

# Catalytic hydroesterification of lignin: A versatile and efficient entry into fully biobased tunable materials

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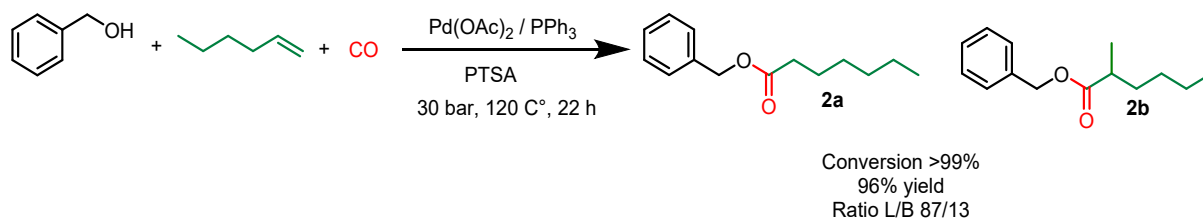
## Supporting information

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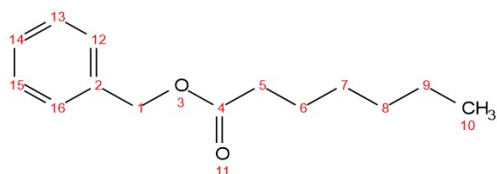
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## Model molecules

### Hydroesterification of 1-hexene with benzyl alcohol



Benzyl alcohol (0.375 mL, 3.6 mmol), palladium acetate (6 mg, 0.027 mmol), triphenylphosphine (175 mg, 0.67 mmol), and paratoluenesulfonic acid (115 mg, 0.67 mmol) were introduced into an autoclave under a nitrogen stream. Distilled and degassed THF (10 mL) and degassed hexene (3 mL, 24 mmol) were added to the autoclave. The autoclave was pressurized with carbon monoxide (30 bar) and kept under stirring at 120 °C for 22 hours. After cooling the reactor to room temperature and release of carbon monoxide, the solvent was evaporated under vacuum, and the crude product was purified by column chromatography on silica using petroleum ether/ethyl acetate mixtures as eluent to afford the desired product in 96% yield. CAUTION: Carbon monoxide is a highly toxic gas and should be handled with extreme care and proper equipment.

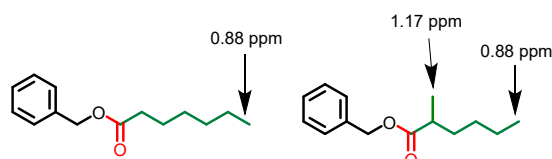


**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.30 (m, 5H, [12-13-14-15-16]), 5.12 (s, 2H, [1a-1b]), 2.36 (t, *J* = 7.5 Hz, 2H, [5a-5b]), 1.65 (p, *J* = 7.7 Hz, 2H, [9a-9b]), 1.37 – 1.21 (m, 6H, [6a-6b-7a-7b-8a-8b]), 0.88 (t, *J* = 5.3 Hz, 3H, [10a-10b-10c]).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 173.8 [4], 136.3 [2], 128.7 [12-16], 128.29 [13-15], 128.27 [14], 66.2 [1], 34.5 [5], 31.6 [8], 28.9 [7], 25.1 [6], 22.6 [9], 14.1 [10].

**HMRS** *m/z*: Calcd for [M+H]<sup>+</sup> C<sub>14</sub>H<sub>21</sub>O<sub>2</sub> 221.15415; Found 221.0836 ( $\Delta m$  = 0.07055 *m/z*).

**General method for determination of L/B ratio** on the hydroesterification of 1-hexene products: Comparison between the integration of the terminal CH<sub>3</sub> of both isomers (at 0.88 ppm) and the CH<sub>3</sub> of the branched compound (at 1.17 ppm) on <sup>1</sup>H NMR spectrum. See example in figure SI 1. **Ratio L/B: 87/13**



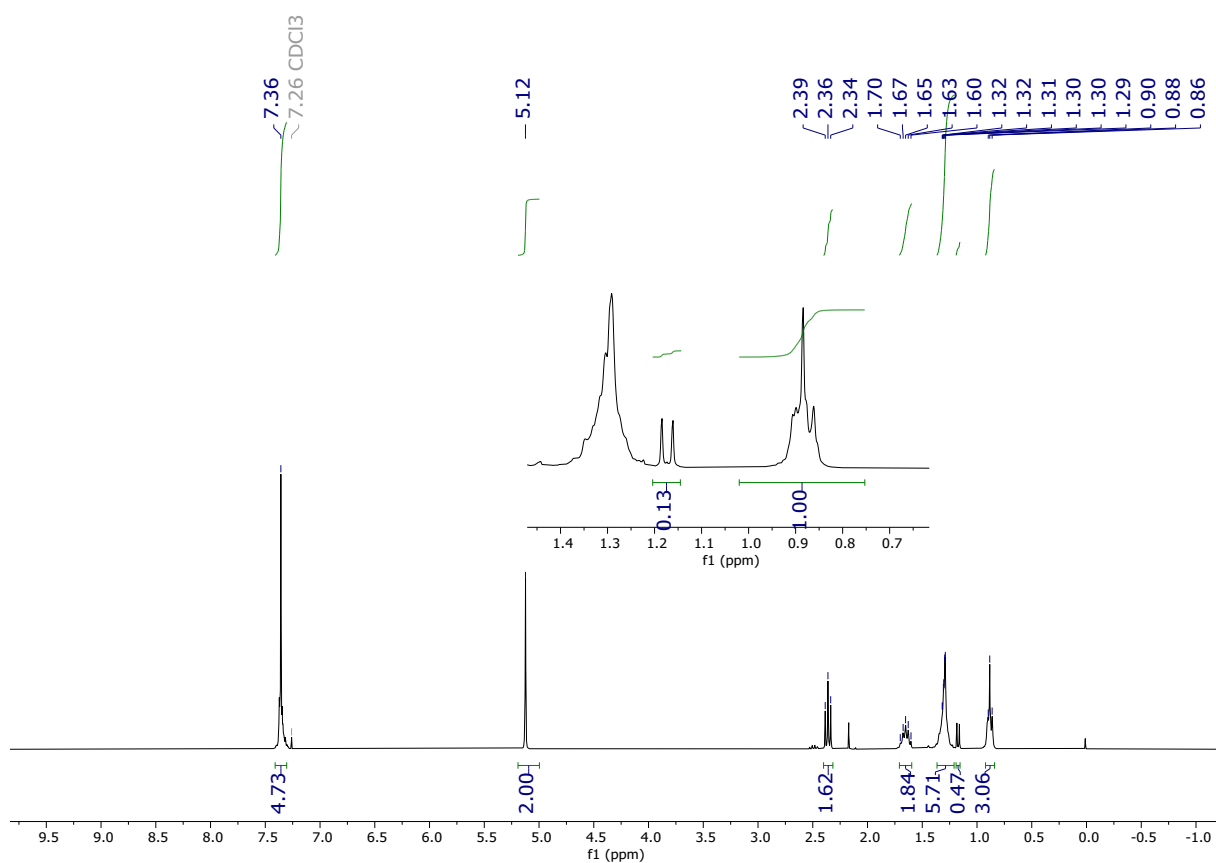


Figure SI 1:  $^1\text{H}$  NMR spectrum of the compound **2a + 2b** in  $\text{CDCl}_3$ .

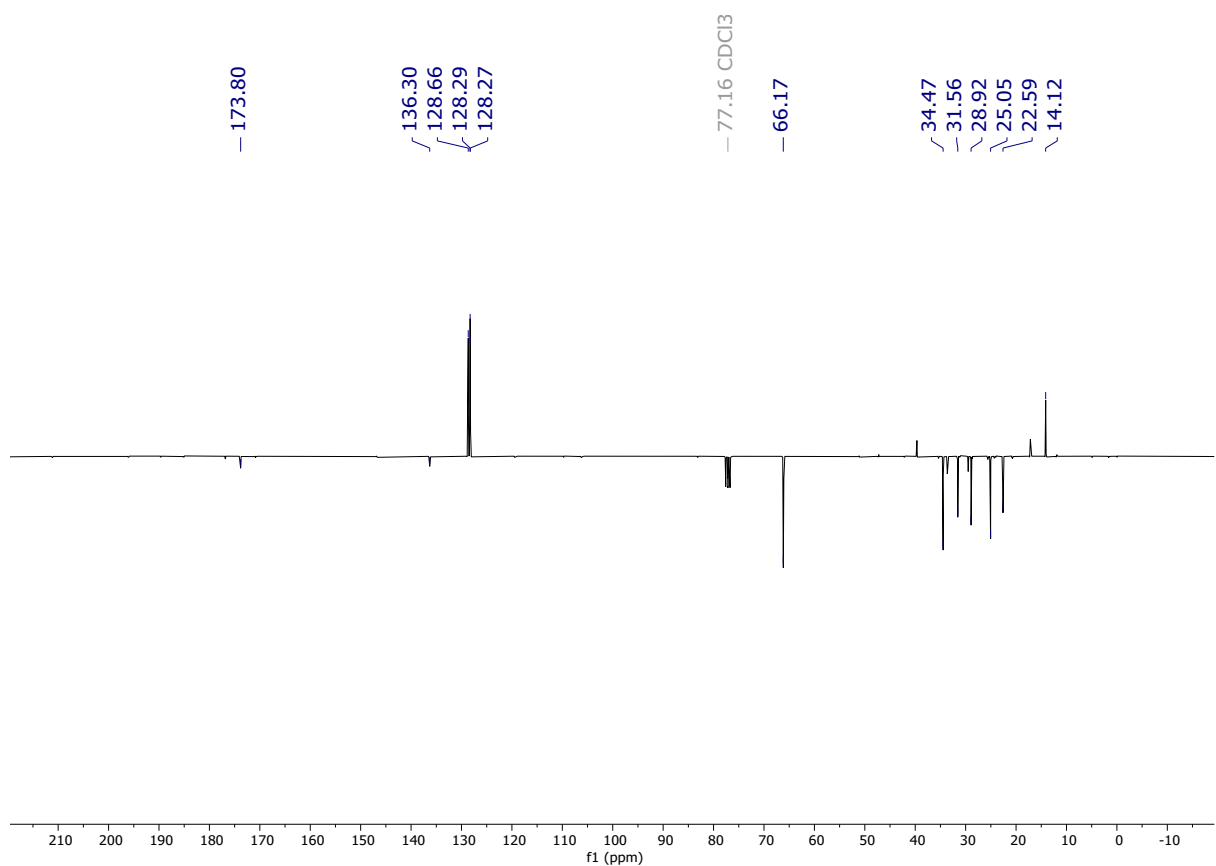
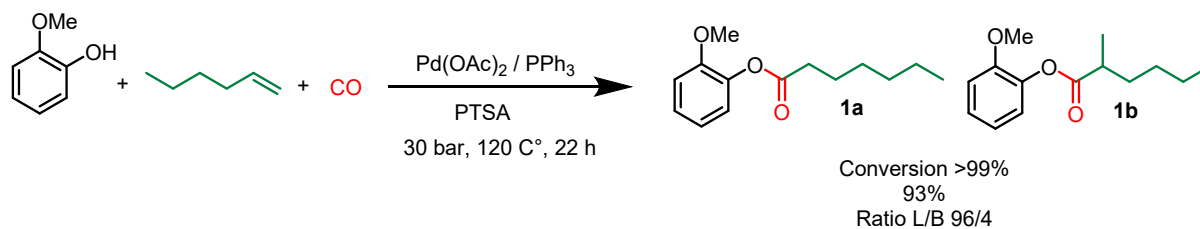
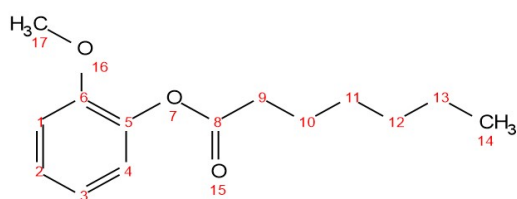


Figure SI 2:  $^{13}\text{C}$  NMR spectrum of the compound **2a + 2b** in  $\text{CDCl}_3$ .

### Hydroesterification of 1-hexene with Guaiacol



This product was synthesized using the same procedure as the one used for the synthesis of compound **1** with benzyl alcohol and was obtained in (93% yield).



$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 – 7.15 (m, 1H, [1]), 7.06 – 6.90 (m, 3H, [2-3-4]), 3.82 (s, 3H, [17a-17b-17c]), 2.59 (t,  $J = 7.5$  Hz, 2H, [9a-9b]), 1.78 (p,  $J = 7.2$  Hz, 2H, [13a-13b]), 1.49 – 1.25 (m, 6H, [10a-10b-11a-11b-12a-12b]), 0.92 (t,  $J = 6.8$  Hz, 3H, [14a-14b-14c]).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.0 [8], 151.3 [6], 140.0 [5], 126.9 [2], 123.0 [3], 120.9 [4], 112.5 [1], 55.9 [17], 34.2 [9], 31.6 [12], 28.9 [11], 25.1 [10], 22.7 [13], 14.16 [14].

HMRS  $m/z$ : Calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{14}\text{H}_{21}\text{O}_3$  237.14907; Found 237.1481 ( $\Delta m = 0.001$   $m/z$ ).

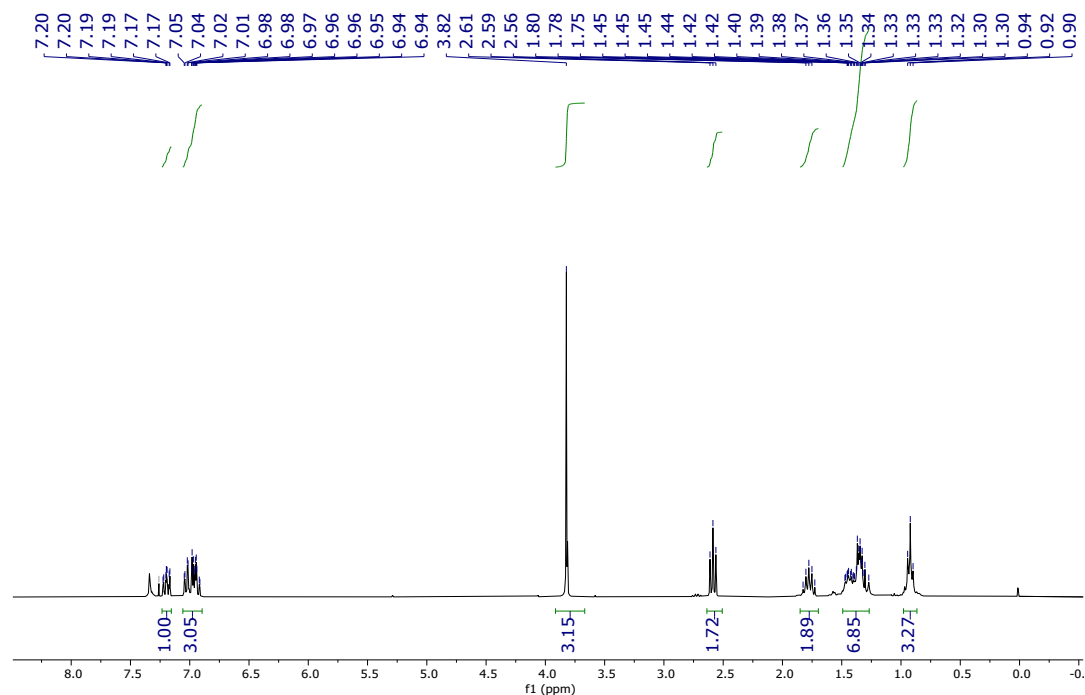
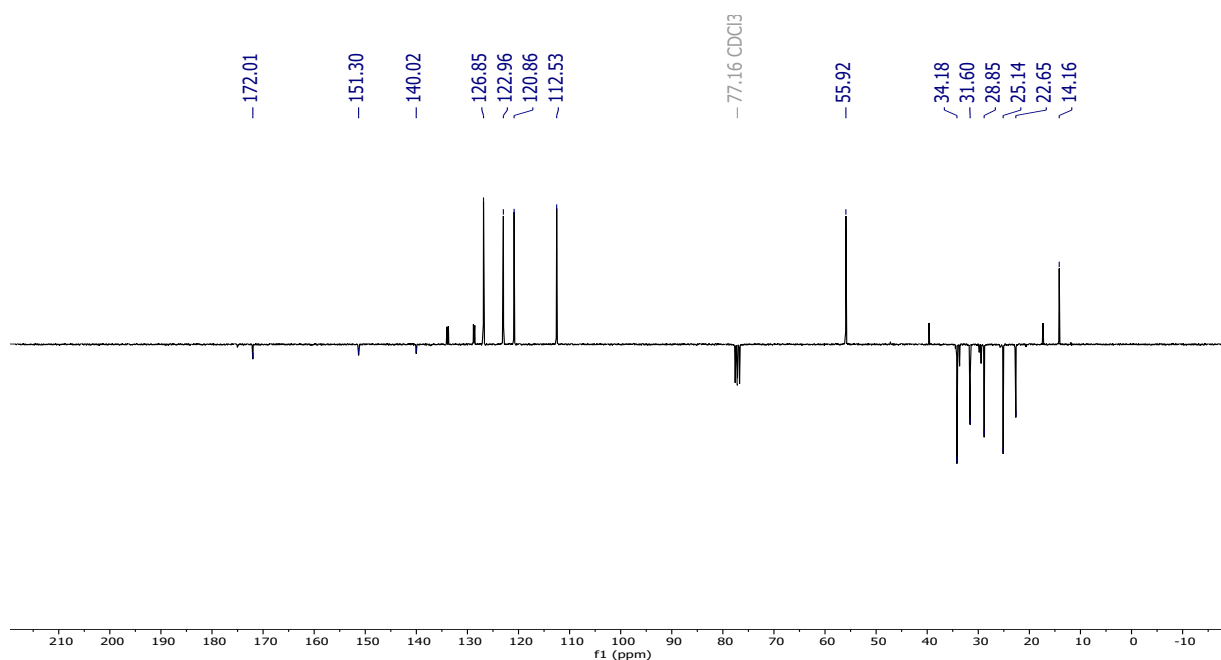
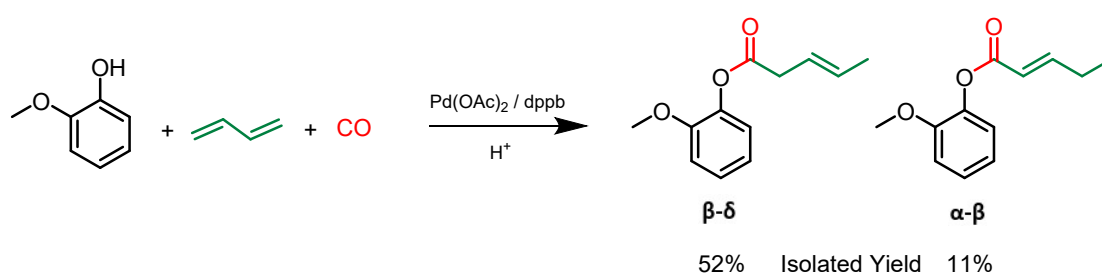


Figure SI 3:  $^1\text{H NMR}$  spectrum of the compound **1a + 1b** in  $\text{CDCl}_3$ .

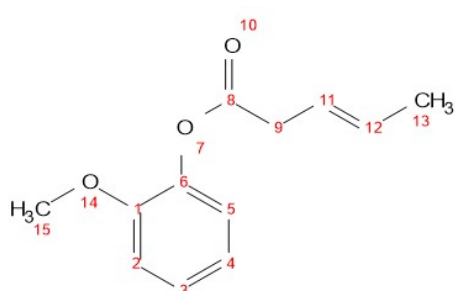


**Figure SI 4:**  $^{13}\text{C}$  NMR spectrum of the compound **1a + 1b** in  $\text{CDCl}_3$

### Hydroesterification of butadiene with guaiacol



An autoclave was charged with palladium acetate (20 mg, 0.09 mmol), 1,4-bis(diphenylphosphino)butane (230 mg, 0.54 mmol) and benzoic acid (330 mg, 2.7 mmol). After performing three vacuum/ $\text{N}_2$  cycles, dry THF (3 mL) and degassed guaiacol (1 mL, 9 mmol) were added to the autoclave. The reactor was cooled to  $-40^\circ\text{C}$ , and then (6 mL, 3.6g, 66 mmol) of butadiene was condensed in a Schlenk tube at  $-40$  and added to the reaction mixture *via* a cannula. The autoclave was pressurized with 25 bar of carbon monoxide and heated at  $120^\circ\text{C}$  for 24 h. After cooling, the excess gas was evacuated, the solvent was evaporated and the crude was purified on silica gel chromatographic column (95/5, petroleum ether/ethyl acetate). Two isomers have been isolated, 2-methoxyphenyl-pent-3-enoate ( $\beta\text{-}\delta$ ) in 52% yield and 2-methoxyphenyl-pent-2-enoate ( $\alpha\text{-}\beta$ ) in 11% yield. CAUTION: Carbon monoxide is a highly toxic gas and should be handled with extreme care and proper equipment.



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.12 (m, 1H, [2]), 7.10 – 6.90 (m, 3H, [3-4-5]), 5.72 – 5.64 (m, 2H, [11-12]), 3.82 (s, 3H, [15a-15b-15c]), 3.32 – 3.28 (m, 2H, [9a-9b]), 1.78 – 1.70 (m, 3H, [13a-13b-13c]).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0 [8], 151.0 [6], 139.7 [1], 129.6 [11], 126.7 [3], 122.7 [12], 122.3 [4], 120.6 [5], 112.3 [2], 55.6 [15], 37.5 [9], 17.9 [3].

HMRS  $m/z$ : Calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{12}\text{H}_{15}\text{O}_3$  207,1021; Found 207,1020, ( $\Delta m = 0,0001$   $m/z$ ).

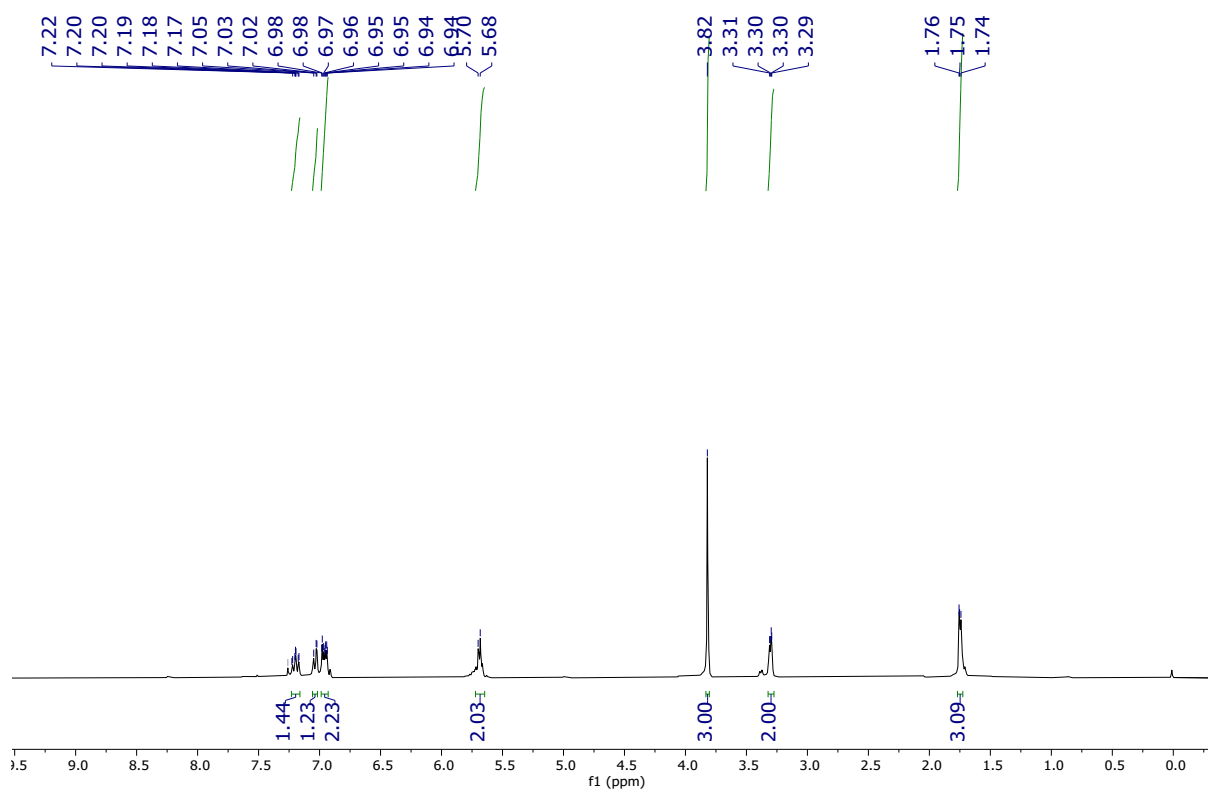
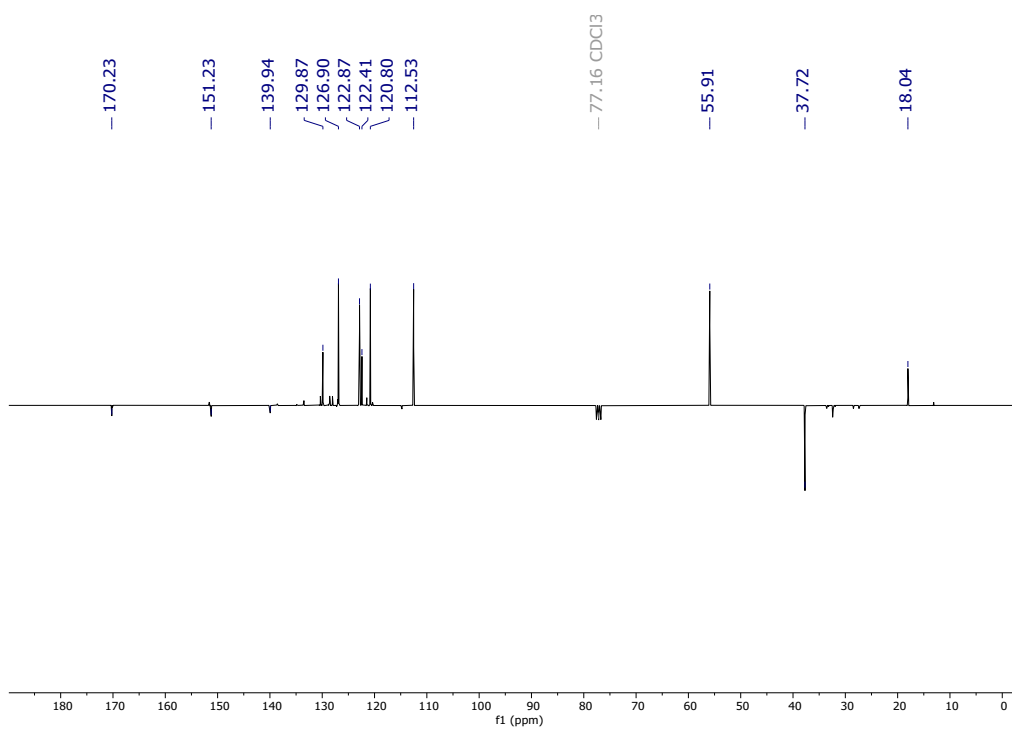
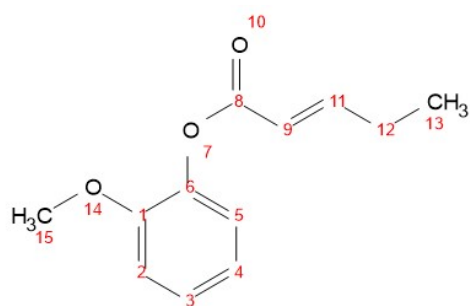


Figure SI 5:  $^1\text{H}$  NMR spectrum of the compound  $\beta$ - $\delta$  in  $\text{CDCl}_3$ .



**Figure SI 6:**  $^{13}\text{C}$  NMR spectrum of the compound  $\beta\text{-}\delta$  in  $\text{CDCl}_3$ .

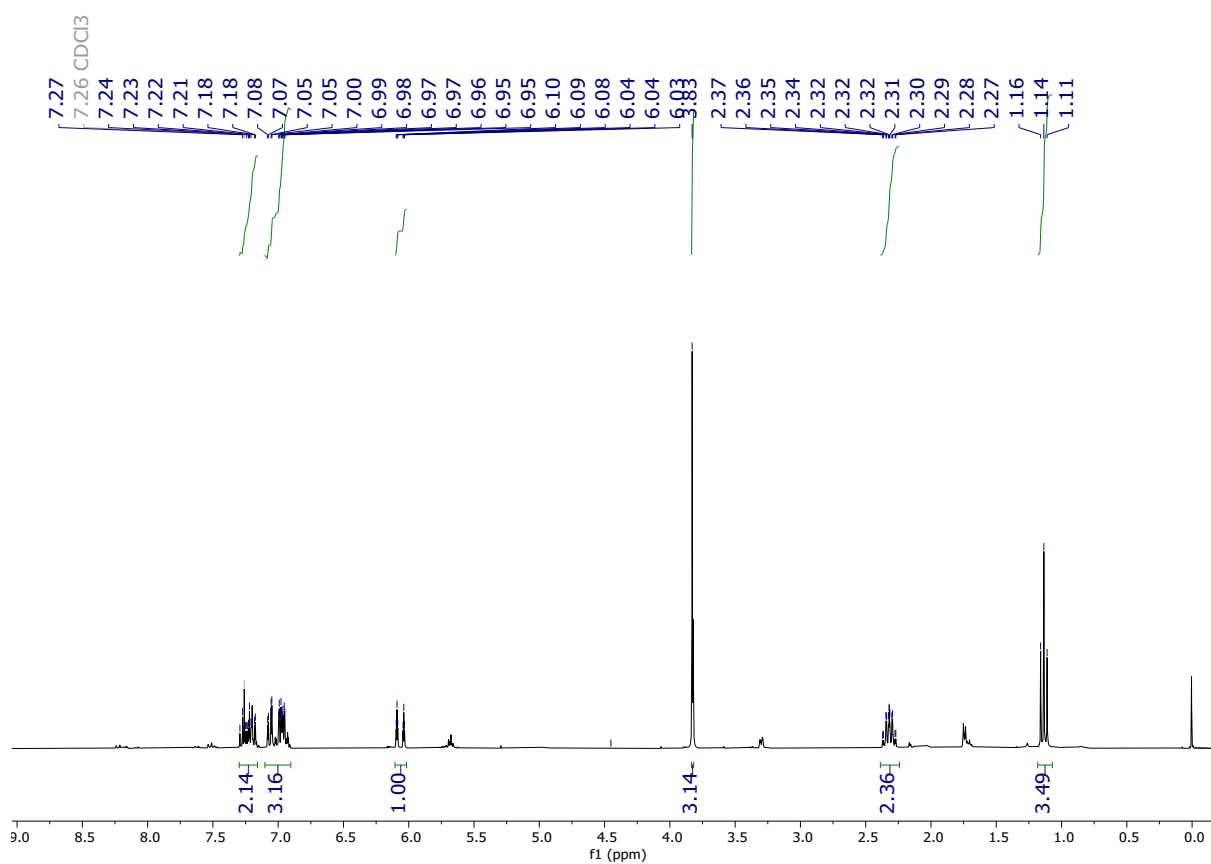


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.16 (m, 2H, [4-5]), 7.10 – 6.90 (m, 3H [2-3-11]), 6.06 (dt,  $J = 15.7, 1.7$  Hz, 1H, [9]), 3.83 (s, 3H, [15]), 2.39 – 2.24 (m, 2H, [12]), 1.14 (t,  $J = 7.4$  Hz, 3H, [13]).

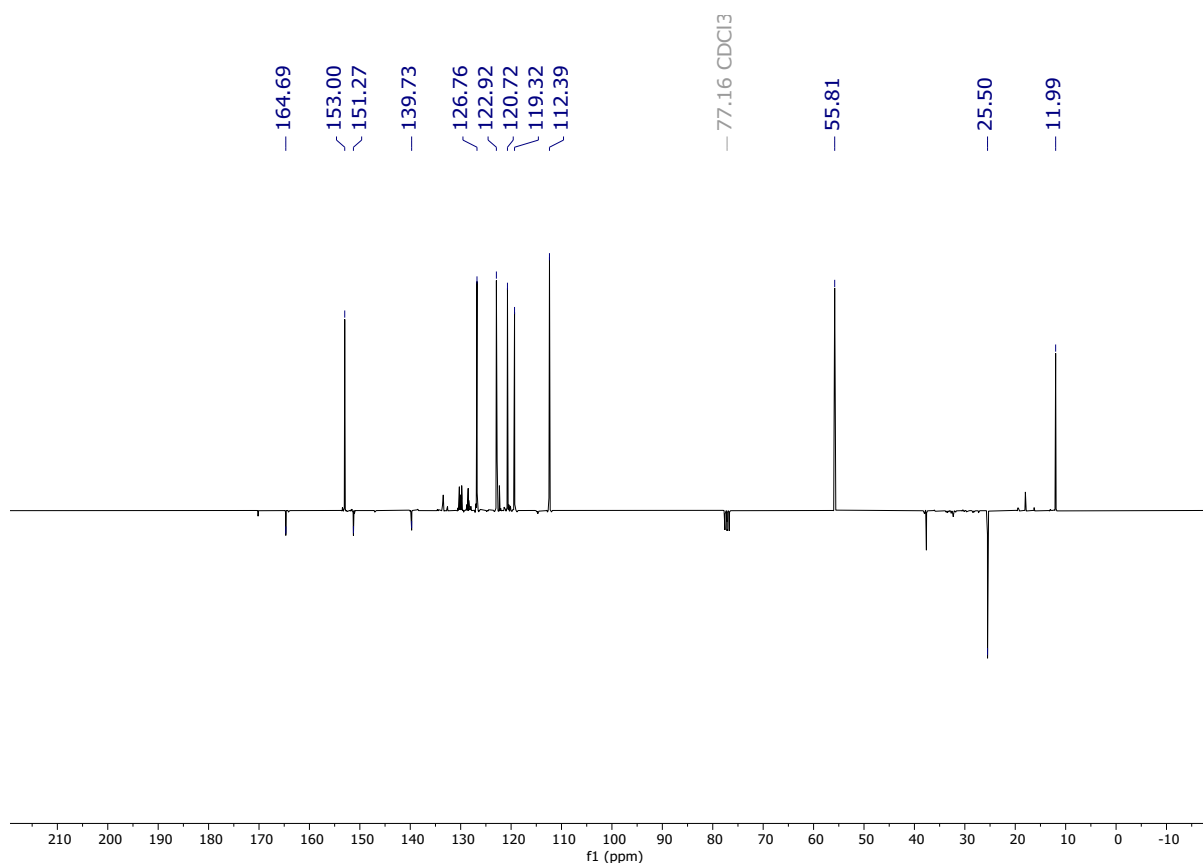
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  164.69 [8] 153.00 [10], 151.27 [6], 139.37 [5], 126.76 [2], 122.92 [3], 120.72 [4], 119.32 [9], 112.39 [1], 55.81 [15], 25.50 [11], 11.99 [12].

HMRS  $m/z$ : Calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{12}\text{H}_{15}\text{O}_3$  207,1021; Found 207,1020,

( $\Delta m = 0,0001$   $m/z$ ).



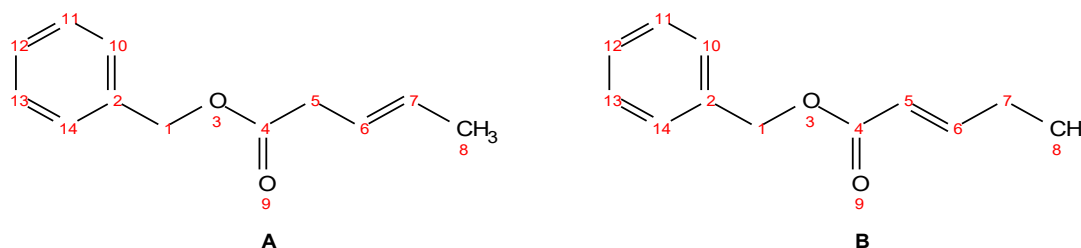
**Figure SI 7:**  $^1\text{H}$  NMR spectrum of the compound  $\alpha\text{-}\beta$  in  $\text{CDCl}_3$ .



**Figure SI 8:**  $^{13}\text{C}$  NMR spectrum of the compound  $\alpha\text{-}\beta$  in  $\text{CDCl}_3$ .

**Model molecule synthesis (benzyl alcohol hydroesterification with butadiene)**

An autoclave was charged with palladium acetate (20 mg, 0.09 mmol), 1,4-bis(diphenylphosphino)butane (230 mg, 0.54 mmol) and benzoic acid (330 mg, 2.7 mmol). After performing three vacuum/ $\text{N}_2$  cycles, dry THF (3 mL) and degassed benzyl alcohol (1 mL, 9 mmol) were added to the autoclave. The reactor was cooled to  $-40^\circ\text{C}$ , and then (6 mL, 3.6g, 66 mmol) of butadiene was condensed in a Schlenk tube at  $-40$  and added to the reaction mixture *via* a cannula. The autoclave was pressurized with 25 bar of carbon monoxide and heated at  $120^\circ\text{C}$  for 24 h. After cooling, the excess gas was evacuated, the solvent was evaporated and the crude was purified on silica gel chromatographic column (95/5, petroleum ether/ethyl acetate). A mixture of two isomers A and B was obtained in **94% yield with ratio of 60% A and 40% B**. CAUTION: Carbon monoxide is a highly toxic gas and should be handled with extreme care and proper equipment.



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.29 (m, 5H, [10-11-12-13-14, A and B]), 7.08 (dt,  $J$  = 15.7, 6.3 Hz, 1H, [6, A]), 5.93- 5.83 (m, 1H, [5, B]), 5.62 – 5.52 (m, 2H, [6-7, A]), 5.18 (s, 2H, [1, B]), 5.13 (s, 2H, [1, A]), 3.20 – 3.00 (m, 2H, [5, A]), 2.30 – 2.18 (m, 2H, [7, B]), 1.72 – 1.68 (m, 3H, [8, A]), 1.07 (t,  $J$  = 7.4 Hz, 3H, [8, B]).



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 172.02 [4, A], 166.62 [4, B] 151.37 [6, B], 136.22 [2, A], 136.0 [2, B], 129.55 [6, A], 128.55 [10-14, A], 128.21 [11-13, B], 128.15 [12, A+B], 122.62 [7, A], 120.11 [5, B], 66.35 [1, A], 66.01 [1, B], 38.04 [5, A], 25.34 [7, B] 17.92 [8, A], 12.11 [8, B].

HMRS m/z: Calcd for [M+H]<sup>+</sup> C<sub>12</sub>H<sub>15</sub>O<sub>2</sub> 191,1072; Found 191,1068, (Δm = 0,0004 m/z).

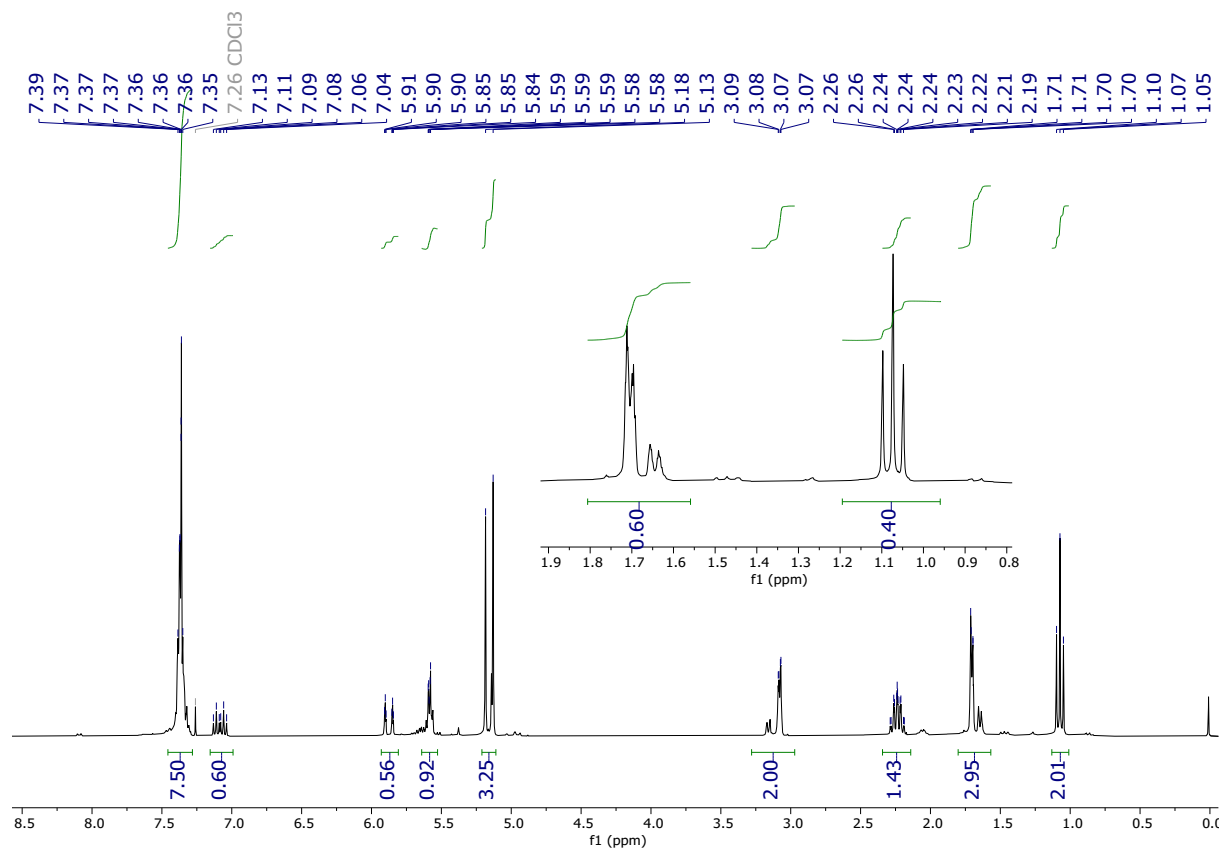
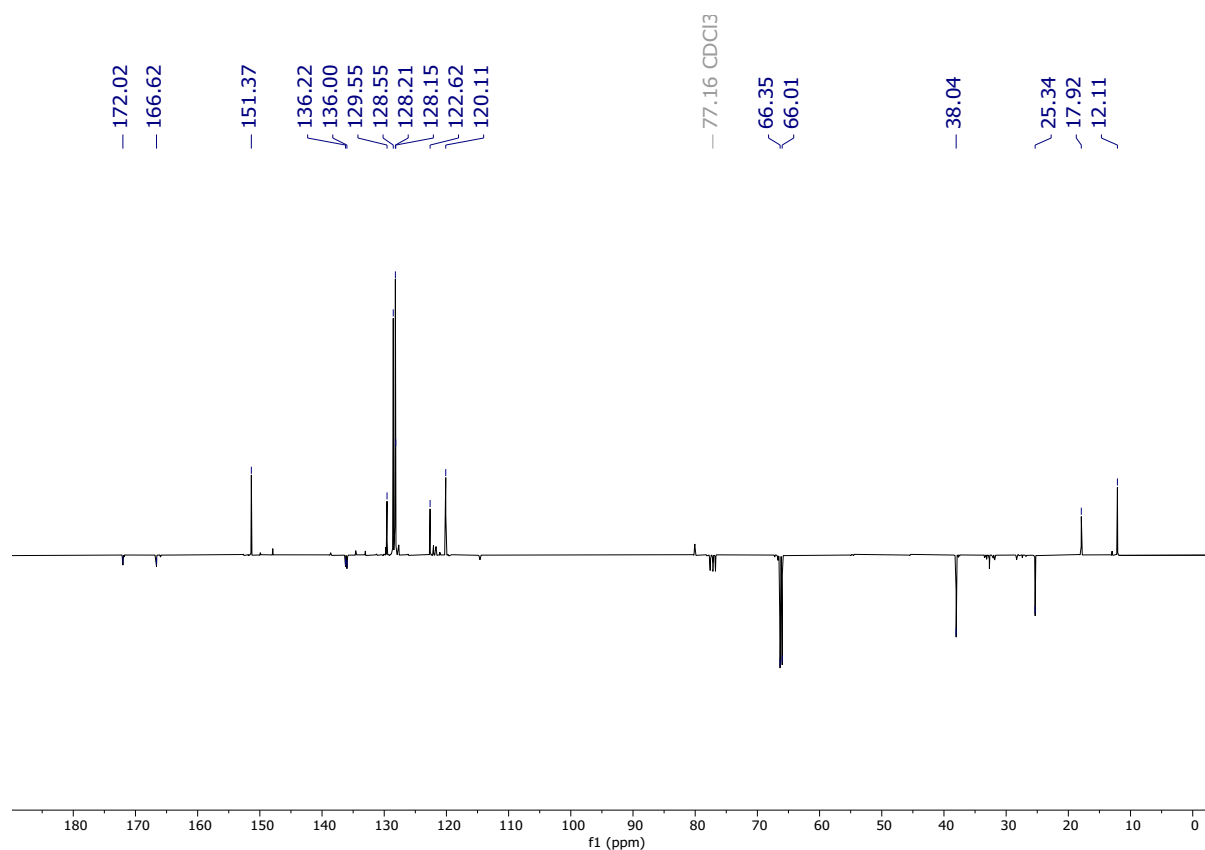


Figure SI 9: <sup>1</sup>H NMR spectrum of the compound A + B 60/40 ratio in CDCl<sub>3</sub>.



**Figure SI 10:**  $^{13}\text{C}$  NMR spectrum of the compound **A + B** in  $\text{CDCl}_3$ .

**Table SI 1: Supplementary experiments of Table 1 – Optimization of the palladium catalyzed hydroesterification of 1-hexene with lignin**

| Entry               | $\text{Pd}(\text{OAc})_2$ (Eq/OH) | $\text{PPh}_3$ (eq/Pd) | PTSA (eq/Pd) | T ( $^\circ\text{C}$ ) | THF (mL) | t (h) | Conv <sup>[a]</sup><br>OH <sup>total</sup> | %W <sup>[b]</sup> |
|---------------------|-----------------------------------|------------------------|--------------|------------------------|----------|-------|--|-------------------|
| 1                   | 1 %                               | 11                     | 25           | 120                    | 10       | 22 h  | 9 %  | 52 %              |
| 2                   | 1 %                               | 15                     | 25           | 120                    | 10       | 22 h  | 9 %  | 52 %              |
| 3                   | 1 %                               | 25                     | 25           | 120                    | 5        | 22 h  | 42 %                                       | 58 %              |
| 4                   | 1 %                               | 25                     | 25           | 120                    | 20       | 22 h  | 56 %                                       | 35 %              |
| 5 <sup>[c]</sup>    | 2 %                               | 13                     | 13           | 120                    | 10       | 22 h  | 57 %                                       | 96 %              |
| 6 <sup>[c]</sup>    | 2 %                               | 13                     | 13           | 120                    | 10       | 48 h  | 59 %                                       | 81 %              |
| 7 <sup>[c][d]</sup> | 2 %                               | 13                     | 13           | 120                    | 10       | 22 h  | 60 %                                       | 74 %              |

Conditions: 0.5g of Kraft lignin, 8 eq/OH of 1-hexene, 30 bars of CO a) by  $^1\text{H}$  NMR with pentafluorobenzaldehyde as internal standard: Conversion of total OH groups - comparison of the amount of chains grafted onto the lignin with the quantity of available hydroxyl groups. b) Weight of lignin recovered in proportion to the amount of starting lignin. c) reaction with 3 eq/OH of 1-hexene d) reaction with 10 bars of CO

Reducing the amount of  $\text{PPh}_3$  considerably decreases the substitution degree of the hydroxyl groups. 61% of lignin's hydroxyl groups were converted with 25 equivalents of  $\text{PPh}_3$  and this value was reduced to 9% with 11 or 15 equivalents of phosphine (entries **1** and **2**). The large amount of ligand required for the reaction can be explained by the oxidation and sulphidation of phosphine caused by impurities present in the kraft lignin as this

has been previously demonstrated in the case of the telomerization reaction with the same material.<sup>1</sup> It is elsewhere known that the presence of large quantities of strong acid is responsible of phosphine protonation, thus limiting the availability of the ligand to coordinate the metal.

### **<sup>31</sup>P NMR spectrum of technical lignins (Kraft, Organosolv, Soda) and modified lignins.**

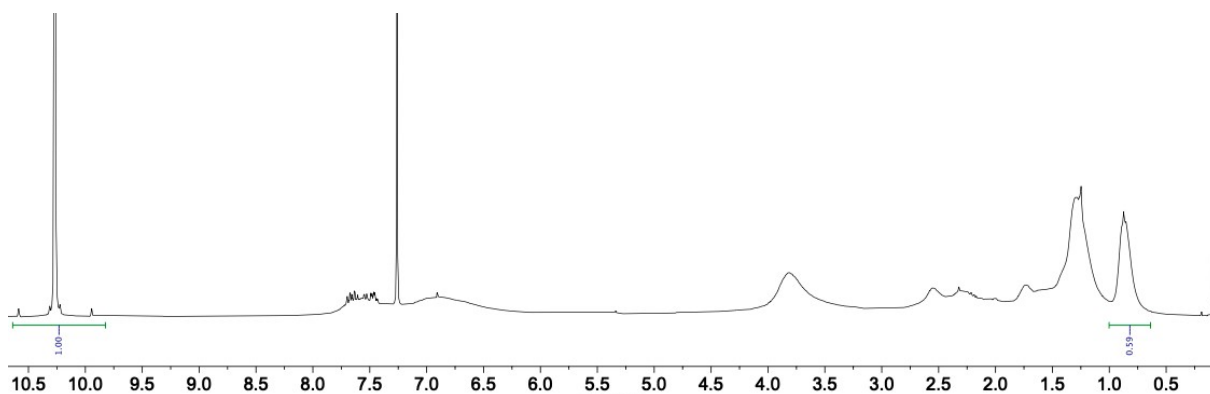
<sup>31</sup>P NMR experiments method: Lignin (30 mg) was dissolved in a CDCl<sub>3</sub> / Pyridine mixture (1:1.6 v/v, 0,5 mL). The phosphitylation reagent, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (150 μL), and the internal standard N-hydroxy-6-norbornene-2,3-dicarboximide (100 μL of 0.1 M solution in 1:1.6 v/v CDCl<sub>3</sub> / Pyridine mixture) were added successively. Chromium(III) acetylacetonate (100 μL of 0.014M solution) in the same CDCl<sub>3</sub> / Pyridine mixture was added to the solution in order to homogenize and accelerate phosphorus relaxation. Spectra were recorded with a 15 sec relaxation time and an average number of 512 scans. Chemical shifts are relative to the signal of the phospholane hydrolysis product at 132.2 ppm. The integrated value of the internal standard was used for calculation of the absolute amount of each functional group. This method includes a correction factor for integrations of modified lignins considering the reduced lignin content.

### **Correction factor calculation in <sup>31</sup>P NMR**

The calculation of this coefficient is performed by calculating the mass of initial lignin in the final product by the calculation of the esters weight added.

$$\% \text{ lignin weight} = 1 - \left( \frac{n_{\text{esters/g}}}{M_{\text{esters}}} \right)$$

The mole content of esters per gram of lignin is determined by <sup>1</sup>H NMR using pentafluorobenzaldehyde as internal standard.



$$n_{\text{esters/g}} = \frac{n_{\text{PFB}} \times I_{\text{CH}_3}}{3}$$

<sup>1</sup> C. Dumont, R. M. Gauvin, F. Belva and M. Sauthier, *ChemSusChem*, 2018, **11**, 1649–1655.

$\%_{\text{ligninweight}}$ : mass percentage of lignin in the product after hydroesterification

$n_{\text{esters/g}}$ : number of moles of esters per gram of product after hydroesterification

$M_{\text{esters}}$ : molar mass of the atoms added through the hydroesterification (depends on the olefin used)

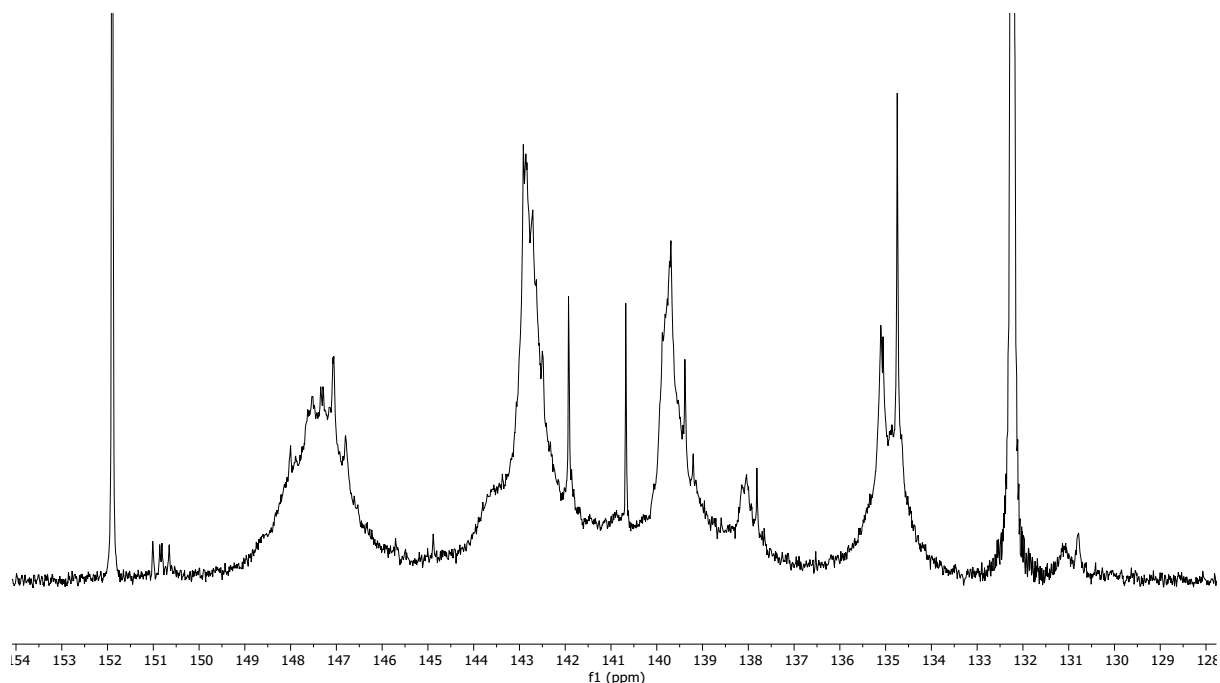
$n_{\text{PFB}}$ : number of moles of internal standard pentafluorobenzaldehyde added to the sample

$\text{ICH}_3$ : Integration of the  $^1\text{H}$  NMR signal between 0.6 - 1 ppm corresponding to the terminal  $\text{CH}_3$  of the ester chains.

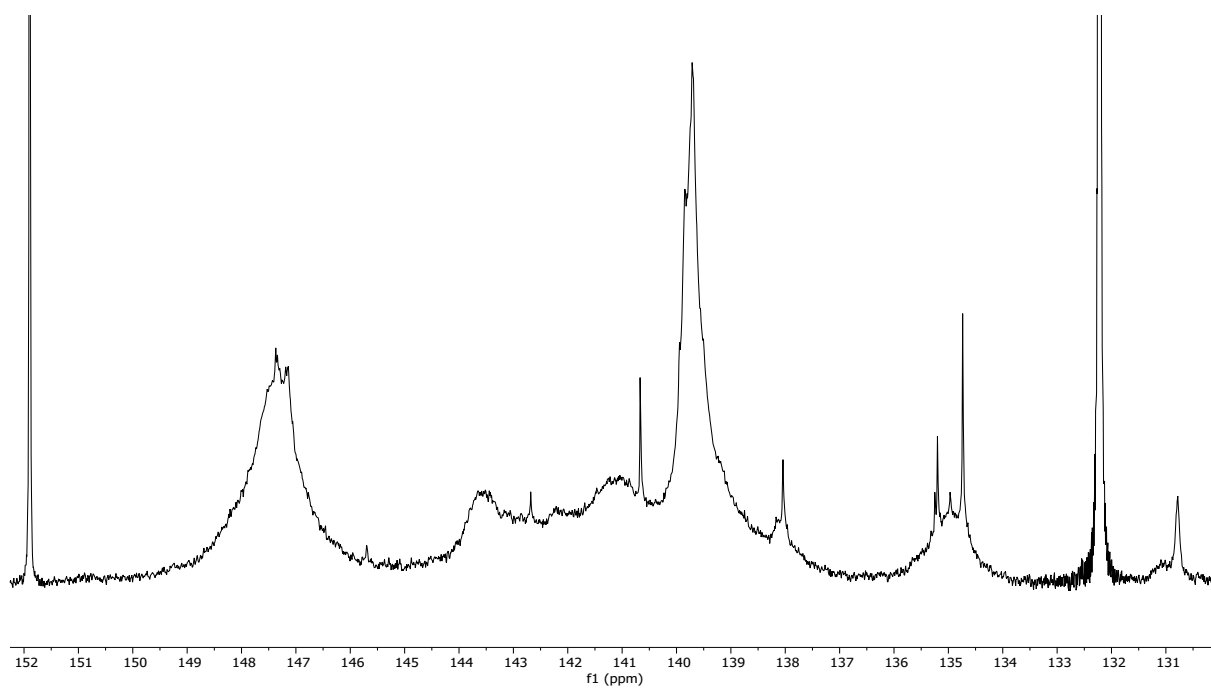
**Table SI 2  $^{31}\text{P}$  Analysis of Technical lignins : Kraft, Organosolv, and Soda Lignins – titration of the hydroxyl groups**

| Entry | Technical Lignin | mmol/g of hydroxyl groups |             |          |                 |
|-------|------------------|---------------------------|-------------|----------|-----------------|
|       |                  | Aliphatic OH              | Phenolic OH | Total OH | Carboxylic Acid |
| 1     | Kraft            | 1.9                       | 4.2         | 6.1      | 0.5             |
| 2     | Soda             | 1.5                       | 3.9         | 5.4      | 1.0             |
| 3     | Organosolv       | 2.3                       | 3.7         | 6.0      | 2.3             |

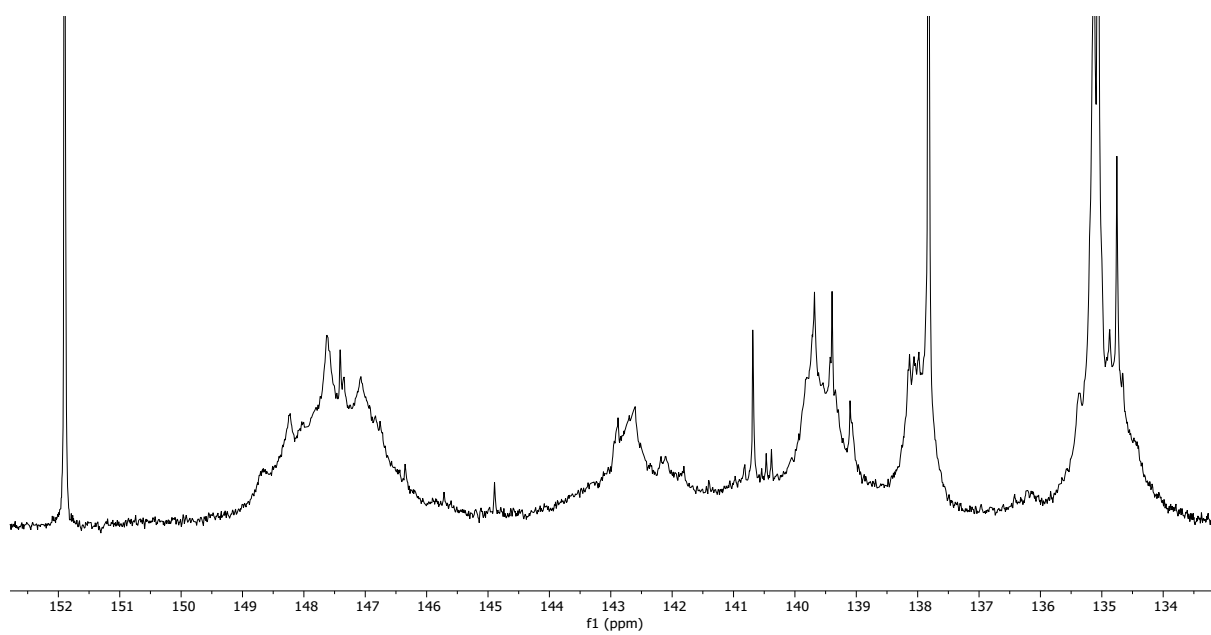
**$^{31}\text{P}$  NMR spectra of Technical lignins : Kraft, Organosolv, and Soda Lignins**



**Figure SI 11:**  $^{31}\text{P}$  NMR spectrum of native Kraft lignin.

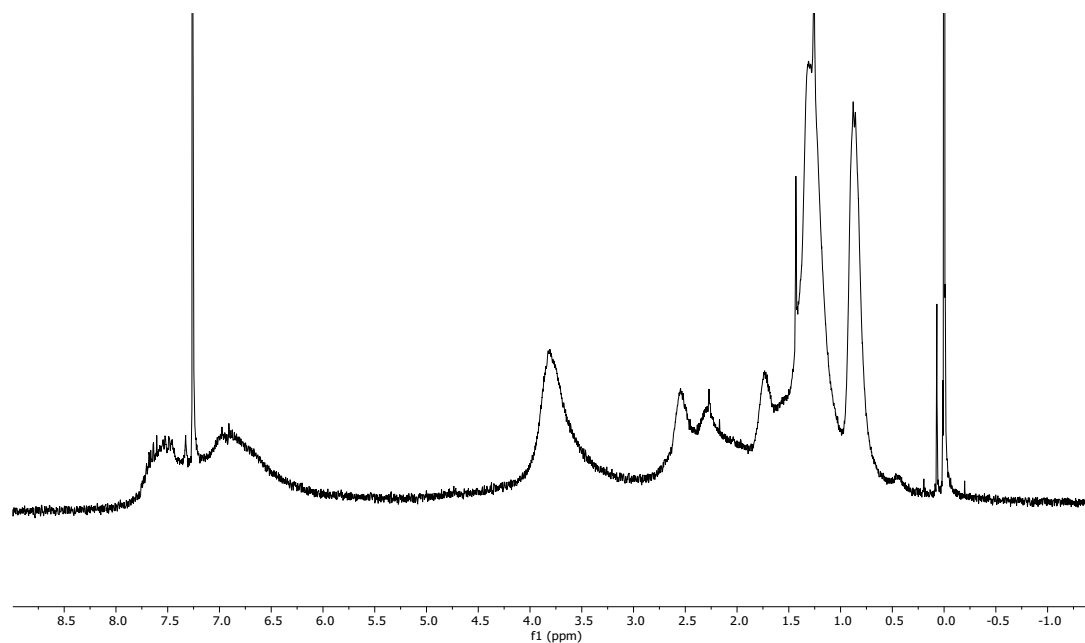


**Figure SI 12:**  $^{31}\text{P}$  NMR spectrum of native organosolv lignin.

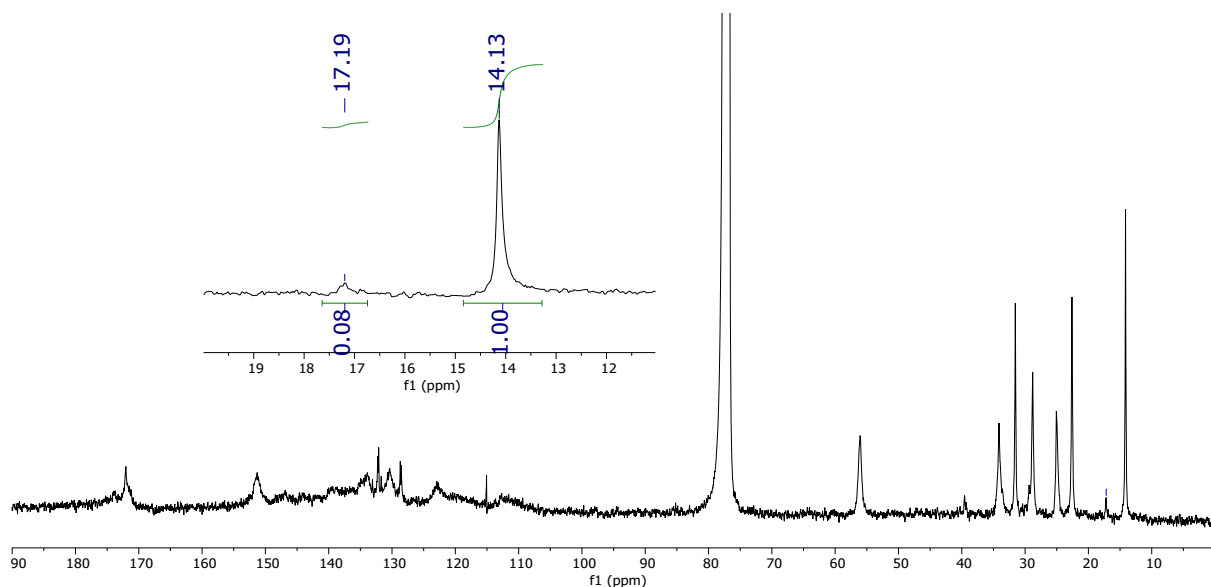


**Figure SI 13:**  $^{31}\text{P}$  NMR spectrum of native soda lignin.

**NMR spectra and DSC of Table 2: Scope of the hydroesterification of 1-hexene on lignins from different extraction processes**

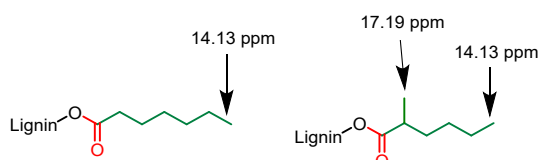


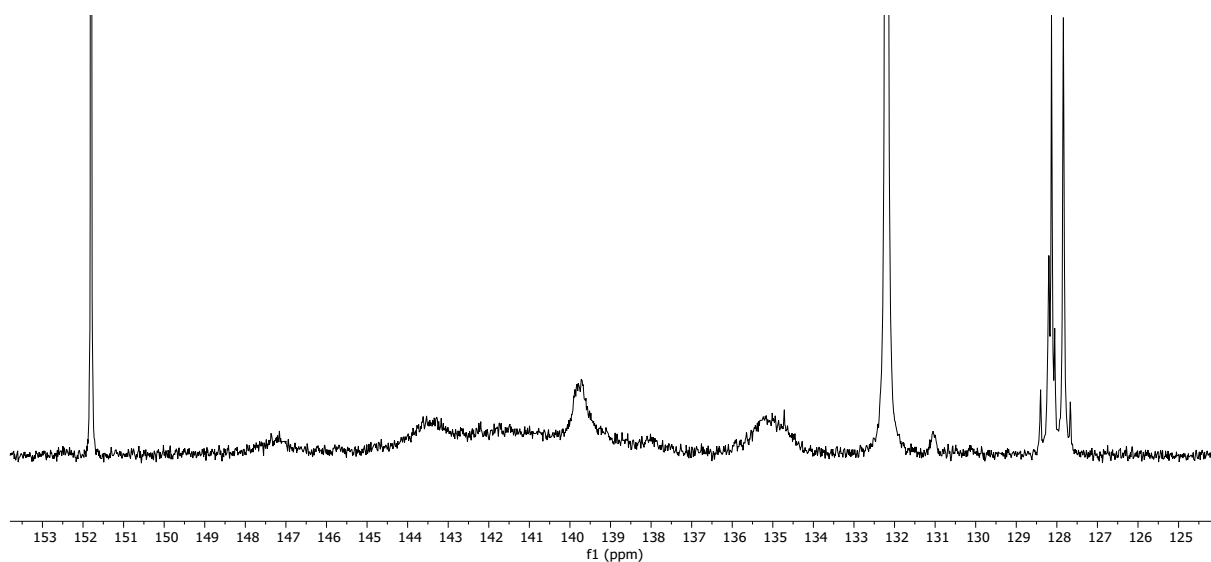
**Figure SI 14:**  $^1\text{H}$  NMR spectrum of the reaction with **Kraft lignin** in  $\text{CDCl}_3$ .



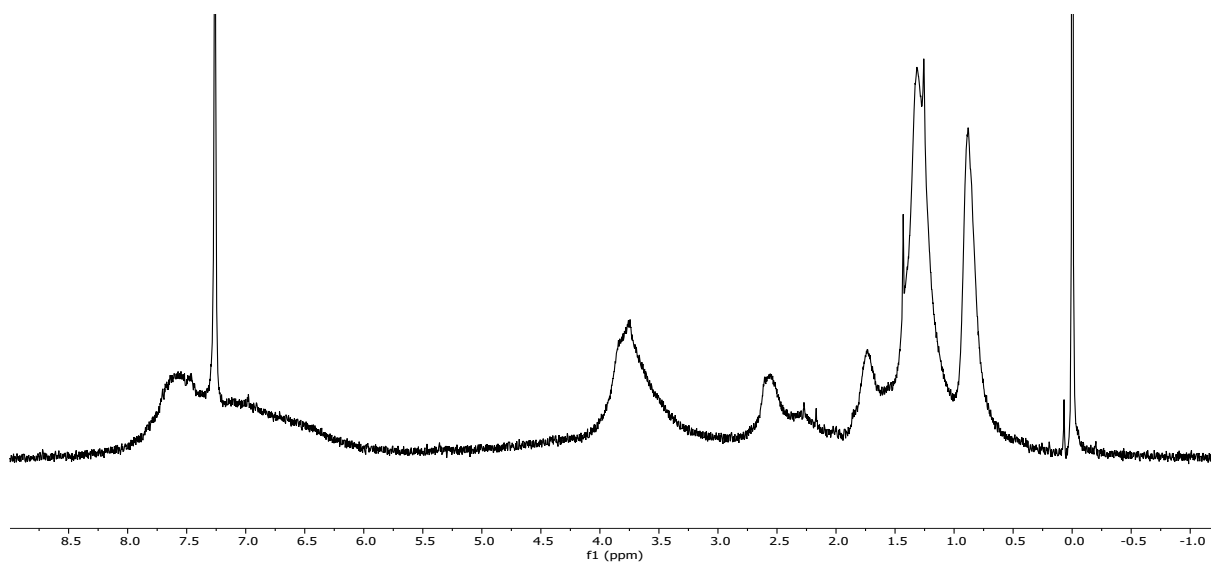
**Figure SI 15:**  $^{13}\text{C}$  Quantitative NMR spectrum of the reaction with **Kraft lignin** in  $\text{CDCl}_3$ .

General method for determination of L/B ratio on lignins: Comparison between the integration of the terminal  $\text{CH}_3$  of both isomers (at 14.13 ppm) and the  $\text{CH}_3$  of the branched compound (at 17.19 ppm) on  $^{13}\text{C}$  quantitative NMR spectrum. See example in figure SI 16. **Ratio L/B : 92/8**





**Figure SI 16:**  $^{31}\text{P}$  NMR spectrum of the reaction with **Kraft lignin**.



**Figure SI 17:**  $^1\text{H}$  NMR spectrum of the reaction with **Organosolv lignin** in  $\text{CDCl}_3$ .

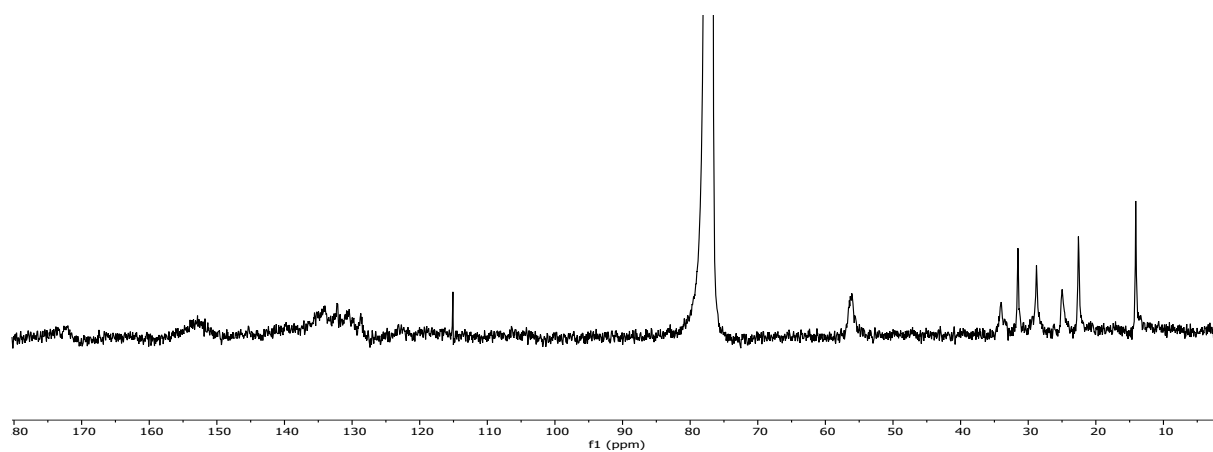


Figure SI 18: <sup>13</sup>C Quantitative NMR spectrum of the reaction with **Organosolv lignin** in CDCl<sub>3</sub>.

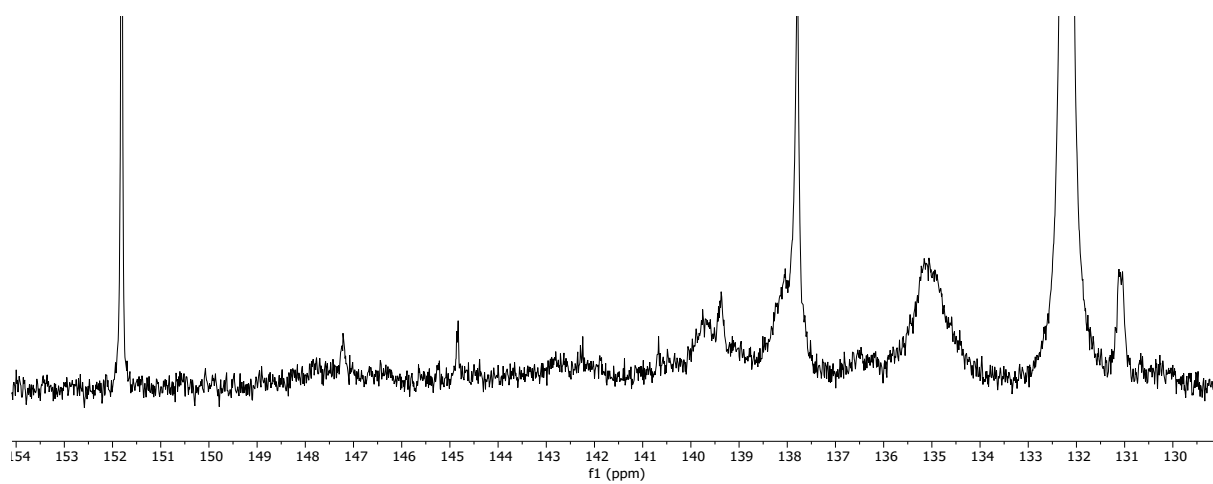


Figure SI 19: <sup>31</sup>P NMR spectrum of the reaction with **Organosolv lignin**.

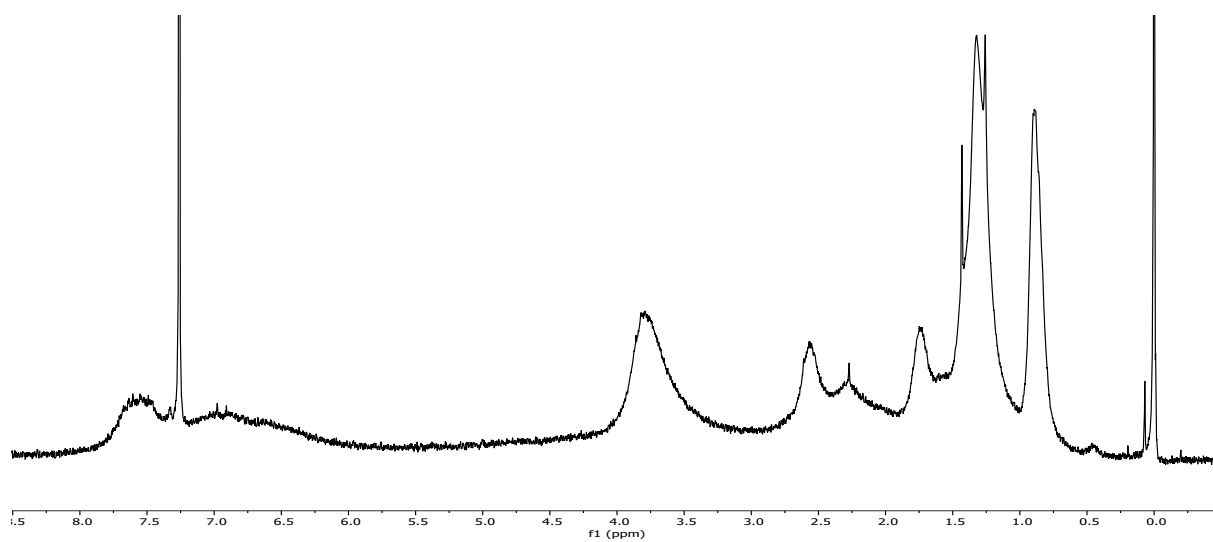
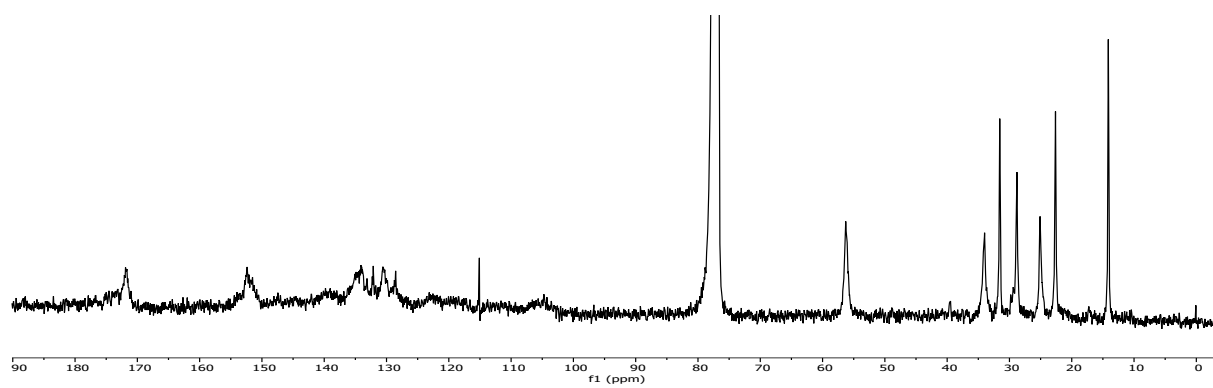
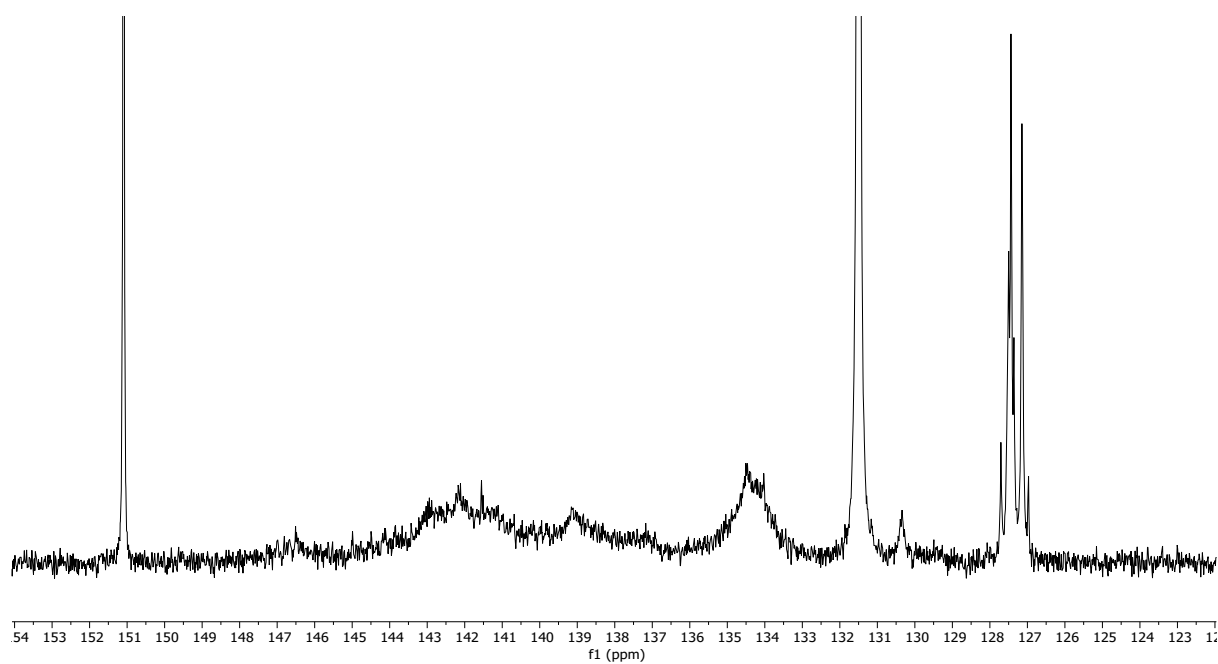


Figure SI 20: <sup>1</sup>H NMR spectrum of the reaction with **Soda lignin** in CDCl<sub>3</sub>.



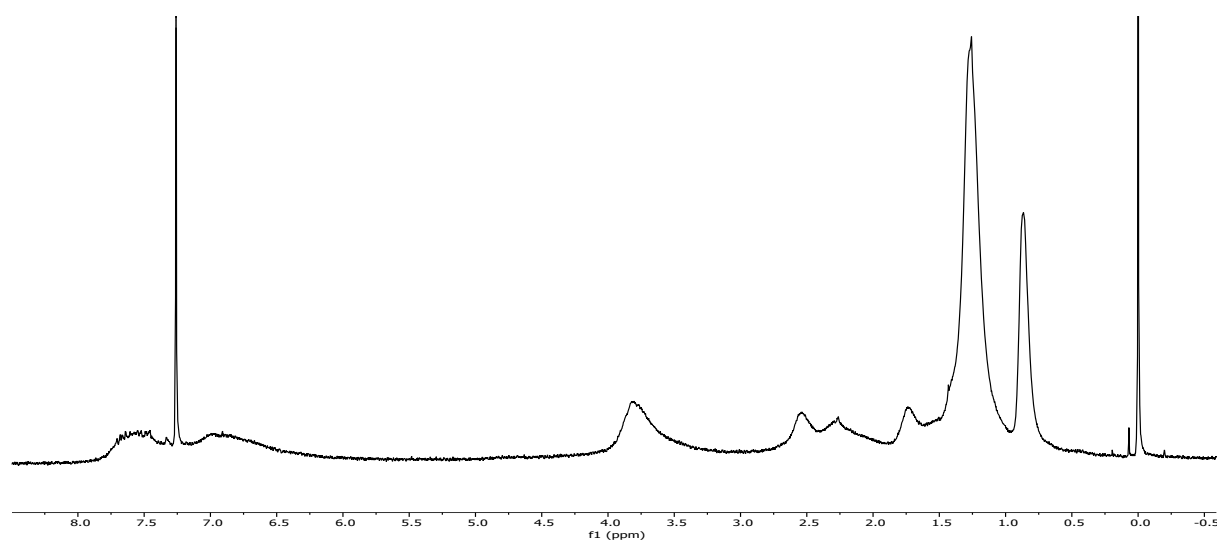


**Figure SI 21:**  $^{13}\text{C}$  Quantitative NMR spectrum of the reaction with Soda lignin in  $\text{CDCl}_3$ .

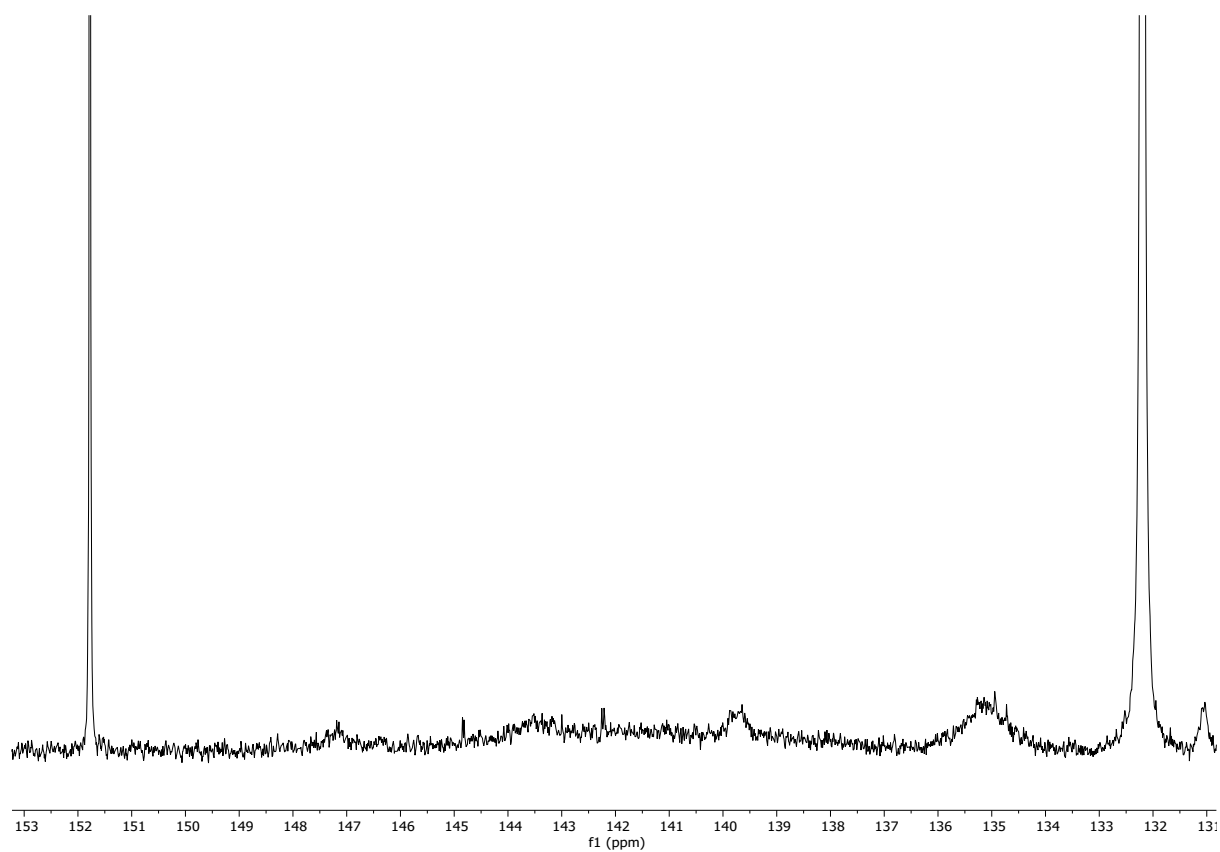


**Figure SI 22:**  $^{31}\text{P}$  NMR spectrum of the reaction with Soda lignin.

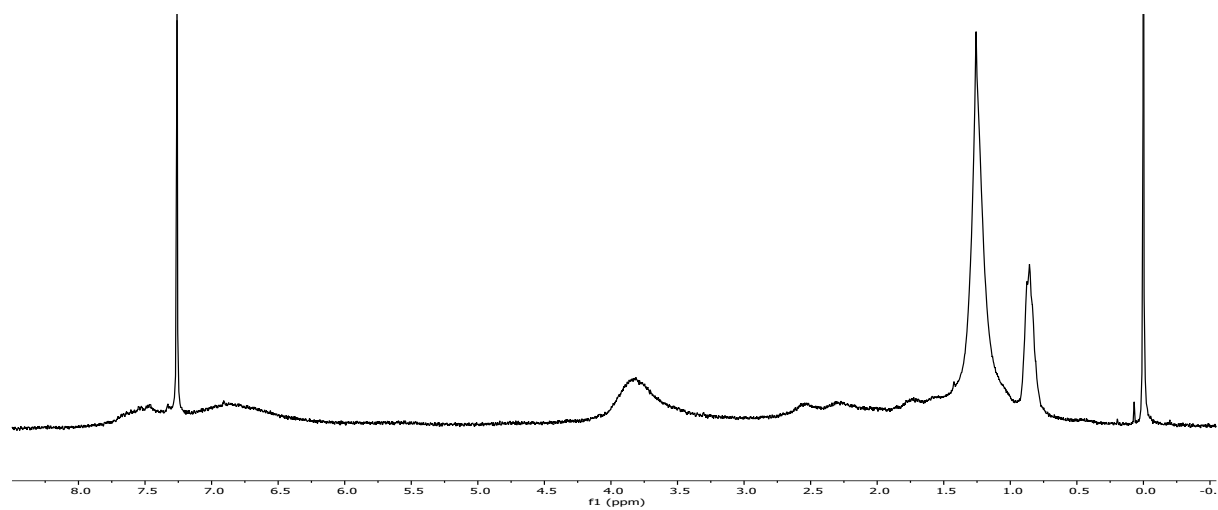
**NMR spectra of Table 3: Scope of olefin length in hydroesterification on Kraft lignin**



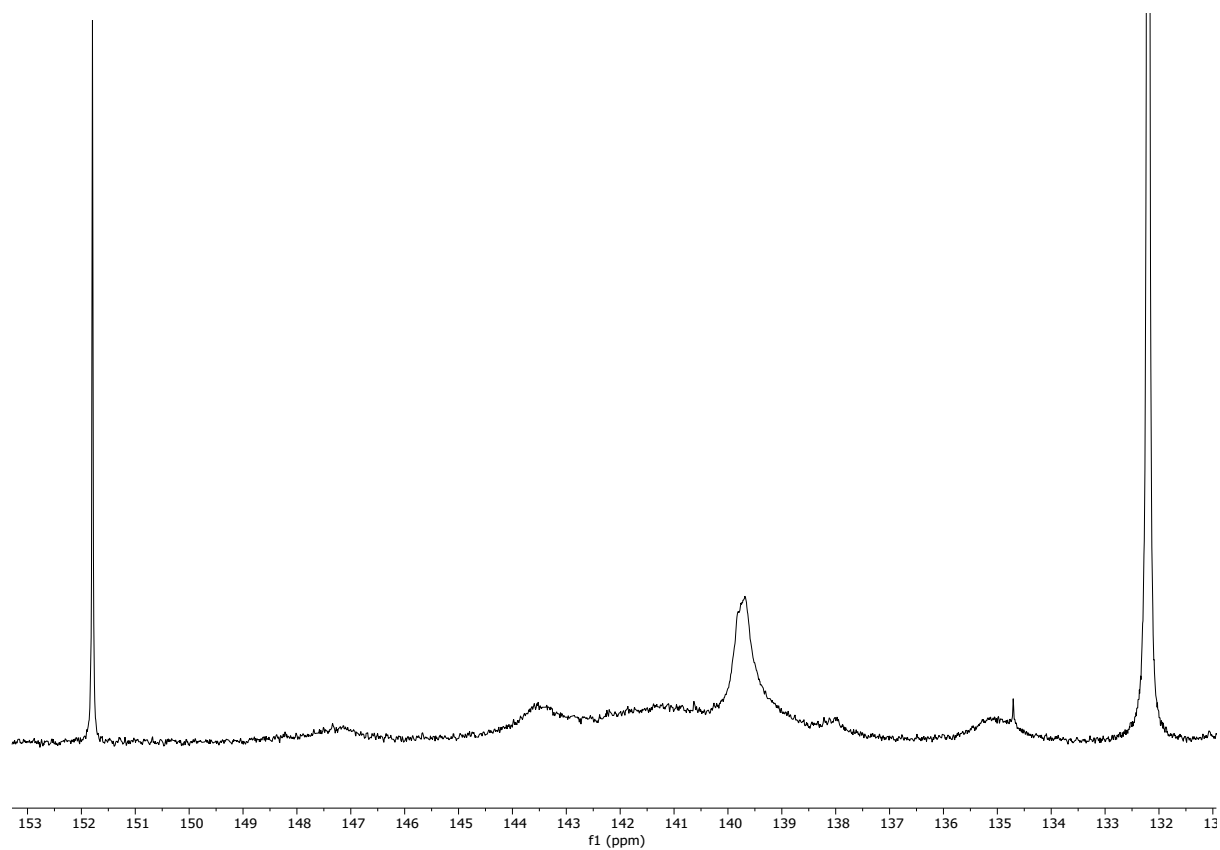
**Figure SI 23:**  $^1\text{H}$  NMR spectrum of the **1-octene** hydroesterification on lignin in  $\text{CDCl}_3$ .



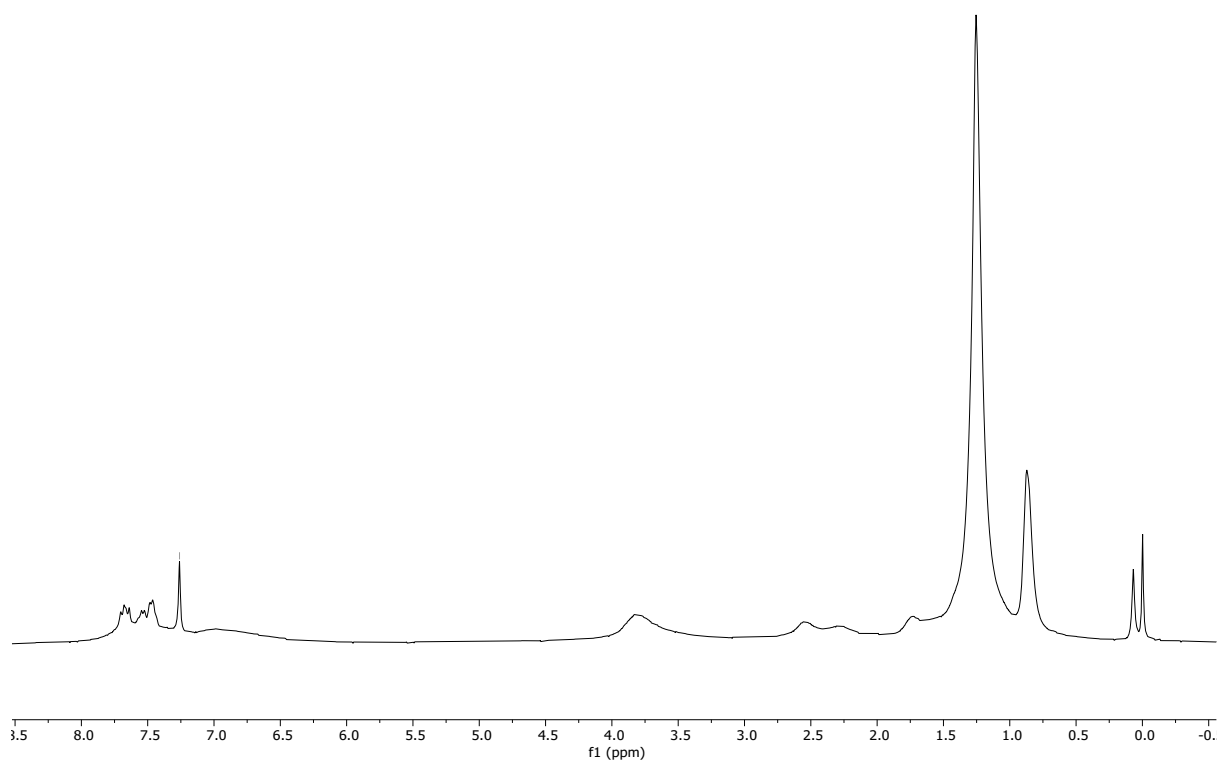
**Figure SI 24:**  $^{31}\text{P}$  NMR spectrum of the **1-octene** hydroesterification on lignin.



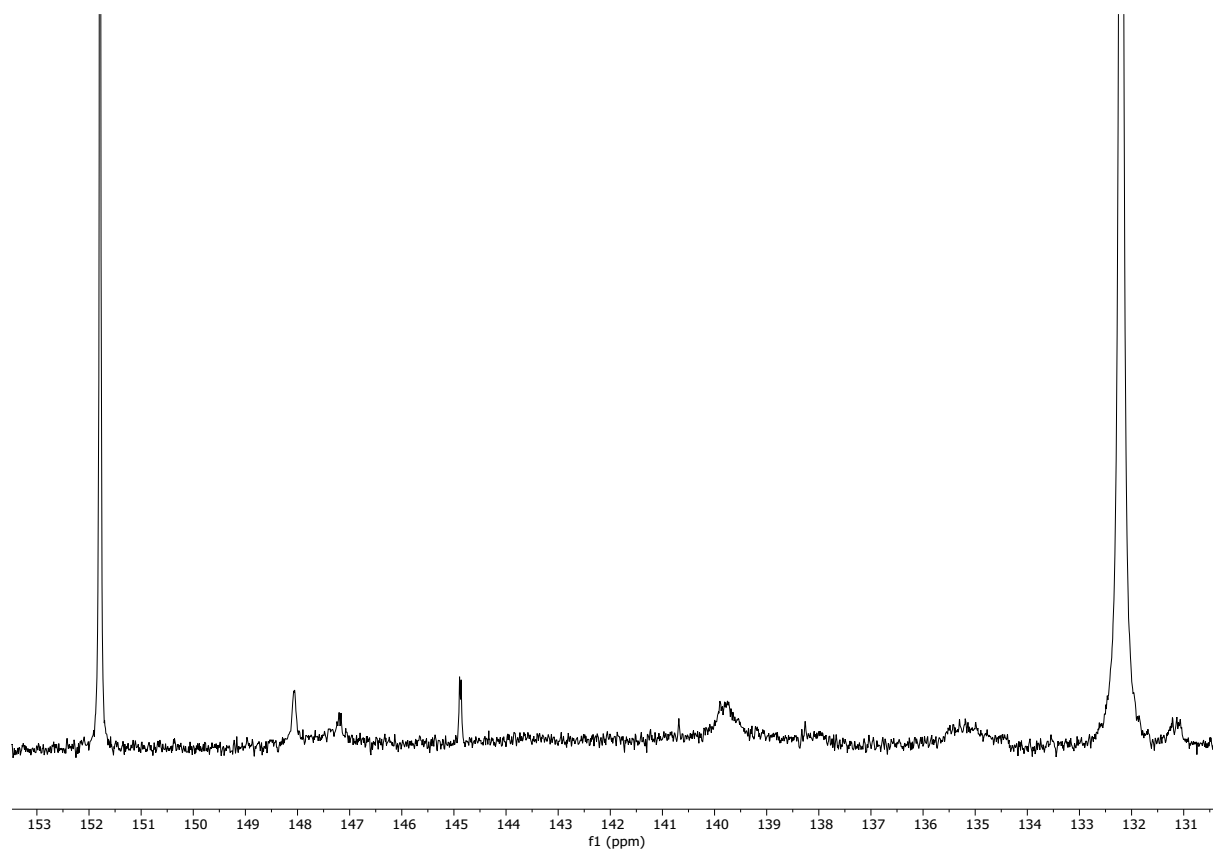
**Figure SI 25:**  $^1\text{H}$  NMR spectrum of the **1-decene** hydroesterification on lignin in  $\text{CDCl}_3$ .



**Figure SI 26:**  $^{31}\text{P}$  NMR spectrum of the **1-decene** hydroesterification on lignin.



**Figure SI 27:**  $^1\text{H}$  NMR spectrum of the **1-dodecene** hydroesterification on lignin in  $\text{CDCl}_3$ .



**Figure SI 28:**  $^{31}\text{P}$  NMR spectrum of the **1-dodecene** hydroesterification on lignin.

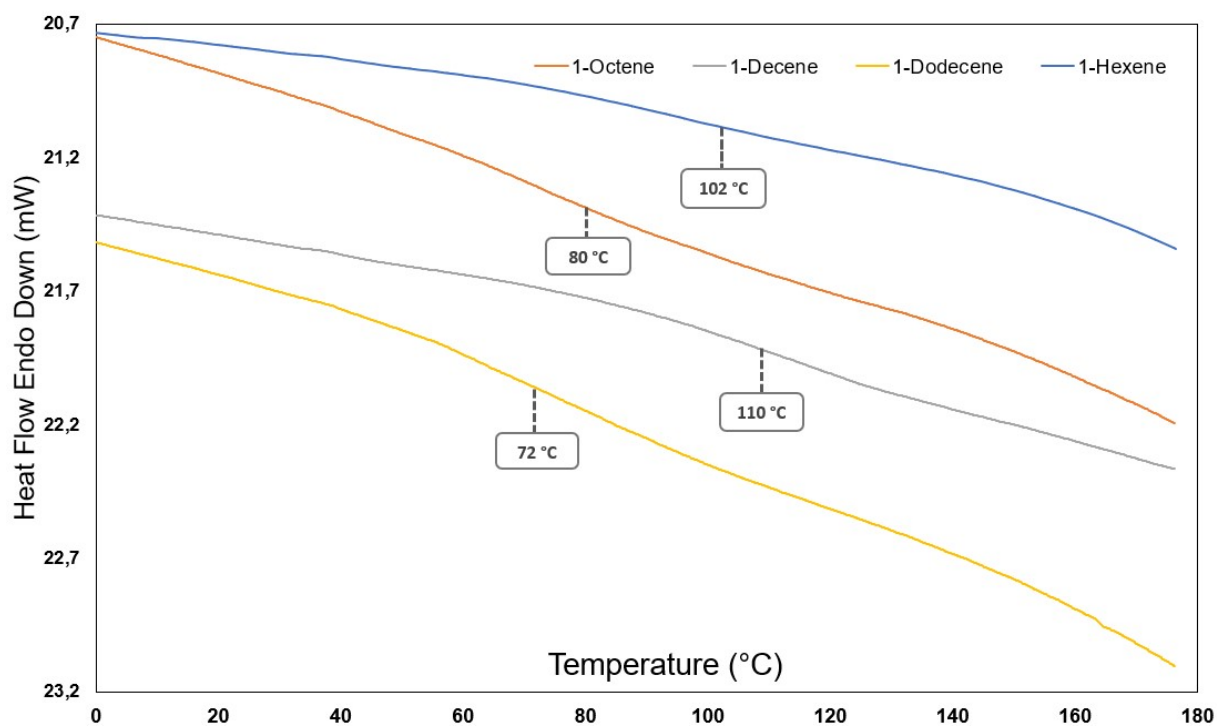
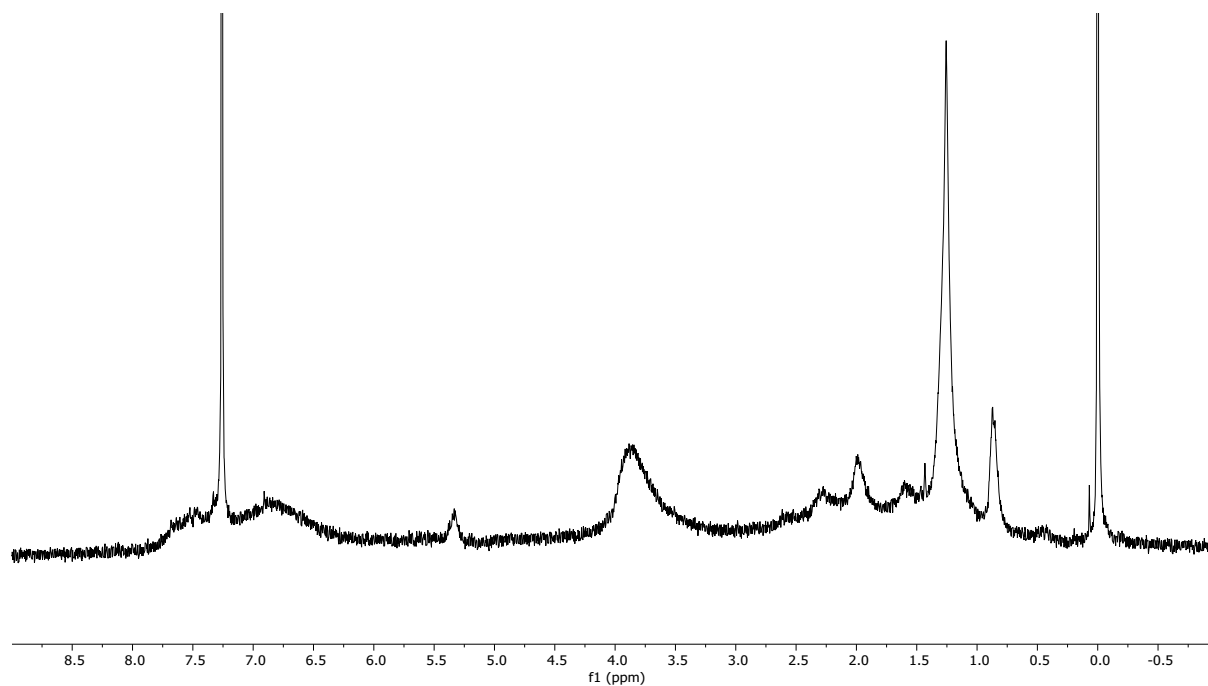
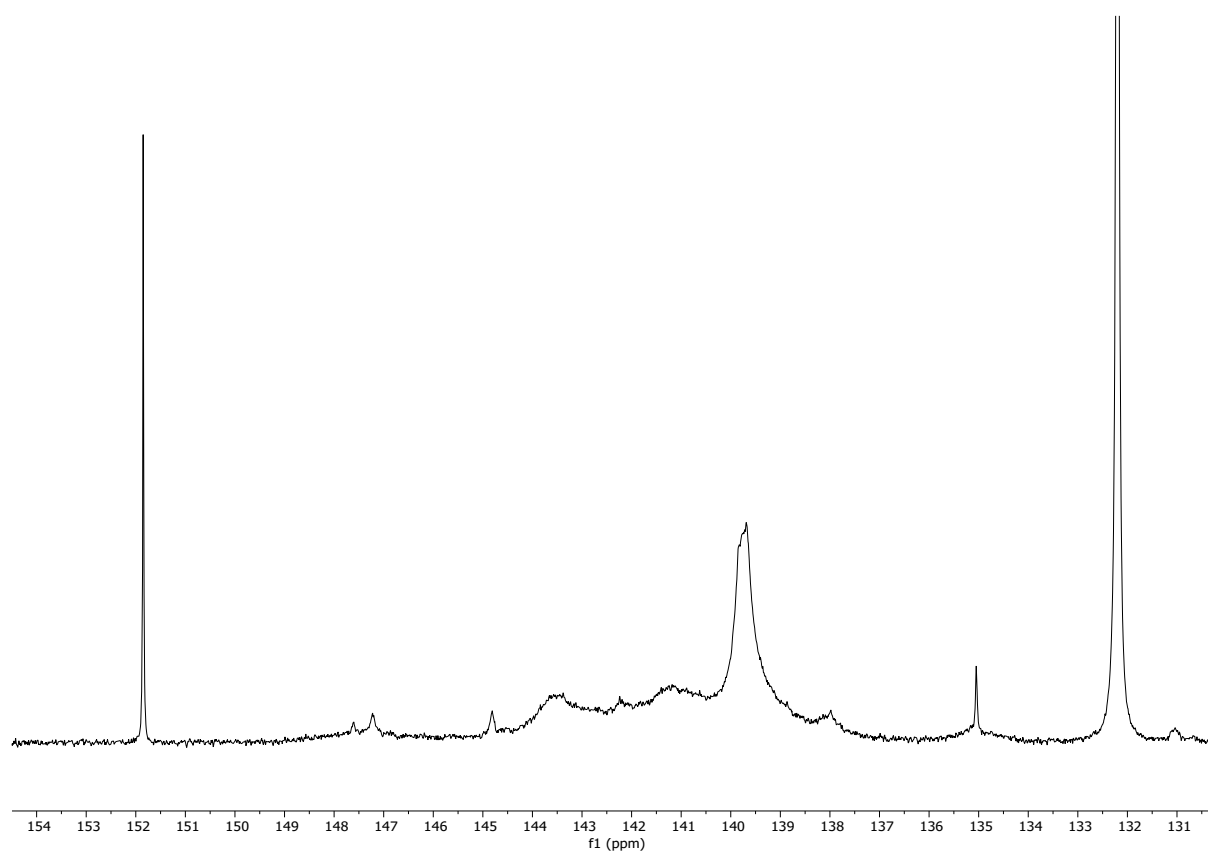


Figure SI 29: DSC Comparison of modified Kraft lignin with olefins.

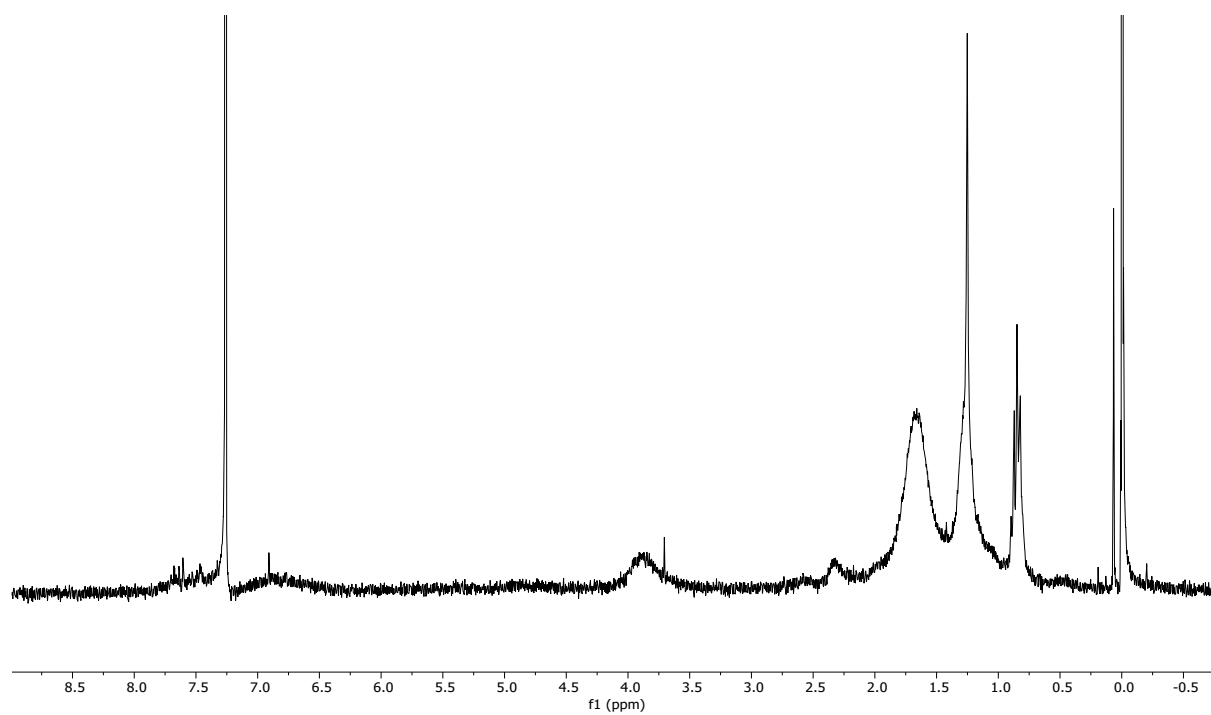
**NMR spectra of Table 4: hydroesterification of fatty acids, fatty ester and estragole on kraft lignin**



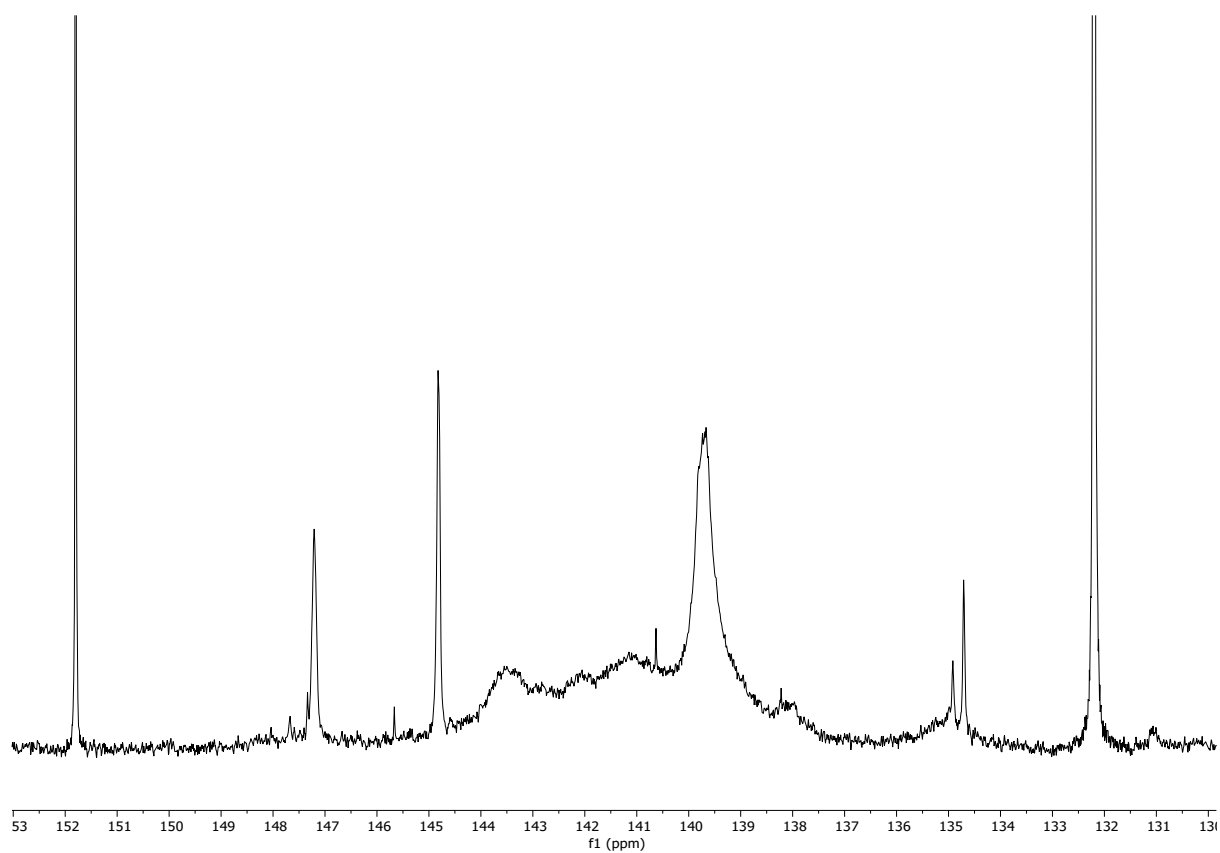
**Figure SI 30:** <sup>1</sup>H NMR spectrum of the **oleic acid** hydroesterification on lignin in CDCl<sub>3</sub>.



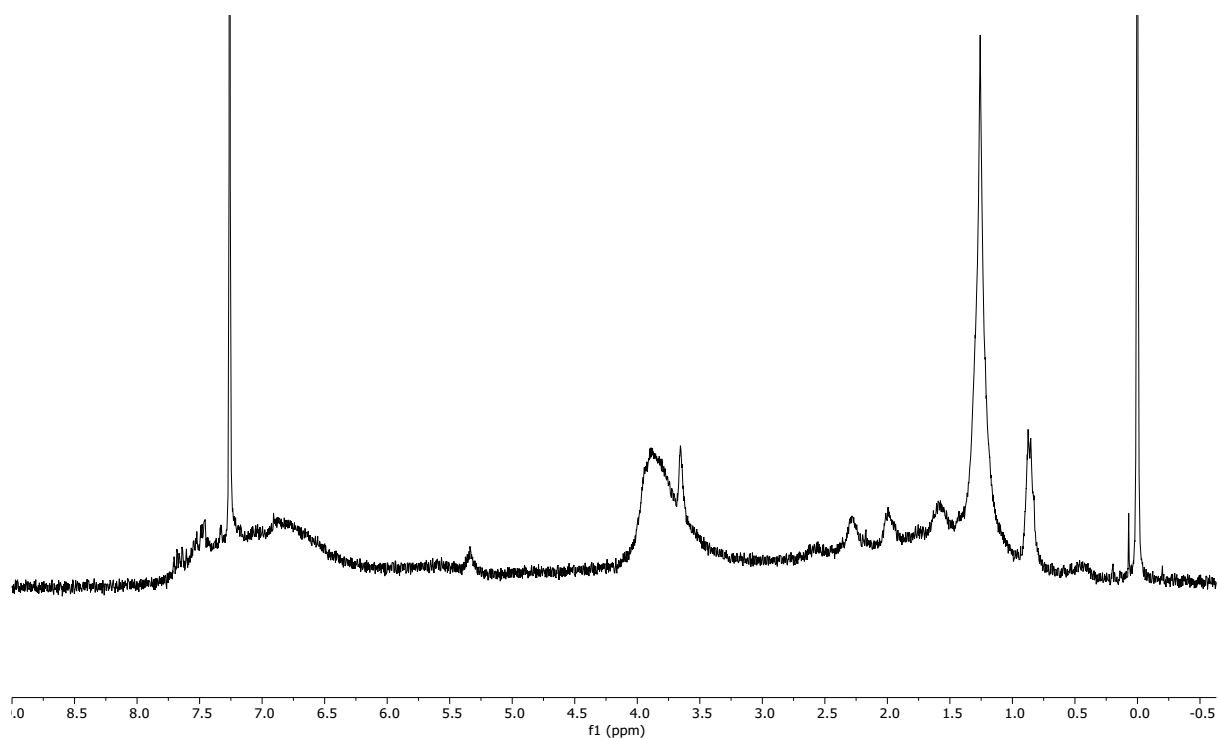
**Figure SI 31:** <sup>31</sup>P NMR spectrum of the **oleic acid** hydroesterification on lignin.



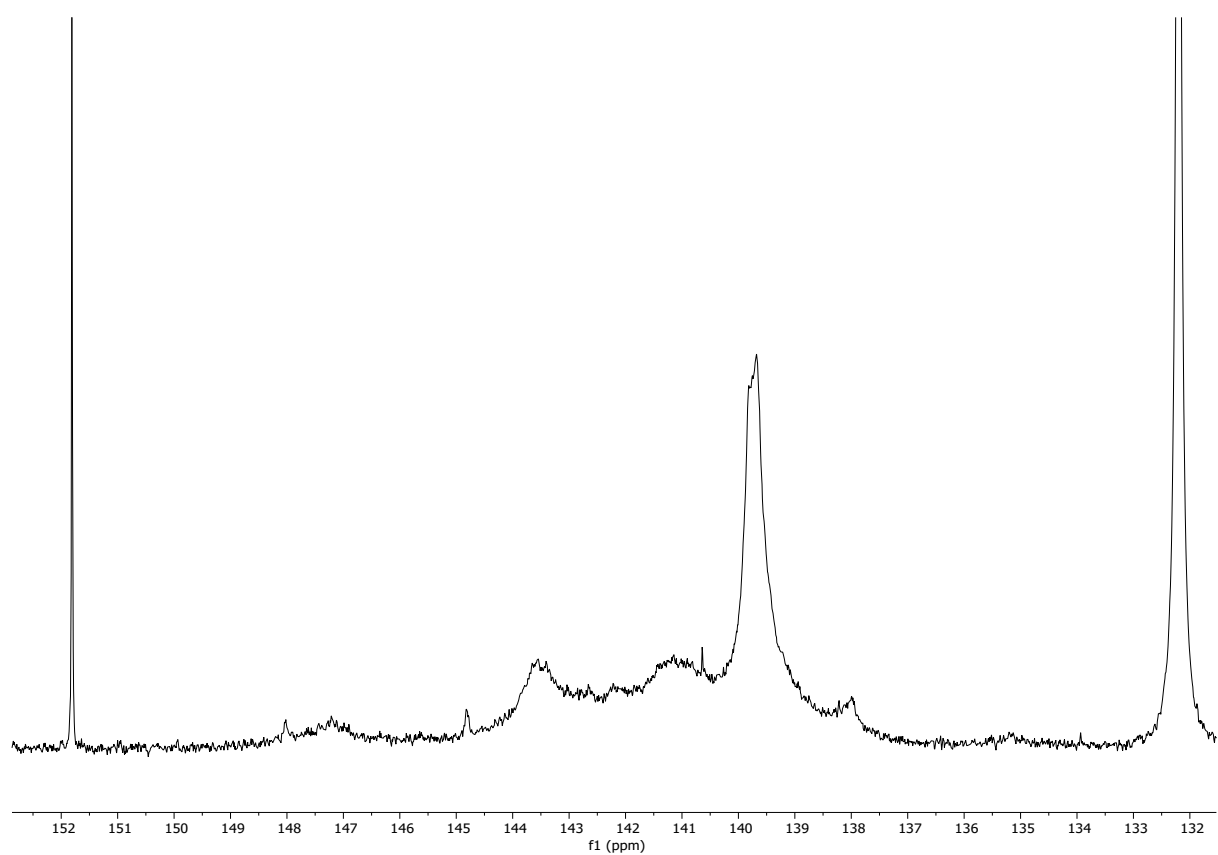
**Figure SI 32:** <sup>1</sup>H NMR spectrum of the **undecylenic acid** hydroesterification on lignin in CDCl<sub>3</sub>.



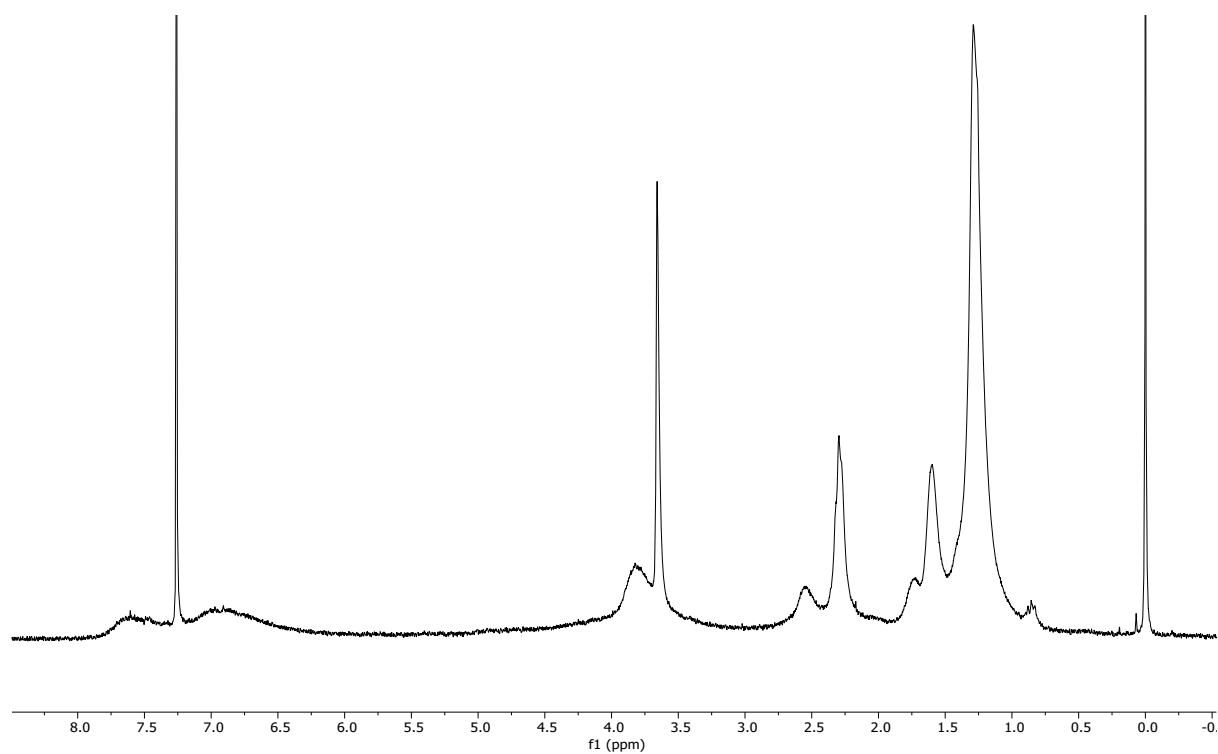
**Figure SI 33:** <sup>31</sup>P NMR spectrum of the **undecylenic acid** hydroesterification on lignin.



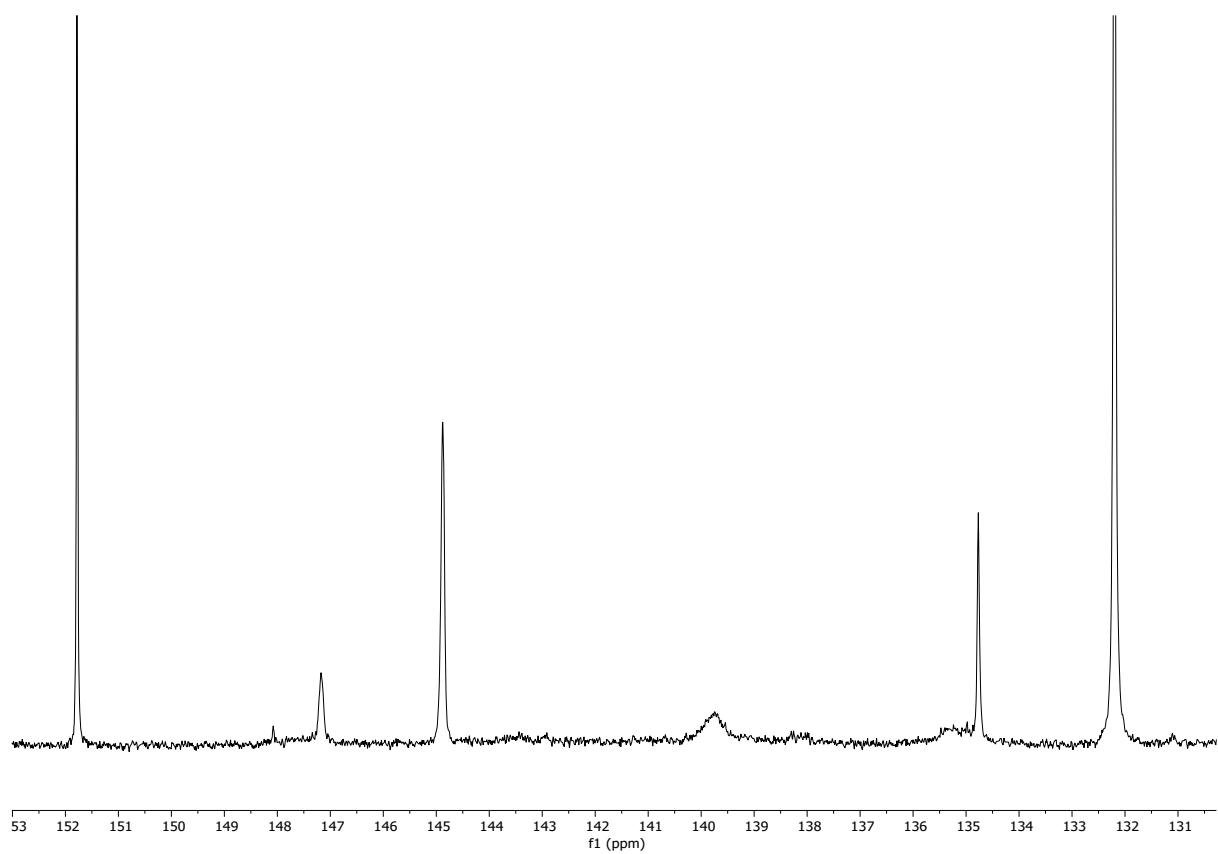
**Figure SI 34:** <sup>1</sup>H NMR spectrum of the **methyl oleate** hydroesterification on lignin in CDCl<sub>3</sub>.



**Figure SI 35:** <sup>31</sup>P NMR spectrum of the **methyl oleate** hydroesterification on lignin.

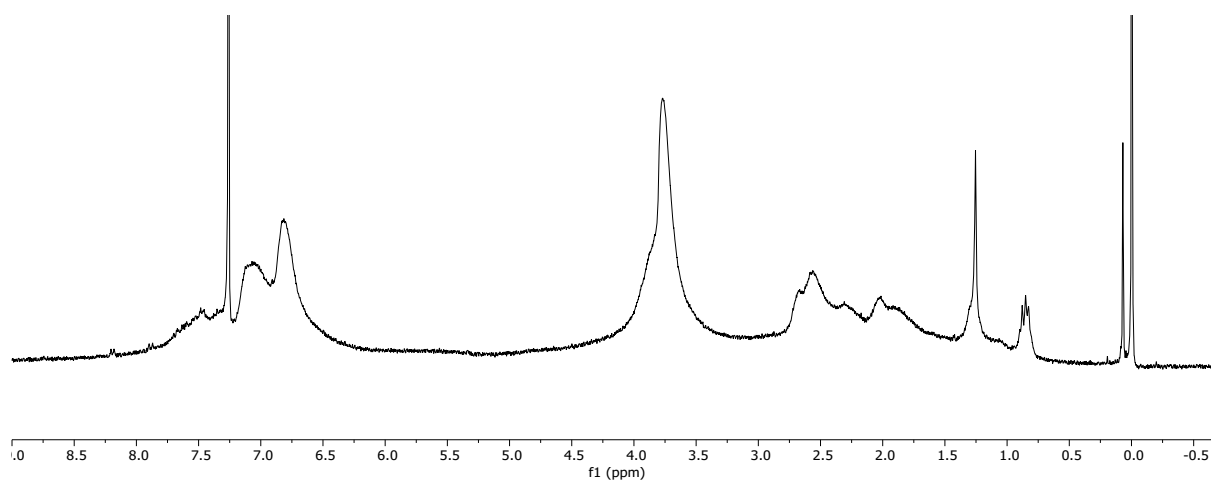


**Figure SI 36:** <sup>1</sup>H NMR spectrum of the **Methyl 10-undecenoate** hydroesterification on lignin in CDCl<sub>3</sub>.

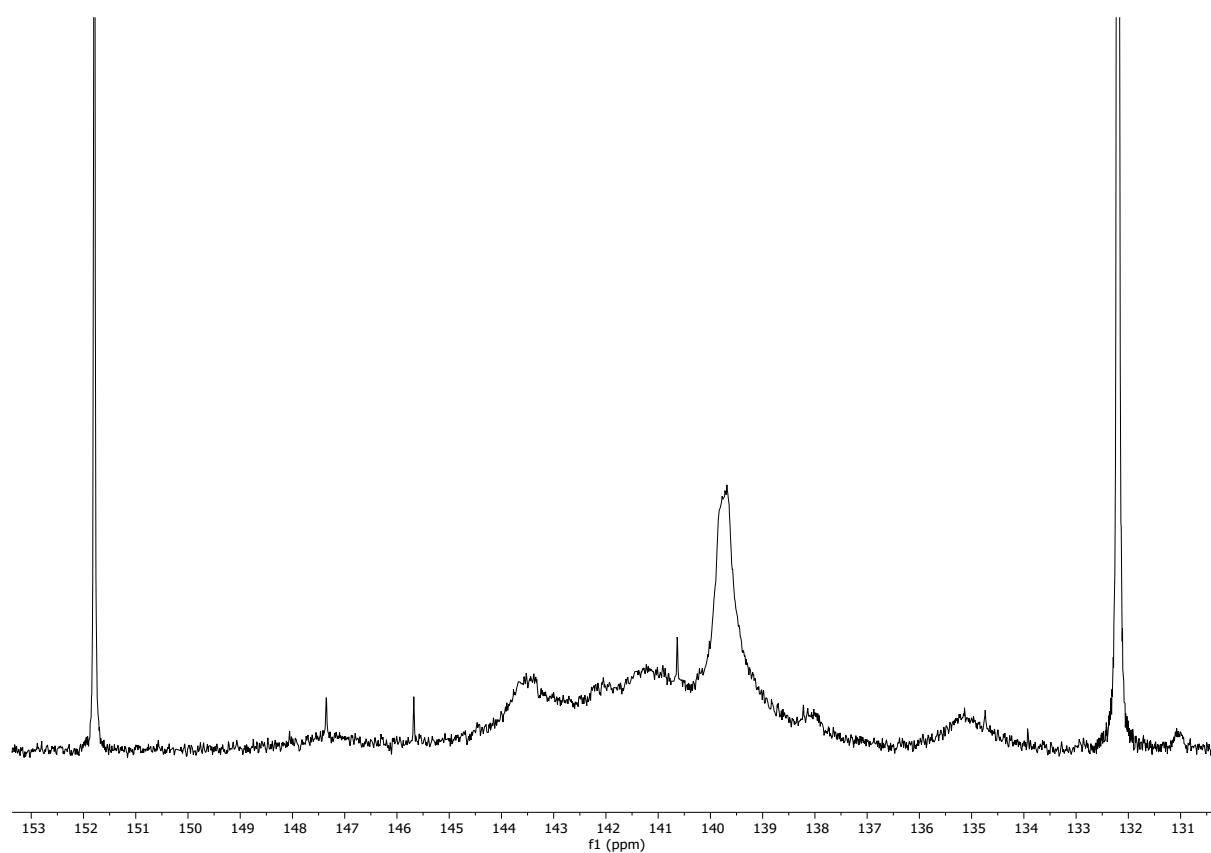


**Figure SI 37:** <sup>31</sup>P NMR spectrum of the **Methyl 10-undecenoate** hydroesterification on lignin.





**Figure SI 38:**  $^1\text{H}$  NMR spectrum of the **estragole** hydroesterification on lignin in  $\text{CDCl}_3$ .



**Figure SI 39:**  $^{31}\text{P}$  NMR spectrum of the **estragole** hydroesterification on lignin.

**Table SI 3: Supplementary catalytic experiments of butadiene hydroesterification with Kraft lignin**

| Entry | $\text{Pd}(\text{OAc})_2$ (eq/OH) | Benzoic Acid (eq/Pd) | T ( $^\circ\text{C}$ ) | Time | Substitution rate <sup>[a]</sup> |
|-------|-----------------------------------|----------------------|------------------------|------|----------------------------------|
| 1     | 1%                                | 30                   | 80                     | 15 h | 0 %                              |
| 2     | 1%                                | 30                   | 90                     | 15 h | 5 %                              |
| 3     | 1%                                | 30                   | 100                    | 15 h | 5 %                              |

|    |      |    |     |      |      |
|----|------|----|-----|------|------|
| 4  | 1%   | 30 | 120 | 15 h | 43 % |
| 5  | 1%   | 0  | 120 | 15 h | 6 %  |
| 7  | 0,5% | 30 | 120 | 15 h | 13 % |
| 8  | 1%   | 30 | 120 | 15 h | 43 % |
| 9  | 1,6% | 30 | 120 | 15 h | 67 % |
| 10 | 0,5% | 30 | 110 | 48 h | 47 % |
| 11 | 1%   | 30 | 110 | 48 h | 46 % |

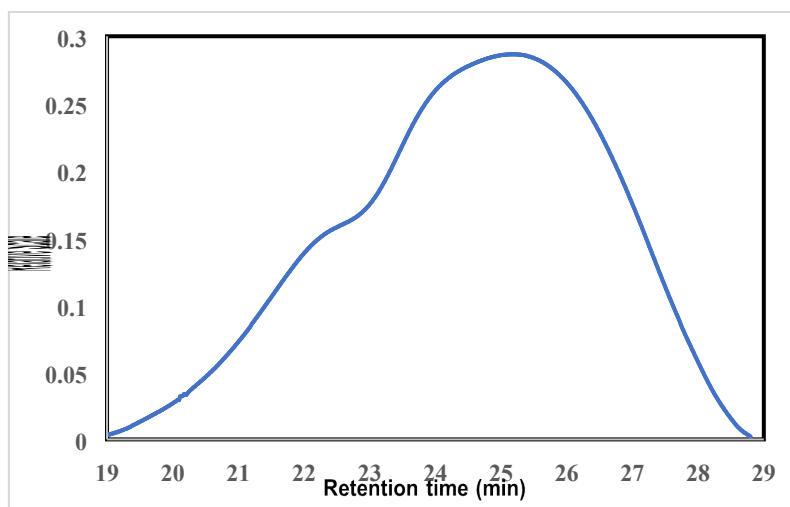
Conditions: 500 mg Kraft lignin, 6eq/Pd dppb, 7 eq/OH butadiene, 10 mL distilled and degassed THF, 50 bar CO. (a) determined by  $^1\text{H}$  NMR with pentafluorobenzaldehyde as internal standard using the  $\alpha$   $\text{CH}_2$  of the ester between 2.8 ppm and 3.45 ppm. Substitution rate as a function of total alcohols present in lignin.

[b] 400 mg of Kraft lignin.

**Table SI 4 - SEC analyses: the number-average molecular weight ( $M_n$ ), the weight-average molecular weight ( $M_w$ ), and molar mass dispersity ( $\mathfrak{D}$ ), for native and modified lignins**

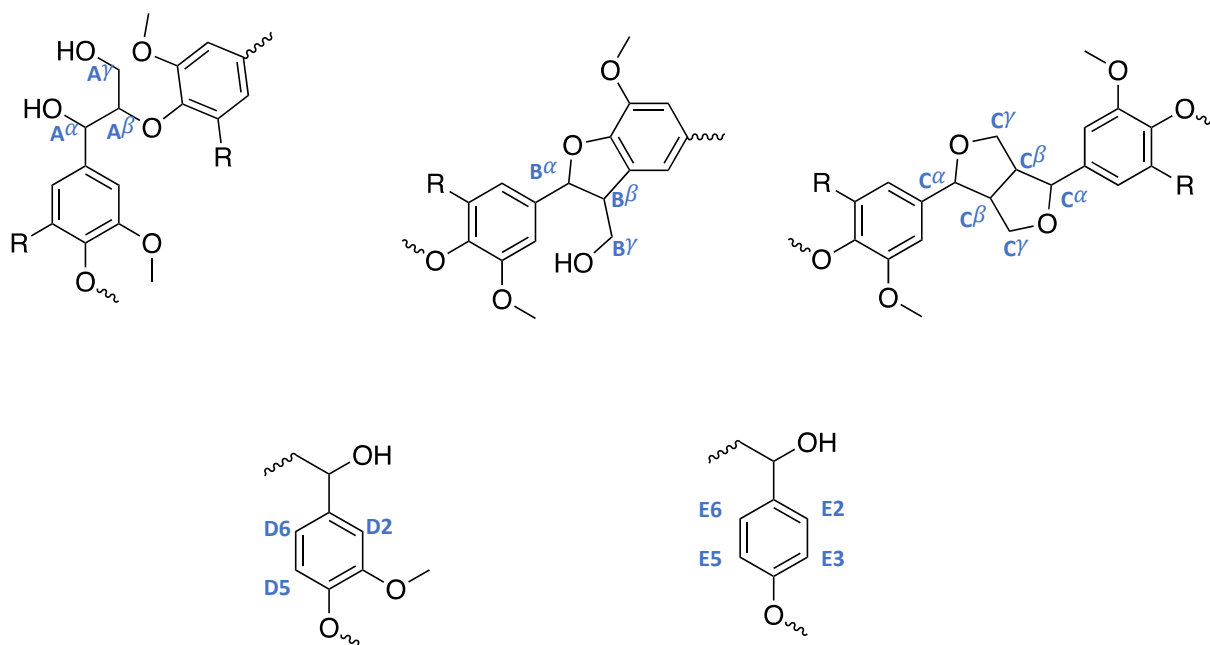
| Lignin                | olefin                | $M_n$ | $M_w$ | Dispersity<br>$\mathfrak{D} = M_w/M_n$ |
|-----------------------|-----------------------|-------|-------|--|
| Acetylated Kraft      | -                     | 1800  | 5600  | 3.1                                    |
| Acetylated Soda       | -                     | 1100  | 2700  | 2.5                                    |
| Acetylated Organosolv | -                     | 1400  | 3700  | 2.6                                    |
| Kraft                 | Hexene                | 2600  | 4400  | 1.7                                    |
| Soda                  | Hexene                | 2800  | 5100  | 1.8                                    |
| Organosolv            | Hexene                | 2100  | 3500  | 1.6                                    |
| Kraft                 | Octene                | 3000  | 5100  | 1.7                                    |
| Kraft                 | Decene                | 2500  | 4000  | 1.6                                    |
| Kraft                 | Dodecene              | 3100  | 6700  | 2.2                                    |
| Kraft                 | Methyl oleate         | 1800  | 2900  | 1.6                                    |
| Kraft                 | Methyl 10-undecenoate | 4000  | 7700  | 1.9                                    |
| Kraft                 | Oleic acid            | 2000  | 3300  | 1.7                                    |
| Kraft                 | 4-Allylanisole        | 2300  | 4400  | 1.9                                    |
| Kraft                 | Undecylenic acid      | 2600  | 4700  | 1.8                                    |
| Kraft                 | Butadiene             | 5100  | 12000 | 2.3                                    |

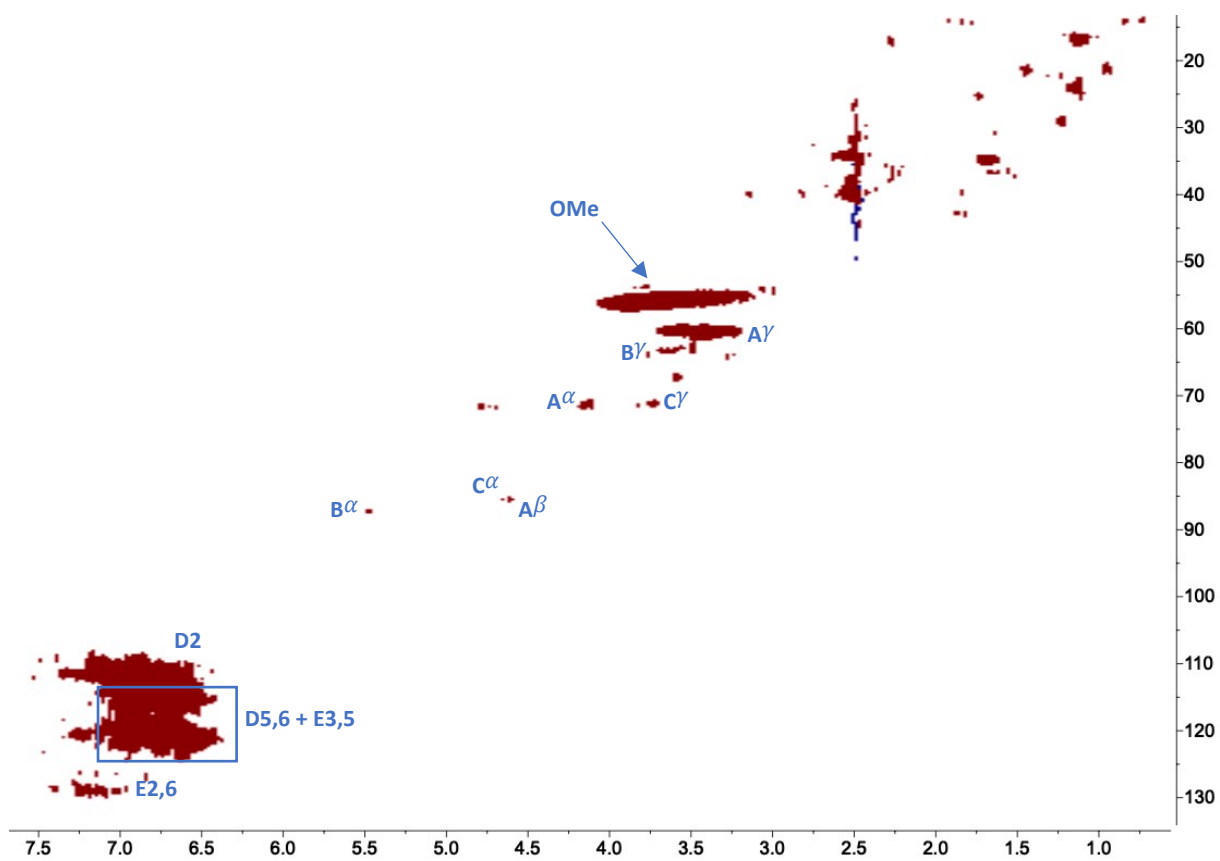
Figure SI 40 - Size exclusion chromatography (SEC) of lignin modified by hydroesterification of butadiene



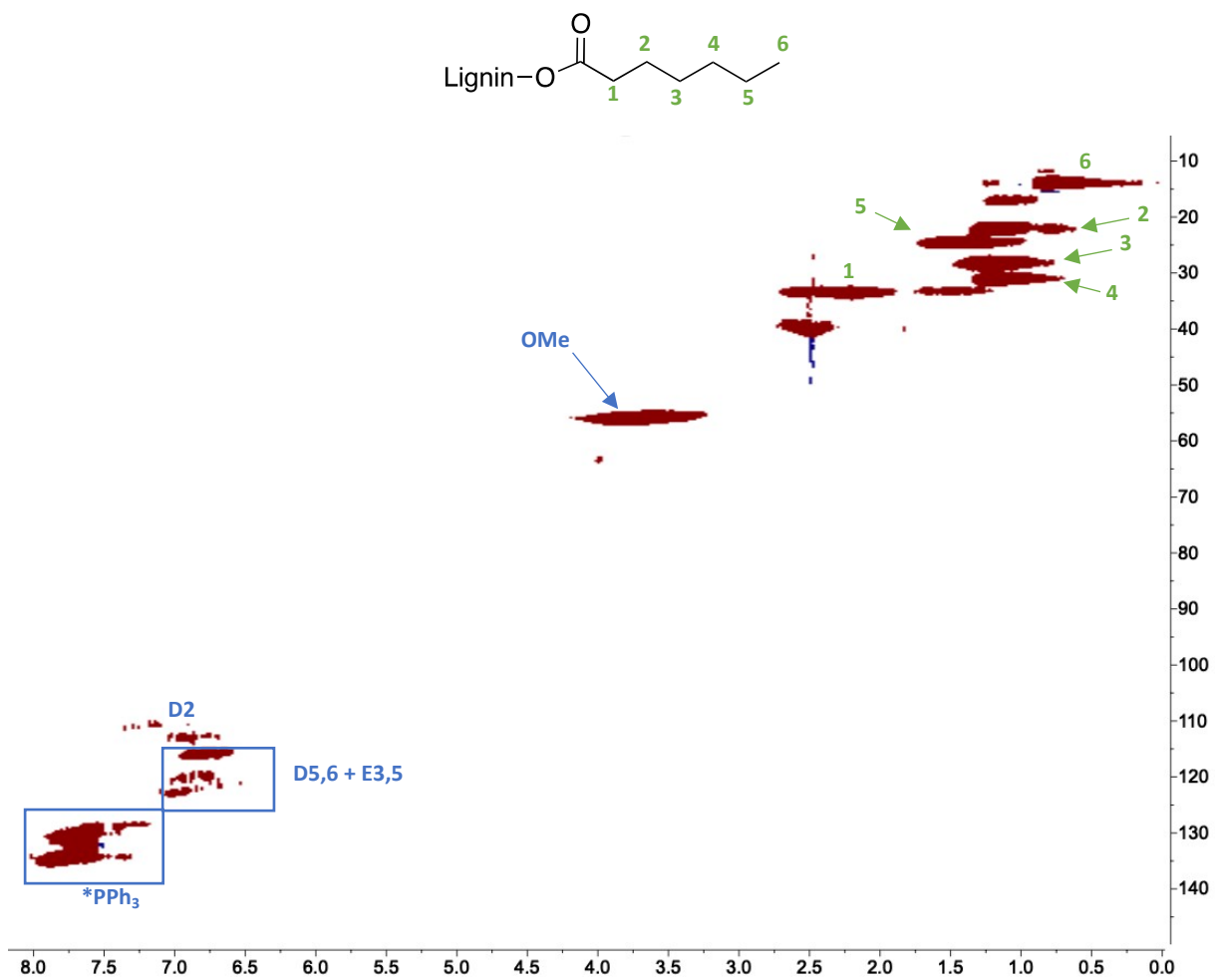
## 2D HSQC NMR of Technical and modified lignin by 1-hexene hydroesterification

NMR interpretation based on the study: S. Constant, H. L. J. Wienk, A. E. Frissen, P. de Peinder, R. Boelens, D. S. van Es, R. J. H. Grisel, B. M. Weckhuysen, W. J. J. Huijgen, R. J. A. Gosselink and P. C. A. Bruijninx, *Green Chem.*, 2016, 18, 2651–2665.





**Figure SI 41:** 2D HSQC NMR spectrum of technical Kraft lignin.



**Figure SI 42:** 2D HSQC NMR spectrum of the **1-hexene** hydroesterification on Kraft lignin