Efficient *N*-Formylation of Primary Aromatic Amines Using Novel Solid Acid Magnetic Nanocatalyst

Jitendra Kumar Yadav[a], Priyanka Yadav[b], Satish K. Awasthi[b*], Alka Agarwal[a*]

Table of contents

^{1}H and ^{13}C NMR chemical shifts for 3a-3m

(The compounds are having mixture of rotamers) [1]

N-(2,3-dichlorophenyl)formamide (3a)

White solid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.71 (s, 1H), 8.51 (s, 1H), 8.36 (s, 1H), 7.81 (s, 1H), 7.34 (s, 6H)

^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.12, 159.39, 136.65, 135.33, 133.19, 129.97, 128.06, 125.70, 124.59, 119.78, 115.77; Elemental analysis for $C_7H_5Cl_2NO$: Calculated: C 44.25, H 2.65, Cl 37.31, N 7.37, O 8.42; Found: C 44.30, H 2.75, Cl 37.39, N 7.38, O 8.45

LC-MS (m/z): 189.98 $[M+H]^+$

N-(4-methoxyphenyl)formamide (3b)

Yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$)δ: 8.50-8.41 (2H), 8.36 (s, 2H), 7.47-7.40 (4H), 7.04-7.01 (2H), 6.88-6.86 (2H), 3.80 (s, 6H)

^{13}C-NMR (101 MHz, $CDCl_3$) δ: 162.45, 158.81, 131.81, 121.52, 115.25, 114.08, 55.33; Elemental analysis for $C_8H_9NO_2$: Calculated: C 63.56, H 6.00, N 9.27, O 21.17; Found: C 63.59, H 6.02, N 9.31, O 21.19

LC-MS (m/z): 152.07 $[M+H]^+$

N-(4-chloro-2-fluorophenyl)formamide (3c)

Light black solid, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 8.80-8.48 (2H), 8.27 (s, 2H), 8.08 (s, 1H), 6.95 (s, 2H), 6.79 (s, 1H), 6.69 (s, 1H), 6.52 (s, 1H)

^{13}C-NMR (101 MHz, $CDCl_3$) δ: 169.91, 133.40, 124.77, 122.73, 117.34, 115.25, 99.54; Elemental analysis for C_7H_5Cl FNO: Calculated: C 48.44, H 2.90, Cl 20.42, F 10.95, N 8.07, O 9.22; Found: C 48.47, H 2.89, Cl 20.44, F 10.92, N 8.09, O 9.25

LC-MS (m/z): 174.01 $[M+H]^+$

N-phenylformamide (3d)

Black oil, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 8.76 (s, 2H), 8.40 (s, 4H), 7.85 (s, 1H), 7.12 (s, 7H)

^{13}C-NMR (101 MHz, $CDCl_3$) δ: 163.96, 159.98, 136.85, 135.88, 130.15, 128.38, 125.54, 124.21, 120.58, 118.84; Elemental analysis for C_7H_7NO: C 69.41, H 5.82, N 11.56, O 13.21; Found: C 69.38, H 5.79, N 11.54, O 13.23

LC-MS (m/z): 122.06 $[M+H]^+$

N-(3,5-dimethylphenyl)formamide (3e)

Black oil, **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.50 (s, 1H), 8.33 (s, 1H), 7.10 (s, 1H), 6.85-6.72 (6H), 2.34 (s, 12H)

^{13}C-NMR (101 MHz, $CDCl_3$) δ: 162.27, 159.01, 139.08, 136.82, 117.72, 116.59, 95.12, 59.56; Elemental analysis for $C_9H_{11}NO$: C 72.46, H 7.43, N 9.39, O 10.72; Found: C 72.44, H 7.45, N 9.37, O 10.75

LC-MS (m/z): 150.09 $[M+H]^+$

N-(4-phenoxyphenyl)formamide (3f)

Light black oil, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.07-8.90 (1H), 8.73 (s, 1H), 8.53 (s, 1H), 8.22 (s, 2H), 7.47 (s, 7H), 6.86-6.99 (m, 10H)

^{13}C-NMR (101 MHz, $CCCl_3$) δ: 163.04, 159.56, 157.23, 154.59, 153.54, 132.99, 129.80, 123.08, 121.65, 120.73, 119.82, 118.39; Elemental analysis for $C_{13}H_{11}NO_2$: C 73.23, H 5.20, N 6.57, O 15.01; Found: C 73.21, H 5.19, N 6.60, O 15.04

LC-MS (m/z): 214.08 $[M+H]^+$

N-(3-hydroxyphenyl)formamide (3g)

Black oil, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.02 (s, 1H), 8.80 (s, 2H), 8.34 (s, 1H), 7.91 (s, 2H), 7.68 (s, 1H), 6.98 (s, 2H), 6.70 (s, 3H), 6.31 (s, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$) δ: 162.82, 161.54, 159.74, 157.71, 156.53, 138.26, 129.34, 128.20, 111.97, 110.41, 109.30, 107.37, 105.12, 103.94; Elemental analysis for $C_7H_7NO_2$: C 61.31, H 5.15, N 10.21, O 23.33; Found: C 61.33, H 5.12, N 10.18, O 23.29

LC-MS (m/z): 138.05 $[M+H]^+$

N-(2-chlorophenyl)formamide (3h)

Black oil, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 8.70-8.62 (1H), 8.47-8.33 (1H), 8.16 (s, 1H), 7.43 (s, 1H), 7.07-7.01 (2H), 6.76-6.63 (6H)

^{13}C-NMR (101 MHz, $CDCl_3$) δ: 162.08, 159.94, 142.94, 134.17, 130.37, 127.81, 126.23, 124.96, 122.67, 119.34, 116.50; Elemental analysis for C_7H_6ClNO: C 54.04, H 3.89, Cl 22.79, N 9.00, O 10.28; Found: C 54.06, H 3.86, Cl 22.77, N 9.03, O 10.25

LC-MS (m/z): 156.02 $[M+H]^+$

N-(4-chlorophenyl)formamide (3i)

White solid, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 8.91 (s, 1H), 8.70 (s, 1H), 8.33 (s, 1H), 8.03 (s, 1H), 7.55-7.36 (3H), 7.31 (s, 3H), 7.04 (s, 2H)

^{13}C-NMR (101 MHz, $CDCl_3$) δ: 159.02, 135.66, 130.80, 129.20, 128.00, 120.58, 119.70; Elemental analysis for C_7H_6ClNO: C 54.04, H 3.89, Cl 22.79, N 9.00, O 10.28; Found: C 54.06, H 3.86, Cl 22.77, N 9.03, O 10.25

LC-MS (m/z): 156.02 $[M+H]^+$

N-(2-cyanophenyl)formamide (3j)

Brown oil, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 8.79 (s, 1H), 8.44 (s, 2H), 8.24 (s, 1H), 7.27-7.17 (4H), 6.71-6.64 (6H)

^{13}C-NMR (101 MHz, $CDCl_3$) δ: 160.15, 139.57, 134.24, 132.66, 125.15, 121.92, 117.88, 102.90; Elemental analysis for $C_8H_6N_2O$: C 65.75, H 4.14, N 19.17, O 10.95; Found: C 65.77, H 4.17, N 19.15, O 10.93

LC-MS (m/z): 147.05 $[M+H]^+$

N-(4-hydroxyphenyl)formamide (3k)

Black solid, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 8.81 (s, 1H), 8.41 (s, 1H), 8.28 (s, 2H), 8.06 (s, 2H), 7.36 (s, 2H), 6.98-6.94 (2H), 6.85-6.80 (4H)

^{13}C-NMR (101 MHz, CHLOROFORM-D) δ: 164.97, 161.89, 132.63, 121.91, 116.34; Elemental analysis for $C_7H_7NO_2$: C 61.31, H 5.15, N 10.21, O 23.33; Found: C 61.33, H 5.18, N 10.19, O 23.35

LC-MS (m/z): 138.06 $[M+H]^+$

N-(2-fluorophenyl)formamide (3l)

Grey solid, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 9.38-9.01 (2H), 8.73 (s, 2H), 8.34 (s, 2H), 7.57 (s, 3H), 6.88-6.73 (3H); Elemental analysis for C_7H_6FNO: C 60.43, H 4.35, F 13.66, N 10.07, O 11.50; Found: C 60.39, H 4.36, F 13.68, N 10.07, O 11.53;

13C NMR (101 MHz, CHLOROFORM-D) δ: 161.47, 158.43, 139.32, 130.71, 128.79, 126.14, 123.21, 122.08, 119.79, 117.32, 115.79; Elemental analysis for C_7H_6BrNO: Calculated: C 42.03, H 3.02, Br 39.95, N 7.00, O 8.00; Found: C 42.05, H 3.06, Br 39.97, N 7.11, O 8.09.

LC-MS (m/z): 140.05 $[M+H]^+$

N-(2,4-difluorophenyl)formamide (3m)

Brown solid, **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 8.55 (s, 1H), 8.43 (s, 1H), 8.32-8.24 (2H), 7.67-7.42 (1H), 7.18 (s, 1H), 6.96 (s, 4H)

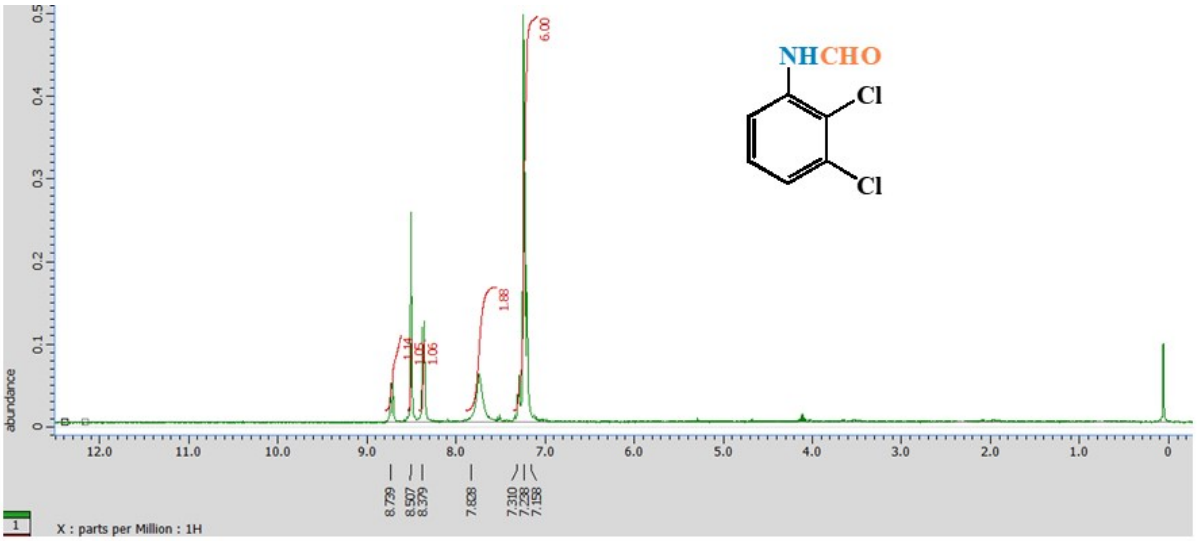
^{13}C-NMR (101 MHz, $CDCl_3$) δ :162.46, 158.62, 123.28, 121.53, 111.75, 105.86, 103.79; Elemental analysis for $C_7H_5F_2NO$: C 53.51, H 3.21, F 24.18, N 8.91, O 10.18; Found: C 53.53, H 3.24, F 24.19, N 8.93, O 10.19

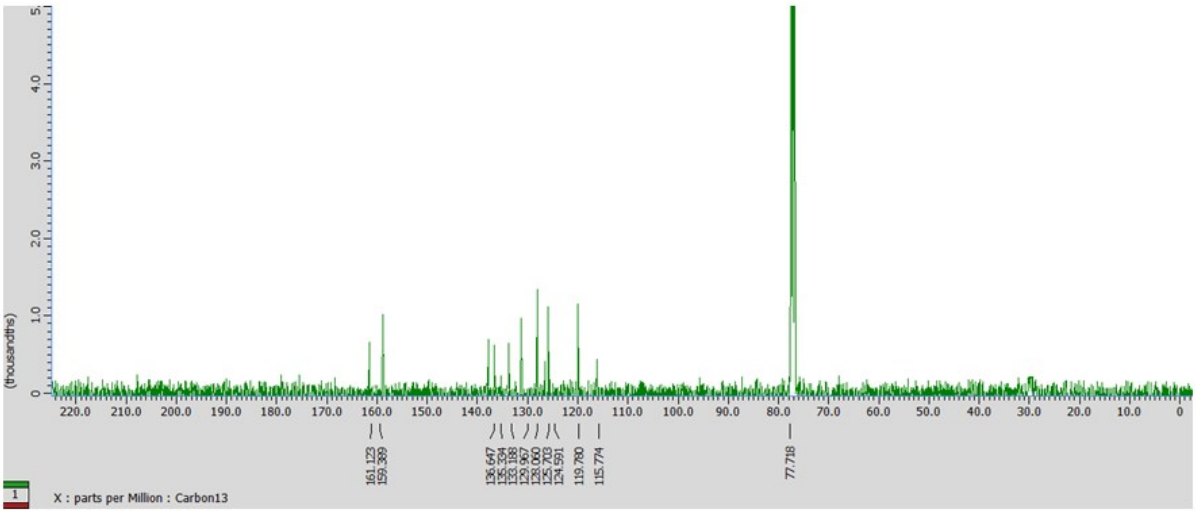
LC-MS (m/z): 158.04 $[M+H]^+$

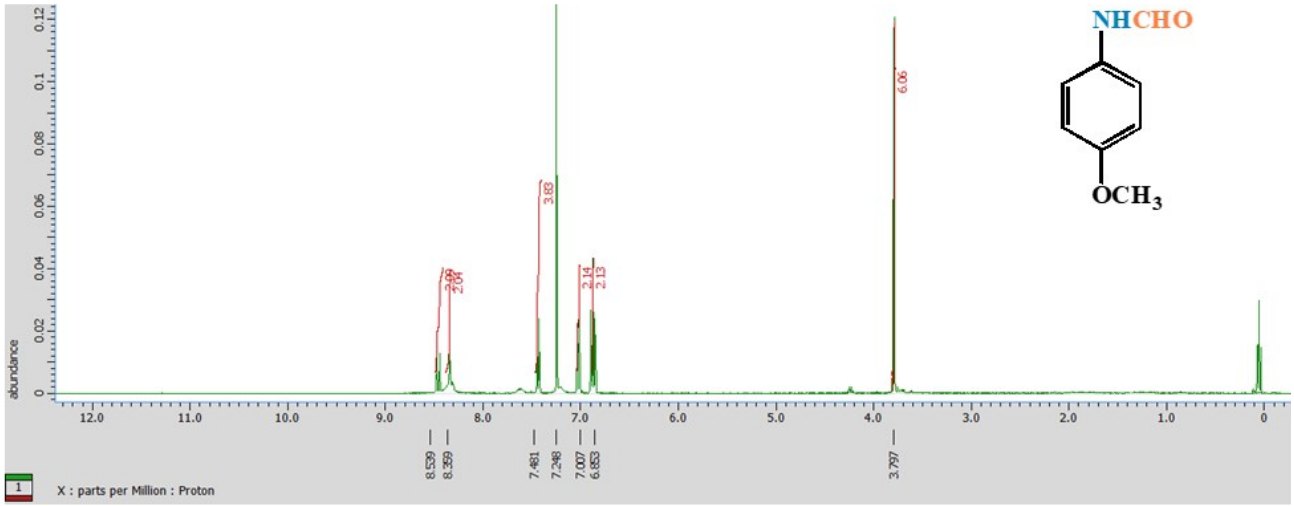
References:

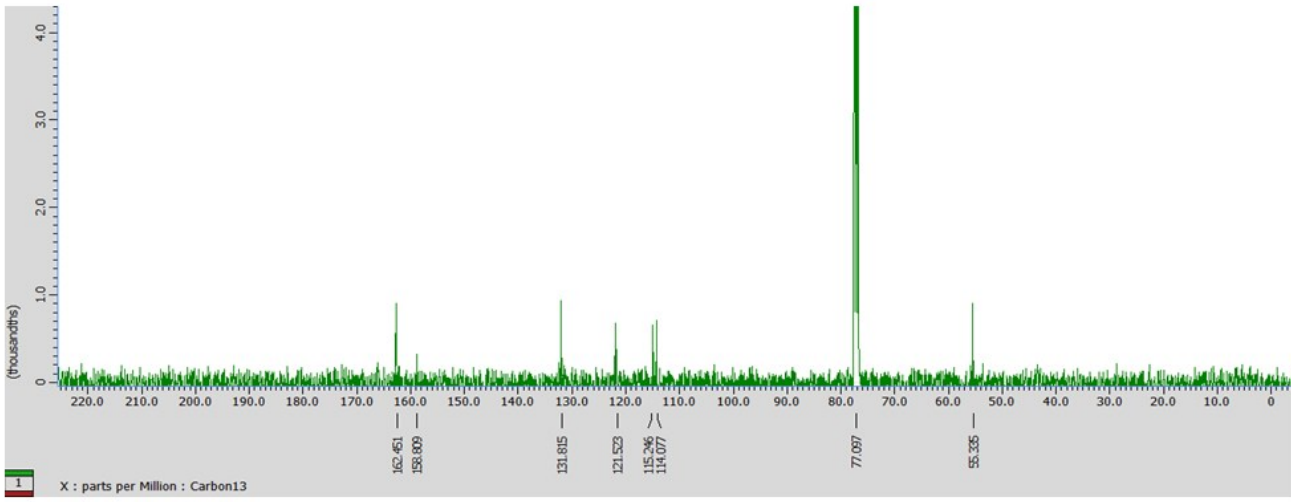
[1] Mutra MR, Dhandabani GK, Wang JJ. Mild Access to N-Formylation of Primary Amines using Ethers as C1 Synthons under Metal-Free Conditions. Advanced Synthesis & Catalysis. 2018 Oct 18;360(20):3960-8.

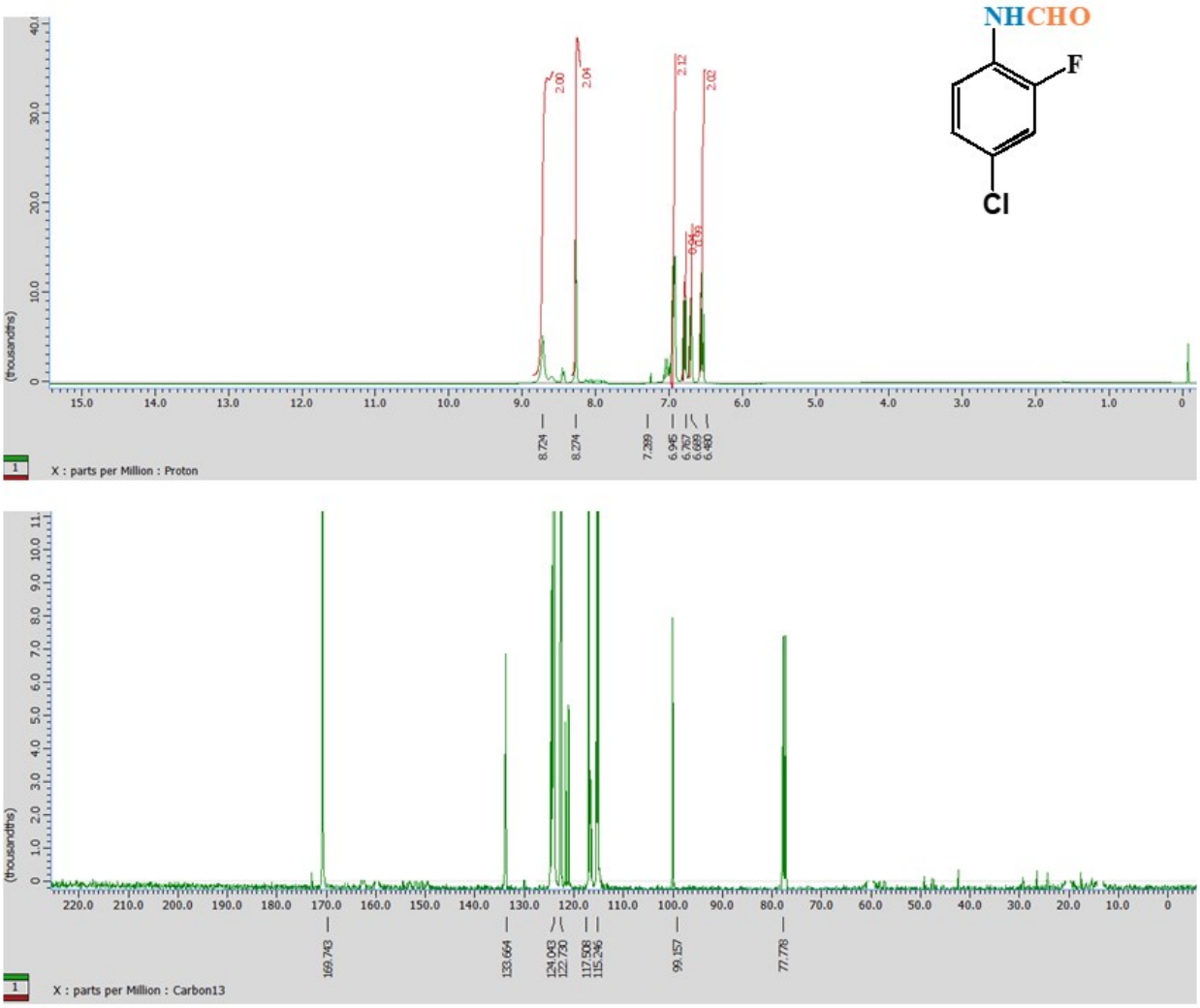
^{1}H and ^{13}C NMR spectra for 3a-3m

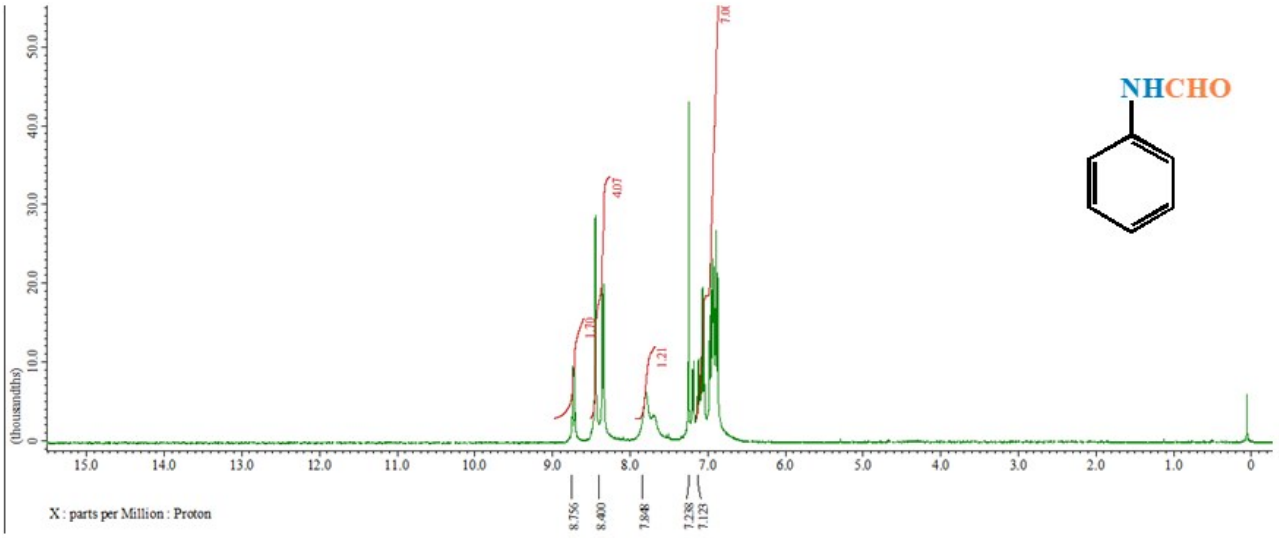


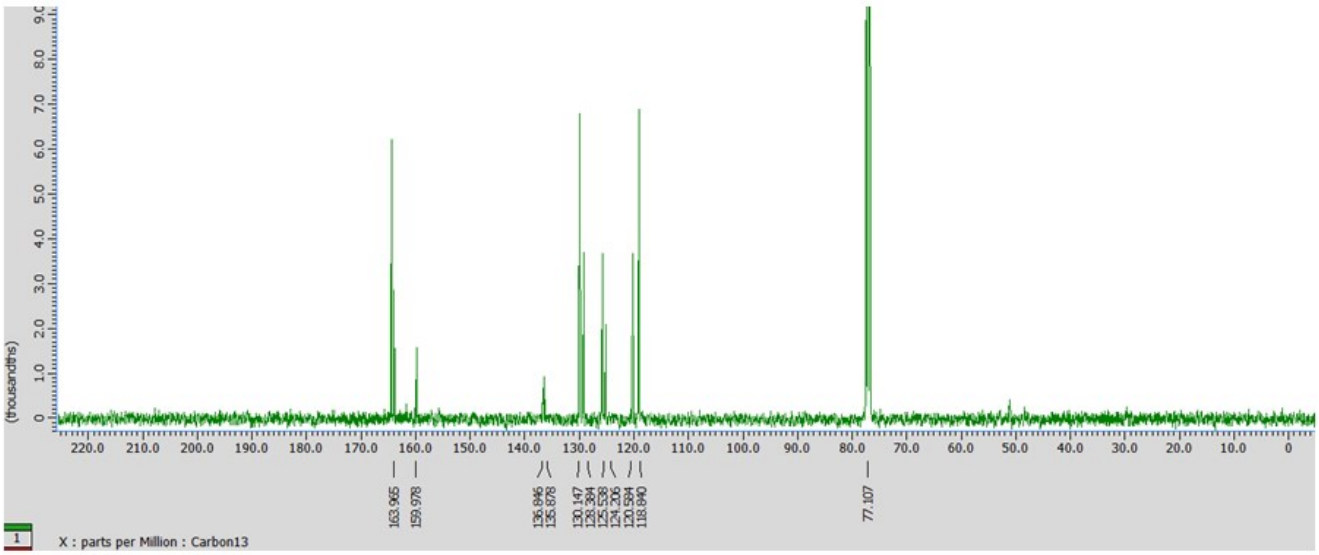


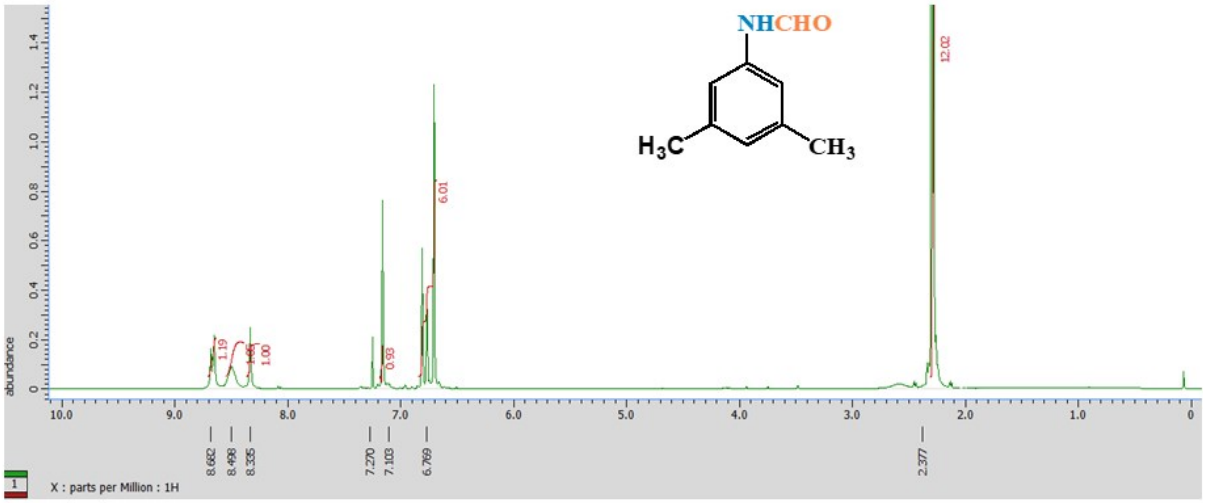

NHCHO
OCH3
abundance
6.06
3.83
2.14
2.13
2.09
2.04
8.539
8.399
7.481
7.248
7.007
6.653
3.797
X : parts per Million : Proton

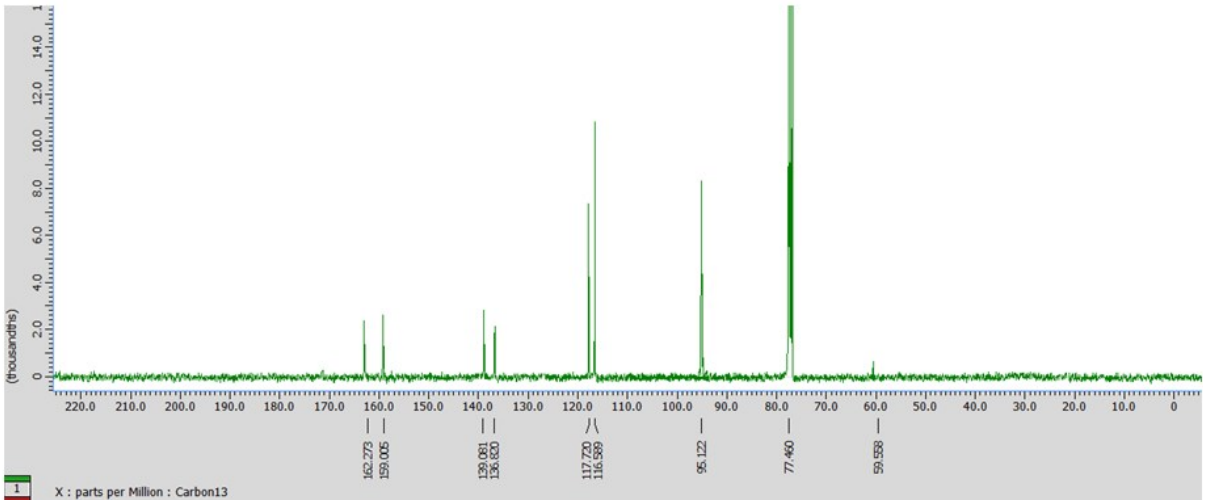

(thousandths)
162.451
158.809
131.815
121.529
115.246
114.077
77.097
55.335
X : parts per Million : Carbon13

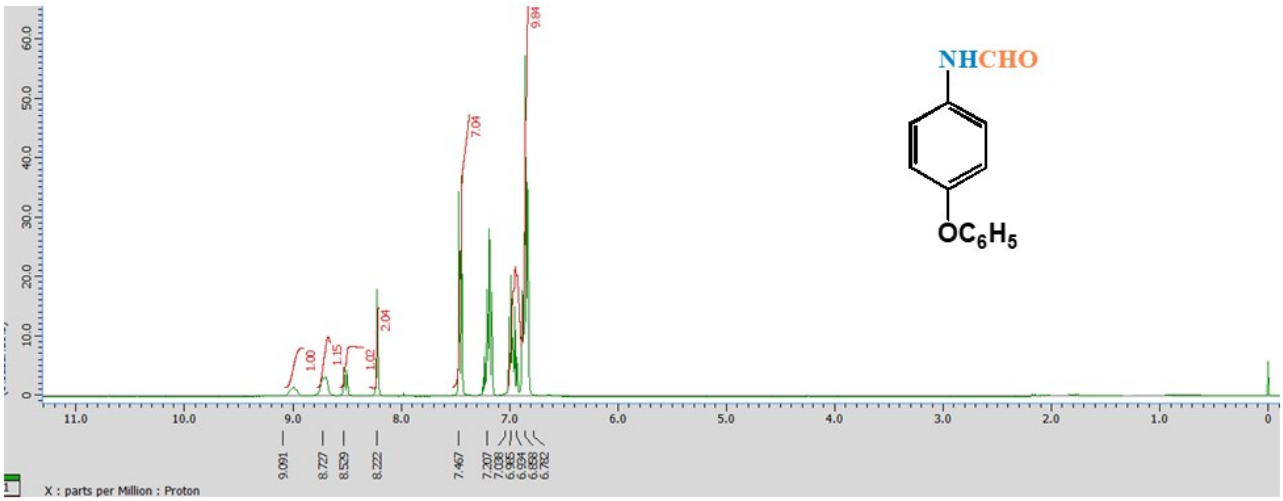

NHCHO
F
Cl
(thousandths)
X : parts per Million : Proton
X : parts per Million : Carbon13

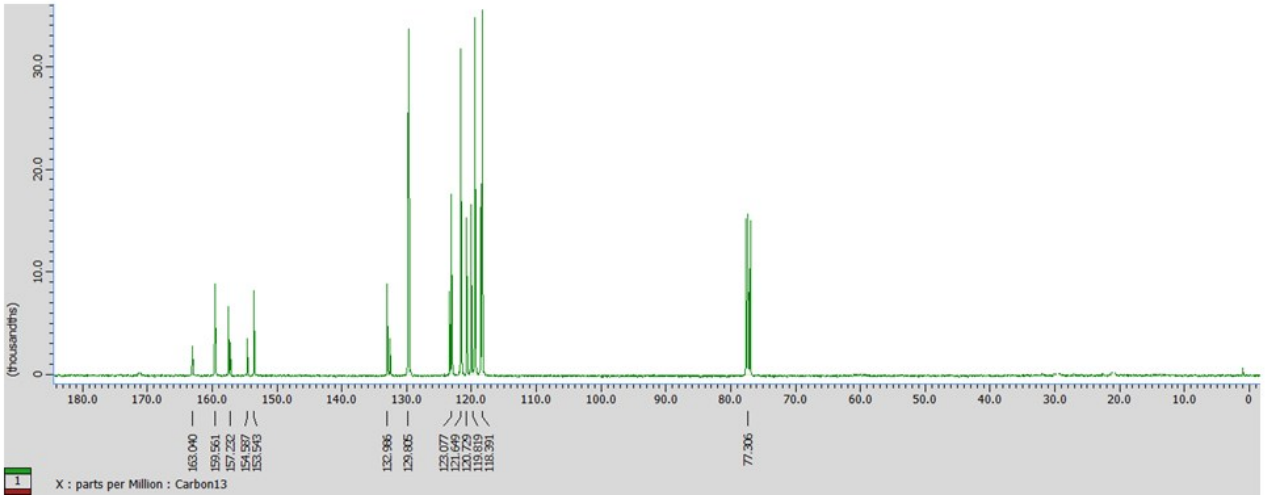

NHCHO
(thousandths)
X : parts per Million : Proton
8.756
8.400
7.848
7.238
7.123

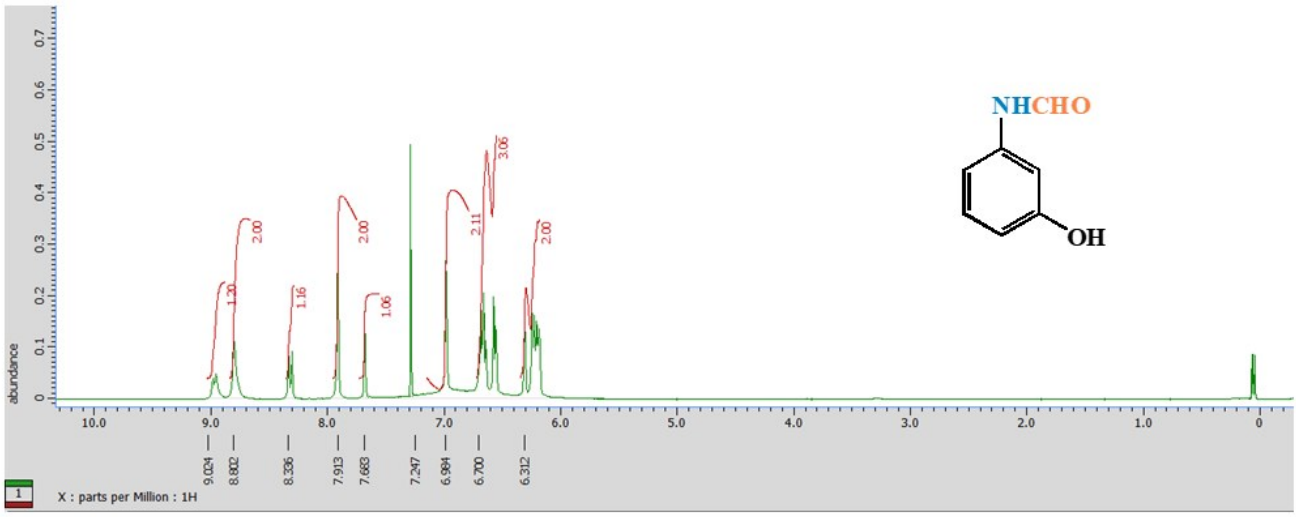

(thousandths)
X : parts per Million : Carbon13
163.965
159.978
136.946
135.678
130.147
128.394
125.538
124.206
120.594
118.890
77.107

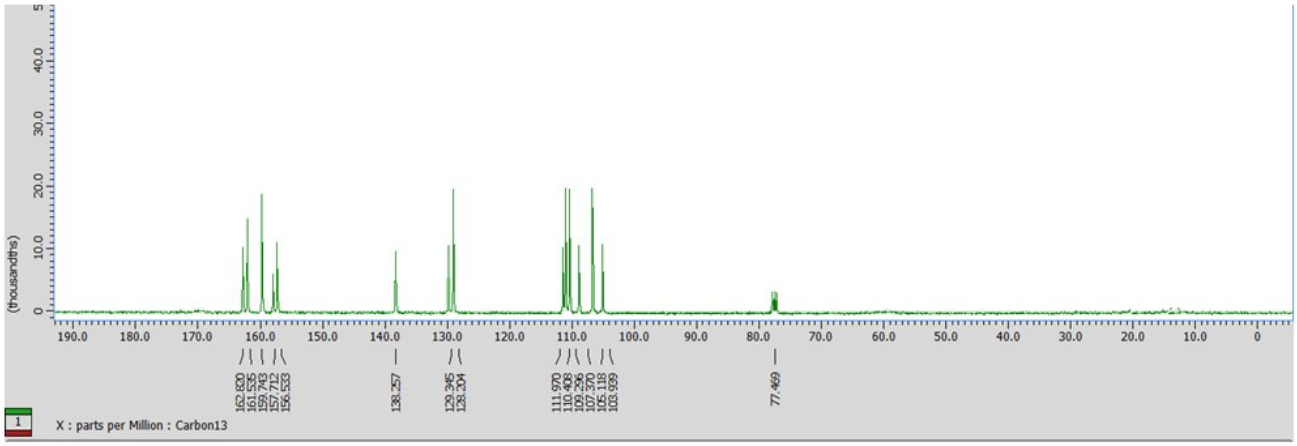

NHCHO
H3C
CH3
abundance
X : parts per Million : 1H

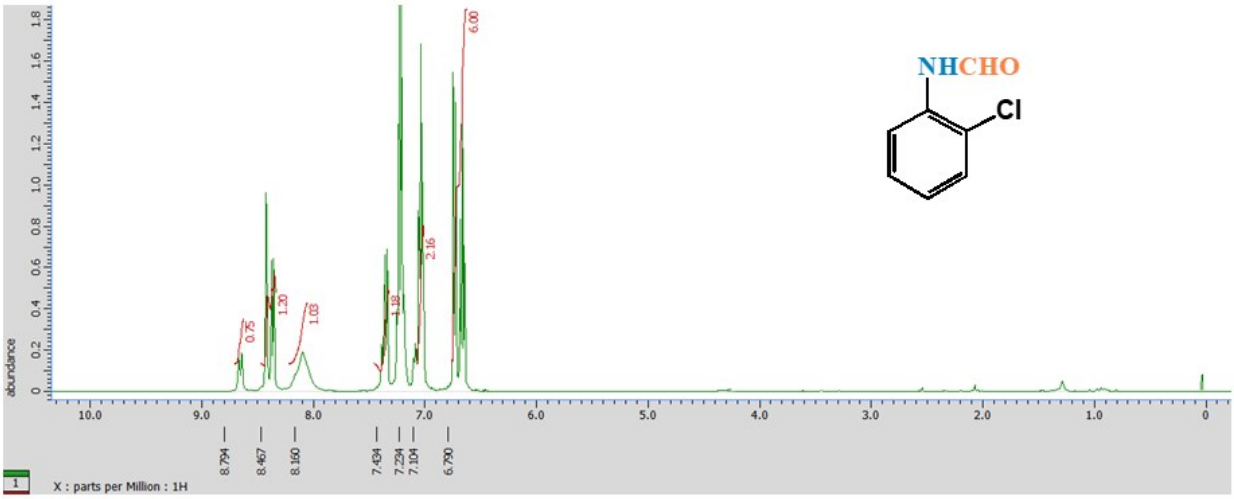

(thousandths)
X : parts per Million : Carbon13

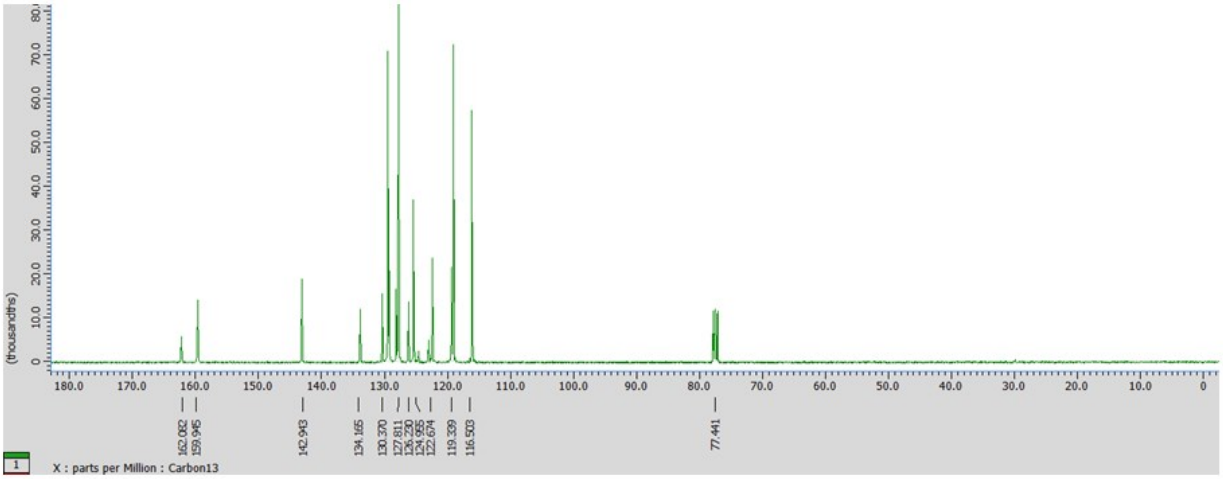

NHCHO
OC6H5
X : parts per Million : Proton

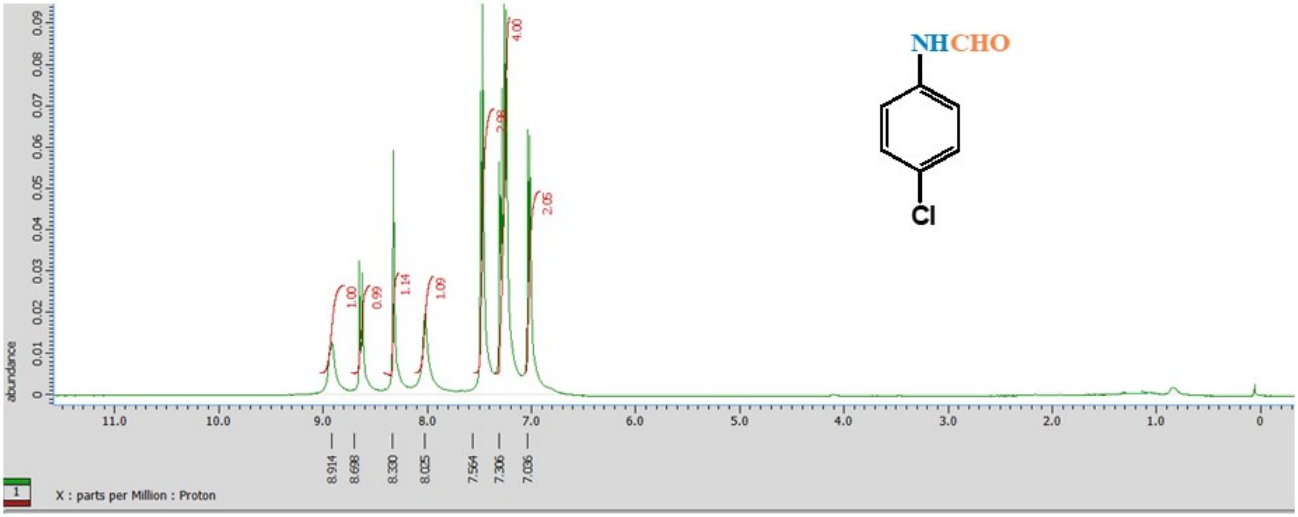

X : parts per Million : Carbon13

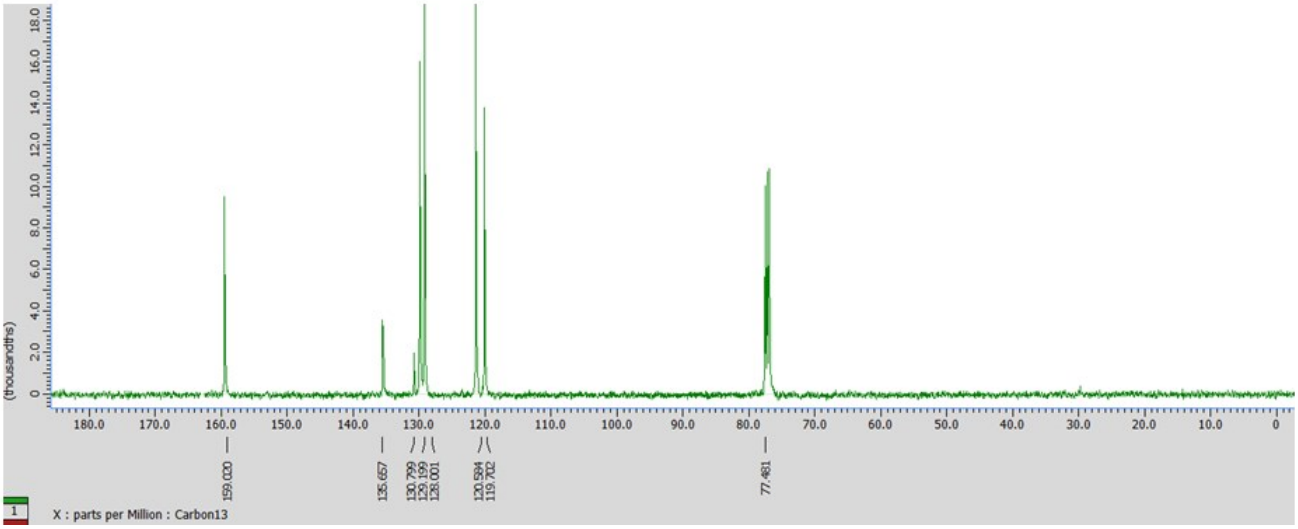

NHCHO
OH
abundance
1.20
2.00
1.16
2.00
1.06
2.11
3.06
2.00
9.024
8.802
8.336
7.913
7.683
7.247
6.984
6.700
6.312
X : parts per Million : 1H

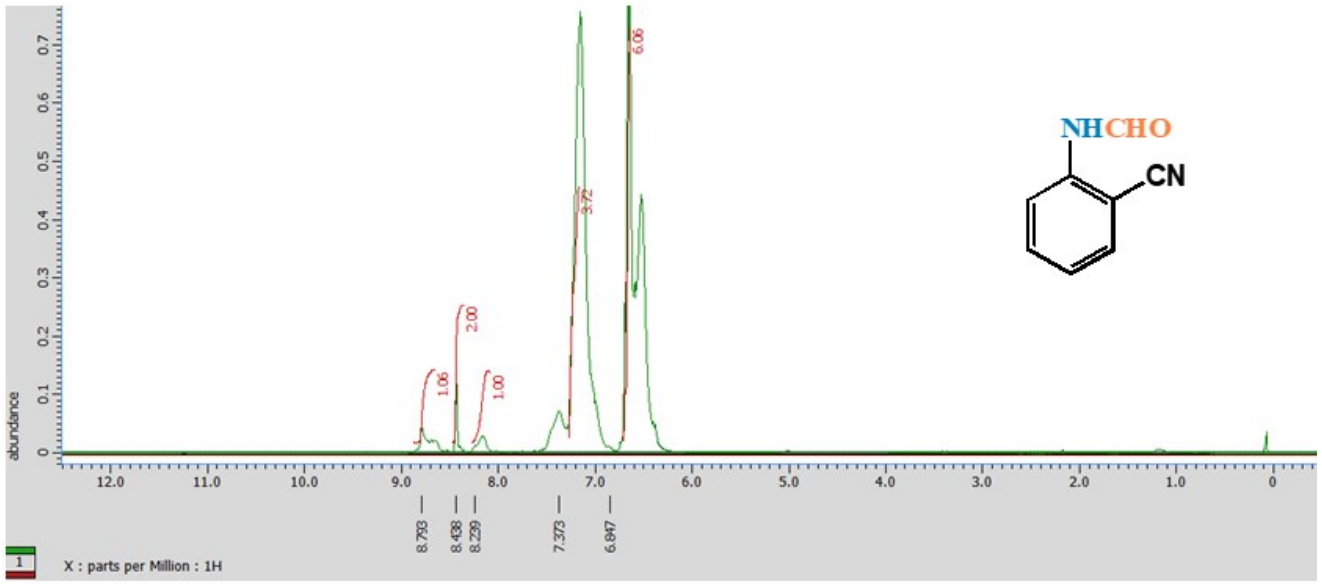

(thousandths)
162.800
161.535
159.742
157.712
156.533
138.257
129.365
128.204
111.970
110.408
109.296
107.370
105.118
103.999
77.469
X : parts per Million : Carbon13

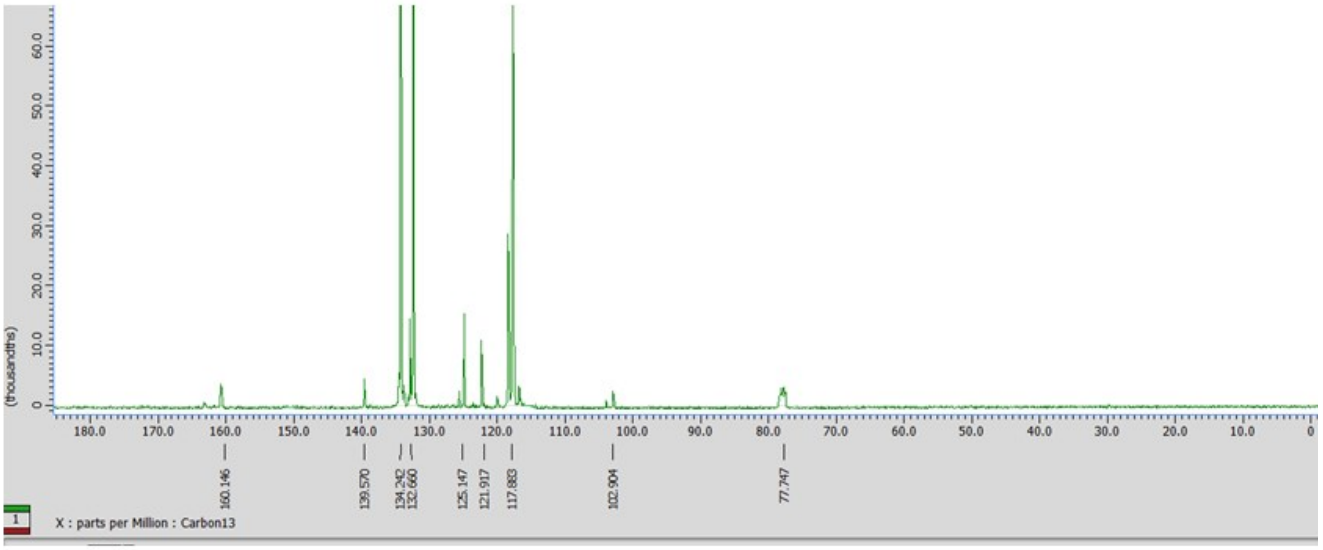

NHCHO
Cl
abundance
0.75
1.20
1.03
1.18
2.16
6.00
8.794
8.467
8.160
7.494
7.234
7.104
6.790
X : parts per Million : 1H

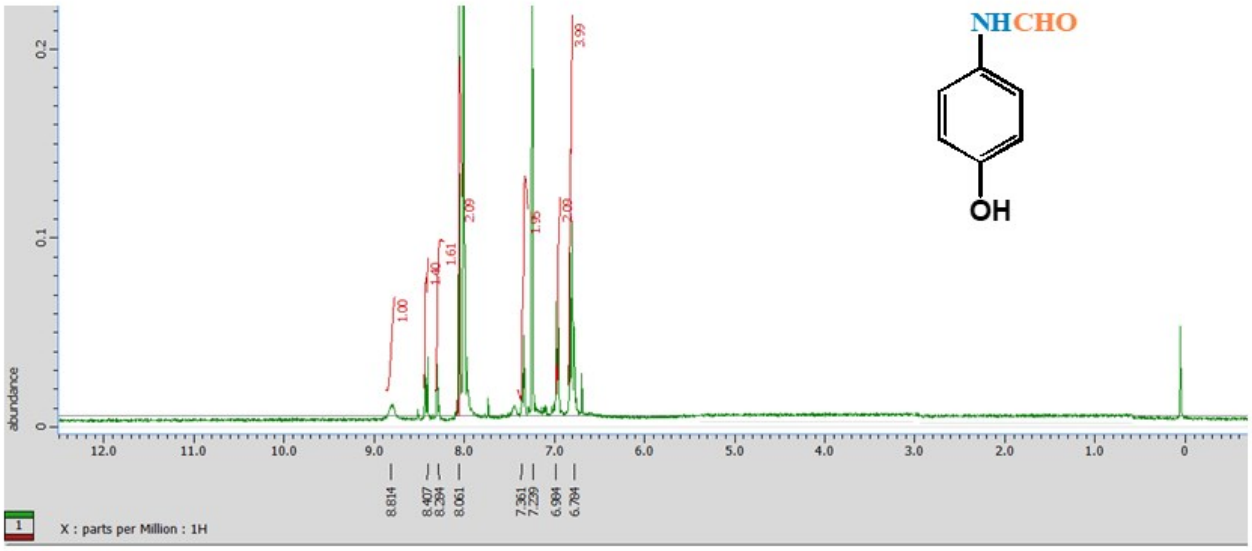

(thousandths)
162.082
159.945
142.943
134.165
130.370
127.811
126.590
124.165
122.674
119.339
116.503
77.441
X : parts per Million : Carbon13

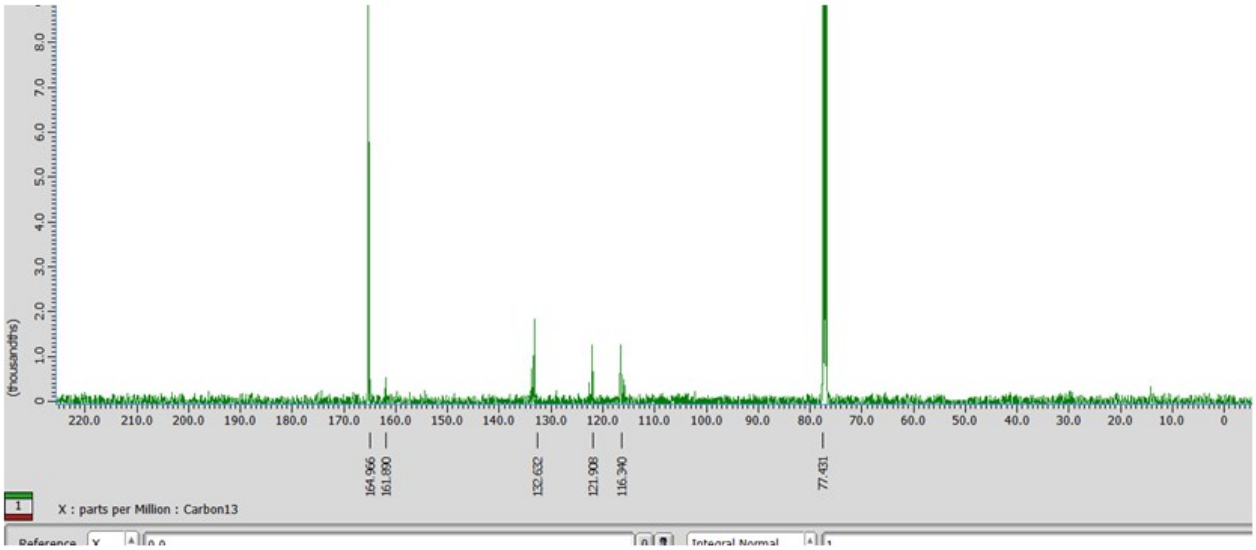

NHCHO
Cl
abundance
1.00
0.99
1.14
1.09
2.88
4.00
2.05
8.914
8.698
8.330
8.025
7.564
7.306
7.036
X : parts per Million : Proton

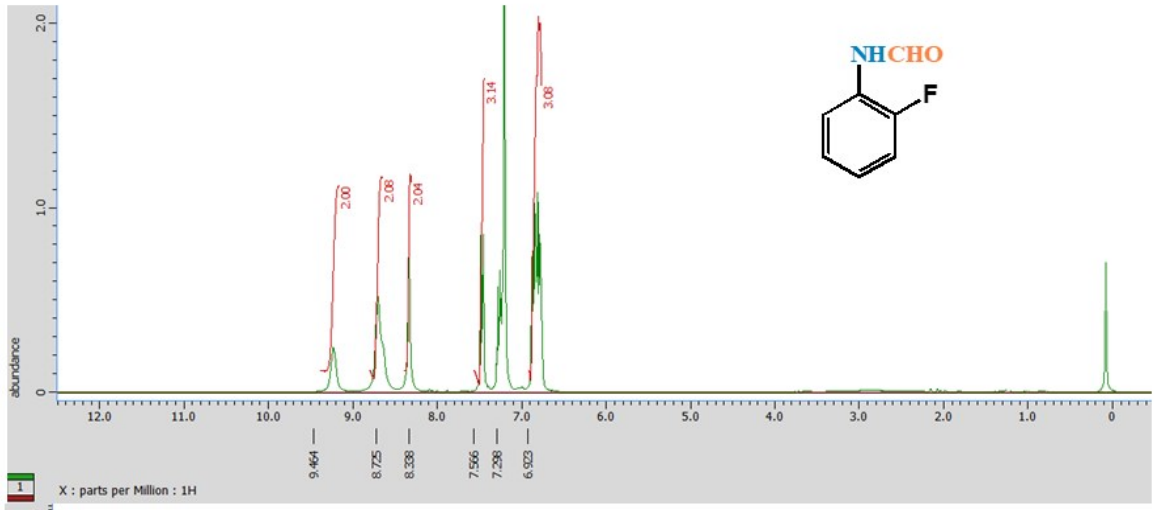

(thousandths)
159.020
135.657
130.799
129.189
128.001
120.594
119.702
77.481
X : parts per Million : Carbon13

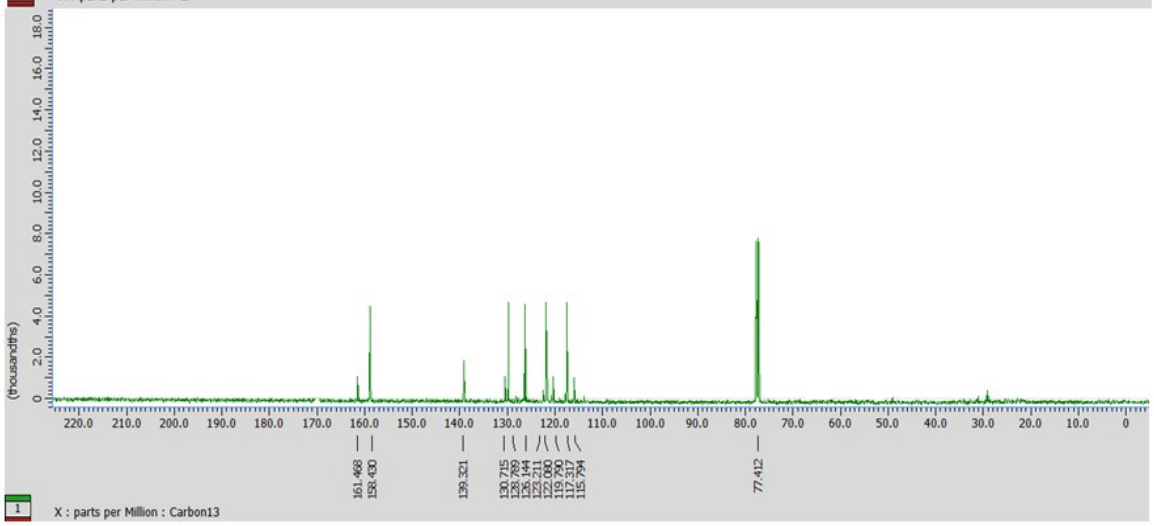

NHCHO
CN
abundance
6.06
3.72
2.00
1.06
1.00
8.793
8.438
8.239
7.373
6.847
X : parts per Million : 1H

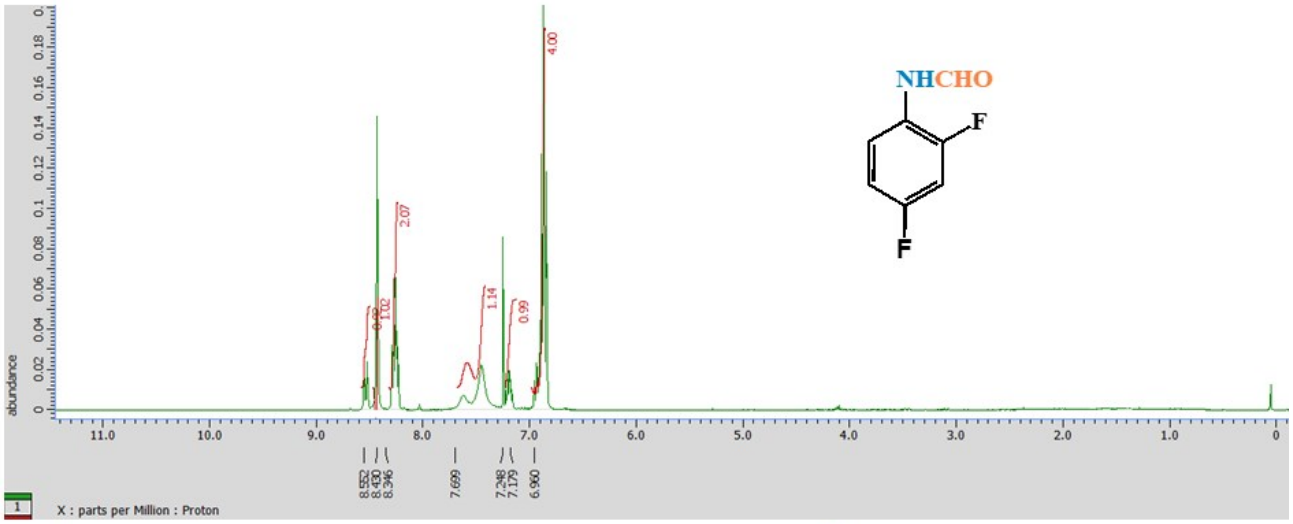

(thousandths)
160.146
139.570
134.242
132.660
125.147
121.917
117.883
102.904
77.747
X : parts per Million : Carbon13

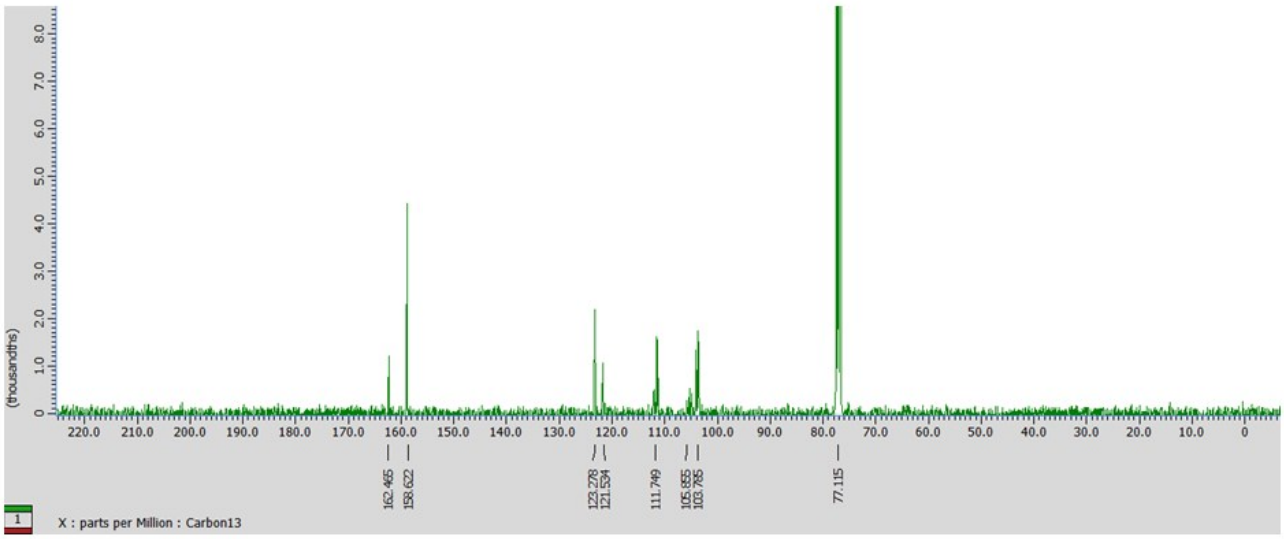

NHCHO
OH
abundance
X : parts per Million : 1H


(thousandths)
X : parts per Million : Carbon13


NHCHO
F
abundance
2.00
2.08
2.04
3.14
3.08
9.464
8.725
8.338
7.566
7.238
6.923
X : parts per Million : 1H

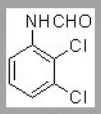

(thousandths)
161.468
158.400
139.321
130.715
128.789
124.144
122.211
122.080
119.790
117.737
115.794
77.412
X : parts per Million : Carbon13


NHCHO
F
F
abundance
4.00
2.07
1.14
1.02
0.99
0.98
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.552
8.430
8.346
7.699
7.248
7.179
6.960
X : parts per Million : Proton


(thousandths)
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.465
158.622
123.278
121.534
111.749
105.855
103.765
77.115
X : parts per Million : Carbon13

Qualitative Compound Report

Data File	J5.d	**Sample Name**	J5
Sample Type	Sample	**Position**	P1-D4
Instrument Name	Instrument 1	**User Name**	
Acq Method	Damo JK.m	**Acquired Time**	03-04-2019 11:49:24
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			



Info.

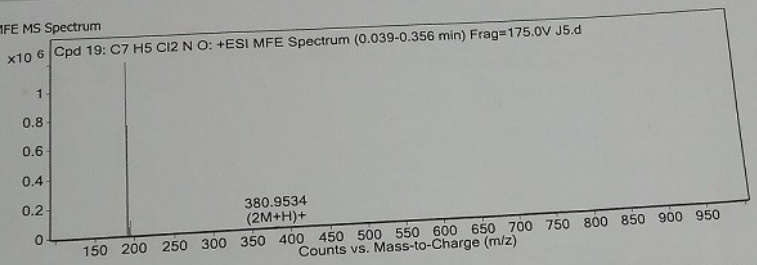
Sample Group	
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)

Compound Table

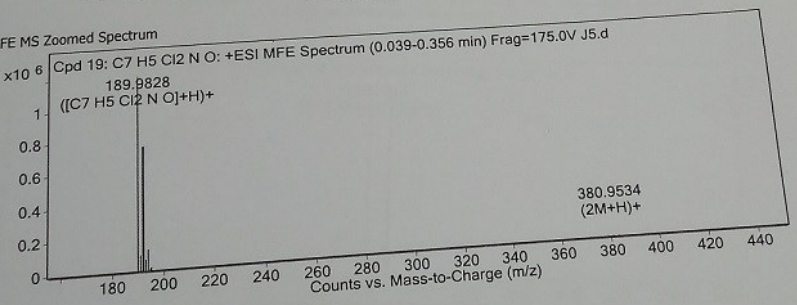
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 19: C7 H5 Cl2 N O	0.136	188.9756	C7 H5 Cl2 N O	C7 H5 Cl2 N O	-4.01	C7 H5 Cl2 N O

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 19: C7 H5 Cl2 N O	189.9828	0.136	Find by Molecular Feature	188.9756

MFE MS Spectrum



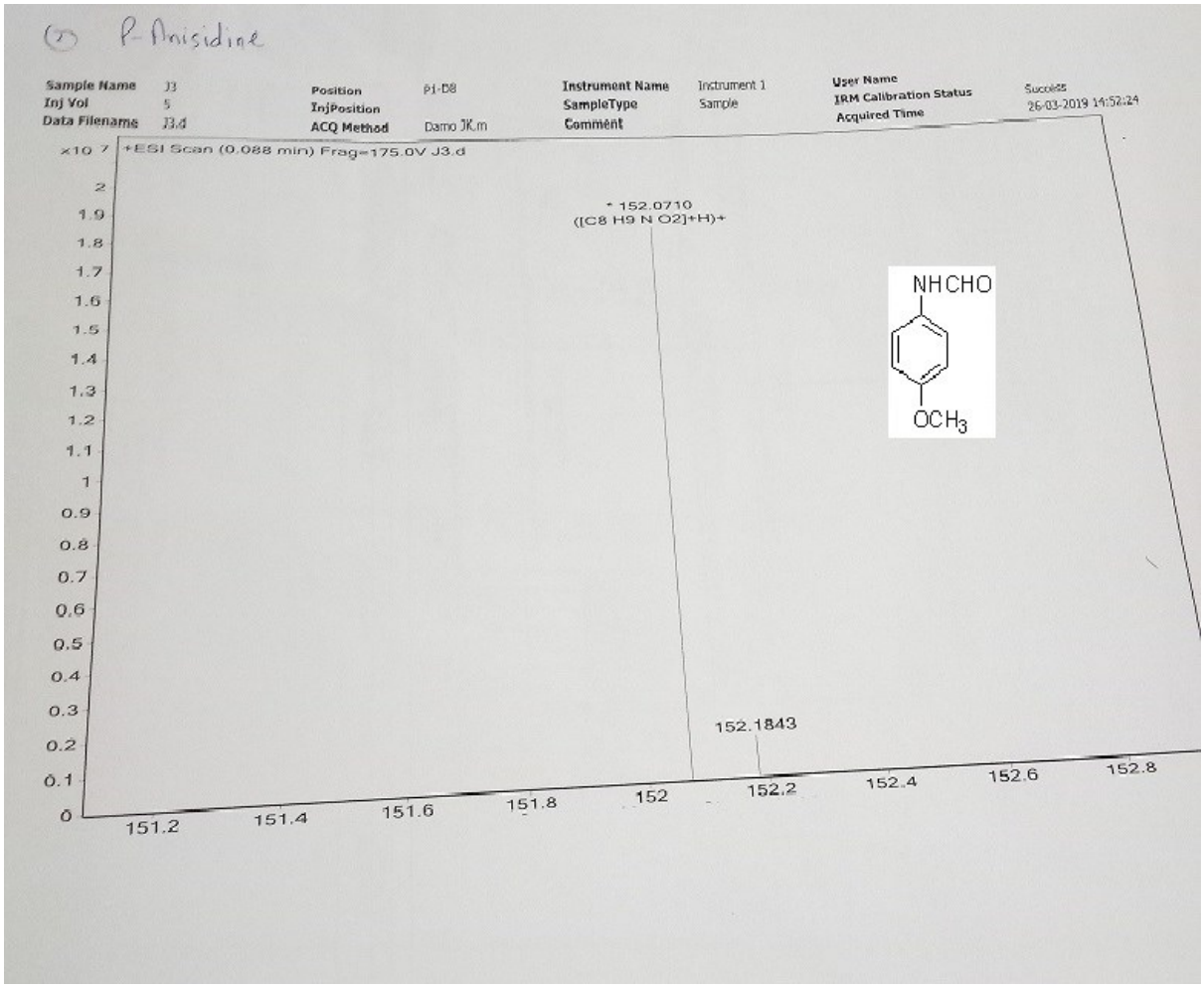
MFE MS Zoomed Spectrum

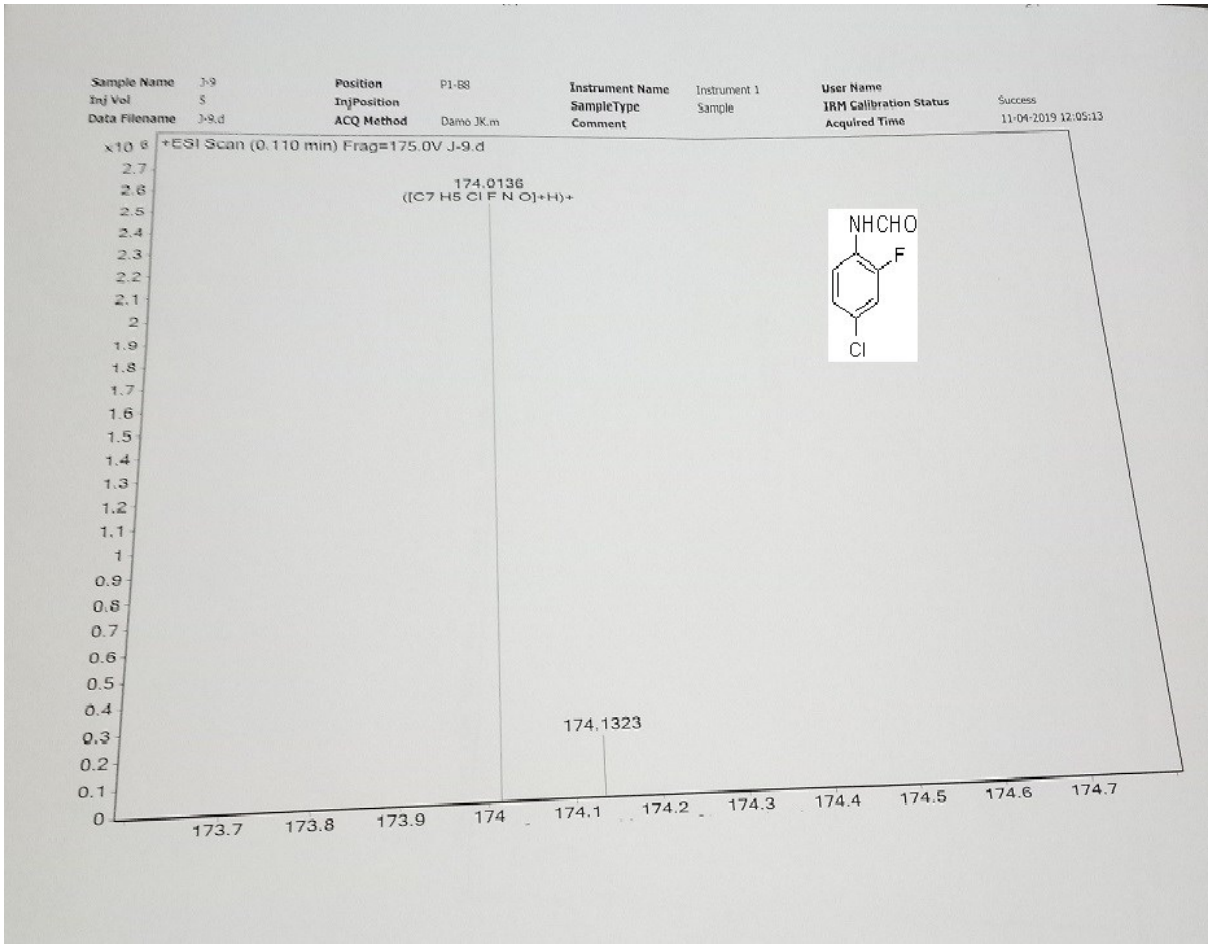


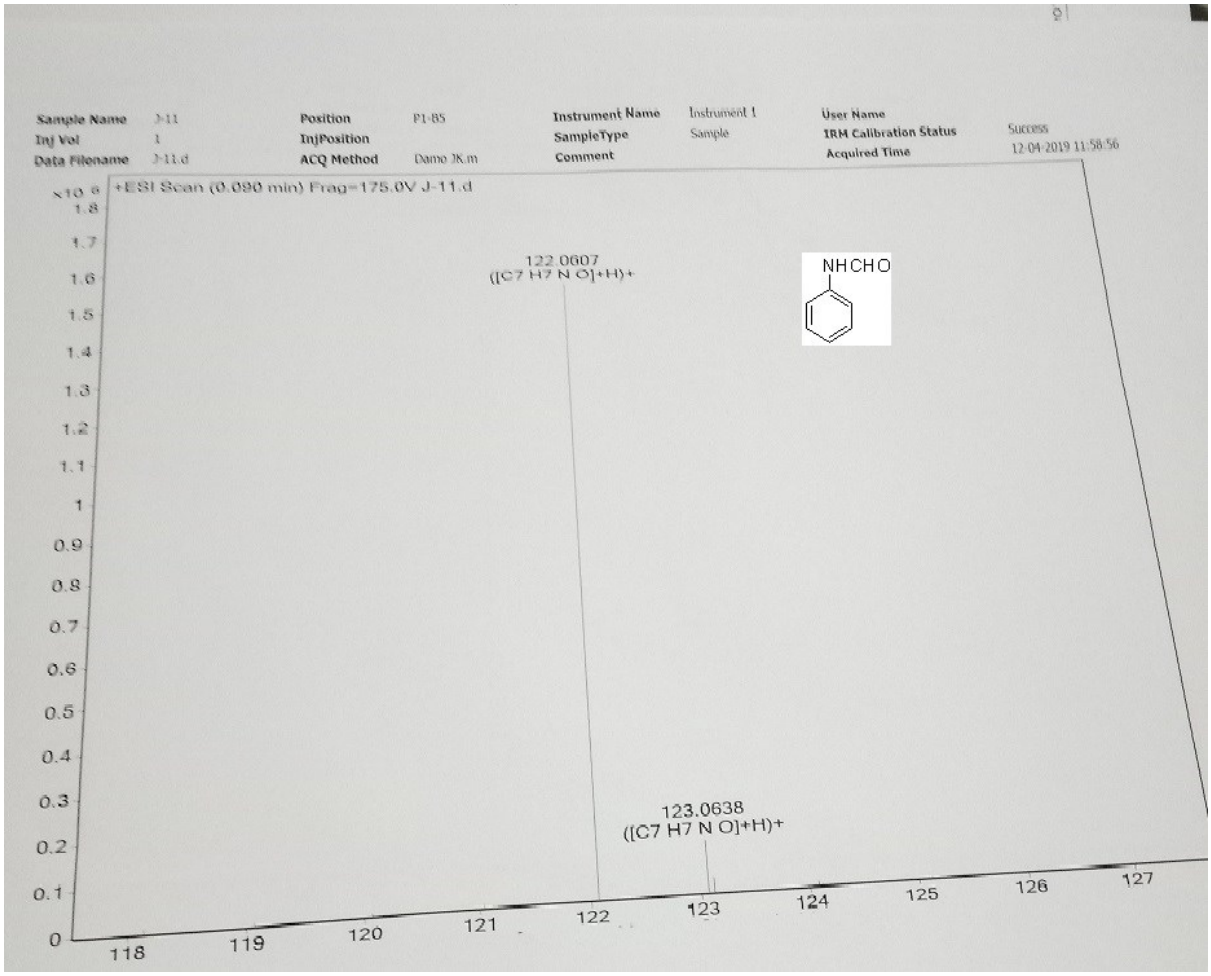
MS Spectrum Peak List

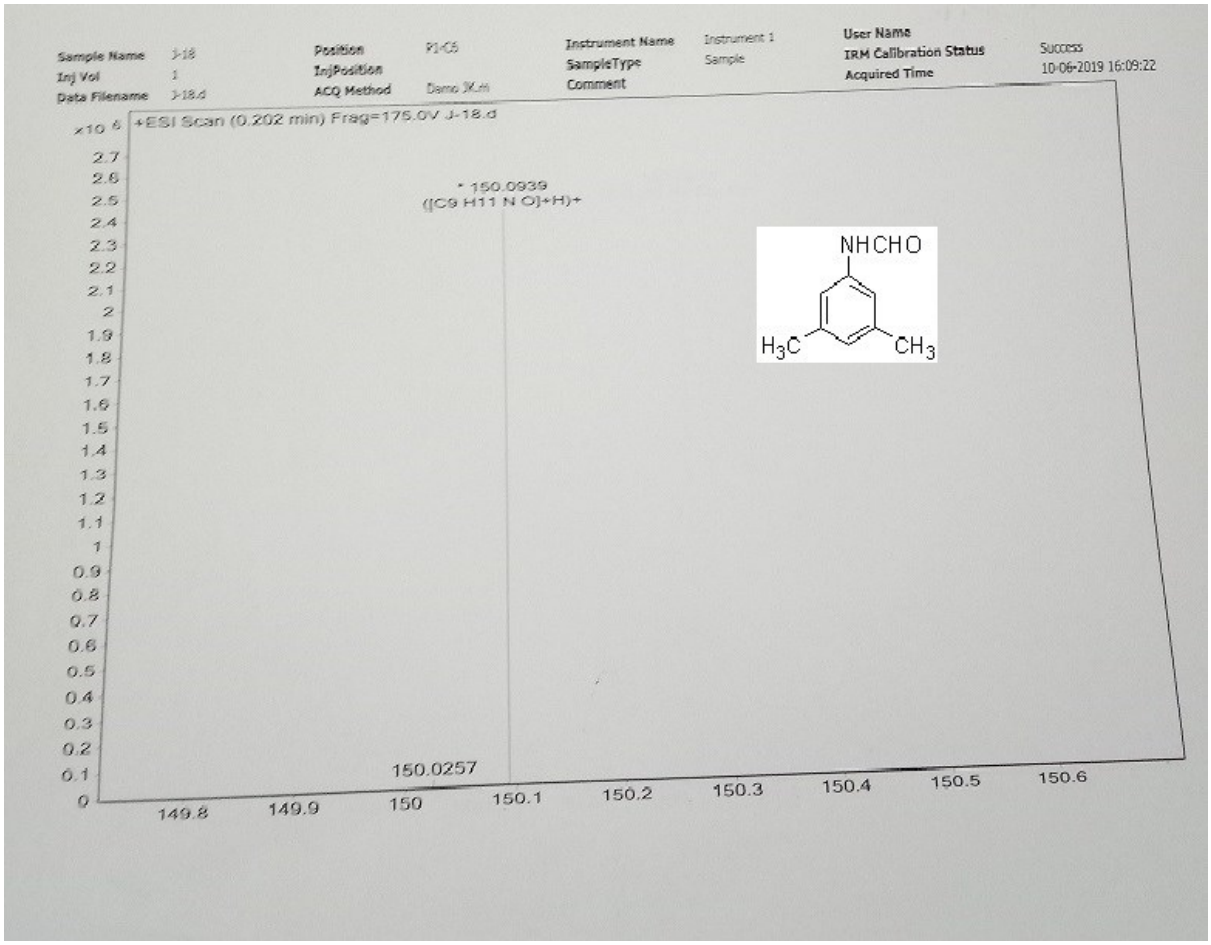
m/z	z	Abund	Formula	Ion
189.9828	1	1204090.38	C7 H5 Cl2 N O	(M+H)+
190.9858	1	88383.25	C7 H5 Cl2 N O	(M+H)+
191.98	1	756670.95	C7 H5 Cl2 N O	(M+H)+
192.9829	1	55435.12	C7 H5 Cl2 N O	(M+H)+
193.9776	1	97557.2	C7 H5 Cl2 N O	(M+H)+
194.9808	1	7994.61	C7 H5 Cl2 N O	(M+H)+
378.9582	1	6267.47		(2M+H)+
380.9534	1	8402.63		(2M+H)+
381.962	1	2677.96		(2M+H)+
382.9555	1	5488.57		(2M+H)+

--- End Of Report ---


(5) P-Anisidine
Sample Name J3
Inj Vol 5
Data Filename J3.d
Position P1-D8
InjPosition
ACQ Method Damo JK.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 26-03-2019 14:52:24
x10 7
+ESI Scan (0.088 min) Frag=175.0V J3.d
+ 152.0710
([C8 H9 N O2]+H)+
152.1843
NHCHO
OCH3
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
151.2
151.4
151.6
151.8
152
152.2
152.4
152.6
152.8


Sample Name J-9
Inj Vol 5
Data Filename J-9.d
Position P1-B8
InjPosition
ACQ Method Damo JK.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 11-04-2019 12:05:13
+ESI Scan (0.110 min) Frag=175.0V J-9.d
x10 6
174.0136
([C7 H5 Cl F N O]+H)+
174.1323
NHCHO
F
Cl
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
173.7
173.8
173.9
174
174.1
174.2
174.3
174.4
174.5
174.6
174.7


Sample Name J-11
Inj Vol 1
Data Filename J-11.d
Position P1-B5
InjPosition
ACQ Method Damo JK.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 12/04/2019 11:58:56
+ESI Scan (0.090 min) Frag=175.0V J-11.d
x10 6
122.0607
([C7 H7 N O]+H)+
123.0638
([C7 H7 N O]+H)+
NHCHO
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
118
119
120
121
122
123
124
125
126
127

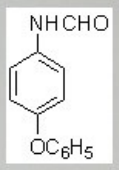

Sample Name J-18
Inj Vol 1
Data Filename J-18.d
Position P1-C5
InjPosition
ACQ Method Demo JK.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 10-06-2019 16:09:22
+ESI Scan (0.202 min) Frag=175.0V J-18.d
x10 6
* 150.0939
([C9 H11 N O]+H)+
NHCHO
H3C
CH3
150.0257
149.8
149.9
150
150.1
150.2
150.3
150.4
150.5
150.6

Qualitative Compound Report

Data File	Y-12.d	**Sample Name**	Y-12
Sample Type	Sample	**Position**	P1-A3
Instrument Name	Instrument 1	**User Name**	
Acq Method	Damo JK.m	**Acquired Time**	16-04-2019 11:36:48
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group **Info.**

Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)

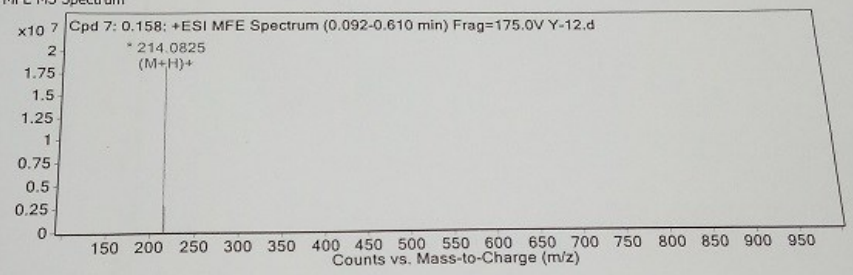


Compound Table

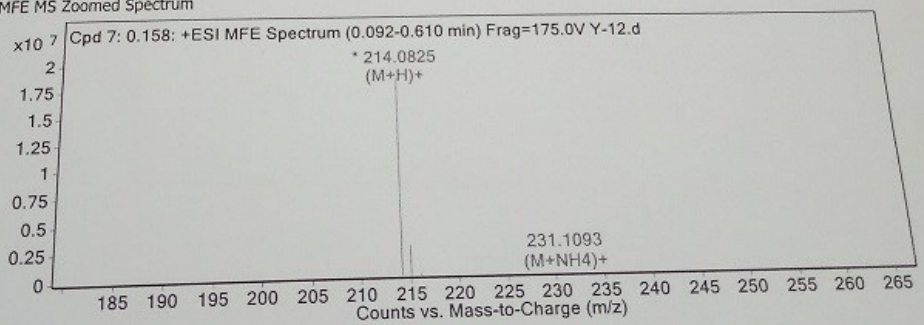
Compound Label	RT	Mass	MFG Formula
Cpd 7: 0.158	0.158	213.0752	<none>

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 7: 0.158	214.0825	0.158	Find by Molecular Feature	213.0752

MFE MS Spectrum



MFE MS Zoomed Spectrum



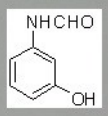
MS Spectrum Peak List

m/z	z	Abund	Ion
214.0825	1	18417204	(M+H)+
215.0858	1	2734168.5	(M+H)+
216.0884	1	215376.57	(M+H)+
217.0912	1	7948.41	(M+H)+
231.1093	1	11041.07	(M+NH4)+

Qualitative Compound Report

Qualitative Compound Report

Data File	J-14.d	**Sample Name**	J-14
Sample Type	Sample	**Position**	P1-D1
Instrument Name	Instrument 1	**User Name**	
Acq Method	Damo JK.m	**Acquired Time**	24-04-2019 12:53:47
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			
Sample Group		**Info.**	
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)		

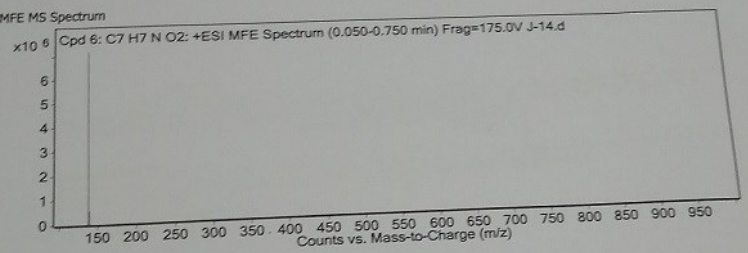


Compound Table

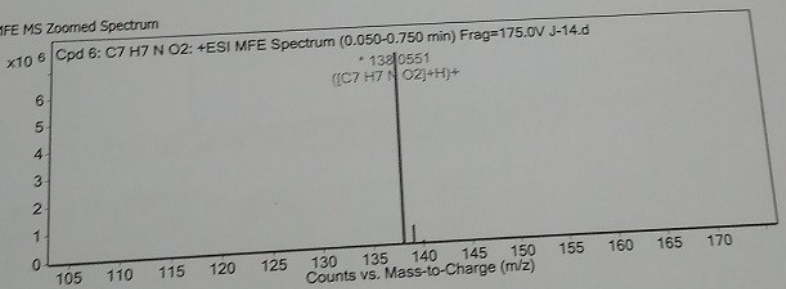
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 6: C7 H7 N O2	0.144	137.0479	C7 H7 N O2	C7 H7 N O2	-1.44	C7 H7 N O2

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 6: C7 H7 N O2	138.0551	0.144	Find by Molecular Feature	137.0479

MFE MS Spectrum



MFE MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
138.0551	1	7180816.5	C7 H7 N O2	(M+H)+
139.0583	1	561636.4	C7 H7 N O2	(M+H)+
140.0599	1	48960.28	C7 H7 N O2	(M+H)+
141.0663	1	5006.88	C7 H7 N O2	(M+H)+

--- End Of Report ---

Compound Report

Qualitative Compound Report

Data File	J-15.d	Sample Name	J-15
Sample Type	Sample	Position	P1-B2
Instrument Name	Instrument 1	User Name	
Acq Method	Damo JK.m	Acquired Time	22-04-2019 17:08:36
IRM Calibration Status	Success	DA Method	Default.m
Comment			

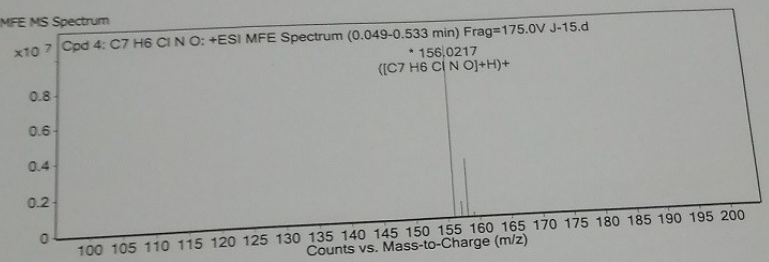
Sample Group	Info.
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)

Compound Table

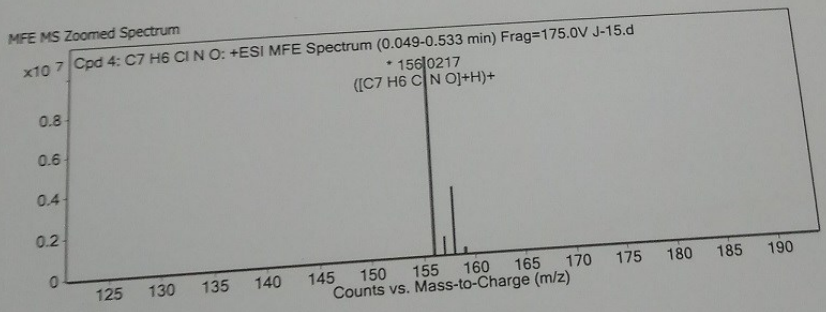
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 4: C7 H6 Cl N O	0.112	155.0145	C7 H6 Cl N O	C7 H6 Cl N O	-4.35	C7 H6 Cl N O

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 4: C7 H6 Cl N O	156.0217	0.112	Find by Molecular Feature	155.0145

MFE MS Spectrum



MFE MS Zoomed Spectrum



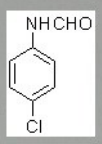
MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
156.0217	1	10123298	C7 H6 Cl N O	(M+H)+
157.025	1	810488.96	C7 H6 Cl N O	(M+H)+
158.0189	1	3295670.77	C7 H6 Cl N O	(M+H)+
159.022	1	217971.73	C7 H6 Cl N O	(M+H)+

--- End Of Report ---

Qualitative Compound Report

Data File	J-16.d	**Sample Name**	J-16
Sample Type	Sample	**Position**	P1-C9
Instrument Name	Instrument 1	**User Name**	
Acq Method	Damo JK.m	**Acquired Time**	26-04-2019 12:43:03
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			



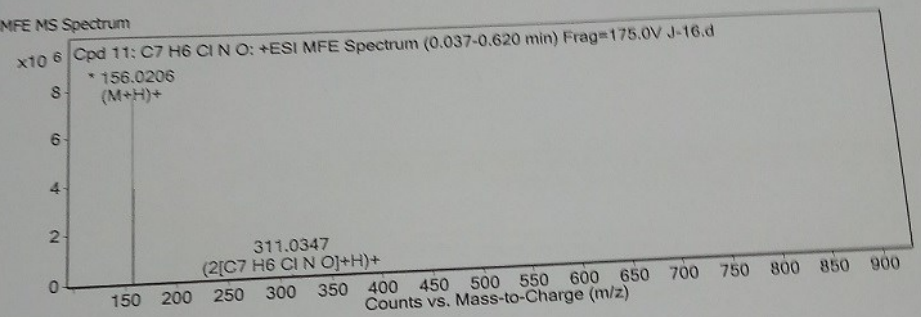
Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)

Compound Table

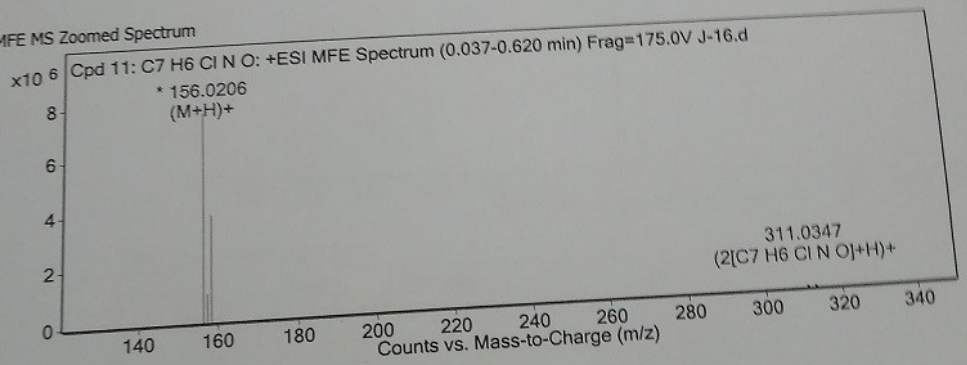
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 11: C7 H6 Cl N O	0.136	155.0129	C7 H6 Cl N O	C7 H6 Cl N O	5.44	C7 H6 Cl N O

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 11: C7 H6 Cl N O	156.0206	0.136	Find by Molecular Feature	155.0129

MFE MS Spectrum

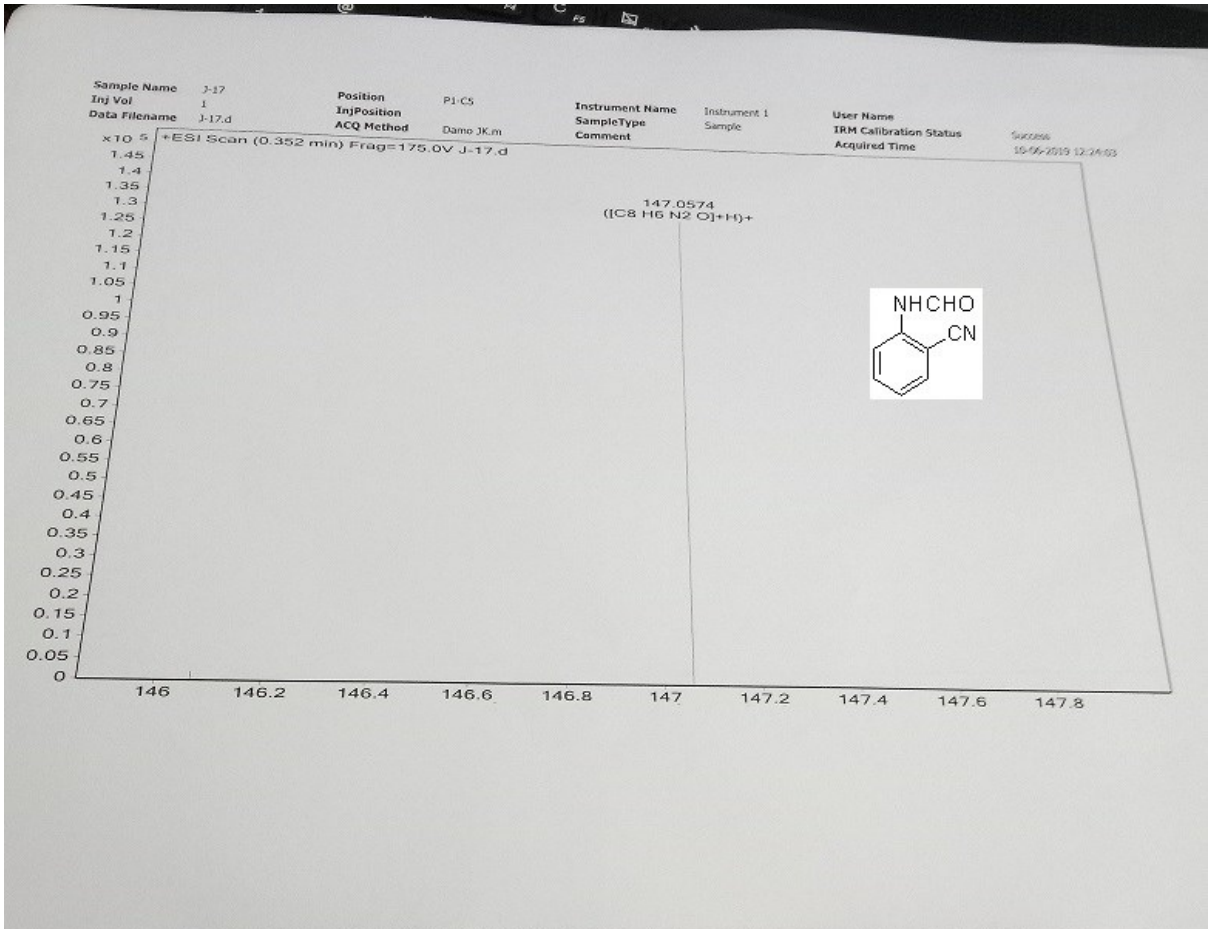


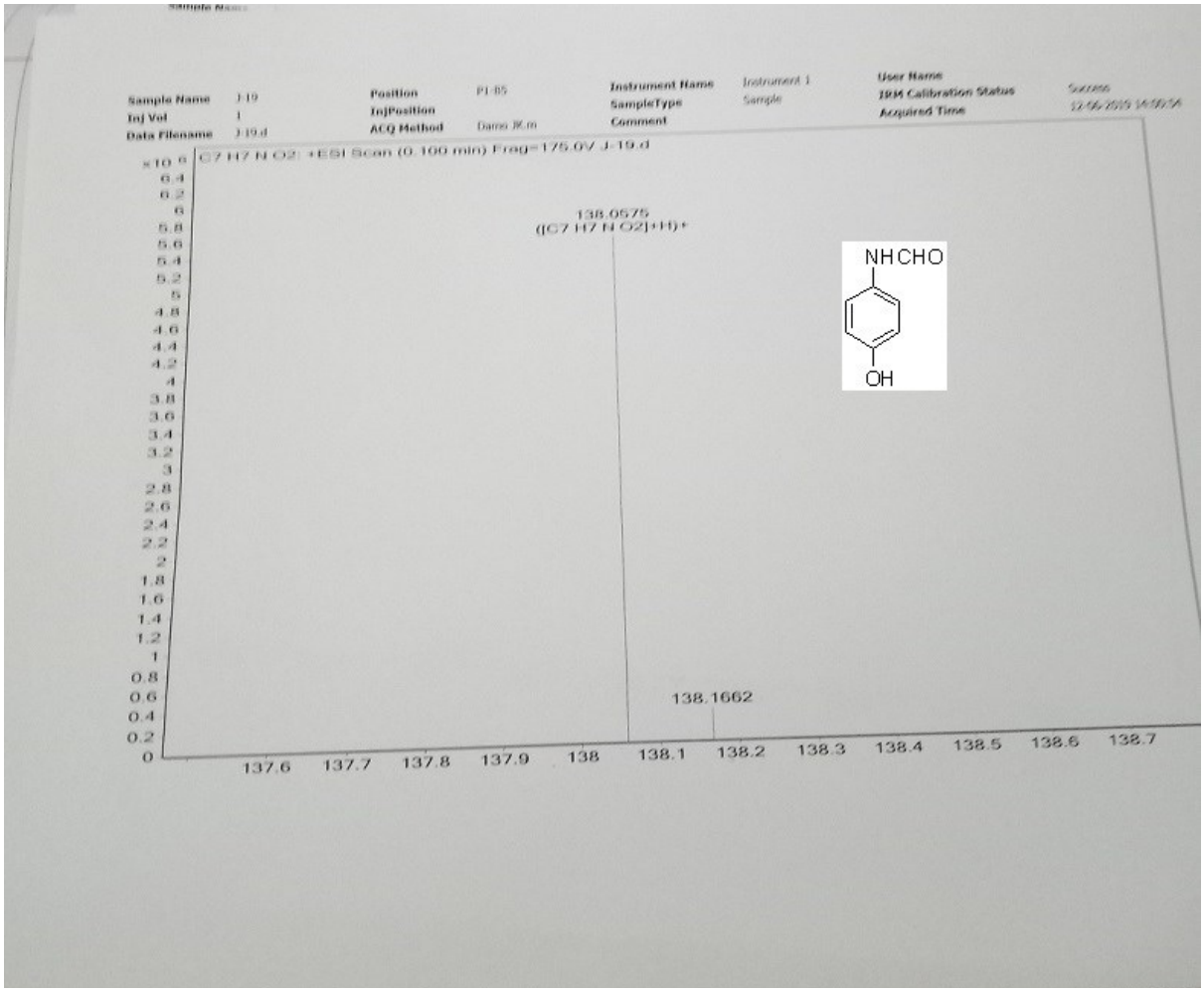
MFE MS Zoomed Spectrum

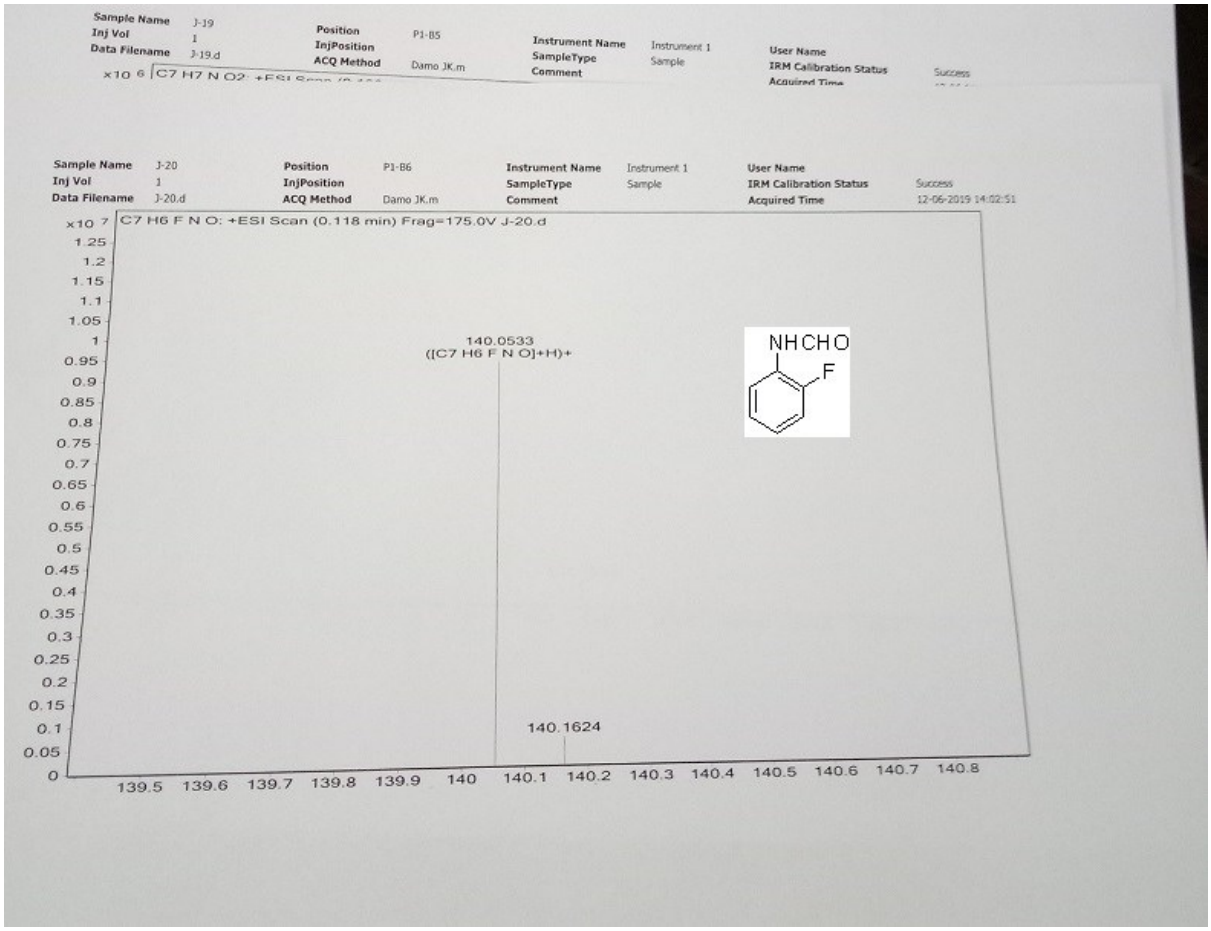


MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
156.0206	1	7679205.5		(M+H)+
157.024	1	991405.76		(M+H)+
158.0179	1	3840436.83		(M+H)+
311.0347	1	36477.41	C7 H6 Cl N O	(2M+H)+
312.0386	1	5798.96	C7 H6 Cl N O	(2M+H)+
313.0309	1	24653.76	C7 H6 Cl N O	(2M+H)+
314.0264	1	4049.43	C7 H6 Cl N O	(2M+H)+
315.0302	1	6145.02	C7 H6 Cl N O	(2M+H)+

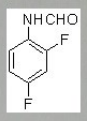

Sample Name J-17
Inj Vol 1
Data Filename J-17.d
Position P1-C5
InjPosition
ACQ Method Damo JK.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status
Acquired Time
+ESI Scan (0.352 min) Frag=175.0V J-17.d
x10 5
147.0574
([C8 H6 N2 O]+H)+
NHCHO
CN
1.45
1.4
1.35
1.3
1.25
1.2
1.15
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
146
146.2
146.4
146.6
146.8
147
147.2
147.4
147.6
147.8


Sample Name J-19
Inj Vol 1
Data Filename J-19.d
Position P1-B5
InjPosition
ACQ Method Damo 3K.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time
C7 H7 N O2 +ESI Scan (0.100 min) Frag=175.0V J-19.d
x10 6
138.0575
([C7 H7 N O2]+H)+
138.1662
NH CHO
OH
137.6
137.7
137.8
137.9
138
138.1
138.2
138.3
138.4
138.5
138.6
138.7


Sample Name J-19
Inj Vol 1
Data Filename J-19.d
Position P1-B5
InjPosition
ACQ Method Damo JK.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status
Sample Name J-20
Inj Vol 1
Data Filename J-20.d
Position P1-B6
InjPosition
ACQ Method Damo JK.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 12-06-2019 14:02:51
x10 7
C7 H6 F N O: +ESI Scan (0.118 min) Frag=175.0V J-20.d
140.0533
([C7 H6 F N O]+H)+
140.1624
NHCHO
F
1.25
1.2
1.15
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
139.5
139.6
139.7
139.8
139.9
140
140.1
140.2
140.3
140.4
140.5
140.6
140.7
140.8

Qualitative Compound Report

Data File	J-22.d	**Sample Name**	J-22
Sample Type	Sample	**Position**	P1-A8
Instrument Name	Instrument 1	**User Name**	
Acq Method	Damo JK.m	**Acquired Time**	18-04-2019 12:37:23
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			



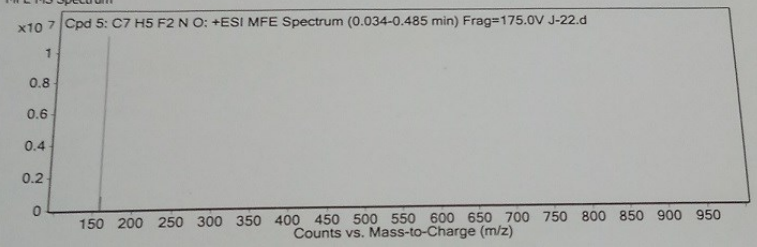
Sample Group		**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.1)	

Compound Table

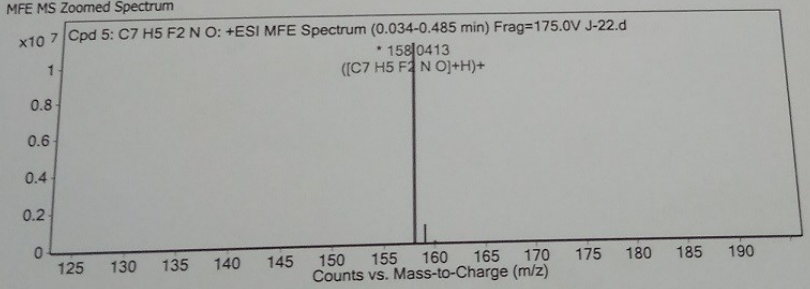
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 5: C7 H5 F2 N O	0.095	157.0341	C7 H5 F2 N O	C7 H5 F2 N O	-1.01	C7 H5 F2 N O

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 5: C7 H5 F2 N O	158.0413	0.095	Find by Molecular Feature	157.0341

MFE MS Spectrum



MFE MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
158.0413	1	11120520	C7 H5 F2 N O	(M+H)+
159.0447	1	877089.98	C7 H5 F2 N O	(M+H)+
160.0468	1	49743.66	C7 H5 F2 N O	(M+H)+
161.0515	1	2288.19	C7 H5 F2 N O	(M+H)+

--- End Of Report ---

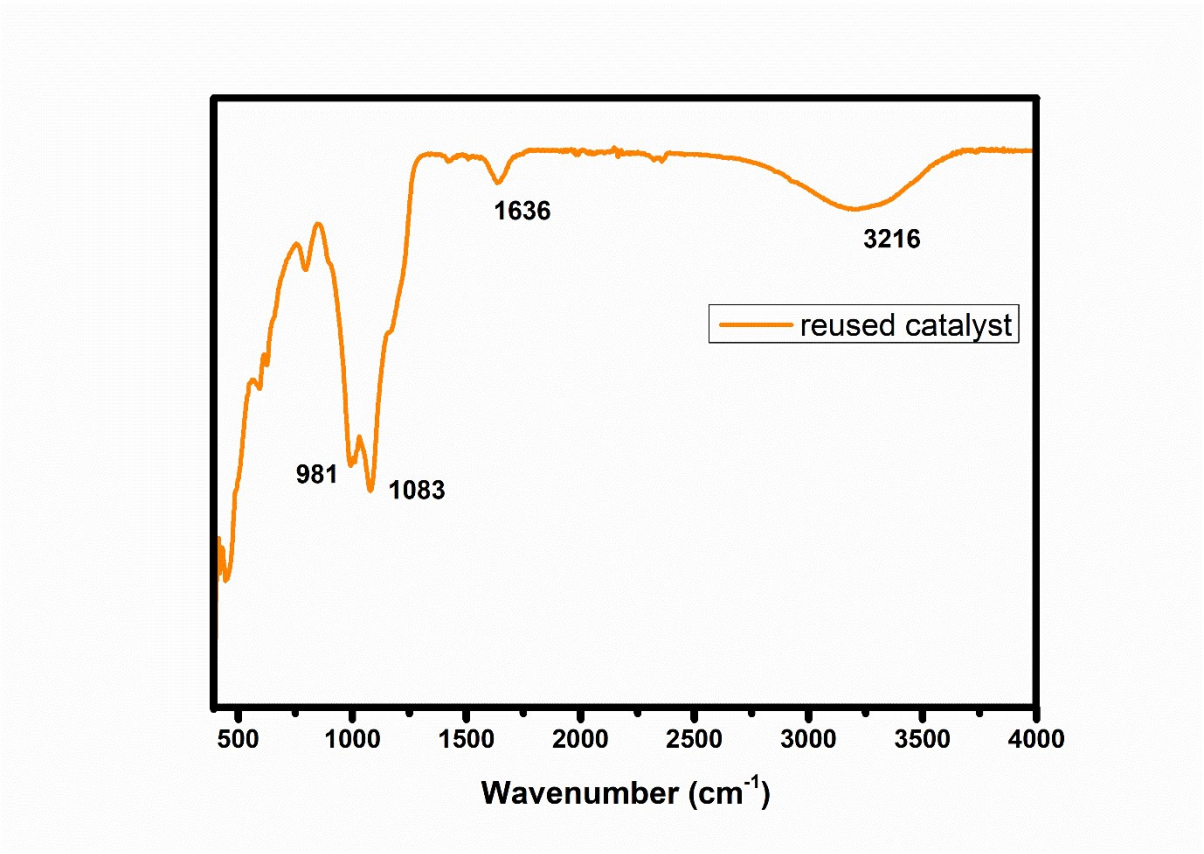


Figure S1: FT-IR of reused catalyst (NP@SO_3H) after 6 serial runs.

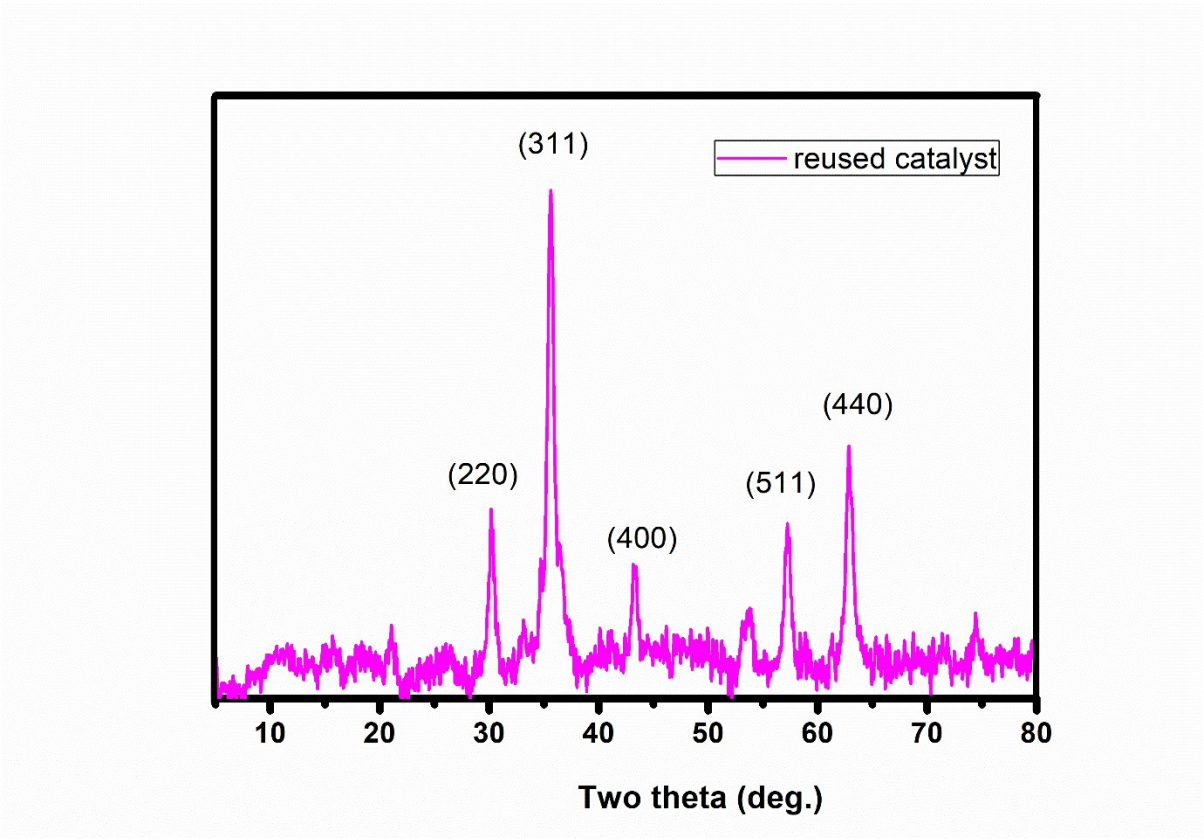


Figure S2: Powder XRD analysis of reused catalyst (NP@SO_3H) after 6 serial runs.