Photosensitized oxidative addition to gold(1) enables alkynylative cyclization of *o*-alkylnylphenols with iodoalkynes

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The well-established oxidative addition-reductive elimination pathway is the most followed one in transition metal-catalysed cross-coupling reactions. While readily occurring with a series of transition metals, gold(1) complexes have shown some reluctance to undergo oxidative addition unless special sets of ligands on gold(1), reagents or reaction conditions are used. Here we show that under visible-light irradiation, an iridium photocatalyst triggers—via triplet sensitization—the oxidative addition of an alkynyl iodide onto a vinylgold(1) intermediate to deliver $C(sp)^2-C(sp)$ coupling products after reductive elimination. Mechanistic and modelling studies support that an energy-transfer event takes place, rather than a redox pathway. This particular mode of activation in gold homogenous catalysis was applied in several dual catalytic processes. Alkynylbenzofuran derivatives were obtained from o-alkynylphenols and iodoalkynes in the presence of catalytic gold(1) and iridium(11) complexes under blue light-emitting diode irradiation.

ver the past two decades, homogeneous gold catalysis has been extensively used to efficiently and selectively promote a variety of cyclization processes¹⁻³. The typical casting involves bifunctional substrates bearing an unsaturation prompt to electrophilic activation and a judiciously positioned internal nucleophile. Protodemetalation of the organogold intermediates to afford hydrofunctionalized products generally terminates the catalytic cycles⁴. To pursue the step economy principle and aim for higher levels of molecular complexity, some in situ postfunctionalization reactions of the organogold⁵ intermediate have been devised, such as electrophilic halogenation or cross-coupling reactions. Although palladium-catalysed crosscoupling from an organogold(1) intermediate has been rendered possible^{6,7}, this transformation still needs generality and most of the described coupling reactions have transited through a Au(I) to Au(III) oxidation, necessitating an oxidant in stoichiometric quantity, transmetalation and a reductive elimination cycle^{8,9}. A notable breakthrough in this area was achieved by Glorius^{10,11} and Toste^{12,13}, who bypassed the burden of stoichiometric oxidants by merging gold catalysis with photoredox catalysis, ensuring that the oxidation states shuttle¹⁴⁻¹⁶. Arylative cyclization and related transformations, as well as cross-coupling processes that rely on the use of easily reduced aryl diazonium salts, have been devised (Fig. 1a)¹⁷⁻²⁴. Two mechanism pathways have been proposed (Fig. 1b) that both feature the reductive elimination from a vinylgold(III) intermediate of type D but differ by the stage of addition of the radical on gold (intermediate A versus F). Pathway I has been recently supported by stoichiometric reactions and calculations^{9,25,26}. A ground-breaking advance in these reactions would be to promote the oxidative addition step by energy transfer (photosensitization) as this has found more

relevance in visible-light catalysis involving organometallic complexes²⁷. Useful photophysical guidelines for Dexter versus Förster and exergonic versus endergonic energy transfers have been drawn²⁸.

Extending the scope of possible partners in these transformations is also highly desirable, and we aimed to develop alkynylative cyclization processes that correspond to a formal $C(sp)^2 - C(sp)$ cross-coupling reaction, which has little precedent in this type of dual catalytic transformation^{13,29-31}. Thus, replacing aryl diazoniums with alkynyl iodide partners in our recent dual photoredox/ gold-catalysed arylative cyclization of o-alkynylphenols, which leads to benzofurans³², would constitute an appropriate base for exploration as well as provide valuable scaffolds. We were also aware that alkynyl iodides are much less reactive than aryl diazoniums and that we would probably have to devise a distinct mode of activation of gold(I) complexes to promote the C-C bond formation step (Fig. 1c). Indeed, gold(I) complexes are notoriously resistant to oxidative addition³³. This can be rendered feasible only by using special sets of electrophilic reagents³⁴⁻³⁶ and/or certain conditions. For instance, Toste and collaborators³⁷ showed that CF₃I adds to arylgold(1) complexes under UV irradiation. Substrates bearing a directing group or with inherent ring strain^{38,39} can also undergo oxidative addition to provide cyclometallated gold(III) intermediates. Recently, Amgoune and Bourissou^{40,41} and Russell⁴² have demonstrated that bidentate ligands on gold(I) with particular features promote oxidative addition and that the resulting gold(III) intermediate can react with a nucleophile to provide cross-coupling products⁴², notably through a catalytic cycle⁴¹. In this work, we uncover a mode of C–C bond formation via photosensitized energy transfer that promotes oxidative addition of a gold(I) complex (Fig. 1c).

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Fig. 1 Gold-catalysed additions to alkynes. a, General scheme of the dual gold-photoredox catalysed difunctionalization of alkynes. **b**, Proposed mechanistic pathway I in dual gold-photoredox catalysis. The key Au(III) intermediate **b** is generated via radical addition on the Au(I) precatalyst and the resulting Au(II) complex **A** is oxidized through single electron transfer (SET) by the oxidized photocatalyst. Pathway I has been supported by calculations and the isolation of intermediates. **c**, Alternate mechanistic pathway II implies the initial formation of a vinyl Au(I) intermediate **E**. **d**, Dual gold and photoinduced alkynylative *O*-cyclization via photosensitized oxidative addition.

Results and discussion

Optimization studies. We surveyed the feasibility of such a transformation by examining the model reaction between 2-(p-tolylethynyl)phenol 1a and iodoethynyl benzene 2a under various conditions (see Supplementary Section III for detailed conditions optimization). Preliminary negative results based on the previous arylation protocol using a catalytic mixture of Ru(bpy)₃Cl₂ and PPh₃AuCl in MeOH drove us to use other conditions. The first hits in the formation of benzofuran 3aa (structure confirmed by X-ray diffraction analysis, Cambridge Crystallographic Data Centre (CCDC) accession code no. 1850903) were obtained in acetonitrile and by adding a base (see Supplementary Section III. 2 and Table 1, entry 1). This finding was consolidated by using $Ir[dF(CF_3)]$ ppy]₂(dtbbpy)PF₆ ([**Ir-F**]) as a photocatalyst (entry 3, 26% of **3aa**). A substantial gain of yield was observed (56% of 3aa) by switching PPh₃AuCl to (p-CF₃Ph)₃PAuCl [Au-CF₃] (entry 4). Finally, after substantial optimization it was found that the combination of [Au-CF₃] (5 mol%), ([Ir-F]) (1 mol%), 1,10-phenanthroline (10 mol%), K₂CO₃ (2.5 equiv.) in degassed MeCN at room temperature overnight under a blue light-emitting diode (LED) light gave the best result, since a 71% isolated yield of 3aa was obtained (entry 5). The reaction can work without a photocatalyst (entry 8) and the use of a more reductive photocatalyst such as fac-Ir(ppy)₃ was not beneficial (entry 2). Control experiments regarding the

role of 1,10-phenanthroline were also performed. A stoichiometric amount of 1,10-phenanthroline proved detrimental to the yield (entry 6); however, other amines, such as quinuclidine (entry 7) or tetramethylethylenediamine (TMEDA), 1,4-diazabicyclo[2.2.2] octane (DABCO) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (see Supplementary Section III. 4), could also be used to improve the reaction. In sharp contrast, no desired product could be obtained in the absence of the base (K_2CO_3 , entry 11), [Au-CF₃] (entry 10) or light (entry 12). Finally, it is worth noting that the iodoetherification product **4a** and diyne **5a** were the side compounds in almost all conditions. Diyne **5a** was present in a lower quantity (<20%) and its formation presumably requires gold catalysis (see Supplementary Section III. 6). When (bromoethynyl)benzene **2a-Br** was subjected to the reaction, only 9% of **3aa** was obtained.

Mechanistic investigations. This preliminary set of findings drove us to delineate a plausible mechanism for the further development of the reaction. We first considered the addition of a radical intermediate stemming from the photocatalytic cycle to produce the corresponding intermediate of type **B** through **A** (Fig. 1). Alkynyl radicals remain an elusive species, but they have been noted sporadically in the literature to be generated from alkynyl iodides^{43,44}. Nevertheless, by using alkynyl iodide **2b** as a probe (as it bears a fluorine label), this hypothesis was rapidly discarded. First, as the



Table 1 | Defining the key parameters of the alkynylative cyclization

a[Au-CF₃] = (p-CF₃Ph)₃PAuCl; [Ir-F] = lr[dF(CF₃)ppy]₃(dtbbpy)PF₆; phen. = 1,10-phenanthroline. ^bOnly 1equiv. of K₂CO₃ was used. ^cYields were determined by ¹H NMR using 1,3,5-trimethoxybenzene as the internal standard, the vield in parentheses is the isolated vield. «No K₂CO₂, «No light, ¹Isolated vield

reductive potential of 1-fluoro-4-(iodoethynyl)benzene at the ground state $(E_{1/2}(\mathbf{2b}) = -1.47 \text{ V}$ versus saturated calomel electrode (SCE) is substantially higher than the reduction potential of the excited state of the [Ir-F] catalyst ($E^{\star}_{1/2} = -0.89$ V versus SCE), photoreductive formation of an alkynyl radical seemed unlikely. This was corroborated by fluorescence quenching studies that showed no quenching of excited [Ir-F] (³T₁), denoted ³[Ir-F], by 2b, therefore precluding a photocatalysed electron transfer event. Another pathway for the formation of the gold(III) intermediate of type B was investigated due to the fact that alkynyl iodide 2b and the gold complex [Au-CF₃] convert into a new unstable gold species under blue LED irradiation, but the catalytic role of the latter remains elusive (see Supplementary Section V.5).

Literature reports^{9,14,16} indicate that a vinylgold(III) intermediate of type D of Fig. 1, which would undergo reductive elimination to provide benzofurans 3, is presumably involved. To investigate this, vinylgold(1) 6 of type E was prepared in 82% yield by an independent route⁴⁵ as shown in Fig. 2a. An X-ray diffraction analysis of suitable crystals of 6 confirmed its structure (CCDC 1850902, Fig. 2b) and provided useful structural data for further modelling studies. No conversion of 6 when reacted with one equivalent of alkynyliodide 2b was observed after 3 h at room temperature (25 °C) in the absence of irradiation with a blue LED. However, blue LED irradiation changed the scenario. A low conversion (<10%) was observed after 2h at room temperature, while overnight irradiation resulted in the formation of 33% of benzofuran 3ab (accompanied by 20% of 4a and 35% of protodeauration product 7 as determined by ¹H NMR (Fig. 2c)). The addition of 10 mol% of [Ir-F] markedly altered the outcome and yielded **3ab** almost quantitatively (Fig. 2d). Therefore, experimental conditions to trigger the key C-C bond formation were successfully found. Although benzofuran formation could be achieved under direct irradiation conditions without photocatalyst [Ir-F] (Fig. 2c,d), which brings some rationalization for the finding in entries 8 and 9 of Table 1, benzofuran formation seems to be greatly enhanced in its presence. This was confirmed by measuring the steady-state luminescence spectra of mixtures of [Ir-F] and 6. We observed a drop in the [Ir-F] luminescence signal

when the concentration of 6 was increased, which suggested that 6 acts as a quencher of ³[Ir-F] (Fig. 2e). In parallel, we recorded the luminescence lifetime of the same solutions and observed that it decreased from 2.4 µs in the absence of 6 (in agreement with previous reports^{46,47}) to 290 ns in the presence of $745 \,\mu\text{M}$ of 6, thereby confirming the quenching of ³[Ir-F] by 6 (see Supplementary Fig. 3). Values of 2.9×10^9 moll⁻¹s⁻¹ and 4.1×10^9 moll⁻¹s⁻¹ were extracted for the bimolecular quenching rate constant (k_{a}) from the luminescence intensity (I_0/I) and lifetime (τ_0/τ) Stern–Volmer plots respectively (see inset of Fig. 2e and Supplementary Fig. 4). These k_a values are almost in the range of the encounter rate under the control of molecular diffusion. This observation suggests that no major molecular reorganization occurs during the reaction between ³[Ir-F] and 6, which would be reasonably in line with a Dexter-type energy transfer according to equation (1) (ref. 28), while considering that the triplet level of ³[Ir-F] is considerably higher than that of ³6 (ref. ⁴⁸).

$${}^{3}[\mathbf{Ir} - \mathbf{F}] + \mathbf{6} \rightarrow [\mathbf{Ir} - \mathbf{F}] + {}^{3}\mathbf{6}$$
(1)

We also recorded the transient absorption spectra of [Ir-F] solutions containing various concentrations of 6 (Fig. 2f). The differential spectrum of ³[Ir-F] exhibited a maximum at around 480-500 nm, which is in agreement with the literature⁴⁹. The addition of an equimolar amount of 6 yields a decrease in the 3[Ir-F] signal, consistent with the ³[Ir-F] luminescence quenching observed in Fig. 2e. In the presence of a ninefold excess of 6, the ³[Ir-F] signal almost disappears and is replaced by a broad differential absorption tentatively attributed to ³6 (new contributions below 450 nm and above 550 nm). The formation of **3ab** is also enhanced by the presence of 10 mol% benzophenone in the reaction medium, which presumably also acts as a sensitizer (Fig. 2d). Another important point to check was the formation of **6** in the reaction conditions. This was achieved by exposing 1a to a stoichiometric amount of [Au-CF₃] in CD₃CN overnight. After this reaction time in the dark, the formation of 6 was observed by NMR in 26% yield (See Supplementary Section V. 4).



Fig. 2 | A vinylgold(:) species as a plausible intermediate. a, Preparation of **6** according to Hashmi's method⁴⁵. **b**, X-ray diffraction structure of complex **6**. **c**, Alkynylation from **2b** and **6** under blue LED irradiation. **d**, Alkynylation of **6** by **2b** by direct irradiation and sensitization. **e**, Quenching of **3[Ir-F]** by **6** monitored by steady-state fluorimetry. **f**, Differential absorption spectra of **3[Ir-F]** (500μ M in N₂-saturated acetonitrile) in the presence of increasing amounts of **6**, showing the quenching of the absorption of **3[Ir-F]** at 500 nm and the appearance of new contributions assigned to **36** below 450 nm and above 550 nm. Spin density (difference between the α and β densities) isosurface (isovalue 0.0006 a.u.). **g**, **3[Ir-F]** in the vicinity of **6**. **h**, Isolated **3[Ir-F]** complex.

All these studies converge to imply an excited state of **6**, whose formation is promoted by the long-lived triplet state ³[**Ir**-**F**] (ref. ⁵⁰). This finding is in line with a recent study on excited-state organometallic catalysis by McCusker and MacMillan⁵¹, who reported an energy-transfer-mediated reductive elimination of an excited arylnickel(II) intermediate, in the same vein as other related reports on copper^{52,53} and nickel intermediates^{54–56}. Further support for these conclusions was provided by calculations. The spin densities of ³[**Ir**-**F**] in isolation or in the vicinity of **6** were compared (Fig. 2g,h and Supplementary Sections VIII. 2–3 for calculation details). As shown in Fig. 2g, part of the ³[**Ir**-**F**] spin density is transferred to the approaching furan moiety of **6**, intimating that energy transfer is taking place. This would lead to the formation of **6** in

an excited electronic state, which may further react with **2a**. Note that the same calculations performed on ³**[Ir-F]** approached by **2a** show that no transfer is occurring to **2a** (see Supplementary Fig. 7). This finding is consistent with the quenching studies carried out on **[Ir-F]** in the presence of **6** or **2a**. Note that **[Au-CF₃]** also does not quench the fluorescence of **[Ir-F]**. To determine which electronic states of **6** are accessible via this energy transfer, time-dependent density functional theory calculations were carried out. Results show that only ³**6** was accessible within the blue LED energy range (470 nm, see Supplementary Section VIII. 3 for details).

Modelling studies. Following these findings, we conducted a detailed theoretical study of the reaction of ³6 with **2a**. The ground

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Fig. 3 | Potential surface energy of the reaction of ³**6 with 2a.** The reaction of ³**6** with **2aa** proceeds via several steps to lead to intermediate ³**IV**. Final formation of **3aa** follows either the dissociative decay of ³**IV** or occurs after rearrangement and dissociation of ³**IV** into ³**3aa**. Optimized geometries of intermediates ³**II** and ³**IV** are given in the inset (top right). Salient features of complex ³**II** are the I-C-C angle of 115° and a C-Au bond of 2.12 Å. Gibbs free energies (CH₃CN) are given relative to the starting products and are in kcal mol⁻¹.

state reactivity of **6** was also checked to help rationalize the role of blue LED in the mechanism efficiency. For the sake of clarity, we will now refer to **6** either as ${}^{1}\mathbf{6}$ or as ${}^{3}\mathbf{6}$ to unambiguously point to the ${}^{1}S_{0}$ ground state or the ${}^{3}T_{1}$ excited state of **6**, respectively. All calculations presented below were obtained at the PBE0/ SDD(Au), 6–311G*(I), 6–31G** (other atoms) level of theory, taking into account solvent effects by SMD procedure. If not stated otherwise, reported energies are Gibbs free energies in CH₃CN DGCH₃CN (ΔG_{MeCN}).

On the singlet potential energy surface, the reaction pathway was quite straightforward to determine. However the barrier to formation of the oxidative addition adduct, gold(III) complex 'I is



Fig. 4 | Mechanism proposal. Two intertwined catalytic cycles are responsible for the alkynylative cyclization of *o*-alkylnylphenols with iodoalkynes. The connecting points involve the interaction of ³**[Ir-F]** with **6** to promote the formation of ³**6**, which is prone to undergoing oxidative addition.

prohibitive: almost 28 kcal mol⁻¹ (see Supplementary Section VIII. 4) and renders the overall pathway unlikely. On the other hand, the reaction on the triplet potential energy surface seemed to be more sinuous, but also more favourable thermodynamically (see Fig. 3). The approach of 2a to ³6 (along the Au-C (bearing the iodine) bond reaction coordinate) leads to the formation of an intermediate complex ³II, located 18.5 kcal mol⁻¹ below the reagents. Interestingly, the geometry adopted by 2a in this complex is bent (I-C-C angle of 115°) and reminiscent of that of modelled 32a (I-C-C angle of 129° versus 180° for 2a in its ground state, see Supplementary Fig. 15). This feature suggests that the ³6 complex may transfer energy to 2a when these reactants approach each other. Checking the spin density along the Au-C (bearing the iodine) bond reaction coordinate effectively confirms that a transfer is occurring at a relatively long distance (from 3.6 Å, see Supplementary Fig. 16). Therefore, ³6 could act as a relay for transferring energy to 2a, which would provide access to a reactive bent structure of the acetylenic compound. From complex ³II and by approaching the iodine atom to gold, intermediate ³III is localized on which Au(I) is oxidized to Au(III) and organic precursors lie in the trans position. This step occurs with a low activation energy of 2.2 kcal mol⁻¹ via TS3. By reducing the C-Au-C angle on ³III (that is bringing together the two C atoms involved in the forthcoming new C-C bond), it was possible to localize a transition structure **TS4**, requiring a formation barrier of 18.8 kcal mol⁻¹. TS4 connects to the Au(III) complex intermediate ³IV, on which the formation of the key C-C bond between 6 and 2a is observed but with the iodine still interacting with the slightly elongated triple bond (d(I-C) = 2.29 Å). Finally, two pathway variants can be envisaged from ³IV. First, the ³IV complex may further rearrange to lead to a ³V complex (-27 kcal mol⁻¹ below ³IV) via an inexpensive TS5 transition structure (+0.001 kcal mol⁻¹ compared with ³IV). Then ³V easily dissociates to lead to ³3aa+ (p-CF₃Ph)₃PAuI (barrier TS6 of 6 kcal mol⁻¹). An electronic decay of ³3aa can then be envisaged to lead to the final coupling product $3aa + (p-CF_3Ph)_3PAuI$. Another possible pathway would imply a direct electronic decay of ³IV from S_0 to T_1 leading to a complex that was revealed to be dissociative. It would therefore directly provide the final coupling products.

The proposed reaction pathway using ${}^{3}\mathbf{G}$ as a starting product seems to be extremely favourable from a thermodynamic point of view, as all intermediate complexes and transition structures have

lower energies than the starting products. This would be consistent with the great efficiency of the observed reaction of Fig. 2d. The aforementioned data all support the plausible catalytic pathway of Fig. 4.

In addition to the use of the photosensitizer [**Ir-F**], two other factors seem to optimize this process. First, the substitution of Ph_3PAuCl by [**Au-CF**₃] seemed to be highly beneficial (Table 1, entry 3 versus 4), perhaps due to the higher electrophilicity of [**Au-CF**₃]²⁵. Second, the adjunction of 1,10-phenanthroline gave a significant yield increase regardless of the pathway followed (compare entry 4 versus 5 and entry 8 versus 9 in Table 1). The reason for this is not clearly established and several hypotheses have been proposed. For instance, some halogen bonding between phenanthroline and the alkynyl iodides **2** (which are known halogen-bonding donors)⁵⁷ might be at work and explain the increased reactivity of the system.

Scope of the reaction. We then explored the scope of this transformation. For this, a series of substituted arvl iodoalkynes 2 were reacted with 2-(phenylethynyl)phenols 1 under optimized reaction conditions (Fig. 5a). Aryl iodoethynyl bearing electron-withdrawing groups in the para position, such as F and CF₃, produced the corresponding benzofurans **3ab** and **3ac** in good yields. *Meta* F or *ortho* Cl-substituted arvl iodoalkynes reacted smoothly with 2-(phenylethynyl)phenol 1a, providing 3ad and 3ae in 78% and 63% yields, respectively. The presence of the electron-donating groups (-Me, -t-Bu, -OMe) at the para position, or no substitution, furnished the alkynylbenzofurans in slightly lower (3af, 3ag and 3ba) to moderate (3ah) yields. No reaction was observed with an iodoalkyne bearing a 4-nitro arylgroup, instead the protodeauration cyclization product 7 was obtained. In addition, alkylalkynes bearing n-pentyl, cyclohexyl, and 3-nitrile butyl groups could be incorporated into the benzofuran scaffold (3aj-3al) from the corresponding alkyl iodoalkynes, albeit in significantly lower yields (25-42%).

The effect of substitution on both aromatic rings of *o*-alkynylphenols **1** was then investigated in reactions with 1-(iodoethynyl)-4-(trifluoromethyl)benzene **2c** (Fig. 5b). Arylalkynes with no substitution or bearing a CH_3F group or F atom at the *para* or *meta* position to the alkyne gave good yields of benzofurans (**3bc**, **3ac**, **3ec** and **3fc**). Similarly, precursors with an electron-withdrawing ester group on the phenol moiety at the *para* or *meta* position of the alkyne delivered corresponding ethynylbenzofurans in good yields (**3cc** and **3dc**).

Postfunctionalization and other systems. The benzofurans **3** are valuable scaffolds for further elaboration, notably through the potential reactivity of the alkyne moiety. For instance, the product **3aa** can be hydrogenated by formic acid under palladium(0) catalysis. Depending on the reaction conditions *Z*-alkene **8** or the *E*-isomer **9** can be selectively obtained. Triazole **10** could also be formed in thermal conditions through a Huisgen type of reaction between **3aa** and sodium azide (Fig. 5c, see Supplementary Section VI for details).

Finally, the sensitization protocol is not restricted to substrates 1 and 2. Other organogold intermediates such as vinylgold 11 and arylgold 13 can undergo the oxidative addition (reductive elimination sequence to provide respectively 12 and 14 as shown in Fig. 5d). One pot reactions are also possible using a vinyliodide electrophile (15) or an *o*-alkynyl tosylaniline (17) as nucleophilic precursor. In the latter case, a new route to 2,3-disubstituted indoles is available.

Conclusions

This study describes a dual catalysis transformation, involving electrophilic gold catalysis and iridium photosensitization to allow a $C(sp)^2-C(sp)$ cross-coupling reaction, useful for the alkynylation of benzofurans. A thorough luminescence study, supported by density functional theory calculations, revealed the mechanistic pathway.

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Fig. 5 | Scope of the alkynylation process. a, Variation of the iodoalkynes **2. b**, Variation of the *o*-alkynylphenols **1. c**, Post-functionalization of benzofuran **3aa** by stereoselective hydrogenation and [3+2] cycloaddition. **d**, Other working systems involving other nucleophilic and electrophilic partners. Experimental details: ^a5 mol% **[Au-CF₃]**, 1mol% **[Ir-F]**, K₂CO₃ (2.5 equiv.), 1,10-phenanthroline (10 mol%) MeCN, blue LED, room temperature, overnight; ^b1 mol% **[Ir-F]**, 1,10-phenanthroline (10 mol%) MeCN, blue LED, room temperature, overnight. ^cNMR yield.

Blue LED-excited [Ir-F] interacts with a vinylgold(I) intermediate, stemming from a gold(I)-promoted 5-endo-dig O-cyclization via energy transfer, to trigger oxidative addition at gold(I). In other words, the triplet excited state of the vinylgold(I) intermediate and the alkynyl iodide partner readily engage in an oxidative addition-*trans/cis* isomerization sequence that forges the desired

 $C(sp)^2-C(sp)$ bond, followed by reductive elimination that delivers the benzofuran product. The process described in this Article enables the oxidative addition–reductive elimination pathway to be used with organogold intermediates and, because other nucleophilic and electrophilic partners are competent, it opens new avenues in the field of excited-state gold catalysis.

Methods

General procedure for alkynylative cyclization of o-alkynylphenols with

iodoalkynes. A Schlenk tube was equipped with a magnetic stirring bar and charged with the photocatalyst [Ir-F](1 mol%) before the addition of the gold(1) complex [Au-CF₃] (5 mol%), K₂CO₃ (2.5 equiv), 1,10-phenanthroline (10 mol%), the appropriate iodoalkyne 2 (0.15 mmol) and *o*-alkynylphenol derivative 1 (0.1 mmol), with MeCN (2 ml). The mixture was degassed using three freeze pump-thaw cycles and purged with Ar, then irradiated for 16 h (unless otherwise stated) with blue LED light (see Supplementary Section VI for set-up). The stirring speed was \geq 1,200 r.p.m. The reaction was then extracted by Et₂O (3 xDl) and a 2 M HCl solution (3 ml) and the solution was then extracted by Et₂O (3×5 ml). The combined organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure to give the crude product. The residue was purified by flash chromatography (FC) on silica gel to afford 3.

Data availability

Crystallographic data for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers 1850903 (**3aa**) and 1850902 (**6**). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/. All other data supporting the findings of this study are available within the Article and the Supplementary Information, or from the corresponding authors on reasonable request.

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Author contributions

Z.X., V.C. and F.Z. performed the synthetic experiments and undertook all the physicochemical analyses. C.P. conducted the MS analyses. A.E., L.J. and T.L.S. performed and analysed the luminescence and transient absorption experiments. Y.G. and H.D. carried out computational studies and V.M-M., C.O. and L.F. designed the experiments, collated the data and prepared the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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