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Copper-Catalyzed Oxidative Cleavage of the C−C Bonds of β-Alkoxy Alcohols and β-1 Compounds

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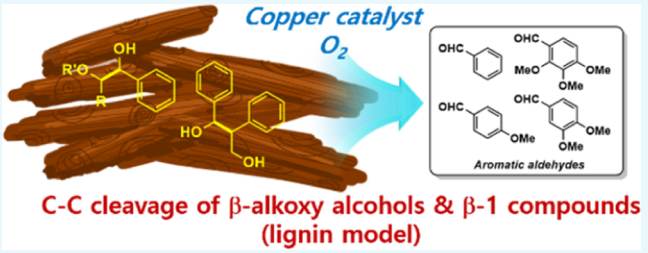
ABSTRACT: Copper-catalyzed aerobic oxidation conditions were employed to promote the C−C bond cleavage of β-alkoxy alcohols and β-1 compounds (lignin model compounds). Besides these compounds, various 1,2 and 1,3-diols were successfully converted to aldehydes. We propose the Cu(I)-catalyzed mechanism explaining the C−C cleavage of these 1,2 and 1,3-dihydroxy compounds and β-alkoxy alcohols based on XPS data. Although our reaction conditions do not include large excess of bases and elaborated ligand-modified catalysts, copper salts with/without Me-TBD show good catalytic activities for C−C bond cleavage of various lignin model compounds.



1. INTRODUCTION

Lignin, a key material for the formation of plant cell walls, is composed of various aromatic building blocks that make it attractive as a renewable feedstock for forming aromatic compounds via chemical processes. Compared to the chemical utilization of other biomass-based feedstocks such as cellulose and hemicellulose, the chemical conversion of lignin is not intensively conducted owing to the difficulty of depolymerizing the randomly connected chemical bonds in the complex structure. Investigating efficient and selective catalysts for the depolymerization of lignin to afford industrially useful aromatic compounds is imperative for replacing fossil fuel-based aromatic compound production.[1,2] The finite availability of petroleum along with the carbon balance achieved by using biomass waste has increased the importance of catalytic processes for converting lignin.

To develop the depolymerization process of lignin, modeling of the metal-catalyzed cleavage of the C−C or C−O bonds has been attempted by many researchers.[3−7] C−C and C−O bonds are commonly found in the β-O-4 linkage and β-1 linkage of lignin.[8−10] For C−O cleavage, Ni,[11] V,[12,13] Pd,[14,15] Co,[16] Ru,[17,18] and Zn,[19,20] as well as metal-free conditions,[21] have been employed, and for C−C cleavage, V,[22−24] Fe,[25] Ru,[26,27] Ir,[28] and Cu[29−35] catalyzed reactions, as well as metal-free[36−38] ones, have been reported. The cleavage of the C−C bonds is not as facile as that of the C−O bonds because of the robustness of the former, but the judicious choice of catalysts has been shown to promote the efficient cleavage of C−C bonds of model lignin compounds.

Our research group has been developing copper-catalyzed oxidative coupling reactions and simple oxidation for tandem asymmetric reactions.[39−41] Based on previous copper-catalyzed oxidation reactions, we decided to investigate copper-catalyzed aerobic oxidative C−C cleavage of β-alkoxy alcohols and β-1 compounds (Figure 1). The β-alkoxy alcohols possessing OR_1 (R_1 = alkyl) and the aromatic group on the carbon backbone undergo the facile C−C bond cleavage compared to the slow reaction of β-O-4 compounds having OAr (Ar = aromatic).[13] Thus, the reactions of β-alkoxy alcohols have been examined to investigate a catalyst. Copper-catalyzed oxidative cleavage reactions of β-alkoxy alcohols and β-1 compounds were reported by Baker/Hanson and Li (Figure 1). Copper catalysts modified with 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) or saturated 1,3-dimesitylimidazol-2-ylidene were used in the presence of large excess of bases such as pyridine, 2,6-lutidine, and quinoline. Compared to previous reports, our reactions do not require large quantity of bases, and in the case of β-1 compounds, CuCl without both ligands and bases promoted the oxidative cleavage. The reaction optimization, the scope of the C−C bond cleavage including β-alkoxy alcohols, β-1 compounds, 1,2-diol, and 1,3-diols, and the proposed catalytic cycles are presented herein.

2. RESULTS AND DISCUSSION

The copper-catalyzed oxidative cleavage reactions of 2-methoxy-1,2-diphenylethan-1-ol (**1a**) were conducted as listed in Table 1. The combination of $CuBr_2$ (10 mol %) and 1,5,7-triazacyclo[4.4.0]dec-5-ene (TBD) under 1 bar of oxygen

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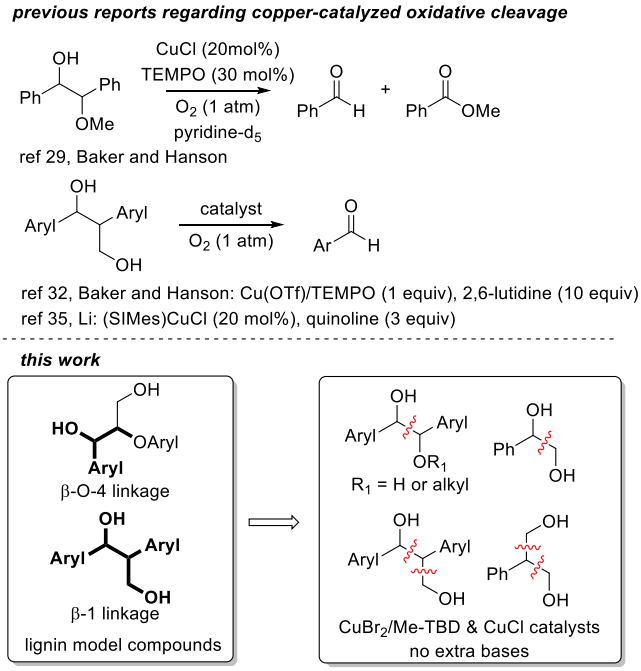
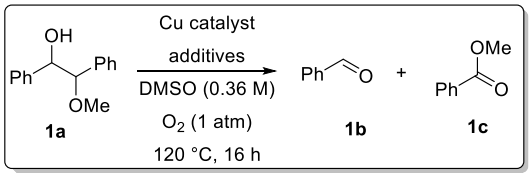


Figure 1. Copper-catalyzed oxidative cleavage reactions.

Table 1. Optimization of Oxidative Cleavage of 1a



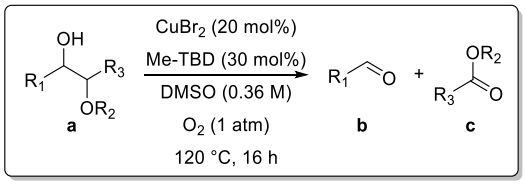
entry	Cu catalyst (mol %)	additives (mol %)	yield (**1b**) (%)	yield (**1c**) (%)
1	$CuBr_2$ (10)	TBD (15)	28	27
2	$CuBr_2$ (20)	TBD (30)	62	59
3		TBD (30)		
4	$CuBr_2$ (20)	TEA (30)	3	2
5	$CuBr_2$ (20)	TEMPO (30)	0.4	0.1
6	$CuBr_2$ (20)	DBU (30)	31	23
7	$CuBr_2$ (20)	Me-TBD (30)	88	73
8	CuBr (20)	Me-TBD (30)	24	27
9	$Cu(OAc)_2$ (20)	Me-TBD (30)	4	11
10	$Cu(OTf)_2$ (20)	Me-TBD (30)	5	4
11[a]	$CuBr_2$ (20)	Me-TBD (30)	94	88

[a]O_2 was bubbled through the solution. Reaction condition: the mixture of **1a** (0.25 mmol), copper catalyst (20 mol %), and additives (indicated amounts) in DMSO (0.36 M) was allowed to react at 120 °C under 1 atm of oxygen. The yields were determined by ^{1}H NMR using maleic acid as an internal standard.

promoted the desired oxidative cleavage to afford aldehyde **1b** and ester **1c** with 28% and 27% yields, respectively (entry 1). The yield of each product was determined by ^{1}H NMR using an internal standard (see the Supporting Information). Higher catalyst loadings increased the yields of **1b** and **1c** (62 and 59%, respectively) (entry 2). In the absence of copper catalysts, the reaction did not proceed (entry 3). Instead of TBD, triethylamine (TEA), TEMPO, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), and *N*-methyl TBD (Me-TBD) were examined, from which the reaction involving Me-TBD afforded products with the highest yields (entries 4−7). CuBr, $Cu(OAc)_2$, and $Cu(OTf)_2$ were inferior to $CuBr_2$ for C−C bond cleavage (entries 8−10). Oxygen gas was bubbled through the solution to increase the oxygen content in the reaction media, resulting in the highest yields (entry 11). Because the yield of **1c** was slightly lower than that of **1b**, we re-exposed the same amount of **1b** and **1c** to the optimized reaction conditions. Compounds **1b** and **1c** were recovered quantitatively, implying that **1b** and **1c** were not decomposed under the reaction conditions (see Supporting Information, Scheme S1).

After optimizing the conditions to cleave the C−C bond in compound **1a**, compounds possessing different substituents were examined (Table 2). 2-Ethoxy-1,2-diphenylethan-1-ol

Table 2. Substrate scope of Copper-catalyzed C−C Cleavage I



entry	reactants	R_1	R_2	R_3	yield
1	**1a**	C_6H_5	CH_3	C_6H_5	94% (**1b**), 88% (**1c**)
2	**2a**	C_6H_5	C_2H_5	C_6H_5	95% (**1b**), 93% (**2c**)
3	**3a**	C_6H_5	C_3H_7	C_6H_5	96% (**1b**), 91% (**3c**)
4	**4a**	4-Cl-C_6H_4	CH_3	C_6H_5	80% (**2b**), 71% (**1c**)
5	**5a**	4-OMe-C_6H_4	CH_3	C_6H_5	97% (**3b**), 71% (**1c**)
6	**6a**	3,4-diOMe-C_6H_3	CH_3	C_6H_5	98% (**4b**), 78% (**1c**)
7	**7a**	C_6H_5	CH_3	4-Me-C_6H_4	71% (**1b**), 76% (**4c**)

and 2-isopropoxy-1,2-diphenylethan-1-ol were converted to benzaldehyde and ethyl- and isopropyl benzoate with good yields, respectively (entries 2 and 3). Whereas the reactions of **1a** showed lower yield of ester **1c** than aldehyde **1b**, compounds **2a** and **3a** possessing ethoxy and propyl alkoxide groups showed similar yields of aldehydes and esters. The electron-deficient aromatic group at the α-carbon (R_1) of **4a** decreased the yield compared to electron-rich aromatic substituted compounds (**1a**, **5a**, and **6a**) (entries 1 and 4−6). The electron-rich substitution at the β-carbon (R_3) of **7a** also reduced the yields of aldehydes and esters (entry 7).

After the oxidative cleavage of β-alkoxy alcohols including **1a**, the copper-catalyzed oxidative cleavage of 1-phenyl-2-(*p*-tolyl)propane-1,3-diol (**1d**), a β-1 model compound, was attempted, as listed in Table 3. The reactions involving $CuBr_2$ with/without Me-TBD afforded products **1b** and **5b** with low yields (entries 1 and 2). Other than indicated products, the starting materials remained the same (see the Supporting Information). Compared to the result for **1a** involving C−C bond cleavage, **1d** undergoes two successive C−C bond cleavages to afford **1b** and **5b**. Thus, the copper catalyst, bases, and temperature were varied to improve the yield. Changing copper catalysts to copper(I) increased the yield of each product (entries 3 and 4). The increasing temperature during the shorter reaction time promoted the C−C bond cleavage of

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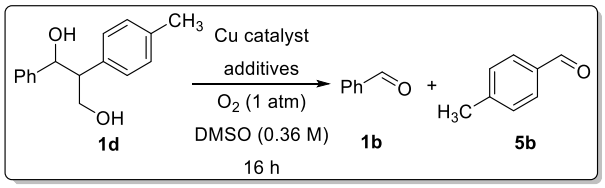
Table 3. Optimization of the Oxidative Cleavage of 1d



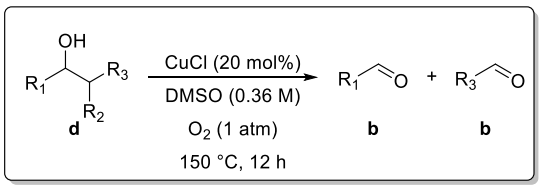
entry	Cu catalyst (mol %)	additives (mol %)	temp (°C)	yield (**1b**) (%)	yield (**1c**) (%)
1	$CuBr_2$ (10)	Me-TBD (30)	120	9	14
2	$CuBr_2$ (20)		120	2	
3	CuBr (20)		120	20	28
4	CuCl (20)		120	25	36
5	CuCl (20)		150	38	55
6[a]	CuCl (20)		150	46	65
7[a]	CuCl (30)		150	44	59
8[a]	CuCl (20)	Me-TBD (30)	150	17	24

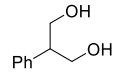
[a]Reaction time: 12 h. Reaction condition: the mixture of **1d** (0.25 mmol), copper catalyst (indicated amounts), and additives (indicated amounts) in DMSO (0.36 M) was allowed to react at the indicated temperature under 1 atm of oxygen. The yields were determined by ^{1}H NMR using 1,3-trimethoxybenzene as the internal standard.

1d with yields of 46% (**1b**) and 65% (**5b**) (entries 5 and 6). Further increasing the catalyst load and addition of Me-TBD did not improve the yield of the product (entries 7 and 8). Products were observed with the remaining starting materials (see Supporting Information, Table S2).

The scope of cleaving the β-1 model compounds was examined, as listed in Table 4. As the number of electron-donating substituents was increased, the overall yields of bond-cleavage products increased. Compound **2d** possessing two methoxy groups underwent cleavage to afford **4b** and **1b** with 49 and 41% yields, respectively, which was similar to the result for **1d** having a methyl group (entries 1 and 2). Compound **3d** having a methoxy and a methyl group was converted to **3b** and **5b** with 50 and 52% yields, respectively (entry 3). Based on the oxidative cleavage yields of **4d**, **5d**, **6d**, and **7d**, as the number of electron-donors increases, better yields were observed (entries 4–7). In addition to lignin model compounds, various 1,2- and 1,3-diols were examined, thereby demonstrating that our copper-catalyzed aerobic C–C cleavage protocol could be expanded to the reactions of these compounds. The transition-metal-catalyzed oxidative cleavage of 1,2-diols was reported using ruthenium, vanadium, and silver catalysts.[42−45] Homogeneous copper catalysts for this transformation has not been reported. In addition, transition-metal catalyzed aerobic cleavage of simple 1,3-diol **11d** has not been reported yet. The reactions of 1,2-diols were successful with both $CuBr_2$ and CuCl (entries 8–10), but the cleavage yields of 1,3-diols were variable depending on the copper catalyst (entry 11). The CuCl-catalyzed reaction afforded benzaldehyde **1b** with a 73% yield, whereas the reaction with $CuBr_2$ and Me-TBD provided **1b** with a 10% yield. The oxidative cleavage of 1,2 and 1,3-alcohols also afforded only aldehydes without forming carboxylic acids. Finally, the reaction of **1a** was conducted under the conditions of Table 4 to compare the catalytic performance between $CuBr_2$/Me-TBD and CuCl. The C–C cleavage of **1a** afforded **1b** with 98% yield and **1c** with 55% yield in the presence of CuCl, showing that CuCl was inferior to $CuBr_2$/Me-TBD for the formation of **1c** (entry 11 of Table 1).

Table 4. Substrate Scope of Copper-Catalyzed C–C Cleavage II



entry	reactants	R_1	R_2	R_3	yield
1	**1d**	C_6H_5	CH_2OH	4-Me-C_6H_5	46% (**1b**), 65% (**5b**)
2	**2d**	3,4-diOMe-C_6H_3	CH_2OH	C_6H_5	49% (**4b**), 41% (**1b**)
3	**3d**	4-OMe-C_6H_4	CH_2OH	4-Me-C_6H_5	50% (**3b**), 52% (**5b**)
4	**4d**	3,4-diOMe-C_6H_3	CH_2OH	4-OMe-C_6H_4	67% (**4b**), 75% (**3b**)
5	**5d**	3,4-diOMe-C_6H_3	CH_2OH	4-Me-C_6H_5	64% (**4b**), 61% (**5b**)
6	**6d**	4-OMe-C_6H_4	CH_2OH	3,4-diOMe-C_6H_3	68% (**3b**), 65% (**4b**)
7	**7d**	2,3,4-triOMe-C_6H_2	CH_2OH	3,4-diOMe-C_6H_3	82% (**6b**), 68% (**4b**)
8	**8d**	C_6H_5	OH	H	71% (**1b**) (70% (**1b**)[a])
9	**9d**	C_6H_5	OH	C_6H_5	73% (**1b**) (68% (**1b**)[a])
10	**10d**	4-OMe-C_6H_4	OH	4-OMe-C_6H_4	93% (**3b**) (93% (**3b**)[a])
11	**11d**				73% (**1b**) (10% (**1b**)[a])

[a]$CuBr_2$ (20 mol%), Me-TBD (30 mol%) at 120 °C

The reaction mechanisms of the C–C bond cleavage of **1a** and **1d** were probed (Scheme 1). Since the reaction was carried out under copper-catalyzed aerobic oxidation conditions, it could be initiated by the oxidation of alcohols,[46−49] followed by C–C bond cleavage. To assess our hypothesis, independently prepared α-oxyketone **5a′** was subjected to the reaction conditions (Scheme 1, eq 1). **5a′** underwent C–C bond cleavage to produce acid **3b′** instead of aldehyde **3b** under the optimized conditions. Even in the absence of $CuBr_2$, the same combination of products was observed with similar yields. In the previous copper-catalyzed C–C cleavage of lignin models, aldehydes were formed rather than acids.[30,32] The starting materials were retained without both $CuBr_2$ and Me-TBD. In the case of **1d′**, aldehydes **1b** and **5b** were obtained with low yields, and no cleavage was observed without CuCl (Scheme 1, eq 2). Besides, ketones formed by the oxidation of **1a** and **1d** were not found during the copper-catalyzed cleavage reactions. Accordingly, it was concluded that the C–C cleavage reactions of **1a** and **1d** might not begin with the oxidation of *sec*-alcohols.[35]

Plausible reaction mechanisms to account for C–C cleavage of **1a** and **1d** are illustrated in cycle A of Scheme 2.[50,51] The reaction of **1a** was promoted by $CuBr_2$ and Me-TBD. Based on XPS data of the mixtures of $CuBr_2$/Me-TBD and $CuBr_2$/Me-TBD/**1a**, Me-TBD is presumed to reduce Cu(II) to Cu(I) (Figure 2). The Cu $2p_{3/2}$ core levels taken from $CuBr_2$/Me-TBD (Figure 2a) and $CuBr_2$/Me-TBD/**1a** (Figure 2b) show the presence of Cu(I) and Cu(II) chemical states at 932.7 and 934 eV, respectively. Along with the observation of Br 3d at 69 eV as well as the survey spectra (Figure S1), the results indicate that two Cu chemical states can be associated with CuBr and $CuBr_2$ species, respectively.[52,53] The presence of Cu(I) [not Cu(0)] as well as Cu(II) is further corroborated by the Cu $L_3M_{4,5}M_{4,5}$ Auger features (Figure S2), which overlap well with the reference Auger spectra of CuBr and $CuBr_2$; the Auger features of CuBr and Cu are well resolved despite the

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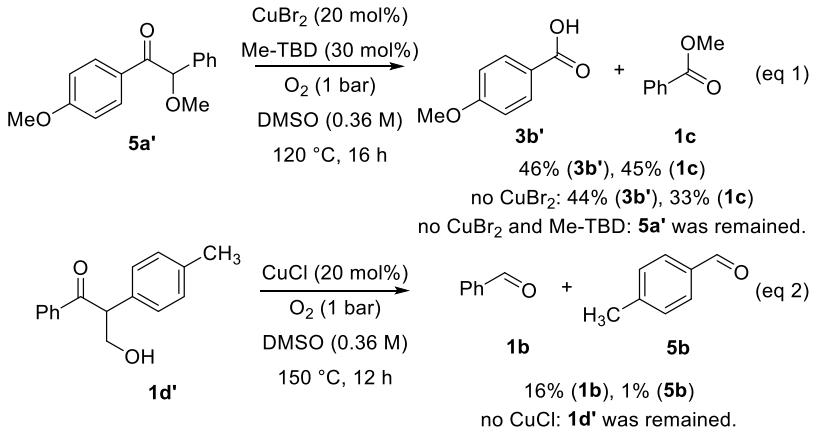
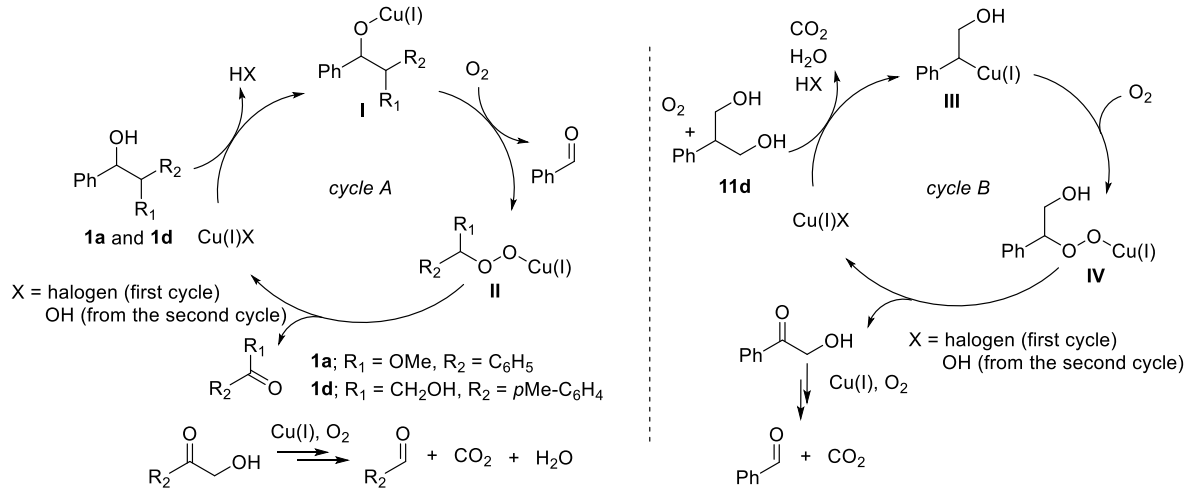
Scheme 1. Control Experiments



Scheme 2. Plausible Catalytic Cycles for the Cleavage of 1a, 1d, and 11d



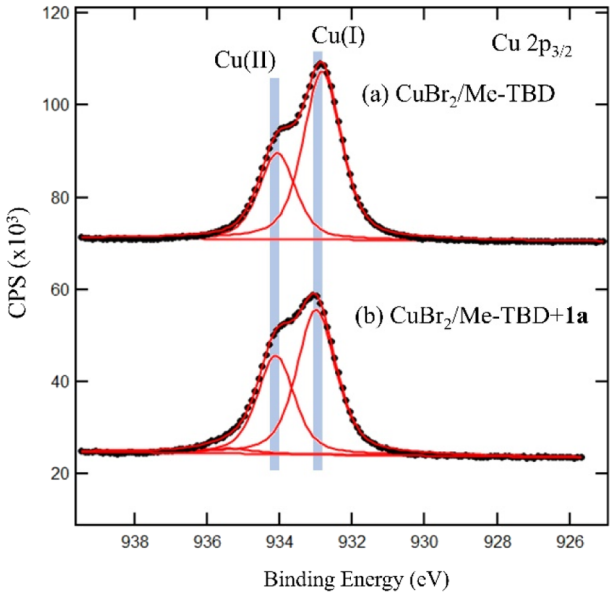


Figure 2. XPS spectra of (a) $CuBr_2$ and Me-TBD and (b) $CuBr_2$, Me-TBD, and **1a**.

similar Cu $2p_{3/2}$ binding energies of the Cu(I) and Cu(0) oxidation states (Figure S2). The relative intensity of Cu(I) to that of Cu(II) differs between (a) and (b) in Figure 2, but higher Cu(I)-to-Cu(II) ratio is maintained even after the reaction of **1a** (b), suggesting the dominant role of Cu(I) in the catalytic cycle of the oxidative C−C cleavage of **1a**. Thus, both reactions (**1a** and **1d**) begin with the cleavage by Cu(I). A free hydroxy group coordinates with the copper catalyst to form intermediate **I**, which undergoes oxygen-mediated cleavage to afford benzaldehyde and copper-coordinated peroxide intermediate **II**.[54] Next, the fragmentation of **II** provides methyl benzoate along with Cu(I) regeneration (CuOH). In the case of **1d**, α-hydroxy ketones released from the cycle undergo decarboxylation to afford aldehydes.[50] Compound **11d** which does not include a secondary hydroxy group undergoes decarboxylation to form intermediate **III**, which is followed by copper-peroxide **IV** formation and fragmentation (cycle B).

3. CONCLUSIONS

We report the copper-catalyzed oxidative C−C cleavage of various alcohols, including lignin model compounds. The optimal copper catalyst was varied depending on the structure of the alcohols. $CuBr_2$/Me-TBD was efficient for vicinal dioxy compounds (β-alkoxy alcohols and 1,2-diols), whereas CuCl was valid with β-1 compounds and 1,2- and 1,3-diols. The yields of CuCl-catalyzed oxidative cleavage of β-1 compounds are somewhat lower than those of $CuBr_2$/Me-TBD-catalyzed cleavage of β-alkoxy alcohols. However, electron-rich β-1

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compounds abundant in lignin undergo oxidative cleavage with improved yields. The reaction mechanisms involving copper-(I)-catalyzed aerobic oxidative cleavage were presented based on XPS data. Compared to previously reported catalytic systems using large amounts of bases and showing good catalytic activities on a specific linkage, our catalysts can cleave the C−C bonds of β-alkoxy alcohols, 1,2-diols, 1,3-diols, and β-1 substrates without extra bases and elaborated ligands. This finding could be a general and useful tool for depolymerizing lignin, which possesses various linkages and bonds, to afford different aromatic feedstocks.

4. EXPERIMENTAL SECTION

4.1. Synthetic Procedure for the Synthesis of 1a−3a. Compounds **1a−3a** were known and prepared according to literature procedure.[48] 2-Methoxy-1, 2-diphenylethan-1-one (3.185 mmol), $Al(O^iPr)_3$ (0.956 mmol), and ^{i}PrOH (35.04 mmol) were dissolved in toluene (4.0 mL, 1.3 M) and stirred overnight at 50 °C. After reaction, the reaction mixture was cooled down, quenched with 1 N HCl, and extracted with ethyl acetate. The organic layer was washed with H_2O and evaporated in vacuo. The residue was purified by column chromatography (ethyl acetate: hexane) to afford **1a** as a white solid with 91% yield. Compounds **2a** and **3a** were obtained with 70 and 76% yields, respectively.

4.2. Synthetic Procedure for the Synthesis of 4a−7a. Copper oxide (5.0 mmol) and iodine (5.0 mmol) were added to a well-stirred solution of 1-(4-chlorophenyl)-2-phenylethan-1-one (5.0 mmol) in MeOH (0.25 M). The mixture was refluxed overnight. Then, the mixture was filtered. Iodine was removed by $Na_2S_2O_3$ solution. The mixture was extracted with ethyl acetate, and the organic layer was dried with Na_2SO_4. The residue was further purified by column chromatography (ethyl acetate: hexane) using silica gel to form 1-(4-chlorophenyl)-2-methoxy-2-phenylethan-1-one as a white solid with 60% yield. 1-(4-Chlorophenyl)-2-methoxy-2-phenylethan-1-one (3.4 mmol) and $NaBH_4$ (5.1 mmol) were dissolved in MeOH (0.13 M) and stirred for 4 h at room temperature. The solution was washed with aqueous NH_4Cl and extracted with ethyl acetate. The organic phase was extracted and dried with $MgSO_4$. The product was purified by column chromatography (ethyl acetate: hexane) to afford **4a** as a colorless oil with 69% yield. Compounds **5a**, **6a**, and **7a** were obtained via reduction of ketone compounds with yields of 89, 81, and 99%, respectively.

*4.2.1. 1-(4-Chlorophenyl)-2-methoxy-2-phenylethan-1-ol (**4a**).* ^{1}H NMR (DMSO-d_6, 600 MHz, diastereomeric mixture): δ 7.32−7.18 (m, 8H), 7.04 (m, 1H), 5.52 (d, J = 4.1 Hz, 0.23H), 5.42 (d, J = 5.4 Hz, 0.77H), 4.69 (dd, J = 6.6, 4.2 Hz, 0.23H), 4.65 (t, J = 5.5 Hz, 0.77H), 4.25 (d, J = 6.6 Hz, 0.23H), 4.20 (d, J = 6.0 Hz, 0.77H), 3.15 (s, 0.69H), 3.03 (s, 2.3H). ^{13}C NMR (DMSO-d_6, 151 MHz, diastereomeric mixture): δ 142.01, 140.82, 139.08, 138.37, 131.28, 131.22, 129.04, 128.98, 127.97, 127.73, 127.65, 127.38, 127.23, 87.62, 87.02, 75.45, 74.94, 56.57, 56.36. HRMS (FAB, $[M - H_2O + H]^+$) calcd for $C_{15}H_{14}ClO$, 245.0733; found, 245.0736. FTIR (neat) 3436, 2932, 1901, 1089, 700 cm^{-1}.

*4.2.2. 2-Methoxy-1-(4-methoxyphenyl)-2-phenylethan-1-ol (**5a**).* ^{1}H NMR (DMSO-d_6, 600 MHz, diastereomeric mixture): δ 7.30−7.15 (m, 6.64H), δ 7.01 (d, J = 7.2 Hz, 0.18H), 6.95 (d, J = 8.4 Hz, 0.18H), 6.82 (m, 1.82H), 6.69 (d, J = 9.0 Hz, 0.18H), 5.26 (d, J = 4.2 Hz, 0.09H), 5.17 (d, J = 4.8 Hz, 0.91H), 4.60 (dd, J = 4.2 Hz, 7.2 Hz, 0.09H), 4.57 (dd, J = 4.8 Hz, 6.0 Hz, 0.91H), 4.20 (d, J = 6.6 Hz, 0.09H), 4.16 (d, J = 6.0 Hz, 0.91H), 3.72 (s, 2.73H), 3.66 (s, 0.27H), 3.14 (s, 0.27H), 3.01 (s, 2.73H). ^{13}C NMR (DMSO-d_6, 151 MHz): δ 158.2, 139.5, 135.1, 128.3, 128.0, 127.6, 127.2, 112.8, 87.4, 75.2, 56.3, 54.9. HRMS (FAB, $[M - H_2O + H]^+$) calcd for $C_{16}H_{17}O_2$, 241.1229; found, 241.1228. FTIR (neat) 3454, 2934, 2057, 1099 cm^{-1}.

*4.2.3. 1-(3,4-Dimethoxyphenyl)-2-methoxy-2-phenylethan-1-ol (**6a**).* ^{1}H NMR (DMSO-d_6, 600 MHz, diastereomeric mixture): δ 7.27−7.20 (m, 4.78H), δ 7.03−7.02 (m, 0.22H), 6.83 (d, J = 8.4 Hz, 0.89H), 6.78−6.74 (m, 1.78H), 6.71 (d, J = 8.4 Hz, 0.11H), 6.58 (dd, J = 1.2 Hz, 8.4 Hz, 0.11H), 6.51 (d, J = 2.4 Hz, 0.11H), 5.30 (d, J = 4.2 Hz, 0.11H), 5.19 (d, J = 4.8 Hz, 0.89H), 4.60 (t, J = 5.4 Hz, 0.89H), 4.58 (t, J = 3.6 Hz, 0.11H), 4.20 (d, J = 7.8 Hz, 0.11H), 4.18 (d, J = 6.0 Hz, 0.89H), 3.72 (s, 2.67H), 3.66 (s, 0.33H), 3.64 (s, 2.67H), 3.53 (s, 0.33H), 3.16 (s, 0.33H), 3.04 (s, 2.67H). ^{13}C NMR (DMSO-d_6, 151 MHz): δ 147.9, 147.7, 139.4, 135.5, 128.1, 127.5, 127.2, 119.3, 111.0, 110.9, 87.3, 75.3, 56.3, 55.4, 55.3. HRMS (FAB, $[M - H_2O + H]^+$) calcd for $C_{17}H_{19}O_3$, 271.1334; found, 271.1336. FTIR (neat) 3440, 2908, 1944, 1136 cm^{-1}. mp 74 °C.

*4.2.4. 2-Methoxy-1-phenyl-2-(p-tolyl)ethan-1-ol (**7a**).* ^{1}H NMR (DMSO-d_6, 600 MHz, diastereomeric mixture): δ 7.25 (m, 4.15H), 7.14−7.11 (m, 0.51H), 7.09 (s, 3.32H), 7.05 (m, 0.34H), 6.99 (d, J = 7.8 Hz, 0.34H), 6.90 (d, J = 7.2 Hz, 0.34H), 4.62 (d, J = 6.6 Hz, 0.17H), 4.60 (d, J = 7.2 Hz, 0.83H), 4.19 (d, J = 7.2 Hz, 0.17H), 4.16 (d, J = 6.6 Hz, 0.83H), 3.12 (s, 0.51H), 2.98 (s, 2.49H), 2.28 (s, 2.49H), 2.21 (s, 0.51H). ^{13}C NMR (DMSO-d_6, 151 MHz, diastereomeric mixture): δ 143.18, 141.81, 136.32, 136.28, 135.61, 128.21, 128.00, 127.73, 127.44, 127.32, 127.25, 127.23, 126.77, 87.84, 87.11, 76.43, 75.66, 56.38, 56.17, 20.77, 20.72. HRMS (FAB, $[M - H_2O + H]^+$) calcd for $C_{16}H_{17}O$, 225.1279; found, 225.1281. FTIR (neat) 3431, 2929, 1899, 1103 cm^{-1}. mp 90 °C.

4.3. Synthetic Procedure for the Synthesis of 1d−7d. Compounds **2d**, **4d**, and **6d** were known and prepared according to literature procedure.[49,50] 1,2-Diaryl-1-ethanone (2 mmol), formaldehyde (2.15 mmol), and K_2CO_3 (3.65 mmol) were dissolved in acetone (0.185 M) and stirred for 3 h at room temperature. The solid was filtered and extracted with ethyl acetate. The product was purified by column chromatography (ethyl acetate/hexane) with 98% yield. 3-Hydroxy-1,2-diphenyl-1-propanone (1.97 mmol) and $NaBH_4$ (2.167 mmol) were dissolved in MeOH (0.13 M) and stirred for 3 h at room temperature. The solution was washed with aqueous NH_4Cl and extracted with ethyl acetate. The organic phase was extracted and dried with $MgSO_4$. The product was purified by column chromatography (ethyl acetate/hexane) to afford **1d** as a white solid with 80% yield. Compounds **2d**, **3d**, **4d**, **5d**, **6d**, and **7d** were obtained via the reduction of ketone compounds with yields of 63, 93, 67, 93, 92, and 77%, respectively.

*4.3.1. 1-Phenyl-2-(p-tolyl)propane-1,3-diol (**1d**).* ^{1}H NMR (DMSO-d_6, 600 MHz): δ 7.20 (t, J = 7.5 Hz, 2H), 7.13 (m, 3H), 6.96 (m, 4H), 5.13 (d, J = 4.8 Hz, 1H), 4.97 (t, J = 4.8 Hz, 1H), 4.49 (t, J = 5.1 Hz, 1H), 3.71−3.68 (m, 1H), 3.49−3.46 (m, 1H), 2.85 (dd, J = 6.6 Hz, 12 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 145.1, 137.2, 134.5, 129.3, 127.9, 127.5, 126.3, 126.2, 72.0, 62.7, 55.2, 20.6. HRMS (FAB, $[M - H_2O + H]^+$) calcd for $C_{16}H_{17}O$, 225.1279; found, 225.1282. FTIR (neat) 3295, 2932, 1903 cm^{-1}. mp 132 °C.

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*4.3.2. 1-(4-Methoxyphenyl)-2-(p-tolyl)propane-1,3-diol (**3d**).* ^{1}H NMR (DMSO-d_6, 600 MHz) 7.05 (m, 2H), 6.97 (m, 4H), 6.77 (m, 2H), 5.01 (d, J = 4.8 Hz, 1H), 4.89 (t, J = 4.8 Hz, 1H), 4.43 (t, J = 5.1 Hz, 1H), 3.69 (s, 3H), 3.67−3.63 (m, 1H), 3.46−3.43 (m, 1H), 2.81 (q, J = 6.2 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (DMSO-d_6, 151 MHz): δ 157.8, 137.5, 137.1, 134.5, 129.3, 127.9, 127.3, 112.9, 71.8, 62.8, 55.3, 54.9, 20.7. HRMS (FAB, $[M - H_2O + H]^+$): calcd for $C_{17}H_{19}O_2$, 255.1385; found, 255.1387. FTIR (neat) 3398, 2889, 1981 cm^{-1}. mp 112 °C.

*4.3.3. 1-(3,4-Dimethoxyphenyl)-2-(p-tolyl)propane-1,3-diol (**5d**).* ^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.97−6.91 (m, 4H), 6.76−6.58 (m, 3H), 5.02 (d, J = 4.2 Hz, 1H), 4.87 (t, J = 5.1 Hz, 1H), 4.42 (t, J = 5.4 Hz, 1H), 3.69−3.67 (m, 1H), 3.66 (s, 3H), 3.54 (s, 3H), 3.48−3.45 (m, 1H), 2.79 (dd, J = 6.9 Hz, 11.7 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (DMSO-d_6, 151 MHz): δ 147.99, 147.32, 137.60, 137.54, 134.58, 129.46, 127.93, 118.25, 110.93, 110.32, 72.10, 62.77, 55.42, 55.39, 55.14, 20.67. HRMS (FAB, $[M - H_2O + H]^+$): calcd for $C_{18}H_{21}O_3$, 285.1491; found, 285.1489. FTIR (neat) 3298, 2961, 1903 cm^{-1}. mp 115 °C.

*4.3.4. 2-(3,4-Dimethoxyphenyl)-1-(2,3,4-trimethoxyphenyl)propane-1,3-diol (**7d**).* ^{1}H NMR (DMSO-d_6, 600 MHz): δ 6.73 (d, J = 7.2 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 6.59−6.57 (m, 3H), 5.18 (t, J = 4.8 Hz, 1H), 4.85 (d, J = 4.2 Hz, 1H), 4.43 (t, J = 5.1 Hz, 1H), 3.81 (s, 3H), 3.76−3.73 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 3.60 (s, 3H), 3.56 (m, 1H), 2.86 (dd, J = 6.9 Hz, 11.7 Hz, 1H). ^{13}C NMR (DMSO-d_6, 151 MHz): δ 151.7, 149.8, 147.6, 147.0, 140.9, 133.0, 130.5, 121.9, 121.4, 113.7, 111.1, 107.1, 66.4, 63.0, 60.7, 60.2, 55.7, 55.4, 55.2, 53.8. HRMS (FAB, $[M - H_2O + H]^+$): calcd for $C_{20}H_{25}O_6$, 361.1651; found, 361.1648. FTIR (neat) 3466, 2937, 1994 cm^{-1}.

4.4. Synthetic Procedure for the Synthesis of 9d−10d. Compounds **9d** and **10d** were known and prepared according to literature procedure.[51,55] Benzoin (6 mmol) and $NaBH_4$ (9.0 mmol) were dissolved in MeOH (0.13 M) and stirred for 1 h at 0 °C. The solution was washed with aqueous NH_4Cl and extracted with ethyl acetate. The organic phase was extracted and dried with anhydrous Na_2SO_4. The product was purified by column chromatography (ethyl acetate: hexane) to afford **9d** as a white solid with 99% yield. The yield of **10d** was 99%.

4.5. Catalytic Reaction Procedure of Tables 1 and 2. The mixture of **1a** (0.25 mmol), copper catalyst (indicated amounts), and additives (indicated amounts) in DMSO (0.36 M) was allowed to react at 120 °C for 16 h under 1 atm of oxygen.

4.6. Catalytic Reaction Procedure of Tables 3 and 4. The mixture of **1d** (0.25 mmol), copper catalyst (indicated amounts), and additives (indicated amounts) in DMSO (0.36 M) was allowed to react at the indicated temperature for the given time under 1 atm of oxygen.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04162.

Experimental procedures of catalytic reactions, representative NMR spectra of the reaction mixture for the quantitative analysis of yields using an internal standard, and XPS data (PDF)

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Notes

The authors declare no competing financial interest.

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