Catalytic Hydrogenation and Hydrogenolysis of Lignin Model Compounds in Ionic Liquid Environment

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Tiivistelmä/Referat – Abstract

Lignin (wood in Latin) is a natural amorphous, aromatic polymer that acts as the essential glue and support that gives vascular plants their structural rigidity and colour. It is found mostly between but also within the plant cells and in the cell walls. Lignin consists of p-coumaryl (almost exclusively in grasses), coniferyl (common in softwoods) and sinapyl alcohol (common in hardwoods) monomers that form dimers with different linkage types depending on the types of monomer radicals combined together. As the result of lignin biosynthesis is a complex aromatic network where the β – aryl ether (β-O-4) linkage type is the most abundant one between monomer units. Within each type there is a lot of variation: lignins differ from species to species, and from one tissue to the next in the same plant--even within different parts of the same cell.

Pulping industry separates lignin from biomass and the lignin waste is combusted on-site as energy for steam generation. Lignin is however potentially a renewable source of aromatic platform compounds that are important in other fields of industry. Many of these platform chemicals are currently obtained from fossil fuel sources. Hence there is an environmentally friendly need to develop efficient methods to convert lignin into high-value products. Rigid molecular structure of lignin and the abundant amount of hydrogen bonds in it makes it highly recalcitrant towards conventional solvents and mild reaction conditions. In addition a considerable sulfur content from the pulping processes establishes a catalyst poison. Thus the processing methods for lignin valorization need to be optimized with proper reaction conditions and effective catalysts while keeping the costs as reasonable as possible.

This thesis is divided into literature and experimental sections. The literature section discusses about the chemical structure and biosynthesis of lignin, industrial view of lignin and a short review of recently examined studies of processing methods on lignin concentrating on hydrogen-dependent methods and ionic liquids as the hydrogen source. The experimental section concentrates on a novel ionic liquid in the studies with hydrogenation and hydrogen lysis of aileron, a widely used lignin model compound.

Avainsanat – Nyckelord – Keywords

lignin, lignin valorization, hydrogenation, hydrogenolysis, catalysis, ionic liquids, super bases, MTBD, adlerol

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Tiivistelmä/Referat – Abstract

Ligniini (*lat*. puu) on amorfinen ja aromaattinen luonnonpolymeeri, joka toimii kasvisolukoissa tuki- ja liima-aineena. Se antaa varsinkin puuainekselle lujan rakenteen ja sille tyypillisen kellertävän värin. Selluloosa, hemiselluloosa ja ligniini muodostavat yhdessä biomassan tärkeimmät komponentit, joista ligniinin osuus on toisiksi runsain. Ligniini koostuu p-kumaryyli-, koniferyyli- ja sinapyylialkoholien monomeereista, jotka muodostavat erilaisia sidostyyppejä riippuen siitä minkä tyyppiset monomeeriradikaalit yhdistyvät keskenään. Biosynteesissä muodostuu monimutkainen verkkopolymeeri, jossa β-O-4 (β-aryyli eetteri) – tyyppinen sidos on runsain monomeeriyksiköiden välillä.

Selluteollisuudessa biomassasta erotetaan hemiselluloosa ja ligniini. Ligniinijäte hyödynnetään sellutehtaassa energiana polttamalla. On kuitenkin todettu, että ligniinillä on potentiaalia toimia uusiutuvana aromaattisten, muussa teollisuudessa arvokkaiden lähtöaineiden lähteenä. Ligniinin tehokas kemiallinen jalostaminen tällaiseksi raaka-aineeksi on kuitenkin vaativa tehtävä. Ligniinin verkkomainen rakenne tekee siitä kemiallisesti kestävän, minkä vuoksi se ei liukene mihinkään tavanomaiseen liuottimeen eikä se reagoi miedoissa reaktio-olosuhteissa. Ligniinin laatu myös vaihtelee riippuen siitä minkä puun biomassasta se on eroteltu. Lisäksi biomassan käsittelystä ligniinin jäänyt rikkipitoinen aines voi hidastaa tai jopa estää katalyyttien toiminnan. Ligniinin kemiallinen prosessointi vaatii siis huolellista optimointia reaktio-olosuhteiden, katalyyttien ja kustannusten suhteen.

Tämä pro gradu – tutkielma sisältää kaksi osiota, kirjallisen ja kokeellisen. Kirjallisessa osuudessa käydään läpi ligniinin biosynteesiä ja kemiallista rakennetta, tarkastellaan ligniiniä teollisuuden näkökulmasta ja lopuksi tarkastellaan keinoja, joilla ligniinin kemiallinen jalostaminen on jo saatu onnistumaan. Kokeellisessa osiossa keskitytään ligniinin malliaineiden vedytykseen ioniliuotin ympäristössä. MTBD-formiaatin odotetaan toimivan sekä liuottimena, että vetylähteenä reaktiossa.

Avainsanat – Nyckelord – Keywords

ligniini, ligniinin jalostus, hydrogenaatio, hydrogenolyysi, katalyysi, ioniliuottimet, superemäkset, MTBD, adleroli

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ABBREVIATIONS

4CL	4-coumarate coenzyme A ligase
BDE	bond dissociation energy
BTX	mixture of benzene, toluene and xylene
C3H	*p*-coumarate 3-hydroxylase
C4H	cinnamate 4-hydroxylase
CAD	cinnamyl alcohol dehydrogenase
CCoAOMT	caffeoyl-CoA *O*-methyltransferase
CCR	cinnamoyl coenzyme A reductase
COMT	caffeic acid *O*-methyltransferase
CSE	caffeoyl shikimate esterase
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DFT	discrete Fourier transform or density functional theory
DMP	1,2-dimethyl-1,4,5,6-tetrahydropyrimidine
DMSO	dimethylsulphoxide
DRIFT	diffuse reflectance infrared Fourier transform
DSC	differential scanning calorimetry
DT	decomposition temperature
F5H	ferulate 5-hydrohylase
FA	formic acid
GC/MS	gas chromatography / mass spectroscope
HCALDH	hydroxycinnamaldehyde dehydrogenase

HCT	shikimate/quinate hydroxycinnamoyltransferase
HDO	hydrodeoxygenation
HMPI	N,N,N',N',N”,N”-hexamethylphosphorimidic triamide
IL	ionic liquid
IR	infrared spectroscopy
MTBD	methyldiazabicyclo[4.4.0]decene
MTG	methanol to gasoline
MTO	methanol to olefins
NMR	nuclear magnetic resonance
PAL	phenylalanine ammonia-lyase
TAL	tyrosine ammonia-lyase
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
TEM	transmission electron microscopy
TLC	thin layer chromatography
TMG	1,1,3,3-tetramethylguanidine
TMPD	N,N,N',N'-tetramethyl-1,3-propanediamine
TPD	thermal desorption spectroscopy
TPR	temperature programmed reduction
WGS	water gas shift with catalyst
XRD	X-ray crystallography

1 LITERATURE SECTION

1.1 Introduction

Lignin (wood in Latin) is a natural amorphous, aromatic polymer that acts as the essential glue and support that gives vascular plants their structural rigidity and colour. It is found mostly between but also within the plant cells and in the cell walls. Lignin consists of p-coumaryl (almost exclusively in grasses), coniferyl (common in softwoods) and sinapyl alcohol (common in hardwoods) monomers that form dimers with different linkage types depending on the types of monomer radicals combined together. As the result of lignin biosynthesis is a complex aromatic network where the β – aryl ether (β-O-4) linkage type is the most abundant one between monomer units. Within each type there is a lot of variation: lignins differ from species to species, and from one tissue to the next in the same plant--even within different parts of the same cell.

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section concentrates on a novel ionic liquid in the studies with hydrogenation and hydrogen lysis of aileron, a widely used lignin model compound.

1.2 Lignin

Biomass consists of three major components: cellulose, hemicellulose and lignin. After cellulose, lignin is the second most naturally abundant polymer with up to 30% of the organic carbon in the biosphere.[1] It gives wood its typical colour, rigidity and it also acts as protection against some pathogens albeit it is biodegraded by some fungi. This can of course be a benefit when planning biological or enzymatic methods for lignin valorization.

Lignin is biosynthesized in plants from the three main monomers, monolignols: sinapyl alcohol (common in hardwood), coniferyl alcohol (common in softwoods) and *p*-coumaryl alcohol (common in grasses).[2] Monolignols first couple to dilignol dimers with a range of different linkages. The chemical structure of the monolignols provide numerous branching sites and alternate ring units to build up a complex, chemically strong aromatic network. This is the polymerization process called lignification. From the different bond types (see Figures 1 and 2) the β-O-4 (β-aryl ether) linkage is the most abundant with up to 50% of all the bonding types in lignin macromolecules.[2] This bond type is sensitive to cleavage under acidic conditions[3] but the chemical complexity of lignin makes it recalcitrant to dissolution in common laboratory solvents. Numerous studies have been made to cleave the β-O-4 linkages in order to make, isolate and extract a variety of aromatic platform chemicals which in turn have many useful applications[4-8].

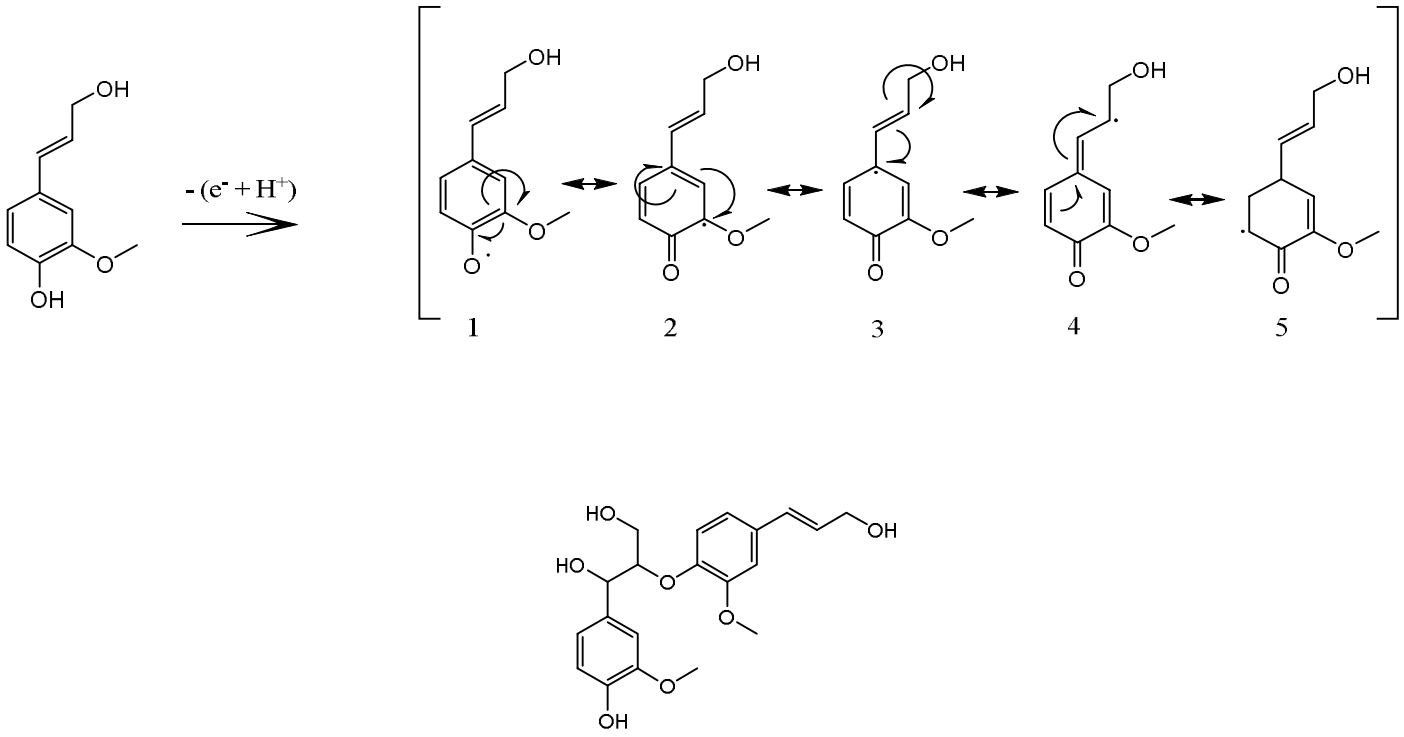
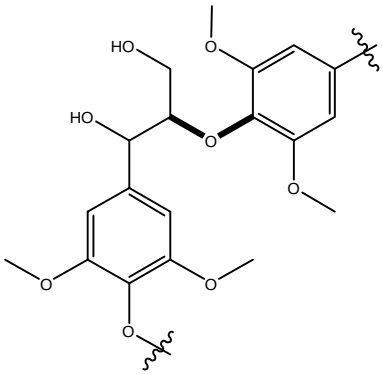
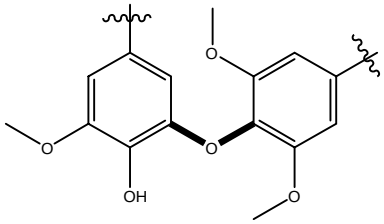


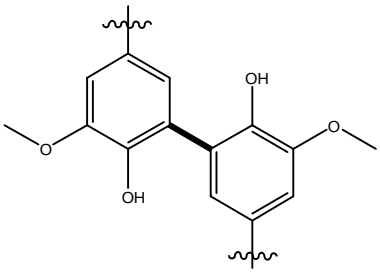
Figure 1. A simplified depiction of the formation of a dilignol. In this example the coniferyl radicals 1 and 4 have reacted and formed the β-aryl ether, the β-*O*-4 linkage. Monolignols form in the cytosol where glucose is added to make them water-soluble. These glucosides are transported through the cell membrane to the apoplast, the space outside the plasma membrane (cell wall), where glucose is removed and lignification takes place.



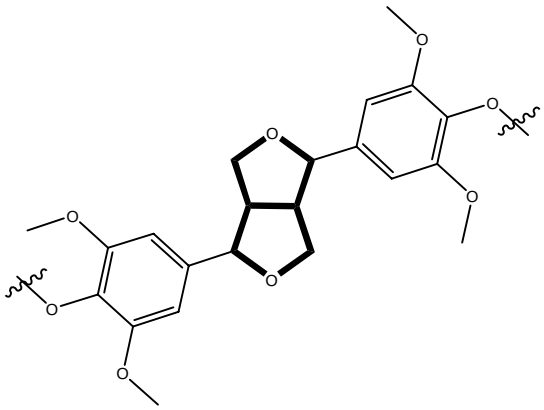
β-aryl ether: β–O–4



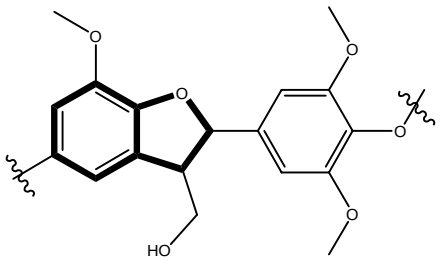
Diaryl ether: 4-O-5



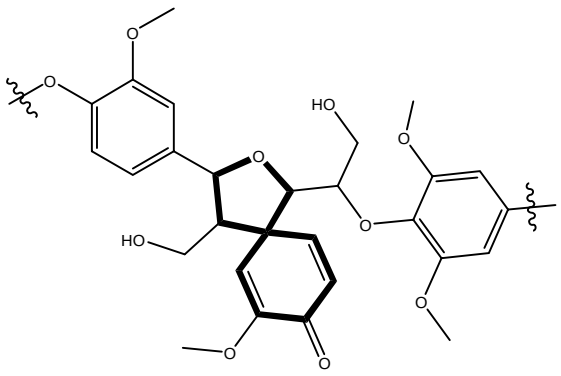
Biphenyl: 5-5



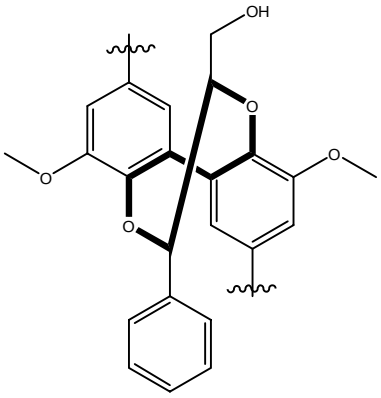
Resinol



Phenylcoumaran



Spirodienone



Dibenzodioxocin

Figure 2. Some of the linkage types in lignin. β-O-4 is the most abundant one (see Table 1) [2]. The enthalpy values of self- or cross-coupling reactions of dilignols gradually become less exothermic in order: β-O-4 > β-β > β-5 > 5-5 > β-1 > 4-O-5[9]. This does not however mean that β-O-4 is the most stable type of these bonds. Biphenyl and dibenzodioxocin bonds have bond dissociation energy (BDE) of 481-494 kcal/mol while β-O-4 have BDE around 188-209 kcal/mol[2, 20-23]. This is based on density functional theory (DFT) predictions.[2]

Table 1. The distribution of certain bond types in lignin (Figure 1) depending on the biomass source.[2]

Beta-aryl ether		**Phenylcoumaran**		**Resinol**	
Type	Occurence (%)	Type	Occurence (%)	Type	Occurence (%)
Softwood	45–50	Softwood	9-12	Softwood	2-6
Hardwood	60–62	Hardwood	3-11	Hardwood	3-12
Grasses	74–84	Grasses	5-11	Grasses	1-7
BDE (kcal/mol)	188-209	BDE (kcal/mol)	210–164	BDE (kcal/mol)	285–339

Biphenyl & Dibenzodioxocin		**Diaryl Ether**		**Spirodienone**	
Type	Occurence (%)	Type	Occurence (%)	Type	Occurence (%)
Softwood	5-7	Softwood	2	Softwood	1-9
Hardwood	< 1	Hardwood	2	Hardwood	1-7
Grasses	-	Grasses	-	Grasses	-
BDE (kcal/mol)	489-494	BDE (kcal/mol)	326–347	BDE (kcal/mol)	272–289

Plants have different amounts of lignin. The least amount being in the grass and the most abundant occurrence in hardwoods and softwoods.[2] the biosynthesis of lignin begins with phenylpropanoid pathway[2] leading to three building blocks of lignin (Figures 3-5). The phenylpropanoid pathway starts with *L*-phenylalanine but in some plants the amino acid *L*-tyrosine might also be consumed[2, 10].

The lignification itself and the absolute structure of lignin is not yet completely understood despite the studies that have been taken on the subject[11-19, 108-112]. The structure of lignin and its monomer moiety contribution depends on the conditions in what the plant has grown and on the age of the plant. Other various factors such as temperature, pressure, salinity and light may drastically affect the lignification process in the plant. To get some clue of the lignification process genetic engineering has managed to change the structure of lignin by altering the enzymes and substrates in the lignin formation pathway. For example, if the monomeric alternative in the biosynthesis pathway is ferulic acid it enables new acetal branch-points in lignin.[2] This has increased the understanding of the lignin formation but there is still a lot of work on this field.

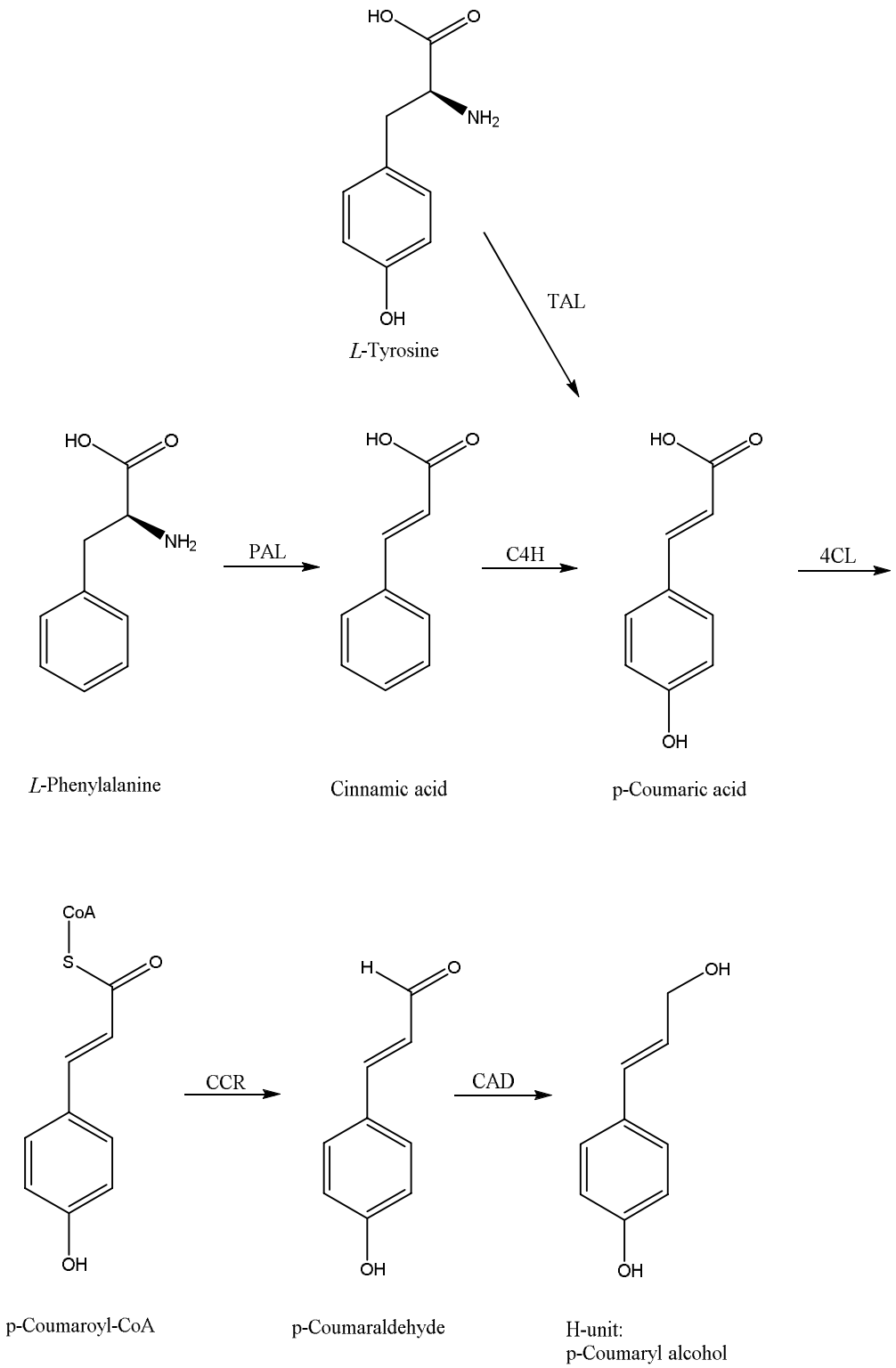


Figure 3. Phenylpropanoid pathway begins with reduction of the amino group of *L*-phenylalanine. Some plants, like can also consume *L*-tyrosine and get the *p*-coumaric acid directly. In this figure is shown the pathway to p-Coumaryl alcohol, the H-unit of lignin monomers. The full names of enzymes abbreviated in this figure can be found in the abbreviation list at the beginning of this thesis. The biosynthesis route of other monomers are shown in the figures 3 and 4.[2]

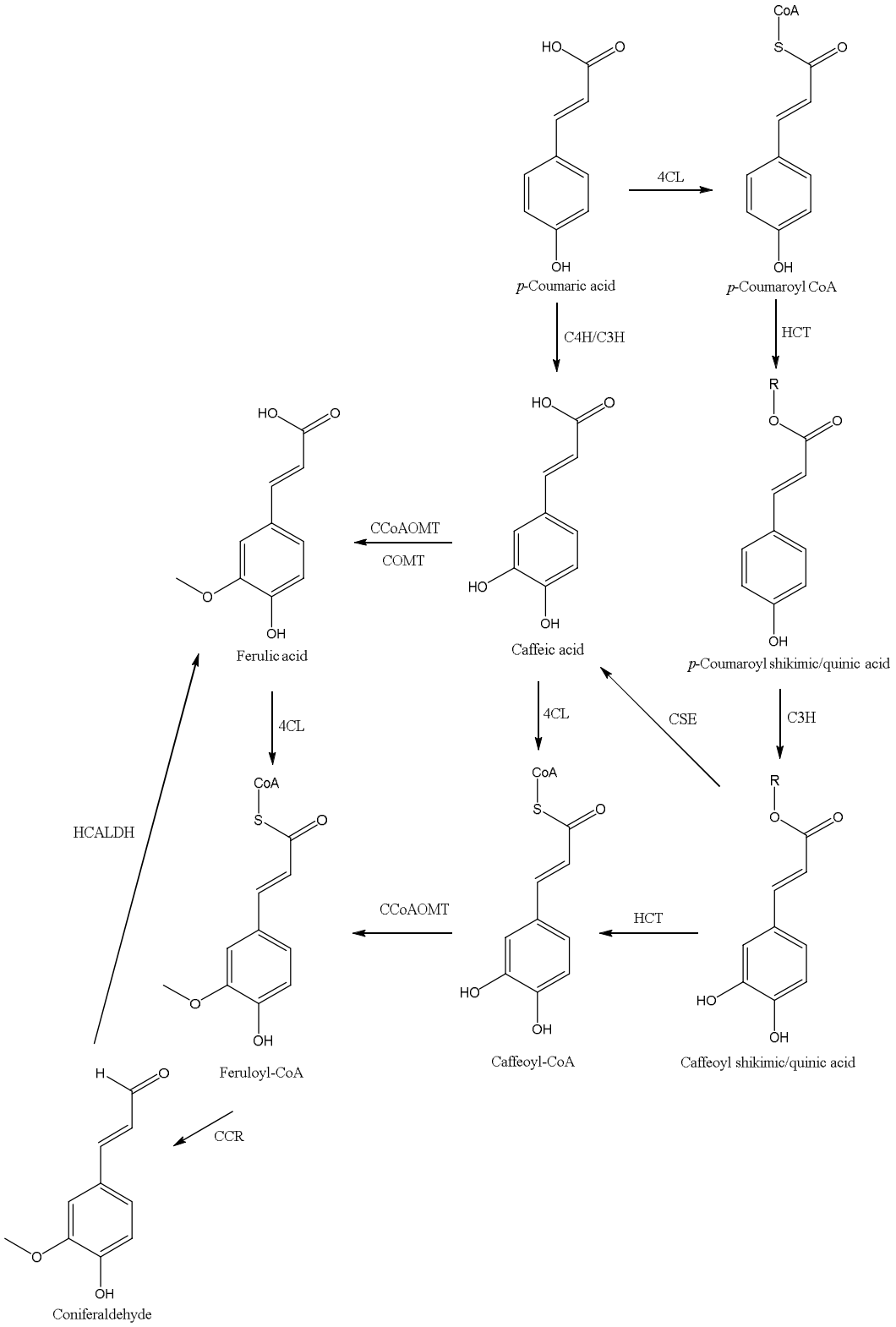


Figure 4. Phenylpropanoid intermediate pathway to show how *p*-Coumaric acid or *p*-Coumaroyl CoA is turned into coniferaldehyde whose reaction pathways into G- and S-units of lignin monomers is shown in figure 4. The full names of enzymes abbreviated in this figure can be found in the abbreviation list at the beginning of this thesis.[2]

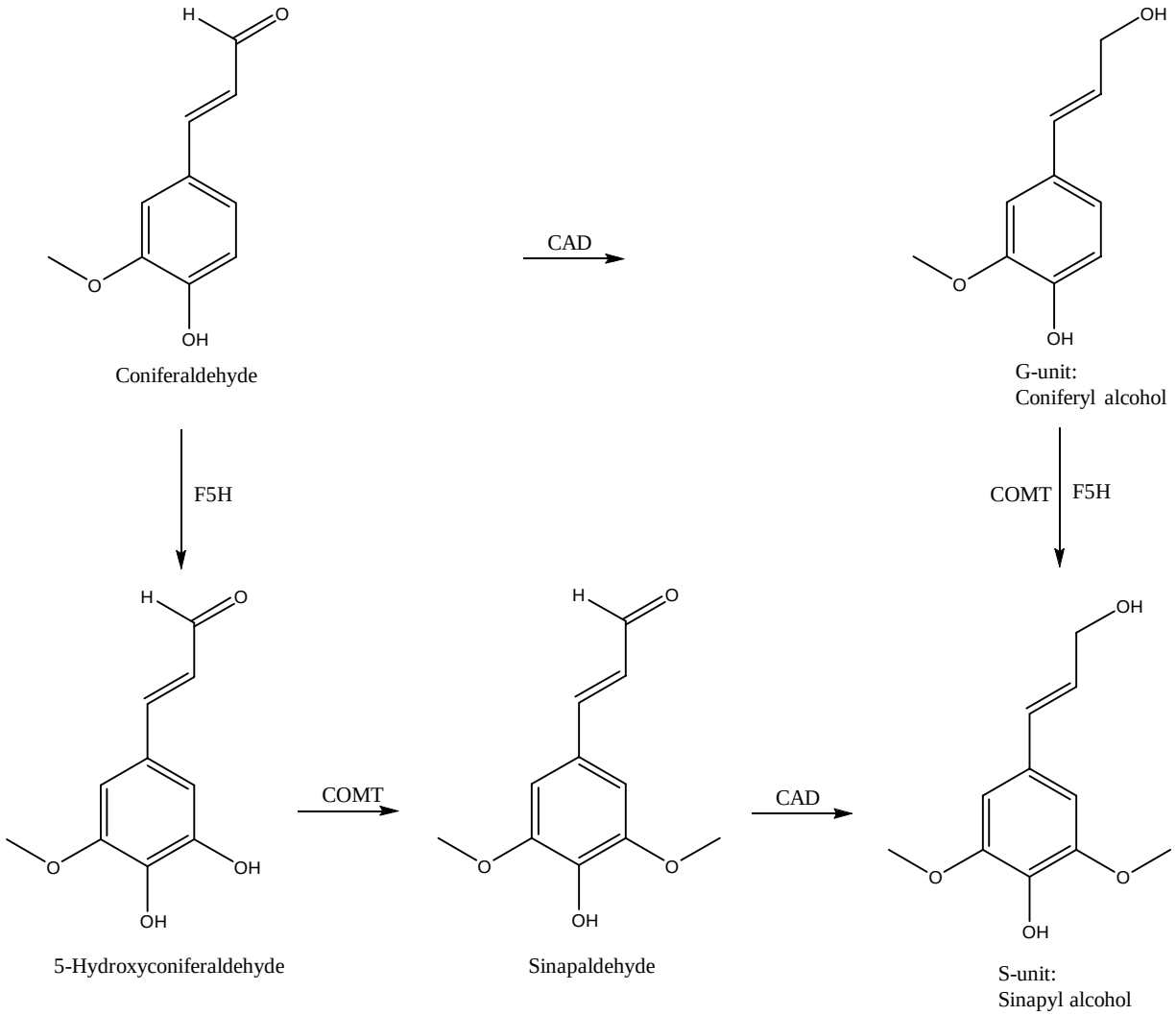


Figure 5. The phenylpropanoin pathway from coniferalcohol to conifeyl alcohol and sinapyl alcohol. The beginning of the phenylpropanoid route is shown in figures 2 and 3. The full names of enzymes abbreviated in this figure can be found in the abbreviation section at the beginning of this thesis.[2]

1.3 Lignin in Industry

Whenever biomass is mentioned it means the mixture of cellulose, hemicellulose and lignin that we got by processing wood material. Pulping industry needs only the cellulose from the biomass so the lignin has to be separated. Production of high quality paper involves low-yield, lignin-free chemical pulp and high yield lignin-rich mechanical pulp leads to lower quality paper.[40]

Kraft pulping is the dominant pulping process all over the world. The kraft process consists of treatment of wood chips with a hot mixture of water, sodium hydroxide and sodium sulfide, known as the white liquor. It breaks the bonds that link the components of biomass together. The technology entails several steps, both mechanical and chemical: impregnation, cooking, recovery process, blowing, screening, washing and bleaching.

The black liquor, the waste product from the kraft process, is usually used as energy source for the pulp mill or as a biofuel feedstock as the source of syngas via gasification process[26,27]. The black lignin liquor plays a key role as an internal energy supply for the mills. It also recovers the inorganic chemicals used in the pulping process. Lignin must be separated from the black liquor if it is needed for more delicate processing.[28, 29]

Because biomass has high O/C ratios and low H/C ratios its biorefinery requires large amounts of hydrogen for reduction regardless of the pathway chosen for the conversion of lignocellulosic biomass[24]. There are several routes for hydrogen production such as steam reforming, pyrolysis and water electrolysis. Onsite hydrogen production is more advantageous[8,25], due to savings in hydrogen transportation. Syngas consists of carbon monoxide and hydrogen and it is produced by gasification of lignin. Hydrogen thus formed can be used to produce electricity as fuel cell applications or as a reagent for hydrogenation and hydrogenolysis reactions. Syngas itself can be converted to methanol or dimethyl ether and methanol can be converted to green gasolines via the MTG (methanol to gasoline) or MTO (methanol to olefins) processes.

Kraft separation of biomass raw material could allow lignin, via syngas in the thermochemical platform, to become a viable feedstock. Disadvantages that rises are the complexity of lignin, malodourous organosulfur products[30, 31], expenses, effluents and large recycle of chemical handling and recovery.[8] In addition the presence of sulfur in black liquor and in conventionally isolated kraft lignin contributes serious problems for any catalytic process. The search for more environmentally benign alternatives lead to the term organosolv and the first report of pulping with organic solvents was published 1931[32] as an alternative to processes based on sulfurous chemicals. Yet the research on this matter intensified not until late 1960s[33]. One notable example of the organosolv process is the Alcell process developed by Repap Enterprises Inc. that was acquired by UPM Kymmenen Corporation in 2000. But the process is still commercially evaluated only at pilot-scale[8].

The interest in lignin and biomass processing is not novel. Studies have been at least 50 years[38] but recent studies have discovered new reaction conditions and new catalysts to cleave bonds in lignin model compounds and lignin itself.[4, 5, 6, 38] Lignin has near-, medium and long-term opportunities[8]. Combustion, gasification, pyrolysis and liquefaction are near-term utilization methods that provide instant benefits from lignin and just few processing steps. Medium-term utilization comprises the use of lignin to produce macromolecules. Examples of opportunities from macromolecules include: carbon fiber, polymer modifiers, adhesives and resins. Medium-term utilization requires a bit more processing and the benefits are not instant. Long-term utilization, the production of aromatic platform products or BTX (mixture of benzene, toluene and xylene) chemicals for other industries, requires a lot more processing, chemicals and research and the benefits will pay off in the future.

One significant technical problem is that lignin from different biomass sources and isolation processes have significantly different reactivity, molecular weight distributions, melting points and polyelectrolyte properties. Another technical challenge is to deal with lignin molecular weight polydispersity. Certain molecular weight fractions may need to be selectively removed. A final barrier is the development of practical new methods to process, stabilize and derivatize lignin and thus optimize its thermal properties.

Lignin is unique among biomass components because of its aromatic nature. Cellulose may be separated from the parent biomass either intact or directly as sugars. Oils are separated as triglycerides or as free fatty acids. In either case, processes for production of carbohydrate-derived chemical products via catalysis or fermentation deal with a fairly consistent and uniform feedstock largely independent of the recovery process. Lignin, however, will come out of any biorefinery recovery process as a complex, polydisperse, high-molecular weight material with uncertain reactivity. This variability is the result of the different basic building block components that make up lignin, which depend on biomass source.

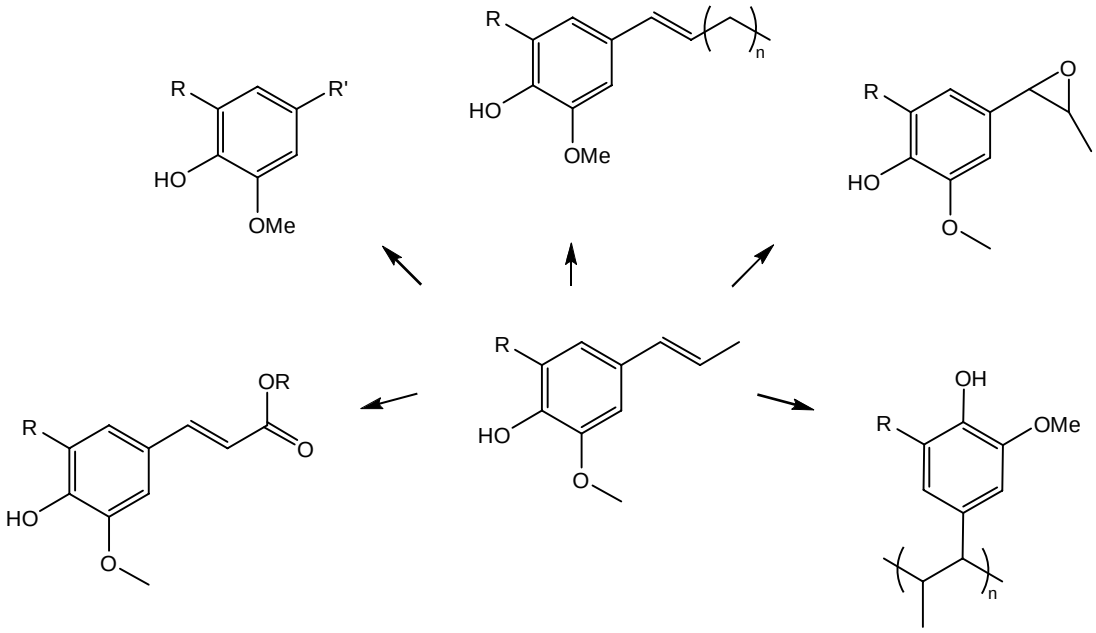


Figure 6. Alternative reactions from starting material derived from organosolv lignin. In this case the reactions done on the starting material are (starting from left) carbonylation, Coupling reaction, two different polymerizations and epoxidation. C=C group is very valuable for rubber and plastic industry because it contributes polymerization.

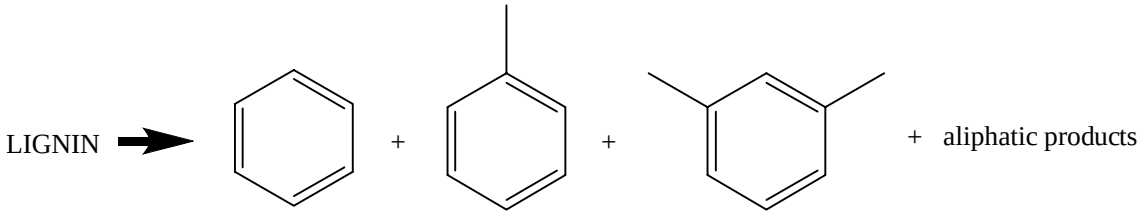


Figure 7. With new technology it is possible to convert lignin into a mixture of benzene, toluene and xylene (BTX chemicals) which in turn are versatile starting materials[8]. From benzene one can get phenol, cyclohexane, cyclohexanol, cyclohexanone, caprolactam, adipic acid, 1,6-diaminohexane, cumene and styrene. Toluene can be converted into dinitrotoluene, diaminotoluene, toluene diisocyanate and benzoic acid. Xylene into isophtalic acid and terephthalic acid.

1.4 Processing Lignin

1.4.1 Hydrogenation, Hydrogenolysis, Transfer Hydrogenolysis and HDO

Palladium-catalyzed coupling reactions comprise of cross-coupling and hydrogenation reactions that employ palladium complexes as catalysts. Widely used coupling reactions be that of Negishi[41], Hech[42], Suzuki[43], Stille[44] and Sonogashira[45] couplings. Typical palladium catalysts used include palladium acetate $Pd(OAc)_2$, tetrakis(triphenylphosphine)palladium(0) $Pd(PPh3)_4$, bis(triphenylphosphine)palladium(II) dichloride $PdCl2(PPh_3)_2$, [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride. Pd(0)/C, Palladium on charcoal is commonly used as the catalyst in hydrogenation reactions.

Hydrogenation and hydrogenolysis are of particular significance for the biomass processing and also a great challenge. Generally, hydrogenation is performed on biomass platform molecules in order to saturate C=C and C=O bonds and hydrogenolysis describes an overall chemical transformation in which a C-C or C-heteroatom bond is broken by insertion of hydrogen. The use of hydrogen not for the conversion electricity but rather as a feedstock in biorefineries appears to be very promising alternative. Alpha-beta unsaturated compounds are important chemical intermediates for the synthesis of fine chemicals such as furfural, isophorone, citral, crotonaldehyde, mesityl oxide and cinnamaldehyde.

Thermodynamically C=C bond should be easier to hydrogenate than C=O bond however due to the conjugation in alpha-beta-unsaturated carbonyl compounds the C=O bonds are sometimes easier to react. Noble metal catalysts such as Pt, Pd, Ir, Rh, Ag, Au , base metals Cu, Ni, Co, Sn and alloy catalysts have been extensively applied to the hydrogenation of alpha-beta-unsaturated carbonyl compounds.

The activity and selectvity of biomass conversion by hydrogenolysis can be significantly increased with pendent hydroxyl groups which are attached to ligands surrounding the central

ruthenium. [51, 52]. In addition to β-O-4 cleavage[50, 53] ruthenium catalysts are prone to cleave the C-C bonds as well.[49] Ruthenium based catalysts are also promising to convert CO_2 into formic acid.[55] (see Figures 10 and 11)

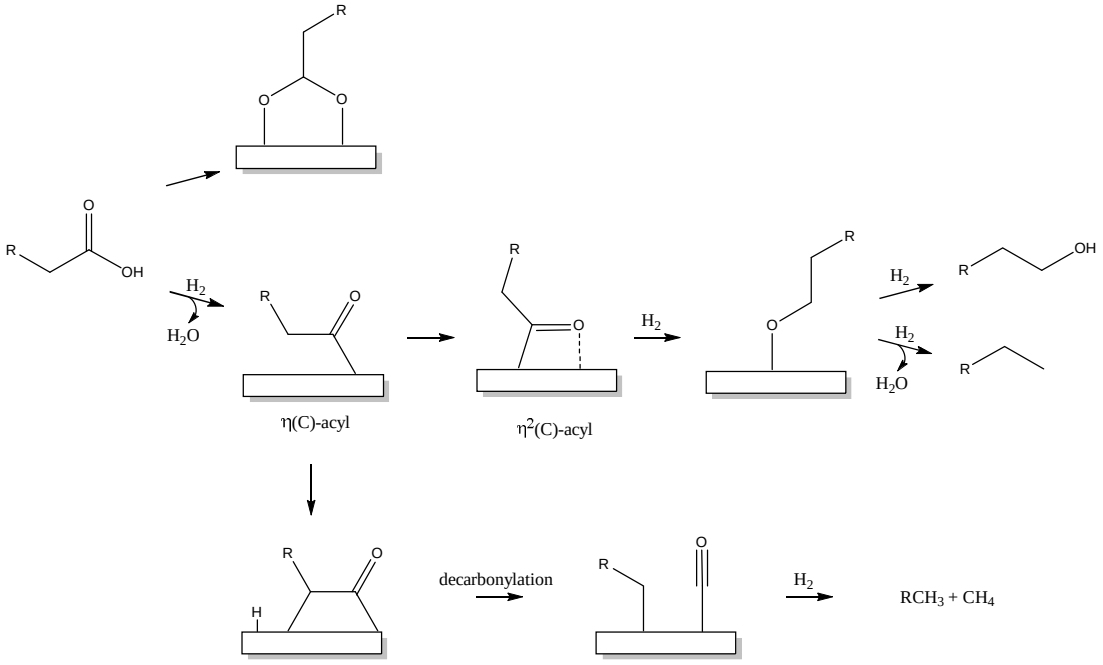


Figure 8. Reaction mechanism for the hydrogenation of carboxylic acid over Ru catalyst. Same behavior is found in the reactions of polyols[46, 48, 49] which might indicate that lignin model compounds behave the same way.

Many oxidation methods lead to the degradaton of propylbenzene skeleton (always present in the lignin structure) via a C-C bond cleavage. For instance, vanillin production exploits this but in other applications it conserves the propylbenzene structure. The major challenge in lignin chemistry is the selective oxidation of secondary alcohols without C-C bond cleavage.[59]

Pd(0)/C-catalyzed transfer hydrogenolysis of lignin model compounds by addition of ammonium formate and formic acid as a hydrogen source to reductively cleave the β-O-4´-ethanoaryl ether linkage has been reported. The initial rate-limiting dehydrogenation generated a ketone intermediate that underwent a fast hydrogenolysis of the β-O-4´-ethanoaryl ether linkage to give aryl ethyl ketone and phenol.[60] Stopping the reaction at the benzylic

oxidation opens up the possibility to obtain the aryl ethyl ketone and these compounds are highly valuable as substrates for fine chemical synthesis.[61,62]

Oxidation is enhanced by certain additives such as catalytic amounts of $NaBH_4$ or glucose whose role is to prevent deactivation of palladium. Metal hydrides are not useful in the large-scale synthesis in which glucose turned out to be the best additive.[63] Lignin model compounds has been successfully cleaved under redox-neutral conditions. N the redox-neutral reaction the hydrogen source is in one of the starting materials so no external hydrogen source is needed.[64-67]

Due to high oxygen content in lignin polymer it is prone to undergo depolymerization and then reduction and/or hydrodeoxygenation (HDO). This allows its utilization as feedstock for the production of chemicals and fuels. Because of the robust structure of the polymer severe conditions are often needed for the decomposition in addition to the hydrodeoxygenation of the molecular species formed. The most favorable choices or the processing of biomass are the precious-metal catalysts due to their remarkable ability to activate the rates of reduction reactions.[57]

Catalytic hydrogenolysis and subsequent HDO of lignin generally produces a mixture of gases, solids and liquid products such as phenols, catechols, aromatics, cycloalkanes, cycloalkanols and cycloalkanones. Current major targets are aliphatic/aromatic hydrocarbons for fuel applications, aromatic commodity chemiclas (phenols, toluene, xylene) in addition to some value-added chemicals (vanillin). There are a few efficient method to convert lignin-related phenols into upgrade biofuels and aromatic commodity chemicals. One of them is the direct C-O bond hydrogenolysis of phenols into benzenes.

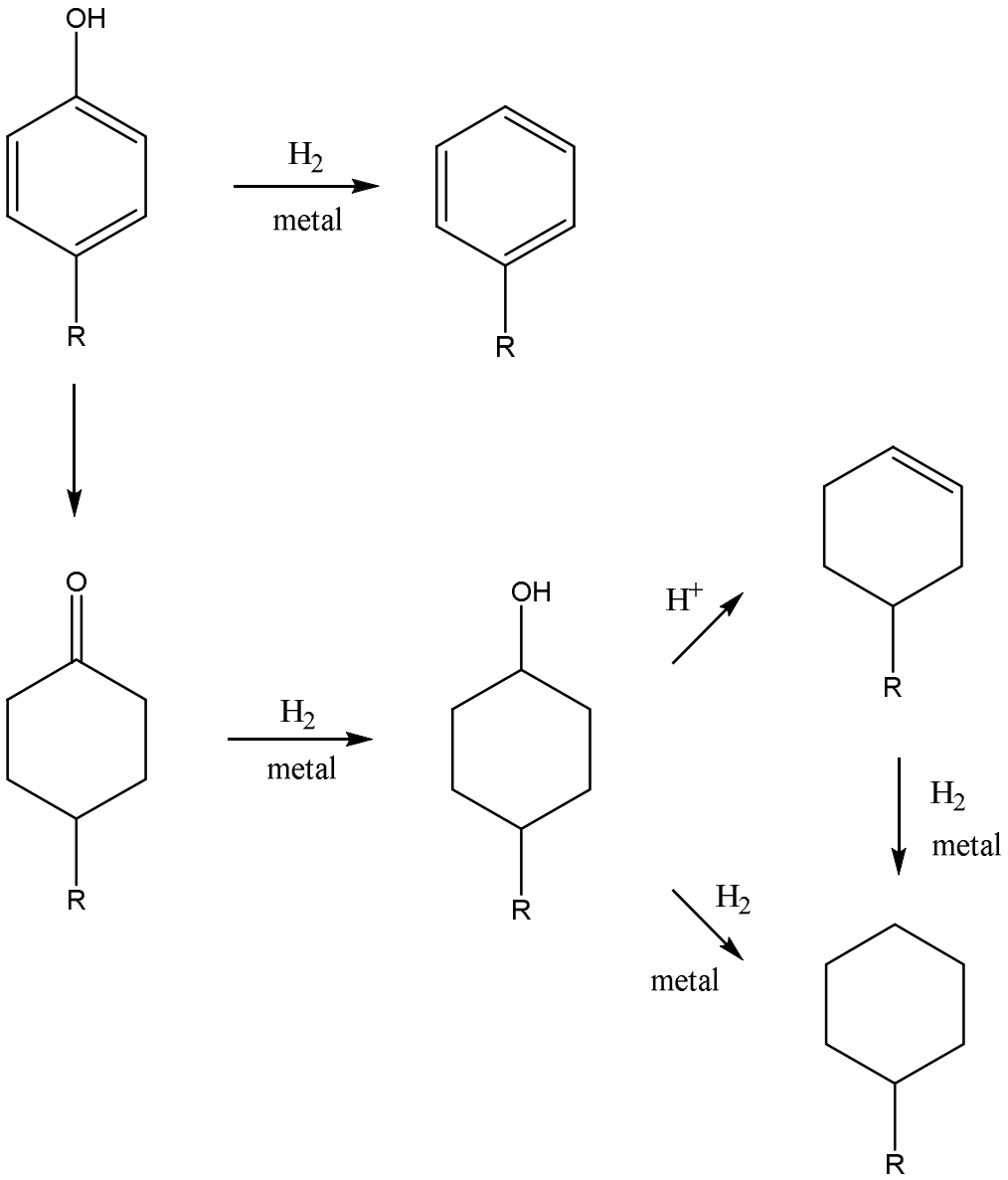


Figure 9. Reaction pathways for the hydrodeoxygenation of phenols.[57]

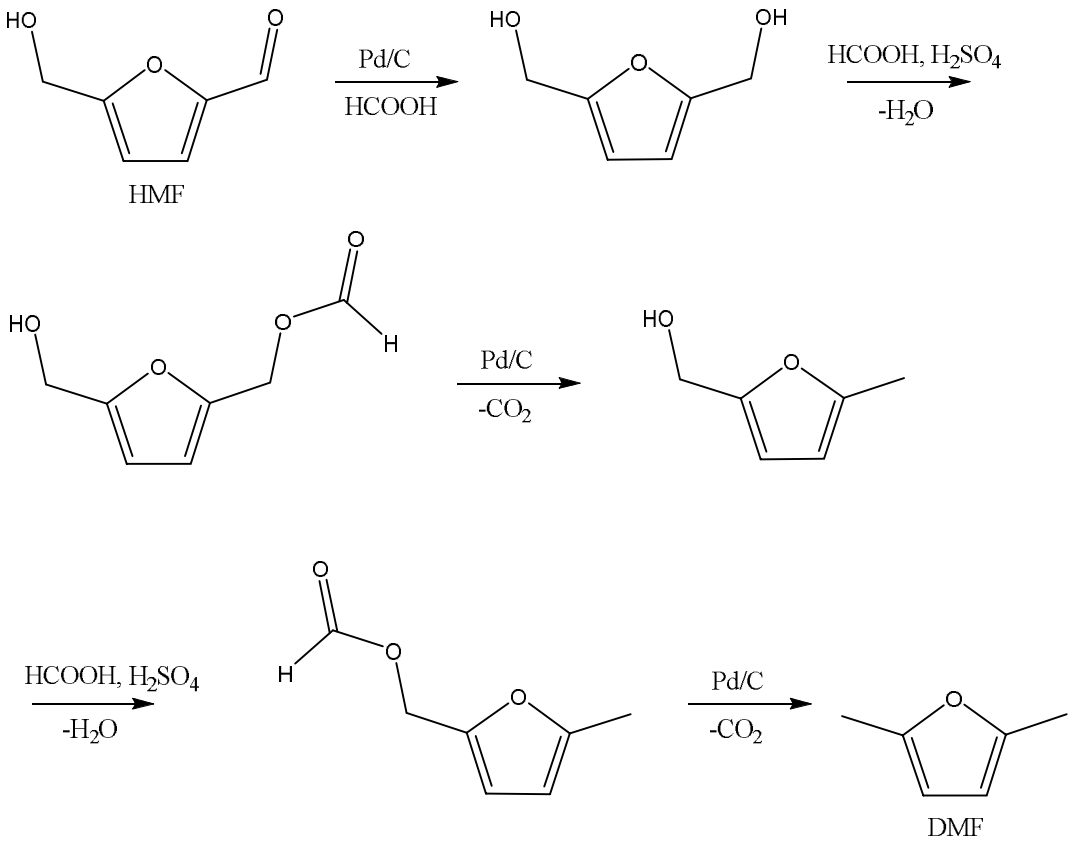


Figure 10. Mechanism of hydrodeoxygenation of HMF to DMF *via* hydrogen-transfer reaction in the presence of a Pd/C catalyst using formic acid as hydrogen source.[70]

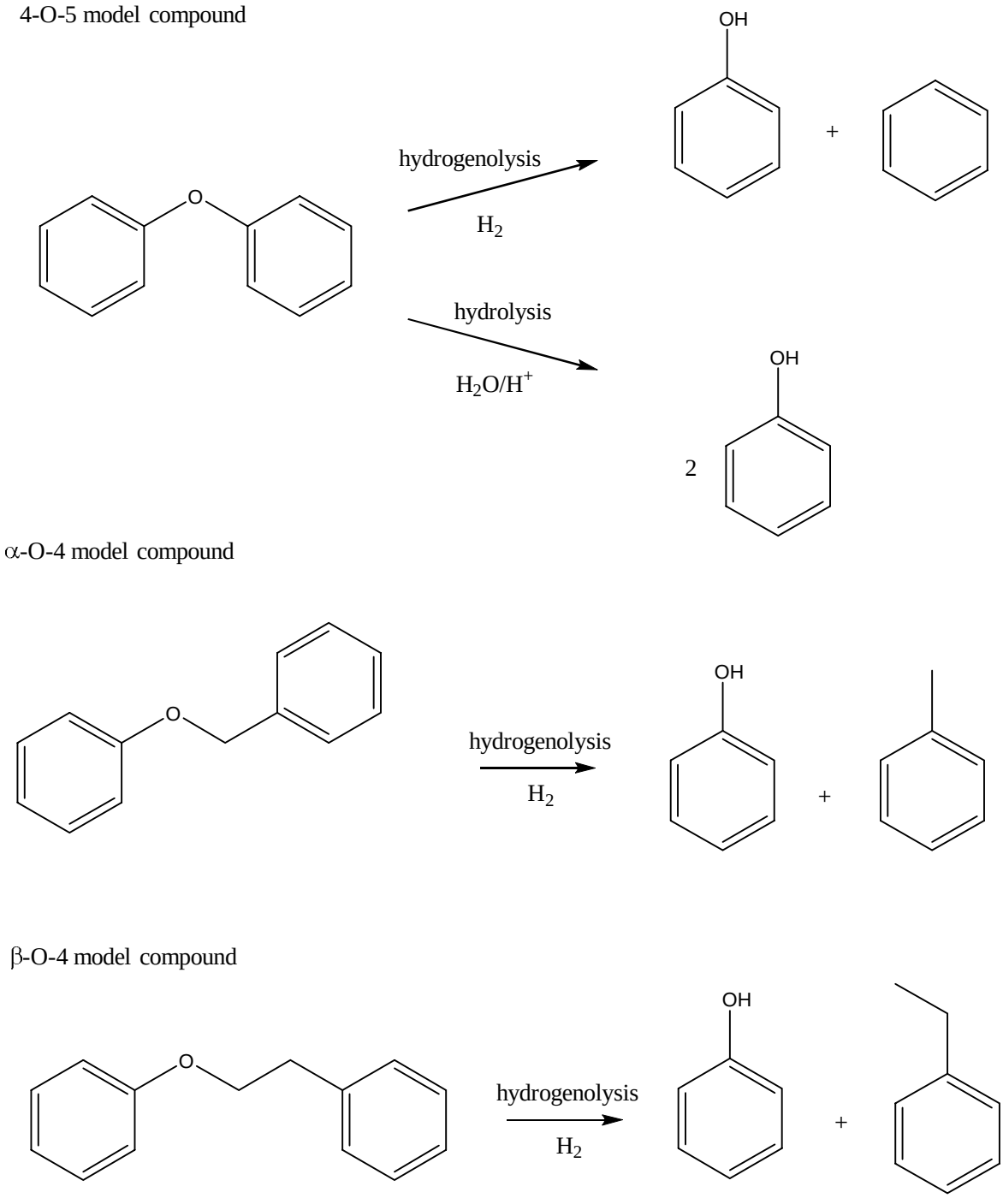


Figure 11. Reaction pathways for the cleavage of ether linkages in lignin model compounds.[7]

1.4.2 Ionic Liquids

Ionic liquids have been under great investigation since the synthesis of the first true room temperature ionic liquid, ethylammonium nitrate in 1914 by Paul Walden[72] and they have found their way to the study of biomass[80,81,82] in the form of selective lignin dissolution[83,84,85], lignin fragmentation and isolaton[86] and cellulose dissolution[74, 78, 79]. Because of the high structural versatility of ILs they have been given the status of "designer solvents" due to their ability to act as acids, bases and nucleophiles as well as recyclable solvents with negligible vapour pressures[87]. By changing only the cation while the anion stays the same they can have a drastic change in its physical properties and its specificity to facilitate certain types of reactions. Also the acidity of the anion is an important property in some cases. Ionic liquids have drawn attention to the biomass field because it has been shown that certain ionic liquids can solvate cellulose and lignins alike.

De Gregorio *et al.* have been investigating the question of acidity of ionic liquid anions with different 1-butyl-3-methylimidazolium hydrogen sulfate [C_4C1im][HSO^4] systems. By varying acid and water concentrations it was found out that these features were correlated to lignin model compund reactivity. In the studies they find out that the rate of ether cleavage increases with an increase in acidity and the initial dehydration of the model compound is the rate-determining step of the reaction.[73]

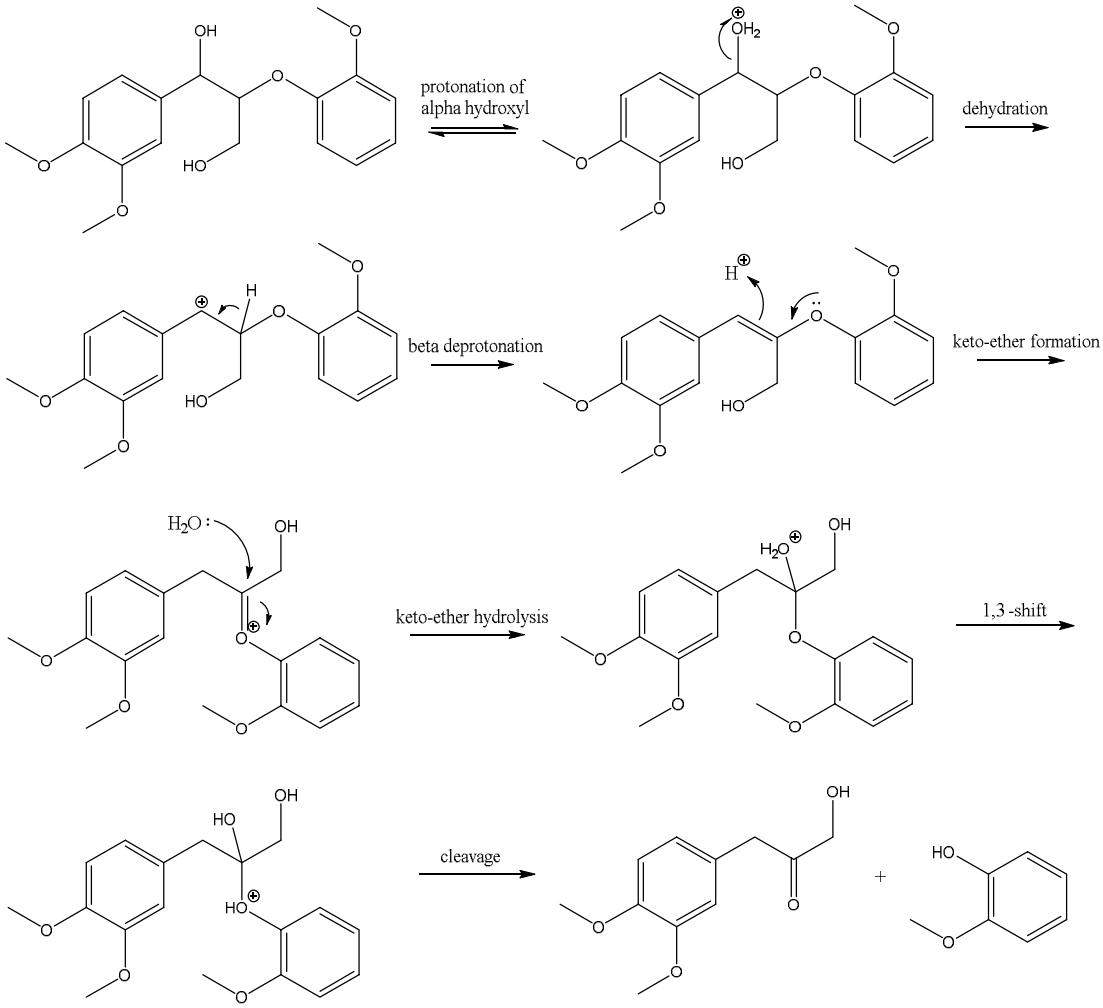


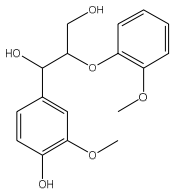
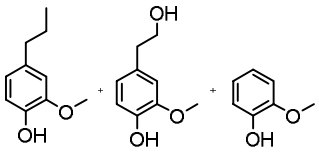
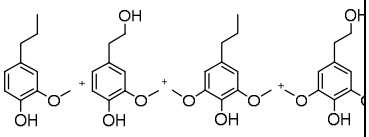
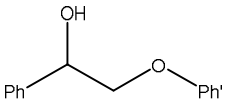
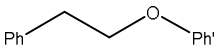
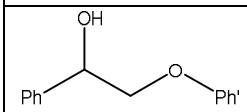
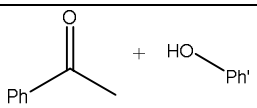
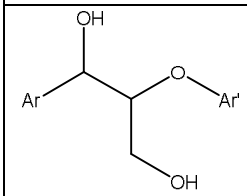
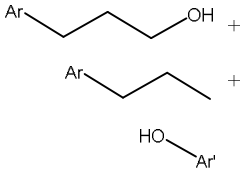
Figure 12. The findings from Cox[76] and Binder[77] show the importance of the acidity in the reactivity of lignin model compounds. Ether cleavage occurs as a consequence of a dehydration reaction after protonation of the hydroxy group located on the α carbon leading to stabilized carbocation. In this figure the hypothetical ether cleavage is done on adlerol which is studied for more detail in the experimental section of this thesis. The overall rate depends on the rate determining step of the reaction. The two distinct steps in the cleavage of the ether linkage can be summarized as dehydration involving protonation and subsequent loss of water. This is then followed by hydrolysis involving tautomerization of the enol-ether to a keto-ether and nucleophilic attack at the β carbon to liberate guaiacol. This can then form an unsaturated enol-ether which can subsequently undergo acid hydrolysis to form guaiacol and the lesser understood "Hibbert ketone" or another hydrolysis product for example an aldehyde if deformylation occurs.[73]

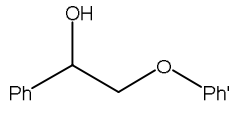
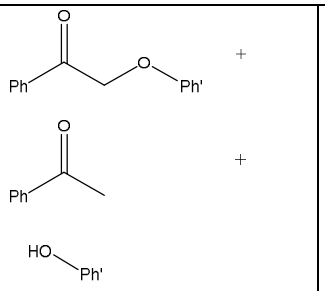
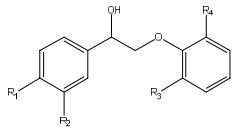
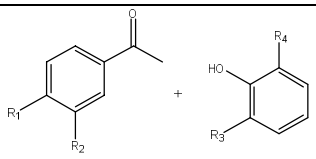
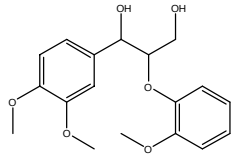
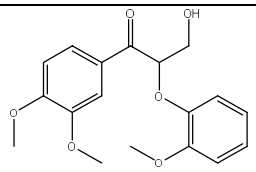
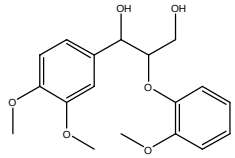
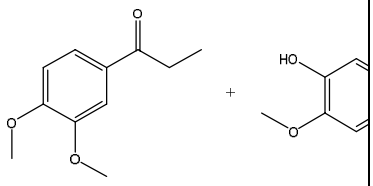
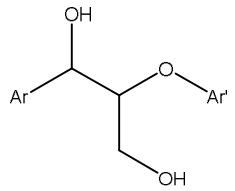
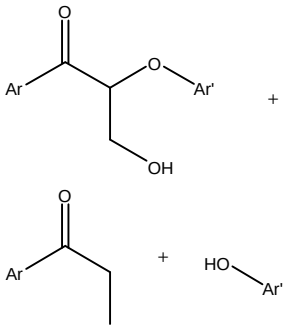
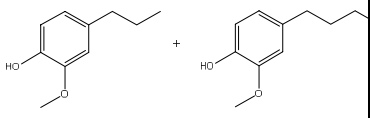
It was found that the mechanism of lignin's β-O-4 linkage hydrolysis in all of the [HSO4] − ILs proceeded via reaction that is catalysed in acidic conditions. The rate determining step involves initial protonation followed by dehydration. The observed high enthalpies of activation indicated that dehydration occurs via an E1 mechanism and the differences in these values were compensated by the entropic component. These differences are attributed to the associative forces between the cation and anion, influenced primarily by hydrogen bonding, determining the degree of solvation of the protonated solute. Whilst the [HSO4] − anion is effective at cleaving the β-O-4 ether linkage, anion–cation association plays a significant role in determining solvation of the solute and therefore the rate of reactivity. This provides possibilities for the appropriate design of IL cations for successful lignin depolymerisation and processing at lower temperatures, with these results suggesting that this would be favoured by ILs with increased cation–anion association.

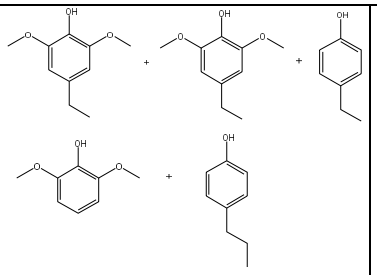
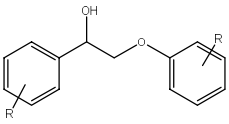
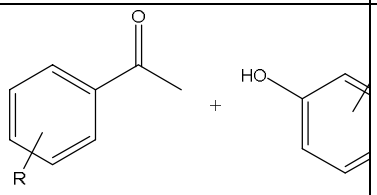
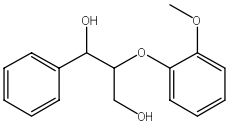
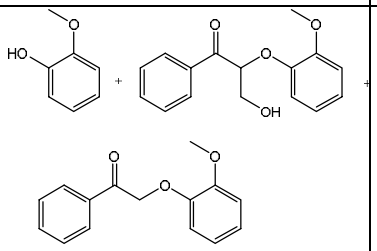
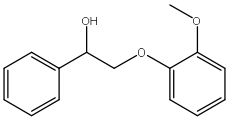
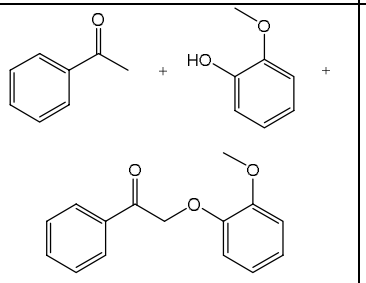
Computational investigations with density functional theory has shown that the carbocation formed during the dehydration exhibits the highest energy along the reaction pathway. Experimental observations have shown that the presence of electron donating groups, such as methoxy or hydroxy substituents that are commonly found in lignin, promotes the cleavage of the ether linkage.[88]

1.4.3 Summary

Table 2. Summary of Catalytic Reactions with Lignin and Lignin Model Compounds

Substrate	Reaction Conditions (time/h, temperature/ ^{o}C ,solvent and/or IL and other reagents, pressure/psi)	Catalyst / Co-Catalyst	Major Products	Ref.
	8-12h, 150^{o}C-225 ^{o}C, MeOH, 500 psig H_2	Pd/C, Zn(OAc)2·2 H2O		**92**
Poplar type WT-717	12h, 225^{o}C, MeOH, 500 psig H_2	Pd/C / $Zn(OAc)_2$ or $FeCl_3$ or $NiCl_2$ or $AlCl_3$		**92**
	1h, 80^{o}C, EtOH/H_2O, HCOOH, base 25 mol%	Pd/C		**60**
	1h, 80^{o}C, EtOH/H_2O, HCOOH, base 1 equiv.	Pd/C		**60**
	EtOAc, Δ ,$HCOONH_4$ 4 equiv. 24h, HCOOH 2 equiv. 12h	Pd/C		**60**

	1h, 80°C, EtOAc/H_2O, 0.4 equiv H_2	Pd/C		**4**
	1h, 80°C, EtOAc/H_2O, $NaBH_4$ (10%)	Pd/C		**4**
	12-24h, 80°C, EtOAc/H_2O, 0.4 equiv. additive (glucose)	Pd/C		**6**
	80°C, EtOAc/H_2O, 0.4 equiv. glucose 12h, K_2CO_3 2.5 equiv. 3h, HCOOH 1 equiv. and $HCOONH_4$ 2 equiv. 4h	Pd/C		**6**
	1h, 195°C, EtOH/H_2O, HCOOH 2 equiv.	Pd/C		**93**
Organosolv lignin from pine	36h, 120°C, EtOAc/H_2O, $HCOONH_4$ 4 equiv., HCOOH 2 equiv.	Pd/C		**93**

Poplar wood	3h, 180°C, 2-PrOH/H_2O	Raney-Ni		**94**
	18h, 140°C, toluene, EtOAc 25 mol%, K*t*amylate 25 mol%,	$(Ph_3P)_3RuCl_2$		**61**
	20h, 135°C, toluene-d_8	$(Ph_3P)_3RuCl_2$ /xanthos		**95**
	20h, 135°C, toluene-d_8	$(Ph_3P)_3RuCl_2$ /xanthos		**95**

2 EXPERIMENTAL SECTION

2.1 Introduction

The aim of this study is to examine if the ionic liquids made from formic acid and selected superbases can act as hydrogen donors in the transfer hydrogenation reaction of cinnamaldehyde and cinnamyl alcohol and in transfer hydrogenolysis of adlerol, a widely used lignin model compund. There has been studies concerning this ability of the formic acid in the transfer hydrogenolysis of alcohols.[96] Some evidences show that formic acid promotes elimination and the alkene thus formed is followed by hydrogenation.[97]

This study is divided into six parts. First a series of ionic liquids were made for thermal experiments. In the second part two superbase candidates, MTBD and allyl-MTBD were synthesized from TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene). followed by pre-experiments with the hydrogenation of cinnamyl alcohol with [MTBDH][CO_2H] catalyzed by Pd(0)/C, Raney-Nickel and $Pd(OAc)_2$. The pre-experiment reactions were monitored by GC-MS.

Adlerol was chosen as the lignin model compound and synthesized. The synthesis route is explained in chapter 2.2.5. First only the ionic liquid, [MTBDH][CO_2H] was left overnight with selected catalysts: Pd(0)/C, $Pd(OAc)_2$ and Ru. Reactions were monitored by NMR and GC/MS. This was then followed by reactions with adlerol in three different conditions monitored by NMR and GC/MS.

2.2 Experimental

2.2.1 Study with Superbases

By definition a superbase is a base that is stronger than a proton sponge [1,8-bis(dimethylamino)naphthalene: DMAN]. That is, they have an absolute proton affinity larger than 245.3 kcal/mol and gas phase basicity over 239 kcal/mol.[98, 99] At the end of the acid-base reaction we have only the formate salt of superbases as products. The ratio for the superbase and acid has to be exactly 1:1. If excess formic acid is added the resulting ionic liquid mixture forms an eutectic liquid.[5]

The selected superbases were: 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, **1**), N,N,N',N'-tetramethyl-1,3-propanediamine (TMPD, **2**), 1,1,3,3-tetramethylguanidine (TMG, **3**), N,N,N',N',N",N"-hexamethylphosphorimidic triamide (HMPI, **4**), 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine (DMP, **5**), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, **6**), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, **7**), phosphazene base (P_1-t-Bu, **8**) and 1,4-diazabicyclo[2.2.2]octane (DABCO, **9**) (Figure 1). The NMR data for the ILs formed can be found in the appendix sections 4.4.1 and 4.4.2 of this thesis.

The normal procedure to prepare the ILs: to a 4ml vial liquid superbases were pipetted via µl Transferpette and solid superbases were weighed with 0,0001 g accuracy followed by addition of formic acid in µl. The formic acid and the bases 1,3,6-9 were taken directly from the commercial bottles. The bases **4** and **5** were first distilled using microdistillation equipment *in vacuo* using water pump.

The reactions were very exothermic and gave off lots of heat. All ILs turned out to be solids at room temperature except for $[TMPDH_2][CO_2H]_2$ that stayed liquid at room temperature. Every time any vial was opened it was flushed with argon gas before closing the vial to make sure that the IL stayed as dry as possible.

TMPD and formic acid in 1:1 ratio formed a two-phase system. ^{1}H-NMR shows that the upper layer is the TMPD free base and the lower layer is the IL in which the acid/base ratio is 0,5 (see appendix section 4.1.2 of this thesis). Thus TMPD cannot act as a proton Shponge probably due to the lack of rigid carbon skeleton.[99] The acid/base -ratio has to be 2:1 as the Figure 2 suggests. On the other hand DABCO formed a solid salt with the 1:1 acid/base ratio so DABCO shows some proton sponge ability even though its proton affinity and gas phase basicity might not be as strong as that of DMAN.

TGA measurements were done on the IL samples and the results can be found in the appendix section 4.2 of this thesis. TGA measurements shows us the temperature range with which we can operate in each case. Our intended reaction is transfer hydrogenolysis of lignin model compound and the reaction might need high temperatures so it is reasonable to choose a superbase formate that has a wide temperature range. This condition was met with TBD and MTBD. MTBD was selected for further experiments. In addition allyl-TBD formate was predicted to act as well in the reaction as MTBD formate. Allyl-TBD formate salt is liquid at room temperature due to its unsymmetrical lattice structure.

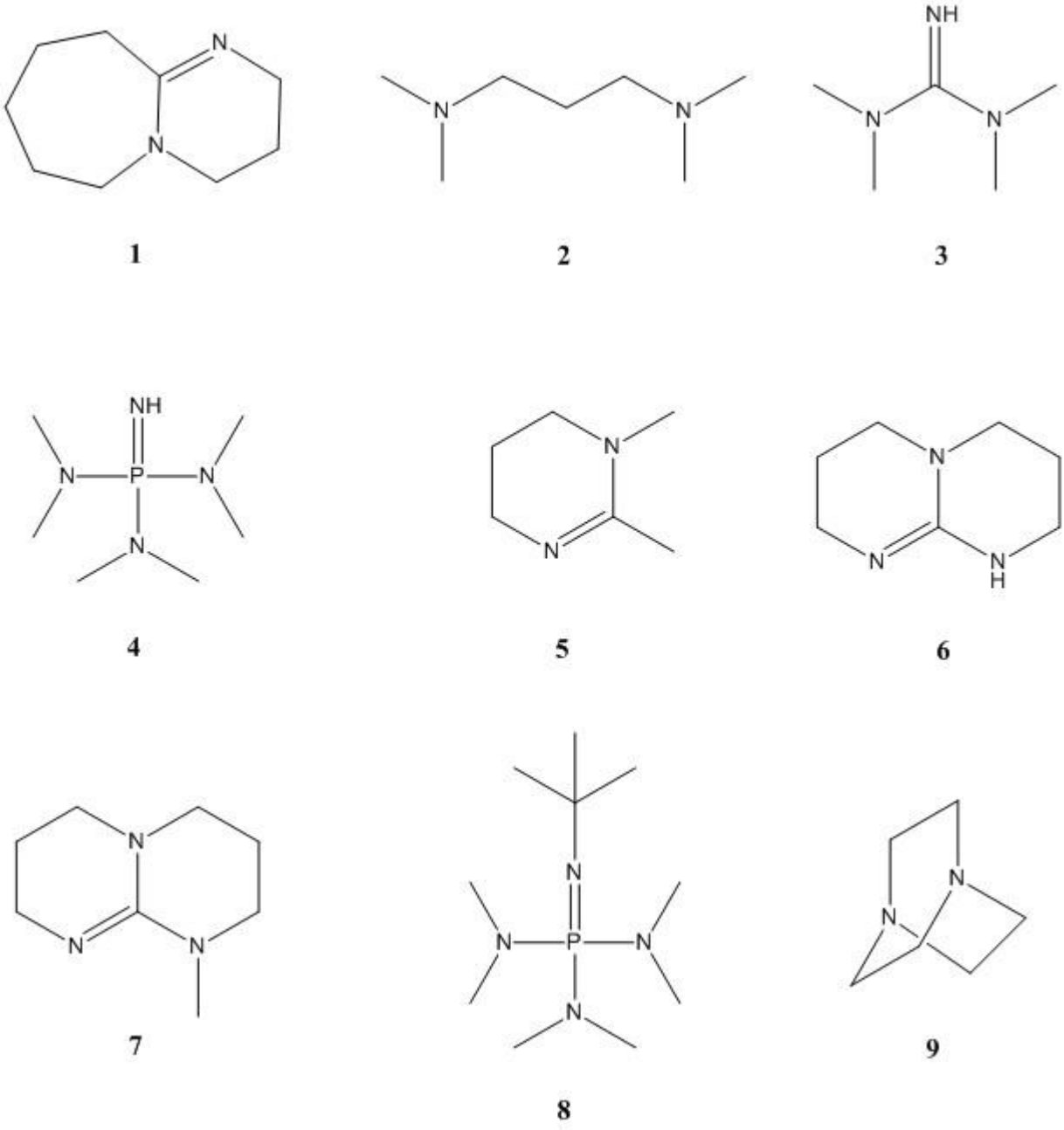


Figure 13. List of used superbases.

1 = 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

2 = N,N,N',N'-tetramethyl-1,3-propanediamine (TMPD)

3 = 1,1,3,3-tetramethylguanidine (TMG)

4 = N,N,N',N',N",N"-hexamethylphosphorimidic triamide (HMPI)

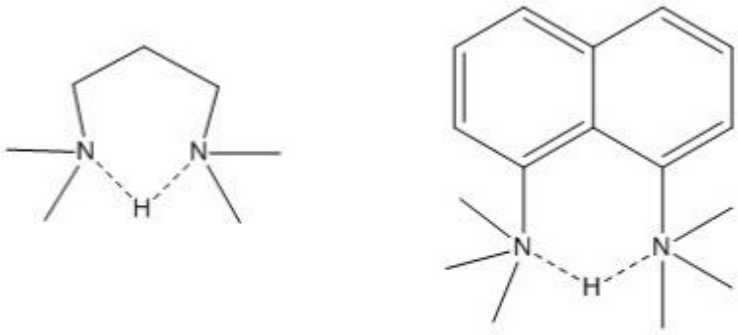
5 = 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine (DMP)

6 = 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)

7 = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD)

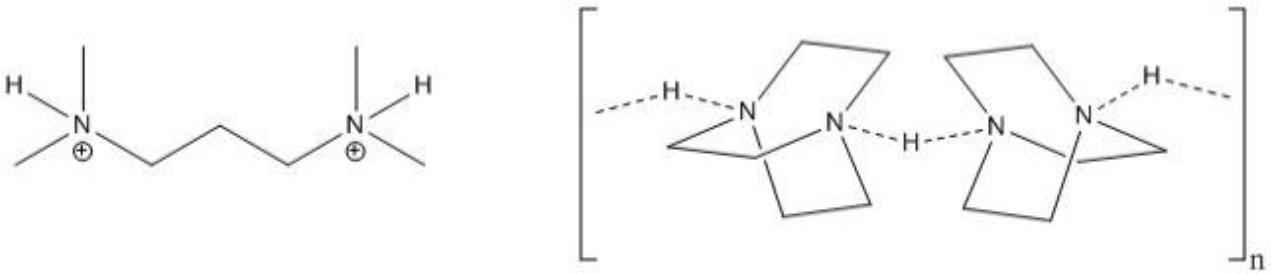
8 = phosphazene base (P_1-t-Bu)

9 = 1,4-diazabicyclo[2.2.2]octane (DABCO)



TMPD **DMAN**

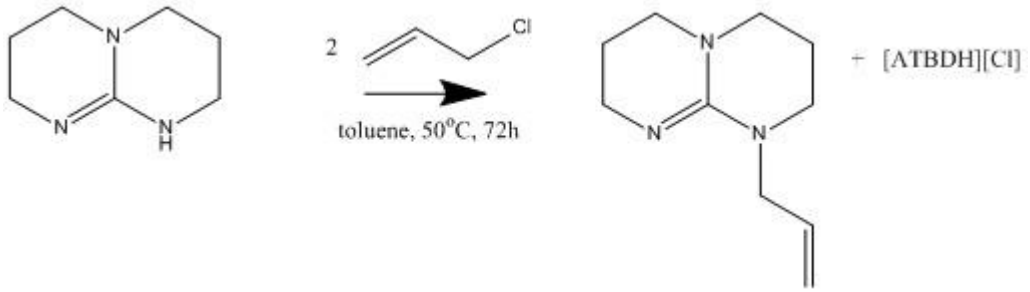
Figure 14. TMPD cannot act as a proton sponge (DMAN)[99] because it lacks the rigid carbon skeleton that keeps the nitrogen ligands firmly in the favorable distance.



$[TMPDH_2]^{2+}$ **$[DABCOH]^{+}$**

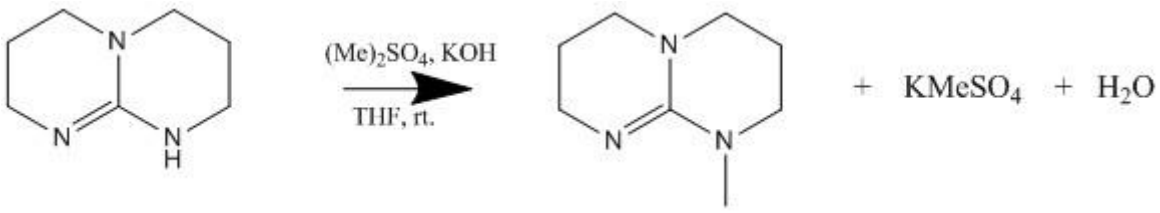
Figure 15. The acid-base ration in TMPD hast to be 2:1. TMPD needs two equivalents of formic acid whereas DABCO forms a salt already with acid/base 1:1 ratio. The figure on the right is one polymorph of [D6]*D*ABCOH]$^{+}$.[101, 102 ,103] TMPD is not a superbase and it is mentioned here only for comparison.

2.2.2 Synthesis of MTBD And Allyl-TBD



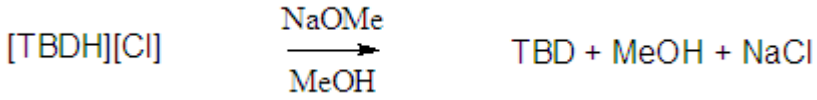
Scheme 1. Synthesis of allyl-TBD.

Allyl-TBD: To the 50 ml flask was measured 1,0267g TBD and it was dissolved to approx. 30 ml of toluene. The mixture was stirred for about 20 min. and then 0,905 ml of allylchloride was added. After 30 min the mixture was opaque and grey. The mixture was heated in 50°C over three days. To the flask was precipitated white/greyish powder that was decanted from toluene. ^{1}H-NMR showed no allyl group in solid material so the solid material is [TBDH][Cl]. After evaporation of the toluene layer yellow oil was left in the flask. ^{1}H-NMR showed allyl group and COSY, NOESY, HSQC and HMBC showed that the product is monoalkylated allyl-TBD in its free base form (see appendix section 4.1.1 of this thesis). The yield was around 45%.



Scheme 2. Synthesis of MTBD.

MTBD[104]: 32,69 g of TBD; 15,810 g of ground KOH and 225 ml of THF were added to 1L two-necked flask. The mixture was stirred for 1h. $(Me)_2SO_4$ was slowly added dropwise into the mixture via addition funnel. The mixture was left stirring over night at room temperature. The solid material thus formed was then filtrated and the solid was washed three times with 100 ml THF. The filtrate was evaporated. During this procedure solid precipitated so it was filtrated and THF phase poured into smaller flask before continuing the evaporation. To the flask was left yellow oil which was then microdistillated *in vacuo* using oil pump. The pressure during distillation was 2-5 mmHg and the substance boiled at 90°C-100°C. The yield was 46% .



Scheme 3. Recovery of TBD from its chloride salt formed in the synthesis of allyl-TBD (Scheme 1).

TBD from [TBDH][Cl]: Sodium methoxide was prepared in the two-necked flask equipped with a condenser. 11,6556g of metallic sodium was weighed into the flask. MeOH was added slowly into the flask via addition funnel and the flask was kept in ice bath. 175,658g [TBDH][Cl] was added to a round bottomed flask. 21,3007g NaOMe in approximately 400 ml MeOH was added to the flask and stirred for 15 min. Toluene was then added and the mixture and it was stirred for one hour. The flask was put to the fridge for 30 min. The mixture was then concentrated with rotary evaporator followed by recrystallization from toluene.

2.2.3 Hydrogenation Of Cinnamaldehyde

Cinnamaldehyde is a common model substance in hydrogenation reactions. It is normally reduced[105] with LAH or $NaBH_4$. In this hydrogenation reaction only the C=O is expected to react. Before any systematic reaction series was done several pre-experiments were carried out. The results from GC-MS can be found in the appendix 2.4.4 of this thesis.

R1: This reaction was freely modified from a synthesis[106] that uses Raney-Nickel and the starting material resembling cinnamaldehyde. 39,72 mmol both MTBD and formic acid and excess ethanol (150 ml) was let stirring for 15 min and 39,72 mmol of cinnamaldehyde was added. The mixture was heated until the inner temperature of the mixture was 70°C. The flask was lifted off from the oil bath and 0,05 mol% Raney-Nickel was added. The mixture was heated so that the inner temperature was at 70°C-75°C range. GC-MS shows nothing but cinnamaldehyde. Excess ethanol might have inhibited the reaction.

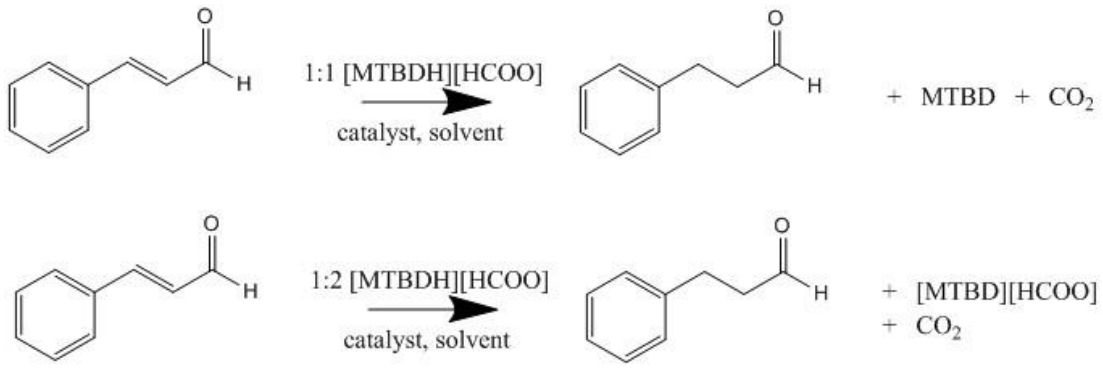
R2: The IL was made by mixing the MTBD and formic acid (both 0,3 mmol) in a flask with a condenser and water cooling without heating. After the salt had formed cinnamaldehyde (0,3 mmol) was added. The mixture was left stirring a few minutes and the Raney-Nickel (0,05 mol%) was added. The mixture was left stirring and heating for 1,5h in 90°C oil bath. To the condenser was attached a tube that led to a beaker full of water. By this we can arbitrarily follow the reaction by following the gas formation. GC-MS detected only cinnamaldehyde.

R3: This reaction is similar to R2 but it was done in the pressure tube. Again GC-MS detected only cinnamaldehyde.

R4: Catalyst was changed to Pd(0)/C (10% Palladium on charcoal) and the amount of formic acid was doubled (0,6 mmol). The ionic liquid was thus 1:2 MTBD and formic acid. The conditions were otherwise identical to R2 and R3. GC-MS showed two peaks: cinnamaldehyde and benzenepropanal. The reaction needs excess formic acid to scavenge the free base of MTBD back to its IL form. Free

base is probably causing side reactions (see Scheme 4). The benzenepropanal peak is is only 2.5 % of the total area.

R5: The catalyst was changed to $Pd(OAc)_2$ and the amount of formic acid was again used in 1:2 ration to MTBD. Otherwise the conditions were the same as in R2-R4. GC-MS shows benzenepropanal but also a couple of new impurities. The reaction mixture was kept reacting overnight. The amount of cinnamaldehyde was decreased and the amount of benzenepropanal increased as well as the amount of impurities.



Scheme 4. The effect of the amount of formic acid in the reaction mixture. In the first case there is only 1 equivalent of acid that converts into CO_2 during the reaction. MTBD is now in its free base form and it can cause unwanted side reactions with starting material and/or products. In the second below the extra amount of formic acid converts the free base back to its IL form.

$Pd(OAc)_2$ and Pd(0)/C seemed to work best for this reaction and they were chosen for the reaction series. Cinnamaldehyde was abandoned as the model substance because it contains the aldehyde group that often causes troubles in the reactions for instance because of its tendency to form polymers in condensation reactions. Cinnamyl alcohol was chosen as a more convenient compound for pre-experiments.

A problem arouse with allyl-TBD. Because it contains a double bond, it is also hydrogenated during the reaction. This means that we have to use extra amount of IL to be sure that the wanted reaction happens and because the allyl-TBD is changed into propyl-TBD it changes the IL completely. The hydrogenation of allyl-TBD was monitored with GC-MS and the data can be found in the appendix 2.4.4 of this thesis. The allyl-TBD was dismissed and only the MTBD was used in the following experiments.

2.2.4 Reaction Series of Cinnamyl Alcohol

RS1: the amount of MeOH and its effects to the reaction, $Pd(OAc)_2$ as catalyst

RS2: the amount of MeOH and its effects to the reaction, Pd(0)/C as catalyst

RS3: the amount of formic acid and its effects to the reaction, Pd(0)/C as catalyst

RS4: If we used equimolar amount of formic acid should we then use MeOH? Is the reaction happening at room temperature?

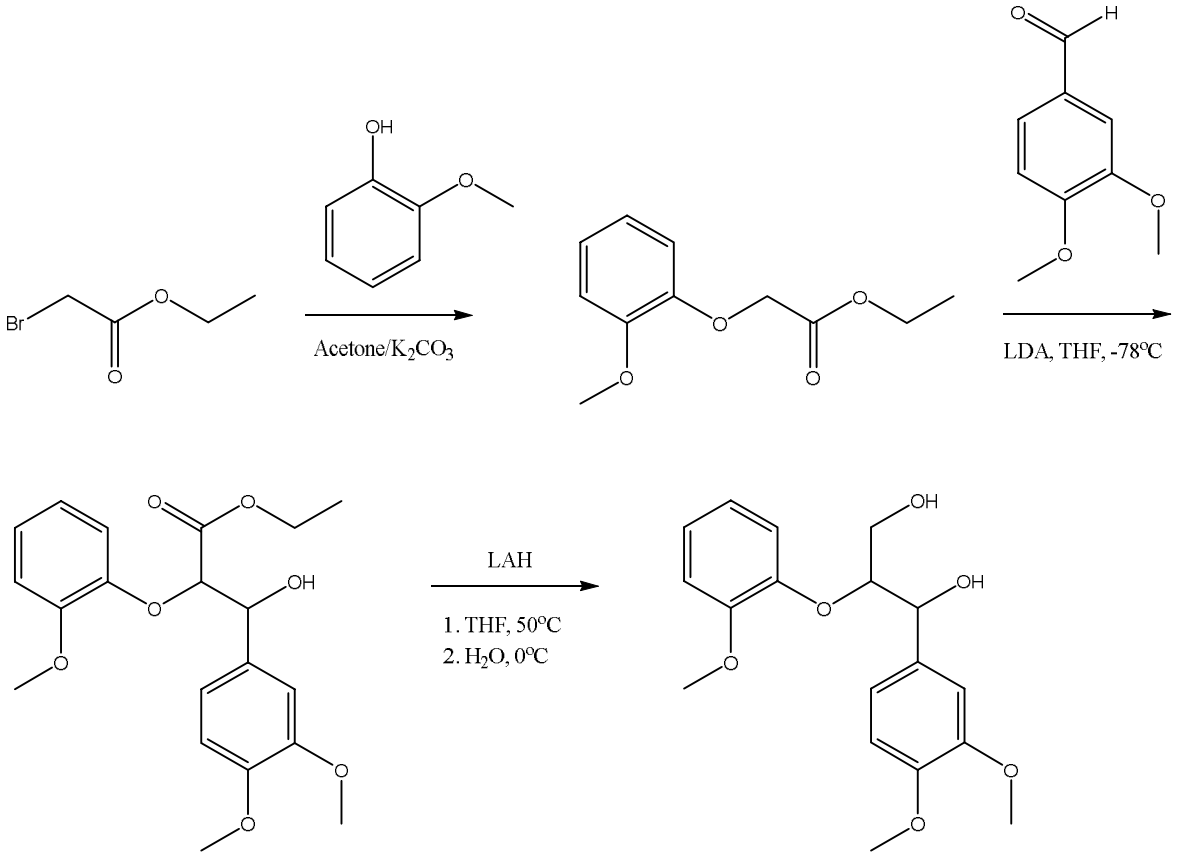
Table 3. Reaction series, reaction condition and results according to GC-MS measurements.

Reaction Series, RS	catalyst	formic acid : MTBD ratio	MeOH / (mmol)	temperature / °C	time / (h)	starting material left (Area% in GC-MS)	product (Area% in GC-MS)	impurities[1]
RS1_ST	5 mol % $Pd(OAc)_2$	2:1	-	90	1	28.430	22.665	yes
RS1_1	5 mol % $Pd(OAc)_2$	2:1	0.3	90	1	48.223	34.316	yes
RS1_2	5 mol % $Pd(OAc)_2$	2:1	0.6	90	1	37.645	25.784	yes
RS1_3	5 mol % $Pd(OAc)_2$	2:1	0.15	90	1	41.413	38.371	yes
RS1_4	5 mol % $Pd(OAc)_2$	2:1	0.075	90	1	40.212	44.910	yes
RS1_5	5 mol % $Pd(OAc)_2$	2:1	excess (1ml)	90	1	42.737	37.762	yes
RS2_ST	5 mol% Pd(0)/C	2:1	-	90	1	-	92.765	few
RS2_1	5 mol% Pd(0)/C	2:1	0.3	90	1	-	90.234	few
RS2_2	5 mol% Pd(0)/C	2:1	0.6	90	1	-	89.772	few

RS2_3	5 mol% Pd(0)/C	2:1	0.225	90	1	-	90.742	few
RS2_4	5 mol% Pd(0)/C	2:1	0.15	90	1	-	95.679	few
RS2_5	5 mol% Pd(0)/C	2:1	0.075	90	1	-	90.382	few
RS2_6	5 mol% Pd(0)/C	2:1	excess (1ml)	90	1	-	65.413	yes
RS3_1	5 mol% Pd(0)/C	1:1	-	90	1	61.383	33.496	yes
RS3_2	5 mol% Pd(0)/C	0,5:1	-	90	1	61.185	6.291	yes
RS3_3	5 mol% Pd(0)/C	excess (1ml)	-	90	1	-	-	yes
RS4_1	5 mol% Pd(0)/C	1:1	1 eq. to IL	90	1	41.623	22.696	yes
RS4_2	5 mol% Pd(0)/C	2:1	-	rt.	1	33.934	30.844	yes

1 – See appendix 2.4.4 of this thesis for more details

2.2.5 Synthesis of Adlerol[107]



Scheme 5. The reaction route of adlerol.

Adlerol (*1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol)*[107]**:** To 1 liter round bottomed flask was measured 36 ml guaiacol (0.33 mol), 40 ml ethylbromoacetate (0.36 mol), 50 g of dry K_2CO_3 and 700 ml of dry acetone. The mixture was left refluxing for 19 h. K_2CO_3 had been in the desiccator and the dryness of acetone was measured by Karl-Fischer –titration. The purity of guaiacol and ethylbromoacetate was checked by refractive index.

Reaction mixture was filtrated and the solids washed twice with 200 ml of acetone. The filtrate was evaporated with rotary evaporator and dissolved to 200 ml of ethyl acetate. Organic layer was washed twice with 200 ml 2 M NaOH and twice with 200 ml of brine, left drying over $MgSO_4$ and solvent evaporated.

The crude ester product, ethyl-2-methoxyphenoxyacetate, was distilled *in vacuo* using oil pump. The product distilled in 113°C in 0.7 mbar pressure.

To a 1 liter round bottomed flask in ice bath was measured 33 ml of distilled di-isopropylamine (distilled at 83°C, normal pressure) in 200ml of dry THF (water content 47 ppm according to Karl-Fischer titration). To this was slowly added 175 ml of 1.59 M BuLi-solution.

Dry ice/ethanol bath -60- (-68) °C was made. 40 ml of ester in 200 ml of THF was slowly added within 1.5 hours. Immediately after this 33,6 mg veratraldehyde in 200 ml of THF was added within 2 hours and the reaction mixture left stirring for 1h.

The reaction mixture was poured into 400 ml of saturated NH_4Cl solution until neutral. EtOAc was then added and the organic layer was washed twice with 400 ml 2 M HCl, twice with 400 ml of 10% $NaHCO_3$ solution and twice with 400 ml of brine. (20 ml 3:1 EtOH/toluene would have crystallized this thing) EtOAc was evaporated and the solids dried with oil pump. The product was characterized by TLC, GC-MS, NMR and IR.

To 3.9363g LAH in 200 ml of THF 9,75 g of ester in 100 ml of ester at 50°C was slowly added slowly under argon. Then cooled to 0°C and 1:1 20 ml H2O/THF mixture was slowly added. 8 ml of 2 M NaOH added. About 8 ml water added until the solds turned white in colour. Filtration. Washed twice with 200 ml EtOAv. The filtrate was extracted , dried over Na2SO4 and evaporated. The crude product is syrup. That bubbled in oil pump vacuum as if it were polymer. TLC, NMR and GC-MS shows it is adlerol. Finaly 4,65 g of adlerol for the hydrogenation reactions. Syrup is a mixture of two diastereoisomers of adlerol. The crude product precipitated into white crystals with 100 ml diethylether. The solid material was pure enough. No further recrystallization was made. NMR-data is found in the appendix section 4.1.3 of this thesis.

2.2.6 How [MTBDH][CO_2H] Is Reacting with Selected Catalysts

First experiments with IL and selected catalysts were performed. Catalyst amount was 5 mol% that of ionic liquid (MTBD:FA 1:2). It was shown by the GC-MS and NMR that $[(Ph)_3P]Ru(II)Cl_2$ catalyst affected the ionic liquid the least. Pd(OAc)2 and Pd/C caused hydrolysis of MTBD and there is even a trace of amide formation to MTBD. The NMR analyses are found in the appendix section 4.1.4.

2.2.7 Reaction Series with Adlerol

Reaction series were done on adlerol. Adlerol was weighed in 1:1 ratio to IL and the IL was MTBD:FA in 1:2 ratio. Temperature was 100°C and the reaction time around 14h. GC-MC, TLC and NMR showed no significant decrease of the starting material so these reactions are not included in this thesis because of the lack of information from the analysis data. The reaction procedure prescribed and the table 5 showed below are considered the main results of this preliminary study on lignin model compound cleavage in reductive environment. The main difference in the cases below is that the concentration of adlerol is lower (7-20 mol% to IL vs. equimolar amount to IL) and the temperatures in some cases are higher than 100°C.

General procedure for preparing reaction mixtures, synthesis and extraction:

[MTBDH][CO_2H] in 1:2 ratio was made a larger quantity to make sure that the quality of IL is the same in each reaction. To a round bottomed flask was weighed 9,50 of MTBD and pipetted 4,70 ml of FA. Three identical 4 ml vials were made at a time with same amount of adlerol, IL and the same catalyst but each of them were put in separate oil baths. The temperatures of oil baths were 100°C, 150°C and 180°C. So A, B and C were reacting at the same time, D, E and F at the same time etc. The reaction time in all cases was 14h. After the reaction to the mixture was poured 1 ml ethyl acetate and the solids were separated by filtration. To the filtrate was poured 1 ml citric acid buffer (pH 4,8) and the layers were separated with a tiny separatory funnel. The ethyl acetate layer was a ready source for aliquots for GC-MS and TLC. For the NMR measurements the ethyl acetate had to be evaporated first.

Table 5. Reaction Series with adlerol in three different temperatures. NMR-data from cases P and Q are found in the appendix section 4.3.2 of this thesis. The reaction time in all cases was 14h.

Table 4. Reaction Series of Hydrogenolysis of Adlerol.

Sample	mol% of adlerol[2]	Catalyst	mol% of catalyst[3]	temperature / °C	GC-MS
A[1]	-	no catalyst	-	**180**	esterification
B[1]	-	no catalyst	-	150	esterification
C[1]	-	no catalyst	-	100	esterification
D	7,3	no catalyst	-	**180**	no reaction
E	6,2	no catalyst	-	150	no reaction
F	4,2	no catalyst	-	100	no reaction
G	12,9	$[(Ph)_3P]Ru(II)Cl_2$	8,5	**180**	guaiacol, 1,2-dimethoxybenzene catalyst impurities
H	14,4	$[(Ph)_3P]Ru(II)Cl_2$	7,4	150	guaiacol, 1,2-dimethoxybenzene catalyst impurities
I	18	$[(Ph)_3P]Ru(II)Cl_2$	12,3	100	guaiacol, 1,2-dimethoxybenzene catalyst impurities
J	8,9	$Pd(OAc)_2$	24,5	**180**	hydrogenation
K	9,3	$Pd(OAc)_2$	43,4	150	hydrogenation
L	7,2	$Pd(OAc)_2$	47,8	100	hydrogenation

M	9,6	Pd(0)/C	13,7	**180**	no reaction
N	4,2	Pd(0)/C	27,4	150	no reaction
O	5,5	Pd(0)/C	32,7	100	no reaction
P	21,4	$[(Ph)_3P]Ru(II)Cl_2$	5,3	**165**	guaiacol, 1,2-dimethoxybenzene
Q	20,2	$Pd(OAc)_2$	5,3	**165**	hydrogenation
R	20,0	Pd(0)/C	5,0	**165**	no reaction

[1]= reactions in formic acid (100 µl) only, no MTBD or catalyst present

[2]= 1:2 ratio MTBD : FA in each case, mol% of adlerol is calculated in comparison to IL using the following formula

$$mol\% = \frac{mol(adlerol)}{mol(adlerol) + mol(IL)} \quad (1)$$

[3]= in this case the formula (1) is

$$mol\% = \frac{mol(catalyst)}{mol(catalyst) + mol(adlerol)} \quad (1)$$

2.3 Conclusions

From the pre-experiments the best reaction condition for the studied hydrogenation of cinnamyl alcohol was 5 mol% of Pd(0)/C (10% Pd) as catalyst at 90°C, reaction time 1h and [MTBDH][CO_2H] used as the ionic liquid with 1 mol extra of formic acid. The reaction conditions depends mainly on the acid/base ratio of the IL. The 1 mol extra formic acid scavenges the free base form of the superbase back to its IL form and thus prevents its possibly harmfull side reactions. The excess of formic acid leads to unwanted side reactions. MeOH is not needed to bind the formed CO_2. From the selected catalysts the used Raney Nickel was not active enough and $Pd(OAc)_2$ was too reactive and it caused too much side reactions. With Pd(0)/C (10% Pd) the reaction went into completion with only trace of propylbenzene as an impurity. The superbase used can´t contain any double bonds or other groups that are easily affected by the hydrogenation reaction (for instance hydrogenolysis of benzyl-*O*-ethers, double bond in allyl-TBD). The reaction also proceeds at room temperature.

The hydrogenolysis of lignin model compound adlerol was successful at 180°C, 14 h reaction time, concentration of adlerol in the IL 5-20 mol% and the $[(Ph)_3P]Ru(II)Cl_2$ as the catalyst. The reaction conditions needed are quite harsh and the amount of ionic liquid needed is huge compared to tha amount of adlerol. In addition the catalyst may interfere with the cation part of the IL albeit the Ru catalyst affected the IL the least. This study was only for the preliminary emperiments on this matter. It was shown that the hydrogenolysis is possible in the chosen conditions but the analysis of the reaction products need to be done more accurately.

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[113] Last but not least I´d like to thank Jussi Helminen for his help and support and for helping me interpreting this HSQC and many other NMR and GC-MS spectra.

4 APPENDIX

4.1 NMR-Data

4.1.1 Study with Superbases

The formic acid and the bases 1, 3, 6-9 were taken directly from the commercial bottle. The bases 4 and 5 were distilled using microdistillation equipment *in vacuo* using water pump. All the IL samples showed exchangeable proton at approximately 13 ppm.

1. [DBUH][CO2H]

1H-NMR (600 MHz, d6-DMSO): *d*=1.555 (4H, quin, CH2), 1.658 (2H, quin, CH2), 1.841 (2H, quin, CH2), 2.648 (2H, t, CH2C=N), 3.188 (2H, t, CH2N), 3.399 (2H, t, CH2N), 3.468 (2H, t, CH2N) 8.477 (1H, s, $HCOO^-$)

13C-NMR (600 MHz, d6-DMSO):*d*=19.126, 23.575, 26.123, 28.305, 31.380, 47.785, 53.096, 165.060, 265.358

2. [TMPDH][CO2H]

1H-NMR (600 MHz, d6-DMSO): *d*=1.76 (2H, qv, CH2), 2.40 (12 H, s, Me), 2.5 (4H, t, CH2N), 9.6 (1H, s, CO2H)

13C-NMR (600 MHz, d6-DMSO):*d*=24.1 (CH2), 47.0 (4C, H3CN), 59.3 (2C, NCH2)

3. [TMGH][CO2H]

1H-NMR (600 MHz, d6-DMSO): *d*=2.826 (12H, s, CH3CN), 8.497 (1H, s, $HCOO^-$)

13C-NMR (600 MHz, d6-DMSO):*d*=162.023, 165.220

4. [HMPIH][CO2H]

1H-NMR (600 MHz, d6-Methanol): *d*=2.083 (18H, d, CH3NP), 3.278 (1H, s, NH), 8.53016 (1H, s, $HCOO^-$)

13C-NMR (600 MHz, d6-Methanol):*d*=38.090, 171.442

5. [DMPH][CO2H]

1H-NMR (600 MHz, d6-DMSO):*d*=1.841 (2H, quin, CH2), 2.199 (3H, s, CH3C=N), 3.014 (3H, s, CH3N), 3.189 (2H, t, CH2N), 3.324 (2H, t, CH2N=C)

13C-NMR (600 MHz, d6-DMSO):*d*=17.539, 18.676, 37.591, 38.568, 47.366, 160.406, 165.625

6. [TBDH][CO2H]

1H-NMR (600 MHz, d6-DMSO):*d*=1.817 (4H, quin, CH2), 3.085 (4H, t, CH2), 3.196 (4H, t, CH2N), 8.399 (1H, s, $HCOO^-$)

13C-NMR (600 MHz, d6-DMSO):*d*=20.446, 37.134, 46.061, 151.249, 167.532)

7. [MTBDH][CO2H]

1H-NMR (600 MHz, d6-DMSO):*d*=1.820 (2H, quin, CH2), 1.881 (2H, quin, CH2), 2.865 (3H, s, CH3N), 3.249 (6H, t, CH2N), 3.318 (2H, t, CH2N), 8.219 (1H, s, $HCOO^-$)

13C-NMR (600 MHz, d6-DMSO):*d*=20.187, 20.340, 36.943, 38.331, 46.503, 46.976, 47.503, 150.746, 164.167

9. *[D6]*ABCOH][CO2H]

1H-NMR (600 MHz, d6-DMSO): *d*=2.772 (12H, s, CH2N), 8.280 (1H, s, HOO^-)

13C-NMR (600 MHz, d6-DMSO):*d*=48.261, 168.443

10. MTBD, free base

1H-NMR (600 MHz, d6-DMSO):*d*=1.96 (2H, qv, CH2), 1.77 (2H, qv, CH2), 3.04 (3H, s, NCH3), 3,45 (6H, t, CH2N), 3.53 (2H, t, CH2N=C)

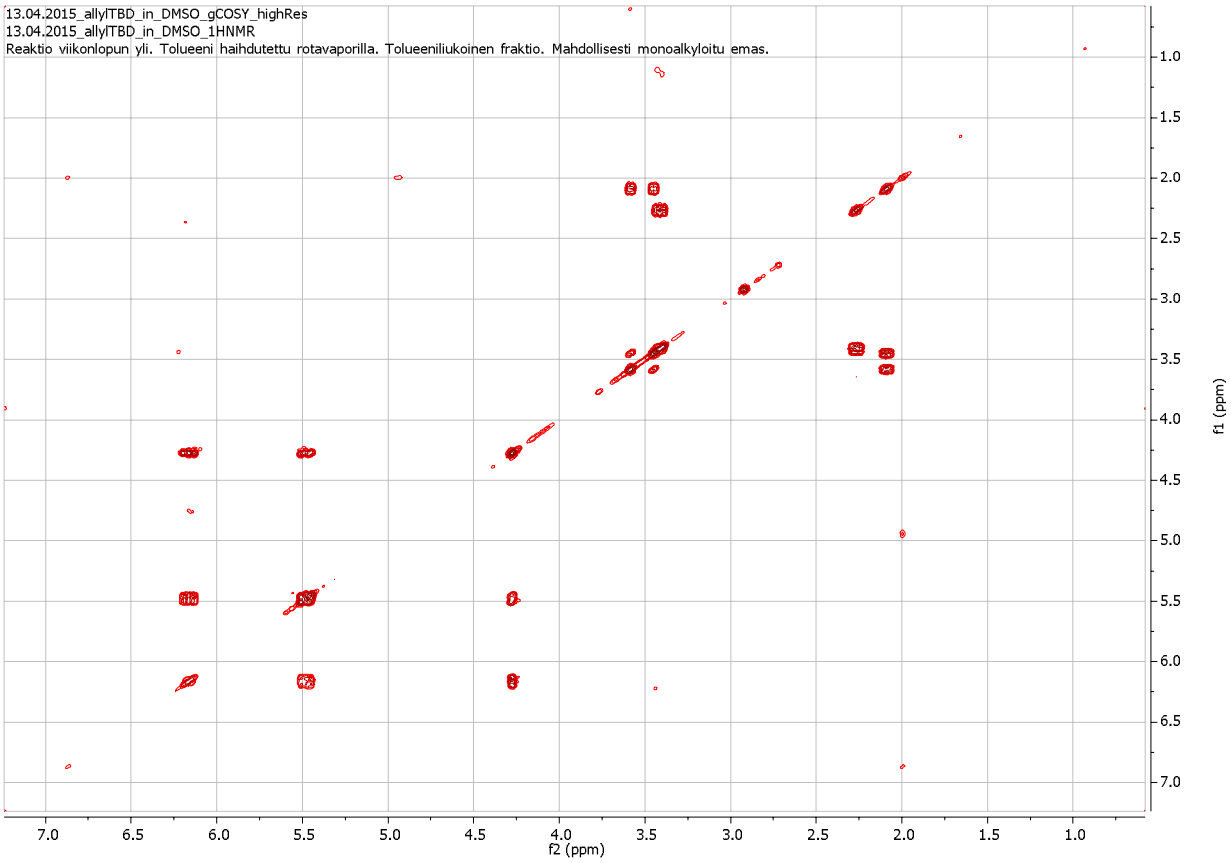
13C-NMR (600 MHz, d6-DMSO):*d*=21.6, 22.7, 35.8, 42.1, 43.6, 44.5, 153.3

11. allylTBD, free base

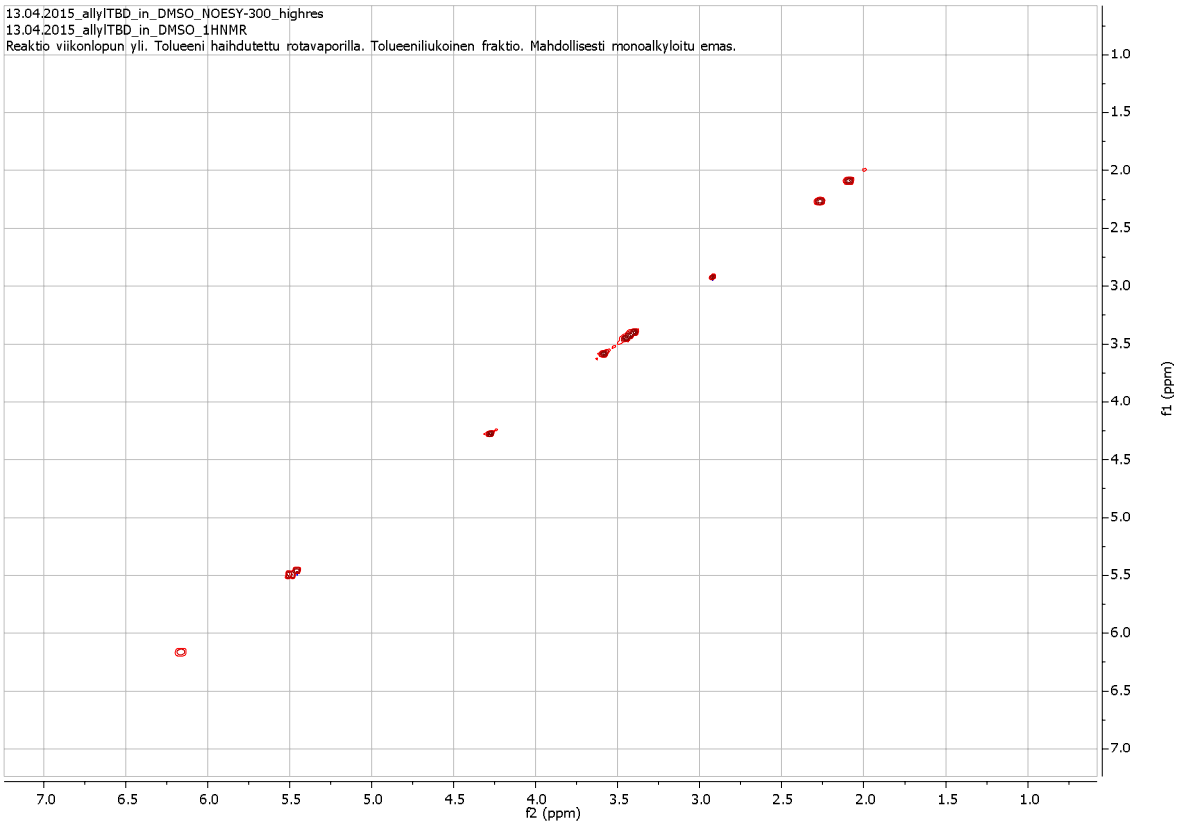
1H-NMR (600 MHz, d6-DMSO):*d*=1.646 (2H, quin, CH2), 1.824 (2H, quin, CH2), 2.975 (6H, m, CH2), 3.141 (2H, t, CH2), 3.832 (2H, d, CH2), 5.022 (1H, t, C-CH=C), 5.065 (1H, s/, C=CH), 5.720 (1H, m, C=CH)

13C-NMR (600 MHz, d6-DMSO):*d*=25.752, 26.034, 43.080, 46.567, 47.605, 50.924, 51.168, 53.114, 118.672, 138.777, 152.634

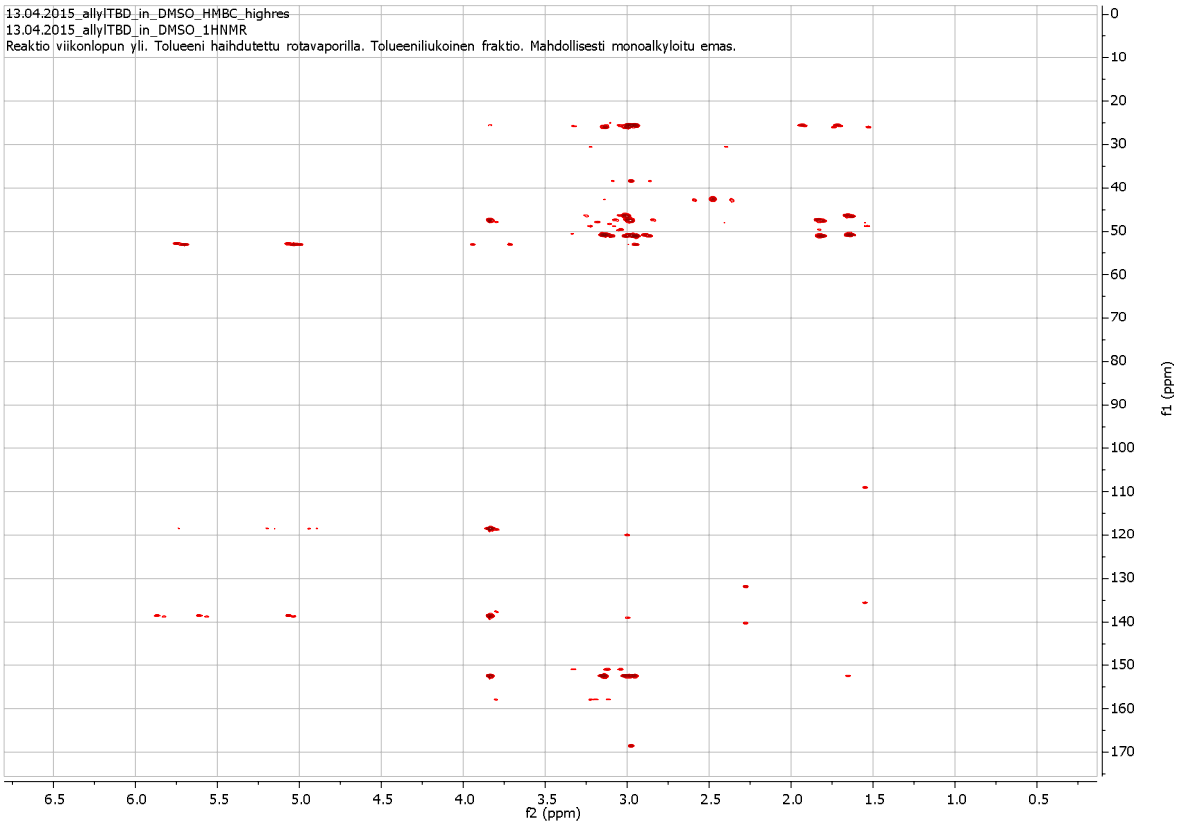
COSY of monoalkylated allyl-TBD: 600 MHz, d6-DMSO[113]



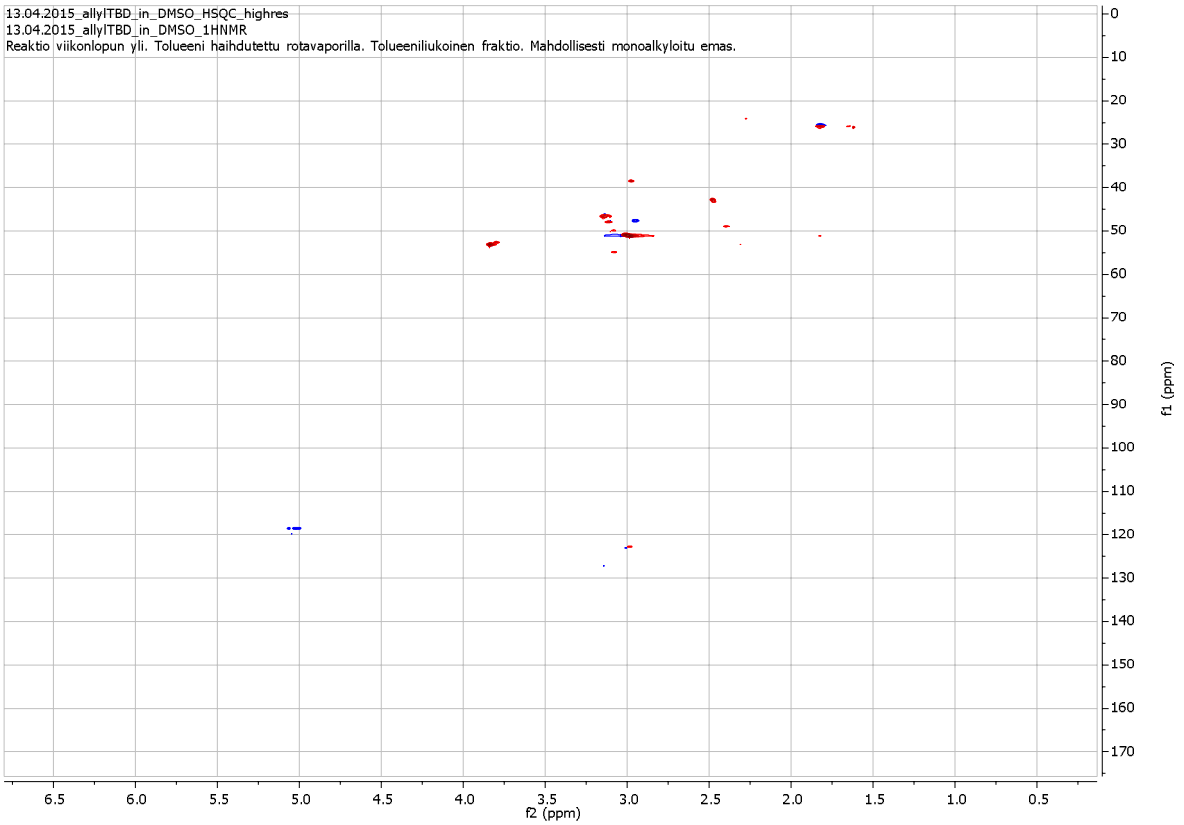
NOESY of monoalkylated allyl-TBD: 600 MHz, d6-DMSO



HMBC of monoalkylated allyl-TBD: 600 MHz, d6-DMSO



HSQC of monoalkylated allyl-TBD: 600 MHz, d6-DMSO



4.1.2 ^{1}H-NMR Data from TMPD/Formic Acid 1:1 and 1:2 Mixtures

TMPD + formic acid (2:1), upper layer in deuterated DMSO

integral nro	ppm	value	multiplicity
1	8,3819	0,410	s
2	2,20764	23,458	t
3	2,09849	65,014	s
4	1,52874	11,118	quin

- 1 proton = 5,4178333
- acid/base ratio about 0,08
- no exchangable proton

TMPD + formic acid (2:1), lower layer in deuterated DMSO

integral nro	ppm	value	multiplicity
1	8,35644	6,589	s
2	2,53788	26,685	t
3	2,33686	57,378	s
4	1,74178	3,348	quin

- 1 proton = 4,7815
- acid/base ratio about 1,4
- exchangable proton present at about 13 ppm

TMPD + formic acid (1:2) in deuterated DMSO

integral nro	ppm	value	multiplicity
1	8,33606	9,580	s
2	2,53788	20,734	t
3	2,38937	59,913	s
4	1,76055	9,773	quin

- 1 proton = 4,99375
- acid/base ratio about 1,9
- exchangable proton present at about 13 ppm

4.1.3 Adlerol Synthesis

1. ethyl 3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate
”adlester”, (adlerol with ester group in its secondary hydroxyl, intermediate in the adlerol synthesis)

1H-NMR (600 MHz, d6-DMSO): *d* = 1.093 (3H, t, CH3), 3.692 (3H, s, CH3), 3.800 (6H, s, CH3), 4.219 (2H, quad., CH2), 4.857 (1H, d, R3H), 6.111 (1H, d, R2H-OH), 6.863 (7H, m, aromatic protons), exchangeable proton at 5.987

13C-NMR (600 MHz, d6-DMSO):*d* = 4.1, 56.1, 61.6, 74.6, 95.9, 109.4, 110.7, 112.6, 115.4, 119.3, 121.3, 121.6, 133.9, 143.2, 146.7, 149.5, 170.8

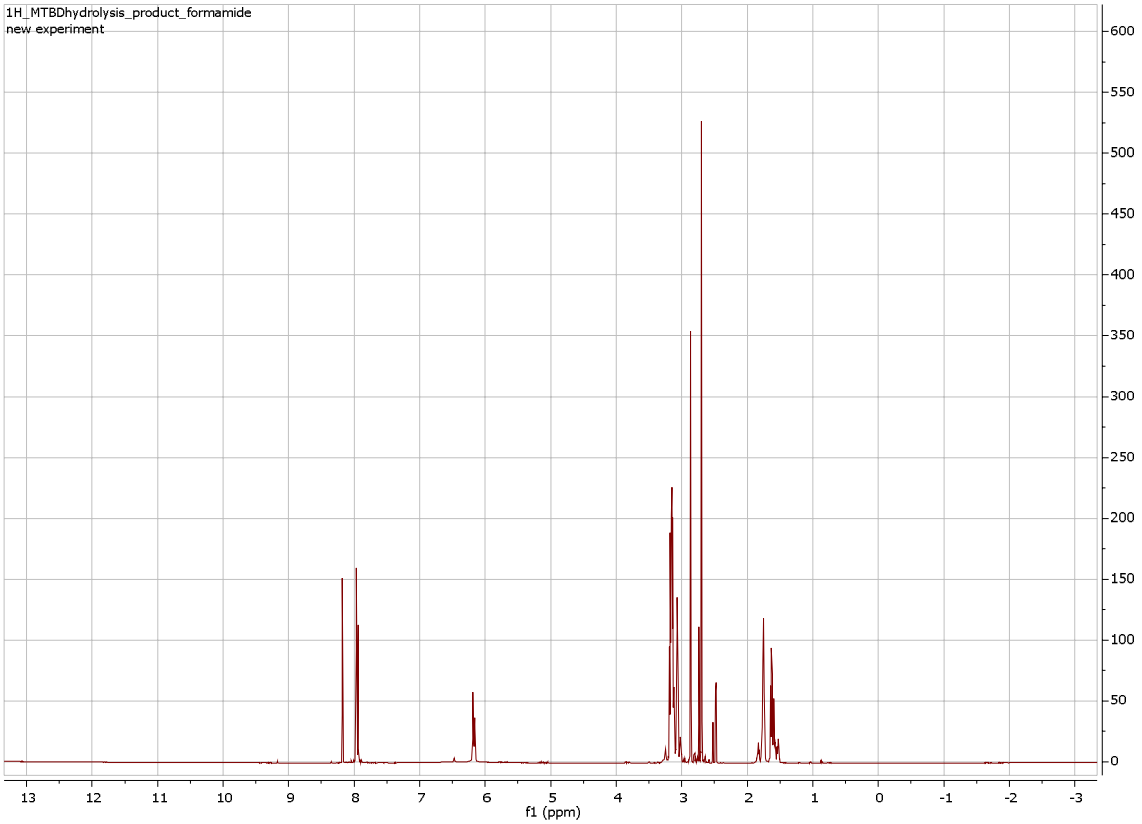
2. adlerol

1H-NMR (600 MHz, d6-DMSO): *d* = 3.760 (2H, d, CH2-OH), 3.854 (9H, s, CH3), 4.081 (1H, quad. R3H), 5.289 (1H, d, R2H-OH), 6.877 (7H, m, aromatic protons), exchangeable protons at 4.001 and 5.178

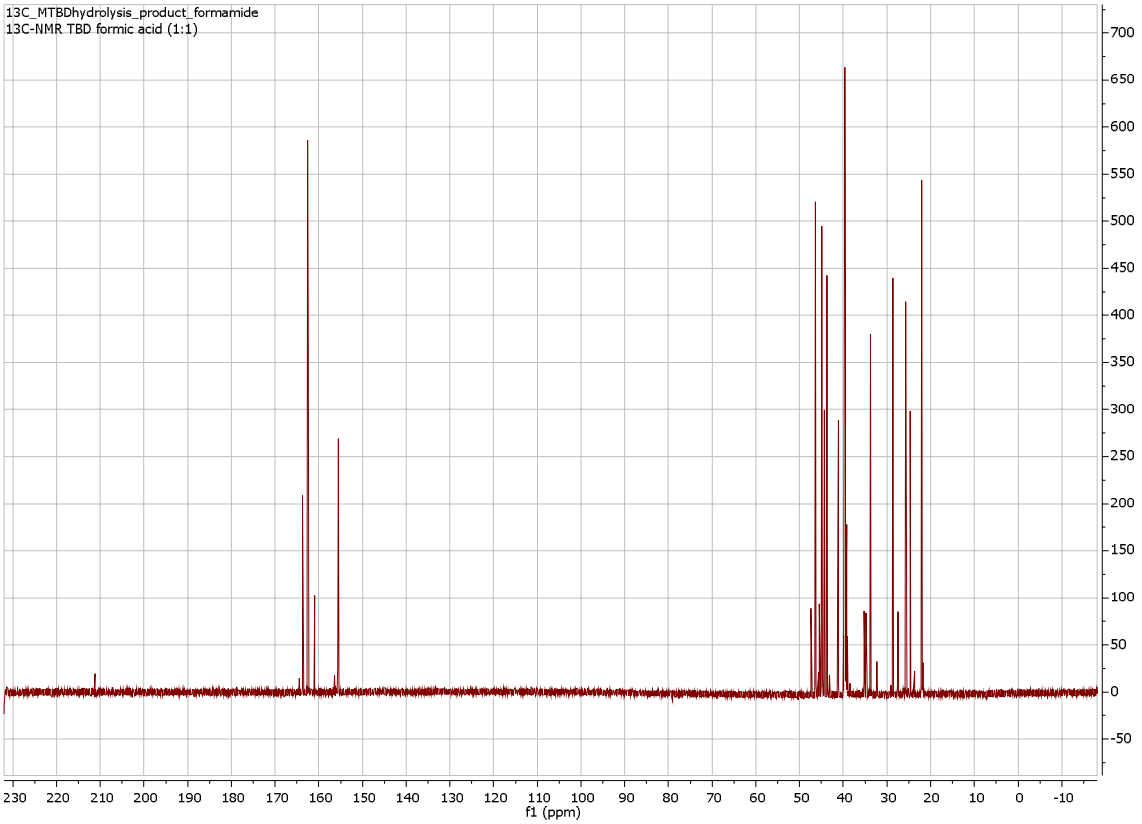
13C-NMR (600 MHz, d6-DMSO):*d* = 56.1, 61.1, 72.8, 91.1, 110.4, 110.7, 112.5, 118.3, 120.3, 121.3, 131.8, 147.1, 148.0, 149.9

4.1.4 [MTBDH][CO_2H] (1:2) + catalyst

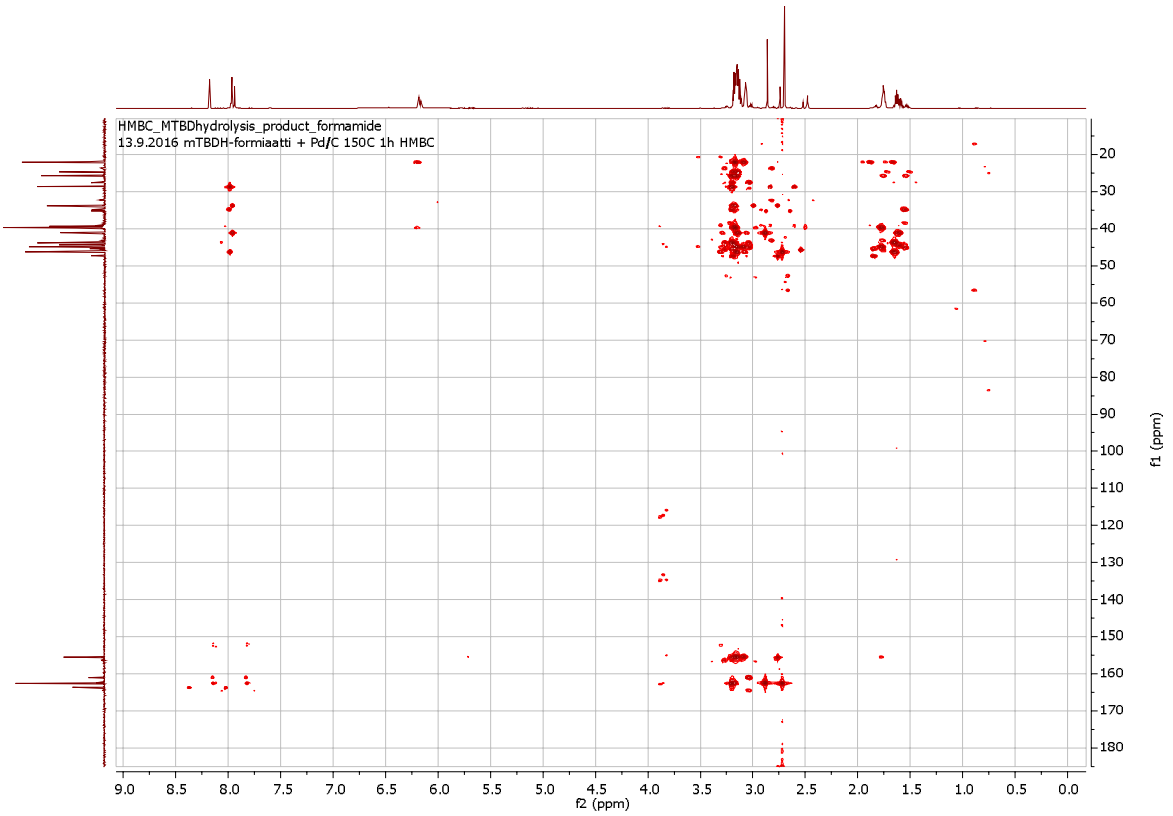
1H-NMR of the formamide product of MTBD hydrolysis product as a reference: 600MHz, d6-DMSO



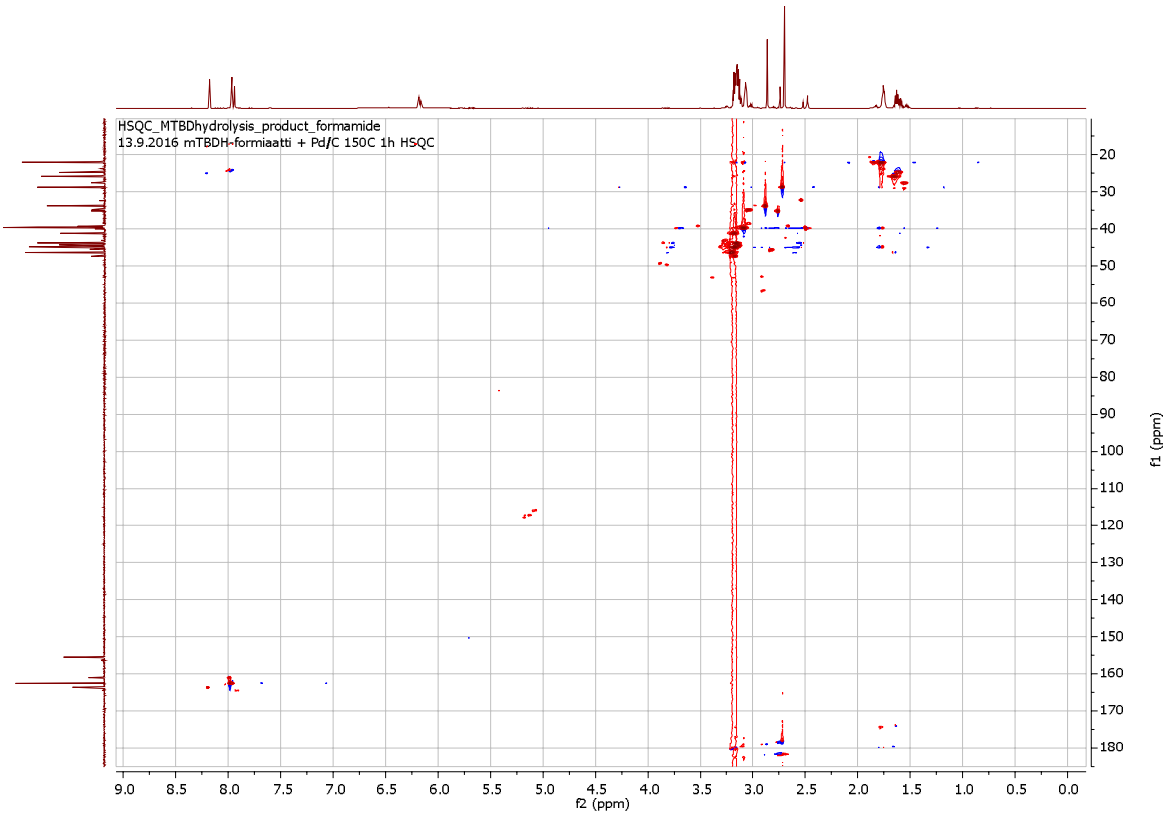
13C-NMR of the formamide product of MTBD hydrolysis product as a reference: 600MHz, d6-DMSO



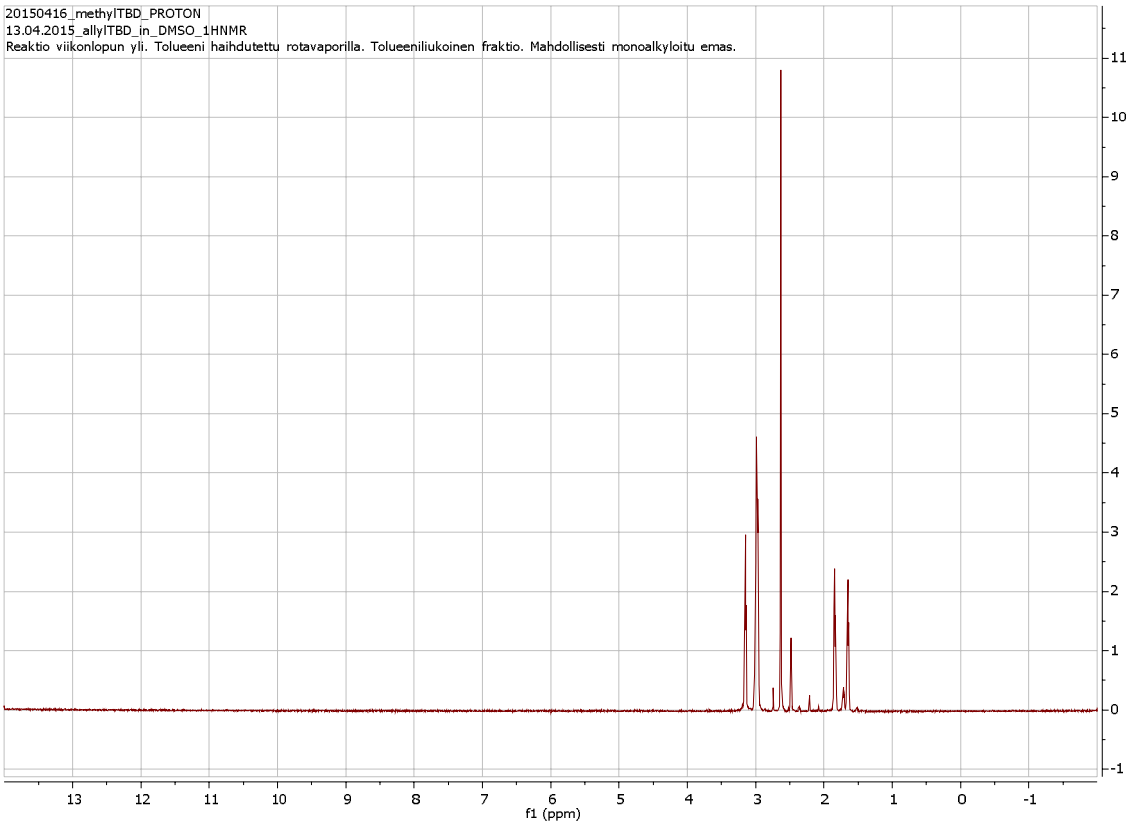
HMBC of the formamide product of MTBD hydrolysis product as a reference: 600MHz, d6-DMSO



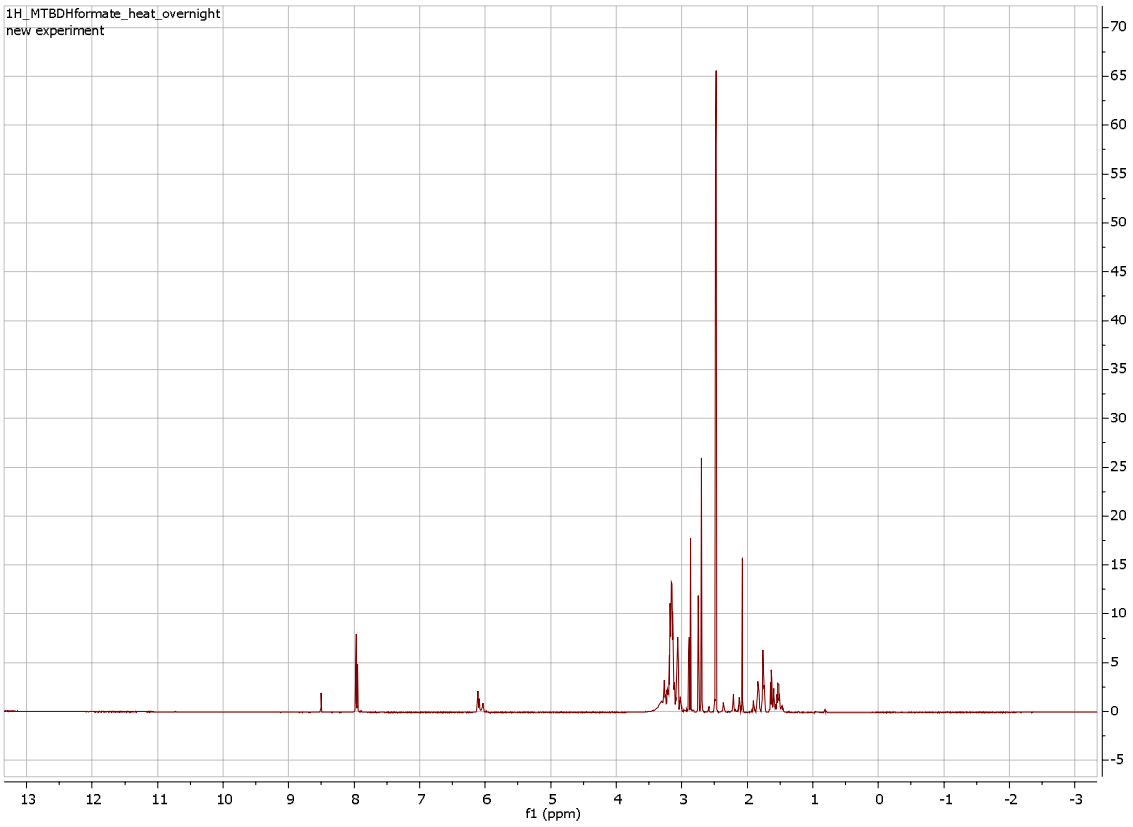
HSQC of the formamide product of MTBD hydrolysis product as a reference: 600MHz, d6-DMSO



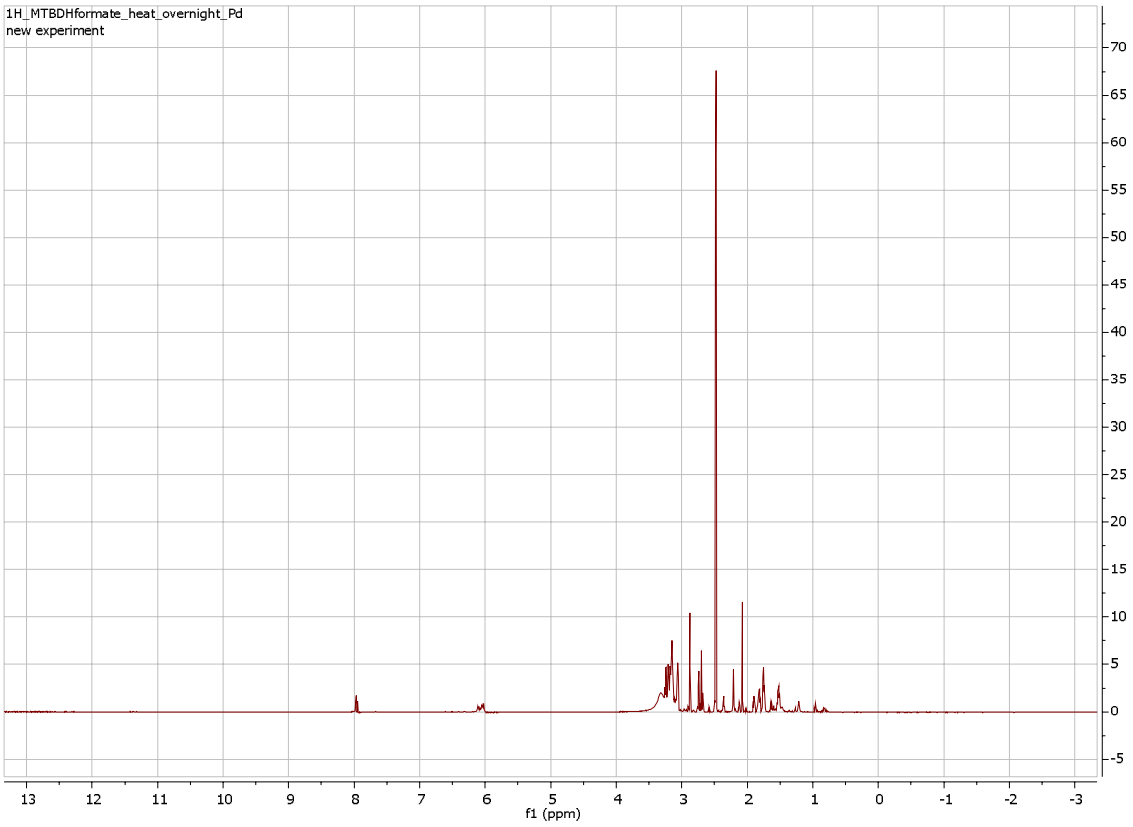
1H-NMR: 600 MHz, d6-DMSO, MTBD:FA 1:2 mixture



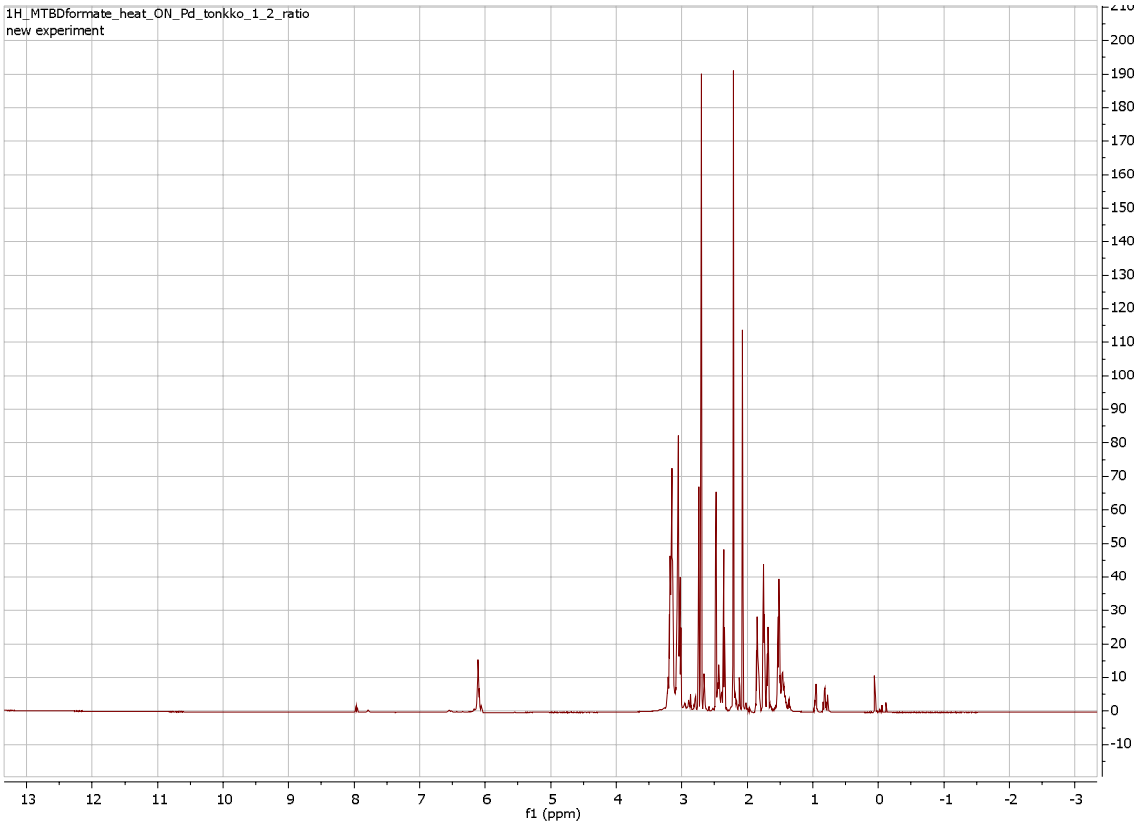
1H-NMR: 600 MHz, d6-DMSO, MTBD:FA 1:2 mixture heated 14 h without catalyst 150ºC



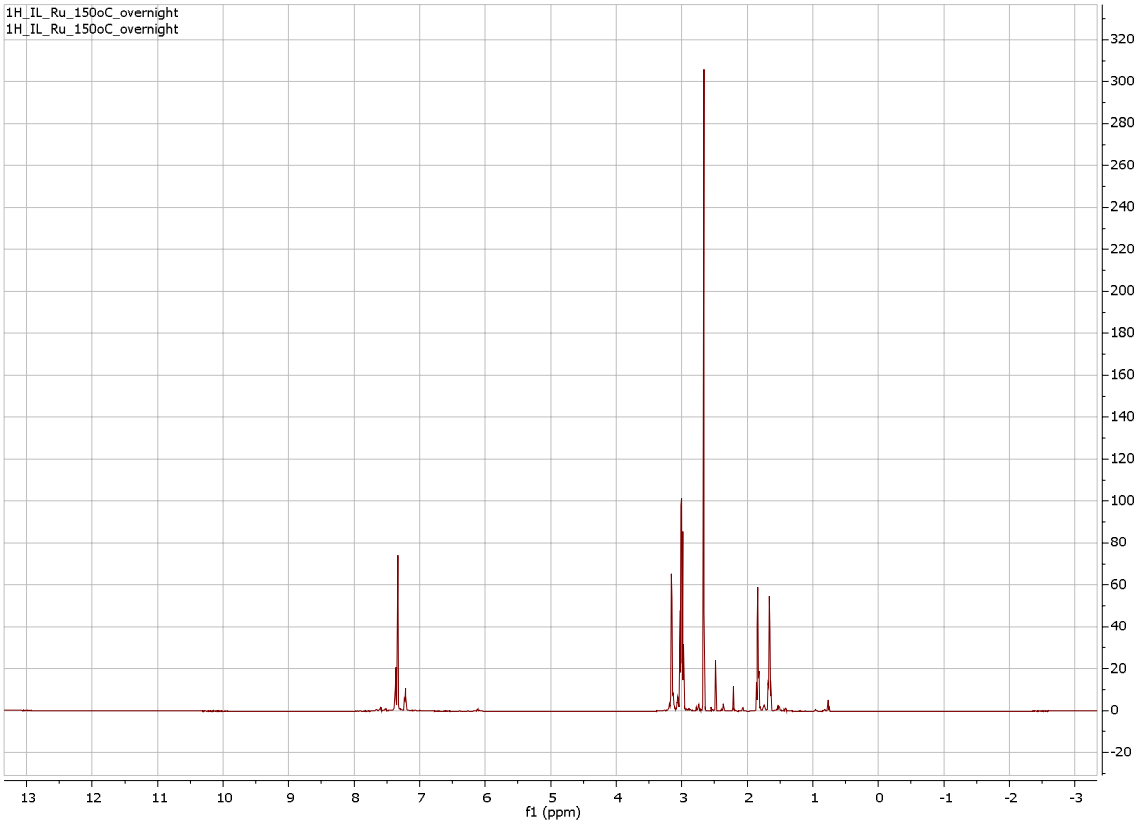
1H-NMR: 600 MHz, d6-DMSO, MTBD:FA 1:2 mixture heated 14 h with Pd(0)/C catalyst, 150ºC



1H-NMR: 600 MHz, d6-DMSO, MTBD:FA 1:2 mixture heated 14 h with $Pd(OAc)_2$ catalyst, 150ºC

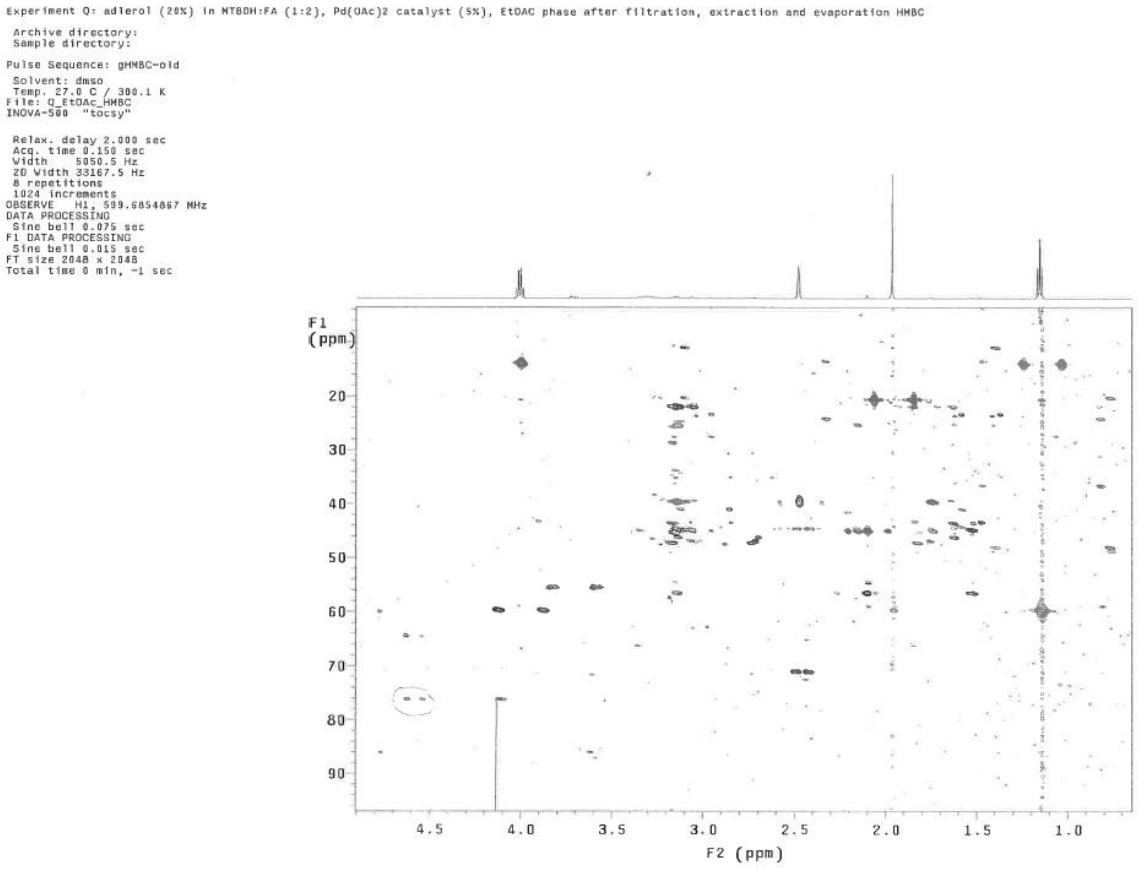


1H-NMR: 600 MHz, d6-DMSO, MTBD:FA 1:2 mixture heated 14 h with $[(Ph)_3P]Ru(II)Cl_2$ catalyst, 150ºC

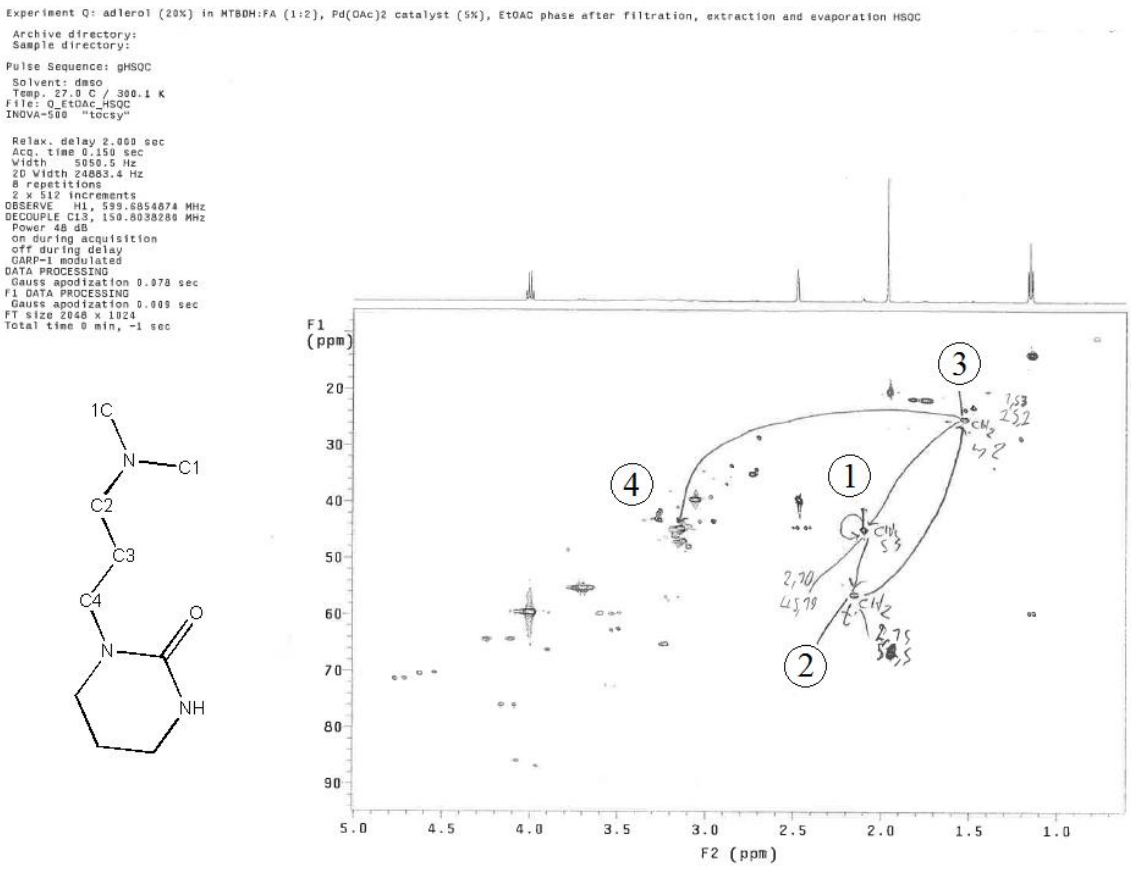


4.1.5 Reaction Series with Adlerol

HMBC of Case Q in the Reaction Series of Adlerol: 600 MHz, d6-DMSO

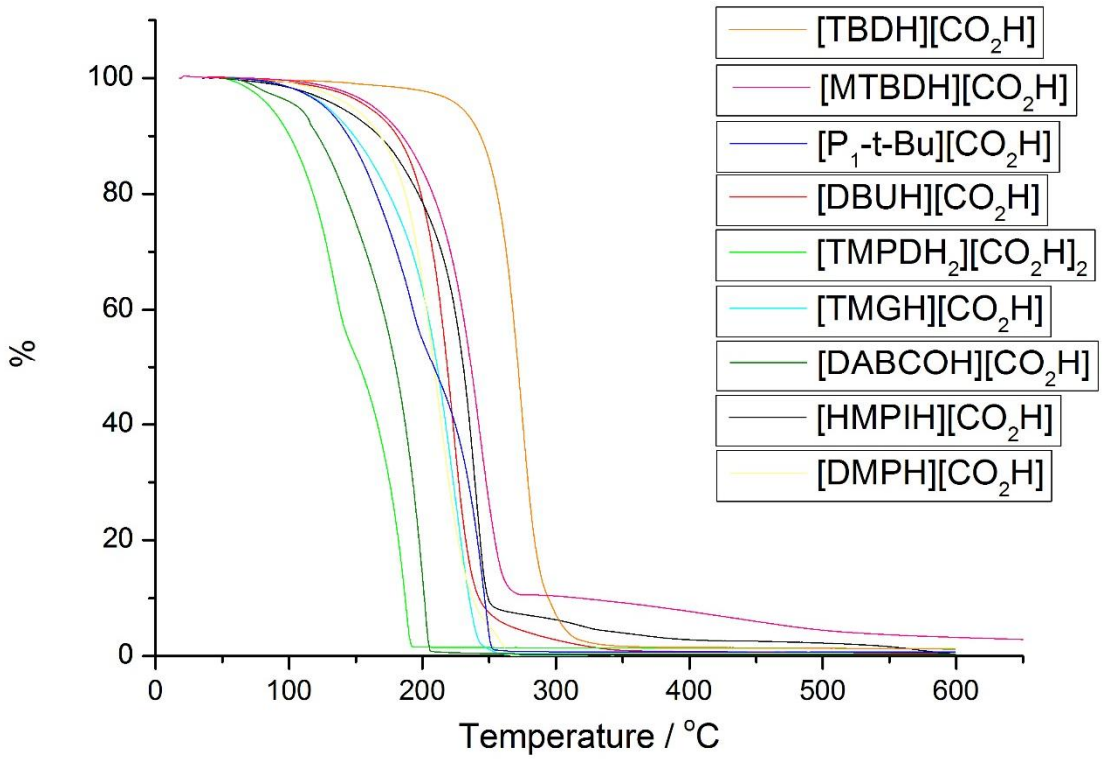


HSQC of Case Q in the Reaction Series of Adlerol[108]: 600 MHz, d6-DMSO



4.2 TGA Measurements

The TGA measurements of the bases 1-6 and 8-9 can be found in the figure below. TBD and MTBD showed the highest temperature range.



4.3 GC-MS

The GC-MS used was Bruker GC/MS with Scion MS.40, CombiPal.24, 456-GC.44, Pyrola 2000 Filament Pulse Pyrolyser and Bruker Autosampler. The sofware used Ms Data Review, Method Builder and MS Workstation. The concentration of the samples was in 1mg-3mg range in 1 ml EtOAc. The split ratio was 50 in every sample. The temperature program in every sample: 50°C for 2.00 min, the temperature was then raised with 30°C/min to 180°C and immediately continued to raise the temperature to 280°C in 40°C/min rate and kept there for 8.00 min. The total measure time was 16.83 and the measurement started at 3.00 min. The concentrations are reported in area-% because no control samples were used.

4.3.1 Pre-experiments with Cinnamaldehyde and Cinnamic alcohol

Substance	Ms	Retention time (min)
toluene	92	3.126
ethylbenzene	106	3.958
propylbenzene	120	4.693
propenylbenzene	118	5.213
benzenepropanal	134	6.006
benzenepropanol	136	6.386
cinnamaldehyde	132	6.602
cinnamyl alcohol	134	6.775
MTBD [1)]	153	7.500
1-propenyl-TBD (ATBD)	179	8.140
propyl-TBD	181	7.706

[1)] omitted from the following reaction reports

Pre-experiments

R1

Area-%	Substance
96.262	cinnamaldehyde

R2

Area-%	Substance
80.174	cinnamaldehyde

R3

Area-%	Substance
100.000	cinnamaldehyde

R4

Area-%	Substance
2.541	benzenepropanal
96.093	cinnamaldehyde

R5

Area-%	Substance
2.207	ethylbenzene
33.038	benzenepropanal
49.642	cinnameldehyde

R5 overnight

Area-%	Substance
7.066	benzenepropanal
8.333	benzenepropanol
12.901	cinnamaldehyde

Reaction series

RS1_ST

Area-%	Substance
1.005	ethylbenzene
21.394	propylbenzene
4.730	propenylbenzene
22.665	benzenepropanol
28.430	cinnamyl alcohol

RS1_1

Area-%	Substance
1.007	ethylbenzene
3.456	propylbenzene
12.992	propenylbenzene
34.316	benzenepropanol
48.223	cinnamyl alcohol

RS1_2

Area-%	Substance
1.090	ethylbenzene
3.858	propylbenzene
12.312	propenylbenzene
25.784	benzenepropanol
37.645	cinnamyl alcohol

RS1_3

Area-%	Substance
0.785	ethylbenzene
2.002	propylbenzene
12.574	propenylbenzene
38.371	benzenepropanol
41.413	cinnamyl alcohol

RS1_4

Area-%	Substance
0.816	toluene
2.704	propylbenzene
10.201	propenylbenzene
44.910	benzenepropanol
40.212	cinnamyl alcohol

RS1_5

Area-%	Substance
1.481	toluene
2.185	propylbenzene
13.985	propenylbenzene
37.762	benzenepropanol
42.737	cinnamyl alcohol

RS2_ST

Area-%	Substance
7.049	propylbenzene
92.765	benzenepropanol

RS2_1

Area-%	Substance
9.766	propylbenzene
90.234	benzenepropanol

RS2_2

Area-%	Substance
10.228	propylbenzene
89.772	benzenepropanol

RS2_3

Area-%	Substance
9.257	propylbenzene
90.742	benzenepropanol

RS2_4

Area-%	Substance
4.321	propylbenzene
95.679	benzenepropanol

RS2_5

Area-%	Substance
9.618	propylbenzene
90.382	benzenepropanol

RS2_6

Area-%	Substance
10.390	propylbenzene
24.198	benzenepropanal
65.413	benzenepropanol

RS3_1

Area-%	Substance
1.151	ethylbenzene
1.410	propylbenzene
2.660	propenylbenzene
33.496	benzenepropanol
61.383	cinnamylalcohol

RS3_2

Area-%	Substance
6.291	benzenepropanol
61.185	cinnamylalcohol

RS3_3

Area-%	Substance
0.136	ethylbenzene
16.840	propylbenzene
18.267	propenylbenzene

RS4_1

Area-%	Substance
22.696	benzenepropanol
41.623	cinnamyl alcohol

RS4_2

Area-%	Substance
2.615	propylbenzene
2.446	propenylbenzene
30.844	benzenepropanol
33.934	cinnamyl alcohol

Hydrogenation of allyl-TBD

allyl-TBD control

Area%	Substance
100	1-propenyl-TBD

allyl-TBD after hydrogenation

Area%	Substance
100	propyl-TBD

4.3.2 Reaction Series with Adlerol

Reaction	retention times	Suggested Compound(s)
adlerol (reference)	10.649	adlerol
guaiacol (reference)	5.546	guaiacol
A	10.357	adlerol monoester (1º alcohol)
B	10.357	adlerol monoester (1º alcohol)
C	10.360	adlerol monoester (1º alcohol)
D	10.612	adlerol
E	10.609	adlerol
F	10.603	adlerol
G	10.367	adlerol monoester (1º alcohol)
	9.521	catalyst impurity
	5.842	1,2-dimethoxybenzene
	5.544	guaiacol
H	10.365	adlerol monoester (1º alcohol)
	9.528	catalyst impurities
	5.545	guaiacol
I	10.314	adlerol monoester (1º alcohol)
	9.531	catalyst impurities
	5.844	1,2-dimethoxybenzene
	5.543	guaiacol
J	10.295	[1]
K	10.616	no reaction
L	10.614	no reaction
M	10.649	no reaction
N	10.615	no reaction
O	10.612	no reaction
P	10.316	adlerol monoester (1º alcohol)
	9.530	catalyst impurities
	5.843	1,2-dimethoxybenzene
	5.550	guaiacol
Q	10.286	[1]
R	10.616	no reaction

1 = 1,2-dimethoxy-4-(2-(2-methoxyphenoxy)propyl)benzene