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COMMUNICATION

Palladium-Catalyzed Formal Cross-Coupling of Diaryl Ethers with Amines: New Tactic to Slice 4-O-5 Linkage in Lignin Models

Huiying Zeng,[a],* Dawei Cao,[a] Zihang Qiu[b] and Chao-Jun Li[a],[b],*

Abstract: Lignin, the second most abundant organic matter on Earth, is an under-utilized renewable source for valuable aromatic chemicals. For future sustainable aromatic products, it is highly desirable to convert lignin into higher value-added platform chemicals instead of using the fossil-based resources. Lignins are aromatic polymers linked by three types of ether bonds (*α*-O-4, *β*-O-4 and 4-O-5 linkages) and other C–C bonds. Among those ether bonds, the bond dissociation energy of 4-O-5 linkage is the highest and the most challenging to cleave. Up to date, the 4-O-5 ether linkage model compounds have been cleaved to obtain phenol, cyclohexane, cyclohexanone, and cyclohexanol. Herein, we report the first example of direct formal cross-coupling of the 4-O-5 linkage model compounds, diaryl ethers, with amines via dual C(Ar)-O bond cleavages to generate valuable nitrogen-containing derivatives.

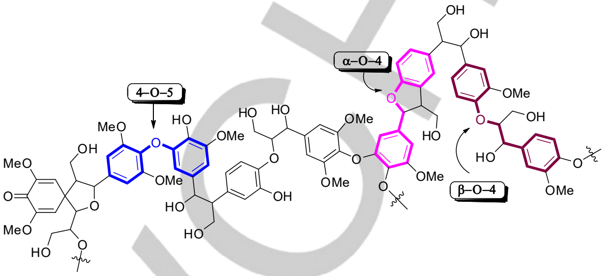
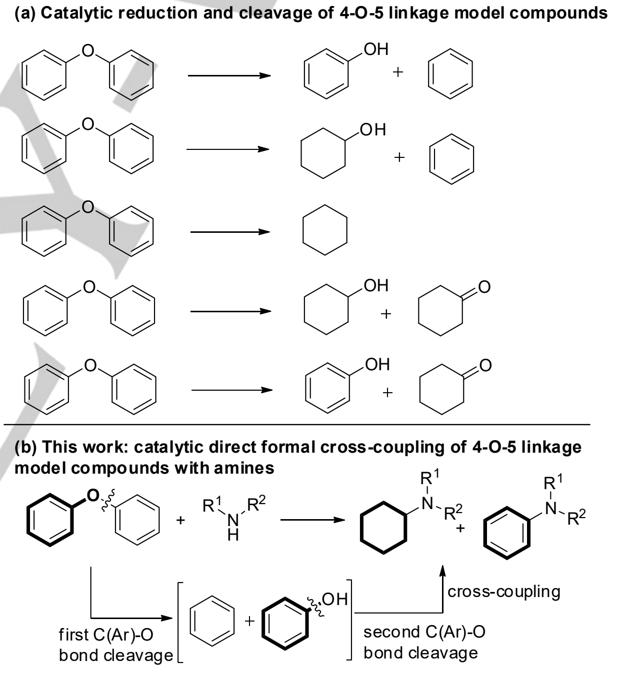


Figure 1. Common Ether Linkages in Lignins



Scheme 1. Strategies for Cleavage of Lignin 4-O-5 Linkage Model Compounds

Lignin, the most recalcitrant of the three components of lignocellulosic biomass,[1] accounts for ca. 30% of the organic carbon on Earth.[2] Until now, lignin has been treated as a waste product in the pulp and paper industry, mostly being burned to recover its thermo-energy. Lignin has the potential to provide one of the few renewable sources of aromatic chemicals in the future.[3] Consequently, valorization of lignin is becoming more and more important for social, economic, and resource sustainability.[4] Structurally, lignin is a complex polyphenolic substance containing a large number of C–O ether bonds (including *α*-O-4, *β*-O-4 and 4-O-5 linkages) (Fig. 1).[5] Therefore, cleavage of C–O ether bonds in lignins is a crucial step for the degradation and valorization of lignin biomass to obtain bio-fuels and commercial chemicals[6] and is challenging because of the strength and stability of these ether linkages.[1a, 7] 2-Phenylethyl phenyl ether, benzyl phenyl ether, and diphenyl ether have been commonly selected as model compounds for the cleavage of *β*-O-4, *α*-O-4 and 4-O-5 linkages, respectively.[8] Among these three types of C–O ether bonds, the bond dissociation energy (BDE) of diphenyl ether bond of 4-O-5 (BDE = 314 kJ·mol^{-1}) is much stronger than the aliphatic ether bonds of *α*-O-4 (BDE =218 kJ·mol^{-1}) and *β*-O-4 (BDE = 289 kJ·mol^{-1}).[9] Thus, while the cleavage of C–O aliphatic ether bond (*α*-O-4 linkage and *β*-O-4 linkage) were extensively reported through oxidation,[10] reduction,[11] hydrolysis/solvolysis,[3a, 12] and others,[13] the cleavage of diphenyl ether bond (4-O-5 linkage) is the most challenging. A milestone to overcome the challenge of cleaving the most difficult diphenyl ether C–O bond (4-O-5 linkage) via hydrogenolysis to form phenol and benzene was achieved by Hartwig and co-workers.[8b, 8c, 8f] Since then, several important progresses have been made in cleavage of diaryl ether bonds to form small molecules, including: a) phenol and benzene,[14] b) cyclohexanol,[8d] c) cyclohexane[8e, 15], d) cyclohexanol and cyclohexanone[8g] and e) cyclohexanone and phenol[8h] (Scheme 1a). It will be highly desirable to generate other important structural motifs such as nitrogen-containing compounds, a

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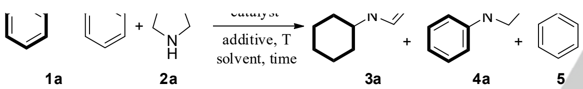
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) general feature shared by >90% of leading pharmaceutical agents[16], from diaryl ethers directly.

Recently, our group reported a palladium-catalyzed formal cross-coupling of phenols with amine to form amine derivatives via a hydrogen-borrowing strategy.[17] Inspired by this strategy, we contemplated the possibility of directly cleaving the most challenging C(Ar)–O bond of diphenyl ethers to generate the nitrogen-containing products, via the phenol intermediate generated in situ (Scheme 1b). *Herein we report, for the first time, a palladium-catalyzed direct conversion of biaryl ethers into amine derivatives via dual C(Ar)–O bond cleavages.* The amine derivatives are important building blocks for pharmaceuticals, fine chemicals, and electronic materials.[18]

Diphenyl ether was used as a model compound for the 4-O-5 linkage of lignin for our investigation. The diphenyl ether was reacted with pyrrolidine with Pd/C (20 mol%) as catalyst in toluene at 160°C under argon atmosphere for 24h using sodium formate as hydride source. Fortunately, the desired nitrogen-containing compound, 1-cyclohexyl-1H-pyrrole was detected by ^{1}H NMR in 18% yield with 26% conversion (Table 1, entry 1). Encouraged by this result, other palladium catalysts were examined for this transformation; lower conversion or no product was obtained when $Pd(OAc)_2$ and $Pd(PPh_3)_2Cl_2$ were used as catalysts (Table 1, entries 2-3). To our delight, higher conversion (35%) and yield (22%) were obtained when $Pd(OH)_2/C$ was used as catalyst (Table 1, entry 4). The addition of various additives such as Lewis acids and Lewis bases failed to produce any desired coupling products, with only small amounts of starting material being converted (Table 1, entries 5-8). The reaction showed a strong dependence on the solvent, among which *o*-xylene, *m*-xylene and *p*-xylene were more effective than toluene (Table 1, entries 9-11). It is interesting to note that the different substituted position of xylene is important to this transformation. The highest yield (48%) and highest conversion (71%) were obtained when *m*-xylene was used as solvent (Table 1, entry 10). More polar solvents, such as dioxane and water, were less effective (Table 1, entries 12-13). A small amount of water (10 µL) was found beneficial to this reaction (Table 1, entry 15), whereas a higher or lower amount of water resulted in a lower yield (Table 1, entries 14 and 16). The ratio of pyrrolidine and diphenyl ether at 3.5: 1 appeared to be optimal for this reaction (Table 1, entries 17-19). The amount of air was also important for both the yield and the conversion. A higher yield (66%) and higher conversion (93%) were achieved when 1 mL air was added in this reaction system (Table 1, entry 20). Further increasing the amount of air (2 mL) decreased the yield slightly (Table 1, entry 21). Decreasing the amount of $Pd(OH)_2/C$ to 10%, both the yield and the conversion were reduced significantly (Table 1, entry 22). No improvement in yield was observed when increasing the amount of catalyst; and almost the same yields were observed with 30 mol% or 40 mol% $Pd(OH)_2/C$ (Table 1, entries 23-24). For economical reason, we choose the amount of 30 mol% $Pd(OH)_2/C$ as the optimal conditions for the following optimization process. It was found that much better result (77% yield, 99% conversion) was obtained when $NaBH_4$ was used as an alternative hydride source (Table 1, entry 25). Further increasing the amount of $NaBH_4$ gave the best result in 83% yield (Table 1, entry 26). When 1 atm H_2 was used, instead of $NaBH_4$ and argon atmosphere, both lower yield and conversion were observed (Table 1, entry 27). For details of studies on the reaction temperature, reaction time and others, please see Supporting Information.



1a **2a** **3a** **4a** **5**

Entry	Catalyst	Additive	Solvent	Conv./%	3a^b/%	4a^b/%	5^c/%
1	Pd/C		toluene	26	18	6	-
2	$Pd(PPh_3)_2Cl_2$		toluene	13	n.p.	n.p.	-
3	$Pd(OAc)_2$		toluene	12	n.p.	n.p.	-
4	$Pd(OH)_2/C$		toluene	35	22	5	-
5	$Pd(OH)_2/C$	$AlCl_3$	toluene	22	n.p.	n.p.	-
6	$Pd(OH)_2/C$	CF_3CO_2H	toluene	5	n.p.	n.p.	-
7	$Pd(OH)_2/C$	DBU	toluene	14	n.p.	n.p.	-
8	$Pd(OH)_2/C$	Cs_2CO_3	toluene	8	n.p.	n.p.	-
9	$Pd(OH)_2/C$		*o*-xylene	60	30	22	-
10	$Pd(OH)_2/C$		*m*-xylene	71	48	20	-
11	$Pd(OH)_2/C$		*p*-xylene	62	20	19	-
12	$Pd(OH)_2/C$		1,4-dioxane	11	n.p.	n.p.	-
13	$Pd(OH)_2/C$		H_2O	20	trace	n.p.	-
14	$Pd(OH)_2/C$	H_2O (5 uL)	*m*-xylene	85	47	26	-
15	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	81	52	25	-
16	$Pd(OH)_2/C$	H_2O (15 uL)	*m*-xylene	65	42	18	-
17^d	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	88	39	23	-
18^e	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	90	57	25	-
19^f	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	82	36	20	-
20^{e,g}	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	93	66	18	-
21^{e,h}	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	92	62	17	-
22^{e,g,i}	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	65	22	13	-
23^{e,g,j}	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	99	70	22	-
24^{e,g,k}	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	99	71	24	-
25^{e,g,j,l}	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	99	77	15	82
26^{e,g,j,m}	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	>99	83 (79)	13 (11)	83
27^{e,g,j,n}	$Pd(OH)_2/C$	H_2O (10 uL)	*m*-xylene	93	68	10	78

a. General conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), catalyst (20 mol%), HCO_2Na (1 equiv), additive (0.5 equiv) and solvent (1 mL) at 160°C for 24 h under argon atmosphere. b. Yields were determined by 1H NMR with nitromethane as internal standard; isolated yields in brackets. c. The yields of benzene and cyclohexane were determined by GC-MS. d. Pyrrolidine (0.3 mmol). e. Pyrrolidine (0.7 mmol). f. Pyrrolidine (0.9 mmol). g. Air (1 mL) was added. h. Air (2 mL) was added. i. $Pd(OH)_2/C$ (10 mol%). j. $Pd(OH)_2/C$ (30 mol%). k. $Pd(OH)_2/C$ (40 mol%). l. $NaBH_4$ was used instead of sodium formate. m. $NaBH_4$ (1.5 equiv). n. 1 atm H_2 was used instead of argon atmosphere, in absence of sodium formate.

With the optimized reaction conditions in hand, the substrate scope was explored with 3.5 equiv of pyrrolidine at 160□ under argon (with 1 mL air and 10 µL water) using 30 mol% of $Pd(OH)_2/C$ as the catalyst and 1.5 equiv of sodium borohydride as the hydride source in *m*-xylene (1 mL) for 24 h. As shown in Table 2, symmetrical diaryl ether reacted with pyrrolidine in good to excellent conversions and moderate to excellent yields (Table 2, entries 1-8). Various diaryl ethers bearing electron-donating and electron-withdrawing groups at different positions were all effective for the transformation. It is noteworthy that with strong electron-donating group—methoxyl group substituted at different positions (*ortho*-, *meta*- or *para*-) of diphenyl ether, the same major product 1-cyclohexylpyrrole **3a** was obtained with demethoxylation at the same time, and the minor product 1-phenylpyrrolidine **4a** was also obtained with demethoxylation (Table 2, entries 4-6). The corresponding products were obtained in good total yield without ester-amide exchange when the

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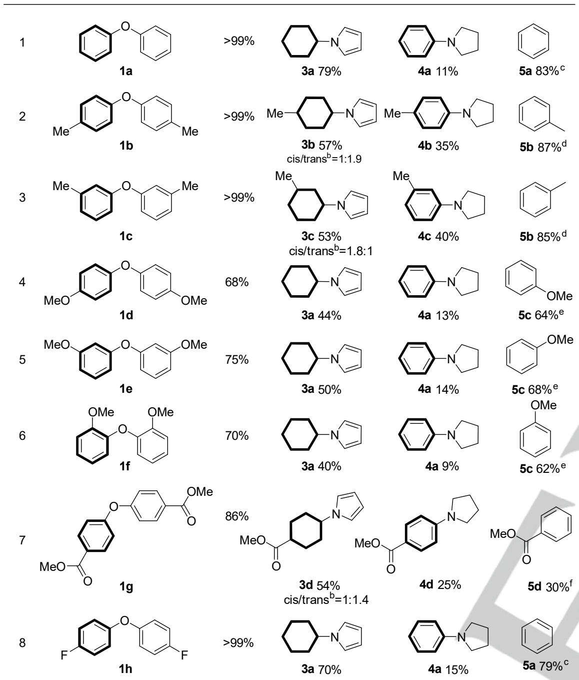
substrate contained an ester group (Table 2, entry 7). When fluorine-containing diphenyl ether was used, defluorination products were obtained with excellent conversion and high total yield (Table 2, entry 8). For all substrates, the corresponding arenes were also obtained with good to high yields (Table 2, entries 1-8).

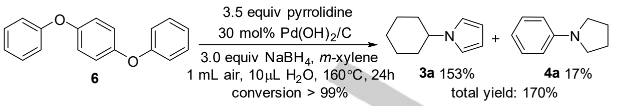


	Substrate	Conversion			
1	**1a**	>99%	**3a** 79%	**4a** 11%	**5a** 83%[c]
2	**1b**	>99%	**3b** 57% cis/trans[b]=1:1.9	**4b** 35%	**5b** 87%[d]
3	**1c**	>99%	**3c** 53% cis/trans[b]=1.8:1	**4c** 40%	**5b** 85%[d]
4	**1d**	68%	**3a** 44%	**4a** 13%	**5c** 64%[e]
5	**1e**	75%	**3a** 50%	**4a** 14%	**5c** 68%[e]
6	**1f**	70%	**3a** 40%	**4a** 9%	**5c** 62%[e]
7	**1g**	86%	**3d** 54% cis/trans[b]=1:1.4	**4d** 25%	**5d** 30%[f]
8	**1h**	>99%	**3a** 70%	**4a** 15%	**5a** 79%[c]

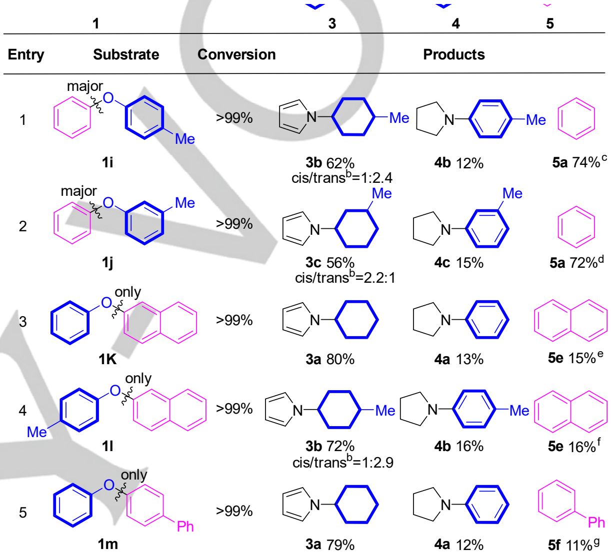
[a] Reaction conditions: diaryl ether (0.2 mmol), pyrrolidine (0.7 mmol), $Pd(OH)_2/C$ (30 mol%), and $NaBH_4$ (0.3 mmol) in *m*-xylene (1 mL). All reactions were carried out at 160°C in a sealed tube under argon (with air (1 mL) and water (10 μL)) for 24 h; yields of isolated products were given; conversions were determined by ^1H NMR with nitromethane as internal standard. [b] Cis/trans (isomer) ratio was determined by crude ^1H NMR. c. Yields of benzene and cyclohexane were determined by GC-MS; a small peak of cyclohexane overlapped within the big peak of benzene. d.Yield was determined by GC-MS; no methylcyclohexane was detected. e. Yield was determined by GC-MS; no cyclohexylmethyl ether was detected. f. Isolated yield. In addition, 52% of methyl cyclohexanecarboxylate was obtained.

Non-symmetrical diaryl ethers were then used to investigate the regioselectivity of the reactions (Table 3). We found that nitrogen-containing products were obtained with high total yields (71-74%), excellent conversions (>99%) and highly regioselective cleavage of C(Ar)–O bond with only a small difference in substitution of phenyl ring (Table 3, entries 1-2). Similar excellent total yields (88-93%), excellent conversions (>99%) and regioselective cleavage of C(Ar)–O bond were observed for compound **1k**, **1j** and **1m** as starting materials (Table 3, entries 3-5).

To further investigate the scope of this catalytic system, oligomeric phenylene oxide **6** containing four C(Ar)-O bonds was tested under the standard reaction conditions with increasing sodium borohydride to 3.0 equiv; 1-cyclohexyl-1H-pyrrole **3a** and 1-phenylpyrrolidine **4a** were obtained in high total yields (170%) and excellent conversion (>99%) (Eq. 1).



Equation 1. Cross-Coupling of Oligomeric Phenylene Oxide with Pyrrolidine



Entry	Substrate	Conversion	Products		
1	**1i**	>99%	**3b** 62% cis/trans[b]=1:2.4	**4b** 12%	**5a** 74%[c]
2	**1j**	>99%	**3c** 56% cis/trans[b]=2.2:1	**4c** 15%	**5a** 72%[d]
3	**1K**	>99%	**3a** 80%	**4a** 13%	**5e** 15%[e]
4	**1l**	>99%	**3b** 72% cis/trans[b]=1:2.9	**4b** 16%	**5e** 16%[f]
5	**1m**	>99%	**3a** 79%	**4a** 12%	**5f** 11%[g]

a. Reaction conditions: diaryl ether (0.2 mmol), pyrrolidine (0.7 mmol), $Pd(OH)_2/C$ (30 mol%), and $NaBH_4$ (0.3 mmol) in *m*-xylene (1 mL). All reactions were carried out at 160°C in a sealed tube under argon with air (1 mL) and water (10 μL)) for 24 h; yields of isolated products were given; conversions were determined by ^1H NMR with nitromethane as internal standard. [b]. Cis/trans (isomer) ratio was determined by crude ^1H NMR. [c]. In addition, 10% of 1-cyclohexyl-1*H*-pyrrole and 9% of toluene were also obtained. [d]. In addition, 14% of 1-cyclohexyl-1*H*-pyrrole and 10% of toluene were also obtained. e. Isolated yield, in addition, 77% of 1,2,3,4-tetrahydronaphthalene was obtained. f. Isolated yield, in addition, 75% of 1,2,3,4-tetrahydronaphthalene was obtained. g. Isolated yield, in addition, 85% of cyclohexylbenzene was obtained.

To further exploit the potentials of this method, different amines were examined to cross-couple with diphenyl ether. Different diaryl ethers were successfully sliced and cross-coupled with pyrrolidine to give higher value-added nitrogen-containing chemicals—pyrrolidines and pyrroles (Table 4). The optimized conditions were obtained by elevating the reaction temperature to 150□, with 3.5 equiv of amines under argon using 30 mol% of $Pd(OH)_2/C$ as the catalyst and 1.25 equiv of sodium borohydride as the hydride source in toluene (0.5 mL) (with 10 μL water) for 24 h (Please see the details in SI). As shown in Table 4, diphenyl ether reacted with different amines in high to excellent conversion, to generate the corresponding anilines and cyclohexyl amines[19] in high to excellent total yields. Piperidine reacted very well with diphenyl ether, generating phenyl piperidine **7b** and cyclohexyl piperidine **8b** in high conversion and excellent total yield (Table 4, entry 1). Piperidine bearing methyl groups at different positions (*2*-, *3*- or *4*-) were all effective for the transformation (Table 4, entries 2-4). Excellent conversion and high yield were also obtained with linear primary amine **2f** (Table 4, entry 5).

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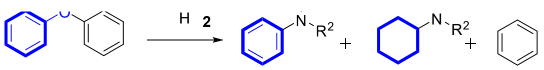
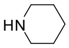
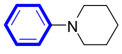
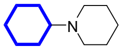
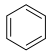
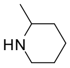
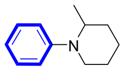
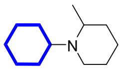
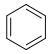
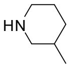
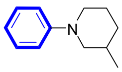
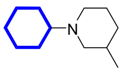
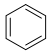
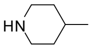
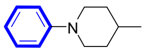
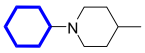
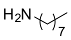
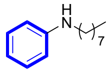
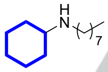
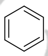
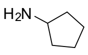
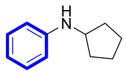
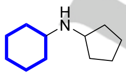
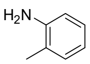
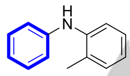
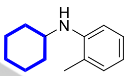
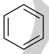
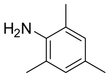
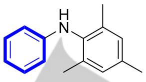
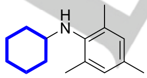
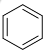
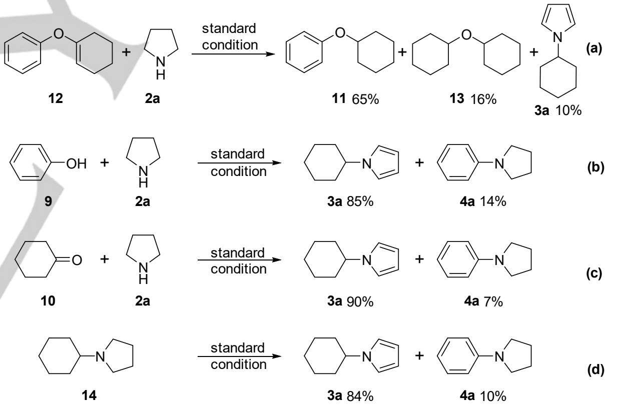
Cyclopentylamine **2g** also reacted smoothly with diphenyl ether to afford the corresponding products in high yield (Table 4, entry 6). Likewise, aryl amines also reacted very well with diphenyl ether efficiently (Table 4, entries 7-8). Despite bearing two methyl groups at 2,6-positions, the sterically hindered 2,4,6-trimethylaniline reacted smoothly (Table 4, entry 8).

Table 4. Direct Formal Cross-Coupling of Diphenyl Ether with Amines[a]



Entry	Amines	Conversion	Products		
1	 **2b**	>99%	 **7b** 28%	 **8b** 56%	 **5a** 85%[b]
2	 **2c**	>99%	 **7c** 32%	 **8c** 53%	 **5a** 84%[b]
3	 **2d**	>99%	 **7d** 33%	 **8d** 54%	 **5a** 87%[b]
4	 **2e**	>99%	 **7e** 30%	 **8e** 60%	 **5a** 86%[b]
5	 **2f**	>99%	 **7f** 65%	 **8f** 23%	 **5a** 84%[b]
6	 **2g**	>99%	 **7g** 74%	 **8g** 2%	 **5a** 82%[b]
7	 **2h**	>99%	 **7h** 68%	 **8h** 22%	 **5a** 83%[b]
8	 **2i**	>89%	 **7i** 50%	 **8i** 26%	 **5a** 78%[b]

[a] Reaction conditions: diaryl ether (0.2 mmol), amines (0.7 mmol), $Pd(OH)_2/C$ (30 mol%), and $NaBH_4$ (0.25 mmol) in toluene (0.5 mL). All reactions were carried out at 150°C in a sealed tube under argon with water (10 μL)) for 24 h; yields of isolated products were given; conversions were determined by ^1H NMR with nitromethane as internal standard. b. Yields of benzene and cyclohexane were determined by GC-MS; a little peak of cyclohexane overlapped with the big peak of benzene.



Scheme 2. Control Experiments

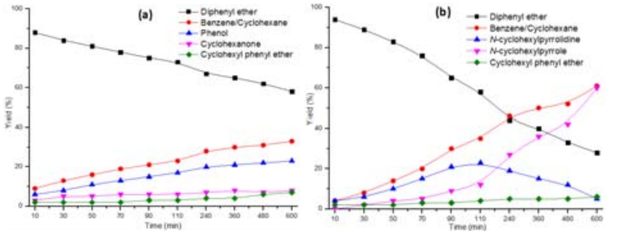


Figure 2. Product Distributions vs Time for the Reaction of Diphenyl Ether without Amine (a) and with Amine (b) under the Standard Reaction Conditions

To explore the reaction mechanism, diphenyl ether was examined without amine under the standard reaction conditions (Figure 2a). Phenol (**9**), cyclohexanone (**10**), benzene (**5**) and a trace amount of cyclohexane were detected by GC-MS. The total yields of phenol (**9**) and cyclohexanone (**10**) were almost the same as the total yields of benzene (**5**) and cyclohexane. To further investigate the potential pathway of C(Ar)-O cleavage, cyclohexenyl phenyl ether (**12**), which was proposed as a partial hydrogenation intermediate in the literatures[8g-h,20], was explored under the standard reaction conditions (Scheme 2a). The direct C=C bond hydrogenation products cyclohexanyl phenyl ether (**11**) (65%) and dicyclohexanyl ether **13** (16%) were obtained as major products with only a small amount of the cross-coupling product **3a** (10%). These results suggest that the C(Ar)–O bond was cleaved via the $Pd(OH)_2/C$ catalyzed hydrogenolysis of diphenyl ether to form phenol and benzene instead of hydrolysis of compound **12** under our standard conditions. The phenol can be reduced to form to cyclohexanone.[21] The reaction of phenol (**9**) and cyclohexanone (**10**) proceeded well under the standard conditions (Scheme 2b and 2c) to give N-cyclohexylpyrrole (**3a**) and N-phenylpyrrolidine (**4a**) in high total yields (99% and 97%, respectively), suggesting their being the possible intermediates in the conversion of diphenyl ether. N-Cyclohexylpyrrolidine **14** was also explored under standard reaction conditions; oxidative aromatization products **3a** and **4a** were also obtained with high total yields (Scheme 2d). The cross-coupling of diphenyl ether with pyrrolidine was then investigated in different reaction times under the standard conditions (Figure 2b). The nitrogen-containing products (N-cyclohexylpyrrolidine and N-cyclohexylpyrrole) and hydrocarbon products (benzene and cyclohexane) were formed in ca. 1:1 ratio. The results indicated that one Ar-O bond was reductively cleaved to form benzene and cyclohexane and the remaining fragment predominantly became phenol and cyclohexanone. This rationale is also in agreement with the results in Figure 2a. Then the phenol and cyclohexanone were transformed into the nitrogen-containing products (N-cyclohexylpyrrolidine and N-cyclohexylpyrrole).

Based on these experimental results, a tentative mechanism for this cross-coupling reaction is proposed in Figure 3: firstly, sodium borohydride reacts with the $Pd(OH)_2/C$ catalyst to form the $HPd^{II}H$ species. Subsequently, hydrogenolysis of diphenyl ether generates phenol **A** via C(Ar)–O bond cleavage, which is further reduced by $HPd^{II}H$ species to form cyclohexanone **B**.[17a, 19] Intermediate **B** reacts with amine to form iminium intermediate **C**. Intermediate **C** is reduced to form compound **D** (path a), and then **D** is oxidized to generate intermediate **E** or **H**. The intermediate **E**, upon loosing H^+, tautomerizes to form enamine **F**. Finally, enamine **F** is oxidatively aromatizes to form the product pyrrole **G**, as well as regenerates $HPd^{II}H$ species. Another intermediate **H** undergoes oxidative aromatization to form product **I** and regenerates the $HPd^{II}H$ species. It is also possible that intermediate **C** can also undergo [1,3] hydride shift to generate intermediate **E** (path b).[22] Furthermore, a small portion of intermediate **C** can also tautomerize to form enamine **H** (path c).

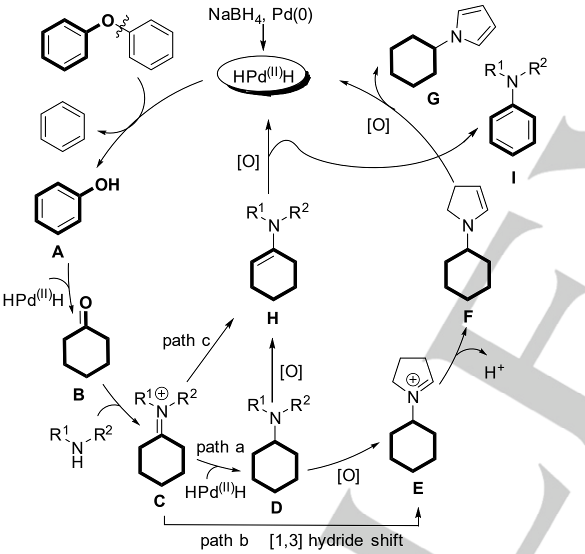


Figure 3. Proposed Reaction Pathway for Cross-Coupling Diaryl Ethers with Amines

In conclusion, we have developed a novel direct cross-coupling of diaryl ethers with amines via dual C(Ar)–O bond cleavage. The 4-O-5 linkage lignin models can be converted into amine derivatives directly and efficiently. This research illustrated potential applications for converting renewable lignin biomass to higher value-added nitrogen-containing chemicals. Further researches on obtaining high-valued chemicals from lignin biomass feedstock are in progress.

Experimental Section

General procedure for the coupling of phenol with pyrrolidine: In a 20 mL oven-dried vial was charged with a magnetic stir-bar, $Pd(OH)_2/C$(42 mg, 30 mol% based on Pd contents) and $NaBH_4$ (12 mg, 0.3 mmol). The tube was then evacuated and backfilled with argon. The evacuation/backfill sequence was repeated two additional times. *M*-xylene (1 mL), diphenyl ether (0.2 mmol) and pyrrolidine (0.7 mmol) were added by syringe, followed by the addition of H_2O (10 uL) and air (1 mL) by syringe. The tube was placed in a preheated oil bath at 160 °C and the mixture was stirred under an argon atmosphere for 24 h. The reaction mixture was cooled to room temperature and filtered through a pad of silica gel. The filtrate was concentrated and the resulting residue was purified by preparative thin layer chromatography to give N-cyclohexylpyrrole and phenylpyrrolidine.

Acknowledgements

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Keywords: Lignin • diaryl ethers • cross-coupling • amines • C-O bond cleavage

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Entry for the Table of Contents (Please choose one layout)

Layout 2:

COMMUNICATION

From waste to value: A potential strategy for converting renewable lignin biomass to higher value-added nitrogen-containing chemicals is reported. The 4-O-5 linkage model compounds of lignin was cross-coupled with amines via dual C(Ar)-O bond cleavages to generate valuable nitrogen-containing derivatives.

Huiying Zeng, Dawei Cao, Zihang Qiu and Chao-Jun Li**

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Palladium-Catalyzed Formal Cross-Coupling of Diaryl Ethers with Amines: New Tactic to Slice 4-O-5 Linkage in Lignin Models