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Letter

Organocatalytic Approach to Photochemical Lignin Fragmentation

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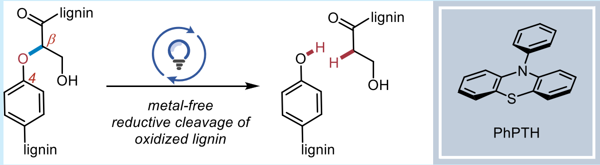
ABSTRACT: Herein, an organocatalytic method for photochemical C−O bond cleavage of lignin systems is reported. The use of photochemistry enabled fragmentation of the *β*-O-4 linkage, the primary linkage in lignin, provides the fragmentation products in good to high yields. The approach was merged with reported oxidation conditions in a one-pot, two-step platform without any intermediary purification, suggesting its high fidelity. The future utility of the organocatalytic method was illustrated by applying the visible light-mediated protocol to continuous flow processing.



Utilization of biomass for the production of fuels and chemicals is of the utmost priority in order to sustain a global economy that is intimately tied to its energy usage.[1−3] Conversion processes in the petrochemical industry are well-established; however, efficient biotechnologies and catalytic processes for converting biomass to useful fuels and fine chemicals are lacking. Lignin, identified as an underutilized renewable source for the production of value-added chemicals, is largely produced as a waste product by the paper and pulping industry.[4] As the use of renewable sources for the production of commodity chemicals and energy sources in an attempt to replace nonrenewable fossil fuels as the source for aromatic chemicals has become a focus, lignin has gained increasing attention in recent years.[5]

Lignin, a component of lignocellulosic biomass alongside cellulose and hemicellulose, is a biopolymer composed of three phenylpropanol subunits (coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) that are oxidatively polymerized to afford various linkages that constitutes 30% of the organic carbon in the biosphere and is the largest source of aromatic building blocks on the planet (Figure 1).[6−8] One of the two strategies for lignin valorization is hydrogenolysis.[9] The other approach involves the selective and mild deconstruction of the polymeric network to its aromatic small molecule products while maintaining native functionality.[10]

The *β*-O-4 linkage is the most investigated linkage moiety for fragmentation due to its abundance in lignin (around 45−60% of all lignin linkages).[8] Various advancements have been made for the cleavage of lignin model systems, as well as native lignin polymers.[11] Despite the variety of methods that have been reported for lignin functionalization and depolymerization, achieving high yields and selectivity under ambient conditions still remains a challenge. An example is the conversion of lignosulfonate to vanillin. The production of vanillin from a renewable source is of high interest to food companies, as well as the flavor and fragrance industries.[12] However, several drawbacks exist in current methods, including moderate yields, as well as the use of high temperatures and pressures.[13,14] Even during the advent of newly developed catalytic approaches, technologies for lignin depolymerization that afford predictable monomeric units are still underdeveloped.[15]

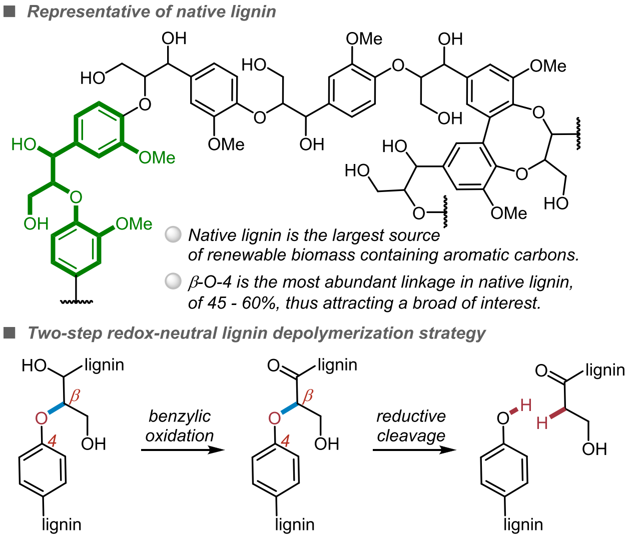


Figure 1. Photocatalytic depolymerization of lignin.

The Stephenson group has been interested in the depolymerization of lignin employing redox-based methods. Our previous studies on lignin fragmentation have exploited the unique reactivity of the *β*-O-4 linkage by targeting the

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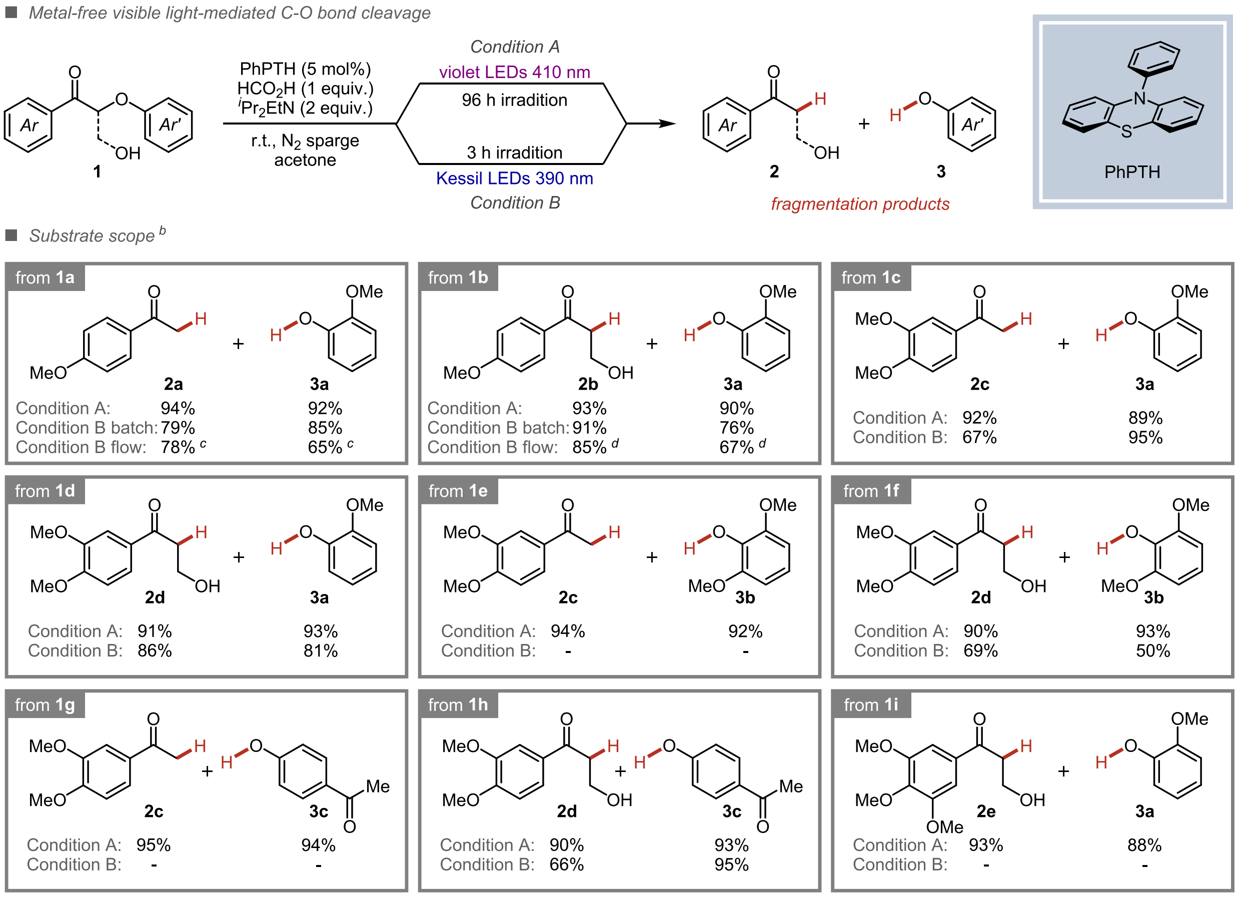

Figure 2. Organocatalytic photochemical C−O bond cleavage. [a]Reaction conditions: **1** (0.25 mmol), *N*-phenylphenothiazine (PhPTH, 0.0125 mmol), formic acid (HCO_2H, 0.25 mmol), diisopropylethylamine ($^iPr_2EtN$, 0.5 mmol), acetone (5 mL), N_2 protection. Reactions were irradiated by violet LED strips (Method A) or Kessil 390 nm LED light (Method B). [b]Isolated yields are reported. [c]1 mmol reaction was carried out in continuous flow. [d]0.25 mmol reaction was carried out in continuous flow.

benzylic alcohol for oxidation. Capitalizing on this oxidation event, several two-step oxidation−fragmentation sequences were developed (Figure 1).[16] However, one major drawback of our reported methods for biomass valorization is the necessity of using iridium-based photocatalysts, which has limited the practical application of photochemical depolymerization of lignin in industry. In comparison with the production of pharmaceuticals and other fine chemicals, biomass valorization is anticipated to operate on a much larger scale, wherein catalyst cost becomes a critical factor in process development. In this paper, an organocatalytic approach to photochemical fragmentation of oxidized lignin substrates is reported.

Initially, several reducing photocatalysts were evaluated. Photocatalyst perylene di-imide (PDI), which has previously been used for reductive dehalogenation reactions via a presumed reductive quenching cycle,[17] resulted in no reactivity with the irradiation of blue LEDs (see the Supporting Information (SI), Table S1). Subsequently, *N*-phenylphenothiazine (PhPTH) was identified as a photocatalyst (E^0 (PhPTH$^{\bullet+}$/PhPTH*) = −2.1 V vs SCE)[18] and resulted in fragmentation products in reasonable yield. The absorbance spectrum of PhPTH was obtained (Figure S1) and showed a maximum absorbance at the wavelength 315 nm, suggesting the need for more violet-centered light sources. Thus, a violet LED strip (λ_{max} = 400−410 nm) was utilized initially. Upon optimization of the reaction conditions, paying particular attention to solvent, concentration, and equivalence of additives (Table S1), full conversion of the oxidized lignin substrate **1a** was obtained after 96 h.

To increase reaction efficiency, a higher-powered LED source (Kessil, PR160−390 nm) was used, in which photon flux is determined to be 16 times larger than that of the violet LED strip (SI).[19] This provided a nearly 30-fold reduction in reaction time, allowing the reaction to proceed in merely 3 h to afford full conversion. The observation is consistent with reports that demonstrate the dependence of reaction efficiency on photon flux.[20]

The organocatalytic photochemical fragmentation of a variety of oxidized lignin model substrates was performed. The fragmentation products were isolated in good yields, ranging from 66% to 95% (Figure 2). In addition, the organocatalytic photochemical C−O bond fragmentation could also be carried out in continuous flow and similar yields were obtained in an even shorter reaction time of 28 min (Figure 2). A scaled-up reaction of **1a** (1 mmol) was performed, and acceptable yields were achieved (Figure 2).

To explore further application of this method, compatibility with oxidation conditions was studied. The organocatalytic photochemical approach was successfully merged with Stahl's disclosed aerobic[21] and our electrochemical[10a] oxidation manifolds of lignin into a one-pot, two-step platform. After chemical or electrochemical oxidation, the solvent was evaporated. Without any additional workup or purification, the crude residue dissolved in acetone was directly subjected to

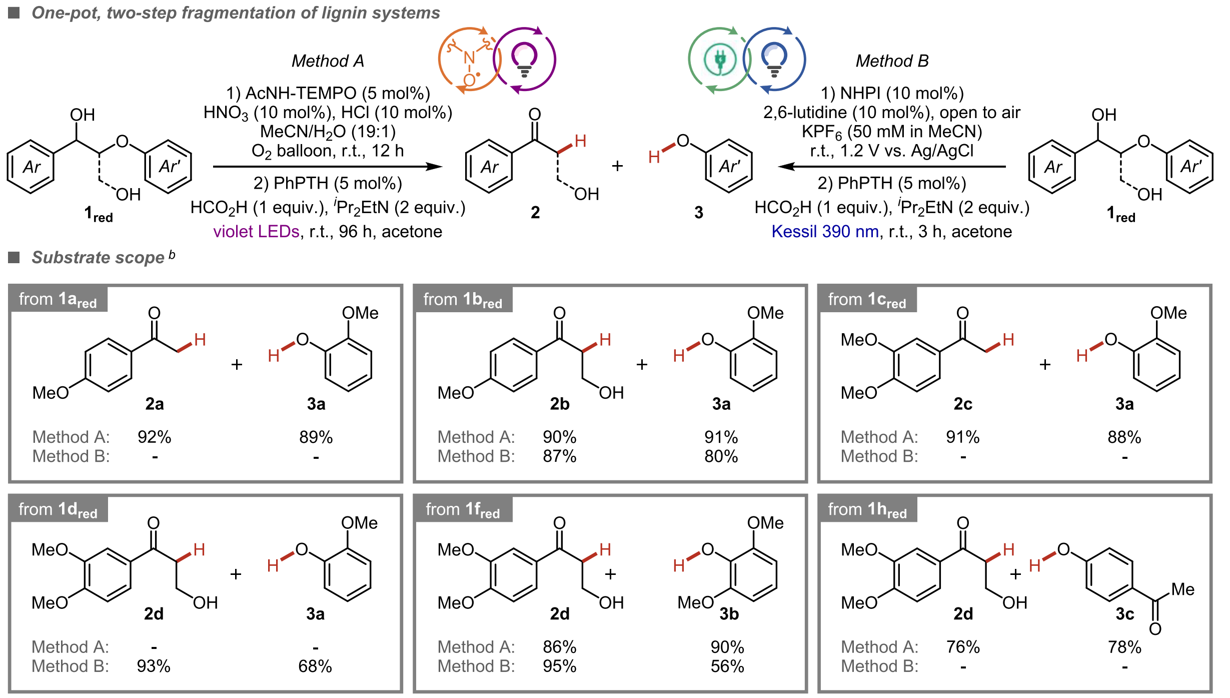

Figure 3. Organocatalytic one-pot, two-step fragmentation of lignin systems. [a]All reactions were performed on a 0.25 mmol substrate scale in a one-pot, two-step platform without any intermediary purification. Method A is carried out according to ref 21 and condition A (irradiated by violet LED strips). Method B is carried out according to ref 10a and condition B (irradiation by Kessil 390 nm LED light). Detailed procedures are described in the Supporting Information. [b]Isolated yields are reported.

the photochemical conditions. The one-pot, two-step oxidation/reduction approach afforded the fragmentation products in good to high yields (Figure 3).

In conclusion, the disclosed methods will add to the growing field of lignin depolymerization and valorization as investment in green technologies continues to rise. Using organic photocatalysts, the fragmentation of oxidized lignin strategies under mild conditions is viable. We anticipate the incorporation of these strategies and principles for lignin valorization to be of great value to the lignin community in the venture to convert renewable biomass feedstocks into useful chemicals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03029.

Experimental Procedures, characterization data for all compounds along with copies of spectra (PDF)

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Notes

The authors declare no competing financial interest.
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