Chapter 2
Dual Gold and Visible Light Photoredox-Catalyzed Heteroarylations of Non-activated Alkenes

2.1 Introduction

2.1.1 General Properties of Homogeneous Gold Catalysts

Gold (Au) is a third row noble transition metal belonging to group 11 of the periodic table and is situated below silver in the coinage metal series. Gold with the ground state electronic configuration $[Xe]4f^{14}5d^{10}6s^1$ has highest first ionization potential ($E^0_{Au(I)/Au(0)}$ = +1.69 V vs. SHE) among d-block elements, due to the relativistic contraction of 6s atomic orbital [1]. As a consequence, elemental gold is very stable in the presence of air and moisture and was long thought to be inactive to perform chemical reactions. Among possible oxidation states (−I to +V), Au(I) and Au(III) species are stable, existing as salts or complexes, while Au(II) is generally unstable and easily undergoes disproportionation to Au(I) and Au(III). In the presence of a strong oxidant, Au(I) can be oxidized to Au(III) ($E^0_{Au(III)/Au(I)}$ = +1.41 V vs. SHE) [1]. Some commercially available Au(I) and Au(III) precursors are listed in Fig. 2.1. In general for catalysis, gold(I) complexes are often employed along with a co-catalyst silver(I) salt with an appropriate, non-coordinating counter-anion is added to the reaction mixture to abstract a halide from the gold center, creating a vacant coordination site accessible to the substrates for binding. In 2005, Gagosz and co-workers developed air stable cationic (phosphine)gold(I) complexes with a loosely bound NTf_2 anion which easily dissociates in solution [2].

The cationic gold(I) complex $[LAu]^+$ (i.e. L = neutral, ligand e.g. a phosphine or NHC) thus generated is most often employed as a highly efficient carbophilic π-Lewis acid catalyst capable of activating carbon-carbon multiple bonds. The π-activation of multiple bonds can be attributed to the strong in-plane σ-donation

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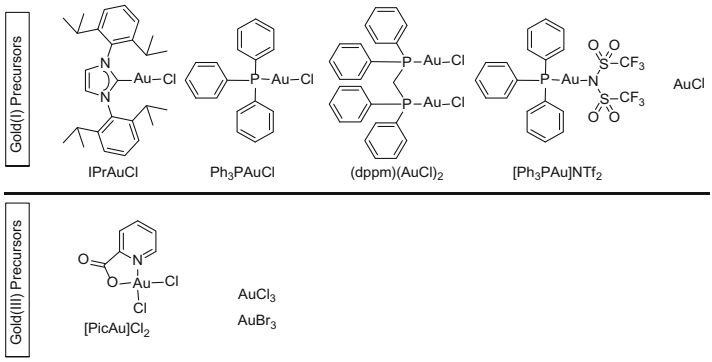


Fig. 2.1 Some common commercially-available Au(I) and Au(III) precursors

from the substrate π-orbital onto the metal [π(alkyne) → d(Au)] with a comparatively weak back-bonding interaction from the gold to the substrate π*-orbital [π*(alkyne) ← d(Au)]. With alkyne substrates, which have an additional out-of-plane double bond, further weak π(alkyne) → d(Au) bonding and π*(alkyne) ← d(Au) back-bonding interactions are possible [3, 4]. Due to the stronger σ-acceptance compared to π-back donation [3, 4], overall charge density in the ligated alkyne/alkene is reduced and electrophilicity is enhanced. The predominance of carbophilic behavior observed with soft LAu^+ species can be rationalized by the fact that it forms kinetically more labile complexes with hard basic heteroatoms (e.g. O and N) [5]. Due to the high redox potential of the Au(I)/Au(III) couple ($E_{1/2}$[Au(III)/Au(I)] = +1.41 V vs. SHE) [1], LAu^+-catalyzed reactions can be conducted under aerobic conditions and no undesired redox processes hamper the desired reactivity. As a result, a wide spectrum of functional groups are tolerated in these types of reactions [5]. Alongside alkynes, this activation approach can be extended to organic substrates containing π-system such as allenes and alkenes [5].

Since the last decade of the twentieth century, a significant amount of interest has been devoted to the development of highly emissive luminescent gold(III) complexes [6, 7], which can absorb photons in visible range of spectrum, and recently some polypyridyl gold(III) complexes have been shown to participate in visible light photoredox catalysis [8]. However, the vast majority of organic reactions are catalyzed by gold(I) complexes rather than gold(III) complexes and the absorption abilities of mononuclear gold(I) complexes (e.g. Ph_3PAuCl, Et_3PAuCl or Me_3PAuCl), and coordinatively-saturated bimetallic gold(I) complexes [e.g. $(dppm)_2(AuCl)_2$, dppm = 1,1-bis(diphenylphosphino)methane] are usually confined to the UV range of the spectrum [9–12]. This phenomenon limits their applications in visible light induced gold-catalyzed organic transformations [11, 13, 14].

2.1.2 Gold-Catalyzed Organic Transformations

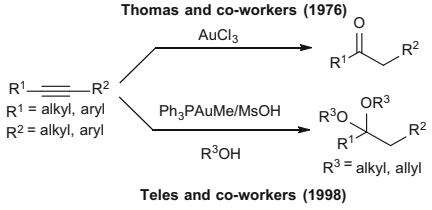
2.1.2.1 Historical Background

Over the last several years, gold catalysis has played an outstanding role in various areas of chemistry [4, 5, 15–32]. $AuCl_3$-catalyzed hydration of alkynes to ketones reported by Thomas and co-workers in 1976 was one of the earliest reports on gold catalysis (Scheme 2.1) [33]. However, the real breakthrough in gold(I) catalysis was made by a group of scientists in BASF in 1998, who developed a highly efficient (phosphine)gold(I)-catalyzed method for the addition of alcohols onto alkynes with very high TON and TOF replacing toxic mercury(II) catalysts (Scheme 2.1) [34].

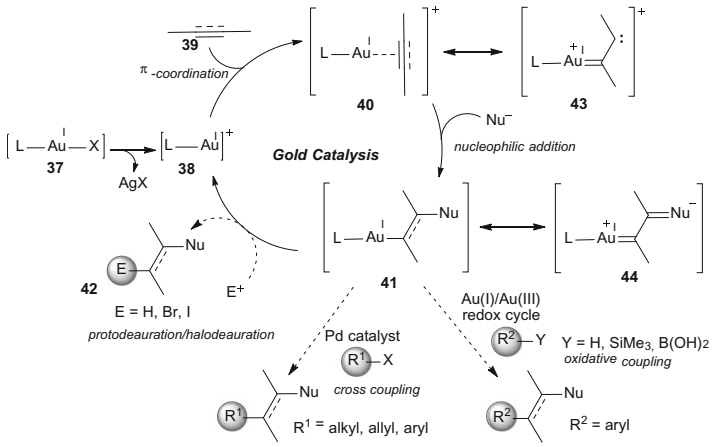
Since then, this field has been explored enormously with highly efficient and stable gold(I) (pre)catalysts being applied [17, 35, 36] to access synthetically important reactivity and mechanistic insight [18, 21, 28, 30, 31]. The compatibility of gold catalysis with other reagents has also been extensively explored and studies devoted to extending the scope of these reactions beyond their current limitations, such as overcoming protodeauration, have been conducted [23, 24, 27, 37]. Novel methodologies exploring many aspects of the chemistry of gold continue to be reported at a fast rate [5, 25, 26, 38], including applications in asymmetric catalysis [20, 32, 39, 40] and natural product synthesis [29].

2.1.2.2 Difunctionalizations of Carbon–Carbon Multiple Bonds: Mechanistic Hypothesis

Gold(I)-catalyzed nucleophilic addition type reactions have emerged as an enabling technology for selective difunctionalizations of alkynes, allenes and alkene substrates. A general mechanistic scenario for these transformations exemplified for alkynes is shown in Scheme 2.2 [16]. In an initial step, commercially available or self-prepared gold(I) complexes of the form [LAuX] (**37**) (L = neutral ligand, e.g. phosphine, NHC and X = charged ligand, e.g. Cl, Br) loses its charged ligand (X) in the presence of a scavenger (e.g. Ag^+) to generate the catalytically-active cationic species $[LAu]^+$ (**38**). This cationic species $[LAu]^+$ (**38**) then enters the catalytic cycle and coordinates to an alkyne (**39**), generating the alkyne-ligated gold (I) intermediate **40** and activating it towards an internal or external nucleophile. The



Scheme 2.1 Early examples of gold catalysis: hydration of alkynes and addition of alcohols onto alkynes [33, 34]



Scheme 2.2 General mechanistic cycle of Au(I)-catalyzed difunctionalization of carbon-carbon multiple bonds [5]

addition of the nucleophile results in the alkenylgold intermediate **41**, which is then quenched in the presence of an electrophile releasing the product **42** and regenerating the cationic species $[LAu]^+$ (**38**). In a different scenario, the alkyne bound to Au(I) in the coordination sphere of intermediates **40** and **41** could behave as *vic*-dicarbene synthons **43** and **44,** respectively, and their great potential in synthesis has been explored over the last few years [5]. It is worth mentioning that allenes and alkenes can be activated in a similar manner, resulting in vinylgold(I) and alkylgold (I) intermediates respectively.

In the vast majority of the cases, the alkenylgold intermediate **41** undergoes protodeauration releasing hydrofunctionalized products, while in a few cases, halonium ions (I^+, Br^+) have been used to quench the alkenylgold intermediate **41** delivering halofuntionalized products [41–43].

Hydrofunctionalizations of alkynes, allenes and to some extent alkenes, undoubtedly, deserve an important position among gold-catalyzed organic transformations and many impressive reactions based on these processes have enriched the library of synthetic organic chemistry [4, 5, 15, 16, 18, 22, 25, 31]. However, in many cases, rapid protodeauration limits the synthetic potential of gold catalysis. In this regard, organic chemists have invested significant efforts to develop alternative routes for the decomplexation of organogold intermediates which can compete with the protodeauration pathway.

One inspiring approach was the use of dual metal catalytic systems where organogold intermediates obtained under redox-neutral gold catalysis hand over organic fragments to other metals through transmetallation process (see Section "Organogold Reactivity in Dual Metal Catalysis") [23].

Another approach that has captured the attention of researchers is oxidative coupling strategy, where organogold intermediates obtained under redox-neutral gold catalysis conditions take part in an oxidative coupling step delivering

complex products (see Section "Nucleophilic Addition/Rearrangement-Oxidative Coupling") [24, 27, 37].

Organogold Reactivity in Dual Metal Catalysis

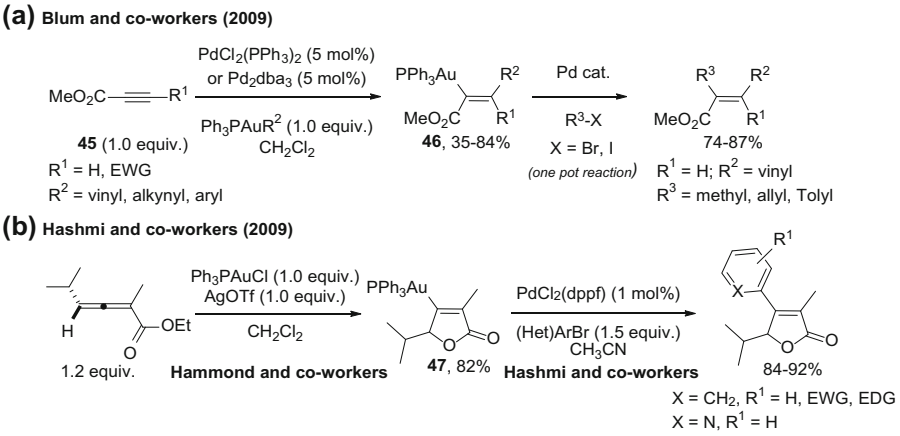
Over the past decades, dual catalysis has become a powerful tool in organic synthesis. The concept of combining two privileged catalytic activation modes together to promote a single transformation, which is not possible in the presence of either catalyst alone, has recently captured the attention of synthetic chemists [44, 45]. In the field of transition metal catalysis, transmetallation is a common step involved in most cross-coupling reactions. There has been a huge progress of developing efficient transmetallating reagents such as organo-magnesium, tin, boron, zinc, silicon, lithium, etc., which have been applied in many famous metal-catalyzed cross-coupling and other reactions (Table 2.1).

In gold catalysis, most of the reactions proceed via alkenylgold intermediates (for alkynes and allenes) or alkylgold intermediates (alkenes), being involved in one of the steps in catalytic cycle. To extend the scope of gold catalysis beyond protodeauration, a group of scientists, including Blum, Hashmi and others have been interested in using in situ generated organogold intermediates in other transition metal-catalyzed processes, mostly in cross-coupling type reactions, as potential transmetallating agents in either a stoichiometric or catalytic manner [23, 46–49]. A seminal report [41] on stable alkenylgold intermediate isolation from Hammond and co-workers in 2008 has enhanced the interest of organic chemists more in this line of research.

In 2009, Blum and co-workers reported the method for the carboauration of alkynes **45** catalyzed by palladium to generate alkenylgold intermediates **46**, which could be subsequently used in palladium-catalyzed cross-coupling chemistry (Scheme 2.3a) [47]. In the same year, Hashmi and co-workers also developed a protocol for cross-coupling reactions with a catalytic amount of palladium and stoichiometric amounts of stable alkenylgold intermediates (Scheme 2.3b) [46]. One set of organogold intermediates **47** used in this study were prepared according to the procedure previously developed by Hammond and co-workers in 2008 [41]. Moreover, Blum and co-workers also reported a carboauration with palladium

Table 2.1 Organometallic reagents used in related cross-coupling reactions

Organometallic reagent	Cross-coupling reaction
R–MgX	Kumada coupling
R–**Sn**	Migita-Kosugi-Stille coupling
R–**B**	Suzuki-Miyaura coupling
R–**Zn**	Negishi coupling
R–**Si**	Hiyama coupling
R–**Cu**	Sonogashira-Hagihara coupling
R–**Au**	??



Scheme 2.3 Palladium-catalyzed cross-coupling reactions of organogold reagents [46, 47]

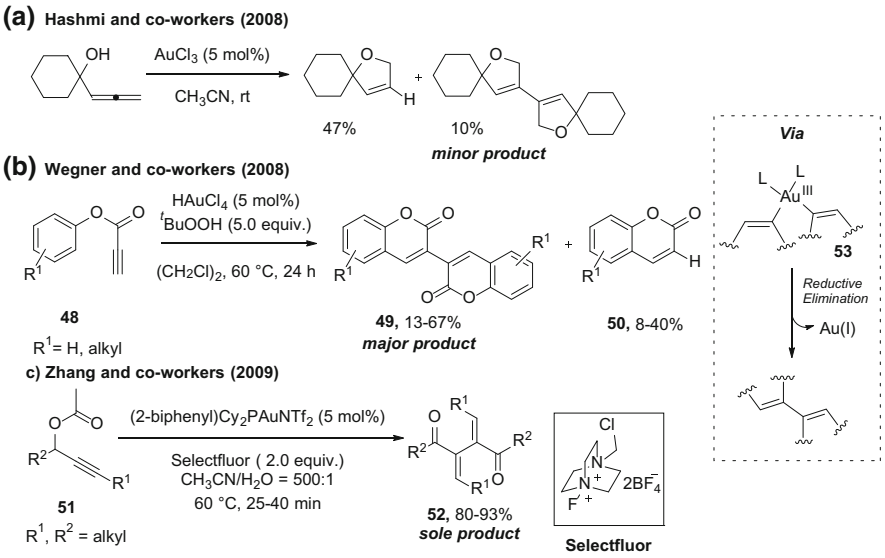
catalysis [47]. In addition to palladium catalysis, organogold intermediates have also been applied in nickel-catalyzed cross-coupling reactions as transmetallating reagents [49].

Although significant contributions have been made to the development of novel organic transformations using dual metal systems with gold and other transition metals, the vast majority of them reported to date are limited to the use of stoichiometric amount of gold [23]. Another limitation is that, in the cases where the other transition metal catalysts (e.g. Ni and Pd) can react via single electron transfer, the substrate scope of the reaction is somewhat limited to compounds, which undergo fast oxidative addition as alternative competing deactivation pathways resulting in the reduction of organogold(I) intermediates to inactive gold(0) can otherwise occur [23]. Another serious concern is the choice of an appropriate ligand, which is crucial to avoid the poisoning of the gold catalysts via the formation of coordinatively-saturated gold complexes (e.g. $[Ph_3P\text{-}Au\text{-}PPh_3]^+$) through ligand exchange between gold and another metal catalyst [23].

Nucleophilic Addition/Rearrangement-Oxidative Coupling

Cascade difunctionalization processes constitute a new class of gold-catalyzed organic transformations, where a carbon–carbon or heteroatom-carbon bond formation generated upon nucleophilic addition onto a carbon–carbon multiple bond activated by gold is accompanied by the formation of a new carbon–carbon or heteroatom-carbon bond under oxidative conditions [24, 27, 37].

An interesting observation by Hashmi and co-workers in early 2008 of a Au(III)-mediated oxidative coupling of vinyl gold intermediates derived from allenyl carbinols upon cyclization disclosed the concept of gold mediated cascade nucleophilic addition oxidative coupling for the first time (Scheme 2.4a) [50]. In late



Scheme 2.4 Au-mediated/catalyzed oxidative coupling reactions of allenes and alkynes [50–52]

2008, Wegner and co-workers reported the first catalytic version of this type of oxidative coupling reaction, where cyclization-oxidative dimerization of arylpropionic esters **48** with $HAuCl_4$ (5 mol%) afforded dicoumarin derivatives **49** (13–67 %) in the presence of the oxidant ^{t}BuOOH (5.0 equiv.) (Scheme 2.4b) [51]. Unfortunately, they could not suppress the competitive protodeauration pathway leading to coumarin **50** formation. Thereby, gold-catalyzed oxidative coupling reactions remained challenging to the scientific community until 2009 when Zhang and co-workers successfully developed a catalytic cascade method for the rearrangement-oxidative homocoupling of propargylic acetates **51** to (*E,E*)-dienones **52** in the presence of (2-biphenyl)$Cy_2PAuNTf_2$ (5 mol%) and 2.0 equiv. of Selectfluor as an oxidant at 60 °C in a mixture of acetonitrile and water (500:1, Scheme 2.4c) [52]. In all the above cases, the homocoupled products are generated upon reductive elimination from a gold(III) intermediate **53**. In 2009 prior to homocouling report, Zhang and co-workers described an exciting oxidative gold catalyzed cross coupling of propargylic acetates with arylboronic acids furnishing α-arylated enones [53].

Since then, over the last six years, the versatility of this novel approach has been exploited in many impressive organic transformations, particularly cascade nucleophilic addition-oxidative cross-coupling processes for the difunctionalization of multiple bonds. Although alkynes and allenes have been used in most of these transformations, alkenes have also been successfully employed [24, 27, 37].

Oxidative gold catalysis is an indispensable tool for the difunctionalization of alkenes where nucleophilic addition-carboauration of C=C bond results in an alkylgold intermediate forming a C(sp^3)–Au bond which then reacts with an aryl

precursor (arylboronic acid, arylsilane or simple arene) under oxidative conditions to release an alkylated arene product via C(sp^3)–C(sp^2) bond formation. It is worth mentioning that alternative well-established palladium-catalyzed reactions of this type typically suffer from side-reactions involving competitive β-hydride elimination of an alkylpalladium intermediate. This elementary step is not favoured with gold catalysts.

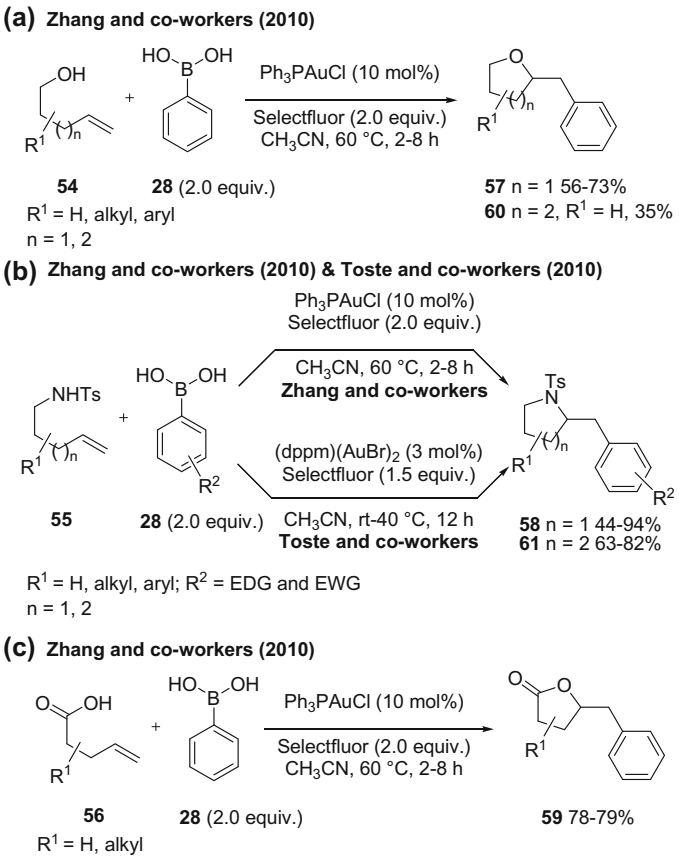
In 2010, Zhang and co-workers reported heteroarylations of non-activated alkenes in an intramolecular fashion, where 4-penten-1-ol **54** was treated with phenylboronic acid **28** (2.0 equiv.) as an aryl precursor in the presence of a privileged gold catalyst (triphenylphosphine)gold(I) chloride (Ph_3PAuCl, 10 mol%) and an exogenous oxidant, Selectfluor (2.0 equiv.) in acetonitrile at 70 °C to deliver the oxyarylated product, 2-benzyl tetrahydrofuran **57** (Scheme 2.5a) [54]. In order to show the broad scope of the developed method, the reactions were performed with different alkene substrates **54–56** with γ-hydroxy, γ-tosyl amine and β-carboxylic acid groups as nucleophiles and also longer tethers between the nucleophile and the alkene to afford the desired 2-benzyl substituted tetrahydrofurans **57**, pyrrolidines **58**, lactones **59** and six membered 2-benzyl substituted tetrahydropyrans **60** and pyrimidines **61** respectively in moderate to excellent yields (Scheme 2.5).

In the same year, Toste and co-workers also reported similar aminoarylations of non-activated alkenes under slightly different reaction conditions (Scheme 2.5b).

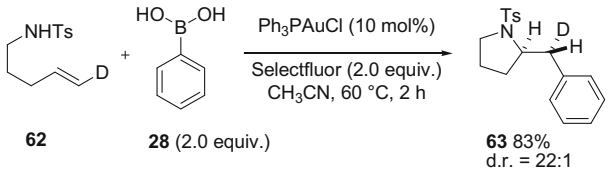
In contrast to Zhang's reaction conditions, they employed a lower amount of oxidant (1.5 equiv.), lower temperature (rt-40 °C) and a slightly lower catalyst loading of a bimetallic phosphinegold complex $(dppm)(AuBr)_2$ (3 mol%, dppm = 1,1-bis(diphenylphosphino-methane)), which was found to be the best catalyst for these studies [55]. The preference for bimetallic gold catalysts was thought to be based on beneficial aurophilic stabilization of Au(III) through Au^{III}–Au^{I} interactions [56].

For the mechanistic illustration of the developed gold-catalyzed intramolecular aminoarylation of alkene, Toste and co-workers and other research groups performed some theoretical calculations and control experiments to identify the intermediates and also the sequence of steps involved in the catalytic cycle [55–57]. In a study focused on elucidating the stereochemical arrangement of the amino and aryl groups in the final products **58**, the deuterium labelled γ-aminoalkene substrate **62** was reacted under the standard conditions. This reaction delivered the expected pyrrolidine product **63** in high diastereoselectivity with conformational analysis of the ^{1}H NMR spectrum revealing that the amino and aryl groups were in an *anti*-orientation (Scheme 2.6) [54].

Based on the mechanistic studies by means of theoretical calculations and control experiments, a general plausible reaction mechanism is shown in Scheme 2.7 [54–57]. In an initial step, the neutral linear gold catalyst [LAuX] gets oxidized to the square planner gold(III) intermediate **A** by the F^+ oxidant, selectfluor. At this point, coordination of the gold(III) metal center to the alkene is followed by a nucleophilic attack onto the activated alkene **55** to obtain intermediate **B**. In next step, aryl group transfer from the arylboronic acid to the

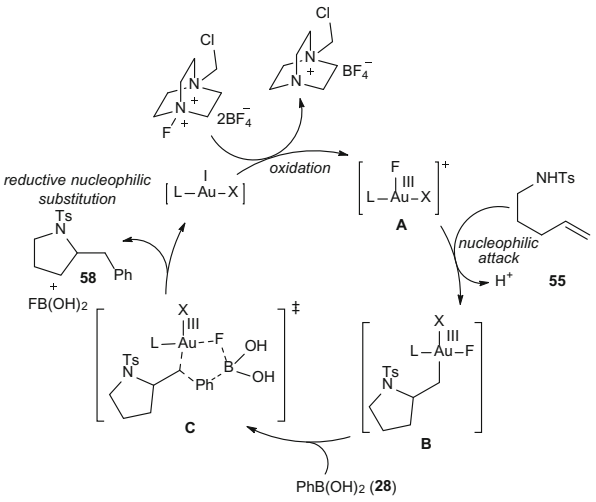


Scheme 2.5 Oxidative gold-catalyzed intramolecular heteroarylation of non-activated alkenes [54, 55]



Scheme 2.6 Aminoarylation of deuterium labelled γ-aminoalkene under Zhang's reaction conditions [54]

sp^3-hybridized carbon attached to Au(III) in a concerted five membered transition state assisted by the fluoride ion bound to Au(III) in intermediate **C** gives rise to the heteroarylation product **58**. The *anti*-relationship of nucleophile and aryl groups could be explained by *syn*-nucleophilic-auration of the C=C bond followed by S_N2

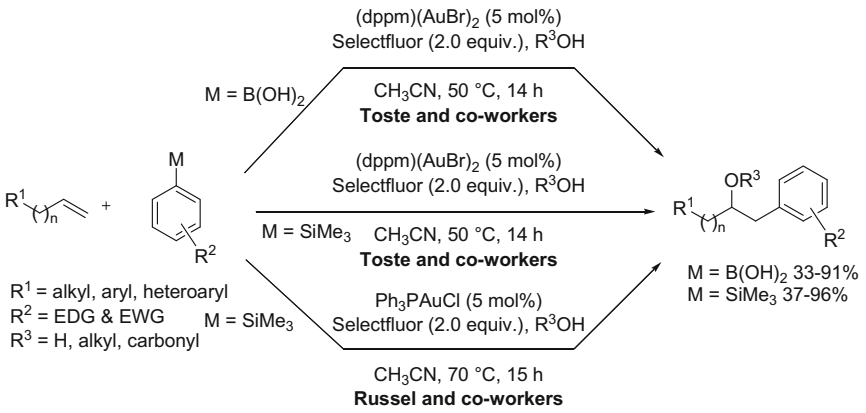


Scheme 2.7 Proposed mechanism for the gold-catalyzed heteroarylation of non-activated alkenes [54–56]

type aryl transfer with inversion of configuration assisted by the fluoride ligand bound to the Au(III) activating the boron center of the boronic acid. An alternative possibility is *anti*-aminoauration of the alkene followed by transmetallation-reductive elimination or a S_Ni-type substitution mechanism.

To show the versatility of this approach, Toste and co-workers extended this reactivity to relatively more difficult selective three component intermolecular oxyarylations of terminal alkenes using arylboronic acids as aryl precursors (Scheme 2.8) [58]. However, all these methods where arylboronic acids were used as aryl precursors suffer from oxygen and nitrogen based functional groups tolerance on the aryl rings. To solve this problem, Toste and co-workers and Russell and co-workers independently developed methods where easily synthesized arylsilanes were successfully employed in place of arylboronic acids (Scheme 2.8) [59, 60]. The next advancement in this strategy was accomplished by Gouverneur and co-workers and Nevado and co-workers using simple arenes as potential aryl precursors in intramolecular processes [61, 62].

This strategy for difunctionalizations of alkenes suffers from some serious limitations such as a lack of substrate scope. For example, electron rich alkene substrates (e.g. styrenes) and boronic acids featuring electron rich substituents (e.g. oxygen, nitrogen substituents) on the aryl ring are not well tolerated under the harsh oxidative reaction conditions implicit to the use of the very strong oxidant, Selectfluor. Moreover, these methods have been so far limited to mono-substituted terminal alkenes.



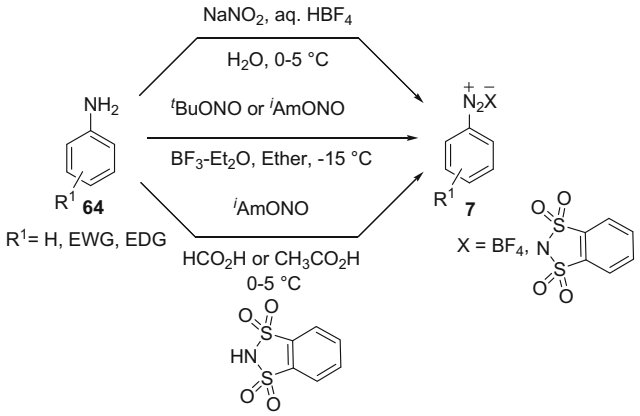
Scheme 2.8 Oxidative gold-catalyzed intermolecular oxyarylation of non-activated alkenes [58–60]

2.1.3 Aryldiazonium Salts: Synthesis and Reactivity

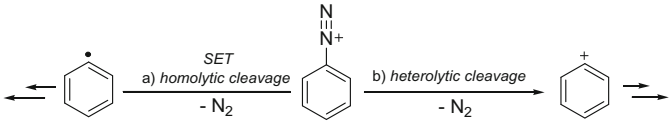
Aryldiazonium salts are attractive reactants used in different fields of chemistry, such as nucleophilic aromatic substitution reactions [63], transition metal catalysis as alternatives to aryl halides and aryl triflates [64], material chemistry for surface modification [65] and most importantly, radical chemistry [66] as excellent aryl radical sources. The chemistry of diazonium salts benefits from (a) very easy preparation, even in large scale, (b) typically high chemoselectivity in cross-coupling reactions due to their superior reactivity compared to aryl halides, (c) ambient reaction conditions and (d) easy removal of a gaseous leaving group (nitrogen gas) without interfering reaction components [67].

Aryldiazonium salts **7** can be prepared from commercially available anilines **64** in an aqueous medium with sodium nitrite and a strong acid (e.g. HBF_4) (Scheme 2.9) [68]. In organic solvents (Et_2O, DME or THF), aryldiazonium salts are prepared using organic nitrites (^tBuONO or ^iAmONO) and BF_3-Et_2O (Scheme 2.9) [69]. The stability of the aryldiazonium salts can be tuned by choosing an appropriate counteranion, such as the *o*-benzenedisulphonimide anion, which results in a high degree of stabilization and can be reused [70]. In many recent studies, aryldiazonium salts are generated in situ using organic nitrites (^tBuONO or ^iAmONO) in organic solvents (e.g. CH_3CN) and directly used in the next step [71–74].

Depending on the reaction conditions (counteranion, nucleophilic additive, solvent, reducing agent and wavelength of light), aryldiazonium salts can undergo homolytic cleavage or heterolytic cleavage to obtain aryl radicals or cations respectively (Scheme 2.10) [66]. Single electron reduction of aryldiazonium salts with subsequent loss of dinitrogen delivers aryl radicals, which participate in classical name reactions: (a) the Sandmayer reaction [75–77], (b) the Pschorr



Scheme 2.9 Synthesis of aryldiazonium salts [68, 69]



Scheme 2.10 Reactivity of diazonium salts: (a) homolytic cleavage; (b) heterolytic cleavage

cyclization [78], (c) the Gomberg-Bachmann reaction [79–81] and (d) the Meerwein arylation [82, 83] and also many conceptually novel and synthetically important organic transformations [66, 67, 71, 84]. There are many single electron reductants known such as Cu(I) salts [75, 76, 85, 86], $FeSO_4$ [87], ferrocene [87], ascorbic acid [72, 87], $TiCl_3$ [88–90], Bu_4NI [73, 74] and TEMPONa [91] to generate aryl radicals from aryldiazonium salts at ambient temperature [81]. In this direction of research, under visible light irradiation, polypyridyl metal complexes (e.g. $[Ru(bpy)_3]Cl_2$) and organic dyes (e.g. eosin Y or fluorescein) are highly efficient at generating aryl radicals from aryldiazonium salts allowing for milder conditions for subsequent reactions [67, 92–94].

2.1.4 Diaryliodonium Salts: Synthesis and Reactivity

Since the seminal report on diaryliodonium salts was published by Hartmann and Meyer [95] in 1894, diaryliodonium salts, IUPAC nomenclature "diaryl-λ^3-iodinanes", constitute a synthetically highly important class of hypervalent iodine compounds, which are widely applied in many different fields of chemistry such as in synthetic organic chemistry as arylating agents [96, 97], in polymer chemistry as

cationic photoinitiators [98, 99] and as precursors to ^{18}F-labelled compounds used in Positron Emission Tomography (PET) imaging [100].

Some important features of diaryliodonium compounds, which highlight its importance in practical applications are listed below: (a) these reagents are non-toxic, mild and moisture and air stable; (b) symmetrical diaryliodoniums have no issue of selectivity, whereas unsymmetrical examples typically selectively transfer one aryl group over another one depending on electronic factors, sterics (e.g. the use of a bulkier dummy aryl group generally favours transfer of the other aryl moeity) [101] and also the reaction conditions; (c) diaryliodonium salts have very high electrophilicity and possess a strong aryl iodide leaving group [102]; (d) easy counteranion exchange has given access to a wide variety of these compounds, which allows for judicious selections to be made to avoid potential nucleophilic attack by the counteranion under the reaction conditions or to improve solubility. Typically diaryliodonium salts with halide counteranions are sparingly soluble in organic solvents while non-coordinating BF_4 and OTf lead to improved solubility in many widely-employed solvents [96, 97].

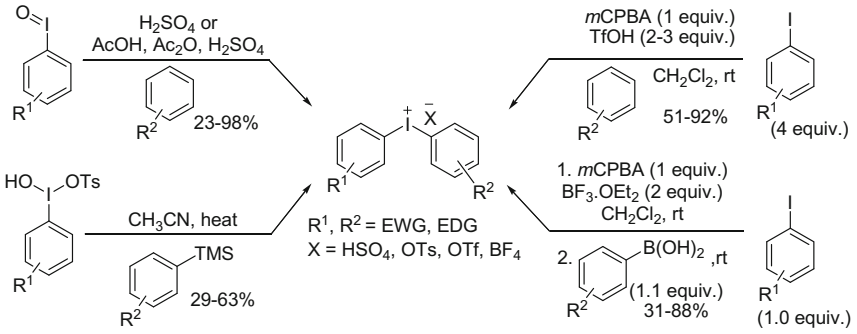
There are many synthetic routes already developed giving access to diaryliodonium salts for practical applications in organic synthesis [96, 97]. Some selected routes starting from different arene precursors are shown in Scheme 2.11 [103–108].

These compounds are highly electrophilic in nature at the iodine center due to the presence of a node of a non-bonding orbital that resides on iodine. Thereby diaryliodoniums react with many different nucleophiles at the iodine center. The reaction occurs through initial Nu–I bond formation followed by reductive elimination of one aryl group and nucleophile from the iodine center (Scheme 2.12a) [96]. Moreover, oxidative addition of these compounds to transition metals (e.g. copper, palladium, etc.) results in aryl–metal intermediates, which can take part in subsequent steps of the transformation such as in cross-coupling (Scheme 2.12b) [96]. In the presence of single electron reductants, diaryliodonium salts can afford aryl radicals (Scheme 2.12c) [66]. Very recently, diaryliodonium salts have been used by the scientific community in photoredox catalysis as aryl precursors to generate aryl radicals for arylation of alkenes and arenes under mild conditions (Scheme 2.12c) [109, 110].

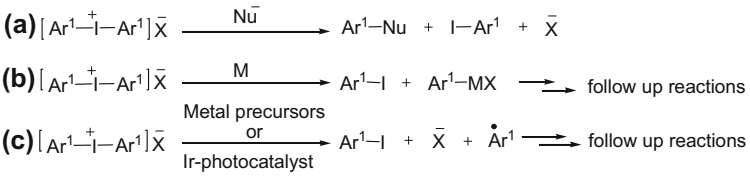
2.2 Results and Discussion

2.2.1 Inspiration

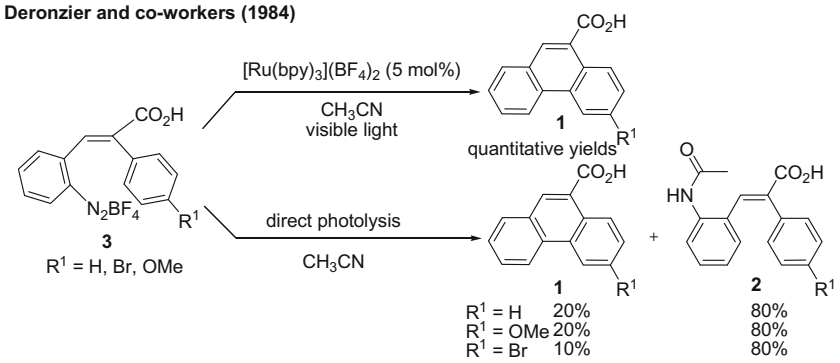
In one of the earlier reports of photoredox catalysis in 1984, Deronzier and co-workers described the Pschorr reaction for the synthesis of phenanthrene derivatives **1** from aryldiazonium salts **3** in the presence of $[Ru(bpy)_3](BF_4)_2$ (5 mol %) in acetonitrile under visible light irradiation (>410 nm) from a 250 W Hg lamp



Scheme 2.11 Synthesis of diaryliodonium salts [103–108]



Scheme 2.12 Reactivity of diaryliodonium salts: **a** nucleophilic substitution; **b** oxidative addition to metals; **c** aryl radical formation under visible light photoredox catalysis

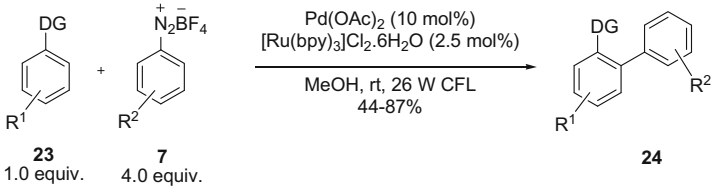


Scheme 2.13 Pschorr reaction under photoredox catalysis and direct photolysis [111]

(Scheme 2.13 and see Sect. 1.4.1.1) [111]. This method avoids the formation of the undesired byproduct **2** under direct photolysis (>360 nm) and benefits from milder reaction conditions compared to previously reported electrochemical processes [112] or thermal methods (Scheme 2.13) [113, 114].

After several intervening years, in 2011, Sanford and co-workers realized the potential of Deronzier's system and successfully applied it to their well-established

Sanford and co-workers (2011)



23 1.0 equiv. **7** 4.0 equiv. **24**

DG = Directing Group; R^1 = H, EDG; R^2 = H, EWG, EDG

Scheme 2.14 Dual palladium and visible light-mediated photoredox-catalyzed directed C–H arylation [115]

directed *ortho*-selective C–H arylation process, combining photoredox with palladium catalysis to access Pd(II)/Pd(IV) catalytic cycles (Scheme 2.14 and see Sect. 1.4.1.2) [115].

Inspired by these two seminal reports, we were interested in developing a dual catalytic system combining photoredox catalysis and gold catalysis and anticipated that in analogy to Pd(II)/Pd(IV) cycles, photoredox-generated aryl radicals from aryldiazonium salts may facilitate Au(I)/Au(III) catalytic cycles and enable the oxyarylation of alkenes while avoiding strong external oxidants and benefiting from milder reaction conditions.

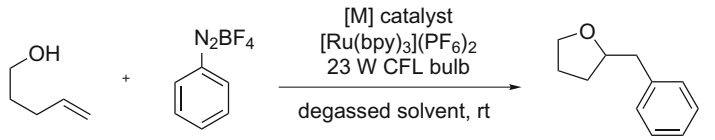
2.2.2 Intramolecular Oxy- and Aminoarylation of Alkenes

2.2.2.1 Preliminary Tests and Optimization Studies

In a preliminary test, 4-penten-1-ol (**54**) was treated with 4.0 equiv. of phenyldiazonium tetrafluoroborate (**65**) in the presence of 10 mol% of the gold(I) precatalyst (triphenylphosphine)gold(I) chloride (Ph_3PAuCl) and 5 mol% of $[Ru(bpy)_3](PF_6)_2$ in degassed methanol (0.1 M) under visible light irradiation from a 23 W compact fluorescent light (CFL) bulb for 6 h. To our delight, we observed the 5-*exo-trig* cyclization-arylation product 2-benzyl tetrahydrofuran (**57**) in 51 % NMR yield as the major product (Table 2.2, entry 1).

As the next step, we performed exhaustive optimization studies of this cascade cyclization-arylation reaction (Table 2.2). Our first attempt to improve the yield involved the screening of different gold catalysts with various ligands and counteranions. The reaction efficiency was highly dependent on the gold catalysts used for these studies. Neutral (dimethylsulfide)gold(I) chloride (Me_2SAuCl) delivered the product **57** in only 20 % NMR yield, while the electron-rich NHC-gold complex IPrAuCl (IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene) was an inefficient catalyst for this process, delivering only a trace amount of product **57**

Table 2.2 Optimization studies[a]



54 **65** **57**

Entry	[M] catalyst (mol%)	mol% $[Ru(bpy)_3]^{2+}$	Equiv. of 65	Solvent	Time (h)	Yield (%)[b]
1	Ph_3PAuCl (10)	5.0	4	MeOH	6	51
2	$(Me_2S)AuCl$ (10)	5.0	4	MeOH	12	26
3	IPrAuCl (10)	5.0	4	MeOH	12	Trace
4	$[dppm(AuCl)_2]$ (10)	5.0	4	MeOH	12	22
5	AuCl (10)	5.0	4	MeOH	12	Trace
6	$AuCl_3$ (10)	5.0	4	MeOH	12	Trace
7	$[(Pic)AuCl_2]$ (10)	5.0	4	MeOH	12	Trace
8	$[Ph_3PAu]NTf_2$ (10)	5.0	4	MeOH	4	84
9	$[Ph^tBu_2PAu(CH_3CN)]SbF_6$ (10)	5.0	4	MeOH	12	–
10	$[(Ph_3P)_2Au]OTf$ (10)	5.0	4	MeOH	12	50
11	$[IPrAu]NTf_2$ (10)	5.0	4	MeOH	12	Trace
12	$[Ph_3PAu]NTf_2$ (10)	5.0	4	CH_3CN	12	20
13	$[Ph_3PAu]NTf_2$ (10)	5.0	4	1,4-Dioxane	12	20
14	$[Ph_3PAu]NTf_2$ (10)	5.0	4	Acetone	12	14
15	$[Ph_3PAu]NTf_2$ (10)	5.0	4	CH_2Cl_2	12	3
16	$[Ph_3PAu]NTf_2$ (10)	5.0	4	DMA	12	17
17	$[Ph_3PAu]NTf_2$ (10)	5.0	4	EtOH	12	66
18	**$[Ph_3PAu]NTf_2$ (10)**	**2.5**	**4**	**MeOH**	**4**	**88(79)**
19	$[Ph_3PAu]NTf_2$ (10)	1.0	4	MeOH	12	61
20	$[Ph_3PAu]NTf_2$ (5)	2.5	4	MeOH	12	50
21	$[Ph_3PAu]NTf_2$ (1)	2.5	4	MeOH	7.5	22
22	$[Ph_3PAu]NTf_2$ (5)	1.2	4	MeOH	12	70
23	$[Ph_3PAu]NTf_2$ (5)	1.2	3	MeOH	12	60
24	$Pd(OAc)_2$ (10)	2.5	4	MeOH	6	–
25	$Cu(OAc)_2$ (10)	2.5	4	MeOH	8	–
26	$PtCl_2$ (10)	2.5	4	MeOH	8	–
27	$[Ph_3PAu]NTf_2$ (10)	–	4	MeOH	4	4
28	–	2.5	4	MeOH	4	–
29[c]	$[Ph_3PAu]NTf_2$ (10)	4	4	MeOH	4	6

[a]Alkenol **54** (0.2 mmol), phenyldiazonium salt **65**, $[Ru(bpy)_3](PF_6)_2$, the transition metal catalyst and the solvent were added to a flame-dried Schlenk flask in the absence of light. The mixture was degassed with three freeze-pump-thaw cycles, flushed with argon, sealed and stirred at rt under visible light irradiation (23 W CFL bulb) for the designated time

[b]NMR yield using diethyl phthalate as an internal reference. Isolated yields in parentheses

[c]The reaction was conducted in the dark. *dppm* diphenylphosphinomethane; *IPr* 1,3-bis (2,6-diisopropylphenyl)imidazol-2-ylidene); *Pic* picolinato

(Table 2.2, entry 2–3). The bimetallic gold complex (dppm)$(AuCl)_2$, (dppm = diphenylphosphinylmethane), which is known to be a good catalyst in oxidative Au(I)/Au(III) catalysis [55], was less efficient in our study, affording product **57** in 22 % NMR yield (Table 2.2, entry 4). Simple gold chloride (AuCl) without any ligand was unsuitable for the reaction (Table 2.2, entry 5). In a similar way, gold(III) precatalysts $AuCl_3$ and (Pic)$AuCl_2$ (Pic = picolinato) were also inefficient catalysts for this reaction (Table 2.2, entry 6–7). Changing the counteranions from tightly bound chloride to loosely bound NTf_2 led to a dramatic change in the reaction efficiency. The Gagosz catalyst $[Ph_3PAu]NTf_2$, which is considered to generate cationic $[Ph_3PAu]^+$ upon solvation, furnished product **57** in 84 % NMR yield (Table 2.2, entry 8). In a screen of cationic gold catalysts, $[Ph^tBu_2PAu(CH_3CN)]SbF_6$ showed no reactivity, whereas coordinatively saturated $[(Ph_3P)_2Au]OTf$, which is considered to be inactive in redox neutral gold catalysis, catalyzed this reaction in moderate efficiency, delivering product **57** in 50 % NMR yield (Table 2.2, entry 9–10). Again, the cationic NHC-gold complex $IPrAuNTf_2$ remained ineffective to promote this reaction (Table 2.2, entry 11). After screening of 11 different gold catalysts, the Gagosz catalyst $[Ph_3PAu]NTf_2$ was found to be the best for this transformation. In a solvent screen, methanol remained the best solvent for this process. On moving from methanol to other non-alcoholic solvents such as CH_3CN, 1,4-dioxane, acetone, CH_2Cl_2 and DMA, the efficiency of the reaction dropped dramatically (Table 2.2, entry 12–16). In another alcoholic solvent, ethanol, a significant drop of reaction efficiency was also observed with the product **57** being afforded in 66 % NMR yield (Table 2.2, entry 17). Lowering the loading of the photocatalyst $[Ru(bpy)_3](PF_6)_2$ from 5 to 2.5 mol% furnished the product **57** in 88 % NMR yield enhancing the reaction efficiency, however further lowering the loading to 1 mol% reduced the reaction efficiency again (Table 2.2, entry 18–19). Lowering the gold catalyst loading from 10 to 5 and 1 mol% had an adverse effect on the efficiency of the reaction (Table 2.2, entry 20–21). When loadings of gold and photocatalyst were reduced to 5 and 1.2 mol% respectively keeping the ratio between the gold catalyst and photocatalyst same, the efficiency of the reaction decreased (Table 2.2, entry 22). A similar effect was also observed when the stoichiometry of the phenyldiazonium salt **65** was reduced to 3.0 equiv. (Table 2.2, entry 23). On the other hand, the other transition metal catalysts $Pd(OAc)_2$, CuOAc and $PtCl_2$ did not catalyze the reaction at all (Table 2.2, entry 24–26). As a result of these studies, the combination of 10 mol% $[Ph_3PAu]NTf_2$, 2.5 mol% $[Ru(bpy)_3](PF_6)_2$ and 4.0 equiv. of the phenyldiazonium salt in methanol (0.1 M) as the solvent was identified as the optimized conditions for this transformation.

Control reactionss confirmed the necessities of all three components: the photoredox catalyst $[Ru(bpy)_3](PF_6)_2$, the gold catalyst $[Ph_3PAu]NTf_2$ and light (Table 2.2, entry 27–29). Without $[Ru(bpy)_3](PF_6)_2$, the reaction gave only 4 % yield of the product while without $[Ph_3PAu]NTf_2$ no reactivity was observed (Table 2.2, entry 27–28). In the absence of light, a trace amount of product **57** (6 %) was observed (Table 2.2, entry 29).

2.2.2.2 Substrate Scope and Limitations[1]

With these optimal reaction conditions in hand, we next investigated the scope and limitations of the developed dual catalytic method for the oxyarylation of alkenes, which are summarized in Tables 2.3 and 2.4.

Varying the alkene substrates

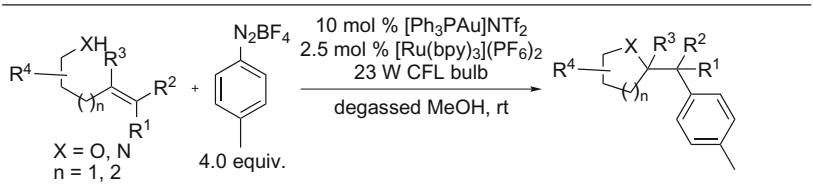
At the beginning, the scope and limitations of the process with respect to the alkene substrates was explored by treating 4-methylphenyldiazonium tetrafluoroborate (**86**) with various substituted alkenol substrates **66**–**75**. The reaction conducted with (±) 3-phenylpent-4-en-1-ol **66,** a primary alcohol, afforded the cyclization-arylation product (±) 2-(4-methylbenzyl)-3-phenyltetrahydro-furan **76** in 70 % yield and 1.6:1 d.r., while (±) *trans*-2-allylcyclohexenol **67**, a secondary alcohol, delivered (±) 2-(4-methylbenzyl)octahydro-benzofuran **77** in 66 % yield and 2.8:1 d.r. showing the tolerance of the process towards substituents on the alkyl tether (Table 2.3, entry 1–2). Under the same reaction conditions, a tertiary alcohol, 3-ethylhept-6-en-3-ol **68**, was reacted with 4-methylphenyldiazonium salt **86** to obtain the corresponding oxyarylation product 2,2-diethyl-5-(4-methylbenzyl) tetrahydro-furan **78** in 56 % yield (Table 2.3, entry 3). The reactions of 1,1-disubstituted alkenes **69** and **70**, which are unsuitable substrates for previously reported gold-catalyzed heteroarylations of alkenes under oxidative conditions [54, 55], were successful coupling partners in this study affording the desired oxyarylation products **79** (39 %) and **80** (63 %) respectively (Table 2.3, entry 4–5). In contrast to previously-reported oxidative gold-catalyzed heteroarylations of alkenes [54, 55], internal alkenes (*E*)-**71** and (*Z*)-**72** were successfully employed in this oxyarylation process under dual catalytic conditions to furnish the expected oxyarylation products (±) (*R*,*R*)-**81** (59 %) and (±) (*R*,*S*)-**82** (56 %) with excellent diastereoselectivities (in both cases d.r. > 25:1) respectively (Table 2.3, entry 6–7). This high diastereoselectivity supports the involvement of the gold catalyst in the stereochemistry-determining steps and provides mechanistic evidence for the process (vide infra). The alkenol **75** with an extra CH_2 tether was suited for this process affording the product **85** in 34 % yield (Table 2.3, entry 10). Alkene substrates with nitrogen nucleophiles were also successfully employed in this process. Substrates **73** and **74** with pendant protected amine nucleophiles delivered the corresponding pyrrolidine products **83** (84 %) and **84** (54 %) respectively (Table 2.3, entry 8–9).

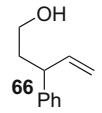
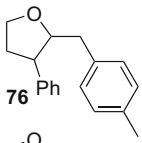
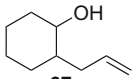
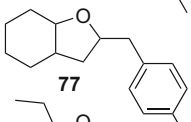
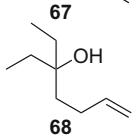
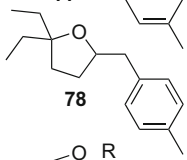
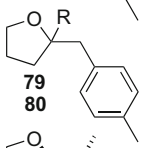
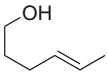
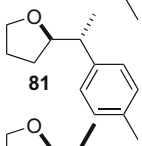
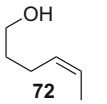
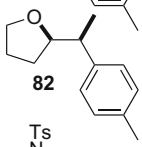
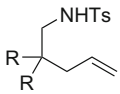
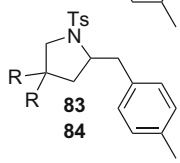
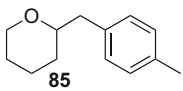
Varying the aryldiazonium salts

Aryldiazonium salts **86**–**92**, with diverse substitution patterns, were investigated in this study using 4-penten-1-ol as the alkene under the optimized reaction conditions (Table 2.4). Aryldiazonium salts **86** and **87**, bearing electron-neutral methyl and phenyl substituents respectively, were well suited for this transformation giving rise to the corresponding products **93** (78 %) and **94** (64 %) (Table 2.4, entry 2–3).

[1]A part of the substrate scope studies was carried out by Dr. Matthew N. Hopkinson (WWU).

Table 2.3 Scope of alkene substrates[a]



Entry	Alkenols	Product	Yield(d.r.)[%][b]
1	 **66**	 **76**	70 (1.6:1)
2	 **67**	 **77**	66 (2.8:1)
3	 **68**	 **78**	56
4 5	 R = Me **69** R = Ph **70**	 **79** **80**	39% 63%
6	 **71**	 **81**	59 (>25:1)
7[c]	 **72**	 **82**	56 (>25:1)
8[d] 9[d]	 R = H **73** R = Me **74**	 **83** **84**	84 54
10	 **75**	 **85**	34

[a]General conditions: **66–75** (0.2 mmol, 1 equiv.), $[Ph_3PAu]NTf_2$ (0.02 mmol), $[Ru(bpy)_3](PF_6)_2$ (0.005 mmol), **86** (4.0 equiv.), degassed MeOH (0.1 M), rt, 4–16 h, 23 W fluorescent light bulb

[b]Isolated yields. *d.r.* determined by ^1H NMR

[c]Reaction performed on a 0.4 mmol scale

[d]5.0 equiv. of **74** used

The aryldiazonium salt **88**, with an electron-withdrawing ester functionality was the most efficient coupling partner among the tested aryldiazonium salts furnishing the desired product **95** in 83 % yield (Table 2.4, entry 4). Aryldiazonium salts **89–91**, featuring electron-withdrawing halogen functional groups such as fluoride, bromide and also bromide and chloride together, were successfully employed in this process to obtain the oxyarylation products **96–98**, in which chloride and bromide functionalities are available for further functionalization (Table 2.4, entry 5–7). Aryldiazonium salt **92**, bearing both an electron-withdrawing trifluoromethyl group and an electron-donating methoxy group was tolerated under the reaction conditions giving rise to the desired product **99** in 32 % yield (Table 2.4, entry 8). In none of the cases was the protodeauration product detected in the reaction mixture.

2.2.3 Intermolecular Oxyarylation of Alkenes

Since a multicomponent intermolecular process is more difficult than its intramolecular version, it is highly encouraging to develop methodologies for the intermolecular difunctionalization of alkenes for constructing important complex building blocks. One of the common methods for the arylation of alkenes in an intermolecular fashion is the palladium-catalyzed Mizoroki-Heck reaction involving aryl halides and alkenes as coupling components to deliver styrene derivatives. However, there has been a significant research attention paid to the development of methodologies for the addition of two functional groups across the C=C double bond, instead of maintaining the alkene functionality. In this regard, we extended our previously developed dual catalytic methodology to the selective three component oxyarylation of terminal alkenes under milder reaction conditions compared to previously-reported methods [58–60].

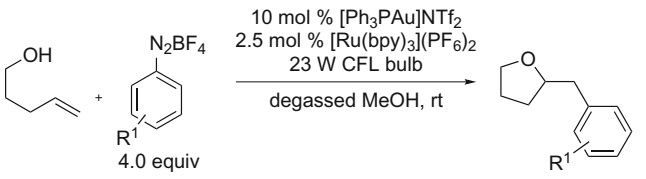
2.2.3.1 Preliminary Tests and Optimization Studies

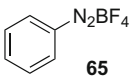
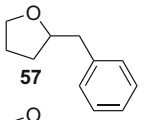
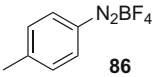
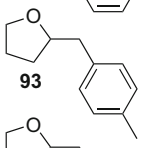
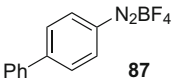
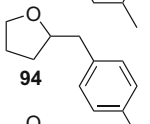
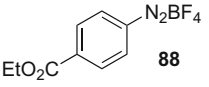
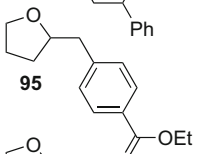
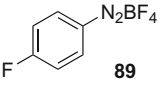
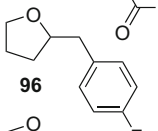
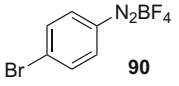
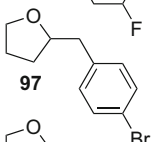
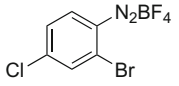
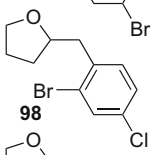
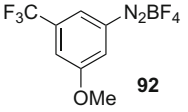
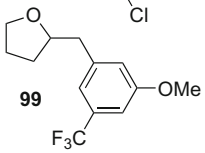
In a preliminary test, we employed our previously-developed standard reaction conditions where a terminal alkene, 1-octene (**100**), was reacted with 4.0 equiv. of phenyldiazonium tetrafluoroborate (**65**) in the presence of 10 mol% of $[Ph_3PAu]NTf_2$ and 2.5 mol% of $[Ru(bpy)_3](PF_6)_2$ in degassed methanol (0.1 M) under visible light irradiation from a 23 W CFL bulb for 16 h. We were delighted to observe selective formation of the oxyarylation product, (2-methoxyoctyl)benzene (**102**) in 90 % NMR yield and 84 % isolated yield as the major product.

In order to optimize this reaction,[2] various gold catalysts with electron-rich phosphines (tricyclohexylphosphine and tris(4-methoxyphenyl)phosphine) and an electron-poor phosphine (tris(4-trifluoromethylphenyl)phosphine) were screened

[2]The optimization studies were carried out by Dr. Matthew N. Hopkinson (WWU Münster).

Table 2.4 Scope of aryldiazonium salts for the Au/Ru-catalyzed oxyarylation of alkenes[a]

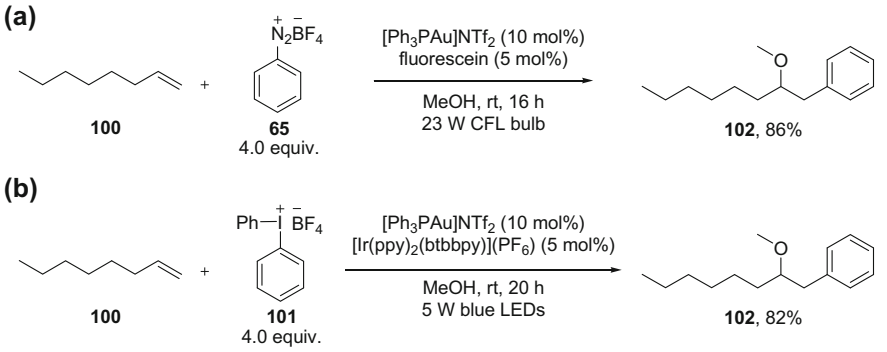


Entry	[Ar-N_2]BF_4	Product	Yield (%)[b]
1	 **65**	 **57**	79
2	 **86**	 **93**	78
3	 **87**	 **94**	64
4	 **88**	 **95**	83
5	 **89**	 **96**	75
6	 **90**	 **97**	60
7	 **91**	 **98**	42
8	 **92**	 **99**	32

[a]Alkenol **54** (0.2 mmol), aryldiazonium salt **65**, **86-92** (0.8 mmol), $[Ph_3PAu]NTf_2$ (0.02 mmol), $[Ru(bpy)_3](PF_6)_2$ (0.005 mmol) and MeOH (2 mL) were added to a flame-dried Schlenk flask in the absence of light. The mixture was degassed with three freeze-pump-thaw cycles, flushed with argon, sealed and stirred at rt under visible light irradiation (23 W compact fluorescent light bulb) 4–12 h

[b]Isolated yield

because our previous intramolecular oxyarylation reactions were highly ligand dependant, favouring phosphine ligands. In the survey of different photoredox catalysts such as the polypyridyl metal complexes ($[Ru(bpy)_3](PF_6)_2$ and $[Ir(ppy)_2(dtbbpy)](PF_6)$) and organic dyes (eosin Y, fluorescein, rhodamine B and rose bengal) and light sources (23 W CFL, blue LEDs, green LEDs), we found that a combination of 10 mol% of $[Ph_3PAu]NTf_2$ and 5 mol% of fluorescein in degassed methanol (0.1 M) under visible light irradiation from a 23 W CFL bulb could catalyze the reaction of 1-octene (**100**) with 4.0 equiv. of the phenyldiazonium salt with the highest efficiency, delivering (2-methoxyoctyl)benzene (**102**) in 88 % NMR yield and 86 % isolated yield (Scheme 2.15a). The use of an inexpensive photoredox catalyst, fluorescein dye (404 times cheaper than previously used $[Ru(bpy)_3](PF_6)_2$, according to the prices offered by Sigma Aldrich in June, 2014) made this protocol more attractive. In order to replace comparatively less stable aryldiazonium salts, air and moisture stable diaryliodonium salts were tested in the same reaction. After an exhaustive screening of many different gold catalysts with a variety of ligands, various photoredox catalysts, light sources, mixture of solvents and diaryliodonium salts with different counteranions, we were delighted to find optimized reaction conditions for this process where treating 1-octene (**100**) with 4.0 equiv. of diphenyliodonium tetrafluoroborate (**101**) in the presence of 10 mol% of $[Ph_3PAu]NTf_2$ and 5 mol% of $[Ir(ppy)_2(dtbbpy)](PF_6)$ in degassed methanol (0.1 M) under visible light irradiation from 5 W blue LEDs furnished (2-methoxyoctyl)benzene (**102**) in 91 % NMR yield and 82 % isolated yield as the major product (Scheme 2.15b). It is worth mentioning that organic dyes did not catalyze this reaction with diaryliodonium salts and that a more strongly reducing iridium photocatalyst was required.



Scheme 2.15 Intermolecular oxyarylation of alkenes: **a** Oxyarylation with aryldiazonium tetrafluoroborate; **b** oxyarylation with diaryliodonium tetrafluoroborate

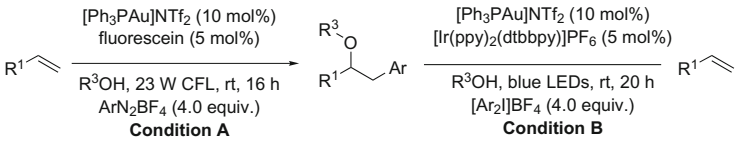
2.2.3.2 Substrate Scope and Limitations[3]

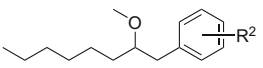
Having optimized reaction conditions for both the methods in hand, we explored the scope and limitations of both protocols for intermolecular oxyarylation in terms of alkene substrates and arylprecursors (conditions A: with aryldiazonium and conditions B: with diaryliodonium salts) (Table 2.5).

In contrast to previously reported oxyarylations of activated alkenes which proceed via radical-addition [91, 110, 116, 117], we could successfully employ unactivated alkenes without requiring any radical stabilizing groups in these dual catalytic methods. In none of the cases were styrene-type products resulting from Mizoriki-Heck coupling or hydroetherification could be detected under the optimized reaction conditions. Electron-withdrawing and electron-donating functional groups on the aryl ring in the aryldiazonium and diaryliodonium salts were well tolerated. Substrates bearing a methyl substituent at the *ortho*-, *meta*- or *para*-positions of the aryl ring were all suitable for this process under both reaction conditions employing aryldiazonium and diaryliodonium salts, but a different trend of tolerance was observed in these studies. The *para*-methyl-substituted aryldiazonium salt reacted efficiently delivering the desired ether product **103** in 62 % yield, while the corresponding diaryliodonium salt afforded same product **103** in a poor yield (26 %). An opposite trend of reactivity was observed for *ortho*-methyl-substituted substrates, with the aryldiazonium salt producing the desired ether product **104** in 28 % yield (conditions A) and the diarylaiodonium salt leading to **104** in 75 % yield (conditions B). A *meta*-methyl substituent in both the cases was well tolerated under both sets of reaction conditions. Electron-withdrawing bromide functionality was also well tolerated under both reaction conditions furnishing the expected ether product **106**, susceptible for further functionalization, in good yield (conditions A: 69 % and conditions B: 65 %). Diaryliodonium salts featuring electron-withdrawing fluorine and trifluoromethyl functional groups were successfully applied for this process only under the reaction conditions B, affording the ether products **107** (82 %) and **108** (36 %), respectively. Ethyl ester functionality at the *para*-position on the aryl ring of the aryldiazonium salt and at the *meta*-position on the aryl ring of the diaryliodonium salt was tolerated in these oxyarylation processes delivering the corresponding products **109** (64 %) and **110** (50 %), respectively, in good to moderate yields. Both compounds were isolated with contamination with small amounts of the corresponding methyl esters resulting from transesterification with the methanol solvent. Diverse functional groups on the alkenes were tolerated in these dual-catalyzed oxyarylation reactions under both sets of reaction conditions, affording the ether products **111–114** in moderate to good yields. Alkene substrates having pendant 4-methoxyphenol and a protected amine *N*-phthalimide group were also successful in this process under reaction conditions B, giving products **115** (26 %) and **116** (52 %), respectively, in low to moderate yields. Apart from methanol, other oxygen nucleophiles such as ethanol

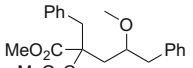
[3]A part of the substrate scope was carried out by Dr. Matthew N. Hopkinson (WWU Münster).

Table 2.5 Scope of intermolecular oxyarylation of alkenes with aryldiazonium salts and diaryliodonium salts[a]

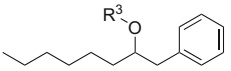




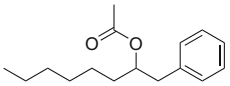
102 (R^2 = H) **A:** 86%, **B:** 82%
(**B:** 2.0 mmol scale, 91%)
103 (R^2 = *p*-Me) **A:** 62%, **B:** 26%
105 (R^2 = *m*-Me) **A:** 70%, **B:** 60%
104 (R^2 = *o*-Me) **A:** 28%, **B:** 75%
106 (R^2 = *p*-Br) **A:** 69%, **B:** 65%
107 (R^2 = *p*-F) **B:** 82%
108 (R^2 = *p*-CF_3) **B:** 36%
109 (R^2 = *p*-CO_2Et) **A:** 50%[a]
110 (R^2 = *m*-CO_2Et) **B:** 50%[b]



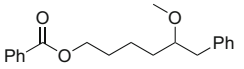
114
A: 76%, **B:** 67%



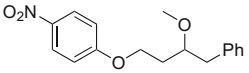
117 (R^3 = Et) **B:** 75%
118 (R^3 = iPr) **B:** 26%



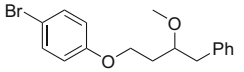
119
B: 26%



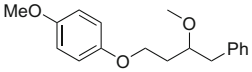
111
A: 75%, **B:** 78%



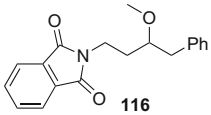
112
A: 60%, **B:** 66%



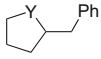
113
A: 84%, **B:** 82%



115
B: 26%



116
B: 52%



57 (Y = O) **B:** 68%
120 (Y = NTs) **B:** 79%

Reaction conditions A Alkene (0.2 mmol), aryldiazonium salt (0.8 mmol), $[Ph_3PAu]NTf_2$ (10 mol %) and fluorescein (5 mol%) in degassed MeOH (0.1 M) reacted in the presence of visible light from a 23 W CFL for 16 h at rt. Isolated yields

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

Reaction conditions B Alkene (0.2 mmol), diaryliodonium salt (0.8 mmol), $[Ph_3PAu]NTf_2$ (10 mol%) and $[Ir(ppy)_2(dtbbpy)]PF_6$ (5 mol%) in degassed MeOH (0.1 M) reacted in the presence of visible light from blue LEDs at rt for 20 h. Isolated yields

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

and isopropanol and even acetic acid were successfully employed in these studies to give access to ether **117–118** and ester **119** compounds, although these nucleophiles were used as solvent. We repeated the intramolecular oxy- and aminoarylation of alkenes **54** and **73** under reaction conditions B using diaryliodonium salts. These reactions delivered the corresponding tetrahydrofuran and pyrrolidine products **57** and **120,** showing that diaryliodonium salts are suitable aryl sources for our previously-developed intramolecular heteroarylations of alkenes. Finally, we repeated the parent reaction with 1-octene, diphenyliodonium tetrafluoroborate (**101**) and methanol on a 2.0 mmol scale, which produced the expected product **102** in 91 % yield. This showed that the reaction efficiency does not drop upon scaling-up the reaction.

In order to investigate the selectivity of aryl transfer from diaryliodonium salts, we employed an unsymmetrical diaryliodonium salt (**121**) having electronically slightly different phenyl and *para*-bromophenyl groups (Scheme 2.16). Interestingly, the electron-deficient *para*-bromophenyl group was transferred in a slight preference over the electron-neutral phenyl group furnishing product **106** and **102** in a ratio of 1.3:1 and in 90 % combined NMR yield.

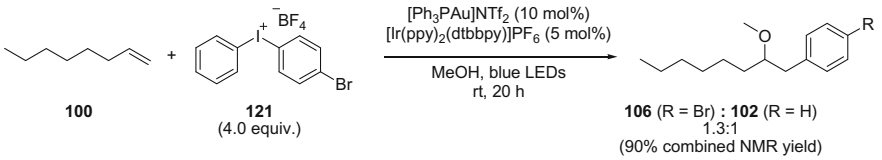
2.2.4 Mechanistic Studies on Heteroarylations of Alkenes[4]

In order to gain insight into the reaction mechanism, we conducted a literature survey and performed control experiments. The results obtained from control experiments confirmed that all the components (the gold catalyst, photoredox catalyst and visible light) are essential for this process (Table 2.2, entry 27–29). In the absence of one of these three components, either the reaction shut down or the reaction efficiency dropped dramatically.

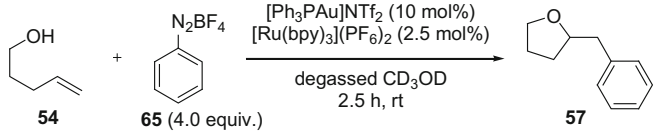
In order to investigate whether visible light irradiation is required throughout the reaction or only to initiate the process, a light off-on experiment was conducted. In this test, the reaction between 4-penten-1-ol (**54**) and phenyldiazonium tetrafluoroborate (**65**) was performed under the optimized reaction conditions on a 0.2 mmol scale in degassed deuterated methanol (Scheme 2.17). The reaction mixture was subjected to stirring for sequential periods of time under visible light irradiation from a 23 W CFL bulb followed by stirring in the dark. At each time point, an aliquot (200 μL) of the reaction mixture was taken out under argon atmosphere, which was then quenched with D_2O (50 μL) and diluted with a $CDCl_3$ solution (500 μL) containing the internal standard diethyl phthalate. The measured NMR yields of tetrahydrofuran **57** are displayed in Fig. 2.2.

The outcome of this experiment indicated that the reaction proceeds smoothly under visible light irradiation. The reaction shut down when irradiation of the reaction mixture was stopped and the reactivity could be recovered upon switching

[4]A part of the mechanistic studies was carried by Dr. Matthew N. Hopkinson (WWU Münster).



Scheme 2.16 Oxyarylation of 1-octene with an unsymmetrical diaryliodonium salt **121**



Scheme 2.17 Dual gold and photoredox-catalyzed oxyarylation of 4-penten-1-ol (**54**) with phenyldiazonium salt **65** in deuterated methanol (MeOH-d_4)

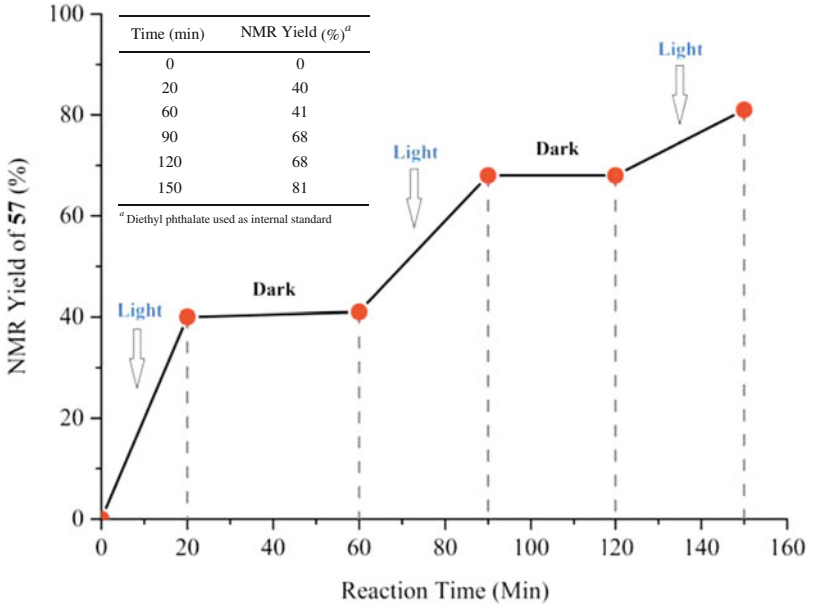
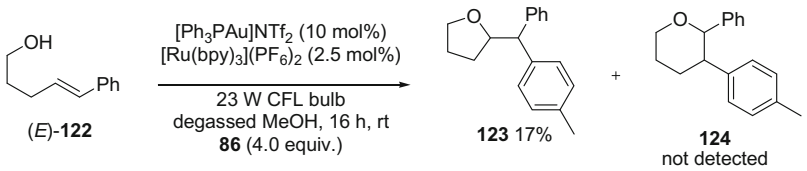


Fig. 2.2 Effect of visible light irradiation on the reaction efficiency

on the light again. This experiment confirmed that continuous visible light irradiation is mandatory for the completion of this process.

The reaction with the activated styrene substrate **70**, which could potentially react with aryl radicals directly in a Meerwein-type arylation process, with aryldiazonium salt **86** under the standard reaction conditions afforded the corresponding

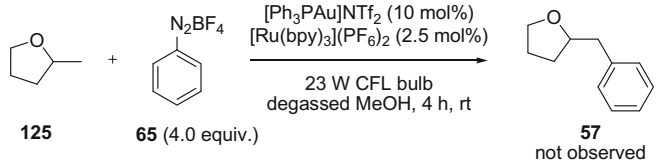


Scheme 2.18 Dual gold and photoredox-catalyzed oxyarylation of styrene-type alkenol *E*-**122** with aryldiazonium salt **86**

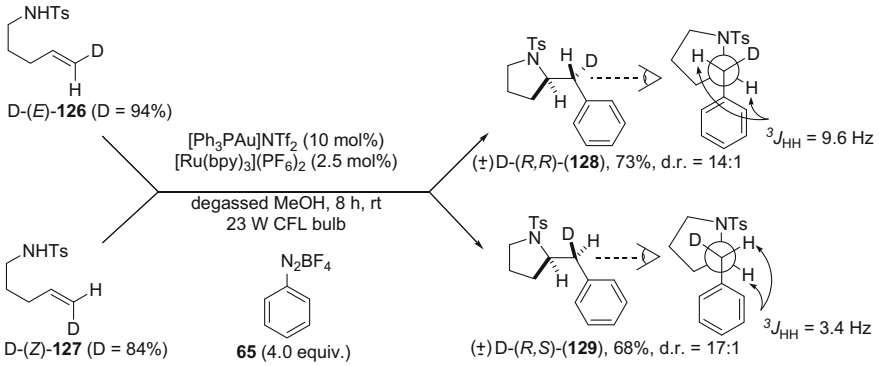
product **80** in 63 % yield, whereas only 14 % yield of the product **80** was obtained omitting the gold catalyst (Table 2.3, entry 5). These results suggested that while the Meerwein-type aryl radical addition to this activated alkene is possible, this process is less favorable than the gold-catalyzed process. As shown by a control reaction with 4-penten-1-ol **54** and from previous-studies on aryl radical addition reactions, unactivated alkenes are poor substrates for this type of process, implying that such a radical addition pathway is unlikely to be operating in this dual-catalyzed reaction [84, 91, 118]. In an analogous test, employing another activated styrene **122**, where Meerwein-type addition would preferentially give rise to a 6-membered ring product (**124**), resulted in the exclusive formation of the 5-membered ring oxyarylation product **123** albeit in a low yield of 17 % with no products resulting from Meerwein-type radical addition being detected. In a control reaction without the gold catalyst, no reactivity was observed with this substrate. From the above two results it seemed that the gold-catalyzed process does not involve a Meerwein-type radical addition and even predominates over this pathway with activated alkenes (Scheme 2.18).

Although during the substrate scope study, no protodeauration products [e.g. 2-methyltetrahydrofuran (**125**)] were detected in any of the reaction mixtures, still the possibility remained that products resulting from protodeauration might be formed under these acidic conditions and become arylated in a subsequent step. In that situation we would not be able to detect protodeauration products. In order to rule out this possibility, we treated 2-methyltetrahydrofuran (**125**) with phenyldiazonium salt **65** under the standard reaction conditions and no formation of the oxyarylated product **57** was observed (Scheme 2.19). The lack of 2-methyltetrahydrofuran or pyrrolidine products observed throughout this study suggests that protodeauration of the alkylgold intermediate formed in this transformation is not an efficient process. In a relevant mechanistic study, Toste and co-workers isolated various alkylgold(I) complexes and tested their stability upon treatment with *p*-toluenesulfonic acid and, in analogy to our experminental observations, obtained no protodeauration product [57].

In a study focused on elucidating the stereochemical relationship between the nucleophile and the aryl group in the final products, the deuterium-labelled γ-aminoalkene substrates (D)-(*E*)-**126** and (D)-(*Z*)-**127** were reacted under the standard conditions, delivering the expected pyrrolidine products **128** and **129** with high diastereoselectivities, respectively, with the amino and aryl group being in an



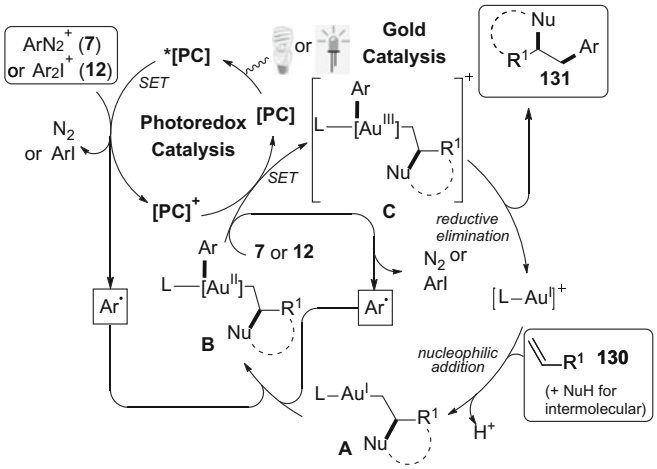
Scheme 2.19 Control experiment of 2-methyltetrahydrofuran **125** with phenyldiazonium salt **65** under the standard reaction conditions



Scheme 2.20 Dual gold and photoredox-catalyzed aminoarylation of deuterated γ-amino-alkenes (**126**–**127**) with phenyldiazonium salt **65**

anti-relationship in both cases (Scheme 2.20) [54]. This fact was determined by comparing the ^{1}H NMR spectra for these compounds with those reported by Zhang et al. [54] who in turn determined the stereochemistry by an analysis of the differences in the vicinal $^{3}J_{HH}$ coupling constants resulting from restricted rotation around the formerly olefinic C–C bond. Similar results were also obtained when internal γ-hydroxyalkenes (*E*)-**71** and (*Z*)-**72** were employed in the intramolecular oxyarylation process under the standard conditions, where the expected oxyarylation products (±) (*R*,*R*)-**81** (59 %) and (±) (*R*,*S*)-**82** (56 %) were furnished with excellent diastereoselectivities (d.r. > 25:1 in the both cases) respectively (Table 2.3, entry 6–7). The above stereochemical observations imply that the nucleophile and the aryl group add in a *trans*-fashion across the C=C double bond of the alkenes. This stereochemical event can be rationalized by an initial *anti*-aminoauration or oxyauration of the alkenes followed by an arylation event occurring with retention of stereochemistry [e.g. via reductive elimination from gold(III)].

Based on previous literature reports [109, 115] and our mechanistic experiment studies, we hypothesized a reaction mechanism of the type shown in Scheme 2.21. According to the previously reported studies on alkene activation with cationic gold (I), [57] we propose that a cationic gold(I) species derived from Gagosz's catalyst



[PC] = photoredox catalyst (i.e. fluorescein, $[Ru(bpy)_3]^{2+}$ or $[Ir(ppy)_2(dtbbpy)]^+$), Nu = O or NTs.

Scheme 2.21 A plausible reaction mechanism for intra- and intermolecular oxyarylation of alkenes with aryldiazonium and diaryliodonium salts

could coordinate to the alkene **130** and activate it towards *anti*-attack of an internal or external hydroxy or amine nucleophile leading to the formation of the alkylgold intermediate **A**. In a parallel photoredox catalytic cycle, single electron reduction of the aryldiazonium salt or diaryliodonium salt with the photo-excited photoredox catalyst (*PC) would release a nucleophilic aryl radical upon extrusion of dinitrogen or an aryl iodide molecule and generate the oxidized photoredox catalyst (PC^+). At this stage, the aryl radical could oxidize the alkylgold(I) intermediate **A** to obtain the highly reactive gold(II) intermediate **B** bearing both coupling fragments. Spectroscopic and theoretical studies on the trapping of nucleophilic phenyl radicals by gold(I) species to generate phenylgold(II) intermediates by Corma, Garcia and co-workers strengthened this speculation [119]. In the next step, the unstable gold (II) intermediate **B** is expected to transfer an electron to the oxidized photoredox catalyst (PC^+) via SET to regenerate the photoredox catalyst (PC) and deliver the gold(III) intermediate **C**. Alternatively SET could occur with another molecule of the aryldiazonium or diaryliodonium salt in a radical chain process. Fast reductive elimination from gold(III) intermediate **C** at this point would furnish the oxy- or aminoarylation product **131** and regenerate the gold(I) catalyst.

2.3 Summary

In conclusion, we have successfully combined two different catalytic modes, gold catalysis and photoredox catalysis, in a novel dual catalytic system, demonstrating their compatibility. This novel dual catalytic system catalyzes oxyarylation and aminoarylation reactions of non-activated γ-hydroxyalkenes, γ-aminoalkenes and also a δ-hydroxyalkene with aryldiazonium salts to give access to substituted saturated heterocyclic compounds (tetrahydrofurans, pyrrolidines and a tetrahydropyran). In contrast to previous reports on oxidative gold-catalyzed heteroarylations of alkenes [54, 55], internal alkenes could successfully be employed using this system. This method avoids the use of strong external oxidizing agents such as Selectfluor, hypervalent iodine reagent or ^{t}BuOOH, which limit the substrate scope of previously-reported related processes. Moreover, this transformation benefits from milder reaction conditions and the use of readily available visible light sources. This concept can be extended to multicomponent intermolecular oxyarylation of non-activated alkenes, simple alcohols and aryldiazonium salts using inexpensive fluorescein dye as the photocatalyst in place of expensive transition metal-based photocatalysts such as $[Ru(bpy)_3](PF_6)_2$. The combination of the more oxidizing photocatalyst $[Ir(ppy)_2(dtbbpy)](PF_6)$ and a gold catalyst in the presence of visible light irradiation from blue LEDs enabled diaryliodonium salts, which are readily prepared and air and moisture stable, to be applied in both intra- and intermolecular oxyarylation processes, extending the scope of these reactions. In this later method, acetic acid could also be applied as a nucleophile in addition to various alcohols.

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