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Electrochemical Cleavage of Aryl Ethers Promoted by Sodium Borohydride

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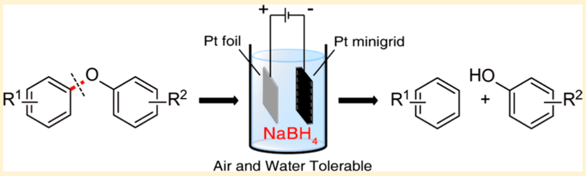
Supporting Information

ABSTRACT: The $NaBH_4$ (or $TBABH_4$)-promoted electrochemically reductive cleavage of aryl C−O bonds in diaryl ethers to produce phenols and arenes with high yields and excellent selectivities at room temperature was reported. Air- and water-tolerable, this process also works on the cleavage of aryl alkyl and benzyl ethers. The application to break the β-O-4, α-O-4, and 4-O-5 lignin model compounds is also illustrated, which highlights the advance toward the goal of lignin conversion.



Air and Water Tolerable

INTRODUCTION

With the growing demand and limited fossil fuel resources, to look for renewable sources of energy such as biomass is important.[1] Lignin, the main constituent of lignocellulosic biomass (15−30% by weight, 40% by energy), is an abundant, cheap, and renewable resource for fuels and bulk chemicals.[2] The β-O-4, α-O-4, and 4-O-5 linkages are three of the most predominant types of ether linkages of lignin. However, selective degradation of lignin into its small building blocks is still challenging mainly due to the high strength and stability of its aromatic ether C−O bonds.[3] The bond dissociation enthalpies (BDE) of the ether linkages reveal that the aryl ether bond of 4-O-5 (314 kJ mol^{-1}) is much stronger than the aliphatic ether bonds of α-O-4 (218 kJ mol^{-1}) and β-O-4 (289 kJ mol^{-1}).[4] The reductive cleavage of aromatic C−O bonds in aryl ethers often requires drastic conditions (high temperature or high pressure), which leads to low reaction selectivities by further reduction to cyclohexane and cycloalkanols.[2a] Recent advances by applying transition-metal catalysts for the selectively reductive cleavage of aryl C−O bonds have been reported under rather milder conditions. Ni catalyst is the most promising and explored.[4b,5] Most recently, an iron catalyst was also used to reductively cleave aryl C−O bonds.[6] Grubbs reported a transition-metal-free process for the efficient reductive scission of diaryl and aryl alkyl ethers by the combination of triethylsilane with *t*BuOK at 165 °C.[7] Other alternative methods for transition-metal-free cleavage of aryl ethers at relatively low temperatures involved reduction by stoichiometric alkali metals[8] and photochemical processes.[9]

The electrochemical method is an excellent method for the generation of reactive species under mild conditions. It serves as “greener” procedures for many transformations.[10,11] Only limited efforts had focused on the electrochemical cleavage of C−O bonds in diaryl ethers. In 1986, Kariv-Miller reported a Birch-type reductive cleavage of diphenyl ether in a divided cell by using a platinum foil anode and mercury pool cathode.[12] Bis(2,5-dihydrophenyl)ether and phenol were obtained as products. Later, an anodic cleavage of diaryl ether at a constant current with MeOH−0.5 M MeONa as electrolyte solution to produce bisacetalcyclohexane-1,4-diene was reported.[13] Another method is electrocatalytic hydrogenation, a process in which hydrogen is generated by electrolysis of water and then reacts with the organic substrate. Lessard and Ménard reported an electrocatalytic hydrogenation of 4-phenoxyphenol to produce 2 equiv of phenol by using a reticulated vitreous carbon (RVC) cathode, which was pretreated with transition-metal particles.[14] A series of intensive studies were reported by Bartak on the carbon−oxygen bond-cleavage reactions, which focused on the mechanical aspects of the electrochemical formation and subsequent reaction pathways of some phenyl ether radicals.[15] These studies were carefully undertaken in the strictly air-free conditions in the glovebox. A general, easy operating, and highly selective electrochemical method for reductive cleavage of diaryl ether bonds, which would further expand the utility to cleavage of a lignin model compound, is highly desirable. As part of our work to aim to explore new organic electrochemical methods,[16] we present a highly selective electrochemical cleavage of diaryl and aryl alkyl ethers promoted by $NaBH_4$ in the undivided cell under air.

RESULTS AND DISCUSSION

As a preliminary experiment, diphenyl ether (**1a**) was treated in a one-compartment cell with platinum foil as the anode and a platinum minigrid as the electrode (represented as Pt (g)) as cathode in DMF−0.2 M $TBABF_4$ (tetrabutylammonium tetrafluoroborate) solution. The electrolysis was carried out at constant current (30 mA) for 105 min at room temperature. The diphenyl ether was not completely electrolyzed, with benzene in 25% yield and phenol in 10% yield only (Table 1,

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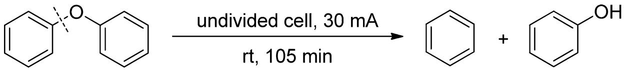
Table 1. Optimization of the Reaction Conditions for the Electrochemical Cleavage of Aryl Ethers[a]



entry	anode–cathode	electrolyte	additive (equiv)	conv (%)[b]	yield (%)[b]	
					benzene	phenol
1	Pt–Pt (g)	DMF–0.2 M $TBABF_4$		26	25	10
2	Pt–RVC[c]	DMF–0.2 M $TBABF_4$		25	23	12
3	Pt–Pt (g)	DMF–0.2 M $TBABF_4$	$NaBH_4$, 3.0	100	80	81
4	Pt–Pt[d]	DMF–0.2 M $TBABF_4$	$NaBH_4$, 3.0	20	20	20
5	Pt–Pt (g)	diglyme–0.2 M $TBABF_4$	$NaBH_4$, 3.0	100	92	82
6	Pt–Pt (g)	NMP–0.2 M $TBABF_4$	$NaBH_4$, 3.0	100	94	95
7	Pt–Pt (g)	NMP–0.2 M $TBABF_4$	$TBABH_4$, 3.0	100	92	94
8	C[e]–Pt (g)	NMP–0.2 M $TBABF_4$	$NaBH_4$, 3.0	96	90	91
9	Pt–RVC	NMP–0.2 M $TBABF_4$	$NaBH_4$, 3.0	90	84	85
10	Pt–Pt (g)	NMP–0.2 M $TBAPF_6$	$NaBH_4$, 3.0	85	82	84
11	Pt–Pt (g)	NMP–0.2 M $NaBF_4$	$NaBH_4$, 3.0	100	94	96
12	Pt–Pt (g)	NMP–0.2 M $NaBF_4$		65	65	40
13	Pt–Pt (g)	NMP–0.2 M $TBABF_4$	H_2[f]	55	55	43

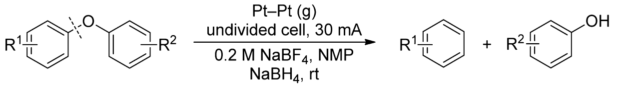
[a] Diphenyl ether (0.5 mmol) in solvent with 0.2 M electrolyte (5 mL) was electrolyzed at constant current (30 mA) in an undivided cell at rt, 105 min, air. Anode: Pt foil (1 × 1.5 cm^2). Cathode is Pt (g): Pt minigrid electrode (52 mesh, 1 × 1.5 cm^2, 4 pieces in parallel). [b] Based on GC analysis with *n*-tetradecane as an internal standard after acidification and aqueous workup. [c] Cathode: RVC electrode. [d] Cathode: Pt foil (1 × 1.5 cm^2). [e] Anode: graphite electrode. [f] H_2 gas in balloon.

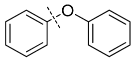
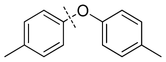
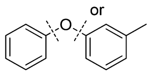
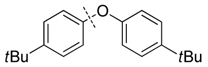
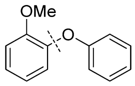
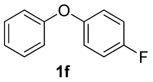
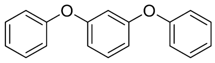
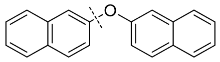
entry 1). Using a RVC electrode instead of Pt (g) as cathode showed no improvement on the conversion of **1a** (Table 1, entry 2). When $NaBH_4$ (3.0 equiv) was added as an additive (Table 1, entry 3), the yield of benzene increased sharply to 80%. Replacement of Pt (g) with single piece of Pt foil, the yields decreased to 20%, which indicated the importance of the working area of the cathode (Table 1, entry 4). Studies on the effect of solvents showed that acetonitrile, THF, and 1,4-dioxane could give only trace amounts of desired products. It was noted that the solubility of $NaBH_4$ was sparse in the above three solvents. Although $NaBH_4$ dissolved in DMSO well, the yield was obtained in 45%. When solvents diglyme or NMP were employed (Table 1, entries 5 and 6), to our delight, the yields reached over 90% and NMP was the best solvent, giving the desired product in an excellent yield of 95%. In the case of employing $TBABH_4$ (tetrabutylammonium borohydride) as a borohydride source (Table 1, entry 7), the reaction occurred at the same reactivity and selectivity as those of $NaBH_4$. It demonstrated that the cations of Na^+ and TBA^+ did not affect the reaction. Change of anode with a graphite electrode resulted in a slight decrease in the yield of phenol and benzene (Table 1, entry 8). It is noted that, by conducting the reaction by using RVC as the cathode, a comparable activity and selectivity were found with a phenol yield of 85% and benzene yield of 84% (Table 1, entry 9), and it implicated that the metal (Pt) electrode does not work as a catalyst or promoter for this reaction. Using $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) as supporting electrolyte could give a good yield at 84% of phenol and 82% of benzene (Table 1, entry 10). Excellent yields of phenol and benzene were obtained with $NaBF_4$ as supporting electrolyte (Table 1, entry 11). Due to its lower price, $NaBF_4$ was a good alternative to $TBABF_4$ for this reaction. When the AR-grade NMP was replaced by the anhydrous NMP under the optimized conditions, no significant effect on the absolute yields of benzene and phenol was observed. It indicated that little amount of water did not affect the transformation. It is noteworthy that the yields of phenol and benzene decreased to 40 and 65%, respectively, when the reaction was performed without $NaBH_4$ (Table 1, entry 12). Furthermore, it was observed that hydrogen gas did not promote the present reaction (Table 1, entry 13). Analyses of the electrolyzed solution by GC-MS and GC indicated that a trace amount of 1,4-cyclohexadiene (<3%), the Birch reduction product of benzene, was formed under the above conditions. It was noticeable that no cyclohexene, cyclohexane, and cyclohexanol were detected in our reactions.

After suitable conditions have been identified, a variety of diaryl ethers were examined to generate the corresponding phenol and arene products (Table 2). The symmetrical diaryl ethers were demonstrated to be good substrates for these conditions and underwent C–O cleavage with good to excellent yields (entries 1, 2, and 4). For the unsymmetrical diaryl ethers with a methyl group, 3-methylphenyl phenyl ether (**1c**), the reaction proceeded with good overall yield with approximately a 1:1 ratio of phenol and *m*-cresol, benzene, and toluene (entry 3). For 2-methoxyphenyl phenyl ether (**1e**), containing an electron-donating group, the cleavage occurred regiospecifically at the C–O bond adjacent to the methoxyl-substituted phenyl ring (entry 5). The ether bearing fluorine group (**1f**) proceeded with the aryl carbon–fluorine bond broken (entry 6). For the 1,3-diphenoxybenzene (**1g**), which contained four C–O bonds, conversion was completed and benzene, phenol, and 3-phenoxyphenol were observed (entry 7). Likewise, cleavage of dinaphthyl ether (**1h**) gave 2-naphthol in 84% yield and naphthalene in 48%. GC and ^1H NMR analyses of the crude reaction mixture indicated that 34% yield of 1,2,3,4-tetrahydronaphthalene was formed (entry 8).

With the promising results on the scission of diaryl ether bonds, we next extended this electrochemical method to aryl alkyl ethers (Table 3). Depending on the nature of the substrate, the yield varied from 74 to 94%. The cleavage of phenyl *tert*-butyl ether (**2b**) and phenyl allyl ether (**2c**) could be furnished at room temperate with good to excellent yields (entries 2 and 3). It might be due to the higher stability of *tert*-butyl and allylic radicals. In some other cases, higher temperature (60 or 80 °C) was applied. For example, anisole

Table 2. Electrochemical Cleavage of Diaryl Ethers[a]

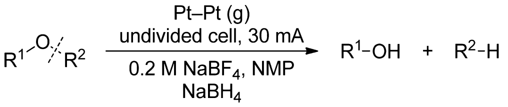


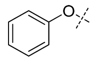
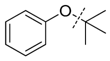
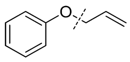
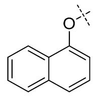
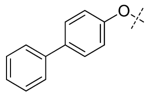
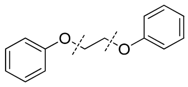
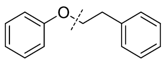
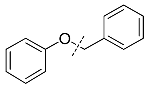
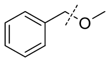
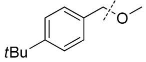
entry	diaryl ether	NaBH$_4$ (equiv)	t (min)	yield (%)[b]	
				ArH	ArOH
1	 **1a**	3.0	105	94[c]	96
2	 **1b**	3.0	105	89	89
3	 **1c**	3.0	105	93[d]	94[e]
4	 **1d**	3.0	120	90	90
5	 **1e**	3.0	120	90	96
6[f]	 **1f**	4.0	180	85	88
7	 **1g**	6.0	150	0.95 (equiv)	1.54 (equiv)[g]
8[h]	 **1h**	4.0	180	48[i]	82

[a] Conditions: diaryl ether (0.5 mmol) and NaBH$_4$, NMP (5 mL, 0.2 M NaBF$_4$ as electrolyte). Anode: Pt foil (1 × 1.5 cm^2). Cathode was presented as Pt (g): Pt minigrid electrode (52 mesh, 1 × 1.5 cm^2, 4 pieces in parallel), constant current (30 mA), undivided cell, rt, air. [b] GC yield with *n*-tetradecane as an internal standard after acidification and aqueous workup. [c] 1,4-Cyclohexadiene (<3%) as a side product, which was detected by GC and GC-MS. [d] Benzene (50%) and toluene (43%). [e] Phenol (44%) and *m*-cresol (50%). [f] Benzene and phenol were obtained as products. [g] With 3-phenoxyphenol (0.17 equiv) as a side product, determined by ^{1}H NMR analysis. [h] At 60 °C. [i] 1,2,3,4-Tetrahydronaphthalene (34%) as byproduct; the yield was determined by GC analysis and identified by ^{1}H NMR spectroscopy.

(**2a**) showed poor reactivity under the optimized condition and only 3% conversion was detected. When the temperature was increased to 80 °C, anisole was completely cleaved to give 74% of phenol by treatment with 6.0 equiv of NaBH$_4$ for 4 h (entry 1). It is also worth noting that 2-phenylethyl phenyl ether (**2g**) could give good yields at 88% of phenol and 80% of ethylbenzene (entry 7). For **2a** and **2g**, traces of Birch reduction products (<3%) were detected. Additionally, phenyl benzyl ether (**2h**), benzyl methyl ether (**2i**), and 4-*tert*-butylbenzyl methyl ether (**2j**) can also be cleaved under room temperature to give moderate to good yields, each with about 5% of 1,2-diphenylethane compound observed. The cleavage occurred at the benzyl C−O bond, which might have generated a more stabilized benzyl radical in the electrolysis process.

Table 3. Electrochemical Cleavage of Aryl Alkyl Ethers and Benzyl Ethers[a]

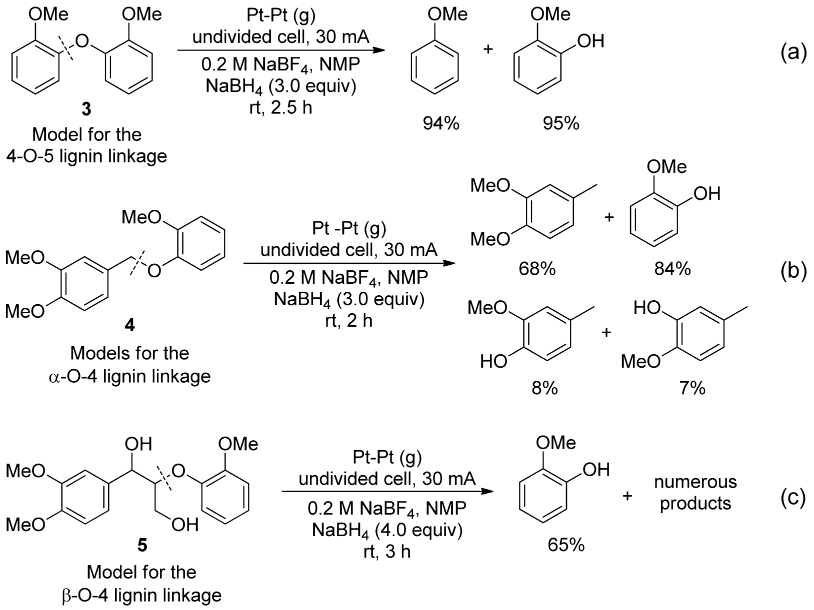


entry	ether	NaBH$_4$ (equiv)	T (°C)	t (h)	yield (%)[b]	
					R^{1}OH	R^{2}H
1[c]	 **2a**	6.0	80	4	74[d,h]	–
2	 **2b**	4.0	rt	3	87	–
3	 **2c**	3.0	rt	1.75	94	–
4[e]	 **2d**	4.0	60	2	85	–
5[e]	 **2e**	4.0	80	2	93[f]	–
6[c]	 **2f**	5.0	60	3	1.80 (equiv)	–
7[c]	 **2g**	5.0	60	3	88	80[g,h]
8	 **2h**	3.0	rt	1.75	94	83
9	 **2i**	3.0	rt	1.75	–	80
10	 **2j**	3.0	rt	1.75	–	75

[a] Conditions: aryl alkyl ether or benzyl ether (0.5 mmol) and NaBH$_4$, NMP (5 mL, 0.2 M NaBF$_4$ as electrolyte). Anode: Pt foil (1 × 1.5 cm^2). Cathode was presented as Pt (g): Pt minigrid electrode (52 mesh, 1 × 1.5 cm^2, 4 pieces in parallel), constant current (30 mA), undivided cell, air. [b] GC yield with *n*-tetradecane as an internal standard after acidification and aqueous workup. [c] With 0.03 M NaBF$_4$ as electrolyte. [d] 1-Methoxy-1,4-cyclohexadiene (<3%) as a side product. [e] With 0.2 M TBABF$_4$ as electrolyte. [f] Isolated yield. [g] 1-Ethyl-1,4-cyclohexadiene (<3%) as a side product. [h] Byproducts were determined by GC and GC-MS.

Depending on the above results, the ability of this reaction system to cleave lignin model compounds was tested. Cleavage of these ether linkages by electrochemical methods would illustrate the possibility of conducting the depolymerization of lignin into small molecules, which could be further converted to fuels and value-added chemicals. Di-2-methoxyphenyl ether (**3**) was chosen as the model of one of the most recalcitrant lignin

Scheme 1. Electrochemical Reductive Cleavage of Lignin Model Compounds



linkages, the 4-O-5 linkage. It was smoothly cleaved to produce anisole and guaiacol in excellent yields at room temperature with 3.0 equiv of $NaBH_4$ for 2.5 h under our electrochemical conditions (Scheme 1a). Reduction of the α-O-4 lignin model compound (**4**) afforded 3,4-dimethoxytoluene in 68% yield and guaiacol in 84% yield, with 2-methoxy-4-methylphenol (8%) and 2-methoxy-5-methylphenol (7%) from further cleavage of 3,4-dimethoxytoluene (Scheme 1b). Cleavage of the β-O-4 model compound (**5**) at room temperature afforded guaiacol in 65% yield, with numerous other products which were not identified (Scheme 1c).

Scheme 2. Plausible Reaction Mechanism

$$\text{PhOPh} + e^- \rightleftharpoons \text{PhOPh}^{\cdot -} \qquad (1)$$

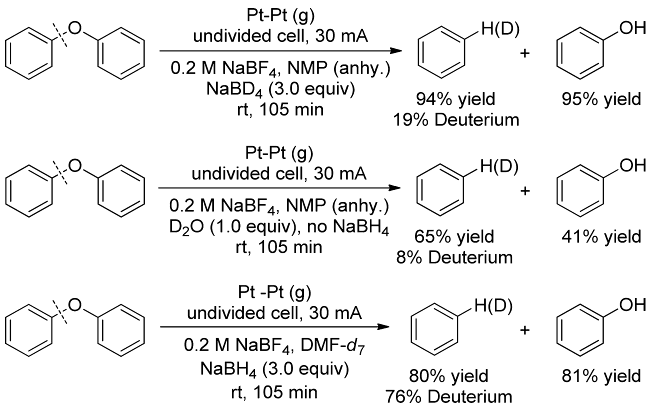
$$\text{PhOPh}^{\cdot -} \longrightarrow \text{PhO}^- + \text{Ph}^{\cdot} \qquad (2)$$

$$\text{Ph}^{\cdot} \xrightarrow{\text{Solvent}} \text{PhH} \qquad (3)$$

Minor path:

$$\text{Ph}^{\cdot} + \text{BH}_4^- \longrightarrow \text{PhH} + \text{BH}_3^{\cdot -} \qquad (4)$$

Scheme 3. Deuterium-Labeling Experiments



According to reported works, the mechanistic paths have been considered (Scheme 2, eqs 1−4).[8,15c,17] Electrochemical formation and decomposition of the diphenyl ether radical anion had been studied by Bartak's group under strictly air-free conditions, and the results supported that the reaction proceeded through eq 3.[15c] To probe the reaction mechanism under our reaction conditions, deuterium-labeling experiments were carried out (Scheme 3).[18] When the reaction was promoted by $NaBD_4$ under the standard reaction conditions, 19% of the benzene was in the monodeuterated form, suggesting that the part of the H atom of benzene was from $NaBH_4$. Reduction of diphenyl ether in the presence of 1.0 equiv of D_2O resulted in minor (8%) deuteration of benzene. This excluded the possibility of D_2O as a major H donor. Furthermore, this result indicated the absence of significant further reduction of the phenyl radical to the anion. Reaction carried out in deuterated DMF resulted in 76% incorporation of deuterium into the benzene, demonstrating that the solvent is the major source of hydrogen for the reductive cleavage process. According to the above results, a one-electron mechanism (Scheme 2, eqs 1−3) might be considered as the major path for the electrochemical reductive ether cleavage. At the current stage, with the preliminary results from the control experiments in Table 1 and the deuteration experiments in Scheme 3, we propose that, besides preventing the oxidation of phenol products by the anode, $NaBH_4$ contributed about 20% of the protons on the product of benzene (Scheme 2, eq 4)[17] and 80% of protons are from solvent according to the deuteration experiments. Meanwhile, several bases were employed to investigate if $NaBH_4$ could act as a base to promote the reaction. Very low yields with very low conversions were obtained when $NaBH_4$ was replaced with Et_3N, NaOH, or K_2CO_3 (see Supporting Information Table S1).

■ CONCLUSIONS

In conclusion, a highly efficient electrochemical reductive cleavage of diaryl ether C−O bonds promoted by $NaBH_4$ has been developed. Operating in an undivided cell with two electrodes system, the reaction occurred highly selectively with minimum further reduction on the aryl ring. The reaction was carried out at room temperature in the air without pretreatment of solvents. This reaction system was also workable on the cleavage of alkyl C−O bonds in aryl alkyl ethers and benzyl ethers. The remarkable substrate scope, including 4-O-5, α-O-4, and β-O-4 model compounds of lignin, air-tolerable reaction conditions, and readily available $NaBH_4$, makes this method a great advance toward the scission of lignin model compounds. Further investigation of the mechanism is underway in our laboratory.

■ EXPERIMENTAL SECTION

General Information. Solvents and reagents were commercially available and used as received without further treatment. GC analyses were carried out using a DB-5 (30 m × 0.25 mm i.d. × 0.25 μm) capillary column with the following temperature programs: (A) 40 °C hold for 2 min, ramp 20 °C/min to a final temperature of 300 °C, and hold for 3 min; or (B) 80 °C, ramp 20 °C/min to a final temperature of 300 °C, and hold for 3 min. GC-MS analyses were carried out on a GC apparatus coupled with a single quadrupole mass spectrometer (EI, 70 eV) and a TG-5MS (30 m × 0.25 mm i.d. × 0.25 μm) capillary column. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts of ^{1}H NMR and ^{13}C NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0 ppm) and relative to the signal of $CDCl_3$ (δ 7.26 ppm for ^{1}H NMR and δ 77.1 ppm for ^{13}C NMR). Multiplicities were given as s (singlet); br s (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. The number of protons (*n*) for a given resonance is indicated by *n*H.

General Procedures for Electrochemical Reductive Cleavage of Aryl Ethers. In a round-bottom flask cell, diphenyl ether (0.5 mmol) and $NaBH_4$ (1.5 mmol) were dissolved in 5 mL of *N*-methyl-2-pyrrolidone (NMP) with $NaBF_4$ (0.2 M) electrolyte. The reaction flask was equipped with a Pt foil anode (1 × 1.5 cm^2) and a Pt minigrid cathode (52 mesh, 1 × 1.5 cm^2, 4 pieces in parallel). The solution was electrolyzed at a constant current (30 mA) for 105 min at ambient temperature. Then, *n*-tetradecane (0.5 mmol) was added to the reaction mixture and stirred for 5 min. The solution was poured into ice water, quenched carefully under 0 °C by aqueous solution of 1 M HCl, and then extracted with diethyl ether (3 × 20 mL). Organic layers were gathered, dried over Na_2SO_4, filtered, and then subjected to GC and GC-MS analyses. All of the products were known compounds and were identified by GC-MS and GC by comparison of the mass spectra and retention times of the products with those of authentic compounds. Conversions and product yields were determined by GC with the *n*-tetradecane internal standard integration. Calibration curves were obtained from authentic compounds.

Quantification of H/D Exchange Reactions. H/D exchange reactions were quantified by GC-MS analyses. The mass data were deconvoluted using a method developed by Periana and co-workers.[18] An important assumption of this method is that there are no isotope effects on the fragmentation pattern of each benzene isotopomers. Known mixtures of pure samples of each isotopomer were analyzed to calibrate the program. The calculated percents of each isotopomer are within the reported error of the method.

Di-4-*tert*-butylphenyl Ether (1d). Prepared according to the reported procedure[5c] as follows: An oven-dried 50 mL round-bottom flask equipped with a stir bar was charged with copper(I) iodide (260 mg, 1.37 mmol), pyridine-2-carboxylic acid (335 mg, 2.72 mmol), 4-iodo-*tert*-butylbenzene (2.36 g, 9.08 mmol), 4-*tert*-butylphenol (2.05 g, 13.7 mmol), and anhydrous potassium phosphate (3.80 g, 17.9 mmol). The reaction flask was sealed and purged with nitrogen. Anhydrous DMSO (25 mL) was added, and the mixture was allowed to stir at 100 °C for 24 h. The reaction mixture was cooled to room temperature and quenched with a 1:1 solution of saturated aqueous ammonium chloride (100 mL) and water (100 mL). The crude product was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed successively with a 5% aqueous solution of potassium hydroxide (100 mL), water (100 mL), and brine (50 mL) and dried over anhydrous sodium sulfate. The solution was evaporated, and the residue was purified by column chromatography (hexane/ethyl acetate 10:1) to give di-4-*tert*-butylphenyl ether (1.92 g, 6.81 mmol) in 75% yield as white crystals: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.35 (m, 4H), 7.00−6.96 (m, 4H), 1.36 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 145.9, 126.5, 118.3, 34.4, 31.6.

2-Methoxyphenyl Phenyl Ether (1e). The same procedure as **1d** with copper(I) iodide (213 mg, 1.12 mmol), pyridine-2-carboxylic acid (276 mg, 2.24 mmol), iodobenzene (1.52 g, 7.45 mmol), guaiacol (1.31 g, 10.5 mmol), anhydrous potassium phosphate (3.56 g, 16.8 mmol), and anhydrous DMSO (16 mL) gave 2-methoxyphenyl phenyl ether (1.06 g, 5.29 mmol) in 71% yield as white crystals: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 8.0 Hz, 2H), 7.22−7.18 (m, 1H), 7.12−6.97 (m, 6H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 151.5, 145.1, 129.5, 124.8, 122.4, 121.1, 121.1, 117.2, 112.9, 55.9.

Phenyl *tert*-Butyl Ether (2b). Prepared according to the reported procedure[19] as follows: Phenol (940 mg, 10.0 mmol) and anhydrous magnesium perchlorate (223 mg, 1.00 mmol) were dissolved in 15 mL of CH_2Cl_2, followed by a slow addition of Boc_2O (5.70 g, 26.1 mmol); the mixture was stirred at 40 °C for 20 h. The crude reaction mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed successively with a 5% aqueous solution of potassium hydroxide (50 mL), water (50 mL), and brine (30 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (hexane/ethyl acetate 10:1) to give phenyl *tert*-butyl ether (1.28 g, 8.52 mmol) in 85% yield as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.2 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.4 H, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 128.9, 124.3, 123.4, 78.4, 29.0.

2-Phenylethyl Phenyl Ether (2g). Prepared according to the reported procedure[5c] as follows: A 250 mL two-necked flask equipped with a stir bar and a condenser coil was charged with anhydrous potassium carbonate (9.10 g, 65.8 mmol), evacuated, and filled with nitrogen. Phenol (6.12 g, 65.0 mmol), acetone (150 mL), and (2-bromoethyl)benzene (9.25 g, 50.0 mmol) were added. The mixture was refluxed until TLC analysis indicated complete consumption of the (2-bromoethyl)benzene. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and dissolved in ethyl acetate (300 mL). The resulting solution was washed with 5% aqueous solution of potassium hydroxide (200 mL) and brine (100 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (hexane/ethyl acetate 10:1) to give 2-phenylethyl phenyl ether (8.96 g, 45.2 mmol) in 90% yield as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.16 (m, 7H), 6.90−6.84 (m, 3H), 4.06 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 138.4, 129.5, 129.1, 128.6, 126.6, 120.8, 114.7, 68.7, 35.9.

Benzyl Phenyl Ether (2h). The same procedure as **2g** with anhydrous potassium carbonate (8.46 g, 61.2 mmol), phenol (5.41 g, 57.5 mmol), acetone (100 mL), and benzyl bromide (7.56 g, 44.2 mmol) gave benzyl phenyl ether (7.33 g, 39.8 mmol) in 90% yield as white crystals: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.38−7.34 (m, 3H), 7.08−7.02 (m, 3H), 5.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 137.2, 129.5, 128.6, 128.0, 127.5, 121.0, 114.9, 69.9.

Di-2-methoxyphenyl Ether (3). Prepared according to the reported procedure[20] as follows: An oven-dried 100 mL round-bottom flask equipped with a stir bar and a condenser coil was charged with copper(I) chloride (1.03 g, 0.010 mol), 2-chloroanisole (14.78 g, 0.104 mol), guaiacol (19.04 g, 0.153 mol), and potassium carbonate (13.80 g, 0.100 mol). Anhydrous pyridine (5 mL) was added, and the mixture was heated under reflux at 150 °C until TLC analysis indicated complete consumption of the 2-chloroanisole. The reaction mixture was cooled to room temperature and diluted with water (300 mL). The crude product was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were washed successively with a 5% aqueous solution of potassium hydroxide (200 mL), water (200 mL), and brine (100 mL) and dried over anhydrous sodium sulfate. The solution was evaporated, and the residue was purified by column chromatography (hexane/ethyl acetate 10:1) to give di-2-methoxyphenyl ether (10.77 g, 46.8 mmol) in 45% yield as white crystals: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08−7.04 (m, 2H), 6.98 (d, J = 7.6 Hz, 2H), 6.89−6.83 (m, 4H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.9, 123.7, 120.8, 118.7, 112.5, 55.8.

3,4-Dimethoxybenzyl 2-Methoxyphenyl Ether (4, the α-O-4 Lignin Model Linkage). Prepared according to the reported procedure[5c,21] as follows: $NaBH_4$ (3.42 g, 90.3 mmol) was added slowly to a solution of 3,4-dimethoxybenzaldehyde (10.0 g, 60.2 mmol) in methanol (100 mL) at 0 °C. After 3 h of stirring at 0 °C, the reaction mixture was warmed to room temperature. Methanol was evaporated, and the mixture was quenched by slow addition of water (300 mL) and extracted with CH_2Cl_2 (3 × 150 mL). The combined organic layers was washed successively with water (300 mL) and brine (200 mL) and dried over anhydrous sodium sulfate. The solution was concentrated to afford the desired alcohol (9.92 g, 59.0 mmol, 98% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, J = 1.6 Hz, 1H), 6.67−6.61 (m, 2H), 4.36 (s, 2H), 3.77 (br s, 1H), 3.65 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 147.7, 133.4, 118.7, 110.6, 110.0, 64.0, 55.3, 55.2. Next, the newly formed alcohol was dissolved in 100 mL of diethyl ether, and the solution was cooled to 0 °C. Then, a solution (1.0 M) of PBr_3 in diethyl ether (61 mL) was added slowly to the flask via syringe. The resulting mixture was warmed to room temperature and stirred for another 4 h. The reaction was quenched carefully with ice water (200 mL) and extracted with diethyl ether (3 × 150 mL). The combined organic layers were washed successively with saturated sodium bicarbonate (200 mL), water (200 mL), and brine (100 mL) and dried over anhydrous sodium sulfate. The solution was concentrated to afford the desired benzyl bromide (13.3 g, 57.8 mmol, 98% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92−6.90 (m, 2H), 6.77 (d, J = 8.0 Hz, 1H), 4.46 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 149.0, 130.1, 121.5, 112.0, 111.0, 55.8, 55.8, 34.3. A 250 mL two-necked flask equipped with a stir bar and a condenser coil was charged with anhydrous potassium carbonate (11.2 g, 81.0 mmol), evacuated, and filled with nitrogen. Guaiacol (9.32 g, 75.1 mmol), acetone (120 mL), and the newly formed benzyl bromide were added, and the reaction mixture was refluxed for 24 h. The mixture was cooled and filtered. The filtrate was evaporated and dissolved in CH_2Cl_2 (300 mL). The resulting solution was washed with 5% aqueous solution of potassium hydroxide (200 mL), water (200 mL), and brine (100 mL) and dried over anhydrous sodium sulfate. The solution was evaporated, and the crude product was purified by column chromatography (hexane/ethyl acetate 10:1) to give 3,4-dimethoxybenzyl 2-methoxyphenyl ether as white crystals (12.5 g, 45.6 mmol) in 79% yield, and an overall yield for three steps was 76%: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01−6.83 (m, 7H), 5.08 (s, 2H), 3.88 (s, 6H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.1, 148.8, 148.2, 129.8, 121.5, 120.8, 120.1, 114.6, 111.9, 111.1, 110.9, 71.2, 55.9, 55.8.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The effect of base, cyclic voltammograms, and copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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