Development of Catalysts for Biomass Transformation Reactions

M.Sc. Thesis

by

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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A THESIS

Submitted in partial fulfilment

of the requirements for the award of the degree

of
Master of Science

by

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CANDIDATE’S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Development of catalyst for biomass transformation reactions** in the partial fulfilment of the requirements for the award of the degree of **Master of Science** and submitted in the **Department of Chemistry, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from **July 2020** to **June 2021** under the supervision of **Dr. Sanjay Kumar Singh**, Associate Professor, Department of Chemistry, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Pranav

Pranav Pathak

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Dr. Sanjay Kumar Singh

Pranav Pathak has successfully given his M.Sc. Oral Examination held on **8 June 2021**

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Date: 9/6/2021

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Department of Chemistry

DEDICATED TO MY FAMILY, FRIENDS,

AND TEACHERS……

ABSTRACT

World's growing population and increasing energy consumption is resulting in the scarcity of fossil fuels. This depletion of fossil resources and growing reliance on fossil fuels have led current researchers to look forward for another renewable energy sources for sustainable future. Biomass is an excellent alternative renewable energy source. In this project, we have done a detailed study on the topic 'Development of catalyst for biomass transformation reactions.' We have synthesized a variety of biomass derived substrates from bio derived platform chemicals like furfural, 5-methyl furfural, methyl furan etc. and demonstrated their catalytic hydrogenation and hydrodeoxygenation over $Ni_{0.9}Pd_{0.1}$ nanoparticles at room temperature under H_2 atmosphere using H_2 balloon and high-pressure reactor (5 bar H_2 pressure) respectively to obtain long chain (C_8-C_{15}) fuel components.

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Acronyms

PXRD	Powdered X-ray Diffraction
NMR	Nuclear magnetic resonance
LCMS	Liquid Chromatography Mass spectroscopy
ESI	Electrospray ionization
SILP	Supported ionic liquid phase
TMS	Tetramethylsilane
SEM	Scanning electron microscopy
NP	Nanoparticles
HDO	Hydrodeoxygenation
PVP	Polyvinylpyrrolidone
XPS	X-ray photoelectron spectroscopy
IL	Ionic liquid
$CDCl_3$	Chloroform-d
HMF	Hydroxymethylfurfural

NOMENCLATURE

mL	Milliliter
g	Gram
°C	Degree Celsius
Ȧ	Angstrom
λ	Lambda
K	Kelvin
V	Volt
pH_2	Pressure of H_2 gas
MHz	Mega Hertz
Rpm	Rotation per minute
Min	Minutes
h	Hour
RB	Round bottom
Ppm	Parts per million
Ref.	Reference
mmol	Millimole
Conv.	Conversion
Temp.	Temperature

Chapter-1

INTRODUCTION

1.1 General Introduction

In today's world, the demand of fossil fuel has increased, and the world's biggest oil sources have been in production decline. We need clean and renewable alternatives of fossil fuels to meet the rising demand for energy. Biomass is one of the most abundant natural sources of carbon-rich materials for the generation of fuel and a variety of compounds with a wide range of uses, from medications to value added chemicals.[1,2]

Nature has a vast amount of biomass, of which three - quarters can be classified as lignocellulose and only 3-4 percent is utilized by humans for living. The practical pathway to produce a variety of synthetic compounds and fuel is to depolymerize lignocellulose into monosaccharides by acidic hydrolysis. These monosaccharides upon dehydration give rise to furfural (C_5) and 5-HMF (C_6).[3-6] These furfurals and 5-HMF are considered as bio platform molecules as they can be converted to fuels and a number of highly value-added components by various processes like hydrogenation, hydrodeoxygenation (HDO), oxidation, reductive amination etc.

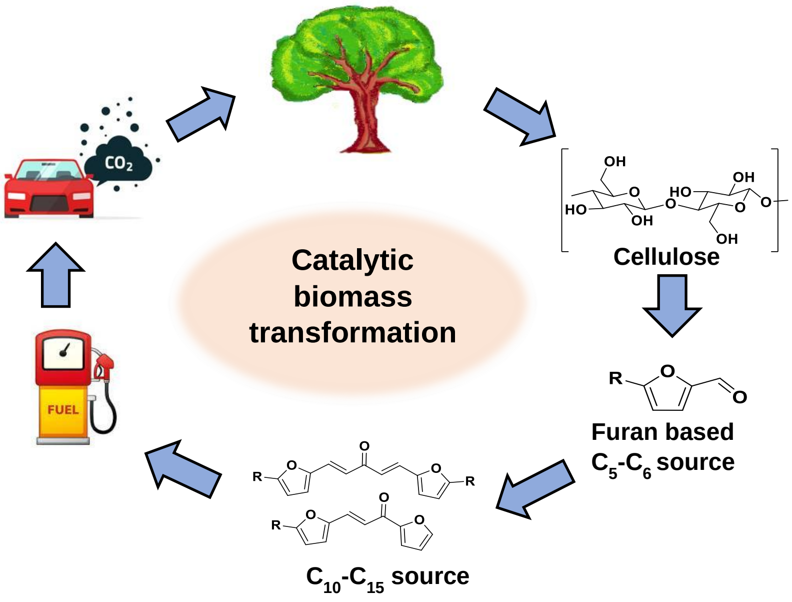


Figure 1. Sustainable pathway for catalytic biomass transformation

Hydrodeoxygenation (HDO) is a process of removing oxygen in the presence of hydrogen from different types of oxygenates. However, hydrodeoxygenation of 5-HMF and furfural gives short chain alkanes which is not suitable for fuel applications because of their insufficient energy density and volatile nature. So, efforts are being made to increase the chain length of furfural and 5-HMF by various processes like aldol condensation, Michael addition, benzoin condensation etc.

To form large organic compounds ($>C_7$), aldol condensation of 5-HMF, furfurals with ketones is preferably used. This technique has been suggested as a promising method to increase the carbon chain length. The monomer and dimer of the furfural-acetone adduct can be formed in the presence of an acid or base catalyst at lower temperature.

These furfural aldol adducts (C_8-C_{15}) contain three different kinds of double bond: ketonic, olefinic, and furanic. Hydrogenation of olefinic (C=C) bond is more favorable than ketonic (C=O) bond.[7-9] These furfural aldol adducts are hydrodeoxygenated to obtain valuable hydrocarbons at higher temperature and higher hydrogen pressure. This process undergoes different reaction pathways like hydrogenation, dehydration, and ring opening, yielding a variety of intermediates.[10-13] In all these reaction pathways, selection of right catalyst is very crucial. Due to the complexity of hydrodeoxygenation process some researchers suggest carrying out the hydrogenation step individually and then performing deoxygenation step.

Various heterogeneous monometallic and bimetallic catalysts have been broadly studied in several catalytic reactions. In which bimetallic heterogeneous catalyst shows higher activity compared to monometallic. The second metal in bimetallic catalyst has huge special impact in the catalytic activity. It alters the catalytic action by changing the geometry and electron density at the catalyst active sites.

It also plays a vital role in the interaction of substrate and distinctive intermediates with the surface of the catalyst.[14]

1.2 Literature review

Literature has revealed that several efficient catalysts based on Ru, Ir, Pt, Pd and Ni have been widely investigated for the hydrodeoxygenation of furanic compounds. However, most of the catalytic reactions were performed under high pressure of H_2, which may have several safety concerns. Pd based catalysts have been extensively investigated as highly active catalysts for hydrogenation as well as deoxygenation of furan ring derivatives.

In similar direction, Nakagawa *et al.* explored Ni-Pd/SiO_2 catalyst (Ni/Pd = 7) for complete hydrogenation of furan derivatives in the presence of acetic acid at 40 °C and 80 bar H_2 pressure, but the Ni-Pd/SiO_2 catalyst quickly deactivated due to substantial Ni leaching in the acetic acid.[15]

Our research group has recently achieved complete hydrogenation of a variety of furan-based compounds to tetrahydrofuran analogous over $Ni_{0.9}Pd_{0.1}$ in water using H_2 balloon as H_2 source at room temperature.[14] In another work when this $Ni_{0.9}Pd_{0.1}$ catalyst was supported on various SiO_2 rich supports we observed selective hydrogenation of C=C bonds over C=O bonds using H_2 balloon at room temperature displayed the role of support in tuning activity and selectivity.[16]

Sutton *et al.* achieved one pot two step selective conversion of biomass derived furan aldol adducts to linear alkane where hydrogenation of aldol adducts was carried out in the presence of Pd catalyst at 100 °C under 0.34 MPa H_2 pressure in glacial acetic acid which resulted in the complete conversion of aldol adduct to polyketones.[17] Later, Addition of $La(OTf)_3$ transformed these polyketones into alkane at 2.07 MPa H_2 and 200 °C.

Faba *et al.* explored total hydrodeoxygenation of furfural acetone (F_2A) adducts over Pt catalyst supported on different supports (activated carbon, alumina and graphite-MgZr oxide composite), to yield tridecane in a batch reactor for 24 h.[18] The best result was obtained with Pt/Al_2O_3 catalyst at 220 ˚C and 55 bar H_2 pressure having yield 21.5%.

Kylie L. Luska *et al.* explored the deoxygenation of furfural aldol adducts over bifunctional catalysts composed of an acid-functionalized supported ionic liquid phase i.e., RuNPs@SILP catalyst. It was found that maximum C_8-OL (linear chain alcohol) was obtained with RuNPs@SILP-1.00 at 150 ˚C under 120 bar H_2 pressure. The selectivity for over hydrogenated product, n-octane was very less with small amount of yield (<3%) was observed.[19]

Feedstock	**Target compound**	**Catalyst**	**Temp (°C)**	**pH_2 (bar)**	**Time (h)**	**Conv. (%)**	**Yield (%)**	**Ref.**
Furan derivative	n-nonane	Pd/C, $La(OTf)_3$	200	20.7	16	>99	90	17
Furan derivative	Tridecane	Pt/Al_2O_3	220	55	24	>99	21.5	18
Furan derivative	Octanol	RuNps@SILP-1.00	150	120	16	>99	60	19
Furan derivative	Octane	$Pd/Nb_2O_5/SiO_2$	170	25	24	>99	95.5	20
Furan derivative	Octane	$Pd/NbOPO_4$	170	20	24	>99	>90	21
Furan derivative	C_8-C_{13}	Pt/MgZr	220	45	24	>99	50	22
Furan derivative	C_9–C_{15} alkanes	$Pd/Hf(OTf)_4$	225	50.7	24	>99	97	23

Table 1: Literature review of HDO of furan aldol derivatives.

Over a variety of bifunctional catalysts, HDO of biomass-derived furanic compounds was achieved. All of the findings based on recent research are listed in above table.

1.3 Challenges in hydrodeoxygenation of biomass

HDO is an important step in synthesis of biofuels from biomass derived chemicals. The unsaturated furan aldol adducts are converted into linear hydrocarbon chain but this process is very challenging to accomplish because of involvement of various steps.

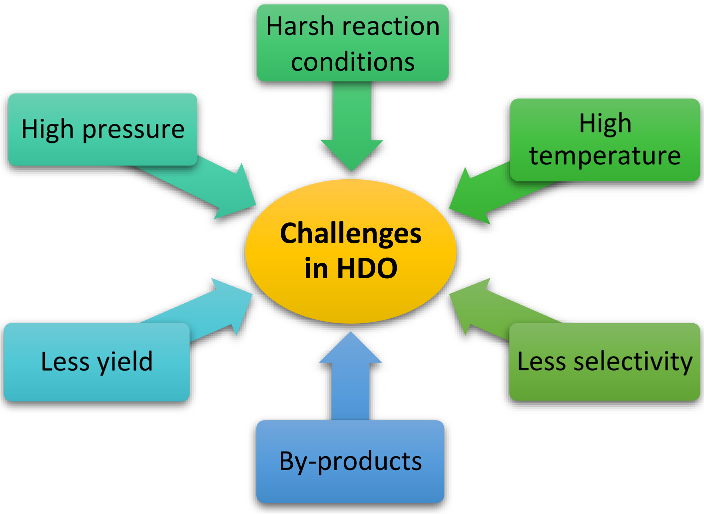


Figure 2. Challenges in performing HDO

Therefore, an efficient catalyst needs to be developed which can carry out HDO at lower pressure and lower temperature under environment benign conditions and shows higher catalytic activity.

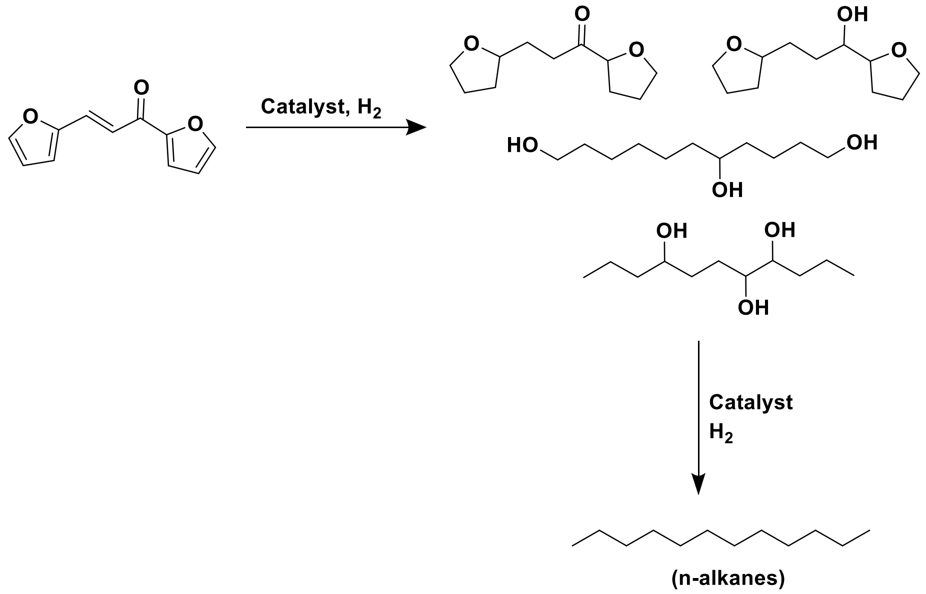
Herein, we have synthesized various biomass derived substrates from platform chemicals like furfural, 5-methylfurfural, 5-methyl furan by aldol condensation to increase the carbon chain length and demonstrated hydrogenation reaction of furanic aldol adducts and later their HDO over $Ni_{0.9}Pd_{0.1}$ in water using H_2 balloon at room temperature.

1.4 Objectives of the project

Depletion of fossil fuel resources made us to look at renewable source as another option.

In this regard, the bio-derived short chain chemicals are transformed into various useful fuel grade compounds which is a prominent route to decrease the worldwide reliance on fossil assets. Thus, lignocellulosic biomass (most naturally plentiful low-cost carbon-source) seen as best alternative to substitute non-renewable fossil assets. This conversion of bio- derived compounds to various chemicals has been the subject of exceptional examination endeavours during the last decade.

This project aimed the preparation of novel, active and stable heterogeneous catalysts for the conversion of bio-derived furan aldol adducts into long chain alkanes to produce high density fuel components and chemical feedstocks.



Scheme 1: Schematic representation for the conversion of furans into long chain alkanes

Chapter-2

EXPERIMENTAL SECTION

2.1 Materials and Instrumentation

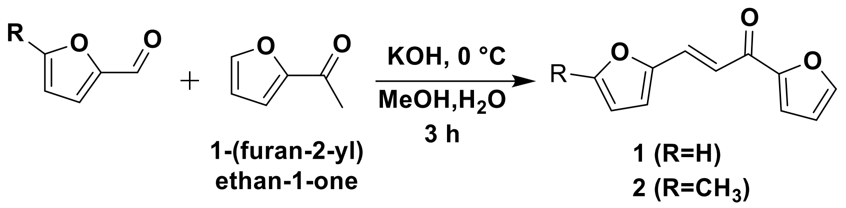
All chemicals and metal salts were purchased from Alfa Aesar, Sigma-Aldrich, and Spectrochem which were used without any further purification. The mass spectrometry (ESI-MS) was performed using a Bruker MicrOTOF-Q II that used positive-mode electron spray ionization. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in deuterated solvent (D_2O) using Bruker Avance 400. Chemical shifts were referenced to the internal solvent resonances and were reported relative to tetramethylsilane. Powder X-ray diffraction (P-XRD) measurements were performed using Rigaku Smart Lab, Automated Multipurpose X-ray diffractometer at 40 kV and 30 mA (Cu_{α} λ=1.5418 Å).

2.2 Synthesis of $Ni_{0.9}Pd_{0.1}$ catalyst

Metal nanoparticles were prepared by previously reported method.[24,25] Typically, 50 mg of PVP was added to 5 mL aqueous solution of $NiCl_2{\cdot}6H_2O$ (0.0107 g, 0.045 mmol) and K_2PdCl_4 (0.0016 g, 0.005 mmol). In which $NaBH_4$ aqueous solution (0.025 g in 5 mL H_2O) was added dropwise. The content of the flask was sonicated for 10 minutes at room temperature to obtain black suspension of $Ni_{0.9}Pd_{0.1}$ nanoparticles, which were then recovered by centrifugation and washed with distilled water several times then dried overnight and then used as catalyst.

2.3 General procedure for synthesis of furan-based aldol adducts

2.3.1 Synthesis of compounds 1 and 2



Scheme 2: Synthesis of compounds **1** and **2**

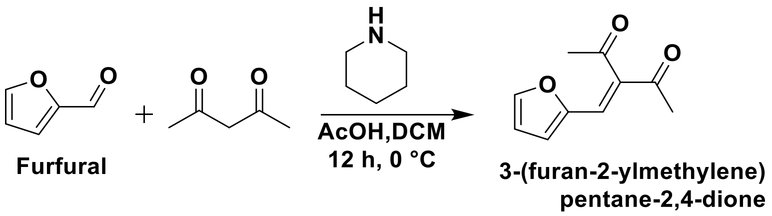
For the synthesis of **compound 1**, In a 50 mL RB flask Furfural (10 mmol) was typically added to 1.2 equivalent 85% KOH solution in MeOH (50 mL) and H_2O (10 mL) under stirring. The mixture was continued to stir at 0 °C for 3 h. The volatiles were extracted under reduced pressure after the reaction was completed, resulting in a solid product that was washed with cold methanol and then dried.

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.65-7.61 (m, 2H), 7.53 (s, 1H), 7.34-7.31 (m, 2 H), 6.73-6.72 (d, 1 H), 6.59-6.58 (m, 1 H), 6.52-6.51 (m, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.74, 153.71, 151.57, 146.54, 145.01, 129.86, 118.85, 117.39,116.34, 112.68, 112.46 ppm; LCMS (ESI): observed m/z for $C_{11}H_8O_3$ $[M+K]^+$ = 227.0107, calculated m/z = 227.0105.

Compound 2 was synthesized using the same procedure as compound 3, but instead of furfural, 5-methylfurfural (5 mmol) was used.

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.64 (m, 1 H), 7.58-7.55 (d, 1 H), 7.30 (d, 1 H), 7.25-7.22 (d, 1H) 6.63 (d, 1 H), 6.57 (d, 1 H), 6.13 (d, 1 H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl3): δ= 177.86, 156.02, 153.82, 150.18, 146.31, 129.95, 118.39, 117.04, 116.99 112.34, 109.37, 14.02 ppm; LCMS (ESI): observed m/z for $C_{12}H_{10}O_3$ $[M+K]^+$ = 241.0264, calculated m/z =241.0262

2.3.2 Synthesis of compound 3

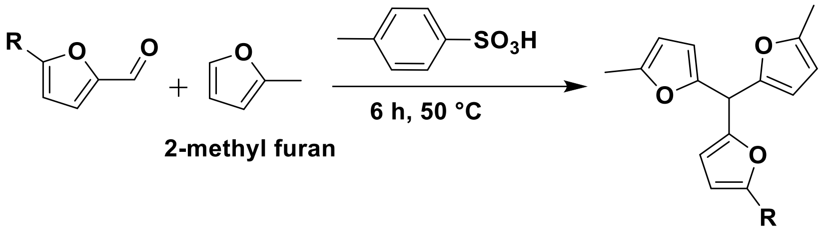


Scheme 3: Synthesis of compound **3**

Acetylacetone (2.5 mmol), piperidine (0.10 mmol), and acetic acid (0.10 mmol) were added to furfural (2 mmol) dissolved in dichloromethane (3 mL) at 0 °C. At room temperature, the reaction mixture was continued to stir for 12 h. After the reaction was completed, 10 mL of brine solution was added to the reaction mixture. Dichloromethane was used for extraction (3 x 10 mL). The volatiles were evaporated under reduced pressure after the organic layer was dried over Na_2SO_4. Hexane and ethyl acetate (9:1 v/v) were used as eluents in column chromatography to purify the sample.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, 1 H), 7.15 (m, 1 H), 6.77 (d, 1 H), 6.51 (dd, 1 H), 2.44 (s, 3 H), 2.37 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ= 204.34, 195.85, 148.68, 146.47, 138.16, 124.91, 118.28, 112.87, 31.34, 25.95 ppm; LCMS (ESI): observed m/z for $C_{10}H_{10}O_3$ $[M+Na]^+$ = 201.0537, calculated m/z 201.0522.

2.3.3 Synthesis of compound 4 and 5



4 (R = H)
5 (R = CH_3)

Scheme 4: Synthesis of compound **4** and **5**

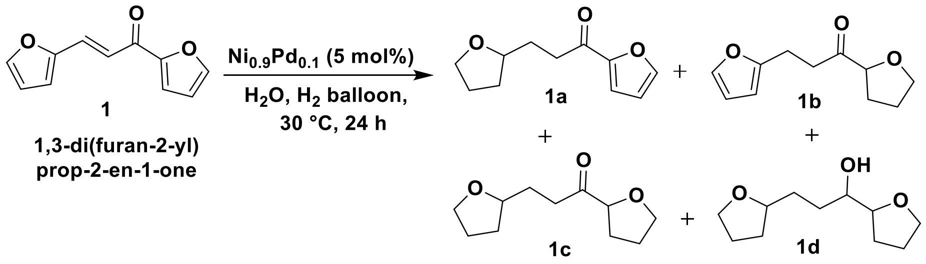
Compound 4: Furfural (2 mmol) was added dropwise to a solution containing 2-methylfuran (10 mmol) and p-toluene sulfonic acid (0.11 mmol) at room temperature under stirring. The reaction mixture was then heated to 50 °C and stirred for 6 h. Following the completion of the reaction, 5 mL of water was added, and dichloromethane extraction was carried out. All the volatiles were evaporated under reduced pressure after being treated with $NaHCO_3$. To obtain the desired compound 5, excess 2-methylfuran was extracted using a rotary evaporator.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (m, 1 H), 6.32-6.33 (m, 1 H), 6.11 (dd, 1 H), 5.97-5.98 (d, 2 H), 5.90 (dd, 2 H), 5.42 (s, 1 H), 2.26 (s, 6 H) ppm; ^{13}C NMR (100 MHz, CDCl3): δ = 152.57, 151.53, 150.31, 141.83, 110.28, 107.89, 107.06, 106.22, 39.06, 13.59 ppm; LCMS (ESI): observed m/z for $C_{15}H_{14}O_3$ $[M+Na]^+$ = 265.1015, calculated m/z = 265.0835.

Compound 5 was synthesized using the same process as compound 4, but instead of furfural, 5-methy-2-furfuraldehyde (2 mmol) was used.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.96-5.97 (m, 3 H), 5.89 (m, 3 H), 5.36 (s, 1 H), 2.26 (s, 9 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.41, 150.67, 107.76, 106.17, 39.12, 13.60 ppm; LCMS (ESI): observed m/z for $C_{16}H_{16}O_3$ $[M+Na]^+$ = 279.1187, calculated m/z = 279.9992

2.4 Hydrogenation of furfural aldol adducts over $Ni_{0.9}Pd_{0.1}$ catalyst at room temperature



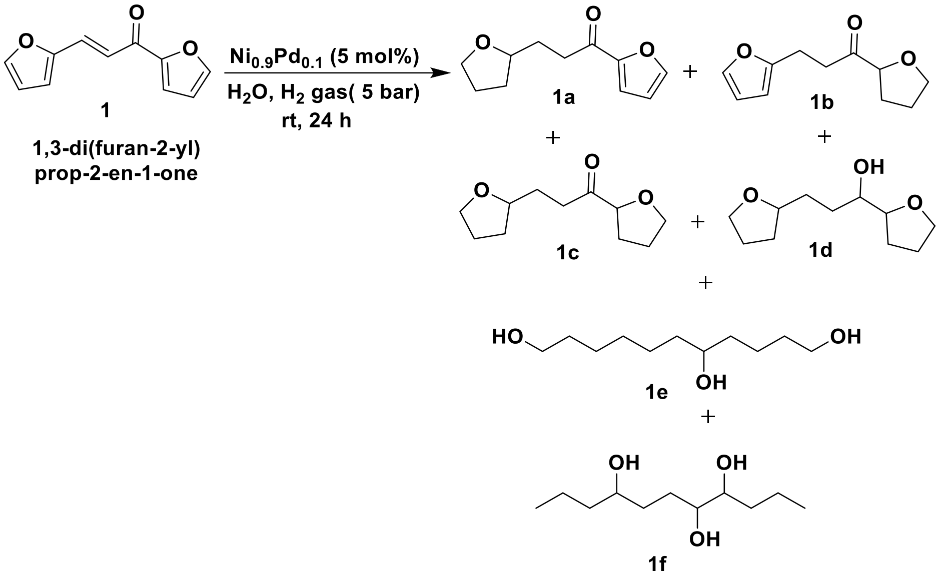
Scheme 5: Hydrogenation of compound **1**

For the hydrogenation process, furan-aldol substrate (1 mmol, 188 mg) was taken in 50 mL RB and an aqueous suspension of 5 mol % NiPd nanoparticles in 10 mL water was added to it and sonicated for 5 min for dispersion of nanoparticles. The reaction vessel was equipped with H_2 balloon and stirred for 24 h at room temperature. After the completion of reaction, catalyst was recovered by centrifugation and product was extracted from the aqueous solution using ethyl acetate (3x10 mL).

The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. To examine different obtained products and the conversion ^1H NMR was used.

2.5 Hydrogenation of furfural aldol adducts over $Ni_{0.9}Pd_{0.1}$ catalyst in a high-pressure reactor

For the hydrogenation process, in the Teflon lined autoclave, furan-aldol substrate (1 mmol, 188 mg) was taken and an aqueous suspension of 5 mol % NiPd nanoparticles in 10 mL water was added to it. Then the autoclave was placed in the high-pressure reactor and H_2 gas (5 bar) was purged into it. The reaction was continued for 24 h at room temperature. After the completion of reaction, catalyst was recovered by centrifugation and product was extracted from the aqueous solution using ethyl acetate (3x10 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. To examine different obtained products and the conversion ^1H NMR was used.



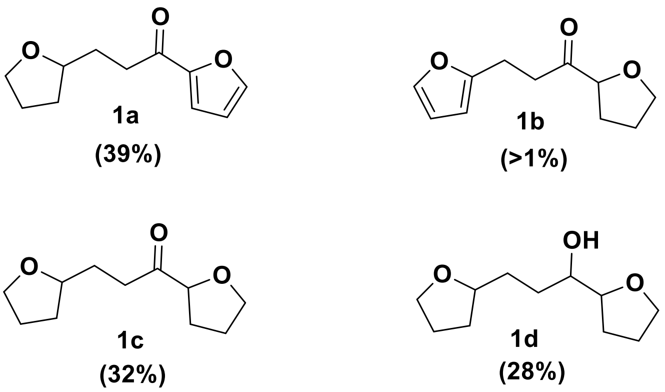
Scheme 6: Hydrogenation of compound **1** in a high-pressure reactor

Chapter-3

RESULTS AND DISCUSSIONS

3.1 Hydrogenation of furfural aldol adducts over $Ni_{0.9}Pd_{0.1}$ catalyst at room temperature

Hydrogenation was carried out for the compound 1 over $Ni_{0.9}Pd_{0.1}$ catalyst at room temperature for 24 h under H_2 atmosphere. After the reaction completion, four different products were obtained with the conversion >99%. Among which, high selectivity (39%) was observed for the product 1-(furan-2-yl)-3-(tetrahydrofuran-2-yl)propan-1-one **(1a).**



1a (39%)

1b (>1%)

1c (32%)

1d (28%)

Figure 3: Selectivity of different hydrogenated products

3.2 Hydrogenation of compound 1 over $Ni_{0.9}Pd_{0.1}$ catalyst in a high-pressure reactor

For the hydrogenation reaction of compound 1 carried out in a high-pressure reactor for 24 h at room temperature and H_2 pressure (5 bar), variety of products were obtained. Conversion of the substrate was found to be 88% with the high selectivity (24%) for the product 3-(furan-2-yl)-1-(tetrahydrofuran-2-yl)propan-1-one **(1b).**

Interestingly, complete hydrogenation of compound 1 was also observed with ring opening of the furan aldol adducts to give linear chain alcohols **(1e)** and **(1f)**.

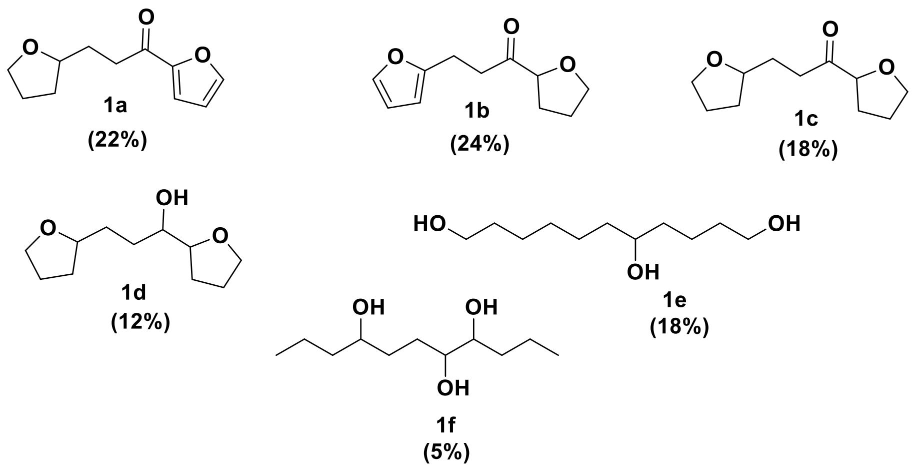


Figure 4: Selectivity of different hydrogenated products

The reduction of particular bond may rely upon the particle size of catalyst, nature of the support system and the noncovalent attachment of the substrate with the surface of catalyst. Considering earlier investigations on bimetallic NiPd catalyst, it is well documented that when the non-noble metal Ni was placed in close proximity to Pd, it will have a significant influence on the electronic structure of Pd and therefore, the bimetallic NiPd catalyst due to the e^- transfer effect driven by the differences in the electronegativity of two metals is highly active.[17,26] So, the electron density transfer from Ni to Pd centre makes it more electron rich helping in dissociation of H_2 in hydrogenation process. When we increase the ratio of Ni, more number of Ni surrounds the Pd centre hence more negative charge is accumulated to it which makes NiPd catalyst very effective.

From the previous research, we know that Pd has high tendency to adsorb C=C bond while the electropositive Ni centre have affinity towards C=O bond.[27,28] Therefore, the furan aldol adducts easily adsorbed over catalyst surface.

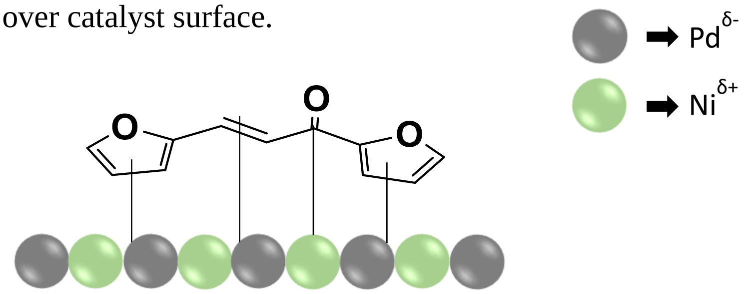


Figure 5: Interaction of substrate over NiPd catalyst surface

The exocyclic C=C bond hydrogenated first and then furanic C=C may be because of the furanic ring causes steric hindrance. It is also observed that on increasing the H_2 pressure to 5 bar, open furan ring products were also observed along with total hydrogenated products.

Chapter-4

CONCLUSION

In conclusion, we have synthesized various long chain (C_8-C_{16}) furan aldol adducts from bio derived chemicals such as furfural, 5-methylfurfural, methyl furan and acetone via aldol condensation. We carried out hydrogenation reaction of these furan aldol adducts over $Ni_{0.9}Pd_{0.1}$ catalyst at room temperature using H_2 balloon. Similar reaction was carried out in a high-pressure reactor for 24 h at room temperature and 5 bar H_2 pressure. We found variety of hydrogenated products including long chain alcohols via ring opening of furans. This is an efficient approach to yield alkane compounds. Though the yield is not significant but in future, on increasing H_2 pressure or by adding support to the catalyst we can get long chain alkanes selectively in high yield. Our current research will provide a thorough understanding of other high-performance, low-cost catalysts that can be used in mild, eco-friendly conditions for transforming biomass derived bio-oil to fuel grade compounds.

APPENDIX

^{1}H, ^{13}C and LCMS spectrum of compounds

1. Compound 1: 1,3-di(furan-2-yl)prop-2-en-1-one

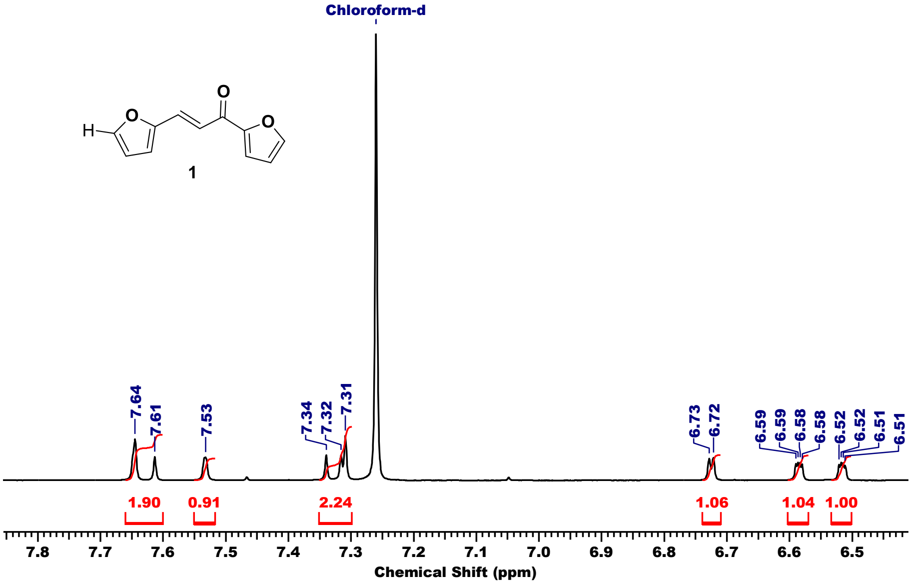


Figure 6: ^{1}H NMR of compound **1**

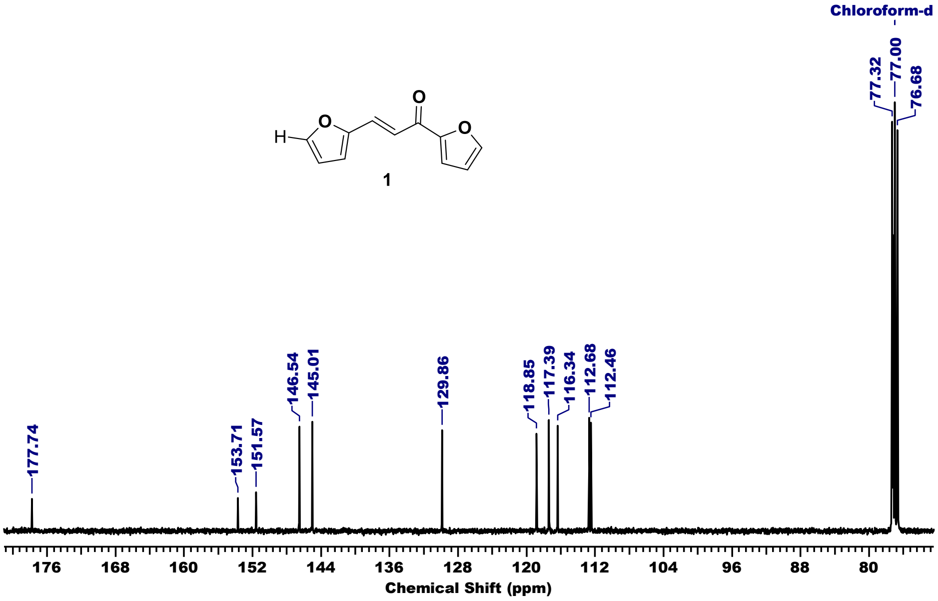


Figure 7: ^{13}C NMR of compound **1**

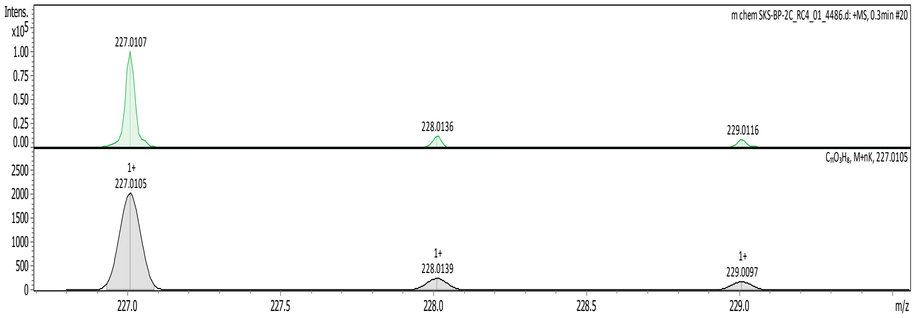


Figure 8: LCMS of compound **1**

2. Compound 2: 1-(furan-2-yl)-3-(5-methylfuran-2-yl)prop-2-en-1-one

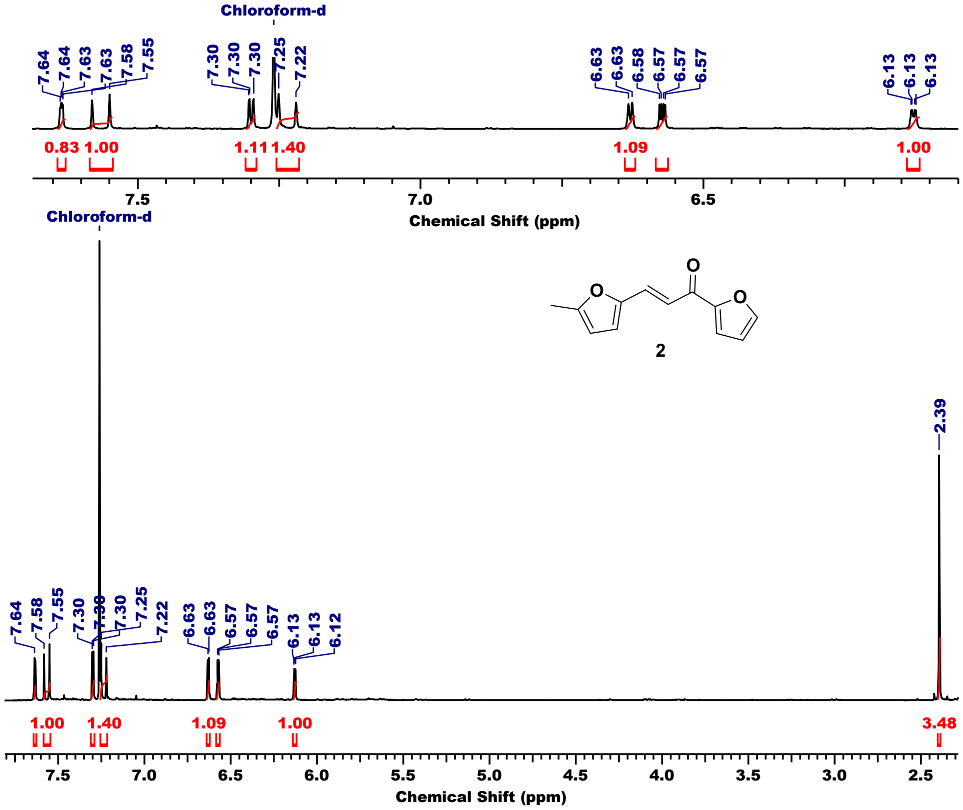


Figure 9: ^{1}H NMR of compound **2**

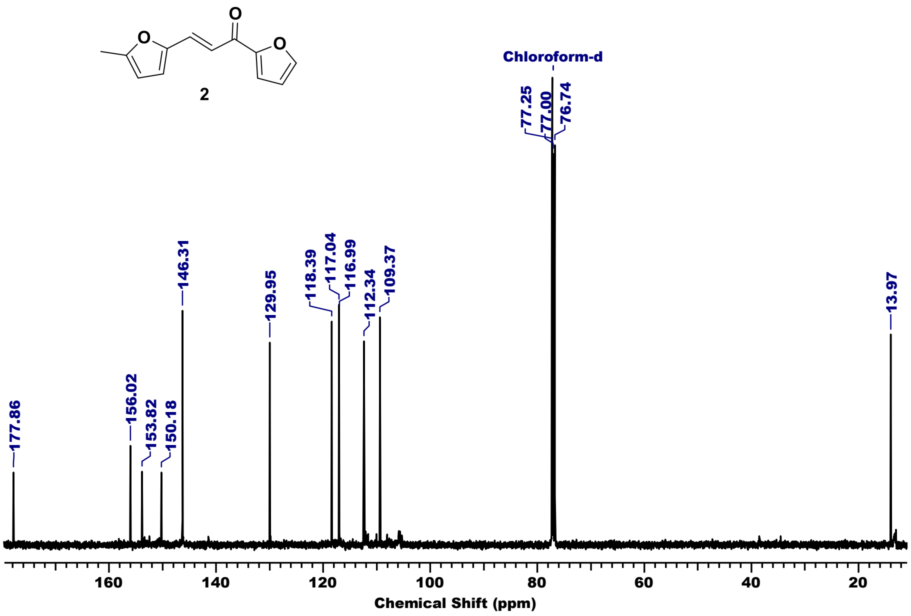


Figure 10: ^{13}C NMR of compound **2**

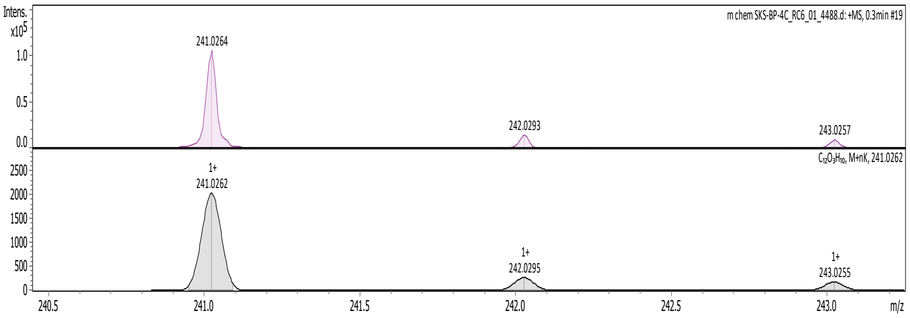


Figure 11: LCMS of compound **2**

3. Compound 3: 3-(furan-2-ylmethylene)pentane-2,4-dione

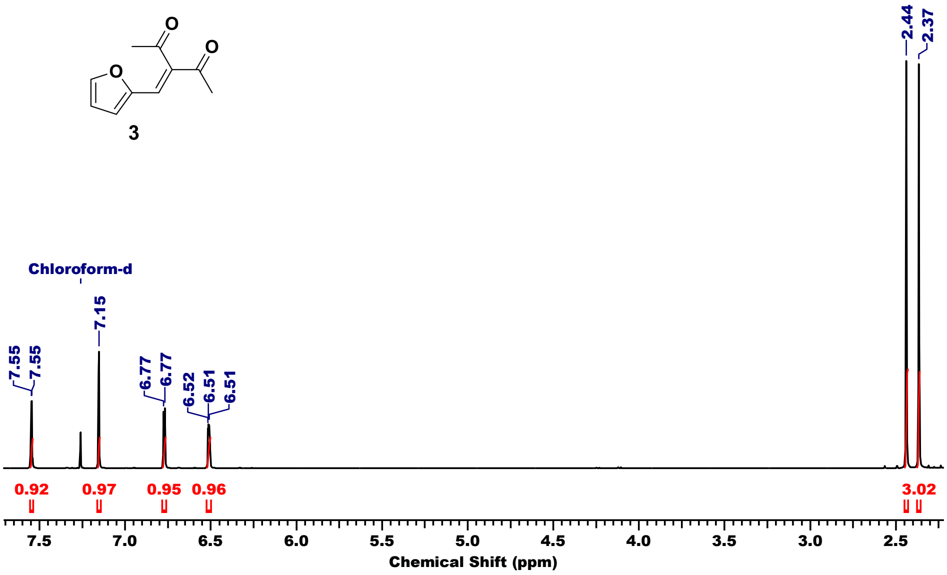


Figure 12: ^{1}H NMR of compound **3**

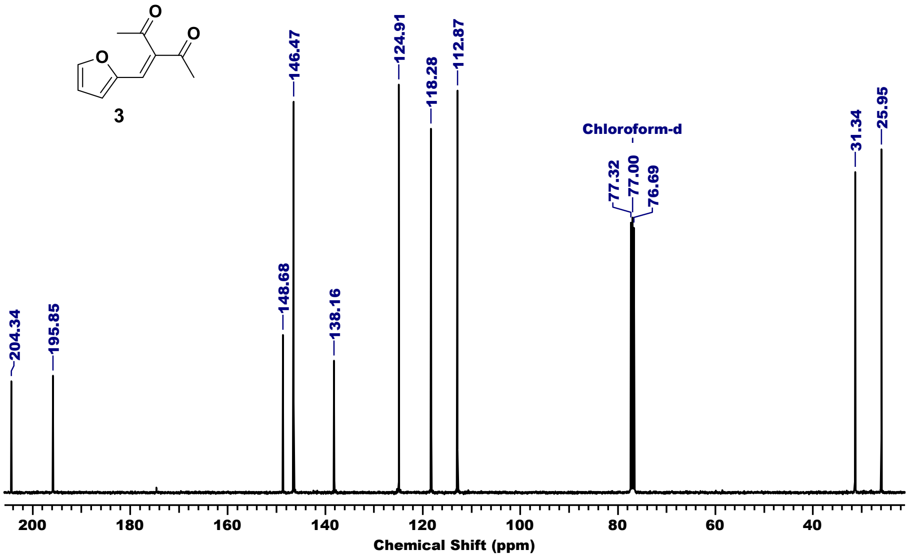


Figure 13: ^{13}C NMR of compound **3**

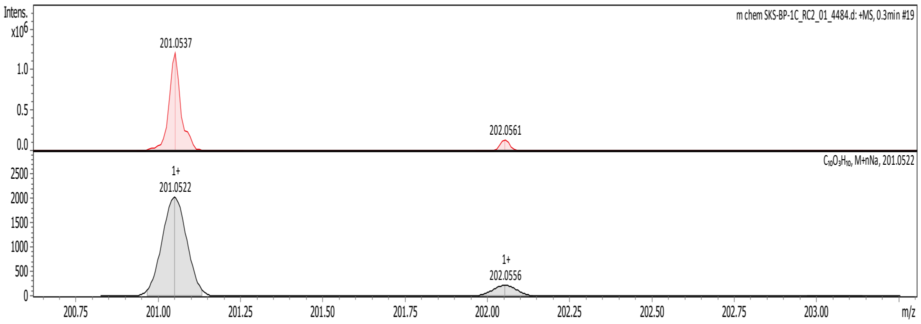


Figure 14: LCMS of compound **3**

4. Compound 4: 5,5'-(furan-2-ylmethylene)bis(2-methylfuran)

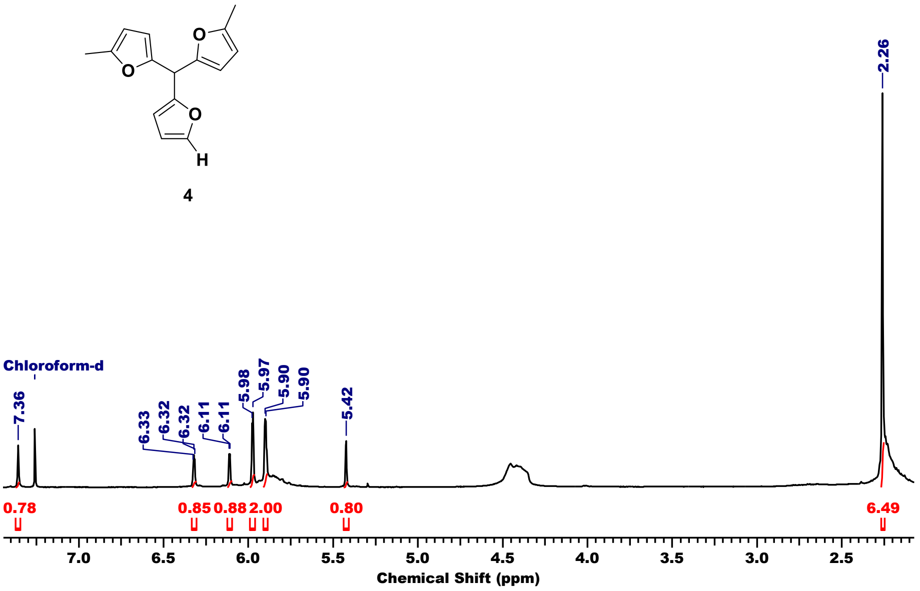


Figure 15: ^{1}H NMR of compound **4**

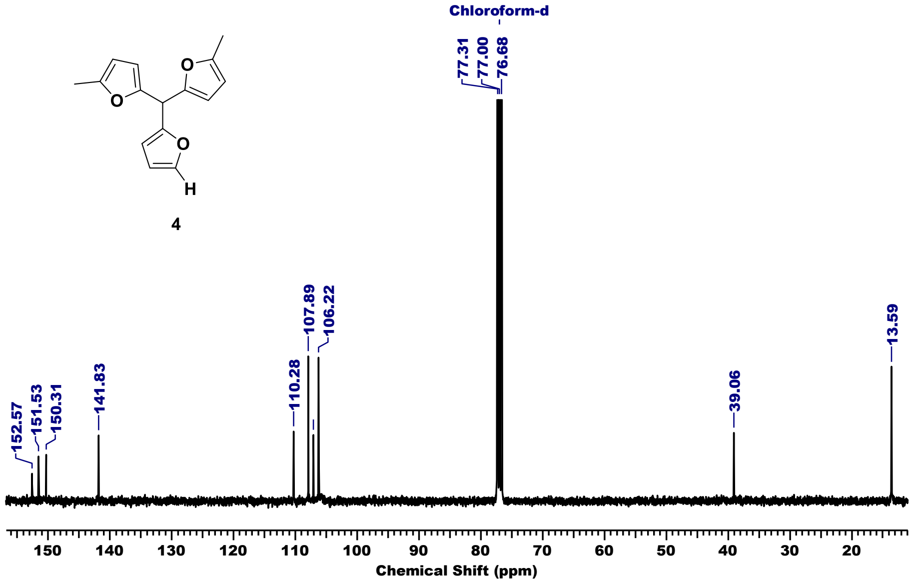


Figure 16: ^{13}C NMR of compound **4**

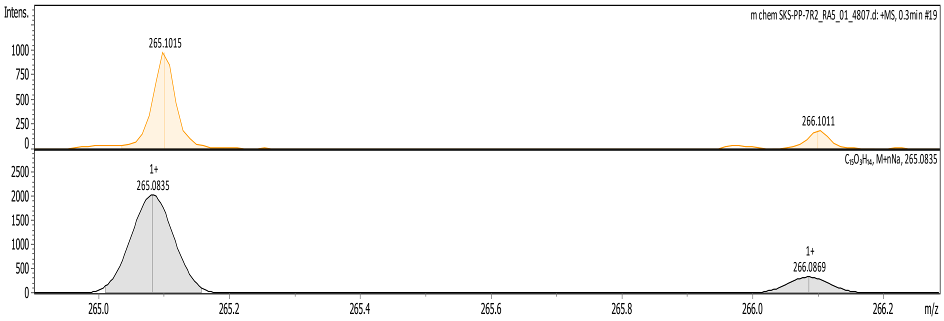


Figure 17: LCMS of compound **4**

5. Compound 5: tris(5-methylfuran-2-yl)methane

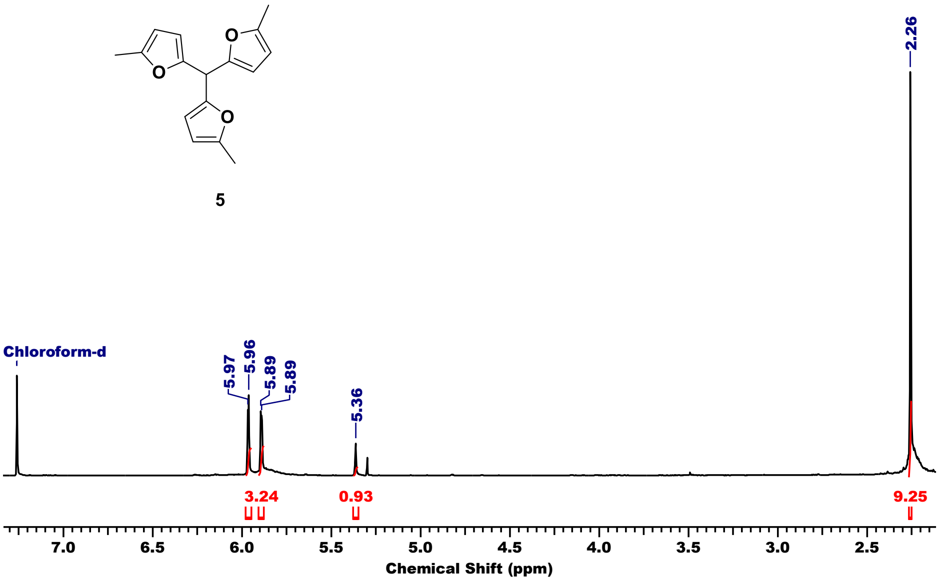


Figure 18: ^{1}H NMR of compound **5**

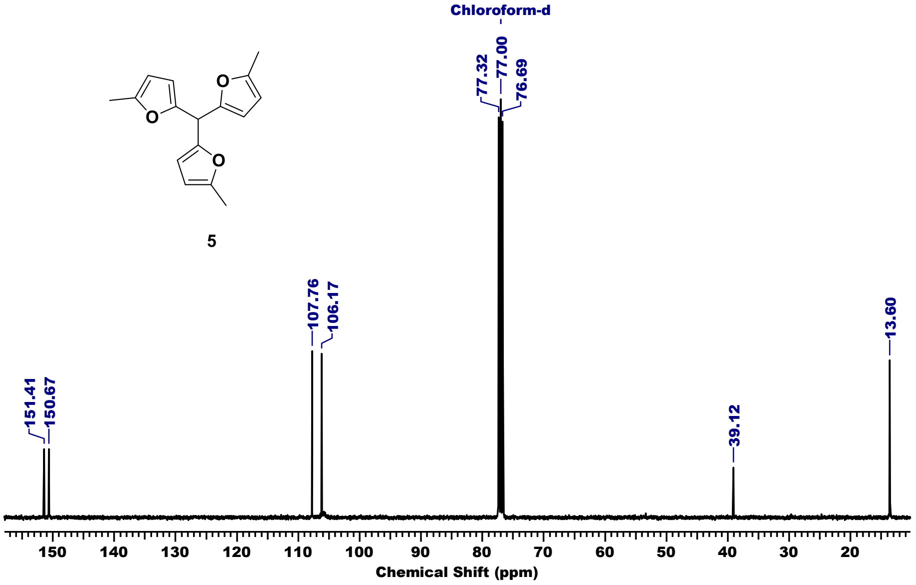


Figure 19: ^{13}C NMR of compound **5**

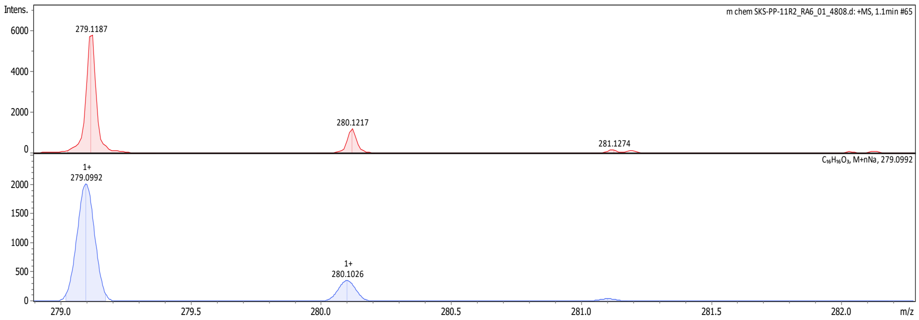


Figure 20: LCMS of compound **5**

6. Hydrogenation of compound 1

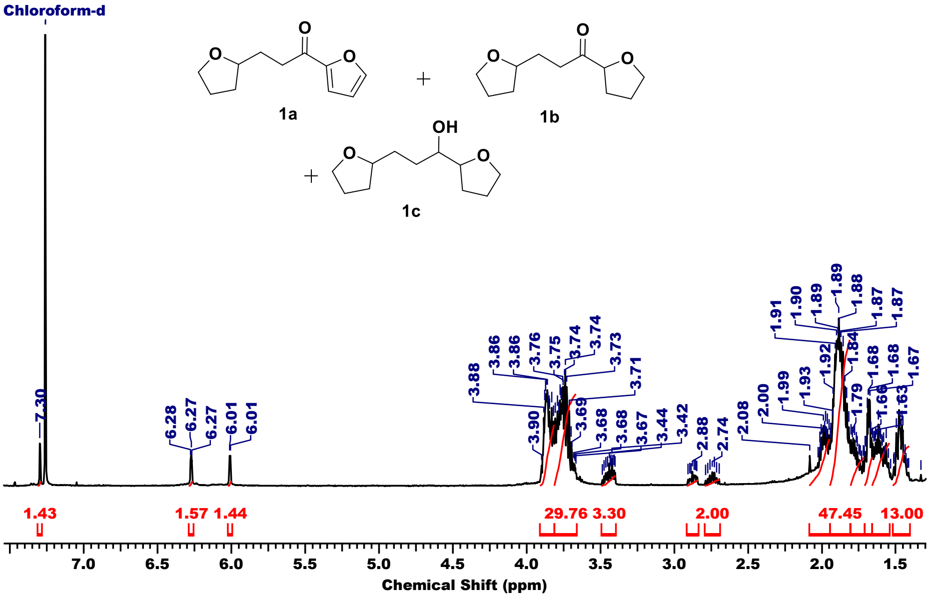


Figure 21: ^{1}H NMR of reaction mixture of hydrogenation of compound 1

7. Hydrogenation of compound 1 in a high-pressure reactor

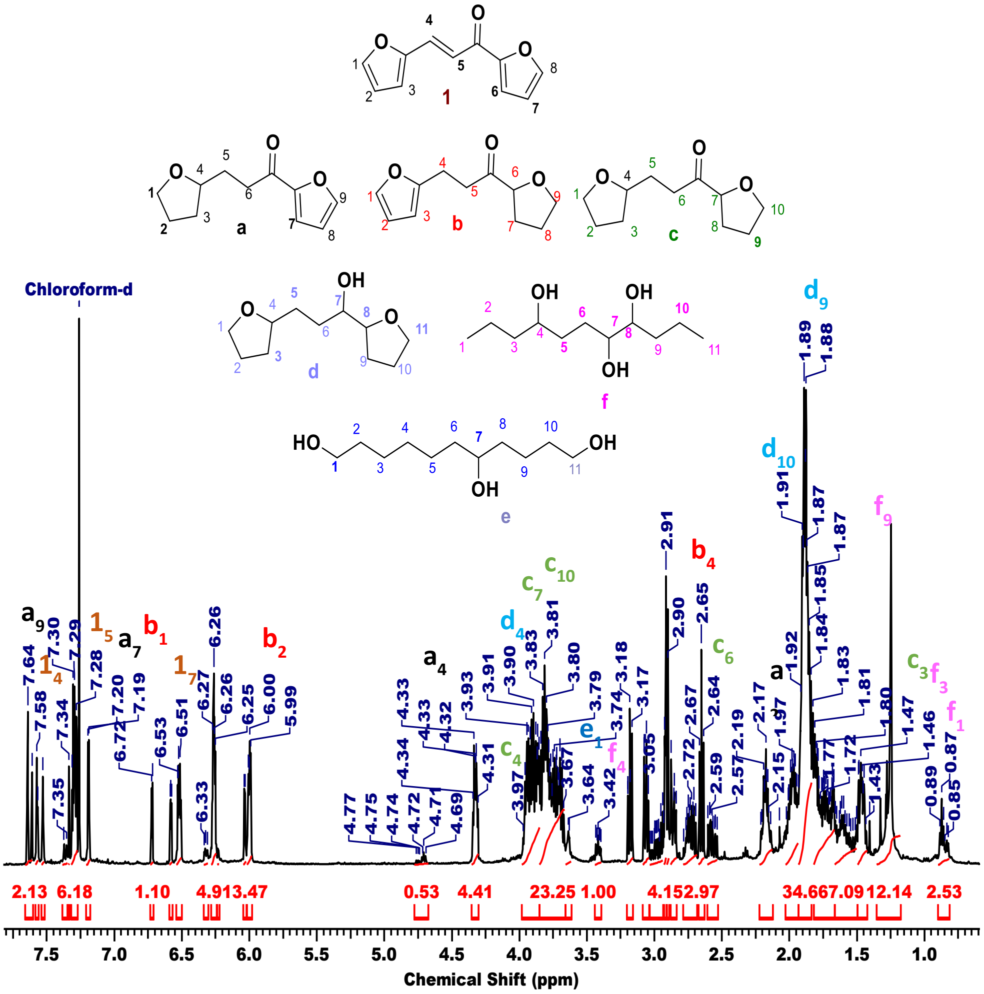


Figure 22: ^{1}H NMR of reaction mixture compound 1

REFERENCES

1. A. Corma, S. Iborra, A. Velty, *Chem. Rev.,* **2007**, 107, 2411-2502.

2. M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.*, **2014**, 114, 1827-1870.

3. S.K. Singh, *Asian J. Org. Chem.,* **2018**, 7, 1901-1923.

4. X. Li, P. Jia, T. Wang, *ACS Catal.,* **2016**, 6, 7621-7640.

5. S. Nishimura, N. Ikeda, K. Ebitani, *Catal. Today*, **2014**, 232, 89-98.

6. R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sadaba, M. L. Granados, *Energy Environ. Sci.*, **2016**, 9, 1144-1189.

7. R. Zanella, C. Louis, S. Giorgio and R. Touroude, *J. Catal.*, **2004**, 223, 328-339.

8. M. Englisch, A. Jentys and J. A. Lercher, *J. Catal.*, **1997**, 166, 25-35.

9. J. Lee, Y. Xu and G. W. Huber, *Appl. Catal.*, B, **2013**, 140, 98-107.

10. W. Xu, Q. Xia, Y. Zhang, Y. Guo, Y. Wang and G. Lu, *ChemSusChem*, **2011**, 4, 1758-1761.

11. Q. N. Xia, Q. Cuan, X. H. Liu, X. Q. Gong, G. Z. Lu and Y. Q. Wang, *Angew. Chem., Int. Ed*., **2014**, 53, 9755-9760.

12. R. Xing, A. V. Subrahmanyam, H. Olcay, W. Qi, G. P. van Walsum, H. Pendse and G. W. Huber, *Green Chem.*, **2010**, 12, 1933-1946.

13. L. Faba, E. Díaz and S. Ordóñez, *Catal. Sci. Technol*., **2015**, 5, 1473-1484.

14. K. Gupta, R. K. Rai, S. K. Singh, *ChemCatChem,* **2018**, 10, 2326-2349.

15. Y. Nakagawa, K. Tomishige, *Catal. Commun*., **2010**, 12, 154-156.

16. S. K. N. H. M. Dostagir, M. K. Awasthi, A. Kumar, K. Gupta, S. Behrens, A. Shrotri, and S. K. Singh, *ACS Sustainable Chem. Eng.*, **2019**, 7, 10, 9352-9359

17. A. D. Sutton, F. D. Waldie, R. Wu, M. Schlaf, L. A. 'Pete' Silks and J. C. Gordon, *Nat. Chem.*, **2013**, 5, 428-432.

18. L. Faba, E. Díaz, A. Vega, S. Ordóñez, *Catal. Today*, **2016**, 269, 132-139.

19. K. L. Luska, J. Julis, E. Stavitski, D. N. Zakharov, A. Adams, W. Leitner, *Chem. Sci.*, **2014**, 5, 4895-4905.

20. Y. Shao, Q. Xia, X. Liu, G. Lu and Y. Wang, *ChemSusChem*, **2015**, 8, 1761-1767.

21. Q. Xia, Q. Cuan, X. Liu, X. Gong, G. Lu, and Y. Wang *Angew. Chem., Int. Ed.*, **2014**, 53, 9755-9760.

22. L. Faba, E. Díaz, S. Ordóñez, *ChemSusChem***, 2014,** 7**,** 2816-2820.

23. S. Dutta and B. Saha, *ACS Catal.*, **2017**, 7, 5491-5499.

24. R. K. Rai, K. Gupta, S. Behrens, J. Li, Q. Xu, S. K Singh, *ChemCatChem.*, **2015**, 7, 1806-1812.

25. K. Gupta, R. K. Rai, S. K Singh, *Inorg. Chem. Front.*, **2017**, 4, 871-880.

26. R. K. Rai, K. Gupta, D. Tyagi, A. Mahata, S. Behrens, X. Yang, Q. Xu, B. Pathak, S.K. Singh, *Catal. Sci. Technol.*, **2016**, 6, 5567-5579.

27. Y. Gao, C. A. Chen, H. M. Gau, J. A. Bailey, E. Akhadov, D. Williams, H. L. Wang, *Chem. Mater.*, **2008**, 20, 2839-2844.

28. K. H. Dostert, C. P. O'Brien, F. I. Barceló, S. Schauermann, H. J. Freund, *J. Am. Chem. Soc.*, **2015**, 137, 13496-13502.