



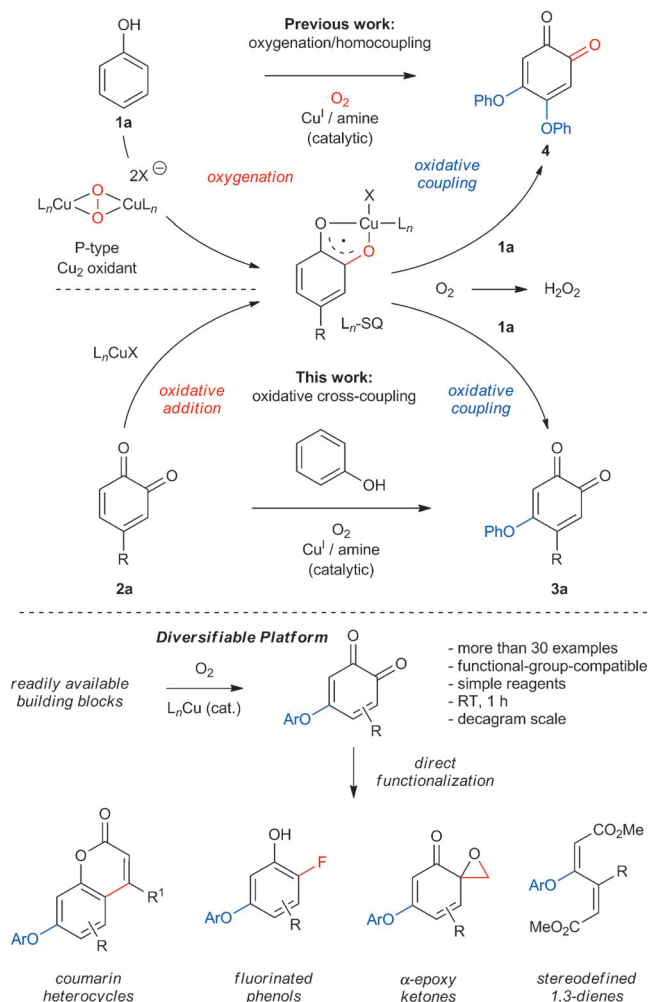
A Catalyst-Controlled Aerobic Coupling of *ortho*-Quinones and Phenols Applied to the Synthesis of Aryl Ethers

Zheng Huang and Jean-Philip Lumb*

Abstract: *ortho*-Quinones are underutilized six-carbon-atom building blocks. We herein describe an approach for controlling their reactivity with copper that gives rise to a catalytic aerobic cross-coupling with phenols. The resulting aryl ethers are generated in high yield across a broad substrate scope under mild conditions. This method represents a unique example where the covalent modification of an *ortho*-quinone is catalyzed by a transition metal, creating new opportunities for their utilization in synthesis.

In spite of their occurrence in nature,^[1] materials science,^[2] catalysis,^[3] organometallic chemistry,^[4] and synthesis,^[5] *ortho*-benzoquinones have remained underexplored functional groups.^[6,7] Their redox lability, complex coordination chemistry, and sensitivity towards nucleophiles are amongst the obstacles that complicate their utilization.^[8] Methods that overcome these challenges benefit from downstream transformations that dramatically alter the topology and polarity of the *ortho*-quinone.^[9] This can diversify chemical space around a key functional group, which we recently illustrated for oxindole heterocycles.^[8] In this previous work, *ortho*-quinones were formed by *ortho*-oxygenation of a phenol with a P-type dinuclear Cu oxidant (Scheme 1).^[10] This forms a Cu^{II} semiquinone radical (L_n -SQ) following atom transfer, which undergoes coupling with the starting phenol prior to dissociation of L_n Cu^I.^[11] While the resulting *ortho*-quinones are versatile,^[12] this method is currently limited to the homocoupling of phenols (**1a** to **4**, Scheme 1).^[13]

Cu^{II} semiquinones can also be formed by oxidation of Cu^I with an *ortho*-quinone,^[4b,10] which suggested to us that a cross-coupling between a phenol and an *ortho*-quinone might provide a more versatile fragment coupling. Existing addition reactions to *ortho*-quinones are either low-yielding or limited in scope, and have not been investigated as general synthetic methods.^[14] Successful reaction development would require chemoselectivity for cross-C–O bond formation over oxidative homocoupling^[15] or *ortho*-oxygenation of the phenol,^[16] while avoiding decomposition of the *ortho*-quinone. Herein, we overcome these challenges and describe a catalytic aerobic synthesis of vinyl aryl ethers by an *ortho*-quinone/phenol cross-coupling. Ligand and counterion effects have a pronounced impact on rate and selectivity, and provide parameters for optimization that extend the method to a broad



Scheme 1. Synthesis and reactivity of *ortho*-quinones.

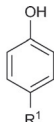
selection of coupling partners. Aryl ethers are omnipresent in natural products, pharmaceuticals, agrochemicals, and materials,^[17] justifying continued efforts to improve the efficiency of their synthesis.^[18] Our reactions employ commercially available components, occur at room temperature in 1 h, and provide access to a diverse array of aryl ethers by post-coupling diversification of the *ortho*-quinone (Scheme 1).

The challenges of utilizing *ortho*-quinones are highlighted by the reaction of phenol (**1a**) and 4-*tert*-butyl-*ortho*-quinone (**2a**; Table 1). As a homogenous solution in CH_2Cl_2 , **1a** and **2a** undergo about 25% decomposition upon standing for 1 h (entry 1). Upon addition of catalytic amounts of either *N,N'*-di-*tert*-butyl-ethylenediamine (DBED) or 4-methoxypyridine (4-MeO-Py; see below for why these amines were chosen),

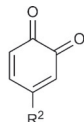
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Table 1: Optimization of the reaction conditions.^[a]



1a: R¹ = H
1b: R¹ = OMe
1c: R¹ = CN



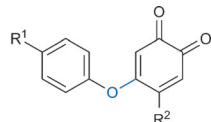
2a: R² = *t*Bu
2b: R² = Me

O₂ (2 atm)

→

CuX (cat.)
 amine (cat.)

CH₂Cl₂, RT
 1 h



3a: R¹ = H / R² = *t*Bu
3b: R¹ = H / R² = Me
3c: R¹ = OMe / R² = Me
3d: R¹ = CN / R² = Me

Entry	Phenol	Quinone	CuX (mol %)	Amine (mol %)	Conv. [%] 1/2	3 a–3 d ^[b] (yield [%])
1 ^[c]	1 a	2 a	–	–	8/17	–
2 ^[c]	1 a	2 a	–	DBED (5)	33/81	3 a (20)
3 ^[c]	–	2 a	–	DBED (20)	–/40	–
4 ^[c,d]	–	2 b	–	DBED or 4-MeO-Py (20)	–/100	–
5 ^[e]	1 a	2 a	CuPF ₆ (4)	DBED (5)	58/48	3 a (40)
6	1 a	2 a	CuBr (4)	DBED (5)	100/100	3 a (97)
7^[f]	1 a	2 a	CuBr (4)	4-MeO-Py (10)	97/100	3 a (97)
8^[f,g]	1 a	2 b	CuCl (10)	4-MeO-Py (20)	81/100	3 b (73)
9 ^[f,g]	1 b	2 b	CuCl (10)	4-MeO-Py (20)	> 95 / > 95	3 c (74)
10 ^[g]	1 b	2 b	CuCl (10)	DBED (10)	> 95 / > 95	3 c (< 5)
11 ^[g]	1 c	2 b	CuCl (10)	DBED (10)	86 / > 95	3 d (79)
12 ^[f,g]	1 c	2 b	CuCl (10)	4-MeO-Py (20)	22 / > 95	3 d (< 10)

[a] The reactions were performed with 0.5 mmol of **1** and 0.5 mmol of **2**. [b] Yield determined by ¹H NMR spectroscopy using hexamethylbenzene as an internal standard. [c] Reactions performed under N₂. [d] Reaction time: 5 min. [e] Reaction time: 4 h. [f] With 4 Å M.S. (100 mg). [g] 0.75 mmol of **2** were slowly added over 10 min.

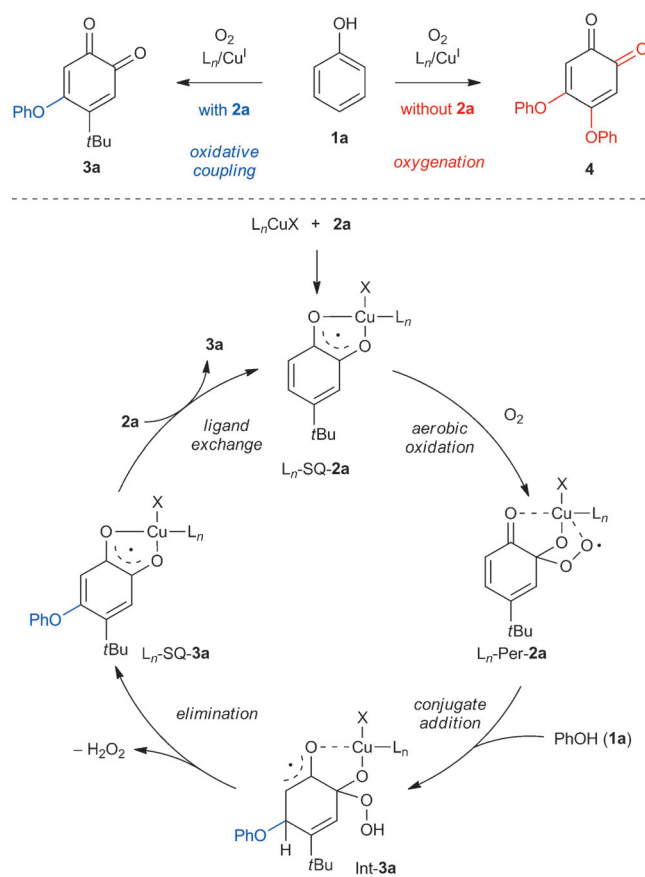
a complex mixture quickly evolves, from which **3 a** is isolated in low yield (entry 2). Factors leading to decomposition include the sensitivity of **2 a** towards the amine (entry 3), and redox exchange between **3 a** and quinone **2 a**.^[19] These problems are amplified for 4-methyl-*ortho*-quinone (**2 b**), which undergoes complete decomposition within 5 min under similar conditions (entry 4).

The addition of Cu^I salts and molecular oxygen (O₂) has a dramatic impact on the selectivity and rate of the reaction. In the presence of [Cu(CH₃CN)₄](PF₆) (abbreviated as CuPF₆), DBED, and 2 atm of O₂, the addition becomes selective for **3 a** at about 50 % conversion after 4 h (entry 5). By simply changing to a halide counterion, the reaction is complete after only 1 h, and the yield of **3 a** is > 95 % (entry 6). An equally pronounced effect is observed for the ligand. After an extensive survey (> 20 amines; see the Supporting Information, Table S2), only 4-MeO-Py emerged as an equally efficient ligand for the coupling of **1 a** and **2 a** in the presence of 4 Å molecular sieves (M.S.; entry 7).

DBED and 4-MeO-Py display a surprising, yet highly desirable, complementarity that enables couplings of either electron-rich or electron-poor phenols. This is illustrated with quinone **2 b**, whose overall sensitivity requires slow addition to the reaction mixture over 10 min (entry 8). **2 b** undergoes a relatively clean coupling with electron-rich phenol **1 b** in the presence of 4-MeO-Py (entry 9), whereas the use of DBED leads to complete decomposition (entry 10). In contrast, DBED promotes the coupling of **2 b** with electron-poor phenol **1 c** (entry 11), whereas 4-MeO-Py does not (entry 12). Fine-tuning reaction conditions by ligand design is a hallmark of traditional metal-catalyzed cross-coupling reactions.^[20] Our

results suggest that a similar opportunity may extend to metal semi-quinones.

A working mechanistic hypothesis that considers the ligand and counterion effects, the requirement for O₂, and the complete absence of **4** is presented in Scheme 2. The catalytic cycle begins with oxidation of L_nCuX with **2 a** to provide L_n-SQ-**2 a**. Stack, Pierpont, and our group have previously shown that amines influence the geometry, nuclearity, and electronic structure of Cu semi-quinones,^[4b,21] which helps explaining the pronounced ligand and counterion effects on rate and selectivity.^[22] The requirement of O₂ for selective C–O coupling leads us to propose an aerobic oxidation of L_n-SQ-**2 a** prior to C–O bond formation, which should be accelerated by more-coordinating counterions, such as Cl or Br, relative to PF₆. The resulting peroxide (L_n-Per-**2 a**)

**Scheme 2.** Mechanistic proposal for the catalytic aerobic coupling of **1 a** and **2 a** to **3 a**.

resembles complexes of Fe,^[23] Cu,^[24] Co,^[25] Rh,^[26] and Ir,^[27] involved in both the enzymatic and non-enzymatic cleavage of semiquinones to muconic esters.^[24a,28] Oxidative cleavage is avoided under our conditions by trapping of L_n -Per-**2a** with **1a**, in what we tentatively describe as a radical addition.^[29] Elimination of H_2O_2 would then provide L_n -SQ-**3a**,^[26–27] and would form the key C–O bond of the product while avoiding redox exchange.^[8] Ligand exchange with **2a** would then release **3a** and close the catalytic cycle. The chemoselectivity for **3a** over **4** (Scheme 2) results from the sequestration of Cu^I as a Cu^{II} semiquinone, preventing O_2 activation as a P-type oxidant, and thus *ortho*-oxygenation of **1a** (Scheme 1).^[11] This is a rare example of chemoselective oxidation over oxygenation,^[16] which finds parallels in the work of Kozłowski and Stahl.^[30]

Coupling remains efficient across a broad range of phenols (Table 2) and can include substituents that are used in more traditional cross-coupling reactions (**3i**, **3j**, and **3r**) or groups that are sensitive to aerobic oxidation (**3g**, **3j**, **3m**, **3p**, and **3u–3w**). The scope of the *ortho*-quinone is equally broad (Table 3), and includes alkyl, aryl, and heteroatom substitution (**3y**, **3z**, **3ae**, and **3ag**), demonstrating regioselectivity for either the less sterically encumbered (**3ah**) or more electrophilic position of the quinone (**3af**). Fused quinones, including *ortho*-naphthoquinone and the 4,5- and 6,7-quinones of

Table 3: Quinone scope.^[a]

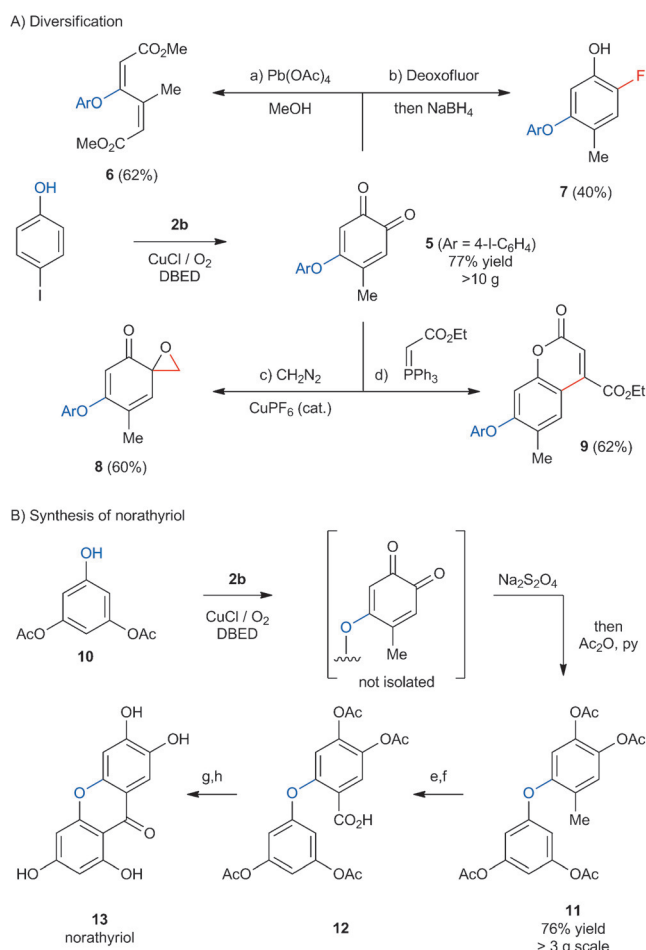
Entry	Yield (%)
3y	87
3z	94
3aa	50
3ab	56
3ac	60
3ad	44

[a] The reactions were performed with 1 mmol of **1** and 1.5 mmol of **2**. **2** was added to the reaction mixture over 10 min. [b] $CuCl$ (20 mol %) and 4-methoxyphenylpyridine (40 mol %) were used. [c] 1 mmol of **2** was used; reaction time: 4 h.

Table 2: Phenol scope.^[a]

Entry	Yield (%)
3e	96
3f	99
3g	94
3h	87
3i	95
3j	74
3k	39/63 ^[b]
3l	< 5/31 ^[b]
3m	97
3n	65
3o	99
3p	99
3q	78/90 ^[b]
3r	84

[a] The reactions were performed with 1.0 mmol of **1** and 1.0–1.5 mmol of **2**. [b] 4-Methoxyphenylpyridine (10 mol %) with 200 mg of 4 Å M.S. [c] DBED (10 mol %) without 4 Å M.S. [d] Reaction performed on 0.1 mmol scale, with a catalyst loading of 15 mol %.



Scheme 3. Diversification of *ortho*-quinone **5** and synthesis of norathyriol (**13**). Conditions: a) $\text{Pb}(\text{OAc})_2$ (2.2 equiv), MeOH/PhMe , RT, 18 h, 62%; b) Deoxofluor, CHCl_3 , $0^\circ\text{C} \rightarrow \text{RT}$, 1 h, then NaBH_4 , DBU, MeOH , 50°C , 30 min, 40%; c) $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$ (4 mol %), CH_2N_2 , THF, $-78^\circ\text{C} \rightarrow \text{RT}$, 30 min, 60%; d) $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$ (2 equiv), CH_2Cl_2 , $40 \rightarrow 100^\circ\text{C}$, 4 h, 62%; e) benzoyl peroxide (10 mol %), *N*-bromosuccinimide (1.2 equiv), CCl_4 , 80°C , 4 h, then *N*-methylmorpholine *N*-oxide (3 equiv), MeCN , RT, 12 h, 73 % yield; f) NaClO_2 (3 equiv), NaH_2PO_4 , $\text{DMSO}/\text{H}_2\text{O}$, RT, 2 h, 71 % yield; g) $(\text{CF}_3\text{CO})_2\text{O}$ (2 equiv), CH_2Cl_2 , RT, 30 min, then $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (5 equiv), RT, 2 h, 87 %; h) K_2CO_3 (5 equiv), RT, 12 h, 87 % yield over two steps.

indole (**3aj** and **3ak**), are also tolerated, whereas *para*-quinones are not.

The decagram synthesis and diversification of **5** highlights the versatility of *ortho*-quinones (Scheme 3A). As the two carbonyl groups in **5** are electronically differentiated, deoxy-fluorination,^[31] Wittig olefination,^[32] and nucleophilic addition^[33] occur selectively at the more electrophilic carbon atom, directly elaborating **5** into *ortho*-fluorophenol **7**, coumarin **9**, or α -epoxy ketone **8**. Alternatively, cleavage of the diketone with lead tetraacetate in methanol^[34] provides muconic ester **6** as a single geometric isomer, which underscores the diversity of aryl ethers that can be accessed from a single *ortho*-quinone precursor.

Our method also provides a unique and convergent synthesis of the xanthone norathyriol (**13**; Scheme 3B).^[35]

Norathyriol and its C-glycosylated analogue mangiferin^[36] are xanthone natural products isolated from the skin of mangoes that exhibit a broad range of biological activities.^[37] The synthesis of **13** is accomplished by cross-coupling of phloroglucinol **10** with **2a** on multigram scale (Scheme 3B). Oxidation of the C5 methyl group to the carboxylic acid provides **12**, which is subsequently converted into **13** by a Friedel–Crafts acylation.

In summary, we have developed a mild and diversifiable synthesis of aryl ethers that highlights the synthetic value of *ortho*-quinones. An important future direction will explore the reactivity of metal–quinone complexes more generally, as they provide a unique mechanism for controlling covalent modification. Metal semiquinones have been studied as non-innocent ligands with unique electronic properties, but mainly for applications in materials science. Our work makes an important departure from this precedent, and demonstrates that these non-innocent ligands can also be viewed as redox-active substrates that are suitable for dehydrogenative coupling.^[38] This highlights the increasingly popular trend of controlling organic radical chemistry with organometallic complexes as the reactivity of these species can be carefully tuned by ligand design.^[39]

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Keywords: aerobic oxidation · aryl ethers · copper catalysis · *ortho*-quinones · phenols

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