Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Sustainable pathway to furanics from biomass via heterogeneous organo-catalysis

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1. Synthesis of g-CN and Sg-CN catalyst

a) Synthesis of g-CN

The pure urea obtained from Aldrich was calcinated at 500 ^{o}C for 2 hours in a closed furnace. A pale-yellow solid of pure graphitic carbon nitride (g-CN) was obtained and used without any purification.

b) Synthesis of Sg-CN catalyst

Graphitic carbon nitride, g-CN (1.0 g) and dichloromethane (50 mL) were taken in a round bottom flask. Chlorosulfonic acid (0.5 mL) was added to the reaction mixture over the period of 10 min under continuous stirring and then stirring was continued for 3 hours. The ensuing white solid was filtered off, washed with water, methanol and dried under vacuum at 50 °C. The Sg-CN catalyst was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA).

2. General procedure for the synthesis of carbohydrates to value added chemicals

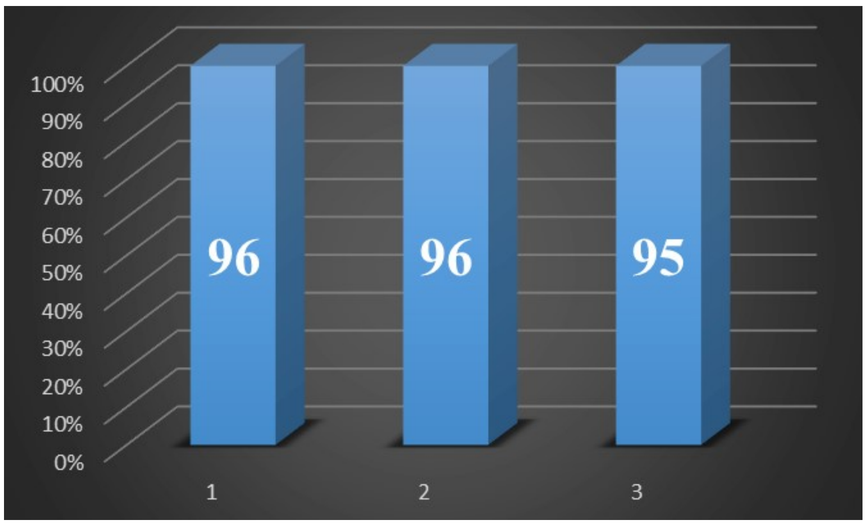
A reaction tube equipped with a stir bar was charged with the desired amount of carbohydrate (2 mmol), catalyst (25 mg of Sg-CN and 5.0 mg of KBr, if required) and water (2 mL). The glass tube was then heated in oil bath at 100 °C. After the completion of the reaction, the reaction temperature was brought down to room temperature, the catalyst was recovered *via* filtration/centrifugation and the product was isolated using solvent extraction using ethyl acetate, dried over sodium sulfate, concentered, and characterized.

3. General procedure for the synthesis of levulinic acid from glucose

A reaction tube equipped with a stir bar was charged with the desired amount of glucose (2 mmol), catalyst (25 mg), and water (2 mL). The glass tube was sealed and placed in an oil bath and heated at 150 °C over a period of 8 hours. After completion of the reaction, the reaction temperature was allowed to come at room temperature. The catalyst was recovered using a centrifuge and the product was isolated using solvent extraction.

4. Recycling of the catalyst

After the completion of each reaction, the Sg-CN catalyst was recovered using a centrifuge,

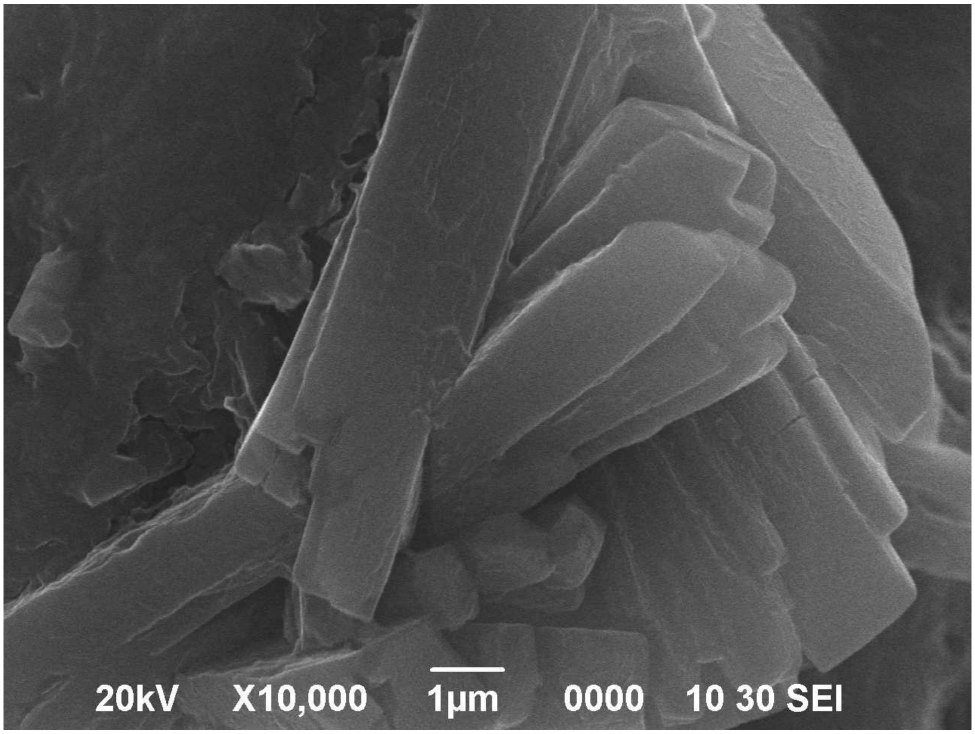


S1. Recycling of the catalyst

washed with water followed by acetone, and dried under vacuum and used for the fresh set

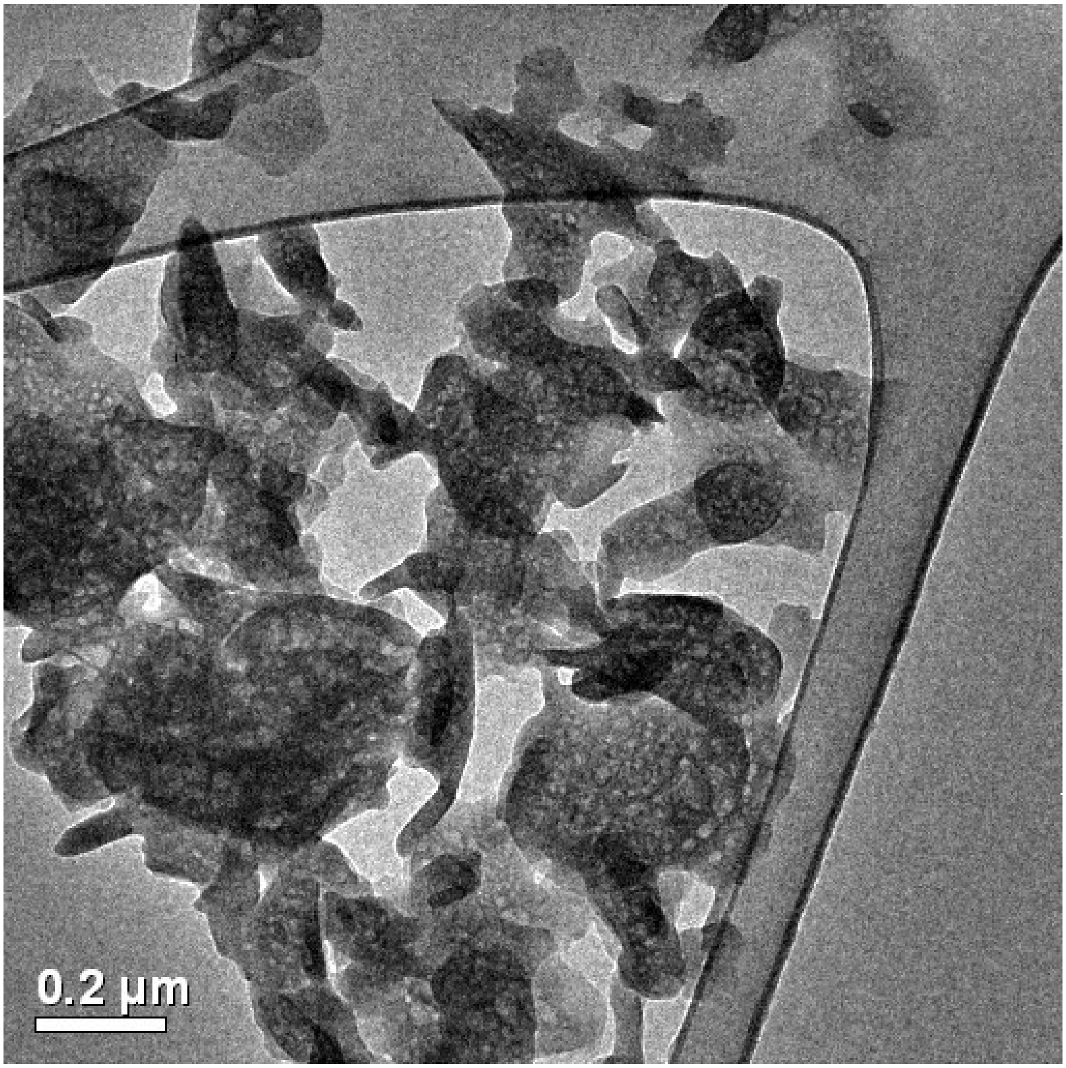
of reactants. It was observed that the catalyst remains active even 3rd cycle of the reaction.

5. Higher magnification SEM image of Sg-CN catalyst



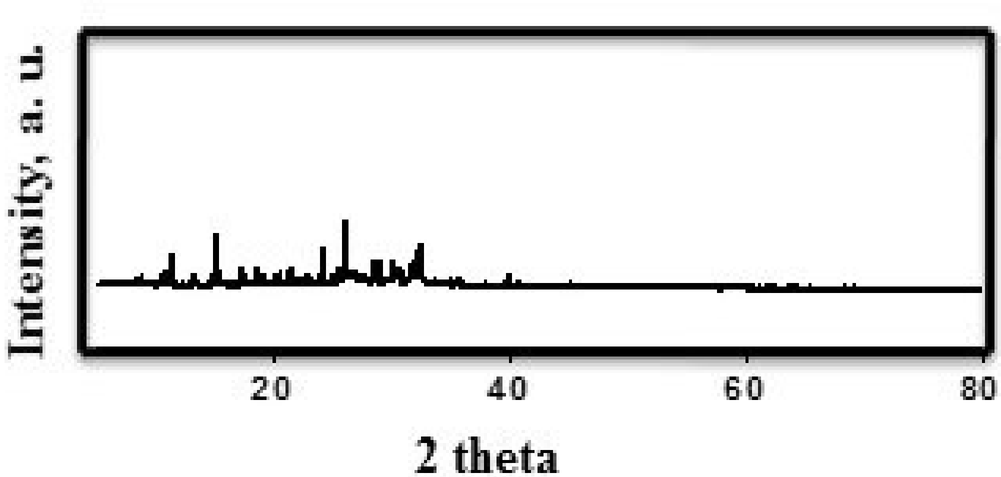
S2. Higher magnification SEM image of Sg-CN catalyst

6. TEM image (different view) of Sg-CN catalyst.



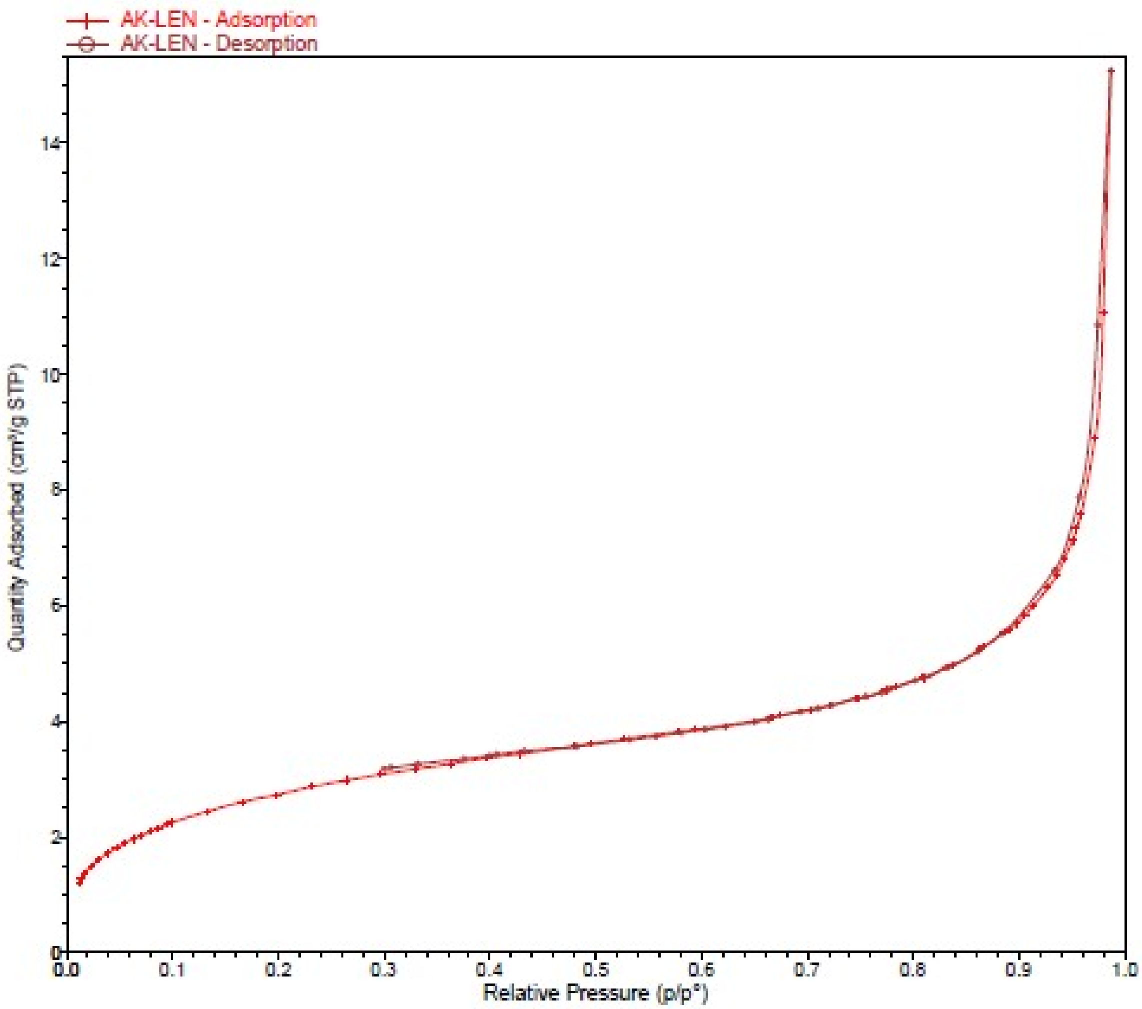
S3. TEM image (different view) of Sg-CN catalyst.

7. XRD of Sg-CN catalyst



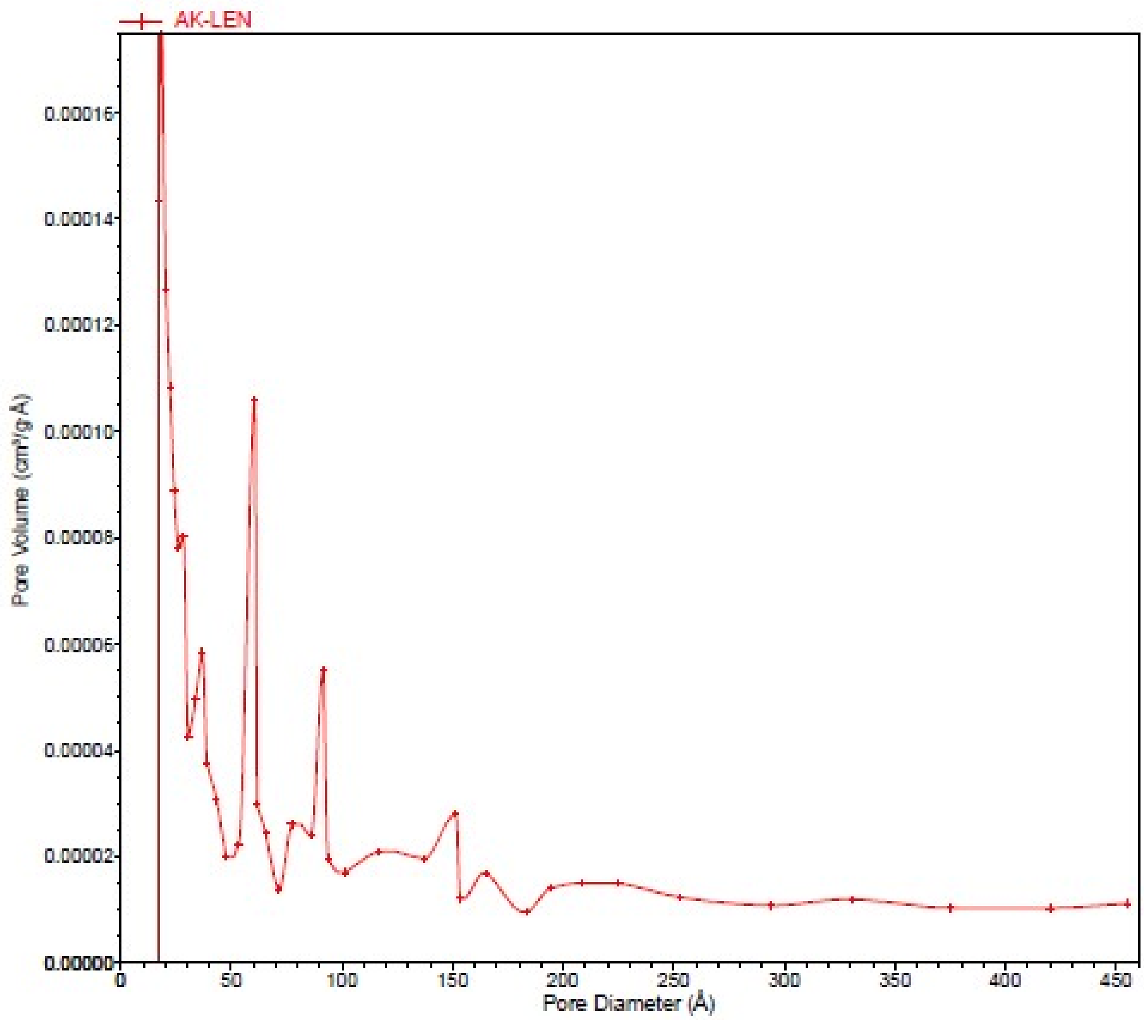
S4. XRD of Sg-CN catalyst

8. N_2 sorption isotherms of Sg-CN



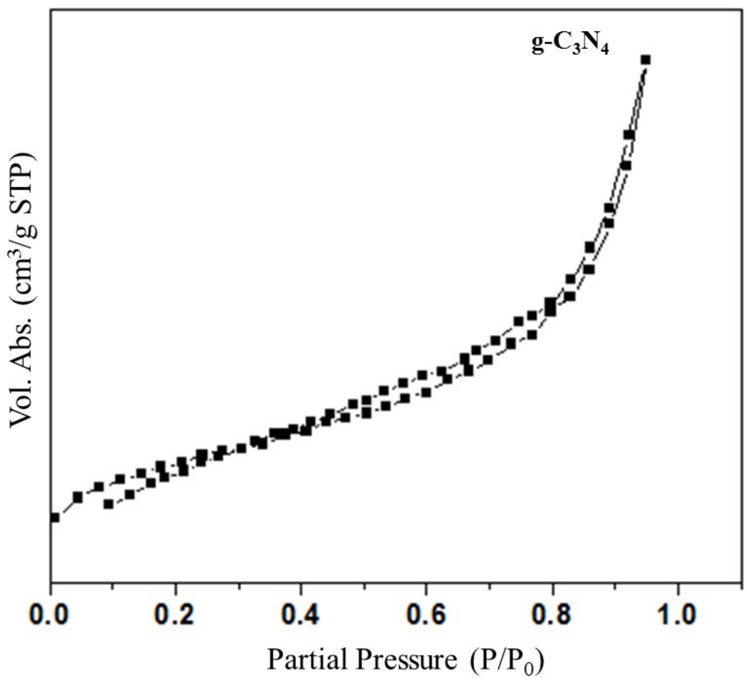
S5. N_2 sorption isotherms of Sg-CN

9. **Distribution of pore diameter of Sg-CN**



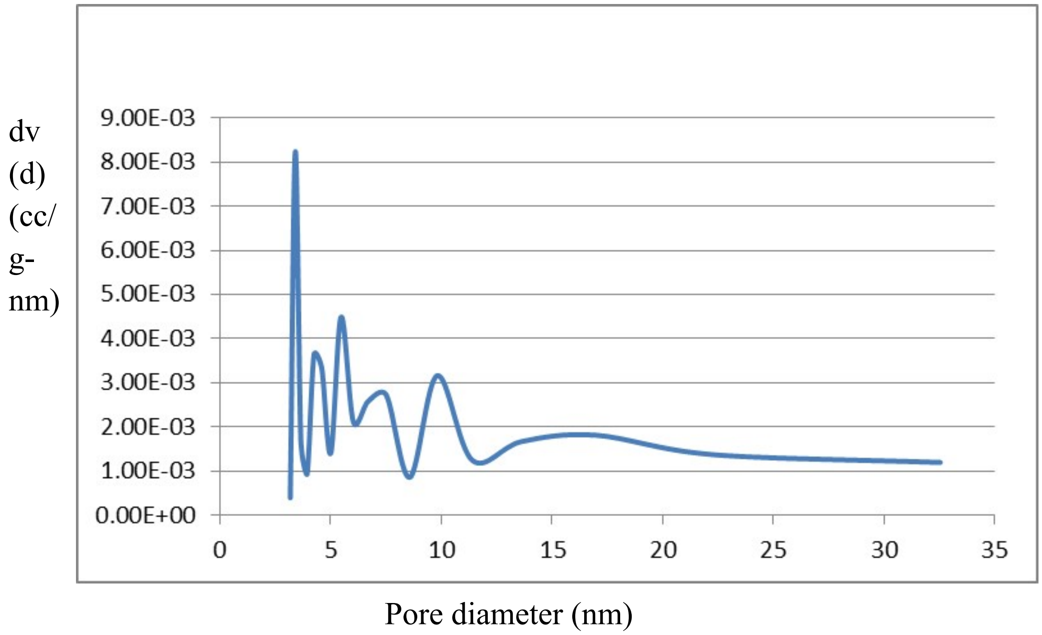
S6. Distribution of pore diameter of Sg-CN

10. N_2 sorption isotherms of g-CN



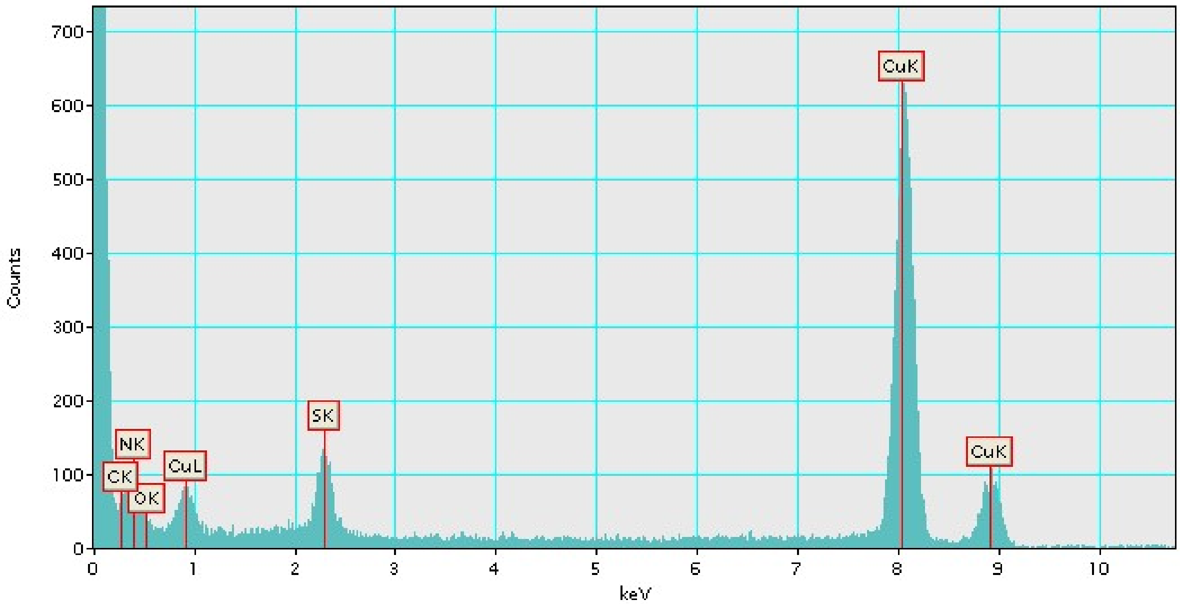
S7. N_2 sorption isotherms of g-CN

11. Distribution of pore diameter of g-CN



S8. Distribution of pore diameter of g-CN

12. EDX of Sg-CN catalyst



S9. EDX of Sg-CN catalyst

13. GC-MASS data of the product

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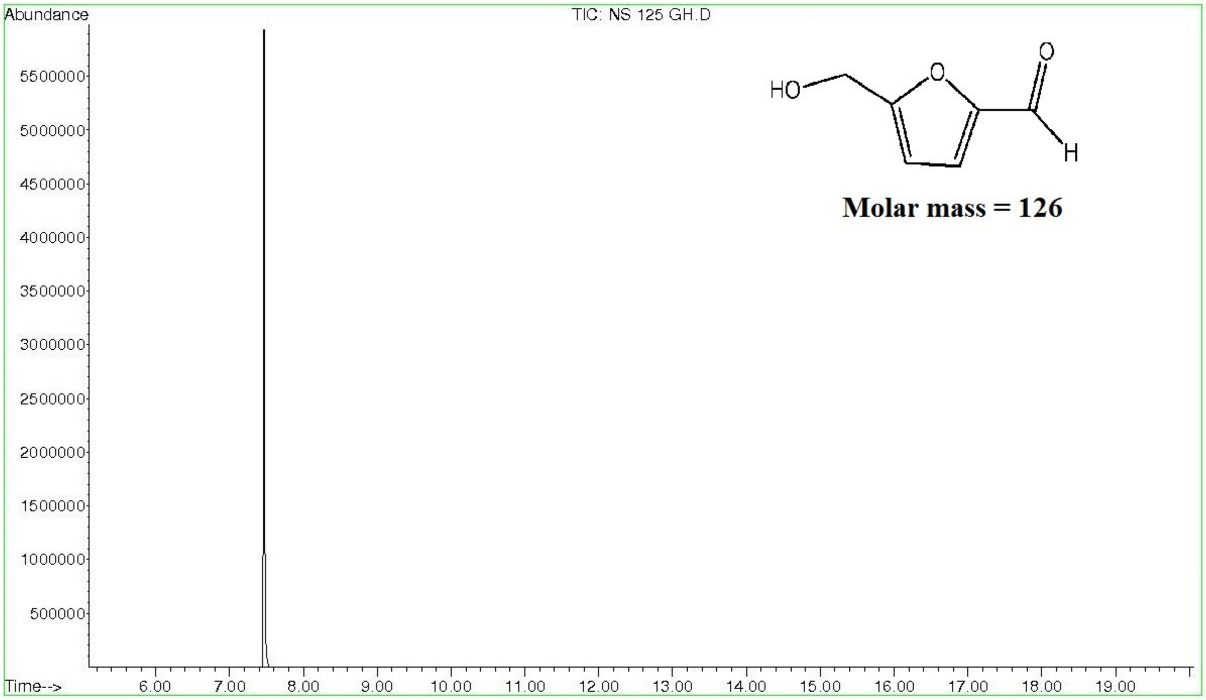

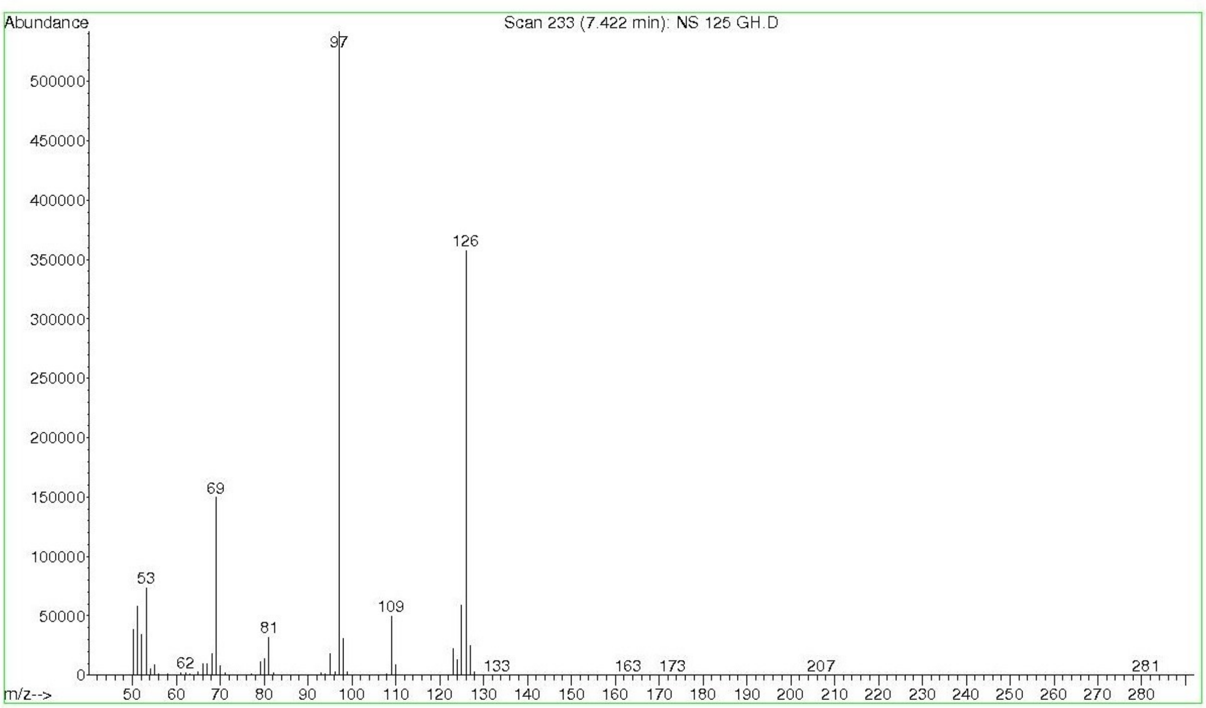

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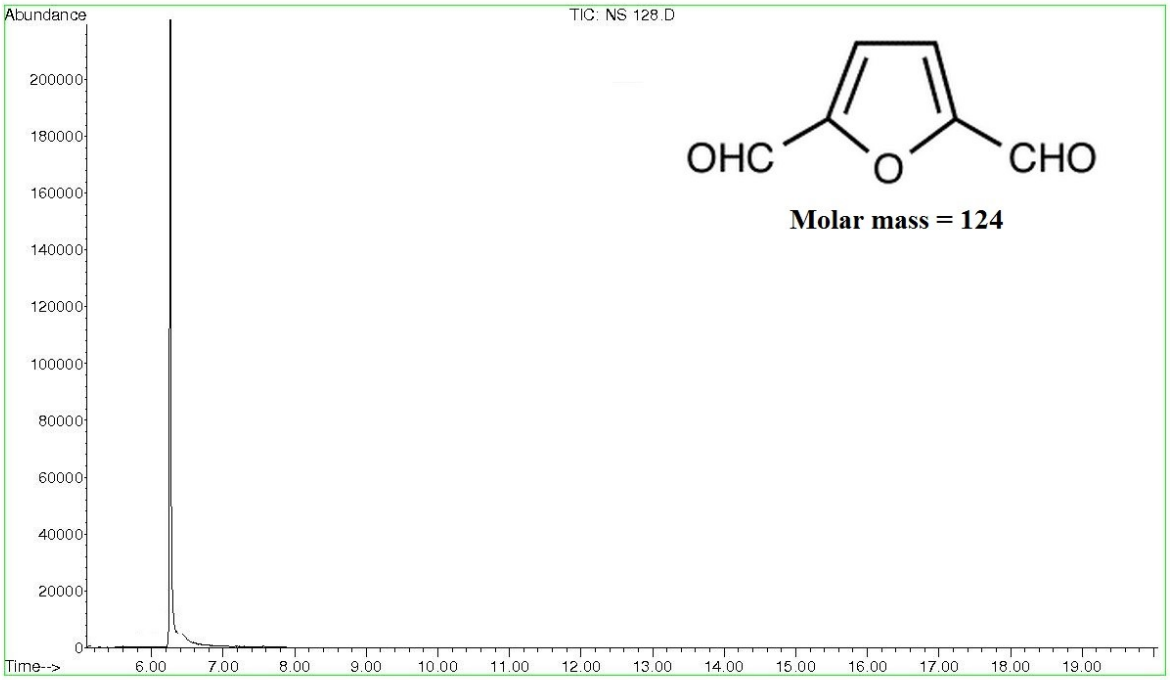

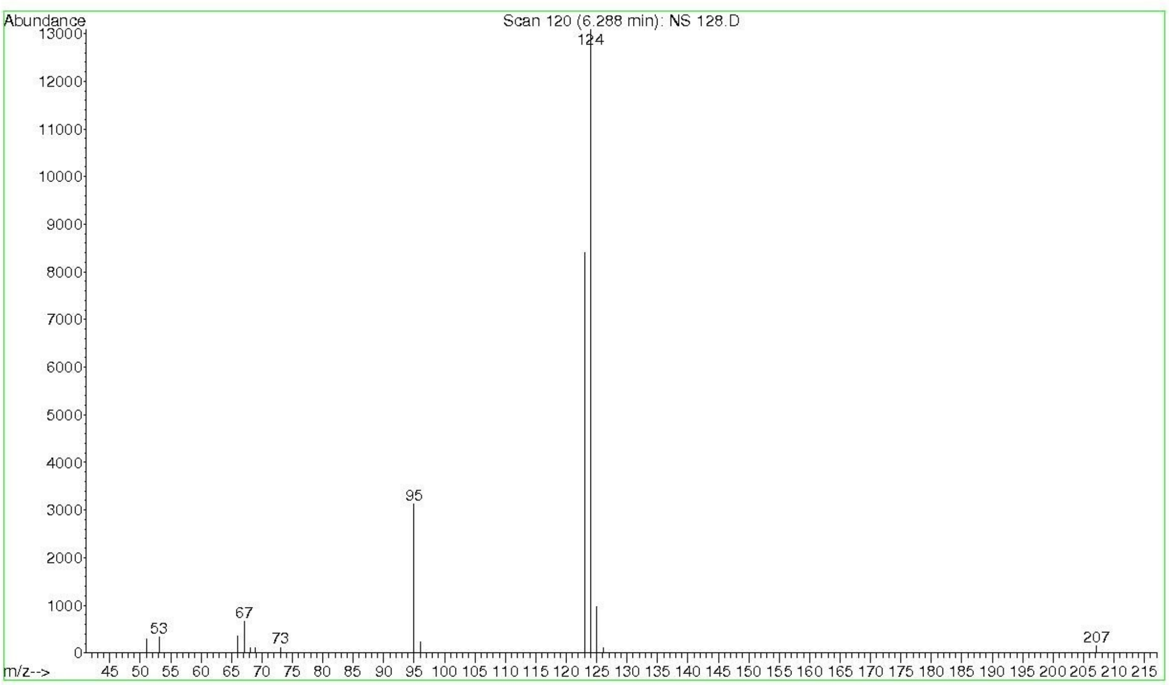

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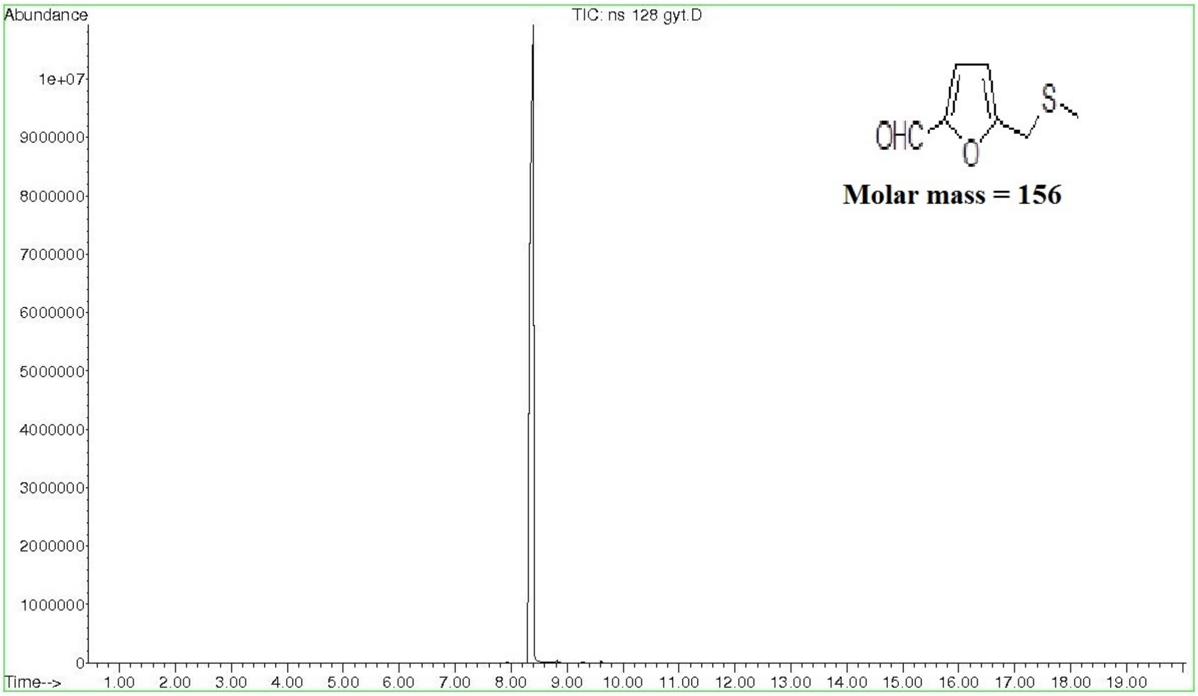
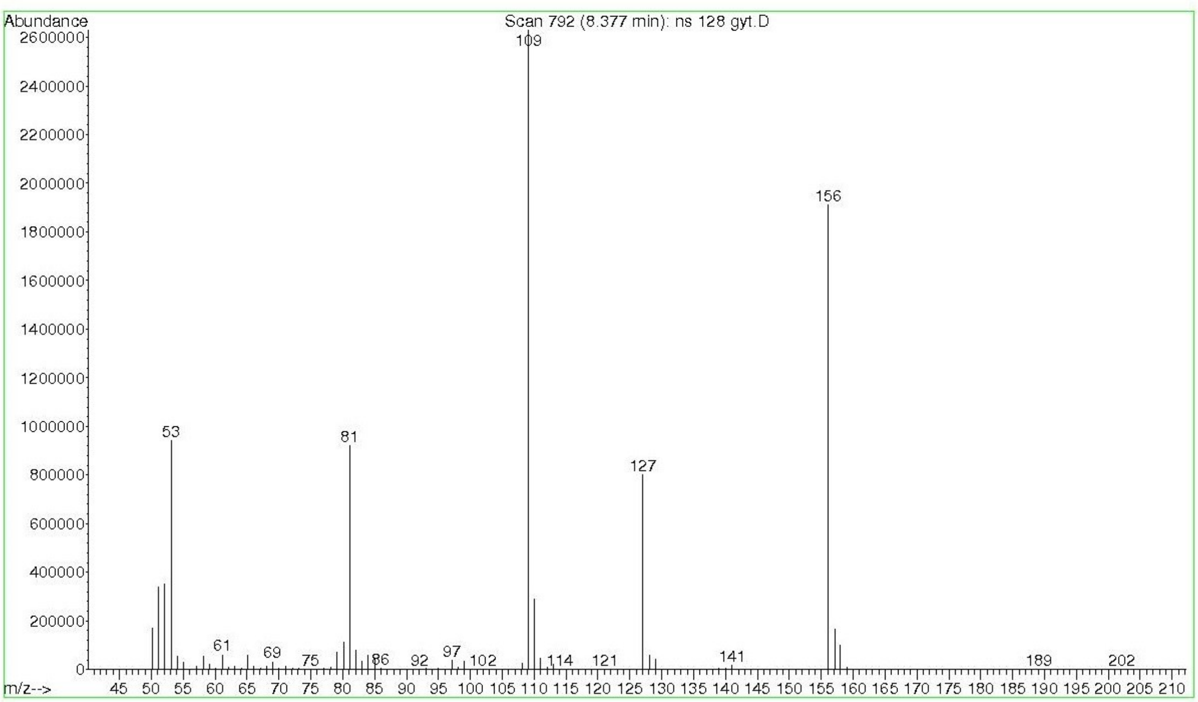
Sample Name: ns 128 gyt
Misc Info :
Vial Number: 6





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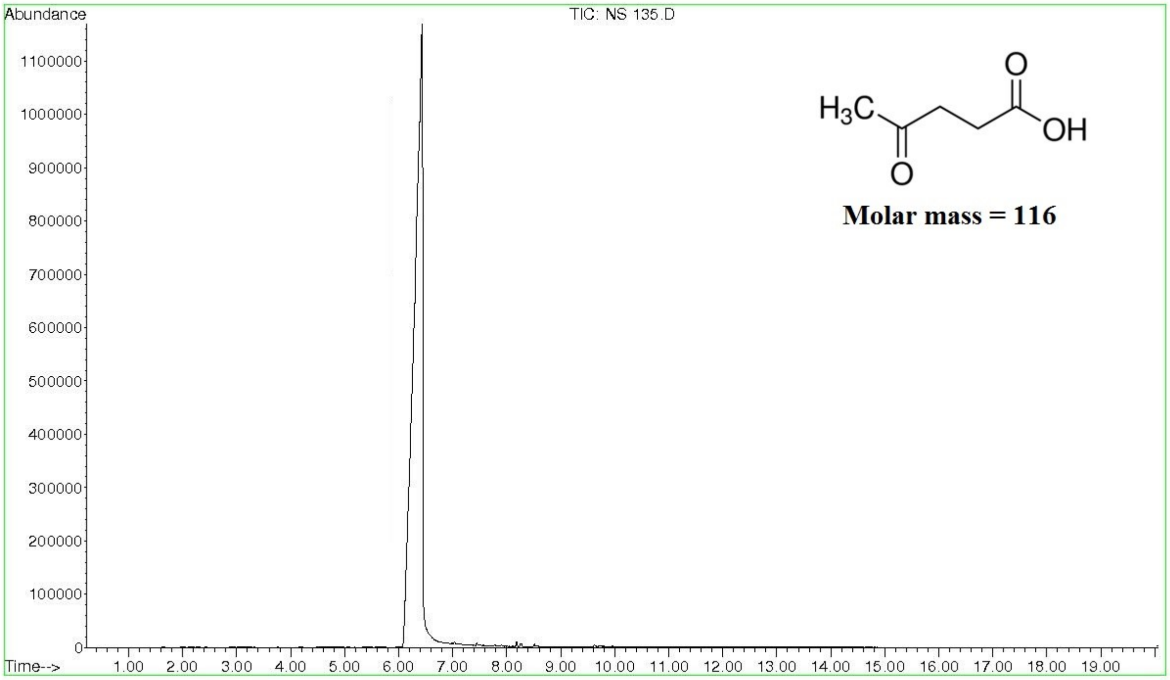
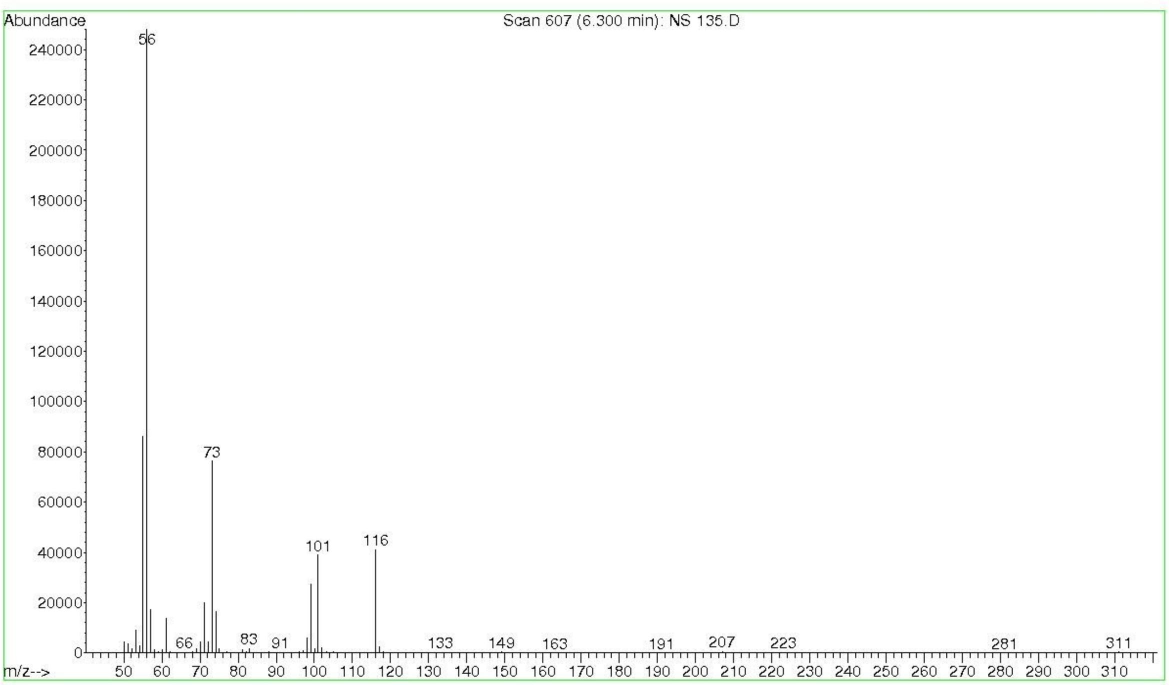
Vial Number: 13





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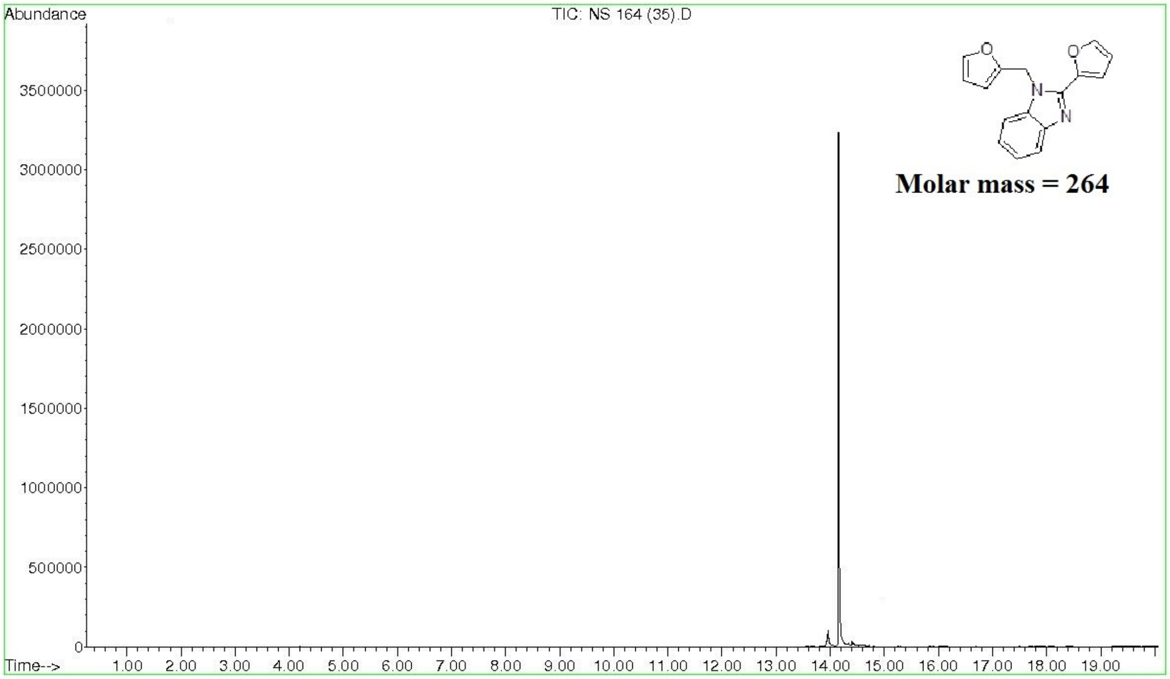
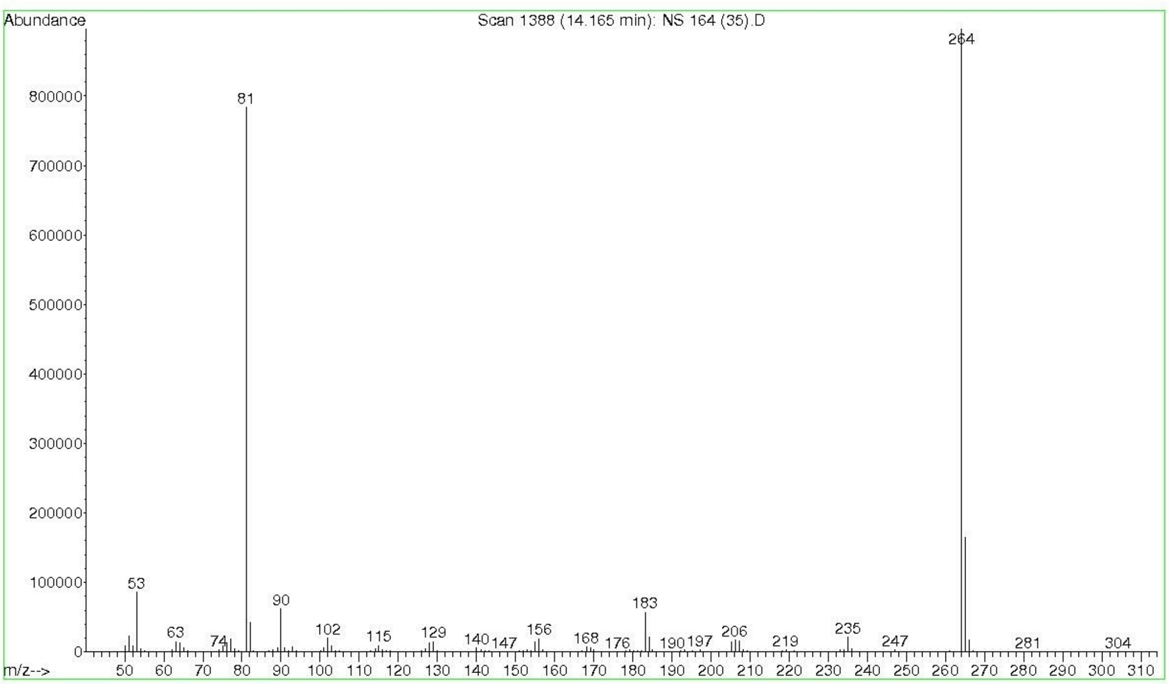
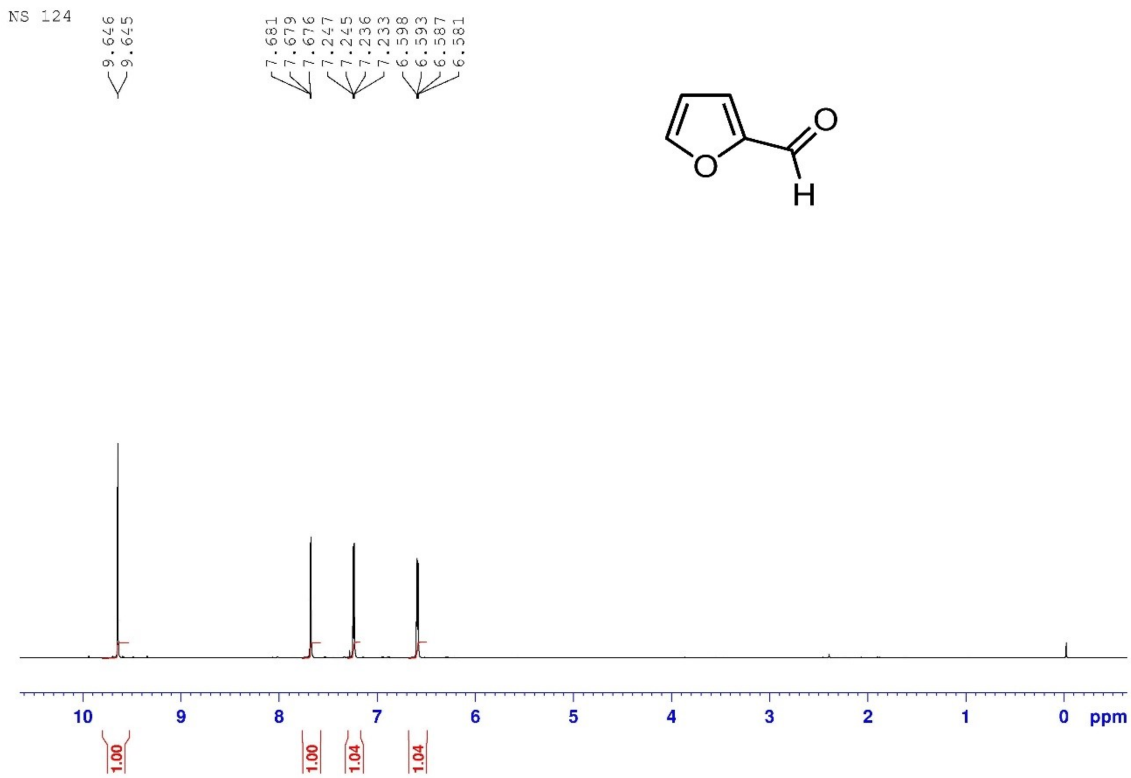
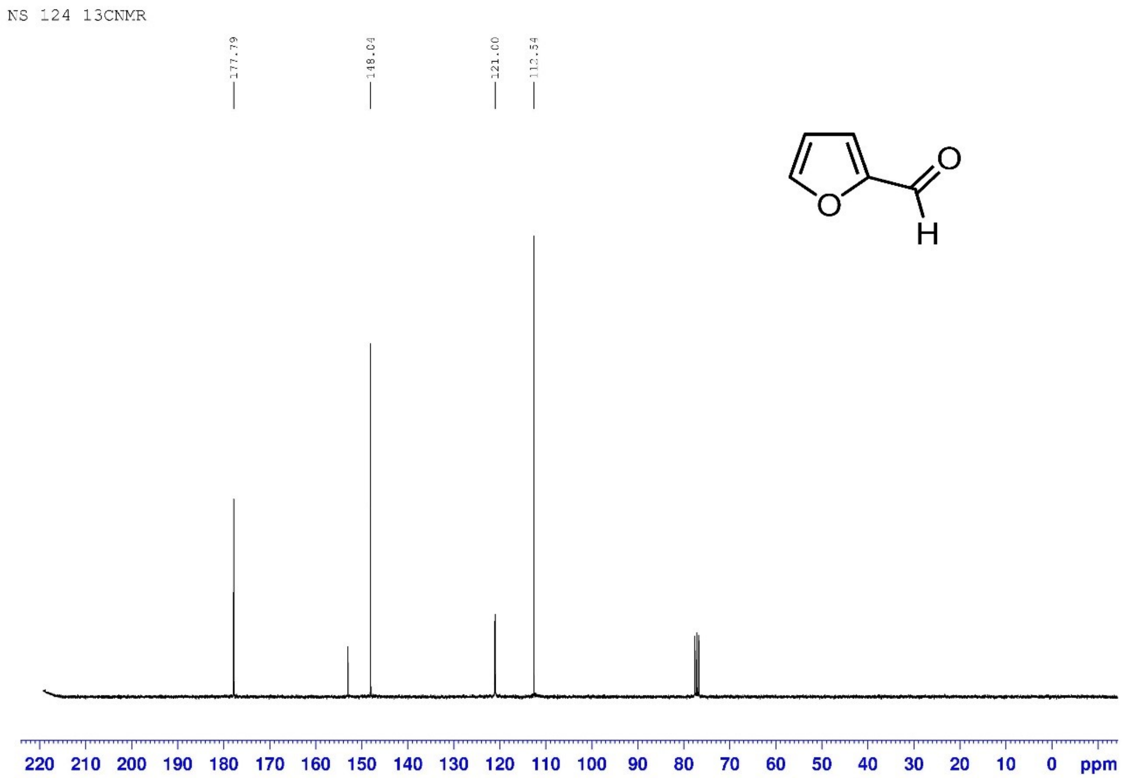
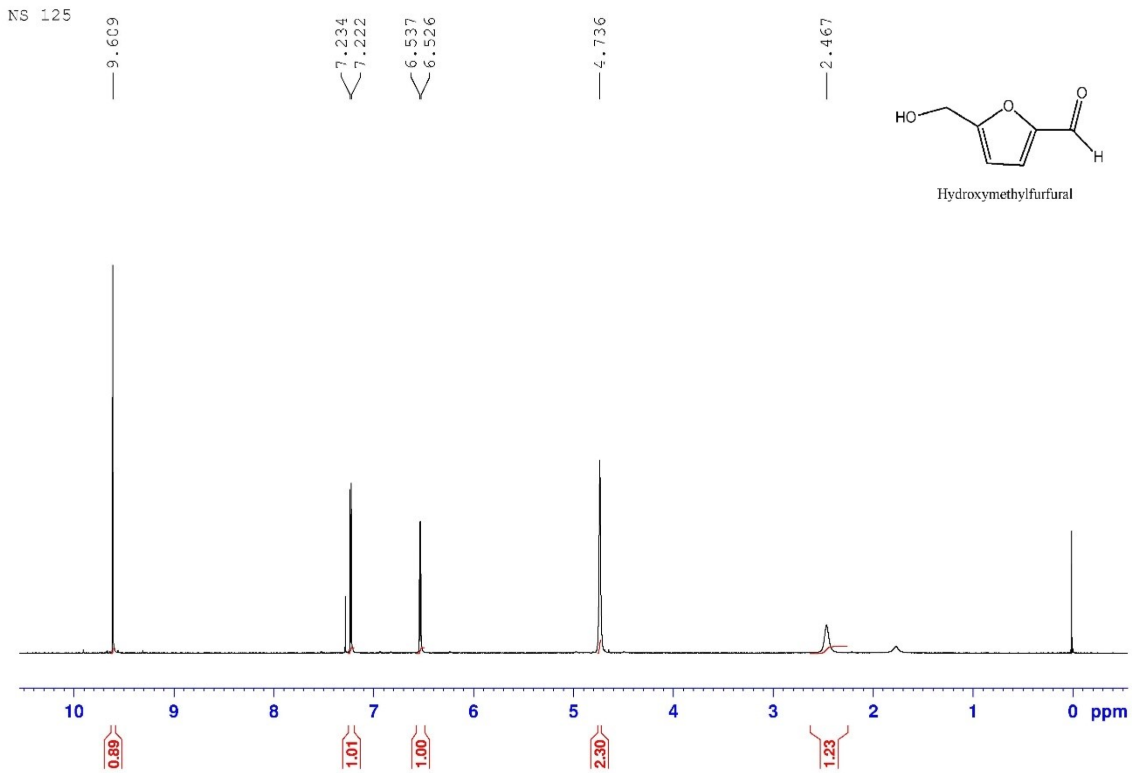




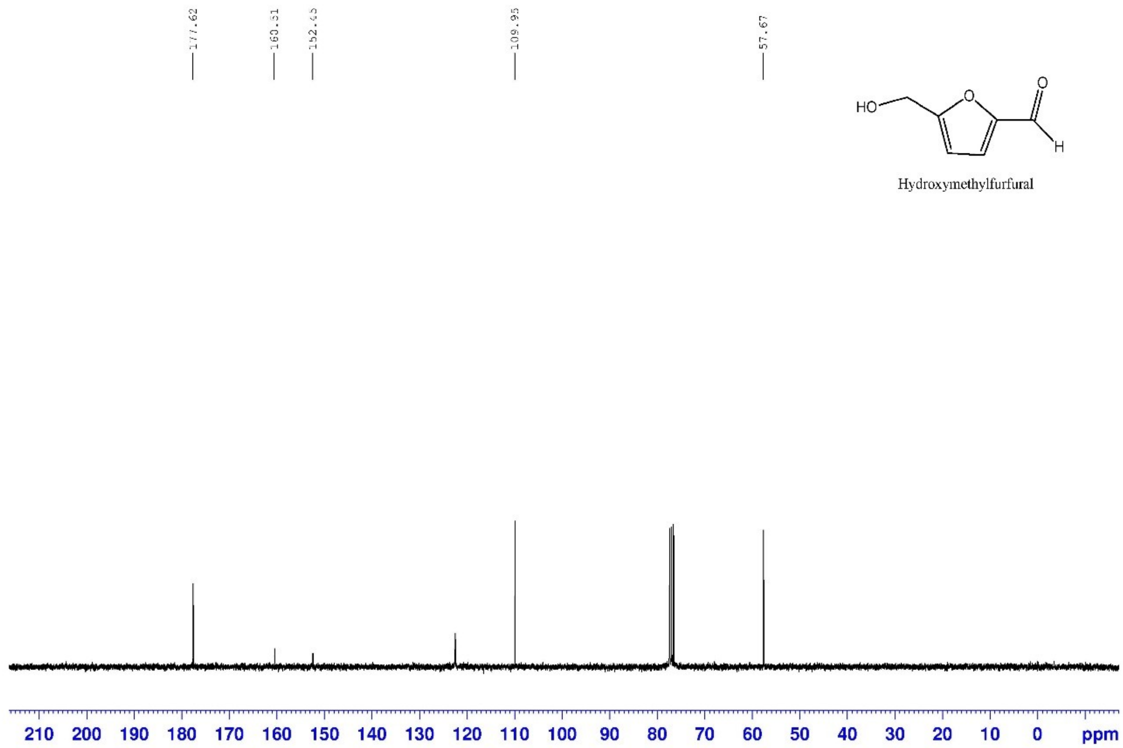
14. ^{1}H and ^{13}C NMR of the product

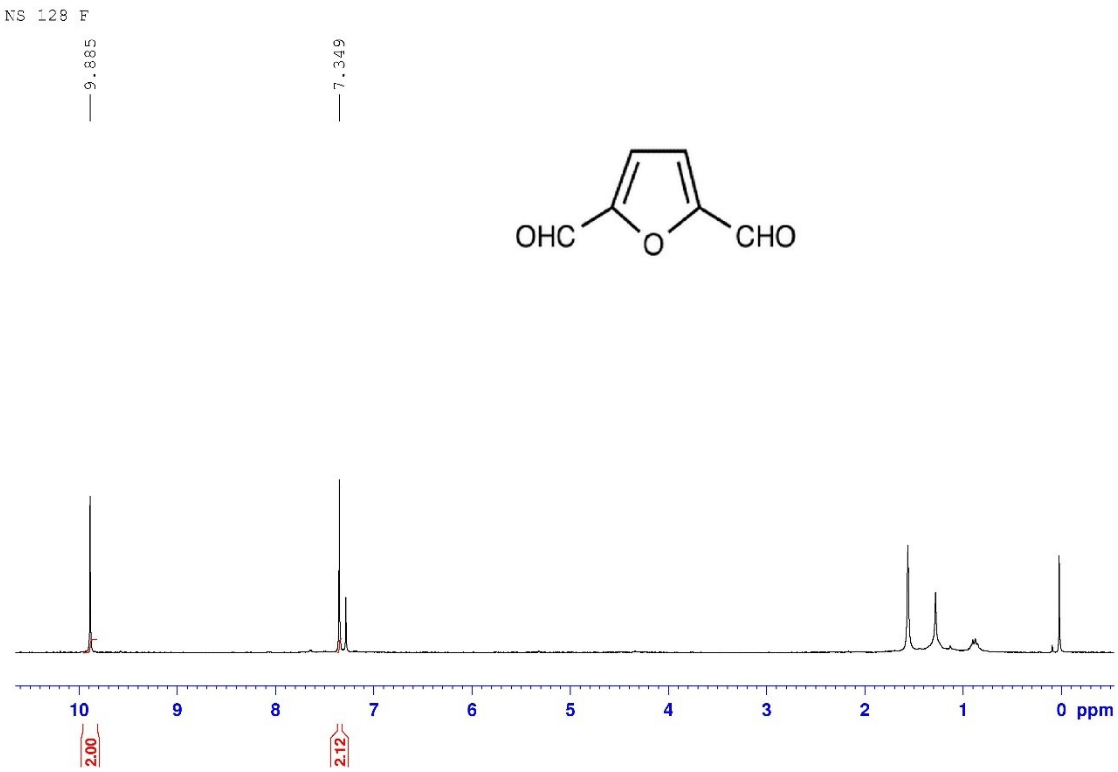


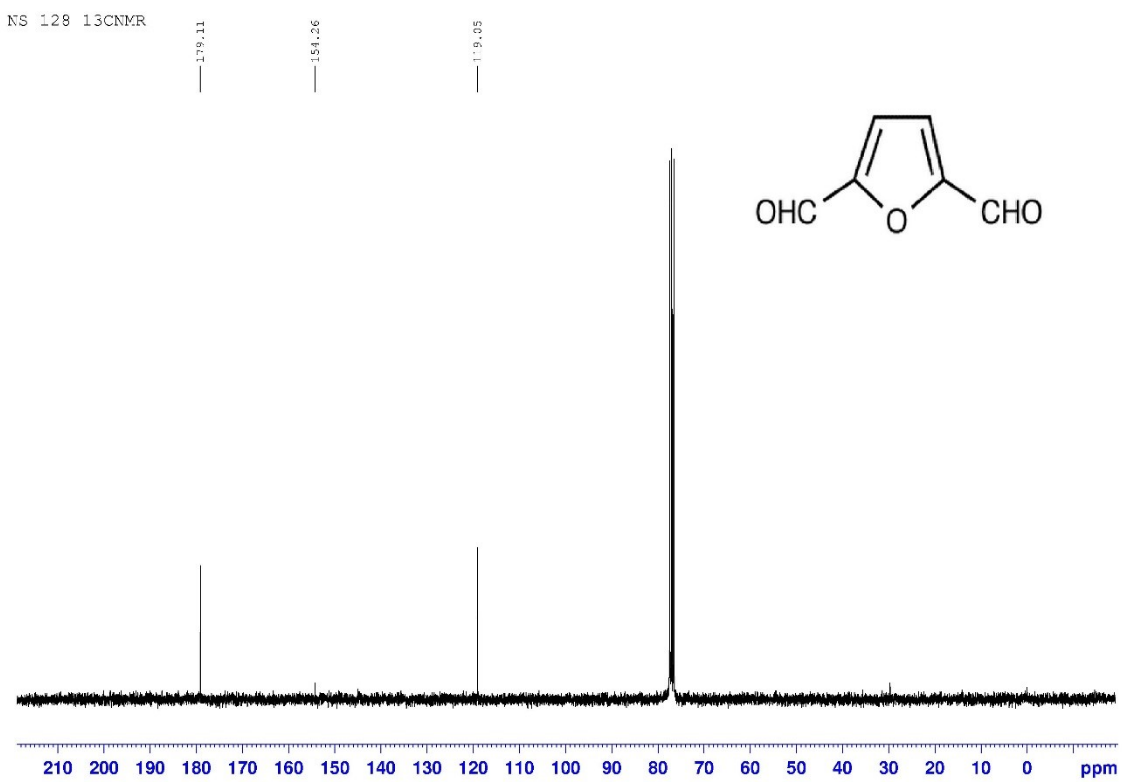

NS 124 13CNMR
177.79
148.04
121.00
112.54
O
H
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



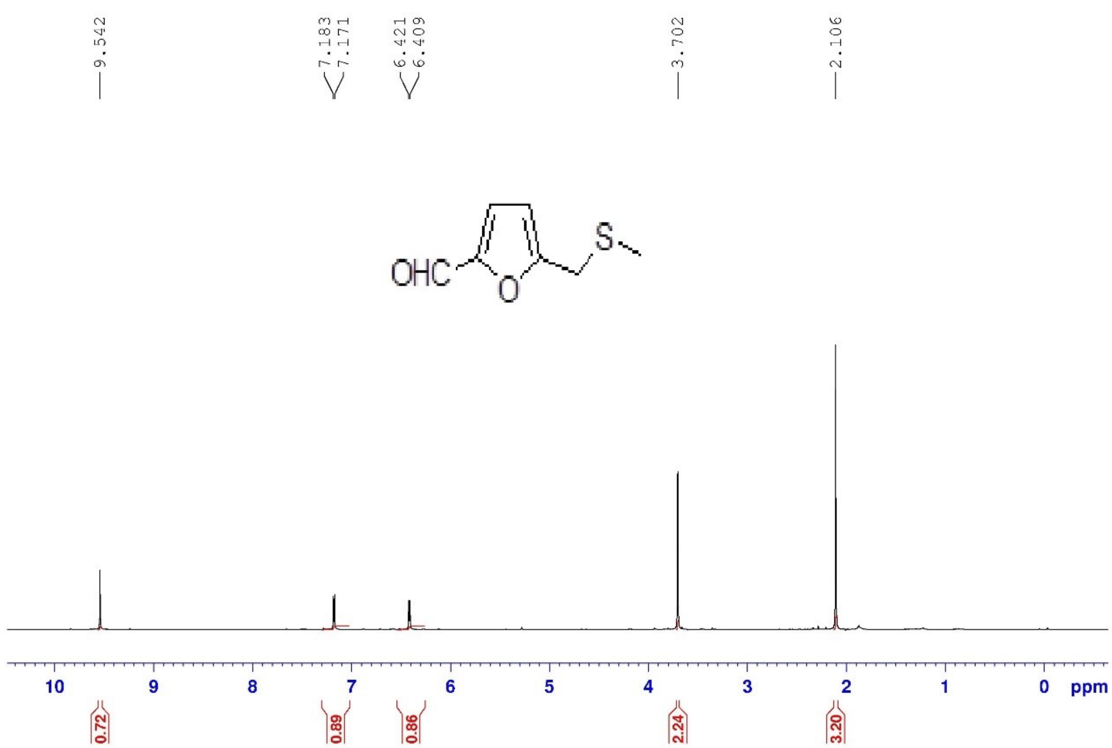
NS 125
9.609
7.234
7.222
6.537
6.526
4.736
2.467
HO
O
O
H
Hydroxymethylfurfural
10
9
8
7
6
5
4
3
2
1
0 ppm
0.89
1.01
1.00
2.30
1.23

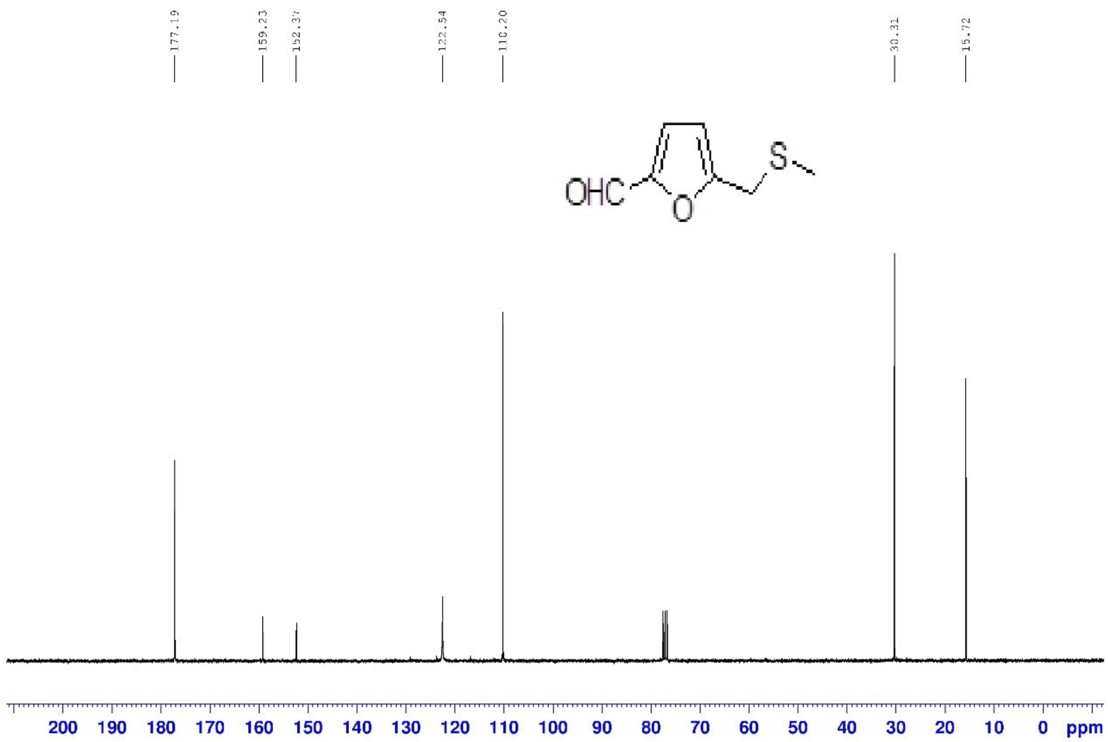

177.62
160.31
152.45
109.95
57.67
HO
O
O
H
Hydroxymethylfurfural
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

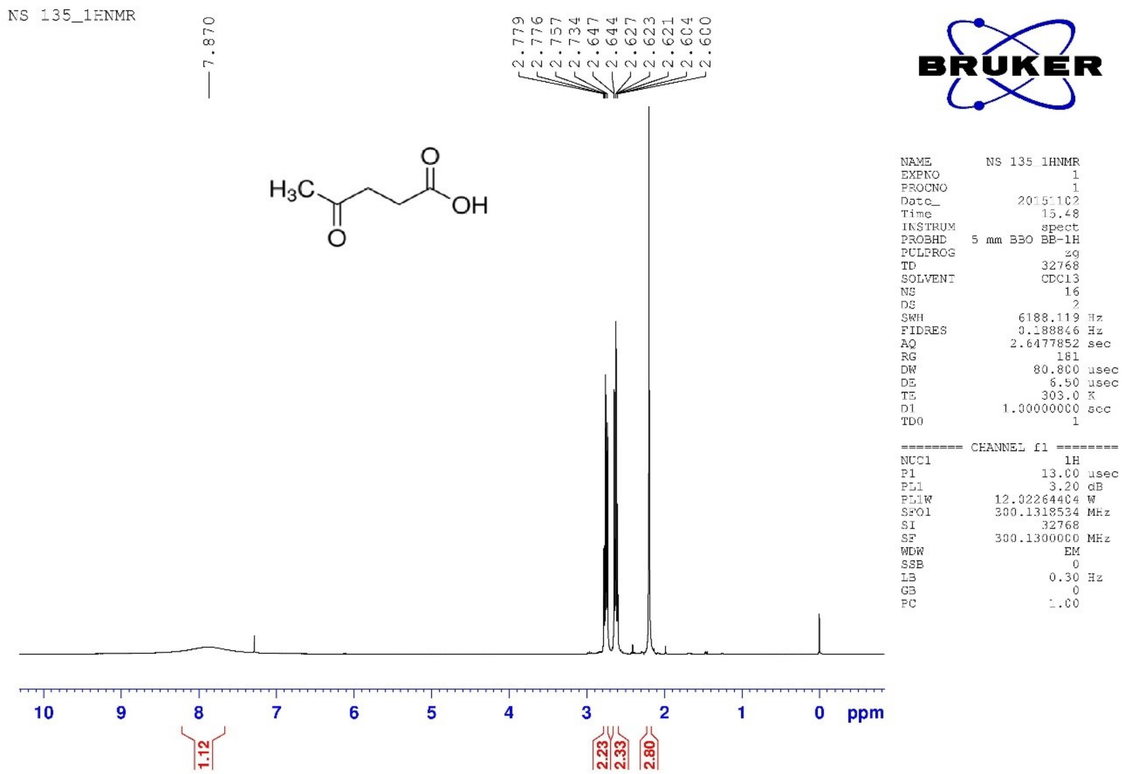

NS 128 F
9.885
7.349
OHC
O
CHO
10
9
8
7
6
5
4
3
2
1
0 ppm
2.00
2.12

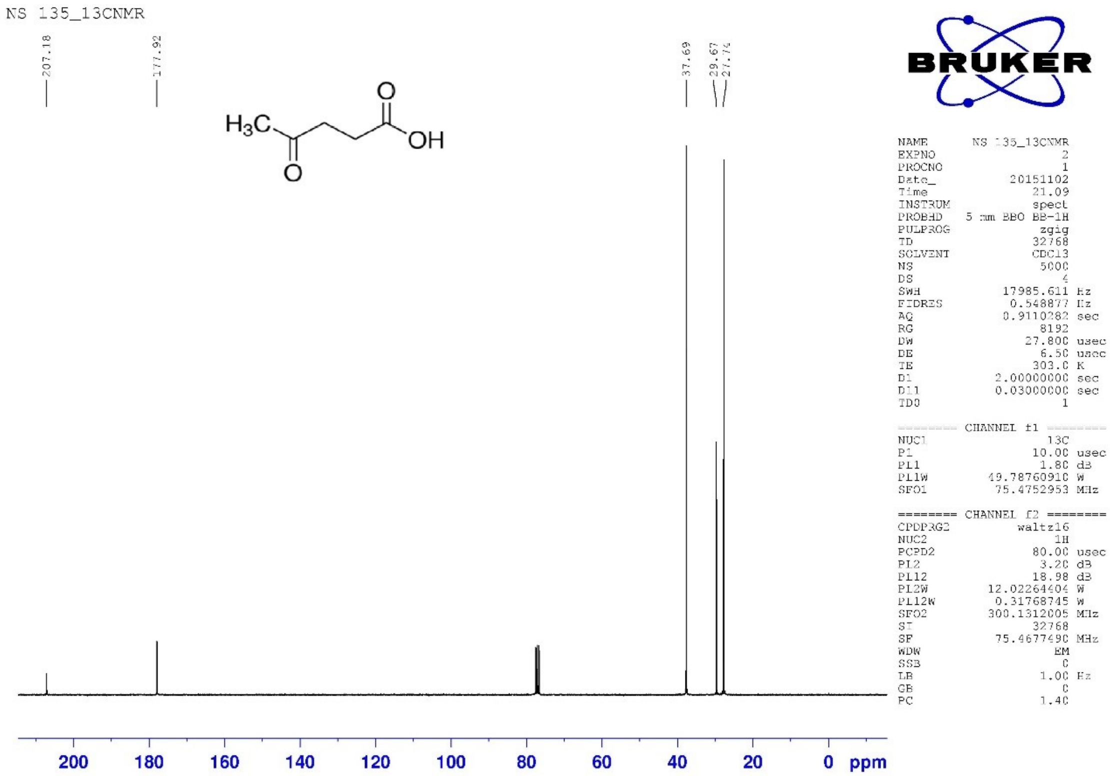


NS 128 13CNMR
179.11
154.26
1̈9.05
OHC
O
CHO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.542
7.183
7.171
6.421
6.409
3.702
2.106
OHC
O
S
10
9
8
7
6
5
4
3
2
1
0
ppm
0.72
0.89
0.86
2.24
3.20


177.19
159.23
152.37
122.54
110.20
30.31
15.72
OHC
O
S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


NS 135_1HNMR
7.870
2.779
2.776
2.757
2.734
2.647
2.644
2.627
2.623
2.621
2.604
2.600
BRUKER
H3C
O
O
OH
NAME NS 135 1HNMR
EXPNO 1
PROCNO 1
Date_ 20151102
Time 15.48
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.188846 Hz
AQ 2.6477852 sec
RG 181
DW 80.800 usec
DE 6.50 usec
TE 303.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 3.20 dB
PL1W 12.02264404 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0
ppm
1.12
2.23
2.33
2.80


NS 135_13CNMR
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177.92
37.69
29.67
27.74
H3C
O
O
OH
NAME NS 135_13CNMR
EXPNO 2
PROCNO 1
Date_ 20151102
Time 21.09
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgig
TD 32768
SOLVENT CDCl3
NS 5000
DS 4
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110282 sec
RG 8192
DW 27.800 usec
DE 6.50 usec
TE 303.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 1.80 dB
PL1W 49.78760910 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 3.20 dB
PL12 18.98 dB
PL2W 12.02264404 W
PL12W 0.31768745 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm