These cause the catalyst, Zn(Meri-Ald-Py) is very stable and capable to remain intact its activity after several reactions runs.

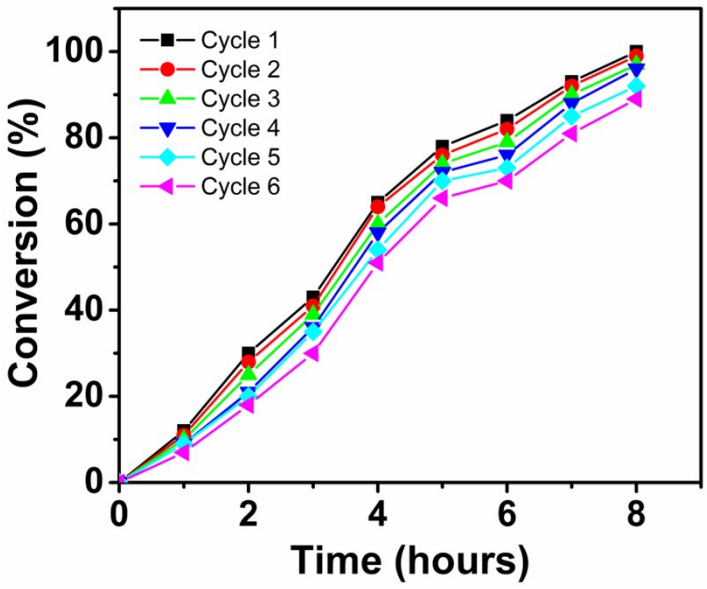


Figure S3: Comparison of conversion percentage of different recycling runs of benzimidazolone synthesis.

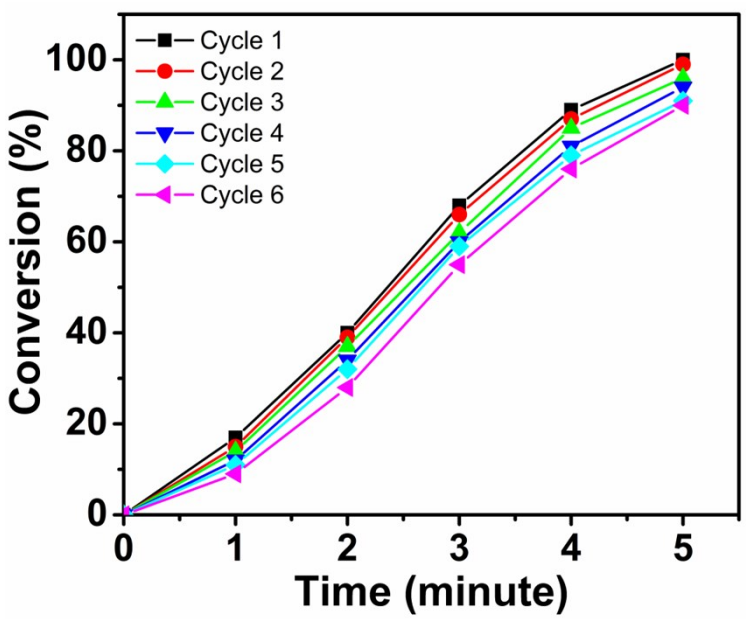
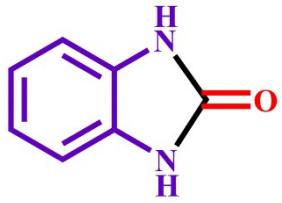
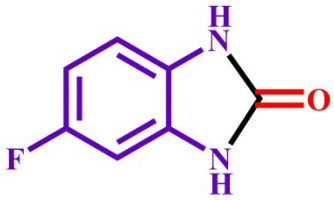
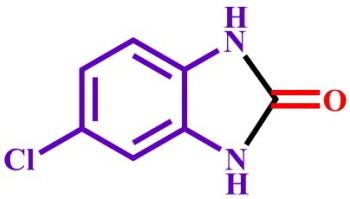
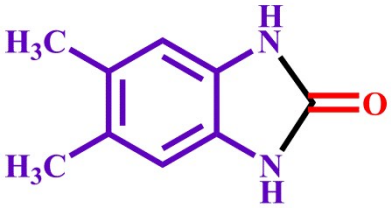
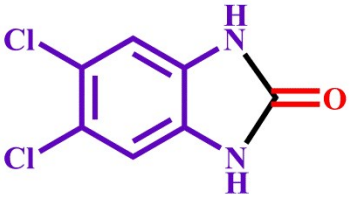
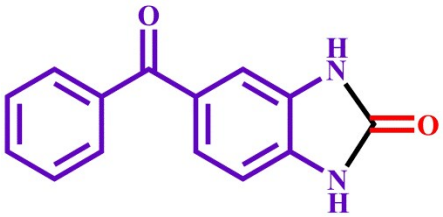
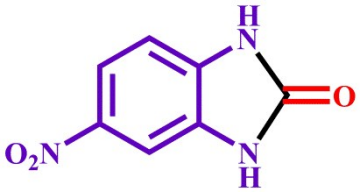


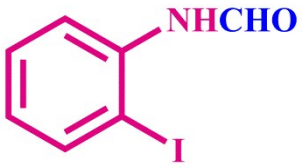
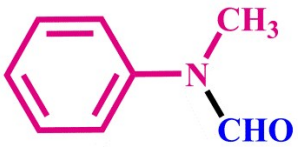
Figure S4: Comparison of conversion percentage of different recycling runs of N-phenyl formamide synthesis.

4. ^{1}HNMR data of benzimidazolone derivatives[2]

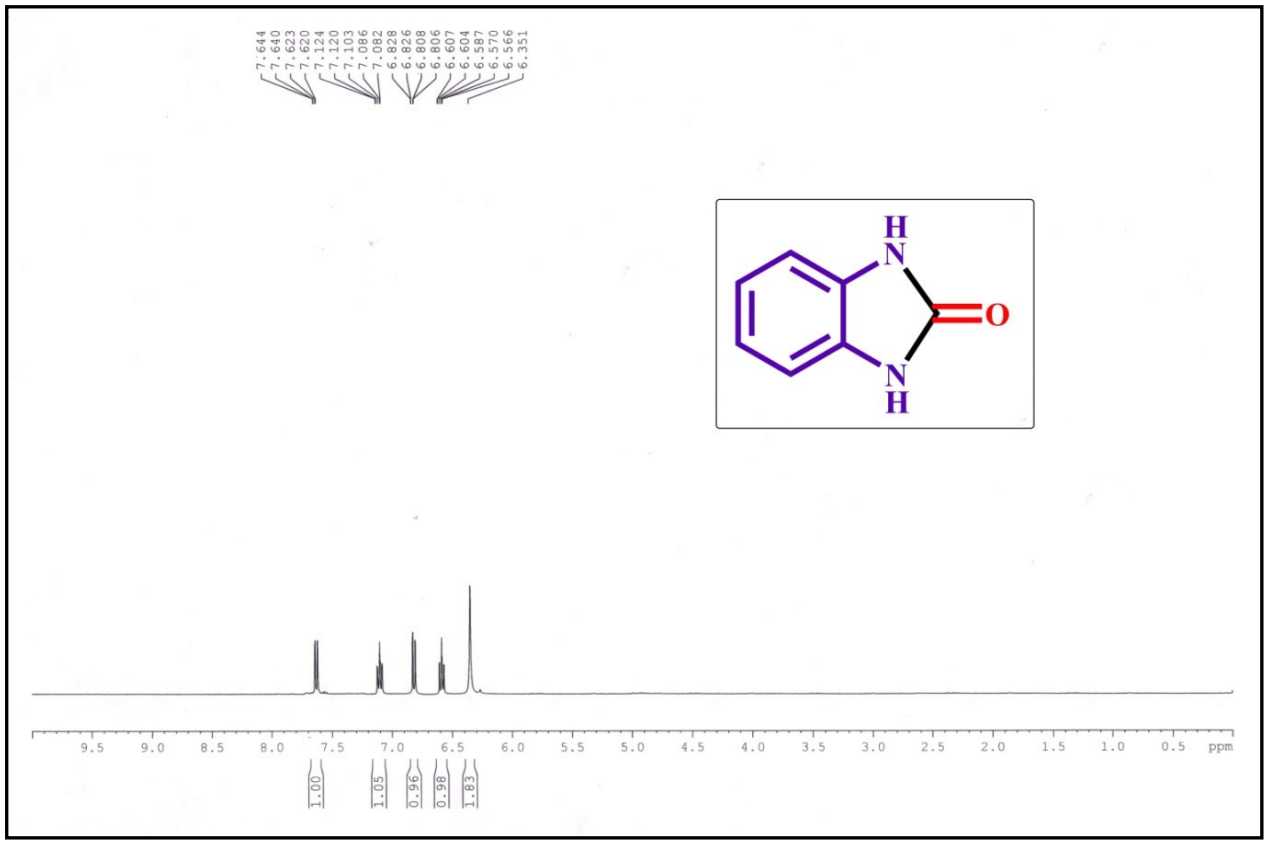
	^{1}HNMR (400 MHz, $CDCl_3$) δ 6.351 (s, 2H), 6.566-6.607 (m, 1H), 6.806-6.828 (m, 1H), 7.082-7.124 (m, 1H), 7.620-7.644 (m, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 4.080 (brs, 1H), 7.079 (d, *J*=6.4 Hz, 1H), 7.414-7.466 (m, 2H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 5.507 (brs, 2H), 6.654-6.697 (m, 2H), 7.498 (d, *J*=7.6 Hz, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 2.481 (s, 6H), 7.871 (s, 2H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 7.862 (s, 2H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 6.678 (d, *J*=8 Hz, 1H), 7.228-7.320 (m, 2H), 7.428-7.604 (m, 4H), 7.716-7.845 (m, 2H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 7.523 (d, *J*=8.8 Hz, 1H), 8.082-8.104 (t, *J*=6.8 Hz, 1H), 8.440 (d, *J*=2 Hz, 1H) ppm.

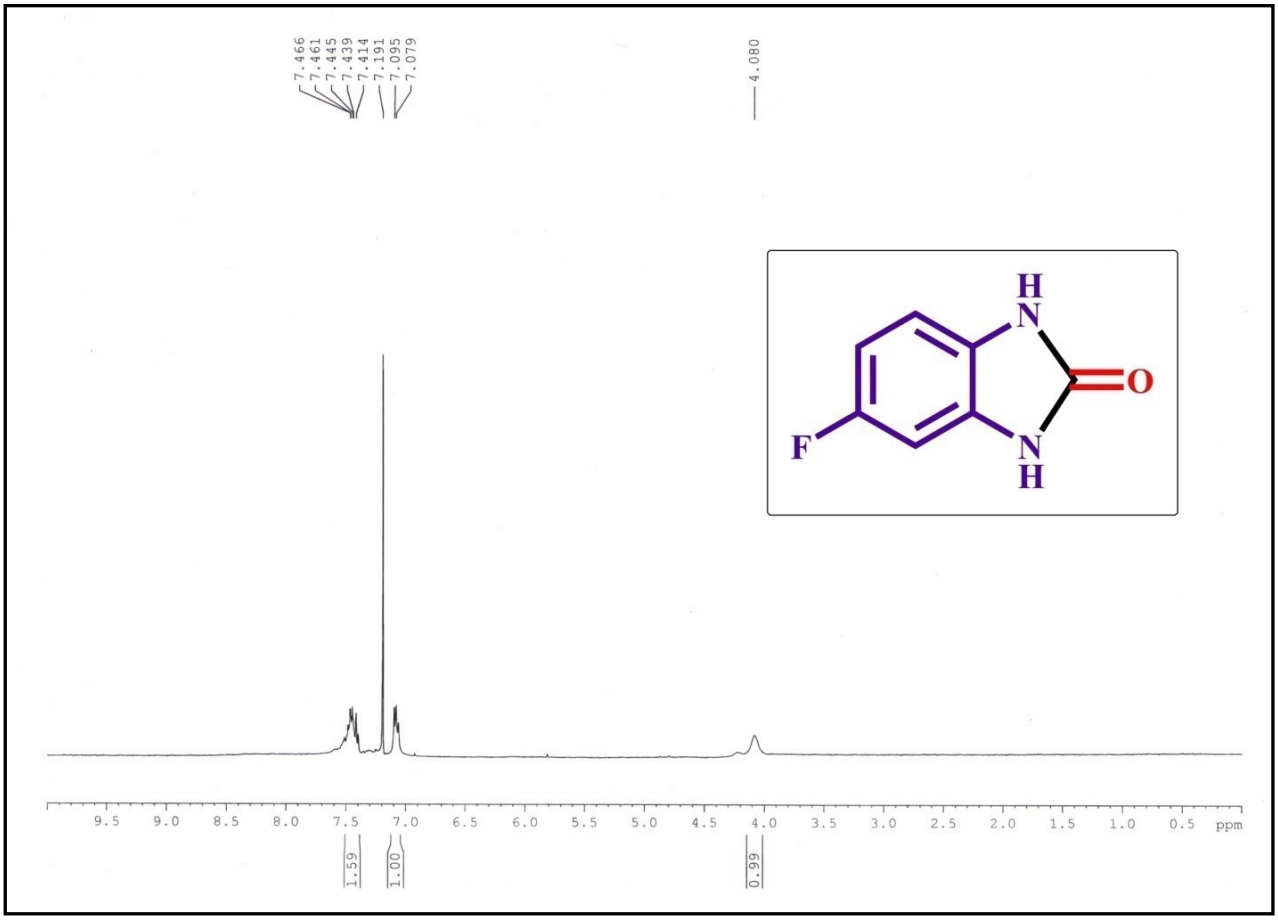
5. ^{1}HNMR data of N-phenyl formamide derivatives[3]

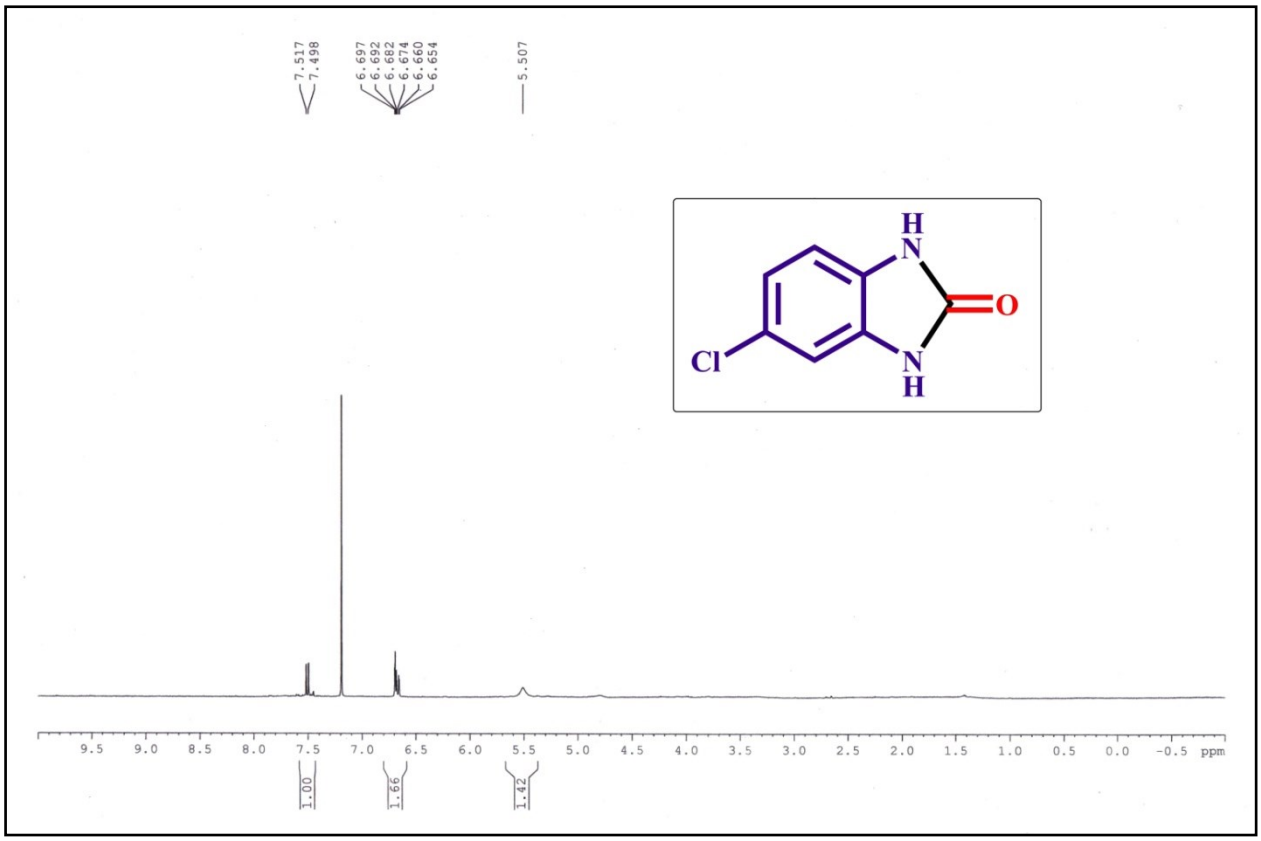
	^{1}HNMR (400 MHz, $CDCl_3$) *(mixture of rotamers)* δ 6.980-7.080 (m, 4H), 7.155-7.240 (m, 4H), 7.442-7.465 (t, *J*=8.4 Hz, 2H), 8.203 (d, *J*=2 Hz, 1H), 8.491 (s, 1H), 8.567-8.596 (m, 1H), 9.127 (brs, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) *(mixture of rotamers)* δ 6.949 (d, *J*=8.8 Hz, 2H), 7.223-7.279 (m, 4H), 7.414-7.442 (t, *J*=8.4 Hz, 2H), 7.784 (brs, 1H), 8.309 (s, 1H), 8.561 (d, *J*=11.6 Hz, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) *(mixture of rotamers)* δ 6.898-6.927 (m, 2H), 7.233 (brs, 1H), 7.378-7.422 (m, 6H), 7.975 (brs, 1H), 8.312 (s, 1H), 8.574 (d, *J*=11.2 Hz, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 7.732-7.754 (m, 2H), 8.104-8.140 (m, 2H), 8.340 (d, *J*=1.2 Hz, 1H), 10.001 (brs, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) *(mixture of rotamers)* δ 3.693 (d, *J*=8 Hz, 6H), 6.749-6.808 (m, 4H), 6.946 (d, *J*=8.8 Hz, 2H), 7.355 (d, *J*=8.8 Hz, 2H), 7.932 (brs, 1H), 8.197 (d, *J*=1.2 Hz, 1H), 8.413 (d, *J*=1.6 Hz, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) *(mixture of rotamers)* δ 6.894-7.194 (m, 6H), 7.291 (d, *J*=7.6 Hz, 1H), 7.571 (d, *J*=2 Hz, 1H), 8.254 (d, *J*=1.6 Hz, 1H), 8.380 (s, 1H), 8.590 (d, *J*=11.2 Hz, 1H), 9.034 (d, *J*=8 Hz, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) *(mixture of rotamers)* δ 6.954-7.385 (m, 7H), 7.718-7.727 (t, *J*=2 Hz, 1H), 8.106 (brs, 1H), 8.270 (d, *J*=2 Hz, 1H), 8.597 (d, *J*=11.2 Hz, 1H), 8.895 (d, *J*=10 Hz, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 7.683-7.726 (m, 2H), 8.267-8.292 (m, 1H), 8.606 (s, 1H), 8.827 (d, *J*=8.4 Hz, 1H), 10.360 (brs, 1H) ppm.

	^{1}HNMR (400 MHz, $CDCl_3$) δ 6.755-6.793 (m, 1H), 6.862-6.886 (m, 1H), 6.927-6.969 (m, 1H), 7.650-7.670 (t, *J*=6.8 Hz, 1H), 8.239 (d, *J*=1.6 Hz, 1H), 8.721 (brs, 1H), 9.229 (s, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) *(mixture of rotamers)* δ 6.770 (d, *J*=8.4 Hz, 2H), 7.253 (d, *J*=8.8 Hz, 2H), 7.563-7.612 (m, 4H), 8.325 (s, 1H), 8.577 (d, *J*=11.2 Hz, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 4.236-4.270 (t, *J*=7.6 Hz, 2H), 6.875 (brs, 1H), 7.038-7.267 (m, 5H), 7.999 (s, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) δ 3.257 (s, 3H), 7.097 (d, *J*=8.4 Hz, 2H), 7.186-7.231 (m, 1H), 7.329-7.367 (t, *J*=7.6 Hz, 2H), 8.412 (s, 1H) ppm.
	^{1}HNMR (400 MHz, $CDCl_3$) *(mixture of rotamers)* δ 2.181-2.239 (m, 12H), 6.711 (brs, 1H), 6.826 (brs, 1H), 7.021-7.081 (m, 6H), 8.011 (d, *J*=11.6 Hz, 1H), 8.348 (d, *J*=1.2 Hz, 1H) ppm.

6. [1]HNMR copies of benzimidazolone derivatives



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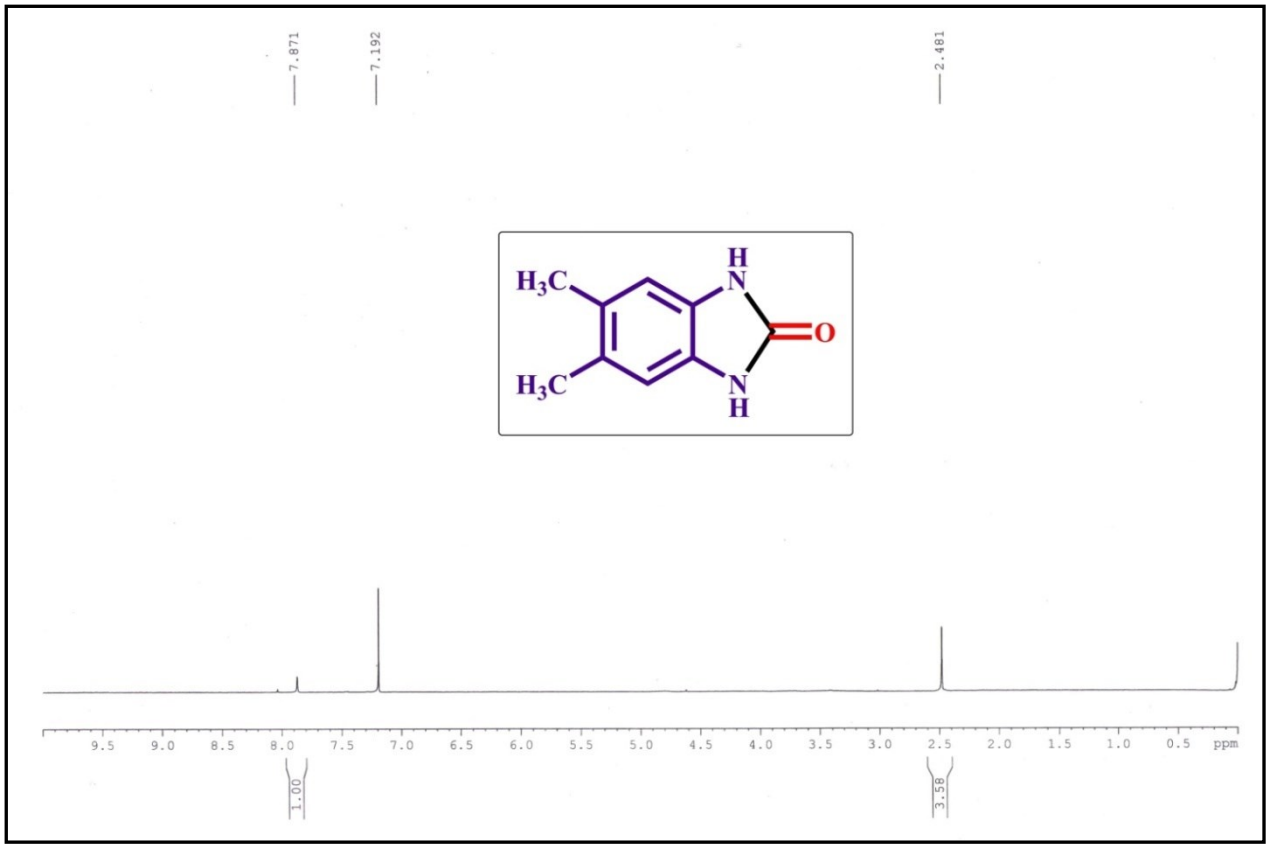
7.498
6.697
6.692
6.682
6.674
6.660
6.654
5.507
H
N
O
Cl
N
H
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.00
1.66
1.42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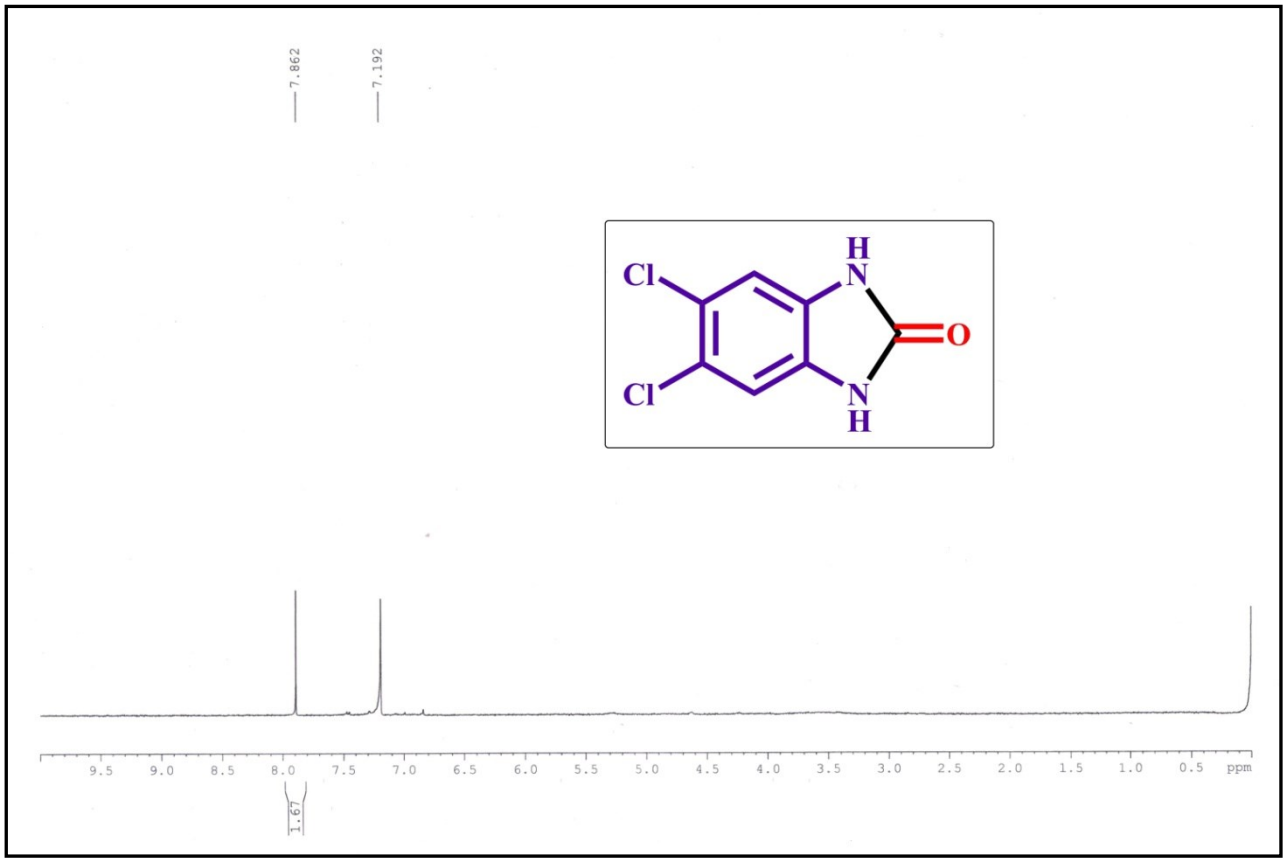
7.192
2.481
H
N
H3C
O
H3C
N
H
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
3.58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7.192
Cl
Cl
H
N
O
N
H
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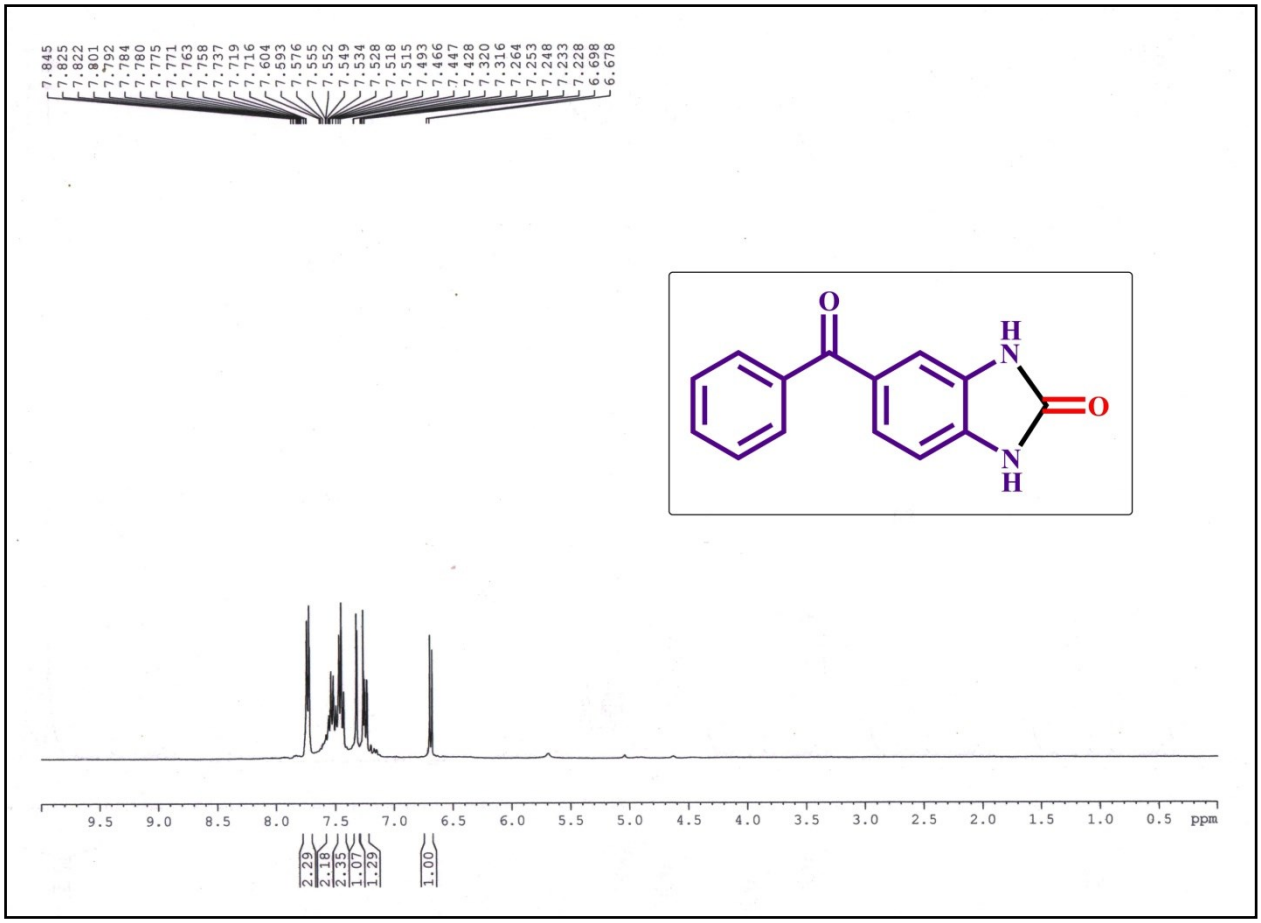
1.67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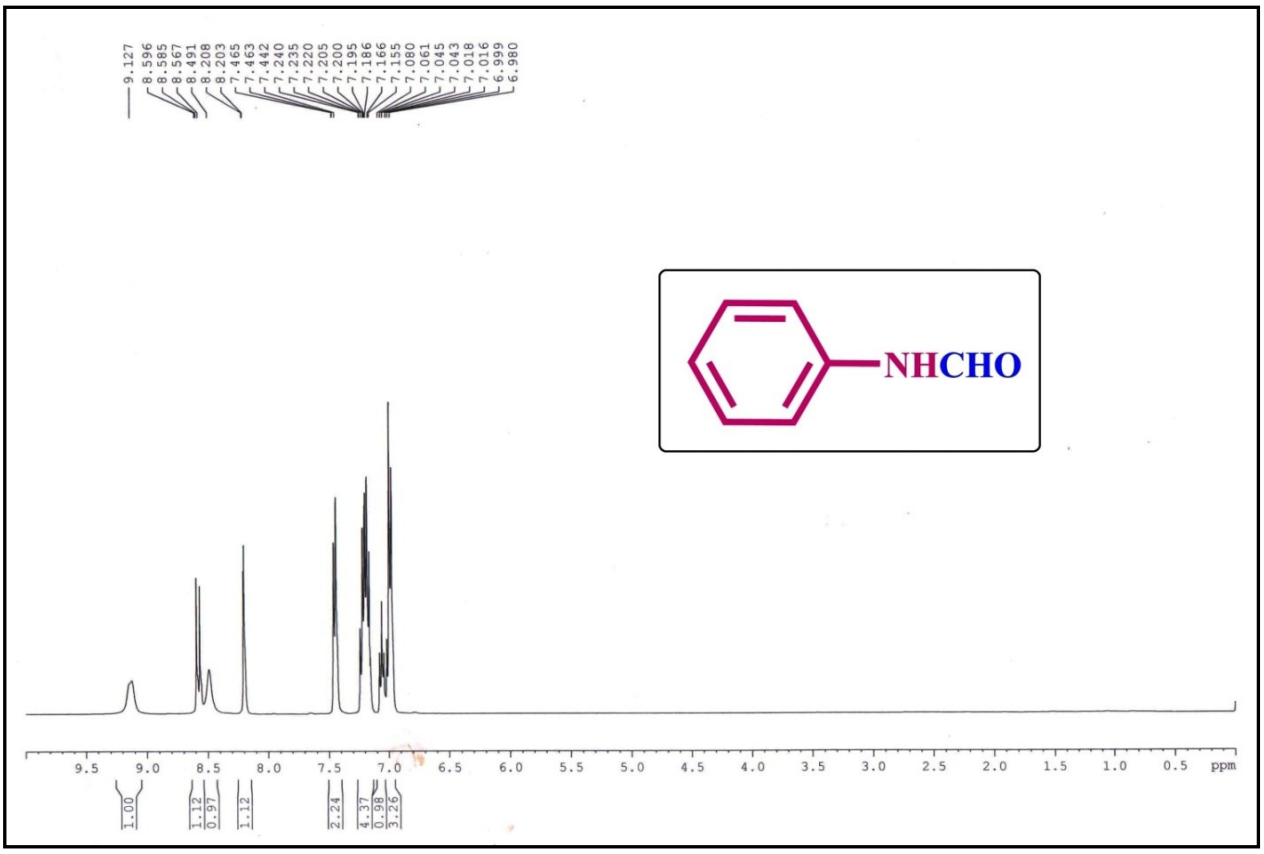
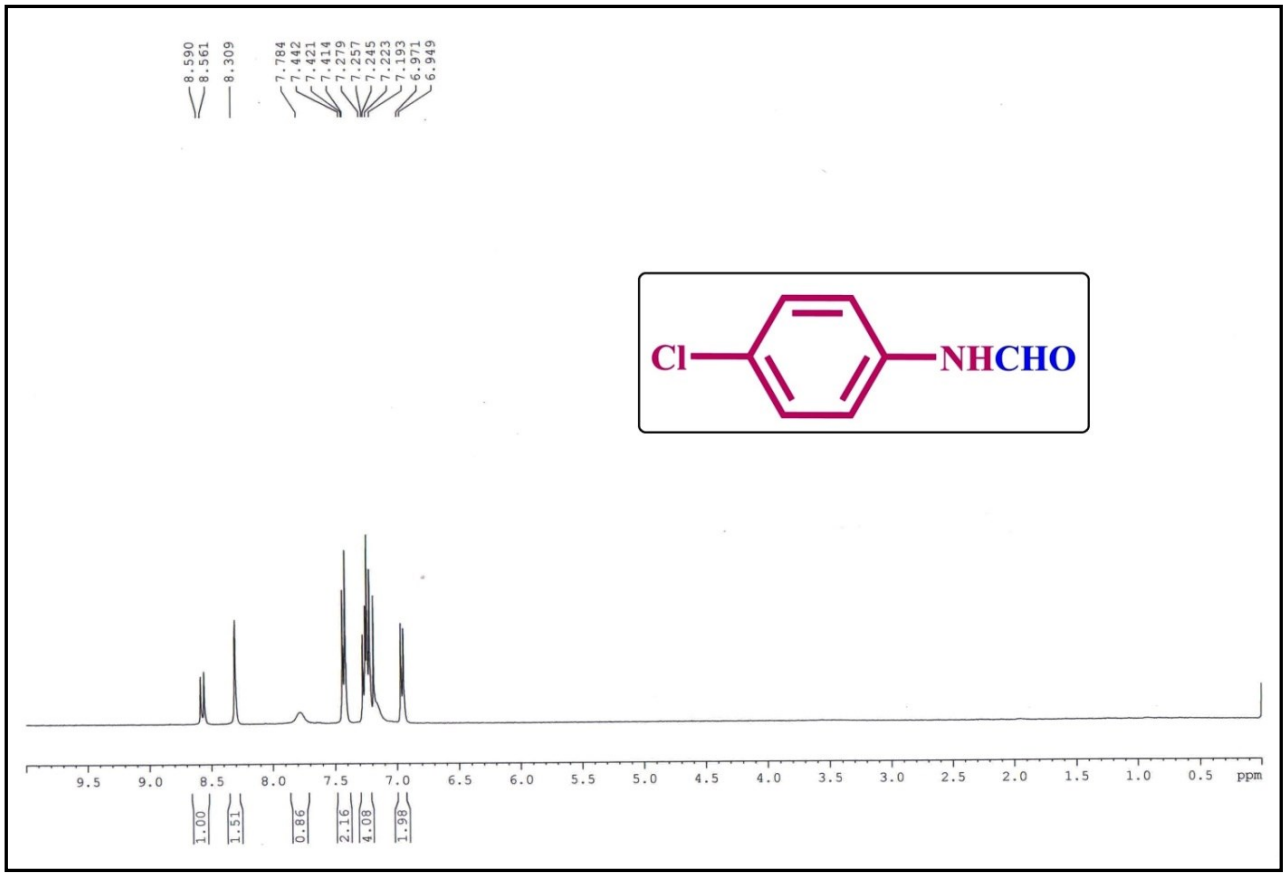
7.822
7.801
7.792
7.784
7.780
7.775
7.771
7.763
7.758
7.737
7.719
7.716
7.604
7.593
7.576
7.555
7.552
7.549
7.534
7.528
7.518
7.515
7.493
7.466
7.447
7.428
7.320
7.316
7.264
7.253
7.248
7.233
7.228
6.698
6.678
O
H
N
O
N
H
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.29
2.18
2.35
1.07
1.29
1.00

7. [1]HNMR copies of N-phenyl formamide derivatives

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8.561
8.309
7.784
7.442
7.421
7.414
7.279
7.257
7.245
7.223
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6.971
6.949
Cl
NHCHO
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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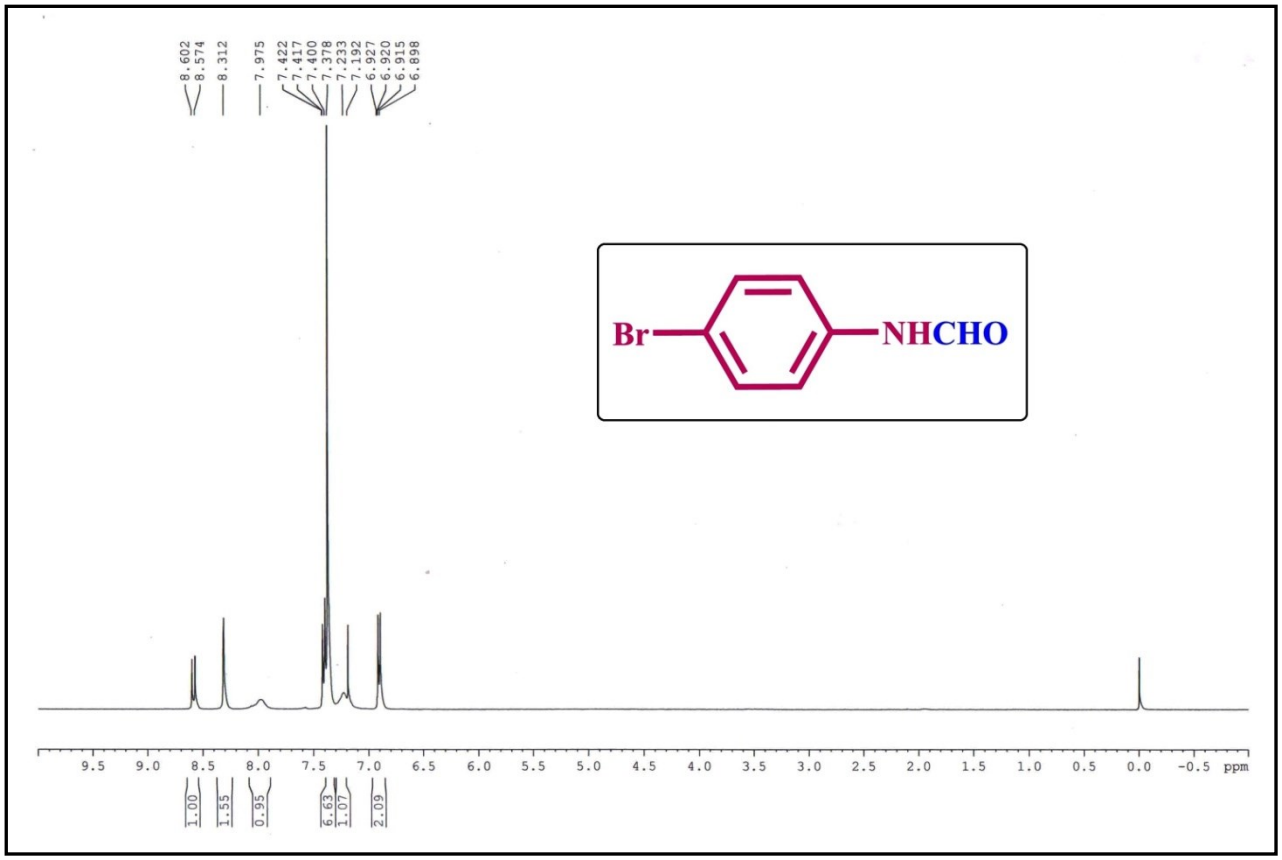
1.51
0.86
2.16
4.08
1.98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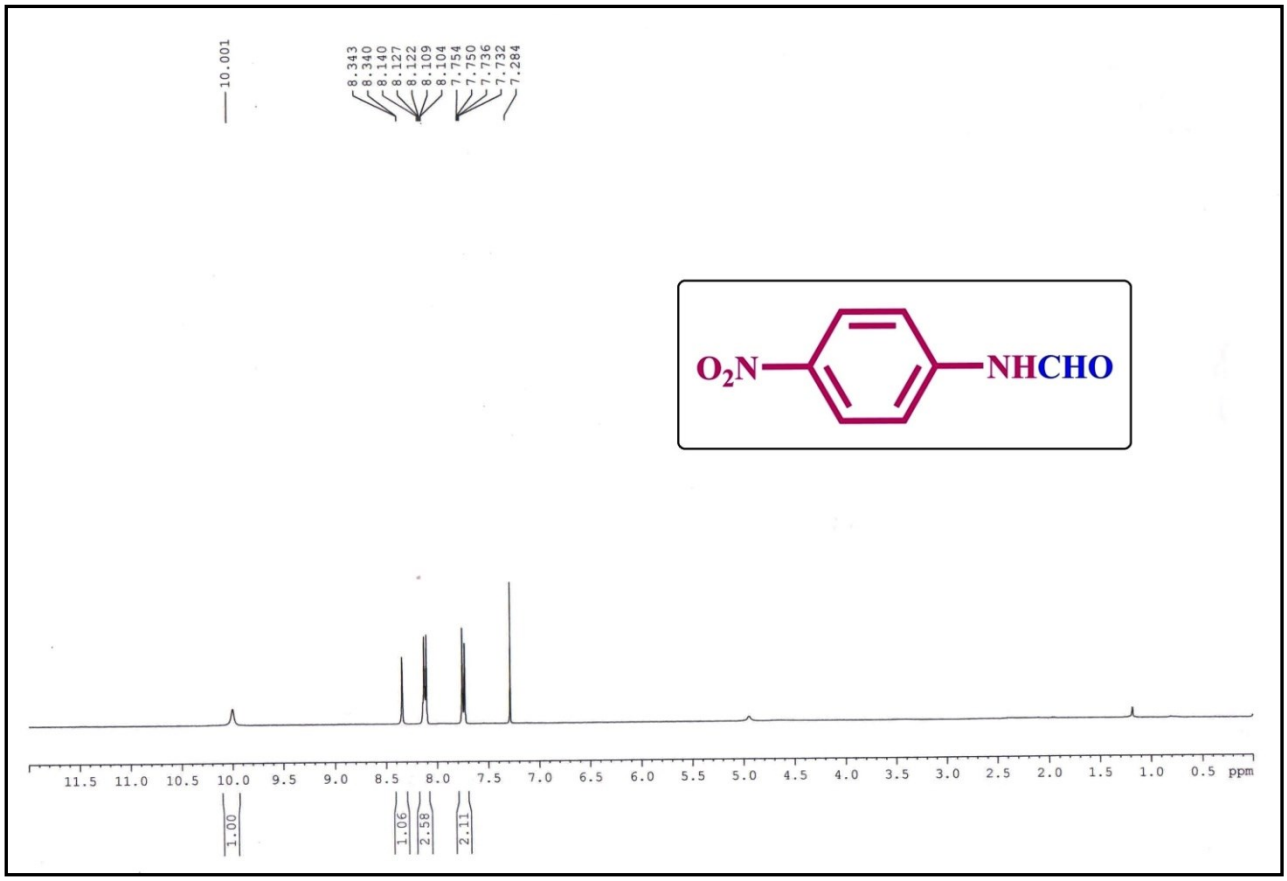
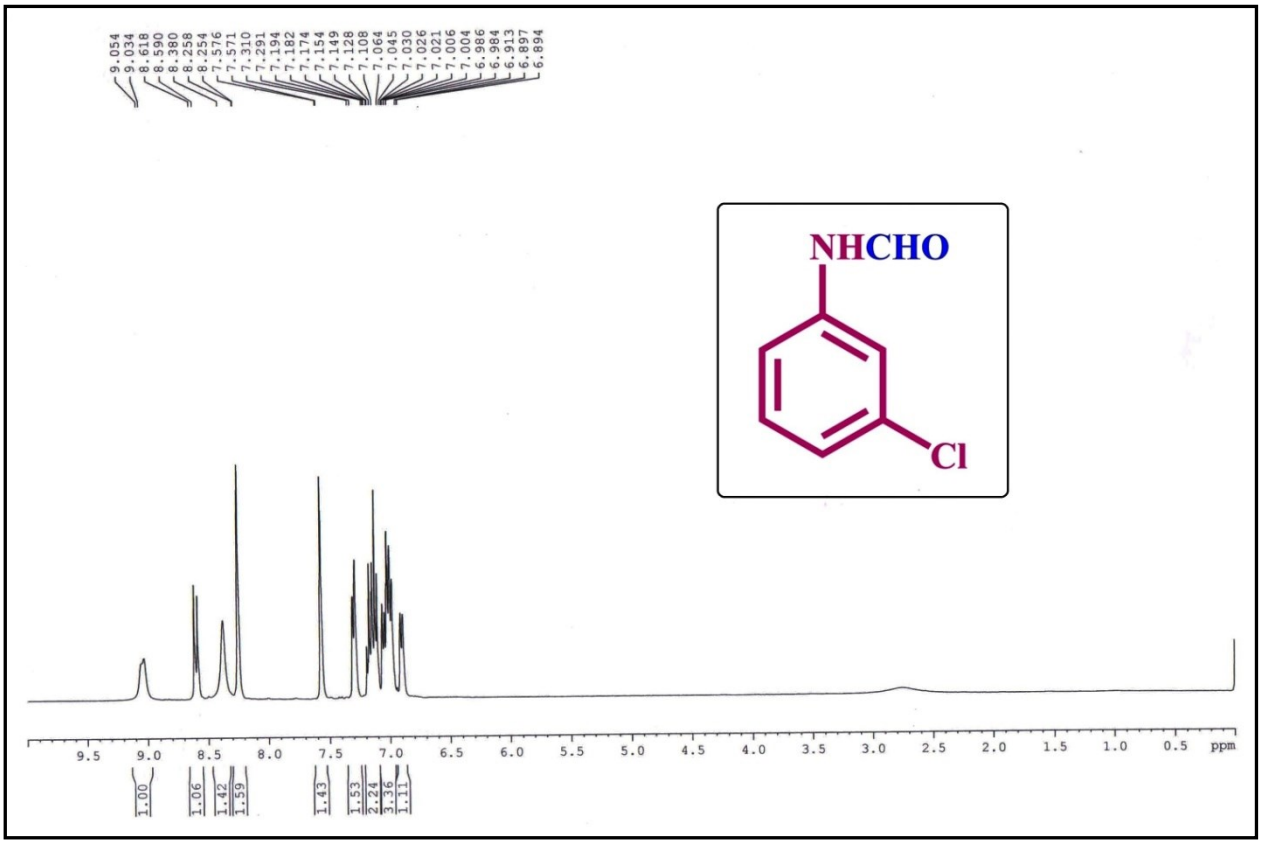
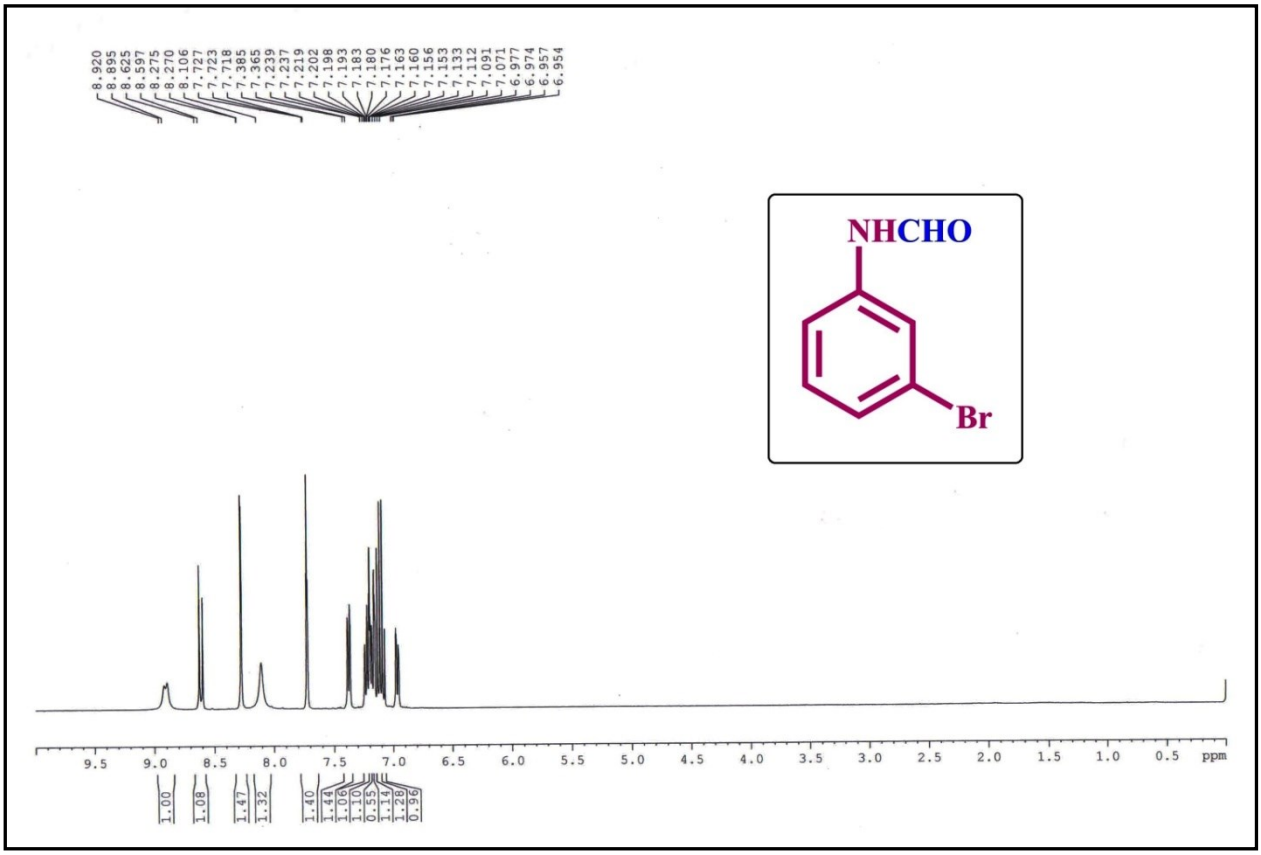
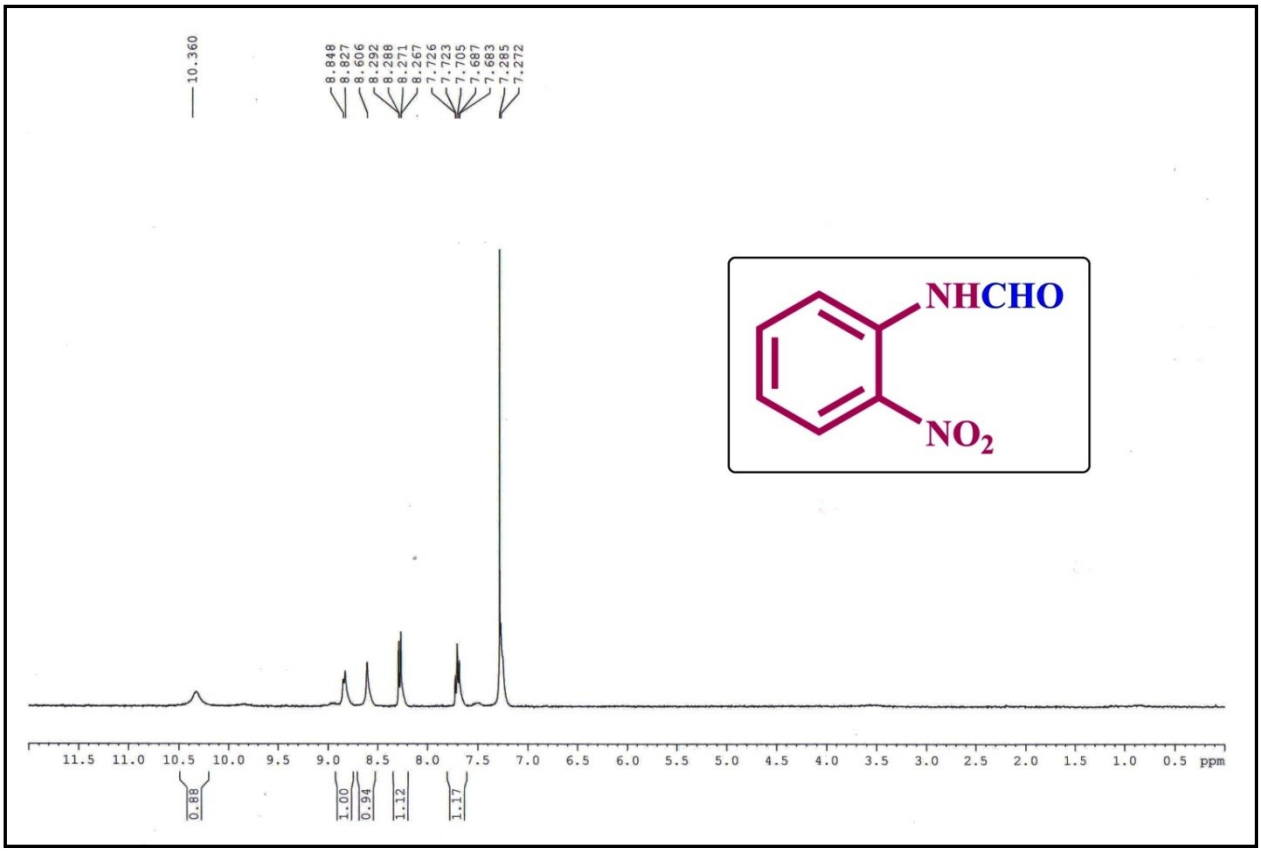
8.574
8.312
7.975
7.422
7.417
7.400
7.378
7.233
7.192
6.927
6.920
6.915
6.898
Br
NHCHO
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.00
1.55
0.95
6.63
1.07
2.09

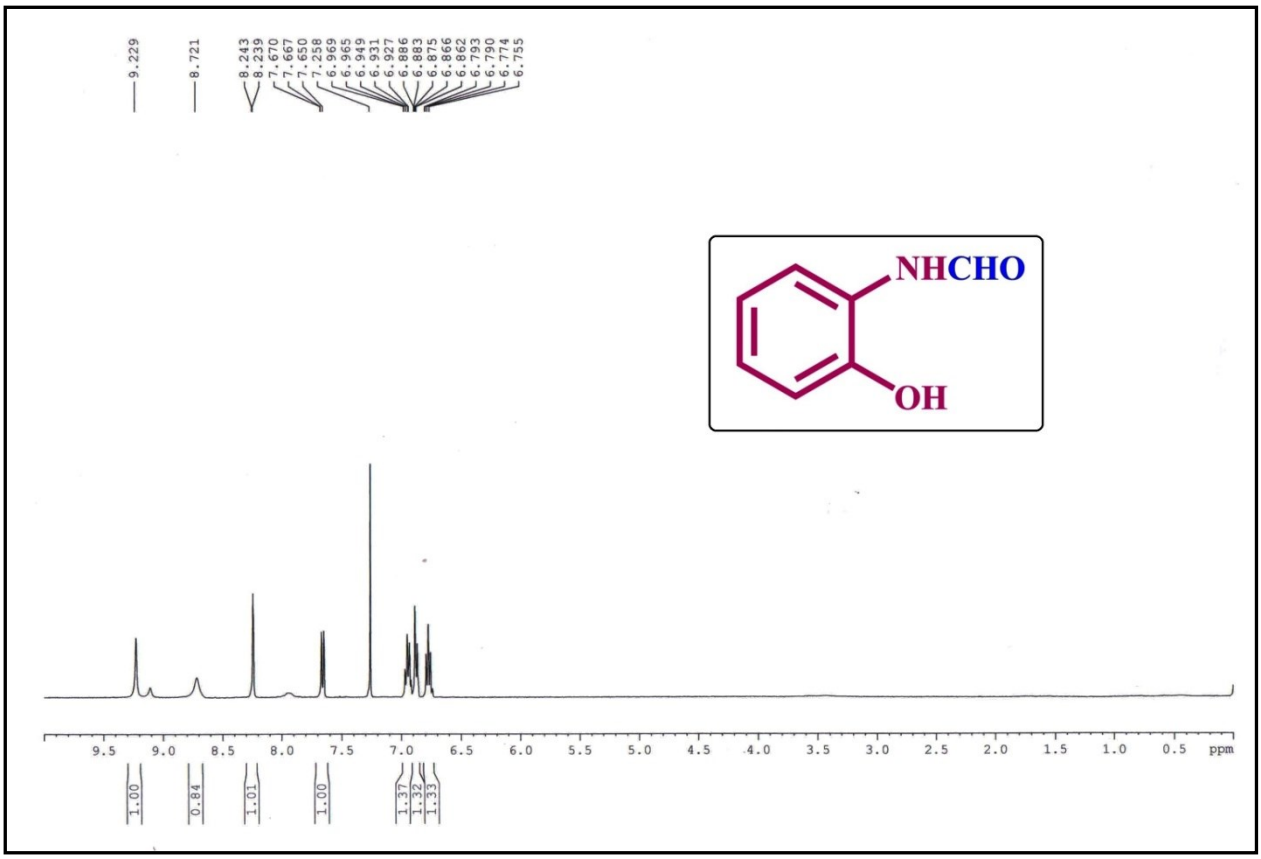

10.001
8.343
8.340
8.140
8.127
8.122
8.109
8.104
7.754
7.750
7.736
7.732
7.284
O2N
NHCHO
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.06
2.58
2.11

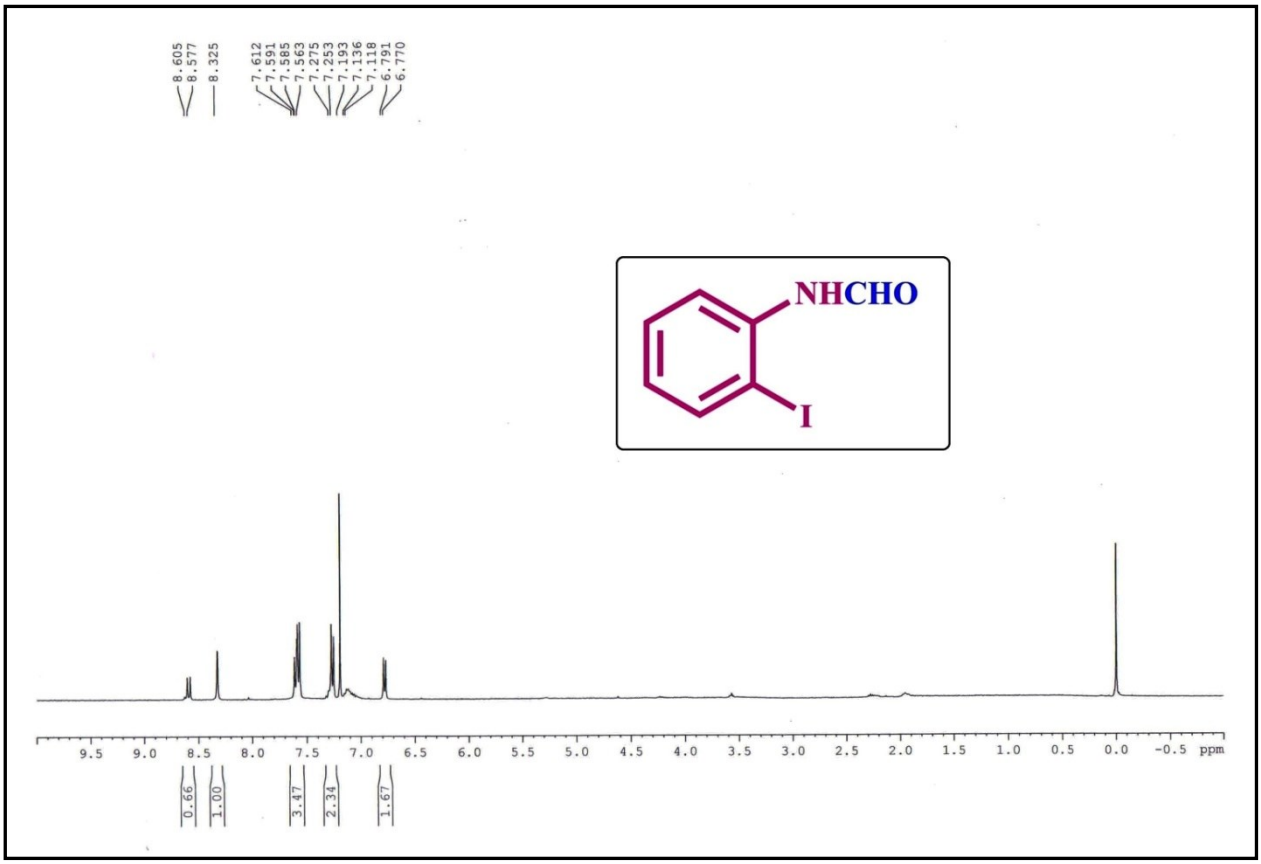

8.442
8.413
8.200
8.197
7.932
7.377
7.355
6.968
6.946
6.808
6.786
6.778
6.771
6.749
3.713
3.693
H3CO
NHCHO
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.11
1.00
2.18
1.96
4.17
6.35

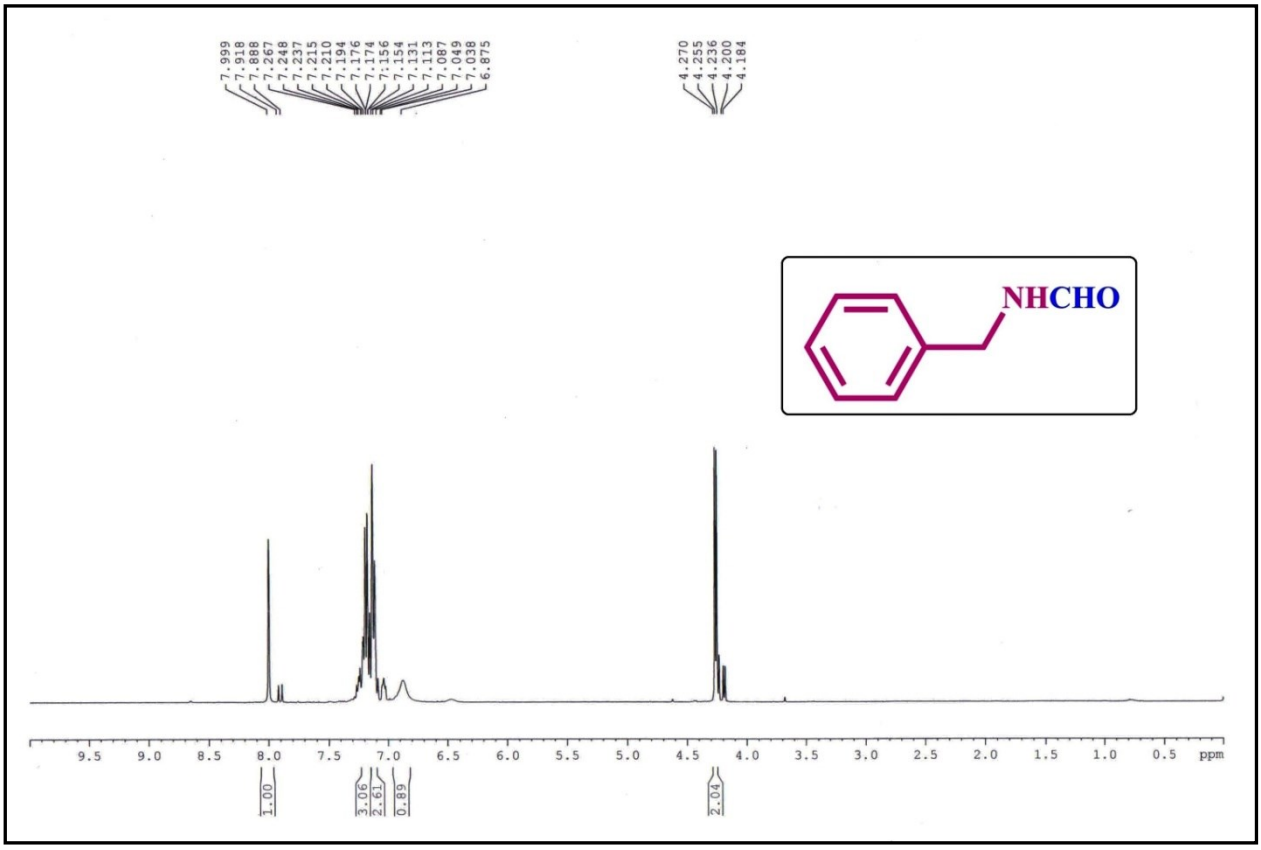

9.054
9.034
8.618
8.590
8.380
8.258
8.254
7.576
7.571
7.310
7.291
7.194
7.182
7.174
7.154
7.149
7.128
7.108
7.064
7.045
7.030
7.026
7.021
7.006
7.004
6.986
6.984
6.913
6.897
6.894
NHCHO
Cl
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.06 1.42 1.59 1.43 1.53 2.24 3.36 1.11

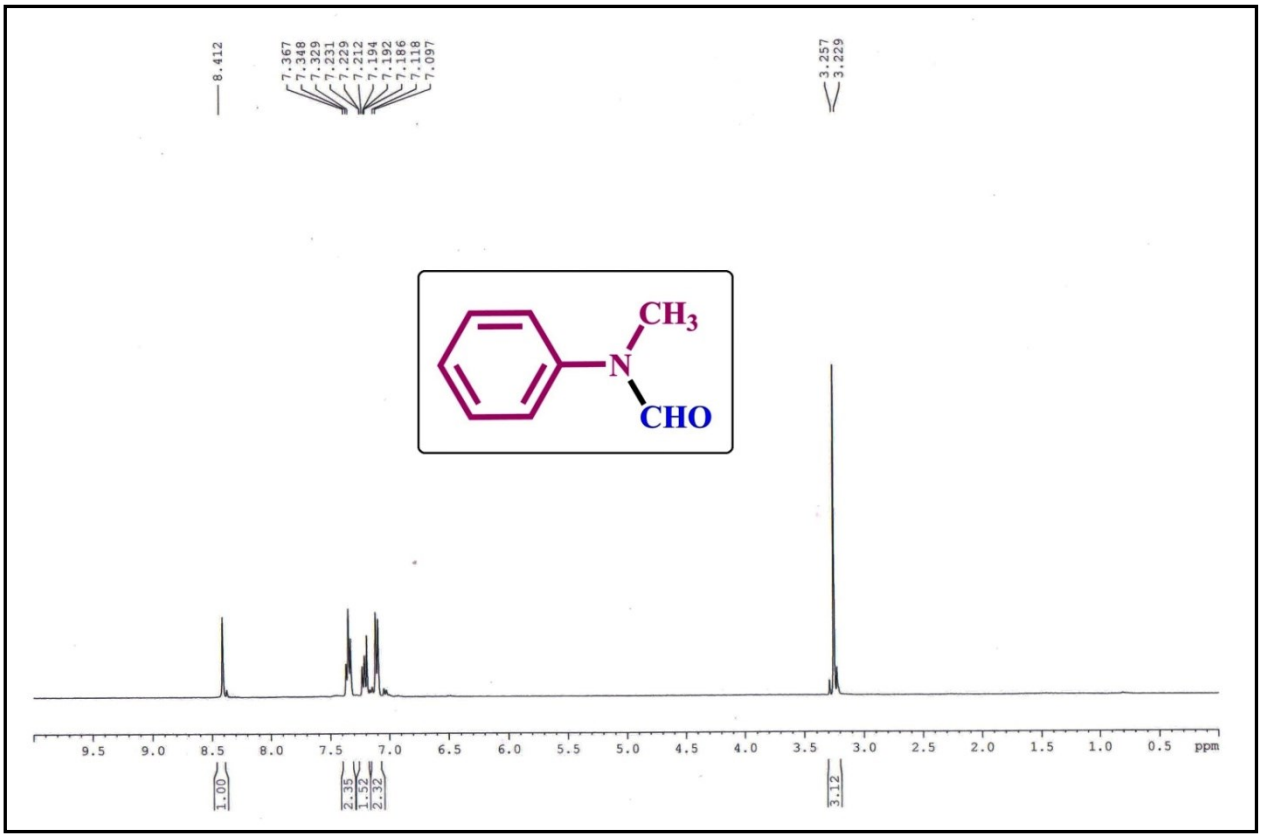

8.920
8.895
8.625
8.597
8.275
8.270
8.106
7.727
7.723
7.718
7.385
7.365
7.239
7.237
7.219
7.202
7.198
7.193
7.183
7.180
7.176
7.163
7.160
7.156
7.153
7.133
7.112
7.091
7.071
6.977
6.974
6.957
6.954
NHCHO
Br
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.08 1.47 1.32 1.40 1.44 1.06 1.10 0.55 1.14 1.28 0.96

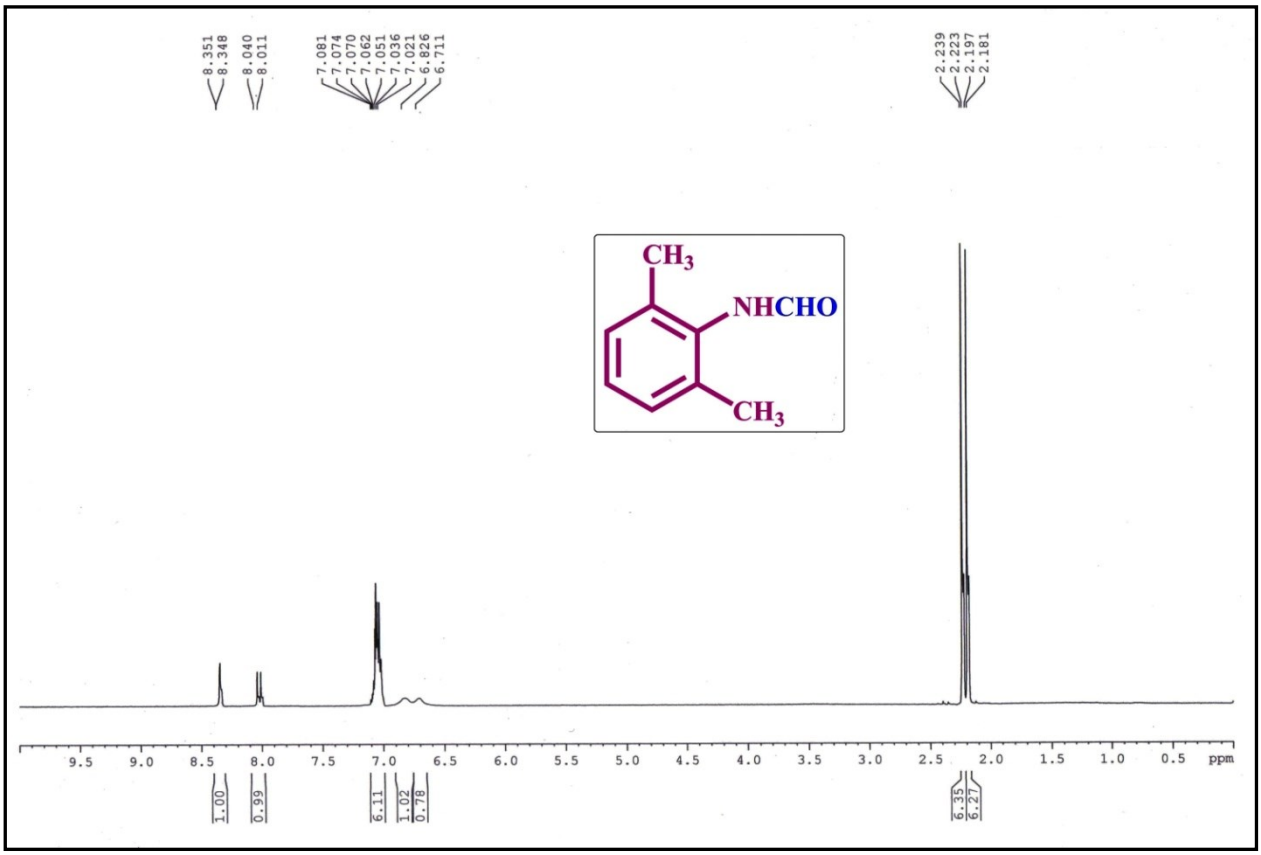

10.360
8.848
8.827
8.606
8.292
8.288
8.271
8.267
7.726
7.723
7.705
7.687
7.683
7.285
7.272
NHCHO
NO2
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.88
1.00
0.94
1.12
1.17


9.229
8.721
8.243
8.239
7.670
7.667
7.650
7.258
6.969
6.965
6.949
6.931
6.927
6.886
6.883
6.875
6.866
6.862
6.793
6.790
6.774
6.755
NHCHO
OH
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.84
1.01
1.00
1.37
1.32
1.33


8.605
8.577
8.325
7.612
7.591
7.585
7.563
7.275
7.253
7.193
7.136
7.118
6.791
6.770
NHCHO
I
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
0.66
1.00
3.47
2.34
1.67


7.999
7.918
7.888
7.267
7.248
7.237
7.215
7.210
7.194
7.176
7.174
7.156
7.154
7.131
7.113
7.087
7.049
7.038
6.875
4.270
4.255
4.236
4.200
4.184
NHCHO
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
3.06
2.61
0.89
2.04


8.412
7.367
7.348
7.329
7.231
7.229
7.212
7.194
7.192
7.186
7.118
7.097
3.257
3.229
CH3
N
CHO
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.35
1.32
2.32
3.12


8.351
8.348
8.040
8.011
7.081
7.074
7.070
7.062
7.051
7.036
7.021
6.826
6.711
2.239
2.223
2.197
2.181
CH3
NHCHO
CH3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.99
6.11
1.02
0.78
6.35
6.27

8. References

1. K. P. Dhake, P. J. Tambade, R. S. Singhal and B. M. Bhanage, *Green Chem. Lett. Rev*., 2011, **4**, 151.

2. (a) T. Kimura, K. Kamata and N. Mizuno, *Angew. Chem. Int. Ed*., 2012, **51**, 6700; (b) X. Cao, H. A. Zhong, P. Zhang and H. Zheng, *J. CO_2 Util.,* 2018, **24**, 250.

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