

Electronic Supplementary Information

for

Sustainable access to biobased biphenol epoxy resins by electrochemical dehydrogenative dimerization of eugenol

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1. Electrochemical Cells

Beaker-type cell (25 mL)

The beaker-type cell (25 mL) consists of a simple glass beaker with cooling jacket and is closed by a PTFE plug. This cap allows precise arrangement of the electrodes in a distance of 12 mm. Dimensions of the used reticulated vitreous carbon (RVC) anode were 2.0 x 6.0 x 0.5 cm with a porosity of 100 ppi. Dimensions of the used glassy carbon (GC) cathode were 7.0 x 2.0 x 0.2 cm. The immersed part of the RVC anode had dimensions of 2.0 x 3.5 x 0.5 cm. A current of 32 mA was applied, resulting in a geometrical current density of 4.5 mA/cm². Terminal voltage in 25 mL beaker-type cells typically is in the range of 2-3 V.



Figure S1 View of an undivided beaker-type cell of 25 mL.

Beaker-type cell (150 mL or 600 mL)

A modular stacked arrangement of alternating GC cathode and RVC anode was set up as shown in Figure S2. The electrodes were separated by PTFE spacers and contacted by thin stainless steel sheets resulting in a set of three GC cathodes and two RVC anodes. The electrode stack was immersed in a beaker-type cell of 150 or 600 mL. The immersed part of one RVC electrode had dimensions of 2.8 x 6.5 x 0.5 cm. A current of 130 mA was applied, resulting in a geometrical current density of 3.5 mA/cm². Terminal voltage in typically is in the range of 2-3 V.

The PTFE frames as mechanical support for the RVC anodes were prepared as shown in Figure S3.

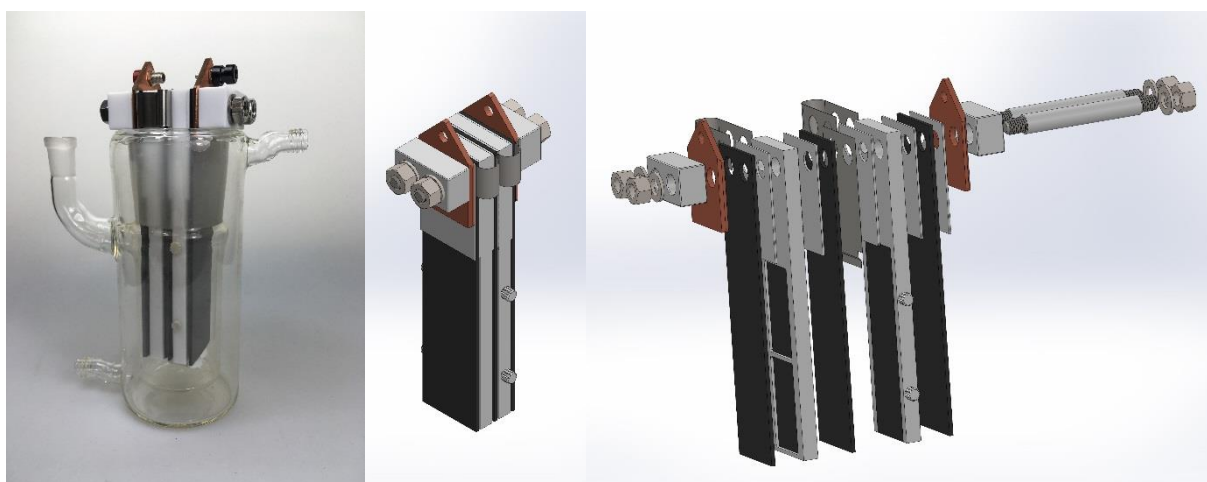


Figure S2 Stacked electrode arrangement for electrolysis in undivided beaker-type cells. Left: 150 mL cell with stacked electrode setup; center: schematic drawing of the electrode setup; right: exploded schematic drawing of the electrode setup.

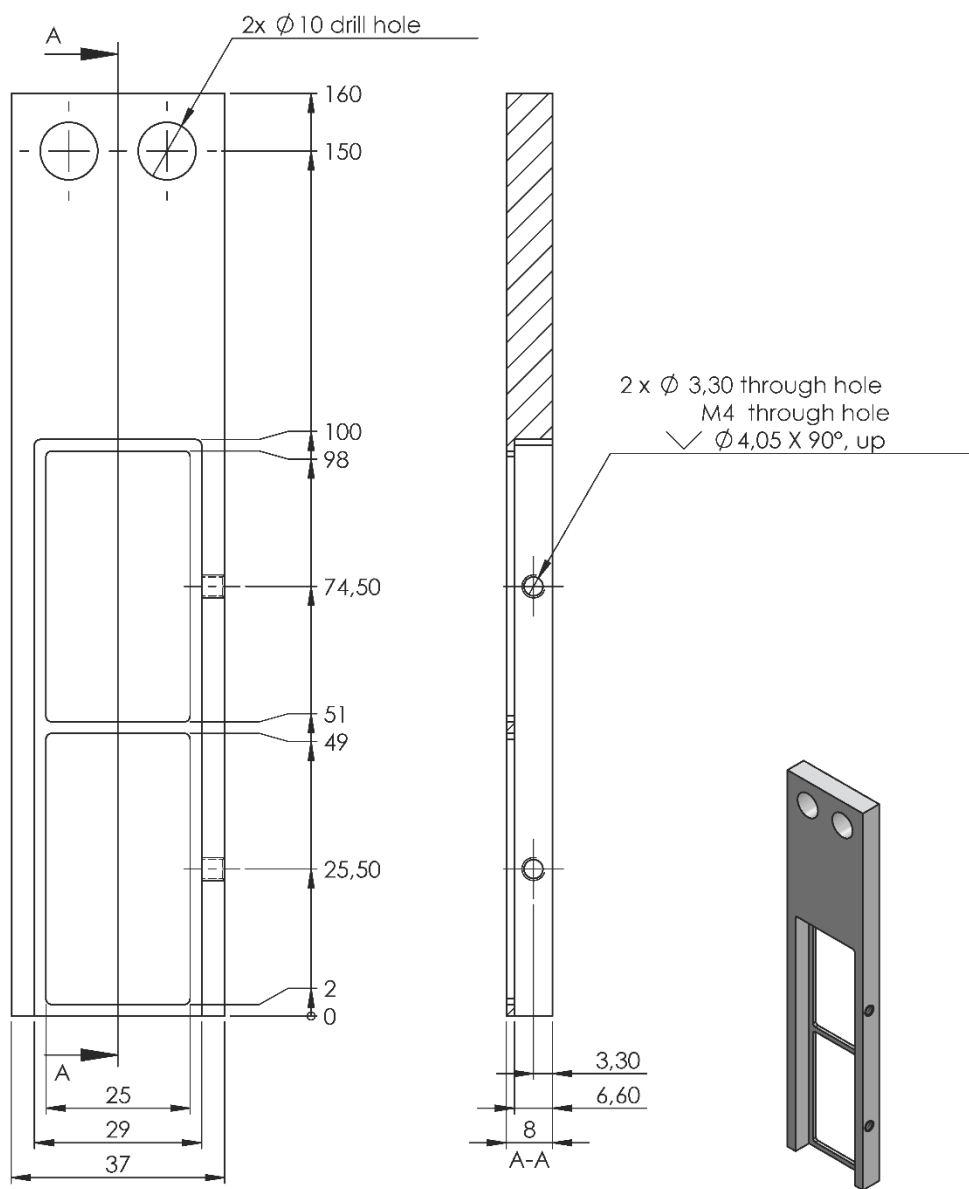


Figure S3 Technical drawing for the PTFE frames. Left: front view, center: profile view; right: 3D model view.

2. Electrochemical Parameter Screening

General Protocol: Parameter Screening for the Anodic Dehydrogenative Dimerization of Eugenol

Eugenol (410 mg, 2.5 mmol), sodium hydroxide (200 mg, 5.0 mmol) and MTBS (78 mg, 0.5 mmol) were dissolved in 22.5 mL methanol and 2.5 mL H₂O and transferred to an undivided beaker-type cell (25 mL) equipped with a RVC anode and glassy carbon cathode (Figure S1). Under vigorous stirring, a current of 32 mA was applied until a charge of 1.5 F (362 C) had passed. The solution was concentrated under reduced pressure, H₂O (15 mL) was added and adjusted to pH 3 by addition of aqueous HCl (10%). The aqueous layer was extracted three times with EtOAc (30 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. Concentration under reduced pressure gave a pale brown residue from which DDE was obtained by column chromatography (SiO₂, CH₂Cl₂ + 0.5-1% MeOH) as a colourless solid.

Table S1 Variation of the General Protocol using different bases.

Entry	Base	Applied Charge / F	Yield ^[a]
1	5% Piperidine	1.5	76%
2	2 eq. Piperidine, 5 vol% Pyridine	1.5	76%
3	2 eq. NBU ₄ OH (40% in MeOH)	1.25	77%

Constant current electrolysis (32 mA) of eugenol (2.5 mmol) was performed following the general protocol in an undivided beaker-type cell. [a] Isolated yields.

Table S2 Scale-up of the dehydrogenative dimerization of eugenol using the stacked electrode setup.

Entry	Volume / mL	Current / I	Yield ^[a]
1	150	130	79%
3	600	214	73%

Constant current electrolysis of eugenol (0.1 mol/L) was performed in methanol and 10% H₂O in an undivided beaker-type cell. The crude product was purified by recrystallization from cyclohexane. [a] Isolated yields.

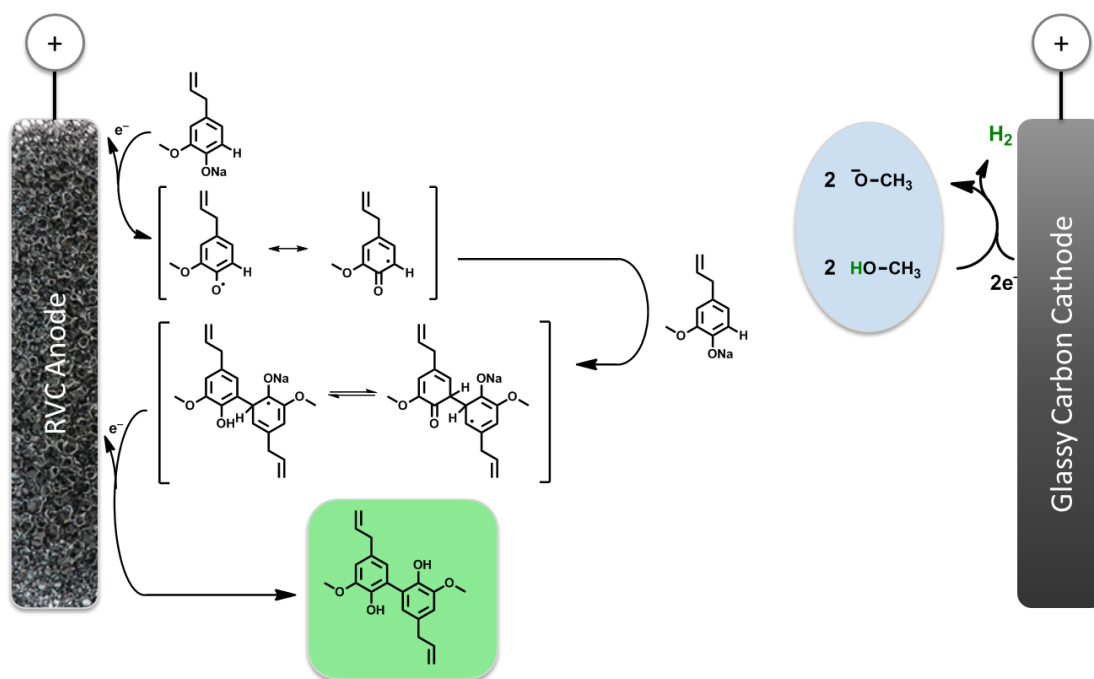


Figure S4 Postulated mechanism of the dehydrogenative phenol-phenol coupling reaction of eugenol.¹

3. Cyclovoltammetric Studies on Eugenol

Cyclic voltammetry protocol: A 4 mM solution of the substrate in 5 mL MeOH (0.1 M *N*-methyl-*N,N,N*-tributylammonium methylsulfate (MTBS)) was placed in a 20 mL beaker-type glass cell. Degassing of the solution was carried out by bubbling argon through the solution for 1 minute. Cyclic voltammetry was performed with a 100 mV/s scan rate using a glassy carbon working electrode, glassy carbon counter electrode, and Ag/AgCl reference electrode in saturated LiCl in EtOH. The peak potentials were referenced versus FcH/FcH⁺.

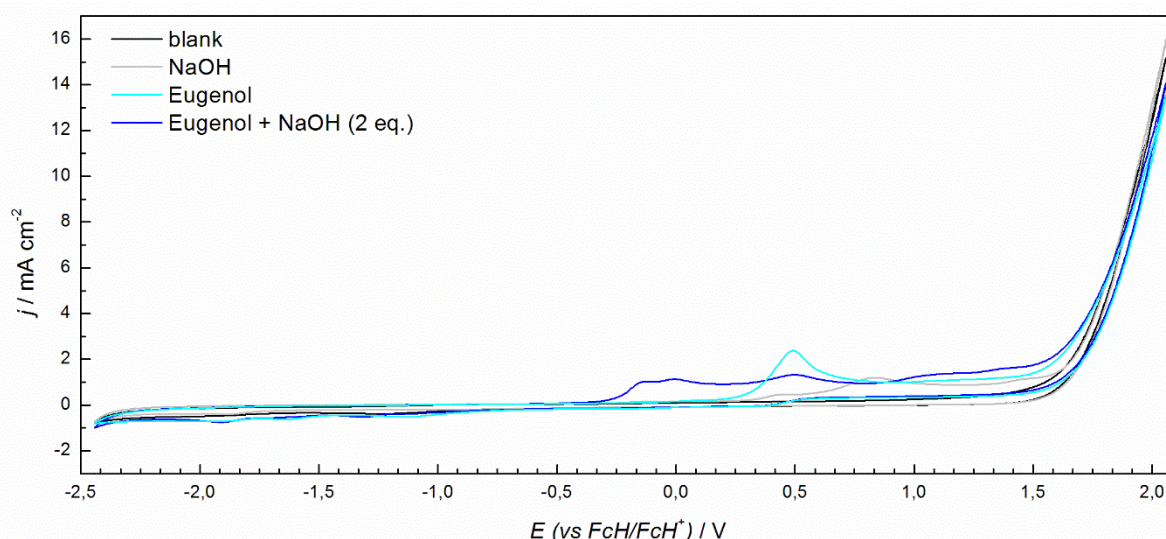


Figure S5 Cyclovoltammetric data of sodium hydroxide (grey), eugenol (light blue) and eugenol in presence of 2 eq. sodium hydroxide (blue) in methanol (0.1 M MTBS).

As expected, the oxidation potential of eugenol ($E^{ox} = 0.5$ V vs FcH/FcH⁺) is greatly reduced by about 0.5 V after deprotonation. This is in agreement with the literature.²

4. Sustainability Considerations for the Oxidative Dehydrodimerization of Eugenol

To assess the sustainability of the electrochemical dehydrodimerization in comparison to the use of potassium ferricyanate³, we used different sustainability metrics for quantification (Table S3). For the calculations, the mass of electrons is neglected.

Atom Economy (AE):

$$AE = \frac{MW_{product}}{MW_{reactants}} = \frac{326,4}{2 \times 164,2}$$

E-Factor:^{4,5}

$$E = \frac{total\ waste}{product}$$

For the calculation of the E-factor were considered: 1) electrochemical: NaOH (1.20 g), MTBS (0.47 g), methanol (17.8 g), water (15 g) and 0.53 g loss ($m_{Eugenol} - m_{Dehydrodieugenol}$) as waste and dehydrodieugenol as product (1.93 g); 2) using potassium ferricyanate: $K_3[Fe(CN)_6]$ (31.0 g), NH_4OH (25%, 362 g), acetone (235 g), water (150 g) and 0.6 g loss ($m_{Eugenol} - m_{Dehydrodieugenol}$) as waste and dehydrodieugenol as product (14.8 g).

Water is explicitly included in the calculation of the E-factor,⁵ as in contrast to organic solvents, it is commonly disposed and requires cost-intensive pre-treatment before releasing into the environment.

Reaction mass efficiency (RME):^{6,7}

$$RME = \frac{m_{product}}{\sum m_{reactants}}$$

For the calculation of RME were considered: 1) electrochemical: Dehydrodieugenol as product (1.93 g) and eugenol (2.46 g), NaOH (1.20 g) and MTBS (0.47 g) as reactants; 2) using potassium ferricyanate: Dehydrodieugenol as product (14.8 g) and eugenol (15.4 g), $K_3[Fe(CN)_6]$ (31.0 g) and NH_4OH (90.6 g) as reactants.

Table S3 Comparison of sustainability metrics for the oxidative dehydrodimerization of eugenol using $K_3[Fe(CN)_6]$ and electric current as oxidizer.

	Atom Economy (AE)	E Factor ^{4,5, a}	E Factor ^{4,5, b}	Reaction Mass Efficiency (RME) ^{6,7, a}
Electrochemically	99.4 %	63	9	47 %
$K_3[Fe(CN)_6]$	99.4 %	53	37	11 %

a) Work-up procedures may vary and were not considered. b) Organic solvents are neglected as they are ideally recycled.

5. Curing of Epoxy Resins

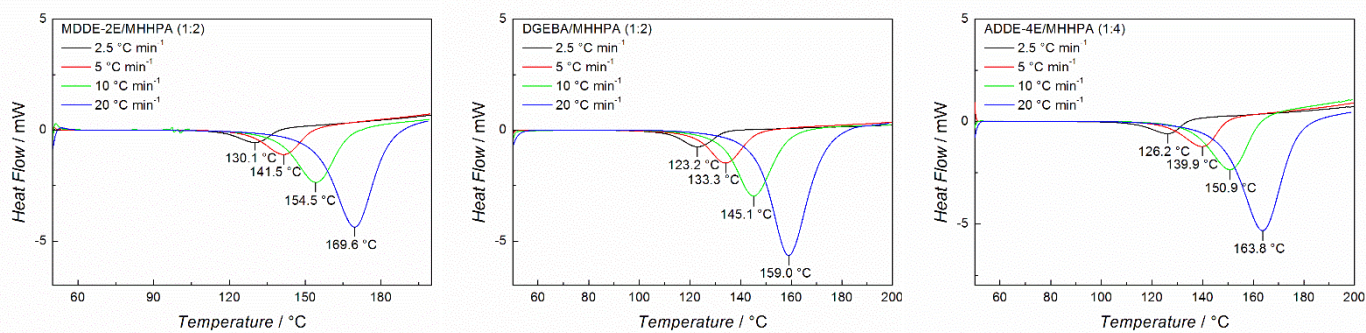
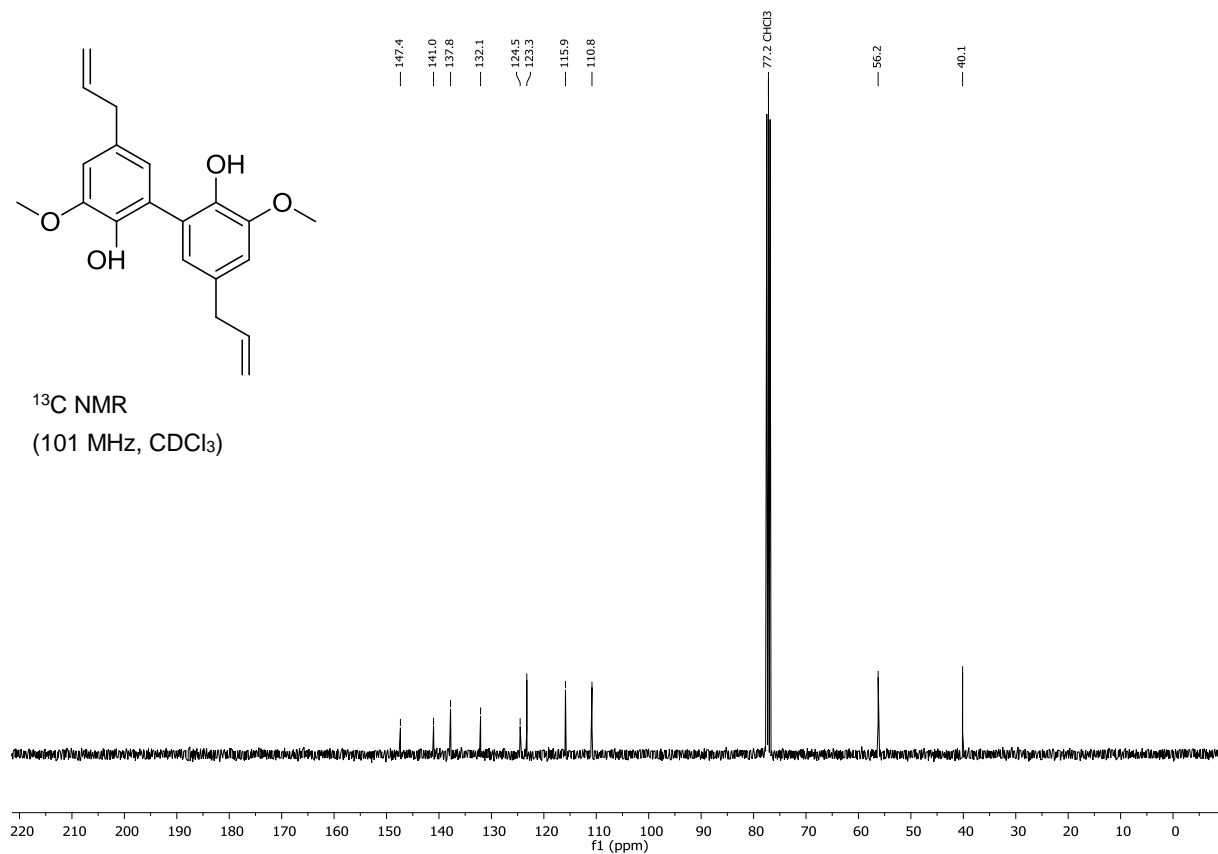
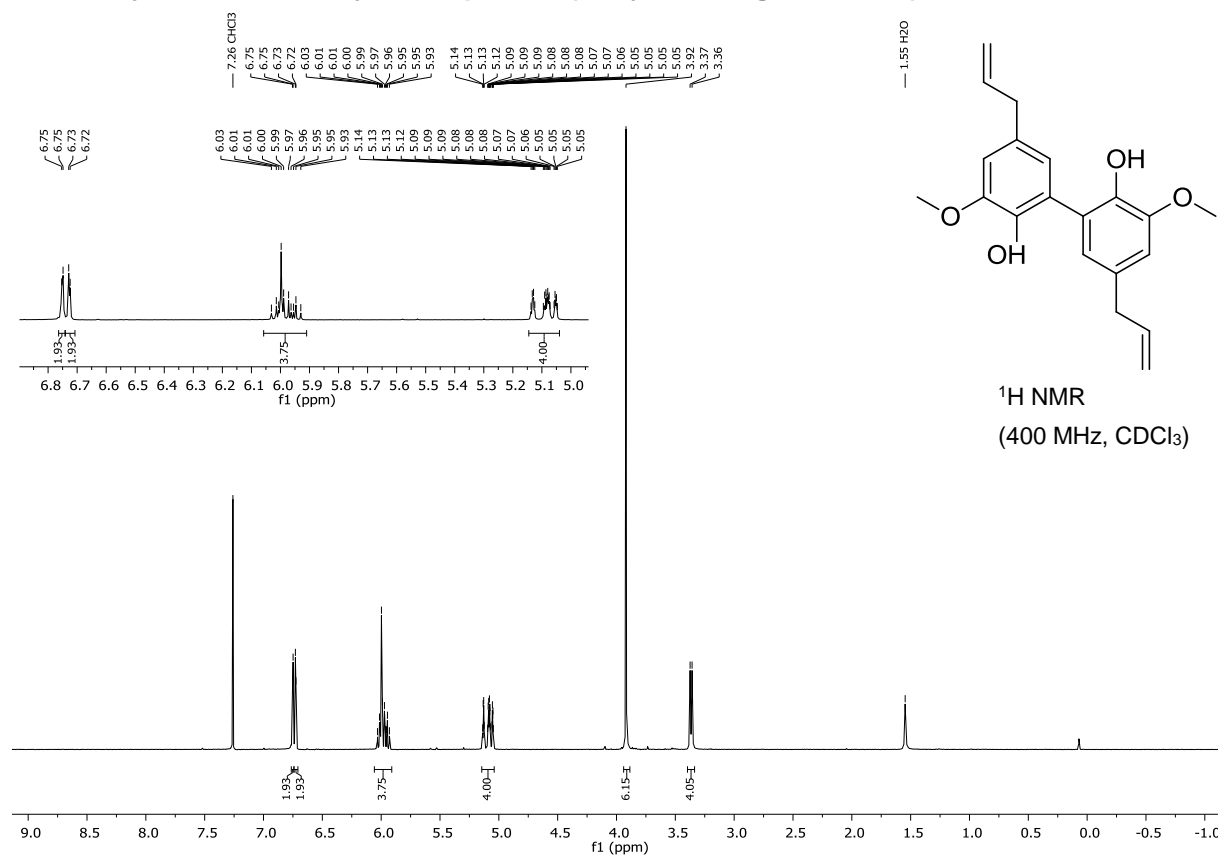


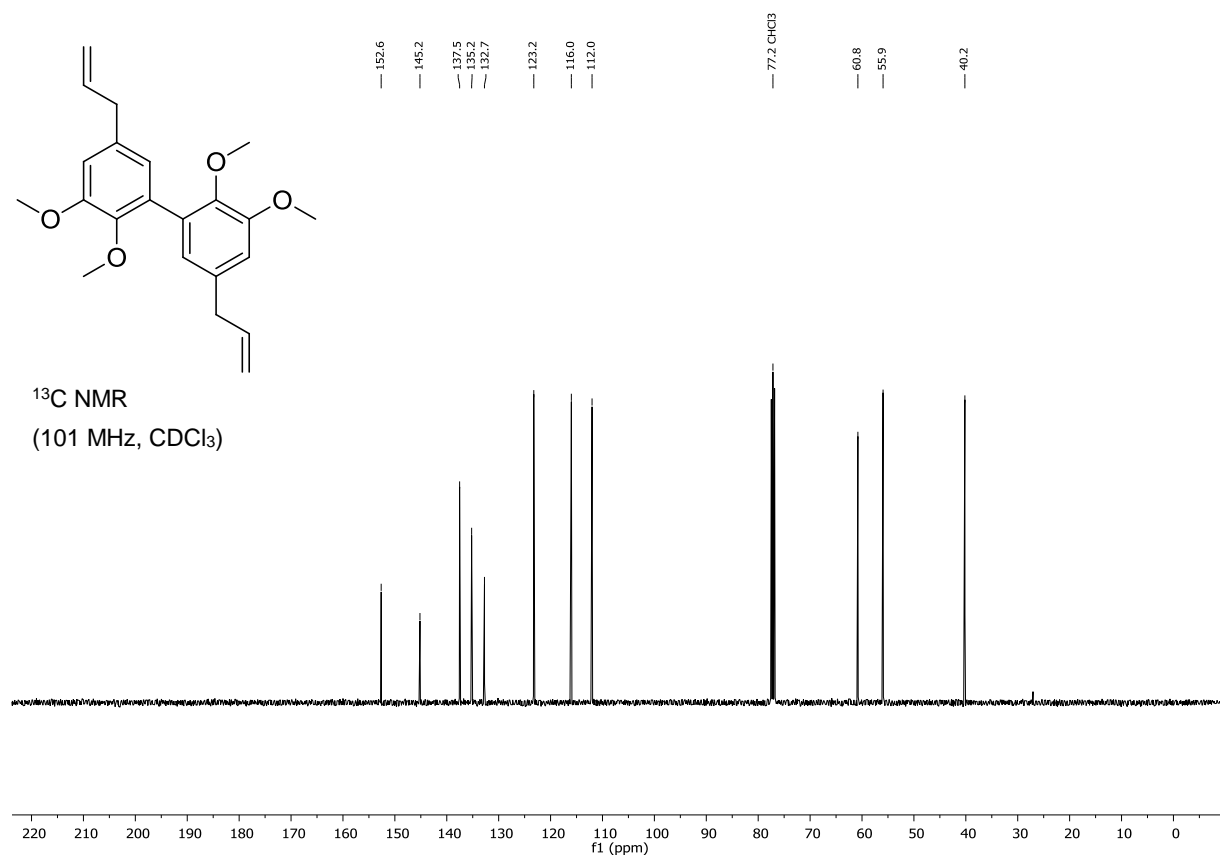
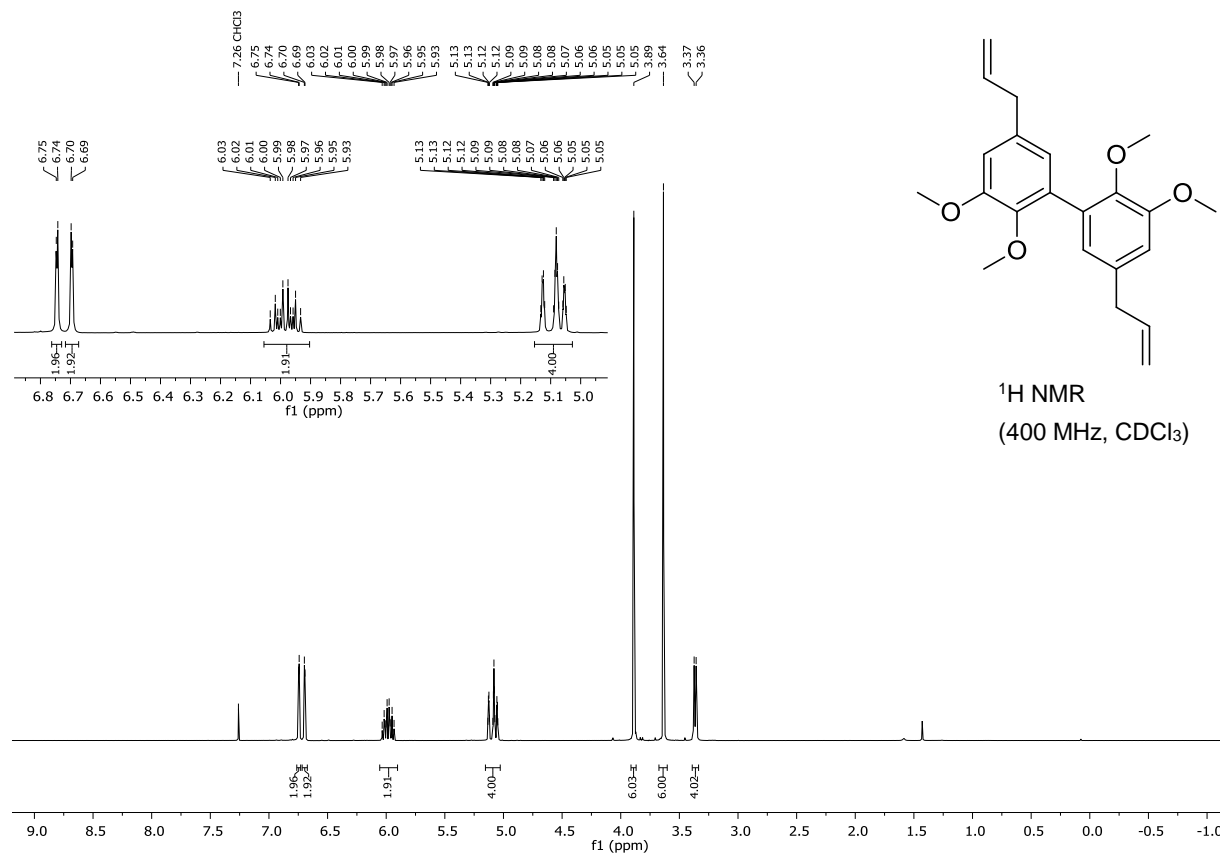
Figure S3 Curing of MDDE-2E, ADDE-4E and DGEBA was monitored by DSC at heating rates of 2.5, 5, 10, and 20 °C/min.

6. NMR Spectra

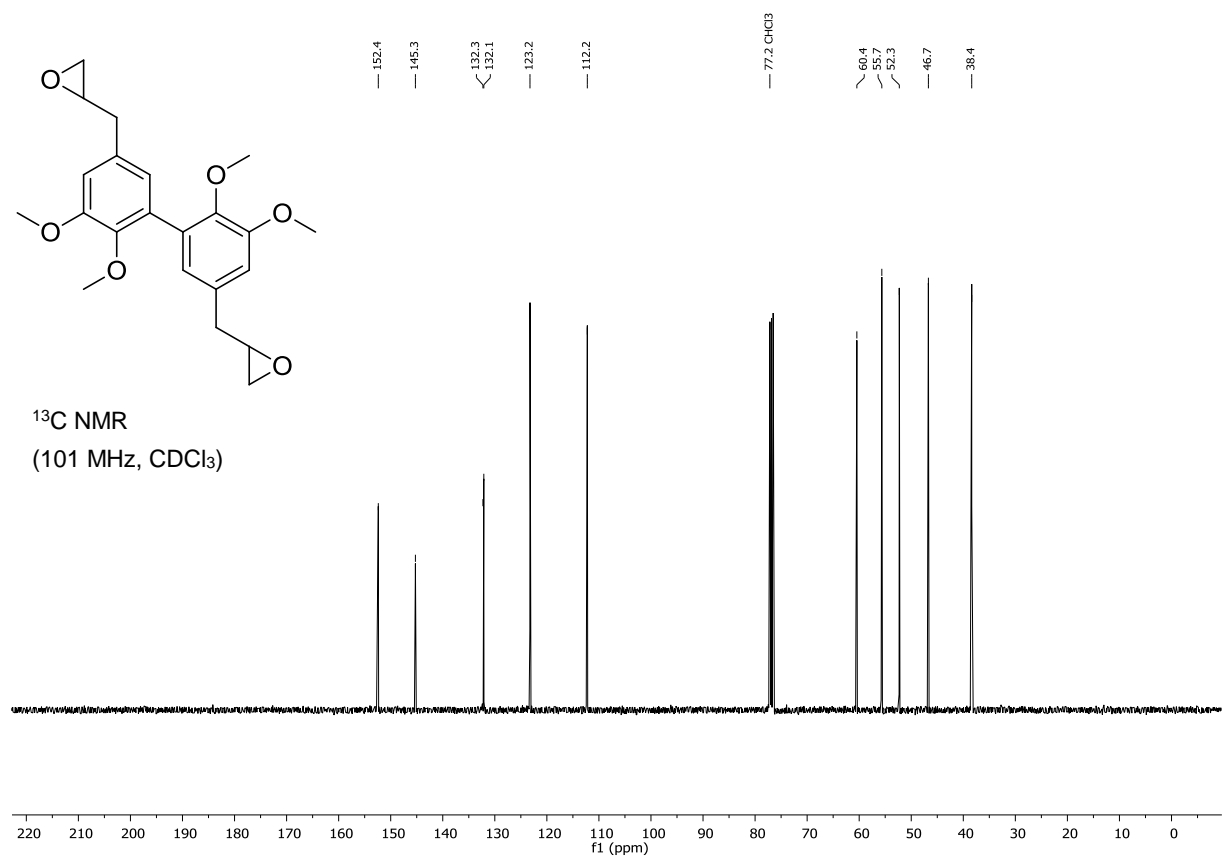
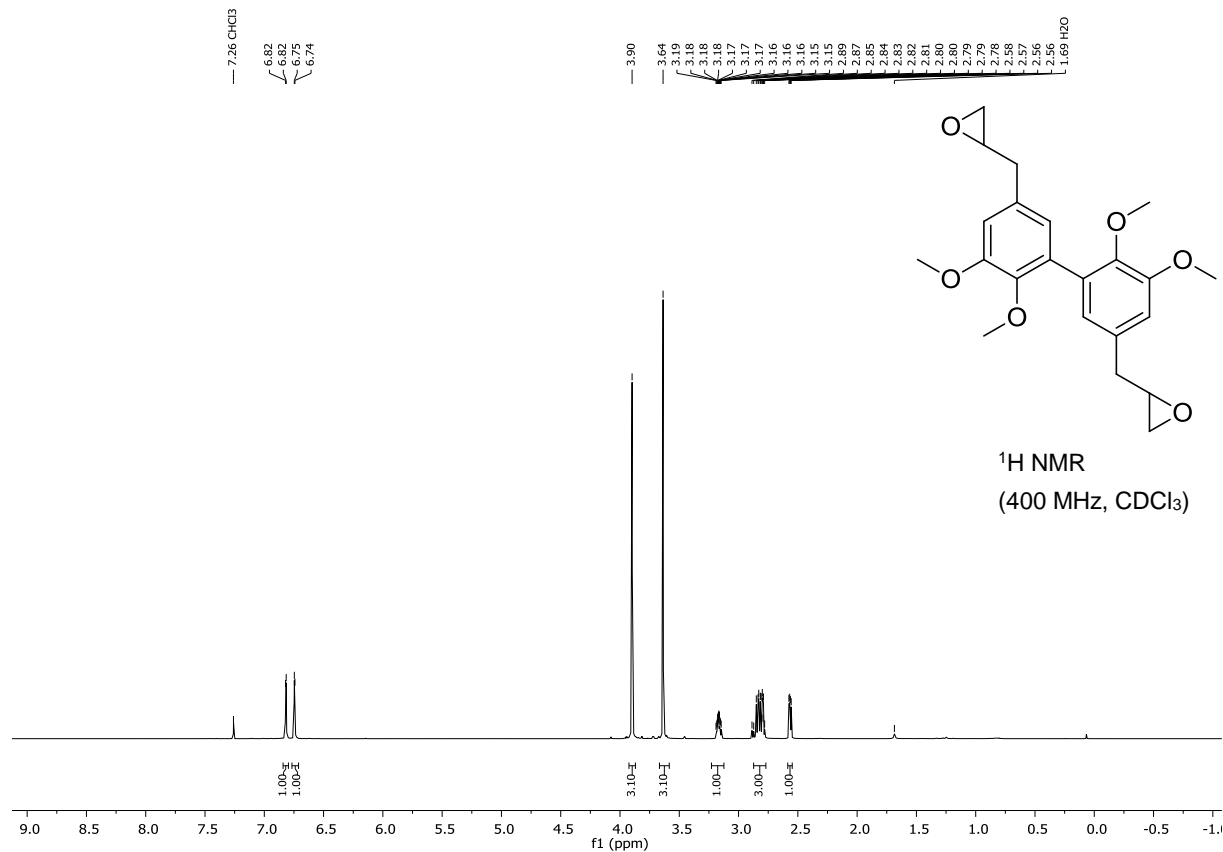
5,5'-Diallyl-3,3'-dimethoxy-2,2'-biphenol (dehydrodieugenol, DDE)



Synthesis of 5,5'-diallyl-2,2',3,3'-tetramethoxy-1,1'-biphenol (MDDE)



MDDE diepoxide (MDDE-2E)



7. References

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