Electronic Supplementary Material (ESI) for Green Chemistry.

Combined lignin defunctionalisation and synthesis gas formation by acceptorless dehydrogenative decarbonylation

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Contents

S 1.0 Analytical procedures

Gas chromatography with a flame ionization detector (GC-FID) was performed with a Hewlett Packard 6890 series equipped with a 6890N FID, a HP-5 capillary column (30m×0.25mm) with 0.25 µm-film using nitrogen as carrier gas. The temperature program started with an isothermal step at 60 °C for 5 minutes followed by a 10 °C/min ramp for 20 minutes, finishing the ramp at 260 °C and holding for 15 minutes at 260 °C. The final temperature was changed to 320 °C for lignin samples. The other method parameters are as follows: 1 µL injection, a split ratio of 50:1, a nitrogen flow of 1 mL/s.

Gas chromatography with a thermal conductivity detector (GC-TCD) was performed using a Hewlett Packard 5890 Series II GC apparatus equipped with a thermal conductivity detector (TCD), using a Porablot Q Al_2O_3/Na_2SO_4 column and a molecular sieve column (5 Å) connected in series.

Gas chromatography-mass spectrometry (GC-MS) was performed using an Agilent 6890 series GC system equipped with a HP973 mass detector with helium as carrier gas.

NMR: For small molecules ^1H and ^{13}C NMR spectra were recorded either on a Varian Oxford Mercury AS 400 or an Agilent Technologies 400/54 Premium shielded spectrometer using $CDCl_3$ as solvent at room temperature. Chemical shift values are reported in part per million (ppm) with the solvent resonance as the internal standard. Data report followed the bellowing pattern: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br. = broad, m = multiplet), coupling constants (Hz), and integration.

NMR: For NMRs of lignin $CDCl_3$ were used as solvents as appropriate and were recorded with a Bruker Avance II 400 for lignin model compounds and with a Bruker Ascend 600 for the lignin samples. HSQC and HMBC were recorded using methods described in the following reference unless otherwise stated.[1]

Thin layer chromatography was performed on pre-coated aluminum plates (60/kieselguhr F_{254} Merk) and visualized under UV light (254 nm) or by staining with $KMnO_4$.

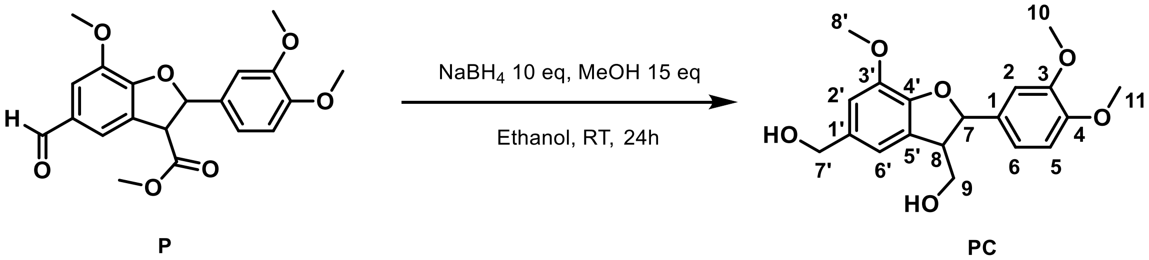
S 2.0 Reaction setup and temperature comparison

The reactions were performed in sealed 20 mL pressure vials (Biotage) heated by a metal synthesis heating block (IKA, H 135.104 Block 4 x 20 ml, hole Ø 28.5 mm, dimensions 79 x 79 mm) placed on a hot plate. There is temperature difference between the set temperature of heating blocks and the inside temperature, because of refluxing present in this setup as well as the low boiling point compared to the setting temperature. Therefore, the inside temperature was measured separately and the temperature difference is provided in the below table for reference. All temperatures presenting in the main text are set temperatures of the heating block, if not otherwise specified. For lignin dehydrogenative decarbonylation reactions, the maximum loading amount of lignin is 200 mg to prevent the pressure from reaching specified maxima.

Table S1: Comparison of the setting temperature of heating block and the measured inside temperature in 1,4-dioxane and diethyl carbonate.

Set T/ °C	Actual inside T in 1,4-dioxane/ °C	Actual inside T in diethyl carbonate/ °C
165	130	139
180	138	145
190	142	148
200	146	154
205	148	157
210	150	159

S 3.0 Procedure for the synthesis of the phenylcoumaran model compound



Scheme S1: synthesis of phenyl coumaran model compound (**PC**)

Methyl-2-(3,4-dimethoxyphenyl)-5-formyl-7-methoxy-2,3-dihydrobenzofuran-3-carboxylate (**P**) was synthesized via reported procedure.[2] **P** (300 mg, 0.81 mmol 1 eq) was dissolved in 10 mL EtOH. $NaBH_4$ (305 mg, 8.1 mmol, 10 eq) was added in 5 minutes. MeOH (387mg, 12.1 mmol, 15 eq) was added slowly under N_2. The reaction was stirred for 24 hours after which time no starting material (**P**) was visible by TLC. The reaction was quenched with an aqueous solution of sat. NH_4Cl. Additional water was added to solubilize the precipitated salts. The quenched reaction was then extracted (x3) with EtOAc. The organic layers were combined, washed with H_2O and brine prior to being dried over $MgSO_4$, filtered and concentrated in *vacuo*. Purification was carried out by column chromatography to afford (2-(3,4-dimethoxyphenyl)-7-methoxy-2,3-dihydrobenzofuran-3,5-diyl)dimethanol (**PC**) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 – 6.91 (m, 2H, Ar-$\underline{H}$), 6.86 – 6.79 (m, 3H, Ar-$\underline{H}$), 5.57 (d, 1H, H7), 4.59 (s, 2H, H7'), 3.94 (dd, *J* = 6.0 Hz, 1H, H9), 3.90 – 3.86 (m, 4H, H9&-OC$\underline{H}_3$), 3.85 (s, 3H, -OC$\underline{H}_3$), 3.83 (s, 3H, -OC$\underline{H}_3$), 3.60 (t, *J* = 6.0 Hz, 1H, H8).

Data is consistent with literature.[3]

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.28 (C4), 149.14 (C3), 148.06 (C4'), 144.51(C3'), 134.57 (C1'), 133.67 (C1), 128.14 (5'), 118.79 (C2), 115.54 (C6'), 111.66 (C2'), 111.16 (C5), 109.45 (C6), 88.06 (C7), 65.57 (C7'), 63.97 (C9), 56.13 (C8'), 56.05 (C10+C11), 53.73 (C8).

S 4.0 Procedure for the isolation of high alcohol incorporation organosolv lignin

S 4.1 Ethanosolv lignin

20 grams of finely ground walnut shell were added to a round-bottom flask equipped with a magnetic stirring bar. 160 mL ethanol, 40 mL water and 4 mL of a 12 M HCl in water solution were added and the mixture was heated at 80 °C for 5 hours. The mixture was allowed to cool down to room temperature. The mixture was filtered and the residue was washed twice with 20 mL of ethanol. The residue was concentrated by rotary evaporation until a sticky solid remained. The solid was redissolved in a minimal amount of acetone, after which lignin was

precipitated in water (300 mL demi water + 100 mL demi water saturated with Na_2SO_4). The product was obtained by filtration and air dried overnight.

Similar with reported procedure[4, 5], to obtain higher alcohol incorporation, 1.2 grams of ethanosolv lignin was placed in a 100 mL round-bottom flask and dissolved in 40 mL ethanol and 10 mL 1,4-dioxane. 3 mL of HCl in 1,4-dioxane solution was added and the mixture was heated for 4 hours at 80 °C. Afterwards the mixture was concentrated by rotary evaporation and the solid was redissolved is a minimal amount of acetone. Lignin was obtained by precipitation in 150 mL water and obtained by filtration, after which it was air dried overnight.

S 4.2 Butanosolv lignin

20 grams of finely ground walnut shell were added to a round-bottom flask equipped with a magnetic stirring bar. 100 mL 1,4-dioxane, 100 mL n-butanol and 12 mL of a 4N HCl in 1,4-dioxane solution were added and the mixture was heated at 80 °C for 12 hours. The mixture was allowed to cool down to room temperature. The mixture was filtered and the residue was washed twice with 20 mL of n-butanol. The residue was concentrated by rotary evaporation until a sticky solid remained. The solid was redissolved in a minimal amount of acetone, after which lignin was precipitated in water (300 mL demi water + 100 mL demi water saturated with Na_2SO_4). The product was obtained by filtration and air dried overnight.

S 4.3 Pentanosov lignin

20 grams of finely ground walnut shell were added to a round bottom flask equipped with a magnetic stirring bar. 100 mL 1,4-dioxane, 100 mL n-pentanol and 12 mL of a 4N HCl in 1,4-dioxane solution were added and the mixture was heated at 60 °C for 16 hours. The mixture was allowed to cool down to room temperature. The mixture was filtered and the residue was washed twice with 20 mL of 1,4-dioxane. The residue was concentrated by rotary evaporation until a sticky solid remained. The solid was redissolved in a minimal amount of acetone, after

which lignin was precipitated in water (300 mL demi water + 100 mL demi water saturated with Na_2SO_4). The product was obtained by filtration and air dried overnight.

S 4.4 Linkages contents of starting lignins and defunctionalized lignins

All the linkages are expressed per 100 aromatics units based on 2D-HSQC. The appearance of a new signal was observed in the aromatic region (6.4,104 ppm, Fig. S13-S18) which is assumed to be unrelated to S and G moieties as this would affect the S/G ratio between the original lignin and the defunctionalized lignin. This is also in correspondence with our earlier experience that the number of β-β linkages is stable throughout the entire reaction sequence.[5] A 1.3 correction factor was applied on the number of linkages as was established in earlier work.[1] Values are based on the β-protons for **LA-OR**, **LB-OR** and **LC** (corrected for 1, 2 and 2 protons) and on the α-protons for **LD** (corrected for 2 protons). The relative T1 values are unknown and therefor no additional correction could be applied to accommodate this. So please note that the integration of the new linkages are thus estimations.

Table S2: Linkages content of starting lignin **LA-OR**, R = Et, Bu or Pn and the linkages in these defunctionalized lignin.

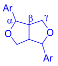
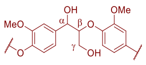
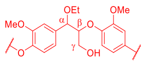
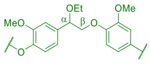
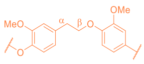
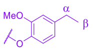
Types of linkages	β-β 	**LA**, β-O-4 a-OH 	**LA-OR**, β'-O-4 a-OR, R=Et, Bu or Pn 	**LB-OR**, R=Et, Bu or Pn 	**LC** 	**LD** 
LA-OEt	10	3	48	none	none	none
LA-OBu	8	3	54	none	none	none
LA-OPn	9	8	49	none	none	none
Defunctionalized LA-OEt	9	0	3	7	18	10
Defunctionalized LA-OBu	9	0	1	4	13	9
Defunctionalized LA-OPn	9	0	2	6	14	11

Table S3: Comparison of S/G ratio and β-β:-OMe ratio lignin of the **LA-OR**, R = Et, Bu or Pn, and the corresponding defunctionalized lignin.

Lignin type	*S/G ratio*[a]		*β-β : -OMe ratio*[a]	
	Initial	*Defunctionalized*	*Initial*	*Defunctionalized*
Ethanosolv	*79/21*	*76/24*	*1:67*	*1:72*
Butanosolv	*74/26*	*72/28*	*1:84*	*1:78*
Pentanosolv	*71/29*	*73/27*	*1:65*	*1:63*

[a] As determined by 2D-HSQC NMR integration

S 5.0 GC-MS data relating to the dehydrogenative decarbonylation of model compounds

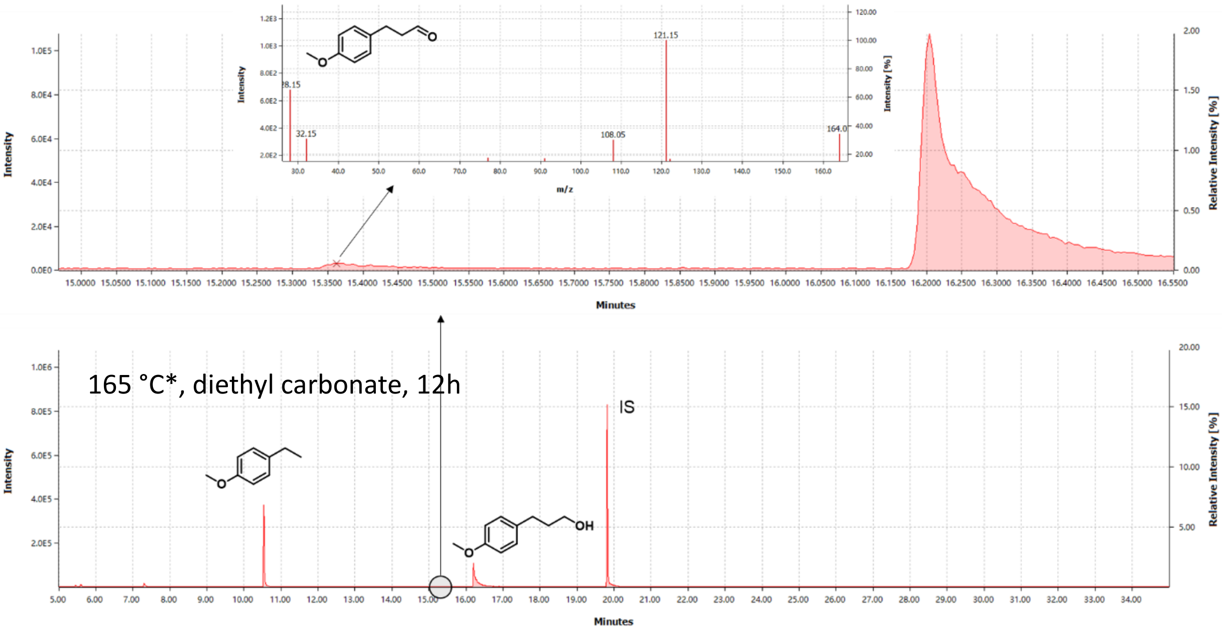


Figure S1: GC spectra of crude product for dehydrogenative decarbonylation of 4-methoxybenzenepropanol (**BP1**) and the MS spectra of the intermediate aldehyde (**BPA**)

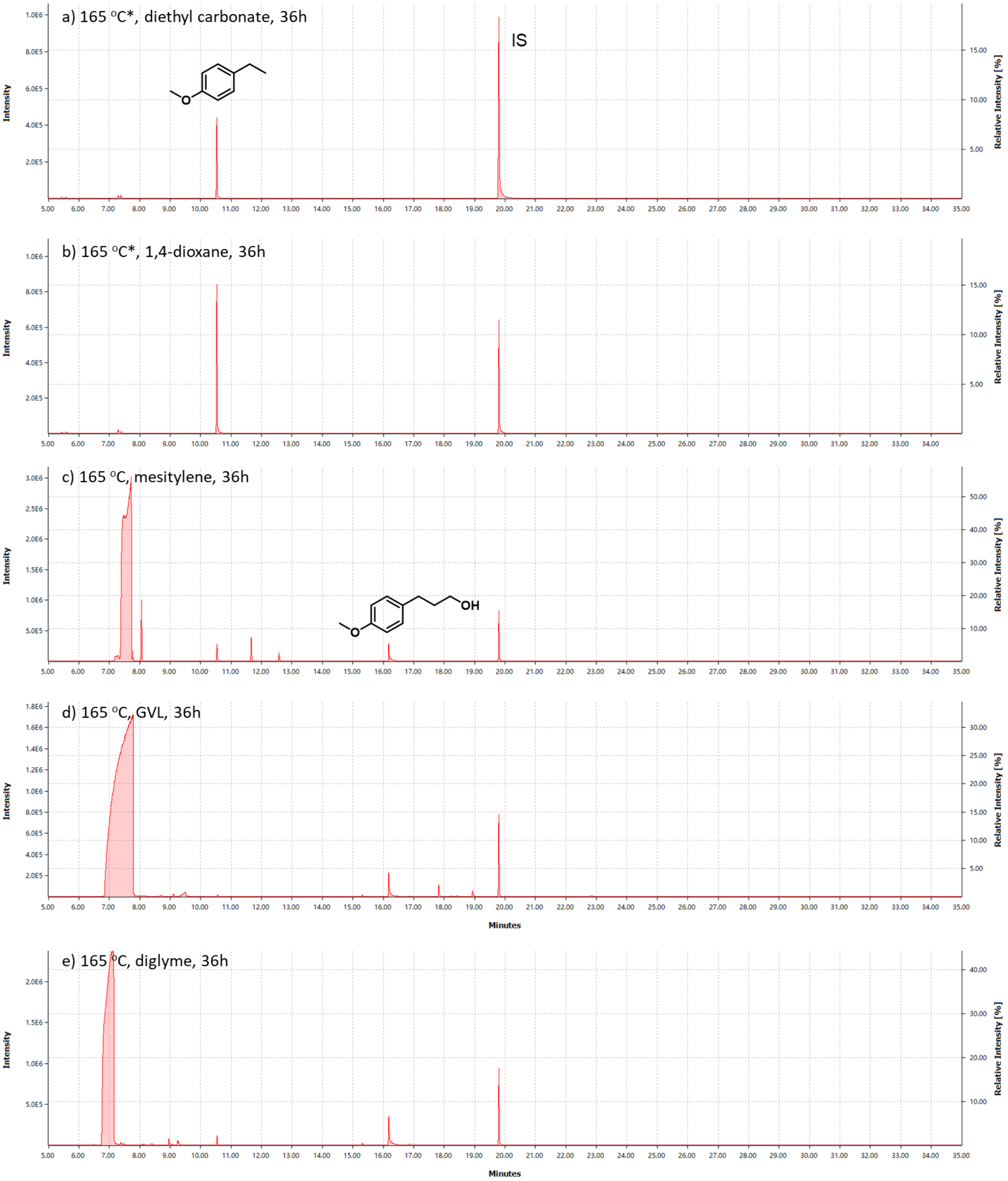


Figure S2: GC spectra of crude product for dehydrogenative decarbonylation of 4-methoxybenzenepropanol (**BP1**) in different solvent

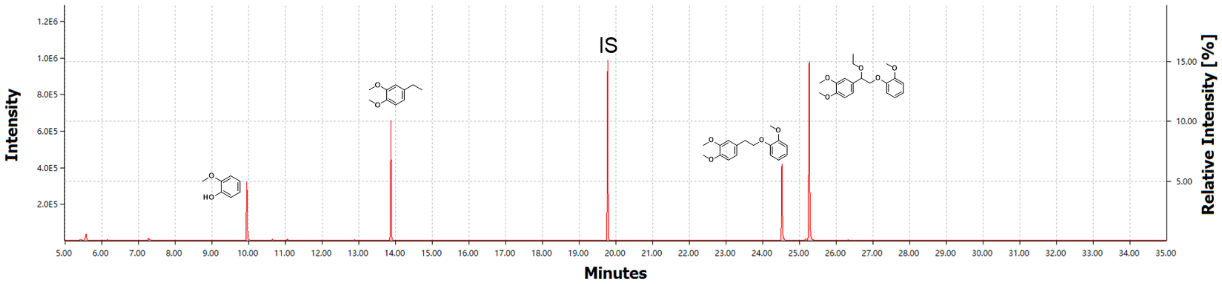


Figure S3: GC spectra of crude product from the dehydrogenative decarbonylation of **A-OEt**. Reaction was performed in 1,4-dioxane at set temperature of 200 °C for 48 hours

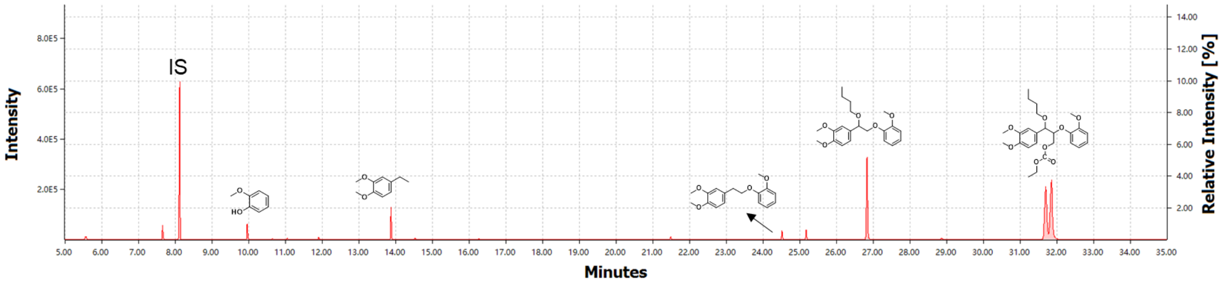


Figure S4: GC spectra of crude product from dehydrogenative decarbonylation of **A-OBu**.

Reaction was performed in diethyl carbonate at set temperature of 200 °C for 48 hours

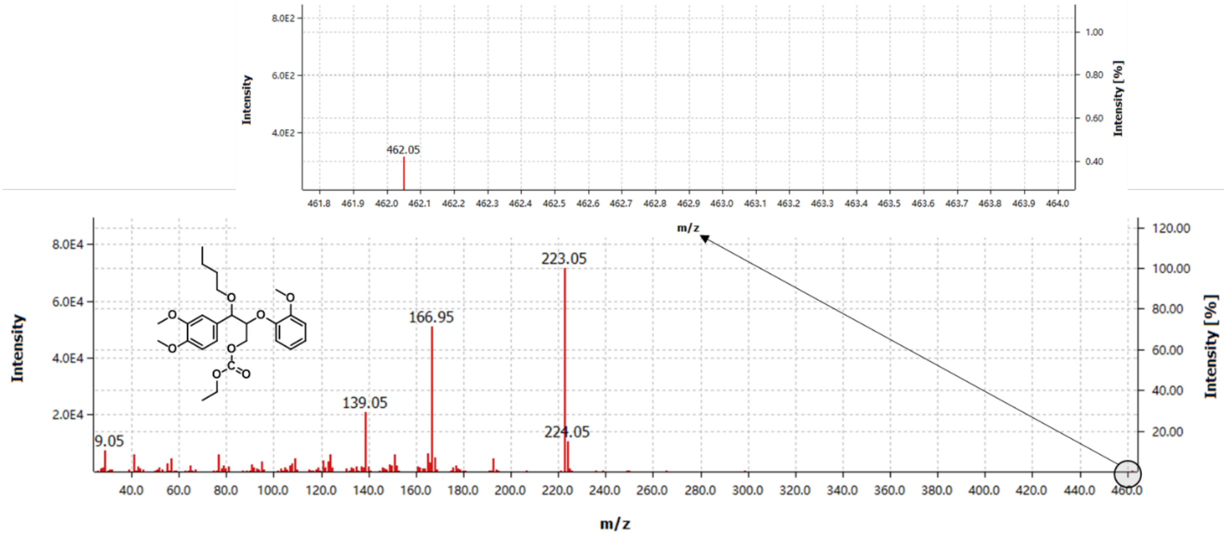


Figure S5: MS spectra of the product of which diethyl carbonate got attached on the γ position of the β-O-4 motif

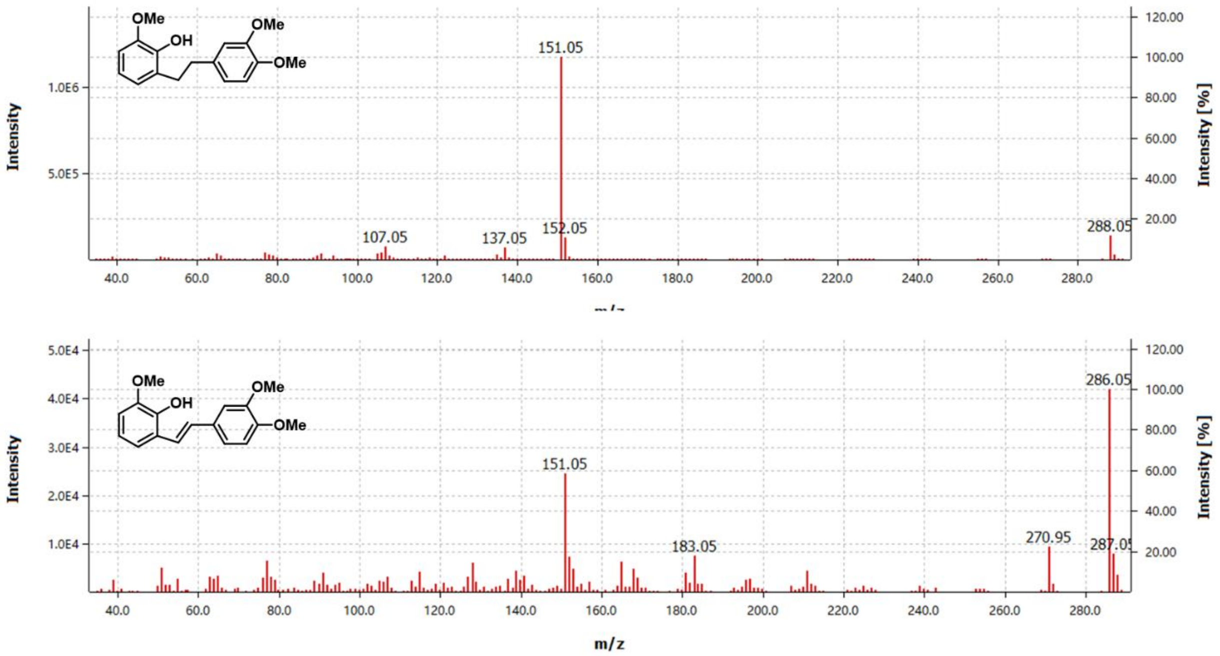


Figure S6: MS spectra of **PC1** and **PC2**

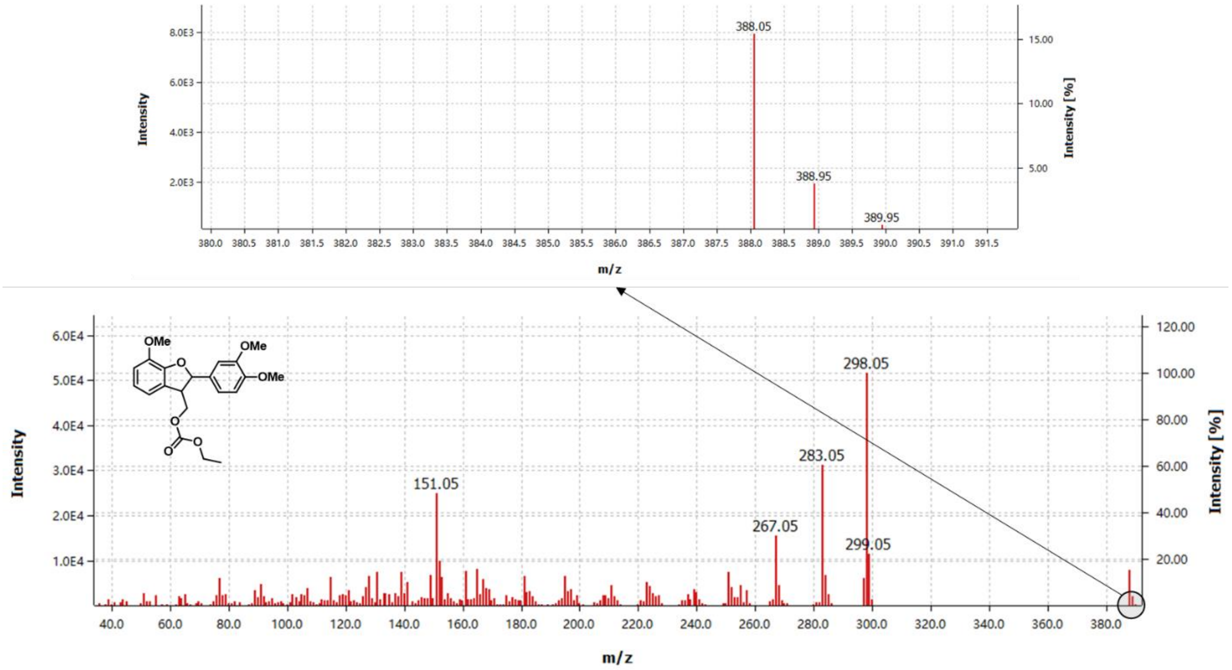


Figure S7: MS spectra of **PC3**

S 6.0 NMRs of the phenyl coumaran model compound

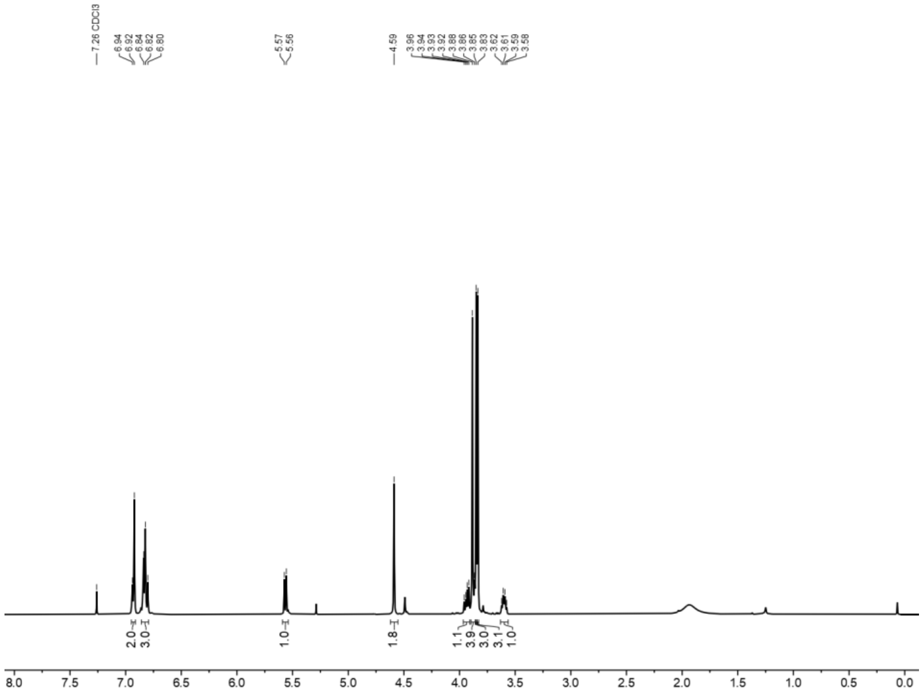


Figure S8: Phenylcoumaran compound **PC**: ^{1}H NMR, 400 MHz, CDCl$_3$

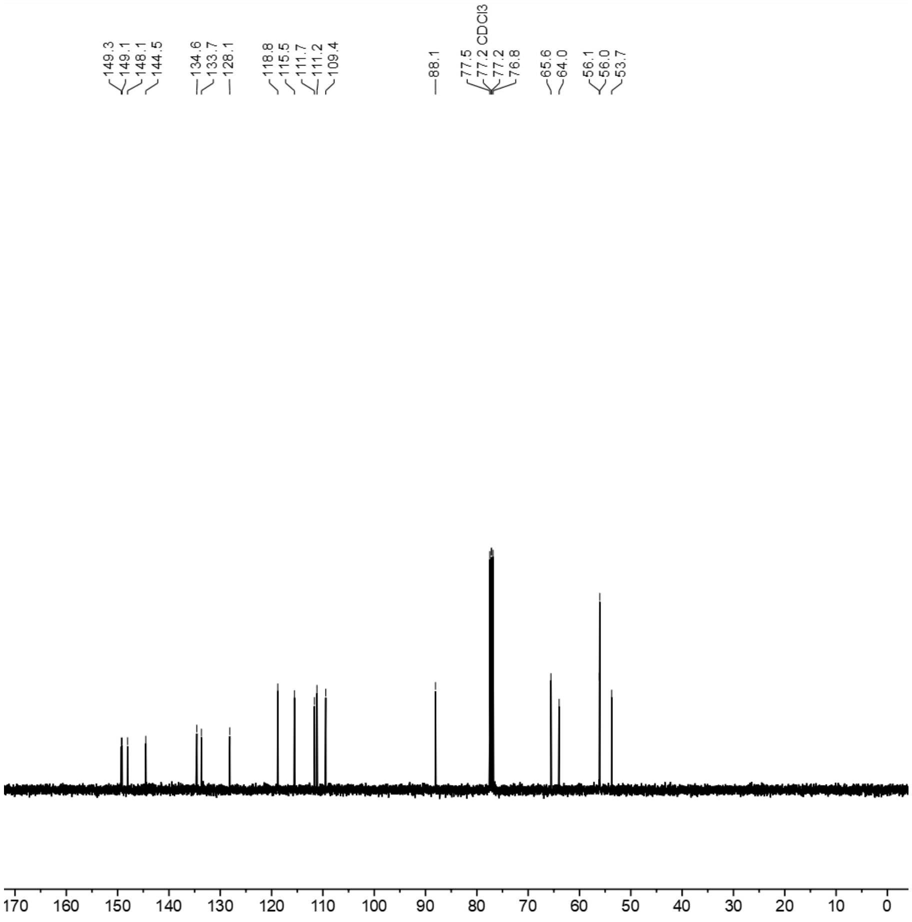


Figure S9: Phenylcoumaran model compound **PC**: ^{13}C NMR, 101 MHz, CDCl$_3$

S 7.0 HSQC of high alcohol incorporation organasolv lignin and the dehydrogenative decarbobylation products

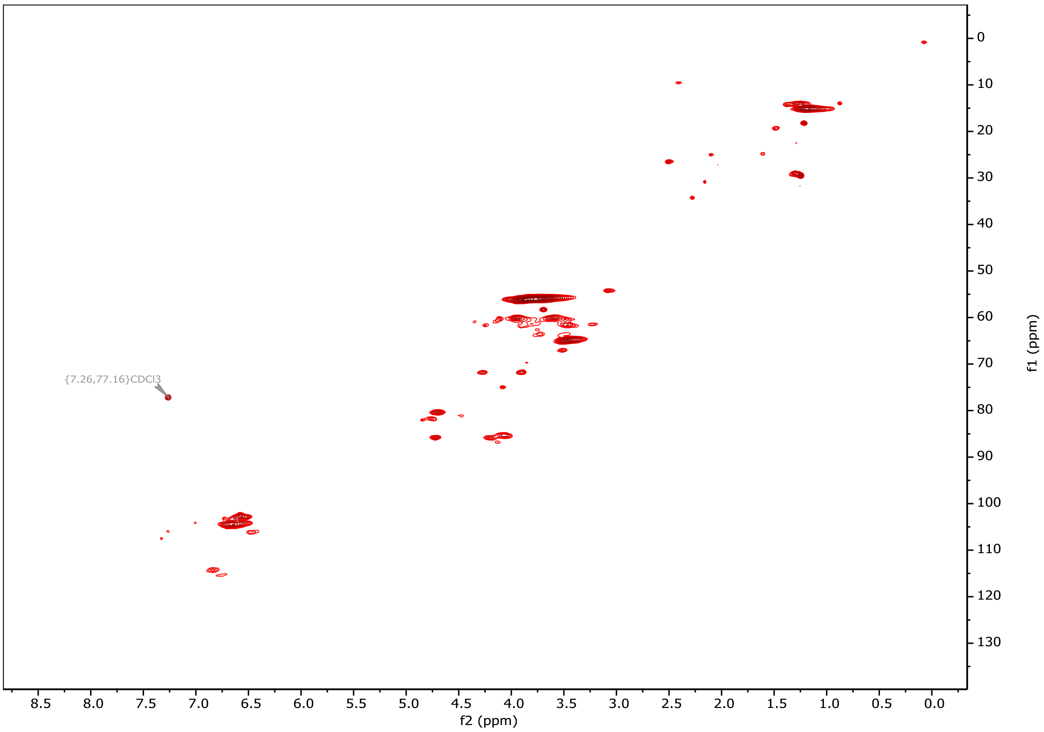


Figure S10: 2D HSQC spectra of α-ethoxylated lignin (**LA-OEt**)

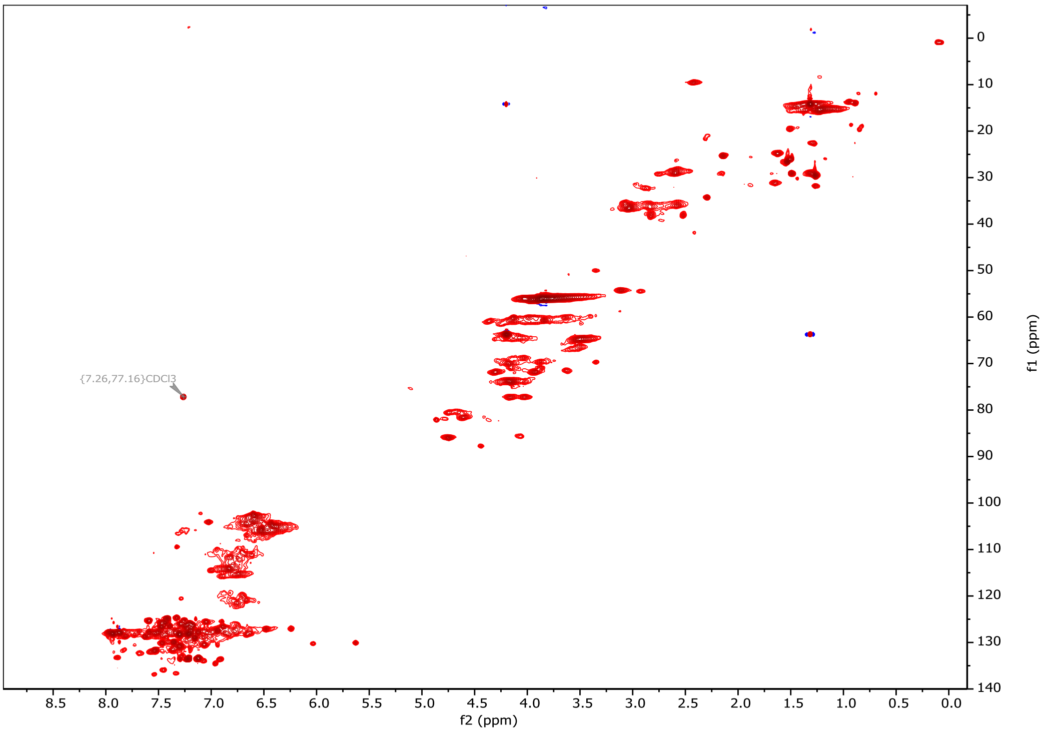


Figure S11: 2D HSQC spectra of the crude product of dehydrogenative decarbonylation of α-ethoxylated lignin (**LA-OEt**). Temperature setting at 205 °C for 48 hours in diethyl carbonate

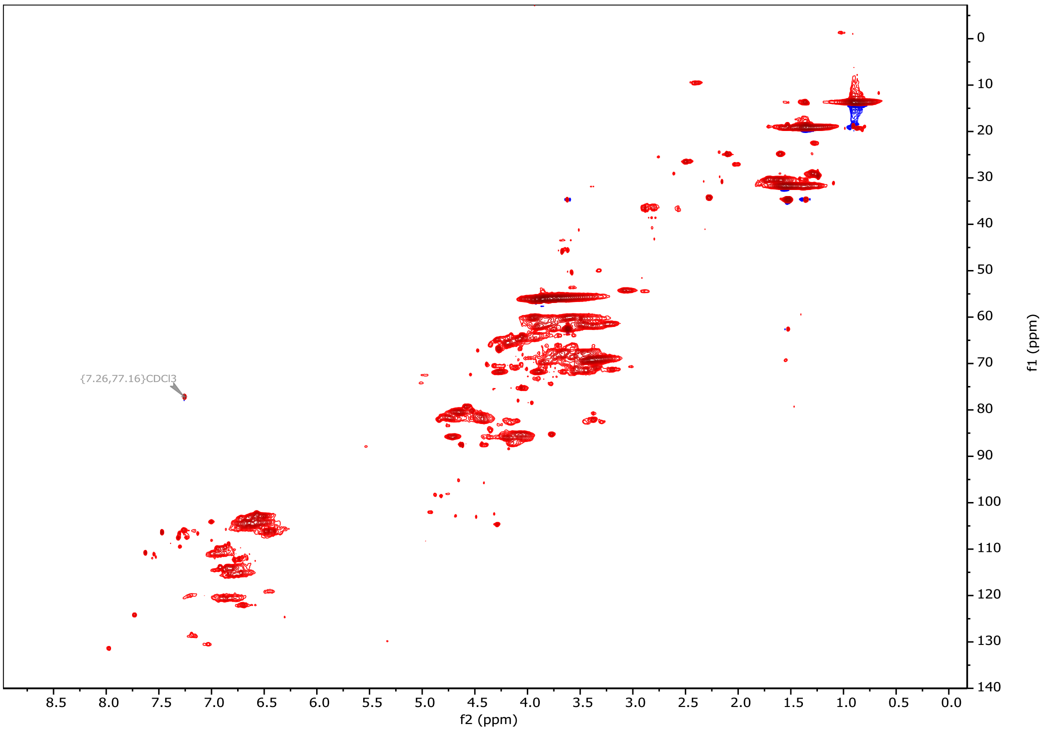


Figure S12: 2D HSQC spectra of α-butoxylated lignin (**LA-OBu**)

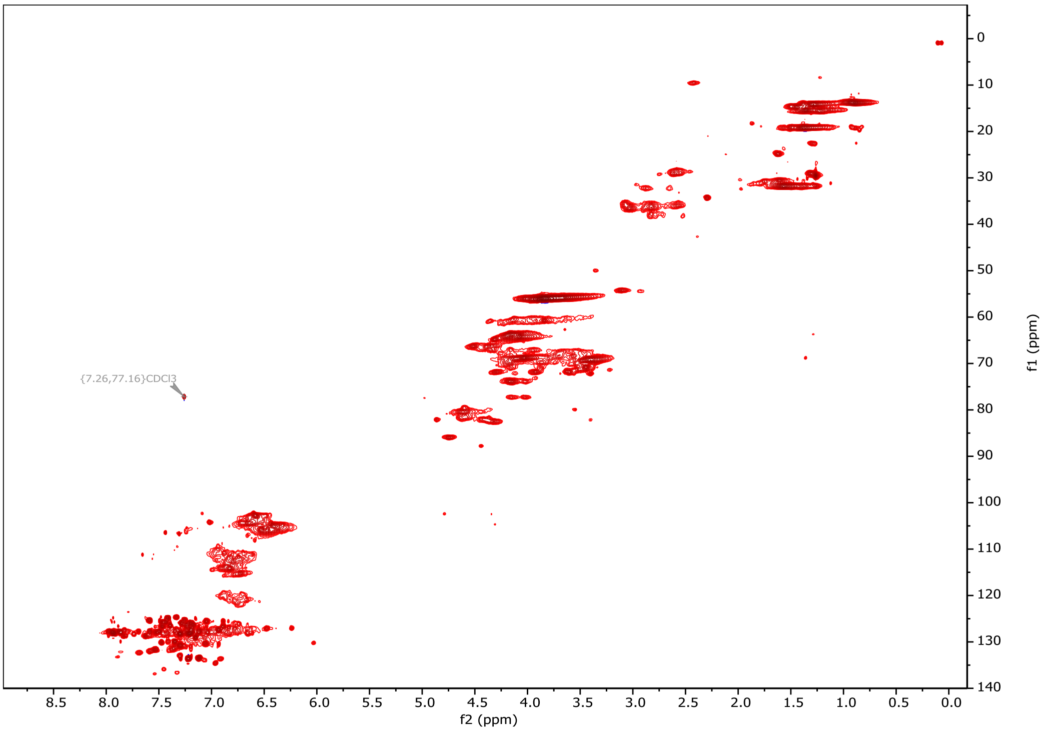


Figure S13: 2D HSQC spectra of crude product of dehydrogenative decarbonylation of α-butoxylated lignin (**LA-OBu**). Temperature setting at 205 °C for 48 h in diethyl carbonate

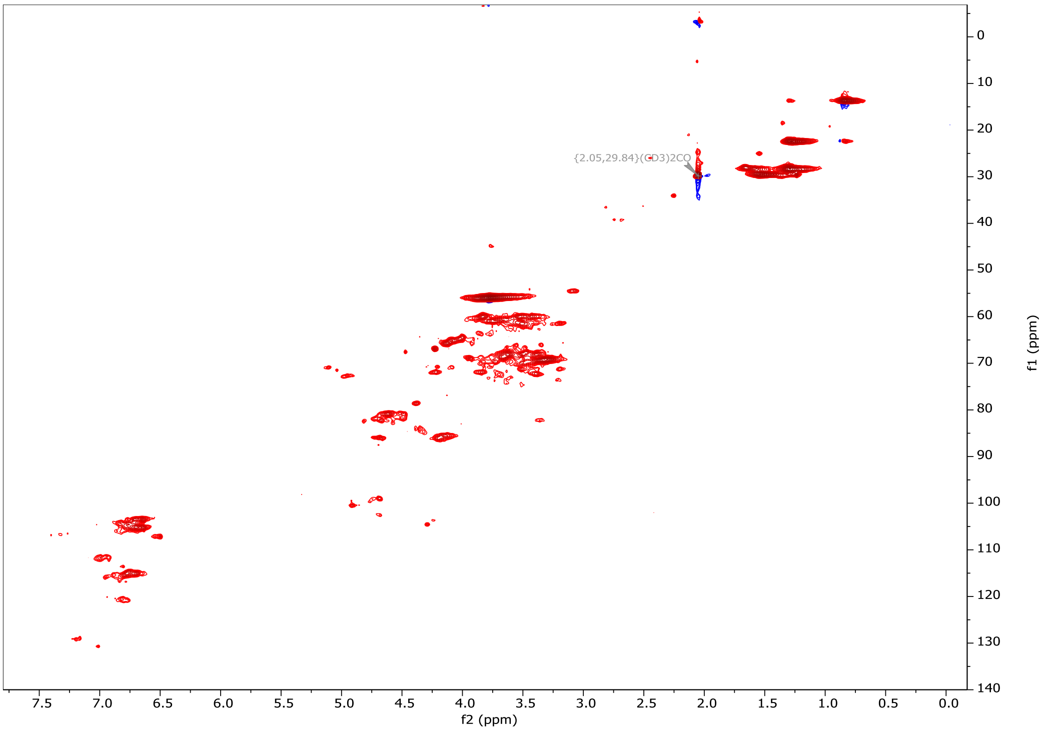


Figure S14: 2D HSQC spectra of α-pentoxylated lignin (**LA-OPn**)

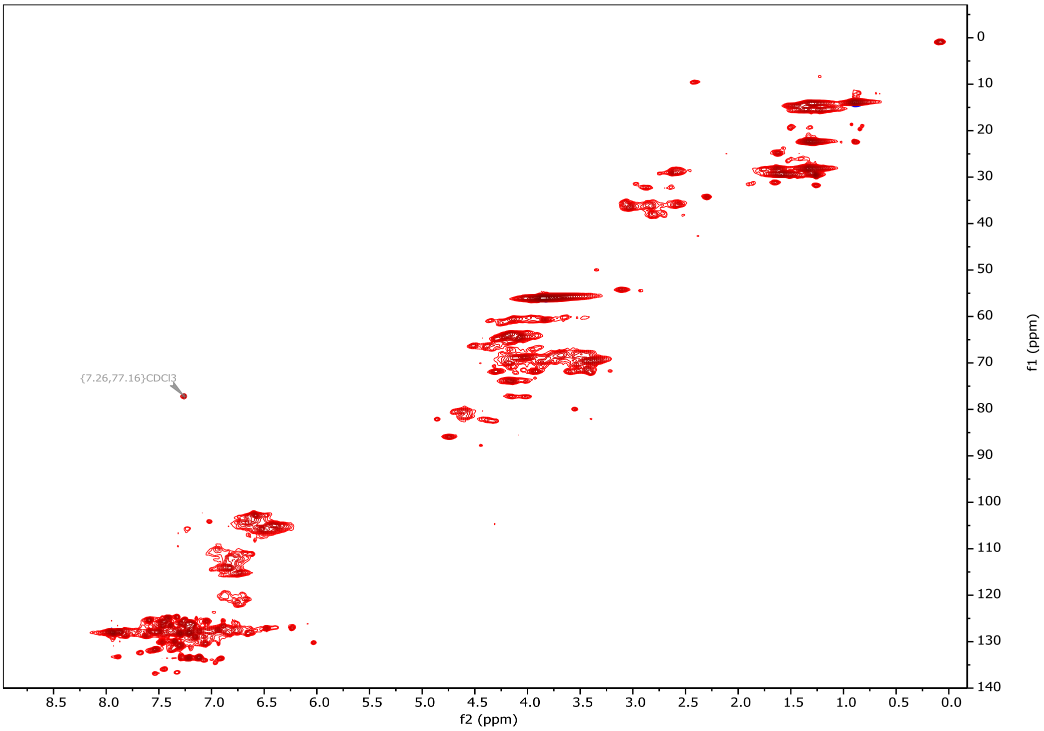


Figure S15: 2D HSQC spectra of the crude product of dehydrogenative decarbonylation of α-pentoxylated lignin (**LA-OPn**). Temperature setting at 205 °C for 48 h in diethyl carbonate

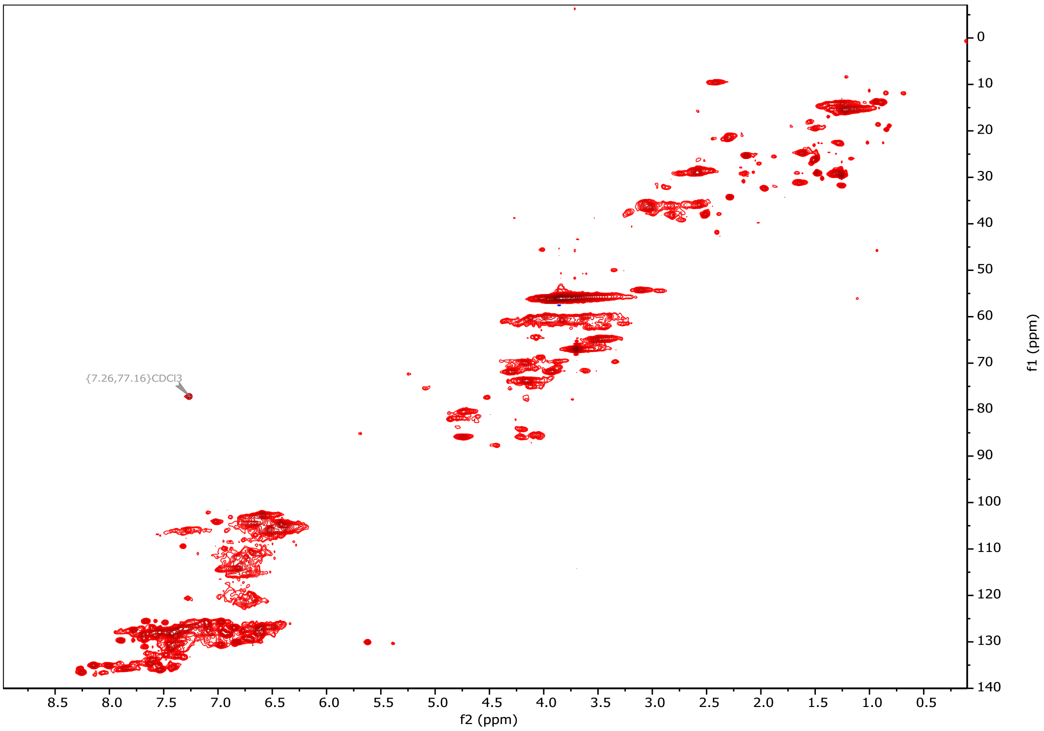


Figure S16: 2D HSQC spectra of the crude product of dehydrogenative decarbonylation of α-ethoxylated lignin (**LA-OEt**). Reaction temperature setting at 205 °C for 48 h in 1,4-dioxane

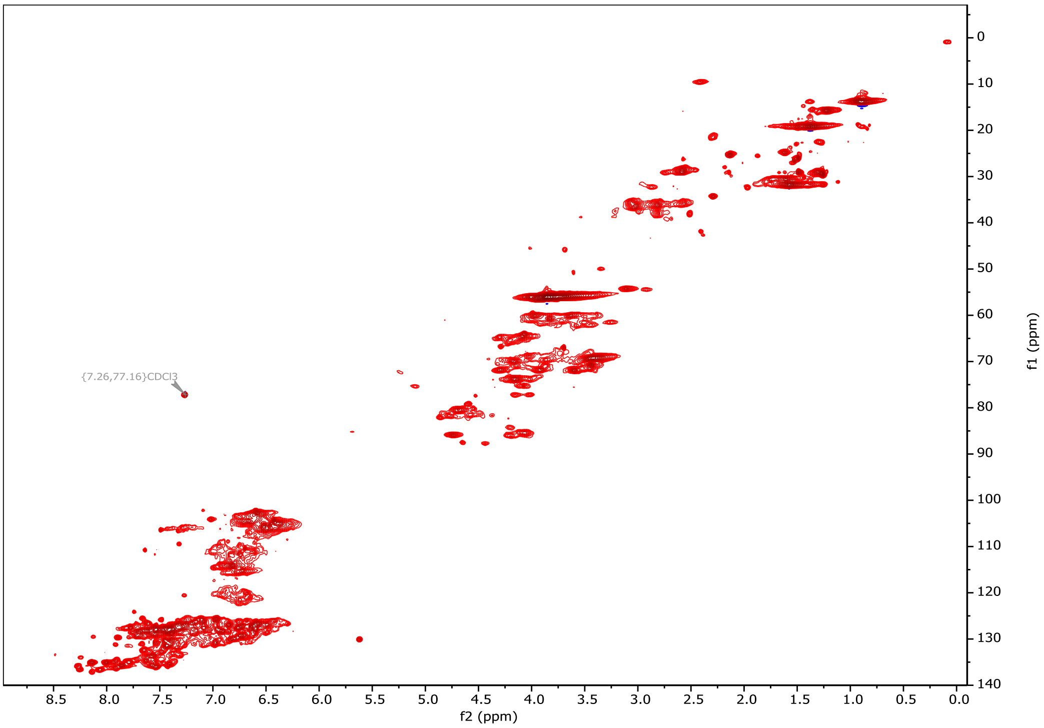


Figure S17: 2D HSQC spectra of the crude product of dehydrogenative decarbonylation of α-butoxylated lignin (**LA-OBu**). Reaction temperature setting at 205 °C for 48 h in 1,4-dioxane

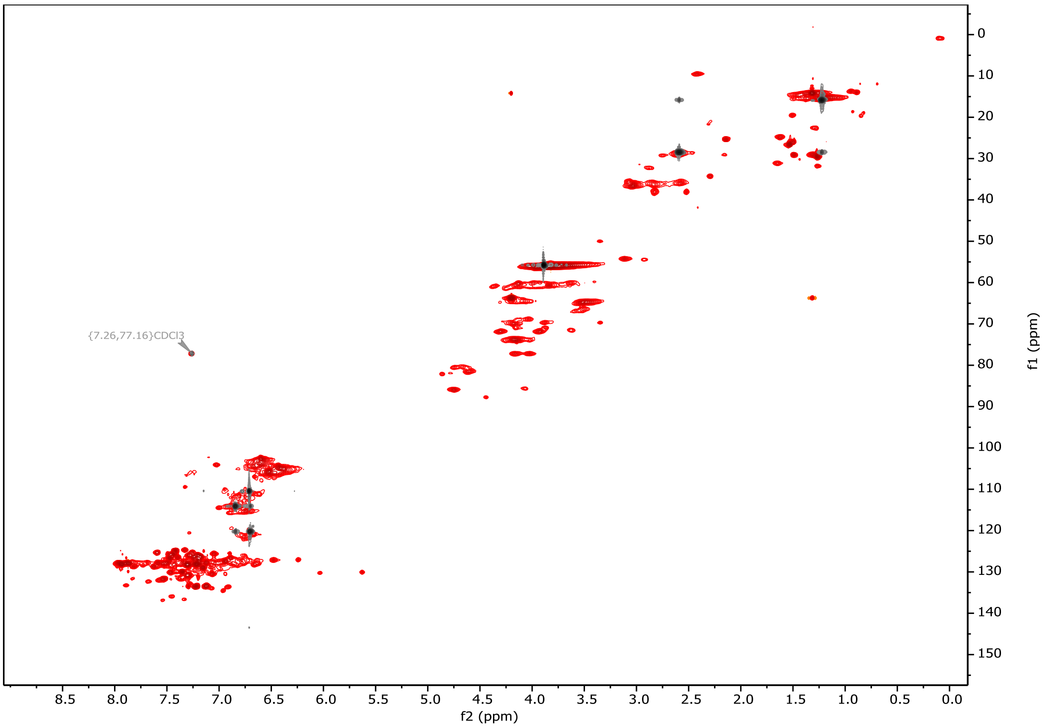


Figure S18: 2D HSQC spectra overlap of α-ethoxylated lignin (**LA-OEt**) after dehydrogenative decarbonylation (red) and the model compound 4-ethylguaiacol (gray)

S 8.0 References

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4. C. S. Lancefield, I. Panovic, P. J. Deuss, K. Barta and N. J. Westwood, *Green Chemistry*, 2017, **19**, 202-214.
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