ACS Catalysis

NOTTINGHAM TRENT UNIVERSITY

Subscriber access provided by Nottingham Trent University

Article

Photocatalytic Cleavage of Aryl Ether in Modified Lignin to Non-phenolic Aromatics

Hongji Li, Anon Bunrit, Jianmin Lu, Zhuyan Gao, Nengchao Luo, Huifang Liu, and Feng Wang

ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.9b02719 • Publication Date (Web): 14 Aug 2019

Downloaded from pubs.acs.org on August 14, 2019

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Photocatalytic Cleavage of Aryl Ether in Modified Lignin to Non-phenolic Aromatics

Hongji Li,[†, ‡] Anon Bunrit,[†] Jianmin Lu,[†] Zhuyan Gao,[†, ‡] Nengchao Luo,[†, ‡] Huifang Liu,[†] and Feng Wang*, [†]

[†] State Key Laboratory of Catalysis (SKLC), Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, Dalian 116023, China.

[‡] University of Chinese Academy of Sciences, Beijing 100049, China.

ABSTRACT: Depolymerization of lignin meets the difficulty in cleaving robust aryl ether bond. Herein through installing an internal nucleophile in β-O-4' linkage, the selective cleavage of aryl ether was realized by the intramolecular substitution on aryl rings affording non-phenolic arylamine products. In particular, nitrogen-modified lignin models and lignin samples were employed to generate the iminyl radical under photocatalytic reduction, which acted as the internal nucleophile inducing aryl migration from O to N atom. The following hydrolysis released primary arylamines and α-hydroxy ketones. Mechanism studies including electron spin resonance (ESR), fluorescence quenching experiments and density functional theory (DFT) calculations proved the aryl migration pathway. This method enables access to non-phenolic arylamine products from lignin conversion.

KEYWORDS: lignin • photocatalytic • aryl ether cleavage • amination • aryl migration

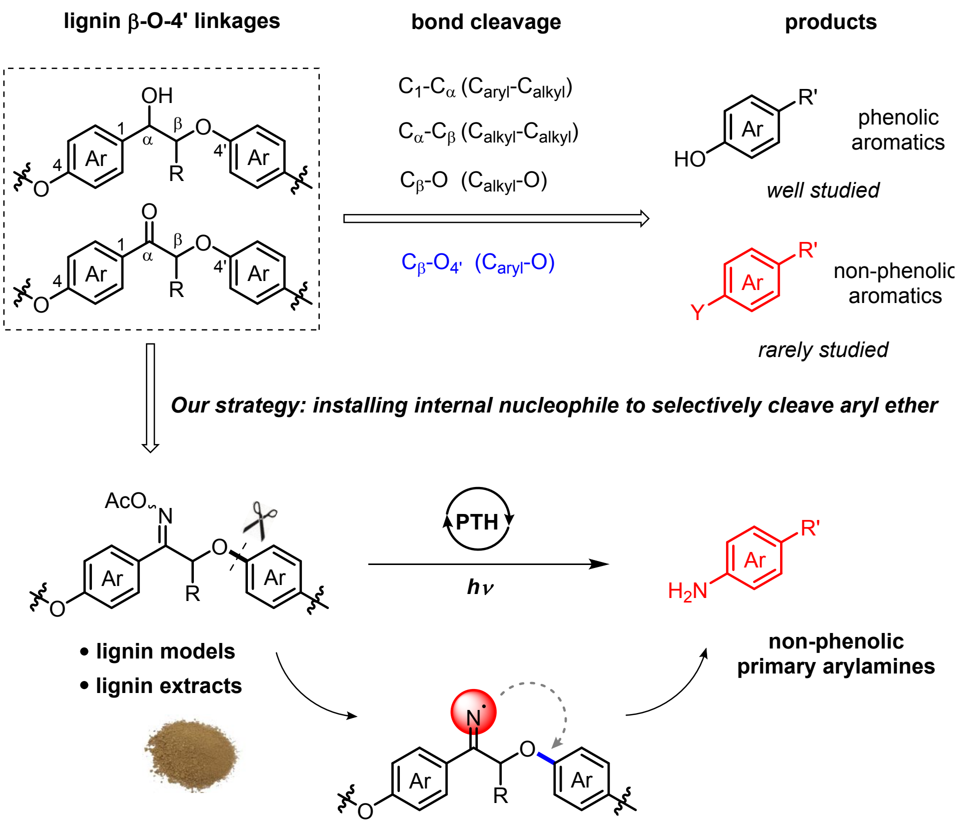
INTRODUCTION

Lignin, the richest resource of aromatic polymers in nature, has a great potential to produce various aromatic compounds via sustainable pathways.[1-7] Phenolic units including syringyl (S), guaiacyl (G) and *p*-hydroxy phenyl (H) units are connected by many types of linkages, in which the β-O-4' linkage is the richest and its cleavage is the key to depolymerize lignin.[8-11] Hydrogenolysis using internal hydrogen donors[12-14] or external hydrogen donors[15-26] and hydrolysis methods[27-30] have been developed to cleave the aliphatic ether bond ($C_β$–O) affording the alkyl-substituted phenols, aromatic ketones, etc. Aerobic oxidation,[31-40] retro-aldol reaction,[41] decarbonylation[42] and hydrogenation[43] methods have been performed to cleave the aliphatic C–C bond and afford the aromatic acids, aldehydes, etc. Using sodium azide,[44] oxidation[31] and rearrangement reactions[45] could induce the cleavage of C_{aryl}–$C_α$ bond. Despite their versatility, most of these transformations did not involve the cleavage of aryl ether bond ($C_{4'}$–O) thus the depolymerized products were limited to phenolic monomers. Obtaining the non-phenolic aromatics will extend the application of lignin conversion,[46,47] however, selective activation of desired aryl ether is retarded by its high bond energy and co-existed aliphatic ethers.[48]

Recently the cation radical-accelerated nucleophilic aromatic substitution was established to cleave the aryl ether bond, in which single electron oxidation activated the arene ring and imidazole as the external nucleophile finished the substitution of methoxy- and benzyloxy-groups.[49] Despite its feasibility partly shown by the cleaving aryl ether in lignin β-O-4' ketone models, complicated chemical environment neighboring β-O-4’ linkage may affect its application in lignin samples. In contrast, one alternative method using an internal nucleophile in β-O-4’ linkage may overcome the effect of chemical environment via kinetically-favorable intramolecular reaction.[50] Pre-modification of lignin has emerged as a strategy to deliver functionalized monomers and polymers,[51-53] and we considered that the precursor of internal nucleophile could be constructed during modification.

Herein we developed the internal nucleophile to selectively cleave aryl ether in lignin based on nitrogen-modification (Scheme 1). The lignin β-O-4’ linkage was modified from an alcohol structure to an acyl oxime structure, namely α-oximated β-aryl ether, from which the iminyl radical was generated under photocatalytic conditions and participated in intramolecular amination of aryl ether to deliver non-phenolic primary arylamines. Aliphatic C−O bond kept stable and the α-hydroxy ketones were obtained as another part of products. Both lignin models and preliminary modified lignin conversion exhibited the feasibility of this method in non-phenolic arylamines generation from lignin.

Otherwise, nitrogen-containing reagents have been utilized to promote the cleavage of lignin linkages where nitrogen-containing reagents could act as the strong nucleophile to attack the inert C−O bonds or C−C bonds.[44,46,47,54] Meanwhile, the generated nitrogen-containing products are useful chemicals such as aniline, which is the key chemical for the manufacture of polyurethane, etc.[26,55] In this work, primary arylamines instead of phenolic products were obtained via amination of aryl ethers and these products could be readily derived to other nitrogen-containing compounds, thus



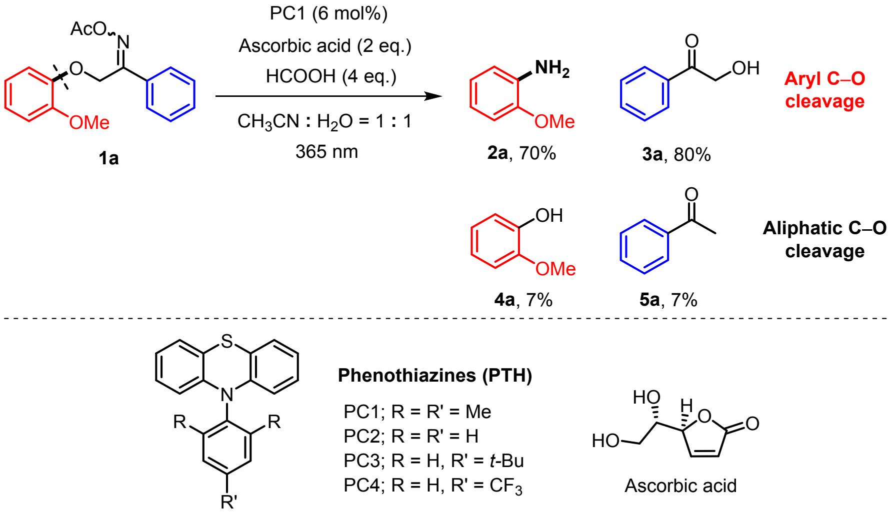
Scheme 1. Cleavage of different bonds in lignin β-O-4’ linkage and the installing internal nucleophile strategy to cleave aryl ether bond.

this work may connect lignin conversion with production of abundant nitrogen-containing chemicals.

RESULTS AND DISCUSSION

The α-oximated β-aryl ether models which were prepared via oximation and acetylation of β-O-4’ ketone models could be used to generate the iminyl radical under photocatalytic reduction. In previous reports the iminyl radical could act as a versatile intermediate to trigger useful transformations.[56] In this case, we explored the iminyl radical to induce the aryl migration from oxygen to nitrogen atom which cleaved the aryl ether bond and constructed aryl C−N bond, and following hydrolysis afforded primary arylamine and α-hydroxy ketone. It was found that phenothiazine (PTH) used as the catalyst in previous photocatalytic reduction (E_{red} ($PTH^{\bullet+}/PTH^{*}$) near −2.1 V vs SCE)[57-60] exhibited good results in the reductive cleavage of N−O bond for the generation of iminyl radical from acetyl oxime **1a**. The highest yields of primary arylamine **2a** (70%) and 2-hydroxyacetophenone **3a** (80%) were obtained from aryl ether cleavage when using PTH PC1 as the photocatalyst, ascorbic acid (HA) as the

Table 1. Optimization of reaction conditions.



Entry	Deviation from above	Yields from aryl C−O cleavage, %		Yields from aliphatic C−O cleavage, %	
		2a	**3a**	**4a**	**5a**
1	CH_3CN/H_2O (4/1) as solvent	67	40	9	11
2	CH_3CN as solvent	5	0	13	1
3	Without ascorbic acid	10	23	0	1
4	$Na_2S_2O_3$ instead of ascorbic acid	46	61	4	1
5	Without HCOOH	66	77	12	8
6	NaH_2PO_4 instead of HCOOH	71	77	12	10
7	PC2 instead of PC1	64	65	14	15
8	PC3 instead of PC1	66	77	7	7
9	PC4 instead of PC1	40	54	4	4
10	Without PC1	28	33	4	4
11	Dark reaction	0	0	0	0

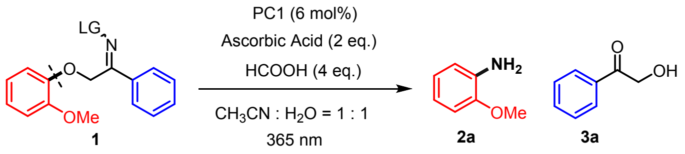
Conditions: substrate (0.05 mmol), solvent (1 mL), argon atmosphere, room temperature, 4 h. The yields were determined by HPLC with 4’-methylacetophenone as the internal standard.

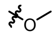
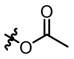
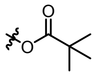
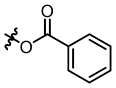
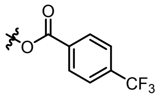
reductant, formic acid, and a mixture of acetonitrile and water (1:1, v/v) as the solvent (Table 1). Only 7% yields of guaiacol and acetophenone, which were main products in previously reported photo-reduction of β-O-4’ ketones, were generated from aliphatic C−O bond cleavage.[61-63] Substitution of adjacent methoxyl on phenolic motif was not observed under the optimal conditions, indicating the good selectivity of desired aryl ether cleavage.

Then control experiments were performed to identify the roles of each additive during this reaction. The formation of **2a** and **3a** were diminished or inhibited with decrease of water content, which may be ascribed to insufficient hydrolysis of the possible imine intermediate (Table 1, entries1 and 2). Further solvent screening indicated that CH_3CN/H_2O (1/1, v/v) was the better solvent than other solvents in this system (Supporting Information, Table S1). The desired products were produced in low yields in the absence of ascorbic acid (10% and 23%, **2a** and **3a**, respectively; entry 3). Replacing ascorbic acid with sodium thiosulfate retained the products moderately (entry 4), indicating the ascorbic acid could act as the reductant to participate in the oxidative cycling step of PTH catalyst.[64] The addition of formic acid was proposed to promote the hydrolysis of imine intermediate to release arylamine and ketone products. Without formic acid the yields of desired products slightly decreased (entry 5) and it could be replaced by sodium dihydrogen phosphate (entry 6). Other phenothiazines could also act as the efficient photocatalyst (entries 7-9), among which the catalysts bearing electron-donating groups (Me, *t*-Bu) behaved better than the catalyst bearing electron-withdrawing group (CF_3). Less overlapping between the UV-Vis absorption spectrum of PTH PC4 with the emission of selected lamp than that of PC1, PC2 and PC3 indicated PC4 might undergo a worse photo excitation under this irradiation condition (Supporting Information, Figure S1).[59] The reaction in the absence of photocatalyst delivered 28-33% yields of desired products which could be rationalized as a pure photoreaction since the substrate itself absorbed the LED irradiation (entry 10). No products were obtained under dark condition confirming this transformation to be photo-triggered (entry 11).

The effect of leaving group (LG) including ether and esters in oxime derivatives on this transformation was studied. Poor yields (9% and 10%, **2a** and **3a**, respectively; Table 2, entry 1) of desired products were obtained using methoxyl group as LG indicating methoxyl group was an inferior LG. Simple acetate (**2a**, 70%), pivalate (**2a**,

Table 2. Investigation of leaving groups.



Entry	Leaving group	Yield of **2a**, %	Yield of **3a**, %
1		9	10
2		70	80
3		76	51
4		70	73
5		59	58

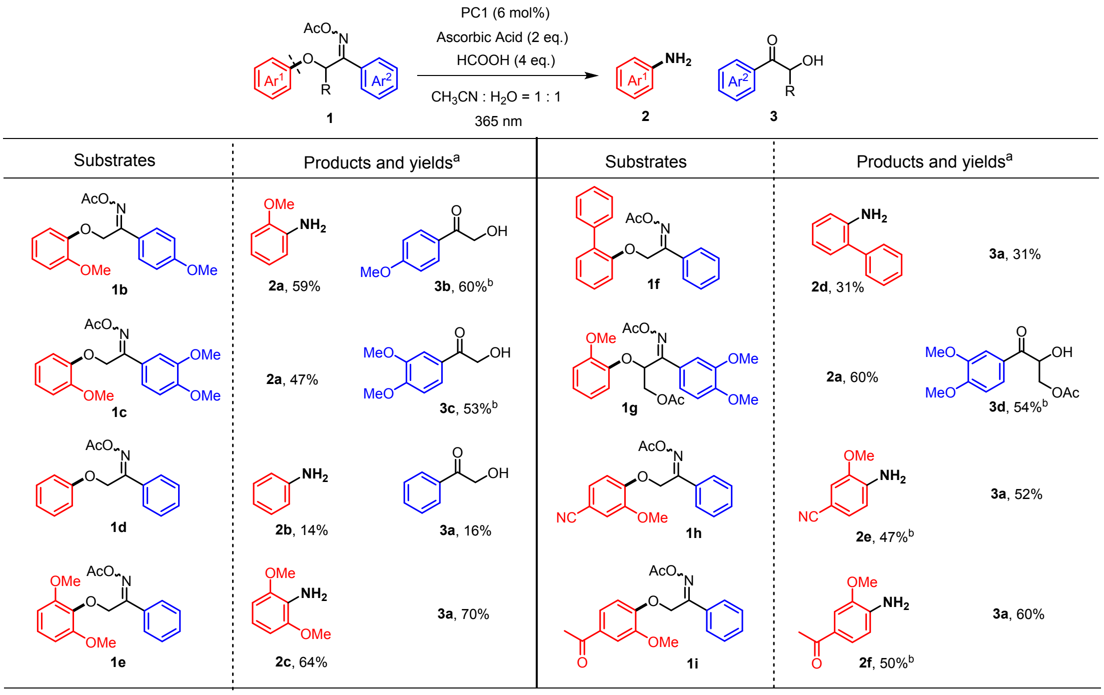
Conditions: substrate (0.05 mmol), solvent (1 mL), argon atmosphere, room temperature, 4 h. The yields were determined by HPLC with 4'-methylacetophenone as the internal standard. LG, leaving group.

76%) and benzoate (**2a**, 70%) behaved better than 4-(trifluoromethyl) benzoate (**2a**, 59%) even though electron-deficient benzoate exhibited the unique validity in previous Iridium photocatalytic systems,[65] which could be explained by the more negative reduction potential of excited PTH catalyst.[58]

After confirmation of optimal conditions, diverse α-oximated β-aryl ethers based on lignin models were investigated (Table 3). Methoxyl group on the benzene ring Ar^2 adjacent to oxime (**1b** and **1c**) showed a minor effect on the aryl migration. It is well accepted that σ-type unpaired electron of iminyl radical could not be delocalized into π-systems of aryl iminyl.[66] Therefore limited effect from substituents on benzene ring Ar^2 will be shown on the property of iminyl radical. However, substituents on migrated benzene ring Ar^1 obviously affected the intramolecular amination. Substrate **1d** delivered **2b** in poor yield (14%), where less steric phenolic motif might be not favorable to formation of spiro intermediate. In contrast, dimethoxy substituted Ar^1 (**1e**) proceeded the amination smoothly (**2c**, 64% yield). Model **1f** containing an *ortho*-phenyl on Ar^1 was a modest substrate compared to **1a**. Then complex model **1g** was also tested. Gratifyingly, selective cleavage of aryl ether bond proceeded over cleavages of aliphatic ether and ester to deliver 54% yield of **3d** and 60% yield of **2a**.

Model **1h** and **1i** were prepared to mimic the possible fragments during modified lignin conversion. 47-50% yields of corresponding primary arylamines were afforded indicating the conjugated structure induced by carbonyl or cyano group did not affect the migration of Ar^1 motif. Product **2f** is of particular note, as the ketone carbonyl group of **2f** would not be tolerated under the reductive amination conditions.[67,68] During the

Table 3. Amination of lignin models.



^{a} HPLC yields on 0.05 mmol scale. ^{b} Isolated yields on 0.3 mmol scale.

amination reaction, α-hydroxy ketones were generated in similar yields with primary arylamines.

After the test of lignin models, we explored the application of this amination method in modified lignin. The modified poplar lignin was prepared via pre-oxidation, oximation and acylation based on dioxasolv poplar lignin (Supporting Information). Among these steps, the oxidation step was carried out using the stoichiometric 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[69] which could provide the consecutive oxidized β-O-4’ motif avoiding the possible disconnected oxidized lignin species in other oxidation systems.[35] The modified lignin exhibited a better solubility in acetonitrile than dioxasolv lignin and oxidized lignin (Figure 1, a-c). Previous studies indicated during the acylation step all hydroxyl groups including aliphatic and phenolic hydroxyls could be acetylated leading to decreased exposed-hydroxyl groups and thus

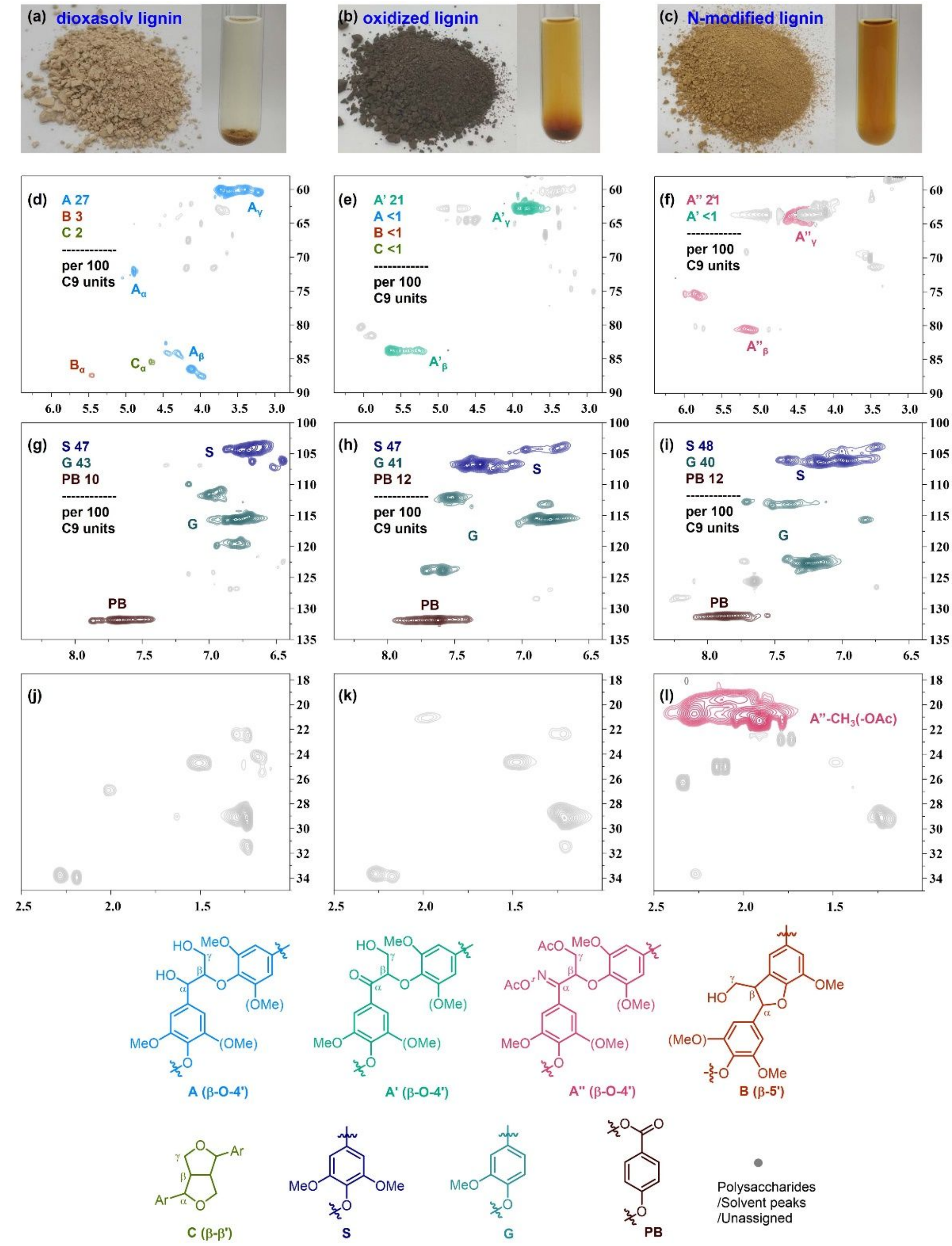


Figure 1. N-modification of lignin samples. (a-c) The pictures of samples and corresponding CH_3CN solutions from dioxasolv lignin, pre-oxidized lignin and modified lignin, respectively. (d-l) 2D NMR spectra of lignin samples in DMSO-d_6. (d, g and i) from dioxasolv lignin. (e, h and k) from pre-oxidized lignin. (f, i, and l) from N-modified lignin.

acylated lignin showed a good solubility in most organic solvents.[70]

Then qualitative and semi-quantitative analysis was conducted on lignin samples by 2D ^{13}C-^{1}H HSQC NMR, where the peaks were assigned based on the lignin model (Supporting Information, Figure S2) and previous literatures.[54,69,71,72] The lignin sidechain regions indicated that β-carbon and γ-carbon in β-O-4’ linkage were stepwise shifted after oxidation and acylation steps (Figure 1, d-f). The amount of total β-O-4’ linkage per 100 aromatic units decreased from 27 to 21 after modification, which suggested the theoretical yield of monomers based on β-O-4’ linkage cleavage would decrease from 7.3% to 4.4%. The aromatic regions indicated these lignin samples were rich in S and G units, and S/G ratio was 1.1-1.2 (Figure 1, g-i). Meanwhile, the amount of H unit per 100 aromatic units was 10-12 in the form of *p*-hydroxybenzoate (PB). In addition, strong methyl peaks appeared in the aliphatic regions which proved the modified lignin was successfully acetylated (Figure 1, j-l).

Then modified lignin was subjected to the amination conditions. To dissolve the modified lignin sufficiently, $CH_3CN/H_2O/HCOOH$ (18:1:1, v/v/v) was used as the solvent. Under this condition, 1.9 wt% primary arylamine monomers (1.5 wt% G monomer and 0.4 wt% S monomer) were obtained (Supporting Information, Figure S3). By-products were phenol monomers (2.7 wt%) and 4-acetoxybenzoic acid (1.8 wt%) as the product of PB unit. The moderate yields of desired arylamine monomers could be ascribed to low percentage of α-oximated β-aryl ethers after modification and more restricted polymerized structures in real lignin than free dimer models. Besides, the isolated large fragments also contained trace amount of arylamine motifs which could

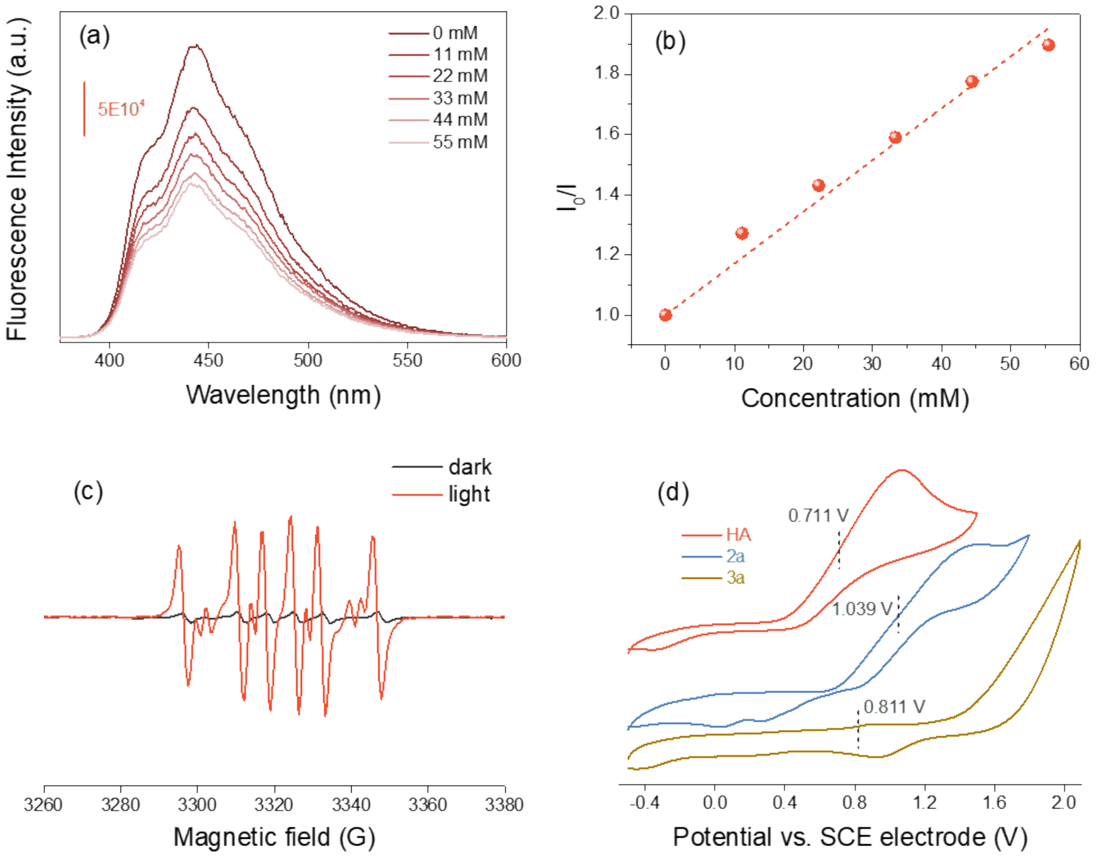


Figure 2. Mechanism studies. (a) and (b) Stern-Volmer quenching study with substrate **1a** (quencher) and PC1 (3.15 mM in CH$_3$CN). (c) The ESR spectra of DMPO capturing radical produced by substrate **1a** and PC1 with or without light irradiation. (d) Cyclic Voltammetry curves of ascorbic acid, product **2a** and **3a**.

not be further depolymerized under this system (Supporting Information, Figure S4).

Several experiments were conducted to get insight into the mechanism of the reaction. Firstly, the electron transfer event between PC1 and substrate **1a** was studied. The emission intensity of the excited state of PC1 was weakened in the presence of **1a** which is followed by the linear Stern–Volmer behavior (Figure 2, a-b). Photo-induced generation of radical was observed using electron spin resonance (ESR) in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the trapping agent compared with the

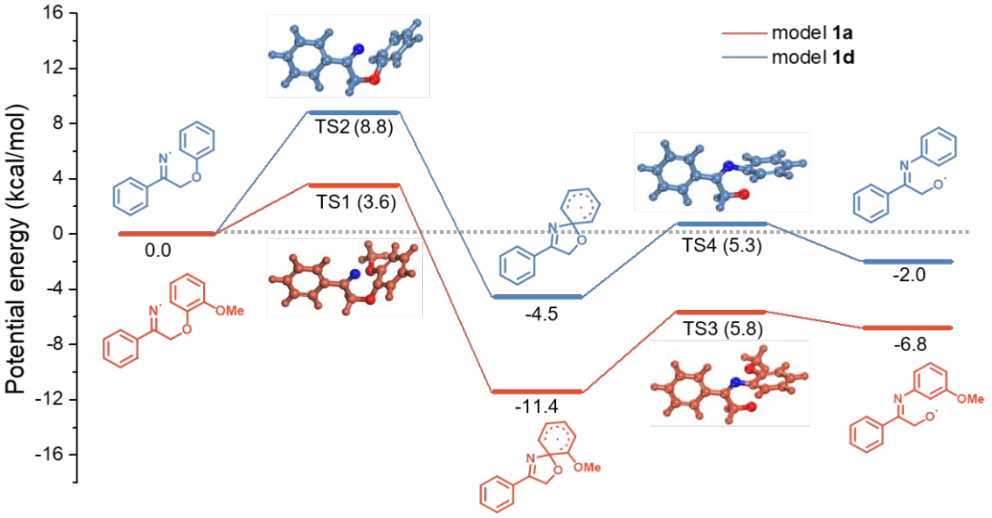
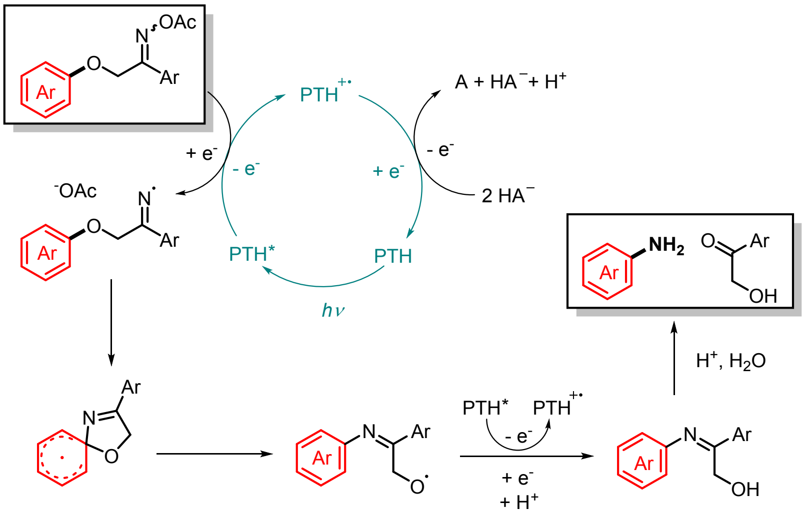


Figure 3. DFT calculations for the aryl migration pathway from oxygen to nitrogen.

signal under dark condition (Figure 2, c).[73] Analysis for the mixture of ESR experiments by HPLC-MS (Supporting Information, Figure S5) proved the existence of several DMPO adducts with the radicals (MW. 240). To further prove the role of HA, the oxidation potentials were measured by cyclic voltammetry (Figure 2, d). Compared to **2a** and **3a**, HA exhibited a lower oxidation potential, implying HA could act as the reductant to protect the products from oxidation in the cycling of PTH catalyst.

The aryl migration from oxygen to nitrogen was further investigated by DFT calculations and comparison of migration pathways between **1a** and **1d** was used to elucidate their different reaction behaviors (Figure 3). The spiro-cyclization and aryl C−O bond cleavage for both substrates are exothermic. However, the whole migration pathway of substrate **1a** is more thermodynamically favorable. Compared to **1a**, the spiro cyclization of substrate **1d** exhibits a higher activation barrier (TS1 and TS2), and activation energies of both following C−O bond cleavages are similar (TS3 and TS4). Therefore, the methoxyl substituent at *ortho* position could favor the twisting of phenol



Scheme 2. Proposed pathway for amination of aryl ether to primary arylamine.

segment to achieve spiro-cyclization. These calculation results accorded well with the experimental results that both aminations occurred while **1a** afforded better yields of desired products. When the electron-withdrawing groups coexist with *ortho*-methoxyl on the migrated ring (**1h** and **1i**), moderate yields of desired products could be still obtained which suggested the effect of *ortho*-methoxyl could be mainly ascribed to the steric effect rather than the electronic effect.

Based on the mechanism studies and previous reports,[50,56,74] a possible pathway for the intramolecular amination of aryl ether was proposed (Scheme 2). This reaction starts with the reduction of N−O bond by the excited PTH, then the generated iminyl radical attacks the aryl C−O bond where *ortho*-substituent promotes the spiro-cyclization. After aryl C−O bond cleavage, primary arylamine and α-hydroxy ketone are released via further hydrogen abstraction and hydrolysis. HA could act as the final reductant and protect the products from being oxidized.

CONCLUSIONS

In conclusion, we developed the aryl ether cleavage to obtain non-phenolic products by installing an internal nucleophile in modified lignin models and extracts. Through constructing the acetyl oxime in modified lignin, the internal iminyl radical was generated under photocatalytic reduction and induced intramolecular spiro cyclization to cleave the aryl ether bond in α-oximated β-aryl ethers. The obtained non-phenolic primary arylamines are readily derived to other nitrogen-containing compounds thus this method enables the access of non-phenolic nitrogen-containing aromatics from lignin conversion.

EXPERIMENTAL SECTION

Chemicals and Materials. All chemicals were of analytical grade, purchased from Aladdin Chemicals and used without further purification. The synthesis of lignin models and modified lignin, NMR spectra and HRMS were provided in the Supporting Information.

Catalytic Test. Typically, a 6 mL quartz reactor tube equipped with a stir bar was loaded with substrate (0.05 mmol), catalyst, and additives. Solvent was added and the atmosphere was changed to argon before sealing the tube. The reaction mixture was irradiated at room temperature with lamps (λ_{max}= 365 nm) for specified time. After the completing of the reaction, internal standard was added. Reaction mixture was analyzed by HPLC after 5 times dilution. Quantification of 2-hydroxyacetophenone, 2-methoxyaniline, 2, 6-dimethoxyaniline, 2-phenylaniline, and aniline were performed using corresponding standard work curves. Quantification of other compounds were performed using isolated yields.

As to the modified lignin conversion, a 6 mL quartz reactor tube equipped with a stir bar was loaded with lignin sample (30 mg), PC1 (1 mg), and ascorbic acid (17.6 mg). Solvent ($CH_3CN/H_2O/HCOOH$, 18:1:1, 2 mL) was added and the atmosphere was changed to argon before sealing the tube. The reaction mixture was irradiated at room temperature with lamps (λ_{max} = 365 nm) for 8 h. After the completing of the reaction, internal standard (vanilline) was added. Reaction mixture was analyzed by GC-MS after 5 times concentration.

AUTHOR INFORMATION

Corresponding Author

*E-mail for F.W.: wangfeng@dicp.ac.cn

ASSOCIATED CONTENT

Supporting Information

ESR, fluorescence quenching experiments, UV-Vis absorption spectra, cyclic voltammetry, HPLC-MS and DFT calculations were provided in the Supporting Information.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (21711530020, 21721004, 21690084, 21690082, 21690080), the "Strategic Priority Research Program of the Chinese Academy of Sciences" Grant No. XDB17020300, XDB17000000.

REFERENCES

(1) Zakzeski, J.; Bruijnincx, P. C.; Jongerius, A. L.; Weckhuysen, B. M. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chem. Rev.* **2010**, *110*, 3552-3599.

(2) Li, C.; Zhao, X.; Wang, A.; Huber, G. W.; Zhang, T. Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. *Chem. Rev.* **2015**, *115*, 11559-11624.

(3) Ma, R.; Xu, Y.; Zhang, X. Catalytic Oxidation of Biorefinery Lignin to Value-Added Chemicals to Support Sustainable Biofuel Production. *ChemSusChem* **2015**, *8*, 24-51.

(4) Galkin, M. V.; Samec, J. S. Lignin Valorization through Catalytic Lignocellulose Fractionation: A Fundamental Platform for the Future Biorefinery. *ChemSusChem* **2016**, *9*, 1544-1558.

(5) Li, S.-H.; Liu, S.; Colmenares, J. C.; Xu, Y.-J. A Sustainable Approach for Lignin Valorization by Heterogeneous Photocatalysis. *Green Chem.* **2016**, *18*, 594-607.

(6) Das, A.; König, B. Transition Metal- and Photoredox-Catalyzed Valorisation of Lignin Subunits. *Green Chem.* **2018**, *20*, 4844-4852.

(7) Liu, C.; Wu, S.; Zhang, H.; Xiao, R. Catalytic Oxidation of Lignin to Valuable Biomass-Based Platform Chemicals: A Review. *Fuel Process. Technol.* **2019**, *191*, 181-201.

(8) Rinaldi, R.; Jastrzebski, R.; Clough, M. T.; Ralph, J.; Kennema, M.; Bruijnincx, P. C.; Weckhuysen, B. M. Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. *Angew. Chem. Int. Ed.* **2016**, *55*, 8164-8215.

(9) Sun, Z.; Fridrich, B.; de Santi, A.; Elangovan, S.; Barta, K. Bright Side of Lignin Depolymerization: Toward New Platform Chemicals. *Chem. Rev.* **2018**, *118*, 614-678.

(10) Van den Bosch, S.; Koelewijn, S. F.; Renders, T.; Van den Bossche, G.; Vangeel, T.; Schutyser, W.; Sels, B. F. Catalytic Strategies Towards Lignin-Derived Chemicals. *Top. Curr. Chem.* **2018**, *376*, 1-40.

(11) Deuss, P. J.; Barta, K. From Models to Lignin: Transition Metal Catalysis for Selective Bond Cleavage Reactions. *Coord. Chem. Rev.* **2016**, *306*, 510-532.

(12) Galkin, M. V.; Dahlstrand, C.; Samec, J. S. Mild and Robust Redox-Neutral Pd/C-Catalyzed Lignol beta-O-4' Bond Cleavage Through a Low-Energy-Barrier Pathway. *ChemSusChem* **2015**, *8*, 2187-2192.

(13) Luo, N.; Wang, M.; Li, H.; Zhang, J.; Hou, T.; Chen, H.; Zhang, X.; Lu, J.; Wang, F. Visible-Light-Driven Self-Hydrogen Transfer Hydrogenolysis of Lignin Models and Extracts into Phenolic Products. *ACS Catal.* **2017**, *7*, 4571-4580.

(14) Wu, X.; Fan, X.; Xie, S.; Lin, J.; Cheng, J.; Zhang, Q.; Chen, L.; Wang, Y. Solar Energy-Driven Lignin-First Approach to Full Utilization of Lignocellulosic Biomass under Mild Conditions. *Nat. Catal.* **2018**, *1*, 772-780.

(15) Parsell, T. H.; Owen, B. C.; Klein, I.; Jarrell, T. M.; Marcum, C. L.; Haupert, L. J.; Amundson, L. M.; Kenttämaa, H. I.; Ribeiro, F.; Miller, J. T.; Abu-Omar, M. M. Cleavage and Hydrodeoxygenation (HDO) of C–O Bonds Relevant to Lignin Conversion Using Pd/Zn Synergistic Catalysis. *Chem. Sci.* **2013**, *4*, 806-813.

(16) Song, Q.; Wang, F.; Cai, J.; Wang, Y.; Zhang, J.; Yu, W.; Xu, J. Lignin Depolymerization (LDP) in Alcohol over Nickel-Based Catalysts via a Fragmentation–Hydrogenolysis Process. *Energy Environ. Sci.* **2013**, *6*, 994.

(17) Zhang, J.; Teo, J.; Chen, X.; Asakura, H.; Tanaka, T.; Teramura, K.; Yan, N. A Series of NiM (M = Ru, Rh, and Pd) Bimetallic Catalysts for Effective Lignin Hydrogenolysis in Water. *ACS Catal.* **2014**, *4*, 1574-1583.

(18) Feghali, E.; Carrot, G.; Thuéry, P.; Genre, C.; Cantat, T. Convergent Reductive Depolymerization of Wood Lignin to Isolated Phenol Derivatives by Metal-free Catalytic Hydrosilylation. *Energy Environ.*

Sci. **2015**, *8*, 2734-2743.

(19) Parsell, T.; Yohe, S.; Degenstein, J.; Jarrell, T.; Klein, I.; Gencer, E.; Hewetson, B.; Hurt, M.; Kim, J. I.; Choudhari, H.; Saha, B.; Meilan, R.; Mosier, N.; Ribeiro, F.; Delgass, W. N.; Chapple, C.; Kenttämaa, H. I.; Agrawal, R.; Abu-Omar, M. M. A Synergistic Biorefinery Based on Catalytic Conversion of Lignin Prior to Cellulose Starting from Lignocellulosic Biomass. *Green Chem.* **2015**, *17*, 1492-1499.

(20) Klein, I.; Marcum, C.; Kenttämaa, H.; Abu-Omar, M. M. Mechanistic Investigation of the Zn/Pd/C Catalyzed Cleavage and Hydrodeoxygenation of Lignin. *Green Chem.* **2016**, *18*, 2399-2405.

(21) Shuai, L.; Amiri, M. T.; Questell-Santiago, Y. M.; Heroguel, F.; Li, Y.; Kim, H.; Meilan, R.; Chapple, C.; Ralph, J.; Luterbacher, J. S. Formaldehyde Stabilization Facilitates Lignin Monomer Production During Biomass Depolymerization. *Science* **2016**, *354*, 329-333.

(22) Bosque, I.; Magallanes, G.; Rigoulet, M.; Karkas, M. D.; Stephenson, C. R. J. Redox Catalysis Facilitates Lignin Depolymerization. *ACS Cent. Sci.* **2017**, *3*, 621-628.

(23) Lan, W.; Amiri, M. T.; Hunston, C. M.; Luterbacher, J. S. Protection Group Effects During alpha,gamma-Diol Lignin Stabilization Promote High-Selectivity Monomer Production. *Angew. Chem. Int. Ed.* **2018**, *57*, 1356-1360.

(24) Lancefield, C. S.; Teunissen, L. W.; Weckhuysen, B. M.; Bruijnincx, P. C. A. Iridium-Catalysed Primary Alcohol Oxidation and Hydrogen Shuttling for the Depolymerisation of Lignin. *Green Chem.* **2018**, *20*, 3214-3221.

(25) Li, Y.; Shuai, L.; Kim, H.; Motagamwala, A. H.; Mobley, J. K.; Yue, F.; Tobimatsu, Y.; Havkin-Frenkel, D.; Chen, F.; Dixon, R. A.; Luterbacher, J. S.; Dumesic, J. A.; Ralph, J. An "Ideal Lignin" Facilitates Full Biomass Utilization. *Sci. Adv.* **2018**, *4*, eaau2968.

(26) Sun, Z.; Bottari, G.; Afanasenko, A.; Stuart, M. C. A.; Deuss, P. J.; Fridrich, B.; Barta, K. Complete Lignocellulose Conversion with Integrated Catalyst Recycling Yielding Valuable Aromatics and Fuels. *Nat. Catal.* **2018**, *1*, 82-92.

(27) Sturgeon, M. R.; Kim, S.; Lawrence, K.; Paton, R. S.; Chmely, S. C.; Nimlos, M.; Foust, T. D.; Beckham, G. T. A Mechanistic Investigation of Acid-Catalyzed Cleavage of Aryl-Ether Linkages: Implications for Lignin Depolymerization in Acidic Environments. *ACS Sustainable Chem. Eng.* **2013**, *2*, 472-485.

(28) Deepa, A. K.; Dhepe, P. L. Lignin Depolymerization into Aromatic Monomers over Solid Acid Catalysts. *ACS Catal.* **2014**, *5*, 365-379.

(29) Rahimi, A.; Ulbrich, A.; Coon, J. J.; Stahl, S. S. Formic-Acid-Induced Depolymerization of Oxidized Lignin to Aromatics. *Nature* **2014**, *515*, 249-252.

(30) Lahive, C. W.; Deuss, P. J.; Lancefield, C. S.; Sun, Z.; Cordes, D. B.; Young, C. M.; Tran, F.; Slawin, A. M.; de Vries, J. G.; Kamer, P. C.; Westwood, N. J.; Barta, K. Advanced Model Compounds for Understanding Acid-Catalyzed Lignin Depolymerization: Identification of Renewable Aromatics and a Lignin-Derived Solvent. *J. Am. Chem. Soc.* **2016**, *138*, 8900-8911.

(31) Hanson, S. K.; Wu, R.; Silks, L. A. C-C or C-O Bond Cleavage in a Phenolic Lignin Model Compound: Selectivity Depends on Vanadium Catalyst. *Angew. Chem. Int. Ed.* **2012**, *51*, 3410-3413.

(32) Zhang, G.; Scott, B. L.; Wu, R.; Silks, L. A.; Hanson, S. K. Aerobic Oxidation Reactions Catalyzed by Vanadium Complexes of Bis(Phenolate) Ligands. *Inorg. Chem.* **2012**, *51*, 7354-7361.

(33) Gazi, S.; Hung Ng, W. K.; Ganguly, R.; Putra Moeljadi, A. M.; Hirao, H.; Soo, H. S. Selective Photocatalytic C-C Bond Cleavage under Ambient Conditions with Earth Abundant Vanadium Complexes. *Chem. Sci.* **2015**, *6*, 7130-7142.

(34) Hanson, S. K.; Baker, R. T. Knocking on Wood: Base Metal Complexes as Catalysts for Selective Oxidation of Lignin Models and Extracts. *Acc. Chem. Res.* **2015**, *48*, 2037-2048.

(35) Lancefield, C. S.; Ojo, O. S.; Tran, F.; Westwood, N. J. Isolation of Functionalized Phenolic Monomers through Selective Oxidation and C-O Bond Cleavage of the beta-O-4 Linkages in Lignin. *Angew. Chem. Int. Ed.* **2015**, *54*, 258-262.

(36) Das, A.; Rahimi, A.; Ulbrich, A.; Alherech, M.; Motagamwala, A. H.; Bhalla, A.; da Costa Sousa, L.; Balan, V.; Dumesic, J. A.; Hegg, E. L.; Dale, B. E.; Ralph, J.; Coon, J. J.; Stahl, S. S. Lignin Conversion to Low-Molecular-Weight Aromatics via an Aerobic Oxidation-Hydrolysis Sequence: Comparison of Different Lignin Sources. *ACS Sustainable Chem. Eng.* **2018**, *6*, 3367-3374.

(37) Lee, T. W.; Yang, J. W. Transition-Metal-Free Conversion of Lignin Model Compounds to High-Value Aromatics: Scope and Chemoselectivity. *Green Chem.* **2018**, *20*, 3761-3771.

(38) Liu, H.; Li, H.; Lu, J.; Zeng, S.; Wang, M.; Luo, N.; Xu, S.; Wang, F. Photocatalytic Cleavage of C–C Bond in Lignin Models under Visible Light on Mesoporous Graphitic Carbon Nitride through π–π Stacking Interaction. *ACS Catal.* **2018**, *8*, 4761-4771.

(39) Schutyser, W.; Kruger, J. S.; Robinson, A. M.; Katahira, R.; Brandner, D. G.; Cleveland, N. S.; Mittal, A.; Peterson, D. J.; Meilan, R.; Román-Leshkov, Y.; Beckham, G. T. Revisiting Alkaline Aerobic Lignin Oxidation. *Green Chem.* **2018**, *20*, 3828-3844.

(40) Zhou, W.; Nakahashi, J.; Miura, T.; Murakami, M. Light/Copper Relay for Aerobic Fragmentation of Lignin Model Compounds. *Asian J. Org. Chem.* **2018**, *7*, 2431-2434.

(41) vom Stein, T.; den Hartog, T.; Buendia, J.; Stoychev, S.; Mottweiler, J.; Bolm, C.; Klankermayer, J.; Leitner, W. Ruthenium-Catalyzed C-C Bond Cleavage in Lignin Model Substrates. *Angew. Chem. Int. Ed.* **2015**, *54*, 5859-5863.

(42) Jastrzebski, R.; Constant, S.; Lancefield, C. S.; Westwood, N. J.; Weckhuysen, B. M.; Bruijnincx, P. C. Tandem Catalytic Depolymerization of Lignin by Water-Tolerant Lewis Acids and Rhodium Complexes. *ChemSusChem* **2016**, *9*, 2074-2079.

(43) Dong, L.; Lin, L.; Han, X.; Si, X.; Liu, X.; Guo, Y.; Lu, F.; Rudić, S.; Parker, S. F.; Yang, S.; Wang, Y. Breaking the Limit of Lignin Monomer Production via Cleavage of Interunit Carbon–Carbon Linkages. *Chem* **2019**, *5*, 1521-1536.

(44) Liu, J.; Qiu, X.; Huang, X.; Luo, X.; Zhang, C.; Wei, J.; Pan, J.; Liang, Y.; Zhu, Y.; Qin, Q.; Song, S.; Jiao, N. From Alkylarenes to Anilines via Site-Directed Carbon-Carbon Amination. *Nat. Chem.* **2019**, *11*, 71-77.

(45) Wang, Y.; Du, Y.; He, J.; Zhang, Y. Transformation of Lignin Model Compounds to N-Substituted Aromatics via Beckmann Rearrangement. *Green Chem.* **2018**, *20*, 3318-3326.

(46) Cao, D.; Zeng, H.; Li, C.-J. Formal Cross-Coupling of Diaryl Ethers with Ammonia by Dual C(Ar)–O Bond Cleavages. *ACS Catal.* **2018**, *8*, 8873-8878.

(47) Zeng, H.; Cao, D.; Qiu, Z.; Li, C. J. Palladium-Catalyzed Formal Cross-Coupling of Diaryl Ethers with Amines: Slicing the 4-O-5 Linkage in Lignin Models. *Angew. Chem. Int. Ed.* **2018**, *57*, 3752-3757.

(48) Cornella, J.; Zarate, C.; Martin, R. Metal-Catalyzed Activation of Ethers via C-O Bond Cleavage: A New Strategy for Molecular Diversity. *Chem. Soc. Rev.* **2014**, *43*, 8081-8097.

(49) Tay, N. E. S.; Nicewicz, D. A. Cation Radical Accelerated Nucleophilic Aromatic Substitution via Organic Photoredox Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 16100-16104.

(50) Chen, Z. M.; Zhang, X. M.; Tu, Y. Q. Radical Aryl Migration Reactions and Synthetic Applications. *Chem. Soc. Rev.* **2015**, *44*, 5220-5245.

(51) Zhang, Z.; Lahive, C. W.; Zijlstra, D. S.; Wang, Z.; Deuss, P. J. Sequential Catalytic Modification

of the Lignin α-Ethoxylated β-O-4 Motif To Facilitate C–O Bond Cleavage by Ruthenium-Xantphos Catalyzed Hydrogen Transfer. *ACS Sustainable Chem. Eng.* **2019**, *7*, 12105-12116.

(52) Xiao, G.; Lancefield, C. S.; Westwood, N. J. Selective Depolymerisation of γ-Oxidised Lignin via NHC Catalysed Redox Esterification. *ChemCatchem* **2019**, *11*, 3182-3186.

(53) Panovic, I.; Miles-Barrett, D. M.; Lancefield, C. S.; Westwood, N. J. Preparation and Reaction of β-O-4 γ-Aldehyde-Containing Butanosolv Lignins. *ACS Sustainable Chem. Eng.* **2019**, *7*, 12098-12104.

(54) Li, H.; Wang, M.; Liu, H.; Luo, N.; Lu, J.; Zhang, C.; Wang, F. NH_2OH–Mediated Lignin Conversion to Isoxazole and Nitrile. *ACS Sustainable Chem. Eng.* **2018**, *6*, 3748-3753.

(55) Downing, R. S.; Kunkeler, P. J.; van Bekkum, H. Catalytic Syntheses of Aromatic Amines. *Catal. Today* **1997**, *37*, 121-136.

(56) Chen, J. R.; Hu, X. Q.; Lu, L. Q.; Xiao, W. J. Visible Light Photoredox-controlled Reactions of N-radicals and Radical Ions. *Chem. Soc. Rev.* **2016**, *45*, 2044-2056.

(57) Treat, N. J.; Sprafke, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Read de Alaniz, J.; Fors, B. P.; Hawker, C. J. Metal-free Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* **2014**, *136*, 16096-16101.

(58) Discekici, E. H.; Treat, N. J.; Poelma, S. O.; Mattson, K. M.; Hudson, Z. M.; Luo, Y.; Hawker, C. J.; Read de Alaniz, J. A Highly Reducing Metal-Free Photoredox Catalyst: Design and Application in Radical Dehalogenations. *Chem. Commun.* **2015**, *51*, 11705-11708.

(59) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116*, 10075-10166.

(60) Wang, H.; Jui, N. T. Catalytic Defluoroalkylation of Trifluoromethylaromatics with Unactivated Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 163-166.

(61) Luo, N.; Wang, M.; Li, H.; Zhang, J.; Liu, H.; Wang, F. Photocatalytic Oxidation–Hydrogenolysis of Lignin β-O-4 Models via a Dual Light Wavelength Switching Strategy. *ACS Catal.* **2016**, *6*, 7716-7721.

(62) Luo, J.; Zhang, X.; Lu, J.; Zhang, J. Fine Tuning the Redox Potentials of Carbazolic Porous Organic Frameworks for Visible-Light Photoredox Catalytic Degradation of Lignin β-O-4 Models. *ACS Catal.* **2017**, *7*, 5062-5070.

(63) Magallanes, G.; Kärkäs, M. D.; Bosque, I.; Lee, S.; Maldonado, S.; Stephenson, C. R. J. Selective C–O Bond Cleavage of Lignin Systems and Polymers Enabled by Sequential Palladium-Catalyzed Aerobic Oxidation and Visible-Light Photoredox Catalysis. *ACS Catal.* **2019**, *9*, 2252-2260.

(64) Pandey, G.; Rao, K. S. S. P.; Rao, K. V. N. Photosensitized Electron Transfer Promoted Reductive Activation of Carbon-Selenium Bonds to Generate Carbon-Centered Radicals: Application for Unimolecular Group Transfer Radical Reactions. *J. Org. Chem.* **1996**, *61*, 6799-6804.

(65) Jiang, H.; An, X.; Tong, K.; Zheng, T.; Zhang, Y.; Yu, S. Visible-Light-Promoted Iminyl-Radical Formation from Acyl Oximes: A Unified Approach to Pyridines, Quinolines, and Phenanthridines. *Angew. Chem. Int. Ed.* **2015**, *54*, 4055-4059.

(66) McBurney, R. T.; Walton, J. C. Interplay of ortho- with Spiro-Cyclisation During Iminyl Radical Closures onto Arenes and Heteroarenes. *Beilstein J. Org. Chem.* **2013**, *9*, 1083-1092.

(67) Yang, P.; Lim, L. H.; Chuanprasit, P.; Hirao, H.; Zhou, J. S. Nickel-Catalyzed Enantioselective Reductive Amination of Ketones with Both Arylamines and Benzhydrazide. *Angew. Chem. Int. Ed.* **2016**, *55*, 12083-12087.

(68) Liang, G.; Wang, A.; Li, L.; Xu, G.; Yan, N.; Zhang, T. Production of Primary Amines by Reductive Amination of Biomass-Derived Aldehydes/Ketones. *Angew. Chem. Int. Ed.* **2017**, *56*, 3050-3054.

(69) Guo, H.; Miles-Barrett, D. M.; Neal, A. R.; Zhang, T.; Li, C.; Westwood, N. J. Unravelling the Enigma of Lignin(OX): Can the Oxidation of Lignin Be Controlled? *Chem. Sci.* **2018**, *9*, 702-711.

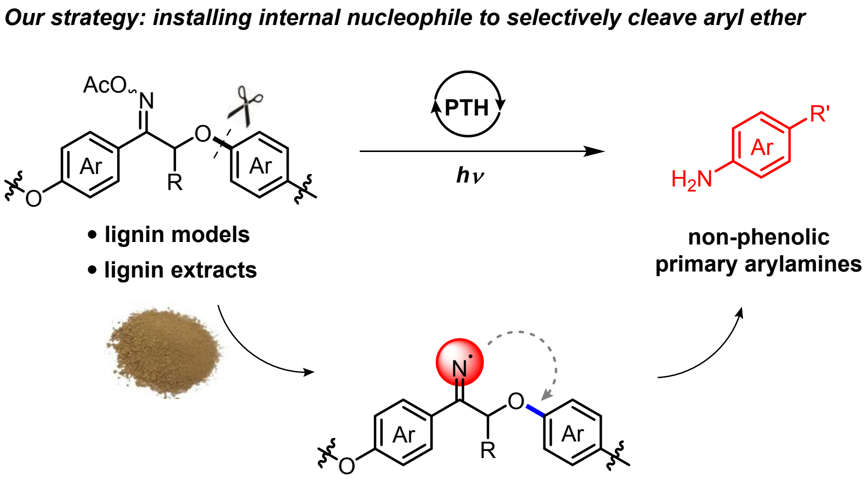
(70) Sameni, J.; Krigstin, S.; Sain, M. Solubility of Lignin and Acetylated Lignin in Organic Solvents. *BioResources* **2017**, *12*, 1548-1565.

(71) Yuan, T. Q.; Sun, S. N.; Xu, F.; Sun, R. C. Characterization of Lignin Structures and Lignin-Carbohydrate Complex (LCC) Linkages by Quantitative 13C and 2D HSQC NMR Spectroscopy. *J. Agric. Food. Chem.* **2011**, *59*, 10604-10614.

(72) Si, X.; Lu, F.; Chen, J.; Lu, R.; Huang, Q.; Jiang, H.; Taarning, E.; Xu, J. A Strategy for Generating High-Quality Cellulose and Lignin Simultaneously from Woody Biomass. *Green Chem.* **2017**, *19*, 4849-4857.

(73) Xie, L. N.; Shao, J.; Huang, C. H.; Li, F.; Xu, D.; Kalyanaraman, B.; Zhu, B. Z. An Unusual Double Radical Homolysis Mechanism for the Unexpected Activation of the Aldoxime Nerve-Agent Antidotes by Polyhalogenated Quinoid Carcinogens under Normal Physiological Conditions. *Free Radical Biol. Med.* **2019**, *130*, 1-7.

(74) Leardini, R.; McNab, H.; Minozzi, M.; Nanni, D. Thermal Decomposition of tert-Butyl ortho-(Phenylsulfanyl)- and ortho-(Phenylsulfonyl)phenyliminoxyperacetates: The Reactivity of Thio-Substituted Iminyl Radicals. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1072-1078.



The photocatalytic amination of aryl ether in modified lignin models and extracts to non-phenolic primary arylamines was developed. Through constructing the acetyl oxime in modified lignin, internal iminyl radical was generated under photocatalytic reduction and induced intramolecular aryl migration to cleave the aryl ether bond in β-O-4’ linkages.