Supporting Information for

Electrochemical oxidation mechanisms for selective products from C−O and C−C cleavages of a *β*−O−4 linkage in lignin model compounds

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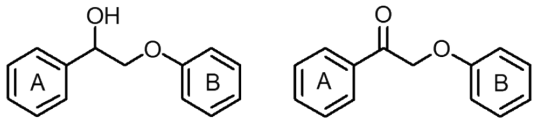
I. Synthesis of lignin model compounds

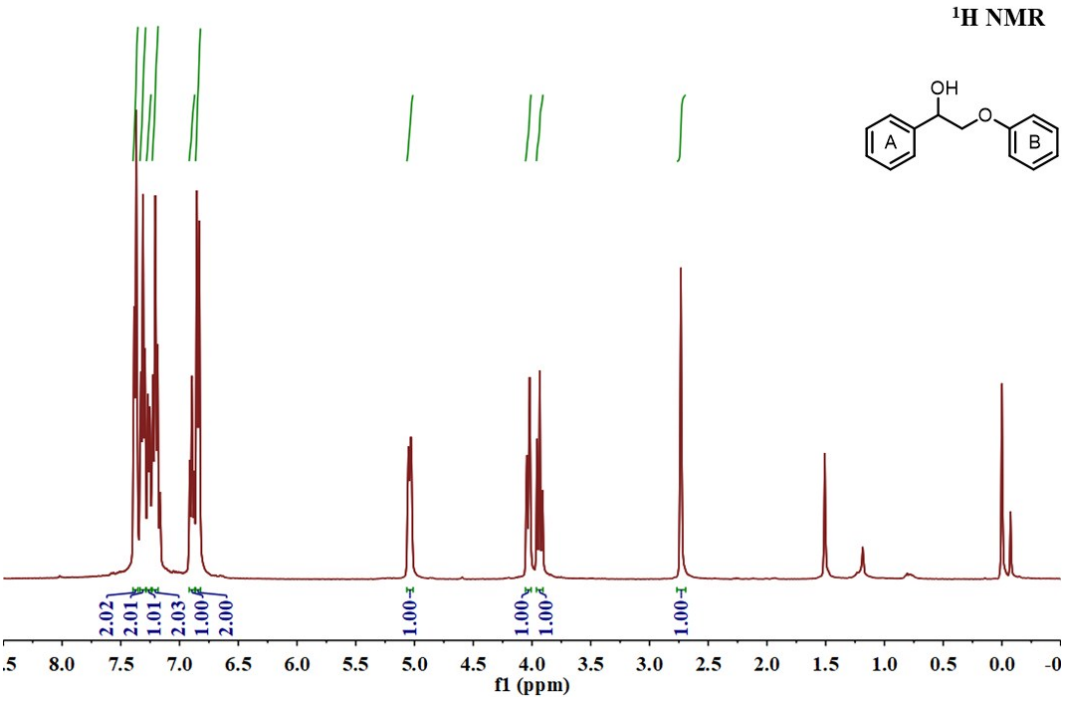


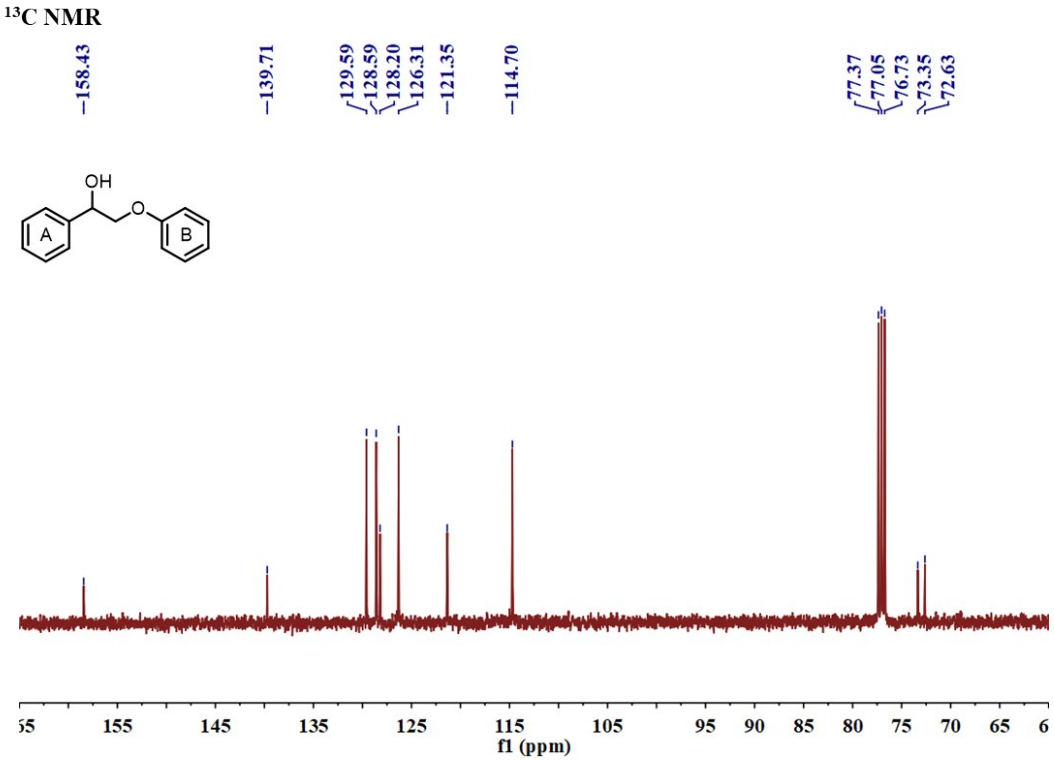
6 7

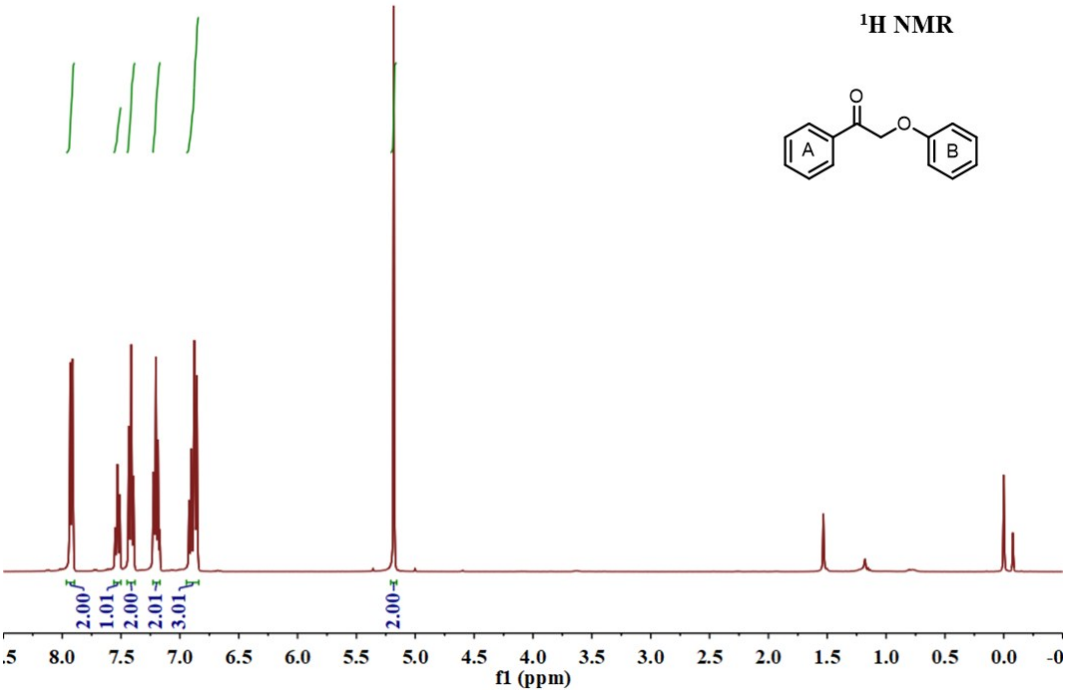
2-phenoxy-1-phenethanol (6): according to the reported literature, model 6 was prepared from **2-phenoxyacetophenone (7).** Step 1: Phenol (5.9 g, 62.7 mmol), potassium carbonate (12.3 g, 89.1 mmol), 2-bromoacetophenone (10.0 g, 50.2 mmol), and acetone (250 mL) were mixed in a round-bottomed flask, and the resulting suspension was heated reflux under stirring for 3 h. And then suffered filtration, vacuum concentration and recrystallization to give 2-phenoxyacetophenone (**7**). Step 2: 2-phenoxyacetophenone (2.00 g, 9.42 mmol), tetrahydrofuran (28 mL) and water (7 mL) were mixed in a round bottom flask. Sodium borohydride (469 mg, 12.4 mmol) was added to the mixture in batches, and the reaction mixture was held under a mild gas for 5 min. Subsequently, the reaction mixture was stirred at room temperature for 3 h. The reaction was quenched with a saturated aqueous NH_4Cl solution, and the reaction mixture was diluted with deionized water. After that, extraction (the aqueous phase is extracted with ether, the organic extract and organic phase were washed twice with saturated sodium chloride), drying in $MgSO_4$, filtration and vacuum drying were performed to give 2-phenoxy-1-phenethanol (**6**).

II. Characterization of lignin model compounds

1.NMR spectra of dimers







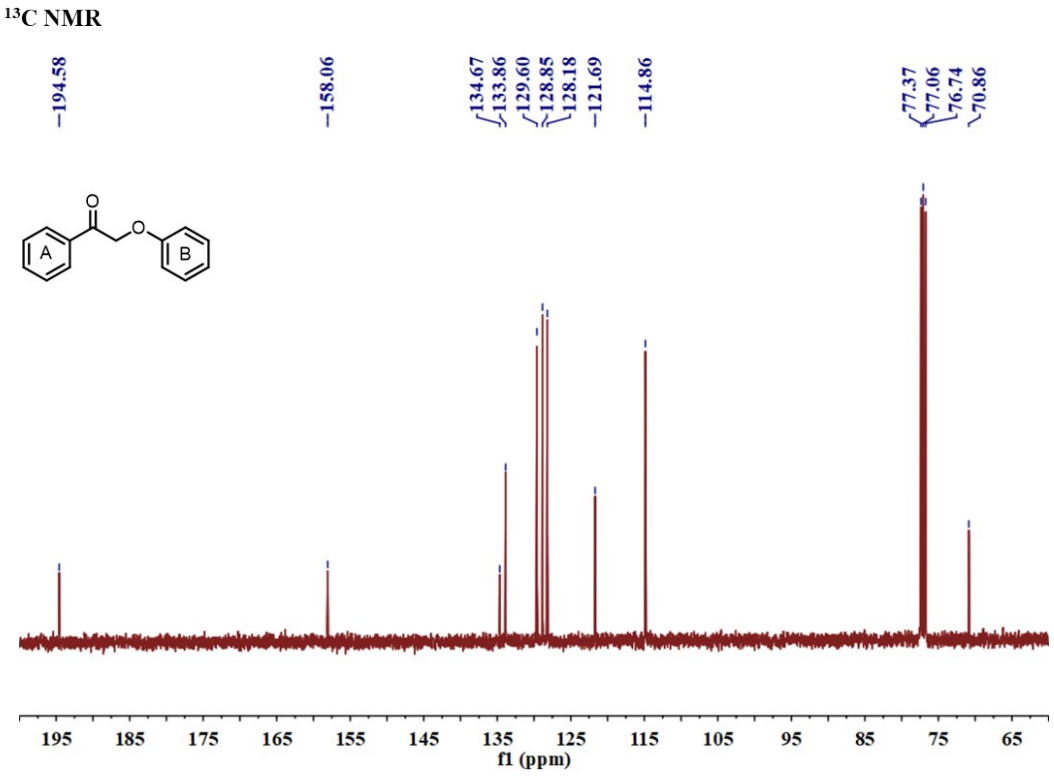


Fig. S1 NMR spectral of 2-phenoxy-1-phenethanol (**6**) and 2-phenoxyacetophenone (**7**).

2. FTIR spectra of dimers

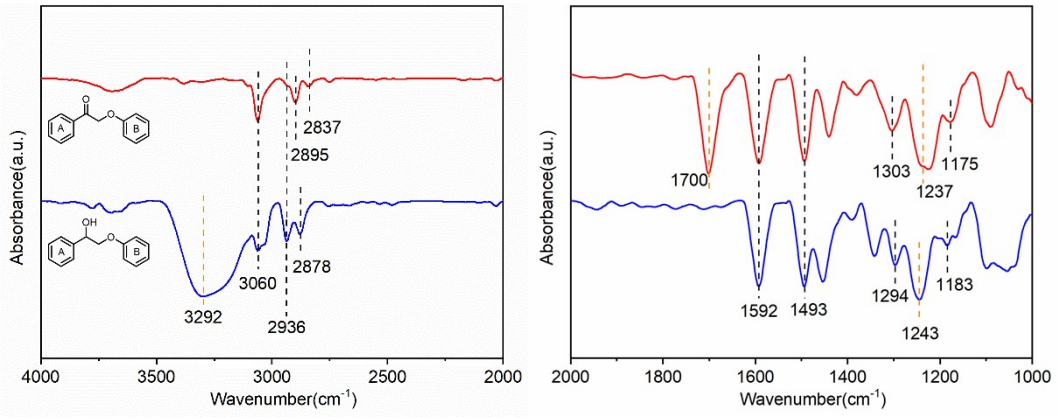


Fig. S2 FTIR spectral of 2-phenoxy-1-phenethanol (**6**) and 2-phenoxyacetophenone (**7**).

3. *In situ* IR spectra of monomers

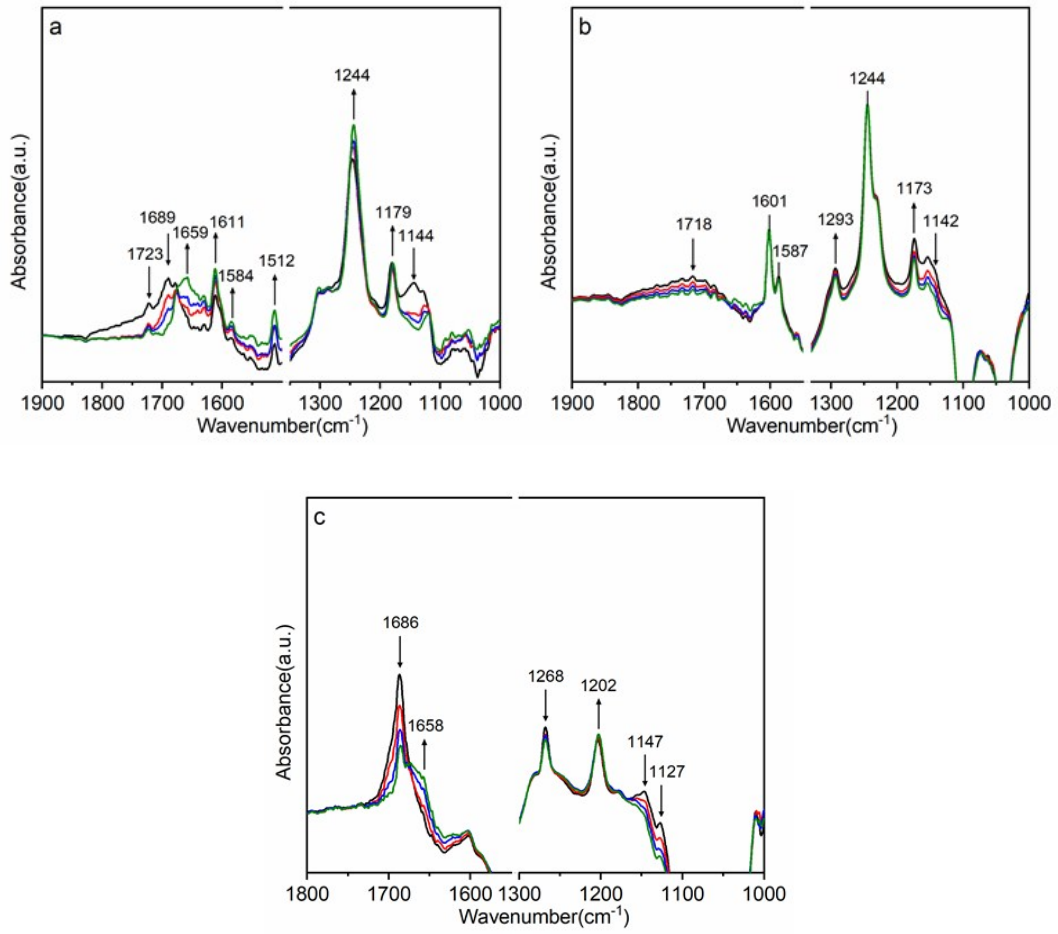


Fig. S3 FT-IR spectra recorded at 0 (black line), 2 (red line), 5 (blue line), and 8 min (green line) during the initial reduction of oxidation state $\mathbf{1}^{++}$ (a), $\mathbf{4}^{+}$ (b) and $\mathbf{5}^{+}$ (c) in $CH_3CN/1\times10^{-1}$ mol dm^{-3} $LiClO_4$ within an OTTLE cell.

III. Vibrational frequencies calculations

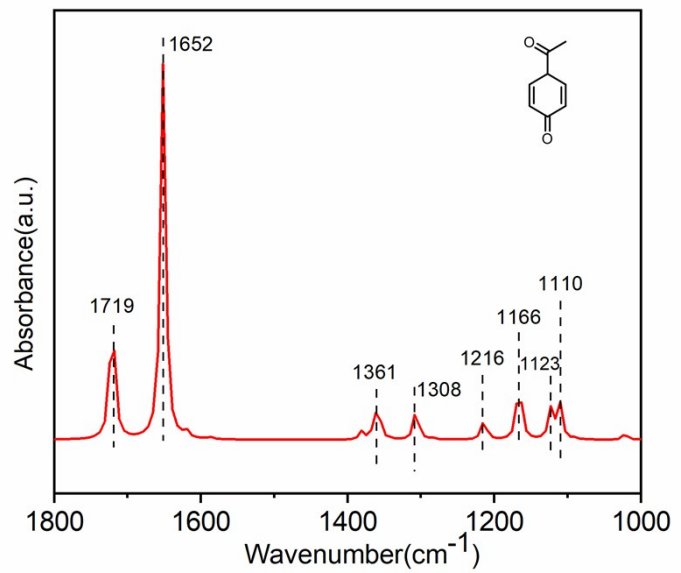


Fig. S4 IR simulation spectra of a possible quinone structure.

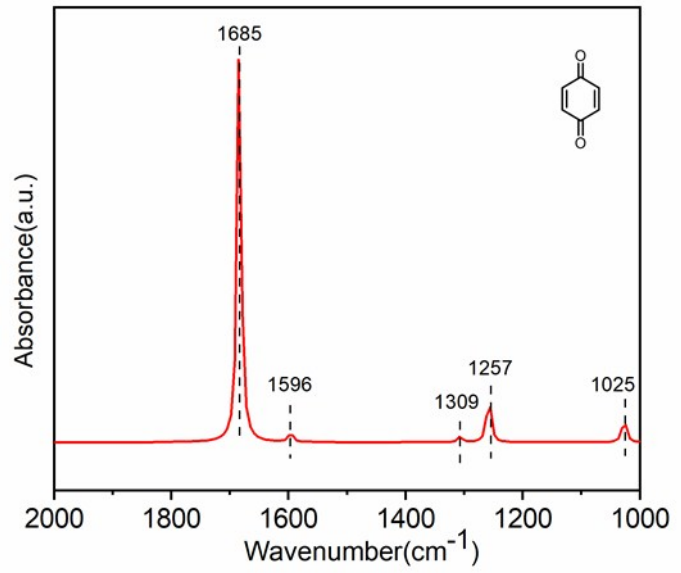


Fig. S5 IR simulation spectra of benzoquinone.

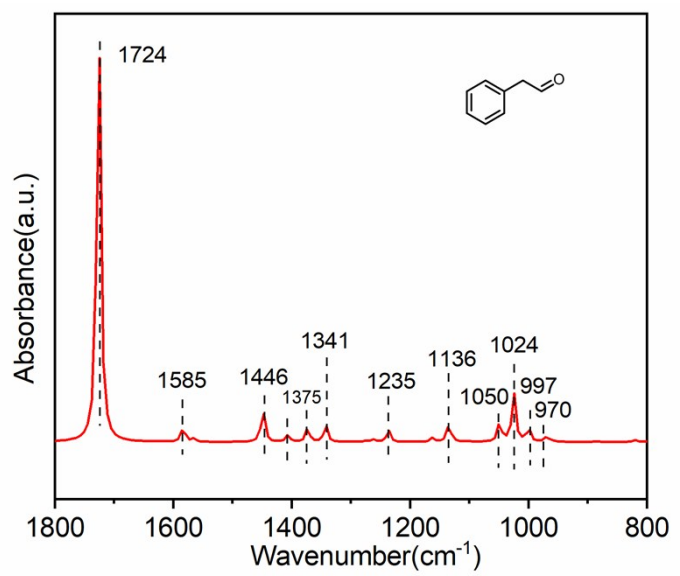
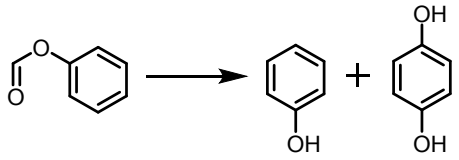


Fig. S6 IR simulation spectra of phenylacetaldehyde.

Ⅳ. GC-MS of the electrolytic products of phenyl formate



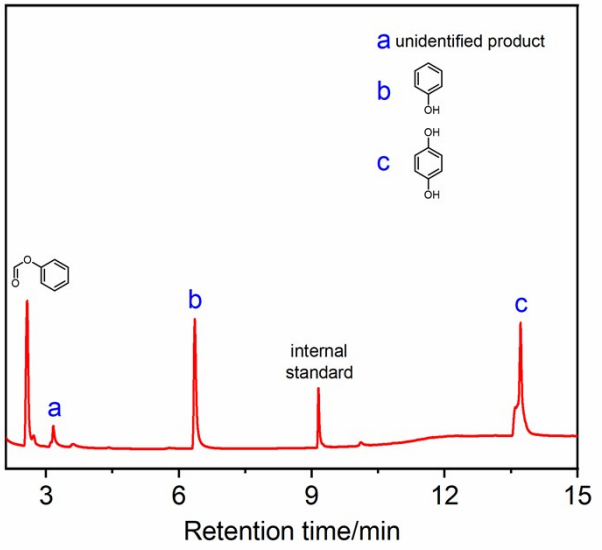


Fig. S7 GC-MS spectra of the electrolyte products from phenyl formate.