Copper Catalysis Hot Paper

International Edition: DOI: 10.1002/anie.201606359
German Edition: DOI: 10.1002/ange.201606359

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

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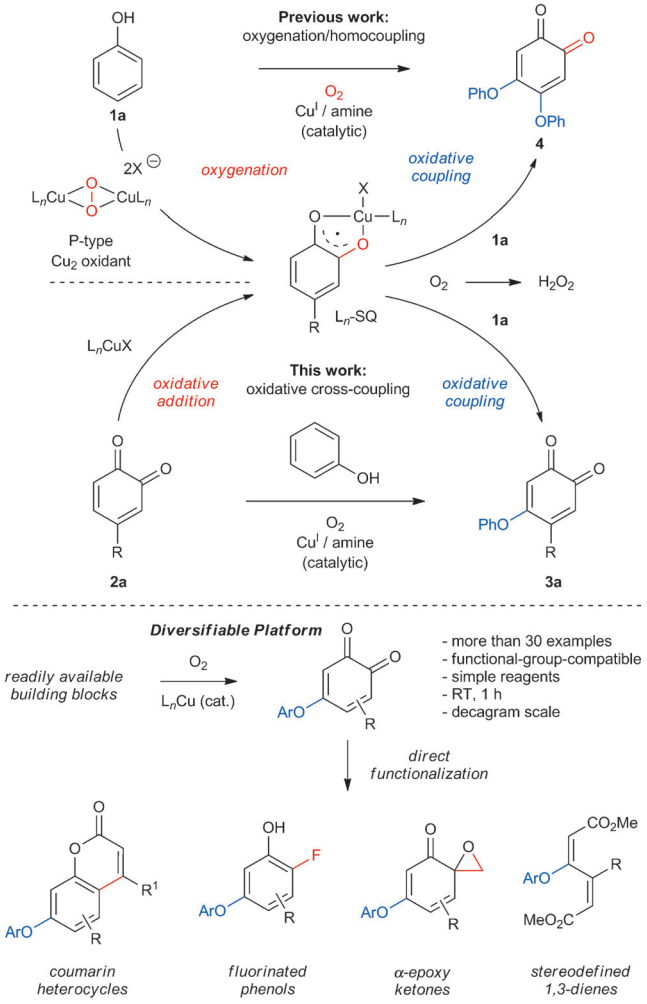
Abstract: *ortho-Quinones are underutilized six-carbon-atom building blocks. We herein describe an approach for controlling their reactivity with copper that gives rise to a catalytic aerobic cross-coupling with phenols. The resulting aryl ethers are generated in high yield across a broad substrate scope 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_nCu^{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 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).



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

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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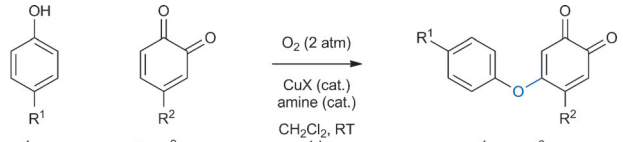
Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201606359.

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



1a: R^1 = H
1b: R^1 = OMe
1c: R^1 = CN

2a: R^2 = *t*Bu
2b: R^2 = Me

3a: R^1 = H / R^2 = *t*Bu
3b: R^1 = H / R^2 = Me
3c: R^1 = OMe / R^2 = Me
3d: R^1 = CN / R^2 = Me

Entry	Phenol	Quinone	CuX (mol%)	Amine (mol%)	Conv. [%] **1**/**2**	**3a–3d**[b] (yield [%])
1[c]	**1a**	**2a**	–	–	8/17	–
2[c]	**1a**	**2a**	–	DBED (5)	33/81	**3a** (20)
3[c]	–	**2a**	–	DBED (20)	–/40	–
4[c,d]	–	**2b**	–	DBED or 4-MeO-Py (20)	–/100	–
5[e]	**1a**	**2a**	$CuPF_6$ (4)	DBED (5)	58/48	**3a** (40)
6	**1a**	**2a**	**CuBr (4)**	**DBED (5)**	**100/100**	**3a (97)**
7[f]	**1a**	**2a**	**CuBr (4)**	**4-MeO-Py (10)**	**97/100**	**3a (97)**
8[f,g]	**1a**	**2b**	**CuCl (10)**	**4-MeO-Py (20)**	**81/100**	**3b (73)**
9[f,g]	**1b**	**2b**	CuCl (10)	4-MeO-Py (20)	>95/>95	**3c** (74)
10[g]	**1b**	**2b**	CuCl (10)	DBED (10)	>95/>95	**3c** (<5)
11[g]	**1c**	**2b**	CuCl (10)	DBED (10)	86/>95	**3d** (79)
12[f,g]	**1c**	**2b**	CuCl (10)	4-MeO-Py (20)	22/>95	**3d** (<10)

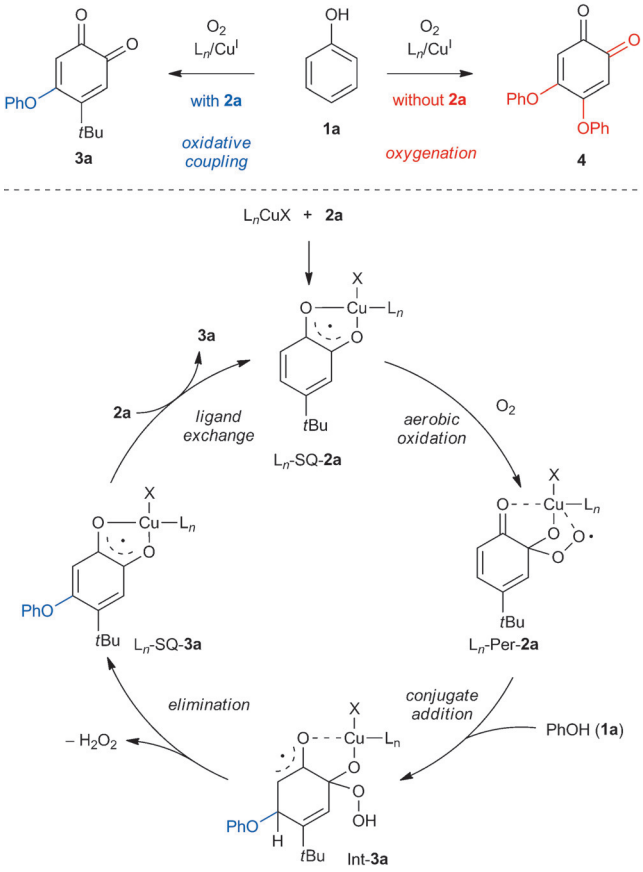
[a] The reactions were performed with 0.5 mmol of **1** and 0.5 mmol of **2**. [b] Yield determined by ^{1}H NMR spectroscopy using hexamethylbenzene as an internal standard. [c] Reactions performed under N_2. [d] Reaction time: 5 min. [e] Reaction time: 4 h. [f] With 4 Å M.S. (100 mg). [g] 0.75 mmol of **2** were slowly added over 10 min.

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

The addition of Cu^I salts and molecular oxygen (O_2) has a dramatic impact on the selectivity and rate of the reaction. In the presence of $[Cu(CH_3CN)_4](PF_6)$ (abbreviated as $CuPF_6$), DBED, and 2 atm of O_2, the addition becomes selective for **3a** 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 **3a** 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 **1a** and **2a** 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 **2b**, whose overall sensitivity requires slow addition to the reaction mixture over 10 min (entry 8). **2b** undergoes a relatively clean coupling with electron-rich phenol **1b** 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 **2b** with electron-poor phenol **1c** (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 semiquinones.

A working mechanistic hypothesis that considers the ligand and counterion effects, the requirement for O_2, and the complete absence of **4** is presented in Scheme 2. The catalytic cycle begins with oxidation of L_nCuX with **2a** to provide L_n-SQ-**2a**. Stack, Pierpont, and our group have previously shown that amines influence the geometry, nuclearity, and electronic structure of Cu semiquinones,[4b,21] which helps explaining the pronounced ligand and counterion effects on rate and selectivity.[22] The requirement of O_2 for selective C–O coupling leads us to propose an aerobic oxidation of L_n-SQ-**2a** prior to C–O bond formation, which should be accelerated by more-coordinating counterions, such as Cl or Br, relative to PF_6. The resulting peroxide (L_n-Per-**2a**)

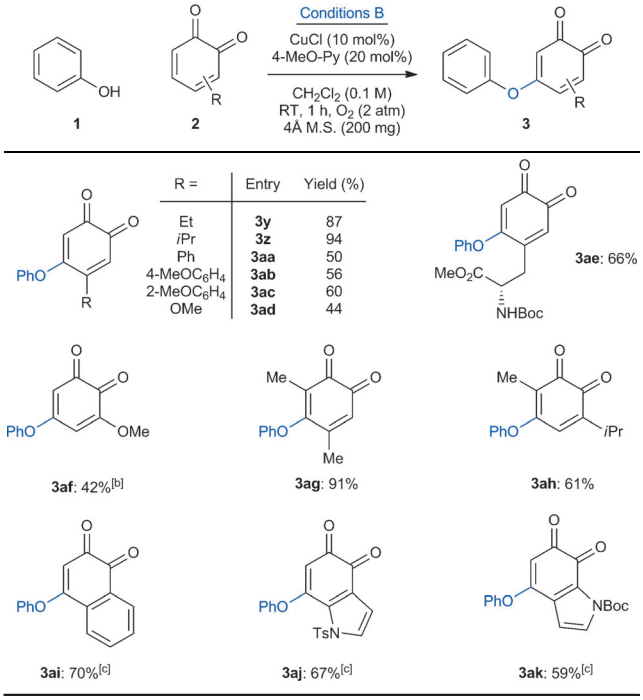


Scheme 2. Mechanistic proposal for the catalytic aerobic coupling of **1a** and **2a** to **3a**.

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 Kozlowski and Stahl.[30]

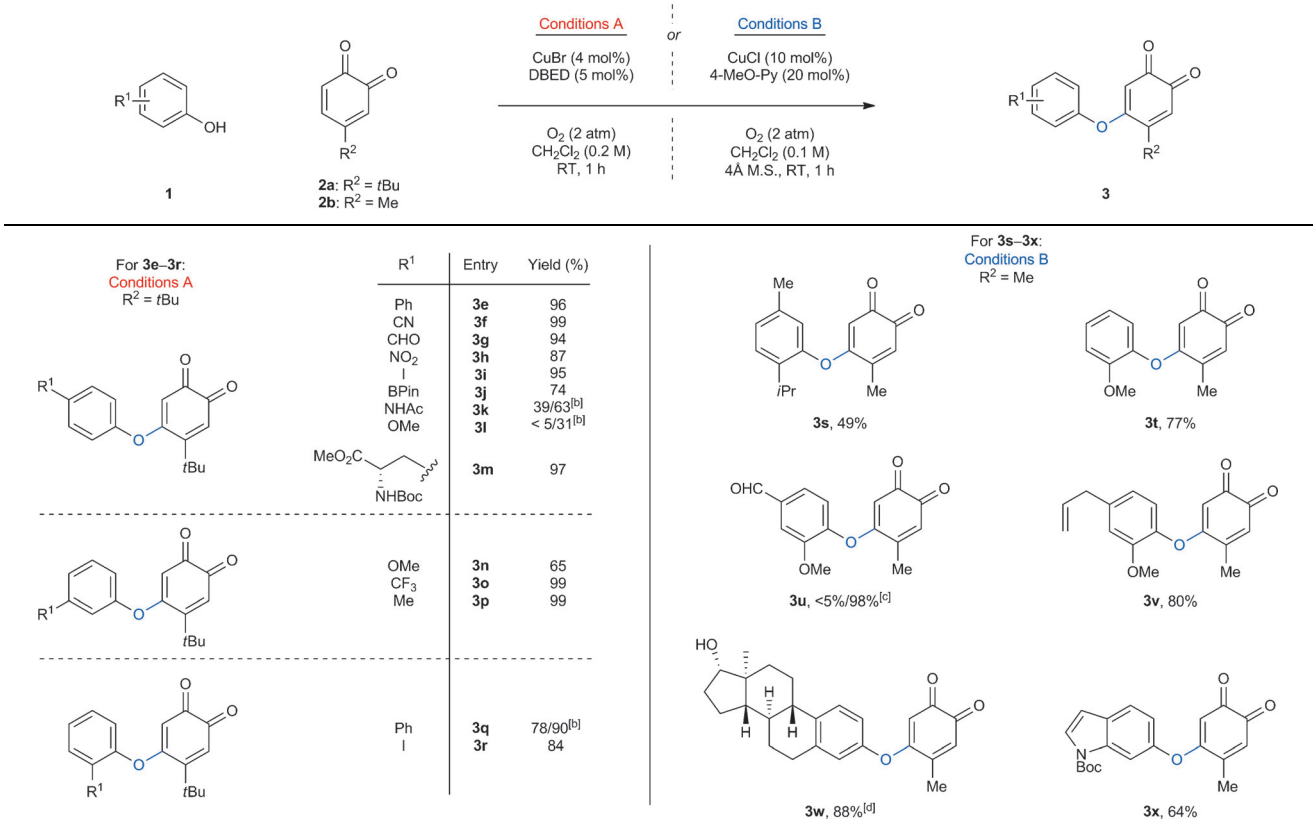
Coupling remains efficient across a broad range of phenols (Table 2) and can include substituents that are used in more traditional cross-coupling reactions (**3i**, **3j**, and **3r**) or groups that are sensitive to aerobic oxidation (**3g**, **3j**, **3m**, **3p**, and **3u**–**3w**). The scope of 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]

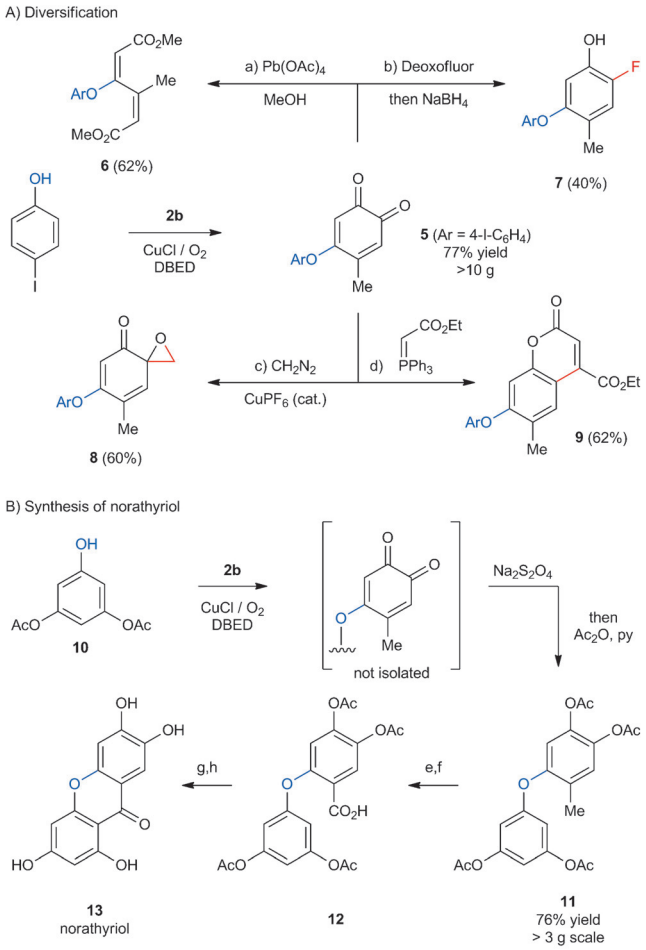


[a] The reactions were performed with 1 mmol of **1** and 1.5 mmol of **2. 2** was added to the reaction mixture over 10 min. [b] CuCl (20 mol%) and 4-methoxypyridine (40 mol%) were used. [c] 1 mmol of **2** was used; reaction time: 4 h.

Table 2: Phenol scope.[a]



[a] The reactions were performed with 1.0 mmol of **1** and 1.0–1.5 mmol of **2**. [b] 4-Methoxypyridine (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) $Pb(OAc)_2$ (2.2 equiv), MeOH/PhMe, RT, 18 h, 62%; b) Deoxofluor, $CHCl_3$, 0 °C→RT, 1 h, then $NaBH_4$, DBU, MeOH, 50 °C, 30 min, 40%; c) $[Cu(MeCN)_4](PF_6)$ (4 mol%), CH_2N_2, THF, −78 °C→RT, 30 min, 60%; d) $Ph_3P{=}CHCO_2Et$ (2 equiv), CH_2Cl_2, 40→100 °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, $DMSO/H_2O$, RT, 2 h, 71% yield; g) $(CF_3CO)_2O$ (2 equiv), CH_2Cl_2, RT, 30 min, then $BF_3{\cdot}Et_2O$ (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, deoxyfluorination,[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]

Acknowledgements

Financial support was provided by the Natural Sciences and Engineering Council of Canada (NSERC, Discovery Grant to J.-P.L.), the Fonds de Recherche du Québec—Nature et Technologies (FRQNT, Team Grant to J.-P.L.), the FRQNT Center for Green Chemistry and Catalysis at McGill University (graduate fellowship for Z.H.), and the NSERC CREATE Program in Green Chemistry at McGill University. We wish to thank Prof. James Gleason, Prof. Bruce Arndtsen, and Prof. Xavier Ottenwaelder for helpful discussions.

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

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 11543–11547
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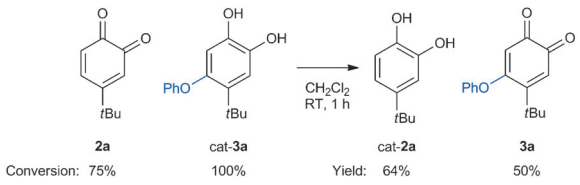

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Received: June 30, 2016
Published online: August 11, 2016

