Preparation and characterization of WO_3 bonded imidazolium sulfonic acid chloride as novel and green ionic liquid catalyst for the synthesis of adipic acid

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SUPPORTING INFORMATION

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Experimental section

All commercially available reagents were used without purification unless otherwise noted. All the yields refer to isolated yields after crystallization. Melting points were determined on a Buchi melting point apparatus and are uncorrected. IR spectra were recorded on Bruker 3000 Hyperion Microscope with Vertex 80 FTIR System. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE III 500 MHz (AV 500) multi nuclei solution NMR Spectrometer, TMS as internal reference; chemical shifts (δ scale) are reported in parts per million (ppm). ^{1}H NMR Spectra are reported in the order: multiplicity, coupling constant (J value) in hertz (Hz) and no of protons; signals were characterized as s (singlet), d (doublet), t (triplet), m (multiplet). Elemental analyses were carried out using Flash 2000 Thermo Scientific instrument. All ^{1}H NMR spectra were recorded on in CD_3OD at 500 Hz on Bruker spectrometer.

Oxidation of cyclohexene to adipic acid

An amount of 1.01 ml (10 mmol) of cyclohexene was dissolved in 10 ml of acetonitrile. This was followed by addition of 50 mg of the catalyst. Subsequently, 2.8 ml (120 mmol) of H_2O_2 (30% aq. solution) was slowly added to the above reaction mixture over a period of 30 minutes and stirred at 90 °C in an oil bath fitted to a condenser till the complete conversion was achieved as confirmed by TLC. The catalyst was then recovered under hot conditions from the reaction mixture through filtration. The product (adipic acid) thus formed in the reaction mixture was then cooled to room temperature to obtain the white solid precipitate and recrystallized with methanol. The obtained solid product was characterized by melting point, ^{1}H NMR, ^{13}C NMR, FTIR, and Elemental analyses.

Oxidation of cyclohexanol to adipic acid

An amount of 1.04 ml (10 mmol) of cyclohexanol was dissolved in 10 ml of acetonitrile. This was followed by addition of 50 mg of the catalyst. Subsequently, 2.8 ml (120 mmol) of H_2O_2 (30% aq. solution) was slowly added to the above reaction mixture over a period of 30 minutes and stirred at 90 °C in an oil bath fitted to a condenser till the complete conversion was achieved as confirmed by TLC. The catalyst was then recovered under hot conditions from the reaction mixture through filtration. The product thus formed in the reaction mixture was then cooled to room temperature to obtain the white solid precipitate and recrystallized with methanol. The obtained solid product was characterized by melting point, ^{1}H NMR, ^{13}C NMR, FTIR, and Elemental analyses.

Oxidation of cyclohexanone to adipic acid

An amount of 1.03 ml (10 mmol) of cyclohexanone was dissolved in 10 ml of acetonitrile. This was followed by addition of 50 mg of the catalyst. Subsequently, 2.8 ml (120 mmol) of H_2O_2 (30% aq. solution) was slowly added to the above reaction mixture over a period of 30 minutes and stirred at 90 °C in an oil bath fitted to a condenser till the complete conversion was achieved as confirmed by TLC. The catalyst was then recovered under hot conditions from the reaction mixture through filtration. The product thus formed in the reaction mixture was then cooled to room temperature to obtain the white solid precipitate and recrystallized with methanol. The obtained solid product was characterized by melting point, ^{1}H NMR, ^{13}C NMR, FTIR, and Elemental analyses.

Oxidation of cycloheptanol to heptanedioic acid

An amount of 1.2 ml (10 mmol) of cycloheptanol was dissolved in 10 ml of acetonitrile. This was followed by addition of 50 mg of the catalyst. Subsequently, 2.8 ml (120 mmol) of H_2O_2 (30% aq. solution) was slowly added to the above reaction mixture over a period of 30 minutes and stirred at 90 °C in an oil bath fitted to a condenser till the complete conversion was achieved as confirmed by TLC. The catalyst was then recovered under hot conditions from the reaction mixture through filtration. The product thus formed in the reaction mixture was then cooled to room temperature to obtain the white solid precipitate and recrystallized with methanol. The obtained solid product was characterized by melting point, ^1H NMR, ^{13}C NMR, FTIR, and Elemental analyses.

Oxidation of cycloheptanone to heptanedioic acid

An amount of 1.8 ml (10 mmol) of cycloheptanone was dissolved in 10 ml of acetonitrile. This was followed by addition of 50 mg of the catalyst. Subsequently, 2.8 ml (120 mmol) of H_2O_2 (30% aq. solution) was slowly added to the above reaction mixture over a period of 30 minutes and stirred at 90 °C in an oil bath fitted to a condenser till the complete conversion was achieved as confirmed by TLC. The catalyst was then recovered under hot conditions from the reaction mixture through filtration. The product thus formed in the reaction mixture was then cooled to room temperature to obtain the white solid precipitate and recrystallized with methanol. The obtained solid product was characterized by melting point, ^1H NMR, ^{13}C NMR, FTIR, and Elemental analyses.

Oxidation of cyclooctanol to octanedioic acid

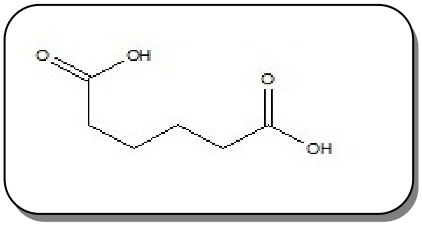
An amount of 1.31 ml (10 mmol) of cyclooctanol was dissolved in 10 ml of acetonitrile. This was followed by addition of 50 mg of the catalyst. Subsequently, 2.8 ml (120 mmol) of H_2O_2 (30% aq. solution) was slowly added to the above reaction mixture over a period of 30 minutes and stirred at 90 °C in an oil bath fitted to a condenser till the complete conversion was achieved as confirmed by TLC. The catalyst was then recovered under hot conditions from the reaction mixture through filtration. The product thus formed in the reaction mixture was then cooled to room temperature to obtain the white solid precipitate and recrystallized with methanol. The obtained solid product was characterized by melting point, ^{1}H NMR, ^{13}C NMR, FTIR, and Elemental analyses.

Oxidation of cyclooctanone to octanedioic acid

An amount of 1.3 ml (10 mmol) of cyclooctanone was dissolved in 10 ml of acetonitrile. This was followed by addition of 50 mg of the catalyst. Subsequently, 2.8 ml (120 mmol) of H_2O_2 (30% aq. solution) was slowly added to the above reaction mixture over a period of 30 minutes and stirred at 90 °C in an oil bath fitted to a condenser till the complete conversion was achieved as confirmed by TLC. The catalyst was then recovered under hot conditions from the reaction mixture through filtration. The product thus formed in the reaction mixture was then cooled to room temperature to obtain the white solid precipitate and recrystallized with methanol. The obtained solid product was characterized by melting point, ^{1}H NMR, ^{13}C NMR, FTIR, and Elemental analyses.

Spectral data of representative compounds

Adipic Acid (S1)



Nature : White crystals

Molecular formula : $C_6H_{10}O_4$

Melting Point : 151-152^{o}C

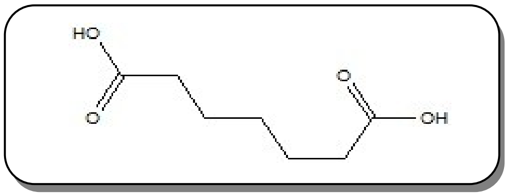
^{1}H NMR (500 MHz, CH$_3$OD) : δ 1.72 (m,4H), 2.42 (m,4H), 5.30 (s,2H)

^{13}C NMR (500 MHz, CH$_3$OD) :δ 175.9, 33.1, 24.1

FTIR : 1696, 2959 cm^{-1}

Elemental analyses (%) : calculated:C, 49.31; H, 6.90 found: C, 49.38; H, 6.79

Heptanedioic acid (S2)



Nature : White Solid

Molecular formula : $C_7H_{12}O_4$

Melting Point : 103-104^{o}C

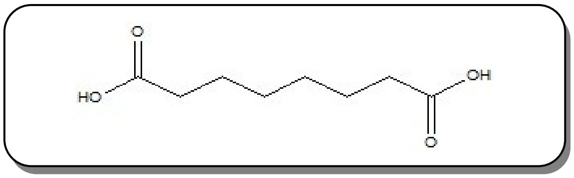
^{1}H NMR (400 MHz, CH$_3$OD) : δ 1.43(m,2H),1.67 (m,4H),2.33 (m, 4H), 5.2 (s,2H)

^{13}C NMR (400 MHz, CH$_3$OD) : δ 176.1, 33.3, 28.3, 24.3

FTIR :1700, 2942 cm^{-1}

Elemental analyse (%) : calculated: C, 52.49; H, 7.55 found: C, 52.54; H, 7.51

Octanedioic acid (S3)



Nature : crystalline solid

Molecular formula **:** $C_8H_{11}O_4$

Melting Point : 141-141^{o}C

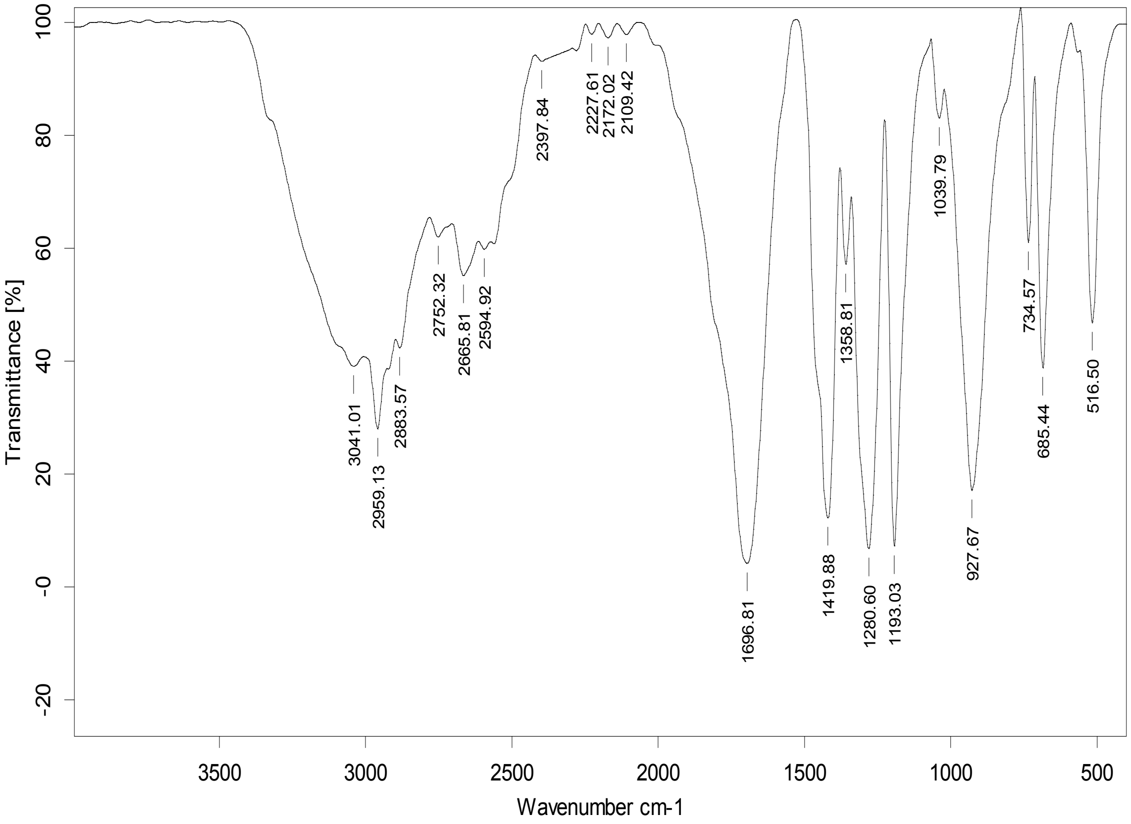
^{1}H NMR (400 MHz, CH_3OD) : δ 1.41 (m,4H), 1.65 (m,4H), 2.32 (m,4H), 5.0 (s,2H)

^{13}C NMR (400 MHz, CH_3OD) : δ 17.2, 33.4, 28.4, 24.5.

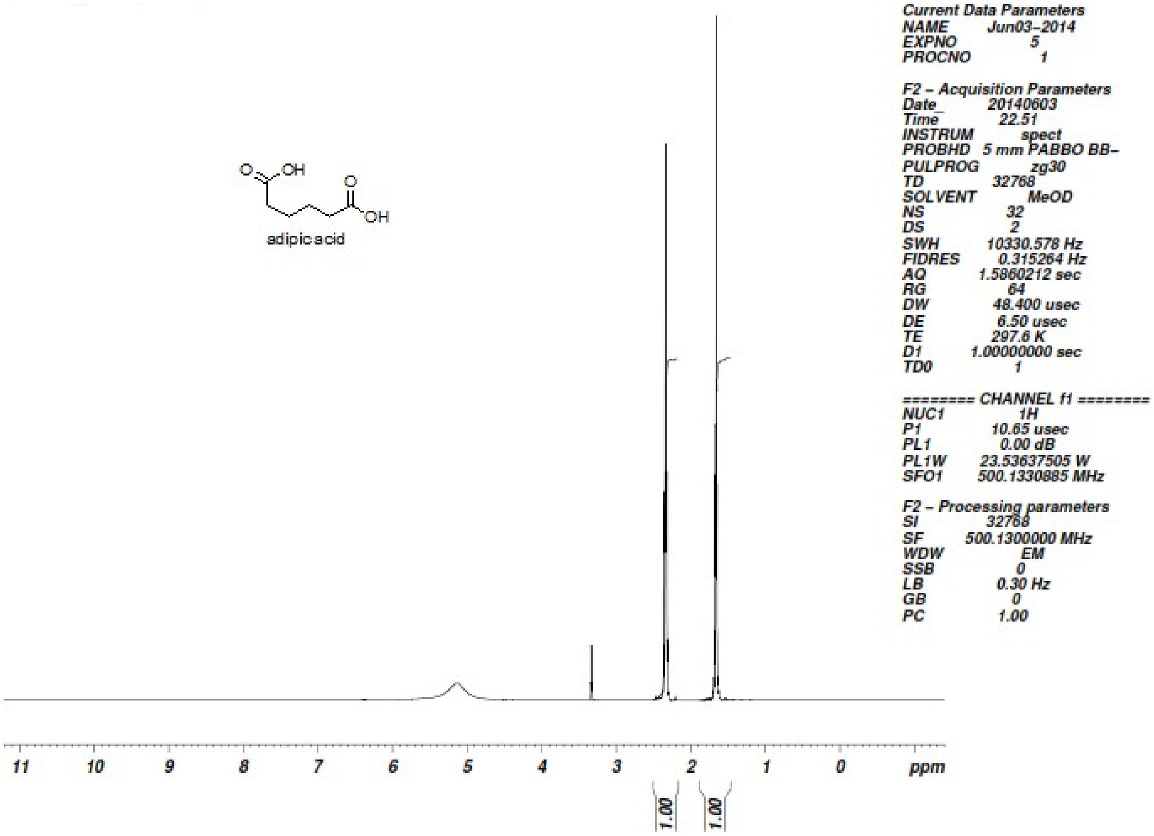
FTIR **:** 1698, 2945 cm^{-1}

Elemental analyses (%) **:** calculated: C, 56.14; H, 6.47 found: C, 56.19 ; H, 6.42

FTIR, ^{1}H NMR, ^{13}C NMR Spectra



S1: FT-IR Spectra of adipic acid



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PROCNO             1

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TE            297.6 K
D1       1.00000000 sec
TD0               1

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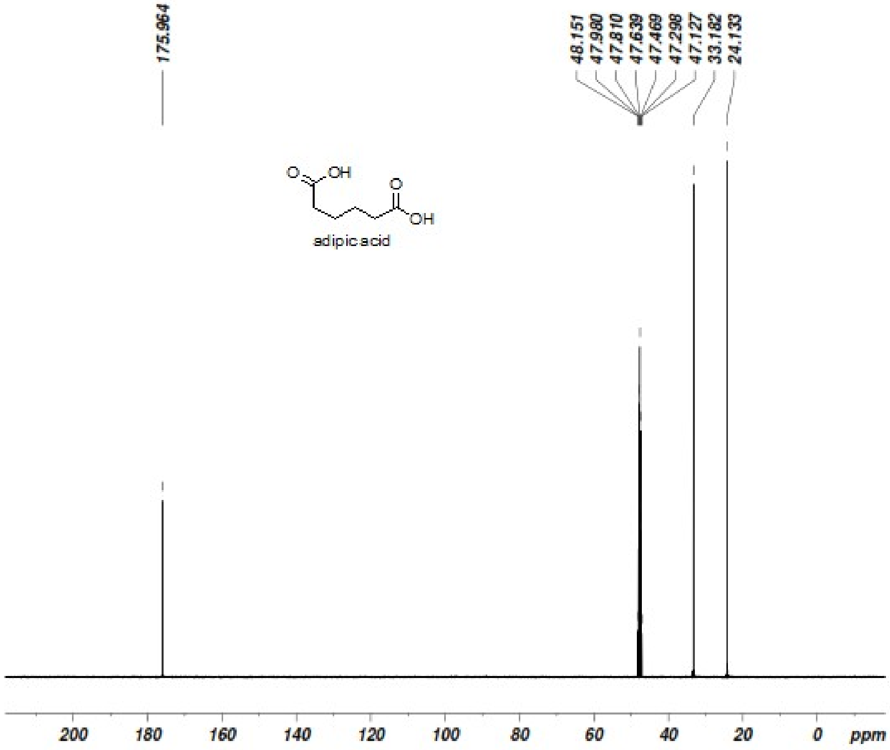
S1: ^{1}H NMR Spectra of adipic acid



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SOLVENT           MeOD
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DS                   4
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FIDRES     0.908261 Hz
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RG                 203
DW          16.800 usec
DE            6.50 usec
TE             299.1 K
D1      2.00000000 sec
D11     0.03000000 sec
TD0                  1

======== CHANNEL f1 ======
NUC1               13C
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PL1            0.00 dB
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SFO1    125.7703643 MHz

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NUC2                1H
PCPD2       80.00 usec
PL2            0.00 dB
PL12          17.51 dB
PL13          18.00 dB
PL2W     23.53637505 W
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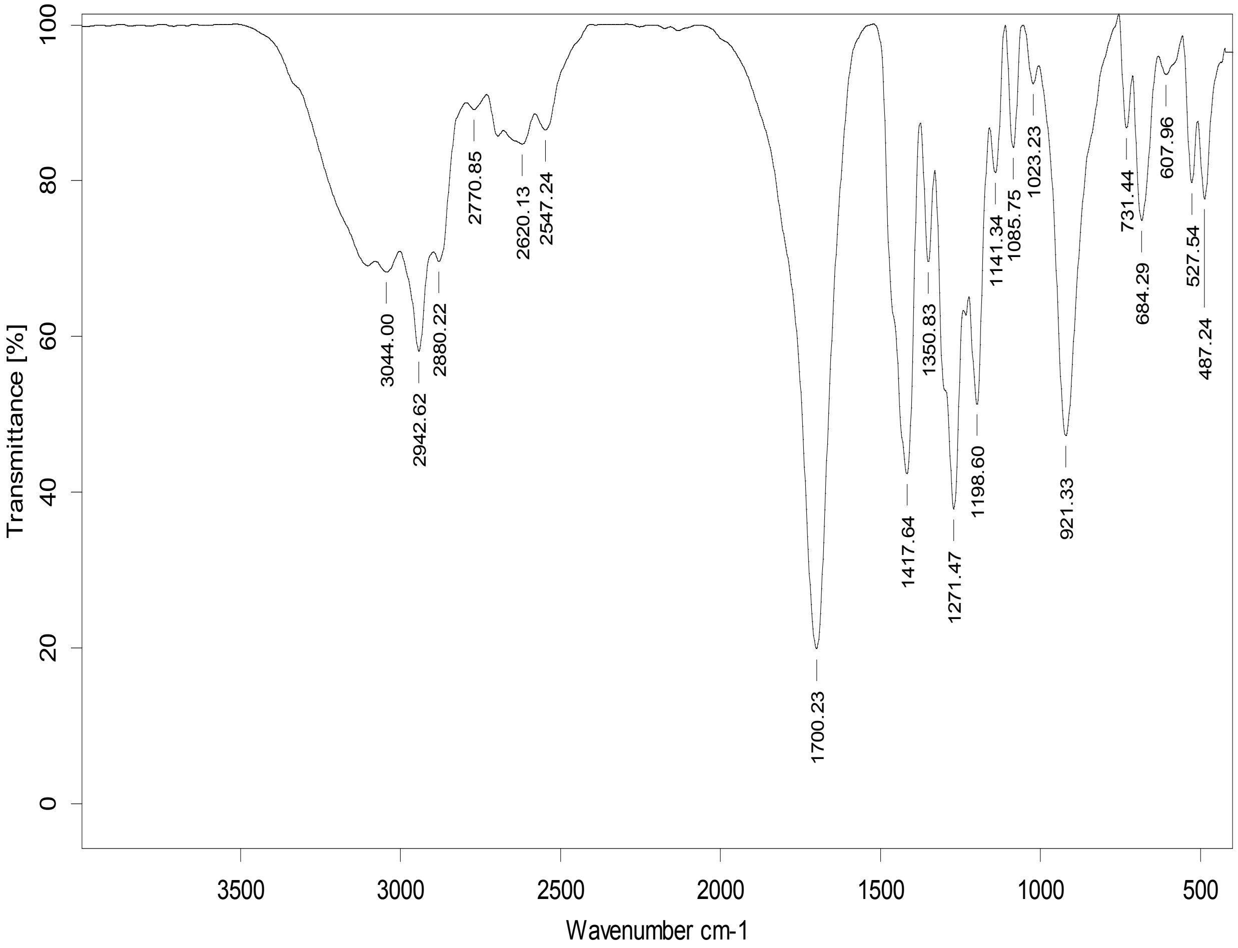
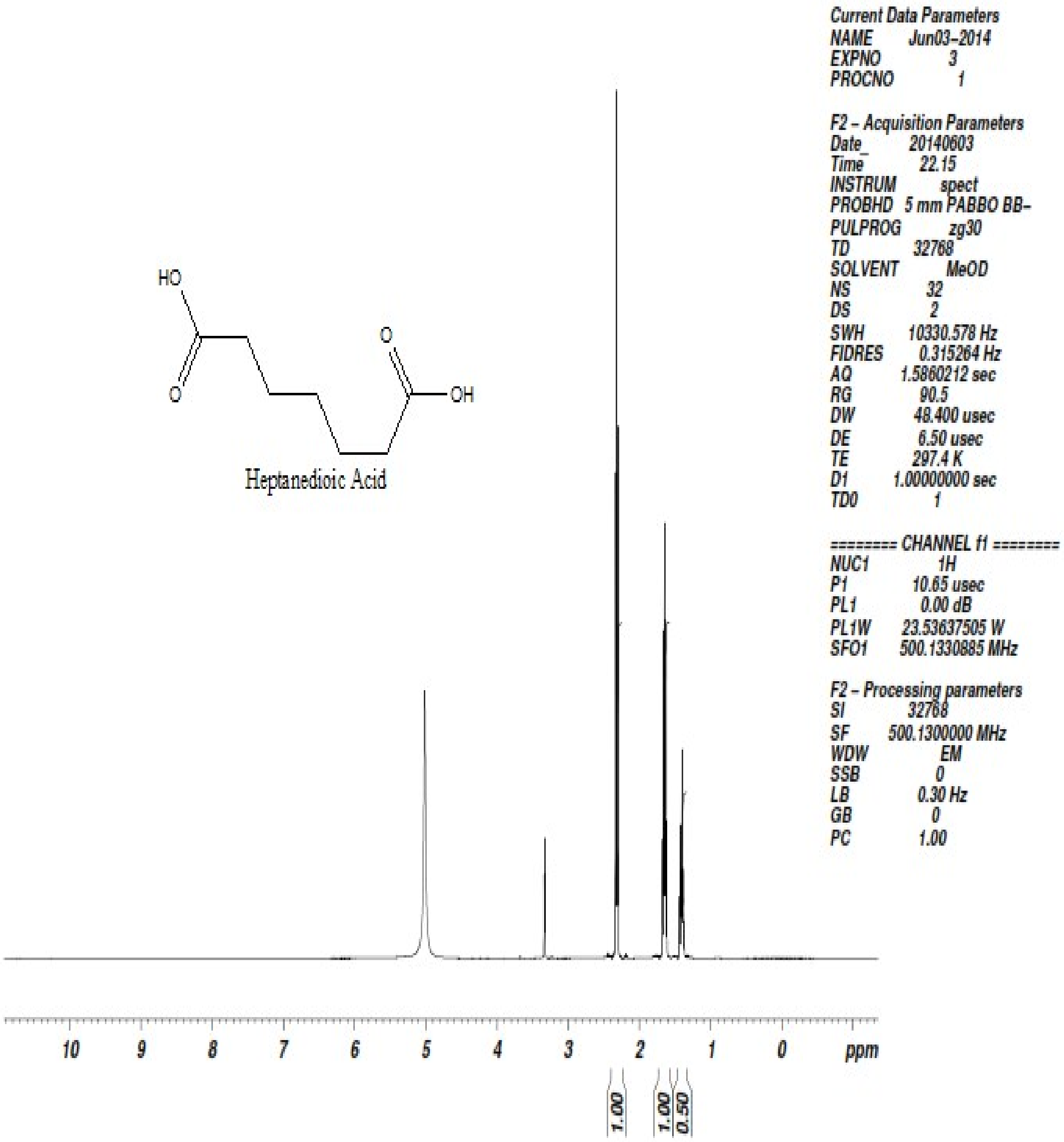
S1: ^{13}C NMR Spectra of adipic Acid



S2: FT-IR spectra of heptanedioic Acid



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SOLVENT         MeOD
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FIDRES   0.315264 Hz
AQ     1.5860212 sec
RG              90.5
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DE          6.50 usec
TE           297.4 K
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TD0                1

======== CHANNEL f1 ========
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PL1          0.00 dB
PL1W  23.53637505 W
SFO1  500.1330885 MHz

F2 - Processing parameters
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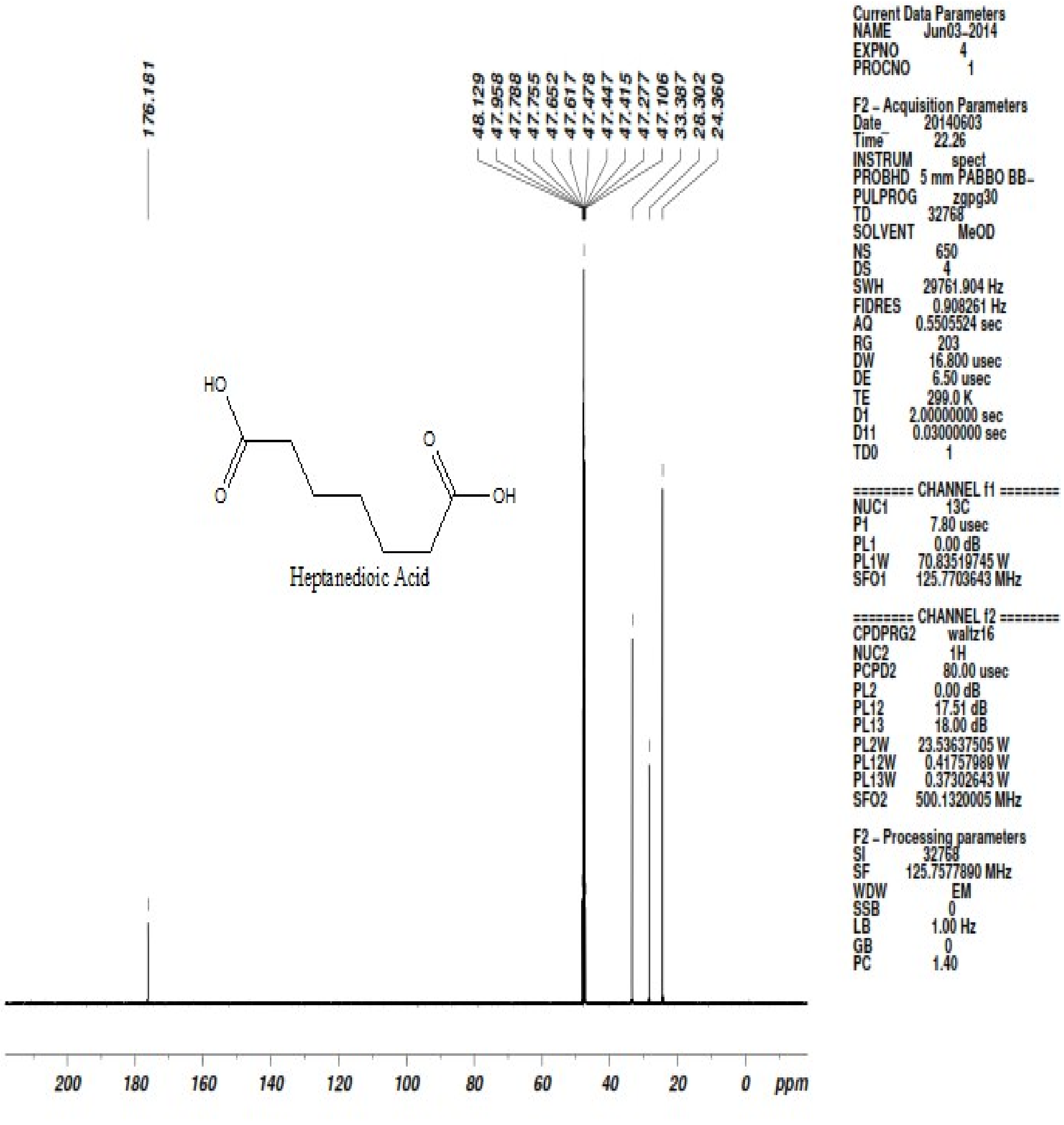
S2: ^{1}H NMR spectra of heptanedioic Acid



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PULPROG         zgpg30
TD               32768
SOLVENT           MeOD
NS                 650
DS                   4
SWH        29761.904 Hz
FIDRES      0.908261 Hz
AQ         0.5505524 sec
RG                 203
DW          16.800 usec
DE            6.50 usec
TE             299.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1            7.80 usec
PL1            0.00 dB
PL1W     70.83519745 W
SFO1     125.7703643 MHz

======== CHANNEL f2 ========
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NUC2                 1H
PCPD2        80.00 usec
PL2             0.00 dB
PL12           17.51 dB
PL13           18.00 dB
PL2W      23.53637505 W
PL12W      0.41757989 W
PL13W      0.37302643 W
SFO2     500.1320005 MHz

F2 - Processing parameters
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GB                    0
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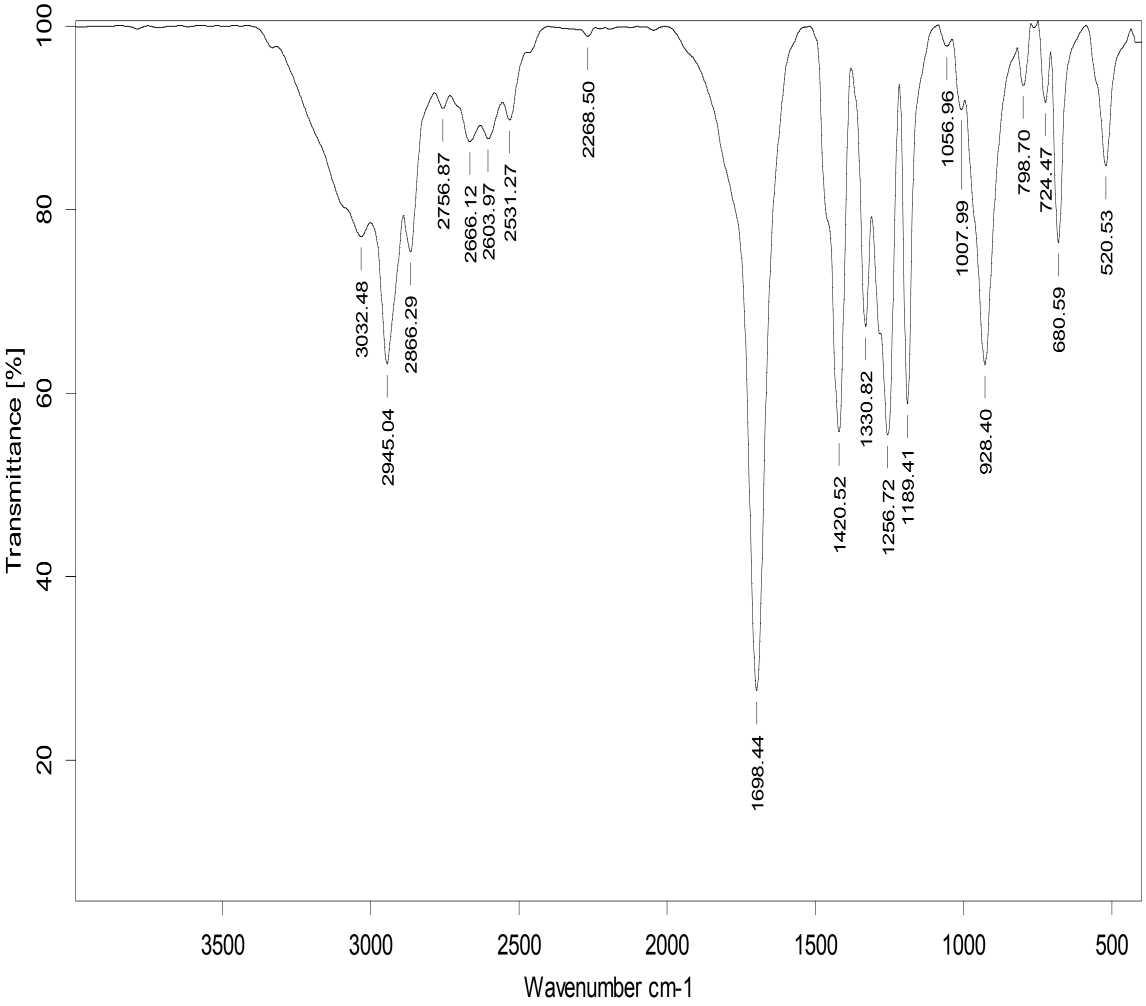
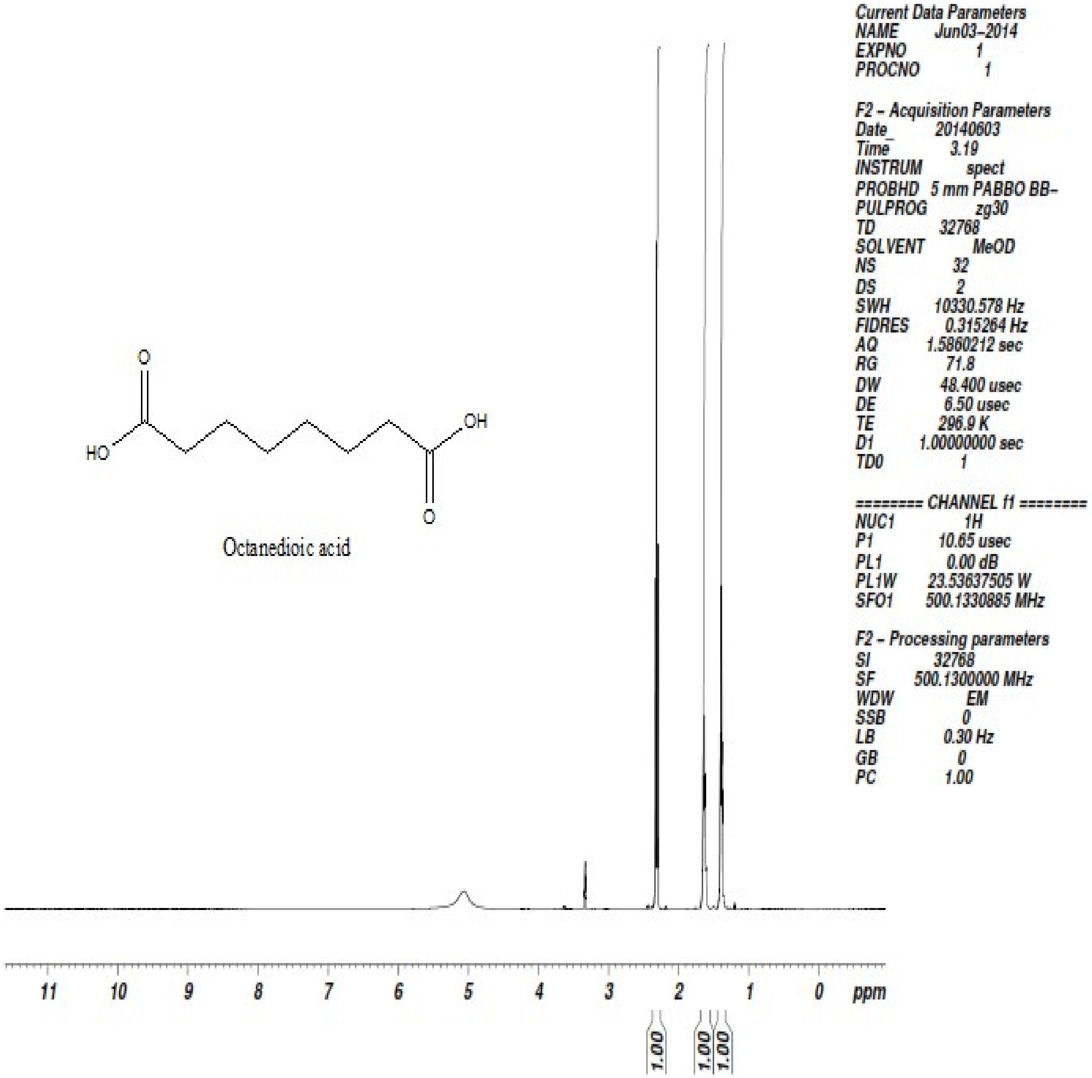
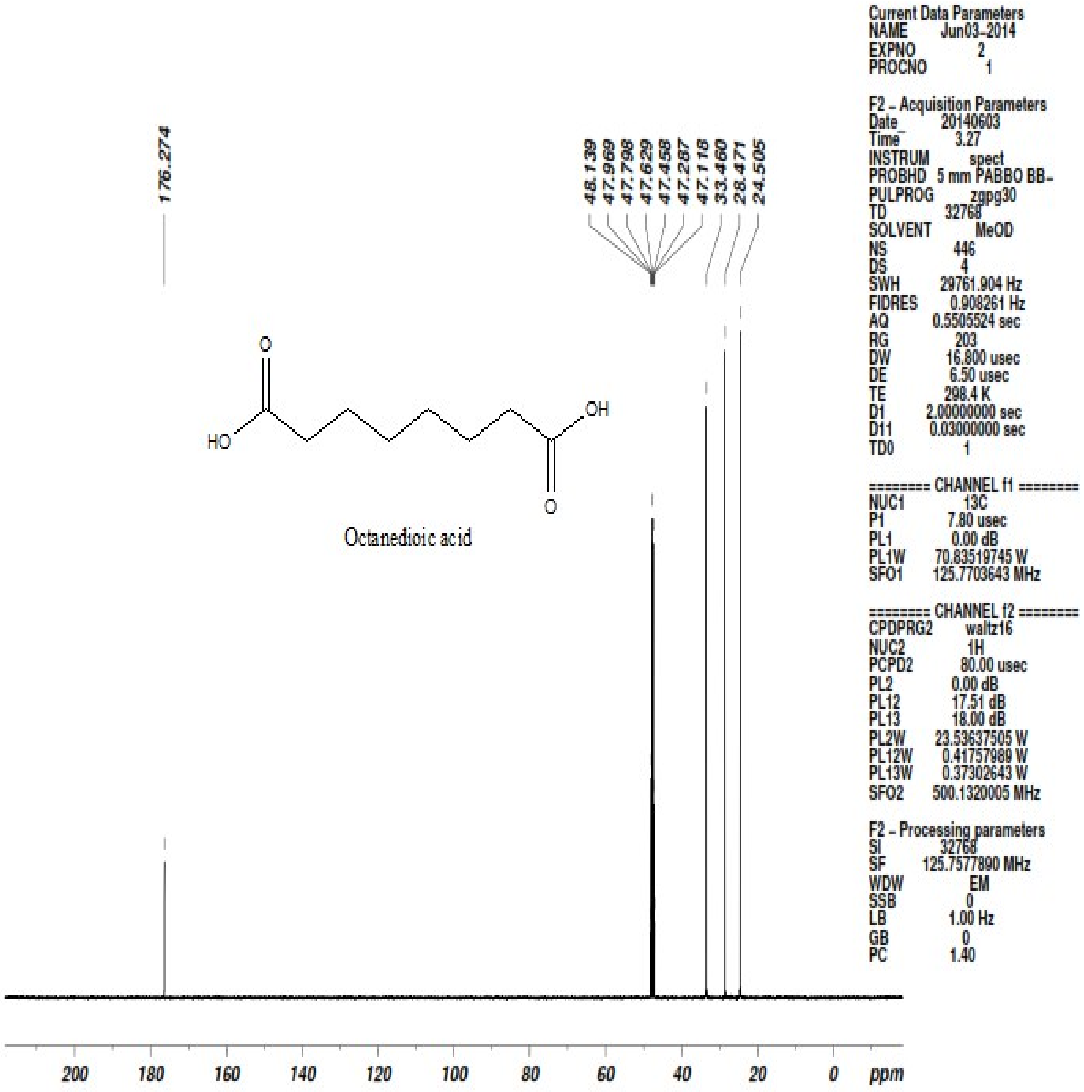
S2: ^{13}C NMR spectra of heptanedioic Acid



S3: FT-IR Spectra of octanedioic acid



S3: ^{1} H NMR Spectra of octanedioic acid



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PROCNO           1

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PULPROG       zgpg30
TD             32768
SOLVENT         MeOD
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SWH       29761.904 Hz
FIDRES     0.908261 Hz
AQ        0.5505524 sec
RG               203
DW            16.800 usec
DE              6.50 usec
TE             298.4 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1             13C
P1              7.80 usec
PL1             0.00 dB
PL1W     70.83519745 W
SFO1     125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2      waltz16
NUC2              1H
PCPD2          80.00 usec
PL2             0.00 dB
PL12           17.51 dB
PL13           18.00 dB
PL2W     23.53637505 W
PL12W     0.41757989 W
PL13W     0.37302643 W
SFO2     500.1320005 MHz

F2 - Processing parameters
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WDW               EM
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GB                 0
PC              1.40
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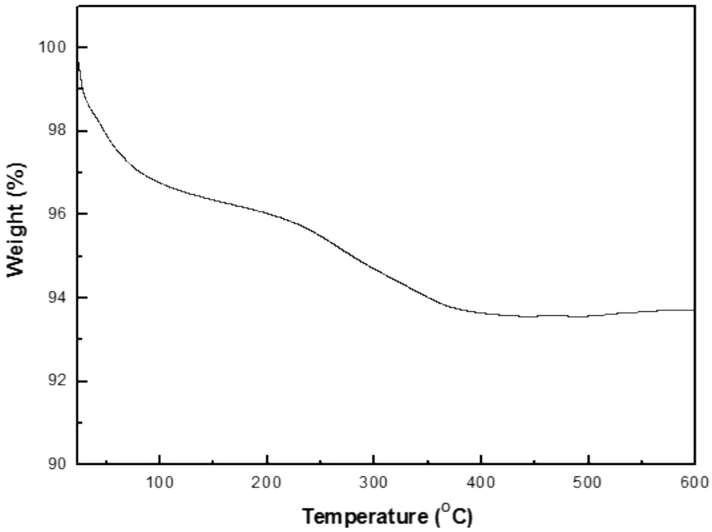
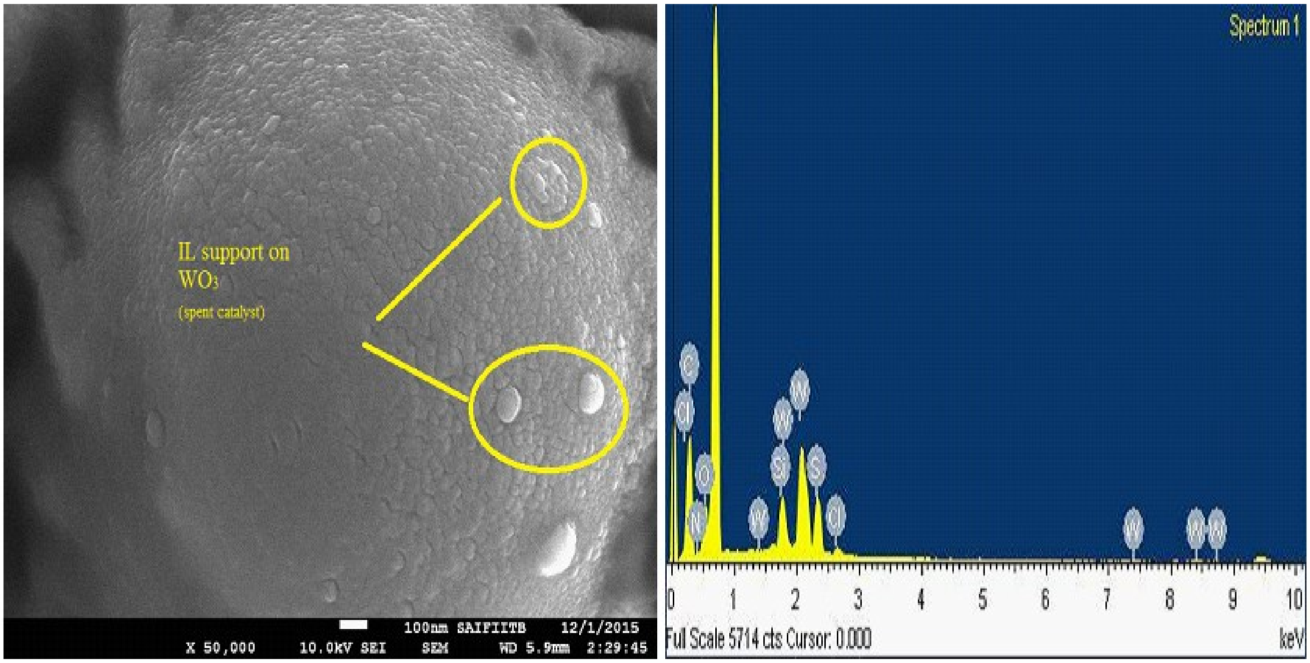
S3: ^{13}C NMR Spectra of octanedioic acid

TGA analysis of the spent catalyst:



S4: **TGA curve of the spent catalyst**

SEM image and EDX pattern of the spent catalyst:



S5: **SEM image and EDX pattern of the spent catalyst**