Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting Information

**Degradation of three β-O-4 lignin model compounds via organic electrolysis and elucidation of the degradation mechanisms**

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# I General Information

Unless otherwise stated, Cyclic voltammetry was recorded on a ALS/CH Instruments Electrochemical Analyzer Model 600A. Calculations were carried out using the Gaussian 16 program package. The structures of closed shell species were optimized at the restricted B3LYP/6-31G(d) level, while the structures of open shell species such as **1a**$^{\bullet+}$, **2a**$^{\bullet+}$, and **3a**$^{\bullet+}$ were optimized using the unrestricted theory at the same level. Frequency analysis was performed for each optimized structure to confirm that no imaginary frequency was obtained for the energy-minimum structures. These calculations were performed in MeOH solution using the polarizable continuum model (PCM).

# II. Spectral Data

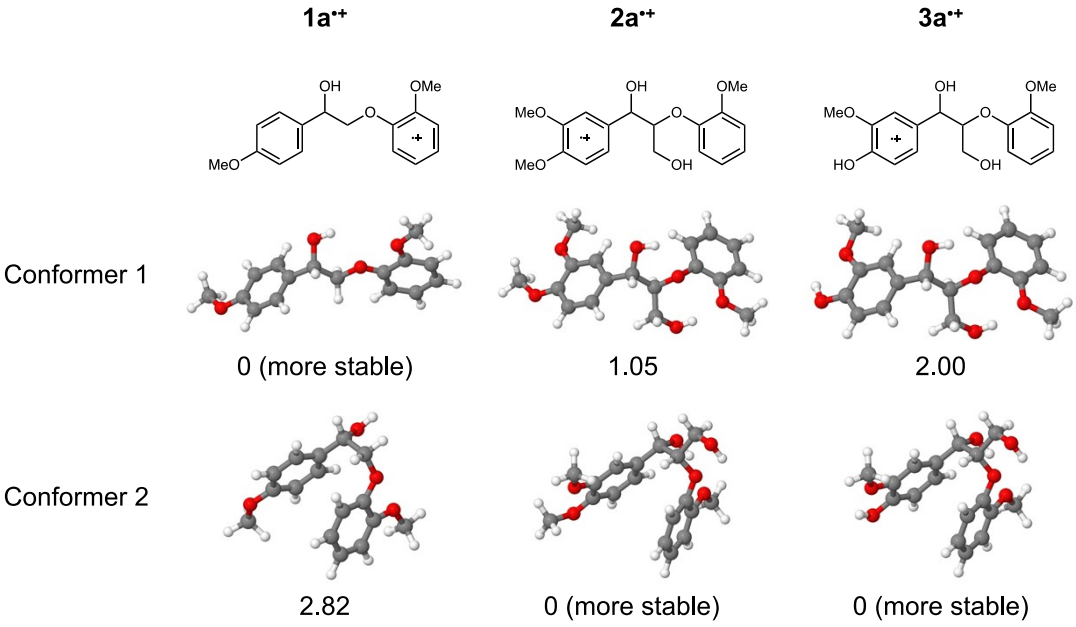



Figure S1. Optimized structures and relative free energies at 298 K between conformers ($\Delta G_{298}$ / kcal mol$^{-1}$) of the radical cations calculated at B3LYP/6-31G(d) level with PCM solvation model (in MeOH).

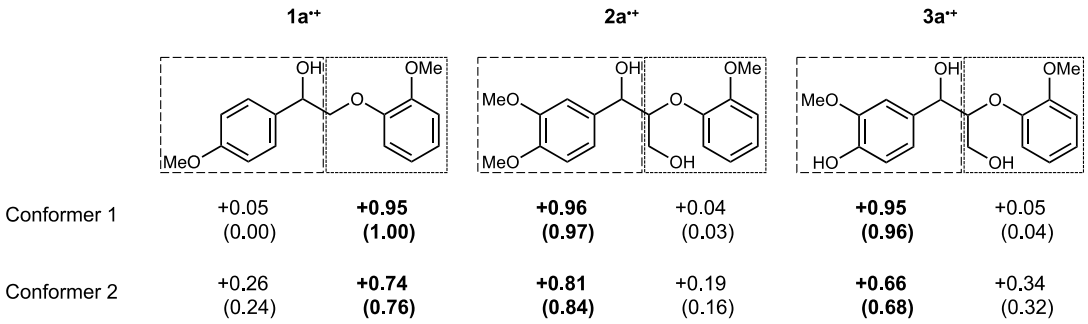
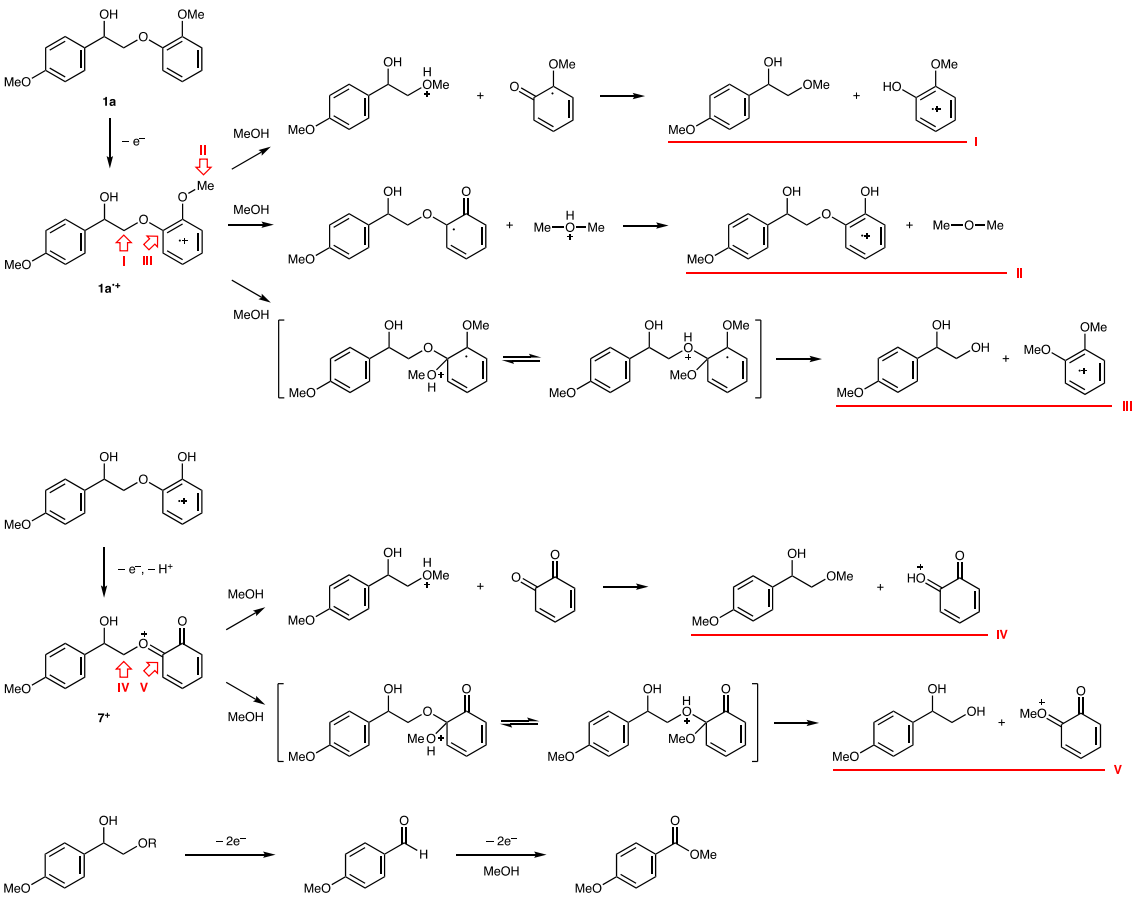



Figure S2. Charge and spin distribution by natural population analysis in the radical cations calculated at B3LYP/6-31G(d) level with PCM solvation model (in MeOH). The values indicate the sum of atomic charges or spins in each part of the radical cations. Spin values are presented in parentheses.




Scheme S1. The possible pathways of the decomposition from **1a**$^{\bullet+}$

Table S1. Free energy changes at 298 K ($\Delta G_{298}$ / kcal mol$^{-1}$) to the products **I** – **V** indicated in Scheme S1 [a]

| Reaction | $\Delta G_{298}$ / kcal mol$^{-1}$ |
|---|---|
| **1a**$^{\bullet+}$ + MeOH → **I** | –4.42 |
| **1a**$^{\bullet+}$ + MeOH → **II** | –1.03 |
| **1a**$^{\bullet+}$ + MeOH → **III** | +2.03 |
| **7**$^{+}$ + MeOH → **IV** | –3.52 |
| **7**$^{+}$ + MeOH → **V** | +1.37 |

[a] Calculated at B3LYP/6-31G(d) level with PCM solvation model (in MeOH).

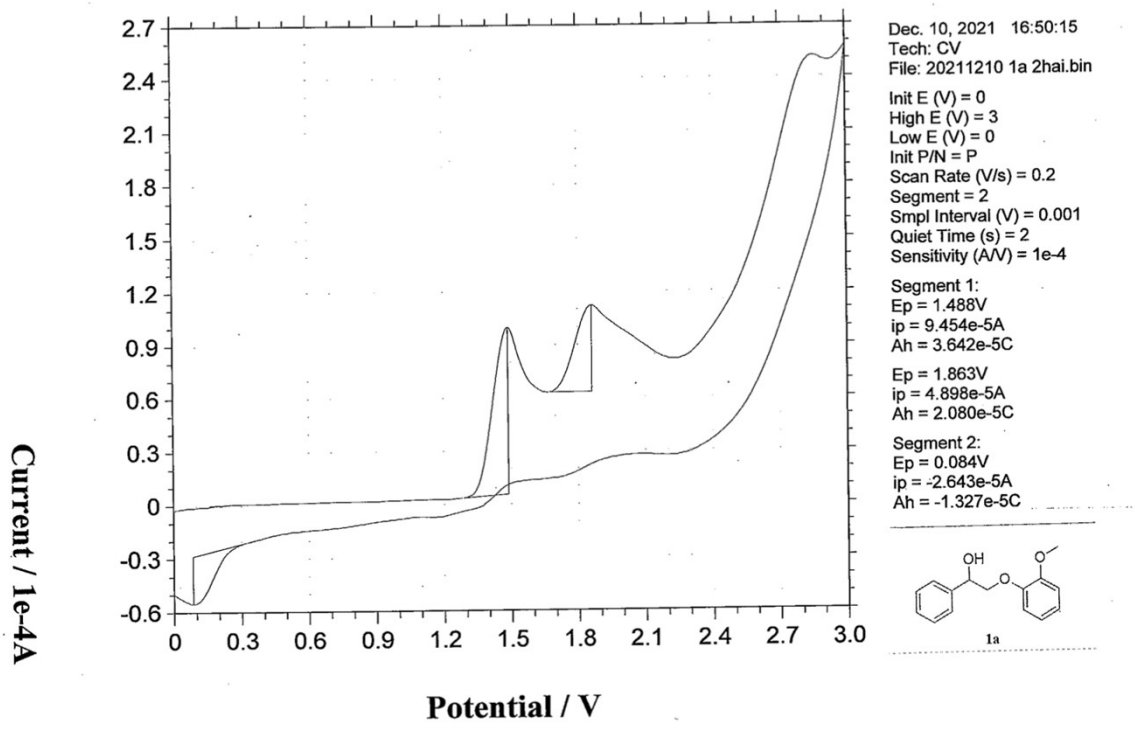



Figure S3 Cyclic voltammograms of a reference sample #**1a**.

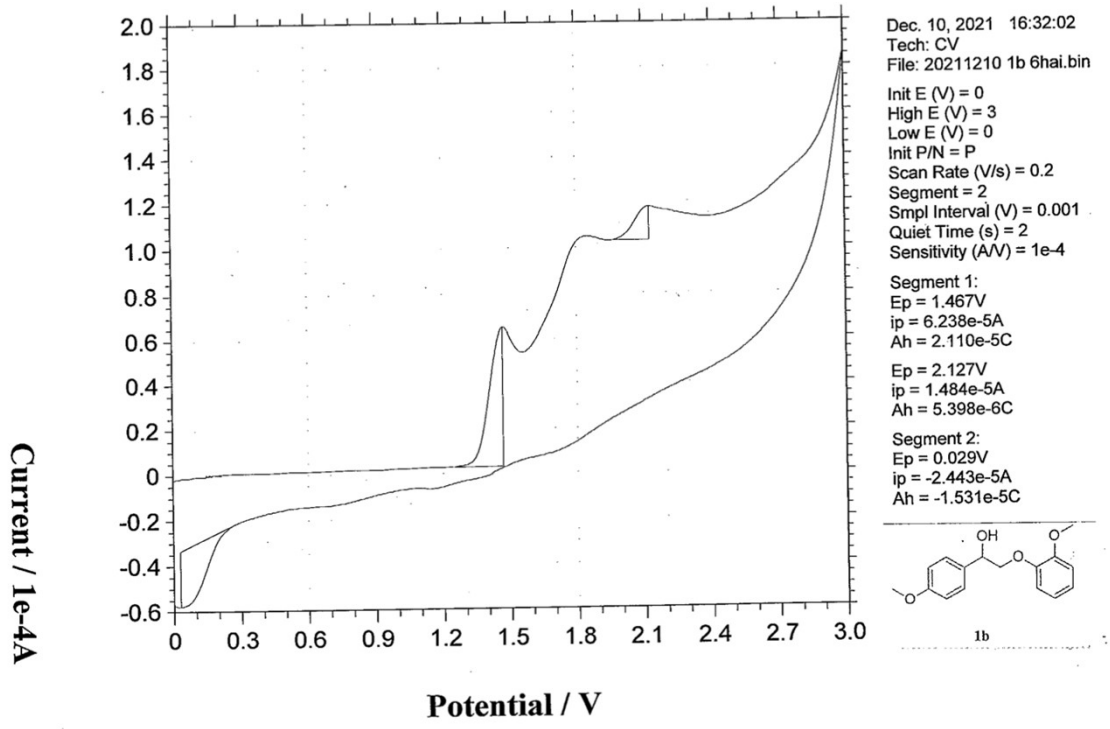



Figure S4 Cyclic voltammograms of a reference sample #**1b**

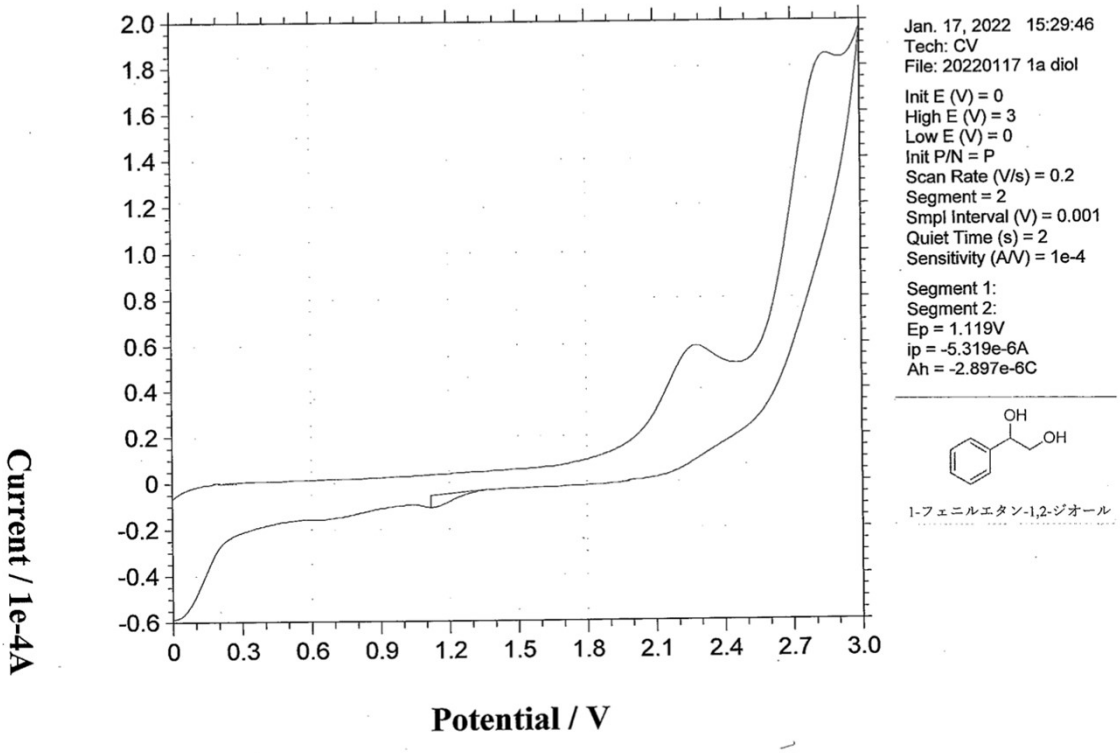



Figure S5 Cyclic voltammograms of 1-phenylethane-1,2-diol as reference sample

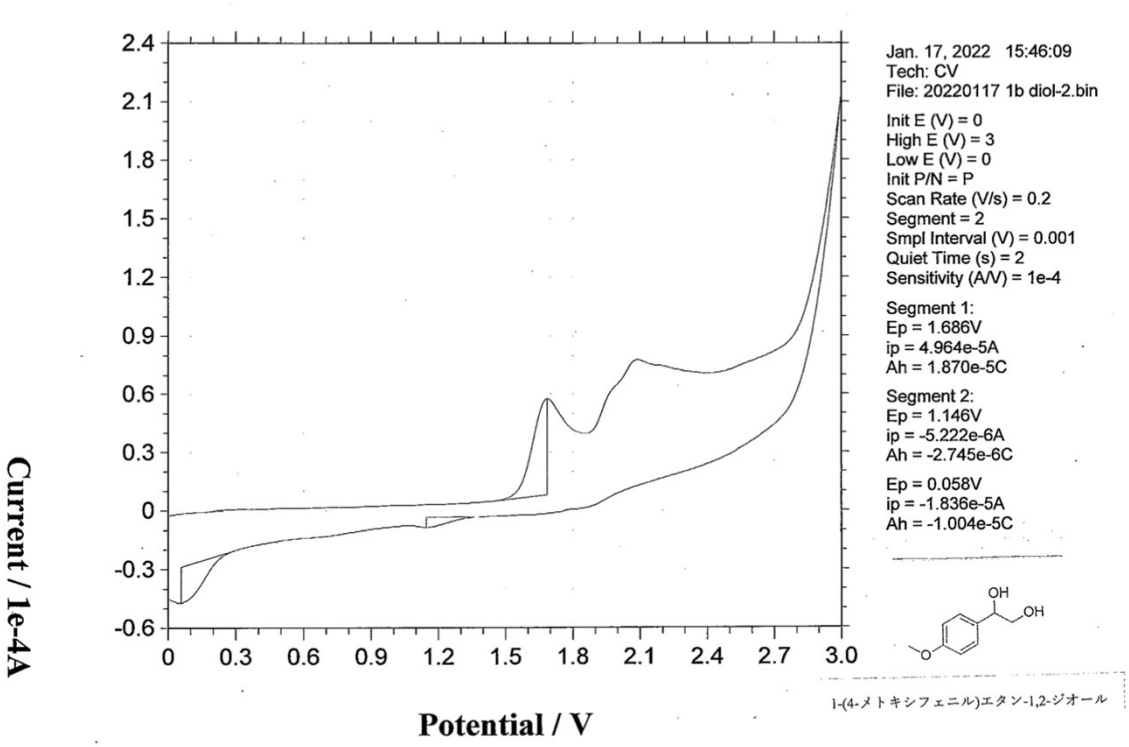



Figure S6 Cyclic voltammograms of 1-(4-methoxyphenyl)ethane-1,2-diol as reference sample

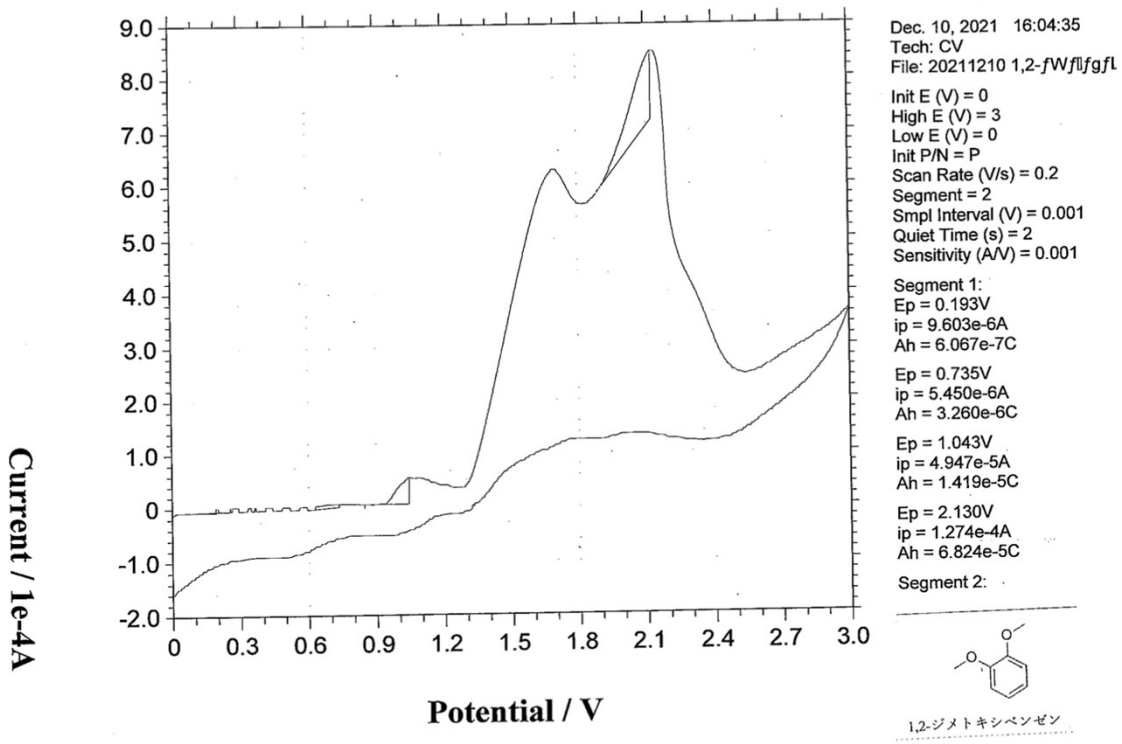



Figure S7 Cyclic voltammograms of 1,2-dimethoxybenzene as reference sample

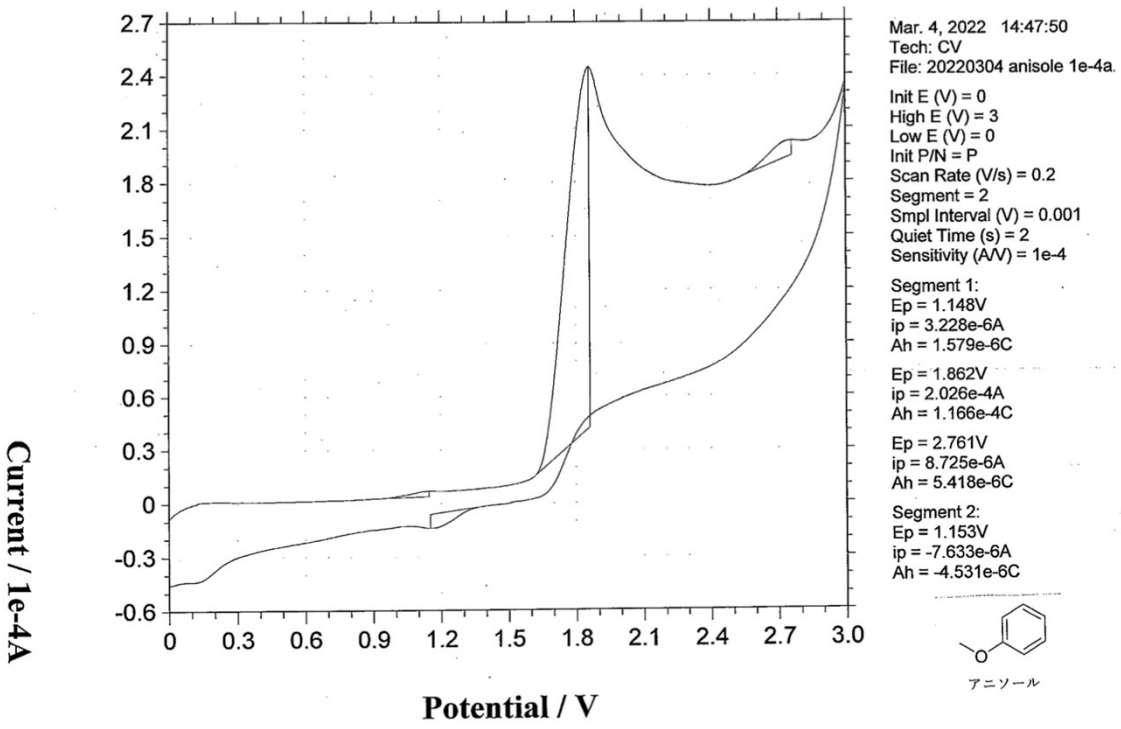



Figure S8 Cyclic voltammograms of anisole as reference sample

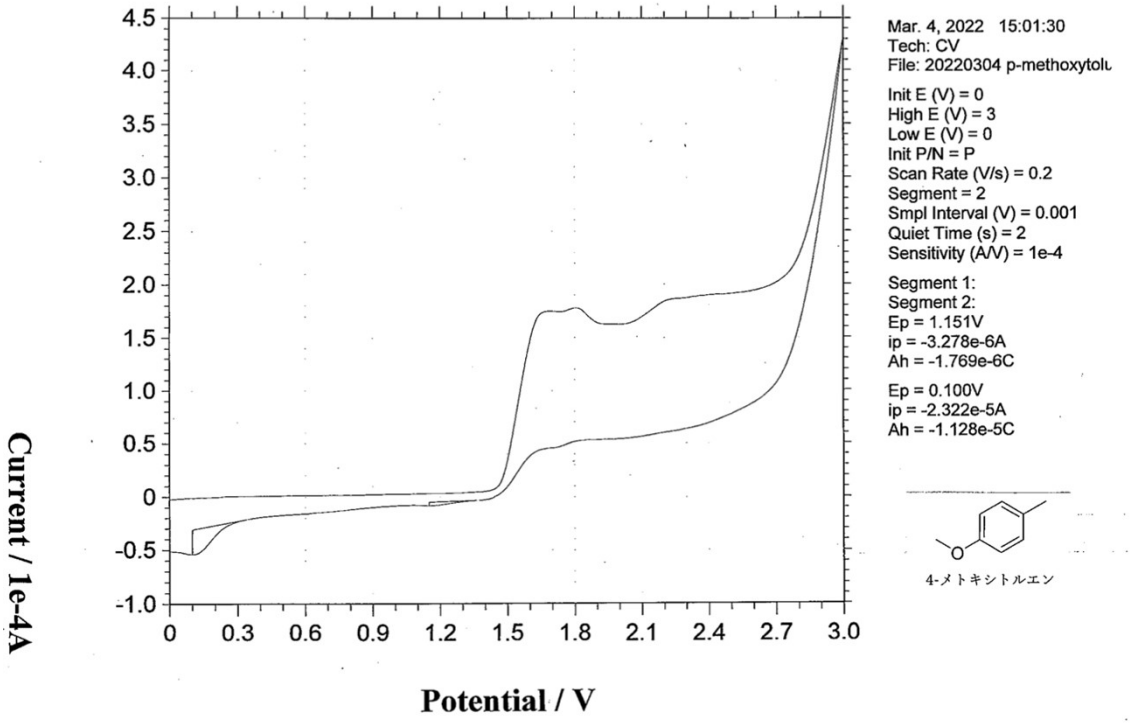



Figure S9 Cyclic voltammograms of 4-methoxytoluene as reference sample