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Photoinduced Gold-Catalyzed Domino C(sp) Arylation/Oxyarylation of TMS-Terminated Alkynols with Arenediazonium Salts

Benito Alcaide,*[,†] Pedro Almendros,*[,‡] Eduardo Busto,*[,†] and Carlos Lázaro-Milla[†]

[†]Grupo de Lactamas y Heterociclos Bioactivos, Departamento de Química Orgánica I, Unidad Asociada al CSIC, Facultad de Química, Universidad Complutense de Madrid, 28040-Madrid, Spain

[‡]Instituto de Química Orgánica General, IQOG-CSIC, Juan de la Cierva 3, 28006-Madrid, Spain

E-mail: alcaideb@quim.ucm.es; palmendros@iqog.csic.es; bbusto@ucm.es

ORCID

Benito Alcaide: 0000-0002-2180-9605

Pedro Almendros: 0000-0001-6564-2758

Eduardo Busto: 0000-0002-1637-0079

Carlos Lázaro-Milla: 0000-0003-3698-1405

Dedicated to Prof. Vicente Gotor on the occasion of his 70th birthday

ABSTRACT

A selective and convenient synthesis of tri- and tetrasubstituted α,β-unsaturated ketones, as well as 2,3-diarylbenzofurans has been developed with the aid of light and taking

advantage of a cooperative gold/photoredox-catalyzed twofold arylation reaction of TMS-terminated alkynols. The reaction of 3-(trimethylsilyl)prop-2-yn-1-ols was competent to generate diarylated α,β-unsaturated ketones; whereas the photoredox sequence involving 2-[(trimethylsilyl)ethynyl]phenol exclusively afforded 2,3-diarylbenzofurans. The reaction of terminal alkynes proceeded in poor yields while the use of bulkier silyl groups such as TIPS resulted unproductive. Apparently, the C(sp) arylation reaction is the first event on the domino bis-arylative sequence. These results could be explained through the intermediation of arylgold(III) species and several single electron transfer processes.

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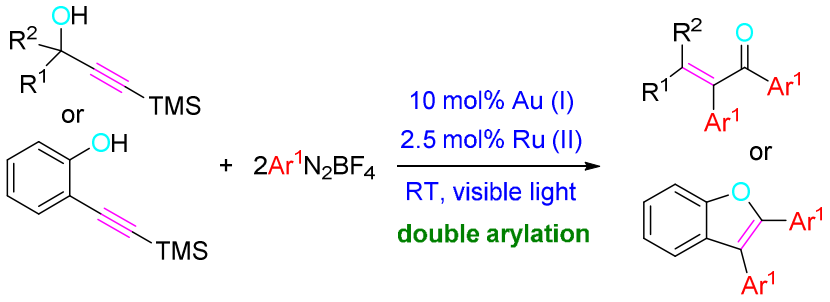


INTRODUCTION

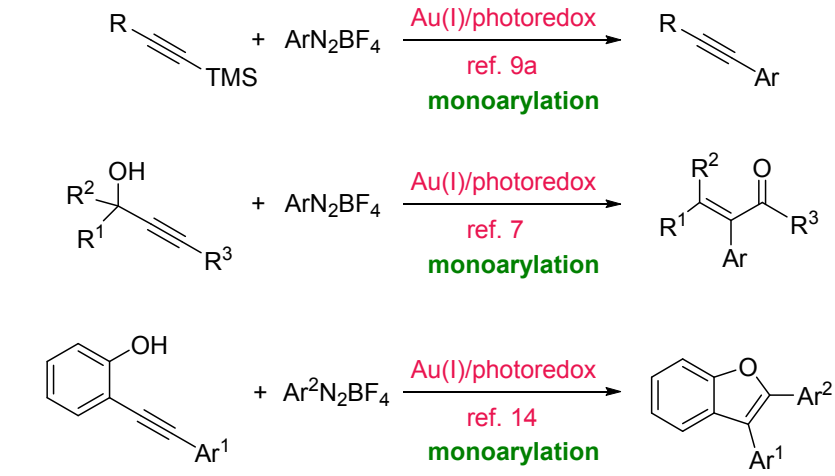
The ready availability of diazonium salts makes these compounds as widely applicable building blocks in organic chemistry.[1] Arenediazonium salts react without the assistance of any ligand or base and are one of the most sustainable and convenient alternatives to aryl halides. Aiming to reduce waste, organic chemists have been trying to develop visible-light photoredox catalysis as a tool in synthetic chemistry.[2] Organometallic complexes (ruthenium- and iridium-based) and metal-free organic dyes (eosin Y, rose bengal, rhodamine B, fluorescein) have been successfully incorporated in the recently developed gold-catalyzed photoredox chemistry.[3] Early work in gold catalysis

demonstrated that even dinuclear complexes of gold can serve as photoredox catalysts,[4] a principle which has been taken up very successully in gold-only photoredox chemistry.[5] This new approach represents an attractive, eco-friendly alternative to the addition of strong oxidants in stoichiometric excess for accessing to Au(I)/Au(III) catalytic cycles.[6]

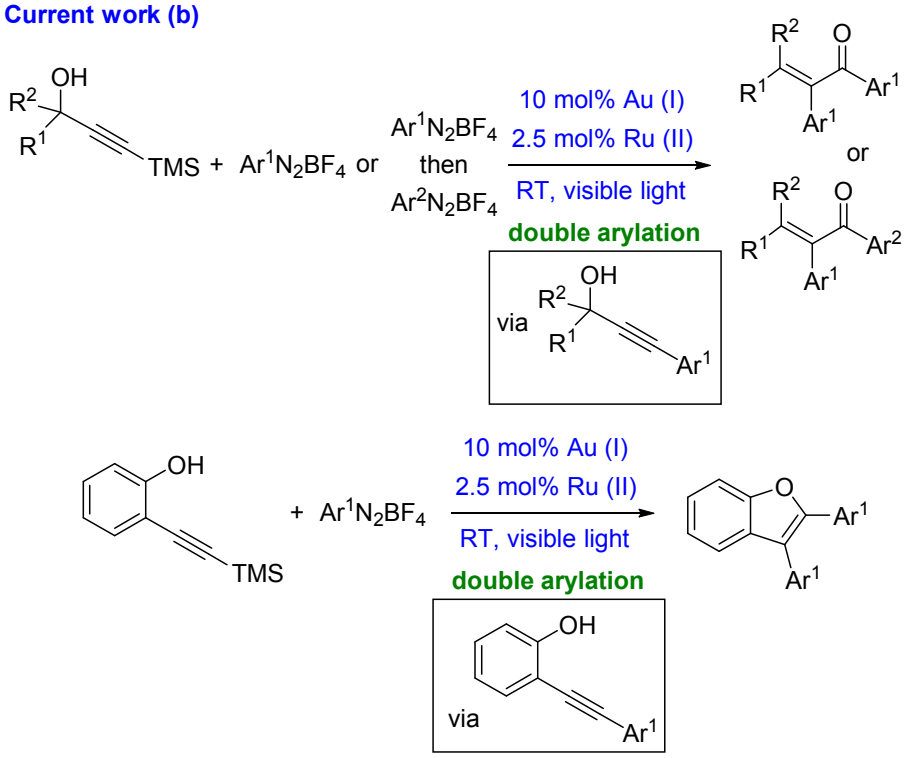
The α,β-unsaturated ketone as well as the benzofuran motifs constitute an important class of compounds because they are found in numerous biologically active natural products and serve as starting materials to prepare a variety of organic compounds. We and others have recently established that, with the aid of a photoredox catalyst, an array of α,β-unsaturated ketones can be obtained from alkynols through a gold-catalyzed Meyer–Schuster/arylation reaction sequence promoted by visible light (Scheme 1a).[7] Domino reactions are practical one-step methods for accessing organic compounds which require less energy and labor.[8] Herein, we take advantage of a photocatalyzed system to develop a selective domino gold-catalyzed twofold arylation reaction of TMS-terminated alkynols to produce different diarylated α,β-unsaturated ketones and 2,3-diarylbenzofurans (Scheme 1b).

Scheme 1. Generic Scheme Delineating the Photopromoted Mono- and Bis-Arylative Reactions of Alkynols

Previous literature (a)



Current work (b)



RESULTS AND DISCUSSION

Several challenges had to be considered in the design of the double arylation sequence, mainly to address the chemoselectivity issue. Depending on the reactivity of the terminal alkynol, two different isomeric products can be initially produced, the aryl-substituted alkynol through Hiyama–Sonogashira-type coupling, and the monoarylated

α,β-unsaturated ketone through Meyer–Schuster-type reaction (or the monoarylated benzofuran through intramolecular alkoxylation). For the success of the domino sequence, the reaction should give access first to the C(sp) arylation event.[9] We set out to probe the validity of our design by using terminal alkynol **1a** as starting material and six equivalents of 4-bromophenyldiazonium salt **2b** under the visible light-driven optimal conditions identified earlier in our laboratory, namely, in the presence of both Gagosz's catalyst [$(Ph_3P)AuNTf_2$] and the photoactive ruthenium complex $[Ru(bpy)_3](PF_6)_2$ (bpy = 2,2'-bipyridine) (Scheme 2). In this case, the desired diarylated product **3ab** was obtained in only 35% yield (Table 1, entry 1). To improve the yield of the required diaryl adduct, other alkynic substrates were screened. To our delight, with TMS-derivative **4a** as precursor, the double arylation reaction was more efficient, giving rise to **3ab** in a great 82% yield without apparent impact on the reaction rate (Table 1, entry 2). Besides, the reaction proceeded with total stereochemical control, giving rise exclusively to the *E*-isomer. The catalyst loading of the gold salt could be reduced to 5% without considerable erosion in the reaction yield. Further reduction of the gold catalyst loading to 2% resulted in a reaction mixture which includes appreciable amounts of unreacted starting material. The reaction yield could not be improved when PPh_3AuCl was applied as catalyst (Table 1, entry 3). The use of twice (12 equiv.) as much arenediazonium salt **2b** neither did increase the yield of the target product (Table 1, entry 4), as the reaction was then complicated by chromatographic separation. It is shown that arylative Meyer–Schuster rearrangement is not in competition with the C(sp) arylation (Hiyama–Sonogashira-type coupling), because α,β-unsaturated ketone formation did not occur with the addition of just one equivalent of arenediazonium salt (Table 1, entry 5). On the other hand, sterically more demanding

TIPS greatly retarded the reaction, resulting in a low conversion with the formation of only trace amounts of **3ab** (Table 1, entry 6).

Scheme 2. Selective Gold-Photoredox Cocatalyzed Domino C(sp) Arylation/Oxyarylation of Alkynols with Arenediazonium Salts

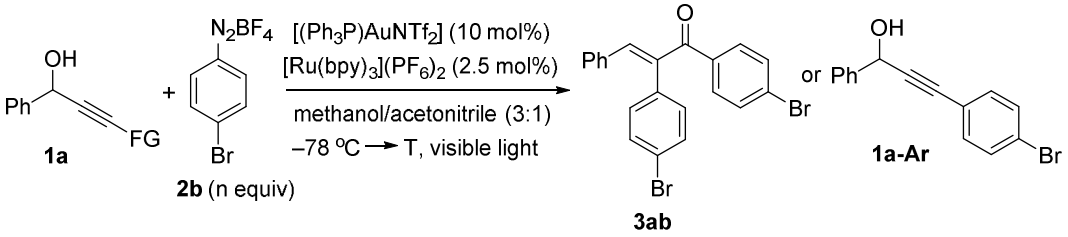


Table 1 Modified Conditions for the Gold-Photoredox Cocatalyzed Domino C(sp) Arylation/Oxyarylation of Alkynols with Arenediazonium Salts

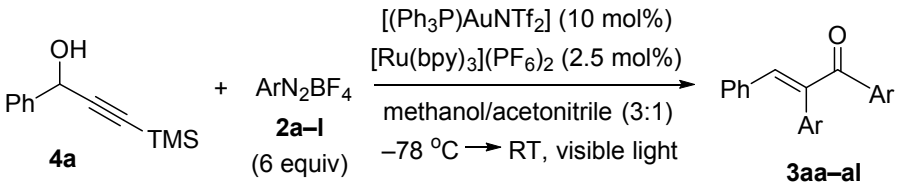
entry	FG	n	T	t (h)	yield[a]
1	H	6	RT	4	**3ab** (35%)
2	TMS	6	RT	4	**3ab** (82%)
3	TMS	6	RT	4	**3ab** (40%)[b]
4	TMS	12	RT	4	**3ab** (80%)
5	TMS	1	–20 °C	0.5	**1a-Ar** (65%)
6	TIPS	6	RT	4	**3ab** (<5%)

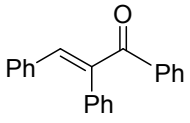
[a]Yield of pure, isolated product with correct analytical and spectral data. [a]Reaction was carried out using PPh_3AuCl as the gold catalyst.

Control experiments proved that the gold salt, the photocatalyst, and ligh are all together required for the twofold arylation sequence to proceed. With the optimized reaction conditions in hand, we examined the scope of the reaction of TMS-alkynol **4a** with differently substituted arenediazonium salts **2**. Several functional groups were well-tolerated under the reaction conditions. The products (**3aa–3al**) were obtained in moderate to good yields, and the results are summarized in Scheme 3. It is observed that

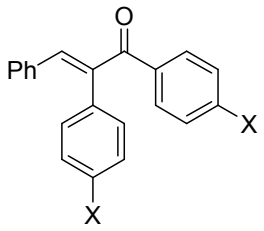
the substituent at the diazonium salts **2a–l** did exert a significant influence. It can be noted that the reaction is much efficient with neutral and somewhat electron poor arenediazonium salts. Strongly electron-withdrawing groups did afford the corresponding NO_2- and CF_3-diarylderivatives **3af** and **3ag** in low yields, while electron-donating groups such as MeO and Me (diazonium salts **2i** and **2j**) did not afford the corresponding diarylated products **3ai** and **3aj**. Additionally, the steric effect was obvious because an *ortho* bromine substituent led to a low yield of the monoarylated α,β-unsaturated ketone **5l**. Probably, the 2-bromoaryl substituent may block the second arylation step. Noteworthy, the carbon–halide bonds in **3aa–3ae** and **3ak**, which could serve as reactive handle for further manipulation, were not affected under the dual gold-photoredox conditions. Taking into account the reactivity of C–X bonds under conventional cross-coupling conditions, our protocol is a promising alternative to these classical reactions.

Scheme 3. Gold-Photoredox Cocatalyzed Domino C(sp) Arylation/Oxyarylation of Alkynol 4a with Arenediazonium Salts

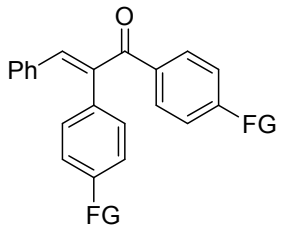




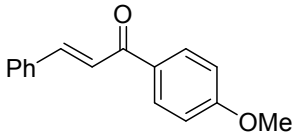
3aa (69%, 4h)



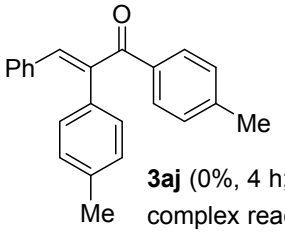
3ab (X = Br, 82%, 4 h)
3ac (X = F, 61%, 4 h)
3ad (X = I, 37%, 4 h)
3ae (X = Cl, 77%, 4 h)



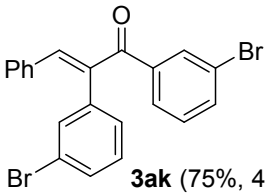
3af (FG = NO_2, 26%, 12 h)
3ag (FG = CF_3, 17%, 12 h)
3ah (FG = CO_2Et, 57%, 3 h)



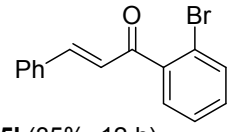
5i (42%, 5 h)



3aj (0%, 4 h; complex reaction)



3ak (75%, 4 h)

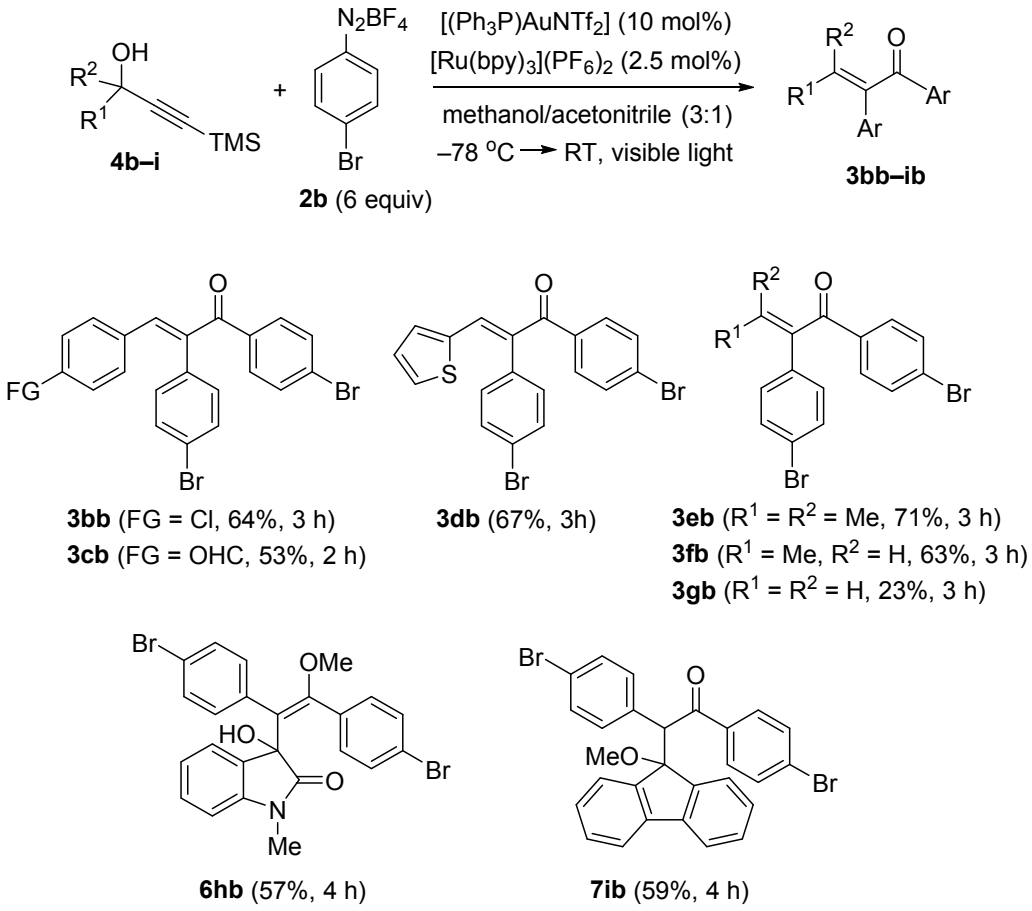


5l (35%, 12 h)

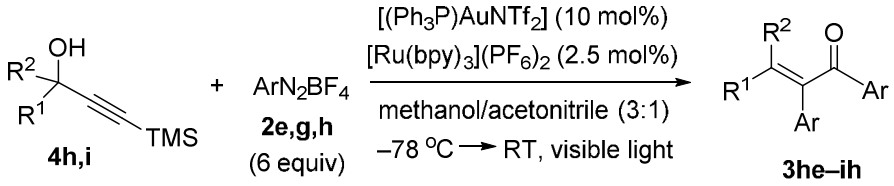
Under the optimized conditions, the scope of the arylation/oxyarylation sequence was investigated through the reaction of arenediazonium salt **2b** with various trimethylsilyl alkynols **4b–i**. Starting from functionalized TMS-alkynols bearing a variety of substituents such as the thiophene ring, the domino reaction also smoothly proceeded and gave rise to the products **3bb–3ib** in reasonable yields (Scheme 4). Noticeably, the diarylation sequence occurred with total stereoselectivity for providing single *E*-isomers. The reactions of the alkyl- or dialkyl-substituted TMS-alkynols **4e** and **4f** also efficiently took place, and the corresponding diarylated α,β-unsaturated ketones **3eb** and **3fb** were obtained in similar yields, while a low yielding reaction was

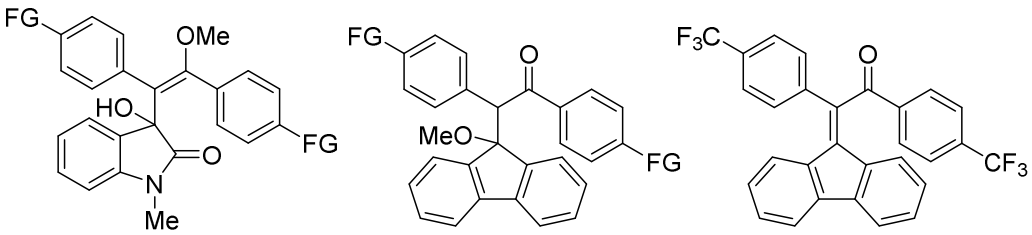
obtained from the primary alcohol counterpart. Curiously, both indolone- and fluorene-tethered TMS-alkynols **4h,i** reacted in a slightly different way than did alkynols **4a–g**, but their transformation into the corresponding products was clean. The initially obtained indolone- and fluorene-based α,β-unsaturated ketones **3hb** and **3ib** evolves under the reaction conditions to afford the allylic alcohol **6hb** and the β-alkoxy ketone **7ib**, respectively (Scheme 4). The formation of fluorene-derived adduct **7ib** must be ascribed to a Michael-type addition of the solvent to the initially obtained tetrasubstituted α,β-unsaturated ketone **3ib**, while the obtention of oxindole-derived adduct **6hb** deals with an 1,2-addition/isomerization sequence in putative ketone **3hb**. The lactam moiety should be responsible for the different evolution of ketone **3hb** in comparison with **3ib**. This general trend for indolone- and fluorene-derivatives was confirmed through the extension of the above reactions to various arenediazonium salts, as summarized in Scheme 5. The exception was the fluorene-linked CF_3-substituted α,β-unsaturated ketone **3ig**.

Scheme 4. Gold-Photoredox Cocatalyzed Domino C(sp) Arylation/Oxyarylation of Alkynols 4 with Arenediazonium Salt 2b



Scheme 5. Gold-Photoredox Cocatalyzed Domino C(sp) Arylation/Oxyarylation of Alkynols 4h,i with Arenediazonium Salts 2e,g,h





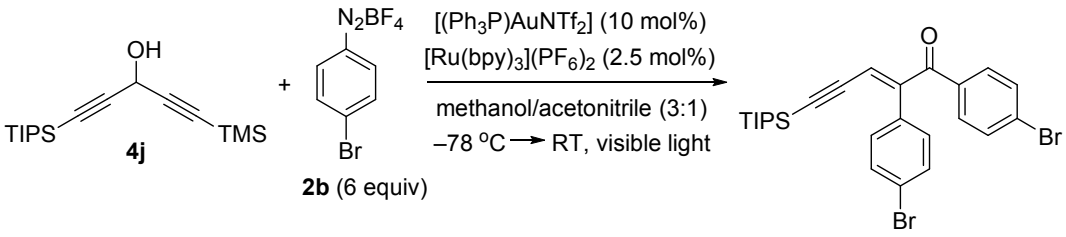
6he (FG = Cl, 45%, 4 h)
6hg (FG = CF_3, 36%, 4 h)
6hh (FG = CO_2Et, 48%, 4 h)

7ie (FG = Cl, 60%, 4 h)
7ih (FG = CO_2Et, 44%, 4 h)

3ig (49%, 4 h)

Aiming to take advantage of the inert reactivity of the triisopropylsilyl-alkyne moiety under the current dual gold-photoredox catalytic conditions in comparison with its highly reactive trimethylsilyl-alkyne counterpart, we infer that the use of a mixed TMS/TIPS-diynol **4** as starting material should afford a conjugate enynone. Indeed, the photoreaction of 1-(triisopropylsilyl)-5-(trimethylsilyl)penta-1,4-diyn-3-ol **4j** produced good results and exquisite chemoselectivity in favor of the TMS-alkyne with the TIPS-alkyne remaining unaltered in (*E*)-1,2-bis(4-bromophenyl)-5-(triisopropylsilyl)pent-2-en-4-yn-1-one **3jb** (Scheme 6).[10]

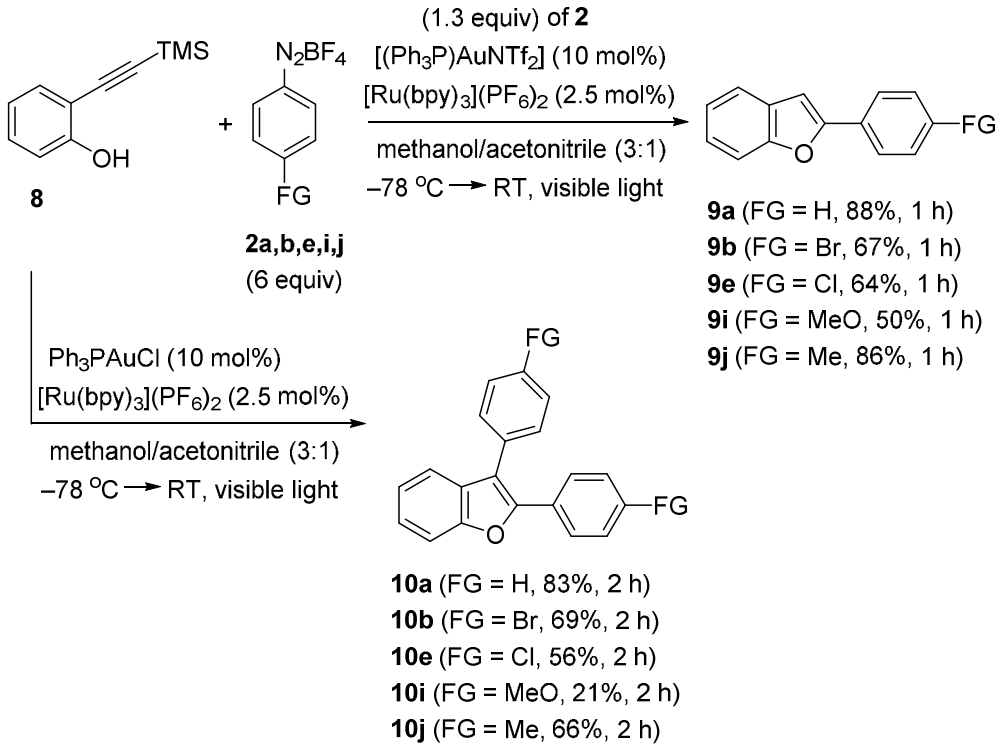
Scheme 6. Chemoselective Gold-Photoredox Cocatalyzed Domino C(sp) Arylation/Oxyarylation of Diynol 4j with Arenediazonium Salt 2b



3jb (44%, 2 h)

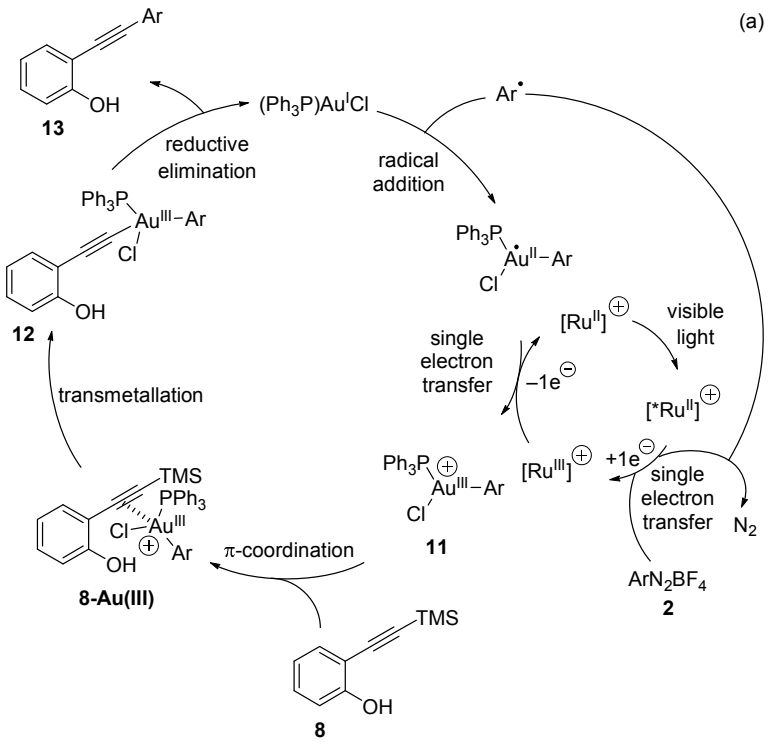
Next, aiming to generate 2,3-diarylbenzofurans we moved to a different type of TMS-alkynol, namely, the 2-[(trimethylsilyl)ethynyl]phenol **8**.[11] Surprisingly, the reaction of TMS-alkynol **8** with various arenediazonium salts **2** under the above optimized conditions using Gagosz's catalyst[12] generated mostly or exclusively the monoarylated 2-arylbenzofurans **9** (Scheme 7), depending on the amount (6 equiv or 1.3 equiv) of diazonium salt **2**.[13] Interestingly, moving to Ph_3PAuCl under otherwise identical conditions allows introducing two aryl motifs in the skeleton of the benzofuran adduct, which grants a divergent preparation of both 2-arylbenzofurans **9** and 2,3-diarylbenzofurans **10** (Scheme 7). The superior performance of Ph_3PAuCl in comparison with $[(Ph_3P)AuNTf_2]$ pointed out to a competitive hydrofunctionalization which overrides the oxyarylation step for the Gagosz's catalyst case.[14] The initial event was the C(sp) arylation reaction of the TMS terminated alkyne, which is preferred over the further oxycyclization step under these dual gold/photoredox-catalyzed conditions.

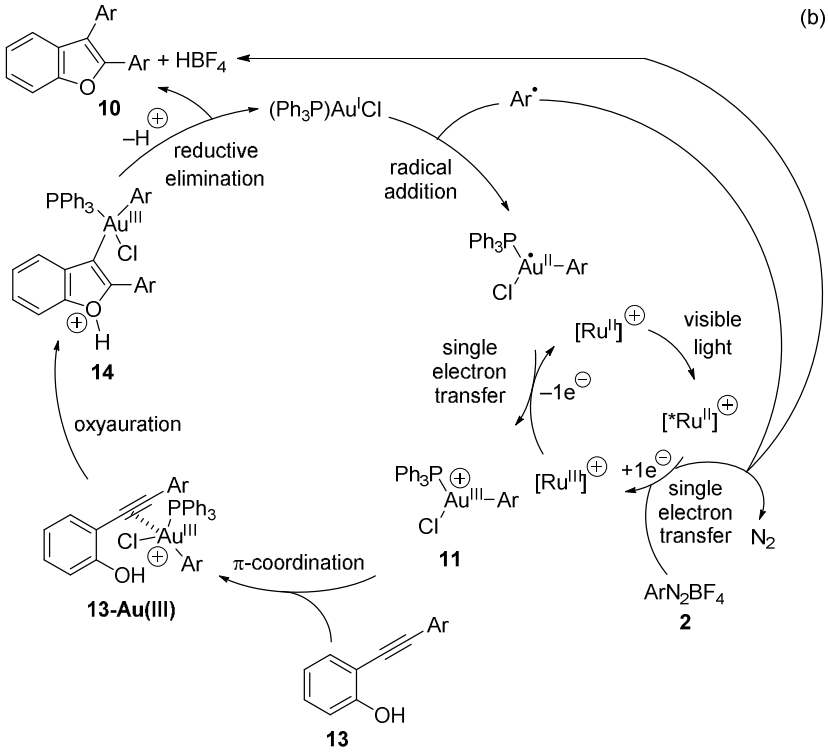
Scheme 7. Gold-Photoredox Cocatalyzed C(sp) Arylation and Domino C(sp) Arylation/Oxyarylation of Alkynol 8 with Arenediazonium Salts 2a,b,e,i,j



A conceivable mechanistic proposal[15] that rationalizes the formation of adducts **10** is shown in Scheme 8. Initially, an aryl radical is formed from the corresponding arenediazonium salt **2** through a single electron transfer (SET) process involving both light and the photoredox catalyst. The so-generated highly reactive radical is added to the gold (I) complex, which after consecutive radical addition to the metallic center and single electron oxidation gives rise to arylgold(III) species **11**. Next, the TMS-terminated alkynol **8** comes into the gold-catalyzed cycle giving rise to the complex **8**-Au(III), which after Si–Au transmetallation generates gold acetylides **12**. Reductive elimination with concomitant aryl transfer delivers intermediate aryl alkynes **13** and releases the gold(I) precatalyst (Scheme 8a). The conversion of alkynes **13** into 2,3-diarylbenzofurans **10** again should require as first event the formation of arylgold(III) species **11** as above, followed by a) alkyne activation through gold π-coordination, b) 5-*endo* oxyauration, and c) reductive elimination associated to deprotonation (Scheme 8b).

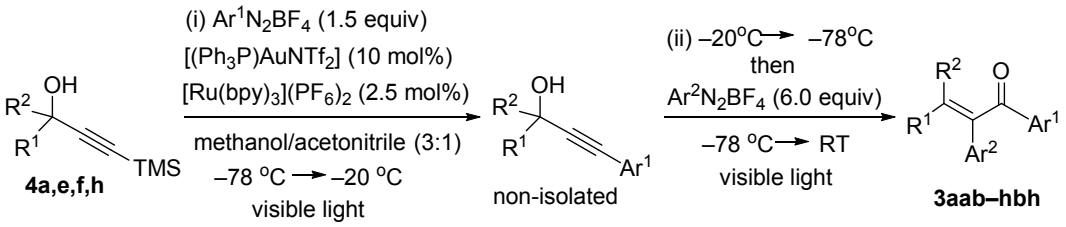
Scheme 8. Mechanistic Outline for the Gold-Photoredox Cocatalyzed C(sp) Arylation and Domino C(sp) Arylation/Oxyarylation of Alkynol 8 with Arenediazonium Salts 2

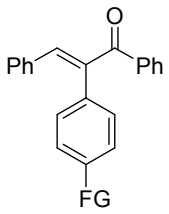




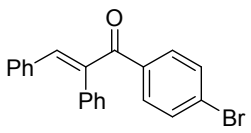
To add value to the proposed synthetic sequence and gain access to adducts bearing two different aryl groups, the crossover experiment of TMS-alkynol **4a** was designed with two similar arenediazonium salts, **2a** and **2b**. As expected, crossover products **4aab** and **4aba** together with adducts **4aa** and **4ab** were observed, supporting the formation of 3-aryl-1-phenylprop-2-yn-1-ol intermediates. In order to selectively obtain cross-adducts, this quickly and in situ generated aryl-1-phenylprop-2-yn-1-ols then should undergo a selective cross-oxyarylation with a different arenediazonium salt. After some experimentation, we managed to furnish cross-coupled adducts as exclusive products in one-pot when both 1.5 equiv of the first diazonium salt and temperature control were used. This cross sequence has a reasonable substrate scope and differently arylated α,β-unsaturated ketones were obtained (Scheme 9). In this case, α,β-unsaturated ketone-linked oxindoles **3hae** and **3hbh** were obtained as the sole reaction products.

Scheme 9. Gold-Photoredox Cocatalyzed Domino Cross C(sp) Arylation/Oxyarylation of Alkynols 4a,e,f,h with Arenediazonium Salts 2a,b,e,h

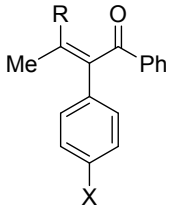




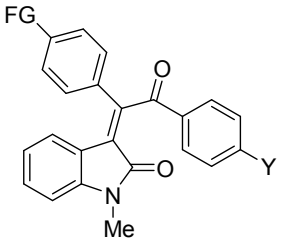
3aab (FG = Br, 46%, (i) 10 min, (ii) 4 h)
3aae (FG = Cl, 41%, (i) 10 min, (ii) 4 h)
3aah (FG = CO_2Et, 53%, (i) 10 min, (ii) 6 h)



3aba (37%, (i) 10 min, (ii) 4 h)



3eab (R = Me, X = Br, 56%, (i) 10 min, (ii) 5 h)
3fae (R = H, X = Cl, 49%, (i) 10 min, (ii) 5 h)



3hae (FG = Cl, Y = H, 36%, (i) 30 min, (ii) 2 h)
3hbh (FG = CO_2Et, Y = Br, 41%, (i) 30 min, (ii) 2 h)

CONCLUSIONS

In conclusion, the controlled preparation of polysubstituted α,β-unsaturated ketones and 2,3-diarylbenzofurans has been accomplished through light promoted dual gold-photoredox cocatalysis starting from 3-(trimethylsilyl)prop-2-yn-1-ols and 2-[(trimethylsilyl)ethynyl]phenol, respectively. The double arylation reaction was not effective using terminal alkynes or TIPS-terminated alkynes as precursors.

EXPERIMENTAL SECTION

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on 300, 500, or 700 MHz spectrometers. NMR spectra were recorded in $CDCl_3$ solutions, except

otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), $CDCl_3$ (^{13}C, 76.9 ppm) and C_6D_6, (^{13}C, 128.4 ppm). Low and high resolution mass spectra were performed on a QTOF LC–MS spectrometer using the electrospray mode (ES) unless otherwise stated. All commercially available compounds were used without further purification. Flash chromatography was performed by using silica gel 60 (230−400 mesh) or neutral alumina. Products were identified by TLC (silica gel). UV light (λ = 254nm) and a solution of phosphomolybdic acid in EtOH (1 g of phosphomolybdic acid hydrate, 100 mL EtOH) was used to develop the plates.

Alkynols 4a, 4b, 4d–g, 4i, 4j, 4a-TIPS and 8 were prepared by known literature procedures.[16]

Procedure for the preparation of alkynol 4c. n-BuLi (1.4 mol, 2.5 M solution in hexane) was added to a solution of trimethylsilylacetylene (1.3 mol) in THF (2.1 mL) cooled at –78 ˚C. The mixture was allowed to warm to room temperature and it was stirred for 1 h at rt. The mixture was cooled at –78 ˚C and then it was added dropwise to a solution of the appropriate aldehyde (1.3 equiv.) in THF (1.6 mL) at –78 ˚C. The reaction mixture was warmed up to room temperature and stirred overnight at rt, before being quenched with NH_4Cl (aq. sat.). The aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography of the residue on silica gel gave analytically pure compound **4c**.

Alkynol 4c. From 100 mg (0.74 mmol) of terephthalaldehyde, and after chromatography of the residue using hexanes/dichloromethane (1:1→0:1) as eluent, gave compound **4c** (72 mg, 42%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 10.0 (s, 1H), 7.89 (m, 2H), 7.71 (m, 2H), 5.53 (s, 1H), 2.75 (s, 1H), 0.20 (s, 9H); ^{13}C

NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 192.0, 146.7, 136.1, 130.0 (2C), 127.1 (2C), 104.0, 92.4, 64.3, –0.30 (3C); IR ($CHCl_3$, cm^{-1}): ν 3440, 2173, 1700; HRMS (ES): calcd for $C_{13}H_{15}O_2Si$ $[M - H]^+$: 231.0836; found: 231.0851.

Procedure for the preparation of alkynol 4h. n-BuLi (1.4 mol, 2.5 M solution in hexane) was added to a solution of trimethylsilylacetylene (1.3 mol) in THF (2.1 mL) cooled at –78 ˚C. The mixture was allowed to warm to room temperature and it was stirred for 1 h at rt. The mixture was cooled at –78 ˚C and then a solution of the appropriate ketone (1.3 equiv.) in THF (1.6 mL) was added dropwise. The reaction mixture was warmed up to room temperature and stirred overnight at rt, before being quenched with NH_4Cl (aq. sat.). The aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography of the residue on silica gel gave analytically pure compound **4h**.

Alkynol 4h. From 300 mg (1.86 mmol) of 1-methylisatin, and after chromatography of the residue using hexanes/ethyl acetate (8:2→1:1) as eluent, gave compound **4h** (301 mg, 62%) as a yellow solid; m.p. 178–180ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.54 (m, 1H), 7.37 (m, 1H), 7.14 (m, 1H), 6.84 (m, 1H), 3.21 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 173.6, 143.1, 130.4, 128.7, 124.6, 123.7, 108.7, 100.9, 92.1, 69.3, 26.6, 0.39 (3C); IR ($CHCl_3$, cm^{-1}): ν 3319, 2165, 1713; HRMS (ES): calcd for $C_{14}H_{18}NO_2Si$ $[M + H]^+$: 260.1101; found: 260.1093.

General procedure for the dual gold-photoredox twofold arylation reaction of TMS-alkynols 4a–j and diazonium salts 2a–l. Preparation of diarylated α,β-unsaturated ketones 3aa–3jb, allylic alcohols 6hb–6hh and β-alkoxy ketones 7ib–-7ih. In a Schlenk tube in the absence of light at –78 ºC under argon atmosphere,

[$(Ph_3P)AuNTf_2$] (10 mol %) and [$Ru(bpy)_{3]}(PF_6)_2$ (2.5 mol %) were sequentially added to a solution of the corresponding arene diazonium salt **2** (6.0 equiv) in a mixture of MeOH/MeCN (3:1, 5.0 mL). Then, a solution of the appropriate TMS-alkynol **4** (1.0 mmol) in MeOH/MeCN (3:1, 2.5 mL) was added dropwise and the reaction was stirred at –78 ºC for 5 min. The reaction mixture was then warmed to room temperature and stirred under irradiation from visible light source (21 W fluorescent light bulb installed in a tool box). After disappearance of the starting material (TLC), the reaction mixture was concentrated under reduced pressure. Chromatography of the residue using hexanes/ethyl acetate or hexanes/toluene mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of compounds **3**, **6**, and **7** follow.

Diarylated α,β-unsaturated ketone 3aa. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (1:1) as eluent, gave compound **3aa** (19 mg, 69%) as a colorless solid; m.p. 99–101ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.89 (m, 2H), 7.50 (m, 3H), 7.29 (m, 9H), 7.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 197.6, 140.7, 140.2, 138.1, 136.4, 134.7, 132.1, 130.3 (2C), 129.7 (2C), 129.6 (2C), 128.9, 128.7 (2C), 128.3 (2C), 128.2 (2C), 127.9; IR ($CHCl_3$, cm^{-1}): ν 1652 (C=O); HRMS (ES): calcd for $C_{21}H_{17}O$ $[M + H]^+$: 285.1274; found: 285.1275.

Diarylated α,β-unsaturated ketone 3ab. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/acetate (95:5) as eluent, gave compound **3ab** (36 mg, 82%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.62 (m, 2H), 7.52 (m, 2H), 7.42 (m, 2H), 7.17 (m, 4H), 7.06 (m, 2H), 7.02 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.1, 141.3, 139.1, 136.7, 135.1, 134.1, 132.1 (2C), 131.7 (2C), 131.4 (2C), 131.2 (2C), 130.3 (2C), 129.4, 128.5 (2C), 127.3,

122.4; IR ($CHCl_3$, cm^{-1}): ν 1654; HRMS (ES): calcd for $C_{21}H_{15}OBr_2$ $[M + H]^+$: 440.9484; found: 440.9467.

Diarylated α,β-unsaturated ketone 3ac. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (4:6) as eluent, gave compound **3ac** (19 mg, 61%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.89 (m, 2H), 7.23 (m, 6H), 7.10 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.0, 165.2 (d, J_{CF} = 254.0 Hz), 165.2 (d, J_{CF} = 247.7 Hz), 140.4, 139.4, 134.4, 134.1 (d, J_{CF} = 3.08 Hz), 132.3 (d, J_{CF} = 9.2 Hz, 2C), 132.2 (d, J_{CF} = 3.78 Hz), 131.5 (d, J_{CF} = 8.1 Hz, 2C), 130.3 (2C), 129.2, 128.4 (2C), 116.0 (d, J_{CF} = 21.5 Hz, 2C), 115.5 (d, J_{CF} = 21.8 Hz, 2C); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^oC): δ = –106.4 (s, 1F), –113.7 (s, 1F); IR ($CHCl_3$, cm^{-1}): ν 1654; HRMS (ES): calcd for $C_{21}H_{15}OF_2$ $[M + H]^+$: 321.1086; found: 321.1097.

Diarylated α,β-unsaturated ketone 3ad. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/acetate (95:5) as eluent, gave compound **3ad** (20 mg, 37%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.82 (m, 2H), 7.70 (m, 2H), 7.54 (m, 2H), 7.22 (m, 4H), 7.10 (m, 2H), 7.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.3, 141.3, 139.2, 138.0 (2C), 137.7 (2C), 137.2, 135.7, 134.2, 131.6 (2C), 131.1 (2C), 130.3 (2C), 129.4, 128.5 (2C), 99.9, 94.1; IR ($CHCl_3$, cm^{-1}): ν 1655; HRMS (ES): calcd for $C_{21}H_{14}OI_2Na$ $[M + Na]^+$: 558.9026; found: 558.9021.

Diarylated α,β-unsaturated ketone 3ae. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (8:2) as eluent, gave compound **3ae** (27 mg, 77%) as a colorless solid; m.p. 124–126ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.79 (m, 2H), 7.44 (m, 2H), 7.35 (m, 2H), 7.23 (m, 6H), 7.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.0, 141.2, 139.2, 138.7, 136.2, 134.6, 134.2, 134.1, 131.1 (4C), 130.3 (2C), 129.4, 129.1 (2C), 128.7 (2C), 128.4

(2C); IR ($CHCl_3$, cm^{-1}): ν 1652; HRMS (ES): calcd for $C_{21}H_{15}OCl_2$ $[M + H]^+$: 353.0494; found: 353.0488.

Diarylated α,β-unsaturated ketone 3af. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/acetate (8:2) as eluent, gave compound **3af** (10 mg, 26%) as a yellow oil; ^1H NMR (500 MHz, $CDCl_3$, 25 ^oC) δ: 8.36 (m, 2H), 8.27 (m, 2H), 7.97 (m, 2H), 7.48 (m, 2H), (s, 1H), 7.33 (m, 1H,), 7.25 (m, 2H), 7.25 (m, 2H), 7.05 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ: 194.7, 149.8, 147.7, 145.2, 143.3, 142.6, 138.0, 133.1, 131.0 (2C), 130.6 (2C), 130.5, 130.3 (2C), 128.8 (2C), 124.1 (2C), 123.7 (2C); IR ($CHCl_3$, cm^{-1}): ν 1647, 1519, 1347; HRMS (ES): calcd for $C_{21}H_{15}O_5N_2$ $[M + H]^+$: 375.0975; found: 375.0965.

Diarylated α,β-unsaturated ketone 3ag. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (8:2→7:3) as eluent, gave compound **3ag** (7 mg, 17%) as a colorless oil; ^1H NMR (700 MHz, $CDCl_3$, 25 ^oC) δ: 7.94 (m, 2H), 7.76 (m, 2H), 7.66 (m, 2H), 7.42 (m, 2H), 7.36 (s, 1H), 7.30 (m, 1H), 7.23 (m, 2H), 7.06 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$, 25 ºC) δ: 195.9, 143.2, 141.2, 139.7, 138.9, 133.7, 133.6 (q, J_{CF} = 32.6 Hz), 130.5 (2C), 130.3 (q, J_{CF} = 32.3 Hz), 130.2 (2C), 129.9, 129.8 (2C), 128.6 (2C), 125.8 (2C), 125.5 (2C), 124.0 (q, J_{CF} = 271.9 Hz), 123.6 (q, J_{CF} = 272.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^oC): δ = –62.9 (s, 3F), –63.3 (s, 3F); IR ($CHCl_3$, cm^{-1}): ν 1659, 1325; HRMS (ES): calcd for $C_{23}H_{15}OF_6$ $[M + H]^+$: 421.1022; found: 421.1006.

Diarylated α,β-unsaturated ketone 3ah. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (4:6) as eluent, gave compound **3ah** (24 mg, 57%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 8.12 (m, 2H), 8.05 (m, 2H), 7.85 (m, 2H), 7.36 (m, 3H), 7.23 (m, 3H), 7.06 (m, 2H), 4.40 (m, 4H), 1.42 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.4, 166.3, 165.8, 142.7, 141.8, 140.1, 139.6, 134.0, 133.4, 130.5 (2C), 130.0 (2C), 129.9

(2C), 129.7, 129.5 (2C), 129.3 (2C), 128.5 (2C), 61.4, 61.1, 14.4, 14.3; IR ($CHCl_3$, cm^{-1}): ν 1719, 1654; HRMS (ES): calcd for $C_{27}H_{25}O_5$ $[M + H]^+$: 429.1697; found: 429.1703.

Diarylated α,β-unsaturated ketone 3ak. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (1:1) as eluent, gave compound **3ak** (33 mg, 75%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.98 (m, 1H), 7.75 (m, 1H), 7.70 (m, 1H), 7.50 (m, 1H), 7.45 (m, H), 7.36 (m, H), 7.27 (m, 2H), 7.45 (m, 4H), 7.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 195.5, 142.3, 139.9, 138.7, 138.1, 135.1, 133.9, 132.5, 132.4, 131.2, 130.5 (2C), 130.4, 129.9, 129.7, 128.5 (2C), 128.4, 128.2, 122.8, 122.7; IR ($CHCl_3$, cm^{-1}): ν 1654; HRMS (ES): calcd for $C_{21}H_{15}OBr_2$ $[M + H]^+$: 440.9484; found: 440.9483.

Diarylated α,β-unsaturated ketone 3bb. From 24 mg (0.10 mmol) of TMS-alkynol **4b**, and after chromatography of the residue using hexanes/toluene (75:15) as eluent, gave compound **3bb** (30 mg, 64%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.69 (m, 2H), 7.60 (m, 2H), 7.50 (m, 2H), 7.20 (m, 3H), 7.13 (m, 2H), 7.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 195.7, 139.7, 139.5, 136.4, 135.3, 134.7, 132.6, 132.2 (2C), 131.7 (2C), 131.5 (2C), 131.3 (2C), 131.2 (2C), 128.8 (2C), 127.5, 122.6; IR ($CHCl_3$, cm^{-1}): ν 1655; HRMS (ES): calcd for $C_{21}H_{14}OBr_2Cl$ $[M + H]^+$: 474.9094; found: 474.9109.

Diarylated α,β-unsaturated ketone 3cb. From 23 mg (0.10 mmol) of TMS-alkynol **4c**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent, gave compound **3cb** (35 mg, 53%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 9.97 (s, 1H), 7.73 (m, 4H), 7.61 (m, 2H), 7.50 (m, 2H), 7.27 (m, 2H), 7.24 (s, 1H), 7.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 195.5, 191.4, 141.7,

140.3, 138.1, 136.1, 135.9, 134.3, 132.3 (2C), 131.8 (2C), 131.3 (2C), 131.2 (2C), 130.6 (2C), 129.6 (2C), 127.9, 122.9; IR ($CHCl_3$, cm^{-1}): ν 1699, 1655; HRMS (ES): calcd for $C_{22}H_{15}Br_2O_2$ $[M + H]^+$: 468.9433; found: 468.9442.

Diarylated α,β-unsaturated ketone 3db. From 21 mg (0.10 mmol) of TMS-alkynol **4d**, and after chromatography of the residue using hexanes/toluene (6:4) as eluent, gave compound **3db** (30 mg, 67%) as a yellow oil; ^1H NMR (300 MHz, C_6D_6, 25 ^oC) δ: 7.49–7.43 (m, 5H), 7.28 (d, 2H, J = 8.4 Hz), 7.03 (d, 2H, J = 8.4 Hz), 6.72 (dd, 1H, J = 13.8 Hz, J = 5.1 Hz), 6.55 (dd, 1H, J = 5.1 Hz, J = 3.7 Hz); ^{13}C NMR (75 MHz, C_6D_6, 25 ºC) δ: 193.7, 138.5 (2C), 137.6, 136.6, 135.1, 133.8, 132.7 (2C), 132.3 (2C), 131.8 (2C), 131.2 (2C), 131.1, 126.9, 126.8, 123.3; IR ($CHCl_3$, cm^{-1}): ν 1689; HRMS (ES): calcd for $C_{19}H_{13}Br_2OS$ $[M + H]^+$: 446.9048; found: 446.9041.

Diarylated α,β-unsaturated ketone 3eb. From 16 mg (0.10 mmol) of TMS-alkynol **4e**, and after chromatography of the residue using toluene as eluent, gave compound **3eb** (28 mg, 71%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.79 (d, 2H, J = 8.8 Hz), 7.56 (d, 2H, J = 8.8 Hz), 7.44 (d, 2H, J = 8.7 Hz), 7.15 (d, 2H, J = 8.7 Hz), 1.87 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 197.3, 137.2, 135.8, 135.5, 135.2, 132.1 (2C), 131.7 (2C), 131.1 (2C), 130.9 (2C), 128.6, 121.5, 22.7, 21.4; IR ($CHCl_3$, cm^{-1}): ν 1658; HRMS (ES): calcd for $C_{17}H_{15}Br_2O$ $[M + H]^+$: 392.9484; found: 392.9498.

Diarylated α,β-unsaturated ketone 3fb. From 14 mg (0.10 mmol) of TMS-alkynol **4f**, and after chromatography of the residue using hexanes/toluene (6:4) as eluent, gave compound **3fb** (24 mg, 63%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.63–7.57 (m, 4H), 7.53 (d, 2H, J = 8.6 Hz), 7.12 (d, 2H, J = 8.6 Hz), 6.63 (q, 1H, J = 7.3 Hz), 1.88 (d, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 195.6,

141.6, 141.0, 136.9, 134.3, 131.6 (2C), 131.6 (2C), 131.3 (2C), 131.1 (2C), 127.0, 121.9, 15.7; IR ($CHCl_3$, cm^{-1}): ν 1655; HRMS (ES): calcd for $C_{16}H_{13}Br_2O$ $[M + H]^+$: 378.9328; found: 378.9339.

Diarylated α,β-unsaturated ketone 3gb. From 13 mg (0.10 mmol) of TMS-alkynol **4g**, and after chromatography of the residue using toluene as eluent, gave compound **3gb** (9 mg, 23%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.74 (d, 2H, J = 8.6 Hz), 7.59 (d, 2H, J = 8.6 Hz), 7.49 (d, 2H, J = 8.6 Hz), 7.28 (d, 2H, J = 8.6 Hz), 6.10 (s, 1H), 5.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 195.9, 146.9, 136.6, 136.5, 131.9 (2C), 131.4 (2C), 128.7 (2C), 128.5, 122.9, 122.2; IR ($CHCl_3$, cm^{-1}): ν 1685; HRMS (ES): calcd for $C_{15}H_{11}Br_2O$ $[M + H]^+$: 364.9171; found: 364.9173.

Diarylated α,β-unsaturated ketone 3ig. From 28 mg (0.10 mmol) of TMS-alkynol **4i**, and after chromatography of the residue using hexanes/toluene (8:2) as eluent, gave compound **3ig** (24 mg, 49%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 8.27 (d, 2H, J = 8.2 Hz), 7.77–7.69 (m, 8H), 7.37–7.33 (m, 2H), 7.20 (d, 1H, J = 8.0 Hz), 7.06–7.00 (m, 2H), 6.67 (d, 1H, J = 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.0, 141.4, 140.9, 139.3, 137.6, 137.3, 136.4, 136.4, 135.8, 135.4, 131.1, 130.3 (2C), 129.7 (2C), 129.6, 129.5, 127.5, 127.2, 126.4 (2C), 126.3 (2C), 125.3, 124.9, 123.8 (q, J_{CF} = 270 Hz), 123.4 (q, J_{CF} = 270 Hz), 120.0, 119.9; ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^oC): δ = –63.0 (s, 3F), –63.5 (s, 3F); IR ($CHCl_3$, cm^{-1}): ν 1643, 1612; HRMS (ES): calcd for $C_{29}H_{17}F_6O$ $[M + H]^+$: 495.1178; found: 495.1184.

Diarylated α,β-unsaturated ketone 3jb. From 31 mg (0.10 mmol) of TMS-alkynol **4j**, and after chromatography of the residue using hexanes/toluene (8:2) as eluent, gave compound **3jb** (24 mg, 44%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.65 (m, 2H), 7.57 (m, 2H), 7.48 (s, 4H), 6.35 (s, 1H), 1.04 (m, 21H); ^{13}C

NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 195.1, 148.1, 135.8, 134.0, 131.8 (2C), 131.4 (2C), 131.3 (2C), 130.8 (2C), 128.1, 122.9, 118.7, 106.8, 102.6, 18.5 (6C), 11.2 (3C); IR ($CHCl_3$, cm^{-1}): ν 1662; HRMS (ES): calcd for $C_{26}H_{31}OBr_2Si$ $[M + H]^+$: 545.0505; found: 545.0469.

Diarylated α,β-unsaturated ketone 6hb. From 26 mg (0.10 mmol) of TMS-alkynol **4h**, and after chromatography of the residue using hexanes/ethyl acetate (7:3) as eluent, gave compound **6hb** (30 mg, 57%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.33–7.26 (m, 6H), 7.06 (d, 1H, J = 7.1 Hz), 7.02 (d, 2H, J = 8.2 Hz), 6.92 (d, 2H, J = 8.2 Hz), 6.84 (d, 1H, J = 7.1 Hz), 3.73 (s, 1H), 3.25 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 177.0, 153.6, 143.9, 134.2, 133.7 (2C), 132.0, 131.5 (2C, 131.4, 131.2 (2C), 131.0 (2C), 129.6, 124.0, 123.8, 122.9, 122.6, 121.6, 108.2, 77.0, 57.1, 26.3; IR ($CHCl_3$, cm^{-1}): ν 3360, 1610; HRMS (ES): calcd for $C_{24}H_{19}Br_2NNaO_3$ $[M + Na]^+$: 549.9624; found: 549.9632.

Diarylated α,β-unsaturated ketone 6he. From 26 mg (0.10 mmol) of TMS-alkynol **4h**, and after chromatography of the residue using hexanes/ethyl acetate (7:3) as eluent, gave compound **6he** (20 mg, 45%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC) δ: 7.33 (td, 1H, J = 7.1 Hz, J = 1.3 Hz), 7.28 (d, 1H, J = 7.1 Hz), 7.15 (d, 2H, J = 8.3 Hz), 7.12 (d, 2H, J = 8.2 Hz), 7.08 (d, 2H, J = 8.2 Hz), 7.04 (d, 1H, J = 7.2 Hz), 6.99 (d, 2H, J = 8.3 Hz), 6.84 (d, 1H, J = 7.1 Hz), 3.76 (s, 1H), 3.25 (s, 3H), 3.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 177.0, 153.6, 143.9, 134.2, 133.9, 133.3 (2C), 133.3, 131.5, 131.4, 131.2 (2C), 129.5, 128.2 (2C), 128.0 (2C), 123.8, 123.8, 122.9, 108.2, 77.0, 57.2, 26.2; IR ($CHCl_3$, cm^{-1}): ν 3363, 1611; HRMS (ES): calcd for $C_{24}H_{19}Cl_2NNaO_3$ $[M + Na]^+$: 462.0634; found: 462.0636.

Diarylated α,β-unsaturated ketone 6hg. From 26 mg (0.10 mmol) of TMS-alkynol **4h**, and after chromatography of the residue using hexanes/ethyl acetate (7:3) as eluent, gave compound **6hg** (18 mg, 36%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.45 (d, 2H, *J* = 8.2 Hz), 7.40 (d, 2H, *J* = 8.2 Hz), 7.35 (t, 1H, *J* = 7.2 Hz), 7.30 (d, 2H, *J* = 8.2 Hz), 7.26 (d, 1H, *J* = 7.1 Hz), 7.16 (d, 2H, *J* = 8.2 Hz), 7.07 (t, 1H, *J* = 7.2 Hz), 6.87 (d, 1H, *J* = 7.4 Hz), 3.54 (s, 1H), 3.28 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 176.9, 153.4, 144.0, 139.0, 136.6, 132.5 (2C), 131.2, 130.3, 129.8 (2C), 129.4, 125.2, 125.0 (2C), 124.7 (2C), 123.9 (q, J_{CF} = 270 Hz, CF_3), 123.8, 123.4 (q, J_{CF} = 270 Hz, CF_3), 123.0 (2C), 108.4, 77.0, 57.3, 26.3; ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –62.9 (s, 3F), –63.2 (s, 3F); IR ($CHCl_3$, cm^{-1}): ν 3365, 1614; HRMS (ES): calcd for $C_{26}H_{20}F_6NO_3$ $[M + H]^+$: 508.1342; found: 508.1357.

Diarylated α,β-unsaturated ketone 6hh. From 26 mg (0.10 mmol) of TMS-alkynol **4h**, and after chromatography of the residue using hexanes/ethyl acetate (7:3) as eluent, gave compound **6hh** (25 mg, 48%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.82–7.76 (m, 4H), 7.33–7.25 (m, 2H), 7.21 (d, 2H, *J* = 8.3 Hz), 7.11 (d, 2H, *J* = 8.2 Hz), 7.03 (t, 1H, *J* = 7.4 Hz), 6.83 (d, 1H, *J* = 7.1 Hz), 4.33–4.28 (m, 4H), 3.24 (s, 3H), 3.14 (s, 3H), 1.32-1.39 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 177.0, 166.2, 165.8, 153.8, 143.9, 140.2, 137.5, 131.0 (2C), 131.2, 130.2, 129.8 (2C), 129.5, 129.2, 129.0 (2C), 128.8 (2C), 125.1, 124.0, 122.8, 108.3, 77.1, 61.0, 61.0 (2C), 57.2, 26.2, 14.2 (2C); IR ($CHCl_3$, cm^{-1}): ν 3368, 1680, 1614; HRMS (ES): calcd for $C_{30}H_{29}NNaO_7$ $[M + Na]^+$: 538.1836; found: 538.1833.

Diarylated α,β-unsaturated ketone 7ib. From 28 mg (0.10 mmol) of TMS-alkynol **4i**, and after chromatography of the residue using hexanes/toluene (8:2) as eluent, gave compound **7ib** (32 mg, 59%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$,

25 °C) δ: 7.78–7.72 (m, 3H), 7.54–7.50 (m, 4H), 7.37–7.25 (m, 5H), 7.14 (d, 2H, *J* = 8.4 Hz), 6.85 (d, 2H, *J* = 8.4 Hz), 5.42 (s, 1H), 2.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.6, 143.7, 142.3, 141.6 (2C), 141.3, 137.2, 132.4, 132.0 (2C), 131.7 (2C), 130.6 (2C), 130.0 (2C), 129.3, 127.9, 127.2, 127.1, 126.4, 124.6, 121.8, 119.9, 119.7, 90.1, 59.7, 51.5; IR ($CHCl_3$, cm^{-1}): ν 1655; HRMS (ES): calcd for $C_{28}H_{20}Br_2NaO_2$ [*M* + Na]$^+$: 570.9704; found: 570.9714.

Diarylated α,β-unsaturated ketone 7ie. From 28 mg (0.10 mmol) of TMS-alkynol **4i**, and after chromatography of the residue using hexanes/toluene (6:4) as eluent, gave compound **7ie** (27 mg, 60%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.78 (d, 2H, *J* = 8.4 Hz), 7.68 (d, 1H, *J* = 7.3 Hz), 7.43 (d, 2H, *J* = 7.3 Hz), 7.18-7.30 (m, 7H), 6.90 (d, 2H, *J* = 8.4 Hz), 6.84 (d, 2H, *J* = 8.4 Hz), 5.36 (s, 1H), 2.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.5, 143.7, 142.3, 141.7, 141.3, 139.2, 136.7, 133.5, 132.0, 131.7 (2C), 130.0 (2C), 129.3 (2C), 128.8 (2C), 127.7 (2C), 127.2, 127.2, 125.6, 124.6, 119.9, 119.8, 90.2, 59.7, 51.6; IR ($CHCl_3$, cm^{-1}): ν 1644; HRMS (ES): calcd for $C_{28}H_{20}Cl_2NaO_2$ [*M* + Na]$^+$: 481.0732; found: 481.0747.

Diarylated α,β-unsaturated ketone 7ih. From 28 mg (0.10 mmol) of TMS-alkynol **4i**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent, gave compound **7ih** (23 mg, 44%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.96 (d, 2H, *J* = 8.4 Hz), 7.87 (d, 2H, *J* = 8.4 Hz), 7.69 (d, 2H, *J* = 7.0 Hz), 7.60 (d, 2H, *J* = 8.4 Hz), 7.41 (d, 2H, *J* = 8.1 Hz), 7.18-7.30 (m, 5H), 6.98 (d, 2H, *J* = 8.2 Hz), 5.51 (s, 1H), 4.31 (q, 2H, *J* = 7.0 Hz), 4.22 (q, 2H, *J* = 7.0 Hz), 1.32 (t, 3H, *J* = 7.0 Hz), 1.27 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 197.2, 166.4, 165.7, 143.5, 142.2, 141.8, 141.6, 141.3, 138.4, 133.8, 130.4 (2C), 129.6 (2C), 129.5, 129.4 (2C), 128.7 (2C), 128.4 (2C), 127.3, 127.2, 126.5, 124.6, 119.9, 119.8, 90.3, 60.9,

60.8, 60.8, 51.5, 14.3 (2C); IR ($CHCl_3$, cm^{-1}): ν 1660; HRMS (ES): calcd for $C_{34}H_{31}O_6$ $[M + H]^+$: 535.2115; found: 535.2135.

General procedure for the dual gold-photoredox arylation/oxyarylation reaction of 2-[(trimethylsilyl)ethynyl]phenol 8 and diazonium salts 2. Preparation of 2-arylbenzofurans 9. In a Schlenk tube in the absence of light at –78 ºC under argon atmosphere, $[(Ph_3P)AuNTf_2]$ (10 mol %) and $[Ru(bpy)_{3]}(PF_6)_2$ (2.5 mol %) were sequentially added to a solution of the corresponding arene diazonium salt **2** (1.3 equiv) in a mixture of MeOH/MeCN (3:1, 5.0 mL). Then, a solution of TMS-alkynol **8** (1.0 mmol) in MeOH/MeCN (3:1, 2.5 mL) was added dropwise and the reaction was stirred at –78 ºC for 5 min. The reaction mixture was then warmed to room temperature and stirred under irradiation from visible light source (21 W fluorescent light bulb installed in a tool box). After disappearance of the starting material (TLC), the reaction mixture was concentrated under reduced pressure. Chromatography of the residue using hexanes gave analytically pure compounds. Spectroscopic and analytical data for pure forms of compounds **9** follow.

2-Arylbenzofuran 9a. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **9a** (17 mg, 88%) as a colorless solid; m.p. 120–121ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.89 (d, 1H, J = 7.6 Hz), 7.61 (dd, 1H, J = 8.5 Hz, J = 1.3 Hz), 7.55 (d, 1H, J = 7.6 Hz), 7.50–7.45 (m, 2H), 7.38 (d, 1H, J = 7.2 Hz), 7.35–7.23 (m, 3H), 7.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 155.9, 154.9, 130.5, 129.2, 128.8 (2C), 128.6, 124.9 (2C), 124.3, 122.9, 120.9, 115.2, 101.3; IR ($CHCl_3$, cm^{-1}): ν 1477, 1445; HRMS (ES): calcd for $C_{14}H_{11}O$ $[M + H]^+$: 195.0810; found: 195.0828.

2-Arylbenzofuran 9b. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **9b** (16 mg, 67%) as a colorless solid; m.p. 158–160ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.72 (d, 2H, *J* = 8.5 Hz), 7.59–7.56 (m, 3H), 7.51 (d, 1H, *J* = 7.6 Hz), 7.33–7.21 (m, 2H), 7.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 154.8, 150.6, 131.9 (2C), 129.3, 128.9, 126.3 (2C), 124.5, 123.0, 122.4, 121.0, 111.1, 101.8; IR ($CHCl_3$, cm^{-1}): ν 1479, 1447; HRMS (ES): calcd for $C_{14}H_{10}BrO$ $[M + H]^+$: 272.9909; found: 272.9918.

2-Arylbenzofuran 9e. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **9e** (15 mg, 64%) as a colorless solid; m.p. 143–145ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.80 (d, 2H, *J* = 8.4 Hz), 7.61–7.52 (m, 2H), 7.43 (d, 2H, *J* = 8.4 Hz), 7.34–7.22 (m, 2H), 7.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 154.9, 154.8, 134.3 (2C), 129.1 (2C), 129.0, 128.2 (2C), 124.6, 123.1, 121.0, 112.2, 101.8; IR ($CHCl_3$, cm^{-1}): ν 1480, 1448; HRMS (ES): calcd for $C_{14}H_{10}ClO$ $[M + H]^+$: 229.0415; found: 229.0424.

2-Arylbenzofuran 9i. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **9i** (12 mg, 50%) as a colorless solid; m.p. 150–151ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.81 (d, 2H, *J* = 8.4 Hz), 7.58–7.56 (m, 2H), 7.28–7.20 (m, 2H), 6.99 (d, 2H, *J* = 8.4 Hz), 6.90 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 160.0, 156.1, 154.7, 129.5, 126.4 (2C), 123.8, 123.4, 122.8, 120.6, 114.3 (2C), 110.0, 99.70, 55.4; IR ($CHCl_3$, cm^{-1}): ν 1475, 1445; HRMS (ES): calcd for $C_{15}H_{13}O_2$ $[M + H]^+$: 225.0910; found: 225.0909.

2-Arylbenzofuran 9j. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **9j** (18 mg, 86%) as a colorless solid; m.p. 129–131ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.78 (d, 2H, *J* = 7.6 Hz), 7.59 (d, 1H, *J* = 7.6 Hz), 7.52 (d, 1H, *J* = 7.6 Hz), 7.29–7.24 (m, 4H), 6.99 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 156.5, 155.2, 139.0, 129.9 (2C), 128.2, 125.3 (2C), 124.4, 123.3, 121.1, 111.5, 101.0, 21.8; IR ($CHCl_3$, cm^{-1}): ν 1485, 1443; HRMS (ES): calcd for $C_{15}H_{13}O$ $[M + H]^+$: 209.0961; found: 209.0952.

General procedure for the dual gold-photoredox twofold arylation/oxyarylation reaction of 2-[(trimethylsilyl)ethynyl]phenol 8 and diazonium salts 2. Preparation of 2,3-diarylbenzofurans 10. In a Schlenk tube in the absence of light at –78 ºC under argon atmosphere, Ph_3PAuCl (10 mol %) and $[Ru(bpy)_3](PF_6)_2$ (2.5 mol %) were sequentially added to a solution of the corresponding arene diazonium salt **2** (6.0 equiv) in a mixture of MeOH/MeCN (3:1, 5.0 mL). Then, a solution of TMS-alkynol **8** (1.0 mmol) in MeOH/MeCN (3:1, 2.5 mL) was added dropwise and the reaction was stirred at –78 ºC for 5 min. The reaction mixture was then warmed to room temperature and stirred under irradiation from visible light source (21 W fluorescent light bulb installed in a tool box). After disappearance of the starting material (TLC), the reaction mixture was concentrated under reduced pressure. Chromatography of the residue using hexanes/ethyl acetate or hexanes/toluene mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of compounds **10** follow.

2,3-Diarylbenzofuran 10a. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **10a** (23

mg, 83%) as a colorless solid; m.p. 120–122ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.68 (dd, 2H, *J* = 8.1 Hz, *J* = 2.5 Hz), 7.58 (d, 1H, *J* = 8.1 Hz), 7.57–7.45 (m, 6H), 7.43–7.24 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 154.0, 150.4, 133.3, 130.5, 130.2, 129.8 (2C), 129.0 (2C), 128.4 (2C), 128.4, 127.5, 127.0 (2C), 125.1, 122.8, 120.0, 117.4, 111.0; IR ($CHCl_3$, cm^{-1}): ν 1495, 1453; HRMS (ES): calcd for $C_{20}H_{15}O$ [*M* + H]$^{+}$: 271.1117; found: 271.1127.

2,3-Diarylbenzofuran 10b. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **10b** (29 mg, 69%) as a colorless solid; m.p. 116–117ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.62 (d, 2H, *J* = 8.0 Hz), 7.58–7.46 (m, 6H), 7.39–7.35 (m, 3H), 7.30–7.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 154.0, 149.4, 132.4 (2C), 131.8 (2C), 131.4, 131.3 (2C), 129.5, 129.3, 128.4 (2C), 125.1, 123.3, 122.8, 122.0, 119.8, 116.7, 111.2; IR ($CHCl_3$, cm^{-1}): ν 1496, 1450; HRMS (ES): calcd for $C_{20}H_{13}Br_2O$ [*M* + H]$^{+}$: 426.9328; found: 426.9344.

2,3-Diarylbenzofuran 10e. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **10e** (19 mg, 56%) as a colorless solid; m.p. 106–108ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.51–7.46 (m, 3H), 7.40–7.35 (m, 5H), 7.31–7.15 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 154.0, 149.7, 134.5, 133.8, 131.1, 131.0 (2C), 129.4, 129.4 (2C), 128.4 (2C), 128.3 (2C), 125.2, 123.3, 120.0, 116.8, 111.3; IR ($CHCl_3$, cm^{-1}): ν 1497, 1451; HRMS (ES): calcd for $C_{20}H_{13}Cl_2O$ [*M* + H]$^{+}$: 339.0343; found: 339.0327.

2,3-Diarylbenzofuran 10i. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **10i** (7 mg,

21%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.61 (d, 2H, J = 8.5 Hz), 7.55–7.44 (m, 2H), 7.43 (d, 2H, J = 8.2 Hz), 7.22–7.20 (m, 2H), 7.01 (d, 2H, J = 8.2 Hz), 6.86 (d, 2H, J = 8.2 Hz), 3.90 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 159.6, 159.0, 153.8, 150.5, 130.9 (2C), 130.6, 128.4 (2C), 125.2, 124.2, 123.5, 123.2, 119.7, 115.7, 114.5 (2C), 113.9 (2C), 110.9, 55.3; IR ($CHCl_3$, cm^{-1}): ν 1490, 1450; HRMS (ES): calcd for $C_{22}H_{19}O_3$ $[M + H]^+$: 331.1328; found: 331.1326.

2,3-Diarylbenzofuran 10j. From 19 mg (0.10 mmol) of TMS-alkynol **8**, and after chromatography of the residue using hexanes as eluent, gave compound **10j** (20 mg, 66%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.58 (d, 2H, J = 8.5 Hz), 7.52–7.50 (m, 2H), 7.41 (d, 2H, J = 8.5 Hz), 7.36–7.22 (m, 4H), 7.15 (d, 2H, J = 8.4 Hz), 2.46 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 153.8, 150.7, 138.3, 137.3, 130.4, 129.9, 129.7 (2C), 129.5 (2C), 129.0 (2C), 128.0, 126.9 (2C), 124.4, 122.8, 119.9, 116.8, 111.0, 21.4 (2C); IR ($CHCl_3$, cm^{-1}): ν 1498, 1448; HRMS (ES): calcd for $C_{22}H_{19}O$ $[M + H]^+$: 299.1430; found: 299.1416.

General procedure for the dual gold-photoredox cross double arylation reaction of TMS-alkynols 4 and diazonium salts 2. Preparation of crossed-diarylated α,β-unsaturated ketones 3aab–3hbh. In a Schlenk tube in the absence of light at –78 ºC under argon atmosphere, $[(Ph_3P)AuNTf_2]$ (10 mol %) and $[Ru(bpy)_{3]}(PF_6)_2$ (2.5 mol %) were sequentially added to a solution of the first arene diazonium salt **2** (1.5 equiv) in a mixture of MeOH/MeCN (3:1, 4.0 mL). Then, a solution of the appropriate TMS-alkynol **4** (1.0 mmol) in MeOH/MeCN (3:1, 1.5 mL) was added dropwise and the reaction was stirred at –78 ºC for 5 min. The reaction mixture was then warmed to –20 ºC and stirred under irradiation from visible light source (21 W fluorescent light bulb installed in a tool box). After disappearance of the

starting material (TLC, typically 20 min), the reaction mixture was cooled at –78 ºC and protected from the light. Then, a solution of the second arene diazonium salt **2** (6.0 equiv) in a mixture of MeOH/MeCN (3:1, 2.5 mL) was added, and the reaction was stirred at –78 ºC for 5 min. The reaction mixture was then warmed to room temperature and stirred under irradiation from visible light source (21 W fluorescent light bulb installed in a tool box). After disappearance of the starting material (TLC), the reaction mixture was concentrated under reduced pressure. Chromatography of the residue using hexanes/ethyl acetate or hexanes/toluene mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of crossed adducts **3** follow.

Diarylated α,β-unsaturated ketone 3aab. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (7:3) as eluent, gave compound **3aab** (16 mg, 46%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.85 (m, 2H), 7.52 (m, 6H), 7.20 (m, 5H), 7.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 197.2, 141.0, 139.5, 137.9, 135.4, 134.4, 132.3, 132.0 (2C), 131.5 (2C), 130.3 (2C), 129.7 (2C), 129.2, 128.4 (2C), 128.3 (2C), 122.2; IR ($CHCl_3$, cm^{-1}): ν 1653; HRMS (ES): calcd for $C_{21}H_{16}OBr$ $[M + H]^+$: 363.0379; found: 363.0376.

Diarylated α,β-unsaturated ketone 3aae. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (7:3) as eluent, gave compound **3aae** (13 mg, 41%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.86 (m, 2H), 7.57 (m, 1H), 7.47 (m, 3H), 7.35 (m, 2H), 7.24 (m, 5H), 7.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 197.3, 141.1, 139.5, 138.0, 134.9, 134.5, 134.0, 132.3, 131.2 (2C), 130.3 (2C), 129.8 (2C), 129.2, 129.1 (2C), 128.5 (2C), 128.4 (2C); IR ($CHCl_3$, cm^{-1}): ν 1654; HRMS (ES): calcd for $C_{21}H_{16}OCl$ $[M + H]^+$: 319.0884; found: 319.0899.

Diarylated α,β-unsaturated ketone 3aah. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (6:4) as eluent, gave compound **3aah** (19 mg, 53%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.05 (m, 2H), 7.87 (m, 2H), 7.56 (m, 1H), 7.46 (m, 2H), 7.38 (m, 2H), 7.33 (s, 1H), 7.21 (m, 3H), 7.08 (m, 2H), 4.39 (q, 4H, J = 7.1), 1.41 (m, 3H, J = 7.1); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 197.0, 166.4, 141.4, 141.3, 139.8, 137.9, 134.3, 132.3, 130.3 (2C), 130.0 (2C), 129.9, 129.8 (2C), 129.7 (2C), 129.3, 128.4 (2C), 128.6 (2C), 61.0, 14.3; IR ($CHCl_3$, cm^{-1}): ν 1717, 1654; HRMS (ES): calcd for $C_{24}H_{21}O_3$ $[M + H]^+$: 357.1485; found: 357.1499.

Diarylated α,β-unsaturated ketone 3aba. From 20 mg (0.10 mmol) of TMS-alkynol **4a**, and after chromatography of the residue using hexanes/toluene (7:3) as eluent, gave compound **3aba** (13 mg, 37%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.72 (m, 2H), 7.58 (m, 2H), 7.35 (m, 3H), 7.22 (m, 6H), 7.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.4, 140.5, 140.4, 136.9, 136.2, 134.6, 131.6 (2C), 131.3 (2C), 130.4 (2C), 129.6 (2C), 129.1, 128.9 (2C), 128.3 (2C), 128.1, 127.1; IR ($CHCl_3$, cm^{-1}): ν 1657; HRMS (ES): calcd for $C_{21}H_{16}OBr$ $[M + H]^+$: 363.0379; found: 363.0379.

Diarylated α,β-unsaturated ketone 3eab. From 16 mg (0.10 mmol) of TMS-alkynol **4e**, and after chromatography of the residue using hexanes/toluene (7:3) as eluent, gave compound **3eab** (17 mg, 56%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.95 (m, 2H), 7.53 (m, 1H), 7.43 (m, 4H), 7.19 (m, 2H), 1.87 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 198.4, 136.7, 136.3, 136.0, 135.6, 133.3, 131.5 (2C), 130.9 (2C), 129.7 (2C), 128.7 (2C), 121.3, 22.6, 21.3; IR ($CHCl_3$, cm^{-1}): ν 1662; HRMS (ES): calcd for $C_{17}H_{16}OBr$ $[M + H]^+$: 315.0379; found: 315.0390.

Diarylated α,β-unsaturated ketone 3fae. From 15 mg (0.10 mmol) of TMS-alkynol **4f**, and after chromatography of the residue using hexanes/toluene (7:3) as eluent, gave compound **3fae** (12 mg, 49%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.75 (m, 2H), 7.53 (m, 1H), 7.40 (m, 4H), 7.21 (m, 2H), 6.63 (q, 1H, J = 7.1 Hz), 1.88 (d, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 196.9, 141.8, 140.6, 138.2, 134.1, 133.5, 132.0, 131.0 (2C), 129.5 (2C), 128.5 (2C), 128.2 (2C), 15.6; IR ($CHCl_3$, cm^{-1}): ν 1656; HRMS (ES): calcd for $C_{16}H_{14}OCl$ $[M + H]^+$: 257.0728; found: 257.0721.

Diarylated α,β-unsaturated ketone 3hae. From 26 mg (0.10 mmol) of TMS-alkynol **4h**, and after chromatography of the residue using hexanes/ethyl acetate (7:3) as eluent, gave compound **3hae** (13 mg, 36%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.04 (m, 2H), 7.56 (m, 3H), 7.45 (m, 4H), 7.31 (m, 1H), 7.00 (m, 1H), 6.84 (m, 2H), 3.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 195.8, 166.3, 147.6, 145.0, 136.0, 135.2, 133.5, 132.2, 130.6, 129.7 (2C), 129.6 (2C), 129.0 (2C), 128.8 (2C), 126.7, 123.2, 122.1, 120.4, 108.5, 26.0; IR ($CHCl_3$, cm^{-1}): ν 1709, 1669; HRMS (ES): calcd for $C_{23}H_{17}ClNO_2$ $[M + H]^+$: 374.0942; found: 374.0929.

Diarylated α,β-unsaturated ketone 3hbh. From 26 mg (0.10 mmol) of TMS-alkynol **4h**, and after chromatography of the residue using hexanes/ethyl acetate (7:3) as eluent, gave compound **3hbh** (25 mg, 41%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.14 (m, 2H), 7.90 (m, 2H), 7.70 (m, 2H), 7.59 (m, 2H), 7.30 (m, 1H), 6.92 (m, 1H), 6.82 (m, 2H), 4.41 (q, 2H, J = 7.13 Hz), 3.17 (s, 3H), 1.88 (t, 3H, J = 7.13 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 194.6, 166.3, 165.8, 147.0, 145.1, 137.8, 134.1, 132.2 (2C), 131.7, 130.9, 130.4 (2C), 130.3 (2C), 128.9, 128.2 (2C), 127.3,

123.4, 122.2, 120.1, 108.6, 61.4, 26.0, 14.3; IR ($CHCl_3$, cm^{-1}): ν 1714, 1610; HRMS (ES): calcd for $C_{26}H_{21}BrNO_4$ $[M + H]^+$: 490.0648; found: 490.0671.

ASSOCIATED CONTENT

Supporting Information. Copies of NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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