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Supporting Information

Deprotection of oximes, imines, and azines to the corresponding carbonyls using Cu-nano particles on cellulose template as green reusable catalyst

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Experimental

General Methods. Chromatographic separations were performed using silica gel 60-120. Infrared (IR) spectra were recorded using an FT-IR spectrometer as chloroform solutions on sodium chloride disks. NMR spectra were recorded in Bruker Avance DPX 300 MHz and Avance-III 500 MHz FTNMR spectrometer using tetramethylsilane (TMS) as an internal standard in indicated solvent. All microwave irradiation experiments were carried out in a CEM-Discover LabMate system (standard configuration, temperature control, external IR temperature sensor, fixed hold time).

Preparation of Cu-nano particle using $NaBH_4$ reduction method:

To a suspension of standard cellulose (200 mg) in water (20 mL), copper(II) acetate (50 mg) was added. The mixture was stirred for 30 minutes at room temperature and then cooled to 0 °C. $NaBH_4$ (20 mg) was added slowly portion wise under nitro gen atmosphere when the solution turned black. The whole mixture was stirred at that temperature for another 1 hour. The black suspension was filtered, washed, vacuum dried, and finally stored under N_2 atmosphere.

Preparation of Cu-nano particle using hydrazine hydrate/ NaOH reduction method

To a suspension of standard cellulose (200 mg) in water (20 mL), copper(II) acetate (50 mg) was added and the mixture was stirred for 30 minutes at room temperature. NaOH (10%) solution and Hydrazine Hydrate was added to the above suspension until the pH value exceeds 10. The resulting solution was kept in a thermostatic bath (50-60 °C) for 3-4 h. The black suspension was then filtered, washed and vacuum dried and finally stored under N_2 atmosphere.

General procedure for deprotection of oximes/imines/azines

In a 10 mL microwave reaction vial oxime/imine/azine (1 mmol), H_2O (5 mL), and Cu-nano catalyst (20 mol%) were taken. The mixture was heated under microwave at 80–100 ^oC for 5-10 min. After the completion of the reaction, as checked by TLC, the catalyst was filtered while washing with ethyl acetate. The filtrate was extracted with ethyl acetate (2 × 20 mL).

The organic layer was washed with brine (15 mL), dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography.

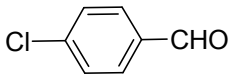
General procedure for preparation of oximes:

To a solution of aldehyde/ketone (1 mmol) in ethanol (5 mL), hydroxylamine (1.5 mmol) and pyridine (0.5 mL) was added. The mixture was heated on a water bath at 70-80 °C for 30 minutes to 3 hours. After this, the reaction was cooled in an ice batch when crystals of oximes separated. Filtration and washing with 70% cold ethanol provided oxime. Further purification was done by recrystallization from ethanol (95%).

General procedure for preparation of imines and azines:

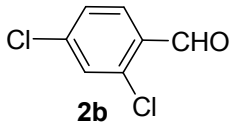
A mixture of aldehyde (1 mmol), amine (1 mmol), and ethanol (5 mL) was warmed in a water bath for 2-5 minutes and then cooled in an ice bath when crystals of imines/azines separated. Filtration, washing with 70% ethanol and recrystallization from ethanol (95%) provided pure imines/azines.

Characterization of aldehydes:



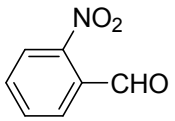
2a

4-Chlorobenzaldehyde (2a). Semi solid; R_f: 0.6 (1:20 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 1699, 1589, 1386, 1207, 1094; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.99 (s, 1H), 7.84 (d, 2H, J = 8.4 Hz), 7.52 (d, 2H, J = 8.4 Hz).



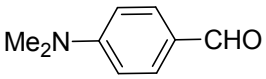
2b

2, 4-Dichlorobenzaldehyde (2b). Solid; Mp: 68-70 °C (lit.[1] 71-72 °C); R_f: 0.75 (1:20 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 1678, 1584, 1375, 1199, 1047; ^1H NMR ($CDCl_3$, 300 MHz): δ 10.42(s, 1H), 7.87 (d, 2H, J = 8.4), 7.49(s, 1H), 7.38 (d, 2H, J = 8.4).



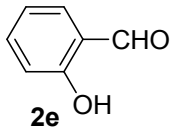
2c

2-Nitrobenzaldehyde (2c). Semi solid; R_f: 0.6 (1:10 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 1694, 1524, 1344, 1188; ^1H NMR ($CDCl_3$, 500 MHz): δ 10.43 (s, 1H), 8.13 (dd, 1H, J = 8.0, 1.5 Hz), 7.96 (d, 1H, J = 8.0, 1.5 Hz), 7.88-7.71 (m, 2H).



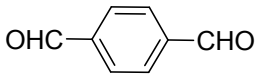
2d

4-(Dimethyl)aminobenzaldehyde (2d). Solid; Mp: 70-72 °C (lit.[2] 70-72 °C); R_f: 0.4 (1:10 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 1661, 1598, 1375, 1231, 1170, 1065; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.74(s, 1H), 7.75 (d, 2H, J = 8.7), 6.72 (d, 2H, J = 8.7 Hz), 3.087(s, 6H).



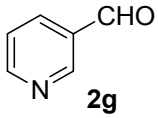
2e

Salicylaldehyde (2e). Oil; R_f: 0.6 (1:20 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 3062, 1664, 1580, 1459, 1386, 1278, 1150, 1029; ^1H NMR ($CDCl_3$, 300 MHz): δ 11.02 (s, 1H), 9.89 (s, 1H), 7.58 -7.50 (m, 2H), 7.05-6.96 (m, 2H).



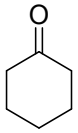
2f

Benzene-1,4-dicarbaldehyde (2f). Solid; Mp: 110-112 °C (lit.[3] 113-114 °C); R_f: 0.5 (1:5 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 1692, 1497, 1384, 1301, 1199, 1013; ^1H NMR ($CDCl_3$, 300 MHz): δ 10.14 (s, 2H), 8.06 (s, 4H).



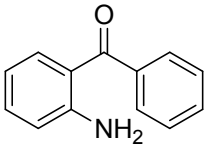
2g

Pyridine-3-aldehyde (2g). Oil; R_f: 0.3 (1:10 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 1704, 1590, 1428, 1216, 1026; ^1H NMR ($CDCl_3$, 300 MHz): δ 10.14 (s, 1H), 9.10 (s, 1H), 8.86 (d, 1H, J = 8.0 Hz), 8.21 (d, 1H, J = 8.0 Hz), 7.54-7.44 (m, 1H).



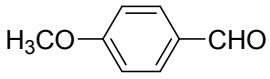
2h

Cyclohexanone (2h). Oil; R_f: 0.7 (1:20 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 1714, 1450, 1311, 1222, 1119; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.38-2.28 (m, 4H), 1.91-1.83 (m, 4H), 1.75-1.68 (m, 2H).



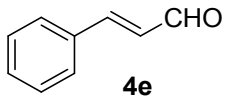
2i

(2-Aminophenyl)(phenyl)methanone (2i). Solid; Mp: 101-103 °C (lit.[4] 103-104 °C); R_f: 0.65 (1:10 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 3470, 3349, 1615, 1548, 1303, 1248, 1160; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.66 (d, 2H, J = 8.0 Hz), 7.58-7.45 (m, 4H), 7.32 (t, 1H, J = 8.0 Hz), 6.76 (d, 1H, J = 8.0 Hz), 6.62 (t, 1H, J = 8.0 Hz), 6.12 (s, 2H).



4d

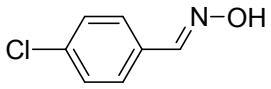
4-Methoxy benzaldehyde (4d). Oil; R_f: 0.35 (1:20 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 1694, 1601, 1513, 1316, 1182, 1025; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.88 (s, 1H), 7.84 (d, 1H, J = 7.5 Hz), 7.02 (d, 1H, J = 7.5 Hz), 3.86 (s, 3H).



4e

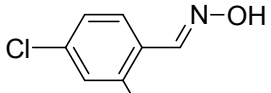
Cinnamaldehyde (4e). Oil; R_f: 0.3 (1:20 :: Ethyl acetate:Hexane); IR (KBr): cm^{-1} 1678, 1626, 1450, 1127, 973; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.88 (d, 1H, J = 8.0 Hz), 7.98-7.52 (m, 2H), 7.48-7.40 (m, 4H), 6.71 (dd, 1H, J = 16.0, 8.0 Hz).

Characterization of oximes:



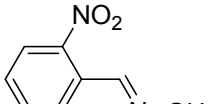
1a

4-Chlorobenzaldehyde oxime (1a). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.12(s, 1H), 7.52 (d, 2H, J = 9.0 Hz), 7.36 (d, 2H, J = 9.0 Hz).



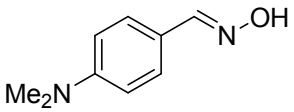
1b

2, 4-Dichlorobenzaldehyde oxime (1b). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.28(s, 1H), 7.78 (d, 1H, J = 7.5 Hz), 7.42 (s, 1H), 7.25 (d, 1H, J = 7.5 Hz).



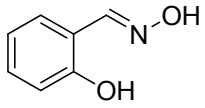
1c

2-Nitro benzaldehyde oxime (1c). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.69(s, 1H), 8.07 (d, 1H, J = 7.0 Hz), 7.92 (d, 1H, J = 7.0 Hz), 7.71-7.53 (m, 2H).



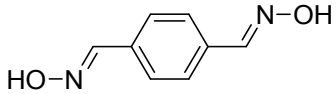
1d

4-(Dimethylamino)benzaldehyde oxime (1d). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.06 (s, 1H), 7.44 (d, 2H, J = 8.5 Hz), 6.68 (d, 2H, J = 8.5 Hz), 2.99 (s, 6H).



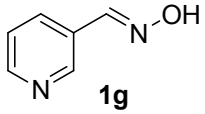
1e

2-Hydroxybenzaldehyde oxime (1e). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.33 (s, 1H), 7.48 (d, 1H, J = 8.0 Hz), 7.28-7.18 (m, 1H), 6.98-6.75 (m, 2H).



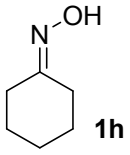
1f

Benzene-1,4-dicarbaldehyde oxime (1f). ^{1}H NMR (MeOH-$d6$, 300 MHz): δ 11.35 (s, 2H), 8.15 (s, 2H), 7.61 (s, 4H).



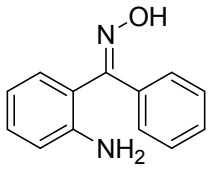
1g

Nicotinaldehyde oxime (1g). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.01 (s, 1H), 8.89-8.82 (m, 1H), 8.66-8.58(m, 1H), 8.34 (s, 1H), 7.99-7.94 (m, 1H).



1h

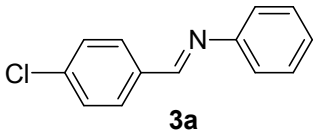
Cyclohexanone oxime (1h). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.52 (t, 2H, J = 6.5 Hz), 2.22 (t, 2H, J = 5.5 Hz), 1.72-1.55 (m, 6H).



1i

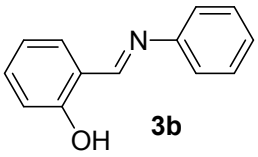
(2-Aminophenyl)(phenyl)methanone oxime (1i). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.63 (d, 2H, J = 7.0 Hz), 7.54-7.41 (m, 4H), 7.29 (t, 1H, J = 7.0 Hz), 6.73 (d, 1H, J = 8.0 Hz), 6.60 (t, 1H, J = 7.0 Hz)

Characterization of imines:



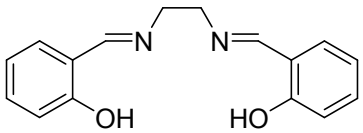
3a

4-Chlorobenzylidene-phenylamine (3a). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.42 (s, 1H), 7.84 (d, 2H, J = 8.3 Hz), 7.49-7.34 (m, 4H), 7.28-7.18 (m, 3H).



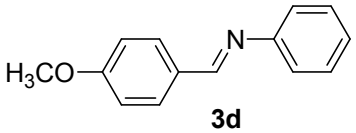
3b

2-Phenyliminomethyl-phenol (3b). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 13.28 (s, 1H), 8.62 (s, 1H), 7.55-7.25 (m, 5H), 7.03 (d, 1H, J = 8.4 Hz), 6.95 (t, 1H, J = 7.5 Hz).



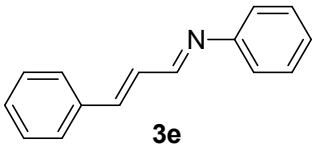
3c

SalenH_2 (3c). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 13.23 (s, 2H), 8.36 (s, 2H), 7.32-7.21 (m, 4H), 6.95-6.82 (m, 4H), 3.93 (s, 4H).



3d

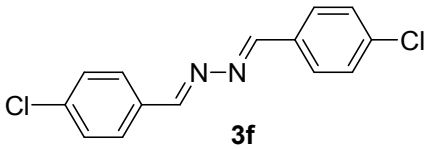
4-Methoxybenzylidenephenylamine (3d). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.38 (s, 1H), 7.84 (d, 2H, *J* = 8.7 Hz), 7.43-7.35 (m, 2H), 7.24-7.18 (m, 3H), 6.97 (d, 2H, J = 8.6 Hz), 3.87 (s, 3H).



3e

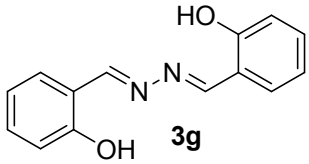
Phenyl-(3-phenyl-allylidene)-amine (3e). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.27 (d, 1H, *J* = 6.4 Hz), 7.54 (d, 2H, J = 7.8 Hz), 7.53-7.33 (m, 5H), 7.25-7.07 (m, 5H).

Characterization of azines:



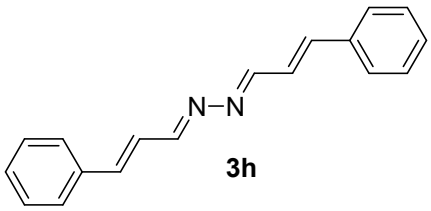
3f

N,N'-Bis-(4-chlorobenzylidene)-hydrazine (3f). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.61 (s, 2H), 7.77 (d, 4H, *J* = 8.4 Hz), 7.42 (d, 4H, *J* = 8.4 Hz).



3g

N,N'-Bis-(2-hydroxybenzylidene)-hydrazine (3g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.28 (brs, 2H), 8.64 (s, 2H), 7.37-7.26 (m, 4H), 7.04-6.85 (m, 4H).



3h

N,N'-Bis-(3-phenylallylidene)-hydrazine (3h). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.43-8.32 (m, 2H), 7.53-7.50 (m, 4H), 7.44-7.33 (m, 6H), 7.09-7.07 (m, 4H)

References:

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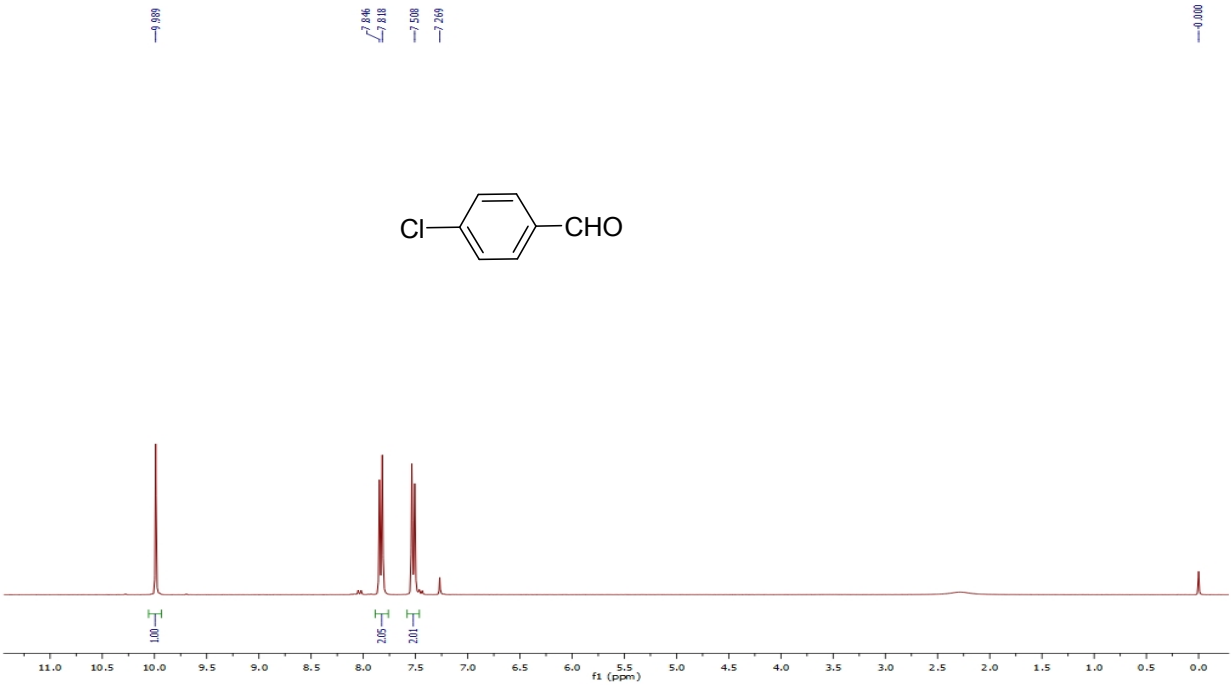
Spectra: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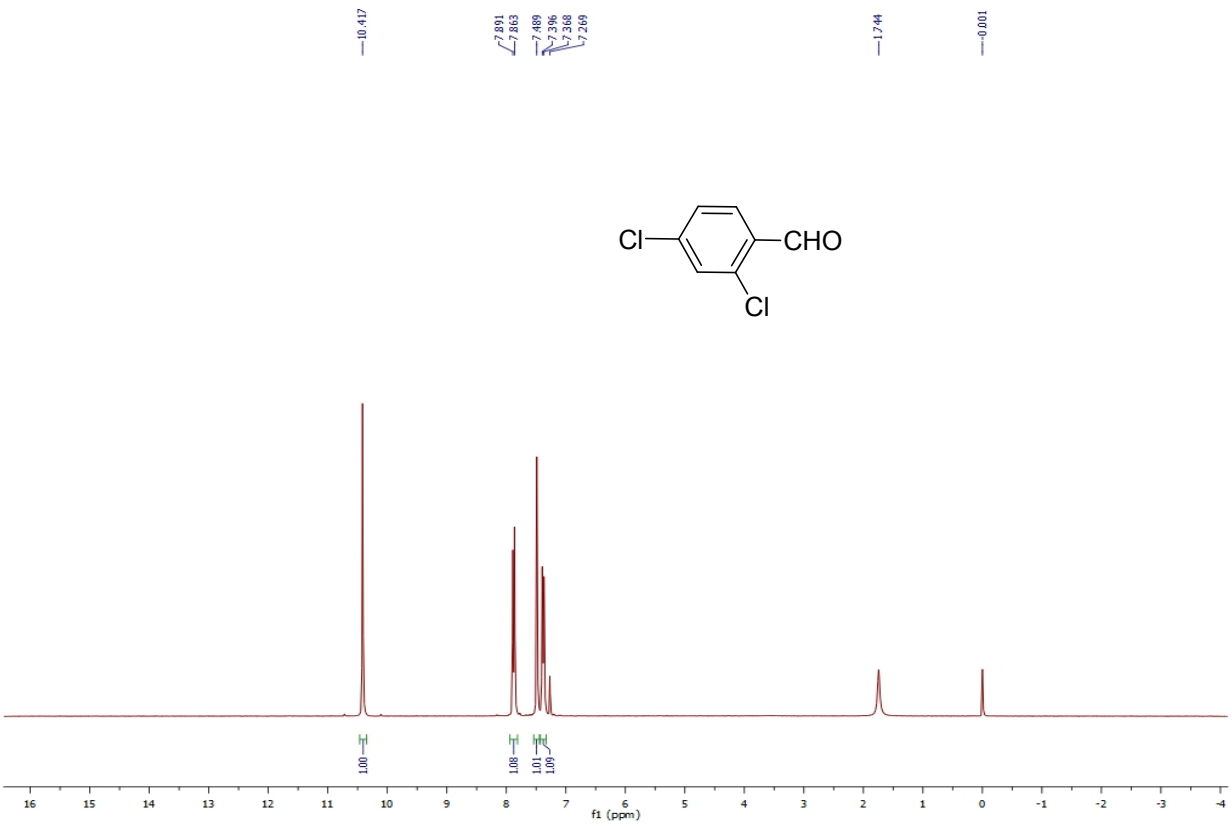
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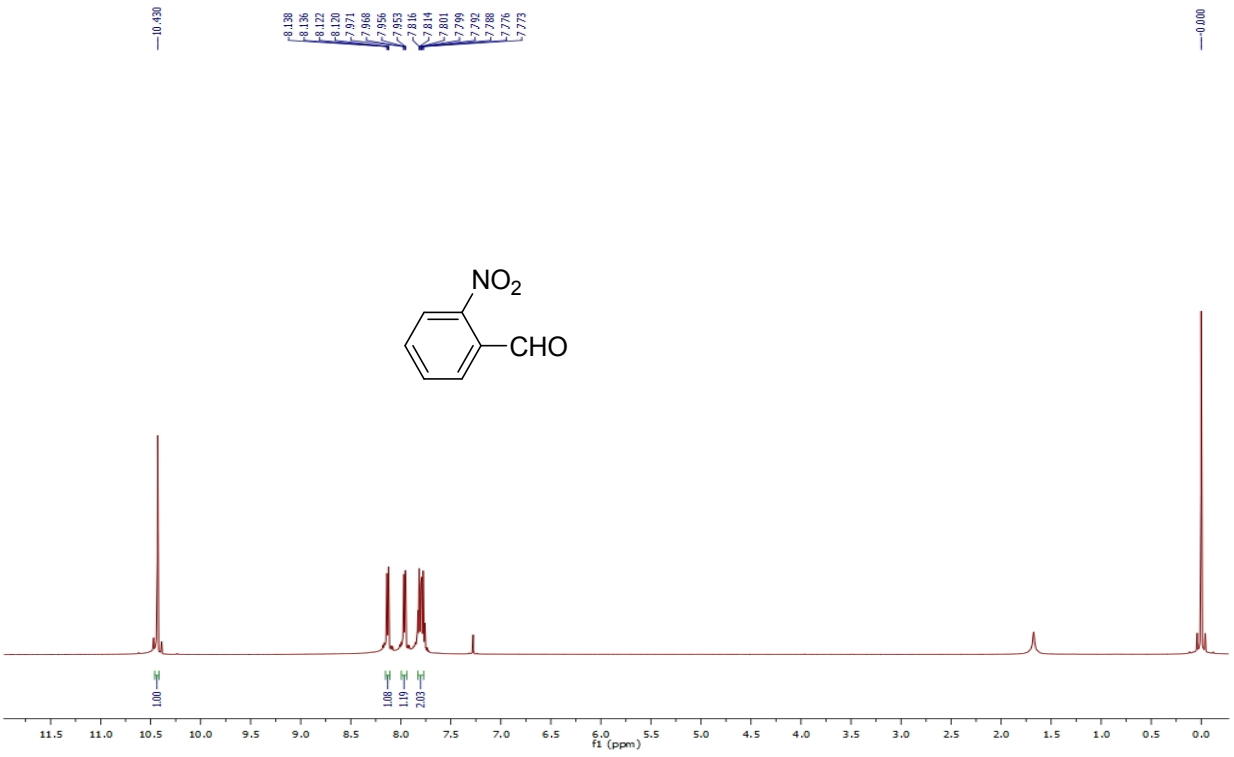
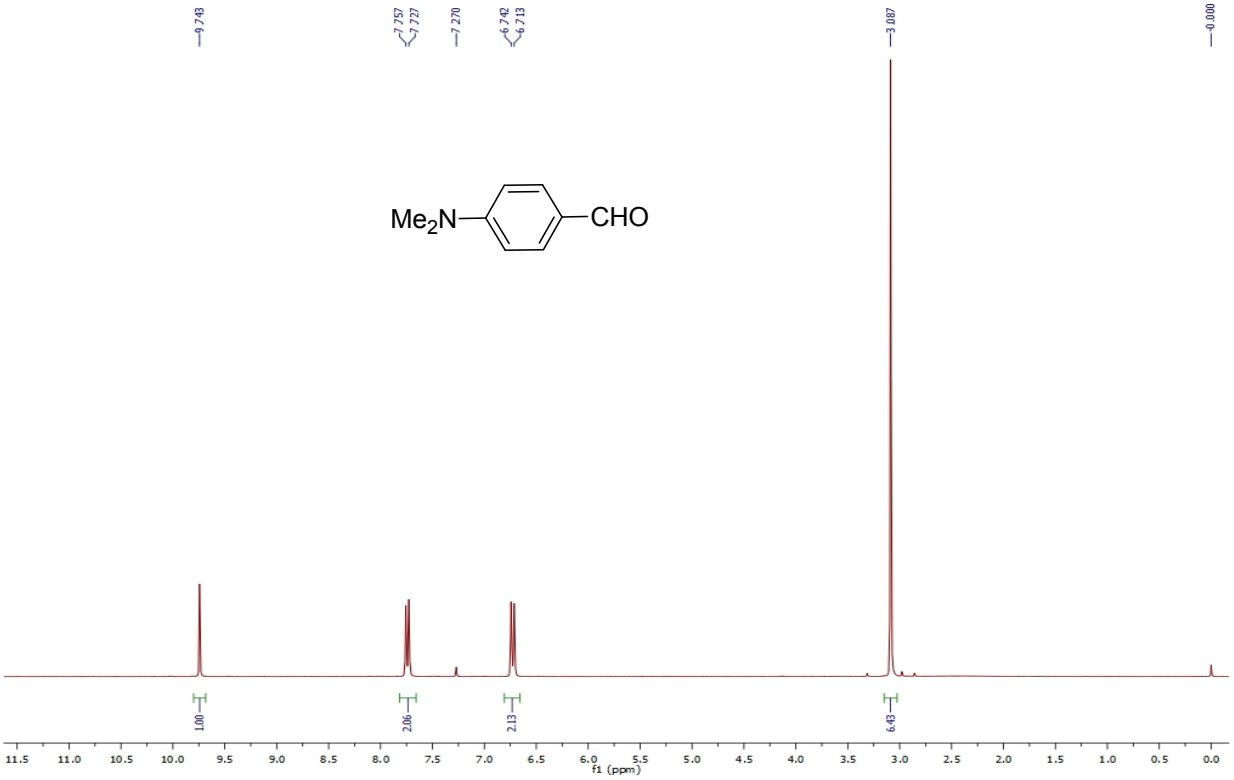
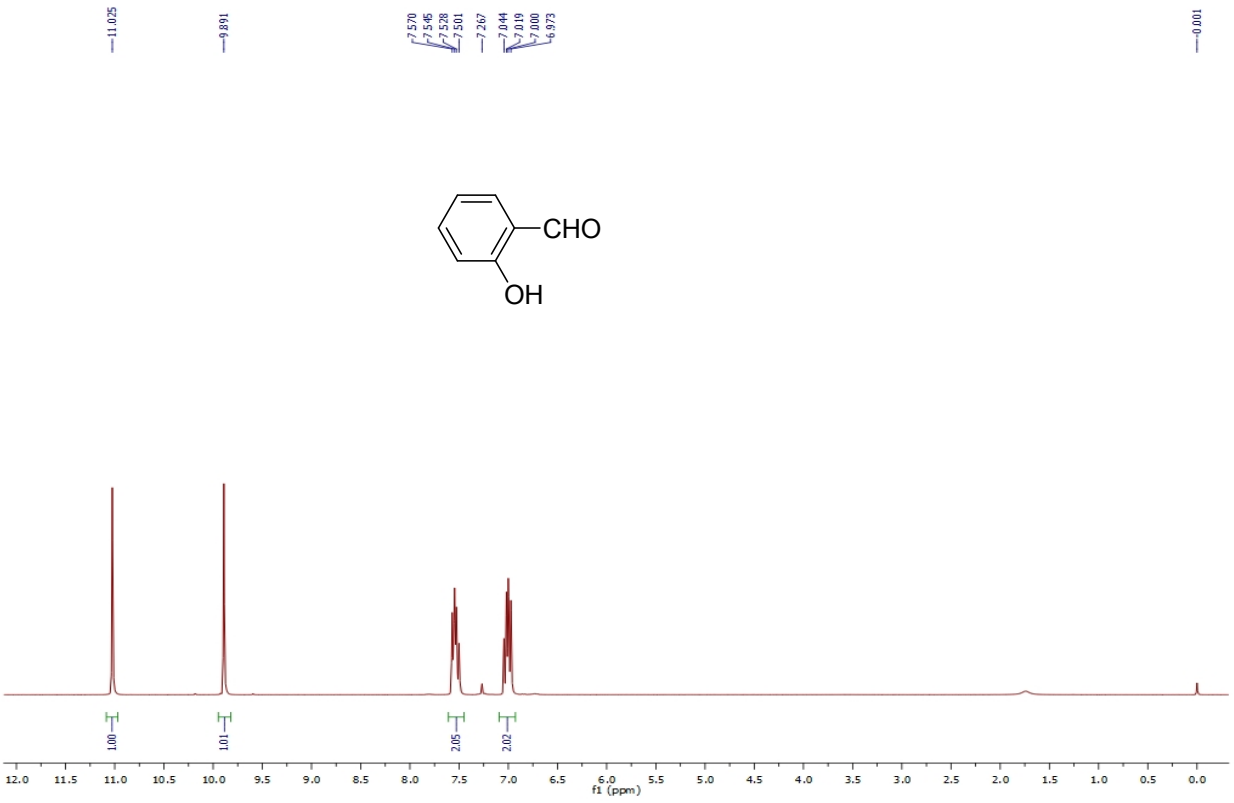
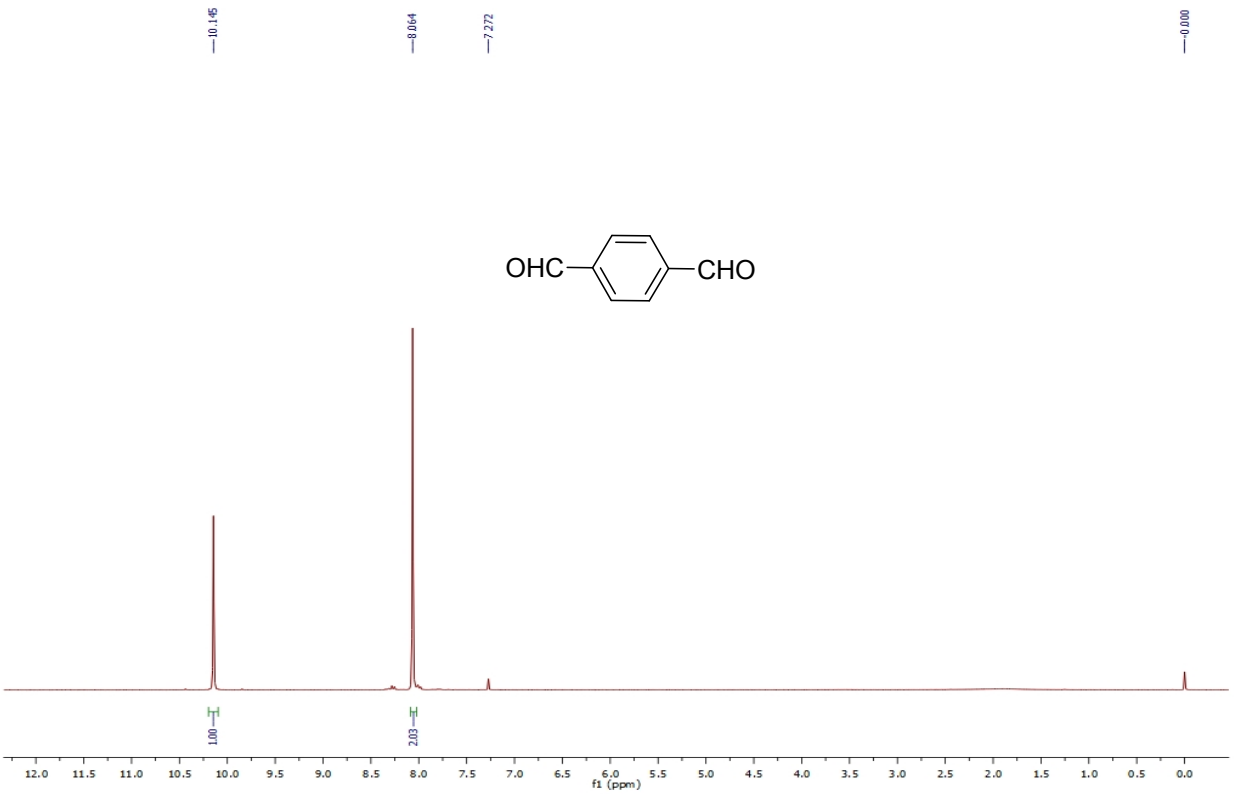
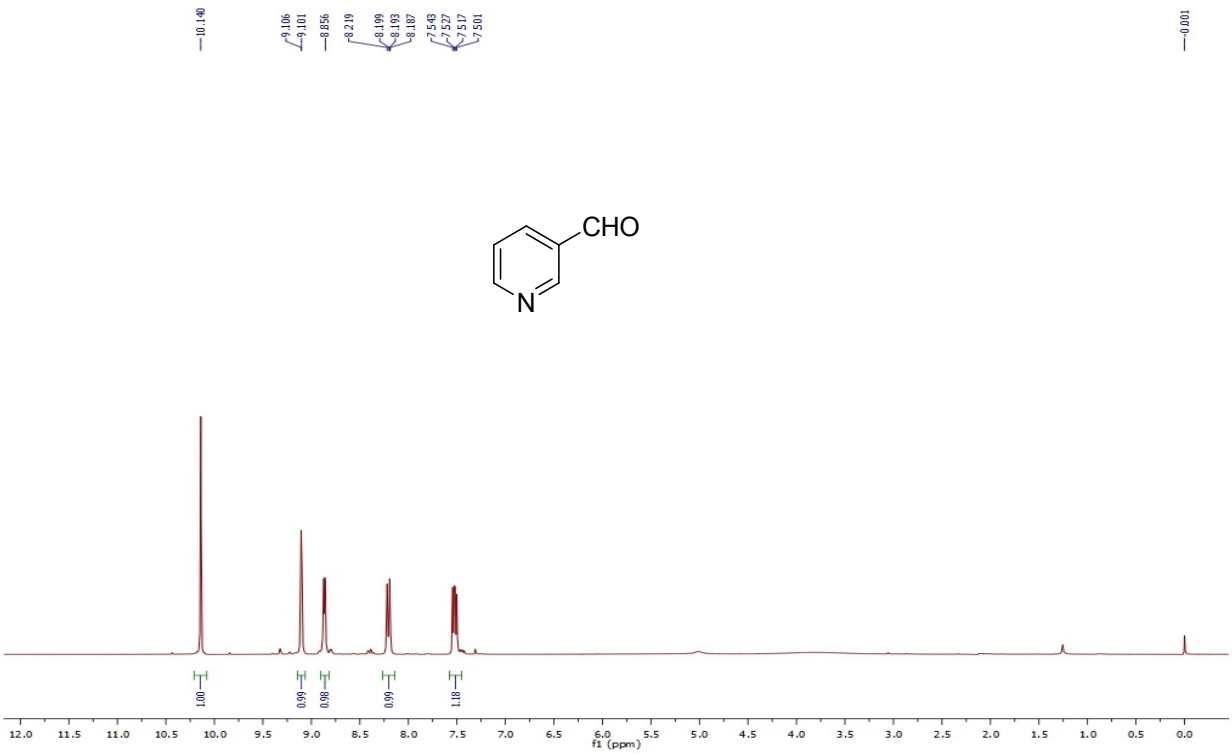
7.863
7.489
7.396
7.368
7.269
1.744
0.001
Cl
CHO
Cl
1.00
1.08
1.01
1.09
f1 (ppm)

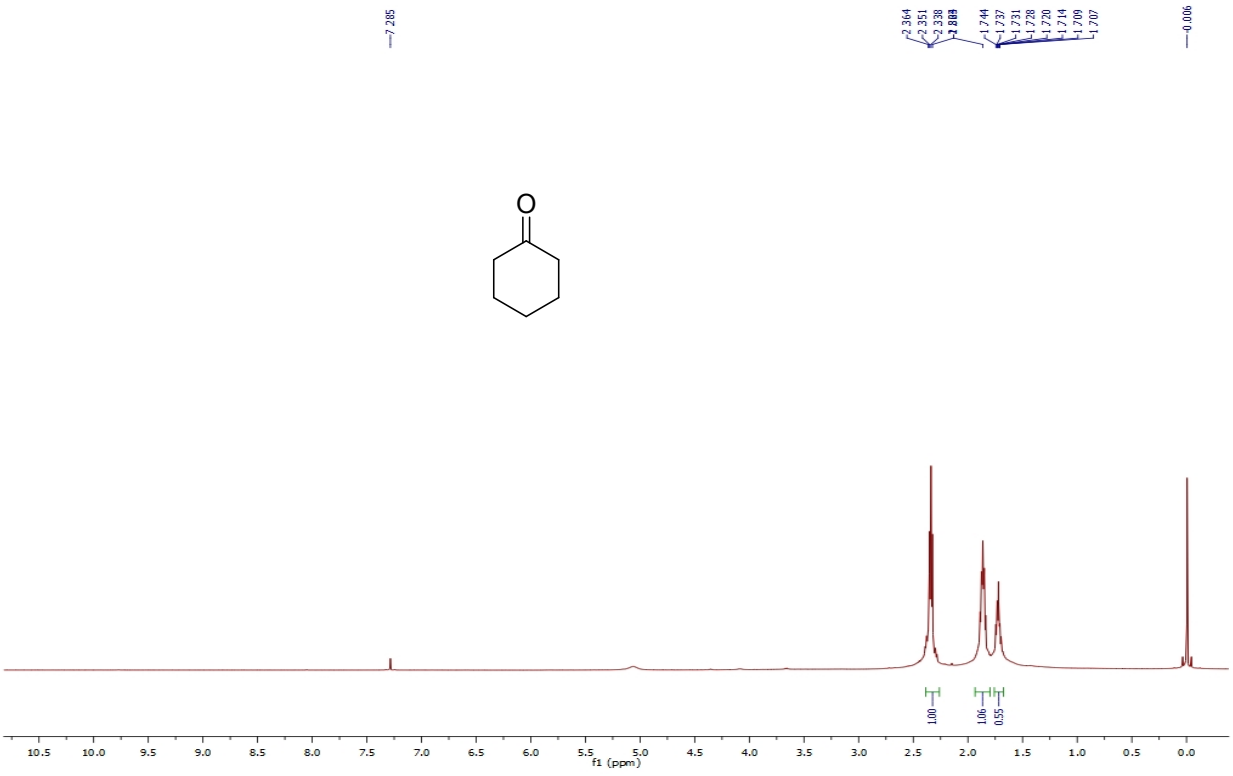

10.430
8.138
8.136
8.122
8.120
7.971
7.968
7.956
7.953
7.816
7.814
7.801
7.799
7.792
7.788
7.776
7.773
0.000
NO2
CHO
1.00
1.08
1.19
2.03
f1 (ppm)

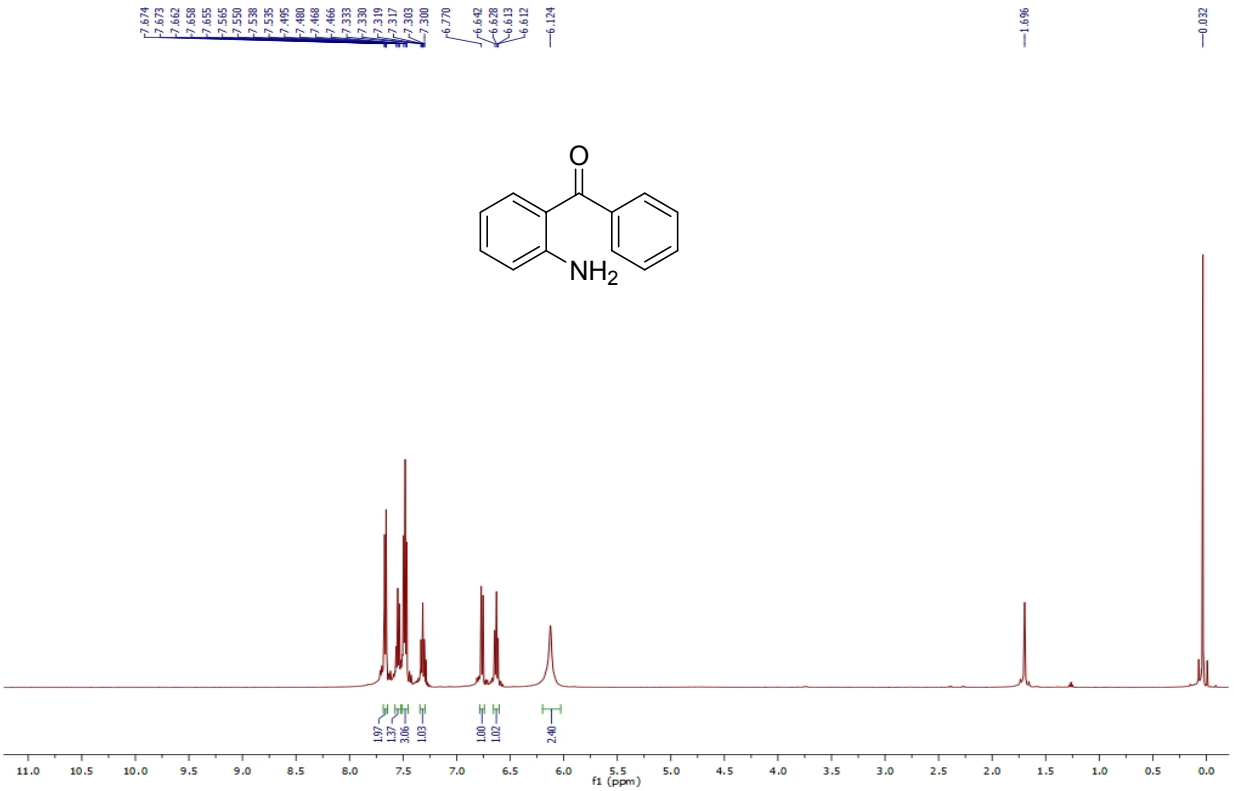

9.743
7.757
7.727
7.270
6.742
6.713
3.087
0.000
Me2N
CHO
1.00
2.06
2.13
6.43
f1 (ppm)

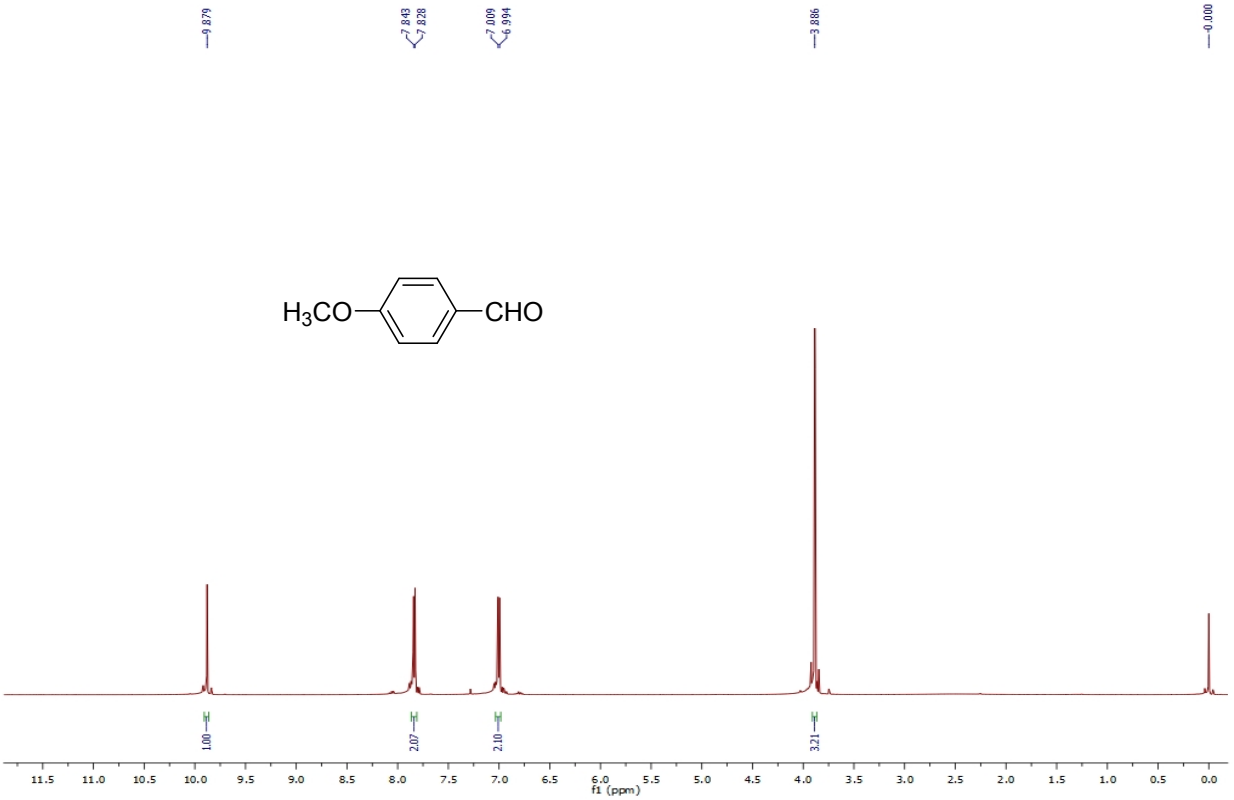

11.025
9.891
7.570
7.545
7.528
7.501
7.267
7.044
7.019
7.000
6.973
0.001
CHO
OH
1.00
1.01
2.05
2.02
f1 (ppm)

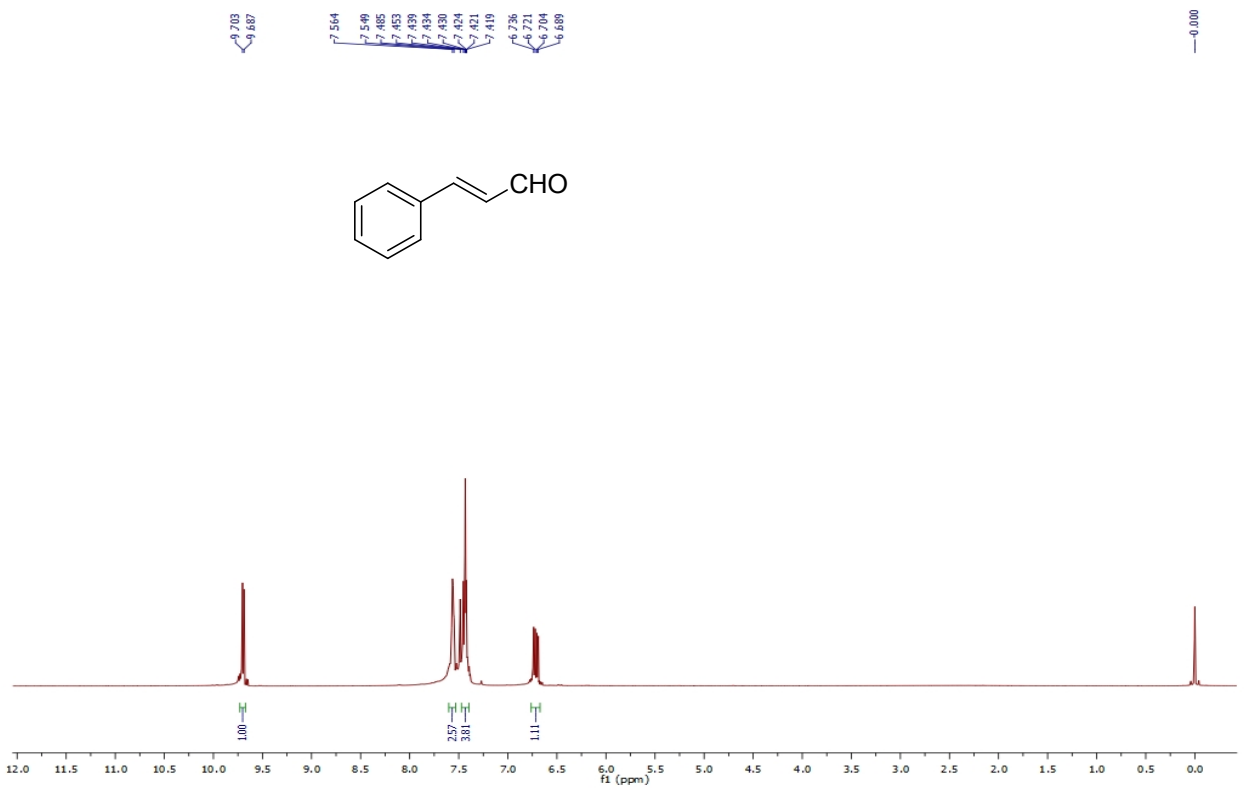

10.145
8.064
7.272
0.000
OHC
CHO
1.00
2.03
f1 (ppm)

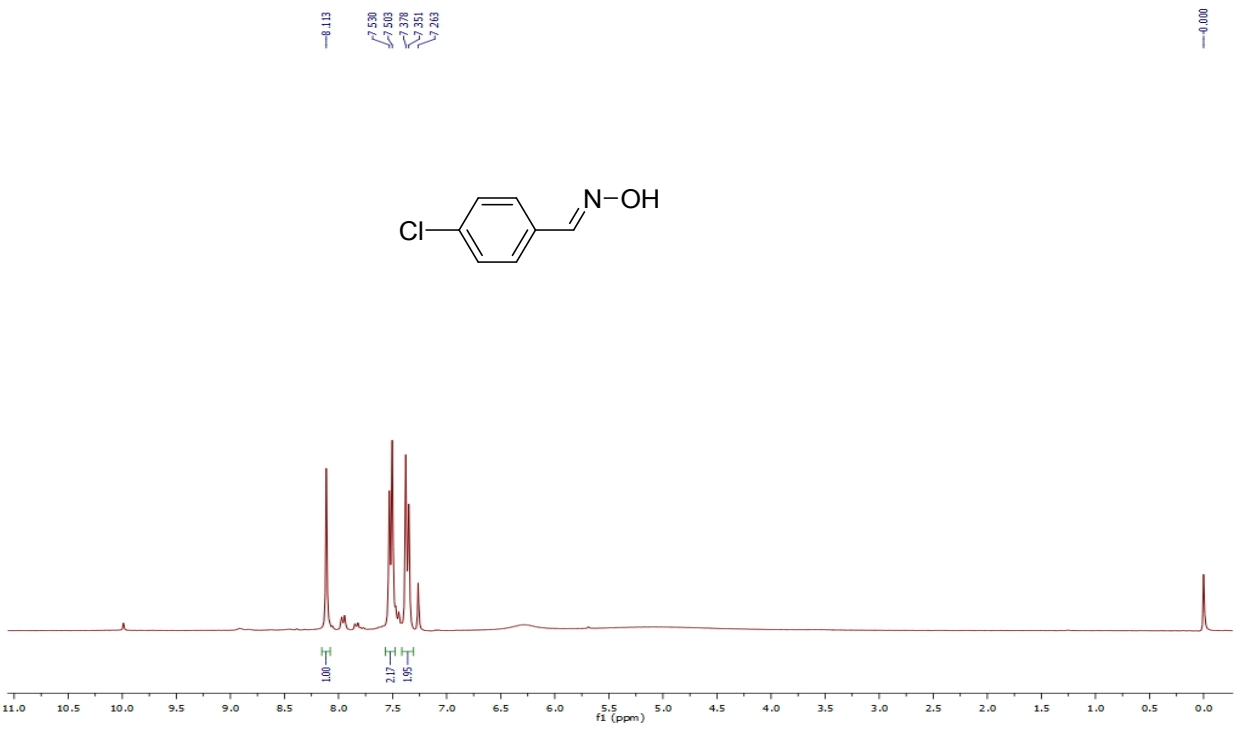

10.140
9.106
9.101
8.856
8.219
8.199
8.193
8.187
7.543
7.527
7.517
7.501
0.001
CHO
N
1.00
0.99
0.98
0.99
1.18
f1 (ppm)

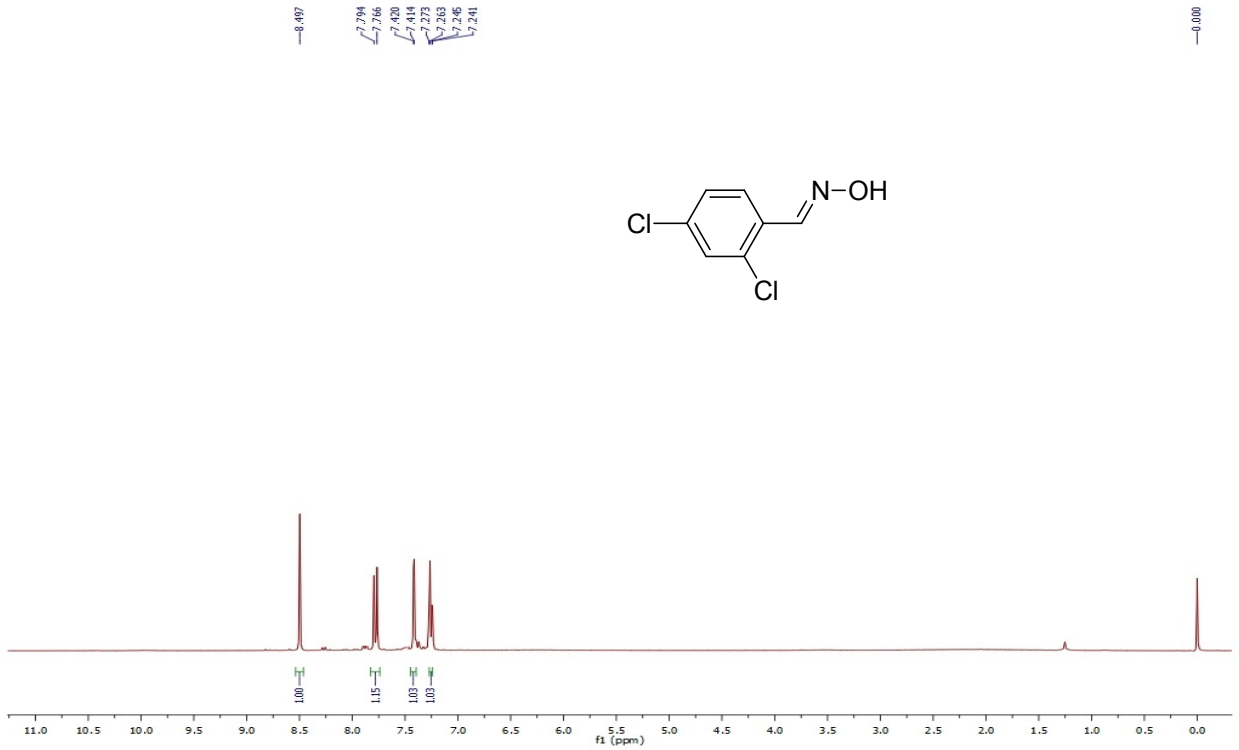

7.285
2.364
2.351
2.338
1.744
1.737
1.731
1.728
1.720
1.714
1.709
1.707
0.006
O
1.00
1.06
0.55
f1 (ppm)

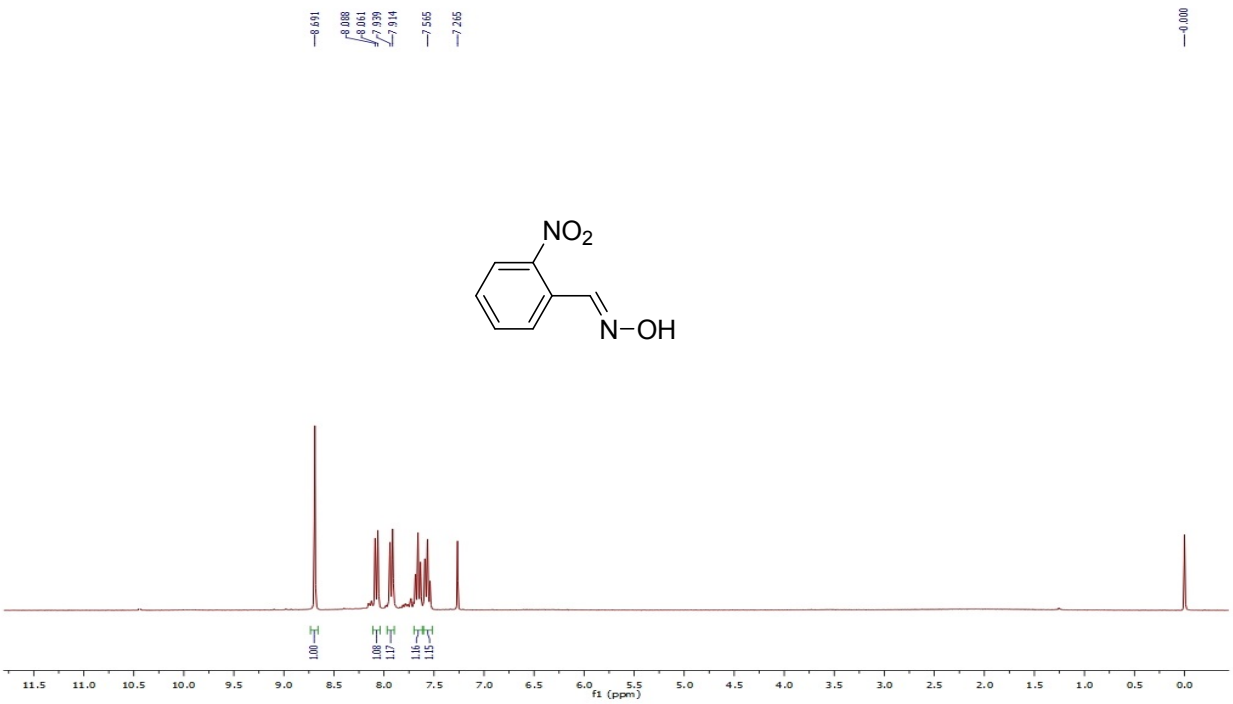

7.674
7.673
7.662
7.658
7.655
7.565
7.550
7.538
7.535
7.495
7.480
7.468
7.466
7.333
7.330
7.319
7.317
7.303
7.300
6.770
6.642
6.628
6.613
6.612
6.124
1.696
0.032
O
NH2
1.97
1.37
3.06
1.03
1.00
1.02
2.40
f1 (ppm)

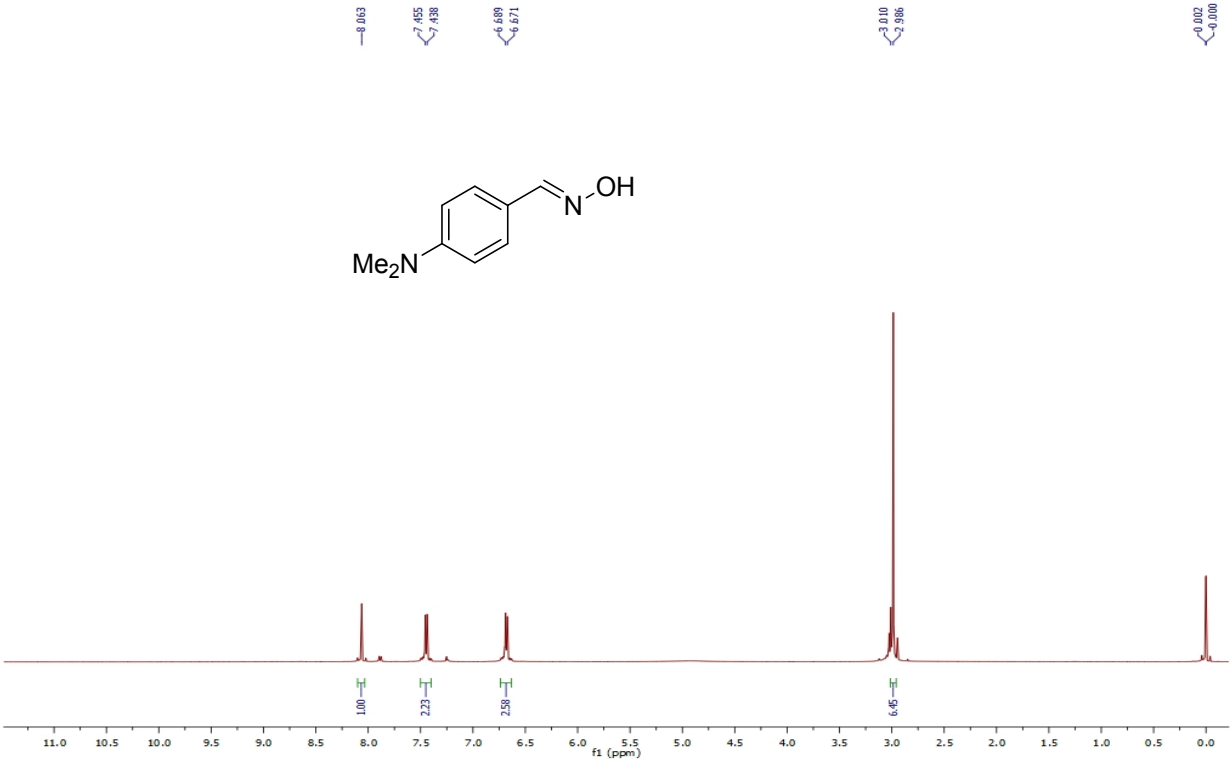

9.879
7.845
7.828
7.009
6.994
3.886
0.000
H3CO
CHO
1.00
2.07
2.10
3.21
f1 (ppm)

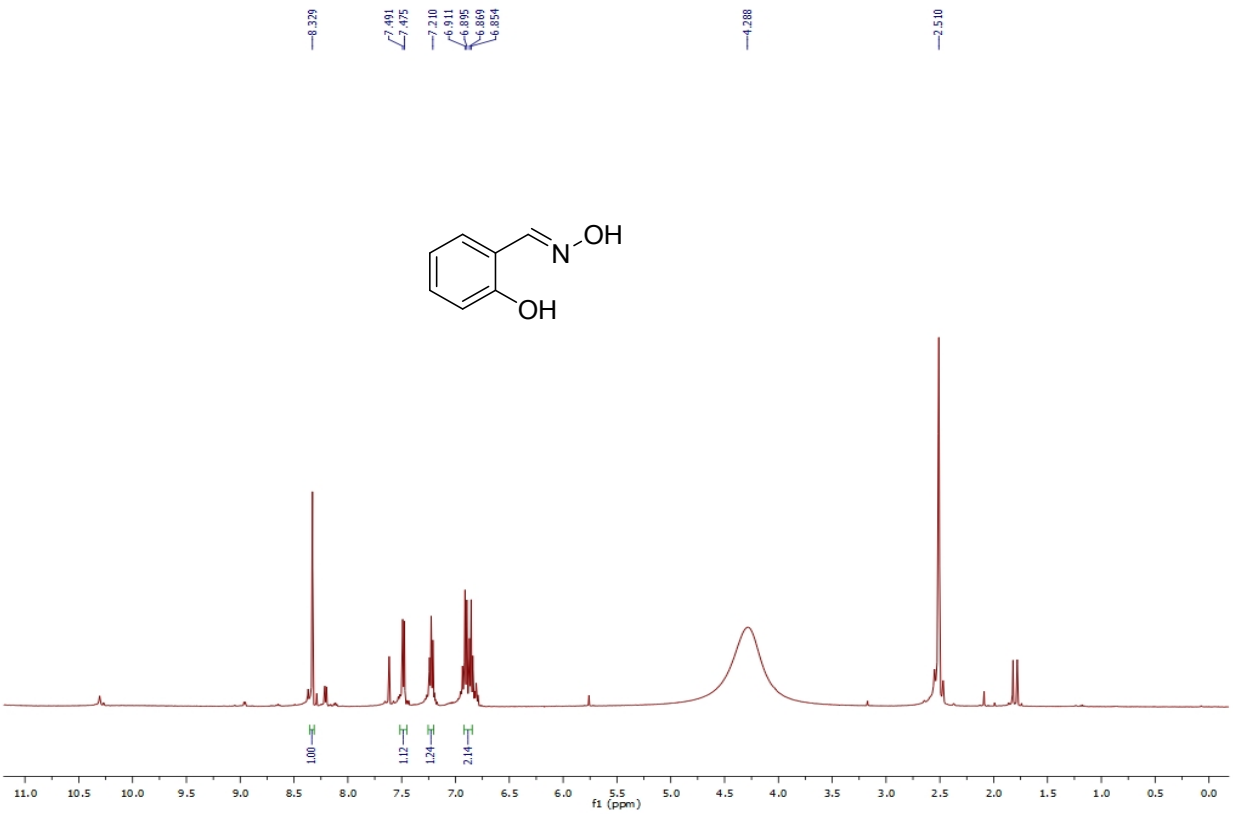

9.703
9.687
7.564
7.549
7.485
7.453
7.439
7.434
7.430
7.424
7.421
7.419
6.736
6.721
6.704
6.689
0.000
CHO
1.00
2.57
3.81
1.11
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

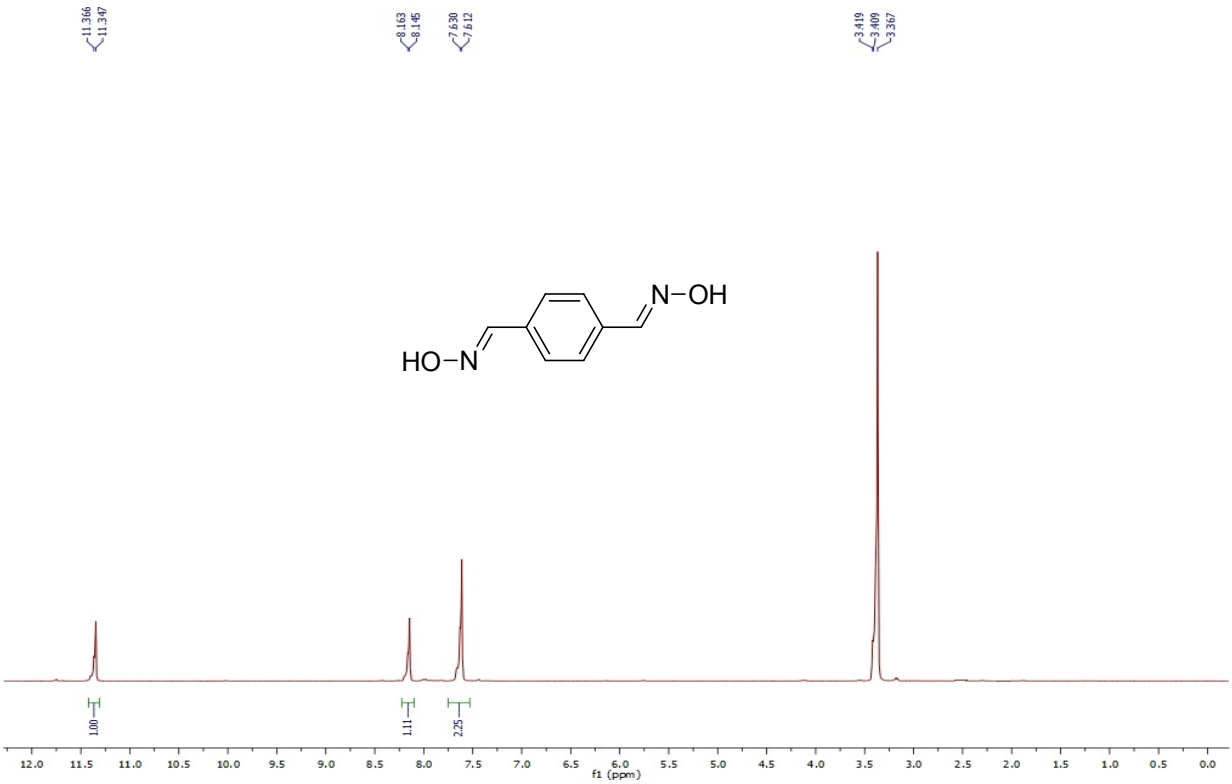

8.113
7.530
7.508
7.378
7.351
7.263
0.000
N−OH
Cl
1.00
2.17
1.95
f1 (ppm)

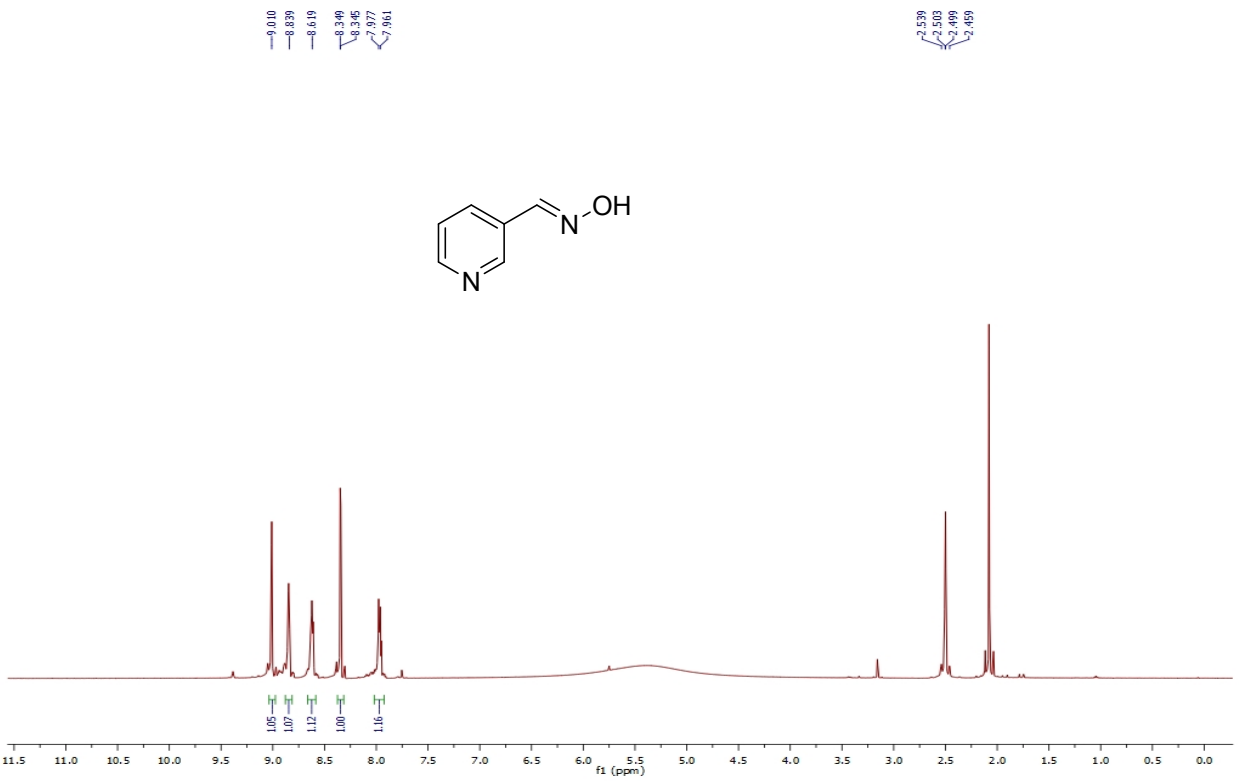

8.497
7.794
7.766
7.420
7.414
7.273
7.263
7.245
7.241
0.000
N−OH
Cl
Cl
1.00
1.15
1.03
1.03
f1 (ppm)

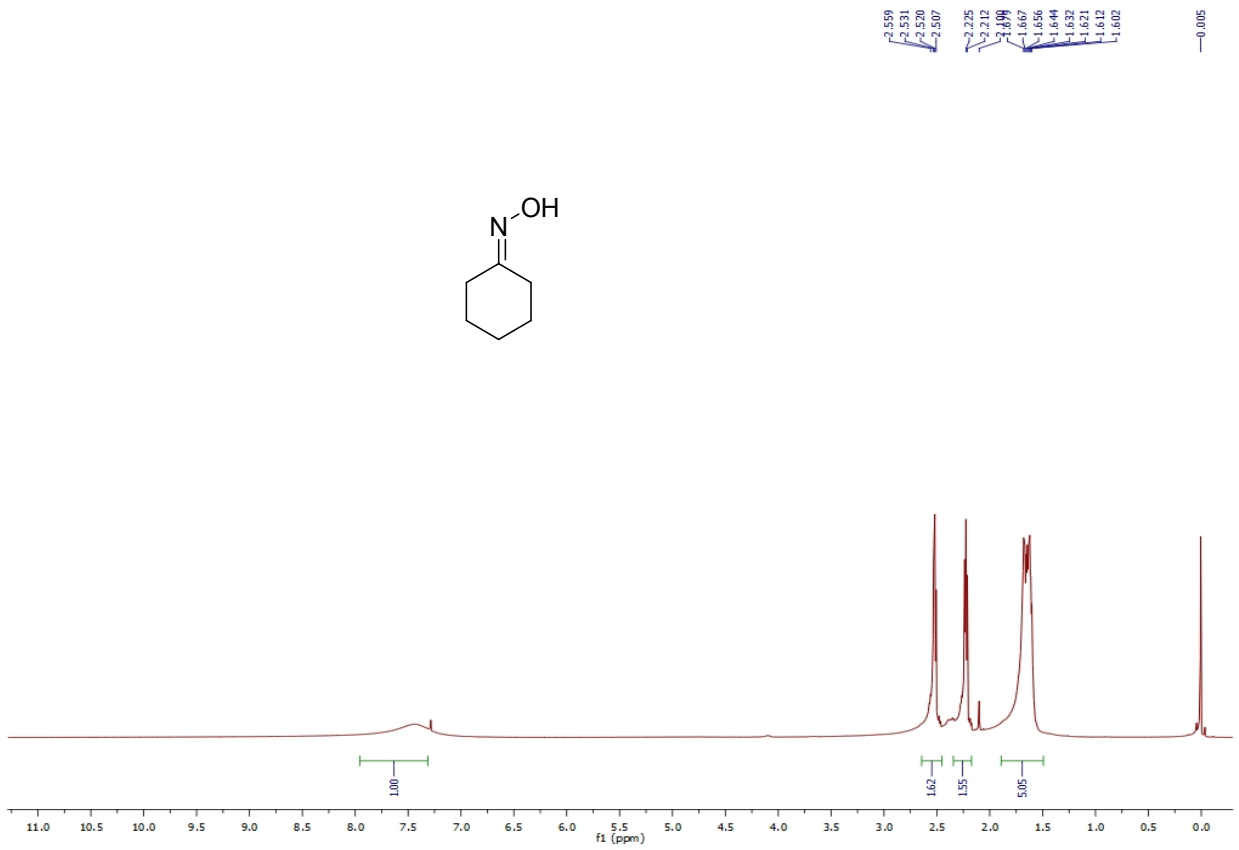

8.691
8.088
8.061
7.939
7.914
7.565
7.265
0.000
NO2
N−OH
1.00
1.08
1.17
1.16
1.15
f1 (ppm)

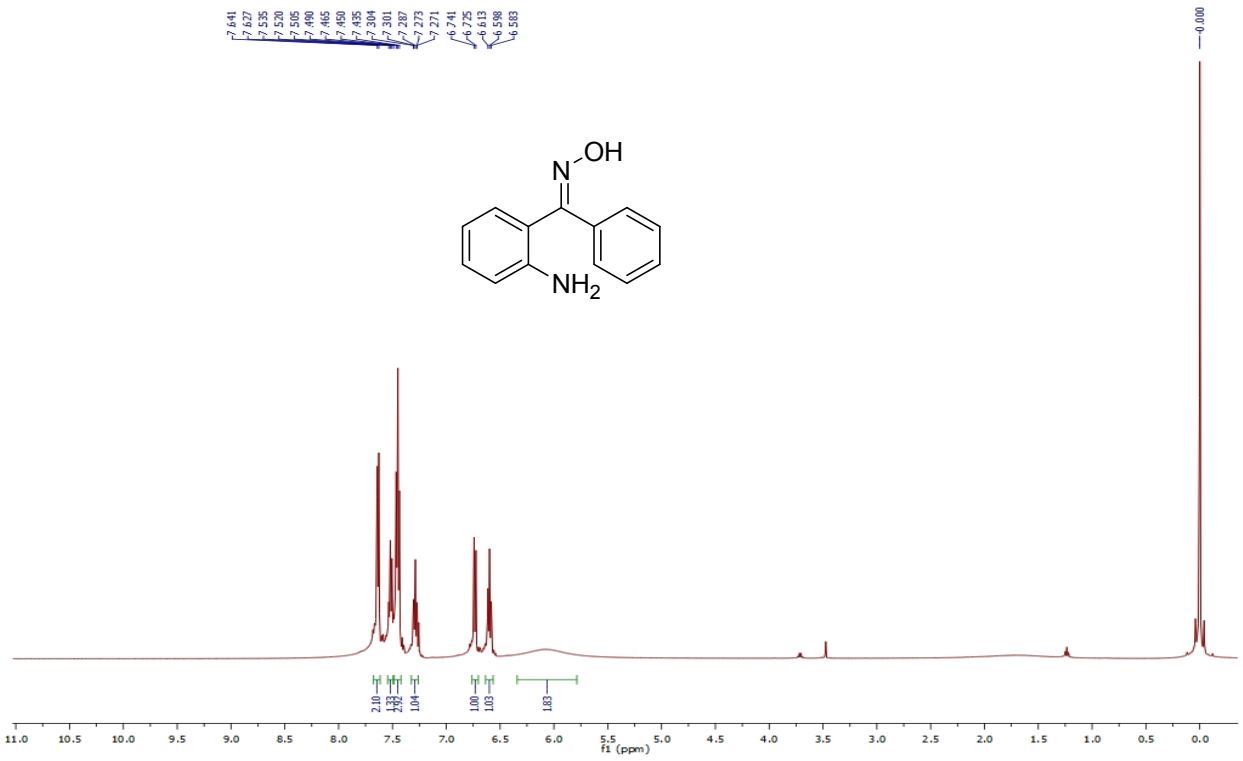

8.063
7.455
7.438
6.689
6.671
3.010
2.986
0.002
0.000
N-OH
Me2N
1.00
2.23
2.58
6.45
f1 (ppm)

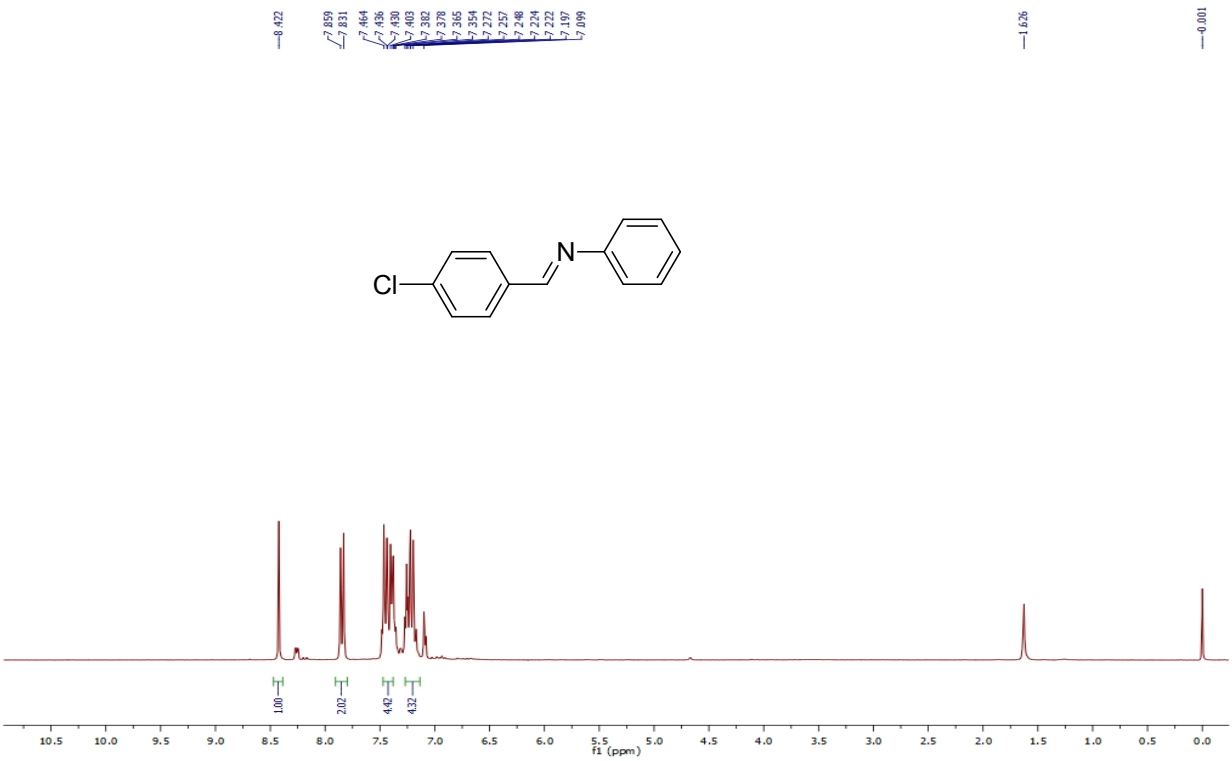

8.329
7.491
7.475
7.210
6.911
6.895
6.869
6.854
4.288
2.510
OH
N
OH
1.00
1.12
1.24
2.14
f1 (ppm)

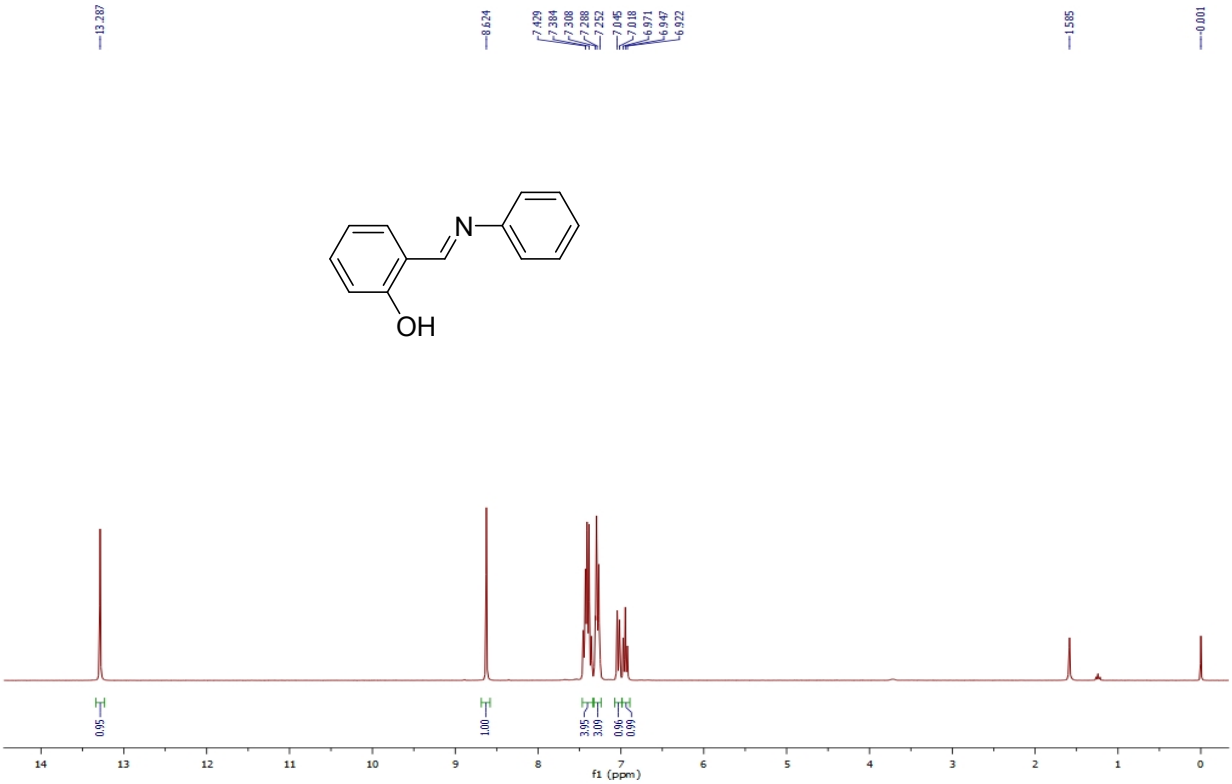

11.366
11.347
8.163
8.145
7.630
7.612
3.419
3.409
3.367
N–OH
HO–N
1.00
1.11
2.25
f1 (ppm)

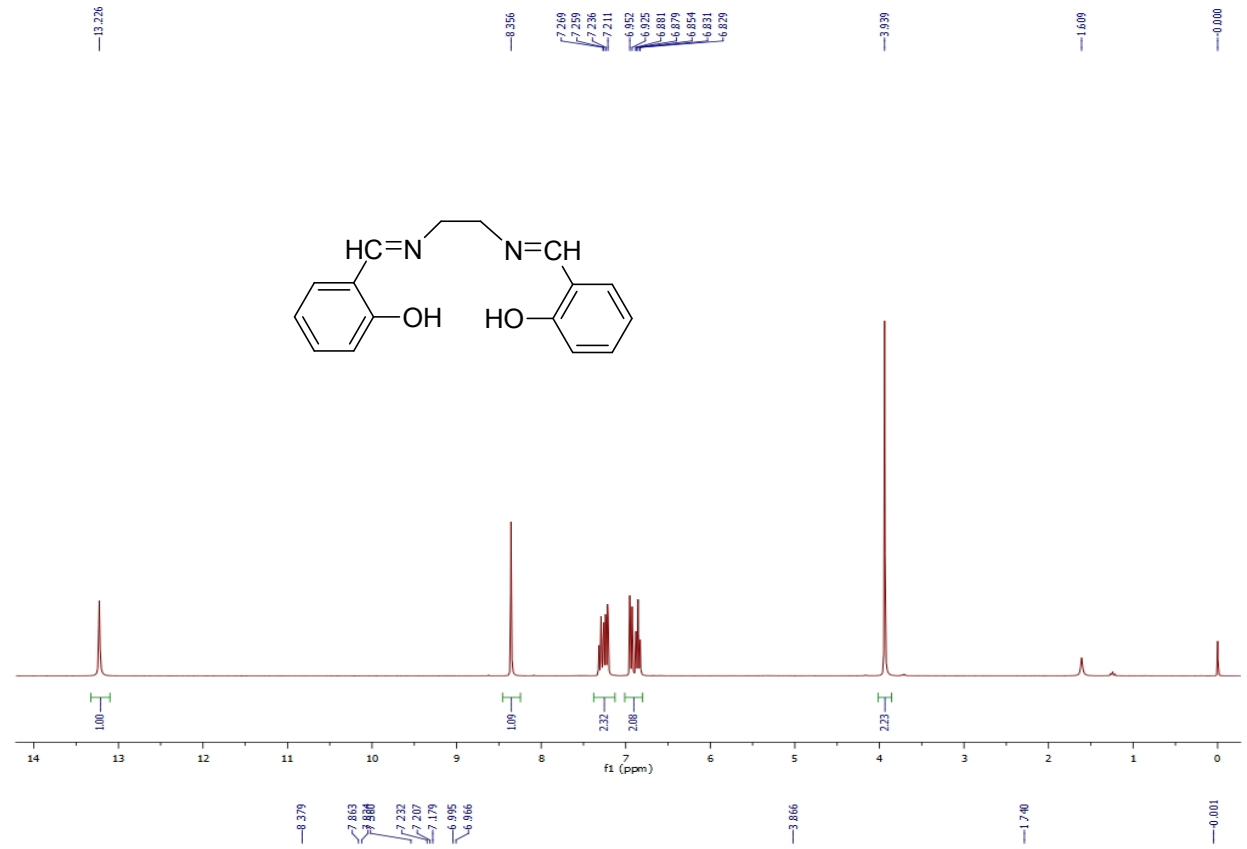

9.010
8.839
8.619
8.349
8.345
7.977
7.961
2.539
2.503
2.499
2.459
N
OH
N
1.05
1.07
1.12
1.00
1.16
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

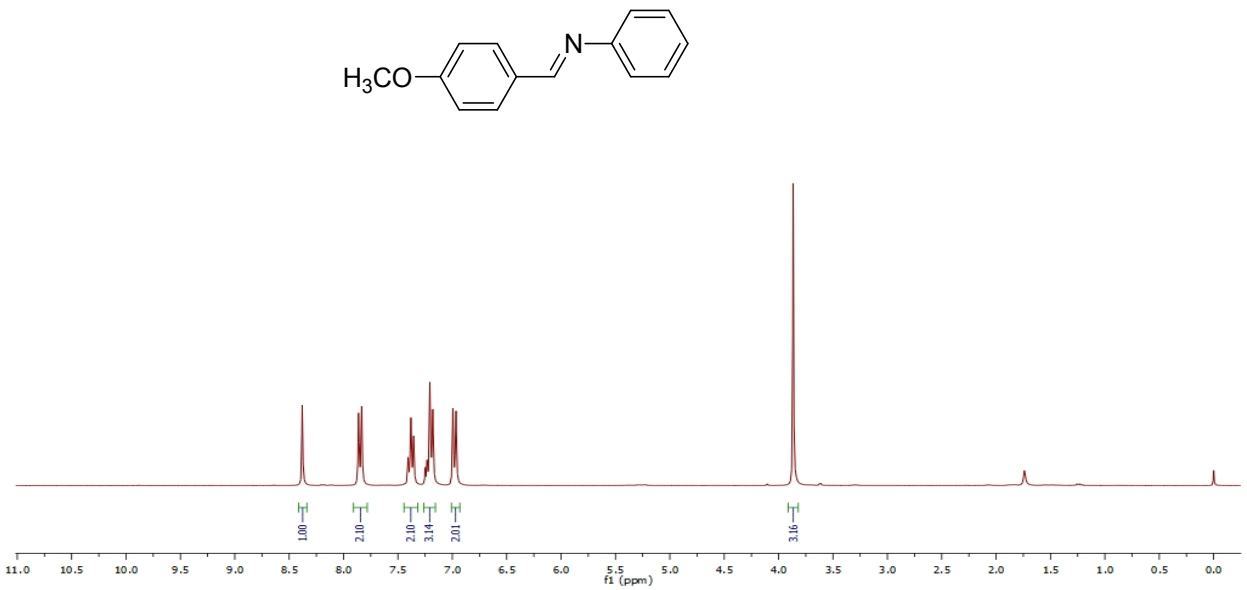

2.559
2.531
2.520
2.507
2.225
2.212
1.667
1.656
1.644
1.632
1.621
1.612
1.602
0.005
N
OH
1.00
1.62
1.55
5.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

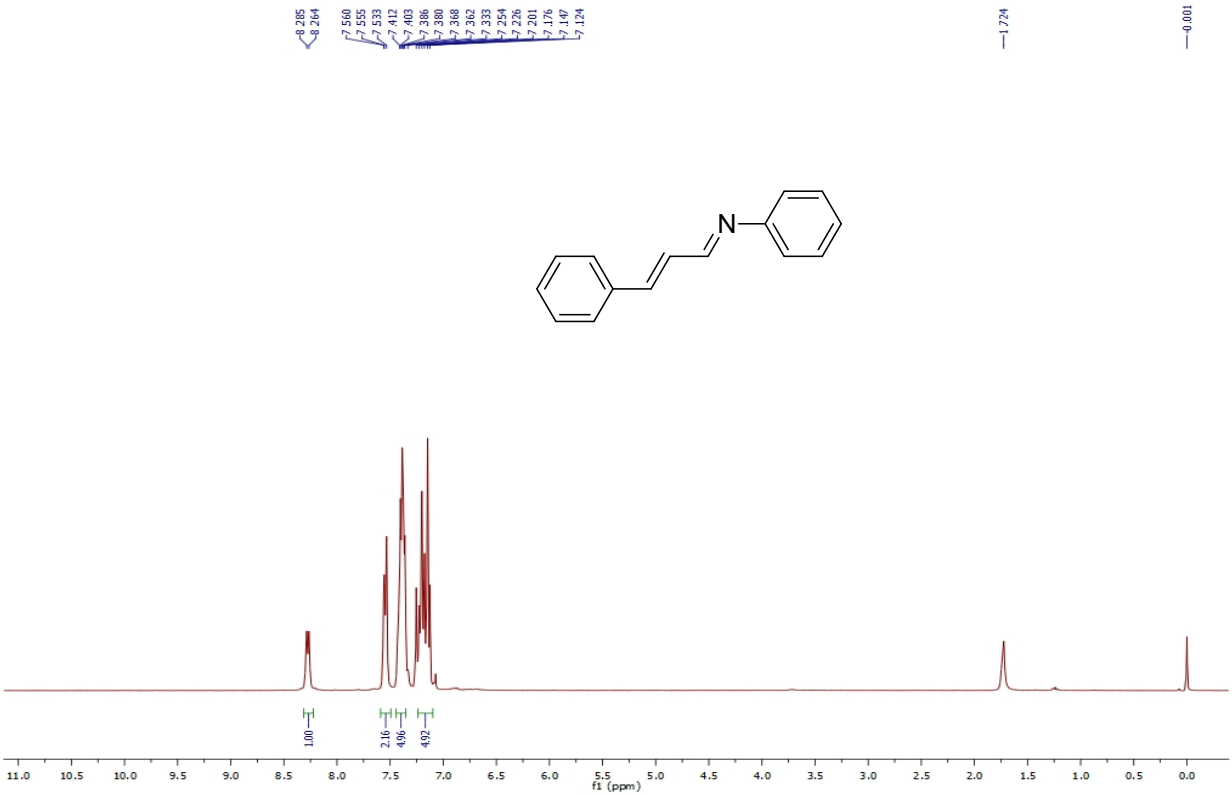

7.641
7.627
7.535
7.520
7.505
7.490
7.465
7.450
7.435
7.304
7.301
7.287
7.273
7.271
6.741
6.725
6.613
6.598
6.583
0.000
OH
N
NH2
2.10
1.33
2.02
1.04
1.00
1.03
1.83
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

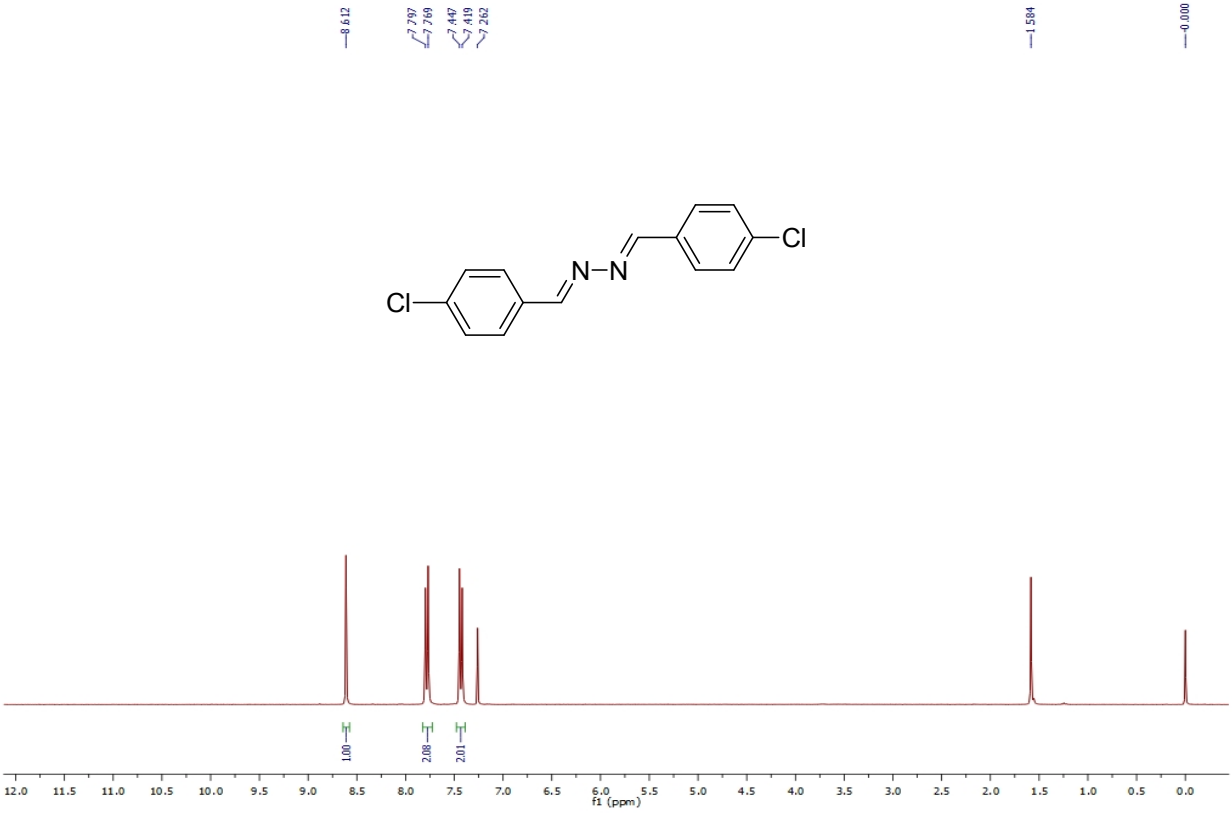

8.422
7.859
7.831
7.464
7.436
7.430
7.403
7.382
7.378
7.365
7.354
7.272
7.257
7.248
7.224
7.222
7.197
7.099
1.626
0.001
Cl
N
1.00
2.02
4.42
4.32
f1 (ppm)

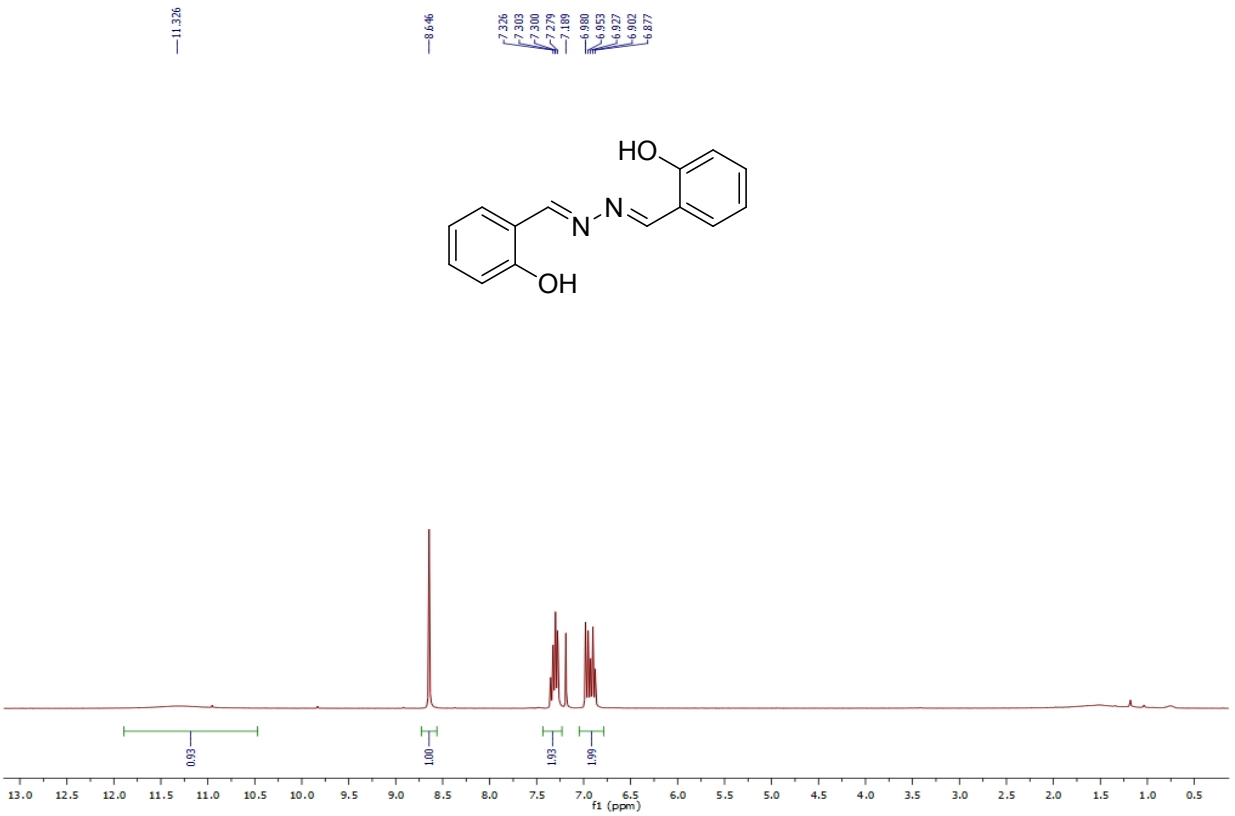

13.287
8.624
7.429
7.384
7.308
7.288
7.252
7.045
7.018
6.971
6.947
6.922
1.585
0.001
OH
N
0.95
1.00
3.95
3.09
0.96
0.99
f1 (ppm)

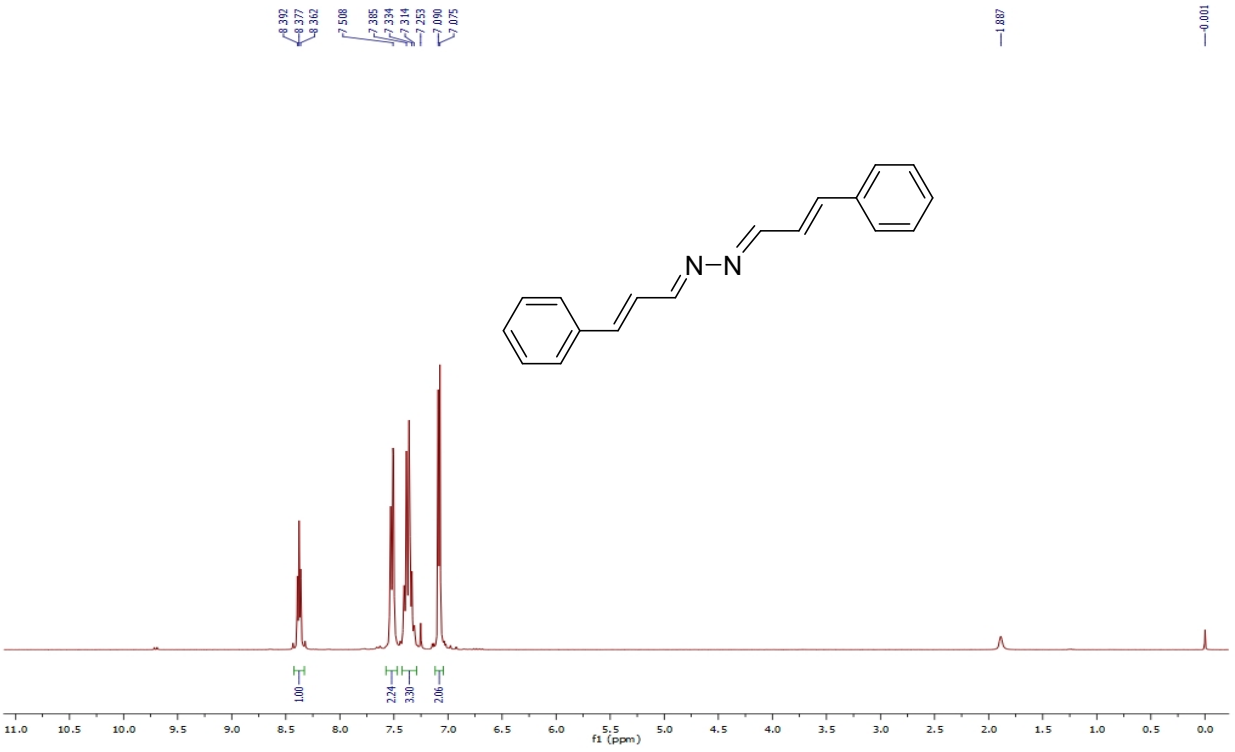

13.226
8.356
7.269
7.259
7.236
7.211
6.952
6.925
6.881
6.879
6.854
6.831
6.829
3.939
1.609
0.000
HC=N
N=CH
OH
HO
1.00
1.09
2.32
2.08
2.23
f1 (ppm)
8.379
7.863
7.232
7.207
7.179
6.995
6.966
3.866
1.740
0.001


H3CO
N
1.00
2.10
2.10
3.14
2.01
3.16
f1 (ppm)


8.285
8.264
7.560
7.555
7.533
7.412
7.403
7.386
7.380
7.368
7.362
7.333
7.254
7.226
7.201
7.176
7.147
7.124
1.724
0.001
N
1.00
2.16
4.96
4.92
f1 (ppm)


8.612
7.797
7.769
7.447
7.419
7.262
1.584
0.000
Cl
N–N
Cl
1.00
2.08
2.01
f1 (ppm)

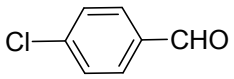

11.326
8.646
7.326
7.303
7.300
7.279
7.189
6.980
6.953
6.927
6.902
6.877
HO
N
N
OH
0.93
1.00
1.93
1.99
f1 (ppm)


8.392
8.377
8.362
7.508
7.385
7.334
7.314
7.253
7.090
7.075
1.887
0.001
N–N
1.00
2.24
3.30
2.06
f1 (ppm)

Instrument Model: Spectrum 100 Resolution: 4.0 cm-1 Data Type: PE IR Spectrum Instrument Serial Number: 80473

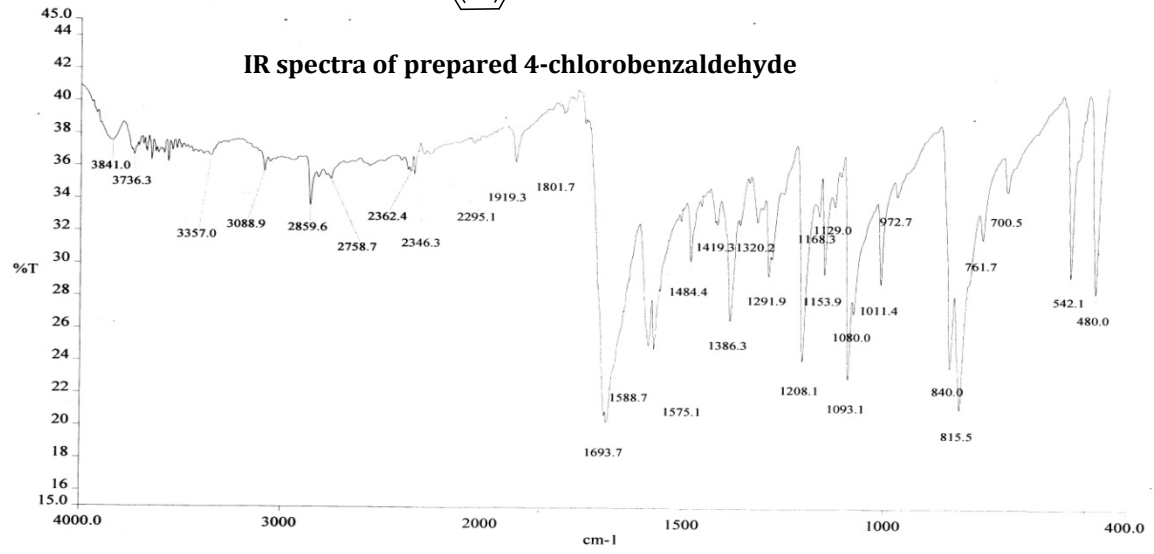
Software Version: Report Builder, Rev. 2.01 Date Created: Friday, September 19, 2014 10:48 AM India Standard Time

Comments: D.Baruah
Sample-P-Cl-D



Anal. Chem. Divn., NEIST-Jorhat

IR spectra of prepared 4-chlorobenzaldehyde



Spectrum Pathname: C:\pel_data\spectra\ES-14-0665.002

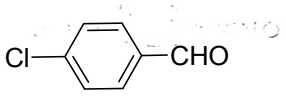
Analyst: Ankana

Instrument Model: Spectrum 100 Resolution: 4.0 cm-1 Data Type: PE IR Spectrum Instrument Serial Number: 80473

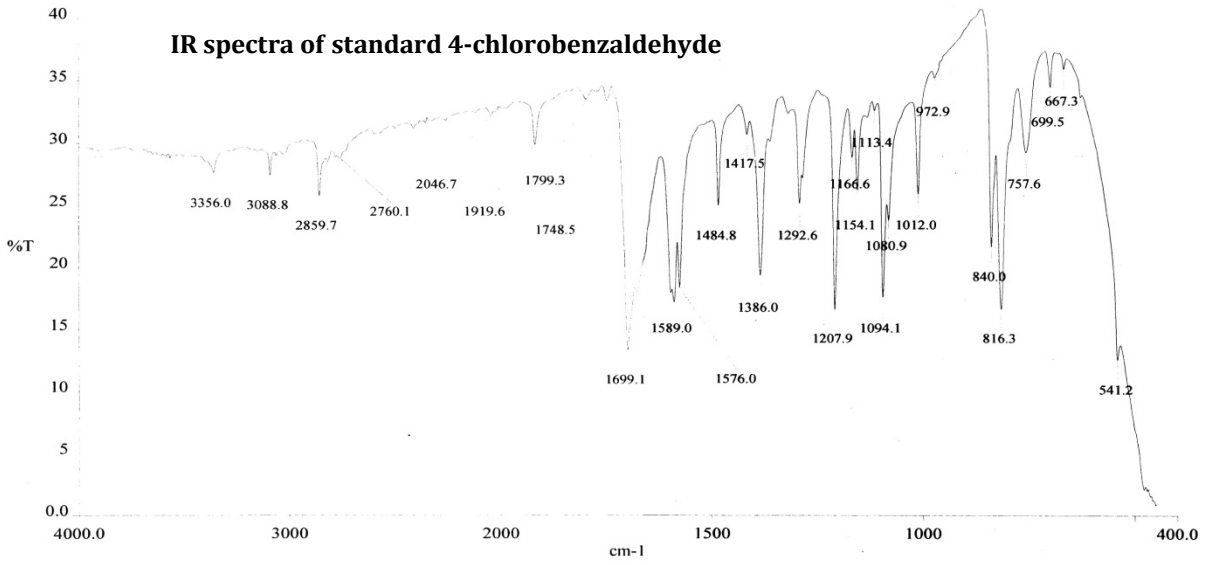
Software Version: Report Builder, Rev. 2.01 Date Created: Thursday, July 03, 2014 9:24 AM India Standard Time

Comments: D.Baruah
Sample-JB-1

Anal. Chem. Divn., NEIST-Jorhat



IR spectra of standard 4-chlorobenzaldehyde



Spectrum Pathname: C:\pel_data\spectra\ES-14-0281.001

Analyst: Ankana