

Supplementary Information for

Solid-State Structures and Properties of Lignin Hydrogenolysis Oil Compounds: Shedding a Unique Light on Lignin Valorization

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Comparison between PGGE and EGE

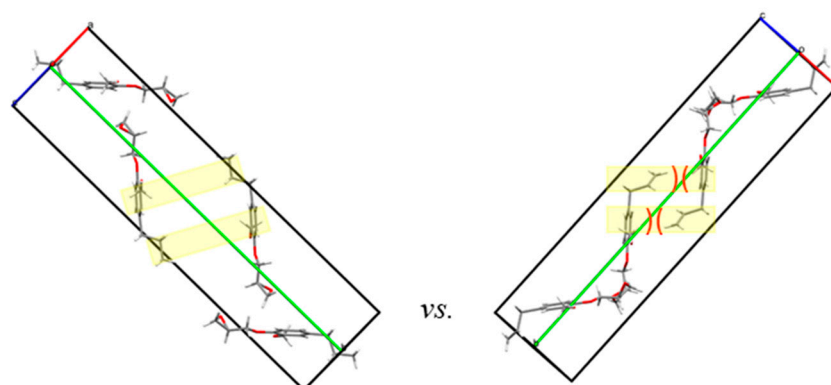


Figure S1. Comparison of PGGE and EGE respectively; the propyl side-arms for EGE are pointing towards the benzene ring of the adjacent molecule causing greater, possible steric repulsive interactions (highlighted in yellow with steric repulsion highlighted in red).

Materials and Methods

All the chemicals were commercially obtained from Merck[®] (Sigma–Aldrich[®]) or VWR[®] and used as received unless stated otherwise. Propyl guaiacol glycidyl ether, propyl guaiacol glycidyl ether dimer, eugenyl glycidyl ether and dihydroconiferyl alcohol glycidyl ether were prepared, *via* glycidylation, following previously reported protocols.^{1,2} The Differential Scanning Calorimetry (DSC) analyses were recorded on a TA Instruments Discovery DSC instrument with the samples placed in T_{zero} pans with T_{zero} hermetic lids. The sample was cooled to -60 °C at 5 °C/min, equilibrated and held at this temperature for 2 minutes, heated to 70–200 °C at 5 °C/min (1st heating cycle), held at this temperature for 1 minutes, cooled to -60 °C at 5 °C/min, equilibrated and held at this temperature for 2 minutes and heated to 70–200 °C at 5 °C/min (2nd heating cycle). Unless stated otherwise, T_g , T_c and T_m values were determined from the 2nd heating cycle between -60 °C to 70–200 °C. As mentioned in the main text, the DCA sample was analyzed again at a slower cooling rate of 0.5 °C/min, however there was no change in the thermogram.

NMR spectroscopy was recorded on a Bruker AVIII 400 MHz or benchtop Magritek Spinsolve 80 MHz Ultra series Phosphor instrument and referenced to residual solvent signals such as CHCl₃. Phosphitylation and quantitative ³¹P {¹H} NMR spectroscopy, using chromium acetylacetonate, endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide, pyridine, deuterated chloroform (CDCl₃) and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, was conducted and analyzed following reported literature.^{3–6} The Fourier-transform infrared spectroscopy (FT-IR) was performed using a Bruker Tensor 27 spectrometer and was measured using attenuated total reflectance mode (ATR-FTIR) under standard atmospheric conditions on a diamond crystal with a spectral range of 400–4000 cm⁻¹. The scan resolution was 4 cm⁻¹ with 32 scans per sample and the spectra was baseline corrected. LC-MS was performed by Dr. J. Jordens, as part of the GOAL team at VITO N.V., on a Thermo Orbitrap Q Exactive coupled with a dionex UPLC-MS. A reversed phase LC measurement was performed using an Acquity BEH C18 100 x 2.1 mm 1.7 μm column with 10 mM H₄Ac as buffer A and CH₃CN as buffer B. With gradient: t = 0 min: 2% B, t = 2 min: 2% B, t = 10 min 100% B, t = 12 min 100% B, t = 12.1 min: 2% B, t = 15 min: 2% B. The column temperature was 60 °C and 5 μl was injected. Measurements were performed using ESI in positive and negative ion mode.

For propyl guaiacol glycidyl ether (PGGE), eugenyl glycidyl ether (EGE) and the methylene propyl guaiacol dimer (MPGD), suitable, single crystals were mounted on a LithoLoop and X-ray intensity data were collected on a SuperNova, Dual, Cu at home/near, Atlas diffractometer using Cu-*K*_α (λ = 1.54184 Å) radiation and recorded at 100(2) K (see *Table S1*). The images were interpreted and integrated with the program CrysAlisPro⁷. Using Olex2⁸, the structures were solved by Intrinsic Phasing using the ShelXT structure solution program and refined by full-matrix least-squares on F² using the ShelXL program package^{9,10}. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode

with isotropic temperature factors fixed at 1.2 times $U(\text{eq})$ of the parent atoms (1.5 times for methyl groups). The structures were determined by Prof. K. Van Hecke.

For dihydroconiferyl alcohol (DCA), the propyl guaiacol dimer (PGD), the P-1 polymorph of EGE and the eugenol dimer (ED), suitable, single crystals were mounted on a Mitegen 200 μm kapton loop and X-ray diffraction data were collected at room temperature (293(2)K) or 100(2)K with $\text{Cu-K}\alpha$ ($\lambda = 1.54184 \text{ \AA}$) radiation (See *Table S1*) via ω -scans on a Rigaku R-Axis Rapid-S diffractometer, using CrystalClear 2.1.¹¹ Data reduction was done with HKL3000¹², the structure was solved with SHELXT-2018/3 and refined with SHELXL-2018/3^{9,10}, using the shelXle graphical interface.¹³

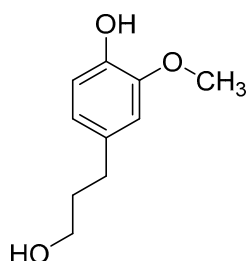
Hydrogen atoms for OH groups were geometrically calculated in idealized positions with O-H distances and H-bonding interactions freely refined (HFIX 148) and unnormalized. All other hydrogen atoms were refined using a riding model.

CCDC numbers 2359588–2359590 and 2361560–2361563 contain the supplementary crystallographic experimental data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

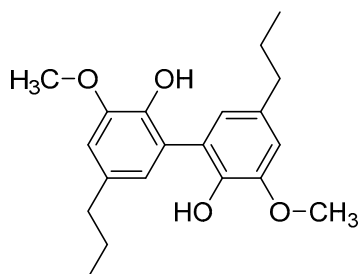
CLP intermolecular energy calculations using the SCXRD solid-state structures were made with CrystalEplorer 3.0¹⁴, based on B3LYP/6-31G(d,p) electron densities, but calibrated against a set of high-level ab initio calculations according to the methodology described in literature.¹⁵ The molecule of interest was surrounded by a 3.8 \AA radius sphere, and all molecules (partially) within this radius were completed. B3LYP/6-31G(d,p) electron densities were calculated with Tonto according to the crystal geometry from the input CIF file resulting from the refinement against the SCXRD data, and the resulting theoretical electron density grid was used directly for the CLP calculations (implemented with CrystalEplorer 3.0).¹⁶ For crystal structures with two independent molecules in the unit cell, the process was repeated for the other independent molecule. Sublimation enthalpies were summed up from the individual

intermolecular contributions, and the result was divided by 2 to arrive at a figure per mole. If disorder was present in the structure, with the exception of the *P*-1 conformer of EGE, only the major configuration for every disorder present was taken into account. For EGE, we also removed the major conformer and kept the minor, but this led, as expected, to unrealistically small stabilization energies due to strong interference of the minor conformations with their neighbors. Images of interaction networks were made with CrystalExplorer 3.0.

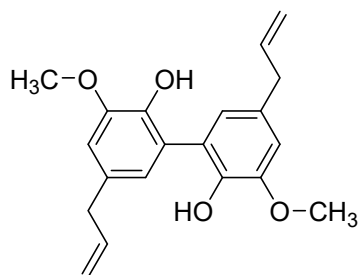
Lignin Model Compound Synthesis and Characterization



Dihydroconiferyl alcohol (DCA). This compound has previously been well reported in literature^{4,17–20} and was prepared according to the following procedures.^{18,20} ¹H NMR (400 MHz, CDCl₃) δ: 6.90–6.64 (m, 3H, ArH), 5.71 (s, 1H, OH), 3.85 (s, 3H, OCH₃), 3.67 (t, *J* = 6.4 Hz, 2H, CH₂CH₂CH₂OH), 2.68–2.57 (m, 2H, CH₂CH₂CH₂OH), 1.90–1.81 (m, 2H, CH₂CH₂CH₂OH), 1.74 (s, 1H, OH). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ: 146.6 (ArC–OCH₃), 143.8 (ArC–OH), 133.8 (ArC–CH₂CH₂CH₂OH), 121.0 (ArC), 114.4 (ArC), 111.2 (ArC), 62.3 (CH₂CH₂CH₂OH), 56.0 (OCH₃), 34.5 (CH₂CH₂CH₂OH), 31.8 (CH₂CH₂CH₂OH). FT–IR is shown in *Figure S2*. DSC curve is shown in *Figure S9*. ³¹P {¹H} NMR spectroscopy: found = 11.03 mmol total OH/g (5.42 mmol aliphatic OH/g and 5.61 mmol phenolic OH/g), theoretical = 11.0 mmol total OH/g. Recrystallisation and solid–state structure confirmed by using dichloromethane / petroleum ether to obtain crystals for single–crystal X–ray diffraction.

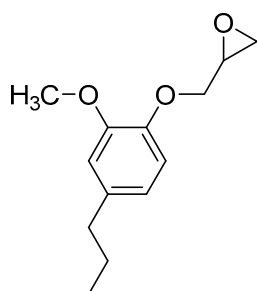


Propyl guaiacol dimer (PGD). This compound has been previously reported in literature^{21,22} and was prepared according to the following literature using the enzyme Laccase (*Trametes versicolor*).^{23–26} ¹H NMR (400 MHz, CDCl₃) δ: 6.79–6.67 (m, 4H, ArH), 6.06 (s, 2H, OH), 3.92 (s, 6H, OCH₃), 2.57 (t, *J* = 7.7 Hz, 4H, CH₂CH₂CH₃), 1.66 (sextet, *J* = 7.4 Hz, 4H, CH₂CH₂CH₃), 0.97 (t, *J* = 7.4 Hz, 6H, CH₂CH₂CH₃). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ: 147.3 (ArC–OCH₃), 140.6 (ArC–OH), 134.8 (ArC–CH₂CH₂CH₃), 124.6 (ArC), 123.1 (ArC), 110.8 (ArC), 56.2 (OCH₃), 38.0 (CH₂CH₂CH₃), 24.9 (CH₂CH₂CH₃), 14.0 (CH₂CH₂CH₃). FT–IR is shown in *Figure S3*. DSC curve is shown in *Figure S10*. Recrystallisation and solid–state structure confirmed by using hot ethanol to obtain crystals for single–crystal X–ray diffraction.



Eugenol dimer (ED) or dieugenol. This compound has been previously reported in literature and is commercially available.^{22,27–29} The compound was prepared according to the following literature using the enzyme Laccase (*Trametes*

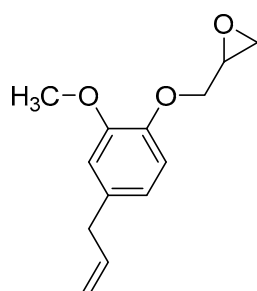
versicolor).^{23–26} ¹H NMR (400 MHz, CDCl₃) δ: 6.78–6.67 (m, 4H, ArH), 6.05–5.91 (m, 4H, CH₂CH=CH₂ + OH), 5.15–5.02 (m, 4H, CH₂CH=CH₂), 3.92 (s, 6H, OCH₃), 3.37 (d, J = 6.7 Hz, 4H, CH₂CH=CH₂). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ: ArC–OCH₃ (147.4), 141.1 (ArC–OH), 137.8 (CH₂CH=CH₂), 132.1 (ArC–CH₂CH=CH₂), 124.5 (ArC), 123.3 (ArC), 115.9 (CH₂CH=CH₂), 110.8 (ArC), 56.2 (OCH₃), 40.1 (CH₂CH=CH₂). FT–IR is shown in *Figure S4*. DSC curve is shown in *Figure S11*. Recrystallisation and solid–state structure confirmed by using hot ethanol to obtain crystals for single–crystal X–ray diffraction.



Propyl guaiacol glycidyl ether (PGGE). The compound was prepared following a previously reported epoxidation protocol² and similar epoxidized guaiacol classed compounds are reported in literature.^{30–33} ¹H NMR (400 MHz, CDCl₃) δ: 6.88–6.64 (m, 3H, ArH), 4.19 (dd, J = 11.3,

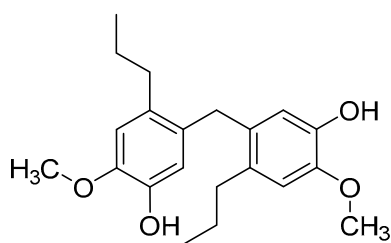
3.6 Hz, 1H, CH₂–glycidyl ether), 4.01 (dd, J = 11.4, 5.5 Hz, 1H, CH₂–glycidyl ether), 3.85 (s, 3H, OCH₃), 3.39–3.34 (m, 1H, CH of the glycidyl ether), 2.87 (dd, J = 5.0, 4.0 Hz, 1H, CH₂ of the glycidyl ether), 2.72 (dd, J = 5.0, 2.6 Hz, 1H, CH₂ of the glycidyl ether), 2.56–2.48 (m, 2H, CH₂CH₂CH₃), 1.61 (sextet, J = 14.7, 7.3 Hz, 2H, CH₂CH₂CH₃), 0.93 (t, J = 7.3 Hz, 3H, CH₂CH₂CH₃). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ: 149.5 (ArC–OCH₃), 146.1 (ArC–OCH₂–glycidyl ether), 136.8 (ArC–CH₂CH₂CH₃), 120.4 (ArC), 114.5 (ArC), 112.5 (ArC), 70.6 (ArC–OCH₂–glycidyl ether), 56.0 (OCH₃), 50.4 (CH of the glycidyl ether), 45.1 (CH₂ of the glycidyl ether), 37.8 (CH₂CH₂CH₃), 24.8 (CH₂CH₂CH₃), 13.9 (CH₂CH₂CH₃). LC–MS: Calcd product = [C₁₃H₁₈O₃], found = [C₁₃H₁₈O₃]. FT–IR is shown in *Figure S5*. DSC curve is shown in *Figure S12*. Elemental analysis: Calcd for C₁₃H₁₈O₃ (found): C, 70.24 (68.28); H, 8.16 (8.05); N, 0.00

(<0.3). Recrystallisation and solid-state structure confirmed by using hot toluene to obtain crystals, that were stable at room temperature, for single-crystal X-ray diffraction.



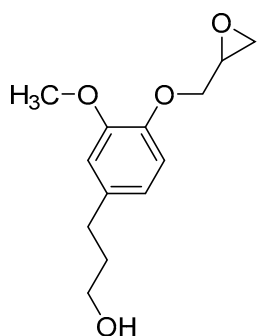
Eugenyl glycidyl ether (EGE). These compound, and similar compounds, have been previously reported in literature.^{30–32} In this instance, it was prepared according to the following a previously reported epoxidation protocol.² ¹H NMR (400 MHz, CDCl₃) δ: 6.89–

6.68 (m, 3H, *ArH*), 5.95 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H, CH₂CH=CH₂), 5.13–4.99 (m, 2H, CH₂CH=CH₂), 4.20 (dd, *J* = 11.4, 3.6 Hz, 1H, CH₂–glycidyl ether), 4.02 (dd, *J* = 11.4, 5.5 Hz, 1H, CH₂–glycidyl ether), 3.85 (s, 3H, OCH₃), 3.37 (m, 1H, CH of the glycidyl ether), 3.33 (d, *J* = 6.7 Hz, 2H, CH₂CH=CH₂), 2.88 (dd, *J* = 5.0, 4.0 Hz, 1H, CH₂ of the glycidyl ether), 2.72 (dd, *J* = 5.0, 2.6 Hz, 1H, CH₂ of the glycidyl ether). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ: 149.7 (ArC–OCH₃), 146.4 (ArC–OCH₂–glycidyl ether), 137.6 (CH₂CH=CH₂), 134.0 (ArC–CH₂CH=CH₂), 120.6 (ArC), 115.8 (CH₂CH=CH₂), 114.6 (ArC), 112.6 (ArC), 70.6 (ArC–OCH₂–glycidyl ether), 56.0 (OCH₃), 50.4 (CH of the glycidyl ether), 45.1 (CH₂ of the glycidyl ether), 39.9 (CH₂CH=CH₂). LC–MS: Calcd product = [C₁₃H₁₆O₃], found = [C₁₃H₁₆O₃]. FT–IR is shown in *Figure S6*. DSC curve is shown in *Figure S13*. Elemental analysis: Calcd for C₁₃H₁₆O₃ (found): C, 70.89 (65.12); H, 7.32 (7.80); N, 0.00 (<0.3). Recrystallisation achieved by using toluene to obtain crystals with the *P*2₁/*n* space group and using n-propanol to obtain crystals with the *P*-1 space group. These crystals were less stable at room temperature and had to be stored in a fridge to prevent melting. The solid-state structure was confirmed *via* placing the crystal on ice before mounting for single-crystal X-ray diffraction.



Methylene propyl guaiacol dimer (MPGD). This compound has previously been reported in literature and was prepared according to the following procedure.³⁴ ¹H NMR (80 MHz, CDCl₃) δ: 6.67 (s, 2H, *ArH*), 6.48 (s, 2H, *ArH*), 5.34 (s, 2H,

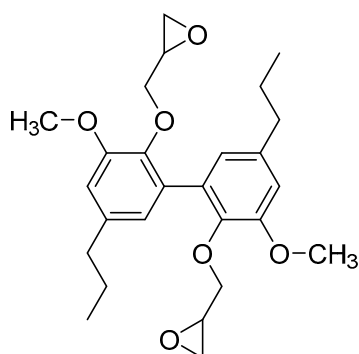
OH), 3.87 (s, 6H, OCH₃), 3.78 (s, 2H, Ar-CH₂-Ar), 2.49 (t, *J* = 7.2 Hz, 4H, CH₂CH₂CH₃), 1.88–1.24 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 6H, CH₂CH₂CH₃). Consistent with that reported in literature.³⁴ Recrystallisation and solid-state structure confirmed by using diethyl ether / heptane to obtain crystals for single-crystal X-ray diffraction. DSC curve is shown in *Figure S14*. Melting point (measured *via* the DSC) = 81 °C and consistent with literature.³⁴



Dihydroconiferyl alcohol glycidyl ether (DCAGE). The compound was prepared from the synthesized dihydroconiferyl alcohol (DCA) following a previously reported epoxidation protocol² and similar epoxidized guaiacol classed compounds are reported in literature.^{30–33}

¹H NMR (400 MHz, CDCl₃) δ: 6.92–6.65 (m, 3H, ArH), 4.21 (dd, *J* = 11.4, 3.6 Hz, 1H, CH₂-glycidyl ether), 4.02 (dd, *J* = 11.4, 5.5 Hz, 1H, CH₂-glycidyl ether), 3.86 (s, 3H, OCH₃), 3.73–3.63 (m, 2H, CH₂CH₂CH₂OH), 3.42–3.33 (m, 1H, CH of the glycidyl ether), 2.89 (dd, *J* = 4.9, 4.1 Hz, 1H, CH₂ of the glycidyl ether), 2.73 (dd, *J* = 4.9, 2.6 Hz, 1H, CH₂ of the glycidyl ether), 2.69–2.57 (m, 2H, CH₂CH₂CH₂OH), 1.94–1.82 (m, 2H, CH₂CH₂CH₂OH). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ: 149.5 (ArC-OCH₃), 146.2 (ArC-OCH₂-glycidyl ether), 135.9 (ArC-CH₂CH₂CH₂OH), 120.4 (ArC), 114.6 (ArC), 112.5 (ArC), 70.6 (ArC-OCH₂-glycidyl ether), 62.1 (CH₂CH₂CH₂OH), 55.9 (OCH₃), 50.4 (CH of the glycidyl ether), 45.1 (CH₂ of the glycidyl ether), 34.3 (CH₂CH₂CH₂OH), 31.8 (CH₂CH₂CH₂OH). In both the ¹H NMR and ¹³C {¹H} NMR spectra was also observed a small amount of minor aliphatic resonance signals related to residual ethyl acetate solvent and also most likely DCA synthesis and/or undesired glycidylation side-products. Phosphitylation and quantitative ³¹P {¹H} NMR (32 MHz, CDCl₃): found = 4.87 mmol aliphatic OH/g, theoretical = 4.23 mmol aliphatic OH/g. LC-MS: Calcd product = [C₁₃H₁₈O₄], found = [C₁₃H₁₈O₄]. FT-IR is shown in *Figure S7*. DSC curve is shown in *Figure S15*. Elemental analysis: Calcd for

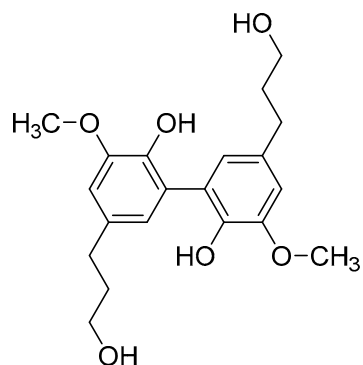
C₁₃H₁₈O₄ (found): C, 65.53 (68.09); H, 7.61 (7.46); N, 0.00 (<0.3). Attempts at recrystallisation to obtain crystals for single-crystal X-ray diffraction were unsuccessful.



Propyl guaiacol dimer diglycidyl ether (PGD diepoxide).

The compound was prepared from the synthesized propyl guaiacol dimer (PGD) following a previously reported epoxidation protocol for DSC analysis.² Similar diglycidyl ether dimer compounds are reported in literature.^{28,35–38} ¹H

NMR (80 MHz, CDCl₃) δ: 6.67 (m, 4H, ArH), 4.29–3.64 (m, 10H, OCH₃ + CH₂–glycidyl ether), 3.18–2.90 (m, 2H, CH of the glycidyl ether), 2.74–2.30 (m, 8H, CH₂CH₂CH₃ + CH₂ of the glycidyl ether), 1.90–1.40 (m, 4H, CH₂CH₂CH₃), 0.95 (t, J = 7.3 Hz, 6H, CH₂CH₂CH₃). DSC curve is shown in *Figure S16*. Elemental analysis: Calcd for C₂₆H₃₄O₆ (found): C, 70.56 (69.3); H, 7.74 (8.0); N, 0.00 (<0.1).



Dihydroconiferyl alcohol dimer (DCA dimer).

The compound was prepared as part of a three-step synthesis: 1) Enzymatic acetate protection of the aliphatic OH group using enzyme Novozymes 51003 (*Aspergillus Oryzae*). 2) Dimerization using the enzyme Laccase (*Trametes versicolor*).

3) Deprotection of the acetate group. This was following reported literature.^{23–26,39} ¹H NMR (400 MHz, DMSO–d₆) δ: 8.08 (s, 2H, ArOH), 6.70 (d, J = 2.0 Hz, 2H, ArH), 6.50 (d, J = 2.0 Hz, 2H, ArH), 4.38 (t, J = 5.2 Hz, 2H, CH₂CH₂CH₂OH), 3.76 (s, 6H, OCH₃), 3.40–3.35 (m, 4H, CH₂CH₂CH₂OH), 1.71–1.59 (m, 4H, CH₂CH₂CH₂OH). ¹³C {¹H} NMR (101 MHz, DMSO–d₆) δ: 147.6 (ArC–OCH₃), 141.4 (ArC–OH), 132.2 (ArC–CH₂CH₂CH₂OH), 125.9 (ArC), 122.7 (ArC), 110.7 (ArC), 60.2 (CH₂CH₂CH₂OH), 55.8 (OCH₃), 34.6 (CH₂CH₂CH₂OH), 31.3 (CH₂CH₂CH₂OH). FT–IR is shown in *Figure S8*. DSC curve is shown in *Figure S17*.

IR Spectra of Lignin Model Compounds

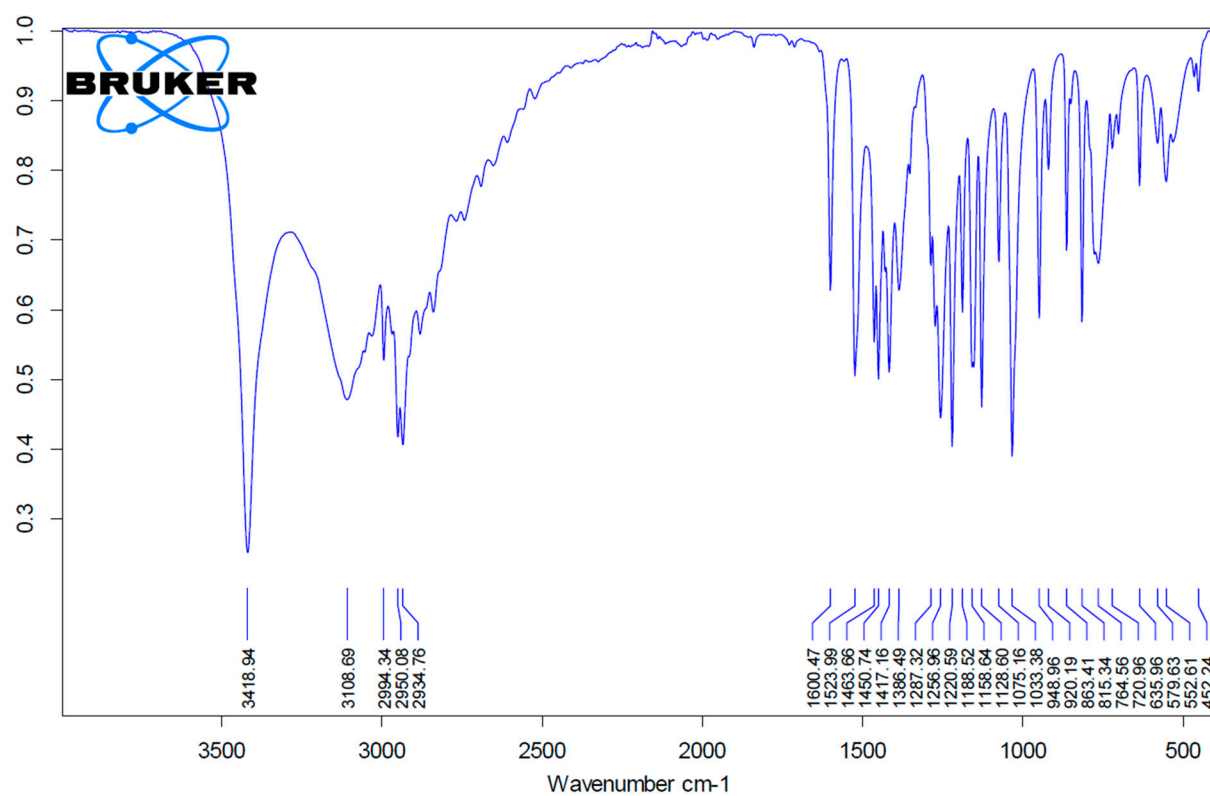


Figure S2. FT-IR of dihydroconiferyl alcohol (DCA).

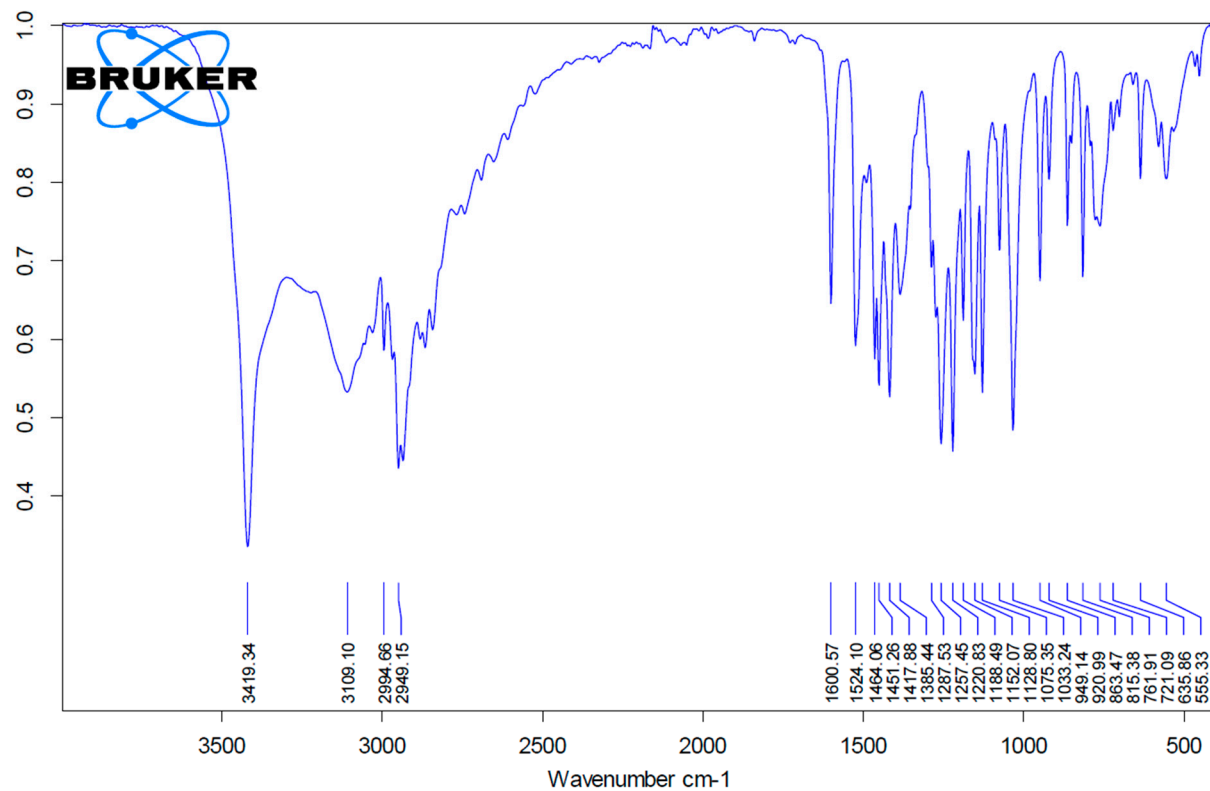


Figure S3. FT-IR of propyl guaiacol dimer (PGD).

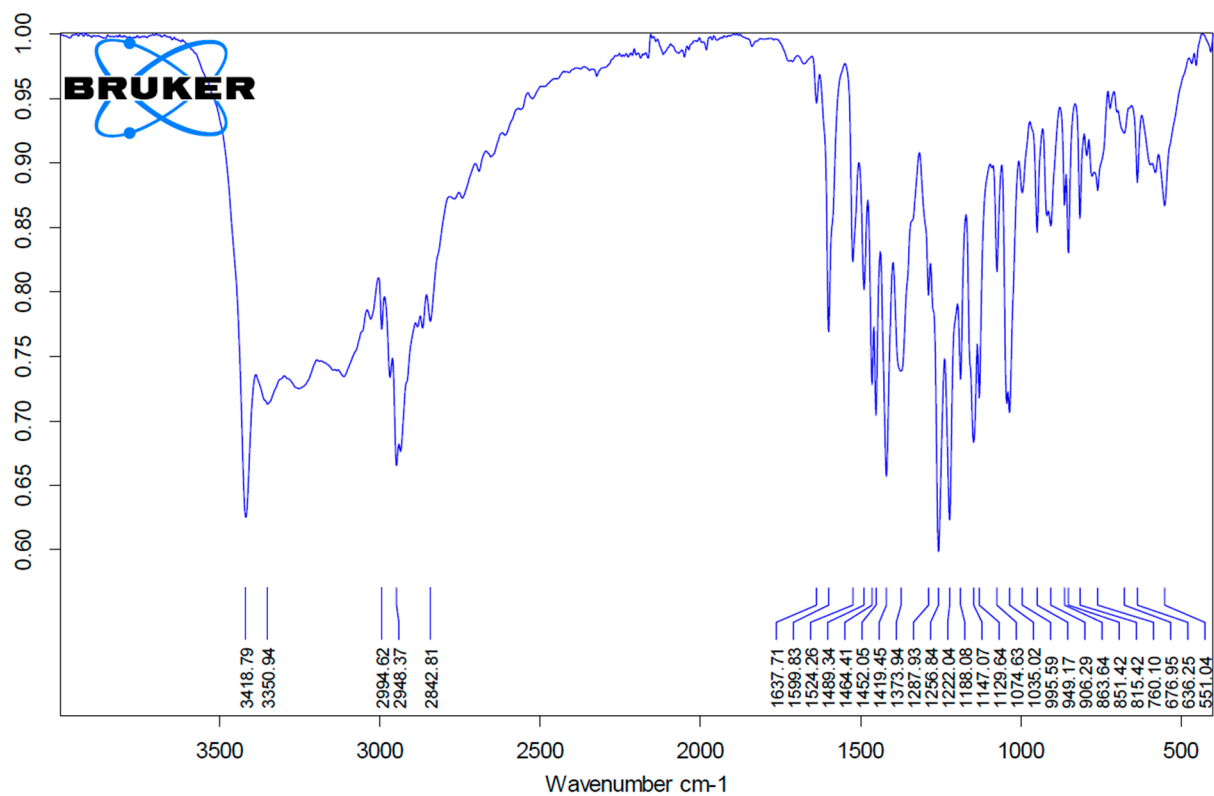


Figure S4. FT-IR of eugenol dimer (ED).

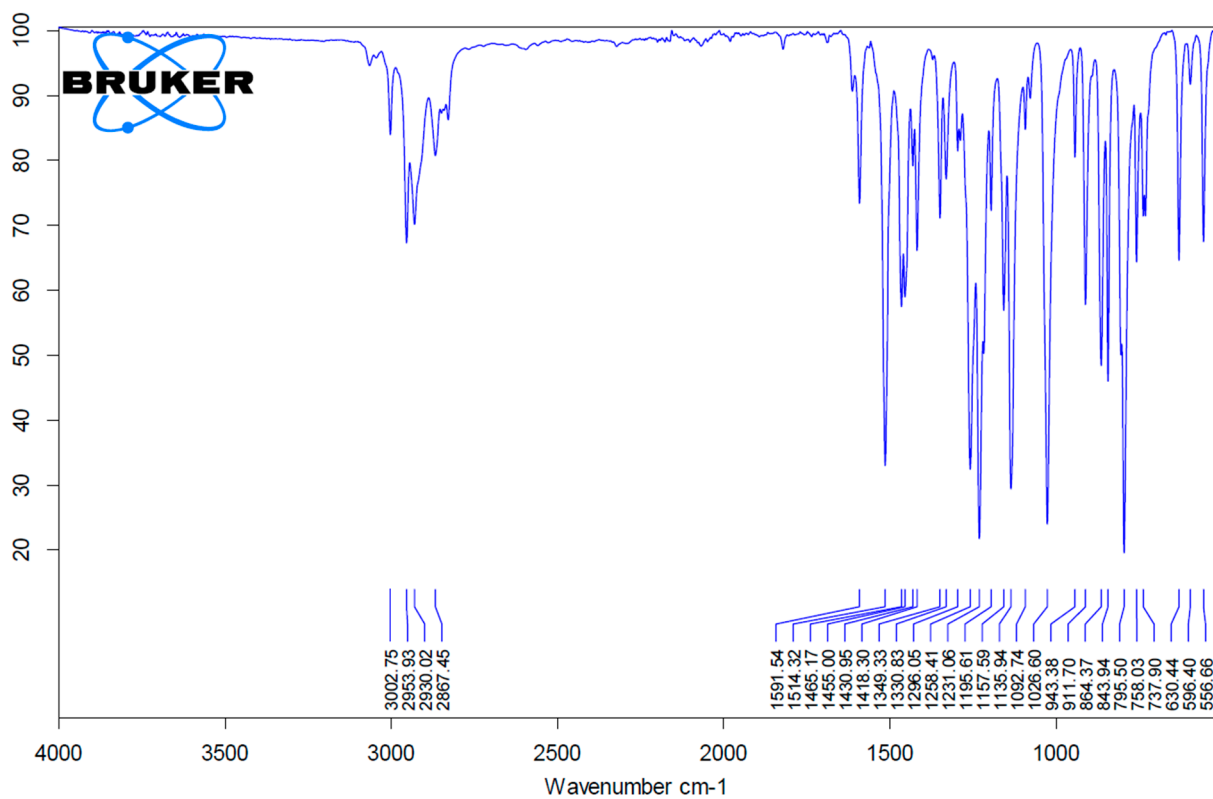


Figure S5. FT-IR of propyl guaiacol glycidyl ether (PGGE).

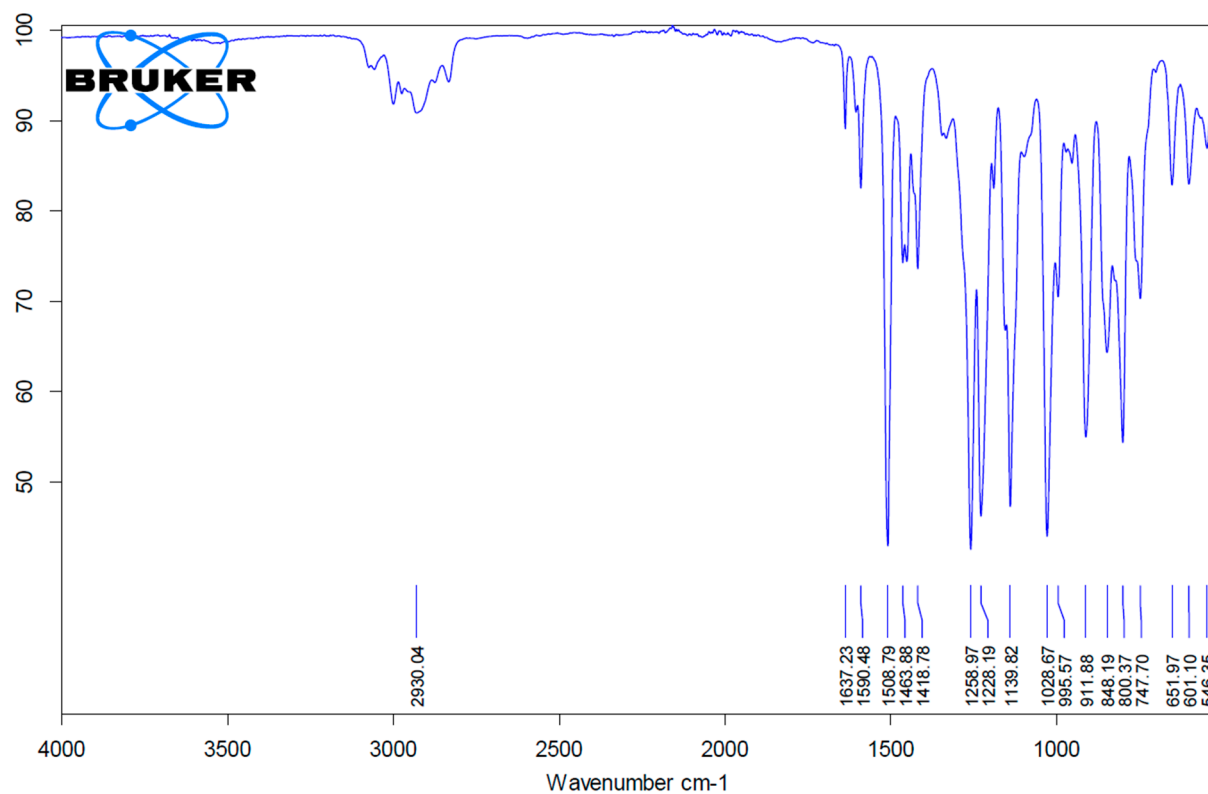


Figure S6. FT-IR of eugenyl glycidyl ether (EGE).

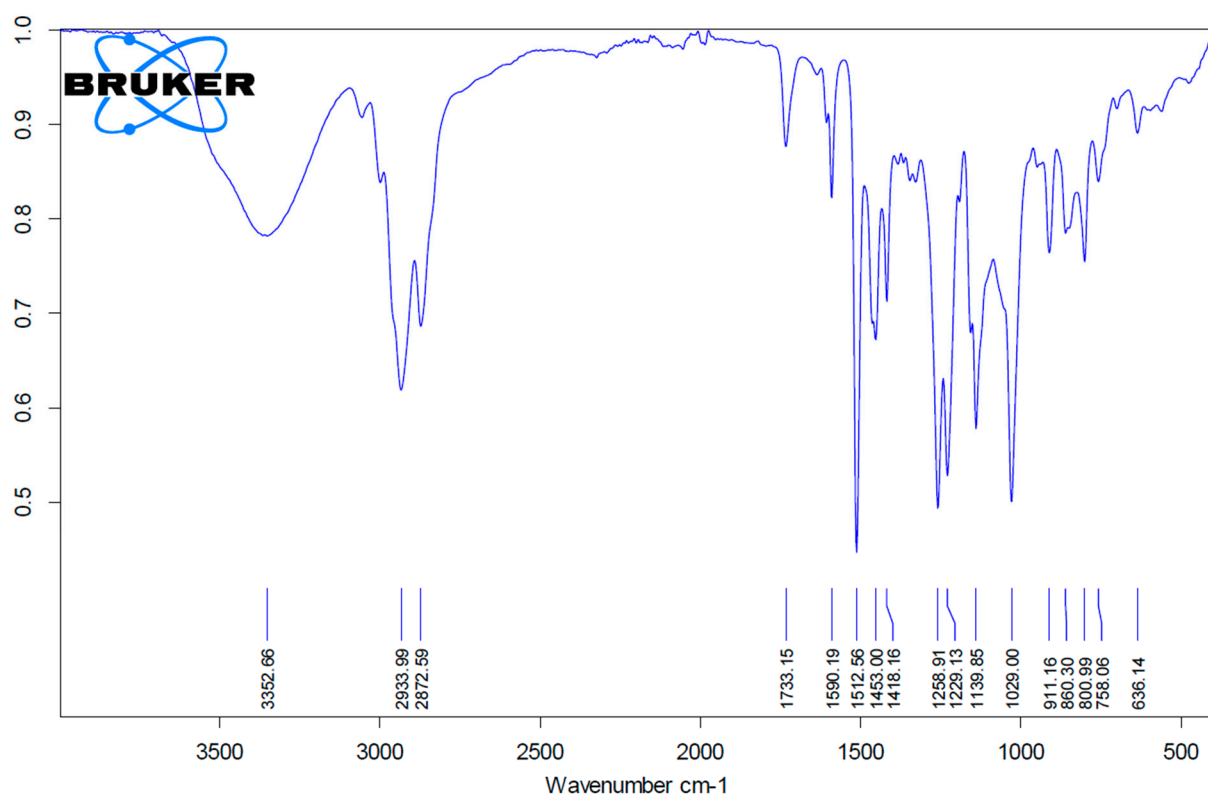


Figure S7. FT-IR of dihydroconiferyl alcohol glycidyl ether (DCAGE).

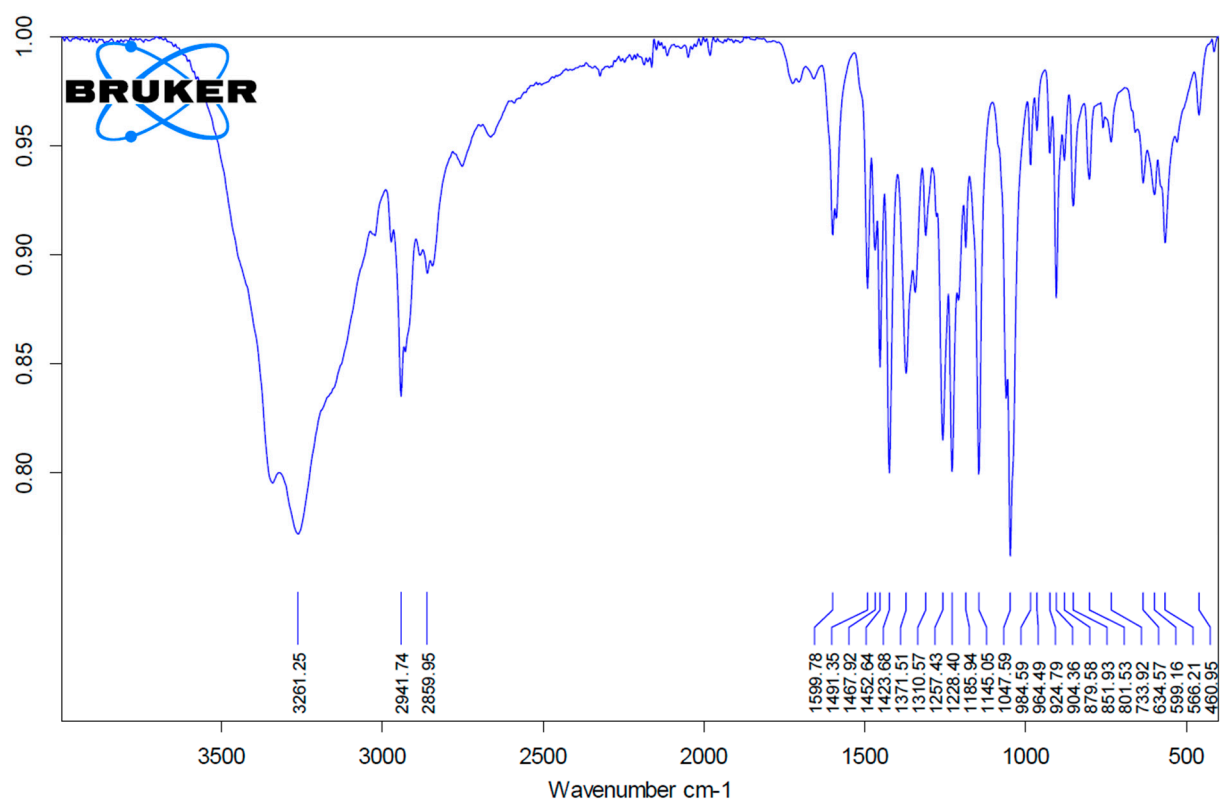


Figure S8. FT-IR of dihydroconiferyl alcohol dimer (DCA dimer).

DSC Curves of Lignin Model Compounds

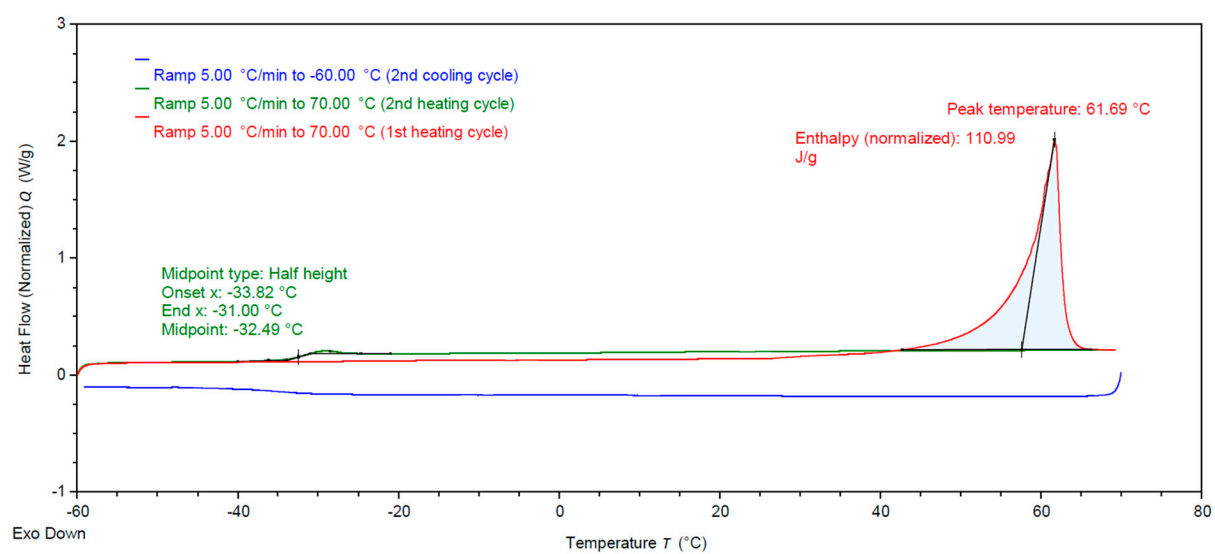


Figure S9. DSC curve of dihydroconiferyl alcohol (DCA).

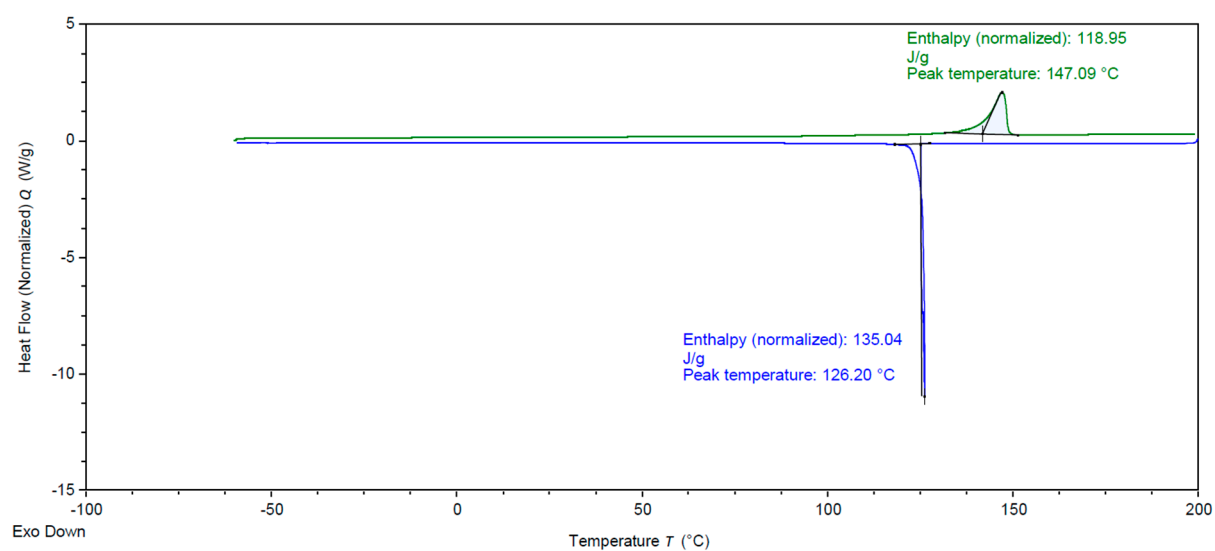


Figure S10. DSC curve of propyl guaiacol dimer (PGD).

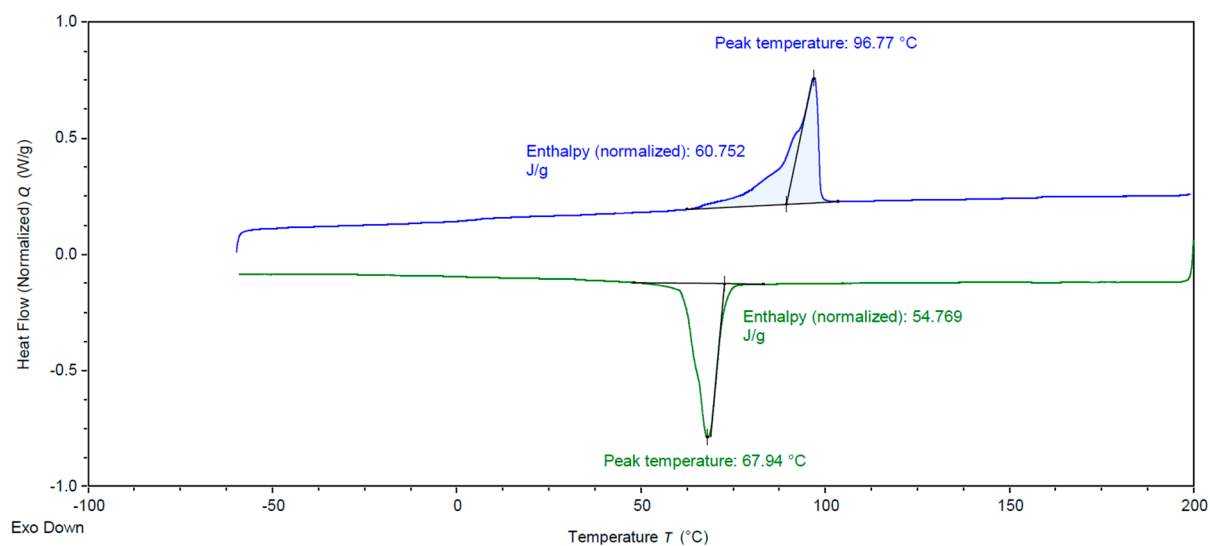


Figure S11. DSC curve of eugenol dimer (ED).

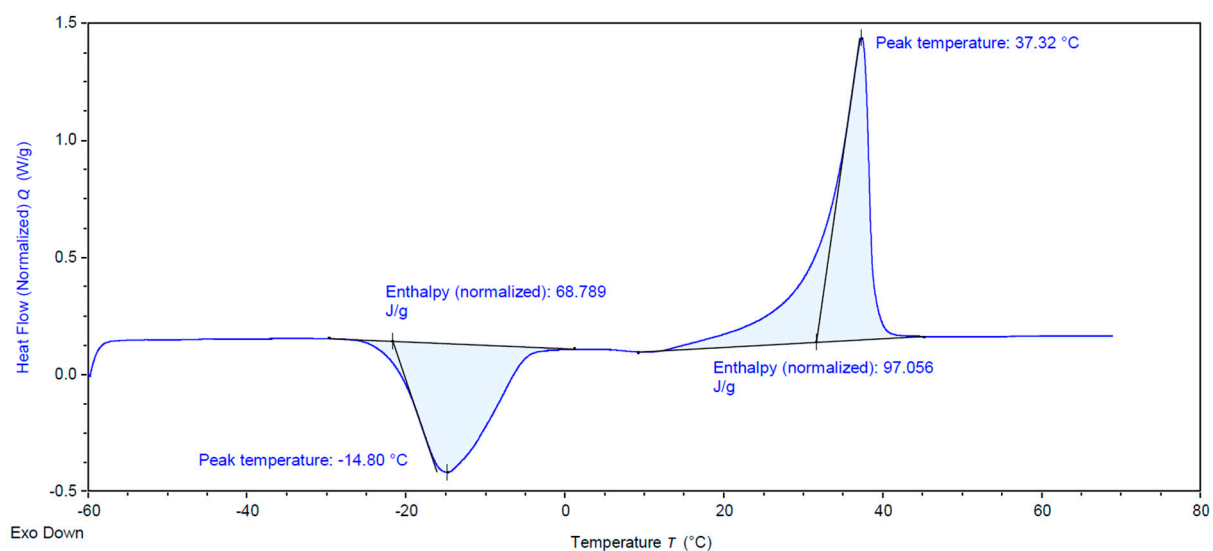


Figure S12. DSC curve of propyl guaiacol glycidyl ether (PGGE).

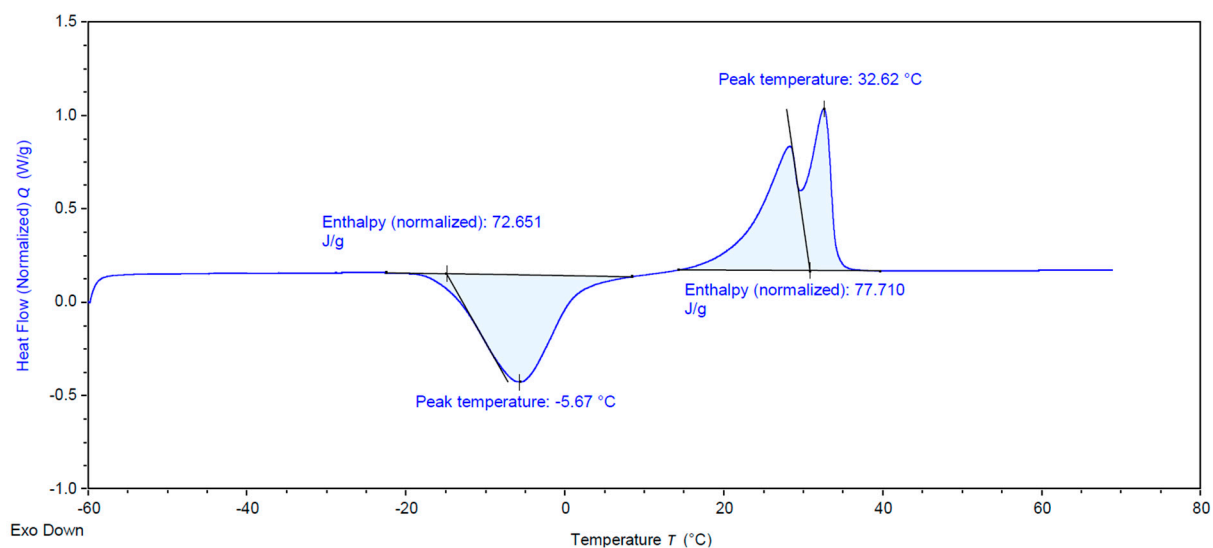


Figure S13. DSC curve of eugenyl glycidyl ether (EGE).

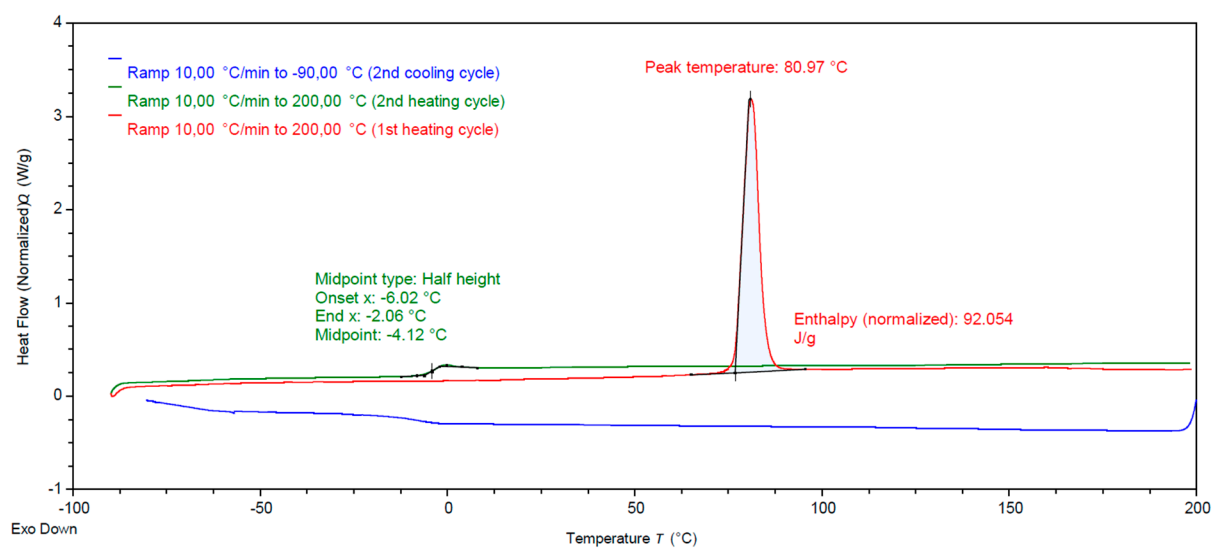


Figure S14. DSC curve of methylene propyl guaiacol dimer (MPGD).

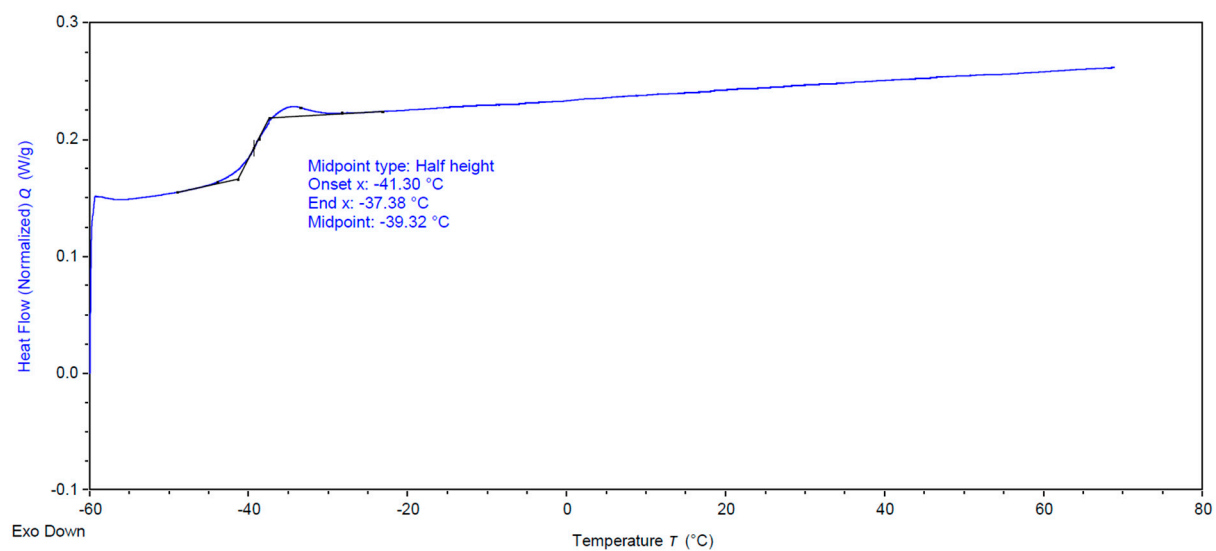


Figure S15. DSC curve of dihydroconiferyl alcohol glycidyl ether (DCAGE).

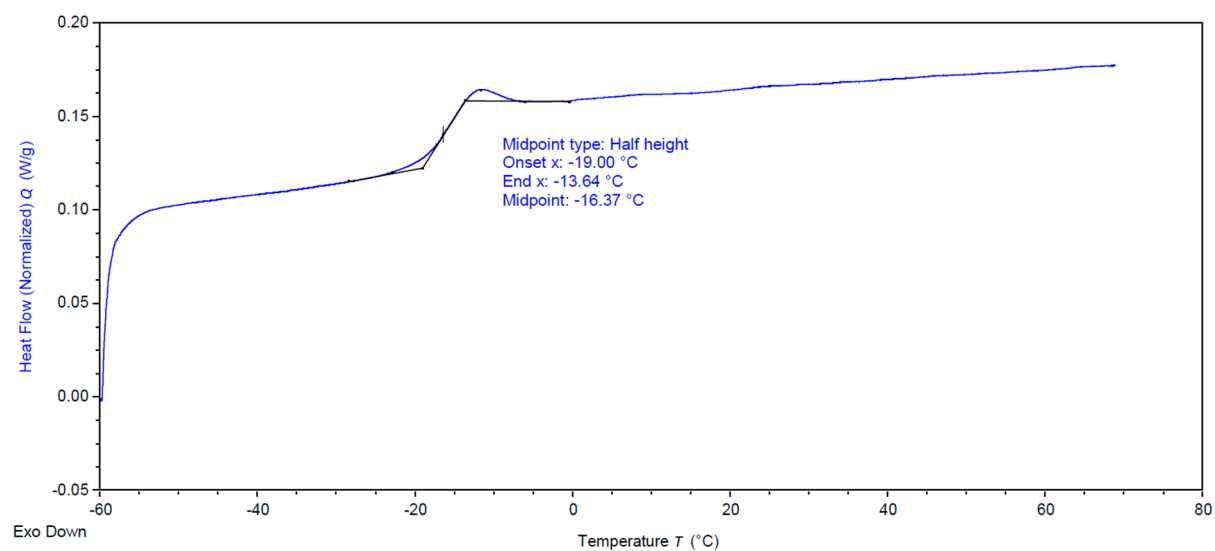


Figure S16. DSC curve of propyl guaiacol dimer diglycidyl ether (PGD diepoxide).

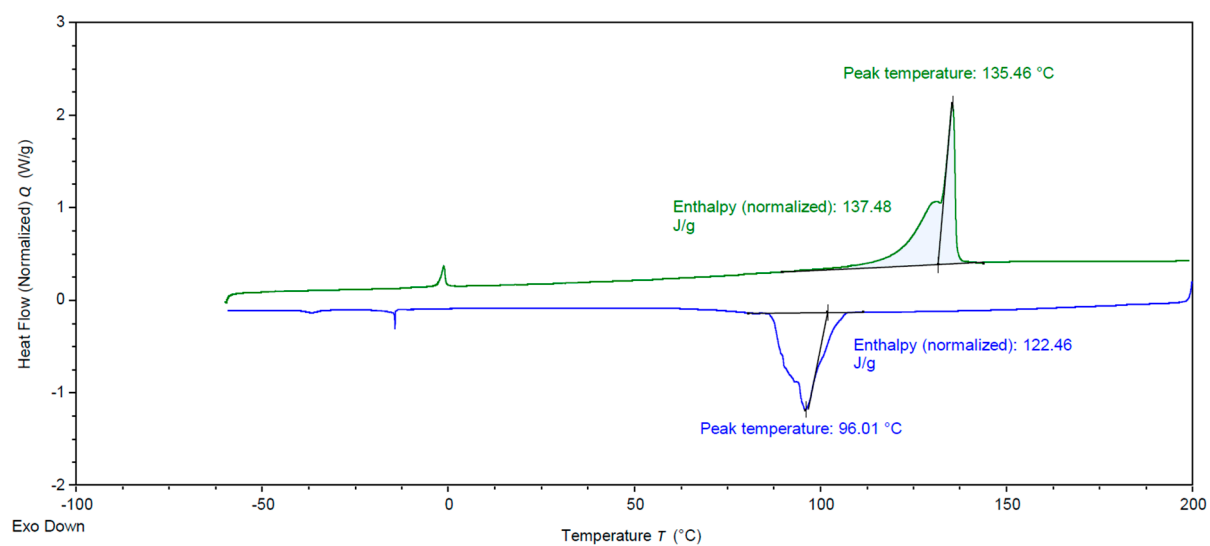


Figure S17. DSC curve of dihydroconiferyl alcohol dimer (DCA dimer).

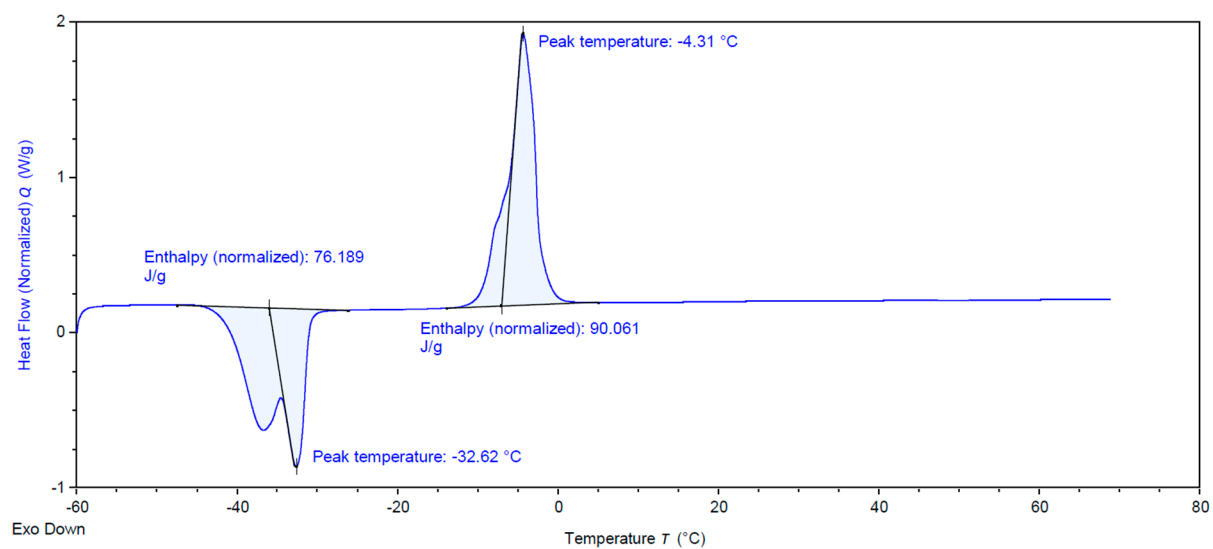


Figure S18. DSC curve of commercial propyl guaiacol (PG).

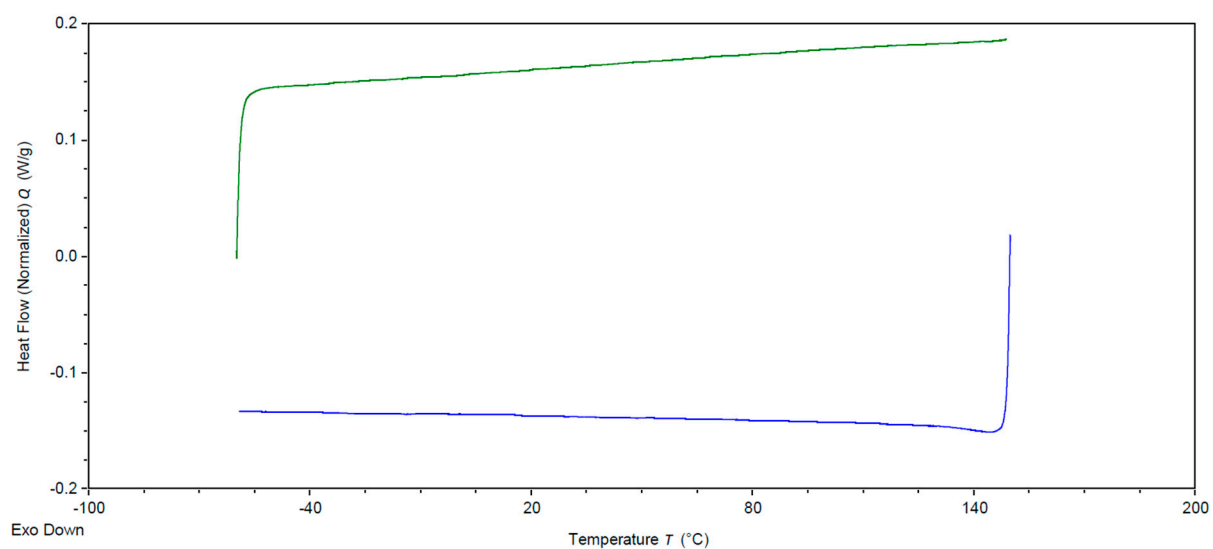


Figure S19. DSC curve of commercial eugenol (E).

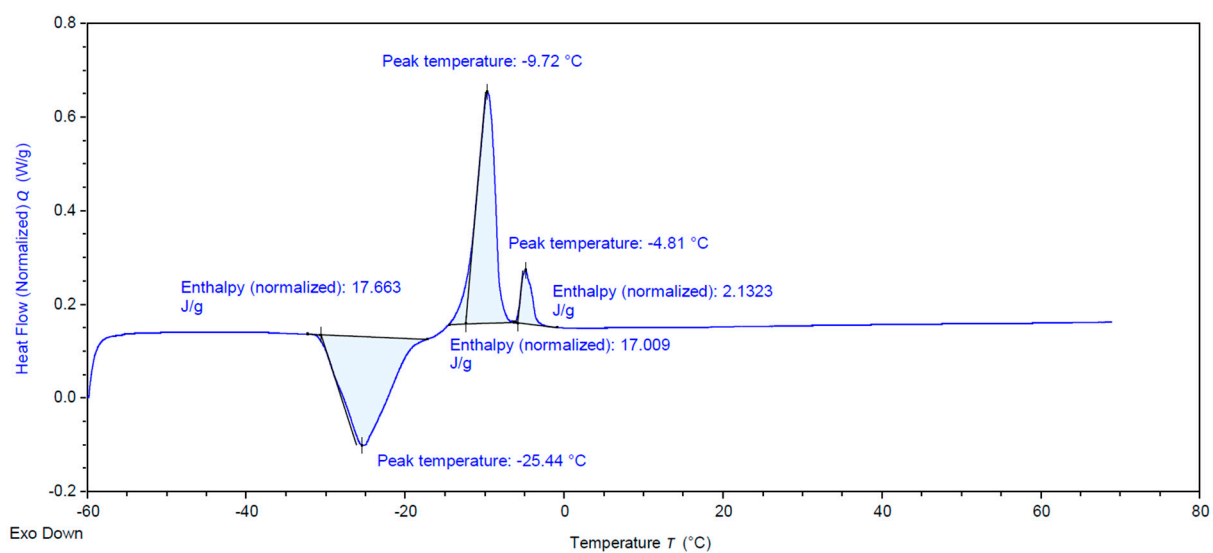


Figure S20. DSC curve of commercial phenyl glycidyl ether (PGE).

Crystallographic Tables and Additional Data for Observed Interactions

Table S1. Data collection and refinement statistics of all solid-state X-ray structures obtained in this study.

Compound reference	DCA	PGGE	EGE	EGE	PGD	ED	MPGD
Chemical formula	C ₂₀ H ₂₈ O ₆	C ₁₃ H ₁₈ O ₃	C ₁₃ H ₁₆ O ₃	C ₁₃ H ₁₆ O ₃	C ₂₀ H ₂₆ O ₄	C ₂₀ H ₂₂ O ₄	C ₂₁ H ₂₈ O ₄
Formula Mass	364.44	222.27	220.26	220.26	330.42	326.39	344.43
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P-1</i>	<i>P2₁/n</i>	<i>P-1</i>	<i>Pbcn</i>
<i>a</i> /Å	16.8772(8)	4.69745(4)	4.57278(5)	4.800(1)	12.1330(8)	8.9744(10)	14.29790(10)
<i>b</i> /Å	6.6647(3)	32.1516(2)	31.8895(3)	9.808(2)	9.0268(5)	12.4696(17)	8.83350(10)
<i>c</i> /Å	17.2045(7)	7.88843(8)	7.85762(9)	12.398(2)	33.6388(16)	16.4182(18)	30.3232(3)
α /°	90	90	90	87.37(2)	90	79.393(9)	90
β /°	90	98.0546(9)	96.3333(10)	82.33(2)	99.617(4)	81.097(10)	90
γ /°	90	90	90	82.20(2)	90	88.283(10)	90
Unit cell volume/Å ³	1935.47(14)	1179.641(17)	1138.83(2)	572.9(2)	3632.4(4)	1784.2(4)	3829.84(6)
Temperature/K	293(2)	100(2)	100(2)	100(2)	293(2)	293(2)	100(2)
No. of formula units per unit cell, <i>Z</i>	4	4	4	2	8	4	8
Radiation type	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α
No. of reflections measured	14555	33721	32507	6794	30635	31959	32143
No. of independent reflections	1880	2385	2304	1934	6903	6203	3864
<i>R</i> _{int}	0.0385	0.0354	0.0620	0.053	0.0488	0.0526	0.0486
Final <i>R</i> ₁ values [(<i>I</i> > 2 σ (<i>I</i>)]	0.0388	0.0377	0.0426	0.087	0.0555	0.0583	0.0379
Final <i>wR</i> ₂ values [(<i>I</i> > 2 σ (<i>I</i>)]	0.1042	0.0928	0.1165	0.2298	0.1553	0.1696	0.1018
Final <i>R</i> ₁ values (all data)	0.0398	0.0429	0.0488	0.1013	0.0728	0.0769	0.0451
Final <i>wR</i> ₂ values (all data)	0.1054	0.0969	0.1236	0.2516	0.1738	0.1963	0.1086

Eugenyl glycidyl ether (EGE)

C–H \cdots Cg(π) intermolecular interactions (Å, °) (*Figure 4b* of the main text)

X–H \cdots Cg	H \cdots Cg	Symmetry code
C7–H7A \cdots Cg2	2.90	1+x, y, z

Cg2 the centroid of the C1–C6 ring.

Hydrogen–bond geometry (Å, °) (*Figure 4b* of the main text)

$D-H\cdots A$	$H\cdots A$	$D-H\cdots A$
C9–H9A \cdots O2	2.623 Å	158.26°

Symmetry code: 1/2+x, 3/2-y, 1/2+z

Eugenol dimer (ED)

Hydrogen–bond geometry (Å, °)

$D-H\cdots A$	Type	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 \cdots O2	Intramolecular	0.85(3)	2.17(3)	2.638(3)	114(2)
O1–H1 \cdots O21 ⁱ	Intermolecular	0.85(3)	2.18(3)	2.964(2)	152(2)
O1–H1 \cdots O22 ⁱ	Intermolecular	0.85(3)	2.45(3)	2.965(3)	120(3)
O31–H1A \cdots O11 ⁱⁱ	Intermolecular	0.84(3)	2.24(3)	2.974(2)	147(2)
O31–H1A \cdots O12 ⁱⁱ	Intermolecular	0.84(3)	2.39(3)	2.951(3)	125(3)
O31–H1A \cdots O32	Intramolecular	0.84(3)	2.21(3)	2.655(3)	113(2)
O21–H1B \cdots O31	Intramolecular	0.86(4)	1.90(4)	2.694(2)	153(2)
O11–H11 \cdots O1	Intramolecular	0.84(4)	1.88(4)	2.660(2)	155(2)

Symmetry codes: (i) 1+x,y,-1+z, (ii) x,y,1+z

C–H \cdots Cg(π) intermolecular interactions (Å, °)

X–H \cdots Cg	H \cdots Cg	X \cdots Cg	X–H \cdots Cg
C40–H40A \cdots Cg4 ⁱ	2.99	3.651(4)	127

Symmetry codes: (i): 2-x,-y,1-z. Cg4 the centroid of the C11–C16 ring.

$Cg(\pi) \cdots Cg(\pi)$ intermolecular interactions (\AA , $^\circ$)

$Cg(I) \cdots Cg(J)$	$Cg \cdots Cg$	α	β	γ	$Cg(I)$ perpendicular	$Cg(J)$ perpendicular
$Cg(2) \cdots Cg(4)^i$	5.6488(16)	81.70(12)	21.5	85.1	0.4785(10)	5.2564(10)
$Cg(3) \cdots Cg(1)^{ii}$	5.5484(17)	81.42(13)	17.7	89.2	0.0818(10)	5.2868(11)
$Cg(4) \cdots Cg(2)^{iii}$	5.8196(16)	81.70(12)	33.7	89.1	0.0944(10)	4.8416(10)

Symmetry codes: (i): 1-x,-y,1-z, (ii) 1-x,1-y,1-z, (iii) 2-x,-y,1-z. Cg1 the centroid of the C21–C26 ring, Cg2 the centroid of the C31–C36 ring, Cg3 the centroid of the C1–C6 ring and Cg4 the centroid of the C11–C16 ring. The Fractional Atomic Coordinates for the Cg rings are below.

Fractional Atomic Coordinates of the Cg centroids.

$Cg(X)$	x	y	z
Cg1	0.35288(13)	0.43164(9)	0.79603(7)
Cg2	0.73410(11)	0.21543(8)	0.78196(6)
Cg3	1.11743(12)	0.27095(8)	0.22970(6)
Cg4	0.74147(11)	0.07065(8)	0.21930(7)

Coulomb–London–Pauli (CLP) Intermolecular Energy Calculations

DCA

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
2	x, y, z	6,66	B3LYP/6-31G(d,p)	-4,6	-0,7	-15,7	8	-14,1	-28,2
1	-x, -y, -z	5,48	B3LYP/6-31G(d,p)	-112,5	-25,9	-35,5	144,8	-79,6	-79,6
2	-x+1/2, y+1/2, z	5,51	B3LYP/6-31G(d,p)	-6,7	-1,6	-32,1	19,5	-24,1	-48,2
2	x, -y+1/2, z+1/2	8,61	B3LYP/6-31G(d,p)	-35,4	-3	-18,1	40,7	-30,3	-60,6
1	-x, -y, -z	5,21	B3LYP/6-31G(d,p)	-8,8	-1,6	-28	13,5	-26,6	-26,6
2	-x, y+1/2, -z+1/2	10,98	B3LYP/6-31G(d,p)	-2,2	-0,3	-2,3	0,2	-4,5	-9
2	-x+1/2, -y, z+1/2	10,15	B3LYP/6-31G(d,p)	-0,1	-0,2	-4,7	1,1	-3,7	-7,4
2	x, -y+1/2, z+1/2	10,75	B3LYP/6-31G(d,p)	0,4	-0,2	-3	0,9	-1,7	-3,4

E_{subl}
(kJ/mol) -131,50

PGGE

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
2	x, y, z	4,7	B3LYP/6-31G(d,p)	-18,5	-4,1	-61	40,8	-50,5	-101
2	x, y, z	7,89	B3LYP/6-31G(d,p)	-2,9	-0,3	-10,5	6,3	-8,6	-17,2
2	x, y, z	8,6	B3LYP/6-31G(d,p)	-1,5	-2,9	-8,2	5,1	-7,7	-15,4
1	-x, -y, -z	9,07	B3LYP/6-31G(d,p)	-3,1	-0,3	-22	11,9	-15,3	-15,3
1	-x, -y, -z	10,75	B3LYP/6-31G(d,p)	-4,2	-4,4	-23,1	14,9	-18,6	-18,6
2	x+1/2, -y+1/2, z+1/2	8,38	B3LYP/6-31G(d,p)	-13,7	-1,2	-18	11,7	-23,8	-47,6
2	x+1/2, -y+1/2, z+1/2	10,45	B3LYP/6-31G(d,p)	-3,3	-3,8	-6,4	4,1	-9,3	-18,6
1	-x, -y, -z	11,21	B3LYP/6-31G(d,p)	-2,2	-1,5	-17,5	9,5	-12,8	-12,8
1	-x, -y, -z	13,02	B3LYP/6-31G(d,p)	-2	0	-7,5	0	-8,7	-8,7
2	x+1/2, -y+1/2, z+1/2	8,69	B3LYP/6-31G(d,p)	5	-2	-14,6	7,8	-4,2	-8,4
E _{subl} (kJ/mol)									-131,8

EGE (monoclinic, $P2_1/n$)

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
2	x, y, z	8,64	B3LYP/6-31G(d,p)	-1,2	-0,5	-7,8	4,5	-5,7	-11,4
2	x, y, z	4,57	B3LYP/6-31G(d,p)	-18,6	-0,3	-59,1	38,4	-47,6	-95,2
1	-x, -y, -z	10,08	B3LYP/6-31G(d,p)	-7,4	-2,2	-26,6	20,5	-19,9	-19,9
2	x+1/2, - y+1/2, z+1/2	10,42	B3LYP/6-31G(d,p)	-3	-0,6	-6,1	3,9	-6,6	-13,2
1	-x, -y, -z	12,46	B3LYP/6-31G(d,p)	-2,2	-0,1	-7	0	-8,5	-8,5
2	x+1/2, - y+1/2, z+1/2	8,41	B3LYP/6-31G(d,p)	-13,9	-9,8	-17,7	11,2	-30,4	-60,8
2	x, y, z	7,86	B3LYP/6-31G(d,p)	-2,7	-0,5	-10,2	5,7	-8,5	-17
1	-x, -y, -z	8,8	B3LYP/6-31G(d,p)	-5,8	-0,9	-24,3	16,5	-17,7	-17,7
2	x+1/2, - y+1/2, z+1/2	8,64	B3LYP/6-31G(d,p)	4,1	-8,4	-15,5	8,9	-9,9	-19,8
1	-x, -y, -z	11,11	B3LYP/6-31G(d,p)	-4,1	-0,4	-15,9	12	-11	-11
									E_{subl} (kJ/mol) -137,25

EGE (triclinic, *P*-1) major conformer

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
2	x, y, z	9,81	B3LYP/6-31G(d,p)	-1,5	-0,4	-8,1	5,1	-5,7	-11,4
1	-x, -y, -z	8,49	B3LYP/6-31G(d,p)	-0,5	-0,4	-11	6	-6,7	-6,7
1	-x, -y, -z	10,17	B3LYP/6-31G(d,p)	-3,9	0	-19,8	14,1	-12,7	-12,7
2	x, y, z	4,8	B3LYP/6-31G(d,p)	-20,1	-3,7	-59,4	38,7	-51,9	-103,8
2	x, y, z	10,32	B3LYP/6-31G(d,p)	-1,7	0	-7	3,3	-5,9	-11,8
1	-x, -y, -z	5,68	B3LYP/6-31G(d,p)	-11,4	-2,1	-32,1	26,6	-25,2	-25,2
1	-x, -y, -z	15,24	B3LYP/6-31G(d,p)	0,1	0	-4,7	0	-4	-4
1	-x, -y, -z	10,73	B3LYP/6-31G(d,p)	0,3	-0,1	-2,1	0,3	-1,4	-1,4
1	-x, -y, -z	9,05	B3LYP/6-31G(d,p)	-20,7	-2,3	-27,8	26,2	-31,6	-31,6
1	-x, -y, -z	8,01	B3LYP/6-31G(d,p)	-7,3	-1,2	-29,6	18,4	-23	-23
1	-x, -y, -z	7,41	B3LYP/6-31G(d,p)	-5,3	-3,5	-20,4	13	-17,9	-17,9
									E_{subl} (kJ/mol) -124,75

PGD

Molecule 1

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
1	-	7,56	B3LYP/6-31G(d,p)	-9,3	-3,5	-57	34,9	-40,5	-40,5
1	-	7,57	B3LYP/6-31G(d,p)	-12,4	-2,3	-58,6	36,9	-43	-43
1	-	7,55	B3LYP/6-31G(d,p)	-10,2	-3,6	-58,7	37,1	-41,7	-41,7
1	-	7,57	B3LYP/6-31G(d,p)	-12,5	-2,2	-58,7	37	-43,1	-43,1
1	-	13,76	B3LYP/6-31G(d,p)	0	0	-3,3	0	-2,9	-2,9
1	-	13,01	B3LYP/6-31G(d,p)	-2,8	-0,6	-7,4	0	-9,8	-9,8
1	-	11,22	B3LYP/6-31G(d,p)	-0,4	0	-6,6	1,7	-5,1	-5,1
1	-	13,01	B3LYP/6-31G(d,p)	-4,6	-0,6	-7,4	0	-11,8	-11,8
1	-	10,51	B3LYP/6-31G(d,p)	-1,3	-0,1	-9,2	4,6	-6,5	-6,5
1	-x, -y, -z	10,03	B3LYP/6-31G(d,p)	-1,2	0	-13,5	6,1	-9,3	-9,3
2	x, y, z	15,12	B3LYP/6-31G(d,p)	0,2	-0,1	-1,7	0	-1,3	-2,6
2	x, y, z	12,13	B3LYP/6-31G(d,p)	0,6	-0,1	-7,2	0	-5,7	-11,4
2	-x+1/2, y+1/2, -z+1/2	8,45	B3LYP/6-31G(d,p)	-35,4	-10	-26,9	32,7	-48,1	-96,2
2	x, y, z	9,03	B3LYP/6-31G(d,p)	-9,1	-2,7	-18,3	5,1	-24,4	-48,8
1	-x, -y, -z	12,98	B3LYP/6-31G(d,p)	-1,2	-0,1	-6,9	0	-7,4	-7,4
									E_{subl} (kJ/mol) -190,05

Molecule 2

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
1	-	7,56	B3LYP/6-31G(d,p)	-9,3	-3,5	-57	34,9	-40,5	-40,5
2	x, y, z	12,13	B3LYP/6-31G(d,p)	-0,1	-0,1	-7,4	0	-6,6	-13,2

1	-x, -y, -z	10,02	B3LYP/6-31G(d,p)	-1,5	-0,1	-14,4	6	-10,5	-10,5
2	x, y, z	15,12	B3LYP/6-31G(d,p)	-0,6	-0,1	-1,6	0	-2,1	-4,2
2	-x+1/2, y+1/2, - z+1/2	8,45	B3LYP/6-31G(d,p)	-35,9	-10,1	-27,3	33,7	-48,4	-96,8
2	x, y, z	9,03	B3LYP/6-31G(d,p)	-9	-2,7	-18,4	5,2	-24,3	-48,6
2	-x+1/2, y+1/2, - z+1/2	15,31	B3LYP/6-31G(d,p)	0,4	-0,1	-1	0	-0,5	-1
1	-x, -y, -z	15,32	B3LYP/6-31G(d,p)	-0,5	0	-1,6	0	-1,9	-1,9
1	-	7,57	B3LYP/6-31G(d,p)	-12,4	-2,3	-58,6	36,9	-43	-43
1	-	7,55	B3LYP/6-31G(d,p)	-10,2	-3,6	-58,7	37,1	-41,7	-41,7
1	-x, -y, -z	13	B3LYP/6-31G(d,p)	-0,4	0	-2,2	0	-2,3	-2,3
1	-	7,57	B3LYP/6-31G(d,p)	-12,5	-2,2	-58,7	37	-43,1	-43,1
1	-	13,76	B3LYP/6-31G(d,p)	0	0	-3,3	0	-2,9	-2,9
1	-	13,01	B3LYP/6-31G(d,p)	-2,8	-0,6	-7,4	0	-9,8	-9,8
1	-	11,22	B3LYP/6-31G(d,p)	-0,4	0	-6,6	1,7	-5,1	-5,1
1	-	13,01	B3LYP/6-31G(d,p)	-4,6	-0,6	-7,4	0	-11,8	-11,8
1	-	10,51	B3LYP/6-31G(d,p)	-1,3	-0,1	-9,2	4,6	-6,5	-6,5

E_{subl}
(kJ/mol) -191,45

ED (major conformer)

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
1	-	7,51	B3LYP/6-31G(d,p)	-3,6	-3,5	-51,4	28,1	-33,8	-33,8
2	x, y, z	8,97	B3LYP/6-31G(d,p)	-9	-2,6	-17,5	4,6	-23,8	-47,6
1	-	8,28	B3LYP/6-31G(d,p)	-35,1	-8,9	-26,9	31,5	-47,6	-47,6
1	-x, -y, -z	12,34	B3LYP/6-31G(d,p)	-5,3	-0,9	-9,7	0	-14,6	-14,6
1	-	15,1	B3LYP/6-31G(d,p)	0,6	-0,1	-1,1	0	-0,4	-0,4
1	-	7,64	B3LYP/6-31G(d,p)	-12,7	-0,2	-46,6	24,2	-39,1	-39,1
1	-	9,85	B3LYP/6-31G(d,p)	-0,5	-0,1	-10,4	2,8	-7,8	-7,8
1	-	7,62	B3LYP/6-31G(d,p)	-6	-2,1	-52	30,1	-34,5	-34,5
2	x, y, z	12,47	B3LYP/6-31G(d,p)	-0,9	-0,2	-6,9	0	-7,1	-14,2
1	-x, -y, -z	13,26	B3LYP/6-31G(d,p)	-0,1	-0,7	-7	0	-6,7	-6,7
1	-	7,96	B3LYP/6-31G(d,p)	-13,1	-5,3	-44,7	26,3	-40,5	-40,5
1	-	12,87	B3LYP/6-31G(d,p)	-0,9	-0,1	-5,8	0	-6	-6
1	-x, -y, -z	9,67	B3LYP/6-31G(d,p)	-2,1	-4,1	-13	5,5	-13,1	-13,1
1	-	8,37	B3LYP/6-31G(d,p)	-33,9	-2,1	-26	29,4	-41,9	-41,9
1	-	15,26	B3LYP/6-31G(d,p)	0,7	-0,1	-1	0	-0,3	-0,3
E _{subl} (kJ/mol)									-174,05

MPGD

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot	
2	-x+1/2, y+1/2, z	7,56	B3LYP/6-31G(d,p)	-15,2	-0,1	-46,2	27	-39,6	-79,2
2	x+1/2, y+1/2, -z+1/2	10,33	B3LYP/6-31G(d,p)	-38,3	-0,4	-15,2	53,7	-20,9	-41,8
2	-x+1/2, y+1/2, z	9,29	B3LYP/6-31G(d,p)	-5,3	-1,9	-24,8	13,7	-20,2	-40,4
2	x, y, z	8,83	B3LYP/6-31G(d,p)	-8,3	-1,5	-42,7	26	-30,9	-61,8
1	-x, -y, -z	9,95	B3LYP/6-31G(d,p)	-1,9	-0,7	-23,1	7,4	-18	-18
2	x+1/2, -y+1/2, -z	11,63	B3LYP/6-31G(d,p)	-0,5	0	-4	1,3	-3,2	-6,4
2	-x, y, -z+1/2	10,73	B3LYP/6-31G(d,p)	-3,5	-1	-10,6	4,3	-11	-22
2	x+1/2, -y+1/2, -z	14,22	B3LYP/6-31G(d,p)	-2,7	-0,3	-6,4	0	-8,6	-17,2
1	-x, y, -z+1/2	6,1	B3LYP/6-31G(d,p)	-82,8	-19,9	-60,3	121,1	-80	-80
1	-x, -y, -z	10,5	B3LYP/6-31G(d,p)	-1,2	-0,1	-8,7	6,1	-5,1	-5,1
E _{subl} (kJ/mol)									-185,95

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