ChemComm

COMMUNICATION

CrossMark
click for updates

Gold-catalysed cross-coupling between aryldiazonium salts and arylboronic acids: probing the usefulness of photoredox conditions†

Thomas Cornilleau, Philippe Hermange* and Eric Fouquet*

The synthesis of biaryl compounds from aryldiazonium salts and arylboronic acids was achieved using PPh₃AuCl as catalyst, CsF as base and acetonitrile as solvent. Combined to photosensitizers, irradiation by blue LEDs allowed accelerating the reaction and expanding its scope. Various functional groups were compatible including bromoaryls, iodoaryls, aldehydes and alcohols. A 2-iodobenzyl alcohol moiety was smoothly introduced by this method, enabling its consecutive isotopic labelling by a Pd-catalysed alkoxycarbonylation.

The field of homogeneous gold catalysis has been intensively explored in the last few decades and is now a well-established area.[1] First employed for pi-activation and cascade reactions,[2] many efforts have focused on catalytic cycles requiring changes in the Au oxidation state.[3] This led to the development of novel, successful strategies for coupling reactions implying the formation of gold(III) intermediates, using for example external oxidants[4] or radical partners. The latter approach has been recently extremely fruitful, especially when merged with radical generation through visible light photoredox catalysis.[5e] Being prone to single-electron reduction,[5] aryldiazonium salts proved to be ideal reactants for gold catalysed couplings under photoredox conditions[6] and have already been combined to various substrates (Scheme 1).[7] Indeed, under visible light and in the presence of a photosensitizer [Ru(bpy)₃²⁺, fluorescein,...], they give *in situ* the desired aryl-radicals, allowing consecutive oxidative addition onto Au(I) species. After another one-electron oxidation, the reductive elimination from the resulting Au(III) complexes produces the desired compounds while regenerating the gold(I) catalyst.[8] After the seminal work of Glorius *et al.* exploiting the intramolecular cyclization of alkenes,[7a] a wide range of reactions were also found to be suitable for this strategy including methanol addition to alkenes,[7b] ring expansion,[7c] allenoate cyclization,[7d] Meyer–Schuster rearrangements[7h–j]

Univ. Bordeaux, Institut des Sciences Moléculaires, UMR-CNRS 5255,
351, Cours de la Libération, 33405 Talence Cedex, France.
E-mail: philippe.hermange@u-bordeaux.fr, eric.fouquet@u-bordeaux.fr
† Electronic supplementary information (ESI) available: General experimental procedures and spectroscopic data (¹H NMR and ¹³C NMR). See DOI: 10.1039/c6cc04239b
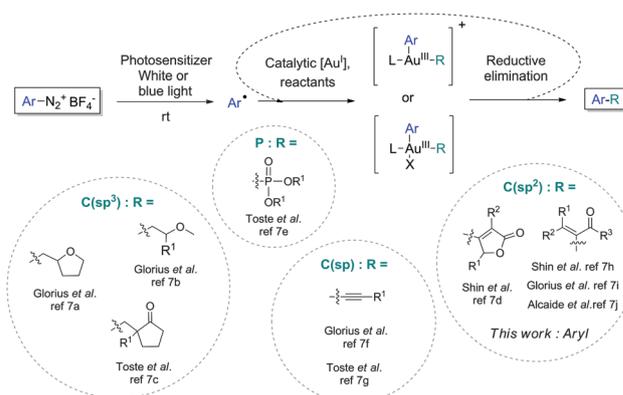
Scheme 1 Gold-catalysed couplings with aryldiazonium salts under photoredox conditions.

and others.[7e–g] Both phosphorus- and carbon-based partners (sp³, sp or sp²) were described but surprisingly, no biaryl formation was reported under photoredox conditions.[9]

However, it should be noted that the line between photoredox catalysis and photoredox activation may be thin.[10] When light only plays a role in radical initiation, other methods of activation can become competitive, as demonstrated by a few reports describing gold-catalysed coupling of diazonium salts without visible light and PS.[7d,11] For example, Shin *et al.* proved that simple thermal activation of diazonium salts at 60 °C was sufficient to induce the cross coupling of vinyl golds in the dark (which was previously developed at room temperature under blue LED irradiation).[7d] In a different manner, Shi *et al.* recently published an elegant method employing cationic Au(I) catalysts which were able to promote direct N₂ extrusion of diazonium salts under the assistance of 2,2′-bipyridine.[11] Under this set of conditions, the couplings of terminal alkynes or arylboronic acids with the aryl moiety of diazonium species were achieved in good yields. Unfortunately, these conditions led to much lower yields when using *p*-iodide diazonium salts (Scheme 2).[12]

Within this context, we were looking for methods allowing the synthesis of biaryl compounds from boronic acids and aryldiazonium salts that would be compatible with free benzyl

Ar–N$_2^+$ BF$_4^-$ + Ar'–B(OH)$_2$ $\xrightarrow[\text{Na}_2\text{CO}_3\ (2\ \text{equiv}),]{\begin{array}{c}\text{[PPh}_3\text{Au](TA)OTf}\\(5\ \text{mol \%})\end{array}}$ Ar–Ar'

(TA = triazole, bpy = 2,2'-bipyridine) · **bpy** (20 mol %), CH$_3$CN, rt · 42–91% (^{1}H NMR yields) (Iodoaryls : <15%)[12]

Scheme 2 Gold-catalysed coupling of aryldiazonium salts with arylboronic acids without photoredox conditions (Shi et al., ref. 11).

alcohols and iodoaryls. Considering the scarce reports of Pd-catalysed Suzuki–Miyaura reactions potentially meeting these criteria[13] and the limited results obtained in our case,[14] the possibilities offered by gold-catalysis were re-examined.

Hypothesizing a potential detrimental effect of the cationic gold source towards iodoaryls, the cross-coupling of 4-methoxy-benzene-diazonium tetrafluoroborate **1a** with phenylboronic acid **2** was investigated with PPh$_3$AuCl. This one was less active,[15] and only small amounts of the desired product **3a** could be obtained without photoredox conditions. However, when combined with blue LED irradiation and a catalytic amount of 9-mesityl-10-acridinium tetrafluoroborate (**6**),[7d,e,16] more interesting results were observed. Indeed, the use of 10 mol% of PPh$_3$AuCl and 2 equivalents of Na$_2$CO$_3$ in CH$_3$CN at 30 °C under photoredox conditions led to a 57% conversion of the diazonium **1a**. The desired coupling product **3a** was produced in this case concomitantly with anisole **5a** in a 2/1 ratio, as determined by ^{1}H NMR analysis of the crude mixture (Table 1, entry 1). KOH[17] instead of Na$_2$CO$_3$ slightly improved this result (entry 2) but CsF was demonstrated to be the best base,[18] allowing full conversion of **1a** to a **3a**/**5a** mixture in a 7 : 3 ratio (entry 3). A control experiment in the dark with bpy as an additive (20 mol%) gave only 40% conversion, demonstrating the importance of the photoredox process under this set of conditions (entry 4). The use of (IPr)AuCl instead of PPh$_3$AuCl was investigated but no biaryl products were formed in this case (entry 5). An excess or catalytic amount of CsF was detrimental (entries 6–8), and the quantity of base was set to 1.05 equivalents

for further experiments. In combination with slightly increased quantities of diazonium **1a** (1.5 equivalent) and acridinium **6** (4 mol%), the desired biaryl **3a** was isolated in 55% yield (entry 9). Interestingly, exchanging the organic photosensitizer by 2 mol% of Ru(bpy)$_3$(PF$_6$)$_2$ allowed access to **3a** in 63% yield (entry 10). Finally, control experiments were performed in the absence of any photosensitizer either under blue light irradiation or in the dark (entries 11 and 12). Both experiments led to almost identical results (i.e. lower conversion and limited formation of **3a**), indicating that no direct effect of the visible light could be detected in this case.[19]

In contrast, the substitution on the aryl ring of the diazonium appeared to be crucial. Indeed, the 4-nitrobenzene-diazonium tetrafluoroborate **1b** was able to react with phenylboronic acid without any photoredox conditions, producing the cross-coupling product **3b** in 81% yield within 16 h (entry 13). The course of this reaction was monitored when performed in the dark or under irradiation with blue LEDs in the presence of a photosensitizer (Fig. 1, see the ESI† for details).

At 30 °C in the dark, pure thermal initiation was sufficient to ensure smooth formation of **3b** (Fig. 1, orange line). Indeed, the easiness of the 4-nitro-substituted diazonium salt to undergo one electron reduction[20] allowed thermal initiation and innate radical chains to operate efficiently.[21] This mechanism difference between the two substrates was confirmed by quantum yield measurement, which were determined to be 1.4 and 9.6 when employing **1a** (4-MeO–) or **1b** (4-NO$_2$–), respectively (see the ESI† for details). However, in the latter, the use of photoredox conditions allowed completion of the reaction within 1 h 30 (Fig. 1, blue line) whereas only 50% of **3b** was formed at the same time in the dark (orange line). Thus, the benefits of the photoredox initiation process[10c] were demonstrated in this case by a strong acceleration of the reaction.

Then, the scope was investigated with the 9-mesityl-10-acridinium **6** (conditions A) or with Ru(bpy)$_3$(PF$_6$)$_2$ (conditions R)

Table 1 Optimization of the reaction conditions^a

Ar–N$_2^+$ BF$_4^-$ + Ph–B(OH)$_2$ $\xrightarrow[\text{CH}_3\text{CN, 30 °C, 16 h}]{\begin{array}{c}\text{PPh}_3\text{AuCl (10 mol \%)}\\\text{Base, PS, Blue LEDs}\end{array}}$ Ar–Ph + Ar–Ar + Ar–H

1a : Ar = 4-CH$_3$O-C$_6$H$_4$ **2** **3a-b** **4a-b** **5a-b**
1b : Ar = 4-NO$_2$-C$_6$H$_4$

	Ar (x equiv.)	Photosensitizer^b (y mol%)	Base (z equiv.)	**1**/**3**/**4**/**5** ratio^c (yield, %)^d
1	**1a** (1 equiv.)	Acrid (2 mol%)	Na$_2$CO$_3$ (2 equiv.)	43/**35**/0/22
2	**1a** (1 equiv.)	Acrid (2 mol%)	**KOH** (1 equiv.)	24/**46**/10/20
3	**1a** (1 equiv.)	Acrid (2 mol%)	**CsF** (1 equiv.)	0/**70**/0/30
4^e	**1a** (1 equiv.)	bpy (20 mol%)	CsF (1 equiv.)	60/**11**/10/19
5^f	**1a** (1 equiv.)	Acrid (2 mol%)	CsF (1 equiv.)	30/**0**/0/60
6	**1a** (1 equiv.)	Acrid (2 mol%)	CsF (**1.5 equiv.**)	0/**33**/13/54
7	**1a** (1 equiv.)	Acrid (2 mol%)	CsF (**2.0 equiv.**)	0/**25**/11/64
8	**1a** (1 equiv.)	Acrid (2 mol%)	CsF (**0.5 equiv.**)	48/**32**/3/17
9	**1a** (**1.5 equiv.**)	Acrid (**4 mol%**)	CsF (**1.05 equiv.**)	13/**60**/5/22 (55%)
10	**1a** (1.5 equiv.)	**Ru** (2 mol%)	CsF (1.05 equiv.)	0/**73**/2/25 (63%)
11	**1a** (1.5 equiv.)	None	CsF (1.05 equiv.)	60/**15**/5/20
12^e	**1a** (1.5 equiv.)	None	CsF (1.05 equiv.)	62/**15**/5/18
13^e	**1b** (1.5 equiv.)	None	CsF (1.05 equiv.)	33/**57**/0/10 (81%)

^{a} Reactions run on a 0.25 mmol scale. ^{b} Acrid = 9-Mesityl-10-acridinium tetrafluoroborate **6**, bpy = 2,2'-bipyridine, Ru = Ru(bpy)$_3$(PF$_6$)$_2$. ^{c} Ratio determined by ^{1}H NMR analysis of the crude mixture. ^{d} Isolated yields of **3** after purification by column chromatography. ^{e} Reaction performed at 30 °C in the dark. ^{f} (IPr)AuCl was used instead of PPh$_3$AuCl.
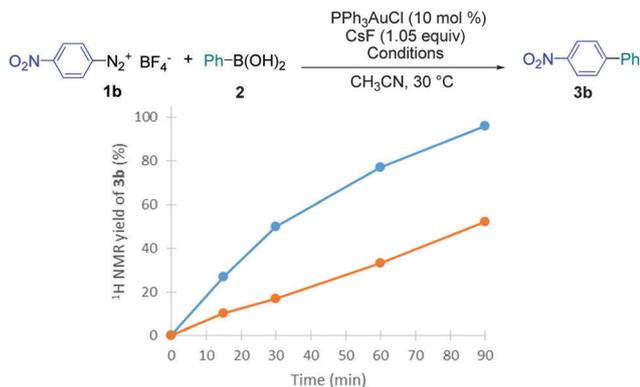
Fig. 1 Evolution in time of the ^{1}H NMR yield of **3b** in the dark (orange line) or with Ru(bpy)$_3$(PF$_6$)$_2$ (2 mol%) under blue LED irradiation (blue line).

as photosensitizers. Under both conditions, the mixture was stirred for 16 h under blue light irradiation to ensure the full completion of the reaction.

Interestingly, both conditions gave good results for 4-nitro-benzenediazonium **1b** with phenylboronic **2**, 2-methyl-phenyl and 2-bromophenylboronic acids as partners. Compound **3b** was isolated in 75–76% yields, and products **3c** and **3d** were obtained in 90–92% and 73–80% yields, respectively. The reaction was also compatible with highly hindered nucleophiles, and product **3e** was synthesized from 9-anthraceneboronic acid in yields up to 55% (conditions A). When switching to 4-methoxybenzene-diazonium tetrafluoroborate **1a**, the Ru(bpy)$_3$$^{2+}$-based conditions gave the best yield (63% of **3a**) and were employed with other arylboronic acids. Compound **3f** was isolated in a 55% yield whereas 2-methyl- and 2-nitrophenylboronic led to the cross-coupling products **3g** and **3h** with excellent results (respectively, 90% and 92% isolated yields). Similarly to **3b**, identical yields of **3i** were obtained from 4-(methoxycarbonyl)-benzenediazonium with the two sets of conditions (65%). With this diazonium, conditions A and R were compatible with aldehydes (50% of **3k**) and iodoaryls (up to 55% of **3l**), demonstrating the mildness of this method. 2-Nitro- and 4-iodobenzene-diazonium were also suitable, providing **3m**, **3n** and **3o** with moderate to good yields. Finally, the most noticeable achievements were the syntheses of the desired model compounds **3p**, with a yield of 50% with both photosensitizers, and **3q**, in a 47% yield under conditions R.[22] Indeed, introduction of the 2-iodobenzyl alcohol moiety occurred smoothly, allowing its further isotopic labelling by a palladium-catalysed alkoxycarbonylation (Scheme 3, 90% isolated yield of **7**, based on a limiting amount of ^{13}CO).[23]

To investigate the reaction mechanism, ^{31}P and ^{1}H NMR spectroscopies were realised on stoichiometric amounts of PPh$_3$AuPh in CD$_3$CN. Acridinium **6** and **1a** or **1b** were added to the mixture, which was then irradiated with blue LEDs for 3 h. Under these conditions, the gold complex was able to produce the desired **3a** and **3b** as the main products (see the ESI† for details). Based on these results, and on the previous reports of gold-catalysed cross-couplings with diazonium salts,[7,8,11] the mechanism in Scheme 4 was proposed. After transmetalation with the arylboronic acids,[24] the triphenylphosphine-aryl-gold species undergo oxidative addition by
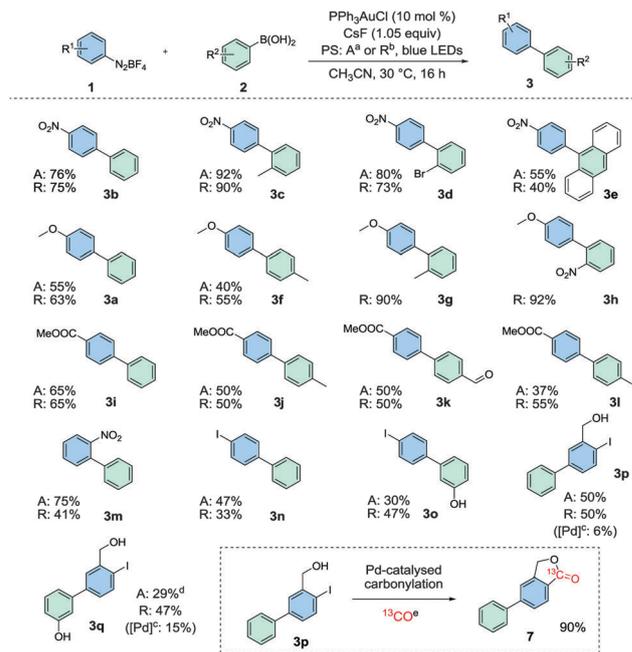
Scheme 3 Substrate screening and carbonylation of **3p**. Isolated yields. Conditions: Arylboronic acid (0.25 mmol), aryldiazonium tetrafluoroborate (1.5 equiv.), PPh$_3$AuCl (10 mol%), CsF (1.05 equiv.), CH$_3$CN (2 mL) at 30 °C for 16 h. [a]Conditions A: 9-mesityl-10-acridinium tetrafluoroborate (4 mol%). [b]Conditions R: Ru(bpy)$_3$(PF$_6$)$_2$ (2 mol%). [c]Conditions from ref. 13b: Pd/BaCO$_3$ (0.5 mol%), MeOH, rt, 12 h, see the ESI† for details. [d]Reaction time: 8 h. [e]Limiting amount of ^{13}CO, see the ESI† for details.

the aryl radical. The latter is consecutively regenerated by a one-electron oxidation of the gold(ɪɪ) intermediates. Then, the reductive elimination from the resulting Au(ɪɪɪ) complexes produces the biaryl compound[25] and regenerates the gold(ɪ) catalyst. It should be noted that the radical initiation step can occur through thermal processes, but these are highly dependent on the substitution onto the diazonium salts. In any case, the photoredox cycle allows an acceleration of the reaction, thus expanding its scope to less active substrates.

In summary, we described the gold-catalysed coupling of aryldiazonium salts with arylboronic acids under photoredox conditions. Employing the convenient PPh$_3$AuCl as the gold source, the conditions proved to be extremely mild (30 °C) and compatible with a wide range of functional groups such as
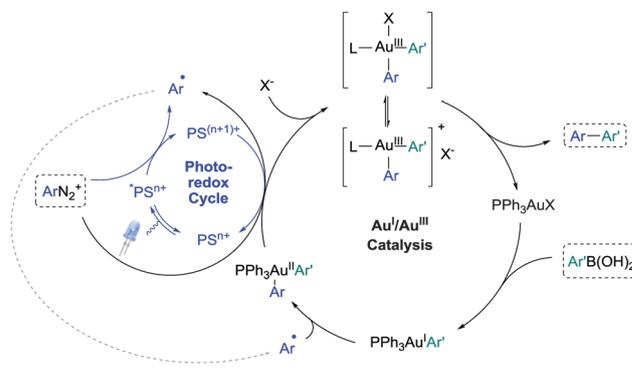
Scheme 4 Proposed mechanism of the reaction.

bromoaryls, iodoaryls, aldehydes and alcohols. The utility of this method was demonstrated by performing the synthesis of a biaryl with a 2-iodobenzyl alcohol moiety, which could not be efficiently obtained using the methods described previously in the literature. The resulting compound **3o** was efficiently labelled by ^{13}C–carbon monoxide, confirming the orthogonality with Pd-catalysed reactions. Aiming toward the synthesis of new potential biotracers,[23a] gold-catalysed couplings of this 3-(hydroxymethyl)-4-iodobenzenediazonium salt **1o** with biomolecule-based boronic acids are being currently explored.

Notes and references

1 *Modern Gold Catalyzed Synthesis*, ed. A. S. K. Hashmi and F. D. Toste, Wiley-VCH, Weinheim, Germany, 2012.

2 For selected recent reviews, see: (*a*) N. D. Shapiro and F. D. Toste, *Synlett*, 2010, 675; (*b*) M. Rudolph and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2012, **41**, 2448; (*c*) C. Obradors and A. M. Echavarren, *Chem. Commun.*, 2014, **50**, 16; (*d*) A. Fürstner, *Acc. Chem. Res.*, 2014, **47**, 925; (*e*) R. Dorel and A. M Echavarren, *Chem. Rev.*, 2015, **115**, 9028.

3 M. Joost, A. Amgoune and D. Bourissou, *Angew. Chem., Int. Ed.*, 2015, **54**, 15022.

4 For reviews, see: (*a*) M. N. Hopkinson, A. D. Gee and V. Gouverneur, *Chem. – Eur. J.*, 2011, **17**, 8248; (*b*) K. M. Engle, T.-S. Mei, X. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2011, **50**, 1478. For a selected example, see: (*c*) L. T. Ball, G. C. Lloyd-Jones and C. A. Russel, *Science*, 2012, **337**, 1644.

5 (*a*) D. F. DeTar and T. Kosuge, *J. Am. Chem. Soc.*, 1958, **80**, 6072; (*b*) M. P. Doyle, J. K. Guy, K. C. Brown, S. N. Mahapatro, C. M. VanZyl and J. R. Pladziewicz, *J. Am. Chem. Soc.*, 1987, **109**, 1536; (*c*) M. N. Weaver, S. Z. Janicki and P. A. Petillo, *J. Org. Chem.*, 2001, **66**, 1138; (*d*) G. Schmidt, S. Gallon, S. Esnouf, J.-P. Bourguoin and P. Chenevier, *Chem. – Eur. J.*, 2009, **15**, 2101; (*e*) M. D. Levin, S. Kim and F. D. Toste, *ACS Cent. Sci.*, 2016, **2**, 293.

6 For recent reviews on photoredox catalysis, see: (*a*) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322; (*b*) M. N. Hopkinson, B. Sahoo, J.-L. Li and F. Glorius, *Chem. – Eur. J.*, 2014, **20**, 3874; (*c*) R. A. Angnes, Z. Li, C. R. Correia and G. B. Hammond, *Org. Biomol. Chem.*, 2015, **13**, 9152; (*d*) S. Fukuzumi and K. Ohkubo, *Org. Biomol. Chem.*, 2014, **12**, 6059; (*e*) D. A. Nicewicz and T. M. Nguyen, *ACS Catal.*, 2014, **4**, 355; (*f*) T. Koike and M. Akita, *Synlett*, 2013, 2492.

7 (*a*) B. Sahoo, M. N. Hopkinson and F. Glorius, *J. Am. Chem. Soc.*, 2013, **135**, 5505; (*b*) M. N. Hopkinson, B. Sahoo and F. Glorius, *Adv. Synth. Catal.*, 2014, **356**, 2794; (*c*) X.-Z. Shu, M. Zhang, Y. He, H. Frei and F. D. Toste, *J. Am. Chem. Soc.*, 2014, **136**, 5844; (*d*) D. V. Patil, H. Yun and S. Shin, *Adv. Synth. Catal.*, 2015, **357**, 2622; (*e*) Y. He, H. Wu and F. D. Toste, *Chem. Sci.*, 2015, **6**, 1194; (*f*) A. Tlahuext-Aca, M. N. Hopkinson, B. Sahoo and F. Glorius, *Chem. Sci.*, 2016, **7**, 89; (*g*) S. Kim, J. Rojas-Martin and F. D. Toste, *Chem. Sci.*, 2016, **7**, 85; (*h*) J. Um, H. Yun and S. Shin, *Org. Lett.*, 2016, **18**, 484; (*i*) A. Tlahuext-Aca, M. N. Hopkinson, R. A. Garza-Sancheza and F. Glorius, *Chem. – Eur. J.*, 2016, **22**, 5909; (*j*) B. Alcaide, O. Almendros, E. Busto and A. Luna, *Adv. Synth. Catal.*, 2016, **358**, 1526.

8 For a DFT study, see: Q. Zhang, Z.-Q. Zhang, Y. Fu and H.-Z. Yu, *ACS Catal.*, 2016, **6**, 798.

9 For gold-catalysed biaryl syntheses with boronic acids and external oxidants, see: (*a*) N. P. Mankad and F. D. Toste, *J. Am. Chem. Soc.*, 2010, **132**, 12859; (*b*) M. Hofer, E. Gomez-Bengoa and C. Nevado, *Organometallics*, 2014, **33**, 1328; (*c*) Q. Wu, C. Du, Y. Huang, X. Liu, Z. Long, F. Song and J. You, *Chem. Sci.*, 2015, **6**, 288.

10 For interesting discussions on radical propagation with aryldiazonium salts, see: (*a*) M. Majek, F. Filace and A. Jacobi von Wangelin, *Beilstein J. Org. Chem.*, 2014, **10**, 981; (*b*) M. A. Cismesia and T. Yoon, *Chem. Sci.*, 2015, **6**, 5426. For a general discussion on catalysis in radical reactions, see: (*c*) A. Studer and A. S. Curran, *Angew. Chem., Int. Ed.*, 2016, **55**, 58.

11 R. Cai, M. Lu, E. Y. Aguilera, Y. Xi, N. G. Akhmedov, J. L. Petersen, H. Chen and X. Shi, *Angew. Chem., Int. Ed.*, 2015, **54**, 8772.

12 The yields for iodoaryl substrates were described as "low" in note (19) of ref. 11. In our hands, **3n** and **3o** were isolated, respectively; in 14% yield and 10% yield with Shi's conditions. See the ESI† for details.

13 For Pd-catalysed Suzuki–Miyaura reactions with diazonium salts with conditions compatible with iodoaryls, see: (*a*) S. Sengupta and S. K. Sadhukhan, *Tetrahedron Lett.*, 1998, **39**, 715; (*b*) F.-X. Felpin and E. Fouquet, *Adv. Synth. Catal.*, 2008, **350**, 863. For a review on Pd-catalysed Suzuki–Miyaura reactions with diazonium salts, see: (*c*) H. Bonin, E. Fouquet and F.-X. Felpin, *Adv. Synth. Catal.*, 2011, **353**, 3063.

14 See Scheme 3 for results obtained for **3p** and **3q** using the best conditions for *p*-iodoaryldiazonium tetrafluoroborate [Pd/BaCO$_3$ (0.5 mol%), MeOH, rt, 12 h, ref. 13*b*]. See the ESI† for details.

15 In their cross-coupling of vinyl golds with diazonium salts under photoredox conditions, Shin *et al.* measured quantum yields of 0.31 and 1.21 employing, respectively, PPh$_3$AuCl or a PPh$_3$AuCl/AgOTf mixture as catalyst. This indicates that radical chain processes are probably favoured by cationic gold species. See ref. 7*d*.

16 This catalyst was selected as a photosensitizer to rule out any potential 2,2′-bipyridine leaching.

17 S. Dupuy, L. Crawford, M. Bühl, A. M. Z. Slawin and S. P. Nolan, *Adv. Synth. Catal.*, 2012, **354**, 2380.

18 For the transmetalation of boronic acids with gold fluoride complexes, see ref. 9*a*.

19 For an example of visible-light-mediated gold-catalysis with diazonium salts, see: L. Huang, F. Rominger, M. Rudolph and A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, 2015, **55**, 4808.

20 Second-order rate constants for the reduction of **1a** (4-MeO–) and **1b** (4-NO$_2$–) by potassium ferrocyanide have been previously measured in aqueous, phosphate-buffered solution at pH 7.0 (ref. 5*b*). The values were 7.1×10^{-5} M^{-1} s^{-1} and 6.95 M^{-1} s^{-1}, respectively, indicating a faster reduction of almost 10^5 fold.

21 Compared to results obtained at 30 °C in the dark, conversion and yield were significantly lower when performed at 18 °C in the dark.

22 Reduction and homocoupling of the diazonium salts are the main by-products in these reactions. However, depending on the photosensitizer, degradation of the biaryl products was observed in some cases, probably due to a prolonged exposure to photoredox conditions. For example, using conditions A, **3q** was isolated in 29% yield of after 8 h and in 20% yield after 16 h.

23 (*a*) T. Cornilleau, H. Audrain, A. Guillemet, P. Hermange and E. Fouquet, *Org. Lett.*, 2015, **17**, 354; (*b*) P. Hermange, A. T. Lindhardt, R. H. Taaning, K. Bjerglung, D. Lupp and T. Skrydstrup, *J. Am. Chem. Soc.*, 2011, **133**, 6061; (*c*) S. D. Friis, R. H. Taaning, A. T. Lindhardt and T. Skrydstrup, *J. Am. Chem. Soc.*, 2011, **133**, 18114; (*d*) S. D. Friis, A. T. Lindhardt and T. Skrydstrup, *Acc. Chem. Res.*, 2016, **49**, 594; (*e*) S. Kealey, A. Gee and P. W. Miller, *J. Labelled Compd. Radiopharm.*, 2014, **57**, 195; (*f*) O. Rahman, *J. Labelled Compd. Radiopharm.*, 2015, **58**, 86.

24 The access to organogold(III) complexes by oxidative addition of diazonium salts has been recently described. Thus, oxidative addition prior to transmetalation cannot be completely excluded. See (*a*) L. Huang, F. Rominger, M. Rudolph and A. S. K. Hashmi, *Chem. Commun.*, 2016, **52**, 6435; (*b*) E. O. Asomoza-Solis, J. Rojas-Ocampo, R. A. Toscano and S. Porcel, *Chem. Commun.*, 2016, **52**, 7295.

25 For selected examples of the biaryl reductive elimination of gold complexes, see: (*a*) J. Vicente, M. D. Bermùdez, J. Escribano, M. P. Carrillo and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1990, 3083; (*b*) J. Vicente, M. D. Bermùdez and J. Escribano, *Organometallics*, 1991, **10**, 3380; (*c*) W. J. Wolfe, M. S. Winston and F. D. Toste, *Nat. Chem.*, 2014, **6**, 159.