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Transformations of Bjorkman lignin from European spruce (*Picea abies*) in superacidic media

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1. Instruments

Mass spectrometric analysis was conducted on Fourier Transform (Ion Cyclotron Resonance) Mass Spectrometer (Varian 902-MS) equipped with MALDI and 9.4 T magnet (FTMS). Samples were irradiated by series of 5x5 impulses at 355 nm pulses by third harmonic of neodymium-doped yttrium aluminium garnet (Nd:YAG) laser. The laser power was set to the minimum level necessary to generate a reasonable signal. Signal from 25 shots was recorded. A ProteoMass Peptide MALDI-MS Calibration Kit (Sigma) was used for external calibration. 2,5-Dihydroxybenzoic acid (DHB) was used as a matrix. The Bjorkman lignin and DHB were mixed and dissolved in toluene. The products of Bjorkman lignin destruction and matrix were mixed and dissolved in acetone, and about 1μl of solutions was deposited on the target plate and then dried under room condition.

Other matrixes, CHCA (α-Cyano-4-hydroxycinnamic acid), DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile), HABA (2-(4-Hydroxyphenylazo)-benzoic acid), SA (Sinapinic acid), gave far worse results in MALDI experiments.

Additionally mass spectrometric analysis was run on a machine TOF MS Reflex IV Bruker.

Chromato-mass-spectrometry data were obtained at a machine G2570A GC/MSD Agilent Technologies 6850c with a column HP-5MS (3m×0.25mm), a thickness of the stationary phase 0.25μm. Analysis of reaction mixtures and these mixtures after trimethylsilylation were carried out (see Figure S1 below).

The ^{1}H and ^{13}C NMR spectra of solutions of compounds in $CDCl_3$ were recorded on a Bruker AM-500 spectrometer at 25°C at 500 and 100 MHz correspondingly. The residual proton-solvent peak $CDCl_3$ (δ 7.26 ppm) was used as a reference.

Element analysis was carried out on the instrument EA – 300 EuroVektor.

2. Procedures for conversion of Bjorkman lignin under the action of superacids

2.1. *Conversion of Bjorkman lignin in the superacid CF_3SO_3H*

Mixture of Bjorkman lignin (100 mg) and CF_3SO_3H (3 ml) was stirred at 20°C for 2 h, then quenched with water (~20 ml). The obtained residue was filtered off, and consequently washed with water (5×10 ml), chloroform (3×5 ml), and then dried under the air conditions. The prepared sample was analyzed by MALDI-MS. The yield of the obtained residue was 90 mg

(90%). The water layer was extracted with chloroform (3×10 ml). These extracts and previously obtained chloroform solution were combined, dried over Na_2SO_4, evaporated in vacuum and analyzed by GC-MS (see Figure S1). The yield of this fraction was 6 mg (6%).

2.2. *Conversion of Bjorkman lignin in the system $AlBr_3$-benzene*

Mixture of Bjorkman lignin (60 mg) and solution of $AlBr_3$ (3 g) in benzene (20 ml) was stirred at 20°C for 2 h, then quenched with water (~100 ml). The obtained residue was filtered off, and consequently washed with water (5×10 ml), chloroform (3×5 ml), and then dried under the air conditions. The prepared sample was analyzed by MALDI-MS. The yield of the obtained residue was 50 mg (83%). The water layer was extracted with chloroform (3×30 ml). These extracts and previously obtained chloroform solution were combined, dried over Na_2SO_4, evaporated in vacuum and analyzed by GC-MS (see Figure S1). The yield of this fraction was 5 mg (8%).

2.3. *Conversion of Bjorkman lignin under the action of zeolite CBV-720*

Mixture of Bjorkman lignin (30 mg) and zeolite CBV-720 (1 g) in benzene (5 ml) was stirred at 130°C for 24 h in glass high pressure tube (Ace pressure tube, ALDRICH Z181099), then cooled down, and extracted with hot methanol (4×10 ml). After the extraction the residual mixture of zeolite and converted lignin was analyzed by MALDI-MS. The yield of this fraction was difficult to estimate because lignin was mixed with zeolite. The methanol extracts were combined, evaporated in vacuum and analyzed by GC-MS. The yield of this fraction was 3 mg (10%).

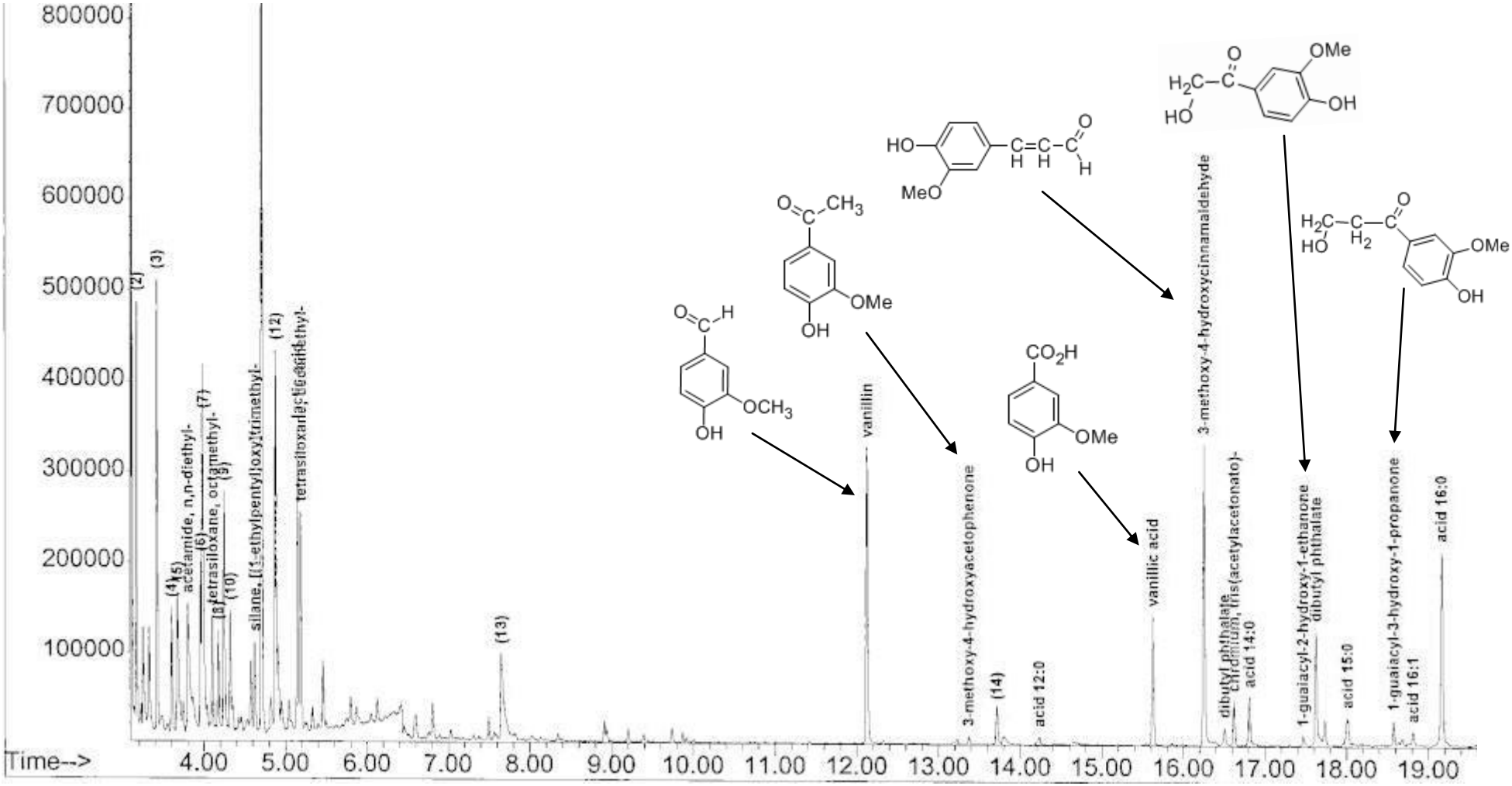


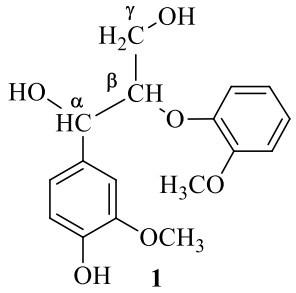
Figure S1 GC-MS spectrum of lignin destruction products (TfOH or $AlBr_3$), that are soluble in chloroform.

*3. Procedure for treatment of lignin model compounds **1-5** in the superacid CF_3SO_3H*

Solution of lignin model compound (50 mg) in CF_3SO_3H (2 ml) was stirred at 20°C for 2 h, then quenched with water (~20 ml). The reaction product was extracted with chloroform (3×20 ml). The combined extracts were washed with water (3×10 ml), dried over Na_2SO_4, evaporated in vacuum and analyzed by GC-MS and ^{1}H NMR.

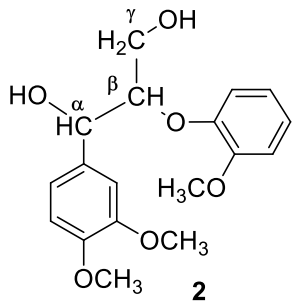
*4. Spectral data of lignin model compounds **1-5***

Compounds **1-5** were synthesized according to procedures from book: G. F. Zakis, *Sintez model'nykh soedinenii lignina (Synthesis of Lignin Model Compounds)*, Zinatne, Riga, 1980 (in Russian).



1

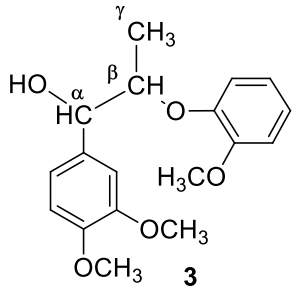
1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy) propane-1,3-diol **1.** Oily mixture of *erythro*- and *threo*-isomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 s (2H, CH_2), 3.47 q (1H, CH, *J* = 7.1 Hz), 3.60 d (1H, CH, *J* = 3.0 Hz), 3.63 d (2H, CH, *J* = 3.0 Hz), 3.66 d (1H, CH, *J* = 3.0 Hz), 3.87 d (6H, *J* = 3.0 Hz, OCH_3), 4.14 q (1H, CH, *J* = 5.0 Hz), 4.96 d (1H, CH, *J* = 3.0 Hz), 6.81-7.13 m ($7H_{arom.}$). Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.78; H, 6.35.



2

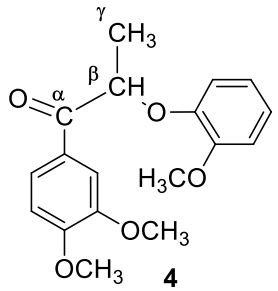
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol **2.** Oily mixture of *erythro*- and *threo*-isomers. ^{1}H NMR (500 MHz, $CDCl_3$, for the mixture of isomers) δ 1.59 s

(2H, CH_2), 3.44 d (2H, CH_2, *J* = 3.0 Hz), 3.60-3.67 m (1H, CH), 3.86 s (3H, OCH_3), 3.87 s (3H, OCH_3), 3.88 s (3H, OCH_3), 4.16 q (1H, CH, *J* = 4.0 Hz), 4.97 q (1H, CH, *J* = 4.0 Hz), 6.82-7.23 m ($7H_{arom.}$). ^{13}C NMR (500 MHz, $CDCl_3$, for the mixture of isomers) δ 55.5, 55.6, 60.6, 60.8, 72.5, 73.5, 86.5, 88.5, 109.3, 109.8, 110.8, 111.9, 112.0, 118.4, 119.3, 120.0, 120.2, 121.4, 123.5, 123.6, 132.2, 132.8, 146.8, 147.5, 148.2, 148.6, 148.7, 148.8, 150.8, 151.0. Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.61; H, 6.58.



3

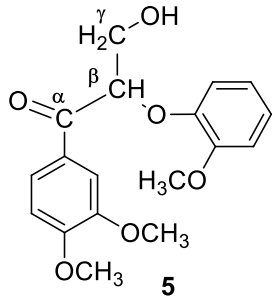
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propan-1-ol **3**. Colorless solid, mp 61-63 °C (for the mixture of *erythro*- and *threo*- isomers). ^1H NMR (500MHz, $CDCl_3$, for the mixture of isomers) δ 1.17 d (3H, CH_3, *J* = 6.4 Hz), 3.85 s (3H, OCH_3), 3.86 s (3H, OCH_3), 3.87 s (3H, OCH_3), 4.35-4.39 m (1H, CH), 4.84 d (1H, CH, *J* = 2.9 Hz), 6.79-7.03 m ($7H_{arom.}$). Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.96; H, 7.02.



4

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propan-1-one **4**. Colorless solid, mp 124-126 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 1.71 d (3H, CH_3, *J* = 6.8 Hz), 3.83 s (3H, OCH_3), 3.90 s (3H, OCH_3), 3.92 s (3H, OCH_3), 5.41 q (1H, CH. *J* = 6.8 Hz), 6.75-7.81 m ($7H_{arom.}$). ^{13}C NMR (500 MHz, $CDCl_3$) δ 19.2, 55.8, 55.9, 56.0, 78.1, 110.1, 111.2, 112.3, 115.9, 120.8, 122.3, 123.6,

127.4, 146.9, 149.0, 149.9, 153.4, 197.5. Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.38; H, 6.41.



5

1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one **5**. Colorless solid, mp 114-116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.04 t (1H, *J* = 6.0 Hz, CH), 3.90 t (9H, *J* = 15.0 Hz, OCH_3), 4.06 t (1H, *J* = 4.0 Hz, CH), 5.38 t (1H, *J* = 5.0 Hz, CH), 6.79-7.75 m ($7H_{arom.}$). ^{13}C NMR (500 MHz, $CDCl_3$) δ 55.6, 55.8, 55.9, 63.5, 83.9, 110.0, 110.8, 112.2, 117.2, 121.0, 123.0, 123.4, 127.9, 146.8, 149.0, 149.9, 153.8, 195.0. Anal. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 65.11; H, 6.12.

*5. Figures of [1]H and [13]C NMR spectra of lignin model compounds **1-5***

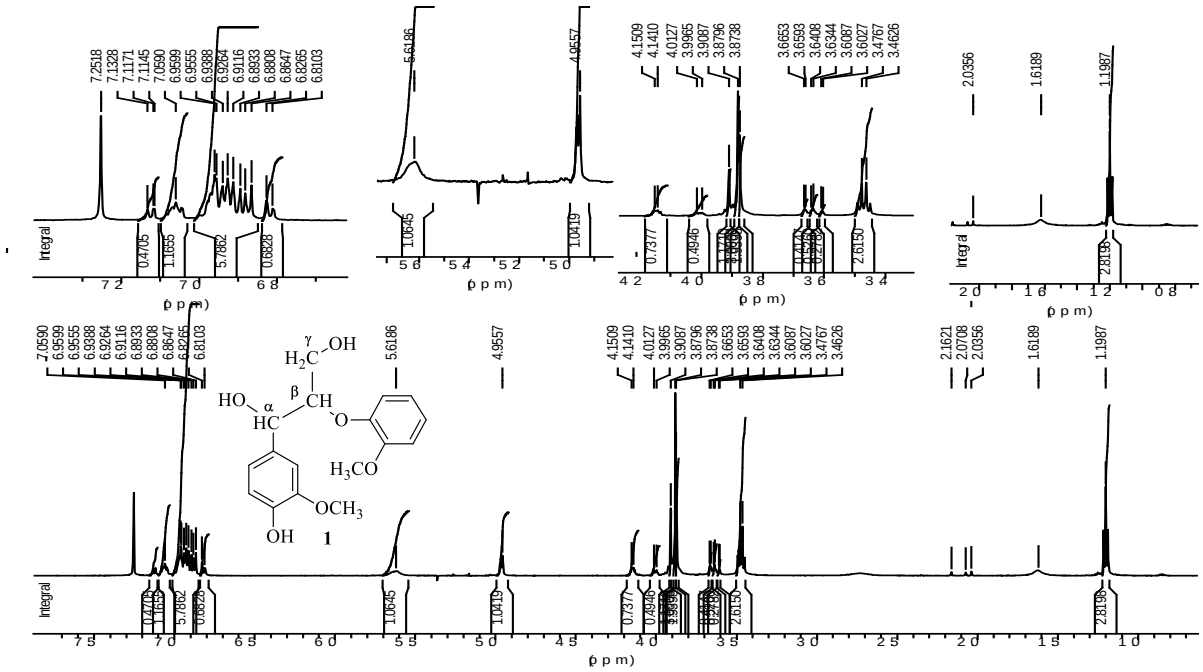


Figure S2 [1]H NMR spectrum of compound **1**.

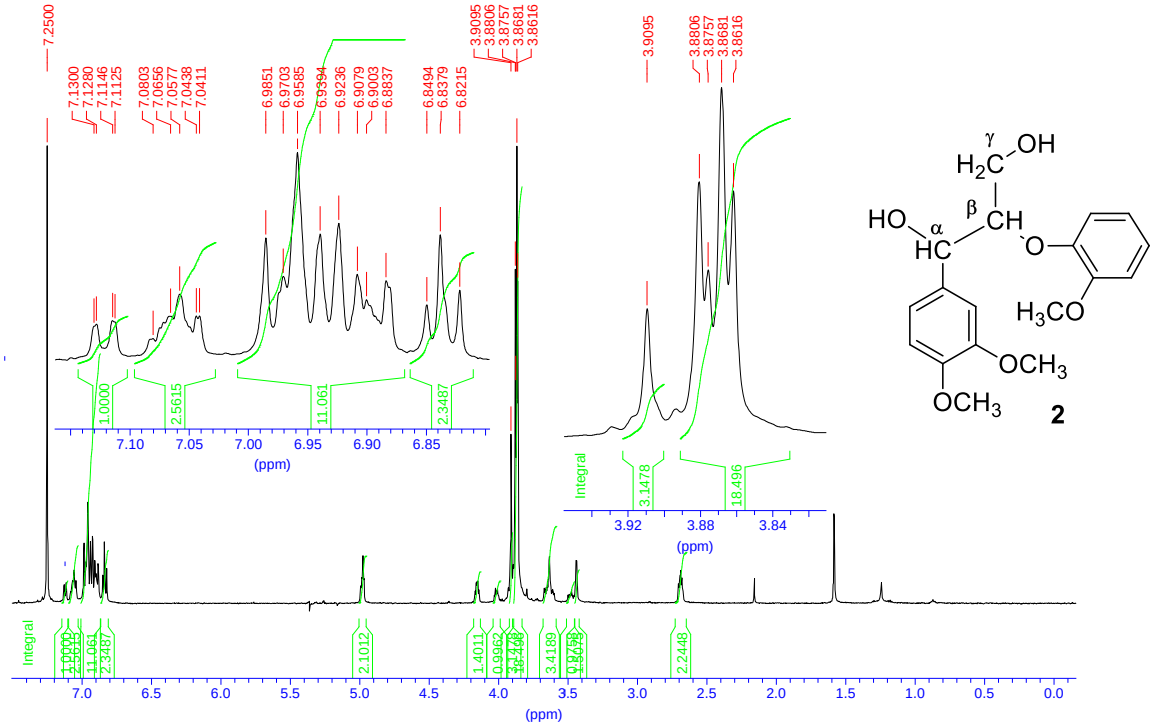


Figure S3 ^{1}H NMR spectrum of compound **2**.

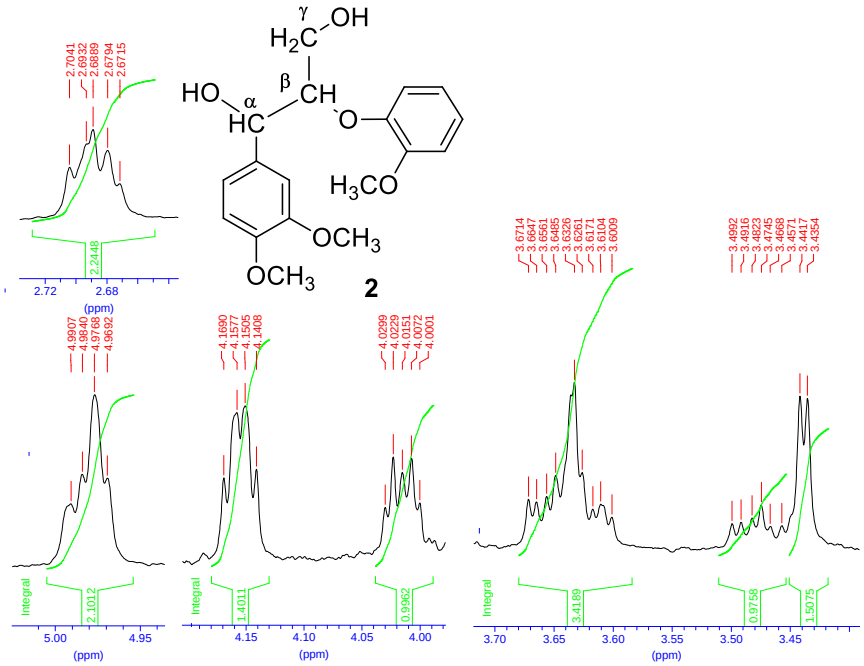


Figure S4 Fragment of ^{1}H NMR spectrum of compound **2**.

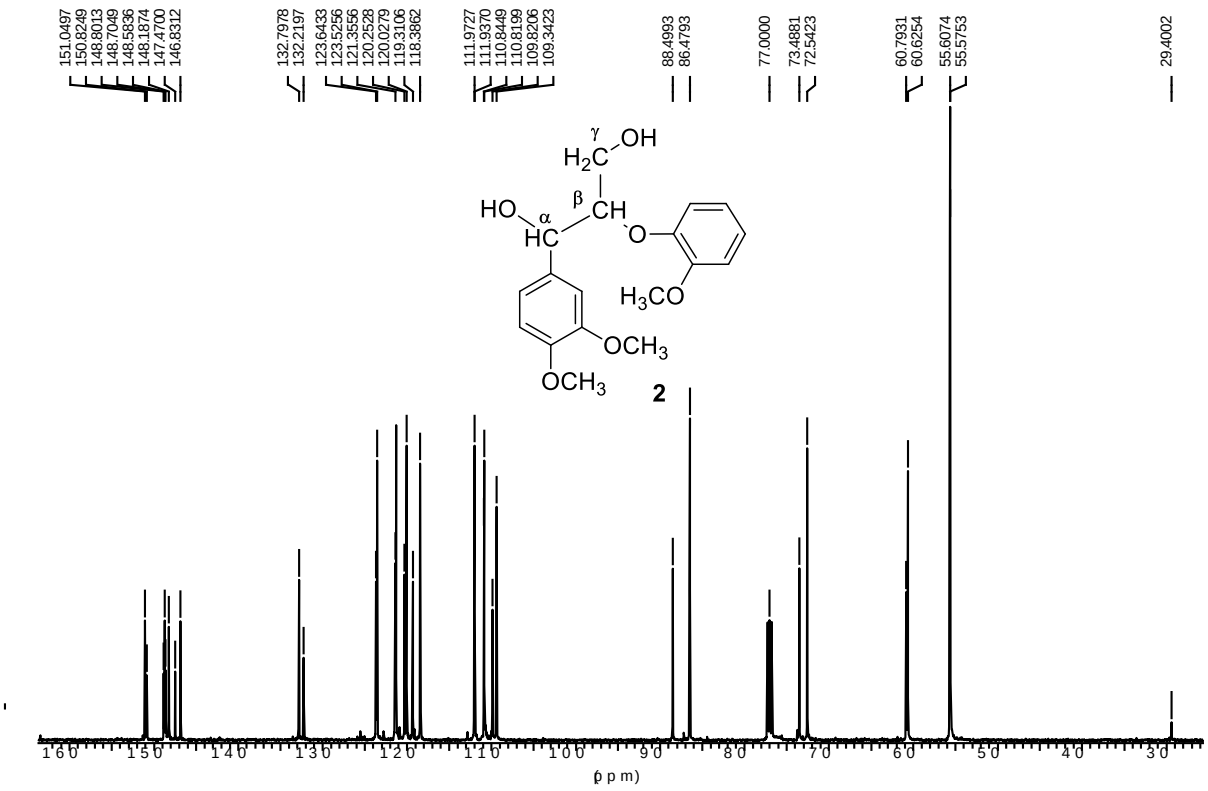


Figure S5 ^{13}C NMR spectrum of compound **2**.

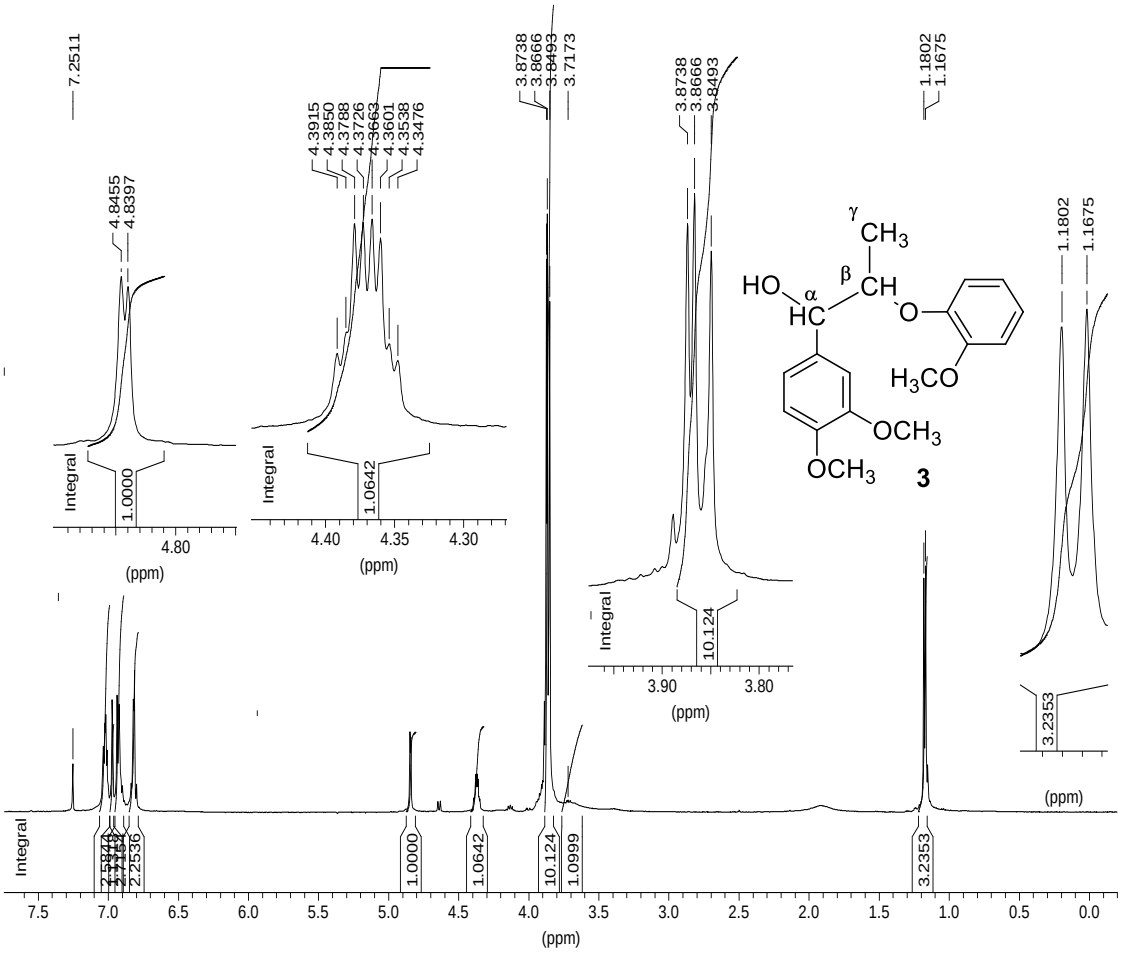


Figure S6 ^{1}H NMR spectrum of compound **3**.

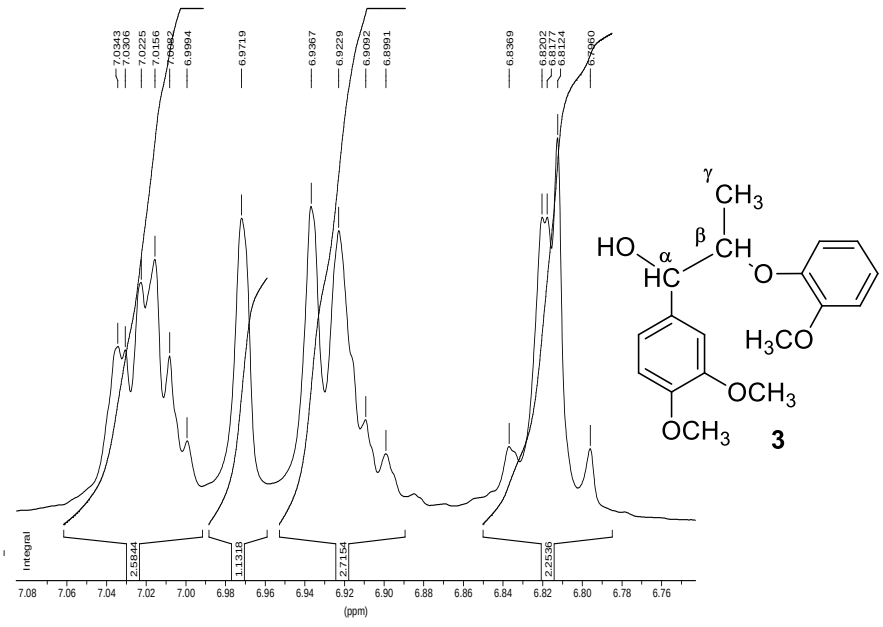


Figure S7 Fragment of ^{1}H NMR spectrum of compound **3**.

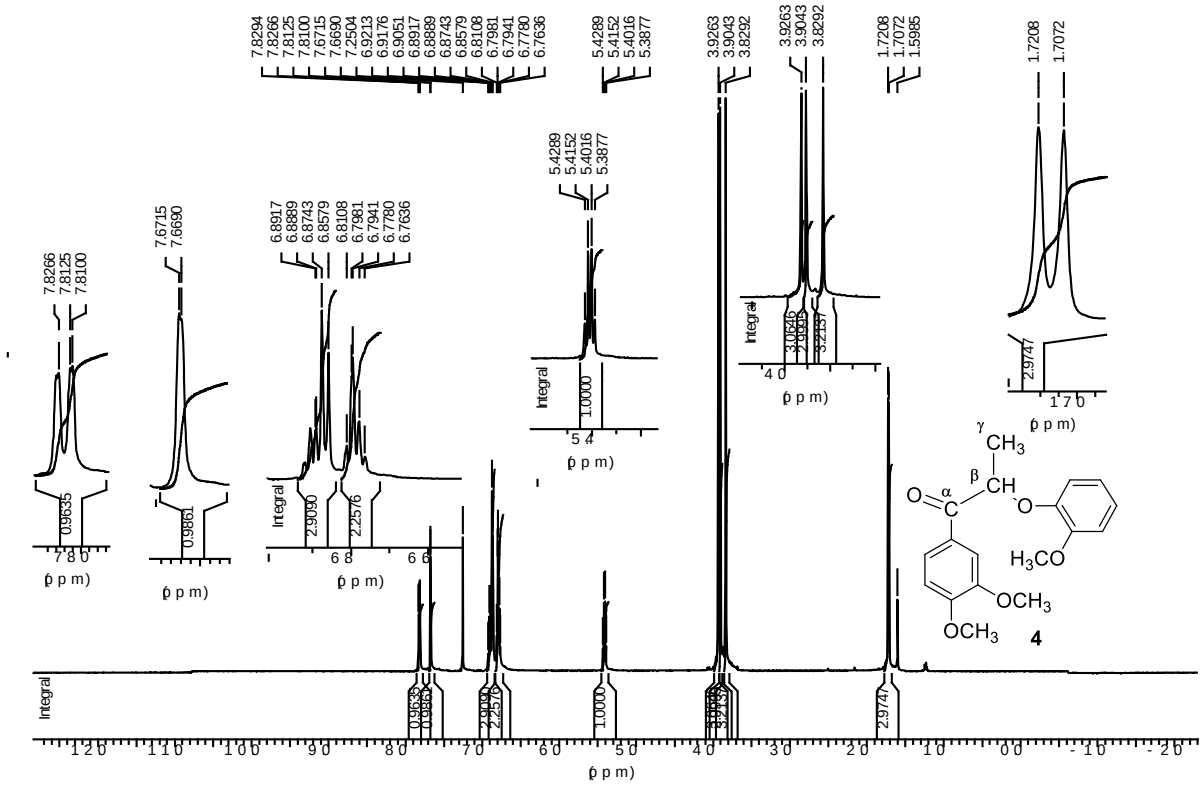


Figure S8 ^{1}H NMR spectrum of compound **4**.

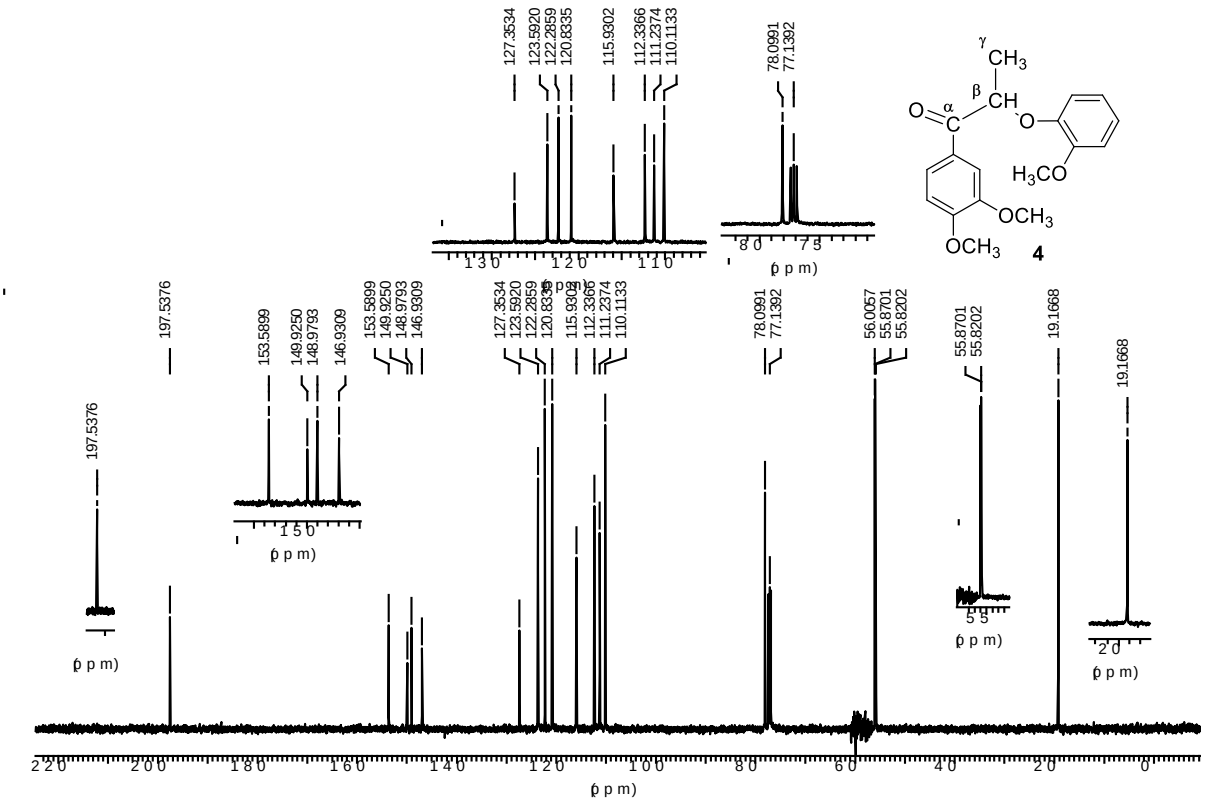


Figure S9 ^{13}C NMR spectrum of compound **4**.

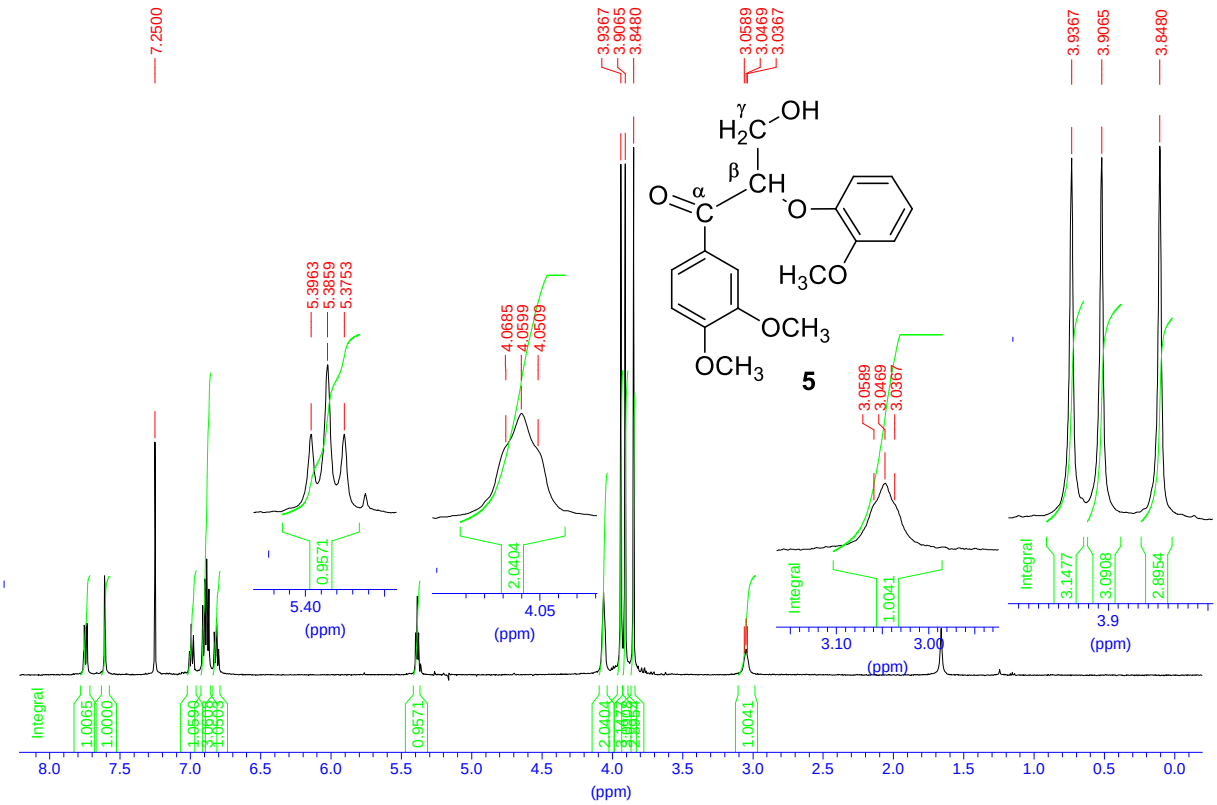


Figure S10 ^{1}H NMR spectrum of compound **5**.

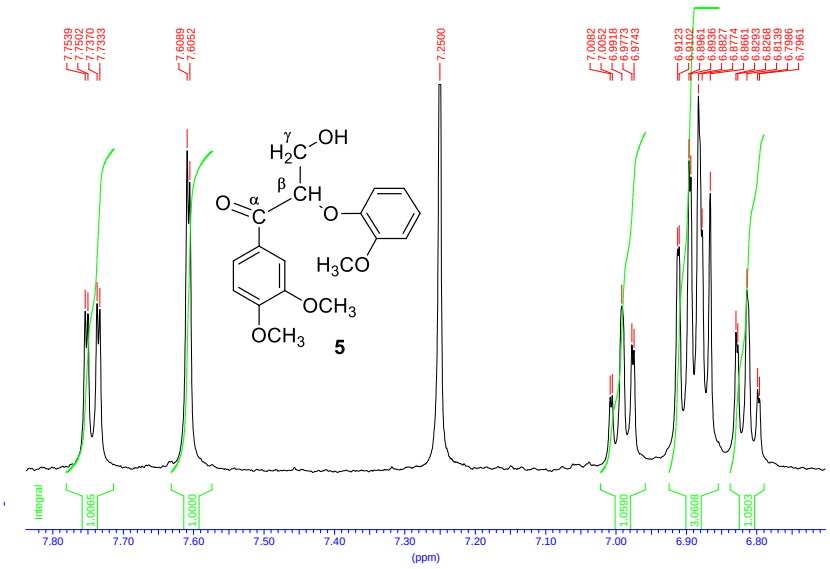


Figure S11 Fragment of ^{1}H NMR spectrum of compound **5**.

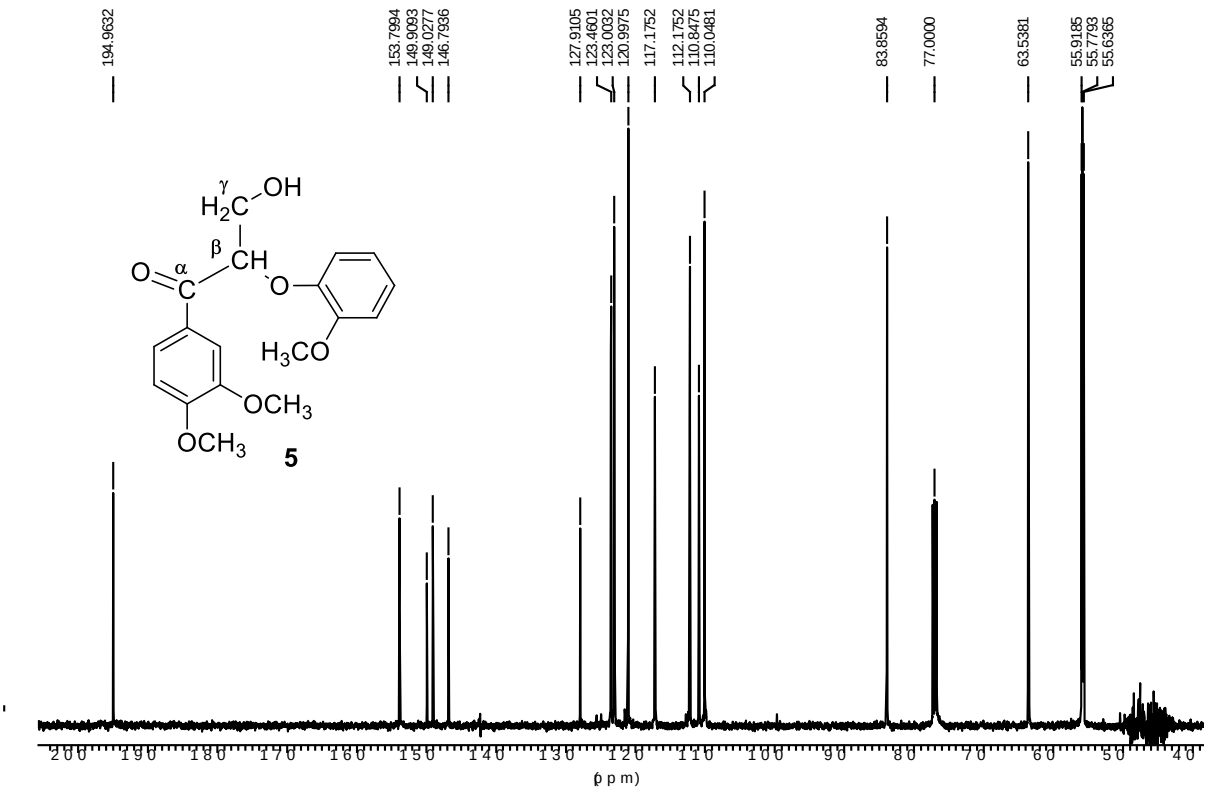


Figure S12 ^{13}C NMR spectrum of compound **5**.

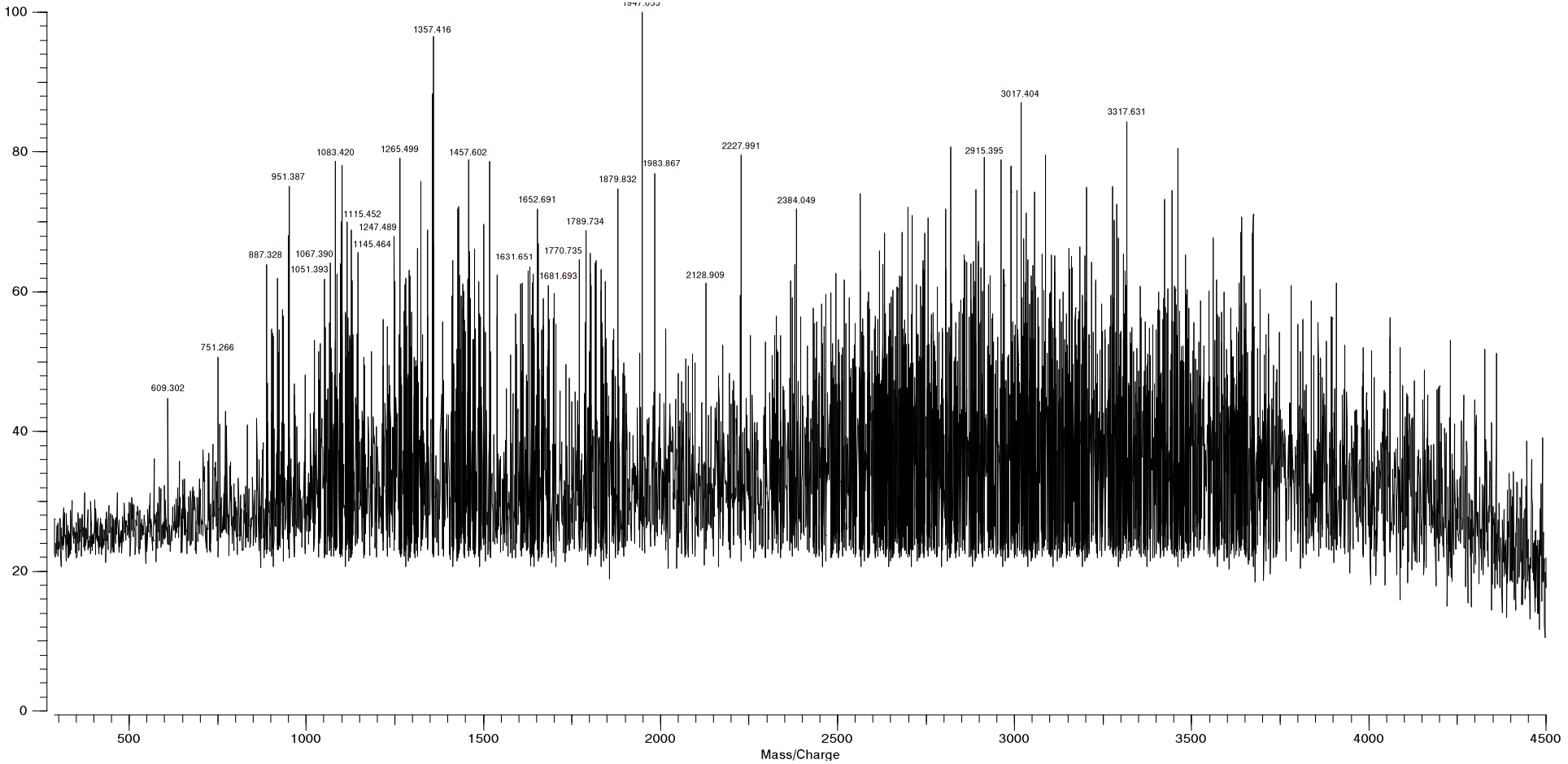


Figure S13 MALDI-MS spectrum of the initial Bjorkman lignin from European spruce (*Picea abies*).

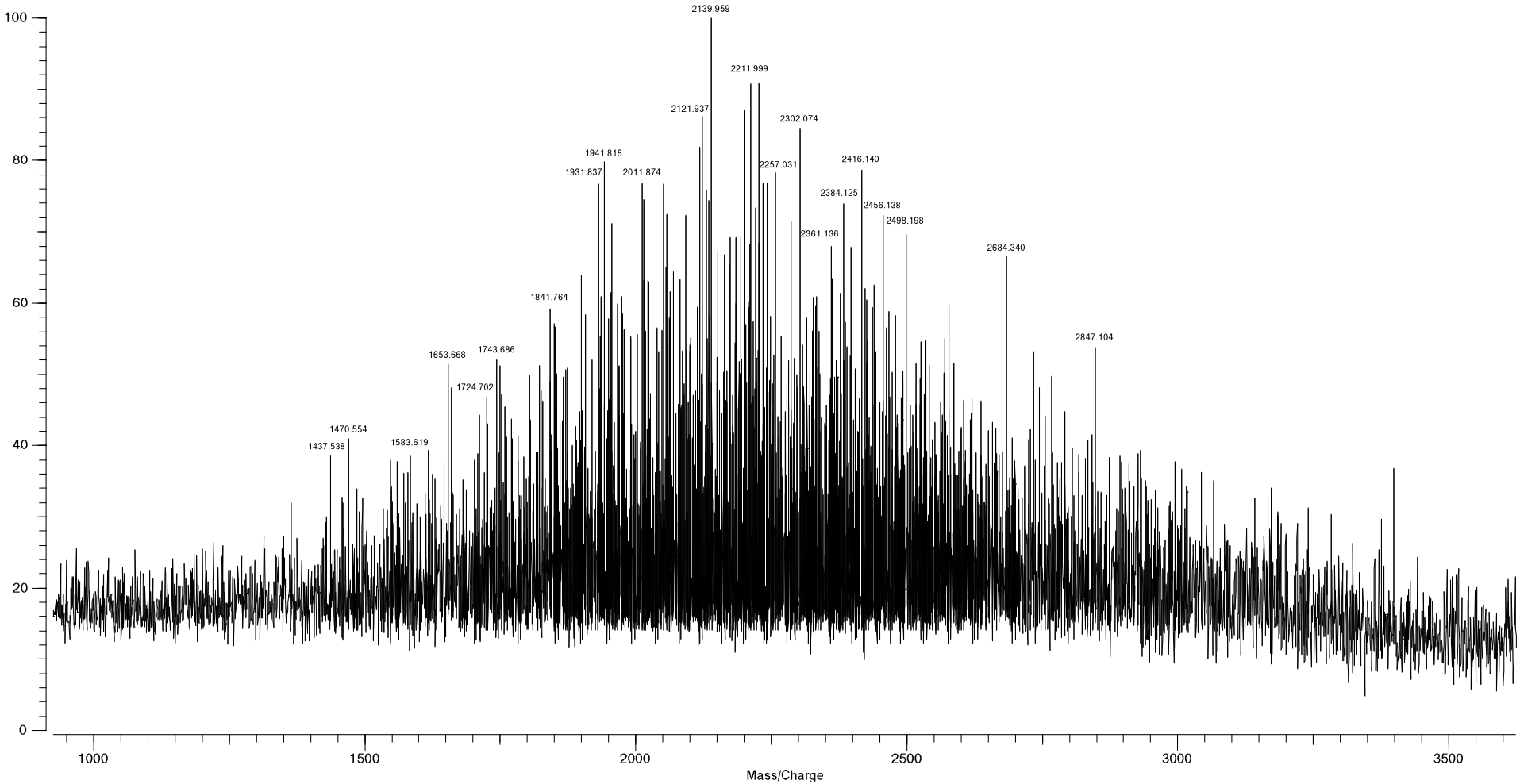


Figure S14 MALDI-MS spectrum of the Bjorkman lignin (*Picea abies*) after the conversion in neat superacid CF_3SO_3H at 20°C for 2 h.

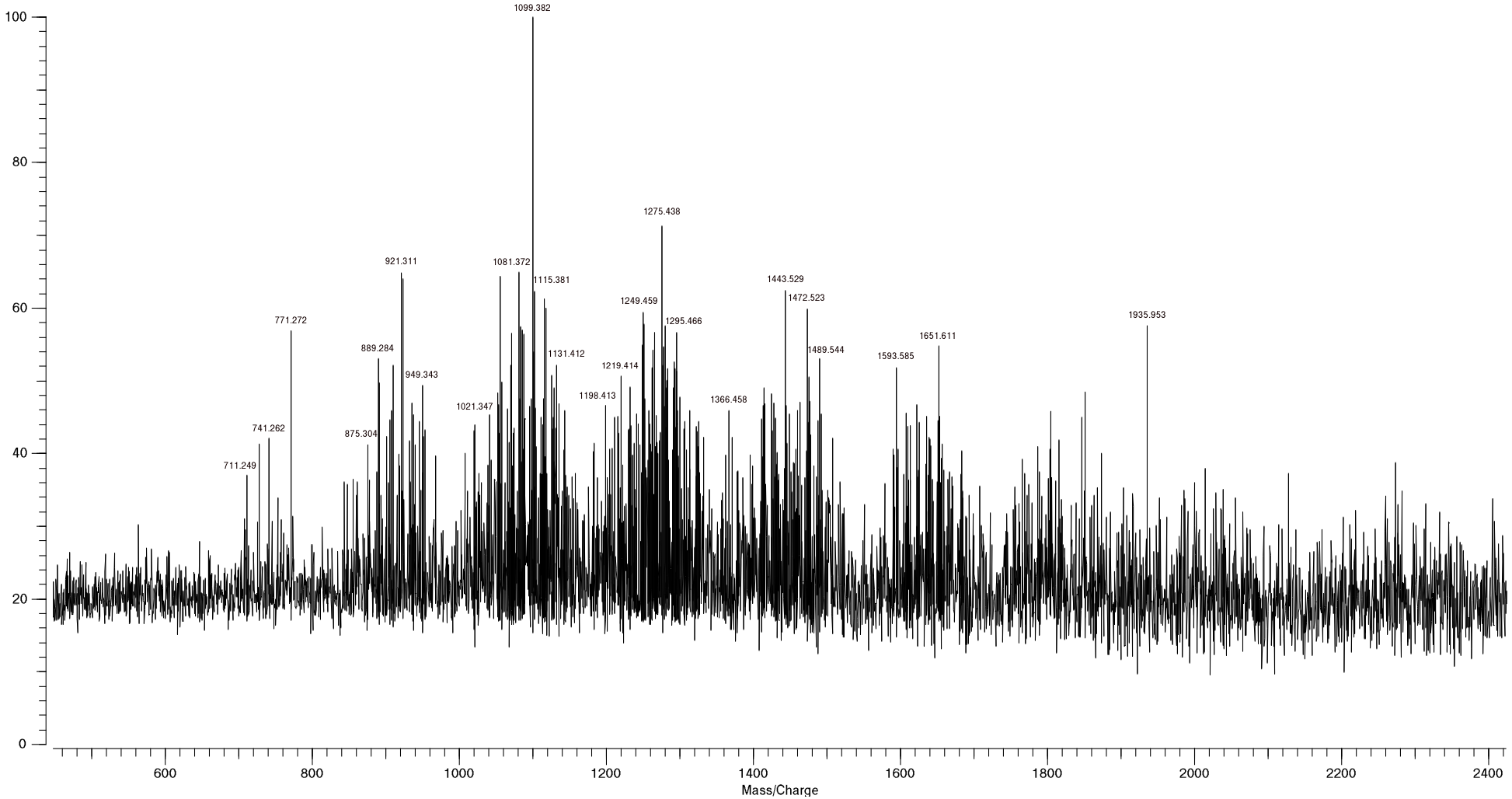


Figure S15 MALDI-MS spectrum of the Bjorkman lignin (*Picea abies*) after the conversion in superacidic system $AlBr_3$-benzene at 20°C for 2 h.

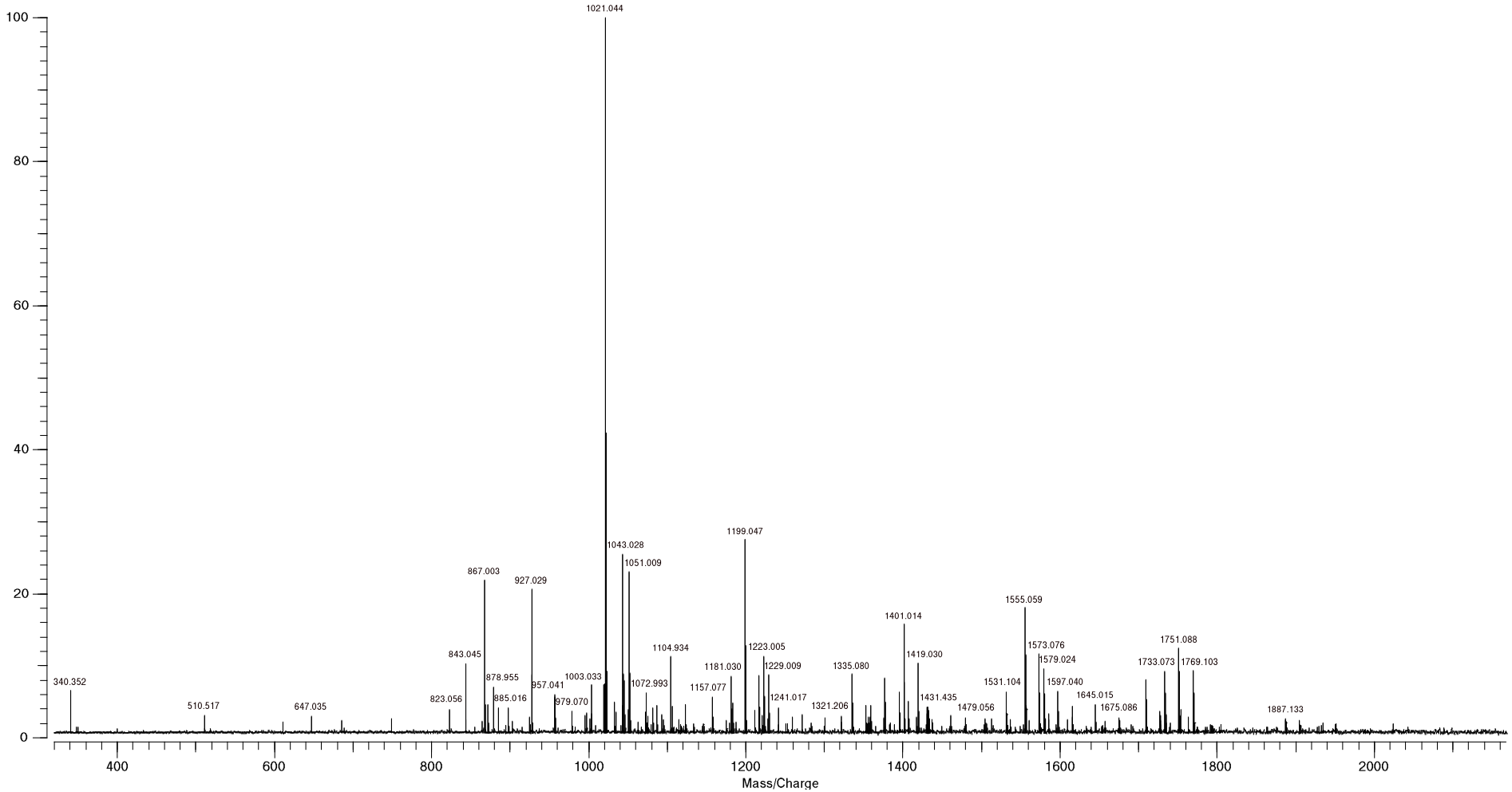


Figure S16 MALDI-MS spectrum of the Bjorkman lignin (*Picea abies*) after the conversion under the action of solid superacidic zeolite CBV-720 at 130°C for 24 h.

7. ^{13}C NMR spectrum of the Bjorkman lignin (Picea abies)

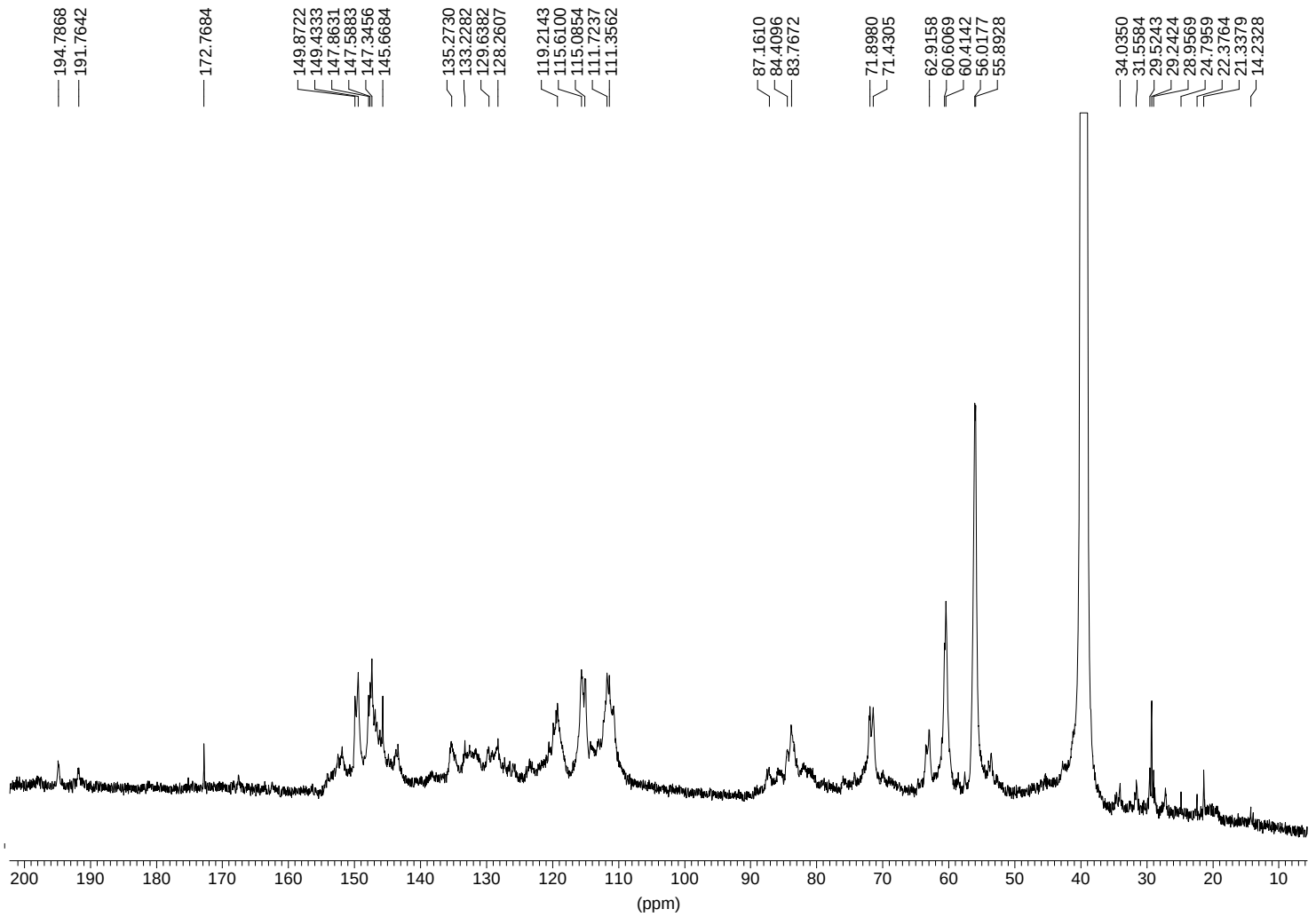


Figure S17 ^{13}C NMR spectrum (DMSO-d_6, 125MHz) from the European Spruce (Picea abies).