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Dual Photoredox and Gold Catalysis: Intermolecular Multicomponent Oxyarylation of Alkenes

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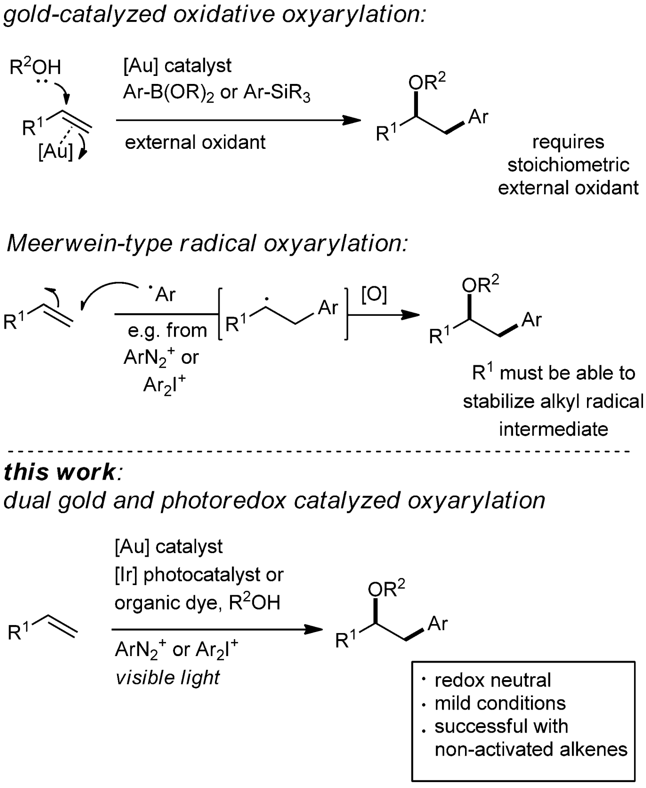
Abstract: Intermolecular three-component oxyarylation reactions of simple alkenes have been developed using a dual gold and photoredox catalytic system. Inexpensive organic dyes could be employed as the photocatalyst using aryldiazonium salts, while the combination of gold and iridium catalysts allowed for diaryliodonium compounds to be employed as the source of the arene coupling partner. In both cases, α-arylated ether products were generated under remarkably mild conditions using readily accessible visible light sources.

Keywords: alkenes; cross-coupling; dual catalysis; gold; photocatalysis

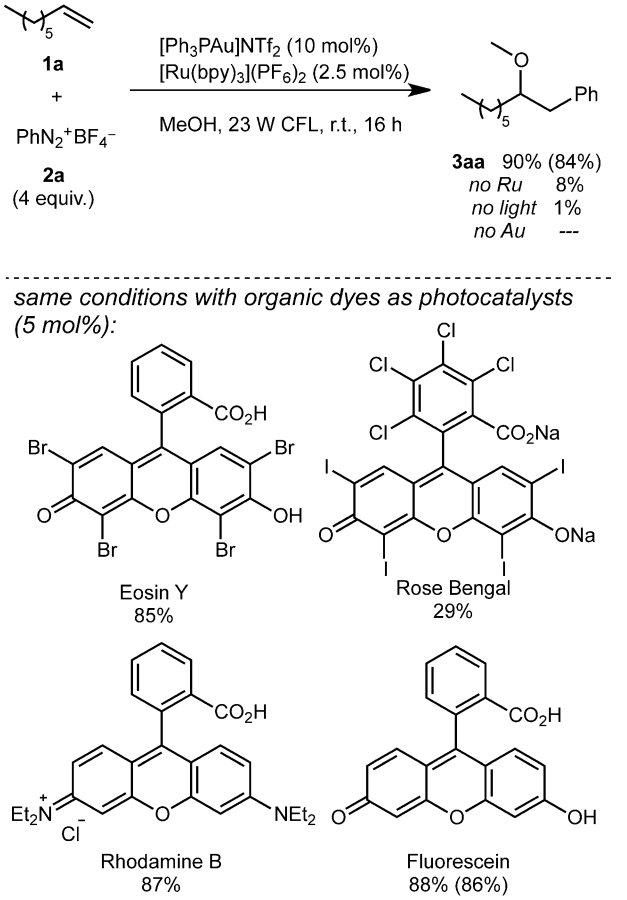
As fundamental building blocks of organic chemistry, methodologies that enable the selective functionalization of alkenes are important weapons in the chemist's armory. The intermolecular arylation of alkenes is most commonly achieved *via* the venerable palladium-catalyzed Mizoroki–Heck reaction between alkenes and aryl halides to afford styrene derivatives. An increasing amount of research attention, however, has been devoted to related transformations which, instead of maintaining the alkene functionality, result in the overall addition of two groups across the double bond. Intermolecular oxyarylation, whereby one aryl group and one oxygen substituent add across an alkene in a multicomponent coupling process, is one such transformation.[1] With palladium catalysts, a major challenge in these reactions is the suppression of the β-hydride elimination step, which results in undesired Mizoroki–Heck-type products. One promising solution to this problem has been the use of gold catalysts, which do not generally react *via* β-hydride elimination.[2] However, gold does not readily undergo oxidative addition with aryl halides and all the examples of Au-catalyzed oxyarylations reported to date have been oxidative processes, requiring super-stoichiometric amounts of a strong external oxidant.[3–5] An alternative approach to oxyarylation involves Meerwein-type addition of highly reactive aryl radicals, generated *in situ* from a suitable precursor.[6] The scope of these transformations, however, is generally limited to activated alkene substrates capable of stabilizing the alkyl radical generated upon addition.

Recently, we reported a novel dual catalytic system capable of mediating intramolecular oxy- and aminoarylation reactions of alkenyl alcohols and amines by combining gold catalysis with visible light photoredox activation.[7–9] In this process, ruthenium-catalyzed photoactivation of aryldiazonium salts is thought to lead to aryl radicals susceptible to gold-catalyzed cross-coupling.[10] Herein we report the successful application of dual gold/visible light photoredox catalysis to the selective *intermolecular* three-component oxyarylation of alkenes with simple alcohols. This redox neutral process benefits from mild reaction conditions and can be applied to a wide range of non-activated terminal alkene substrates. Moreover, judicious selection of the photoredox catalyst and light source allows for readily accessible diaryliodonium salts to be employed as the source of the arene coupling partner (Scheme 1).

In an initial test reaction, the simple alkyl-substituted alkene 1-octene (**1a**) was reacted with benzenediazonium tetrafluoroborate (**2a**, 4 equiv.) in the presence of the gold(I) catalyst [Ph_3PAu]NTf_2 (10 mol%) and the photosensitizer [$Ru(bpy)_3$]$(PF_6)_2$ (2.5 mol%) in methanol. We were delighted to find that, upon irradiation with visible light from a simple household compact fluorescent light bulb (23 W CFL), a single regioisomer of product **3aa**, resulting from selective addition of one phenyl and one methoxy group across the alkene, was generated as the only detectable product in 90% NMR yield (84% isolated yield). Control reactions conducted in the absence of either



Scheme 1. Intermolecular oxyarylation of alkenes.

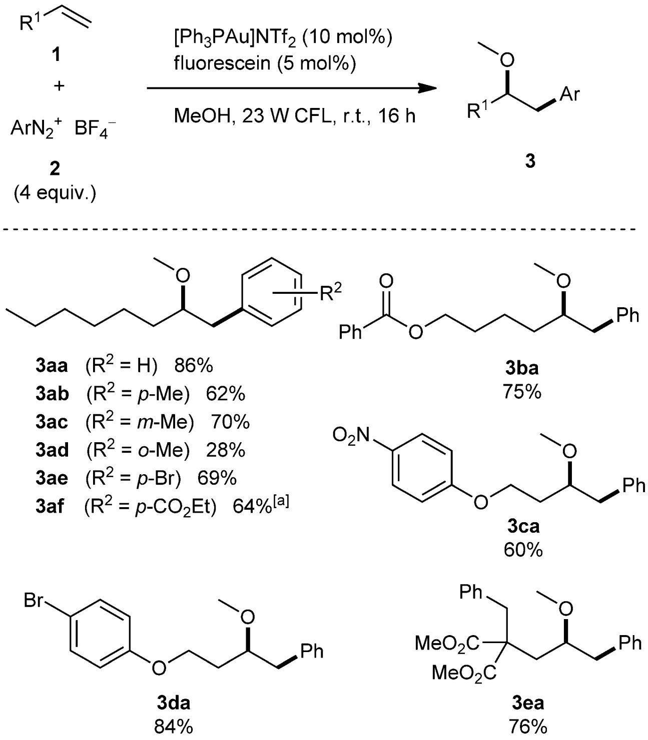


Scheme 2. Gold and organic dye dual-catalyzed intermolecular oxyarylation of alkenes with aryldiazonium salts. *Reaction conditions:* **1a** (0.1 mmol), (**2a**, 0.4 mmol), $[Ph_3PAu]NTf_2$ (10 mol%), photocatalyst in degassed MeOH (0.1 M) reacted under visible light irradiation (23 W CFL) for 16 h at room temperature. NMR yields using diethyl phthalate as internal standard, isolated yields in parentheses.

the photoredox catalyst or in the dark resulted in a dramatic drop in the reaction efficiency (<8% NMR yield) while no product was observed in the absence of gold.[11] With the feasibility of the dual catalyzed intermolecular oxyarylation reaction validated, our attention turned to improving the attractiveness of the process by employing an organic dye as photosensitizer. In comparison to transition metal-based photocatalysts such as $[Ru(bpy)_3](PF_6)_2$, organic dyes are considerably less expensive and benefit from lower toxicity and improved environmental characteristics.[12,13] The results of a short screen of some commercially available organic dyes are shown in Scheme 2. Pleasingly, inexpensive fluorescein (5 mol%) was found to be an effective substitute for $[Ru(bpy)_3](PF_6)_2$, selectively delivering the oxyarylated product **3aa** in 88% NMR yield (86% isolated yield). Changing the light source or gold catalyst failed to lead to an improvement of the reaction outcome while reducing the loadings of either catalyst or equivalents of the diazonium salt resulted in a diminished yield of the oxyarylated product.[11]

The dual gold and organic dye co-catalyzed intermolecular oxyarylation reaction was found to be general for a selection of different terminal alkenes and aryldiazonium salts, selectively delivering arylated ether products **3** in good yields (Scheme 3). In contrast to oxyarylation processes proceeding *via* radical addition, non-activated alkyl alkenes could be successfully employed and there was no requirement for radical-stabilizing substituents. A range of functional groups either on the alkene substrates or the aryldiazonium salts was tolerated including a bromoaryl moiety (**3da**, **3ae**), which could serve as a handle for further functionalization *via* cross-coupling methodologies. *ortho*-, *meta*- and *para*-substitution patterns on the aryl coupling partner were all tolerated while in no case were products resulting either from Mizoroki–Heck-type arylation or hydroetherification detected in the reaction mixture.

Having established a dual gold and photoredox catalytic system capable of mediating three-component oxyarylation reactions with aryldiazonium salts, we next sought to identify alternative sources of the arene coupling partner. In this regard, we were inspired by previous reports demonstrating that diaryliodonium salts can serve as precursors for aryl radicals upon photoredox activation with visible light.[6h,14]

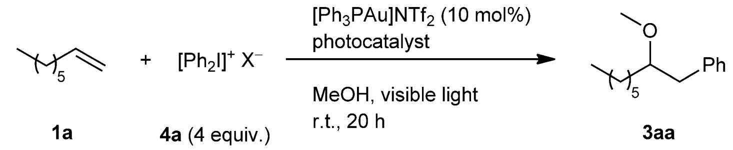


[a] Isolated as a 92:8 mixture with the corresponding methyl ester.

Scheme 3. Scope and limitations of the gold and fluorescein dual-catalyzed intermolecular oxyarylation of alkenes with aryldiazonium salts. *Reaction conditions:* **1** (0.2 mmol), (**2**, 0.8 mmol), $[Ph_3PAu]NTf_2$ (10 mol%), fluorescein (5 mol%) in degassed MeOH (0.1 M) reacted under visible light irradiation (23 W CFL) for 16 h at room temperature. Isolated yields given.

In contrast to aryldiazonium salts, diaryliodonium compounds may be stored for extended periods with many derivatives being commercially available. Substituting the aryldiazonium salt **2a** with diphenyliodonium trifluoromethanesulfonate in the intermolecular oxyarylation reaction of 1-octene (**1a**), however, led to very low yields of **3aa** using either the organic dye fluorescein or $[Ru(bpy)_3](PF_6)_2$ as the photocatalyst (3% and 7% NMR yields, respectively, Table 1, entries 1 and 2). Envisaging that photoredox catalysts with more reducing excited states might be beneficial for these less oxidizing arene sources, the iridium(III) complex $[Ir(ppy)_2(dtbbpy)]PF_6$ (ppy = 2-phenylpyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) was tested. Using this photocatalyst, which exhibits an excited state reduction potential of E^0 (Ir^{IV}/Ir^{III*}) = −0.96 V {*cf.* E^0 (Ru^{III}/Ru^{II*}) = −0.81 V for $[Ru(bpy)_3]^{2+}$},[9h] a small but notable improvement in the reaction efficiency was observed with **3aa** being delivered in 16% NMR yield after 20 h (Table 1, entry 3). A much more significant effect was observed, however, upon changing the source of visible light. Switching to a more powerful 32 W compact fluorescent light bulb (CFL) led to an increase in the oxyarylation yield to 29% (NMR) while **3aa** was produced in a respectable 62% NMR yield upon irradiation with blue LEDs (5 W, Table 1, entries 4 and 5). This figure could be further increased to 91% (NMR yield, 82% isolated yield) upon increasing the photoredox catalyst loading to 5 mol% and switching the iodonium salt anion to tetrafluoroborate (**4a**, Table 1, entries 6 and 7). An extensive survey of alternative gold catalysts, photocatalysts and light sources did not

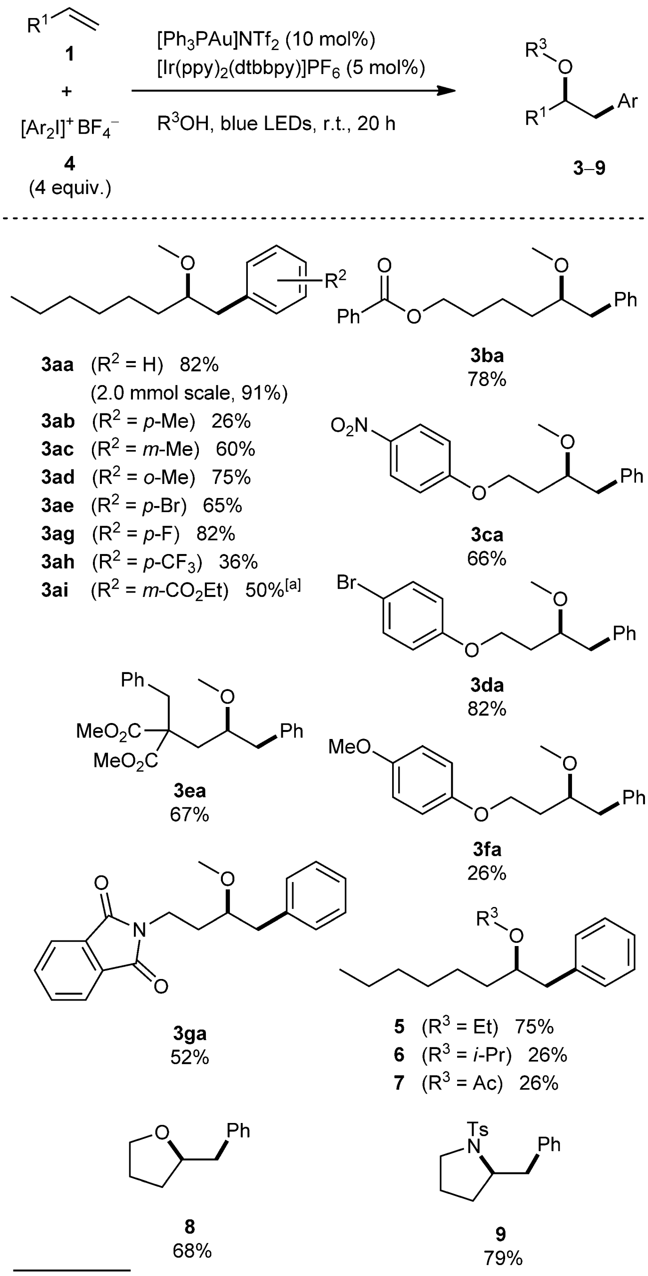
Table 1. Optimization of the oxyarylation reaction with diaryliodonium salts.



Entry[a]	Gold Catalyst (mol%)/Photocatalyst (mol%)	Light Source	X^-	Yield[b]
1	$[Ph_3PAu]NTf_2$ (10)/$[Ru(bpy)_3](PF_6)_2$ (2.5)	23 W CFL	OTf	7%
2	$[Ph_3PAu]NTf_2$ (10)/fluorescein (5)	23 W CFL	OTf	3%
3	$[Ph_3PAu]NTf_2$ (10)/$[Ir(ppy)_2(dtbbpy)]PF_6$ (2.5)	23 W CFL	OTf	16%
4	$[Ph_3PAu]NTf_2$ (10)/$[Ir(ppy)_2(dtbbpy)]PF_6$ (2.5)	32 W CFL	OTf	29%
5	$[Ph_3PAu]NTf_2$ (10)/$[Ir(ppy)_2(dtbbpy)]PF_6$ (2.5)	blue LEDs	OTf	62%
6	$[Ph_3PAu]NTf_2$ (10)/$[Ir(ppy)_2(dtbbpy)]PF_6$ (5)	blue LEDs	OTf	85%
7	$[Ph_3PAu]NTf_2$ (10)/$[Ir(ppy)_2(dtbbpy)]PF_6$ (5)	blue LEDs	BF_4	91% (82%)
8	Ph_3PAuCl (10)/$[Ir(ppy)_2(dtbbpy)]PF_6$ (5)	blue LEDs	BF_4	36%
9	Cy_3PAuCl (10)/$[Ir(ppy)_2(dtbbpy)]PF_6$ (5)	blue LEDs	BF_4	52%
10	–/$[Ir(ppy)_2(dtbbpy)]PF_6$ (5)	blue LEDs	BF_4	9%
11	$[Ph_3PAu]NTf_2$ (10)/–	blue LEDs	BF_4	<5%
12	$[Ir(ppy)_2(dtbbpy)]PF_6$ (5)	–	BF_4	<5%

[a] *Reaction conditions:* **1a** (0.1 mmol), (**4a**, 0.4 mmol), $[Ph_3PAu]NTf_2$ (10 mol%), photocatalyst in degassed MeOH (0.1 M) reacted under visible light irradiation for 20 h at room temperature.

[b] NMR yield using diethyl phthalate as internal standard, isolated yield in parentheses.



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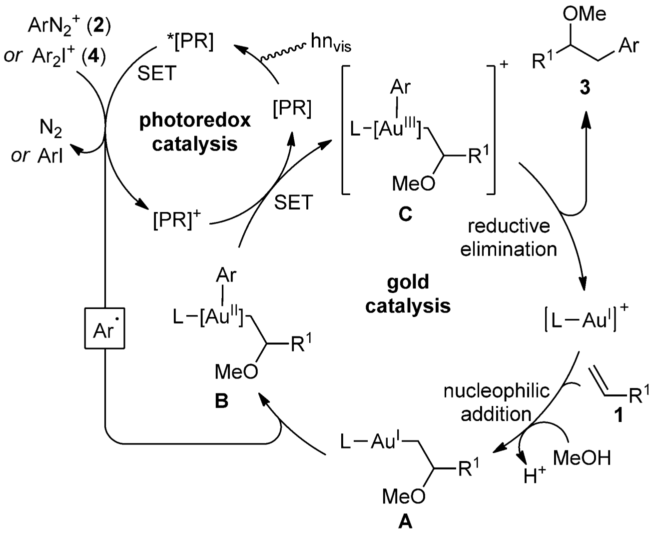
[a] Isolated as a 81:19 mixture with the corresponding methyl ester.

Scheme 4. Scope and limitations of the gold and iridium dual-catalyzed intermolecular oxyarylation of alkenes with diaryliodonium salts. *Reaction conditions:* **1** (0.2 mmol), (**4**, 0.8 mmol), $[Ph_3PAu]NTf_2$ (10 mol%), $[Ir(ppy)_2(dtbbpy)]PF_6$ (5 mol%) in degassed MeOH (0.1 M) reacted under visible light irradiation (blue LEDs) for 20 h at room temperature. Isolated yields given.

reveal superior reaction conditions while control reactions again confirmed the necessity for both catalysts and visible light (Table 1, entries 8–12).[11]

The scope and limitations of the dual gold and iridium-catalyzed three-component oxyarylation reaction with diaryliodonium salts are displayed in Scheme 4. As for the process with aryldiazonium compounds, a range of non-activated terminal alkenes could be successfully employed, delivering homobenzyl-substituted ethers **3** in generally good yields up to 82%. In most cases where the same products were obtained using both sets of conditions, the yields were largely comparable. Significant variations were observed, however, for the *para-* and *ortho*-methyl-substituted derivatives **3ab** and **3ad**. The more sterically congested *ortho*-substituted substrate was seemingly better tolerated as the iodonium salt, delivering **3ad** in 75% yield compared to 28% with diazonium salt **2d**. The opposite trend was observed for the *para*-methyl substituted aryl group with **3ab** being delivered in only 26% using diaryliodonium salt **4b** (*cf.* 62% yield with **2b**). The *para*-halogen-substituted diaryliodonium salts **4e** and **4g** reacted smoothly, however, affording **3ae**, which bears a bromoaryl group amenable to further functionalization, and **3ag** in 65% and 82% yields, respectively. A broad range of functional groups was also tolerated under these conditions although **3fa**, which bears an electron-rich and potentially photoredox active methoxyphenyl ether motif, was formed in a comparatively low yield of 26%. A selection of different alcohols was successfully coupled with 1-octene (**1a**) and diphenyliodonium salt **4a** when employed as the solvent in place of methanol. Acetic acid was also a suitable oxygen nucleophile, furnishing the corresponding acetoxylated product **7**, albeit in a modest yield of 26%. Diaryliodonium salts were also shown to be suitable sources of the aryl coupling partner in intramolecular oxy- and aminoarylation reactions. Reacting alkenyl alcohol **1h** and amine **1i** with diphenyliodonium salt **4a** under the optimized conditions with $[Ph_3PAu]NTf_2$ and $[Ir(ppy)_2(dtbbpy)]PF_6$ under blue LED irradiation delivered the corresponding heterocyclic products **8** and **9** in 68% and 79% yields, respectively. The oxyarylation process was also found to be readily scalable with **3aa** being obtained in 91% isolated yield when the reaction was run on a 2.0 mmol scale. Finally the degree of selectivity afforded by the process using an unsymmetrical diaryliodonium salt was tested using (phenyl)(*para*-bromophenyl)iodonium tetrafluoroborate (**4j**). Reacting this substrate with 1-octene (**1a**) under the optimized conditions in methanol afforded a mixture of **3aa** and **3ae** in a ratio of 1:1.3, indicating a slight preference for the more electron-deficient bromo-substituted aryl group (90% combined NMR yield, see the Supporting Information for more details).

A mechanistic hypothesis for the dual-catalyzed process is shown in Scheme 5. In accordance with previous reports on the activation of alkenes with sources of cationic gold(I),[15] we envisage that initial coordination of the gold to the double bond followed by nucleophilic attack of the methanol solvent would lead



Scheme 5. Mechanistic hypothesis for the dual catalyzed oxyarylation process. [PR] = photoredox catalyst {fluorescein for diazonium salts **2**, $[Ir(ppy)_2(dtbbpy)]^+$ for iodonium salts **4**}.

to the alkylgold(I) complex **A**.[16] Concurrently, in the case of the reaction with aryldiazonium salts **2**, excitation of the fluorescein photocatalyst by visible light followed by single electron transfer (SET) to the diazonium compound and subsequent extrusion of nitrogen would generate an aryl radical. With diaryliodonium salts **4**, this species would be generated by SET from the excited state of the iridium catalyst $[Ir(ppy)_2(dtbbpy)]^+$ and loss of an aryl iodide molecule. At this stage, oxidation of the gold(I) complex **A** by the aryl radical would afford the gold(II) species **B**, bearing both the alkyl and aryl coupling partners.[17] SET between this complex and the oxidized photocatalyst would then deliver the gold(III) species **C** and complete the photoredox catalytic cycle. Subsequent reductive elimination from **C** would then result in product formation and regeneration of the gold(I) catalyst.

In conclusion, we have developed a novel dual catalyzed multicomponent oxyarylation of alkenes combining gold catalysis and visible light photoredox catalysis. Using aryldiazonium salts as sources of the aryl coupling partner, the inexpensive organic dye fluorescein can be used as the photocatalyst while the combination of the iridium complex $[Ir(ppy)_2(dtbbpy)]PF_6$ and visible light from blue LEDs allows for diaryliodonium salts to be employed. In both cases, the oxyarylation reactions proceed at room temperature under irradiation from readily accessible visible light sources and deliver arylated ether products from simple, non-activated alkenes.

Experimental Section

General Procedure for Oxyarylation with Aryldiazonium Salts

Fluorescein (3.3 mg, 10.0 μmol, 5 mol%), $[Ph_3PAu]NTf_2$ (14.8 mg, 20.0 μmol, 10 mol%), the aryldiazonium salt **2** (0.80 mmol, 4.0 equiv.) and the alkene substrate **1** (0.20 mmol, 1.0 equiv.) were added to a flame-dried Schlenk flask containing a stirring bar. In the absence of light, anhydrous methanol (2.0 mL, 0.10 M) was added and the mixture was degassed using three freeze-pump-thaw cycles. The flask was then flushed with argon, sealed and the mixture was stirred under irradiation from a desk lamp fitted with a 23 W fluorescent light bulb (situated ~5 cm away from the reaction vessel). After evolution of nitrogen had ceased (16 h), the mixture was stirred for a further 30 min before being filtered through a short pad of silica gel (eluent = EtOAc) and the solvent was removed under vacuum. The crude products were purified by column chromatography over silica gel.

General Procedure for Oxyarylation with Diaryliodonium Salts

$[Ir(ppy)_2(dtbbpy)](PF_6)$ (9.2 mg, 10.0 μmol, 5 mol%), $[Ph_3PAu]NTf_2$ (14.8 mg, 20.0 μmol, 10 mol%), the diaryliodonium salt **4** (0.80 mmol, 4.0 equiv.) and the alkene substrate **1** (0.20 mmol, 1.0 equiv.) were added to a flame-dried Schlenk flask containing a stirring bar. In the absence of light, anhydrous methanol (or other alcohol, 2.0 mL, 0.10 M) was added and the mixture was degassed using three freeze-pump-thaw cycles. The flask was then flushed with argon, sealed and the mixture was stirred under irradiation from blue LEDs (situated ~5 cm away from the reaction vessel in a custom-made "light box"). After 20 h of irradiation, the mixture was filtered through a short pad of silica gel (eluent = EtOAc) and the solvent was removed under vacuum. The crude products were purified by column chromatography over silica gel.

Acknowledgements

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