

## Supplementary Information

# Halogen-Free Bleaching of Shellac Using Electrochemically Generated Peroxodicarbonate

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## 1. General information

All employed chemicals are of analytical grade, were purchased from commercial suppliers and were used as received unless stated otherwise. Seedlac and dewaxed shellac were provided by A.F. Suter. All reactions were carried out at ambient atmosphere unless otherwise stated. Electrodes were obtained from commercial suppliers: boron-doped diamond (DIACHEM®, 15 µm boron-doped diamond layer on 3 mm silicon support/wafer, CONDIAS GmbH, Itzhoë, Germany).

**<sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}-, and <sup>13</sup>C APT-NMR spectra** were recorded on a Bruker Avance III HD 500 MHz spectrometer using CD<sub>3</sub>OD as deuterated solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative the corresponding deuterated solvent.

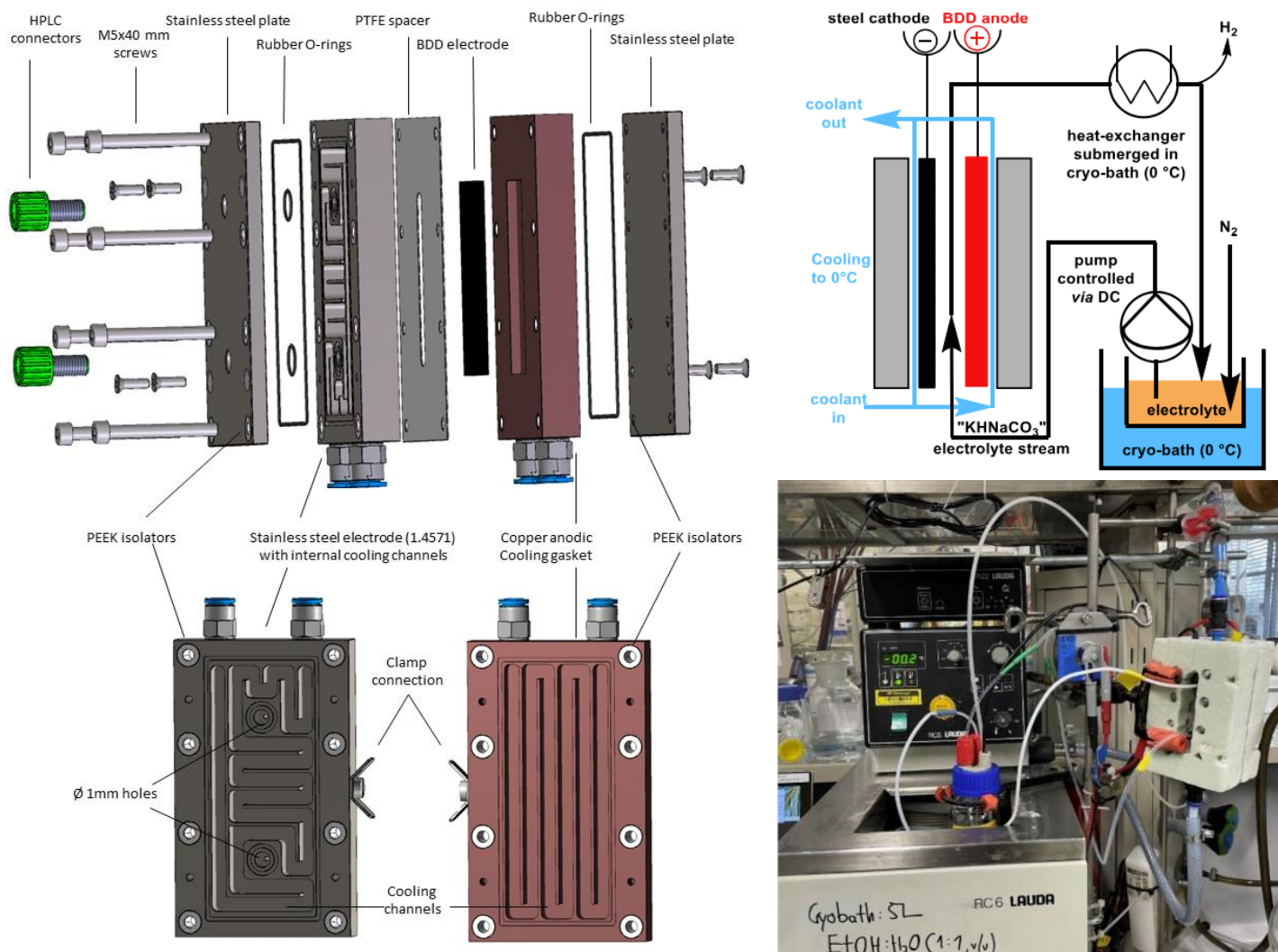
**UV-vis spectroscopy** (Shimadzu UV-3600i plus Spectrophotometer, Tokyo, Japan) was used for the determination of the bleaching efficiency. Absorbance spectra were measured between 400 nm and 700 nm with a medium scan speed and 0,5 nm intervals. All spectra were corrected for background intensities by subtracting the spectra of pure solvent measured under identical conditions.

**Fourier-transformed infrared (FT-IR)** spectra for characterization of shellac were recorded at 20 °C on a Bruker ALPHA ATR spectrometer. Shellac samples were grinded and measured as solids.

### **Electrochemical setup**

The electro-synthesis of peroxodicarbonate was performed in circular flow cell in a set-up slightly adapted from previous work.<sup>1</sup> A Diachem™ boron-doped diamond electrode (A= 2 cm x 6 cm x 0.3 cm, 15 µm BDD on silicon support, CONDIAS GmbH, Itzhoë, Germany) embedded in a copper cooling casting served as the anode, while a stainless-steel plate with internal cooling casting was used as a cathode. A Teflon™ spacer with a thickness off 0.5 mm was placed between the electrodes to ensure a constant interelectrode gap of 0.5 mm and to restrict the active electrode surface to 3.0 cm<sup>2</sup>. The electrolyte was pumped through the cell with Teflon™ tubing (1 mm inner diameter). The tubing was fixed in a coiled state and also functioned as a heat exchanger. The cell is cooled with a cryostat (RC6 cryostat, Lauda, Lauda-Königshofen, Germany) to 0 °C. An ethanol/water mixture (1/1, v/v) served as cooling media. Both, the heat exchanger and the electrolyte reservoir (a 100 mL Schott flask) were immersed in the cooling bath of the cryostat. The temperature was constantly monitored using a DS18B20 temperature sensor with a USB-connected cortex-M microcontroller (Diamex Produktion und Handel GmbH, Heidelberg, Germany). A gentle nitrogen stream was connected to the electrolyte reservoir to ensure sufficient safety by diluting and purging the hydrogen evolved. The electrolyte is pumped through the cell with a membrane pump (Aquamarin 1210 LC PP/EPDM membrane pump, Gardner Denver Thomas GmbH, Memmingen Germany) with a flow rate of 100 mL/min (applied

potential 10 V at 120-130 mA via a HMP4040 galvanostat, Rohde & Schwarz, München, Germany). The applied current of the electrolysis was controlled using a HMP4040 galvanostat (Rohde & Schwarz, München, Germany) in constant current mode as a power source. The electrolysis can be controlled remotely via an open-source python-based user interface ([https://github.com/marcodyga/power\\_supply\\_gui](https://github.com/marcodyga/power_supply_gui)). A schematic drawing of the electrolysis set up and an exploded view of the flow electrolyser are depicted in Figure S1.



**Figure S1** Left: Exploded view of narrow-gap flow electrolyser. Right top: schematic drawing of electrochemical setup. Right bottom: Electrolysis set-up.

## 2. Experimental procedures

### 2.1. Measurement of bleaching efficiency (%Bleach)

#### Calibration curve

A dilution series of unbleached shellac was prepared. 1 g unbleached shellac was dissolved in ethanol to obtain a 100 mL solution of 1% shellac. This stock solution was further diluted to different concentrations. The absorbance spectra of all diluted shellac solutions were measured between 400 nm and 700 nm, using ethanol as a blank sample (Figure S2a). The absorbance of shellac at 430 nm was selected for bleaching quantification as stated in literature.<sup>2</sup> A calibration curve was plotted with on the x-axis the absorbance at 430 nm and on the y-axis the bleaching efficiency (%bleach), defined as:

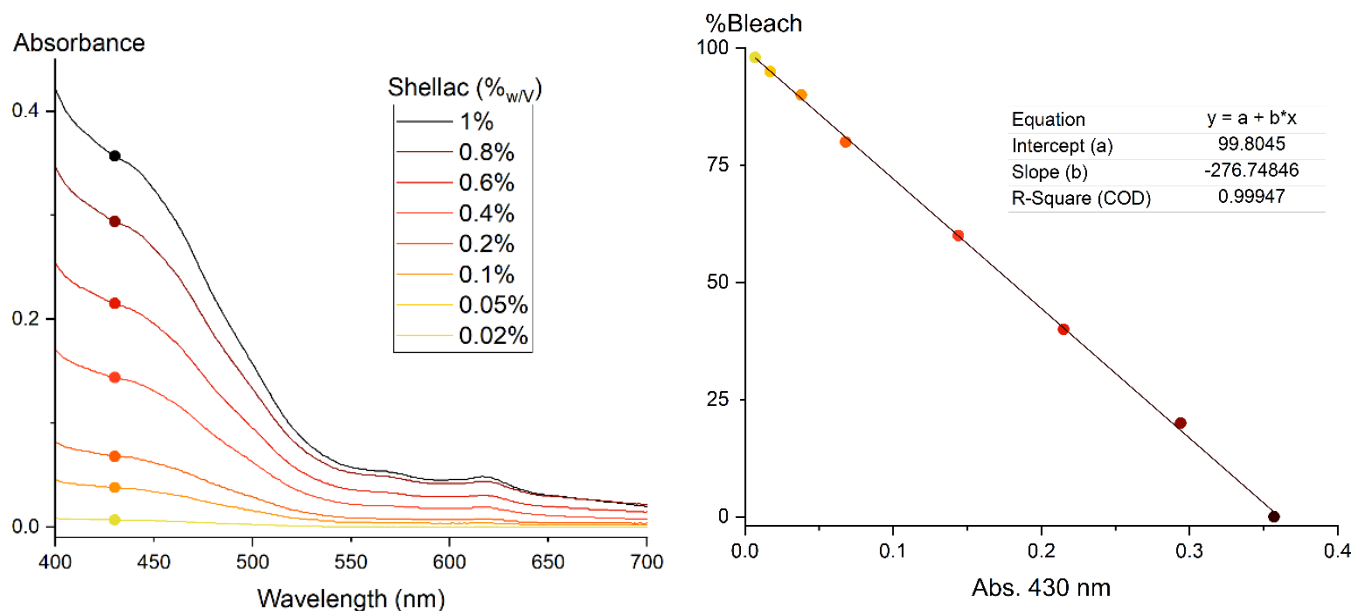
$$\%Bleach = \left(1 - [shellac]_{\frac{w}{v}}\right) \times 100$$

With  $[Shellac]_{w/v}$  being the weight concentration of the solution in % (Figure S2b). A linear fit was obtained with following parameters:

$$y = a + bx$$

$$a = 99.8045$$

$$b = -276.74846$$



**Figure S2 a.** UV-vis spectra of different concentrations of unbleached shellac in ethanol. **b.** Calibration curve at 430 nm expressing the absorbance at the x-axis and the bleaching efficiency (%bleach) at the y-axis

## **Quantification of the bleaching efficiency**

Precisely 100 mg bleached shellac was weighted in a 10 mL volumetric flask. 8 mL Ethanol was added, and the volumetric flask was shaken with a shaking plate for 3 hours until complete dissolution. The volume was adjusted precisely to 10 mL and a UV-vis spectra was measured between 400 nm and 700 nm. The absorbance at 430 nm was used to calculate the bleaching efficiency according to the calibration curve (Figure S2B).

### **2.2. Acid Value**

Acid values were determined using an acid-base titration adapted from the European Pharmacopoeia 2008.<sup>3</sup> Exactly 2 g of shellac was dissolved in 50 mL ethanol and titrated with 0.1 M NaOH at room temperature. In all cases, a pH-meter was used to titrate the solution to the endpoint (pH = 8.3). The acid value was expressed in mg<sub>KOH</sub> required to neutralize 1 g of shellac according to following formula:

$$Acid\ Value = \frac{5.61056 \times V}{m_{shellac}}$$

With V, the volume of titration in mL, and  $m_{shellac}$  the weighted amount of shellac in gram.

### **2.3. Electrosynthesis of peroxodicarbonate (11)**

#### **Synthesis of peroxodicarbonate solution (11):**

95.4 g Na<sub>2</sub>CO<sub>3</sub>, 155.5 g K<sub>2</sub>CO<sub>3</sub> and 22.5 g KHCO<sub>3</sub> were added into a 1000 mL volumetric flask and filled with water. This resulted in a 0.90 M Na<sub>2</sub>CO<sub>3</sub>, 1.125 M K<sub>2</sub>CO<sub>3</sub> and 0.225 M KHCO<sub>3</sub>. 35 mL of this solution was transferred into a 100 mL screw cap glass container, which was placed in the coolant mixture of the cryostat. A USB temperature sensor was placed inside of the electrolyte. The solution was circulated through the electrolysis system at a constant flow rate of 100 mL/min until the electrolyte temperature reached 0 °C. An interelectrode gap of 0.5 mm and an available anode surface of 3 cm<sup>2</sup> were used. Then, the solution was electrolyzed using the circular flow cell at a constant current density of 3.33 A/cm<sup>2</sup> for 60.0 minutes, corresponding to an applied charge of 36000 C (4.7 F) relative to total carbonate. After the electrolysis, the sample container was placed in an ice bath.

#### **Determination of the peroxodicarbonate concentration:**

Directly after the electrolysis a 2 mL volumetric pipette was pre-cooled by pumping 2 mL of cold electrolyte solution into the pipette and immediately returning it into the electrolyte three times. Next, 2 mL of the electrolyte was transferred into an Erlenmeyer flask containing 5 mL H<sub>2</sub>SO<sub>4</sub> (20%<sub>v/v</sub> in water). 5 mL off an

aqueous solution of KI (6%<sub>w/v</sub> in H<sub>2</sub>O) and three drops of ammonium heptamolybdate solution (3%<sub>w/v</sub> in H<sub>2</sub>O) were added. The brown solution was titrated against a standard solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.1 M). The endpoint of the titration was determined by the complete disappearance of the yellow colour of free I<sub>2</sub>. Titration was conducted three times, and the resulting average concentration of total oxidizer was then calculated by standard error calculations. Concentrations between 800 – 900 mM of **11** could be achieved.

#### **pH adjustment of peroxodicarbonate:**

The correct volume of a freshly prepared and titrated peroxodicarbonate solution was transferred with a glass volumetric pipette to a pre-cooled Erlenmeyer flask placed in an ice-bath. A pH electrode was placed in the cooled solution and the pH of **11** was adjusted by dropwise addition of a pre-cooled solution of H<sub>2</sub>SO<sub>4</sub> (5%<sub>v/v</sub> in water) while gently swirling the Erlenmeyer flask.

### **2.4. Bleaching optimisation**

#### **General procedure for optimisation:**

Bleaching optimisation was performed on a 5 g scale of dewaxed shellac (A.F. Suter AFS 750 Dewaxed Shellac). In a 250 mL round-bottom flask equipped with a magnetic stir bar was added 5 g shellac, 0.5 g Na<sub>2</sub>CO<sub>3</sub> and 100 mL distilled water. The flask was stirred for 30 min at 85 °C. Afterwards, the solution was cooled to the stated temperature and acetonitrile was added. To the vigorously stirred shellac solution was added dropwise 10 mmol of a freshly prepared, titrated and pH adjusted peroxodicarbonate **11** solution, continuously cooled to 0 °C, using a glass Pasteur pipette. During addition, a precipitation may be formed, and the addition is paused to circumvent coagulation of shellac. The precipitate rapidly re-dissolves. The bleaching solution was stirred at the stated temperature for the required time. Next, the reaction is cooled to 20 °C and shellac is precipitated by dropwise addition of 5% H<sub>2</sub>SO<sub>4</sub> in water to a pH of 4 (measured using pH stripe). The precipitate was stirred vigorously for 10 minutes and big clumps were broken with a spatula to ensure complete precipitation and protonation. Shellac was filtered through a glass filters (G4 sintered glass) using a membrane vacuum pump. The precipitate was excessively washed with distilled water and broken to small particles with a spatula to ensure complete removal of excess acid. Washing is repeated until the filtrate reaches neutral pH. The bleached shellac is dried in the glass filter under a constant stream of air followed by storage in a desiccator with CaCl<sub>2</sub> under vacuum for two days before quantification of the bleaching efficiency and acid value.

#### **Optimisation of the acetonitrile quantity:**

Reactions were performed according to the general optimisation procedure without pH adjustment of the freshly generated high concentration peroxodicarbonate (pH ~12) at room temperature for 4 hours with different amounts of acetonitrile (Table S1)

Eq. (acetonitrile)	n(acetonitrile)	V (acetonitrile)	Absorbance	%Bleach	Acid value
eq.	mmol	mL	AU	%	mg <sub>KOH</sub> /g
0	0	0.00	0.362	0	77
0.3	3	0.16	0.236	34	84
0.5	5	0.26	0.186	48	87
1	10	0.52	0.163	55	90
<b>1.5</b>	<b>15</b>	<b>0.78</b>	<b>0.137</b>	<b>62</b>	<b>92</b>
2	20	1.04	0.133	63	93
5	50	2.60	0.138	61	95

**Table S1** Optimisation table for the acetonitrile quantity.

#### **Optimisation of the peroxodicarbonate pH:**

Reactions were performed according to the general optimisation procedure with pH adjustment of the freshly generated high concentration peroxodicarbonate at room temperature for 4 hours with 0.78 mL acetonitrile (15 mmol) (Table S2):

pH	Absorbance	%Bleach	Acid value
	AU	%	mg <sub>KOH</sub> /g
9.50	0.247	32	86
10.00	0.187	48	87
10.50	0.157	56	89
11.00	0.142	61	91
11.50	0.144	60	91
<b>12.00</b>	<b>0.137</b>	<b>62</b>	<b>92</b>

**Table S2** Optimisation table for the pH of the peroxodicarbonate solution.

#### **Optimisation of the bleaching temperature:**

Reactions were performed according to the general optimisation procedure without pH adjustment of the freshly generated high concentration peroxodicarbonate at various temperatures for 4 hours with 0.78 mL acetonitrile (15 mmol) (Table S3):

Temperature	Absorbance	%Bleach	Acid value
°C	AU	%	mg <sub>KOH</sub> /g
0	0.242	33	81
<b>20*</b>	<b>0.137</b>	<b>62</b>	<b>92</b>
<b>30*</b>	<b>0.128</b>	<b>64</b>	<b>93</b>
40	0.135	62	95
50	0.152	58	97
60	0.161	55	102

**Table S3** Temperature optimisation. \* A temperature range of 25-30 was chosen to be optimal.



### Optimisation of the bleaching time

Reactions were performed according to the general optimisation procedure without pH adjustment of the freshly generated high concentration peroxod carbonate at ambient temperature for various times with 0.78 mL acetonitrile (15 mmol) (Table S4):

<b>Time</b>	<b>Absorbance</b>	<b>%Bleach</b>	<b>Acid value</b>
hours	AU	%	mg <sub>KOH</sub> /g
0	0.337	6	76
1	0.209	42	81
2	0.164	54	84
4	0.131	64	93
6	0.109	70	95
<b>8*</b>	<b>0.106</b>	<b>70</b>	<b>98</b>
20	0.115	68	107

**Table S4** Time optimisation

### **2.5. Optimised bleaching procedure with peroxod carbonate**

Optimised bleaching is following the general procedure for optimisation using 1.5 equivalents of acetonitrile relative to **11**, without pH adjustment at a temperature range between 25 °C and 30 °C, for 8 hours.

<b>11</b>	<b>Absorbance</b>	<b>%Bleach</b>	<b>Acid value</b>
mmol/g(shellac)	AU	%	mg <sub>KOH</sub> /g
1	0.166	54	90
2	0.109	70	95
3	0.086	76	96
4	0.053	85	98
5	0.032	91	104
6	0.023	94	109

**Table S5** Bleaching with different amounts of **11**

### **2.6. Bleaching procedure with NaOCl**

Bleaching with NaOCl (12%) was performed in a similar procedure as described in 2.5. However, no acetonitrile was added and instead of **11**, various amounts of NaOCl were added. Bleaching time was shortened to two hours as described in literature.<sup>2</sup> Drying of the bleached shellac was done as described in 2.5.

NaOCl	Absorbance	%Bleach	Acid value
mmol/g(shellac)	AU	%	mg <sub>KOH</sub> /g
0.3	0.136	62	73
0.5	0.022	94	74
1.0	0.014	96	77
1.5	0.007	98	83
2.0	0.006	98	88

**Table S6** Bleaching with different amounts of NaOCl.

## 2.7. Bleaching procedure with H<sub>2</sub>O<sub>2</sub>

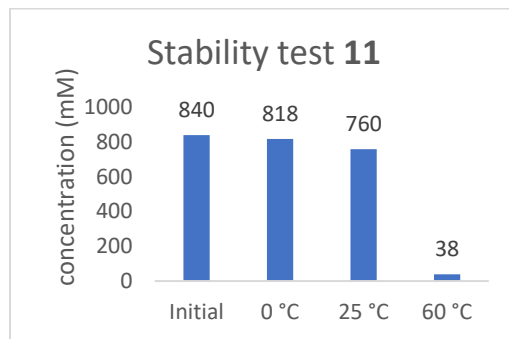
Bleaching with hydrogen peroxide was performed according to a modified literature procedure.<sup>4</sup> In a 250 mL round-bottom flask equipped with a magnetic stir bar was added 5 g shellac, 0.5 g Na<sub>2</sub>CO<sub>3</sub> and 100 mL distilled water. The flask was stirred for 30 min at 85 °C. Afterwards, the temperature was increased to 90 °C and a pH electrode was placed in the solution. The pH was adjusted to 10 by addition of 0.1 M NaOH. Next, 100 mg Na<sub>2</sub>SiO<sub>3</sub> and 25 mg MgSO<sub>4</sub> were added as stabilizers followed by the dropwise addition of various amounts of H<sub>2</sub>O<sub>2</sub> (35%) within 2 hours, while maintaining a pH of 10. After 7 hours, the solution was filtered over Celite™. Precipitation, filtration and drying of shellac was done according to the procedure described in 2.5.

H <sub>2</sub> O <sub>2</sub>	Absorbance	%Bleach	Acid value
mmol/g(shellac)	AU	%	mg <sub>KOH</sub> /g
3.0	0.208	42	104
6.0	0.117	68	132
9.0	0.088	76	142
12.0	0.061	83	164
15.0	0.039	89	176

**Table S7** Bleaching with different amounts of hydrogen peroxide.

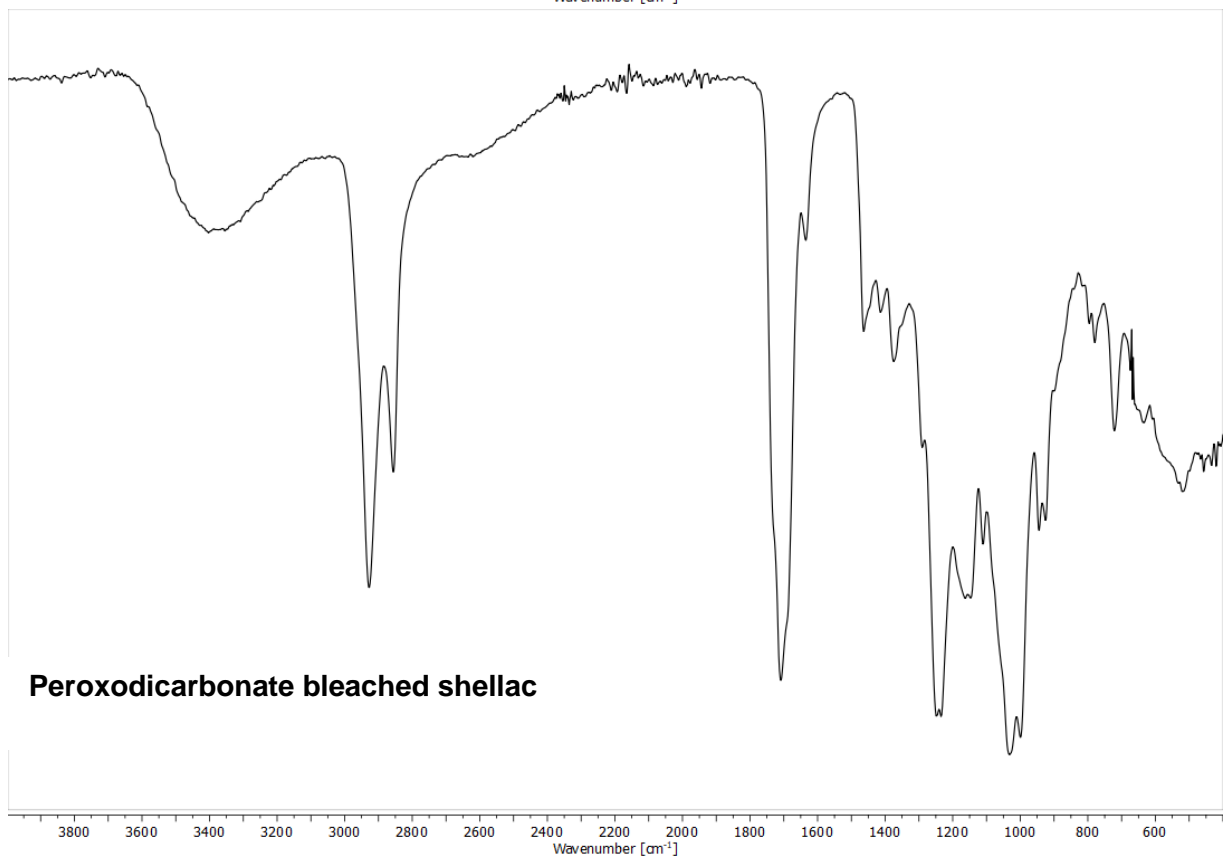
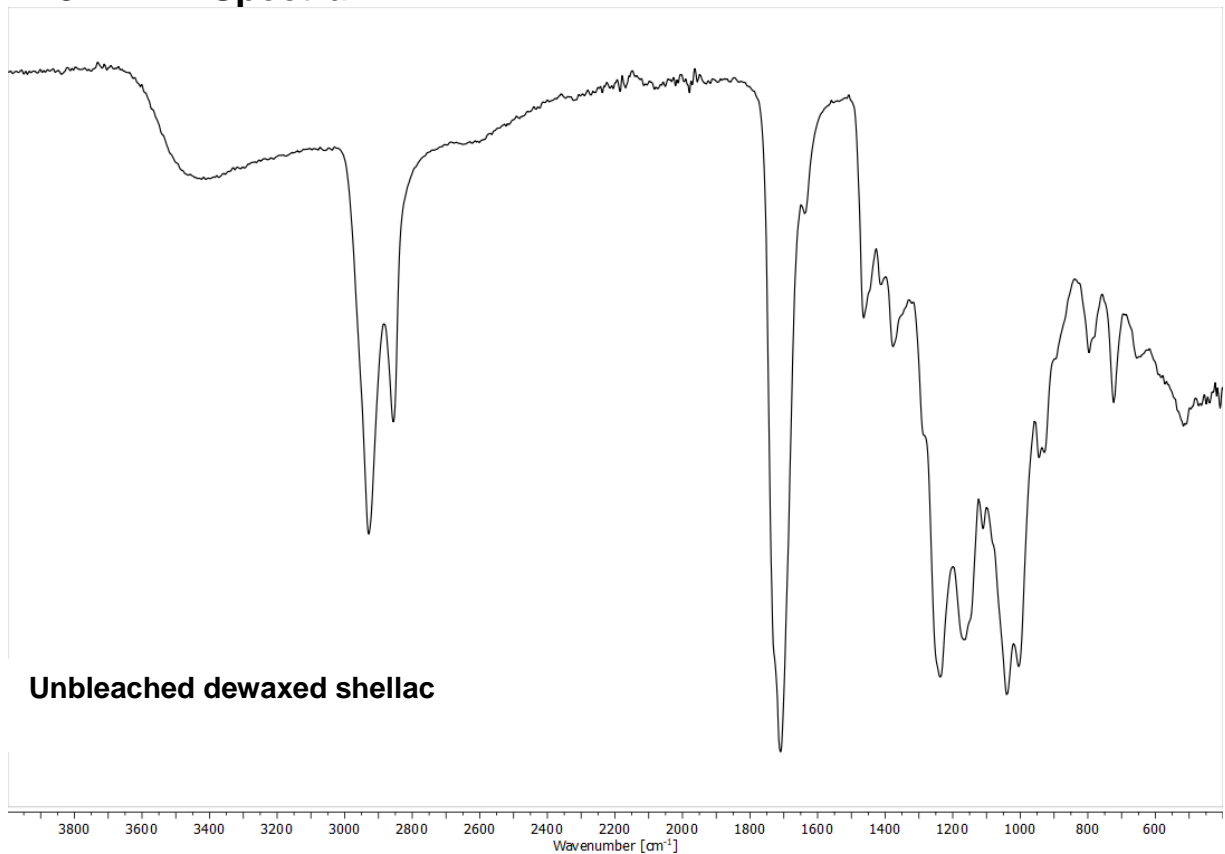
## 2.8. Stability test 11

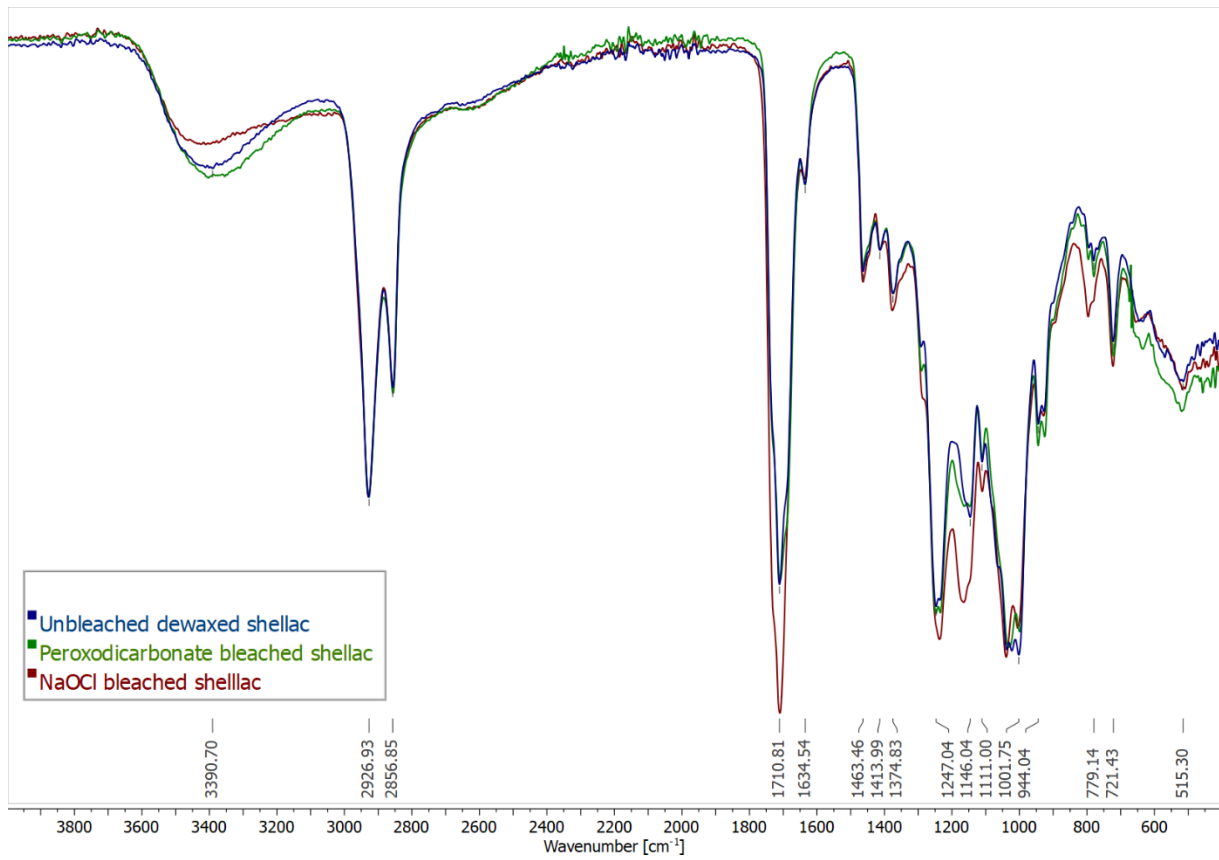
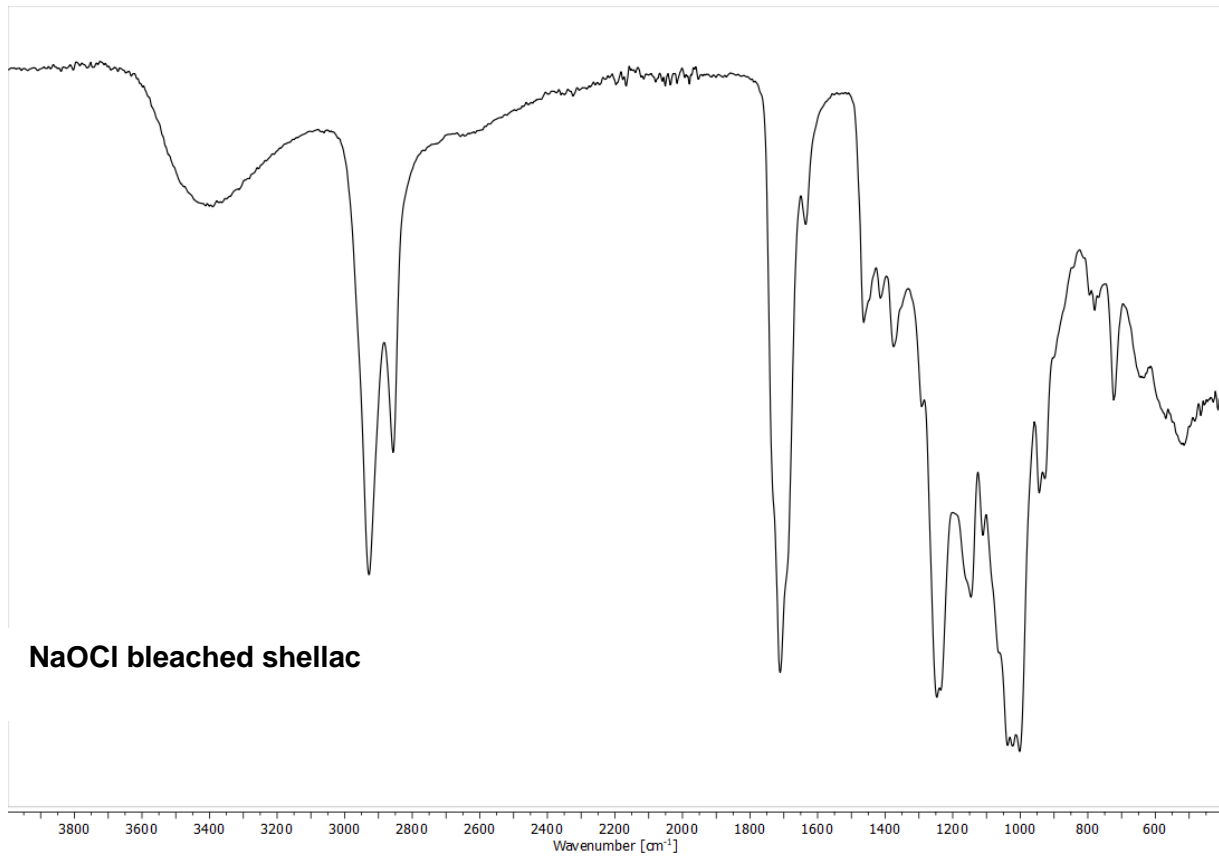
A solution of **11** was prepared and titrated according to the procedure described in 2.3. Next, two times 2 mL of the freshly prepared solution was transferred into 2 reaction tube while the reservoir of **11** was kept in the cryo-bath. One reaction tube was kept at room temperature for 20 min while to other one was heated to 60 °C in an oil bath. Afterward, the solutions at 0 °C, 25 °C and 60 °C where titrated according to the procedure 2.3 and the results are presented in Figure S4.



**Figure S4** Stability test of **11** at various temperatures.

### 3. FT-IR Spectra

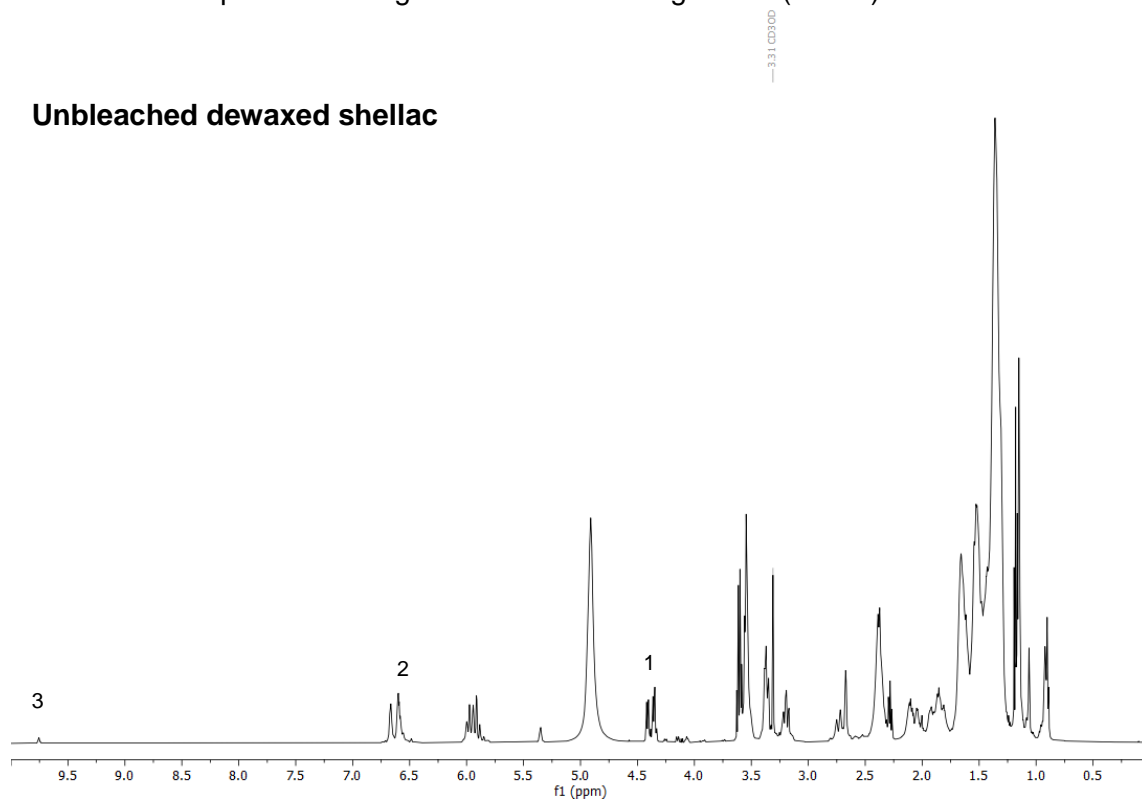




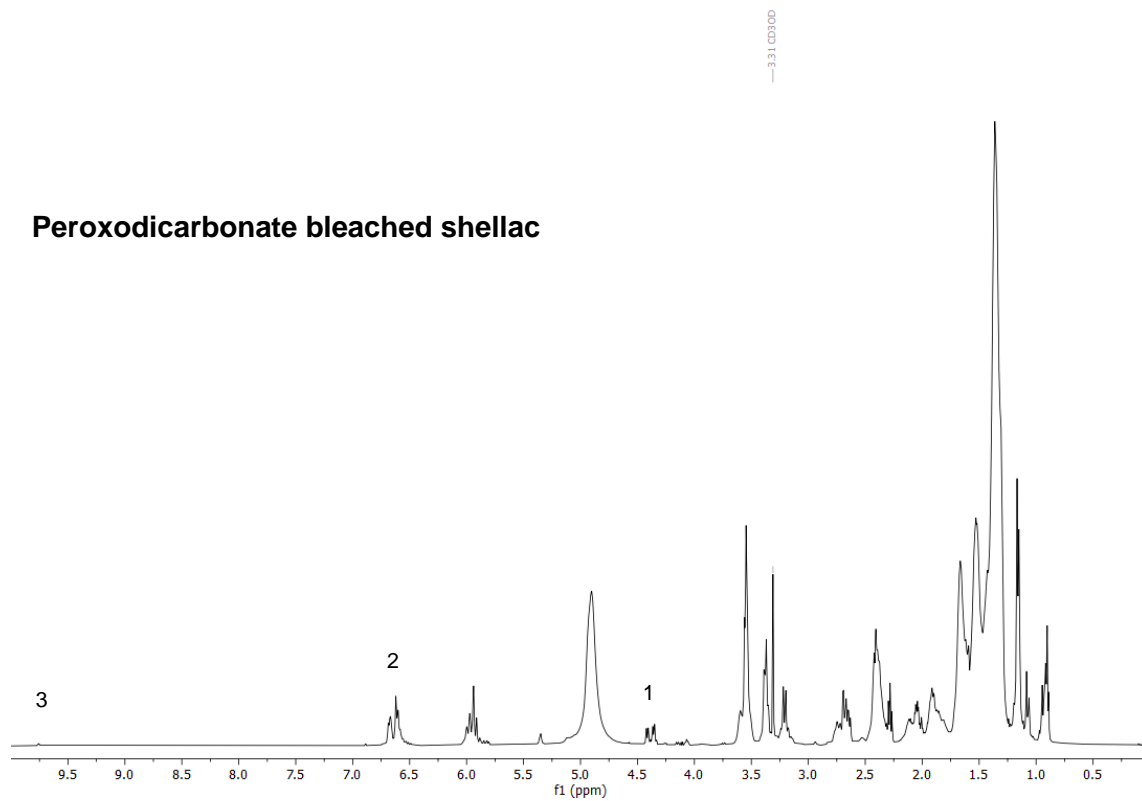
## 4. $^1\text{H}$ NMR Spectra

Numbers correspond the assigned  $^1\text{H}$  and  $^{13}\text{C}$  in Figure S3 (Below)

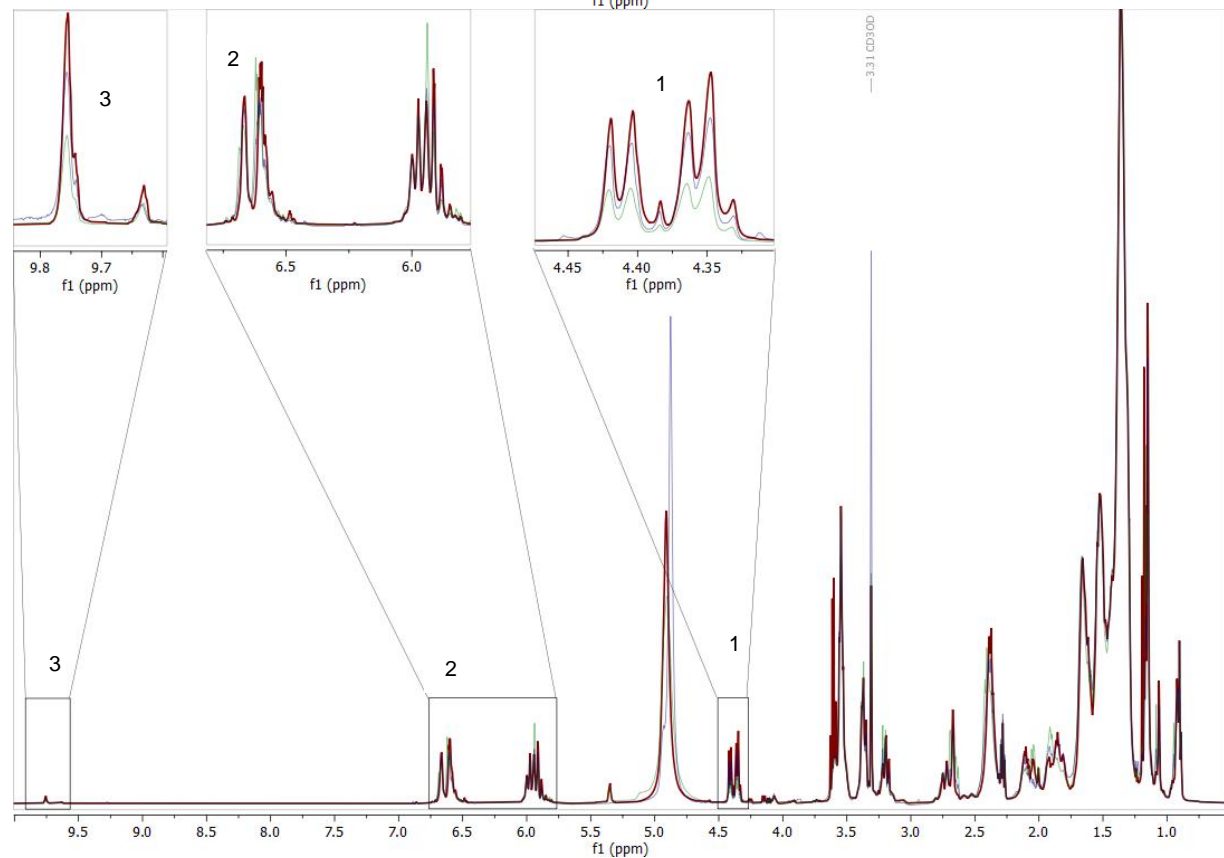
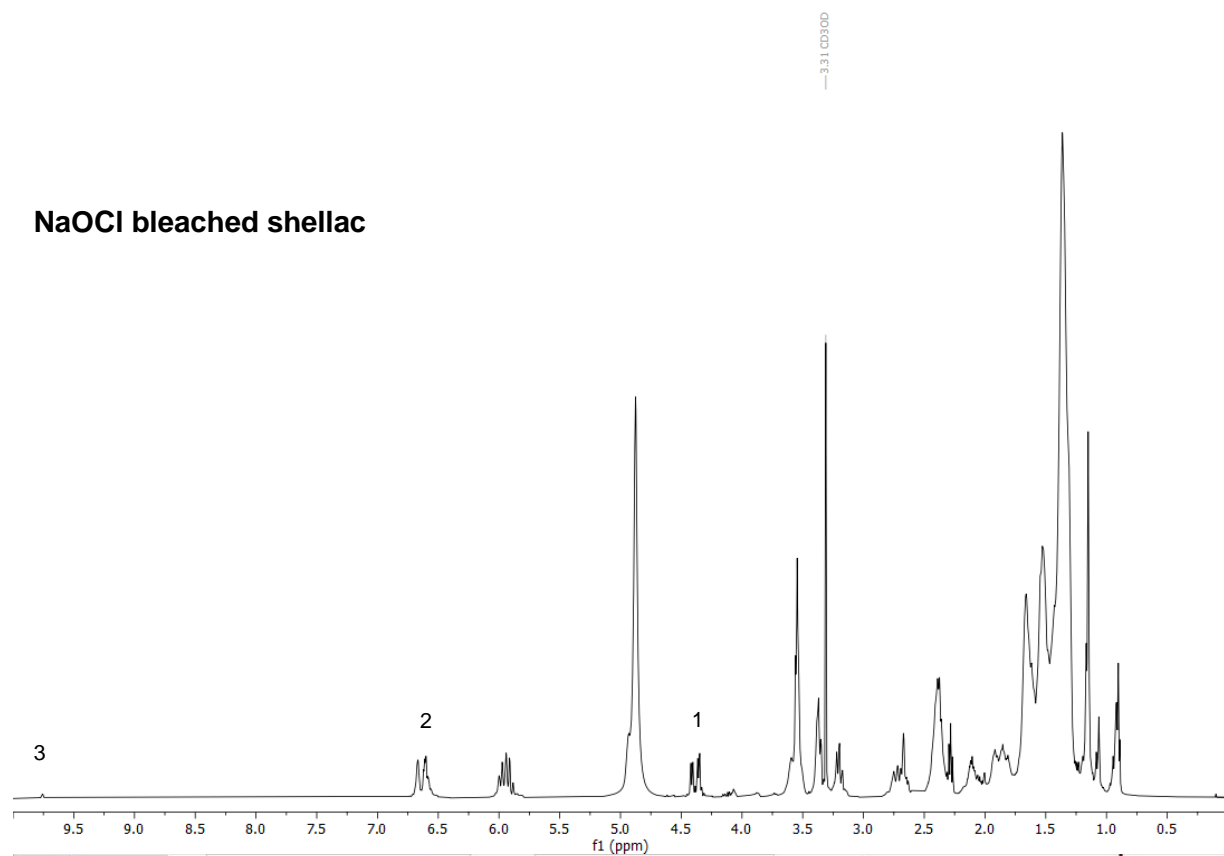
### Unbleached dewaxed shellac



### Peroxodicarbonate bleached shellac



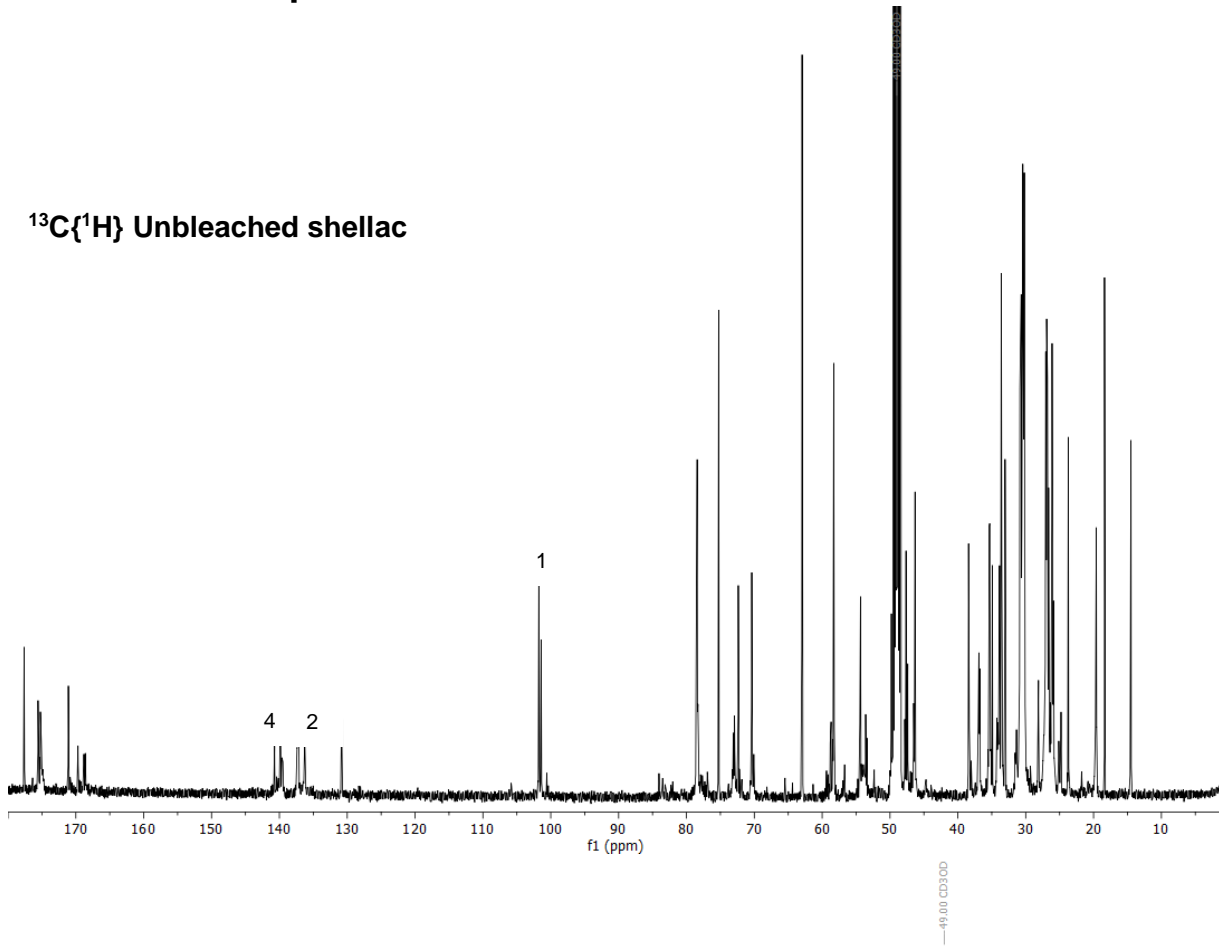
# NaOCl bleached shellac



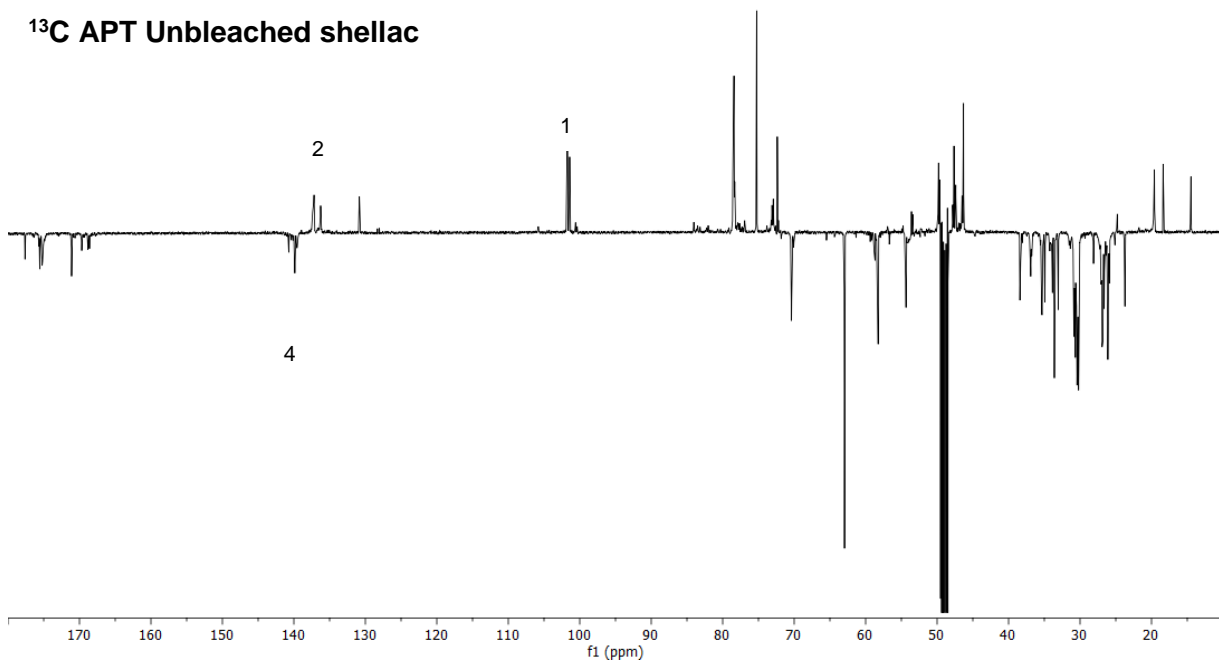
Stacked view of <sup>1</sup>H NMR: Unbleached (Red); Bleached with 11 (green); Bleached with NaOCl (blue)

## 5. $^{13}\text{C}$ NMR Spectra

$^{13}\text{C}\{^1\text{H}\}$  Unbleached shellac

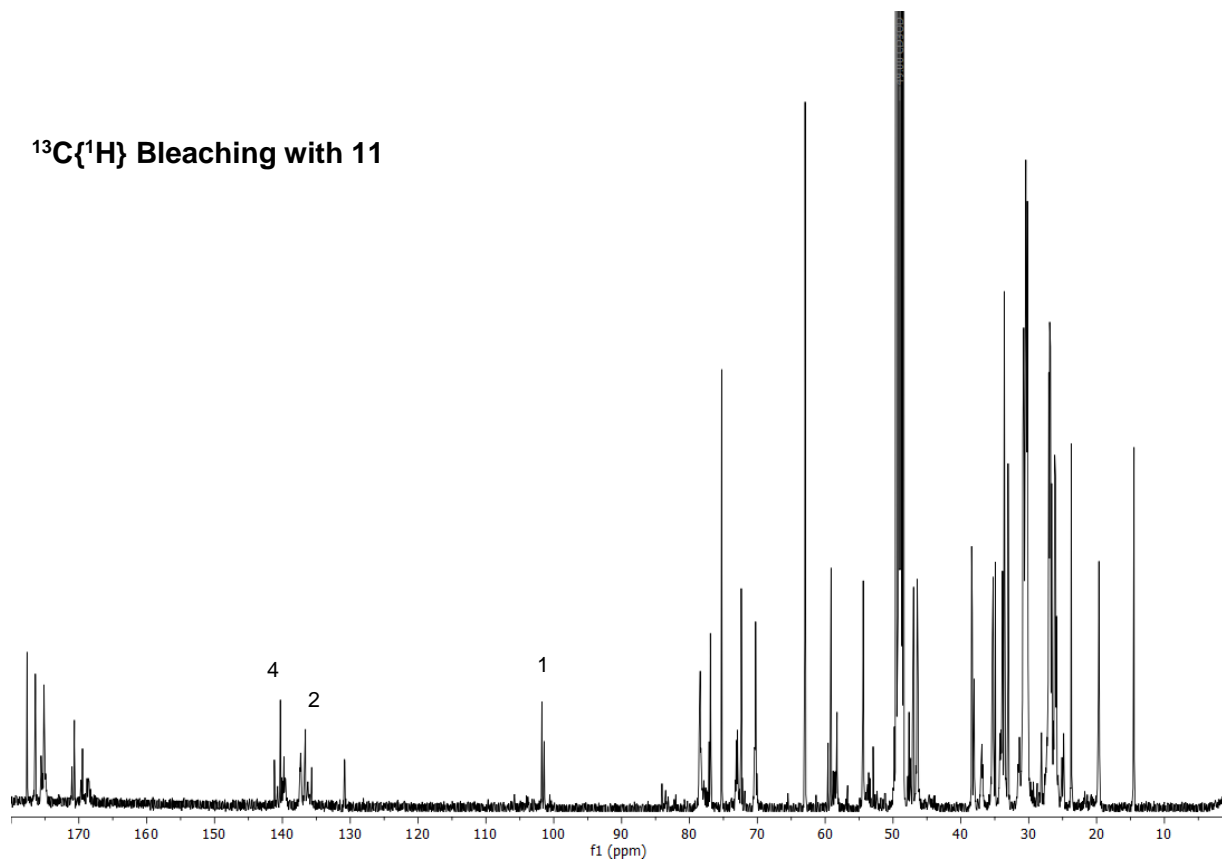


$^{13}\text{C}$  APT Unbleached shellac

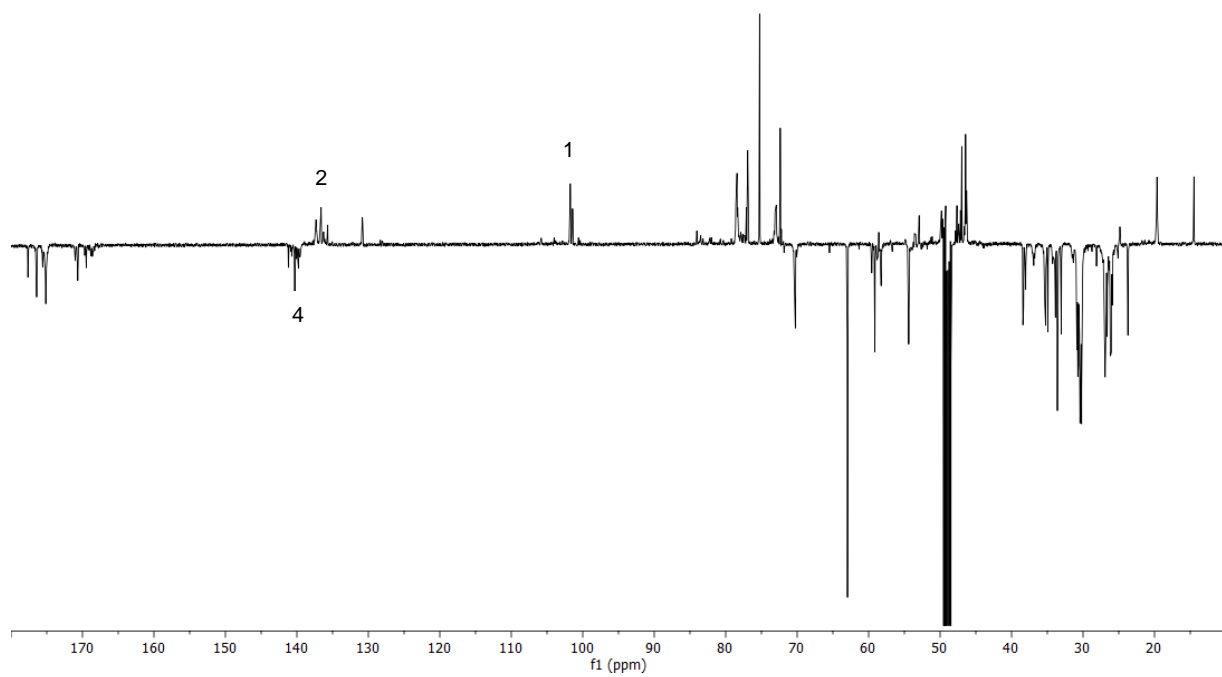




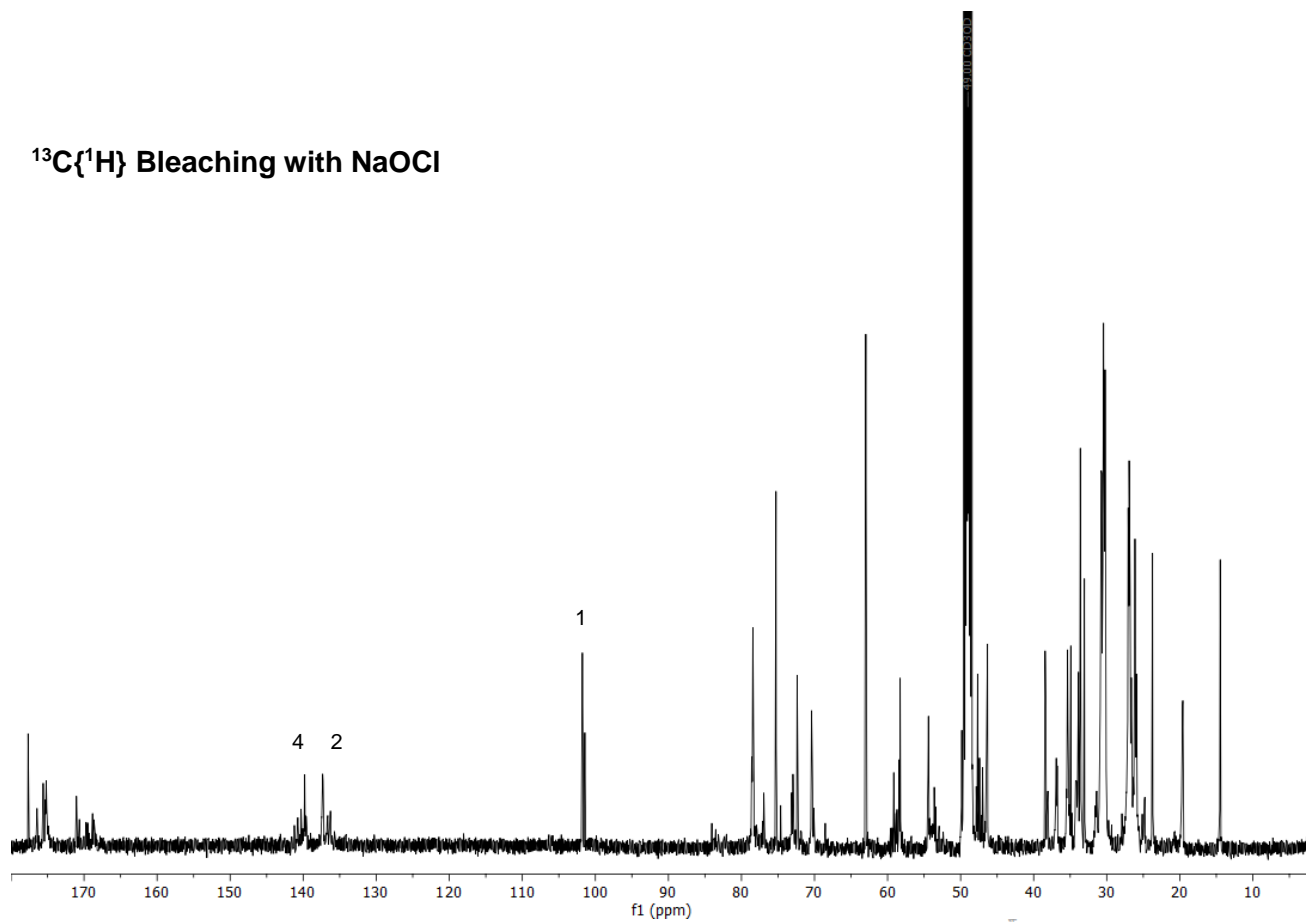
**$^{13}\text{C}\{^1\text{H}\}$  Bleaching with 11**



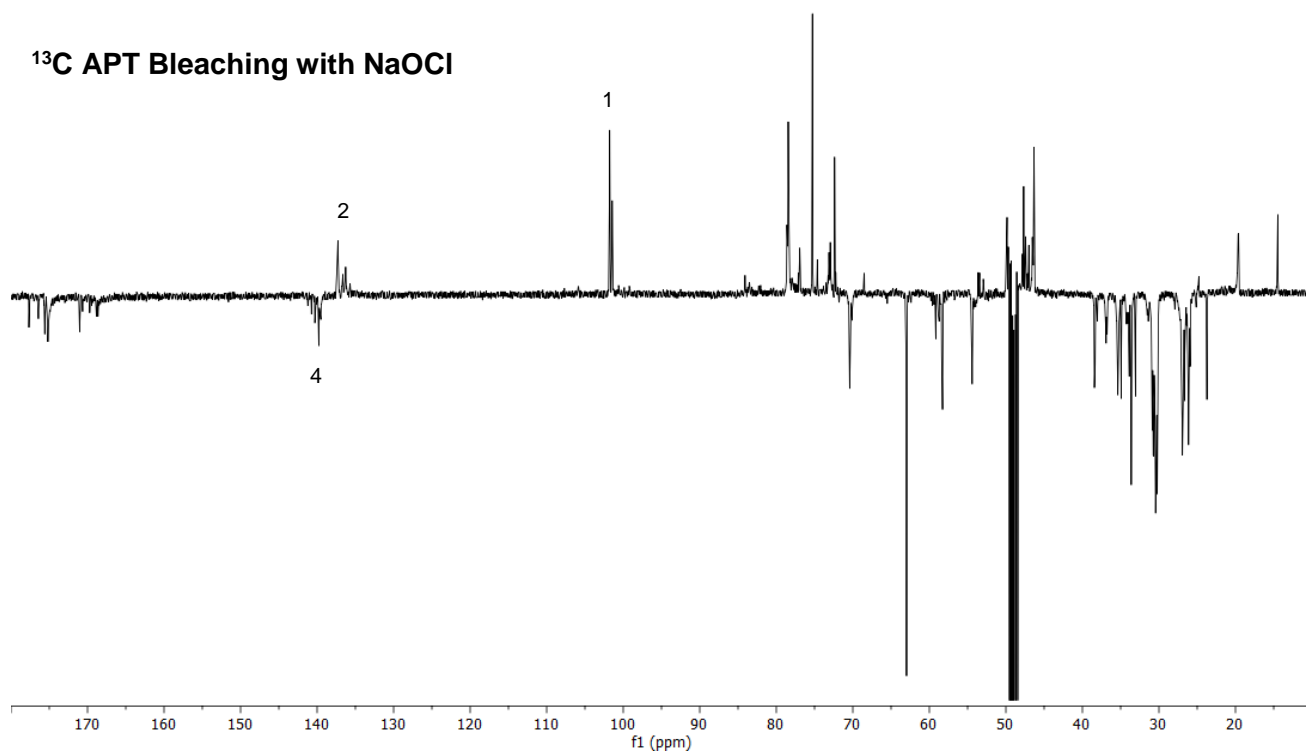
**$^{13}\text{C}$  APT Bleaching with 11**

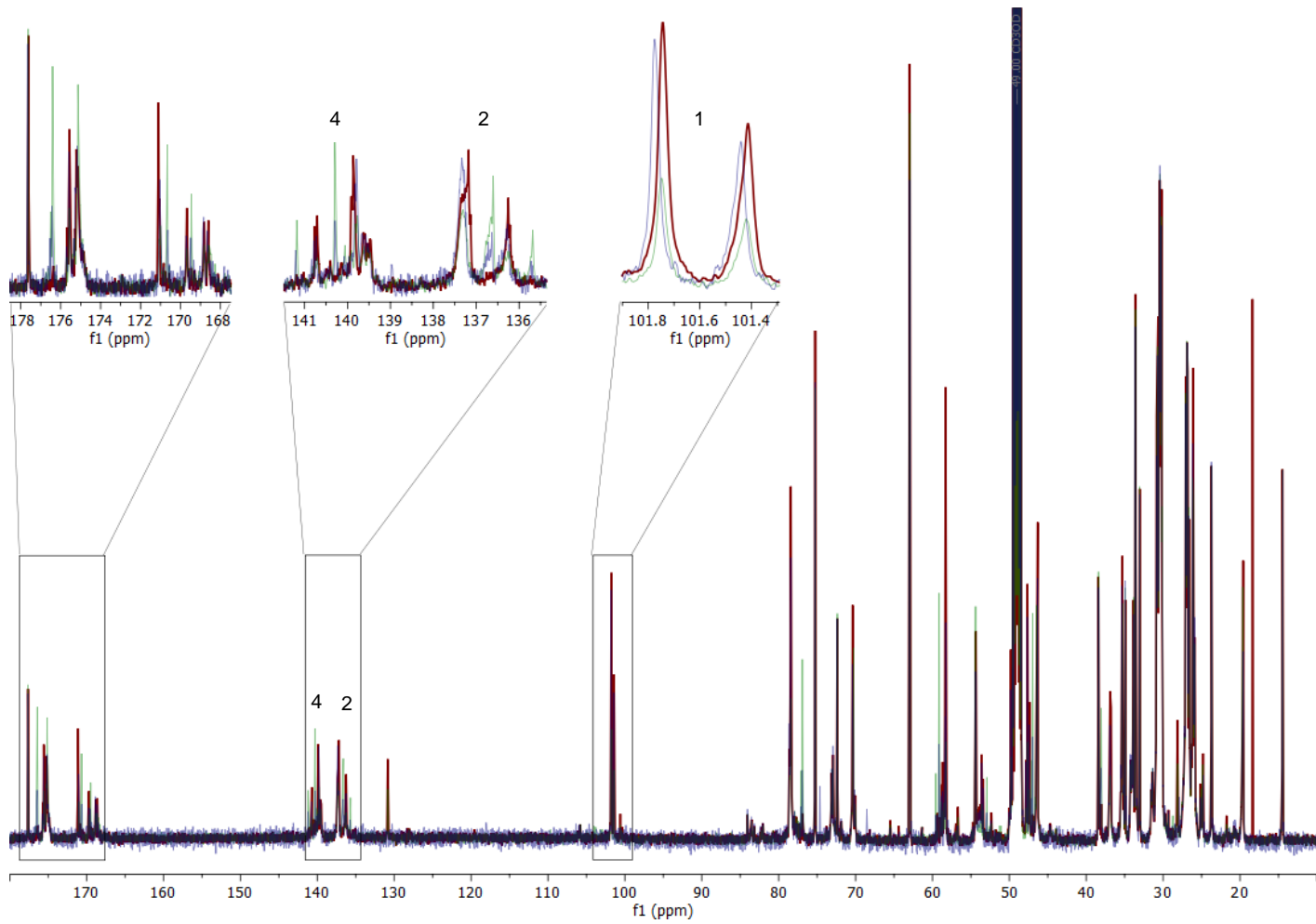


**$^{13}\text{C}\{^1\text{H}\}$  Bleaching with NaOCl**



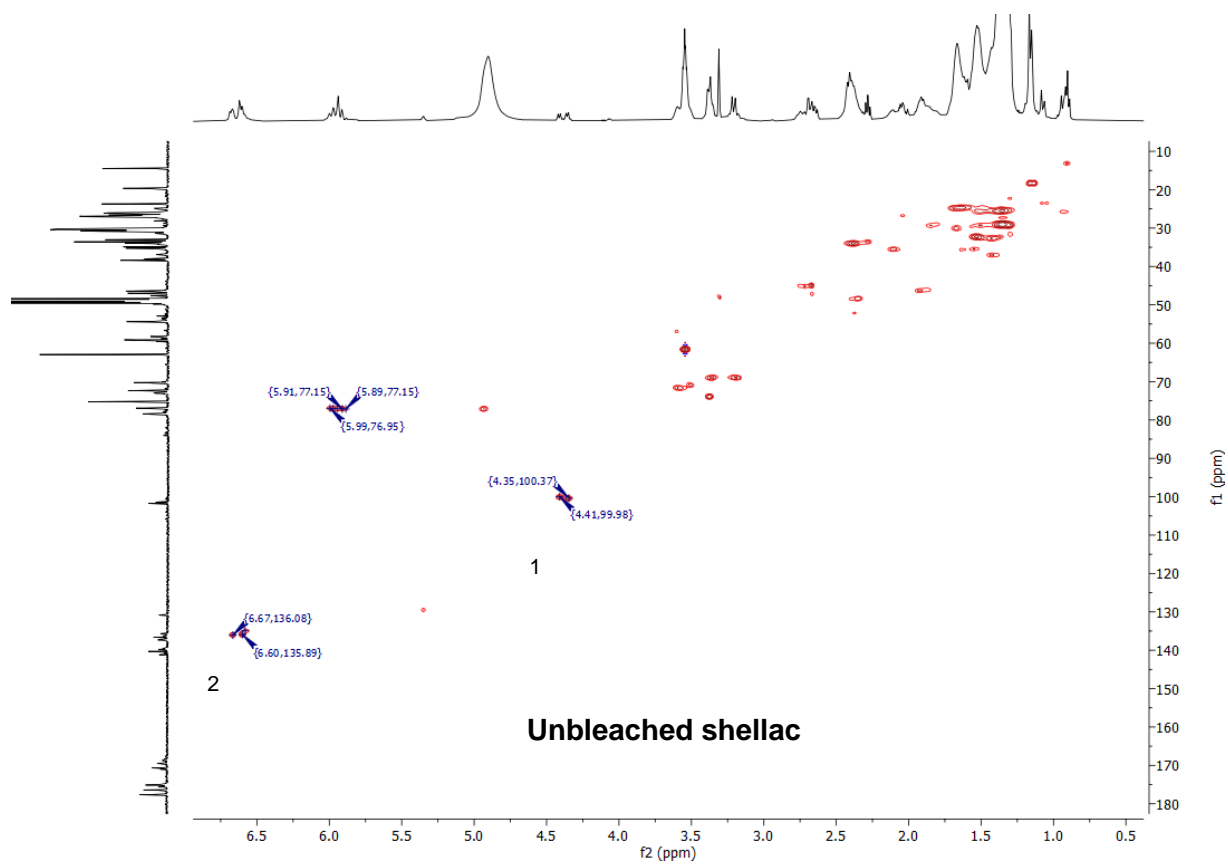
**$^{13}\text{C}$  APT Bleaching with NaOCl**

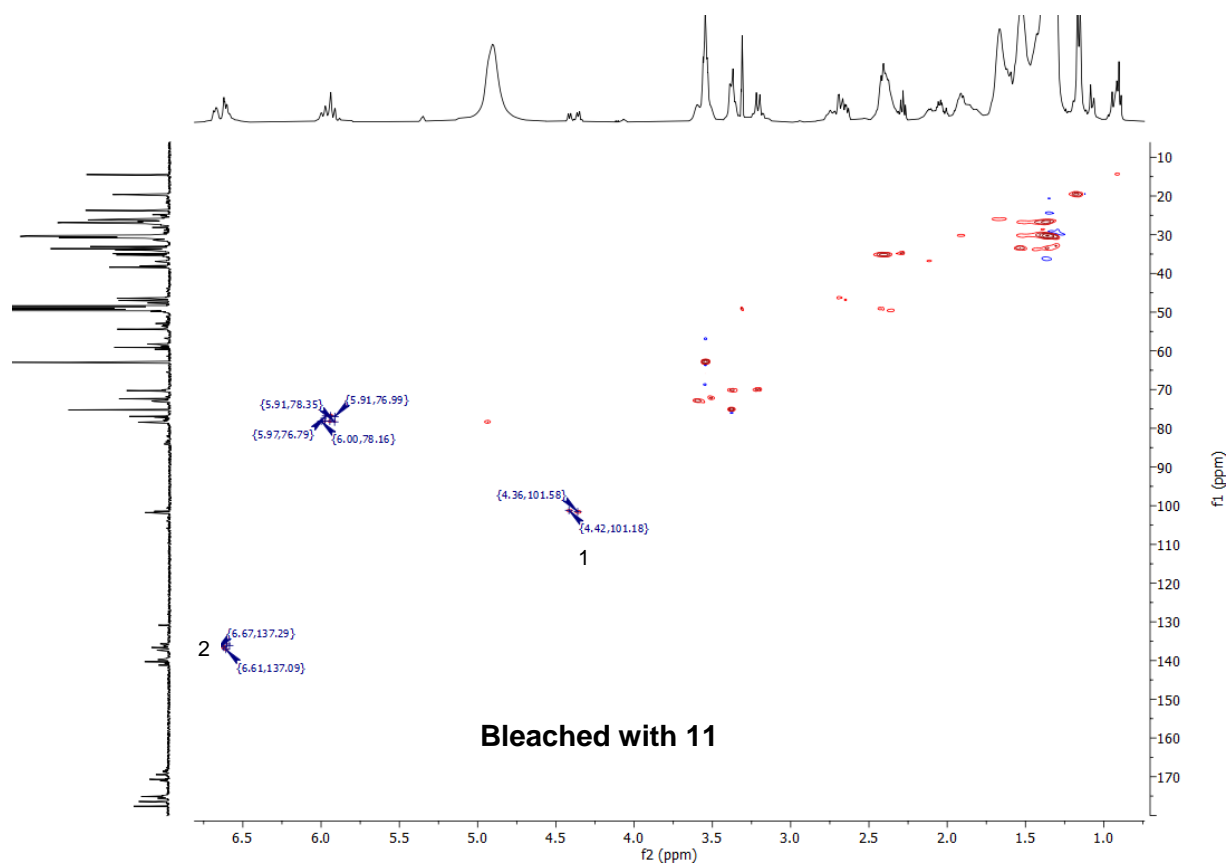


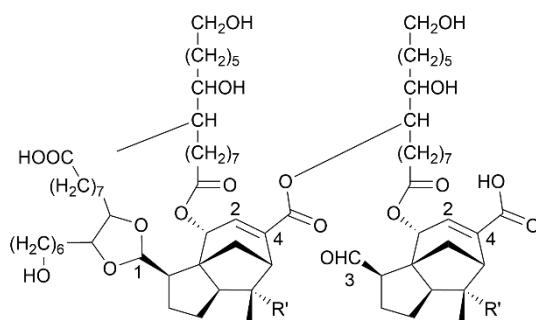
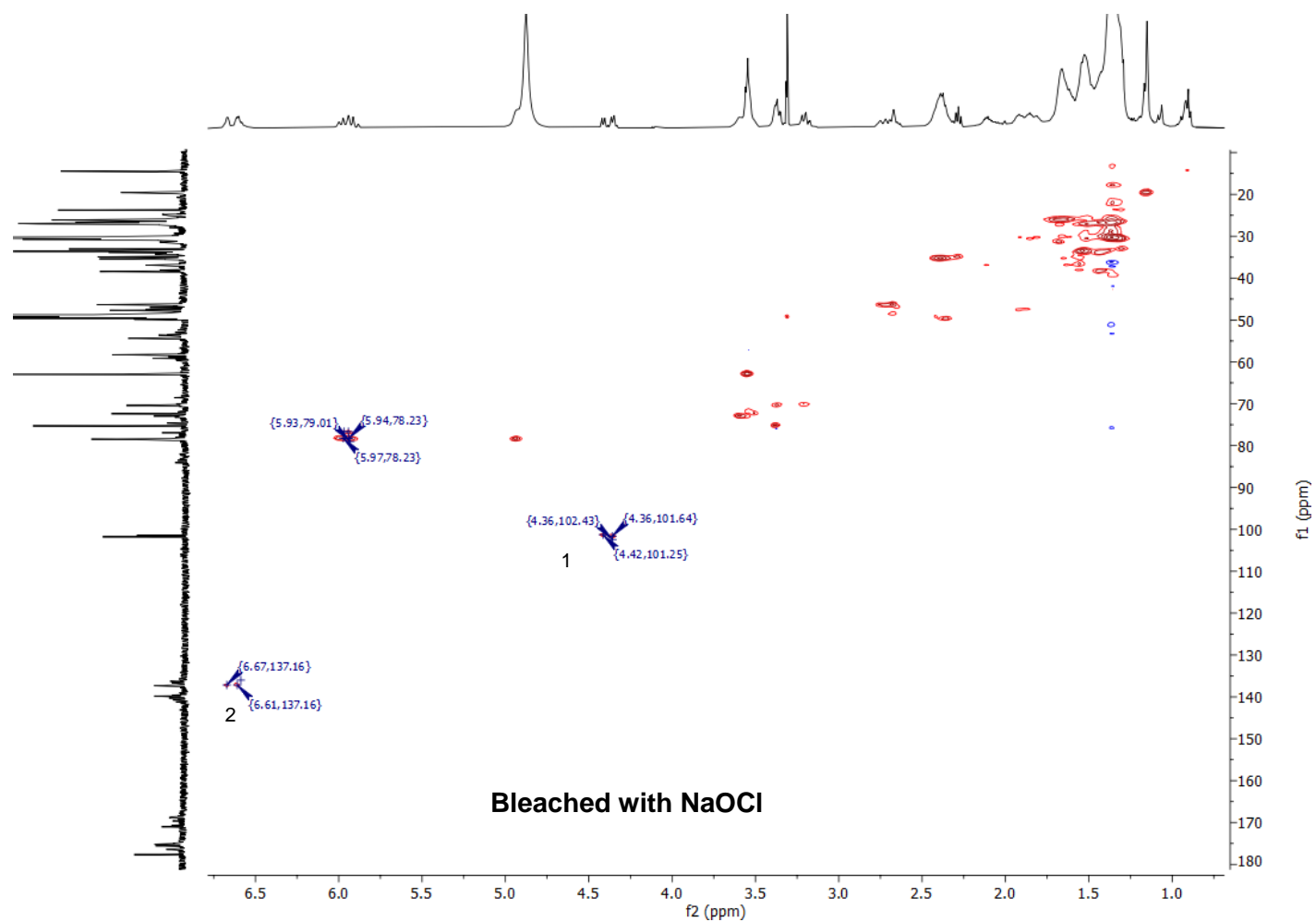


Stacked view of  $^{13}\text{C}\{^1\text{H}\}$ : Unbleached (Red); Bleached with 11 (green); Bleached with NaOCl (blue)

## 6. HSQC NMR







**Figure S3** General structure of shellac with assigned  $^1\text{H}$  and  $^{13}\text{C}$

## 7. References

1. A.-K. Seitz, P. J. Kohlpaintner, T. van Lingen, M. Dyga, F. Sprang, M. Zirbes, S. R. Waldvogel and L. J. Gooßen, *Angew. Chem. Int. Ed.*, 2022, **61**, e202117563.
2. S. Saengsod, S. Limmatvapirat and M. Luangtana-anan, *J. Food Process. Eng*, 2019, **42**, e13291.
3. Ph. Eur. 7.0, 20502 (01/2008).
4. K. Li, H. Zheng, H. Zhang, W.-w. Zhang, K. Li and J. Xu, *RSC Advances*, 2016, **6**, 55618–55625.