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Photopromoted Entry to Benzothiophenes, Benzoselenophenes, 3*H*-Indoles, Isocoumarins, Benzosultams, and (Thio)flavones by Gold-Catalyzed Arylative Heterocyclization of Alkynes

Benito Alcaide,[a]* Pedro Almendros,[b]* Eduardo Busto,[a] Fernando Herrera,[a] Carlos Lázaro-Milla,[a] and Amparo Luna[a]

[a] 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, Fax: (+34) 91-3944103, E-mail: alcaideb@quim.ucm.es

[b] Instituto de Química Orgánica General, Consejo Superior de Investigaciones Científicas, IQOG-CSIC, Juan de la Cierva 3, 28006 Madrid, Spain, Fax: (+34) 91-5644853, E-mail: Palmendros@iqog.csic.es

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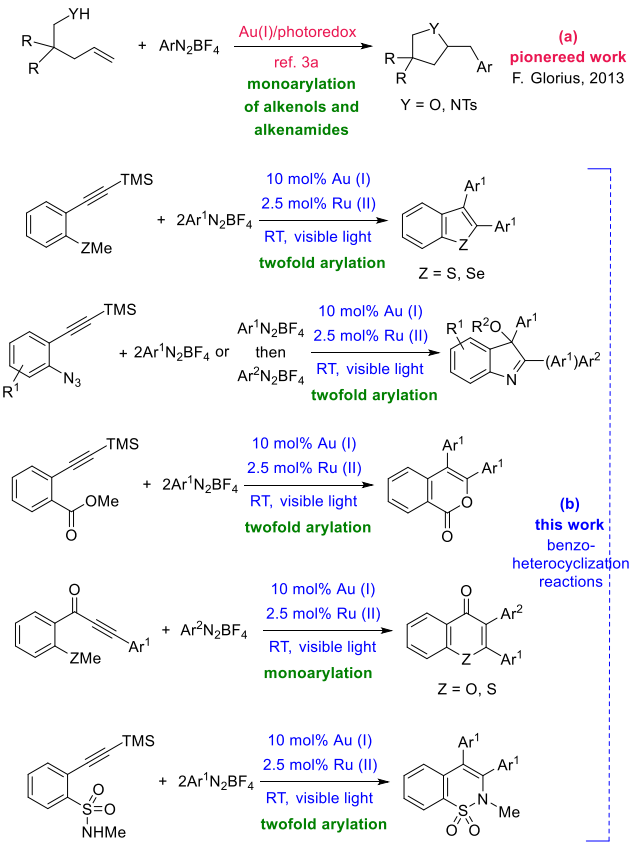
Abstract: Visible light-promoted and gold-photoredox catalyzed reactions of heteroatom (N, S, Se, O) tethered alkynes with arenediazonium salts selectively reacted to build vicinal diaryl-substituted 2*H*-benzo[*e*][1,2]thiazine 1,1-dioxides (benzosultams), benzoselenophenes, benzothiophenes, 4*H*-chromen-4-ones (flavones), 3*H*-indoles, 1*H*-isochromen-1-ones (isocoumarins), and 4*H*-thiochromen-4-ones (thioflavones). Moreover, the utility of functionalized 3*H*-indoles as precursors for further elaboration has been demonstrated with the switchable and facile preparation of 1*H*-indoles, 2-oxindoles, and 3-oxindolines.

Keywords: alkynes; cyclization; gold; heterocyclic compounds; synthetic methods

Introduction

Homogeneous gold catalysis has been developed as a potent tool in the field of synthetic organic chemistry. Particularly attractive is the activation of alkenes, alkynes and allenes by cationic gold(I) species.[1] However, Au(I)/Au(III) catalytic cycles cannot be accessed through the traditional gold(I)-catalyzed processes, and super-stoichiometric amounts of a strong oxidant are required for surpassing the high redox potential Au(I)/Au(III).[2] Taking into account the above limitations, it is not surprising that gold-catalyzed cross-coupling strategies are a less explored field. Glorius and, later, Toste developed a smart strategy for avoiding the drawback of the inclusion of strong oxidants,[3] which takes advantage of a photoredox catalyst and a diazonium salt.[4] Hashmi and Barriault developed gold-only photoredox chemistry through the use of dinuclear complexes of gold as photoredox catalysts.[5]

On the other hand, the widespread presence of heterocycles in both natural products and synthetic drugs as well as in advanced materials, explains the interest in the preparation of these cyclic frameworks. This area is clearly dominated by palladium catalysis, which usually demands elevated temperatures and the use of ligands and bases. Besides, the incorporation of aryl substituents to the heterocyclic core is performed by the use of aryl halides, which are not always readily available. Aiming to surmount these deficiencies, we were motivated to include diazonium salts and visible light in a comprehensive gold-catalyzed arylative heterocycle formation. Due to environmental concerns, the development of a photocatalyzed arylative synthesis at room temperature may be a great achievement. We wish to describe herein the unique use of diazonium salts as a radical source in the cooperative gold-photoredox catalyzed synthesis of benzo-fused heterocycles (Scheme 1).[6]

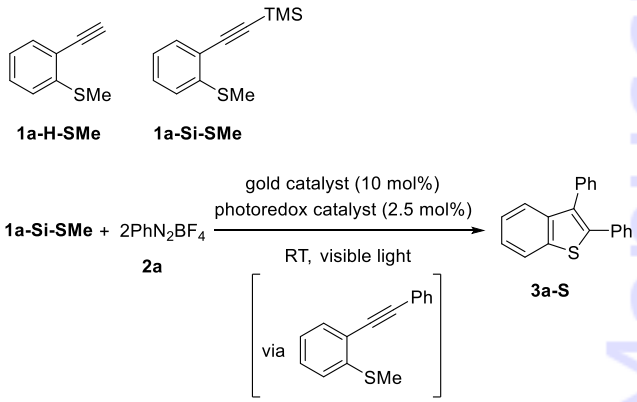


Scheme 1. Dual gold- and photoredox-catalyzed heterocyclization reactions: Previous and current strategies. TMS = Trimethylsilyl.

Results and Discussion

(2-Ethynylphenyl)(methyl)sulfane **1a-H-SMe** and phenyldiazonium salt **2a** were chosen as model substrates to examine their reactivity under cooperative gold and photoredox catalysis.[7] Our aim was the in situ generation of a methyl[2-(arylethynyl)phenyl]sulfane from a gold-catalyzed sila-Sonogashira-type coupling, which can be further trapped by the nucleophile sulfur with a concomitant second arylation in a domino sequence. This premise deals with difficulties and presents an initial challenge because the photoredox gold-catalyzed arylation of sulfur derivatives has not yet been reported. Besides, we need that the starting material undergoes a relatively fast coupling at the alkyne site, in comparison with the heterocyclization event. Substrate **1a-H-SMe** provided benzothiophene **3a-S** in a promising 27% yield. A significant improvement was detected with the use of TMS-capped alkyne **1a-Si-SMe**,[8] which was considered as viable precursor in the synthesis of 2,3-diaryl benzothiophenes. We initiated our optimization studies using various gold(I) complexes and the ruthenium salt $[Ru(bpy)_3](PF_6)_2$ (bpy = 2,2'-bipyridine) as shown in Table 1. After the evaluation of different conditions, PPh_3AuCl (10 mol%) in combination with $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%) provided an impressive yield (94%) of 2,3-diphenyl benzothiophene **3a-S** (entry 3, Table 1). When the loading of PPh_3AuCl was increased from 10 mol% to 20 mol%, it resulted in just a little improvement of the yield (95%) (entry 5, Table 1). Decreasing the amount of PPh_3AuCl from 10 mol% to 5 mol% produced an appreciable reduction of the yield (64%) (entry 6, Table 1). Inferior results were obtained when the reaction was carried out in presence of other photoactive complexes such as $[Ir(ppy)_2(dtbbpy)](PF_6)_2$ (ppy = 2-phenylpyridine; dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) (entry 4, Table 1). Also, alternative gold(I) sources such as [AuClIPr] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and $[(Ph_3P)AuNTf_2]$ were inefficient (entries 1 and 2, Table 1).

Table 1. Screening of reaction conditions for benzothiophene formation through light-driven gold/photoredox-co-catalyzed diarylative thiacyclization.[a]



Entry	Gold Catalyst	Photocatalyst[b]	Yield (%)[c]
1	[IPrAuCl]	[Ru]	–
2	$[(Ph_3P)AuNTf_2]$	[Ru]	–
3	$[(PPh_3)AuCl]$	[Ru]	94
4	$[(PPh_3)AuCl]$	[Ir]	63
5	$[(PPh_3)AuCl]$[d]	[Ru]	95
6	$[(PPh_3)AuCl]$[e]	[Ru]	64
7	$[(PPh_3)AuCl]$	[Ru]	5[f]

[a] Unless otherwise noted, all reactions were carried out in methanol/acetonitrile (3:1) at room temperature.
[b] [Ru] = $[Ru(bpy)_3](PF_6)_2$. [Ir] = $[Ir(ppy)_2(dtbbpy)](PF_6)_2$.
[c] Yield of pure, isolated product with correct analytical and spectral data.
[d] Catalyst loading of 20 mol%.
[e] Catalyst loading of 5 mol%.
[f] The reaction was carried out in DMF.

We applied the above reaction conditions to differently functionalized arenediazonium salts **2** (Scheme 2). Substitution was tolerated in the diarylative thiacyclizations of **1a-Si-SMe**, with the presence at the arenediazonium salt of electron withdrawing groups (CO_2Et, CF_3) as well as halogens (Br) and weakly electron donating groups (Me). The results depicted in the above Scheme show the effectiveness of this methodology for the smooth

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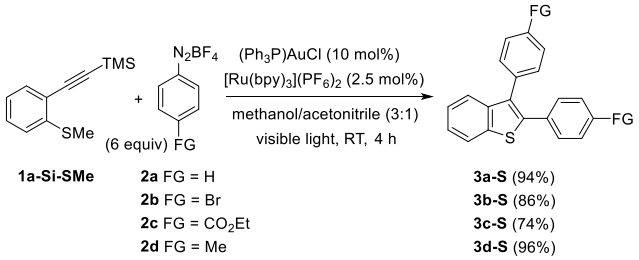
preparation of a variety of 2,3-diaryl benzothiophenes **3-S**.[9]



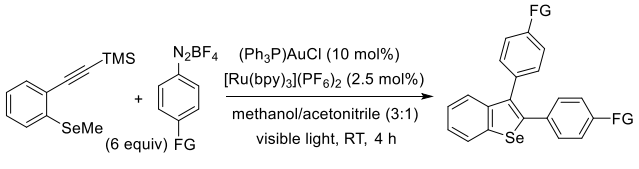
1a-Si-SMe

2a FG = H
2b FG = Br
2c FG = CO_2Et
2d FG = Me

3a-S (94%)
3b-S (86%)
3c-S (74%)
3d-S (96%)

Scheme 2. Cooperative gold-photoredox catalysis for the synthesis of 2,3-diaryl benzothiophenes **3-S**.

To further probe the scope and versatility of the arylative carbon−chalcogen cyclization reaction, trimethyl[(2-methylselanylphenyl)ethynyl]silane **1a-Si-SeMe** was used to react with phenyldiazonium salt **2a** under the optimized conditions for the formation of 2,3-diaryl benzothiophenes **3-S**. As depicted in Scheme 3, the diarylation/C−Se bond formation sequence proceeded to afford 2,3-diaryl benzoselenophene **3a-Se**, but less efficiently. Precursor **1a-Si-SeMe** reacted well with several arenediazonium salts **2** bearing diverse substitution and gave rise under mild conditions to the desired selenoheterocycles **3-Se**, a type of organic molecules which are prevalent both in drugs and in advanced materials (Scheme 3).



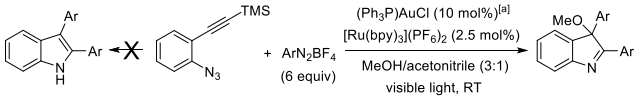
1a-Si-SeMe

2a FG = H
2d FG = Me
2e FG = Cl
2f FG = CF_3

3a-Se (44%)
3d-Se (60%)
3e-Se (52%)
3f-Se (53%)

Scheme 3. Cooperative gold-photoredox catalysis for the synthesis of 2,3-diaryl benzoselenophenes **3-Se**.

Continuing to explore different functionalities at the TMS-protected alkynes and taking into account that the azide moiety is a versatile nitrogen source,[10] we decided to test azidobenzene-tethered alkynes.[11] The above reaction conditions for TMS-sulfane **1a-Si-SMe** was also applicable for TMS-(ethynyl)azidobenzene **4a-Si**,[12] but it exhibited different reactivity. The lack of formation of expected 2,3-diaryl 1*H*-indoles of type **5** was observed, which should point to a marked directing effect of the heteroatomic nucleophile functionality. In view of the structure of adduct **6a**, the participation of methanol as a nucleophile is apparent. Noteworthy, this interesting reactivity switch allowed the obtention of functionalized 3*H*-indoles **6aa–ah** through a diarylative aminocyclization/hydroalkoxylation sequence (Scheme 4). Halogenated or weakly activated arenediazonium salts turned out to be suitable coupling partners. However, diazonium salts having strong electron withdrawing groups (NO_2 and CF_3) failed to give the desired indole. Instead, alkenes **7** were formed (Scheme 5). Apparently, the electron poor aryl alkyne intermediate disfavors the aminocyclization with the azide moiety and the competitive intermolecular nucleophilic addition of methanol dominates.



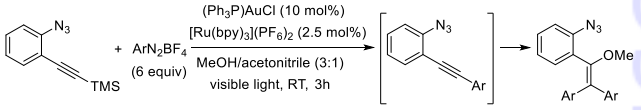
5aa
5ab
5ad
5ae
5ag
5ah

4a-Si

2a Ar = Ph
2b Ar = 4-BrC_6H_4
2d Ar = 4-MeC_6H_4
2e Ar = 4-ClC_6H_4
2g Ar = 4-FC_6H_4
2h Ar = 4-IC_6H_4

6aa (43%, 3h)
6ab (63%, 3h)
6ad (55%,3h)
6ae (49%, 2h)
6ag (42%, 2h)
6ah (45%, 2h)

Scheme 4. Cooperative gold-photoredox catalysis for the synthesis of 2,3-diaryl 3*H*-indoles **6**. [a] For a full conversion, the complex was added in two separated portions with a 30 min spacing.



4a-Si

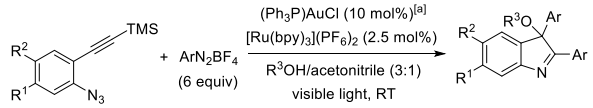
2f Ar = 4-$CF_3C_6H_4$
2i Ar = 4-$NO_2C_6H_4$

4af-Ar
4ai-Ar

7af (38%)
7ai (55%)

Scheme 5. Cooperative gold-photoredox catalysis for the diarylative hydroalkoxylation of (ethynyl)azidobenzene **4a-Si** with strongly deactivated arenediazonium salts.

Next, under the optimized reaction conditions, the reactivities of several TMS-(ethynyl)azidobenzenes **4-Si** with arenediazonium salt **2b** were examined (Scheme 6). The power of this methodology was further demonstrated with the use of different alcohols (ethanol, 2-propanol, *tert*-butanol, and methanol-d_3) instead of methanol to give adducts **6ab-Et**, **6ab-*i*Pr**, **6ab-*t*Bu**, and **6ab-CD_3** (Scheme 6). Besides, several substituents could be incorporated to the starting materials, which grants for the formation of a variety of functionalized 3*H*-indoles. The reaction yields (^{1}H NMR) were excellent before purification because no side-products were detected when the starting material was fully converted. However, partial decomposition was observed on sensitive 3*H*-indoles **6** during chromatographic purification.



4a-Si R^1 = H, R^2 = H
4a-Si R^1 = H, R^2 = H
4a-Si R^1 = H, R^2 = H
4a-Si R^1 = H, R^2 = H
4b-Si R^1 = Cl, R^2 = H
4c-Si R^1 = F, R^2 = H
4d-Si R^1 = H, R^2 = Me
4e-Si R^1 = H, R^2 = CO_2Et
4f-Si R^1 = H, R^2 = Cl

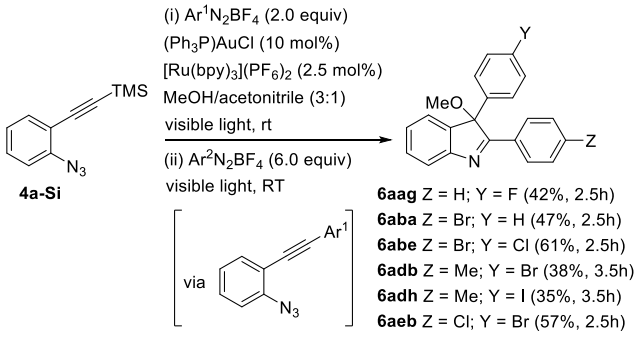
2b

Ar = 4-BrC_6H_4

6ab-Et R^3 = Et (57%, 3h)
6ab-*i*Pr R^3 = *i*Pr (55%, 5h)
6ab-*t*Bu R^3 = *t*Bu (23%, 12h)
6ab-CD_3 R^3 = CD_3 (59%, 2h)
6bb R^3 = Me (49%, 2h)
6cb R^3 = Me (52%, 2h)
6db R^3 = Me (41%, 3h)
6eb R^3 = Me (44%, 3h)
6fb R^3 = Me (46%, 2h)

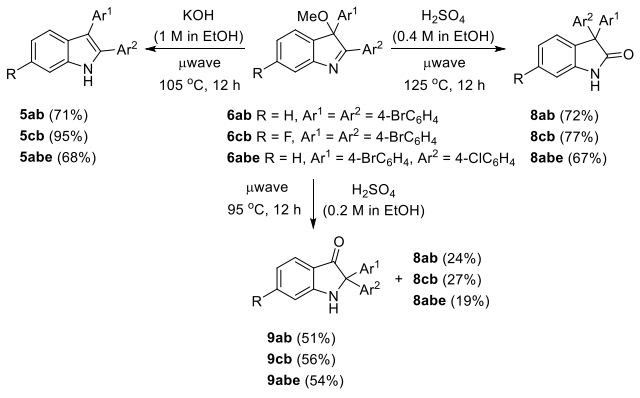
Scheme 6. Cooperative gold-photoredox catalysis for the synthesis of differently substituted 2,3-diaryl 3*H*-indoles **6**. [a] For a full conversion, the complex was added in two separated portions with a 30 min spacing.

To fully exploit the potential of this methodology, we reacted [(2-azidophenyl)ethynyl]trimethylsilane **4a-Si** with a pair of different diazonium salts **2**. Initial Hiyama coupling of TMS-precursor **4a-Si** with the first diazonium salt **2** provided 1-azido-2-(arylethynyl)benzene intermediates. Without the need of isolation, these intermediates afforded the final differently diarylated 3*H*-indoles **6** after a second coupling with another diazonium salt (Scheme 7). Thus, TMS-(ethynyl)azidobenzene **4a-Si** acts as a versatile building block for the double crossed diarylation reaction, and allows for the preparation of crossover adducts in a convenient and modular way.



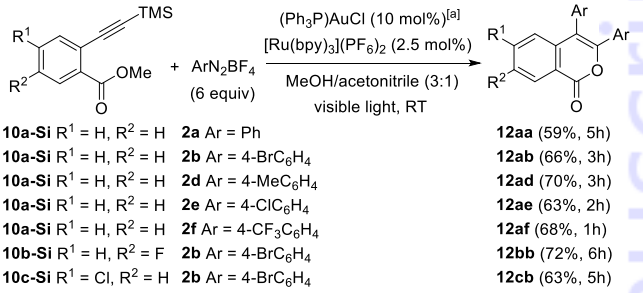
Scheme 7. Cooperative gold-photoredox catalysis for the crossed preparation of 2,3-diaryl 3*H*-indoles **6**.

Besides, the utility of 3-alkoxy-2,3-diaryl-3*H*-indoles **6** as precursors for further elaboration has been demonstrated with the controlled preparation of *N*-unprotected indoles **5**, 2-oxindoles **8** and 3-oxindolines **9** through base- or acid-promoted rearrangement reactions (Scheme 8).[13] Possibly, the driving-force of these reorganizations may be related to the gain in stability associated with the 1*H*-indole, indolinone and indolone formation.

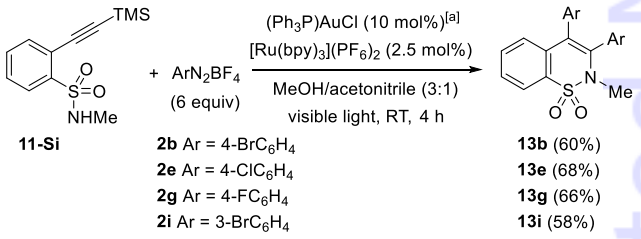


Scheme 8. Synthetic transformations of 3-methoxy-2,3-diaryl-3*H*-indoles **6**.

With thia-, selena-, and azido-(TMS-ethynyl)benzenes **1a-Si-SMe**, **1a-Si-SeMe**, and **4-Si** found to be compatible with the diarylative five-membered heterocyclization reaction, structurally different precursors were investigated to further expand the scope of the reaction to six-membered benzo-fused heterocycles. For the investigation of the scope of the sequence, a pair of potential precursors, esters **10-Si** and sulfonamide **11-Si**, was prepared. Interestingly, isocoumarins **12** were obtained in fair yields by the light-driven gold/photoredox-co-catalyzed double arylation/oxycyclization of 2-[(trimethylsilyl)ethynyl]benzoates **10-Si** (Scheme 9). Notably, regioisomeric five-membered heterocycles were not detected, highlighting the exquisite selectivity of the sequence. Starting from 2-[(trimethylsilyl)ethynyl]benzenesulfonamide **11-Si**, the same diarylative protocol afforded benzosultams **13** with satisfactory yields (Scheme 10). It is apparent that in esters **10-Si** and sulfonamide **11-Si** the 6-*endo* oxy- and aza-cyclizations paths are favoured because competitive 5-*exo* heterocyclizations are not involved.



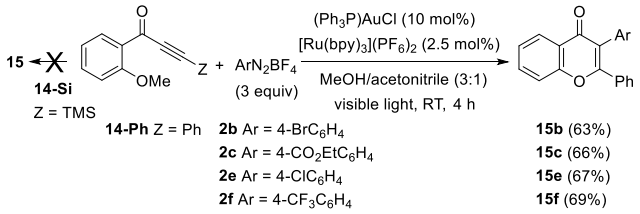
Scheme 9. Cooperative gold-photoredox catalysis for the synthesis of 3,4-diaryl- isocoumarins **12**. [a] For a full conversion, the complex was added in two separated portions with a 30 min spacing.



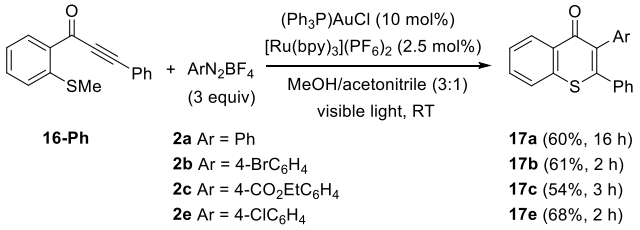
Scheme 10. Cooperative gold-photoredox catalysis for the synthesis of 3,4-diaryl-benzosultams **13**.

Having in hand (trimethylsilyl)prop-2-yn-1-one **14-Si**, we attempted the double arylation with arenediazonium salt **2a** under the above reaction conditions. However, absence of reaction was observed (Scheme 11), which shows that the contiguous ketone group in the (trimethylsilyl)ethyne moiety is critical for the suppression of any Hiyama-Sonogashira reaction. Efforts to modified either the gold catalyst or the diazonium salt led to no improvement in reactivity. We decided to implement our planned synthesis of benzo-fused heterocycles replacing the TMS group by an aryl substituent. Convincing confirmation for the negative effect of the alkynone framework on the sila-coupling but not on the heterocyclization event, was definitively obtained by the fruitful accomplishment of the monoarylative/heterocyclization in aryl-terminated alkynone **14-Ph** by which synthesis of 4*H*-chromen-4-ones **15** has been attained (Scheme 11). The succesful cyclization of the heteroatom-linked alkynone core

was further confirmed by the light-driven gold/photoredox-co-catalyzed arylative thiacyclization reaction of the sulfa-derivative **16-Ph** with several diazonium salts **2** to afford 4*H*-thiochromen-4-ones **17** (Scheme 12). The detected regiochemistry of both ring closures (6-*endo* oxy- and thia-cyclizations) is in agreement with the results of Schemes 9 and 10.

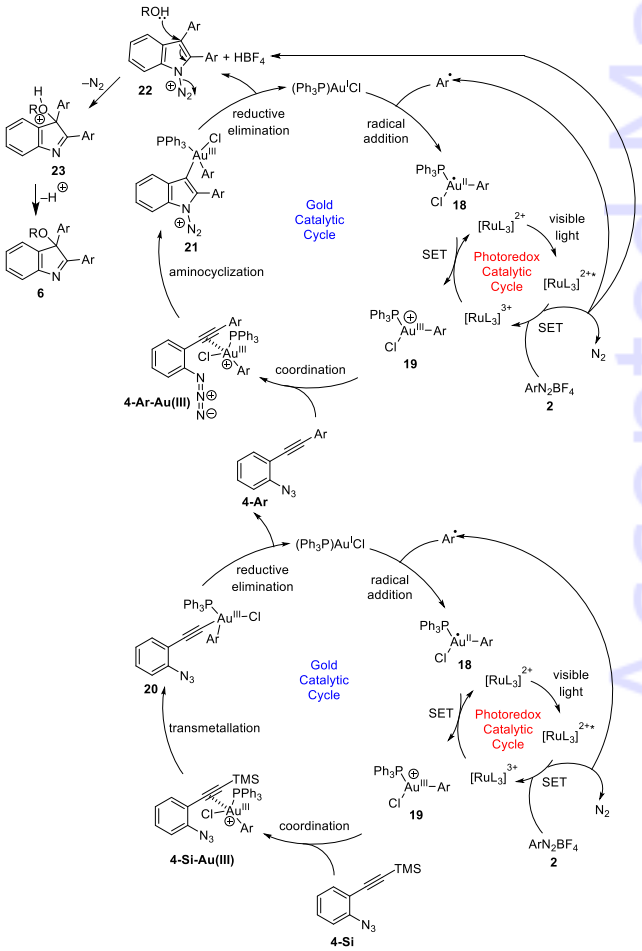


Scheme 11. Cooperative gold-photoredox catalysis for the synthesis of 3-aryl-flavones **15**.



Scheme 12. Cooperative gold-photoredox catalysis for the synthesis of 3-aryl-thioflavones **17**.

Despite that Hashmi[14] and Shi[15] have independently shown that no photoredox catalysts are required for related reactions, a control experiment verified that our reactions operates through $[Ru(bpy)_3](PF_6)_2$ photoredox. Indeed, starting either from **1a-Si-SMe** or **4a-Si** no reaction occurred in the absence of the photosensitizer. The critical role of light in the domino reaction was probed when precursors **1a-Si-SMe** or **4a-Si** were recovered when the reactions were run with all the reagents but without irradiation. A tentative mechanistic proposal for the generation of 3-alkoxy-2,3-diaryl-3*H*-indoles **6** from 2-[(trimethylsilyl)ethynyl]azidobenzenes **4-Si**, diazonium salts **2** and light under dual gold-photoredox cocatalysis is summarized in Scheme 13. Initially, irradiation of the Ru(II)-based photoredox catalyst results in the formation of an aryl radical from diazonium salts **2** after extrusion of dinitrogen (bottom catalytic cycle, right side). This key reactive species is able to be coupled with the gold(I) precatalyst to allow the formation of unstable organogold(II) intermediate **18**, which rapidly evolves to the cationic organogold(III) derivative **19**, a strong electrophile, through the oxidative action of Ru(III) and concomitant liberation of $[Ru(bpy)_3](PF_6)_2$ into the catalytic cycle. Next, TMS-(ethynyl)azidobenzenes **4-Si** enter the gold catalytic sequence (bottom catalytic cycle, left side), forming complexes **4-Si**-Au(III) through alkyne coordination with the gold complex. Either the transmetallation of the C(sp)–Si bond or the nucleophilic attack from the azide group can be effectively produced. Apparently, the silicon/gold interchange is preferred to the amino-auration. Then, Si–Au transmetallation should produce gold acetylide species **20**, which suffers reductive elimination paired to aryl transfer and releases 2-(arylethynyl)azidobenzenes **4-Ar** and the gold(I) salt, closing the first gold catalytic cycle (bottom catalytic cycle). The formation of 3-alkoxy-2,3-diaryl-3*H*-indoles **6** from 2-(arylethynyl)azidobenzenes **4-Ar** requires the participation of the organogold(III) species **19** in the azacyclization event. According to the aforementioned comments, a second molecule of arenediazonium salt **2** affords the corresponding aryl radical helped by light and the photoredox catalyst (top catalytic cycle, right side). The N atom attack to the terminal carbon of the triple bond with respect to the azide moiety is facilitated in intermediate **4-Ar-Au(III)** by the coordination of arylgold(III) species **19** with the alkyne functionality of **4-Ar**. After the 5-*endo*-dig azacyclization, the aryl transfer from the Au atom to the C3 indole carbon lead to intermediate 1*H*-indoles **22**. In concert, the gold(I) precatalyst is regenerated in this pathway (top catalytic cycle, left side). The formation of 3-alkoxy-2,3-diaryl-3*H*-indoles **6** requires the further attack of the alcohol with concomitant nitrogen releases.



Scheme 13. Rationalization for the gold-photoredox cocatalyzed preparation of 3-alkoxy-2,3-diaryl-3*H*-indoles

6 from TMS-(ethynyl)azidobenzenes **4-Si** and diazonium salts **2**.

Conclusions

In conclusion, visible light-promoted and gold-photoredox catalyzed reactions of heteroatom(N, S, Se, O)-tethered alkyne derivatives with diazonium salts are totally selective to build in a controlled manner vicinal diaryl-substituted 2*H*-benzo[*e*][1,2]thiazine 1,1-dioxides (benzosultams), benzoselenophenes, benzothiophenes, 4*H*-chromen-4-ones (flavones), 3*H*-indoles, 1*H*-isochromen-1-ones (isocoumarins), and 4*H*-thiochromen-4-ones (thioflavones). Besides, the usefulness of 3*H*-indoles has been probed with the facile and divergent synthesis of 1*H*-indoles, 2-oxindoles and 3-oxindolines.

Experimental Section

General methods: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance AVIII-700 with cryoprobe, Bruker AMX-500, or a Bruker AMX-500, or a Bruker Avance-300 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), or $CDCl_3$ (^{1}H, 7.27 ppm; ^{13}C, 76.9 ppm), or C_6D_6 (^{1}H, 7.16 ppm; ^{13}C, 128.0 ppm). Low and high resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electrospray mode (ES) unless otherwise stated. IR spectra were recorded on a Bruker Tensor 27 spectrometer. All commercially available compounds were used without further purification.

General procedure for the photopromoted gold-catalyzed twofold arylation reaction of hetero-subtituted TMS-(ethynyl)benzenes 1a-Si-SMe, 1a-Si-SeMe, 4a–f-Si, 10a–c-Si, or 11-Si with diazonium salts 2. Preparation of 2,3-diaryl benzothiophenes 3-S, 2,3-diaryl benzoselenophenes 3-Se, 3-alkoxy-2,3-diaryl-3*H*-indoles 6, 3,4-diaryl-isocoumarins 11, and 3,4-diaryl-benzosultams 13. 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 the appropriate 2-[(trimethylsilyl)ethynyl]benzene **1a-Si-SMe**, **1a-Si-SeMe**, **4a–f-Si**, **10a–c-Si**, or **11-Si** (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. For a full conversion in the case of azides **4**, at the beginning the gold salt was added in two separated portions with a 30 min spacing. 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. The addition of Et_3N (2%) to the eluent was neccesary for the purification of acid sensitive 3*H*-indoles **6**. Spectroscopic and analytical data for pure forms of compounds **1a-Si-SMe**, **1a-Si-SeMe**, **4a–f-Si**, **10a–c-Si**, and **11-Si** follow.[16]

2,3-Diaryl benzothiophene 3a-S. From 22 mg (0.10 mmol) of TMS-alkyne **1a-Si-SMe**, and after chromatography of the residue using hexanes as eluent, gave compound **3a-S** (27 mg, 94%) as a colorless solid; m.p. 107–109 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.85–7.79 (m, 1H, CH^{Ar}), 7.54–7.50 (m, 1H, CH^{Ar}), 7.31–7.15 (m, 12H, $12CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 141.2 ($C^{Ar\text{-}q}$), 139.9 ($C^{Ar\text{-}q}$), 139.2 ($C^{Ar\text{-}q}$), 135.8 ($C^{Ar\text{-}q}$), 134.6 ($C^{Ar\text{-}q}$), 133.6 ($C^{Ar\text{-}q}$), 130.8 ($2CH^{Ar}$), 130.0 ($2CH^{Ar}$), 129.0 ($2CH^{Ar}$), 128.7 ($2CH^{Ar}$), 128.1 (CH^{Ar}), 127.7 (CH^{Ar}), 124.9 (CH^{Ar}), 124.8 (CH^{Ar}), 123.7 (CH^{Ar}), 122.4 (CH^{Ar}); IR ($CHCl_3$, cm^{-1}): ν 1599, 1436; HRMS (ES): calcd for $C_{20}H_{15}S$ [*M* + H]$^{+}$: 287.0889; found: 287.0898.

2,3-Diaryl benzothiophene 3b-S. From 35 mg (0.16 mmol) of TMS-alkyne **1a-Si-SMe**, and after chromatography of the residue using hexanes as eluent, gave compound **3b-S** (60 mg, 86%) as a colorless solid; m.p. 175–177 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.89 (m, 1H, CH^{Ar}), 7.56 (m, 3H, $3CH^{Ar}$), 7.40 (m, 4H, $4CH^{Ar}$), 7.19 (m, 4H, $4CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 140.3 ($C^{Ar\text{-}q}$), 138.8 ($C^{Ar\text{-}q}$), 138.6 ($C^{Ar\text{-}q}$), 134.1 ($C^{Ar\text{-}q}$), 132.9 ($C^{Ar\text{-}q}$), 132.3 ($C^{Ar\text{-}q}$), 132.1 ($2CH^{Ar}$), 132.0 ($2CH^{Ar}$), 131.7 ($2CH^{Ar}$), 131.1 ($2CH^{Ar}$), 124.9 (CH^{Ar}), 124.8 (CH^{Ar}), 123.1 (CH^{Ar}), 122.3 ($C^{Ar\text{-}q}$), 122.2 (CH^{Ar}), 121.8 ($C^{Ar\text{-}q}$); IR ($CHCl_3$, cm^{-1}): ν 1533, 1484; HRMS (ES): calcd for $C_{20}H_{13}Br_2S$ [*M* + H]$^{+}$: 442.9099; found: 442.9087.

2,3-Diaryl benzoselenophene 3d-Se. From 26 mg (0.10 mmol) of TMS-alkyne **1a-Si-SeMe**, and after chromatography of the residue using hexanes as eluent, gave compound **3d-Se** (28 mg, 60%) as a colorless solid; m.p. 140–142 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.08–8.04 (m, 1H, CH^{Ar}), 7.67–7.63 (m, 1H, CH^{Ar}), 7.47–7.30 (m, 8H, $8CH^{Ar}$), 7.21–7.17 (m, 2H, $2CH^{Ar}$), 2.56 (s, CH_3), 2.46 (s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 143.8 ($C^{Ar\text{-}q}$), 143.2 ($C^{Ar\text{-}q}$), 140.2 ($C^{Ar\text{-}q}$), 137.4 ($C^{Ar\text{-}q}$), 136.9 ($C^{Ar\text{-}q}$), 135.9 ($C^{Ar\text{-}q}$), 133.8 ($C^{Ar\text{-}q}$), 133.4 ($C^{Ar\text{-}q}$), 130.4 ($2CH^{Ar}$), 129.7 ($2CH^{Ar}$), 129.4 ($2CH^{Ar}$), 129.1 ($2CH^{Ar}$), 125.6 (CH^{Ar}), 125.2 (CH^{Ar}), 124.6 ($2CH^{Ar}$); ^{77}Se NMR (95 MHz, $CDCl_3$, 25 ºC) δ: 528.9 (s, 1Se); IR ($CHCl_3$, cm^{-1}): ν 1506, 1439, 810; HRMS (ES): calcd for $C_{22}H_{19}Se$ [*M* + H]$^{+}$: 363.0647; found: 363.0632.

2,3-Diaryl benzoselenophene 3e-Se. From 26 mg (0.10 mmol) of TMS-alkyne **1a-Si-SeMe**, and after chromatography of the residue using hexanes as eluent, gave compound **3e-Se** (21 mg, 52%) as a colorless solid; m.p. 198–200 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.97–7.94 (m, 1H, CH^{Ar}), 7.52–7.49 (m, 1H, CH^{Ar}), 7.42–7.27 (m, 4H, $4CH^{Ar}$), 7.26–7.17 (m, 6H, $6CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 143.0 ($C^{Ar\text{-}q}$), 142.3 ($C^{Ar\text{-}q}$), 140.5 ($C^{Ar\text{-}q}$), 135.6 ($C^{Ar\text{-}q}$), 134.9 ($C^{Ar\text{-}q}$), 134.4 ($C^{Ar\text{-}q}$), 133.8 ($C^{Ar\text{-}q}$), 133.6 ($C^{Ar\text{-}q}$), 131.9 ($2CH^{Ar}$), 131.0 ($2CH^{Ar}$), 129.1 ($2CH^{Ar}$), 128.7 ($2CH^{Ar}$), 125.5 (CH^{Ar}), 125.4 (CH^{Ar}), 125.2 (CH^{Ar}), 125.0 (CH^{Ar}); ^{77}Se NMR (95 MHz, $CDCl_3$, 25 ºC) δ: 538.9

(s, 1Se); IR ($CHCl_3$, cm^{-1}): ν 1484, 1089, 833; HRMS (ES): calcd for $C_{20}H_{13}Cl_2Se$ $[M + H]^+$: 402.9554; found: 402.9570.

3-Alkoxy-2,3-diaryl-3*H*-indole 6ab. From 30 mg (0.14 mmol) of TMS-azide **4a-Si**, and after chromatography of the residue using hexanes/Et_2O (97:3) containing NEt_3 (2%) as eluent, gave compound **6ab** (40 mg, 63%) as a yellow oil; ^1H NMR (500 MHz, $CDCl_3$, 25 ºC) δ: 7.97 (m, 2H, $2CH^{Ar}$), 7.68 (d, 1H, J = 7.7 Hz, CH^{Ar}), 7.51 (m, 2H, $2CH^{Ar}$), 7.41 (m, 1H, CH^{Ar}), 7.37 (m, 2H, $2CH^{Ar}$), 7.22 (d, 1H, J = 6.6 Hz, CH^{Ar}), 7.19 (m, 2H, $2CH^{Ar}$), 7.11 (d, 1H, J = 6.9 Hz, CH^{Ar}), 3.06 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ: 177.2 (N=C), 153.2 ($C^{Ar\text{-}q}$), 139.7 ($C^{Ar\text{-}q}$), 138.3 ($C^{Ar\text{-}q}$), 131.9 ($2CH^{Ar}$), 130.2 (CH^{Ar}), 130.0 ($C^{Ar\text{-}q}$), 129.9 ($2CH^{Ar}$), 127.2 (CH^{Ar}), 126.4 ($C^{Ar\text{-}q}$), 126.2 ($2CH^{Ar}$), 123.4 (CH^{Ar}), 121.7 ($C^{Ar\text{-}q}$), 121.6 (CH^{Ar}), 92.9 (OC^{q}), 52.6 (OCH_3); IR ($CHCl_3$, cm^{-1}): ν 1728 (N=C), 1079 (C-O); HRMS (ES): calcd for $C_{21}H_{16}Br_2NO$ $[M + H]^+$: 455.9593; found: 455.9601.

3-Alkoxy-2,3-diaryl-3*H*-indole 6ab-CD$_3$. The reaction was runned in CD_3OD instead MeOH. From 30 mg (0.14 mmol) of azide **4a-Si**, and after chromatography of the residue using hexanes/Et_2O (97:3) as eluent containing NEt_3 (2%), gave compound **6ab-CD$_3$** (38 mg, 59%) as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.87 (m, 2H, $2CH^{Ar}$), 7.58 (d, 1H, J = 7.7 Hz, CH^{Ar}), 7.41 (m, 2H, $2CH^{Ar}$), 7.29 (m, 3H, $3CH^{Ar}$), 7.10 (m, 2H, $2CH^{Ar}$), 7.01 (d, 1H, J = 6.8 Hz, CH^{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 177.2 (N=C), 153.3 ($C^{Ar\text{-}q}$), 139.7 ($C^{Ar\text{-}q}$), 138.3 ($C^{Ar\text{-}q}$), 131.9 ($2CH^{Ar}$), 130.2 (CH^{Ar}), 130.1 ($C^{Ar\text{-}q}$), 129.9 ($2CH^{Ar}$), 127.2 (CH^{Ar}), 126.4 ($C^{Ar\text{-}q}$), 126.2 ($2CH^{Ar}$), 123.4 (CH^{Ar}), 121.7 ($C^{Ar\text{-}q}$), 121.6 (CH^{Ar}), 92.9 (OC^{q}); D(^2H) NMR (107 MHz, $CDCl_3$, 25 ºC) δ: 3.04; IR ($CHCl_3$, cm^{-1}): ν 1723 (N=C), 1076 (C-O); HRMS (ES): calcd for $C_{21}H_{13}D_3Br_2NO$ $[M + H]^+$: 458.9782; found: 458.9784.

3,4-Diaryl-isocoumarin 12ad. From 40 mg (0.18 mmol) of TMS-alkyne **10a-Si**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent, gave compound **12ad** (41 mg, 70%) as a colorless solid; m.p. 165–167 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.39 (d, 1H, J = 7.8 Hz, CH^{Ar}), 7.62 (m, 1H, CH^{Ar}), 7.50 (t, 1H, CH^{Ar}), 7.19 (m, 7H, $7CH^{Ar}$), 7.01 (m, 2H, $2CH^{Ar}$), 2.43 (s, 3H, CH_3), 2.30 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 162.4 (C=O), 150.9 (*C*=C), 139.2 ($C^{Ar\text{-}q}$), 139.0 ($C^{Ar\text{-}q}$), 137.8 ($C^{Ar\text{-}q}$), 134.5 (CH^{Ar}), 131.4 ($C^{Ar\text{-}q}$), 131.0 ($2CH^{Ar}$), 130.1 ($C^{Ar\text{-}q}$), 129.8 ($2CH^{Ar}$), 129.4 (CH^{Ar}), 129.0 ($2CH^{Ar}$), 128.6 ($2CH^{Ar}$), 127.8 (CH^{Ar}), 125.3 (CH^{Ar}), 120.3 ($C^{Ar\text{-}q}$), 116.3 (C=*C*), 21.3 (CH_3), 21.2 (CH_3); IR ($CHCl_3$, cm^{-1}): ν 1715 (C=O); HRMS (ES): calcd for $C_{23}H_{19}O_2$ $[M + H]^+$: 327.1380; found: 327.1388.

3,4-Diaryl-isocoumarin 12af. From 35 mg (0.15 mmol) of TMS-alkyne **10a-Si**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent, gave compound **12af** (44 mg, 68%) as a colorless solid; m.p. 155–157 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.45 (dd, 1H, J = 7.9, 1.3 Hz, CH^{Ar}), 7.71 (m, 3H, $3CH^{Ar}$), 7.60 (m, 1H, CH^{Ar}), 7.50 (m, 2H, $2CH^{Ar}$), 7.43 (m, 4H, $4CH^{Ar}$), 7.13 (d, 1H, J = 7.8 Hz, CH^{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 161.4 (C=O), 149.7 (*C*=C), 137.7 (d, J_{CF} = 1.3 Hz, $C^{Ar\text{-}q}$), 137.6 ($C^{Ar\text{-}q}$), 135.9 (d, J_{CF} = 1.0 Hz, $C^{Ar\text{-}q}$), 135.0 (CH^{Ar}), 131.7 ($2CH^{Ar}$), 131.0 (q, J_{CF} = 32.7 Hz, $C^{Ar\text{-}q}$-CF_3), 130.8 (q, J_{CF} = 32.8 Hz, $C^{Ar\text{-}q}$-CF_3), 129.9 (CH^{Ar}), 129.5 ($2CH^{Ar}$), 129.0 (CH^{Ar}), 126.3 (q, J_{CF} = 3.7 Hz, $2CH^{Ar}$), 125.2 (CH^{Ar}), 125.1 (q, J = 3.8 Hz, $2CH^{Ar}$), 123.8 (q, J_{CF} = 272.4 Hz, CF_3), 123.6 (q, J_{CF} = 272.4 Hz, CF_3), 120.5 ($C^{Ar\text{-}q}$), 116.90 (C=*C*), 103.4 (CH^{Ar}); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): –62.9 (s, 3F, CF_3), –63.2 (s, 3F, CF_3); IR ($CHCl_3$, cm^{-1}): ν 1735 (C=O); HRMS (ES): calcd for $C_{23}H_{13}F_6O_2$ $[M + H]^+$: 435.0814; found: 435.0814.

3,4-Diaryl-isocoumarin 12bb. From 41 mg (0.11 mmol) of TMS-alkyne **10b-Si**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent, gave compound **12bb** (37 mg, 72%) as a colorless solid; m.p. 142–144 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.06 (dd, 1H, J = 8.3, 2.8 Hz, CH^{Ar}), 7.60 (m, 2H, $2CH^{Ar}$), 7.39 (m, 3H, 3 CH^{Ar}), 7.16 (m, 5H, $5CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 162.0 (d, J_{CF} = 251.5 Hz, $C^{Ar\text{-}q}$-F), 163.7 (d, J_{CF} = 3.5 Hz, C=O), 149.5 (d, J_{CF} = 2.6 Hz, *C*=C), 134.7 (d, J_{CF} = 2.7 Hz, $C^{Ar\text{-}q}$), 132.7 ($2CH^{Ar}$), 132.6 ($2CH^{Ar}$), 131.4 ($2CH^{Ar}$), 131.2 ($C^{Ar\text{-}q}$), 130.6 ($2CH^{Ar}$), 127.7 (d, J_{CF} = 7.8 Hz, CH^{Ar}), 123.8 ($C^{Ar\text{-}q}$), 123.3 ($C^{Ar\text{-}q}$), 123.1 (d, J_{CF} = 22.8 Hz, CH^{Ar}), 122.9 ($C^{Ar\text{-}q}$), 122.2 (d, J_{CF} = 8.2 Hz, $C^{Ar\text{-}q}$), 115.5 (d, J_{CF} = 0.9 Hz, C=*C*), 115.3 (d, J_{CF} = 23.3 Hz, CH^{Ar}); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): –110.31 (s, 1F, C–F); IR ($CHCl_3$, cm^{-1}): ν 1737 (C=O); HRMS (ES): calcd for $C_{21}H_{11}Br_2FO_2$ $[M + H]^+$: 472.9183; found: 472.9192.

3,4-Diaryl-benzosultam 13e. From 26 mg (0.10 mmol) of TMS-alkyne **11-Si**, and after chromatography of the residue using hexanes/ethyl acetate (8:2) as eluent, gave compound **13e** (28 mg, 68%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.00–7.96 (m, 1H, CH^{Ar}), 7.55–7.53 (m, 2H, $2CH^{Ar}$), 7.30–7.28 (m, 3H, $3CH^{Ar}$), 7.24–7.22 (m, 4H, $2CH^{Ar}$), 7.15 (d, 2H, J = 7.9 Hz, $2CH^{Ar}$), 2.99 (s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 140.0 ($C^{Ar\text{-}q}$), 134.9 ($C^{Ar\text{-}q}$), 134.1 ($C^{Ar\text{-}q}$), 133.6 ($C^{Ar\text{-}q}$), 133.4 ($C^{Ar\text{-}q}$), 132.5 ($2CH^{Ar}$), 132.3 ($C^{Ar\text{-}q}$), 131.8 (CH^{Ar}), 131.6 ($C^{Ar\text{-}q}$), 131.3 ($2CH^{Ar}$), 128.6 ($2CH^{Ar}$), 128.5 ($2CH^{Ar}$), 128.2 (CH^{Ar}), 127.0 (CH^{Ar}), 123.4 ($C^{Ar\text{-}q}$), 122.0 (CH^{Ar}), 34.5 (CH_3); IR ($CHCl_3$, cm^{-1}): ν 1588 (C=C), 1485, 1337 (O=S=O); HRMS (ES): calcd for $C_{21}H_{16}Cl_2NO_2S$ $[M + H]^+$: 416.0273; found: 416.0277.

3,4-Diaryl-benzosultam 13g. From 26 mg (0.10 mmol) of TMS-alkyne **11-Si**, and after chromatography of the residue using hexanes/ethyl acetate (8:2) as eluent, gave compound **13g** (25 mg, 66%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.92–7.89 (m, 1H, CH^{Ar}), 7.48–7.46 (m, 2H, $2CH^{Ar}$), 7.31–7.25 (m, 3H, $3CH^{Ar}$), 7.20–7.05 (m, 2H, $2CH^{Ar}$), 7.02–6.91 (m, 4H, $4CH^{Ar}$), 2.94 (s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 162.5 (d, 1H, J_{CF} = 250.0 Hz, $C^{Ar\text{-}q}$ -F), 162.0 (d, 1H, J_{CF} = 250.0 Hz, $C^{Ar\text{-}q}$ -F), 140.3 ($C^{Ar\text{-}q}$), 133.7 ($C^{Ar\text{-}q}$), 132.9 162.0 (d, 2H, J_{CF} = 8.3 Hz, $2CH^{Ar}$), 131.9 (d, 2H, J_{CF} = 8.3 Hz, $2CH^{Ar}$), 131.8 (CH^{Ar}), 131.6 ($C^{Ar\text{-}q}$), 131.5 ($C^{Ar\text{-}q}$), 130.0 ($C^{Ar\text{-}q}$), 128.0 (CH^{Ar}), 127.0 (CH^{Ar}), 123.4 ($C^{Ar\text{-}q}$), 121.9 (CH^{Ar}), 115.2 (d, 4H, J_{CF} = 22.3 Hz, $4CH^{Ar}$), 34.4 (s, CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): –111.4 (s, 1F, C–F), –114.3 (s, 1F, C–F); IR ($CHCl_3$, cm^{-1}): ν 1585 (C=C), 1487, 1335 (O=S=O); HRMS (ES): calcd for $C_{21}H_{16}F_2NO_2S$ $[M + H]^+$: 384.0864; found: 384.0860.

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General procedure for the photopromoted gold-catalyzed cross double arylation reaction of TMS-(ethynyl)azidobenzene 4a-Si with diazonium salts 2. Preparation of crossed-3-methoxy-2,3-diaryl-3*H*-indoles 6aag–6aeb. In a Schlenk tube in the absence of light at –78 ºC under argon atmosphere, Ph_3PAuCl (5 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 2-[(trimethylsilyl)ethynyl]azidobenzene **4a-Si** (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 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, 20–30 min), Ph_3PAuCl (5 mol %) and a solution of the second arene diazonium salt **2** (6.0 equiv) in a mixture of MeOH/MeCN (3:1, 2.5 mL) were sequentially added. The resulting reaction mixture was stirred at rt 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. The addition of Et_3N (2%) to the eluent was neccesary for the purification of acid sensitive 3*H*-indoles **6**. Spectroscopic and analytical data for pure forms of crossed adducts **6** follow.

3-Methoxy-2,3-diaryl-3*H*-indole 6abe. From 30 mg (0.14 mmol) of TMS-azide **4a-Si**, and after chromatography of the residue using hexanes/Et_2O (97:3) containing NEt_3 (2%) as eluent, gave compound **6abe** (35 mg, 61%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 7.99 (m, 2H, 2CH^{Ar}), 7.59 (d, 1H, *J* = 7.7 Hz, CH^{Ar}), 7.42 (m, 2H, 2CH^{Ar}), 7.32 (td, 1H, *J* = 7.6, 1.3 Hz, CH^{Ar}), 7.15 (m, 5H, 5CH^{Ar}), 7.02 (d, 1H, *J* = 7.3 Hz, CH^{Ar}), 2.98 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 177.3 (N=C), 153.3 (*C*$^{Ar\text{-}q}$), 139.8 (*C*$^{Ar\text{-}q}$), 137.7 (*C*$^{Ar\text{-}q}$), 133.5 (*C*$^{Ar\text{-}q}$), 131.9 (2CH^{Ar}), 130.1 (CH^{Ar}), 130.0 (*C*$^{Ar\text{-}q}$), 129.9 (2CH^{Ar}), 129.0 (CH^{Ar}), 127.2 (CH^{Ar}), 126.3 (*C*$^{Ar\text{-}q}$), 125.9 (2CH^{Ar}), 123.4 (CH^{Ar}), 121.6 (CH^{Ar}), 92.9 (O*C*^{q}), 52.6 (OCH_3); IR ($CHCl_3$, cm^{-1}): ν 1693 (N=C), 1085 (C-O); HRMS (ES): calcd for $C_{21}H_{16}BrClNO$ [*M* + H]$^+$: 412.0098; found: 412.0115.

3-Methoxy-2,3-diaryl-3*H*-indole 6aeb. From 30 mg (0.14 mmol) of TMS-azide **4a-Si**, and after chromatography of the residue using hexanes/Et_2O (97:3) containing NEt_3 (2%) as eluent, gave compound **6aeb** (33 mg, 57%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.04 (m, 2H, 2CH^{Ar}), 7.38 (d, 1H, *J* = 7.7 Hz, CH^{Ar}), 7.38 (m, 5H, 5CH^{Ar}), 7.21 (m, 3H, 3CH^{Ar}), 7.11 (d, 1H, *J* = 7.3 Hz, CH^{Ar}), 3.07 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 177.1 (N=C), 153.3 (*C*$^{Ar\text{-}q}$), 139.7 (*C*$^{Ar\text{-}q}$), 138.3 (*C*$^{Ar\text{-}q}$), 137.7 (*C*$^{Ar\text{-}q}$), 131.9 (2CH^{Ar}), 130.1 (CH^{Ar}), 129.7 (2CH^{Ar}), 129.6 (*C*$^{Ar\text{-}q}$), 128.9 (2CH^{Ar}), 127.1 (CH^{Ar}), 126.2 (2CH^{Ar}), 123.4 (CH^{Ar}), 121.6 (*C*$^{Ar\text{-}q}$), 121.5 (CH^{Ar}), 92.9 (O*C*^{q}), 52.6 (OCH_3).; IR ($CHCl_3$, cm^{-1}): ν 1726 (N=C), 1087 (C-O); HRMS (ES): calcd for $C_{21}H_{16}BrClNO$ [*M* + H]$^+$: 412.0098; found: 412.0087.

General procedure for the base-catalyzed rearrangement reaction of 3-methoxy-2,3-diaryl-3*H*-indoles 6. Preparation of 2,3-diaryl-1*H*-indoles 5. A solution of the corresponding 3*H*-indole **6** (1 mmol) in ethanolic potash (115 mL, KOH 1 M in EtOH) was stirred under microwave heating (105 ºC) until the complete disappearance of the starting material (TLC, typically 12 h). After this time, the reaction was cooled down to 0 ºC and neutralized with HCl (3 M) until pH 7. The aqueous phase was extracted with EtOAc (3 × 20 mL), the organic phases combined, dried over $MgSO_4$ and the solvent removed by distillation under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure adducts **5**.

2,3-Diaryl-1*H*-indole 5ab. From 20 mg (0.043 mmol) of 3*H*-indole **6ab**, and after chromatography of the residue using hexanes/DCM (8:2) as eluent, gave compound **5ab** (13 mg, 71%) as a colorless solid; m.p. 175-177 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.21 (s, 1H, NH), 7.62 (d, 1H, *J* = 7.9 Hz, CH^{Ar}), 7.47 (m, 5H, 5CH^{Ar}), 7.27 (m, 5H, 5CH^{Ar}), 7.17 (m, 1H, CH^{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 135.9 (*C*$^{Ar\text{-}q}$), 133.7 (*C*$^{Ar\text{-}q}$), 133.0 (*C*$^{Ar\text{-}q}$), 132.0 (2CH^{Ar}), 131.8 (2CH^{Ar}), 131.6 (2CH^{Ar}), 131.2 (*C*$^{Ar\text{-}q}$), 129.6 (2CH^{Ar}), 128.3 (*C*$^{Ar\text{-}q}$), 123.2 (CH^{Ar}), 122.1 (*C*$^{Ar\text{-}q}$), 120.8 (CH^{Ar}), 120.4 (*C*$^{Ar\text{-}q}$), 119.4 (CH^{Ar}), 114.3 (*C*$^{Ar\text{-}q}$), 111.0 (CH^{Ar}); IR ($CHCl_3$, cm^{-1}): ν 3417 (N-H); HRMS (ES): calcd for $C_{20}H_{14}Br_2N$ [*M* + H]$^+$: 425.9487; found: 425.9484.

General procedure for the acid-catalyzed rearrangement reaction of 3-methoxy-2,3-diaryl-3*H*-indoles 6. Preparation of 2-oxindoles 8. A solution of the corresponding 3*H*-indole **6** (1 mmol) in ethanolic sulfuric acid (115 mL, H_2SO_4 0.4 M in EtOH) was stirred under microwave heating (125 ºC) until the complete disappearance of the starting material (TLC, typically 12 h). After this time, the reaction was cooled down to 0 ºC and neutralized with $NaHCO_3$ (aqueous saturated solution) until pH 7. The aqueous phase was extracted with EtOAc (3 × 10 mL), the organic phases combined, dried over $MgSO_4$ and the solvent removed by distillation under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure adducts **8**.

3,3-Diaryl-2-oxindole 8ab. From 20 mg (0.043 mmol) of 3*H*-indole **6ab**, and after chromatography of the residue using hexanes/AcOEt (97:3 → 80:20) as eluent, gave compound **8ab** (14 mg, 72%) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) δ: 8.48 (s, 1H, NH), 7.44 (m, 4H, 4CH^{Ar}), 7.28 (t, 1H, *J* = 7.6 Hz, CH^{Ar}), 7.16 (m, 5H, 5CH^{Ar}), 7.09 (t, 1H, *J* = 7.6 Hz, CH^{Ar}), 6.98 (d, 1H, *J* = 7.8 Hz, CH^{Ar}). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ: 178.8 (C=O), 140.2 (2*C*$^{Ar\text{-}q}$), 139.9 (*C*$^{Ar\text{-}q}$), 132.4 (*C*$^{Ar\text{-}q}$), 131.7 (4CH^{Ar}), 130.1 (4CH^{Ar}), 128.8 (CH^{Ar}), 126.1 (CH^{Ar}), 123.2 (CH^{Ar}), 121.9 (2*C*$^{Ar\text{-}q}$), 110.5 (CH^{Ar}), 61.0 (*C*^{q}-C=O). IR ($CHCl_3$, cm^{-1}): ν. 3222 (N-H), 1711 (C=O); HRMS (ES): calcd for $C_{20}H_{14}Br_2NO$ [*M* + H]$^+$: 441.9437; found: 441.9446.

General procedure for the acid-catalyzed rearrangement reaction of 3-methoxy-2,3-diaryl-3*H*-indoles 6. Preparation of 3-oxindolines 9. A solution of the corresponding 3*H*-indole **6** (1 mmol) in ethanolic

sulfuric acid (115 mL, H_2SO_4 0.2 M in EtOH) was stirred under microwave heating (95 ºC) until the complete disappearance of the starting material (TLC, typically 12 h). After this time, the reaction was cooled down to 0 ºC and neutralized with $NaHCO_3$ (aqueous saturated solution) until pH 7. The aqueous phase was extracted with EtOAc (3 × 10 mL), the organic phases combined, dried over $MgSO_4$ and the solvent removed by distillation under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure adducts **9** along with compounds **8** as minor components.

2,2-Diaryl-3-oxindoline 9ab. From 20 mg (0.043 mmol) of 3*H*-indole **6ab**, and after chromatography of the residue using hexanes:AcOEt (97:3) as eluent, gave compound **9ab** (10 mg, 51%) yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) δ: 7.66 (d, 1H, *J* = 7.7 Hz, CH^{Ar}), 7.53 (t, 1H, *J* = 7.7 Hz, CH^{Ar}), 7.46 (m, 4H, $4CH^{Ar}$), 7.25 (m, 4H, $4CH^{Ar}$), 6.94 (m, 2H, $2CH^{Ar}$), 5.09 (s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ: 199.8 (C=O), 159.9 ($C^{Ar\text{-}q}$), 139.7 ($2C^{Ar\text{-}q}$), 138.0 (CH^{Ar}), 131.8 ($4CH^{Ar}$), 129.1 ($4CH^{Ar}$), 125.6 (CH^{Ar}), 122.4 ($2C^{Ar\text{-}q}$), 120.3 (CH^{Ar}), 119.8 ($C^{Ar\text{-}q}$), 112.7 (CH^{Ar}), 74.0 (NC^{q}). IR ($CHCl_3$, cm^{-1}): ν 3450 (N-H), 1686 (C=O). HRMS (ES): calcd for $C_{20}H_{14}Br_2NO$ [*M* + H]$^+$: 441.9437; found: 441.9453.

General procedure for the photopromoted gold-catalyzed monoarylation reaction of aryl-terminated alkynones 14-Ph or 16-Ph with diazonium salts 2. Preparation of 3-aryl-flavones 15 and 3-aryl-thioflavones 17. 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** (3.0 equiv) in a mixture of MeOH/MeCN (3:1, 3 mL). Then, a solution of the appropriate aryl-terminated alkynone **14-Ph** or **16-Ph** (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 **15** and **17** follow.

3-Aryl-flavone 15c. From 21 mg (0.10 mmol) of aryl-terminated alkynone **14-Ph**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent, gave compound **15c** (24 mg, 66%) as a colorless solid; m.p. 127–129 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.32 (dd, 1H, *J* = 7.6 Hz, *J* = 1.5 Hz, CH^{Ar}), 8.00 (d, 2H, *J* = 8.3 Hz, $2CH^{Ar}$), 7.77–7.71 (m, 1H, $1CH^{Ar}$), 7.56 (d, 1H, *J* = 8.6 Hz, $1CH^{Ar}$), 7.49–7.27 (m, 8H, $8CH^{Ar}$), 4.38 (q, 2H, *J* = 6.5 Hz, CH_2), 1.40 (t, 3H, *J* = 6.5 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 176.8 (C=O), 166.4 (C=O), 161.8 (*C*=C), 155.9 ($C^{Ar\text{-}q}$), 137.8 ($C^{Ar\text{-}q}$), 133.8 (CH^{Ar}), 132.8 ($C^{Ar\text{-}q}$), 131.3 ($2CH^{Ar}$), 130.3 (CH^{Ar}), 129.5 ($2CH^{Ar}$), 129.4 ($C^{Ar\text{-}q}$), 129.3 ($2CH^{Ar}$), 128.2 ($2CH^{Ar}$), 126.3 (CH^{Ar}), 125.2 (CH^{Ar}), 123.3 ($C^{Ar\text{-}q}$), 122.1 ($C^{Ar\text{-}q}$), 118.0 (CH^{Ar}), 60.9 (CH_2), 14.3 (CH_3); IR ($CHCl_3$, cm^{-1}): ν 1712 (C=O), 1639 (C=O), 1270; HRMS (ES): calcd for $C_{24}H_{19}O_4$ [*M* + H]$^+$: 371.1278; found: 371.12826.

3-Aryl-flavone 15f. From 21 mg (0.10 mmol) of aryl-terminated alkynone **14-Ph**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent, gave compound **15f** (25 mg, 69%) as a colorless solid; m.p. 144–145 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) δ: 8.31 (dd, 1H, *J* = 7.6 Hz, *J* = 1.5 Hz, CH^{Ar}), 7.76–7.73 (m, 2H, $2CH^{Ar}$), 7.57 (d, 1H, *J* = 8.6 Hz, CH^{Ar}), 7.49–7.46 (m, 1H, $1CH^{Ar}$), 7.40–7.31 (m, 5H, $5CH^{Ar}$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ: 176.8 (C=O), 162.1 (*C*=C), 159.0 ($C^{Ar\text{-}q}$), 136.8 ($C^{Ar\text{-}q}$), 134.0 (CH^{Ar}), 131.7 ($2CH^{Ar}$), 130.5 (CH^{Ar}), 129.5 ($2CH^{Ar}$), 129.6 (q, J_{CF} = 32.0 Hz, $C^{Ar\text{-}q}$), 128.3 ($2CH^{Ar}$), 126.5 (CH^{Ar}), 125.4 (CH^{Ar}), 125.4 (q, J_{CF} = 4.3 Hz, $2CH^{Ar}$), 124.1 (q, J_{CF} = 272.0 Hz, CF_3), 123.3 ($C^{Ar\text{-}q}$), 121.7 ($C^{Ar\text{-}q}$), 118.0(CH^{Ar}); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): –62.9 (s, 3F, CF_3); IR ($CHCl_3$, cm^{-1}): ν 1638 (C=O), 1377; HRMS (ES): calcd for $C_{22}H_{14}F_3O_2$ [*M* + H]$^+$: 367.0904; found: 367.0947.

3-Aryl-thioflavone 17b. From 35 mg (0.14 mmol) of aryl-terminated alkynone **16-Ph**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent, gave compound **17b** (33 mg, 61%) as a colorless solid; m.p. 155–157 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ: 8.50 (d, 1H, *J* = 7.7 Hz, CH^{Ar}), 7.52 (m, 3H, $3CH^{Ar}$), 7.20 (m, 7H, $7CH^{Ar}$), 6.91 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ: 179.2 (C=O), 150.8 (*C*=C), 137.2 ($C^{Ar\text{-}q}$), 136.6 ($C^{Ar\text{-}q}$), 134.5 ($C^{Ar\text{-}q}$), 134.4 (C=*C*), 132.8 ($2CH^{Ar}$), 131.6 (CH^{Ar}), 131.1 ($C^{Ar\text{-}q}$), 130.9 ($2CH^{Ar}$), 129.5 (CH^{Ar}), 129.3 (CH^{Ar}), 129.2 ($2CH^{Ar}$), 128.5 ($2CH^{Ar}$), 127.8 (CH^{Ar}), 125.8 (CH^{Ar}), 121.4 ($C^{Ar\text{-}q}$); IR ($CHCl_3$, cm^{-1}): ν 1617 (C=O), 1589 (C=C); HRMS (ES): calcd for $C_{21}H_{14}BrOS$ [*M* + H]$^+$: 392.9943; found: 392.9935.

3-Aryl-thioflavone 17e. From 31 mg (0.12 mmol) of aryl-terminated alkynone **16-Ph**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent, gave compound **17e** (28 mg, 68%) as a colorless solid; m.p. 154–156 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) δ: 8.58 (d, 1H, *J* = 7.8 Hz, CH^{Ar}), 7.62 (m, 3H, $3CH^{Ar}$), 7.28 (m, 3H, $3CH^{Ar}$), 7.21 (m, 4H, $4CH^{Ar}$), 7.05 ($2CH^{Ar}$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ: 179.3 (C=O), 150.8 (*C*=C), 137.2 ($C^{Ar\text{-}q}$), 136.6 ($C^{Ar\text{-}q}$), 134.4 ($C^{Ar\text{-}q}$), 134.0 (C=*C*), 133.1 ($C^{Ar\text{-}q}$), 132.5 ($2CH^{Ar}$), 131.6 (CH^{Ar}), 131.2 ($C^{Ar\text{-}q}$), 129.6 (CH^{Ar}), 129.3 (CH^{Ar}), 129.2 ($2CH^{Ar}$), 128.5 ($2CH^{Ar}$), 128.0 ($2CH^{Ar}$), 127.8 (CH^{Ar}), 125.8 (CH^{Ar}); IR ($CHCl_3$, cm^{-1}): ν 1617 (C=O), 1588 (C=C); HRMS (ES): calcd for $C_{21}H_{13}ClOS$ [*M* + H]$^+$: 349.0448; found: 349.0457.

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[16] Experimental procedures as well as full spectroscopic and analytical data for compounds not included in this Experimental Section are described in the Supporting Information. It contains compound characterization data, experimental procedures, and copies of NMR spectra for all new compounds.

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FULL PAPER

Photopromoted Entry to Benzothiophenes, Benzoselenophenes, 3*H*-Indoles, Isocoumarins, Benzosultams, and (Thio)Flavones by Gold-Catalyzed Arylative Heterocyclization of Alkynes

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Benito Alcaide,* Pedro Almendros,* Eduardo Busto, Fernando Herrera, Carlos Lázaro-Milla, and Amparo Luna