NMR Characterization of LtL oil

by

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ABSTRACT

The need for energy is increasing sharply due to the rapid increase in the world's population and developing technologies, while the current energy resources with limited reserves are decreasing. Lignocellulosic biomass is the most viable choice for producing high value chemicals, liquid fuels, and energy from a renewable source. Lignin, in particular, is of interest because it serves as the only significant source of renewable aromatic carbon.

Lignin can be converted into bio-oil by Lignin-to-Liquid solvolysis, which includes addition of lignin, a hydrogen donor (formic acid) and a solvent into a high pressure/high temperature reactor and heating the reaction mixture, as a closed system.

The bio oil is a very complex mixture containing phenolic compounds, carbohydrates, furans, ketones, aldehydes, carboxylic acids, and water. In this thesis, nuclear magnetic resonance (NMR) spectroscopy, including 1H, ^{13}C, 2D HSQC spectra, was used to characterize the functional groups in LtL oil converted with different solvolysis conditions.

^{13}C NMR suffers from low sensitivity due to its low natural abundance and long relaxation times. The determination of optimum relaxation reagent Cr(acac)3 concentrations for quantitative ^{13}C has also studied.

ABBREVIATIONS

NMR	Nuclear magnetic resonance
$Cr(acac)_3$	Chromium (III) acetylacetonate
D1	Relaxation delay
DMSO-d_6	Deuterated dimethyl sulfoxide
FA	Formic acid
FT	Fourier Transform
FID	Free Induction Decay
FT-IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatography -Mass spectrometry
HSQC	Heteronuclear Single Quantum Coherence
LtL	Lignin-to-Liquid
ns	Number of scans
NOE	Nuclear Overhauser Enhancement
ppm	Parts per million ($x10^{-6}$)
TMS	Tetramethylsilane

CONTENTS

Chapter 1 Introduction

1.1 Potential of biomass

Environmental concerns and growing worldwide energy demands impel scientists to investigate alternative and renewable sources of energy, fuels, and materials to shift dependence away from the fixed supply of fossil fuels. The world is now in a transition state between an energy economy that, in most nations, has an overwhelming dependence on petroleum, natural gas, and coal, to a new energy economy that will be based heavily on alternative, renewable sources of energy, including fuels derived from plants[1]. As world demand for liquid transportation fuels grows, the surplus production capacity of traditional petroleum reservoirs is approaching a vanishingly small margin, resulting in upward pressure on the global price of petroleum. Coupling this with increasing volatility in the price and uncertainty of supply, many national programs encouraging domestic production of fuels have arisen, typically focused on the use of domestic biomass resources to meet demand for liquids[2].

Biomass can be utilized for the production of process heat, steam, motive power, and electricity, and can be converted by thermal or biological routes into a range of useful energy carriers such as liquid fuels and synthesis gas. Figure 1-1 illustrates a fully integrated biorefinery cycle. The term biomass is used to describe any material of recent biological origin and includes plant materials such as trees, grasses, and agricultural crops, as well as animal manure and municipal biosolids. As a raw material, biomass is a nearly universal feedstock due to its domestic availability and renewability. Indeed, until the widespread utilization of crude oil as an energy source in the 19th century, biomass supplied the majority of the world’s energy needs. In one sense, the situation has now come full circle: concern over the environmental effects of fossil-fuel combustion, as well as disquiet about dwindling petroleum reserves - coupled with increasing global energy demand - have brought about a resurgence of interest in the utilization of biomass as an energy source[2].

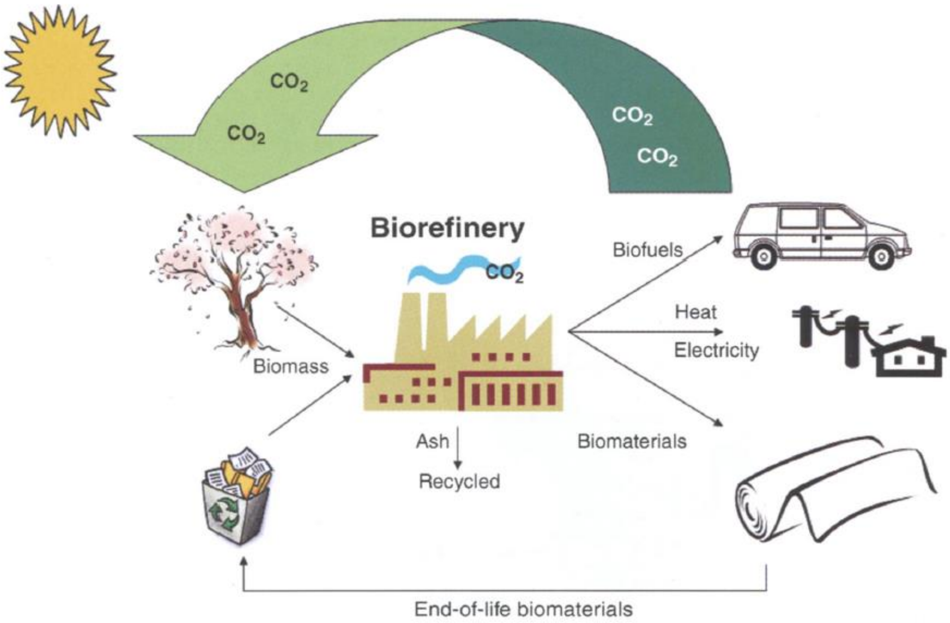


Figure 1-1 The fully integrated agro-biofuel-biomaterial-biopower cycle for sustainable technologies[3]

The benefits most frequently cited for biomass utilization as an energy source can be summarized as follows[4, 5]:

- Fuel-supply diversification: biomass is a widespread resource, the utilization of which can diversify the fuel supply and in turn lead to an energy supply that is more secure, i.e. less subject to geopolitical constraints.

- Reduction of greenhouse gases: substituting fossil fuels with biofuels can lead to a reduction in greenhouse gases, principally CO_2. This stems from the fact that the amount of CO_2 released from combustion of the biomass is inherently equal to that fixed by the plant during its growth. However, the extent of greenhouse-gas reduction is dependent on a number of factors, including the degree to which fossil fuels are used in the production and distribution of biofuels. Another consideration is the extent to which stored CO_2 is released to the atmosphere during the clearing and tilling of grassland and forests that are to be used for biomass cultivation.

- Increased rural income: the increased agricultural activity associated with the production of energy crops can generate employment in rural areas and result in increased farm income, thereby reversing the trend of rural depopulation prevalent in many countries.
- Restoration of degraded land: If appropriate crops are selected, degraded land (currently unsuited for the production of food crops) can be utilized for biofuels production.

Given its abundance and affordability, lignocellulosic biomass (Figure 1-2) that consists of cellulose, hemicellulose and lignin has been extensively investigated and utilized to obtain fuels, such as bioethanol, biodiesel, hydrocarbon fuels, and chemicals[6].

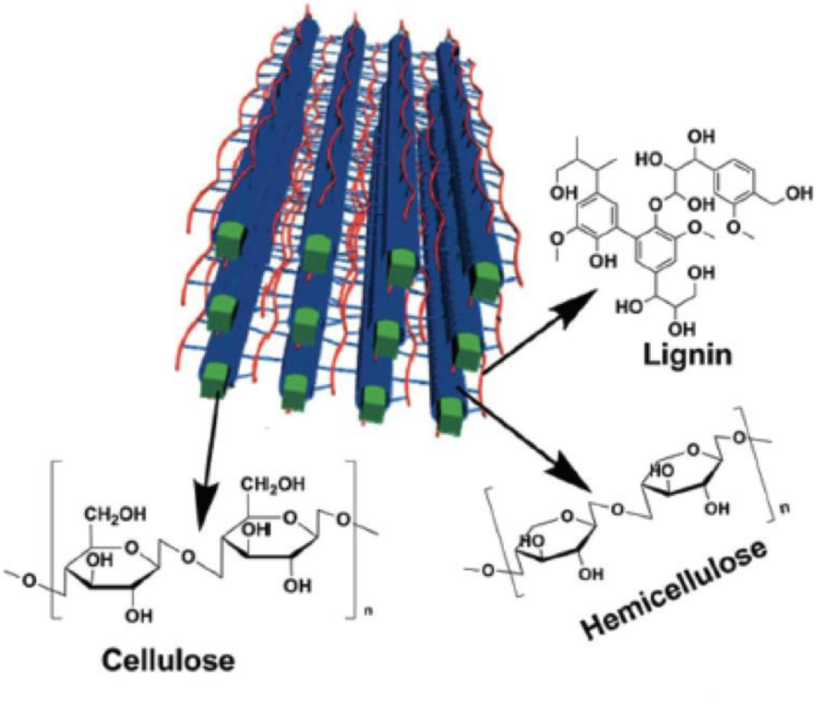


Figure 1-2 Schematic analysis of the location and structure of three components in the lignocellulosic biomass[7]

Cellulose is a high molecular weight polymer that consists of linear β-1,4 glycoside linked chains of D-glucose units[8], whereas hemicellulose is a heterogeneous polymer that comprises several different types of monosaccharides. Lignin is one of the most abundant natural polymers (only second to cellulose), which constitutes 20%-30% of the weight of lignocellulosic biomass[9]. From the perspective of high energy content and polymer structure, lignin is considered a promising source of renewable fuels and chemicals.

1.2 Lignin

Lignin is present in most of the terrestrial plants with content varies from 10-40% and to lend rigidity to cell walls[10, 11].Currently, lignin is a by-product mostly from pulp and paper industry, and the so-called “black liquor” which is the discarded lignin stream has long been underutilized [12]. Also, with the development of biorefinery industry, biorefinery lignin also becomes more available in recent years. Therefore, finding value-added applications for biorefinery lignin is of great importance. Lignin provides all vascular plants, such as woody plants and trees, their rigidity and water-impermeability and protects them against microbial and fungal destruction of cellulosic fibres [13].Lignin has aromatic structures and relatively high carbon content, which make them a good candidate for producing carbon-based materials. Lignin is also bio-degradable and renewable that is desired to maintain an environmentally friendly, sustainable and carbon-neutral community[14].

However, lignin does not have well-defined structures and properties. The complex structure of lignin contains numerous ether linkages, –OH groups, and methoxy groups. This cross-linked macromolecule composed of three types of monolignols, also known as phenolic monomers, including p-coumaryl alcohol (H), coniferyl alcohol (G) and sinapyl alcohol (S) as shown in Figure 1-3 [15].

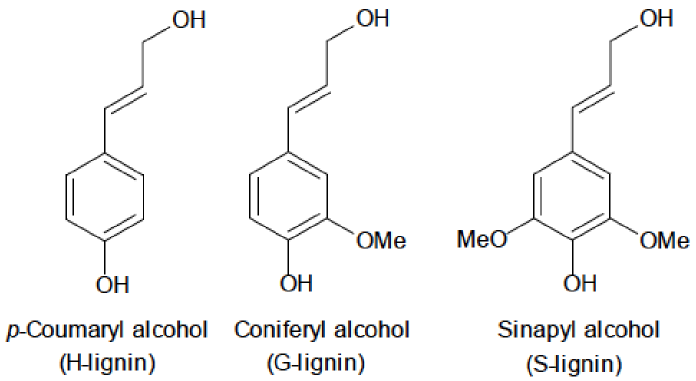


Figure 1-3 The three types of monolignols in lignin

These three units are inter-crosslinked via in-situ free radical polymerization to form a three dimensionally complex network. Figure 1-4 shows these units are interconnected through various interunit linkages α-O-4, β-O-4, β-β, β-1, β-5, 5-5', and 4-O-5 macromolecular lignin.

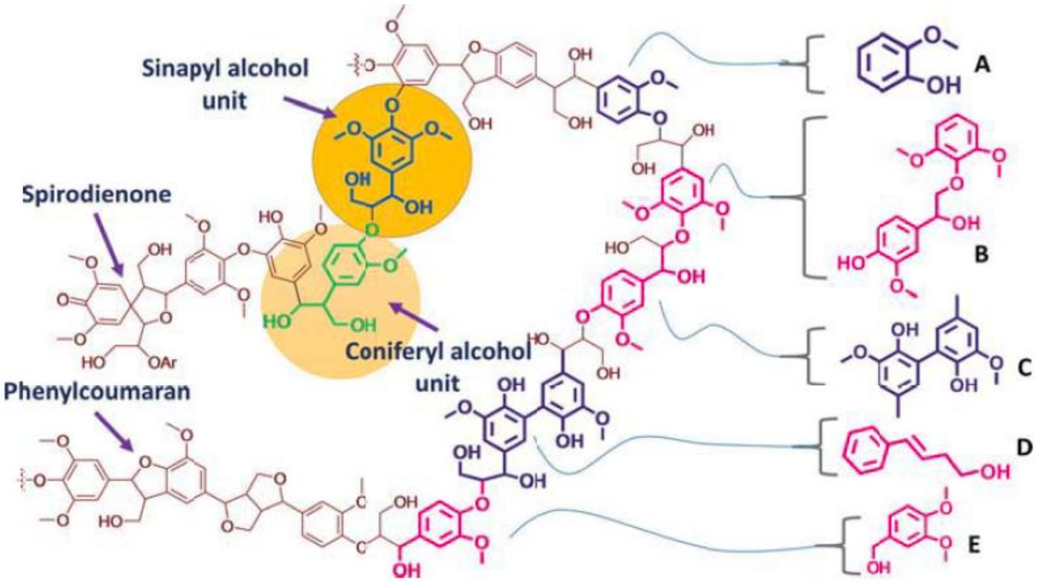


Figure 1-4: Schematic depiction of lignin showing various linkages and lignin model compounds. Model (A) phenol and methoxy functionalities, (B) a β-O-4 linkage, (C) a 5-5' linkage, (D) a propyl side chain, and (E) a benzylic group. [16]

Lignification typically occurs after the polysaccharides have been laid down in the cell wall[17].The units in the lignin polymer are linked by a variety of chemical bonds that have different chemical properties. Lignin composition varies among plant species:

- with some exceptions, lignin from gymnosperms is composed of G-units only (with minor amounts of H-units);
- angiosperm dicot lignin is composed mainly of G- and S-units (with very little H);
- lignin from grasses (monocots) contains G- and S-units at comparable levels, and more H-units than dicots. [18]

The majority of secondary wall formation in most plants occurs in the water conducting cells of the xylem, which tend to be enriched in G lignin, and in the structural fibers, which in angiosperms typically contain higher levels of S subunits[19].Lignified cell walls are also found in sclereid cells, endodermal tissue in roots, and in specialized cells of anthers and some seed pods, where they are important for the dehydration-driven release of pollen and seeds, respectively. The wood of both gymnosperm and angiosperm trees is composed largely of the secondary cell walls of vascular tissue and associate fibers, and as such, of lignin. It is important to note that lignin biosynthesis is also of crucial importance in herbaceous (non-woody) species.

Less abundant units than the three main monolignols have been identified from a variety of species and may be incorporated into the polymer at varying levels[18]. Particularly common, less abundant subunits include ferulates (which form crosslinks between lignin and hemicelluloses), conifer aldehyde, and acylated monolignols containing acetate, p-coumarate, or p-hydroxybenzoate moieties[19]. Lignin composition also varies among cell types and can even be different in individual cell wall layers. Lignin composition is also influenced by environmental conditions; for example, lignin in compression wood is enriched in H-units[17]. Hence, both developmental and environmental parameters influence the composition and, thus, the structure of the lignin polymer.

Following their synthesis in the cytoplasm, lignin monomers are exported to the extracellular space (the apoplast) for incorporation into the lignin polymer[19]. After reaching the apoplast, monolignols undergo single-electron oxidation by wall-bound laccases and/or peroxidases to form radical species. Then bond formation can occur between two such radicals (any combination of two monolignols, a monolignol and an elongating polymer end, or two polymer ends) in a process known as bimolecular radical coupling. Alternatively, activated monolignols can be involved in a radical transfer reaction.

The three different monolignols, and the subunits derived from them can freely form bond with one another[19]. Depending on the ring-substitution pattern of the molecules (H, G and S) and their location (free or attached to the polymer), multiple sites may be available for bond formation, resulting in a variety of potential coupling patterns, mainly including β-O-4, β-5 and β-β linkages as the central (β) carbon of the monolignol tail is most frequently involved, see an example of lignin structure predicted by NMR analysis in Figure 1-5.

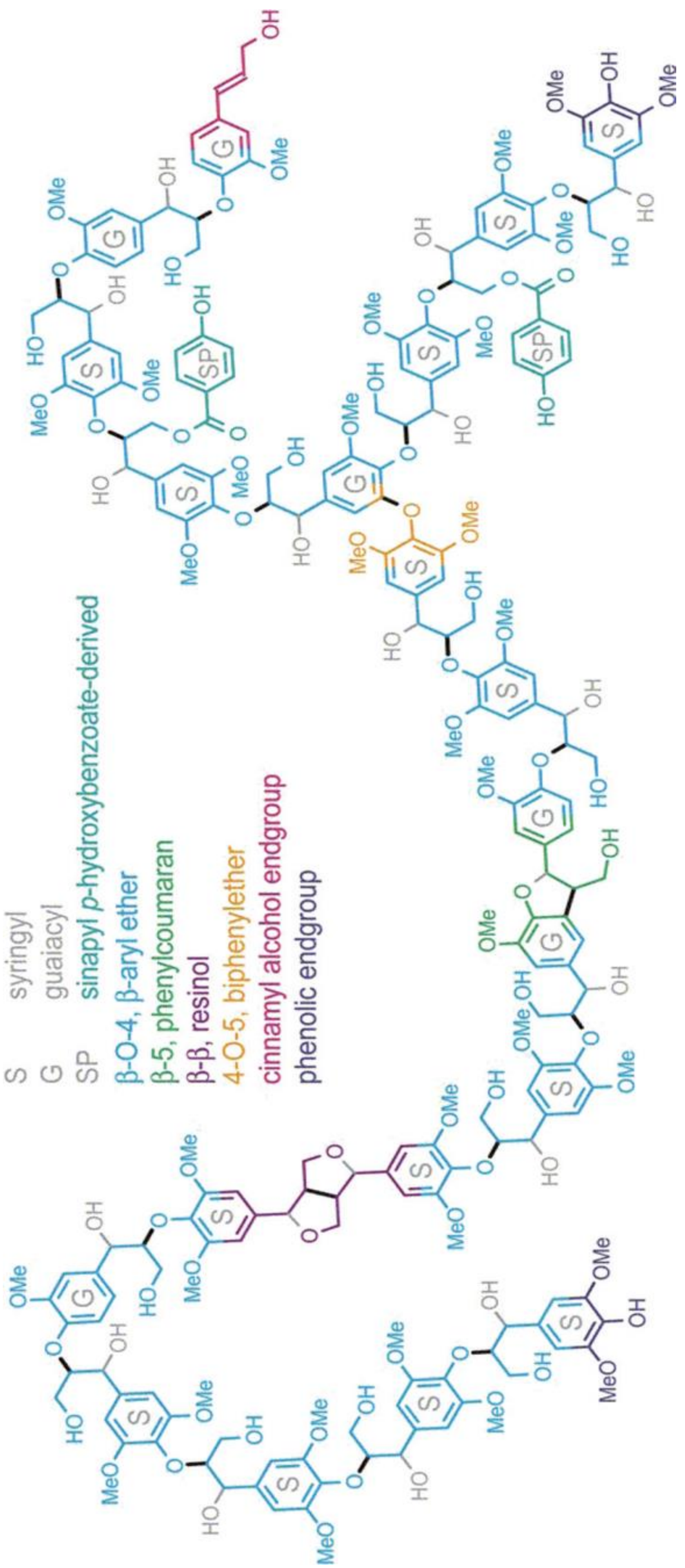


Figure 1-5 Lignin polymer from poplar, as predicted from NMR-based lignin analysis. [18]

1.3 Thermal conversion process

Lignocellulosic biomass feedstock can be converted to biofuels and chemicals through multiple processes. Conversion technologies fall into two main categories: biochemical conversion and thermochemical conversion. The thermochemical platform for conversion of lignocellulosic biomass aims to efficiently produce biofuels and chemicals via processes that use heat and chemistry[20].

There are three main thermal processes available for converting biomass to a more useful energy form – pyrolysis, gasification and combustion. Figure 1-6 summarizes their products and applications[2]. monoxide and hydrogen known as synthesis gas or syngas.

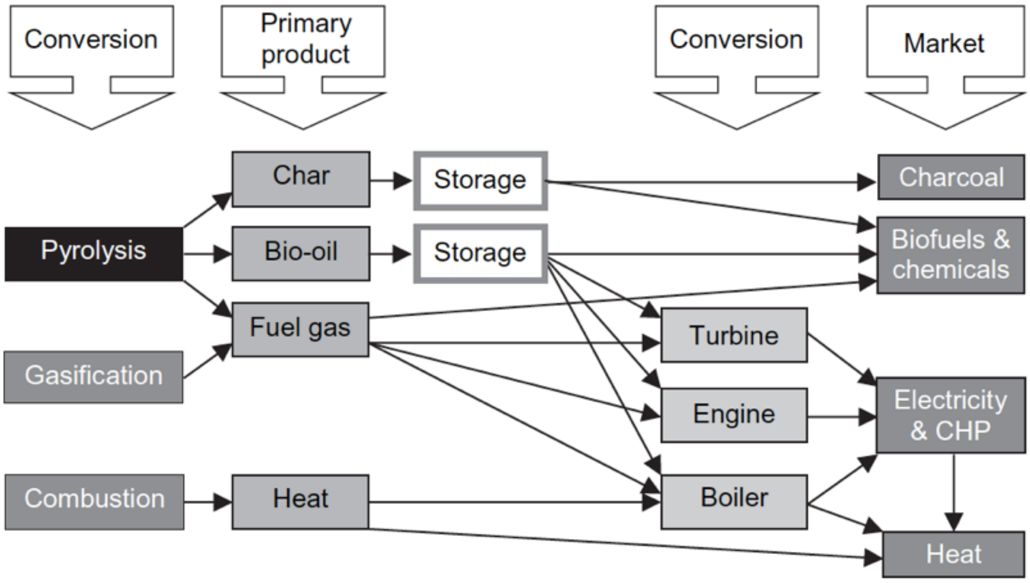


Figure 1-6 Products from thermal biomass conversion.[2]

Combustion is the thermal conversion of organic matter with an oxidant (generally oxygen) to produce primarily carbon dioxide and water. The oxidant is in stoichiometric excess, i.e. complete oxidation. Biomass combustion mainly leads to heat energy which can be utilized for steam and/or electricity production[21].

Gasification is the thermal conversion of organic matter at elevated temperatures and in oxygen-deficient conditions (reducing conditions) to produce primarily permanent gases, with char, water, and condensable as minor products. The main permanent gases resulting from biomass gasification are the mixture of carbon

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is always also the first step in combustion and gasification, but in these processes, it is followed by total or partial oxidation of the primary products. Lower process temperatures and longer vapor residence times favor the production of charcoal. High temperatures and longer residence times increase biomass conversion to gas, and moderate temperatures and short vapor residence time are optimum for producing liquids. Three products are always produced, but the proportions can be varied over a wide range by adjustment of the process parameters.

1.4 Lignin-to-Liquid (LtL) solvolysis

Solvolysis is pyrolysis in the presence of a solvent. The process is known as direct liquefaction although this overlooks the prospects for also fractionating or gasifying biomass via solvolysis [2]. A variety of solvents can be employed, their physical and chemical properties determining the temperature and pressures at which the processes operate. Because water is a major constituent of biomass, it is frequently used as a solvent, in which case solvolysis is referred to as hydrothermal processing. In comparison to atmospheric pyrolysis, solvolysis provides the advantages of milder conditions and a single-phase environment due to the miscibility of the organic products in the (supercritical) solvent. Anthracene, water and ethanol have been shown to have suitable solvent properties in this context. Especially ethanol has been reported to have a very high solvency for biomass and a low critical temperature which makes it attractive for lignin depolymerization[22].

A promising and relatively new lignin reductive conversion methodology is the Lignin-to-Liquid (LtL) process. In the LtL process the lignin is converted at moderate temperatures in the presence of two additional compounds: (i) formic acid (FA) as a substitute of molecular hydrogen, and (ii) a solvent, mostly ethanol or water. Figure 1-7 depicts the main conversion route during LtL solvolysis, excluding aliphatic reaction products from the equation, as the most recent publications report aromatics to be the dominating product structures. solvolysis, excluding aliphatic reaction products from the equation, as the most recent publications report aromatics to be the dominating product structures.

Formic acid (FA) acts, together with a co-solvent, as an in situ hydrogen donor in the liquid reaction medium during LtL-solvolysis, providing depolymerization and hydrodeoxygenation of the lignin copolymer. Thermal degradation products of FA provide CO and H_2O or CO_2 and H_2 with the latter as the preferred decomposition pathway[23]. FA has shown to deliver reactive hydrogen upon degradation during LtL-solvolysis, together with CO_2, in a more reactive way than for H_2 gas[22].

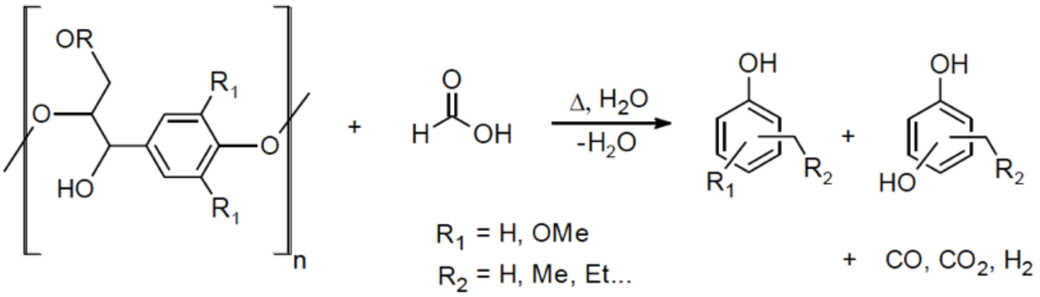


Figure 1-7 :Overview of the main conversion route; Lignin is a methoxylated, phenolic polymer which in course of the solvolytic reaction is degraded to phenol monomers with different substitution patterns and aliphatic compounds. Simultaneously a hydrodeoxygenation occurs in which formic acid (FA) serves as the hydrogen donor. Water is generated during the reaction[24].

The solvent is added to create a more homogeneous reaction environment and increase the mass and heat transfer rates. This allows operating at milder reaction conditions and increases the selectivity towards the production of bio-oil. Water is considered as a promising reaction media due to its abundance, low cost and green nature, although it has a low ability to solubilize most type of lignin. Ethanol has also been identified as one of the most promising alternatives due to is very good solvent properties for biomass and low critical temperature; furthermore, it is one of the main fuel type products obtained from the conversion of lignocellulosic feedstock[25].

1.5 NMR characterization of bio-oil

1.5.1 Analysis methods of bio-oil

To understand the possible decomposition pathways of lignin and to find an effective upgrading method, several analytical techniques have been employed to analyze bio-oil. Popular analytical techniques which have been widely employed for bio-oil analysis are gas chromatography (GC), high performance liquid chromatography (HPLC), GPC, GC–MS, liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS), Fourier transform infrared spectroscopy (FTIR), NMR and thermo gravimetric analysis (TGA)[26]. In bio-oil analysis, results from many analytical techniques complement each other leading to unequivocal identification of its chemical components. Important prerequisite of GC based detection is the volatility of analyses due to which gases, volatile non-polar and chemical derivatives of polar organic compounds in bio-oils are largely amenable. HPLC is usually associated with the analysis of polar and thermo-labile organic compounds. Mass spectrometer is a powerful detector to chromatographic systems as well as an independent technique for studying behavior of molecules and advanced gaseous phase reactions. GC–MS and LC–MS have immensely contributed in the identification of bio-oil components. FTIR analysis reveals presence of functional groups in compounds and helps in establishing molecular structure. NMR is essential in determining the nature and types of covalently bonded nuclei (hydrogen or carbon) within a molecule. It gives an estimated number of such nuclei under observation through peak area integrations.

GC-MS analysis

Mass spectrometry (MS) provides crucial elemental and structural composition of organic molecules. Key technological advancements in sample introduction, ionization, and analyzers in the past two decades have revolutionized the research which has largely focused upon biological perspectives. Bio-oils have comparable degree of compositional complexity; hence sufficient scope exists in the investigations utilizing higher mass resolving power of MS to extract accurate molecular level information. Researchers in of the area of bio-oil analysis have extensively involved quadrupole analyzer based mass spectrometers. This analytical approach is quite suitable for characterization of small molecular weight organic compounds from aliquots obtained after sample preparation and offers labor and cost effectiveness. The analysis may involve GC to introduce sample to achieve chromatographic separations. The obtained results are conclusive in electron ionization (EI) mode since mass spectral database exists.

GC-MS library search gave a tentative identification of the compounds present in the bio-oils. There are approximately a hundred compounds were detected in lignin bio oil by GC-MS and almost all of them contain a phenol structure. Furthermore, phenol, acetovanillone, cresols, guaiacol, 4-ethylphenol, syringaldehyde, acetosyringone, 4-methylguaiacol, catechol, 3-methylcatechol, 4-methylguaiacol, 4-vinylguaiacol, vanillin, syringol, eugenol isoeugenol, and acetovanillone have been reported.[27]

Figure 1-8 depicts an example of GC-MS chromatogram showing a representative structural distribution for the LtL-oils[28].

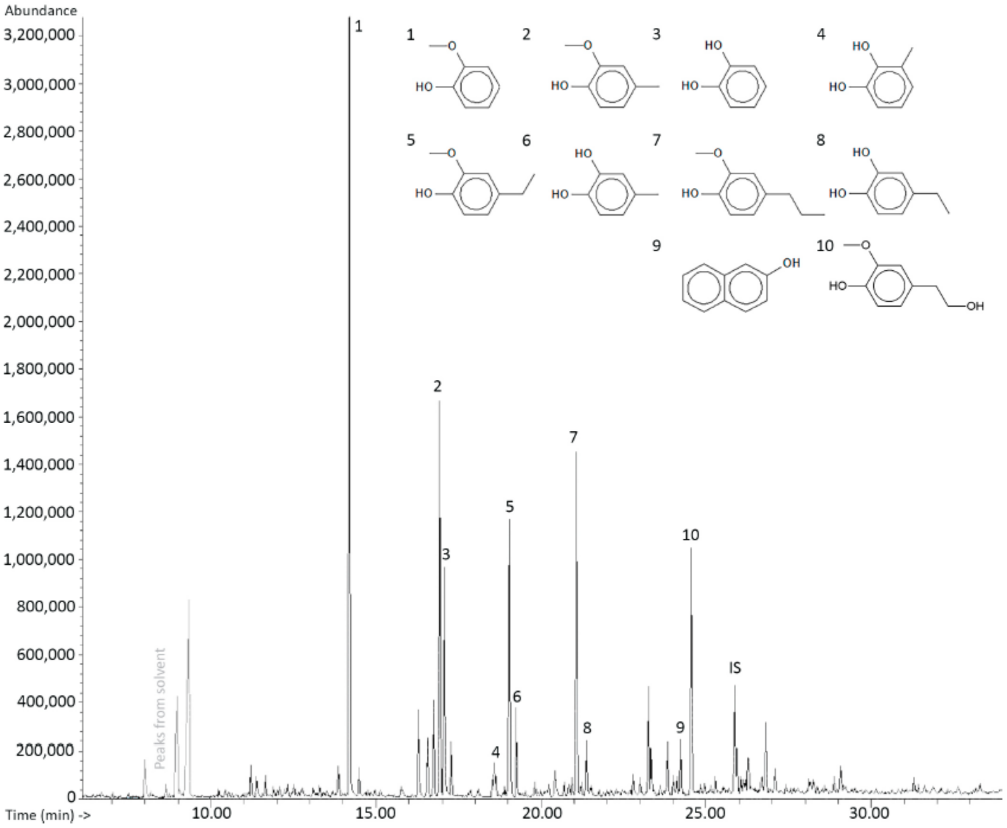


Figure 1-8 Chromatogram of a LtL-oil representing a typical compositional distribution.

FTIR analysis

Due to the limitation of volatility of high molecular weight components in the lignin bio-oil, it has been indicated that there are only about 40 % of lignin bio-oil that could be detected by GC[13]. Therefore, many researchers also try to find alternative characterization method which could analyze the whole portion of pyrolysis oil, such as FTIR. In FTIR analysis, mid-infrared region is extensively utilized to reveal the presence of various functional groups in molecules. FTIR analysis is of vital significance to study the fundamental vibrations and associated rotational–vibrational structure within a molecule. Scientific literature contains huge information on updates and upcoming trends in modern infrared spectroscopy.

1.5.2 NMR analysis of bio-oil

Nevertheless, the complexity of the lignin bio-oil limits the use of these instruments due to different issues and consequently many chemical components could not be identified. Therefore, the main goal of the present study was to investigate the structures of lignin bio-oil under different conversion conditions. Most recently, some research workers introduce NMR, including quantitative ^{1}H, ^{31}P, and ^{13}C-NMR, and semi-quantitative HSQC-NMR to characterize bio oils[29]. Such investigations improve understanding about lignin conversion mechanisms, which leads to more control in the degradation pathways.

Nuclear magnetic resonance (NMR) is one of the important spectroscopic techniques employed in analytical and bioanalytical chemistry. NMR spectrometers are sophisticated and largely present in research and academic institutions across the world. The operating frequencies of modern NMR spectrometers have extraordinarily increased to nearly 1 GHz. The technique is nowadays essentially employed in range of experiments on solid, liquid, and gaseous samples, over a wide temperature span. Inherent limitation associated with NMR is its relatively low sensitivity as compared to other spectroscopic techniques. Hence, trace and ultra-trace level quantitation are always represented by poor limits of detection that is several orders of magnitude poorer than mass spectrometry or emission/absorption/fluorescence based techniques. NMR is exceptionally used in the structural analysis of petroleum fractions. It is an essential tool for carrying out group type analysis and directly measures aromatic and aliphatic carbon and hydrogen distributions. It also provides important information on the carbon and hydrogen structural groupings in a molecule. ^{13}C NMR studies of coal and asphaltenes are the pioneer NMR applications in petroleum analysis[30].

In bio-oil analysis, major advantages of NMR are that the whole bio-oil can be dissolved in a suitable solvent and a qualitative assessment of the oxygen containing functionalities can be determined simply from integration of appropriate regions of the

^{13}C and ^{1}H NMR spectra. Bio-oils have been largely studied with NMR and the ^{13}C NMR spectra are particularly instructive because of their large chemical shift regions. ^{13}C and ^{1}H NMR offer a reasonable trade-off between functional group identification and analytical measurement effort. Accuracy however depends upon selection of chemical shift regions, baseline compensation, and correction for incomplete longitudinal relaxation effects.

NMR techniques are used to quantitatively identify functional groups in bio-oil. NMR methods previously used for biomass and products from thermochemical conversion of biomass[29]. Proton NMR is widely applied in bio-oil characterization. Figure 1-9 presents typical assignments of an ^{1}H NMR spectrum for bio-oil from pinewood[29].

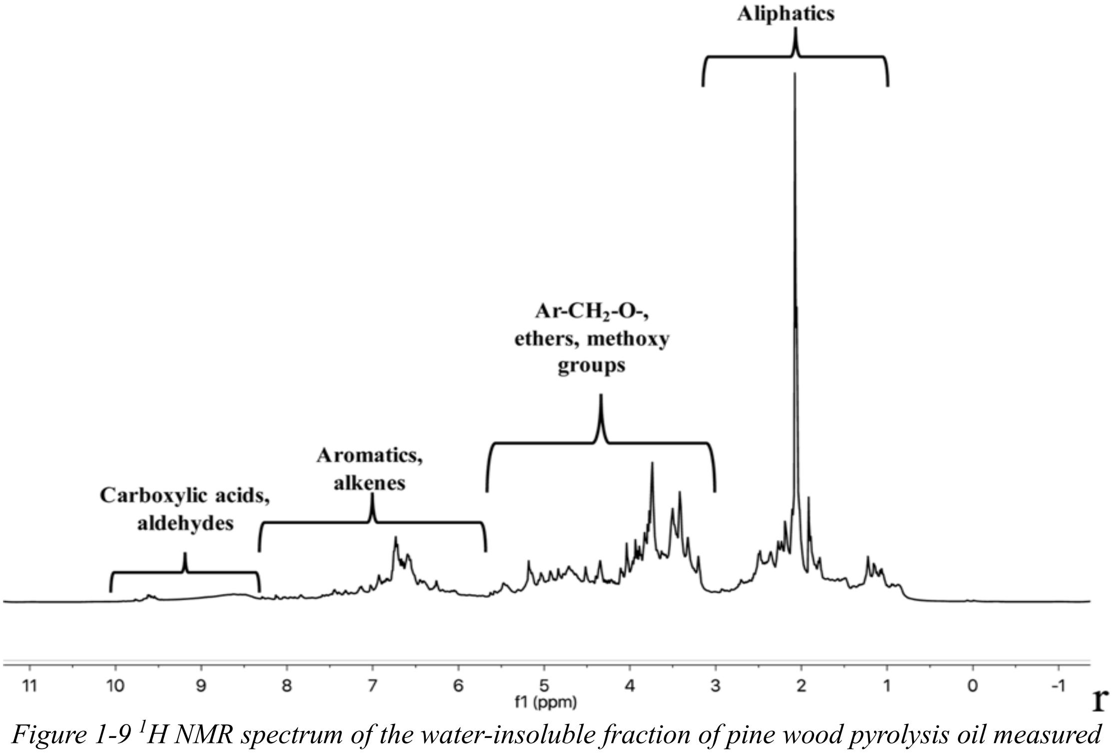


Figure 1-9 ^{1}H NMR spectrum of the water-insoluble fraction of pine wood pyrolysis oil measured in DMSO-d6 [29]

^{13}C NMR spectroscopy provides carbon information on bio-oil components. In comparison to a ^{1}H NMR spectrum, a ^{13}C NMR spectrum benefits from a broader chemical shift range, which means less spectral overlap. The limitation of quantitative ^{13}C NMR is its low sensitivity and long experiment time due to the low natural abundance of ^{13}C nuclei and pulse delay times. An example of the characterization of phenolic compounds of the bio-oil obtained from spruce wood in ^{13}C NMR spectra are shown in Figure 1-10 [31]. A typical structural assignment range of functional groups was developed, and this analysis is summarized Table 1-1 [32].

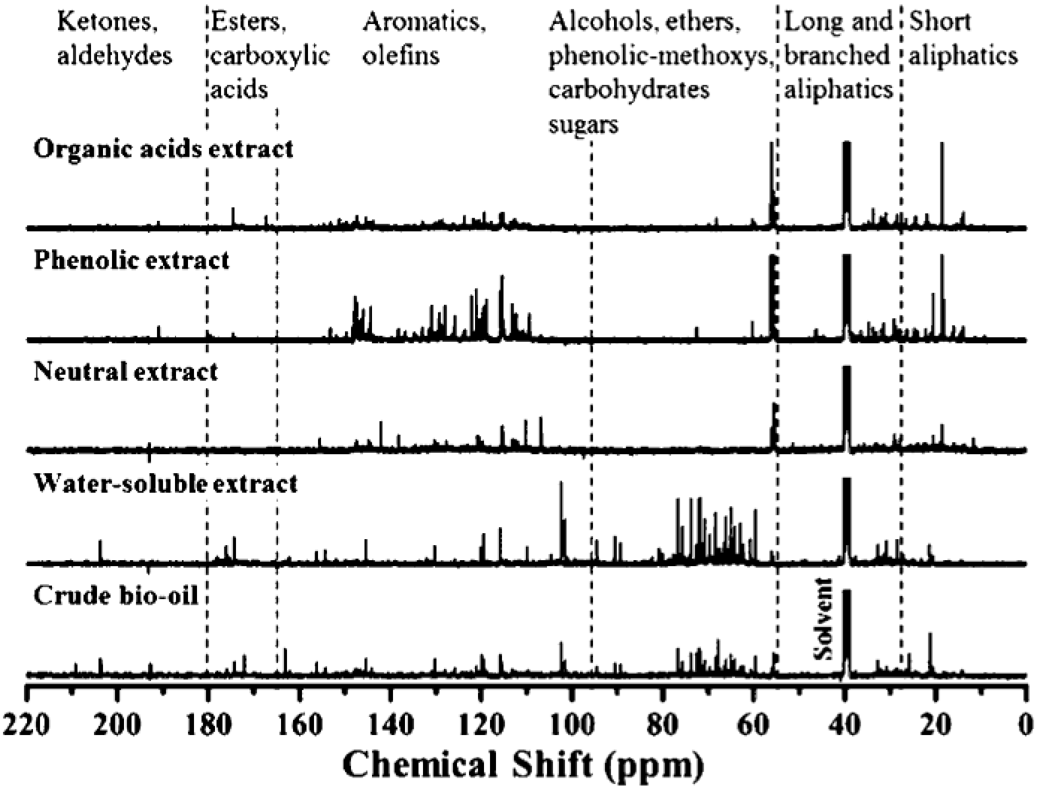


Figure 1-10 ^{13}C NMR spectra of the crude bio-oil, water-soluble extract, neutral extract, phenolic extract, and organic acids extract.[31]

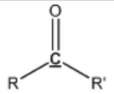
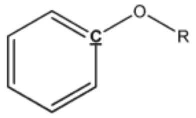
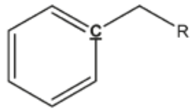
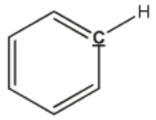
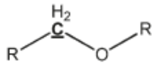
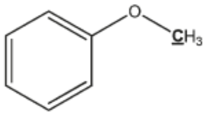
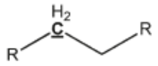
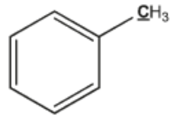
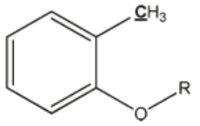
Functional group		Integration region (ppm)	Examples
Carbonyl or Carboxyl bond		215.0 – 166.5	
Aromatic C-O bond		166.5 – 142.0	
Aromatic C-C bond		142.0 – 125.0	
Aromatic C-H bond		125.0 – 95.8	
Aliphatic C-O bond		95.8 – 60.8	
Methoxyl-Aromatic bond		60.8 – 55.2	
Aliphatic C-C bond	General	55.2 – 0.0	
	Methyl – Aromatic	21.6 – 19.1	
	Methyl – Aromatic at ortho position of a hydroxyl or methoxyl group	16.1 – 15.4	

Table 1-1 A ^{13}C NMR Chemical Shift Assignment Range of Lignin bio-oil [32]

The chemical components of bio-oil are very complex, and only about 40 wt % could be analyzed by GC[13]. In addition, FT-IR has a limited ability to quantitatively analyze complex pyrolysis mixtures. In contrast, NMR has a much higher resolution and provides detailed structural information of lignin bio-oils. The possible pathway of primary decomposed functional groups- aliphatic hydroxyl, carboxyl, and methoxyl groups and ether bond, in lignin bio-oil conversion is shown in Figure 1-11[30].

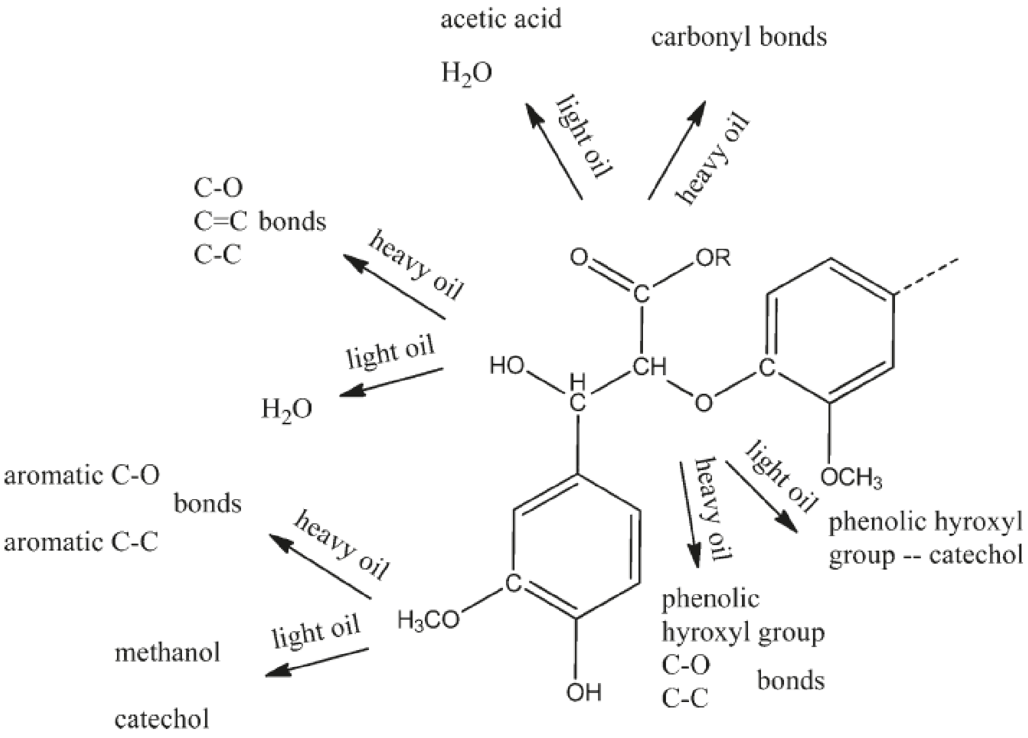


Figure 1-11 Possible pathway of primary decomposed functional groups in lignin bio-oil.[30]

Chapter 2 Method

Various NMR experiments have been employed to better understand the components and structures of thermally generated bio-oils. ^{1}H and ^{13}C NMR analyses have been widely used to investigate the structural hydrogen-carbon framework of bio-oils. Moreover, selective analysis of functional groups in the bio-oils through NMR analysis techniques allows a deep understanding of the characteristics of bio-oils.

2.1 Nuclear magnetic resonance introduction

2.1.1 Basic principle of NMR

Nuclear magnetic resonance, or NMR as it is abbreviated by scientists, is a phenomenon which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon, and others do not, dependent upon whether they possess a property called spin. Most of the matter the composed of molecules can be examined with NMR. Molecules are composed of atoms which can be thought of as a small magnetic field and will cause the nucleus to produce an NMR signal.

The nuclei of many elemental isotopes have a characteristic spin (**I**). Some nuclei have integral spins (e.g. I = 1, 2, 3 ....), some have fractional spins (e.g. I = 1/2, 3/2, 5/2 ....), and a few have no spin, I = 0 (e.g. ^{12}C, ^{16}O, ^{32}S, ...). Isotopes of particular interest and use to organic chemists are ^{1}H, ^{13}C, ^{19}F and ^{31}P, all of which have I = 1/2. Since the analysis of this spin state is straightforward, our discussion of nmr will be limited to these and other I = 1/2 nuclei. The following features lead to the nmr phenomenon:

1) A spinning charge generates a magnetic field, as shown by the animation on the right. The resulting spin-magnet has a magnetic moment (**μ**) proportional to the spin shows in Figure 2-1.

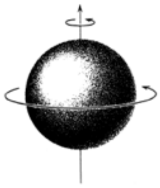


Figure 2-1 Spinning creates a magnetic moment.

2) In the presence of an external magnetic field (**B_0**), two spin states exist, **+1/2** and **-1/2**. The magnetic moment of the lower energy +1/2 state is aligned with the external field, but that of the higher energy -1/2 spin state is opposed to the external field.

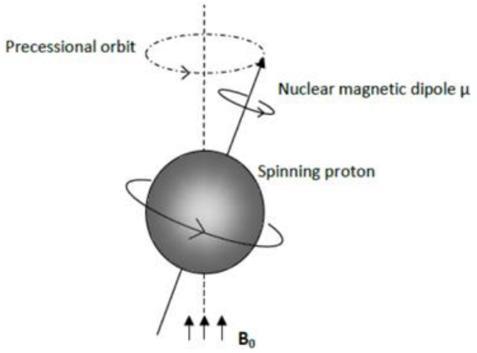


Figure 2-2 Representation of a precessing proton in a stationary magnetic field B_0

3) The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small. The Figure 1-3 illustrates that the two spin states have the same energy when the external field is zero, but diverge as the field increases.

The energy difference **ΔE** between the spin energy states can be rewritten in terms of frequency units **ν**:

$$\Delta E = h\nu \qquad \text{Eq.2-1}$$

where h is Plankcs constant equal to $6.6256 * 10^{-34}$ J s

Transitions between the spin energy states occurs at the Lamor frequency **ν_o**:

$\mathbf{v_o} = \gamma B_0/2\pi$ Eq.2-2

where the proportionality factor gamma is a constant for the isotope of each element and is called the magnetogyric (or gyromagnetic) ratio.

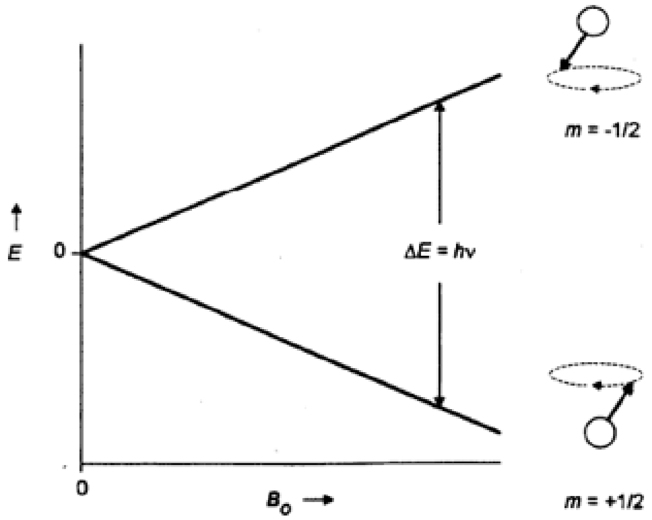


*Figure 2-3 The energy difference Δ**E** between the spin energy states*

The signal in NMR spectroscopy results from the difference between the energy absorbed by the spins which make a transition from the lower energy state to the higher energy state, and the energy emitted by the spins which simultaneously make a transition from the higher energy state to the lower energy state. The signal is thus proportional to the population difference between the states. NMR is a rather sensitive spectroscopy since it is capable of detecting these very small population differences. It is the resonance, or exchange of energy at a specific frequency between the spins and the spectrometer, which gives NMR its sensitivity.

2.1.2 Chemical shift

All proton resonances do not occur at the same position. The Larmor precession frequency (ν_o) varies because the actual magnetic field B at the nucleus is always less than the external field B_o. The origin of this effect is the "superconducting" circulation of electrons in the molecule, which occurs in such a way that a local magnetic field B_e is created, which opposes B_o (B_e is proportional to B_o). Thus $B = B_o - B_e$. We therefore say that the nucleus is shielded from the external magnetic field. The extent of shielding is influenced by many structural features within the molecule, hence the name chemical shift.

The scale most commonly used to assign peaks in an NMR spectrum is the ppm-scale. Chemical shift (**δ**) is defined in terms of a ratio of frequency difference between the resonance and that of TMS and operating frequency:

$$\delta = \frac{(\upsilon_s - \upsilon_{TMS}) \times 10^6}{\upsilon_{spectrometer}} \qquad \textbf{δ (ppm: part per million]}$$

Eq.2-3

2.2 T1 Relaxation

Relaxation is the process by which the bulk magnetization reaches its equilibrium Value. Figure 1-4 illustrates that the z-magnetization grows back along the applied field axis (z-axis). Any transverse magnetization and other coherences decay over time. Phenomenologically, relaxation is categorized into Longitudinal relaxation (or T1 relaxation) that describes the return of the z component of longitudinal (z-)magnetization to its equilibrium value. Transverse relaxation (or T2 relaxation) that describes the decay of transverse (x,y) magnetization.

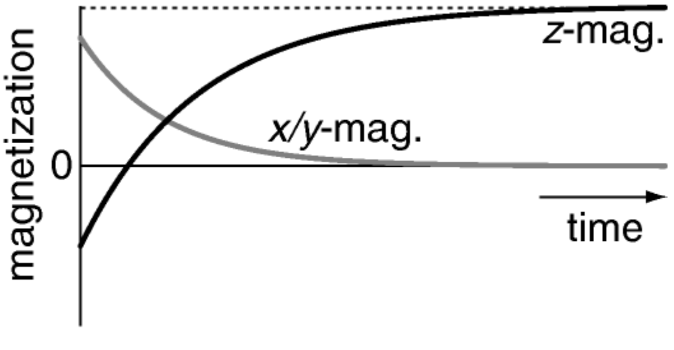


Figure 2-4 The z-magnetization grows back along the applied field axis (z-axis)over time

T_1 Relaxation (Spin-Lattice Relaxation)

The equilibrium distribution of α vs. β -state is governed by the Boltzman distribution:

$$\frac{\#(\alpha)}{\#(\beta)} = e^{-(E_\alpha - E_\beta)/kT}$$

Eq.2-5

Since α and β -states correspond to different energies changing the relative populations of these states changes the energy of the system. Therefore, T1 relaxation is an enthalpic process. The energy is transferred to or taken from other spins. The surrounding of spins is often called the lattice and hence T1 relaxation is often referred to as spin-lattice relaxation.

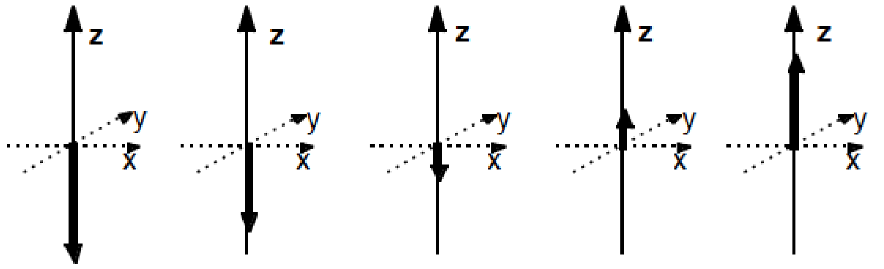


Figure 2-5 Return of the z-component of magnetization to the equilibrium value. The initial state may have been created through population inversion arising from an 180° pulse.

The vectors shown in the figure 2-5 above represent the magnetization vectors rather than magnetic moments from individual spins. Longitudinal magnetization decays exponentially according to:

$$M_z(t) = M_z(t_0)\, e^{-t/T1}$$

Eq.2-6

The T1 relaxation time determines the pulse repetition rate, the delay that must be inserted between individual scans. T1 times for protons are in the range of 0.5 to a few seconds. T1 times for quadrupolar nuclei (I > 1/2) can be rather short (ms range).

T1 relaxation time measurement

T1 relaxation times are usually determined from the inversion recovery sequence: 180 deg pulse-delay-90 deg pulse-delay-acquisition

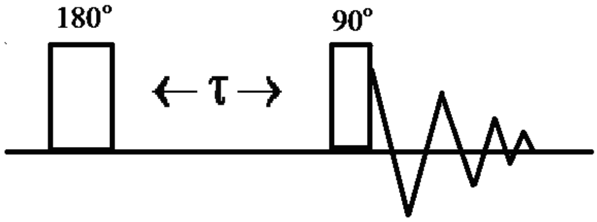


Figure 2-6 Pulse sequence used to measure T₁ using inversion recovery

In this sequence, magnetization is inverted by application of a 180-degree pulse. A delay follows during which T1 relaxation takes place bringing the –z magnetization back towards +z. Afterwards a 90-degree pulse along y turns the magnetization onto the x-axis into observable signal (Figure 2-7). The magnitude and sign of the x-magnetization at the end of the sequence depends on the T1 constant and the relaxation delay Δ.

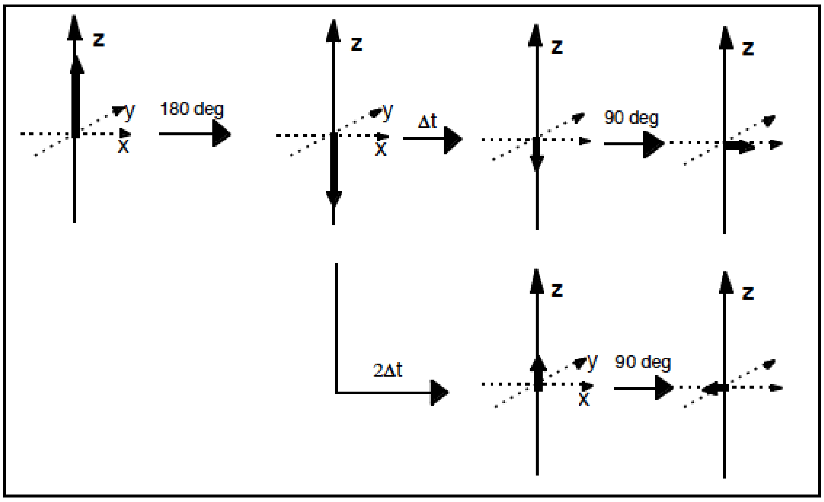


Figure 2-7 Magnetization vectors illustration in inversion recovery pulse sequence

The value for T1 is determined with the help of TopSpin using the fitting function:

$$f(t) = I_0 \cdot [1 - 2\exp(-t/T_1)]$$ Eq.2-7

2.3 The NOE effect

The Nuclear Overhauser Enhancement (NOE) effect increases the intensities of the signals. Two nuclei close in space exhibiting a dipolar coupling will help each other to relax. The NOE effect works through space, not necessarily through scalar couplings. The system for two dipolar coupled nuclei A and X with no scalar coupling is illustrated Figure 2-8 :

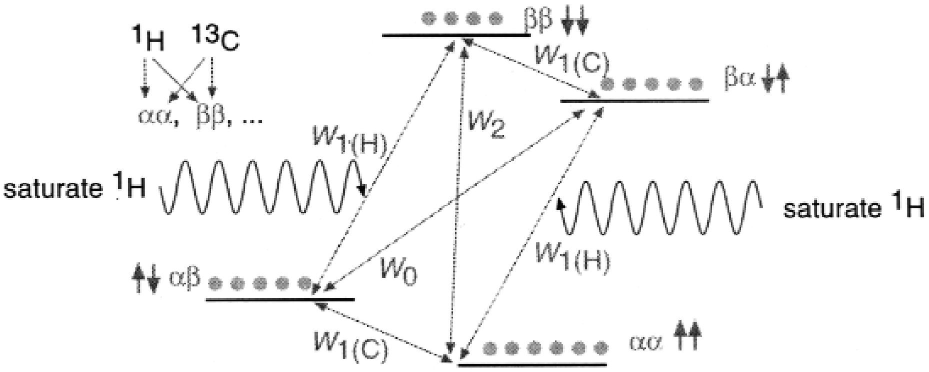


Figure 2-8 The system for two dipolar coupled nuclei ^{1}H and ^{13}C with no scalar coupling [33]

Two nuclei A and X (illustrated with H and C) are dipolar coupled and help relax each other through the pathways W_0 and W_2. The usual relaxation pathway W_1 is irradiated.

Figure 2-8 describes the possible pathways for relaxation. W_2 is a double quantum transition and W_0 a zero-quantum transition. W_0 and W_2 are determined mostly by dipole-dipole relaxation. When non-dipolar mechanisms are relaxing the system, this affects mainly W_1.

Irradiation of the sample with the resonance frequency of A equalizes (i.e. saturates) the populations in the N_1-N_3 and N_2-N_4 levels. The population difference for X has not changed and there seems to be no signal enhancement.

The irradiation shifts the system out of equilibrium, and because the W_{1A} pathway is irradiated and the W_{1X} has not changed from equilibrium, the only pathways to relaxation are W_0 and W_2. When relaxation along W_0 occurs, populations in N_2 are increased and N_3 decreased, thus reducing the difference in populations N_1 - N_2 and N_3 - N_4, thereby reducing the signal intensity from X. Relaxation along W_2, on the other hand, increases population N_1 at the expense of N_4, seemingly increasing the difference between populations N_1 - N_2 and N_3 - N_4 giving enhanced signal intensity from X. As NOE is a relaxation process it needs some time to build up.

The system is not relaxed by W_0 or W_2, but the two pathways in combination. Both W_0 and W_2 relax the system and are therefore competing pathways. What decides whether W_0 or W_2 dominates in the relaxation process is the correlation time, Tc. Small molecules tumble faster than large ones and thus have shorter Tc. W_2 dominates at short correlation times and W_0 at long correlation times. Thus, small molecules give positive NOE effect and large molecules give negative NOE effect.

The frequency of the applied magnetic field is also an important factor. The fluctuating magnetic fields needed to induce the double quantum transition must contain frequencies close to the sum of the Larmor frequencies of A and X. The zero-quantum transition requires much lower frequencies. Thus, it is more likely to find negative NOE amplifications in a high field.

The NOE effect will also depend on the distance between the cross-relaxing molecules and will decrease in inverse proportion to the sixth power of the distance. This is an important tool for calculating distances between molecules through space.

Maximum NOEs cannot be achieved, since the dipole-dipole relaxation process is not the only process relaxing the nuclei. In theory the maximum NOE intensity enhancement is given by:

$$\eta + 1 = 1 + ½ * \gamma_X/\gamma_A$$

Eq.2-8

2.4 The Free Induction Decay (FID)

The signal registered in the apparatus arises from the magnetization in the x´y´-plane. The relaxation of these magnetization vectors induces a signal picked up by the receiver coil in the apparatus. This results in a decaying time dependent signal. This signal is called the Free Induction Decay (FID), it contains all the information from the sample but is rather hard to analyze directly. The FID is therefore Fourier Transformed to obtain a frequency dependent spectrum which is possible to analyze (illustrated in Figure 2-9.

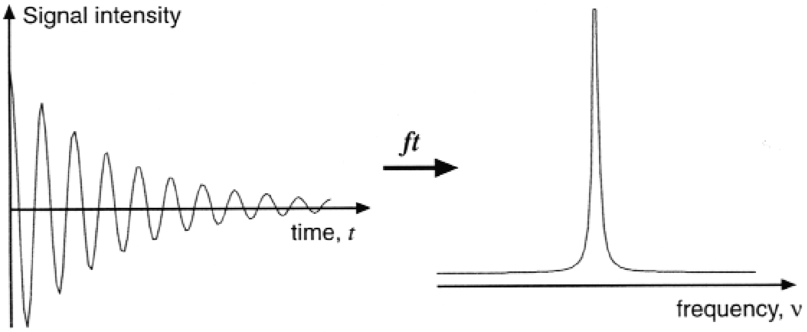


Figure 2-9 From FID to specrum by Fouriere Transformation

The Fourier transformation is described mathematically by:

$$F(\nu) \propto \int_{-\infty}^{\infty} f(t)e^{-i2\pi\nu t}dt$$

Eq.2-9

and this is the mathematical basis of the Fourier Transform (FT) NMR method.

2.5 Quantitative ^{13}C NMR experiment

Many of the molecules studied by NMR contain carbon. Unfortunately, the carbon-12 nucleus does not have a nuclear spin, but the carbon-13 nucleus does due to the presence of an unpaired neutron. Carbon-13 nuclei make up approximately one percent of the carbon nuclei on earth. Therefore, ^{13}C NMR spectroscopy will be less sensitive than proton NMR spectroscopy.

With the appropriate concentration, field strength, and pulse sequences, however, carbon-13 NMR spectroscopy can be used to supplement the previously described proton NMR information and has a much larger chemical shift range. Its low natural abundance and proton decoupling means that spin-spin couplings are seldom observed. This greatly simplifies the spectrum and makes it less crowded. ^{13}C is a low sensitivity nucleus that yields sharp signals and has a wide chemical shift range. A typical analysis of a ^{13}C NMR spectrum consists of matching expected chemical shifts to the expected moieties. Each type of signal has a characteristic chemical shift range that can be used for assignment, shows in Figure 2-10.

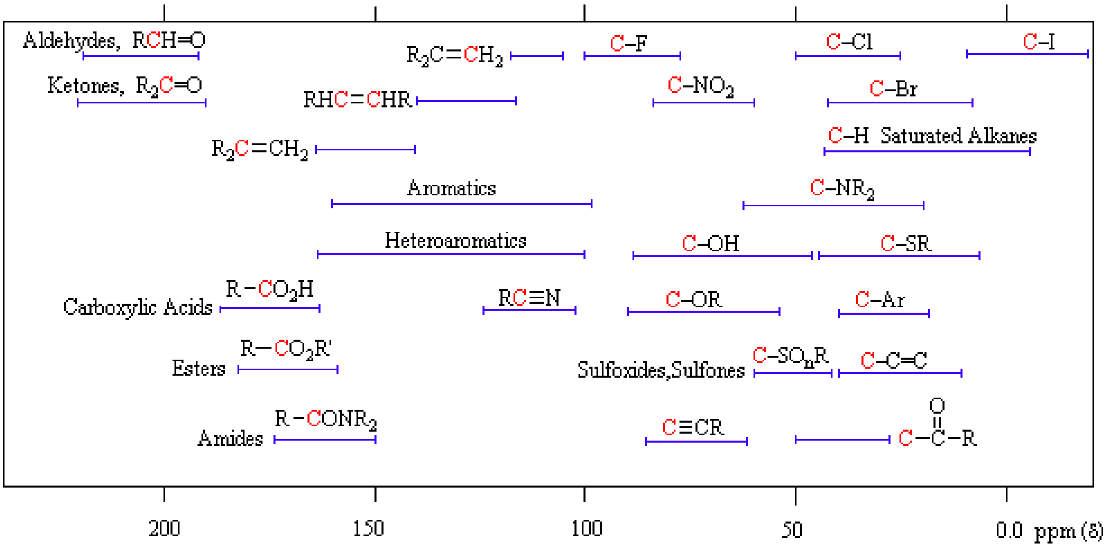


Figure 2-10 The chemical shift range in ^{13}C NMR spectrum[34]

Integration is almost useless in a regular ^{13}C NMR spectrum because of uneven nuclear Overhauser effect (NOE) enhancement of the signals by decoupling and long T1 relaxation times. Quantitative spectra may be obtained by inverse gated decoupling and long delays in the region of 10 minutes between pulses.

An inverse gated decoupling experiment can be carried out for quantitative carbon calculation. Figure 2-11 illustrates the pulse scheme for inverse gated decoupled. The BB decoupling pulses are only switched on when the acquisition of the ^{13}C spectrum starts and stays on for the time of acquisition. The NOE effect will then not have time to build up, but the spectrum will still be decoupled. The ^{13}C spectrum is now not distorted by the NOE enhancement, and can now be integrated to the relative number of ^{13}C atoms in the molecule. When integration is required for a ^{13}C spectrum, this experiment can be used with a long relaxation time, although the sensitivity is dramatically reduced as compared to measuring carbon with regular decoupling.

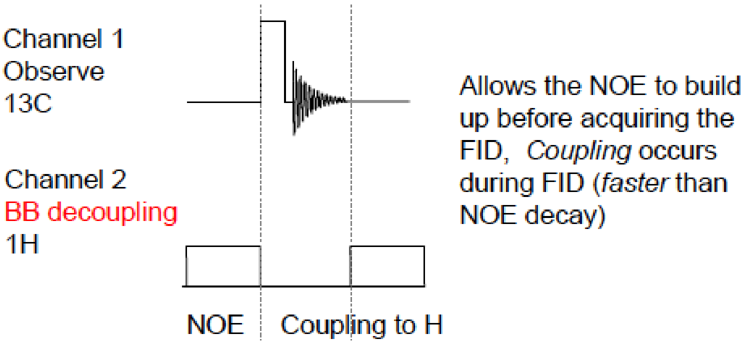


Figure 2-11 Pulse scheme of Inverse gated decoupled ^{13}C NMR experiment[35]

2.6 2D HSQC NMR experiment

The construction of a 2D experiment is simple: In addition to preparation and detection which are already known from 1D experiments the 2D experiment has an indirect evolution time t1 and a mixing sequence. This scheme (Figure 2-12) can be viewed as:

- Preparation: do something with the nulcei
- Evolution: let them process freely
- Mixing: do something else
- Detection: detect the result

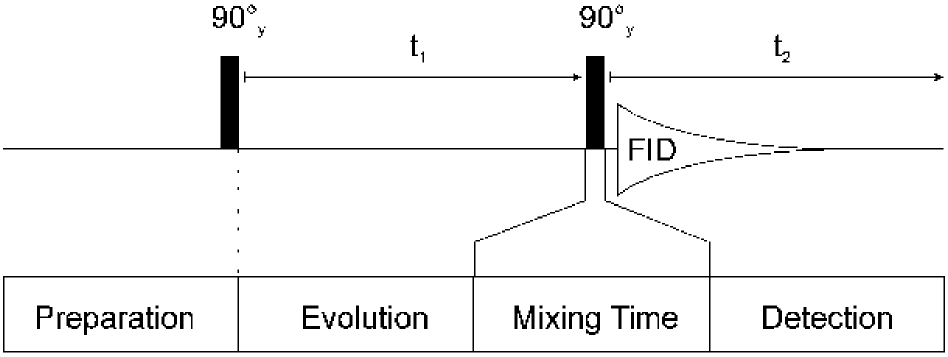


Figure 2-12 Scheme of pulse program of 2D NMR experiment

After preparation the spins can precess freely for a given time t1. During this time the magnetization is labelled with the chemical shift of the first nucleus. During the mixing time magnetization is then transferred from the first nucleus to a second one. Mixing sequences utilize two mechanisms for magnetization transfer: scalar coupling or dipolar interaction (NOE). Data are acquired at the end of the experiment (detection, often called direct evolution time); during this time the magnetization is labelled with the chemical shift of the second nucleus.

Two-dimensional FT yields the 2D spectrum with two frequency axes. A diagonal of signals (A and B) divides the spectrum in two equal halves. Symmetrical to this diagonal, there are more signals (X), called cross signals. The diagonal results from contributions of the magnetization that has not been changed by the mixing sequence (equal frequency in both dimensions) i.e. from contributions which remained on the same nucleus during both evolution times. The cross signals originate from nuclei that exchanged magnetization during the mixing time (frequencies of the first and second nucleus in each dimension, respectively). They indicate an interaction of these two nuclei. Therefore, the cross signals contain the really important information of 2D NMR spectra. Figure 2-13 illustrates the scheme of 2D NMR spectrum.

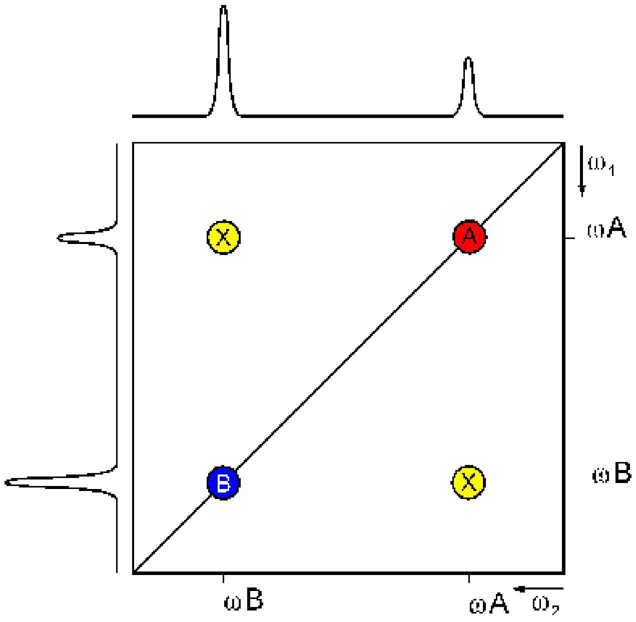


Figure 2-13 Scheme of a 2D NMR spectrum

^1H-^{13}C Heteronuclear Single Quantum Coherence Spectroscopy (HSQC) spectrum correlates chemical shifts of heteronucleus X (F1 dimension) and protons (F2 dimension) via the direct heteronuclear coupling. The HSQC experiment is widely used for recording one-bond correlation spectra between carbon and proton, with the proton being the observed nucleus (i.e. it is an inverse experiment). A ^1H-^{13}C HSQC pulse sequences is shown in Figure 2-14.

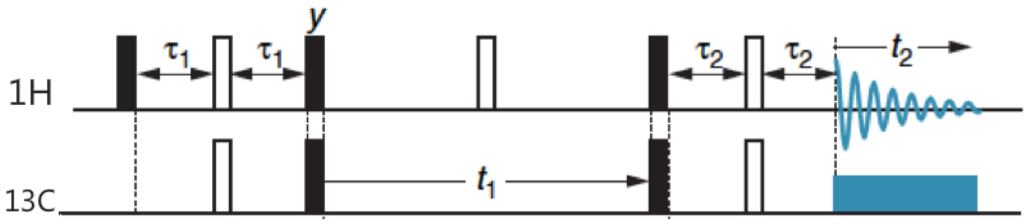


Figure 2-14 A pulse sequences for ^1H and ^{13}C correlation using the HSQC experiment[36]

2.7 Objective

LtL oils are complex mixtures of degradation products from the thermal breakdown of lignin. Considerable efforts are being made to characterize the oil and quantify individual components. However, such analysis is very strenuous and time-consuming. NMR techniques have the potential to characterize mixtures in terms of structural groups, rather than individual compounds, and thus provide quantitative information on the oil composition without requiring complete separation and quantification of individual compounds.

In this Master's project, the aim is to establish analytical protocols for NMR characterization of LtL-oils. The purpose is to quantify the major structural groups like aromatic rings, aliphatic chains, phenol groups, carboxylic groups, ketones and alcohols. ^{13}C NMR will be the most central technique, but proton NMR and 2-D methods of derivatized oils will also be evaluated.

In a pilot phase, standard compounds that correspond to major components based on GC-MS analysis results of the bio-oils will be prepared as mixtures with known concentrations, and the conditions for quantitative NMR spectroscopy including the choice of solvent and relaxation agent will be established. The use of a quantitative internal standard will be considered. When suitable NMR conditions are established, analysis of LtL oils will be attempted and quantification of functional groups of LtL oils converted under different conditions will be calculated.

Chapter 3 Experiment

3.1 Materials

6 standard compounds showed in Figure 3-1 which are compared from the GC-MS analysis results are chosen during the experiment[28]. 3 solvents and 1 relaxation agent listed in Table 3-1 are used for preparation of NMR samples. All the solvents and compounds were purchased from Sigma-Aldrich and used without further upgrading.

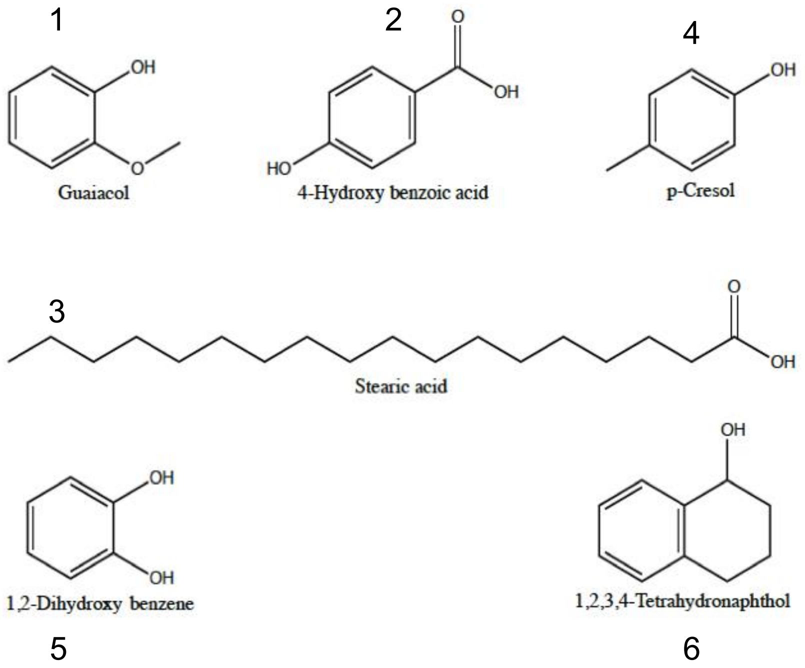


Figure 3-1 Compounds used in the study

Table 3-1 Solvent used in the study

Solvent	Source	Use
$CDCl_3$	Sigma-Aldrich	Solvent for the standard compounds
DMSO-D6	Sigma-Aldrich	Solvent for mixture and LtL-oil
Chromium(III) acetylacetonate	Sigma-Aldrich	Relaxation agent

The LtL-oils are produced by solvolysis method in UiB lab, detailed descriptions of solvolysis system and conditions have been previously published, a simplified flow sheet for LtL-solvolysis laboratory workup is displayed in Figure 3-2[37]. The biomass used in the experimental setups consisted of industrially obtained wood shavings from softwood, comprised by ~90% Norway spruce (Picea abies) and limited amounts of Pine (Pinus sylvestris). It was kindly supplied by Weyland AS in Norway, produced from locally grown wood in the district of Hardanger, Norway, and processed at Granvin Bruk in Hardanger[38]. The LtL oils were produced by Camilla Løhre and Hilde Vik Halleraker, the production conditions of LtL-Oils 1-6 were listed in Table 3-2. The LtL oils were used as received.

Table 3-2 Conditions of the production of LtL oil

LtL-oil samples	Lignin g	Water mL	Formic acid mL	Time h	Temperature °C
1	0.5	4	0.75	2	340
2	0.5	4	0.75 (^{13}C)	2	340
3	0.5	4	0.5	2	320
4	0.5	4	1	2	360
5	0.5	4	0.5	2	320
6	0.5	4	0.5 (^{13}C)	2	320

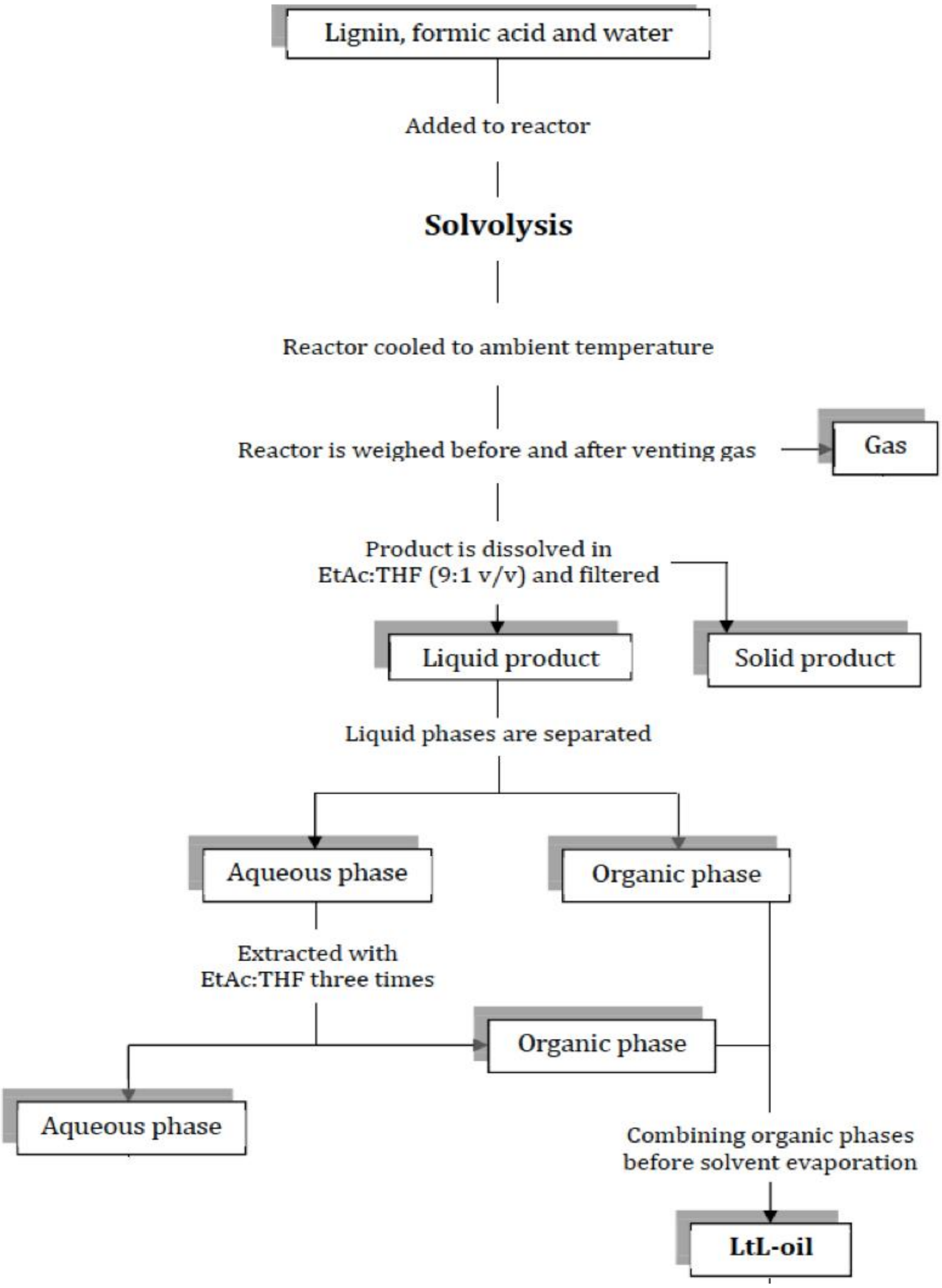


Figure 3-2 Flow sheet for LtL-solvolysis laboratory workup[37]

3.2 Sample preparation

3.2.1 Standard compound samples

Each standard compound showed in Figure 3-1 was weighed 0.06 g by an analytical balance then dissolved in 0.6ml solvent, which made the concentration were around 10%. The samples were shaken vigorously and transferred to NMR tubes. The samples were named Standard 1-7.

3.2.2 Mixture samples

5 mixture samples were prepared with standard compounds according to Table 3-3. The standard compounds were weighed by a total weight of 0.06g, and the weights of each compound in the mixture were equal. Then they were dissolved in 0.6ml DMSO-d6 and transferred to NMR tubes.

Table 3-3 Mixture samples preparation

Sample Name	Standard compounds	Weight of each compound/g	DMSO-d6 /ml
Mix 1	1,2	0.03	0.6
Mix 2	1,2,3	0.02	0.6
Mix 3	1,2,3,4	0.15	0.6
Mix 4	1,2,3,4,5	0.12	0.6
Mix 5	1,2,3,4,5,6	0.10	0.6

3.2.3 Samples with relaxation reagent

Two samples of 10% guaiacol (standard compound 1) with different concentration of Cr(acac)3 were prepared according to Table 3-4:

Table 3-4 Samples with relaxation reagent preparation

LtL-oil samples	Weight of LtL oils /mg	Cr(acac)3	DMSO-d6 /ml
Standard1-2	0.06	0.01M	0.6
Standard1-2	0.06	0.05M	0.6

3.2.4 LtL-oil samples

Each LtL oil showed in Table 3-2 was weighed 0.06 g by an analytical balance and 0.1M Cr(acac)3 were added as relaxation reagent, then dissolved in 0.6ml DMSO-d6. The samples were shaken vigorously and transferred to NMR tubes. The weight of samples LtL-oil 1-6 is shown in Table 3-5.

Table 3-5 LtL-Oil samples preparation

Sample Name	Weight of LtL-Oils /mg	Cr(acac)3	DMSO-d6 /ml
LtL-Oil 1	60.4	0.01M	0.6
LtL-Oil 2	60.1	0.01M	0.6
LtL-Oil 3	60.1	0.01M	0.6
LtL-Oil 4	59.5	0.01M	0.6
LtL-Oil 5	60.2	0.01M	0.6
LtL-Oil 6	60.2	0.05M	0.6

3.3 NMR experiments

3.3.1 NMR spectrometers

Three NMR spectrometers were used for this study are listed in Table 3-6.

Table 3-6 NMR Spectrometers and probes

Spectrometers	Resonance frequency for protons	Probe	Automatic sample changer
Bruker Biospin 850 Ascend	850MHz	TCI CryoProbe	Yes
Bruker Biospin AV600	600MHz	TCI Cryo Probe	No
Bruker Biospin AV500	500MHz	Broadband Observe (BBO) probe	Yes

The Bruker Biospin AV 500 instrument is located at the Department of Chemistry in UiB, it is equipped with BBO probe to perform ^{1}H and ^{13}C experiments. Broadband observe – BBO- means that there are two rf-coils (double resonance, plus lock channel), one for X nucleus (where X can be a different nuclei, including ^{13}C), and one for ^{1}H. The X rf-coil is located inside the ^{1}H rf-coil. Automatic sample changer is applied on AV500 NMR, and samples are put in queue using the IconNMR software.

Figure 3-3 Bruker Biospin AV500

The Bruker Biospin AV600 instrument is located at Department of Chemistry in UiB, it is equipped with a TCI Cryo Probe, and is mainly used for high resolution NMR studies of proteins and macromolecules in the liquid state. The TCI Cryo Probe is a proton-optimized triple resonance (three rf-coils) NMR inverse (the ^{1}H coil on the inside) probe, featuring three fully independent channels (plus lock channel) for simultaneous decoupling on multiple nuclei such as ^{13}C and ^{15}N. Sample is manually inserted for each measurement. It’s preferable to shim the sample manually on AV600. However, the AV600 was discharged in December 2017.

Figure 3-4 Bruker Biospin AV600

The Bruker Biospin 850 Ascend is located at NNP (Norwegian NMR platform), it is also equipped with a TCI Cryo Probe. An automatic sample changer is applied, samples are put in queue using the IconNMR software.

Figure 3-5 Bruker Biospin 850 Ascend

Figure 3-6 NMR samples for AV500 and AV600

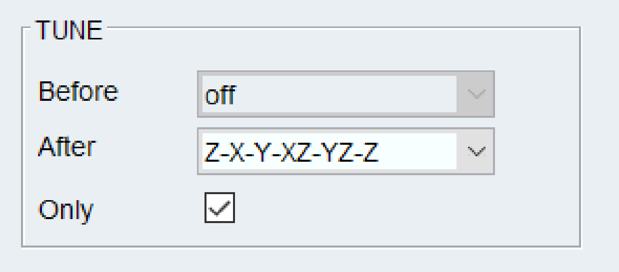
Figure 3-7 NMR samples for 850MHz

3.3.2 Procedure of running a sample on NMR instrument

Each spectrometer is connected to a PC running Windows XP and controlled by a program called Topspin. The procedure to set up and perform the experiment is as following:

- Edit the specific acquisition parameters for selected pulse program by typing *ased*. The detailed information about pulse program are stated in chapter 3.3.3.

- Insert the sample to NMR instrument.
- Perform tuning and matching after the sample had been inserted typing *atma* (followed by atmm only if the automatic tuning and matching was insufficient).
- Turn on and adjust the deuterium lock to lock the signal before the solvent is selected by typing *lock*.
- Correct the phase by using *autophase*.
- Perform shimming on the sample by typing *topshim gui* and the configuration shown in Figure 3-8:



TUNE

Before: off

After: Z-X-Y-XZ-YZ-Z

Only: ☑

Figure 3-8: Configurations for topshim gui.

- Adjust the receiver gain by typing rga.
- Check the estimated experimental time by tying expt.
- Start acquisition by typing zg.

3.3.3 Pulse program

The following pulse sequences were used:

- **^{1}H NMR Experiments:**

Zg: *The Standard ^{1} H NMR pulse program.*

Zg30: *The Standard ^{1} H NMR 30° pulse program.*

1D-sequence, using a 90°(zg) or 30°(zg30) flip angle. Result is a routine proton NMR spectrum. A typical list of acquisition parameters for a standard 1D ^{1}H experiment is shown in Table 3-7, the specific parameters used in the experiments are record in result in chapter 4.

*Table 3-7 Acquisition parameters in ^1H NMR experiment**

Parameter	Description	Typical name/value
PULPROG	pulse program used	zg
TD	number of points in FID	32768
NS	number of scans	32
DS	number of dummy scans	4
SWH	spectral width (Hz)	6000-12000Hz Hz
AQ	acquisition time	3s
RG	receiver gain	10
DW	dwell time	85 μs
DE	Pre scan delay	6 μs
D1	Relaxation delay	1.0 s
TD0	How often write data	1
NUC1	Nucleus for channel 1	^{1}H
P1	90 ° pulse width	5-12 μs
PL1	Relative power level for pulse	0.00 dB
PL1W	Power level for pulse	5-60 W
SFO1	Transmitter frequency	600.1728208

**Acquisition parameters setting is acquired from course "KJEM 251 NMR Spectroscopy I" in UiB, John Georg Seland, Sept.2014*

- **^{13}C NMR Experiments:**

***Zgig**: Inverse gated ^{1}H -decoupled ^{13}C NMR pulse program.*

***Zgig30**: Inverse gated ^{1}H -decoupled ^{13}C NMR 30°pulse program.*

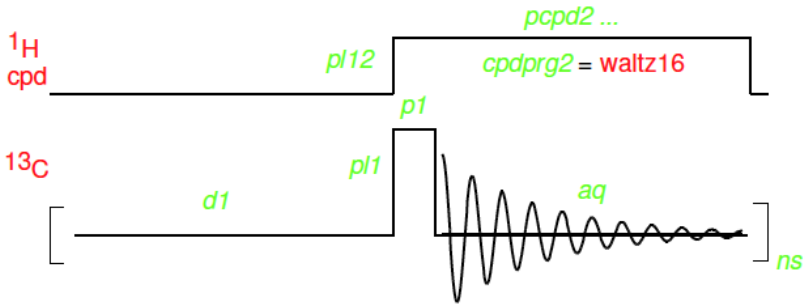


Figure 3-9: Inverse gated ^{1}H -decoupled ^{13}C NMR pulse program
(cpd: composite pulse decoupling sequence)

1D-sequence with inverse gated decoupling, using a 90° (zgig) or 30° (zgig30) pulse. This experiment yields ^{1}H-decoupled NMR spectra of ^{13}C -nuclei without signal enhancement by the nuclear overhauser effect. A typical list of acquisition parameters for a standard 1D 1H -decoupled ^{13}C NMR experiment is shown in Table 3-8, the specific parameters used in the experiments are record in result in chapter 4.

*Table 3-8 Acquisition parameters in 1D ^{13}C experiment**

Parameter	Description	Typical name/value
PULPROG	pulse program used	zgdc
TD	number of points in FID	32768
NS	number of scans	32 or more
DS	number of dummy scans	0
SWH	spectral width (Hz)	100-300 KHz
AQ	acquisition time	2s
RG	receiver gain	1000
DW	dwell time	45 μs
DE	Pre scan delay	50 μs
D1	Relaxation delay	5.0 s or higher
TD0	How often write data	1
NUC1	Nucleus for channel 1	^{13}C
P1	90° pulse width for ^{13}C	10-15μs
PL1	Relative power level for pulse	0.00 dB (AV500)
PL1W	Power level for pulse	5-60 W
SFO1	Transmitter frequency (nucleus 1)	125.7682745 (AV500)
CPDPRG2	Filename for BB decoupling	waltz16
NUC2	Nucleus for channel 2	^{1}H
PCPD2	90° pulse width for BB decoupling	60-100 μs
PL2	Relative power level for pulse	0.00 dB (AV500)
PL2W	Power level for pulse	20-30 W
PL12	Relative power level for BB pulse	15 dB
PL12W	Power level for BB pulse	0.5W
SFO2	Transmitter frequency (nucleus 2)	500.1328208 (AV500)

**Acquisition parameters setting is acquired from course "KJEM 251 NMR Spectroscopy I" in UiB, John Georg Seland, Sept.2014*

- **T1 relaxation NMR experiments:**

T1irpg: *Inversion recovery ^{13}C NMR pulse program*

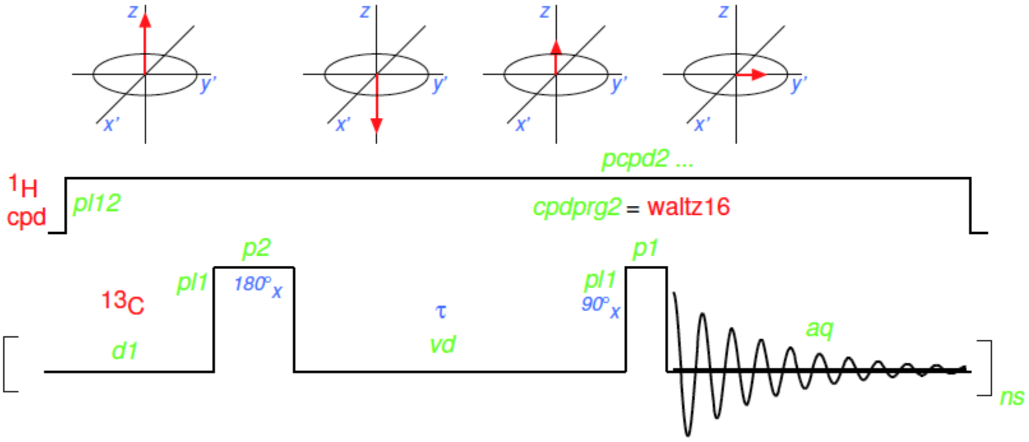
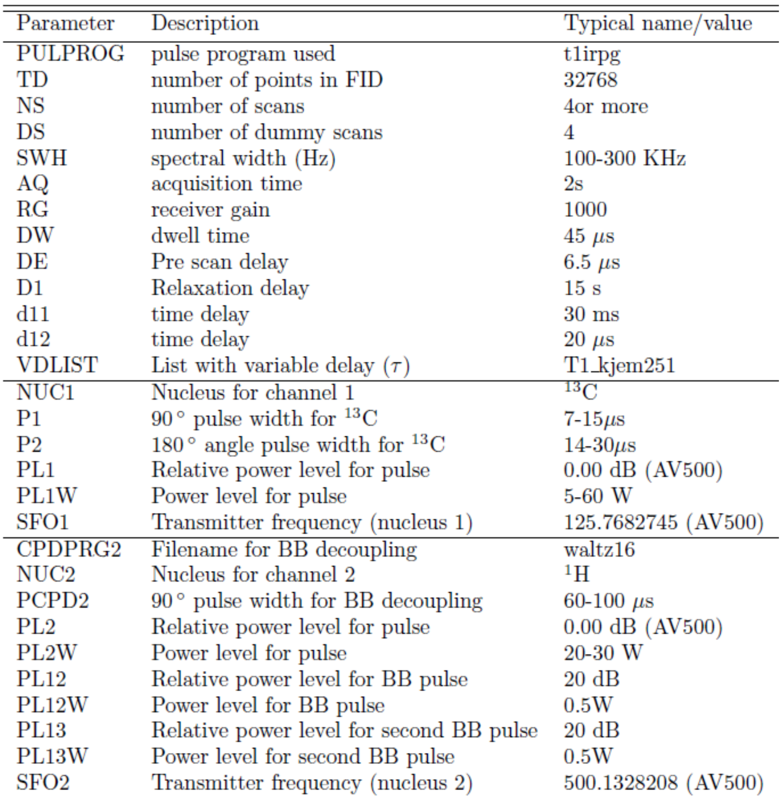


Figure 3-10: Inverse recovery ^{13}C NMR pulse program

*Table 3-9 Acquisition parameters in inversion recovery ^{13}C NMR experiment**



Parameter	Description	Typical name/value
PULPROG	pulse program used	t1irpg
TD	number of points in FID	32768
NS	number of scans	4or more
DS	number of dummy scans	4
SWH	spectral width (Hz)	100-300 KHz
AQ	acquisition time	2s
RG	receiver gain	1000
DW	dwell time	45 μs
DE	Pre scan delay	6.5 μs
D1	Relaxation delay	15 s
d11	time delay	30 ms
d12	time delay	20 μs
VDLIST	List with variable delay (τ)	T1_kjem251
NUC1	Nucleus for channel 1	^{13}C
P1	90 ° pulse width for ^{13}C	7-15μs
P2	180 ° angle pulse width for ^{13}C	14-30μs
PL1	Relative power level for pulse	0.00 dB (AV500)
PL1W	Power level for pulse	5-60 W
SFO1	Transmitter frequency (nucleus 1)	125.7682745 (AV500)
CPDPRG2	Filename for BB decoupling	waltz16
NUC2	Nucleus for channel 2	^{1}H
PCPD2	90 ° pulse width for BB decoupling	60-100 μs
PL2	Relative power level for pulse	0.00 dB (AV500)
PL2W	Power level for pulse	20-30 W
PL12	Relative power level for BB pulse	20 dB
PL12W	Power level for BB pulse	0.5W
PL13	Relative power level for second BB pulse	20 dB
PL13W	Power level for second BB pulse	0.5W
SFO2	Transmitter frequency (nucleus 2)	500.1328208 (AV500)

**Acquisition parameters setting is acquired from course "KJEM 251 NMR Spectroscopy I" in UiB, John Georg Seland, Sept.2014*

T_1 relaxation times for ^{13}C is measured using the Inversion Recovery method. The T_1 data acquisition is somewhat similar to obtaining simple ^{1}H-decoupled ^{13}C NMR spectra. However, a series of spectra for different values of a time delay parameter t were recorded to make it possible to plot each of the ^{13}C signal intensities as functions of time. A typical list of acquisition parameters for an inversion recovery ^{13}C NMR experiment is shown in Table 3-9, the specific parameters used in the experiments are record in result in chapter 4.

- **2D ^{1}H-^{13}C HSQC experiments:**

Hsqcetgpsi2: *Phase-sensitive gs-HSQC with sensitivity enhancement pulse program*

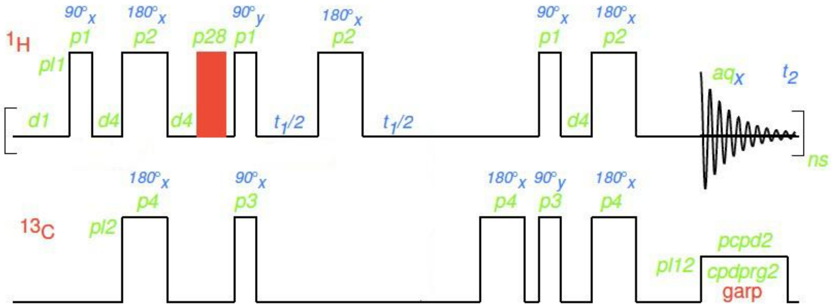


Figure 3-11: 2D gs-HSQC ^1H - ^{13}C NMR pulse program

2D pulse sequence with HSQC (Heteronuclear Single Quantum Coherence) method performs the H, C correlation via the ^{13}C chemical shift evolution of a single quantum coherence. In this case it is a gradient-selected correlation using echo/antiecho selection method. A typical list of acquisition parameters for a standard 2D HSQC NMR experiment is shown in Table 3-10, the specific parameters used in the experiments are record in result in chapter 4.

*Table 3-10 Acquisition parameters in 2D HSQC experiment**

Parameter	Description	Typical name/value
PULPROG	pulse program used	hsqcetgpf
TD	number of points in FID	2048-4096
NS	number of scans	2
DS	number of dummy scans	8 or more
SWH	spectral width (Hz)	15000-30000 Hz
AQ	acquisition time	0.5-2s
RG	receiver gain	10
DW	dwell time	30-200 μs
DE	Pre scan delay	6 μs
CNST2	C-H coupling constant	145 Hz
CNST11	degree of enhancement	3
D0	incremented delay	1-10 μs s
D1	Relaxation delay	1-2 s
d4	$\frac{1}{4J}$ value	1/(4CNST2)
D11	delay	30 ms
D13	delay	4 μs
D16	delay for gradient recovery	0.0005 s
Delta	delay	1.5 ms
Delta1	delay	0.7 ms

in0	increment between FIDs (=INF1)	100-500 μs
INF1	increment between FIDs	100-500 μs
ST1CNT	Loop counter	64
NUC1	Nucleus for channel 1	^{1}H
P1	90° pulse width for ^{1}H	5-12 μs
P2	180° angle pulse width for ^{1}H	14-30μs
PL1	Relative power level for pulse	0.00 or 3.00 dB
P28	trim pulse duration	3 μs
PL1W	Power level for pulse	5-60 W
SFO1	Transmitter frequency	600.1728208
CPDPRG2	Filename for BB decoupling	garp
NUC2	Nucleus for channel 2	^{13}C
P3	90° pulse width for ^{13}C	7-15μs
P4	180° angle pulse width for ^{13}C	14-30μs
PCPD2	90° pulse width for BB decoupling	60-100 μs
PL2	Relative power level for pulse	0.00 or -1.80 dB
PL2W	Power level for pulse	20-30 W
PL12	Relative power level for BB pulse	15 dB
PL12W	Power level for BB pulse	0.5W
SFO2	Transmitter frequency (nucleus 2)	150.1328208 (AV600)
GPNAM1	Shape of pulsed field gradient 1	SINE.100
GPNAM2	Shape of pulsed field gradient 2	SINE.100
GPZ1	Strength of pulsed field gradient 1	80 %
GPZ2	Strength of pulsed field gradient 2	20.1 %
P16	Length of pulsed field gradient	1000 μs

**Acquisition parameters setting is acquired from course “KJEM 251 NMR Spectroscopy I” in UiB, John Georg Seland, Sept.2014*

3.3.4 Data processing in Topspin

The list of processing parameters was accessed by typing *edp*. In order to obtain an NMR spectrum, the FID (time domain signals) had to be transformed to the frequency domain by means of the Fourier transform. Besides, exponential multiplication was applied before Fourier transform to improve upon the signal-to-noise ratio. These two steps were done by typing *ef*. Then the spectrum was phased to obtain pure absorption spectra, i.e. all resonances should have a positive phase. Automatic phase correction was performed by typing *apk*. And an extra manually phasing was always performed using phase correction in toolbox. For LtL-oil sample NMR spectrums, baseline correction was performed. For quantitative ^{13}C NMR spectrums, peaks were manually picked and integration the peaks were manually selected.

Chapter 4 Results

4.1 Deuterated solvent for NMR samples

The standard compounds 1-6 were dissolved in 2 solvents, the solubility results are shown in table 4-1.

Table 4-1 Solubility of standard compounds 1-6 in CDCl3 and DMSO-d6:

Compounds	1	2	3	4	5	6
$CDCl_3$	Y	Y	N*	Y	Y	Y
DMSO-d6	Y	Y	Y	Y	Y	Y

**Compound 3 –stearic acid forms a gel at room temperature in $CDCl_3$*

The ^{1}H NMR experiments was performed on the samples of 10% guaiacol (compound 1) in $CDCl_3$ and 10% guaiacol in DMSO-d6 on Bruker AV600 (pulse program: zg, ns=32, sw=12ppm). The spectra in Figure 4-1 and Figure 4-2 show that the peak from Ar-OH in guaiacol is 5.6006 ppm in CDCl3 while it is 8.8744 ppm in DMSO-d6. It is also observed the Ar-OH signal in DMSO-d6 is stronger than in CDCl3.

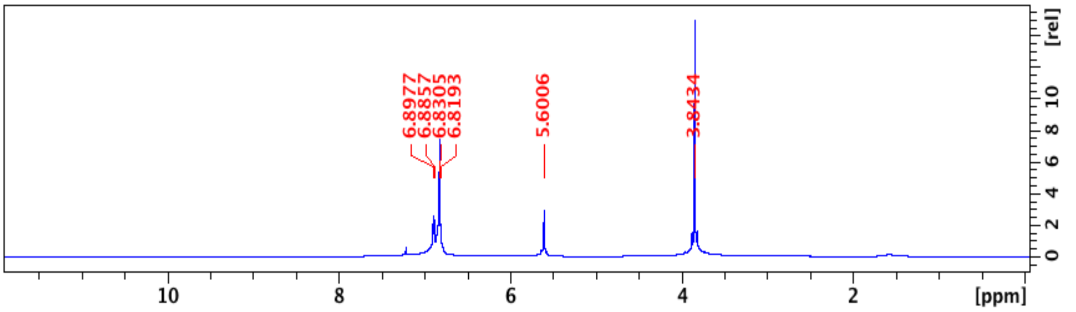


Figure 4-1 1 H NMR spectrum of 10% guaiacol in $CDCl_3$

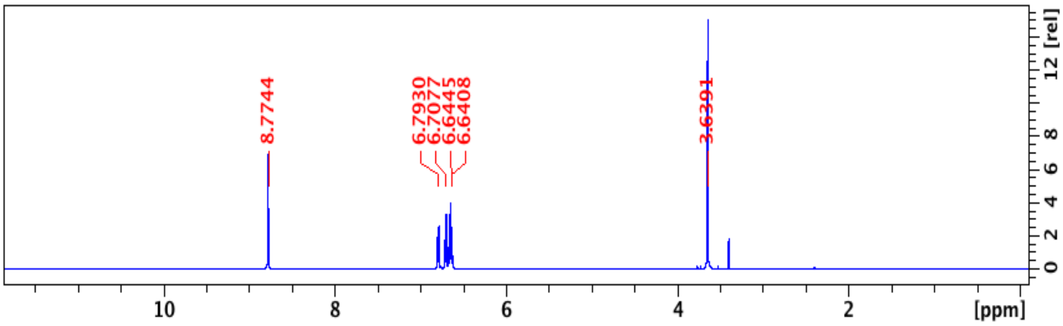


Figure 4-2 I H NMR spectrum of 10% guaiacol in DMSO-d6

4.2 T1 relaxation NMR experiment

T1 relaxation affects the relative integration between signals, since each nucleus (individual spins) in a molecule has a different T1 value, for quantitative purposes is mandatory to wait at least 5 times the longest T1 in the sample between scans in order to recover 99% of the equilibrium magnetization.

T1 relaxation NMR experiment of 10%Guaiacol in DMSO-d6 is performed on Bruker AV600 (pulse program: t1irpg, D1=15, TD=16, ns=4). T1 was calculated by Topspin software and the results shows the longest T1=8.816s, see Figure 4-3. In this case, the d1 should be set higher than 5*T1 (44s), which will result a 12 h experiment time for quantitative ^{13}C NMR experiment of one sample.

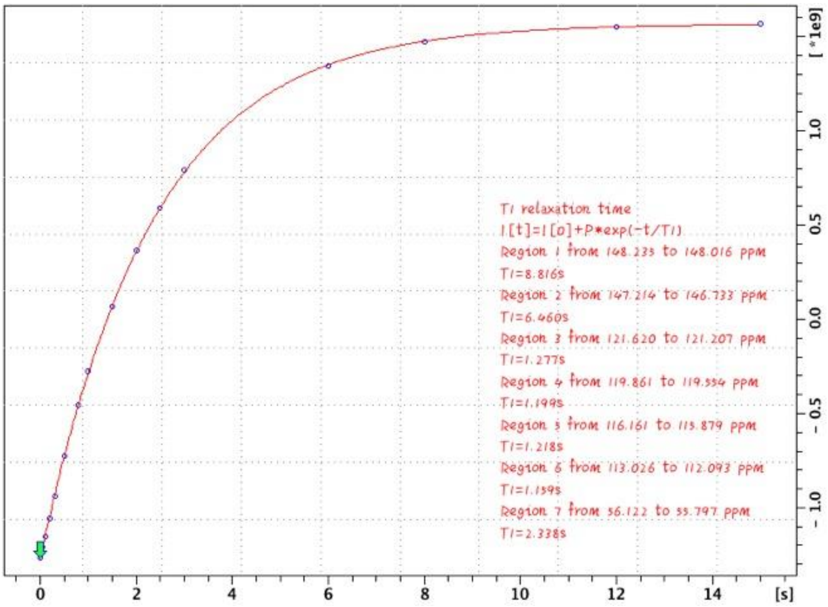


Figure 4-3 ^{13}C T1 measurement of guaiacol

Quantitative ^{13}C NMR spectra for 3 guaiacol samples were acquired from Bruker AV600 (pulse program: zgig30, d1=10, sw=220ppm, ns=1024), and the experiment time for each sample is 3h 16min, see the spectra in Figure 4-4.

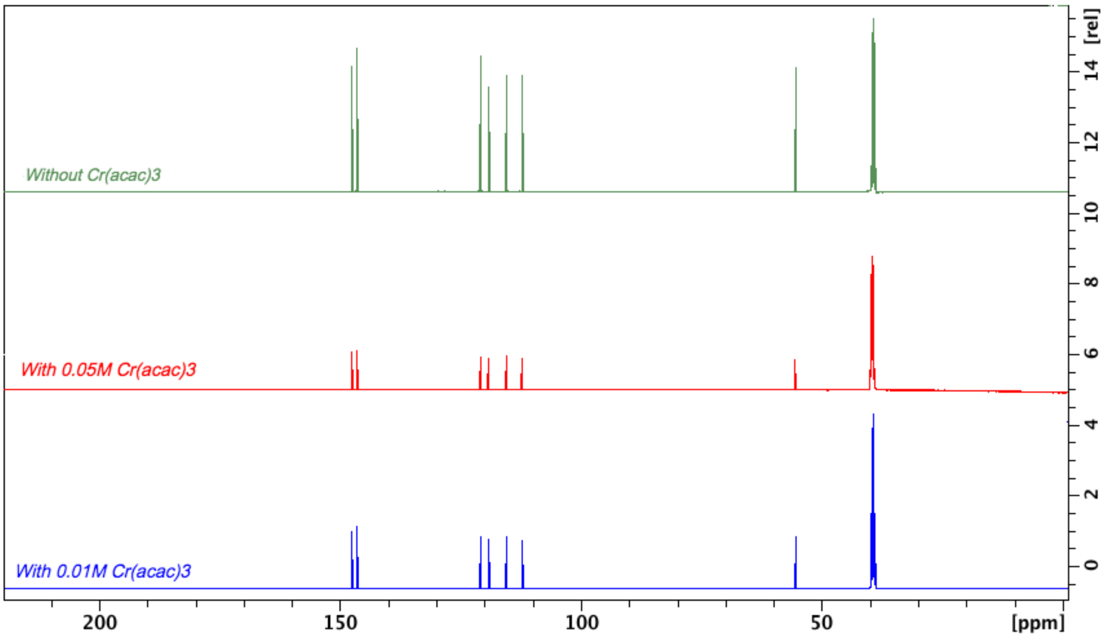


Figure 4-4 Quantitative ^{13}C NMR spectra of Guaiacol (with and without relaxation agent)

4.3 Standard compound NMR experiments

^{1}H NMR (pulse program: zg30, ns=32, sw=16ppm), ^{13}C NMR (pulse program: zgig30, ns=1024, sw=220ppm), 2D HSQC (pulse program: hsqcetgpsi2, td= 256 in F1/1024 in F2, ds=16, ns=8) of the samples of 10% standard compounds in DMSO-d6 were performed on Bruker AV500. (See spectra in Appendix A1-A9)

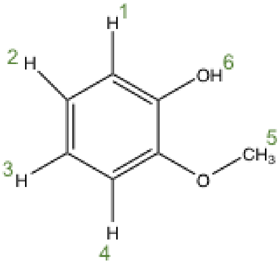
The 2D HSQC pulse sequence utilizes several polarization transfers steps that increase the overall sensitivity of the experiment. The experiment employs pulsed field gradients to select the proper magnetization components to produce 2D ^{1}H -^{13}C HSQC spectra. Such a sequence effectively removes residual ^{1}H signals from hydrogens connected to ^{12}C-containing carbon atoms and suppresses the solvent signal. This 2D experiment correlates the chemical shift of proton with the chemical shift of the directly bonded carbon. On the bottom axis is a proton spectrum and on the other is a carbon.

Cross peaks give the shift of the corresponding proton and carbon.

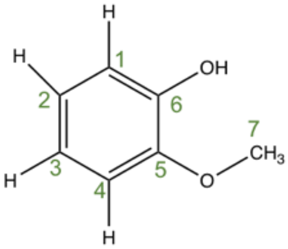
The following results shows the peak identification of each compounds, ^{1}H chemical shift and ^{13}C chemical shift are assigned according to the connection between H and C in 2D HSQC NMR spectra:

Standard 1 - Guaiacol

(Spectra in appendix A1-A5)



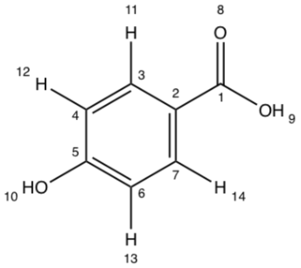
Assign	**^{1}H shift/ppm** **CDCL3**	**^{1}H shift/ppm** **DMSO-d6**
1	6.90	6.79
2	6.89	6.70
3	6.83	6.64
4	6.81	6.64
5	3.84	3.64
6	5.60	8.77



Assign	^{13}C shift/ppm $CDCl_3$	^{13}C shift/ppm DMSO-d6
1	114.5	116.0
2	121.5	121.4
3	120.1	119.7
4	110.7	112.8
5	146.6	148.1
6	145.7	147.0
7	55.9	55.9

Standard 2 - 4-Hydroxy benzoic acid

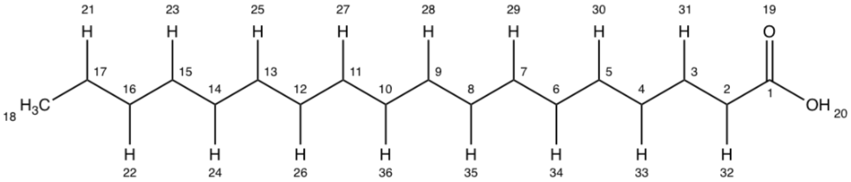
(Spectra in appendix A6-A8)



Assigned H Atom number	^{1}H shift/ppm DMSO	Assign C Atom number	^{13}C shift/ppm DMSO
11	7.80	1	167.1
12	6.83	2	121.3
10	10.24	3	131.5
13	6.81	4	115.1
14	6.81	5	161.6
8	12.39	6	115.1
		7	131.5

Standard 3 - Stearic acid

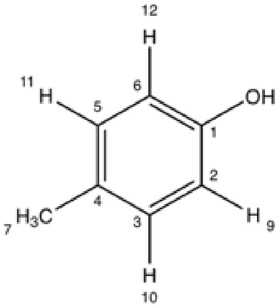
(Spectra in appendix A9-A11)



Assigned **H Atom number**	**^{1}H shift/ppm** **DMSO**	**Assign** **C Atom number**	**^{13}C shift/ppm** **DMSO**
18	0.88	1	180.4
20	11.48	2	34.1
21-30, 33-36	1.26	3	24.7
31	1.63	4-15	29.7
32	2.34	16	31.9
		17	22.7
		18	14.1

Standard 4 – p-Cresol

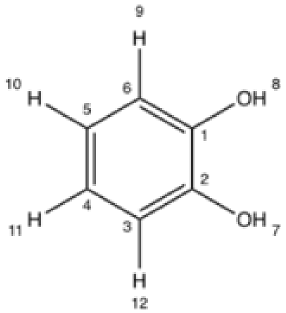
(Spectra in appendix A12-A14)



Assigned **H Atom number**	**^{1}H shift/ppm** **DMSO**	**Assign** **C Atom number**	**^{13}C shift/ppm** **DMSO**
7	2.19	1	155.0
8	9.09	2	115.0
9	6.68	3	127.1
10	6.95	4	129.7
11	6.95	5	127.1
12	6.68	6	115.0
		7	20.0

Standard 5 - 1,2-Dihydroxy benzene

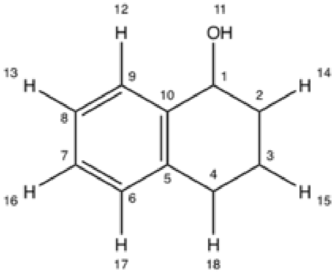
(Spectra in appendix A15-A16)



Assigned **H Atom number**	**^{1}H shift/ppm** **DMSO**	**Assign** **C Atom number**	**^{13}C shift/ppm** **DMSO**
7	8.79	1	145.7
8	8.79	2	145.7
9	6.72	3	116.0
10	6.72	4	119.8
11	6.60	5	119.8
12	6.60	6	116.0

Standard 6 - 1,2,3,4-Tetrahydronaphthol

(Spectra in appendix A17-A19)



Assigned **H Atom number**	**^{1}H shift/ppm** **DMSO**	**Assign** **C Atom number**	**^{13}C shift/ppm** **DMSO**
1	4.58	1	66.8
11	5.09	2	32.8
12	7.40	3	19.5
13,16	7.14	4	29.3
17	7.06	5	136.8
18	2.72	6	128.8
4	2.67	7	126.0
3,15	1.71	8	127.0
2,14	1.90	9	128.7

1	4.58	10	140.8

4.4 Bio-oil based mixture NMR experiments

^{1}H NMR(pulse program: zg30, ns=128, sw=20ppm), ^{13}C NMR (pulse program: zgig30, ns=1024, sw=220ppm), 2D HSQC NMR (pulse program: hsqcetgpsi2, td= 256 in F1/1024 in F2, ds=16, ns=8) experiments for the samples of mixtures 1-5 in DMSO-d6 are performed on Bruker AV600. (See spectra in Appendix A20-A24)

The peaks of ^{1}H chemical shift and ^{13}C chemical shift were assigned in chapter 4.3. Functional group are identified by chemical shift range and 2D HSQC spectra . The standard compounds 1-6 can be identified in 2D HSQC spectra of Mixtures, see the example of Mixture 5 of all the standard compounds in Figure 4-5. Figure 4-6 &4-7 shows the summary of functional group assignment in ^{1}H &^{13}C spectra.

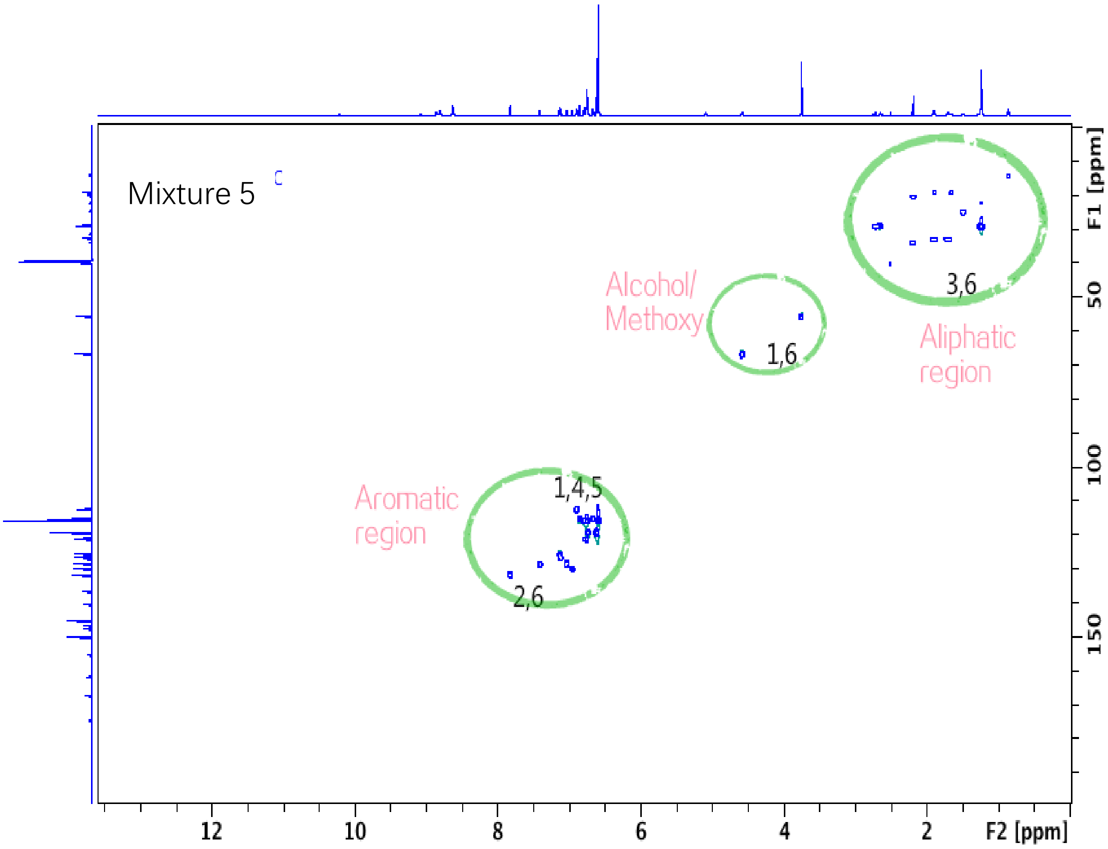


Figure 4-5 Identification of 6 compounds in 2D HSQC NMR spectrum of mixture 5

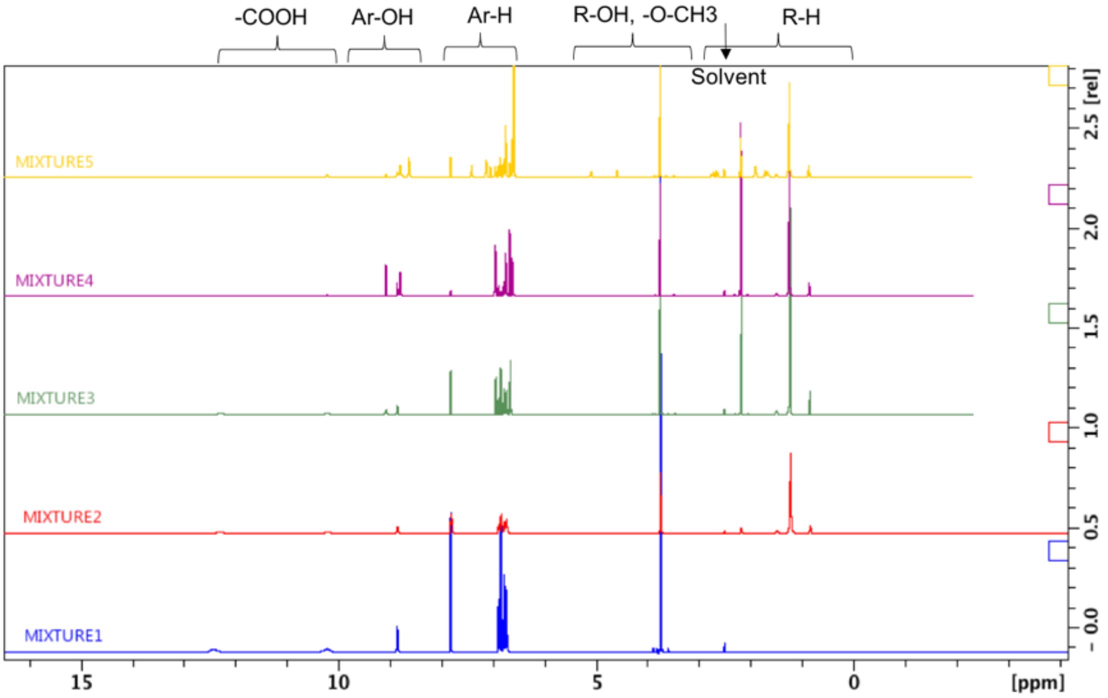


Figure 4-6 ^{1}H NMR chemical shift assignment of functional groups in Mixtures

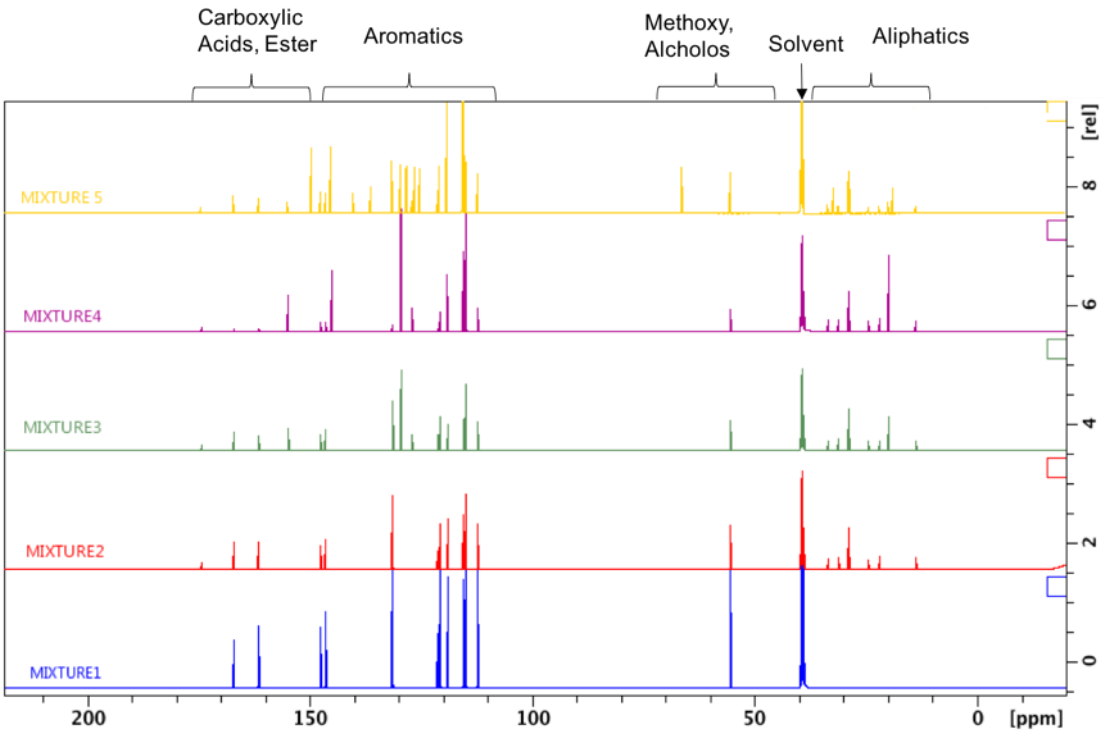


Figure 4-7 ^{13}C NMR chemical shift assignment of functional groups in Mixtures

4.5 LtL-oil NMR experiments

Quantitative ^{13}C NMR spectra of 6 LtL-oil samples in DMSO-d6 with 0.01 M Cr(acac)3 were collected on Bruker Advance 850MHz with an inverse-gated decoupling pulse sequence (pulse program: zgig, sw=238ppm, d1=10, ns=3072). (See spectra in Appendix A25-A30, and integration raw data in Appendix B4-B7)

4.5.1 Two LtL- oils with and without formic acid ^{13}C

Figure 4-8 shows a comparison of ^{13}C NMR spectra of LtL oil-1 and LtL oil-2. Two LtL-oils were converted from same lignin at same condition, while the reaction solvents were standard formic acid and ^{13}C labelled formic acid. The chemical shift of ^{13}C peaks are similar for the two oils. However, it is clear to see two differences in the spectra. The signal from peak at 166.2 ppm in experiment 2 is significant stronger than experiment 1, which is from residual formic acid (One signal at 166.22ppm is acquired in ^{13}C NMR spectra of standard CH_2O_2 [39]). Also, the intensity of the peaks over 170ppm is higher in oil made with ^{13}C-enriched formic acid than the oil made with standard formic acid. This is an evidence demonstrating that the formic acid does not only work as a hydrogen donor but also contributes with carbon to the produced LtL-oil.

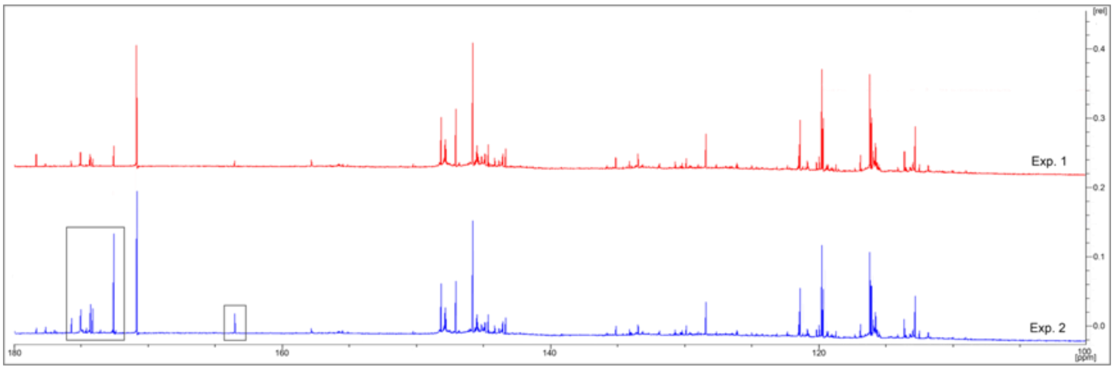


Figure 4-8 ^{13}C NMR spectra of LtL-oil produced on the conditions -360 °C, 0.5 mL, standard formic acid (Exp.1)/ ^{13}C -labeled formic acid (Exp.2)

4.5.2 Four LtL- oils converted under different conditions

Figure 4-9 shows a comparison of quantitative ^{13}C NMR spectra of LtL oil-3,4,5,6.

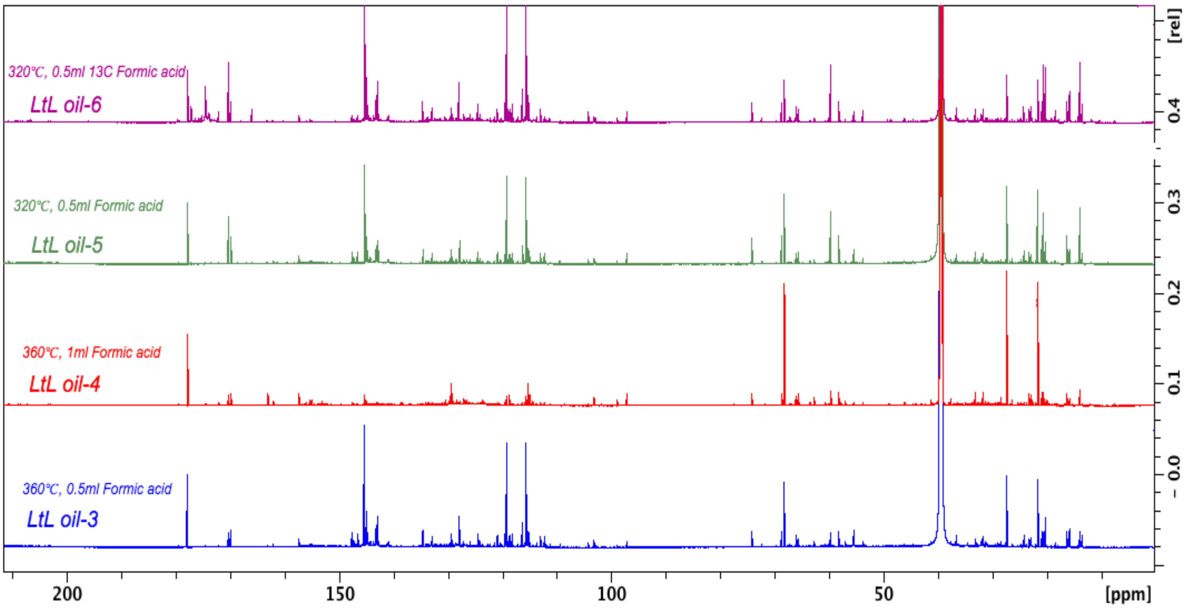


Figure 4-9 Quantitive^{13}C NMR spectra of LtL-oil produced on different conditions

The integration of quantitative ^{13}C NMR spectra were manually calculated using the topspin software, a previous developed structural assignment range of bio-oil in Table 4-2 [40]were used in this study.

Table 4-2 ^{13}C NMR Chemical Shift Assignment Range of Lignin bio-oil

Functional group	**Chemical shift range（ppm）**
Carbonyl or Carboxyl bond	215.0-166.5
Aromatic C-O bond	166.5-142.0
Aromatic C-C bond	142.0-125.0
Aromatic C-H bond	125.0-95.8
Aliphatic C-O bond	95.8-60.8
Methoxyl-Aromatic bond	60.8-55.2
aliphatic C-C	55.2-0

The integration results of functional group in four LtL-oil based on ^{13}C NMR spectra are summarized in table 4-3.

*Table 4-3 Integration Results for LtL-Oils produced under different conditions, detected by quantitative ^{13}C NMR using the assignment range shown in Table 4-2**

Functional group	LtL-Oil 3 *360℃,0.5M FA*	LtL-Oil 4 *360℃,1M FA*	LtL-Oil 5 *320℃,0.5M FA*	LtL-Oil 6 *320℃,0.5M FA-* **^{13}C**
C=O	4.3%	9.1%	6.8%	23.5%
Aromatic C-O	18.2%	8.3%	14.2%	19.5%
Aromatic C-C	5.4%	9.1%	4.5%	6.7%
Aromatic C-H	31.8%	14.6%	26.2%	24.4%
Aliphatic C-O	7.3%	15.1%	9.2%	4.4%
Methoxyl-	11.5%	3.4%	6.0%	3.1%
Aliphatic C-C	21.5%	40.3%	33.2%	18.3%

** The results were shown as the percentage of carbon, which is the relative amounts of carbon, not the absolute amounts, since this depends on the amount of oil produced to.*

On the basis of ^{13}C NMR LtL-oil 3 and LtL-oil 5, the relative number of aromatic carbons increased with increasing temperature from 320°C to 360°C. In the contrast, the number of aliphatic carbons decreased with an increasing temperature. While under the same production temperature 360°C, there are more C=O groups, as well as aliphatic groups and less aromatic groups in LtL-oil 4 than LtL-oil 3 due to double amount of formic acid presented. In LtL-oil 6, significantly higher amount of carbonyl or carboxyl groups were detected, compare with the LtL-oil 5 which was produced under same condition, it's confirmed that some carbon in carbonyl or carboxyl group are transferred from ^{13}C labelled formic acid.

Chapter 5 Discussion

5.1 The choice of deuterated solvent

Before running the samples for NMR experiments, the first step is to choose a suitable solvent. Since deuterium is by far the most popular lock nucleus, the sample is usually dissolved in a deuterated solvent (a deuterated solvent is one in which a large proportion, typically more than 99%, of the hydrogen atoms have been replaced by deuterium). Chloroform-d and DMSO-d6 were compared to be use in this study.

The choice deuterated solvent is decided by solvent solubility, solvent peak overlap, and solvent effect:

a. Solubility

All the samples can be easily dissolved in DMSO-d6. Clearly the more soluble the sample is in the solvent the better. This maximizes the amount of sample within the sensitive volume which increases the sensitivity of the experiment.

b. Interfering peaks

The solvent itself will inevitably produce NMR signals which will obscure regions of the spectrum. These 'residual solvent peaks' should not overlap with signals from the sample. The chemical shifts of solvent signals observed for ^{1}H NMR and ^{13}C NMR spectra are listed in the table 5-1, it shows ^{1}H chemical shift of DMSO-d6 is less overlap than $CDCl_3$ in aromatic area:

Table 5-1: Chemical shift of $CDCl_3$ and DMSO-d6 in ^1H and ^{13}C NMR spectra:*

	^{1}H NMR chemical shift/ppm	^{13}C NMR chemical shift/ppm
$CDCl_3$	7.26	77.3
DMSO-d6	2.50	39.5
Aromatics group	7-8	95-166

Data were acquired from: https://webspectra.chem.ucla.edu/NotesOnSolvents.html

^{1}H chemical shift of DMSO-d6 is 2.5 ppm which is far away from aromatics group 7-8 ppm, while $CDCl_3$ is 7.26ppm. It shows the solvent peak of DMSO-d6 will have less overlap in aromatic area in the ^{1}H NMR spectra.

c. Solvent effect:

The spectra show that the peak from Ar-OH in guaiacol is more intensive and easier to be identified in high chemical shift range (>8ppm) in DMSO-d6. (Spectra in appendix A1&A3). It´s assumed that the Aromatics-OH group is more stable in DMSO-d6 due to hydrogen bond. The difference of ^{1}H NMR chemical shift in Ar–OH group of Guaiacol can be observed in Figure 5-1. The chemical shifts of OH protons vary over a wide range depending on substrate structure, solvent, temperature and concentration. The shifts are very strongly affected by hydrogen bonding, with large downfield shifts of H-bonded groups compared to free OH groups. Thus OH signals tend to move downfield with increased hydrogen bonding solvents like DMSO.

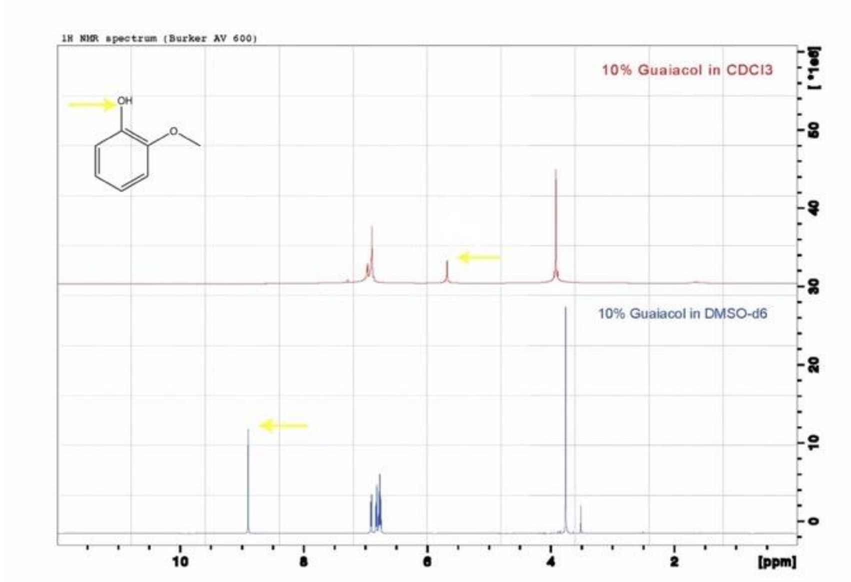


Figure 5-1 A comparison of ^{1}H NMR spectrum for guaiacol in $CDCl_3$ and DMSO-d6

Consequently, DMSO-d6 was chosen as suitable deuterated solvent for the experiments because of the good solubility, less peak overlap in ^{1}H NMR spectra and stable solvent effect.

5.2 The choice of relaxation agent

To get accurate integration of ^{13}C signals, the quantitative ^{13}C NMR were recorded with broad band proton-decoupling only during the acquisition periods ("inverse-gating"), to avoid nonuniform enhancement of carbon signals from proton NOE effects (polarization transfer). As each LtL oil sample was a complex mixture, the concentration of each individual component was very low. These low concentrations, in combination with the intrinsic low sensitivity of the ^{13}C nuclei, required large numbers of transients to achieve visually acceptable signal-to-noise ratios. Such lengthy signal-averaging made the direct determination of accurate carbon T1 relaxation times impractical due to long acquisition times.

It was measured the longest T1 is at least 8,816s in chapter 4.2, which results in that the d1 should be set to 44s (five times the longest T1), which would have allowed the full recovery of all signals and the most accurate measurement of integrated intensities. In that case, a 12 h experiment time is needed (calculated by Topspin with a command "expt" for estimating the experiment time) for one sample with ns=1024.

In order to reduce the experiment time, a relaxation agent Chromium(III) acetylacetonate was considered to add into LtL-oil sample. Relaxation reagents are paramagnetic substances capable of strongly decreasing the relaxation times of substrate nuclei without inducing noticeable shifts. Both an electron nuclear dipolar interaction and an electron-nuclear contact interaction may contribute to the overall relaxation.

Table 5-2: Integral results of Quantitative ^{13}C NMR spectra of three guaiacol samples

	Integral [rel]		
Object	Guaiacol with 0.05M Cr(acac)3	Guaiacol with 0.01M Cr(acac)3	Guaiacol without relexation agent
Peak 1	1.0	1.0	0.9
Peak 2	1.0	1.0	1.1
Peak 3	1.0	1.0	1.0
Peak 4	1.0	1.0	1.0
Peak 5	1.0	1.0	1.0
Peak 6	1.0	1.0	0.9
Peak 7	1.0	1.0	1.1

Guaiacol contains 7 carbons and each carbon gives a peak in the ^{13}C NMR spectrum. During the integration process, the sum of integrals is normalized to be 7, then the results of each peak integrals were calculated by topspin in table 5-2. Two samples with 0.01M and 0.05M Cr(acac)3 got the more accurate carbon integration results than the sample without relaxation agent. Besides, no big difference was observed between 0.01M and 0.05M Cr(acac)3. *(See the integration raw data in Appendix B1-B3)*

It is showed that adding Cr(acac)3 can speeded up the relaxation and the carbons were fully relaxed when d1=10, where d1=55 for without relaxation reagent sample. It reduced the experiment time from 12h to 3h per sample with ns=1024.

Both 0.01M and 0.05M Cr(acac)3 can reduce the NMR acquisition time to get fully relaxed ^{13}C NMR spectra. However, an excess of this relaxation agent deteriorates the spectral resolution. The spectrum with 0.01M Cr(acac)3 has better resolution and quality than spectrum with 0.05M Cr(acac)3. Therefore, 0.01M Cr(acac)3 was added into LtL oil NMR samples as relaxation agent to achieve more accurate quantitative ^{13}C

NMR spectra of LtL oils.

5.3 Comparison of NMR spectra acquired from different magnets

Quantitative ^{13}C NMR spectra of LtL-oil sample 1 in DMSO-d6 with 0.01 M Cr(acac)3 were collected on Bruker Advance 850MHz/AV600 MHz/AV500MHzwith an inverse-gated decoupling pulse sequence (pulse program: zgig 30, sw=238ppm, d1=10, ns=3072). Figure 5-2 shows the quantitative ^{13}C spectra of LtL oil 1 acquired under different magnet field (AV500/AV600/850MHz).

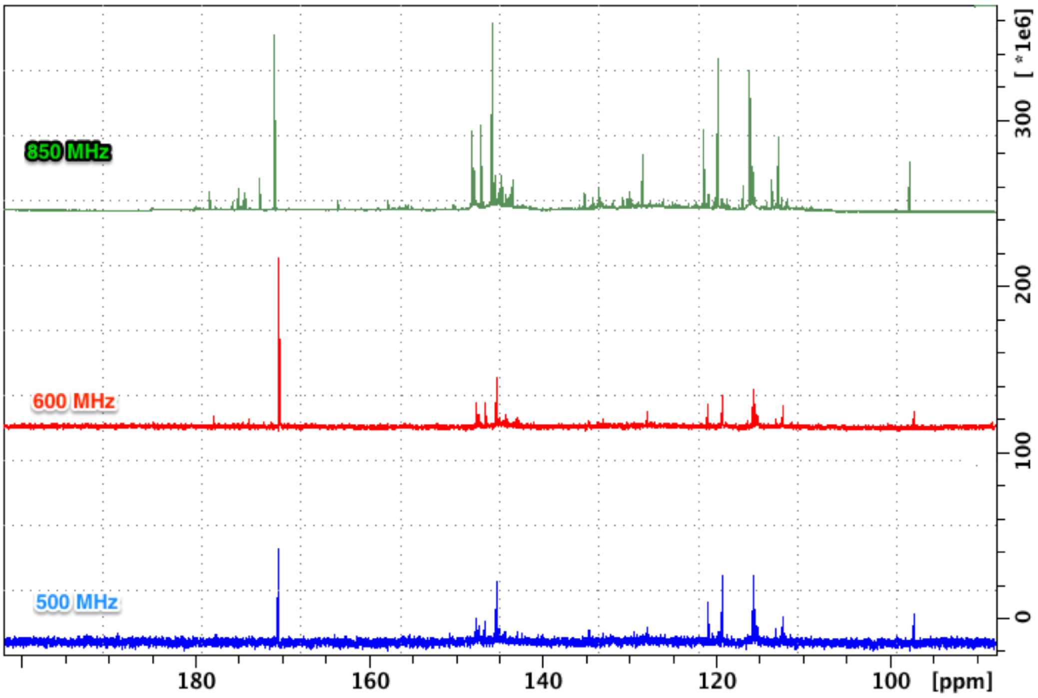


Figure 5-2 A comparison of ^{13}C NMR spectrum for LtL oil 1in DMSO-d6 acquired under different magnet field (AV500/AV600/850MHz)

a. Resolution of NMR spectra

The energy separation between the two spin states of a spin ½ nucleus is directly proportional to the strength of the magnetic field ($\Delta E = \mu B_o$). This in turns affects the Boltzmann population differences of the α and β spin states. Thus, stronger magnetic fields result in large increases in the strength of the NMR signal.

It is obvious that more peaks are visible in 850MHz spectrum than 500 MHz and

600MHz spectra. Also, there is a noticeable difference in the spread of the chemical shifts, peaks are better separated in 850MHz spectrum. The larger the separation is, the more chance one has to be able to fully interpret the spectrum with visual inspection.

b. Sensitivity of NMR spectra

The sensitivity of NMR experiments is given by the signal to noise ratio[35]:

$$S/N = \frac{N\gamma_{exc}T_2(\gamma_{det}B_0)^{3/2}\sqrt{ns}}{T}$$

S/N = signal to noise ratio
N = number of spins in the system (sample concentration)
γ_{exc} = gyromagnetic ratio of the excited nucleus
γ_{det} = gyromagnetic ratio of the detected nucleus
ns = number of scans
B_0 = external magnetic field
T_2 = transverse relaxation time (determines the line width)
T = sample temperature

with same number of scans, high applied magnetic field is recognized as the most straightforward means to enhance NMR sensitivity. It is clearly seen that 850MHz spectra has higher signal-noise ratio than 500 MHz and 600MHz spectra.

Therefore, LtL-oils were analyzed by 850MHz because of its both highest resolution and sensitivity, which gives better spectra for interpretation, especially for integration of ^{13}C spectra. However, 850 MHz NMR is pricy and should be booked for complex samples. For standard compound samples, 500MHz was efficient to analyze ^{1}H NMR and ^{13}C NMR since the component was pure and the concentration was high enough to achieve strong signals, it can be used for routine ^{1}H and ^{13}C experiments where the main goal is identification and characterization of organic compounds.. For mixture samples, 600MHz was chosen to use because its magnet field is higher than 500MHz, and it is allowed to manually shim the sample and try different parameters to achieve preferable spectra.

5.4 Functional groups in LtL-oils

The ^{13}C NMR chemical shift of selected standard compounds was identified in chapter 4.1; however, LtL-oil contains more chemical compounds than used in this study. A complete chemical shift range of different functional groups in LtL-oil cannot be assigned based on only standard compounds, and a previous developed structural assignment range of bio-oil in Table 4-2 [40]were used for integration of quantitative ^{13}C NMR spectra. Several different assignments of ^{13}C NMR chemical shift integration ranges were proposed by researchers, the reason to choose it in this study is that most peaks from standard compounds fits the functional group assigned range in Table 4-2, and the only exceptions came from standard compound 6 - 1,2,3,4-Tetrahydronaphthol. The ^{13}C chemical shift of aromatic C-H in standard compound 6 are 126.0-128.8 ppm, but these peaks would be included into aromatic C-C range (125.0-142.0 ppm) instead of aromatic C-H range (95.8-125.0 ppm) according to Table 4-2. It is considered there would be some overlap in these ranges.

a. Production temperature effect

The integration results of LtL-Oils were calculated in chapter 4.5, Table 5-3 & Table 5-4 show that with an increasing temperature from 320°C to 360°C, the percentage of aromatic carbons increased from 44.9% to 55.4%, while the ratio of C-C: C-O: C-H in aromatic carbons are similar (*0.3: 1: 1.8* and *0.3: 1: 1.7*). Also, Methoxyl C-O increased significantly from 6.0% to 11.5%. In the contrast, the number of aliphatic Carbon with C-C bond decreased from 33.2% to 21.5%, aliphatic carbon with C-O bond decreased from 9.2% to 7.3% and C=O decreased from 6.8% to 4.3%.

Table 5-3 Carbon percentage in functional group of LtL-oils produced from lignin under different temperature (same formic acid amount =0.5ml)

	Temperature	*Aromatic carbon*	*Methoxyl C-O*	*Aliphatic C-C*	*Aliphatic C-O*	*C=O*
LtL-Oil 5	***320℃***	44.9%	6.00%	33.20%	9.20%	6.80%
LtL-Oil 3	***360℃***	55.4%	11.50%	21.50%	7.30%	4.30%

Table 5-4 The ratio of different carbon bond in Aromatic carbons in LtL-oils produced under different temperature (same formic acid amount =0.5ml)

	Temperature	*Aromatic C-C*	*Aromatic C-O*	*Aromatic C-H*
LtL-Oil 5	***320℃***	0.3	1	1.8
LtL-Oil 3	***360℃***	0.3	1	1.7

b. Formic acid amount effect

On the other hand, Table 5-5 & Table 5-6 show that under the same production temperature 360℃, there are more C=O groups, as well as Aliphatic groups and less Aromatic groups in LtL-oil 4 than LtL-oil 3 due to double amount of formic acid presented. With the increasing presented amount of formic acid from 0.5M to 1M, the percentage of aromatic carbons decreased from 55.4% to 32.0%, while the ratio of C-C: C-O: C-H in aromatic carbons are quite different (0.3: 1: 1.7 and 1.1: 1: 1.8) which means significantly more C-C bonds are presented in LtL-oil produced by high amount formic acid. Also, Methoxyl C-O decreased dramatically from 11.5% to 3.4%. In contrast, the number of aliphatic Carbon with C-C bonds increased from 21.5% to 40.3%, aliphatic carbon with C-O bond increased from 7.3% to 15.10% and C=O increased from 4.3% to 9.1%.

Table 5-5 Carbon percentage in functional group of LtL-oils produced from lignin with different amount of formic acid (same production temperature=360℃)

	Formic acid	Aromatic carbon	Methoxyl C-O	Aliphatic C-C	Aliphatic C-O	C=O
LtL-Oil 3	***0.5M***	55.40%	11.50%	21.50%	7.30%	4.30%
LtL-Oil 4	***1M***	32.00%	3.40%	40.30%	15.10%	9.10%

Table 5-6 The ratio of different carbon bond in Aromatic carbons in LtL oil produced with different amount of formic acid (same production temperature=360℃)

	Formic acid	Aromatic C-C	Aromatic C-O	Aromatic C-H
LtL-Oil 3	***0.5M***	0.3	1	1.7
LtL-Oil 4	***1M***	1.1	1	1.8

c. Carbon incorporation from formic acid

From the results calculated in chapter 4.5, the LtL-oil 6 which contains ^{13}C labelled formic acid, significate higher amount of Carbonyl or Carboxyl group were detected with a carbon percentage of 23%, compare with the LtL-oil 5 which was produced under same condition, it's confirmed that some carbon in Carbonyl or Carboxyl group are transferred from ^{13}C labelled formic acid.

It is also noticed in Table 5-7 that the aliphatic carbon ratio of C-C: C-O: C-H bonds are slightly different between 2 oils (*1: 1.5: 5.5* and *1 : 1.5: 5.9*), it seems carbon from the formic acid didn't incorporates in the Methoxyl/ Aliphatic C-O structures, but incorporates in aliphatic C-C structure in LtL-oil. In the aromatic composition, the carbon percentage of aromatic carbon is higher in LtL oil 6 which produced under ^{13}C labeled formic acid than LtL oil 5, and Table 5-8 shows the aromatic carbon ratio of C-C: C-O: C-H bonds are slightly varied. It seems some of carbon in aromatic group are also transferred from ^{13}C labelled formic acid.

Table 5-7 The ratio of different carbon bond in Aliphatic carbons in LtL oil produced with with normal and ^{13}C labelled formic acid

	Production condition	Formic acid	*Methoxyl-C-O*	*Aliphatic C-O*	*Aliphatic C-C*
LtL-Oil 5	320°C, 0.5ml FA	***Normal***	1.0	1.5	5.5
LtL-Oil 6	320°C, 0.5ml FA	^{13}C ***labelled***	1.0	1.5	5.9

Table 5-8 The ratio of different carbon bond in Aromatic carbons in LtL oil produced with normal and ^{13}C labelled formic acid

	Production condition	Formic acid	*Aromatic C-C*	*Aromatic C-O*	*Aromatic C-H*
LtL-Oil 5	320°C, 0.5ml FA	***Normal***	0.3	1	1.8
LtL-Oil 6	320°C, 0.5ml FA	^{13}C ***labelled***	0.3	1	1.3

In summary, more aromatic carbon and less aliphatic carbon are achieved when the experiment temperature is increasing, while the aromatic compositions are not varied under different temperature. On the other hand, less aromatic carbon and more aliphatic carbon are achieved when higher amount formic acid is presented. Also, the aromatic compositions vary with different amount of formic acid added. When more formic acid is present, then more aromatic C-C bonds are produced compared to aromatic C-O bonds and C-H bonds.

Besides, carbon from the formic acid mostly incorporates in the carbonyl structures, while it seems also partly incorporates in aliphatic C-C structures and aromatic group in LtL oils. It's confirmed that the formic acid is a reactant in the lignin conversion in addition to be a hydrogen donor.

In conclusion, the NMR technologies provide a facile way to analyze LtL-oils. NMR analysis is well-known to be an insensitive research tool, and for bio-oils it is better suited to analyze changes in functional group composition than to identify individual compounds.

Quantitative measurements of the chemical constituents in whole bio-oil are difficult because of its viscous, acidic, and unstable nature. Further, bio-oil is a complex mixture containing over 300 compounds, mostly present in low concentrations, including ketones, aldehydes, anhydrous sugars, carboxylic acids, and phenolic compounds. The main advantages of the application of NMR to the analysis of bio-oils are (1) the whole bio-oil can be dissolved in an appropriate solvent and information about the whole spectrum of functional groups can be obtained, which does not depend on the volatility of the components in the bio-oils; and (2) the chemical shift ranges for functional groups can be studied, and quantitative analysis of functional groups can be achieved by integration of peaks based on the proposed chemical shift assignment ranges.

Since most LtL research focuses on reducing the oxygen contents in bio-oils through optimizing the solvolysis experiment parameters (e.g., temperature and solvent atmosphere), ^{1}H, ^{13}C NMR analyses are powerful tools for obtaining structure information about the whole fraction of bio-oils. ^{1}H−^{13}C HSQC NMR provides carbon−hydrogen information, which is useful for elucidating possible reactive pathways during solvolysis reactions.

The 1-D NMR techniques are quantitative in nature; however, the spectral overlap problems usually occur because of the complex constitution of bio-oils. The appropriate NMR experiment parameters should carefully select to let the nucleus fully relax. The inaccuracy of the integration results should also be considered. It took days to perform ^{13}C quantitative NMR of LtL oil samples on 850MHz with ns=3072, but it’s still not enough to get perfect baseline correction and phase correction of spectra due to very low concentration of each component in the LtL oils. Besides, around 300 peaks for each ^{13}C NMR spectrum of LtL oils were manually picked and integrated, some integration from poor signals could be not accurate enough.

Chapter 6 Conclusion

The aim of this thesis was to characterize LtL-oil by Nuclear Magnetic Resonance (NMR) spectroscopy. An appropriate solvent DMSO-d6 was selected for NMR sample preparation because of its good solubility, less peak overlap in ^{1}H NMR spectra and stable solvent effect. The efficiency of quantitative ^{13}C NMR experiments was improved by reducing the duration of the experimental time by means of relaxation agents and by the use of greater magnetic field strengths to improve signal sensitivity. The optimum relaxation Cr(acac)3 concentration was determined to be 0.01M and 850MHz magnet was chosen to use for LtL-oil analysis because of its better resolution and sensitivity.

The ^{1}H NMR, ^{13}C NMR and 2D NMR spectra of 6 standard compounds and mixtures which were predicted to be contained in LtL-oil by previous GC-MS analysis results were achieved and their ^{1}H chemical shift and ^{13}C chemical shift were identified. Then a proposed ^{13}C NMR chemical shift assignment range of Lignin bio-oil was selected to use for quantitative analysis of functional groups in LtL-oils, based on the comparison of standard compounds assignments. The integration results of quantitative ^{13}C NMR spectra about the functional groups in LtL-oils under different conversion conditions were consequently obtained.

It is discovered that both formic acid and reaction temperature in LtL-solvolysis influences the product composition on a functional group level. It is also confirmed that the formic acid is a reactant in the lignin solvolysis conversion in addition to be a hydrogen donor by comparing ^{13}C NMR spectra of normal LtL oil and ^{13}C-labeled formic acid LtL oil, which indicated functionality and position of the incorporated carbons from formic acid in the solvolysis products.

Chapter 7 Further work

- **Make the NMR spectra better processed**

When it comes to ^{13}C quantitative analysis, a clear and well processed NMR spectrum is essential. However, the LtL oils are complicated mixture, in addition to small amounts and poor solubility of LtL oil samples, the NMR spectra acquired were not perfect regarding the baseline correction and integration. To reduce the noise and correct the phase in NMR spectra, larger number of ns (scan of numbers) can be settled if time permits. Also, the concentration of NMR samples can be increased if enough sample is available.

- **Make the functional groups integration more accurate.**

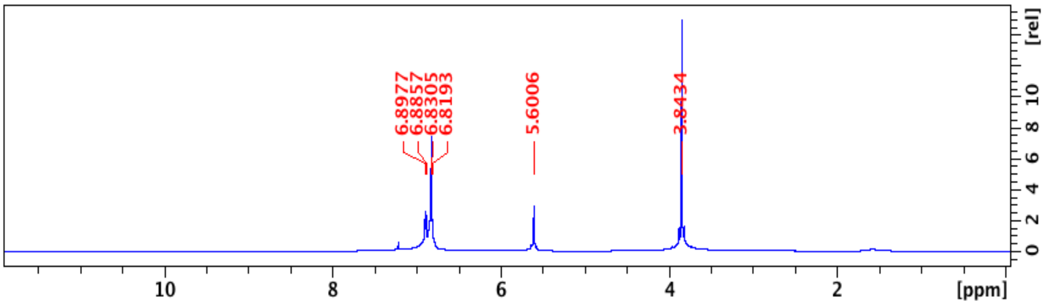
The ^{13}C NMR chemical shift of functional group assignment of Lignin bio-oil is identified based on standard compound NMR spectra assignment and previous published papers. Most peaks from standard compounds fits the functional group assigned range, however, there are a few exceptions and LtL oil contains more chemical compounds than used in this study. In order to find these exceptions to make the functional group integration more accurate, it could be helpful to run NMR experiments of more possible chemical compounds and identify their peaks.

- **Investigation of the role of formic acid**

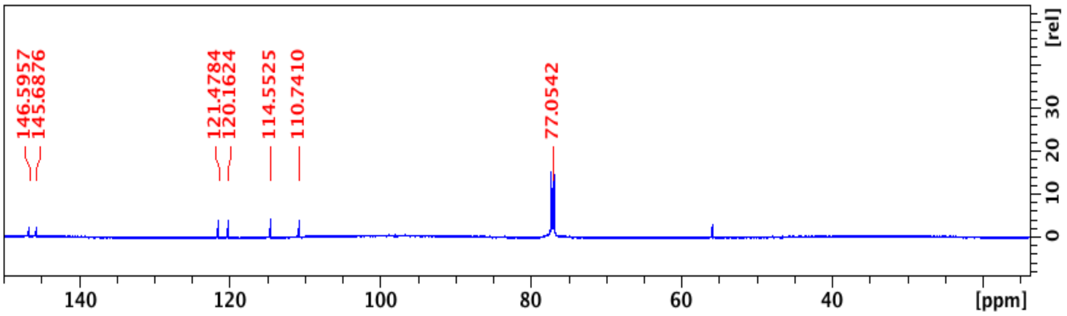
2D NMR, for example HMBC and HSQC can be used further identify relevant functional groups in LtL oil. It will help understand the reaction pathways of producing LtL oils and investigate the role of formic acid.

Appendix A NMR spectra

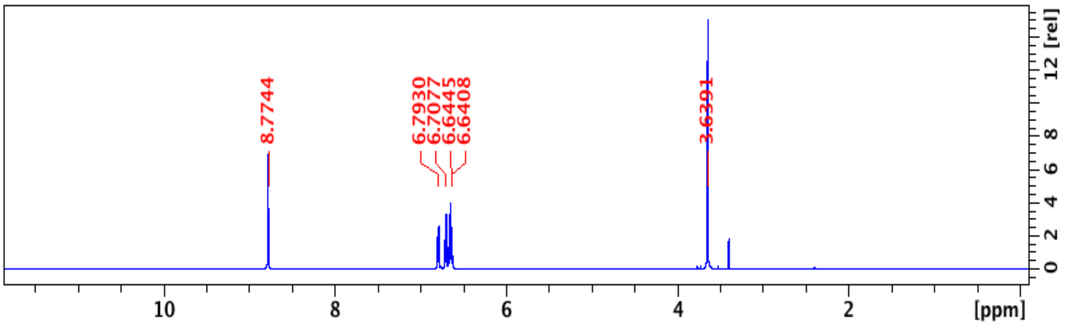
A1. ^{1}H NMR spectrum of compound 1 in $CDCl_3$



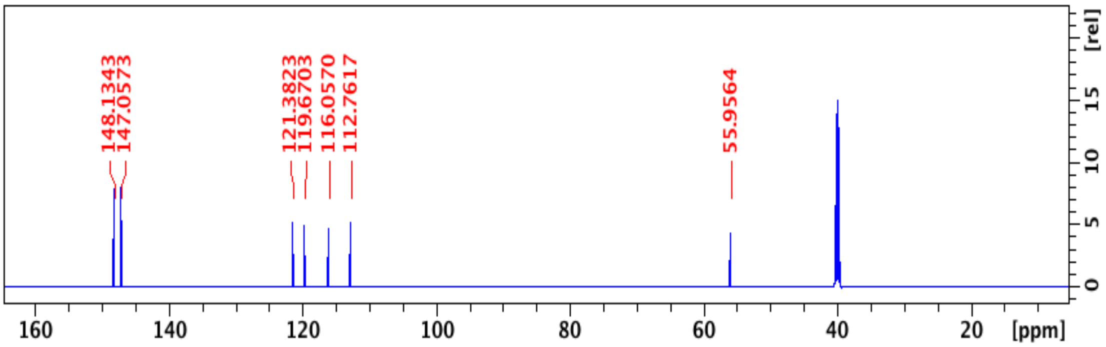
A2. ^{13}C NMR spectrum of compound 1 in CDCl3



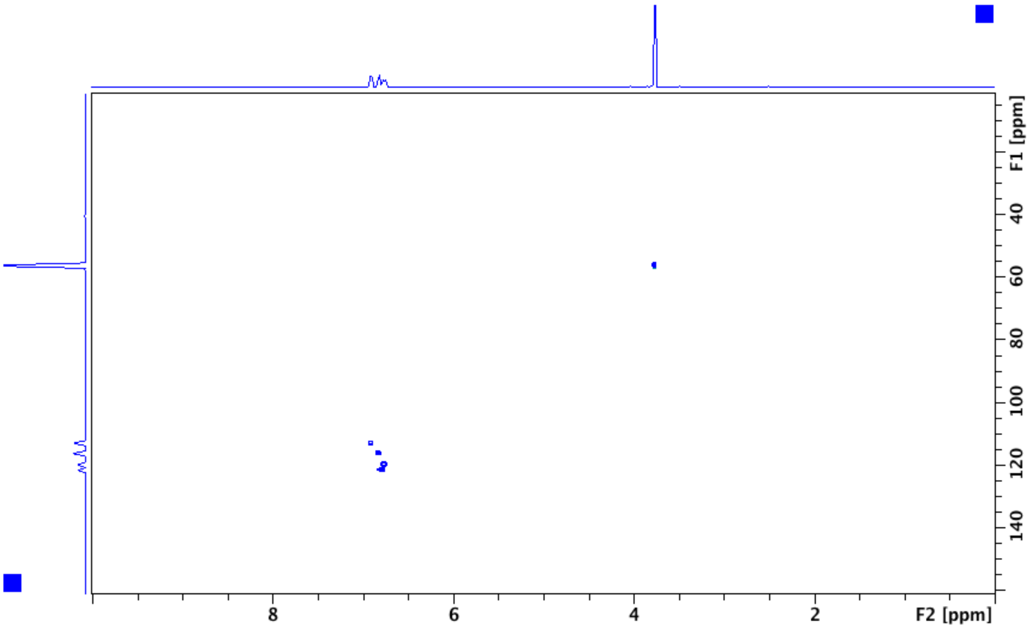
A3. ^{1}H NMR spectrum of compound 1 in DMSO-d6



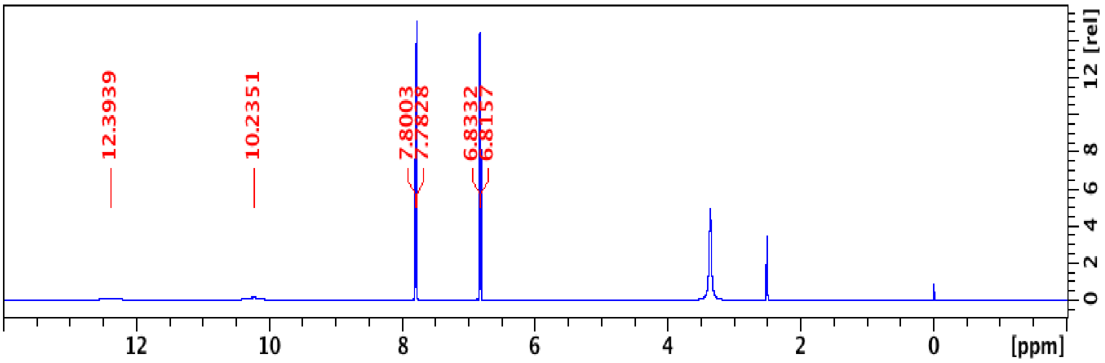
A4. ^{13}C NMR spectrum of compound 1 in DMSO-d6



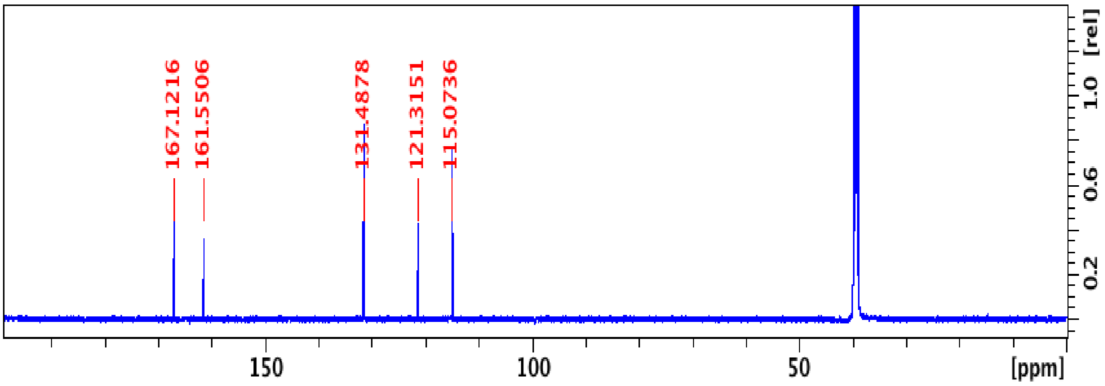
A5. 2D HSQC NMR spectrum of compound 1 in DMSO-d6



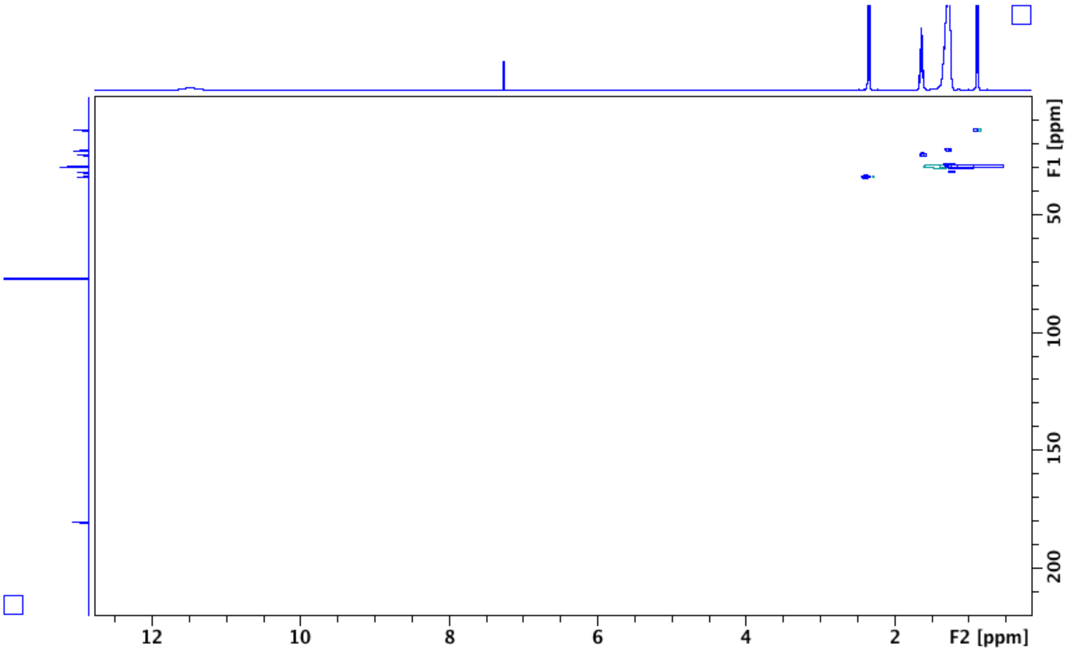
A6. ^{1}H NMR spectrum of compound 2 in DMSO-d6



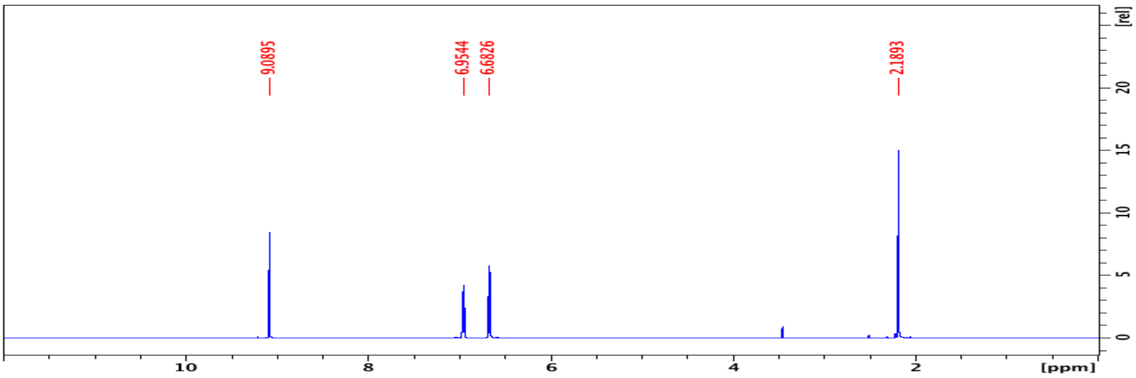
A7. ^{13}C NMR spectrum of compound 2 in DMSO-d6



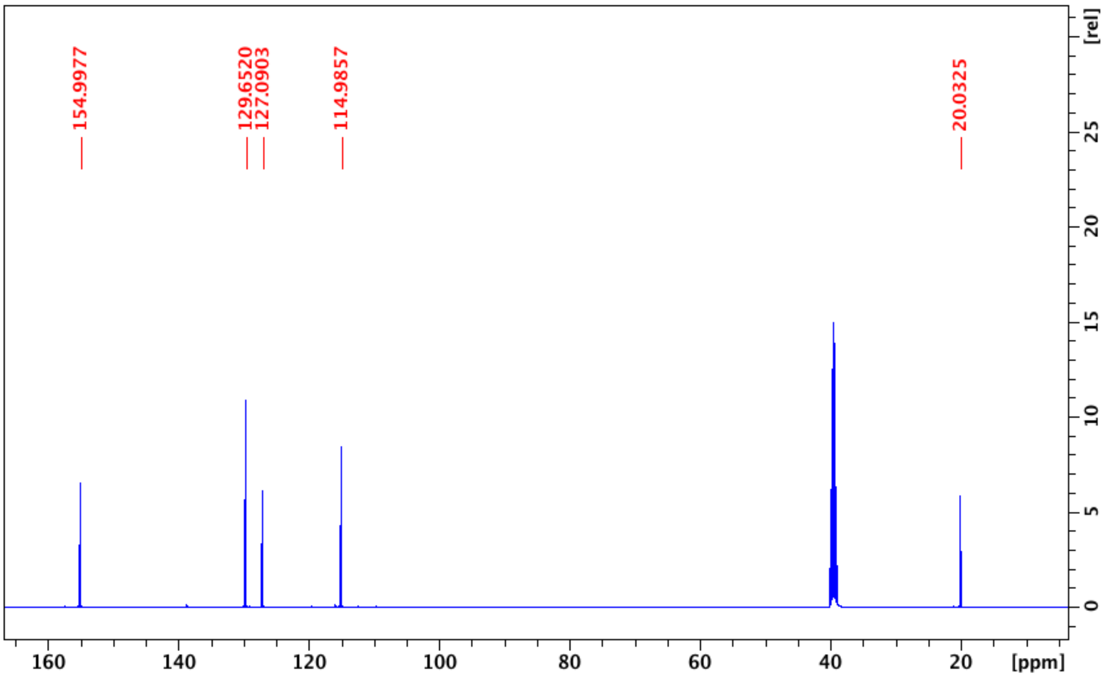
A8. 2D HSQC NMR spectrum of compound 2 in DMSO-d6



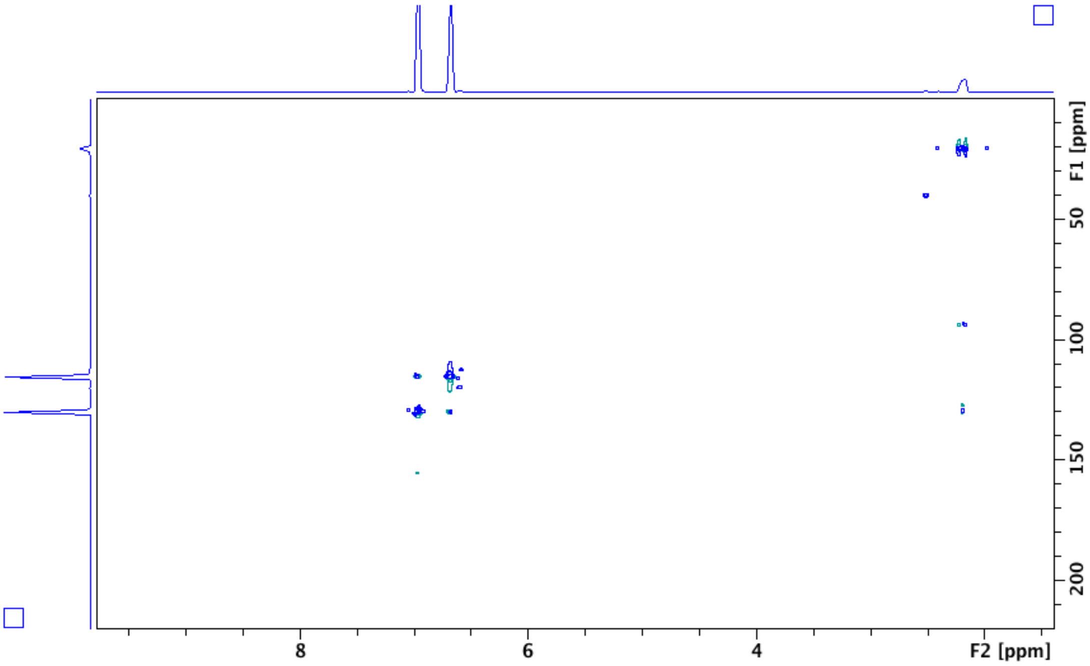
A9. ^{1}H NMR spectrum of compound 3 in DMSO-d6



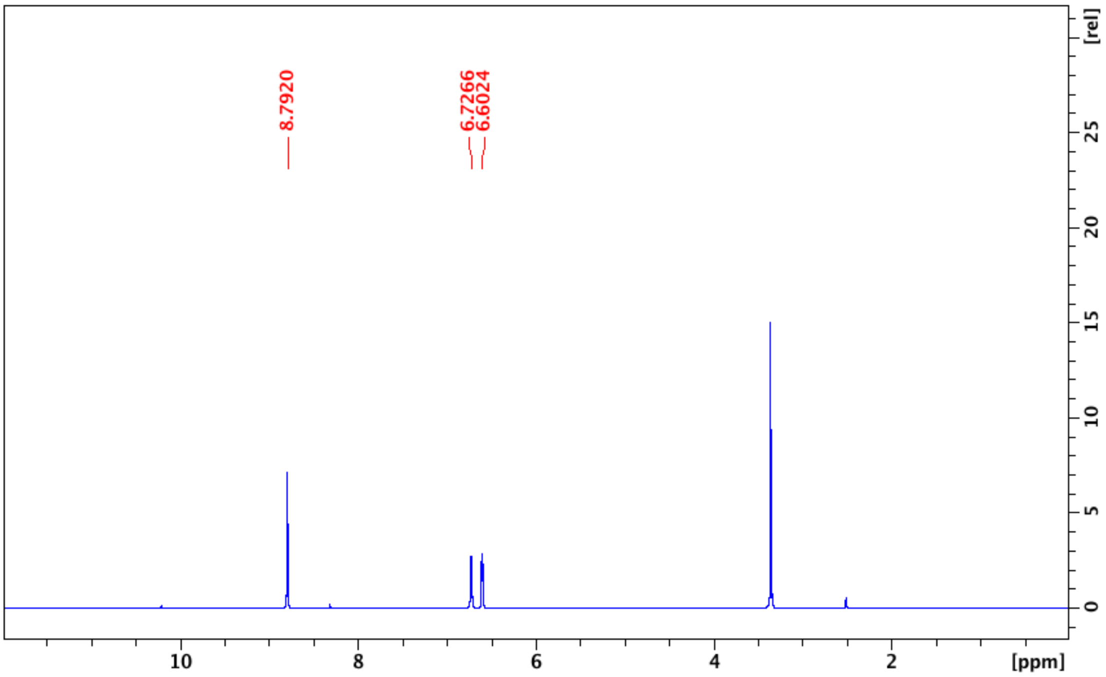
A10. ^{13}C NMR spectrum of compound 3 in DMSO-d6



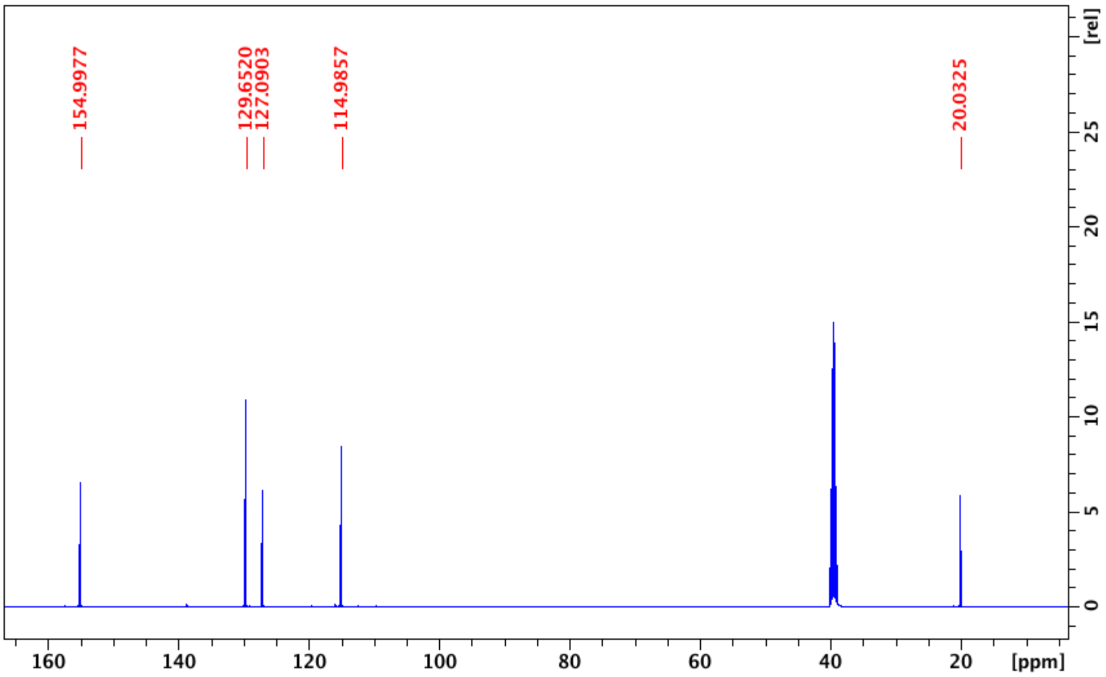
A11. 2D HSQC NMR spectrum of compound 3 in DMSO-d6



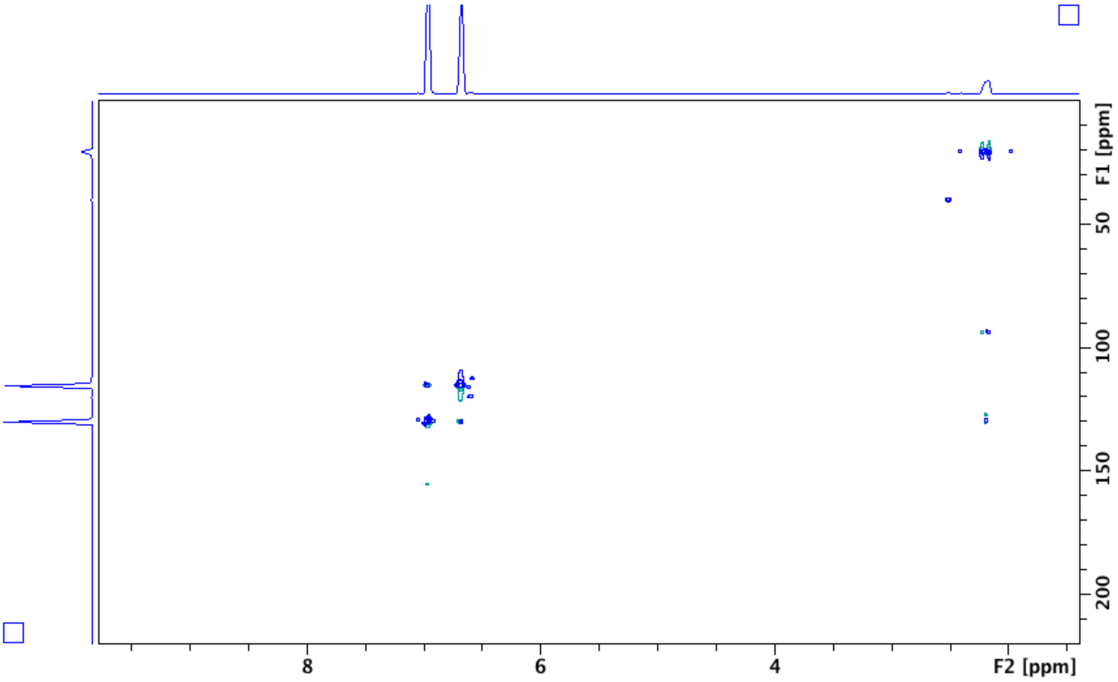
A12. ^{1}H NMR spectrum of compound 4 in DMSO-d6



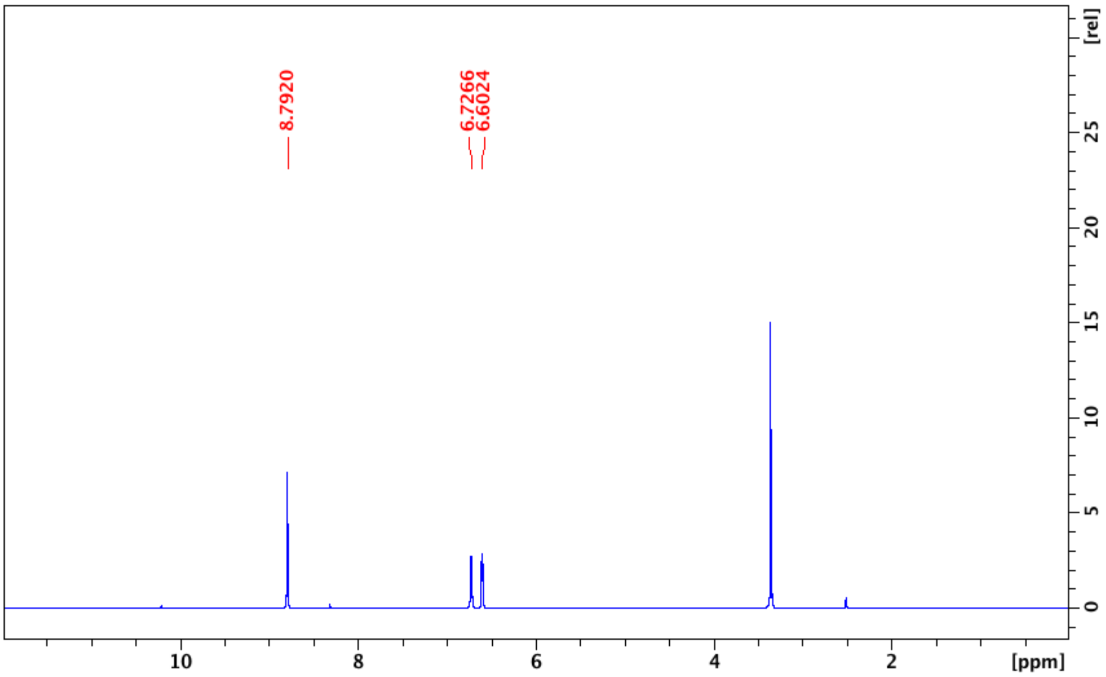
A13. ^{13}C NMR spectrum of compound 4 in DMSO-d6



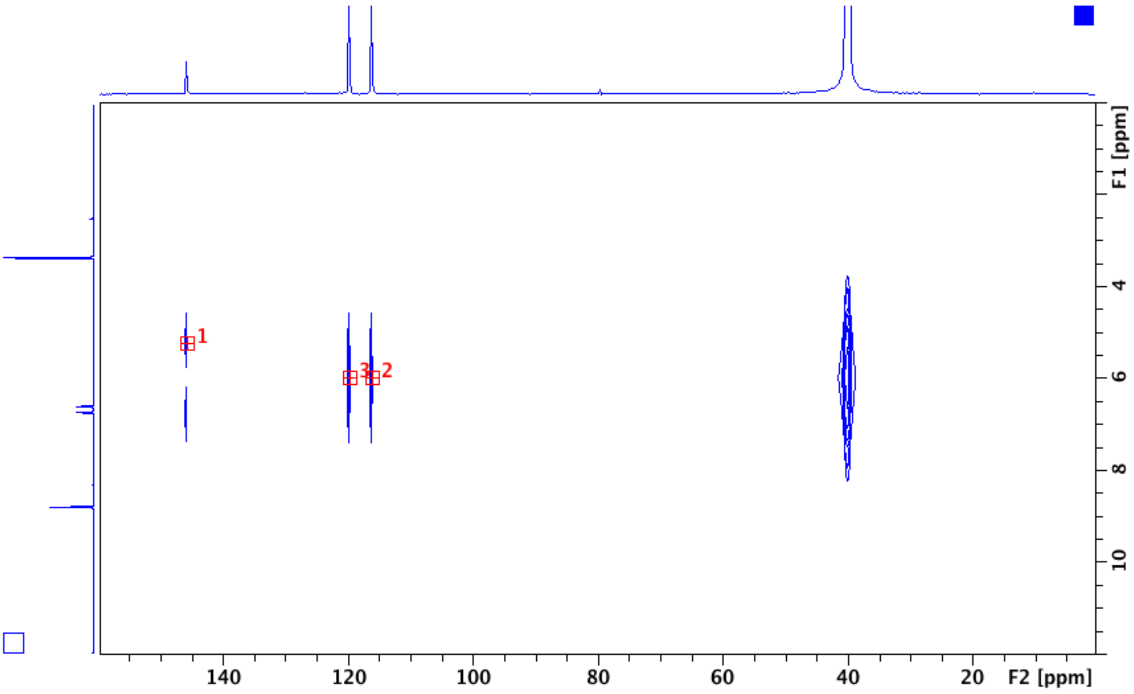
A14. 2D HSQC NMR spectrum of compound 4 in DMSO-d6



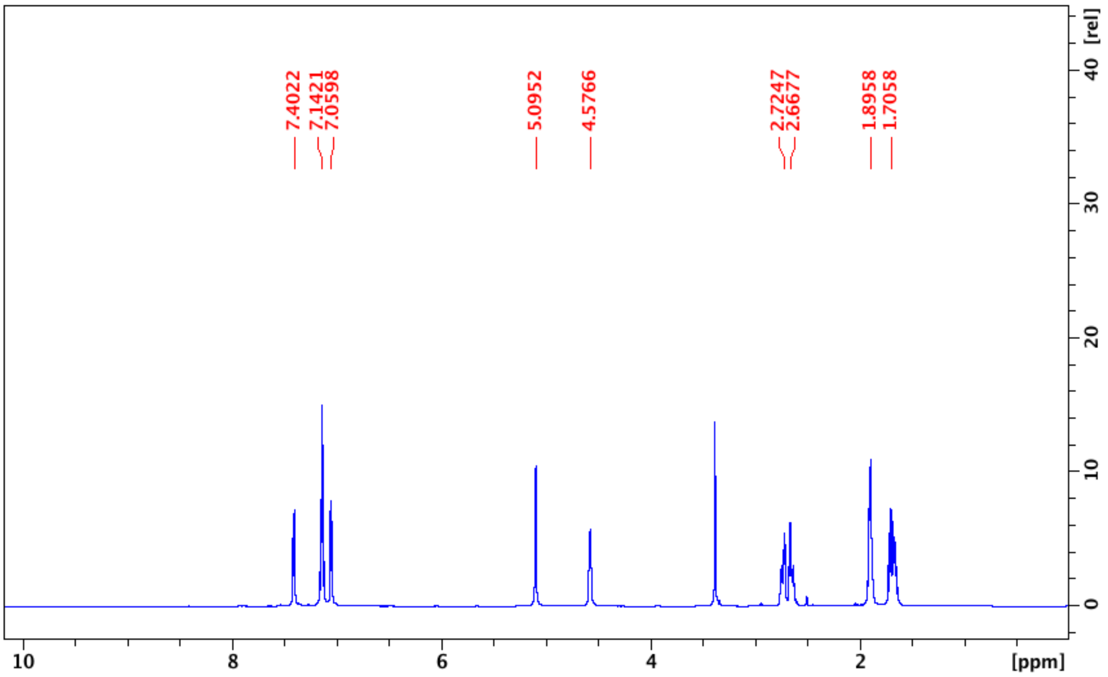
A15. ^{1}H NMR spectrum of compound 5 in DMSO-d6



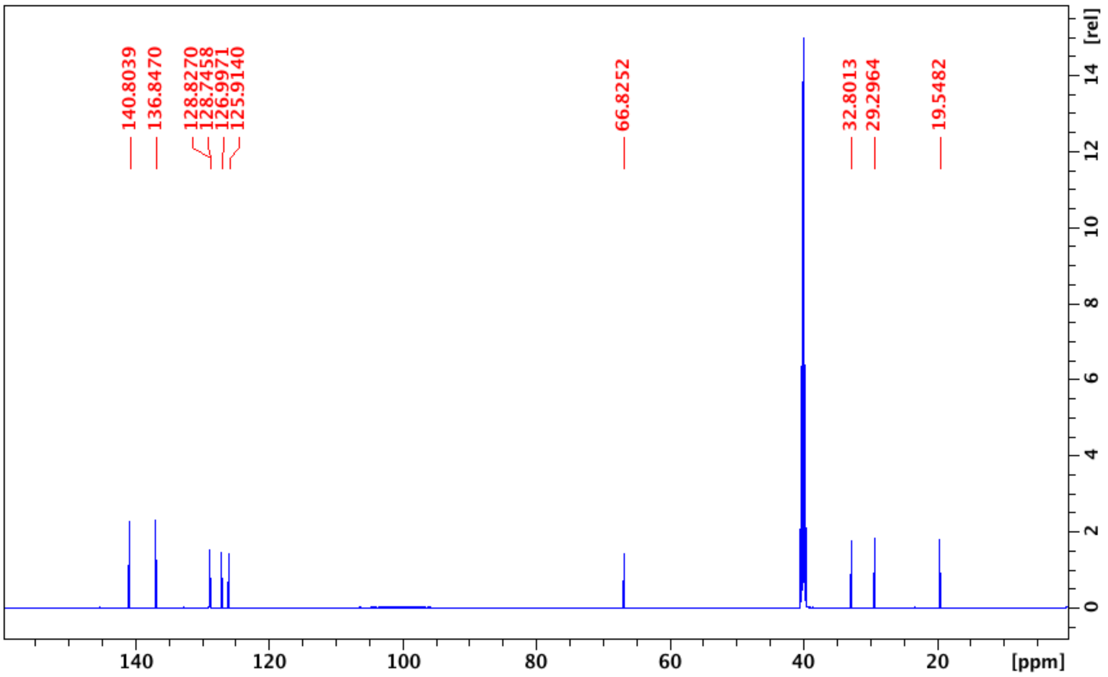
A16. 2D HSQC NMR spectrum of compound 5 in DMSO-d6



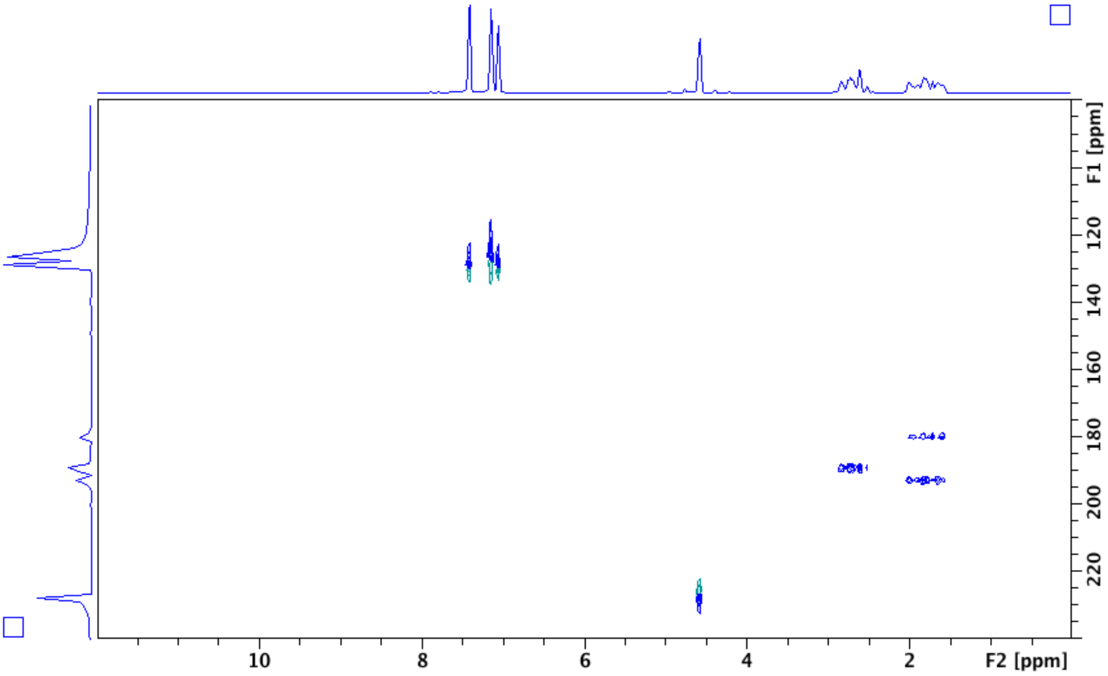
A17. ^{1}H NMR spectrum of compound 6 in DMSO-d6



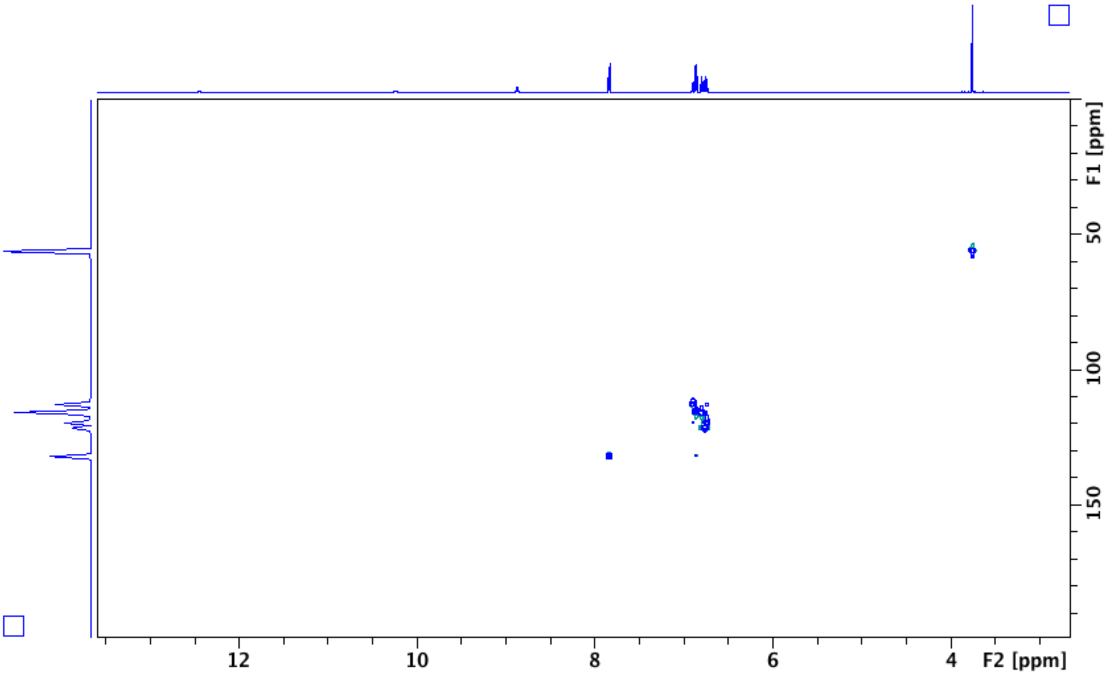
A18. ^{13}C NMR spectrum of compound 6 in DMSO-d6



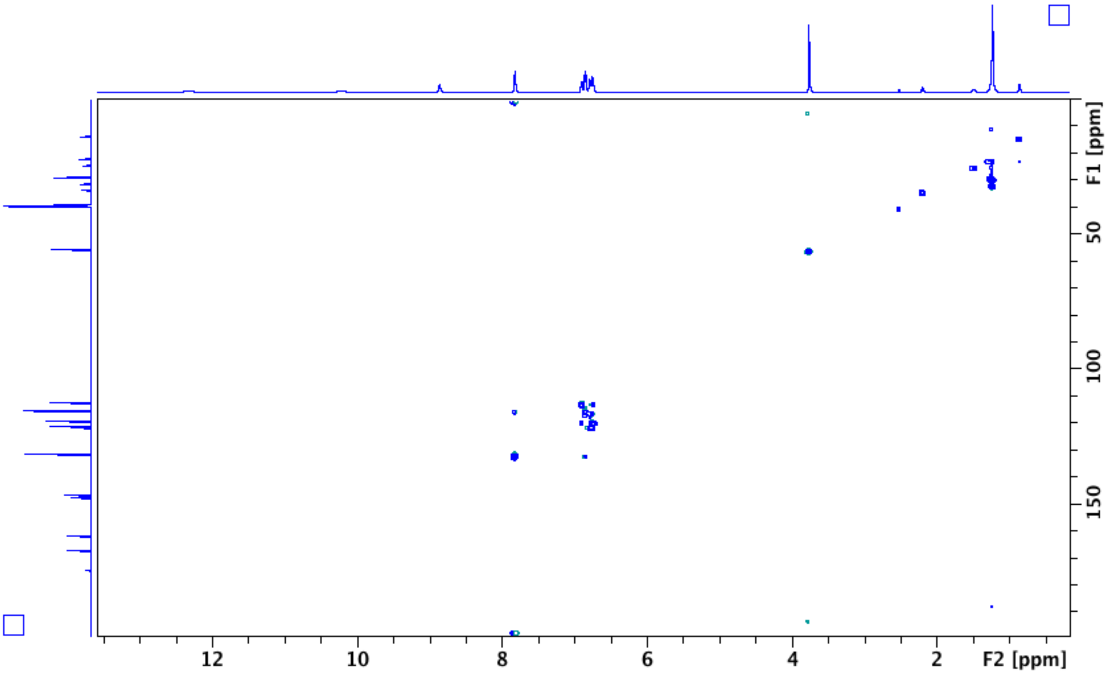
A19. 2D HSQC NMR spectrum of compound 6 in DMSO-d6



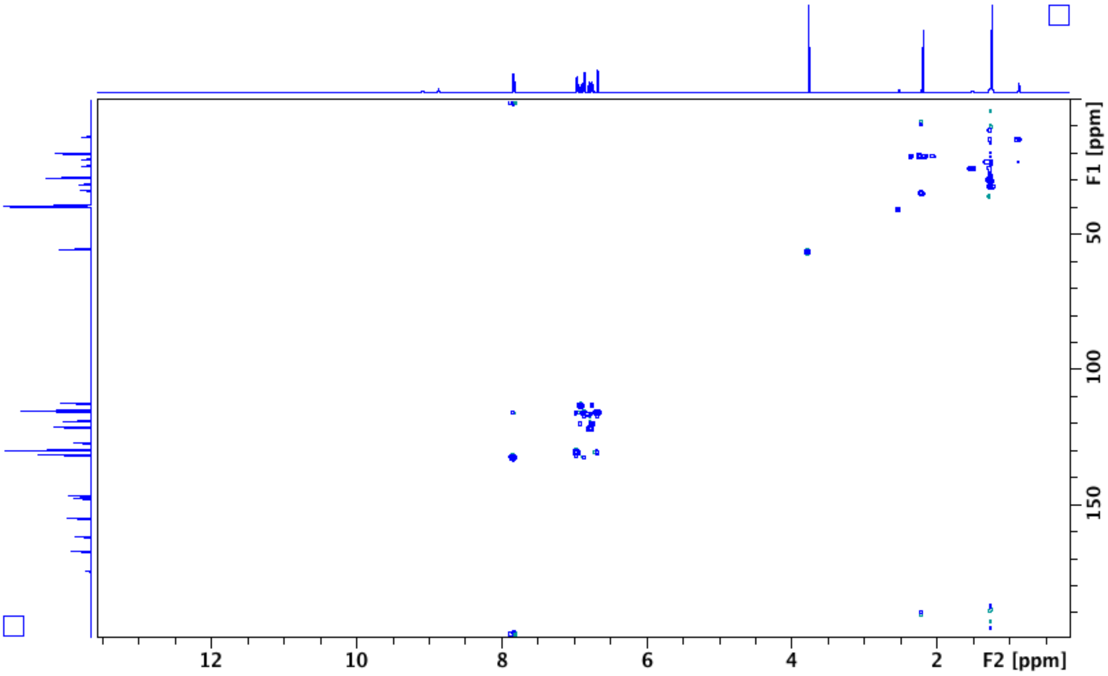
A20. 2D HSQC NMR spectrum of Mixture 1 in DMSO-d6



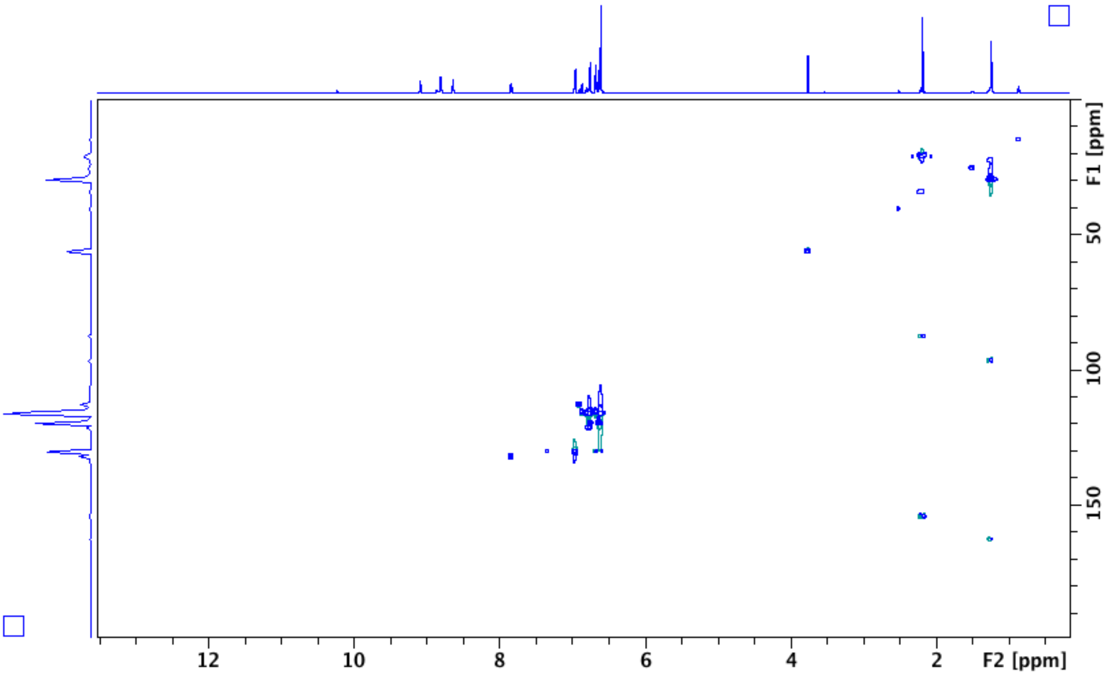
A21. 2D HSQC NMR spectrum of Mixture 2 in DMSO-d6



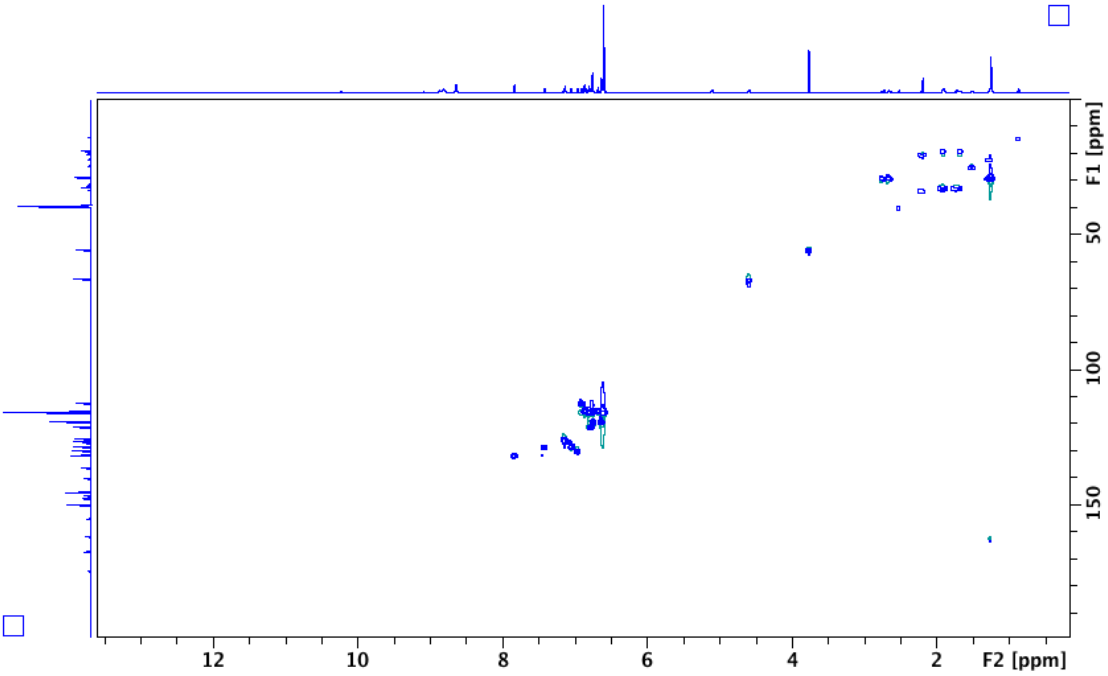
A22. 2D HSQC NMR spectrum of Mixture 3 in DMSO-d6



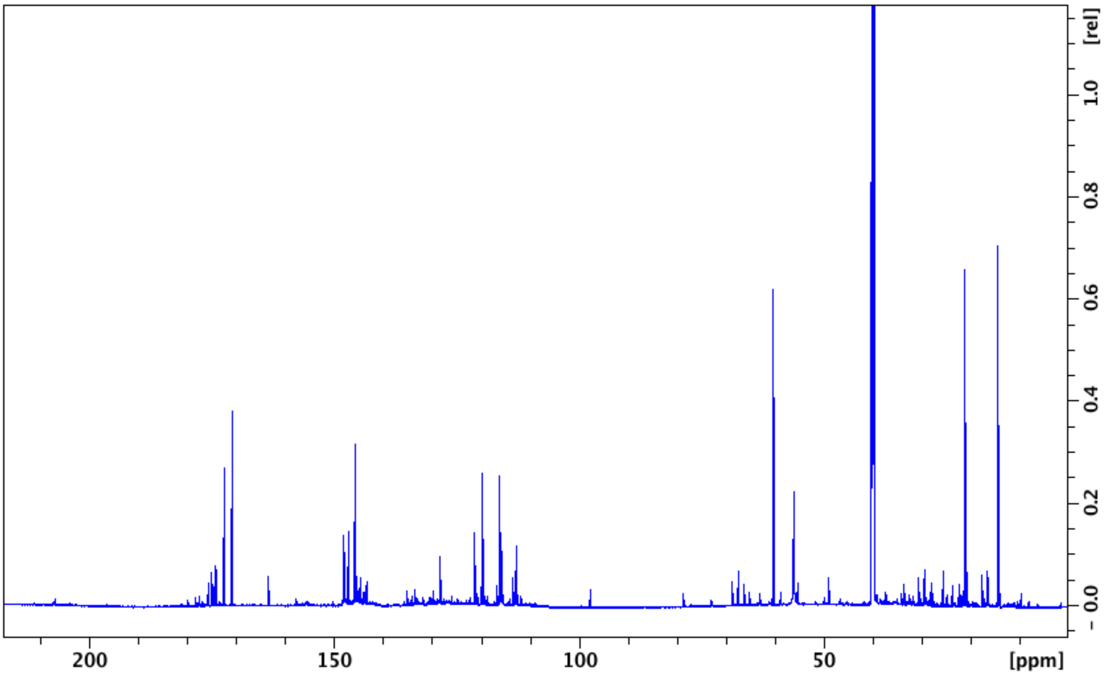
A23. 2D HSQC NMR spectrum of Mixture 4 in DMSO-d6



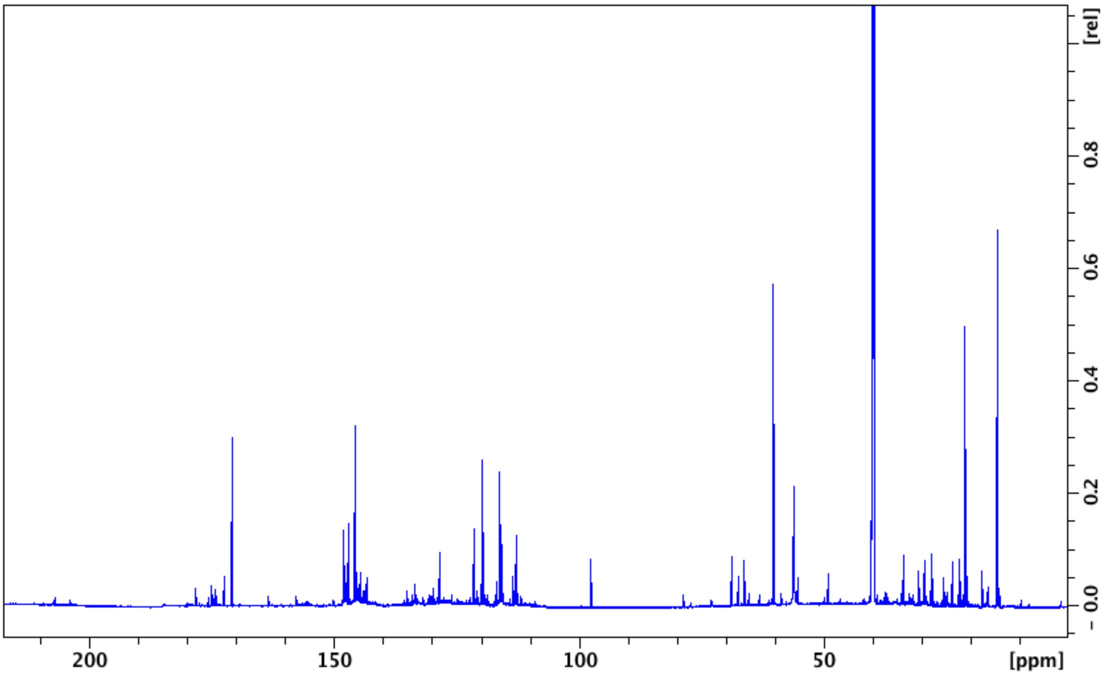
A24. 2D HSQC NMR spectrum of Mixture 5 in DMSO-d6



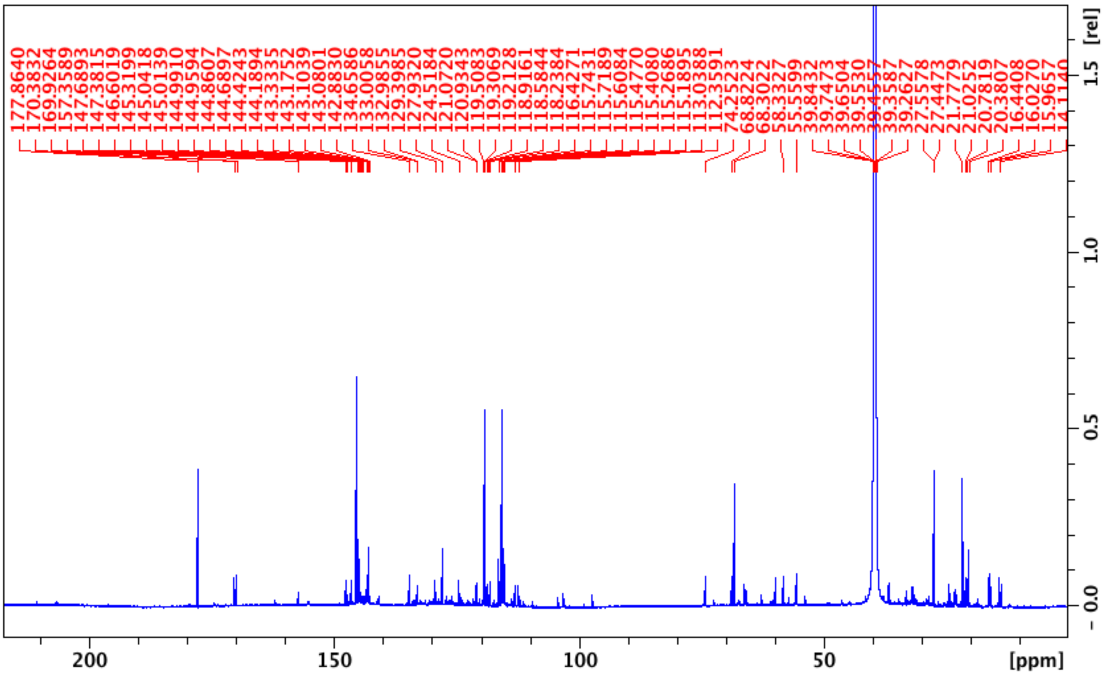
A25. Quantitative ^{13}C NMR spectrum of LtL-oil 1



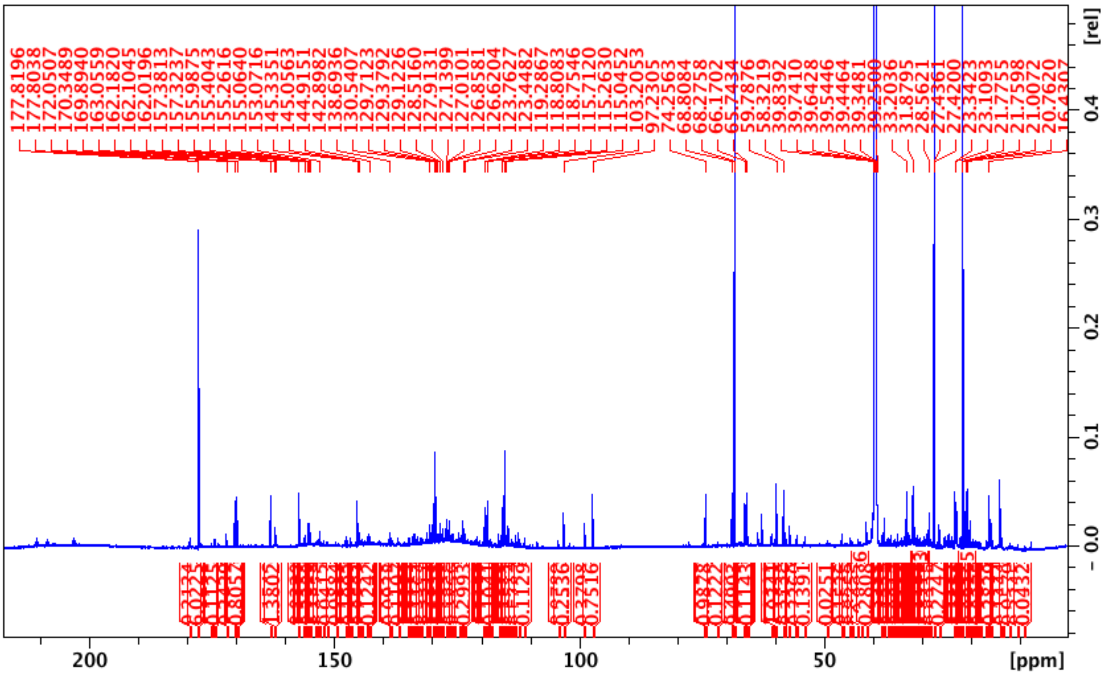
A26. Quantitative ^{13}C NMR spectrum of LtL-oil 2



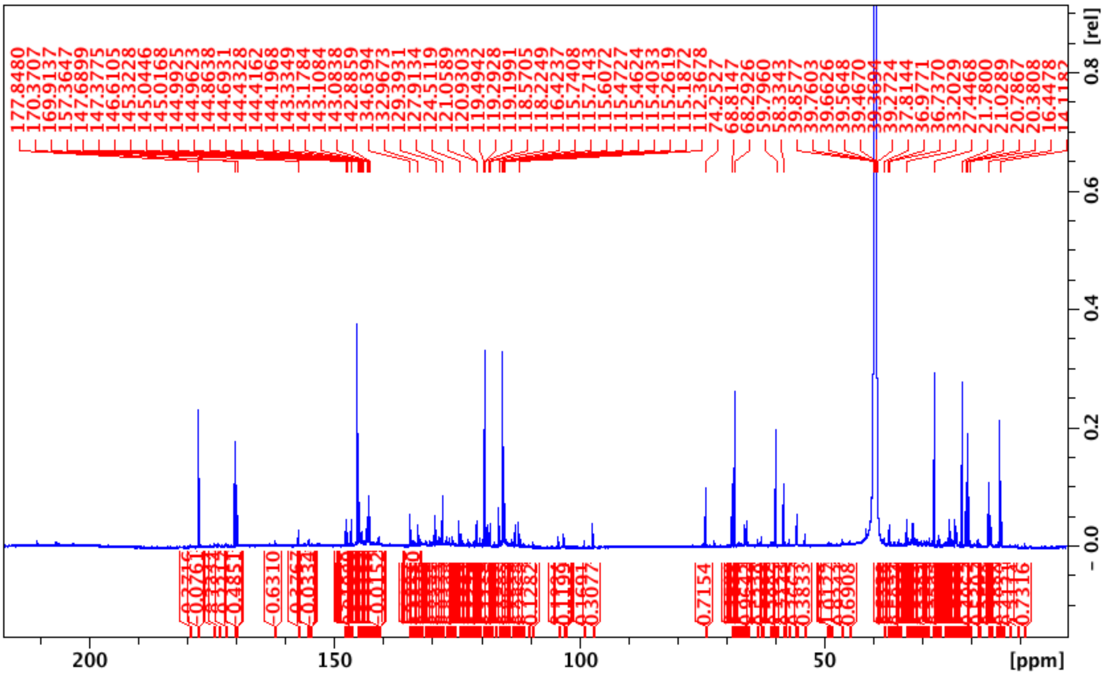
A27. Quantitative ^{13}C NMR spectrum of LtL-oil 3



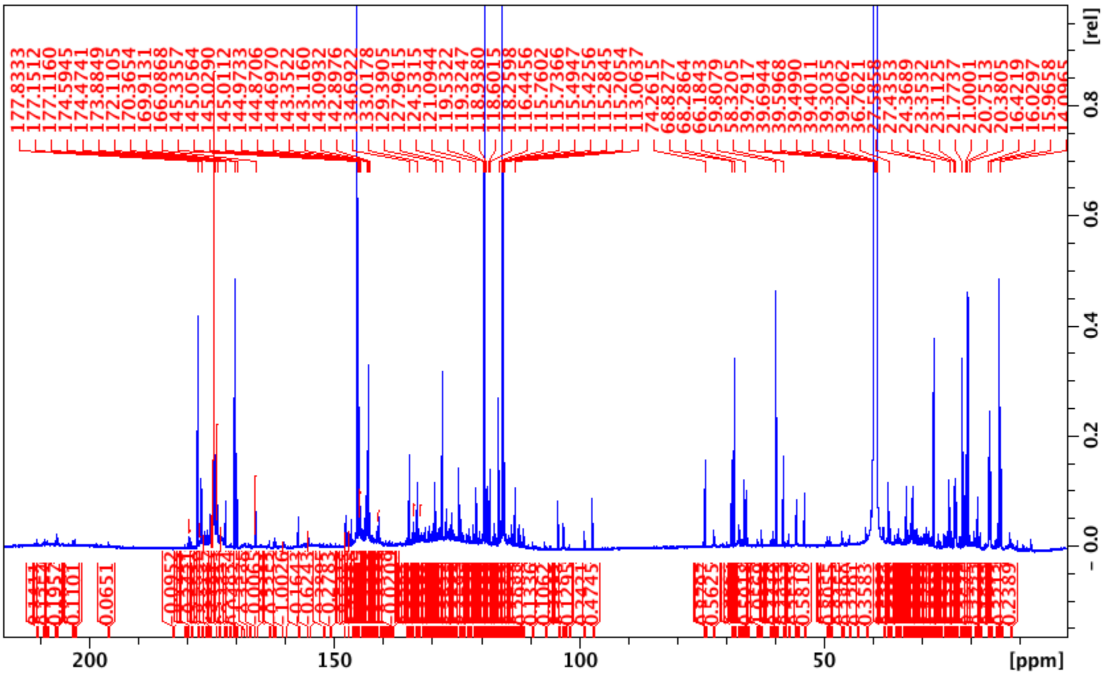
A28. Quantitative ^{13}C NMR spectrum of LtL-oil 4



A29. Quantitative ^{13}C NMR spectrum of LtL-oil 5



A30. Quantitative ^{13}C NMR spectrum of LtL-oil 6



Appendix B NMR spectra integrations

B1. Integrals of Quantitative ^{13}C NMR of guaiacol in DMSO-d6

Object	*Integral [abs]*	*Integral [rel]*	*Peaks*	*Range (F1) from*	*Range (F1) to*	*v(F1) [ppm]*
Integral 7	495338993.5	1.000000267	1	55.53826661	55.4160574	55.477162
Integral 6	488102177	0.985390437	1	112.5584483	111.8340934	112.1962708
Integral 5	455005668	0.918574543	1	115.739311	115.1409308	115.4401209
Integral 4	446036191.5	0.900466784	1	119.2980979	118.9674142	119.1327561
Integral 3	460157866	0.928975903	1	121.0302509	120.6838203	120.8570356
Integral 2	513465909.5	1.036595247	1	146.6916176	146.1853223	146.43847

B2. Integrals of Quantitative ^{13}C NMR of guaiacol with 0.01M Cr(acac)3 in DMSO-d6

Object	*Integral [abs]*	*Integral [rel]*	*Peaks*	*Range (F1) from*	*Range (F1) to*	*v(F1) [ppm]*
Integral 7	231310278.5	1.023627748	1	147.730764	147.5362239	147.6334939
Integral 6	231852651.5	1.026027936	1	146.6458288	146.4662533	146.556041
Integral 5	224416517.5	0.993120478	1	120.9837601	120.8131788	120.8984695
Integral 4	227947103	1.008744537	1	119.3195521	119.0532789	119.1864155
Integral 3	220524783.5	0.975898213	1	115.6470469	115.4999432	115.5734951
Integral 2	219654160.5	0.972045406	1	112.3796118	112.236031	112.3078214

B3. Integrals of Quantitative ^{13}C NMR of guaiacol with 0.01M Cr(acac)3 in DMSO-d6

Object	*Integral [abs]*	*Integral [rel]*	*Peaks*	*Range (F1) from*	*Range (F1) to*	*v(F1) [ppm]*
Integral 7	275862890	1.017773662	1	147.7753862	147.5496977	147.662542
Integral 6	273207266.5	1.007975955	1	146.6800188	146.5010244	146.5905216
Integral 5	269003982.5	0.992468281	1	121.1067041	120.8805622	120.9936331
Integral 4	267485257.5	0.986865069	1	119.4028956	119.1519711	119.2774334
Integral 3	269314169	0.993612689	1	115.7722347	115.505821	115.6390279
Integral 2	273812203	1.010207819	1	112.5195095	112.2654872	112.3924983

B4. Integrals of Quantitative ^{13}C NMR of LtL-oil 3 in DMSO-d6

Object	*Integral [abs]*	*Integral [rel]*	*Peaks*	*Range (F1) from*	*Range (F1) to*	*v(F1) [ppm]*
Integral 1	1128729,556	1	0	179,6930255	179,6614959	179,6772607
Integral 2	2322358,471	2,057497705	1	179,5176422	179,4585242	179,4880832

Integral 3	80138756,1	70,99907654	1	177,925398	177,8032209	177,8643095
Integral 4	1120485,974	0,992696584	1	174,6027505	174,533526	174,5681382
Integral 5	15425659,87	13,66639138	1	170,4308182	170,3523637	170,391591
Integral 6	18009852,45	15,95586149	1	169,9785512	169,8908668	169,934709
Integral 7	12537475,78	11,10759944	2	162,240605	162,1075853	162,1740951
Integral 8	8804552,737	7,80040949	1	157,3921725	157,2890143	157,3405934
Integral 9	1352595,15	1,19833413	1	155,407057	155,3724447	155,3897508
Integral 10	466972,2	0,413714869	0	155,3357964	155,3011841	155,3184903
Integral 11	2554809,92	2,263438489	1	155,2726799	155,2278876	155,2502837
Integral 12	2096570,542	1,85746048	1	155,0690783	155,026322	155,0477002
Integral 13	772040,3333	0,683990536	1	148,885219	148,8590951	148,8721571
Integral 14	3487343,813	3,089618585	1	147,8402638	147,7854036	147,8128337
Integral 15	15765109,42	13,96712733	1	147,7436054	147,6391099	147,6913577
Integral 16	12918344,3	11,4450306	2	147,4562427	147,356972	147,4066074
Integral 17	3606734,788	3,195393237	1	147,2812127	147,2237402	147,2524765
Integral 18	1754143,261	1,554086408	1	147,0591598	147,0199739	147,0395668
Integral 19	2881222,032	2,552623893	1	146,8162077	146,7613475	146,7887776
Integral 20	15746137,06	13,95031873	1	146,6516272	146,5680308	146,609829
Integral 21	3521897,88	3,120231824	1	146,3982256	146,3094044	146,353815
Integral 22	1597649,421	1,415440407	1	145,5441092	145,5121746	145,5281419
Integral 23	152073877,3	134,7301278	1	145,3962019	145,2499754	145,3230886
Integral 24	2695860,6	2,388402595	1	145,2062755	145,1709795	145,1886275
Integral 25	2726252,32	2,415328195	1	145,117195	145,0734951	145,0953451
Integral 26	65400345,74	57,9415551	3	145,0701336	144,9726493	145,0213914
Integral 27	9456110,824	8,37765856	1	144,9726493	144,9138225	144,9432359
Integral 28	16206053,17	14,35778225	2	144,8953341	144,8129767	144,8541554
Integral 29	10489711,86	9,293379279	1	144,7171731	144,6398579	144,6785155
Integral 30	3249557,371	2,878951256	1	144,6297733	144,5692658	144,5995196
Integral 31	7687079,636	6,810382167	2	144,4482508	144,389424	144,4188374
Integral 32	3631706,621	3,217517077	1	144,268409	144,2179861	144,2431975
Integral 33	3784467,636	3,352855977	1	144,2095823	144,1726054	144,1910938
Integral 34	4492900	3,980492916	1	143,7053529	143,6381224	143,6717377
Integral 35	21515262,92	19,06148626	1	143,3944115	143,305331	143,3498713
Integral 36	1009617,462	0,894472424	1	143,2952464	143,2733965	143,2843215
Integral 37	6578073,429	5,827856103	1	143,1994429	143,1372546	143,1683487
Integral 38	40352215,62	35,75011873	2	143,1372546	143,0431318	143,0901932
Integral 39	687230	0,608852667	0	142,9674974	142,9439667	142,955732
Integral 40	39778809,21	35,24210828	1	142,9389244	142,8212709	142,8800976
Integral 41	1501029	1,329839369	1	142,7893364	142,7590826	142,7742095
Integral 42	5936649,162	5,259585109	1	142,7540403	142,6884905	142,7212654
Integral 43	1030385,824	0,912872192	1	141,836343	141,8060892	141,8212161
Integral 44	1666768,692	1,476676751	1	141,3421983	141,2968176	141,3195079
Integral 45	3505888,231	3,106048046	1	141,1102528	141,0413414	141,0757971
Integral 46	5126806,2	4,542103265	1	140,8799881	140,8262036	140,8530958

Integral 47	482983,2308	0,427899871	1	135,1284124	135,1065625	135,1174874
Integral 48	24089509,11	21,34214435	1	134,7082213	134,6124177	134,6603195
Integral 49	2398878,364	2,125290644	1	134,1535691	134,1149115	134,1342403
Integral 50	3832182,677	3,395129204	1	133,9031352	133,8493507	133,876243
Integral 51	2824795,125	2,502632372	1	133,6577436	133,6157245	133,636734
Integral 52	18769993,89	16,62931018	2	133,0257762	132,9635879	132,994682
Integral 53	3150875,217	2,791523622	1	132,5753313	132,5366738	132,5560026
Integral 54	2021164,923	1,790654735	1	132,2307746	132,1837132	132,2072439
Integral 55	3134765	2,777250746	1	131,4240078	131,3752656	131,3996367
Integral 56	1488842,25	1,319042496	1	130,6794291	130,6441331	130,6617811
Integral 57	1449480,455	1,284169842	1	130,3752108	130,3365532	130,355882
Integral 58	1273884,063	1,128599899	0	130,2289843	130,2020921	130,2155382
Integral 59	1294089,889	1,146501288	1	129,8726622	129,8407277	129,856695
Integral 60	3575930,189	3,168101847	1	129,7550087	129,6894589	129,7222338
Integral 61	13668081,36	12,10926151	1	129,4306212	129,3533061	129,3919636
Integral 62	1549208,3	1,372523907	1	129,1583374	129,0877453	129,1230413
Integral 63	621078,3871	0,550245525	0	129,0742992	129,0205147	129,0474069
Integral 64	3750338,919	3,322619577	1	128,5650276	128,4994778	128,5322527
Integral 65	1237403,913	1,096280244	1	128,2137478	128,1734095	128,1935786
Integral 66	42811758,95	37,92915561	1	127,9885254	127,8742334	127,9313794
Integral 67	7217101,808	6,394004456	2	127,1935239	127,1010818	127,1473028
Integral 68	1857774,88	1,645899029	1	127,0708281	127,0271282	127,0489781
Integral 69	3539957,529	3,136231803	1	126,6724869	126,6119794	126,6422331
Integral 70	2783385,273	2,465945238	1	126,5245796	126,4859221	126,5052508
Integral 71	14607157,08	12,94123734	1	124,5480007	124,4757279	124,5118643
Integral 72	3367921,143	2,983815854	1	124,2269748	124,2034441	124,2152094
Integral 73	4797696,25	4,250527707	1	124,2034441	124,1614249	124,1824345
Integral 74	1082619	0,95914827	0	124,1614249	124,1278097	124,1446173
Integral 75	3559735,55	3,153754177	1	124,1244481	124,053856	124,0891521
Integral 76	5034735,396	4,460532969	1	123,8168683	123,7311493	123,7740088
Integral 77	1130320,188	1,001409223	0	122,8823633	122,855471	122,8689172
Integral 78	3248874,923	2,878346639	1	122,6924369	122,6470563	122,6697466
Integral 79	3347363,927	2,965603152	0	122,4117492	122,3125841	122,3621667
Integral 80	590121,4286	0,522819152	0	122,2218229	122,1982922	122,2100575
Integral 81	1179417,7	1,044907254	0	121,7091897	121,6738937	121,6915417
Integral 82	4119230,406	3,649439661	1	121,5579209	121,500775	121,529348
Integral 83	15722145,14	13,92906304	1	121,1192415	121,0150341	121,0671378
Integral 84	3808537,714	3,374180906	1	121,0133533	120,9763765	120,9948649
Integral 85	13206575,5	11,70038955	1	120,9595688	120,8973806	120,9284747
Integral 86	4687129,75	4,152571116	1	120,4082781	120,3292822	120,3687802
Integral 87	3492610,296	3,094284436	0	120,2906246	120,2418825	120,2662535
Integral 88	2443994,077	2,165260992	0	119,7208455	119,6754649	119,6981552
Integral 89	33792507,69	29,93853357	1	119,5561306	119,4586463	119,5073884
Integral 90	2206032	1,954438057	0	119,4569655	119,4048618	119,4309136

Integral 91	148065180,2	131,1786153	1	119,3813311	119,2384661	119,3098986
Integral 92	11351425,6	10,05681613	1	119,2384661	119,1846817	119,2115739
Integral 93	2457806,765	2,177498368	0	119,104005	119,0451782	119,0745916
Integral 94	15058542,19	13,34114281	1	118,9846707	118,8737403	118,9292055
Integral 95	9102342,118	8,064236533	2	118,875421	118,8149135	118,8451673
Integral 96	2336040	2,069618881	0	118,8031482	118,7476829	118,7754155
Integral 97	3007927,056	2,664878439	0	118,7426406	118,6787716	118,7107061
Integral 98	964883	0,854839846	0	118,6552409	118,6266679	118,6409544
Integral 99	14760241,04	13,07686236	1	118,6233064	118,5426297	118,582968
Integral 100	488177,3684	0,432501626	0	118,5392682	118,5056529	118,5224605
Integral 101	4289495,629	3,800286444	0	118,4989298	118,4367415	118,4678357
Integral 102	1420858,667	1,258812317	0	118,4249762	118,3728725	118,3989243
Integral 103	1344036,235	1,190751344	0	118,3442995	118,283792	118,3140457
Integral 104	16204469,3	14,35637901	1	118,2770689	118,1963922	118,2367306
Integral 105	349716,8788	0,309832304	0	118,1678192	118,1106732	118,1392462
Integral 106	2600971,854	2,304335738	0	118,1089925	118,0350388	118,0720157
Integral 107	1641227	1,454048042	0	117,4854289	117,4551751	117,470302
Integral 108	4167233,867	3,691968414	0	117,2400373	117,1879336	117,2139855
Integral 109	2966245,733	2,627950795	0	116,8551423	116,8030386	116,8290904
Integral 110	38281243,13	33,91533689	1	116,4937779	116,3542745	116,4240262
Integral 111	1397511,475	1,23812783	0	116,3357861	116,1912403	116,2635132
Integral 112	9241488,397	8,187513432	0	116,1072021	115,9761025	116,0416523
Integral 113	179116202,8	158,6883252	2	115,8181107	115,6533957	115,7357532
Integral 114	16038440,14	14,20928517	1	115,6533957	115,5760806	115,6147382
Integral 115	100717161	89,2305517	2	115,5760806	115,3643043	115,4701924
Integral 116	6698437,765	5,934493105	1	115,3609427	115,3004352	115,330689
Integral 117	16339022,58	14,47558674	1	115,3105198	115,2466508	115,2785853
Integral 118	18859971,36	16,70902588	1	115,2332047	115,1390819	115,1861433
Integral 119	15289053,6	13,54536481	1	115,1189127	114,9609208	115,0399168
Integral 120	1395563,862	1,236402339	0	114,6045988	114,5541759	114,5793873
Integral 121	6370681,547	5,644116889	0	113,754132	113,6600092	113,7070706
Integral 122	6001656,915	5,317178845	0	113,2028413	113,1188031	113,1608222
Integral 123	22797299,64	20,19730902	1	113,0885493	112,9440036	113,0162765
Integral 124	3733411,667	3,307622848	0	112,5372586	112,4733896	112,5053241
Integral 125	2237196,96	1,98204871	0	112,4868357	112,4431358	112,4649858
Integral 126	19091592,21	16,9142308	1	112,4296897	112,3019516	112,3658207
Integral 127	4086696,04	3,62061578	0	112,0700061	112,0263063	112,0481562
Integral 128	2882824,514	2,554043614	0	112,0094986	111,9456296	111,9775641
Integral 129	3390829,375	3,004111444	0	111,3909773	111,3338313	111,3624043
Integral 130	2409975,277	2,135121974	0	109,5522211	109,4681829	109,510202
Integral 131	1719497,067	1,52339155	0	109,1353915	109,0816071	109,1084993
Integral 132	5555557,061	4,921955869	0	104,2981517	104,2410057	104,2695787
Integral 133	10411495,73	9,224083556	1	103,2628009	103,1350628	103,1989318
Integral 134	3315676,4	2,937529529	0	103,1417858	103,0711937	103,1064898

Integral 135	1961432,156	1,737734382	0	102,9165634	102,8594174	102,8879904
Integral 136	6921887,875	6,132459136	0	97,2624721	97,20532611	97,2338991
Integral 137	20117713,23	17,82332457	1	74,33012314	74,12843142	74,22927728
Integral 138	8737009,892	7,740569784	0	72,51489763	72,38043648	72,44766706
Integral 139	19156482,51	16,97172048	1	68,91133884	68,74998546	68,83066215
Integral 140	85582728,84	75,82217407	1	68,39366342	68,21214086	68,30290214
Integral 141	34081741,47	30,19478076	0	66,2389235	66,03050872	66,13471611
Integral 142	13425716,57	11,89453798	0	65,83890159	65,70444044	65,77167101
Integral 143	756338,5263	0,670079491	0	63,68080015	63,64718486	63,6639925
Integral 144	1644072,079	1,456568645	0	63,56650817	63,45221619	63,50936218
Integral 145	6821725,381	6,043719992	0	62,84041796	62,76646433	62,80344115
Integral 146	8899080,93	7,884156915	0	60,87728519	60,72265487	60,79997003
Integral 147	2306913,368	2,043814089	0	60,27893308	60,2117025	60,24531779
Integral 148	18510099,28	16,39905608	1	59,87554963	59,72091931	59,79823447
Integral 149	19948377,31	17,67330111	1	58,41664616	58,28218501	58,34941559
Integral 150	1612247,947	1,428373998	0	58,07377023	58,00653966	58,04015495
Integral 151	1497124,022	1,326379747	0	57,91913991	57,83846322	57,87880157
Integral 152	6783105,538	6,009504673	0	57,19304971	57,0989269	57,14598831
Integral 153	15889613,19	14,07743166	0	55,7879307	55,61313121	55,70053095
Integral 154	40418317,94	35,8086822	1	55,64002344	55,35093197	55,4954777
Integral 155	4860385,652	4,306067497	0	53,88530544	53,80462875	53,8449671
Integral 156	1427753,538	1,264920841	0	48,69285584	48,64638764	48,66962174
Integral 157	2172897,074	1,925082109	0	46,45076561	46,32878661	46,38977611
Integral 158	7158900,471	6,342440876	0	46,31136104	46,18938204	46,25037154
Integral 159	3191510,909	2,827524887	0	44,76629368	44,70820844	44,73725106
Integral 160	3187797,917	2,824235355	0	37,00051078	36,95886879	36,97968978
Integral 161	10811722,77	9,578665426	1	36,76347175	36,71862653	36,74104914
Integral 162	2532371	2,243558687	0	36,47197781	36,42392936	36,44795359
Integral 163	3833077,732	3,395922179	0	34,67496573	34,60129144	34,63812859
Integral 164	6227965	5,517676904	0	33,24312188	33,16624436	33,20468312
Integral 165	3624679,548	3,21129143	0	32,95162794	32,89717303	32,92440049
Integral 166	2294711,452	2,033003779	0	32,82349874	32,76904383	32,79627128
Integral 167	12131382,07	10,74781998	0	32,17324303	32,0739429	32,12359297
Integral 168	3062677,606	2,713384788	0	32,0419106	31,98425246	32,01308153
Integral 169	28653882,17	25,38595896	1	31,95542339	31,83049741	31,8929604
Integral 170	6735899,385	5,967682295	0	31,81768449	31,77283927	31,79526188
Integral 171	3624439,667	3,211078906	0	31,49736148	31,44931303	31,47333726
Integral 172	13033935,45	11,54743879	0	31,35641936	31,26993215	31,31317575
Integral 173	2584090,259	2,289379459	0	31,1482094	31,10016095	31,12418518
Integral 174	7363326,938	6,523552876	0	31,07773834	30,96242206	31,0200802
Integral 175	1543080,094	1,367094612	0	30,7205193	30,66282583	30,69167257
Integral 176	1267190,789	1,122669982	0	30,26649677	30,19876965	30,23263321
Integral 177	1810576,267	1,604083332	0	29,57919193	29,52651529	29,55285361
Integral 178	1263421,133	1,119330248	0	28,9972404	28,97215628	28,98469834

Integral 179	7833544,147	6,940142666	0	28,6586048	28,53569263	28,59714871
Integral 180	2775440,156	2,458906248	0	27,83082891	27,77564385	27,80323638
Integral 181	2544474,478	2,254281786	0	27,63266438	27,59252979	27,61259708
Integral 182	16538964	14,6527252	1	27,58751297	27,52480267	27,55615782
Integral 183	82967305,74	73,50503523	1	27,50724379	27,3818232	27,44453349
Integral 184	2038035,436	1,805601196	0	27,37931479	27,31158767	27,34545123
Integral 185	2816129,385	2,494954944	0	26,5114043	26,46625289	26,4888286
Integral 186	670702,1818	0,594209816	0	25,47543023	25,43780405	25,45661714
Integral 187	1114930,741	0,987774915	0	25,19448811	25,14682828	25,1706582
Integral 188	875962	0,776060125	0	25,00635722	24,97625628	24,99130675
Integral 189	2592109,348	2,296483985	0	24,83829363	24,79815904	24,81822634
Integral 190	4503588,813	3,989962689	0	24,45450663	24,39681316	24,42565989
Integral 191	14819425,84	13,12929724	1	24,39932157	24,31152716	24,35542436
Integral 192	1485291,75	1,315896924	0	24,27390098	24,23878321	24,2563421
Integral 193	3512688,333	3,112072609	0	23,96787474	23,92523174	23,94655324
Integral 194	6111314,917	5,414330551	0	23,35833067	23,31568767	23,33700917
Integral 195	6298220,63	5,579920007	0	23,21284279	23,16518296	23,18901288
Integral 196	7148282,435	6,333033807	0	23,1300652	23,08993061	23,1099979
Integral 197	4417755,75	3,913918731	0	22,99711937	22,95447637	22,97579787
Integral 198	1988857	1,762031472	0	22,83908943	22,8114969	22,82529316
Integral 199	1286381,96	1,139672434	0	22,75380343	22,70865202	22,73122772
Integral 200	3377484,424	2,992288461	0	22,15930983	22,10161636	22,1304631
Integral 201	86842837,74	76,93856984	1	21,85328359	21,70277888	21,77803124
Integral 202	1779277,963	1,576354543	0	21,18102923	21,13336941	21,15719932
Integral 203	2270631,2	2,011669836	0	21,11581052	21,06313388	21,0894722
Integral 204	16064130,37	14,23204548	1	21,05811705	20,99540676	21,02676191
Integral 205	14595523,38	12,93093045	1	20,8122927	20,74707399	20,77968334
Integral 206	3780500,667	3,349341433	0	20,62917863	20,59406087	20,61161975
Integral 207	35427751,48	31,38728077	1	20,43352251	20,35827016	20,39589634
Integral 208	2005230,12	1,776537267	0	20,15007198	20,10742898	20,12875048
Integral 209	2938817,75	2,603650924	0	18,64753331	18,58983984	18,61868658
Integral 210	18863524,63	16,71217391	1	16,47023187	16,37491222	16,42257205
Integral 211	9602565,389	8,507410249	0	16,14413834	16,08142804	16,11278319
Integral 212	46107312,75	40,84885748	2	16,06888598	15,94848222	16,0086841
Integral 213	2662488,636	2,358836644	0	15,93844857	15,90082239	15,91963548
Integral 214	2547748,353	2,257182281	0	15,87573828	15,81553639	15,84563733
Integral 215	15209155	13,4745785	1	14,14242572	14,0746986	14,10856216
Integral 216	2964573,815	2,626469556	0	14,01449672	13,9668369	13,99066681
Integral 217	15565880,28	13,79061991	1	13,71097889	13,64074336	13,67586113

B5. Integrals of Quantitative ^{13}C NMR of LtL-oil 4 in DMSO-d6

Object	*Integral [abs]*	*Integral [rel]*	*Peak*	*Range (F1) from*	*Range (F1) to*	*v(F1) [ppm]*
Integral 1	833745,0909	0,207403118	0	179,5897375	179,5509832	179,5703604
Integral 2	4019925,538	1	1	179,4917119	179,4461186	179,4689153
Integral 3	124378017,9	30,94037855	6	177,8480734	177,7432088	177,7956411
Integral 4	1510538,087	0,375762703	0	175,2378568	175,1968228	175,2173398
Integral 5	1086316,571	0,270233008	0	174,6269066	174,5904319	174,6086692
Integral 6	11153136,94	2,774463564	1	174,5813133	174,4354147	174,508364
Integral 7	2033367,871	0,505822272	1	174,3305501	174,2758381	174,3031941
Integral 8	4662618,943	1,159876943	1	172,078241	171,982495	172,030368
Integral 9	17844418,51	4,438992299	1	170,3912888	170,2864242	170,3388565
Integral 10	1415604,571	0,352146963	1	170,1861189	170,1359663	170,1610426
Integral 11	16556006,24	4,118485799	1	169,9125591	169,8396098	169,8760845
Integral 12	24127912,8	6,002079533	1	163,0879458	163,016719	163,0523324
Integral 13	29181094,34	7,259113152	3	162,2100335	162,0013223	162,1056779
Integral 14	19383844	4,821941057	1	157,4129882	157,3384485	157,3757184
Integral 15	4918524,833	1,223536303	1	157,3334792	157,2920682	157,3127737
Integral 16	774142,4615	0,192576319	1	157,2771603	157,2556266	157,2663934
Integral 17	2648581,953	0,658863436	1	156,2286348	156,1524387	156,1905368
Integral 18	3429981,714	0,853245087	2	156,1027455	156,0530524	156,0778989
Integral 19	3122451,467	0,776743608	1	156,0033592	155,9768562	155,9901077
Integral 20	7531448,632	1,873529387	1	155,4335445	155,3672869	155,4004157
Integral 21	6494967,442	1,61569347	2	155,3142809	155,2380847	155,2761828
Integral 22	7457952,098	1,855246329	1	155,095631	155,0227478	155,0591894
Integral 23	1004681,778	0,24992547	1	153,8662493	153,8359219	153,8510856
Integral 24	1213150,222	0,301784252	1	153,5872369	153,5569095	153,5720732
Integral 25	1336477,818	0,332463327	1	153,2869953	153,2687988	153,2778971
Integral 26	4070120,889	1,012486637	1	153,0838015	153,0524631	153,0681323
Integral 27	1237179,294	0,307761744	1	152,2902038	152,2611697	152,2756868
Integral 28	1351660	0,336240059	1	152,2227699	152,1918626	152,2073162
Integral 29	1090773,778	0,271341787	1	151,5400011	151,5090939	151,5245475
Integral 30	1016045,846	0,252752405	1	151,4510258	151,4294844	151,4402551
Integral 31	2321838,971	0,577582582	1	149,6386971	149,5766554	149,6076763
Integral 32	3199502	0,795910762	1	147,7213129	147,6563168	147,6888148
Integral 33	4415008,276	1,098281108	1	147,4613285	147,3579257	147,4096271
Integral 34	3877725,905	0,964626302	1	146,7847785	146,7109193	146,7478489
Integral 35	2731159,871	0,679405587	1	146,6547863	146,6016077	146,628197
Integral 36	17037156,24	4,238177069	1	145,3560784	145,2950205	145,3255494
Integral 37	2151931,556	0,535316273	1	145,1829692	145,1514337	145,1672014
Integral 38	8283974,788	2,060728416	2	145,0715888	145,0125438	145,0420663
Integral 39	1455642,4	0,362106807	1	144,9816793	144,9662471	144,9739632
Integral 40	3600085,333	0,895560204	1	144,9273311	144,8910989	144,909215
Integral 41	1689977,143	0,420400111	1	144,7146348	144,6777317	144,6961833

Integral 42	1363132	0,339093843	1	144,4663774	144,4435645	144,454971
Integral 43	1189940,364	0,296010549	1	144,4422226	144,4241065	144,4331646
Integral 44	1404900,615	0,349484238	1	144,3892163	144,3664034	144,3778099
Integral 45	2203520,952	0,548149694	1	143,3680059	143,3331157	143,3505608
Integral 46	1953829,25	0,486036179	1	143,1304839	143,1029743	143,1167291
Integral 47	1906032	0,474146096	1	143,1036453	143,0794905	143,0915679
Integral 48	2856435,111	0,710569159	1	142,9198006	142,8875942	142,9036974
Integral 49	4118155,636	1,0244358	1	138,7088175	138,6699014	138,6893594
Integral 50	2252380,6	0,56030406	1	138,3760183	138,341128	138,3585732
Integral 51	2660359,667	0,66179327	1	136,9320993	136,8891575	136,9106284
Integral 52	2592776,077	0,64498112	1	134,9461906	134,8544944	134,9003425
Integral 53	5132882,75	1,276860156	1	134,6683234	134,5543979	134,6113606
Integral 54	3794335,478	0,94388203	1	134,1431545	134,062573	134,1028637
Integral 55	1949290,909	0,484907218	0	133,9958849	133,9375328	133,9667088
Integral 56	14238623,34	3,542011712	1	133,8875167	133,6680016	133,7777591
Integral 57	6744064,93	1,677659167	1	133,6402149	133,4846093	133,5624121
Integral 58	7393912,727	1,839315842	1	133,4762733	133,3567904	133,4165318
Integral 59	6616431,563	1,645908985	1	133,0344645	132,9205389	132,9775017
Integral 60	2320849,872	0,577336533	1	132,4870661	132,403706	132,4453861
Integral 61	3061367,915	0,761548413	0	132,2230923	132,1397322	132,1814122
Integral 62	5160377,514	1,283699776	1	131,1714366	131,1065158	131,1389762
Integral 63	7315083,059	1,819706109	1	130,574584	130,5138517	130,5442179
Integral 64	18210765,52	4,530125086	2	129,7452731	129,6698812	129,7075772
Integral 65	35751058,81	8,893462944	2	129,4353287	129,3389946	129,3871616
Integral 66	2350958,4	0,584826355	1	129,190305	129,1567975	129,1735512
Integral 67	8183840,818	2,035819007	2	129,1484206	129,0709345	129,1096775
Integral 68	7915630,737	1,969098846	1	128,5369085	128,4698935	128,503401
Integral 69	6170836,706	1,53506244	1	128,2248698	128,1641374	128,1945036
Integral 70	4648948,457	1,156476261	1	127,9442444	127,8814178	127,9128311
Integral 71	9618941,917	2,392815943	2	127,1610063	127,0751433	127,1180748
Integral 72	4263599,833	1,060616619	1	127,0269763	126,9850919	127,0060341
Integral 73	5452333,625	1,35632702	1	126,8782867	126,8217428	126,8500147
Integral 74	7332102,872	1,823939971	1	126,6353572	126,566248	126,6008026
Integral 75	4660567,882	1,159366719	1	126,5138925	126,3924278	126,4531601
Integral 76	4507367,322	1,121256421	1	126,2919052	126,1871943	126,2395497
Integral 77	13128186,68	3,265778572	2	126,0259394	125,8835324	125,9547359
Integral 78	4245900,211	1,056213646	1	125,6573567	125,5903417	125,6238492
Integral 79	6848811,676	1,703716054	1	124,5495146	124,4845938	124,5170542
Integral 80	13682340,62	3,403630364	1	123,8039725	123,6427176	123,723345
Integral 81	6670736,286	1,659417873	1	123,47518	123,3746575	123,4249188
Integral 82	4481986,621	1,114942697	0	119,6280989	119,5757434	119,6019211
Integral 83	4670106,2	1,161739479	0	119,5212937	119,4500902	119,4856919
Integral 84	17745246,61	4,414322215	1	119,343285	119,2616105	119,3024477
Integral 85	2327601,231	0,579016006	0	119,2113492	119,1673706	119,1893599

Integral 86	1946682,074	0,484258242	0	118,9181585	118,8720856	118,8951221
Integral 87	15394201,85	3,829474377	1	118,8343897	118,7904111	118,8124004
Integral 88	6562303,484	1,632444039	1	118,7778458	118,7233961	118,7506209
Integral 89	1865801,625	0,464138355	0	118,5830834	118,5265394	118,5548114
Integral 90	524300,75	0,130425488	0	118,4511475	118,4239227	118,4375351
Integral 91	2282531,84	0,567804507	0	118,398792	118,3548134	118,3768027
Integral 92	2286410,167	0,568769283	0	118,2480082	118,2061238	118,227066
Integral 93	2244444,167	0,558329786	0	118,0804707	118,0385863	118,0595285
Integral 94	6743810,359	1,67759584	0	116,4700159	116,4009067	116,4354613
Integral 95	4263107,179	1,060494066	0	115,9255188	115,8564096	115,8909642
Integral 96	20057041,92	4,989406328	1	115,7663582	115,6784009	115,7223796
Integral 97	3608958,545	0,897767511	0	115,6260455	115,5883495	115,6071975
Integral 98	3179711,125	0,790987568	0	115,487827	115,431283	115,459555
Integral 99	2569864,593	0,63928164	0	115,4166235	115,3705507	115,3935871
Integral 100	1938903,4	0,482323213	0	115,3454201	115,3119125	115,3286663
Integral 101	32559438,38	8,099512808	1	115,297253	115,2051073	115,2511802
Integral 102	2992639,833	0,744451559	0	115,2009189	115,1590345	115,1799767
Integral 103	24054549,6	5,983829643	1	115,0815484	115,0019681	115,0417582
Integral 104	3104751,833	0,772340633	0	115,0019681	114,9600837	114,9810259
Integral 105	2054612,131	0,511107012	0	114,8176767	114,7087773	114,763227
Integral 106	3719835,059	0,925349244	0	114,6857409	114,6250086	114,6553747
Integral 107	8302232	2,065270095	1	114,6061606	114,5454282	114,5757944
Integral 108	8802163,525	2,189633475	1	114,5119207	114,4072097	114,4595652
Integral 109	1148581,143	0,285721995	0	114,4009271	114,3653253	114,3831262
Integral 110	3128242,615	0,778184219	0	113,9360103	113,8438647	113,8899375
Integral 111	3302524	0,8215386	0	113,7265884	113,6595734	113,6930809
Integral 112	12008396,69	2,987218687	0	113,1255474	113,0208364	113,0731919
Integral 113	11312211,23	2,814035018	0	112,4218897	112,3381209	112,3800053
Integral 114	2289958,526	0,569651976	0	111,2072424	111,1737349	111,1904886
Integral 115	1582133,143	0,393572748	0	104,2754991	104,2641811	104,2698401
Integral 116	20880178,48	5,194170458	1	103,2345488	103,1612512	103,1979
Integral 117	4988172	1,24086179	0	103,1361205	103,0900477	103,1130841
Integral 118	7681000	1,910731909	1	98,96263098	98,93589164	98,94926131
Integral 119	15218021,63	3,78564764	1	97,25572489	97,20825009	97,23198749
Integral 120	1859027,2	0,462453143	0	74,60855267	74,55574647	74,58214957
Integral 121	19639615,1	4,885566888	1	74,28841511	74,19930465	74,24385988
Integral 122	2044398,667	0,508566302	0	71,82962666	71,77682046	71,80322356
Integral 123	18353199,17	4,565556998	1	68,83446462	68,78284147	68,80865304
Integral 124	196771151,4	48,94895427	2	68,30667568	68,23964263	68,27315916
Integral 125	7083066,261	1,761989418	0	66,32650404	66,28566781	66,30608593
Integral 126	12391355,11	3,082483741	1	66,18781497	66,15776568	66,17279033
Integral 127	2064232	0,513500059	0	66,15006073	66,13388034	66,14197053
Integral 128	2209631,333	0,549669717	0	66,11847044	66,09843758	66,10845401
Integral 129	1424801,5	0,354434799	0	66,08456867	66,07069976	66,07763422

Integral 130	6478509,091	1,611599277	0	66,0653063	66,02755206	66,04642918
Integral 131	16607616	4,131324285	1	65,75864937	65,71781315	65,73823126
Integral 132	2213957,067	0,55074579	0	65,61071437	65,58528804	65,5980012
Integral 133	4166113,787	1,03636591	0	60,87423354	60,79022695	60,83223024
Integral 134	8690423,149	2,161836846	0	60,76349758	60,67949098	60,72149428
Integral 135	3256932,242	0,810197157	0	60,12581115	60,06853393	60,09717254
Integral 136	1810547,273	0,450393236	0	60,06089696	60,02271215	60,04180456
Integral 137	2068433	0,514545103	0	59,99598278	59,96161644	59,97879961
Integral 138	21387397,23	5,320346615	1	59,80887718	59,7630554	59,78596629
Integral 139	24019071,53	5,975004089	1	58,3731281	58,25093669	58,31203239
Integral 140	3245272,485	0,807296666	0	58,07910502	58,02182779	58,0504664
Integral 141	3796808,444	0,944497207	0	57,91109183	57,86527005	57,88818094
Integral 142	6500588,941	1,617091879	0	57,15885095	57,09775525	57,1283031
Integral 143	2208557,231	0,549402522	0	55,76510517	55,6963725	55,73073884
Integral 144	6836157,647	1,700568227	0	55,57418109	55,51308539	55,54363324
Integral 145	3108570,4	0,773290542	0	53,8663652	53,77615357	53,82125939
Integral 146	779098,087	0,193809084	0	49,28561922	49,24552516	49,26557219
Integral 147	3175364	0,789906174	0	46,40636477	46,37880011	46,39258244
Integral 148	3485415,6	0,867034866	0	46,2284474	46,1933651	46,21090625
Integral 149	1793460,48	0,446142712	0	44,73494378	44,69234385	44,71364382
Integral 150	1564101,333	0,389087141	0	44,37660315	44,34653261	44,36156788
Integral 151	968654,0909	0,240963192	0	44,18114462	44,10346239	44,14230351
Integral 152	1246337,333	0,310039905	0	43,14120503	43,10862861	43,12491682
Integral 153	856913,4884	0,213166508	0	42,48215897	42,40698261	42,44457079
Integral 154	6263975,368	1,558231691	0	41,37205478	41,33947835	41,35576657
Integral 155	3027160,69	0,753038996	0	38,22688239	38,1761752	38,2015288
Integral 156	3068114	0,763226575	0	38,11912962	38,07159163	38,09536062
Integral 157	3900528,941	0,970298804	0	38,00503844	37,94482365	37,97493105
Integral 158	11062682,67	2,751962085	1	37,82439408	37,76734849	37,79587128
Integral 159	3769606,244	0,937730365	0	37,04160184	36,96871026	37,00515605
Integral 160	2886979	0,718167283	0	36,7753891	36,73418951	36,7547893
Integral 161	2977489,418	0,740682729	0	36,64228272	36,49966875	36,57097574
Integral 162	4154751,158	1,033539333	0	36,47748436	36,41093117	36,44420777
Integral 163	3852927,364	0,958457396	0	36,32536279	36,24613281	36,2857478
Integral 164	1422030,452	0,353745471	0	35,87216729	35,8182909	35,84522909
Integral 165	2906584,69	0,72304441	0	35,43798698	35,3334034	35,38569519
Integral 166	4768327,636	1,186173125	0	35,07669825	35,01965266	35,04817546
Integral 167	803569,44	0,199896598	0	34,87703869	34,8326699	34,8548543
Integral 168	869610,4286	0,216325009	0	34,78513191	34,73759392	34,76136292
Integral 169	1485773,6	0,369602269	0	34,25587562	34,22101443	34,23844503
Integral 170	12573201,74	3,127720058	0	33,79317252	33,65689695	33,72503474
Integral 171	1387690,769	0,345203103	0	33,50160618	33,45723739	33,47942179
Integral 172	21993475,6	5,471115171	1	33,25123943	33,14348666	33,19736305
Integral 173	1400068,2	0,348282123	0	33,11496386	33,08010267	33,09753327

Integral 174	5330943,111	1,326129815	0	32,9406579	32,89311991	32,9168889
Integral 175	5670182,146	1,410519198	0	32,82656672	32,75367514	32,79012093
Integral 176	3088351,04	0,768260758	0	32,74416754	32,65542996	32,69979875
Integral 177	2203697,455	0,5481936	0	32,57619998	32,53816958	32,55718478
Integral 178	2990870,323	0,744011374	0	32,53500038	32,481124	32,50806219
Integral 179	3771959,75	0,938315825	0	32,25928004	32,17371166	32,21649585
Integral 180	2661345,744	0,662038567	0	32,16420406	32,09448168	32,12934287
Integral 181	1419068	0,353008529	0	32,05328209	32,0089133	32,03109769
Integral 182	36257231,46	9,019378869	1	31,92651411	31,82193053	31,87422232
Integral 183	11826022,44	2,941851119	1	31,81876133	31,75537735	31,78706934
Integral 184	5104861,419	1,269889547	0	31,65396297	31,54304099	31,59850198
Integral 185	6836825,63	1,700734395	0	31,5208566	31,47331861	31,4970876
Integral 186	3005502,815	0,747651365	0	31,45113421	31,40359622	31,42736522
Integral 187	3566158,37	0,887120504	0	31,37507343	31,32753544	31,35130443
Integral 188	1931366,316	0,480448281	0	31,30218184	31,27048985	31,28633585
Integral 189	2027225,333	0,50429425	0	31,07083029	31,0454767	31,05815349
Integral 190	3011903,2	0,74924353	0	31,0106155	30,97575431	30,99318491
Integral 191	3867242,074	0,962018335	0	30,84898634	30,80144835	30,82521734
Integral 192	3459789,867	0,860660187	0	30,5384048	30,48452841	30,51146661
Integral 193	2805282,326	0,69784435	0	30,39896003	30,32289925	30,36092964
Integral 194	1998903,31	0,49724884	0	30,25000766	30,19930047	30,22465407
Integral 195	470911,4667	0,117144326	0	30,12007049	30,0947169	30,10739369
Integral 196	-160383,75	-0,039897194	0	30,0883785	30,0598557	30,0741171
Integral 197	623871,8333	0,155194873	0	30,03133291	29,99013332	30,01073311
Integral 198	1701437,867	0,42325109	0	29,98062572	29,92674933	29,95368753
Integral 199	816174,8	0,203032318	0	29,87287294	29,83801175	29,85544235
Integral 200	1562891,636	0,388786215	0	29,78730456	29,74927417	29,76828936
Integral 201	3046662,824	0,757890362	0	29,74293577	29,68272098	29,71282838
Integral 202	3212526,4	0,799150723	0	29,5749682	29,53059941	29,55278381
Integral 203	2377192,833	0,591352454	0	29,49890742	29,45770783	29,47830763
Integral 204	3605674,947	0,896950681	0	28,81436036	28,74780718	28,78108377
Integral 205	12773804,67	3,177622208	1	28,57983961	28,51645563	28,54814762
Integral 206	1874958,065	0,466416118	0	28,22805849	28,1741821	28,20112029
Integral 207	205558323,9	51,13485858	3	27,46998927	27,39697826	27,43348376
Integral 208	6107772,615	1,519374565	0	26,49813152	26,47703945	26,48758549
Integral 209	17214331,17	4,282251251	1	23,35541289	23,31485121	23,33513205
Integral 210	3345940,923	0,83233903	0	23,18343138	23,16071684	23,17207411
Integral 211	2606128,8	0,648302755	0	23,16071684	23,13637984	23,14854834
Integral 212	10049900,92	2,500021661	1	23,12015517	23,0990631	23,10960913
Integral 213	3826373,412	0,951851813	0	23,09744063	23,06823622	23,08283843
Integral 214	7221259,529	1,79636649	1	23,03254195	23,00171507	23,01712851
Integral 215	2905063,733	0,722666056	0	22,99360274	22,96764327	22,980623
Integral 216	6533114,857	1,625183052	1	22,75347762	22,72914061	22,74130912
Integral 217	2182885,684	0,543016447	0	22,2375331	22,20508376	22,22130843

Integral 218	3728886	0,927600764	0	22,16127715	22,12720535	22,14424125
Integral 219	206024538,3	51,25083446	3	21,82218154	21,71185379	21,76701767
Integral 220	7781841,875	1,935817418	0	21,09856125	21,0417749	21,07016808
Integral 221	20914810,32	5,202785503	1	21,03852997	20,97038635	21,00445816
Integral 222	18880920,47	4,696833384	1	20,78704758	20,7270163	20,75703194
Integral 223	-117347	-0,029191337	0	20,52096299	20,50798325	20,51447312
Integral 224	3411465,037	0,848638863	0	20,39116562	20,34411408	20,36763985
Integral 225	12183984	3,030897932	1	20,12832597	20,08127442	20,10480019
Integral 226	3270517,143	0,813576548	0	20,06018235	20,02286561	20,04152398
Integral 227	2450154,286	0,609502406	0	19,59777925	19,56046251	19,57912088
Integral 228	2712656,444	0,67480266	0	19,07638735	19,04483005	19,0606087
Integral 229	1764928	0,439044948	0	18,66877223	18,64510426	18,65693825
Integral 230	988967,6364	0,246016407	0	18,62143629	18,60302786	18,61223207
Integral 231	1729142,435	0,430142901	0	18,41894362	18,37949699	18,3992203
Integral 232	2394418,947	0,595637637	0	18,19804252	18,16648522	18,18226387
Integral 233	1171344,2	0,291384551	0	18,13492792	18,10074085	18,11783439
Integral 234	2342654,957	0,582760784	0	16,91997191	16,88052528	16,90024859
Integral 235	418209,8462	0,104034227	0	16,78585338	16,74114721	16,7635003
Integral 236	554937,3333	0,13804667	0	16,71484946	16,68329216	16,69907081
Integral 237	1687459,5	0,41977382	0	16,62543711	16,58336071	16,60439891
Integral 238	19357632,56	4,815420676	1	16,46502084	16,40190624	16,43346354
Integral 239	3535489,412	0,879491269	0	16,40190624	16,34142142	16,37166383
Integral 240	1821679,333	0,453162457	0	16,1231501	16,0810737	16,1021119
Integral 241	5056669,2	1,25790121	0	16,06266528	16,0284782	16,04557174
Integral 242	1202260,75	0,299075378	0	16,02584843	15,99955068	16,01269955
Integral 243	7414420,889	1,844417469	1	15,99955068	15,96799338	15,98377203
Integral 244	6157343,294	1,531705808	0	15,96799338	15,93906586	15,95352962
Integral 245	8071578,225	2,007892472	0	15,83650463	15,53145074	15,68397769
Integral 246	24312093,03	6,047896359	1	14,12452115	14,06140656	14,09296385
Integral 247	5865010,667	1,458984902	0	13,99829196	13,94043691	13,96936443
Integral 248	6870986,595	1,709232305	0	13,70638694	13,64064257	13,67351475
Integral 249	2103405,905	0,523244992	0	13,64064257	13,60382572	13,62223414
Integral 250	3178610,462	0,790713766	0	13,59330662	13,52493247	13,55911954
Integral 251	1154732	0,287252087	0	12,15481973	12,12589221	12,14035597
Integral 252	4241828,7	1,055200814	0	10,48491265	10,41390873	10,44941069
Integral 253	940987,2727	0,234080772	0	9,13583811	9,117429685	9,126633898
Integral 254	331838,4	0,082548395	0	9,046425762	8,993830264	9,020128013

B6. Integrals of Quantitative ^{13}C NMR of LtL-oil 5 in DMSO-d6

Object	*Integral [abs]*	*Integral [rel]*	*Peak*	*Range (F1) from*	*Range (F1) to*	*v(F1) [ppm]*
Integral 1	3179721,846	0,173213134	1	179,549799	179,361522	179,4556605
Integral 2	55765692,81	3,037797289	1	177,9437914	177,5943491	177,7690702
Integral 3	3930884,5	0,214132196	1	174,6102967	174,4663202	174,5383085
Integral 4	1074013,25	0,058506124	1	173,691062	173,591386	173,641224
Integral 5	4691190,757	0,25554935	1	172,1183954	171,985494	172,0519447
Integral 6	33776957,13	1,839976222	3	170,4501951	170,2172336	170,3337143
Integral 7	21718494,68	1,183099876	1	170,0813393	169,7513105	169,9163249
Integral 8	11694124,5	0,63702929	2	162,2383007	161,9082719	162,0732863
Integral 9	10258938,03	0,558848507	2	157,4625891	157,249041	157,3558151
Integral 10	661065,7778	0,036011098	1	155,3957184	155,380865	155,3882917
Integral 11	847983,1667	0,046193293	1	155,2555028	155,2358964	155,2456996
Integral 12	1027489,333	0,055971766	1	155,0546855	155,0356733	155,0451794
Integral 13	988534,2222	0,053849713	1	147,8264028	147,7963629	147,8113829
Integral 14	7816154	0,425779547	1	147,7062432	147,6681926	147,6872179
Integral 15	2928308,087	0,159517544	1	147,4499026	147,4098494	147,429876
Integral 16	7375589,077	0,40178008	1	147,4038414	147,3577802	147,3808108
Integral 17	2305084,667	0,125567882	1	147,2636551	147,2336152	147,2486352
Integral 18	2141549,4	0,116659413	1	147,0794104	147,0093172	147,0443638
Integral 19	1734408,087	0,094480673	1	146,8070485	146,7669953	146,7870219
Integral 20	8051793,778	0,43861586	1	146,6248064	146,5927638	146,6087851
Integral 21	86420397,1	4,707690962	5	145,3766821	145,2489007	145,3127914
Integral 22	1454981,412	0,079259099	1	145,1934484	145,1645167	145,1789825
Integral 23	840070,8571	0,045762275	0	145,1633112	145,140407	145,1518591
Integral 24	1301317,818	0,070888382	1	145,0970095	145,0777218	145,0873657
Integral 25	10180568,92	0,554579404	1	145,0753108	145,0295024	145,0524066
Integral 26	13940766,27	0,759413536	1	145,0295024	145,0041872	145,0168448
Integral 27	691038,5714	0,037643845	1	145,0005707	144,9897214	144,9951461
Integral 28	545734	0,02972848	0	144,9897214	144,976461	144,9830912
Integral 29	7244159,111	0,394620524	1	144,9752555	144,9439129	144,9595842
Integral 30	928590,2857	0,050584309	0	144,941502	144,9185977	144,9300499
Integral 31	7118257,9	0,387762143	1	144,8776113	144,8438577	144,8607345
Integral 32	657076,8333	0,035793803	1	144,8330083	144,8125151	144,8227617
Integral 33	357384	0,019468245	1	144,7908163	144,7715286	144,7811724
Integral 34	5836398,229	0,31793373	1	144,7136653	144,6521855	144,6829254
Integral 35	-7228,222222	-0,000393752	0	144,6497746	144,6341033	144,6419389
Integral 36	556072,1667	0,030291644	0	144,6232539	144,6039661	144,61361
Integral 37	1018410,4	0,055477197	1	144,5907058	144,573829	144,5822674
Integral 38	2218610,933	0,120857286	1	144,4460476	144,4219379	144,4339927
Integral 39	1099996,857	0,059921563	1	144,4219379	144,409883	144,4159105
Integral 40	221261,1111	0,012053045	0	144,4050611	144,3905953	144,3978282
Integral 41	1153439,778	0,062832829	1	144,2495535	144,2362932	144,2429233

Integral 42	2202908,941	0,120001931	1	144,210978	144,1832518	144,1971149
Integral 43	1109827,778	0,060457095	1	144,1217721	144,091635	144,1067035
Integral 44	744798,5714	0,040572384	1	143,7010578	143,6757426	143,6884002
Integral 45	802147,4118	0,043696422	1	143,4720156	143,4442895	143,4581525
Integral 46	1397782,571	0,076143232	1	143,3707549	143,3466452	143,3587
Integral 47	7420473,565	0,404225131	1	143,3478507	143,3080696	143,3279601
Integral 48	1096662,154	0,059739907	1	143,2972203	143,276727	143,2869737
Integral 49	3203720	0,174520416	1	143,2080144	143,1622059	143,1851102
Integral 50	506280	0,027579251	0	143,1634114	143,1453292	143,1543703
Integral 51	300054	0,016345233	0	143,1321039	143,1207806	143,1264422
Integral 52	4945024	0,269376739	1	143,1205172	143,1012938	143,1109055
Integral 53	9243404,933	0,503528048	1	143,0970805	143,0712737	143,0841771
Integral 54	236470,4	0,01288156	0	143,0736438	143,0578437	143,0657437
Integral 55	503046,5	0,027403108	0	142,9651501	142,9509301	142,9580401
Integral 56	16527223,33	0,900308984	1	142,9019499	142,8661365	142,8840432
Integral 57	1187117,231	0,064667385	1	142,7934562	142,7713362	142,7823962
Integral 58	1602005,167	0,087268116	1	142,7428961	142,7218294	142,7323627
Integral 59	504049,5	0,027457746	0	142,7202494	142,7076093	142,7139293
Integral 60	722744,8	0,03937102	0	142,276268	142,2499346	142,2631013
Integral 61	475474,1818	0,025901125	1	142,0582274	142,0392673	142,0487473
Integral 62	310909,8462	0,016936597	1	141,8338667	141,8117466	141,8228067
Integral 63	1214236,8	0,066144704	1	141,0757712	141,0590201	141,0673956
Integral 64	1983938,375	0,108073662	1	140,8704626	140,8438326	140,8571476
Integral 65	15002237,33	0,817236433	1	134,6681042	134,5993121	134,6337081
Integral 66	2227816,667	0,121358762	1	134,1491721	134,1192625	134,1342173
Integral 67	489339,6667	0,026656438	1	133,8635352	133,8425984	133,8530668
Integral 68	95528,90909	0,005203871	0	133,8470849	133,8291391	133,838112
Integral 69	438896,3636	0,023908574	1	133,8052114	133,7872656	133,7962385
Integral 70	1320437,059	0,071929889	1	133,6347265	133,6048169	133,6197717
Integral 71	4024515,333	0,219232671	1	133,0081198	132,9767147	132,9924172
Integral 72	5187227,294	0,282570595	1	132,9767147	132,9483005	132,9625076
Integral 73	1561387,04	0,085055472	1	132,5579799	132,5146109	132,5362954
Integral 74	2090182,483	0,113861235	1	132,2185056	132,1676592	132,1930824
Integral 75	862366,8	0,046976831	1	131,3929998	131,3660812	131,3795405
Integral 76	828699,4286	0,045142824	1	131,1537228	131,1297951	131,1417589
Integral 77	711166,6667	0,038740309	1	130,6721778	130,651241	130,6617094
Integral 78	1208081,9	0,06580942	1	130,573476	130,5375844	130,5555302
Integral 79	621101,75	0,033834085	1	130,2145605	130,1876418	130,2011011
Integral 80	471149,5556	0,025665544	0	130,1502548	130,1352999	130,1427773
Integral 81	2907853,091	0,158403273	1	129,7494657	129,7120787	129,7307722
Integral 82	383803,2	0,020907412	0	129,7120787	129,6956284	129,7038535
Integral 83	9365177,067	0,5101615	1	129,4114869	129,3591451	129,385316
Integral 84	446745,6364	0,024336157	1	129,1303364	129,1123906	129,1213635
Integral 85	1197591,143	0,065237944	1	129,0435985	129,0077069	129,0256527

Integral 86	1960631,852	0,106804055	1	128,5500896	128,5022342	128,5261619
Integral 87	18746749,04	1,021216101	1	127,9399332	127,8920778	127,9160055
Integral 88	1605198,842	0,087442089	1	127,1667693	127,1323732	127,1495712
Integral 89	1690003	0,092061737	1	127,1323732	127,1054545	127,1189139
Integral 90	1544631,405	0,08414272	2	127,0800313	127,0142302	127,0471308
Integral 91	1815653,263	0,098906447	1	126,6463417	126,6134411	126,6298914
Integral 92	2640287,84	0,143827842	1	126,5281987	126,4848297	126,5065142
Integral 93	2022591,429	0,11017926	1	126,0182395	125,9943118	126,0062757
Integral 94	312116,9091	0,017002351	1	125,5980092	125,5606222	125,5793157
Integral 95	743960,5714	0,040526734	0	124,5556587	124,5302355	124,5429471
Integral 96	6153044,421	0,335182811	1	124,5227581	124,4898575	124,5063078
Integral 97	88944,8	0,004845206	0	124,4898575	124,4734072	124,4816323
Integral 98	163127,6364	0,008886264	0	124,2356256	124,2176799	124,2266527
Integral 99	2057273,077	0,112068518	1	124,2206708	124,1997341	124,2102024
Integral 100	3477978,444	0,189460454	1	124,1982386	124,1668335	124,182536
Integral 101	927266,4167	0,050512192	0	124,1638425	124,1204736	124,142158
Integral 102	1374558,833	0,074878135	1	124,0860775	124,0666362	124,0763569
Integral 103	1132084,737	0,061669528	0	123,8138999	123,7809993	123,7974496
Integral 104	1263379,273	0,068821706	1	123,7735219	123,7555761	123,764549
Integral 105	1272143,6	0,069299137	1	123,7555761	123,7301529	123,7428645
Integral 106	386266,4615	0,021041597	0	123,4594708	123,438534	123,4490024
Integral 107	478090,5455	0,02604365	0	122,9839077	122,9644664	122,974187
Integral 108	401802	0,021887884	0	122,8687556	122,8523053	122,8605304
Integral 109	2419401,556	0,131795215	1	122,6758385	122,6444334	122,6601359
Integral 110	899698,6667	0,049010458	0	122,3931925	122,3737512	122,3834719
Integral 111	738980,8889	0,040255469	0	122,2167257	122,1853206	122,2010231
Integral 112	567998,2667	0,03094131	0	121,6948027	121,6693795	121,6820911
Integral 113	2146853,217	0,116948334	1	121,5273087	121,4869307	121,5071197
Integral 114	7643304,786	0,416363707	1	121,0786643	121,0293134	121,0539889
Integral 115	2369784,444	0,129092358	1	121,0008993	120,9694942	120,9851967
Integral 116	7777173,273	0,423656099	1	120,9500529	120,9111704	120,9306116
Integral 117	435473,7647	0,02372213	0	120,6404882	120,6105786	120,6255334
Integral 118	2942932,261	0,160314186	1	120,3997157	120,3593377	120,3795267
Integral 119	2444358,686	0,133154738	0	120,2725998	120,2097896	120,2411947
Integral 120	3014423,391	0,164208615	1	119,7117943	119,6714163	119,6916053
Integral 121	14952991,85	0,81455382	1	119,5188772	119,4725172	119,4956972
Integral 122	601214,6667	0,03275075	0	119,4695263	119,4426076	119,4560669
Integral 123	206438,6667	0,011245603	0	119,4366257	119,4216709	119,4291483
Integral 124	1133444,375	0,061743593	0	119,4216709	119,3947522	119,4082115
Integral 125	-515644,0952	-0,028089353	0	119,3902657	119,3543742	119,37232
Integral 126	80550045,05	4,387907621	1	119,3274555	119,2586634	119,2930595
Integral 127	476370,8421	0,02594997	1	119,251186	119,2182854	119,2347357
Integral 128	8696237,692	0,473721494	1	119,2227718	119,1779074	119,2003396
Integral 129	689914,125	0,037582592	0	119,0627553	119,0358366	119,049296

Integral 130	6184895	0,336917849	1	118,9326484	118,8907749	118,9117117
Integral 131	1028863,75	0,056046636	1	118,8937659	118,8653518	118,8795588
Integral 132	1228158,588	0,066903084	1	118,8653518	118,8369376	118,8511447
Integral 133	5281303,083	0,287695308	1	118,8354421	118,7935687	118,8145054
Integral 134	1184321,667	0,064515098	0	118,7771184	118,7576771	118,7673977
Integral 135	603931,3333	0,032898739	0	118,7158036	118,6843985	118,7001011
Integral 136	7638766,593	0,416116492	1	118,5856967	118,5378413	118,561769
Integral 137	2306166	0,125626787	0	118,4630673	118,4316621	118,4473647
Integral 138	10008994,1	0,545232985	1	118,2596818	118,1893941	118,224538
Integral 139	1258153,813	0,068537053	0	118,0757376	118,0189093	118,0473234
Integral 140	2322776,786	0,126531648	0	117,2397634	117,1904125	117,215088
Integral 141	19531047,75	1,063940228	1	116,4665995	116,3798616	116,4232306
Integral 142	866402,8	0,047196689	0	116,3275197	116,2931237	116,3103217
Integral 143	816460,4	0,044476112	0	116,2318089	116,2048903	116,2183496
Integral 144	1680143,5	0,091524647	0	116,0628195	116,0284235	116,0456215
Integral 145	673352	0,036680381	0	116,0284235	116,0059912	116,0172073
Integral 146	2221765,913	0,121029151	0	115,9013075	115,8190561	115,8601818
Integral 147	108763717,9	5,924827806	2	115,7906419	115,6500667	115,7203543
Integral 148	7939196,667	0,432482211	1	115,6336164	115,5857609	115,6096887
Integral 149	31413220,08	1,711213293	2	115,5199598	115,4332218	115,4765908
Integral 150	9017879,6	0,491242712	1	115,4332218	115,3539613	115,3935916
Integral 151	5088165,143	0,277174254	1	115,3539613	115,3046104	115,3292859
Integral 152	13148640,8	0,716263053	1	115,2866647	115,2328273	115,259746
Integral 153	-273226,7692	-0,014883838	0	115,2253499	115,2044132	115,2148816
Integral 154	8853192,615	0,482271504	1	115,2044132	115,1580533	115,1812332
Integral 155	695600	0,037892326	0	115,1550623	115,1281436	115,141603
Integral 156	6916313,733	0,376761375	1	115,0743063	115,0219644	115,0481354
Integral 157	3385227,212	0,184407895	0	115,0219644	114,9636407	114,9928026
Integral 158	1170902,444	0,063784095	0	114,5987432	114,5673381	114,5830406
Integral 159	688466,7692	0,037503748	0	114,4581679	114,4357357	114,4469518
Integral 160	1207962,105	0,065802895	0	113,728373	113,6969679	113,7126704
Integral 161	2406792	0,131108318	0	113,1780358	113,1451352	113,1615855
Integral 162	824179,8824	0,044896625	0	113,1286849	113,0987753	113,1137301
Integral 163	8764890,471	0,477461306	1	113,0733521	113,0135329	113,0434425
Integral 164	4162880,909	0,226770039	0	112,5409607	112,5020782	112,5215195
Integral 165	1250516,143	0,068120996	0	112,4975918	112,4482409	112,4729163
Integral 166	937831,0909	0,051087696	0	112,4273041	112,3884216	112,4078629
Integral 167	9018654,714	0,491284936	1	112,3899171	112,3405662	112,3652417
Integral 168	3555470,933	0,193681804	0	112,0803524	112,0265151	112,0534338
Integral 169	577797,125	0,031475096	0	111,3729897	111,3460711	111,3595304
Integral 170	3384268,177	0,184355653	0	110,3067114	110,1631452	110,2349283
Integral 171	1707747	0,093028329	0	109,5514933	109,5170972	109,5342953
Integral 172	2815360,727	0,153364815	0	104,2758704	104,2585053	104,2671878
Integral 173	3147873,429	0,171478213	0	103,2246195	103,1999077	103,2122636

Integral 174	593228,6667	0,032315719	0	103,1999077	103,1915592	103,1957335
Integral 175	1147492,875	0,062508875	0	103,1842125	103,1561613	103,1701869
Integral 176	161626,5	0,008804491	0	103,1387963	103,1267744	103,1327853
Integral 177	2212751,636	0,120538105	0	103,1214313	103,0840297	103,1027305
Integral 178	1071866,667	0,05838919	0	102,9117154	102,885	102,8983577
Integral 179	1837802,222	0,100112996	0	98,96585131	98,93379284	98,94982208
Integral 180	7873377,385	0,428896751	1	97,24270823	97,19729205	97,22000014
Integral 181	22443365,57	1,222586713	1	74,28630546	74,22056673	74,2534361
Integral 182	20081083,68	1,093903052	1	68,82921793	68,79518847	68,8122032
Integral 183	61691194,61	3,360584874	1	68,33965778	68,25303735	68,29634756
Integral 184	807258,4	0,043974839	0	67,73408812	67,70779263	67,72094038
Integral 185	1307549,059	0,071227825	0	67,6196254	67,59023632	67,60493086
Integral 186	1754156,643	0,095556462	0	67,34893653	67,30098594	67,32496124
Integral 187	1613220,313	0,087879053	0	67,25612892	67,20044436	67,22828664
Integral 188	852114,3529	0,046418336	0	67,0705137	67,04267142	67,05659256
Integral 189	1229160,421	0,066957658	0	66,89263245	66,86014978	66,87639112
Integral 190	2968635,368	0,161714345	0	66,3311464	66,29866374	66,31490507
Integral 191	6417383,905	0,34958252	0	66,20121574	66,1640927	66,18265422
Integral 192	647448,6667	0,035269315	0	66,1640927	66,13315683	66,14862477
Integral 193	5567539,263	0,303287825	0	66,13006324	66,09758058	66,11382191
Integral 194	1828844,615	0,099625037	0	66,0929402	66,04808319	66,07051169
Integral 195	168412	0,009174126	0	66,04962998	66,03416204	66,04189601
Integral 196	296856,4211	0,016171047	0	66,02952166	65,997039	66,01328033
Integral 197	1097539,52	0,059787701	0	66,00013259	65,95682237	65,97847748
Integral 198	929289,0769	0,050622375	0	65,95527558	65,90887177	65,93207367
Integral 199	1995584	0,108708049	0	65,90732498	65,854734	65,88102949
Integral 200	112133,1667	0,006108376	0	65,85009362	65,82843851	65,83926606
Integral 201	291687,1667	0,015889455	0	65,82379813	65,80368981	65,81374397
Integral 202	2410276,727	0,131298147	0	65,8052366	65,76811356	65,78667508
Integral 203	8283208,769	0,451222031	0	65,76811356	65,72170975	65,74491166
Integral 204	25329,81818	0,001379824	0	65,72016296	65,70160144	65,7108822
Integral 205	907341,7037	0,049426808	0	65,70160144	65,65519763	65,67839954
Integral 206	275270,3077	0,014995158	0	65,65674443	65,63508932	65,64591687
Integral 207	1953537,6	0,106417601	0	65,63508932	65,58249834	65,60879383
Integral 208	4516690,645	0,246043578	0	65,56084323	65,45102089	65,50593206
Integral 209	1512493,647	0,082392038	0	63,69076987	63,63199171	63,66138079
Integral 210	3039520,909	0,165575785	0	63,57940073	63,52062258	63,55001166
Integral 211	2132798,813	0,11618273	0	62,81528474	62,75960017	62,78744245
Integral 212	1253301,543	0,068272729	0	62,7286643	62,66679256	62,69772843
Integral 213	2901183,708	0,158039963	0	60,88798001	60,80135958	60,84466979
Integral 214	3486960,564	0,189949749	0	60,77042371	60,70236479	60,73639425
Integral 215	1243100,3	0,067717023	0	60,24703684	60,21208381	60,22956032
Integral 216	926719,1111	0,050482378	0	60,04430927	60,01335087	60,02883007
Integral 217	400335,6667	0,021808007	0	59,98239248	59,96142066	59,97190657

Integral 218	46165690,63	2,514843854	1	59,84757365	59,73372665	59,79065015
Integral 219	1984562,4	0,108107655	0	59,73472531	59,69078436	59,71275483
Integral 220	23044904,81	1,255355145	1	58,41749547	58,2457263	58,33161089
Integral 221	1722342,233	0,093823394	0	58,07395713	57,99805913	58,03600813
Integral 222	2228434,31	0,121392407	0	57,93015039	57,80232217	57,86623628
Integral 223	2749864,681	0,149796964	0	57,16318108	57,07929382	57,12123745
Integral 224	2967665,103	0,16166149	0	55,78902774	55,73709753	55,76306264
Integral 225	2053419,2	0,111858581	0	55,74708411	55,70314316	55,72511364
Integral 226	708655	0,038603488	0	55,70514048	55,67717805	55,69115927
Integral 227	19498707,81	1,062178532	0	55,59728542	55,52338473	55,56033507
Integral 228	2351054	0,12807203	0	55,52538205	55,48543573	55,50540889
Integral 229	4056007,826	0,220948202	0	53,87559911	53,83565279	53,85562595
Integral 230	1258163,636	0,068537588	0	49,4074677	49,35022424	49,37884597
Integral 231	3846025,385	0,209509555	0	49,10852962	48,96860116	49,03856539
Integral 232	3391529,238	0,184751194	0	48,69510462	48,5806177	48,63786116
Integral 233	467973,8298	0,025492549	0	46,54529462	46,46260962	46,50395212
Integral 234	2314656,48	0,1260893	0	46,44352847	46,35448309	46,39900578
Integral 235	3790201,93	0,206468611	0	46,30360001	46,20183385	46,25271693
Integral 236	2275362,233	0,123948773	0	44,78254182	44,70646421	44,74450301
Integral 237	5445284,435	0,296628078	1	37,84391835	37,76185812	37,80288824
Integral 238	3014994,133	0,164239706	1	36,99501933	36,94125573	36,96813753
Integral 239	6633885,789	0,36137631	1	36,75166828	36,72054198	36,73610513
Integral 240	1433834,286	0,078107124	1	36,48002059	36,44323497	36,46162778
Integral 241	2348593,556	0,127937999	1	36,33853742	36,27628483	36,30741113
Integral 242	990992,7586	0,053983641	0	35,87730229	35,82636835	35,85183532
Integral 243	3044528,25	0,165848557	0	35,45568244	35,38494086	35,42031165
Integral 244	1768346,526	0,096329446	0	35,09914485	35,03123293	35,06518889
Integral 245	3082300,824	0,167906191	0	34,67469534	34,61527241	34,64498388
Integral 246	9663770,769	0,526427184	1	33,24571532	33,15233643	33,19902588
Integral 247	2915088,211	0,158797401	0	32,95425999	32,88634807	32,92030403
Integral 248	358221,5385	0,019513869	0	32,86654043	32,82126581	32,84390312
Integral 249	1868675,833	0,101794815	0	32,80994716	32,76750221	32,78872468
Integral 250	3713173,481	0,20227254	0	32,74769457	32,65148601	32,69959029
Integral 251	778004,8	0,04238127	0	32,6288487	32,44775024	32,53829947
Integral 252	1075526,5	0,058588557	0	32,17893222	32,12233895	32,15063559
Integral 253	789430,8485	0,043003696	0	32,12233895	32,06291602	32,09262749
Integral 254	1674001,838	0,091190085	0	32,04310838	31,97802612	32,01056725
Integral 255	2564152,615	0,139680428	0	31,95538881	31,9101142	31,93275151
Integral 256	13449528,09	0,732653679	1	31,9101142	31,83371329	31,87191374
Integral 257	8505985,489	0,463357637	0	31,83088362	31,74599372	31,78843867
Integral 258	2326149,241	0,12671536	0	31,51396132	31,46302738	31,48849435
Integral 259	2510322,914	0,136748093	0	31,37530781	31,31305522	31,34418152
Integral 260	2268440,35	0,123571709	0	31,31305522	31,24231363	31,27768443
Integral 261	1742079,739	0,094898581	0	31,23665431	31,15459407	31,19562419

Integral 262	1500472,154	0,081737176	0	31,14610508	31,10083046	31,12346777
Integral 263	3423800,507	0,186509149	0	31,08668215	30,96783628	31,02725922
Integral 264	1821341,9	0,099216332	0	30,73014456	30,65940297	30,69477377
Integral 265	4288962,03	0,23363822	0	30,59149105	30,47264519	30,53206812
Integral 266	1908018,353	0,103937971	0	30,2858874	30,22646447	30,25617594
Integral 267	1465665,467	0,079841106	0	30,22646447	30,17270087	30,19958267
Integral 268	5480258,17	0,298533248	0	30,07649231	29,90671251	29,99160241
Integral 269	2834348,077	0,154399138	0	29,60393852	29,51055963	29,55724908
Integral 270	5653574,159	0,307974516	0	29,14545064	29,03165971	29,08855517
Integral 271	2378665,784	0,129576162	0	28,99872023	28,93284127	28,96578075
Integral 272	3270771,646	0,178173008	0	28,83402283	28,546551	28,69028691
Integral 273	4783654,239	0,260586234	0	27,9027339	27,78295397	27,84284393
Integral 274	1986268,588	0,108200598	0	27,63622356	27,5763336	27,60627858
Integral 275	10447705,42	0,569131478	1	27,5733391	27,53141613	27,55237761
Integral 276	59513662,74	3,241965341	1	27,48050966	27,41762519	27,44906743
Integral 277	1545234,667	0,084175583	0	27,37570222	27,34575724	27,36072973
Integral 278	1418748,688	0,077285347	0	26,87262653	26,81573106	26,8441788
Integral 279	3714198,56	0,202328381	0	26,52825924	26,43842429	26,48334177
Integral 280	2244318,7	0,122257699	0	25,48317938	25,37537745	25,42927841
Integral 281	4727470,693	0,257525674	0	25,24062503	25,05796064	25,14929284
Integral 282	4684259,586	0,25517178	0	24,88427975	24,77947231	24,83187603
Integral 283	1334898,513	0,072717667	0	24,72557134	24,65669789	24,69113462
Integral 284	3391430	0,184745788	0	24,45007751	24,39617655	24,42312703
Integral 285	11331850,29	0,617294655	1	24,39617655	24,3093361	24,35275632
Integral 286	609793,4667	0,033218075	0	24,27939112	24,22549015	24,25244063
Integral 287	3172692,767	0,172830229	0	23,9859303	23,87812836	23,93202933
Integral 288	1185242,194	0,064565243	0	23,77631543	23,72241446	23,74936494
Integral 289	9303874,192	0,506822069	1	23,37804717	23,28521773	23,33163245
Integral 290	12671864,81	0,690291013	0	23,24030026	23,12650932	23,18340479
Integral 291	4437258,645	0,241716575	1	23,12650932	23,07260836	23,09955884
Integral 292	737626,25	0,040181676	0	23,04266338	23,0007404	23,02170189
Integral 293	5458108,56	0,297326664	0	23,0097239	22,91988895	22,96480642
Integral 294	752037,4118	0,040966714	0	22,91389996	22,85400999	22,88395497
Integral 295	1131807,692	0,061654436	0	22,848021	22,80310352	22,82556226
Integral 296	505957,3793	0,027561676	0	22,76716955	22,71626308	22,74171631
Integral 297	483420,8889	0,026334016	0	22,47071423	22,42280226	22,44675824
Integral 298	806909,0435	0,043955808	0	22,3449453	22,30601683	22,32548107
Integral 299	1271045,619	0,069239325	0	22,23714337	22,16228092	22,19971214
Integral 300	3240248,679	0,176510291	0	22,16228092	22,06346248	22,1128717
Integral 301	65252700,72	3,554595439	1	21,83288612	21,72508418	21,77898515
Integral 302	3020765,306	0,164554087	0	21,2160195	21,12917905	21,17259927
Integral 303	2321485,905	0,126461328	0	21,12917905	21,0543166	21,09174782
Integral 304	22981573,8	1,251905232	1	21,06629459	20,99442663	21,03036061
Integral 305	43794170,21	2,385656931	1	20,82374024	20,7219273	20,77283377

Integral 306	2684212	0,14622058	0	20,62310886	20,56920789	20,59615838
Integral 307	20813262,08	1,13378796	1	20,43744997	20,34162603	20,389538
Integral 308	2856577,724	0,155610083	0	20,16195614	20,11104967	20,13650291
Integral 309	1411864,621	0,076910342	0	18,68566855	18,63476208	18,66021531
Integral 310	2353205,636	0,128189239	0	18,63775658	18,5988281	18,61829234
Integral 311	2316190	0,126172838	0	18,22451583	18,15564237	18,1900791
Integral 312	24160824,65	1,316144101	1	16,49369589	16,38289946	16,43829767
Integral 313	7378432	0,401934946	0	16,17029009	16,06847715	16,11938362
Integral 314	582037,4286	0,031706084	0	16,07147165	16,04751566	16,05949366
Integral 315	8521478,609	0,464201614	1	16,04751566	16,00858719	16,02805143
Integral 316	3758195,2	0,204725067	0	16,00607602	15,98068457	15,9933803
Integral 317	9939427,7	0,541443404	1	15,97919096	15,94433994	15,96176545
Integral 318	1669004,842	0,090917877	0	15,93936122	15,90650169	15,92293146
Integral 319	250794,1176	0,013661835	0	15,9010251	15,87214855	15,88658683
Integral 320	484526	0,026394216	0	15,87015706	15,85522091	15,86268899
Integral 321	2997837,692	0,163305121	0	15,8537273	15,80742523	15,83057626
Integral 322	1615151,742	0,087984267	0	14,90030307	14,84653293	14,873418
Integral 323	5713902,822	0,311260878	0	14,53984398	14,41039735	14,47512067
Integral 324	1125178,4	0,06129331	0	14,40840587	14,38251654	14,3954612
Integral 325	502443,2308	0,027370245	0	14,23713801	14,21523166	14,22618484
Integral 326	3013037,85	0,164133139	0	14,21124869	14,13955517	14,17540193
Integral 327	43756966,44	2,383630281	1	14,13955517	14,0598957	14,09972544
Integral 328	3180099,28	0,173233694	0	14,03599786	13,94638096	13,99118941
Integral 329	499497,1	0,027209757	0	13,94638096	13,91252569	13,92945333
Integral 330	15545475,14	0,846828935	1	13,72134297	13,62176864	13,67155581
Integral 331	2347274,316	0,127866134	0	13,59986229	13,53215174	13,56600702
Integral 332	2009310,188	0,109455773	0	12,02641383	11,96902808	11,99772095
Integral 333	6180998,022	0,336705564	0	10,52618633	10,35812806	10,4421572
Integral 334	1384250,746	0,075406096	0	9,103839505	8,997265967	9,050552736

B7. Integrals of Quantitative ^{13}C NMR of LtL-oil 6 in DMSO-d6

Object	*Integral [abs]*	*Integral [rel]*	*Peak*	*Range (F1) from*	*Range (F1) to*	*v(F1) [ppm]*
Integral 1	5938010,531	1	0	210,9180267	210,6521808	210,7851037
Integral 2	816159,2632	0,137446584	0	209,5683476	209,3638508	209,4660992
Integral 3	1529111,934	0,2575125	0	209,0980049	208,9344074	209,0162062
Integral 4	5311435,717	0,894480683	0	208,6481119	208,4436151	208,5458635
Integral 5	1704645,77	0,287073551	0	207,0734863	206,8689895	206,9712379
Integral 6	9393441,774	1,581917332	1	206,7258417	206,4395462	206,5826939
Integral 7	2667269,059	0,44918564	0	203,4743422	203,290295	203,3823186
Integral 8	2310798,789	0,389153703	0	203,1471473	202,8813014	203,0142243
Integral 9	6498050,198	1,094314361	0	196,2556042	195,9079596	196,0817819

Integral 10	1139617,913	0,191919147	0	183,1064583	182,9837602	183,0451092
Integral 11	1389837,912	0,234057839	0	180,5706976	180,4479995	180,5093486
Integral 12	1606865,516	0,270606714	0	180,0594556	179,8958581	179,9776568
Integral 13	27695153,81	4,664045924	3	179,77316	179,384616	179,578888
Integral 14	2745839,496	0,462417418	0	179,3641664	179,1187702	179,2414683
Integral 15	98761927,22	16,63215764	2	177,9725456	177,7879028	177,8802242
Integral 16	23380486,71	3,937427627	2	177,6417273	177,2032007	177,422464
Integral 17	63655630,38	10,72002652	3	177,2032007	176,8800759	177,0416383
Integral 18	14557175,37	2,451524007	7	176,8569956	176,1722786	176,5146371
Integral 19	21320967,59	3,590591072	1	175,9030079	175,6183503	175,7606791
Integral 20	39522533,37	6,655854376	2	175,5183355	175,2413714	175,3798534
Integral 21	644434430	108,5269934	5	175,1413565	174,1181279	174,6297422
Integral 22	188607802,3	31,76279351	6	174,1335148	173,5795865	173,8565506
Integral 23	23679873,67	3,987846359	1	173,5411192	173,2641551	173,4026372
Integral 24	47427226,34	7,987056623	1	173,2487682	172,6255989	172,9371835
Integral 25	1981770,87	0,333743239	0	172,3871019	172,2640068	172,3255544
Integral 26	40996439,41	6,904069839	1	172,1793788	172,0332033	172,1062911
Integral 27	5626091,459	0,947470778	0	171,4092398	171,1024946	171,2558672
Integral 28	119711738,3	20,16024352	4	170,6117022	170,2436079	170,4276551
Integral 29	45268513,71	7,623515229	1	170,0391111	169,8141646	169,9266378
Integral 30	35419707,99	5,964911616	0	169,0575263	168,0145925	168,5360594
Integral 31	4026003,137	0,678005389	0	167,4829008	167,2988536	167,3908772
Integral 32	126140113,8	21,24282421	2	166,3581682	165,6833287	166,0207484
Integral 33	18194027,96	3,063993887	1	163,3725145	163,0657693	163,2191419
Integral 34	11428776,65	1,924681101	1	162,5136279	162,2682317	162,3909298
Integral 35	23755556,22	4,000591797	2	162,2273323	161,9001374	162,0637349
Integral 36	32653398,54	5,499046923	1	160,6527068	159,8756188	160,2641628
Integral 37	15324830,51	2,580802178	2	157,4830059	157,2989588	157,3909824
Integral 38	16143466,3	2,718665825	4	155,4584874	154,967695	155,2130912
Integral 39	746318,4425	0,125684931	0	152,3296859	152,1251891	152,2274375
Integral 40	659216,1053	0,111016325	0	150,7959597	150,5914629	150,6937113
Integral 41	39466067,44	6,646345141	6	147,9534538	147,1354665	147,5444602
Integral 42	25100058,76	4,227014862	2	147,1354665	146,4401773	146,7878219
Integral 43	9723300,266	1,63746767	3	146,4294065	146,198603	146,3140048
Integral 44	34238852,68	5,766047821	4	145,8447044	145,4215647	145,6331346
Integral 45	342407178,2	57,66361923	3	145,460032	145,2830827	145,3715573
Integral 46	3663575,315	0,616970161	2	145,2600023	145,1292137	145,194608
Integral 47	231388189,3	38,96729184	4	145,1292137	144,929184	145,0291989
Integral 48	96556740,04	16,26078963	5	144,929184	144,5675919	144,748388
Integral 49	29960092,02	5,045476404	6	144,5137378	144,0829047	144,2983212
Integral 50	17764930,96	2,991731131	3	144,0213571	143,6136043	143,8174807
Integral 51	39935786,35	6,725448892	3	143,5828305	143,2904795	143,436655
Integral 52	143558930,7	24,17626745	4	143,2673991	143,0058219	143,1366105
Integral 53	96050211,2	16,17548684	2	142,9981284	142,8442595	142,921194

Integral 54	19859274,34	3,344432321	3	142,8211791	142,7057774	142,7634783
Integral 55	287167,8636	0,048360956	0	142,6596167	142,5826822	142,6211495
Integral 56	13798971,46	2,323837485	2	142,5596019	142,3595722	142,459587
Integral 57	2562501,657	0,431542121	1	142,3057181	142,2441705	142,2749443
Integral 58	6248880,225	1,0523525	2	142,1749294	142,013367	142,0941482
Integral 59	1954296,458	0,329116368	1	141,8825784	141,7979505	141,8402644
Integral 60	1403416,933	0,236344635	0	141,6902422	141,5286798	141,609461
Integral 61	7410892,681	1,248043034	1	141,4209715	141,2517156	141,3363435
Integral 62	40482012,63	6,817436989	3	141,2594091	140,6977873	140,9785982
Integral 63	4211513,533	0,709246559	1	140,6900939	140,5823856	140,6362397
Integral 64	857237,9574	0,144364506	1	140,451597	140,366969	140,409283
Integral 65	3858227,778	0,649750915	0	140,1515525	139,9899901	140,0707713
Integral 66	2196352,512	0,369880198	0	139,8976687	139,8207342	139,8592014
Integral 67	2287639,436	0,385253516	0	139,5206897	139,4514487	139,4860692
Integral 68	2380259,318	0,400851313	0	139,0744697	138,9975352	139,0360024
Integral 69	2216028,567	0,373193775	0	138,7667317	138,6590234	138,7128776
Integral 70	1065176,35	0,179382698	0	138,1435624	138,0743214	138,1089419
Integral 71	2598227,771	0,437558633	1	135,1815847	135,1200371	135,1508109
Integral 72	3456944,385	0,582172155	0	134,9430878	134,8507664	134,8969271
Integral 73	52109611,97	8,775601137	1	134,7892188	134,5814957	134,6853573
Integral 74	6666088,567	1,122613126	1	134,1737429	134,0660347	134,1198888
Integral 75	24929212,98	4,198243309	4	134,0121805	133,4120915	133,712136
Integral 76	10378271,83	1,747769186	2	133,3890112	133,0889667	133,2389889
Integral 77	43156261,08	7,267798004	2	133,112047	132,9581781	133,0351125
Integral 78	22061723,67	3,715339263	2	132,9274043	132,4888777	132,708141
Integral 79	19517288,43	3,286839645	2	132,4657974	132,0734315	132,2696144
Integral 80	18831610,39	3,171366958	2	132,0888184	131,7272263	131,9080223
Integral 81	2158184,9	0,363452521	0	131,7041459	131,5964377	131,6502918
Integral 82	4264749,674	0,718211875	1	131,5887442	131,5118097	131,550277
Integral 83	15636239,31	2,633245466	1	131,5195032	131,3848678	131,4521855
Integral 84	1549737,077	0,260985909	0	131,1194439	131,0271225	131,0732832
Integral 85	1810470,545	0,304895139	0	130,9848085	130,9271076	130,9559581
Integral 86	16867789,18	2,840646558	4	130,7232313	130,3539457	130,5385885
Integral 87	6843416,139	1,152476255	1	130,015434	129,8077109	129,9115724
Integral 88	11083412,5	1,866519509	2	129,7692436	129,6115279	129,6903858
Integral 89	27626929,46	4,652556495	1	129,4499655	129,3499507	129,3999581
Integral 90	11833798,62	1,992889463	2	129,1576145	129,0306726	129,0941435
Integral 91	1849262,97	0,311428038	1	128,7075477	128,6498469	128,6786973
Integral 92	6798124,26	1,144848805	1	128,592146	128,4536639	128,522905
Integral 93	9884181,113	1,664561062	1	128,3998098	128,1766998	128,2882548
Integral 94	5576296,436	0,939084969	1	128,1228456	128,0228308	128,0728382
Integral 95	86070608,54	14,49485616	1	128,0112906	127,9112758	127,9612832
Integral 96	1473434,171	0,248135998	1	127,7727937	127,7112461	127,7420199
Integral 97	1415661,31	0,238406669	1	127,3034934	127,253486	127,2784897

Integral 98	12960582,84	2,182647331	1	127,211172	127,1342375	127,1727047
Integral 99	4204645,243	0,708089893	1	127,1226973	127,057303	127,0900002
Integral 100	2700661,742	0,454809187	1	126,9649816	126,9111275	126,9380546
Integral 101	6133073,333	1,032849858	2	126,7110978	126,6149297	126,6630138
Integral 102	3776659,455	0,636014274	1	126,5264551	126,4687542	126,4976046
Integral 103	14095354,5	2,373750337	1	126,0840818	125,9840669	126,0340744
Integral 104	10417678,06	1,754405453	1	125,6917159	125,5032264	125,5974712
Integral 105	2290568,308	0,385746757	1	125,3147369	125,2685762	125,2916566
Integral 106	35048179,17	5,90234372	1	124,5800126	124,4723043	124,5261584
Integral 107	1428339,73	0,240541798	0	124,3569026	124,2915083	124,3242054
Integral 108	27176225,36	4,576654963	4	124,2568877	124,0914786	124,1741832
Integral 109	5374439,742	0,905090975	1	124,0683982	124,0145441	124,0414712
Integral 110	3546963,286	0,597331929	1	123,8145144	123,764507	123,7895107
Integral 111	12910618,67	2,174233036	1	123,7452734	123,5606306	123,652952
Integral 112	3506199,419	0,590467026	0	122,9028408	122,8489867	122,8759137
Integral 113	5364334,103	0,903389119	0	122,7989792	122,7297382	122,7643587
Integral 114	3926965,234	0,661326755	0	122,7105046	122,6258766	122,6681906
Integral 115	7143002,103	1,2029285	1	122,4220003	122,3527592	122,3873797
Integral 116	1983909,636	0,334103422	0	122,2412042	122,202737	122,2219706
Integral 117	9452479,268	1,591859634	1	121,5795676	121,5064799	121,5430238
Integral 118	1039165,622	0,17500232	0	121,2795231	121,2141288	121,246826
Integral 119	26881976,34	4,527101493	1	121,1333476	121,0487197	121,0910337
Integral 120	2429940,897	0,409218017	0	121,0217926	120,9717852	120,9967889
Integral 121	10801873,17	1,819106436	1	120,9563983	120,9063909	120,9313946
Integral 122	1917501,091	0,322919786	0	120,6794342	120,6409669	120,6602005
Integral 123	3676271,892	0,619108348	0	120,4178569	120,3524626	120,3851598
Integral 124	10808532,61	1,820227929	1	120,3216888	120,2332141	120,2774515
Integral 125	1565131,304	0,263578398	0	119,9524033	119,913936	119,9331696
Integral 126	3080139,478	0,518715732	0	119,7485269	119,6677457	119,7081363
Integral 127	2830312,387	0,476643208	0	119,6485121	119,5946579	119,621585
Integral 128	73686464,78	12,40928496	1	119,5850411	119,4946431	119,5398421
Integral 129	2280228,2	0,384005415	1	119,4869496	119,4523291	119,4696394
Integral 130	332757583,8	56,03856411	2	119,3907815	119,2426826	119,3167321
Integral 131	8101212,632	1,364297451	1	119,2388359	119,2061388	119,2224873
Integral 132	820089,8333	0,138108518	0	119,1926752	119,1715182	119,1820967
Integral 133	5522833,684	0,93008149	1	119,0868903	119,0541931	119,0705417
Integral 134	26573411,19	4,475137094	2	118,9695652	118,9137877	118,9416765
Integral 135	3340500	0,562562155	1	118,9060943	118,8830139	118,8945541
Integral 136	10547957,57	1,77634538	1	118,8541635	118,8041561	118,8291598
Integral 137	3843236,32	0,647226255	0	118,8022327	118,7579954	118,780114
Integral 138	3200387,778	0,538966336	0	118,7541487	118,7214515	118,7378001
Integral 139	1200754,533	0,202214955	0	118,7060646	118,6810609	118,6935627
Integral 140	26436744,65	4,452121551	1	118,6310535	118,554119	118,5925862
Integral 141	3508077,286	0,590783271	0	118,4887247	118,4406406	118,4646827

Integral 142	3704077,846	0,623791054	0	118,3983267	118,352166	118,3752463
Integral 143	40741936,65	6,861209902	1	118,3040819	118,2156073	118,2598446
Integral 144	793126,75	0,133567757	0	118,1540597	118,1271326	118,1405961
Integral 145	1109479,333	0,186843612	0	118,0944354	118,0694317	118,0819336
Integral 146	5652349,636	0,951892828	1	118,0636616	118,0251944	118,044428
Integral 147	3621107,818	0,609818356	0	117,5135801	117,4751128	117,4943465
Integral 148	10571897,05	1,780376946	1	117,2520028	117,1846851	117,218344
Integral 149	1775714,941	0,299042067	0	116,8634837	116,8346332	116,8490585
Integral 150	3608924,957	0,607766682	0	116,7653922	116,7250016	116,7451969
Integral 151	80784503,05	13,60464126	1	116,5153551	116,4018768	116,4586159
Integral 152	16572370,67	2,79089614	2	116,0883687	116,0248978	116,0566333
Integral 153	386491060,4	65,08763473	2	115,8267915	115,6786926	115,752742
Integral 154	1118780,941	0,188410064	1	115,6652291	115,6363786	115,6508038
Integral 155	8440149,333	1,421376619	1	115,6344553	115,6036815	115,6190684
Integral 156	1645910,571	0,277182158	1	115,5921413	115,569061	115,5806011
Integral 157	132282620,9	22,27726276	1	115,5498273	115,4498125	115,4998199
Integral 158	23345383,63	3,931516036	1	115,4498125	115,394035	115,4219237
Integral 159	5703663,75	0,960534462	1	115,3709546	115,3151771	115,3430659
Integral 160	21630563,28	3,64272902	1	115,2997903	115,2555529	115,2776716
Integral 161	38408127,82	6,468181156	1	115,2324726	115,1747717	115,2036221
Integral 162	11676710,53	1,966434797	1	115,1016839	115,0497532	115,0757186
Integral 163	777925,4545	0,131007759	0	115,0497532	115,0305196	115,0401364
Integral 164	3392351,5	0,571294288	0	115,0228261	114,9728187	114,9978224
Integral 165	3979457,886	0,670166862	0	114,6266135	114,5650659	114,5958397
Integral 166	862936,3158	0,145324147	0	114,4862081	114,4535109	114,4698595
Integral 167	3759701,714	0,633158479	0	114,3727297	114,3361858	114,3544578
Integral 168	1674720,5	0,282033939	0	113,8438051	113,816878	113,8303416
Integral 169	7279953,724	1,225992054	1	113,7649473	113,7149398	113,7399436
Integral 170	2646591,765	0,445703447	0	113,1456247	113,1148509	113,1302378
Integral 171	29085094,52	4,898121074	1	113,0879238	113,0340696	113,0609967
Integral 172	4047141,474	0,681565223	0	113,0340696	113,0013725	113,0177211
Integral 173	7148357,083	1,203830314	0	112,5089918	112,4666778	112,4878348
Integral 174	10683375,18	1,799150595	1	112,3724331	112,3128088	112,342621
Integral 175	5015486,182	0,844640837	0	112,0339213	111,9954541	112,0146877
Integral 176	1653900	0,27852763	0	111,591548	111,5607742	111,5761611
Integral 177	8527890,6	1,436152825	1	111,410752	111,3395876	111,3751698
Integral 178	2354065,789	0,396440151	0	109,5143169	109,4816198	109,4979684
Integral 179	1796972,286	0,302621943	0	107,023563	106,9985593	107,0110611
Integral 180	17968310	3,025981498	1	104,309699	104,2500748	104,2798869
Integral 181	18665724,04	3,143430605	1	103,3037806	103,2018424	103,2528115
Integral 182	1619746,737	0,272775996	0	103,2018424	103,1691452	103,1854938
Integral 183	11907337,96	2,005273971	0	103,1691452	103,0902874	103,1297163
Integral 184	8579421,613	1,444830987	0	102,9364184	102,8825643	102,9094913
Integral 185	1445145,067	0,243371927	0	101,9266533	101,8997262	101,9131898

Integral 186	6887780,952	1,159947581	0	98,97621576	98,93967188	98,95794382
Integral 187	20597783,56	3,468802128	1	97,28173372	97,22595621	97,25384496
Integral 188	2036002,444	0,342876193	0	74,61106416	74,58029037	74,59567727
Integral 189	36045072,76	6,070227154	1	74,29370941	74,21869829	74,25620385
Integral 190	9874641,829	1,662954583	0	72,49536581	72,43381822	72,46459201
Integral 191	35855162,38	6,038244997	1	68,86213472	68,78904696	68,82559084
Integral 192	88139616,03	14,84329062	1	68,34475031	68,23511867	68,28993449
Integral 193	12088798,23	2,035833073	0	67,38306924	67,30421139	67,34364031
Integral 194	5867407,1	0,988109918	0	67,26766751	67,19650311	67,23208531
Integral 195	3172626,583	0,534291168	0	67,08879483	67,04840423	67,06859953
Integral 196	2757269,846	0,464342364	0	66,90607543	66,85991474	66,88299508
Integral 197	2020170,333	0,340209961	0	66,64065145	66,60026085	66,62045615
Integral 198	2134080,783	0,35939323	0	66,44062179	66,40023118	66,42042649
Integral 199	1026280,375	0,17283236	0	66,3790742	66,35214713	66,36561067
Integral 200	6447637,091	1,085824462	0	66,34637704	66,3079098	66,32714342
Integral 201	21330885,93	3,592261384	1	66,21558842	66,16750437	66,19154639
Integral 202	1964500,769	0,330834841	0	66,165581	66,14442402	66,15500251
Integral 203	9705342,64	1,634443487	0	66,14250066	66,09826333	66,12038199
Integral 204	754028,4	0,126983338	0	66,10018669	66,08479979	66,09249324
Integral 205	1303482,364	0,219514997	0	66,08672316	66,04825591	66,06748953
Integral 206	27180738,55	4,577415012	1	65,82899263	65,75013478	65,7895637
Integral 207	3373215,333	0,568071632	0	65,6270396	65,57510883	65,60107421
Integral 208	1168874,857	0,196846208	0	65,53279486	65,47124727	65,50202106
Integral 209	1865620,182	0,3141827	0	63,70944755	63,65174669	63,68059712
Integral 210	1395855,333	0,235071212	0	63,57096548	63,50749452	63,53923
Integral 211	8097971,072	1,363751551	0	62,82470096	62,70160579	62,76315338
Integral 212	3929272,75	0,661715356	0	60,88787529	60,81671089	60,85229309
Integral 213	4875150,5	0,821007385	0	60,79363054	60,70900261	60,75131658
Integral 214	7454871,5	1,255449357	0	60,32625354	60,2473957	60,28682462
Integral 215	2162499,167	0,364179072	0	60,09545009	60,05313612	60,0742931
Integral 216	1055595,1	0,177769153	0	60,03197914	59,99735862	60,01466888
Integral 217	112231160,8	18,9004651	1	59,85887654	59,74732154	59,80309904
Integral 218	2385546	0,401741625	0	59,74539818	59,6934674	59,71943279
Integral 219	33663168,5	5,669098821	1	58,3625008	58,28364295	58,32307187
Integral 220	1996266,923	0,33618447	0	58,12208053	58,07591984	58,09900019
Integral 221	1416019,2	0,23846694	0	57,96821156	57,91628078	57,94224617
Integral 222	5910589,484	0,995382116	0	57,19117325	57,13539575	57,1632845
Integral 223	11984256,88	2,018227624	0	55,7563451	55,66210035	55,70922273
Integral 224	18942024,9	3,189961486	1	55,56208552	55,51207811	55,53708181
Integral 225	2813520,5	0,473815344	0	55,51207811	55,48515104	55,49861457
Integral 226	996535,3333	0,1678231	0	55,39667638	55,36590258	55,38128948
Integral 227	17870963,1	3,00958764	1	53,86760348	53,81374934	53,84067641
Integral 228	4614567,459	0,777123489	0	49,42656029	49,36116598	49,39386314
Integral 229	3508846,732	0,590912851	0	49,0553514	48,98226364	49,01880752

Integral 230	5425573,143	0,913702176	0	48,70145277	48,60143793	48,65144535
Integral 231	4614363,907	0,777089209	0	46,42803872	46,35110423	46,38957147
Integral 232	10231987,23	1,723133897	0	46,29340337	46,19146517	46,24243427
Integral 233	4910490,37	0,826958852	0	44,76048374	44,71432305	44,73740339
Integral 234	722355,7778	0,121649461	0	43,1467829	43,11600911	43,13139601
Integral 235	4272597,077	0,719533429	0	41,37151965	41,32728232	41,34940098
Integral 236	5201692,87	0,875999267	0	37,87100055	37,83060995	37,85080525
Integral 237	5395208,75	0,908588613	0	37,82676322	37,78444925	37,80560624
Integral 238	2661956,842	0,448291028	0	37,02279785	36,95548017	36,98913901
Integral 239	1477252,643	0,248779054	0	36,8573887	36,80930465	36,83334668
Integral 240	25285823,89	4,258298931	1	36,78814767	36,72082999	36,75448883
Integral 241	5421711,643	0,913051874	0	36,45155929	36,40347524	36,42751726
Integral 242	6206479,463	1,045211933	0	36,35923791	36,28615015	36,32269403
Integral 243	3183612,72	0,536141306	0	35,42256055	35,38024658	35,40140356
Integral 244	1845367,077	0,310771944	0	35,12828614	35,08212545	35,10520579
Integral 245	1450623,467	0,244294526	0	35,07827872	35,02634794	35,05231333
Integral 246	2369706	0,399074065	0	34,88786587	34,8455519	34,86670889
Integral 247	9540076,154	1,606611525	0	34,72053336	34,62821198	34,67437267
Integral 248	1497668,417	0,252217205	0	34,42241223	34,38009827	34,40125525
Integral 249	2188258,267	0,368517074	0	33,77423919	33,72038505	33,74731212
Integral 250	901318,1818	0,151787906	0	33,49150496	33,47227134	33,48188815
Integral 251	21321721,56	3,590718044	1	33,23954452	33,17607357	33,20780904
Integral 252	7611624,375	1,281847571	0	32,95104019	32,89333933	32,92218976
Integral 253	750704	0,126423487	0	32,82217493	32,79140114	32,80678803
Integral 254	1468862,3	0,247366065	0	32,77024415	32,73562364	32,75293389
Integral 255	912211,8333	0,153622468	0	32,51059026	32,4682763	32,48943328
Integral 256	34558621,02	5,81989891	2	32,17977198	32,07398706	32,12687952
Integral 257	8848088,923	1,490076327	1	32,04898335	32,00282266	32,02590301
Integral 258	5637103,412	0,949325264	1	31,94896852	31,92011809	31,9345433
Integral 259	18576174,6	3,128349892	1	31,91627136	31,83933688	31,87780412
Integral 260	28096698,63	4,731668711	2	31,82394998	31,75663231	31,79029114
Integral 261	4067725,6	0,685031726	0	31,51044195	31,45658781	31,48351488
Integral 262	16271068,58	2,740154888	0	31,38734677	31,2642516	31,32579919
Integral 263	2898170,609	0,488070978	0	31,23732453	31,19693392	31,21712923
Integral 264	5677689,826	0,956160282	0	31,17193021	31,13153961	31,15173491
Integral 265	6756347,692	1,137813356	0	31,08153219	31,03729486	31,05941353
Integral 266	2482190,267	0,418017155	0	30,6699327	30,64492899	30,65743084
Integral 267	2003186,889	0,337349838	0	30,54106743	30,51029364	30,52568054
Integral 268	2523554,5	0,424983163	0	30,23332949	30,17755199	30,20544074
Integral 269	1201182,8	0,202287078	0	29,66016757	29,61593024	29,63804891
Integral 270	5001178,615	0,842231348	0	29,59092654	29,54476584	29,56784619
Integral 271	6431531,25	1,083112133	0	29,46975472	29,38512679	29,42744075
Integral 272	8993894,541	1,514630952	0	29,11777945	29,05238514	29,08508229
Integral 273	4033210,889	0,679219221	0	28,96391048	28,91774979	28,94083013

Integral 274	1563566,435	0,263314864	0	28,85235547	28,81388823	28,83312185
Integral 275	1131622,545	0,190572674	0	28,79273125	28,77542099	28,78407612
Integral 276	5176740,533	0,871797129	0	28,59270158	28,54077081	28,5667362
Integral 277	1555951,636	0,262032482	0	28,44652606	28,40805882	28,42729244
Integral 278	3373725,882	0,568157612	0	28,2311095	28,16956191	28,20033571
Integral 279	3334066,571	0,561478723	0	27,85220716	27,81566328	27,83393522
Integral 280	47448355,47	7,990614908	1	27,66179431	27,56754956	27,61467194
Integral 281	86416551,39	14,55311521	1	27,46368801	27,40021706	27,43195253
Integral 282	1523408,516	0,256552006	0	26,88283264	26,8289785	26,85590557
Integral 283	5059014,476	0,851971287	0	26,51739383	26,48084995	26,49912189
Integral 284	2488619,846	0,419099938	0	26,20580917	26,15964848	26,18272882
Integral 285	7355649,042	1,238739642	0	25,49608854	25,40953724	25,45281289
Integral 286	4893937,302	0,824171206	0	25,23258792	25,1575768	25,19508236
Integral 287	3772780,767	0,635361077	0	25,09987594	24,99216766	25,0460218
Integral 288	7989318,667	1,345453772	0	24,81329498	24,74405394	24,77867446
Integral 289	1904049,375	0,320654429	0	24,44977953	24,42285246	24,436316
Integral 290	24795794,87	4,175774823	1	24,39400203	24,35361143	24,37380673
Integral 291	774156	0,130372958	0	24,35361143	24,33822453	24,34591798
Integral 292	3932610,6	0,662277472	0	24,25551996	24,22089944	24,2382097
Integral 293	3282170,667	0,552739112	0	23,95162874	23,92085494	23,93624184
Integral 294	4397139,059	0,740507117	0	23,92085494	23,89200451	23,90642973
Integral 295	2436471,538	0,41031782	0	23,43809105	23,4150107	23,42655087
Integral 296	22832957,31	3,845220078	1	23,37846682	23,31499587	23,34673135
Integral 297	1463136	0,246401719	0	23,25921837	23,22844457	23,24383147
Integral 298	4520166,706	0,761225781	1	23,22459785	23,19574742	23,21017263
Integral 299	2086762,4	0,351424503	1	23,19574742	23,17843716	23,18709229
Integral 300	1439956,923	0,24249821	0	23,17074371	23,14766336	23,15920354
Integral 301	435926	0,073412803	0	23,14189328	23,12650638	23,13419983
Integral 302	19845350,22	3,342087408	1	23,13227647	23,10150267	23,11688957
Integral 303	992691,3333	0,167175745	0	23,10150267	23,08034569	23,09092418
Integral 304	7207760	1,213834156	1	23,04187845	23,00918129	23,02552987
Integral 305	15592142,9	2,625819342	1	23,00672819	22,95219848	22,97946334
Integral 306	3416988,8	0,575443372	0	22,90729165	22,87361154	22,8904516
Integral 307	3731782,615	0,628456719	0	22,86398865	22,84153523	22,85276194
Integral 308	6631415,492	1,116773953	0	22,24972745	22,14547946	22,19760345
Integral 309	84285286,29	14,19419616	1	21,80386684	21,73009134	21,76697909
Integral 310	4659271,111	0,784651877	0	21,19441708	21,14790645	21,17116176
Integral 311	32732980,5	5,512449049	1	21,02441268	20,96827915	20,99634591
Integral 312	2361448,5	0,397683448	0	20,85921972	20,83195486	20,84558729
Integral 313	99379888,16	16,73622633	1	20,78223659	20,71648017	20,74935838
Integral 314	2967318,706	0,499715972	0	20,60742074	20,57855207	20,59298641
Integral 315	4725418,526	0,795791537	0	20,54807958	20,51600328	20,53204143
Integral 316	1623461,273	0,273401548	0	20,47270027	20,4550583	20,46387929
Integral 317	11732730,3	1,975868894	1	20,43581252	20,40052859	20,41817056

Integral 318	90627434,65	15,26225563	1	20,39892477	20,34439506	20,37165992
Integral 319	4502952,4	0,758326779	0	20,12948383	20,08618082	20,10783233
Integral 320	3927691,833	0,661449119	0	19,29389614	19,25219695	19,27304655
Integral 321	3508175,926	0,590799883	0	19,04690861	19,00039797	19,02365329
Integral 322	15908406,7	2,679080243	1	18,63152049	18,59142511	18,6114728
Integral 323	6173548,5	1,039666142	0	18,02207074	17,95791813	17,98999443
Integral 324	29633187,11	4,990423469	1	16,43589756	16,40542507	16,42066132
Integral 325	3093444,588	0,5209564	0	16,38938692	16,36051825	16,37495259
Integral 326	13575346,32	2,286177541	1	16,12315361	16,08947349	16,10631355
Integral 327	23548629,45	3,96574397	1	16,05739719	16,01890563	16,03815141
Integral 328	5346781,111	0,90043308	1	16,02211326	16,00767892	16,01489609
Integral 329	6871402,167	1,157189286	1	16,0060751	15,98682932	15,99645221
Integral 330	43392332,93	7,307554054	1	15,98362169	15,93390342	15,95876256
Integral 331	2149508,267	0,361991319	0	15,92748816	15,90182712	15,91465764
Integral 332	371097,4286	0,062495246	0	15,85852411	15,84729741	15,85291076
Integral 333	1668083,5	0,280916225	0	15,84408977	15,82484399	15,83446688
Integral 334	1646195,091	0,277230073	0	15,82484399	15,80559821	15,8152211
Integral 335	1723751,333	0,290291054	0	14,87698924	14,85774346	14,86736635
Integral 336	3315393,467	0,55833405	0	14,50490413	14,47924309	14,49207361
Integral 337	8177634,727	1,377167434	1	14,41990193	14,38301418	14,40145806
Integral 338	92018925,64	15,49659186	1	14,11196942	14,07508167	14,09352555
Integral 339	647632	0,109065485	0	13,69978893	13,67412789	13,68695841
Integral 340	18958766,74	3,192780922	1	13,67092026	13,63724014	13,6540802
Integral 341	5613324,783	0,945320786	0	11,99814107	11,95804569	11,97809338

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