Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2019

Supplementary Information

Visible light mediated and water-assisted selective hydrodeoxygenation of lignin derived guaiacol to cyclohexanol

Sanny Verma[a], Mallikarjuna N. Nadagouda[b] and Rajender S. Varma[c*]

[a]Oak Ridge Institute for Science and Education, P. O. Box 117, Oak Ridge TN, 37831, USA.

[b]Department of Mechanical and Materials Engineering, Wright State University, Dayton, Ohio 45324, United States.

[c]Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacky University, Šlechtitelů 27, 78371 Olomouc. E-mail: varma.rajender@epa.gov

1. Synthesis of materials

- **a) Synthesis of CN_X**
- **b) Synthesis of $AgPd/Fe@CN_X$ catalyst**
- **c) Hydrodeoxygenation of lignin derived guaiacol**

2. XRD analysis of $AgPd/Fe@CN_X$ as compared with JCPDS standards (S3)

3. XPS full spectrum of carbon nitride (S4)

4. XPS full spectrum of $AgPd/Fe@CN_X$ (S5)

5. Detailed XPS analysis for carbon nitride (CN_X) catalyst. a) C1s spectra. b) N1s spectra (S6)

6. Detailed XPS analysis for $AgPd/Fe@CN_X$ catalyst. a) C1s spectra. b) N1s spectra (S7)

7. Detailed XPS analysis for $AgPd/Fe@CN_X$ catalyst. c) O1s spectra. d) Ag3d spectra (S8)

8. Detailed XPS analysis for $AgPd/Fe@CN_X$ catalyst. e) Pd3d spectra. f) Fe2p spectra (S9)

9. Recycling of $AgPd/Fe@CN_X$ catalyst (S5)

10. FT-IR analysis of CN_X and $AgPd/Fe@CN_X$ catalyst (S6)

11. GC-MS monitoring results

12. ^{1}H and ^{13}C NMR of the product

Chemicals and characterization. Chitosan, sodium borohydride, $Pd(NO_3)_2$, $AgNO_3$, $HAuCl_4$, $CuSO_4$, $CoCl_2.6H_2O$, $PtCl_2$, $FeSO_4$, Formic acid (>99%), and all organic solvents and guaiacol were received from Sigma-Aldrich chemicals. For each experiment, deionized water (18.2 mS conductivity) was used. Analytical thin-layer chromatography (TLC) was performed using analytical chromatography silica gel 60 F254 pre-coated plates (0.25 mm). A theta-theta diffractometer (PANalytical X'Pert Pro, PANalytical B.V.; The Netherlands) with a copper X-ray tube was used to identify crystalline phases of the synthesized solids. The XRD tube was operated at 45 keV and 40 mA for the analyses. Scans were performed over a 2-theta range between 2° to 90° with a step of 0.02° and a one-second count time at each step. Pattern analysis was performed following ASTM procedures using computer software (Materials Data, Incorporated. Jade+ v.5-8 XRD Processing Software; Livermore, California) with reference to the 2002 ICDD PDF-2 data files (International Center for Diffraction Data, Incorporated; Newtown Square, PA). The amorphous morphology and crystallinity of experimentally developed solid samples were investigated using A JEOL (JEM-2010F) high resolution-transmittance electron microscope (HR-TEM) with field transmission of 200 kV. To prepare the samples for HR-TEM, the copper solid samples were suspended in water and sonicated for 30 min, then fixed on a Lacy Carbon-Copper grid (LC300-Cu, EMS) by the drop-casting method. The TEM sample was prepared by dispersing dry powder of catalyst in water. For scanning electron microscopy (SEM), gold sputter coating was carried out on desired samples at a pressure ranging in between 1 and 0.1 Pa. The Sample was loaded in the chamber of Philip XL30 SEM and recorded by operating at 10-2 to 10-3 Pa with EHT 15.00 kV with 300 V collector bias. Sonication (Power Sonic 405) and centrifugation (Gyrogen 1236 MG) were used for re-dispersing and separating of the catalysts, respectively. X-ray photoelectron spectroscopy (XPS) was used to identify the oxidation states of metals. GC-MS analysis was conducted using an Shimadzu technology GCMS-QP2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard) and an in-built MS 5975C VL MSD system with triple axis detector (Heater=290C, Pressure (He)= 7.02 psi, Total Flow= 23.6 mL/min; injection volume=0.5ul, syringe size= 5.0 uL).

1. Synthesis of materials

a) Synthesis of CN_X

The nitrogen enriched carbon nitride (CN_X) was synthesized by the calcination of chitosan (5.0 g, 4 h) with heating rate of 50 °C/min in a dynamic nitrogen flow of 20 mL/min using silica crucible in a furnace (KSL-1100X) operating at 600 ^{o}C.

b) Synthesis of AgPd/Fe@CN_X catalyst

1.0 g CNx support was first dispersed in 1000 ml water and sonicated for 3 h. Then the solution of $FeSO_4$ (500 mg in 100 ml) was added dropwise at room temperature (RT). Aqueous solution of $AgNO_3$ (0.5 mM, in 25 ml water) was added to colloidal solution and stirring for 10 min. Then aqueous solution of $Pd(NO_3)_2$ (0.5 mM, in 25 ml water) was added to the dispersed solution at RT and reaction mixture was further stirring for 3 h. 1.0g Sodium borohydride ($NaBH_4$) was added, in portions, at 50 °C to reduce the iron sulfate, Ag (I) and Pd (II) to magnetic ferrites, Ag(0) and Pd(0), respectively. This reaction mixture was stirred for next 12 h. The ensuing black colored solid was isolated as AgPd/Fe@CN_X using an external magnet, washed with water and methanol; finally dried at 60 °C in vacuum. The obtained AgPd/Fe@CN_X composite powder was further analyzed by various instrumental techniques such as X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray

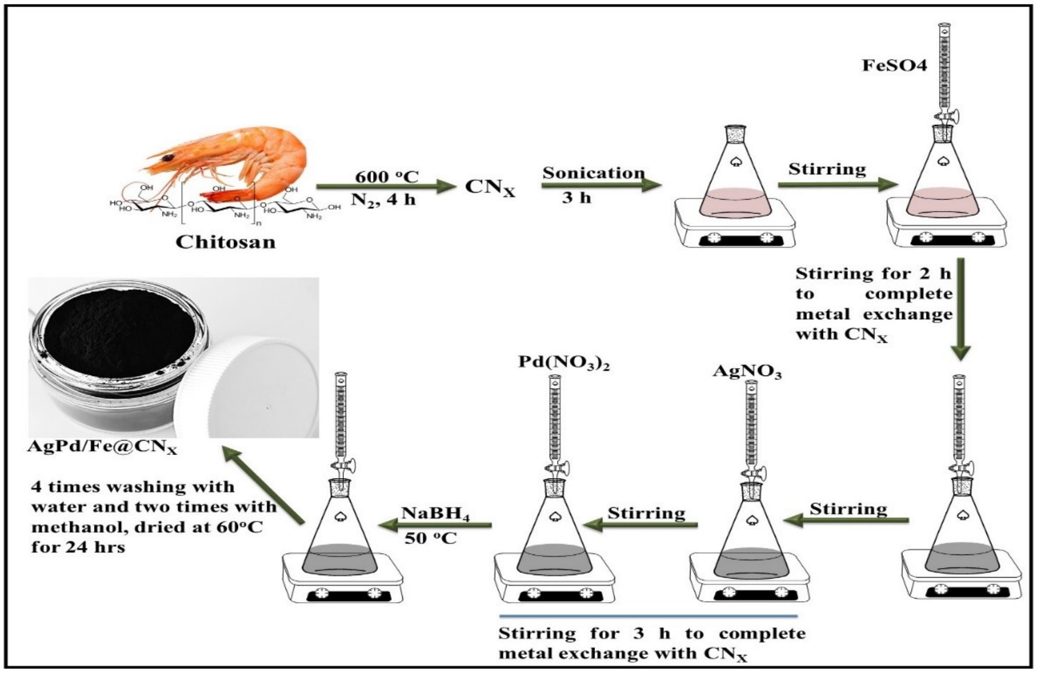


Figure S1: Pictorial representation of the synthesis of AgPd/Fe@CN_X

photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area analysis and Inductive coupled plasma atomic emission spectroscopy (ICP-AES).

c) Screening of AgPd/Fe@CN$_X$ catalyst for upgrading of guaiacol

Guaiacol (1.0 mmol), catalyst (20 mg), H_2O (1.0 mL), formic acid (5.0 mmol) and internal standard n-hexadecane (5.0 mmol) were placed in a reaction tube (10 mL) which was sealed with rubber septa. The reaction mixture was exposed to visible light using 20 W domestic bulb at ambient temperature and pressure. During the reaction, the temperature was monitored carefully to ensure that a 30 °C temperature was maintained. Reaction was monitored by TLC (ethyl acetate: hexane = 10:90; Rf = 0.40). After completion of reaction, 10 mL dichloromethane (DCM) was added and the catalyst was separated using an external magnet. DCM and water layer were separated with the help of separating funnel. DCM solvent was evaporated from the extracted solution and analyzed by GC-MS and NMR.

Figure S2. Pictorial representation of the experimental set-up for transformation of guaiacol

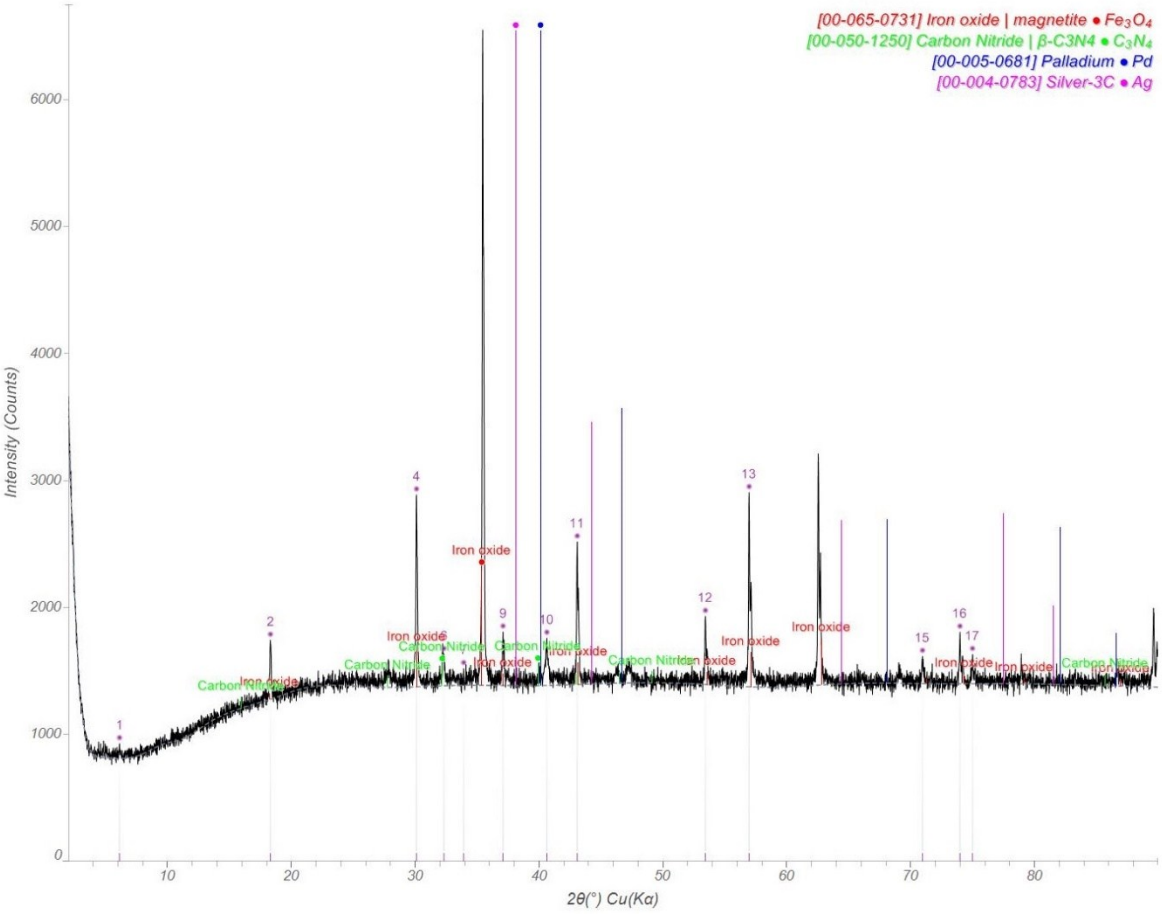


Figure S3. XRD analysis of AgPd/Fe@CN_X as compared with JCPDS standards

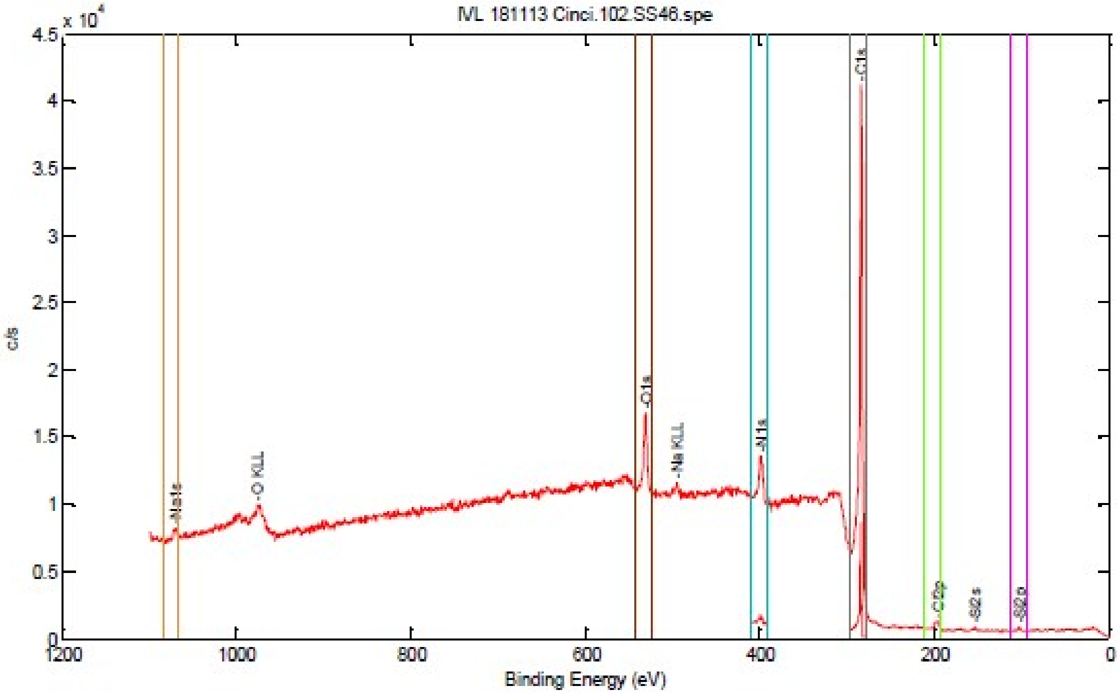


Figure S4. XPS full spectrum of carbon nitride (CN_X)

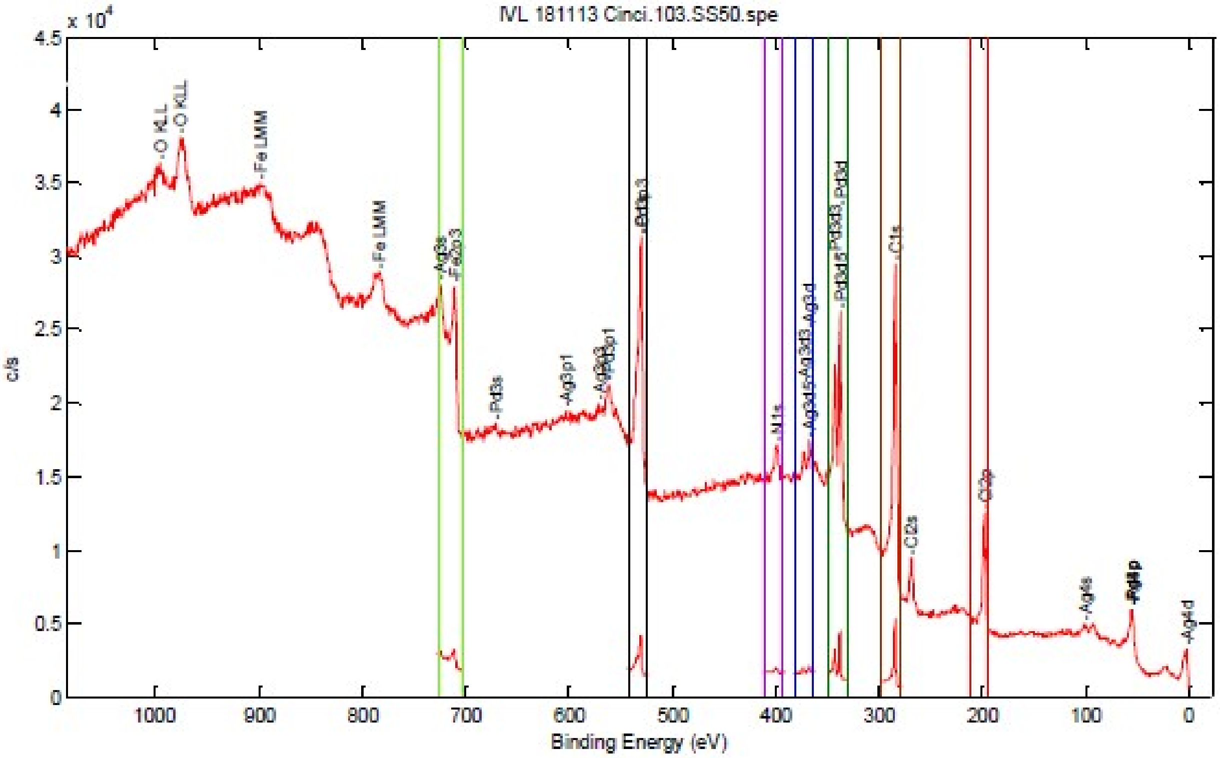


Figure S5. XPS full spectrum of AgPd/Fe@CN_X

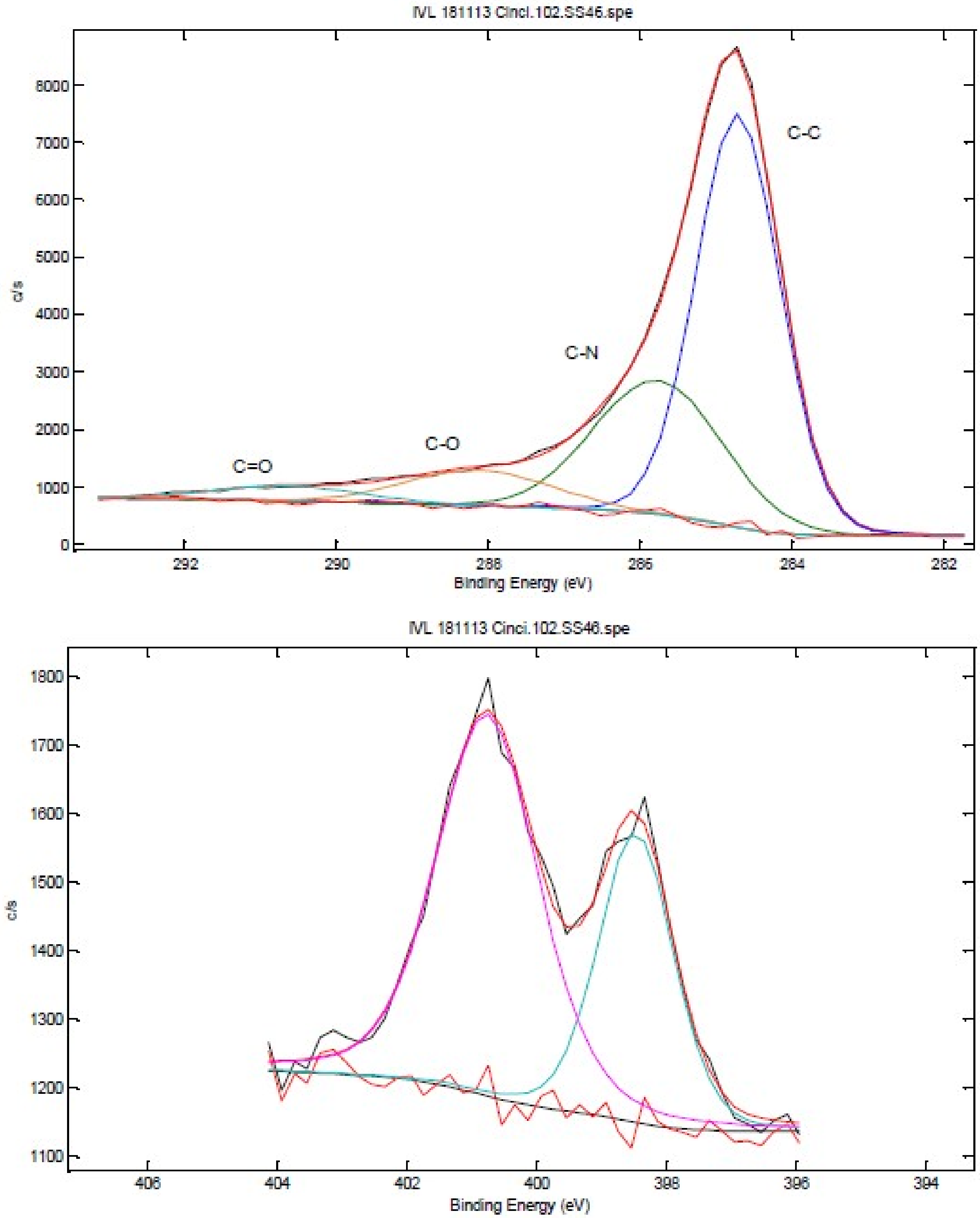


Figure S6. Detailed XPS analysis for carbon nitride (CN_X) catalyst. a) C1s spectra. b) N1s spectra.

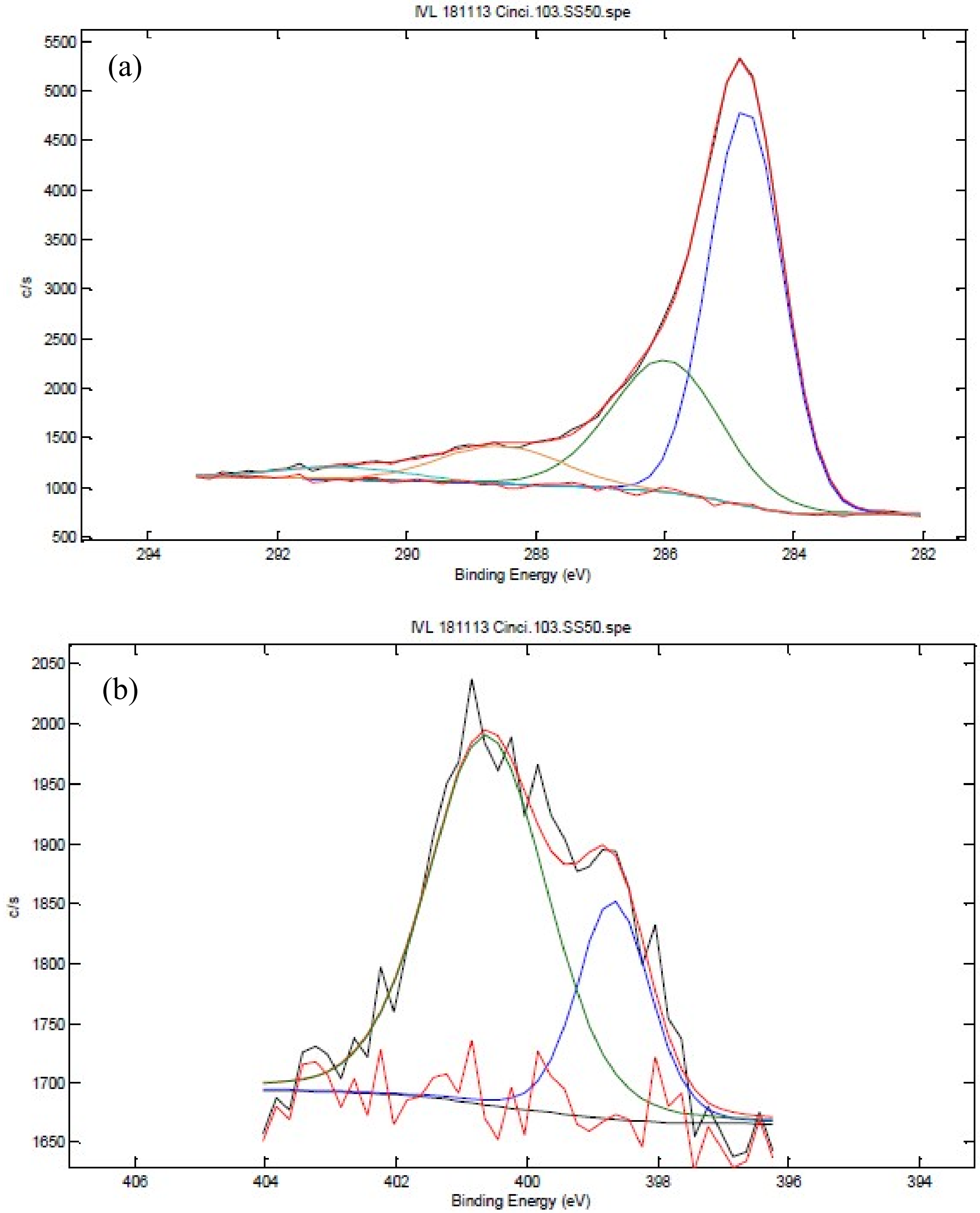


Figure S7. Detailed XPS analysis for AgPd/Fe@CN_X catalyst. a) C1s spectra. b) N1s spectra.

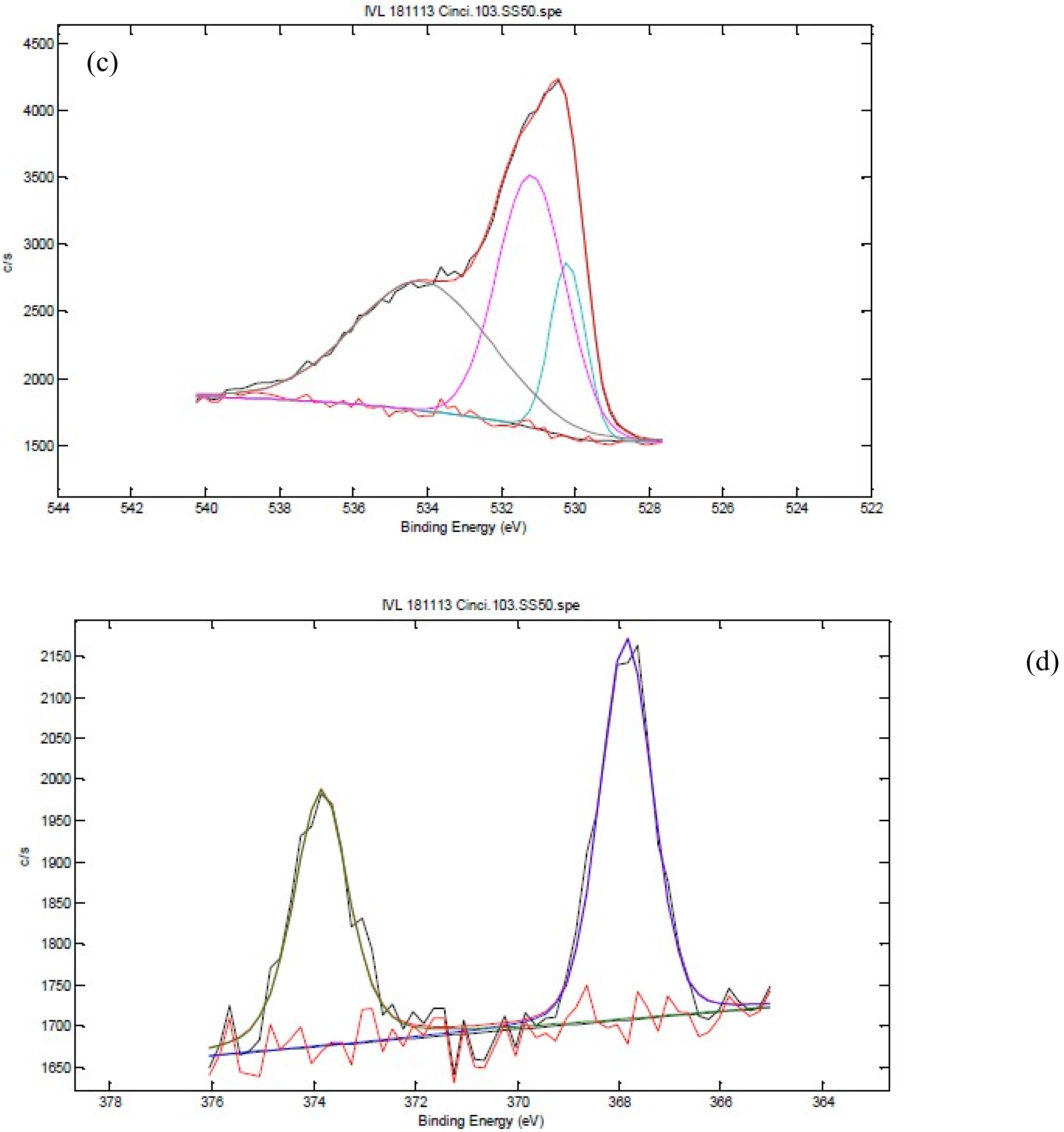
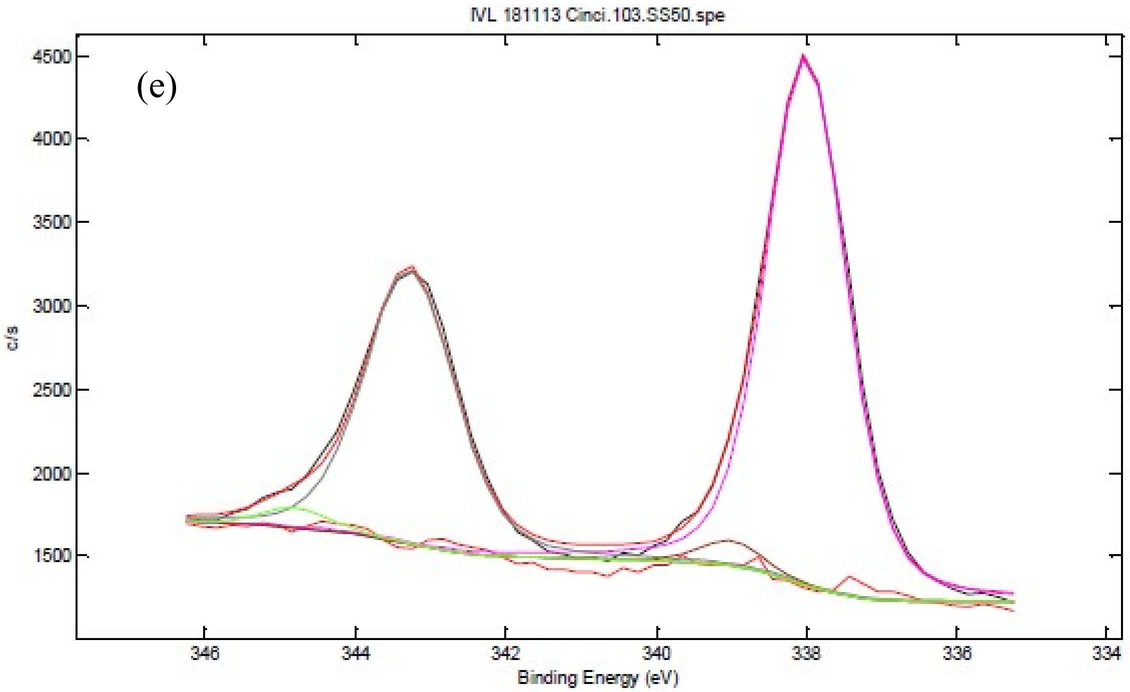
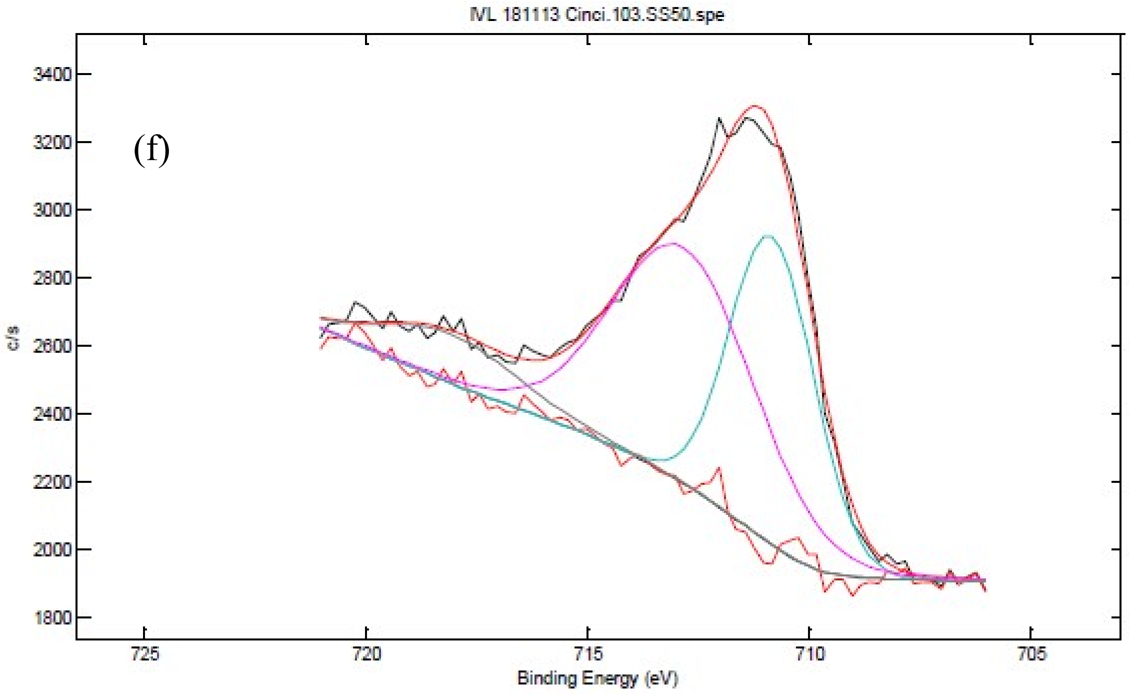


Figure S8. Detailed XPS analysis for AgPd/Fe@CN$_X$ catalyst. c) O1s spectra. d) Ag3d spectra


IVL 181113 Cinci.103.SS50.spe
(e)
4500
4000
3500
3000
2500
2000
1500
c/s
346
344
342
340
338
336
334
Binding Energy (eV)


IVL 181113 Cinci.103.SS50.spe
(f)
3400
3200
3000
2800
2600
2400
2200
2000
1800
c/s
725
720
715
710
705
Binding Energy (eV)

(e)

Figure S9. Detailed XPS analysis for AgPd/Fe@CNX catalyst. e) Pd3d spectra. f) Fe2p spectra

9. Recycling of AgPd/Fe@CN$_X$ catalyst:

After each reaction, the catalyst AgPd/Fe@CN$_X$ was recovered using an external magnet, washed with water followed by methanol and dried under vacuum at 60 °C. The recovered catalyst was then used for a new reaction using a fresh substrate. It was observed that the catalyst remained active after the reaction; could be recycled and reused over 6 times without much loss in activity.

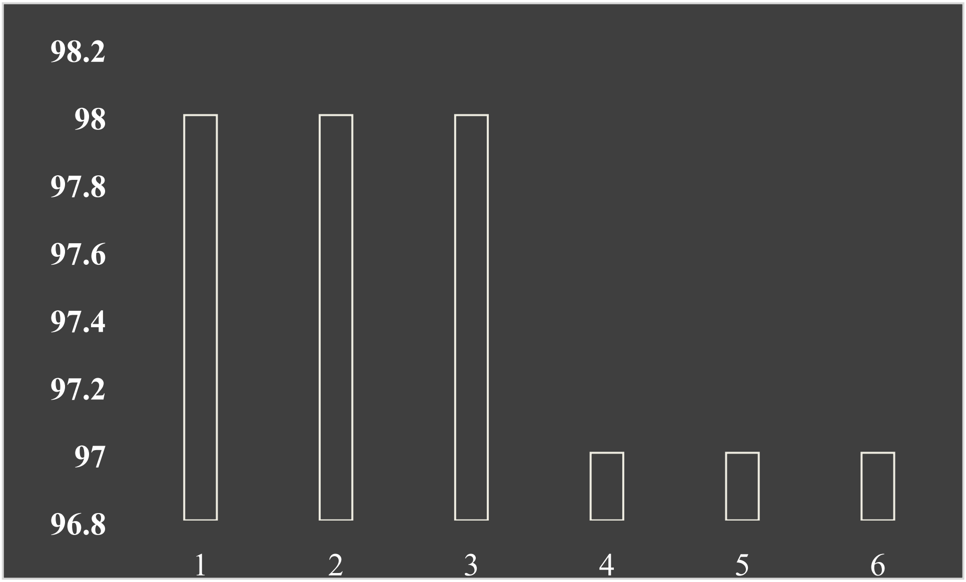


Figure S10: Recycling of AgPd/Fe@CN$_X$ catalyst

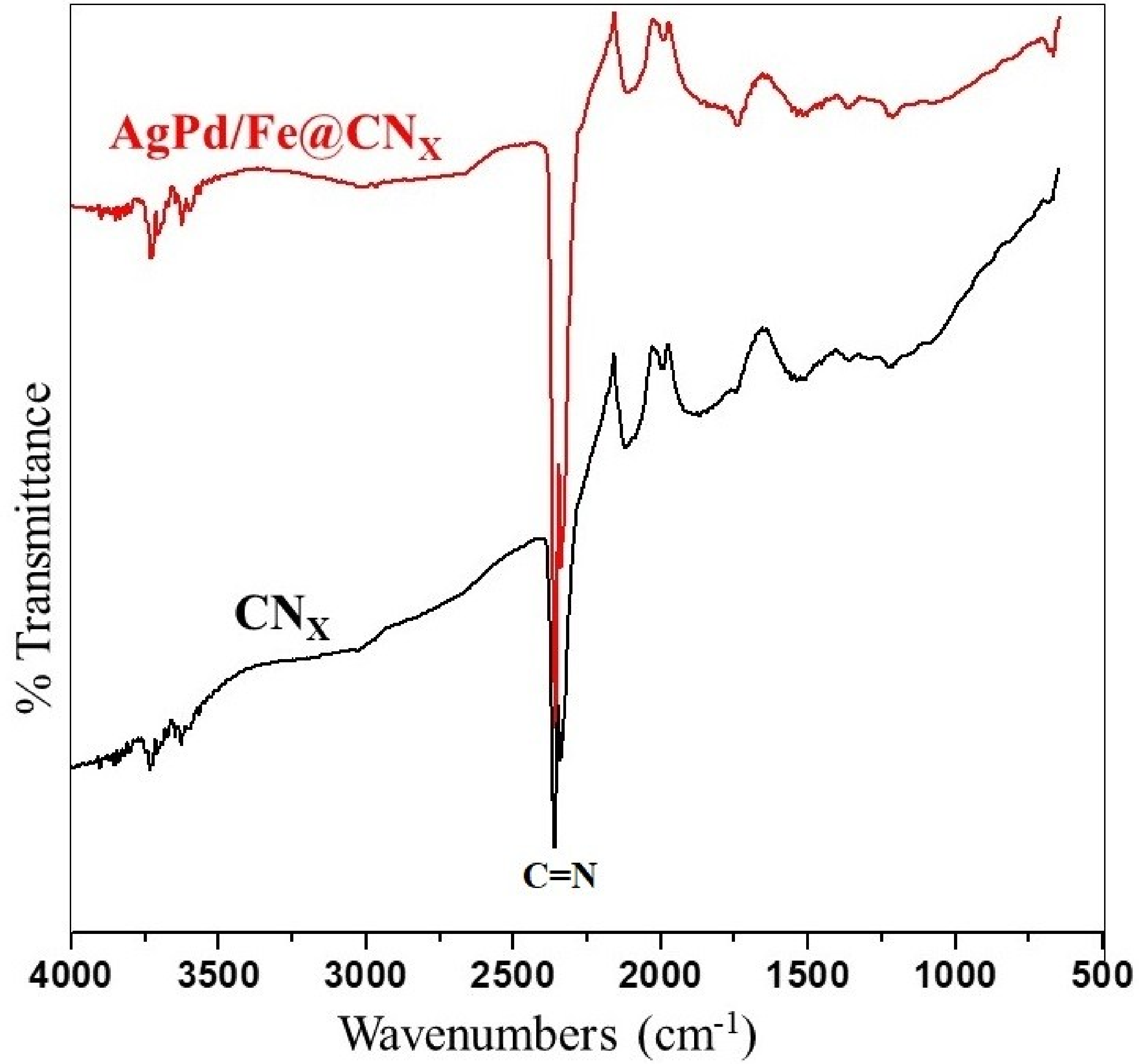
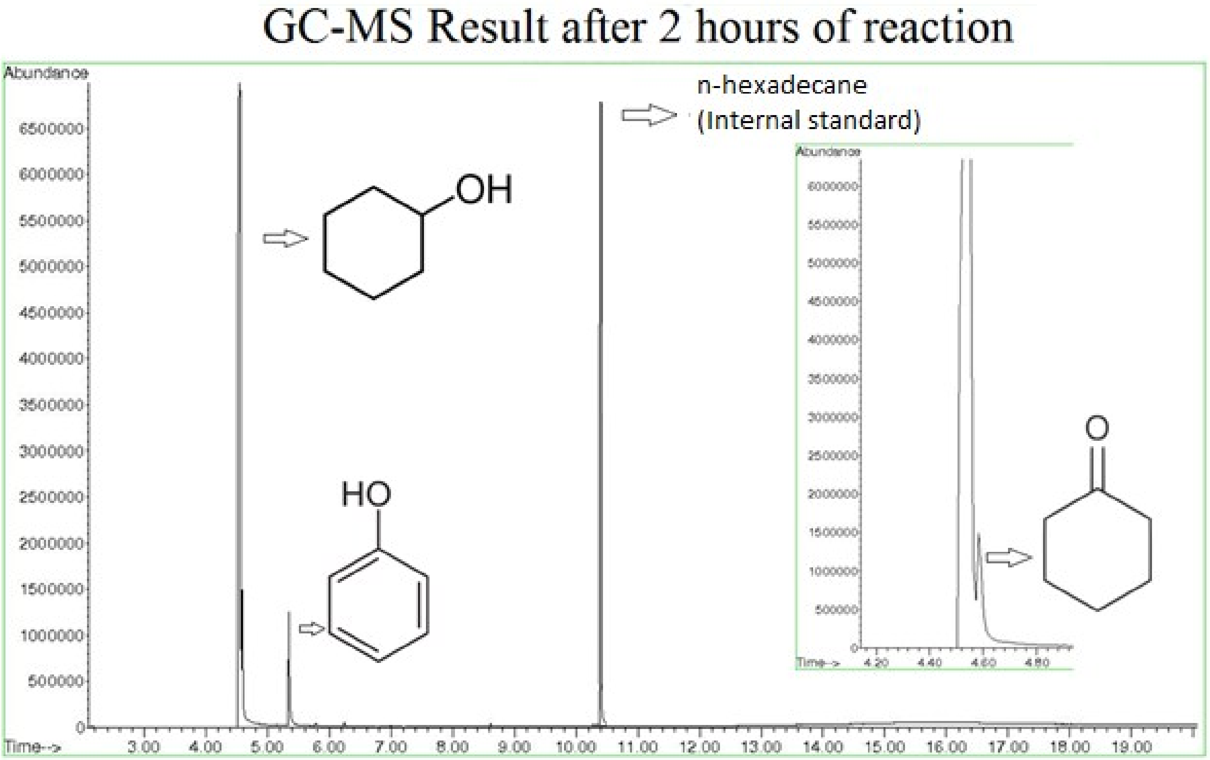


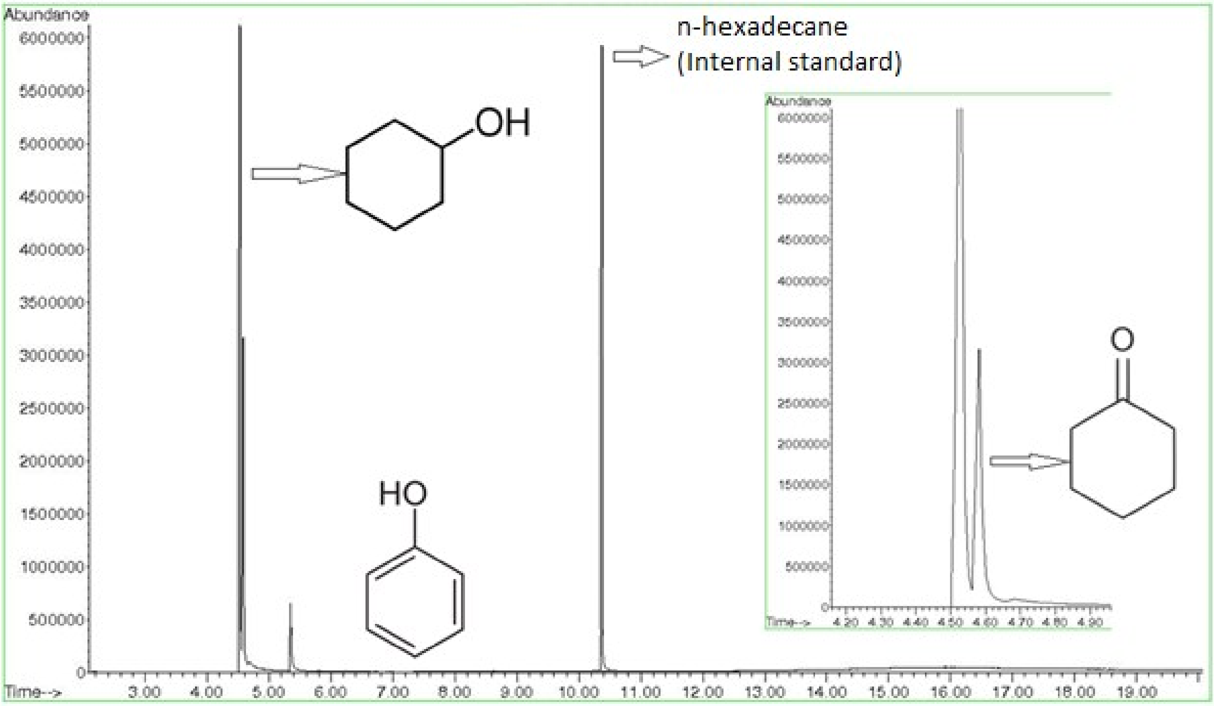
Figure S10. FT-IR of CN$_X$ and AgPd/Fe@CN$_X$ catalyst

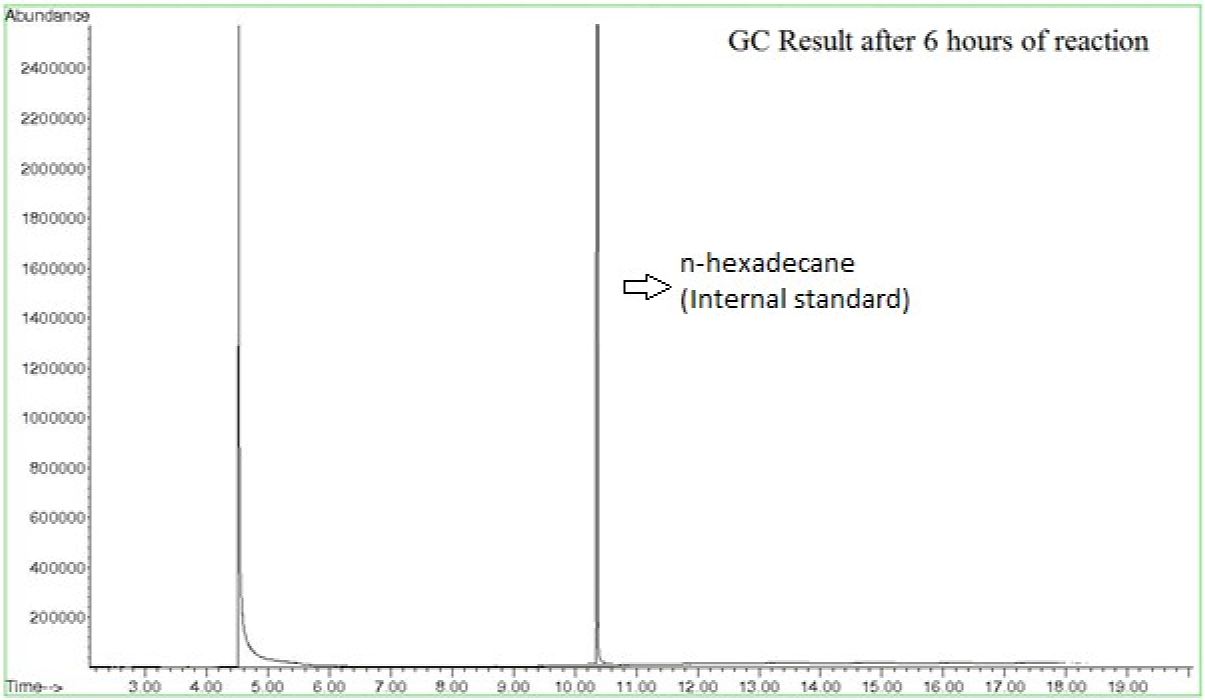
GC-MS monitoring results

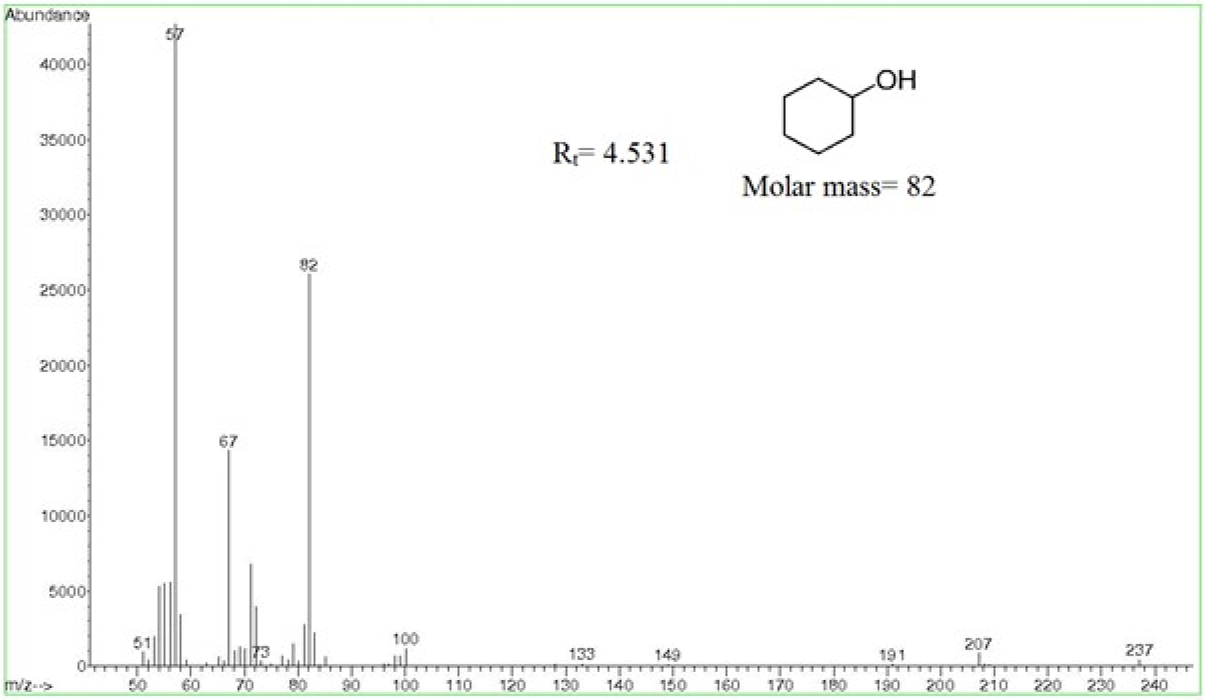


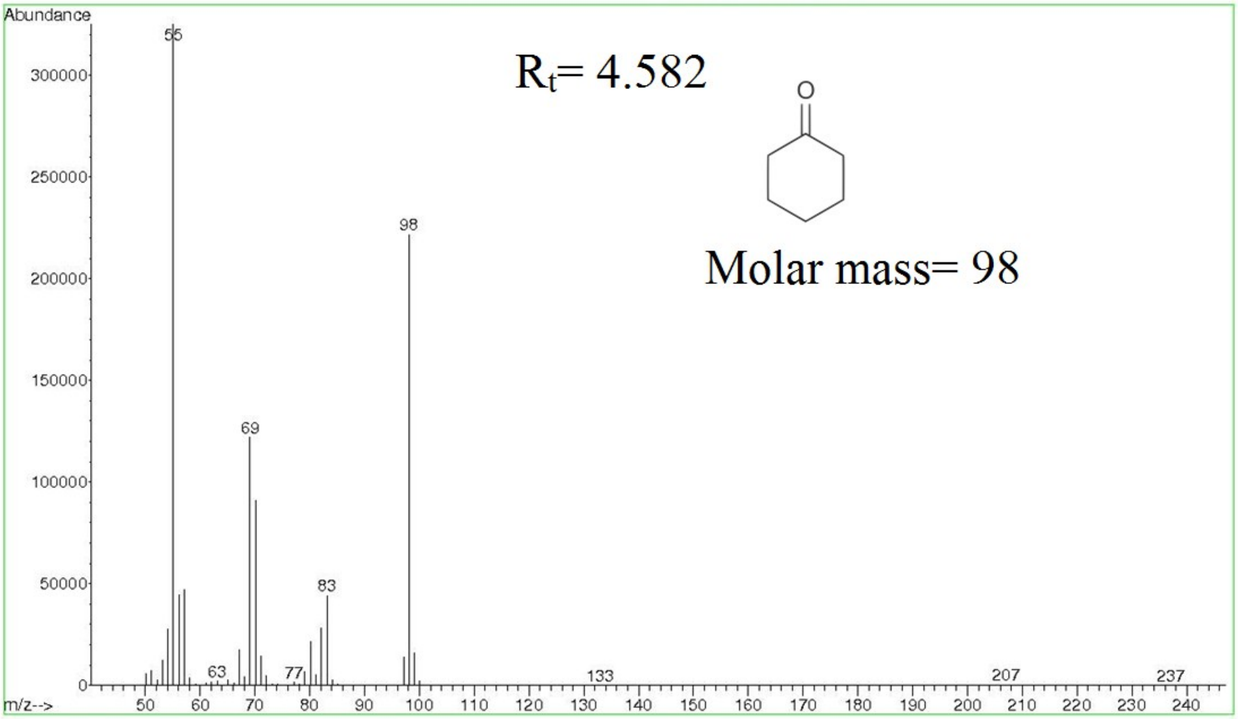
GC-MS Result after 2 hours of reaction

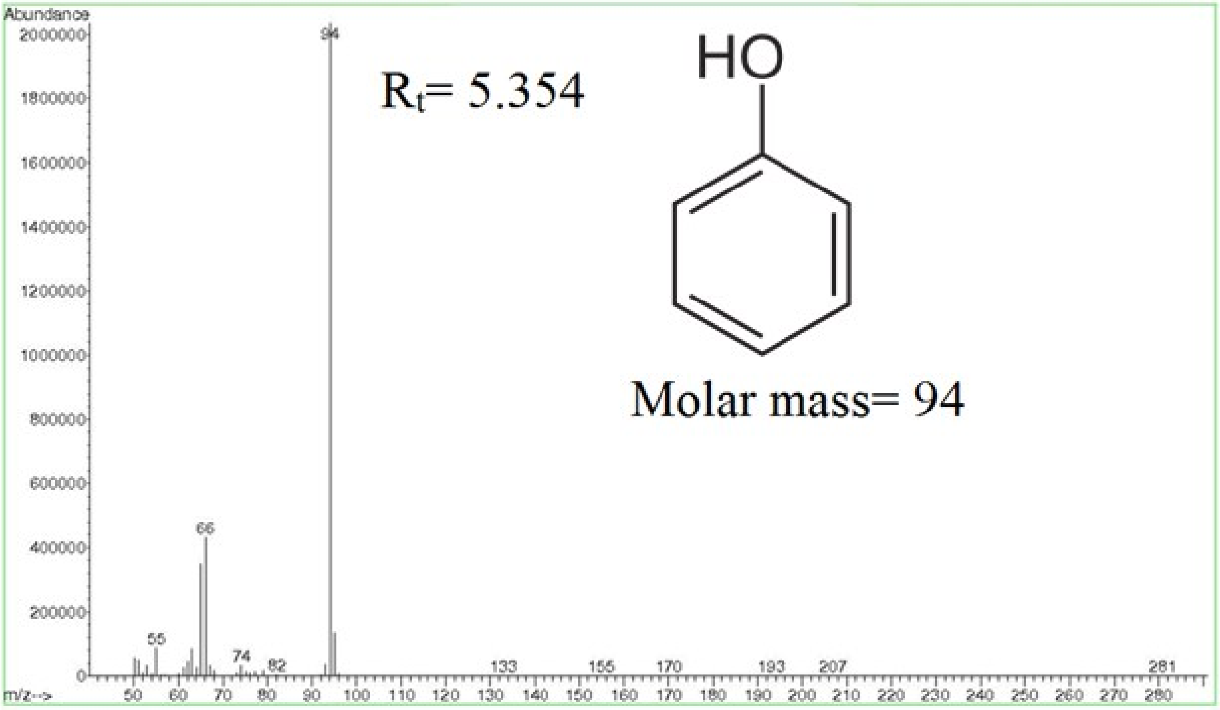
GC-MS Result after 4 hours of reaction



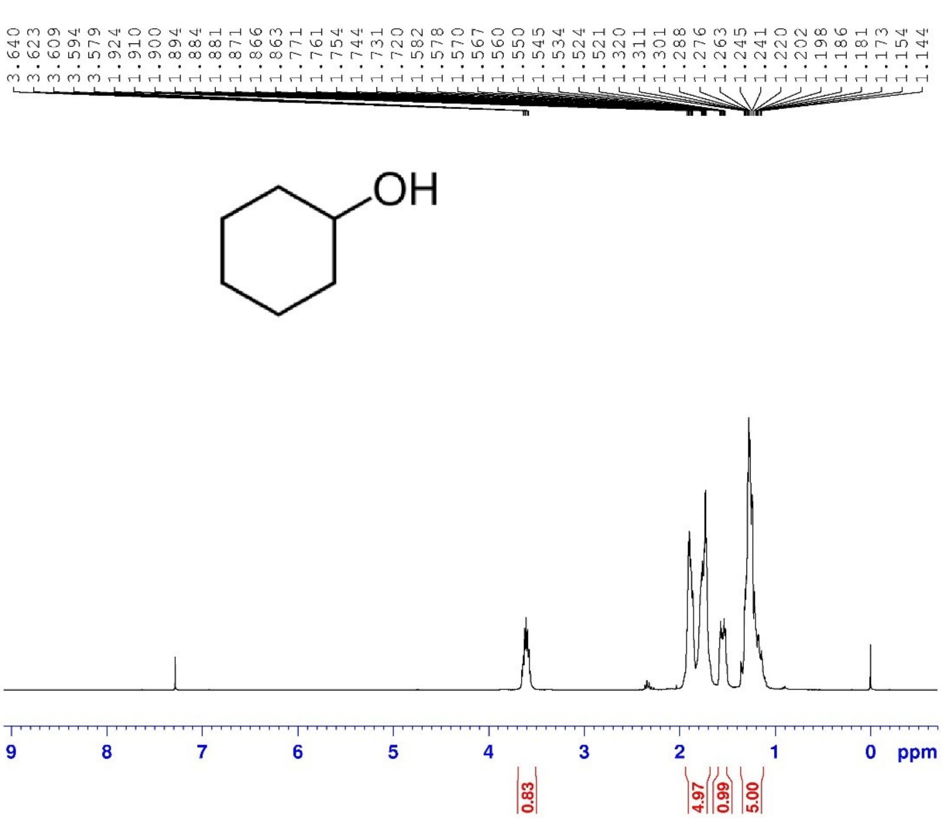

GC Result after 6 hours of reaction
Abundance
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
Time-->
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
16.00
17.00
18.00
19.00
n-hexadecane
(Internal standard)


Abundance
40000
35000
30000
25000
20000
15000
10000
5000
0
m/z-->
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
57
82
67
51
73
100
133
149
191
207
237
Rt= 4.531
OH
Molar mass= 82


Abundance
300000
250000
200000
150000
100000
50000
0
m/z-->
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
55
98
69
83
63
77
133
207
237
R_t= 4.582
O
Molar mass= 98

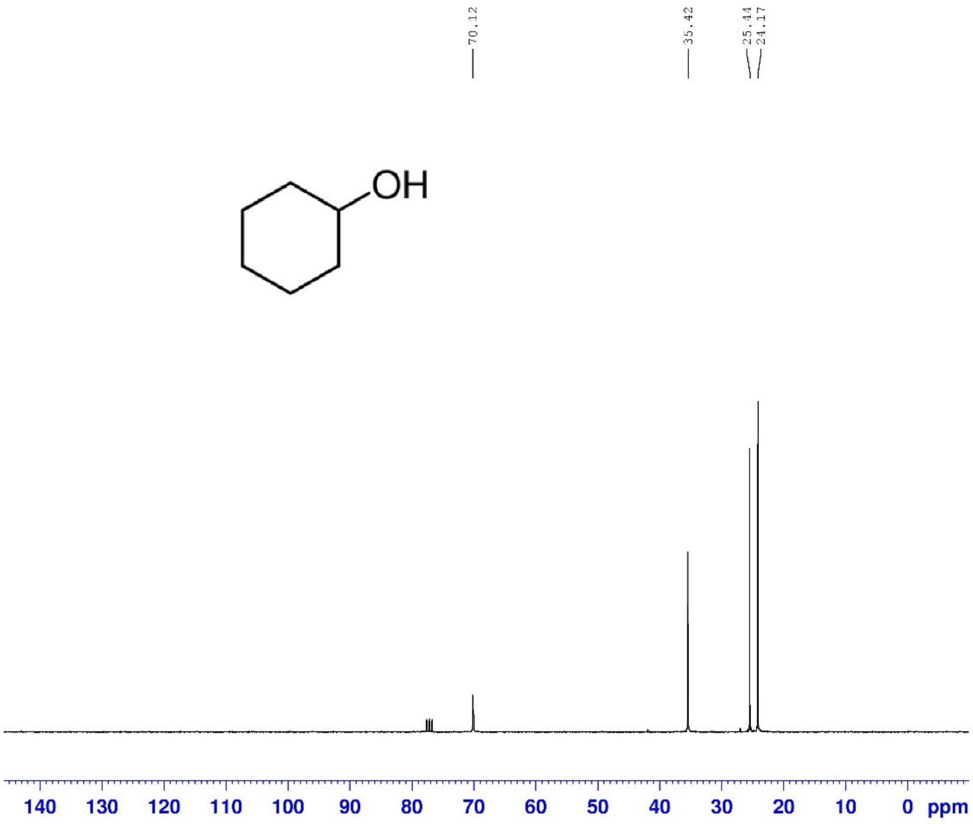

Abundance
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
m/z-->
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
94
66
55
74
82
133
155
170
193
207
281
R_t= 5.354
HO
Molar mass= 94

^{1}NMR and ^{13}CNMR



```
NAME              SS-110_P
EXPNO                    4
PROCNO                   1
Date_             20180206
Time                 15.24
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                   300.0 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
```



```
NAME              SS-110_P
EXPNO                    3
PROCNO                   1
Date_             20180206
Time                 13.49
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zgig
TD                   32768
SOLVENT              CDCl3
NS                    1024
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                   298.0 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
```