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Combining Gold and Photoredox Catalysis: Visible Light-Mediated Oxy- and Aminoarylation of Alkenes

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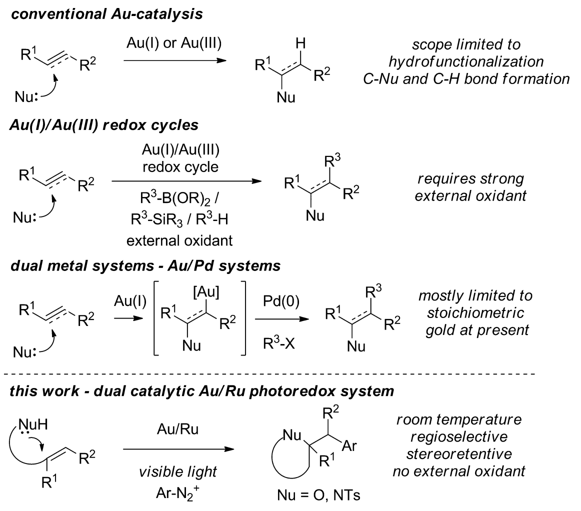
Ⓢ *Supporting Information*

ABSTRACT: A room-temperature intramolecular oxy- and aminoarylation of alkenes with aryldiazonium salts has been developed using a novel gold and photoredox dual-catalytic system. The compatibility of these two catalytic modes has been established for the first time and demonstrates the potential of this system as a method to expand the scope of nucleophilic addition reactions to carbon−carbon multiple bonds.

The selective functionalization of carbon−carbon multiple bonds remains a highly attractive and widely applied method for the preparation of complex organic molecules. Nucleophilic addition processes catalyzed by gold complexes have emerged as powerful tools for the direct functionalization of alkynes and allenes, while alkenes have also been successfully employed as substrates.[1] In these transformations, Au acts as a highly carbophilic π-Lewis acid, activating C−C multiple bonds toward intra- or intermolecular nucleophiles with often remarkable levels of chemo-, regio-, and/or stereocontrol. In the vast majority of cases, however, nucleophilic attack onto the π-system is followed by proto-deauration, leading to products of hydrofunctionalization. In recent years, several approaches have been developed which seek to expand the scope of these transformations by extending the range of demetalation pathways beyond protonation. Several publications have focused on cascade nucleophilic addition−oxidative coupling processes involving Au^I/Au^{III} redox cycles facilitated by strong external oxidants such as $PhI(OAc)_2$ or Selectfluor (a trademark of Air Products and Chemicals).[2] Recently, an alternative strategy has been disclosed whereby Au is used in combination with another catalyst in a dual-metal system. Stoichiometric organogold intermediates generated upon nucleophilic attack onto C−C multiple bonds have been employed as coupling partners in palladium-catalyzed cross-coupling processes, leading to products not accessible using either metal in isolation.[3] The extension of this methodology toward dual-catalytic systems, however, has proved challenging.[4]

We sought to evaluate the viability of dual catalysis as a means of expanding the scope of Au-catalyzed functionalization reactions of C−C multiple bonds. In this regard, our attention was drawn to the recent reports of dual-catalytic systems[5] involving photoredox catalysis.[6] In these transformations, the combination of organo-,[7] Lewis acid,[8] or transition metal catalysts such as palladium[9] or copper[10] with photoactive complexes of ruthenium or iridium led to novel synthetic processes under mild conditions when performed in the presence of visible light. In this paper, we report the successful development of a dual Au and photoredox catalytic system applicable to the intramolecular oxy- and aminoarylation of alkenes with aryldiazonium salts.[11−13] This process involves the formation of new C−Nu and C−C bonds across the alkene and occurs at room temperature upon irradiation with a simple household light bulb (Scheme 1).

Scheme 1. Gold-Catalyzed Addition to C−C Multiple Bonds



In a preliminary experiment, 4-penten-1-ol (**1a**) was reacted in the presence of 4 equiv of phenyldiazonium tetrafluoroborate (**2a**), which is known to act as a source of phenyl radicals in the presence of $[Ru(bpy)_3](PF_6)_2$ under visible light irradiation.[14,15] Upon treatment with 5 mol% of this photoredox catalyst and 10 mol% of the Au(I) precatalyst Ph_3PAuCl in degassed methanol for 6 h in the presence of light from a 23 W fluorescent light bulb, the tetrahydrofuran **3aa** resulting from a cascade 5-*exo-trig* cyclization−arylation process was observed as the major product in 51% NMR yield. In contrast to previously reported Au-catalyzed alkene oxyarylation processes, this dual-catalyzed reaction proceeds at room temperature and does not require stoichiometric amounts of a strong external oxidant.[11] With the aim of identifying a set of standard reaction conditions, an optimization study was conducted (Table 1).[16] The reaction efficiency was found to be highly dependent on the Au catalyst

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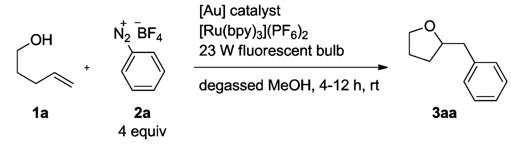
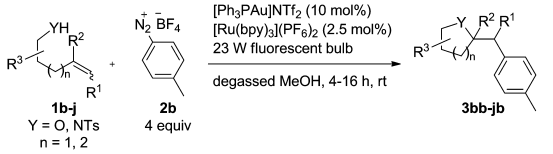
Table 1. Optimization Studies

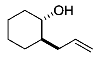
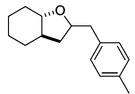
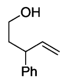
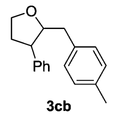
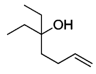
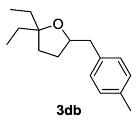
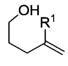
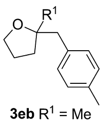
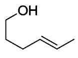
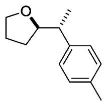
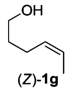
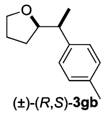
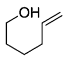
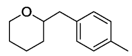
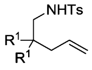
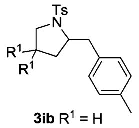


entry[a]	[Au] catalyst	[Au]/[Ru] (mol%)	yield (%)[b]
1	Ph_3PAuCl	10/5	51
2	$[dppm(AuCl)_2]$	10/5	22
3	$AuCl_3$	10/5	trace
4	$(pic)AuCl_2$	10/5	trace
5	IPrAuCl	10/5	trace
6	$[Ph_3PAu]NTf_2$	10/5	84
7	$[Ph_3PAu]NTf_2$	10/2.5	88 (79)
8	$[Ph_3PAu]NTf_2$	10/1	61
9	$[Ph_3PAu]NTf_2$	5/2.5	50
10	$[Ph_3PAu]NTf_2$	1/2.5	22
11[c]	$[Ph_3PAu]NTf_2$	10/2.5	6
12	$[Ph_3PAu]NTf_2$	10/—	4
13	—	—/2.5	0

[a] General conditions: **1a** (0.2 mmol), [Au] catalyst, $[Ru(bpy)_3](PF_6)_2$, **2a** (0.8 mmol), degassed MeOH (2 mL), rt, 4−12 h, 23 W fluorescent light bulb. [b] Yield determined by ^1H NMR using diethyl phthalate as an internal standard. Isolated yields in parentheses. [c] Reaction was performed in the absence of light. dppm = bis(diphenylphosphanyl)-methane, IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene, pic = picolinato.

Table 2. Scope of Alkene Substrates



Entry[a]	Alkenol **1**	Product **3**	Yield (dr)[b]
1	 (±)-(*S*,*R*)-**1b**	 (±)-(*R*,*S*)-**3bb**	66% (2.8:1)
2	 **1c**	 **3cb**	70% (1.6:1)
3	 **1d**	 **3db**	56%
4 5	 **1e** R^1 = Me **1f** R^1 = Ph	 **3eb** R^1 = Me **3fb** R^1 = Ph	39% 63%
6	 (*E*)-**1g**	 (±)-(*R*,*R*)-**3gb**	59% (>25:1)
7[c]	 (*Z*)-**1g**	 (±)-(*R*,*S*)-**3gb**	56% (>25:1)
8	 **1h**	 **3hb**	34%
9[d] 10[d]	 **1i** R^1 = H **1j** R^1 = Me	 **3ib** R^1 = H **3jb** R^1 = Me	84% 54%

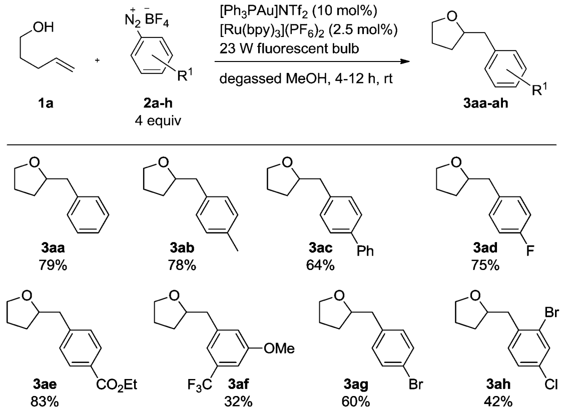
[a] General conditions: **1b−j** (0.2 mmol, 1 equiv), $[Ph_3PAu]NTf_2$ (10 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%), **2b** (4 equiv), degassed MeOH (0.1 M), rt, 4−16 h, 23 W fluorescent light bulb. [b] Isolated yields. dr determined by ^1H NMR. [c] Reaction performed on a 0.4 mmol scale. [d] 5 equiv of **2b** used.

employed. Au(III) precatalysts such as $AuCl_3$ or $(pic)AuCl_2$ led to only trace amounts of the oxyarylated product **3aa**, while the N-heterocyclic carbene-stabilized Au(I) complex IPrAuCl was also unsuitable (Table 1, entries 1−5). The highest yield of **3aa** (84% NMR yield) was obtained using the Gagosz catalyst $[Ph_3PAu]NTf_2$, which is thought to dissociate to afford a cationic Au(I) species upon solvation (Table 1, entry 6). With the optimal Au catalyst identified, the effect of changing the relative loadings of each reactant and catalyst was investigated. A 10:2.5 mol% ratio of Au to Ru was found to give the highest yield of the desired product (88% NMR yield, 79% isolated yield, Table 1, entry 7), while lowering the equivalents of the aryldiazonium salt **2a** or changing solvents from methanol had a detrimental effect on the reaction efficiency. The dual-catalyzed nature of the process was confirmed by control experiments. Performing the reaction in the absence of light or in the absence of $[Ru(bpy)_3](PF_6)_2$ led to a dramatic reduction in the yield of **3aa** (NMR yields not exceeding 6%), while no product was observed in the absence of Au (Table 1, entries 11−13).

With a set of optimized reaction conditions in hand, we turned our attention to an evaluation of the scope and limitations of the dual-catalyzed process with a range of different alkenes and aryldiazonium salts.[17] The results of these studies are summarized in Tables 2 and 3, respectively.

The reaction with (4-methylphenyl)diazonium salt **2b** proceeded readily with a range of substituted 4-penten-1-ol derivatives **1a−g**, delivering the corresponding tetrahydrofuran products **3ab−gb** in generally moderate to good yields (Table 2, entries 1−7). In addition to tolerating substituents on the alkyl tether, the reaction was also successful for substrates bearing methyl groups on the alkene itself (Table 2, entries 4−7). In contrast to previously reported Au-catalyzed alkene oxyarylation processes,[11] internal alkenes were also suitable substrates, with (*E*)-4-hexen-1-ol (*E*)-**1g** and (*Z*)-4-hexen-1-ol (*Z*)-**1g** delivering tetrahydrofurans (±)-(*R*,*R*)-**3gb** and (±)-(*R*,*S*)-**3gb** with high diastereoselectivity in 59% and 56% yield, respectively (Table 2, entries 6 and 7). In all cases, selective 5-*exo-trig* cyclization was observed without contamination with products resulting from 6-*endo-trig* cyclization. Similarly, 5-hexen-1-ol **1h**, which possesses an extra CH_2 unit between the alkene and alcohol functionalities, cyclized exclusively in a 6-*exo-trig* fashion to afford the oxyarylated pyran product **3hb** in a moderate 34% yield (Table 2, entry 8). In no case were 2-methyl-substituted heterocycles resulting from conventional cyclization−protodeauration isolated from the reaction mixture. The cascade nucleophilic addition−arylation process was also successful with alkene substrates **1i,j** bearing a pendant nitrogen nucleophile. These

Table 3. Scope of Aryldiazonium Salts



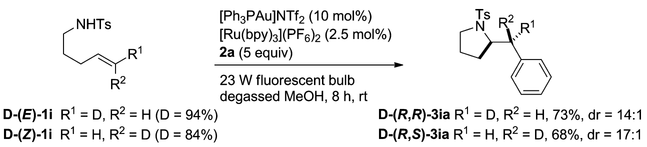
[a]General conditions: **1a** (0.2 mmol, 1 equiv), $[Ph_3PAu]NTf_2$ (10 mol %), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%), **2a**–**h** (4 equiv), degassed MeOH (0.1 M), rt, 4–12 h, 23 W fluorescent light bulb. Isolated yields.

reactions delivered pyrrolidine products in good yields up to 84% (Table 2, entries 9 and 10).

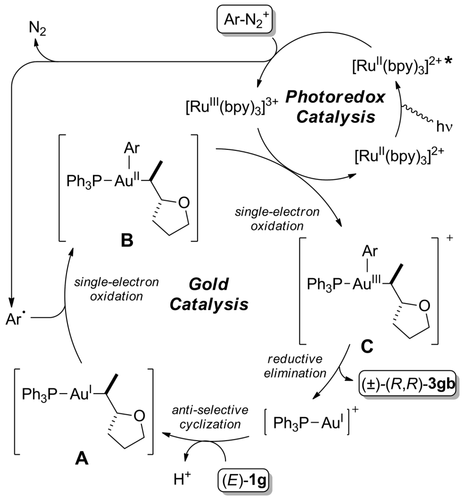
The oxyarylation process was also successful with a range of diversely substituted aryldiazonium salts **2a**–**h**. Under the standard reaction conditions with 4-penten-1-ol (**1a**), arylated tetrahydrofurans **3aa**–**ah** were delivered in generally moderate to good yields up to 83% (Table 3). Aryldiazonium salts bearing an electron-withdrawing substituent were the most efficient coupling partners, while comparatively electron-neutral groups such as 4-methyl and 4-phenyl were also well tolerated. Notably, halogenated substrates **2g**,**h** also reacted successfully to afford the corresponding products **3ag**,**ah** possessing bromo or chloro groups amenable to further functionalization.

Alongside scope and limitation studies, control experiments were conducted to shed light on the reaction mechanism. In an initial experiment, the effect of suspending the irradiation of light during the reaction of alkene **1a** and aryldiazonium salt **2a** was investigated. Whereas 40% conversion to product (NMR) was observed after 20 min of visible light irradiation, the reaction shut down once the light was switched off (1% conversion over 40 min stirring in the dark). Reapplying the light irradiation led to a recovery of the catalytic activity, implying that the photoredox and Au catalysts operate in tandem throughout the course of the reaction.[16] Insight into the reaction mechanism was also provided by the stereochemical outcome of the reactions of aryldiazonium salt **2a** with deuterated alkene substrates D-(*E*)- and D-(*Z*)-**1i**. These reactions proceeded in a diastereoselective fashion to afford the corresponding pyrrolidines with stereochemistry consistent with an overall *trans*-addition across the alkene in each case (Scheme 2). Similar selectivity was observed for internal alkene substrates (*E*)- and (*Z*)-**1g** (Table 2, entries 6 and 7). This observation is in line with previously reported Au-catalyzed aminoarylation processes whereby an initial *trans*-aminoauration is followed by oxidative arylation proceeding with retention of stereochemistry.[11,18]

Scheme 2. Aminoarylation of Deuterated Substrates



Scheme 3. Mechanistic Hypothesis



A tentative mechanistic hypothesis consistent with the above observations is shown in Scheme 3. In this scenario, the cationic Au(I) catalyst initially reacts with the alkene substrate to afford the alkylgold(I) intermediate **A** resulting from *anti*-selective cyclization. At this stage, aryl radicals generated upon Ru-catalyzed photoredox decomposition of the diazonium salt could react with this species to afford the Au(II) intermediate **B** bearing both coupling partners.[14,19] This unstable species would be expected to rapidly donate an electron to Ru^{III}, regenerating the Ru^{II} photoredox catalyst and affording a highly electrophilic Au(III) species, **C**. Reductive elimination at this stage would deliver the product and regenerate the Au(I) catalyst.[20] Although further studies are required to determine whether a redox mechanism of this type is operating in this system,[21,22] the implication that organic radicals generated via photoredox catalysis could act as oxidants for Au(I) is an intriguing possibility.[23]

In conclusion, a novel Au and visible light-mediated photoredox dual-catalytic system has been applied to the intramolecular oxy- and aminoarylation of alkenes with aryldiazonium salts. This transformation gives access to arylated heterocyclic compounds and occurs at room temperature under irradiation from a simple household light bulb. Moreover, we believe the apparent compatibility of Au and photoredox catalysis demonstrated herein could lead to the development of a wide range of novel, dual-catalyzed transformations of broad synthetic appeal.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization data, and details of optimization and control reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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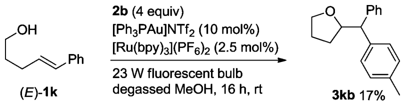

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