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Photosensitizer-Free Visible-Light-Mediated Gold-Catalyzed 1,2-Difunctionalization of Alkynes

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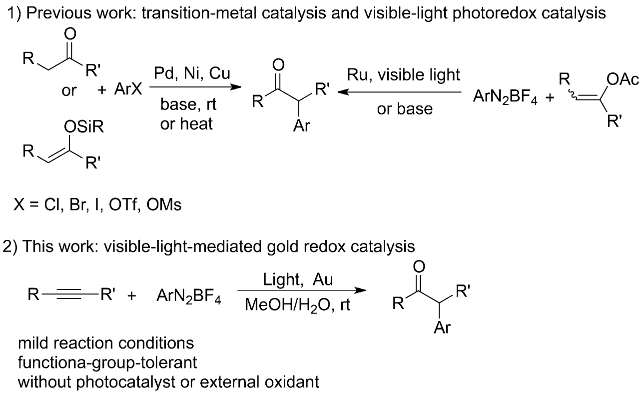
Abstract: *Under visible-light irradiation, the gold-catalyzed intermolecular difunctionalization of alkynes with aryl diazonium salts in methanol affords a variety of α-aryl ketones in moderate to good yields. In contrast to previous reports on gold-catalyzed reactions that involve redox cycles, no external oxidants or photosensitizers are required. The reaction proceeds smoothly under mild reaction conditions and shows broad functional-group tolerance. Further applications of this method demonstrate the general applicability of the arylation of a vinyl gold intermediate instead of the commonly used protodemetalation step. This step provides facile access to functionalized products in one-pot processes. With a P,N-bidentate ligand, a stable aryl gold(III) species was obtained, which constitutes the first direct experimental evidence for the commonly postulated direct oxidative addition of an aryl diazonium salt to a pyridine phosphine gold(I) complex.*

The synthesis of α-aryl ketone derivatives is of great importance in organic synthesis because of their utility as a core structural component of numerous pharmaceuticals, bioactive natural products, and functional materials.[1] Thus, considerable attention has been devoted to the construction of this moiety. Over the last two decades, the transition-metal-catalyzed α-arylation of carbonyl compounds and their equivalents with aryl halides or pseudohalides was studied particularly well, and both the substrate scope and the functional-group tolerance were substantially broadened. However, the vast majority of α-arylation methods still suffer from some drawbacks, such as harsh reaction conditions (elevated temperatures or the use of strong bases). Alternatively, visible-light- and base-mediated couplings of prefunctionalized enol ether derivatives with aryl diazonium salts as the aryl radical source have been developed.[2] Despite this progress, the development of a new efficient synthetic method that utilizes readily available starting materials to afford the desired products with high selectivity under mild conditions is still highly desirable (Scheme 1).



Scheme 1. Known strategies for the synthesis of α-aryl ketones and our alternative approach.

Homogeneous gold catalysis has made significant progress in the past decade.[3] In contrast to the frequently applied concept of using gold as a mild carbophilic π Lewis acid, fewer examples of reactions based on gold(I)/gold(III) redox cycles have been reported. Strong external oxidants, such as hypervalent iodine reagents or F^+ donors, are required in stoichiometric amounts owing to the high redox potential of gold.[4,5] Recently, work by the groups of Glorius and Toste demonstrated that the oxidation of gold can also be achieved by combining the use of photosensitizers and aryl radical sources (aryl diazonium or diaryl iodonium salts) with visible-light irradiation (Scheme 2).[6]

The gold-catalyzed hydration of alkynes represents an important method for C–O bond formation.[7] Previous work by the groups of Utimoto and Laguna has demonstrated that organometallic Au^{III} complexes can efficiently catalyze the hydration of alkynes.[7e,h] A beautiful expansion of this method was published by Hammond and co-workers, who reported on the gold-catalyzed trifunctionalization of alkynes. In this case, a gold(III) intermediate is generated by oxidation with Selectfluor as the external oxidant, and the functionalization proceeds by transmetalation from a boronic acid followed by reductive elimination. The third functionalization is then induced by the electrophilic fluorinating reagent.[4e] Inspired by this success and based on the recent work of our group in the context of photocatalysis,[8] we envisioned that highly electrophilic aryl gold(III) intermediates, generated by photoredox processes, could also serve as efficient activators of C≡C bonds for nucleophilic additions. The generated mixed aryl/vinyl gold(III) intermediates could then deliver the desired α-aryl ketones after reductive elimination and hydrolysis. Thus, in contrast to known methods, a major

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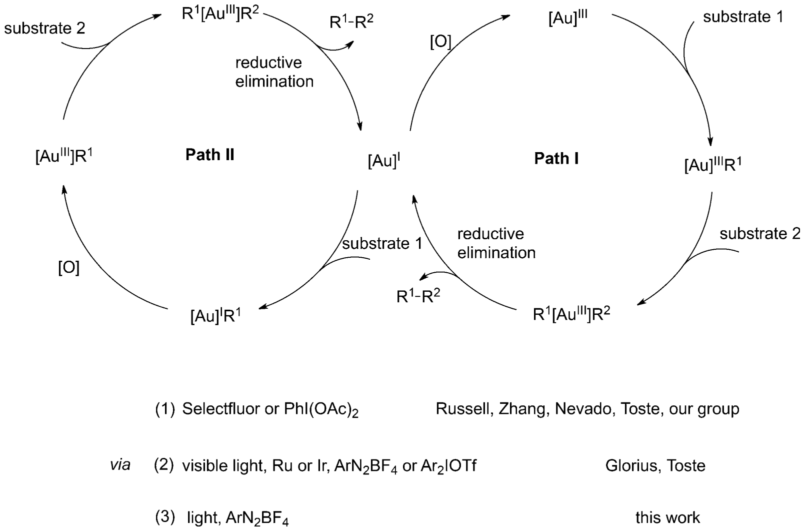
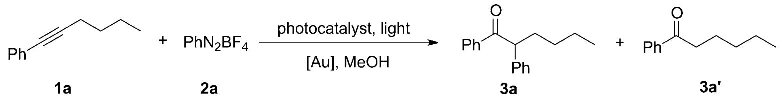


Scheme 2. Au^I/Au^{III} redox cycles under different conditions.

drawback would be avoided: The additional functionalization would not require an external oxidant.

To test this hypothesis, we initially performed an experiment with 1-phenyl-1-hexyne (**1a**) and phenyldiazonium tetrafluoroborate (**2a**) in the presence of 5 mol% [Ru(bpy)$_3$]Cl$_2$•6H$_2$O and 10 mol% Ph$_3$PAuCl as the catalytic system at room temperature under irradiation with UVA light in methanol. These conditions afforded the desired product **3a** in 27% after 24 h (Table 1, entry 1). Using [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ as the photosensitizer improved the yield to 57% (entry 2). The successful use of dimeric gold complexes as photosensitizers was recently demonstrated by Barriault and co-workers and by our group.[8] Thus we decided to explore the feasibility of a process in which gold not only acts as a π-activator but also serves as a photosensitizer. Indeed, the employment of dinuclear gold photocatalysts also produced **3a** in 47% and 65% yield (depending on the counterion; entries 3 and 4). Control experiments confirmed that the transformation does not occur in the absence of a catalyst, and only a trace amount of the product was observed in the presence of [Au$_2$(μ-dppm)$_2$](NTf$_2$)$_2$ (entries 5 and 6). To our surprise, the yield of **3a** dramatically increased to 76% when simple Ph$_3$PAuCl was used (entry 7). Further control experiments showed that light was essential for the success of this reaction (entry 8). Next, different light sources were examined, and blue LEDs turned out to be most effective, affording **3a** in 79% yield (entries 9–11). The reaction also proceeds smoothly under sunlight irradiation, albeit in a slightly reduced yield (entry 11). A survey of different basic and acidic additives failed to give better results (entries 12–14). Other transition-metal salts, such as Pd(OAc)$_2$ or Cu(OAc)$_2$, could not afford the desired product

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



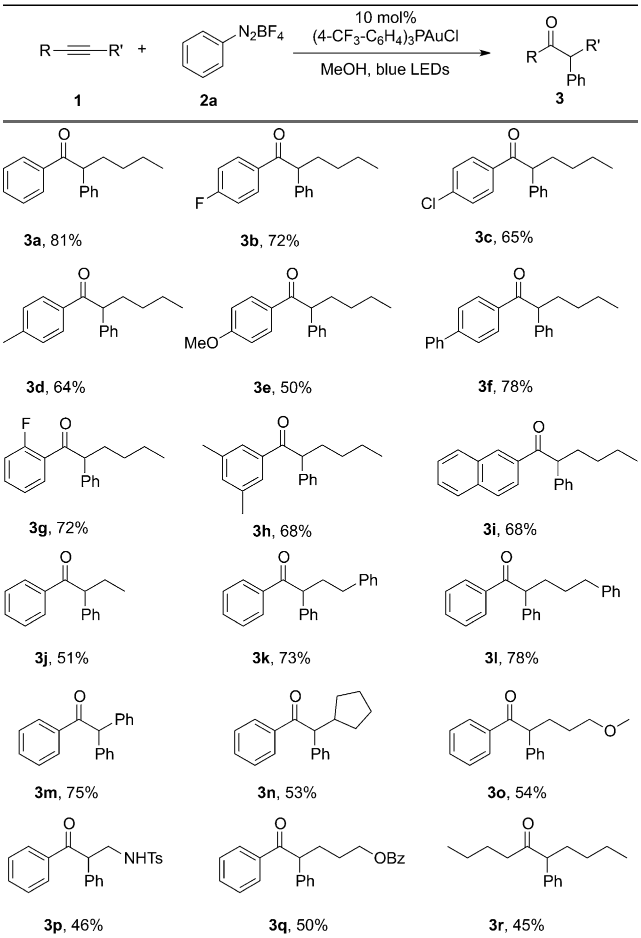
Entry	Photocatalyst (5 mol%)	Light source	Au (10 mol%)	Additive	Yield of **3a**[b,c]	Ratio **3a/3a′**
1	[Ru(bpy)$_3$]Cl$_2$·6H$_2$O	UVA	Ph$_3$PAuCl	–	27%	5:1
2	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	UVA	Ph$_3$PAuCl	–	57%	9:1
3	[Au$_2$(μ-dppm)$_2$]Cl$_2$	UVA	Ph$_3$PAuCl	–	47%	4:1
4	[Au$_2$(μ-dppm)$_2$](NTf$_2$)$_2$	UVA	Ph$_3$PAuCl	–	65%	11:1
5	–	UVA	–	–	–	–
6	[Au$_2$(μ-dppm)$_2$](NTf$_2$)$_2$	UVA	–	–	trace	–
7	–	UVA	Ph$_3$PAuCl	–	76%	14:1
8	–	–	Ph$_3$PAuCl	–	–	–
9	–	20 W CFL	Ph$_3$PAuCl	–	9%	6:1
10	–	blue LEDs	Ph$_3$PAuCl	–	79%	>20:1
11	–	sunlight	Ph$_3$PAuCl	–	71%	16:1
12	–	blue LEDs	Ph$_3$PAuCl	Na$_2$CO$_3$	trace	–
13	–	blue LEDs	Ph$_3$PAuCl	NaOMe	62%	6:1
14	–	blue LEDs	Ph$_3$PAuCl	MsOH	71%	>20:1
15	–	blue LEDs	Pd(OAc)$_2$	–	–	–
16	–	blue LEDs	Cu(OAc)$_2$	–	–	–
17	–	blue LEDs	(4-CH$_3$C$_6$H$_4$)$_3$PAuCl	–	71%	13:1
18	–	blue LEDs	(4-FC$_6$H$_4$)$_3$PAuCl	–	83%	16:1
19	–	blue LEDs	(4-CF$_3$C$_6$H$_4$)$_3$PAuCl	–	87% (81%)	15:1
20	–	blue LEDs	AuCl	–	trace	–
21[d]	–	blue LEDs	Ph$_3$PAuCl	–	–	–

[a] Reaction conditions: 1-Phenyl-1-hexyne (**1a**, 0.1 mmol), phenyldiazonium salt **2a** (0.4 mmol), photocatalyst (5 mol%), and gold catalyst (10 mol%) in MeOH (0.25 mL) were reacted at room temperature under irradiation with various light sources. [b] The yields and ratios were determined by 1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as the internal standard. [c] Yield of isolated product given in parentheses. [d] Ph$_2$IOTf was used instead of **2a**.

(entries 15 and 16). Variations of the ligand at the gold center revealed that electron-poor ligands provided better results. The yield of **3a** improved to 87% with $(4\text{-}CF_3C_6H_4)_3P$, whereas the electron-rich ligand $(4\text{-}CH_3C_6H_4)_3P$ gave the worst result (entries 17–19). When simple AuCl was employed, only a trace amount of the product was observed (entry 20). Finally, diphenyliodonium triflate was tested as the aryl source as well, but no reaction was observed (entry 21).

Under the optimized reaction conditions (Table 1, entry 19), we next examined the scope of the difunctionalization reaction with respect to the alkyne substrate. As shown in Table 2, 1-aryl-1-hexynes with various substituents on the aryl ring underwent the difunctionalization smoothly, affording the desired α-aryl ketones **3a**–**3i** in moderate to good yields, independent of their electronic nature. Encouraged by these results, we further explored the scope of this transformation by using a series of alkynes bearing different R′ groups. Different alkyl, cycloalkyl, and aryl substituents were examined first, and the corresponding α-aryl ketones **3j**–**3n** were formed in 51–75% yield. Remarkably, this method also exhibits good functional-group tolerance without affecting a methyl ether, benzoyl ether, or sulfonamide, providing **3o**–**3q** in 46–54% yield. Encouraged by these results, we extended this catalytic process to 5-decyne; the arylation was successful, and afforded the product **3r** in 45% yield.

Table 2: Reaction scope with respect to various alkynes.[a]

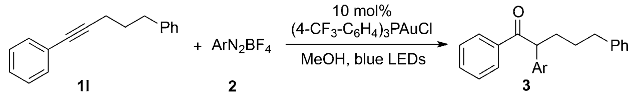


3a, 81% **3b**, 72% **3c**, 65%
3d, 64% **3e**, 50% **3f**, 78%
3g, 72% **3h**, 68% **3i**, 68%
3j, 51% **3k**, 73% **3l**, 78%
3m, 75% **3n**, 53% **3o**, 54%
3p, 46% **3q**, 50% **3r**, 45%

[a] All reactions were carried out using **1** (0.2 mmol) and **2a** (0.8 mmol) in the presence of 10 mol% $(4\text{-}CF_3C_6H_4)_3PAuCl$ in MeOH (0.5 mL).

We then turned our attention to the use of various aryl diazonium salts **2b**–**2i** in combination with alkyne **1l** under the standard reaction conditions (Table 3). With 4-methylphenyldiazonium tetrafluoroborate and 4-*tert*-butylphenyldiazonium tetrafluoroborate, the difunctionalized products **3s** and **3t** were obtained in 61% and 40% yield, respectively (entries 1 and 2). A variety of functional groups attached to the aromatic ring of the aryl diazonium substrate, namely fluoro, chloro, bromo, and ester moieties, were also tolerated, providing α-aryl ketones **3u**–**3x** in moderate yields (entries 3–6). Among the tested starting materials, 4-trifluoromethylphenyldiazonium tetrafluoroborate failed to produce any product, probably because of its tendency to decompose (entry 7). The aryl diazonium salt with a methyl substituent at the *meta* position produced **3z** in 65% yield (entry 8).

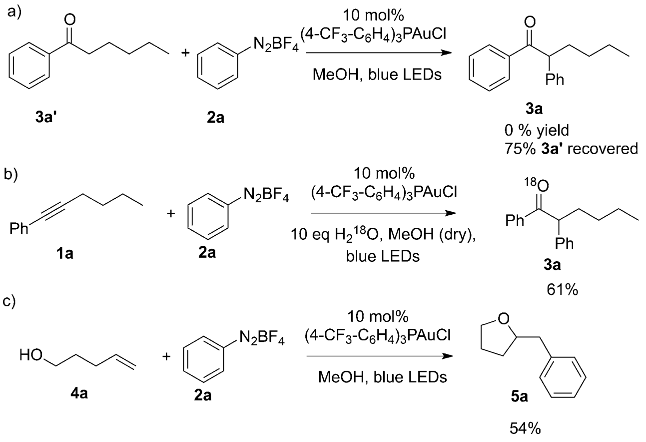
Table 3: Reaction scope with respect to various aryl diazonium tetrafluoroborate salts.[a]



Entry	Aryl diazonium salt	Product	Yield [%]
1	$4\text{-}CH_3C_6H_4$, **2b**	**3s**	61
2	$4\text{-}t\mathrm{Bu}C_6H_4$, **2c**	**3t**	40
3	$4\text{-}FC_6H_4$, **2d**	**3u**	61
4	$4\text{-}ClC_6H_4$, **2e**	**3v**	41
5	$4\text{-}BrC_6H_4$, **2f**	**3w**	55
6	$4\text{-}(CO_2Me)C_6H_4$, **2g**	**3x**	57
7	$4\text{-}CF_3C_6H_4$, **2h**	**3y**	–
8	$3\text{-}CH_3C_6H_4$, **2i**	**3z**	65

[a] All reactions were carried out using **1l** (0.2 mmol) and **2** (0.8 mmol) in the presence of $(4\text{-}CF_3C_6H_4)_3PAuCl$ (10 mol%) in MeOH (0.5 mL).

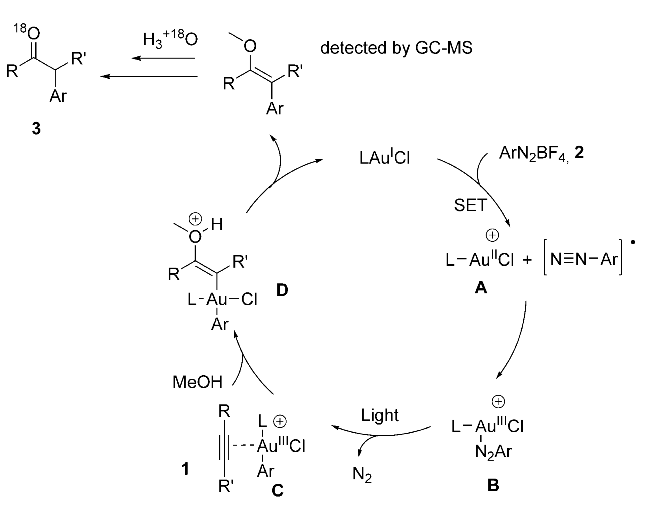
A recent report showed that the α-arylation of carbonyl compounds can be enabled through a radical process.[1k] To exclude the possibility that our transformation proceeds by hydration followed by ketone arylation, we examined the reaction of **3a′** with phenyldiazonium tetrafluoroborate **2a** under the standard reaction conditions, but α-aryl ketone **3a** was not obtained (Scheme 3a). During the optimization studies, we had observed the formation of an arylated enol ether by GC-MS analysis, which is believed to be transformed into the corresponding ketal upon hydrolysis to produce the final product. To gain insight into the reaction mechanism, we thus further investigated the reaction by isotope labeling experiments. With $H_2{}^{18}O$ (10 equiv) as an additive, the ^{18}O-labeled α-aryl ketone **3a** was obtained in 61% yield under the standard reaction conditions (Scheme 3b). The reduced yield was attributed to the decomposition of phenyldiazonium tetrafluoroborate in the presence of excess water. In a previous report,[6d] a dual Au and photoredox catalytic system was used for the intramolecular oxyarylation of alkenes with aryl diazonium salts. The photocatalyst was claimed to be essential in these reactions for the generation of an electro-



Scheme 3. Mechanistic investigation.

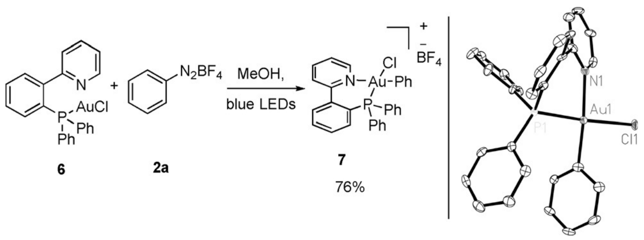
philic aryl gold(III) species by a photoredox process. Even in the absence of a photocatalyst under our optimized reaction conditions, the reaction of 4-penten-1-ol (**4a**) with phenyldiazonium salt **2a** provided tetrahydrofuran **5a** in 54% yield. This finding underlines that these types of reactions can be performed in the absence of a photocatalyst (Scheme 3c).[6e] The UV/Vis absorption spectrum of (4-CF$_3$C$_6$H$_4$)$_3$PAuCl showed a very weak absorption band at 450 nm ($\varepsilon = 17$), which excludes the possibility of (4-CF$_3$C$_6$H$_4$)$_3$PAuCl being a photosensitizer itself. A light on/off experiment showed that the transformation required continuous irradiation with blue LEDs (see the Supporting Information), excluding the possibility that an efficient radical-chain propagation mechanism is operating.

Based on this experimental evidence in combination with literature reports,[7,9] a highly speculative mechanism that accounts for the α-aryl ketone synthesis is depicted in Scheme 4. We assume that the reaction is initiated by gold-induced single electron transfer (SET) to the aryl diazonium salt, generating an aryl diazo radical and gold(II) species **A**. Then, the phenyldiazonium radical recombines with the gold(II) center, which oxidizes the latter to gold(III) species **B**. However, the direct addition of the diazonium species to the gold(I) center is also conceivable. Efforts to isolate this species failed as it is too sensitive. Then, assisted by light irradiation, N$_2$ is extruded, and the aryl gold(III) species **C** is formed. In the next step, methanol adds to the π-activated alkyne to form vinyl gold species **D**. Reductive elimination then provides arylated enol ether **E**, which delivers the final products upon hydrolysis. Methanol as the solvent might also play a crucial role in the reaction mechanism. It has been reported that under basic conditions, aryl diazonium salts can form azo ethers that absorb light in the visible range.[10] The observation of these species as key intermediates in photocatalyzed reactions was recently reported by Rueping and coworkers for a titanium dioxide catalyzed C–H arylation of heteroarenes.[11] However, despite the fact that these species might also be formed in the gold-catalyzed process, their role in the reaction remains unclear.



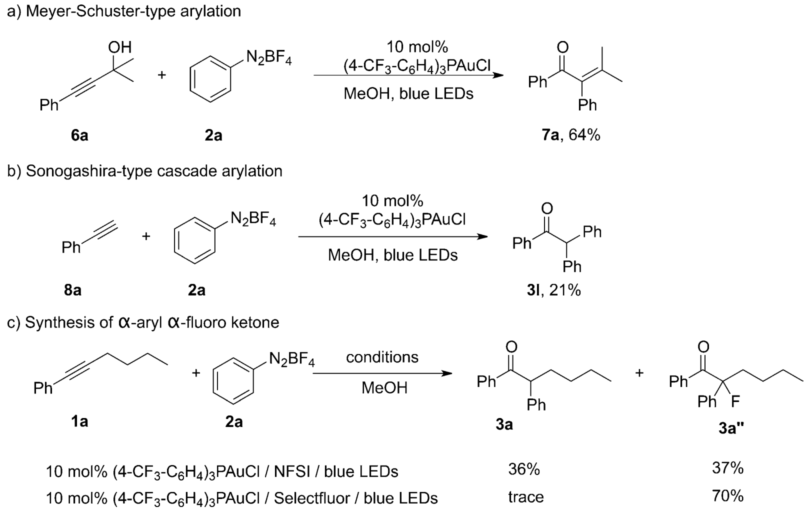
Scheme 4. Proposed mechanism.

Attempts to isolate intermediates directly from the catalytic reactions failed. Therefore, we used P,N-bidentate ligands as alternatives that can improve the thermal stability of transition-metal complexes.[12] The stoichiometric reaction between pyridine phosphine gold(I) complex **6** and phenyldiazonium tetrafluoroborate (**2a**) provided the stabilized chelated gold(III) complex **7** in 76% yield. The structure of **7** was confirmed unequivocally by X-ray crystallography[13] (Scheme 5, right). Compared to previously reported procedures, which are based on the combination of oxidative addition and transmetalation under harsh conditions,[14] this is a rather facile and efficient way to synthesize aryl gold(III) complexes from gold(I) precursors. Moreover, it is the first direct experimental evidence of a gold(III) species being formed in gold-mediated reactions with aryl diazonium salts.



Scheme 5. Synthesis of the P,N-chelate-stabilized gold(III) complex by direct oxidative addition of the phenyldiazonium salt to gold.

Next, we explored further applications of this light-assisted gold-catalyzed intermolecular arylation step. Under the standard reaction conditions, propargylic alcohol **6a** was converted into the α-arylated, α,β-unsaturated carbonyl compound **7a** in 64% yield (Scheme 6a). This reaction can be rationalized by a Meyer–Schuster rearrangement[15] that is enabled by the electrophilic aryl Au$^{\text{III}}$ intermediate acting as the catalyst followed by reductive elimination to form the additional C–C bond. On the basis of a previous report on gold(III)-catalyzed Sonogashira-type cross-coupling reactions,[4c] we next envisioned the development of a tandem reaction that involves a cross-coupling reaction followed by the difunctionalization using a terminal alkyne as the starting



Scheme 6. Combining the arylation strategy with other reactions.

material. When the reaction of phenylacetylene (**8a**) with 5 equiv **2a** was performed in MeOH under irradiation with blue LEDs at room temperature for 18 hours, **3l** was isolated in 21% yield (Scheme 6b). In good agreement with the results obtained by the Hammond group,[4e] the addition of an electrophilic fluorinating reagent (NFSI or Selectfluor) delivered the trifunctionalized product **3a**′′ in yields of up to 70% (with Selectfluor as the fluorinating agent; Scheme 6c).

In conclusion, the difunctionalization of alkynes with aryl diazonium tetrafluoroborate derivatives as the aryl source to afford α-aryl ketones in moderate to good yields under very mild reaction conditions can be achieved by the use of mononuclear gold(I) catalysts only. Explorative experiments indicate that this method will enable the future development of a number of synthetically useful[16] tandem and cascade reactions that transform readily available alkynes into α-aryl ketones and their derivatives. While further investigations of the reaction mechanism are ongoing, initial results suggest that this reaction is a rare example of gold(I)/gold(III) redox catalysis without the need for a photosensitizer or external oxidants.

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