Supplementary Information (SI) for Green Chemistry.

Supporting Information

O-Demethylation of biobased Anisole-like Derivatives induced by acoustic energy: role of the Cavitation Bubble-Water Interface

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1-Description of the ultrasonic reactor

The ultrasonic reactor was purchased from Sinaptec Ultrasonic Technology (Fig.S1) (ultrasonic generator NexTgen LAB1000, $P_{electric}$= 75 W). This reactor is equipped with three piezoelectric materials (3 cm diameter) which generate the ultrasonic waves at a frequency of 550 kHz. During ultrasonic irradiation, piezoelectric materials were continuously cooled down thanks to a flow of air. The temperature of the solution was monitored with a thermocouple and maintained at 30°C thanks to a cooling jacket.

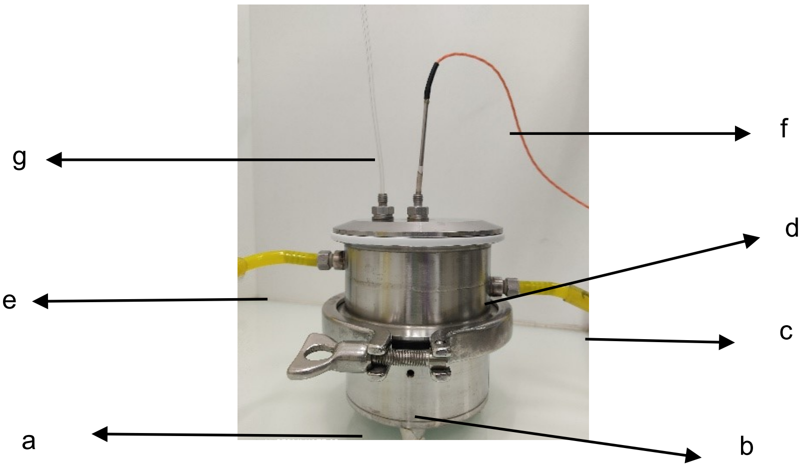


Fig.S1. *Photo of the ultrasonic reactor. (a) Transducer (location of piezoelectric materials), (b) compressed air inlet for piezoelectric materials cooling, (c) Inlet cooling solution, (d) Cooling jacket, (e) Outlet cooling solution, (f) Thermocouple, (g) Gas inlet.*

2-General procedure for the *O*-Dealkylation of syringol in water

In a typical procedure, a 50 mL aqueous solution of syringol (5 mM in ultrapure water) was subjected to a continuous ultrasonic irradiation (550 kHz) at an acoustic power density of 0.20 W/mL. Unless mentioned in the article text, the reaction was carried out under an air atmosphere. The solution temperature was continuously maintained at 30 °C by circulating a cooling liquid (at 14 °C) through the reactor jacket. During the reaction, aliquots were taken and analyzed by HPLC to determine the conversion, yield, and selectivity. Results were double confirmed by ^{1}H NMR (500 MHz with 128 scans) and mass spectroscopy analysis (ESI/Q-TOF).

<u>**Note:**</u> This procedure was adapted when temperatures (16-62°C range) and atmospheres (Ar, He, N_2, O_2, H_2) were varied. A similar procedure was also employed with other anisole-like derivatives tested in Table 1.

3- General procedure for the *O*-Dealkylation of syringol in the presence of DMPO as a ●OH radical scavenger

In order to identify the relative contributions of thermal decomposition at cavitation interfaces *versus* •OH-mediated pathways, radical-scavenging experiments were performed. To do so, an aqueous syringol solution (50 mL at 5 mM) was prepared and then 28-557 µL (5 mM-0.1 M) of DMPO was added. The resulting mixture was placed in an ultrasonic bath (20 kHz) for 5 min to ensure complete dissolution, and then subjected to continuous ultrasonic irradiation at 550 kHz.

4- Analytical methods

High liquid performance chromatography analyses

Samples were analyzed using high-performance liquid chromatography (HPLC) from SHIMADZU LC-40D equipped with a UV-Visible detector (wave length at 225 nm) and a C18 Agilent column (4.6 mm × 250 mm). The eluent was composed of a mixture of acetonitrile/water (25:75) flowing through the column at a flow rate of 0.8 mL min^{-1}. The injection volume was 20 µL, and the temperature of the column was set at 25 °C. For calibration, standard solutions of syringol, 3-methoxycatechol, and pyrogallol, were prepared in water, at concentrations ranging from 0.001 to 1 mM. Calibration curves are provided in Fig. S2-S4 and were used for the determination of conversion, yield and selectivity provided in the article text. Data were given with an uncertainty of ± 5%.

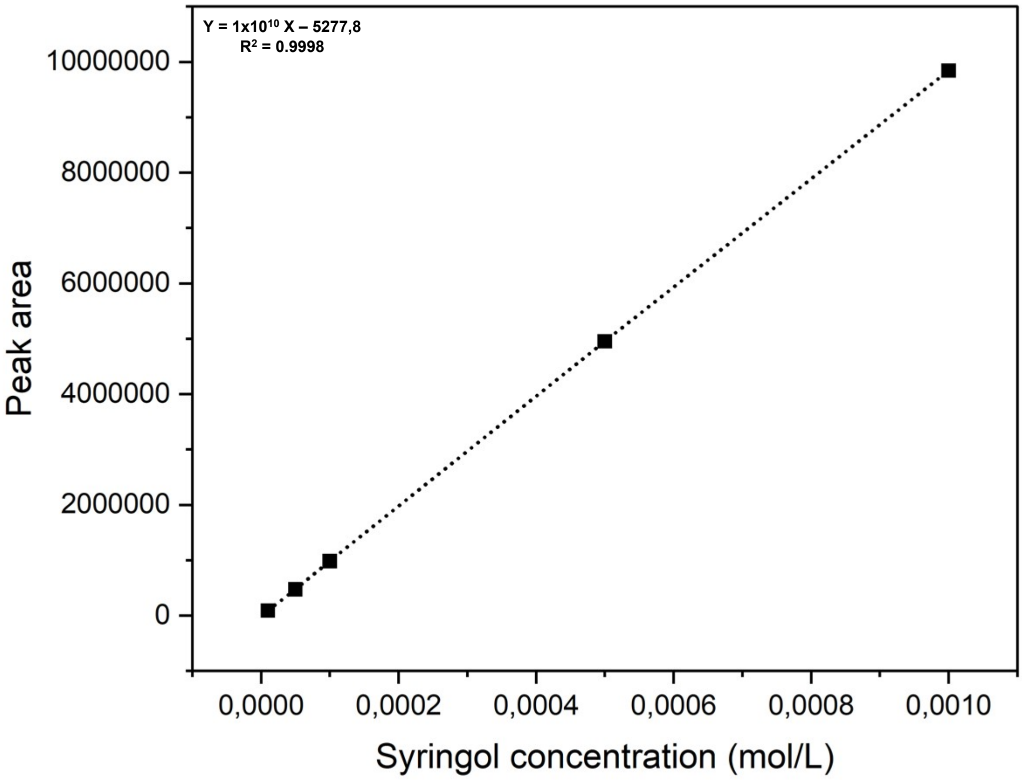


Fig.S2. *Calibration curve of syringol*

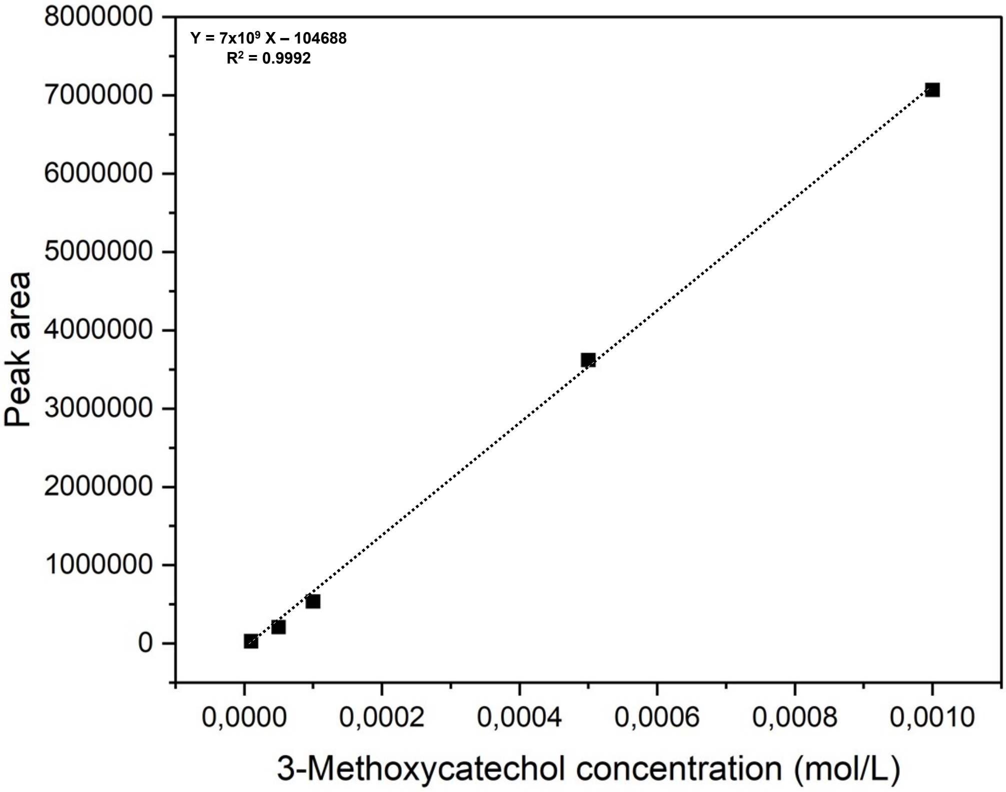


Fig.S3. *Calibration curve of 3-methoxycatechol*

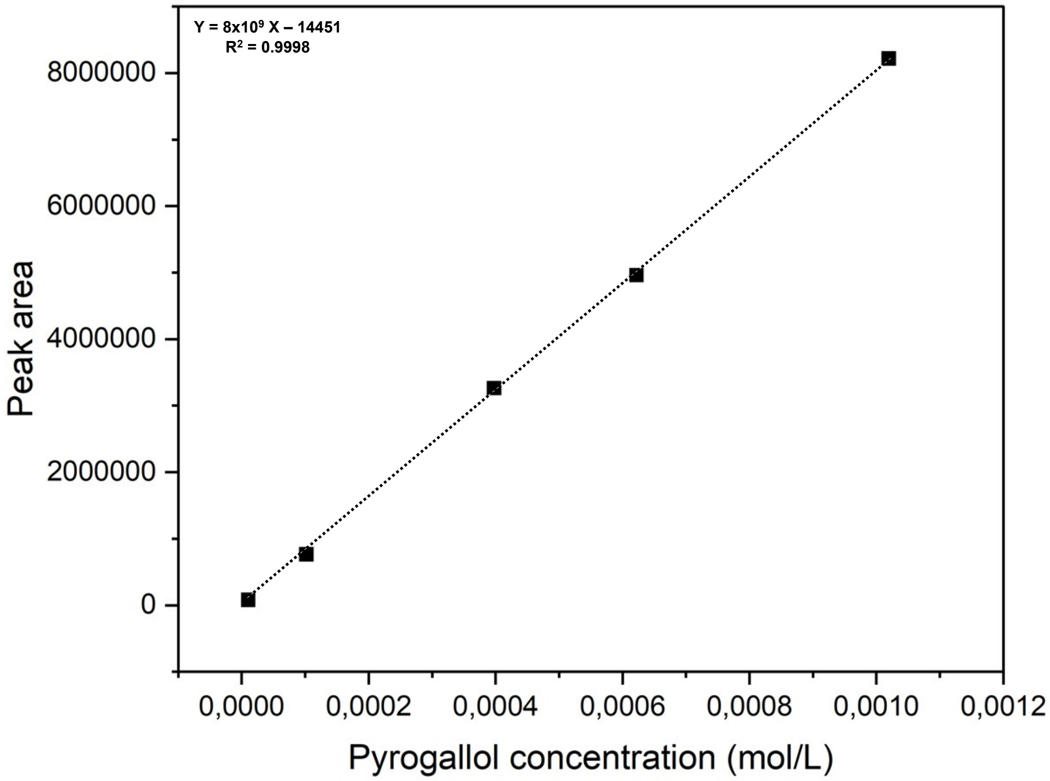


Fig.S4. *Calibration curve of pyrogallol*

Nuclear Magnetic Resonance (NMR) analyses

Nuclear Magnetic Resonance (NMR) spectroscopy analysis was performed on a 500 MHz spectrometer (Bruker) equipped with a cryoprobe. All spectra were recorded at 500 MHz with 128 scans for ^{1}H. For the monitoring of the reaction by ^{1}H NMR, the ultrasonic irradiation of syringol was performed in D_2O instead of H_2O (Fig S7, S15).

High-resolution mass spectrometry analyses

High-resolution mass spectrometry (HRMS) analyses were carried out on a QTOF Impact HD mass spectrometer (Thermo Scientific) equipped with an electrospray ionization (ESI) source operating in negative ion mode**.** The mobile phase was composed of acetonitrile/water (1:1, v/v) containing 0.1% formic acid**.** The capillary voltage was set to 2.8 kV**,** and the desolvation temperature to 150 °C. Spectra were recorded over an m/z range of 50–1000 (Fig S6)**.**

Online analysis of the gas phase by gas chromatography

The gaseous products formed during the ultrasonic irradiation of syringol were monitored online using a Micro GC Fusion Gas Analyzer (INFICON) connected to the gas outlet of the ultrasonic reactor (Fig. S16). Gas sampling was performed directly at the reactor outlet through a heated injection loop (90 °C) to prevent condensation. The GC was equipped with two capillary columns mounted in parallel, allowing for simultaneous and complementary separation of the various gases. The first column, Rt-Msieve 5A (30 m, 0.53 mm ID, 50 µm; column temperature 80 °C; carrier gas: Ar), was used for H_2, O_2, N_2, CH_4, and CO, while the second column, Rt-Q-BOND (30 m, 0.53 mm ID, 20 µm; temperature programmed from 50 to 160 °C at 1 $°C \cdot s^{-1}$; carrier gas: He), was used for CH_4, CO_2, light hydrocarbons, and H_2S. Detection was performed using a thermal conductivity detector (TCD) at 70 °C. This setup enabled on line identification and quantification of the main gaseous products (H_2, CO, CO_2, CH_4, etc.).

Determination of total organic carbon in the liquid phase

The total organic carbon (TOC) content was determined on a Shimadzu TOC-L CSH/CSN analyzer. The analytical principle is based on the complete oxidation of dissolved organic compounds to carbon dioxide (CO_2), which is then detected by a non-dispersive infrared (NDIR) detector. The equipment was calibrated using standard solutions of potassium hydrogen phthalate (KHP). After 4 h of ultrasonic irradiation of syringol, 0.5 mL aliquots were taken and diluted in 50 mL of ultrapure water (Table S2).

6- Additional figures and Tables

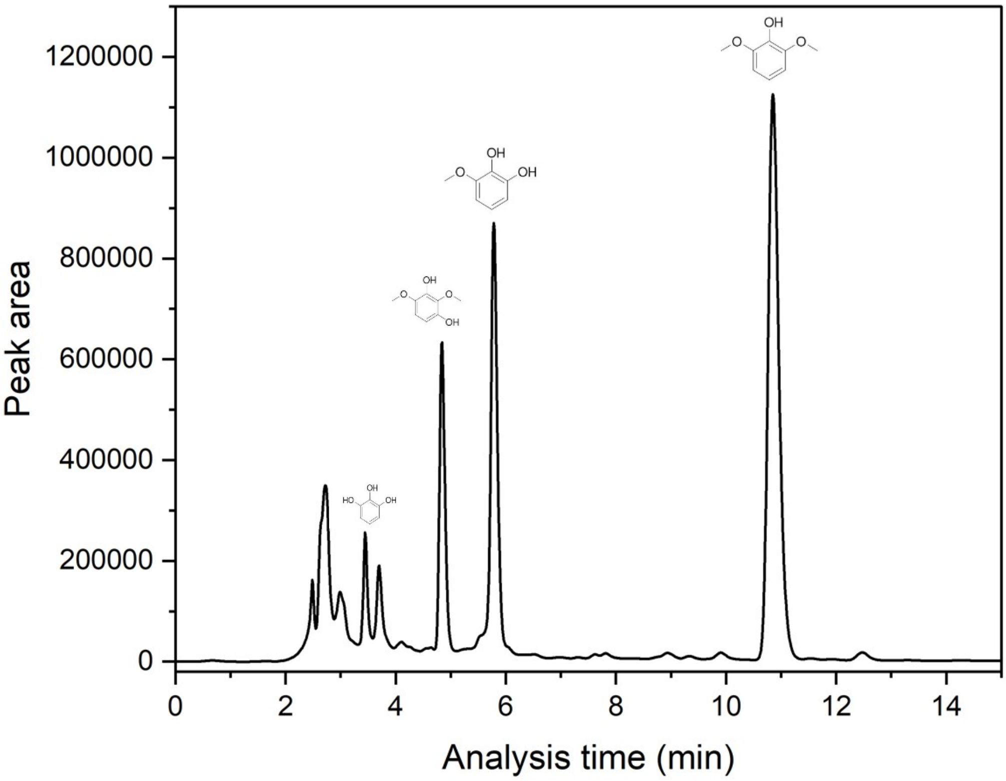


Fig.S5. Example of HPLC chromatogram obtained after 2 hours of ultrasonic irradiation. Reaction conditions: 5 mM of syringol in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 30 °C.

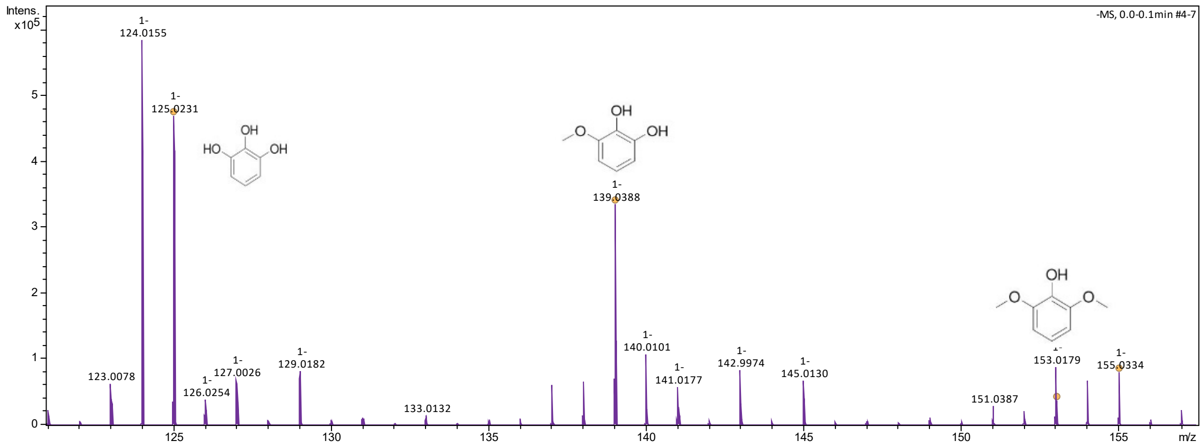


Fig.S6. Analysis of the liquid phase by High Resolution Mass Spectrometry. Reaction conditions: 5 mM of syringol in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 30 °C and 2h. MS analysis was performed in negative mode (ESI/Q-TOF). 3-methoxycatechol (calculated mass for $C_7H_7O_3$ [M-H] = 139.0395, found 139.0388), pyrogallol (calculated mass for $C_6H_5O_3$ [M-H] = 125.0238, found 125.0231)

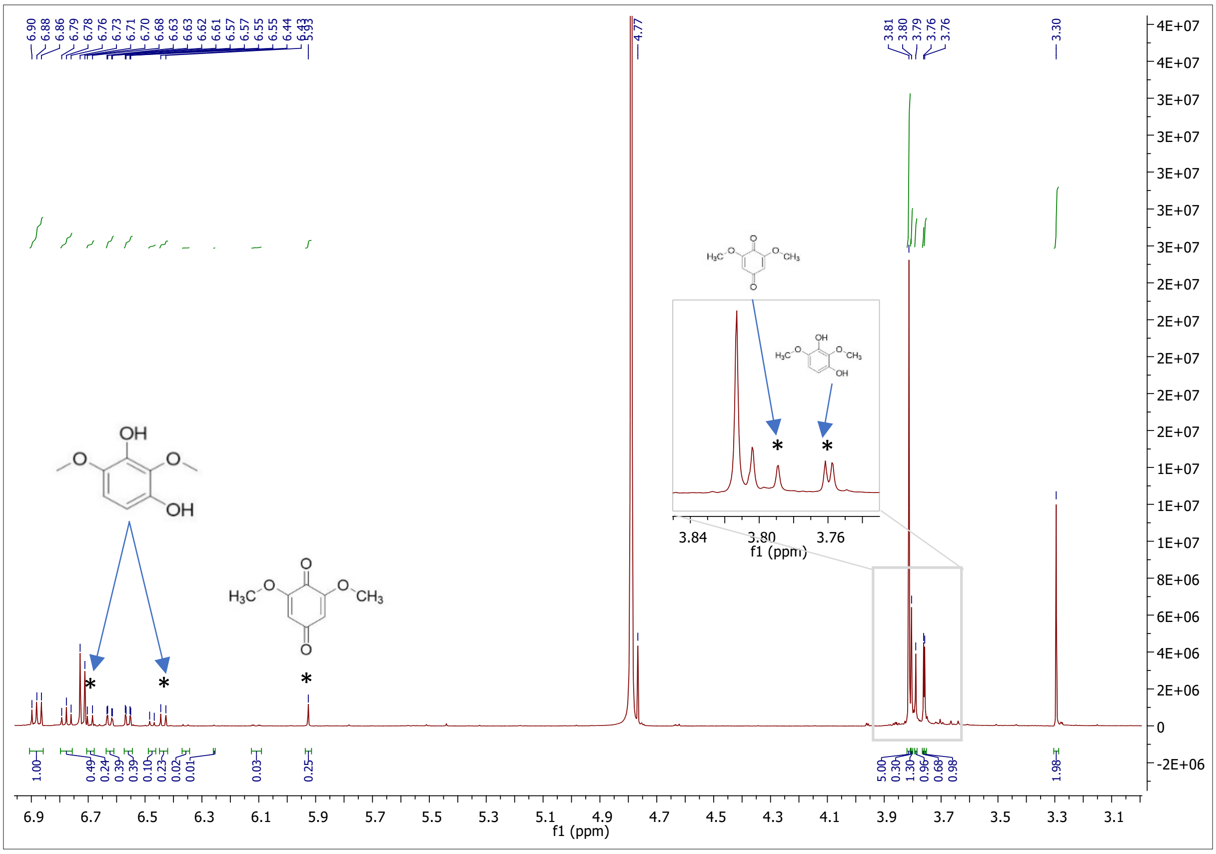


Fig.S7. *^1H* NMR (500 MHz) of syringol after ultrasonic irradiation showing the formation of 2,6-dimethoxybenzoquinone and 3-hydroxysyringol. Reaction conditions: 5 mM of syringol in 50 mL D_2O, 550 kHz, irradiation time: 2h, reaction under air atmosphere, 0.20 W/mL, 30 °C.

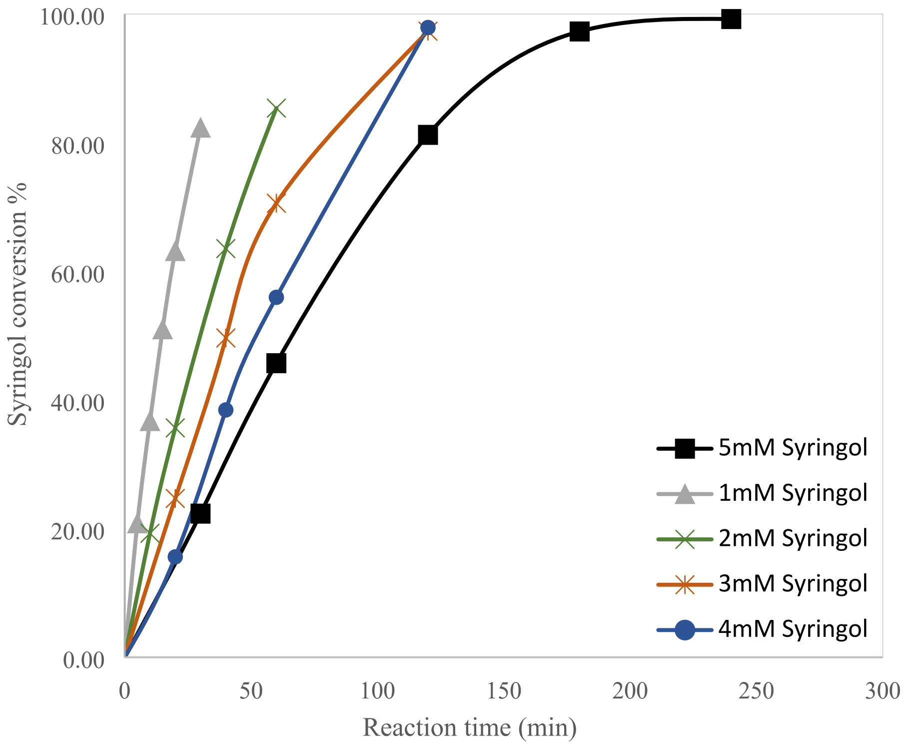


Fig.S8. Kinetic profile obtained by changing the syringol concentration. Reaction conditions: 1-5 Mm of Syringol in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C.

Table S1. Initial reaction rate as a function of the syringol concentration

Syringol concentration (mM)	**Initial Conv. Rate (mol/l/s)**
1	7,36x10^{-7}
2	6,59x10^{-7}
3	6,42x10^{-7}
4	5,15x10^{-7}
5	6,33x10^{-7}

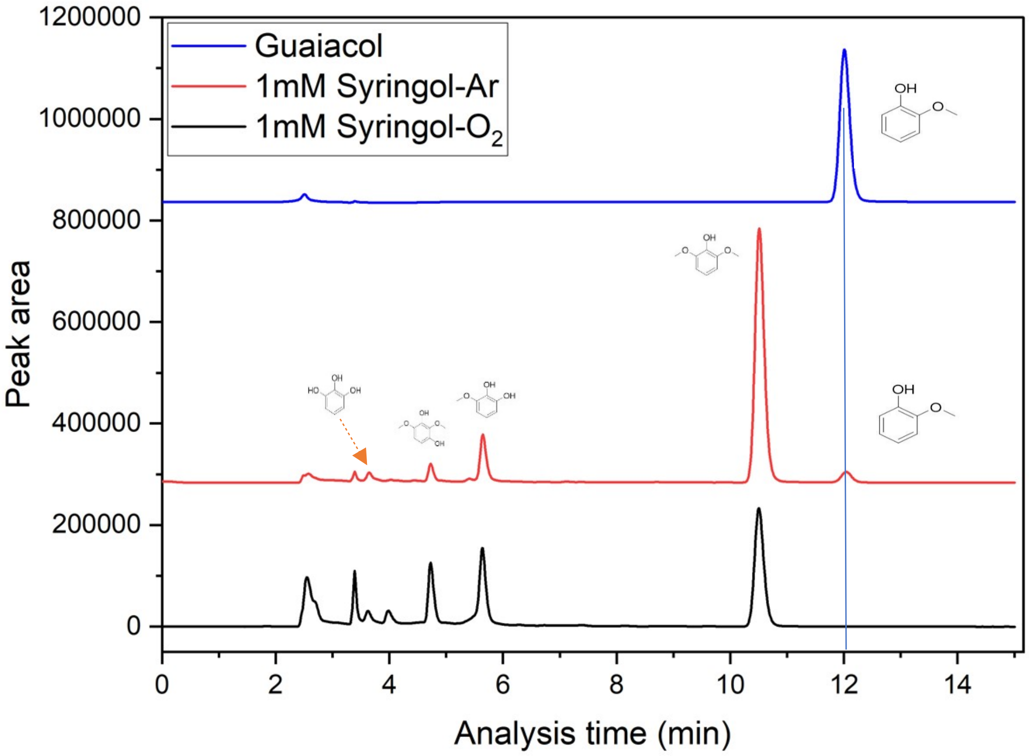


Fig.S9. Example of HPLC chromatogram obtained after 30 minutes of ultrasonic irradiation of syringol under Ar and O_2 atmosphere. Reaction conditions: 1 mM of syringol in 50 mL H_2O, 550 kHz, 0.20 W/mL, 50 °C.

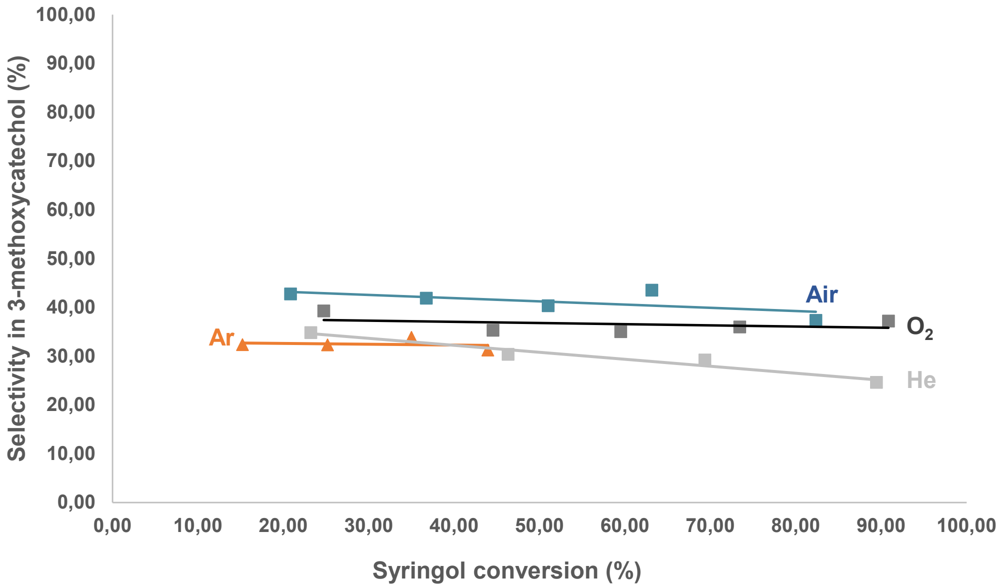


Fig. S10. *Plot of the selectivity to 3-methoxycatechol as a function of the syringol conversion under different atmospheres.* Reaction conditions: 1 mM of syringol in 50 mL H_2O, 550 kHz, 0.20 W/mL, 50 °C, gas flow = 20 mL/min.

Table S2: Total organic carbon in the liquid phase over time. Reaction conditions: 50 mL 5 mM of syringol in H_2O, 550 kHz, irradiation time: 4 h, reaction under air atmosphere, 0.20 W/mL, 50 °C.

	Carbon concentration (mmol/L)	% carbon loss
T0	4.88	0
T + 4h	4.40	9.8%

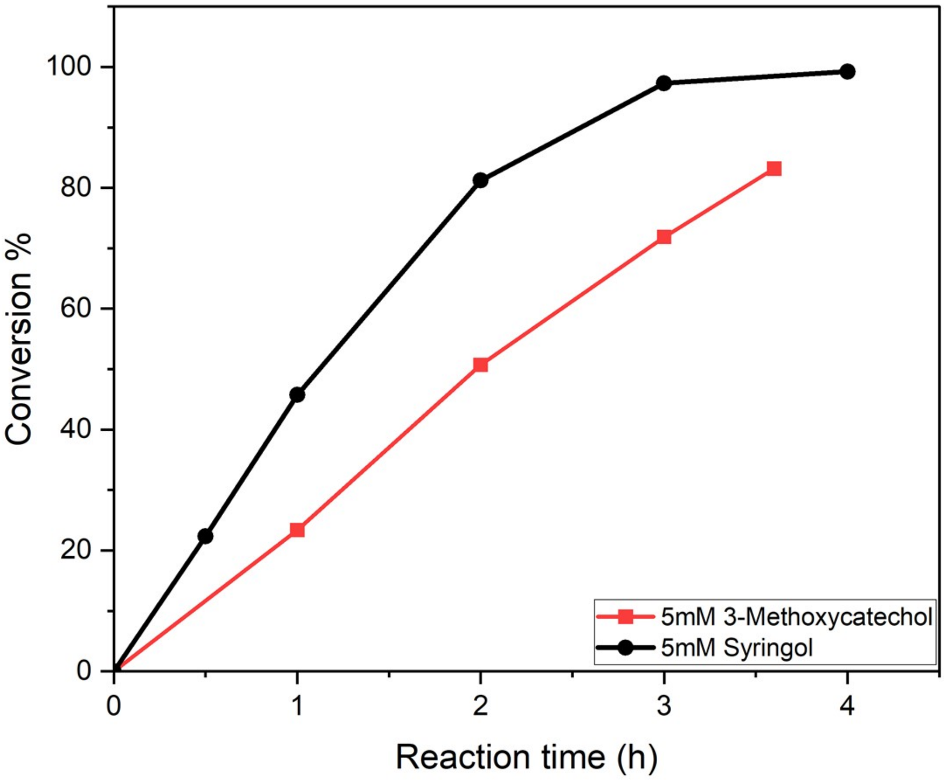


Fig.S11. 3-methoxycatechol and syringol conversion as a function of the reaction time. Reaction conditions: 5 mM 3-Methoxycatechol in 50 mL H_2O or 5 mM syringol in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C.

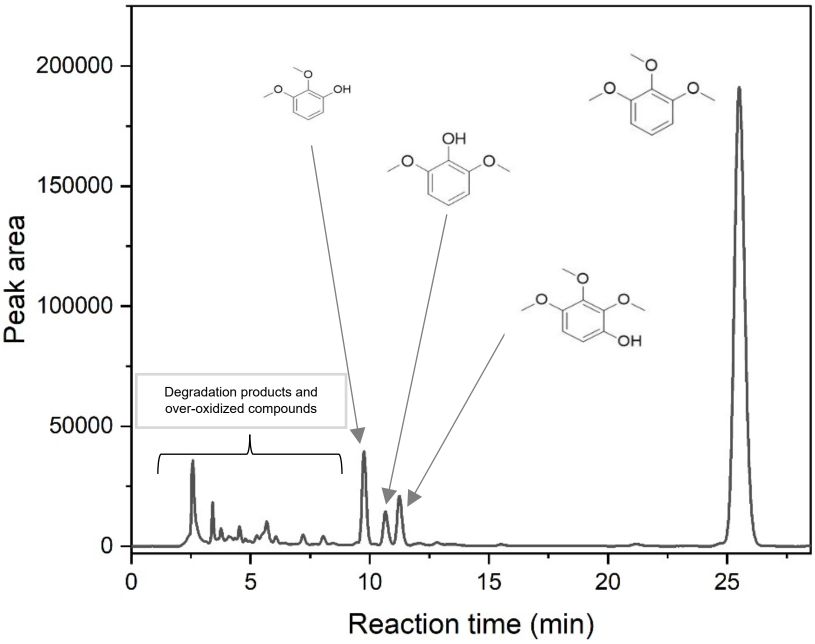


Fig.S12. HPLC chromatogram obtained after 10 minutes of ultrasonic irradiation of 1,2,3-trimethoxybenzene. Reaction conditions: 1 mM of 1,2,3-trimethoxybenzene in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C.

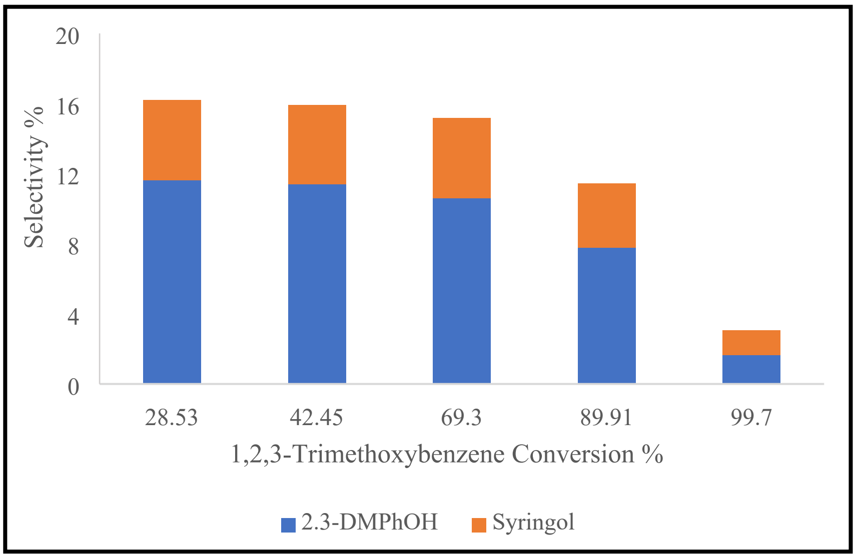


Fig.S13. 2,3-Dimethoxyphenol (2,3-DMPhOH) and syringol selectivity as a function of 1,2,3-trimethoxybenzene conversion. Reaction conditions: 1 mM of 1,2,3-trimethoxybenzene in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C*.*

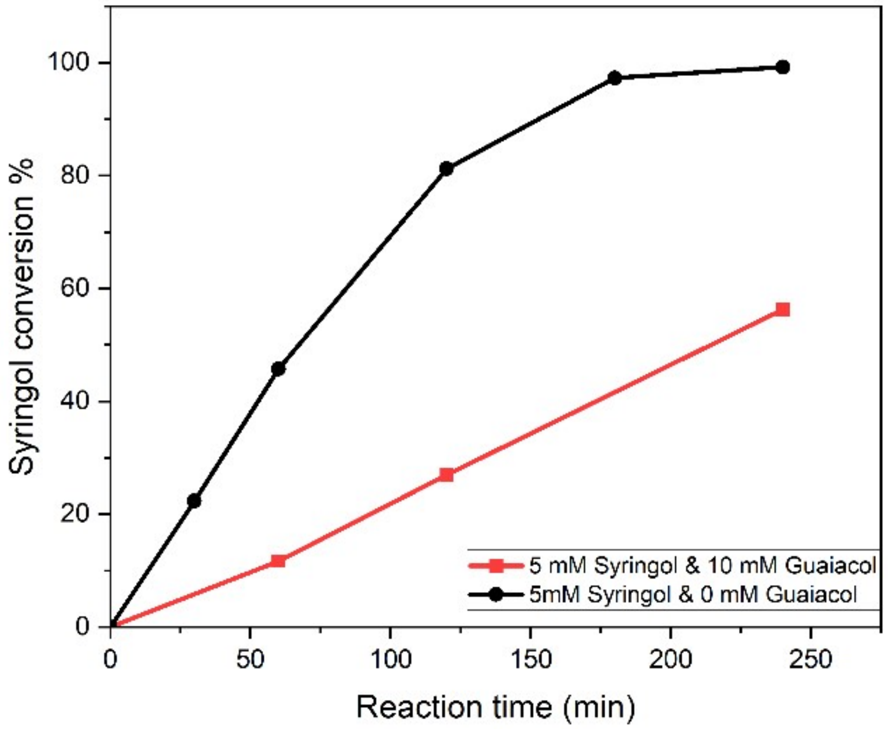


Fig.S14. Conversion of syringol over time, with (red line) and without guaiacol (black line). Reaction conditions: The solution was made of a mixture of syringol (1 eq, 5 mM) and guaiacol (2 eq, 10 mM) in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C.

Note: While independently syringol and guaiacol were converted at a similar rate under ultrasonic irradiation (Fig. S20), in a mixture guaiacol/syringol (2/1), the conversion rate of guaiacol was nearly two times higher than that of syringol, suggesting that both chemicals co-adsorb at the cavitation bubble interface.

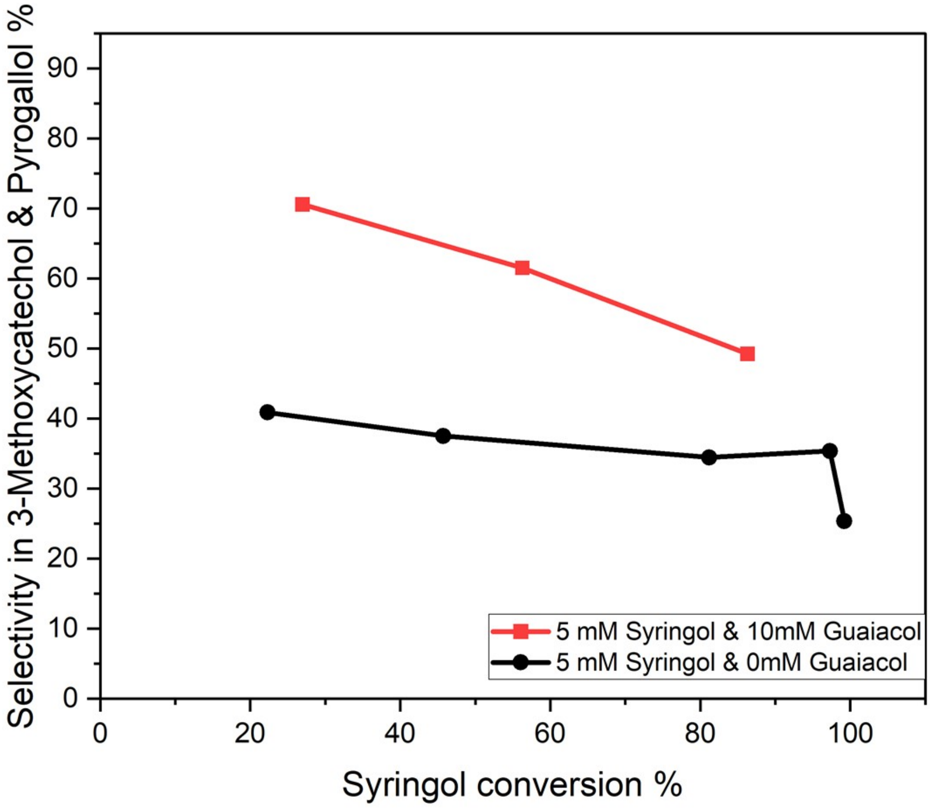


Fig.S15. Effect of guaiacol on the (3-Methoxycatechol + pyrogallol) selectivity. Reaction conditions: The solution was made of a mixture of syringol (1 eq, 5 mM) and guaiacol (2 eq, 10 mM) in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C.

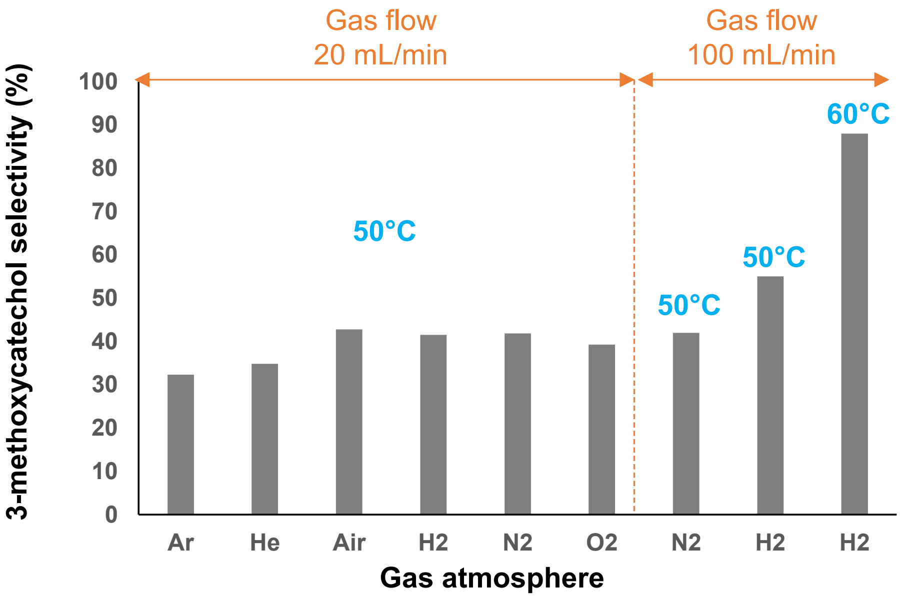


Fig. S16. Impact of the gas atmosphere, temperature and gas flow on the selectivity to 3-methoxycatechol at 25-30% conversion of syringol. Reaction conditions: 1 mM of syringol in 50 mL H_2O, 550 kHz, 0.20 W/mL.

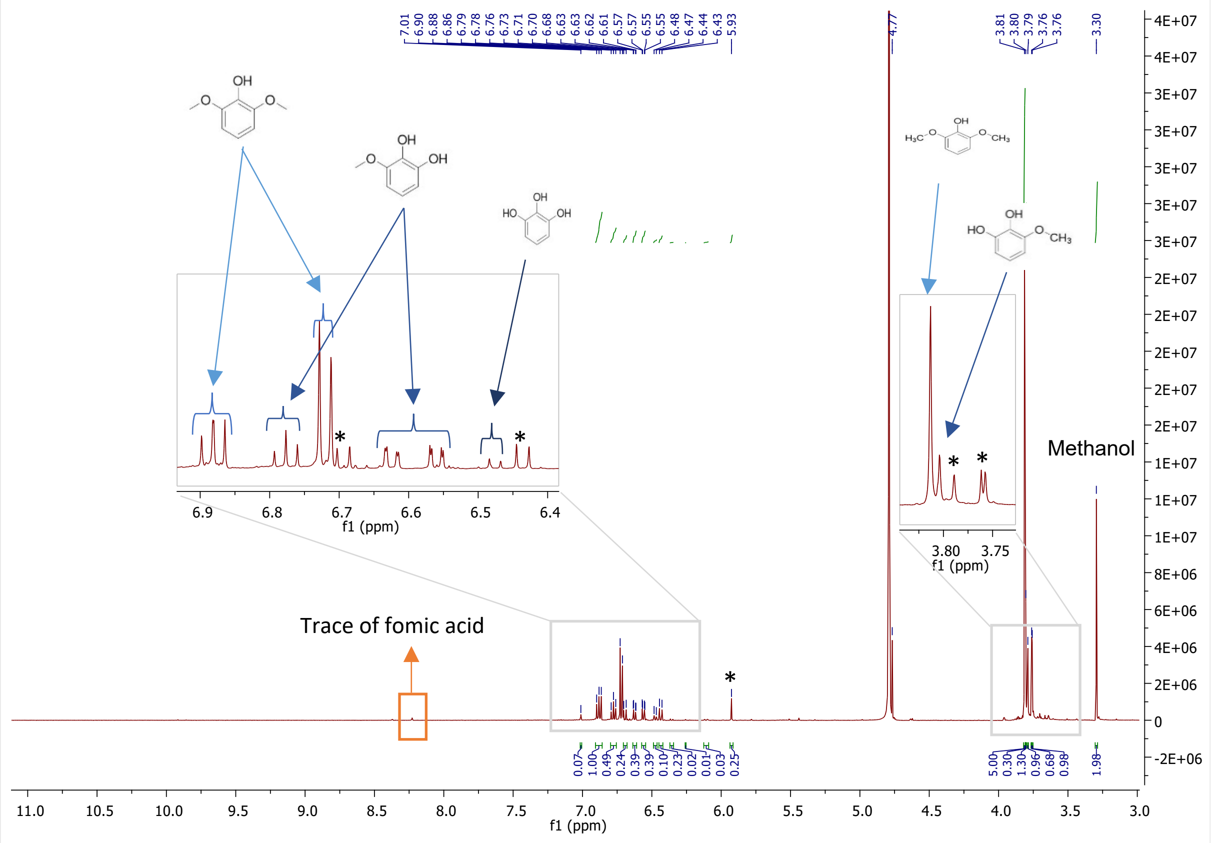


Fig.S17 *^1H* NMR (500 MHz) of syringol after ultrasonic irradiation showing the formation of 3-methoxycatechol, pyrogallol. Reaction conditions: 5 mM of syringol in 50 mL D_2O, 550 kHz, ultrasonic irradiation time: 2 h, reaction under air atmosphere, 0.20 W/mL, 30 °C.

Note: * = Assigned to 2,6-dimethoxybenzoquinone and 3-hydroxysyringol as the two main side products (more information on Fig. S5 and S7).

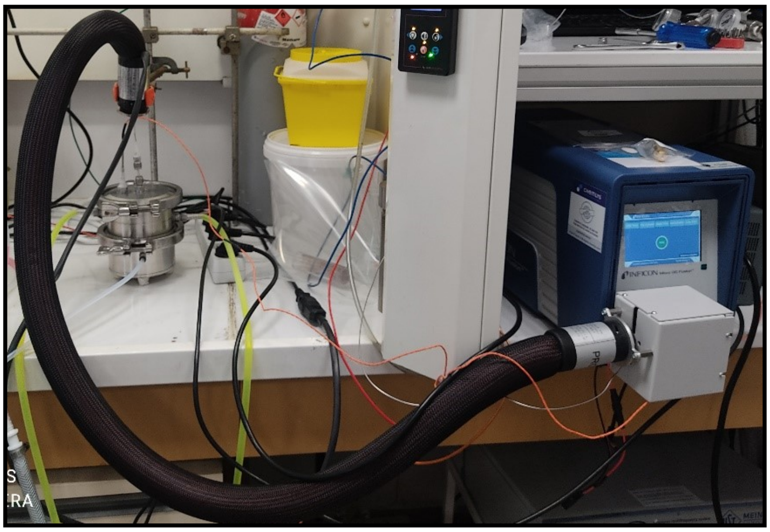


Fig. S18. Picture of online gas phase analysis setup by GC.

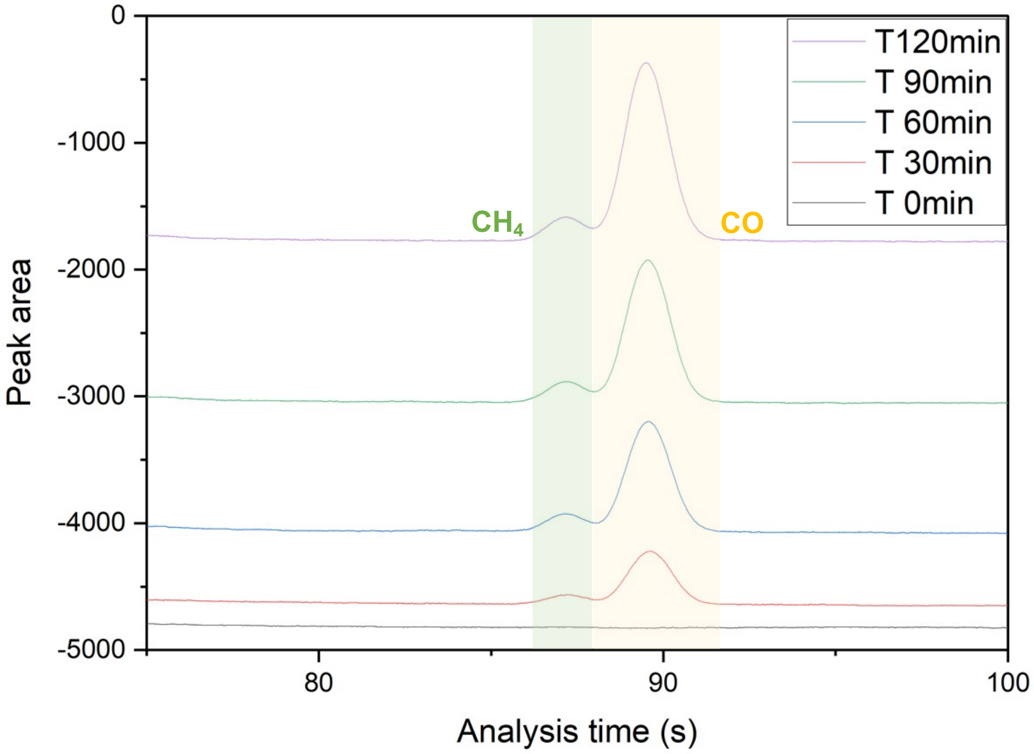


Fig.S19. Chromatogram of online gas phase analysis showing methane and carbon monoxide production over irradiation time on column A. Reaction conditions: 5 mM of syringol in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C.

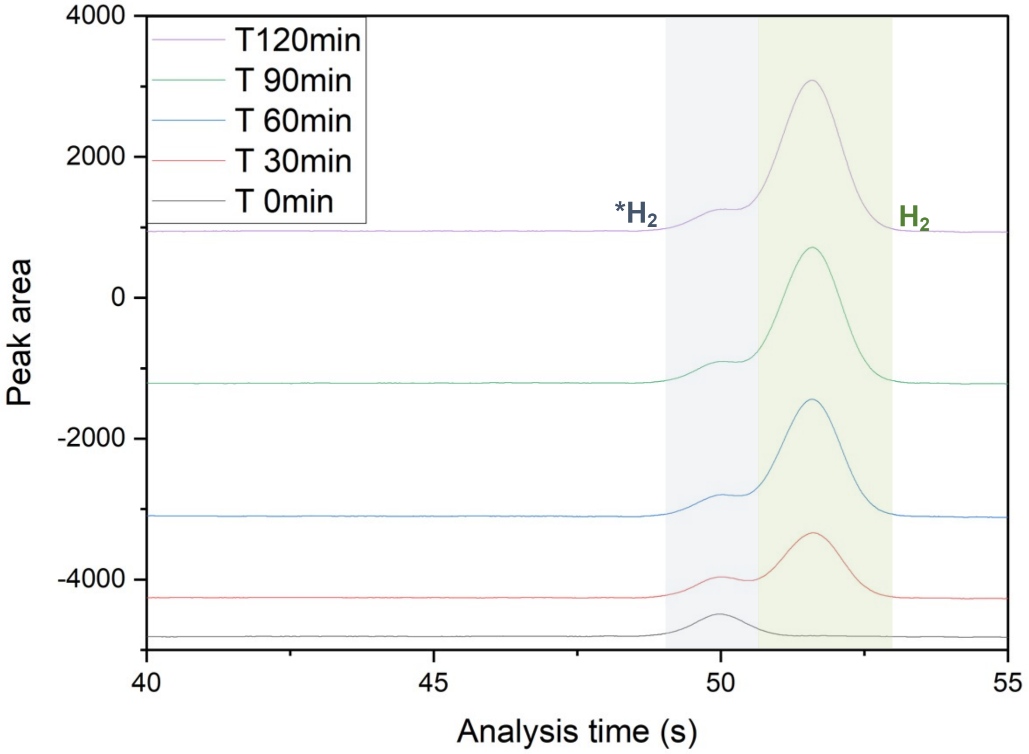


Fig.S20. Chromatogram of online gas phase analysis showing hydrogen production over irradiation time on column A. Reaction conditions: 5 mM of syringol in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C. (**H_2: Hydrogen from the air that remains trapped in the column during the analysis*)

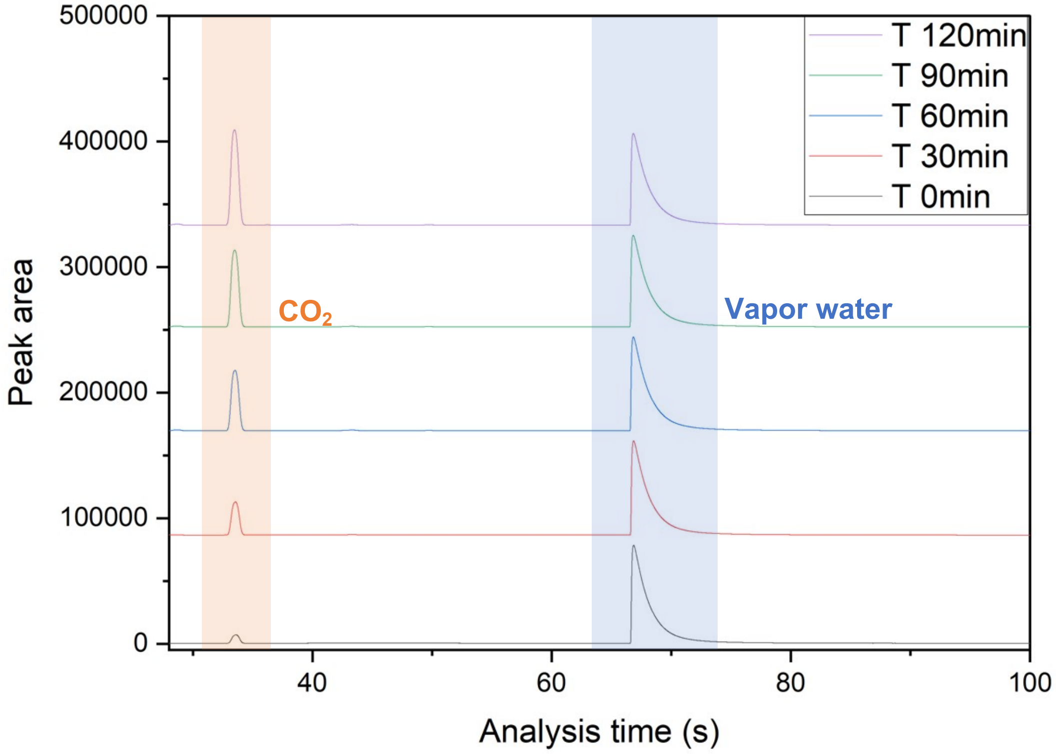


Fig.S21. Chromatogram of online gas phase analysis showing carbon dioxide formation over irradiation time. Reaction conditions: 5 mM of syringol in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C.

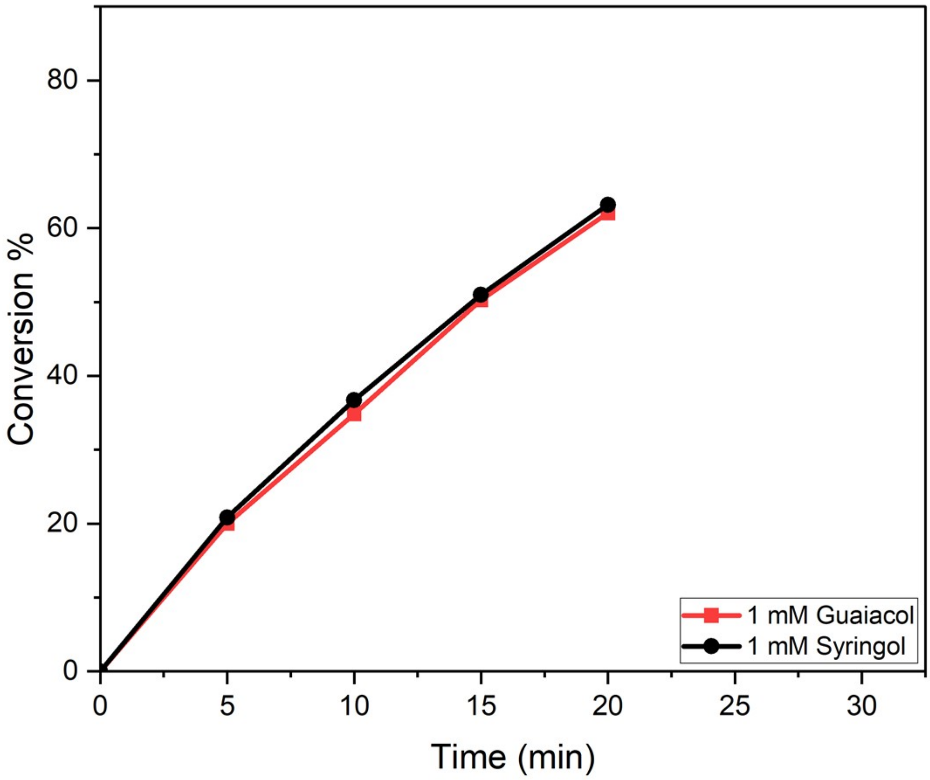


Fig.S22. Syringol and guaiacol conversion as a function of the reaction time. *Reaction conditions: 1 mM syringol in 50 mL H_2O and 1 mM guaiacol in 50 mL H_2O, 550 kHz, reaction under air atmosphere, 0.20 W/mL, 50 °C.*

Table S3. ln(k) as a function of the gas atmosphere. Data were calculated based on the previous work of Goto and co-workers.[1] Reaction conditions: 1 mM syringol in 50 mL H_2O, 550 kHz, 0.20 W/mL, 50 °C. Before ultrasonic experiments, the solution was first degassed with the desired gas (continuous bubbling) for 30 min. Then, during ultrasonic irradiation, the desired gas was continuously bubbled into the solution at a flow rate of 20 mL/min.

Gas	**ln(k)**	**1/T**	**T°C**
N_2	-3,96	0,00279	358
Ar	-3,44	0,00247	404
Air*	-2,85	0,00211	473
O_2^*	-2,53	0,00191	522

** in this example, the temperature is over-estimated due to the formation of oxygenated radical species in a higher amount, thus increasing the contribution of radical reactions over thermal cracking reactions*

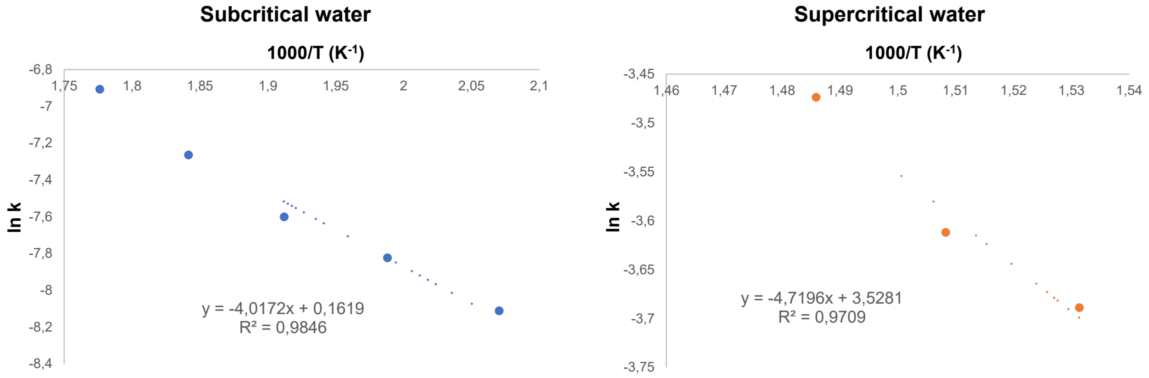


Fig. S23. Arrhenius plot of the rate constants for the decomposition of guaiacol in subcritical and supercritical water, reproduced from the work of Goto[1]

Table S4. Estimation of the energy consumption based on scheme 6 in the main article

Acoustic power density (W/mL)	Acoustic energy per hour (kJ/h))	Energy consumption ($kJ/g_{syringol}$)
0.2	720 000	2057
0.38	1 368 000	13.7

Detail of calculation

► 0.2 W per mL = 200 000 W per m^3 *i.e.* 200 000 x 3600 = 720 000 KJ per hour

The productivity if 0.35 kg/m3/h meaning that the energy consumption is 720 000 / 350 = 2057 kJ/g

► 0.38 W per mL = 380 000 W per m^3 *i.e.* 380 000 x 3600 = 1 368 000 KJ per hour

The productivity if 100 kg/m3/h meaning that the energy consumption is 1 368 000 / 100 000 = 13.7 kJ/g

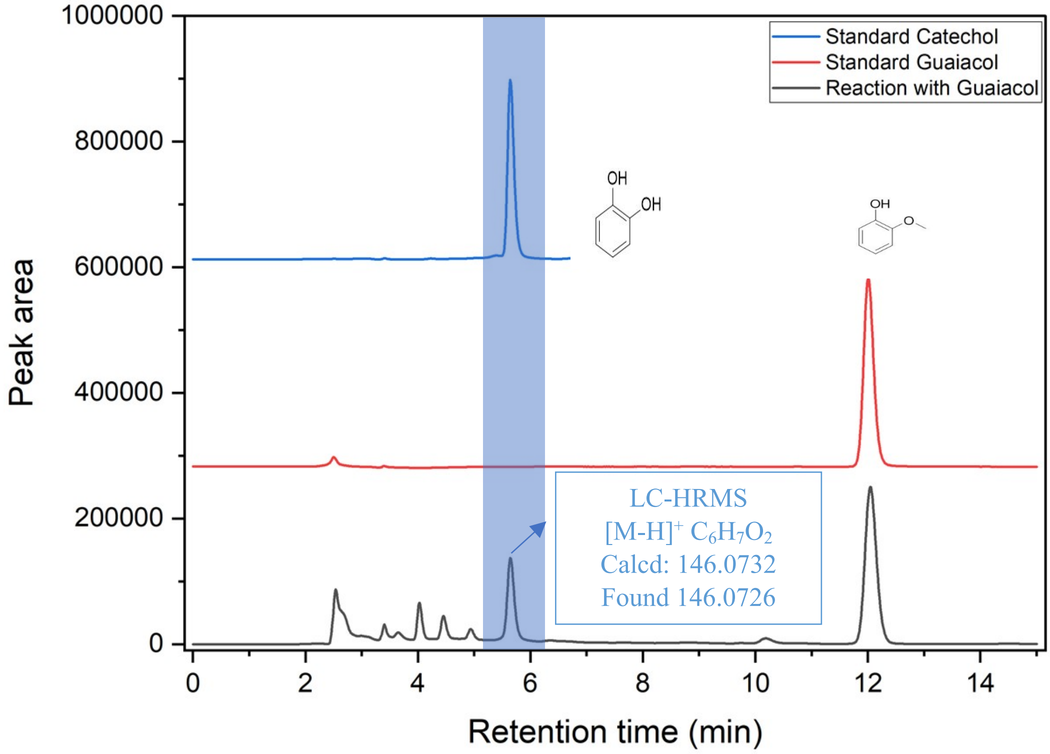
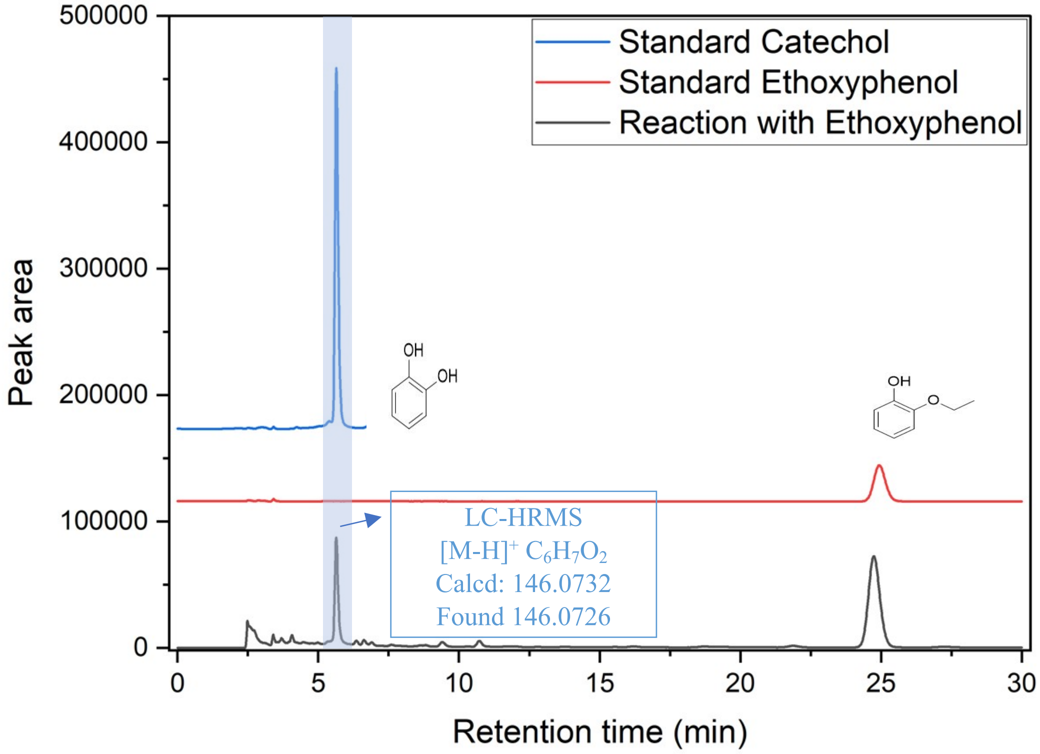


Fig.S24. Example of HPLC chromatogram (and HRMS within the blue dashed rectangle) obtained after 10 minutes of ultrasonic irradiation of guaiacol under Air atmosphere*.* Reaction conditions: 1 mM of guaiacol in 50 mL H_2O, 550 kHz, 0.20 W/mL, 50 °C*.*



LC-HRMS
$[M-H]^+$ $C_6H_7O_2$
Calcd: 146.0732
Found 146.0726

Fig.S25. Example of HPLC chromatogram (and HRMS within the blue dashed rectangle) obtained after 120 minutes of ultrasonic irradiation of ethoxyphenol under Air atmosphere. Reaction conditions: 5 mM of ethoxyphenol in 50 mL H_2O, 550 kHz, 0.20 W/mL, 50 °C.

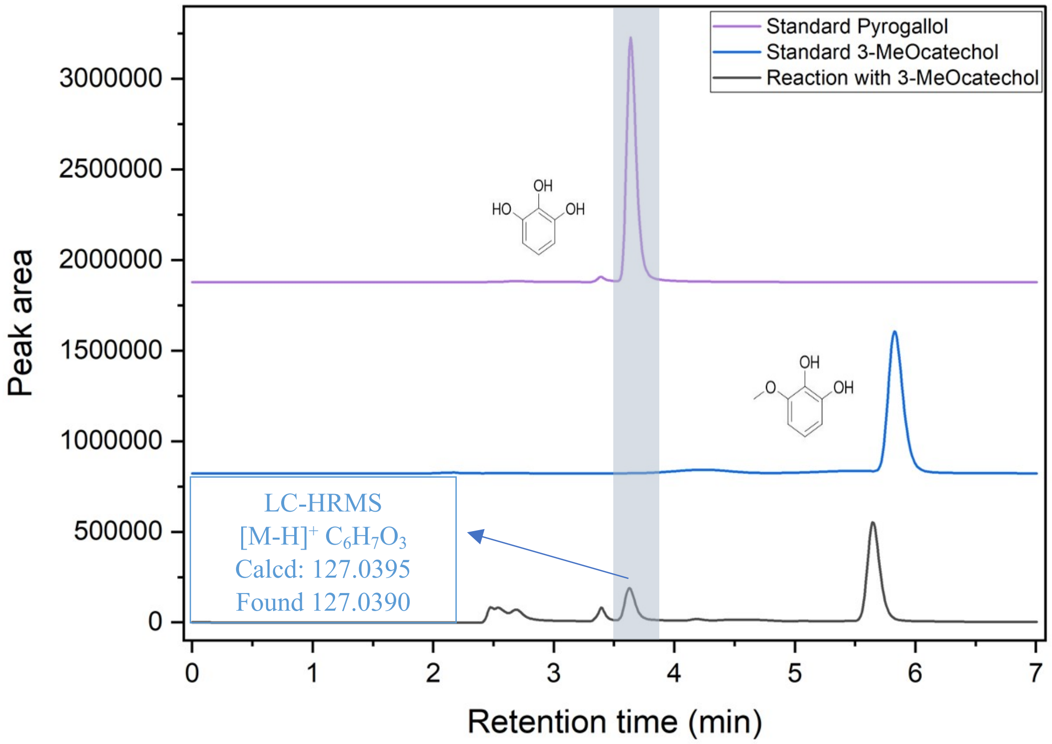
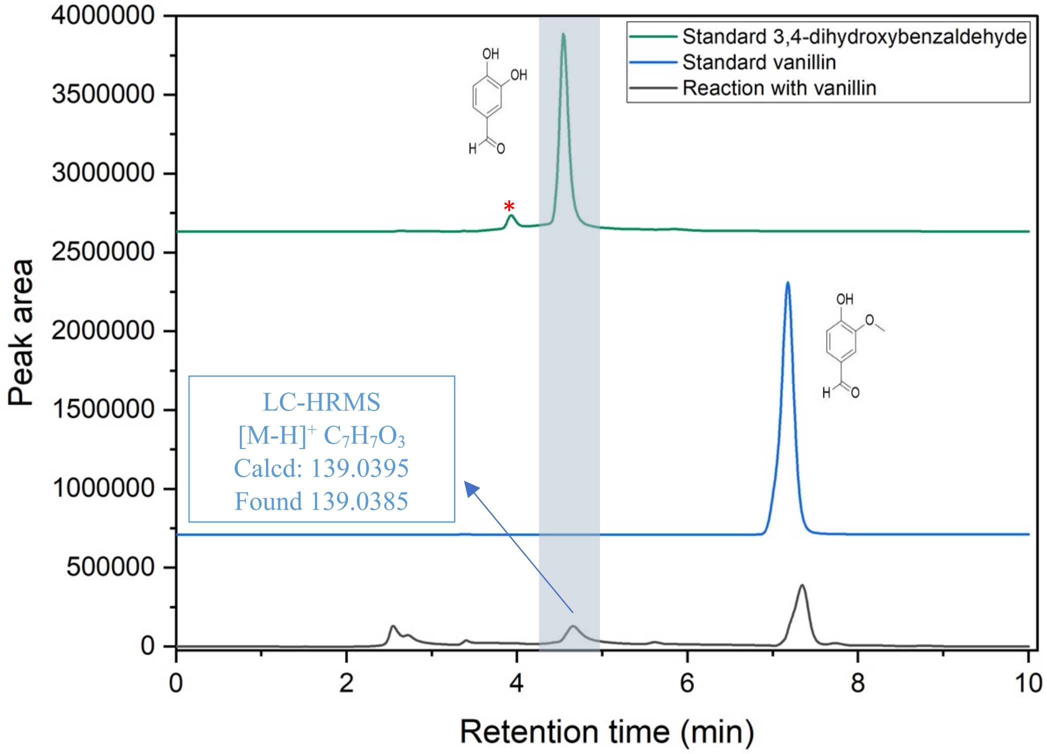


Fig.S26. Example of HPLC chromatogram (and HRMS within the blue dashed rectangle) obtained after 120 minutes of ultrasonic irradiation of 3-methoxycatechol under Air atmosphere. Reaction conditions: 5 mM of 3-methoxycatechol in 50 mL H_2O, 550 kHz, 0.20 W/mL, 50 °C.



LC-HRMS
$[M-H]^+$ $C_7H_7O_3$
Calcd: 139.0395
Found 139.0385

Fig.S27. Example of HPLC chromatogram (and HRMS within the blue dashed rectangle) obtained after 30 minutes of ultrasonic irradiation of vanillin under Air atmosphere. Reaction conditions: 1 mM of vanillin in 50 mL H_2O, 550 kHz, 0.20 W/mL, 50 °C*.* (*=impurity contained in commercial product).

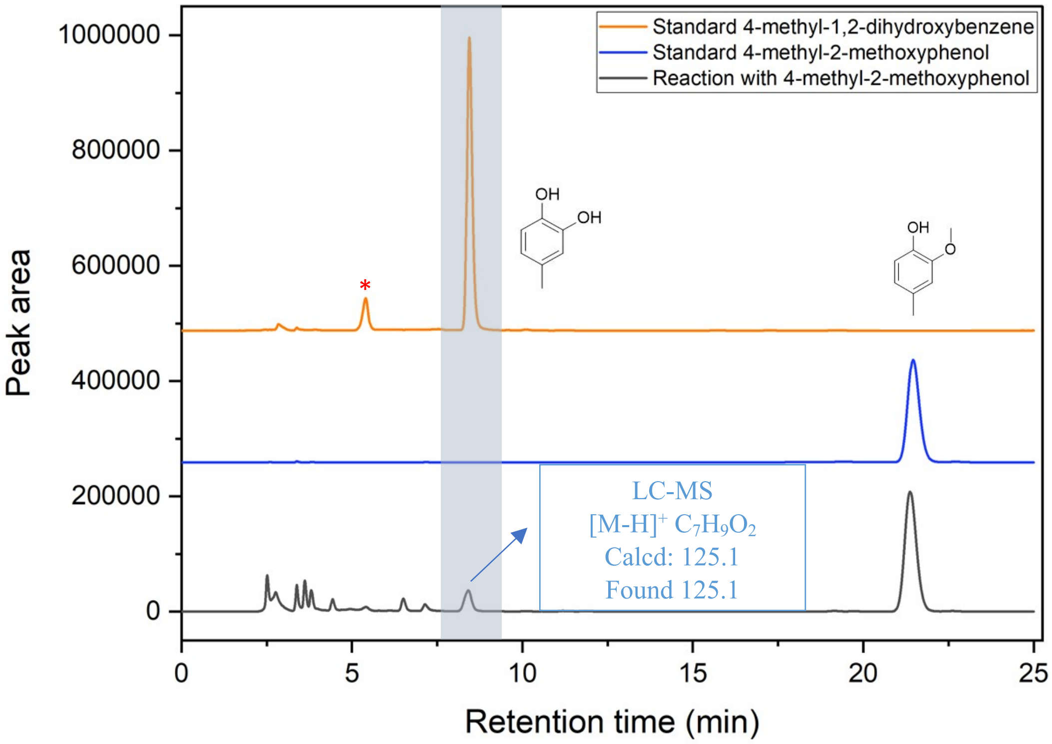


Fig.S28. Example of HPLC chromatogram (and MS within the blue dashed rectangle) obtained after 10 minutes of ultrasonic irradiation of 4-methyl-2-methoxyphenol under Air atmosphere. Reaction conditions: 1 mM of 4-methyl-2-methoxyphenol in 50 mL H_2O, 550 kHz, 0.20 W/mL, 50 °C. (*=impurity contained in commercial product).

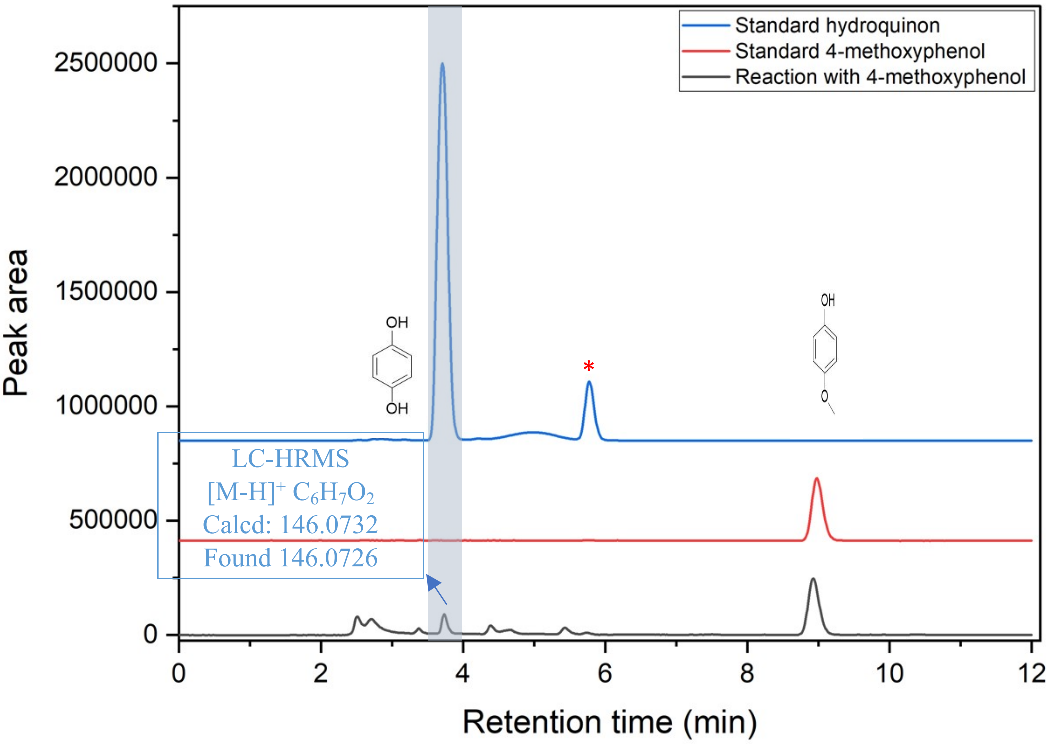


Fig.S29. Example of HPLC chromatogram obtained after 10 minutes of ultrasonic irradiation of 4-methoxyphenol under Air atmosphere. Reaction conditions: 1 mM of 4-methoxyphenol in 50 mL H_2O, 550 kHz, 0.20 W/mL, 50 °C. (*=impurity contained in commercial product).

Reference

1. Wahyudiono, M. Sasaki, M. Goto, *J. Mater. Cycles Waste Manag.*, 2011, **13**, 68-79