Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Thio-assisted reductive electrolytic cleavage of lignin β-O-4 models and authentic lignin

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General Condition of Thio-assisted Cathodic Electrolysis of 2-phenoxyacetophenone

Reactions were conducted at room temperature up to 2.5 h in an H-type electrochemical cell (separated by a Nafion 117 membrane) wherein a platinum wire in 20 mL of pH 8 phosphate buffer was placed in the anode half-cell and the reticulated vitreous carbon (RVC) cathode had 2 cm^2 immersed in the catholyte, consisting of 50 mM $LiBF_4$ in 20 mL of DMF. Current (5 mA) was then applied for the duration of the experiment.

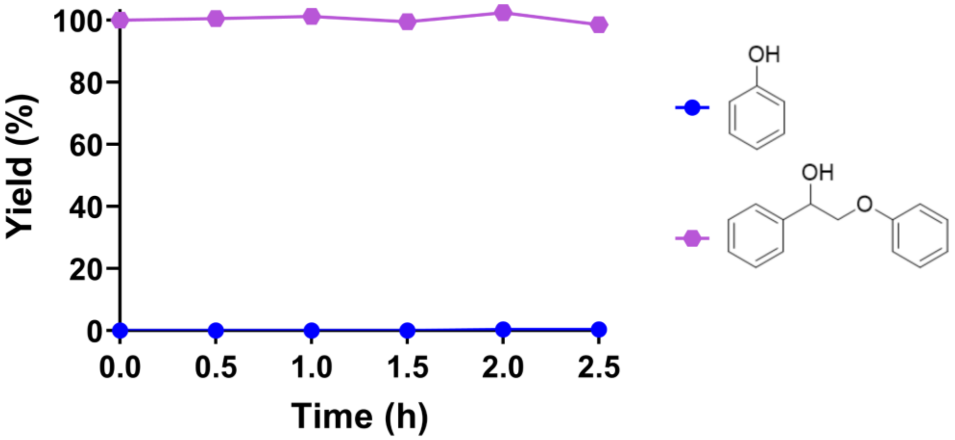


Figure S1. Electrolysis of 2-phenoxy-1-phenylethanol (parent alcohol analog of 2-phenoxyacetophenone) only (no thiol or disulfide). Procedure: 2-phenoxy-1-phenylethanol (4.7 mM) was added to the catholyte at t = 0 and current (5 mA) and stirring were applied for the duration of the experiment.

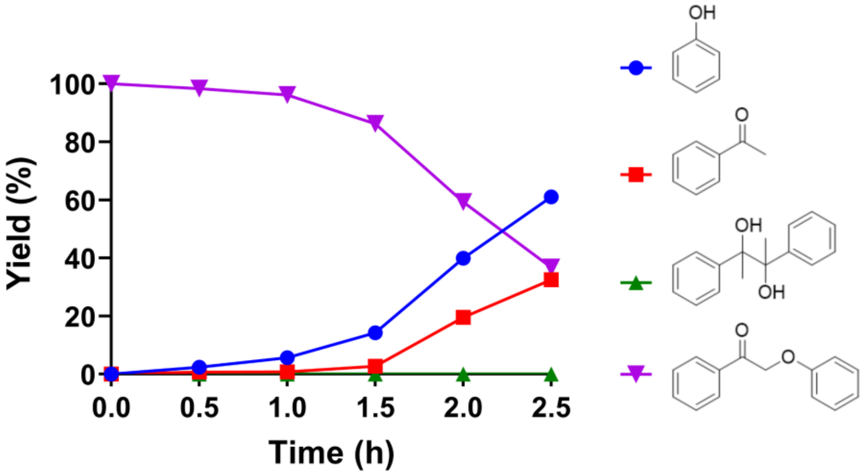


Figure S2. Cleavage of 2-phenoxyacetophenone electrolysis in the presence of cystine . Procedure: cystine (4.7 mM) and 2-phenoxyacetophenone (4.7 mM) were added to the catholyte at t = 0. Current (5 mA) and stirring were then applied for the duration of the experiment.

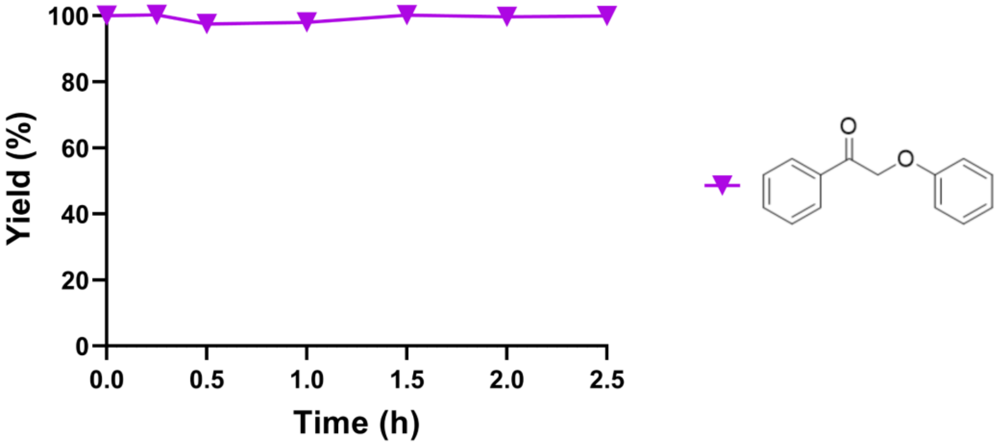


Figure S3. Simple (no electrolysis) treatment of 2-phenoxyacetophenone (4.7 mM) with β-mercaptoethanol (9.4 mM), $LiBF_4$ (4.7 mM) and K_2CO_3 (2 eq) in DMF (20 mL) at room temperature. No phenol product was detected at any time.

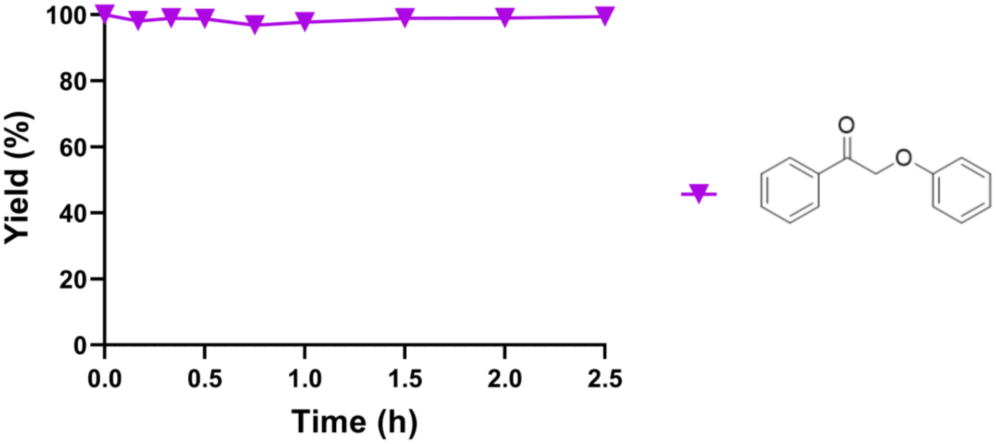


Figure S4. Simple (no electrolysis) treatment of 2-phenoxyacetophenone (4.7 mM) with β-mercaptoethanol (9.4 mM) and Et_3N (9.4 mM) in DMF (20 mL) at room temperature. No phenol product was detected at any time.

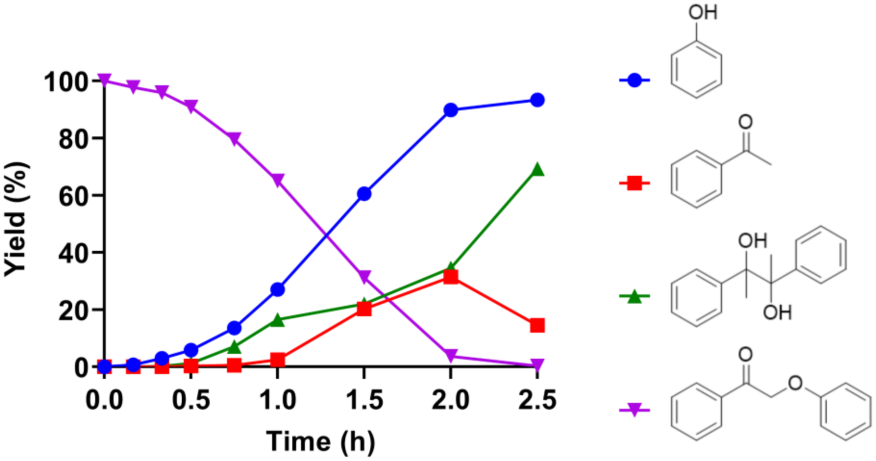


Figure S5. Cleavage of 2-phenoxyacetophenone with 2,2'-dithiodiethanol, pre-electrolyzed for 30 min. Procedure: 2,2'-dithiodiethanol (4.7 mM) was pre-electrolyzed at 5 mA in the stirring catholyte for 30 min; 2-phenoxyacetophenone (4.7 mM) was then added at t = 0. The 5 mA current and stirring were maintained throughout the entire reaction.

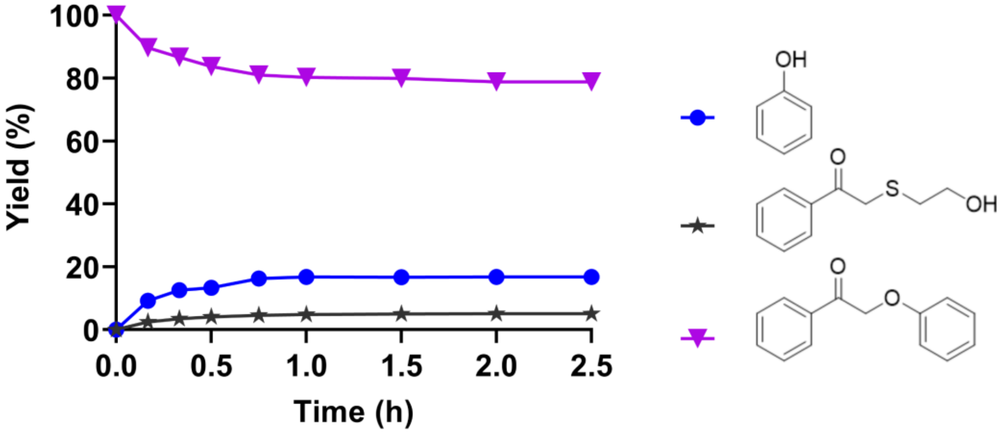


Figure S6. Cleavage of 2-phenoxyacetophenone/BHT mixture with 2,2’-dithiodiethanol, pre-electrolyzed for 1 h. Procedure: 2,2’-dithiodiethanol (4.7 mM) was pre-electrolyzed in the stirring catholyte at 5 mA for 1 h; the current was then turned off, and BHT (4.7 mM) and 2-phenoxyacetophenone (4.7 mM) were added to the stirred solution at t = 0. Stirring, but no current, was continued for the duration of the experiment.

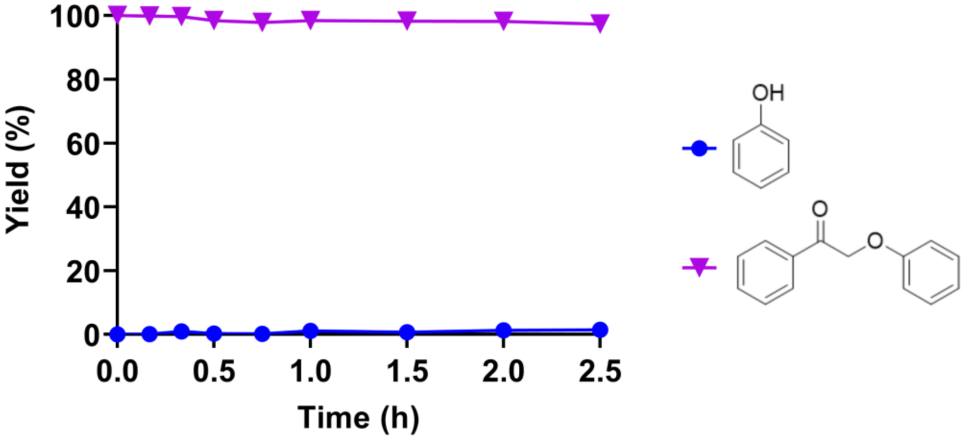


Figure S7. Reaction of 2-phenoxyacetophenone with 2,2’-dithiodiethanol, pre-electrolyzed for 1 h, modified by BHT addition and a waiting period. Procedure: 2,2’-dithiodiethanol (4.7 mM) was pre-electrolyzed at 5 mA with stirring in the catholyte for 1 h; the current was then turned off, BHT (4.7 mM) was added, and the mixture was stirred for 30 min; 2-phenoxyacetophenone (4.7 mM), was then added, defining t = 0. Stirring, but no current, was continued for the duration of the experiment.

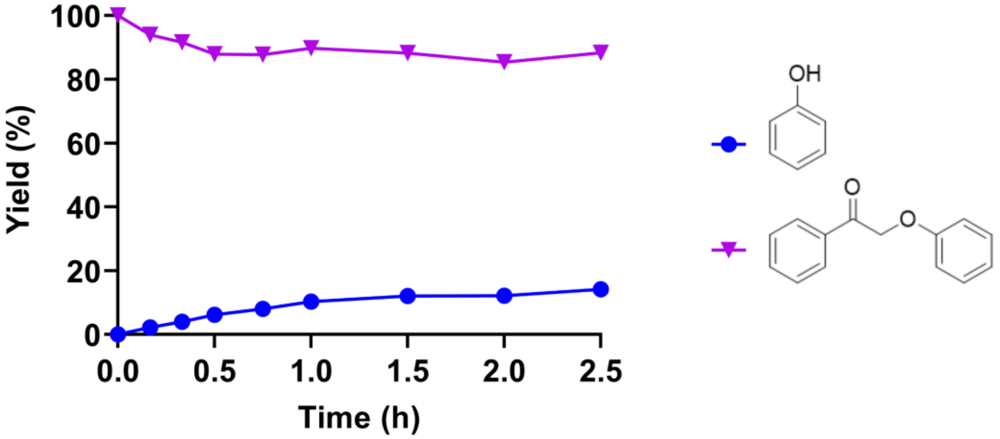


Figure S8. Reaction of 2-phenoxyacetophenone with 2,2’-dithiodiethanol, pre-electrolyzed for 1 h without addition of BHT. Procedure: 2,2’-dithiodiethanol (4.7 mM) was pre-electrolyzed at 5 mA with stirring in the catholyte for 1 h; stirring was continued with the current off for 30 min; 2-phenoxyacetophenone (4.7 mM) was then added at t = 0. Stirring, but no current, was continued for the duration of the experiment.

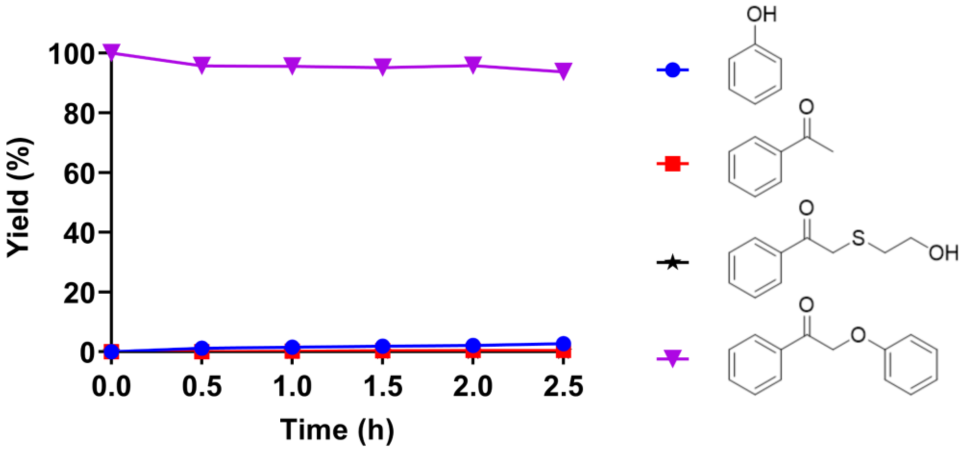


Figure S9. Reaction of 2-phenoxyacetophenone (4.7 mM) with β-mercaptoethanol (9.4 mM) with AIBN (azobisisobutyronitrile, 0.7 mM) in DMF (20 mL) at 100 ºC without any electric current. Only trace amounts of the three products were detectable.

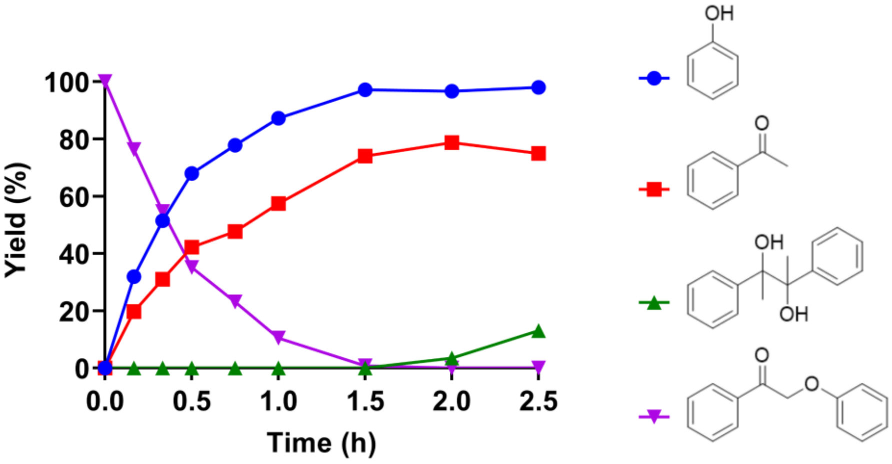


Figure S10. Cleavage of a 2-phenoxyacetophenone/BHT mixture with 2,2’-dithiodiethanol, pre-electrolyzed for 30 min. Procedure: 2,2’-dithiodiethanol (4.7 mM) was pre-electrolyzed at 5 mA in the stirring catholyte for 30 min; BHT (9.4 mM) and 2-phenoxyacetophenone (4.7 mM) were then added together at t = 0, and current and stirring were continued for the duration of the reaction.

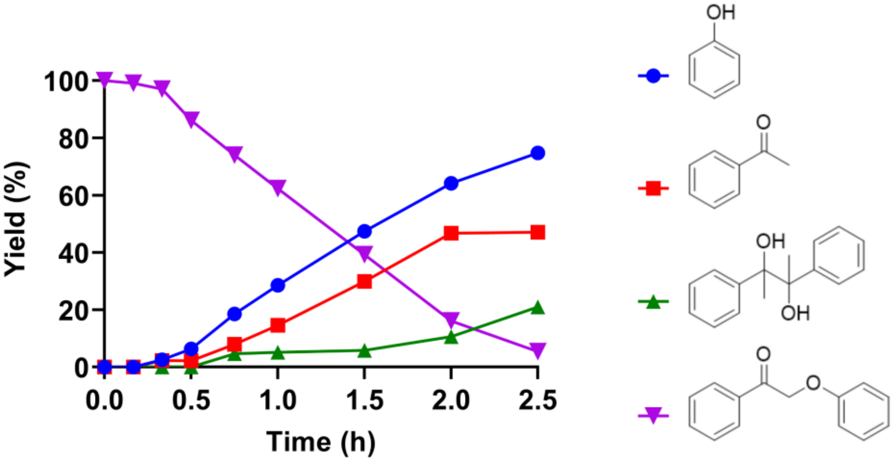


Figure S11. Cleavage of 2-phenoxyacetophenone by electrolysis of 2,2’-dithiodiethanol (4.7 mM) and BHT (4.7 mM) with 5 mA current. Procedure: 2,2’-dithiodiethanol (4.7 mM), BHT (4.7 mM) and 2-phenoxyacetophenone (4.7 mM) were solubilized with stirring in the catholyte. At t=0, current was applied and continued with stirring for the duration of the reaction.

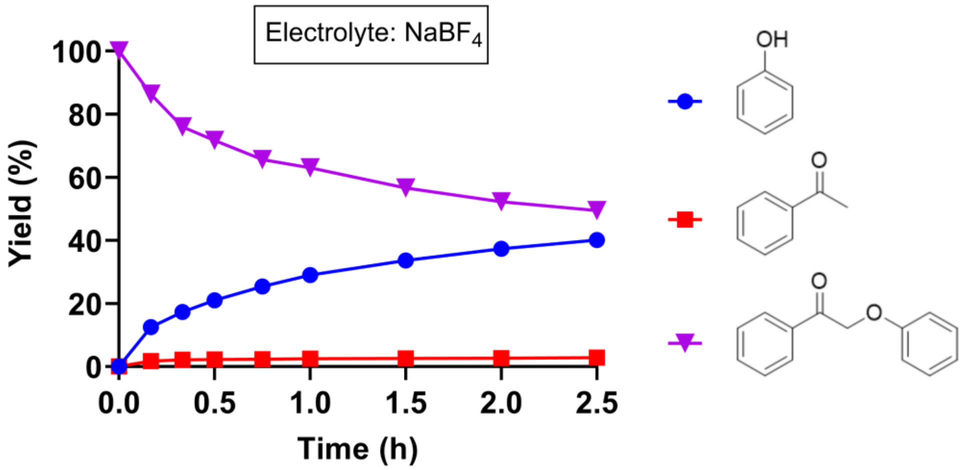


Figure S12. Cleavage of 2-phenoxyacetophenone with 2,2'-dithiodiethanol, pre-electrolyzed for 1 h, and using NaBF$_4$ as electrolyte. Procedure: 2,2'-dithiodiethanol (4.7 mM) was pre-electrolyzed at 5 mA for 1 h in a stirred catholyte (20 mL) in which NaBF$_4$ (50 mM) was employed instead of LiBF$_4$; 2-phenoxyacetophenone (4.7 mM) was then added at t = 0 and current and stirring were continued for the duration of the reaction. Though only traces of acetophenone were seen, no pinacol product was observed.

Various controls of thio-assisted electrolysis of dimer 1a-c

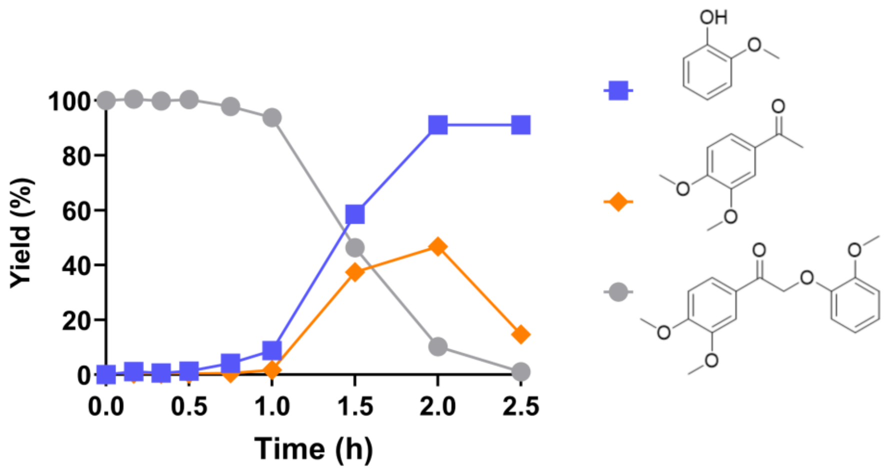


Figure S13. Cleavage of dimer **1a** with current alone. Procedure: dimer **1a** (3.3 mM) was added to the catholyte at t = 0, and current (5 mA) and stirring were continued for the duration of the reaction.

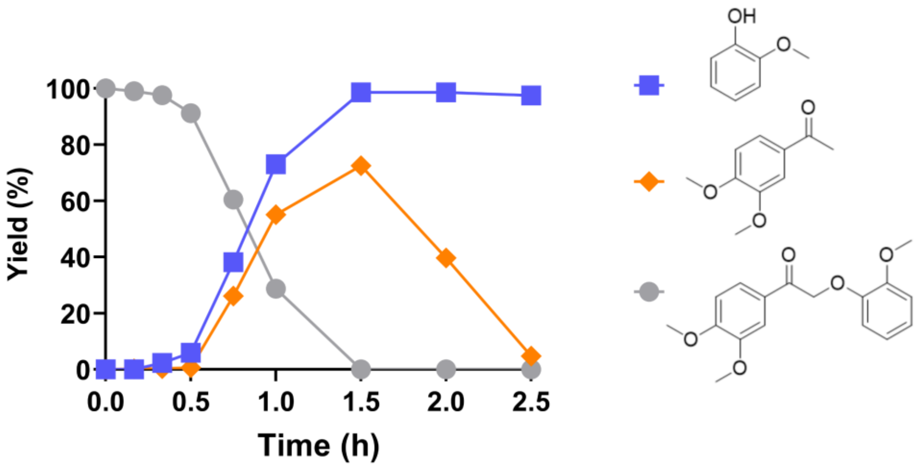


Figure S14. Cleavage of dimer **1a** with 2,2'-dithiodiethanol, pre-electrolyzed for 43 min. Procedure: 2,2'-dithiodiethanol (3.3 mM) was pre-electrolyzed at 5 mA for 43 min (the time required to pass 2 eq of electrons); dimer **1a** (3.3 mM) was then added to the stirring catholyte at t = 0, and current and stirring were continued for the duration of the reaction.

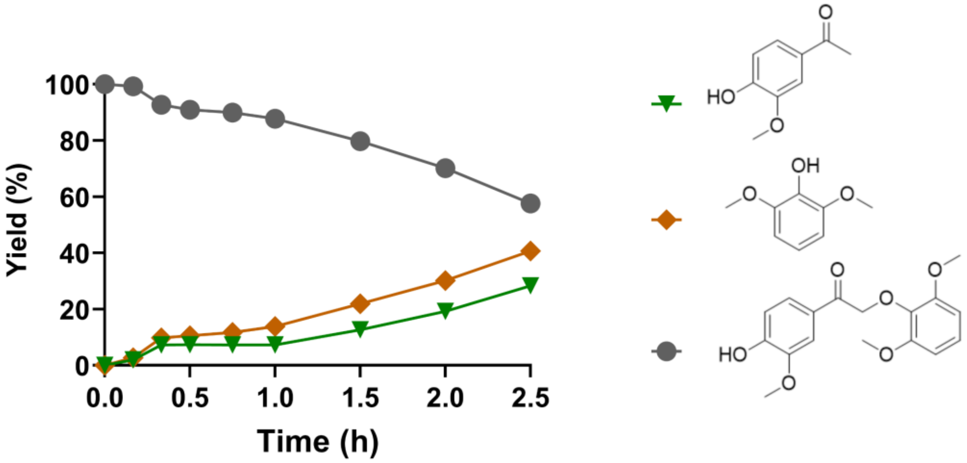


Figure S15. Cleavage of dimer **1b** with current alone. Procedure: dimer **1b** (3.1 mM) was added to the catholyte at t = 0, and current (5 mA) and stirring were continued for the duration of the reaction.

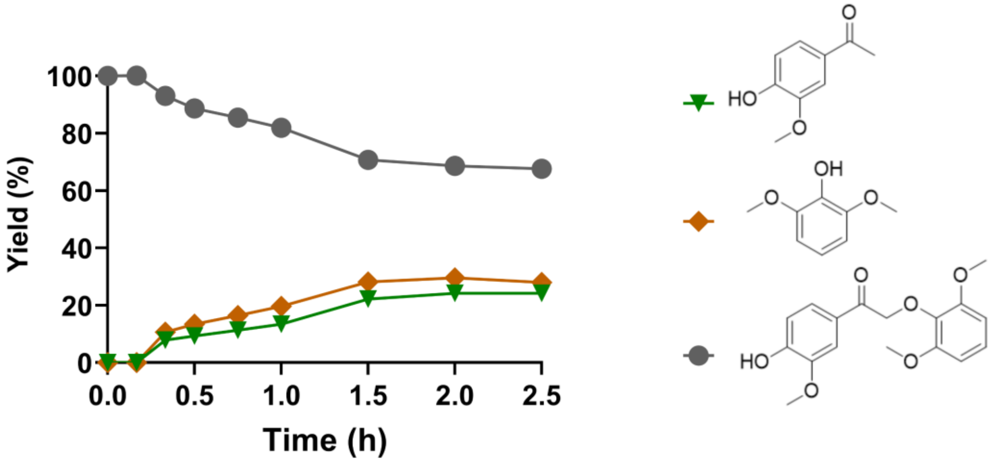


Figure S16. Cleavage of dimer **1b** with 2,2’-dithiodiethanol, pre-electrolyzed for 40 min. Procedure: 2,2’-dithiodiethanol (3.1 mM) was pre-electrolyzed at 5 mA for 40 min (the time required to pass 2 eq of electrons); dimer **1b** (3.1 mM) was then added to the stirring catholyte at t = 0, and current and stirring were continued for the duration of the reaction.

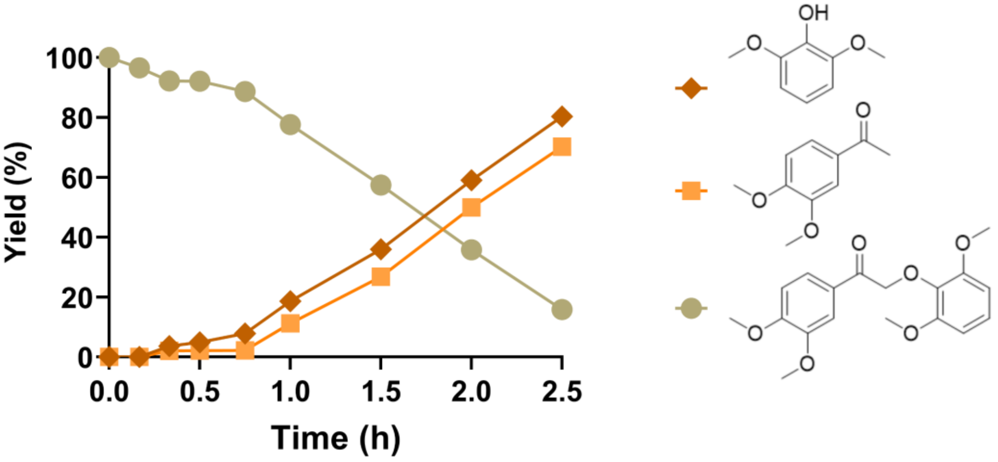


Figure S17. Cleavage of dimer **1c** with current alone. Procedure: dimer **1c** (3.0 mM) was added to the catholyte at t = 0, and current (5 mA) and stirring were continued for the duration of the reaction.

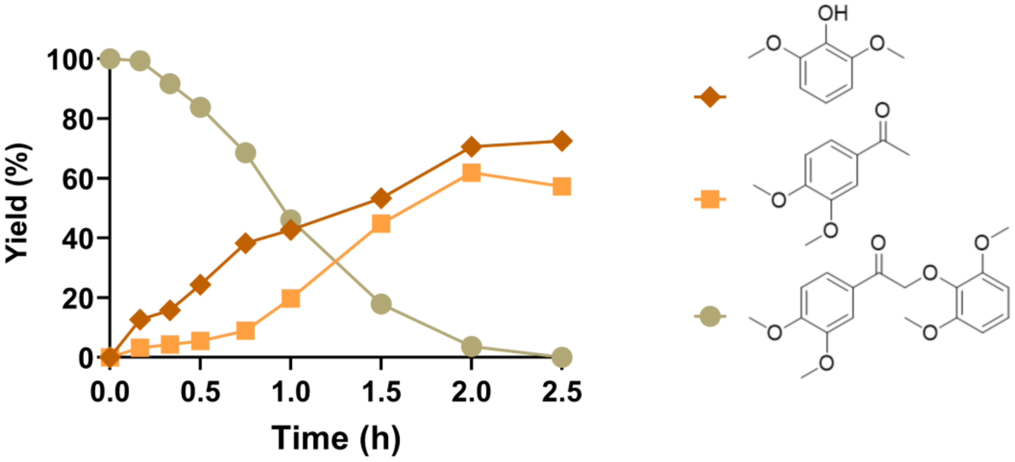


Figure S18. Cleavage of dimer **1c** with 2,2’-dithiodiethanol, pre-electrolyzed for 40 min. Procedure: 2,2’-dithiodiethanol (3.0 mM) was pre-electrolyzed at 5 mA for 40 min (the time required to pass 2 eq of electrons); dimer **1c** (3.0 mM) was then added to the stirring catholyte at t = 0, and current and stirring were continued for the duration of the reaction.

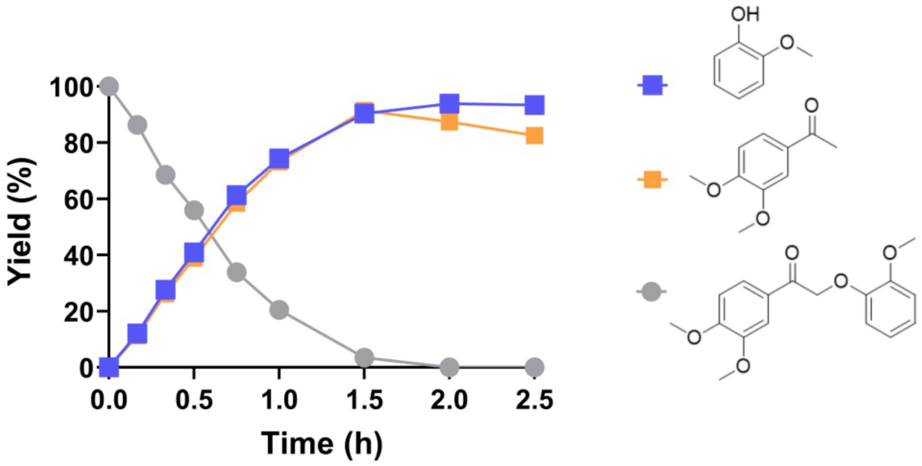


Figure S19. Cleavage of dimer **1a** with 2,2’-dithiodiethanol and BHT, pre-electrolyzed for 43 min,. Procedure: 2,2’-dithiodiethanol (3.3 mM) and BHT (3.3 mM) were pre-electrolyzed at 5 mA for 43 min (the time required to pass 2 eq of electrons); dimer **1a** (3.3 mM) was then added to the stirring catholyte at t = 0, and current and stirring were continued for the duration of the reaction.

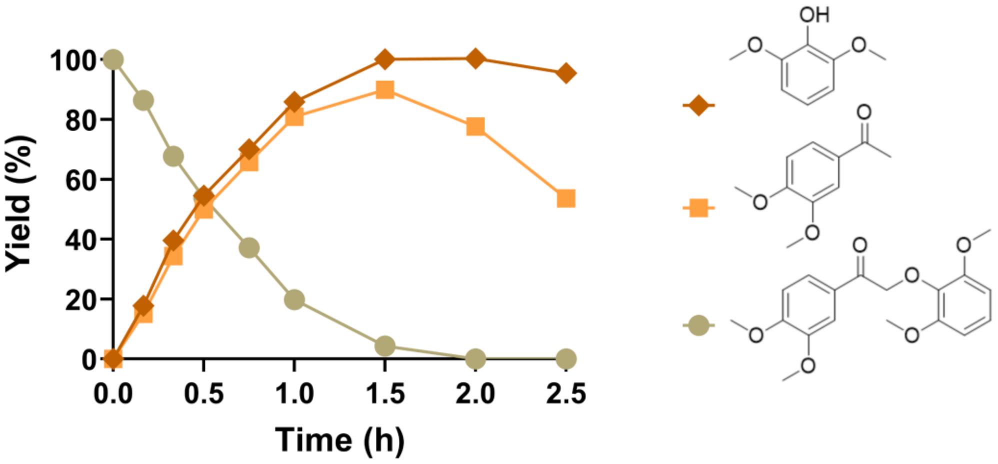


Figure S20. Cleavage of dimer **1c** with 2,2’-dithiodiethanol and BHT, pre-electrolyzed for 40 min,. Procedure: 2,2’-dithiodiethanol (3.0 mM) and BHT (3.0 mM) were pre-electrolyzed at 5 mA for 40 min (the time required to pass 2 eq of electrons); dimer **1c** (3.0 mM) was then added to the stirring catholyte at t = 0, and current and stirring were continued for the duration of the reaction.

Characterization of thio-assisted electrolysis of lignin^{ox}

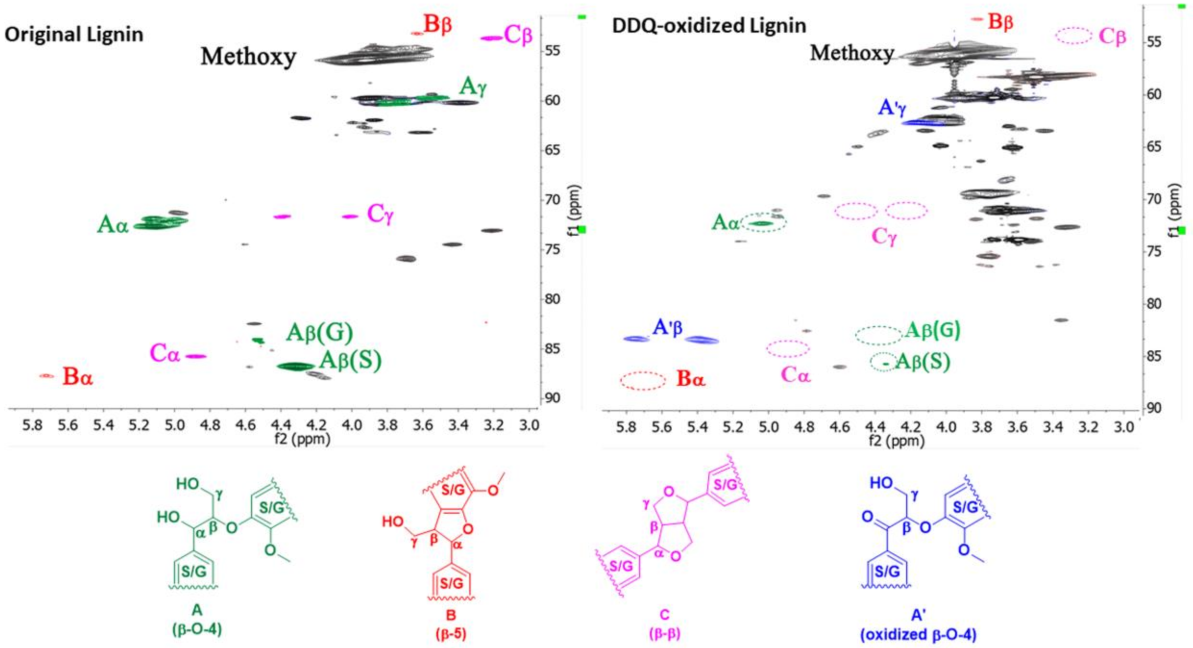


Figure S21. 2D HSQC spectra of original lignin and DDQ-oxidized lignin; depletion of the Aα cross-peak at 5.1/73 ppm (δ_H/δ_C) indicates that majority of the α-OH in the β-O-4 linkages was successfully oxidized to corresponding keto form. As expected, given the benzylic C-H selectivity of DDQ, the primary Aγ sites are retained in the oxidized product.

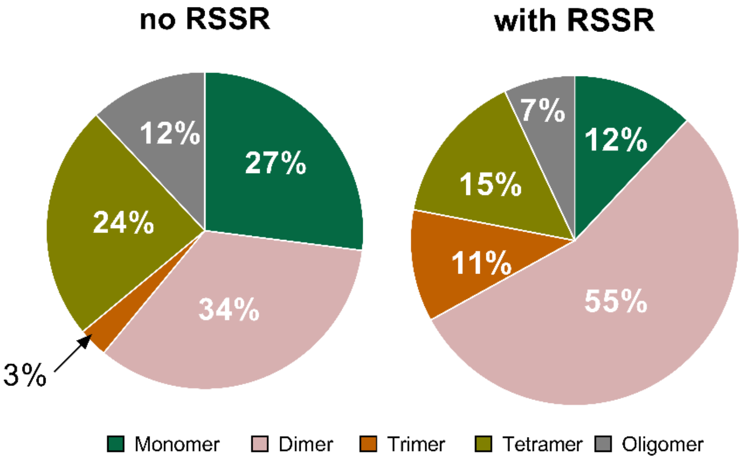


Figure S22. Composition of ethyl acetate (EA) soluble fractions from different reactions. Based on relative intensities of molecular weights, the EA-soluble products were categorized as follows: monomer 88-199 g/mol; dimer 200-299 g/mol; trimer 300-399 g/mol; tetramer 400-499 g/mol; oligomer >500 g/mol. Percentage of each category was directly calculated based on the integrated area of each peak using a high-resolution LCMS-QTOF. These pie charts represent the 24 wt% (left) and 36 wt% (right) of ethyl acetate soluble products obtained from the electrolytic cleavage of lignin, respectively.

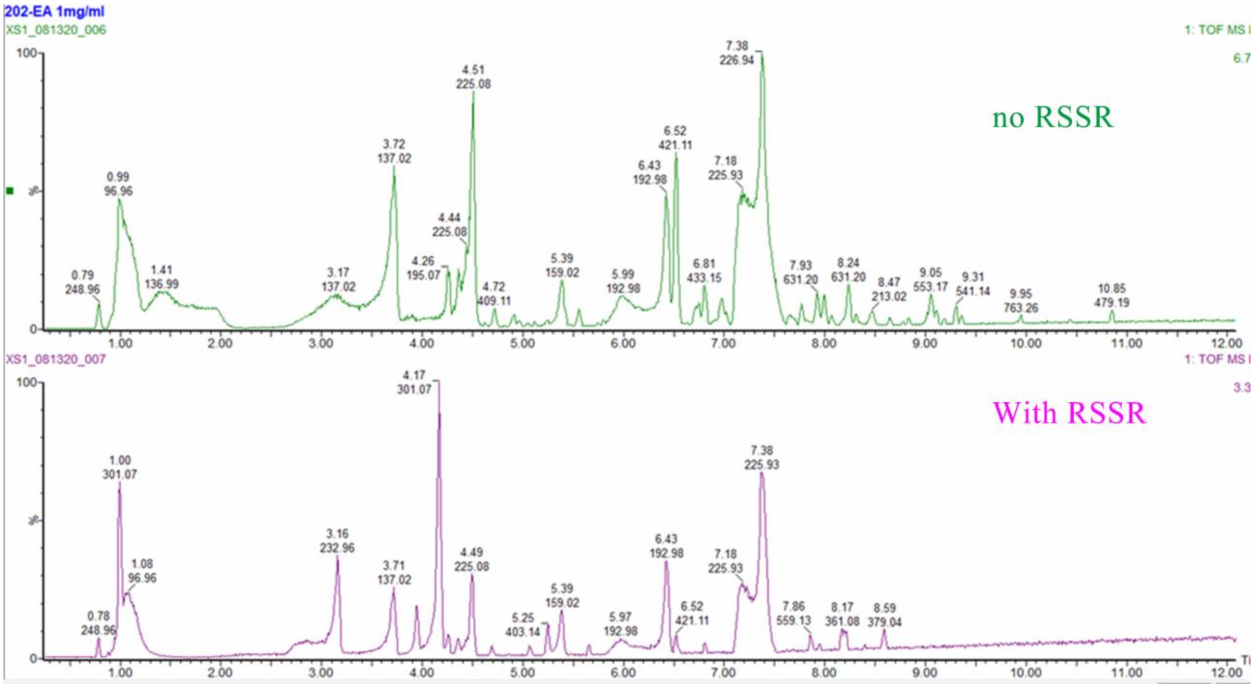


Figure S23. LCMS-QTOF chromatograph of the EA-soluble fraction from reaction: without RSSR (top) and with RSSR (bottom).

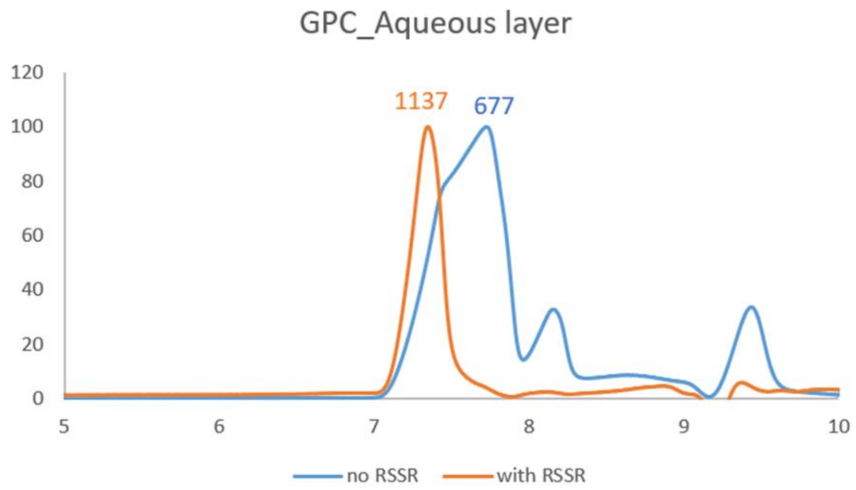
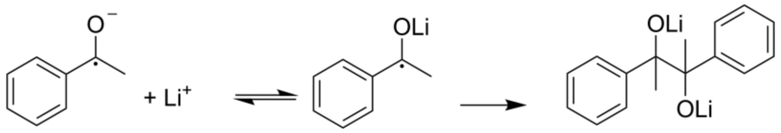
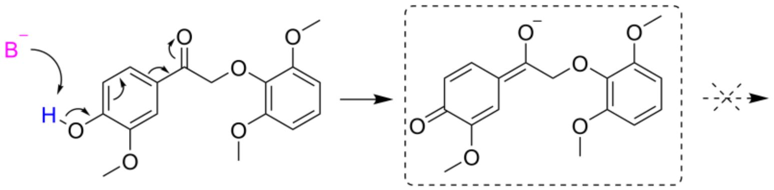


Figure S24. GPC chromatogram of the aqueous soluble products from different control reactions. Blue: Mn (number molecular weight) = 651, Mw (weight molecular weight) = 850; Orange: Mn (number molecular weight) = 1159, Mw (weight molecular weight) = 1160; Conditions: Anode: 20 mL of pH 8 phosphate buffer; Cathode: 20 mL of pH 8 phosphate buffer/isopropanol (2:1, v/v).



Scheme S1. Li$^+$ favored the formation of pinacol



1b

Scheme S2. Proposed formation of the quinone methide intermediate, inhibiting the further cleavage of **1b**.

NMR spectra of dimer 1a-c

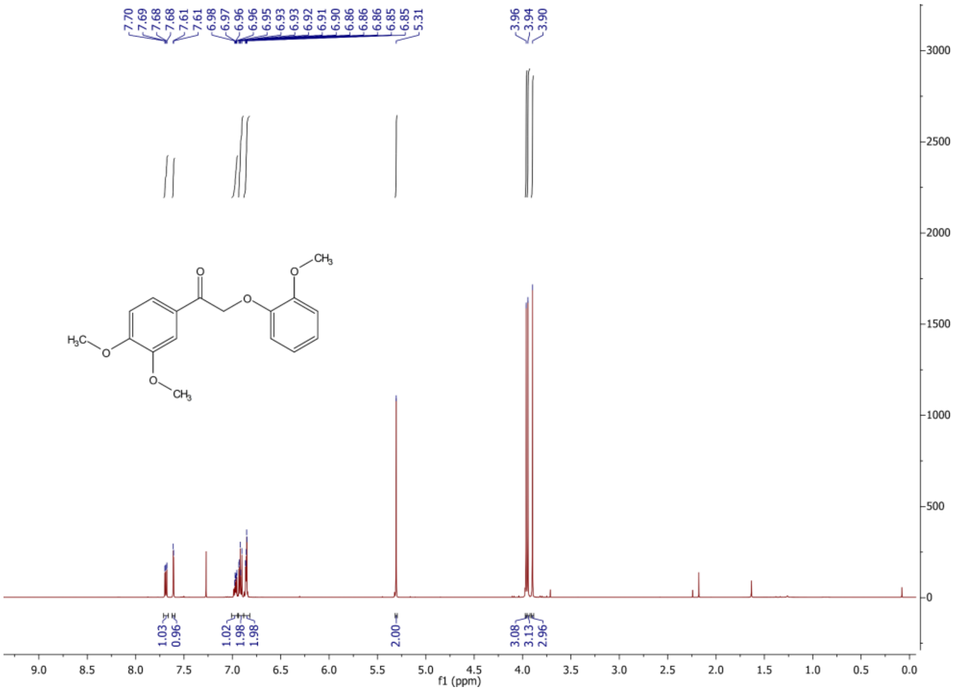


Figure S25. ^{1}H NMR of dimer **1a**

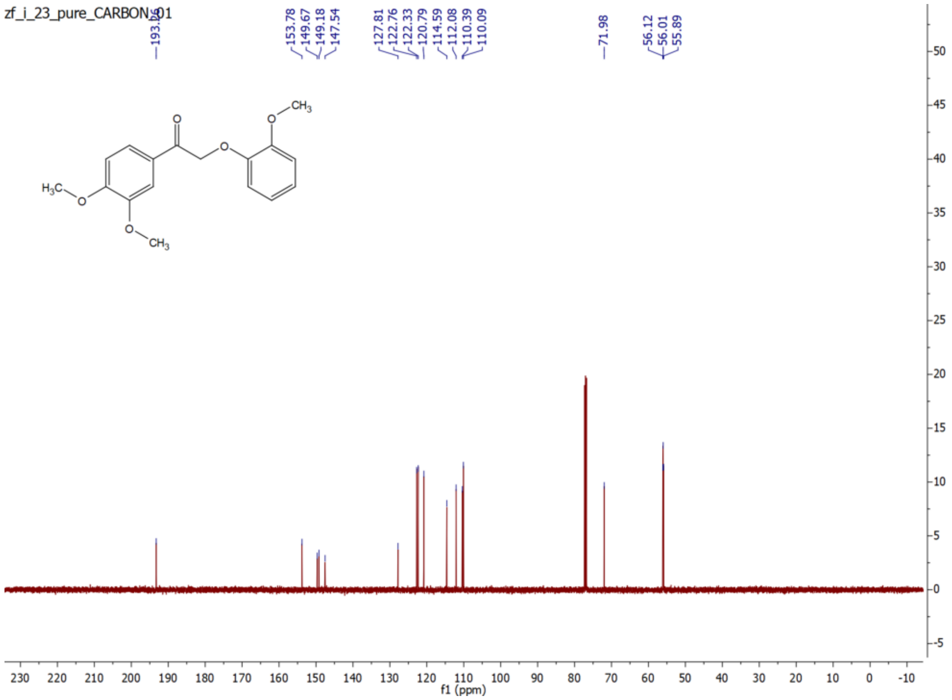


Figure S26. ^{13}C NMR of dimer **1a**

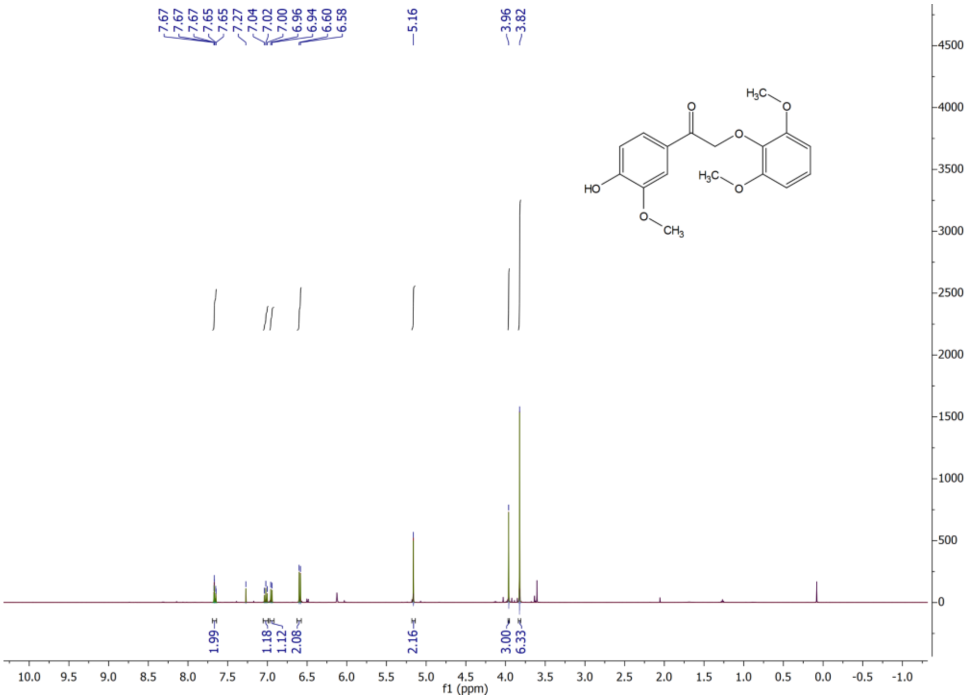


Figure S27. ^{1}H NMR of dimer **1b**

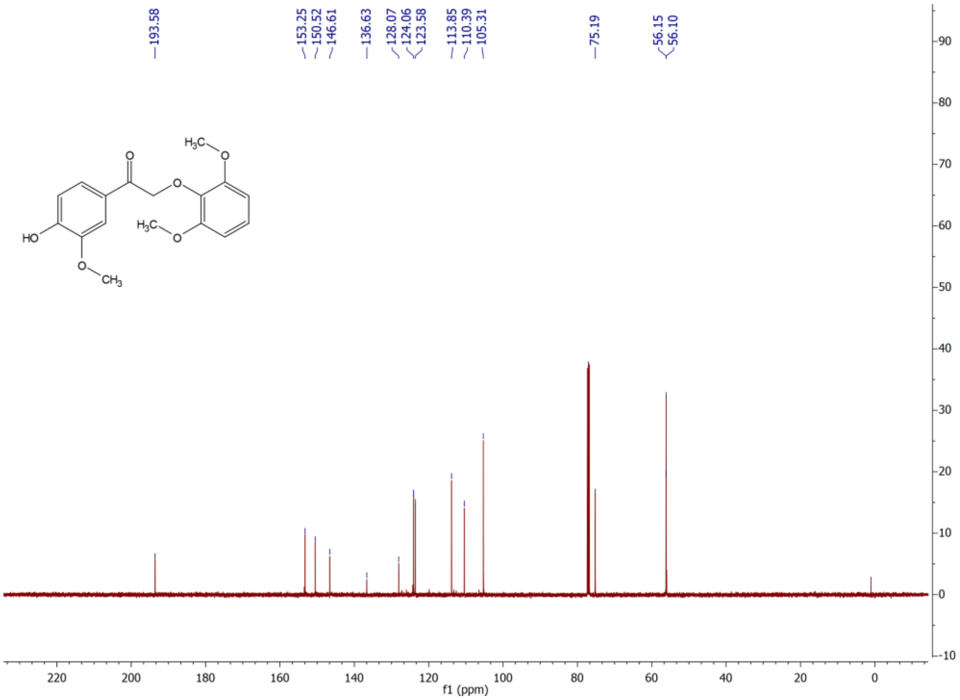


Figure S28. ^{13}C NMR of dimer **1b**

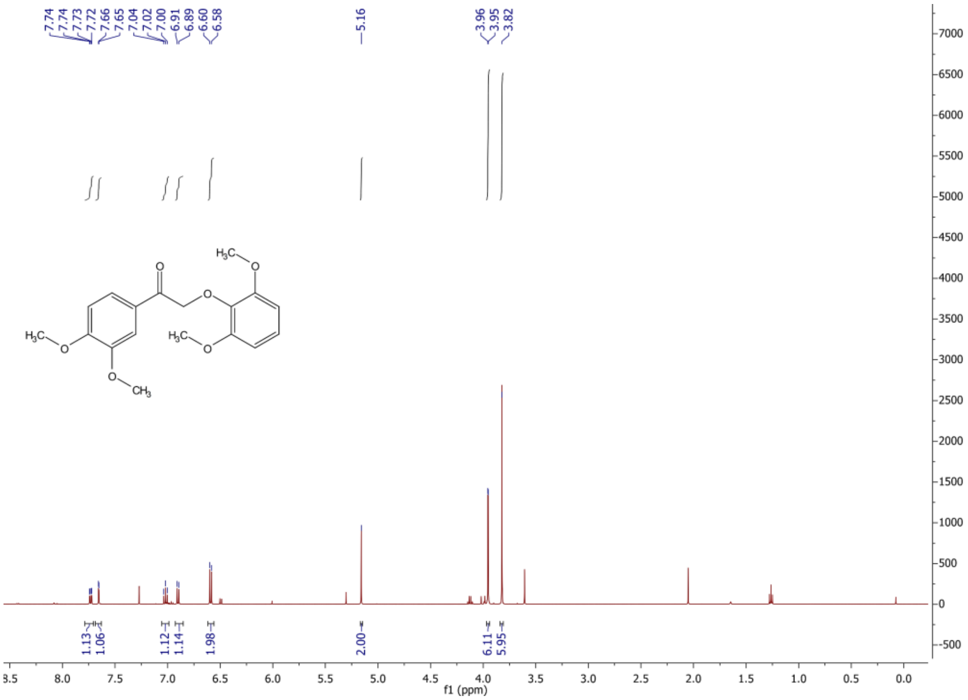


Figure S29. ^{1}H NMR of dimer **1c**

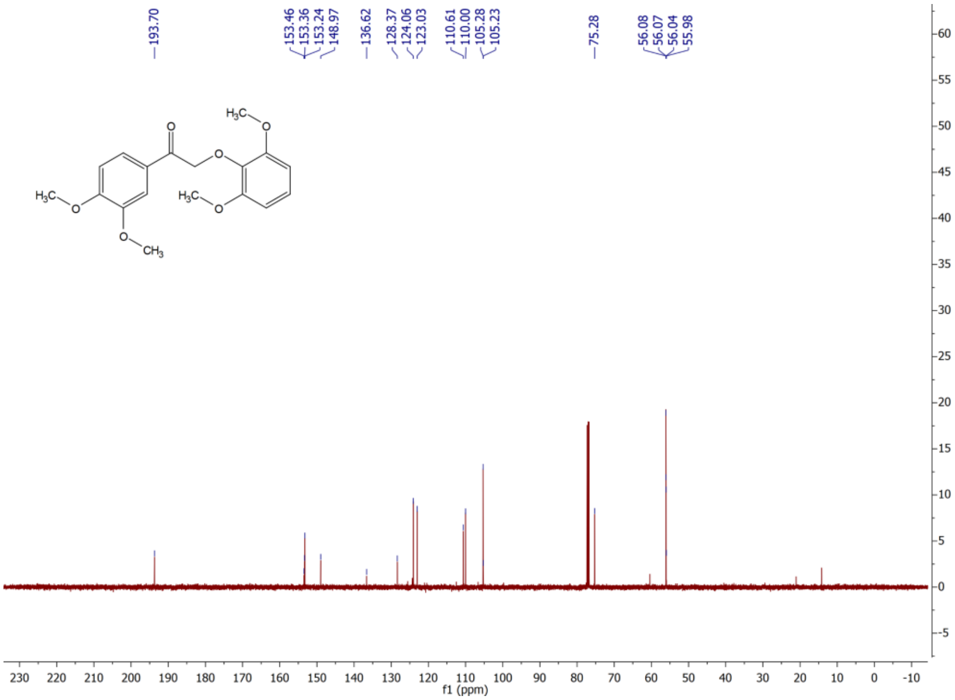


Figure S30. ^{13}C NMR of dimer **1c**

Cyclic voltammetry of 2,2’-dithiodiethanol

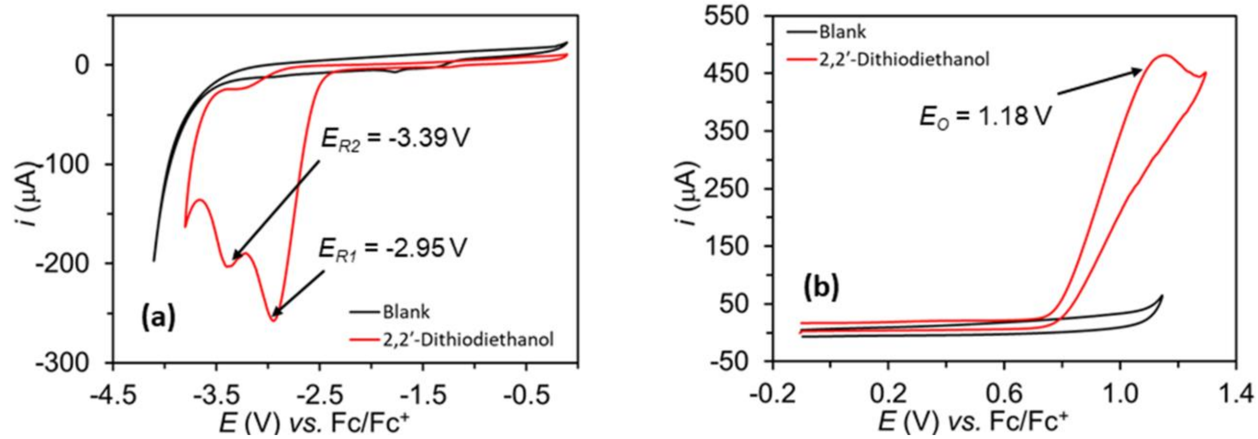


Figure S31. CV of 10 mM 2,2′-Dithiodiethanol in DMF containing 0.1 M LiBF$_4$ (red trace) and blank solution (black trace). CV condition: working electrode: glassy carbon disk (F = 0.07 cm^2); counter electrode: Pt disk; reference electrode: Ag/AgNO$_3$ in CH$_3$CN. Reported Potential vs. Fc/Fc$^+$. Scan rate: 100 mV/s. (a) Two reduction peaks at -2.95 and -3.39 V were observed. (b) An oxidative potential of 1.18 V was also observed.