# Chemical Science

## ARTICLE

# Oxygen Nucleophiles as Reaction Partners in Photoinduced, Copper-Catalyzed Cross-Couplings: O-Arylations of Phenols at Room Temperature

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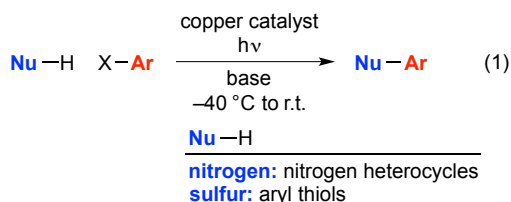
Most copper-catalyzed cross-couplings require an elevated reaction temperature. Recently, a photoinduced variant has been developed that enables C–X bond-forming reactions of certain nitrogen and sulfur nucleophiles to proceed under unusually mild conditions (–40 °C to room temperature). In view of the importance of carbon–oxygen bond construction in organic chemistry, the expansion of this photochemical approach to oxygen nucleophiles is an important objective. In this report, we establish that, in the presence of light and an inexpensive copper pre-catalyst (CuI), a wide array of phenols and aryl iodides can be coupled to generate diaryl ethers under mild conditions (room temperature) in the presence of a variety of functional groups. Our studies indicate that a Cu(I)–phenoxide complex is a competent intermediate in photoinduced C–O bond-formation.

## Introduction

We have recently determined that, with the aid of light, copper-catalyzed couplings of both nitrogen and sulfur nucleophiles with aryl electrophiles can be achieved under unusually mild conditions [eqn (1)].[1,2] Naturally, we are interested in expanding the scope of this approach to C–X bond-forming processes other than C–N and C–S.



$$\mathbf{Nu}\!-\!H \quad X\!-\!\mathbf{Ar} \xrightarrow[\substack{\text{base} \\ -40\,°C\ \text{to r.t.}}]{\substack{\text{copper catalyst} \\ h\nu}} \mathbf{Nu}\!-\!\mathbf{Ar} \qquad (1)$$

**Nu**—H

**nitrogen:** nitrogen heterocycles
**sulfur:** aryl thiols

As indicated in the simplified pathway outlined in Scheme 1, our current hypothesis is that a copper–nucleophile complex undergoes excitation in the presence of light, and the resulting complex engages with the electrophile in an electron-transfer process to generate an aryl radical.[3] Because the structure of the nucleophile is expected to have a significant impact on the photophysics of the copper–nucleophile complex, the extension of this strategy to new families of nucleophiles cannot be taken for granted.
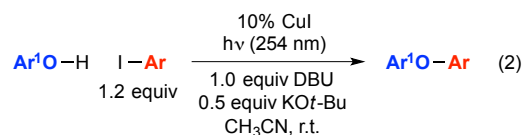
Diaryl ethers are a common subunit in important classes of organic compounds, such as pharmaceuticals, agricultural chemicals, and polymers.[4,5] Although palladium-catalyzed cross-coupling reactions provide a very powerful approach to the synthesis of these targets from the union of phenols with aryl electrophiles,[6] copper catalysts can be advantageous from the standpoints of cost and toxicity.[7] Recent reports on copper-catalyzed Ullmann C–O coupling have established that the use of appropriate ligands can enable diaryl ether formation under much milder conditions than described in Ullmann's original report (>180 °C).[8,9] Despite these

important advances, an elevated reaction temperature (≥60 °C) is employed in virtually all methods that have been reported to date.[10]
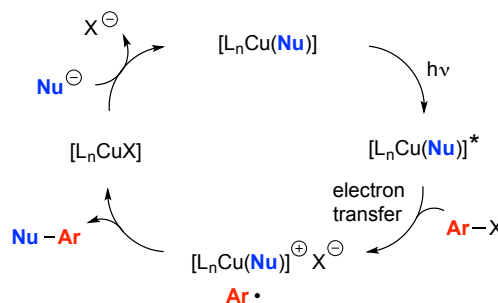


**Scheme 1** Outline of one possible pathway for photoinduced, copper-catalyzed cross-coupling.

In our pursuit of further evidence for the generality of photoinduced, copper-catalyzed C–X bond formation, we therefore chose to investigate the use of oxygen nucleophiles.[11] In this report, we establish that this third family of nucleophiles can indeed be employed as useful reaction partners, specifically, that C−O coupling between a variety of phenols and aryl iodides can be achieved under unusually mild conditions in the presence of light and CuI [eqn (2)]. Furthermore, our data are consistent with the hypothesis that this new photoinduced, copper-catalyzed process may follow an initial pathway analogous to that suggested for the corresponding C–N and C–S couplings, thereby providing support for the postulate that the reaction manifold outlined in Scheme 1 may have considerable generality.

$$\mathbf{Ar^1O}\!-\!H \quad I\!-\!\mathbf{Ar} \xrightarrow[\substack{1.0\ \text{equiv DBU} \\ 0.5\ \text{equiv KO}t\text{-Bu} \\ CH_3CN,\ \text{r.t.}}]{\substack{10\%\ \text{CuI} \\ h\nu\ (254\ \text{nm})}} \mathbf{Ar^1O}\!-\!\mathbf{Ar} \qquad (2)$$

1.2 equiv

## Results and discussion

Our previously described conditions for the arylation of nitrogen heterocycles and of aryl thiols were not effective for the coupling of phenol with 3-iodotoluene (<2%).[1] Optimization led to a method that furnishes the desired diaryl ether in good yield at room temperature (80%; Table 1, entry 1). Several control reactions established the importance of CuI and light for efficient coupling under these conditions (entries 2–4); the use of longer-wavelength light also resulted in less efficient C–O bond formation (entries 5–7). While our standard method employs a combination of DBU and KO$t$-Bu as the Brønsted base, either DBU or KO$t$-Bu alone also provided a fairly good yield of the coupling product (entries 8 and 9), although the use of excess KO$t$-Bu led to substantially less diaryl ether (entry 10). The identity of the alkali-metal cation associated with the $t$-butoxide base has a significant impact on coupling efficiency (entries 11 and 12); indeed, we have determined that, when PhOK, PhONa, or PhOLi was used in place of phenol and exogenous base, only PhOK furnished a substantial amount of the desired product (75%, 16%, and <5% for PhOK, PhONa, and PhOLi, respectively). Use of less CuI resulted in considerably less C–O bond formation (entry 13), whereas replacement of CuI with CuCl or CuCl$_2$ led to comparable or slightly diminished yield (entries 14 and 15).[12] Cu powder and Cu nanoparticles afforded some coupling product (<25%), whereas Cu$_2$O nanoparticles did not (entries 16–18). The process is modestly air- and moisture-sensitive (entries 19 and 20). Under our standard conditions, the O-arylation of phenol with an aryl bromide or an aryl chloride is less efficient than with an aryl iodide (entries 21 and 22; heating the reaction of PhBr to 60 °C led to a small increase in yield (50%)).[13]

**Table 1** Photoinduced, copper-catalyzed coupling of an oxygen nucleophile: Effect of reaction parameters
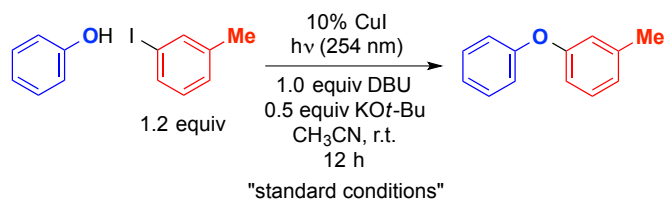


| entry | variation from the "standard conditions" | yield (%)[a] |
|---|---|---|
| 1 | none | **80** |
| 2 | no CuI | 10 |
| 3 | no hν | <1 |
| 4 | no CuI and no hν | <1 |
| 5 | hν (300 nm) | 64 |
| 6 | hν (100-watt Hg lamp) | 3 |
| 7 | hν (ambient light) | <1 |
| 8 | 1.5 equiv DBU, no KO$t$-Bu | 74 |
| 9 | 1.0 equiv KO$t$-Bu, no DBU | 70 |
| 10 | 1.5 equiv KO$t$-Bu, no DBU | 14 |
| 11 | NaO$t$-Bu, instead of KO$t$-Bu | 15 |
| 12 | LiO$t$-Bu, instead of KO$t$-Bu | 18 |
| 13 | 5% CuI | 42 |
| 14 | CuCl, instead of CuI | 78 |
| 15 | CuCl$_2$, instead of CuI | 65 |
| 16 | Cu powder, instead of CuI | 23 |
| 17 | Cu nanoparticles (60–80 nm), instead of CuI | 22 |
| 18 | Cu$_2$O nanoparticles (<50 nm), instead of CuI | <1 |
| 19 | under air, instead of under nitrogen | 51 |
| 20 | 0.1 equiv of H$_2$O | 64 |
| 21 | PhBr, instead of 3-iodotoluene | 42 (50)[b] |
| 22 | PhCl, instead of 3-iodotoluene | 20 |

[a] Yield determined by GC analysis with the aid of a calibrated internal standard (average of two runs). [b] Coupling conducted at 60 °C.

With reaction conditions in hand, we examined the scope of this photoinduced, copper-catalyzed method for coupling oxygen nucleophiles. With respect to the electrophilic partner, a variety of aryl iodides are suitable, including a highly hindered 2,6-disubstituted substrate (Table 2, entry 10; 20% CuI). A variety of functional groups, including an ester, ketone, ether, nitrile, acetal, and pyridine, are compatible with the coupling process.

**Table 2** Photoinduced, copper-catalyzed coupling of an oxygen nucleophile: Scope with respect to the electrophile

PhO—H   I—Ar   —see eqn (2)→   PhO—Ar

| entry | I—Ar | | yield (%)[a] |
|---|---|---|---|
| 1 | I—C₆H₅ | | 81 |
| 2 | I—C₆H₄—R | R = t-Bu | 63 |
| 3 | | CO₂Et | 71 |
| 4 | | COMe | 74 |
| 5 | I—C₆H₄—R | R = OMe | 70 |
| 6 | | CN | 77[b] |
| 7 | | CO₂Et | 55 |
| 8 | I—(3,5-Me₂C₆H₃) | | 70 |
| 9 | I—(2-EtO₂C-C₆H₄) | | 61[b] |
| 10 | I—(3,4,5-Me₃C₆H₂) | | 61[b] |
| 11 | I—(1-naphthyl) | | 51[b] |
| 12 | I—(benzodioxole) | | 52[b] |
| 13 | I—(2-pyridyl) | | 76 |

[a] Yield of purified product (average of two runs). [b] 20% CuI.

Ar¹O—H   I—Ph   —see eqn (2)→   Ar¹O—Ph

| entry | Ar¹O—H | | yield (%)[a] |
|---|---|---|---|
| 1 | R—C₆H₄—OH | R = Me | 60 |
| 2 | | Ph | 70 |
| 3 | | F | 67 |
| 4 | | CH₂CH₂OH | 68 |
| 5 | (3-R-C₆H₄)—OH | R = OMe | 76 |
| 6 | | CO₂Et | 62 |
| 7 | (3,5-Me₂C₆H₃)—OH | | 69 |
| 8 | (2-OMe-C₆H₄)—OH | | 65 |
| 9 | Me-(2,6-Me₂)-C₆H₂—OH | | 58 |

[a] Yield of purified product (average of two runs).

**Table 4** Photoinduced, copper-catalyzed coupling of an oxygen nucleophile: Functional-group compatibility

C₆H₅OH + I—(3-Me-C₆H₄) —see eqn (2), additive (1.0 equiv), 12 h→ C₆H₅O—(3-Me-C₆H₄)

| entry | additive | yield (%)[a] | recovery of additive (%)[a] |
|---|---|---|---|
| 1 | none | 80 | – |
| 2 | CH₂=CH—n-Hex | 80 | 88 |
| 3 | HC≡C—n-Hex | 76 | 81 |
| 4 | 3-Me-pyridine | 80 | >95 |
| 5 | N-Me-imidazole | 80 | >95 |
| 6 | benzoxazole | 71 | >95 |
| 7 | Me-CO-CH₂-(2-furyl) | 50[b] | >95 |
| 8 | 4-Cl-toluene | 55 | 54 |
| 9 | nitrobenzene | 11 | >95 |

[a] Yield determined by GC analysis with the aid of a calibrated internal standard (average of two runs). [b] Yield after 24 h: 63%.

With respect to the oxygen nucleophile, the scope of this photoinduced method for C–O coupling is also fairly broad (Table 3). Thus, phenols that bear a variety of substitution patterns serve as suitable coupling partners, including hindered (e.g., entry 9), electron-rich, and electron-poor substrates. In the case of a substrate with two different oxygens that can potentially serve as nucleophiles, the phenol reacts in preference to the aliphatic alcohol (entry 4).[14]

To provide additional data about the functional-group compatibility of this photoinduced coupling process, we examined the reaction of phenol with 3-iodotoluene in the presence of an array of additives (Table 4).[15] In the case of an alkene, alkyne, pyridine, imidazole, and benzoxazole, C–O bond formation proceeded in similar yield as for the additive-free coupling, and the additive was largely intact at the end of the reaction (entries 2–6). In contrast, the presence of 2-propionylfuran and 4-chlorotoluene significantly inhibited the O-arylation process (entries 7 and 8), and nitrobenzene (a powerful electron-acceptor) virtually shut down C–O coupling (entry 9).

**Table 3** Photoinduced, copper-catalyzed coupling of an oxygen nucleophile: Scope with respect to the nucleophile

According to the mechanistic hypothesis outlined in Scheme 1, C–O bond formation is initiated by photoexcitation of a Cu(I)–phenoxide complex, followed by electron transfer from an excited state of the Cu(I)–phenoxide to the aryl iodide, resulting in cleavage of the C–I bond. To gain insight into whether a Cu(I)–phenoxide complex can serve as a chemically competent intermediate, we

examined the reaction of [Cu(OPh)$_2$][N($n$-Bu)$_4$] (**1**; for excitation spectra, see Fig. 1)[3e] with an aryl iodide [eqn (3)]. Carbon–oxygen bond formation did indeed proceed upon irradiation (62%; in the absence of DBU: 35%), whereas no product was formed in the dark (<1%).
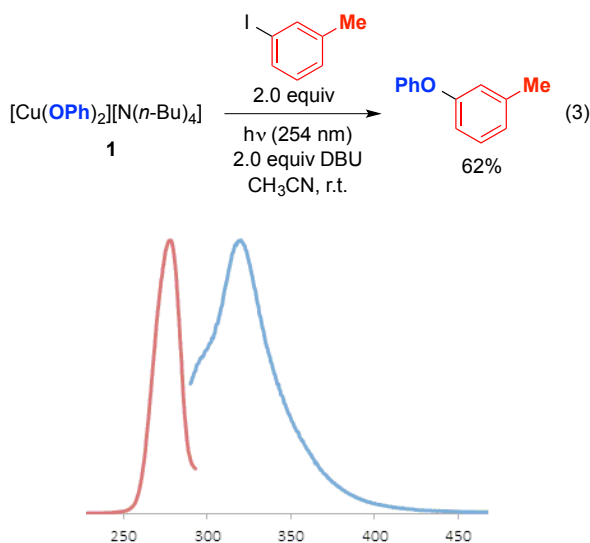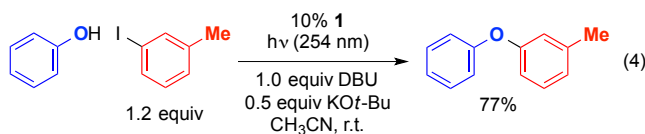
$$\text{[Cu(OPh)}_2\text{][N}(n\text{-Bu})_4\text{]} \quad \xrightarrow[\substack{\text{2.0 equiv} \\ h\nu\ (254\ \text{nm}) \\ \text{2.0 equiv DBU} \\ \text{CH}_3\text{CN, r.t.}}]{} \quad \text{PhO}\!-\!\text{C}_6\text{H}_4\!-\!\text{Me} \quad (3)$$

**1**        2.0 equiv                              62%



**Fig. 1** Excitation spectra of complex **1** at 320 nm emission (red) and emission spectra of complex **1** at 276 nm excitation (blue) in MeCN at room temperature.

In addition, we have determined that Cu(I)–phenoxide **1** serves as a competent (pre)catalyst for the coupling of phenol with 3-iodotoluene [eqn (4)]. The $^1$H NMR and excitation spectra of complex **1** in CH$_3$CN are essentially unchanged upon addition of DBU, suggesting that DBU is not bound to this complex under these conditions. We have not determined whether DBU binds to other copper species under the cross-coupling conditions.

$$\text{PhOH} + \text{I}\!-\!\text{C}_6\text{H}_4\!-\!\text{Me} \quad \xrightarrow[\substack{\text{1.0 equiv DBU} \\ 0.5\ \text{equiv KO}t\text{-Bu} \\ \text{CH}_3\text{CN, r.t.}}]{\substack{10\%\ \textbf{1} \\ h\nu\ (254\ \text{nm})}} \quad \text{Ph}\!-\!\text{O}\!-\!\text{C}_6\text{H}_4\!-\!\text{Me} \quad (4)$$

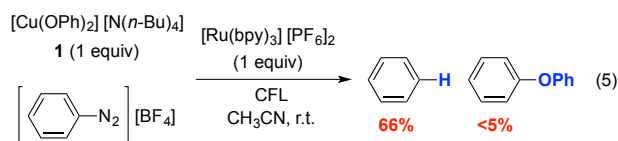1.2 equiv                              77%

Reaction pathways other than that presented in Scheme 1 also warrant consideration. While a complete mechanistic study is beyond the scope of the present contribution, one scenario that we have considered is whether direct photolysis of ArI at 254 nm in CH$_3$CN generates free Ar·, which in turn reacts with a Cu(I)–phenoxide species such as **1** (rather than a Cu(II)–phenoxide, as illustrated in Scheme 1) to afford C–O coupled product and Cu(0).[16] We therefore examined the generation of Ar· by means other than that shown in Scheme 1.

Photolysis of an aryl iodide at 254 nm in CH$_3$CN at room temperature can generate Ar·. For example, irradiation of 2-(allyloxy)iodobenzene at 254 nm leads to efficient cyclization over a 12-hour period to produce 2,3-dihydro-3-(iodomethyl)benzofuran (>90%). In contrast, under the same conditions, a simpler aryl iodide (3,5-dimethyliodobenzene) can be recovered almost quantitatively (>95%; in the presence of DBU and KO$t$-Bu: >80%), presumably due to relatively rapid in-cage recombination of Ar· and I·.

To explore whether free Ph· can react with a Cu(I)–phenoxide to generate a C–O coupling product, a solution of diazonium salt [PhN$_2$][BF$_4$], [Ru(bpy)$_3$][PF$_6$]$_2$, and complex **1** in CH$_3$CN was irradiated with a compact fluorescent light (CFL) bulb for 12 hours

[eqn (5)].[17] The predominant product was PhH, with only a trace of the diaryl ether (<5%).[18]

$$\text{[Cu(OPh)}_2\text{][N}(n\text{-Bu})_4\text{]} \atop \textbf{1}\ (1\ \text{equiv})}$$

$$\left[\text{C}_6\text{H}_5\!-\!\text{N}_2\right]\text{[BF}_4\text{]} \quad \xrightarrow[\substack{\text{CFL} \\ \text{CH}_3\text{CN, r.t.}}]{\substack{\text{[Ru(bpy)}_3\text{][PF}_6\text{]}_2 \\ (1\ \text{equiv})}} \quad \text{Ph}\!-\!\text{H} \quad \text{Ph}\!-\!\text{OPh} \quad (5)$$

66%        <5%

Although these experiments do not rule out radical-based pathways for photoinduced, copper-catalyzed cross-coupling that differ from that outlined in Scheme 1, they also do not provide support for the hypothesis that free Ar· that is generated by homolysis of ArI at 254 nm can react efficiently with a Cu(I)–phenoxide to produce a diaryl ether. Additional studies are required to obtain a clearer understanding of the mechanism(s) of photoinduced, copper-catalyzed cross-couplings, and it is likely that the details will vary considerably as a function of the coupling partners and the reaction conditions.

## Conclusions

We have provided further evidence for the suggestion that photoinduced, copper-catalyzed cross-coupling may be a versatile strategy for achieving C–X bond formation under unusually mild conditions. Specifically, we have demonstrated that oxygen nucleophiles can be employed as reaction partners, thereby expanding the scope of this approach to C–O bond-forming processes, an important bond construction in organic chemistry. Thus, using inexpensive CuI as the pre-catalyst, the cross-coupling of phenols with aryl iodides (with diverse steric and electronic properties) can be accomplished at room temperature. An array of functional groups are compatible with the reaction conditions, including an acetal, aliphatic alcohol, alkene, alkyne, benzoxazole, ester, ether, ketone, imidazole, nitrile, and pyridine. Our studies indicate that a Cu(I)–phenoxide is a viable intermediate in a photoinduced C–O bond-forming process. Ongoing studies are focused on the development of new classes of photoinduced coupling reactions and elucidating the mechanisms of these processes.

## Experimental section

In air, the phenol (1.0 mmol), CuI (19 mg, 0.10 mmol), and KO$t$-Bu (56 mg, 0.50 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. The quartz tube was fitted with a rubber septum, the joint was wrapped with electrical tape, and the quartz tube was evacuated and backfilled with nitrogen (3 cycles). DBU (154 mg, 1.0 mmol), the aryl iodide (1.2 mmol), and CH$_3$CN (6.5 mL) were added in turn via syringe. Then, the quartz tube was detached from the nitrogen line, and the puncture holes in the septum were immediately covered with vacuum grease. The resulting mixture was stirred for 5 minutes, and then the tube transferred to a Luzchem LZC–4V photoreactor (a Honeywell UV100A1059 UV Surface Treatment System, which can be purchased for ~$160 from common vendors such as Amazon.com, can also be used), where it was irradiated at 254 nm (UVC lamps) for 12 hours. Next, the reaction mixture was passed through a long plug of silica gel (monitored by TLC), the solvent was removed, and the residue was purified by column chromatography.

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Electronic supplementary information (ESI) available: Experimental details and characterization data (  pages).  See DOI: 10.1039/b000000x/

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10  We are aware of only three reports of copper-catalyzed cross-couplings of phenols with aryl halides that proceed at room temperature: (*a*) Q. Cai, B. Zou, D. Ma, *Angew. Chem. Int. Ed.,* 2006, **45**, 1276–1279 (requires an amide directing group ortho to the halide).  (*b*) Huffman, L. M.; Casitas, A.; Font, M.; Canta, M.; Costas, M.; Ribas, X.; Stahl, S. S. *Chem.–Eur. J.* 2011, **17**, 10643–10650.  (*c*) S. G. Babu, R. Karvembu, *Tetrahedron Lett.*, 2013, **54**, 1677–1680.

11  For a recent example of a photoinduced C–O bond-forming process that is *not* metal-catalyzed, see: Z. Xiao, S. Cai, Y. Shi, B. Yang, S. Gao, *Chem. Commun.* 2014; DOI: 10.1039/c3cc47426g.

12  Under the reducing conditions of these photoinduced cross-couplings, we anticipate that $CuCl_2$ is reduced to Cu(I).

13  Under the standard conditions: (a) The concentration of the aryl iodide is 0.15 M.  Use of a higher concentration (0.5 M) led to a decreased yield, whereas a lower concentration (0.05 M) provided a somewhat higher yield (88%; three times the amount of solvent).  (b) A small amount of unreacted phenol is often observed.

14  No product resulting from arylation of the aliphatic alcohol was detected.

15  (*a*) See footnote 15 in: A. C Bissember, A. Levina, G. C. Fu, *J. Am. Chem. Soc*., 2012, **124**, 14232–14237.  (*b*) For a recent discussion, see: K. D. Collins, F. Glorius, *Nature Chem.*, 2013, **5**, 597–601.

16  Our observation that Cu powder and Cu nanoparticles afford some C–O coupling product (Table 1, entries 17 and 18) may be relevant in this context.  Alternatively, Cu powder and Cu nanoparticles may provide a source of soluble Cu(I) under the reaction conditions.  For example, we have determined that, when PhSH and PhI are subjected to the standard conditions described herein, using Cu powder or Cu nanoparticles in place of CuI, analysis of the reaction mixture by ESI/MS reveals the presence of a significant quantity of $Cu(SAr)_2^-$ and $Cu_2(SAr)_3^-$ (which we have also identified during photoinduced, copper-catalyzed C–S cross-couplings: ref 1b), indicating that a homogenous Cu(I)–Nu adduct can be generated from these copper sources.  The corresponding experiments using PhOH and PhI do not lead to the positive identification by ESI/MS

of a Cu(I)–phenoxide in either the Cu powder/nanoparticles experiment or in the CuI-catalyzed C–O coupling reaction.

17  Under these conditions, photoreduction of the diazonium salt by the Ru photosensitizer liberates Ph·: (*a*) H. Cano–Yelo, A. Deronzier, *J. Chem. Soc. Perkin Trans. II*, 1984, 1093–1098. (*b*) H. Cano–Yelo, A. Deronzier, *J. Chem. Soc. Faraday Trans. I*, 1984, **80**, 3011–3019.

18  To explore whether Ph· can be trapped in a bimolecular process under these conditions, a solution of [PhN$_2$][BF$_4$] and Bu$_3$SnD in CH$_3$CN was irradiated with a CFL bulb in the presence [Ru(bpy)$_3$][PF$_6$]$_2$, resulting in a high yield of PhD (81%). Under otherwise identical conditions in the absence of [Ru(bipy)$_3$][PF$_6$]$_2$, a lower yield of PhD was observed (26%).