

# **Catalytic conversion of renewable carbohydrates and furans into valuable chemicals**

**Thesis Submitted to AcSIR for the Award of the Degree  
of  
DOCTOR OF PHILOSOPHY  
In  
Chemical Science**



**By  
Suhas Hanmant Shinde  
Registration Number: 10CC13A26009**

**Under the guidance of  
Dr. Chandrashekhar V. Rode**

**Chemical Engineering & Process Development Division,  
CSIR-National Chemical Laboratory,  
Pune- 411008, INDIA**

**June 2018**

Dedicated to  
My Beloved Mother  
and  
Wife



# सीएसआईआर - राष्ट्रीय रासायनिक प्रयोगशाला

(वैज्ञानिक तथा औद्योगिक अनुसंधान परिषद)

डॉ. होमी भाभा मार्ग, पुणे - 411 008, भारत



## CSIR - NATIONAL CHEMICAL LABORATORY

(Council of Scientific & Industrial Research)

Dr. Homi Bhabha Road, Pune - 411 008, India

### CERTIFICATE

This is to certify that the work incorporated in the thesis, “**Catalytic conversion of renewable carbohydrates and furans into valuable chemicals**” submitted by **Mr. Suhas Shinde**, for the degree of **Doctor of Philosophy**, was carried out by him under my supervision at CSIR-National Chemical Laboratory, Pune, India. The material that has been obtained from other sources is duly acknowledged in the thesis.

June-2018

Pune

**Dr. Chandrashekhar V. Rode**

(Research Supervisor)

डॉ. चं. व. रोडे/DR. C. V. RODE

वैज्ञानिक 'जी'/SCIENTIST 'G'

सीएसआईआर-राष्ट्रीय रासायनिक प्रयोगशाला

CSIR-NATIONAL CHEMICAL LABORATORY

पुणे/PUNE-411008.

#### Communication Channels

NCL Level DID : 2590  
NCL Board No. : +91-20-25902000  
EPABX : +91-20-25893300  
: +91-20-25893400



#### FAX

Director's Office : +91-20-25902601  
COA's Office : +91-20-25902660  
SPO's Office : +91-20-25902664

#### WEBSITE

[www.ncl-india.org](http://www.ncl-india.org)

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I hereby declare that the thesis entitled “**Catalytic conversion of renewable carbohydrates and furans into valuable chemicals**” submitted to Academy of Scientific and Innovative Research (AcSIR) for the award of degree of Doctor of Philosophy (Ph. D.) in chemical science is the outcome of experimental investigations carried out by me under the supervision of **Dr. Chandrashekhar V. Rode**, Chief Scientist, Chemical Engineering and Process Development Division, CSIR–National Chemical Laboratory, Pune. I affirm that the work incorporated is original and has not been submitted to any other academy, university or institute for the award of any degree or diploma.

**June-2018**

**Pune**



**Suhas Hanmant Shinde**

(Research Student)

CE & PD Division,

CSIR-National Chemical Laboratory,

Dr. Homi Bhabha Road, Pune – 411 008,

INDIA.



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***Part-II: C-O and C-C bond forming reactions of bioderived aldehydes***

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*My sincere thanks go to all my best friends, one of the biggest assets of life. I always enjoyed their company and all were there for me at every stage. I would like to thank Mr. Vikas Pable, Mr. Anirudhha Jagtap, Mr. Amol Yadav, Mr. Ganesh Pavle, Mr. Pravin Shinde, Mr. Santosh Shinde, Mr. Prakash Buchude, Mr. Swagat Thavai, Mr. Pritam Tighare, Mr. Sanjay Kudpane, Miss. Dipti Kakade, Mrs. Archana Jagdale-Kamathe, Mr. Saidu Mukhade and Mr. Akil Shaikh for their life time help. I would also like to acknowledge my friends, Miss. Vaishali Shende, Mr. Taufeeq Shaikh, Mr. Rohit Kamble, Dr. Hanumant Gurav, Mr. Sandip Wagh and Mr. Manoj Patil. I will never forget the encouragement and support obtained from Dr. Appaji Mandhare and Mr. Shankar Jadhav especially during preparation of NET examination.*

*No word would suffice to express my gratitude to my parents. They have been always the source of inspiration and thanks for given opportunity to see this beautiful world. I am very thankful to my Mother, Smt. Chhaya for her belief in my abilities. I always feel that I am lucky to have mother like her. Without her constant support, encouragement, positive thinking and inspiration, I cannot stand with this dissertation. I would like to equally thank to my elder brother Mr. Shrikant for supporting me in any situation. I am also thankful to my cousin sister Mrs. Supriya Shinde-Jadhav for continuous encouragement. The blessings showered on me by my grandfather, Mr. Hanmant and grandmother, Late Indumati are magnanimous and always supported and encouraged me at any stage.*

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*Last but not the least I feel very happy to express my sincere gratitude and appreciation to all the people whose direct or indirect contribution helped me during this work.*

*With many thanks,*

*Suhas H. Shinde*

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## ABBREVIATIONS

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aq.	Aqueous
Å	Angstrom
AMF	5-(Acetoxymethyl)furfural
AgNO <sub>3</sub>	Silver nitrate
Al(OTf) <sub>3</sub>	Aluminium triflate
AlCl <sub>3</sub> · 6H <sub>2</sub> O	Aluminium (III) chloride hexa hydrate
Al(OH) <sub>3</sub>	Aluminium hydroxide
BAMF	2,5-bis(alkoxymethyl)furan
BHMF	2,5-bishydroxymethylfuran
[Bmim][Cl]	1-butyl-3-methylimidazolium chloride
C <sub>4</sub> mimBr	1-butyl-3-methylimidazolium bromide
BET	Brunauer–Emmett–Teller
<i>n/i/t</i> -BuOH	<i>n/iso/tert</i> -Butanol
<i>t</i> -BMF	5-( <i>tert</i> -butoxymethyl)furfural
ca.	Calculated
<sup>13</sup> C	13-Carbon
C-C	Carbon-Carbon
C-O	Carbon-Oxygen
CH <sub>3</sub> COOH	Acetic acid
CMF	5-(Chloromethyl)furfural
CTH	Catalytic transfer hydrogenation
cm	Centimetre
CaO	Calcium oxide
CO <sub>2</sub>	Carbon dioxide
CDCl <sub>3</sub>	Deuterated chloroform
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane
CrCl <sub>3</sub>	Chromium Chloride
CrPO <sub>4</sub>	Chromium Phosphate
Conc.	Concentrated
°C	Degree Celsius



CH <sub>3</sub> NO <sub>2</sub>	Nitromethane
d	Doublet
dd	Doublet of doublet
DFF	2,5-(diformyl)furan
DNP	Dinitrophenylhydrazine
2,5-DMF	2,5-Dimethylfuran
DMF	N,N-Dimethylformamide
DMA	N,N-Dimethylacetamide
DMSO	Dimethyl sulfoxide
DMSO-d <sub>6</sub>	Deuterated dimethyl sulfoxide
e.g.	For example
eV	Electron volt
EmimCl	Ethyl(methylimidazolium chloride)
EtOH	Ethanol
EFE	Ethyl Furfuryl Ether
EtOAc	Ethyl acetate
FTIR	Fourier Transformed Infrared
FDCA	2,5-Furandicarboxylic acid
FMF	5-(Formyloxymethyl)furfural
FUR	Furfural
FAL	Furfuryl alcohol
FeCl <sub>3</sub>	Iron (III) chloride
FeCl <sub>3</sub> 6H <sub>2</sub> O	Iron (III) chloride hexa hydrate
g	Gram
GCMS	Gas Chromatography mass spectroscopy
GVL	γ-Valerolactone
1G/2G	First generation/second generation
HMF	5-(Hydroxymethyl)furfural
He	Helium
HMFA	5-(Hydroxymethyl)furoic acid
HCl	Hydrochloric acid

h or hrs	Hours
HCO <sub>2</sub> H	Formic acid
HI	Hydroiodic acid
H <sub>2</sub> O	Water
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
Hz	Hertz
HF	Hydrofluoric acid
HRMS	High resolution mass spectrometry
HPLC	High performance liquid chromatography
<sup>1</sup> H	Proton
H <sub>2</sub>	Hydrogen
ILs	Ionic liquids
InCl <sub>3</sub>	Indium(III)Chloride
i-Pro	Isopropyl
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
KBr	Potassium bromide
KMnO <sub>4</sub>	Potassium permanganate
kJ	Kilo Joule
Kg	Kilo gram
K <sub>2</sub> CO <sub>3</sub>	Potassium carbonate
LA	Levulinic acid
LE	Levulinic ester
MgO	Magnesium oxide
MeOH	Methanol
Me <sub>2</sub> SO <sub>2</sub>	Methylsulfonylmethane
Me <sub>2</sub> S	Dimethylsulfur
<i>m</i>	Multiplate
mm	Milimeter
MF	5-Methylfurfural
mg	Miligram
MHz	Mega Hertz

MIBK	Methylisobutylketone
min	Minute
mL/ $\mu$ L	Mililiter/Microliter
mmol	Milimole
MPV	Meerwein-Pondorf-Verley
MPa	Mega Pascal
MTMF	5-((methylthio)methyl)-2-furfural
NaCl	Sodium chloride
NaOCl	Sodium hypochloride
NaOH	Sodium hydroxide
NMe <sub>3</sub>	Trimethylamine
NMP	N-methyl pyrrolidine
NHC	N-Heterocyclic carbene
NH <sub>3</sub>	Sodium azide
Na <sub>2</sub> SO <sub>4</sub>	Sodium Sulfate
NaHCO <sub>3</sub>	Sodium hydrogen carbonate
NMR	Nuclear magnetic resonance
Ni(OH) <sub>2</sub>	Nickel hydroxide
OBMF	5,5-oxy(bis-methylene)-2-furfuraldehyde
O <sub>2</sub>	oxygen
N <sub>2</sub>	Nitrogen
Pd	Palladium
PG	Propyl guaiacol
ppm	Parts per million
<i>p</i> -TSA	<i>p</i> -Toluene sulfonic acid
PeD	Pentane diol
Pr	Propyl
Py-FTIR	Pyridine Fourier Transform Infrared spectroscopy
RON	Research Octane Number
RI	Refractive index
rt	Room temperature

$\text{RuCl}_3$	Ruthenium tri-Chloride
$s$	Singlet
SEM	Scanning electron microscopy
SPB	Sec-butyl phenol
Si	Silicon
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	Tin chloride penta hydrate
Sn-Mont	Tin montmorillonite
$\text{Sn}(\text{OH})_4$	Tin hydroxide
$\text{SnO}_2$	Tin oxide
TMS-Cl	Trimethylsilylchloride
$t$	Triplet
$t$	Time
T	Temperature
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
THFA	Tetrahydrofurfuryl alcohol
TLC	Thin layer chromatography
TPD	Temperature programmed desorption
$\theta$	Theta
U.S.	United States
UV	Ultra violet
u	unit
wt	Weight
XPS	X-ray photo electron microscopy
XRD	X-ray diffraction
$\text{ZnCl}_2$	Zinc(II)chloride
$\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$	Zirconium (IV) oxychloride octahydrate
$\text{ZrO}(\text{OH})_2$	Zirconium hydroxide
$\text{ZrO}_2$	Zirconium oxide

## **GENERAL REMARKS**

All the reactions were carried out in an oven dried glass apparatus.

1) Speciality chemicals and A. R. Grade dried solvents were procured from authentic suppliers like Aldrich (US), Alfa Aesar (US), Chem Labs and Thomas Baker (India) etc.

2) TLC plates were purchased from Merck and Loba, India.

3) 60-120, 100-200 and 230-400 mesh sized silica was utilized for the column chromatography using ethyl acetate in pet ether as a mobile phase.

4) Conversion of substrates and yield of products were calculated by liquid analysis using Thermo Scientific GC (FID detector and a capillary column HP5) and Agilent HPLC (column: Hi-Plex USP L17, detector: RI and mobile phase: millipore water with 0.6 mL/min flow; for carbohydrates analysis and column: Poroshell 120 EC-C18 2.7  $\mu$ m, detector: UV and mobile phase: 0.1 % acetic acid in Millipore water: acetonitrile (85:15, v/v) with 0.6 mL/min flow; for yield calculation of dehydration product).

5) Products were characterized by  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR using  $\text{CDCl}_3$  (0.01 % TMS) and DMSO- $d_6$  (0.01 % TMS) as solvents on 50 and 200 MHz frequency Bruker instrument.

6) The confirmation of the products was carried out using QP-Ultra 2010 GC-MS Shimadzu instrument on a RTX-5 column using helium as a carrier gas, in EI mode and at ionization source temperature of about 200  $^\circ\text{C}$ .

8) Micromeritics chemisorbed 2120 instrument was used for measuring BET surface area,  $\text{CO}_2$ -TPD and  $\text{NH}_3$ -TPD analysis.

9) Functional group characterization of various compounds and catalysts was done on Perkin Elmer frontier FT-IR instrument in ATR (PIKE make) mode at room temperature.

10) Pyridine-FTIR was done using Harrick Diffuse reflectance praying mantis assembly with temperature controller (30-850  $^\circ\text{C}$ ) attached with Perkin Elmer frontier under 150 mL/min flow of nitrogen as a carrier gas.

11) Wide angle X-ray diffraction (WAXRD) were recorded on a PAnalytical PXRD model X-Pert PRO-1712, using Ni filtered Cu-K $\alpha$  radiation ( $\lambda$ = 0.154 nm) as a source (current intensity, 30 mA; voltage, 40 kV) and a Xcelerator detector.

12) TEM analysis was carried out with JEOL, JEM-2100 LaB6 operated at high tension up to 200 kV with electron wavelength 2.5 pm.

14) ICP-OES carried out on Thermo Fisher instrument.

15) EDAX for determining the weight % of elements was studied on AMTEK make EDAX connected with the JEOL SEM machine.

## ABSTRACT

### Catalytic conversion of renewable carbohydrates and furans into valuable chemicals

Name of the research student : Mr. Suhas Hanmant Shinde  
AcSIR enrolment number : 10CC13A26009  
Date of Registration : August-2013  
Research Supervisor : Dr. Chandrashekhar V. Rode

The thesis entitled “**Catalytic conversion of renewable carbohydrates and furans into valuable chemicals**” is divided into two parts with a total of seven chapters. **Chapter 1** deals with the general introduction of biorefinery and literature on conversions of biomass derived carbohydrates and furans into advanced furan derivatives. Then **Chapters 2, 3 and 4** are included under section-I, which is focused on “Carbohydrate conversion to furan derivatives.” **Chapter 2** involves the direct synthesis of 5-(Acetoxymethyl)furfural (AcMF) from carbohydrates over Sn-Mont catalyst. **Chapter 3** describes the production of 5-((methylthio)methyl)-2-furfural (MTMF) and 2,5-Diformylfuran (DFF) directly from carbohydrates over Sn-Mont and H<sub>2</sub>SO<sub>4</sub> respectively, in DMSO. **Chapter 4** deals with “Carbohydrate dehydration followed by C-C bond forming reactions” and is subdivided into three sections as **4.1, 4.2 and 4.3**. Section **4.1** deals with the production of diesel fuel precursors from carbohydrates and 2-methylfuran. Section **4.2** describes the production jet fuel precursors from carbohydrates *via* dehydration-aldol condensation reaction sequence while; section **4.3** presents the Friedel-Crafts alkylation over Zr-Mont catalyst for the production of diesel fuel precursor. Section-II is focused on “C-O and C-C bond forming reactions of bioderived aldehydes.” In this section, **Chapter 5** discusses the etherification reactions of the bioderived aldehydes and it is subdivided into two sections as **5.1 and 5.2**. Section **5.1** is on self etherification of 5-(hydroxymethyl)furfural (HMF) over Sn-Mont catalyst and the section **5.2** is on cascade reductive etherification of bioderived aldehydes over Zr-based catalysts. **Chapter 6** demonstrates the C-C bond forming reactions between furans and bioderived aldehydes in presence - SO<sub>3</sub>H functionalized ionic liquids. In **Chapter 7** conclusions and future scope of this work is discussed.

## 1. Introduction

Valorisation of carbohydrates and furans to the advanced chemicals is a hot topic nowadays because of its potential to develop sustainable processes in near future. In the area of carbohydrates conversion, isomerisation of the glucose like carbohydrates without using mineral acids is a key challenge [1]. This can be surmounted by developing metal exchanged montmorillonite having suitable Lewis and Brønsted acid strengths as catalysts [2]. In this work, a novel strategy involving integrated/direct production of diesel fuel precursors from carbohydrates was developed using Sn-Mont catalyst in formic acid medium. Formic acid was employed as a co-catalyst as well as a reactive solvent. The biphasic solvent system containing MIBK: H<sub>2</sub>O+DMSO were also developed for the dehydration of carbohydrates over Sn-Mont catalyst which facilitated the easy separation of HMF. The HMF formed in MIBK could undergo aldol condensation over CaO to form jet fuel precursor. Apart from that the pure HMF was converted into important ether derivatives over metal exchanged montmorillonite catalysts. These ethers have applications in polymers and fuel additives [3, 4]. Further, the hydroxyalkylation-alkylation of furfural with furan was explored over SO<sub>3</sub>H functionalised ionic liquids and a method for clean isolation of condensation product was also developed [5].

## 2. Statement of problem

The selective conversion of oxygen rich biomass to value-added chemicals is the key issue for development of fossil-independent chemical technologies for the production of fuel additives and chemicals. 5-(Hydroxymethyl)furfural (HMF) is an important and a versatile platform molecule in the biorefinery. Although several technologies are available for the production of HMF, its isolation and purification is still a biggest challenge due to its solubility in water making it difficult to extract from the aqueous solution. During distillation at high temperature, unwanted impurities were formed which results in significant loss of HMF yield. On the other hand, although furfural is produced commercially but its long time stability is a major concern. Therefore, this work deals with direct conversion of carbohydrates to the desired products without isolation of unstable furfural derivatives. Similarly, conversion of furan to more stable and value added



products could be achieved by catalyst design and developing new reaction pathways.

### 3. Objectives of Study

The overall objective of the thesis is the conceptual development and optimization of environment friendly and cost efficient strategies that will enable the conversion of biomass derived molecules to value added products. The objectives of thesis are divided into two parts I and II.

#### I. Based on carbohydrates utilization

Direct/integrated conversion of carbohydrates (*e.g.* fructose, glucose, sucrose, xylose) into advanced furan derivatives (*e.g.* fuel additives and chemicals) without isolation of unstable intermediates (furfural derivatives). It will eliminate the tedious isolation and purification processes of furfural derivatives (HMF/furfural).

To this end, the specific aims are as follows:

- Development of catalysts possessing both Lewis and Brønsted acid sites, by simple preparation techniques.
- Catalyst characterization and parametric study of reaction conditions in order to understand structure-property-reactivity relationships for the optimization of the carbohydrates dehydration reaction.
- Careful selection of biphasic solvent system for dehydration of carbohydrates to HMF. Subsequent utilization organic phase for further conversion of in-situ formed HMF to advanced chemicals/fuel additives.
- Development of integrated technologies for the production of advanced chemicals and fuel precursors from carbohydrates.

#### II. Based on utilization of furan derivatives

- To find out catalytic upgradation processes of pure HMF/furfural to advanced chemicals.
- Development of cascade protocol for the conversion of HMF into fuel additives.
- Development of sustainable technologies/processes for the upgradation of furan derivatives.

## 4. Methodology Used

The prepared metal exchanged montmorillonite catalysts and other catalysts used in this work were thoroughly characterised using XRD, Py-FTIR, NH<sub>3</sub>-TPD, BET, EDS, SEM, TEM and ICP techniques. All the synthesized products and their structures were characterized and confirmed using advanced analytical and spectroscopic techniques such as high field NMR (<sup>1</sup>H and <sup>13</sup>C), FTIR, HRMS.

## 5. Sample results

### Chapter 1

#### General Introduction

**Chapter 1** is focused on general introduction of biorefinery and literature on conversion of biomass derived carbohydrates and furans into advanced furan derivatives.

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#### *Part-I: Carbohydrate conversion to furan derivatives*

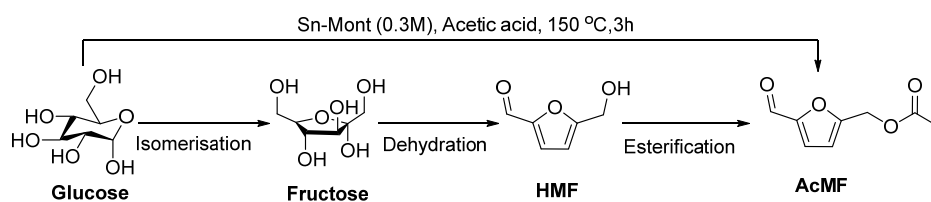
The part-I of the thesis contains three chapters such as Chapter 2, 3 and 4.

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### Chapter 2

#### Direct synthesis of 5-(acetoxymethyl)furfural from carbohydrates

In this chapter, we describe the direct and cascade synthesis of 5-(acetoxymethyl)furfural from carbohydrates such as glucose, fructose and sucrose *via* cascade sequence involving isomerisation-dehydration-esterification over Sn-Mont catalyst and in acetic acid as a reactive medium. The Sn-Mont catalyst was prepared by simply mixing of aq. SnCl<sub>4</sub>·5H<sub>2</sub>O and montmorillonite clay. The unique combination of Brønsted + Lewis acid sites present in Sn-Mont facilitates the isomerisation-dehydration-esterification of glucose like carbohydrates (**Scheme 1**). The critical features of the Sn-Mont catalyst is well characterised. The Sn-Mont shows phenomenal stability and recyclability.

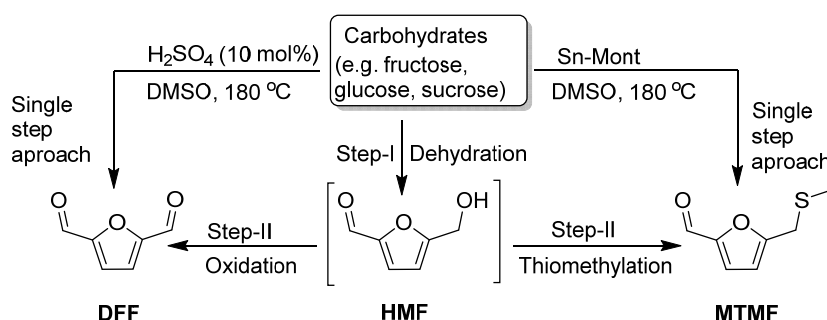


**Scheme 1** Direct synthesis of AcMF from glucose

### Chapter 3

#### Direct production of 2,5-di(formyl)furan and 5-((methylthio)methyl)-2-furfural from carbohydrates

A direct conversion of carbohydrates to DFF and MTMF is demonstrated over  $\text{H}_2\text{SO}_4$  and Sn-Mont catalysts, respectively (**Scheme 2**). The DFF was obtained in 33-48 % and MTMF was obtained in 36-45 % from carbohydrates. DMSO was acted as solvents as well as sacrificial reagent for oxidation and thiomethylation.



**Scheme 2** Direct conversion of carbohydrates to DFF and MTMF

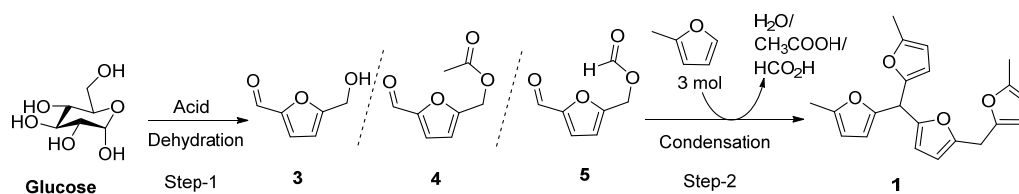
### Chapter 4

#### Dehydration of carbohydrate followed by C-C bond forming reactions

The Chapter 4 is organized in three section as follows:

##### 4.1 An integrated process for production of diesel fuel precursors from carbohydrates and 2-methylfuran over Sn-Mont catalyst

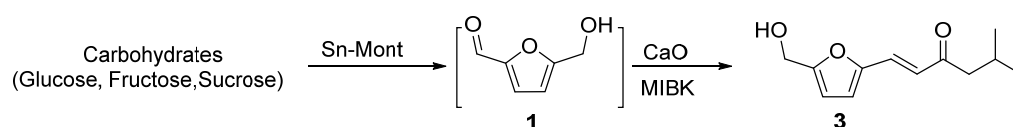
An integrated production of diesel fuel precursors from carbohydrates is demonstrated using Sn-Mont and formic acid (**Scheme 3**). The Sn-Mont catalyst facilitates the isomerisation of glucose like carbohydrates to fructose and formic acid dehydrates in-situ generated fructose to 5-(formyloxymethyl)furfural and subsequently latter was treated with 2-methylfuran in same pot to afford diesel fuel precursor of  $\text{C}_{21}$  unit.



**Scheme 3** Integrated conversion of carbohydrates to diesel fuel precursor

#### 4.2 Clean production of jet-fuel precursor from carbohydrates through an integrated dehydration and aldol condensation

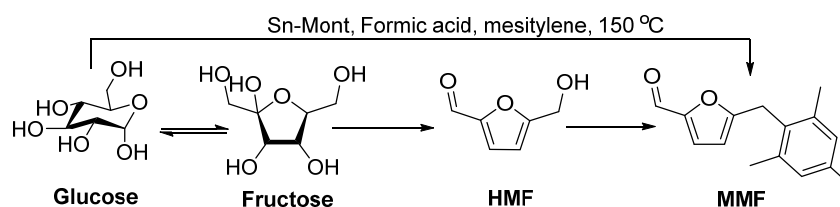
Jet-fuel precursor is produced cleanly in MIBK: H<sub>2</sub>O+DMSO biphasic solvent system *via* an integrated dehydration of carbohydrates over Sn-Mont followed by aldol condensation over CaO (**Scheme 4**). MIBK acted as a solvent for the extraction of product as well as a reactant. 80% recovery of MIBK could be possible from the reaction crude.



**Scheme 4** Integrated conversion of carbohydrates to jet fuel precursor.

#### 4.3 Friedel-Crafts alkylation over Zr-Mont catalyst for the production of diesel fuel precursors

In this work, a novel strategy was developed for the direct production of diesel fuel precursors from carbohydrates and mesitylene, xylene or toluene using Zr-Mont and formic acid (**Scheme 5**). Mesitylene acted as a solvent to extract product as well as reactant for FC alkylation reaction.



**Scheme 5** Direct conversion of glucose to diesel fuel precursor *via* FC alkylation

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## ***Part II: C-O and C-C bond forming reactions of bioderived aldehydes***

The part-II of the thesis contains two chapters such as Chapter 5 and 6

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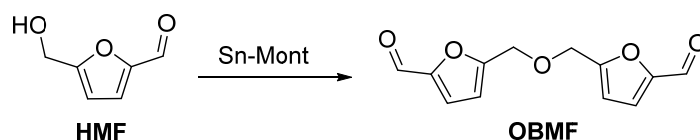
### **Chapter 5**

#### **Etherification reactions of biomass derived platform molecules**

Chapter 5 is subdivided into 2 sections as follows

##### **5.1 Selective self-etherification of 5-(hydroxymethyl)furfural over Sn-Mont catalyst**

Sn-Mont is  $\text{Sn}(\text{OH})_4$  species enwrapped into montmorillonite layers imparting active Brønsted acid sites for the selective self etherification of HMF (**Scheme 6**). Self etherification of HMF was attempted using Dean-Stark assembly to get high selectivity of OBMF (98%).

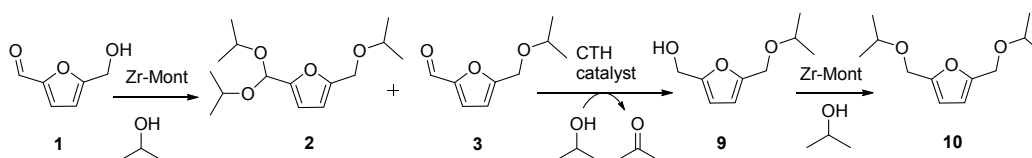


**Scheme 6** Selective self etherification of HMF to OBMF

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##### **5.2 Cascade reductive-etherification of bio-derived aldehydes over Zr-based catalysts**

A cascade protocol is developed for the reductive etherification of bioderived aldehydes over a mixture of Zr-Mont and  $\text{ZrO}(\text{OH})_2$  (**Scheme 7**).  $\text{ZrO}(\text{OH})_2$  has a unique acid base character making it a very good catalyst for transfer hydrogenation of aldehydes to alcohols and Zr-Mont catalyst is an acidic catalyst which promotes the etherification of bio-derived aldehydes with alcohols.



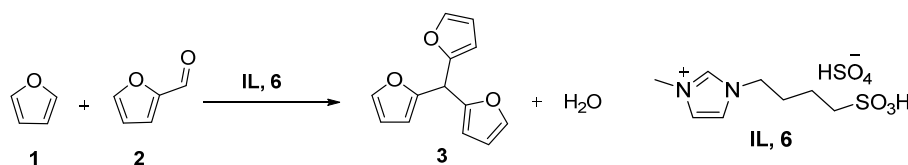
**Scheme 7** Cascade-reductive-etherification of HMF to 2,5-(bisalkoxymethylfuran)

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## Chapter 6

### C-C bond forming reaction for synthesis of furylmethane derivatives over -SO<sub>3</sub>H functionalized ionic liquids

An efficient method is investigated for the clean production of furylmethane derivatives from bioderived aldehydes and furans in biphasic solvent system. The sulfonic acid functionalized ionic liquid was used as catalyst for the hydroxyalkylation-alkylation (HAA) reaction (**Scheme 8**). The dilution of the reaction medium with water significantly reduces the side reactions which produces unwanted polymers. Furan was acted as a reactant as well as product extraction phase.



**Scheme 8** Synthesis of furylmethane derivatives using SO<sub>3</sub>H functionalized IL

## References

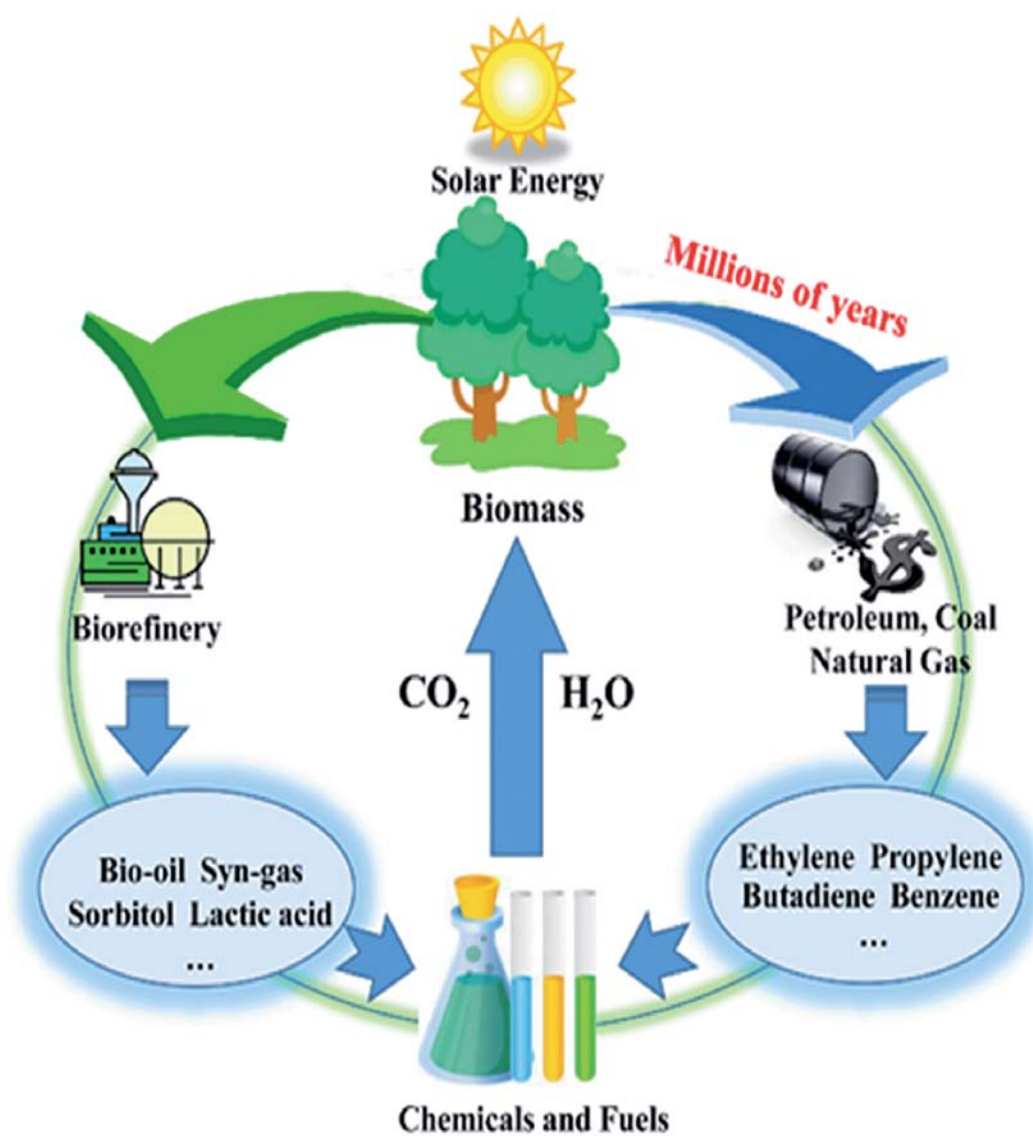
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## Chapter 1

### General Introduction

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## 1.1. Motivation for this study

At present energy and chemicals requirement of the whole world is dependent on fossil resources like petroleum, coal and natural gas. However, use of fossil resources is exponentially increasing in transportation and industrial sectors leading to quick depletion of these sources. In addition to this, the global warming caused by the emission of CO<sub>2</sub> from these sources is becoming a serious threat to the society. The use of non-degradable materials, hazardous, toxic and polluting chemicals is also on rise with world civilization and developments. This has surely imposed far reaching, severe health hazards to human beings and also threat to the environment. Therefore, the primary challenges to the scientists and technologists are to look for the alternative options for fuels, chemicals and materials. Lignocellulosic biomass is one of the sustainable and eco-friendly alternatives, as it is highly abundant on earth and most importantly a renewable resource of organic carbon.

India is a biomass rich country in both quantity and diversity, producing around 600-700 million tonnes of the agro waste in the form of straw [1]. Indian agriculture contributes to about 8 % of global agricultural domestic products to satisfy the need of 18 % of the world population on only 9 % of world's arable land and 2.3 % of geographical areas [2]. India with its strong roots in agriculture and diverse availability of enormous agro-resources is likely to generate non-edible biomass which potentially can be explored for the production of power and biofuel. According to the IEA's (International Energy Agency) medium term oil market report 2009, the production of biofuel in India reached to 1.08 billion litres of biodiesel in 2008. The current share of biofuel in total fuel consumption is extremely low and is confined mainly to 5 % blending of ethanol in gasoline, which the government has made mandatory in only 10 states. Currently, biodiesel is not sold in the Indian fuel market, but the government plans to meet 20 % of the country's diesel requirement by 2020 using biodiesel (planning commission, 2003). Since the demand for edible oil seeds exceeds current production, the government promotes the use of non-edible oils from *Jatropha curcas* and *Pongamia pinnata* as feedstock for biodiesel production [3]. Unfortunately, around 116 million metric tonnes of crop residue in the crop field is currently burnt on the respective field locations in India (12 million metric tons of rice straw is burnt in Punjab region alone) [4]. In this



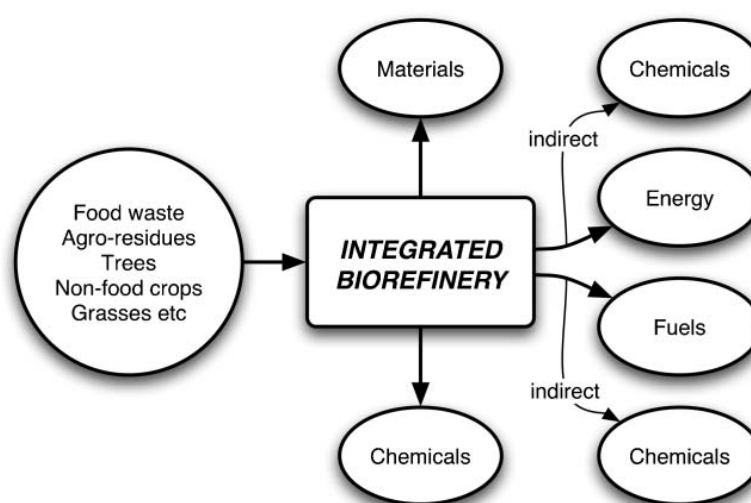
regard, India and Europe made collaboration on Biomass Research and Biowaste conversion through SAHYOG project. In this program following are the twinning research themes [5].

- Bioethanol production from lignocellulosic biomass
- Thermochemical conversion technologies (pyrolysis, gasification)
- Anaerobic digestion technologies (biogas, biomethane, hydrogen)
- Algae production and conversion system
- Biomass to chemicals-the biorefinery approach
- Feedstock production and genetic improvement of plants
- Sustainable and life cycle assessment

The U.S. Department of Energy (DOE) has set goals to replace 30 % of the liquid petroleum transportation fuel with biofuels and to replace 25 % of industrial organic chemicals with biomass-derived chemicals by 2025. It also screened thousands of future possible outcome chemicals from biomass and finalized 12 chemicals based on their importance on daily life, ease of production and quantities required.

## 1.2. Biorefinery at a glance

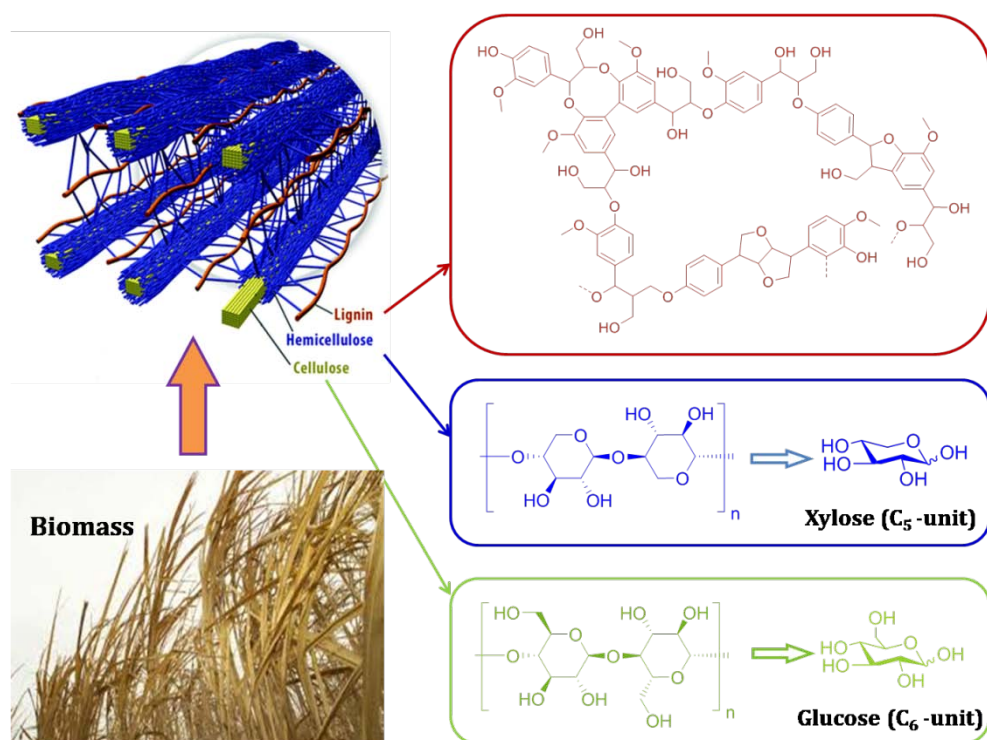
A biorefinery is an integral unit that can accept different biological feedstocks and convert them into a range of useful products including biochemicals, bioenergy and biomaterials (Figure 1.1) [6].



**Figure 1.1.** The integrated biorefinery. Reproduced from Ref. [7].

### 1.3. Lignocellulosic biomass

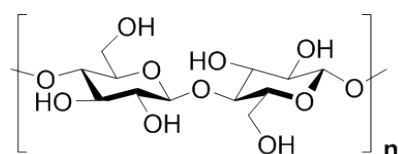
Biodiesel and ethanol can be produced from the first generation (1G) biorenewable feedstock (*e.g.* vegetable oil and starch/sucrose) but then it becomes a food competitive process. Moreover, at present the quantity of these feedstocks is rather limited as compared to the current production of fuels and chemicals from petro-feedstock. Hence, they can only be qualified as a transitional solution to the overall energy and materials requirements needed by a growing world population. From the long-term perspective, it is predicted that second generation (2G) bio renewable feedstocks derived from lignocellulosic biomass can meet current carbon demands. The estimated annual production of lignocellulosic biomass is  $\sim 2 \times 10^{11}$  metric tons [8]. Typically, lignocellulosic biomass is comprised of about 40-50 % cellulose, 20-30 % hemicellulose and 10-25 % lignin (Figure 1.2.) [9].



**Figure 1.2.** Lignocellulose biomass compositions: cellulose, hemicellulose and lignin.

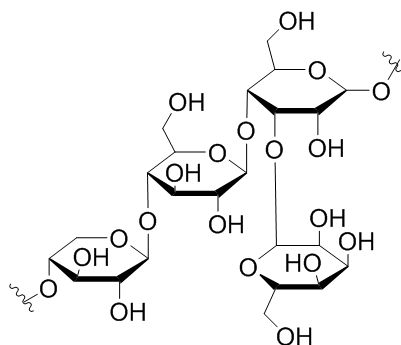
Cellulose is derived from D-glucose units condensed through  $\beta(1 \rightarrow 4)$ -glycosidic bonds (Figure 1.3.). Cellulose is a straight chain polymer adopts an extended and rather stiff rod like conformation, aided by the equatorial conformation of the glucose residue. Cellulose is mainly used to produce paperboard and paper. Smaller

quantities are converted into a wide variety of derivative products such as cellophane and rayon. Conversion of cellulose from energy crops into biofuels such as cellulosic ethanol is under investigation as an alternative fuel source. Cellulose for industrial use is mainly obtained from wood pulp and cotton [10]. It can be broken down into its glucose units by hydrolysis treatment.



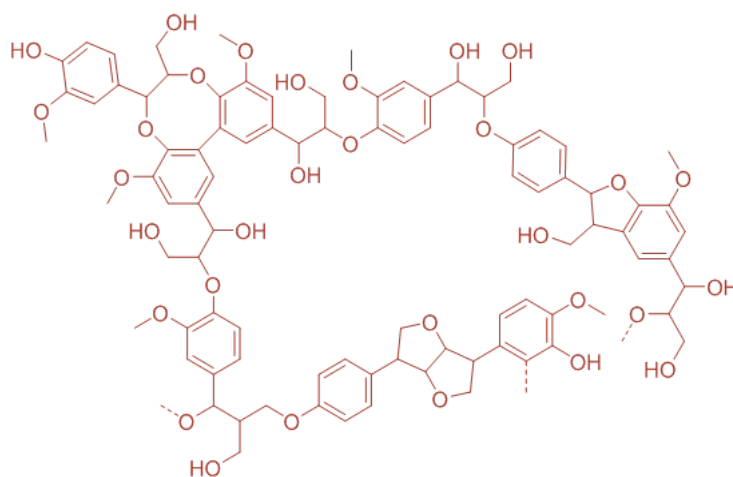
**Figure 1.3.** Structure of Cellulose

Hemicellulose is another component of lignocellulosic biomass. It is any of several heteropolymers (matrix polysaccharides), such as arabinoxylans, present along with cellulose in almost all plant cell walls [11]. Hemicellulose includes xylan, glucuronoxylan, arabinoxylan, glucomannan and xyloglucan (Figure 1.4). These polysaccharides contain many different sugar monomers such as xylose, mannose, galactose, rhamnose and arabinose. Hemicellulose contains most of the D-pentose sugars, and occasionally small amount of L-Sugars as well. Hemicellulose found in the hardwood trees is predominantly xylan with some glucomannan, while in softwood it is mainly rich in galactoglucomannan and contains only a small amount of xylan. Xylan is a polysaccharides made from units of xylose (a pentose sugar). Typically, xylan is present in 10-35 % of the total hemicellulose in hardwood and in softwood they are 10-15 % of the total hemicellulose content. In softwood mannose can be the most abundant sugar. Thus, hemicellulose is rich source of xylose monomers compared to other sugar monomers.

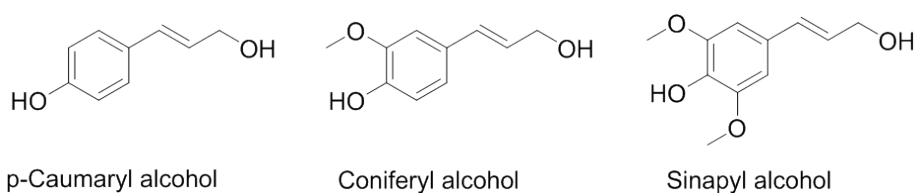


**Figure 1.4.** Structure of Hemicellulose

Lignin is the third component of lignocellulosic biomass which is recalcitrant in nature. It is a class of complex organic polymers that forms important structural materials in the support tissues of vascular plants and some algae [12]. Lignin is a cross-linked racemic macromolecule with molecular masses in excess of 10,000 u (Figure 1.5). It is relatively hydrophobic and aromatic in nature. There are three monolignol monomers, methoxylated to various degrees: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [13] (Figure 1.6). These lignols are incorporated into lignin in the form of the phenylpropanoids *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively [14].



**Figure 1.5.** Possible lignin structure



**Figure 1.6.** Structures of Lignols

## 1.4. Processing of lignocellulosic biomass

Lignocellulose is generally considered as a promising feedstock, as it is abundant, inexpensive and potentially sustainable [15]. However, structural and chemical complexity of lignocellulosic biomass forced to employ various processes to convert it into fuels and chemicals. The conversion of lignocellulosic biomass into higher value added products like fine chemicals or bio-fuel production normally requires a

multi-step processing (pretreatment) that includes gasification, pyrolysis/liquefaction and hydrolysis (Figure 1.7.). Gasification is well-suited for the production of fuels, whereas pyrolysis/liquefaction and hydrolysis provide attractive paths for the production of biomass derivatives sugar monomers and their dehydration products (*e.g.* furan derivatives) which can be subsequently upgraded to useful chemicals and/or fuels for the transportation sector.

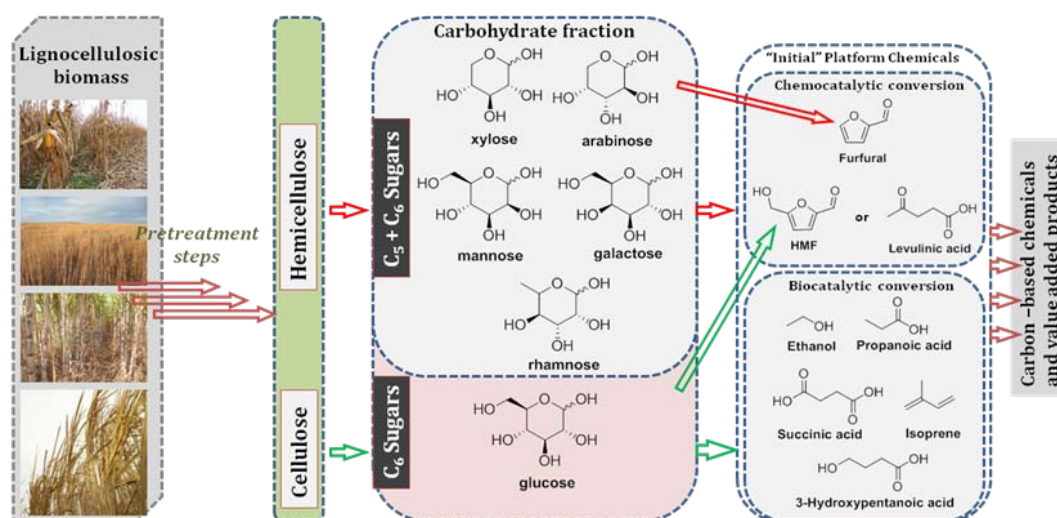


Figure 1.7. Lignocellulose derived initial platform chemicals

To the date hydrolysis treatment is the most studied technique that has extensively been used for delignification of lignocellulosic materials. It is an important method for the recovery of sugar monomers from cellulose and hemicellulose polymers. In this process, cellulose decomposes into glucose while, hemicellulose decomposes into sugar monomers like xylose, galactose, arabinose, mannose and rhamnose. Glucose is a C<sub>6</sub> carbohydrate and it is a cheap and potential source for production of a versatile platform molecule such as 5-(hydroxymethyl)furfural (HMF). On the other hand, xylose is obtained as a major component after pretreatment of hemicellulosic feedstock. Thus, xylose is used as commercial starting material for the bulk production of furfural (an important platform molecule). Although the arabinose is also a potential substrate for furfural production, its contribution to commercial processes is usually negligible, because of its low proportions in the hemicellulose and its slow reaction rate as compared to xylose [16]. Xylose is a sugar, first isolated from wood and named for it as “wood sugar”. Xylose is

classified as a monosaccharide of the aldopentose type, containing five carbon atoms and an aldehyde functional group.

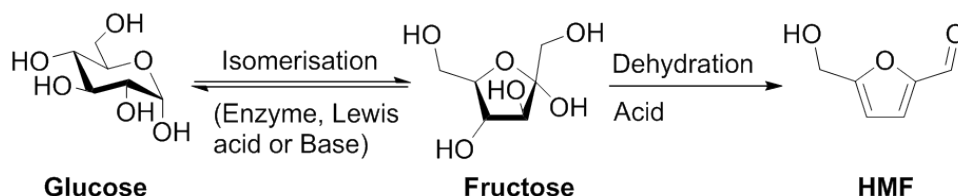
### 1.5. 5-(Hydroxymethyl)furfural (HMF)

5-(Hydroxymethyl)furfural, is a natural substance that occurs in honey, vegetables, coffee and other beverages in small amounts. It is one of the constituents of aroma in liqueurs [17]. HMF is a heterocyclic furanic molecule substituted in 2,5-positions with hydroxide and aldehyde functionalities. The global market for HMF is expected to reach about 125000 million USD by 2022 from 116750 million USD in 2016 [18]. The current price of HMF is estimated between 500 and 1500 USD/kg, which is three times higher than that of currently utilized fossil-based bulk chemicals. A price around 1 USD/kg would be economically acceptable. The most effective protocol to obtain HMF is the multistep acid-catalyzed dehydration of hexoses, preferably fructose, glucose, as well as cellulose, representing the C<sub>6</sub>-fraction of biomass.

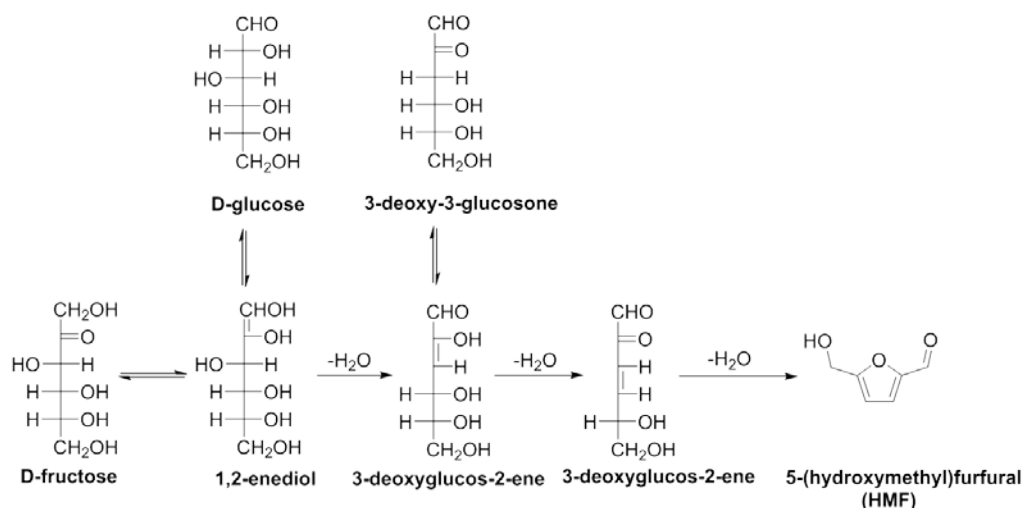
#### 1.5.1. HMF production from mono and disaccharides

Fructose is one of the C<sub>6</sub>-carbohydrates found in honey, tree and vine fruits, flowers, berries, and most root vegetables. Commercially, it is derived from sugar cane, sugar beets and maize. Fructose is a hydrolysis product of sucrose and it could also be produced from glucose *via* isomerisation. The highest reported yields of HMF from hexoses use fructose as the starting reactant. The fructose dehydration reaction has been carried out using homogeneous and heterogeneous catalysts in monophasic and biphasic systems, as well as in ionic liquid solutions. Glucose can be obtained by hydrolysis of carbohydrates such as milk sugar (lactose), cane sugar (sucrose), maltose, cellulose, glycogen, etc. It is commercially manufactured from cornstarch by hydrolysis *via* pressurized steaming at controlled pH in a jet followed by further enzymatic depolymerisation [19]. In principal, cellulose could be hydrolysed to glucose but this process is not yet practiced commercially [20]. Dilute acid hydrolysis and enzymatic hydrolysis are commonly used to liberate the monosaccharide glucose units [21]. The challenge of using glucose as a raw material for the production of HMF is the stability of the glucose ring, which makes the dehydration processing much more difficult. It has been reported that the conversion of glucose into HMF could proceed in two steps: the first isomerization of glucose to

fructose in the presence of an enzyme, Lewis acid or base catalysts (Scheme 1.1), followed by the dehydration of fructose to HMF. The reaction pathway for glucose to HMF is presented in Scheme 1.2.



**Scheme 1.1.** Schematic representation of the glucose isomerization to fructose using enzyme, Lewis acid or base catalysts and the fructose dehydration to HMF with acid catalysts



**Scheme 1.2.** Reaction pathway for dehydration of hexoses to HMF

The production of HMF from mono- and polysaccharides, including pre-treated biomass substrates is reported using homogeneous mineral acids, Brønsted acidic ionic liquids (IL), Lewis acidic metal halides and recyclable heterogeneous catalysts in pure organic or aqueous solvents has been reported [22]. Besides the effectiveness of the catalyst for high yield and high selective in HMF production, solvents also play an important role in enhancing HMF yield, purity and ease of separation to make the process economically and environmentally competitive. Although the chemistry and engineering aspects of HMF production and its effective separation technology have advanced in recent years, most research efforts over the past decade were limited to achieving higher carbohydrate conversions in high boiling point



organic solvents such as dimethylsulfoxide (DMSO), N,N-dimethylformide (DMF), N,N-dimethylacetamide (DMA), methyl isobutyl ketone (MIBK) and ILs. Among these, DMSO is the most studied solvent along with variety of catalytic systems for the conversion of mono-, di-, polysaccharides and cellulose into HMF [23]. The use of high boiling point solvents such as DMSO and DMF also pose similar challenges of HMF separation thus these processes are economically not feasible on a commercial scale. Additionally, high concentrations of oligomeric species (humins) are also formed as by-products in these organic solvent mediated dehydration reactions [24]. On the other hand, IL mediated processes are expensive and separation of HMF from high boiling ILs is energy intensive. In addition to that, ILs gets deactivated by water formed during the carbohydrate dehydration reaction. To overcome these challenges, HMF production is attempted in pure water by Zhu and co-workers using  $\text{ZnCl}_2$  from mono- and disaccharides [25]. However, HMF production in pure water is not a viable option due to the slow rate of HMF formation and rapid rehydration to furan ring opening products such as levulinic acid and formic acid [26]. The use of monophasic solvent system including high boiling point organic solvents, ILs or pure water has several disadvantages. Therefore, utilization of biphasic reaction systems including reactive aqueous phase and organic phase for acid catalyzed dehydration of carbohydrates to HMF has got tremendous attention (Table 1.1). The organic layer of the biphasic system acts as an extracting phase for HMF, immediately after its formation in the reactive aqueous phase. Thus, ultimately HMF would have lower concentration in the aqueous phase which avoids/limits the rate of side reactions and thereby improves the HMF yields [27]. This method allows easy separation and reusability of the reactive aqueous phase containing spent homogeneous or heterogeneous catalysts. The partition coefficient (R), which is the ratio of HMF in the organic phase to that in the aqueous phase, is an important parameter in determining overall effectiveness of the biphasic media. Higher partitioning of HMF into the organic layer improves effective extraction and hence increases HMF selectivity. Besides the nature of the organic solvents in determining effective extraction, the presence of inorganic salt, *e.g.* NaCl, in the aqueous phase also plays an important role in improving the partition coefficient of HMF. The distinct benefits of the biphasic reaction systems are: (i) high HMF yield



and selectivity by preventing undesired side reactions, (ii) easy separation and reusability of the reactive phase containing spent catalysts and (iii) cost-effective separation of the desired product from lower boiling point extracting solvents. Much more efforts being made over the past few years describe the beneficial effect derived from the choice of organic phase on homogeneous and heterogeneous catalyzed conversions of carbohydrates and lignocellulosic biomass.

**Table 1.1.** Dehydration of mono and disaccharides to 5-(hydroxymethyl)furfural in biphasic solvent system

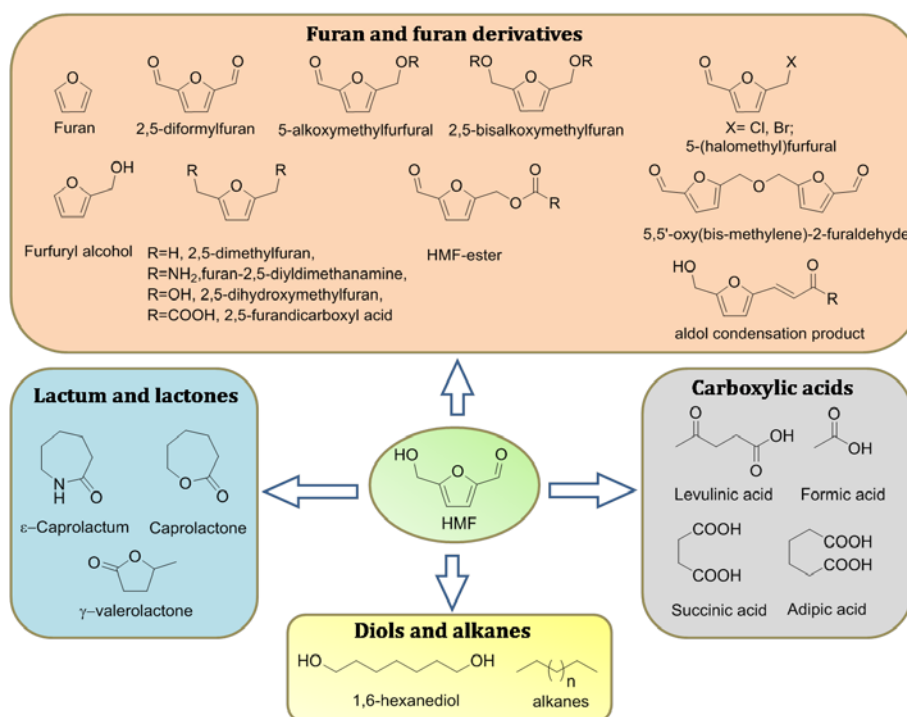
Substrate	Catalyst	Biphasic system	T [°C]	t	Yield [%]	ref
Glucose	C <sub>6</sub> H <sub>4</sub> (SO <sub>3</sub> H)(NH <sub>2</sub> )	water: DMSO: 2-BuOH: MIBK	150	1 h	78	[28b]
Glucose	NbPO	water: MIBK	135	400 min	55	[29a]
Fructose	LpSnP-1	water: MIBK	150	20 min	77	[29b]
Glucose					50	
Sucrose					51	
Fructose	No catalyst	water: MIBK	160	2 h	74	[29c]
Glucose	Al-MCM-41	water: MIBK	195	150 min	63	[29d]
Fructose	SO <sub>3</sub> H-MCM-41	water: MIBK	190	80 min	83	[29e]
Fructose	PA-PBI	water: MIBK	180	1h	71	[29f]
Fructose	HCl	water: MIBK	180		89	[29g]
Glucose	AlCl <sub>3</sub>	water/CHCl: MIBK	150	15 min	70	[29h]
Glucose	PBnNH <sub>3</sub> Cl	water: DMSO: MIBK	140	12h	53	[29i]
Sucrose				11h	56	
Glucose	TiO <sub>2</sub>	water: <i>n</i> -BuOH	175	3h	81	[30a]
Fructose	(C <sub>16</sub> )H <sub>4</sub> PW <sub>11</sub> Ti	water: <i>n</i> -BuOH	130	90 min	75.6	[30b]
Glucose					77.2	
Sucrose					66.4	
Fructose	WO <sub>3</sub> -Ta <sub>2</sub> O <sub>5</sub>	water: 2-BuOH	180	90 min	62	[30c]
Fructose	HCl	water: <i>n</i> -BuOH	170	10-60 min	82	[30d]
Glucose	AlCl <sub>3</sub> + HCl	water: <i>sec</i> -butyl phenol	170	40 min	97 (62) <sup>a</sup>	[31a]
Glucose	Al(OTf) <sub>3</sub>	water: <i>sec</i> -butyl phenol	160	25 min	45	[31b]
Glucose	AlCl <sub>3</sub> + HCl + NaCl	water: <i>sec</i> -butyl phenol	170		67	[31c]
		water: PG			58	
Fructose	SBA-15-PrSO <sub>3</sub> H	water: CH <sub>3</sub> NO <sub>2</sub>	140	30 min	70	[32a]
Fructose	[MBClM][SO <sub>3</sub> Cl]	water: acetonitrile	80	4h	89	[32b]
Glucose	CrCl <sub>3</sub> + KBr	water: Toluene + acetone	140	2h	47	[32c]
Fructose	Ce(PO <sub>4</sub> ) <sub>1.5</sub> (H <sub>2</sub> O) (H <sub>3</sub> O) <sub>0.5</sub> (H <sub>2</sub> O) <sub>0.5</sub>	water: Dimethyl carbonate	150	6h	70	[32d]
Fructose	BHC	CHCl/BHC: MIBK	110	1h	84	[32e]
Fructose	PTSA-POM	water: GVL	130	30 min	78	[32f]
Glucose	TiO <sub>2</sub> -ZrO <sub>2</sub> /Amberlyst-15	water: THF	180	3 h	86	[32g]
Sucrose					86.5	
Glucose	AlSiO-20	water: THF + NaCl	160	90 min	63.1	[32h]
Sucrose					49	
Fructose	CrPO <sub>4</sub>	water: THF + NaCl	140	15 min	83	[32i]
Glucose				30 min	63	
Fructose	Sn-Mont	water: DMSO: THF + NaCl	160	3 h	78.8	[32j]
Glucose					53.5	
Sucrose					43.6	
Glucose	Nb <sub>0.2</sub> WO <sub>3</sub>	water: THF	120	3 h	59	[32k]
Fructose	Beta-Cal750	water: DMSO: THF	180	3 h	55 <sup>s</sup>	[32l]
Glucose					66 <sup>s</sup>	
Sucrose					67 <sup>s</sup>	

[a] Isolated yield; [S] selectivity

To address the limitation of the HMF production due to poor product selectivity and separation issues, researchers have designed a modified biphasic reaction system using high boiling point polar aprotic solvents (*e.g.* MIBK, 2-BuOH etc.) modified aqueous medium as a reactive phase [28]. MIBK forms a biphasic system with water, was also widely studied as an extracting agent for carbohydrate conversion [29]. Alcohols, preferably butanols, which could easily be obtained from biomass, were also applied as extracting compounds in biphasic systems [30]. Lignin-based extractive solvents containing alkyl substituted phenolics [*i.e.* *sec*-butylphenol (SBP) or propyl guaiacol (PG)] and water mixtures were also introduced into transformation of C<sub>6</sub> sugars to HMF [31]. Several groups performed solvent screening focusing on a combination of common organic solvents (*e.g.* Acetonitrile, Tetrahydrofuran *etc.*) and/or ionic liquids to form biphasic systems for hexose transformation [32].

### 1.5.2. Carbohydrates and HMF to fuels and chemicals

Although, full commercial production of the HMF from biomass is not being practiced, extensive research is being focused in this direction. Nevertheless, as 5-HMF is a very versatile platform molecule, it is highly prudent to be equipped with process options for HMF utilization for the production of commodity chemicals must since commercial availability of HMF is going to be inevitable in near future. HMF is a  $\alpha,\omega$ -bifunctional molecule with aldehyde substituents at C-2 position and hydroxymethyl substituent at C-5 positions. Aldehyde functionality can be oxidised to carboxylic acid or reduced to alcohol or it can undergo carbon upgradation through condensation (C-C bond formation) reactions. Hydroxymethyl functionality of HMF could be oxidised to aldehydes/carboxylic acids or it can be produce ethers with alcohols or esters with carboxylic acids. An unsaturated aromatic ring of HMF could be converted into saturated ring through hydrogenation. The heterocyclic structure of furans can be found in an array of biologically active molecules with pharmaceutical applications. It was identified as a high potential initial C<sub>6</sub>-platform chemical serving biomass-based alternatives for polymers, pharmaceuticals, agrochemicals, flavors and fragrances, macro- and heterocycles, and natural products as well as it could be a precursor for fuel components [33]. The most important HMF-based chemicals are summarized on Figure 1.8.



**Figure 1.8.** Utilization of 5-(hydroxymethyl)furfural to advanced chemicals and fuel additives

### 1.5.2.1. C-C bond forming reactions

The aldehyde functionality of HMF is susceptible for carbon upgradation process via C-C bond forming reactions such as aldol [34] and furoin condensation,[35] hydroxyalkylation-alkylation [36] coupling with isoprene [37] and Baylis–Hillman reaction [38] (Scheme 1.3).

**1.5.2.1.1. Aldol condensation:** Aldol condensation is one of the most important C-C bond formation reactions of HMF for synthesis of fine chemicals, plasticizers and fragrances [34a]. The Mg-Al-oxide and Cu/MgAl<sub>2</sub>O<sub>4</sub> catalyst were explored for aldol condensation of HMF with acetone [34a, b].

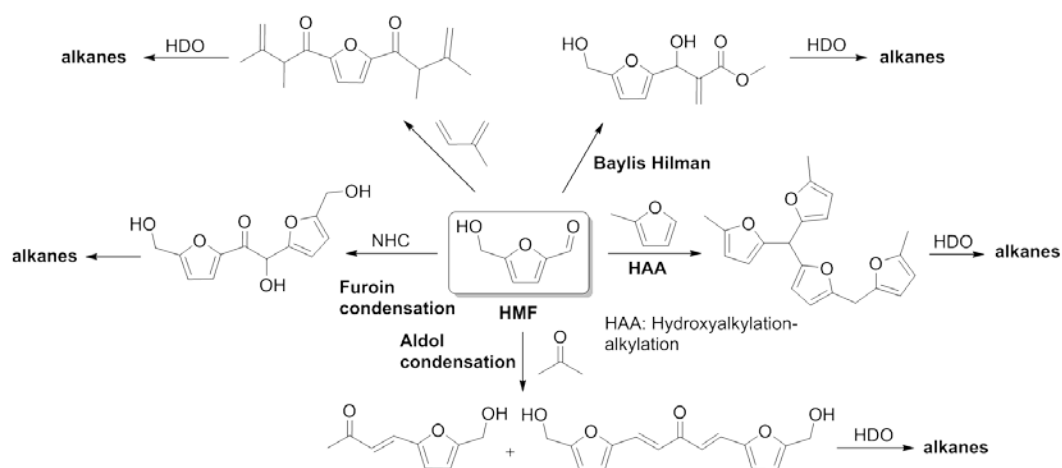
**1.5.2.1.2. Furoin condensation:** In 2012 Liu et al, disclosed an efficient method for HMF upgradation to self-coupling product with 98 % yield using ionic liquid and organocatalyst [35a]. Immediately, after a year they have not only improved the process for self coupling of HMF but also attempted further processing to alkanes [35b].

**1.5.2.1.3. Hydroxyalkylation-alkylation (HAA):** In 2014, Balakrishnan et al. reported sulfonic acid functionalized silica solid acid catalyst for HAA reaction of 2-methylfuran with HMF to produce polyfuranic compound [36a]. In the same year, same author reported ring hydrogenation of same kind of polyfuranic compounds to fuel additives using  $\text{Pd/IL}(\text{PF}_6)^-\text{SiO}_2$  catalyst under  $\text{H}_2$  pressure [36b].

**1.5.2.1.4. Coupling with isoprene:** Nicklaus et al. reacted HMF with isoprene in presence of ruthenium catalyst to afford a double coupling product with 48 % isolated yield [37].

**1.5.2.1.5. Baylis–Hillman Reaction:** In 2010, Huber et al. performed a Baylis–Hillman reaction between HMF and methyl acrylate with an aqueous  $\text{NMe}_3$  and DABCO to obtain good yield of coupling product [38].

All above reactions were performed by utilized pure HMF; the crude HMF prepared from carbohydrates is also not yet explored for above application. The cheap and abundant HMF precursors such as glucose, fructose or sucrose can undergo carbon upgradation *via* direct/integrated approach.



**Scheme 1.3.** C-C bond forming reactions of HMF

### 1.5.2.2. Hydrogenation and hydrogenolysis reactions

In these processes, important polymer precursors such as 2,5-bis(hydroxymethyl)furan (BHMF) and 2,5-bis(hydroxymethyl)tetrahydrofuran and

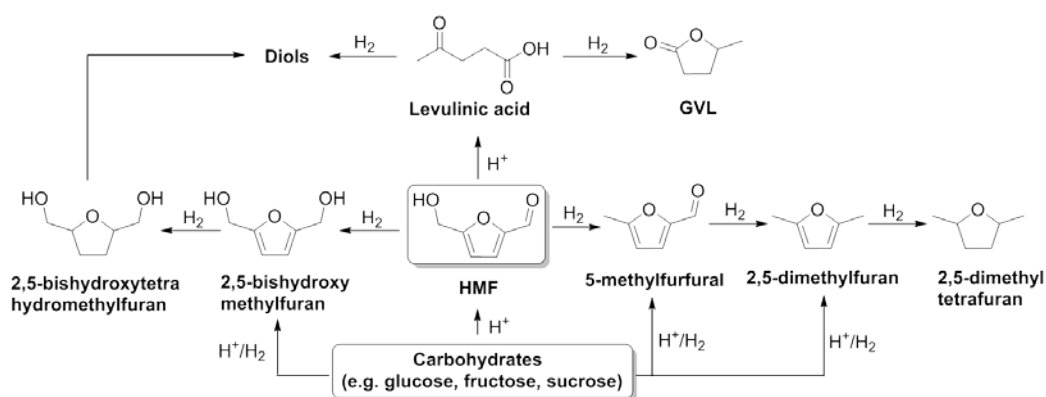
fuel components such as 2,5-dimethylfuran (2,5-DMF) and  $\gamma$ -valerolactone (GVL) can be produced from HMF (Scheme 1.4.).

**1.5.2.2.1. 2,5-bis(hydroxymethyl)furan (BHMF):** It is used as a monomer for the synthesis of heat insulating material,[39] resins, crown ethers, [40] shape memory and self-healing polymers [41]. The 1,6-hexanediol, an important polymer precursor can also be prepared from BHMF [41]. Commercially, BHMF is produced from HMF *via* Cannizzaro reaction [42]. During the course of reaction, 5-(hydroxymethyl)furanoic acid (HMFA) is also formed in an equimolar amount, which is difficult to separate from the reaction mass. For the selective production of BHMF from HMF the hydrogenation performed using noble (*e.g.* Pt/MCM-41[43] and Ru/Co<sub>3</sub>O<sub>4</sub> [44]) and non-noble (*e.g.* Cu–ZnO [45], ZrO(OH)<sub>2</sub> [46] and Fe<sub>3</sub>O<sub>4</sub>@HAP [47] catalysts with external hydrogen or *via* transfer hydrogenation. In the pioneered work of the Thananattathanachon et al, they showed that, BHMF can be directly produced from a cheap and abundant carbohydrate such as fructose using homogeneous Ir catalyst in formic acid as hydrogen donor [48]. However, selective production of BHMF *via* direct/integrated way from carbohydrates and using heterogeneous catalyst system is not yet explored.

**1.5.2.2.2. 5-(methyl)furfural (MF):** It is a useful intermediate for the production of pharmaceuticals, chemicals for agriculture, perfumes, flavoring component [50] and other applications [49]. It is also considered a potential anti-tumor agent. [51] MF is produced on industrial scale by formylation of 5-methylfuran with N,N-dimethylformamide and phosphorus oxychloride or phosgene [52]. In this process an excess amount of expensive and poisonous reagents were used. MF can be produced from biomass-derived carbohydrates (hexoses) *via* a two-step process. In the first step, 5-(chloromethyl)furfural (CMF) is obtained from carbohydrates in high concentrations of chloride ion and then MF is obtained in 98 % yield by hydrogenation of CMF with Pd catalyst under H<sub>2</sub> pressure [53]. In another report, a convenient method is presented for conversion of biomass-derived carbohydrates directly to MF using HI, RuCl<sub>3</sub> or Pd/C under hydrogen pressure [54]. Besides, huge importance of the MF, it's synthesis is attempted by only few researchers using

homogeneous catalyst systems. The researchers working in heterogeneous catalysis can have opportunity to do further development in this area.

**1.5.2.2.3. 2,5-dimethylfuran (DMF):** It is particularly attractive because of its nearly ideal boiling point (92–94 °C), its high energy density (30 kJ cm<sup>-3</sup>), and its high research octane number (RON=119) [55]. Furthermore it is immiscible with water and is easier to blend with gasoline. Several noble metal-based catalysts such as CuRu/C, [55] Ru/Co<sub>3</sub>O<sub>4</sub>, [56] Ru/CoFe-LDO, [57] Ru–Na–Y, [58] Pt–Co/C [59] and Pd/C [60] were commonly used for pure HMF conversion into DMF. Binder et al. utilized crude HMF obtained from corn stover for hydrogenolysis to DMF with a 49 % yield over CuRu/C type of catalyst [61]. Upare et al. successfully produced DMF from fructose with a 92 % yield in 1-butanol at 240 °C over a combination of Amberlyst-15 and Ru–Sn/ZnO catalysts [62]. In another attempt, 22% yield of DMF was obtained from fructose over ZnCl<sub>2</sub> and Pd/C catalysts [63]. Xiang et al. utilized HY and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> for fructose dehydration-hydrogenolysis into DMF with 40.6 % yield [64]. Recently, Wei et al. have proposed a direct conversion of fructose to DMF with a 66 % yield using a combination of AlCl<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> and Ru/C catalysts [65]. Recently, Insyani et al. utilized fructose and glucose for direct conversion into DMF with 70.5 and 45.3% yields, respectively using a bifunctional catalyst, Pd/Uio-66@SGO [66]. The DMF production from pure HMF is well explored using heterogeneous catalysts. In case of fructose conversion to DMF, most of the attempts were accomplished by using homogeneous catalyst systems which are non-recyclable, hazardous and harmful to environment.



**Scheme 1.4.** Hydrogenation and hydrogenolysis of HMF and carbohydrates

Uptil now only a single report is available for fructose as well as glucose conversion to DMF using heterogeneous catalyst. Further development in this area is needed by utilizing real biomass and carbohydrates as a feed with heterogeneous catalyst system.

### 1.5.2.3. Oxidation reactions

2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA) are the important oxidation products of HMF (Scheme 1.5).

**1.5.2.3.1. 2,5-diformylfuran (DFF):** Selective oxidation of the hydroxyl group of HMF into 2,5-diformylfuran (DFF), has been attracting much attention due to its versatile uses as a monomers, an intermediate of pharmaceuticals, antifungal agents and ligands [67]. DFF synthesis from HMF had been extensively studied using classical oxidants (*e.g.* NaOCl, [68] BaMnO<sub>4</sub> [69] and pyridinium chlorochromate (PCC)[70]. In recent years, there has been growing attention on the synthesis of DFF from pure HMF by oxidation with molecular oxygen catalyzed by heterogeneous or homogeneous metal catalysts such as Co/Ce/Ru,[71] Ru,[72] Cu,[73] Cu/V,[74] Mn,[75] Mo/V,[76] and V[77]. These catalysts often give a relatively high yield of DFF; however, the catalysts applied in this transformation are usually expensive, toxic, and difficult to remove [78]. Lv et al. reported that, graphene oxide (GO) and N<sub>2</sub> doped GO along with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as an efficient carbocatalyst for selective oxidation of HMF into DFF [79]. Recently, a photocatalyst Nb<sub>2</sub>O<sub>5</sub>-800 showed 90.6 % selectivity to DFF, but with only 20 % conversion of HMF [80]. The combination of benzoic acid and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) shown maximum 86.7 % conversion of HMF with 77.8 % DFF yield [81]. However, the production of DFF from pure HMF is an uneconomical and energy-intensive process. The direct synthesis of DFF from carbohydrates provides an alternative and cheap approach *via* acid catalyzed dehydration of carbohydrates to HMF and oxidation of crude HMF to DFF using a combination of acid and oxidation catalysts. For instance, H-form cation-exchange resin and V-based catalysts,[82] Amberlyst-15 + Ru/HT,[83] CrCl<sub>3</sub>·6H<sub>2</sub>O/NaBr + NaVO<sub>3</sub>·2H<sub>2</sub>O,[84] Fe<sub>3</sub>O<sub>4</sub>-SBA-SO<sub>3</sub>H + K-OMS-2,[85] and Amberlyst-15 + polymer-supported 2-iodoxybenzoic acid (IBX) amide[86] have been investigated

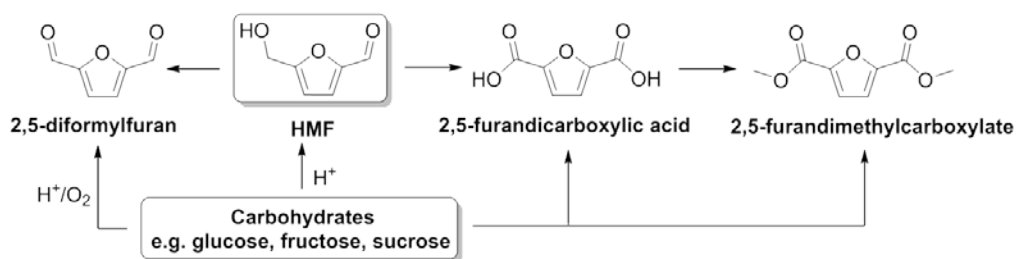


for the one-pot, two-step production of DFF from fructose. However, an oxidation catalyst promoted the oxidative degradation of fructose to humins. Thus, to obtain the highest yield of DFF the oxidation catalyst must be added into the reaction after HMF is formed by acid catalyzed dehydration of fructose. In this direction, for one-pot, one-step fructose conversion to DFF, several other authors have reported single bifunctional catalysts such as GO,[87] PMA–MIL-101,[88] HPMoV,[89] NaBr,[90] Cs<sub>3</sub>HPMo<sub>11</sub>VO<sub>40</sub> [91] Cs<sub>0.5</sub>H<sub>2.5</sub>PMo<sub>12</sub> [92]. There are only few catalysts combinations (CrCl<sub>3</sub>·6H<sub>2</sub>O/NaBr + NaVO<sub>3</sub>·2H<sub>2</sub>O, [84] Hydrotalcite + Amberlyst-15 + Ru/HT [93] and AlCl<sub>3</sub>·6H<sub>2</sub>O/NaBr + MVO<sub>3</sub> [94]) were employed for glucose conversion to DFF. Huge efforts were putted by the researchers for the production of DFF from HMF and fructose. But, there are very few reports are available starting from cheap carbohydrates such as glucose. From the economic point of view further investigations need to be conducted in this area.

**1.5.2.3.2. 2,5-furandicarboxylic acid (FDCA):** It is an important renewable building block, as it has a potential to substitute the terephthalic acid for production of polyesters [95]. Polyethylene furanoate (PEF), made from FDCA and ethylene glycol, has similar physical, mechanical and chemical properties to the petroleum-based analog, polyethylene terephthalate (PET) [96]. FDCA is produced through an oxidation of HMF. Several precious metal supported catalysts have been investigated for the FDCA production from HMF under oxygen pressure and in presence of excess base. For instance, Au/CeO<sub>2</sub> or Au/TiO<sub>2</sub>, [97] Au-Cu/TiO<sub>2</sub>, [98] Pt/C or Pd/C or Au/TiO<sub>2</sub>, [99] 2%Pd/HT-5 or 2%Pd/HT-6, [100] Au-Pd/ZOC, [101] Pt/Ce<sub>0.8</sub>Bi<sub>0.2</sub>O<sub>2-δ</sub> [102] and Fe<sub>3</sub>O<sub>4</sub>@C@Pt [103]. Recently, few researchers have addressed this problem and FDCA was produced in excellent yields over catalysts such as Pt/CNT, [104] Au/HT-AC [105] and Fe<sup>III</sup>-porphyrin complex supported on porous carbon materials [106] without using a base. Although, FDCA could be produced from HMF with nearly quantitative yields, the cost of HMF is high. Carbohydrates such as fructose, glucose, and cellulose are much cheaper and more abundant than HMF. Therefore, it is more attractive to carry out the oxidative conversion of carbohydrates into FDCA by one-pot reaction over multiple functional catalysts combining acidic and metal sites. In 2000, Kröger and co-workers realized the one-pot conversion of fructose to FDCA in water/methyl isobutyl ketone (MIBK)



using membrane reactor [107]. Fructose first dehydrated into HMF in water with a Lewatit SPC108 as the solid acid catalyst. Then HMF was extracted into MIBK, followed by the oxidation into FDCA over metal catalysts. This process produced a maximum 25 % yield of FDCA. Later, Ribeiro and Schuchardt reported a 99 % selectivity of FDCA and 72 % conversion of fructose over  $\text{Co}(\text{acac})_3$  encapsulated in sol-gel silica catalyst [108]. Zhang and co-workers reported a 83 % yield of FDCA fructose using HCl and Au/HT catalyst [109]. Later, they have used a combination of polybenzyl ammonium chloride resins and Au/HT to afford 72 % yield of FDCA [110]. More recently, triphasic reactor that can convert sugars into FDCA in a one-pot process is reported [111]. A two-step strategy was applied for the synthesis of FDCA with 59.8 % yield from fructose using  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$  as a acid catalyst and *t*-BuOOH over nano- $\text{Fe}_3\text{O}_4\text{-CoO}_x$  as oxidation catalyst.[112] Although, the direct conversion of carbohydrates into FDCA is much more attractive, but the current results are not very much satisfactory. The FDCA production is more focused on carbohydrates such as fructose. Much more work should be paid to the design of novel catalysts with multiple catalytic sites and technology to avoid side reactions. The conversion of carbohydrates such as glucose or even cellulose into FDCA should also be attempted.



**Scheme 1.5.** Oxidation of HMF and carbohydrates

#### 1.5.2.4. Etherification reactions

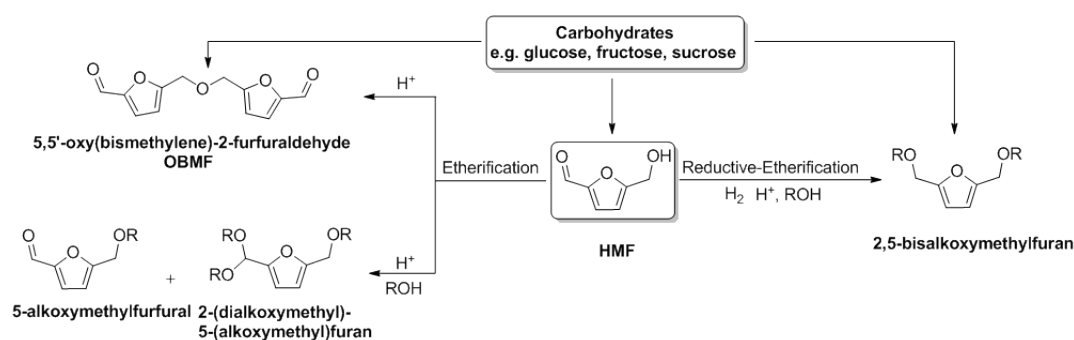
In recent years, processing HMF into drop-in biofuel candidates has attracted much interest. Ethers of HMF have received tremendous attention as they are potential biofuel candidates [113] and flavoring agents [114].

**1.5.2.4.1. 5-(alkoxymethyl)furfural (AMF):** HMF ethers are considered to be the most potential biofuel candidates. One of the HMF ether derivatives such 5-(ethoxymethyl)furfural (EMF) is considered to be an excellent diesel additive. EMF has a high energy density of 8.7 kWh/L, which is similar to gasoline (8.8 kWh/L), nearly as good as diesel (9.7 kWh/L).[115] EMF has been used as a blend in commercial diesel in engine tests, and EMF generated positive results with a significant reduction of soot (fine particulates) and a reduction of the SO<sub>x</sub> emissions [116]. In addition to that, EMF has been widely established as a flavor and aroma additive in wines and beers [114]. Therefore, there is a great interest in the synthesis of EMF from renewable resources. EMF was first synthesized by a simple nucleophilic substitution reaction between 5-(chloromethyl)furfural (CMF) and ethanol.[115] Following this, the preparation, EMF was synthesized from carbohydrates and HMF using a variety of acids such as metal halides,[115, 116] mineral acids,[117] organic acids and resins,[118] solid acids, [119] and acidic ionic liquids [120]. Interestingly, ethers of HMF obtained from branched alcohols have superior blending properties as compared to ethers obtained from linear analogues. For example, up to 40:60 v/v 5-(tert-butoxymethyl)furfural (*t*-BMF)/diesel did not show any mixing or flocculation problems and leads to a substantial increase in the cetane number and does not decrease the oxidation stability of commercial diesel.[121] The preparation of *t*-BMF was achieved by reacting HMF with *tert*-butanol in the presence of montmorillonite K10 and zeolite HY [121]. However, the major concern about AMF is the presence of an aldehyde functionality, which reduces the stability of the molecule. Hence, it is desirable to first hydrogenate the aldehyde functionality to an alcohol [122] followed by subsequent etherification to form stable 2,5-bis(alkoxymethyl)furan [123].

**1.5.2.4.2. 2,5-bis(alkoxymethyl)furan (BAMF):** The two ether linkages in the BAMF is enhancing its miscibility in commercial diesel and lowering of the crystallization temperature compared with that of AMF [124]. Therefore Balakrishnan et al., attempted synthesis of these types of ethers from HMF /Fructose using combination of Pt (noble metal) and acid catalysts under external H<sub>2</sub> [125]. However, use of unsafe, non-renewable and high cost H<sub>2</sub> is deterring factors for its widespread usage. While, few others have used zeolite based catalysts for BAMF

production from HMF through transfer hydrogenation–etherification in secondary alcohols [126]. However, the certain amount of HF is generally used during preparation of zeolites. The simple and non hazardous catalysts system and high yield of BAMF without using external H<sub>2</sub> could improve the economy of process.

**1.5.2.4.3. 5,5'-oxy(bis-methylene)-2-furaldehyde (OBMF):** It is used for making multiheteromacrocycles (16-crown-6), polyurethanes, polyamides and imine polymers [127]. OBMF and 1, 4-diaminobenzene gives a polymer with high glass transition temperature, thermal and electrical conductivities and having solubility in polar solvents [128]. OBMF possesses wide range of anti-virus, anti-tuberculosis and anti-oxidant activity [129]. OBMF can be synthesized by a conventional Williamson reaction between HMF and CMF giving only 42.7 % yield [129]. Thermal dehydration of HMF in DMSO also gives OBMF while, carbohydrates conversion using BF<sub>3</sub>·OEt<sub>2</sub>/DMSO gives low to moderate yield of OBMF [130]. Large amount of waste is generated when homogeneous acids or bases are used [130b, 131]. Therefore, solid acids such as Amberlite IR120 and Amberlyst-15 were also explored however; they have a lower thermal stability especially, during their regeneration step [132]. This was overcome by Casanova et al. with an excellent performance of Al-MCM-41 [133]. Recently, graphene oxide was explored for this reaction to give 86 % yield of OBMF in dichloromethane however; dichloromethane exerts a high vapour pressure under reaction conditions [134]. Recently, Paez et al. reported preyssler heteropolyacids for OBMF production from HMF, but catalyst doesn't show an efficient recyclability [135]. More recently, Amarasekara et al. converted fructose to OBMF with 75% yield over Dowex 50 W X8 in DMSO by keeping reaction flask open [136]. Water molecules produced after dehydration of carbohydrates is the major hurdle for the production of OBMF from carbohydrates. The technology with continuous removal of water after dehydration of carbohydrates will be helpful for the production of the OBMF from carbohydrates.

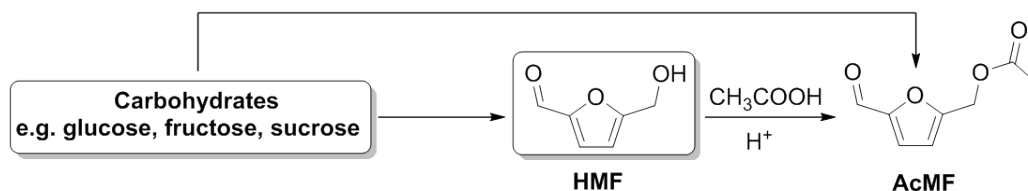


**Scheme 1.6.** Etherification and reductive-etherification of HMF and carbohydrates

### 1.5.2.5. Esterification reaction

**1.5.2.5.1. 5-(acetoxymethyl)furfural (AcMF):** It is a HMF-based chemical with diverse properties, such as fuel blending agents,[137] additives for bulk chemicals, [138] polymer precursor, [138] natural surfactants,[138] fungicides [138] and as building blocks of therapeutic agents for osteoporosis or protein tyrosine phosphatase 1B (PTP1B) inhibitors [139]. AcMF is more stable than HMF and offer some important advantages over HMF for industrial production. Compared with the HMF, their ester derivatives are hydrophobic, less reactive, more stable, readily isolable from the aqueous reaction mixture and potentially making them even more useful than HMF itself. Several reports on the production of AcMF are available using various starting materials. For example, AcMF was obtained in moderate to good yields from CMF and acetic acid in the presence  $K_2CO_3$  [140]. Recently, Kang et al. converted CMF into AcMF with 84 % yield using alkyl ammonium acetate salt wherein acetate anion acted as an acetylating agent [141]. Krystof et al. reported lipase catalyst for the production of HMF esters in good yields from HMF [138]. However, use of expensive enzymes would not be feasible for the commercial production of AcMF. Making AcMF directly from carbohydrates without isolating HMF is much more rewarding. Several patents described the production of HMF-ester (including AcMF), by acid-catalyzed dehydration of carbohydrates [142]. For example, 5.1 % yield of AcMF was obtained when glucose dehydration was performed in a mixture of EmimCl and Acetic acid over  $CrCl_2$  catalyst [142] Sanborn et al. produced AcMF in 41 % yield from fructose by using Amberlyst-15 catalyst [143]. However in the above cases, low to moderate yield of AcMF was obtained. Recently, an improved yield of 36 % of AcMF was reported from cellulose

acetate using stoichiometric amount of  $\text{H}_2\text{SO}_4$  [144]. Nevertheless, further development is necessary to replace homogeneous catalyst with improved yield of AcMF directly from carbohydrates.



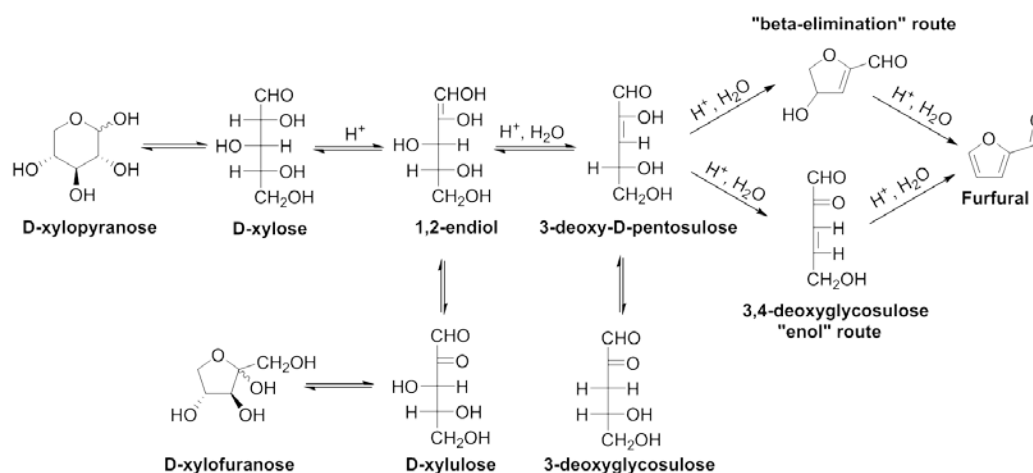
**Scheme 1.7.** Esterification of HMF and carbohydrates

## 1.6 Furfural

Furfural was first isolated as an aromatic odour reminiscent of almonds in 1831 by J. W. Döbereiner. In 1845, G. Fownes prepared the same substance with a molecular formula  $\text{C}_5\text{H}_4\text{O}_2$  and named it furfural. Furfural is the most common industrial chemical derived from lignocellulosic biomass, with an annual production volume of more than 200 000 tonnes [145]. Recently, the furfural production is exclusively based on the acid-catalyzed conversion of pentosane sugars present in agricultural and forestry residues [146]. The main producers of furfural are the Republic of South Africa (ca. 20 kTonne/year), Dominican Republic (32 kTonne/year), and China (200 kTonne/year), representing 90 % of the global capacity [147]. The price of furfural has shown significant fluctuations of USD 500 to 1500 per metric ton since 2000. However, due to the low feedstock costs accompanied by continuously increased capacity in China, a slight price drop has been observed for the past decade. Recently, the market price is ca. 1000 USD compared with 1740 USD/Tonne in 1990 and 1760 USD/Tonne for furfuryl alcohol. Both USA and EU have increased the import rate of furfural from China to minimize differences in prices; however, the market currently depends on China's supply [148]. According to a report published by Allied Market Research, the global furfural market is expected to reach 1434 million USD by 2022 from 663 million USD in 2015 [149]. The first commercial production of furfural was discovered at the Quaker Oats Company in 1921 [150]. At that time the company had obtained vast quantities of oat hulls from the manufacture of oatmeal. Quaker Oats produced furfural in 50 % yield (based on xylan) from hulls by treating them with dilute sulfuric acid and steam pressure [151].

### 1.6.1. Furfural production from C<sub>5</sub> carbohydrates

The dehydration of C<sub>5</sub> sugars can yield furfural, which is commercially produced as a platform chemical having applications ranging from solvents to resins and fuel additives [152].



**Scheme 1.8.** Proposed mechanism for xylose dehydration *via* enolization.

Since xylose is produced as an aqueous stream its conversion to furfural in water would be preferable. After this initial discovery, many others have examined the conversion of pentoses (*e.g.* xylose) into furfural [153]. In addition to these studies in water, numerous other studies have been explored the potential of the dehydration of xylose to furfural in various media and using Lewis or Brønsted solid acids as catalysts (Table 1.2). Concerning the catalyst's activity and selectivity, it can generally be stated that catalysts with a higher number of Lewis-acid sites were more effective for the formation of furfural, but its selectivity strongly depended on the Brønsted-acid sites [155]. Heterogeneous catalysis combined with facile catalyst/product separation is of utmost importance due to its potential applications in greener and economically viable processes at an industrial scale. Thus, another elegant approach is the application of combined solid acid catalyst having Lewis and Brønsted acidity to accelerate pentose isomerization and conversion, respectively. By combining dual catalysts with a biphasic solvent system, it could result in facile product separation and catalyst recycling. An extraction of furfural is easier in toluene therefore it is the most utilized organic solvent in a biphasic reaction system

for the production of furfural over heterogeneous catalysts [156]. Other bioderived solvents such as GVL,[157] MeTHF [158] and SBP [159] were also employed.

**Table 1.2** Dehydration of C<sub>5</sub>-carbohydrates to furfural in biphasic solvent system

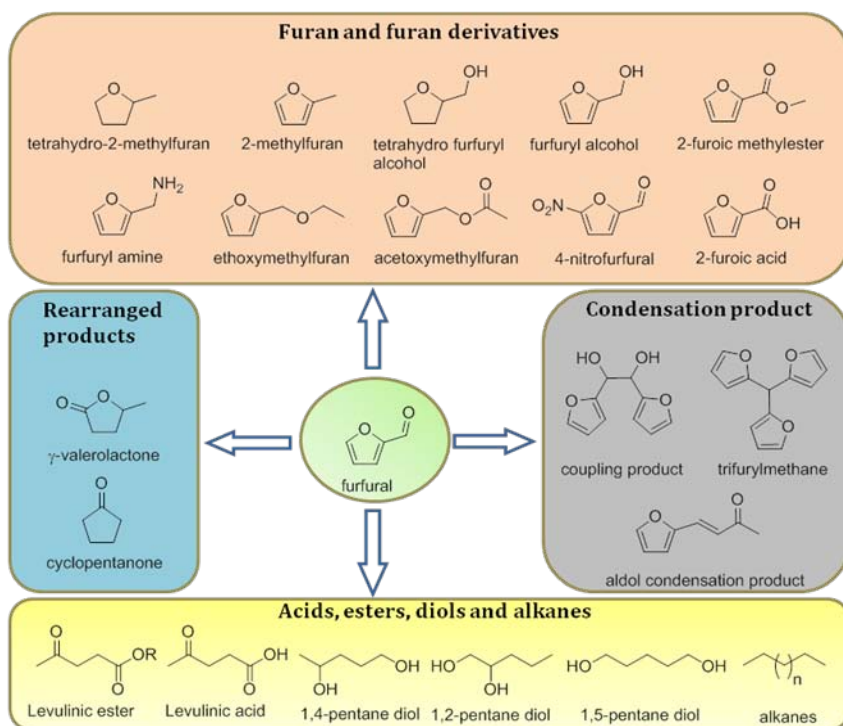
Substrate	Catalyst	Biphasic solvent system	T (°C)	<i>t</i>	Yield (%)	Ref
Xylose	Formic acid	water: <i>o</i> -nitrotoluene	190	75 min	74	[154]
	Nb <sub>2</sub> O <sub>5</sub>	water: toluene	120	3 h	71	[156a]
	SBA-12Nb	water: toluene	160	24 h	84	[156b]
	TaOPO <sub>4</sub> -m	water: toluene	140	2 h	35	[156c]
hemicellulose	SAPO-44	water: toluene	170	8h	63	[156d]
	WO <sub>3</sub> /SiO <sub>2</sub>	water: toluene	170	8 h	61	[156e]
	Ga <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>		170	8 h	54	
	TiO <sub>2</sub> /CB	water: toluene	170	3.5 h	69	[157]
xylose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	water: toluene	160	4 h	50	[156h]
	MCM-41-SO <sub>3</sub> Hc	water: toluene	140	24 h	76	[156g]
	Ar-SO <sub>3</sub> H-SBA-15	water: toluene	160	20 h	80	[158]
	Amberlyst-70	water: toluene	175	4 h	54	[157]
	Zeolite Nu-6	water: toluene	170	4 h	47	[160]
	[Bmim][HSO <sub>4</sub> ]	water: toluene	140	6 h	71	[159]
	SO <sub>4</sub> <sup>2-</sup> /sporopollenin	water: CPME, MI	190	40 min	69	[161]
	SO <sub>4</sub> <sup>2-</sup> /Sn-Mont	water: MeTHF, NaCl	160	2 h	79.6	[162]
	Glu-TsOH-Ti	water: MeTHF	180	30 min	51	[156f]

CPME: cyclopentylmethyl ether, MeTHF: 2-methyltetrahydrofuran, CB: carbon black, MI: Microwave irradiation.

### 1.6.2 Furfural conversion to fuels and chemicals

The chemo-catalytic transformation of furfural has a wide scope for producing a variety fuel components and useful chemicals. Reportedly, over 80 chemicals have been derived directly or indirectly from furfural, making it a versatile biomass-based top C<sub>5</sub>-platform molecule [163]. Figure 1.9 shows the broad spectrum of furfural based chemistry. Its world market currently is estimated to be ca. 205 kilotons per year of which about 60 % is used for the production of furfuryl alcohol [164]. Additional transformations of furfural are highly desired, that is to find new pathways for converting furfural to those products which could be integrated into the bio refinery product chain. Furfural can be further transformed into downstream chemicals/fuel additives *via* C-C bond forming reactions, hydrogenation-hydrogenolysis, oxidation etc.





**Figure 1.9.** Utilization of furfural to chemicals and fuels

### 1.6.2.1. C-C bond forming reactions

As like HMF, FUR also undergo carbon upgradation of furfural *via* C-C bond formation reactions (Scheme 1.9)

**1.6.2.1.1. Aldol condensation:** The aldol condensation of FUR and acetone is widely studied reaction. The condensation product furfurylidene acetone (4-(2-furyl)-3-buten-2-one, FAc) of FUR and acetone is of particular importance. These C<sub>8</sub> monomers can further condense with another FUR molecule to form the C<sub>13</sub> dimer, difurfurylidene acetone (1,5-bis-(2-furyl)-1,4-pentadien-3-one, DFAc). The final products of the reaction have interesting applications in the preparation of polymers with high thermal and chemical resistance, as well as organo-mineral concretes [165]. FAc is a flavouring agent used in the food industry [166]. This reaction was initially focused for the increasing the number of carbon atoms [167]. Early studies focused on the condensation of FUR and acetone in H<sub>2</sub>O with NaOH as a catalyst [165, 168]. The use of solid catalysts is preferred due to the facile catalyst recovery and recyclability. For instance, hydrotalcites, [167c] MgO, [167c] CaO, [167c] La-ZrO<sub>2</sub>, [167c] Y-ZrO<sub>2</sub>, [167c] MgO-ZrO<sub>2</sub>, [167c] MgO-TiO<sub>2</sub>, [167c] ion-exchange resins, [167c] and NH<sub>3</sub>-functionalised SiO<sub>2</sub>, [167c] N-substituted Na-Y, [169] Co-Al

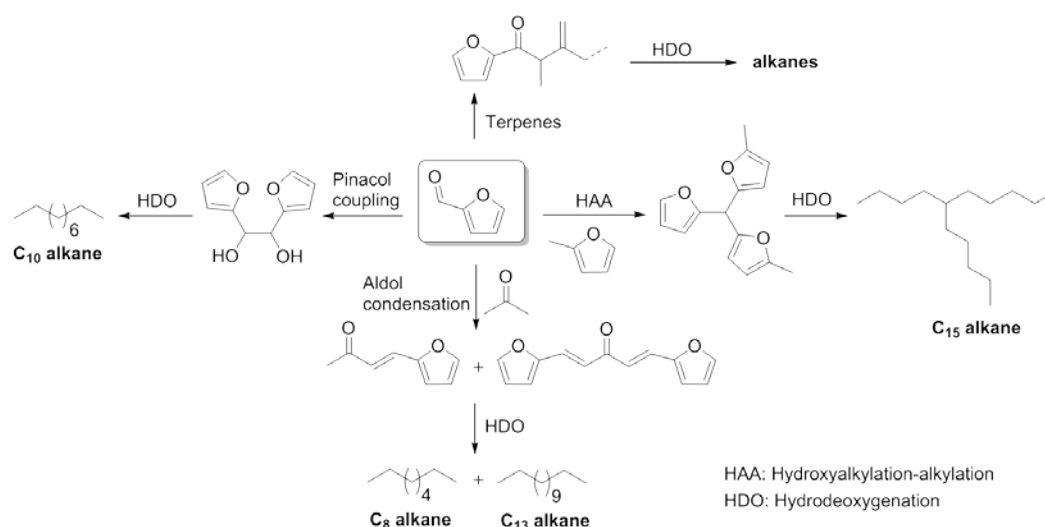


spinel, [170] mixed oxides such as Mg–Al, [171] Ca–Zr, [172]  $\text{WO}_3\text{--ZrO}_2$ , [173] other MgO–ZrO<sub>2</sub> species, [173, 174] supported Mg–Zr oxides on graphite [175] or MgO/Na–Y, [176] dolomites, [177] chitosan, [178] and zeolites [179]. The condensation of FUR with other ketones such as dihydroxyacetone, hydroxyacetone and glyceraldehyde, [180] LA, [181] methyl isobutyl ketone (MIBK), [182] 2-pentanone and 2-heptanone, [183] and cyclopentanone [184] has also been studied. Further hydrogenation and dehydro-deoxygenation of the condensation products affords molecules in the range of diesel or jet fuels.

**1.6.2.1.2. Pinacol coupling:** Fu et al. proposed a 2-step route for the synthesis of biofuels in the range of linear C<sub>8</sub>–C<sub>10</sub> alkanes *via* pinacol coupling of two FUR molecules [185]. The dimer was obtained in 95 % yields by reacting FUR with powdered Zn (reductant) and 10 % NaOH aqueous solution at room temperature. Subsequent dehydration/hydrogenation was performed over a mixture of Pd/C and TaOPO<sub>4</sub> or NbOPO<sub>4</sub> to obtain 84 % yield of mixed alkanes. This pathway still requires additional efforts to overcome some of the limitations of the process. For instance, the metal powders used in the first self-condensation step should be substituted by less expensive and more sustainable reductant. Additional investigation on the reutilisation of the catalysts in the second step is also required.

**1.6.2.1.3. Hydroxyalkylation-alkylation (HAA):** Huber et al. established another elegant route for carbon upgradation by forming a C–C bond between FUR and furan with conc. H<sub>2</sub>SO<sub>4</sub> to afford 79 % yield of the C<sub>13</sub> dimer [186]. In 2014, Balakrishnan *et al.*, reported sulfonic acid functionalized silica as a solid acid catalyst for HAA reaction of 2-methylfuran with furfural [36a] and later they have performed ring hydrogenation HAA products into diesel additives [36b].

**1.6.2.1.4. Coupling with Terpenes:** Furfural was reacted with terpenes (*e.g.* isoprene and myrcene) in presence of ruthenium catalyst to afford the coupling products which were isolated in <90 % yields [37].



**Scheme 1.9.** C-C bond forming reactions of furfural and subsequent hydrodeoxygenation

### 1.6.2.2. Hydrogenation and hydrogenolysis reactions

Variety of valuable chemicals and fuel components could be produced from FUR through hydrogenation and hydrogenolysis (Scheme 1.10.).

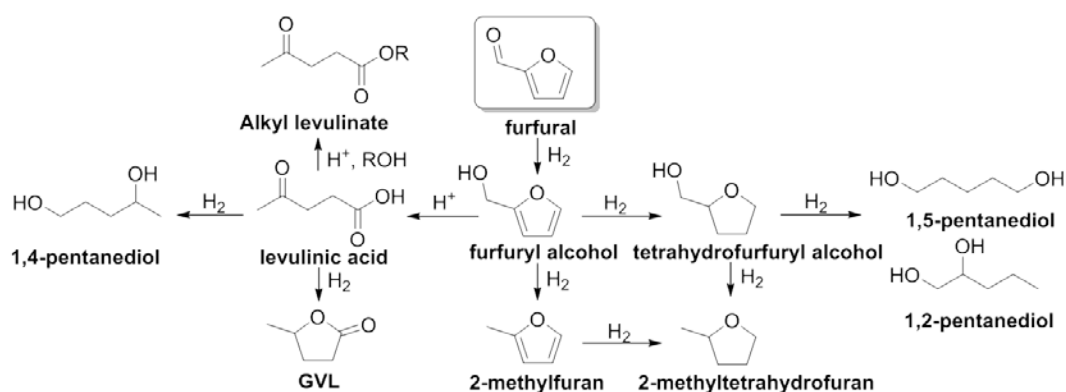
**1.6.2.2.1. Furfuryl alcohol (FAL):** Furfuryl alcohol (FAL) is the most important chemical derived from FUR, having a broad spectrum of applications in the chemical industry. FAL is primarily used for the production of resins for use as high-quality cores and moulds for metal casting in the foundry industry, as a reactive solvent for phenolic resins in the refractory industry, as a viscosity reducer for epoxy resins, in the manufacture of polyurethane foams and polyesters, as a chemical building block for the synthesis of tetrahydrofurfuryl alcohol (THFA) and pharmaceuticals (such as antiulcer ranitidine), and in the manufacture of fragrances [187]. Other relevant chemicals that can be obtained from FAL include ethyl furfuryl ether (EFE), levulinic acid (LA),  $\gamma$ -valerolactone (GVL). The industrial synthesis of FAL is performed *via* the catalytic hydrogenation of FUR, which can be accomplished in gas or liquid phase. The gas-phase Cu-catalyzed hydrogenation of FUR is the preferred industrial route. The gas-phase process was first reported in 1929 by using Cu on asbestos as the catalyst, [188] whereas the use of copper chromite was patented in 1937 by Du Pont de Nemours [189]. Quaker Oats Company achieved furfuryl alcohol yields of 99% by employing  $\text{Cu}/\text{Na}_2\text{O} \cdot x\text{SiO}_2$  [190]. Since then, many other catalytic systems based on Cu and other metals (Pd, Pt, Co, Fe, Ni, and

Zn) have been proposed for this process, mainly to overcome the environmental concerns associated with the presence of chromium in copper chromite catalysts. An 85 % FAL yield was obtained by gas-phase MPV reduction of FUR coupled with cyclohexanol over Cu–MgO–Cr<sub>2</sub>O<sub>3</sub> [191]. The liquid phase hydrogenation of FUR was first reported in 1933 by Quaker Oats company over Ni/MgO catalyst.[192] The FAL selectivity was further improved to 98 % by adding alkaline earth oxides (CaO, BaO) in copper chromite [193]. An extensive effort has been devoted to developing more environmentally friendly Ni, [194] Cu, [195] Co, [196] Ru,[197] Rh, [194c] Pt,[198] Pd [199] and Ir [200] based catalysts with external H<sub>2</sub> or *via* transfer hydrogenation. Thananattathanachon et al, shown that, FAL can be directly produced xylose using homogeneous Ir based catalyst in formic acid as hydrogen donor [48].

**1.6.2.2.2. Levulinic acid (LA) and ester (LE):** The most investigated route for production of LA from FUR involves several steps conducted in different reactors. FUR is first hydrogenated to FAL and then later is transformed into LA *via* acid-catalysed ring-opening in H<sub>2</sub>O [201]. The ring opening of FAL can also be conducted in the presence of alcohols rather than H<sub>2</sub>O to afford alkyl levulinate [201] which can be later hydrolysed to furnish LA. Remarkably, the one-pot direct transformation of FUR into alkyl levulinate with 76 % yield by avoiding the isolation of FAL, has been reported by Chen et al. using a bifunctional catalyst Pt/ZrNbPO<sub>4</sub> [202]. However, a slight deactivation of the catalyst was noticed with almost 17% of the initial catalyst activity was lost. Hence, more research is needed in this direction.

**1.6.2.2.3.  $\gamma$ -Valerolactone ( $\gamma$ -GVL):** It is used as a fuel additive,[203] food ingredient, [204] an intermediate for the production of chemicals [205] and high-grade alkene fuels,[206] nylon intermediate, [208] or in a wide range of niche applications (*e.g.* cutting oils and brake fluids), [209] and a renewable solvent for processing of lignocellulosic biomass, [207, 210] However, the commercial use of GVL is still limited, primarily because of its high production costs. Remarkably, the direct conversion of FUR into GVL has been reported by Roman-Leshkov et al. [211] *via* one-pot conversion of FUR into GVL through a cascade reaction sequence over Zr-Beta zeolite and Al-MFI. A GVL yield as high as 68 % was obtained.

**1.6.2.2.4. Pentanediols (PeD):** Linear diols are of utmost importance in chemistry and find nowadays many applications in our society. In particular, diols are widely employed as solvent in cosmetic industry [212]. They also serve as intermediates in the manufacture of fine/specialty chemicals, as monomers in the fabrication of polymers and as polar head in the synthesis of bio-surfactants [213]. Liu *et al.* [214] reported the one-pot selective conversion of furfural to 1,5-PeD over a Pd-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst with THFA as the intermediate and obtained a maximum 71.4 % yield of 1,5-PeD. Similar result was obtained using a Re-Rh-Ir alloy catalyst [215]. Additionally, Xu *et al.* [216] developed a novel process for the direct conversion of FUR to 1,5-PeD by hydrogenolysis of the furan ring over the Pt/Co<sub>2</sub>AlO<sub>4</sub> catalyst under mild conditions. In contrast, Mizugaki *et al.* [217] found that Pt-hydrotalcite catalyzed the direct transformation of FUR to 1,2-PeD with a high yield of 73 %. In addition to 1,5-PeD and 1,2-PeD, another pentanediol, 1,4-PeD, can also be synthesized from furfural over Pt-Mo/hydroxyapatite catalysts *via* LA, to get 70 % yield of 1,4-PeD yield [218]. Recently, Liu *et al.* disclosed a catalytic pathway for selective conversion of furfural to 1,4-PeD in a one-pot process over Ru/CMK-3 catalyst under the mild reaction conditions. The yield of 1,4-PeD obtained in as high as yield up to 90 % [219].



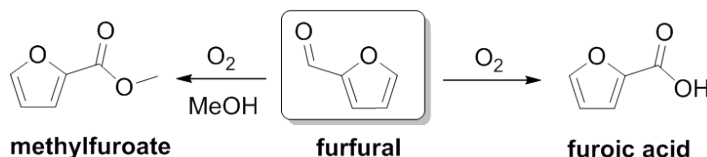
**Scheme 1.10.** Hydrogenation and hydrogenolysis products of furfural

### 1.6.2.3. Oxidation reactions

The oxidation and oxidative-esterification of furfural provided furoic acid and methylfuroate (Scheme 1.11.)

**1.6.2.3.1. Furoic acid:** Furoic acid has applications in the pharmaceutical, agrochemical, flavour and fragrance industries [220]. Furoic acid is industrially produced by the Cannizzaro reaction of FUR in aqueous NaOH solution [221]. Furfuryl alcohol and sodium furoate are formed in this reaction later one is acidified with sulfuric acid to yield furoic acid. Other oxidation processes use strong oxidative reactants such as  $\text{KMnO}_4$ ,  $\text{MnO}_2$ , or  $\text{NaOCl}$ . None of the above processes can be considered green syntheses. Hence, investigations have been directed at achieving selective production to furoic acid with cheaper and less polluting and non-toxic oxidative reactants. A number of catalysts based on noble metals (Ag, Au, Pt, or Pd) supported on different metal oxides have been explored and the highest selectivity of 96 % for furoic acid was achieved with the use of a Ag/CuO–CeO<sub>2</sub> catalyst [222]. The complete conversion of FUR to furoic acid was achieved using a Pb–Pt/C catalyst in the aqueous phase under conditions [223]. These methods required co-feeding of strong bases to maintain high pH of reaction mass to produce soluble furoate species. The addition of base is a serious drawback for the environmental sustainability of the process.

**1.6.2.3.2. Furoate esters:** The oxidative esterification of FUR to methyl furoate in the presence of O<sub>2</sub>, base (NaOCH<sub>3</sub>) and methanol. However, the base was used in a considerably smaller concentration than that used in the FUR to furoic acid transformation. Indeed, furoic acid can be produced by hydrolysis of methyl furoate. The ester also finds application in the fine chemicals industry (flavour and fragrances). Christensen et al., produced methyl furoate with almost 100 % yield at room temperature over Au/TiO<sub>2</sub> catalyst [224]. Very remarkable results have recently been obtained by Signoretto et al. using Au-based catalysts with low pressure air (0.05 MPa) as an oxidant and without external base [225].



**Scheme 1.11.** Oxidation of furfural

## 1.7. Statement of problem

The selective conversion of oxygen rich biomass to value-added chemicals is the key issue for development of fossil-independent chemical technologies for the production of fuel additives and chemicals. 5-(hydroxymethyl)furfural (HMF) is an important and a versatile platform molecule in the biorefinery. Uptil now several technologies are available for the production of HMF. Unfortunately, its isolation and purification is still a biggest challenge due to its solubility in water, making it difficult to extract from the aqueous solution. During distillation at high temperature, unwanted impurities were formed which results in significant loss of HMF yield. Therefore, further development for isolation and purification of HMF is needed. Instead of using pure HMF, the crude HMF can also be used as a starting material for the production of valuable chemicals/fuel. Alternatively, direct/integrated technologies should be developed for transformation of cheap HMF precursors (e.g. glucose, fructose and sucrose) into valuable chemicals/fuel without isolation of intermediate HMF. The utilization of pure HMF for production of advanced chemicals through single step/cascade/integrated process is also an interesting and hot area.

On the other hand, although furfural is produced commercially in industries, its long time stability (shelf life) is a major concern. The transformation of pure furfurals to value added chemicals is also well explored. Still there are plenty of opportunities to find out advanced technologies.

Therefore, this work is deals with the direct/integrated conversion of carbohydrates without isolation of intermediate furfurals to the desired products. Similarly, conversion of furan to more stable and value added products could be achieved by catalyst design and developing new reaction pathways.

## 1.8 Objectives of the study

The overall objective of the thesis is the conceptual development and optimization of environment friendly and cost efficient strategies that will enable the conversion of biomass derived molecules to value added products. The objectives of thesis are divided into two parts I and II.

### I. Based on carbohydrates utilization

Direct/integrated conversion of carbohydrates (*e.g.* fructose, glucose, sucrose and xylose) into advanced furan derivatives (*e.g.* fuel additives and chemicals) without isolation of unstable intermediates (furfural derivatives; *e.g.* HMF or furfural). It will eliminate the tedious isolation and purification processes of furfural derivatives (*e.g.* HMF/furfural).

To this end, the specific aims are as follows:

- Development of catalysts possessing both Lewis and Brønsted acid sites, by simple preparation techniques.
- Catalyst characterization and parametric study of reaction conditions in order to understand structure-property-reactivity relationships for the optimization of the carbohydrates dehydration reaction.
- Careful selection of biphasic solvent system for dehydration of carbohydrates to HMF. Subsequent utilization organic phase for further conversion of in-situ formed HMF to advanced chemicals/fuel additives.
- Development of integrated technologies for the production of advanced chemicals and fuel precursors from carbohydrates.

## **II. Based on utilization of furan derivatives**

- To find out catalytic upgradation processes of pure HMF/furfural to advanced chemicals.
- Development of cascade protocol for the conversion of HMF into fuel additives.
- Development of sustainable technologies/processes for the upgradation of furan derivatives.

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## *Part-I*

### *Carbohydrate conversion to furan derivatives*

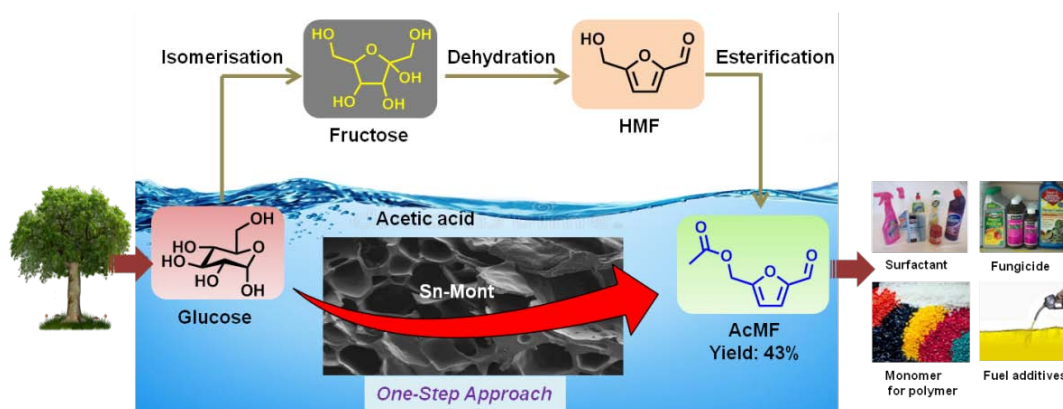


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## Chapter 2

### Direct synthesis of 5-(Acetoxymethyl)furfural from carbohydrates

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An ester derivative of 5-(hydroxymethyl)furfural (HMF) such as 5-(Acetoxymethyl)furfural (AcMF) has emerged as an important alternative for HMF. The AcMF can be converted into those products which are typically prepared from HMF. The growing importance of AcMF encouraged us to prepare it directly from cheap and abundant carbohydrates. Making AcMF from glucose and glucose-like carbohydrates is an exigent assignment, owing to tough isomerisation of glucose to fructose. We employed Sn-Mont catalysts for glucose conversion directly into AcMF. The Sn-Mont has a unique combination of Lewis as well as Brønsted acid sites. Lewis acid sites of Sn-Mont facilitate the isomerisation of glucose to fructose. At the same time, dehydrative-esterification of fructose to AcMF is catalysed by Brønsted acid sites of Sn-Mont. Sn-Mont catalysts were prepared by simply mixing of montmorillonite clay with an aqueous solution of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  with different concentrations (*e.g.* 0.1M-0.4M). Different types of acid sites of Sn-Mont (0.1-0.4M) catalysts were identified by Py-FTIR analysis and their strength was estimated by using the Emeis equation. The AcMF was produced in 43 % yield directly from glucose over Sn-Mont(0.3M) catalyst due to its highest acid strength. Furthermore, the efficacy of Sn-Mont(0.3M) catalyst was probed for sucrose which resulted in 53 % yield of AcMF. From fructose, 58 % yield of AcMF was achieved. Critical properties of all the prepared Sn-Mont catalysts were thoroughly investigated through BET, temperature-programmed desorption of  $\text{NH}_3$  and pyridine-FTIR techniques.

Suhas Shinde, Kashmira Deval, Rajeev Chikate, Chandrashekhar Rode, **Submitted to ChemCatChem.**

## 2.1. Introduction

Multiple functionality of HMF makes it a versatile precursor for the making of a broad domain of chemicals. Despite of that, its bulk production from renewable feedstock is only practised by AVA BIOCHEM [1]. Indeed, major hurdle for commercial production of HMF is its tedious purification by distillation which generates large amount of tarry degradation products. As a result, its market price is also too high. Thus, instead of isolating HMF, its further conversion to higher value commercial chemicals *via* direct/integrated process is highly desirable. In this regards, 5-(Acetoxymethyl)furfural (AcMF) which is an advanced HMF- derived chemical with divergent properties. The AcMF potentially can be a fuel blending agent, additive for bulk chemicals, monomers for synthesis of polymers, natural surfactant and a fungicide [2-6]. In addition to that, AcMF is also used as building block for synthesis of therapeutic agents for osteoporosis or protein tyrosine phosphatase 1B (PTP1B) inhibitors [7]. Interestingly, AcMF shows energy content ca.  $8.7 \text{ KWhL}^{-1}$  which is higher than that of ethanol (ca.  $6.1 \text{ KWhL}^{-1}$ ) and similar to that of gasoline (ca.  $8.8 \text{ KWhL}^{-1}$ ) [8-11], hence making it suitable as a fuel blending agent. The AcMF is relatively more stable than HMF and thus represents an extremely good substitute for HMF. The esters of HMF offer some important advantages over HMF from the point of view of its industrial production. Compared with the HMF, its ester derivatives are aquaphobic, less reactive, more stable and could be easily extracted from the aqueous reaction mixture. Hence, these esters are comparatively more useful than HMF itself. Whereas, HMF is known to be prepared from carbohydrates in acidic medium and it is comparatively not stable under acidic environment and also it is hard to extract from the aqueous reaction mixture [12-14]. The AcMF can be converted into promising chemicals, such as FDCA, BHMF and HFCA [15] and also into liquid fuel (2,5-dimethylfuran) [2] (Scheme 2.2). Also from the safety perspective, AcMF is preferred to HMF as the latter possesses weak cytotoxicity and mutagenicity in humans [15].

## 2.2. Literature survey

Several reports on the production of AcMF are available using various starting materials. For example, AcMF was obtained in moderate to good yields from 5-(chloromethyl)furfural (CMF) and acetic acid in the presence potassium carbonate

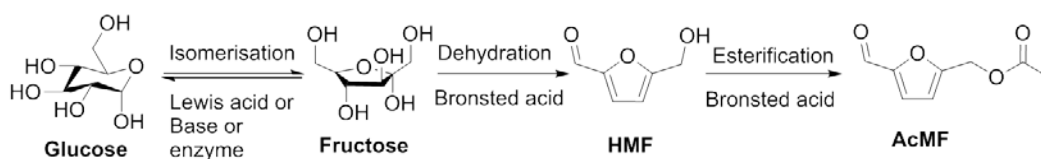
[16]. Recently, Kang et al. converted CMF into AcMF with 84 % yield using alkyl ammonium acetate salt wherein acetate anion acted as an acetylating agent [15]. Krystof et al. reported lipase catalyst for the production of HMF esters in good yields from HMF [17]. However, use of expensive enzymes would not be feasible for the commercial production of AcMF. Making AcMF directly from carbohydrates without isolating HMF is much more rewarding. Several patents described the production of HMF-ester (including AcMF), by acid-catalyzed dehydration of carbohydrates [18]. For example, only 5.1 % yield of AcMF was obtained when glucose dehydration was performed in a mixture of EmimCl and Acetic acid over  $\text{CrCl}_2$  catalyst [18]. Sanborn et al. produced AcMF in 41 % yield from fructose by using Amberlyst-15 catalyst [19]. However in the above cases, low to moderate yield of AcMF was obtained. Recently, a 36 % yield of AcMF was reported from cellulose acetate using stoichiometric amount of  $\text{H}_2\text{SO}_4$  [20]. Nevertheless, further development is necessary to replace homogeneous catalyst with improved yield of AcMF.

### 2.3. Scope of the present work

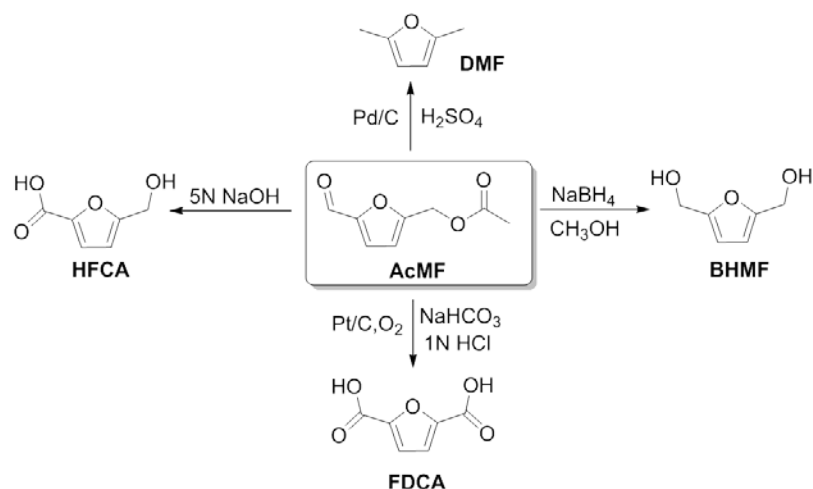
Among several options, tin (Sn) containing heterogeneous catalysts have been explored quite extensively for the conversion of glucose-based carbohydrates to HMF and its derivatives. Nikola et al. shown that Sn-beta could be an efficient catalyst for the isomerization of glucose to fructose and then generated fructose was converted to HMF rapidly by using HCl [21]. In another attempt, 5-(ethoxymethyl)furfural was produced directly from glucose using a combination of Sn-BEA and Amberlyst-15 [22]. However, certain amount of highly corrosive hydrofluoric acid (HF) was used while preparing Sn-beta catalyst [21]. To circumvent this problem, Sn-Mont catalyst prepared simply by mixing of aq.  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and montmorillonite was reported for the production of alkyl lactate from triose sugars [23] and HMF from carbohydrates [24].

In this direction, we established a method for the production of AcMF directly from carbohydrates using heterogeneous Sn-Mont catalysts. Glucose was efficiently converted to AcMF over Sn-Mont(0.3M) catalyst in acetic acid as a reactive medium. Sn-Mont(0.3M) has a unique balance of Lewis and Brønsted acidities which facilitate the glucose conversion into AcMF in a three step process

involving a) isomerisation of glucose to fructose on Lewis acid sites, b) in-situ formed fructose dehydration to HMF on Brønsted acid sites and c) esterification of in-situ formed HMF (Scheme 2.1). This protocol was further explored for sucrose and fructose for their transformation into AcMF. The AcMF is recognised as an alternative to HMF and it is a well established starting material for production of other valuable furan derivatives (Scheme 2.2). The possibility of producing some more advanced furan compounds from AcMF is discussed later.



**Scheme 2.1.** Synthetic pathways and applications of OBMF



**Scheme 2.2.** Conversion of 5-(acetoxymethyl)furfural (AcMF) into useful furans. BHMf: 2,5-bis(hydroxymethyl)furan; FDCA: 2,5-furandicarboxylic acid; HFCA: 5-(hydroxymethyl)furan-2-carboxylic acid; 2,5-DMF: 2,5-dimethylfuran.

## 2.4. Experimental section

### 2.4.1. Materials

All the materials/chemicals used in this work were as obtained from the authentic supplier. SnO<sub>2</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, H<sub>2</sub>SO<sub>4</sub> (98 %), acetic acid (99.9 %), K<sub>2</sub>CO<sub>3</sub>, NaOH and carbohydrates such as sucrose, glucose and fructose were obtained from Thomas Baker, India. All the solvents and inorganic solids such as NaHCO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>

were purchased from ChemLabs, India. Inorganic metal precursors such as  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , Amberlyst-15, Amberlite IRN78 hydroxide form resin and montmorillonite clay  $[(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}]$  (CAS No. 1302-78-9) with the composition (mass %)  $\text{SiO}_2$  (66.5)  $\text{Al}_2\text{O}_3$  (8.79)  $\text{Fe}_2\text{O}_3$  (1.64)  $\text{CaO}$  (1.64)  $\text{MgO}$  (3.03)  $\text{TiO}_2$  (2.06)  $\text{K}_2\text{O}$  (0.19)  $\text{Na}_2\text{O}$  (0.14) were of Sigma-Aldrich make. Hydrotalcite ( $\text{Mg}/\text{Al} = 3$ ) was produced by following the literature procedure [25]. The key compound (for the HPLC quantification studies), 5-(acetyloxymethyl)furfural (AcMF) was prepared according to the procedure reported in literature [26].

#### 2.4.2. Catalysts preparation

The catalyst was prepared by following previous report [27, 28]. In a representative preparation, montmorillonite (5 g) was slowly added into the various concentration of 80 mL aqueous solution of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (0.1, 0.2, 0.3 and 0.4M) under stirring. The mixture was further stirred for 4 h at room temperature. Then mixture was filtered, the residue was washed with distilled water until washing was neutral ( $\text{pH} = 7$ ) and completely free from chloride ions. The filtrate was treated with  $\text{AgNO}_3$  to detect the presence of chloride ion. The resultant residue of Sn-Mont was dried overnight at  $100^\circ\text{C}$ . Finally, it was powdered and stored in a glass bottle. Resultant catalysts were denoted Sn-Mont(0.1M), Sn-Mont(0.2M), Sn-Mont(0.3M) and Sn-Mont(0.4M).  $\text{Sn}(\text{OH})_4$  was prepared by precipitation of aq.  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (0.3 M, 50 mL) with 30 % aq. ammonia.

#### 2.4.3. Catalyst characterization

Micromeritics ChemiSorb 2720 instrument was used for the Temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) analysis. In a representative experiment, U-shaped, flowthru, quartz sample tube was filled with 0.05 g of a catalyst. Initially, the catalyst was pre-treated in He ( $30 \text{ cm}^3/\text{min}$ ) at  $200^\circ\text{C}$  for period of 2 h. Then a mixture of  $\text{NH}_3$  in He (10 %) was passed through the U-shaped tube with flow rate of  $30 \text{ cm}^3/\text{min}$  at  $50^\circ\text{C}$  for the period of 30 min. The sample was subsequently flushed with He with flow rate of  $30 \text{ cm}^3/\text{min}$  at  $50^\circ\text{C}$  for the period of 1 h. The Temperature-programmed desorption of ammonia was measured in the range 50 to  $700^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$ . The desorbed ammonia concentration was recorded with a gold-plated, filament thermal conductivity

detector. The nitrogen adsorption experiment was also performed on same instrument, Micromeritics ChemiSorb 2720 sorption analyzer instrument. Before analysis, the catalyst samples were de-gassed at 200 °C for the period of 2 h. FTIR spectrometer (Perkin Elmer 2000) in the 4000–400 cm<sup>-1</sup> wave number range attached with a Harrick's diffuse reflectance praying mantis assembly was used for the pyridine FT-IR spectra recording of the prepared catalysts. Pyridine was injected into the port, from where under nitrogen flow pyridine was driven and adsorbed on the sample for half an hour. Physically adsorbed pyridine was removed by heating the sample at 100 °C for a half an hour. Then the sample was analysed for the presence of acid sites using spectrum software. The quantitative analysis of Brønsted acid and Lewis acid sites was determined by using equations (I and II) developed by Emeis [29]. Before sample filling the disk was heated at 400 °C for the period of 1 h under vacuum in order to remove physisorbed water. After that the cell was cooled to room temperature, then KBr was placed into the disk and IR spectrum was recorded as a background. Then KBr sample was replaced with catalyst sample and pressed into self-supporting disks (0.25 cm, radius, 50 mg, wt) and placed in an IR cell attached to a closed glass-circulation system. Then at room-temperature pyridine vapour was introduced into the cell until equilibrium was reached, and then a second spectrum was recorded. Subsequently evacuation was performed by heating at different temperature for the period of 10 min followed by spectral acquisition. The spectrum is obtained by subtracting the spectra recorded before and after pyridine adsorption.

$$C_L = K_L \times A_{1450} = (\pi / \text{IMEC}_L) \times (r^2/w) \times A_{1450} \quad \text{----- (I)}$$

$$C_B = K_B \times A_{1540} = (\pi / \text{IMEC}_B) \times (r^2/w) \times A_{1540} \quad \text{----- (II)}$$

Where,

$C_L$  and  $C_B$  = concentration of pyridine on Lewis and Brønsted acid sites.

$A_{1450}$  and  $A_{1540}$  = integrated area of band at 1450 cm<sup>-1</sup> and 1540 cm<sup>-1</sup>

$K_L$  and  $K_B$  = molar extinction constant for Lewis acid sites and Brønsted acid sites

$\text{IMEC}_L$  = integration molar extinction coefficient for Lewis acid sites which is 2.22 cm/μmol

$\text{IMEC}_B$  = integration molar extinction coefficient for Brønsted acid sites which is 1.67 cm/ $\mu\text{mol}$

$r$  = radius of self supporting disk of praying mantis assembly

$w$  = weight of sample pressed into self supporting disk of praying mantis assembly.

The energy dispersive X-ray analysis (EDX) was performed on a model Leica-440 for the quantitative elemental analysis of catalyst.

#### 2.4.4. Catalyst testing

##### 2.4.4.1. Synthesis of AcMF from carbohydrates

A mixture of carbohydrate (*e.g.* sucrose/glucose/fructose) (5 wt %), acetic acid (10 mL) and Sn-Mont(0.3M) (0.2 g) was heated at 150 °C for the period of 3h. Then the reaction mixture was filtered and catalyst bed was thoroughly washed with ethyl acetate (20 mL x 3). Further, mother-liquor was treated with saturated solution of  $\text{NaHCO}_3$  (10 mL x 1),  $\text{H}_2\text{O}$  (10 mL x 2) and saturated solution of  $\text{NaCl}$  (10 mL x 1). The separated organic phase was treated with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated on rotary evaporator. The obtained crude residue was passed through silica bed to afford orange oil of pure AcMF. Yield: 0.084 g (50 %, from fructose), 0.055 g (33 %, from glucose) and 0.148 g (44 %, from sucrose).

##### 2.4.4.2. Catalyst recycling

Mixture of glucose (5 wt %), Sn-Mont(0.3M)(0.2 g), acetic acid (10 mL) was heated at 150 °C for 3h. Further reaction mixture was filtered, the catalyst bed was washed with ethyl acetate (10 mL x 3). Then the catalyst was dried at 110 °C for the period of 2 h before it was reused for the next run. After each run, fresh starting materials (glucose and acetic acid) were loaded into the reactor and treated with the reused catalyst. The same procedure was repeated for each recycle.

##### 2.4.4.3. Transformations of AcMF

###### 2.4.4.3.1. Synthesis of 2a-d from AcMF

A solution of AcMF (1.0 g, 0.0059 mol), Sn-Mont(0.3M) (0.4 g) and alcohol (10 mL) was stirred at 80 °C for 3 h. Further, reaction mixture was filtered, catalyst bed was washed with ethyl acetate (20 mL x 3). The mother liquor was treated with saturated solution of  $\text{NaHCO}_3$  (10 mL x 1), water (10 mL x 2) and saturated solution of  $\text{NaCl}$  (10 mL x 1) and then diluted with ethyl acetate (20 mL x 1). The collected



organic layers were treated with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated using rotary evaporator to yield orange oil of **2a-d** without purification.

#### **2.4.4.3.2. Synthesis of 3 from AcMF**

A mixture of AcMF (1.0 g, 0.0059 mol), Sn-Mont(0.3M) (0.4 g) and 2-methylfuran (1.61 g, 0.0196 mol) was stirred at 65 °C for 3 h. Then reaction mixture was filtered and catalyst bed was washed with ethyl acetate (20 mL x 1). The mother liquor was treated with saturated solution of  $\text{NaHCO}_3$  (10 mL x 1), water (10 mL x 2) and saturated solution of NaCl (10 mL x 1). Further, collected organic layers were treated with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to yield light pink oil of product, **3** without purification. Yield: 0.71 g (94 %).

#### **2.4.4.3.3. Synthesis of 4 from AcMF**

A stirred mixture of AcMF (1.0 g, 0.0059 mol), Sn-Mont(0.3M)(0.4 g), mesitylene (5 mL) and nitroethane (5 mL) was heated at 110 °C for 5 h. Then reaction mixture was filtered and catalyst bed was washed with ethyl acetate (20 mL). The mother liquor was treated with saturated solution of  $\text{NaHCO}_3$  (10 mL x 1), water (10 mL x 2) and saturated solution of NaCl (10 mL x 1). Then collected organic layers were treated with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to yield orange oil of product, **4** without purification. Yield: 0.71 g (94 %)

#### **2.4.4.3.4. Hydrolysis of AcMF to HMF**

A solution of AcMF (0.5 g) in methanol (10 mL) was treated with  $\text{K}_2\text{CO}_3$  (0.065 g) at room temperature for 15 h. After that, reaction mixture was filtered and then the filtrate was evaporated. The obtained residue was diluted with ethyl acetate (20 mL x 1) and washed with brine solution (10 mL x 2). Further, organic layer was dried over anhydrous sodium sulfate and subsequently evaporated under reduced pressure to obtain crude oil of HMF with the yield of 95 % (0.38 g).

#### **2.4.5. Analysis of reaction products**

Merck 5554 aluminium-backed silica plates were used for TLC analysis, and compounds were visualized under UV light (254 nm). The conversion of carbohydrates was calculated by using Agilent HPLC (column: Hi-Plex H USP L17, detector: RI and mobile phase: millipore water with 0.6 mL/min flow). The yield of dehydration product of carbohydrates was calculated by using Agilent HPLC



(column: Poroshell 120 EC-C18 2.7  $\mu\text{m}$ , detector: UV and mobile phase: 0.1 % acetic acid in millipore water: acetonitrile (85:15, v/v) with 0.6 mL/min flow) using an external standard calibration curve method. Purified products were characterised and structures were confirmed by  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR using deuterated chloroform (0.01 %, TMS) as solvent on 200 and 50 MHz frequency Bruker instrument, respectively. The purified products were also analyzed by QP-Ultra 2010 GC-MS Shimadzu instrument having RTX-5 column.

The product yield and carbohydrate conversion were calculated using following equations (III and IV).

$$\text{AcMF yield} = \frac{\text{Moles of AcMF formed}}{\text{Moles of starting carbohydrates}} \times 100 \% \quad \text{----- (III)}$$

$$\text{Carbohydrates conversion} = \frac{(\text{Moles of starting carbohydrates} - \text{Moles of carbohydrates remained})}{\text{Moles of starting carbohydrates}} \times 100 \% \quad \text{----- (IV)}$$

## 2.5. Results and discussion

### 2.5.1. Catalyst Characterisation

#### 2.5.1.1. XRD

Figure 2.1 shows the XRD patterns of parent montmorillonite and Sn containing montmorillonite catalysts. The  $d_{001}$  basal spacing for the reflection at  $2\theta = 7.196^\circ$  of parent montmorillonite is shifted to  $2\theta = 5.9^\circ$  after treatment with  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . Additionally, the  $d$  spacing value was also expanded from 12.27 to 14.96 Å indicated the delamination of montmorillonite layers due to a higher extent of polarizability of  $\text{Sn}^{4+}$  cations [30]. The sharp peak at  $2\theta = 28.26^\circ$  of parent montmorillonite was broadened in Sn-Mont samples due to the formation of  $\text{Sn}(\text{OH})_4$  species into the layers of montmorillonite (Figure 2.2). Thus from the above observations it was revealed that Sn-Mont samples have lost multilayered regularity in the perpendicular direction to each montmorillonite unit. These facts imply that the Sn-Mont would not be composed of the intrinsic aluminosilicate unit layers neatly stacked in a layer-upon-layer fashion. However, the  $(k\ l\ 0)$  peaks, such as  $(0\ 2\ 0)$ ,  $(1\ 1\ 0)$  and  $(0\ 6\ 0)$  of the parent Mont, were still observed in Sn-Mont. The  $(k\ l\ 0)$  peaks are ascribed to the

reflections parallel to the montmorillonite unit layers. Delamination was also evidenced from increase in surface area of parent montmorillonite from 19 to 159-182 m<sup>2</sup>/g after Sn<sup>4+</sup>-exchange. Therefore, it can be concluded that although the neatly-stacked arrangement of intrinsic aluminosilicate unit layer of montmorillonite was disturbed, but each layer of the montmorillonite was intact during Sn<sup>4+</sup>-exchange process as shown schematically in Figure 2.2 [28].

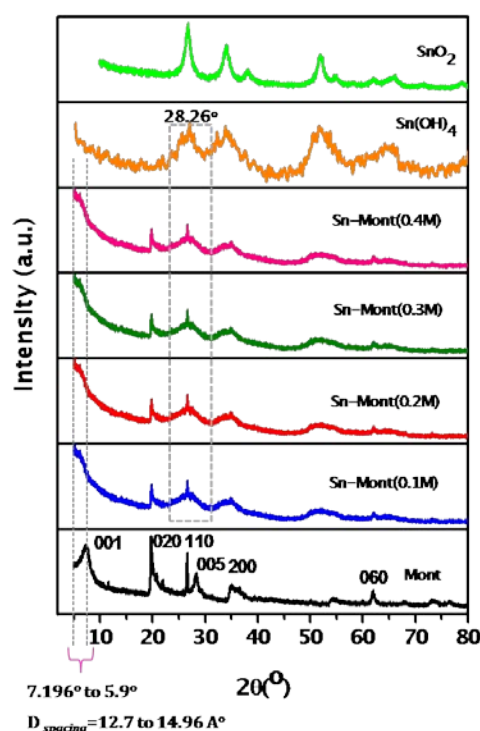


Figure 2.1. XRD patterns of montmorillonite and Sn containing catalysts.

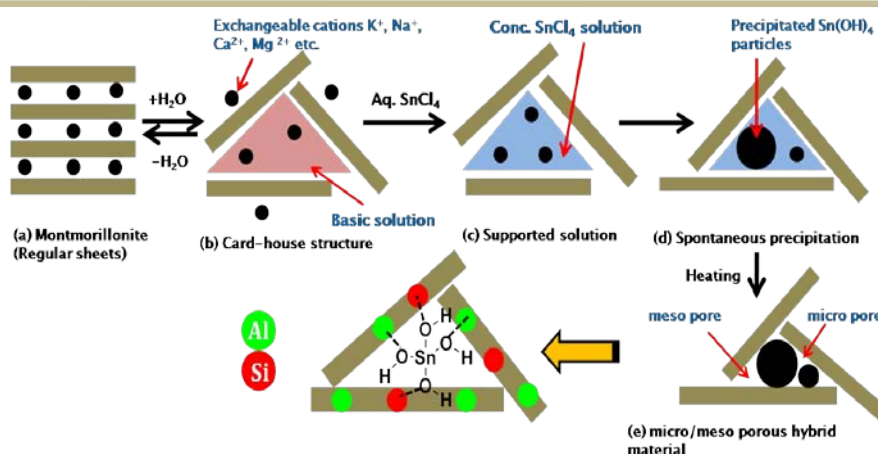
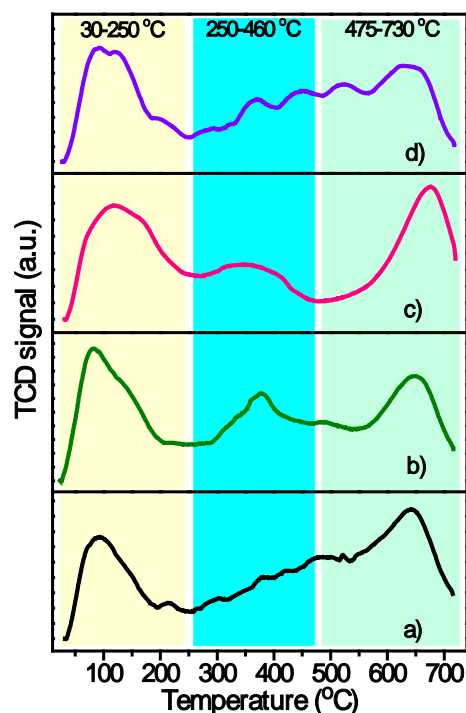


Figure 2.2. The formation of Sn(OH)<sub>4</sub> species into the layers of montmorillonite.

### 2.5.1.2. $\text{NH}_3$ -TPD

The  $\text{NH}_3$ -TPD profiles of Sn-Mont(0.1-0.4M) catalysts are presented in Figure 2.3 and the values of their acid strengths in terms of  $\mu\text{mol}$  of  $\text{NH}_3$  desorbed are provided in Table 2.1.



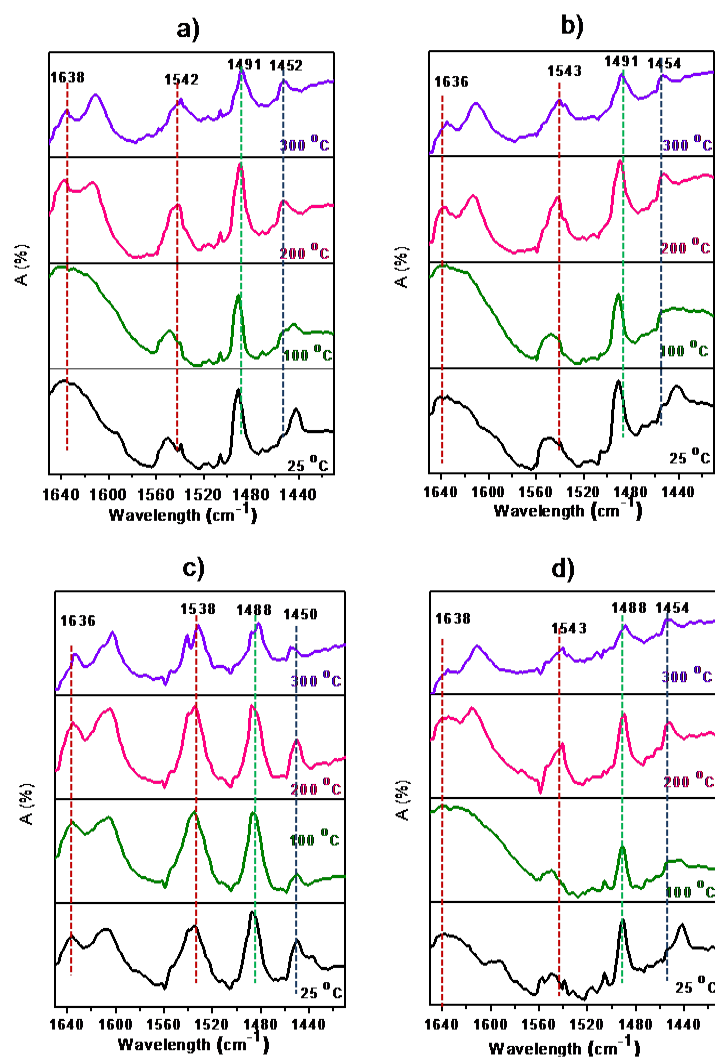
**Figure 2.3.**  $\text{NH}_3$ -TPD profile of a) Sn-Mont(0.1M), b) Sn-Mont(0.2M) c) Sn-Mont(0.3M) and d) Sn-Mont(0.4M).

Acid sites were distributed over three temperature regions *viz.* weak, moderate and strong acid sites in the ranges of 30-250 °C (region-I), 250-460 °C (region-II) and 475-730 °C (region-III), respectively. For Sn-Mont(0.1M) catalyst, significant peaks were observed in the regions I and III suggesting the abundance of weak and strong acidity. The quantitative acid sites distribution in these regions were 154.1  $\mu\text{mol}$  (region-I) and 149.2  $\mu\text{mol}$  (region-III). As the loading of Sn was increased from 0.1M to 0.2M the acid strength of montmorillonite in region-I was found to be enhanced along with appearance of a new peak in region-II, indicating the formation of moderate acidity sites with higher Sn loadings. For Sn-Mont (0.2M) catalyst, quantitative acid sites distribution was 234.9  $\mu\text{mol}$  (region-I), 85.0  $\mu\text{mol}$  (region-II) and 129.39  $\mu\text{mol}$  (region-III). Similarly, For Sn-Mont(0.3M) catalyst, acid sites

distribution was 258.24  $\mu\text{mol}$  (region-I), 88.0  $\mu\text{mol}$  (region-II) and 175.10  $\mu\text{mol}$  (region-III). Surprisingly, acid strength of Sn-Mont(0.4M) catalyst was found to be lower than that of Sn-Mont (0.2M) and Sn-Mont (0.3M). This could be attributed to the partial surface saturation/blocking of pores of montmorillonite by Sn species ( $\text{SnO}_2/\text{SnCl}_4$ ) leading to comparatively less access to acid sites. The acidity trend of Sn-Mont catalysts with their total acidities are as follows: Sn-Mont (0.1M) (309.00  $\mu\text{mol}$ ) < Sn-Mont(0.4M) (356.44  $\mu\text{mol}$ ) < Sn-Mont(0.2M) (449.29  $\mu\text{mol}$ ) < Sn-Mont(0.3M) (521.34  $\mu\text{mol}$ ). Among all the prepared catalysts, Sn-Mont(0.3M) catalyst possessed highest acid strength. It could be ascribed to maximum amount of  $\text{Sn}(\text{OH})_4$  species being precipitated/generated into the montmorillonite layers.

### 2.5.1.3. Py-FTIR

An Identification of the nature of acids sites present in our catalysts was performed using pyridine FTIR. The pyridine FTIR spectrum of  $\text{Sn}^{4+}$ -exchanged montmorillonite samples is depicted in Figure 2.4. In order to identify/evaluate the acidity of these catalysts, difference spectra were obtained by subtracting the spectrum before pyridine adsorption from that was obtained after pyridine adsorption of the respective catalyst. Desorption of pyridine from catalyst was carried out at various temperature ranges such as 25  $^{\circ}\text{C}$ , 100  $^{\circ}\text{C}$ , 200  $^{\circ}\text{C}$  and 300  $^{\circ}\text{C}$  using the method proposed by the Emeis [29] and the outcome is provided in Table 2.1. The band at 1441  $\text{cm}^{-1}$  signifies the Lewis acidity, 1490  $\text{cm}^{-1}$  represents the combination of Lewis and Brønsted acidity and the bands at 1548  $\text{cm}^{-1}$  and 1638  $\text{cm}^{-1}$  signify the Brønsted acidity [31]. The Sn-Mont (0.3M) catalyst having highest total acidity of 532  $\mu\text{mol g}^{-1}$  was distributed as 390  $\mu\text{mol g}^{-1}$  of Brønsted acid sites and 142  $\mu\text{mol g}^{-1}$  of Lewis acid sites. The acid strength determined by evacuation of the pyridine at 100  $^{\circ}\text{C}$  referred to weak acid sites. When evacuation of pyridine was performed at 200  $^{\circ}\text{C}$ , resultant acid strength referred to medium acid sites. Strong acid sites could be observed if the evacuation of pyridine was performed at 300  $^{\circ}\text{C}$ . All the Sn-Mont catalysts possessed significantly large amount of medium acid sites compared to their weak and strong acid sites.



**Figure 2.4.** Pyridine-FTIR analysis of a) Sn-Mont(0.1M), b) Sn-Mont(0.2M), c) Sn-Mont(0.3M) and d) Sn-Mont(0.4M).

**Table 2.1.** Catalysts characterisation

Catalyst	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	V ( $\text{cm}^3/\text{g}$ )	Acidity by PyFTIR <sup>[a]</sup> ( $\mu\text{mol}_{\text{pyridine}} \text{g}^{-1} \text{cat.}$ )						Acidity by $\text{NH}_3$ -TPD ( $\mu\text{mol}_{\text{ammonia}} \text{desorbed} \text{g}^{-1} \text{cat.}$ )				
			100 °C		200 °C		300 °C		Total	30-250 °C	250-460 °C	475-730 °C	Total
			B	L	B	L	B	L					
Sn-Mont (0.1M)	159	180	43	20	143	44	51	20	321	154.1	5.7	149.2	309.00
Sn-Mont (0.2M)	175	190	81	35	190	67	69	21	463	234.9	85.00	129.39	449.29
Sn-Mont (0.3M)	182	197	95	41	220	76	75	25	532	258.24	88.0	175.1	521.34
Sn-Mont (0.4M)	181	191	49	30	162	61	63	22	387	227.9	24.15	104.39	356.44

[a] Acidity at different temperatures calculated from the extinction coefficients given in Ref. [15]. B=Brønsted acid sites. L= Lewis acid sites.

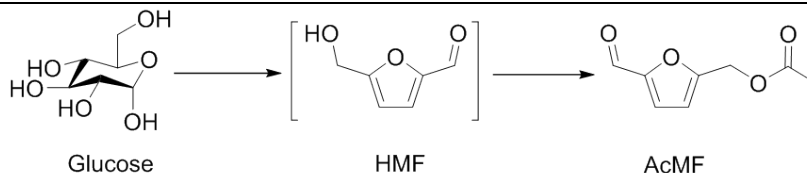
## 2.5.2. Activity Results

### 2.5.2.1. Dehydrative-esterification of glucose to AcMF

Currently, HMF is mainly obtained from the acid-promoted dehydration of carbohydrates (*e.g.* glucose or fructose). However, the process of making HMF is expensive due to tedious separation and purification and also the waste acid is harmful for the environment. Therefore, production of AcMF from HMF would not be an economic process. In contrast, direct synthesis of AcMF from hexoses (*e.g.* fructose and glucose) without isolation of HMF is highly advantageous. Here, we aimed to produce AcMF directly from glucose by treating it with acetic acid and catalyst at 150 °C. For this purpose, several catalysts were explored and their activity results are presented in Table 2.2. Without a catalyst, glucose not reacted with acetic acid eliminating the possibility of any autocatalytic reaction (Table 2.2, entry 1). Glucose was subjected for dehydrative-esterification with acetic acid in presence of catalytic amount of conc.  $\text{H}_2\text{SO}_4$  to afford AcMF with 31 % yield along with polymeric products (Table 2.2, entry 2) thus, having major lacunae in terms of polymer formation, ease of separation and recycling. In an attempt to overcome this, Amberlyst-15, a heterogenized para-toluene sulfonic acid on polystyrene backbone was used for glucose to AcMF conversion. However, Amberlyst-15 was not found to be effective for this transformation due to its inefficiency for glucose isomerisation to fructose (Table 2.2, entry 3). Therefore, we planned to use protocol developed by Ebitani et al. wherein glucose was converted into HMF by using a physical mixture of solid acid (Amberlyst-15) and base (hydrotalcite, HT,  $\text{Mg}:\text{Al}=3$ ) [32]. AcMF was produced in 25 % yield from glucose and acetic acid using combination of Amberlyst-15 + HT (Table 2.2, entry 4). Phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ), a solid acid having Lewis as well as Brønsted acid sites was tested for glucose conversion to AcMF. After heating the mixture of glucose,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and acetic acid at 150 °C for the period of 3h, AcMF was obtained in 17 % yield (Table 2.2, entry 5). Further, in presence of montmorillonite clay AcMF was not obtained, but glucose conversion was reached to 50 % (Table 2.2, entry 6). Acidity of montmorillonite clay could be augmented by metal incorporation into the layers. We have already explored that the Sn-Mont catalyst possesses  $\text{Sn}^{4+}$  species (Lewis acid sites) and  $\text{Sn}(\text{OH})_4$

species (Brønsted acid sites) enwrapped between montmorillonite layers, for the selective self etherification reaction of HMF [27].

**Table 2.2.** Dehydrative-acetylation of glucose over different catalyst <sup>[a]</sup>



Entry	Catalyst	Loading	t	Conv,	Yield, <sup>[c]</sup> [%]	
			[h]	[%]	HMF	AcMF
1	No catalyst	--	4	<10	00	00
2	H <sub>2</sub> SO <sub>4</sub>	10 mol%	3	100	00	31
3	Amberlyst-15	0.2 g	3	80	00	04
4	Amberlyst-15 + HT	0.2 g + 0.1 g	3	98	04	25
5	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	10 mol%	3	82	09	17
6	Mont	0.2 g	4	50	00	00
7	Sn-Mont(0.1M)	0.2 g	3	87	03	35
8	Sn-Mont(0.2M)	0.2 g	3	96	00	41
9	Sn-Mont(0.3M)	0.2 g	3	99	trace	43
10	Sn-Mont(0.4M)	0.2 g	3	92	00	39
11	Sn(OH) <sub>4</sub>	0.2 g	3	00	00	00
12	SnO <sub>2</sub>	0.2 g	3	30	00	00
13 <sup>[b]</sup>	---	---	4	99	trace	95

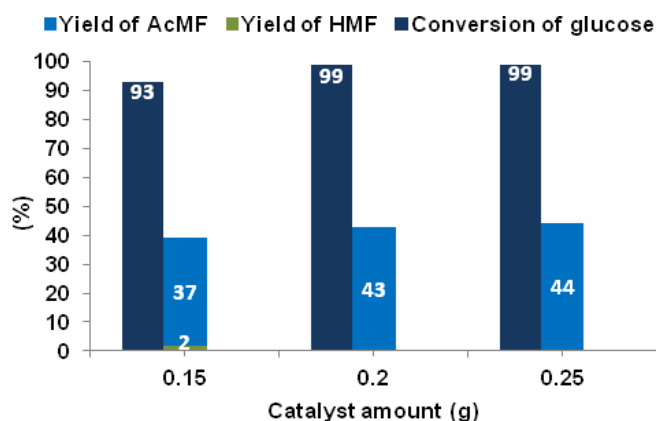
[a] Reaction conditions: glucose (5 wt %), catalyst, acetic acid (10 mL), 150 °C. [b] Reaction conditions: HMF (0.2 g), acetic acid (99.9 %, 10 mL), 50 °C. [c] Yield was determined by using HPLC. HT= Hydrotalcite (Mg/Al= 3).

$\text{Sn}^{4+}$  species are responsible for glucose isomerisation to fructose and  $\text{Sn}(\text{OH})_4$  species catalyze the dehydration of fructose to HMF and further HMF to AcMF. Here, we have prepared different Sn-Mont catalysts from montmorillonite clay by treating it with 0.1-0.4 M solution of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . The catalytic activity of Sn-Mont (0.1-0.4M) was investigated for AcMF production from glucose. Over Sn-Mont(0.1M) catalyst, 87 % conversion of glucose was obtained with 35 % of AcMF (Table 2.2, entry 7). When Sn-Mont(0.2M) catalyst was used, conversion of glucose and yield of AcMF increased to 96 and 41 %, respectively (Table 2.2, entry 8). Sn-

Mont(0.3M) showed complete conversion of glucose with 43 % yield of AcMF (Table 3.2, entry 9). Conversion of glucose and yield of the AcMF dropped down to 92 % and 39 %, respectively, when Sn-Mont(0.4M) was used (Table 2.2, entry 10). Above results obtained with Sn-Mont(0.1-0.3M) catalysts are in well agreement with their acid strengths as discussed above. The activity trend of these catalysts was as follows: Sn-Mont(0.3M) > Sn-Mont(0.2M) > Sn-Mont(0.4M) > Sn-Mont(0.1M). In a control experiment, prepared Sn(OH)<sub>4</sub> and SnO<sub>2</sub> catalysts were found to be ineffective for this transformation (Table 2.2, entries 11, 12). From the above experiments, it was concluded that Sn-Mont catalyst bearing both Brønsted and Lewis acidic sites are responsible for the direct conversion of glucose to AcMF in a single-pot process. In a control experiment, pure HMF was treated with acetic acid (99.9 %) at 50 °C for the period of 4 h, to achieve 95 % yield of AcMF. Sn-Mont(0.3M) was found to be the superior catalyst hence, it was used for further experiments. In a control experiment, pure HMF was treated with acetic acid (99.9 %) at 50 °C for 4 h, to achieve 95 % yield of AcMF.

#### 2.5.2.1.1. Effect of catalyst amount

Effect of Sn-Mont(0.3M) catalyst amount was also studied for glucose conversion to AcMF (Figure 2.5). When the amount of Sn-Mont(0.3M) was decreased from 0.2 g to 0.15 g, the glucose conversion and yield of AcMF decreased to 93 and 37 %, respectively, owing to insufficient active sites. The yield of AcMF did not improve if the amount of Sn-Mont(0.3M) was increased from 0.2 to 0.25 g, indicating that the optimal Sn-Mont(0.3M) amount required for the reaction was 0.2 g.

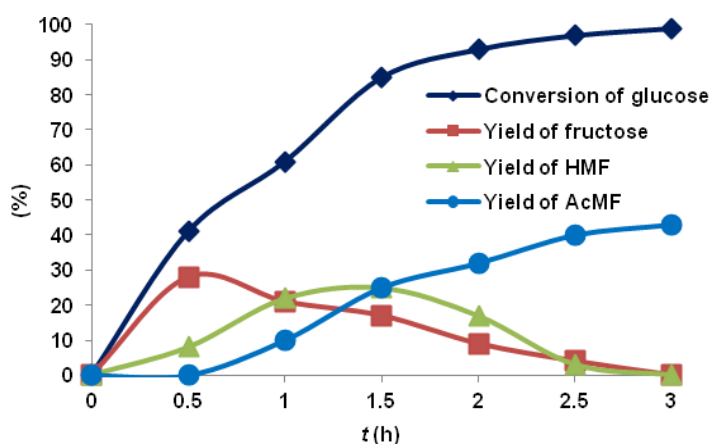


**Figure 2.5.** Influence of catalyst amount on conversion of glucose into AcMF. Reaction conditions: glucose (5 wt %), Sn-Mont(0.3M) (0.15-0.25 g), acetic acid (10 mL), 3 h.



### 2.5.2.1.2. Influence of time

Effect of residence time was studied for the direct transformation of glucose into AcMF by withdrawing samples periodically with an interval of 0.5 h (Figure 2.6). Under experimental conditions in first half hour of the reaction, glucose was isomerised to 28 % of fructose along with 8 % of HMF. After 1 h, 61 % glucose was consumed with product distribution as follows: fructose (21 %), HMF (22 %) and AcMF (10 %). After 1.5 h, concentration of fructose and HMF started decreasing due to their conversion into AcMF. At the end of 3<sup>rd</sup> hour, AcMF precursors such as glucose, fructose and HMF were consumed completely to afford a maximum of 43 % yield of AcMF.

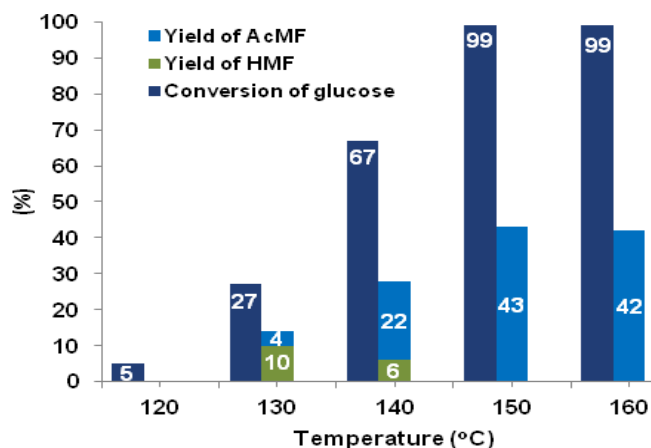


**Figure 2.6.** Progress of glucose conversion into AcMF with time. Reaction conditions: glucose (5 wt %), Sn-Mont(0.3M) (0.2 g), acetic acid (10 mL), 150 °C.

### 2.5.2.1.3. Influence of temperature

Effect of change in temperature on the behaviour of reaction was also investigated (Figure 2.7). At 120 °C, no any significant conversion of glucose was observed. The conversion of glucose increased to 27 % when temperature was raised to 130 °C and importantly AcMF formation was also initiated. Interestingly, when temperature was further raised to 140 °C, the glucose conversion was significantly increased to 67 % and AcMF was formed in 22 % yield. Thus, temperature higher than 140 °C was required to promote this reaction to completion. Almost complete conversion of glucose could be achieved at 150 °C, with a maximum yield of AcMF (43 %).

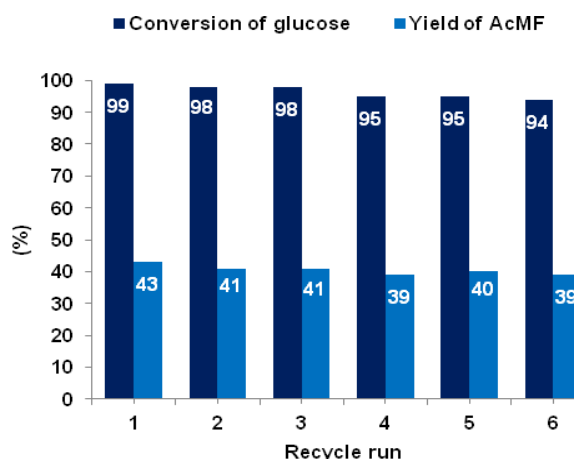
Furthermore increase in temperature to 160 °C, did affected neither glucose conversion nor the yield of AcMF.



**Figure 2.7.** Influence of temperature on conversion of glucose into AcMF. Reaction conditions: glucose (5 wt %), Sn-Mont(0.3M) (0.2 g), acetic acid (10 mL), 3 h.

#### 2.5.2.1.4. Recycle studies of Sn-Mont(0.3M)

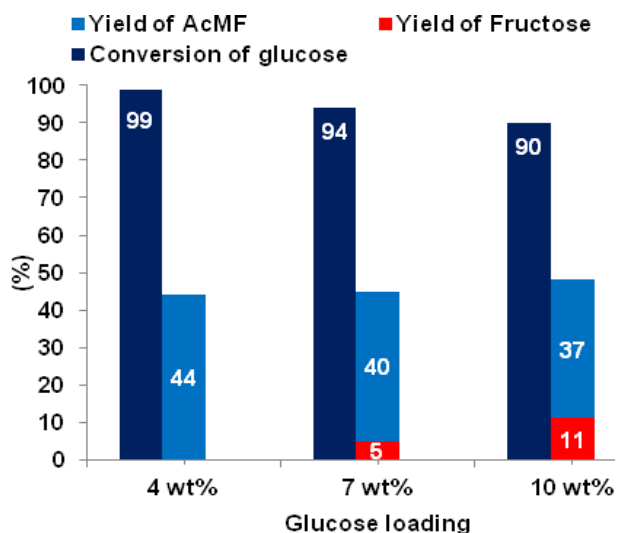
The stability and reusability of Sn-Mont(0.3M) catalyst was established for the dehydrative-esterification of glucose to AcMF. It was found that the catalytic activity of Sn-Mont(0.3M) was very much consistent after being used for six times (Figure 2.8). The Figure 2.8 indicated that the Sn-Mont(0.3M) catalyst has a reasonable stability. When Sn-Mont (0.3M) was used for six times at 150 °C for the period of 3 h, the glucose conversions slightly dropped from 99-94 % after sixth reuse while AcMF yield were also showed slight drop in yield from 43-38 %. Such a slight loss in activity could be attributed to the humin deposition on the catalyst surface.



**Figure 2.8.** Recycle experiments for conversion of glucose into AcMF; Reaction conditions: glucose (5 wt %), Sn-Mont(0.3M) (0.2 g), acetic acid (10 mL), 150 °C, 3 h.

#### 2.5.2.1.5. Effect of glucose concentration

In case of heterogeneous catalytic reaction, yield of the desired product could be significantly influenced by the substrate concentration. Thus, the effect of an initial glucose concentration was studied in the range of 4–10 wt %, for the dehydrative-esterification of glucose to AcMF (Figure 2.9). It was observed that both conversion of glucose and yield of AcMF were partially influenced by the change in initial glucose concentration.

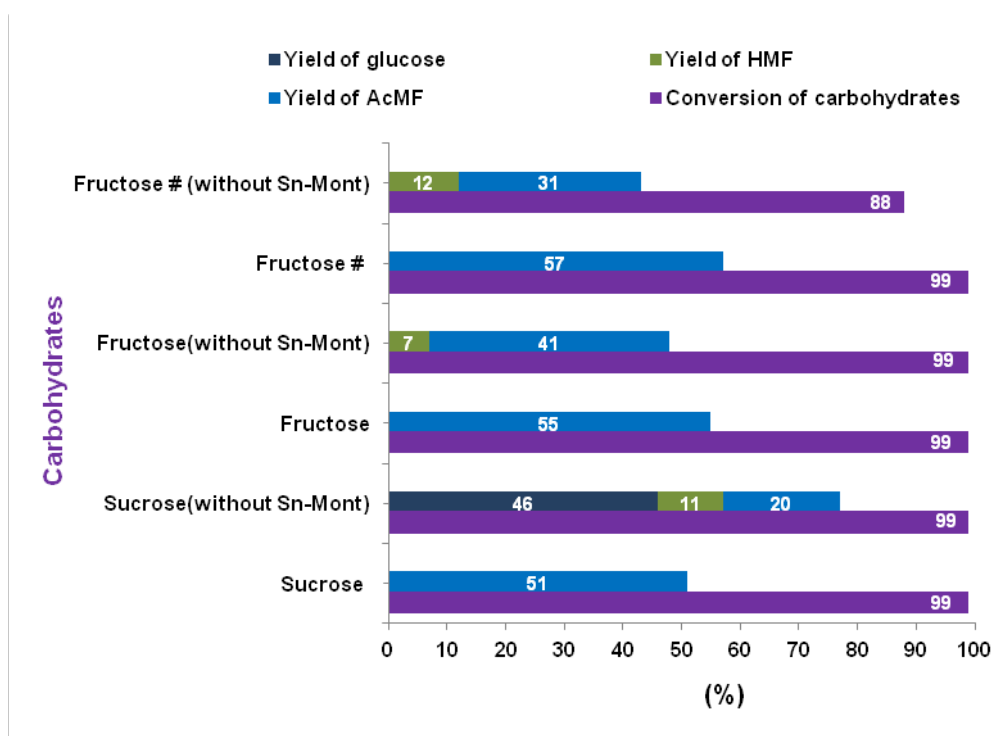


**Figure 2.9.** Effect of glucose concentration; Reaction conditions: glucose (4-10 wt %), Sn-Mont(0.3M) (0.2 g), acetic acid (10 mL), 150 °C, 3 h.

As high as 44 % yield of AcMF was obtained when 4 wt % of initial glucose concentration was used. When 7 wt % of glucose concentration was used still 40 % yield of AcMF was noticed. It indicates the high efficiency of Sn-Mont(0.3M) catalyst. At high glucose concentration partial loss of HMF is observed it could be due to the increased rates of side-reactions which lead to formation of undesired by-products [24].

#### ***2.5.2.2. Synthesis of AcMF from Sucrose and fructose***

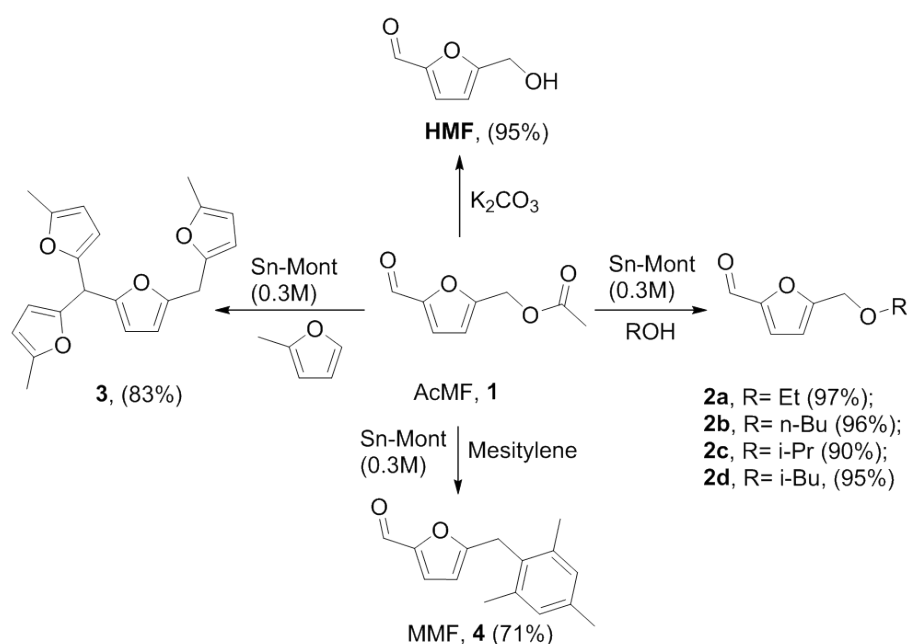
Encouraged by the results obtained for synthesis of AcMF directly from glucose and acetic acid over Sn-Mont(0.3M) catalyst, we further explored the possibility of using more complex carbohydrate, such as disaccharide (sucrose) as renewable raw materials. Under optimized reaction conditions, sucrose could be converted into AcMF with our catalyst and the 51 % yield of AcMF was obtained (Figure 2.10). While, without using Sn-Mont(0.3M) sucrose was fully consumed with 46 % of glucose, 11 % of HMF and 20 % of AcMF yield. In absence of Sn-Mont (0.3M), fructose part of sucrose was hydrolysed in acetic acid while glucose part was left unreacted which was confirmed by HPLC analysis. Further objective was to convert fructose into AcMF. We performed some experiments for dehydration of fructose in acetic acid with and without using Sn-Mont(0.3M) catalyst. The conversion of fructose was nearly up to 100 % with 55 % yield of AcMF at 150 °C in just 1 h. It means that the dehydration of fructose to HMF and further esterification was very fast and the Brønsted acid sites of the Sn-Mont(0.3M) were active enough for the dehydration of generated fructose to HMF. In fact, fructose is relatively more reactive as compared to glucose or sucrose. Therefore, fructose dehydration could be achieved at relative milder temperature of 130 °C in presence of Sn-Mont(0.3M), to give higher yield of AcMF (57 %) in 1.5 h with >99 % conversion of fructose. Without using Sn-Mont(0.3M) at 130 °C, upto 88 % conversion of fructose was observed with 31 % yield of AcMF.



**Figure 2.10.** AcMF yield from sucrose and fructose. Reaction conditions: Carbohydrate (5 wt %), Sn-Mont(0.3M) (0.2 g), acetic acid (10 mL), 150 °C. #Reaction was carried out at 130 °C. Conversion and yields were determined using HPLC.

### 2.5.3. Transformation of AcMF into useful furan derivatives

HMF is a versatile platform chemical for the synthesis of various valuable chemicals. HMF is derived from the two functionalities attached at C<sub>2</sub> and C<sub>5</sub> of its furan ring. The functionalities such as hydroxymethyl and formyl of HMF could be converted into diverse and useful furan derivatives (Scheme 2.3). Other furan derivatives such as 5-(alkoxymethyl)furfural (**2**) [33], condensation product (**3**) [34] and mesitylmethylfurfural (**4**) [26] are potential fuel blenders or precursors. Recently, we have produced condensation product (**3**) from AcMF using -SO<sub>3</sub>H functionalized ionic liquid [34]. There is no report on transformation of AcMF into 5-(alkoxymethyl)furfural (**2**) and mesitylmethylfurfural (**4**). With this in the mind, we have probed the conversion of AcMF to valuable furan derivatives to signify its utility (Scheme 2.3). Alcoholysis of AcMF at 80 °C in presence of Sn-Mont (0.3M) catalyst provided selectively respective ethers in significantly high yield (**2a-d**). Importantly, for alcoholysis of AcMF competing reaction such as acetalization was not observed.



**Scheme 2.3.** Transformation of AcMF into useful furan derivatives. Isolated yields are represented in parenthesis.

However, acetalization product is usually formed in alcoholysis of HMF in presence of acid which needs to be further hydrolysed in  $H_2O$  [33]. Treatment of AcMF with three moles of 2-methylfuran afforded condensation product (**3**) in 83 % yield.  $C_{21}$  unit of condensation product could be a potential precursor for production of liquid alkanes. Friedel-Crafts alkylation of mesitylene with AcMF was performed over Sn-Mont(0.3M) catalyst to give 71 % yield of hybrid diesel fuel precursor such as mesitylmethylfurfural (**4**). While using AcMF as starting material the yields of **2a-d**, **3** and **4** were significantly higher than that using HMF as a starting material. Thus it is revealed that AcMF has potential to produce those products which are traditionally prepared from HMF. Hence, AcMF could be considered as a sustainable substitute/alternative for HMF. AcMF could be selectively transformed back to HMF in high yield and high purity after hydrolysis with base catalyst. Hydrolysis of AcMF was performed using NaOH,  $K_2CO_3$  and Amberlite IRN78 hydroxide resin to get 73, 95 and 85 % yield of HMF, respectively.

## 2.6. Conclusions

We have presented a productive method for the AcMF production from carbohydrates through sequential isomerisation–dehydration–esterification reactions in one-pot over Sn-Mont(0.3M) catalyst. The Sn-Mont(0.1-0.4M) catalysts were prepared by simple mixing of montmorillonite clay with an aqueous solution of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  of different concentrations (*e.g.* 0.1M-0.4M). Types of acid sites of the Sn-Mont(0.1-0.4M) catalysts were identified by Py-FTIR analysis and their strength was estimated by using Emeis equation. Among all the tested catalysts, Sn-Mont(0.3M) showed highest acid strength; hence AcMF was produced in high yield (43 %) directly from glucose. It was reveals that the presence of combination of Lewis and Brønsted acid sites in Sn-Mont catalyst is the key for the direct conversion of the glucose-unit carbohydrates into AcMF. In a one-pot reaction system, the combination of Brønsted acid and Lewis acid sites facilitated isomerization + dehydration. Sn-Mont has green preparation method, it is a highly active and reusable catalyst.

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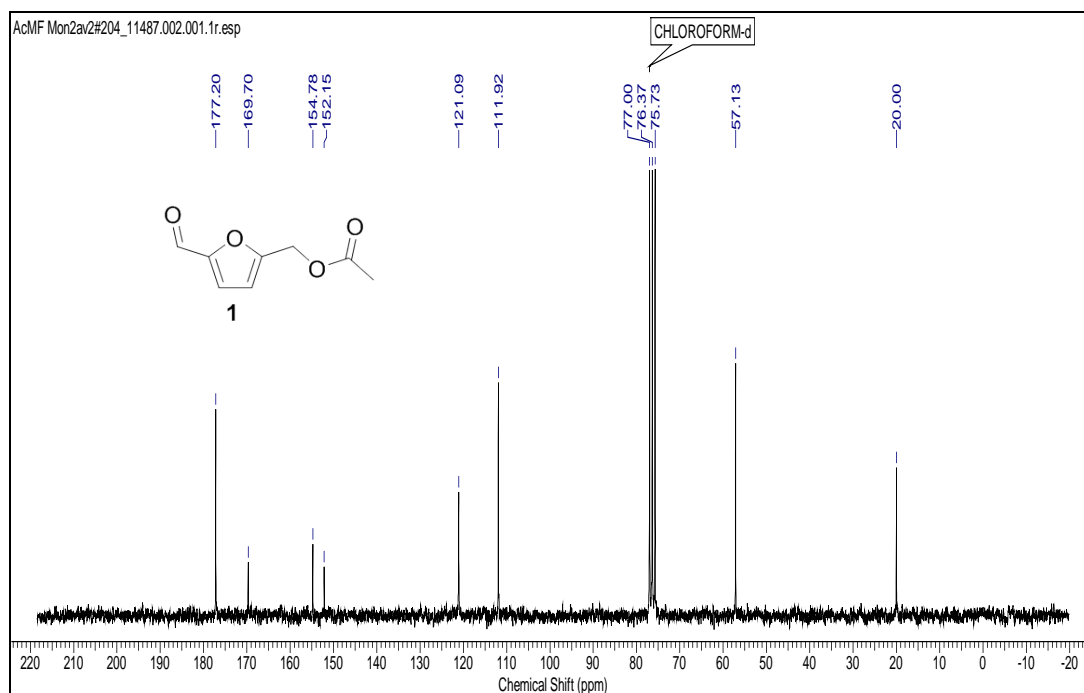
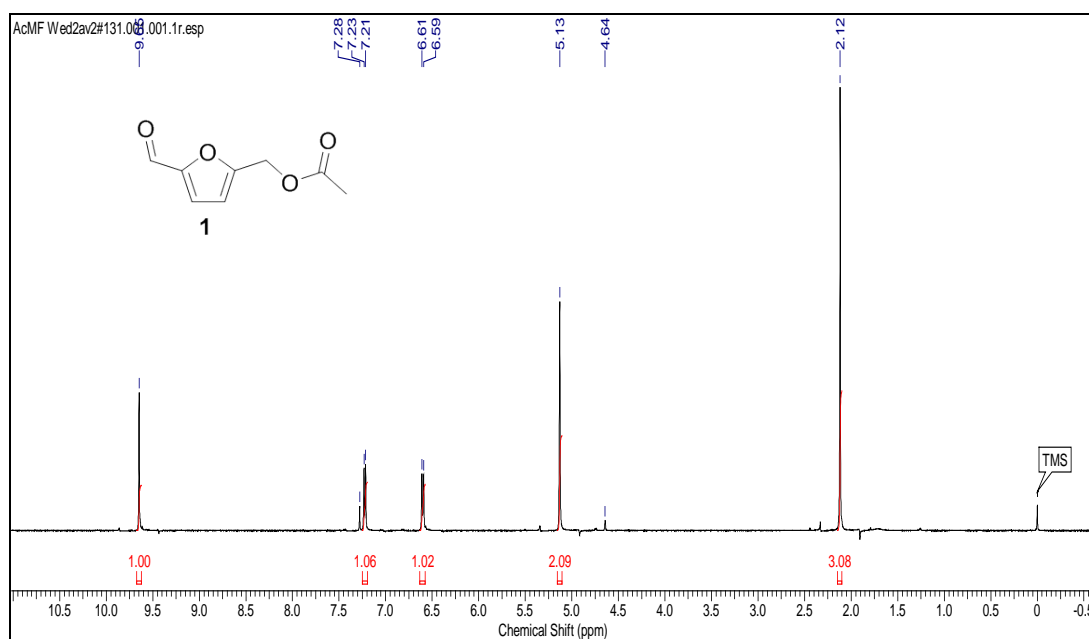
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## 2.8. NMR data of the synthesized compound

### 5-Acetoxymethylfurfural (1): Orange oil

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 2.12 (s, 3 H) 5.13 (s, 2 H) 6.60 (d,  $J=3.54$  Hz, 1 H) 7.22 (d,  $J=3.54$  Hz, 1 H) 9.65 (s, 1 H).

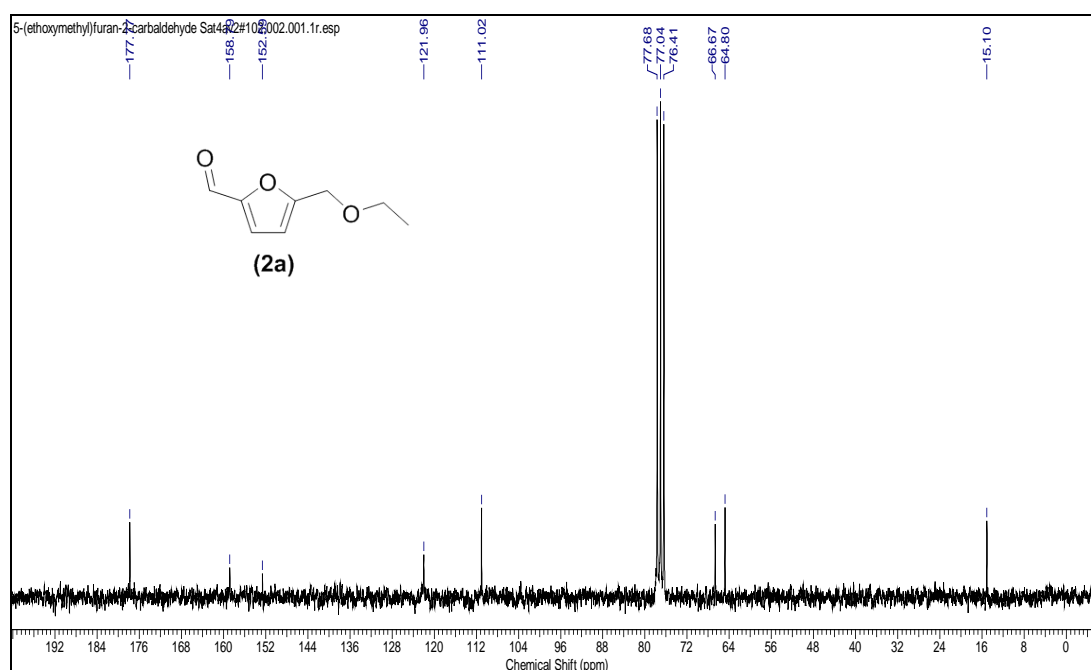
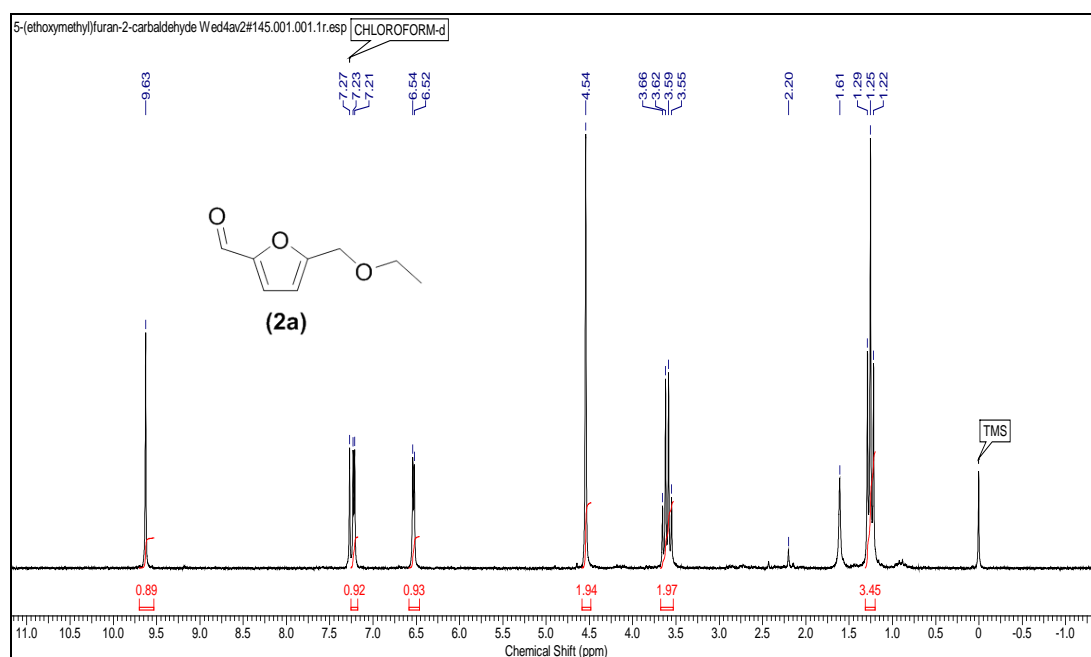
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 20.00, 57.13, 111.92, 121.09, 152.15, 154.78, 169.70, 177.20.



**5-(Ethoxymethyl)furan-2-carbaldehyde (2a):** Orange oil

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 1.25-1.29 (t,  $J=7.01$  Hz, 3 H) 3.55-3.66 (q,  $J=6.95$  Hz, 2 H) 4.54 (s, 2 H) 6.52-6.54 (d,  $J=3.54$  Hz, 1 H) 7.21-7.23 (d,  $J=3.54$  Hz, 1 H) 9.63 (s, 1 H).

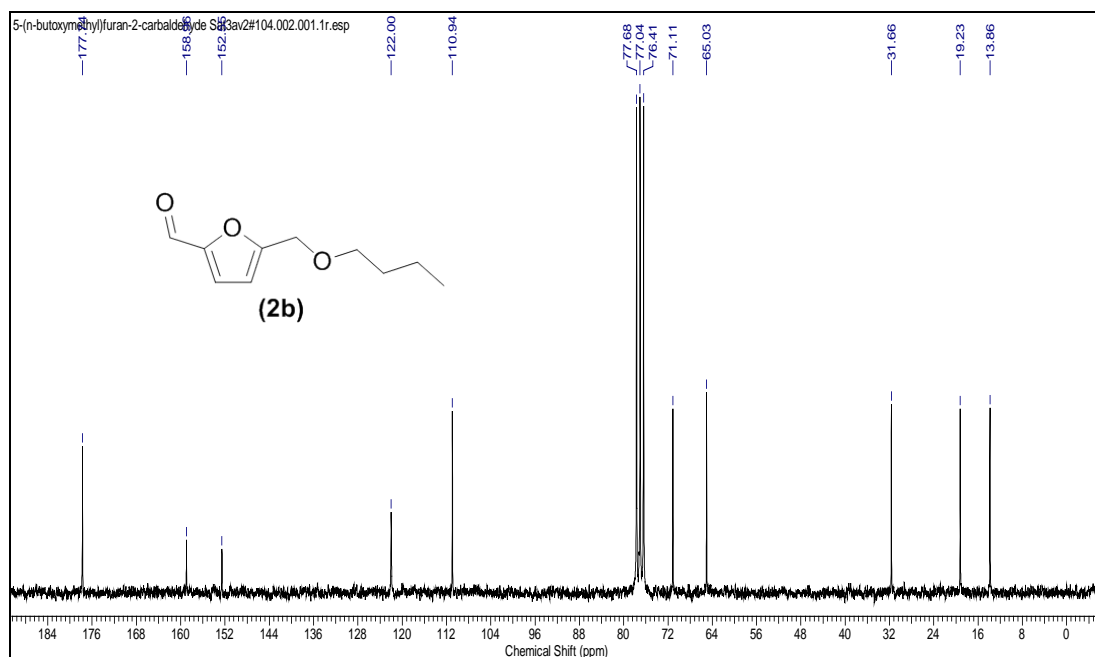
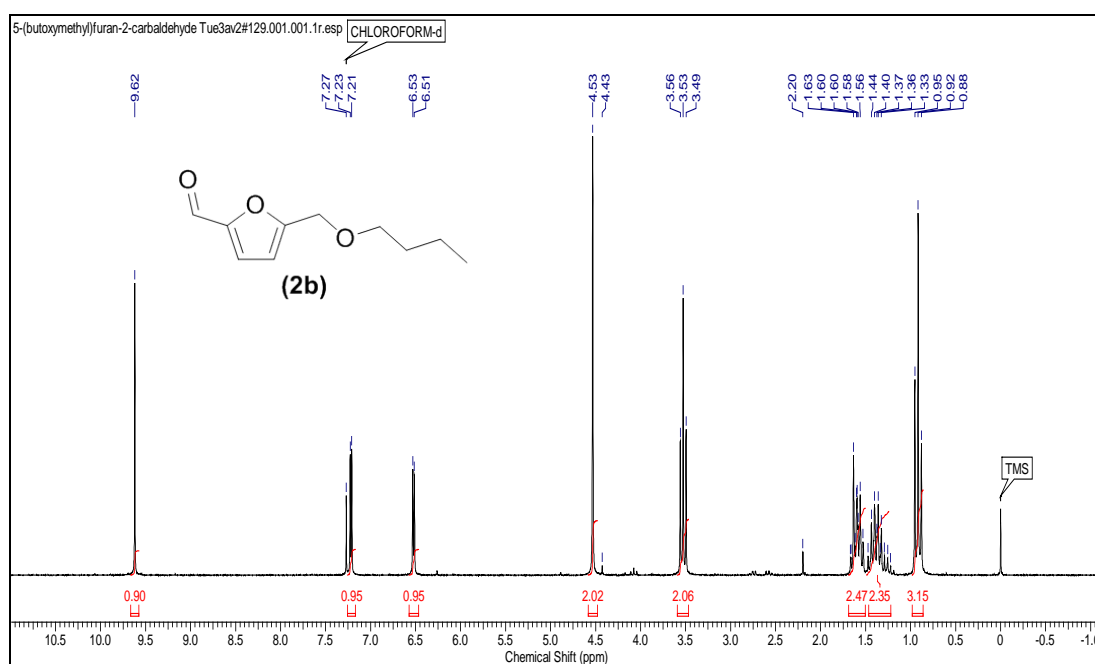
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 15.10, 64.80, 66.67, 111.02, 121.96, 152.59, 158.79, 177.77.



**5-(Butoxymethyl)furan-2-carbaldehyde (2b):** Yield: 96%,

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.88 - 0.95 (m, 3 H) 1.33 - 1.44(m, 2 H) 1.56 - 1.63 (m, 2 H) 3.49 - 3.56 (t,  $J=6.51$  Hz, 2 H) 4.53 (s, 2 H) 6.51–6.53 (d,  $J=3.54$  Hz, 1 H) 7.21 - 7.23 (d,  $J=3.54$  Hz, 1 H) 9.62 (s, 1 H);

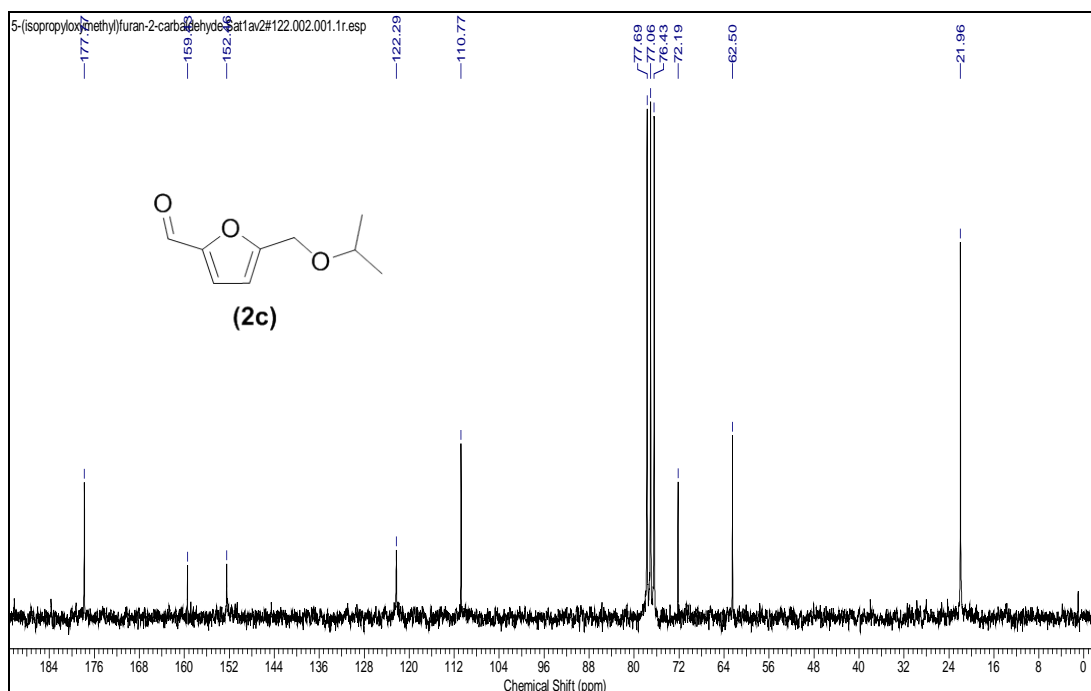
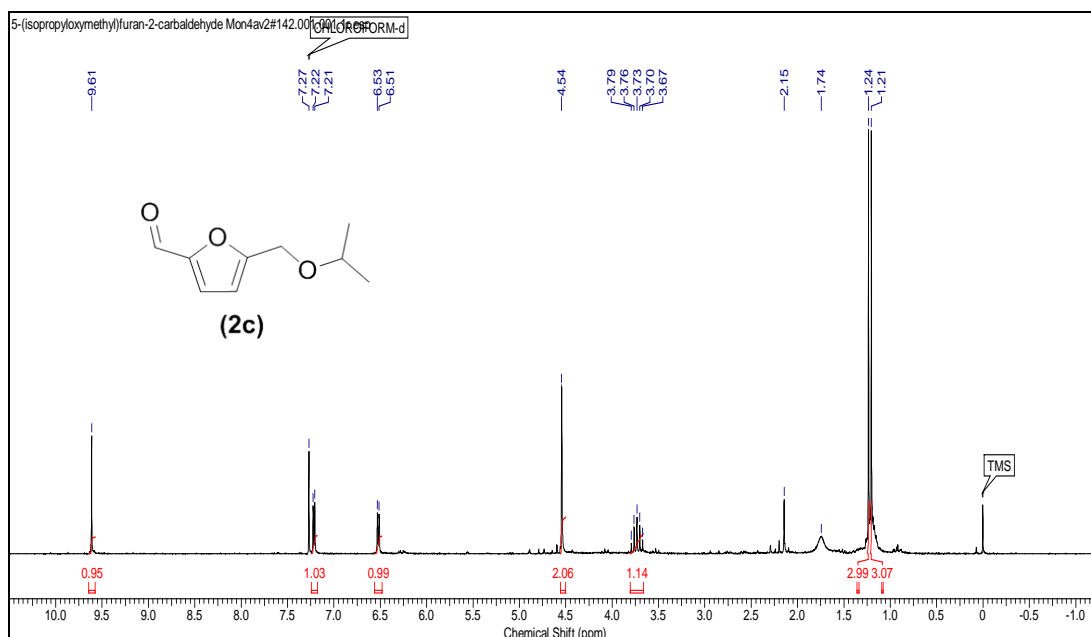
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.86, 19.23, 31.66, 65.03, 71.11, 110.94, 122.00, 152.55, 158.96, 177.74.



**5-(Isopropoxymethyl)furan-2-carbaldehyde (2c):** Yield: 90%,

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 1.21 (s, 3 H) 1.24 (s, 3 H) 3.67-3.79 (quin,  $J=6.09$  Hz, 1 H) 4.54 (s, 2 H) 6.51-6.53 (d,  $J=3.54$  Hz, 1 H) 7.21-7.22 (d,  $J=3.54$  Hz, 1 H) 9.61 (s, 1 H).

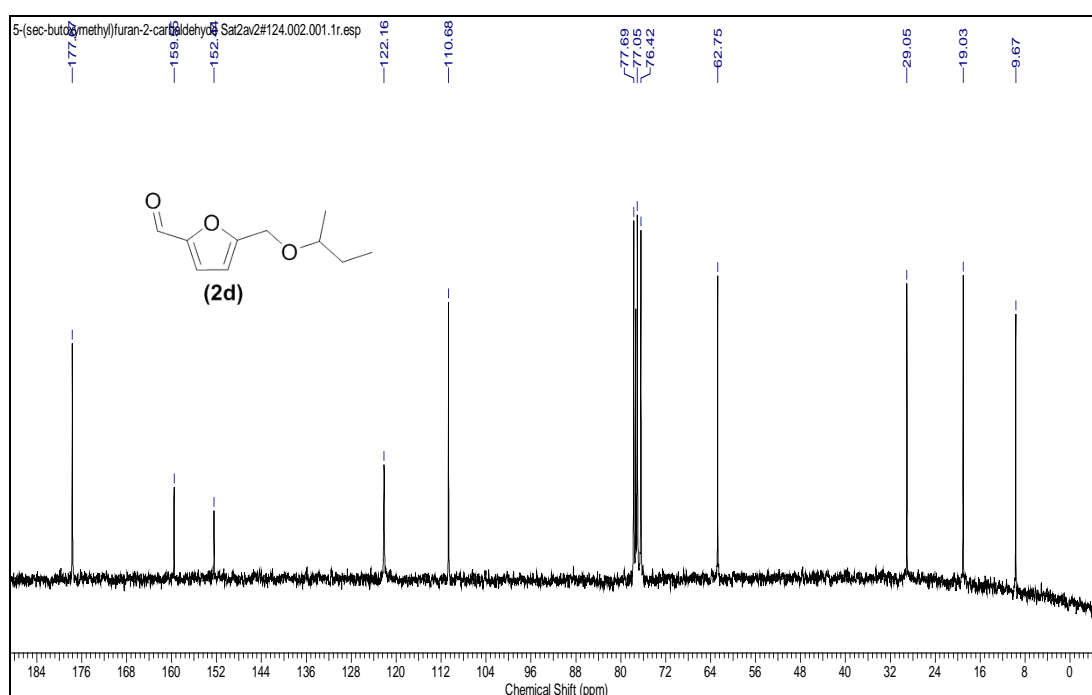
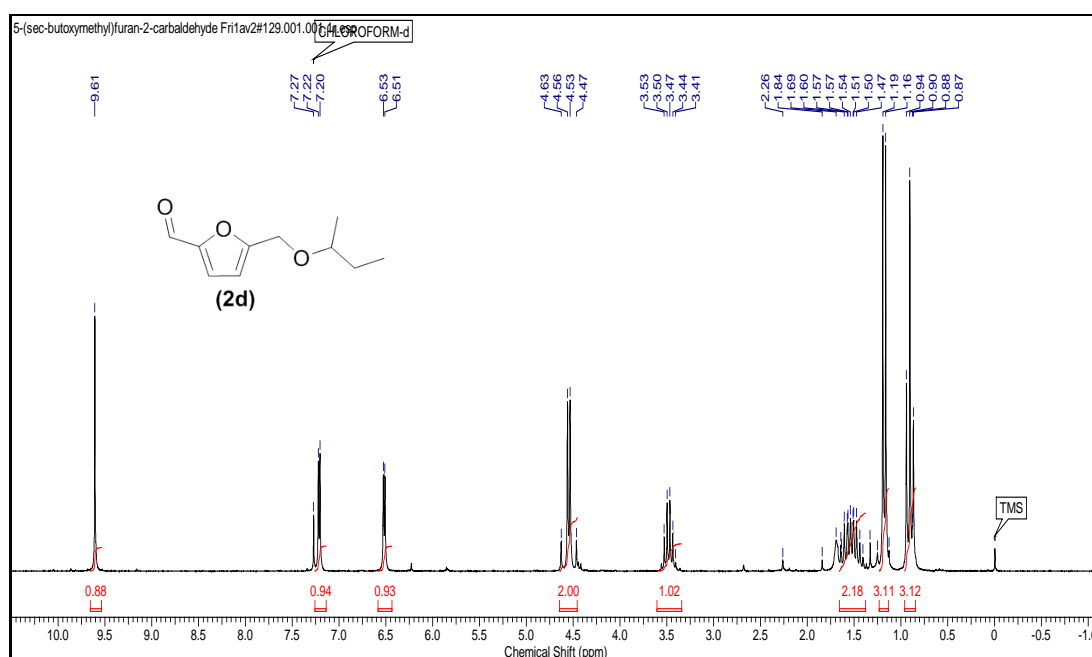
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 21.96, 62.50, 72.19, 110.77, 122.29, 152.46, 159.43, 177.77

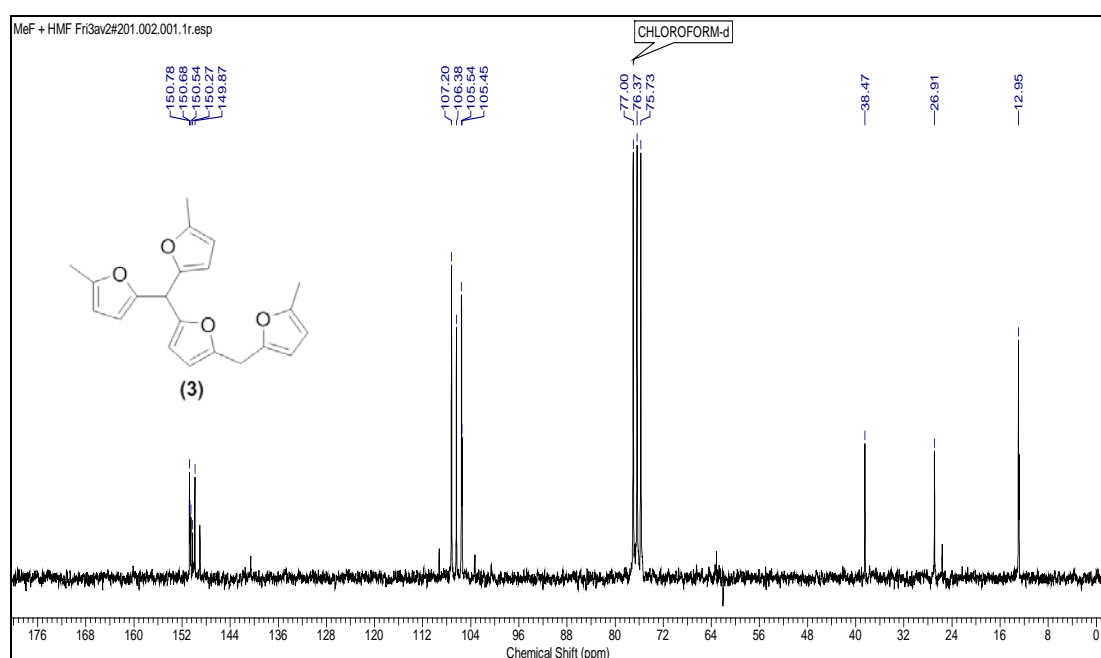
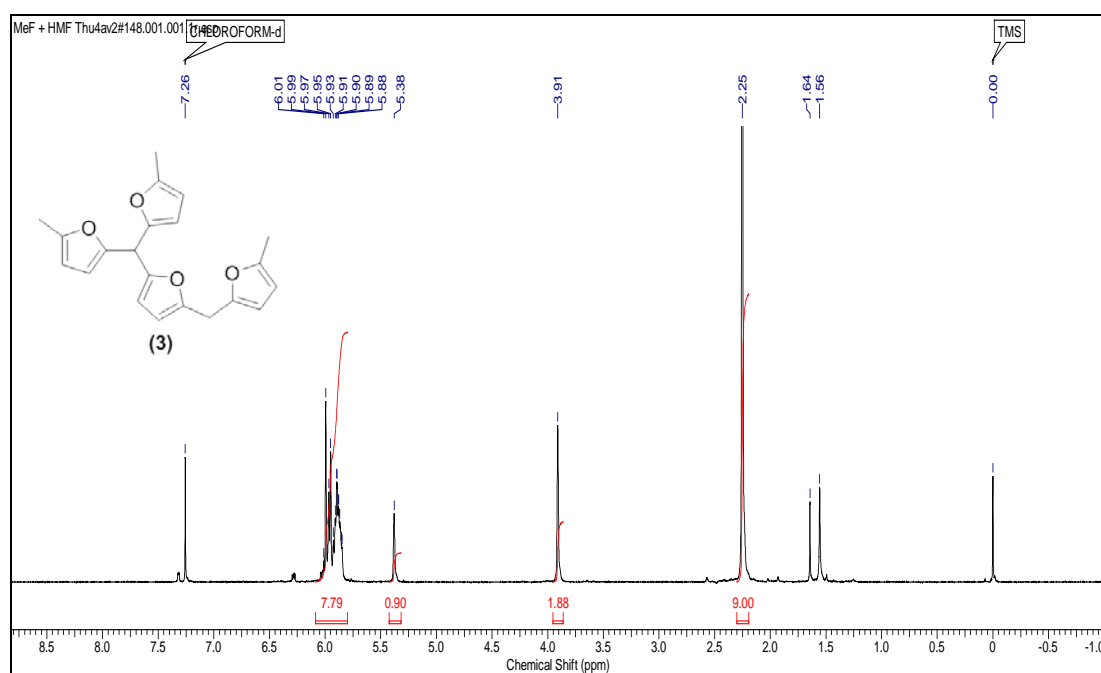


**5-(*sec*-Butoxymethyl)furan-2-carbaldehyde (2d):** Yield: 95%,

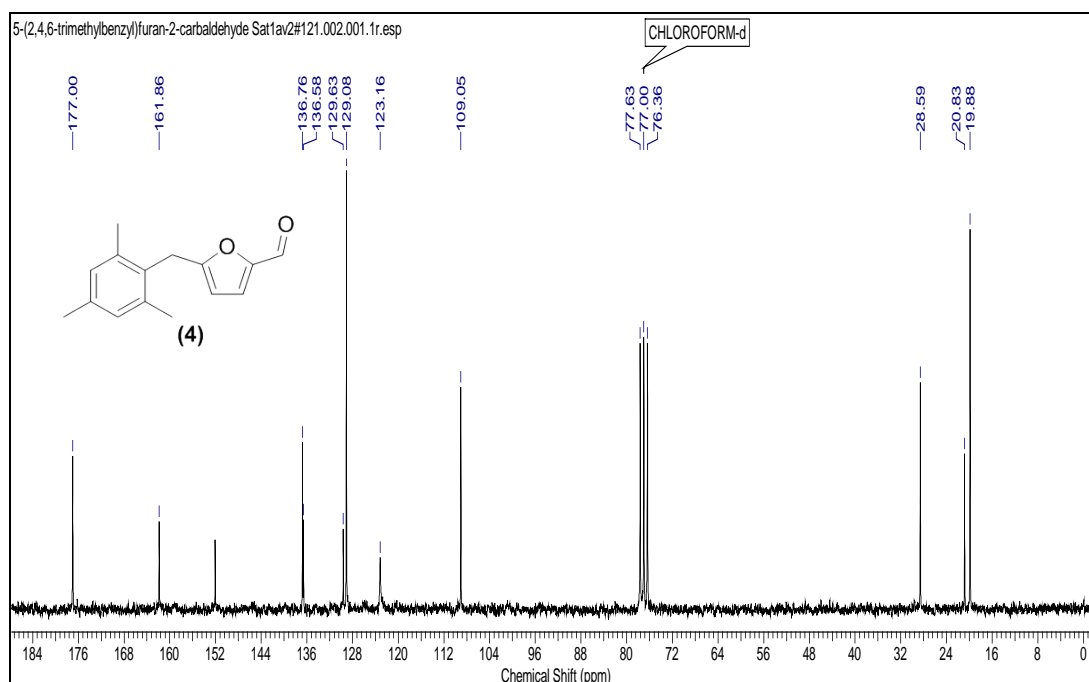
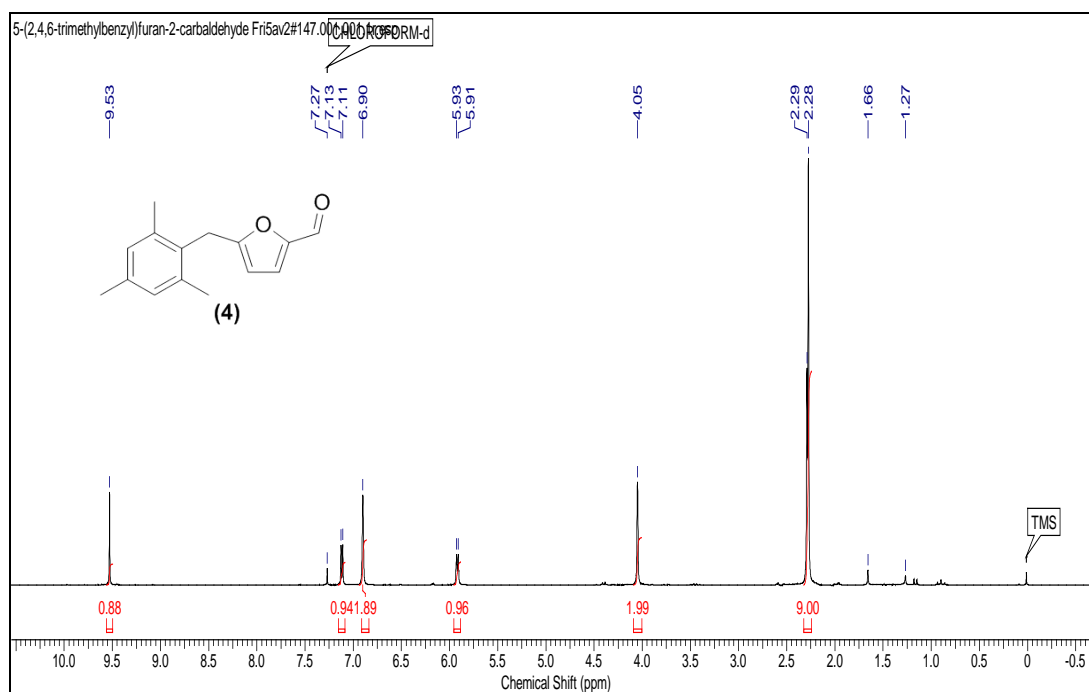
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 0.87-0.94 (t, 3 H) 1.16-1.19 (d,  $J=6.19$  Hz, 3 H) 1.41-1.64(m, 2 H) 3.41 - 3.56 (m, 1 H) 4.47-4.63 (m, 2 H) 6.51-6.53 (d,  $J=3.54$  Hz, 1 H) 7.20-7.22 (d,  $J=3.54$  Hz, 1 H) 9.61 (s, 1 H).

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 9.67, 19.03, 29.05, 62.75, 76.42, 77.34, 77.69, 110.68, 122.16, 152.44, 159.55, 177.67.



**5,5'-((5-((5-methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran)****(3):** Yield: 0.71 g (94%),<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ ppm: 2.25 (s, 9 H) 3.91 (s, 2 H) 5.38 (s, 1 H) 5.88-6.01 (m, 8 H).<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ ppm: 13.52, 13.62, 27.59, 39.15, 106.12, 106.22, 107.06, 107.88, 149.71, 150.55, 150.95, 151.21, 151.36, 151.45.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ ppm: 2.28 - 2.29 (m, 9 H, -CH<sub>3</sub>) 4.05 (s, 2 H) 5.91-5.93 (d, J=3.54 Hz, 1 H) 6.90 (s, 2 H) 7.11-7.13 (d, J=3.54 Hz, 1 H) 9.53 (s, 1 H).  
<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ ppm: 19.88, 20.83, 28.59, 109.05, 123.16, 129.08, 129.63, 136.58, 136.76, 152.00, 161.86, 177.00



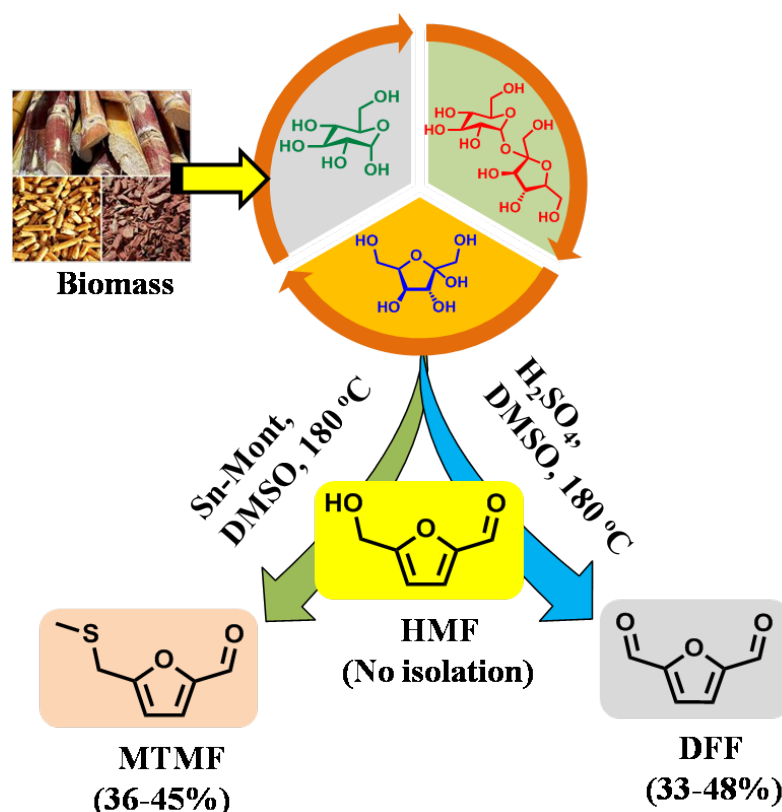


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## Chapter 3

### Direct production of 2,5-di(formyl)furan and 5-((methylthio)methyl)-2-furfural from carbohydrates

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2,5-di(formyl)furan (DFF) and 5-((methylthio)methyl)-2-furfural (MTMF) were directly produced from carbohydrates (*e.g.* fructose, glucose and sucrose) in DMSO as a sacrificial solvent. DFF was produced in moderate yield (33-48 %) from carbohydrates in a mixture of catalytic amount of concentrated H<sub>2</sub>SO<sub>4</sub> and DMSO which is acting as an oxidant, without an external O<sub>2</sub> or additional oxidation catalyst. While, MTMF was produced in good to moderate yield (36-45 %) from carbohydrates in DMSO over solid Sn-Mont catalyst. DMSO decomposed to give dimethylsulfide at 180 °C in presence of Sn-Mont catalyst, which reacted with in situ formed HMF to form MTMF.

Suhas Shinde and Chandrashekhar Rode, Patent application number **INV-2017-009**

### 3.1. Introduction

2,5-Diformylfuran (DFF) is one of the most important derivatives of HMF which has wide range applications in the synthesis of polymers, antifungal agents, drugs and ligands. DFF can also be used to produce unsubstituted furans. In spite of its proven usefulness, DFF is not readily available commercially. Selective oxidation of HMF is the only industrially feasible route to DFF. However, there is currently only one industrial process which uses biomass-derived feedstock for bulk production of HMF [1]. Indeed, lab scale purification of HMF has also proved to be a troublesome operation. HMF could be distilled out by long exposure to temperatures but impurities associated with the synthetic mixture tend to form tarry degradation products. A process that directly converts carbohydrate to DFF avoiding the costly HMF isolation step, would definitely have economic as well as process advantages.

### 3.2. Literature survey

Few researchers have already attempted direct carbohydrate conversion to DFF. For example, Takagaki et al. reported glucose conversion to DFF with 25 % yield in one-pot process using three different catalysts comprising hydrotalcite (HT) for glucose isomerisation to fructose, Amberlyst-15 for fructose dehydration to HMF and Ru/HT for HMF oxidation to DFF in  $O_2$  atmosphere [2]. In another attempt, a complex homogeneous catalytic system ( $AlCl_3 \cdot 6H_2O/NaBr$  and vanadium compound) has been reported with molecular  $O_2$  in DMF solvent for DFF formation from glucose [3]. Xiang et al. achieved DFF yield of 55 % based on glucose in one-pot, two-step conversion of glucose over homogeneous catalyst system of  $CrCl_3 \cdot 6H_2O/NaBr/NaVO_3 \cdot 2H_2O$ , [4]. Another one-pot DFF synthesis involves acid catalyzed dehydration of fructose followed by aerobic oxidation using a combination of  $Fe_3O_4$ -SBA- $SO_3H$  and K-OMS-2 catalyst [5]. Ghezali et al. reported that mixture of Choline Chloride and DMSO promoted the direct conversion of fructose to DFF with 84 % yield in the presence of a bifunctional acid/redox HPMoV catalyst [6]. Graphene oxide, a metal-free carbon based material was also demonstrated to be an efficient and recyclable bifunctional catalyst in the direct synthesis of DFF with 53-72 % yield from fructose. [7] A combination of Amberlyst-15 + SBA-15-Biimidazole-Ru catalyst system in presence of  $O_2$  under pressure was found to give 72.4 % DFF yield from conversion. [8] Similarly, Halliday et al. reported two step

procedures for conversion of fructose to DFF using fructose dehydration over BioRad AG 50W-X8, 100-200 mesh cation-exchange resin followed by oxidation over vanadium compound. [9] Chen et al. reported a bifunctional catalyst V-g-C<sub>3</sub>N<sub>4</sub> (H<sup>+</sup>) for fructose conversion to DFF with 45 % yield [10]. The simple salts like NaBr have been also reported for one-pot transformations, which could replace transition-metal catalysts for the conversion of fructose into DFF in DMSO solvent [11]. In another two step procedure for synthesis of DFF from fructose, H<sub>2</sub>SO<sub>4</sub> (10 mol %) was used as an acid catalyst for dehydration and then [Pip\*(O)][BF<sub>4</sub>] as a oxidation agent in ionic liquids. [12] Liu et al. reported a bifunctional acid/redox polyoxometalate (Cs<sub>3</sub>HPMo<sub>11</sub>VO<sub>40</sub>) catalyst for dehydrative-oxidation of fructose to DFF with 60 % yield [13]. An integrated conversion of fructose to DFF was achieved using combination two catalysts such as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-SO<sub>3</sub>H and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@HAP-Ru, under O<sub>2</sub> flow [14]. A satisfactory yield of 69.3 % to DFF could be obtained from fructose over a bifunctional acid/redox polyoxometalate (Cs<sub>0.5</sub>H<sub>2.5</sub>PMo<sub>12</sub>) [15]. Xu et al. used Amberlyst-15 for the acid-catalyzed dehydration of fructose into HMF, followed by the in situ oxidation of HMF to DFF catalyzed by polyaniline-VO(acac)<sub>2</sub> with 71 % yield [16].

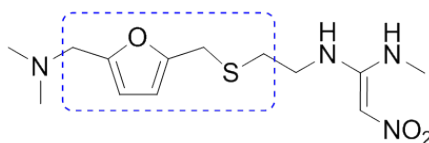
There are only three methods existed for glucose conversion to DFF. However, all of these strategies have used two or more catalyst systems for separate purposes (*e.g.* oxidation catalyst and dehydration catalyst) with external source of oxygen. The methods reported on fructose conversion to DFF are limited for fructose molecule but not applicable for more complex carbohydrates such as glucose or sucrose. Therefore, there is need in the art to develop a process which will overcome prior arts drawbacks.

### 3.3. Scope of the present work

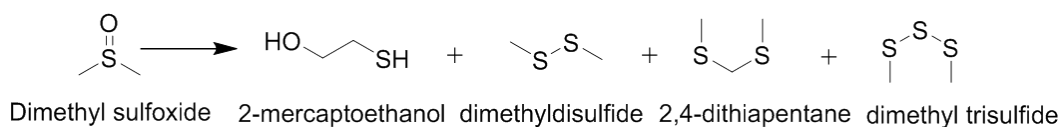
As can be seen from the literature, if glucose is the starting material, first step involves its isomerization to fructose followed by dehydration and finally the oxidation to give DFF. Hence, two or more catalysts have been used for example, Lewis acid or base for glucose isomerisation to fructose, Brønsted acid for dehydration of fructose to HMF and oxidation catalyst for oxidation of HMF to DFF with an external source of oxygen. The methods reported on the fructose conversion to DFF are mostly limited to fructose as a starting material only and not applicable

for complex carbohydrates such as glucose or sucrose. Therefore, our objective of the present work was to provide a single catalyst, single solvent, no oxidation source and simple catalytic process that can convert a series of carbohydrate to DFF without the isolation of HMF. In this work, we have produced DFF in 33-48 % yield from glucose, sucrose and fructose using catalytic amount of conc.  $\text{H}_2\text{SO}_4$  in DMSO.

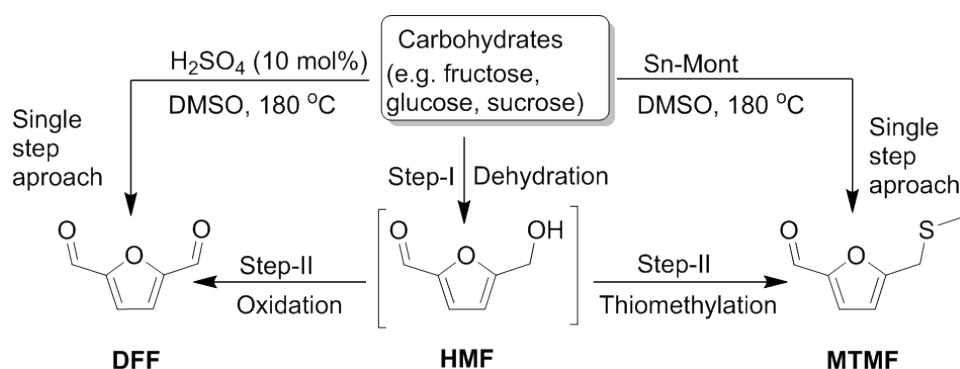
Another valuable furan derivatives such as 5-((methylthio)methyl)-2-furfural (MTMF) is a new class of sulfur derivative of HMF. This molecule presently not having known applications, but in future it may be a valuable intermediate due to its sulfur functionality. The introduction of sulfur makes MTMF, a precursor for the synthesis of some pharmaceutical intermediates. Especially, this molecule could be a starting material for the cheap production of Ranitidine (Zantac) (Scheme 3.1). Hu et al. [17] performed dehydration of levoglucosan with Amberlyst-70 in DMSO and they found MTMF as a major product. But, they have not quantified the abundance of MTMF in reaction. The polysulfides produced from the decomposition of DMSO could further react with HMF to produce 5-[(methylthio)methyl]-2-furancarboxaldehyde (Scheme 3.2). In this work, a solid acid Sn-Mont catalyst was found to be most suitable for conversion of carbohydrates to MTMF. The Sn-Mont promotes dehydration of carbohydrates and also decomposition of DMSO to polysulfide's which was further reacted with HMF to produce MTMF. We are the first to synthesize MTMF in high yield directly from carbohydrates. A schematic of production of DFF and MTMF from carbohydrates without isolation of the intermediate, HMF is presented in Scheme 3.3.



**Scheme 3.1.** Structure of Ranitidine (Zantac)



**Scheme 3.2.** Thermal decomposition of DMSO in acid medium



**Scheme 3.3.** Direct conversion of carbohydrates to DFF and MTMF

### 3.4. Experimental section

#### 3.4.1. Materials

All the materials/chemicals used in this work were as obtained from the authentic suppliers.  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_2\text{SO}_4$  (98%), and carbohydrates such as sucrose, glucose and fructose were obtained from Thomas Baker, India. All the solvents and inorganic solids such as  $\text{NaHCO}_3$  and  $\text{Na}_2\text{SO}_4$  were purchased from ChemLabs, India. Inorganic metal precursors such as  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , Amberlyst-15 and montmorillonite clay were of Sigma-Aldrich make. Sn-Mont(0.3M) is prepared by following method reported in section 2.4.2 of **Chapter 2**.

#### 3.4.2. Catalyst characterization

The instrumentation used for the characterisation of Sn-Mont(0.3M) is already presented in section 2.4.3 of **Chapter 2**.

#### 3.4.3. Catalyst testing

##### 3.4.3.1. Synthesis of DFF from carbohydrates

A solution of carbohydrates (*e.g.* fructose/glucose/sucrose, 10 g) in DMSO (10 mL) was heated at 180 °C for 24 h, under stirring in the presence of conc.  $\text{H}_2\text{SO}_4$  (0.54 g or 0.3 mL, 10 mol %). Because small quantities of  $\text{Me}_2\text{SO}_2$  and  $\text{Me}_2\text{S}$  (**ATTENTION!** Unpleasant odour) were produced during the reaction, the outgoing gas was bubbled through bleach ( $\text{NaOCl}$ ) to oxidize the  $\text{Me}_2\text{S}$  and fully destroy the odour. The reaction was monitored by quantitative HPLC analysis with an external standard. Once the highest yield of DFF was achieved, the reaction mixture was cooled to room temperature. Then reaction mixture was diluted with

dichloromethane (300 mL) and washed with saturated solution of  $\text{NaHCO}_3$  (100 mL x 1) and water (100 mL x 2). Separated organic phase was evaporated and passed through silica (60-120 mesh size). The yield of pure DFF as a yellow crystalline solid was 2.88 g (42 % calculated on fructose used), 1.84 g (27 % calculated on glucose used) and 2.24 g (31 % calculated on sucrose used).

#### 3.4.3.2. Synthesis of MTMF from carbohydrates

A solution of carbohydrates (*e.g.* fructose/glucose/sucrose, 10 g) in DMSO (10 mL) was heated at 180 °C for the period of 24 h, under stirring in the presence of Sn-Mont (4 g). Because, small quantities of decomposition products of DMSO (**ATTENTION!** Unpleasant odour) were produced during the reaction, the outgoing gas was bubbled through bleach ( $\text{NaOCl}$ ) to oxidize the  $\text{Me}_2\text{S}$  and fully destroy the odour. The reaction was monitored by quantitative HPLC analysis with an external standard. Once the highest yield of MTMF was achieved, the reaction mixture was cooled to room temperature and filtered to separate the catalyst. Catalyst bed was washed with dichloromethane (300 mL) further mother liquor was washed with water (100 mL x 2). Separated organic phase was evaporated and passed through silica (60-120 mesh size). The yield of pure MTMF as a brown crystalline solid was 3.29 g (38 % calculated on fructose used), 2.42 g (28 % calculated on glucose used) and 3.0 g (33 % calculated on sucrose used).

#### 3.4.4. Analysis of reaction products

Analysis of reaction products of this work is done by using methods provided in section 2.4.5 of **Chapter 2**. The product yield and carbohydrate conversion were calculated using following equations (I-III).

$$\text{DFF yield} = \frac{\text{Moles of DFF formed}}{\text{Moles of starting carbohydrates}} \times 100 \% \quad \text{----- (I)}$$

$$\text{MTMF yield} = \frac{\text{Moles of MTMF formed}}{\text{Moles of starting carbohydrates}} \times 100 \% \quad \text{----- (II)}$$

$$\text{Carbohydrates conversion} = \frac{(\text{Moles of starting carbohydrates} - \text{Moles of carbohydrates remained})}{\text{Moles of starting carbohydrates}} \times 100 \% \quad \text{----- (III)}$$

### 3.5. Results and discussion

#### 3.5.1. Dehydration of glucose

Glucose is a complex and stable molecule thus its dehydration is challenging due to difficult isomerisation step. Its dehydration to HMF follows two steps, *i*) isomerisation to fructose, *ii*) fructose dehydration to HMF. Different acid catalysts were screened for the dehydration of glucose and the results are presented in Table 3.1. Initially, dehydration of glucose was studied over Sn-Mont catalyst at 150 °C in DMSO. After 24 h, glucose was consumed completely with 38 % yield of HMF (Table 3.1, entry 1). Next experiment was performed at 170 °C, the product distribution was, 19 % HMF and 21 % MTMF [5-((methylthio)methyl)-2-furfural] (Table 3.1, entry 2). Interestingly, the selectivity to MTMF was increased at 180 °C with its 36 % yield (Table 3.1, entry 3). Presence of Lewis and Brønsted acid sites are unique features of Sn-Mont which facilitate the glucose isomerisation to fructose on its Lewis acid sites and dehydration of in-situ formed fructose to HMF on its Brønsted acid sites. Very interestingly, DMSO decomposed at high temperature (180 °C) on Sn-Mont to polysulfides which reacted with in-situ formed HMF to give MTMF. In presence of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 5-(chloromethyl)furfural (CMF) was formed directly from glucose *via* dehydration followed by chlorination (Table 3.1, entry 6). Amberlyst-15 and heteropoly acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) were found to be ineffective for this reaction (Table 3.1, entries 7 and 8). Interestingly, in presence of conc.  $\text{H}_2\text{SO}_4$ , glucose was directly converted to DFF in 33 % yield (Table 3.1, entry 9). Under experimental conditions, DMSO behaves as an oxidation agent as well as a reaction medium. Further work on effect of parameters was done using conc.  $\text{H}_2\text{SO}_4$  and DMSO system.

**Table 3.1.** Catalyst optimisation for thermal dehydration of glucose in DMSO <sup>[a]</sup>

Entry	Catalyst	Loading	T [°C]	<i>t</i> [h]	Conv. [%]	Yield [%] <sup>[b]</sup>		
						HMF	MTMF	DFF
1	Sn-Mont	0.2 g	150	24	100	38	0	0
2	Sn-Mont	0.2 g	170	24	100	19	21	0
3	Sn-Mont	0.2 g	180	24	100	06	<b>36</b>	trace
4	Sn-Mont	0.2 g	180	12	100	30	06	trace
5	Mont	0.2 g	180	24	61	09	07	0

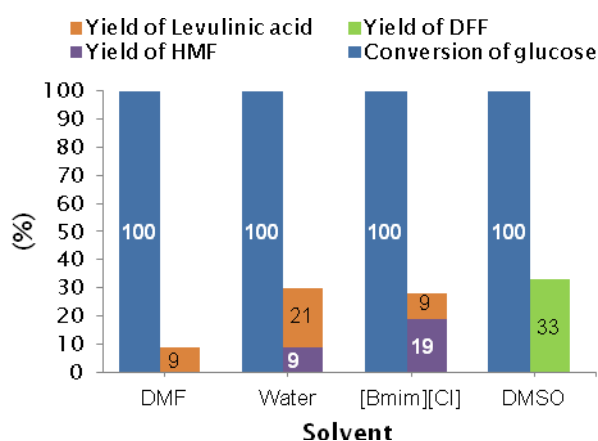
6	SnCl <sub>4</sub> ·5H <sub>2</sub> O	10 mol %	180	24	100	09 [12] <sup>[c]</sup>	0	0
7	Amberlyst-15	0.2 g	180	24	71	07	0	0
8	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	10 mol %	180	24	80	09	06	08
9	H <sub>2</sub> SO <sub>4</sub>	10 mol %	180	24	100	0	0	33
10	---	---	180	24	00	0	0	0

[a] Reaction conditions: Glucose (0.5 g, 0.277 mmol), DMSO (10 mL), catalyst. [b] yields reported on HPLC, [c] yield of 5-(chloromethyl)-2-furfural

### 3.5.2. Parameters study for the glucose dehydration over H<sub>2</sub>SO<sub>4</sub>

#### 3.5.2.1. Effect of solvents

The basic criterion for the solvent selection is that glucose should have significant solubility. Therefore some solvents such as N,N-dimethylformamide (DMF), H<sub>2</sub>O and 1-Butyl-3-methylimidazolium chloride [Bmim][Cl] were chosen for glucose dehydration reaction (Figure 3.1). When glucose was conducted in DMF and 10 mol % H<sub>2</sub>SO<sub>4</sub> by heating reaction mixture at 180 °C for the period of 24 h, the levulinic acid was formed in 9 % yield along with excess humin. On the other hand, under experimental conditions (e.g. 10 mol % H<sub>2</sub>SO<sub>4</sub>, 180 °C, 24 h) in presence of water, HMF and levulinic acid were formed in 09 and 21 %, respectively. In presence of 1-Butyl-3-methylimidazolium chloride ([Bmim][Cl]), DFF was not formed at all. Thus from above experiments it is concluded that other than DMSO no other solvent was suitable for the production of DFF from glucose.

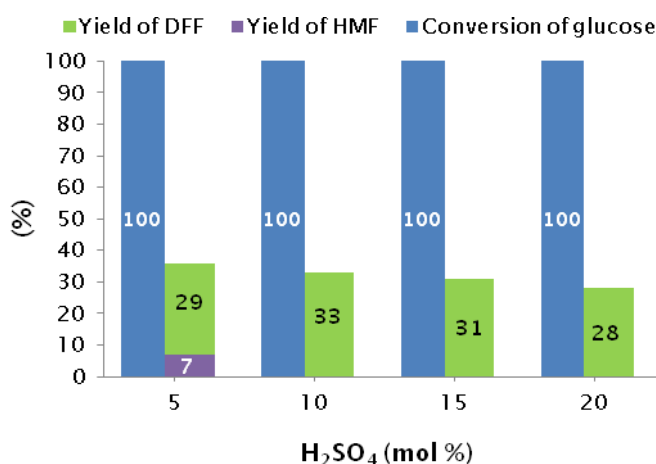


**Figure 3.1.** Dehydration of glucose with H<sub>2</sub>SO<sub>4</sub> (10 mol %) in different solvents. Reaction conditions: glucose (0.5 g), H<sub>2</sub>SO<sub>4</sub>, solvent (10 mL), 180 °C, 24 h.



### 3.5.2.2. Effect of concentration of $H_2SO_4$

Effect of concentration of  $H_2SO_4$  was studied in the range of 5-20 mol % (Figure 3.2). With 5 mol % of  $H_2SO_4$ , glucose was consumed completely with 07 % yield of HMF and 29 % yield DFF. While using 15 mol % of  $H_2SO_4$ , DFF was produced in 31 % yield. On the other hand, in presence of 20 mol % of  $H_2SO_4$ , DFF yield was dropped to 28 %. Higher catalyst concentration than 10 mol % has induced negative effect on DFF yield due to excess humin formation.

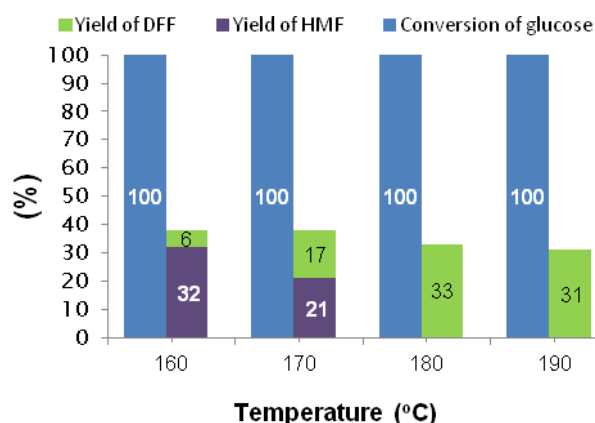


**Figure 3.2.** Dehydration of glucose with different concentrations of  $H_2SO_4$  in DMSO.

Reaction conditions: glucose (0.5 g),  $H_2SO_4$  (5-20 mol %), DMSO (10 mL), 180 °C, 24 h.

### 3.5.2.3. Effect of temperature

Effect of temperature on glucose conversion and yield of DFF was studied in the range of 160-190 °C and the results are shown in Figure 3.3. At 160 °C, product distribution was, 32 % of HMF and 06 % of DFF with complete conversion of glucose. While increasing the temperature to 170 °C, DFF yield increased to 17 %. However, at 190 °C, DFF was obtained in 31 % yield which was comparable to the result obtained at 180 °C.

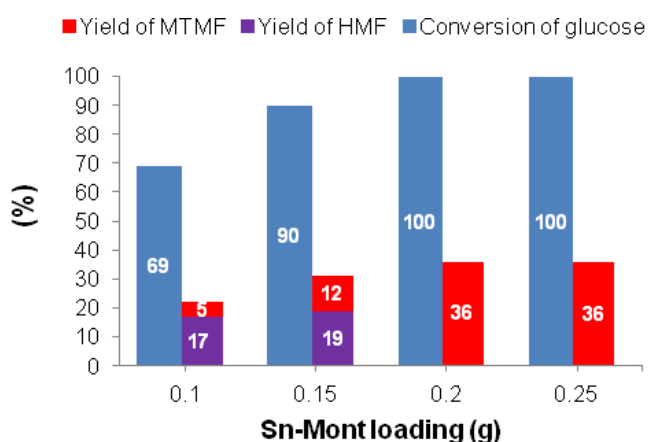


**Figure 3.3.** Dehydration of glucose with  $\text{H}_2\text{SO}_4$  (10 mol %) in DMSO at different temperature. Reaction conditions: glucose (0.5 g),  $\text{H}_2\text{SO}_4$ , DMSO (10 mL), 160-190 °C, 24 h.

### 3.5.3. Parameter study for the glucose dehydration over Sn-Mont

#### 3.5.3.1. Effect of catalyst loading

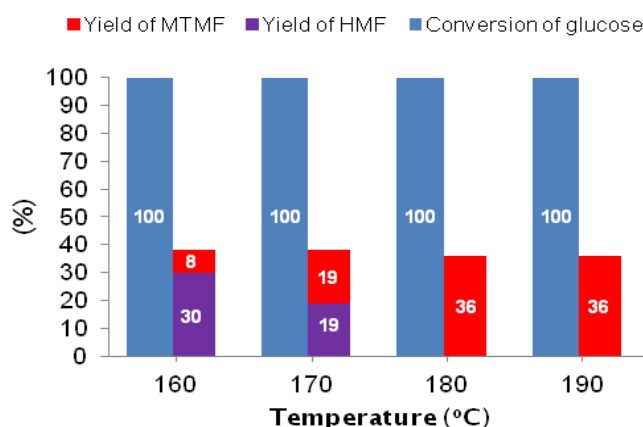
Effect of Sn-Mont loading was studied for the MTMF production in DMSO and the results are presented in Figure 3.4. When lower than 0.2 g loading of Sn-Mont was used, conversion of glucose was < 70 %. While, with  $\geq 0.2$  g of Sn-Mont loading MTMF was produced in 36 % yield. Thus, 0.2 g loading was found to be the optimum loading and same amount was used for further experiments.



**Figure 3.4.** Dehydration of glucose with different loading of Sn-Mont in DMSO. Reaction conditions: glucose (0.5 g), Sn-Mont (0.1-0.25 g), DMSO (10 mL), 24 h.

### 3.5.3.2. Effect of temperature

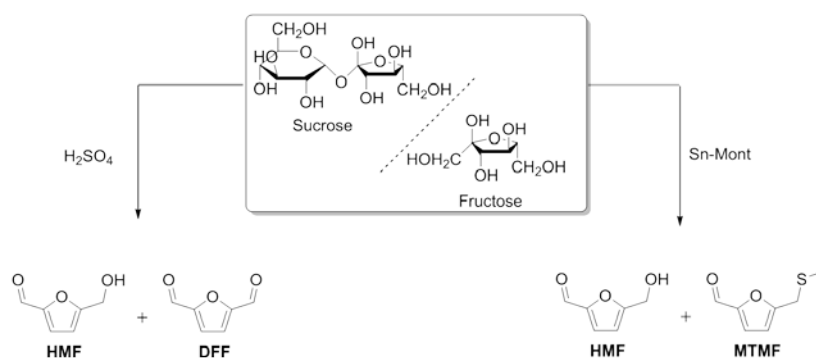
Dehydration of glucose was studied over Sn-Mont in a temperature range of 160-190 °C in DMSO solvent (Figure 3.5). At 160 °C, product distribution was, 30 % of HMF and 08 % of MTMF. With increase in temperature to 170 °C, formation of MTMF dramatically increased to 19 % at the cost of HMF. With further increase in temperature to 180 °C, MTMF was obtained in maximum yield of 36 % which was remained constant even at 190 °C.



**Figure 3.5.** Dehydration of glucose with Sn-Mont in DMSO at different temperature. Reaction conditions: glucose (0.5 g), Sn-Mont (0.2 g), DMSO (10 mL), 160-190 °C, 24 h.

### 3.5.4. Dehydration of fructose and sucrose

After successful optimisation of dehydration of glucose, dehydration of fructose and sucrose was also studied using the same catalyst and solvent systems (Scheme 3.4 and Table 3.2).



**Scheme 3.4.** Dehydration of fructose and sucrose over  $\text{H}_2\text{SO}_4$  and Sn-Mont.

In DMSO, fructose and sucrose were heated at 180 °C with Sn-Mont to give MTMF in 45 and 40 %, respectively (Table 3.2, entries 1 and 2). Similarly, with concentrated H<sub>2</sub>SO<sub>4</sub> fructose and sucrose were transformed into DFF with 48 and 39 %, respectively (Table 3.2, entry 3 and 4).

**Table 3.2.** One-pot synthesis of 2,5-diformylfuran and 5-((methylthio)methyl)-2-furfural from carbohydrates in DMSO <sup>[a]</sup>

Entry	Substrates	Catalyst	Loading	Conversion [%]	Yield [%] <sup>[b]</sup>		
					MTMF	DFF	HMF
1	Fructose	Sn-Mont	0.2 g	100	45	2	06
2	Sucrose			>99	40	2	04
3	Fructose	H <sub>2</sub> SO <sub>4</sub>	10 mol %	100	0	48	Trace
4	Sucrose			>99	0	39	Trace

[a] Reaction conditions: Carbohydrate (0.5 g), DMSO (10 mL), catalyst, 180 °C, 24 h. [b] yields reported on HPLC.

### 3.6. Conclusions

Two different acid catalysts (Sn-Mont and conc.  $\text{H}_2\text{SO}_4$ ) were evaluated under identical conditions for the dehydration of carbohydrates to produce DFF and MTMF. In presence of Sn-Mont, DMSO decomposes to polysulfide which was responsible for MTMF formation from carbohydrates. On the other hand, mixture of  $\text{H}_2\text{SO}_4$  and DMSO were responsible for dehydration and it is worked as an oxidising agent to produce DFF from carbohydrates.

### 3.7. References

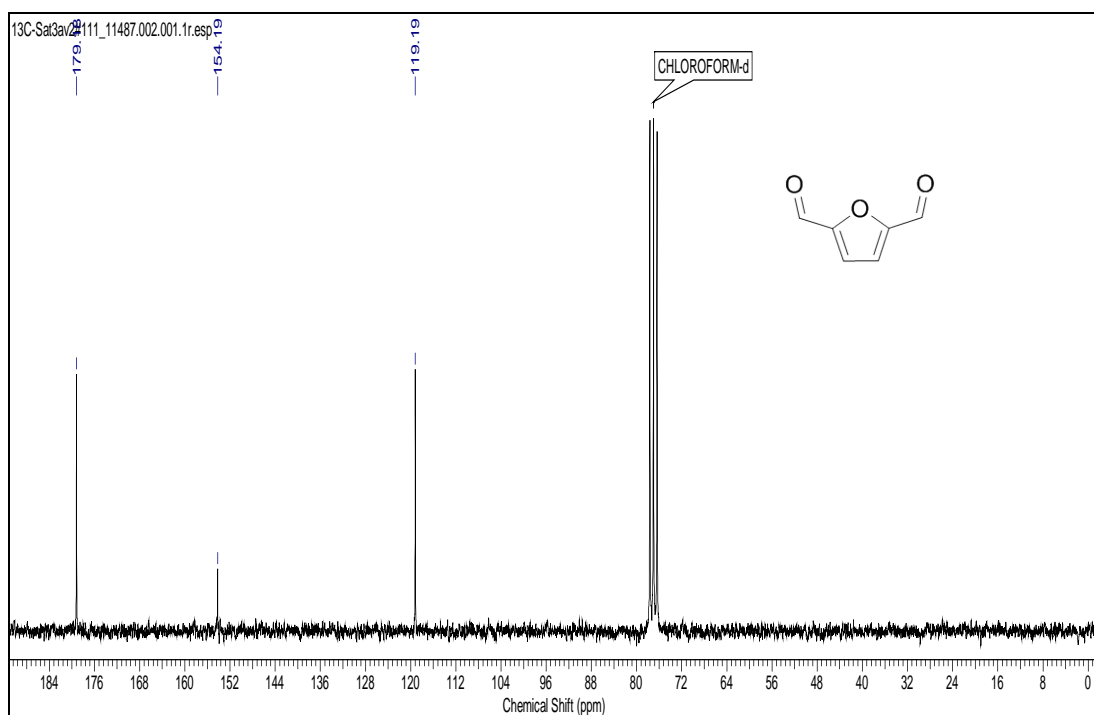
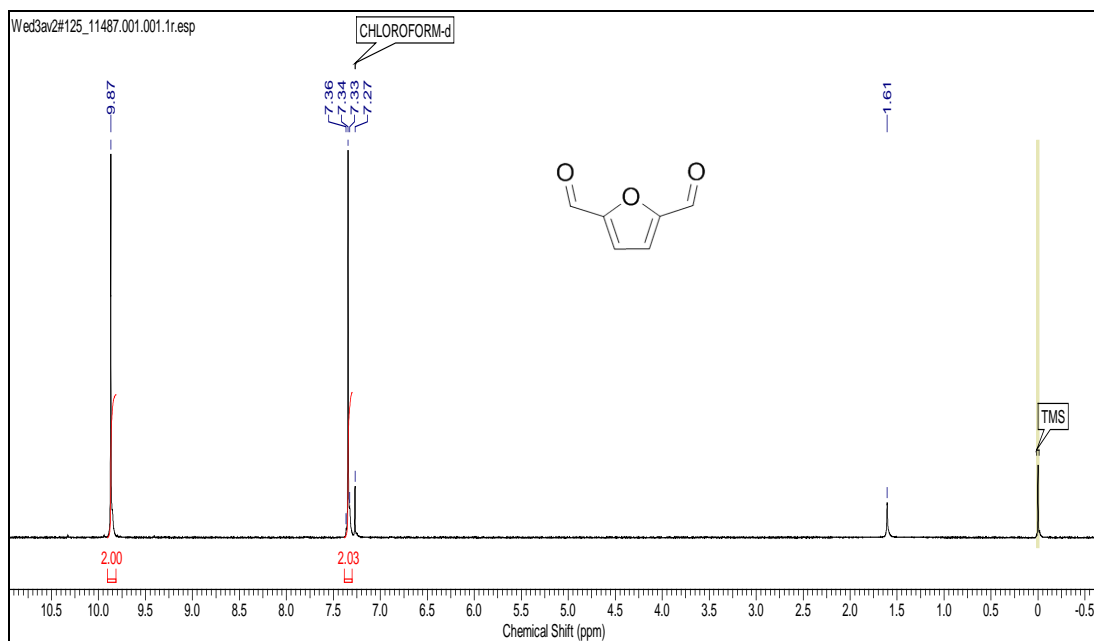
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### 3.8. NMR data of the synthesized compound

#### 2,5-(diformyl)furan

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ),  $\delta$  ppm: 7.4 (s, 2H), 9.8 (s, 2H)

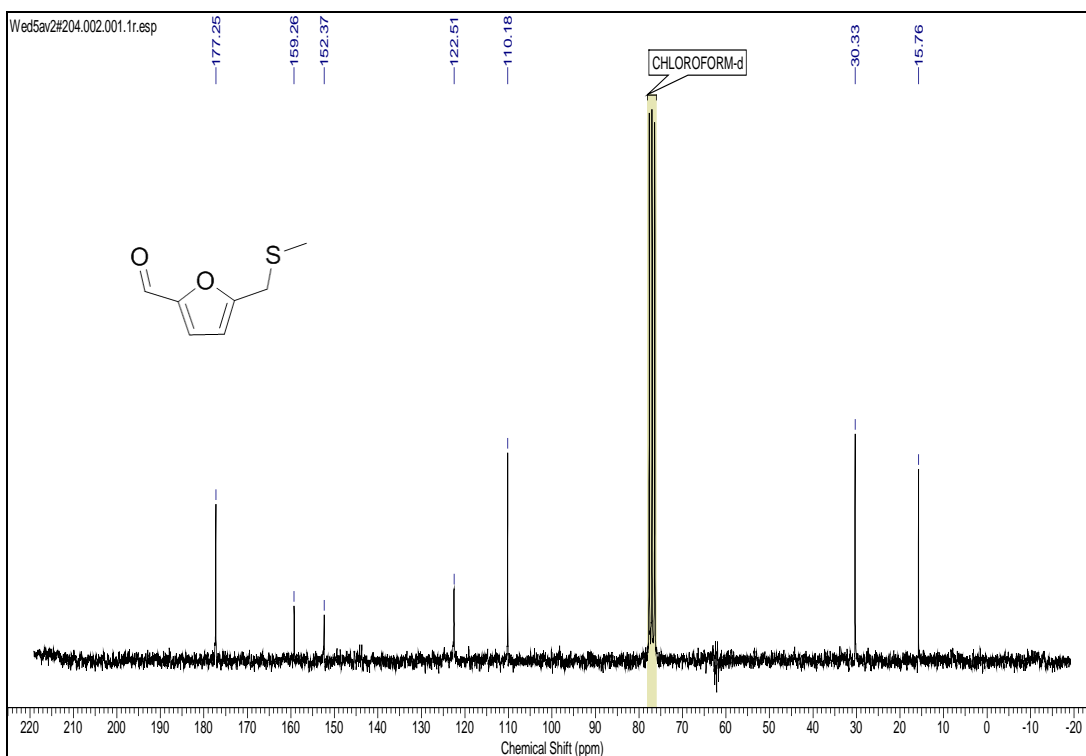
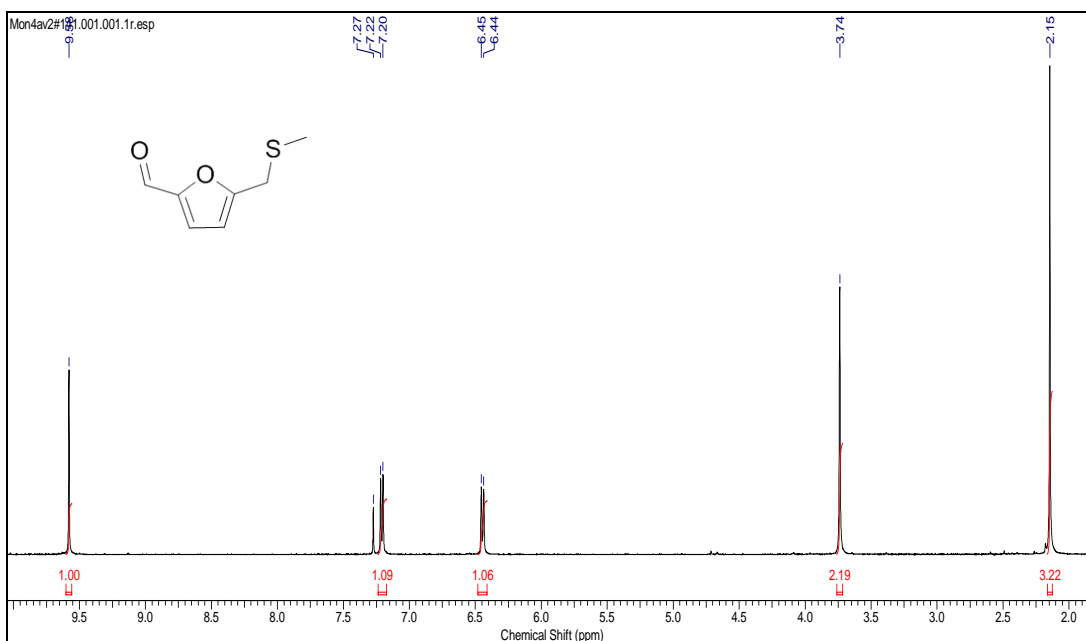
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 119.19, 154.19, 179.18.



**5-((methylthio)methyl)-2-furfural**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 2.15 (s, 3 H) 3.74 (s, 2 H) 6.44-6.45 (d,  $J=3.54$  Hz, 1 H) 7.20-7.22 (d,  $J=3.54$  Hz, 1 H) 9.58 (s, 1 H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 15.81, 30.38, 110.23, 122.56, 152.41, 159.31, 177.30.





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## **Chapter 4**

### **Dehydration of carbohydrates followed by C-C bond forming reactions**

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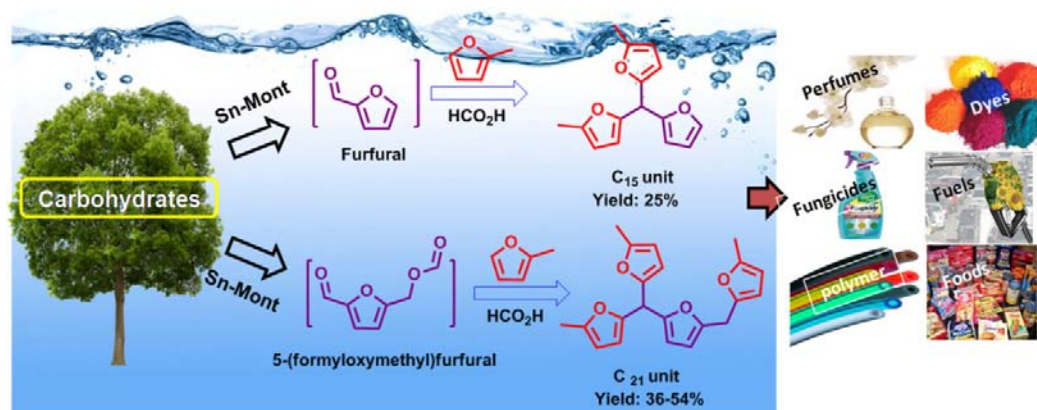
**This Chapter is organized in three sections:**

**4.1 An integrated production of diesel fuel precursors from carbohydrates and 2-methylfuran over Sn-Mont catalyst**

**4.2 Clean production of jet-fuel precursors from carbohydrates through an integrated dehydration and aldol condensation**

**4.3 Friedel-Crafts alkylation over Zr-Mont catalyst for the production of diesel fuel precursors**

### 4.1. An integrated production of diesel fuel precursors from carbohydrates and 2-methylfuran over Sn-Mont catalyst



Condensation of 5-(hydroxymethyl)furfural (HMF) with 2-methylfuran provides the precursor of diesel fuel. However, HMF production is critical due to its tedious isolation and purification steps. Therefore, an integrated process has been developed for the production of diesel precursors directly from cheap HMF precursors and 2-methylfuran. This process involves dehydration of carbohydrates to HMF followed by latter's condensation with 2-methylfuran to give 5,5'-((5-((5-methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran) (**1**). Over Sn-Mont catalyst, in solvents like water, DMSO and C<sub>4</sub>mimBr, product **1** was produced in negligible yields. The yield of **1** was significantly improved to 36 % in formic acid medium. Sn-Mont facilitates the isomerization of glucose to fructose with its Lewis acid sites and formic acid promotes the dehydration of fructose to a mixture of HMF + 5-(formyloxymethyl)furfural (FMF) which was further treated with 2-methylfuran in the same pot. The product **1** was obtained with 40 and 54 % yields from sucrose and fructose, respectively. Using this strategy xylose was converted into 5,5'-(furan-2-ylmethylene)bis(2-methylfuran) (**2**) in 25 % yield.

Suhas Shinde, Chandrashekhar Rode, *ChemistrySelect*, **2018**, 3, 4039-4046.

### 4.1.1. Introduction

The aldehyde functionality present on HMF and furfural is prone to C-C bond forming reactions such as aldol-condensation, [1] pinacol coupling, [2] umpolung benzoin condensation [3] and hydroxyalkylation-alkylation (HAA) reaction [4-7]. Sugars and dehydrated sugar derivatives can also be used to produce additional platform molecules, such as 5-methylfurfural and 2-methylfuran (MeF) through sequential or one-pot reactions [8, 9]. MeF is a byproduct in large-scale production of furfuryl alcohol (FAL) from FUR and is a major product when same reaction was carried out at 250 °C [10]. MeF is an electron rich aromatic ring thus, it undergoes selective electrophilic substitution at the C<sub>4</sub> position of furan ring. Hydroxyalkylation-alkylation (HAA) reaction of MeF with furfurals (HMF and FUR) provides condensation products [bis/tris(furyl)alkanes] containing C<sub>15</sub> and C<sub>21</sub> units, respectively. Bis/tris(furyl)alkanes have wide range of industrial applications [1-7, 11-18].

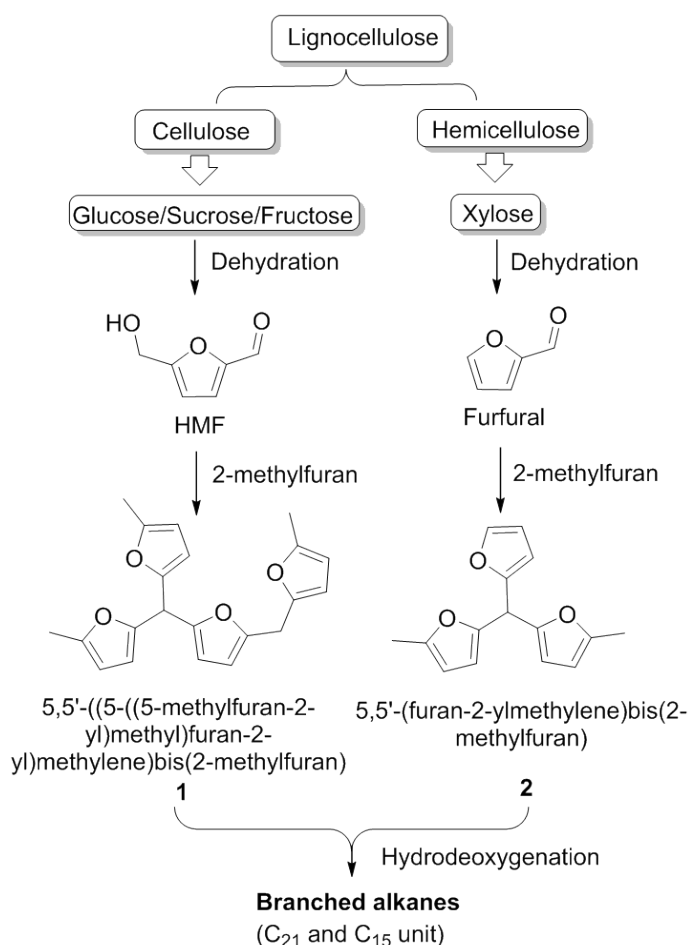
### 4.1.2. Literature Survey

Numerous synthetic methods are available on synthesis of bis/tris(furyl)alkanes by condensation of MeF with carbonyl compounds over mineral acids, [4,19,20] acidic resins, [4,6,21] functionalized silica and carbon, [22-25] AuCl<sub>3</sub> [26,27] zeolites, [28] Cu(OTf)<sub>2</sub> [29] I<sub>2</sub> [30] and TFA/ZrO<sub>2</sub> [31]. Recently, we have invented a biphasic reaction system for the clean isolation of tris(furyl)alkanes with high yield using -SO<sub>3</sub>H functionalized ionic liquids [32].

### 4.1.3. Scope of the present work

Production of bis/tris(furyl)alkanes from pure HMF or furfural could be achieved by simple treatment with MeF in acid medium. Although the large scale production of furfural is practiced, still its long time stability is one of the concerns due to its vulnerability to polymerize. On the other hand, HMF production from carbohydrates is not yet commercialized due its troublesome isolation and purification. As a result, its market price is also too high. Thus, instead of isolating these furfural derivatives, their further conversion to higher value commercial chemicals *via* integrated process is highly desirable. In this direction, we propose here production of diesel fuel

precursors [bis/tris(furyl)alkanes] directly from carbohydrates and 2-methylfuran (Figure 4.1.1).



**Figure 4.1.1.** Process path for production of liquid alkanes from biomass derived molecules.

However, making diesel fuel precursors from carbohydrates is a hard task due their stable ring structure. In addition, carbohydrates like glucose are much more difficult to dehydrate to HMF due to its critical isomerisation to fructose. Thus, conversion of glucose into HMF would proceed in two steps: first isomerisation of glucose to fructose in presence of an enzyme, Lewis acid or base catalysts, [33, 34] followed by the dehydration of fructose to HMF over Brønsted acid. In our new approach, we produced condensation products such as 5,5'-((5-((5-methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran) (1) and 5,5'-(furan-2-ylmethylene)bis(2-methylfuran) (2) from carbohydrates and 2-methylfuran *via* an integrated process using our well established Sn-Mont catalyst. This process involved acid catalyzed

dehydration of carbohydrates to furfural derivatives (*e.g.* HMF/FMF or FUR) followed by their in-situ condensation with MeF. HMF could be produced from fructose at relatively milder conditions in acid medium but on the other hand, glucose and sucrose are much more difficult to dehydrate due much more stability of the glucose ring. Glucose was effectively isomerized to fructose over Lewis acid sites of Sn-Mont and further dehydrative-esterification of in-situ formed fructose to 5-(formyloxymethyl)furfural (FMF) on Brønsted acid sites of reactive solvent such as formic acid. Then in-situ formed FMF was subsequently treated with MeF in the same reaction pot. The same protocol was further applied for the different starting materials such as fructose, sucrose as well as for xylose. Here, formic acid served as a reactive solvent which also helped to promote the condensation step.

#### 4.1.4. Experimental Section

##### 4.1.4.1. Materials

All the reactants and reagents were used as procured. 2-methylfuran, furfural, 5-(hydroxymethyl)furfural, C<sub>4</sub>mimBr, SnCl<sub>4</sub>·5H<sub>2</sub>O and montmorillonite clay (CAS No. 1302-78-9) were procured from Sigma-Aldrich, Bangalore, India. Sucrose, glucose, fructose, xylose, acetic acid (100 %), formic acid (98-100 %) and HCl (35-38 %) were obtained from Thomas Baker. Dimethylsulfoxide (DMSO), ethyl acetate, petroleum ether, NaHCO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> were purchased from ChemLabs, India. SnO<sub>2</sub> purchased from LOBA Chemie.

##### 4.1.4.2. Catalyst preparation

Metal exchanged montmorillonite catalysts were prepared according to the literature report [34, 35]. Into the aqueous solution of precursors such as SnCl<sub>4</sub>·5H<sub>2</sub>O, ZrOCl<sub>2</sub>·8H<sub>2</sub>O, AlCl<sub>3</sub>·6H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O, montmorillonite were added and resultant catalysts denoted as Sn-Mont, Zr-Mont, Al-Mont and Fe-Mont, respectively.

##### 4.1.4.3. Catalyst characterization techniques

The instruments used for the characterisation of catalysts are described in **Chapter 2**, section 2.4.3.

#### 4.1.4.4. Analysis of reaction products

The formation of product was initially detected with TLC by visualizing under UV light (254 nm). The conversion of carbohydrates was calculated by using Agilent HPLC (column: Hi-Plex USP L17, detector: RI and mobile phase: millipore water with 0.6 mL/min flow). The yield of dehydration product of carbohydrates calculated by using Agilent HPLC (column: Poroshell 120 EC-C18 2.7  $\mu$ m, detector: UV and mobile phase: 0.1 % acetic acid in Millipore water: acetonitrile (85:15, v/v) with 0.6 mL/min flow) using an external standard calibration curve method. Purified products were characterised and established by  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR using deuterated chloroform (0.01 %, TMS) as solvent on 200 and 50 MHz frequency Bruker instrument, respectively.

#### 4.1.4.5. Synthetic procedures

##### 4.1.4.5.1. Synthesis of condensation product (1) from HMF

A mixture of HMF (0.252 g, 2 mmol), 2-methylfuran (0.530 g, 6.5 mmol) and Sn-Mont (0.1 g) was heated to 65 °C for 2h. Reaction was monitored by TLC analysis by visualizing under UV light. After completion of reaction, it was filtered to separate the catalyst. Filtrate was diluted with ethyl acetate (20 mL) and subsequently washed with water (10 mL) and brine (10 mL). Separated organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. The residue was passed through silica bed with pet ether mobile phase to afford orange oil as a pure product (Yield: 0.477 g, 71 %).

##### 4.1.4.5.2. Synthesis of condensation product (2) from furfural

A mixture of furfural (0.192 g, 2 mmol), 2-methylfuran (0.344 g, 4.2 mmol) and Sn-Mont (0.1 g) was heated to 65 °C for 2h. Reaction was monitored by TLC analysis by visualizing under UV light. After completion of reaction, it was filtered to separate the catalyst. Filtrate was diluted with ethyl acetate (20 mL) and subsequently washed with water (10 mL) and brine (10 mL). Separated organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. The residue was passed through silica bed with pet ether mobile phase to afford orange oil as a pure product (Yield: 0.387 g, 80 %).

**4.1.4.5.3. Synthesis of condensation product (1) from sucrose or glucose**

In a typical experiment, glucose or sucrose (1 mmol) was dissolved in formic acid (5 mL), Sn-Mont (0.1 g) was added and reaction mixture was heated at 150 °C for 3 h. Then reaction was cooled to 65 °C and 2-methylfuran (0.246 g, 3 mmol for glucose and 0.492 g, 6 mmol for sucrose) was introduced into the reaction mixture and stir for 2 h. After complete conversion of FMF/HMF, reaction mixture was filtered to separate the catalyst. Filtrate was neutralized with saturated solution of NaHCO<sub>3</sub> (20 mL) and diluted with ethyl acetate (20 mL). Separated organic layer was partitioned by H<sub>2</sub>O (10 mL) and subsequently treated with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was evaporated under reduced pressure and residue was purified by column chromatography eluted in petroleum ether to afford orange oil (0.121 g, 36 % from glucose and 0.208 g, 31 % from sucrose).

**4.1.4.5.4. Synthesis of condensation product (1) from glucose using HCl via CMF**

In a typical experiment, Glucose (0.180 g), concentrated HCl (18 mL), and 1,2-dichloroethane (36 mL) were introduced into a 100 mL vessel, and the mixture was heated with vigorous stirring in a closed system at an oil bath temperature of 100 °C. After 2 h the reaction was cooled to 65 °C and 2-methylfuran (0.246 g, 3 mmol) was introduced into the reaction mixture and stir for next 2 h. After complete conversion of 5-(chloromethyl)furfural (CMF), reaction mixture was cooled to room temperature. Reaction was neutralised with 1N NaOH and diluted with dichloromethane (50 mL). Separated organic layer was partitioned by H<sub>2</sub>O (30 mL) and subsequently treated with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was evaporated under reduced pressure and residue was purified by column chromatography eluted in petroleum ether to afford orange oil (Yield: 0.170 g, 55 %).

**4.1.4.5.5. Synthesis of condensation product (1) from fructose**

In a typical experiment, fructose (1 mmol) was dissolved in formic acid (5 mL) and mixture was heated at 150 °C for 3 h. Then reaction was cooled to 65 °C and 2-methylfuran (0.246 g, 3 mmol) was introduced into the reaction mixture and stir for 2 h. After complete conversion of FMF/HMF, reaction mixture was filtered to separate the catalyst. Filtrate was neutralized with saturated solution of NaHCO<sub>3</sub> (20 mL) and diluted with ethyl acetate (20 mL). Separated organic layer was partitioned by H<sub>2</sub>O (10 mL) and subsequently treated with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer

was evaporated under reduced pressure and residue was purified by column chromatography eluted in petroleum ether to afford orange oil (Yield: 0.181 g, 54 %).

#### ***4.1.4.5.6. Synthesis of condensation product (2) from xylose***

In a typical experiment, xylose (1 mmol) was dissolved in formic acid (5 mL), Sn-Mont (0.2 g) was added and reaction mixture was heated at 150 °C for 3 h. Then reaction was cooled to 65 °C and 2-methylfuran (0.164 g, 2 mmol) was introduced into the reaction mixture and stir for 2 h. After complete conversion of furfural, reaction mixture was filtered to separate the catalyst. Filtrate was neutralized with saturated solution of NaHCO<sub>3</sub> (20 mL) and diluted with ethyl acetate (20 mL). Separated organic layer was partitioned by H<sub>2</sub>O (10 mL) and subsequently treated with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was evaporated under reduced pressure and residue was purified using column chromatography by eluting in petroleum ether to afford orange oil (Yield: 0.06 g, 25 %).

#### ***4.1.4.5.7. Sn-Mont recycling studies***

##### ***4.1.4.5.7.1. For condensation between HMF and MeF***

In a typical recycle experiment, after desired time of condensation reaction between HMF and MeF mixture was filtered to separate the catalyst. After each reuse, the recovered Sn-Mont catalyst was washed with water (10 mL) and acetone (10 mL) and subsequently dried in oven at 110 °C for 1 h. Then dried Sn-Mont catalyst was again loaded into the reactor and reacted with the fresh HMF and MeF.

##### ***4.1.4.5.7.2. For dehydrative-esterification of glucose***

In a typical recycle experiment, after desired time of dehydrative-esterification reaction mixture was filtered to separate the catalyst. After each reuse the recovered Sn-Mont catalyst was washed with water (10 mL) and acetone (10 mL) and subsequently dried in oven at 110 °C for 1 h. Then dried Sn-Mont catalyst was again loaded into the reactor and reacted with the fresh glucose and formic acid.

#### ***4.1.4.5.8. HMF production***

##### ***4.1.4.5.8.1. HMF from bagasse***

In a typical experiment, mixture of bagasse (50 g), water (100 mL), DMSO (25 mL), MIBK (125 mL) and conc. H<sub>2</sub>SO<sub>4</sub> (5 mL) were heated at 150 °C for 3 h. After that,



the reaction mixture was filtered and the filtrate was neutralized with saturated solution of  $\text{NaHCO}_3$  (250 mL x 3) and then aqueous layer was extracted with ethyl acetate (250 mL x 1). Subsequently, organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  (50 g) and evaporated to obtain brown oil of crude HMF (0.5 g). Without purifying this crude HMF was used as it is for the hydroxyalkylation-alkylation reaction

#### **4.1.4.5.8.2. HMF from fructose**

In a typical experiment, mixture of fructose (1 g), DMSO (2 mL), MIBK (8 mL) and Amberlyst-15 (0.4 g) were heated at 120 °C for 3 h. After that, the reaction mixture was filtered and the filtrate was neutralized with saturated solution of  $\text{NaHCO}_3$  (250 mL x 3) and then the aqueous layer was extracted with ethyl acetate (250 mL x 1). Subsequently, the organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  (50 g) and evaporated to obtain brown oil of crude HMF (Yield: 0.357 g, 51 %).

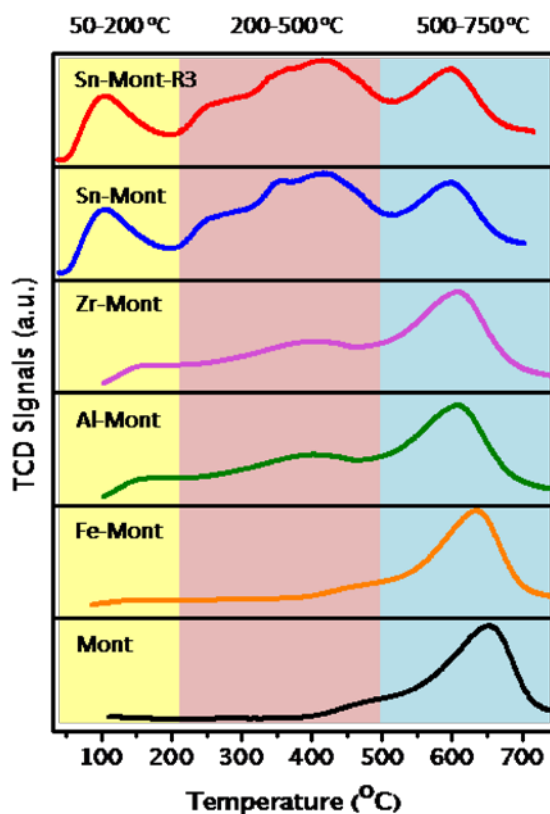
### **4.1.5. Results and Discussion**

#### **4.1.5.1. Catalyst Characterization**

##### **4.1.5.1.1. $\text{NH}_3$ -TPD**

Acidity of montmorillonite catalysts were measured by using  $\text{NH}_3$ -TPD analysis and the TPD profiles are shown in Figure 4.1.2 while their acid strength values in terms of  $\mu\text{mol}$  of  $\text{NH}_3$  desorbed are provided in Table 4.1.1. Acid sites of these catalysts were distributed over three temperature regions viz. weak, moderate and strong acid sites in the ranges of 50-200 °C (region-I), 200-500 °C (region-II) and 500-750 °C (region-III), respectively. The montmorillonite, Fe-Mont, Al-Mont and Zr-Mont showed weak acidities in the region-I and II as compared to Sn-Mont. Sn-Mont showed significantly high volume of  $\text{NH}_3$  desorption in regions -I and II suggesting the abundance of weak and medium acidity. While, at high temperature range of 500-750 °C (region-III), Sn-Mont showed slightly less volume of  $\text{NH}_3$  desorption compared to montmorillonite, Fe-Mont, Al-Mont and Zr-Mont. However, the total acid sites present on Sn-Mont catalyst were much higher than those on montmorillonite, Fe-Mont, Al-Mont and Zr-Mont. The acidity trend of all these catalysts was as follows: montmorillonite ( $90.08 \mu\text{mol g}^{-1}$ ) < Fe-Mont ( $190.63 \mu\text{mol g}^{-1}$ ) < Al-Mont ( $190.63 \mu\text{mol g}^{-1}$ ) < Zr-Mont ( $190.63 \mu\text{mol g}^{-1}$ ) < Sn-Mont ( $190.63 \mu\text{mol g}^{-1}$ )

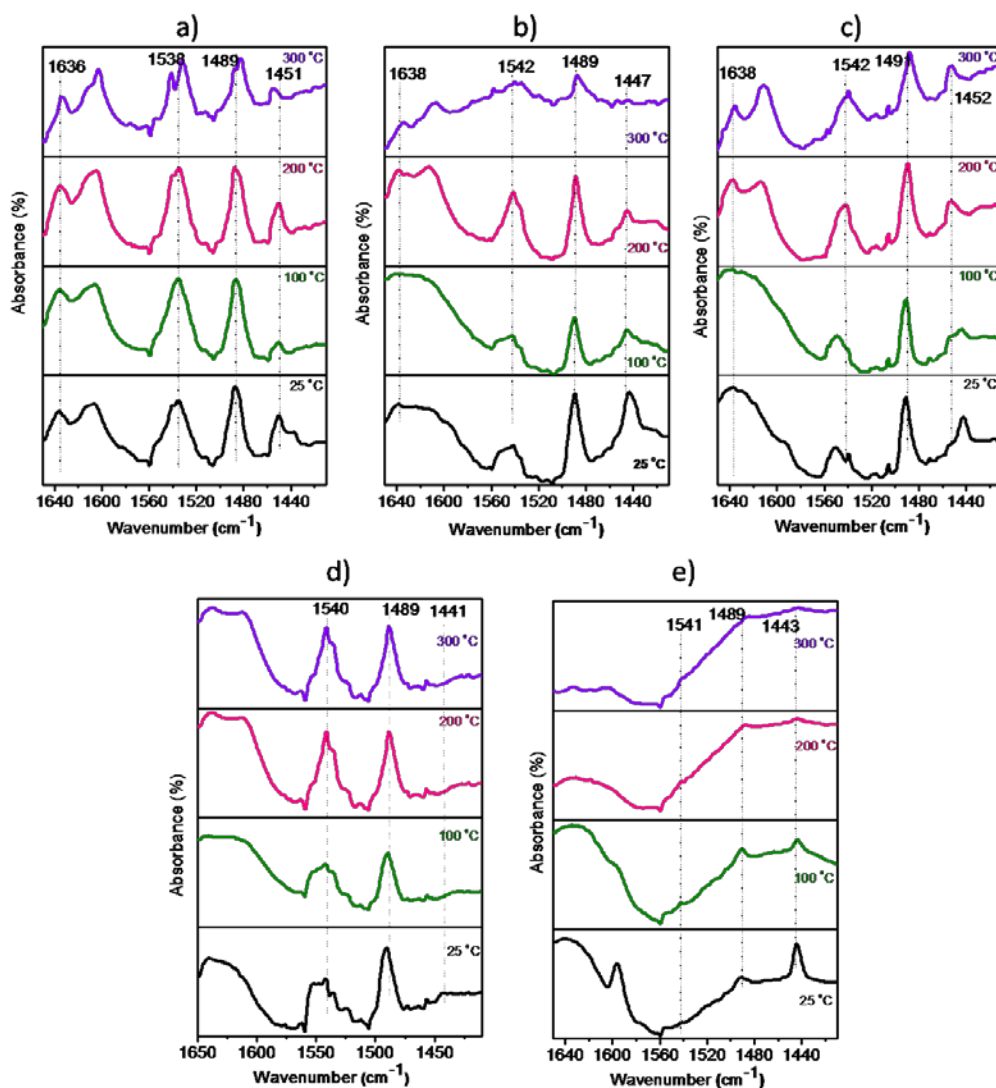
$\text{g}^{-1}) < \text{Al-Mont} (309.17 \text{ } \mu\text{mol g}^{-1}) < \text{Zr-Mont} (380.30 \text{ } \mu\text{mol g}^{-1}) < \text{Sn-Mont-R3} (490.10 \text{ } \mu\text{mol g}^{-1}) < \text{Sn-Mont} (511.90 \text{ } \mu\text{mol g}^{-1})$ .



**Figure 4.1.2.**  $\text{NH}_3$ -TPD profiles of montmorillonite catalysts

#### 4.1.5.1.2. Py-FTIR analysis

The types of acid sites present in our catalysts were identified by using pyridine FTIR spectroscopy. The pyridine FTIR spectra of montmorillonite and metal exchanged montmorillonite samples (Fe-Mont, Al-Mont and Sn-Mont) are depicted in Figure 4.1.3. In order to identify/evaluate the acidity of these catalysts, difference spectra were obtained by subtracting the spectrum before pyridine adsorption from that obtained after pyridine adsorption of the respective catalyst.



**Figure 4.1.3.** Py-FTIR of a) Sn-Mont, b) Zr-Mont, c) Al-Mont, d) Fe-Mont and e) Mont evacuated at different temperatures.

Desorption of pyridine from catalyst was carried out at different temperatures such as 25 °C, 100 °C, 200 °C and 300 °C using the method proposed by the Emeis [36] and the results are summarized in Table 4.1.1. The band at 1441  $\text{cm}^{-1}$  signifies Lewis acidity, 1490  $\text{cm}^{-1}$  represents combination of Lewis and Brønsted acidity and the bands at 1548  $\text{cm}^{-1}$  and 1638  $\text{cm}^{-1}$  signify Brønsted acidity [37]. The Sn-Mont catalyst having highest total acidity of 532  $\mu\text{mol g}^{-1}$  was distributed as 390  $\mu\text{mol g}^{-1}$  of Brønsted acid sites and 142  $\mu\text{mol g}^{-1}$  of Lewis acid sites. The acid strength determined by evacuation of the pyridine at 100 °C referred as weak acid sites. When evacuation of pyridine was performed at 200 °C, resultant acid strength

referred as medium acid sites. Strong acid sites could be observed if evacuation of pyridine was performed at 300 °C. All the metal exchanged montmorillonite catalysts possessed significantly large amount of medium acid sites compared to their weak and strong acid sites.

**Table 4.1.1.** Chemo-physical properties of various montmorillonite catalyst

Catalyst	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Acidity								B/L ratio	V <sub>micro</sub>	V <sub>meso</sub>
		NH <sub>3</sub> -TPD (μmol ammonia desorbed g <sup>-1</sup> cat.)	100 °C		200 °C		300 °C		Total			
			B	L	B	L	B	L				
Mont	19	90.08	08.23	09.00	60.00	21.00	13.00	8.17	119.40	2.13	6	15
Fe-Mont	131	190.63	17.76	11.44	94.00	49.00	33.00	17.00	222.20	1.87	39	93
Al-Mont	141	309.17	24.92	26.53	151.00	59.00	51.00	19.00	331.45	2.29	49	104
Zr-Mont	192	380.30	55.68	31.00	187.00	57.00	57.00	21.46	404.14	2.73	77	151
Sn-Mont	183	511.90	85.10	51.02	210.00	86.05	65.09	35.11	532.37	2.09	69	128
Sn-Mont-R3 <sup>[a]</sup>	169	490.10	80.18	48.00	205.11	83.09	61.19	33.14	509.88	2.11	65	131

[a] After 3<sup>rd</sup> recycle. [b] The quantification of acid sites by pyridine FTIR was determined by using the Emeis equation.[36]

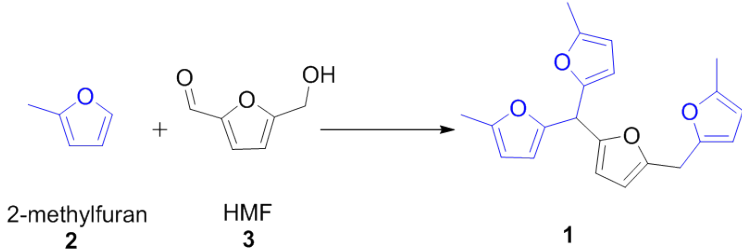
B= Brønsted acid sites and L=Lewis acid sites. V=Pore volume.

#### 4.1.5.2. Catalyst Screening

The multiple functionality of HMF offers sites for multiple C-C bond formation for carbon upgradation process. In the hydroxyalkylation-alkylation (HAA) process carbonyl (C=O) and hydroxyl (–OH) functionality of HMF was reacted with the three molecules of MeF over acid catalyst [32]. The condensation product formed during this reaction is a unit of C<sub>21</sub> which could provide a diesel range branched alkane on hydrodeoxygenation process. Initially, we identified a suitable catalyst system for the reaction between HMF and MeF by evaluating several catalysts for this reaction at 65 °C without using any solvent (Table 4.1.2). A complete conversion of HMF with 68 % yield of condensation product **1**, was observed for conc. H<sub>2</sub>SO<sub>4</sub> after 2h (Table 4.1.2, entry 1). Solid acid such as amberlyst-15 provided

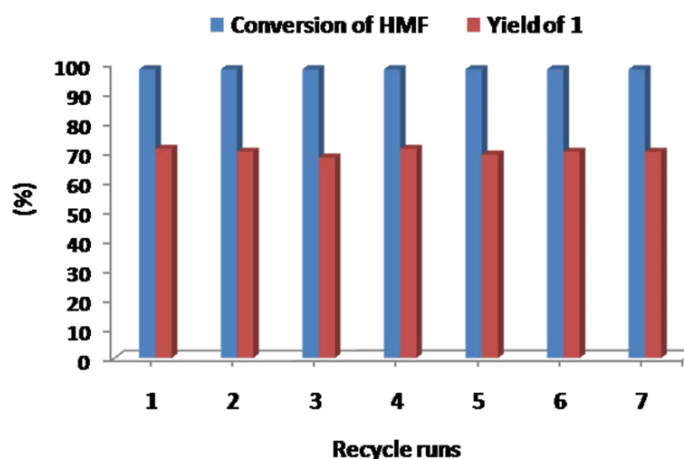
70 % yield of product **1** after 2h (Table 4.1.2, entry 2) while, naturally occurring montmorillonite clay wasn't found to be effective for this reaction as only 24 % yield of product **1** was obtained (Table 4.1.2, entry 3). Since, metal exchanged montmorillonite is more acidic than parent montmorillonite; several metal exchanged clay samples were also evaluated. Samples of Fe-Mont Al-Mont and Zr-Mont provided good to moderate yield of product **1** (Table 4.1.2, entries 4-6). Interestingly, tin exchanged montmorillonite (Sn-Mont) gave the highest yield of 71 % of product **1** with almost complete consumption of HMF (Table 4.1.2, entry 7). The inferior performance of other metal exchanged montmorillonite catalysts could be attributed to their lower acidic strength as compared to the Sn-Mont (Table 4.1.1). Lowering the Sn-Mont loading from 0.1 g to 0.05 g decreased the productivity of product **1** from 71 to 58 % due to insufficient active sites (Table 4.1.2, entry 8). However, increasing the catalyst loading by two time, (0.1 g to 0.2 g) had no significant improvement in the yield of product **1** (Table 4.1.2, entry 9). Sn-Mont possessed unique properties such as appropriate acid strength, large surface area, and pore volume leading to the high efficiency for the condensation reaction. The excellent stability and recyclability of Sn-Mont make it a robust catalyst (Figure 4.1.3). Although, pure HMF condensation with MeF was successfully achieved over a recyclable Sn-Mont catalyst, the present cost of pure HMF is a major deterrent factor for the development of downstream processes.

**Table 4.1.2.** Condensation of HMF with 2-methylfuran over Sn-Mont catalyst<sup>[a]</sup>.

 <div style="display: flex; justify-content: space-around; margin-top: 10px;"> <div style="text-align: center;">2-methylfuran <b>2</b></div> <div style="text-align: center;">+ HMF <b>3</b></div> <div style="text-align: center;">→</div> <div style="text-align: center;"><b>1</b></div> </div>					
Entry	Catalyst	Loading	<i>t</i> [h]	Conv <sup>[b]</sup> . of <b>3</b> [%]	Yield <sup>[c]</sup> of <b>1</b> [%]
1	conc. H <sub>2</sub> SO <sub>4</sub>	10 mol %	2	99	68

2	Amberlyst-15	0.1 g	2	98	70
3	Mont	0.1 g	24	30	24
4	Fe-Mont	0.1 g	3	81	60
5	Al-Mont	0.1 g	3	89	63
6	Zr-Mont	0.1 g	3	91	67
7	Sn-Mont	0.1 g	3	98	71
8	Sn-Mont	0.05 g	5	77	58
9	Sn-Mont	0.2 g	3	99	70
10 <sup>[d]</sup>	Sn-Mont	0.1 g	3	98	63
11 <sup>[e]</sup>	Sn-Mont	0.1 g	3	98	60

[a] Reaction conditions: HMF **3** (0.252 g, 2 mmol), 2-methylfuran (0.530 g, 6.5 mmol), catalyst (0.1 g), 65 °C. [b] Conversion of HMF (**3**) was determined using HPLC. [c] Isolated yield corresponds to HMF. Crude HMF (obtained from [d] fructose and [e] bagasse) **3** (0.252 g, 2 mmol), 2-methylfuran (0.530 g, 6.5 mmol), catalyst (0.1 g), 65 °C. Crude HMF was obtained from fructose and dry bagasse.

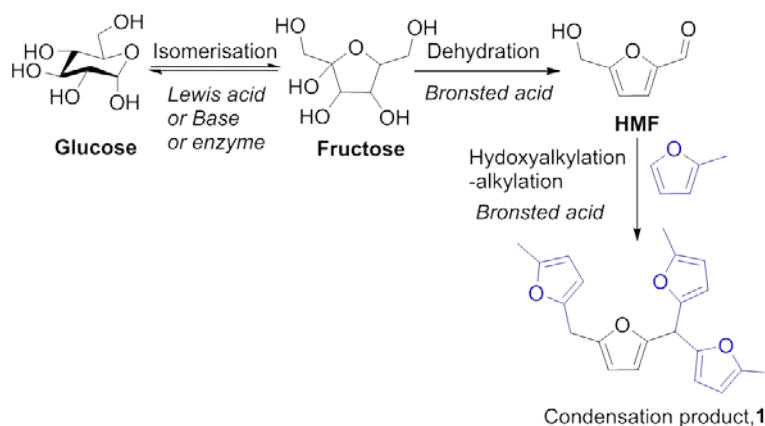


**Figure 4.1.3.** Recycle study of Sn-Mont for the condensation of HMF with MeF. Reaction conditions: HMF **3** (0.252 g, 2 mmol), 2-methylfuran (0.530 g, 6.5 mmol), Sn-Mont (0.1 g), 65 °C, 3h. After each cycle catalyst was washed with acetone and dried in the oven at 110 °C for 1 h prior to use for next cycle. Conversion of HMF was measured using HPLC and reported yields were isolated.

Therefore, crude HMF was obtained from fructose reacted with MeF to obtain 63 % yield of product **1** (Table 4.1.2, entry 10). Another sample of crude HMF was also obtained directly from bagasse by using concentrated  $\text{H}_2\text{SO}_4$ . Using this crude HMF, 60 % yield of condensation product **1** was obtained (Table 4.1.2, entry 11). Use of the crude HMF for synthesis of desired products avoided the energy-intensive separation/purification of HMF. This reaction system is a cost-efficient process for the practical production of product **1** from glucose and bagasse.

#### 4.1.5.3. Integrated glucose dehydration and condensation with MeF

Although, the crude HMF could be utilized for the condensation with MeF, the two separate operations must be carried out. Hence, without isolating HMF, its precursors (*e.g.* Glucose, fructose and sucrose) conversion to condensation product is possible as the whole process is acid catalyzed. Therefore, initially we have selected glucose as a potential HMF precursor which is more abundant and relatively much cheaper than HMF. The production of **1** from glucose requires to undergo three steps, *i*) isomerisation of glucose to fructose, *ii*) dehydration of fructose to HMF, *iii*) condensation of HMF with MeF. As shown in the Scheme 1, this process requires two types of catalysts such as Lewis acid (for glucose isomerisation) and Brønsted acid (dehydration of fructose and condensation reaction). For this purpose, Sn-Mont having unique combination of Lewis and Brønsted acid site was chosen as a catalyst [37]. Firstly, glucose (1 mmol) dehydration was carried out at 150°C in water over Sn-Mont catalyst (0.1 g) after a period of 3 h HMF was produced in 19 % yield with 89 % conversion of glucose.



**Scheme 4.1.1.** Process for the production of condensation product (**1**) from glucose

Further, reaction was cooled to 65 °C and MeF was added into the reaction mixture containing crude HMF. Unfortunately, no any condensation product was observed (Table 4.1.3, entry 1). After unsuccessful attempt in water, we explored the suitability of ionic liquid, C<sub>4</sub>mimBr (1-butyl-3-methyl-1H-imidazol-3-ium bromide) was tested. In C<sub>4</sub>mimBr also condensation between in situ formed HMF and MeF wasn't noticed (Table 4.1.3, entry 2). Further, dehydration of glucose attempted in DMSO where HMF was produced in 41 % yield with complete consumption of glucose. Then in situ formed HMF was treated with MeF at 65 °C for the longer time (24 h).

**Table 4.1.3.** Integrated dehydration of glucose followed by condensation with 2-methylfuran over Sn-Mont catalyst in different solvents

Glucose **8**  $\xrightarrow[\text{Dehydration}]{\text{Acid}}$  HMF **3**  $\xrightarrow[\text{Condensation}]{3 \text{ mol } \text{2-methylfuran}, \text{H}_2\text{O}}$  **1**

Entry	Solvent	Dehydration of glucose (Step-I) <sup>[a]</sup>		Condensation (Step-II) <sup>[b]</sup>	
		Conv <sup>[c]</sup> [%]	Yield <sup>[c]</sup> of <b>3</b> [%]	Conv <sup>[c]</sup> of <b>3</b> [%]	Yield <sup>[e]</sup> of <b>1</b> [%]
1	Water	89	19	11	00
2 <sup>[d]</sup>	C <sub>4</sub> mimBr	100	37	10	00
3	DMSO	100	41	24	08
4	DMSO	100	41	43	13

[a] Step-I: Glucose, **8** (0.180 g, 1 mmol), catalyst (0.1 g), solvent (5 mL), 150°C, 3 h. [b] Step-II: 2-methylfuran (0.246 g, 3.0 mmol), 65°C, 2 h. [c] Conversion of carbohydrates and yield of HMF (**3**) was determined using HPLC. [d] C<sub>4</sub>mimBr (1 g) was used. [e] Isolated yield corresponds to carbohydrates



Even after such a long time, only 24 % of HMF was consumed with 8 % yield of **1** (Table 4.1.3, entry 3). The lowest yield in above cases particularly, in the second step could be attributed to the limited or no activity of Sn-Mont catalyst. Higher loading (0.2 g) of Sn-Mont in DMSO was also attempted; still only 13 % yield of product **1** was obtained (Table 4.1.3, entry 4).

#### 4.1.5.4. Integrated dehydration of glucose and condensation with MeF in reactive medium

Further, we performed the reaction in a suitable acidic solvent which could dissolve the glucose as well as help to promote the condensation step. Hence, in the initial experiment, glucose was dissolved in acetic acid and heated at 150°C for 3 h over Sn-Mont. In this experiment, with complete conversion of glucose 11 % of HMF and 26 % of 5-(acetoxymethyl)furfural (AcMF, **4**) were formed. In the next step, these furfurals were treated with MeF to afford 17 % yield of desired product **1** (Table 4.1.4, entry 1). This implied that in order to improve the yield of product **1**, more acidic medium than acetic acid might be needed. Therefore, glucose dehydration was performed in formic acid and surprisingly, glucose was consumed completely with 3 % of HMF and 40 % of 5-(formyloxymethyl)furfural (FMF, **5**). In condensation step, mixture of HMF+FMF was converted to product **1** in 36 % yield (Table 4.1.4, entry 2). From the entries 1 and 2, it was observed that acidic medium along with Sn-Mont could significantly improve the yield of product **1**. Thus, it was concluded that formation of condensation product (**1**) from glucose was successfully achieved certainly due to the co-operative catalysis between Sn-Mont and formic acid. Lewis acid sites present on Sn-Mont played a crucial role for glucose isomerisation to fructose and further reactions could be promoted by formic acid. The use of formic acid in these processes is attractive because, it is a product from biomass degradation [38, 39] and can be regenerated by hydrogenation of CO<sub>2</sub> [40]. In addition to that formic acid is safe and cheap. [41] For the comparison purpose, several Lewis acids were screened in place of Sn-Mont for this reaction. Calcined Sn-Mont sample (Sn-Mont-600) possessing Lewis acidity was employed for glucose dehydration in formic acid medium. Glucose was consumed upto 61 % with 5 % yield of HMF and 19 % yield of FMF (**5**). This crude mixture of HMF+FMF was condensed with MeF to afford product **1** in low (17 %) yield (Table 4.1.4, entry 3). Parent montmorillonite

and  $\text{SnO}_2$  catalyst were found to be ineffective (Table 4.1.4, entries 4 and 5). Thus, Sn-Mont having  $\text{Sn}(\text{OH})_4$  species can generate the large pore volume into the layers of montmorillonite and also significantly increase the surface area of parent montmorillonite [42]. These unique features of Sn-Mont were responsible for its better performance than other Lewis acids studied in this work. In a control experiment, glucose was treated with hydrated tin chloride to give 5-(chloromethyl)furfural (CMF) as an intermediate which could be converted to FMF in 13 % yield in formic acid medium. With this starting material condensation product (**1**) was formed in 8 % yield (Table 4.1.4, entry 6). In presence of a catalytic amount of mineral acid ( $\text{HCl}$ , 20  $\mu\text{L}$ ), glucose was consumed completely, with 48 % yield of FMF which was further condensed with MeF to afford product **1** in highest yield of 41 % (Table 4.1.4, entry 7).

**Table 4.1.4.** Dehydration of glucose followed by condensation with 2-methylfuran in acidic solvent over various acid catalysts.

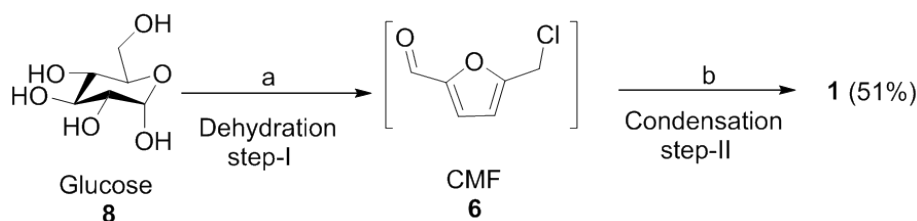
Entry	Solvent	Catalyst	Dehydration of glucose (Step-I) <sup>[a]</sup>		Condensation (Step-II) <sup>[b]</sup>	
			Conv <sup>[c]</sup> [%]	Yield <sup>[c]</sup> of <b>3/4/5</b> [%]	Conv <sup>[c]</sup> of <b>3+4+5</b> [%]	Yield <sup>[c]</sup> of <b>1</b> [%]
1	$\text{CH}_3\text{CO}_2\text{H}$	Sn-Mont	69	11/26/--	100	17
2	$\text{HCO}_2\text{H}$	Sn-Mont	99	03/--/40	99	36
3	$\text{HCO}_2\text{H}$	Sn-Mont-600	61	05/--/19	100	17
4	$\text{HCO}_2\text{H}$	Mont	58	--/--/--	---	00

5	HCO <sub>2</sub> H	SnO <sub>2</sub>	37	--/--/11	100	05
6	HCO <sub>2</sub> H	SnCl <sub>4</sub> ·5H <sub>2</sub> O	41	--/--/13	100	08
7 <sup>[d]</sup>	HCO <sub>2</sub> H	HCl	100	--/--/48	100	41

Reaction conditions: [a] Step-I: Glucose, **8** (0.180 g, 1 mmol), catalyst (0.1 g), solvent (5 mL), 150 °C, 3 h, [b] Step-II: 2-methylfuran (0.246 g, 3.0 mmol), 65 °C, 2 h. [c] Conversion of carbohydrates and yield of HMF (**3**), AcMF (**4**) and FMF (**5**) was determined using HPLC. [d] Reaction condition for step-I: Glucose, **8** (0.180 g, 1 mmol), HCl (20 µL), formic acid (5 mL), 150 °C, 3 h. [e] Isolated yield corresponds to carbohydrates

#### 4.1.5.5. Synthesis of condensation product (**1**) from glucose using HCl

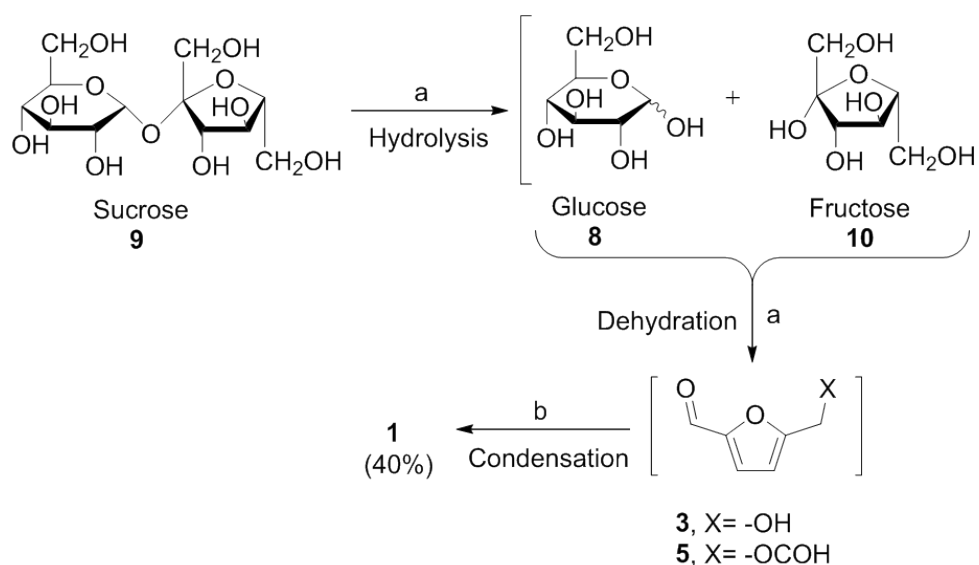
Alternatively, condensation product could be produced from carbohydrates *via* 5-chloromethylfurfural (CMF). CMF is a good starting material for its condensation with MeF. In this work CMF (69 % yield) was produced from glucose, following the strategy developed by Mascall and Nikitin [43], and without isolation it was further treated with MeF to afford product **1** in 51 % yield (Scheme 4.1.2). Although, mineral acid such as conc. HCl offers a high yield of condensation product (**1**), however, its commercial exploitation is generally avoided due to use of stoichiometrically large excess of conc. HCl, its hazardous nature, waste generation and non recyclability.



**Scheme 4.1.2.** One-pot, sequential two steps dehydrative-condensation of glucose with MeF in HCl. Reagents and conditions: a) conc. HCl, dichloroethane, 100 °C, 2 h; b) 2-methylfuran, 65 °C, 2 h.

#### 4.1.5.6. Sucrose dehydration and condensation with MeF

More complex carbohydrate such as disaccharide (sucrose) which contains a single unit of each glucose and fructose was also evaluated (Scheme 4.1.3) for its conversion to product **1** using the above protocol. Initially, sucrose dehydration was attempted in formic acid without using Sn-Mont catalyst that resulted into dehydration of only fructose unit to yield 5-(formyloxymethyl)furfural (FMF) with 28 % then FMF was further transformed into condensation product **1** with only 13 % yield. When sucrose dehydration was performed in formic acid over Sn-Mont catalyst, a mixture of HMF and FMF was obtained in 8 and 44 % yields, respectively. This mixture was then treated with MeF to afford an overall 40 % yield of product **1**. Thus, it was concluded that Sn-Mont was necessary to promote glucose isomerisation to fructose and further reaction proceeded due to formic acid.

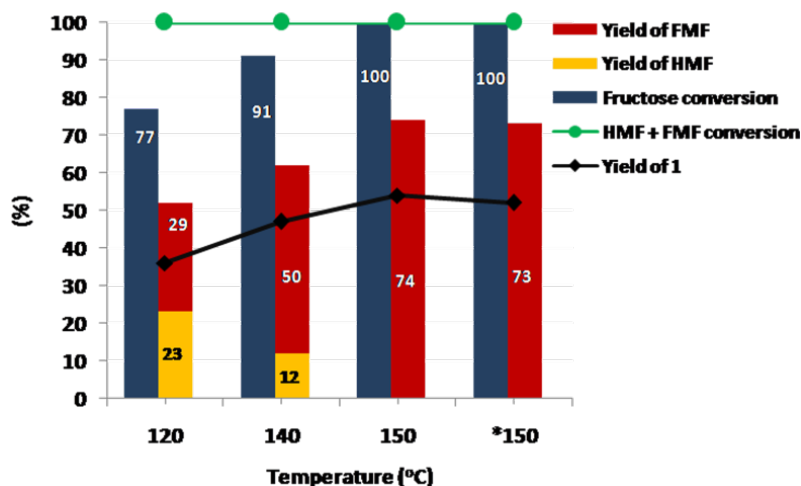


**Scheme 4.1.3.** One-pot, sequential two steps dehydrative-condensation of sucrose with MeF. Reagents and conditions: a) formic acid, Sn-Mont, 150 °C, 3 h; b) 2-methylfuran, 65 °C, 2 h.

#### 4.1.5.7. Fructose dehydration and condensation with MeF

Fructose is relatively more reactive as compared to glucose/sucrose hence, its dehydration was performed under mild temperature of 120 °C, to give HMF (23 %) and FMF (29 %) with 77 % conversion (Figure 4.1.4). At a higher temperature of 140 °C, fructose conversion increased to 91 % with a mixture of HMF (12 %) and FMF (50 %). Further increase in temperature to 150 °C led to completely conversion

with formation of only FMF in 74 % yield which was further converted into product **1** with maximum of 54 % yield. When fructose dehydration was performed over Sn-Mont catalyst in formic acid no any improvement in the yield of FMF was observed. Thus, it was confirmed that Sn-Mont has no role particularly, in fructose dehydration reaction in presence formic acid.

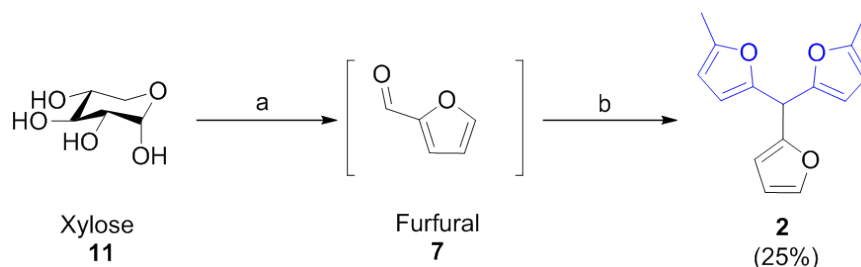


**Figure 4.1.4.** Dehydrative-condensation of fructose with MeF. Step-I: Fructose, **10** (0.180 g, 1 mmol), formic acid (5 mL), 150 °C, 3h, Step-II: 2-methylfuran (0.246 g, 3.0 mmol), 65 °C, 2h. \*Sn-Mont (0.1 g) was used. Yields are isolated corresponds to fructose.

#### 4.1.5.8. Xylose dehydration and condensation with MeF

Inspired by the promising results obtained with carbohydrate feedstock such as glucose, sucrose and fructose, we applied this methodology for conversion of C5-carbohydrate (xylose) (Scheme 4.1.4). In the first step, xylose was dehydrated to furfural over Sn-Mont catalyst (0.2 g) in formic acid medium. After 3 h at 150 °C, furfural was obtained in 33 % yield. In a consecutive step, *in-situ* formed furfural was treated with MeF to afford a total 25 % yield of the corresponding condensation product (**2**). Formation of furfural from xylose can be mainly due to xylose isomerisation to xylulose which is efficiently catalyzed by Lewis acid sites of Sn-Mont catalyst. Once, xylulose is formed it is much easier to dehydrate into furfural over Brønsted acid sites of formic acid. In a control experiment, xylose was treated with formic acid only to give low (11 %) yield of furfural. When, pure furfural was

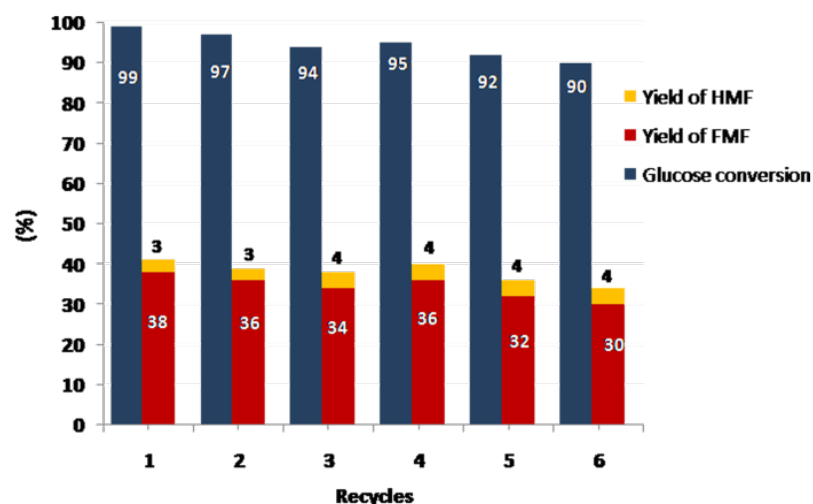
used for condensation with MeF, 93 % yield of (**2**) was obtained in formic acid. While, over Sn-Mont catalyst, (**2**) was formed in 88 % yield.



**Scheme 4.1.4.** One-pot, sequential two steps dehydration-condensation of xylose with MeF. Reagents and conditions: a) formic acid, Sn-Mont, 150 °C, 3 h; b) 2-methylfuran, 65 °C, 2 h.

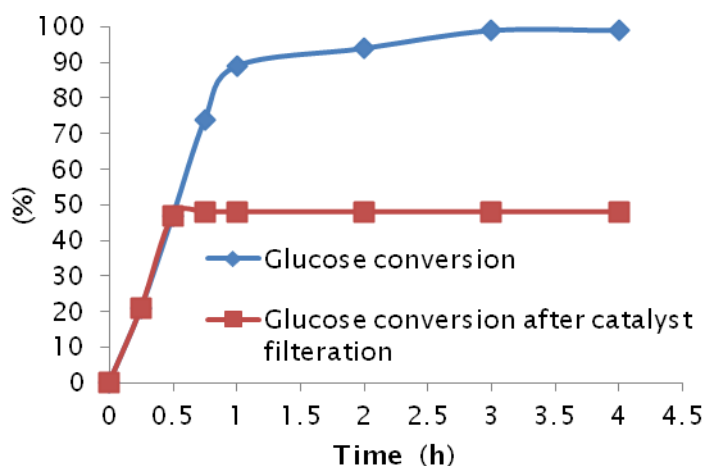
#### 4.1.5.9. Recycle studies of Sn-Mont

The stability and reusability of Sn-Mont catalyst was investigated for the dehydration-esterification of glucose in formic acid medium. As can be seen from Figure 4.1.5, catalyst showed almost similar activity for six recycles. Conversion of glucose was dropped marginally from 99 to 90 % after sixth recycle. The total furfural (HMF+FMF) yield was found to be gradually dropped from 41 to 34 % after sixth reuse of Sn-Mont.



**Figure 4.1.5.** Recycling of Sn-Mont for the production of FMF from glucose in formic acid. Reaction conditions: Glucose (0.180 g, 1 mmol), formic acid (5 mL), Sn-Mont (0.1 g), 150 °C, 3 h. After each cycle catalyst was washed with acetone and dried in the oven at 110 °C

for 1 h prior to use for next cycle. Conversion of glucose was and yields of HMF and FMF were measured using HPLC.



**Figure 4.1.6.** Leaching test of Sn-Mont for dehydration of glucose in formic acid

This slight drop in activity of Sn-Mont could be attributed to the humin deposition on the surface of catalyst which may cause pore blocking of catalyst. The slight loss in acidity of the Sn-Mont catalyst was also observed in  $\text{NH}_3$ -TPD analysis of fresh and reused catalysts. The acidity of the fresh and reused (3<sup>rd</sup> reuse) catalyst was found to be  $511 \mu\text{mol}_{\text{ammonia desorbed}} \text{g}^{-1}_{\text{cat}}$  for fresh and  $490 \mu\text{mol}_{\text{ammonia desorbed}} \text{g}^{-1}_{\text{cat}}$  for reused Sn-Mont catalyst (Table 4.1.1). Further, the stability of Sn-Mont was also confirmed by ICP analysis which showed no leaching of Sn species. In addition to that, hot filtration test also suggest that the active sites of the catalyst were not leached into the reaction mixture (Figure 4.1.6).

#### 4.1.6. Conclusions

In summary, combination of Sn-Mont and formic acid provided an integrated protocol for production of condensation products having C<sub>15</sub> and C<sub>21</sub> units from carbohydrates and 2-methylfuran. Sn-Mont, a heterogeneous catalyst demonstrated efficient isomerisation of glucose to fructose on its Lewis acid site. Further, dehydration of in-situ formed fructose to FMF followed by condensation of FMF with MeF was promoted in presence of formic acid. Formic acid played a versatile role as a solvent to dissolve carbohydrates and as a strong Brønsted acid catalyst. This strategy was further optimized for sucrose to obtained 40 % yield of condensation product (**1**). While, in case of fructose only formic acid was sufficient to bring out conversion into condensation product (**1**) with 54 % yield. Xylose was also successfully transformed into condensation product (**2**) in two sequential steps using above methodology. Additionally, the Sn-Mont catalyst was rather robust and it could be used upto six reaction cycles without significant loss in activity. This new and green approach offers a sustainable route for valorization of biomass to liquid alkane precursors and chemicals.



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### 4.1.8. NMR spectroscopic data of the synthesized compound

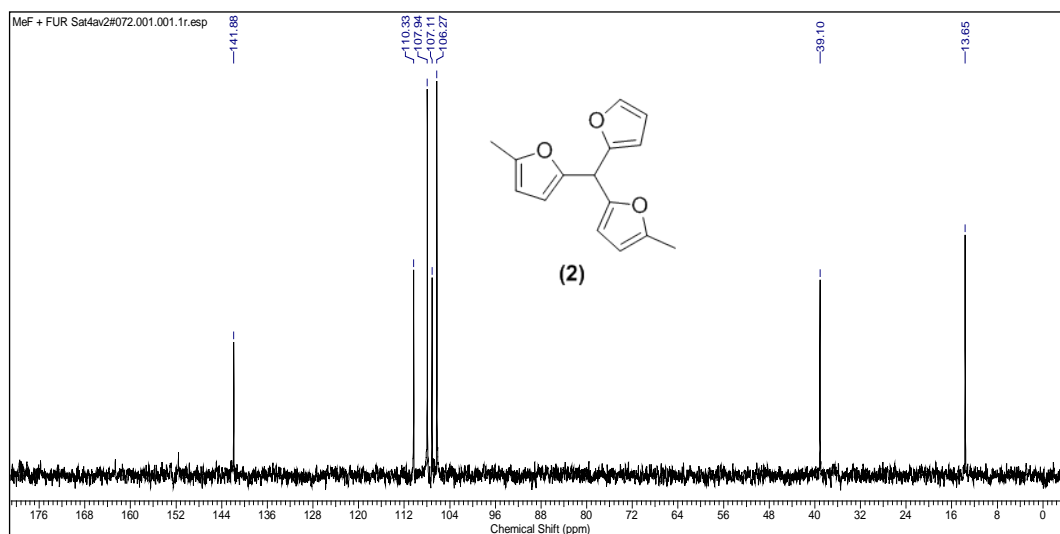
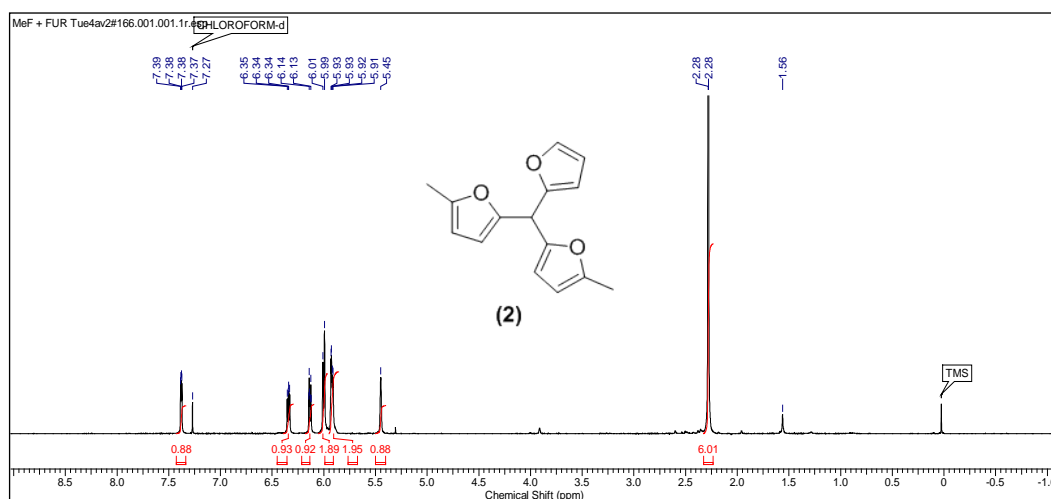
#### 5,5'-((5-((5-methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran)

(1): NMR data of this compound is provided in Chapter 2.

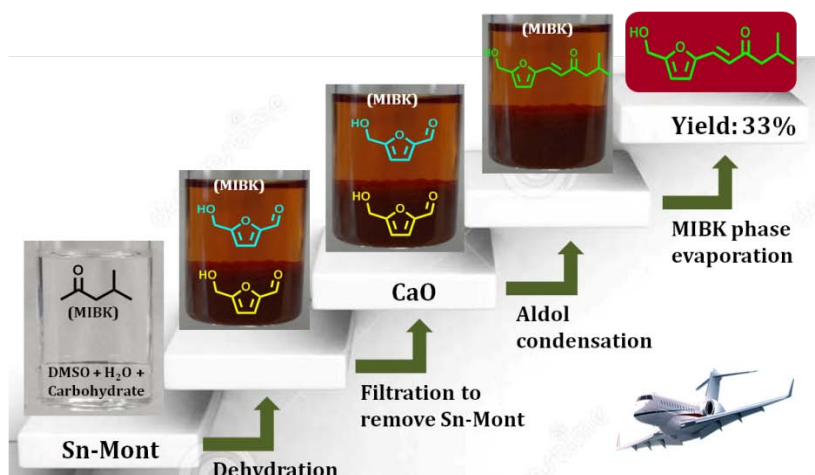
#### 5,5'-(furan-2-ylmethylene)bis(2-methylfuran) (2)

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 2.28 (s, 6 H;  $\text{CH}_3$ ) 5.45 (s, 1 H, CH) 5.91 - 5.93 (m, 2 H; Ar-H) 5.99-6.01 (d,  $J=3.03$  Hz, 2 H; Ar-H) 6.13-6.14 (dt,  $J=3.22$ , 0.79 Hz, 1 H; Ar-H) 6.34-6.35 (dd,  $J=3.03$ , 1.89 Hz, 1 H; Ar-H) 7.37-7.39 (dd,  $J=1.89$ , 0.88 Hz, 1 H; Ar-H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 13.65 ( $\text{CH}_3$ ), 39.10 (CH), 106.27 (Ar-C), 107.11 (Ar-C), 107.94 (Ar-C), 110.33 (Ar-C), 141.88 (Ar-C).



## 4.2. Clean production of jet-fuel precursor from carbohydrates through an integrated dehydration and aldol condensation



A promising and efficient approach is demonstrated for the clean and high yield production of jet-fuel range precursor from carbohydrates *via* dehydration followed by aldol condensation. C<sub>12</sub> branched alkane precursor was produced from carbohydrates through an integrated process which involves two steps such as *i*) isomerisation-dehydration of carbohydrates to 5-(hydroxymethyl)furfural (HMF) over solid acid catalyst in MIBK (methyl isobutyl ketone): water + DMSO biphasic solvent system, *ii*) aldol condensation of crude HMF with MIBK (solvent) over solid base catalyst. Initially, production of HMF was optimized from glucose in MIBK: H<sub>2</sub>O-NaCl (8:2; *v/v*) biphasic solvent system over different acid catalysts at 170 °C. Among those catalysts, Sn-Mont with a combination of Lewis and Brønsted acid sites show 80 % glucose conversion with 34 % yield of HMF. Interestingly, in a modified biphasic solvent system, MIBK: H<sub>2</sub>O-NaCl: DMSO (8:1.5:0.5; *v/v/v*) complete glucose conversion with 42 % HMF yield was achieved. Aldol condensation of HMF with MIBK was optimized over several base catalysts at 80 °C. The CaO exhibited excellent performance to achieve 90 % yield of aldol condensation product. In an integrated sequence, Sn-Mont catalyst was filtered after glucose dehydration and filtrate containing crude HMF was treated with CaO to facilitate aldol condensation with MIBK (solvent). The overall 32 % yield of aldol condensation product was achieved from glucose. More importantly, a product extraction phase (MIBK) was recovered upto its 80 % of initial volume which could be reused. This strategy was further explored for carbohydrates such as fructose and sucrose.

Suhas Shinde and Chandrashekhar Rode, Submitted to ChemSusChem.

### 4.2.1. Introduction

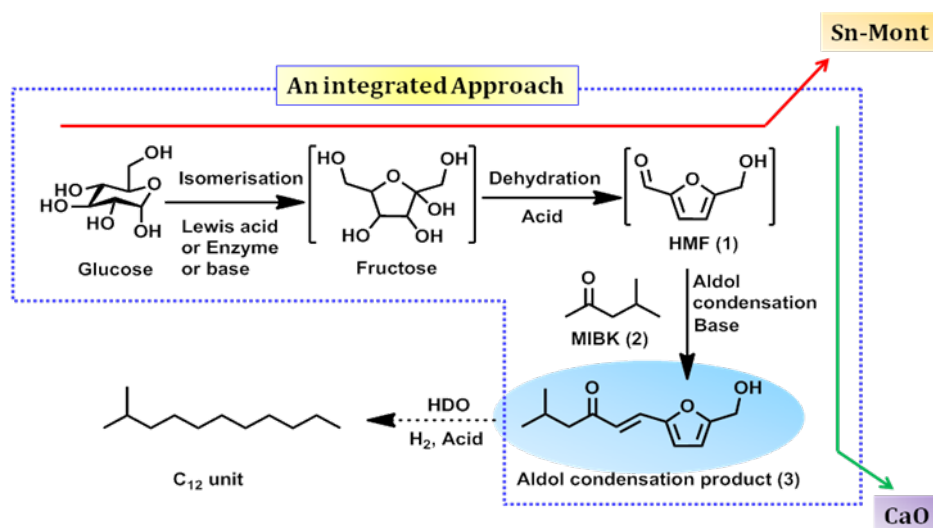
The aldehydes functionality of HMF is susceptible for carbon up-gradation process *via* C-C bond formation for the production of long chain liquid alkanes. For example, the aldol condensation of HMF with aldehydes or ketones has been used as a strategy to obtain hydrocarbons in the diesel fuel range. Several authors reported the aldol condensation reactions of HMF with carbonyl compounds, mainly acetone (which can also be obtained by fermentation of biomass) as a synthetic strategy for the synthesis of pharmacological compounds and useful intermediates for the synthesis of biofuels [1]. However, straight chain alkanes were obtained from the HDO of aldol condensation products of HMF and acetone. These alkanes have relatively high freezing points or low octane numbers thus; they can't be used directly as jet fuel without hydroisomerization [2]. Since, extraction of HMF from aqueous phase is not an easy process due to unfavourable distribution coefficient between organic and aqueous phase [3]. However, this problem has been overcome by the use of organic solvent such as MIBK (methyl isobutyl ketone), which has been reported to be an efficient extraction solvent [4]. MIBK is the hydrogenation product of mesitylene oxide which is self-aldol condensation product of acetone [5]. It has been used as an extracting solvent to increase the selectivity towards furfural in the dehydration of xylose or its oligomers [6]. From the process intensification point of view, it is preferable if MIBK can be directly used as the HMF extraction solvent as well as carbonyl functionality for aldol condensation with extracted HMF. Furthermore, the branched structure of MIBK also renders it as a potential feedstock for the direct synthesis of branched alkanes [7]. More importantly, these branched alkanes have low freezing points and can be blended into jet fuel without hydroisomerization.

### 4.2.2. Literature Survey

Uptil now, integrated conversion of carbohydrates to jet fuel is reported only by Li et al. in 2014 according to which, they produced jet fuel (liquid branched alkane) starting from C<sub>5</sub>-carbohydrates (xylose) and MIBK [8].

### 4.2.3. Scope of the present work

In this direction, we have successfully demonstrated the production of jet fuel precursor from carbohydrates (*e.g.* glucose, sucrose and fructose) and MIBK. As shown in Scheme 4.2.1, jet fuel production from carbohydrates requires three steps, *i*) dehydration of carbohydrates to HMF, *ii*) aldol condensation of HMF with MIBK and *iii*) hydrodeoxygenation (HDO) of aldol condensation product. On the basis of this background, we report here an integrated conversion of carbohydrates into jet fuel precursor. This strategy involves the dehydration of carbohydrates over Sn-Mont catalyst in a biphasic solvent system including MIBK: H<sub>2</sub>O-NaCl + DMSO (8: 1.5 + 0.5; *v/v*) followed by aldol condensation of *in-situ* formed HMF with MIBK (solvent) over CaO catalyst. In this strategy MIBK serves as a solvent for product extraction as well as a reactant (carbonyl compound) for aldol condensation with HMF. In order to establish this integrated approach, initially we have meticulously found out suitable catalysts and reaction conditions for glucose dehydration and aldol condensation reaction of HMF.



**Scheme 4.2.1.** Process for the production of jet-fuel precursor from carbohydrates

## 4.2.4. Experimental

### 4.2.4.1. Materials

All the reactants were used as received without their further purification. Carbohydrates such as fructose, glucose and sucrose, basic oxides such as MgO and CaO,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_2\text{SO}_4$  (98 %) and NaOH were purchased from Thomas Bakers.  $\text{Ba}(\text{OH})_2$  was obtained from Qualigens fine chemicals. Methyl isobutyl ketone (MIBK) was obtained from SD fine chemicals Ltd. Metal chlorides such as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and natural montmorillonite clay  $[(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}]$  (CAS No. 1302-78-9) with the composition (mass %)  $\text{SiO}_2$  (66.5)  $\text{Al}_2\text{O}_3$  (8.79)  $\text{Fe}_2\text{O}_3$  (1.64)  $\text{CaO}$  (1.64)  $\text{MgO}$  (3.03)  $\text{TiO}_2$  (2.06)  $\text{K}_2\text{O}$  (0.19)  $\text{Na}_2\text{O}$  (0.14) was purchased from Sigma-Aldrich. Metal exchanged montmorillonite was prepared in house as per our previous report. [9] Hydrotalcite (HT,  $\text{Mg}/\text{Al} = 3$ ) was prepared according to the procedure reported in literature [10].

### 4.2.4.2. Catalyst preparation

The metal exchanged montmorillonite catalysts were prepared in **Chapter 4.1** are used in this work.

### 4.2.4.3. Synthesis procedures

#### 4.2.4.3.1. Aldol condensation of HMF with MIBK

A mixture of HMF (0.126 g, 1 mmol), MIBK (4.5 mL), water (0.5 mL) and CaO (0.1 g) was heated at 80 °C for 12 h. After desired time, reaction mixture was cooled to ambient temperature, filtered and catalyst bed was washed with ethyl acetate (10 mL x 1). Further, filtrate was washed with water (10 mL x 2) and saturated solution of NaCl (10 mL x 1). Subsequently, organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then organic phase was evaporated under reduced pressure to afford crude residue. This residue was further passed through silica bed to afford orange oil of aldol condensation product. Yield of (E)-1-(5-(hydroxymethyl)furan-2-yl)-5-methylhex-1-en-3-one (**3**): 0.186 g, (90 %).



#### ***4.2.4.3.2. Dehydration of carbohydrates to HMF***

In a pressure reactor, mixture of carbohydrate (e.g. fructose or glucose or sucrose, 0.5 g), H<sub>2</sub>O-NaCl (1.5 mL, 10 wt % NaCl), DMSO (0.5 mL), MIBK (8 mL) and Sn-Mont (0.2 g) was heated at 170 °C for 12 h. After that reactor system was cooled to room temperature. Subsequently, reaction mixture was filtered to separate the catalyst (Sn-Mont). MIBK layer was separate out and aqueous layer was extracted with ethyl acetate (10 mL x 2). Further, MIBK layer and ethyl acetate were combined and washed with saturated solution of NaCl (10 mL x 2). Organic phase was further dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure using rotary evaporator. Crude residue was passed through silica bed to afford orange oil of HMF.

#### ***4.2.4.3.3. Synthesis of aldol condensation product from carbohydrates***

In a pressure reactor mixture of carbohydrate (e.g. fructose or glucose or sucrose) (0.5 g), H<sub>2</sub>O-NaCl (1.5 mL, 10 wt % NaCl), DMSO (0.5 mL), MIBK (8 mL) and Sn-Mont (0.2 g) was heated at 170 °C. After 12 h, the reactor system was quickly cooled to room temperature in an ice water bath. After that reaction mixture was filtered to separate the catalyst (Sn-Mont). Into mother liquor containing in-situ formed HMF, CaO (0.2 g) was added and continued to react at 80 °C for 12 h. After that the reaction mixture was cooled to ambient temperature, filtered and catalyst bed was washed with ethyl acetate (10 mL x 1). Combined mother liquor was washed with water (10 mL x 2) and saturated solution of NaCl (10 mL x 1). Organic phase was further dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure using rotary evaporator. Further crude residue was passed through silica bed to afford orange oil of pure aldol condensation product (3). Yield: 0.219 g, 38 % based on fructose; 0.132 g, 23 % based on glucose; 0.188 g, 31 % based on sucrose.

#### ***4.2.4.3.4. Hot filtration test***

In a typical experiment, mixture of glucose (0.5 g), water-NaCl (1.5 mL, 10 wt % NaCl), DMSO (0.5 mL), MIBK (8 mL) and Sn-Mont (0.2 g) was heated at 170 °C for 1 h. After that reaction mixture was filtered to separate the Sn-Mont catalyst. Then filtrate was continued to heat at 170 °C under stirring for 11h. Conversion of glucose was monitored using HPLC.

#### ***4.2.4.3.5. Recycle studies of Sn-Mont***

In a typical recycle experiment; mixture of glucose (0.5 g), water-NaCl (1.5 mL, 10 wt % NaCl), DMSO (0.5 mL), MIBK (8 mL) and Sn-Mont (0.2 g) was heated at 170 °C for 12 h. After that reactor system was cooled to room temperature. Subsequently, reaction mixture was filtered to separate the catalyst (Sn-Mont). Then catalyst bed was washed with ethyl acetate (10 mL x 2) and acetone (10 mL x 2). Subsequently, catalyst was dried at 110 °C for 2 h before its reuse for the next run. After each run fresh starting materials and solvents were loaded into the reactor and treated with reused Sn-Mont catalyst. The same procedure was repeated each time procedure.

#### ***4.2.4.3.6. Recycle studies of CaO***

Into the mother liquor of dehydration step containing in-situ formed HMF, CaO (0.2 g) was added and continued to react at 80 °C for 12 h. After that reaction mixture was cooled to ambient temperature, filtered and catalyst bed was washed with ethyl acetate (10 mL x 2) and acetone (10 mL x 2). Subsequently, catalyst was dried at 110 °C for 2 h before its reuse for the next run. After each run starting materials obtained from dehydration of glucose was loaded into the reactor and treated with reused CaO catalyst. The same procedure was repeated each time procedure.

#### ***4.2.4.4. Analysis of reaction products***

Conversion of carbohydrates and yields of HMF and aldol product were calculated by using Agilent HPLC. Pure products were characterised and confirmed by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR using CDCl<sub>3</sub> (0.01 %, TMS) as solvent on 200 MHz frequency Bruker instrument. Product yields and carbohydrate conversion were obtained by using following equations.

$$\text{HMF yield from glucose or fructose} = \frac{\text{Moles of HMF formed}}{\text{Moles of starting glucose or fructose}} \times 100 \% \quad \text{----- (I)}$$

$$\text{HMF yield from sucrose} = \frac{\text{Moles of HMF formed}}{\text{Moles of hexose unit in sucrose}} \times 100 \% \quad \text{----- (II)}$$

$$\text{Carbohydrates conversion} = \frac{(\text{Moles of starting carbohydrates} - \text{Moles of carbohydrates remained})}{\text{Moles of starting carbohydrates}} \times 100 \% \quad \text{--- (III)}$$

$$\text{HMF conversion} = \frac{(\text{Moles of starting HMF} - \text{Moles of HMF remained})}{\text{Moles of starting HMF}} \times 100 \% \quad \text{---- (IV)}$$

$$\text{Condensation product yield} = \frac{\text{Moles of condensation product formed}}{\text{Moles of starting HMF}} \times 100 \% \quad \text{----- (V)}$$

## 4.2.5. Results and Discussion

### 4.2.5.1. Dehydration of glucose in MIBK: H<sub>2</sub>O

As carbohydrate dehydration to HMF is one of the important steps in an integrated approach for synthesis of jet fuel precursor, we selected glucose as starting material to optimize the dehydration conditions using the appropriate catalyst. Glucose is rather difficult to dehydrate due to its inertness for isomerisation to fructose. We believe that once reaction conditions are optimized for glucose dehydration those reaction conditions could be used for sucrose and fructose. Dehydration of glucose was conducted in a pressure reactor with biphasic solvent system (MIBK: H<sub>2</sub>O-NaCl; 8:2; v/v) over different acidic catalysts at 170 °C (Table 4.2.2). In presence of mineral acid (H<sub>2</sub>SO<sub>4</sub>, 10 mol %), glucose was consumed completely in just 1h with total 32 % yield of HMF. Concentration of HMF in aqueous and organic phases was determined as 13 and 19 %, respectively (Table 4.2.2, entry 1). Over phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>), glucose conversion was 33 % with 11 % HMF yield (Table 4.2.2, entry 2). While, in presence of montmorillonite clay, no HMF was detected in aqueous and organic phases even after 17 % glucose conversion (Table 4.2.2, entry 3). After treatment of montmorillonite clay with aqueous solution

of  $\text{SnCl}_4 \cdot 8\text{H}_2\text{O}$ , the resultant catalyst (Sn-Mont), showed better catalytic performance for glucose dehydration. In this experiment, glucose conversion was 88 % with combined yield of 34 % of HMF in aqueous and organic phases (Table 4.2.2, entry 4). Sn-Mont possessed  $\text{Sn}(\text{OH})_4$  species enwrapped between montmorillonite layers wherein  $\text{Sn}^{4+}$  species behave as a Lewis acid while,  $\text{Sn}(\text{OH})_4$  species behave as a Brønsted acid.  $\text{Sn}^{4+}$  species are responsible for glucose isomerisation to fructose and  $\text{Sn}(\text{OH})_4$  species are responsible for dehydration of in-situ formed fructose to HMF. Sn-Mont, a heterogeneous solid acid catalyst is well known for the carbohydrate dehydration to HMF in THF/ $\text{H}_2\text{O}$ –NaCl bi-phasic system [11]. The Effect of Sn-Mont catalyst loading was also investigated for glucose conversion into HMF. When, 0.1 g of Sn-Mont was used, only 24 % HMF was formed after 73 % conversion of glucose (Table 4.2.2, entry 5). While, 0.15 g loading of Sn-Mont showed 80 % glucose conversion with 28 % yield of HMF (Table 4.2.2, entry 6). Over Zr-Mont, glucose was consumed upto 72 % with 23 % yield of HMF (Table 4.2.2, entry 7). While, Al and Fe exchanged montmorillonite showed identical results, glucose consumption was <55 % with almost 20% yield of HMF (Table 4.2.2, entries 8 and 9). Solid Lewis acid ( $\text{SnO}_2$ ) wasn't effective for dehydration of glucose (Table 4.2.2, entry 10).

**Table 4.2.2.** Dehydration of glucose over different acid catalysts in biphasic solvent system <sup>[a]</sup>

Entry	Catalyst	Loading	Conv <sup>[c]</sup> [%]	HMF yield <sup>[c]</sup> [%]		
				In MIBK	In $\text{H}_2\text{O}$	Total
1 <sup>[b]</sup>	$\text{H}_2\text{SO}_4$	10 mol %	89	13	19	32
2	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	10 mol %	33	4	7	11
3	Mont	0.2 g	17	00	00	00
4	Sn-Mont	0.2 g	88	19	15	34
5	Sn-Mont	0.1 g	73	15	09	24
6	Sn-Mont	0.15 g	80	17	11	28

7	Zr-Mont	0.2 g	72	13	10	23
8	Fe-Mont	0.2 g	51	11	08	19
9	Al-Mont	0.2 g	54	12	08	20
10	SnO <sub>2</sub>	0.2 g	6	00	00	00

[a] Reaction conditions: Glucose (0.5 g), H<sub>2</sub>O (2 mL), MIBK (8 mL), catalyst, 170 °C, 12 h, [b] Reaction time, 3h. [c] Conversion of glucose was determined using HPLC.

#### 4.2.5.2. Effect of DMSO

The improved HMF yield and glucose dehydration rate was observed in the presence of DMSO. It led us to study the effect of varying amount of DMSO in reaction medium. Glucose dehydration was conducted at 170 °C in the presence of 8: 2 (v/v) MIBK: aqueous phase, solvent system. As shown in Table 4.3.3, the small addition of DMSO (0.2 mL) in reaction medium improved the conversion of glucose from 88 to 94 % and the yield of HMF was also raised from 26 to 34 % (Table 4.2.3, entry 1). Further increase in DMSO level in reaction medium to 0.5 mL raised the conversion to 100 % with 42 % yield of HMF (Table 4.2.3, entry 2). Concentration of DMSO higher than 0.5 mL e.g. 1 mL didn't improve the yield of HMF (Table 4.2.3, entry 3). Due to addition of DMSO, HMF concentration increased in both the aqueous and organic phases. Importantly, addition of DMSO suppresses the formation of condensation by-products (humin) [3a, 12]. However, it should also be noted that increasing the DMSO content in reaction mixture more than a critical concentration decreased the extraction efficiency of the solvent [4d]. A suitable reaction medium comprising 8 mL: 1.5 mL: 0.5 mL, MIBK: H<sub>2</sub>O-NaCl: DMSO, respectively, was used while performing the reaction in conc. H<sub>2</sub>SO<sub>4</sub>. Although significant amount of improvement in the conversion of glucose and yield of HMF were observed, its recyclability and handling difficulty restrict its large scale exploitation.

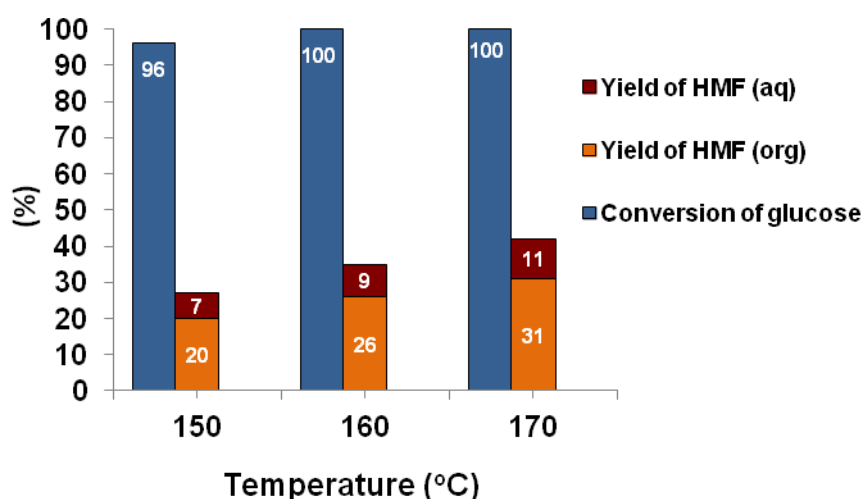
**Table 4.2.3.** Effect of DMSO addition on dehydration of glucose Sn-Mont<sup>[a]</sup>

Entry	Aqueous phase (H <sub>2</sub> O: DMSO; v/v)	Conv. <sup>[c]</sup> [%]	HMF, Yield <sup>[c]</sup> [%]		
			MIBK phase	Aqueous phase	Total
1	1.8 mL: 0.2 mL	94	21	13	34
2	1.5 mL: 0.5 mL	100	28	16	42
3	1 mL: 1 mL	100	21	21	42
4 <sup>[b]</sup>	1.5 mL: 0.5 mL	100	26	18	44

[a] Reaction conditions: glucose (0.5 g), DMSO + H<sub>2</sub>O (2 mL), MIBK (8 mL), Sn-Mont (0.2 g), 170 °C, 12 h. [b] Reaction was performed using 10 mol % of H<sub>2</sub>SO<sub>4</sub> catalyst. [c] Conversion of glucose and yield of HMF were determined using HPLC.

#### 4.2.5.3. Effect of temperature

To arrive at the optimum reaction temperature, glucose dehydration was carried out over Sn-Mont catalyst in a biphasic solvent system including MIBK: H<sub>2</sub>O-NaCl+DMSO; 8: 1.5 + 0.5, (v/v) at different temperatures ranging from 150-170 °C and the results are presented in Figure 4.2.5. At 150 °C, glucose conversion was >90 % with 27 % yield of HMF. The distribution of HMF in organic and aqueous phases was 20 % and 07 %, respectively.

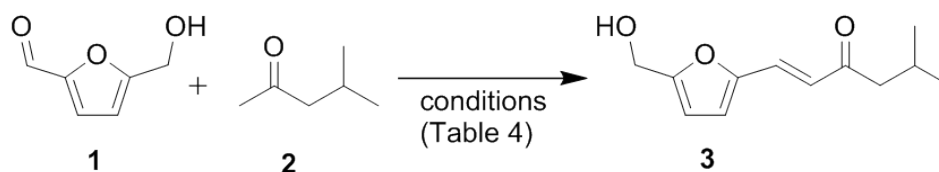


**Figure 4.2.5.** Influence of temperature on conversion of glucose and yield of HMF in MIBK and aqueous phase. Reaction conditions: glucose (0.5 g), H<sub>2</sub>O + DMSO (1.5 mL + 0.5 mL), MIBK (8 mL), Sn-Mont (0.2 g), 12 h.

At 160 °C, glucose conversion reached to 100 % with 35 % yield of HMF where distribution of HMF in organic and aqueous phases was 26 and 09 %, respectively. More than 160 °C, *i.e.* at 170 °C, glucose conversion was 100 % and more importantly, yield of HMF increased marginally to 42 % with distribution of HMF in organic and aqueous phases was 31 and 11 %, respectively. At 180 °C, yield of HMF was distributed in organic and aqueous phase as 31 and 9 %, respectively. Thus, the higher than optimum temperature (*i.e.* 170 °C) was not favourable for the dehydration of glucose as it resulted in decreasing the yield HMF in aqueous phase.

#### 4.2.5.4. Aldol condensation of HMF with MIBK

After optimizing the reaction conditions for glucose dehydration, we then focused on developing an appropriate catalyst and reaction conditions for aldol condensation between HMF and MIBK. Aldol condensation of pure HMF with MIBK was carried out over different base catalysts (Scheme 4.2.2, Table 4.2.4). Initially, HMF and MIBK were heated in presence of catalytic amount of NaOH and in just 1h, complete conversion of HMF was observed with 84 % yield of condensation product (Table 4.2.4, entry 1). Despite of good results obtained with NaOH, it could not be the best choice as it is soluble in reaction medium and difficult to reuse. In addition, it needs to be neutralised with acid which adds to the extra process operation. In this context, we focused our efforts to explore a recyclable and safe catalyst system for aldol condensation of HMF with MIBK. In fact, metal oxides could be a better choice for this reaction. Therefore, we attempted aldol condensation of HMF with MIBK over hydrotalcite (HT, Mg/Al=3) but unfortunately, only 10 % of HMF conversion was observed even after 12 h at 80 °C (Table 4.2.4, entry 3). In presence of MgO, HMF did not react at all with MIBK (Table 4.2.4, entry 4). Under the same experimental conditions, CaO exhibited the best catalytic performance in a model aldol condensation reaction. By using 0.1 g of CaO, aldol condensation product (**3**) was obtained in 80 % yield with 98 % conversion of HMF (Table 4.2.4, entry 5). On the other hand, when 0.05 g of CaO was used, the yield of condensation product and conversion of HMF dropped to 59 and 81 %, respectively (Table 4.2.4, entry 6). Optimum amount



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Entry	Catalyst	Loading	T [°C]	Conv. [%]	Yield <sup>[c]</sup> of <b>3</b> [%]
1 <sup>[b]</sup>	NaOH	10 mol %	80	100	84
2	Ba(OH) <sub>3</sub>	0.1 g	80	06	0
3	HT	0.1 g	80	10	3
4	MgO	0.1 g	80	0	0
5	CaO	0.1 g	80	98	80
6	CaO	0.05 g	80	81	59
7	CaO	0.15 g	80	100	90



8	CaO	0.15 g	70	89	63
9	CaO	0.15 g	90	100	81

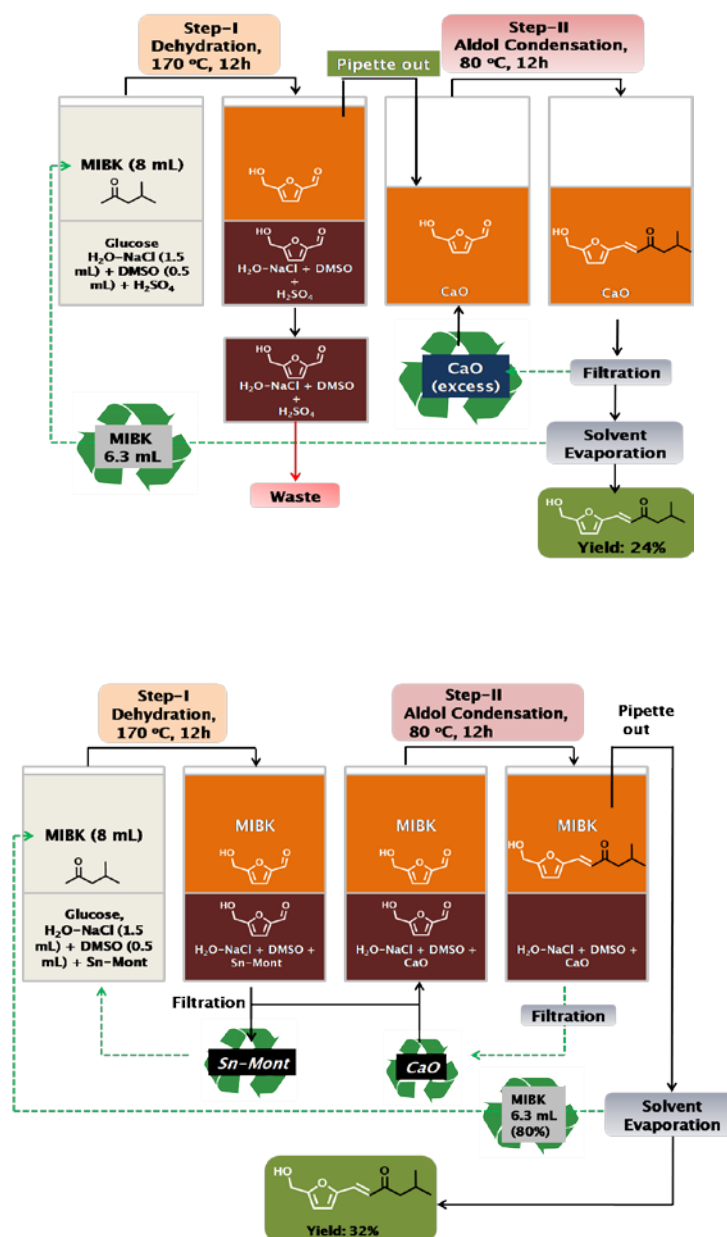
[a] Reaction conditions: HMF (0.126 g, 1 mmol), catalyst, MIBK (4 mL), H<sub>2</sub>O (1 mL), 12 h, [b] Reaction time, 1h. [c] Isolated yield of pure products. HT= Hydrotalcite (Mg: Al= 3).

#### 4.2.5.5. Integrated conversion of glucose into aldol condensation product

Inspired by the promising results obtained in the production of HMF from carbohydrate in MIBK: H<sub>2</sub>O-NaCl: DMSO (8: 1.5: 0.5; v/v/v) medium, we envisioned that role of MIBK could be enhanced as a reactant for aldol condensation with crude HMF. In this direction, we attempted dehydration of glucose with conc. H<sub>2</sub>SO<sub>4</sub> (10 mol %) in MIBK: H<sub>2</sub>O-NaCl: DMSO (8:1.5:0.5; v/v/v) medium. As shown in Table 4.2.3 (entry 4), HMF was obtained in 44 % yield with 18% in aqueous and 26 % in MIBK phase. Very interestingly, after separation of the catalyst (Sn-Mont), the remaining mixture contained MIBK and crude HMF. Therefore, it opens up an opportunity to carry out aldol condensation between crude HMF and MIBK. Thus, our perception was to combine these two methodologies (*e.g.* dehydration of glucose to HMF and aldol condensation between crude HMF and MIBK) in a single pot integrated process. In an integrated two-step approach, jet fuel precursor (aldol product) was produced in MIBK phase which can be isolated by separating and evaporating MIBK (Figure 4.2.6). A schematic reaction flow-charts of glucose dehydration over H<sub>2</sub>SO<sub>4</sub> vs. Sn-Mont and aldol condensation over CaO is presented in Figure 4.2.7. In a pressure reactor, glucose was dissolved in H<sub>2</sub>O-NaCl + DMSO (1.5 mL + 0.5 mL) then MIBK (8 mL) and Sn-Mont (0.2 g) was added.



**Figure 4.2.6.** Formations of aldol product in MIBK phase enabling clean/easy product separation and isolation.



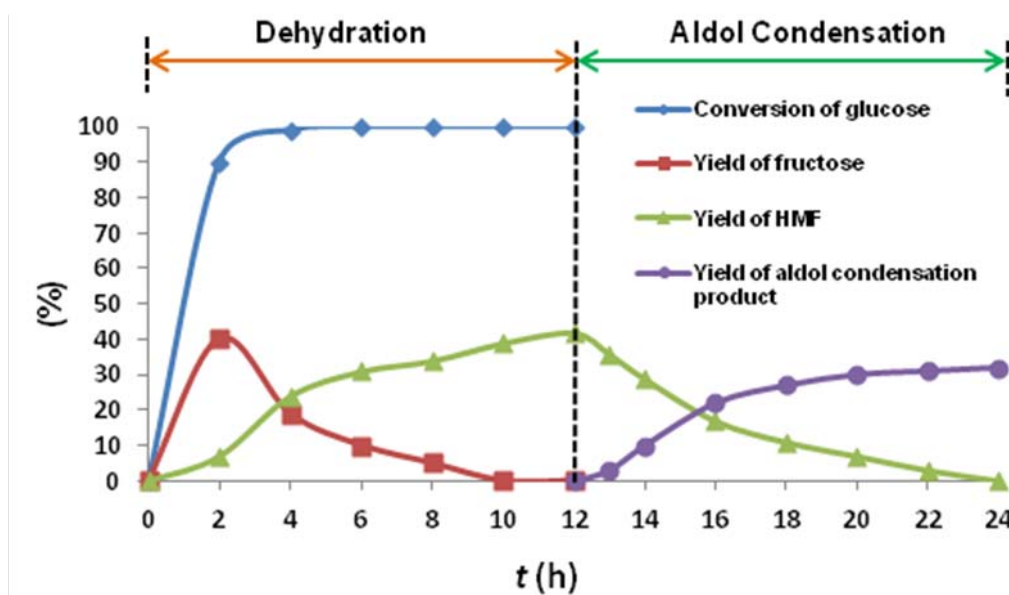
**Figure 4.2.7.** Schematic presentation of reaction flow-chart of integrated conversion of glucose to aldol condensation product over H<sub>2</sub>SO<sub>4</sub> vs. Sn-Mont.

This biphasic reaction mixture was stirred and heated at 170 °C for 12h, which gave a combined 42 % yield of HMF in both organic and aqueous phases. Subsequently, reaction was quickly cooled to ambient temperature and filtered to separate the catalyst (Sn-Mont) and then the resultant biphasic filtrate was reloaded into the same reactor and treated with CaO (0.15 g) at 80 °C for 12h.

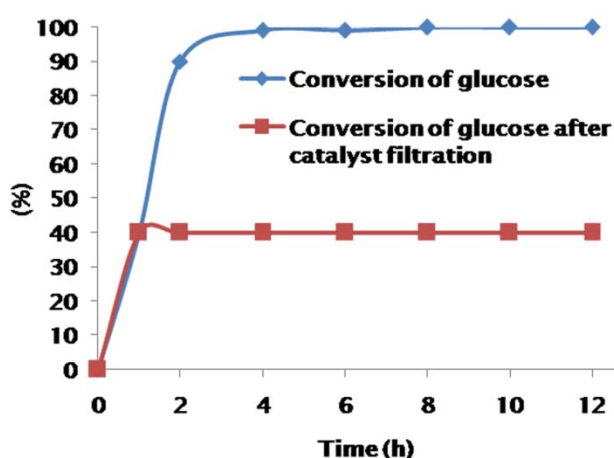
After that, upper organic phase was pipetted out and evaporated under reduced pressure to afford aldol condensation product (**3**) in 32 % yield. Interestingly, evaporated MIBK was collected upto 80 % (6.3 mL) of its initial volume (8 mL) which could be reused for this reaction.

#### 4.2.5.6. Reaction progress monitoring

The progress of glucose dehydration and aldol condensation reaction was monitored by withdrawing and analyzing liquid samples after each 2h (Figure 4.2.8). In the first 2 h, glucose conversion reached to 90 % with 40 % of fructose and <10 % of HMF. After 4<sup>th</sup> hour, glucose was consumed completely and in-situ formed fructose also consumed upto 50% of its initial concentration to produce HMF in 20 % yield. At the end of 12<sup>th</sup> hour, fructose concentration in reaction mixture decreased gradually to nil to achieve maximum of 42 % yield of HMF. After that reaction mixture was cooled to room temperature and filtered to separate the Sn-Mont catalyst. Interestingly, intrinsic stability of Sn-Mont did not leave any acidity in the reaction mixture. Thus, it would avoid the neutralization/deactivation of basic catalyst used for aldol condensation step. The absence of acidity in the reaction mixture was confirmed by hot filtration test. The reaction mixture was filtered at 40 % conversion of glucose, after which, filtrate was subjected under optimized conditions but glucose conversion did not improve (Figure 4.2.9). The progress of aldol condensation reaction between in-situ formed HMF and MIBK (solvent/organic phase) was also monitored by withdrawing and analyzing sample after each 2h (Figure 4.2.8). Filtrate of step-I was subjected for aldol condensation reaction over CaO catalyst. Concentration of HMF in reaction mixture was gradually decreased while, concentration of aldol condensation product (**3**) was increased. At the end of end of 12<sup>th</sup> hour, no HMF was detected into the reaction mixture with maximum of 32 % yield of aldol condensation product (**3**).



**Figure 4.2.8.** Time profile study for integrated conversion of glucose into aldol product. Reaction condition for a): glucose (0.5 g), Sn-Mont (0.2 g), MIBK (8 mL), H<sub>2</sub>O (1.5 mL), DMSO (0.5 mL), 170 °C; Reaction condition for b): CaO (0.2 g), 80 °C.

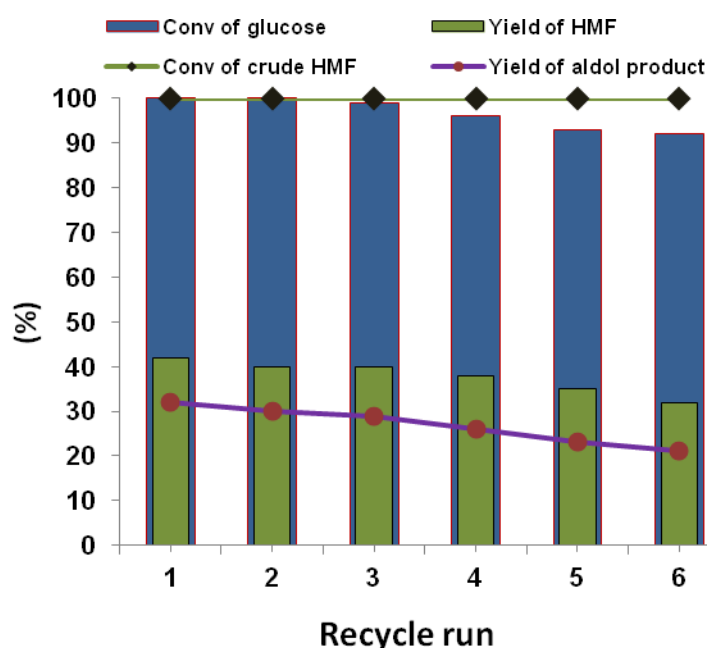


**Figure 4.2.9.** Hot filtration test. Reaction conditions: glucose (0.5 g), Sn-Mont (0.2 g), MIBK (8 mL), H<sub>2</sub>O (1.5 mL), DMSO (0.5 mL), 170 °C, 1 h.

#### 4.2.5.7. Recycle studies of Sn-Mont and CaO catalysts

The stability and reproducibility of activity of Sn-Mont and CaO was examined by recycle experiments (Figure 4.2.10). The Sn-Mont catalyst was washed with water (5 mL x 1) and acetone (5 mL x 2) then dried in oven for 1h at 110 °C before reused for the next cycle. Into the filtrate of first step (glucose dehydration), fresh CaO catalyst

was added to facilitate aldol condensation reaction between in-situ formed HMF and MIBK. After 12 h, CaO catalyst was also separated from the reaction mixture by filtration and subsequently washed with acetone (5 mL x 2) and dried at 110 °C for 1 h, before reused for next cycle. As can be seen from Figure 4.2.9, after each reuse of Sn-Mont glucose conversion was almost 100 % with slight decrease in yield of HMF from 42 to 37 %. Recycling of CaO was also successfully studied for the aldol condensation reaction between in-situ formed HMF and MIBK. The yield of **3** was gradually decreased from 32 to 20 % after 6<sup>th</sup> reuse of CaO.



**Figure 4.2.10.** Recycle experiments of Sn-Mont and CaO for integrated conversion of glucose into **3**. a) Dehydration of glucose to HMF over Sn-Mont and b) aldol condensation of in-situ formed HMF with MIBK over CaO. Reaction conditions: Step-I (dehydration): glucose (0.5 g), Sn-Mont (0.2 g), MIBK (8 mL), H<sub>2</sub>O-NaCl (1.5 mL, 10 wt% NaCl), DMSO (0.5 mL), 170 °C, 12 h; Step- II (aldol condensation): CaO (0.2 g), 80 °C, 12 h.

#### 4.2.5.8. Integrated conversion of carbohydrates to aldol condensation product

After promising results obtained from glucose, we extended this methodology for fructose and more complex carbohydrate such as sucrose. Sucrose molecule is a disaccharide made up of glucose and fructose units which make it more complex than fructose and glucose. Sucrose underwent dehydration

over Sn-Mont catalyst to obtain combined 51 % yield of HMF in both organic and aqueous phases. Subsequently, reaction was filtered to separate the Sn-Mont catalyst and filtrate containing crude HMF was treated with CaO to undergo aldol condensation with MIBK (solvent) to achieve 39 % yield of aldol condensation product (Table 4.2.5, entry 1). Complete dehydration of fructose was achieved within just 7 h with combined 60 % yield of HMF in both organic and aqueous phases. Subsequently, in-situ formed HMF undergoes aldol condensation with MIBK (solvent) to produce **3** in 45 % yield (Table 4.2.5, entry 2). Over Sn-Mont catalyst dehydration of fructose was relatively fast as compared to sucrose.

**Table 4.2.5.** Integrated conversion of carbohydrates to aldol condensation product

Entry	Substrate	Step-I			Step-II		
		(Carbohydrate dehydration)			(Aldol condensation) <sup>[b]</sup>		
		<sup>[a]</sup>					
		<i>t</i> , [h]	Conv. <sup>[c]</sup> [%]	HMF, Yield <sup>[c]</sup> (%)	<i>t</i> , [h]	Conv. <sup>[c]</sup> [%]	Aldol condensation product, Yield <sup>[c]</sup> [%]
1	Sucrose	12	100	51	12	99	39 (88) <sup>[d]</sup>
2	Fructose	07	100	60	12	99	45 (90) <sup>[d]</sup>

Reaction condition: [a] Step-I: carbohydrate (0.5 g), Sn-Mont (0.2 g), MIBK (8 mL), H<sub>2</sub>O-NaCl (1.5 mL, 10 wt % NaCl), DMSO (0.5 mL), 170 °C; [b] Step-II: CaO (0.2 g), 80 °C. [c] Yields of HMF and condensation product were determined using HPLC. [d] Yields are based on crude HMF formed after step- I.

#### 4.2.6. Conclusions

An integrated approach for the synthesis of jet fuel precursors from carbohydrates such as glucose, fructose and sucrose is successfully developed. In the first step, carbohydrates were dehydrated to HMF over Sn-Mont catalyst in biphasic solvent system (MIBK: H<sub>2</sub>O-NaCl: DMSO; 8: 1.5: 0.5; v/v/v) at 170 °C. Importantly, Sn-Mont catalyst having combination of Lewis and Brønsted acid sites with high strength facilitates the isomerisation-dehydration of carbohydrates to HMF. Interestingly, intrinsic stability of Sn-Mont doesn't leave acidity into reaction mixture thus it avoids the possibility of neutralization of basic catalyst used in aldol condensation step. In a second step, MIBK (solvent) was condensed with in- situ generated HMF over CaO to form aldol condensation product. In biphasic solvent system, MIBK (organic phase) turns out to be important as reactant as well as product extraction phase. In addition to that, MIBK could be recovered upto 80 % of its initial volume and could be reused. This protocol provides a single pot facile route to synthesize jet-fuel precursor from complex carbohydrates without performing tedious isolation of HMF (an important intermediate).

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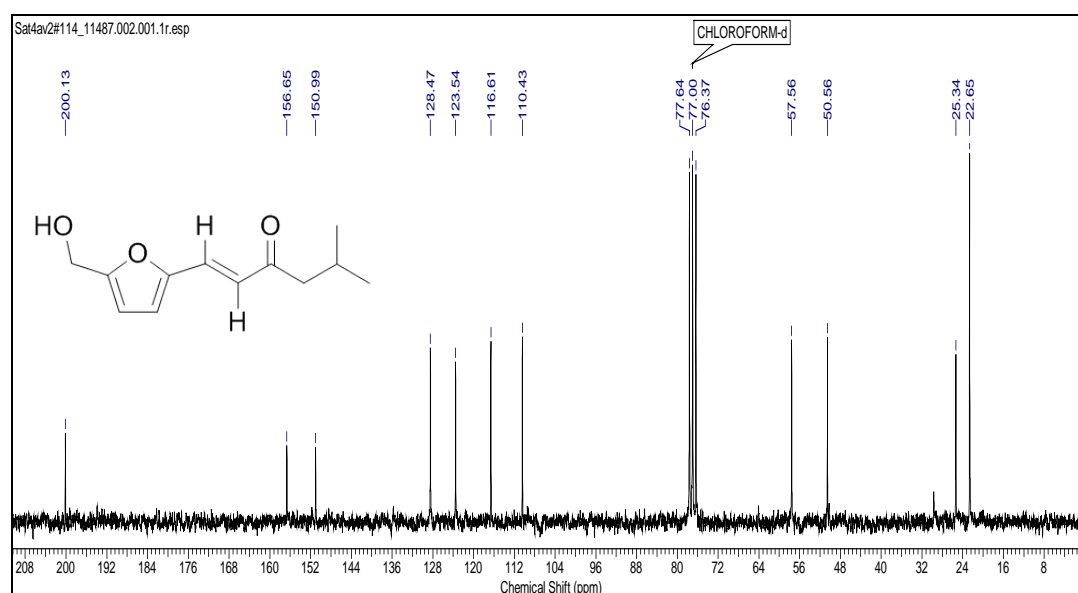
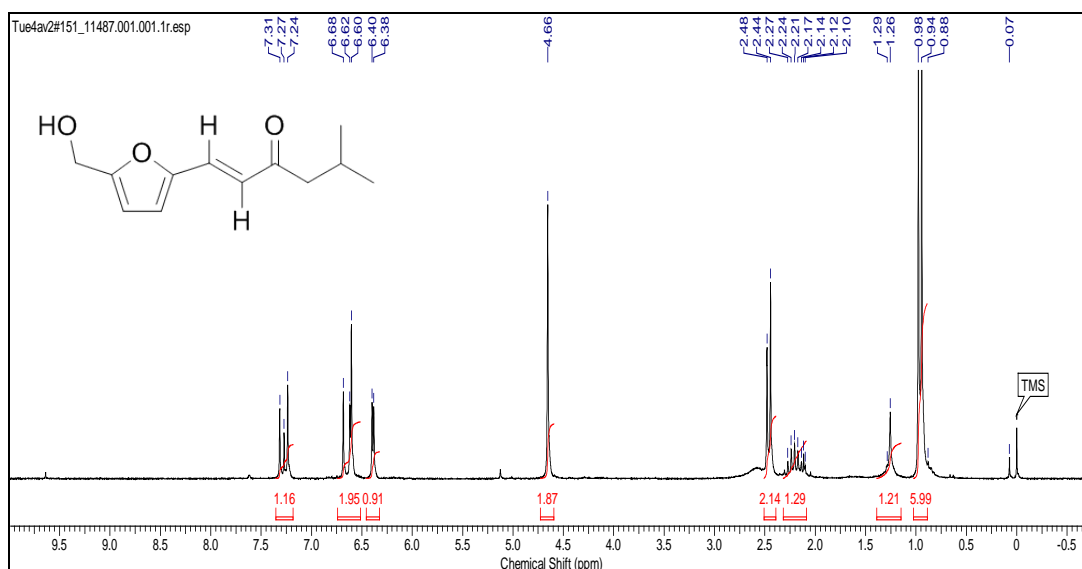
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## 4.2.8. NMR data of the synthesized compound

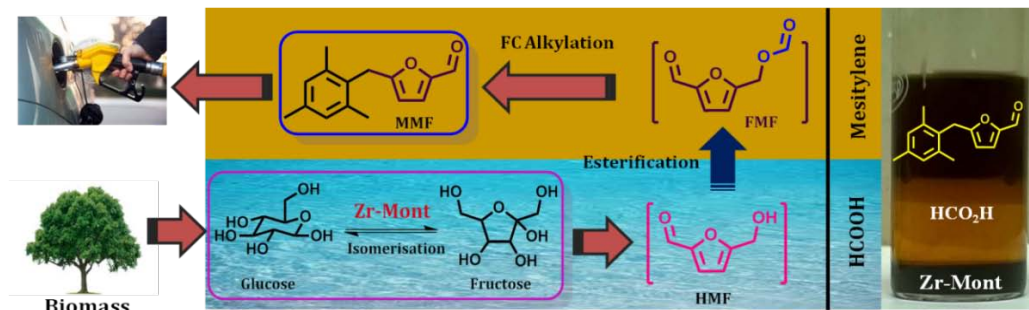
(E)-1-(5-(hydroxymethyl)furan-2-yl)-5-methylhex-1-en-3-one (**3**): 0.186 g, (90%).

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.96 (d,  $J=6.69$  Hz, 6 H) 1.26 (s, 1 H) 2.09 - 2.27 (m, 1 H) 2.44-2.48 (d,  $J=6.95$  Hz, 2 H) 4.66 (s, 2 H) 6.38-6.40 (d,  $J=3.41$  Hz, 1 H) 6.60 - 6.68 (m, 2 H) 7.24 - 7.31 (m, 1 H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 22.65 ( $-\text{CH}_3$ ) 25.34 ( $-\text{CH}_3$ ) 50.56 ( $-\text{CH}_2$ ) 57.56 ( $-\text{OCH}_2$ ) 110.43 (furan,  $-\text{CH}$ ) 116.61 (furan,  $-\text{CH}$ ) 123.54 (olefin,  $-\text{CH}$ ) 128.47 (olefin,  $-\text{CH}$ ) 150.99 (furan,  $-\text{C}$ ) 156.65 (furan,  $-\text{C}$ ) 200.13 (ketone,  $-\text{CH}$ )



### 4.3. Friedel-Crafts alkylation over Zr-Mont catalyst for the production of diesel fuel precursors



Heterogeneous Zr-Mont catalyst prepared by a simple protocol was employed for the production of diesel fuel precursors *via* Friedel Crafts (FC) alkylation of petroleum derived arenes (*e.g.* mesitylene, xylene and toluene) with biomass derived 5-(hydroxymethyl)furfural (HMF), HMF derivatives and carbohydrates. Initially, several acidic catalysts were screened for the FC alkylation of mesitylene with HMF in nitroethane solvent. Among all these, Zr-Mont catalyst gave an exceptionally high yield (80 %) of mesitylmethylfurfural (MMF). Catalytic activity of Zr-Mont was also evaluated for the alkylation of different petroleum derived arenes with ester/halogen derivatives of HMF. Suitable acid strength and high surface area of Zr-Mont were its major attributes to make it the most efficient solid acid catalyst for this FC reaction. Even after several reuses, catalytic activity of Zr-Mont was found to be consistent which was also evidenced by the acidity measurements of fresh and reused Zr-Mont catalysts by  $\text{NH}_3$ -TPD and PyFTIR techniques. Direct conversion of glucose to diesel fuel precursors was also attempted over Zr-Mont catalyst in mesitylene and polar non acidic solvents at 150 °C. However, the activity of Zr-Mont catalyst was limited for glucose dehydration to HMF and MMF not formed. When same experiment was performed in formic acid medium MMF produced in 34 % yield. After addition of formic acid, the reaction becomes biphasic which contains mesitylene as an organic phase and formic acid as an aqueous phase. Formic acid was worked as a solvent, reactant and co-catalyst whereas mesitylene worked as reactant and product extraction phase to enabled easy product isolation. With this strategy, other diesel fuel precursors were also produced in 26-30 % yields from glucose and different arenes. Similar strategy was successfully extended for the conversion of sucrose to diesel fuel precursors.

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### 4.3.1. Introduction

To produce diesel range  $C_{11}$ - $C_{23}$  alkanes from HMF, it needs to undergo carbon up-gradation process *via* C-C bond formation [1]. Some of the efforts made in this direction involving C-C bond forming reactions include *i*) base catalyzed aldol condensation of HMF with acetone, [2] *ii*) amine catalyzed Baylis–Hillman reactions between methylacrylate and HMF, [3] *iii*) Coupling of HMF and isoprene over ruthenium complex [4] and *iv*) Condensation of HMF with 2-methylfuran [5]. These upgraded products are carbon rich hence they can be converted into diesel range liquid hydrocarbons *via* ring opening-dehydration-hydrodeoxygenation processes [2, 6].

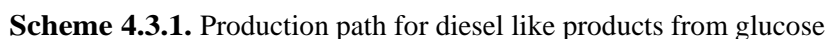
### 4.3.2. Literature survey

In 2014, Corma et al. produced alkyl naphthenic kerosene from HMF and substituted benzenes *via* Friedel-Crafts alkylation using zeolites followed by hydrodeoxygenation process over platinum based catalyst [6]. However, currently there is only one industrial process for the bulk production of HMF from biomass-derived feedstock [7]. Since, HMF has high solubility in aqueous reaction mixture its extraction is a tedious task. In addition to that, HMF has low stability in acidic medium and also produces large amount of tarry degradation products during its recovery by distillation at high temperature. Therefore, researchers have focused their attention on technologies where the carbohydrates can be directly converted into advanced chemicals/fuel precursors without isolating unstable intermediate (HMF). In this direction, Zhou et al. reported an excellent work on production of hybrid diesel fuel precursors from carbohydrates and petrochemicals using formic acid as a reactive solvent to dissolve carbohydrates as well as a reagent for making reactive intermediate named as 5-(formyloxymethyl)furfural [8]. However, in this reaction sequence, catalytic amount of conc. HCl was required for isomerisation of glucose and glucose based other carbohydrates into fructose that limits its commercial exploitation due to its hazardous nature as well as waste formation. Recently, Jadhav et al. reported alkylation of aromatic arenes with fructose over  $\text{Glu-Fe}_3\text{O}_4\text{-SO}_3\text{H}$  catalyst without isolation of HMF intermediate [9]. This approach is limited to the fructose only and not useful for the complex carbohydrates like glucose and sucrose.

Glucose is relatively more stable than fructose, which makes its dehydration much more difficult. Conversion of glucose into HMF proceeds in two steps: the first is glucose isomerization to fructose in the presence of enzyme or Lewis acid or base catalyst [10] and the second step is dehydration of fructose to HMF. Wang et al. reported montmorillonite based (Sn-Mont) catalyst for the isomerisation of glucose to fructose followed by its dehydration to HMF [11]. Very recently, we have produced polyfuran units of C<sub>21</sub> and C<sub>15</sub> from carbohydrates and 2-methylfuran using Sn-Mont and formic acid *via* an integrated process without isolation of intermediate furfural derivatives [12].

#### 4.3.3. Scope of the present work

In this work, Zr-Mont catalyst easily prepared *via* the ion-exchange of natural montmorillonite with an aqueous ZrOCl<sub>2</sub>·8H<sub>2</sub>O solution is employed for the carbon up-gradation processes. The catalytic activity of Zr-Mont was initially evaluated for FC alkylation of arenes (*e.g.* mesitylene, xylene and toluene) with HMF and HMF derivatives. The schematic of our approach for direct production diesel fuel precursor from glucose is elaborated in Scheme 4.3.1. This approach is three steps reaction sequence which involves, *i*) glucose isomerisation to fructose, *ii*) dehydration-esterification of fructose to HMF derivatives and *iii*) FC-alkylation of arenes with HMF derivatives. The Zr-Mont catalyst, due to presence of Zr<sup>4+</sup> ions which act as Lewis acid was also found to be efficient for the isomerisation of complex carbohydrates (*e.g.* glucose and sucrose) to fructose. *In-situ* formed fructose could be dehydrated to HMF/HMF-ester and subsequently undergone FC alkylation with arene molecule in formic acid medium. Formic acid served as a reactive solvent as well as a co-catalyst. Notably, use of formic acid in this process is appealing as it is obtained from biomass degradation, [13] it is regenerable, [14] safe and cheap [15]. The phenomenal stability and recyclability of Zr-Mont makes it a very viable alternative to liquid acid (*e.g.* HCl) usually used in this process.



#### 4.3.4.1. Materials

#### 4.3.4.2. Catalysts preparation

#### 4.3.4.3. Catalyst characterization

2018-Ph. D. Thesis: Mr. Suhas H. Shinde, CSIR-NCL, AcSIR

#### 4.3.4.4. Synthetic procedures

##### 4.3.4.4.1. *Synthesis of arylmethylfurfural from HMF and its derivatives*

HMF or HMF derivatives (*e.g.* FMF/AcMF/CMF/BMF) (1 mmol) was dissolved in nitroethane (5 mL). Subsequently, mesitylene/xylene/toluene (10 mL) and Zr-Mont (0.1 g) was added and the reaction mixture was heated at 110 °C under stirring for the period of 16 h. After complete conversion of starting material, reaction mixture was filtered to separate the catalyst. Mother-liquor was diluted with ethyl acetate (20 mL) and partitioned by H<sub>2</sub>O (10 mL). Subsequently organic phase was treated with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue was purified by column chromatography eluted in petroleum ether.

##### 4.3.4.4.2. *Synthesis of arylmethylfurfural from carbohydrates*

Carbohydrates (*e.g.* sucrose/glucose) (0.5 g) were dissolved in formic acid (5 mL). Subsequently, mesitylene/xylene/toluene (10 mL) and Zr-Mont (0.2 g) was added and the reaction mixture was heated at 150 °C under stirred for the period of 16 h. After complete conversion of FMF (reaction key intermediate), reaction mixture was filtered to separate the catalyst. Mother-liquor was diluted with ethyl acetate (20 mL) and partitioned by H<sub>2</sub>O (10 mL). Subsequently, organic phase was treated with aq. NaHCO<sub>3</sub> (6 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then organic layer was evaporated under reduced pressure. The residue was purified by column chromatography eluted in petroleum ether.

##### 4.3.4.4.3. *Synthesis of HMF derivatives*

###### 4.3.4.4.3.1. *Synthesis of 5-(formyloxymethyl)furfural from HMF*

In a typical experiment [8], mixture of HMF (0.2 g) and formic acid (98 %, 10 mL) was stirred at room temperature for 3 h. After completion of reaction it was neutralized with saturated solution of NaHCO<sub>3</sub>. Further reaction mixture diluted with ethyl acetate (20 mL) and washed with water (10 mL x 1), brine (10 mL x 1). The organic layer was finally dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. Residue was purified using column chromatography by eluting in ethyl acetate: pet ether (90: 10) mobile phase. After purification yellow oil of 5-(formyloxymethyl)furfural (0.212 g, 87 %) was obtained.

#### **4.3.4.4.3.2 .Synthesis of 5-(acetyloxymethyl)furfural from HMF**

The procedure for synthesis of 5-(acetyloxymethyl)furfural from HMF is provided in **Chapter 2, Section 2.4.4.1.**

#### **4.3.4.4.3.3. Synthesis of 5-(chloromethyl)furfural from HMF**

In typical experiment [16], HMF (0.252 g, 2 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and HCl (aq. 37 %, 5 mL) was added drop wise. Biphasic reaction mixture was stirred at room temperature for 24 h, then organic layer was separated, and acidic fraction was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). Organic fractions were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. Residue was purified by filtering through short silica gel column (ethyl acetate: pet ether, 90:10) to yield, 0.23 g (80 %) as yellowish crystals.

#### **4.3.4.4.3.4. Synthesis of 5-(bromomethyl)furfural from HMF**

In a typical experiment [16], HMF (0.252 g, 2 mmol) was dissolved in 1,2-dichloroethane (7 mL) and HBr (aq. 48 %, 7 mL) was added drop wise. Biphasic reaction mixture was stirred at room temperature for 24 h, then organic layer was separated, and acidic fraction was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). Organic fractions were combined, dried with Na<sub>2</sub>SO<sub>4</sub>, and evaporated. Residue was purified by filtering through short silica gel column (ethyl acetate: pet ether, 90:10) to yield, 0.319 g (85 %) as yellowish crystals.

#### **4.3.4.5. Analysis of the reaction products**

Merck 5554 aluminium-backed silica plates were used for TLC analysis, and the compounds were visualized under UV light (254 nm). Conversion of carbohydrates was calculated by using Agilent HPLC (column: Hi-Plex H USP L17, detector: RI and mobile phase: millipore water with 0.6 mL/min flow). Yields of dehydration product of carbohydrates and coupling products were calculated by using Agilent HPLC (column: Poroshell 120 EC-C18 2.7 µm, detector: UV and mobile phase: 0.1 % acetic acid in millipore water: acetonitrile (85:15) with 0.6 mL/min flow). Pure products were characterised and confirmed by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR using CDCl<sub>3</sub> (0.01 %, TMS) as solvent on 200 MHz and 50 MHz frequency Bruker instrument.



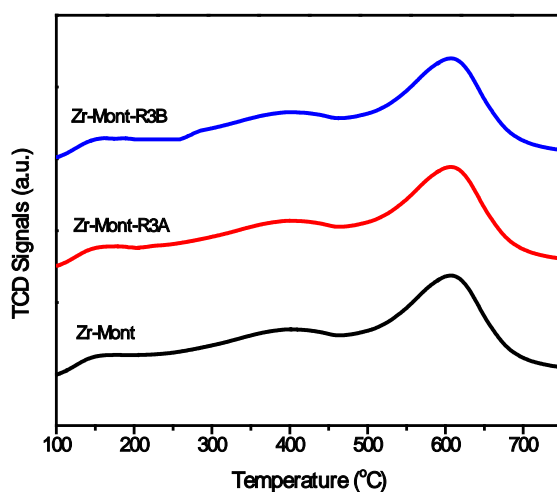
### 4.3.5. Results and discussion

#### 4.3.5.1. Catalyst Characterisation

Catalysts such as montmorillonite, Fe-Mont, Al-Mont, Sn-Mont and Zr-Mont are well characterised with their physico-chemical properties and the characterisation data is already presented in Table 4.1.1 and in Figures 4.1.2 and 4.1.3 of **Chapter 4.1**.

##### 4.3.5.1.1. $\text{NH}_3$ -TPD

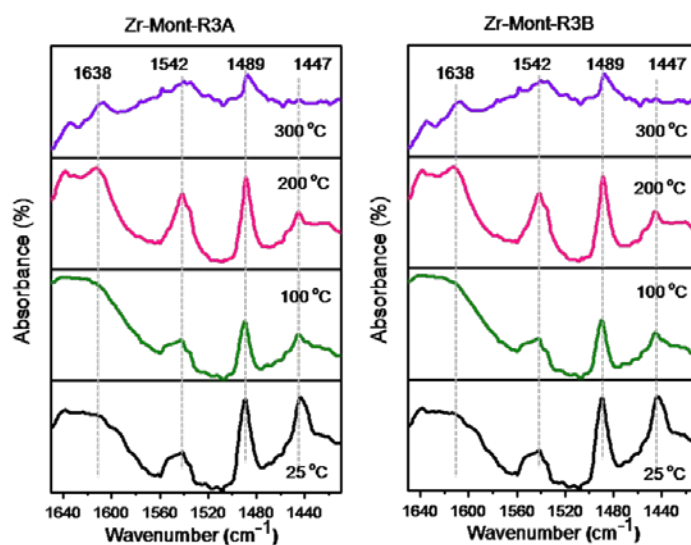
Among various catalysts, total acid strength of Sn-Mont catalyst was much higher than that of montmorillonite, Fe-Mont, Al-Mont and Zr-Mont. The trend of acid strength of all these catalysts was as follows: montmorillonite ( $90.08 \mu\text{mol g}^{-1}$ ) < Fe-Mont ( $190.63 \mu\text{mol g}^{-1}$ ) < Al-Mont ( $309.17 \mu\text{mol g}^{-1}$ ) < Zr-Mont-R3B ( $344.44 \mu\text{mol g}^{-1}$ ) < Zr-Mont-R3A ( $359.10 \mu\text{mol g}^{-1}$ ) < Zr-Mont ( $380.30 \mu\text{mol g}^{-1}$ ) < Sn-Mont ( $511.90 \mu\text{mol g}^{-1}$ ). Although, the Sn-Mont showed the highest acidity, but the Zr-Mont with second highest acidity was found to be the most suitable catalyst for our targeted application therefore; its stability in terms of acidity retention was evaluated by  $\text{NH}_3$ -TPD analysis of the used catalyst samples (Figure 4.3.1). Almost identical  $\text{NH}_3$ -TPD profiles were observed for Zr-Mont-fresh and Zr-Mont-R3A (after reused for three times for HMF to MMF reaction; Figure 4.3.6) and Zr-Mont-R3B (after reused for three times for glucose to MMF reaction; Figure 4.3.9). A very marginal decrease in the total acidities of reused samples was noticed (Table 4.3.1).



**Figure 4.3.1.**  $\text{NH}_3$ -TPD of Zr-Mont, Zr-Mont-R3A and Zr-Mont-R3B.

#### 4.3.5.1.2. Py-FTIR

The types of acid sites present in our catalyst samples were identified by using pyridine FTIR spectroscopy. The pyridine FTIR spectra of montmorillonite and metal exchanged montmorillonite samples (Fe-Mont, Al-Mont and Sn-Mont) are depicted in **Chapter 4.1**. In order to identify/evaluate the acidity of these catalysts, difference in spectrum before pyridine adsorption from that obtained after pyridine adsorption of the respective catalyst was taken. The band at  $1441\text{ cm}^{-1}$  signifies Lewis acidity,  $1490\text{ cm}^{-1}$  represents a combination of Lewis and Brønsted acidities and the bands at  $1548\text{ cm}^{-1}$  and  $1638\text{ cm}^{-1}$  signify Brønsted acidity [17]. The acidity trend of montmorillonite catalysts by Py-FTIR was found to be as follows: montmorillonite ( $119.40\text{ }\mu\text{mol g}^{-1}$ ) < Fe-Mont ( $222.20\text{ }\mu\text{mol g}^{-1}$ ) < Al-Mont ( $331.45\text{ }\mu\text{mol g}^{-1}$ ) < Zr-Mont-R3B ( $379.33\text{ }\mu\text{mol g}^{-1}$ ) < Zr-Mont-R3A ( $388.88\text{ }\mu\text{mol g}^{-1}$ ) < Zr-Mont ( $404.14\text{ }\mu\text{mol g}^{-1}$ ) < Sn-Mont ( $532.37\text{ }\mu\text{mol g}^{-1}$ ). All the metal exchanged montmorillonite catalysts possessed significantly large amount of medium strength acid sites compared to their weak and strong acid sites. To investigate the different types of acidic sites and acid strengths of Zr-Mont-R3A and Zr-Mont-R3B samples, their Py-FTIR spectra (Figure 4.3.2) were recorded at different temperatures using the method proposed by the Emeis [18]. Brønsted acidities of Zr-Mont-R3A and Zr-Mont-R3B samples were found to be



**Figure 4.3.2.** Pyridine FTIR of Zr-Mont-R3A and Zr-Mont-R3B at different evacuation temperatures.

284.22 and 276.8  $\mu\text{mol g}^{-1}$ , respectively. While, the Lewis acidities of these samples were found to be 104.66 and 102.53  $\mu\text{mol g}^{-1}$ . Even after 3<sup>rd</sup> reuse the Brønsted/Lewis acid (B/L) ratio of Zr-Mont-R3A (B/L=2.71) and Zr-Mont-R3B (B/L=2.69) was almost similar to that of fresh Zr-Mont sample (B/L=2.73) (Table 4.3.1).

**Table 4.3.1** .Chemo-physical properties of various montmorillonite catalyst

Catalyst	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Acidity								B/L ratio	V <sub>micro + meso</sub>
		TPD (μmol ammonia desorbed g <sup>-1</sup> cat.)	PyFTIR <sup>[a]</sup> (μmol pyridine g <sup>-1</sup> cat.)								
			100 °C		200 °C		300 °C		Total		
			B	L	B	L	B	L			
Zr-Mont	192	380.30	55.68	31.00	187.00	57.00	57.00	21.46	404.14	2.73	228
Zr-Mont- R3A <sup>[b]</sup>	171	359.10	51.12	30.26	182.03	55.20	51.07	19.20	388.88	2.71	208
Zr-Mont- R3B <sup>[c]</sup>	158	344.44	48.57	29.64	179.23	54.35	49.00	18.54	379.33	2.69	159

[a] The quantification of B and L sites present in catalysts was done by using the Emeis equation.[18] [b] Recovered after 3<sup>rd</sup> reuse from FC alkylation reaction of HMF with mesitylene (Figure 4.3.6). [c] Recovered after 3<sup>rd</sup> reuse from glucose to MMF reaction (Figure 4.3.9) B= Brønsted acid sites and L=Lewis acid sites. V=Pore volume.

#### 4.3.5.2. Catalyst screening

The FC alkylation of mesitylene with HMF was carried out in a nitroethane over different acid catalysts and the results are summarized in Table 4.3.2. FC alkylation of mesitylene with HMF carried out in presence of catalytic amount of conc.  $\text{H}_2\text{SO}_4$  at 80 °C for 3h which showed that HMF was consumed completely to give 75 % yield of coupling product (MMF, **1**) along with 11 % of OBMF (Table 4.3.2, entry 1). Nevertheless, conc.  $\text{H}_2\text{SO}_4$  is hazardous in nature, non-recyclable and produces by-product which limits its further exploitation. When commercially available sulfonic acid functionalized polystyrene (Amberlyst-15) solid acid catalyst was explored, MMF was formed in 79 % yield with 7 % of OBMF (Table 4.3.2, entry 2). In presence of Lewis acid ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ), MMF was produced in 30 % yield after a quite longer reaction time of 16 h (Table 4.3.2, entry 3). The lower yield of MMF in presence of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was attributed to the formation of chlorination product [5-(chloromethyl)furfural (CMF)] of HMF. In order to convert *in-situ* formed CMF into MMF, reaction was prolonged for 16 h. Even after such a long period, yield of MMF did not improved. Performance of naturally occurring montmorillonite clay

possessing Lewis acidity was also evaluated for this reaction but even at elevated temperature of 110 °C, only 21 % yield of product **1** was noticed (Table 4.3.2, entry 4). It is well known that the acidity of the montmorillonite could be significantly enhanced by metal exchange process [19, 20]. In this context, Zr-exchanged montmorillonite clay (Zr-Mont) was used for the FC alkylation of mesitylene with HMF. Over Zr-Mont catalyst (0.1 g) and at 110 °C, HMF was treated with mesitylene to give MMF in 86 % yield with only 2 % of OBMF (Table 4.3.2, entry 5). Decreasing the catalyst (Zr-Mont) amount from 0.1 g to 0.05 g affected the conversion of HMF obviously due to the short fall of the active sites (Table 4.3.2, entry 6). On the contrary, increasing catalyst loading to 0.2 g, the yield of OBMF was increased to 17 % (Table 4.3.2, entry 7).

**Table 4.3.2.** Arylation of HMF with mesitylene over various catalysts <sup>[a]</sup>

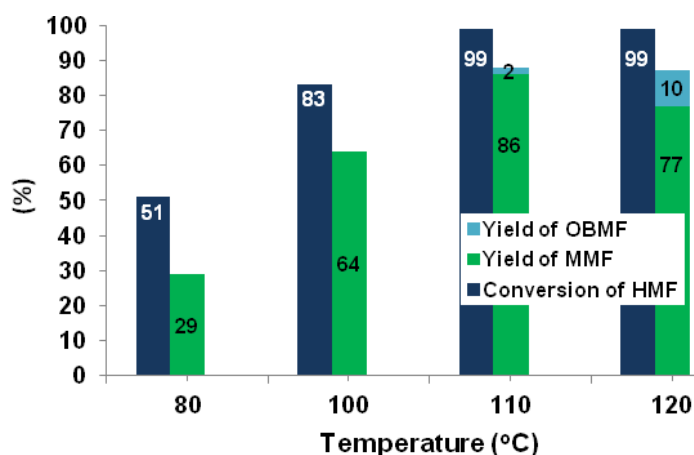
Entry	Catalyst	Loading	T °C	t h	Conv. <sup>[c]</sup> (%) <b>6</b>	Yield <sup>[d]</sup> (%) <b>1</b> <b>4</b>		TOF (h <sup>-1</sup> )
1	H <sub>2</sub> SO <sub>4</sub>	10 mol%	80	3	>99	75	11	0.2
2	Amberlyst-15	0.1 g	80	4	>99	79	07	13.83
3	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	0.1 g	80	16	>99	30	11	0.14
4	Mont	0.1 g	110	16	44	21	09	2.5
5	Zr-Mont	0.1 g	110	12	>99	86	02	2.63
6	Zr-Mont	0.05 g	110	16	64	50	00	3.15
7	Zr-Mont	0.2 g	110	16	>99	75	17	1.57
8	Sn-Mont	0.1 g	110	16	>99	70	21	2.09
9	Al-Mont	0.1 g	110	16	72	57	trace	2.70
10	Fe-Mont	0.1 g	110	16	55	43	-	2.79
11 <sup>[b]</sup>	Zr-Mont	0.1 g	110	16	>99	83	02	2.67

[a] Reaction conditions: HMF (0.252 g, 2 mmol), mesitylene (5 mL), nitroethane (5 mL), catalyst. [b] Crude HMF obtained from fructose. [c] Conversion of HMF was measured using HPLC. [d] Isolated yields.

$\text{Sn}^{4+}$  incorporated montmorillonite catalyst (Sn-Mont, 0.1 g) showed 70 % yield of MMF with 21 % of OBMF (Table 4.3.2, entry 8). This observation well matched with our previous reports.[19b] Surprisingly, even though the acidity of Sn-Mont ( $511.90 \mu\text{molg}^{-1}$ , Table 4.1.1, **Chapter 4.1**) was higher than that of the Zr-Mont ( $380.3 \mu\text{molg}^{-1}$ , Table 4.1.1, **Chapter 4.1**), yield of MMF was found to be lower due to formation of OBMF (**4**), the formation of OBMF was promoted due to the higher acidity of Sn-Mont along with lower B/L ratio (2.09) and low surface area of ( $183 \text{ m}^2\text{g}^{-1}$ , Table 4.1.1, **Chapter 4.1**) than Zr-Mont ( $196 \text{ m}^2\text{g}^{-1}$ , Table 4.1.1, **Chapter 4.1**).  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ -exchanged montmorillonite catalysts were shown 57 and 43% yield of MMF with 72 and 55 % conversion of HMF, respectively (Table 4.3.2, entries 9 and 10). Thus, suitable acid strength and high surface area of Zr-Mont contributed to its excellent activity in terms of the yield of MMF. Although, MMF was produced in high yield from HMF over a recyclable Zr-Mont catalyst, the present cost of pure HMF is a major deterrent factor for the development of downstream processes. Therefore, crude HMF obtained from fructose was reacted with mesitylene, to obtain 83 % yield of MMF (Table 4.3.2, entry 11). Use of crude HMF for the synthesis of desired products avoided the energy-intensive separation/purification of HMF offering a cost-efficient process for the practical production of product **1** from fructose.

#### 4.3.5.3. Effect of temperature

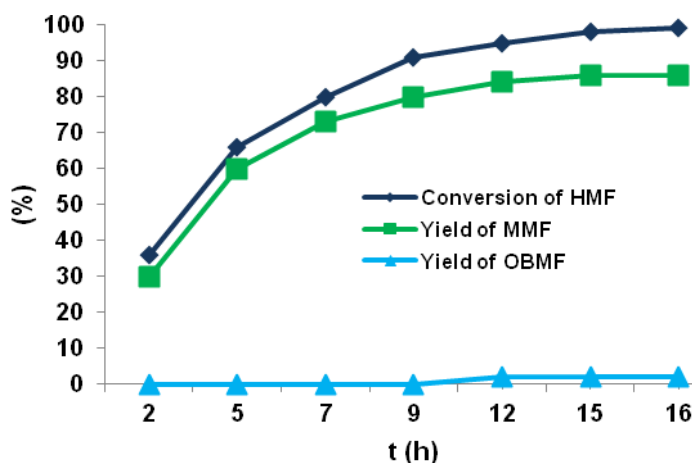
FC alkylation of mesitylene with HMF was carried out over Zr-Mont catalyst for the period of 16 h, under different temperatures ranging from 80 °C to 120 °C (Figure 4.3.3). MMF was produced in 29 and 64 % yields at 80 °C and 100 °C, respectively. Interestingly, when same reaction was conducted at 110 °C, MMF was obtained in significantly high yield of 86 % with complete consumption of HMF. Thus, lower than 110 °C not effective to push reaction to completion. While, at elevated temperature of 120 °C, 77 % yield of MMF was obtained with 10 % of self etherification product (OBMF). Thus, 110 °C is an optimum reaction temperature used for further experiments.



**Figure 4.3.3.** Effect of reaction temperature on FC alkylation of mesitylene with HMF. Reaction conditions: HMF (0.252 g, 2 mmol), mesitylene (5 mL), nitroethane (5 mL), Zr-Mont (0.1 g), 80-120 °C, 16 h. Conversion of HMF was measured using HPLC and reported yields were isolated.

#### 4.3.5.4. Effect of reaction time

Effect of reaction time for FC alkylation of mesitylene with HMF was studied by monitoring the reaction after specific time intervals (Figure 4.3.4). In the first 2h, HMF was consumed upto 36 with 30 % yield of MMF. After 9<sup>th</sup> hour, formation of OBMF began and reached to the maximum of 2 % and remained steady at the end of 16<sup>th</sup> h.

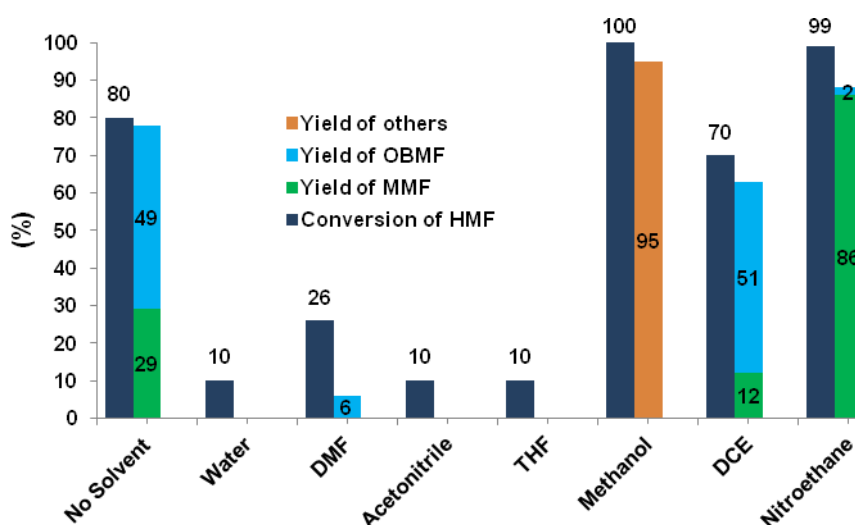


**Figure 4.3.4.** Effect of reaction time on FC alkylation of mesitylene with HMF. Reaction conditions: HMF (0.252 g, 2 mmol), mesitylene (5 mL), nitroethane (5 mL), Zr-Mont (0.1 g), 110 °C, 16 h. Conversion of HMF and Yield of MMF were measured on HPLC.

HMF conversion and yield of MMF gradually increased to 99 and 86 %, respectively, during the time span of 16 h.

#### 4.3.5.5. Role of solvent

Influence of different solvents was studied for the FC alkylation of mesitylene with HMF and the results are presented in Figure 4.3.5. Under experimental conditions and in absence of solvent, MMF was obtained in 29 % yield along with 49 % yield of OBMF. In aqueous medium, reaction doesn't proceed due to equilibrium between HMF and dehydrated HMF. DMF, acetonitrile and THF were not suitable solvents for this reaction. Etherification of HMF was noticed in presence of methanol medium, the ether 5-(methoxymethyl)furfural was formed in 95 % yield. In dichloroethane, only 12 % of MMF was formed along with 51 % of OBMF. After evaluating several solvents, we found out nitroethane as a best choice of solvent to achieve high yield (86 %) of MMF.

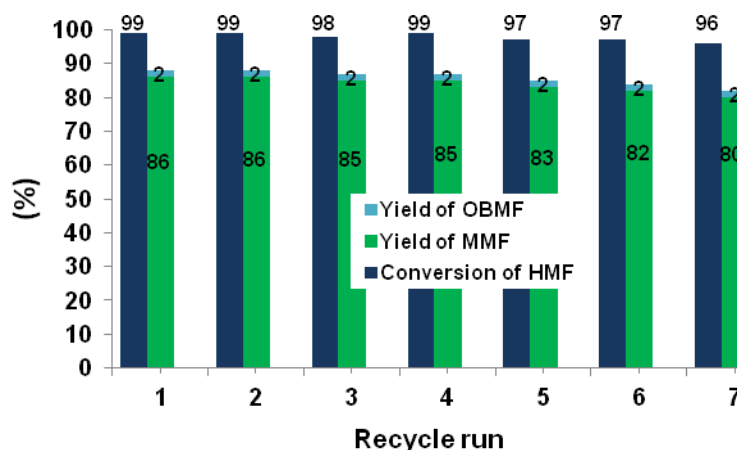


**Figure 4.3.5.** Influence of solvents on production of MMF from HMF. Reaction conditions: HMF (0.252 g, 2 mmol), mesitylene (5 mL), solvent (5 mL), Zr-Mont (0.1 g), 110 °C, 16 h. Conversion of HMF was measured using HPLC and reported yields were isolated.

#### 4.3.5.6. Catalyst recycling studies

The stability and reusability of Zr-Mont was investigated for the FC alkylation of mesitylene with HMF. In a typical recycle experiment, Zr-Mont catalyst was filtered, washed with acetone (5 mL x 2) and dried in oven for 1h at 110 °C before reused for

the next cycle. As can be seen from Figure 4.3.6, after each reuse of Zr-Mont, HMF conversion was almost >95 % with slight decrease in yield of MMF. The retention of acidity of Zr-Mont is also confirmed by  $\text{NH}_3$ -TPD and PyFTIR analysis of fresh and reused Zr-Mont sample (Figures 4.3.1 and 4.3.2).



**Figure 4.3.6.** Recycle study of Zr-Mont for the FC alkylation of mesitylene with HMF. Reaction conditions: HMF (0.252 g, 2 mmol), mesitylene (5 mL), nitroethane (5 mL), Zr-Mont (0.1 g), 110 °C, 16 h. After each cycle catalyst was washed with acetone and dried in the oven at 100 °C for 1 h prior to use for next cycle. Conversion of HMF was measured using HPLC and reported yields were isolated.

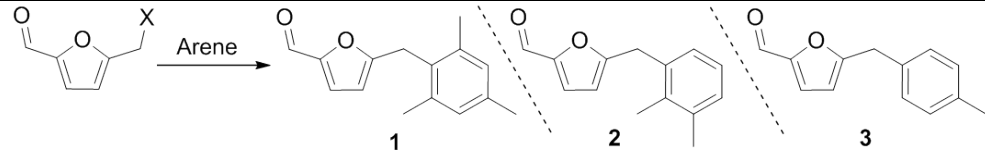
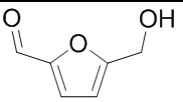
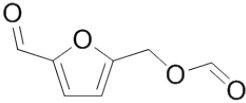
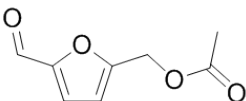
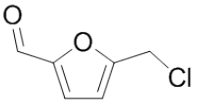
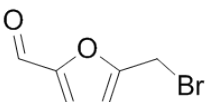
#### 4.3.5.7. Synthesis of arylmethylfurfural from different HMF derivatives

The arylation protocol using acidic Zr-Mont was also extended to the ester and halogen derivatives of HMF, and the results are summarized in Table 4.3.3. Initially, HMF was treated with xylene to afford arylation products **2** in 59 % yield. Our protocol gives higher yield of **2** than reported by Beller et al. using  $\text{FeCl}_3$  under solvent-free condition provides a 37 % yield of the coupled product [21]. When toluene was treated with HMF coupling product **3** was produced in 69 % yield (Table 4.3.3, entry 1). Ester derivatives of HMF offer some important advantages over HMF for industrial production. Compared with the hydroxymethyl functionality of HMF, the ester functionality makes them hydrophobic, stable and more readily isolable from the aqueous reaction mixture, whereas HMF is known to be relatively unstable under acidic conditions (easily undergo polymerisation) and is difficult to isolate from the aqueous reaction mixture [22]. Therefore, we prepared few ester



derivatives of HMF and tested for the reaction with arenes. The formate derivative [5-(formyloxymethyl)furfural] (FMF) of HMF seems to be relatively more active than HMF as it provides high yields 85, 71 and 84% of arylmethylfurfurals **1**, **2** and **3**, respectively (Table 4.3.3, entry 2). Similarly, 5-(acetoxymethyl)furfural (AcMF) also actively reacted with mesitylene, xylene and toluene to give high yield of arylmethylfurfurals **1**, **2** and **3** (Table 4.3.3, entry 2). Electron withdrawing ester functionality on FMF/AcMF makes them more active electrophile to react with nucleophilic arenes. Next, we studied the reactivity of halogen derivative of HMF such as 5-(chloro/bromomethyl)furfural.

**Table 4.3.3.** FC alkylation of arenes with HMF and its derivatives over Zr-Mont catalysts<sup>[a]</sup>

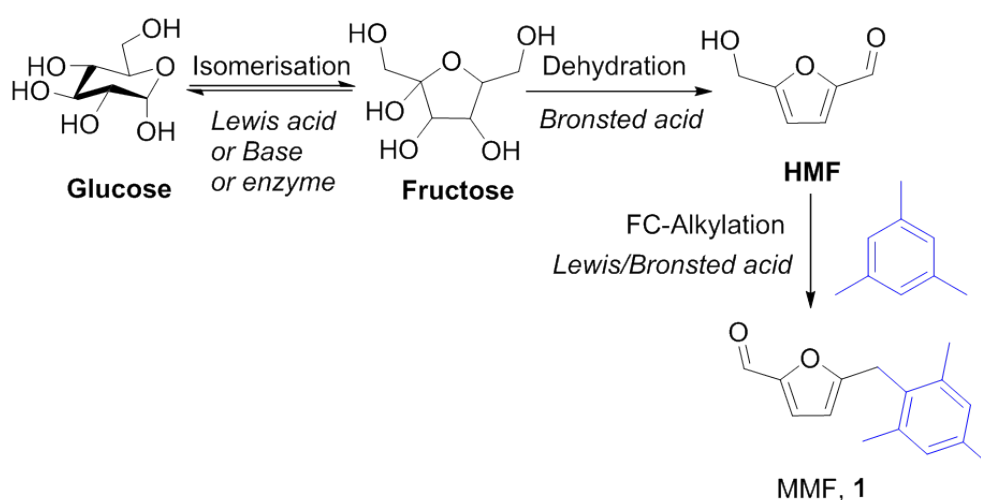
				
Entry	Substrate	Arene	<i>t</i> h	Yield <sup>[b]</sup> [%] <b>1/2/3</b>
1		Xylene	16	--/59/--
		Toluene	16	--/--/69
2		Mesitylene	4	85/--/--
		Xylene	16	--/71/--
		Toluene	8	--/--/84
3		Mesitylene	5	83/--/--
		Xylene	16	--/69/--
		Toluene	12	--/--/81
4		Mesitylene	16	90/--/--
		Xylene	18	--/80/--
		Toluene	3	--/--/92
5		Mesitylene	16	89/--/--
		Xylene	19	--/78/--
		Toluene	3	--/--/94

[a] Reaction conditions: HMF derivative (2 mmol), arene (5 mL), nitroethane (5 mL), Zr-Mont (0.1 g), 110 °C. [b] Isolated yields.

5-(chloromethyl)furfural (CMF) was treated with mesitylene to obtain a product **1** in 90 % yield. While, after reaction with xylene only 80 % yield of **2** was obtained. On the other hand, toluene reacted relatively faster with CMF to give 92 % yield of **3** (Table 4.3.3, entry 4). Under identical reaction conditions, 5-(bromomethyl)furfural (BMF) was treated with different arenes and yields of coupling products **1**, **2** and **3** were comparable with the products formed from CMF (Table 4.3.3, entry 5). The starting materials such as CMF and BMF used in above experiments were prepared from HMF (see section 4.3.4.4.3.3 and 4.3.4.4.3.4).

#### 4.3.5.8. Direct, one-pot synthesis of MMF from glucose and mesitylene

Although, the crude HMF could be utilized for the FC alkylation with mesitylene, the two separate operations must be carried out. Hence, without isolating HMF, direct conversion of its precursors (*e.g.* glucose, fructose and sucrose) to diesel fuel precursor is possible as this cascade process is acid catalyzed. Therefore, initially we selected glucose as a potential HMF precursor which is more abundant and relatively much cheaper than HMF. The production of MMF from glucose requires to undergo three steps, *i*) isomerisation of glucose to fructose, *ii*) dehydration of fructose to HMF, *iii*) coupling of HMF with mesitylene. As shown in the Scheme 4.3.2, this process requires two types of catalysts such as Lewis acid (for glucose isomerisation) and Brønsted acid (dehydration of fructose and FC alkylation reaction).



**Scheme 4.3.2.** Process for the production of MMF (**1**) from glucose.

For this purpose, we employed Zr-Mont catalyst which has unique combination of Lewis + Brønsted acid sites for the purpose of glucose conversion to MMF. At first, glucose dehydration-FC alkylation sequence was carried out in DMSO at 150 °C over Zr-Mont catalyst. But even after 24 h of reaction, only HMF was formed in 34 % yield without formation of MMF (Table 4.3.4, entry 1). As we, found out nitroethane was effective for FC alkylation of arenes with HMF, next experiment with nitroethane + DMSO was carried out in order to promote the FC alkylation reaction. But in this experiment also, only HMF was observed without MMF (Table 4.3.4, entry 2). After unsuccessful attempt in DMSO, we tested ionic liquid, C<sub>4</sub>mimBr (1-butyl-3-methyl-1H-imidazol-3-ium bromide) as a reaction medium which also was found to be ineffective for the promotion of FC alkylation of in-situ formed HMF and mesitylene (Table 4.3.4, entry 3). In above cases MMF was not formed which could be attributed to the limited or no activity of Zr-Mont after glucose dehydration to HMF. This loss in activity of Zr-Mont could be due to blocking of active centres by deposition of polymeric products generated in glucose dehydration step. After the above attempts, we used acidic solvents which could dissolve the glucose as well as help to promote the FC alkylation step. Thus, first experiment conducted in acetic acid at 150 °C for the period of 16 h to give 6 % of MMF (Table 4.3.5, entry 1). Therefore, medium with higher acidity such as formic acid was evaluated and surprisingly, complete consumption of glucose was observed with 34 % yield of MMF (Table 4.3.5, entry 2). Thus, the formation of MMF (**1**) from glucose was successfully achieved due to the co-operative catalysis between Zr-Mont and formic acid. Lewis acid sites present on Zr-Mont played a crucial role for glucose isomerisation to fructose and further reactions could be promoted by formic acid. For the comparison purpose, several other montmorillonite based solid acids were screened in place of Zr-Mont for this reaction. In presence of Sn-Mont catalyst also, MMF was produced with the same yield (34 %) of that obtained over Zr-Mont (Table 4.3.5, entry 3). Al-Mont and Fe-Mont gave 32 and 31 % yield of the MMF, respectively (Table 4.3.5, entries 4 and 5). From these results (Table 4.3.5, entry 6), it is clear that glucose isomerisation to fructose is a key step which is not possible without using Lewis acid catalyst (Scheme 4.3.3). However, 27 %

conversion of glucose seen may be due the esterification of hydroxyl groups of glucose.

**Table 4.3.4.** Direct conversion of glucose into MMF in different solvents over Zr-Mont<sup>[a]</sup>

Entry	Solvent	<i>t</i> [h]	Conv. <sup>[b]</sup> [%]	Yield [%]	
				HMF <sup>[c]</sup>	<b>1</b> <sup>[d]</sup>
1	DMSO	24	89	34	00
2	DMSO (3 mL) + nitroethane (2 mL)	16	87	30	00
3	BmimBr (1 mL)	16	80	21	Trace

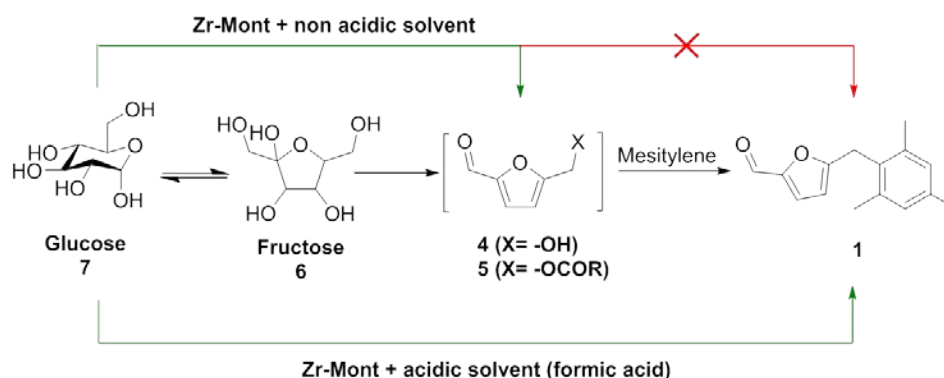
[a] Reaction conditions: glucose (0.5 g), solvent (5 mL), mesitylene (10 mL), Zr-Mont (0.2 g), 150 °C. [b] Conversion of glucose and [c] yield of HMF was measured using HPLC. [d] Isolated yields.

A very important process benefit presented in Figure 4.3.7 is that mesitylene acting as reactant as well as a product extraction phase, formic acid acting as a reactive solvent and Zr-Mont as a solid Lewis acid which settled down and to be separated by simple filtration.

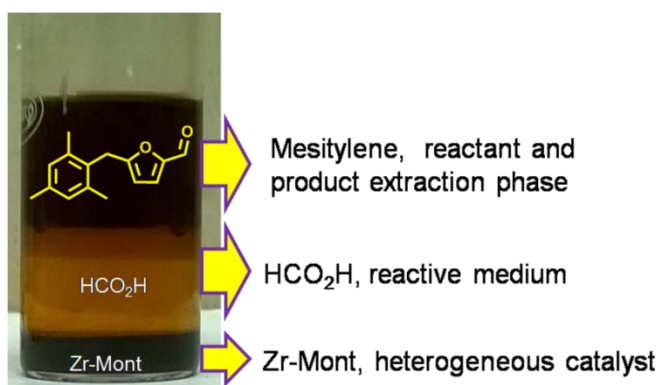
**Table 4.3.5.** Direct conversion of glucose into MMF in acidic solvents over montmorillonite catalysts<sup>[a]</sup>

Entry	Solvent	Catalyst	<i>t</i> [h]	Conv. <sup>[b]</sup> [%]	Yield [%]	
					HMF <sup>[c]</sup>	<b>1</b> <sup>[d]</sup>
1	CH <sub>3</sub> CO <sub>2</sub> H	Zr-Mont	16	95	04	06
2	HCO <sub>2</sub> H	Zr-Mont	16	100	00	34
3	HCO <sub>2</sub> H	Sn-Mont	16	100	00	34
4	HCO <sub>2</sub> H	Al-Mont	16	100	00	32
5	HCO <sub>2</sub> H	Fe-Mont	16	98	00	31
6	HCO <sub>2</sub> H	--	16	27	--	00

[a] Reaction conditions: glucose (0.5 g), solvent (5 mL), mesitylene (10 mL), catalyst (0.2 g), 150 °C. [b] Conversion of glucose and [c] yield of HMF was measured using HPLC. [d] Isolated yields.



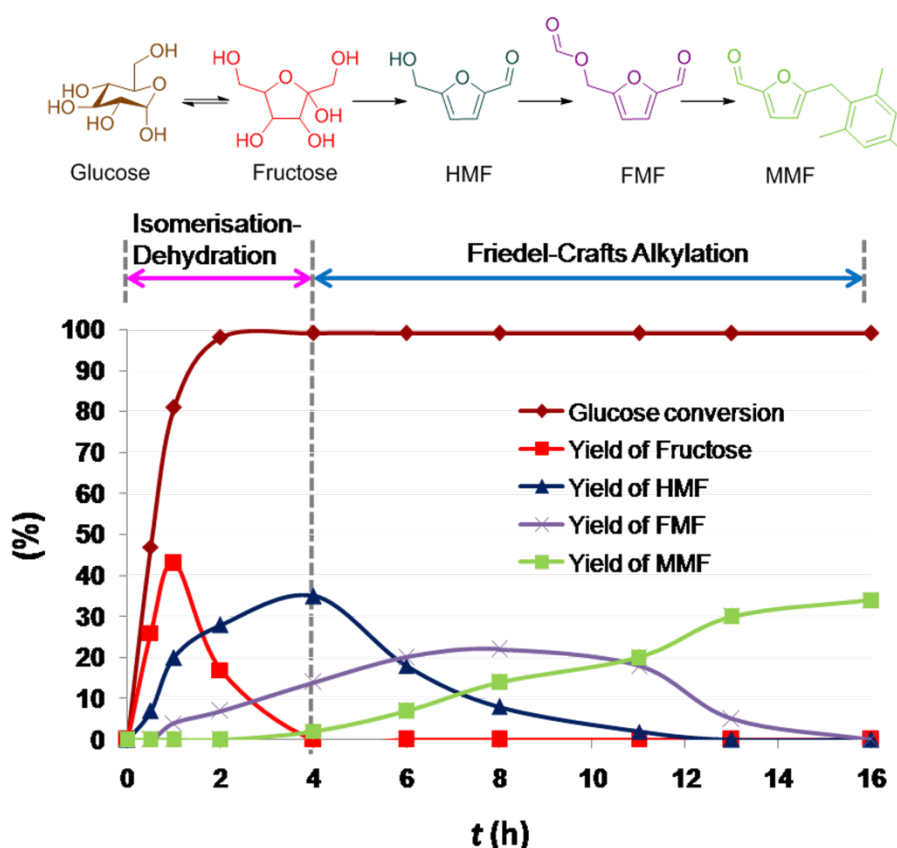
**Scheme 4.3.3.** Glucose to MMF over Zr-Mont in non acidic vs. acidic solvents.



**Figure 4.3.7.** Formation of coupling product in mesitylene phase *via* dehydration followed by arylation of glucose.

#### 4.3.5.9. Effect of reaction time

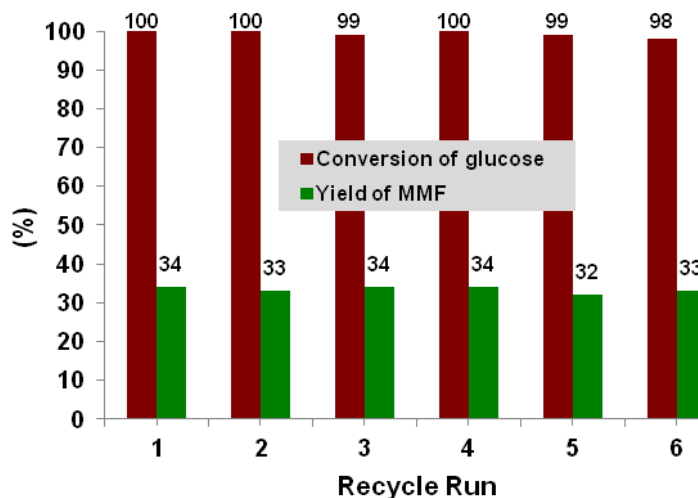
The progress of dehydration-FC alkylation of glucose with mesitylene was monitored by withdrawing samples after specific time and analyzed using HPLC (Figure 4.3.8). Under experimental conditions, in just 1 h, 81 % of glucose was consumed with 43, 20 and 4 % yields of fructose, HMF and FMF, respectively. After 2 h of reaction, glucose was consumed completely with 28, 17 and 7 % yields of fructose, HMF and FMF, respectively. Dehydration of glucose is seems to be rapid. At the end of 4<sup>th</sup> hour, fructose was completely consumed with maximum 35 % yield of HMF along with 14 % of FMF and 2 % of MMF. Then HMF was slowly converted into FMF and later was subsequently converted into MMF. The yield of MMF was gradually increased to 34 % after 16 h of reaction.



**Figure 4.3.8.** Reaction progress of glucose conversion to MMF with time. Reaction conditions: Glucose (0.5 g), mesitylene (10 mL), formic acid (5 mL), Zr-Mont (0.2 g), 150 °C, 16 h.

#### 4.3.5.10. Recycling studies of Zr-Mont

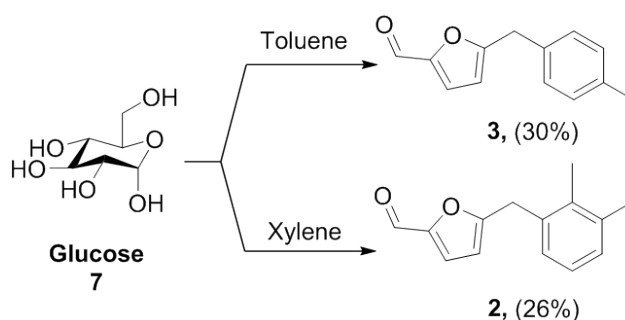
The unending stability and reusability of the catalyst are of great importance for the practical production of MMF to minimize the process cost. The stability and reusability of Zr-Mont was investigated for the production of MMF from glucose in formic acid medium. Because the heterogeneous nature of the Zr-Mont catalyst, it can be easily recovered from the reaction mixture by filtration, we sought to investigate the reusability of recovered catalysts by conducting the MMF production from glucose at 150 °C for the period of 16 h over multiple cycles. In a typical recycle experiment after the reaction Zr-Mont catalyst was filtered, washed with water (5 mL x 2), acetone (5 mL x 2) and dried in oven for 1 h at 110 °C before reuse in the next cycle. Catalyst-recycling studies revealed that the catalyst could be readily recycled six times without any reduction in catalyst activity (Figure 4.3.9). After each reuse of Zr-Mont, glucose conversion was almost >95 % with slight drop in yield of MMF.



**Figure 4.3.9.** Recycle study of Zr-Mont for the MMF production from glucose. Reaction conditions: Glucose (0.5 g), mesitylene (10 mL), formic acid (5 mL), Zr-Mont (0.2 g), 150 °C, 16 h. After each cycle catalyst was washed with acetone and dried in the oven at 100 °C for 1 h prior to use for next cycle.

#### 4.3.5.11. Synthesis of arylmethylfurfural from glucose and arenes

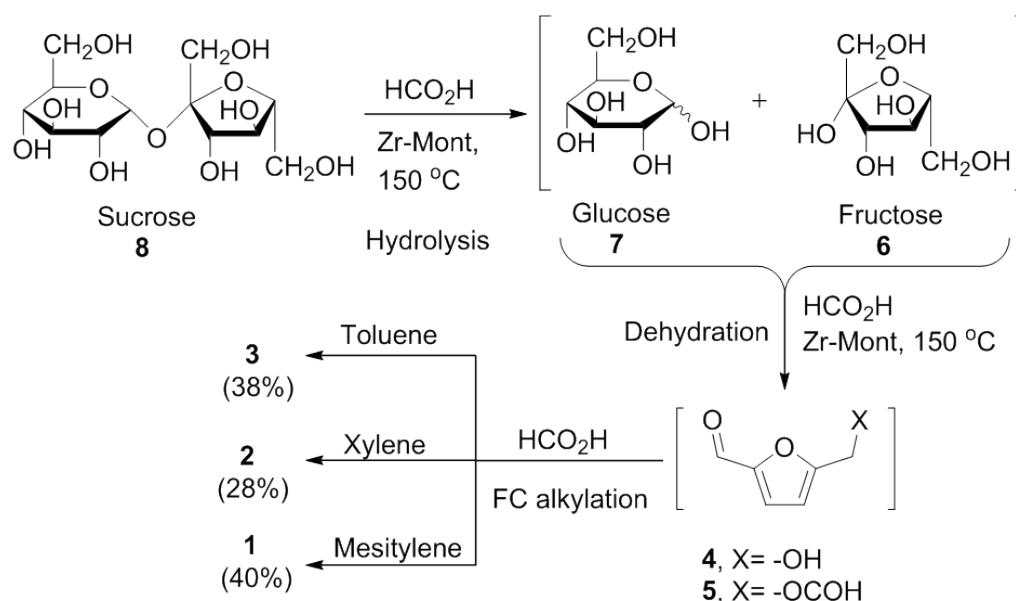
Instead of mesitylene we further conducted reaction of xylene and toluene with glucose in formic acid medium. With toluene, product **2** was formed in 30 % directly from glucose while with xylene coupling product (**3**) was formed in 26 % yield (Scheme 4.3.4).



**Scheme 4.3.4.** Production of arylmethylfurfural from glucose and toluene/xylene.

#### 4.3.5.12. Synthesis of coupling products from sucrose with arenes

After successful conversion of glucose we moved our efforts towards the conversion of more complex carbohydrate such as sucrose (**8**). Sucrose is a disaccharide containing one glucose and one fructose unit. Acid hydrolysis of sucrose breaks the glycosidic bond between glucose and fructose unit in acidic medium. The glucose unit of sucrose was intended to isomerise to fructose over Zr-Mont catalyst. The above protocol was applied for conversion of sucrose, under similar experimental conditions sucrose was dehydrated to FMF and generated FMF was coupled with mesitylene to afford a product **1** in 40 % yield. In the next experiment in place mesitylene, we used xylene for the FC alkylation with in-situ formed HMF/FMF to obtain product **2** in 28 % yield. Similarly, product **3** was formed in 38 % yield from FC alkylation of toluene with in-situ generated HMF/FMF (Scheme 4.3.5).



**Scheme 4.3.5.** Production of arylmethylfurfural from sucrose.



#### 4.3.6. Conclusions

An efficient approach for the production of diesel fuel precursors is demonstrated using a combination of biomass and petroleum derived feedstocks. FC alkylation of arenes (*e.g.* mesitylene, xylene and toluene) with 5-(hydroxymethyl)furfural or its derivatives was successfully achieved over Zr-Mont catalyst. Various solvents were screened for this reaction among which, nitroethane showed an excellent suitability. Appropriate acid strength and high surface area of Zr-Mont catalyst resulted into the highest yield of arylmethylylfurfural. The stability of Zr-Mont was successfully confirmed by its recycle runs. Further, in a one-pot strategy to MMF from glucose, Zr-Mont promoted the sluggish isomerisation of glucose to fructose and formic acid effectively converted in-situ formed fructose into mesitylmethylylfurfural (MMF, **1**) in 34 % yield. Using this protocol, arylmethylylfurfural was successfully produced by treating glucose with xylene and toluene. Sucrose was also efficiently converted to arylmethylylfurfural such as **1**, **2** and **3** with 40, 28 and 38 % yields, respectively. The phenomenal stability and recyclability of solid acid (Zr-Mont) would replace the hazardous mineral acids (*e.g.* conc. HCl) to make the process green. Importantly, use of formic acid was found to be attractive as it acted as solvent to dissolve carbohydrates as well as the co-catalyst to promote FC alkylation.

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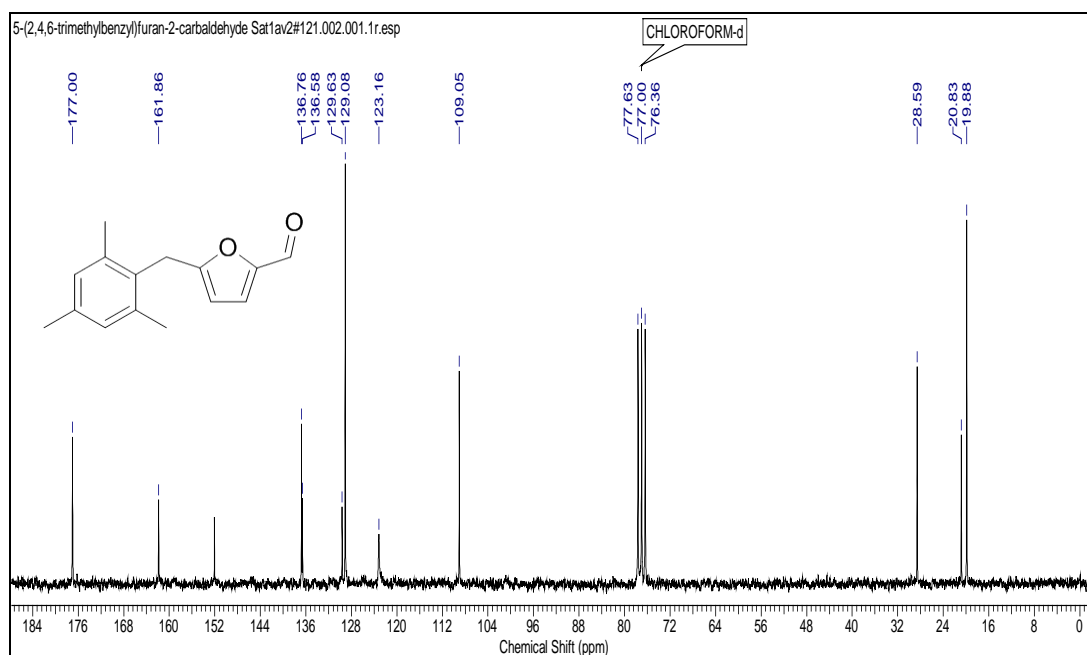
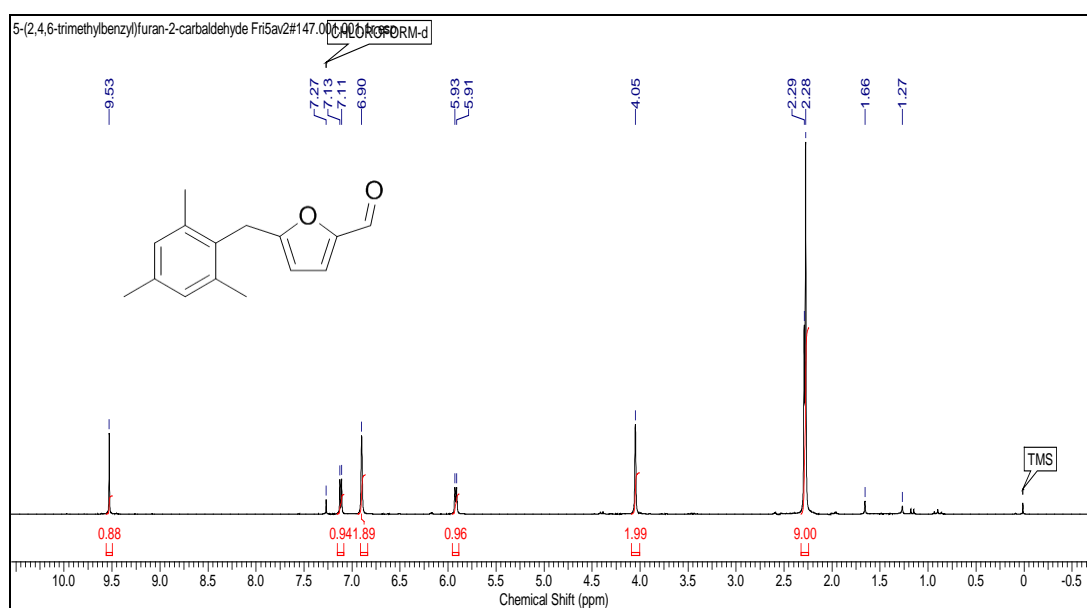
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## 4.3.8. NMR data of synthesized compounds

**5-(2,4,6-trimethylbenzyl)furan-2-carbaldehyde:**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 2.28-2.29 (m, 9 H) 4.05 (s, 2 H) 5.91-5.93 (d,  $J=3.54$  Hz, 1 H) 6.90 (s, 2 H) 7.11-7.13 (d,  $J=3.54$  Hz, 1 H) 9.53 (s, 1 H)

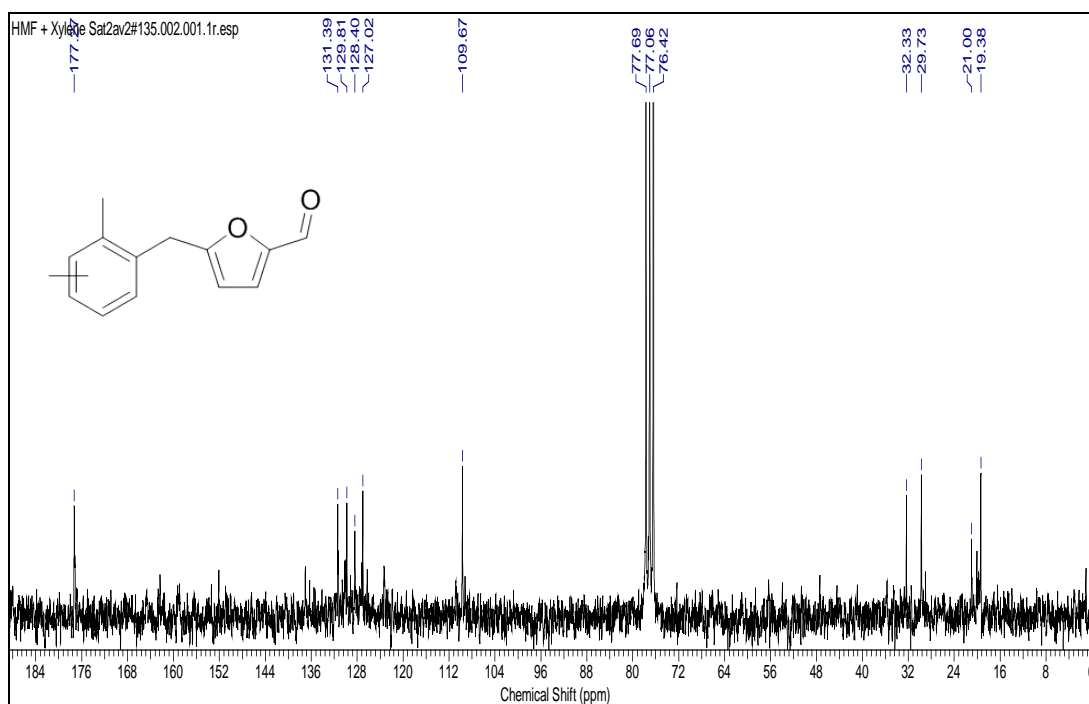
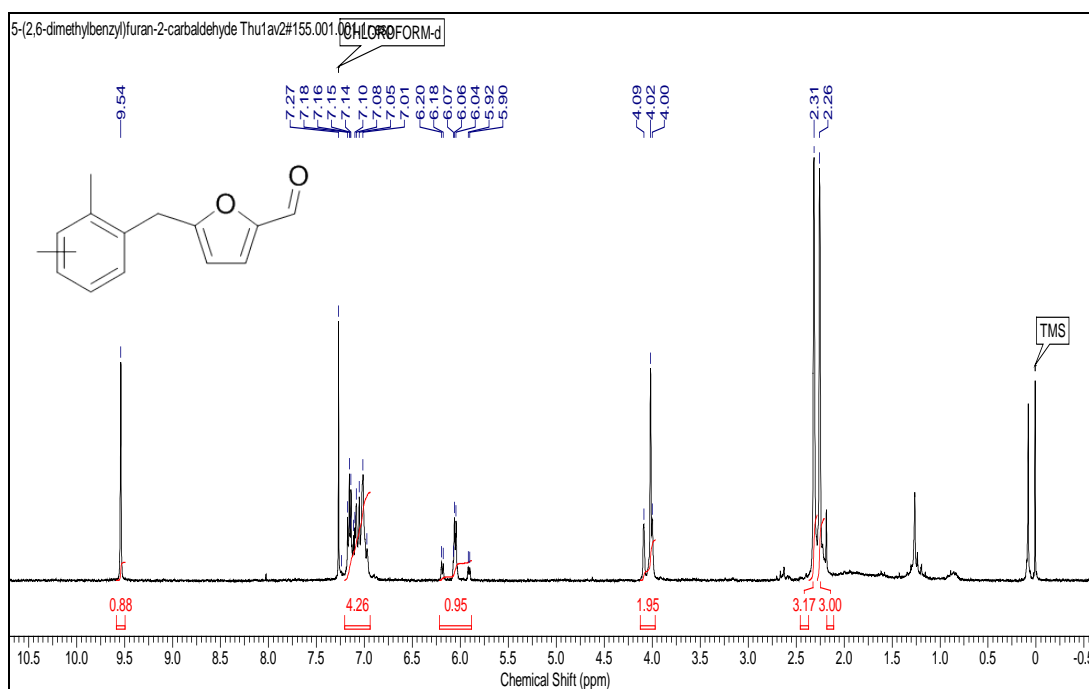
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 19.88, 20.83, 28.59, 109.05, 123.16, 129.08, 129.63, 136.58, 136.76, 161.86, 177.00



**5-(2,6-dimethylbenzyl)furan-2-carbaldehyde:**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.26 (s, 3 H) 2.31 (s, 3 H) 4.00 - 4.09 (m, 2 H) 5.90 - 6.20 (m, 1 H) 6.97 - 7.18 (m, 5 H) 9.54 (s, 1 H)

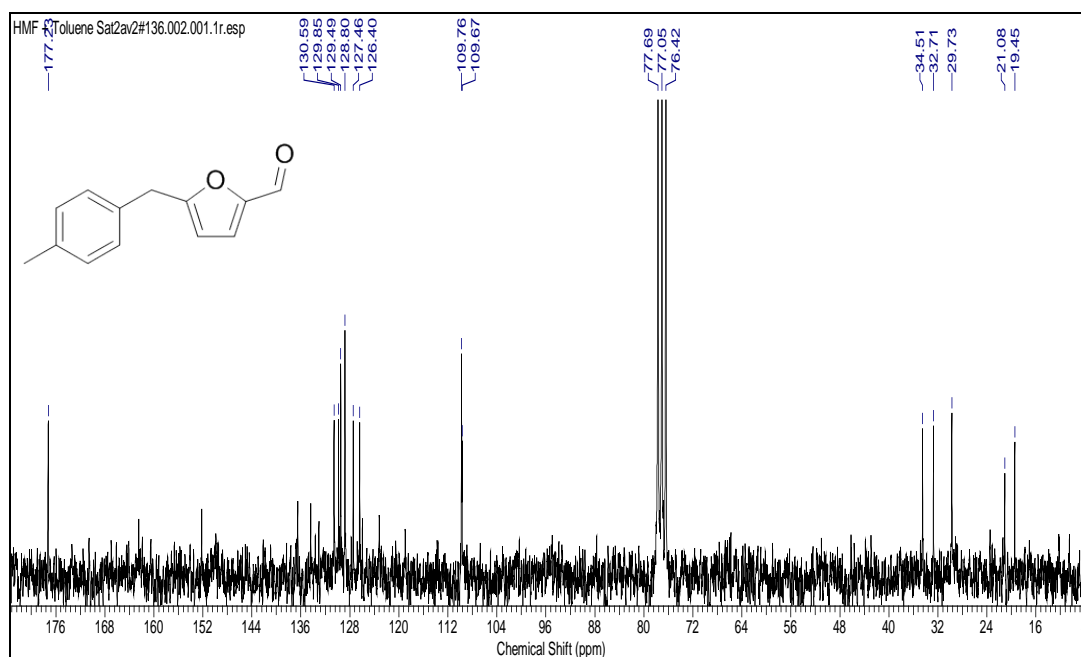
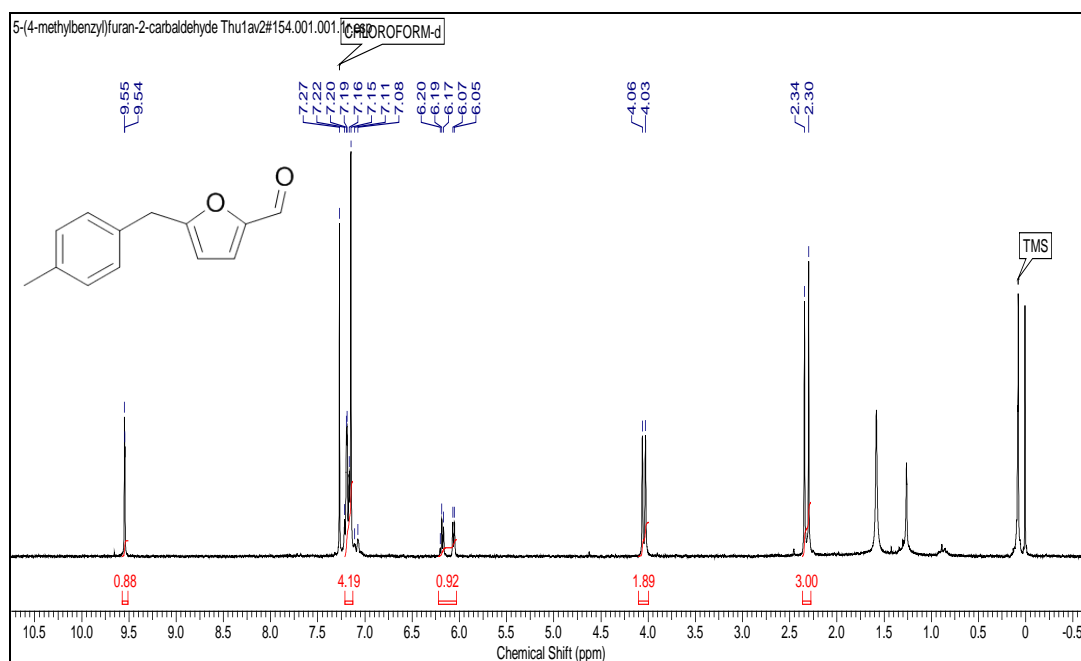
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 19.38, 21.00, 29.73, 32.33, 109.67, 127.02, 128.40, 129.81, 131.39, 177.27



**5-(4-methylbenzyl)furan-2-carbaldehyde:**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.30-2.34 (d,  $J=8.97$  Hz, 3 H) 4.03-4.04 (d,  $J=6.57$  Hz, 2 H) 6.05 - 6.20 (m, 1 H) 7.15 - 7.20 (m, 4 H) 9.54-9.55 (d,  $J=0.88$  Hz, 1 H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 19.45, 21.08, 29.73, 32.71, 34.51, 109.67 109.76, 126.40, 127.46, 128.80, 129.49, 129.85, 130.59, 177.23

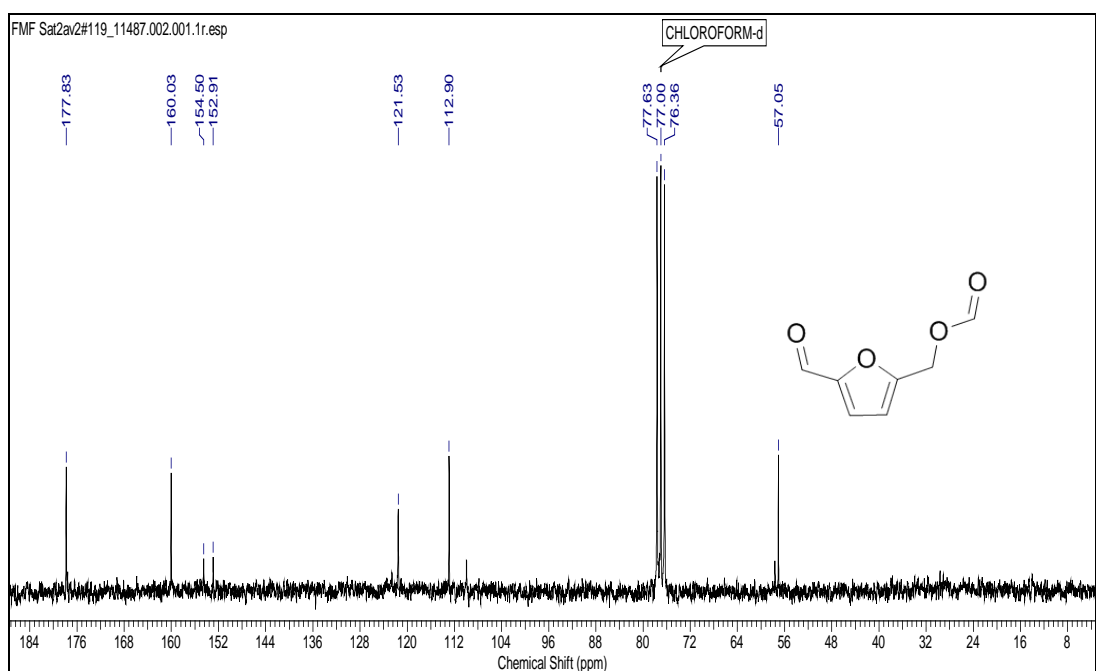
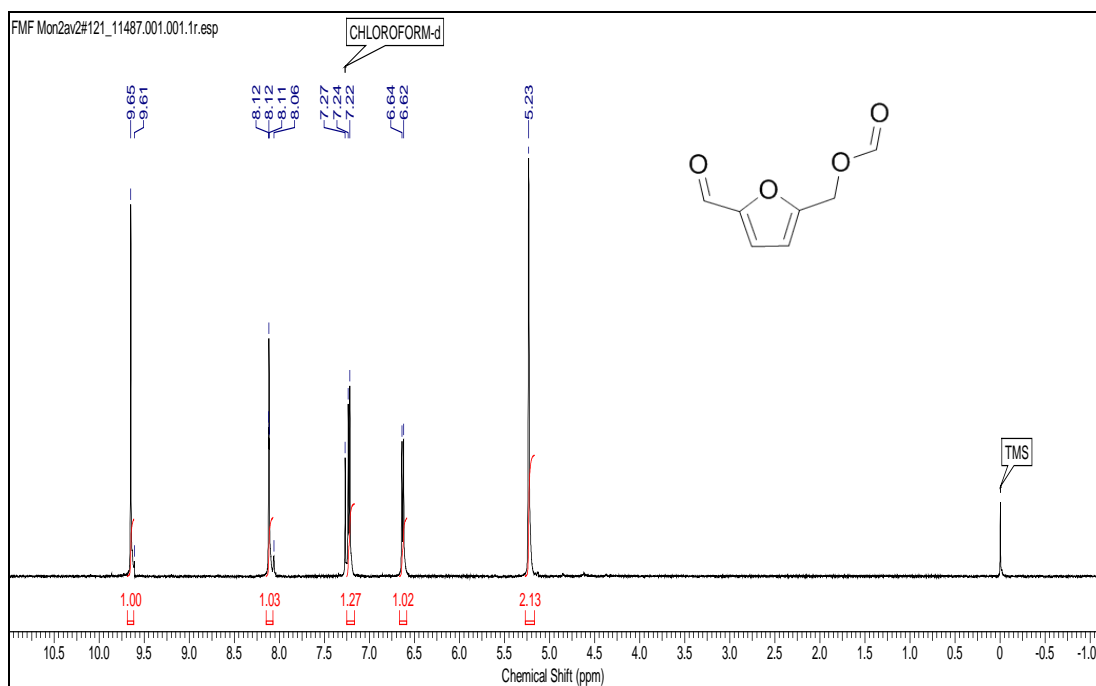


**5-(acetoxymethyl)furfural:** NMR is provided in Chapter 2

**5-(formyloxymethyl)furfural:**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 2.12 (s, 3 H) 5.13 (s, 2 H) 6.60 (d,  $J=3.54$  Hz, 1 H) 7.22 (d,  $J=3.54$  Hz, 1 H) 9.65 (s, 1 H)

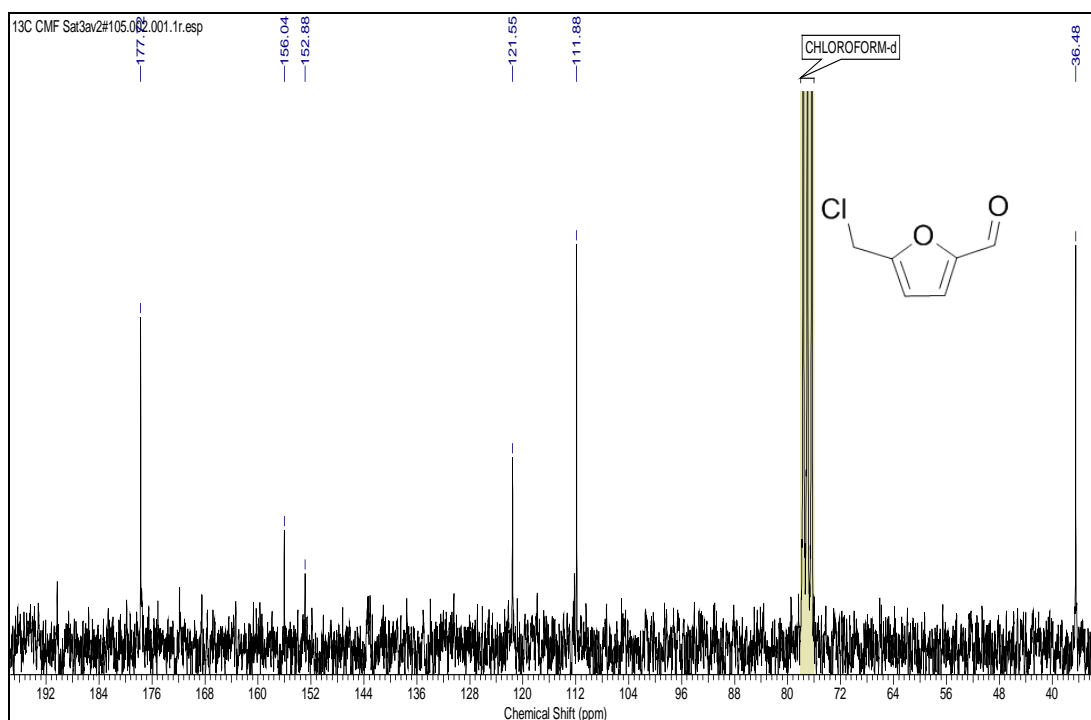
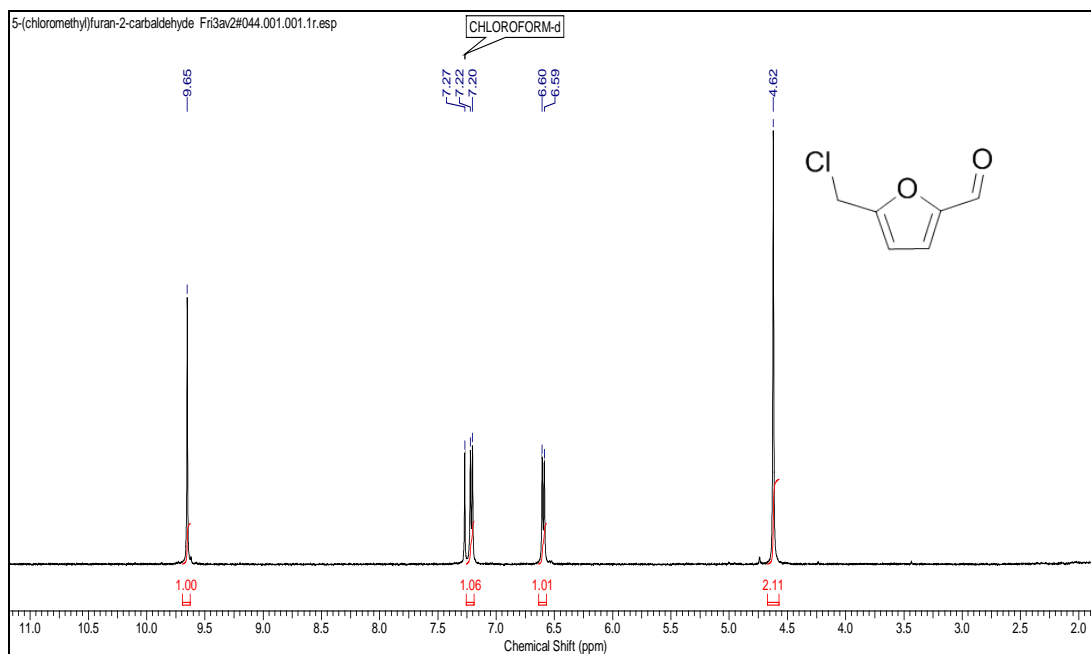
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 57.05, 112.90, 121.53, 152.91, 154.50, 160.03, 177.83



**5-(chloromethyl)furfural:**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 4.62 (s, 2H), 6.59-6.60 (d,  $J=3.54\text{Hz}$ ), 7.20-7.22 (d,  $J=3.54$ , 1H), 9.65 (s, 1H).

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 36.48, 111.88, 121.55, 152.88, 156.04, 177.72.





## *Part-II*

### *C-O and C-C bond forming reactions of bioderived aldehydes*

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## **Chapter 5**

### **Etherification Reactions of biomass derived platform molecules**

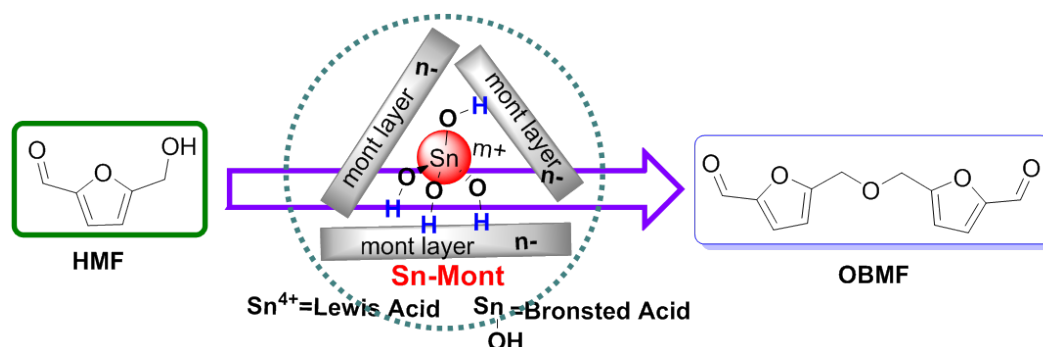
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**This Chapter is organized in two sections:**

**5.1 Selective self-etherification of 5-(hydroxymethyl)furfural over Sn-Mont catalyst**

**5.2 Cascade reductive-etherification of bio-derived aldehydes over Zr-based catalysts**

## 5.1. Selective self-etherification of 5-(hydroxymethyl)furfural over Sn-Mont catalyst

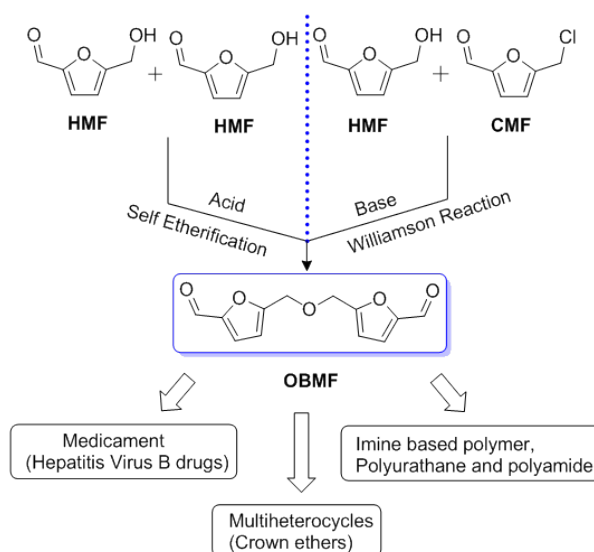


Etherification of biomass derived molecules is one of the important class of reaction producing value added substrates for wide range of applications. Due to obvious disadvantages of conventional homogeneous acid/ base reagents used for etherification, we focused on development of stable solid acid catalysts. In such attempts, in the first part of this chapter, self etherification of 5-(hydroxymethyl)furfural (HMF) over a heterogeneous Sn-Mont catalyst is discussed. Sn-Mont catalyst was found to be a highly efficient for the self-etherification of 5-(hydroxymethyl)furfural (HMF) to give 5,5'-oxy(bis-methylene)-2-furaldehyde (OBMF). Lewis and Brønsted acidity of  $\text{Sn}(\text{OH})_4$  species enwrapped into the layers of montmorillonite was responsible for an excellent activity of Sn-Mont catalyst, which gives almost complete conversion of HMF and 98 % selectivity to OBMF. An aprotic non-polar, dichloroethane was most effective solvent due to the facile formation of oxonium ion mediating etherification reaction. The catalyst showed suitable recyclability confirming its appreciable hydrolytic stability in water and retention of its acidity.

Suhas Shinde, Chandrashekhar Rode, *Catalysis communications*, **2017**, 88, 77-80

### 5.1.1. Introduction

HMF derivatives have wide range of applications as starting materials for plastics, surfactants, solvents, fuels, pharmaceuticals and antifungals [1–3]. Despite of its high cost as a reagent, an extensive research has been focused on obtaining valuable products from HMF believing that its commercial availability at an affordable cost in near future. One such example is 5,5'-oxybis(methylene)difuran-2-carbaldehyde (OBMF) which is used for making multiheteromacrocycles (16-crown-6), polyurethanes, polyamides and imine polymers [4, 5]. The OBMF and 1, 4-diaminobenzene gives a polymer with high glass transition temperature, thermal and electrical conductivities and having solubility in polar solvents [6]. The OBMF possesses wide range of anti-virus, anti-tuberculosis and anti-oxidant activity (Scheme 5.1.1) [7].



**Scheme 5.1.1.** Synthetic pathways and applications of OBMF

### 5.1.2. Literature survey

Considering the wide range applications of the OBMF, Wen et al. synthesized it by employing a conventional Williamson reaction between HMF and 5-(chloromethyl)furfural to give only 42.7 % yield of OBMF [7]. Thermal dehydration of HMF in DMSO also gives OBMF while, carbohydrates conversion using  $\text{BF}_3 \cdot \text{OEt}_2/\text{DMSO}$  gives low to moderate yield of OBMF [8, 9]. Use of the Dean-Stark assembly increases the productivity of OBMF from HMF. However, large

amount of waste is generated when homogeneous acids or bases were used [9–11]. Therefore, solid acids such as amberlite IR120 and amberlyst-15 were also explored by Rapp et al. [12] and Trabelsi et al. [13], respectively. However, these solid acids have a lower thermal stability therefore their recyclability is become difficult. In this direction, Casanova et al. [14] reported a recyclable and very efficient catalyst for self etherification of HMF. They showed 95 % conversion of HMF with 98 % selectivity to OBMF over Al-MCM-41 catalyst in 4-Chlorotoluene solvent. Recently, Hou et al. explored a graphene oxide catalyst for this reaction to give 86 % yield of OBMF in dichloromethane however; dichloromethane exerts a high vapour pressure under reaction conditions [15].

### 5.1.3. Scope of the present work

Considering the drawbacks of the existing methods, we employed our well established Sn-Mont catalyst for HMF etherification reaction. Self-etherification of HMF was conducted in dichloroethane at 100 °C using a Dean-Stark assembly to achieve 98 % OBMF selectivity with almost complete HMF conversion. Effects of solvents, catalyst loading, water removal, reaction time and temperature on the yield of OBMF have been studied in detail.

### 5.1.4. Experimental section

#### 5.1.4.1. Materials

5-(Hydroxymethyl)furfural (99.8 %),  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{SnO}_2$ , montmorillonite (CAS No. 1302-78-9) and amberlyst-15 were purchased from Sigma-Aldrich, India. Organic solvents, conc.  $\text{H}_2\text{SO}_4$  and *p*-toluenesulfonic acid were purchased from Thomas Baker.

#### 5.1.4.2. Catalyst preparation

The Sn-Mont catalyst was prepared by following method provided in **Chapter 2**.

#### 5.1.4.3. Catalytic experiment

A mixture of HMF (0.252 g, 2 mmol), dichloroethane (5 mL) and Sn-Mont (0.1 g) were placed in a 25 mL round bottom flask equipped with an inverse Dean-Stark assembly. Reaction flask was kept in a preheated (100 °C) oil bath and stirred at 1000 rpm for 2 h. Reaction was monitored by TLC (ethyl acetate: petroleum ether, 1:1 and charred in DNP stain). After completion of reaction, catalyst was filtered and

filtrate was evaporated under reduced pressure to afford dark brown coloured solid, which was further recrystallized in hot hexane (2 mL) to get yellow coloured crystals of OBMF with 89 % yield and, mp 112–114 °C (lit., 111–112 °C) [11].

## 5.1.5. Results and discussion

### 5.1.5.1. Catalyst characterization

#### 5.1.5.1.1. Pyridine FTIR

The types of acid sites present in Sn-Mont and Sn-Mont-600 samples were evaluated by Py-FTIR (Figure 5.1.1). The calcined Sn-Mont sample did not show the Brønsted acidity band at 1540  $\text{cm}^{-1}$ . It indicates, the loss of Brønsted acid sites from the Sn-Mont sample after calcination due the dehydration of  $\text{Sn}(\text{OH})_4$  species present between montmorillonite layers.

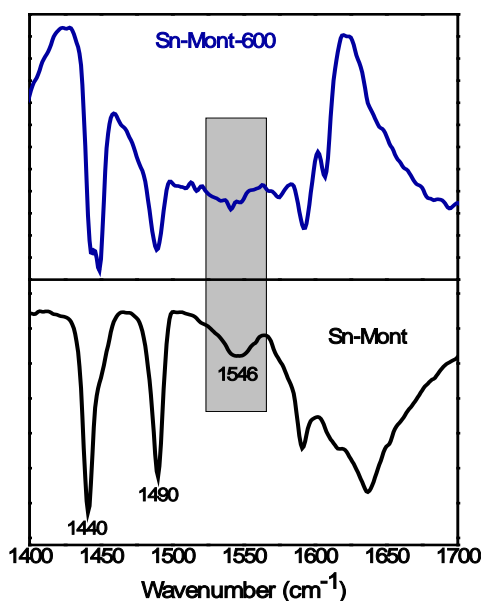


Figure 5.1.1. Pyridine FTIR of Sn-Mont and calcined Sn-Mont

The other properties of catalysts used in this work are summarized in Table 5.1.1.

**Table 5.1.1. Properties of catalysts**

Entry	Catalysts	$S_{\text{BET}}$	$\text{NH}_3$ desorbed	$V_{\text{micro}}$	$V_{\text{meso}}$	$V_{\text{total}}$
		$\text{m}^2 \text{g}^{-1}$	$\text{mmol g}^{-1}$	$\text{mm}^3 \text{g}^{-1}$	$\text{mm}^3 \text{g}^{-1}$	$\text{mm}^3 \text{g}^{-1}$
1	Montmorillonite	19	0.06	6	15	21
2	Sn-Mont	182	0.43	69	128	197
3	Sn-Mont-600	179	0.23	64	136	200
4	$\text{Sn}(\text{OH})_4$	98	0.010	40	6	46
5	$\text{SnO}_2$	11	0.019	36	6	42

### 5.1.5.2. Catalyst screening

A few important criteria for catalyst selection were that the catalyst should interact favourably with the hydrophobic reactants, should not be influenced by by-product water, and should be readily recyclable. While screening various acid catalysts for HMF etherification to OBMF, Sn precursors showed 90% conversion of HMF but only 30–69 % selectivity to OBMF, due to the chlorination of HMF to form CMF (Table 5.1.2, entries 1, 2). Interestingly,  $\text{Sn}^{4+}$ -exchanged montmorillonite showed almost complete HMF conversion with 98 % selectivity to OBMF with small amounts of 2,5-diformylfuran (DFF, **5**) and 2,5-bis(hydroxymethyl)furan (BHMF, **6**) (Table 5.1.2, entry 4, Scheme 5.1.2), which are also useful products [4, 17-21]. Surprisingly, calcined SnMont-600 sample showed much lower HMF conversion of 32 and 98 % OBMF selectivity (Table 5.1.2, entry 8). During the calcination,  $\text{Sn}(\text{OH})_4$  loses  $-\text{OH}$  by dehydration, resulting into loss of Brønsted acidity which was proved by Py-FTIR (Figure 5.1.1). In control experiments,  $\text{SnO}_2$  and  $\text{Sn}(\text{OH})_4$  doesn't show any conversion of HMF (Table 5.1.2, entries 9, 10) due to their weakest acidity indicating that not only  $\text{Sn}(\text{OH})_4$  but also surrounding aluminosilicates layers were necessary for the acid catalysis [22]. Sn-Mont formed an ideal combination of micro and mesopores for the smooth transport of reactant-product to and from the active sites.

**Table 5.1.2.** Catalyst optimization for synthesis of symmetric ether OBMF <sup>[a]</sup>

Entry	Catalyst	Loading	<i>t</i> [h]	Conversion [%]	Selectivity [%]
1	SnCl <sub>2</sub> ·2H <sub>2</sub> O	20 mol %	2	95	69 (31) <sup>[b]</sup>
2	SnCl <sub>4</sub> ·5H <sub>2</sub> O	20 mol %	2	90	30 (70) <sup>[b]</sup>
3	Mont	0.1 g	24	39	98
4	Sn-Mont	0.1 g	2	98	98
5	Sn-Mont	0.05 g	2	76	96
6	Sn-Mont	0.2 g	2	>99	93
7 <sup>[c]</sup>	Sn-Mont	0.1 g	21	75	89
8	Sn-Mont-600	0.1 g	12	32	98
9	SnO <sub>2</sub>	0.1 g	12	0	0
10	Sn(OH) <sub>4</sub>	0.1 g	12	0	0
11	conc. H <sub>2</sub> SO <sub>4</sub>	10 mol %	2	>99	79
12	<i>p</i> -TSA	10 mol %	2	>99	82
13	Amberlyst-15	10 mol %	4	85	94

[a] Reaction condition: HMF (0.252 g, 2 mmol), dichloroethane (5 mL), Dean-Stark assembly, 100 °C. [b] Selectivity of 5-(chloromethyl)-2-furfuraldehyde. [c] Without Dean-Stark assembly at 100 °C.

### 5.1.5.3. Effect of catalyst loading

HMF conversion decreased from 98 to 76 % with decrease in catalyst loading from 0.1 to 0.05 g (Table 5.1.2, entry 5) obviously due to insufficient active sites. When Sn-Mont loading was increased to 0.2 g, HMF conversion remained the same (99 %) while OBMF selectivity decreased to 93 % (Table 5.1.2, entry 6). Hence, 0.1 g was the optimum catalyst loading to achieve almost complete conversion of HMF and 95 % OBMF selectivity.



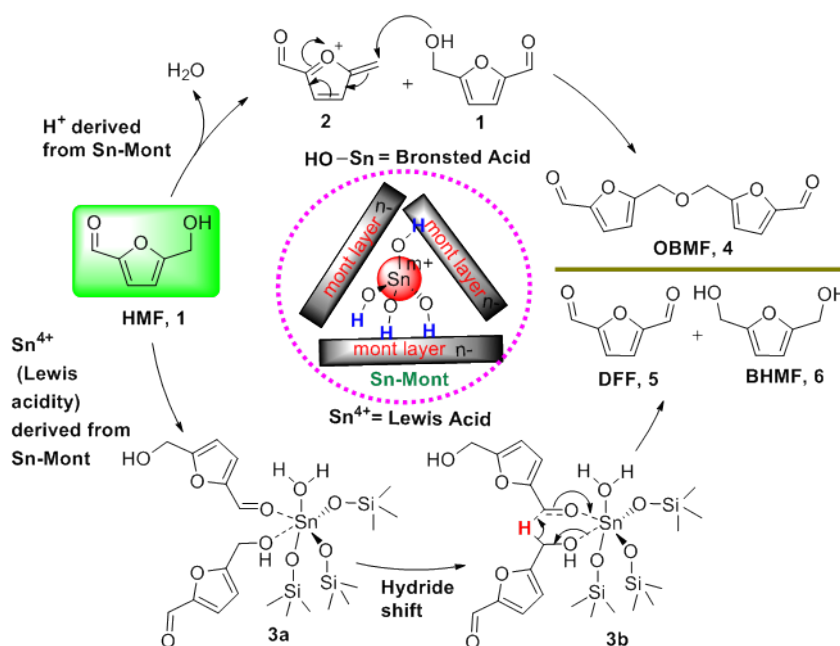
#### 5.1.5.4. Role of solvent

The screening of solvents showed that in polar solvents (water, DMF, acetonitrile), HMF conversion decreased to 40 % which was lower than that in non-polar solvents (dichloroethane, toluene) (Table 5.1.3, entries 2–4). The intermediate **2** formed immediately after dehydration of HMF and although stabilized by the resonance of furan ring electrons (Figure 5.1.2), is not detectable as it immediately converts to OBMF. The formation of **2** is most facile due to the electron withdrawing formyl group of HMF. DFF and BHMF by-products formation is possible *via* Oppenauer oxidation/Meerwein-Ponndorf-Verley process. Both etherification and acetalization of HMF was observed in methanol with trace formation of OBMF and methyl levulinate (Table 5.1.3, entry 5). In non-polar solvent like toluene, conversion of HMF strikingly rose to 80 %, with 61 % selectivity to OBMF (Table 5.1.3, entry 6) due to the alkylation reaction facilitated by an activated aromatic ring [14].

**Table 5.1.3.** Effect of reaction medium on conversion of HMF to OBMF<sup>[a]</sup>

Entry	Solvent	<i>t</i> [h]	Conversion [%]	Selectivity [%]
1	No solvent	24	48	90
2	Water	5	0	0
3	DMF	12	39	80
4	Acetonitrile	12	37	90
5	Methanol	12	90	Trace
6	Toluene	24	80	61(30) <sup>[b]</sup>
7	Xylene	24	81	64(33) <sup>[b]</sup>
8	Mesitylene	24	80	62(36) <sup>[b]</sup>
9	4-Chlorotoluene	12	86	96
10	Dichloroethane	2	98	98

[a] Reaction conditions: HMF (0.252 g, 2 mmol), solvent (5 mL), Sn-Mont (0.1 g), 100 °C, Dean-Stark assembly. [b] Arylation products.



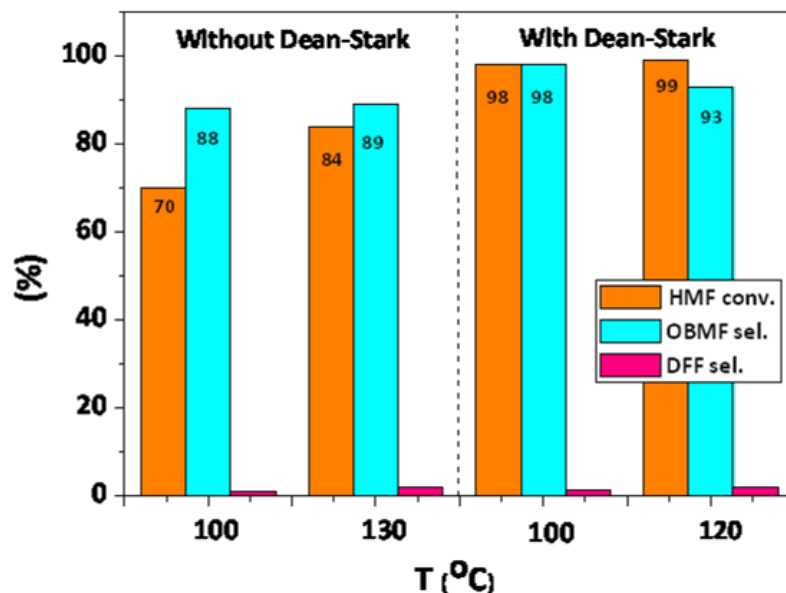
**Figure 5.1.2.** Plausible pathways for the formation of OBMF and DFF.

Similar results were obtained with xylene and mesitylene solvents (Table 5.1.3, entries 7 and 8). In 4-chlorotoluene, both HMF conversion and OBMF selectivity were significantly improved due to the deactivated aromatic ring but with only 86 % conversion even after 12 h (Table 5.1.3, entry 9). Almost complete HMF conversion and 98 % OBMF selectivity could be achieved in dichloroethane (Table 5.1.3, entry 10). Oxonium ion formation is the key step in catalytic dehydration of alcohols to ethers, usually facilitated in solvents with electron withdrawing groups [23, 24]. Increasing solvent polarity decreases the rate of  $\text{S}_{\text{N}}^1$  reaction involving a neutral leaving group hence, neutral solvent would be preferred [25]. Dichloroethane, proved to be the best solvent due to 1) non-polar character, 2) no interaction with the reactant, 3) low vapour pressure (as compared to dichloromethane) and 4) highest yield of OBMF.

#### 5.1.5.5. Effect of water removal

Effect of water removal was also studied at different temperatures since; water is a by-product in this reaction. Water could be removed from the reaction medium by using Dean-Stark assembly which gave complete HMF conversion and 98% selectivity to OBMF at 100 °C, which was substantially higher than the etherification

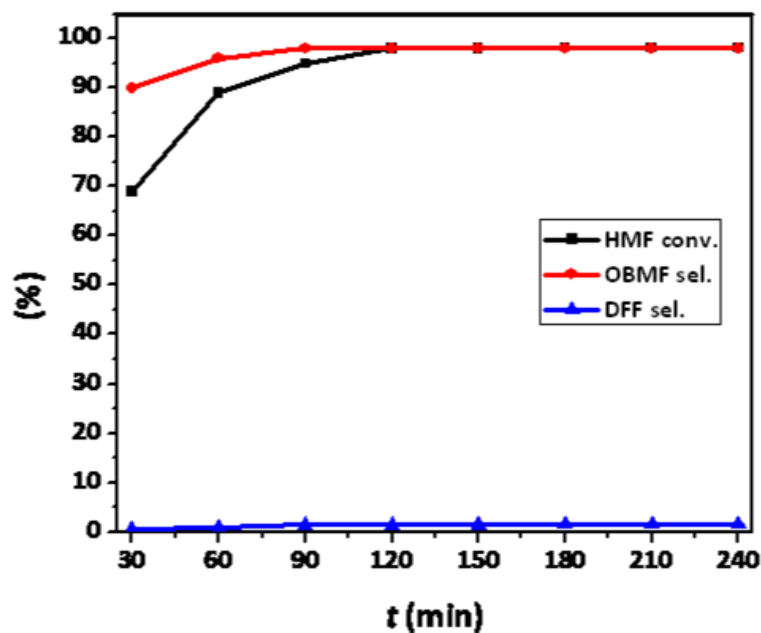
conducted without Dean-Stark assembly (70 % conversion and 88 % selectivity) even at higher temperature of 130 °C (Figure 5.1.3)



**Figure 5.1.3.** Effect of temperature and water removal. Reaction conditions: HMF (0.252 g, 2 mmol), dichloroethane (5 mL), Sn-Mont (0.1 g), 2h, with or without Dean-Stark (water removal) assembly.

#### 5.1.5.6. Effect of reaction time

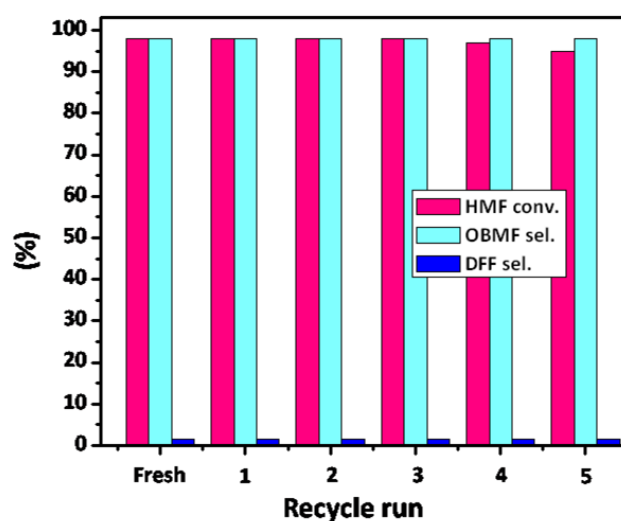
Attempts were also made to achieve complete conversion and higher yield of OBMF, by extending the reaction time up to 4 h under the optimized reaction conditions (Figure 5.1.4). Initially, up to 30 min, 70 % HMF conversion with 90 % selectivity to OBMF was observed, both of which then gradually increased to 98 % in 2 h. Further increase in reaction time beyond 2 h, did not result in enhancement of conversion or OBMF selectivity. This could be attributed to the adsorption of traces of water on the catalyst surface, which could rehydrate intermediate, **2** (Figure 5.1.2).



**Figure 5.1.4.** Effect of reaction time. Reaction conditions: HMF (0.252 g, 2 mmol), dichloroethane (5 mL), Sn-Mont (0.1 g), 100 °C, with Dean-Stark assembly.

#### 5.1.5.7. Catalyst recycle studies

As shown in Figure 5.1.5, the activity of Sn-Mont remained consistent even after five recycles under the optimized reaction conditions. After each cycle catalyst was washed with acetone, dried at 110 °C and reused.



**Figure 5.1.5.** Catalyst recycles experiment. Reaction conditions: HMF (0.252 g, 2 mmol), dichloroethane (5 mL), Sn-Mont (0.1 g), 100 °C, 2 h, with Dean-Stark assembly.

### 5.1.6. Conclusions

Structured micro- and mesoporous Sn-Mont was found to be a very efficient catalyst for self-etherification of HMF to afford selectively, OBMF. Higher  $d$  values (14.96 Å) of Sn-Mont than that of parent Mont (12.7 Å), confirmed that  $\text{Sn}^{4+}$  remained between the montmorillonite layers while, Py-IR evidenced the presence of both Lewis and Brønsted acidity. However, calcined Sn-Mont dramatically affected the conversion of HMF due to loss of Brønsted acid sites. Sn-Mont catalyst could be efficiently recycled for five times confirming its stability under the reaction conditions. The proposed reaction pathway involves formation of OBMF and DFF due to Brønsted  $[\text{Sn}(\text{OH})_4]$  and Lewis ( $\text{Sn}^{4+}$ ) acid sites, respectively. Use of non-polar solvent and continuous water removal assembly is inevitably necessary for this reaction to achieve highest yield of OBMF.

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### 5.1.8. NMR data of the synthesized compound

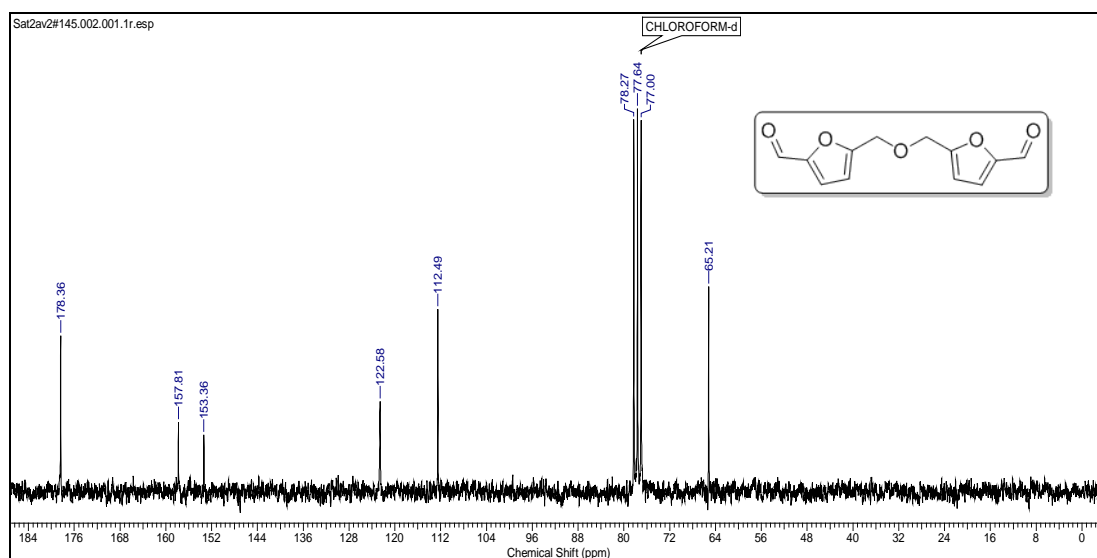
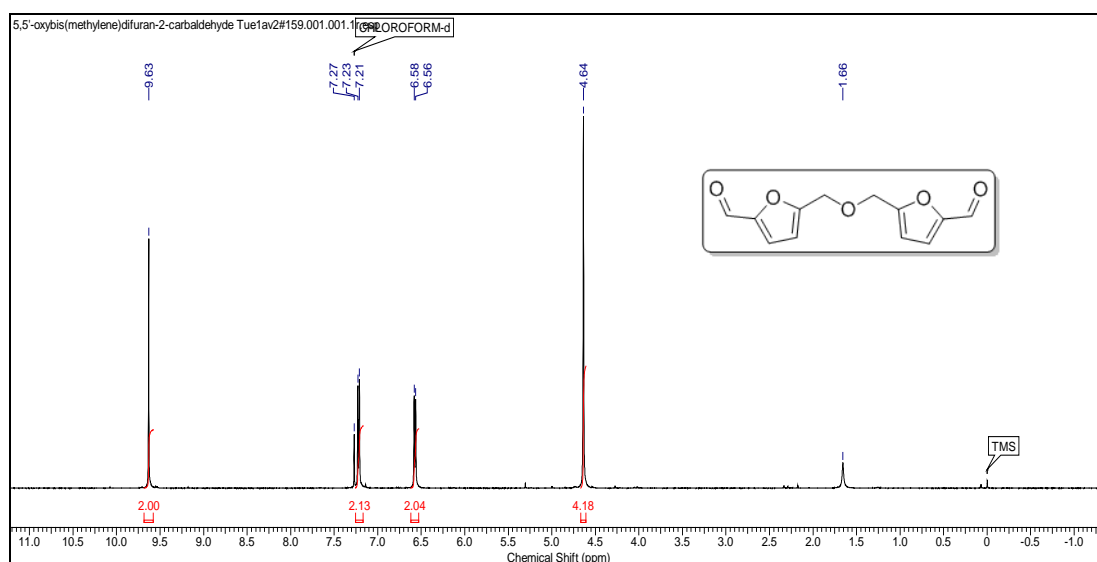
**5,5'-oxybis(methylene)difuran-2-carbaldehyde:** Brownish yellow crystals,  
Melting point= 112-114 °C.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , Relative to TMS,  $\delta$  ppm): 4.64 (s, 4H), 6.56-6.58 (d,  $J=3.54\text{Hz}$ , 2H), 7.21-7.23 (d,  $J=3.54$ , 2H), 9.63 (s, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , Relative to TMS,  $\delta$  ppm): 65.21, 112.49, 122.58, 153.36, 157.81, 178.36.

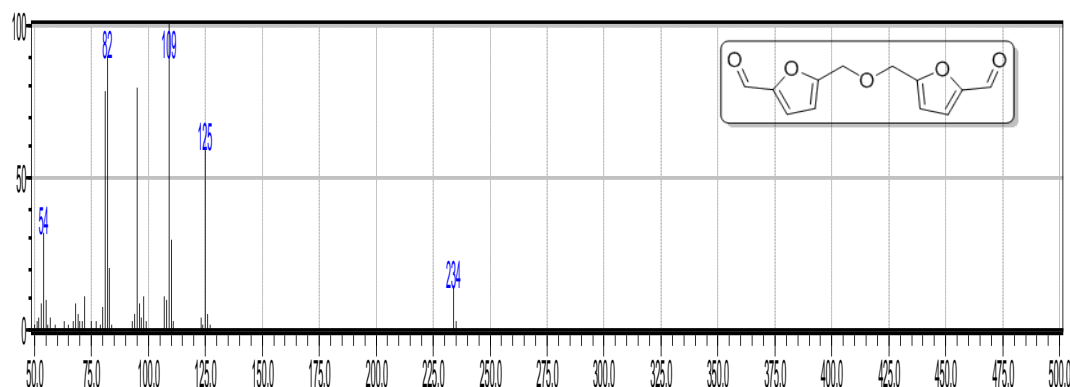
GC-MS data:  $\text{M}^+$  234 ( $\text{C}_{12}\text{H}_{10}\text{O}_5$ ), 125, 123, 110, 109, 96, 95, 82, 81 and 54

FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2924, 2853, 1677, 1523, 1023 and 807

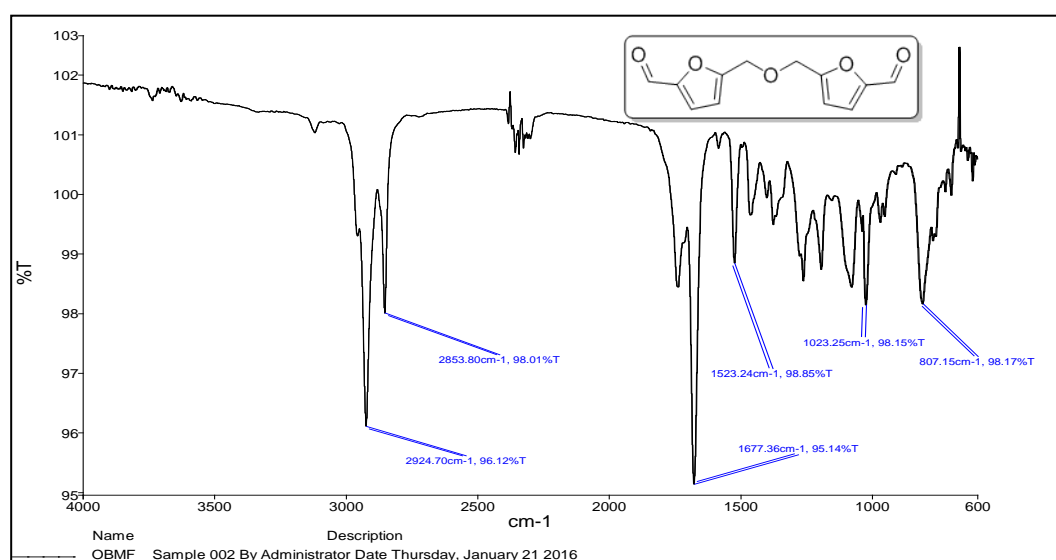




## GCMS



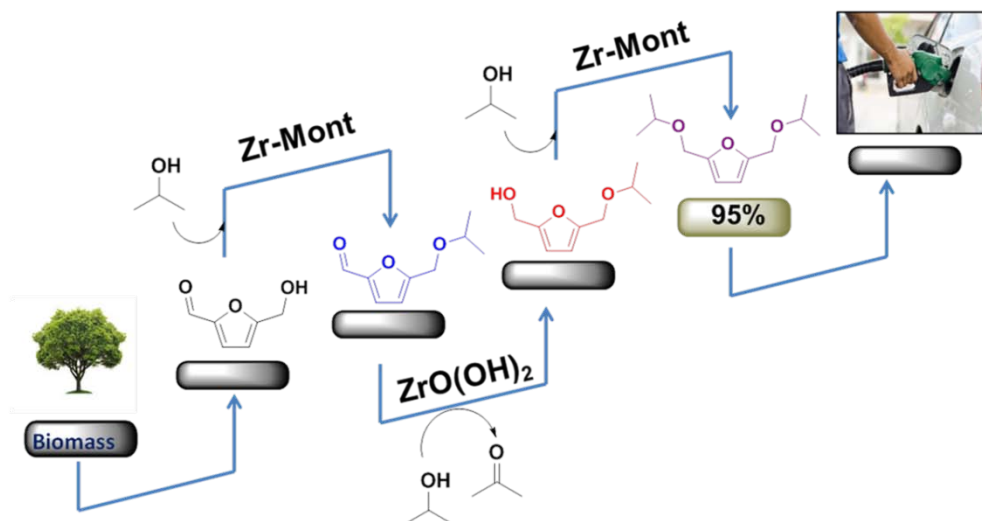
## FTIR



**5-(chloromethyl)furfural:** Brownish-Yellow liquid, The NMR of this compound is provided in **Chapter 4.3**.

**5-(2,4,6-trimethylbenzyl)furan-2-carbaldehyde, 5-(2,6-dimethylbenzyl)furan-2-carbaldehyde and 5-(4-methylbenzyl)furan-2-carbaldehyde:** The NMR of these compounds is provided in **Chapter 4.3**.

## 5.2. Cascade reductive-etherification of bio-derived aldehydes over Zr-based catalysts

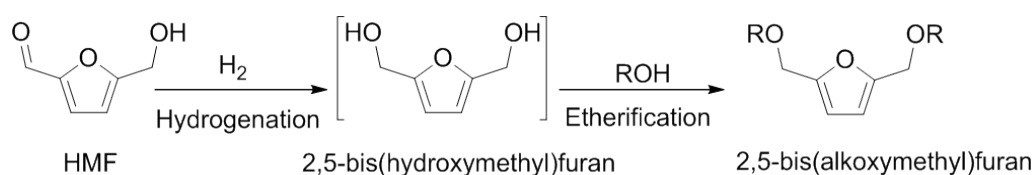


In this part an efficient one-pot catalytic cascade sequence for the production of value-added ethers from bioderived aldehydes is demonstrated. Etherification of 5-(hydroxymethyl)furfural with different aliphatic alcohols over acidic Zr–montmorillonite (Zr-Mont) catalyst produced a mixture of 5-(alkoxymethyl)furfural and 2-(dialkoxymethyl)-5-(alkoxymethyl)furan. The latter was selectively converted back into 5-(alkoxymethyl)furfural by treating it with water over the same catalyst. The synthesis of 2,5-bis(alkoxymethyl)furan was achieved through a cascade sequence involving etherification, transfer hydrogenation, and re-etherification over a combination of acidic Zr-Mont and the charge-transfer hydrogenation catalyst [ $\text{ZrO}(\text{OH})_2$ ]. This catalyst combination was further explored for the cascade conversion of 2-furfuraldehyde into 2-(alkoxymethyl)furan. The scope of this strategy was then extended for the reductive etherification of lignin-derived aryl aldehydes to obtain the respective benzyl ethers in > 80% yield. Additionally, the mixture of Zr-Mont and  $\text{ZrO}(\text{OH})_2$  does not undergo mutual destruction, which was proved by recycling experiments and XRD analysis. Both the catalysts were thoroughly characterized using BET, temperature-programmed desorption of  $\text{NH}_3$  and  $\text{CO}_2$ , pyridine-FTIR, XRD, inductively coupled plasma optical emission spectroscopy and X-ray photoelectron spectroscopy techniques.

Suhas Shinde, Chandrashekhar Rode, *ChemSusChem* **2017**, 10, 4090–4101

### 5.2.1. Introduction

HMF can be transformed into a number of important compounds that are expedient and important intermediates for the production of fine chemicals and monomers, including furan derivatives such as 2,5-furandicarboxylic acid, 2,5-diformylfuran, 2,5-bis(hydroxymethyl)furan, and nonfuranic compounds such as levulinic acid, 1,6-hexanediol, adipic acid, caprolactam and caprolactone [1]. One such example is the HMF ether 5-(ethoxymethyl)furfural (EMF), which can be used directly as a fuel or fuel additive (owing to its high cetane number and high energy density) and also as a flavoring and aroma component. EMF was first synthesized by a simple nucleophilic substitution reaction between 5-(chloromethyl)furfural (CMF) and ethanol at room temperature [2a]. Following this, the preparation of EMF from carbohydrates and HMF was studied using a variety of acids such as metal halides [2], mineral acids [3], organic acids and resins [3b], solid acids [4] and acidic ionic liquids [5]. Interestingly, ethers of HMF obtained from branched alcohols have superior blending properties as compared to ethers obtained from linear analogues. For example, up to 40 vol. % of 5-(tert-butoxymethyl)furfural (*t*-BMF) was completely soluble in commercial diesel and did not have any mixing or flocculation problems [6]. This 40:60 *v/v* *t*-BMF/diesel blend ratio leads to a substantial increase in the cetane number and does not decrease the oxidation stability of commercial diesel [7]. The preparation of *t*-BMF was achieved by reacting HMF with tert-butanol in the presence of montmorillonite K10 and zeolite HY to give HMF conversion of 49 and 59 % with selectivities to *t*-BMF of 76 and 79 %, respectively [7]. However, a major concern about 5-(alkoxymethyl)furfural is the presence of an aldehyde functionality, which reduces the stability of the molecule. Hence, it is desirable to first hydrogenate the aldehyde functionality to an alcohol [8] followed by subsequent etherification to form stable 2,5-bis(alkoxymethyl)furan (Scheme 5.2.1) [3b]. An added advantage of the two ether linkages in the 2,5-bis(alkoxymethyl)furan is its enhanced miscibility in commercial diesel and lowering of the crystallization temperature compared with that of 5-(alkoxymethyl)furfural [8]. Therefore, it is of seminal interest to produce 2,5-bis(alkoxymethyl)furan directly from HMF by a less energy intensive process.



**Scheme 5.2.1.** Process for production of 2,5-bis(alkoxymethyl)furan from HMF.

### 5.2.2. Literature survey

There have been reports on the use of a combination of Pt (noble metal) and acid catalysts under external  $\text{H}_2$  pressure to obtain moderate to good yields of 2,5-bis(alkoxymethyl)furan [3b, 9]. In the hydrogenation process, besides the high cost of external  $\text{H}_2$ , the  $\text{H}_2$  is non renewable and its safe transportation, storage, and handling are the deterring factors for its widespread usage. Therefore, catalytic transfer hydrogenation (CTH) through the Meerwein–Ponndorf–Verley (MPV) reaction using sacrificial alcohols as hydrogen donors is the preferred alternative to the use of external hydrogen. There have been very few studies in this regard; for example, the use of Lewis acids such as Sn- $\beta$  and Hf- $\beta$  zeolites, in either batch or continuous modes, for cascade reductive etherification of HMF to 2,5-bis(alkoxymethyl)-furan [10]. However, for the synthesis of Sn or Hf- $\beta$ , a certain amount of hydrofluoric acid (HF) must be used [11], which is highly corrosive, easy to volatilize, and is very harmful to human beings and the environment. Luo et al. studied various metal oxides with and without an SBA-15 support and zeolites for transfer hydrogenation–etherification of HMF in 2-propanol. Only 80 % conversion of HMF with 60 % selectivity to 2,5-bis-(isopropoxymethyl)furan was achieved [12].

### 5.2.3. Scope of the present work

We report here, a mixed catalyst system, composed of  $\text{ZrO}(\text{OH})_2$  and Zr–montmorillonite (Zr-Mont), showing an excellent performance for a one-pot cascade reductive etherification of HMF with secondary alcohols through MPV reduction. One of the catalysts from the mixed catalyst system is  $\text{ZrO}(\text{OH})_2$ , which was employed for MPV reduction of the aldehyde functionality present in HMF. The  $\text{ZrO}(\text{OH})_2$  catalyst was prepared by simple precipitation from  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  [13]. Zr-

Mont works alongside  $\text{ZrO}(\text{OH})_2$  in the cascade reductive etherification reaction where it catalyzes the etherification of the -OH functionality of reduced aldehydes. Zr-Mont was prepared by simply mixing montmorillonite with aqueous  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  [14] and exhibits Brønsted/Lewis acidity and high thermal and water stability. After proving the efficacy of the mixed catalyst system, the cascade reductive etherification of furfural and vanillin were explored. Moreover, this catalyst mixture does not undergo mutual deactivation and could be efficiently recycled. Most importantly, dehydrogenated products produced from sacrificial H-donors (alcohols) could be easily recycled through hydrogenation or used as industrial chemicals [15].

## 5.2.4. Experimental Section

### 5.2.4.1. Materials

All the materials/chemicals were used as received. 5-(Hydroxymethyl)furfural, 2-furfuraldehyde, furfuryl alcohol and 4-hydroxy-3-methoxybenzaldehyde were purchased from Sigma–Aldrich, India. All the alcohols and solvents used were received from Chem Labs India. Aqueous ammonia (30 %),  $\text{ZrO}_2$ , and the metal precursors  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  were purchased from Thomas Bakers. Montmorillonite  $[(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2 (\text{Si}_4\text{O}_{10}) (\text{OH})_2 \cdot n\text{H}_2\text{O}]$  (CAS No. 1302-78-9) with the composition (mass %)  $\text{SiO}_2$  (66.5),  $\text{Al}_2\text{O}_3$  (8.79),  $\text{Fe}_2\text{O}_3$  (1.64),  $\text{CaO}$  (1.64),  $\text{MgO}$  (3.03),  $\text{TiO}_2$  (2.06),  $\text{K}_2\text{O}$  (0.19),  $\text{Na}_2\text{O}$  (0.14) and Amberlyst-15 were purchased from Sigma–Aldrich India. Conc.  $\text{H}_2\text{SO}_4$  (98 %) was purchased from Thomas Bakers. Reaction intermediates such as 5-(isopropoxymethyl)furan-2-yl)methanol and Alkyl levulinates were prepared in house.

### 5.2.4.2. Preparation of Zr-Mont

Preparation of Zr-Mont is provided in section 4.1.4.2. of **Chapter 4.1.**

### 5.2.4.3. Preparation of metal hydroxides

The hydroxides of Al, Sn, Ni and Zr were prepared by a precipitation process [16]. In atypical preparation, the metal chloride precursor (10 g) was precipitated out as the respective hydroxide by the addition of aqueous  $\text{NH}_3$  until the pH of the solution was 9–10. Then, the mixture was aged for 24 h, filtered, and the residue washed with

plenty of distilled water until the pH of the filtrate was neutral. The residue was subsequently dried at 110 °C for 12 h and ground to a powder in a mortar with a pestle and stored in a glass bottle.

#### 5.2.4.4. Catalyst characterization

The methods and instrumentation used for the BET surface area, XRD, NH<sub>3</sub>-TPD, EDS and ICP analysis of catalysts is provided in **Chapter 2**. CO<sub>2</sub>-TPD was performed on a Micromeritics ChemiSorb 2720 instrument. In the typical experiment, the catalyst (0.05 g) was taken in a U-shaped, flow through, quartz sample tube. The catalyst was pre-treated in He (25 cm<sup>3</sup>min<sup>-1</sup>) at 200 °C for 1h. Then, the helium was replaced by CO<sub>2</sub> gas to adsorb over the surface of the catalyst for 30 min and then again replaced with helium. The temperature was increased to 700 °C with 10 °C min<sup>-1</sup> ramps and the CO<sub>2</sub> concentration in the effluent was monitored with a gold-plated filament thermal conductivity detector.

#### 5.2.4.5. Synthetic procedures

##### 5.2.4.5.1. Synthesis of 5-(alkoxymethyl)furfural from 5-(hydroxymethyl)furfural

A mixture of HMF (0.252 g, 2 mmol), Zr-Mont (0.1 g), and the alcohol (5 mL) was heated at 100 °C for 12 h in a round bottom flask attached with a reflux condenser. After the complete consumption of HMF (analyzed by using HPLC), water (0.5 mL) was added to the reaction mixture and further heated at 100 °C for 2h. After that reaction was cooled to room temperature and filtered, the catalyst was washed with ethyl acetate (10 mL x 2). The mother liquor was further washed with water (10 mL) and the separated organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude residue as passed through a silica bed to afford pure 5-(alkoxymethyl)furfural.

##### 5.2.4.5.2. Synthesis of 2,5-bis(alkoxymethyl)furan from 5-(hydroxymethyl)furfural

In a pressure reactor, a mixture of HMF (0.252 g, 2 mmol), ZrO(OH)<sub>2</sub>/Zr-Mont (1:1 w/w, 0.1:0.1 g) and the alcohol (5 mL) were heated at 150 °C for 1h. The progress of the reaction was monitored by analyzing the sample with HPLC and GC. After the reaction was complete, the reaction mixture was filtered and the catalyst bed was washed with ethyl acetate (10 mL x 3). The mother liquor was washed with water (10 mL) and the separated organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and

evaporated under reduced pressure. The crude residue was passed through a silica bed to afford pure 2,5-bis(alkoxymethyl)furan.

#### ***5.2.4.5.3. Synthesis of 2-(alkoxymethyl)furan from 2-furfuraldehyde***

In a pressure reactor, a mixture of 2-furfuraldehyde (0.192 g, 2 mmol),  $\text{ZrO}(\text{OH})_2/\text{Zr-Mont}$  (1:1 w/w, 0.1:0.1 g) and the alcohol (5 mL) were heated at 100 °C for 1h. The progress of the reaction was monitored by analyzing the sample with HPLC and GC. After that reaction mixture was filtered, the catalyst was washed with ethyl acetate (10 mL x 3). The mother liquor was washed with water (10 mL) and the separated organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure to afford 2-(alkoxymethyl)furan.

#### ***5.2.4.5.4. Synthesis of alkoxymethylbenzene from vanillin***

In a pressure reactor, a mixture of vanillin (0.304 g, 2 mmol),  $\text{ZrO}(\text{OH})_2/\text{Zr-Mont}$  (1:1 w/w, 0.1:0.1 g) and the alcohol (5 mL) were heated at 100 °C for 8h. After completion of the reaction, the mixture was filtered and the catalyst was washed with ethyl acetate (10 mL x 3). The mother liquor was washed with water (10 mL) and the separated organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. The crude residue was passed through a silica bed to afford pure alkoxymethylbenzene.

#### ***5.2.4.5.5. Synthesis of (5-(isopropoxymethyl)furan-2-yl)methanol***

A methanolic solution of 5-(isopropoxymethyl)-2-furfural (0.2 g, 1.19 mmol in 5 mL of methanol) was cooled to 0 °C.  $\text{NaBH}_4$  (0.09 g, 2.38 mmol) was then added lot-wise under stirring. The reaction mixture was allowed to warm at 25 °C over a period of 3 h and stirred overnight at room temperature. The reaction was carefully quenched with saturated solution of NaCl (40 mL) and stirred for next 6 h. The methanol in the reaction mixture was evaporated and remaining mixture was extracted with ethyl acetate (3 x 10 mL). The organic layers was combined and washed with saturated solution of NaCl (15 mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Subsequently, solvent was evaporated to afford colourless oil. Crude residue was passed through silica to obtain pure product in 80 % yield.

**5.2.4.5.6. Synthesis of 2-butyllevulinate**

In a 50 mL round bottom flask mixture of levulinic acid (1 g, 0.0086 mol), 2-butanol (20 mL) and Amberlyst-15 (0.250 g, 25 wt %) was heated at 70 °C for 12 h. Reaction was cooled to room temperature and saturated solution of NaHCO<sub>3</sub> (20 mL) was added. Resultant solution was extracted with ethyl acetate (25 mL x 2) then a combined organic layer was washed with water (25 mL) and brine (25 mL). Organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to afford crude 2-butyllevulinate. Further, crude product was distilled under reduced pressure to obtain pure 1.0 g (yield, 67 %) of 2-butyllevulinate.

**5.2.4.5.7. Synthesis of 2-propyllevulinate**

In a 50 mL round bottom flask mixture of levulinic acid (1 g, 0.0086 mol), 2-propanol (20 mL) and Amberlyst-15 (0.250 g, 25 wt %) was heated at 70 °C for 12 h. Reaction was cooled to room temperature and saturated solution of NaHCO<sub>3</sub> (20 mL) was added. Resultant solution was extracted with ethyl acetate (25 mL x 2) then a combined organic layer was washed with water (25 mL) and brine (25 mL). Organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to afford crude 2-propyllevulinate. Further, crude product was distilled under reduced pressure to obtain pure 2-propyllevulinate. (Yield: 0.98 g 72 %).

**5.2.4.5.8. Catalyst recycle**

In a pressure reactor, a mixture of HMF (0.252 g, 2 mmol), ZrO(OH)<sub>2</sub>/Zr-Mont (1:1 w/w, 0.1:0.1 g) and 2-propanol (5 mL) were heated at 150 °C for 1h. After that reaction mixture was filtered, the catalysts bed was washed with ethyl acetate (10 mL x 3). The catalyst was dried at 110 °C for 2 h before it was reused for the next run. After each run, fresh starting materials (HMF and 2-propanol) were loaded into the reactor and treated with the reused catalyst. The same procedure was repeated for each recycle.

**5.2.4.6. Analysis of the reaction products**

The conversion of 5-(hydroxymethyl)furfural and 2-furfuraldehyde was calculated by using Agilent HPLC (column: Poroshell 120 EC-C18 2.7 mm, detector: UV, and mobile phase : 0.1 % acetic acid in Millipore water/acetonitrile (85 :15 v/v) with 0.6 mL min<sup>-1</sup> flow). The selectivity of the ethers was calculated using GC with a flame ionization detector and a capillary column (HP5).



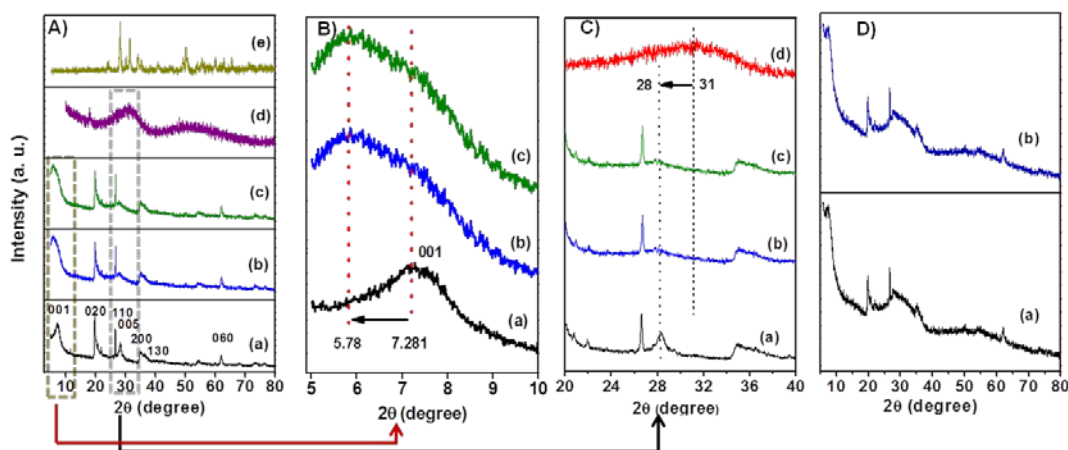
## 5.2.5. Results and Discussion

### 5.2.5.1. Catalyst characterization

#### 5.2.5.1.1. XRD analysis

Powder XRD patterns of montmorillonite,  $\text{Zr}^{4+}$ -exchanged montmorillonite,  $\text{ZrO}(\text{OH})_2$  and  $\text{ZrO}_2$  samples are shown in Figure 5.2.1. The  $d_{001}$  basal spacing for the reflection at  $2\theta = 7.2818^\circ$  corresponds to the  $(0\ 0\ 1)$  plane of the parent montmorillonite [17]. After insertion of  $\text{Zr}^{4+}$  into the montmorillonite layers, the  $(0\ 0\ 1)$  peak was shifted from  $2\theta = 7.2818^\circ$  to  $2\theta = 5.788^\circ$ . In addition, the  $(0\ 0\ 1)$  peak for Zr-Mont was broadened in comparison to the parent montmorillonite (Figure 5.2.1B). An expansion of d spacing from 12.13 to 15.26 Å was also observed for the Zr-Mont sample. These observations clearly indicated that delamination of the montmorillonite layers occurred, owing to a higher extent of polarizability of the  $\text{Zr}^{4+}$  cation. A similar observation was reported for the irregular stacking of the layers in acid-activated montmorillonite clay [18]. Meanwhile, the peak at  $2\theta = 28.08^\circ$  corresponding to the  $(0\ 0\ 5)$  plane of the parent montmorillonite was not detected in Zr-Mont, indicating that Zr-Mont lost multilayered regularity in the perpendicular direction to each montmorillonite unit. Further evidence of delamination was the increase in surface area of the parent montmorillonite from 19 to 196  $\text{m}^2\text{g}^{-1}$  after  $\text{Zr}^{4+}$  exchange [19]. These facts imply that Zr-Mont was not surrounded by parallel and regular aluminosilicate unit layers neatly stacked in a layer upon layer fashion [20]. However, the  $(0\ 2\ 0)$ ,  $(1\ 1\ 0)$ , and  $(0\ 6\ 0)$  peaks of the parent montmorillonite ( $k\ l\ 0$ ), were still observed in Zr-Mont. Therefore, although the neatly stacked arrangement of the aluminosilicate unit layer of montmorillonite was disturbed, each layer of the montmorillonite was intact during the ion-exchange process with aqueous  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ . The higher d value (15.26 Å) and the shifting of the  $(0\ 0\ m)$  peaks to lower  $2\theta$  confirmed that the zirconium species remained between the montmorillonite layers. In addition, a sharp peak at  $2\theta = 28.8^\circ$  in the parent montmorillonite was broadened and the intensity dropped after the  $\text{Zr}^{4+}$  exchange process. A broad peak at  $2\theta = 28.8^\circ$  in Zr-Mont corresponded to the formation of zirconyl hydroxide species in the montmorillonite layers (Figure 5.2.1Ab and Cb) [20], whereas the bulk  $\text{ZrO}(\text{OH})_2$  catalyst showed a broad peak at  $2\theta = 31.8^\circ$  (Figure 5.2.1C). As compared with bulk  $\text{ZrO}(\text{OH})_2$ , zirconyl hydroxide

present in the Zr-Mont catalyst showed a slight shifting of the  $2\theta$  value from  $31.8^\circ$  to  $28.8^\circ$ , which was due to the surrounding aluminosilicate layers (Figure 5.2.1C).

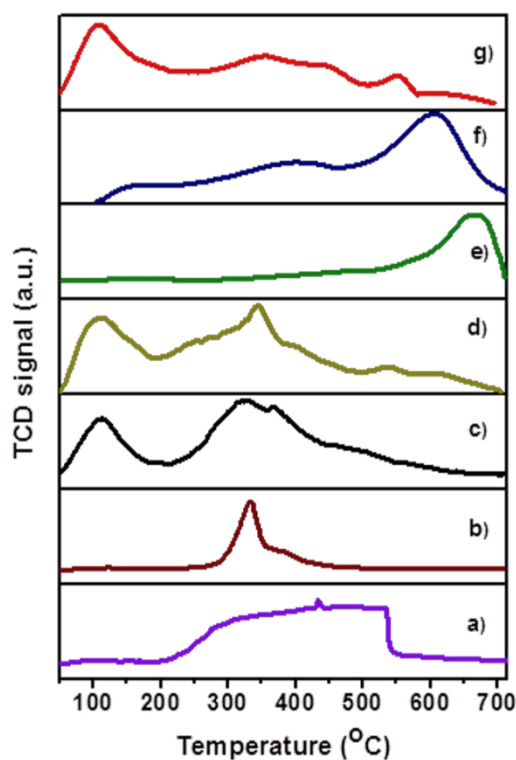


**Figure 5.2.1.** XRD analysis of A) a) montmorillonite, b) Zr-Mont, c) Zr-Mont-400, d)  $\text{ZrO}(\text{OH})_2$  and e)  $\text{ZrO}_2$ . B) Magnified XRD between  $2\theta = 5^\circ$  to  $10^\circ$  of a) montmorillonite, b) Zr-Mont and c) Zr-Mont-400. C) Magnified XRD between  $2\theta = 20^\circ$  to  $40^\circ$  of a) montmorillonite, b) Zr-Mont, c) Zr-Mont-400, d)  $\text{ZrO}(\text{OH})_2$  and e)  $\text{ZrO}_2$ . D) a) XRD of fresh Zr-Mont +  $\text{ZrO}(\text{OH})_2$  mixture and b) XRD of Zr-Mont +  $\text{ZrO}(\text{OH})_2$  mixture after 3<sup>rd</sup> recycle.

#### 5.2.5.1.2. $\text{NH}_3$ -TPD

The total acidity of all the prepared catalysts was estimated by using temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) analysis (Figure 5.2.3, Table 5.2.1). All of the metal hydroxides showed weak and moderate acidity peaks in their TPD profiles. Among these,  $\text{ZrO}(\text{OH})_2$  showed the highest acidity, owing to the highest Lewis acidic character as compared to other hydroxides. This was also confirmed by pyridine-FTIR (PyFTIR) analysis (see below, Figure 5.2.5Bd). The acidity trend was found to be as follows:  $\text{ZrO}(\text{OH})_2 > \text{Al}(\text{OH})_3 > \text{Sn}(\text{OH})_4 > \text{Ni}(\text{OH})_2$ . In the case of montmorillonite, only high acidic sites at 500–750  $^\circ\text{C}$  were observed (Figure 5.2.3e). The acidity of montmorillonite could be augmented by a cation exchange process. The Zr-Mont prepared by this method showed a distribution of acid sites in the three temperature regions: 17.69 % in region I (100–225  $^\circ\text{C}$ ) representing physically adsorbed ammonia or weak acidity, 36.92 % in region II (225–465  $^\circ\text{C}$ ) representing moderate acidity, and 38.46 % in region III (500–750  $^\circ\text{C}$ ) representing the high acidity region (Figure 5.2.3f). The acidity of a recovered mixture of Zr-Mont and

ZrO(OH)<sub>2</sub> catalysts was also estimated to determine the stability of the catalyst mixture (Figure 5.2.3g). Even after it was reused three times, the catalyst possessed acidity equivalent to the fresh catalyst of 0.24 mmol of NH<sub>3</sub>desorbed per gram (Table 5.2.1).



**Figure 5.2.3.** NH<sub>3</sub>-TPD profile for a) Al(OH)<sub>3</sub> b) Ni(OH)<sub>2</sub> c) Sn(OH)<sub>4</sub> d) ZrO(OH)<sub>2</sub> e) Montmorillonite, f) Zr-Mont and g) recovered mixture ZrO(OH)<sub>2</sub> + Zr-Mont after 3<sup>rd</sup> reuse.

**Table 5.2.1.** Textural properties of prepared catalysts

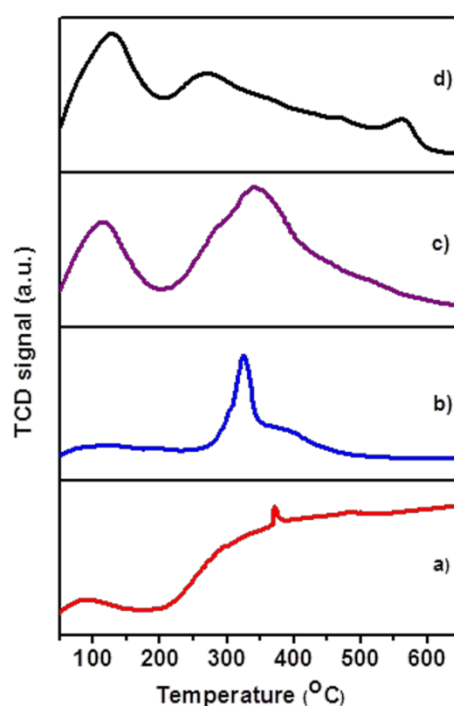
Catalyst	S <sub>BET</sub>	NH <sub>3</sub> desorbed mmol/g	CO <sub>2</sub> desorbed mmol/g	V <sub>micro</sub>	V <sub>meso</sub>
[Zr-Mont+ ZrO(OH) <sub>2</sub>	150	0.24	--	44	97
Zr-Mont	196	0.38	---	77	151
ZrO(OH) <sub>2</sub>	161.13	0.044	0.12	51	9
Sn(OH) <sub>4</sub>	35.49	0.029	0.15	40	6

Al(OH) <sub>3</sub>	85.59	0.041	0.13	38	7
Ni(OH) <sub>2</sub>	38	0.019	---	20	3
Mont	19	0.06	---	6	15

[a] Reused catalyst mixture after 3<sup>rd</sup> cycle

### 5.2.5.1.3. CO<sub>2</sub>-TPD

The basic strength of all the metal hydroxide catalysts was estimated by using temperature-programmed desorption of carbon dioxide (CO<sub>2</sub>-TPD) measurements (Figure 5.2.4). Al(OH)<sub>3</sub> gave rise to two CO<sub>2</sub> desorption peaks at 91 °C and 371 °C, which indicated that this material had weak and moderate basic sites (Figure 5.2.4a). Ni(OH)<sub>2</sub> gave rise to single CO<sub>2</sub> desorption peaks at 326 °C, which indicated moderate basic sites (Figure 5.2.4b). The Sn(OH)<sub>4</sub> sample gave rise to two significant CO<sub>2</sub> desorption peaks, one at 114 °C and another at 341 °C, which were assigned to the weak and medium basic sites (Figure 5.2.4c). In the ZrO(OH)<sub>2</sub> sample there was a significant CO<sub>2</sub> desorption peak at 128 °C, which was assigned to weak basic sites, whereas the peaks at 267 and 560 °C were associated with

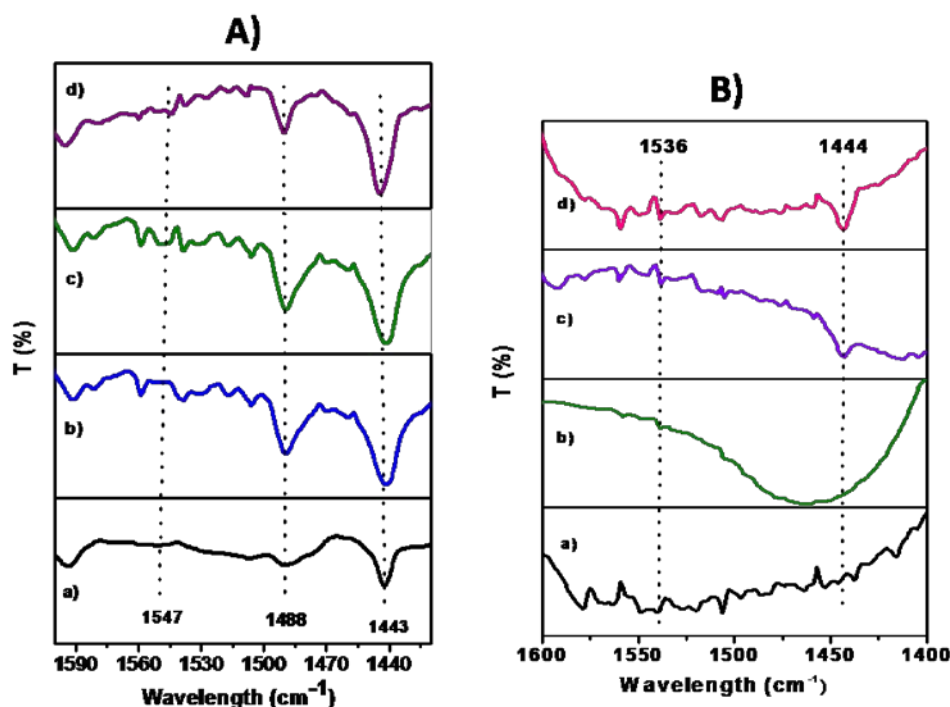


**Figure 5.2.4.** CO<sub>2</sub>-TPD profile for a) Al(OH)<sub>3</sub> b) Ni(OH)<sub>2</sub> c) Sn(OH)<sub>4</sub> and d) ZrO(OH)<sub>2</sub>

moderate and strong basicity, respectively (Figure 5.2.4d). Their basicity trend was as follows:  $\text{ZrO}(\text{OH})_2 < \text{Al}(\text{OH})_3 < \text{Sn}(\text{OH})_4 < \text{Ni}(\text{OH})_2$ .

#### 5.2.5.1.4. Pyridine FTIR

The nature of the acid sites of the prepared catalysts was determined by Py-FTIR (Figure 5.2.5A and B). Among the metal hydroxides, the spectra for  $\text{Al}(\text{OH})_3$  and  $\text{ZrO}(\text{OH})_2$  showed bands at  $1443 \text{ cm}^{-1}$ , which could be assigned to Lewis acid sites. Other metal hydroxides such as  $\text{Ni}(\text{OH})_2$  and  $\text{Sn}(\text{OH})_4$  did not show any visible band at  $1443 \text{ cm}^{-1}$ . The band at  $1548 \text{ cm}^{-1}$ , which indicates Brønsted acidity, was not observed for any of the metal hydroxides. In the case of montmorillonite, the band at  $1443 \text{ cm}^{-1}$  was observed, whereas the Brønsted acidity band at  $1548 \text{ cm}^{-1}$  was absent. Zr-Mont showed intense bands at  $1443 \text{ cm}^{-1}$  and  $1548 \text{ cm}^{-1}$  owing to Lewis ( $\text{Zr}^{4+}$ ) and Brønsted acidity, respectively. The band at  $1490 \text{ cm}^{-1}$  observed in Zr-Mont represented a combination of Lewis and Brønsted acidity (Figure 5.2.5Ac) [21]. The Brønsted acidity in Zr-Mont catalyst was due to the zirconyl hydroxide species surrounded by aluminosilicate layers. Interestingly, for Zr-Mont-400 (Zr-Mont

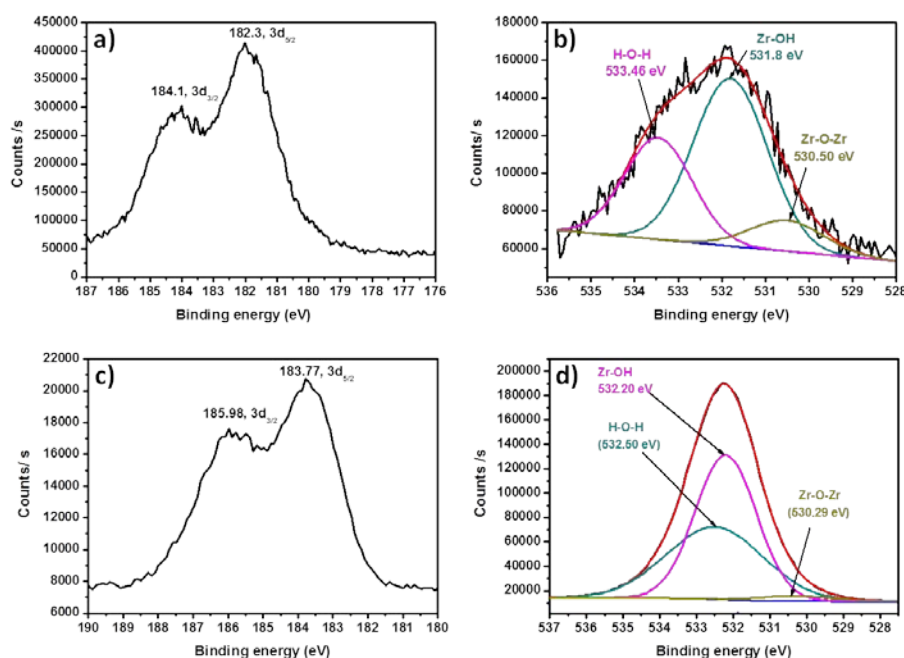


**Figure 5.2.5.** (A) Py-FTIR of Montmorillonite based catalysts a) Montmorillonite, b) Zr-Mont-400, c) Zr-Mont d) recovered mixture Zr-Mont +  $\text{ZrO}(\text{OH})_2$  after 3<sup>rd</sup> reuse and (B) Py-FTIR of metal hydroxide catalysts a)  $\text{Ni}(\text{OH})_2$ , b)  $\text{Sn}(\text{OH})_4$ , c)  $\text{Al}(\text{OH})_3$ , d)  $\text{ZrO}(\text{OH})_2$

calcined at 400 °C), the disappearance of band at 1548 cm<sup>-1</sup> was attributed to the loss of Brønsted acidity during the calcination process (Figure 5.2.5Ab). The bands at 1443 cm<sup>-1</sup> and 1548 cm<sup>-1</sup> were still observed for the recovered Zr-Mont + ZrO(OH)<sub>2</sub> catalyst mixture (Figure 5.2.5Ad). Thus, the combination of catalysts had an excellent stability and retained their acid sites even after it was used 3 times.

#### 5.2.5.1.5. XPS

The chemical status of zirconium in the ZrO(OH)<sub>2</sub> and Zr-Mont was analyzed by X-ray photoelectron spectroscopy (XPS; Figure 5.2.6). For the ZrO(OH)<sub>2</sub> sample, the binding energies of Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub> were recorded to be 182.3 and 184.1 The O1s XPS spectrum of the ZrO(OH)<sub>2</sub> sample showed three peaks (Figure 5.2.6b), which were attributed to Zr-O-Zr (530.50 eV), Zr-O-H (531.8 eV), and H-O-H (533.46 eV) [22]. The XPS of Zr-Mont showed peaks at binding energies of 183.77 and 185.98 eV (Figure 5.2.6c, d) owing to Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub>, respectively. The shifting of the binding energies of Zr in the Zr-Mont sample towards slightly

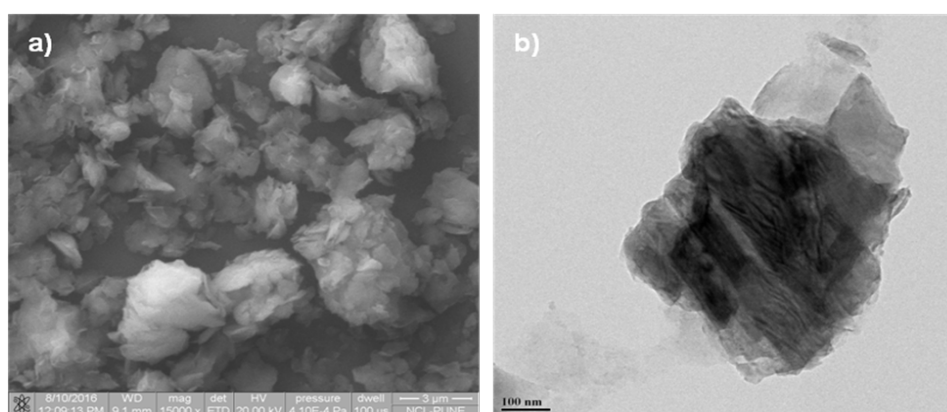


**Figure 5.2.6.** XPS analysis of ZrO(OH)<sub>2</sub> and Zr-Mont. a) XPS spectrum of Zr 3d for ZrO(OH)<sub>2</sub>; b) deconvolution result of XPS O 1s core-level spectra for ZrO(OH)<sub>2</sub>; c) XPS spectrum of Zr 3d for Zr-Mont; d) deconvolution result of XPS O 1s core-level spectra for Zr-Mont.

higher values as compared to bulk  $\text{ZrO}(\text{OH})_2$  was due to the change in the environment around the Zr species. Zr-Mont also showed three kinds of oxygen bonds in the XPS spectrum of O1s, albeit with a slightly different pattern (Figure 5.2.6d). The binding energy of the Zr-O-Zr species was 530.29 eV with reduced intensity. This evidenced the presence of Zr-O-Zr species in the montmorillonite layers. The binding energies of Zr-O-H and H-O-H species were recorded at 531.8 and 533.46 eV, respectively (Figure 5.2.6b). This confirmed that Zr was in the oxidation state IV in the  $\text{ZrO}(\text{OH})_2$  sample.

#### 5.2.5.1.6. SEM and TEM

Irregular arrangements of sheets were observed in the SEM image of Zr-Mont, which supported the fact that delamination of montmorillonite happened owing to  $\text{Zr}^{4+}$  insertion (Figure 5.2.7a). However, TEM analysis only suggested that the layered structure was maintained in montmorillonite even after  $\text{Zr}^{4+}$  insertion (Figure 5.2.7b).



**Figure 5.2.7.** a) SEM image of Zr-Mont, b) TEM image of Zr-Mont

#### 5.2.5.1.7 ICP-OES

The inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the parent montmorillonite and the Zr-Mont samples confirmed that almost all the exchangeable cations from the parent montmorillonite were replaced by  $\text{Zr}^{4+}$  through an ion-exchange process (Table 5.2.2).

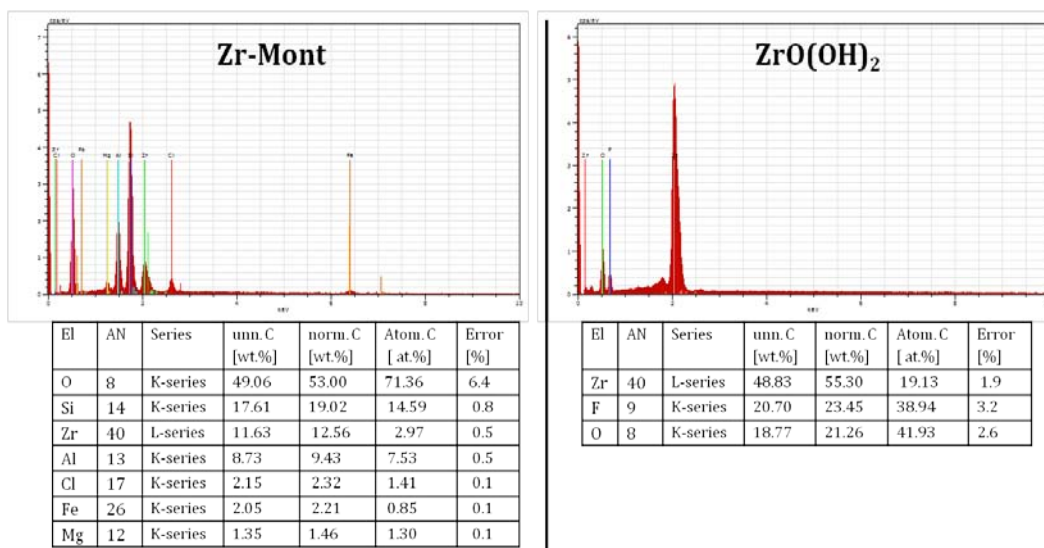


**Table 5.2.2.** ICP analysis of Mont catalysts

	Si	Mg	Ca	Al	K	Fe	Na	Ti	Sr	Ba	Zr	Cl
Mont	29.11	1.19	0.047	9.66	0.110	2.614	1.649	0.25	0.21	0.03	--	---
Zr-Mont	26.51	0.81	0.001	8.12	0.00	1.77	0.0009	0.01	0.008	0.00	9.19	1.91

**5.2.5.1.8. EDS**

The energy-dispersive X-ray spectroscopy analysis also showed that the content of  $\text{Zr}^{4+}$  in Zr-Mont catalyst was 12.56 wt % and all exchangeable cations were fully exchanged (Figure 5.2.8). In the case of the  $\text{ZrO}(\text{OH})_2$  catalyst, 55 % elemental Zr was present (Figure 5.2.8).

**Figure 5.2.8.** EDS spectrum of Zr-Mont and  $\text{ZrO}(\text{OH})_2$ **5.2.4.2. Catalyst screening**

Branched ethers of HMF have superior fuel-blending properties compared to linear ether analogues. Therefore, etherification of HMF was attempted with 2-propanol (branched alcohol) over different acid catalysts (Table 5.2.3). HMF was treated with 2-propanol over Zr-Mont at 100 °C for 12 h and was completely consumed to give a mixture of two products, 2-(diisopropoxymethyl)-5-(isopropoxymethyl)furan (**2**) and 5-(alkoxymethyl)furfural (**3**). Subsequently, product **2** was treated with water at 100 °C for 2 h in the same pot under the same reaction conditions to obtain **3** in 84%



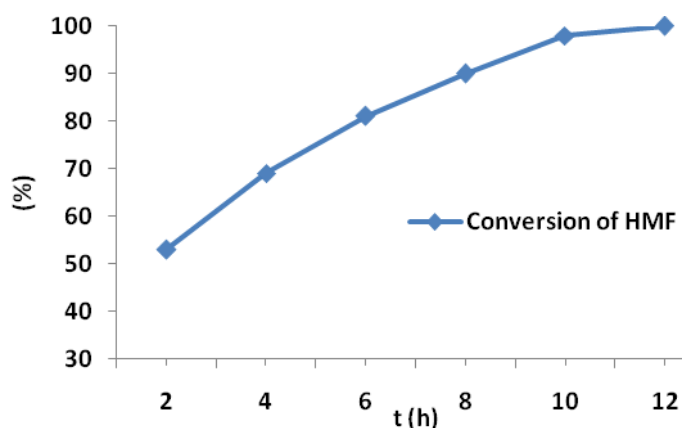
yield (Table 5.2.3, entry 1). However, when the loading of Zr-Mont was decreased from 0.1 g to 0.075 g, the conversion of HMF and yield of **3** were decreased to 89 and 78 %, respectively, owing to insufficient active sites (Table 5.2.3, entry 2). The yield of **3** did not improve even if the Zr-Mont loading was increased to 0.150 g (Table 5.2.3, entry 3), indicating that the optimal Zr-Mont loading was 0.1 g. The conversion versus time profile (Figure 5.2.9) for the reaction with Zr-Mont showed that the initial HMF conversion of < 50 % in the first two hours gradually increased with increasing reaction time and complete conversion of HMF was obtained after 12 h. Surprisingly, a calcined Zr-Mont-400 sample showed much lower HMF conversion of 45 and 34 % yield of **3** (Table 5.2.3, entry 4), because calcination at 400 °C caused the loss of Brønsted acidity owing to dehydration leading to a decrease in catalytic activity. The parent montmorillonite was also found to be an ineffective, owing to weak acid sites (Table 5.2.3, entry 5).  $\text{ZrO}_2$  and  $\text{ZrO}(\text{OH})_2$  individually were also almost ineffective for this reaction (Table 5.2.3, entries 6 and 7). In the presence of Amberlyst-15, HMF was consumed completely and **3** was obtained in 85 % yield, which was slightly higher than that obtained for Zr-Mont (Table 5.2.3, entry 8). However, Amberlyst-15 was no longer active for the next cycle, owing to its deactivation by water present in the reaction medium. A conventional etherification reagent, conc.  $\text{H}_2\text{SO}_4$  (10 mol %), was also evaluated for this transformation and gave complete conversion of HMF and a 79 % yield of **3**, which was lower than that obtained with Zr-Mont (Table 5.2.3, entry 9).

**Table 5.2.3.** Selective etherification of HMF with 2-propanol over different catalysts<sup>[a]</sup>

Entry	Catalyst	Loading	Conv. <sup>[b]</sup> [%]	Yield <sup>[c]</sup> of <b>3</b> [%]	TOF (h <sup>-1</sup> )
1	Zr-Mont	0.100 g	100	84	3.91

2	Zr-Mont	0.075 g	89	78	4.91
3	Zr-Mont	0.150 g	100	84	3.15
4	Zr-Mont-400	0.100 g	45	34	0.45
5	Mont	0.100 g	17	10	7.5
6	ZrO <sub>2</sub>	0.100 g	08	03	2.5
7	Zr(OH) <sub>2</sub>	0.100 g	00	00	00
8	Amberlyst-15	0.050 g	100	79	11.32
9	Conc. H <sub>2</sub> SO <sub>4</sub>	10 mol%	100	79	0.97

[a] Reaction conditions: Step I: HMF (0.252 g, 2 mmol), catalyst, 2-propanol (5 mL), 100 °C, 12 h. Step II: H<sub>2</sub>O (0.5 mL), 2 h. [b] Conversion of HMF determined using HPLC. [c] Yields are isolated after flash column chromatography.

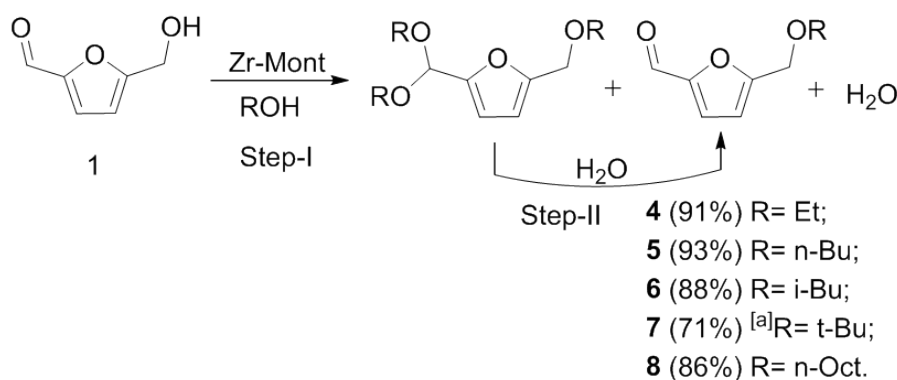


**Figure 5.2.9.** Conversion of HMF at different time. Reaction conditions: HMF (0.252 g, 2 mmol), 2-propanol (5 mL), Zr-Mont (0.1 g), 100 °C.

### 5.2.5.3. Scope of Zr-Mont for etherification of HMF

The scope of Zr-Mont as a solid acid catalyst was further explored for the etherification of HMF with different alcohols (Scheme 5.2.2). When HMF was treated with ethanol and *n*-butanol, the corresponding ethers **4** and **5** were formed in the highest yields (compared with ethers obtained from branched alcohol, such as

isopropyl alcohol) of 91 and 93 %, respectively. Etherification of HMF with 2-butanol provided ether **6** in 88 % yield. At a higher reaction temperature of 120 °C, complete consumption of HMF occurred to give the ether product **7** in 71 % yield, which was significantly higher than that reported previously [6]. However, at temperatures lower than 120 °C, the reaction of HMF with *t*-butanol did not reach completion and a low yield of **7** was obtained. The higher alcohol *n*-octanol also reacted with HMF to afford **8**, which is an important intermediate for the production of biodegradable surfactants, in 86 % yield [23].



**Scheme 5.2.2.** Selective synthesis of 5-(alkoxymethyl)furfural by etherification of HMF over Zr-Mont. Reaction condition: Step-I: HMF (0.252 g, 2 mmol), Zr-Mont (0.1 g), alcohol (5 mL), 100 °C, 12 h. Step-II: H<sub>2</sub>O (0.5 mL), 2 h. [a] HMF (0.252 g, 2 mmol), Zr-Mont (0.1 g), *t*-BuOH (5 mL), 120 °C, 24 h. Yields are isolated after flash column chromatography.

#### 5.2.5.4. Reductive etherification of HMF with 2-propanol

After successful etherification of HMF to 5-(alkoxymethyl)furfural over Zr-Mont, we converted the aldehyde functionality of 5-(alkoxymethyl)furfural to obtain 2,5-bis(alkoxymethyl)furan through CTH. 2,5-bis(alkoxymethyl)furan is inert and has a low freezing point and a high cetane number [24]. We expected the combination of Zr-Mont and the hydrogenation catalyst to catalyze the etherification and hydrogenation, respectively, in the same reactor without mutual destruction. A similar type of cascade reaction of furfural to  $\gamma$ -valerolactone was reported over a combination of silicate and zeolites system [25]. In this work, for the purpose of reductive etherification, 2-propanol was chosen as both hydrogen donor for the

reduction of the aldehyde functionality of HMF to give **9** and as a substrate for the etherification of **9**. This cascade reductive etherification of HMF was carried out at higher temperature (150 °C) over a mixture of Zr-Mont and different metal hydroxides and the results are presented in Table 5.2.4. The combination of Zr-Mont with hydroxides of Sn and Ni was ineffective for the hydrogenation step as only the ether products **2** and **3** were obtained (Table 5.2.4, entries 1 and 2). A combination of Zr-Mont and Al(OH)<sub>3</sub> showed 99 % conversion of HMF with 29 % selectivity to **10** (Table 5.2.4, entry 3). The inappropriate acid-base character, low surface area, and a low pore volume in the case of Sn(OH)<sub>4</sub> and Ni(OH)<sub>2</sub> were attributed to their inactivity for MPV reduction of HMF. However, Al(OH)<sub>3</sub> showed some activity in the MPV reduction of HMF, which could be due to its appropriate acid–base character, higher surface area, and higher pore volume than Sn(OH)<sub>4</sub> and Ni(OH)<sub>2</sub>. An encouraging result was obtained when ZrO(OH)<sub>2</sub> was used as a CTH catalyst in combination with Zr-Mont; HMF was completely consumed with an excellent selectivity of 95 % to the target ether **10** through transfer hydrogenation of **2** and **3** followed by etherification of **9** with 2-propanol in the same reactor (Table 5.2.4, entry 4).

**Table 5.2.4.** Cascade reductive etherification of HMF *via* CTH in 2-propanol <sup>[a]</sup>

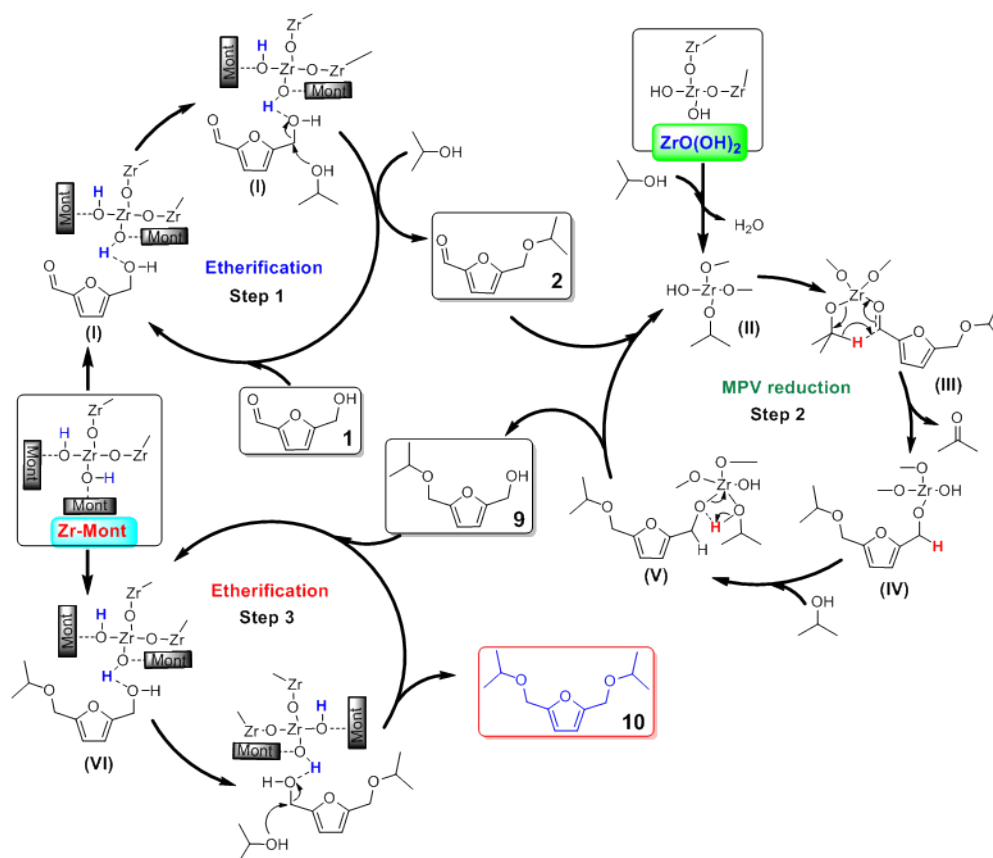
Entry	CTH Catalyst	Loading	<i>t</i> [h]	Conv. <sup>[b]</sup> [%]	Selectivity <sup>[c]</sup> [%]				
					2	3	9	10	Others <sup>[d]</sup>
1	Sn(OH) <sub>4</sub>	0.100 g	12	99	27	73	00	00	00
2	Ni(OH) <sub>2</sub>	0.100 g	12	99	29	71	00	00	00
3	Al(OH) <sub>3</sub>	0.100 g	12	99	19	52	00	29	00
4	ZrO(OH) <sub>2</sub>	0.100 g	1	100	00	Trace	00	95	05
5	ZrO(OH) <sub>2</sub>	0.075 g	1	100	00	07	00	90	03

6	ZrO(OH) <sub>2</sub>	0.150 g	1	100	00	Trace	00	94	06
7[e]	ZrO(OH) <sub>2</sub>	0.100 g	1	98	00	00	00	90	10
8[f]	ZrO(OH) <sub>2</sub>	0.100 g	1	90	00	00	00	92	08
9	ZrO <sub>2</sub>	0.100 g	1	99	19	58	00	23	00
10	---	---	12	100	25	75	00	00	00

[a] Reaction conditions: HMF (0.252 g, 2 mmol), 2-propanol (5 mL), Zr-Mont (0.1 g), CTH catalyst, 150 °C. [b] Conversion of HMF was determined by HPLC. [c] Selectivities of products were determined by GC. [d] Others comprised acetone and unknowns. [e] Using a crude HMF as substrate and reaction conditions for HMF synthesis: Fructose (1 g), Amberlyst-15 (0.4 g), DMSO (2 mL), MIBK (8 mL), 120 °C, 3 h, the crude HMF yield is 51% [f] Crude HMF obtained from bagasse was used as a substrate.

ZrO(OH)<sub>2</sub>, as a typical acid–base catalyst with the appropriate electronegativity, was much more effective for the CTH of HMF through MPV reduction compared to other metal hydroxides. [14] In addition, the high surface area and pore volume of ZrO(OH)<sub>2</sub> could be responsible for its superior activity compared with other metal hydroxides (Table 5.2.1). Therefore, ZrO(OH)<sub>2</sub> was selected as the preferred catalyst for the subsequent experiments. A lower loading (0.075 g) of ZrO(OH)<sub>2</sub> showed 90 % selectivity to **10** along with 7 % selectivity to **3** owing to insufficient active sites for complete hydrogenation of **3** (Table 5.2.4, entry 5). A higher loading of 0.150 g of ZrO(OH)<sub>2</sub> showed 94 % selectivity to **10**, which was similar to that obtained with 0.1 g of ZrO(OH)<sub>2</sub> loading (Table 5.2.4, entry 6). The scope of this tandem strategy was extended to the crude HMF obtained from fructose, in which 90 % selectivity to ether **10** was achieved (Table 5.2.4, entry 7). Another sample of crude HMF was also obtained directly from bagasse by using concentrated H<sub>2</sub>SO<sub>4</sub>. This crude HMF was also converted into **10** by the CTH process with 92 % selectivity (Table 5.2.4, entry 8). Conversion of the crude HMF into the desired products eliminated the necessity of energy-intensive separation/purification of HMF. This cascade reaction system is a cost-efficient process for the practical production of **10** from fructose and bagasse. For comparison, we performed reductive etherification of HMF over a mixture of ZrO<sub>2</sub> and Zr-Mont. In this experiment, only 23 % selectivity of the desired product

(10) was achieved (Table 5.2.4, entry 9). This might be because of the relatively low efficiency of  $\text{ZrO}_2$  for the MPV reduction of intermediates **2** and **3**. Next, without using  $\text{ZrO}(\text{OH})_2$ , **2** and **3** were formed in 24 and 75 % yields, respectively (Table 5.2.4, entry 10). Importantly, a mixture of Zr-Mont and  $\text{ZrO}(\text{OH})_2$  was stable and could be successfully recycled five times (Figure 5.2.6). This confirmed that there was no deactivation of individual active sites because of the mutual interaction of Zr-Mont and  $\text{ZrO}(\text{OH})_2$  under the experimental conditions. This combination catalyst system has one more advantage; both catalysts (Zr-Mont and  $\text{ZrO}(\text{OH})_2$ ) could be prepared from a single metal precursor ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ), which effectively reduces the cost of the process. In addition, both catalysts were prepared by a simple and eco-friendly method from cheap and commercially available raw materials. The proposed mechanism for the formation of 2,5-bis(isopropoxymethyl)furan from HMF is presented in Scheme 5.2.3.



**Scheme 5.2.3.** Plausible reaction mechanism for the cascade synthesis of 2,5-bis(isopropoxymethyl)furan from HMF over Zr-based catalysts.

The Brønsted acid sites present on Zr-Mont protonated the hydroxy group of HMF to form intermediate **I**, which was further reacted with 2-propanol to produce ether **3**. In the next step, ether **3** was a starting material for the MPV reduction, which proceeded over  $\text{ZrO}(\text{OH})_2$ . The six-membered cyclic transition state (**III**) was formed after interaction between **3** and the intermediate alkoxide **II**. Intermediate **IV** was produced by hydride transfer from alkoxide **II** to the carbonyl group of **3** by a concerted pathway releasing acetone. A four-member transition state (**V**) was generated by insertion of a second molecule of 2-propanol. [20] Then, the hydride was coordinated with two oxygen atoms and transferred from one oxygen to another oxygen atom to release alcohol **9**.  $\text{ZrO}(\text{OH})_2$  as a typical acid–base catalyst with the appropriate electronegativity and steric hindrance was much more effective for the MPV reduction of HMF. The -OH group of  $\text{ZrO}(\text{OH})_2$  is important during the reaction process and proposed to act as a site for ligand exchange with 2-propanol to form zirconium propoxide (**V**). In step 3, alcohol **9** underwent etherification with 2-propanol over Zr-Mont to produce 2,5-bis(isopropoxymethyl)furan (**10**).

#### 5.2.5.5. Influence of temperature on reductive etherification of HMF

The influence of reaction temperature on the cascade reductive etherification of HMF was also investigated and the results are shown in Table 5.2.5. At lower temperatures of 120 and 130 °C the yield of **10** was very low 3 and 13 %, respectively (Table 5.2.5, entries 1 and 2). If the reaction temperature was increased to 160 °C, the yield of **10** enhanced several fold to 94 % (Table 5.2.5, entry 3). However, the result obtained at 160 °C was comparable with that obtained at 150 °C (Table 5.2.5, entry 4), which was chosen as the optimum reaction temperature. The kinetics of the cascade reductive etherification of HMF was also studied; the activation energy was estimated to be 111.51 kJ mol<sup>-1</sup>.

**Table 5.2.5** Cascade reductive-etherification of HMF at different temperature <sup>[a]</sup>

Entry	T [°C]	<i>t</i> [h]	Conversion [%]	Selectivity <sup>[c]</sup> [%]			
				<b>2</b>	<b>3</b>	<b>10</b>	Others <sup>[d]</sup>
1	120	24	100	09	88	03	00

2	130	5	100	17	70	13	00
3	160	1	100	00	00	94	06

[a] Reaction conditions: HMF (0.252 g, 2 mmol), 2-propanol (5 mL), Zr-Mont (0.1 g) ZrO(OH)<sub>2</sub> (0.1 g). [b] Conversion of HMF was determined by HPLC. [c] Selectivities of products were determined by GC. [d] Others comprised acetone and unknowns.

#### 5.2.5.6. Screening of alcohols for reductive etherification of HMF

The efficient combination of Zr-Mont and ZrO(OH)<sub>2</sub> catalysts for the synthesis of 2,5-bis(isopropoxymethyl)furan from HMF and 2-propanol opens up the possibility of using different alcohols, such as 2-butanol, *n*-butanol, and ethanol (Table 5.2.6). In this regard, HMF was treated with 2-butanol over a mixture of Zr-Mont and ZrO(OH)<sub>2</sub> at 150 °C to give **10a** with the highest yield of 96 % (Table 5.2.6, entry 1). When HMF was heated at 150 °C with *n*-butanol over these Zr-based catalysts, **10b**

**Table 5.2.6.** Cascade reductive etherification of HMF in different alcohols <sup>[a]</sup>

<div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;"> <b>1</b>  <chem>O=C1C=CC(=O)CO1</chem> </div> <div style="text-align: center;"> <math>\xrightarrow[\text{ROH, 150 } ^\circ\text{C}]{\text{Zr-Mont, ZrO(OH)}_2}</math> </div> <div style="display: flex; gap: 10px;"> <div style="text-align: center;"> <math>\text{RO-CH}_2\text{-C}_4\text{H}_3\text{(O)-CH}_2\text{-C(OR)}_2</math>  <b>2a, R= i-Bu</b>  <b>2b, R= n-Bu</b>  <b>2c, R= Et</b> </div> <div style="text-align: center;"> <math>\text{RO-CH}_2\text{-C}_4\text{H}_3\text{(O)-CH}_2\text{-C(OR)}_2</math>  <b>3a, R= i-Bu</b>  <b>3b, R= n-Bu</b>  <b>3c, R= Et</b> </div> <div style="text-align: center;"> <math>\text{RO-CH}_2\text{-C}_4\text{H}_3\text{(O)-CH}_2\text{-C(OR)}_2</math>  <b>10a, R= i-Bu</b>  <b>10b, R= n-Bu</b>  <b>10c, R= Et</b> </div> </div> </div>							
Entry	Alcohol	t [h]	Conv. <sup>[b]</sup> [%]	Selectivity <sup>[c]</sup> [%]			
				<b>2 (a-c)</b>	<b>3 (a-c)</b>	<b>10 (a-c)</b>	Others <sup>[d]</sup>
1	<i>i</i> -BuOH	1	100	00	00	96	04
2	<i>n</i> -BuOH	3	100	17	31	49	03
3	EtOH	5	100	29	71	00	00

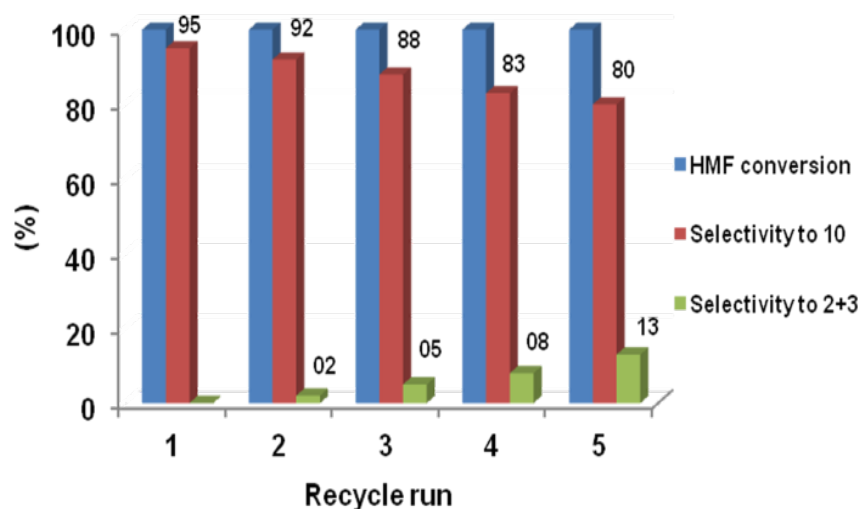
[a] Reaction conditions: HMF (0.252 g, 2 mmol), alcohol (5 mL), Zr-Mont (0.1 g), ZrO(OH)<sub>2</sub> (0.1 g), 150 °C. [b] Conversion of HMF was determined by HPLC. [c] Selectivities of products were determined by GC. [d] Others comprised 2-butanone, *n*-butanal and unknowns.



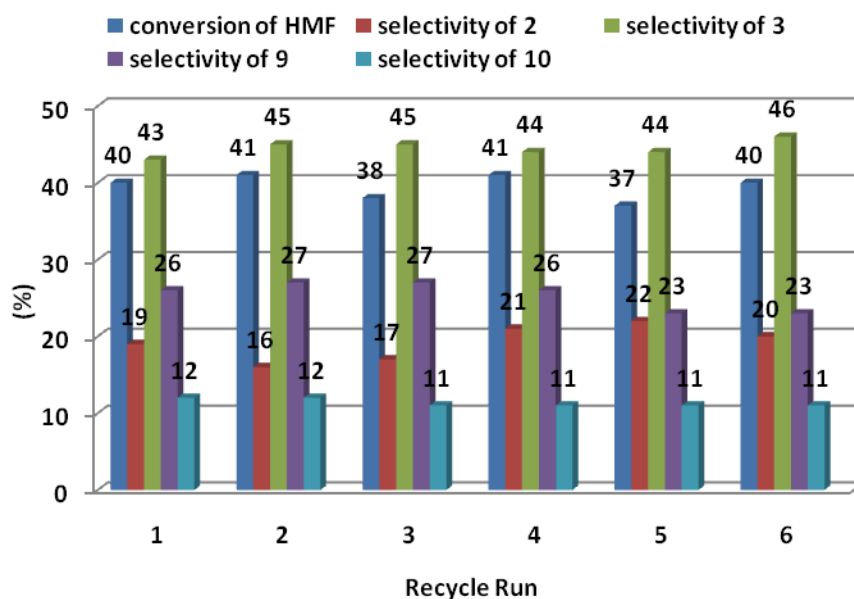
was produced in 49 % yield along with 17 % of **2b** and 31 % of **3b** (Table 5.2.6, entry 2). Under the experimental conditions and in presence of ethanol, **2c** and **3c** were formed in 29 and 71 % yields, respectively, without the formation of **10c** (Table 5.2.6, entry 3). The H-donor capability increased with increasing carbon chain length and degree of substitution of the alcohol. Of the tested alcohols, 2-propanol and 2-butanol demonstrated the highest H-donor activity. These findings are in accordance with previous reports that secondary alcohols have a higher tendency to release hydrogen than primary alcohols [15].

#### 5.2.5.7. Recycle studies of Zr-Mont and ZrO(OH)<sub>2</sub>

In a typical catalyst recycling study, the catalyst mixture was separated from the reaction mixture by filtration after the desired reaction time. The separated catalyst was washed with acetone (3 x 10 mL) and then dried at 110 °C for 2h before it was reused for the next run. The HMF conversion remained constant even after the catalyst mixture was reused 5 times (Figure 5.2.10). However, selectivity to **10** was considerably diminished from 95 to 80 %. The formation of products **2** and **3** started after the 2<sup>nd</sup> recycle and gradually increased to 13 % after the 5<sup>th</sup> recycle. This indicated that the hydrogenation ability of the ZrO(OH)<sub>2</sub> catalyst decreased owing to its partial deactivation, which was probably caused by carbon deposits on the catalyst surface during the reaction [13]. Although the selectivity to product **10** decreased with increasing number of recycles, the HMF conversion remained unchanged. This also implied that catalyst deactivation did not occur. The decreased selectivity to product **10** could be explained by competitive adsorption on the sites of Zr(OH)<sub>2</sub>; after its formation, the hydrogenation product **10** does not get desorbed easily from the sites of the Zr(OH)<sub>2</sub> catalyst and the adsorption of the intermediates **2** and **3** on the hydrogenation sites is retarded. This was indicated by accumulation of the intermediate products **2** and **3**. The catalyst stability was also confirmed by the recycle runs performed at lower conversion levels.



**Figure 5.2.10.** Recycle experiment for the reductive-etherification of HMF with 2-propanol over mixture of Zr-Mont +  $\text{ZrO}(\text{OH})_2$ . Reaction conditions: HMF (0.252 g, 2 mmol), 2-propanol (5 mL), Zr-Mont (0.1 g),  $\text{ZrO}(\text{OH})_2$  (0.1 g), 150 °C, 1 h.



**Figure 5.2.11** Catalyst recycles study at lower conversion of HMF. Reaction conditions: HMF (0.252 g, 2 mmol), 2-propanol (5 mL), Zr-Mont (0.1 g),  $\text{ZrO}(\text{OH})_2$  (0.1 g), 150 °C, 10 min.

As shown in the Figure 5.2.11 (recycling experiments at low conversion), consistent HMF conversion of approximately 40 % and the selectivity pattern confirmed the stability of the catalyst system. The stability of the catalyst mixture was also proved by the XRD patterns of fresh and reused catalysts. The XRD patterns of the fresh

and reused catalysts (after the 3<sup>rd</sup> recycle) in the catalyst mixtures were identical (Figure 5.2.1D). In addition, no leaching of Zr metal from the catalyst mixture was observed, which was confirmed by ICP-OES analysis.

#### 5.2.5.8 Reductive etherification of 2-furfuraldehyde with 2-propanol

Furfural is a key platform molecule that is easily accessible from the hydrolysis of hemicelluloses in acidic media to form xylose (pentose) and its subsequent dehydration [26]. Therefore, after the successful reductive etherification of HMF, we were encouraged to use the same catalyst system for the reductive etherification of 2-furfuraldehyde (bioderived aldehyde) to 2-(alkoxymethyl)furan. Importantly, 2-(alkoxymethyl)furans are valuable ether derivatives that can be used as fuel additives and flavor/aroma products [27]. Because 2-furfuraldehyde is more reactive than HMF, relatively milder reaction conditions were employed (Table 5.2.7).

**Table 5.2.7.** Cascade reductive-etherification of 2-furfuraldehyde over mixture of Zr-Mont and  $\text{ZrO}(\text{OH})_2$  <sup>[a]</sup>

Entry	T [°C]	t [h]	Conv. <sup>[c]</sup> [%]	Selectivity <sup>[d]</sup> [%]			
				12	13 (a-b)	14 (a-b)	Others <sup>[e]</sup>
1	90	4	77	27	47	22	4
2	100	2	100	9	67	20	4
3	120	2	100	7	57	33	3
4 <sup>[b]</sup>	100	2	100	6	69	21	4

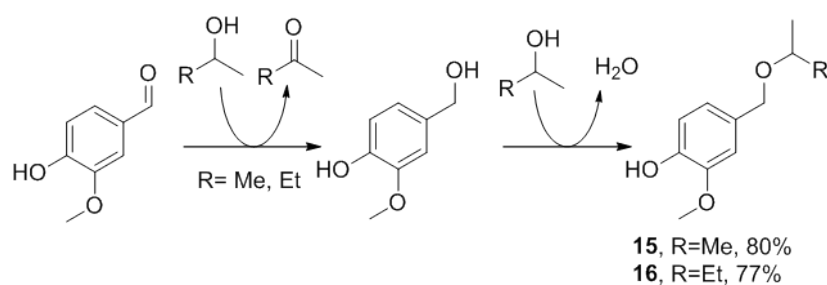
[a] Reaction conditions: 2-furfuraldehyde (0.192 g, 2 mmol), 2-propanol (5 mL), Zr-Mont (0.1 g),  $\text{ZrO}(\text{OH})_2$  (0.1 g). [b] 2-butanol (5 mL) was used as solvent. [c] Conversion

was determined using HPLC. [d] Selectivity was determined on GC. [e] Others comprised acetone, 2-butanone and unknowns.

Initially, the reaction was performed in 2-propanol at 90 °C; after 4 h, the conversion of 2-furfuraldehyde was only 77 % and the product distribution of **12**, **13a**, and **14a** was 27, 47 and 22 %, respectively (Table 5.2.7, entry 1). Therefore, the reaction was conducted at an elevated temperature of 100 °C, which resulted in the complete conversion of 2-furfuraldehyde. Interestingly, at 100 °C, the yield of the valuable ether **13a** was increased from 47 to 67 % (Table 5.2.7, entry 2). At 120 °C, the yield of the ring-opened product (**14a**, alkyl levulinate) was increased to 33 % (Table 5.2.7, entry 3). If 2-butanol was used instead of 2-propanol as a hydrogen donor and etherification agent, 2-furfuraldehyde was converted into **13b** in 69 % yield (Table 5.2.7, entry 4).

#### 5.2.5.9. Reductive etherification of vanillin with alcohols

The scope of the Zr-Mont and ZrO(OH)<sub>2</sub> catalyst system was further explored for the conversion of arylaldehydes, which can be obtained from other renewable materials, such as lignin. By using a mixture of Zr-Mont and ZrO(OH)<sub>2</sub>, 4-hydroxy-3-methoxybenzaldehyde (vanillin) was efficiently converted into the respective ether (Scheme 5.2.4).



**Scheme 5.2.4.** Cascade reductive-etherification of vanillin over mixture of Zr-Mont and ZrO(OH)<sub>2</sub>. Reaction conditions: vanillin (0.304 g, 2 mmol), 2-propanol/2-butanol (5 mL), Zr-Mont (0.1 g), ZrO(OH)<sub>2</sub> (0.1 g), 100 °C, 8 h.

4-Hydroxy-3-methoxybenzaldehyde is a depolymerization product of lignin [28]. The reductive etherification of vanillin was performed over a mixture of Zr-Mont

and  $\text{ZrO}(\text{OH})_2$  in 2-propanol or 2-butanol solvent at 100 °C. The respective ethers (**15** and **16**) were obtained in pure form and in excellent yields. These ethers could be used for making cosmetics, air fresheners, cleaning products, detergents, fabric conditioners, and flavor enhancers [29].

### 5.2.6. Conclusions

Herein, we have presented an efficient method for the production of higher grade fuel 2,5-bis(alkoxymethyl)furan from HMF through sequential etherification–hydrogenation–etherification reactions in one pot over a mixture of the two catalysts, Zr-Mont and  $\text{ZrO}(\text{OH})_2$ . Different sacrificial alcohols were screened for this reaction, among which secondary alcohols (2-propanol/2-butanol) showed excellent activity. The acidic character of Zr-Mont facilitated the etherification of HMF, whereas the acid–base characteristics of  $\text{ZrO}(\text{OH})_2$  facilitated the transfer hydrogenation of the reaction intermediates. The mixture of Zr-Mont and  $\text{ZrO}(\text{OH})_2$  did not undergo mutual deactivation, which was proved by recycling experiments and XRD analysis. This protocol was successfully explored for the conversion of 2-furfuraldehyde into 2-(alkoxymethyl)furan. A mechanistic pathway for the formation of 2,5-bis(isopropoxymethyl)furan was also proposed, in which the Brønsted acid sites of Zr-Mont protonated the hydroxyl group of HMF to form an ether. In the next step, the ether undergoes MPV reduction, which proceeded over  $\text{ZrO}(\text{OH})_2$ . In the third step, the alcohol formed by CTH underwent another etherification with 2-propanol over Zr-Mont to produce 2,5-bis(isopropoxymethyl)furan. The strategy developed here was also extended for the etherification of vanillin to their respective valuable ethers in excellent yields. The combination of Zr-Mont and  $\text{ZrO}(\text{OH})_2$  has the potential to convert a wide variety of bioderived and petroleum-derived substrates into valuable products.

### 5.2.7. References

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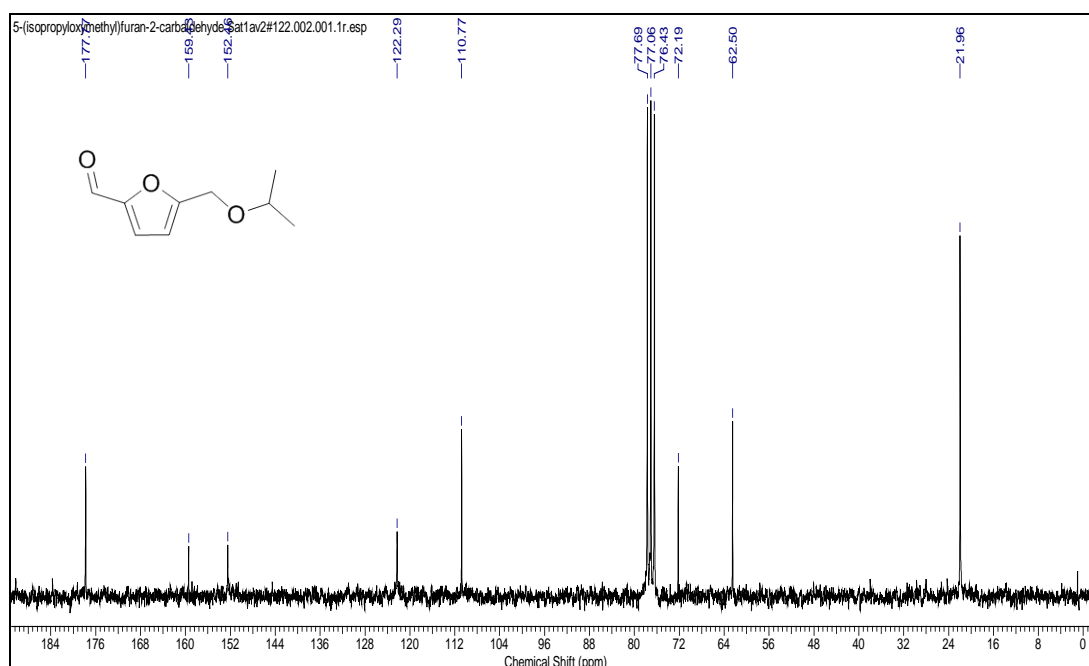
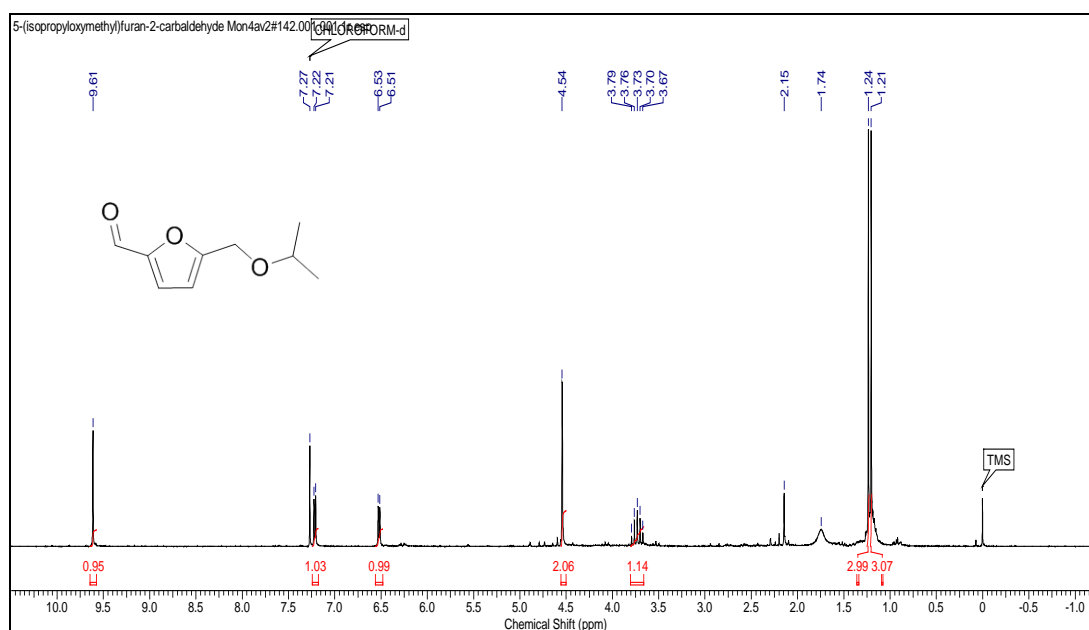
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### 5.2.8. NMR data of the synthesized compound

#### 5-(isopropoxymethyl)furan-2-carbaldehyde (3):

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.21 (s, 3 H) 1.24 (s, 3 H) 3.67-3.79 (quin,  $J=6.09$  Hz, 1 H) 4.54 (s, 2 H) 6.51-6.53 (d,  $J=3.54$  Hz, 1 H) 7.21-7.22 (d,  $J=3.54$  Hz, 1 H) 9.61 (s, 1 H)

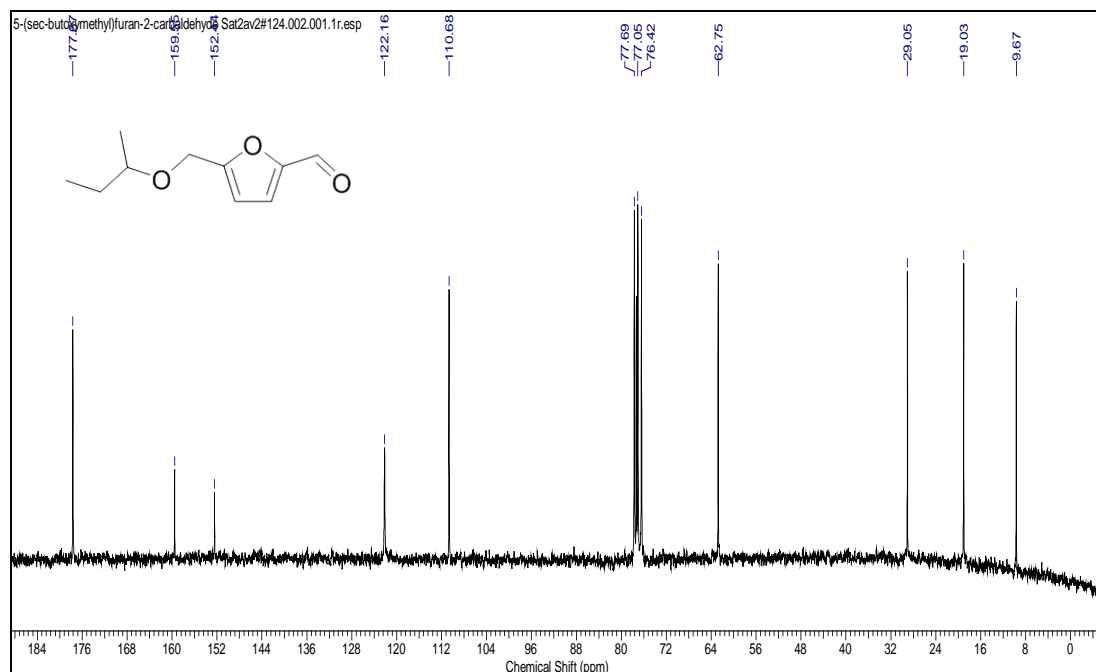
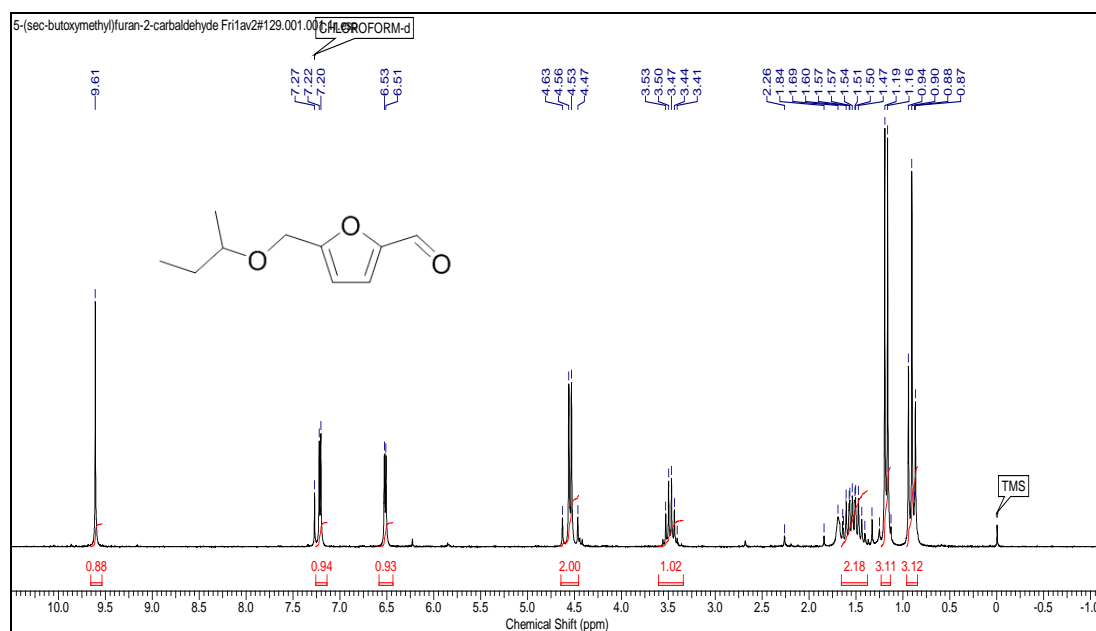
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 21.96, 62.50, 72.19, 110.77, 122.29, 152.46, 159.43, 177.77



**5-(*sec*-butoxymethyl)furan-2-carbaldehyde (6):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.87-0.94 (t, 3 H) 1.16-1.19 (d,  $J=6.19$  Hz, 3 H) 1.41-1.64 (m, 2 H) 3.41-3.56 (m, 1 H) 4.47 - 4.63 (m, 2 H) 6.51-6.53 (d,  $J=3.54$  Hz, 1 H) 7.20-7.22 (d,  $J=3.54$  Hz, 1 H) 9.61 (s, 1 H).

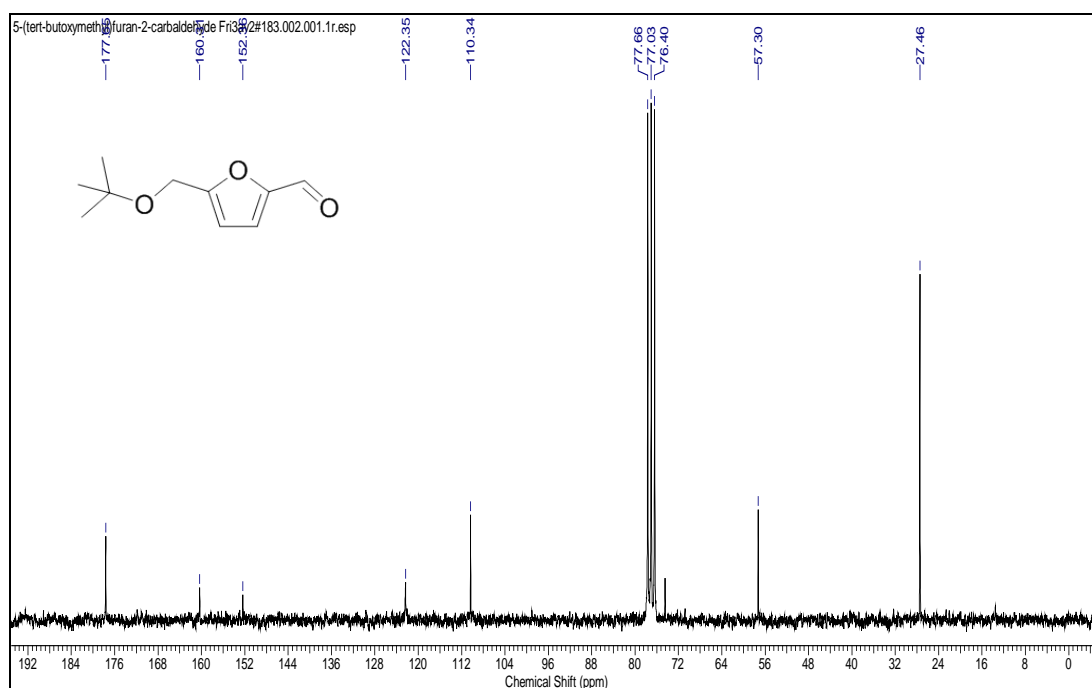
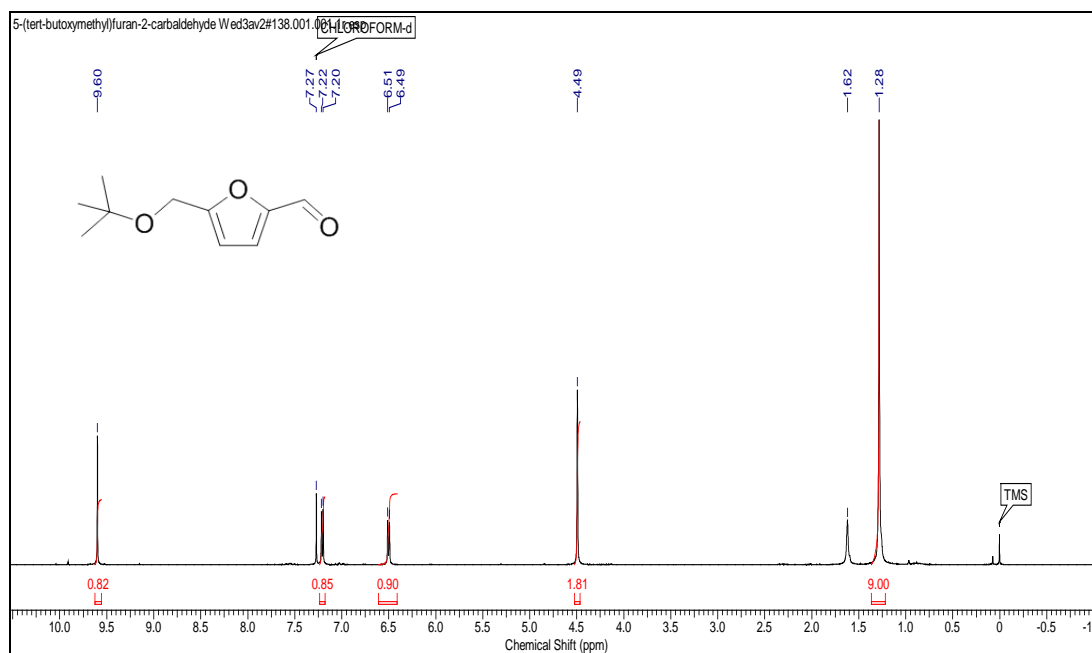
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 9.67, 19.03, 29.05, 62.75, 76.42, 77.34, 77.69, 110.68, 122.16, 152.44, 159.55s, 177.67.



**5-(*tert*-butoxymethyl)furan-2-carbaldehyde (7):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.28 (s, 9 H) 4.49 (s, 2 H) 6.49-6.51 (d,  $J=3.54$  Hz, 1 H) 7.20-7.22 (d,  $J=3.54$  Hz, 1 H) 9.60 (s, 1 H)

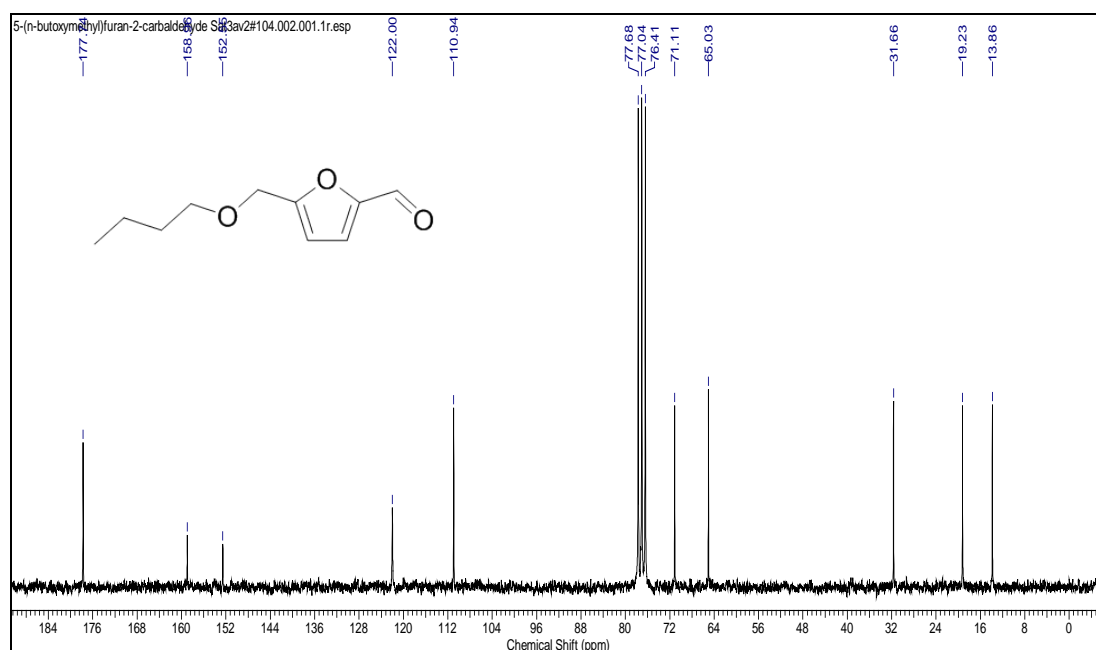
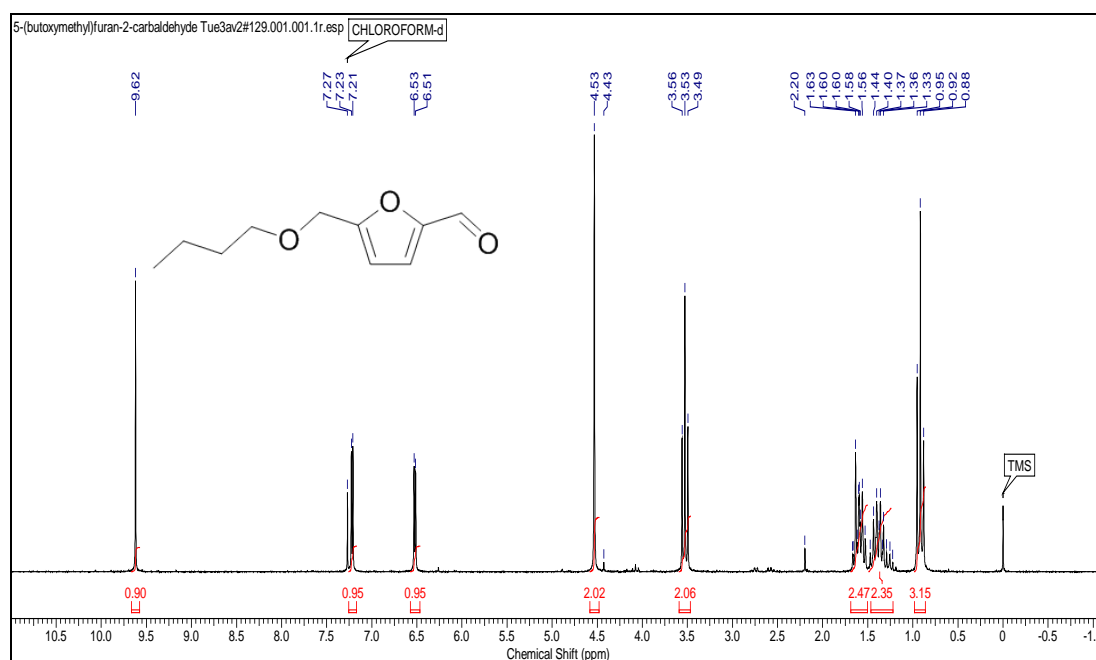
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 27.46, 57.30, 110.34, 122.35, 152.36, 160.3, 177.65.



**5-(butoxymethyl)furan-2-carbaldehyde (5):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.88-0.95 (m, 3 H) 1.33-1.44 (m, 2 H) 1.56-1.63 (m, 2 H) 3.49-3.56 (t,  $J=6.51$  Hz, 2 H) 4.53 (s, 2 H) 6.51–6.53 (d,  $J=3.54$  Hz, 1 H) 7.21–7.23 (d,  $J=3.54$  Hz, 1 H) 9.62 (s, 1 H)

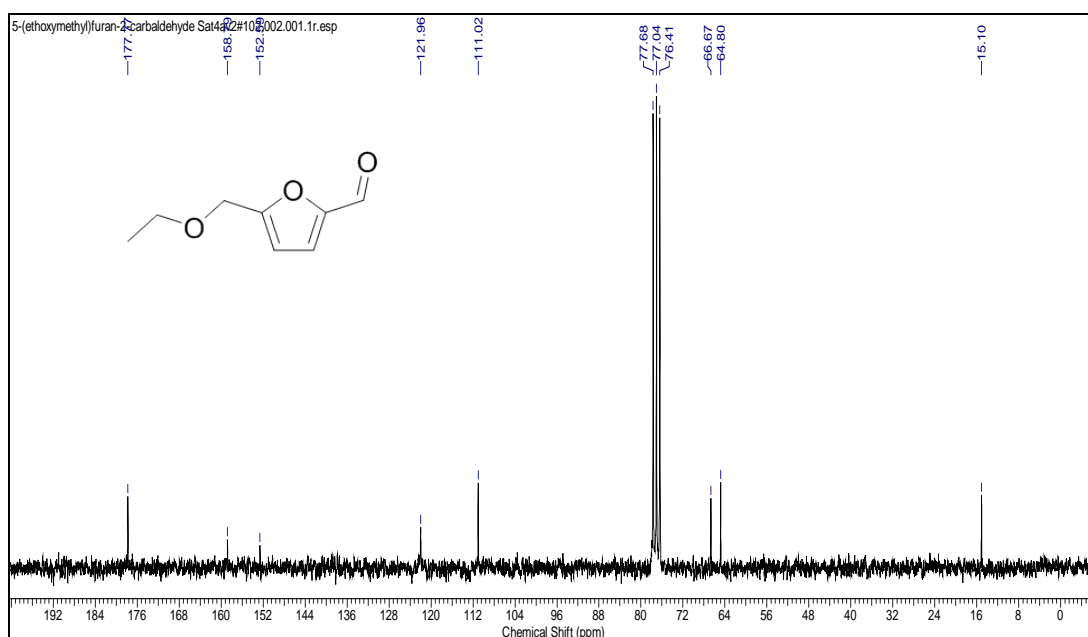
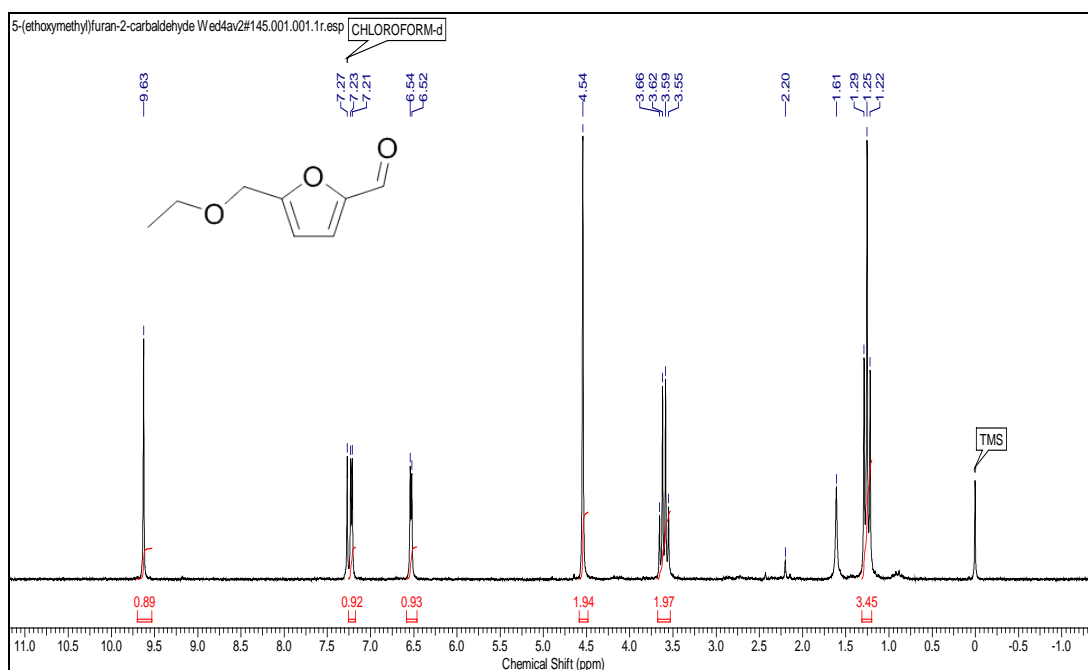
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.86, 19.23, 31.66, 65.03, 71.11, 110.94, 122.00, 152.55, 158.96, 177.74.



**5-(ethoxymethyl)furan-2-carbaldehyde (4):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.25-1.29 (t,  $J=7.01$  Hz, 3 H) 3.55-3.66 (q,  $J=6.95$  Hz, 2 H) 4.54 (s, 2 H) 6.52-6.54 (d,  $J=3.54$  Hz, 1 H) 7.21-7.23 (d,  $J=3.54$  Hz, 1 H) 9.63 (s, 1 H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 15.10, 64.80, 66.67, 111.02, 121.96, 152.59, 158.79, 177.77.



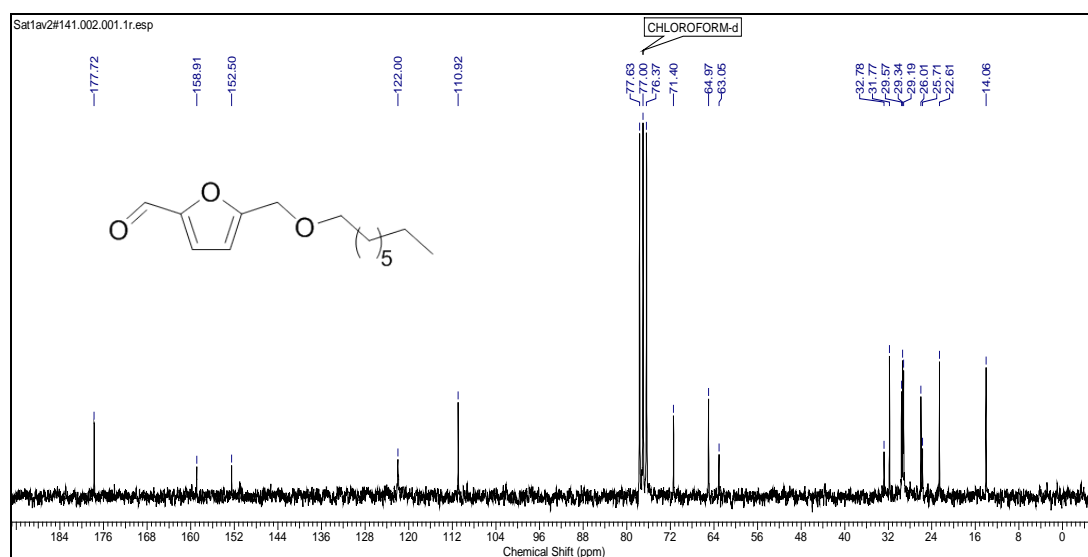
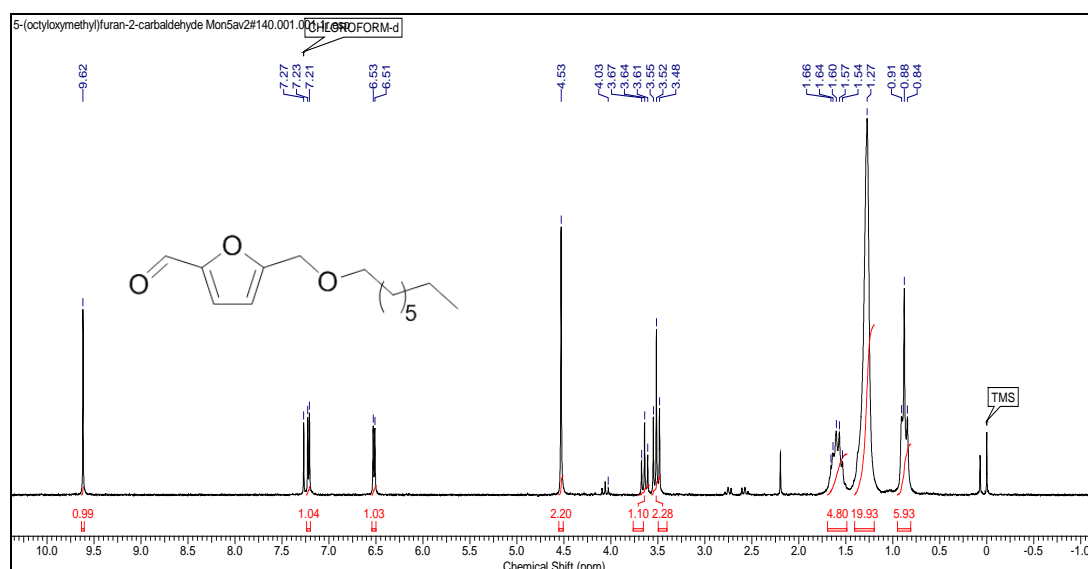
**5-(octyloxymethyl)furan-2-carbaldehyde (8):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.81 - 0.95 (m, 6 H) 1.27 (br. s., 20 H) 1.49 - 1.69 (m, 5 H) 3.52 (t,  $J=6.57$  Hz, 2 H) 3.64 (t,  $J=6.57$  Hz, 1 H) 4.53 (s, 2 H) 6.52 (d,  $J=3.54$  Hz, 1 H) 7.22 (d,  $J=3.54$  Hz, 1 H) 9.62 (s, 1 H)

**Note:** Excess protons signals were observed due to presence of *n*-octanol (almost 50%) in sample.

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 14.06, 22.61, 25.71, 26.01, 29.19, 29.34, 29.57, 31.77, 32.78, 63.05, 64.97, 110.92, 122.00, 152.50, 158.91, 177.72.

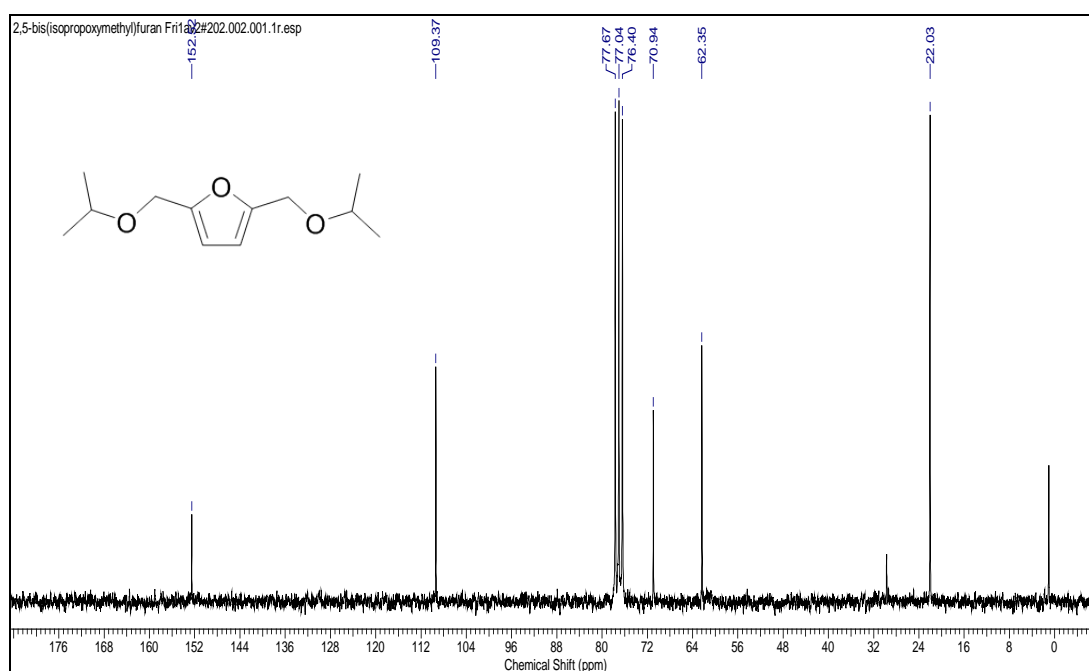
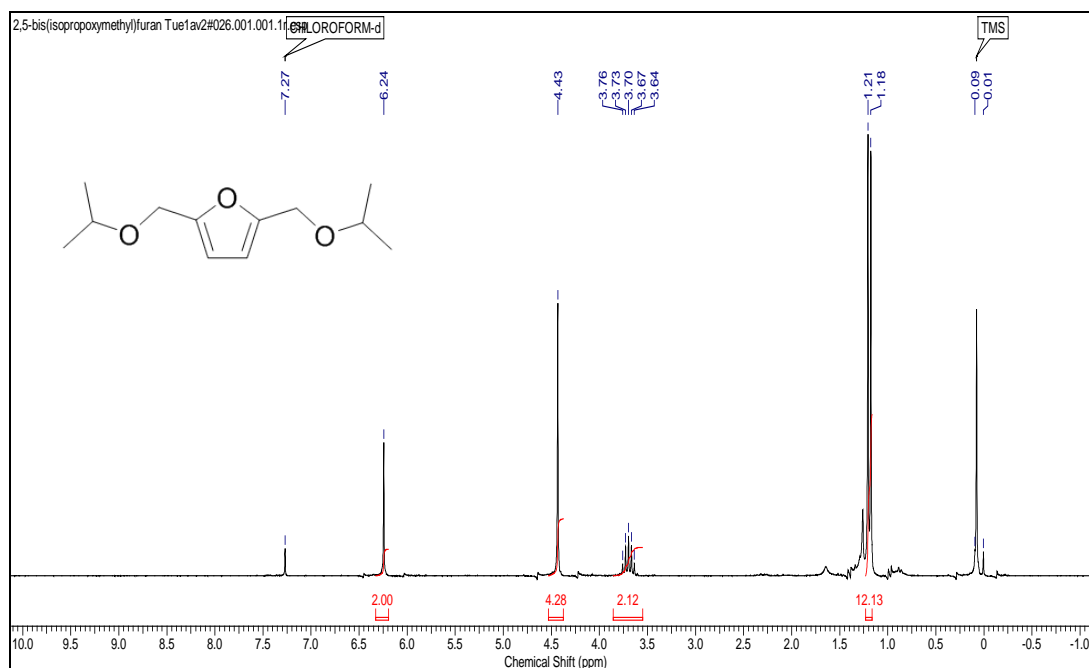
**Note:** Excess carbon signals were observed due to presence of *n*-octanol (almost 50%) in sample.



**2,5-bis(isopropoxymethyl)furan (10):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.18-1.21 (d,  $J=6.06$  Hz, 12 H) 3.64-3.76 (m,  $J=6.06$  Hz, 2 H) 4.43 (s, 4 H) 6.24 (s, 2 H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 22.03, 62.35, 70.94, 109.37, 152.52.

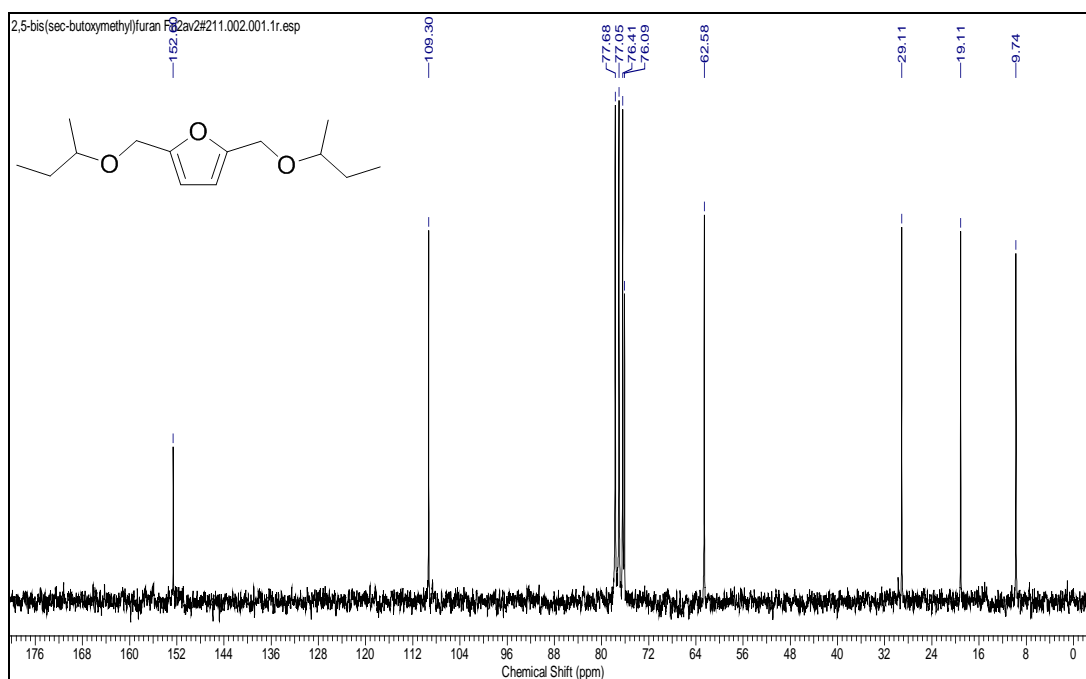
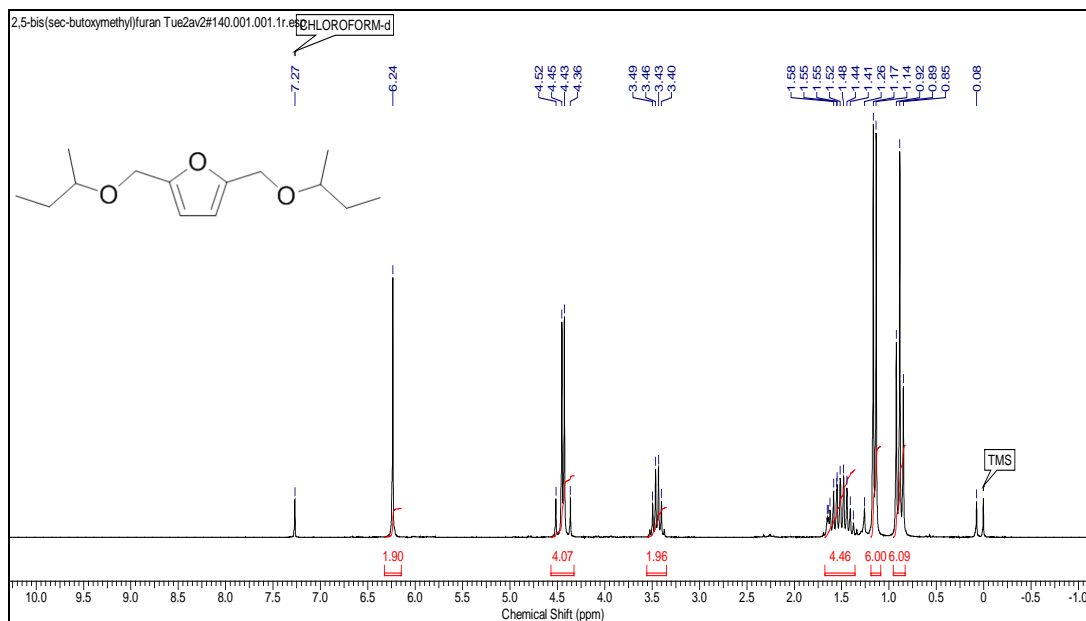




**2,5-bis(*sec*-butoxymethyl)furan (10a):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.85-0.92 (t,  $J=7.39$  Hz, 6 H) 1.14-1.17 (d,  $J=6.06$  Hz, 6 H) 1.41-1.58 (m, 4 H) 3.40 - 3.49 (m, 2 H) 4.36-4.52 (m, 4 H) 6.24 (s, 2 H)

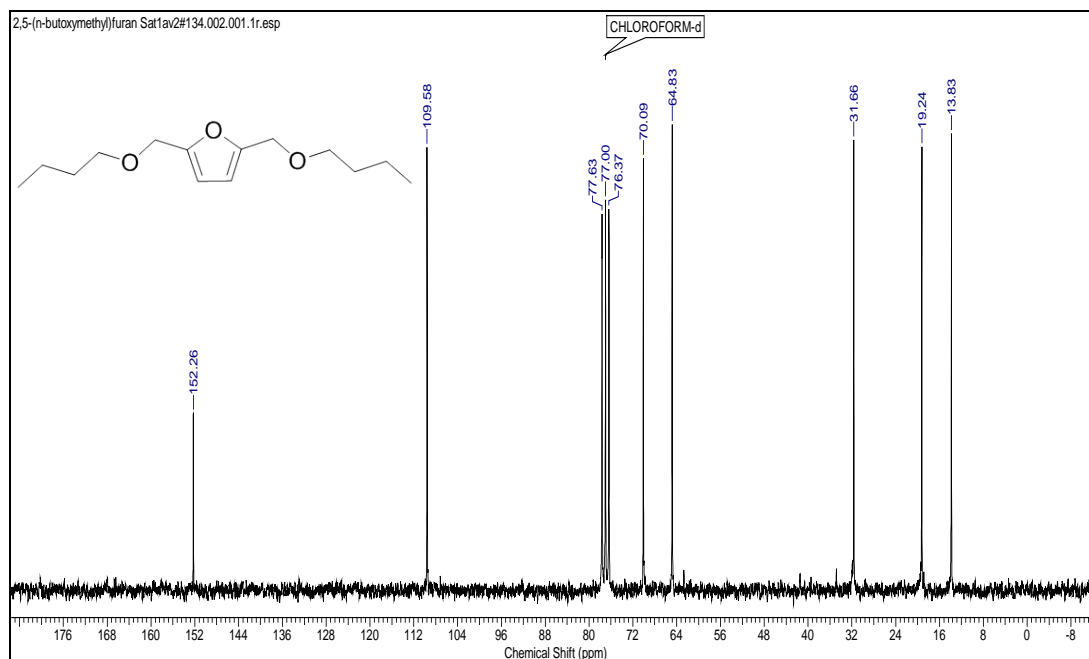
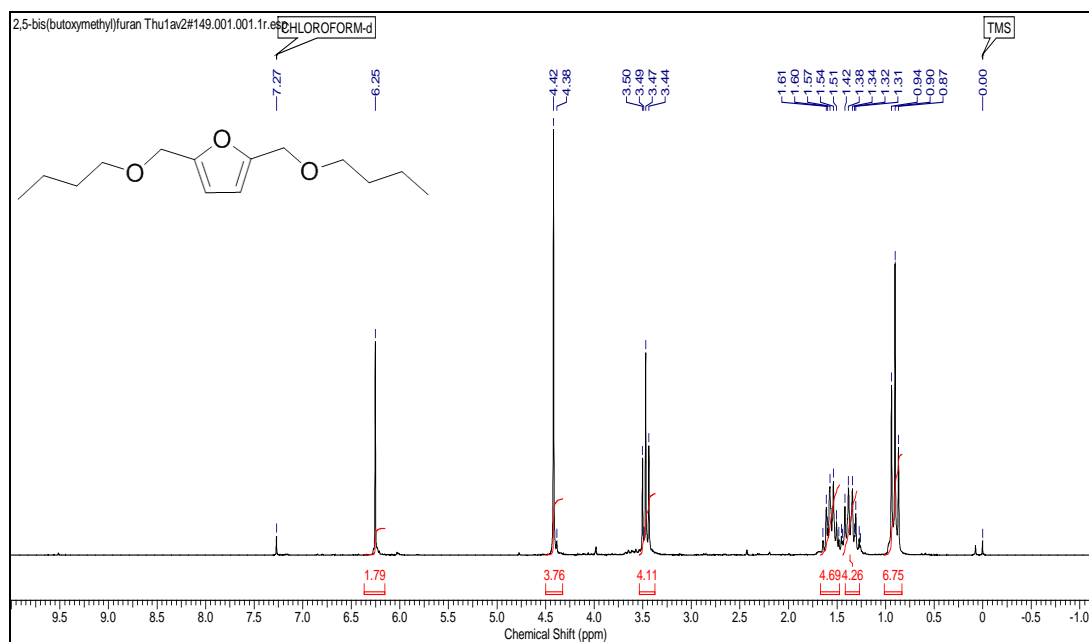
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 9.74, 19.11, 29.11, 62.58, 76.09, 109.30, 152.60.



**2,5-bis(butoxymethyl)furan (10b):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.87 - 0.94 (t, 6 H) 1.31-1.42 (m, 4 H) 1.51-1.61 (m, 4 H) 3.44-3.50 (t, 4 H) 4.42 (s, 4 H) 6.25 (s, 2 H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.83, 19.24, 31.66, 64.83, 70.09, 109.58, 152.26.

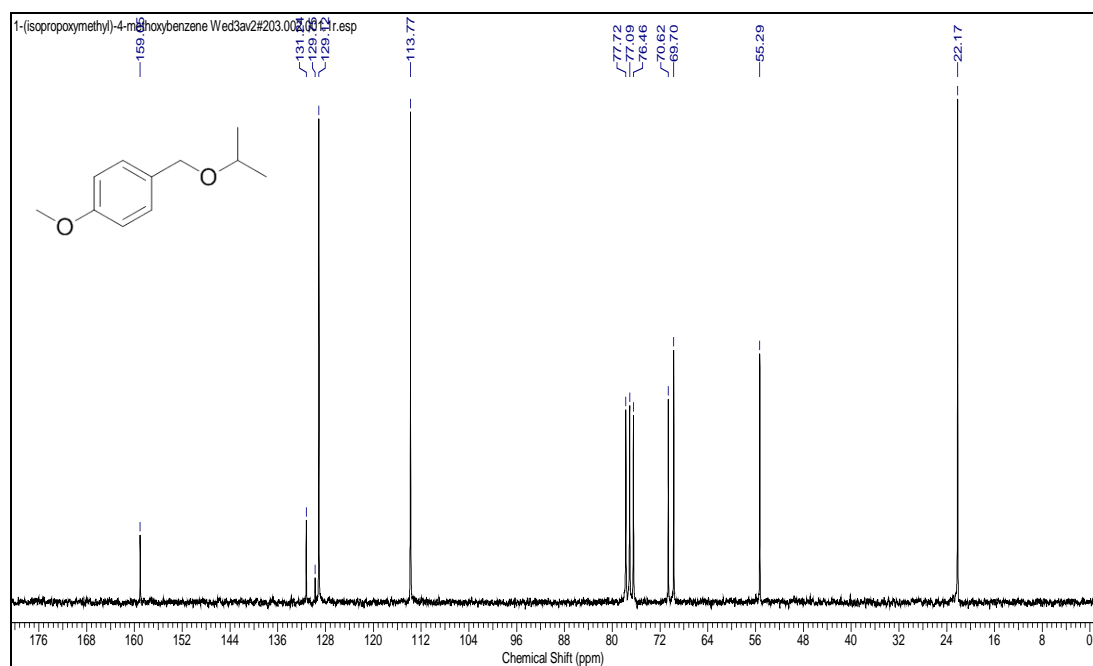
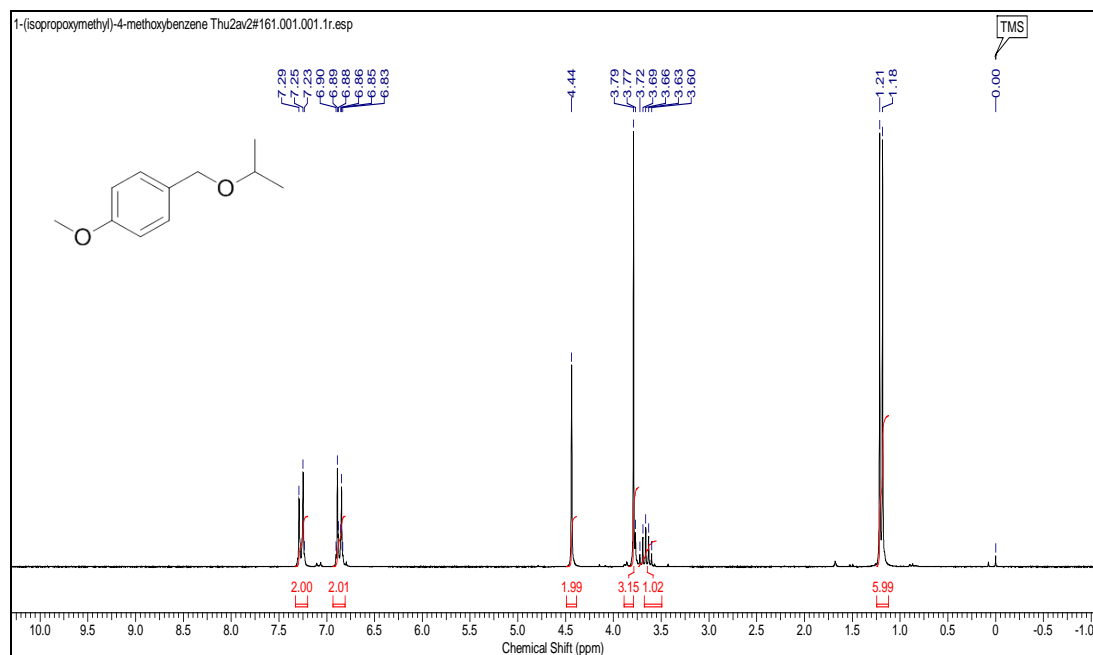


**1-(isopropoxymethyl)-4-methoxybenzene (15):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.18-1.21 (d,  $J=6.06$  Hz, 6 H) 3.60-3.72 (m, 1 H)

3.79 (s, 3 H) 4.44 (s, 2 H) 6.83-6.90 (m, 2 H) 7.23-7.79 (m, 2 H)

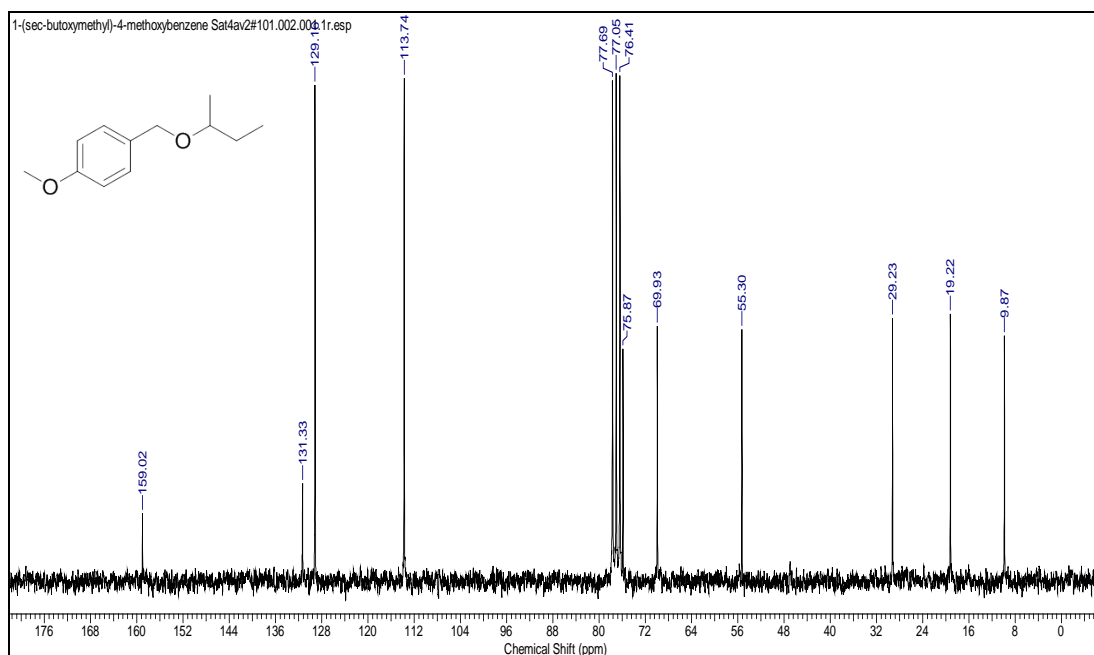
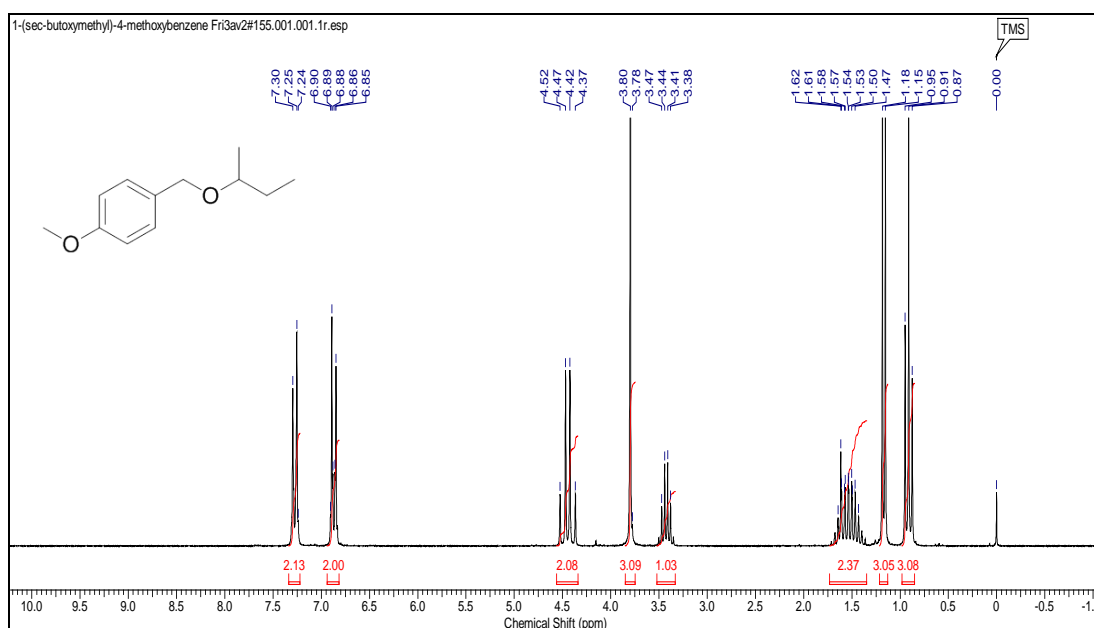
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 22.17, 55.29, 69.70, 70.62, 113.77, 129.12, 129.75, 131.24, 159.05.



**1-(*sec*-butoxymethyl)-4-methoxybenzene (18):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.87-0.95 (t, 3 H) 1.15-1.18 (d,  $J=6.06$  Hz, 3 H) 1.47-1.62 (m, 2 H) 3.38-3.47 (m, 1 H) 3.75-3.80 (s, 3 H) 4.37-4.52 (m, 2 H) 6.85-6.90 (m, 2 H) 7.24-7.30 (m, 2 H)

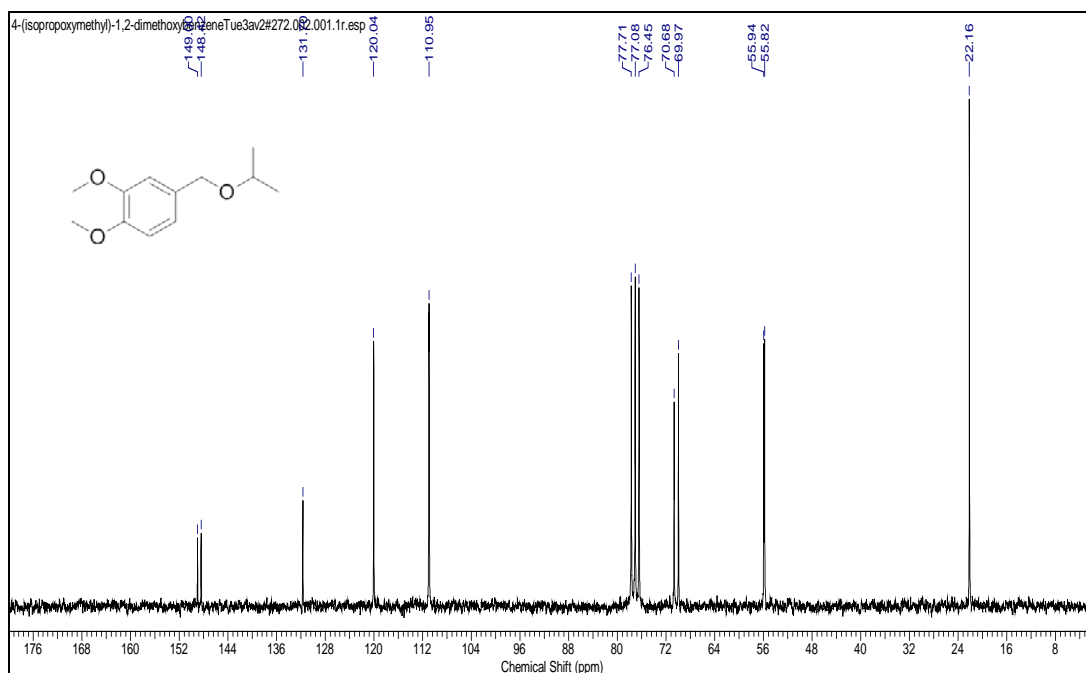
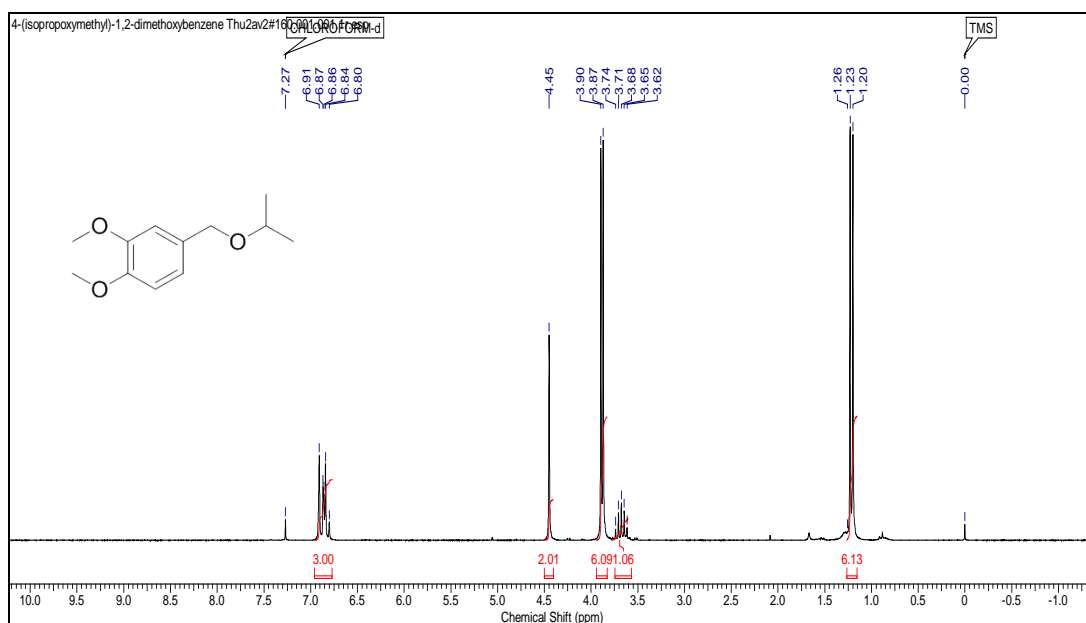
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 9.87, 19.22, 29.23, 55.30, 69.93, 75.87, 113.74, 129.16, 131.33, 159.02.



**4-(isopropoxymethyl)-1, 2-dimethoxybenzene (16):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.20-1.26 (d, 6 H) 3.62-3.74 (m, 1 H) 3.90 (s, 3 H) 3.87-3.90 (d, 6 H) 4.45 (s, 2 H) 6.80-6.91 (m, 3 H).

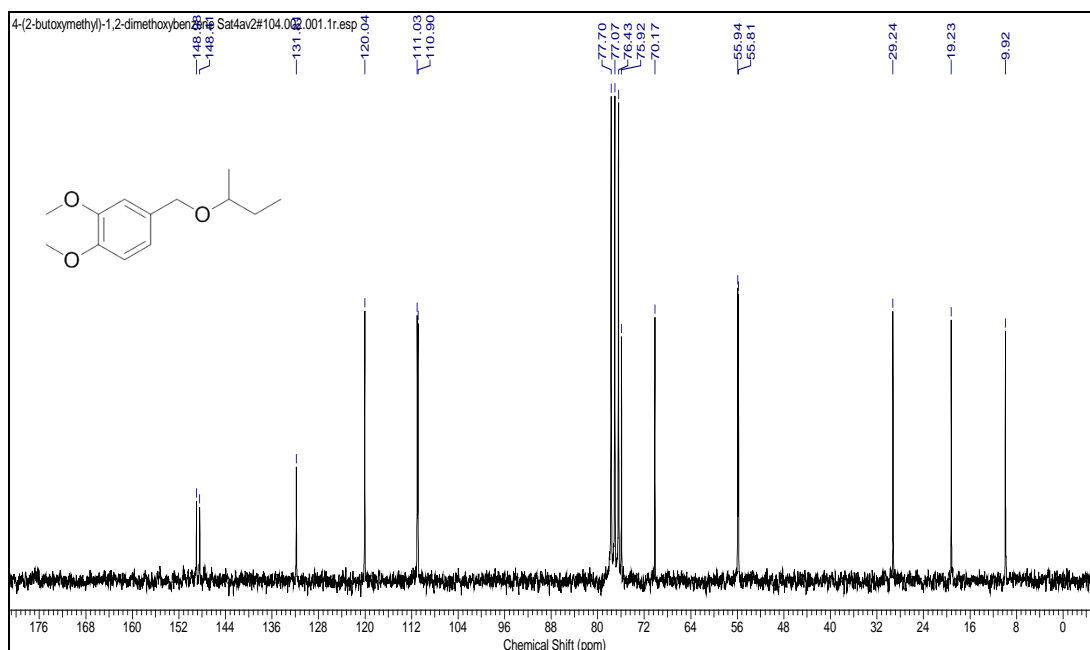
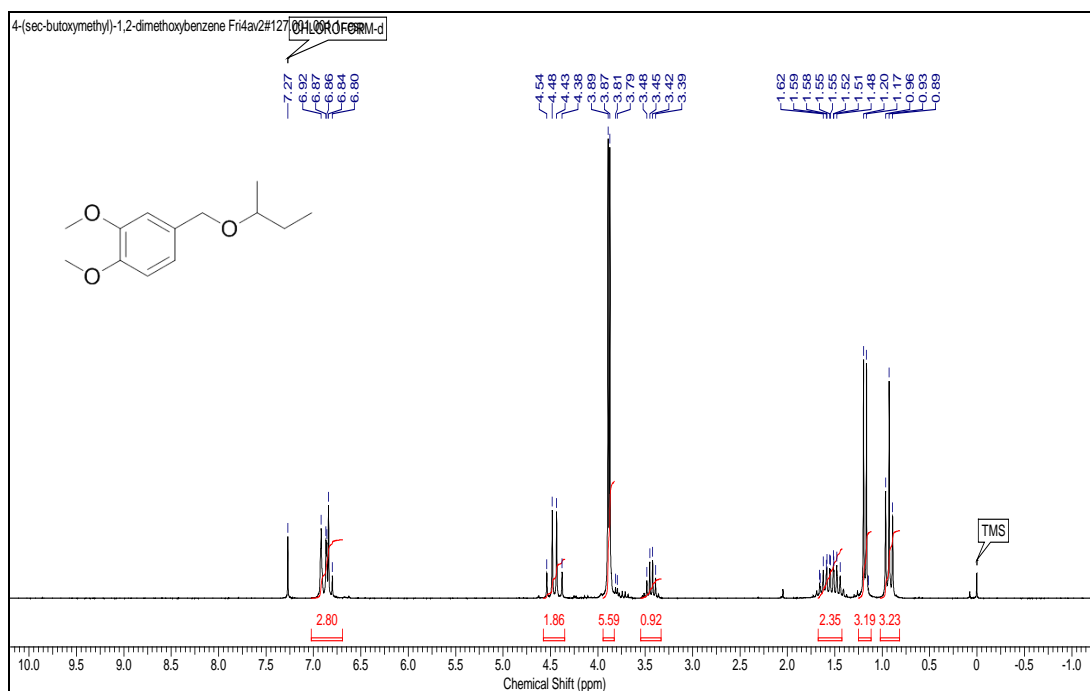
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 22.16, 55.82, 55.94, 69.97, 70.68, 110.95, 110.98, 120.04 131.70, 148.42, 149.00.



**4-(*sec*-butoxymethyl)-1,2-dimethoxybenzene (19):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.89-0.96 (m, 3 H) 1.17-1.20 (d,  $J$  = 6.06 Hz, 3 H) 1.48-1.62 (m, 2 H) 3.39-3.48 (q,  $J$  = 6.19 Hz, 1 H) 3.79-3.89 (d, 6 H) 4.38-4.45 (m, 2 H) 6.80-6.92 (m, 3 H)

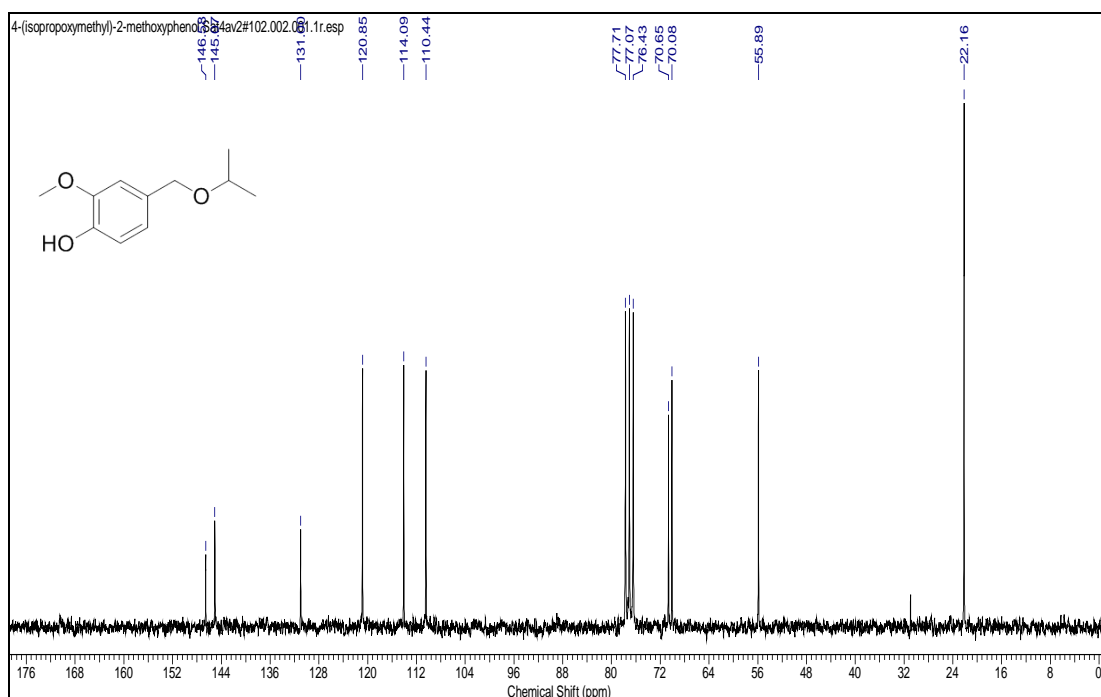
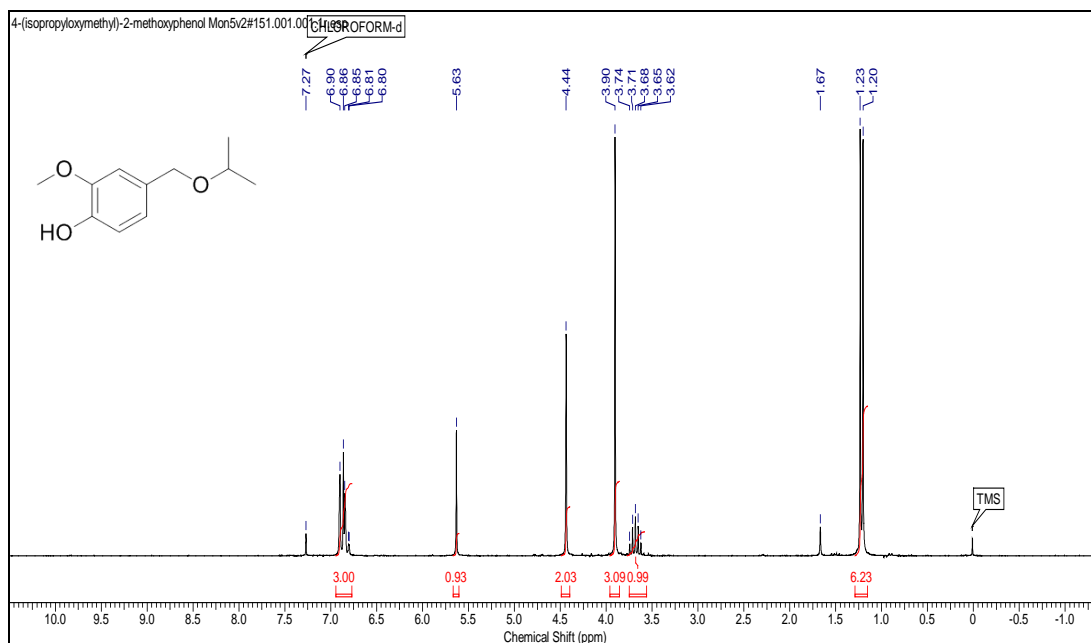
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 9.92, 19.23, 29.24, 55.81, 55.94, 70.17, 75.92, 110.90, 111.03, 120.04, 131.81, 148.41, 148.98.



**4-(isopropoxymethyl)-2-methoxyphenol (17):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.20-1.23 (d, 6 H) 3.62-3.74 (m, 1 H) 3.90 (s, 3 H) 4.44 (s, 2 H) 5.63 (s, 1 H) 6.80 - 6.90 (m, 3 H)

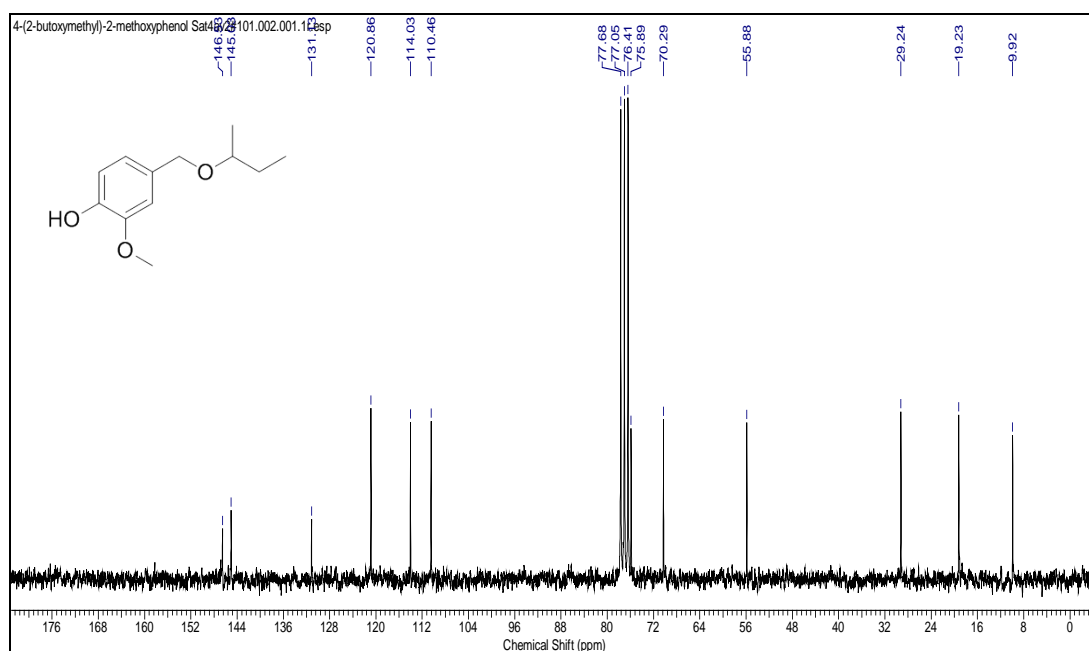
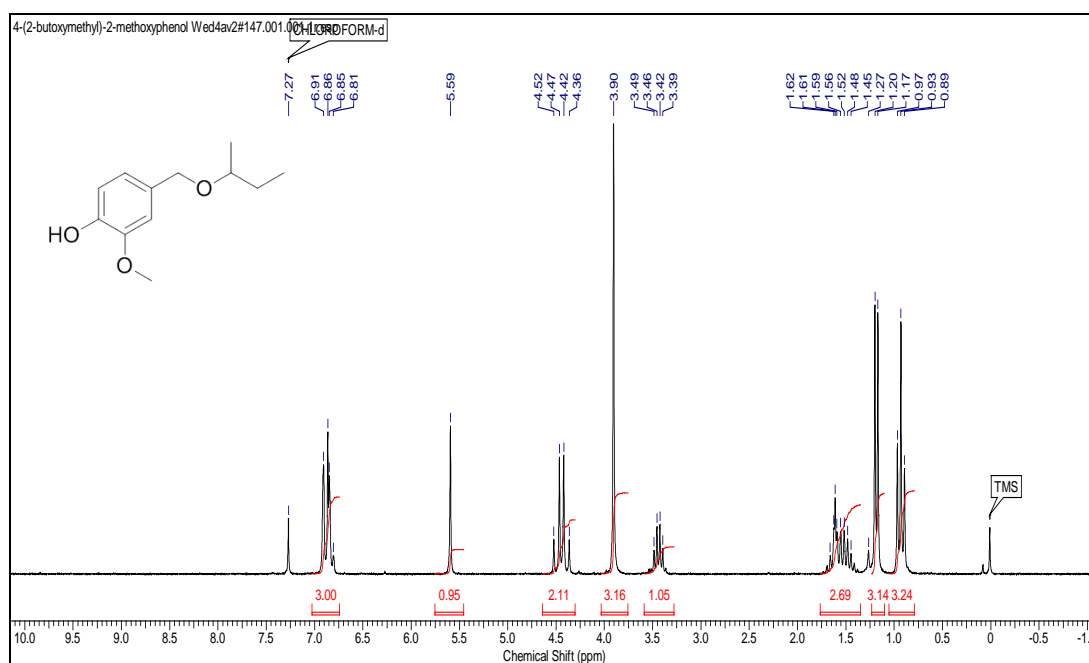
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 22.16, 55.89, 70.08, 70.65, 110.44, 114.09, 120.85, 131.00, 145.07, 146.58.



**4-(*sec*-butoxymethyl)-2-methoxyphenol (20):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.89-0.97 (t,  $J=7.45$  Hz, 3 H) 1.17-1.18 (d,  $J=6.06$  Hz, 3 H) 1.45-1.62 (m, 2H) 3.39-3.49 (m, 1 H) 3.90 (s, 3 H) 4.36-4.52 (m, 2 H) 5.59 (s, 1 H) 6.81–6.91 (m, 3 H).

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 9.92, 19.23, 29.24, 55.88, 70.29, 75.89, 110.46, 114.03, 120.86, 131.13, 145.03, 146.53.

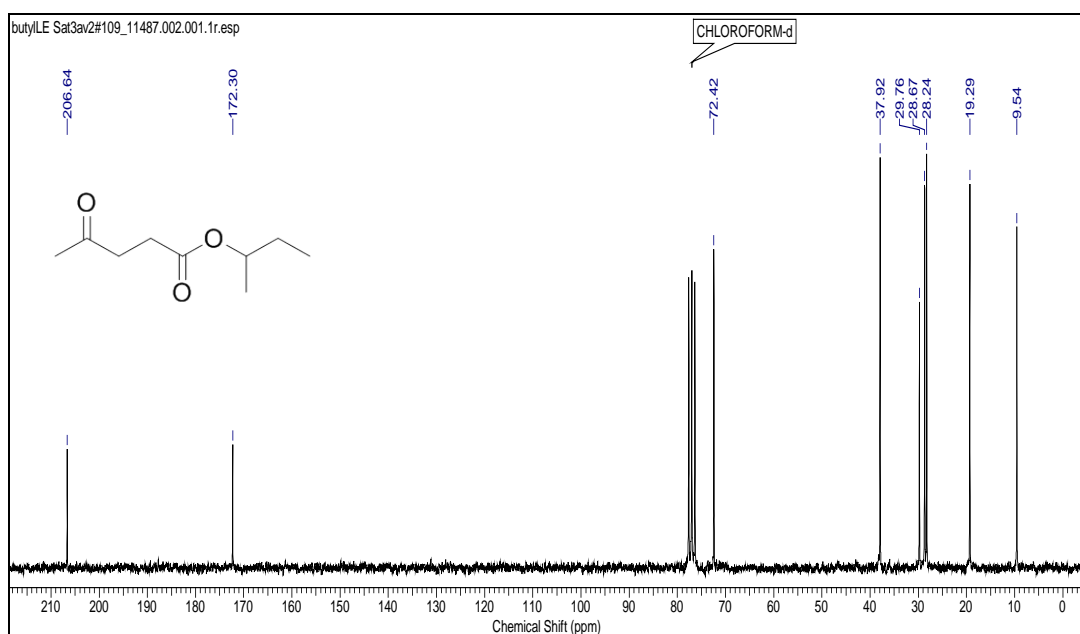
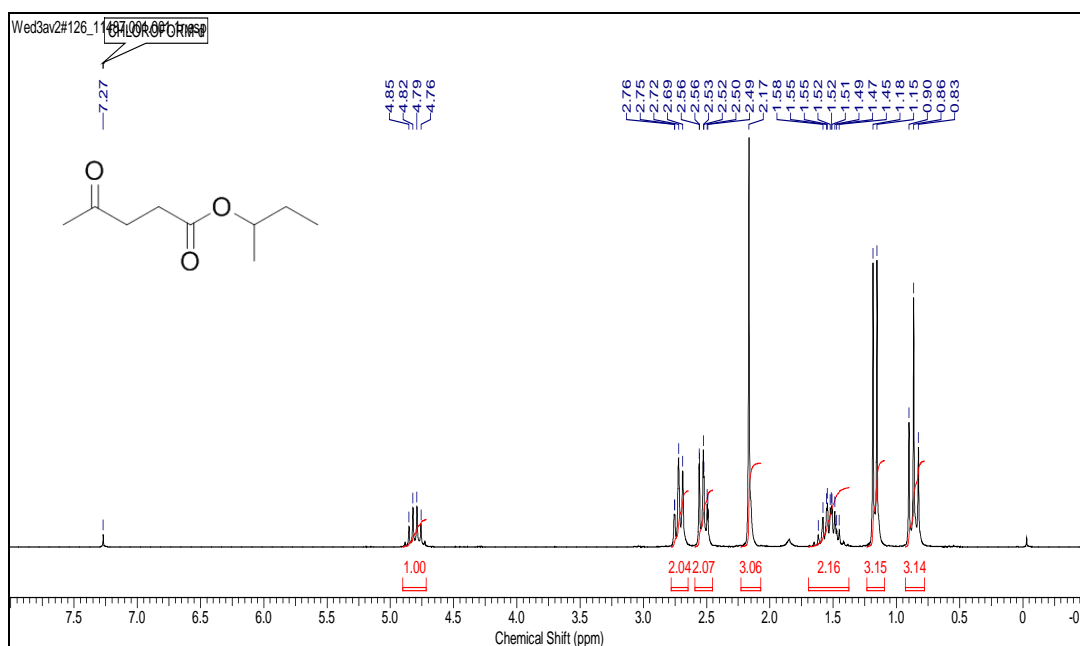




**sec-butyl-4-oxopentanoate (sec-butyl levulinate):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.83-0.9 (t,  $J=7.45$  Hz, 3 H) 1.17-1.18 (d,  $J=6.32$  Hz, 3 H) 1.45-1.65 (m, 2 H) 2.17 (s, 3 H) 2.45-2.56 (m, 2 H) 2.69-2.76 (m, 2 H) 4.76-4.88 (m, 1 H).

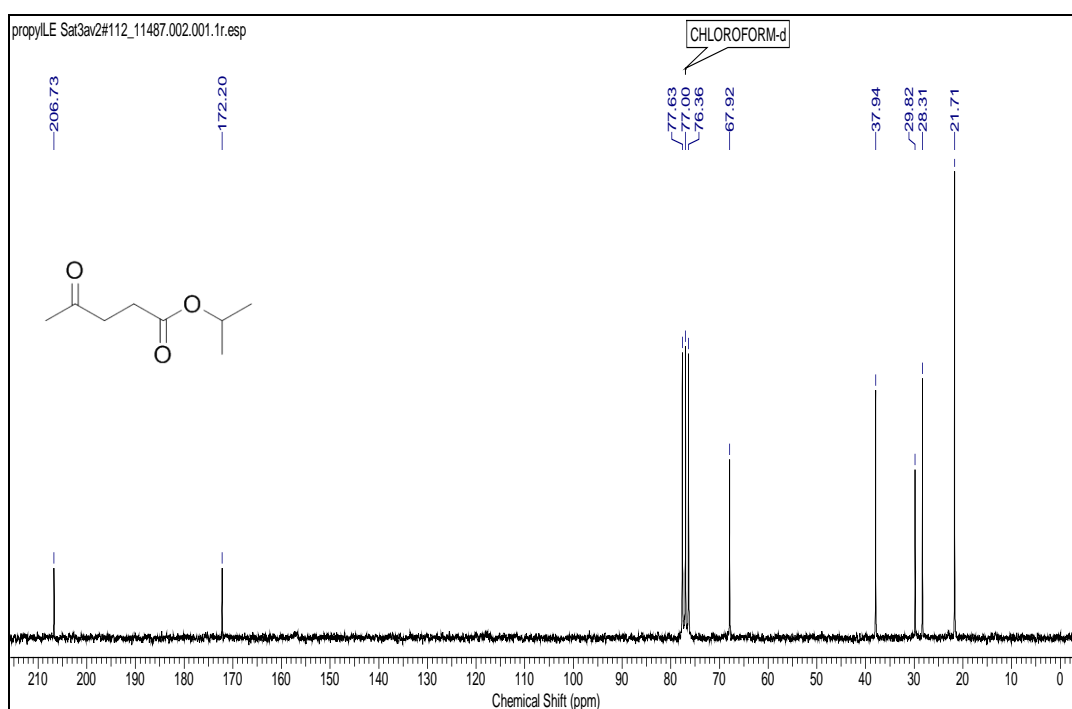
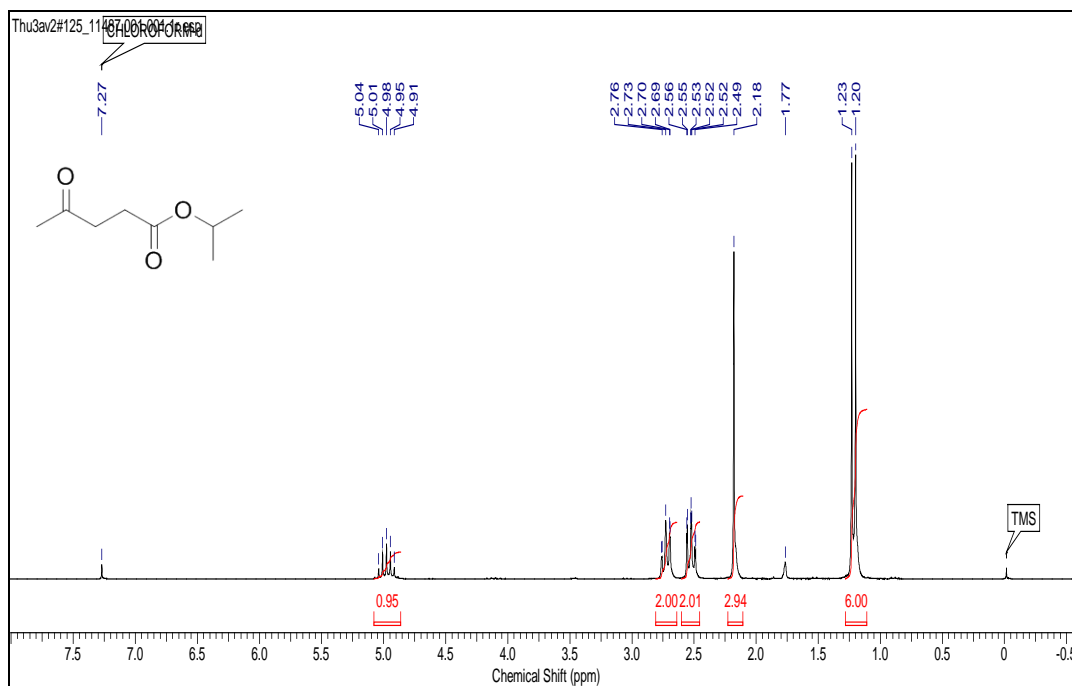
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 9.54, 19.29, 28.24, 28.67, 29.76, 37.92, 72.42, 172.30, 206.64.



**Isopropyl-4-oxopentanoate (Isopropyl levulinate):**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.21-1.23 (d,  $J=6.32$  Hz, 6 H) 2.18 (s, 3 H) 2.49-2.56 (m, 2 H) 2.69-2.76 (m, 2 H) 4.88-5.07 (m, 1 H)

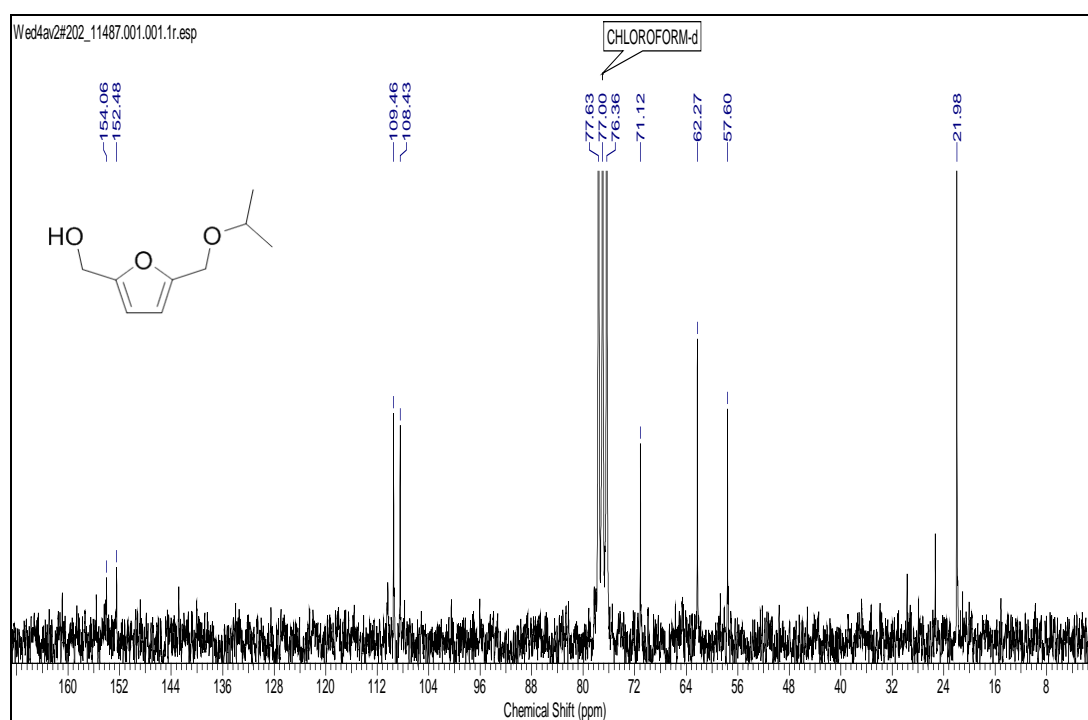
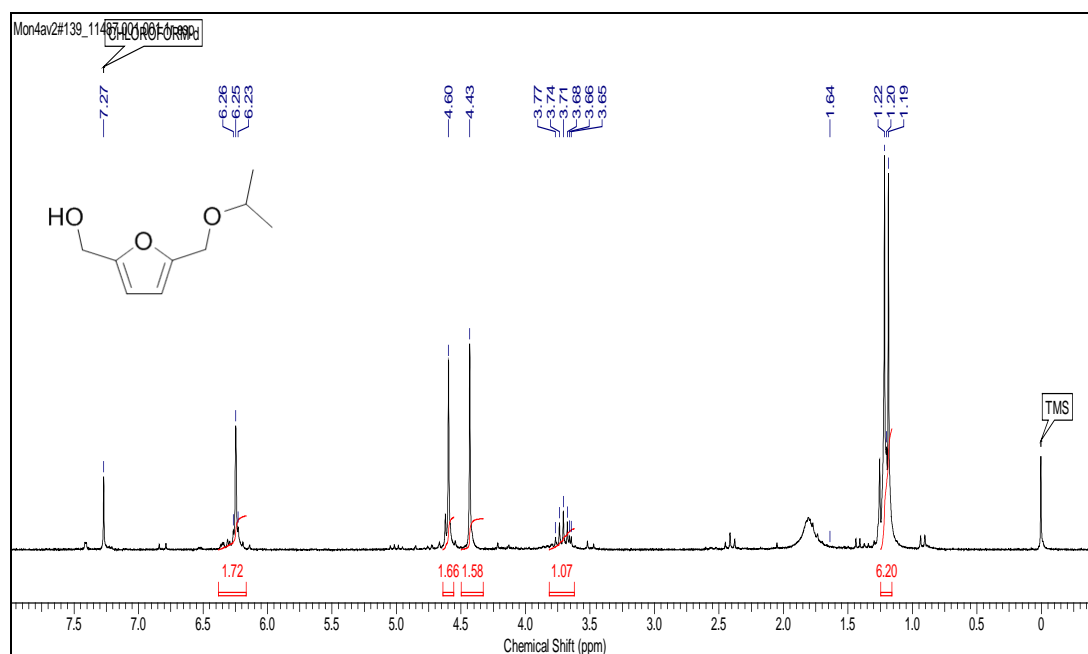
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 21.71, 28.31, 29.82, 37.94, 67.92, 172.20, 206.73



**(5-(isopropoxymethyl)furan-2-yl)methanol:**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.16-1.25 (m, 7 H) 3.62-3.82 (m, 1 H) 4.43 (s, 2 H) 4.60 (s, 2 H) 6.16-6.38 (m, 2 H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 21.98, 57.60, 62.27, 71.12, 76.36, 77.63, 108.43, 109.46, 152.48, 154.06.

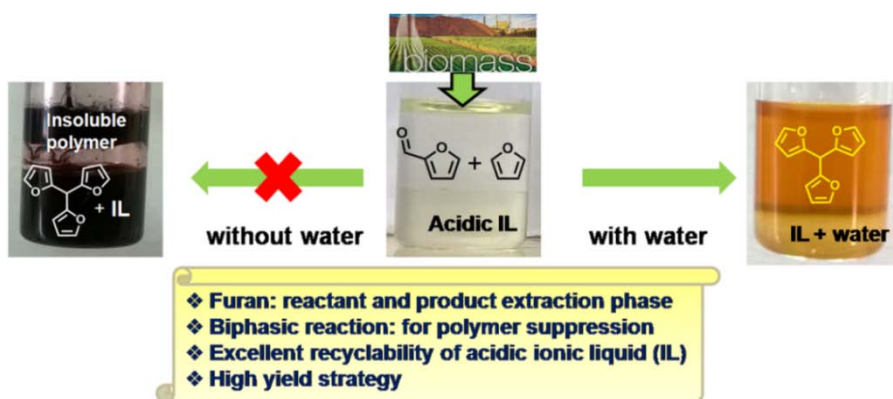


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## Chapter 6

### C-C bond forming reaction for the synthesis of furylmethane derivatives over $-\text{SO}_3\text{H}$ functionalized ionic liquids

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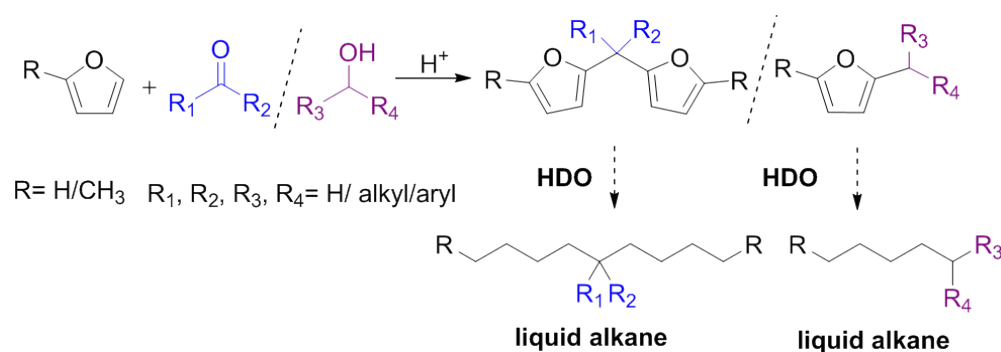


A new and effective unique two-phase reaction system is developed for the high yield production of tri(furyl)methane from furfural and furan. This strategy includes the use of an acidic aqueous phase (water +  $-\text{SO}_3\text{H}$  functionalized IL) and furan phase, which significantly suppresses polymer formation, thereby increasing the yield of tri(furyl)methane. Furan serves as a reactant as well as an extraction solvent for the recovery of the condensation products. Different  $-\text{SO}_3\text{H}$  functionalized ionic liquids were prepared and their performances were compared for the condensation of furan and furfural. The ionic liquids with alkyl chain linkers were found to be more effective and acidic than those with imidazolium linked N-sulfonic acids. In addition, an increase in carbon chain length between imidazole/tri-ethylamine/pyridine and  $-\text{SO}_3\text{H}$ , increases the catalytic activity of the respective ionic liquids. Among the several prepared ionic liquids, the strongly acidic imidazolium based butylsulfonic acid (IL, **6**) show the best activity with a maximum condensation product yield of 84%. This strategy offers a significantly high yield of the condensation products of furan and furfural compared to the traditional mineral acid route. The activity and stability of the  $-\text{SO}_3\text{H}$  functionalized IL **6** was confirmed from seven successful recycles, in which there is no reduction in its activity. Finally, this new strategy was successfully extended for the condensation of furan derivatives (e.g. furan and 2-methylfuran) with several different aldehydes, ketones and alcohols

Suhas Shinde, Chandrashekhar Rode, *Green Chemistry*, **2017**, *19*, 4804-4810

## 6.1. Introduction

Currently, the worldwide production of transportation fuels and chemicals is dependent on crude oil, which may have limited availability in the future due to its depletion and the exponential increase in its consumption. Sustainable and renewable alternatives to petroleum are therefore critically needed to fill the future gap in the supply and demand of transportation fuels and chemical feedstock [1, 2]. Biomass provides an ideal alternative to fossil resources since it is a sustainable, cheap and abundant source of organic molecules. Hence, genuine interest has been aroused for the production of biomass derived platform molecules. One such approach involves catalytic C–C bond forming reactions which include *i*) aldol-condensation of furfural with different ketones [3], *ii*) pinacol coupling of lignocellulose derived aldehydes [4], *iii*) NHC catalyzed umpolung benzoin condensation of 5-(hydroxymethyl)furfural [5] and *iv*) hydroxyalkylation–alkylation (HAA) reaction of 2-methylfuran [6]. Furan, which is an electron rich aromatic ring, is capable of undergoing electrophilic substitution at the C<sub>1</sub> and C<sub>4</sub> positions and hence a starting material in the hydroxyalkylation–alkylation (HAA) reaction. Furans are considered to be more reactive than benzene towards electrophilic substitution reactions due to the electron donating effect of the oxygen heteroatom [7]. Importantly, furan is a biomass derived molecule obtained from the decarbonylation of furfural [8]. Furan ring containing products such as bis/tris (furyl)alkanes have attracted much attention due to their wide range of industrial applications, such as intermediates for the synthesis of tetraoxaquaterenes, which is a very interesting scaffold in supramolecular chemistry [9], polymers [10], macromolecules for metal ions carriers [11], foods [12], dyes [13] and agrochemicals [14]. Apart from these conventional applications recently, bis/tris(furyl)alkanes have been considered as rich carbon sources for the production of bio-fuel *via* hydrodeoxygenation (HDO) (Scheme 6.1) [3–6, 15].



**Scheme 6.1.** Production of liquid alkane from mono/bis/tris(furyl)alkane

## 6.2. Literature survey

Numerous synthetic methods are available for the synthesis of bis/tris(furyl) alkanes, which mainly include the condensation of 2-methylfuran with carbonyl compounds in presence of conc.  $\text{H}_2\text{SO}_4$  [6a],  $\text{HCl}$  [15], acidic resins [6a,c,16,17],  $\text{MCM-SO}_3\text{H}$  [18],  $\text{Mo-Zr-MCM-41}$  [19],  $\text{AuCl}_3$  [20], zeolites [21],  $\text{SiO}_2\text{-Pr-S-Pr-SO}_3\text{H}$  [6d],  $\text{Cu(OTf)}_2$  [22],  $\text{I}_2$  [23],  $\text{CMH-SO}_3\text{H}$  [24],  $\text{SILC}$  [25] and  $\text{TFA-ZrO}_2$  [26]. However, most of these synthetic methods utilize non-recyclable and environmentally incompatible catalyst systems. In addition, some of the solid catalysts need tedious preparation steps. Almost all the above mentioned catalysts were employed for the condensation reaction of the relatively more stable 2-methylfuran with different aldehydes/alcohols. To the best of our knowledge, there is only one report on the condensation of the relatively unstable furan with aldehydes/alcohols in the presence of conc.  $\text{H}_2\text{SO}_4$  [6b], in which the presence of a homogenous phase restricted the yield of the resulting TFM to ~70%.

## 6.3. Scope of the present work

In this study, we developed an efficient process for the production of tri(furyl)methane (TFM, **3**) and mono/bis/tris(furyl) alkanes using hydrophilic,  $-\text{SO}_3\text{H}$  functionalized, recyclable, Brønsted acidic ionic liquids (ILs) as catalysts by devising a two phase reaction system. This strategy has significant advantages as follows: 1) furan acts as a reactant as well as an extraction phase for product isolation in higher yields (up to 84 %). 2) Polymer formation is significantly suppressed due to the indirect contact of acid with the substrates in a two phase furan and IL + water mixture. 3) Partitioning between the reactants/products phase (furan

layer) and IL + water (aqueous layer) phase allows easy product isolation. 4) Acidic ILs can be easily recovered and recycled. The efficiency of this two phase furan and IL + water system is successfully demonstrated by its wide scope for the condensation of various furan derivatives (*e.g.* furan and 2-methylfuran) with lignocellulose derived reactants such as aldehydes, ketones or alcohols.

## 6.4. Experimental Section

### 6.4.1. Materials

All materials/chemicals were used as received. Furan, 2-methylfuran, 5-(hydroxymethyl)furfural, 2-furfuraldehyde, 5-methylfurfuraldehyde, furfuryl alcohol, 4-methoxybenzaldehyde, 3,4-dimethoxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-methoxybenzylalcohol, 3,4-dimethoxybenzylalcohol, 4-hydroxy-3-methoxybenzylalcohol, hydroxyacetone, 1-methylimidazole, 1,3-propanesultone, 1,4-butanedisultone and Amberlyst-15 were purchased from Sigma-Aldrich, India. Acetone, 2-butanone, formaldehyde (37 %), conc.  $\text{H}_2\text{SO}_4$ , *p*-toluenesulfonic acid, pyridine and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  were purchased from Thomas Baker. Triethylamine was purchased from Merk, India. All solvents used were received from Chem Labs India. 5-Methylfurfural alcohol was prepared in house via the reduction of 5-methylfurfuraldehyde.  $[\text{BmimSO}_3\text{H}]_3[\text{PW}_{12}\text{O}_{40}]$  [27], Sn-Mont [28] and  $\text{SO}_4^{2-}/\text{ZrO}_2$  [29] were prepared according to the procedures reported in the literature. The sulfonic acid-functionalized ionic liquid catalysts (**4–8**) were synthesized following literature procedures and characterized *via* FTIR and NMR spectroscopy.

### 6.4.2 Preparation of ionic liquid **4**

Ionic liquid **4** was synthesized using the method reported in the literature [30]. 1-Methylimidazole (0.82 g, 0.01 mol) in acetonitrile (5 mL) was charged in a round-bottom flask and the mixture was stirred at 0 °C for 1 min. Then, a stoichiometric amount of conc. sulfuric acid (0.01 mol) was added drop wise and the mixture stirred for 1 h at 0 °C and then stirred for 2 h at room temperature. The acidic Brønsted ionic liquid was washed repeatedly with diethyl ether to remove non-ionic residues and dried under vacuum. Yield: 95 % (1.71 g).

### 6.4.3 Preparation of ionic liquids 5 and 6

Ionic liquids **5** and **6** were synthesized using a method reported in the literature [30]. 1-Methylimidazole (0.82 g, 0.01 mol) was stirred with 1,3-propanesultone (1.22 g, 0.87 mL, 0.01 mol) and 1,4-butanedisulfone (1.36 g, 1.02 mL, 0.01 mol), respectively, at 40 °C for 24 h. The two white solid zwitterions produced were washed three times with toluene to remove unreacted material and dried under vacuum. A stoichiometric amount of conc. sulfuric acid (0.01 mol) was added drop wise to the zwitterions and the mixture was stirred at 40 °C for 2–3 days until it liquefied, resulting in the formation of the ionic liquids. The ionic liquids were washed repeatedly with toluene and diethyl ether to remove unreacted material and dried under vacuum. Yield of **5**: 91 % (2.78 g) and yield of **6**: 93 % (2.94 g).

### 6.4.4 Preparation of ionic liquid 7

Ionic liquid **7** was synthesized using a method reported in the literature [30]. Triethylamine (1.01 g, 0.01 mol) was stirred with 1,4-butanedisulfone (1.36 g, 1.02 mL, 0.01 mol) at 40 °C for 24 h. The white solid zwitterion produced was washed three times with toluene to remove unreacted material and dried in a vacuum. A stoichiometric amount of conc. Sulfuric acid (0.01 mol) was added drop wise to the zwitterion and the mixture was stirred at 40 °C for 2–3 days until it liquefied, resulting in the formation of the ionic liquid. The ionic liquid was washed repeatedly with toluene and diethyl ether to remove unreacted material and dried under vacuum. Yield: 89 % (2.98 g).

### 6.4.5 Preparation of ionic liquid 8

Ionic liquid **8** was synthesized using a method reported in the literature [30]. Pyridine (0.79 g, 0.01 mol) and 1,4-butanedisulfone (1.36 g, 0.01 mol) were combined and stirred at 40 °C for 24 h. The white solid zwitterion produced was washed three times with toluene to remove unreacted material and dried under vacuum. A stoichiometric amount of conc. sulfuric acid (0.01 mol) was added drop wise to the zwitterion and the mixture was stirred at 40 °C for 2–3 days until it liquefied, resulting in the formation of the ionic liquid. The ionic liquid was washed



repeatedly with toluene and diethyl ether to remove unreacted material and dried under vacuum. Yield: 89 % (2.81 g).

#### 6.4.6 Alkylation of furan with aldehydes/ketone/alcohols

A catalytic amount of sulfonic acid functionalized IL (20 mol %) and water (1 mL) were added to a solution of alcohol, ketone or aldehyde (1 mmol) in furan (5 mL), and the reaction mixture was stirred at room temperature for 3 h. The upper organic phase was pipetted out and the aqueous phase was further washed with ethyl acetate (10 mL  $\times$  2) to extract the entire product from the aqueous phase. The furan and ethyl acetate layers were combined and evaporated under reduced pressure using a rotary evaporator to obtain the crude condensation product which was purified by column chromatography. The aqueous phase was dried at 80 °C under reduced pressure to isolate the ionic liquid prior to reuse for the next recycle.

#### 6.4.7 Alkylation of 2-methylfuran with aldehydes/ketone/alcohols

A catalytic amount of sulfonic acid functionalized IL **6** (20 mol %) and water (0.5 mL) were added to a solution of alcohol (4 mmol), ketone or aldehyde (2 mmol) in 2-methylfuran (4.4 mmol or 6.6 mmol for the HMF and HMF derivatives). The reaction mixture was subsequently heated to 65 °C for 2 h. The upper organic phase was pipetted out and the aqueous phase was further washed with ethyl acetate (10 mL  $\times$  2) to extract the entire product from the aqueous phase. The furan and ethyl acetate layers were combined and evaporated under reduced pressure using rotary evaporator to obtain the crude condensation product which was purified by column chromatography.

#### 6.4.8 Analysis of the reaction products

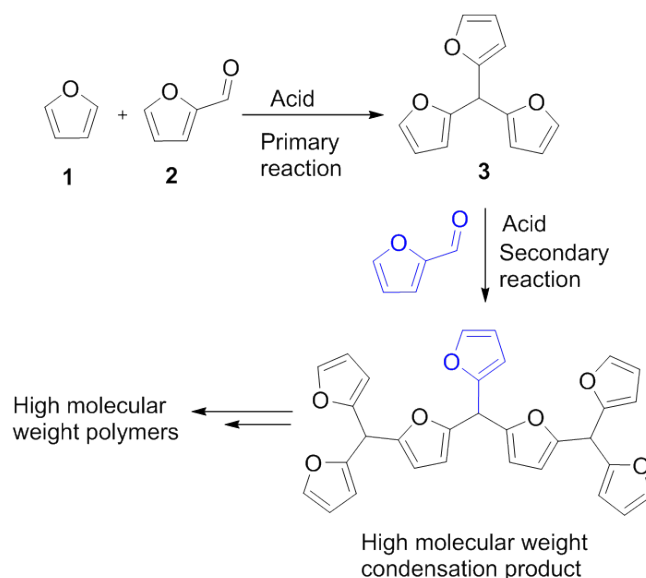
The conversion of the substrates was calculated *via* liquid analysis using a Thermo Scientific Trace 700 gas chromatograph. Products were separated using a Factor Four capillary column (HP-5, 30 m length and 0.25 mm diameter) coated with a 0.25 mm thick stationary phase (5 % phenyl and 95 % dimethylpolysiloxane). The pure products were confirmed by  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR using  $\text{CDCl}_3$  (0.01 % TMS) as the solvent on a 200 MHz Bruker instrument. The products were also characterised

using a QP-Ultra 2010 GC-MS Shimadzu instrument with an RTX-5 column, under helium as the carrier gas, in EI mode and an ionization source temperature of about 200 °C. The approximate molecular weights of a few representative condensation products were analysed using high resolution mass spectroscopy (HRMS) on an HRMS-Q Exactive (ORBITRAP) spectrometer.

## 6.5. Results and discussion

### 6.5.1 Catalyst screening

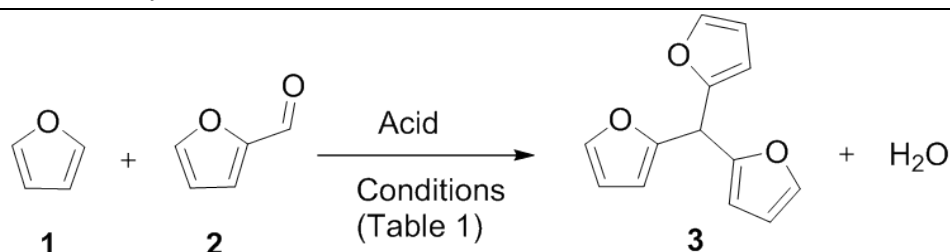
Initially, several solid and liquid acids were explored for the condensation of furan (1) with furfural (2) under solvent free conditions (Table 6.1). In the presence of mineral acid such as conc.  $\text{H}_2\text{SO}_4$  (10 mol %), TFM was produced in 67 % yield at room temperature (Table 6.1, entry 1). However, due to the very strong acidity of conc.  $\text{H}_2\text{SO}_4$ , further condensation (secondary reaction; refer to Figure 6.1) of TFM (3) with furfural facilitated the production of undesired higher-molecular-weight products (insoluble black mass or polymer), which was seen as a black layer on the wall of the flask (Figure 6.3B). The activity of *p*-toluenesulfonic acid (*p*-TSA) was found to be almost similar to that of conc.  $\text{H}_2\text{SO}_4$  (Table 6.1, entry 2).



**Figure 6.1** Schematic presentation of formation of high molecular weight condensation product *via* secondary reaction of 3 with 2 in acid.

Furthermore, over Amberlyst-15, furfural was consumed up to 89 % with an improved yield (71 %) of TFM (Table 6.1, entry 3). Heteropolyacid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ), which is a strong solid acid, gave 74 % yield of TFM with 91 % conversion of furfural (Table 6.1, entry 4). Next, the heterogeneous organo-inorganic hybrid solid acid catalyst  $[\text{BmimSO}_3\text{H}]_3[\text{PW}_{12}\text{O}_{40}]$  showed 86 % furfural conversion and 71 % TFM yield (Table 6.1, entry 5). Sn-Mont and  $\text{SO}_4^{2-}/\text{ZrO}_2$  were found to be ineffective catalysts and gave only a moderate yield (<65 %) of TFM (Table 6.1, entries 6 and 7).

**Table 6.1** Catalyst screening for the condensation of furan (**1**) with furfural (**2**) over various acid catalysts.<sup>[a]</sup>



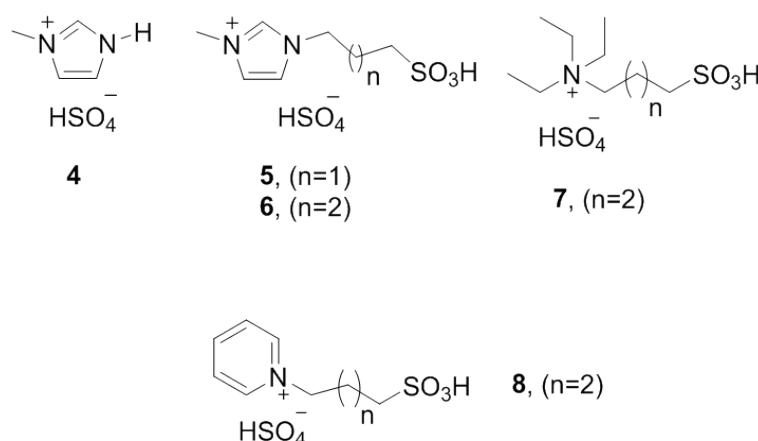
Entry	Acid catalyst	<i>t</i> [h]	Conv. <sup>[c]</sup> of <b>2</b> [%]	Yield <sup>[d]</sup> of <b>3</b> [%]
1	Conc. $\text{H}_2\text{SO}_4$	1	100	67
2	<i>p</i> -TSA	3	100	69
3	Amberlyst-15	3	89	71
4	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	3	91	74
5	$[\text{BmimSO}_3\text{H}]_3[\text{PW}_{12}\text{O}_{40}]$	3	86	71
6 <sup>[b]</sup>	Sn-Mont	3	61	56
7 <sup>[b]</sup>	$\text{SO}_4^{2-}/\text{ZrO}_2$	3	72	63
8	No catalyst	24	--	--

[a] Reaction conditions: furfural, **2** (0.192 g, 2 mmol), furan, **1** (5 mL), catalyst (10 mol %), rt. [b] Acid catalyst, 0.1 g used. [c] Conversion of **2** was measured using GC. [d] Isolated yields after column chromatography.

Without catalyst, the reaction did not proceed even after 24 h (Table 6.1, entry 8). From the above experiments, it was observed that the mineral acid (conc.  $\text{H}_2\text{SO}_4$ ) and *p*-TSA showed only moderate yield of TFM due to the formation of excess polymer (Table 6.1, entries 1 and 2). On the other hand, solid acids (Table 6.1, entries 3–7) showed mostly lower furan conversion with a maximum TFM yield of ~70 %. This is due to the insufficient exposure of surface acidity to the substrates under the reaction conditions at room temperature.

### 6.5.2 Screening of $-\text{SO}_3\text{H}$ functionalized ionic liquids

Nevertheless, the moderate conversions and yields obtained in the above attempts opened up an opportunity to develop other efficient reusable acid catalysts for the targeted furan condensation reaction. Therefore, we focused our efforts on sulfonic acid functionalized ionic liquids (**4–8**) as catalysts for the reaction between furan and furfural. These ionic liquids are strongly acidic due to the presence of the sulfonic acid functionality, and their strong ionic nature makes them immiscible with hydrophobic reaction media, where the substrate furan itself is the reaction medium. For comparison, we prepared several Brønsted acidic ionic liquids (**4–8**; Figure 6.2) *via* the quaternization of 1-methylimidazole, triethylamine or pyridine with 1,3-propane/1,4-butane sultone and their successive protonation with conc.  $\text{H}_2\text{SO}_4$ .



**Figure 6.2.** Sulfonic acid functionalized ionic liquids.

The Brønsted acidity of these ionic liquids was determined in terms of the Hammett acidity function, as given in eqn (1). [31]

$$Ho = pK(I)_{aq} + \log ([I]/[IH^+]) \dots \dots \dots (1)$$

where,  $pK(I)_{aq}$  is the  $pK_a$  value of the indicator, which is (0.99),  $[IH^+]$  is the protonated form of the indicator,  $[I]$  is the molar concentration of the unprotonated form of the indicator and  $[IH^+]$  is the molar concentration of the protonated form of the indicator. The UV-VIS spectra of both the unprotonated and protonated forms of the indicator show a specific absorption at 360 nm in ethanol; however, the intensity is higher for the protonated form. The measured intensity values of absorbance were used to determine the  $[I]/[IH^+]$  ratio from which the value of  $Ho$  was calculated for all four ILs. The acidity trend of the ILs (**4–8**) is in the following order [ionic liquid/Hammett acidity ( $Ho$ )]: **4** ( $Ho = -0.78$ ) < **7** ( $Ho = -1.21$ ) < **5** ( $Ho = -1.55$ ) < **6** ( $Ho = -1.84$ ) < **8** ( $Ho = -1.90$ ). These acidic ILs were investigated to determine their catalytic activity for the condensation of furfural with furan in aqueous and non-aqueous media (Tables 6.2 and 3). Initially, the acidic IL **4** (20 mol %) was tested for furan condensation with furfural for 3 h, which gave only 75 % conversion of furfural with 52 % yield of TFM (Table 6.2, entry 1). Thereafter, the ionic liquid (**5**) containing an  $-SO_3H$  functional group separated from imidazolium by propyl chain linkers was employed, which showed 100 % conversion of furfural with improved yield of the condensation product (TFM) from 52 to 68 % (Table 6.2, entry 2).

**Table 6.2** Condensation of furan with furfural using acidic ionic liquids <sup>[a]</sup>

Entry	Ionic Liquid	Conv. <sup>[b]</sup> of <b>2</b> [%]	Yield <sup>[c]</sup> of <b>3</b> [%]
1	<b>4</b>	75	52
2	<b>5</b>	100	68
3	<b>6</b>	100	72
4	<b>7</b>	98	59
5	<b>8</b>	100	70

[a] Reaction conditions: furfural, **2** (0.192 g, 2 mmol), furan, **1** (5 mL), ionic liquid (20 mol %), rt, 3h. [b] Conversion was measured using GC. [c] Isolated yields after column chromatography.

Moreover, the ionic liquid (**6**) containing an  $-\text{SO}_3\text{H}$  functional group separated from imidazolium by butyl chain linkers showed a slightly higher TFM yield of 72 % (Table 6.2, entry 3). Thus, the ionic liquids (*e.g.* ILs, **5** and **6**) with alkyl chain linkers [32] were found to be more effective and acidic than the imidazolium linked N-sulfonic acids (*e.g.* IL, **4**). In addition, the increase in carbon chain length between imidazole and the  $-\text{SO}_3\text{H}$  functionality increased the acidity as well as the catalytic activity of the ILs (*e.g.* **5** vs. **6**, Table 6.2, entries 2 and 3). Therefore, for comparison, we prepared and evaluated the performances of triethylamine and pyridine based  $-\text{SO}_3\text{H}$  functionalized ionic liquids (*e.g.* **7** and **8**) possessing a butyl chain. In the presence of IL **7**, the yield of TFM was only 59 % with 98 % conversion of furfural (Table 6.2, entry 4), whereas, in the presence of **8**, 70 % yield of TFM with almost complete conversion of furfural was observed (Table 6.2, entry 5). Even though the acidity of IL **8** is higher than that of IL **6** the catalytic activity of **8** is comparable with **6** (Table 6.2, entries 3 and 5). However, in the above cases, the lower yield of the condensation product is due to the significant formation of black insoluble polymeric material (high molecular weight condensation product), as shown in Figure 3B.

### 6.5.3 Role of water

Importantly, we discovered that the addition of water (as an aqueous phase) along with acidic ILs forms a two phase system, which allows easy separation of the product. This strategy minimizes the formation of polymeric products since contact between the TFM formed and furfural is avoided. Thus, the suppression of polymer formation ultimately increased the yield of TFM up to 84 % (Table 6.3, entries 1–5). In addition, the excess furan used served as an extraction phase (organic layer) for product recovery (Figures 6.3A and 6.3C). In water medium and in the presence of IL **4** (20 mol %), the conversion of furfural increased from 75 % (non-aqueous medium, Table 6.2, entry 1) to 84% with enhanced yield (60 %) of TFM (Table 6.3, entry 1). Moreover, IL **5** showed complete furfural conversion with 74 % yield of TFM (Table 6.3, entry 2). On the other hand, the low loading (10 mol %) of IL **6** resulted in 94 % conversion of furfural with 77 % of TFM (Table 6.3, entry 3). When 20 mol % of IL **6** was used, complete consumption of furfural was achieved

with a maximum TFM yield of 84 % (Table 6.3, entry 3). After this experiment, we intentionally analyzed the aqueous phase using GC and GCMS, which showed neither furfural nor TFM. A high catalyst loading (30 mol% of IL **6**), was not required since it increased the acidity of the reaction mixture, which ultimately promoted polymer formation, thereby slightly decreasing the yield of TFM to 81 % (Table 6.3, entry 3). On the other hand, IL **7** showed a relatively low yield of TFM (75 %) (Table 6.3, entry 4). Furthermore, in the presence of IL **8**, 82 % yield of TFM was achieved with complete conversion of furfural (Table 6.3, entry 5).

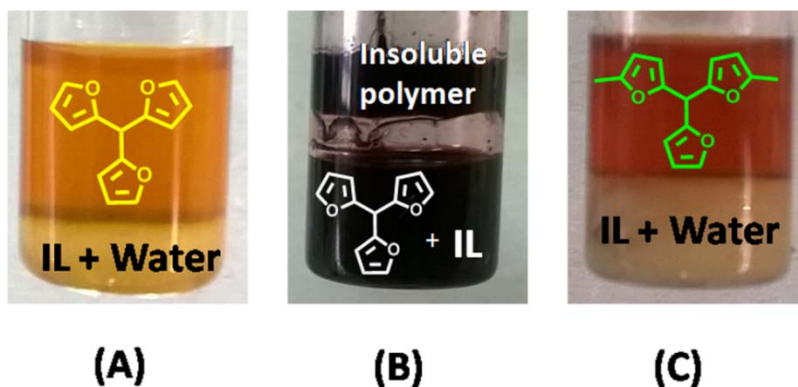
**Table 6.3** Condensation of furan with furfural using acidic catalysts in water <sup>[a]</sup>

Entry	IL/Catalyst	Loading (mol %)	Conv. <sup>[b]</sup> of <b>2</b> [%]	Yield <sup>[c]</sup> of <b>3</b> [%]
1	<b>4</b>	20	84	60
2	<b>5</b>	20	100	74
3	<b>6</b>	10	94	77
		20	100	84
		30	100	81
4	<b>7</b>	20	100	75
5	<b>8</b>	20	100	82
6	H <sub>2</sub> SO <sub>4</sub>	20	100	74
7	<i>p</i> -TSA	20	100	71

[a] Reaction conditions: furfural, **2** (0.192 g, 2 mmol), furan, **1** (5 mL), ionic liquids, water (1 mL), rt, 3h. [b] Conversion was measured using GC. [c] Isolated yields after column chromatography

For comparison, we used conc. H<sub>2</sub>SO<sub>4</sub> (20 mol %) in water for the condensation of furan with furfural, where up to 74 % yield of TFM was obtained (Table 6.3, entry 6). However, polymer formation in this case was significantly reduced compared to the use of conc. H<sub>2</sub>SO<sub>4</sub> without water (Table 6.1, entry 1). An almost similar result was obtained when *p*-TSA was used in water for TFM formation (Table 6.3, entry

7). The high yield of TFM in the presence of IL **6** directed us to explore its activity for further experiments.

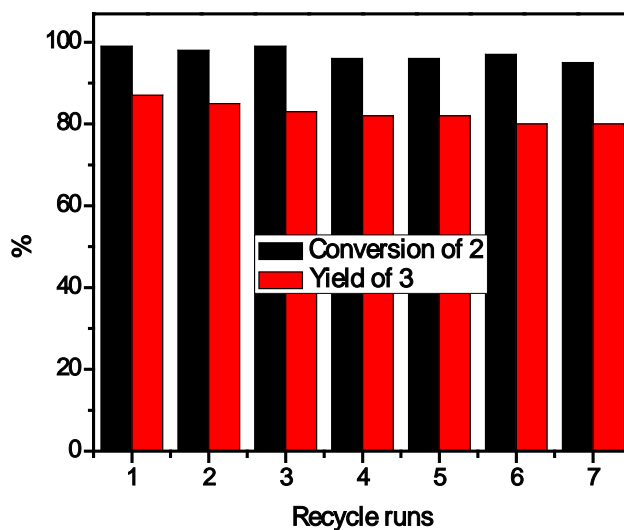


**Figure 6.3** (A) Phase separation between furan (containing product) and mixture of aqueous + IL phase, (B) In the reaction of furan and furfural in absence of water insoluble polymeric compound formed which was stuck on the wall of reactor (C) Phase separation between 2-methylfuran phase (containing product) and mixture of aqueous + IL phase.

#### 6.5.4 Catalyst recycles studies

In a typical recycle experiment, the product was separated from the reaction mixture by pipetting out the furan phase. The aqueous phase was then washed with ethyl acetate and subsequently the ethyl acetate layer was pipetted out and evaporated together with the furan layer to recover the product. Subsequently, the volatile impurities were removed on a rotavap at 80 °C. The same procedure was repeated after each reuse. As can be seen from Figure 6.4, after each reuse of the recovered IL (**6**), a slight decrease in the conversion of furfural was noted. The conversion of furfural gradually decreased from 99 % after the 1<sup>st</sup> reuse to 95 % after the 7<sup>th</sup> reuse. Similarly, a gradual decrease in the yield of TFM was also observed after each reuse of the IL (**6**). The drop in the yield of TFM was from 84 % after the 1<sup>st</sup> reuse to 80 % after the 7<sup>th</sup> reuse. Thus, the catalytic activity of the IL (**6**) was almost similar to its initial activity. This can be attributed to the minimal formation and no deposition of solid polymeric products on the IL (**6**) in aqueous medium.

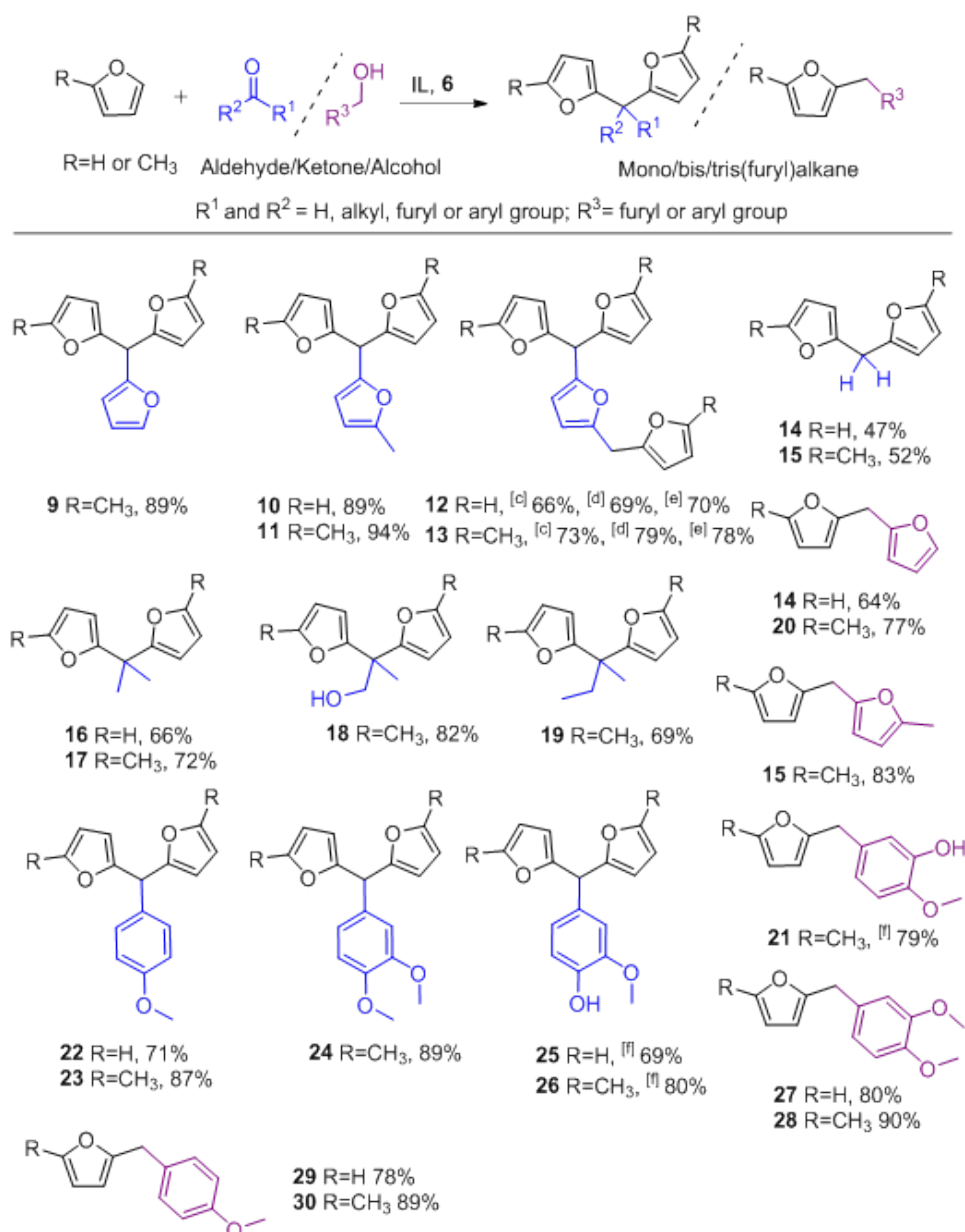




**Figure 6.4** Recycle study for production of TFM in the presence of sulfonic acid functionalized IL, **6**. Reaction conditions: furfural (0.192 g, 2 mmol), furan (5 mL), acid catalyst, **6** (20 mol %), water (1 mL), rt, 3h.

### 6.5.5 Substrate scope

After the successful optimization of the efficient reusable IL, **6** for the production of TFM (**3**), we explored the scope of our protocol for various lignocellulose derived aldehydes, ketones and alcohols for their condensation with furan (Figure 6.5). When 5-methylfurfural was condensed with furan, 89 % yield of product **10** was achieved. The high yield of **10** is due to the stability of 2,5-disubstituted furans, which are not susceptible to further condensation (secondary reaction). HMF itself condensed with three molecules of furan in the presence of IL **6** to produce **12** in 66 % yield with complete conversion of the starting material. Product **12** was also obtained in 69 and 70 % yield using 5-(acetyloxymethyl)furfural (AcMF) and 5-(formyloxymethyl)furfural (FMF) as starting materials, respectively. AcMF and FMF were found to be more active



**Figure 6.5** Substrates scope for the condensation of furans with various bio-derived molecules. [a] Reaction conditions: aldehydes/ketones (2 mmol) or alcohols (2 mmol), furan (5 mL), IL, **6** (20 mol %), water (1 mL), rt, 3h. [b] Reaction conditions: aldehydes/ketones (2 mmol) or alcohols (4 mmol), 2-methylfuran (0.361 g, 4.4 mmol), IL, **6** (20 mol %), water (0.5 mL), 65 °C, 2h. Reaction conditions: [c] HMF/ [d] AcMF/[e] FMF (2 mmol), furan (5 mL), IL, **6** (20 mol %), water (1 mL), rt, 3h. Reaction conditions: [c] HMF/[d] AcMF/[e] FMF (2 mmol), 2-methylfuran (0.541 g, 6.6 mmol), IL, **6** (20 mol %), water (0.5 mL), 65 °C, 2h. [f] Vanillin was dissolved in ethyl acetate prior to reaction. AcMF= 5-(acetoxymethyl)-2-furfural, FMF= 5-(formyloxymethyl)-2-furfural. Yields are isolated after column chromatography. All the products were confirmed using NMR analysis.

than HMF due to the presence of the electron withdrawing ester (acetate or formate) functionality. An aqueous solution of formaldehyde was reacted with furan, which gave a low yield (47 %) of the condensation product **14**. The condensation product **14** was obtained in substantially high yield of 64 % when furfuryl alcohol was condensed with furan. Aliphatic ketones such as acetone condensed with furan gave 66 % yield of **16**. Lignin derived aryl aldehydes such as 3-methoxy-4-hydroxybenzaldehyde (vanillin) and other aldehydes such as 4-methoxybenzaldehyde (anisaldehyde) were chosen as starting materials for condensation with furan. 3-Methoxy-4-hydroxybenzaldehyde (vanillin) is a depolymerisation product of lignin. [33] The condensation products **22** and **25** were obtained in 71 and 69 % yields, respectively. However, in the case of 3-methoxy-4-hydroxybenzaldehyde (vanillin), which was insoluble in both furan and the aqueous phase, ethyl acetate was added as the soluble medium to push the reaction. Furthermore, aryl alcohols such as 3,4-dimethoxybenzyl alcohol and 4-methoxybenzyl alcohol were also reacted with furan which afforded 80 and 88 % yields of the condensation products **27** and **29**, respectively.

The same protocol was successfully employed for the condensation of 2-methylfuran (MeF) and various other bio-derived substrates (Figure 6.5). Unlike furan, which has C<sub>2</sub> and C<sub>4</sub> positions prone to electrophilic substitution, MeF has only one C<sub>4</sub> position for electrophilic substitution. This feature of MeF ceases the production of high molecular weight products via secondary reaction. Due to the higher stability and higher boiling point of MeF than that of furan, the condensation reaction was conducted at 65 °C. When furfural was reacted with MeF, condensation product **9** was produced in 89 % yield. Tri(5-methylfuran)methane, **11** was produced in the significantly higher yield of 94 % due to the higher stability of the electrophile possessing 2,5 substitution (5-methylfurfural). The condensation product **13** was obtained in 73, 79 and 78 % by reacting MeF with HMF, AcMF and FMF, respectively. The activity of acetone and hydroxyacetone was also evaluated for condensation with MeF. The condensation product (**18**) of MeF and hydroxyacetone was obtained in the high yield of 82 % compared to the condensation product (**17**, 72 %) obtained from acetone. It is clear that due to the presence of the electron withdrawing –OH group in hydroxyacetone, the –C=O functionality becomes more

electrophilic and reactive for nucleophilic attack from MeF. [6c] On the other hand, 2-butanone, which is a less electrophilic ketone, reacted slowly with MeF compared to acetone and showed only 69 % yield of **19** after 5 h. Product **15** was obtained in 52 % when MeF was treated with formaldehyde; however, the same product was obtained in significantly higher yield of 83 % when MeF was treated with furfuryl alcohol. The condensation of MeF and lignin derived aldehydes showed >80 % yield of condensation products **23**, **24** and **26**. Similarly, the benzylation of MeF was conducted with aryl alcohols to produce condensation products **21**, **28** and **30** in 80–90 % yield.

## 6.6. Conclusions

In summary, hydrophilic,  $-\text{SO}_3\text{H}$  functionalized, recyclable, Brønsted acidic ionic liquid catalysts integrated with a two phase reaction system were developed for the efficient condensation of furan with furfural for the production of tri(furan-2-yl)methane products. Several Brønsted acidic ionic liquids were prepared *via* the quaternization of an organic base with 1,3-propane/1,4-butane sultone and their successive protonation with sulfuric acid. The Hammett acidity function varied for the four ILs studied here, as determined by the  $[\text{I}]/[\text{IH}^+]$  ratio from the intensity UV-Vis absorbance values at 360 nm. It was found that the ILs with alkyl chain linkers were more acidic and more active. In addition, an increase in the carbon chain length between imidazole and  $-\text{SO}_3\text{H}$  increased the acidity as well as the catalytic activity of the ILs. Similar to mineral acids, for the best performing IL in a homogeneous phase, undesired products (black polymer-like) were observed. This was successfully minimized by introducing water as a second phase since, it significantly suppressed the direct interaction of acid with the product/substrate. Furan as a reactant as well as an extractant enhanced the product isolation up to 84 %, and the IL + aqueous phase could be recycled multiple times. This protocol was successfully demonstrated for a wide variety of bio-derived substrates for condensation with furan as well as with 2-methylfuran.

## 6.7. References

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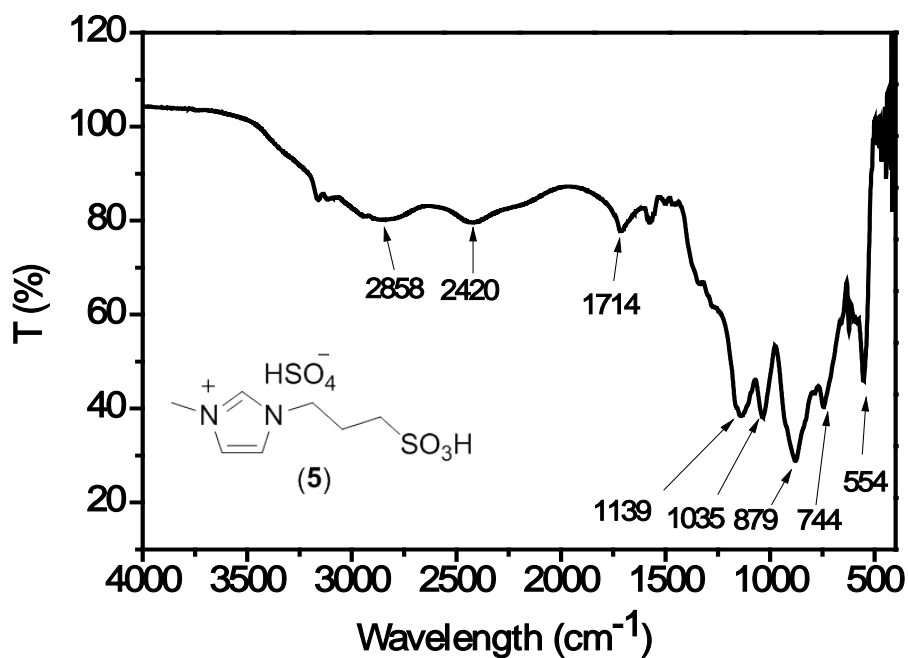
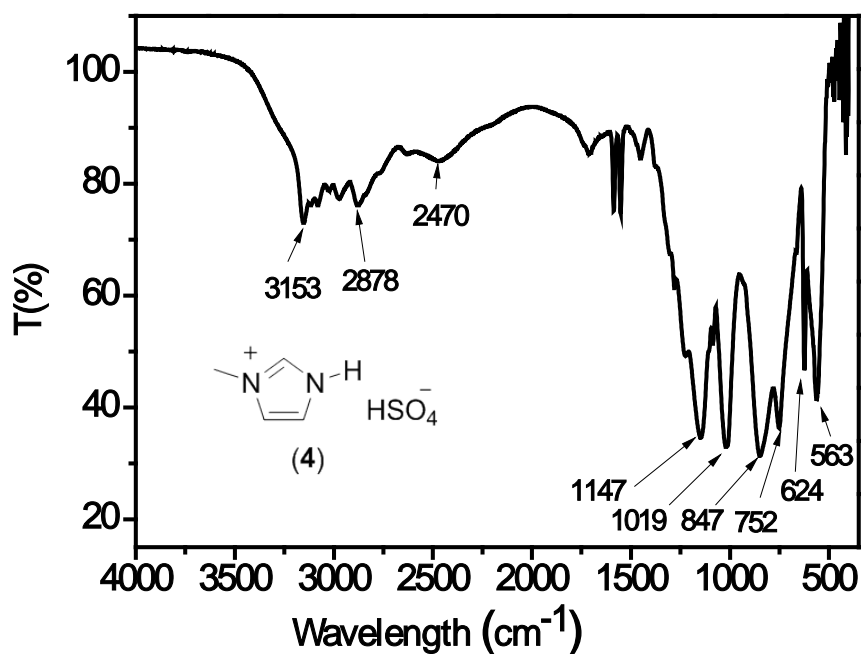
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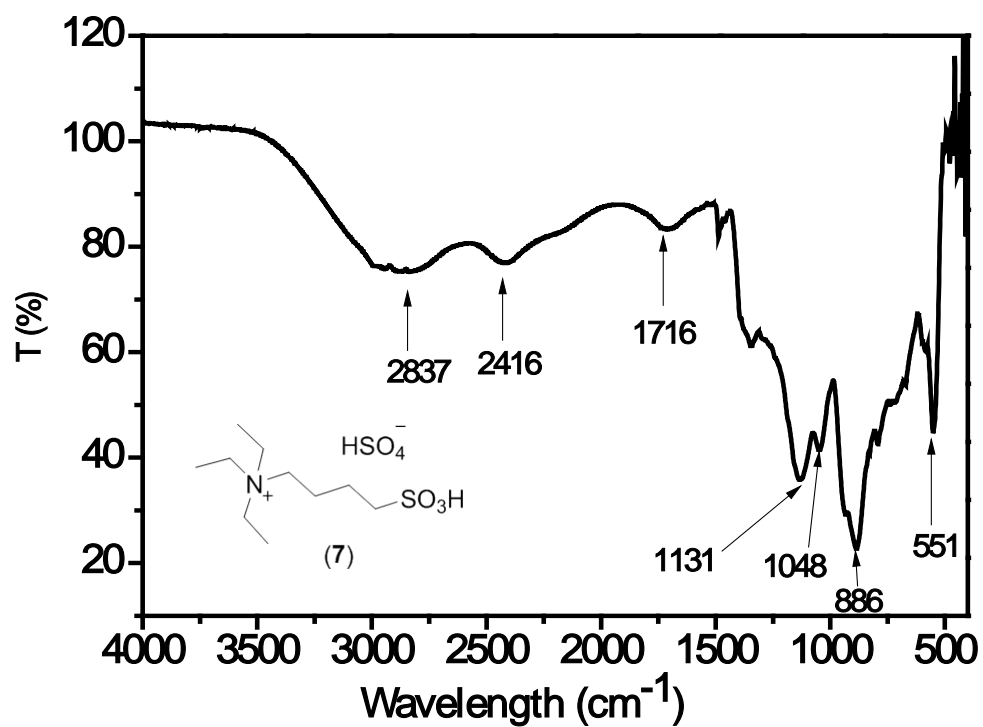
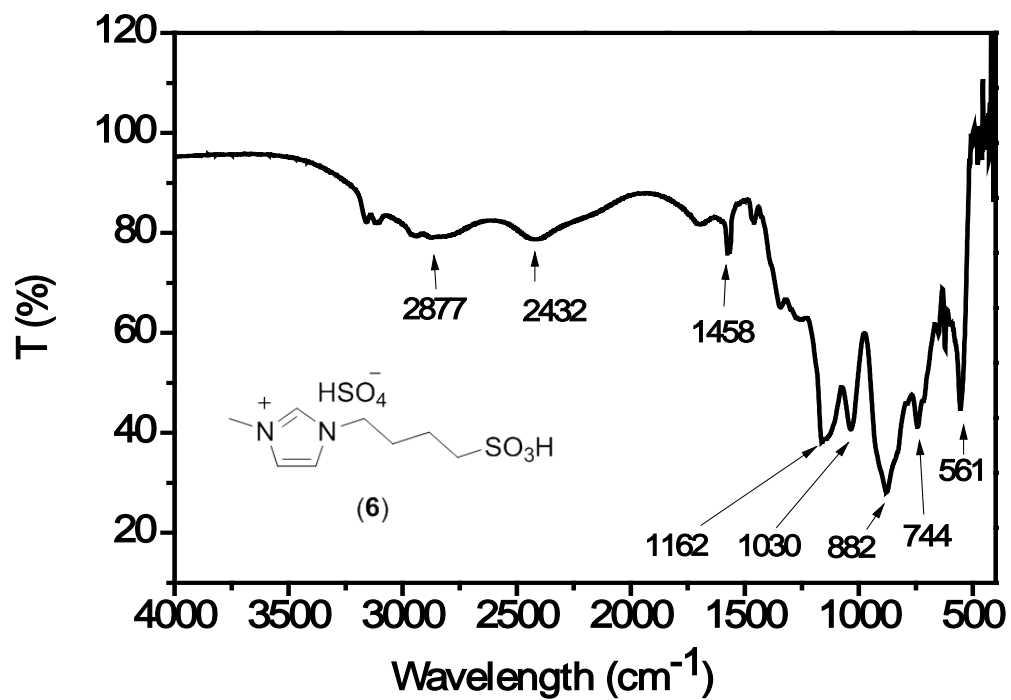
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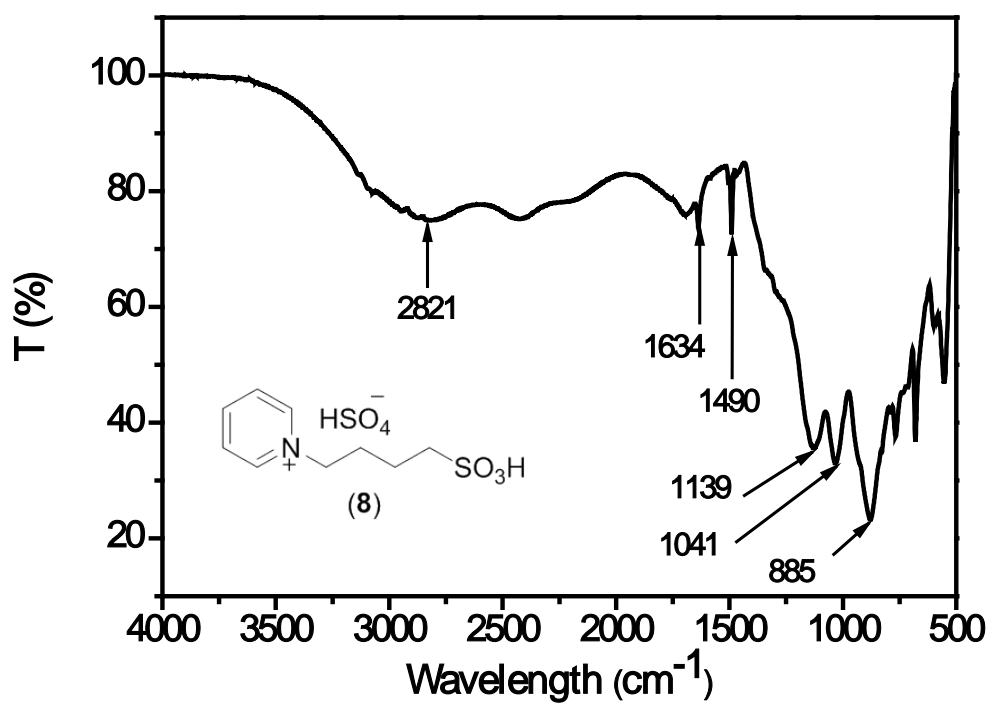


## 6.8. Spectroscopic data of all synthesized compounds

### 6.8.1. FTIR of ILs (4-8)



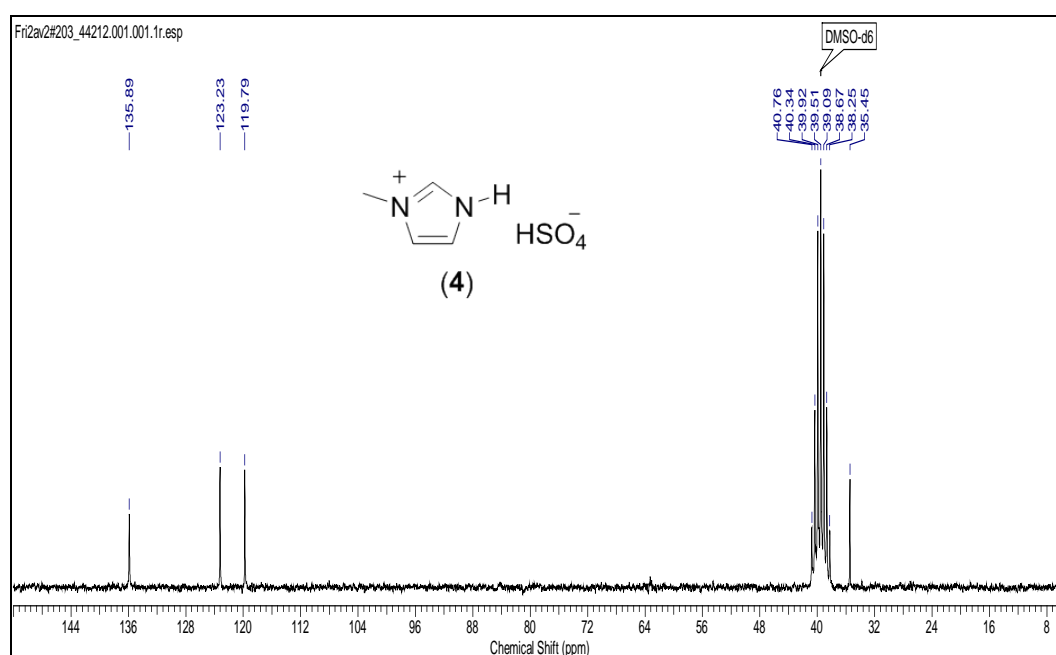
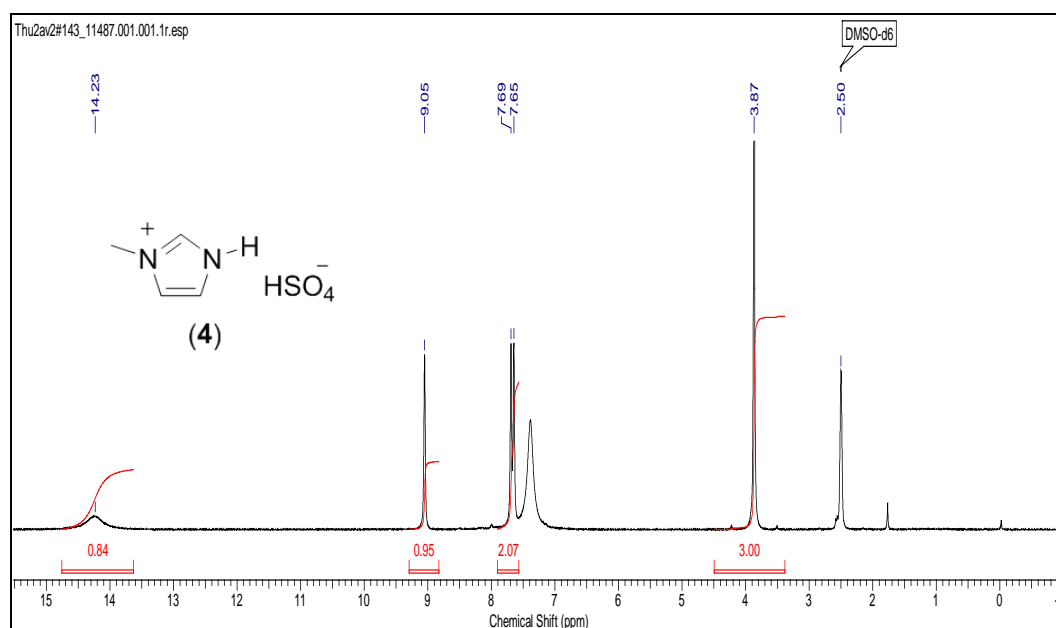




6.8.2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR of ionic liquids and synthesized compounds**N-methylimidazolium hydrogen sulfate:**

$^1\text{H}$  NMR (200 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 3.87 (s, 3 H) 7.67 (d,  $J=9.35$  Hz, 2 H) 9.05 (s, 1 H) 14.23 (br. s., 1 H)

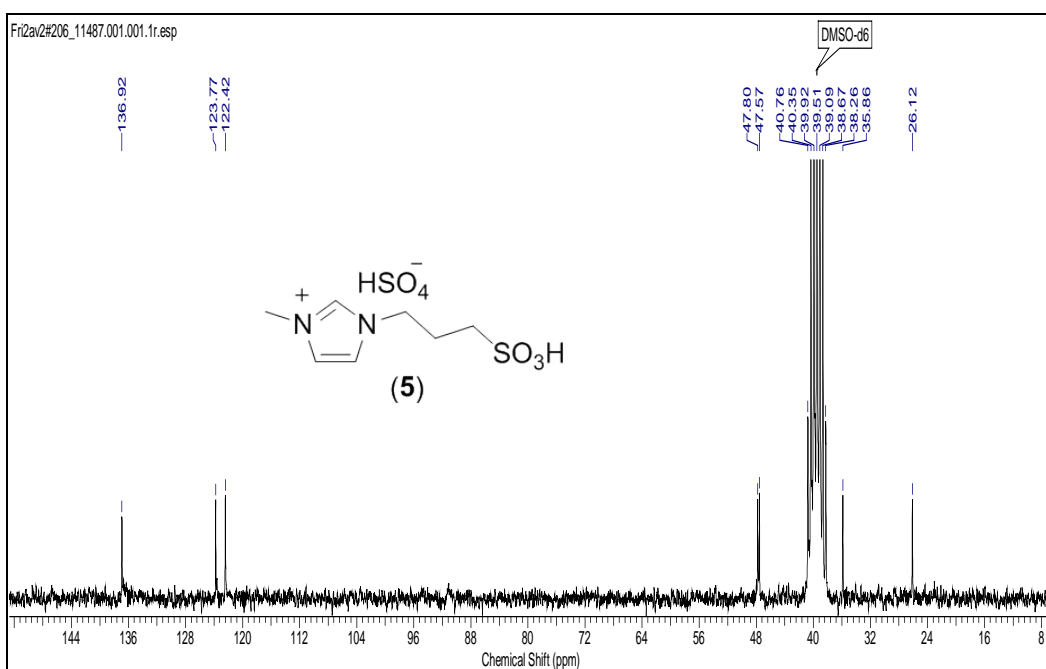
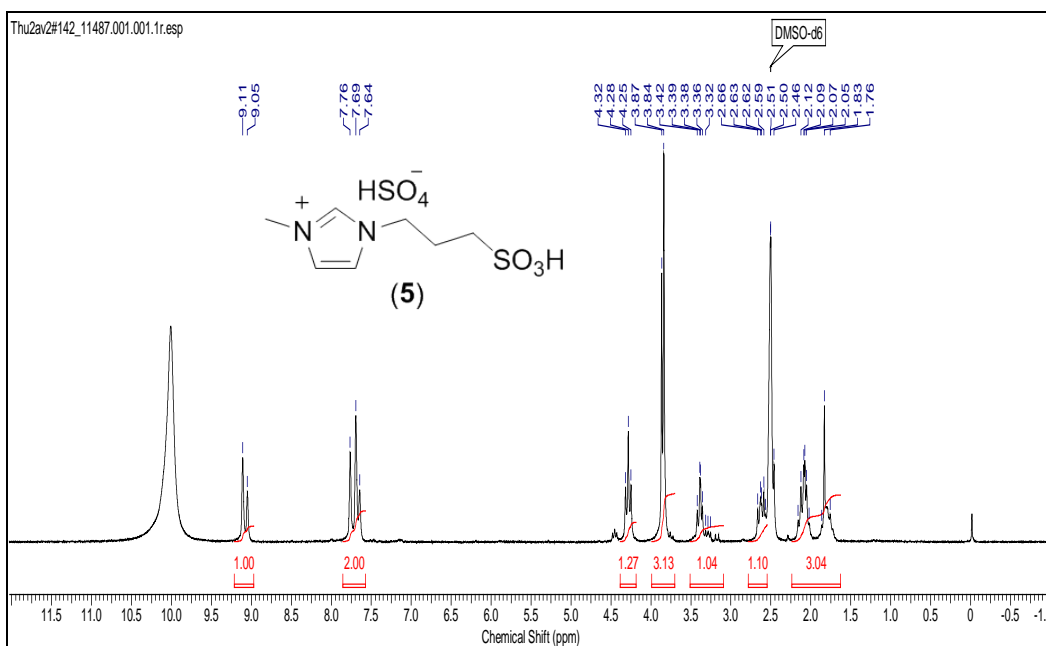
$^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 35.45, 38.25, 38.67, 39.09, 39.92, 40.34, 40.76, 119.79, 123.23, 135.89.



**3-methyl-1-(3-sulfopropyl)-1H-imidazol-3-ium**

$^1\text{H}$  NMR (200 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 1.763 – 2.12 (m, 3 H) 2.55 - 2.78 (m, 1 H) 3.09 - 3.51 (m, 1 H) 3.85 (d,  $J=5.56$  Hz, 3 H) 4.28 (t,  $J=6.88$  Hz, 1 H) 7.57 - 7.85 (m, 2 H) 8.97 - 9.21 (m, 1 H)

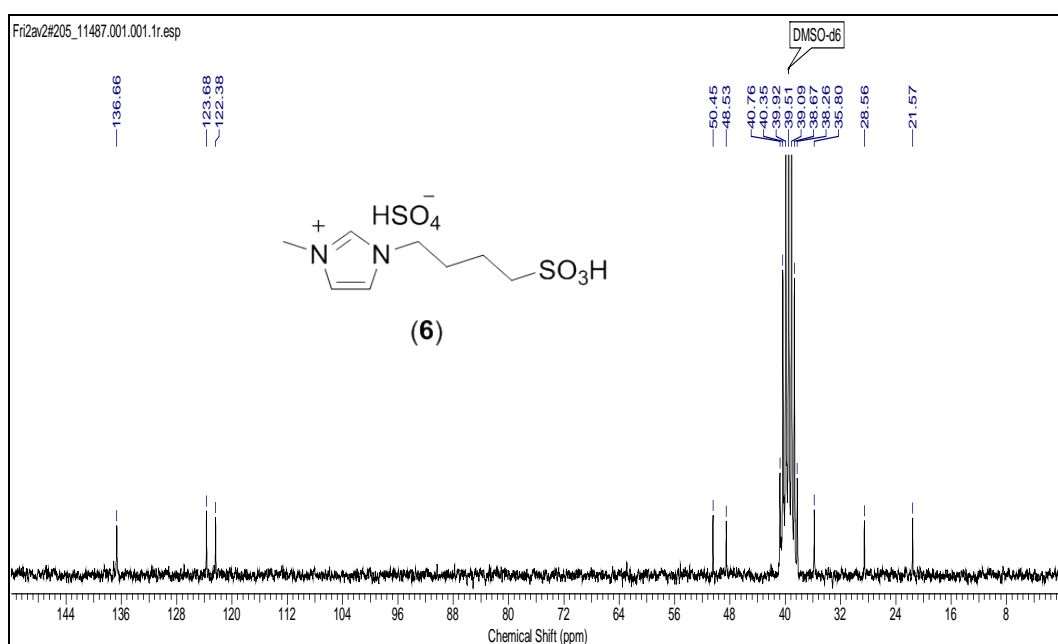
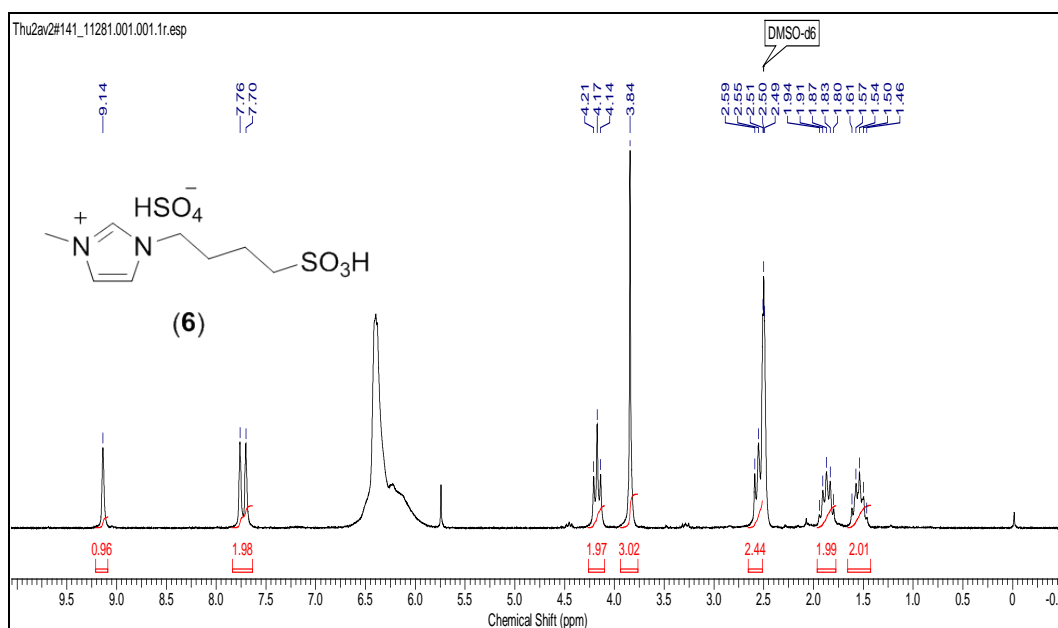
$^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 26.12, 35.86, 38.26, 38.67, 39.09, 39.92, 40.35, 40.76, 47.57, 47.80, 122.42, 123.77, 136.92.



**3-methyl-1-(3-sulfobutyl)-1H-imidazol-3-ium**

$^1\text{H}$  NMR (200 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 1.54 (quin,  $J=7.42$  Hz, 2 H) 1.87 (quin,  $J=7.20$  Hz, 2 H) 2.51-2.66 (m, 3 H) 3.84 (s, 3 H) 4.17 (t,  $J=6.88$  Hz, 2 H) 7.76 (s, 1 H) 7.70 (s, 1 H) 9.14 (s, 1 H)

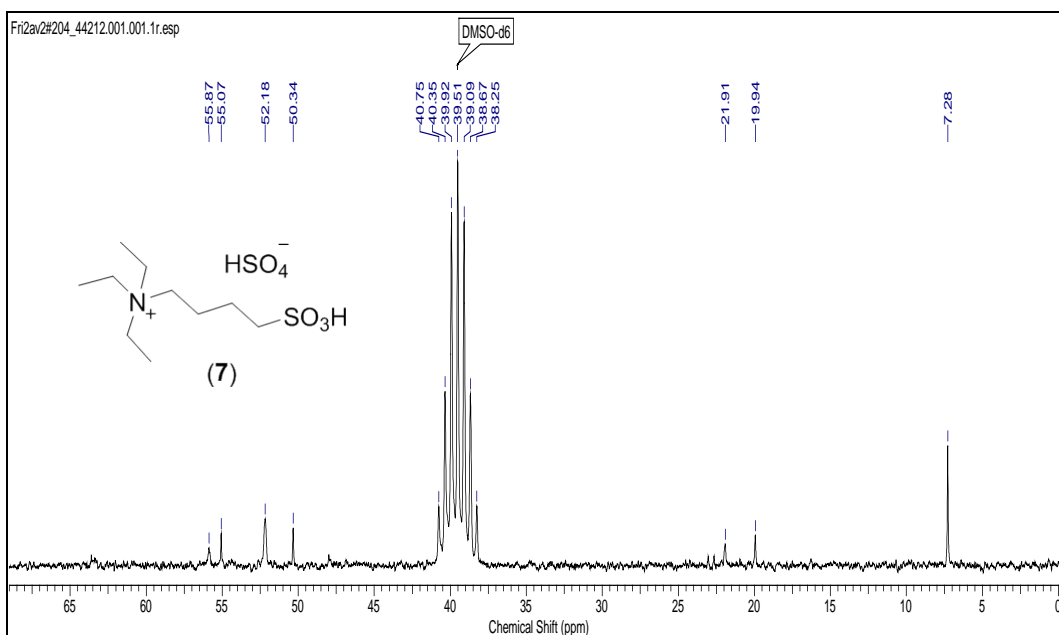
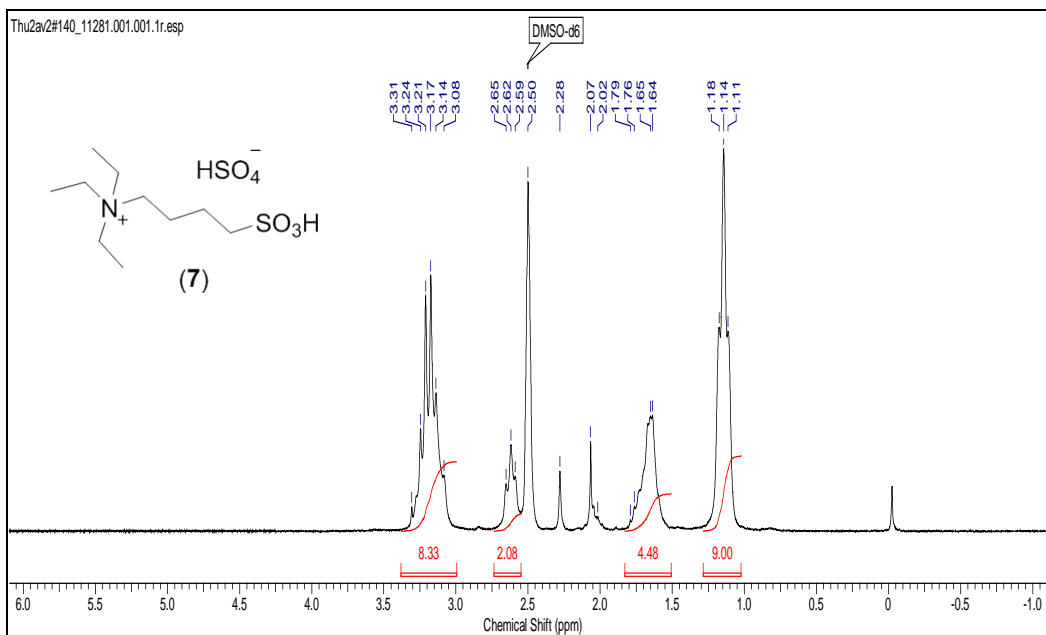
$^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 21.57, 28.56, 35.80, 38.26, 38.67, 39.09, 39.92, 40.35, 40.76, 48.53, 50.45, 122.38, 123.68, 136.66



**N,N,N-triethyl-4-sulfobutan-1-aminium**

$^1\text{H}$  NMR (200 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 1.14 (t,  $J=6.19$  Hz, 9 H) 1.51 - 1.71 (m, 4 H) 1.71 - 1.83 (m, 1 H) 2.62 (t,  $J=6.32$  Hz, 2 H) 2.99 - 3.38 (m, 8 H)

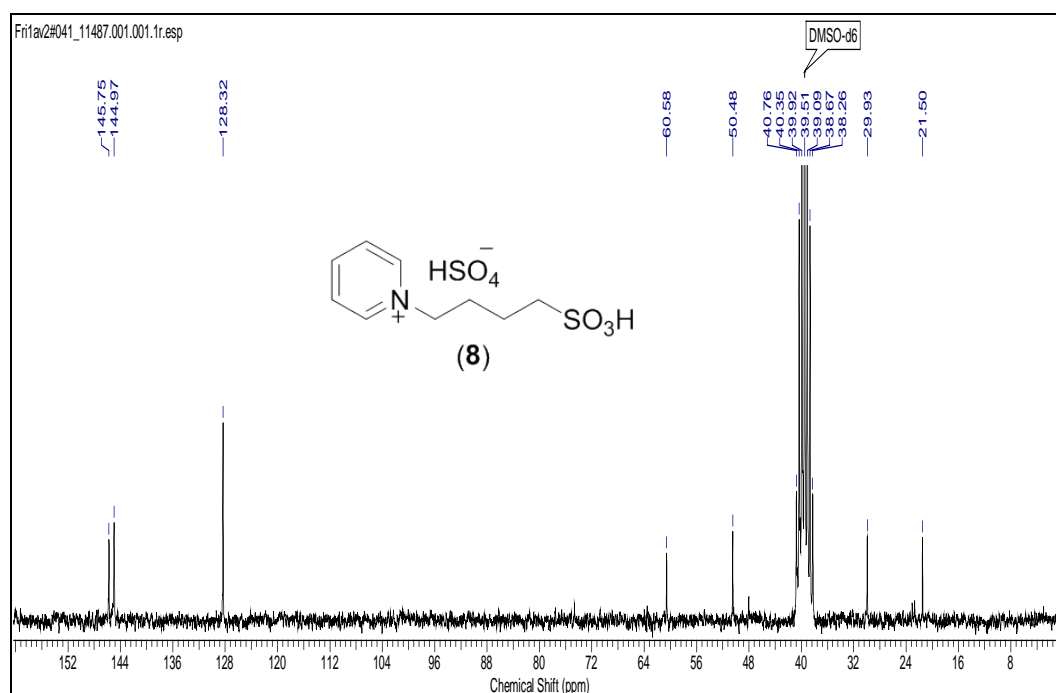
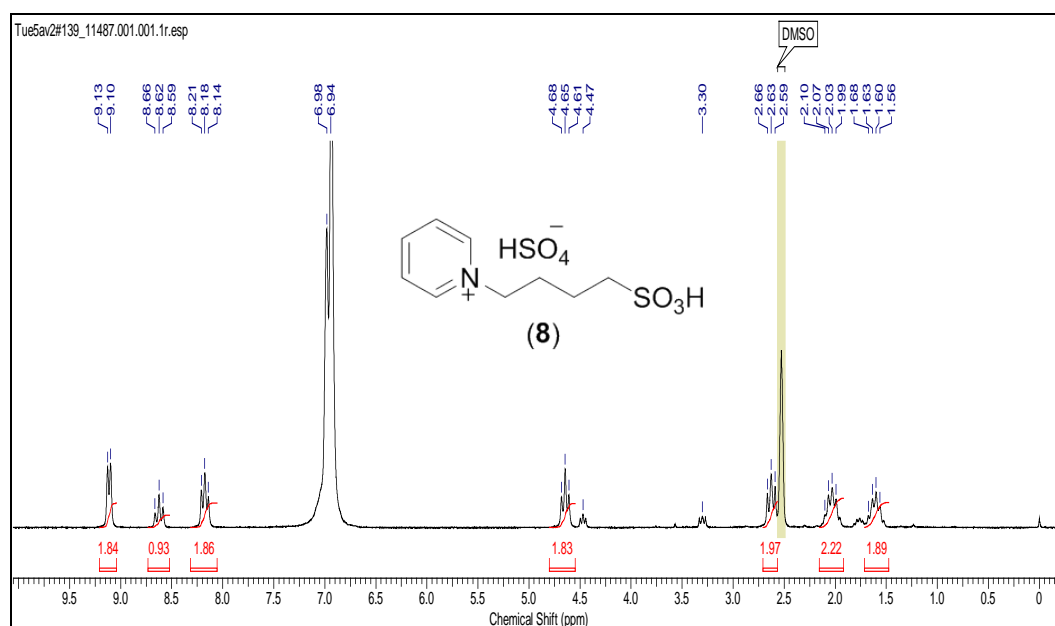
$^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 7.28, 19.94, 21.91, 38.25, 38.67, 39.09, 39.92, 40.35, 40.75, 50.34, 52.18, 55.07, 55.87



## 1-(4-sulfobutyl)pyridin-1-ium

$^1\text{H}$  NMR (200 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm: 1.48-1.71 (m, 2 H) 1.92-2.16 (m, 2 H) 2.63 (t,  $J=7.52$  Hz, 2 H) 4.65 (t,  $J=7.26$  Hz, 2 H) 8.18 (t,  $J=6.88$  Hz, 2 H) 8.52-8.73 (m, 1 H) 9.11 (d,  $J=5.68$  Hz, 2 H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm: 21.50, 29.93, 50.48, 60.58, 128.32, 144.97, 145.75.

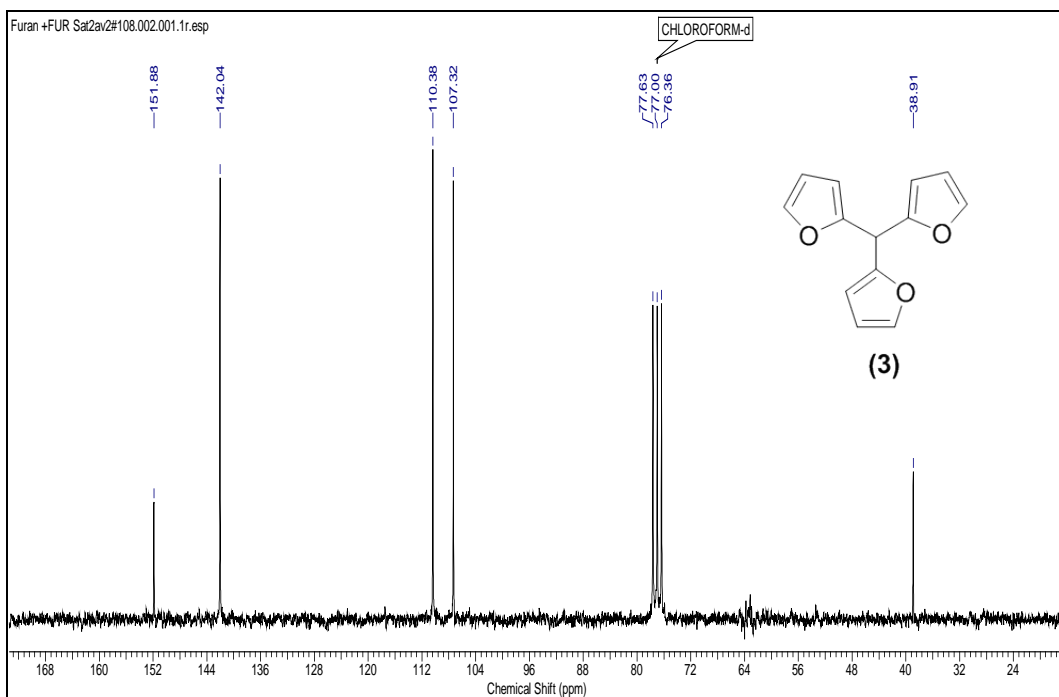
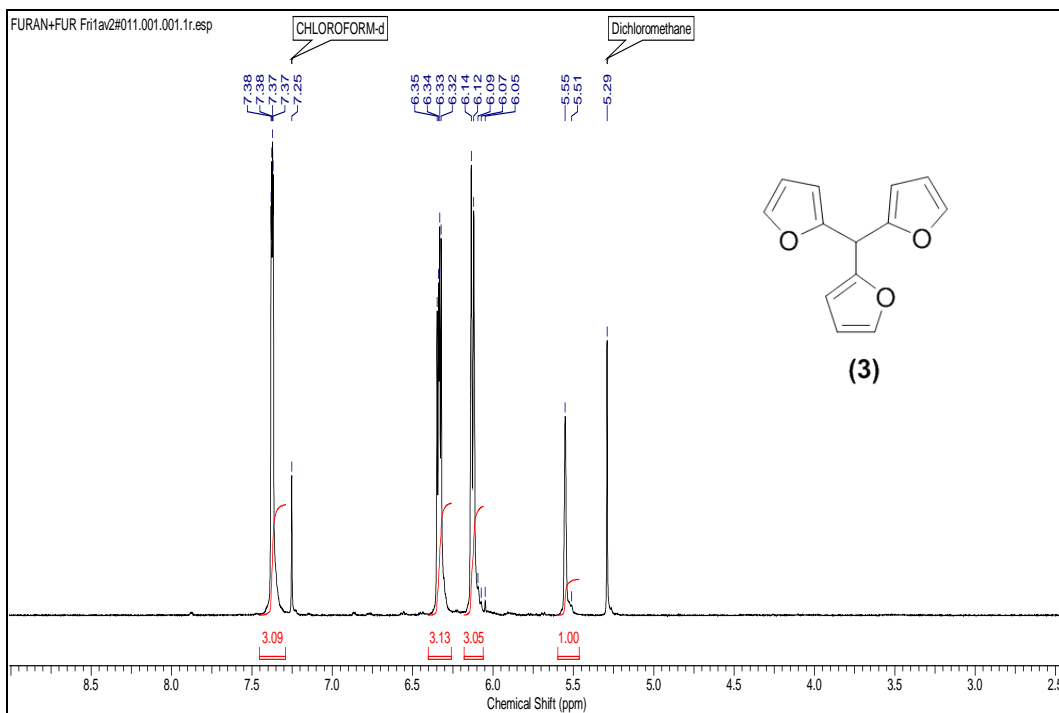




**tri(furan-2-yl)methane**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 5.46-5.60 (m, 1 H) 6.06 -6.18 (m, 3 H) 6.34 (dd,  $J=3.16, 1.89$  Hz, 3 H) 7.37 (dd,  $J=1.77, 0.76$  Hz, 3 H)

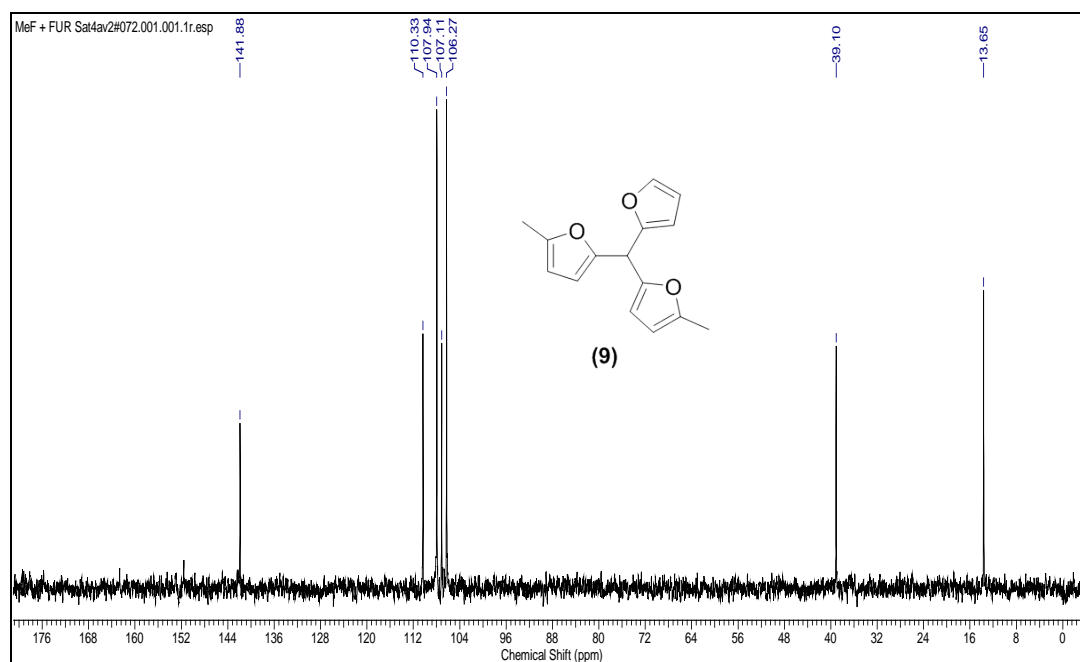
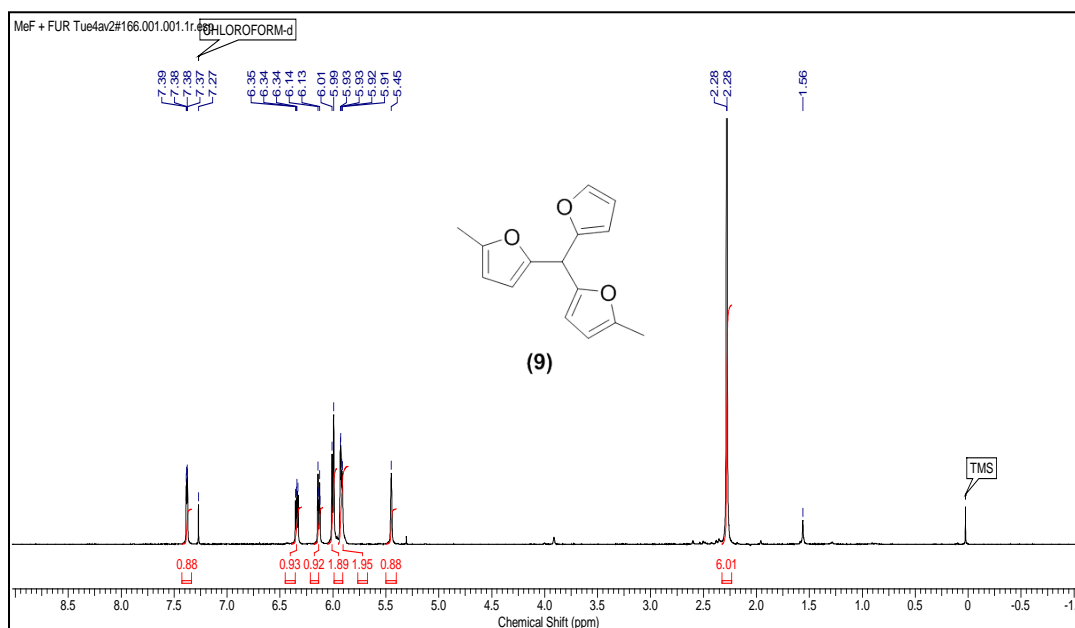
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 38.91, 107.32, 110.38, 142.04, 151.88



**5,5'-(furan-2-ylmethylene)bis(2-methylfuran)**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.28 (s, 6 H) 5.45 (s, 1 H) 5.91-5.93 (m, 2 H) 5.99-6.01 (d,  $J=3.03$  Hz, 2 H) 6.13-6.14 (dt,  $J=3.22$ , 0.79 Hz, 1 H) 6.34-6.35 (dd,  $J=3.03$ , 1.89 Hz, 1 H) 7.37-7.39 (dd,  $J=1.89$ , 0.88 Hz, 1 H)

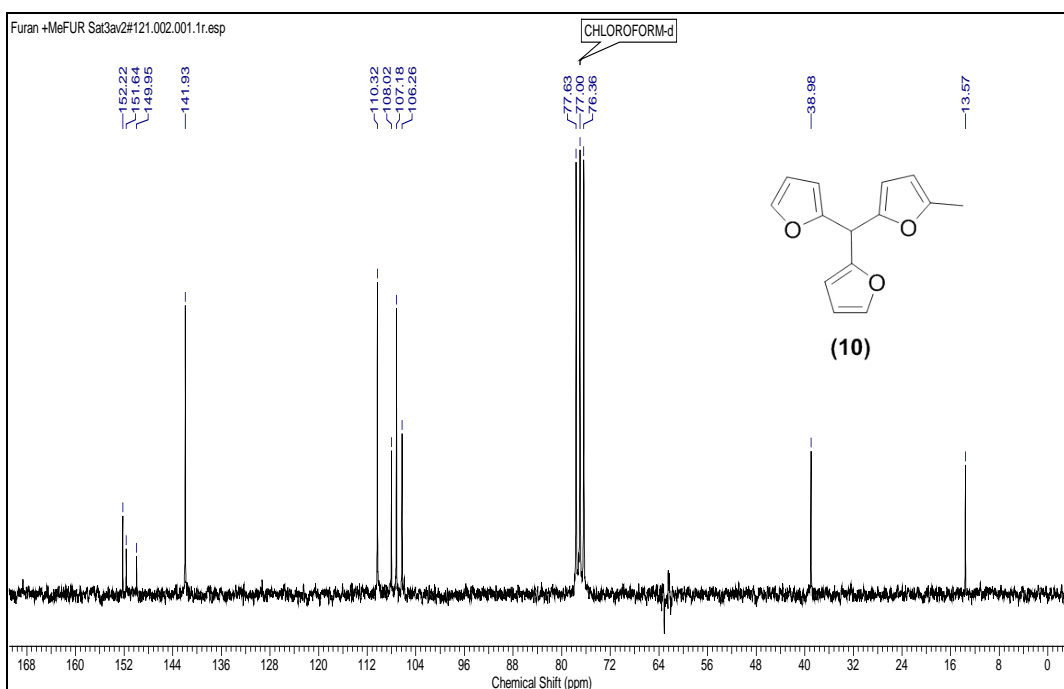
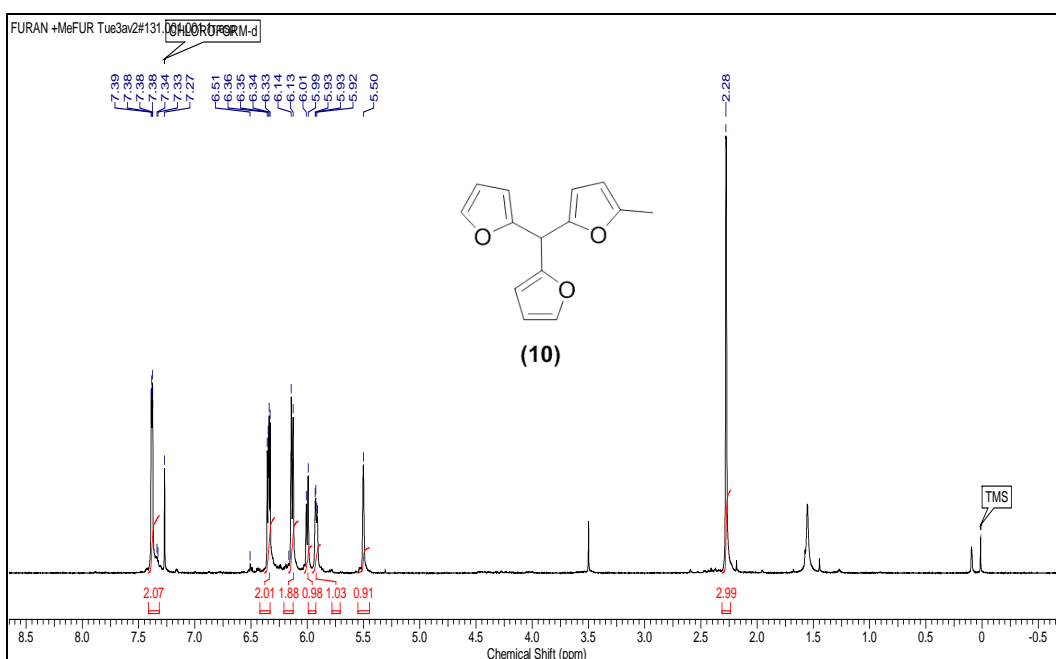
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.65, 39.10, 106.27, 107.11, 107.94, 110.33 and 141.88



**2,2'-((5-methylfuran-2-yl)methylene)difuran**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.28 (s, 3 H) 5.50 (s, 1 H) 5.92-5.93 (dd,  $J=3.03$ , 0.88 Hz, 1 H) 5.99- 6.01 (d,  $J=3.16$  Hz, 1 H) 6.13-6.14 (m, 2 H) 6.33-6.36 (dd,  $J=3.28$ , 1.89 Hz, 2 H) 7.33-7.39 (m, 2 H)

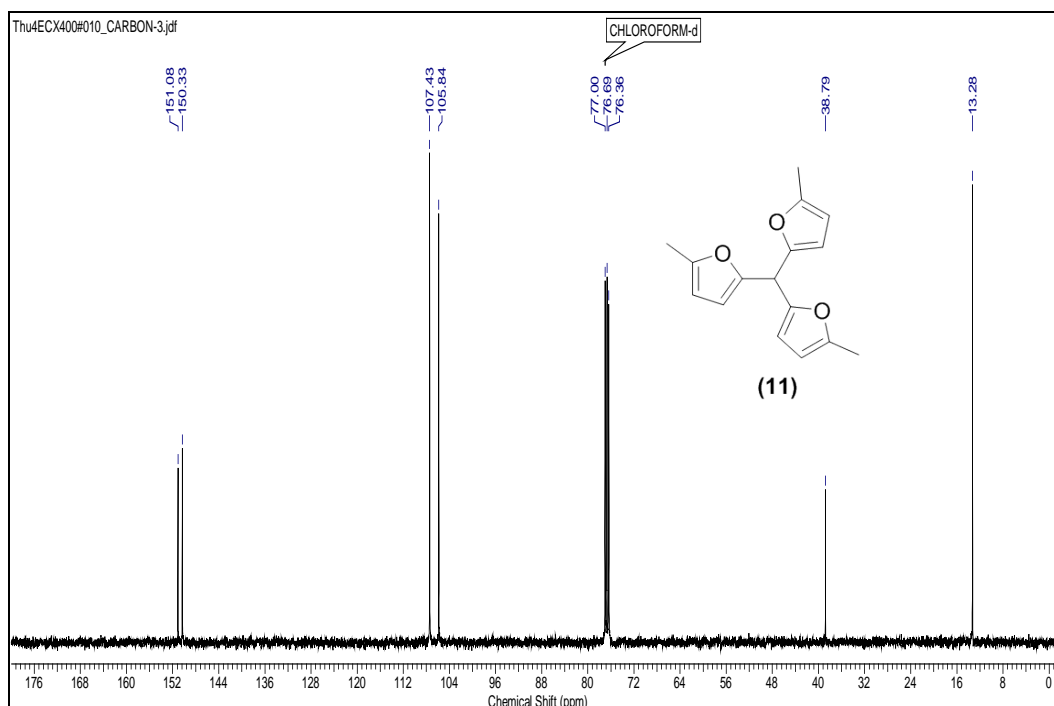
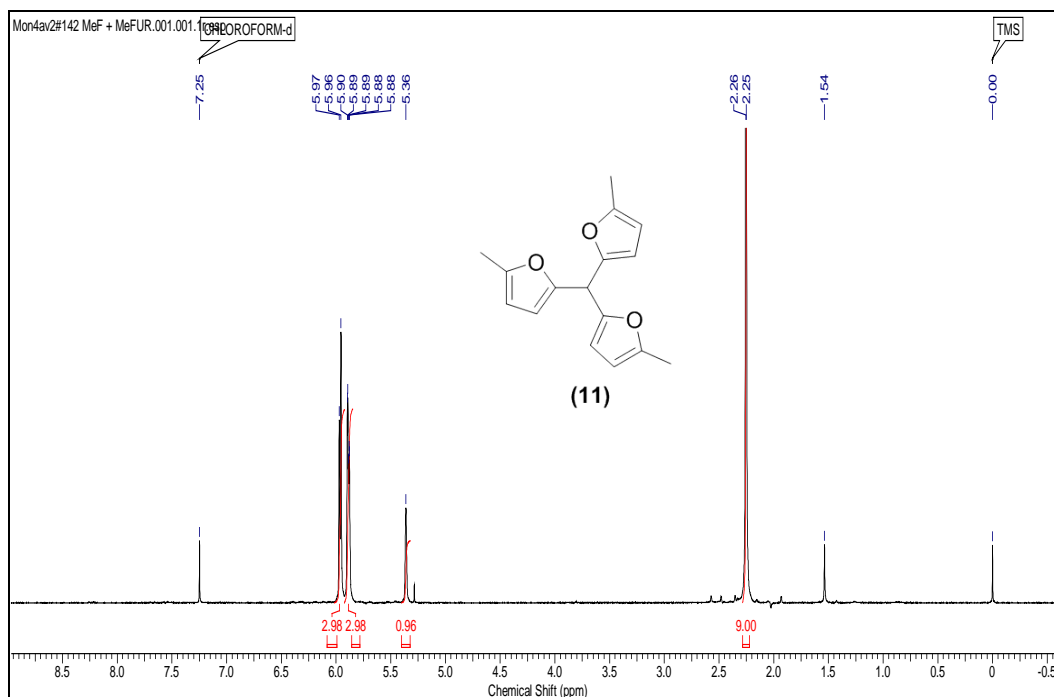
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.57, 38.98, 106.26, 107.18, 108.02, 110.32, 141.93, 149.95, 151.64, 152.22



**tris(5-methylfuran-2-yl)methane**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.22-2.28 (m, 9 H) 5.36 (s, 1 H) 5.88-5.90 (m, 3 H) 5.96-5.97 (d,  $J=3.03$  Hz, 3 H)

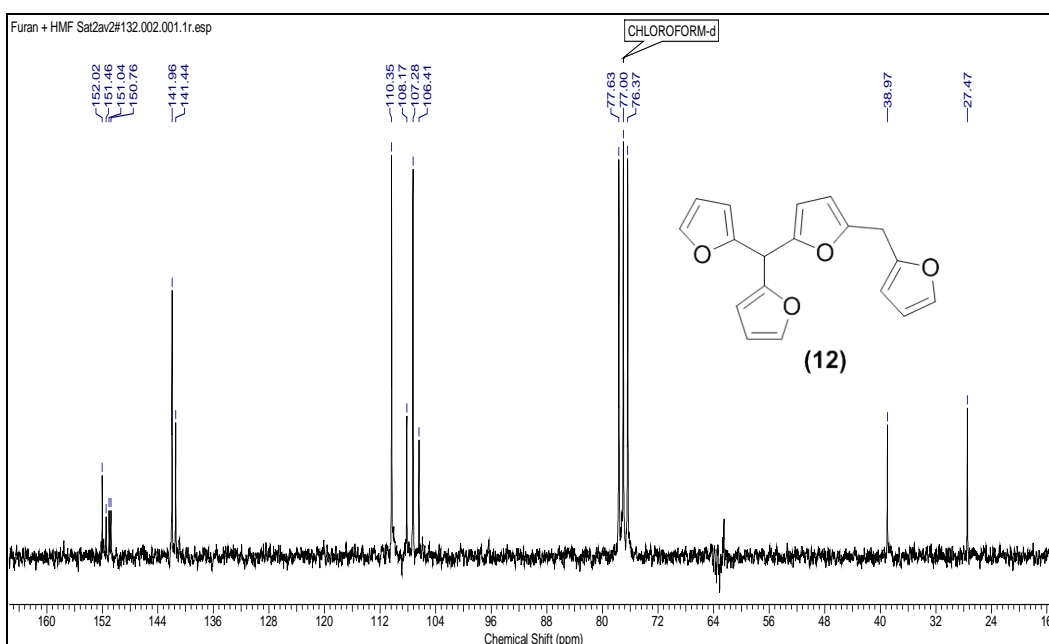
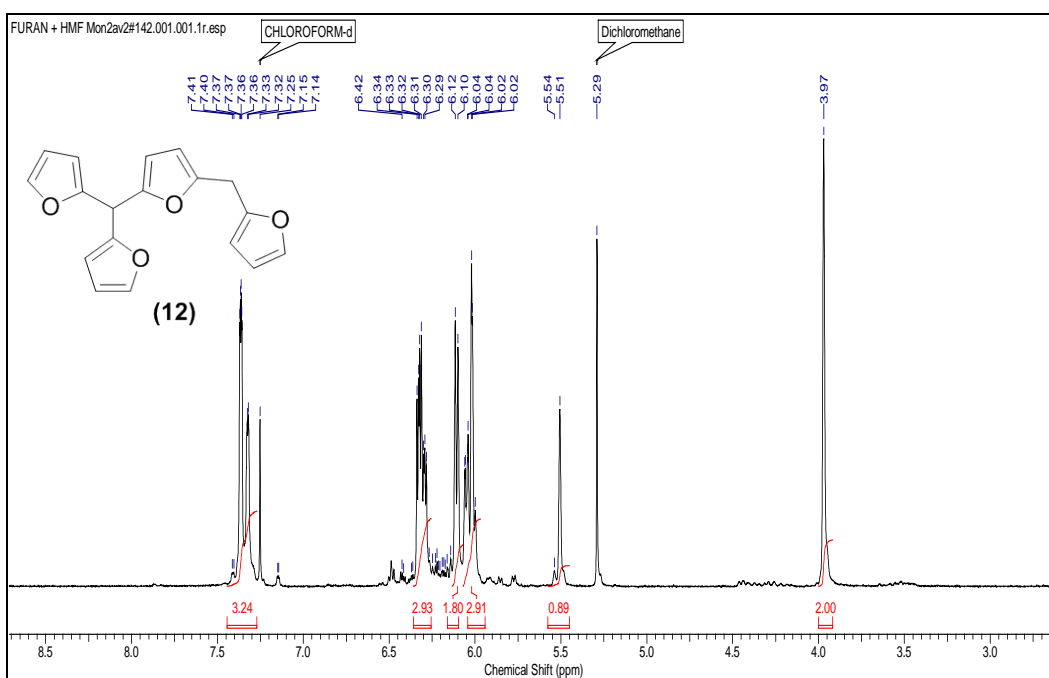
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.71, 39.22, 106.27, 107.86, 150.76, 151.51



**2,2'-((5-(furan-2-ylmethyl)furan-2-yl)methylene)difuran**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 3.97 (s, 2 H) 5.51-5.54 (m, 1 H) 6.02-6.04 (m, 3 H) 6.10-6.12 (d,  $J=3.16$  Hz, 2 H) 6.29-6.34 (m, 3 H) 7.25-7.41 (m, 3 H)

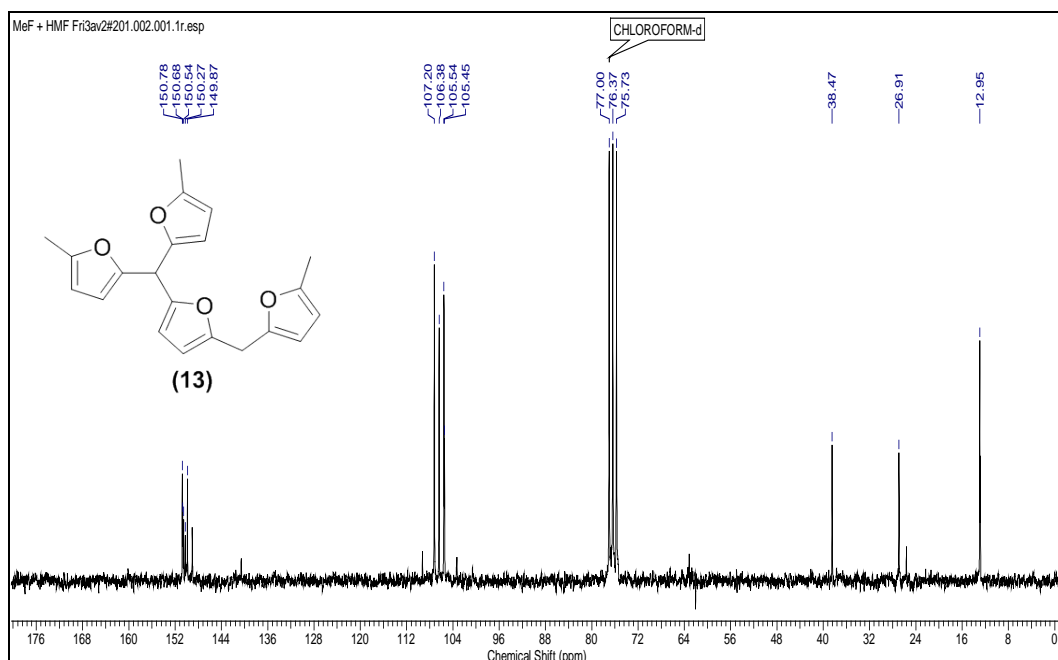
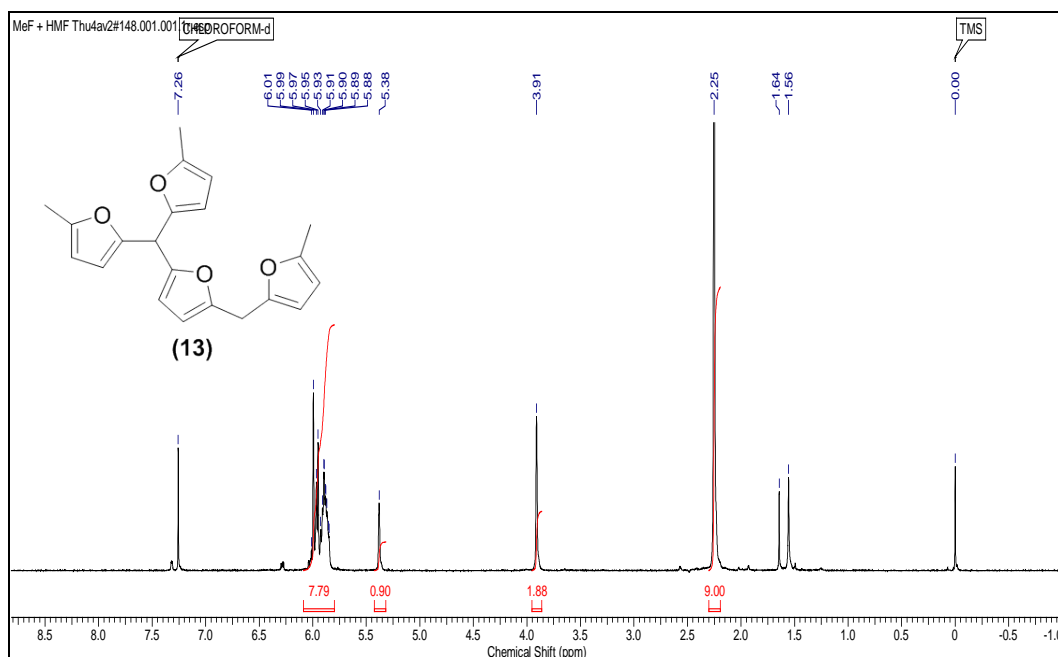
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 27.47, 38.97, 106.41, 107.28, 108.17, 110.35, 141.44, 141.96, 150.76, 151.04, 151.46, 152.02



**5,5'-((5-((5-methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran)**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.25 (s, 9 H) 3.91 (s, 2 H) 5.38 (s, 1 H) 5.88-6.01 (m, 8 H)

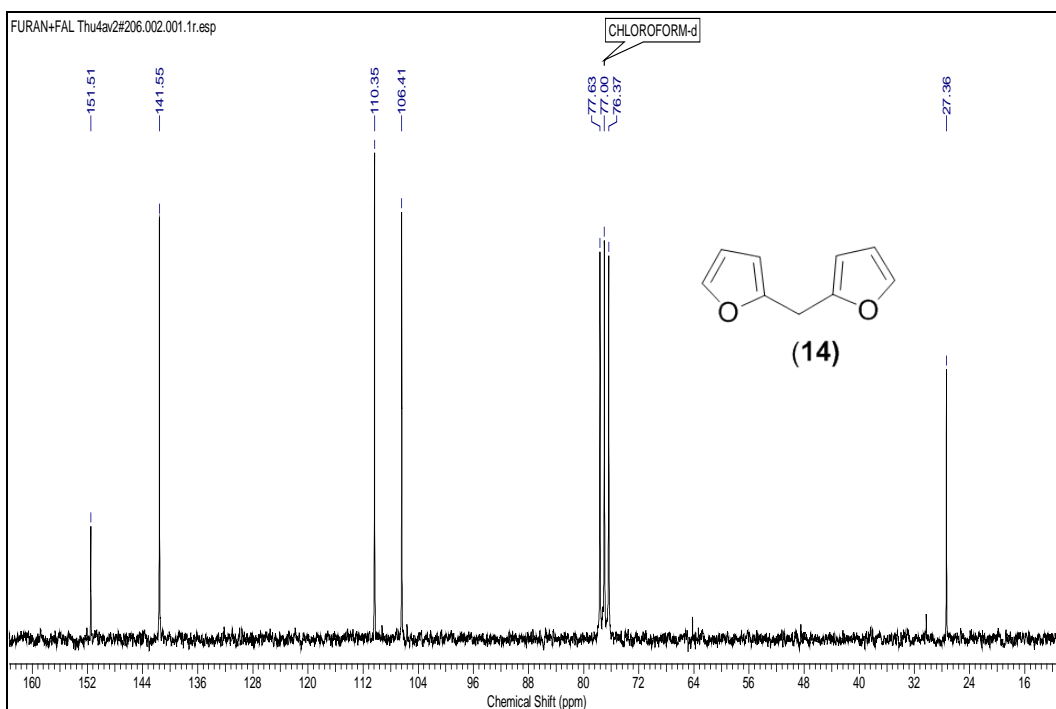
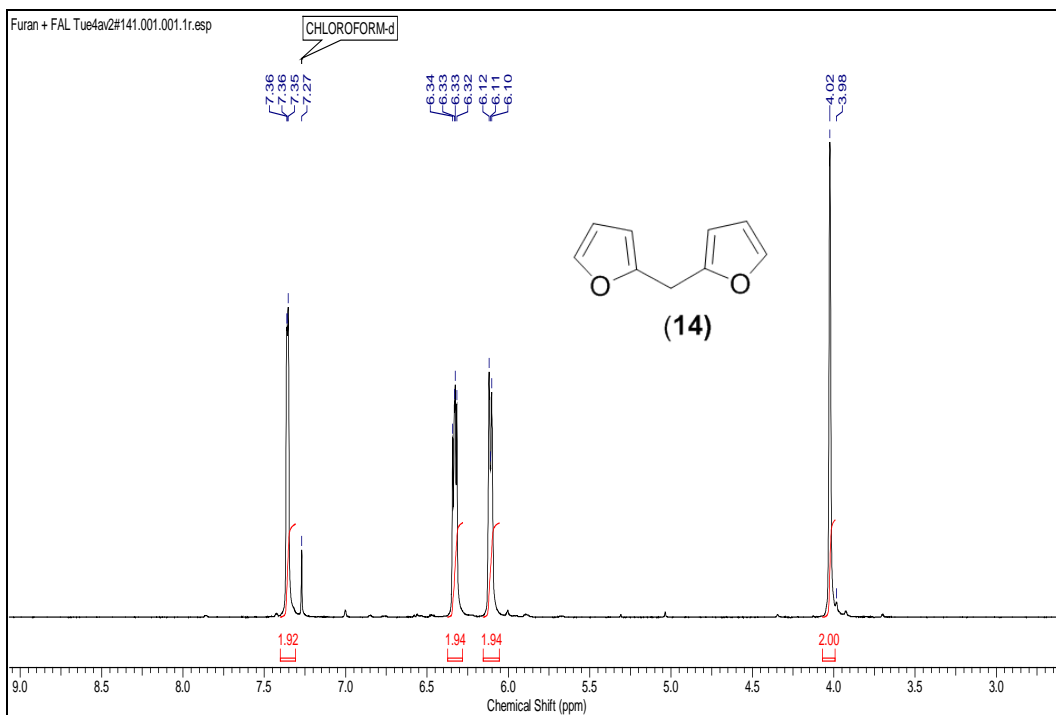
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.52, 13.62, 27.59, 39.15, 106.12, 106.22, 107.06, 107.88, 149.71, 150.55, 150.95, 151.21, 151.36, 151.45



**di(furan-2-yl)methane**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 3.94-4.08 (m, 2 H) 6.05-6.17 (m, 2 H) 6.33 (dd,  $J=3.03, 2.02$  Hz, 2 H) 7.29-7.41 (m, 2 H)

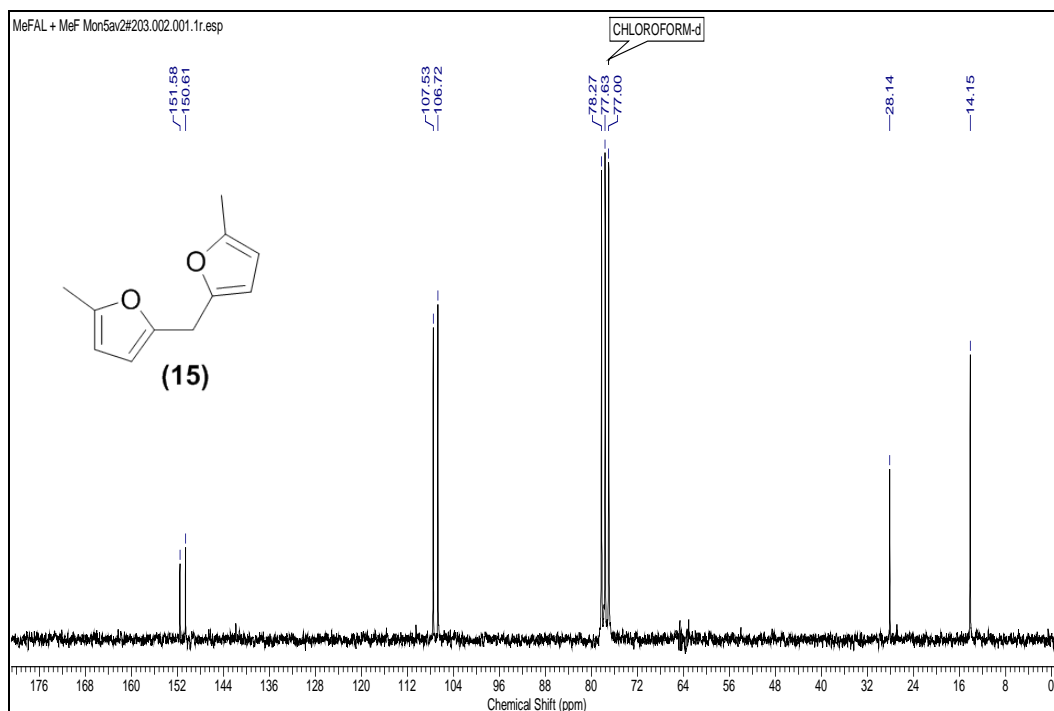
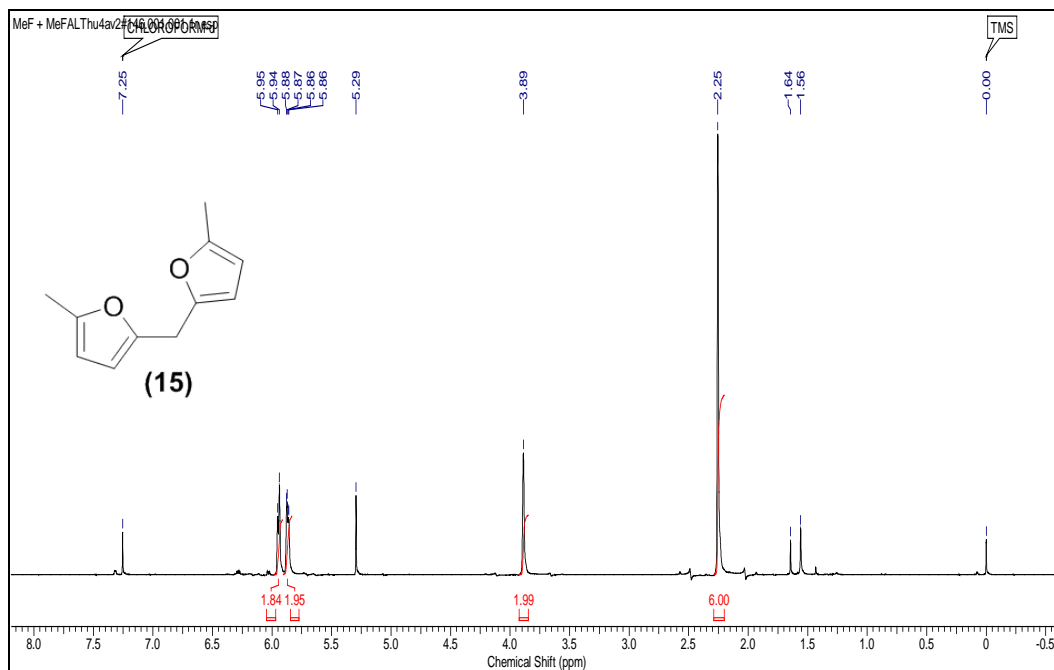
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 27.36, 106.41, 110.35, 141.55, 151.5



**bis(5-methylfuran-2-yl)methane**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.25 (s, 6 H) 3.89 (s, 2 H) 5.86-5.88 (dd,  $J=2.91, 0.88$  Hz, 2 H) 5.94-5.95 (d,  $J=3.03$  Hz, 2 H)

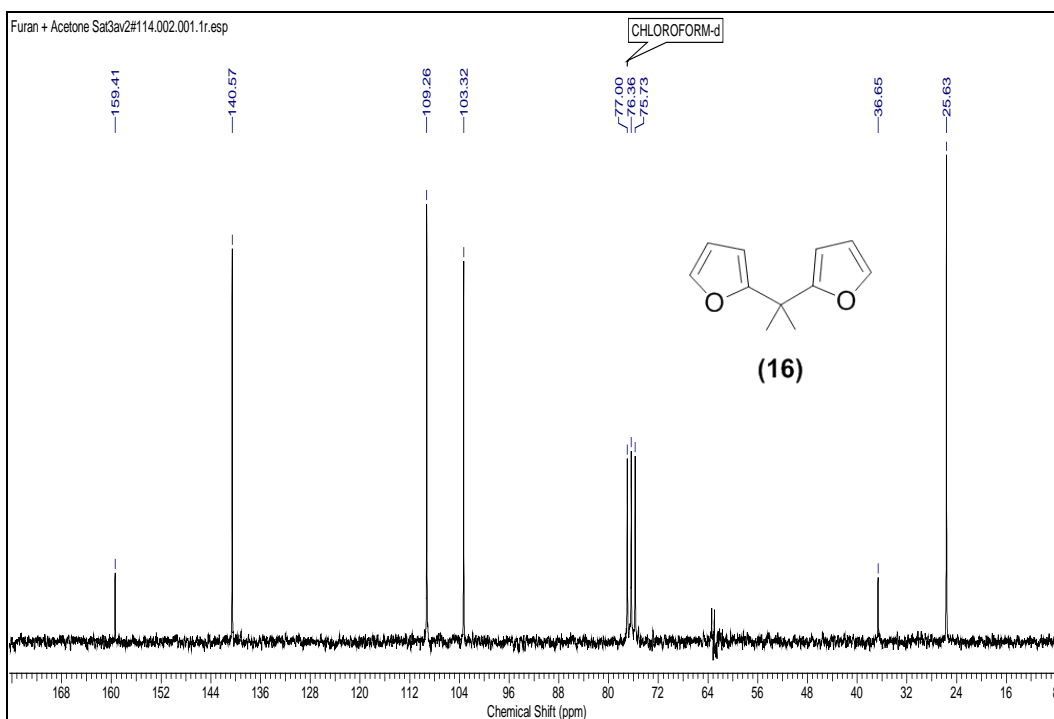
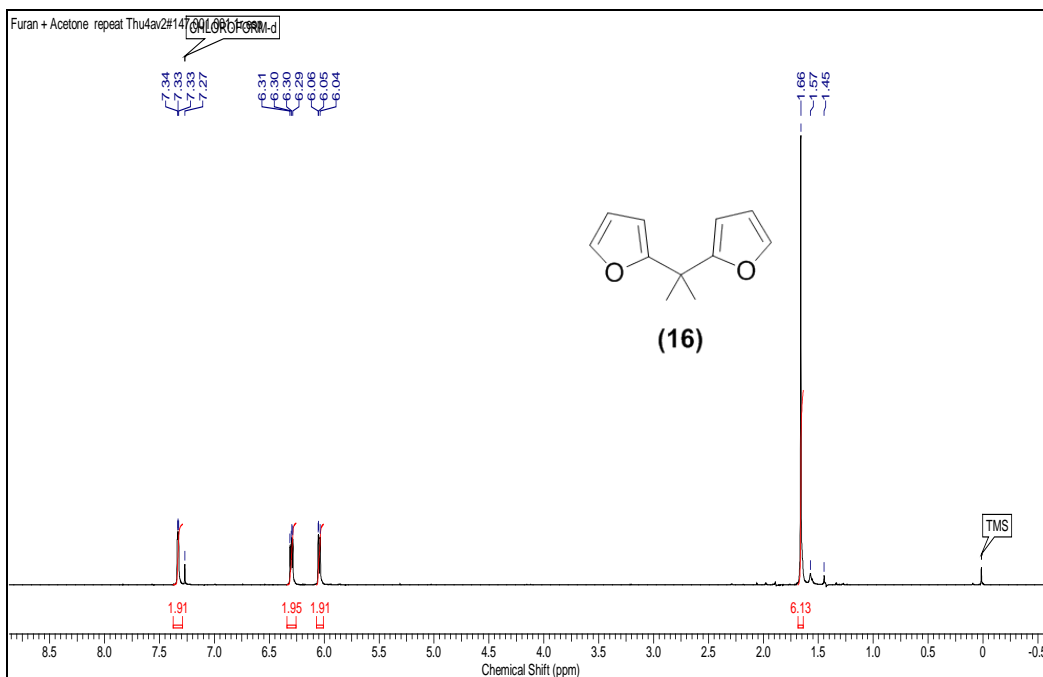
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 14.15, 28.14, 106.72, 107.53, 150.61, 151.58





**2,2'-(propane-2,2-diyl)difuran**

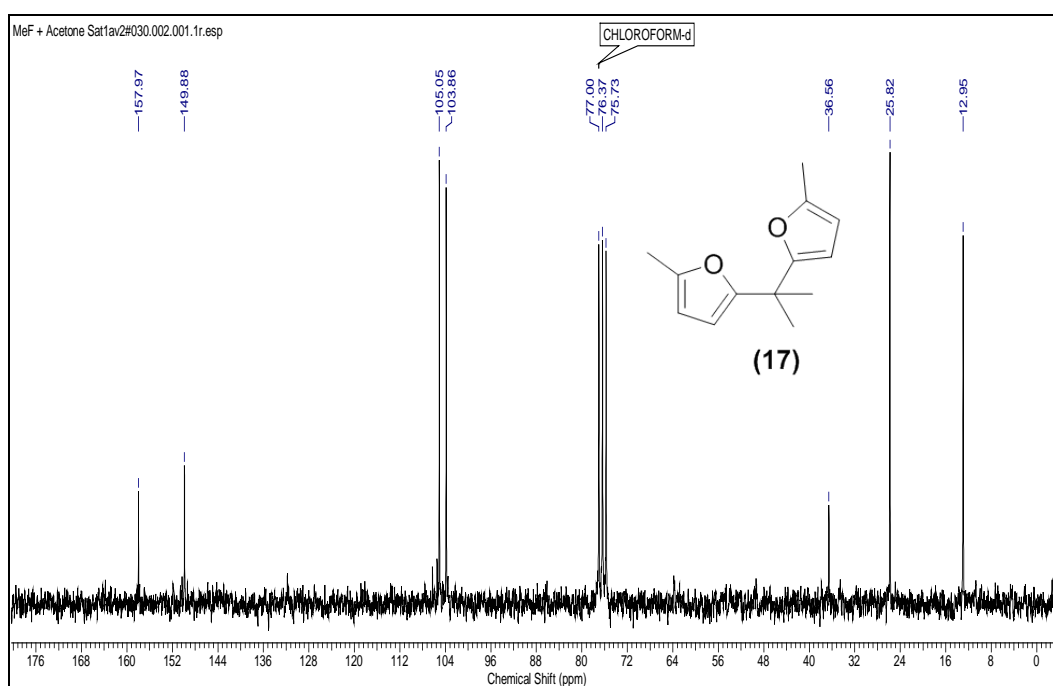
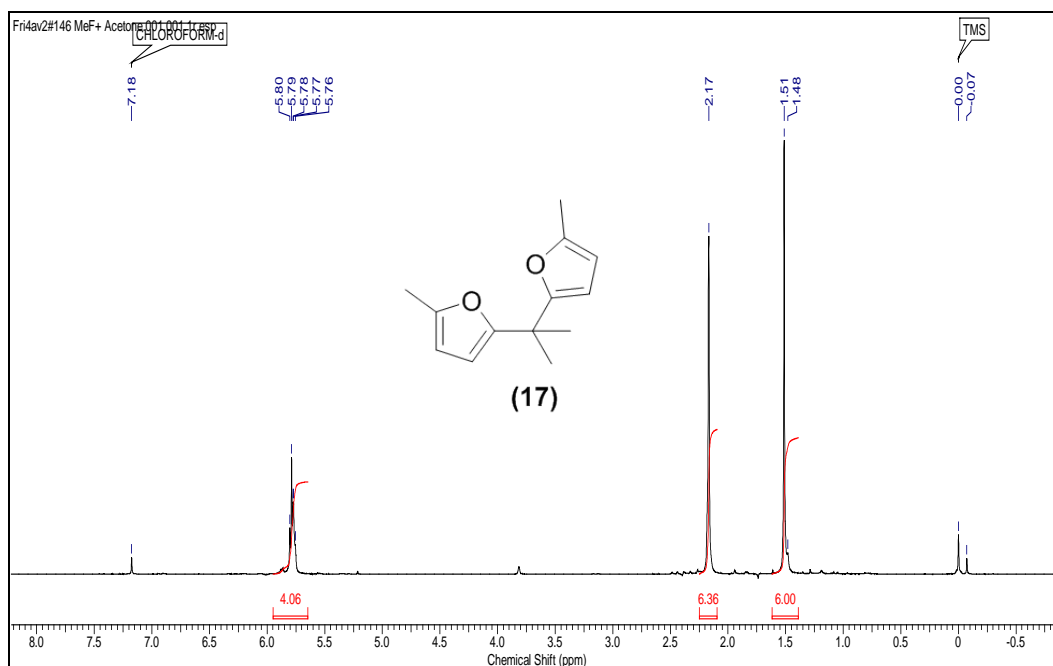
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ ppm 1.66 (s, 6 H) 6.01-6.07 (m, 2 H) 6.30 (dd, *J*=3.22, 1.83 Hz, 2 H) 7.29-7.38 (m, 2 H)

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ ppm 25.63, 36.65, 103.32, 109.26, 140.57, 159.41

**5,5'-(propane-2,2-diyl)bis(2-methylfuran)**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.48-1.51 (m, 6 H) 2.17 (s, 7 H) 5.76-5.90 (m, 4 H)

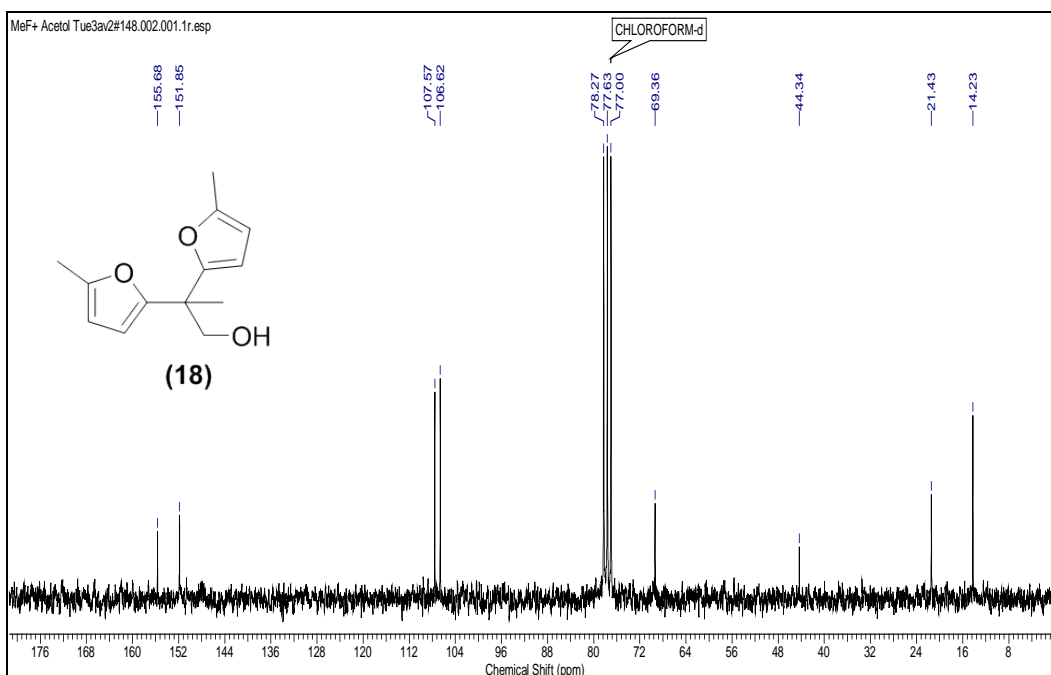
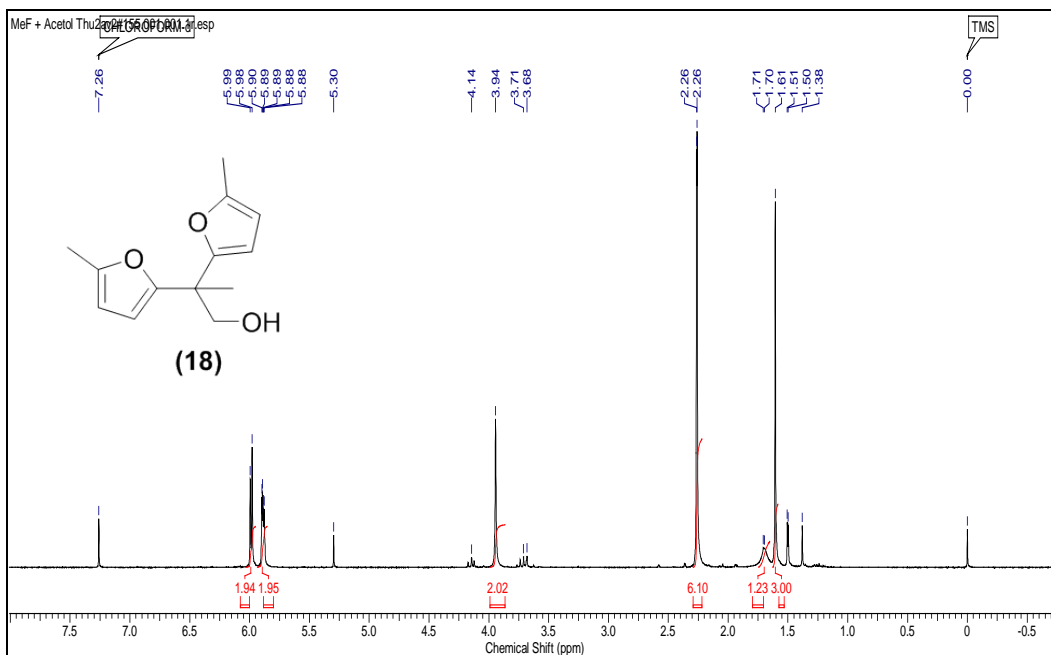
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 12.95, 25.82, 36.56, 103.86, 105.05, 149.88, 157.97



**2,2-bis(5-methylfuran-2-yl)propan-1-ol**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 1.61 (s, 3 H) 1.65-1.74 (m, 1 H) 2.26 (d,  $J=0.76$  Hz, 6 H) 3.94 (s, 2 H) 5.85-5.94 (m, 2 H) 5.99 (d,  $J=3.16$  Hz, 2 H)

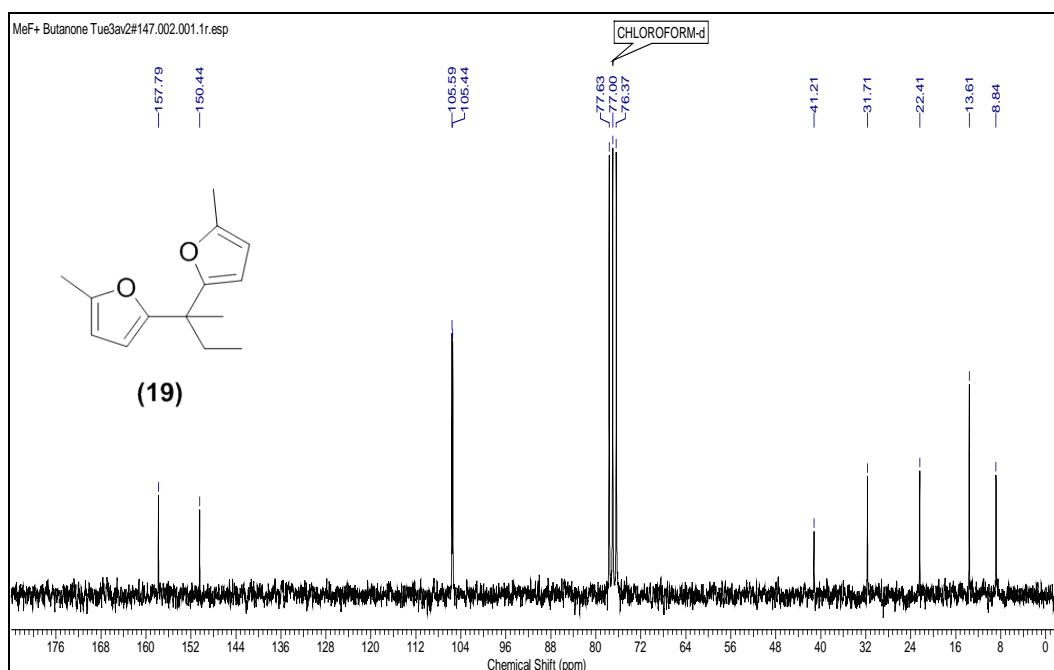
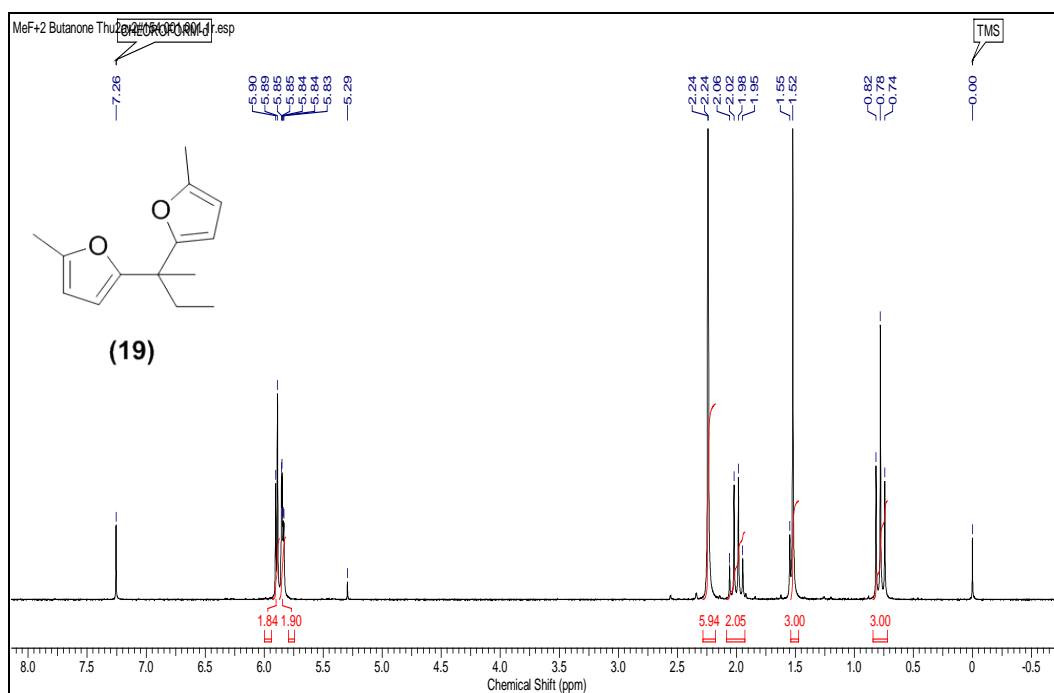
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 14.23, 21.43, 44.34, 69.36, 106.62, 107.57, 151.85 and 155.68



**5,5'-(butane-2,2-diyl)bis(2-methylfuran)**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 0.74-0.82 (t,  $J=7.39$  Hz, 3 H) 1.52 (s, 3 H) 1.95-2.06 (q,  $J=7.37$  Hz, 2 H) 2.24 (d,  $J=0.88$  Hz, 6 H) 5.83-5.85 (m, 2 H) 5.89-5.90 (m, 2 H)

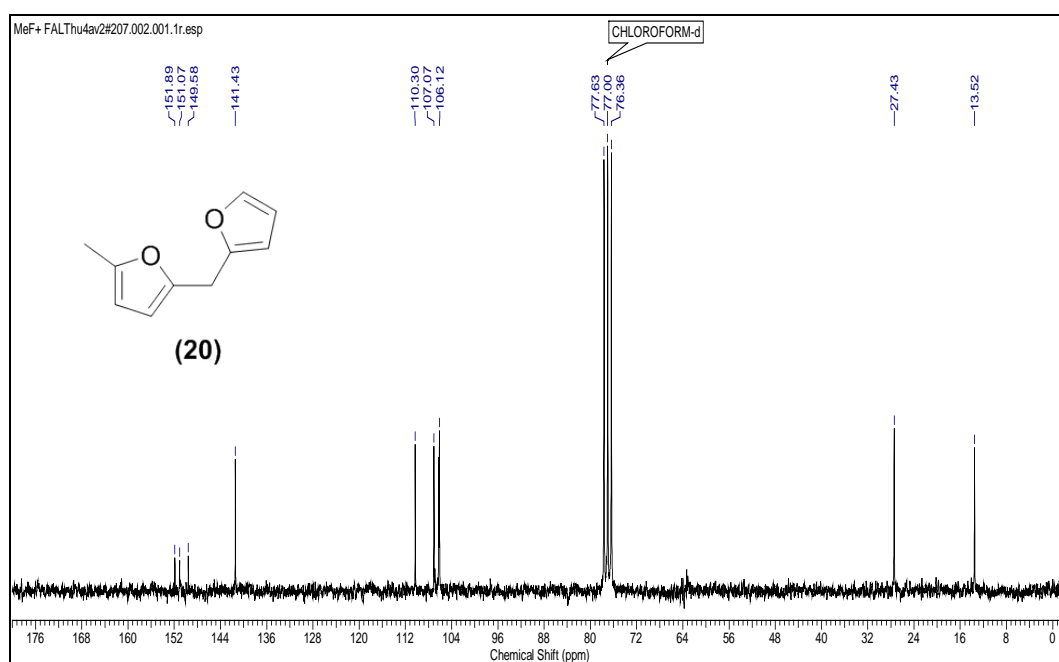
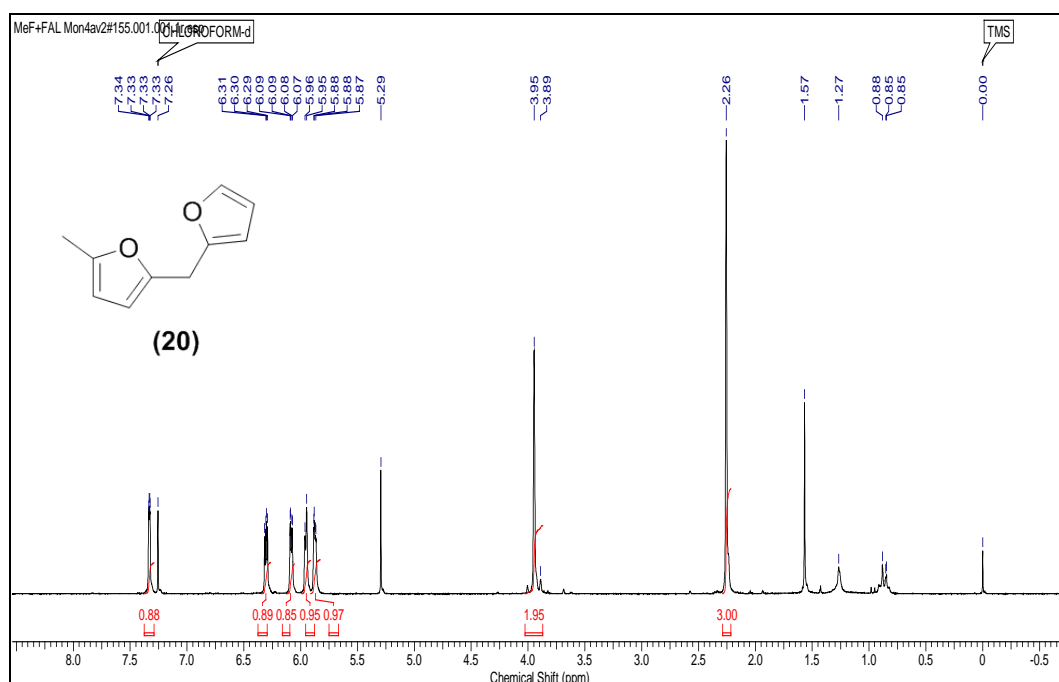
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 8.84, 13.61, 22.41, 31.71, 41.21, 105.44, 105.59, 150.44, 157.79



**2-(furan-2-ylmethyl)-5-methylfuran**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.26 (s, 3 H) 3.89-4.01 (m, 2 H) 5.87-5.88 (m, 1 H) 5.95-5.96 (d,  $J=2.91$  Hz, 1 H) 6.07-6.09 (m, 1 H) 6.29-6.32 (dd,  $J=3.16, 1.89$  Hz, 1 H) 7.33-7.34 (dd,  $J=1.83, 0.69$  Hz, 1 H)

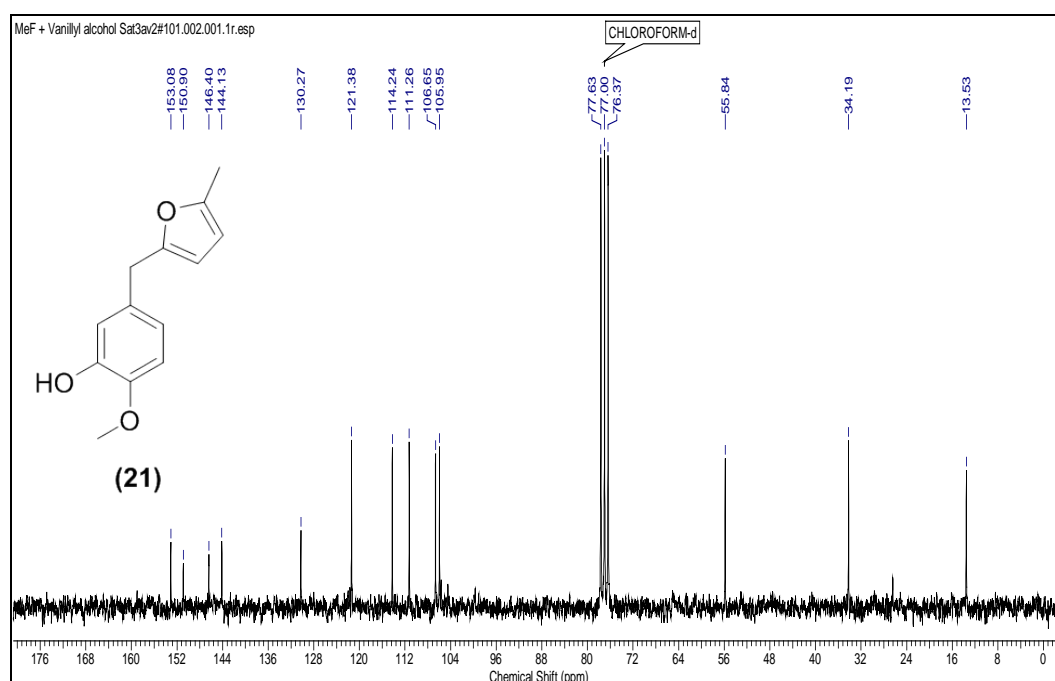
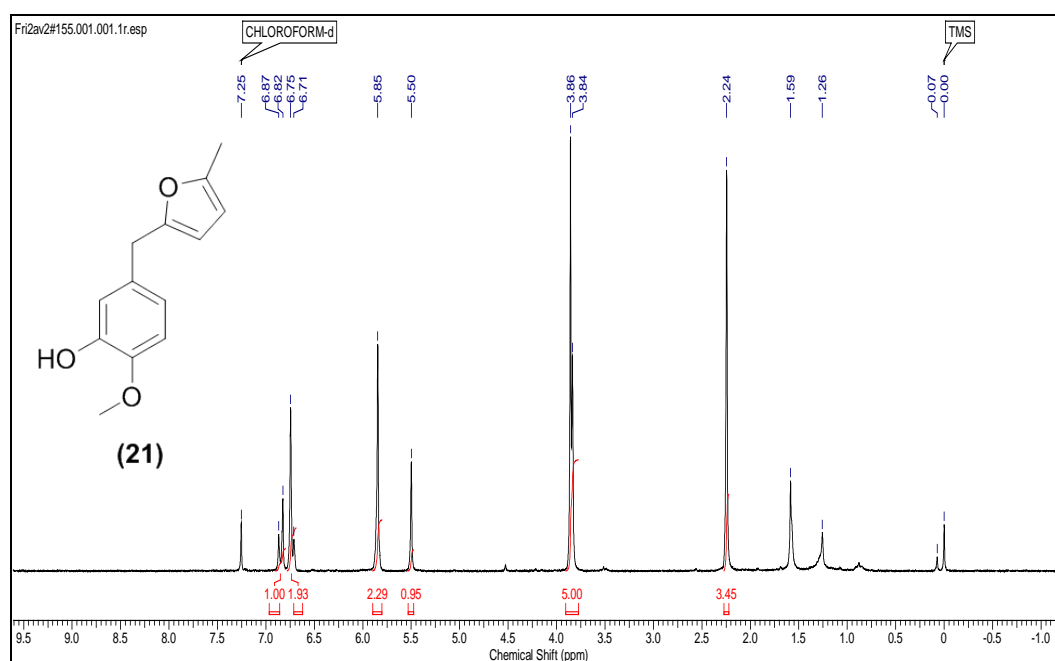
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.52, 27.43, 106.12, 107.07, 110.30, 141.43, 149.58 151.07, 151.89



**2-methoxy-5-((5-methylfuran-2-yl)methyl)phenol**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.24 (s, 4 H) 3.84-3.86 (d, 5 H) 5.50 (s, 1 H) 5.85 (s, 2 H) 6.69-6.78 (d,  $J$ = 8.59 Hz, 2 H) 6.80-6.90 (d,  $J$ =6.82 Hz, 1 H)

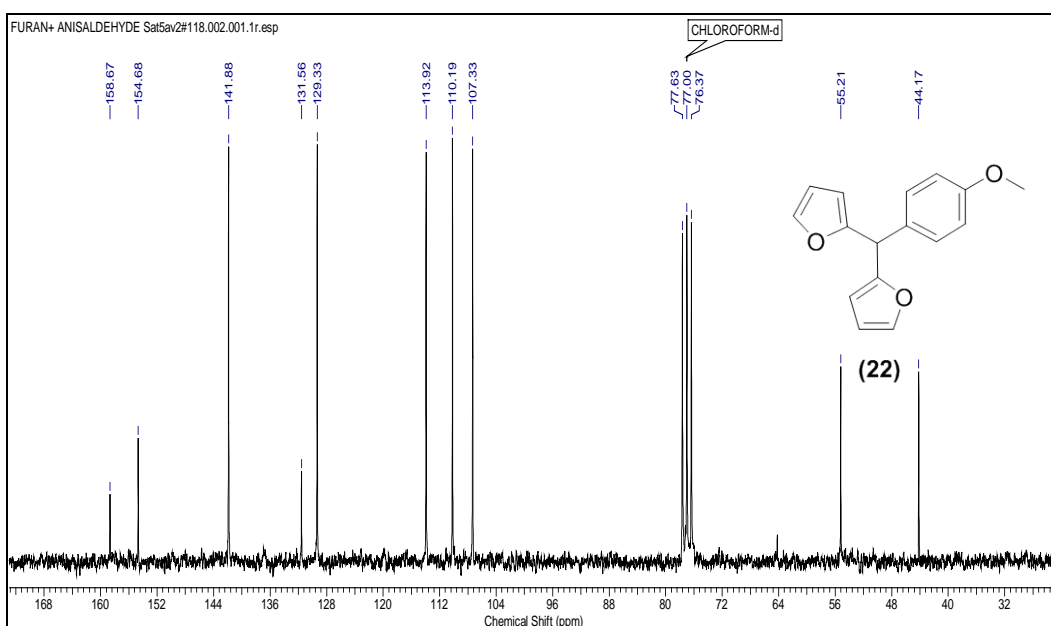
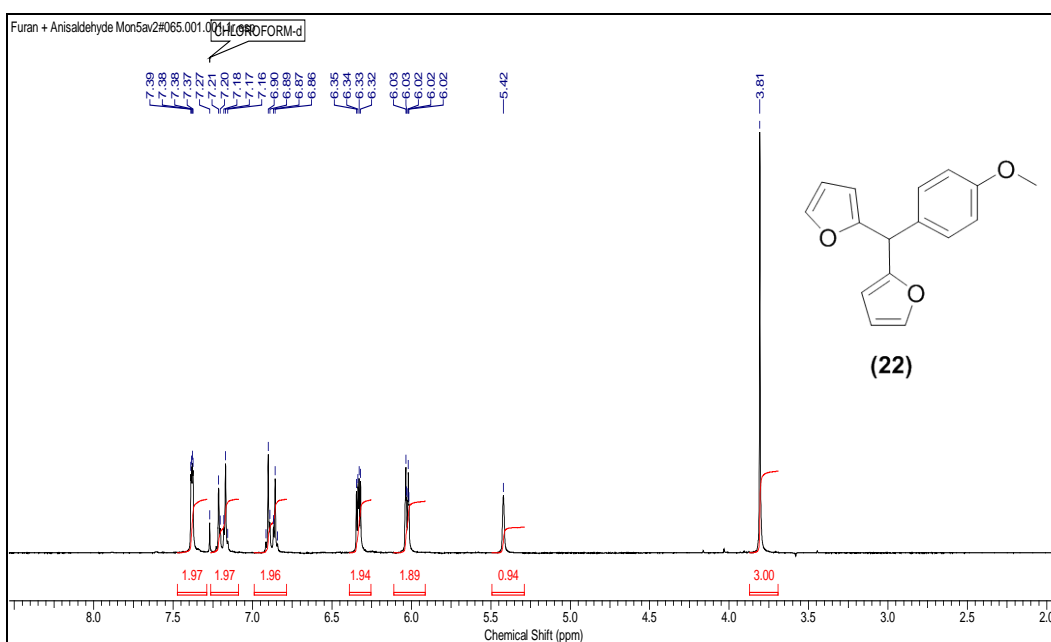
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.53, 34.19, 55.84, 105.95, 106.65, 111.26, 114.24, 121.38, 130.27, 144.13, 146.40, 150.90, 153.08



**2,2'-((4-methoxy phenyl)methylene)difuran**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 3.81 (s, 3 H) 5.42 (s, 1 H) 6.02-6.03 (m, 2 H) 6.32-6.35 (dd,  $J=3.22$ , 1.83 Hz, 2 H) 6.86-6.90 (m, 2 H) 7.16-7.21 (m, 2 H) 7.37-7.39 (dd,  $J=1.83$ , 0.82 Hz, 2 H)

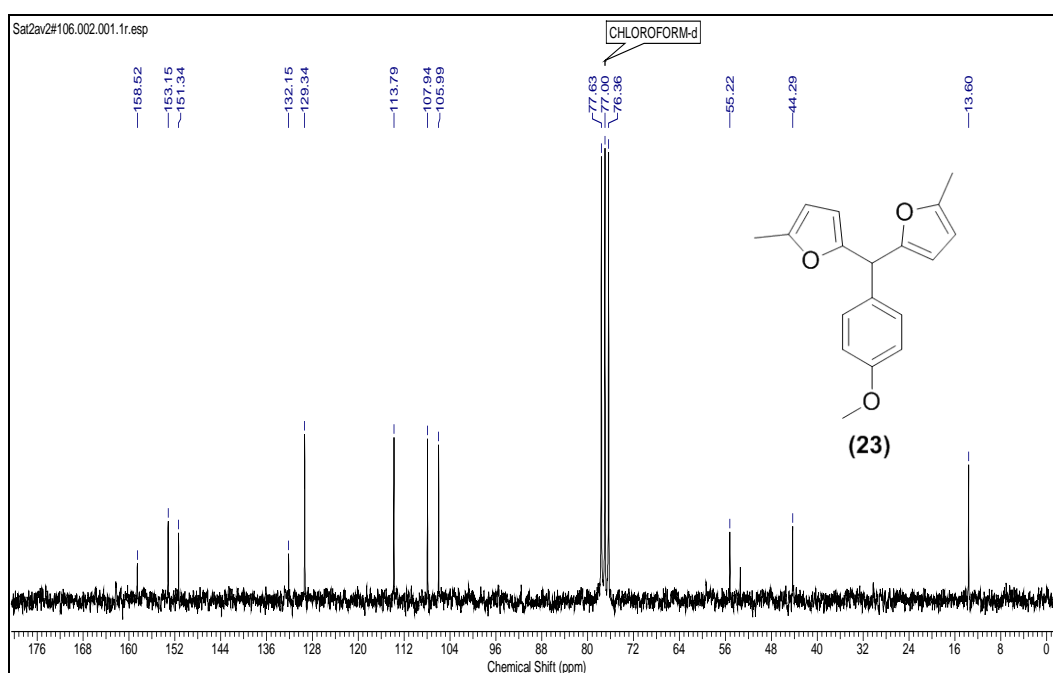
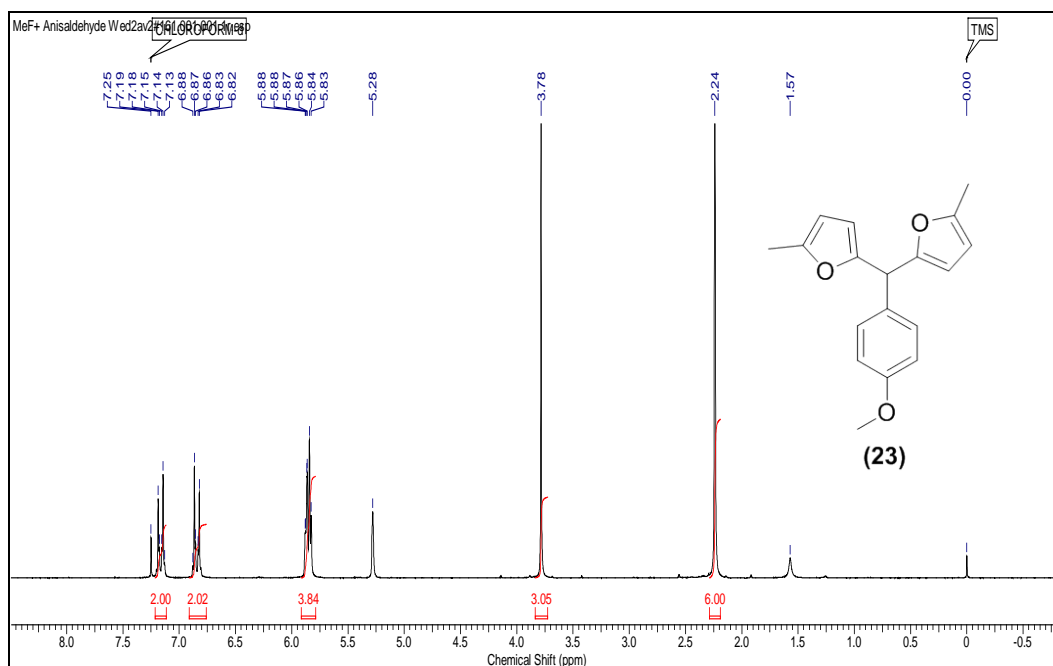
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 44.17, 55.21, 107.33, 110.19, 113.92, 129.33, 131.56, 141.88, 154.68, 158.67



**5,5'-((4-methoxy phenyl)methylene)bis(2-methylfuran)**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.24 (s, 6 H) 3.78 (s, 3 H) 5.83-5.88 (m, 4 H) 6.82-6.88 (m, 2 H) 7.13-7.25 (m, 2 H)

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.60, 44.29, 55.22, 105.99, 107.94, 113.79, 129.34, 132.15, 151.34, 153.15, 158.52.

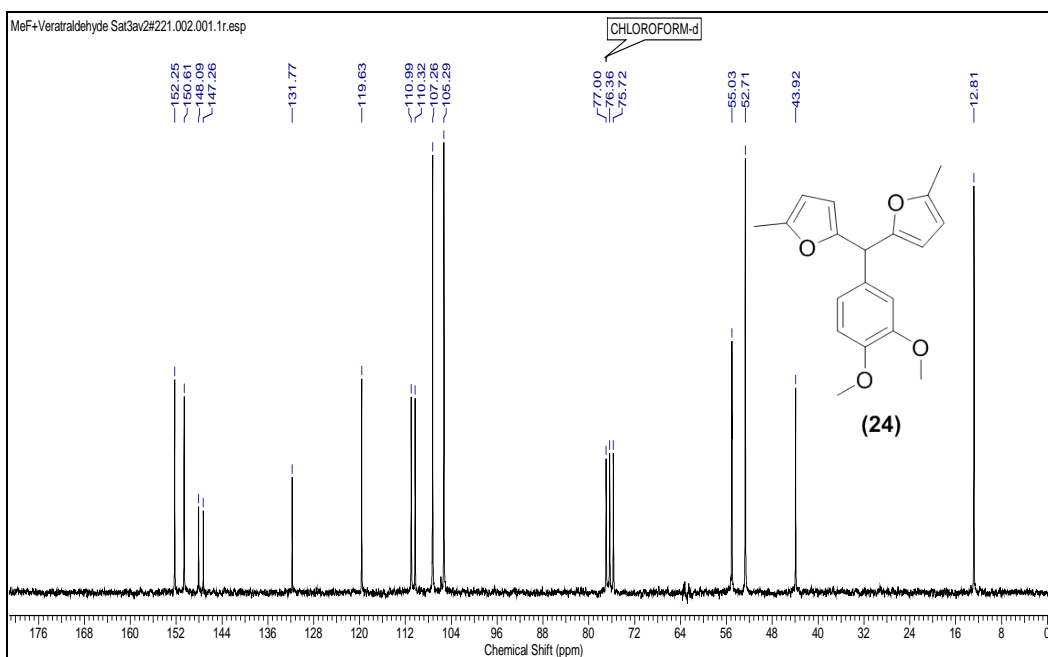
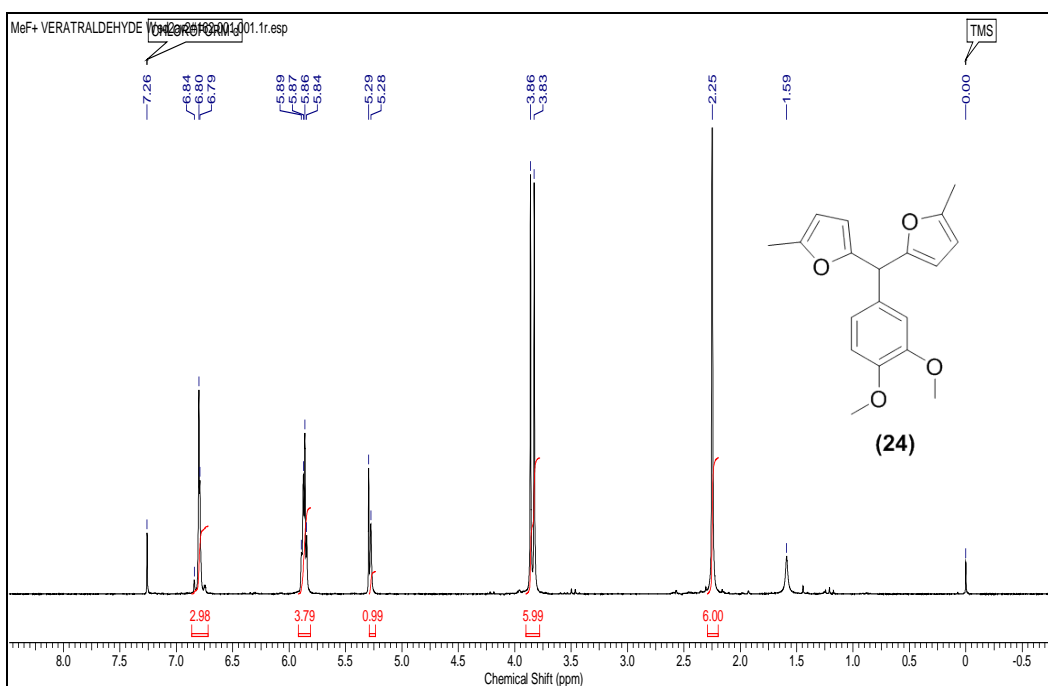




**5,5'-((3,4-dimethoxy phenyl)methylene)bis(2-methylfuran)**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.25 (s, 6 H) 3.86 (s, 3 H) 3.83 (s, 3 H) 5.28 (s, 1 H) 5.84-5.89 (m, 4 H) 6.79 - 6.84 (m, 3 H), (Singlet at 5.3 ppm is of residual dichloromethane).

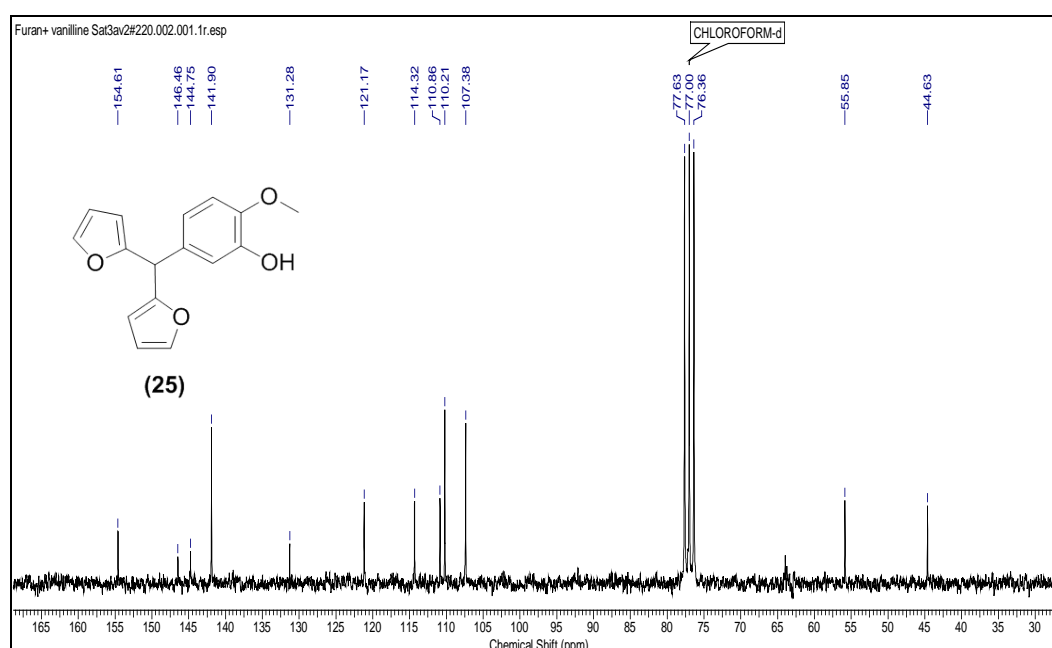
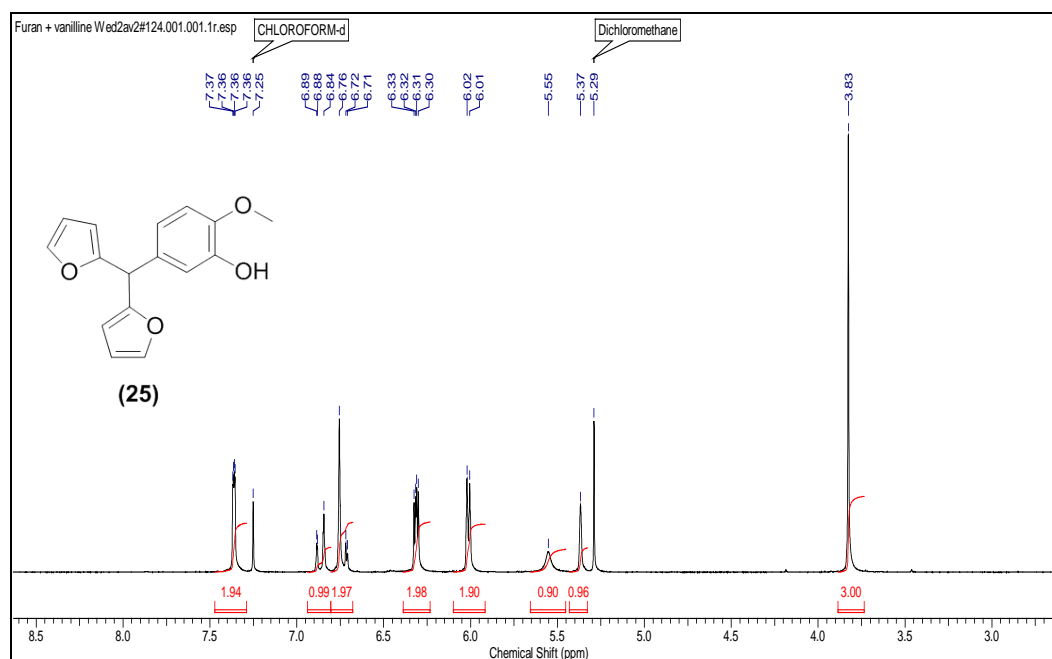
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 12.81, 43.92, 52.71, 55.03, 105.29, 107.26, 110.32, 110.99, 119.63, 131.77, 147.26, 148.09, 150.61 and 152.25



## 5-(di(furan-2-yl)methyl)-2-methoxy phenol

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 3.83 (s, 3 H) 5.37 (s, 1 H) 5.55 (br. s., 1 H) 6.01-6.02 (d,  $J=3.16$  Hz, 2 H) 6.30-6.33 (dd,  $J=3.16$ , 1.89 Hz, 2 H) 6.71 - 6.76 (m, 2 H) 6.84-6.89 (m, 1 H) 7.36 -7.37 (dd,  $J=1.77$ , 0.76 Hz, 2 H)

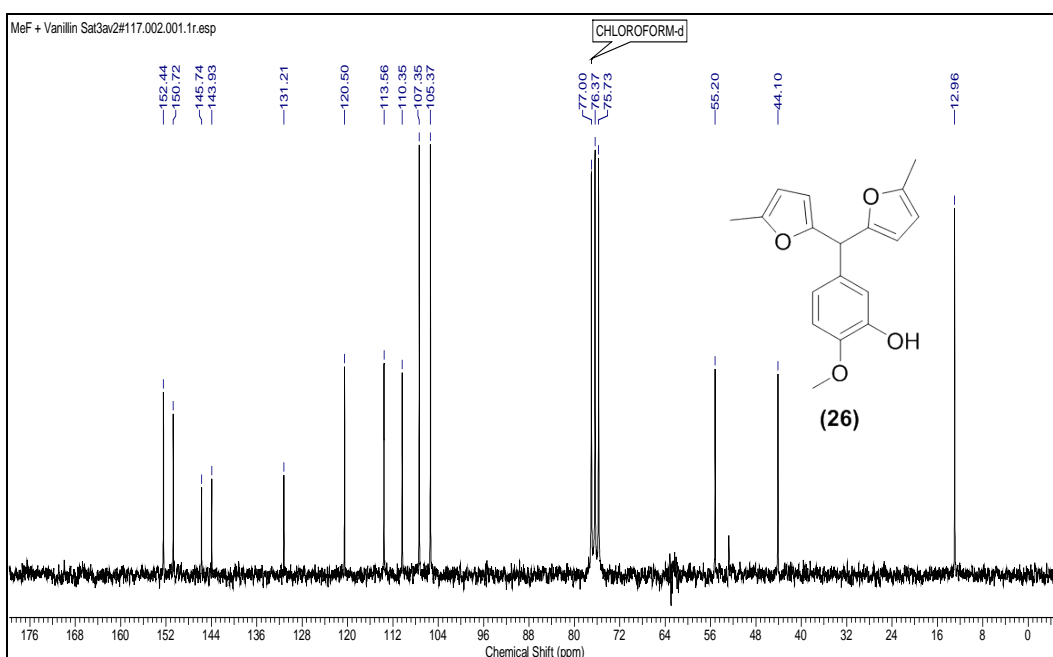
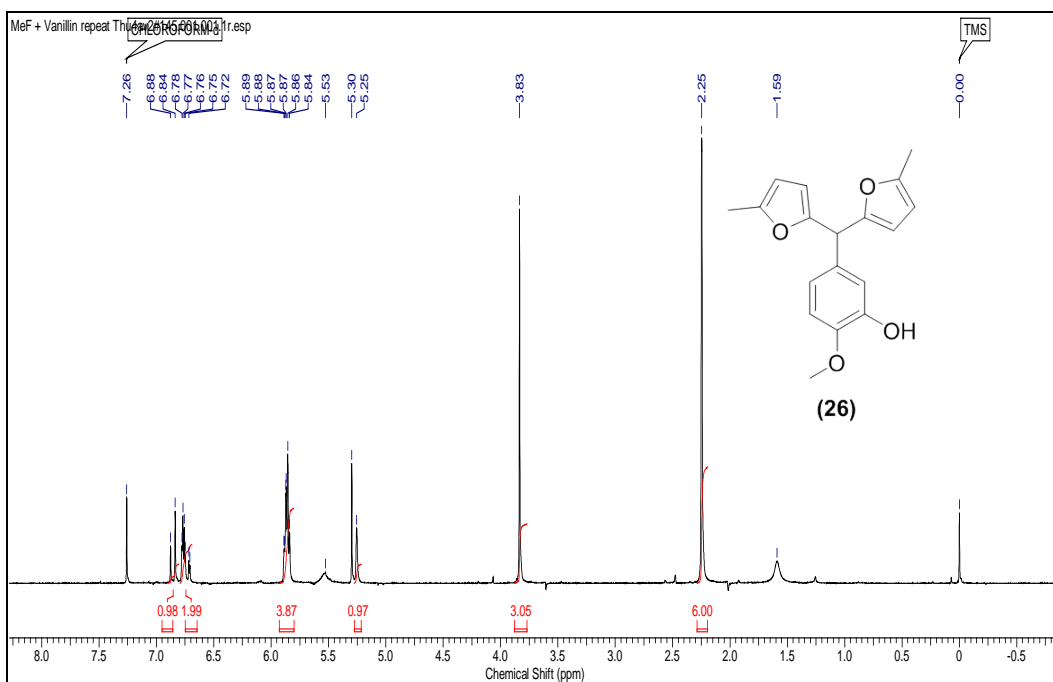
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 44.63, 55.85, 107.38, 110.21, 110.86, 114.32, 121.17, 131.28, 141.90, 144.75, 146.46, 154.61



**5-(bis(5-methylfuran-2-yl)methyl)-2-methoxyphenol**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.25 (s, 6 H) 3.83 (s, 3 H) 5.25 (s, 1 H) 5.84-5.89 (m, 4 H) 6.72-6.78 (m, 2 H) 6.84-6.88 (m, 1 H)

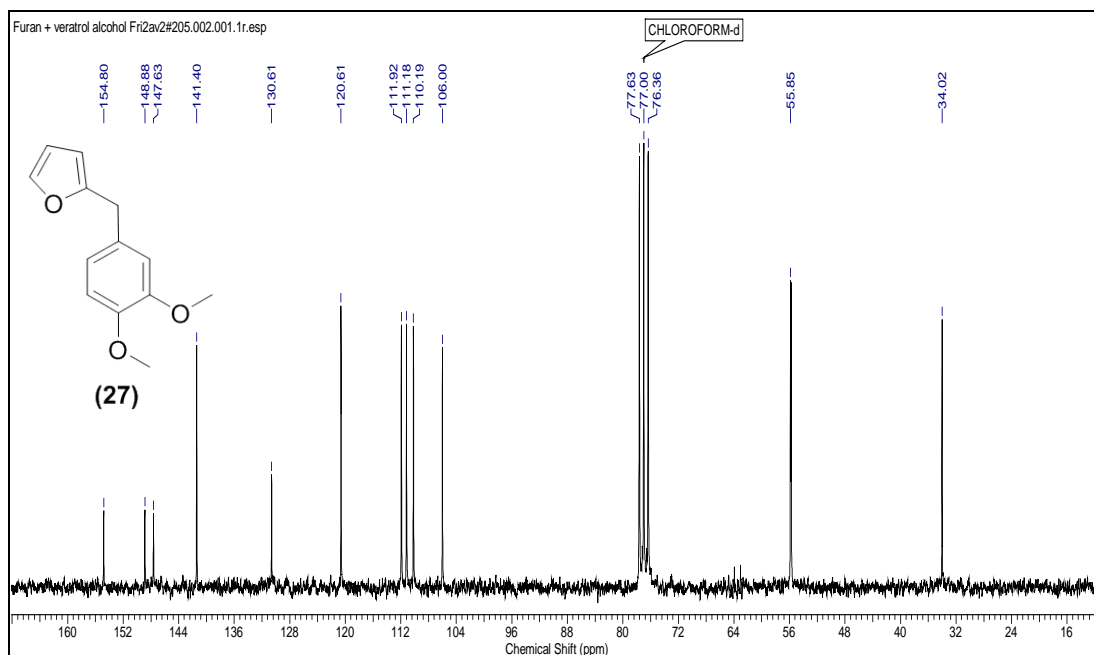
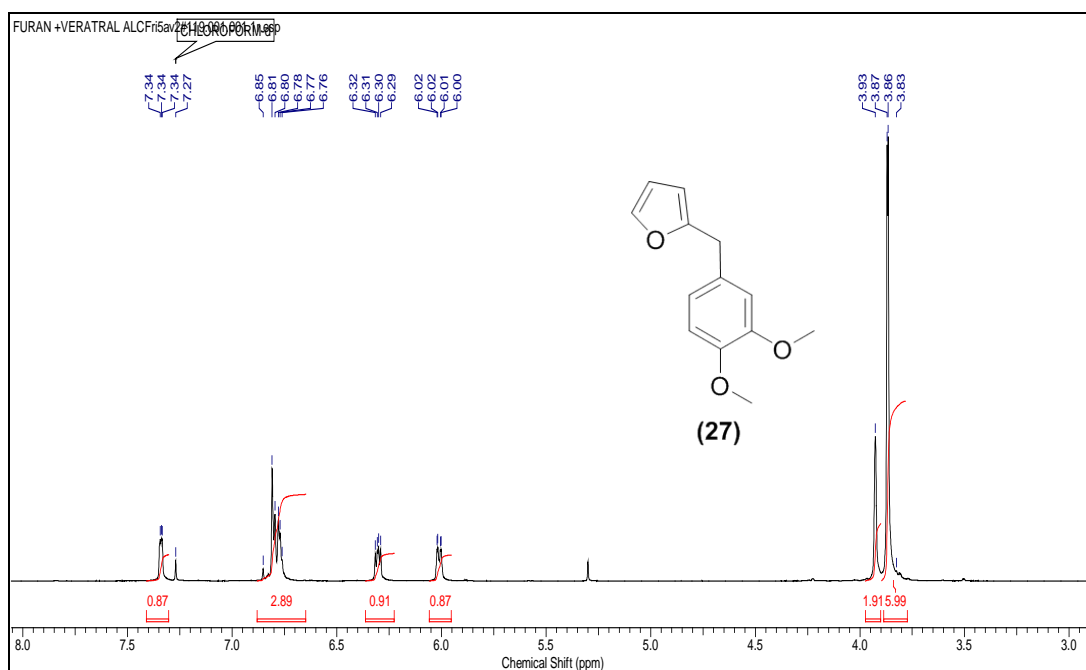
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 12.96, 44.10, 55.20, 105.37, 107.35, 110.35, 113.56, 120.50, 131.21, 143.93, 145.74, 150.72, 152.44



## 2-(3,4-dimethoxy benzyl)furan

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 3.86-3.87 (d, 6 H) 3.93 (s, 2 H) 6.01-6.02 (dd,  $J=3.16, 0.76$  Hz, 1 H) 6.29-6.32 (dd,  $J=3.09, 1.96$  Hz, 1 H) 6.76-6.85 (m, 3 H) 7.34 (m, 1 H)

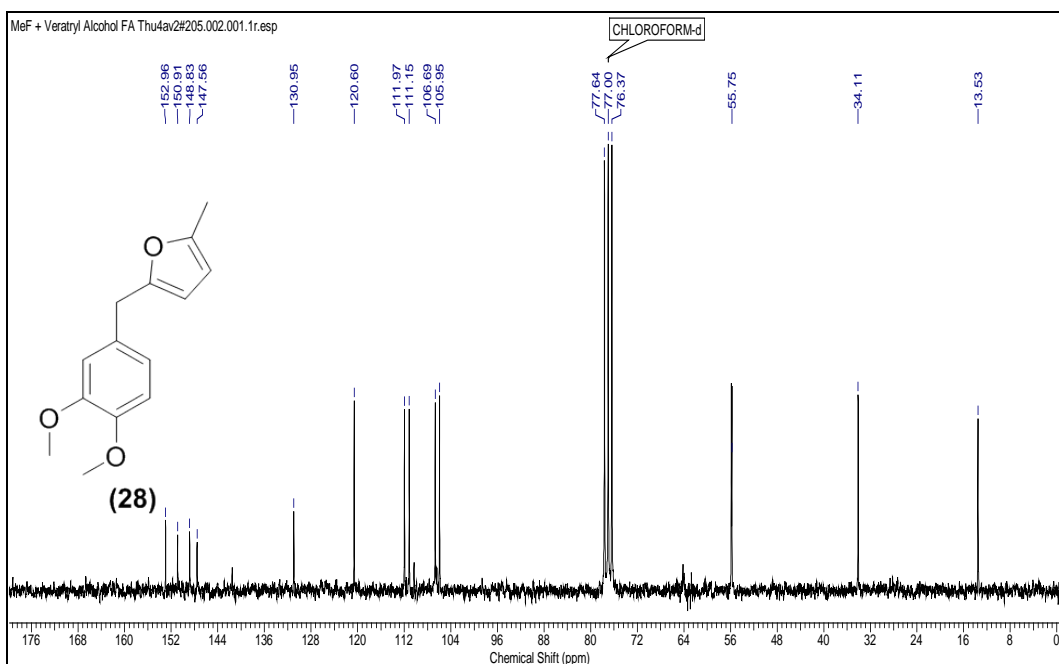
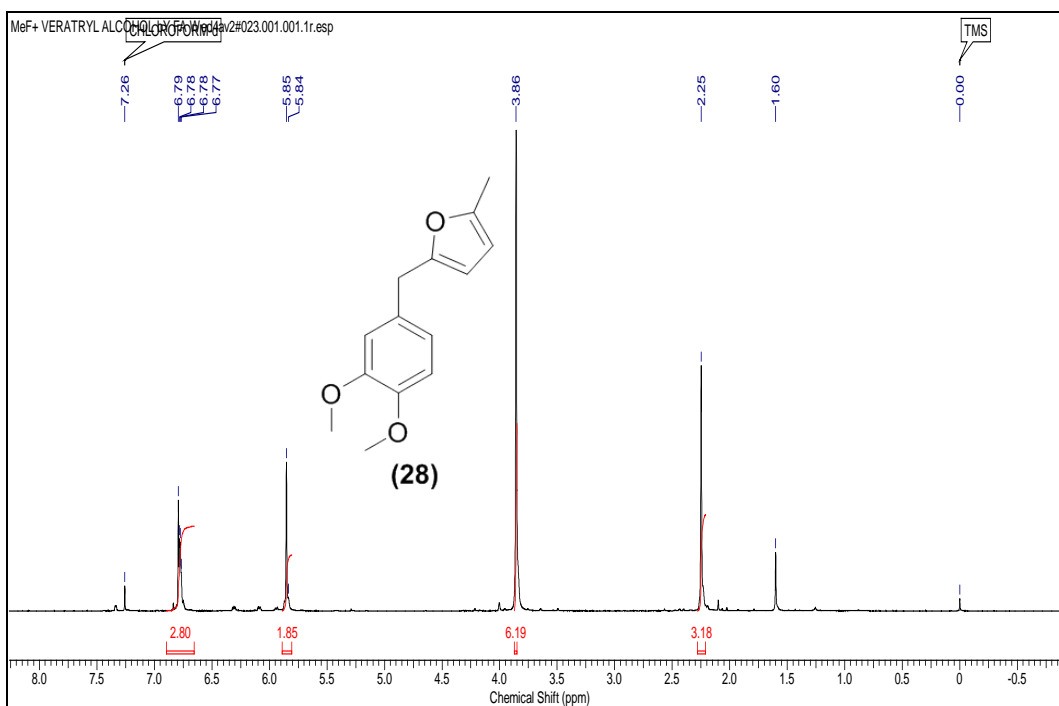
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 34.02, 55.85, 106.00, 110.19, 111.18, 111.92, 120.61, 130.61, 141.40, 147.63, 148.88, 154.80



**2-(3,4-dimethoxy benzyl)-5-methylfuran**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.25 (s, 3 H) 3.86 (s, 6H) 5.84-5.85 (m, 2 H) 6.77-6.79 (m, 3 H)

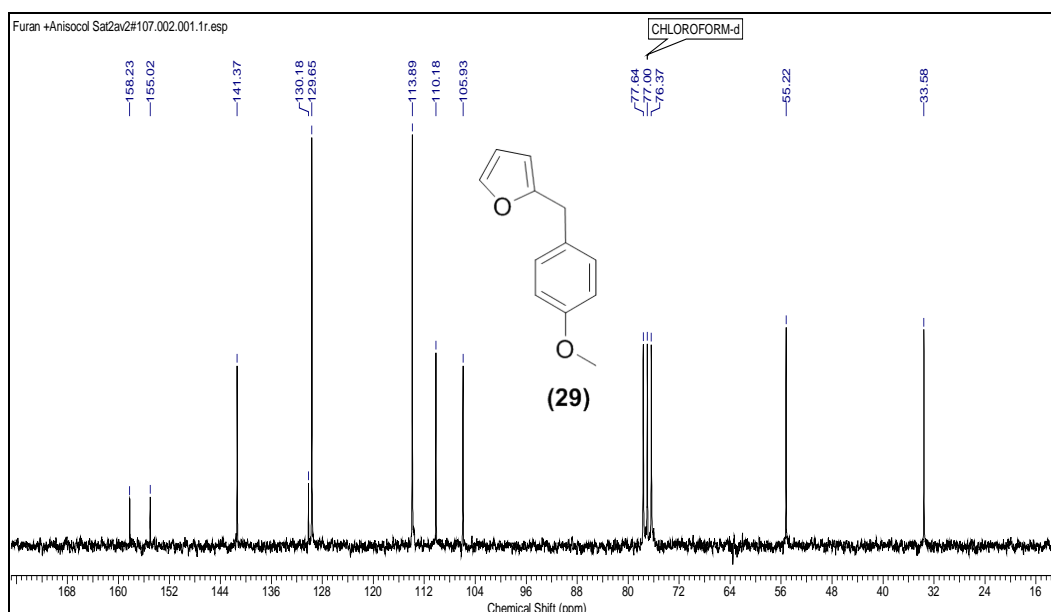
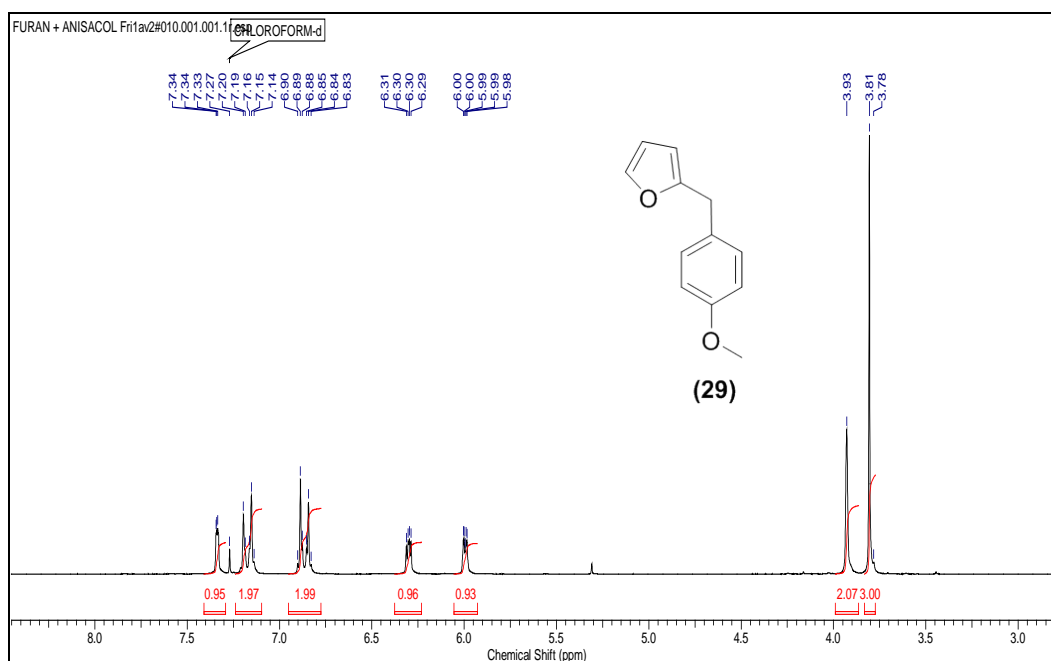
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.53, 34.11, 55.75, 105.95, 106.69, 111.15, 111.97, 120.60, 130.95, 147.56, 148.83, 150.91, 152.96



**2-(4-methoxybenzyl)furan**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 3.81 (s, 3 H) 3.93 (s, 2 H) 5.98-6.00 (m, 1 H) 6.29-6.31 (dd,  $J=3.09$ , 1.96 Hz, 1 H) 6.83-6.90 (m, 2 H) 7.14-7.20 (m, 2 H) 7.33-7.34 (m, 1 H)

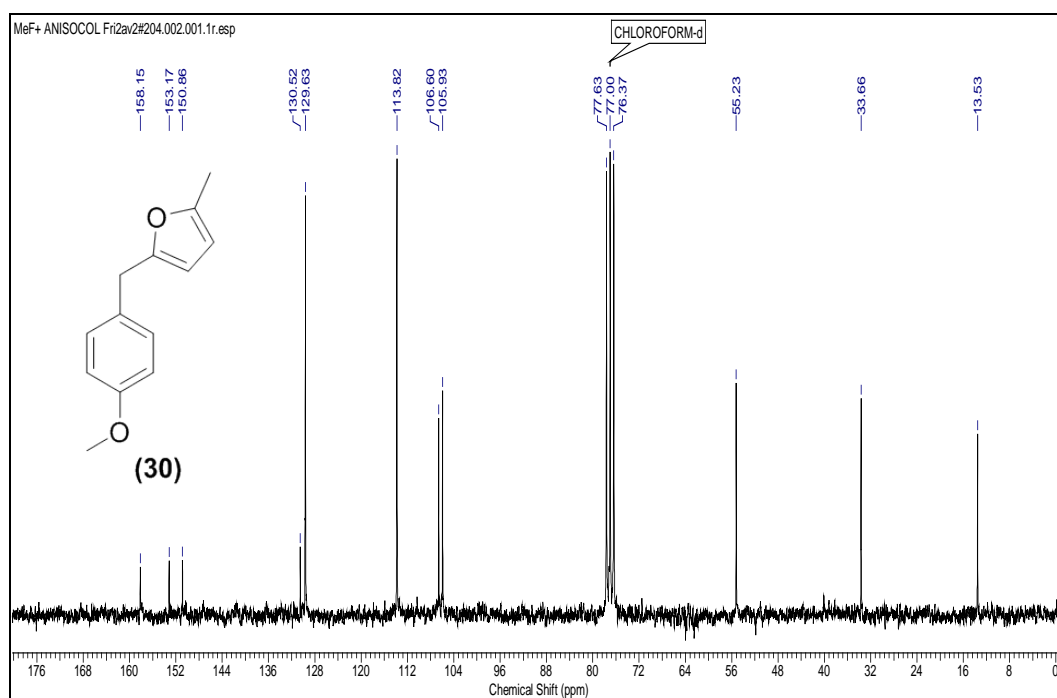
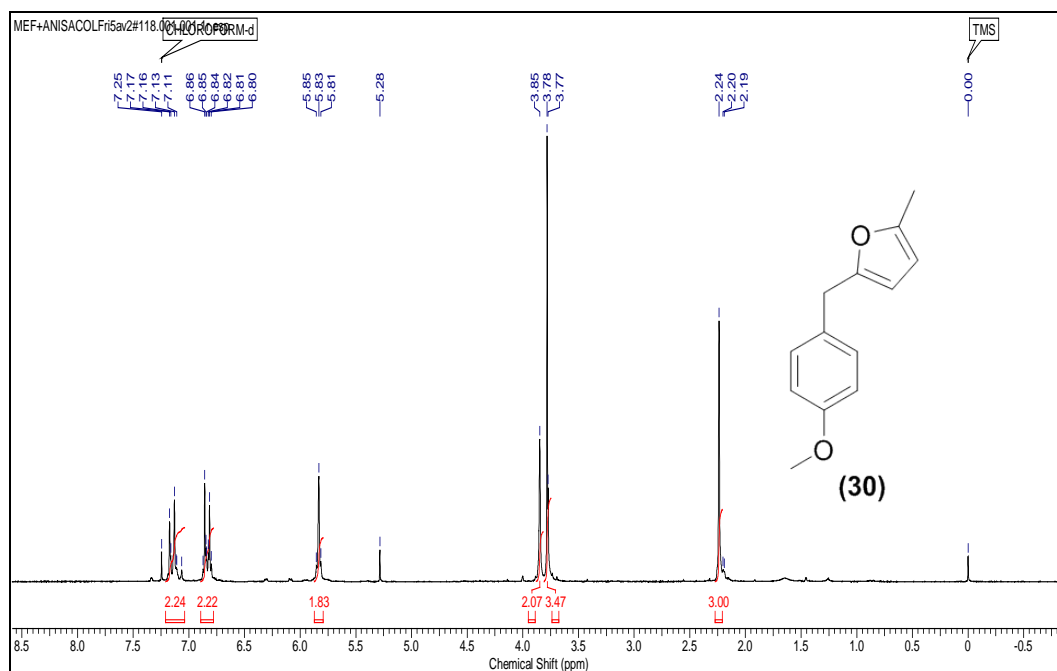
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 33.58, 55.22, 105.93, 110.18, 113.89, 129.65, 130.18, 141.37, 155.02, 158.23



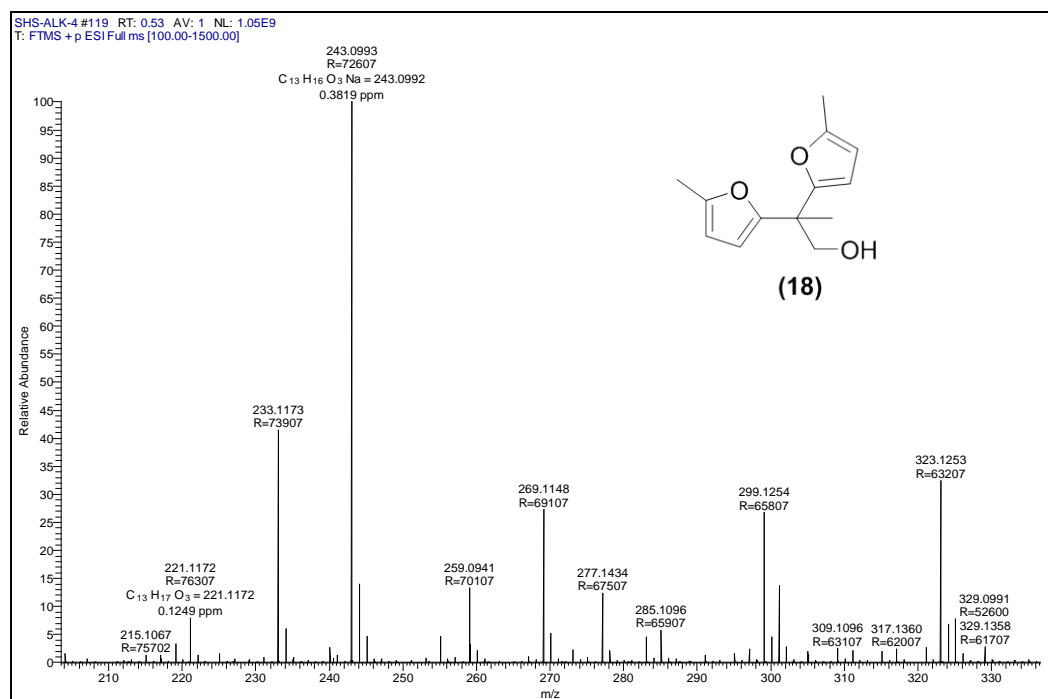
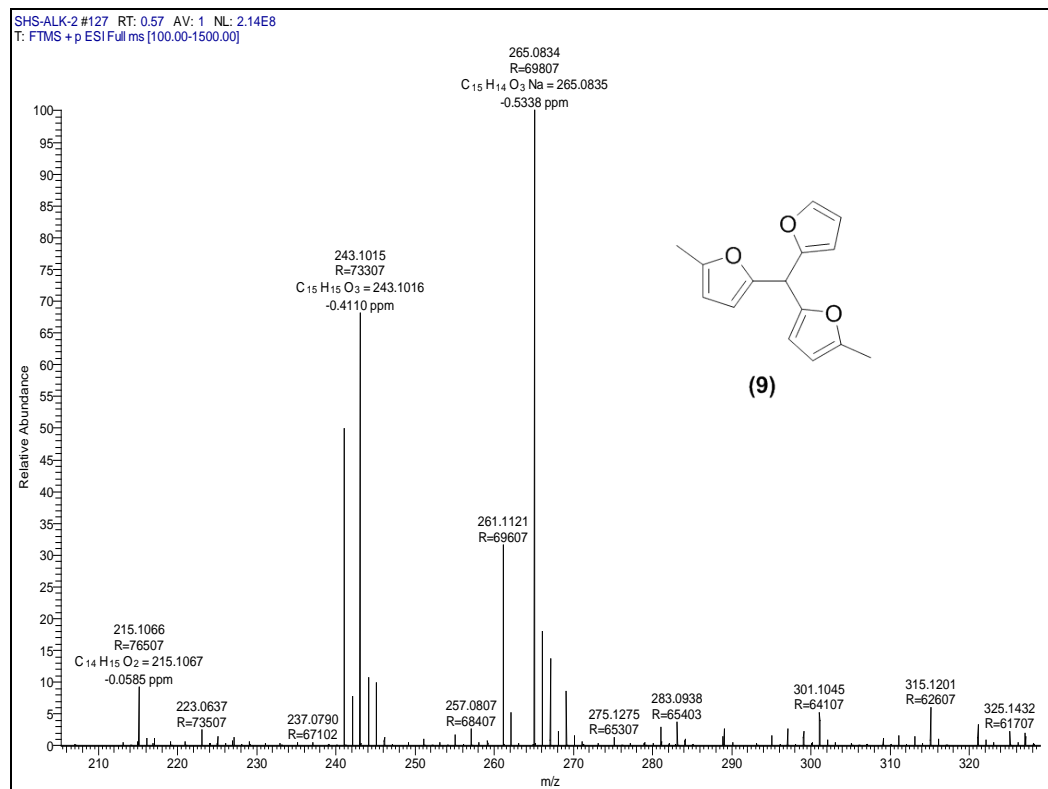
**2-(4-methoxybenzyl)-5-methylfuran**

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 2.24 (s, 3 H) 3.78 (s, 3 H) 3.85 (s, 2 H) 5.81-5.85 (m, 2 H) 6.80-6.87 (m, 2 H) 7.06-7.17 (m, 2 H)

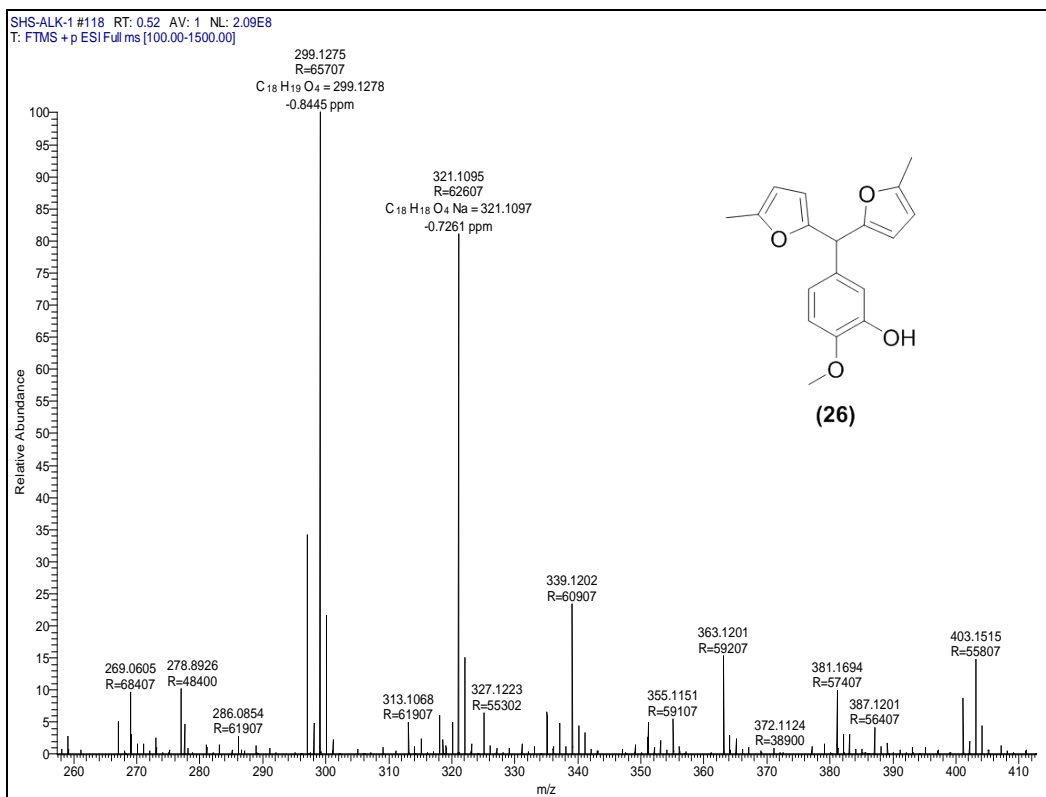
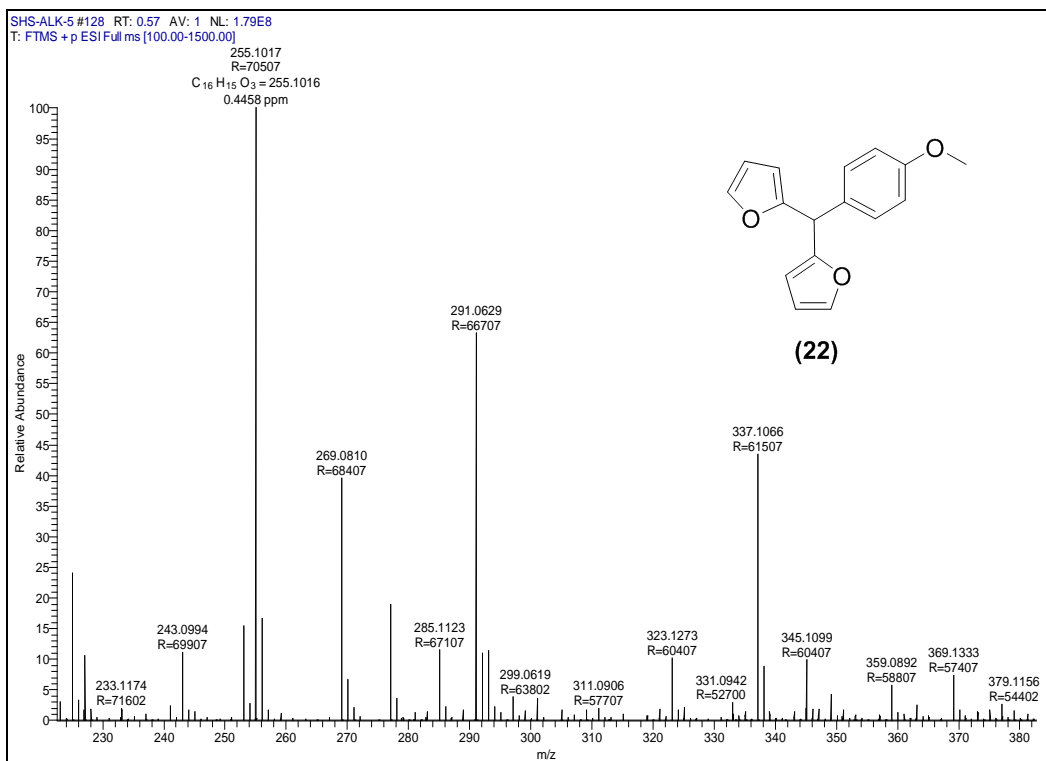
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 13.53, 33.66, 55.23, 105.93, 106.60, 113.82, 129.63, 130.52, 150.86, 153.17, 158.15



## 6.8.3. HRMS







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**Chapter 7**  
**Conclusions**  
**and**  
**Future Scope**

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## 7.1. Conclusions

In summary, conceptual development, environment friendly and cost efficient strategies for the transformation of biomass derived platform molecules to liquid transportation fuels, fuel additives and chemicals has been demonstrated successfully, in this thesis work. The thesis is divided into two parts, in which chemo-catalytic conversion of carbohydrates and furans is explored.

### Part-I

In this section, direct/integrated conversion of carbohydrates into advanced furan derivatives (*e.g.* fuel additives and chemicals) without isolation of unstable intermediates (furfural derivatives; *e.g.* 5-(hydroxymethyl)furfural (HMF) or furfural) is developed. Metal exchanged montmorillonite based solid acid catalysts such as Sn-Mont, Zr-Mont, Al-Mont and Fe-Mont were extensively studied for these transformations. These montmorillonite based catalysts possess unique combination of Lewis as well as Brønsted acid sites. The Lewis acid sites present on these catalysts facilitate the isomerisation of glucose/glucose like carbohydrates to fructose and Brønsted acid site promoted the dehydration of fructose to HMF derivatives. Using Sn-Mont catalyst, 5-(acetoxymethyl)furfural (AcMF) was produced in high yield from glucose, sucrose and fructose. In another attempt, carbohydrates dehydration was carried out over Sn-Mont and DMSO. A sulfur containing product is formed which has potential pharmaceutical applications. At high temperature of 180 °C, DMSO degraded over Sn-Mont to polysulfide compounds which became the source for methylsulfur. Sn-Mont was also explored for the production of polycondensed furan products from carbohydrates and 2-methylfuran in formic acid medium. These polycondensed furan products could be further converted into diesel range liquid alkanes. In yet another work, carbohydrates dehydration to HMF was achieved over Sn-Mont catalyst in MIBK: H<sub>2</sub>O + DMSO biphasic solvent system. Further in-situ produced HMF was treated with CaO to undergo aldol condensation with solvent component to produce the condensation products which is a precursor for the production of Jet fuel. Continuing with Mont based acid catalysts, the Friedel crafts alkylation reactions of HMF, HMF derivatives and carbohydrates with petroleum derived arenes were successfully achieved over Zr-Mont catalyst. As compared to other catalysts, Zr-Mont possesses suitable acid strength and high

surface area which contributed to its excellent activity for Friedel-Crafts reaction. The montmorillonite based catalysts showed very good stability under reaction conditions evidenced by their good recyclability. These approaches eliminated the tedious isolation and purification processes of furfural derivatives (*e.g.* HMF/furfural). However in above developed strategies, the yields of downstream furan derivatives are only moderate to good due to humin formation in the reaction. From a practical perspective, the development of catalysts system and sustainable process which could reduce the humin formation in the reaction is urgently needed.

## Part II

In this section, catalytic upgradation processes were developed for the conversion of furan derivatives into advanced furan compounds through cascade and sustainable technologies. 5,5'-oxy(bis-methylene)-2-furfuraldehyde (OBMF) is a polymer precursor produced in high yield by reacting HMF in dichloroethane solvent over Sn-Mont catalyst. The use of Dean-Stark assembly facilitated the continuous removal of water from the reaction mixture which resulted in high yield of OBMF. A cascade protocol was developed for the conversion of bioderived aldehydes into respective ether derivatives using a combination of Zr-Mont and  $\text{ZrO}(\text{OH})_2$ . The unique balance of acid and base catalytic sites in  $\text{ZrO}(\text{OH})_2$  promoted the transfer hydrogenation of aldehydes to respective alcohols in presence of secondary alcohols as a hydrogen donors. The resultant alcohols were then reacted with the solvent (secondary alcohol) over Zr-Mont catalyst. In another novel approach, the hydrophilic,  $-\text{SO}_3\text{H}$  functionalized, recyclable, Brønsted acidic ionic liquid catalysts integrated with a two phase reaction system were developed for the efficient condensation of furan with furfural for the production of tri(furan-2-yl)methane products. The polymer formation was successfully minimized in water containing two phase system. It avoided direct interaction of acid with the product/substrate. Furan as a reactant as well as an extractant enhanced the product isolation and the IL + aqueous phase could be recycled multiple times. The critical features of all the as prepared catalysts were thoroughly characterized using advanced analytical tools.

Although, we have developed excellent strategies for furan (furfural derivatives) upgradation, isolation of these furfural derivatives (especially HMF) is

extremely difficult. During distillation at high temperature, unwanted impurities were formed which results in significant loss of HMF yield. Therefore, further development for isolation and purification of HMF is needed. Instead of using pure HMF, the crude HMF can also be used as a starting material for the production of valuable chemicals/fuel. On the other hand, although furfural is produced commercially in industries, its long time stability (shelf life) is a major concern. The transformation of pure furfurals to value added chemicals is also well explored. Still there are plenty of opportunities to find out advanced technologies.

## 7.2. Future Scope

During this thesis work, we have prepared several fuel precursors *via* C-C bond forming reactions. These fuel precursors could be converted into liquid alkanes *via* hydrodeoxygenation process. This area is open to work on the catalyst design and process development. The direct or integrated technologies could be developed in future for the production of liquid alkanes from carbohydrates. Development of processes which could utilize the earth abundant cheap cellulose as feedstock will make the production of bulk chemicals in a sustainable way. From a practical perspective, the development of a downstream use or market of HMF to compensate its high production cost is essential to justify the current research effort. In this direction, finding suitable applications of HMF or HMF-derived molecules where their unique properties can be advantageous compared to petroleum based platform chemicals is highly necessary. Along with their application as fuel, fuel additives and commodity chemicals HMF and its derivatives can be explored in other sectors, e.g. pharmaceutical and speciality chemicals.

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**List of Publications**

1. Selective self-etherification of 5-(hydroxymethyl)furfural over Sn-Mont catalyst.

**Suhas Shinde**, Chandrashekhar Rode, *Catalysis Communications*, 2017, 88, 77-80; <http://dx.doi.org/10.1016/j.catcom.2016.09.034>

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2. A two-phase system for the clean and high yield synthesis of furylmethane derivatives over-SO<sub>3</sub>H functionalized ionic liquids.

**Suhas Shinde**, Chandrashekhar Rode, *Green Chemistry*, 2017, 19, 4804-4810; DOI: 10.1039/c7gc01654a.

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3. Cascade Reductive Etherification of Bioderived Aldehydes over Zr-Based Catalysts.

**Suhas Shinde**, Chandrashekhar Rode, *ChemSusChem*, 2017, 10, 4090-4101; DOI:10.1002/cssc.201701275.

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4. An Integrated Production of Diesel Fuel Precursors from Carbohydrates and 2-Methylfuran over Sn-Mont Catalyst.

**Suhas Shinde**, Chandrashekhar Rode, *ChemistrySelect*, 2018, 3, 4039-4046; DOI:10.1002/slct.201800694.

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5. Friedel-Crafts Alkylation over Zr-Mont Catalyst for the Production of Diesel Fuel Precursors.

**Suhas Shinde**, Chandrashekhar Rode, *ACS Omega*, 2018, 3, 5491-5501; DOI:10.102/acsomega.8b00560.

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6. Highly efficient triphenyl(3-sulfopropyl)phosphonium functionalized phosphotungstic acid on silica as a solid acid catalyst for selective mono-allylation of acetals.

Sumit Kamble, **Suhas Shinde**, Chandrashekhar Rode, *Catalysis Science and Technology*, 2015, 5, 4039–4047; DOI: 10.1039/c5cy00531k.

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- 
7. Cascade synthesis of dihydrobenzofuran *via* Claisen rearrangement of allyl aryl ethers using FeCl<sub>3</sub>/MCM-41 catalyst.  
Sachin Sakate, **Suhas Shinde**, Gayatri Kasar, Rajeev Chikate, Chandrashekhar Rode, *Journal of Saudi Chemical Society*, 2018, 22, 396–404;  
<http://doi.org/10.1016/j.jscs.2017.08.006>.
- 
8. Effect of anion variation of imidazolium based ionic liquids on hydrogenation of levulinic acid to  $\gamma$ -valerolactone and pentanoic acid over Ru/C catalyst.  
Virendra Patil, **Suhas Shinde**, Alberto Coronas, Kashinath Patil, Chandrashekhar Rode, *Catalysis in Green Chemistry and Engineering*, 2018, in press
- 
9. Direct production of 2,5-di(formyl)furan and 5-((methylthio)methyl)-2-furfural from carbohydrates in sacrificial DMSO.  
**Suhas Shinde**, Chandrashekhar Rode, **Patent application number INV-2017-009**.
- 
10. Direct Synthesis of 5-(Acetoxymethyl)furfural from Carbohydrates over Sn-Mont Catalyst.  
**Suhas Shinde**, Kashmira Deval, Rajeev Chikate, Chandrashekhar Rode, **Submitted to ChemCatChem**.
- 
11. Clean Production of Jet-fuel Precursor from Carbohydrates through an Integrated Dehydration and Aldol Condensation.  
**Suhas Shinde**, Chandrashekhar Rode, **Submitted to ChemSusChem**.
- 
12. 4-Hydroxypyridine immobilized on silica as an efficient base catalyst for the Knoevenagel condensation of furfural with acetyl acetone.  
**Suhas Shinde**, Sachin Sakate, Chandrashekhar Rode, **to be submitted**.
- 
13. Selective Production of Alkyl levulinate Directly from Furfural *via* Transfer Hydrogenation over Zr-based Heterogeneous Catalysts.  
**Suhas Shinde**, Chandrashekhar Rode, **to be submitted**.
-



## Short communication

# Selective self-etherification of 5-(hydroxymethyl)furfural over Sn-Mont catalyst



Suhas Shinde, Chandrashekhar Rode \*

Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Pune 411008, India

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5-(Hydroxymethyl)furfural

Sn-Mont

Self-etherification

OBMF

## ABSTRACT

Sn-Mont was found to be a highly efficient catalyst for self-etherification of 5-(hydroxymethyl)furfural (HMF) to give 5,5'-oxy(bis-methylene)-2-furaldehyde (OBMF). L-B acidity of  $\text{Sn}(\text{OH})_4$  species enwrapped into the layers of montmorillonite was responsible for the excellent activity of Sn-Mont catalyst giving almost complete conversion of HMF with 98% selectivity to OBMF. Aprotic non-polar, dichloroethane was most effective solvent due to the facile formation of oxonium ion mediating etherification reaction. The catalyst showed suitable recyclability confirming its appreciable hydrolytic stability in water, and retention of its acidity.

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## 1. Introduction

HMF derivatives have wide range applications as starting materials for plastics, surfactants, solvents, fuels, pharmaceuticals and antifungals [1–3]. Despite its high cost as a reagent, extensive research is being focused on obtaining valuable products from HMF believing its commercial availability at an affordable cost in near future. One such example is 5,5'-oxybis(methylene)difuran-2-carbaldehyde (OBMF) which is used for making multiheteromacrocycles (16-crown-6), polyurethanes, polyamides and imine polymers [4,5]. OBMF and 1, 4-diaminobenzene gives a polymer with high glass transition temperature, thermal and electrical conductivities and having solubility in polar solvents [6]. OBMF possesses wide range of anti-virus, anti-tuberculosis and anti-oxidant activity (Scheme 1) [7]. OBMF can be synthesized by a conventional Williamson reaction between HMF and 5-(chloromethyl)-2-furfural giving only 42.7% yield [7]. Thermal dehydration of HMF in DMSO also gives OBMF while, carbohydrates conversion using  $\text{BF}_3 \cdot \text{OEt}_2$ /DMSO gives low to moderate yield of OBMF [8,9]. Although Dean-Stark assembly increased the productivity of OBMF, in HMF self-etherification but large amount of waste is generated when homogeneous acids or bases are used [9–11]. Therefore, solid acids such as amberlite IR120 and amberlyst-15 were also explored however, they have a lower thermal stability especially, during their regeneration step [12,13]. This was overcome by Casanova et al. with an excellent performance of Al-MCM-41 [14]. Recently, graphene oxide was explored for this reaction to give 86% yield of OBMF in dichloromethane however, dichloromethane exerts a high vapour pressure under reaction conditions [15].

Considering these drawbacks of the existing methods, we envisioned HMF etherification by using Sn-Mont catalyst having the following characteristics: 1) ideal combination of micro and mesopores 2) simple preparation 3) excellent stability in presence of water [16] and 4) easy recovery and recyclability. Self-etherification of HMF was conducted in dichloroethane at 100 °C using a Dean-Stark assembly to achieve 98% OBMF selectivity with almost complete HMF conversion. Effects of solvents, catalyst loading, water removal, reaction time and temperature on the yield of OBMF have been studied in detail.

## 2. Materials and methods

### 2.1. Materials

5-(Hydroxymethyl)furfural (99.8%),  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{SnO}_2$ , montmorillonite (CAS No. 1302-78-9) and amberlyst-15 were purchased from Sigma-Aldrich, India. Organic solvents,  $\text{H}_2\text{SO}_4$  and p-toluenesulfonic acid were purchased from Thomas Baker.

### 2.2. Catalyst preparation

The catalyst was prepared as per the literature [17]. In a typical preparation, 5 g of montmorillonite (CAS No. 1302-78-9) was slowly added to the aqueous solution of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (0.3 M, 80 mL) and stirred for 4 h at RT. Mixture was then filtered, residue washed with distilled water till pH neutral and then dried at 100 °C overnight (2 nm particle size). Calcined sample prepared by heating at 600 °C for 4 h was denoted as 'Sn-Mont-600'.  $\text{Sn}(\text{OH})_4$  was prepared by precipitation of aq.  $\text{SnCl}_4$  (0.3 M, 50 mL) with 30% aq. ammonia.

\* Corresponding author.  
E-mail address: [cv.rode@ncl.res.in](mailto:cv.rode@ncl.res.in) (C. Rode).



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## A two-phase system for the clean and high yield synthesis of furylmethane derivatives over $-\text{SO}_3\text{H}$ functionalized ionic liquids†

S. H. Shinde  and C. V. Rode \*

A new and effective unique two-phase reaction system is investigated for the high yield production of tri(furyl)methane from furfural and furan. This strategy includes the use of an acidic aqueous phase (water +  $-\text{SO}_3\text{H}$  functionalized IL) and furan phase, which significantly suppresses polymer formation, thereby increasing the yield of tri(furyl)methane. Furan serves as a reactant as well as an extraction solvent for the recovery of the condensation products. For comparison, different  $-\text{SO}_3\text{H}$  functionalized ionic liquids are prepared and their performances evaluated for the condensation of furan and furfural. The ionic liquids with alkyl chain linkers are found to be more effective and acidic than those with imidazolium linked *N*-sulfonic acids. In addition, an increase in carbon chain length between imidazole/tri-ethylamine/pyridine and  $-\text{SO}_3\text{H}$ , increases the catalytic activity of the respective ionic liquids. Among the several prepared ionic liquids, the strongly acidic imidazolium based butylsulfonic acid **6** shows the best activity with a maximum condensation product yield of 84%. This strategy offers a significantly high yield of the condensation products of furan and furfural compared to the traditional mineral acid route. The activity and stability of the  $-\text{SO}_3\text{H}$  functionalized **6** is confirmed from seven successful recycles, in which there is no reduction in its activity. Finally, this new strategy is successfully extended for the condensation of furan derivatives (e.g. furan and 2-methylfuran) with several different aldehydes, ketones and alcohols.

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### Introduction

Currently, the worldwide production of transportation fuels and chemicals is dependent on crude oil, which may have limited availability in the future due to its depletion and the exponential increase in its consumption. Sustainable and renewable alternatives to petroleum are therefore critically needed to fill the future gap in the supply and demand of transportation fuels and chemical feedstock.<sup>1,2</sup> Biomass provides an ideal alternative to fossil resources since it is a sustainable, cheap and abundant source of organic molecules. Hence, genuine interest has been aroused for the production of biomass derived platform molecules. One such approach involves catalytic C–C bond forming reactions which include (i) aldol-condensation of furfural with different ketones,<sup>3</sup> (ii) pinacol coupling of lignocellulose derived aldehydes,<sup>4</sup> (iii) NHC catalyzed umpolung benzoin condensation of 5-(hydroxymethyl)furfural<sup>5</sup> and (iv) hydroxyalkylation-alkylation (HAA) reaction of 2-methylfuran.<sup>6</sup> Furan, which is an electron rich

aromatic ring, is capable of undergoing electrophilic substitution at the  $\text{C}_1$  and  $\text{C}_4$  positions and hence a starting material in the hydroxyalkylation-alkylation (HAA) reaction. Furans are considered to be more reactive than benzene towards electrophilic substitution reactions due to the electron donating effect of the oxygen heteroatom.<sup>7</sup> Importantly, furan is a biomass derived molecule obtained from the decarbonylation of furfural.<sup>8</sup> Furan ring containing products such as bis/tris(furyl)alkanes have attracted much attention due to their wide range of industrial applications, such as intermediates for the synthesis of tetraoxaquaterenes, which is a very interesting scaffold in supramolecular chemistry,<sup>9</sup> polymers,<sup>10</sup> macromolecules for metal ions carriers,<sup>11</sup> foods,<sup>12</sup> dyes<sup>13</sup> and agrochemicals.<sup>14</sup> Apart from these conventional applications recently, bis/tris(furyl)alkanes have been considered as rich carbon sources for the production of bio-fuel *via* hydrodeoxygenation (HDO) (Scheme 1).<sup>3–6,15</sup> Numerous synthetic methods are available for the synthesis of bis/tris(furyl)alkanes, which mainly include the condensation of 2-methylfuran with carbonyl compounds in presence of conc.  $\text{H}_2\text{SO}_4$ ,<sup>6a</sup>  $\text{HCl}$ ,<sup>15</sup> acidic resins,<sup>6a,c,16,17</sup>  $\text{MCM-SO}_3\text{H}$ ,<sup>18</sup>  $\text{Mo-Zr-MCM-41}$ ,<sup>19</sup>  $\text{AuCl}_3$ ,<sup>20</sup> zeolites,<sup>21</sup>  $\text{SiO}_2\text{-Pr-S-Pr-SO}_3\text{H}$ ,<sup>6d</sup>  $\text{Cu}(\text{OTf})_2$ ,<sup>22</sup>  $\text{I}_2$ ,<sup>23</sup>  $\text{CMH-SO}_3\text{H}$ ,<sup>24</sup>  $\text{SILC}$ <sup>25</sup> and  $\text{TFA-ZrO}_2$ .<sup>26</sup> However, most of these synthetic methods utilize non-recyclable and environmentally incompatible catalyst systems. In addition, some of the solid

Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, India-411008. E-mail: cv.rode@ncl.res.in; Fax: +91 20 2590 2621; Tel: +91 20 2590 2349

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# Cascade Reductive Etherification of Bioderived Aldehydes over Zr-Based Catalysts

Suhas Shinde and Chandrashekhar Rode\*<sup>[a]</sup>

An efficient one-pot catalytic cascade sequence has been developed for the production of value-added ethers from bioderived aldehydes. Etherification of 5-(hydroxymethyl)furfural with different aliphatic alcohols over acidic Zr-montmorillonite (Zr-Mont) catalyst produced a mixture of 5-(alkoxymethyl)furfural and 2-(dialkoxymethyl)-5-(alkoxymethyl)furan. The latter was selectively converted back into 5-(alkoxymethyl)furfural by treating it with water over the same catalyst. The synthesis of 2,5-bis(alkoxymethyl)furan was achieved through a cascade sequence involving etherification, transfer hydrogenation, and re-etherification over a combination of acidic Zr-Mont and the charge-transfer hydrogenation catalyst [Zr(OH)<sub>2</sub>]. This catalyst

combination was further explored for the cascade conversion of 2-furfuraldehyde into 2-(alkoxymethyl)furan. The scope of this strategy was then extended for the reductive etherification of lignin-derived arylaldehydes to obtain the respective benzyl ethers in >80% yield. Additionally, the mixture of Zr-Mont and Zr(OH)<sub>2</sub> does not undergo mutual destruction, which was proved by recycling experiments and XRD analysis. Both the catalysts were thoroughly characterized using BET, temperature-programmed desorption of NH<sub>3</sub> and CO<sub>2</sub>, pyridine-FTIR, XRD, inductively coupled plasma optical emission spectroscopy, and X-ray photoelectron spectroscopy techniques.

## Introduction

A central research challenge in the coming decades will be to develop practical and efficient procedures for the conversion of cellulosic biomass into platform chemicals and biofuels; the latter is estimated to cater for up to one third of the world's demand for transportation fuels.<sup>[1]</sup> Lignocellulosic materials are biopolymers available from nonedible biomass consisting of cellulose (40–50%), hemicellulose (20–30%), and lignin (20–25%).<sup>[2]</sup> One of the prime platform molecules, 5-(hydroxymethyl)furfural (HMF) is produced from the acid-catalyzed dehydration of C<sub>6</sub> sugars (hexoses) and can be used for the production of liquid alkanes.<sup>[3,4]</sup> Therefore, the demand for HMF is predicted to grow as the supply of petroleum feedstock diminishes concurrently with the rise in its price in the near future.<sup>[5]</sup> It has also been shown that 2,5-dimethylfuran, produced from the hydrogenation of HMF, can directly serve as a high heating value fuel.<sup>[6]</sup> HMF can be transformed into a number of important compounds that are expedient and important intermediates for the production of fine chemicals and monomers, including furan derivatives such as 2,5-furandicarboxylic acid, 2,5-diformylfuran, 2,5-bis(hydroxymethyl)furan, and nonfuranic compounds such as levulinic acid, 1,6-hexanediol, adipic acid, caprolactam, and caprolactone.<sup>[7]</sup>

One such example is the HMF ether 5-(ethoxymethyl)furfural (EMF), which can be used directly as a fuel or fuel additive (owing to its high cetane number and high energy density) and also as a flavoring and aroma component. EMF was first synthesized by a simple nucleophilic substitution reaction between 5-(chloromethyl)furfural (CMF) and ethanol at room temperature.<sup>[8a]</sup> Following this, the preparation of EMF from carbohydrates and HMF was studied using a variety of acids such as metal halides,<sup>[8]</sup> mineral acids,<sup>[9]</sup> organic acids and resins,<sup>[9b]</sup> solid acids,<sup>[10]</sup> and acidic ionic liquids.<sup>[11]</sup> Interestingly, ethers of HMF obtained from branched alcohols have superior blending properties as compared to ethers obtained from linear analogues. For example, up to 40 vol. % of 5-(*tert*-butoxymethyl)furfural (*t*-BMF) was completely soluble in commercial diesel and did not have any mixing or flocculation problems.<sup>[12]</sup> This 40:60 v/v *t*-BMF/diesel blend ratio leads to a substantial increase in the cetane number and does not decrease the oxidation stability of commercial diesel.<sup>[12]</sup> The preparation of *t*-BMF was achieved by reacting HMF with *tert*-butanol in the presence of montmorillonite K10 and zeolite HY to give HMF conversion of 49 and 59% with selectivities to *t*-BMF of 76 and 79%, respectively.<sup>[12]</sup> However, a major concern about 5-(alkoxymethyl)furfural is the presence of an aldehyde functionality, which reduces the stability of the molecule. Hence, it is desirable to first hydrogenate the aldehyde functionality to an alcohol<sup>[13]</sup> followed by subsequent etherification to form stable 2,5-bis(alkoxymethyl)furan (Scheme 1).<sup>[9b]</sup> An added advantage of the two ether linkages in the 2,5-bis(alkoxymethyl)furan is its enhanced miscibility in commercial diesel and lowering of the crystallization temperature compared with that of 5-(alkoxymethyl)furfural.<sup>[14]</sup> Therefore, it is of seminal interest to produce

[a] S. Shinde, Dr. C. Rode  
Chemical Engineering and Process Development Division  
CSIR National Chemical Laboratory  
Dr. Homi Bhabha Road, Pune, 411008 (India)  
E-mail: cv.rode@ncl.res.in

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## Catalysis

## An Integrated Production of Diesel Fuel Precursors from Carbohydrates and 2-Methylfuran over Sn-Mont Catalyst

Suhas H. Shinde and Chandrashekhar V. Rode<sup>\*[a]</sup>

Condensation of 5-(hydroxymethyl)furfural (HMF) with 2-methylfuran provides precursor of diesel fuel. However, HMF production is critical due to its tedious isolation and purification. Herein, we have developed an integrated process for production of diesel precursors directly from cheap HMF precursors and 2-methylfuran. This process involves, dehydration of carbohydrates to HMF followed by latter's condensation with 2-methylfuran to give 5,5'-((5-((5-methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran) (1). Over Sn-Mont catalyst, in solvents like water, DMSO and C<sub>4</sub>mimBr the product 1

was produced in negligible yields. The yield of 1 was significantly improved to 36% in formic acid medium. Sn-Mont facilitates the isomerization of glucose to fructose with its Lewis acid sites and formic acid promotes the dehydration of fructose to a mixture of HMF + 5-(formyloxymethyl)furfural (FMF) which was further treated with 2-methylfuran in same pot. The product 1 was obtained with 40% and 54% yields from sucrose and fructose, respectively. Using this strategy xylose was converted into 5,5'-(furan-2-ylmethylene)bis(2-methylfuran) (2) in 25% yield.

## Introduction

Lignocellulosic biomass is a renewable carbon rich source that makes it an ideal alternative to fossil resources for obtaining fuel and chemicals to fulfill at least partially world's current and future requirement.<sup>[1]</sup> Glucose and xylose obtained from cellulose and hemicellulose components of biomass are the precursors of versatile platform molecules like, 5-(hydroxymethyl)furfural (HMF) and furfural (FUR), respectively.<sup>[2–4]</sup> These furan aldehydes can be transformed into liquid fuels via C–C bond formation and hydrodeoxygenation processes. Aldehyde functionality present on HMF and furfural is prone to C–C bond forming reactions such as aldol-condensation,<sup>[5]</sup> pinacol coupling,<sup>[6]</sup> umpolung benzoin condensation<sup>[7]</sup> and hydroxyalkylation-alkylation (HAA) reaction.<sup>[8–11]</sup> Sugars and dehydrated sugar derivatives can also be used to produce additional platform molecules, such as 5-methylfurfural and 2-methylfuran (MeF) through sequential or one-pot reactions.<sup>[12–13]</sup> MeF is a by-product in large-scale production of furfuryl alcohol (FAL) from FUR and is a major product when same reaction was carried out at 250 °C.<sup>[14]</sup> MeF is an electron rich aromatic ring thus, it undergoes selective electrophilic substitution at the C<sub>4</sub> position of furan ring. Hydroxyalkylation-alkylation (HAA) reaction of MeF with furfurals (HMF and FUR) provides condensation products [bis/tris(furyl)alkanes] containing C<sub>15</sub> and C<sub>21</sub> units, respectively. Bis/tris(furyl)alkanes have wide range of industrial applications.<sup>[15–11, 15–22]</sup> Numerous synthetic methods are available

on synthesis of bis/tris(furyl)alkanes by condensation of MeF with carbonyl compounds over mineral acids,<sup>[8, 23, 24]</sup> acidic resins,<sup>[8, 10, 25]</sup> functionalized silica and carbon,<sup>[26–29]</sup> AuCl<sub>3</sub>,<sup>[30, 31]</sup> zeolites,<sup>[32]</sup> Cu(OTf)<sub>2</sub>,<sup>[33]</sup> I<sub>2</sub>,<sup>[34]</sup> and TFA/ZrO<sub>2</sub>.<sup>[35]</sup> Recently, we have invented a biphasic reaction system for the clean isolation of tris(furyl)alkanes with high yield using -SO<sub>3</sub>H functionalized ionic liquids.<sup>[36]</sup> Production of bis/tris(furyl)alkanes from pure HMF or furfural could be achieved by simple treatment with MeF in acid. Although, large scale production of furfural is practiced still its long time stability is also one of the concerns due to its vulnerability to polymerize. On the other hand, HMF production from carbohydrates is not yet commercialized due to its troublesome isolation and purification. As a result, its market price is also too high. Thus, instead of isolating these furfural derivatives, their further conversion to higher value commercial chemicals via integrated process is highly desirable. In this direction, we propose here production of diesel fuel precursors directly from carbohydrates and 2-methylfuran (Figure 1). However, making diesel fuel precursors [bis/tris(furyl)alkanes] from carbohydrates is a hard task due their stable ring structure. In addition, carbohydrates like glucose are much more difficult to dehydrate to HMF due to its critical isomerisation to fructose. Thus, conversion of glucose into HMF would be proceeding in two steps: first isomerisation of glucose to fructose in presence of enzyme, Lewis acid or base catalysts,<sup>[37, 38]</sup> followed by the dehydration of fructose to HMF over Brønsted acid.

The tin (Sn) containing heterogeneous catalysts were explored quite extensively for the conversion of glucose-based carbohydrates to HMF and its derivatives. Nikola et al. shown that Sn-beta could be efficient catalyst for the isomerization of glucose to fructose and then generated fructose was converted to the HMF rapidly by using HCl.<sup>[38]</sup> Lew et al, produced 5-(ethoxymethyl)furfural directly from glucose using a combination of Sn-BEA and Amberlyst-15.<sup>[39]</sup> However, certain amount

[a] S. H. Shinde, Dr. C. V. Rode  
Chemical Engineering and Process Development division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, India-411008  
+9120 2590 2349  
+9120 2590 2621  
E-mail: cvrode@ncl.res.in

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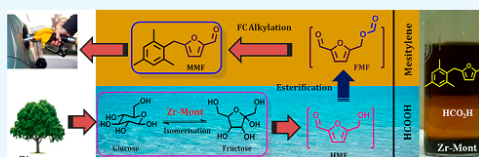
# Friedel–Crafts Alkylation over Zr-Mont Catalyst for the Production of Diesel Fuel Precursors

Suhas H. Shinde and Chandrashekhar V. Rode\*

Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

## Supporting Information

**ABSTRACT:** Heterogeneous Zr-Mont catalyst prepared by a simple protocol was employed for the production of diesel fuel precursors via Friedel–Crafts (FC) alkylation of petroleum-derived arenes (e.g., mesitylene, xylene, and toluene) with biomass-derived 5-(hydroxymethyl)furfural (HMF), HMF derivatives, and carbohydrates. Initially, several acidic catalysts were screened for the FC alkylation of mesitylene with HMF in nitroethane solvent. Among all, Zr-Mont catalyst gave an exceptionally high yield (80%) of mesitylmethylfurfural (MMF). The catalytic activity of Zr-Mont was also evaluated for the alkylation of different petroleum-derived arenes with ester/halogen derivatives of HMF. Suitable acid strength and high surface area of Zr-Mont were its major attributes to make it the most efficient solid acid catalyst for this FC reaction. Even after several reuses, the catalytic activity of Zr-Mont was found to be consistent, which was also evidenced by the acidity measurements of fresh and reused Zr-Mont catalysts by temperature-programmed desorption of ammonia and pyridine Fourier transform infrared spectroscopy techniques. Direct conversion of glucose to diesel fuel precursors was also attempted over Zr-Mont catalyst in mesitylene and polar nonacidic solvents at 150 °C. However, the activity of Zr-Mont catalyst was limited for glucose dehydration to HMF and MMF did not form. When the same experiment was performed in formic acid medium, MMF was produced in 34% yield. After the addition of formic acid, the reaction becomes biphasic which contains mesitylene as an organic phase and formic acid as an aqueous phase. Formic acid worked as a solvent, reactant, and cocatalyst, whereas mesitylene worked as a reactant and product extraction phase to enable easy product isolation. With this strategy, other diesel fuel precursors were also produced in 26–30% yields from glucose and different arenes. Similar strategy was successfully extended for the conversion of sucrose to diesel fuel precursors.



## INTRODUCTION

For chemicals and liquid fuels, the society is heavily relying on crude oil which has certainly a limited stock on the earth. This imminent crisis can be overcome by an alternative feedstock such as cellulosic biomass; the latter has become one of the most exploited research areas.<sup>1</sup> 5-(Hydroxymethyl)furfural (HMF) derived from cellulose is recognized as a principle raw material for the production of liquid fuels<sup>2–6</sup> and a monomer for the polymers.<sup>7,8</sup> To produce diesel-range C<sub>11</sub>–C<sub>23</sub> alkanes from HMF, it needs to undergo carbon upgradation process via C–C bond formation.<sup>9</sup> Some of the efforts made in this direction involving C–C bond-forming reactions include (i) base-catalyzed aldol condensation of HMF with acetone,<sup>10</sup> (ii) amine-catalyzed Baylis–Hillman reactions between methylacrylate and HMF,<sup>11</sup> (iii) coupling of HMF and isoprene over a ruthenium complex,<sup>12</sup> and (iv) condensation of HMF with 2-methylfuran.<sup>13</sup> These upgraded products are carbon-rich; hence, they can be converted into diesel-range liquid hydrocarbons via ring-opening–dehydration–hydrodeoxygenation processes.<sup>10,14</sup>

In 2015, Corma et al. produced alkyl naphthenic kerosene from HMF and substituted benzenes via Friedel–Crafts (FC) alkylation using zeolites followed by hydrodeoxygenation

process over a platinum-based catalyst.<sup>14</sup> However, currently there is only one industrial process for the bulk production of HMF from biomass-derived feedstocks.<sup>15</sup> Because HMF has high solubility in aqueous reaction mixtures, its extraction is a tedious task. In addition to that HMF has low stability in acidic mediums and also produces a large amount of tarry degradation products during its recovery by distillation at high temperature. Therefore, researchers have focused their attention on technologies where the carbohydrates can be directly converted into advanced chemicals/fuel precursors without isolating the unstable intermediate (HMF). In this direction, Zhou and Rauchfuss reported an excellent work on the production of hybrid diesel fuel precursors from carbohydrates and petrochemicals using formic acid as a reactive solvent to dissolve carbohydrates as well as a reagent for making a reactive intermediate named as 5-(formyloxymethyl)furfural (FMF).<sup>16</sup> However, in this reaction sequence, catalytic amount of concd HCl was required for the isomerization of glucose and other glucose-based carbohydrates into fructose, which limits its

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## Highly efficient triphenyl(3-sulfopropyl)phosphonium functionalized phosphotungstic acid on silica as a solid acid catalyst for selective mono-allylation of acetals†

Sumit B. Kamble, Suhas H. Shinde and Chandrashekhar V. Rode\*

Silica supported phosphotungstic acid functionalized with triphenyl(3-sulfopropyl)phosphonium (PW-Si/TPSP) was developed as a solid acid catalyst for C–C bond formation via Hosomi–Sakurai allylation of acetals. Functionalization of PW as well as its binding to silica was confirmed by solid state  $^{31}\text{P}$ -NMR and  $^{29}\text{Si}$ -NMR, respectively. Among the various catalysts prepared, the 30% PW loaded (30PW-Si/TPSP) catalyst gave an excellent yield of homoallyl ethers (HAEs) via selective mono-allylation of acetals with allyltrimethylsilane. A plausible reaction pathway has also been proposed in which the strong Brønsted acid sites of 30PW-Si/TPSP play an important role in activating the acetals to form the corresponding oxonium cations. The versatility of our catalyst was demonstrated for the allylation of a wide variety of acetals while its stability was established in five successful recycling runs.

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### Introduction

Acid catalyzed Hosomi–Sakurai allylation is one of the most important carbon–carbon bond forming reactions which is a key step in natural product synthesis, *e.g.* concise synthesis of nematocidal oxylipid<sup>1</sup> and heliespirone A and C having inhibitory activity in the coleoptile bioassay (Fig. 1).<sup>2</sup> Homoallyl ethers (HAEs) synthesized by the reaction of acetals with allyltrimethylsilane are also used as starting materials for many organic transformations.<sup>3a–e</sup>

Initially, Hosomi and Sakurai reported the allylation of acetals with titanium chloride as a catalyst.<sup>4</sup> Thereafter, conventional Lewis acids in stoichiometric or catalytic quantities were studied which included  $\text{TMSNTf}_2$ ,<sup>5</sup>  $\text{Sc}(\text{OTf})_3$ ,<sup>6</sup> diphenylboryl triflate,<sup>7</sup>  $\text{TMSOTf}$ ,<sup>8a–c</sup>  $\text{Bi}(\text{OTf})_3$ ,<sup>9</sup>  $\text{AlBr}_3/\text{CuBr}$ ,<sup>10</sup>  $\text{TMSI}$ ,<sup>11</sup>  $\text{NbCl}_5/\text{AgClO}_4$ ,<sup>12</sup>  $\text{CuBr}/\text{microwave}$ ,<sup>13</sup> liquid  $\text{SO}_2$ ,<sup>14</sup> trityl perchlorate,<sup>15</sup>  $\text{FeCl}_3$ ,<sup>16</sup> and  $\text{BiBr}_3$ ,<sup>17</sup>  $\text{AlCl}_3$ ,  $\text{BF}_3\cdot\text{Et}_2\text{O}$ ,<sup>18,19</sup>  $\text{TiCp}_2(\text{CF}_3\text{SO}_3)_2$ ,<sup>20</sup> and  $\text{TMSN}(\text{SO}_2\text{F})_2$ .<sup>21</sup> All these catalysts suffered from cumbersome work-up procedures due to unwanted salt formation. Exceptionally, a few Brønsted acids have been studied for the allylation of acetals such as sulfonimides with good yields but about 50% loss of the catalyst was observed up to 3rd recycling run and simultaneously needed aqueous work-up.<sup>22</sup> List *et al.* screened different sulfonic acids among which 2,4-dinitrobenzenesulfonic acid

gave excellent activity but again compromising the recovery of the catalyst.<sup>23</sup> Silicomolybdic acid supported on silica facilitated the allylation of acetals and aldehydes to HAEs but the activity diminished to 15% in the 3rd recycling run.<sup>24</sup> It is very important for a greener approach that the catalyst should be stable for subsequent reuse for several times without compromising the activity under the reaction conditions. Thus, there exists a scope to design a catalyst for allylation of acetals which does not undergo any leaching of the active component and can be recycled several times without losing its activity.

Heteropolyanion based 1-methyl-3-(3-sulfopropyl)imidazolium, 1-(3-sulfopropyl)pyridinium and triphenyl(3-sulfopropyl)phosphonium (TPSP) salts were well reported for acid-catalyzed esterification due to their self-induced phase separation properties.<sup>25–27</sup> Despite their self-separation nature, synthetic utility of these catalysts for new organic transformations is restricted due to

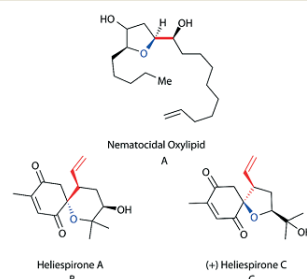


Fig. 1 Nematocidal oxylipid and heliespirones.

Chemical Engineering & Process Development Division, CSIR-National Chemical Laboratory, Pune 411008, India. E-mail: cv.rode@ncl.res.in

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ORIGINAL ARTICLE

# Cascade synthesis of dihydrobenzofuran via Claisen rearrangement of allyl aryl ethers using $\text{FeCl}_3/\text{MCM-41}$ catalyst



Sachin S. Sakate<sup>a,b</sup>, Suhas H. Shinde<sup>a</sup>, Gayatri B. Kasar<sup>a</sup>, Rajeev C. Chikate<sup>c</sup>, Chandrashekhar V. Rode<sup>a,\*</sup>

<sup>a</sup> Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Pashan, Pune 411008, India

<sup>b</sup> P. E. Society's Modern College of Arts, Science and Commerce, Shivajinagar, Pune 411004, India

<sup>c</sup> M. E. Society's Abasaheb Garware College, Karve Road, Pune 411004, India

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## KEYWORDS

Claisen rearrangement;  
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Ferric chloride

**Abstract** Dihydrobenzofuran as one of the active ingredients of the naturally occurring motif is synthesized by using in situ generation of *ortho* allyl phenols. Aryl allyl ethers on reacting with catalytic amounts of non noble metal iron (III) chloride supported on MCM-41 under moderate reaction conditions yield dihydrobenzofuran. First step via Claisen rearrangement gives *ortho* allyl phenol followed by its in situ cyclization to yield dihydrobenzofuran in very good yields. Both Lewis as well as Brønsted acidity of the catalyst as evidenced by Py-FTIR studies was found to catalyze the cascade synthesis of dihydrobenzofuran. The scope of the present strategy was successfully demonstrated for several substrates with varying electronic effects for the synthesis of corresponding dihydrobenzofuran with high yields in a range of 71–86%.

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## 1. Introduction

One of the most important motifs among the wide spectrum of various naturally occurring and medicinally important compounds is dihydrobenzofuran [1–3]. Some of the medicinally

important and biologically active molecules having the backbone of dihydrobenzofuran compounds are shown in Fig. 1. Synthesis of dihydrobenzofuran by a well known Claisen rearrangement is the oldest method for the formation of carbon-carbon bond which can be subsequently cyclized to give dihydrobenzofuran. The latter can be synthesized in two ways, firstly [3, 3] sigmatropic rearrangement of the allyl group at the *ortho* position and secondly, the cyclization of *o*-allyl phenols. In earlier days, Claisen rearrangement of aryl allyl ether was achieved at high temperatures either in the presence of solvents such as DMF, DMSO, *o*-dichloro benzene (ODCB) etc. or without any solvent (neat reaction). In the second step, cyclization of 2-allyl phenol to benzofuran was achieved

\* Corresponding author.

E-mail address: [cv.rode@ncl.res.in](mailto:cv.rode@ncl.res.in) (C.V. Rode).

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