

Supplementary Information

Contact-Electro-Catalyzed Direct Hydroxylation of Aromatic C–H Bonds under Ambient Conditions

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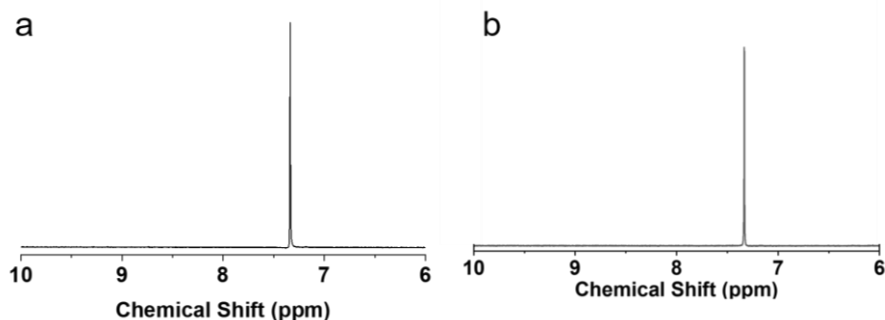


Figure S1. Control experiments for contact-electro-catalytic benzene hydroxylation. ^1H NMR spectra (500 MHz) of control experiments of benzene hydroxylation (a) in the absence of PTFE particles under ultrasonication at 40 kHz and 200 W; and (b) in the absence of ultrasonication, using 20 mg PTFE (3 μm) under high-speed magnetic stirring. Other conditions: 30 mL DI water, 5 mM benzene, 1 h reaction time, air atmosphere, and 25 $^\circ\text{C}$.

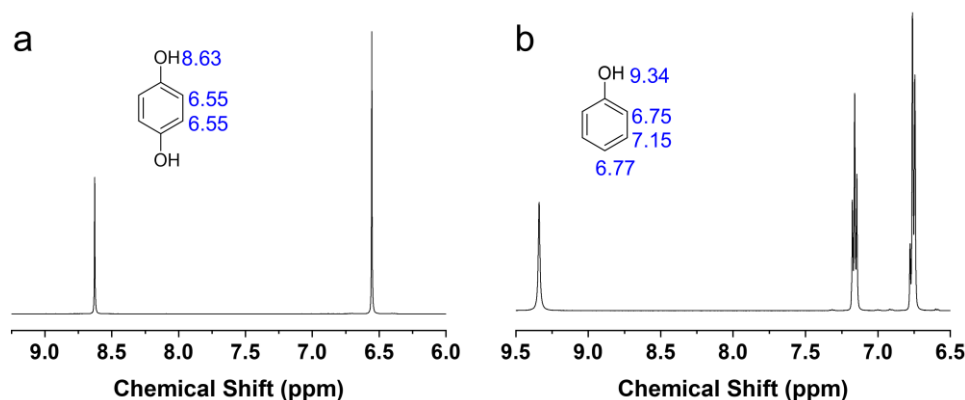


Figure S2. Standard ^1H NMR spectra of hydroquinone and phenol. ^1H NMR (500 MHz) spectra of standard samples for (a) hydroquinone and (b) phenol.

Product analysis for phenol: Due to the conjugation effect of the benzene ring, the ortho- and para-position of the electron-donating group ($-\text{OH}$) are generally activated. The ^1H NMR spectra of phenol after the reaction were shown in Figure S3a-b, which exhibits multiple peaks in the chemical shift of 6.5-7.5 ppm. The peaks of 6.6 and 6.72 ppm are consistent with that of the standard sample for pyrocatechol (Figure S3c), while the intensity of the singlet peaks at 6.55 and 8.61 ppm are stronger, consistent with the standard spectrum for hydroquinone (Figure S3d). These results suggested that the products of hydroxylation reaction were pyrocatechol and hydroquinone. The

quantification of the products was performed using the ^1H NMR internal standard method, with the characteristic peak at 6.55 ppm selected for the integration of hydroquinone.

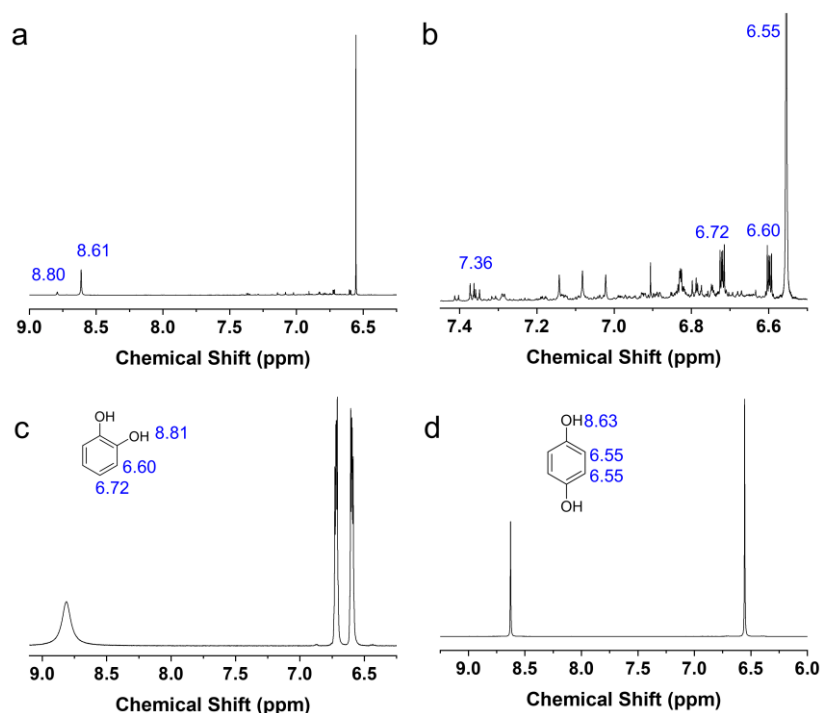


Figure S3. NMR analysis of phenol hydroxylation products. (a) ^1H NMR spectra (850 MHz) of the phenol solution after the reaction. The post-reaction sample was filtered and subjected to solvent evaporation prior to ^1H NMR analysis. (b) Enlarged view of the selected region in panel (a). Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 5 mM phenol, 2 h reaction time, air atmosphere, 25 $^\circ\text{C}$, and ultrasonication at 40 kHz and 200 W. ^1H NMR spectra (500 MHz) of standard samples for (c) pyrocatechol and (d) hydroquinone.

Product analysis for benzoic acid: The samples exhibited numerous new peaks within the range of 6.0~11.0 ppm after reaction. The ^1H - ^1H COSY NMR spectrum (Figure S4a) demonstrated the presence of several sets of ^1H - ^1H correlated signal peaks, among which four groups were observed at 6.78 and 7.28 ppm, 7.0 and 7.28 ppm, 7.28 and 7.37 ppm, 6.82 and 7.79 ppm. Based on the simulated chemical shifts and peak splitting number of the three compounds, the four groups of signal peaks were assigned (Figure S4b). It is hypothesized that the main products were 3-hydroxybenzoic acid, 4-hydroxybenzoic acid and 3,4-dihydroxybenzoic acid. The ^1H NMR spectra of the three

standard samples shown in Figure S4c-f suggest that the para- and meta-positions of the $-\text{CO}_2\text{H}$ group were selectively activated by $\cdot\text{OH}$. The quantification of the products was performed using the ^1H NMR internal standard method, with the characteristic peak at 7.78 ppm selected for the integration of 3-hydroxybenzoic acid.

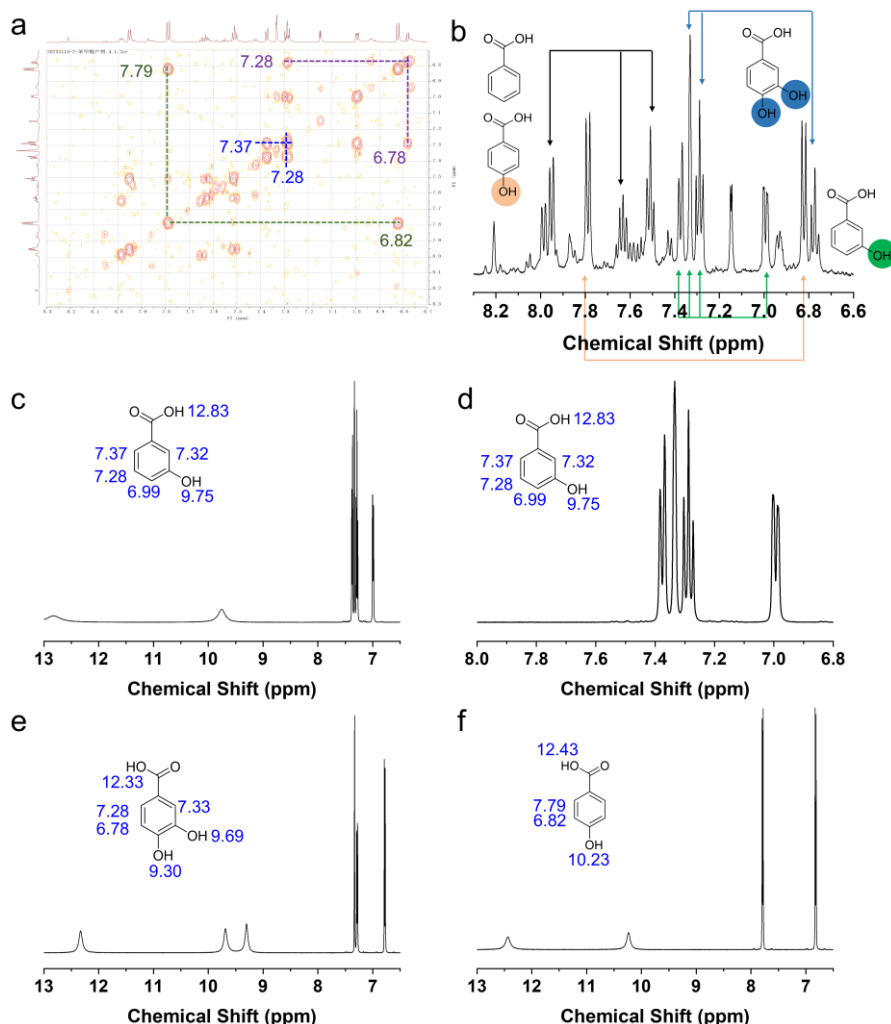


Figure S4. NMR analysis of benzoic acid hydroxylation products. (a) ^1H - ^1H COSY NMR spectra and (b) ^1H NMR spectrum analysis of benzoic acid solution after the reaction, recorded on an 850 MHz NMR spectrometer. The post-reaction sample was filtered and subjected to solvent evaporation prior to ^1H NMR analysis. ^1H NMR spectra (500 MHz) of standard samples of (c-d) 3-hydroxybenzoic acid, (e) 3,4-dihydroxybenzoic acid, and (f) 4-hydroxybenzoic acid, where panel (d) is an enlarged view of panel (c). Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 5 mM benzoic acid, 2 h reaction time, air atmosphere, 25 $^\circ\text{C}$, and ultrasonication at 40 kHz and 200 W.

Product analysis for 4-nitrobenzoic acid: The new peaks after the reaction mainly appear at 6.5-9.0 ppm. The ^1H - ^1H COSY NMR spectrum in Figure S5a indicates the presence of three sets of ^1H - ^1H correlated signal peaks, which were 7.13 and 7.58, 7.47 and 7.94, 7.68 and 7.98 ppm, respectively. These peaks are all doublet peaks, indicating that the molecular composition of the product encompasses not only $\text{H}-\text{C}=\text{C}-\text{H}$ structure, but also different substituent groups on adjacent carbon atoms. Next, the signal peaks were assigned based on the chemical shift and the number of splitting peaks, as shown in Figure S5b. It was hypothesized that the main products were 3-hydroxy-4-nitrobenzoic acid and 2-hydroxy-4-nitrobenzoic acid, respectively. The ^1H NMR spectra of the standard samples were shown in Figure S5c-d, which is in general agreement with the experimental results, confirming the veracity of the speculation. The quantification of the products was performed using the ^1H NMR internal standard method, with the characteristic peak at 7.47 ppm selected for the integration of 3-hydroxy-4-nitrobenzoic acid.

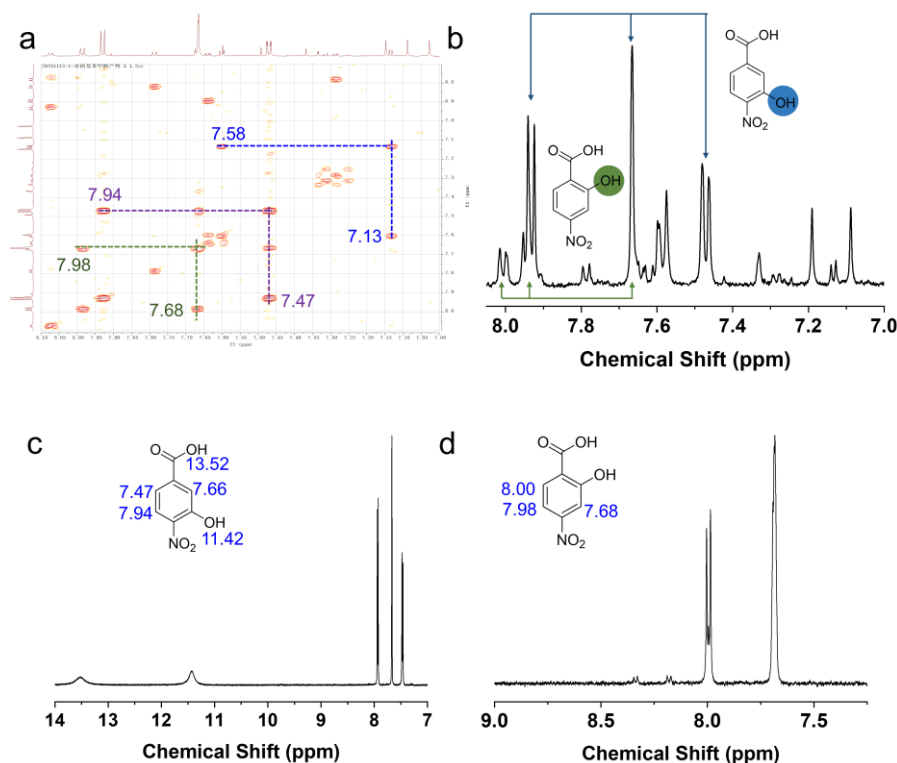


Figure S5. NMR analysis of 4-nitrobenzoic acid hydroxylation products. (a) ^1H - ^1H COSY NMR and (b) ^1H NMR spectral analysis of 4-nitrobenzoic acid solution after reaction, recorded on an 850 MHz NMR spectrometer. The post-reaction sample was

filtered and subjected to solvent evaporation prior to ^1H NMR analysis. ^1H NMR spectra (500 MHz) of standard samples for (c) 3-hydroxy-4-nitrobenzoic acid and (d) 2-hydroxy-4-nitrobenzoic acid. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 5 mM 4-nitrobenzoic acid, 2 h reaction time, air atmosphere, 25 $^\circ\text{C}$, and ultrasonication at 40 kHz and 200 W.

Product analysis for 4-nitrobenzyl alcohol: The spectrum of sample after the reaction is shown in Figure S6a. Many new peaks emerge at 6.5-9.0 ppm, indicating the formation of new products. The ^1H - ^1H COSY NMR spectrum (Figure S6b) revealed the presence of two groups of ^1H - ^1H -related doublet peaks, which were located at 7.6-8.21 ppm and 6.9-7.87 ppm, respectively. The first group was identified as the $\text{H}-\text{C}=\text{C}-\text{H}$ structure in raw material molecules. It is speculated that the second group has $\text{H}-\text{C}=\text{C}-\text{H}$ structure in the 2-hydroxy-4-nitrobenzyl alcohol molecule. In addition, the signal peak was simply attributed to 2-hydroxy-4-nitrobenzyl alcohol, confirmed by the comparison with the LC-MS results in Figure 3e. The quantification of the products was performed using the ^1H NMR internal standard method, with the characteristic peaks at 7.87 and 6.90 ppm were selected for the integration of 2-hydroxy-4-nitrobenzyl alcohol.

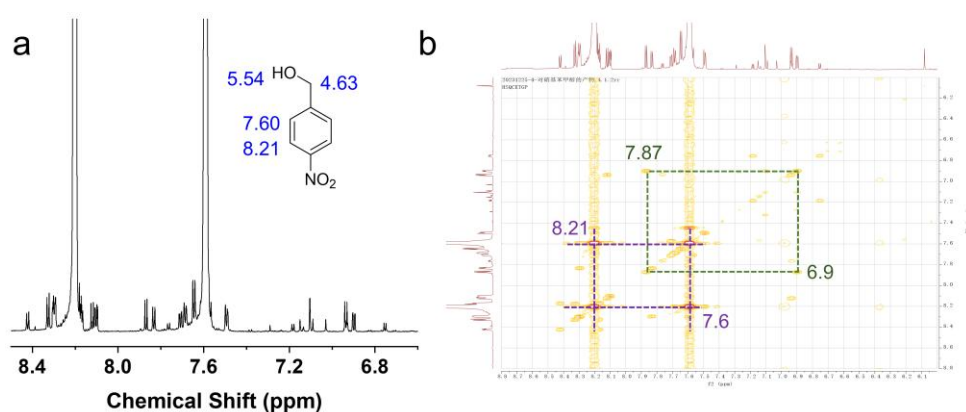


Figure S6. NMR analysis of 4-nitrobenzyl alcohol hydroxylation products. (a) ^1H NMR and (b) ^1H - ^1H COSY NMR spectra of 4-nitrobenzyl alcohol after the reaction, recorded on an 850 MHz NMR spectrometer. The post-reaction sample was filtered and subjected to solvent evaporation prior to ^1H NMR analysis. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 5 mM 4-nitrobenzyl alcohol, 2 h reaction time, air atmosphere, 25 $^\circ\text{C}$, and ultrasonication at 40 kHz and 200 W.

Product analysis for 4-hydroxybenzoic acid: The raw 4-hydroxybenzoic acid exhibits strong C–H peaks of benzene ring at 6.81 and 7.79 ppm (Figure S7a). The chemical shift primarily depends on the density of the extranuclear electron cloud. The –OH and –CO₂H groups are classified as the electron-donating and electron-withdrawing groups respectively. The electron-withdrawing groups reduce the density of the electron cloud at the periphery of the hydrogen nucleus, resulting in the decrease of the shielding effect. Thus, the resonance absorption peak shifts towards the lower field, and the chemical shift increases. On the contrary, the increase of the electron cloud density outside the hydrogen nucleus by electron-donating groups results in higher shift of the resonance absorption peak and the lower chemical shift. Therefore, the doublet peaks at 6.81 and 7.79 ppm belong to the C–H bonds connecting to the –OH and –CO₂H groups, respectively. Four groups of new peaks appeared after the reaction, among which 7.35, 7.3, 6.8 and 6.56 ppm exhibit singlet, doublet and triplet peaks, respectively (Figure S7b), suggesting the formation of new products. In addition, the C–H COSY NMR spectra were shown in Figure S7c-d. The carbon atom chemical shift corresponding to the peaks at 7.35, 7.3 and 6.56 ppm locates at 117, 123 and 117 ppm, respectively, and the chemical shift of the peaks at 6.57 and 117 ppm are consistent with the chemical shift of hydroquinone carbon atoms obtained by simulation. The ¹H-¹H COSY NMR spectra were shown in Figure S7e-f. Two groups of ¹H-¹H-related peaks appear in the 2D NMR, displaying doublet peaks at 7.3 and 6.8 ppm, 6.82 and 7.79 ppm, respectively. The above results indicate the presence of H–C=C–H structure in new product. According to the singlet peak at 7.35 ppm in the ¹H NMR spectrum, we speculate that the C–H bond on the benzene ring of 4-hydroxybenzoic acid may undergo activation and hydroxylation. Based on the location effect of the chemical molecules, we speculate that the resulting product may be 3,4-dihydroxybenzoic acid. Next, the commercially purchased hydroquinone and 3,4-dihydroxybenzoic acid were measured. As shown in Figure S7g-h, the characteristic peaks of C–H bond and the –OH group of hydroquinone appears at 6.55 and 8.63 ppm. Due to the asymmetric molecular structure of 3,4-dihydroxybenzoic acid and the different chemical environments for the benzene C–H bond, three distinct signal peaks

emerge, corresponding to the doublet, singlet, and doublet peaks with chemical shifts at 6.78, 7.28, and 7.33 ppm, respectively. The two –OH and –CO₂H groups exhibit singlet peaks at 9.3, 9.69 and 12.33 ppm. The chemical shift and number of splitting of signal peaks are essentially consistent with the results in Figure S7b, suggesting that the two main products were hydroquinone and 3,4-dihydroxybenzoic acid, respectively. Quantification of the products was performed by the ¹H NMR internal standard method. The characteristic peaks at 7.35 and 7.30 ppm were selected for the integration of 3,4-dihydroxybenzoic acid, while the characteristic peak at 6.56 ppm was selected for the integration of hydroquinone.

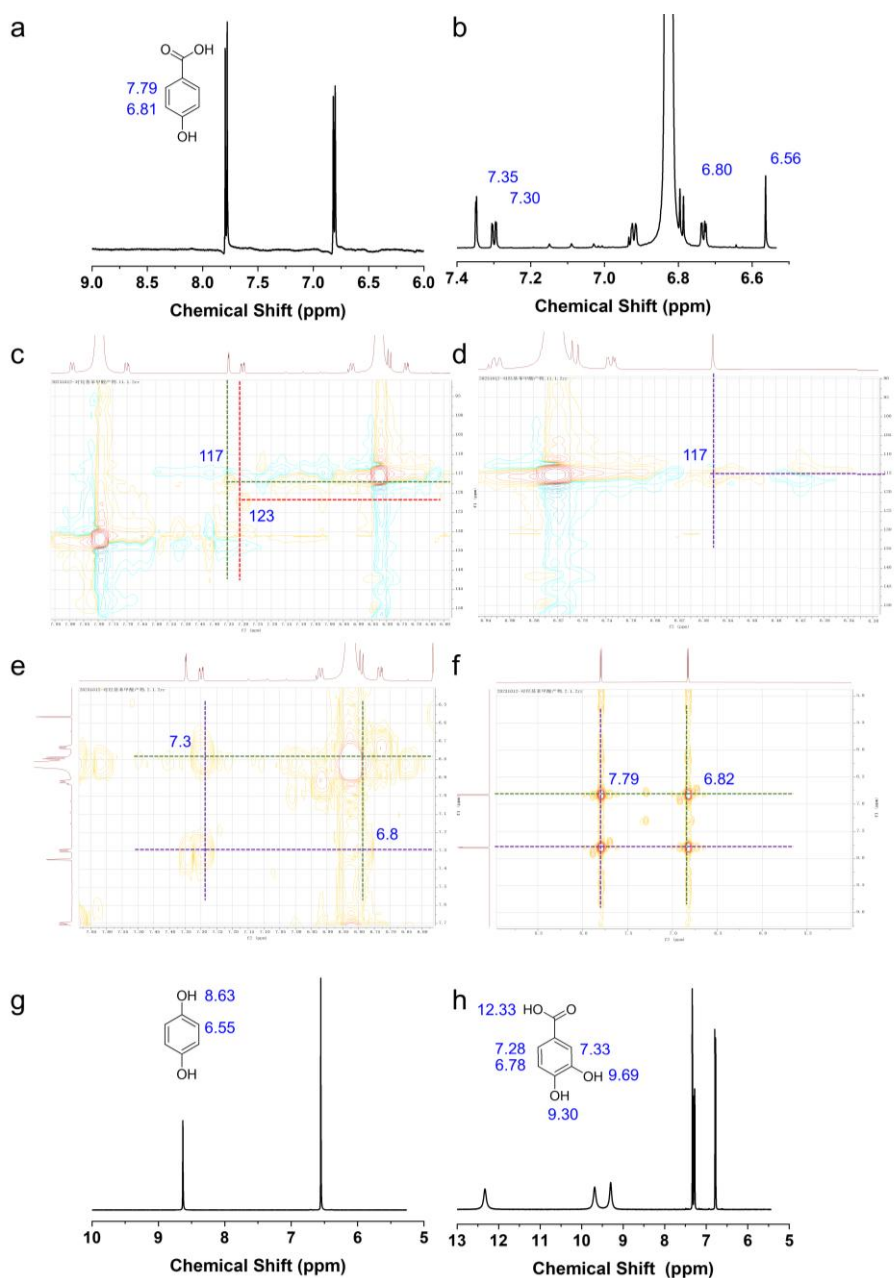
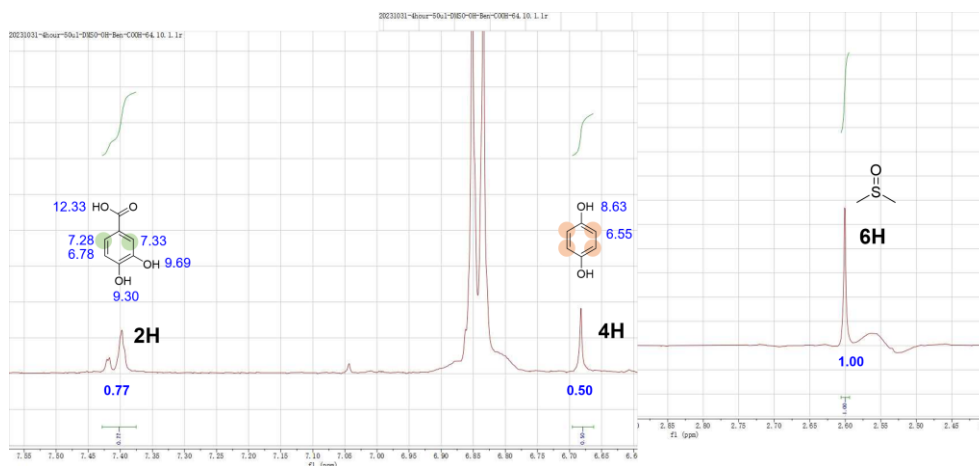


Figure S7. NMR analysis of 4-hydroxybenzoic acid hydroxylation products. (a-b) ^1H NMR spectra (850 MHz) before and after reaction of 4-hydroxybenzoic acid solutions, where panel (b) is an enlarged view of panel (a). ^1H - ^{13}C HSQC (c-d) and ^1H - ^1H COSY NMR spectra (850 MHz) of 4-hydroxybenzoic acid solution (e-f) after reaction. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 5 mM 4-hydroxybenzoic acid, 2 h reaction time, air atmosphere, 25 $^\circ\text{C}$, and ultrasonication at 40 kHz and 200 W. ^1H NMR spectra (500 MHz) of standard samples for (g) hydroquinone and (h) 3,4-dihydroxybenzoic acid.

The reaction sites of hydroxylation products are different when benzene ring has diverse substituents. In general, aromatics with electron-donating groups undergo hydroxylation reactions preferentially at the ortho- and para-site of the group, while aromatics with electron-withdrawing groups prefer to react at the meta position. This can be attributed to the location effect. It is relatively simple to analyze the active sites when the substituents are solely electron-donating or electron-withdrawing groups. In the case of 4-nitrobenzoic acid, the $-\text{CO}_2\text{H}$ and $-\text{NO}_2$ groups are electron-withdrawing groups. Thus, the reactive site is located in the interposition between the two groups. However, it is essential to initially consider the positioning ability of the two groups. For example, the electronegativity of the N atom is stronger than that of the C atom, and the electronegativity of the $-\text{NO}_2$ group is stronger, so the C-H activity of the intermediate site is higher. The $\cdot\text{OH}$ will preferentially activate the site with low energy and the hydroxylation reaction will occur. When substituents have both electron-donating and electron-withdrawing groups, a comprehensive analysis of the molecular structure of hydroxylation products is required. For example, as for 4-hydroxybenzoic acid, the $-\text{CO}_2\text{H}$ group belongs to electron-withdrawing groups, while the $-\text{OH}$ group is the electron-donating group, so the active site is the ortho-site of the overlapping $-\text{OH}$ group. In addition to the location effect, the steric hindrance effect should also be considered. For example, substituents such as carboxyl group and benzene ring have a considerable steric hindrance, resulting in an overlapping electron cloud with neighboring atoms, hindering the reaction of the neighboring atom.

Next, we selected other aromatic compounds with structural composition (such as the introduction of $-\text{OCH}_3$, $-\text{CH}_3$ groups) for experiments, namely, hydroquinone, catechol, resorcinol, 4-methoxyphenol and benzyl alcohol. Based on the localization effect and LC-MS results, the hydroxylation reaction pathway and the product were predicted. The hydroxylation reaction paths of hydroquinone, catechol and resorcinol are shown in Figure S8a-c. The $\cdot\text{OH}$ selectively activated the C–H bond in the benzene ring to generate 1,2,4-trihydroxybenzene ($[\text{C}_6\text{H}_6\text{O}_3\text{-H}]^-$, m/z 125.0246) and 1,2,4,6-tetrahydroxybenzene ($[\text{C}_6\text{H}_6\text{O}_4\text{-H}]^-$, m/z 141.0193). In addition, the hydroxylation reaction paths and mass spectrometry results for 4-methoxyphenol and benzyl alcohol were presented in Figure S9a-b. The hydroxylated products of 4-methoxyphenol were expected to be 3,4-dihydroxyanisole ($[\text{C}_7\text{H}_8\text{O}_3\text{-H}]^-$, m/z 139.0399), 3,4,5-trihydroxyanisole ($[\text{C}_7\text{H}_8\text{O}_4\text{-H}]^-$, m/z 155.0353) and 2,3,4,5-tetrahydroxyanisole ($[\text{C}_7\text{H}_8\text{O}_5\text{-H}]^-$, m/z 171.0425). The hydroxylated products of benzyl alcohol were 4-hydroxybenzyl alcohol ($[\text{C}_7\text{H}_8\text{O}_2\text{-H}]^-$, m/z 123.0451), 3,4-dihydroxybenzyl alcohol ($[\text{C}_7\text{H}_8\text{O}_3\text{-H}]^-$, m/z 139.0399) and 3,4,5-trihydroxybenzyl alcohol ($[\text{C}_7\text{H}_8\text{O}_4\text{-H}]^-$, m/z 155.0327).

Calculation of the yield of products using Test method 1



Quantitative analysis and yield calculation of the reaction products were performed by the ^1H NMR internal standard method.

$$\text{Internal standard concentration} = [2 \times (50 \times 10^{-6})] / [(50 + 100 + 400) \times 10^{-6}] \text{ mM}$$

$$= 0.18181 \text{ mM} = 181.81 \text{ } \mu\text{M}$$

$$\text{Yield of Product 1} = 828.44 \text{ } \mu\text{M}$$

$[(1 \times 78.13)/6]: [(0.77 \times 154.12)/2] = 181.81 \mu\text{M}$: Yield of Product 1 μM

Yield of Product 2 = 192.1 μM

$[(1 \times 78.13)/6]: [(0.50 \times 110.11)/4] = 181.81 \mu\text{M}$: Yield of Product 2 μM

Note: In the ^1H NMR analysis, the integral area of the characteristic peak of the internal standard was normalized to unit 1, and the characteristic peaks of the target product were integrated using this value as the reference.

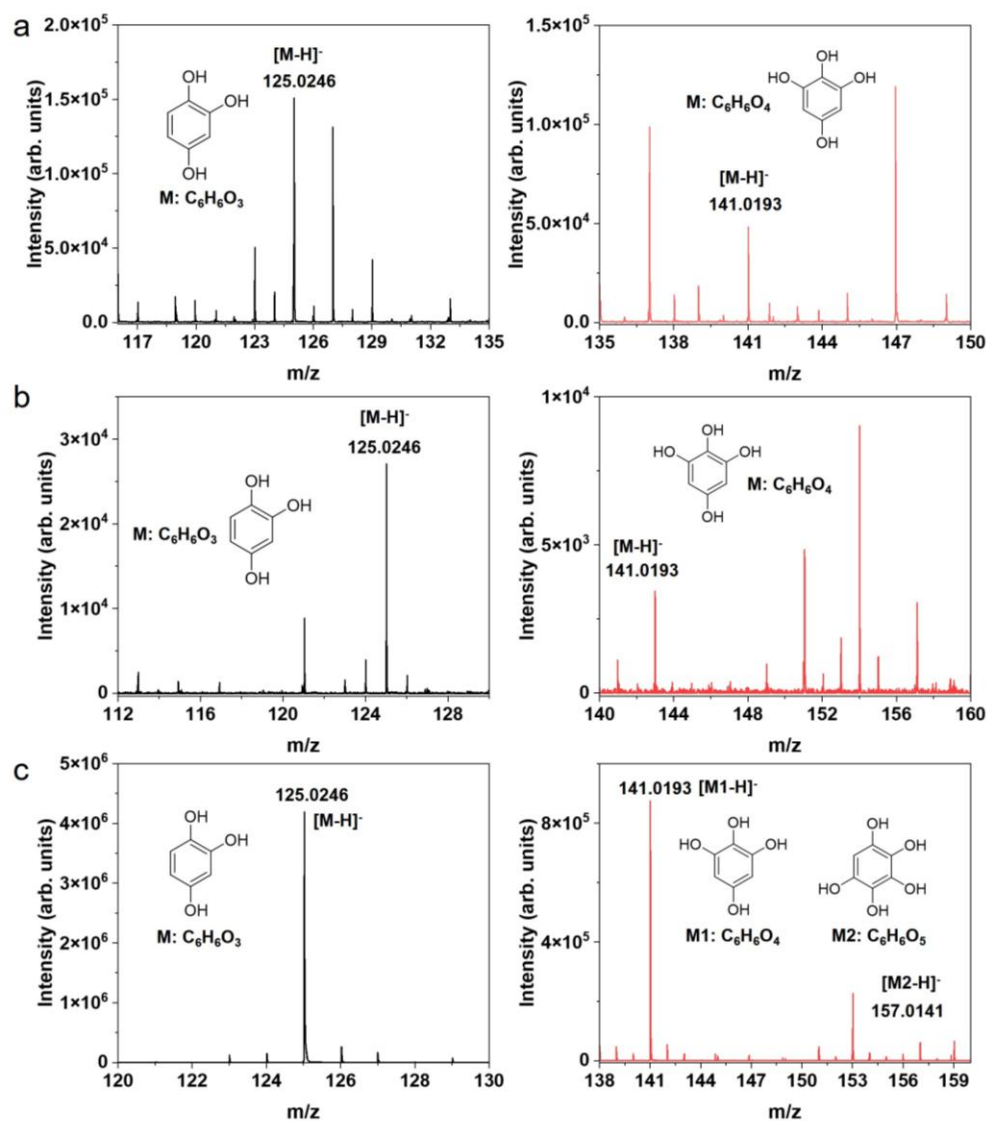


Figure S8. Mass spectrometric analysis of hydroxylation products from phenolic substrates. Mass spectra of hydroxylation products for (a) hydroquinone, (b) pyrocatechol and (c) resorcinol. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μ m), 5 mM reaction substrate, 2 h reaction time, air atmosphere, 25 $^{\circ}$ C, and ultrasonication at 40 kHz and 200 W. The post-reaction samples were filtered prior to LC-MS analysis. $[M-H]^{-}$, deprotonated molecular ion

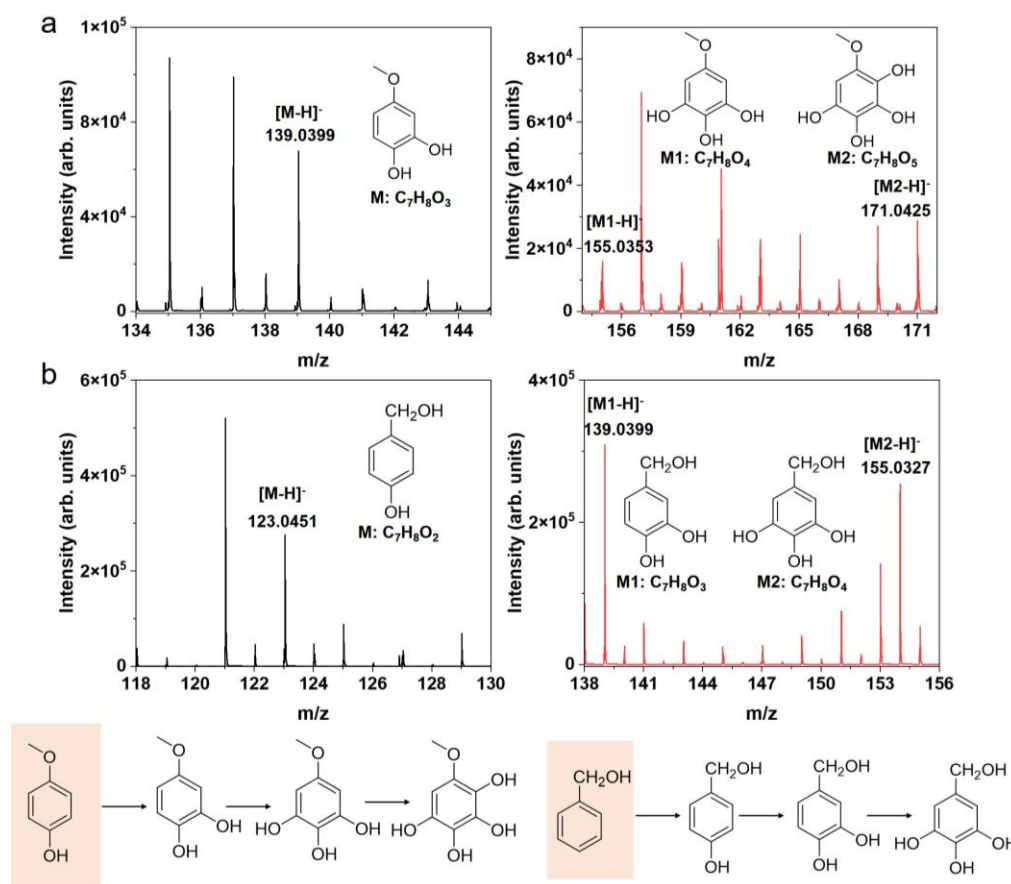


Figure S9. Mass spectrometric analysis of hydroxylation products from 4-methoxyphenol and benzyl alcohol. Mass spectra of the hydroxylation products for (a) 4-methoxyphenol and (b) benzyl alcohol. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μ m), 5 mM reaction substrate, 2 h reaction time, air atmosphere, 25 $^{\circ}$ C, and ultrasonication at 40 kHz and 200 W. The post-reaction samples were filtered prior to LC-MS analysis.

Product analysis of resorcinol: The spectra before and after the reaction were shown in Figure S10a-b. Due to the symmetrical structure of resorcinol, the chemical shifts of

the two –OH peaks are identical, appearing as a singlet peak at 9.2 ppm. After the reaction, the result shows doublet peaks at 6.0 and 6.49 ppm, as well as four singlet peaks at 8.05, 8.49, 8.68 and 8.71 ppm, respectively. Combined with ^1H - ^1H COSY NMR spectrum in Figure S10c, it is hypothesized that –OH groups may have replaced C–H bonds in the benzene ring. Compared with the ^1H NMR spectrum of standard sample for 1,2,4-trihydroxybenzene, it exhibits the same chemical shift and the number of splitting peaks (Figure S10d), indicating that resorcinol has undergone hydroxylation to produce 1,2,4-trihydroxybenzene. Quantification of the products was performed by the ^1H NMR internal standard method. The characteristic peak at 6.49 ppm was selected for the integration of 1,2,4-trihydroxybenzene.

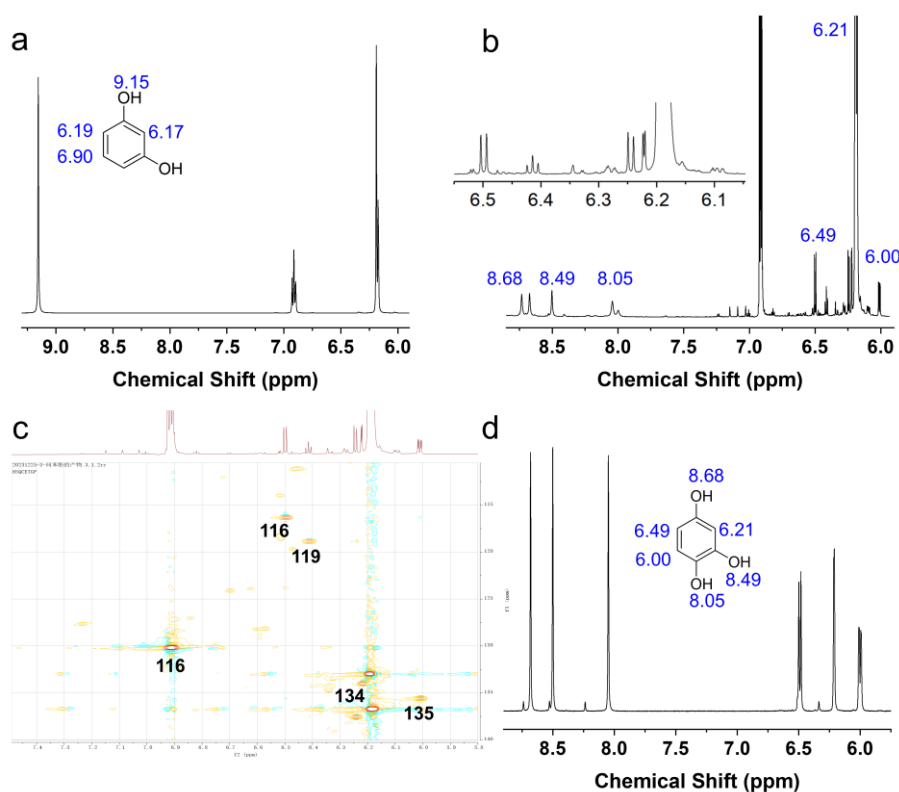


Figure S10. NMR analysis of resorcinol hydroxylation products. (a) ^1H NMR spectrum (500 MHz) of the resorcinol solution before the reaction. (b) ^1H NMR spectrum (850 MHz) of the resorcinol solution after the reaction; the inset shows an enlarged region highlighting the characteristic product signal. (c) ^1H - ^1H COSY NMR spectrum (850 MHz) of the resorcinol solution after the reaction. (d) ^1H NMR spectrum (500 MHz) of the standard sample of 1,2,4-trihydroxybenzene. Reaction conditions: 30 mL DI water,

20 mg PTFE (3 μm), 5 mM resorcinol, 2 h reaction time, air atmosphere, 25 $^{\circ}\text{C}$, and ultrasonication at 40 kHz and 200 W. The post-reaction sample was filtered and subjected to solvent evaporation prior to ^1H NMR analysis.

Product analysis for benzene: Quantification of the products was performed by the ^1H NMR internal standard method. The characteristic peaks at 6.75 and 6.77 ppm were selected for the integration of phenol, while the characteristic peak at 6.55 ppm was selected for the integration of hydroquinone.

The major products formed from resorcinol, phenol, benzoic acid, 4-nitrobenzyl alcohol, and 4-nitrobenzoic acid were quantitatively analyzed using chromatographic acetonitrile as an internal standard. The corresponding products were identified as 1,2,4-trihydroxybenzene, hydroquinone, 4-hydroxybenzoic acid, 2-hydroxy-4-nitrobenzyl alcohol, and 3-hydroxy-4-nitrobenzoic acid, with the yield of 4.63, 3.87, 1.09, 0.77, and 1.04 $\text{mmol L}^{-1} \text{h}^{-1}$, respectively (Figure S11a). With an initial substrate concentration of 20 mM and the theoretical product amount calculated based on 100% substrate conversion, the corresponding 1 h-normalized ^1H NMR-determined yields of these products were 23.2%, 19.4%, 5.5%, 3.9%, and 5.2%, respectively. During post-treatment, benzene may be partially lost during transfer and drying because of its relatively low boiling point. Phenol and hydroquinone may also be partially lost during filtration, transfer, and drying. Therefore, the experimentally detected amounts of phenol and hydroquinone obtained after post-treatment may underestimate their actual formation in the reaction system. The experimentally detected yields were determined to be 47 and 4.14 $\mu\text{mol L}^{-1} \text{h}^{-1}$, respectively (Figure S11b). For this reason, we did not further calculate its apparent isolated yield, to avoid misleading interpretation.

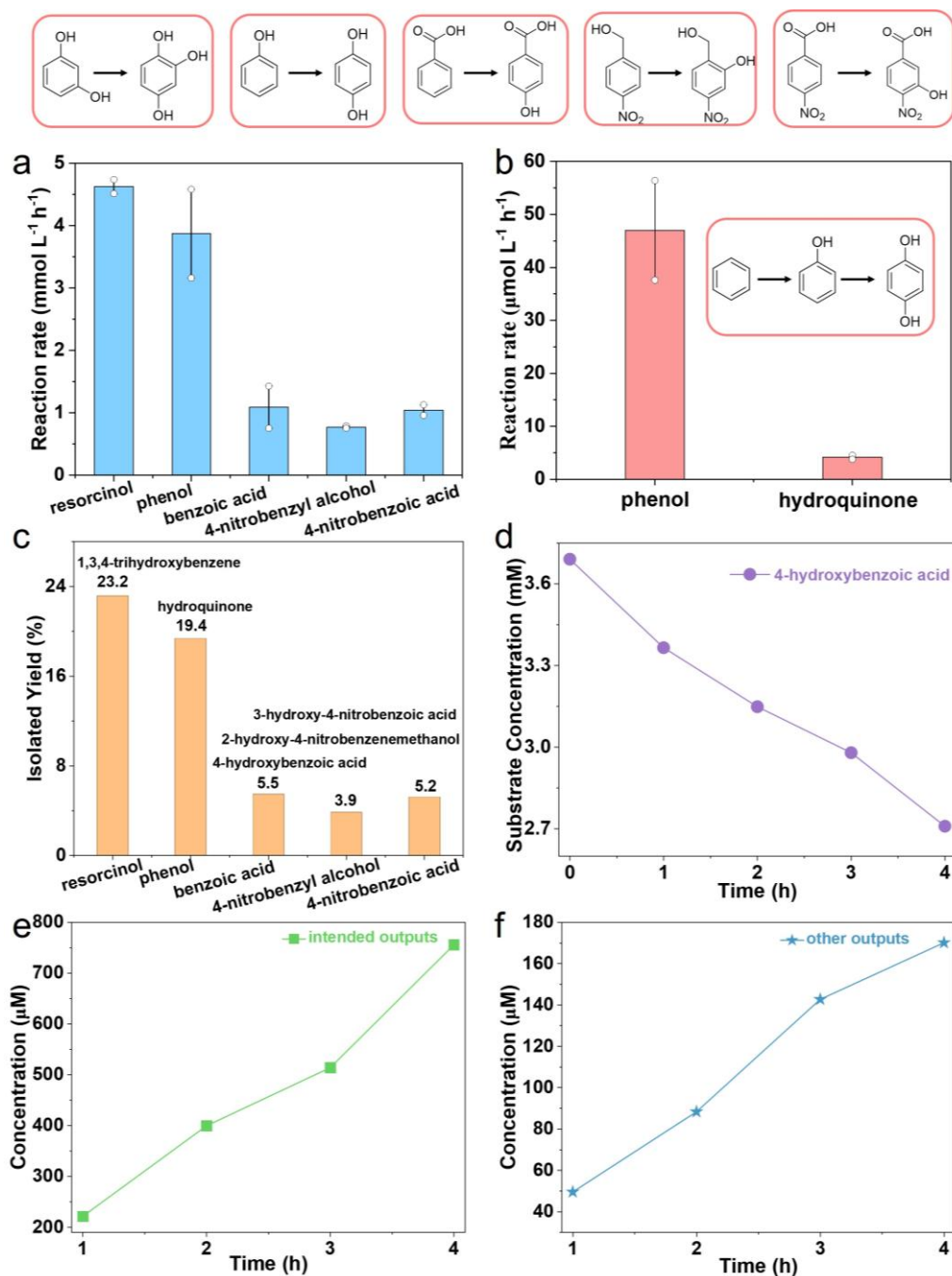


Figure S11. Quantitative analysis of aromatic hydroxylation products. (a) Yields of major products formed from different aromatic substrates. (b) Yields of phenol and hydroquinone derived from benzene, as quantified using Test Method 2. (c) ¹H NMR-based apparent yields of the major products formed from resorcinol, phenol, benzoic acid, 4-nitrobenzyl alcohol, and 4-nitrobenzoic acid. Reaction conditions for (a-c): 30 mL DI water, 20 mg PTFE (3 μm), 20 mM substrate, air atmosphere, 25 °C, and ultrasonication at 40 kHz and 200 W. The post-reaction samples were filtered and subjected to solvent evaporation prior to ¹H NMR analysis. (d) Time-dependent

concentration of 4-hydroxybenzoic acid substrate. (e) Time-dependent combined yield of the target products, 3,4-dihydroxybenzoic acid and hydroquinone. (f) Time-dependent yields of other products. Reaction conditions for (d-f): 30 mL DI water, 20 mg PTFE (3 μ m), 5 mM 4-hydroxybenzoic acid, air atmosphere, 25 °C, and ultrasonication at 40 kHz and 200 W. For (a-b), data are presented as mean $\pm$ standard deviation from two independent measurements (n=2), with individual data points shown. The conversion values in (c) were calculated from the mean values shown in (a).

We have also supplemented the quantitative analysis of the concentration of 4-hydroxybenzoic acid based on ^1H NMR at different reaction times. As shown in Figure S11d, when the reaction time was extended from 1 to 4 h, the concentration of 4-hydroxybenzoic acid decreased from 3.365 mmol L $^{-1}$ to 2.709 mmol L $^{-1}$, confirming continuous substrate consumption during the reaction. Meanwhile, the time-dependent distributions of the target products and by-products indicate that the 3,4-dihydroxybenzoic acid formation pathway exhibits a higher formation rate and selectivity than the hydroquinone pathway (Figure S11e-f). However, side reactions also occurred, leading to the formation of non-target products from the substrate.

The target products from the six substrates were identified through comprehensive ^1H NMR analysis, including chemical shifts, splitting patterns, and integration ratios, in comparison with authentic standards. LC-MS analysis provided complementary evidence. Thus, product assignment was based on combined NMR and LC-MS characterization rather than a single spectroscopic method.

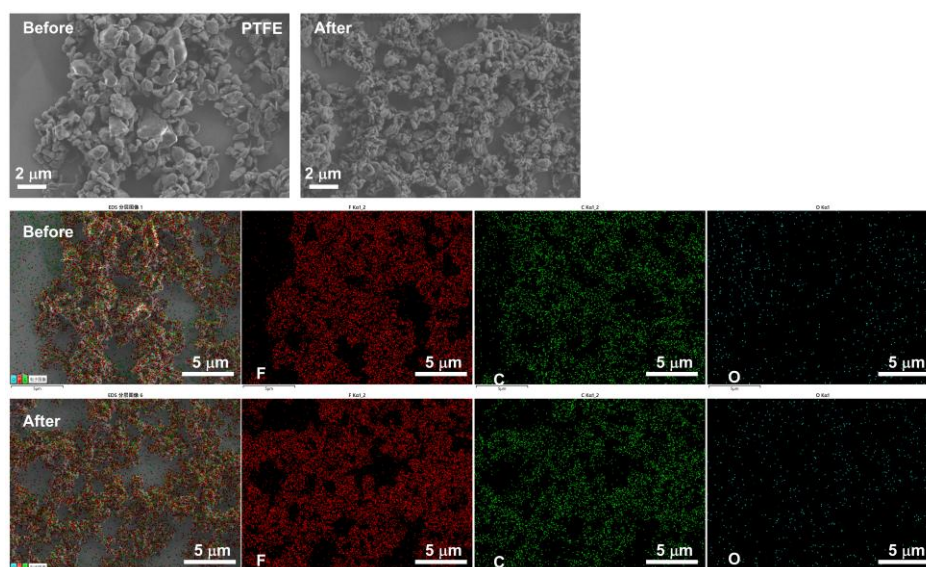


Figure S12. Morphology and elemental distribution of PTFE before and after ultrasonication. SEM images of PTFE particles before and after ultrasonication in the PTFE–H₂O system (upper panel). The corresponding EDS elemental mapping images show the spatial distributions of F, C, and O elements before and after treatment (lower panel). Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 50 h reaction time, air atmosphere, 25 °C, and ultrasonication at 40 kHz and 100 W. PTFE, polytetrafluoroethylene

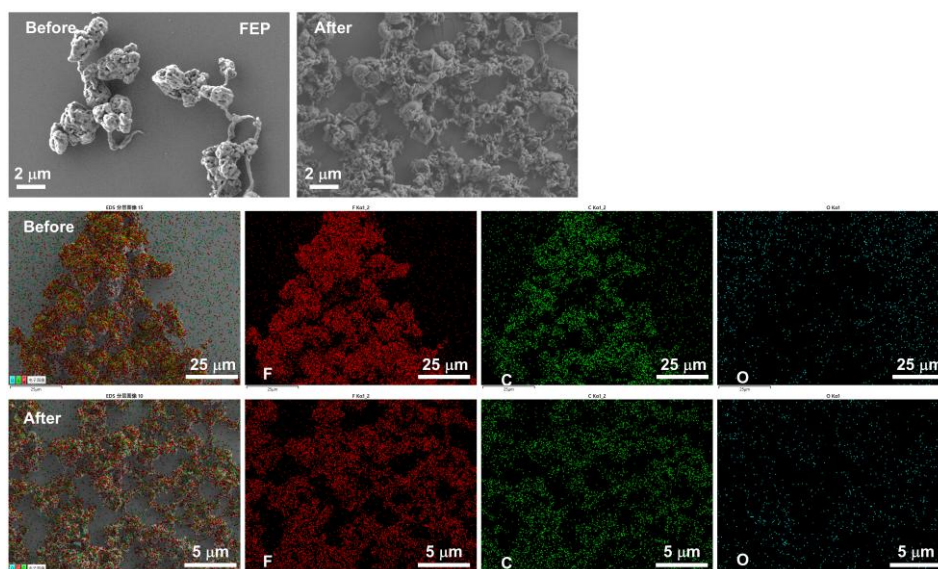


Figure S13. Morphology and elemental distribution of FEP before and after ultrasonication. SEM images of FEP particles before and after ultrasonication in the FEP–H₂O system (upper panel). The corresponding EDS elemental mapping images show the spatial distributions of F, C, and O elements before and after treatment (lower

panel). Reaction conditions: 30 mL DI water, 20 mg FEP (3 μm), 50 h reaction time, air atmosphere, 25 $^{\circ}\text{C}$, and ultrasonication at 40 kHz and 100 W. FEP, fluorinated ethylene propylene.

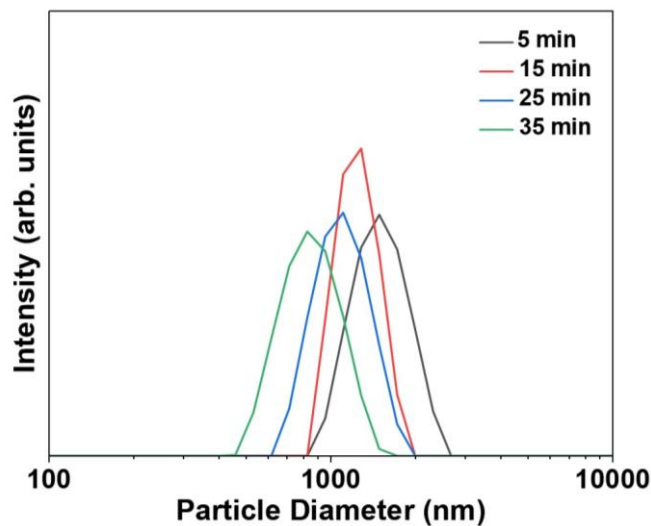


Figure S14. Time-dependent particle size distribution of PTFE in aqueous suspension. Particle size distributions of PTFE particles in aqueous suspension after ultrasonic treatment for different times. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), air atmosphere, 25 $^{\circ}\text{C}$, and ultrasonication at 40 kHz and 100 W.

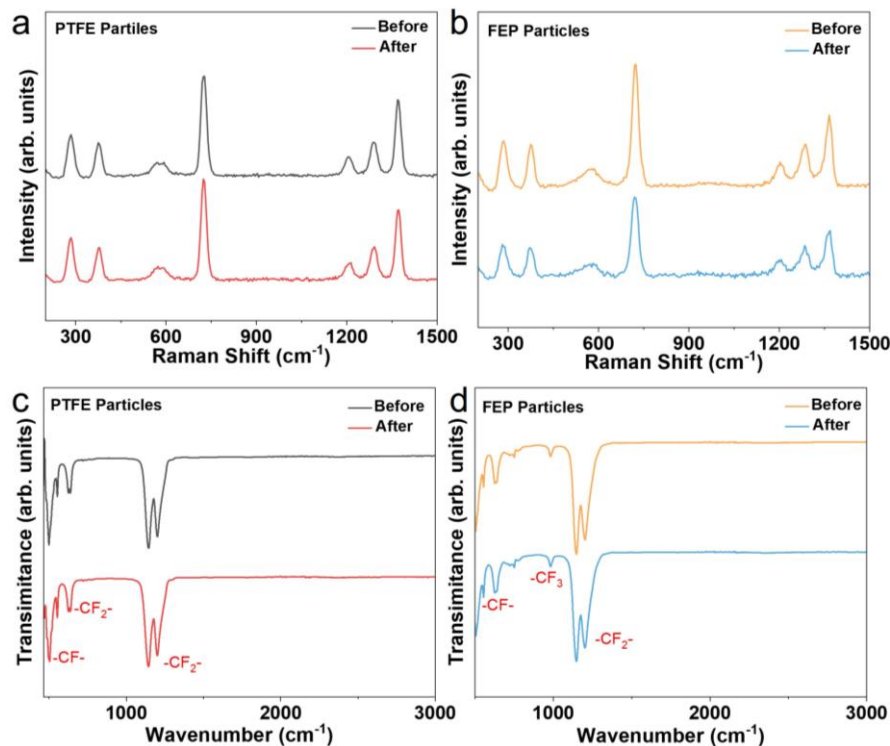


Figure S15. Raman and FTIR characterization of PTFE and FEP before and after ultrasonication. Raman spectra of (a) PTFE and (b) FEP particles before and after ultrasonication. FTIR spectra of (c) PTFE and (d) FEP particles before and after ultrasonication. Reaction conditions: 30 mL DI water, 20 mg PTFE or FEP (3 μ m), 50 h reaction time, air atmosphere, 25 $^{\circ}$ C, and ultrasonication at 40 kHz and 100 W. PTFE, polytetrafluoroethylene; FEP, fluorinated ethylene propylene

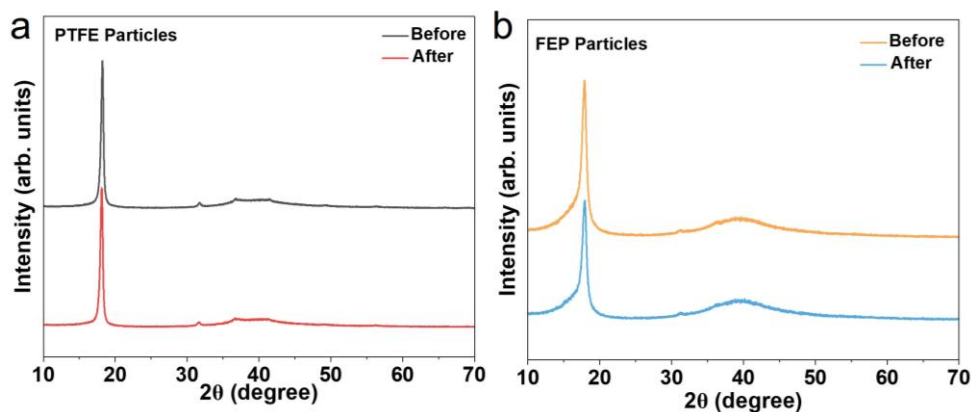


Figure S16. XRD characterization of PTFE and FEP before and after ultrasonication. XRD patterns of (a) PTFE and (b) FEP particles before and after ultrasonic treatment, respectively. Reaction conditions: 30 mL DI water, 20 mg PTFE or FEP (3 μ m), 50 h reaction time, air atmosphere, 25 $^{\circ}$ C, and ultrasonication at 40 kHz and 100 W. PTFE, polytetrafluoroethylene; FEP, fluorinated ethylene propylene

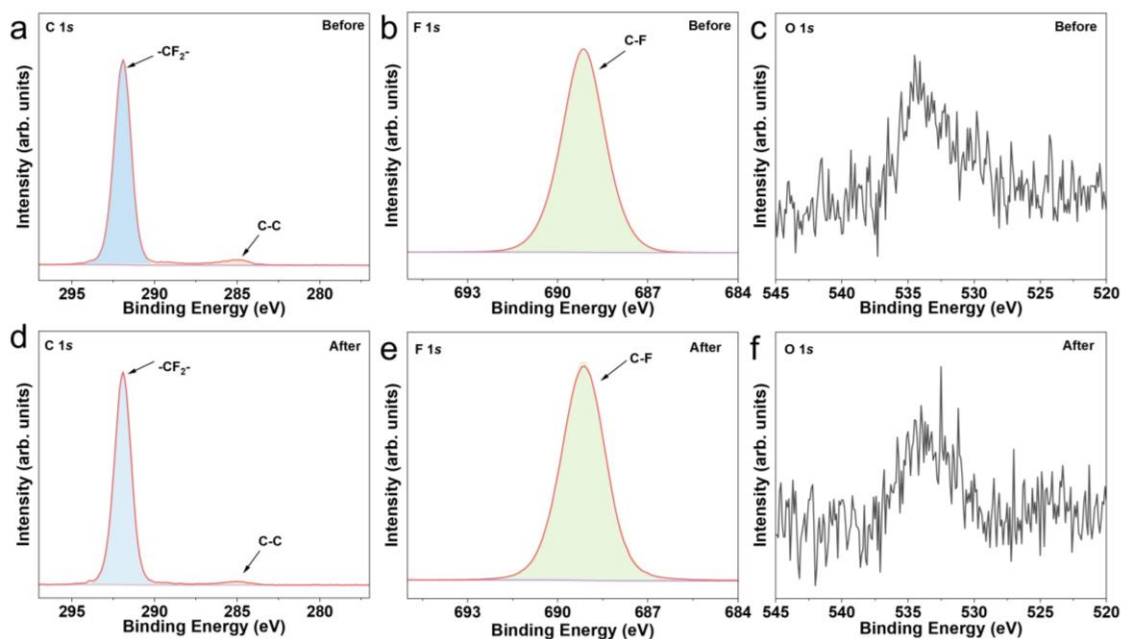


Figure S17. XPS characterization of PTFE before and after ultrasonication. XPS spectra of (a, d) C 1s, (b, e) F 1s, and (c, f) O 1s for PTFE particles before and after ultrasonic treatment. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 50 h reaction time, air atmosphere, 25 $^{\circ}\text{C}$, and ultrasonication at 40 kHz and 100 W.

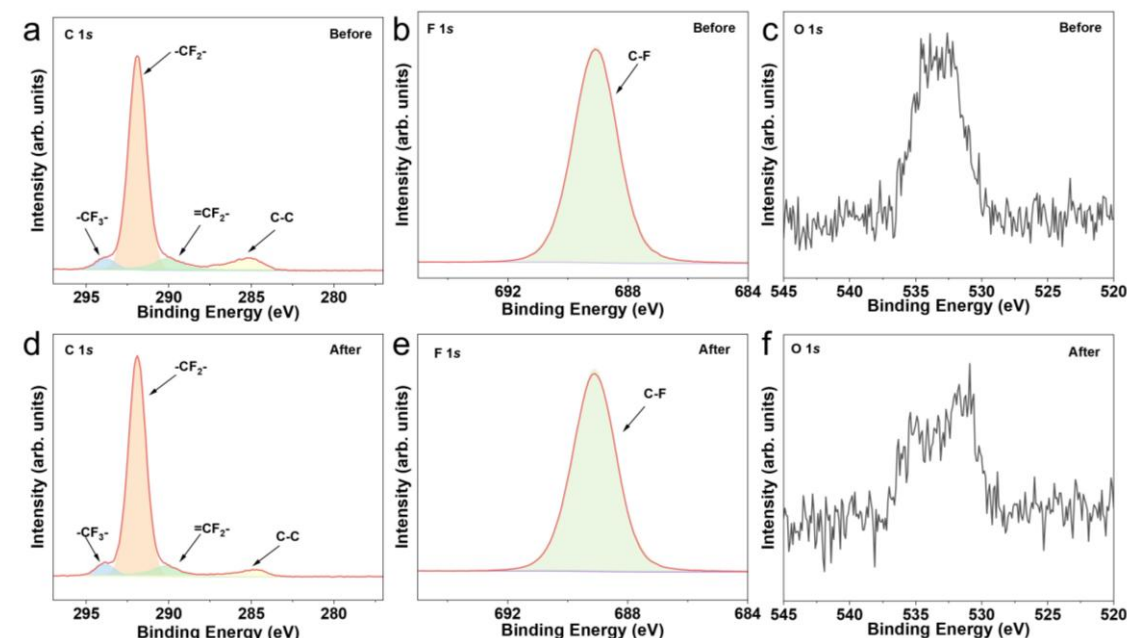


Figure S18. XPS characterization of FEP before and after ultrasonication. XPS spectra of (a, d) C 1s, (b, e) F 1s, and (c, f) O 1s for FEP particles before and after ultrasonic treatment. Reaction conditions: 30 mL DI water, 20 mg FEP (3 μm), 50 h reaction time, air atmosphere, 25 $^{\circ}\text{C}$, and ultrasonication at 40 kHz and 100 W.

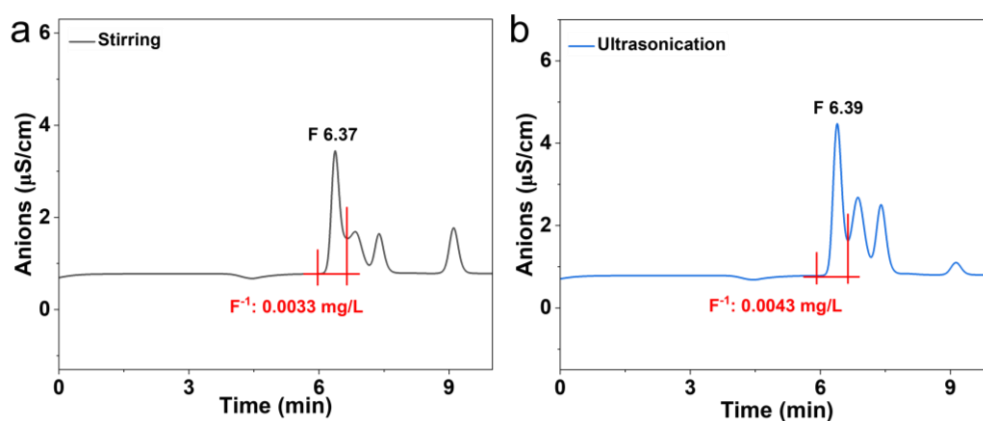


Figure S19. Ion chromatographic analysis of the PTFE-H₂O system. Ion chromatograms of the aqueous phases collected from the PTFE-H₂O system after 30

min treatment of (a) stirring and (b) ultrasonication at 40 kHz and 100 W. The other conditions were identical: 50 mL DI water, 20 mg PTFE (3 μ m), air atmosphere, 25 $^{\circ}$ C.

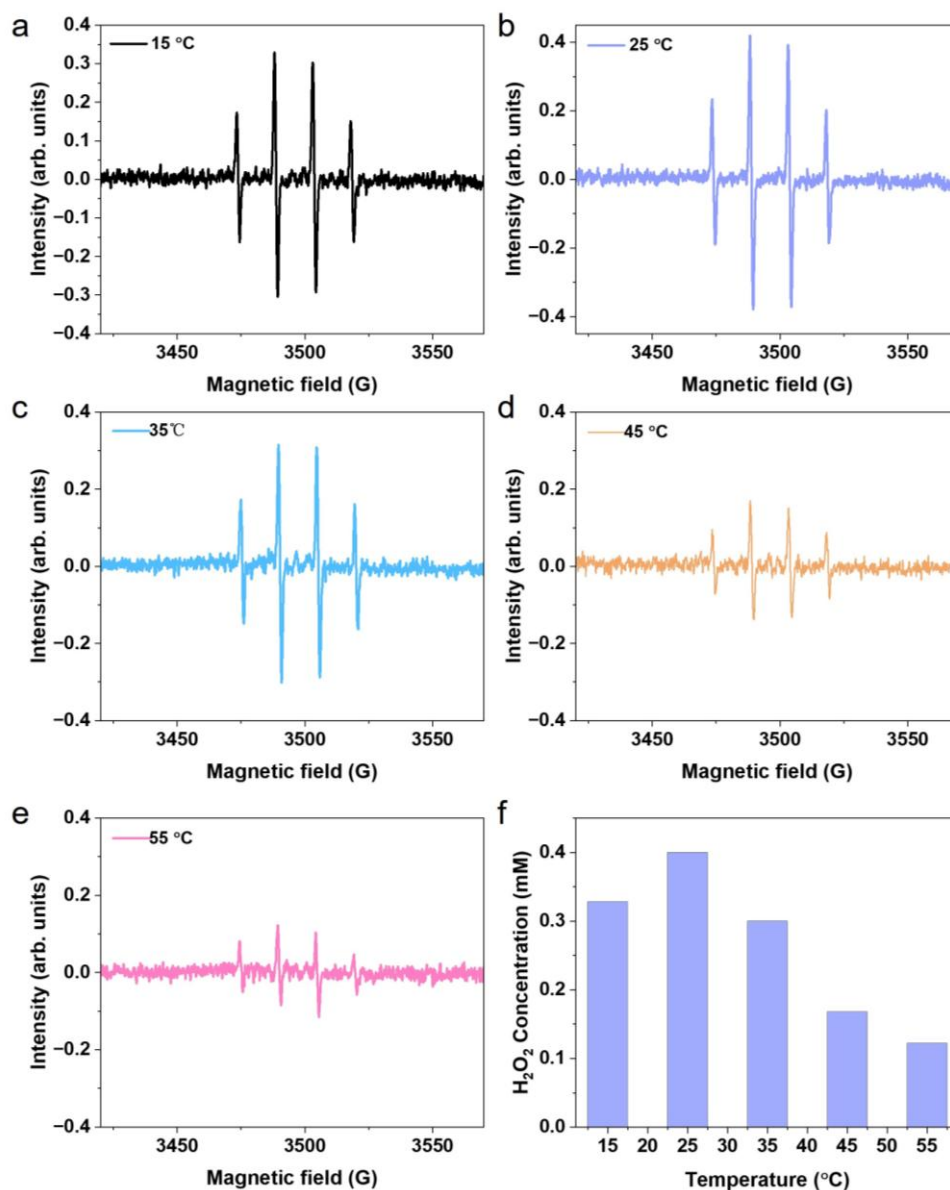


Figure S20. Temperature dependence of $\cdot$ OH and H_2O_2 generation. The intensity of $\cdot$ OH characteristic peaks at (a) 15, (b) 25, (c) 35, (d) 45 and (e) 55 $^{\circ}$ C. (f) The concentration of H_2O_2 at different temperatures. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μ m), 1 h reaction time, air atmosphere, and ultrasonication at 40 kHz and 200 W. The data in (f) are from a single measurement (n=1).

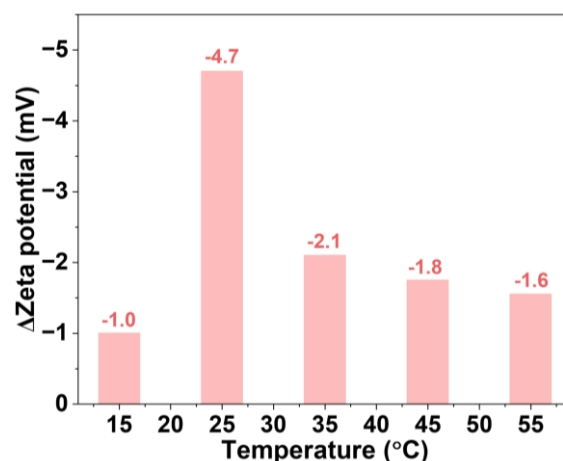


Figure S21. Temperature-dependent zeta potential changes in the PTFE–H₂O system. Comparison of the zeta potential difference in the PTFE–H₂O system at different temperatures after 30 min of ultrasonic treatment under ambient pressure and air atmosphere. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), and ultrasonication at 40 kHz and 100 W. The data are from a single measurement (n=1).

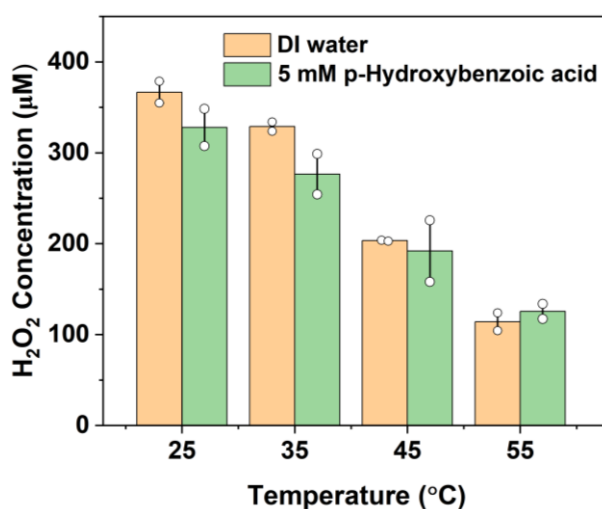


Figure S22. Temperature dependence of H₂O₂ generation in different reaction solutions. Comparison of H₂O₂ concentrations for DI water and 4-hydroxybenzoic acid at different reaction temperatures. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 5 mM 4-hydroxybenzoic acid, 1 h reaction time, air atmosphere, and ultrasonication at 40 kHz and 200 W. Data are presented as mean ± standard deviation from two independent experiments (n=2).

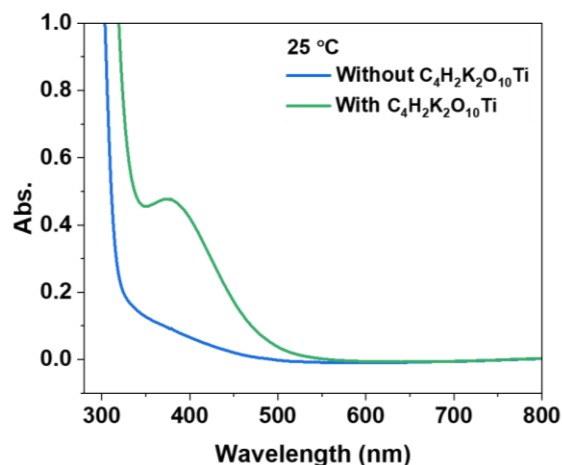


Figure S23. Absorbance analysis for H_2O_2 detection. Comparison of the absorbance with and without $\text{C}_4\text{H}_2\text{K}_2\text{O}_{10}\text{Ti}$ at 25 °C. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 1 mL of 0.1 M $\text{C}_4\text{H}_2\text{K}_2\text{O}_{10}\text{Ti}$ solution, 2 h reaction time, air atmosphere, and ultrasonication at 40 kHz and 200 W.

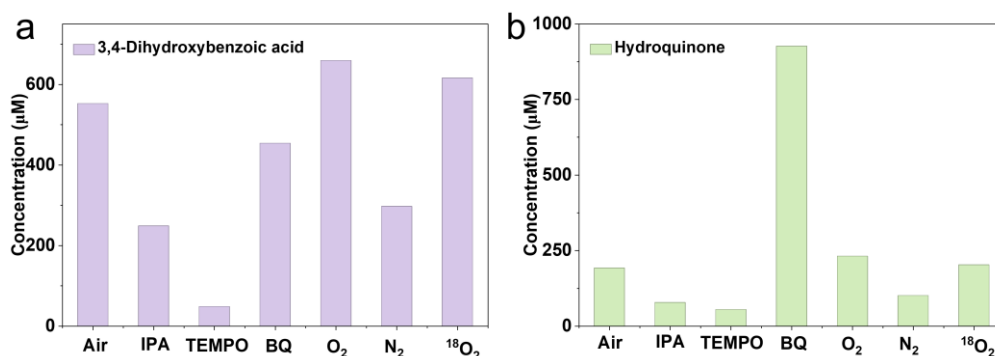


Figure S24. Effects of radical scavengers and gas atmospheres on product formation. Product concentrations of (a) 3,4-dihydroxybenzoic acid and (b) hydroquinone under different reaction conditions, including in air, air with IPA ($\cdot\text{OH}$ scavenger), air with TEMPO (radical scavenger), air with benzoquinone (BQ), as well as O_2 , N_2 and $^{18}\text{O}_2$ atmospheres. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 5 mM 4-hydroxybenzoic acid, 4 h reaction time, 25 °C, and ultrasonication at 40 kHz and 200 W. The data are from a single measurement ($n=1$). PTFE, polytetrafluoroethylene; IPA, 2-propanol; TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl; BQ, benzoquinone.

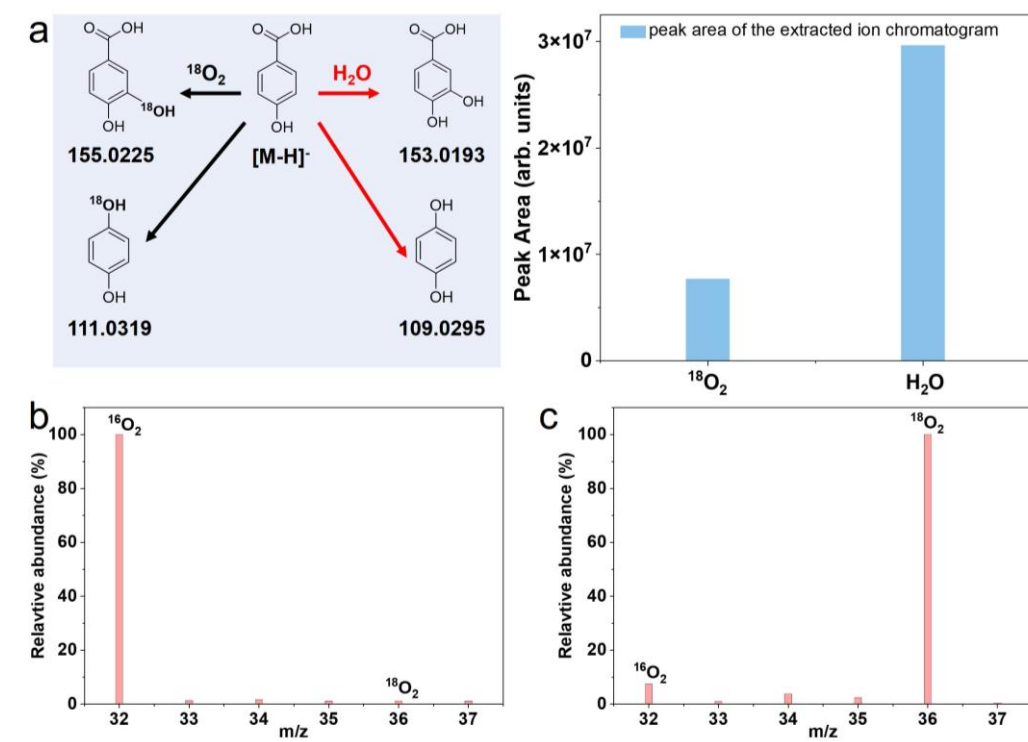


Figure S25. Isotope-labeling analysis of oxygen incorporation in hydroxylation products. (a) LC-MS isotope-labeling analysis of oxygen incorporation into the hydroxylation products under an $^{18}O_2$ atmosphere in H_2O . The left panel shows the detected signals of the ^{18}O -labeled and ^{16}O -containing products, and the right panel shows the corresponding extracted-ion chromatogram peak areas. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μ m), 5 mM 4-hydroxybenzoic acid, 8 h reaction time, 25 $^{\circ}C$, and ultrasonication at 40 kHz and 200 W. GC-MS analysis of the headspace gas before (b) gas exchange and after (c) Ar deoxygenation and $^{18}O_2$ replacement. The signals at m/z = 32 and 36 are assigned to $^{16}O_2$ and $^{18}O_2$, respectively. The data in (a) are from a single measurement ($n=1$). $[M-H]^-$, deprotonated molecular ion.

We performed GC-MS analysis of the headspace gas collected after completion of the gas-replacement procedure to directly assess the replacement efficiency of $^{18}O_2$. The analysis focused on the signals at m/z = 32 and 36, which were assigned to $^{16}O_2$ and $^{18}O_2$, respectively. Before gas replacement (Figure S25b), the m/z = 32 signal was dominant, whereas the m/z = 36 signal ($^{18}O_2$) was only 0.71% of the m/z = 32 ($^{16}O_2$). After Ar bubbling for 30 min followed by $^{18}O_2$ bubbling for 10 min, the m/z = 36 signal ($^{18}O_2$) became dominant (Figure S25c), while the residual m/z = 32 signal ($^{16}O_2$) was

7.44% of the $m/z = 36$ ($^{18}\text{O}_2$). A minor intrinsic contribution from ^{16}O -containing oxygen isotopologues was expected because the $^{18}\text{O}_2$ gas used in this experiment had an isotopic enrichment of 98% ^{18}O atom rather than 100%. Moreover, because the headspace gas was collected using a syringe, a small amount of ambient air may have been introduced during sampling. Therefore, the measured $m/z = 32$ signal likely represents an upper estimate of the residual $^{16}\text{O}_2$ content in the sealed reactor. These results provide direct experimental evidence that the combined Ar-deoxygenation and $^{18}\text{O}_2$ -replacement procedure substantially reduced the contribution of atmospheric $^{16}\text{O}_2$ and established a $^{18}\text{O}_2$ -dominated atmosphere.

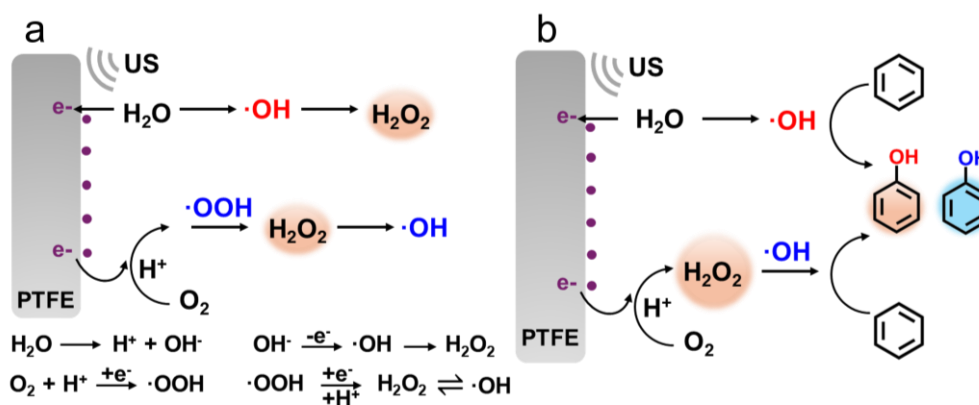


Figure S26. Proposed pathways for H_2O_2 generation and aromatic hydroxylation. (a) The H_2O_2 generation pathway during the contact-electro-catalysis reaction. (b) The proposed reaction pathway for aromatic hydroxylation with $\cdot\text{OH}$. PTFE, polytetrafluoroethylene; US, ultrasonication.

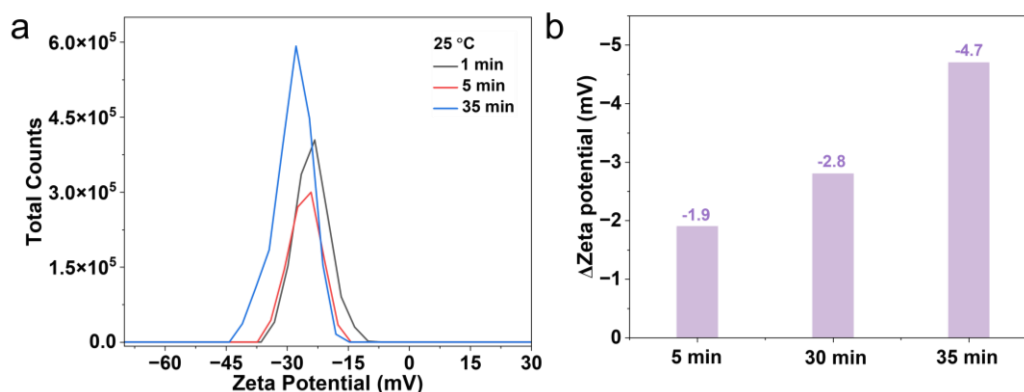


Figure S27. Time-dependent zeta potential evolution of the PTFE– H_2O system. (a) Zeta potential distributions of PTFE– H_2O system after ultrasonication for 1, 5, and 35 min

at 25 °C. (b) Corresponding changes in zeta potential over different ultrasonication intervals (1-5 min, 5-35 min, 1-35 min). Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μ m), air atmosphere, and ultrasonication at 40 kHz and 100 W. The data in (b) are from a single measurement (n=1).

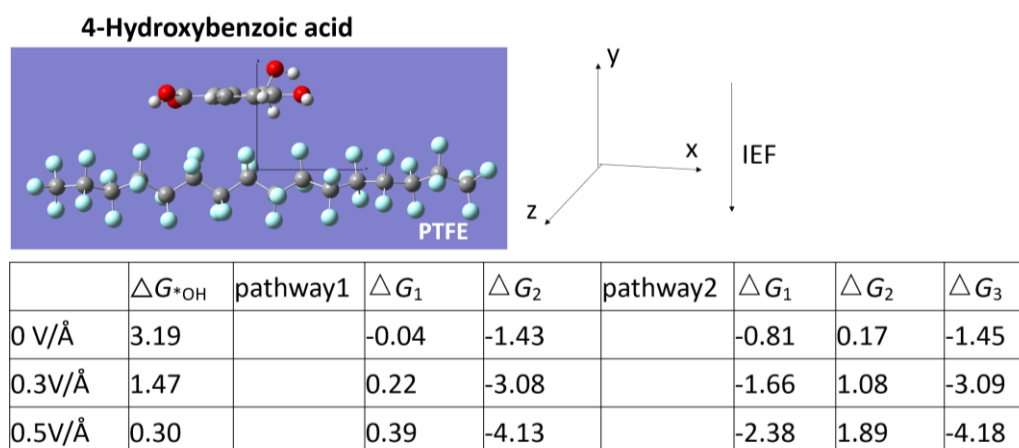


Figure S28. Schematic representation of the external electric field applied to the interfacial model. The required ΔG values for $\cdot OH$ generation from OH^- and the hydroxylation of 4-hydroxybenzoic acid via pathways 1 and 2 under different interfacial electric fields. ΔG values are given in electron volts (eV). PTFE, polytetrafluoroethylene; IEF, interfacial electric field; ΔG , Gibbs free-energy change.

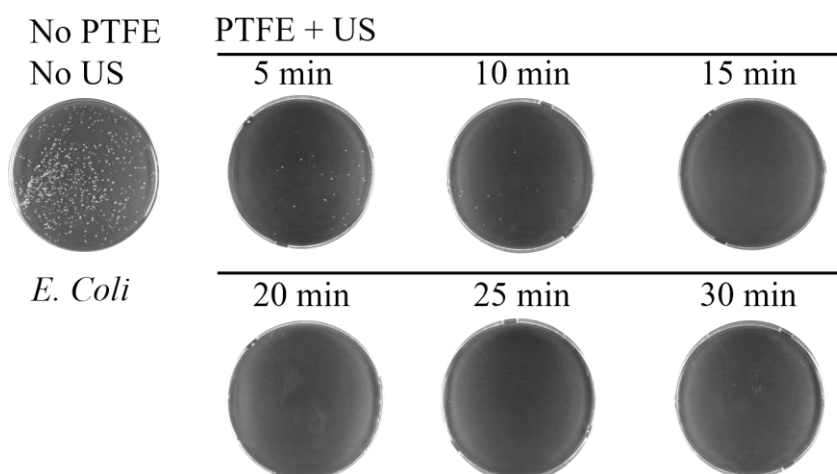


Figure S29. Time-dependent inactivation of *E. coli* under PTFE-assisted ultrasonication. Micrographs of *E. coli* colonies cultured on agar plates after different ultrasonic treatment times in the presence of PTFE particles. Reaction conditions: 50 mL DI water,

50 mg PTFE (25 μ m), air atmosphere, 25 $^{\circ}$ C, and ultrasonication at 40 kHz and 300 W.
 PTFE, polytetrafluoroethylene; US, ultrasonication; *E. coli*, *Escherichia coli*.

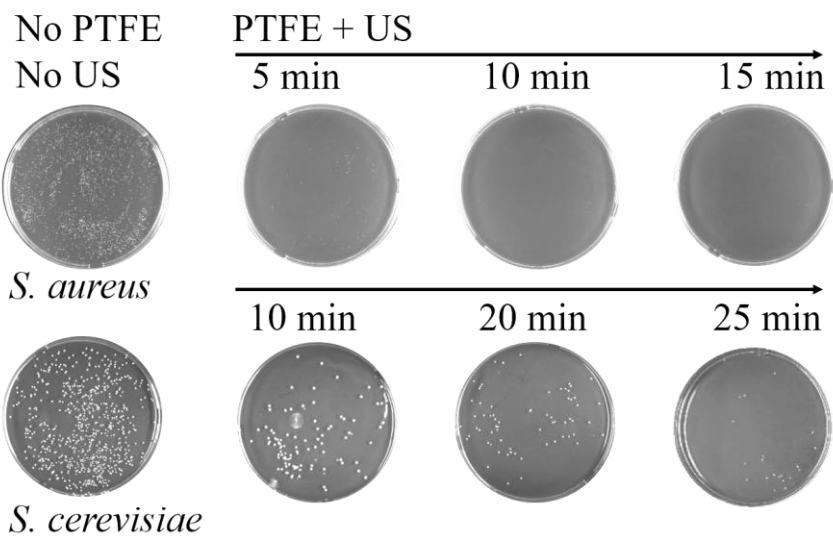


Figure S30. Time-dependent inactivation of *S. aureus* and *S. cerevisiae* under PTFE-assisted ultrasonication. Micrographs of *S. aureus* and *S. cerevisiae* colonies cultured on agar plates after different ultrasonic treatment times in the presence of PTFE particles. Reaction conditions: 50 mL DI water, 50 mg PTFE (25 μ m), air atmosphere, 25 $^{\circ}$ C, and ultrasonication at 40 kHz and 300 W. PTFE, polytetrafluoroethylene; US, ultrasonication; *S. aureus*, *Staphylococcus aureus*; *S. cerevisiae*, *Saccharomyces cerevisiae*.

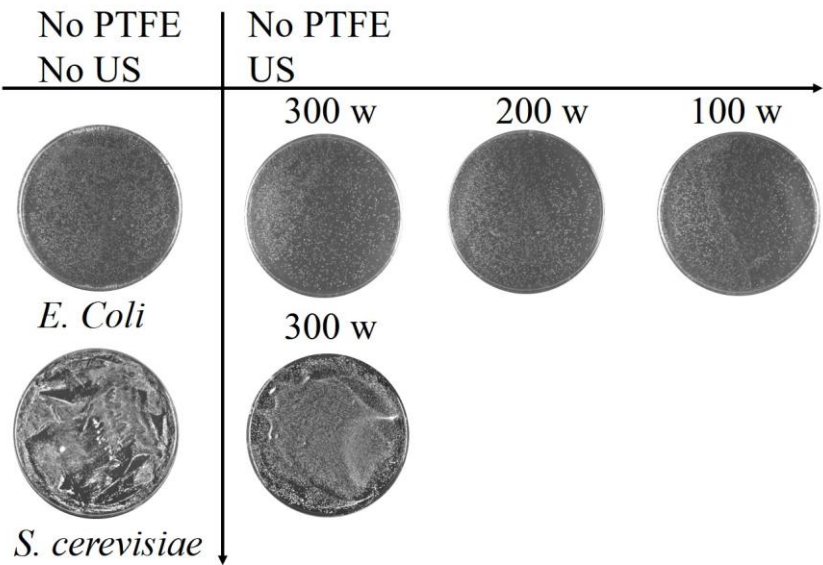


Figure S31. Effects of ultrasonication alone on microbial viability. Micrographs of *E. coli* and *S. cerevisiae* colonies cultured on agar plates before and after 30 min of ultrasonic treatment in the absence of PTFE particles. Reaction conditions: 50 mL DI water, air atmosphere, 25 °C, and ultrasonication at 40 kHz and 300 W. Ultrasonication alone shows no significant bactericidal or fungicidal activity over this short treatment duration. PTFE, polytetrafluoroethylene; US, ultrasonication; *E. coli*, *Escherichia coli*; *S. cerevisiae*, *Saccharomyces cerevisiae*.

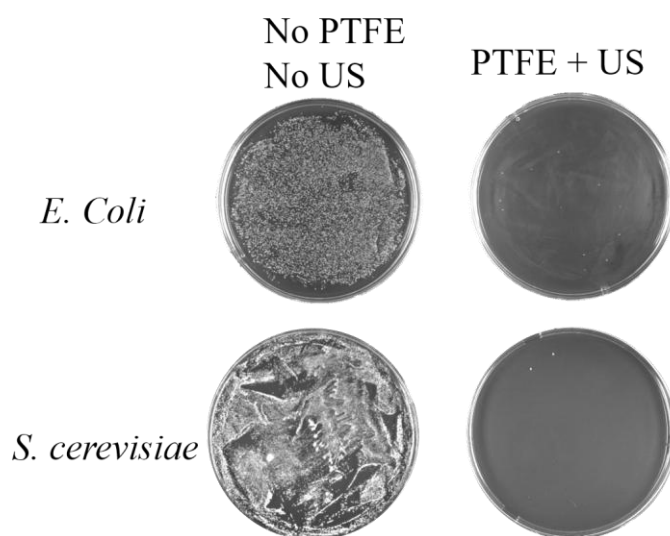


Figure S32. Microbial inactivation under PTFE-assisted ultrasonication. Micrographs of *E. coli* and *S. cerevisiae* colonies cultured on agar plates after 30 min of ultrasonication in the presence of PTFE particles, compared with control samples cultured without ultrasonication or PTFE particles. Reaction conditions: 50 mL DI water, 50 mg PTFE (25 µm), air atmosphere, 25 °C, and ultrasonication at 40 kHz and 300 W. PTFE, polytetrafluoroethylene; US, ultrasonication; *E. coli*, *Escherichia coli*; *S. cerevisiae*, *Saccharomyces cerevisiae*.

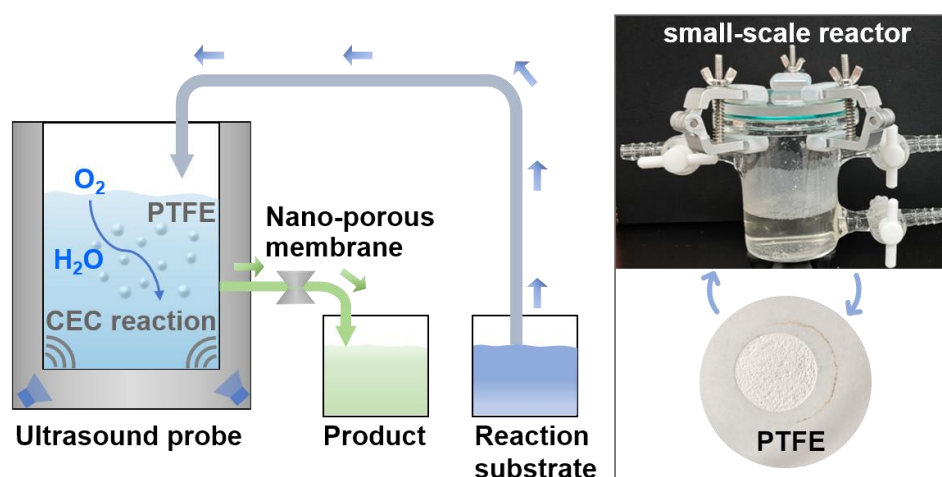


Figure S33. Small-scale recirculating system for PTFE recycling. Schematic illustration of a small-scale recirculating reaction system used to evaluate the recyclability and reusability of PTFE particles. Reaction conditions: 50 mL DI water, 60 mg PTFE (3 μm), 10 mM 4-hydroxybenzoic acid, 2 h reaction time/cycle, air atmosphere, 25 $^{\circ}\text{C}$, and ultrasonication at 40 kHz and 100 W. CEC, contact-electrocatalysis; PTFE, polytetrafluoroethylene.

Cycle	mass of membrane + PTFE (mg)	mass of filter membrane (mg)	PTFE mass (mg)	recycling efficiency (%)
1	228.2	172.9	55.3	92
2	221.2	169.4	51.8	94
3	221.1	171.3	49.8	96
4	220.0	171.4	48.6	98
5	219.3	173.8	45.5	94
6	218.2	175.6	42.6	94

Table S1. Recovery and per-cycle recycling efficiency of PTFE particles in a miniature circulating reaction system at ambient conditions. The initial PTFE amount was 60 mg. The redispersed PTFE mass was determined from the mass difference between the dried PTFE-loaded membrane and the membrane after PTFE redispersion. The per-cycle recycling efficiency was calculated relative to the PTFE mass recovered from the previous cycle, except for cycle 1, which was calculated relative to the initial PTFE mass. Reaction conditions: 50 mL DI water, 60 mg PTFE (3 μm), 1 h reaction time/cycle, air atmosphere, 25 $^{\circ}\text{C}$, and ultrasonication at 40 kHz and 100 W.

Further analysis of the cycling performance shown in Figure 6f indicates that, after six cycles, the recovered PTFE mass decreased from 60.0 mg to 42.6 mg (Table S1), corresponding to a cumulative loss of approximately 29.0%. Nevertheless, the concentrations of 3,4-dihydroxybenzoic acid and hydroquinone remained at approximately 350 μM and 120 μM , respectively, with no evident downward trend. These results suggest that PTFE loss during the first six cycles did not significantly affect the reaction performance. The key question, therefore, is whether the amount of PTFE remaining after the sixth cycle was still sufficient to provide an effective solid-liquid interfacial area and sustain contact electrification activity.

Figure 4f provides further support for this interpretation. Under conditions of 30 mL deionized water containing 5 mM 4-hydroxybenzoic acid, increasing the PTFE loading from 10 to 20 mg enhanced the formation of 3,4-dihydroxybenzoic acid. However, further increasing the PTFE loading to 30 or 40 mg did not improve the yield and instead resulted in a slight decrease. This result indicates that the reaction performance does not increase linearly with PTFE loading, but rather exhibits an optimal loading range. A moderate increase in PTFE loading can enlarge the solid-liquid interfacial contact area, thereby facilitating charge transfer and promoting $\cdot\text{OH}$ generation. In contrast, excessive PTFE loading may lead to the accumulation of interfacial electrostatic fields, which can suppress the contact electrification process.

In the 30 mL system, the optimal PTFE loading was approximately 20 mg, corresponding to 0.67 mg mL^{-1} . Based on the same solid-to-liquid ratio, the corresponding PTFE loading for a 50 mL system would be approximately 33 mg. The 42.6 mg of PTFE recovered after the sixth cycle therefore remained above this optimal loading level. In addition, a control experiment was performed using 42.6 mg of fresh PTFE under otherwise identical conditions to those used in the cycling experiments. As shown in Figure S34, the concentrations of 3,4-dihydroxybenzoic acid and hydroquinone were 374.73 μM and 133.36 μM , respectively, both of which fall within the ranges observed over the six recycling cycles. These results further demonstrate that a PTFE loading of 42.6 mg is sufficient to maintain the reaction performance without a significant decrease. It should be noted, however, that continued PTFE loss over

extended cycling may eventually reduce the PTFE loading below the effective range, at which point a decline in reaction performance could be expected. Therefore, further optimization of reactor configuration and particle recovery strategies will be necessary to minimize PTFE loss and improve the long-term cycling stability of the system.

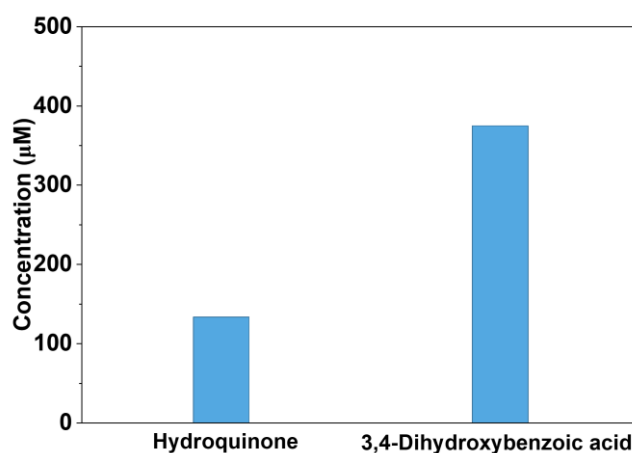


Figure S34. Experimental validation experiment using a small-scale recirculating system. Concentrations of hydroquinone and 3,4-dihydroxybenzoic acid obtained under the same reaction conditions as the recycling experiment, using 42.6 mg of fresh PTFE. The data are from a single measurement (n=1).



Figure S35. Experimental setup for aromatic hydroxylation. The experimental setup

used for aromatic hydroxylation reactions. 20 mg of PTFE particles were added to 30 mL of a 5 mM aromatic substrate solution.

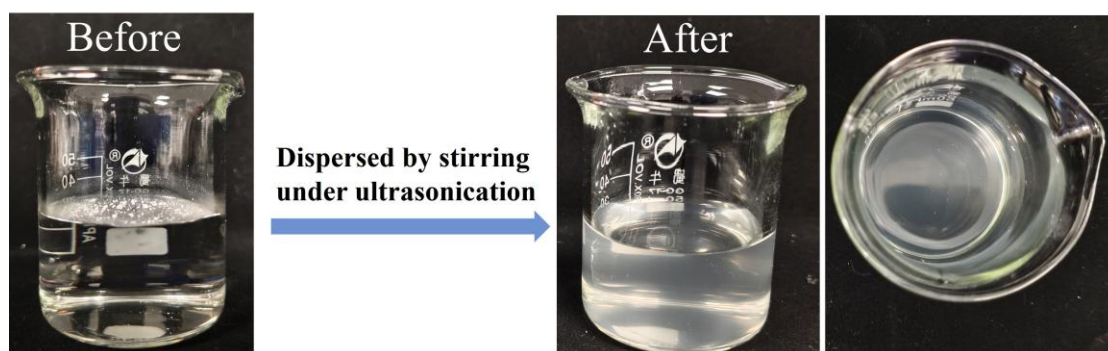


Figure S36. Dispersion of PTFE particles in water by ultrasonication. Initial state of 20 mg PTFE particles in 30 mL DI water and the resulting suspension after dispersion. Reaction conditions: air atmosphere, 25 °C, and ultrasonication at 40 kHz and 100 W.

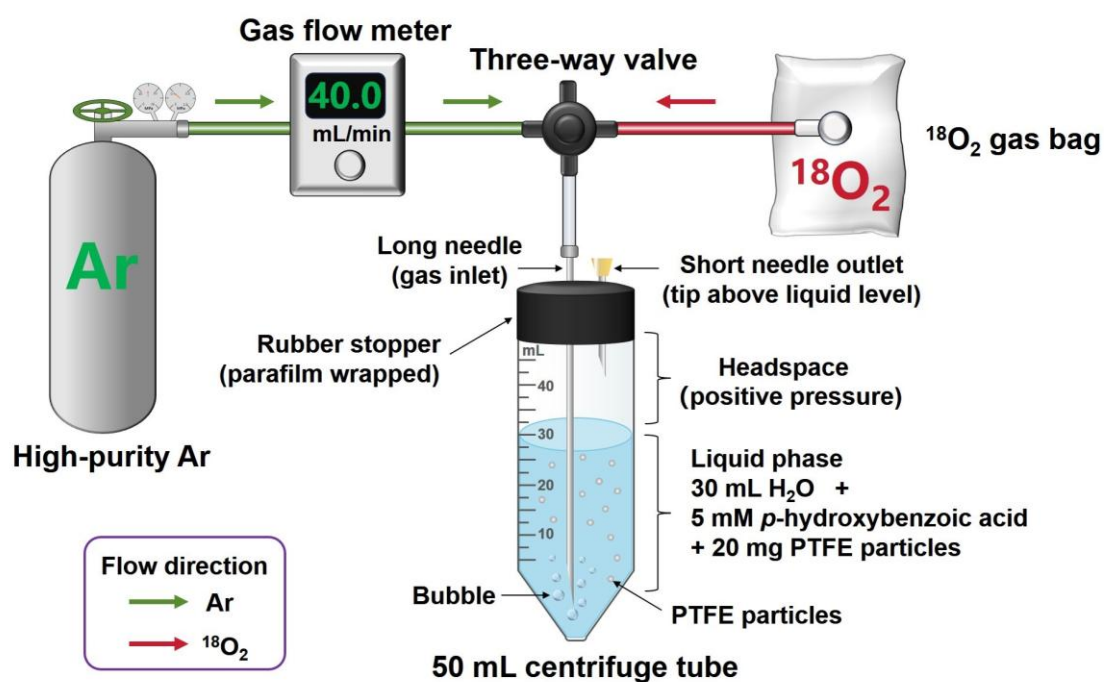


Figure S37. Experimental setup for $^{18}\text{O}_2$ atmosphere control. Experimental setup for replacing the reaction atmosphere with $^{18}\text{O}_2$. Ar, argon; PTFE, polytetrafluoroethylene.



Figure S38. Experimental setup for microbial inactivation. The experimental setup used for microbial inactivation. 50 mg of PTFE particles with a particle size of 25 μm were added to 50 mL of DI water in a 150 mL beaker, followed by ultrasonication to obtain a dispersed suspension.

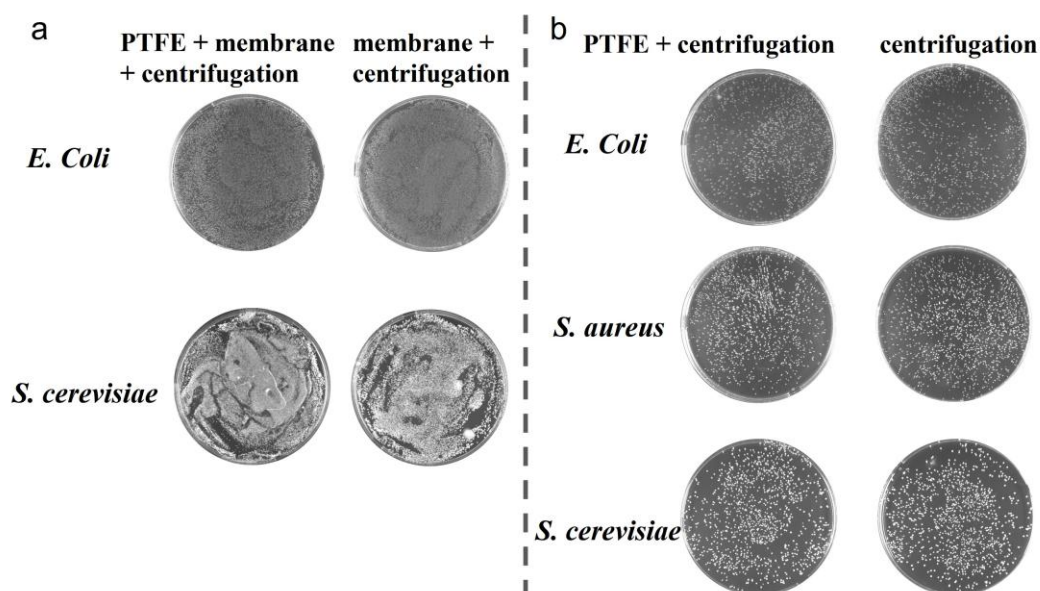


Figure S39. Control experiments for the effects of PTFE on microbial filtration and centrifugation. Control experiments without ultrasonication. (a) Effect of PTFE particles on microbial filtration, with corresponding microscopy images of *E. coli* and *S. cerevisiae* after cultivation on agar plates. (b) Effect of PTFE particles on microbial centrifugation, with corresponding microscopy images of *E. coli*, *S. aureus*, and *S. cerevisiae* after cultivation on agar plates. Reaction conditions: 50 mL DI water, 50 mg PTFE (25 μm), air atmosphere, 25 $^{\circ}\text{C}$. PTFE, polytetrafluoroethylene; *E. coli*, *Escherichia coli*; *S. aureus*, *Staphylococcus aureus*; *S. cerevisiae*, *Saccharomyces cerevisiae*.

Figure S39a represents control experiments designed to evaluate whether PTFE particles affect the filtration of *E. coli* and yeast. Experiments were performed following the same standing, 10 μm membrane filtration, centrifugation, and cultivation procedures as those used for the PTFE-ultrasonication-treated group in Figure S32. Compared with the PTFE-free groups, the presence of PTFE particles caused only a slight decrease in the colony numbers of *E. coli* and yeast. This indicates that PTFE particles and filtration may induce minor cell loss, but cannot account for the significant microbial inactivation observed after PTFE-ultrasonication treatment. Figure S39b represents control experiments designed to evaluate whether PTFE particles affect microbial centrifugation. Experiments were performed following the same standing, sampling, centrifugation, and cultivation procedures as those used for the PTFE-ultrasonication-treated group in Figures 6e and S29-S30. Results showed that the PTFE-containing and PTFE-free groups exhibited no appreciable difference in microbial colony counts, suggesting that neither the PTFE particles nor the centrifugation step significantly affected microbial cell viability or interfered with the results presented in Figures 6e and S29-S30. Thus, the substantial decrease in microbial abundance was mainly attributable to PTFE-assisted ultrasonication.

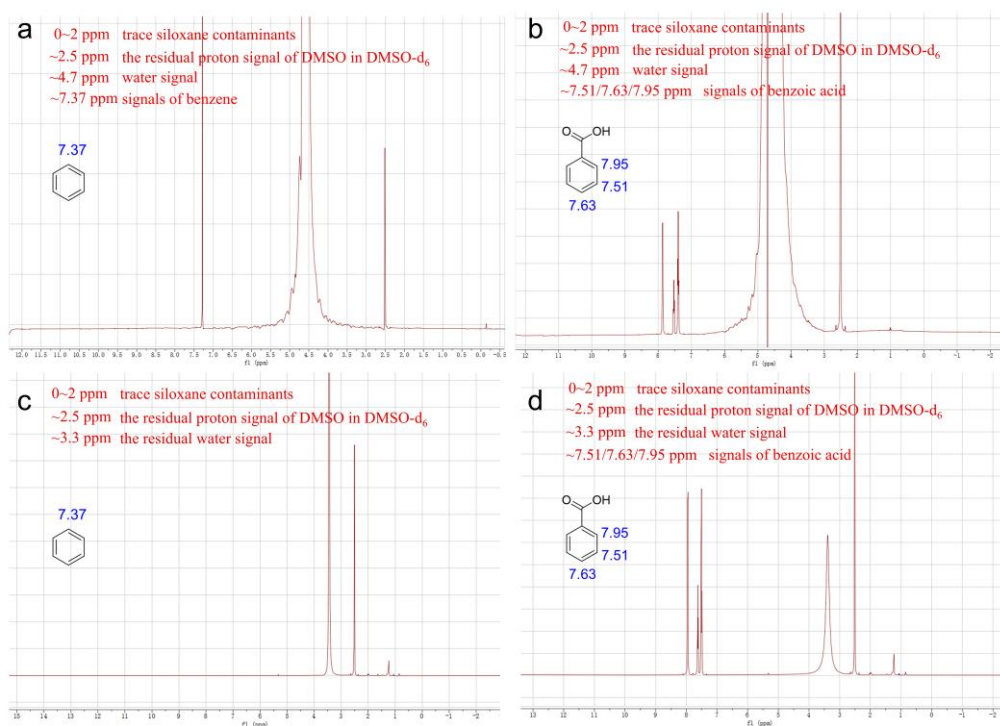


Figure S40. NMR spectra of pre-reaction benzene and benzoic acid controls. ^1H NMR spectra (500 MHz) of (a) benzene and (b) benzoic acid before reaction. ^1H NMR spectra (500 MHz) of post-treated before-reaction control samples containing (c) benzene or (d) benzoic acid and PTFE. The control samples in (c-d) were subjected to the same sample-handling procedure as the after-reaction samples. Control conditions: 30 mL DI water, 5 mM aromatic substrate, 20 mg PTFE (3 μm), without ultrasonication.

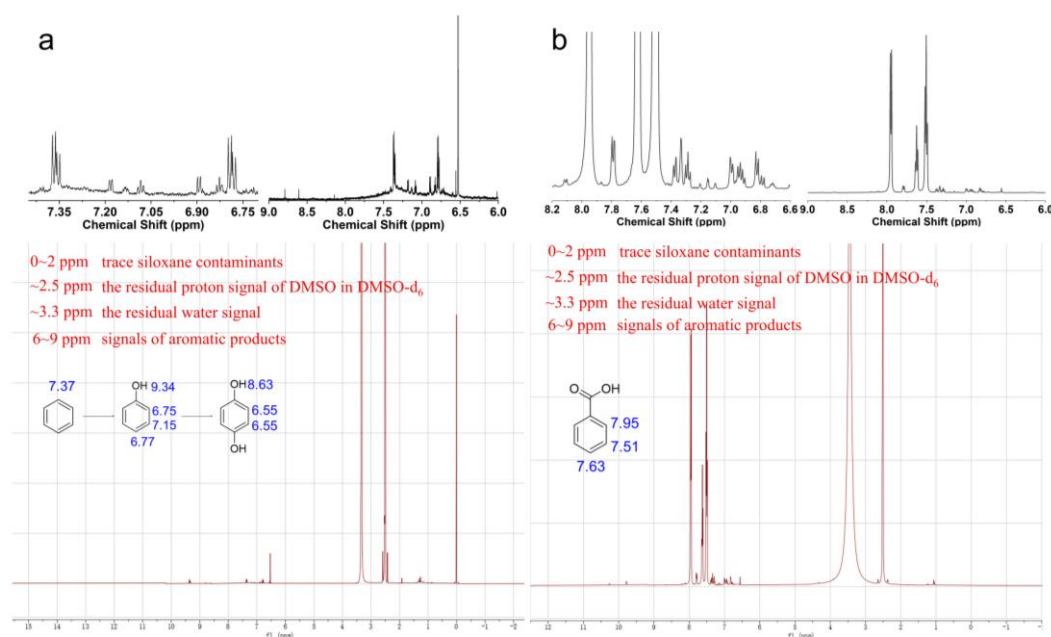


Figure S41. NMR spectra of benzene and benzoic acid reaction mixtures after hydroxylation. (a) ^1H NMR spectrum (850 MHz) of the benzene reaction mixture and (b) ^1H NMR (500 MHz) of the benzoic acid reaction mixture after hydroxylation, including the full spectra and corresponding expanded regions. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 5 mM benzene or benzoic acid, 2 h reaction time, air atmosphere, 25 $^{\circ}\text{C}$, and ultrasonication at 40 kHz and 200 W. The post-reaction sample was filtered and subjected to solvent evaporation prior to ^1H NMR analysis.

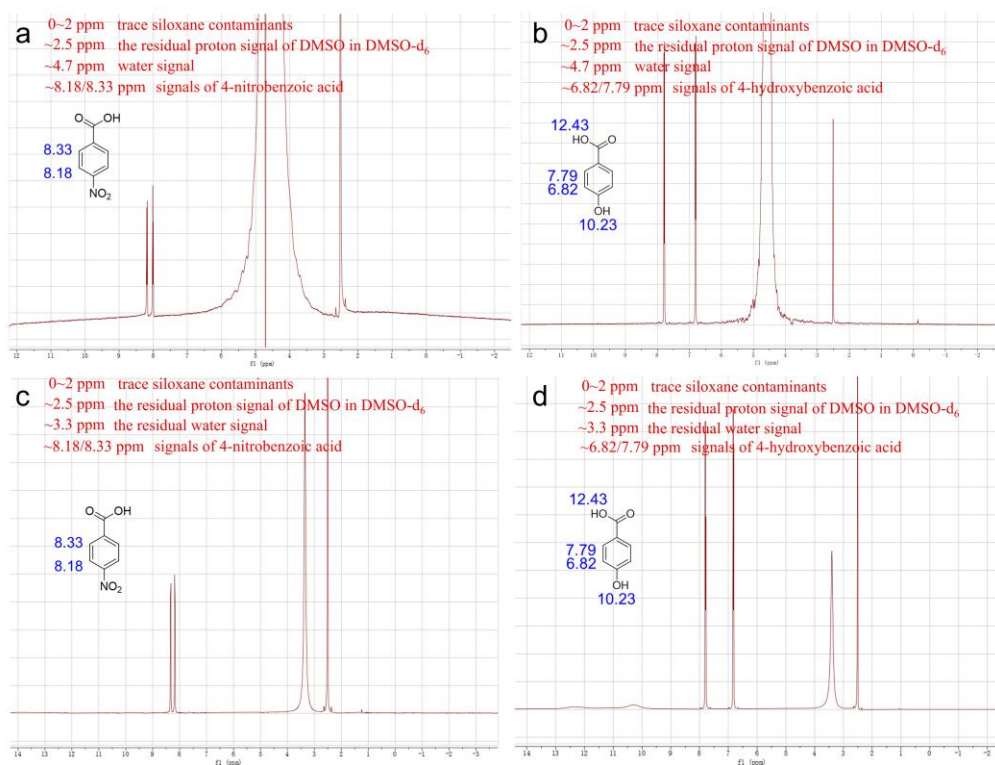


Figure S42. NMR spectra of pre-reaction 4-nitrobenzoic acid and 4-hydroxybenzoic acid controls. ^1H NMR spectra (500 MHz) of (a) 4-nitrobenzoic acid and (b) 4-hydroxybenzoic acid before reaction. ^1H NMR spectra (500 MHz) of post-treated before-reaction control samples containing (c) 4-nitrobenzoic acid or (d) 4-hydroxybenzoic acid and PTFE. The control samples in (c-d) were subjected to the same sample-handling procedure as the after-reaction samples. Control conditions: 30 mL DI water, 5 mM aromatic substrate, 20 mg PTFE (3 μm), without ultrasonication.

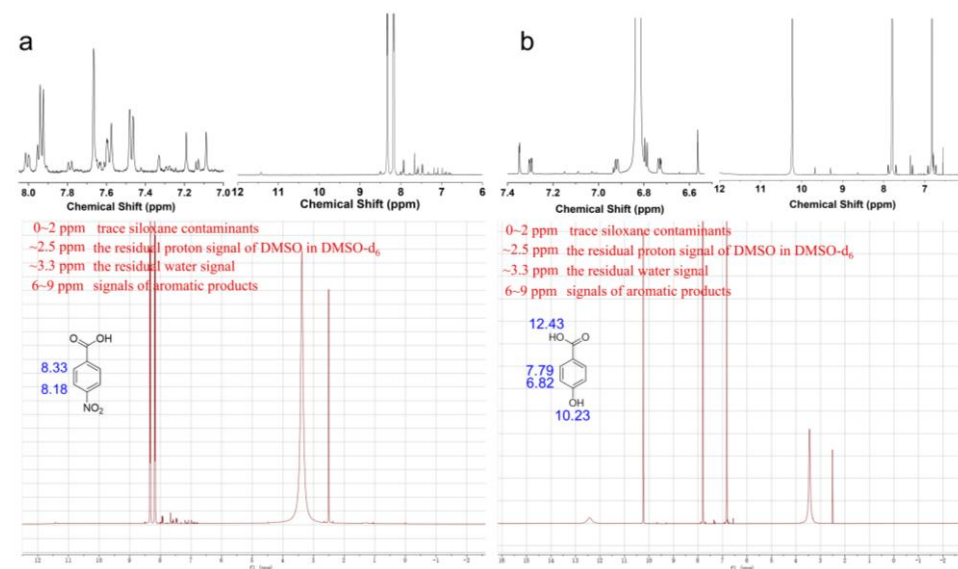


Figure S43. NMR spectra of 4-nitrobenzoic acid and 4-hydroxybenzoic acid reaction mixtures after hydroxylation. ^1H NMR spectra (850 MHz) of the reaction mixtures after hydroxylation of (a) 4-nitrobenzoic acid and (b) 4-hydroxybenzoic acid, including the full spectra and corresponding expanded regions. Reaction conditions: 30 mL DI water, 20 mg PTFE (3 μm), 5 mM 4-nitrobenzoic acid or 4-hydroxybenzoic acid, 2 h reaction time, air atmosphere, 25 $^\circ\text{C}$, and ultrasonication at 40 kHz and 200 W. The post-reaction sample was filtered and subjected to solvent evaporation prior to ^1H NMR analysis.

In Figures S40-S43, the original pre-reaction spectra were directly recorded from the as-prepared aqueous substrate solutions (Figures S40a-b and S42a-b). In contrast, the post-reaction spectra were obtained after solid-liquid separation, solvent evaporation, and drying of the reaction mixtures, followed by redissolution of the residues in DMSO-d_6 for ^1H NMR analysis (Figures S41a-b and S43a-b). To further improve the comparability between the pre- and post-reaction samples for qualitative analysis, additional pre-reaction control samples of the four aromatic substrates were subjected to the same post-treatment and ^1H NMR analysis procedures as those used for the post-reaction samples. The corresponding results are shown in Figures S40c-d and S42c-d. Therefore, these spectra were primarily used for peak assignment, identification of post-reaction components, and structural confirmation of the products, rather than for rigorous quantitative comparison.