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Metallo-Deuteroporphyrin as a Biomimetic Catalyst for the Catalytic Oxidation of Lignin to Aromatics

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A series of metallo-deuteroporphyrins derived from hemin were prepared as models of the cytochrome P450 enzyme. With the aid of the highly active Co^{II} deuteroporphyrin complex, the catalytic oxidation system was applied for the oxidation of several lignin model compounds, and high yields of monomeric products were obtained under mild reaction conditions. It was found that the modified cobalt deuteroporphyrin that has no substituents at the *meso* sites but does have the disulfide linkage in the propionate side chains at the β sites exhibited much higher activity and stability than the synthetic tetraphenylporphyrin. The changes in the propionate side chains can divert the reactivity of cobalt deuteroporphyrins from the typical C–C bond cleavage to C–O bond cleavage. Furthermore, this novel oxidative system can convert enzymolysis lignin into depolymerized products including a significant portion of well-defined aromatic monomers.

Introduction

As a result of the depleting fossil fuel reserves and increasing greenhouse gas emissions, the exploration of feasible pathways for the conversion of abundant and renewable biomass into clean fuels and high-value-added chemicals to supplement or gradually replace the petroleum-based industry is highly desirable.[1] In this context, lignocellulosic biomass is a promising candidate to substitute fossil resources in some industrial processes.[2] The chemical conversion of cellulose and hemicellulose has been extensively studied,[3] whereas that of lignin remains uncommon despite the fact that it is the second most abundant terrestrial polymer after cellulose on earth and constitutes up to 15–30% of the weight and 40% of the energy content of lignocellulosic biomass. At present, plenty of lignin is discharged into paper-making black liquor or burned as a low-calorific-value fuel, which results in enormous resource waste and serious environmental pollution. The other uses of lignin remain limited mainly to low-value products,[4] such as surfactants, dispersants, or emulsifiers,[5] phenolic resins,[6] epoxy resins,[7] carbon fibers,[8] thermoplastic films,[9] and polyurethane foams.[10]

The extraction of more value from lignin is increasingly recognized as crucial to the economic viability of integrated biorefineries.[11] Recently, lignin has received great attention as a sustainable precursor for basic aromatic building blocks that are currently obtained from fossil-based feedstocks,[12] because it is the only large-volume renewable feedstock that is composed of aromatics. Moreover, the utilization of lignin does not compete with food production, an ethical problem often encountered with renewable resources.[13] However, lignin is resistant to normal chemical or biochemical processes for breaking down linkages among the structural units, as a result of its huge molecular weight and robust 3D amorphous network structure.[14] Generally, there are five major strategies for lignin depolymerization: pyrolysis,[15] hydrolysis,[16] enzymolysis,[17] hydrogenolysis,[18] and oxidation.[19] Among these, the oxidative depolymerization of lignin is a very promising way to go, because it leads to highly functionalized monomeric or oligomeric products, which can be used directly as fine chemicals or as platform chemicals.[12,20] However, the low conversions and broad product distributions (usually $<20\%$ yield of well-defined aromatic monomers) are the main problems for the oxidative depolymerization of lignin. The incorporation of catalytic technologies into lignin oxidative depolymerization is a possible option for valorizing the feedstock as a renewable raw material for aromatic chemical production, and the key to achieving this goal is the development of efficient and robust catalysts.

Inspired by the peroxidase degradation of lignin (for example, lignin peroxidase, manganese peroxidase),[21] the application of synthetic metalloporphyrins as biomimetic catalysts for lignin oxidative depolymerization attracted a significant amount of interest in the past.[22] However, there has been very little recent progress in this area. The structures and abbreviated names of representative synthetic metalloporphyrins are given in Figure 1. As can be seen, nearly all of the metalloporphyrins were based on the structure of synthetic *meso*-tetraphenylporphyrin (TPP). These biomimetic catalysts can yield

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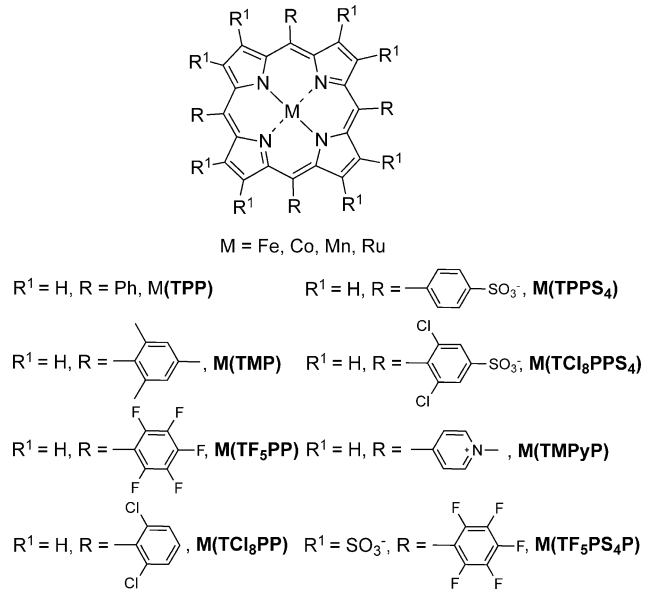


Figure 1. Structures and abbreviated names of representative synthetic metalloporphyrins.

highly oxidized metal–oxo species upon reaction with the oxidant species. However, there are still several drawbacks of using some of these porphyrin complexes from a practical point of view: 1) they are usually unstable under oxidation conditions as a result of their self-destruction or the formation of inactive μ-oxo dimers;[23] 2) it is usually difficult to maintain the aromaticity of the degradation product because of the aromatic nuclei oxidation;[22] and 3) the catalytic potential of the porphyrin complexes still needs to be improved. In view of the aforementioned inadequacies of existing metalloporphyrins, recent significant advances in biomimetic catalysis prompted us to reconsider the metalloporphyrin catalysts and provided an opportunity of designing more reactive and stable catalysts for lignin depolymerization.

Recently, the cytochrome P450 enzyme has drawn considerable attention as a mild and highly efficient catalyst for various organic transformations.[24] Heme is usually considered as the prosthetic group of the cytochrome P450 enzyme.[25] Metallo-deuteroporphyrin, which is derived from natural hemin, is an ideal candidate to mimic the P450 enzyme as a result of its excellent stability, high accessibility, and close relationship to the naturally occurring hemes. To the best of our knowledge, there is no report for the catalytic oxidation of lignin with metallo-deuteroporphyrins as catalysts. We envisaged that the use of metallo-deuteroporphyrins would properly address the efficiency issues in porphyrin catalysts by providing a stable catalyst with reasonably high activity. In a continuation of our efforts to develop new methods for catalytic biomass conversion and synthetic chemistry,[26] we report herein a novel and efficient biomimetic catalytic oxidation system for the oxidation of lignin model compounds and real lignin.

Results and Discussion

Evaluation of the metallo-deuteroporphyrin catalysts

It is well known that lignin is a highly branched macromolecule consisting of *p*-hydroxybenzene, guaiacyl, and syringyl phenylpropane units cross-linked by C–C bonds (β-1, β-5, β-β, 5-5′) and C–O bonds (4-O-5, α-O-4, β-O-4), of which the β-O-4 bonds account for more than 50% of the linkages in most plants.[27] Therefore, initial experiments were carried out with 2-(2-methoxyphenoxy)-1-phenylethanol (**1**) as a simple non-phenolic β-O-4-type model substrate to check the efficiency of the deuteroporphyrin catalysts. Metallo-deuteroporphyrins M(DPDME), M(DPNH$_2$), M(DPBr$_2$), M(DPCl$_2$) and disulphide-derivatized deuteroporphyrins M(DPS$_2$) and M(DPCys) (Figure 2),

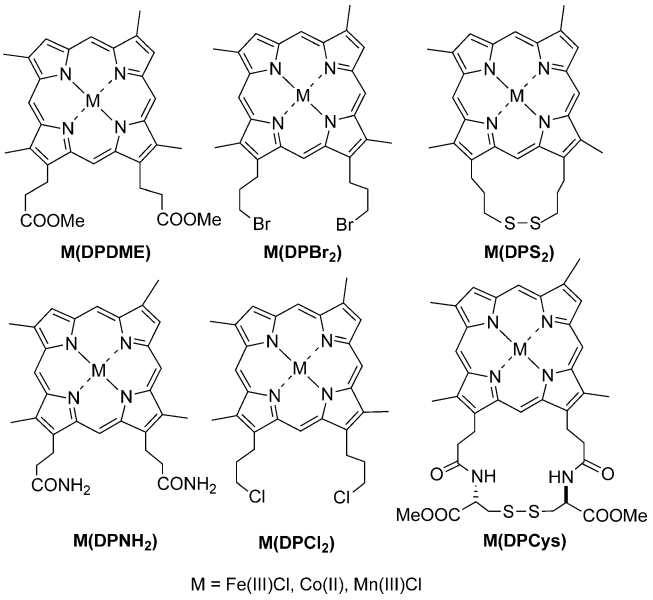


Figure 2. The structures and abbreviated names of the metallo-deuteroporphyrins used in this study.

in which M represents Mn^{III}Cl, Co^{II}, or Fe^{III}Cl, were synthesized from protohemin by using our previous methods (for details, see the Supporting Information).[28] We first examined the effect of the oxidant with Fe(DPDME) as the catalyst. The active oxidant, an iron–oxo-complex radical cation structurally similar to that involved in the enzymatic reactions, is usually formed by reaction of the Fe^{III}–porphyrin with various oxygen donors, such as hydrogen peroxide, *tert*-butylhydroperoxide (TBHP), *m*-chloroperoxybenzoic acid, sodium hypochlorite, iodosylbenzene, magnesium monoperoxyphthalate, and molecular oxygen plus a reducing agent. The choice of the oxygen donor depends on the substrate structure, the catalyst, and the reaction medium. Previous research on the oxidation of lignin usually employed H_2O_2 or TBHP as the oxidant.[22] The results indicated that both are not suitable under the present system (Table 1, entries 1 and 2). The use of PhIO as the oxidant did not show any improvement despite the fact that it is often used as an oxygen donor in the porphyrin catalysis

Table 1. Optimization studies for the catalytic oxidation of lignin model compound **1**.[a]

Entry	Oxidant	Catalyst	Solvent	T [°C]	Conv.[b] [%]
1	H_2O_2	Fe(DPDME)	H_2O	60	<10
2	TBHP	Fe(DPDME)	H_2O	60	<10
3	PhIO	Fe(DPDME)	H_2O	60	16
4	oxone	Fe(DPDME)	H_2O	60	29
5	oxone	Mn(DPDME)	H_2O	60	37
6	oxone	Co(DPDME)	H_2O	60	71
7	oxone	Co(DPNH$_2$)	H_2O	60	78
8	oxone	Co(DPBr$_2$)	H_2O	60	54
9	oxone	Co(DPCl$_2$)	H_2O	60	63
10	oxone	Co(DPS$_2$)	H_2O	60	89
11	oxone	Co(DPCys)	H_2O	60	96
12[c]	oxone	Co(DPCys)	H_2O	60	91
13[d]	oxone	Co(DPCys)	H_2O	RT	90
14	oxone	Co(TPP)	H_2O	RT	48
15	oxone	Co(DPCys)	MeOH	RT	56
16	oxone	Co(DPCys)	CH_2Cl_2	RT	51
17	TBAOX	Co(DPCys)	MeOH	RT	58
18	oxone	Co(DPCys)	MeCN	RT	55
19	oxone	Co(DPCys)	MeOH/H_2O	RT	100
20[e]	oxone	Co(DPCys)	MeOH/H_2O	RT	88
21[f]	oxone	Co(DPCys)	MeOH/H_2O	RT	91

[a] Reactions were performed by using **1** (0.5 mmol), catalyst (0.5 mol%), and oxidant (2.5 mmol) in H_2O (10 mL) for 8 h unless otherwise noted. [b] The conversion was determined by GC analysis. [c] Co(DPCys) (0.1 mol%) was used. [d] This reaction was performed at room temperature for 15 h. [e] Pyridine (0.05 mmol) was added. [f] Imidazole (0.05 mmol) was added.

system (Table 1, entry 3).[29] Other oxidants, such as urea hydrogen peroxide, $K_2S_2O_8$, peracetic acid, or *m*-chloroperoxybenzoic acid were also tested for this reaction; however, all of them were unsatisfactory (data not shown). Recently, oxone ($2\,KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) has been used extensively for a variety of chemical transformations and particularly as a reagent in numerous oxidation reactions as a result of its nontoxic nature, affordability, and safety profile.[30] We were very pleased to find that noticeable conversion was achieved with oxone as the oxidant (Table 1, entry 4). In the control experiments, there was no product formation in the absence of the deuteroporphyrin catalyst or oxone. This high activity of oxone probably occurs because the peroxidic O–O bond is more unsymmetrical in oxone than in H_2O_2 and because SO_4^{2-} is a better leaving group than HO^-; thus, the heterolytic cleavage step leading to a high-valence metal–oxo species is highly favored for oxone.[22k] A similar phenomenon has also been observed in DNA breaks catalyzed by (bleomycin)Fe^{III} and cationic metalloporphyrins.[31] Beyond that, the acidic character of oxone may be another important reason for its high activity (see below), because it will favor the cleavage of inactive μ-oxo metallodeuteroporphyrin dimers, which are known to be formed in the oxidation of porphyrin complexes and represent a dead end in the catalytic cycle.

With the aim of finding an appropriate catalyst for lignin catalytic oxidative depolymerization, we then evaluated the catalytic performance of other deuteroporphyrin catalysts (Table 1, entries 4–6). As shown in Table 1, the conversion of **1** varies markedly with the change of the central metal atom. Co^{II}(DPDME) exhibited the highest activity in the series of M(DPDME). If the central metal atom was Fe or Mn, **1** was oxidized with lower conversion, and the following order of reactivity was observed: Co(DPDME) > ClMn(DPDME) > ClFe(DPDME). This phenomenon may be caused by the different redox potentials of the deuteroporphyrin catalysts; the half-wave potential ($E_{1/2}$) values (versus the SCE in DMF) of these catalysts are in the order: Co(DPDME) (−803.7 mV) > ClMn(DPDME) (−902.8 mV) > ClFe(DPDME) (−915.0 mV).[28] There is a linear relationship between the catalytic activity and the half-wave potential of M(DPDME); this is agreement with earlier observations that the catalytic activity of metalloporphyrins increases with an increase in the redox potential.[32] Also, there is another possibility that ClMn(DPDME) and ClFe(DPDME) both need to drop the axial-ligand Cl group before combination with the oxygen donor to produce the highly oxidized metal–oxo complexes. Seen in this way, Co(DPDME), without the axial-ligand Cl group, is prone to be activated. The split of the axial ligand in the initiation step of the reaction has been proven for ClMn(TTP) porphyrin[32c] and (HO)Fe^{III} porphyrin.[33]

Besides the central metal atom of the complexes, the electronic and geometric effects of the substituents are the other important factors that affect the catalytic activity of deuteroporphyrins. It is well known that the introduction of electron-withdrawing substituents such as F, Cl, Br, or SO_3^- groups into metalloporphyrins increases the redox potential of porphyrin system and hence increases the catalytic activity. Depending on the size of the substituent, it may also exert a steric bulk influence. On the basis of these considerations, a series of Co–deuteroporphyrins with electron-withdrawing groups [Co(DPBr$_2$), Co(DPCl$_2$)], and electron-donating groups [Co(DPDME), Co(DPNH$_2$), Co(DPS$_2$)] on the propionate side chains were synthesized and tested for the reaction. The order of catalytic activity of these deuteroporphyrins is as follows: Co(DPS$_2$) > Co(DPNH$_2$) > Co(DPDME) > Co(DPCl$_2$) > Co(DPBr$_2$) (Table 1, entries 6–10). To our surprise, the order of the catalytic activity is nearly opposite to the earlier observations. The catalytic activities of Co(DPBr$_2$) and Co(DPCl$_2$) were found to be much lower than those of the deuteroporphyrins containing electron-donating groups [Co(DPNH$_2$), Co(DPDME)]. Apparently, the character of electronic effect does not play a pronounced influence on the catalytic properties of the deuteroporphyrins. Based on what has been mentioned above, the catalytic activity of the metalloporphyrins increases with an increase in the redox potential. However, the half-wave potential ($E_{1/2}$) values of these catalysts are in the order: Co(DPNH$_2$) (−711.3 mV) > Co(DPCl$_2$) (−778.8 mV) > Co(DPBr$_2$) (−782.6 mV) > Co(DPS$_2$) (−786.6 mV) > Co(DPDME) (−803.7 mV). No obvious correlation between the two orders is found. If we compare only Co(DPBr$_2$) and Co(DPCl$_2$), they are still consistent with the above rule. We speculate that this simple linear relation just exists within the same character of structure, such as Co(DPBr$_2$) and Co(DPCl$_2$). For other deuteroporphyrins bearing various substituents, the catalytic efficiency does not correlate with the reduction potential. Thus, we be-

lieve that the groups on the propionate side chains play an important role in the reaction. Recently, the effect of the propionate groups in tuning the heme electronic properties and ligand binding in cytochrome P450 monooxygenase has been reported.[34] In accordance with that report, the electron transfer (spin delocalization effect) between the metal center, the deuteroporphyrin system, and the propionate groups of the present Co–deuteroporphyrin is suggested in Figure 3. This intramolecular electron-transfer effect will induce delocalization of the spin density in the active high-valence metal–oxo species, which can be used to explain the high catalytic activity of Co(DMDPE). For $Co(DPNH_2)$ and $Co(DPS_2)$, the greater catalytic activity is probably because the S–S and NH_2 groups on the propionate side chains both have unpaired electrons that are prone to bind the cobalt in another deuteroporphyrin core as axial ligands by forming an intermolecular interaction, and this coordination mode would be responsible for the high catalytic activity of $Co(DPS_2)$ and $Co(DPNH_2)$. Such similar coordination modes have been recently demonstrated for Mn^{III}–aminophenylporphyrins and Zn^{II}–aminophenylporphyrins.[35]

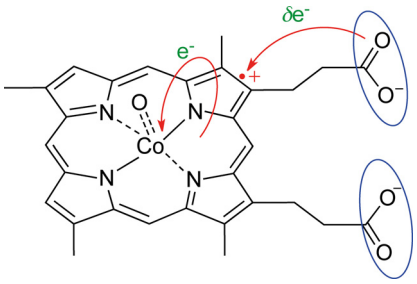


Figure 3. Intramolecular electron transfer from the propionate lone pairs into the deuteroporphyrin system and from the deuteroporphyrin system into the Co metal center.

A significant disadvantage of porphyrin complexes is that they are subject to oxidation degradation in strong oxidizing media, which is the main obstacle to their practical application. In contrast to the central metal atom and the electronic and geometric effects, little attention has been paid to the stability of porphyrins during the oxidation process. The stability of Co(TPP), $Co(DPS_2)$, Co(DPDME), and $Co(DPNH_2)$ was studied in the presence of H_2O_2 (1:100 molar ratio of catalyst to H_2O_2) in MeOH solvent, and the extent of degradation of the catalyst was measured through the change in absorbance at the Soret band of the Co–deuteroporphyrin in the UV/Vis spectrum. As shown in Table 2, the stability of the catalysts is in the order: $Co(DPS_2) > Co(DPNH_2) > Co(DPDME)$. For the purpose of comparison, the traditional Co(TPP) was also treated to the same conditions. The results indicate that approximately 82% of Co(TPP) was degraded 5 h after the addition of H_2O_2. Under the same conditions, only 31% of $Co(DPS_2)$ had been degraded. Interestingly, although the electronegativity of the S–S group was lower than that of OCH_3 and NH_2 groups, $Co(DPS_2)$ is more stable than Co(DPDME) and $Co(DPNH_2)$. Apparently, the groups on the propionate side chains of $Co(DPS_2)$ form a closed ring that contributes to the stability of the Co–deuteroporphyrin toward oxidative degradation.

Table 2. Degradation of Co–deuteroporphyrins in the presence of H_2O_2.[a]

Entry	Catalyst	Soret band [nm]	Degradation [%]
1	Co(DPDME)	390	66
2[b]	$Co(DPNH_2)$	415	56
3	$Co(DPS_2)$	391	31
4	Co(TPP)	410	82
5	Co(DPCys)	397	19

[a] Reactions were performed by using catalyst:H_2O_2 in a 1:100 molar ratio in MeOH at room temperature for 5 h. [b] The $Co(DPNH_2)$ was dissolved in DMF.

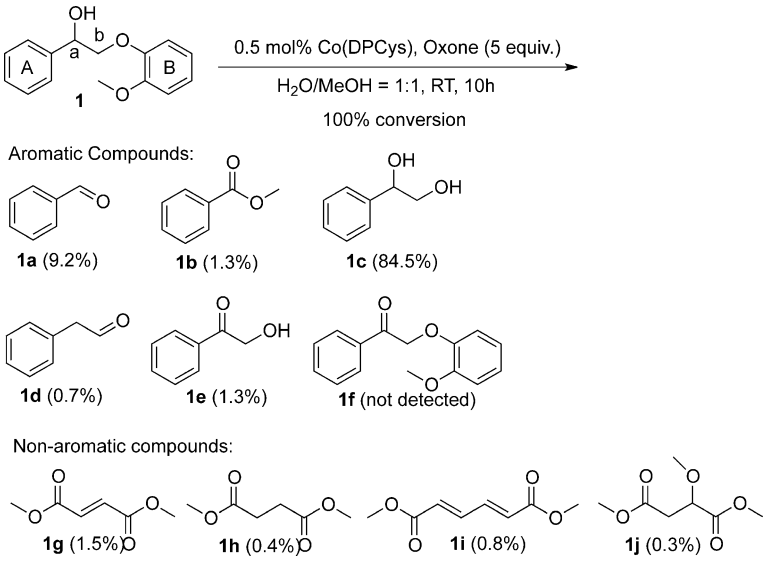
Thus, we conclude that the substitution of the propionate side chains acts in a double role, both to affect the electron transfer and to improve the stability. These results inspired us to develop a more efficient catalyst, which has both NH_2 and S–S groups on the propionate side chains and forms the closed ring to enhance the stability and catalytic activity of the deuteroporphyrin. Based on the observations, Co(DPCys) was synthesized and tested for the reaction. As expected, Co(DPCys) exhibited a much higher stability among the Co–deuteroporphyrins (Table 2, entry 5), and we were very pleased to find that Co(DPCys) shows excellent catalytic activity; the conversion of **1** was 96% (Table 1, entry 11). With regard to the Co(DPCys) dosage, it was possible to decrease the amount of Co(DPCys) to as low as 0.1 mol% without a significant loss in catalytic efficiency (Table 1, entry 12). Notably, the reaction can proceed smoothly even at room temperature as a result of the excellent catalytic activity of Co(DPCys), although a longer reaction time was required (Table 1, entry 13). Under the same conditions, Co(TPP) was also applied for the purpose of comparison; unfortunately, the conversion was much lower (Table 1, entry 14), which clearly demonstrates the superior catalytic activity of Co(DPCys).

Interestingly, the nature of the solvent plays an important role in the present system. Co(DPCys) has good solubility in MeOH or CH_2Cl_2; however, the use of MeOH or CH_2Cl_2 as solvents led to poor conversions (Table 1, entries 15 and 16), which is probably because of the poor solubility of oxone in these solvents. To check this point, tetra-*n*-butylammonium peroxymonosulfate (nBu_4NHSO_5, TBAOX, an organic salt of oxone), which is completely soluble in MeOH and CH_2Cl_2,[36] was synthesized and used in the reaction. However, the use of TBAOX instead of oxone was also unsuccessful (Table 1, entry 17), which clearly indicates that H_2O is essential for this reaction. The use of MeCN as the solvent also did not give a satisfactory result (Table 1, entry 18), despite the fact that it is usually an efficient solvent (or co-solvent) for metalloporphyrin-catalyzed oxidations, because it may act as an axial ligand and limit the formation of inactive μ-oxo dimers or influence the electron transfer between the substrate and the catalyst.[22h,j,23a,37] Further optimization revealed that a minimum of 20 vol% of H_2O was needed to ensure completely conversion of **1**, and a 50 vol% MeOH/H_2O mixture was the best solvent

for the reaction (Table 1, entry 19). Surprisingly, the addition of pyridine or imidazole to accelerate the reaction did not show any improvement, although they are usually used as axial ligands in metalloporphyrin-catalyzed oxidations (Table 1, entries 20 and 21).[38]

Oxidation of lignin model compounds

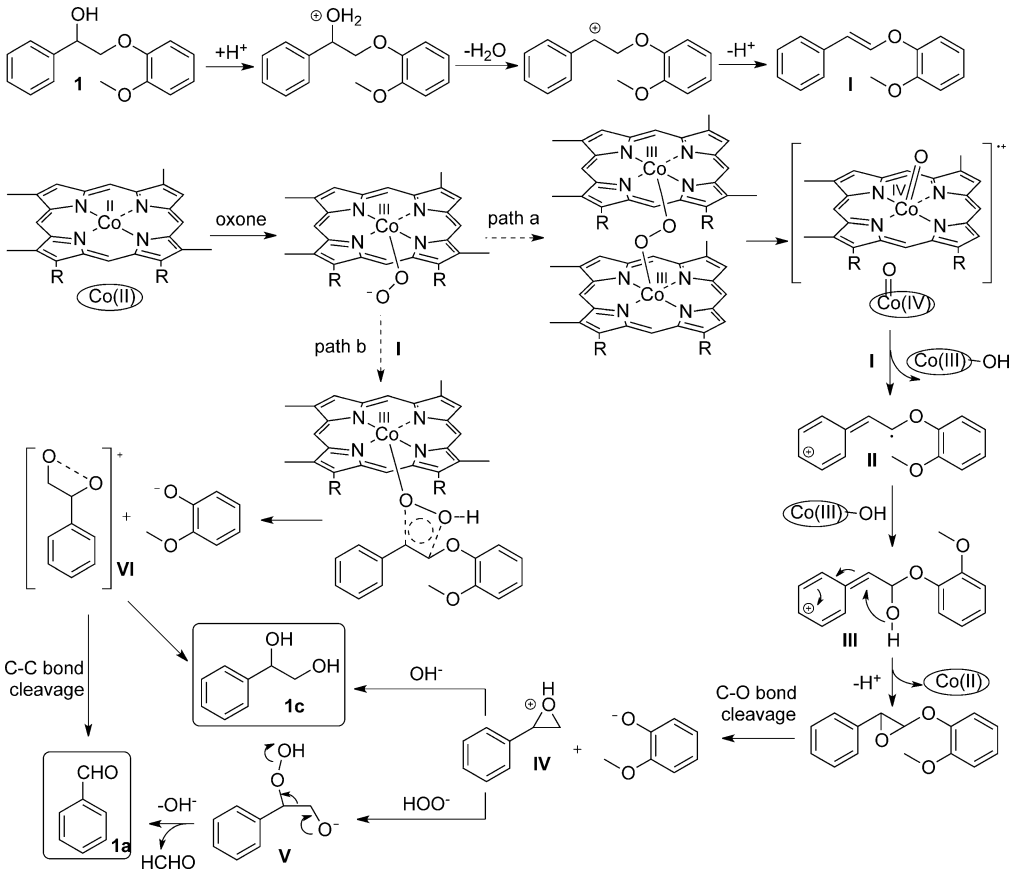
By maintaining all of the key parameters of the reaction, the optimal reaction conditions were applied for the catalytic oxidation of nonphenolic β-O-4-type lignin model compound **1**. Five aromatic compounds were identified after the reaction, with 1-phenyl-1,2-ethanediol (**1 c**) as the dominant product (Scheme 1). Aromatic compounds **1 a** and **1 b** are monoaromatic compounds derived from oxidative C_α–C_β bond breakage, and compounds **1 c**–**1 e** are formed by C_β–O bond breakage. Notably, the fact that **1 c** was identified as the dominant product derived from ring A through hydroxylation indicates that the major reaction pathway involves C_β–O bond cleavage. Diol formation has also been found to be the first step in the degradation of lignin in nature by the basidiomycete fungus *Phanerochaete chrysosporium*.[39] The formation of the diol was very meaningful, because it has great application potential for the synthesis of bio-polyols derived from lignin, which are suitable to replace or partly replace petroleum-based polyols in polyurethane foam synthesis.[40] Surprisingly, the compound 2-(2-methoxyphenoxy)-1-phenylethanone (**1 f**) was not identified after the oxidation; this is quite different from previous reports, in which keto ether **1 f** was often obtained as the major product generated from the oxidation of the benzylic C–OH bond without C–O or C–C bond cleavage;[19] this highlights the fact that Co(DPCys) is an effective catalyst for oxidative decoupling of the lignin model compound by selective cleavage of the C–O bond.



Scheme 1. Degradation of nonphenolic β-O-4-type lignin model compound **1**.

Interestingly, all of the aromatic compounds, which bear only one C6 ring structure, were all derived from ring A through C_β–O bond or C_α–C_β bond cleavage. Guaiacol, which is generated from ring B, was not detected after the oxidation. At the same time, a range of aliphatic dimethyl dicarboxylates, **1 g**–**1 j**, were detected after the oxidation. We speculate that these aliphatic compounds were obtained by the further oxidation of guaiacol. To verify this hypothesis, a confirmatory experiment was carried out with guaiacol as the substrate under the same reaction conditions. The result shows that most of the guaiacol was consumed during the reaction, and the same compounds were detected after the oxidation. A similar phenomenon was previously observed for the nitrogen-containing graphene[19c] or $CuFeS_2$[41] catalyzed oxidation of lignin with TBHP or H_2O_2 as the terminal oxidant. The current hypothesis favors the formation of *o*-quinone in situ by oxidation of guaiacol, which is further oxidized to open the ring and form the dicarboxylic acids. Under our system, the dicarboxylic acids were further transformed into the dimethyl dicarboxylates as a result of the presence of MeOH in the solvent mixture.

Generally, the metalloporphyrin catalysis is believed to involve an electron-transfer mechanism, and the reaction proceeds through two competing pathways that lead to either side-chain oxidation or aromatic nuclei oxidation.[11] For β-O-4-type lignin model compound **1**, the main products were usually aromatic aldehydes or acids by side-chain oxidation through C–C bond cleavage or quinones (or muconates) by aromatic nuclei oxidation. However, under the present Co–deuteroporphyrin catalytic system, 1-phenyl-1,2-ethanediol (**1 c**) was produced as the dominant product through C–O bond cleavage. A plausible mechanism for the present process is proposed in Scheme 2. Compound **1** is first protonated at the α-hydroxy group under the acidic reaction conditions; this is followed by dehydration to form a carbocation. Abstraction of a proton from the carbocation produces enol ether intermediate **I**.[42] Indeed, a trace amount of **I** was detected during the reaction by ^{1}H NMR spectroscopy and GC–MS analysis. Co(DPCys) is activated by oxone to form a cobalt–superoxo species, which can further react with Co(DPCys) to produce the μ-peroxo-bridged cobalt–deuteroporphyrin dimers and then gives the high-valence cobalt–oxo species [(Por)Co^{IV}=O] by homolytic cleavage of the O–O bond.[43] The activated (Por)Co^{IV}=O then abstracts a single electron from the aryl group of **I**, to form the C_β-centered cation radical **II**. The combination of **II** and the reduced (Por)Co^{III}–OH produces β-hydroxyquinonemethide cation ion intermediate **III** through

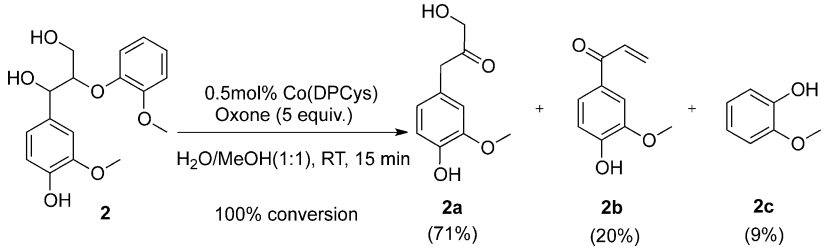


Scheme 2. Plausible mechanism for the oxidation of the simple nonphenolic β-O-4-type lignin model compound **1**.

hydroxyl transfer, and intermediate **III** immediately undergoes intramolecular nucleophilic attack of the resulting β-hydroxy group on the C_α atom with concomitant release of an H^+ ion to produce epoxide **IV** through C–O bond cleavage. Epoxide **IV** then undergoes noncatalytic hydrolysis through nucleophilic attack of a hydroxide anion to produce the final product 1-phenyl-1,2-ethanediol (**1 c**). Additionally, epoxide **IV** can also undergo nucleophilic attack by a hydroperoxide anion (HOO^-) to give the α-hydroperoxyl-β-hydroxide anion intermediate **V**, which immediately decomposes to give the product, benzaldehyde (**1 a**). Another route (path b in Scheme 2) is also possible, in which the Co–superoxo intermediate reversibly binds to the double bond of **I** and attacks the reaction site to produce intermediate **VI** through C–O bond cleavage,[44] which results in the formation of 1-phenyl-1,2-ethanediol (**1 c**) and benzaldehyde (**1 a**).

To check the substituent effects on the lignin model compound conversion, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol, which has an alkyl aryl ether moiety in positions 3 and 4 of the aromatic ring A, was then tested in the reaction. The result shows that the presence of the methoxy group dramatically increased the reactivity of the substrate, probably as a result of the electron-donating property of the methoxy group.[23a,37a] The reaction was finished in 20 min with 100% conversion; however, this substrate was converted into some unfavorable polymers. HPLC-MS shows that a series of high-molecular-weight compounds ($m/z > 500$) was formed during the reaction. The traditional products, such as 3,4-dimethoxybenzaldehyde through C_α–C_β bond cleavage and ketones through benzylic C–OH bond oxidation, were not detected after the reaction.

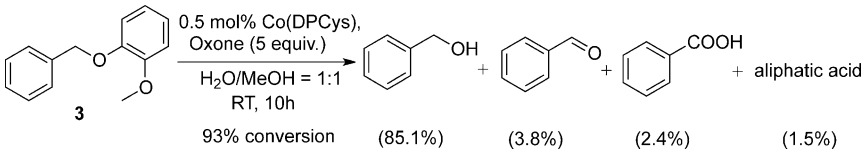
After the study of the nonphenolic β-O-4-type lignin model compound, we were then interested in investigating the reactivity of the present catalytic system with phenolic β-O-4-type lignin model compound **2** (Scheme 3). Phenolic groups are abundant in lignin; for example, spruce lignin is estimated to



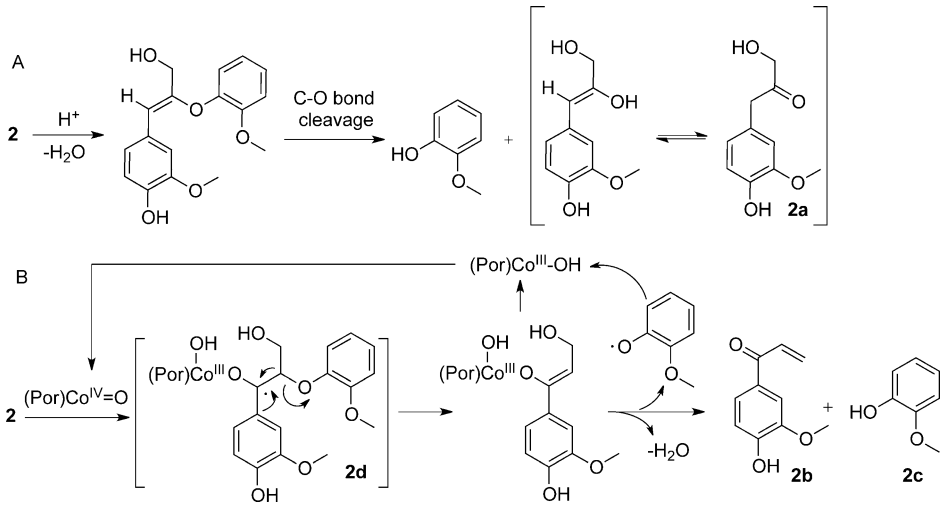
Scheme 3. Degradation of phenolic β-O-4-type lignin model compound **2**.

have 15–30 free phenolic groups per 100 phenylpropanoid units.[45] It has been reported that the phenolic group could influence the course of the reaction.[42a,46] As shown in Scheme 3, the presence of a phenolic hydroxy group dramatically increased the conversion rate, the reaction was finished in 15 min with 100% conversion, and three compounds were identified after the reaction. Compound **2a** was generally considered as the product of acid-catalyzed β-aryl ether cleavage, as illustrated in Scheme 4. However, in the control experiment, the starting material **2** was recovered with a yield of 91% in the absence of Co(DPCys), which clearly demonstrates the important catalytic effect of Co(DPCys) during the reaction. The formation of enone derivative **2b** was surprising. Cobalt complexes such as a Co Schiff base[47] or cobalt salt[48] have been reported to break oxidatively the C–C bonds in similar lignin model compounds, but cobalt-mediated C–O bond cleavage is very rare. Recently, Toste and co-workers investigated the reactivity of a series of vanadium complexes with a nonphenolic β-O-4-type lignin model compound, and a similar enone product was obtained through C–O bond cleavage.[49] An analogous one-electron transfer pathway was proposed for the formation of **2b**: the activated (Por)Co^{IV}=O first abstracts the benzylic hydrogen atom of **2**, to form the cobalt-bound ketyl radical intermediate **2d**, then elimination of the OH group from the resulting enolate produces the product **2b** (Scheme 4).

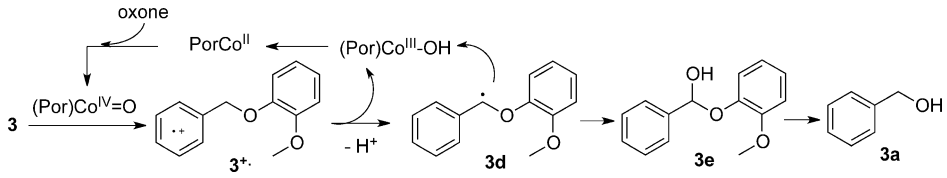
We were excited by this new reactivity for C–O bond cleavage, so the present catalytic system was then tested for another lignin model compound that contains the C–O bond. As shown in Scheme 5, the α-O-4-type lignin model compound 1-(benzyloxy)-2-methoxybenzene (**3**) underwent a smooth transformation to afford benzyl alcohol (**3a**, 85.1%) as the major product through C–O bond cleavage. The control experiment shows that no reaction occurred in the absence of the deuteroporphyrin catalyst (see Figure S6 in the Supporting Information). The reaction pathway can be inferred to be analogous to the above-proposed one. The activated (Por)Co^{IV}=O first abstracts a single electron from the aryl group of **3** to produce the radical cation $\mathbf{3}^{+\bullet}$. The latter underwent proton loss to produce the α-phenoxybenzyl radical **3d**, which further reacts with (Por)-Co^{III}–OH through hydroxyl transfer to form **3e**. Compound **3e** is subsequently hydrolyzed to give the main product benzyl alcohol (**3a**) and the corresponding oxidative products **3b** and **3c** (Scheme 6). The formed guaiacol was further oxidized into aliphatic acids, which is in full agreement with the observations from the reaction of the β-O-4-type model compound. Notably, the 4-O-5-type lignin model compound diphenyl ether **4**, which often resists oxidation by most metalloporphyrin catalytic oxidation systems, also furnished guaiacol with 37% conversion, although a higher reaction temperature (150 °C) and increased catalyst dosage (1 mol%) were required (Scheme 7). In the control experiment, the conversion (9%) was much lower in the absence of the deuteroporphyrin catalyst (see Figure S8 in the Supporting Information). Although the mechanistic details of this transformation are not clear at the moment, on the basis of the results obtained from the control experiment, we believe that the reaction pathway was more than acid-catalyzed aryl ether cleavage; a synergistic catalysis effect might be occurring in this reaction.



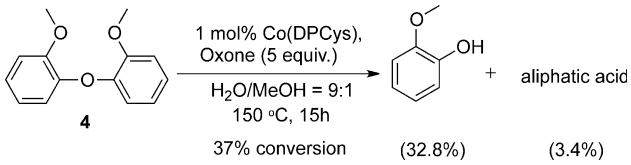
Scheme 5. Degradation of α-O-4-type lignin model compound **3**.



Scheme 4. Proposed mechanisms for A) the formation of **2a** and B) the formation of **2b** and **2c**.



Scheme 6. Proposed mechanism for the formation of **3a**.



Scheme 7. Degradation of 4-O-5-type lignin model compound **4**.

Oxidation of enzymolysis lignin

Based on the promising results obtained from the lignin model compounds, we next conducted reactions on real lignin.

A huge amount of lignin is expected to be available as a by-product in the production of second-generation bioethanol from crop waste.[50] Lignin obtained from the residue of enzymatic hydrolysis, referred as "enzymolysis lignin" (EL), is assumed to be close to its original status and generally exhibits much smaller structural changes than lignin obtained by chemical-treatment methods, such as kraft lignin and lignosulfonate. Therefore, enzymolysis lignin, which is derived from enzymatic hydrolysis of corn stover in bioethanol production, was selected in the present study and purified according to the literature procedure[51] to remove the remaining cellulose, hemicellulose, and sugars. The Co(DPCys) catalytic oxidation system was applied for the oxidation of EL, and two fractions, that is, an oily liquid fraction and a solid residue fraction, were obtained after the reaction. The yield of the reaction was calculated as a percentage of the weight of recovered oily liquid products divided by the weight of dry lignin. The molecular structure of lignin is very complicated, so it is difficult to calculate the molar yield of the product. As can be seen in Table 3, the result obtained from oxidation of EL at room temperature is very poor (Table 3, entry 1). 95.7 wt% of solid residue was recovered after the reaction, which contained unconverted lignin and repolymerized lignin fragments from the reaction mixture. With consideration of the complex structure and low reactivity of real lignin, a higher temperature was employed. Upon an increase in the reaction temperature to 120 °C, the yield was significantly improved (Table 3, entry 2), which indicated that the lignin oxidation was promoted at a higher temperature to overcome the activation energy for the reaction. In the control experiments, the yield of oily liquid fraction was much lower in the absence of the deuteroporphyrin catalyst (Table 3, entry 3), which clearly demonstrates the major catalytic role of Co(DPCys) during the reaction. After the reaction, the solvent was evaporated, the residue was extracted with ethyl acetate, and a variety of aromatic compounds were identified by GC–MS. These compounds could be classified into three types: H-type compounds including benzoic acid, *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, and *p*-hydroxybenzoic acid; G-type compounds including guaiacol, vanillin, acetovanillone, and vanillic acid; and S-type compounds including syringaldehyde, acetosyringone, and syringic acid. Among these three types of aromatic compounds, the main products were vanillin and syringaldehyde. Hence, these two compounds were selected to determine the effects of the reaction conditions.

Table 3. Catalytic oxidative depolymerization of real lignin.[a]

Entry	Product distribution[b] [%]				Yield	Solid residue	Mass balance
	H	G	S	aliphatics	[wt%]	[wt%]	[wt%]
1[c]	–	–	–	–	1.1	95.7	96.8
2[d]	22.8	45.2	24.1	6.1	22.3	64.8	87.1
3[e]	–	–	–	–	5.7	82.8	89.5
4[f]	18.8	48.9	22.7	8.4	31.2	53.3	84.5
5[g]	13.5	41.2	26.8	15.5	37.8	40.2	78.0
6[h]	8.7	37.6	24.4	22.3	39.1	34.7	73.8
7[i]	7.5	32.1	46.1	11.7	33.4	47.9	81.3
8[j]	9.0	38.5	39.3	9.4	29.8	53.7	83.5
9[k]	–	85.2	–	11.3	13.6	71.5	85.1

[a] Reaction were performed by using lignin (0.2 g), Co(DPCys) (0.01 mmol), and oxone (8 mmol) in H_2O (20 mL) at 150 °C for 10 h unless otherwise noted. [b] Product distribution was calculated by GC–MS. [c] The reaction was performed at room temperature. [d] The reaction was performed at 120 °C. [e] The reaction was performed in the absence of Co(DPCys). [f] The yield is the averaged data from three replicated experiments. [g] Oxone (12 mmol) was used in the reaction. [h] The reaction was performed at 180 °C. [i] Ethanol lignin derived from bagasse was used in the reaction. [j] Dioxane lignin derived from bagasse was used in the reaction. [k] Ethanol lignin derived from pine sawdust was used in the reaction.

We then screened a variety of parameters of this reaction, such as the reaction temperature, dosage of oxidant and catalyst, the ratio of mixed solvent, and the reaction time (see Table S1 in the Supporting Information). Under the optimal reaction conditions, a soluble oily liquid fraction corresponding to 31.2 wt% of the original lignin was obtained, together with an insoluble solid fraction that accounted for 53.3 wt% of the lignin (Table 3, entry 4). Notably, 31.2 wt% of the oily liquid fraction is not the highest yield because our target products are aromatics. A further increase in the dosage of oxone or in the reaction temperature has a favorable effect on the yield of the oily liquid fraction (Table 3, entries 5 and 6). However, a subsequent decrease in the selectivity of the aromatics and the formation of coking were observed, probably as a result of the further oxidation of in situ generated aromatics into aliphatic compounds, such as maleic acid, muconic acid, and even carbon dioxide. The soluble oily liquid fraction was analyzed by GC–MS to identify the products of the reaction (Figure 4), and a full listing of characterized products is provided in the Supporting Information (Figure S9).

To elucidate whether the present method could be broadly used in the conversion of other types of lignin, we applied this procedure to several organosolv lignins, including ethanol lignin derived from bagasse, dioxane lignin derived from bagasse, and ethanol lignin derived from pine sawdust. It was found that the source of lignin has a significant effect on the conversion efficiency and the distribution of products. For instance, ethanol lignin derived from bagasse could afford an oily liquid fraction yield of 33.4 wt% (Table 3, entry 7), and all three types of aromatics were identified after the reaction (Figure S10 in the Supporting Information). The different organic solvents (ethanol and dioxane) used for the lignin extraction seem to have had little influence on the reaction (Table 3, entries 7 and 8; Figure S10 and S11 in the Supporting Information). Significantly different from the conversion of grass bio-

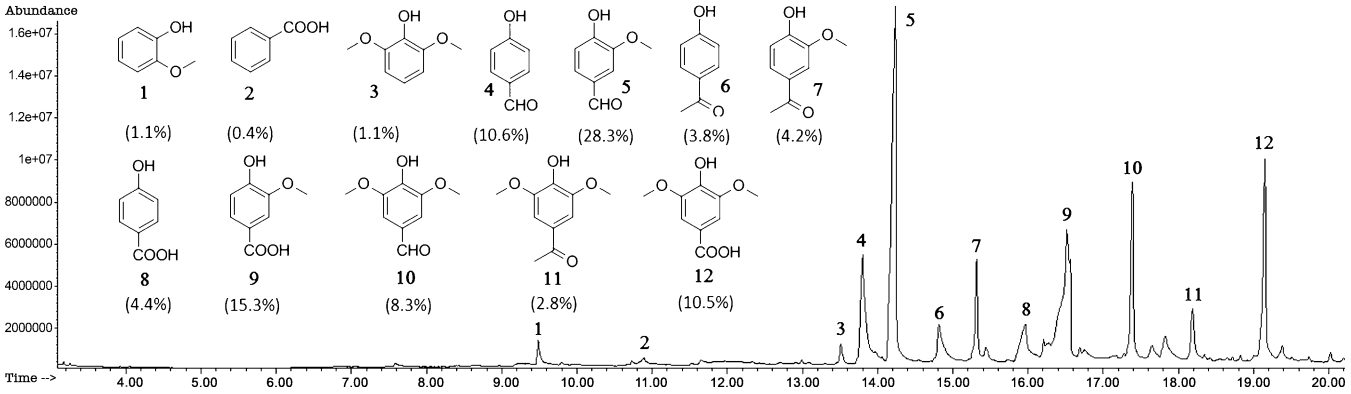


Figure 4. GC–MS chromatography spectrum of the soluble oily liquid fraction. Inset graphics depict the structures and selectivities of the detected aromatics (in minutes). The mass spectra and reference mass spectra are given in the Supporting Information (see Figure S9).

mass lignin, when ethanol lignin derived from pine, a woody-based biomass, was used as the substrate for the reaction under the same conditions, it only gave rise to a relatively poor oily liquid fraction yield (Table 3, entry 9), and only the G-type aromatics were detected after the reaction (Figure S12 in the Supporting Information). Therefore, the different structures of lignin from grass-based biomass (including corn stover and bagasse) and wood biomass might be an important reason for the different results. It has been reported that the composition and the abundance of primary units in wood lignin and grass lignin varies remarkably.[12a] Sinapyl, coniferyl, and *p*-coumaryl alcohols constitute approximately 70%, 25%, and 5% of grass lignin,[52] whereas roughly equal proportions of coniferyl and sinapyl alcohols appear in hard-wood lignin.[12a]

Conclusions

In conclusion, a series of metallo-deuteroporphyrin biomimetic catalysts, which are derived from natural hemin, have been designed and synthesized to mimic the cytochrome P450 enzyme. Various lignin model compounds underwent smooth transformation to afford the corresponding C–O bond cleavage product in moderate to excellent yields under mild reaction conditions. This novel catalytic oxidative system can further convert real lignin into depolymerized products including a significant portion of well-defined aromatic monomers. Some of these products can be used directly as fine chemicals (such as vanillin and syringaldehyde) or as feedstocks for further upgrading. Further studies on immobilizing the metallo-deuteroporphyrins on heterogeneous supports and enhancing the yield of monomeric chemicals from real lignin are under way.

Experimental Section

General procedure for the catalytic oxidation of lignin model compounds

Oxone (2.5 mmol) was added to a stirred solution of lignin model compound (0.5 mmol) and metallo-deuteroporphyrin (0.0025 mmol) in MeOH/H_2O (5/5 mL). The solution was stirred at room temperature for several hours, and the reaction progress was checked by GC–MS or thin-layer chromatography. After completion of the reaction, the mixture was extracted with EtOAc (3×10 mL). The organic phase was dried and analyzed by GC–MS (for details, see the Supporting Information).

Typical procedure for the catalytic oxidation of enzymolysis lignin

A 100 mL thick-walled glass tube with a stirrer bar was charged with dry enzymolysis lignin (0.2 g), Co(DPCys) (0.01 mmol), oxone (8 mmol), and H_2O (20 mL). The tube was sealed with a polytetrafluoroethylene screw cap and heated for 10 h at $T=150\,^{\circ}C$. After completion of the reaction, the mixture was first concentrated under vacuum, and the residue was extracted with EtOAc (3×20 mL). The organic soluble fraction was concentrated under vacuum to afford a viscous oil, which was characterized by GC–MS. The organic insoluble material was washed with hexane and then water to remove all salts and was dried under vacuum. The resulting solid was further treated with acetic anhydride and pyridine (3/3 mL) at room temperature for 48 h to acetylate all of the alcohol groups. After 48 h, the acetylated polymer was extracted with EtOAc and subjected to gel permeation chromatography analysis.

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