

Supporting information

## **Solvent dependent reaction mechanisms in the electro oxidative coupling of phenols: Insights by in-situ Raman spectroelectrochemistry**

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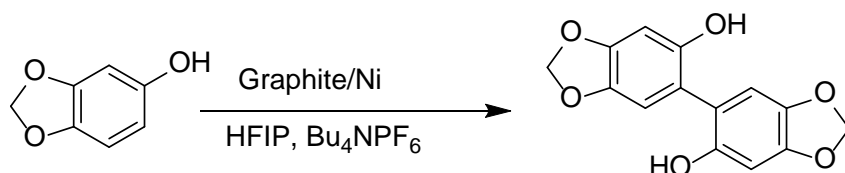
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## General remarks

All chemicals were purchased from commercial suppliers and used without further purification. The electrode materials were purchased from Fischer Scientific (Nickel), Alfa Aesar (Silver) and Merck (Graphite felt). Electrolysis and Cyclovoltametry experiments were performed with an Ivium Vertex One EIS potentiostat with Ivium electrochemical software. NMR-Spectra are obtained by a Bruker Avance II 600 spectrometer.

### S1. Electrolysis



A 25 ml roundbottom flask is filled with Sesamol (1 g, 7,24 mmol) and tetrabutylammoniumhexafluorophosphate (TBAF) (0,697 g, 1,8 mmol) in 18ml 1,1,1,3,3,3-hexafluoroisopropanol (HFIP). The flask is equipped with graphite felt as anode and a nickel sheet as cathode and silver wire as a pseudoreference electrode. The reaction solution is electrolyzed under stirring at a constant current of 5 mA is applied for 38 h (2 F per mole starting material).

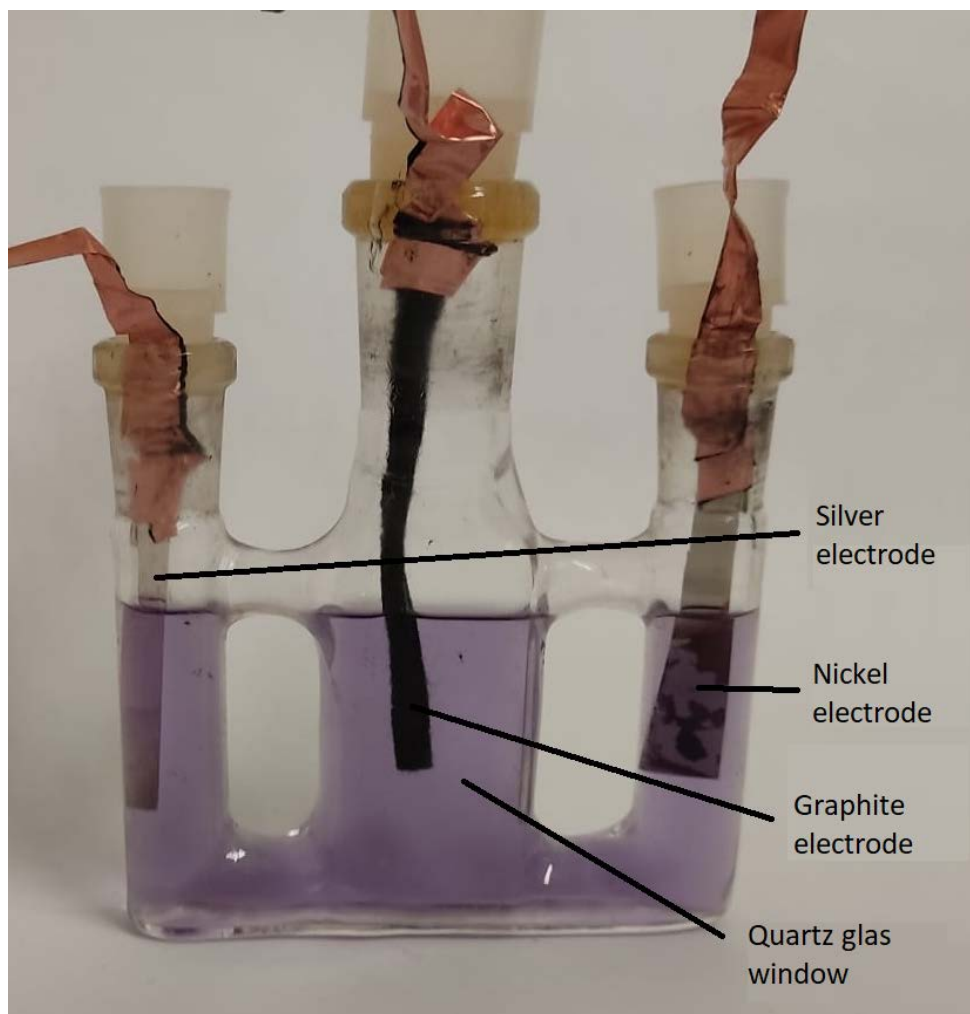
After that the solvent is evaporated and the resulting solid is solubilised by tert-butylmethylether. The organic phase is washed three times with distilled water, once with brine and dried with anhydrous sodium sulfate, resulting in 0,811 g crude product. The Yield is determined by <sup>1</sup>H-NMR-spectroscopy with Toluene as internal standard.

An analytic sample of 200 mg of the crude product is purified by column chromatography on silica gel with an ethylacetat:n-hexane (1:3) solvent mixture.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δH 7.09 (2H, d, J = 0.4 Hz), 6.94 (2H, d, J = 0.4 Hz), 5.95 (4H, s).

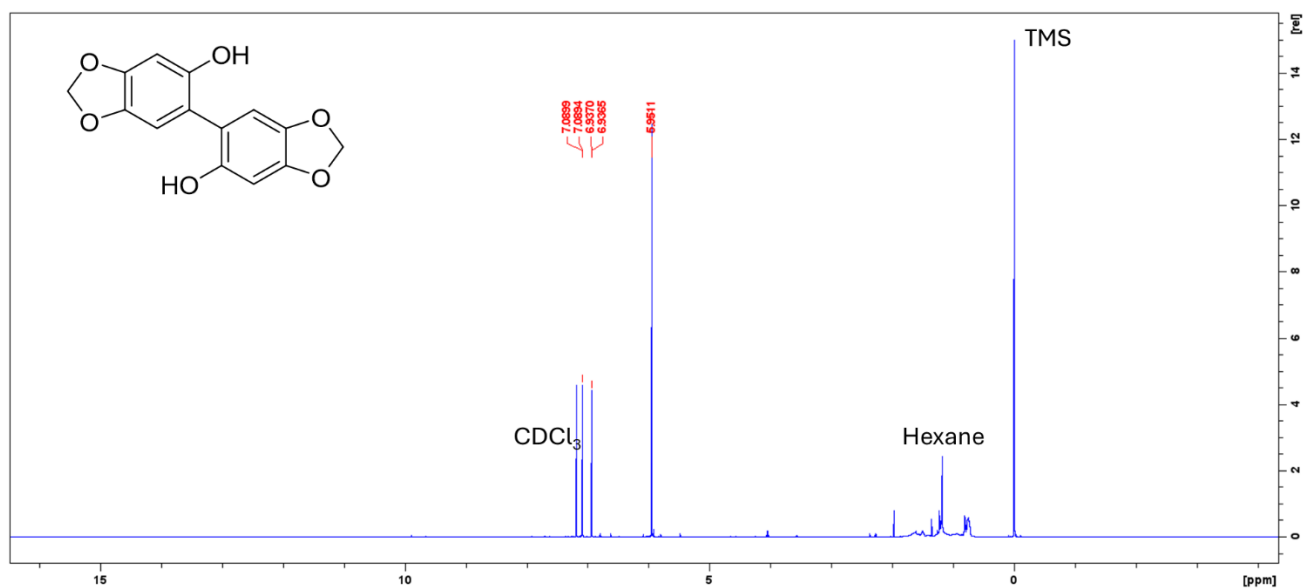
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 600 MHz): δC 150.7 (s), 145.7 (s), 143.2 (s), 116.6 (s), 100.5 (s), 97.5 (s), 93.0 (s).

HRMS(ESI): calc. for [(C<sub>14</sub>H<sub>9</sub>O<sub>6</sub>)] (M<sup>-</sup>) 273.0399, measured 273.0405.

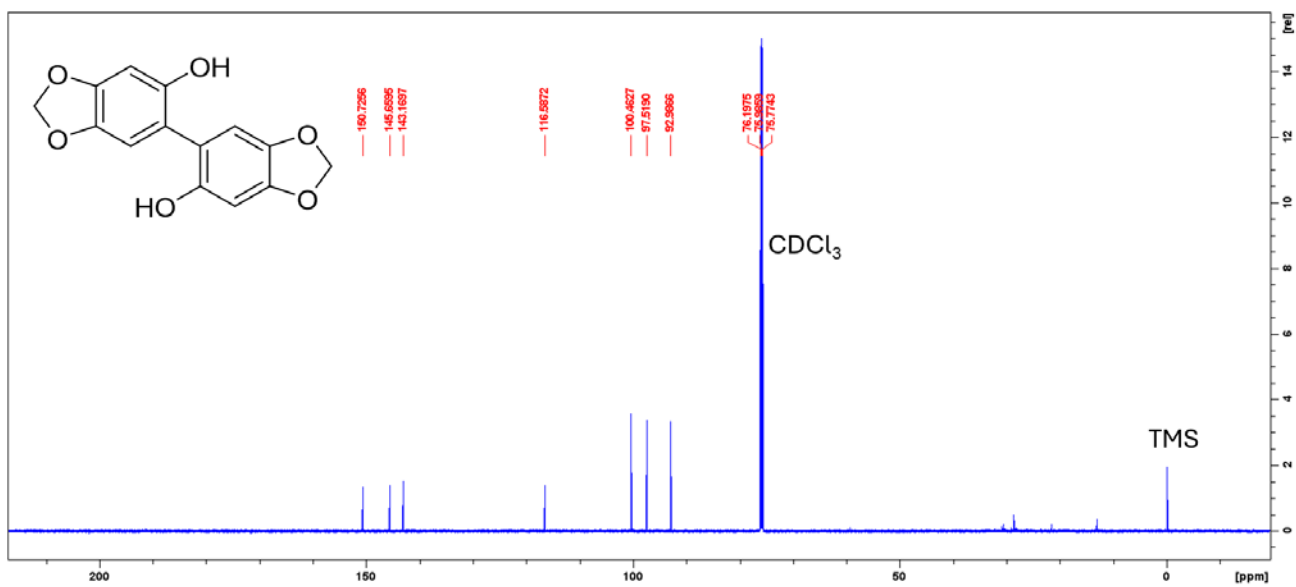


**Figure S1:** Electrochemical setup for operando Raman measurements.

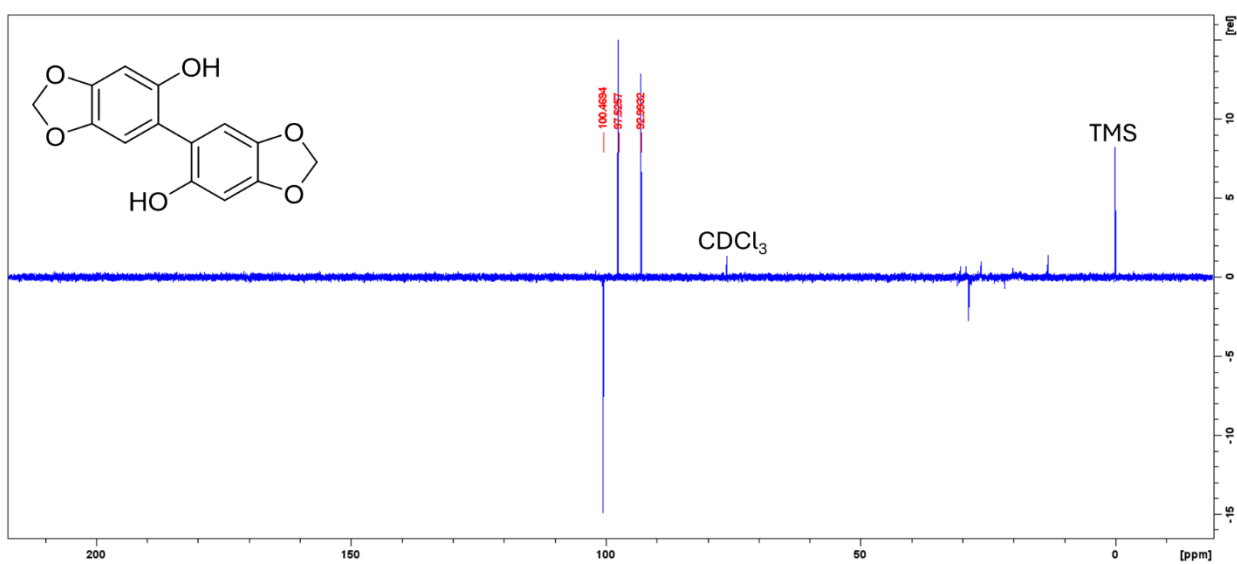
## S2. NMR-Spectra



**Figure S2:** <sup>1</sup>H-NMR-Spectra (600MHz in CDCl<sub>3</sub>) of purified electrolysis product.

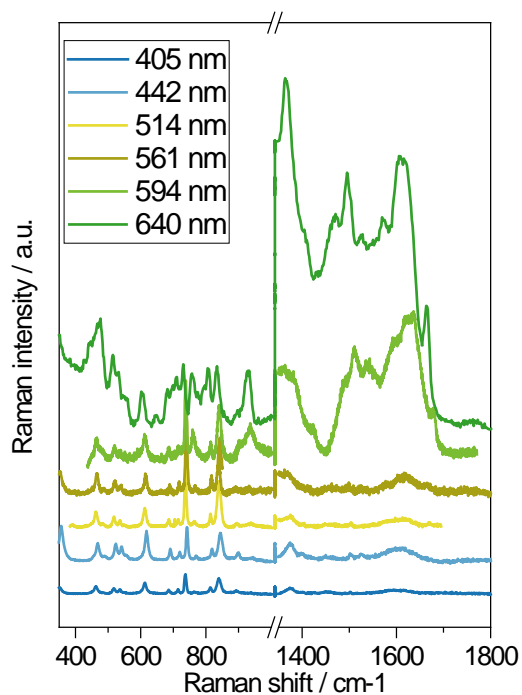


**Figure S3:**  $^{13}\text{C}$ -NMR-Spectra (600MHz in  $\text{CDCl}_3$ ) of purified electrolysis product.

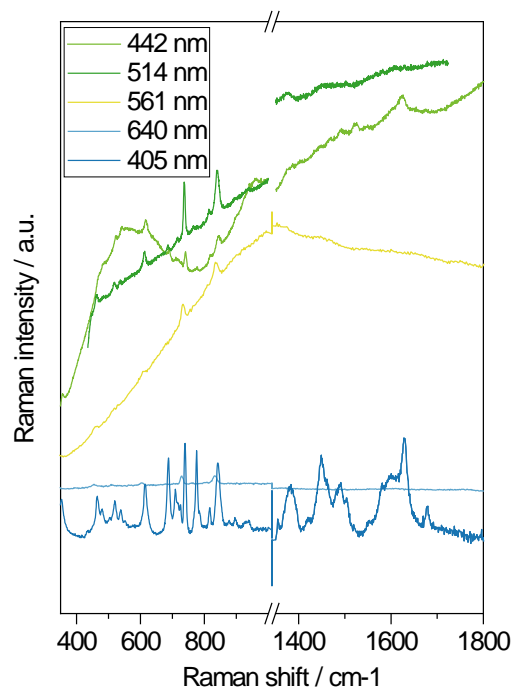


**Figure S4:**  $^{13}\text{C}$ -DEPT 135-NMR-Spectra (600MHz in  $\text{CDCl}_3$ ) of purified electrolysis product.

### S3. Raman Spectroscopy

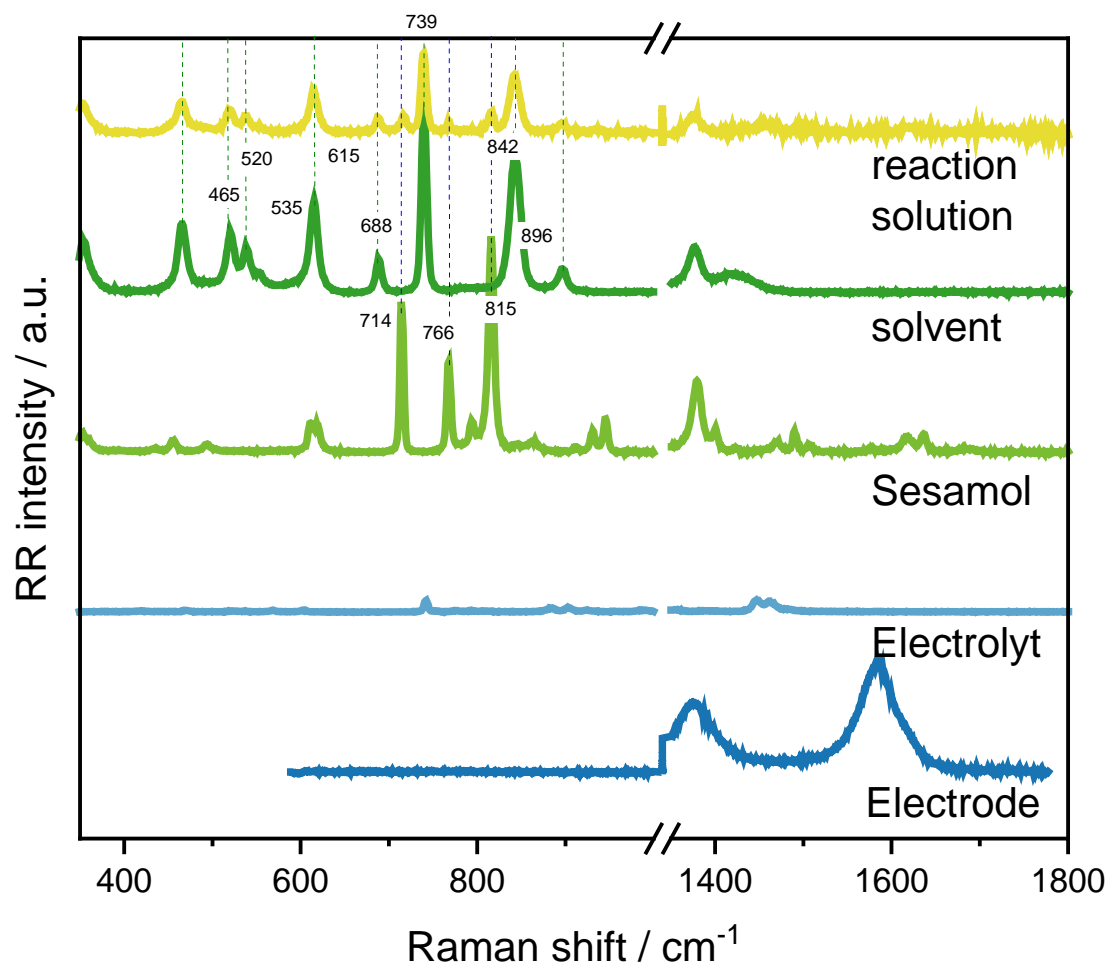


**Figure S5:** Raman spectra of reaction solution with different excitation wavelengths.

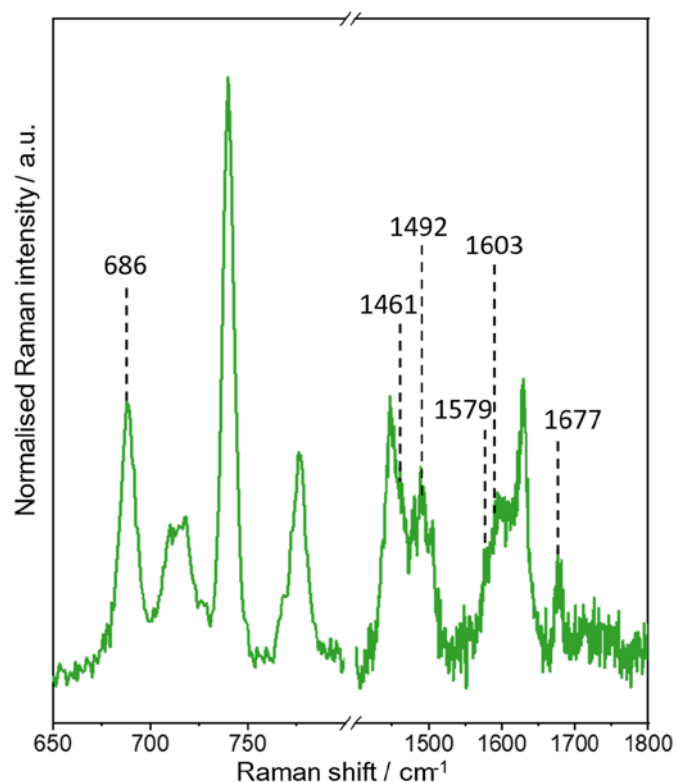


**Figure S6:** Raman spectra of reaction solution with applied potential of 2,5 V vs Ag/Ag+ at different excitation wavelengths without applied baseline.

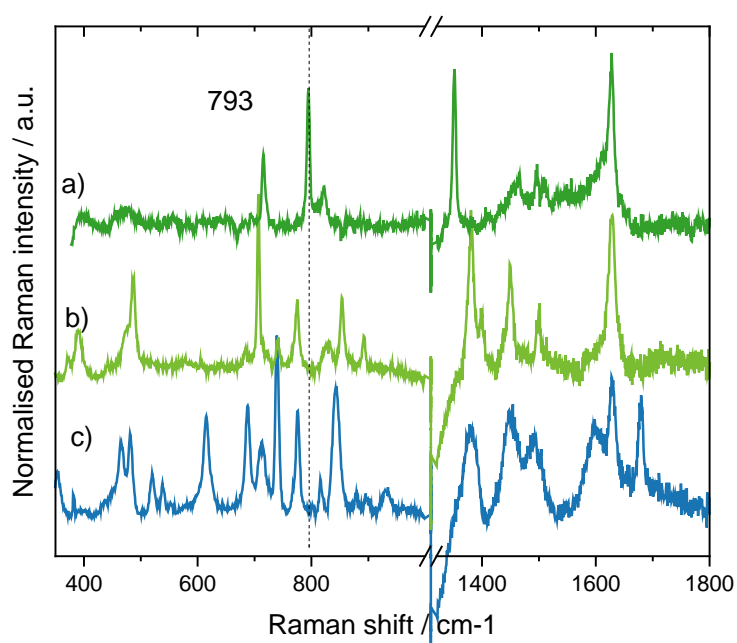
Figure S5 and S6 show that with an excitation wavelength of 405 nm the product formation is better observable than in higher wavelengths, while in higher wavelengths the intensity of the starting material increases, additionally higher wavelengths show higher scattering during the electrolysis. That's why all spectra are measured with an excitation wavelength of 405 nm.



**Figure S7:** Raman spectra of all starting materials and electrodes and reaction solution.



**Figure S8:** Raman spectra of reaction mixture at 2 V vs. Ag|Ag<sup>+</sup> in HFIP with Graphite as working electrode. Unassigned bands are marked by dotted lines.



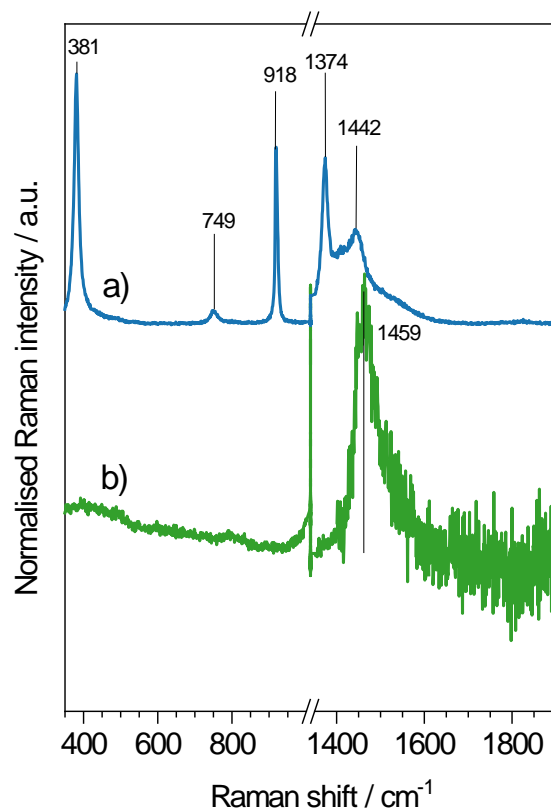
**Figure S9:** Raman spectra of a) crude product, b) purified product c) reaction solution at 2 V vs. Ag|Ag<sup>+</sup>. Intermediate bands are marked with a dotted line. Spectra are measured with 405nm excitation.

The only band, which shows in the crude product but not the product is as 793 cm<sup>-1</sup>, however this band does not correspond to a band in the operando Raman spectra.

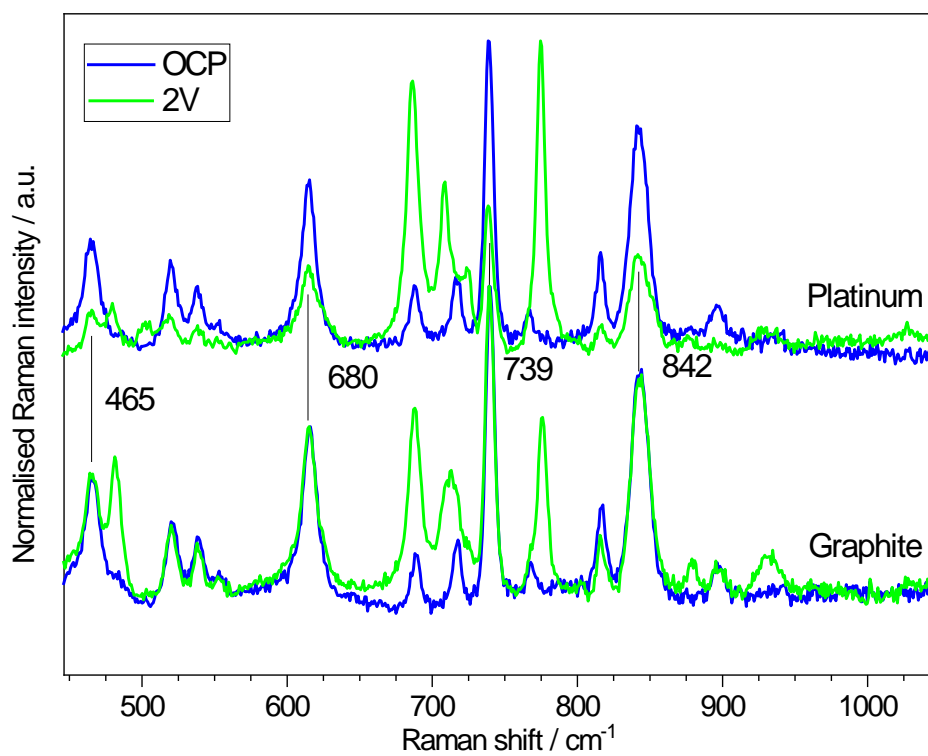
**Table S1:** Selected observed Raman bands in  $\text{cm}^{-1}$  for educt, solvent and product in HFIP solution.

Nr.	Educt (Sesamol)	Solvent and electrolyte	Intermediate	Product
1		465		
2				480
3		520		
4		537		
5		615		
6			686	
7		688		
8				708
9	714			
10		739		
11	766			
12				775
13	815			
14		842		
15		896		
16				1448
17			1461	
18			1492	
19				1501
20			1579	
21			1603	
22				1627
23			1677	



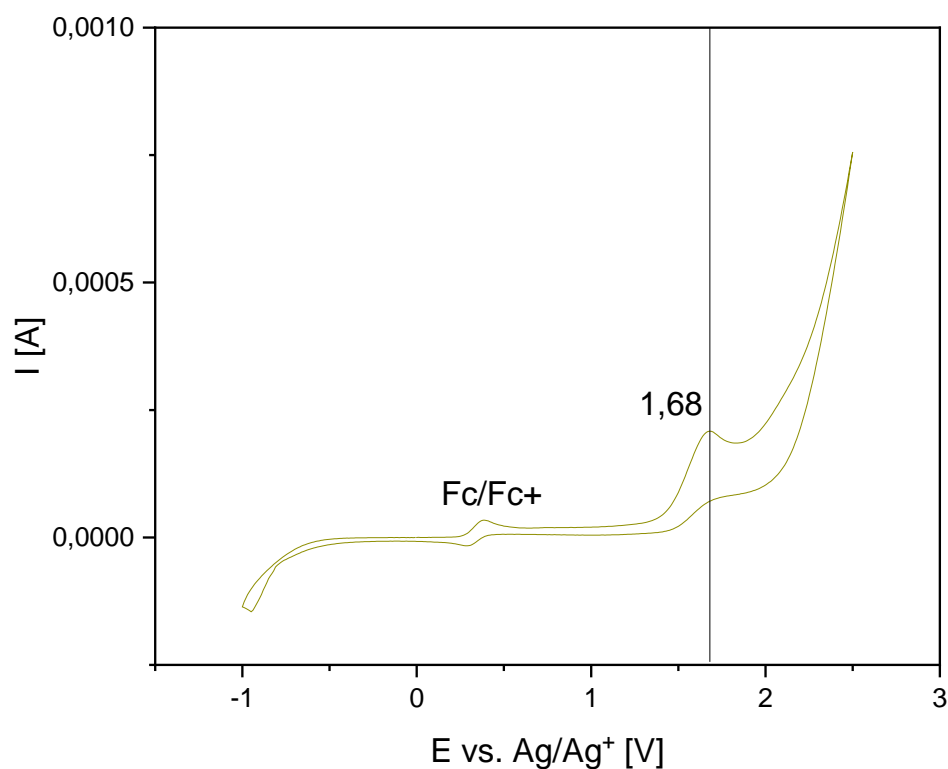


**Figure S10:** Raman spectra of solvents a) acetonitrile and b) methanol.



**Figure S11:** Comparison between Raman spectra of reaction solution on graphite and on platinum at OCP (blue) and 2 V vs.  $\text{Ag}/\text{Ag}^+$  (green).

## S4. Cyclic voltammetry

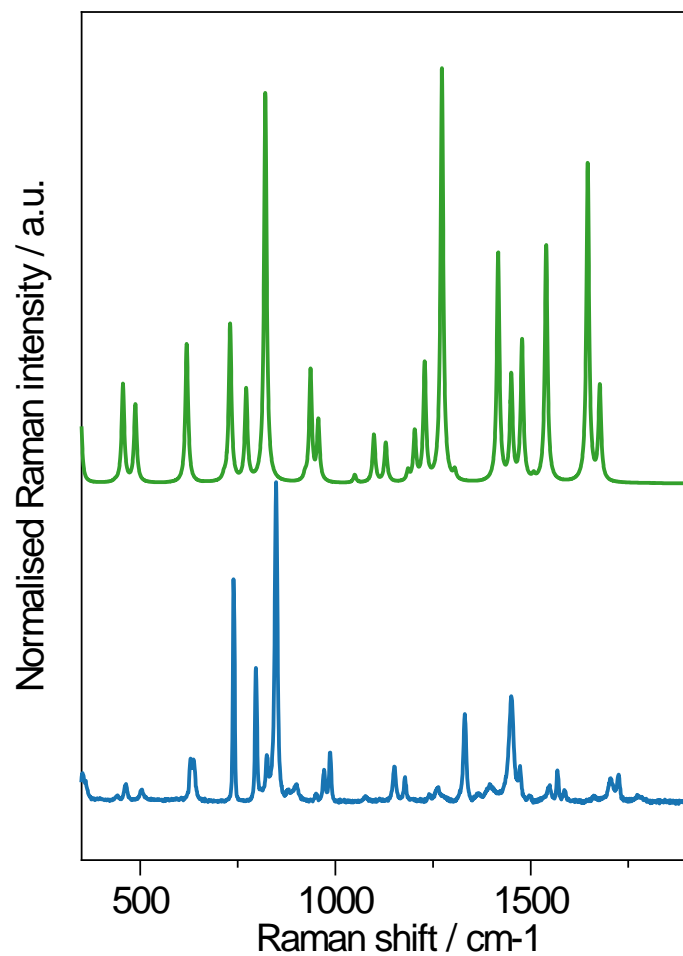


**Figure S12:** Cyclic voltammogram of methanol with Ferrocene (Fc) as internal standard with glassy carbon as working electrode vs. Ag|Ag<sup>+</sup>, recorded in 0,25 M [Bu<sub>4</sub>N][PF<sub>6</sub>] solution, scan rate (v) 0,01 V/s.

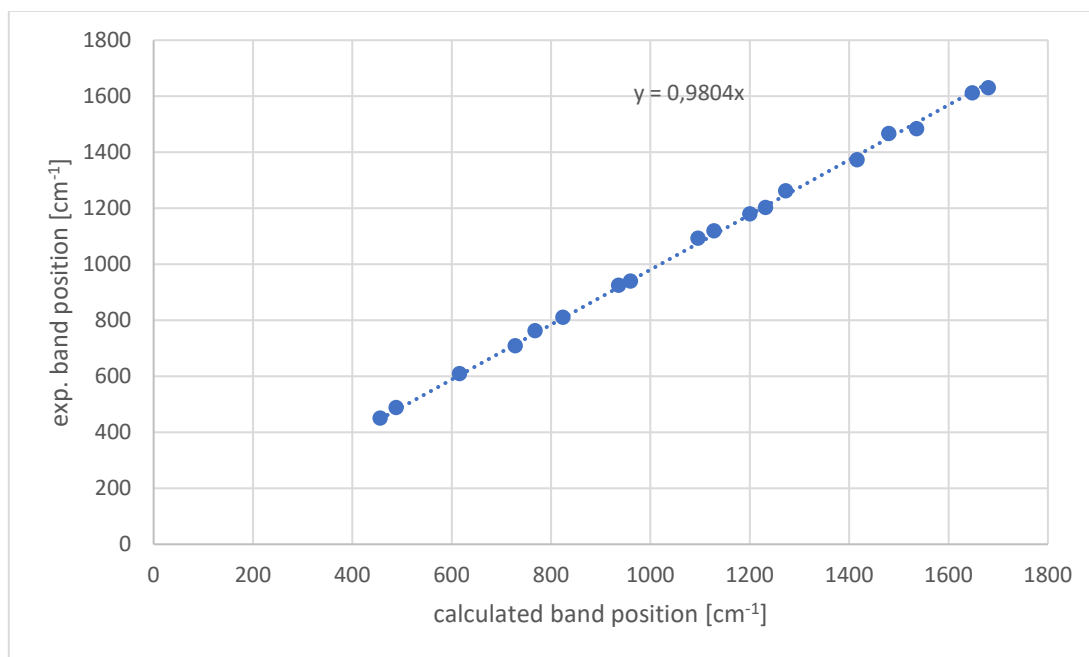
## S5. DFT calculations

The DFT calculation are performed with the programs Gaussian 09W and GaussView 5.0. For each calculation a geometry preoptimisation with Universal Force Field (UFF) is performed followed by a DFT geometry optimisation and the calculation of the vibrational spectra. For the calculations the method Ground State, the functional B3LYP and the basis set 6-311G is chosen.

By comparison of the experimental and calculated spectra of the starting material a correction factor is determined (see Figure S11, Figure S12). This correction factor is applied to the x-axis of the calculated spectra.



**Figure S13:** calculated (red) and experimental (grey) Raman spectra of sesamol.



**Figure S14:** Linear regression of experimental and calculated band positions of sesamol.