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(Article begins on next page)

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Gold catalysed Suzuki-Miyaura coupling of arenediazonium *o*-benzenedisulfonimides

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Keywords: Diazonium salts. C-C coupling. Boronic acids. Gold catalysis. Au(I)/Au(III). Electron transfer agent.

Abstract: Arenediazonium *o*-benzenedisulfonimides have been used as efficient electrophilic partners in Au(I) catalysed Suzuki coupling reactions. The synthetic protocol is general, easy and produced either biaryls or heteroaryl arenes in good yields (51 positive examples, average yield 80%). *o*-Benzenedisulfonimide was recovered at the end of the reactions and was reused to prepare the starting salts for further reactions. Mechanistic insights suggest that the *o*-benzenedisulfonimide anion act as an electron transfer agent and promotes a catalytic cycle which does not require the presence of photocatalysts or external oxidants.

1. Introduction

The use of oxidative gold catalysis as an effective means of facilitating C–C bond-forming reactions has been attracting increasing amount of attention in recent years.[1] The fact that Au (I) and Pd(0) are isoelectronics means that Au (I) species are able to catalyse reactions, including cross-coupling reactions, that are typically promoted by Pd(0). A number of Au(I) catalysts have therefore been successfully used in several of these reactions, such as Suzuki,[2] Sonogashira,[3] Stille[1h,4] and Hiyama[5] couplings.

The higher redox potential that exists between Au(I) and Au(III) could be seen as a drawback. However, the Au(I)/Au(III) redox cycle takes place quite easily in the presence of external oxidants.[1h,2f,6]

A number of research group have recently presentend a new strategy for gold-catalysed cross-coupling reactions.[7] They propose using aryl radicals, which operate as both oxidants and coupling partners, instead of external oxidants. These aryl radicals usually resulted from the light-mediated decomposition of arenediazoniumm salts after nitrogen loss, which generally occurred in the presence of an appropriate photocatalyst. Two efficient gold-catalysed Suzuki-Miyaura couplings of arenediazonium salts that make use of this mechanism have been recently reported.[8a,b] This approach was recently improved into a photocatalyst-free coupling as proposed by Hashmi and co-workers.[8c]

Our own research has produced a large family of dry diazonium salts, the arenediazonium *o*-benzenedisulfonimides **1,** (Fig. 1)[9a] which, have shown significant potential in numerous synthetic applications and in particular have given excellent results in palladium catalysed coupling reactions.[9b-h]

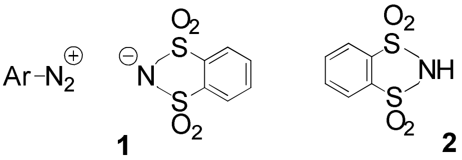
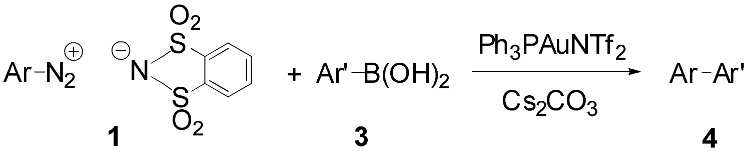


Fig. 1. Arenediazonium *o*-benzenedisulfonimides **1** and *o*-benzenedisulfonimide (**2**).

In fact, they are easy to prepare and isolate, are extremely stable, and can be stored for an unlimited period. Moreover, they react easily both in water and in organic solvents, and *o*-benzenedisulfonimide (**2**; Fig. 1) can be easily recovered and reused at the end of the reactions.

As part of a broader project aimed at exploring the synthetic potential of **1** in metal catalysed reactions we herein describe the reactivity of **1** as electrophilic partners in Au(I) catalysed Suzuki-Miyaura coupling[10] (Scheme 1). It must be stressed that, in our recent paper,[11a] we obtained significant results from using salts **1** in Au(I) catalysed Heck-coupling reactions.



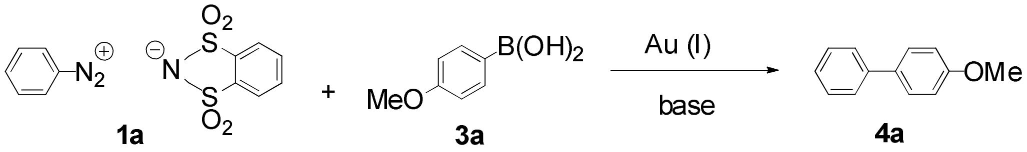
Scheme 1. The gold catalysed Suzuki-Miyaura coupling of arenediazonium *o*-benzenedisulfonimides **1**.

2. Results and discussion

In order to optimise the reaction conditions, the coupling reaction of benzenediazonium *o*-benzenedisulfonimide (**1a**) and 4-methoxyphenylboronic acid (**3a**) in the presence of two different Au(I) catalysts was initially performed and studied under varying conditions, as reported in Table 1. First of all, it must be stressed that better results were achieved using [bis(trifluoromethanesulfonyl)imidate] (triphenylphosphine) gold (Table 1, entries 13−24) than with chloro(triphenylphosphine)gold (Table 1, entries 1−12). A variety of bases, solvent ant temperatures were tested in the presence of the first catalyst and the best result was obtained using Cs_2CO_3 in THF at room temperature (Table 1, entry19).

Table 1

Trial reactions



Entry	Temp (°C)	Time (h)	Solvent	Catalyst	Base	Photocatalyst	Yield (%) of **4a** ^{a,b}
1	50	24	THF	-	-	$Ru(bpy)_3(PF_6)_2^{c}$	-
2	r.t	24	THF	Ph_3PAuCl	-	$Ru(bpy)_3(PF_6)_2^{c}$	20
3	r.t	24	THF	Ph_3PAuCl	-	-	25
4	50	24	THF	Ph_3PAuCl	-	-	15
5	r.t.	24	THF	Ph_3PAuCl	$CaCO_3$	-	35
6	r.t	24	THF	Ph_3PAuCl	NaOH	-	-
7	r.t.	24	THF	Ph_3PAuCl	Na_2CO_3	-	28
8	r.t.	24	THF	Ph_3PAuCl	K_3PO_4		25
9	r.t	24	THF	Ph_3PAuCl	Cs_2CO_3	-	$47^{d,e}$
10	r.t	24	EtOH	Ph_3PAuCl	Cs_2CO_3	-	14
11	r.t.	24	MeCN	Ph_3PAuCl	Cs_2CO_3	-	20
12	r.t.	24	DMSO	Ph_3PAuCl	Cs_2CO_3	-	traces
13	r.t.	24	THF	$Ph_3PAuNTf_2$	-	$Ru(bpy)_3(PF_6)_2^{c}$	42
14	r.t.	24	THF	$Ph_3PAuNTf_2$	-	-	40
15	50	24	THF	$Ph_3PAuNTf_2$	-	-	22
16	r.t.	4	THF	$Ph_3PAuNTf_2$	$CaCO_3$	-	68
17	r.t.	3.5	THF	$Ph_3PAuNTf_2$	K_3PO_4	-	60
18	r.t	7	THF	$Ph_3PAuNTf_2$	Na_2CO_3	-	45
19	r.t.	2	THF	$Ph_3PAuNTf_2$	Cs_2CO_3	-	$88^{d,e}$
20	50	1	THF	$Ph_3PAuNTf_2$	Cs_2CO_3	-	42
21	r.t.	4	EtOH	$Ph_3PAuNTf_2$	Cs_2CO_3	-	58
22	r.t	8	MeCN	$Ph_3PAuNTf_2$	Cs_2CO_3	-	74
23	r.t.	1.5	DMSO	$Ph_3PAuNTf_2$	Cs_2CO_3	-	80
24	r.t.	2	THF	$Ph_3PAuNTf_2$	Cs_2CO_3	dark	87

[a] All the reactions were carried under nitrogen flow, using 0.5 mmol of **1a,** 0.6 mmol of **3a**, 5 mol% of Au catalysts and 1 mmol of various bases.

[b] Yields refer to pure and isolated **4a**, purified on a silica gel chromatography column. The eluent was petroleum ether/diethyl ether (9 : 1).

[c] 5 mol% of photocatalyst were used

[d] Higher amount of base or Au catalyst did not lead to increased yield

[e] No product **4a** was formed when when the reaction was carried out in the presence of 1,3-dinitrobenzene (0.5 mmol, 85 mg) or TEMPO (0.5 mmol, 78 mg).

An excellent yield (88%) of **4a** was achieved in a short reaction time (2 h) and in the presence of and Cs_2CO_3 (2 equiv.) and using 5 mol % of $Ph_3PAuNTf_2$ as the catalyst. It is worth noting that, unlike other gold catalysed Suzuki reactions, no external oxidants, photocatalysts or light were necessary for the completion of the reaction which also occurred in the dark (Table 1, entry 24).

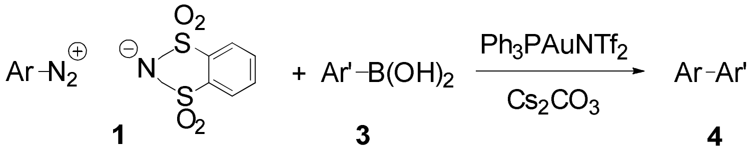
The high yield, short reaction time and simplicity of the procedure encouraged us to further exploit its generality and scope, using a number of variously substituted diazonium salts **1** and boronic acids **3.** The results are collected in Table 2. Most of these examples demonstrate the usefulness and the simplicity of this method, which requires mild reaction conditions and relatively short reaction times. The target products were obtained in good yields and selectivity while producing negligible amounts of by-products, namely symmetrical biphenyls, arenes, *N*-aryl-*o*-benzenedisulfonimides.

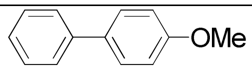
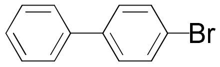
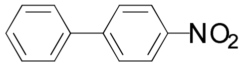
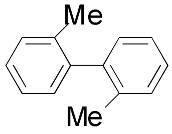
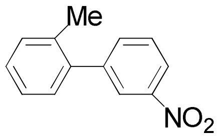
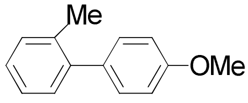
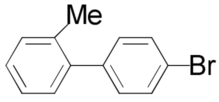
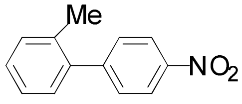
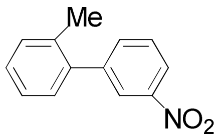
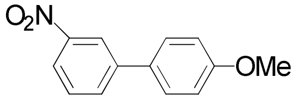
The reaction was chemoselective; diazonium salts which bear a bromine atom **1e** and that could potentially react as a diazonium group, only furnished target products **4b, j, r, s, t, u, v, w (**Table 2; entries 22−30) and no traces of possible terphenyl were detected. On the other hand, the reaction carried out with salt **1i** which bears an iodine atom, provided a complex mixture of products, which included the target 4-iodobiphenyl, but also terphenyl (Table 2, entry 44). It can be stated that the reaction was not affected by electronic effects as biaryls **4** were obtained in satisfactory yields from the reactions between **1** or **3** which bear either electron-donating and/or electron-withdrawing groups. However, steric effects were found to be significant. The presence of a substituent in the *ortho* position of either **1** or **3** drastically reduced the yield; (Table 2, entries 4–8,14, 23, 32, 40, 43) in fact, the preparation of hindered biaryls via a cross-coupling reaction has historically been proven to be difficult.

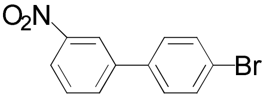
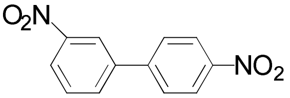
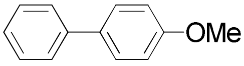
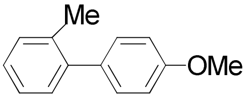
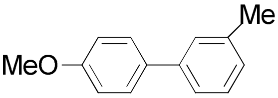
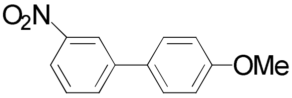
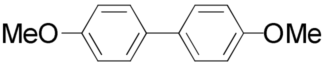
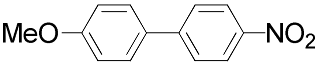
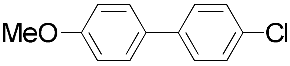
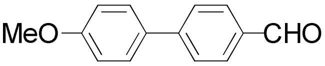
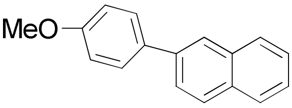
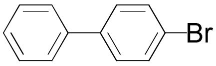
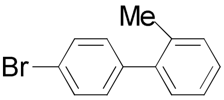
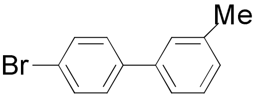
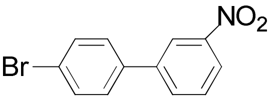
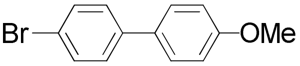
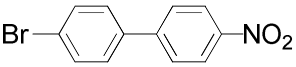
Surprisingly, the reactions carried out with heteroaryl boronic acids **3l–n** failed (Table 2, entries 45–47). Therefore, four heteroarenediazonium salts **5a–d** were synthesized in order to produce heteroaryl arenes **6**. These salts, which are extremely well-stabilized by the anion of **2,** were easy to isolate and handle and were used as electrophilic partners for reactions carried out with six selected arylboronic acids **3a–f** (Table 3). The target heteroaryl arenes **6a-i** were obtained in satisfactory yields.

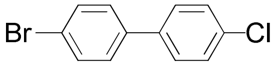
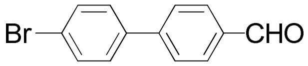
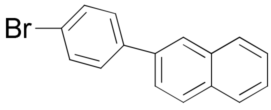
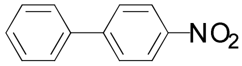
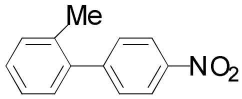
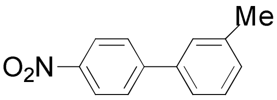
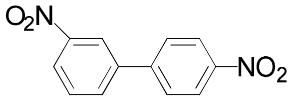
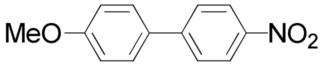
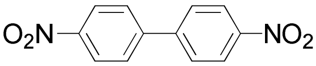
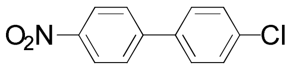
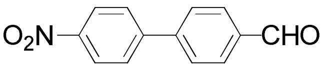
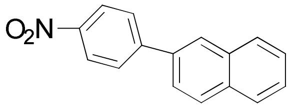
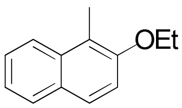
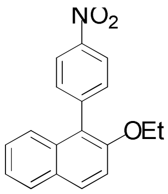
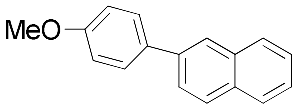
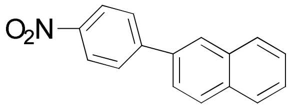
Table 2

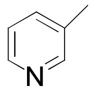
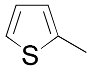
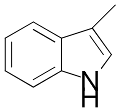
Au catalysed reactions between arenediazonium salts **1** and boronic acids **3**



Entry	Ar in **1**	Ar' in **3**	Time (h)	Products **4** and yields (%)^{a,b}
1	**1a**; C_6H_5	**3a;** $\text{4-MeOC}_6\text{H}_4$	2	 **4a;** 88
2	**1a**	**3b;** $\text{4-BrC}_6\text{H}_4$	2.5	 **4b;** 89
3	**1a**	**3c;** $\text{4-NO}_2\text{C}_6\text{H}_4$	3	 **4c;** 84
4	**1b;** $\text{2-MeC}_6\text{H}_4$	**3d;** $\text{2-MeC}_6\text{H}_4$	24	 **4d**; 60^{c}
5	**1b**	**3e;** $\text{3-NO}_2\text{C}_6\text{H}_4$	7	 **4e;** 76^{c}
6	**1b**	**3a**	6	 **4f;** 65^{c}
7	**1b**	**3b**	7	 **4g**; 62^{c}
8	**1b**	**3c**	6.5	 **4h;** 68^{c}
9	**1c;** $\text{3-NO}_2\text{C}_6\text{H}_4$	**3d**	5	 **4e;** 61^{c}
10	**1c**	**3a**	2	 **4i;** 92

11	**1c**	**3b**	2.5	 **4j;** 90
12	**1c**	**3c**	3	 **4k;** 88
13	**1d;** $4\text{-MeOC}_6\text{H}_4$	**3f;** C_6H_5	2	 **4a;** 91
14	**1d**	**3d**	5.5	 **4f;** 61[c]
15	**1d**	**3g;** $3\text{-MeC}_6\text{H}_4$	3	 **4l;** 79
16	**1d**	**3e**	2.5	 **4i;** 87
17	**1d**	**3a**	2.5	 **4m**; 92
18	**1d**	**3c**	3	 **4n**; 85
19	**1d**	**3h;** $4\text{-ClC}_6\text{H}_4$	2	 **4o**; 93
20	**1d**	**3i;** $4\text{-CHOC}_6\text{H}_4$	3	 **4p**; 87
21	**1d**	**3j;** 2-naphthyl	4	 **4q;** 83
22	**1e;** $4\text{-BrC}_6\text{H}_4$	**3f**	2	 **4b**; 90
23	**1e**	**3d**	8	 **4g**; 62[c]
24	**1e**	**3g**	3.5	 **4r**; 83
25	**1e**	**3e**	3	 **4j**; 86
26	**1e**	**3a**	2	 **4s;** 91
27	**1e**	**3c**	3.5	 **4t;** 93

28	**1e**	**3h**	3.5	 **4u**; 84
29	**1e**	**3i**	3	 **4v**; 87
30	**1e**	**3j**	4	 **4w;** 81
31	**1f;** 4-$NO_2C_6H_4$	**3f**	2.5	 **4c;** 91
32	**1f**	**3d**	7	 **4h;** 64[c]
33	**1f**	**3g**	3	 **4x;** 84
34	**1f**	**3e**	3.5	 **4k;** 82
35	**1f**	**3a**	2.5	 **4n**; 92
36	**1f**	**3c**	2.5	 **4y;** 86
37	**1f**	**3h**	3	 **4z;** 92
38	**1f**	**3i**	3.5	 **4aa;** 84
39	**1f**	**3j**	4.5	 **4ab**; 83
40	**1f**	**3k;** 	24	 **4ac**; 25[c]
41	**1g;** 2-naphthyl	**3a**	6	 **4q;** 87
42	**1g;** 2-naphthyl	**3c**	4	 **4ab**; 83
43	**1h;** 2-BrC_6H_4	**3a**	24	-[d]

44	**1i;** 4-IC_6H_4	**3a**	3	-[e]
45	**1f**	**3l;** 	8	-[d]
46	**1f**	**3m;** 	8	-[d]
47	**1f**	**3n;** 	8	-[d]

[a] All the reactions were performed in THF at room temperature under nitrogen flow in the presence of Cs_2CO_3 (1 mmol) and $Ph_3PAuNTf_2$ (5 mol%). The **1** (0.5 mmol) : **3** ratio was 1:1.1.

[b] Yields refer to pure and isolated **4,** purified from the by-products on a silica gel chromatography column. The eluent was petroleum ether/diethyl ether (9 : 1).

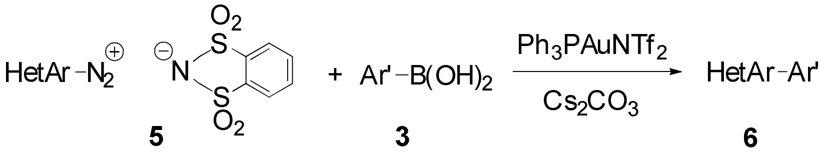
[c] The **1** (0.5 mmol) : **3** ratio was 1:3.

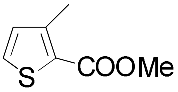
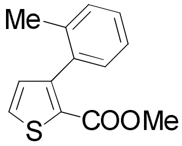
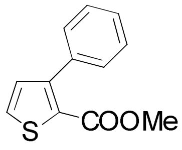
[d] No products **4** were obtained. After 8 hours salts **1** were still present (azo-coupling test with 2-naphthol was positive). Heating at 50 ° C caused the decomposition of **1.**

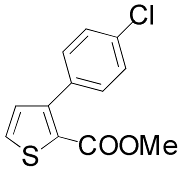
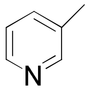
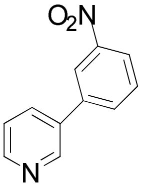
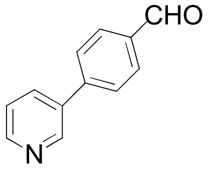
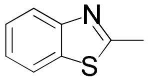
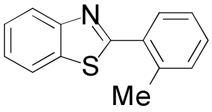
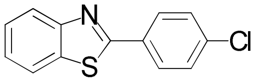
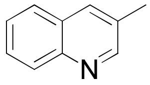
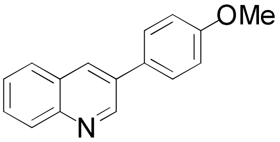
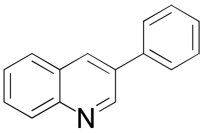
[e] GC-MS analyses of the crude residue showed a complex mixture of products among which 4-iodobiphenyl, MS (EI): *m/z* 280 (M^+) and terphenyl, MS (EI): *m/z* 230 $(M)^+$ were recognized.

Table 3

Au catalysed reactions between heteroaromatic salts **5** and **3**



Entry	HetAr in **5**	Ar' in **3**	Time (h)	Products **6** and yields (%)[a, b]
1	**5a;** 	**3d;** 2-MeC_6H_4	8	 **6a;** 59[c]
2	**5a**	**3f;** C_6H_5	3	 **6b;** 91

3	**5a**	**3h;** 4-ClC$_6$H$_4$	3.5	 **6c;** 84
4	**5b;** 	**3e;** 3-NO$_2$C$_6$H$_4$	4	 **6d**; 81
5	**5b**	**3i;** 4-CHOC$_6$H$_4$	2.5	 **6e;** 78
6	**5c;** 	**3d**	8	 **6f**; 48[c]
7	**5c**	**3h**	3	 **6g;** 70
8	**5d;** 	**3a;** 4-MeOC$_6$H$_4$	4	 **6h;** 79
9	**5d**	**3f**	3.5	 **6i;** 77

[a] All the reactions were performed in THF at room temperature under nitrogen flow in the presence of Cs_2CO_3 (1 mmol) and $Ph_3PAuNTf_2$ (5 mol%). The **5** (0.5 mmol) : **3** ratio was 1:1.1.

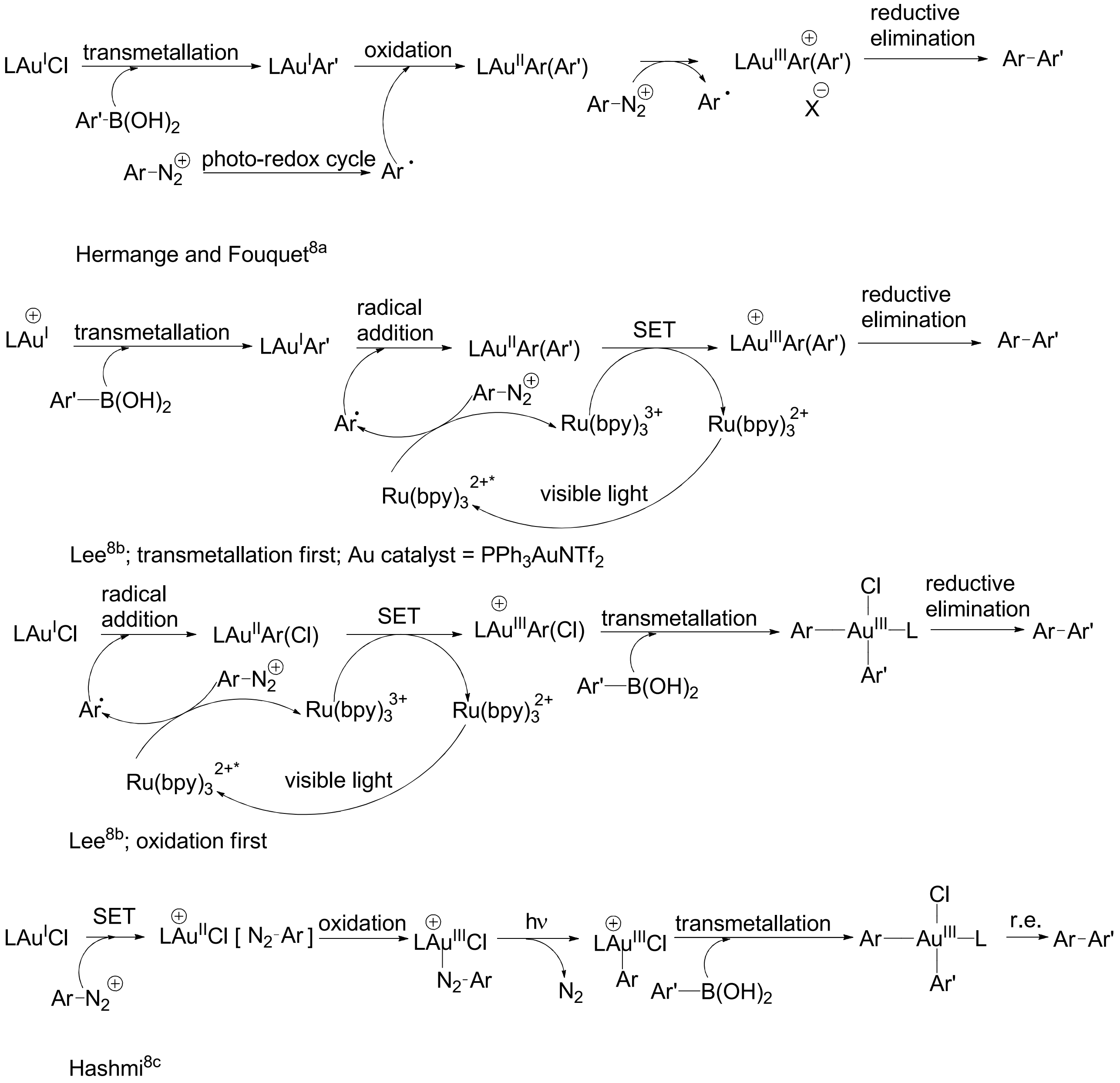
[b] Yields refer to pure and isolated **6,** purified from the by-products on a silica gel chromatography column. The eluent was petroleum ether/diethyl ether (9 : 1).

[c] The **1** (0.5 mmol) : **3** ratio was 1:3.

Finally, it is worth noting that was possible to recover *o*-benzenedisulfonimide (**2**) in more than 80% yield from all the reactions described above. It was also possible to recycle **2** for the preparation of other salts **1** with economic and ecological benefits.

The large amounts of data collected provide a good basis for some remarks on the mechanism involved.

Elegant hypotheses as to the mechanism of the gold-catalysed Suzuki couplings of arenediazonium salts have been proposed by the three different research groups mentioned above and are summarized in Scheme 2.[8] In two of these protocols, aryl radicals, generated by a visible-light photoredox process, enable the oxidation of Au(I) to Au(III). According to Lee hypothesis,[8b] using $Ph_3PAuNTf_2$ as a catalyst means that the transmetallation step occurrs prior to the oxidation step, whereas oxidation precedes transmetallation in the presence of Ph_3PAuCl.



Hermange and Fouquet[8a]

Lee[8b]; transmetallation first; Au catalyst = PPh_3AuNTf_2

Lee[8b]; oxidation first

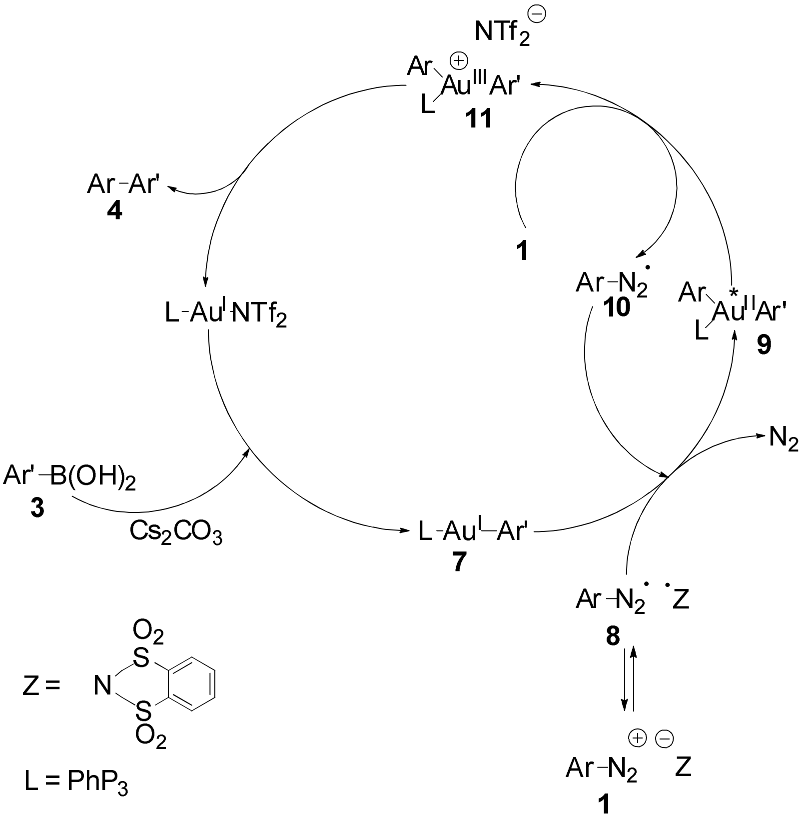
Hashmi[8c]

Scheme 2. Mechanisms proposed in the literature

On the other hand, Hermange and Fouquet,[8a] who only used Ph_3PAuCl, proposed that transmetallation came before gold oxidation in the catalytic cycle. Finally, Hashmi[8c] hypothesized a photosensitizer-free visible-light driven process in which the first step involved the oxidation of Ph_3PAuCl to a Au(III) specie by a diazonium salt in a SET process. It must be noted that the specie that actually undergoes the transmetallation is only formed after the light-mediated elimination of N_2.

In a previous paper,[11a] we obtained significant results from using salts **1** in Au(I) catalysed Heck-coupling reactions. Mechanistic insights highlighted the interesting role that the *o*-benzenedisulfonimide anion played as an electron transfer agent[11b-c] in promoting a pathway that does not require the presence of photocatalysts or external oxidants. Moreover, this reaction also occurred in the dark and without any photocatalysts. With the above-described mechanism in mind, we hypothesize the pathway shown in Scheme 3.

We assume that the transmetallation, namely the interaction between **3** and $Ph_3PAuNTf_2$ leading to the Au(I) intermediate **7**, is the first step.



Scheme 3. Hypothesized mechanism.

At this point, we also believe that the anion of salts **1** may act as a primary electron donor reagent toward the arenediazonium cations also in this coupling reaction, which would most likely give rise to the electron transfer complex **8** (Fig. 2). This would be favoured by the formation of a complex in which the partner of the aryldiazenyl radical is a species that is highly resonance stabilized (**8a**, **8b**, etc)

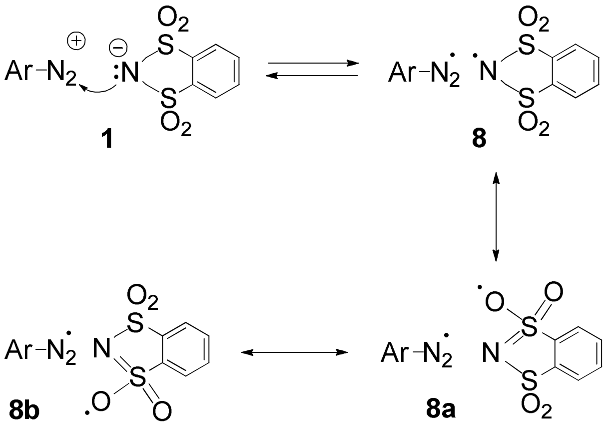


Fig. 2. Electron transfer complex **8**.

We then assume that complex **8** interacts with **7** to form the Au(II) complex **9** by transferring an aryl radical to it. A further oxidation of **9**, most likely due to an electron donated by **1**, gives the Au(III) complex **11** and other radicals **10** which contribute to oxidizing the Au(I) catalyst.

Ultimately, this radical chain enables the oxidation of the Au(I) to Au(III) (even in the dark; Table 1, entry 24) and without the involvement of photocatalysts or external oxidants. Finally, the reductive elimination step allows target **4** to be obtained and the Au catalyst restored.

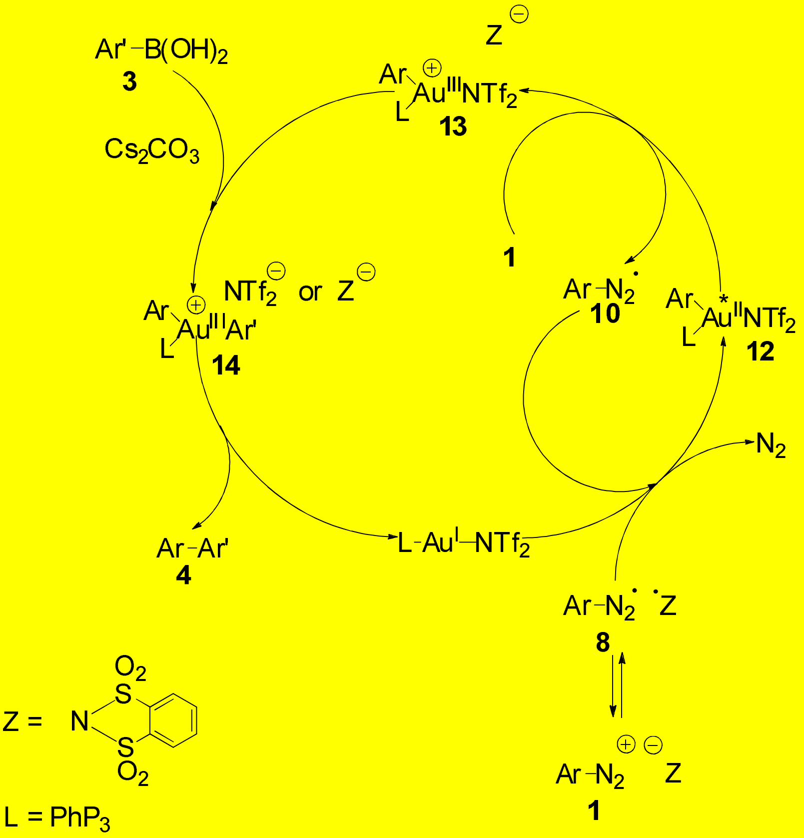
It must be stressed that no product **4a** was formed when the reaction was carried out in the presence of 1,3-dinitrobenzene or TEMPO, known radical scavengers (Table 1; entry 19, note e). This is good evidence that radicals are the actual reactive species.

It is known from the literature that the decomposition of diazonium salts in the presence of toluene furnished three isomers derived from phenylation of toluene at the *ortho*, *meta* and *para* positions. For a heterolytic decomposition the *o:m:p* ratio is 2.4:1.0:1.0 [12a] whereas for a homolytic one the *o:m:p* ratio is 4.0:1.0:0.7.[12b] In a control experiment (Experimental: *control experiment 4.4.1)* carried out under standard conditions, we added toluene in the reaction enviroment (in equimolar amount with respect to arylboronic acid). At the end of the reactions, GC analyses showed the presence of a significant amount of methylbiphenyl *o, m, p* isomers. The ratio was 4.08:1.0:0.61., typical of an homolytic pathway. This can be a further evidence of the formation of aryl radicals resulting from **8.**

The trial reactions (Table 1) clearly indicated that $Ph_3PAuNTf_2$ was a better catalyst than Ph_3PAuCl. The type of the counterion is crucial here. In fact the presence of NTf_2, a strong electron-withdrawing group, makes Au (I) much more electrophilic than when it is bound to Cl[13] and therefore makes it very reactive in the transmetallation step.

A simple control experiment was carried out (Experimental: *control experiment 4.4.2)* in order to confirm that transmetallation really is the first step. First, we prepared PPh_3AuPh by reacting $Ph_3PAuNTf_2$ with **3a** in the presence of Cs_2CO_3 and we then added salt **1**. The reaction completed after 1 h and the usual work-up furnished target **4a** in yields comparable to those obtained under standard conditions. Interestingly, the same reaction provided poor results when carried out with Ph_3PAuCl, confirming that this catalyst is less inclined to undergo the transmetallation reaction.

An alternative mechanism, in which the oxidation step precedes the transmetallation step, is showed in Scheme 4. We believe this alternative mechanism is very unlikely; in fact, the possible intermediate **13,** formed via Au (I) oxidation by aryl radicals, would be highly destabilized by the presence of NTf_2, thus hindering the progress of the reaction. A control experiment (Experimental: *control experiment 4.4.3*) confirmed this hypothesis.



Scheme 4. Alternative mechanism.

3. Conclusions

We have proposed a mild, easy and efficient gold catalysed Suzuki-Miyaura coupling of arenediazonium *o*-benzenedisulfonimides **1** and heteroarenediazonium *o*-benzenedisulfonimides **5**. The target products, biaryls **4** or heteroarenes **6** were generally obtained in satisfactory yields (51 positive examples, 80% average yield). We also confirm the interesting role that the *o*-

benzenedisulfonimide anion plays as an electron transfer agent in enabling a pathway that does not require the presence of photocatalysts or external oxidants.

4. Experimental

4.1. General information

All the reactions were carried out in oven dried glassware and under a nitrogen flow. Analytical grade reagents and solvents were used and reactions were monitored by GC, GC-MS and TLC. Column chromatography and TLC were performed on Merck silica gel 60 (70-230 mesh ASTM) and GF 254, respectively. Petroleum ether refers to the fraction boiling in the range 40–70 °C. Room temperature is 20-25 °C. Mass spectra were recorded on an HP 5989B mass selective detector connected to an HP 5890 GC with a methyl silicone capillary column. ^{1}H NMR, ^{13}C NMR, ^{31}P spectra were recorded on a Jeol ECZR spectrometer at 600, 150 and 243 MHz respectively. IR spectra were recorded on an IR PerkinElmer UATR-two spectrometer. Dry arenediazonium *o*-benzenedisulfonimides **1** and dry heteroarenediazonium *o*-benzenedisulfonimides **5** were prepared as described previously by us.[9a] The crude salts **1** and **5** were virtually pure (by ^{1}H NMR spectroscopy) and were used in subsequent reactions without further crystallization. All the other reagents were purchased from Sigma-Aldrich or Alfa-Aesar. Structures and purity of all the products obtained in this research were confirmed by their spectral (NMR, MS) and physical data, substantially identical to those reported in the literature. Yields of the pure (GC, GC-MS, TLC and NMR) isolated compounds **4**, **6** are collected in Tables 2 and 3. NMR spectra of **4** and **6** are reported in Supplementary material. Satisfactory microanalyses were obtained for new compound **4ac.**

*4.2. Benzenediazonium o-benzenedisulfonimide (**1a**): representative procedure for the preparation of salts **1**.*

A solution of *o*-benzenedisulfonimide (**2**; 2.63 g, 12 mmol) in glacial AcOH (40 mL) was slowly added, over period of 10 min, to a stirred solution of aniline (0.93 g, 10 mmol) in the same solvent, previously cooled to 0-5°C in an ice bath. *i*-Pentyl nitrite (1.28 g, 11 mmol) was added dropwise (about 10 min). A white precipitate of **1a** began to separe at once. After the addition was complete, the cooling bath was removed and the mixture was maintained under stirring for further 10 min. Then anhydrous Et_2O was added to complete the precipitation of **1a**, that was gathered by filtration on a Büchner funnel and washed several times with additional anhydrous Et_2O. After drying under reduced pressure, the title compound **1a** was obtained in 98% yield (3.18 g). Dp 110°C (lit.[9a] dp 110 °C).

*4.3. 4-Methoxybiphenyl (**4a**): representative procedure for the Au catalyzed Suzuki-Miyaura couplings*

In a oven-dried flask and under nitrogen flow, benzenediazonium *o*-benzenedisulfonimide (**1a**, 161 mg, 0.5 mmol) was added to a suspension of 4-methoxyphenylboronic acid (**3a**, 91 mg, 0.6 mmol), [bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold(I) (2:1) toluene adduct (39 mg, 0.025 mmol, 5mol%), Cs_2CO_3 (325 mg, 1 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature for 2 h; the completion of the reaction was confirmed by the absence of azo coupling with 2-naphthol. Then, the reaction mixture was poured into diethyl ether/water (100 mL, 1:1). The aqueous layer was separated and extracted with diethyl ether (50 mL). The combined organic extracts were washed with water (50 mL), dried with Na_2SO_4 and evaporated under reduced pressure. GC-MS analyses of the crude residue showed 4-methoxybiphenyl (**4a**), MS (EI): *m/z* 184 (M^+) as the major product, besides traces of biphenyl, MS (EI): *m/z* 154 (M^+), 4,4'-dimethoxybiphenyl, MS (EI): *m/z* 214 (M^+), *N*-phenyl-*o*-benzenedisulfonimide, MS (EI): *m/z* 295 (M^+). The crude residue was purified on a short column, eluting with petroleum ether/diethyl ether (9:1). The only isolated product was the title compound (**4a**, 81 mg, 88% yield). The aqueous layer and aqueous washings were collected and evaporated under reduced pressure. The tarry residue was passed through a column of Dowex HCR-W2 ion exchange resin (1.6 g/1 g of product), eluting with water (about 50 mL). After removal of water under reduced pressure, virtually pure (^{1}H NMR) *o*-benzenedisulfonimide (**2**) was recovered (89 mg, 81% yield; mp 192–194 °C. Lit. 190–193 °C).

A gram-scale reaction was also carried out between **1a** (1.61 g, 5 mmol) and **1b** (0.91 g, 6 mmol) in the presence of bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold(I) (2:1) toluene adduct 0.39 g, 0.25 mmol, 5mol%) and Cs_2CO_3 (3.25 g, 10 mmol) in THF (20 mL). After the above described work-up, **4a** (0.78 g) was obtained in 85% yield and **2** was recovered (1.00 g, 91%).

*4.3.1 4-Methoxybiphenyl (**4a**).*

4a was obteined as a white solid; 81 mg (88% yield from **1a** and **3a**) or 84 mg (91% yield from **1d** and **3f** ; mp 87–88 °C (MeOH; lit.[14] mp 87–88 °C); R_f (petroleum ether/Et_2O 9:1) 0.43; δ_H (600 MHz, $CDCl_3$) 7.58−7.54 (m, 4H), 7.43 (t, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H); δ_C (150 MHz, $CDCl_3$) 159.3, 140.9, 133.9, 128.8, 128.3, 126.8, 126.7, 114.6, 55.4; MS (EI): *m/z* 184 (100, M^+)

*4.3.2. 4-Bromobiphenyl (**4b**).*

4b was obtained as a pale grey solid; 104 mg (89% yield from **1a** and **3b**) or 105 mg (90% yield from **1e** and **3f**); mp 90–91°C (MeOH; lit.[15] mp 89–90 °C); R_f (petroleum ether/Et_2O 9:1) 0.41; δ_H (600 MHz, $CDCl_3$) 7.58−7.55 (m, 4H), 7.47−7.43 (m, 4H), 7.39−7.36 (m, 1H); δ_C (150 MHz, $CDCl_3$) 140.2, 140.1 131.9, 129.0, 128.9, 127.8, 127.1, 121.7; MS (EI): *m/z* 232 (100, M^+), 234 (100, M^+ +2).

4.3.3 4-Nitrobiphenyl (4c).

4c was obtained as a pale yellow solid; 84 mg (84% yield from **1a** and **3c**) or 91 mg (91 % yield from **1f** and **3f**); mp 114–115 °C (MeOH; lit.[16] mp 112–113 °C); R_f (petroleum ether/Et_2O 9:1) 0.37; δ_H (600 MHz, $CDCl_3$) 8.28 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.62−7.61 (m, 2H), 7.51−7.48

(m, 2H), 7.46–7.44 (m, 1H); δ_C (150 MHz, CDCl$_3$) 147.8, 147.2, 138.9, 129.3, 129.0, 127.9, 127.5, 124.2; MS (EI): *m/z* 199 (100, M$^+$).

*4.3.4. 2,2’-Dimethylbiphenyl (**4d**).*

4d was obtained as a pale yellow viscous oil;[17] 55 mg (60% yield); R_f (petroleum ether/Et$_2$O 9:1) 0.65; δ_H (600 MHz, CDCl$_3$) 7.26–7.20 (m, 6H), 7.11–7.09 (m, 2H), 2.05 (s, 6H); δ_C (150 MHz, CDCl$_3$) 141.6, 135.8, 129.9, 129.4, 127.2, 125.7, 19.9; MS (EI): *m/z* 182 (75, M$^+$).

*4.3.5. 2-Methyl-3’-nitrobiphenyl (**4e**).*

4e was obtained as a pale yellow viscous oil;[18] 81 mg (76% yield from **1b** and **3e**) or 65 mg (61% yield from **1c** and **3d**); R_f (petroleum ether/Et$_2$O 9:1) 0.41; δ_H (600 MHz, CDCl$_3$) 8.21–8.20 (m, 2H), 7.67–7.65 (m, 1H), 7.61–7.57 (m, 1H), 7.33–7.21 (m, 4H), 2.27 (s, 3H); δ_C (150 MHz, CDCl$_3$) 148.2, 143.7, 139.4, 135.4, 135.3, 130.7, 129.7, 129.1, 128.4, 126.2, 124.2, 121.9, 20.6; MS (EI): *m/z* 213 (100, M$^+$).

*4.3.6. 4’-Methoxy-2-methylbiphenyl (**4f**).*

4f was obtained as a pale yellow solid; 64 mg (65% yield from **1b** and **3a**) or 60 mg (61% yield from **1d** and **3d**); mp 52–53 °C (MeOH; lit.[19] mp 51–52 °C); R_f (petroleum ether/Et$_2$O 9:1) 0.49; δ_H (600 MHz, CDCl3) 7.28–7.26 (m, 4H), 7.25–7.23 (m, 2H), 6.97 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H), 2.30 (s, 3H); δ_C (150 MHz, CDCl$_3$) 158.6, 141.6, 135.6, 134.5, 130.4, 130.3, 130.0, 127.1, 125.9, 113.6, 55.8, 21.1; MS (EI): *m/z* 198 (100, M$^+$).

*4.3.7. 4’-Bromo-2-methylbiphenyl (**4g**).*

4g was obtained as a pale yellow viscous oil;[20] 77 mg (62% yield from **1b** and **3b**) or 77 mg (62% yield from **1e** and **3d**); R_f (petroleum ether/Et$_2$O 9:1) 0.58; δ_H (600 MHz, CDCl$_3$) 7.55 (d, *J* = 8.4 Hz, 2H), 7.34–7.24 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.28 (s, 3H); δ_C (150 MHz, CDCl$_3$) 140.9, 140.7, 135.3, 131.4, 131.0, 130.7, 130.6, 127.7, 126.0, 121.1, 20.7; MS (EI): *m/z* 246 (80, M$^+$), 248 (80, M$^+$ +2).

*4.3.8. 2-Methyl-4’-nitrobiphenyl (**4h**).*

4h was obtained as a pale yellow solid; 72 mg (68% yield from **1b** and **3c**) or 69 mg (64% yield from **1f** and **3d**); mp 105–106 °C (MeOH; lit.[21] mp 104–105 °C); R_f (petroleum ether/Et$_2$O 9:1) 0.40; δ_H (600 MHz, CDCl$_3$) 8.27 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.34–7.27 (m, 3H), 7.21 (d, *J* =7.2 Hz, 2H), 2.27(s, 3H); δ_C (150 MHz, CDCl$_3$): δ = 148.9, 146.9, 139.7, 135.2, 130.8, 130.2, 129.5, 128.6, 126.2, 123.7, 20.5; MS (EI): *m/z* 213 (100, M$^+$).

*4.3.9. 4’-Methoxy-3-nitrobiphenyl (**4i**).*

4i was obtained as a pale brown solid; 105 mg (92% yield from **1c** and **3a**) or 100 mg (87% yield from **1d** and **3e**); mp 75–77 °C (MeOH; lit.[22] mp 75–76 °C); R_f (petroleum ether/Et$_2$O 9:1) 0.28; δ_H (600 MHz, CDCl$_3$) 8.38 (t, *J* = 1.8 Hz, 1H), 8.13–8.12 (m, 1H), 7.85–7.84 (m, 1H), 7.57–7.54 (m, 3H), 6.99 (d, *J* =9.0 Hz, 2H), 3.86 (s, 3H); δ_C (150 MHz, $CDCl_3$) 160.2, 148.8, 142.5, 132.6, 131.1, 129.7, 128.3, 121.4, 121.3, 114.7,55.5; MS (EI): *m/z* 229 (100, M^+).

*4.3.10. 4'-Bromo-3-nitrobiphenyl (**4j**).*

4j was obtained as a white solid; 125 mg (90% yield from **1c** and **3b**) or 120 mg (86% yield from **1e** and **3e**); mp 94–95 °C (MeOH; lit.[23] mp 93 °C); R_f (petroleum ether/Et_2O 9:1) 0.35; δ_H (600 MHz, $CDCl_3$): δ = 8.39 (t, J = 1.8 Hz, 1H), 8.21–8.19 (m, 1H), 7.87–7.86 (m, 1H), 7.62–7.58 (m, 3H), 7.47 (d, J =9.0 Hz, 2H); δ_C (150 MHz, $CDCl_3$) 141.7, 137.6, 133.1, 132.9, 132.4, 130.0, 128.8, 123.1, 122.5, 121.8; MS (EI): *m/z* 277 (100, M^+), 279 (100, M^+ +2).

*4.3.11. 3-Nitro-4'-nitrobiphenyl (**4k**).*

4k was obtained as a pale orange solid; 107 mg (88% yield from **1c** and **3c**) or 100 mg (82% yield from **1f** and **3e**); mp 185–186 °C (MeOH; lit.[24] mp 184–187 °C); R_f (petroleum ether/Et_2O 9:1) 0.18; δ_H (600 MHz, $CDCl_3$) 8.48 (t, *J* = 1.8 Hz, 1H), 8.35 (d, *J* = 9.0 Hz, 2H), 8.30–8.29 (m, 1H), 7.95–7.94 (m, 1H), 7.78 (d, *J* = 9.0 Hz, 2H), 7.69 (t, *J* = 7.8 Hz, 1H); δ_C (150 MHz, $CDCl_3$) 148.9, 147.9, 144.9, 140.5, 133.3, 130.4, 128.2, 124.5, 123.6, 122.4; MS (EI): *m/z* 244 (100, M^+).

*4.3.12. 4'-Methoxy-3-methylbiphenyl (**4l**).*

4l was obtained as a pale grey solid; 78 mg (79% yield); mp 50–51 °C (MeOH; lit.[25] mp 51–52 °C); R_f (petroleum ether/Et_2O 9:1) 0.49; δ_H (600 MHz, $CDCl_3$) 7.56 (d, *J* = 8.4 Hz, 2H), 7.45–7.33 (m, 3H), 7.17–7.16 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 2.45 (s, 3H); δ_C (150 MHz, $CDCl_3$) 159.2, 140.9, 138.3, 134.0, 128.8, 128.3, 127.7, 127.6, 123.9, 114.2, 55.3, 21.3; MS (EI): *m/z* 198 (100, M^+).

*4.3.13. 4,4'-Dimethoxybiphenyl (**4m**).*

4m was obtained as a white solid; 98 mg (92% yield); mp 174–175 °C (MeOH; lit.[26] mp 172–174 °C); R_f (petroleum ether/Et_2O 9:1) 0.25; δ_H (600 MHz, $CDCl_3$) 7.48 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H); δ_C (150 MHz, $CDCl_3$) 158.8, 133.6, 127.9, 114.2, 55.8; MS (EI): *m/z* 214 (100, M^+).

*4.3.14. 4-Methoxy-4'-nitrobiphenyl (**4n**).*

4n was obtained as a pale orange solid; 97 mg (85% yield from **1d** and **3c**) or 105 mg (92% yield from **1f** and **3a**); mp 109–110°C (MeOH; lit.[27] mp 109–110 °C); R_f (petroleum ether/Et_2O 9:1) 0.22; δ_H (600 MHz, $CDCl_3$) 8.25 (d, *J* = 9.0 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H); δ_C (150 MHz, $CDCl_3$) 160.5, 147.4, 146.6, 131.1, 128.7, 127.1, 124.4, 114.7, 55.8; MS (EI): *m/z* 229 (100, M^+).

*4.3.15. 4-Chloro-4'-methoxybiphenyl (**4o**).*

4o was obtained as a pale grey solid; 101 mg (93% yield); mp 111–112°C (MeOH; lit.[28] mp 110–111 °C); R_f (petroleum ether/Et_2O 9:1) 0.45; δ_H (600 MHz, $CDCl_3$) 7.49–7.58 (m, 4H), 7.38–7.37 (m, 2H), 6.98 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H); δ_C (150 MHz, $CDCl_3$) 159.5, 139.4, 132.8, 132.5, 129.1, 128.1, 128.0, 114.6, 55.8; MS (EI): *m/z* 218 (100, M^+).

*4.3.16. 4-(4-Methoxyphenyl)benzaldehyde (**4p**).*

4p was obtained as a white solid; 92 mg (87% yield); mp 110–111°C (MeOH; lit.[29] mp 109–110 °C); R_f (petroleum ether/Et_2O 9:1) 0.29; δ_H (600 MHz, $CDCl_3$)10.00 (s, 1H), 7.89 (d, J = 9.0 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H); δ_C (150 MHz, $CDCl_3$) 192.0, 160.2, 146.8, 134.8, 132.1, 130.4, 128.6, 127.1, 114.5, 55.4; MS (EI): *m/z* 212 (100, M^+).

*4.3.17. 2-(4-Methoxyphenyl)naphthalene (**4q**).*

4q was obtained as a grey solid; 97 mg (83% yield from **1d** and **3j**) or 102 mg (87% yield from **1g** and **3a**); mp 132–133°C (MeOH; lit.[30] mp 130–131 °C); R_f (petroleum ether/Et_2O 9:1) 0.38; δ_H (600 MHz, $CDCl_3$) 8.01 (d, J = 2.4 Hz, 1H), 7.91–7.87 (m, 3H), 7.75–7.73 (m, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.55–7.45 d_C (m, 2H), 7.04 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H); δ_C (150 MHz, $CDCl_3$) 159.4, 138.3, 133.7, 133.6, 132.4, 128.6, 128.5, 128.2, 127.8, 126.4, 125.8, 125.6, 125.2, 114.4, 55.6 ; MS (EI): *m/z* 234 (75, M^+).

4.3.18. 4'-Bromo-3-methylbiphenyl (4r).

4r was obtained as a pale yellow viscous oil;[31] 103 mg (83% yield); R_f (petroleum ether/Et_2O 9:1) 0.62; δ_H (600 MHz, $CDCl_3$) 7.57 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.39–7.35 (m, 4H); δ_C (150 MHz, $CDCl_3$) 140.4, 140.1, 138.6, 131.9, 128.9, 128.8, 128.5, 127.8, 124.1, 121.5, 21.6; MS (EI): *m/z* 246 (100, M^+), 248 (100, M^+ +2).

4.3.19. 4-Bromo-4'-methoxybiphenyl (4s).

4s was obtained as a pale grey solid; 120 mg (91% yield); mp 144–145°C (MeOH; lit.[32] mp 143–144 °C); R_f (petroleum ether/Et_2O 9:1) 0.45; δ_H (600 MHz, $CDCl_3$) 7.53 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 9.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H); δ_C (150 MHz, $CDCl_3$) 159.5, 139.8, 132.5, 131.9, 128.3, 128.1, 120.9, 114.5, 54.9; MS (EI): *m/z* 262 (100, M^+), 264 (100, M^+ +2).

4.3.20. 4-Bromo-4'-nitrobiphenyl (4t).

4t was obtained as a yellow solid; 129 mg (93% yield); mp 173–174 °C (MeOH; lit.[33] mp 175–176°C); R_f (petroleum ether/Et_2O 9:1) 0.38; δ_H (600 MHz, $CDCl_3$): δ = 8.28 (d, J = 9.0 Hz, 2H), 7.69 (d, J = 9.0 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H); δ_C (150 MHz, $CDCl_3$) 147.3, 146.4, 137.8, 132.4, 129.0, 127.7, 124.4, 123.0; MS (EI): *m/z* 277 (70, M^+), 279 (70, M^+ +2).

*4.3.21. 4-Bromo-4'-chlorobiphenyl (**4u**).*

4u was obtained as a pale grey solid; 112 mg (84% yield); mp 153–155 °C (MeOH; lit.[34] mp 150–153°C); R_f (petroleum ether/Et_2O 9:1) 0.70; δ_H (600 MHz, $CDCl_3$) 7.55 (d, J = 8.4 Hz, 2H), 7.46 (d,

J = 8.4 Hz, 2H), 7.41–7.39 (m, 4H); δ$_C$ (150 MHz, CDCl$_3$) 138.9, 138.5, 133.8, 132.0, 129.1, 128.7, 128.3, 122.0; MS (EI): *m/z* 266 (80, M$^+$), 268 (100, M$^+$+2).

*4.3.22. 4-(4-Bromophenyl)benzaldehyde (**4v**).*

4v was obtained as a white solid; 113 mg (87% yield); mp 140–141°C (MeOH; lit.[35] mp 140–142 °C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.48; δ$_H$ (600 MHz, CDCl$_3$) 10.04 (s, 1H), 7.93 (d, J = 9.0 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H); δ$_C$ (150 MHz, CDCl$_3$) 191.9, 145.9, 138.7, 135.5, 132.3, 130.4, 129.0, 127.6, 123.0; MS (EI): *m/z* 260 (75, M$^+$), 262 (75, M$^+$+2).

*4.3.23. 2-(4-Bromophenyl)naphthalene (**4w**).*

4w was obtained as a pale orange solid; 115 mg (81% yield); mp 128–129°C (MeOH; lit.[36] mp 129–130°C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.68; δ$_H$ (600 MHz, CDCl$_3$) 8.01 (s, 1H), 7.92–7.87 (m, 3H), 7.70–7.68 (m, 1H), 7.62–7.57 (m, 4H), 7.53–7.51 (m, 2H); δ$_C$ (150 MHz, CDCl$_3$) 140.1, 137.4, 133.7, 132.8, 132.1, 129.0, 128.8, 128.3, 127.8, 126.6, 126.3, 125.8, 125.2, 121.8; MS (EI): *m/z* 282 (65, M$^+$), 284 (65, M$^+$+2).

*4.3.24. 3-Methyl-4'-nitrobiphenyl (**4x**).*

4x was obtained as a pale yellow solid; 89 mg (84% yield); mp 49–50 °C (MeOH; lit.[37] mp 48–49 °C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.42; δ$_H$ (600 MHz, CDCl$_3$) 8.27 (d, J = 9.0 Hz, 2H), 7.71 (d, J = 9.0 Hz, 2H), 7.43–7.37 (m, 4H), 2.45 (s, 3H); δ$_C$ (150 MHz, CDCl$_3$) 147.9, 147.1, 138.9, 138.8, 129.8, 129.2, 128.2, 127.9, 124.6, 124.1, 21.6; MS (EI): *m/z* 213 (100, M$^+$).

*4.3.25. 4,4'-Dinitrobiphenyl (**4y**).*

4y was obtained as a pale yellow solid; 105 mg (86% yield); mp 236–237°C (MeOH; lit.[38] mp 239–240°C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.42; δ$_H$ (600 MHz, CDCl$_3$) 8.34 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H); δ$_C$ (150 MHz, CDCl$_3$) 148.2, 145.1, 128.4, 124.5; MS (EI): *m/z* 244 (100, M$^+$).

*4.3.26. 4-Chloro-4'-nitrobiphenyl (**4z**).*

4z was obtained as a white solid; 107 mg (92% yield); mp 145–146 °C (MeOH; lit.[39] mp 145–146°C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.35; δ$_H$ (600 MHz, CDCl$_3$) 8.27 (d, J = 9.0 Hz, 2H), 7.68 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 9.0 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H); δ$_C$ (150 MHz, CDCl$_3$) 147.4, 146.4, 137.2, 135.3, 129.5, 128.7, 127.8, 124.3; MS (EI): *m/z* 233 (90, M$^+$).

*4.3.27. 4-(4-Nitrophenyl)benzaldehyde (**4aa**).*

4aa was obtained as a pale yellow solid; 95 mg (84% yield); mp 128–130°C (MeOH; lit.[26] mp 127–129 °C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.20; δ$_H$ (600 MHz, CDCl$_3$) 10.01 (s, 1H), 7.89 (d, J = 9.0 Hz, 2H), 7.99–7.97 (m, 2H), 7.77–7.75 (m, 4H); δ$_C$ (150 MHz, CDCl$_3$) 191.8, 147.8, 146.18, 144.5, 136.3, 130.5, 128.3, 128.2, 124.3; MS (EI): *m/z* 227 (100, M$^+$).

*4.3.28. 2-(4-Nitrophenyl)naphthalene (**4ab**).*

4ab was obtained as a pale grey solid; 103 mg (83% yield from **1f** and **3j**) or 103 mg (83% yield from **1g** and **3c**); mp 184–185°C (MeOH; lit.[40] mp 183–184 °C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.35; δ_H (600 MHz, CDCl$_3$) 8.32 (d, *J* = 9.0 Hz, 2H), 8.08 (d, *J* = 1.8 Hz, 1H), 7.96–7.95 (m, 1H), 7.93–7.88 (m, 1H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.74–7.72 (m, 2H), 7.57–7.54 (m, 2H); δ_C (150 MHz, CDCl$_3$) 147.7, 147.2, 136.1, 133.5, 133.4, 129.1, 128.6, 128.1, 127.8, 127.0, 126.9, 124.9, 124.2; MS (EI): *m/z* 249 (75, M$^+$).

*4.3.29. 2-Ethoxy-1-(4-nitrophenyl)naphthalene (**4ac**).*

4ac was obtained as a pale grey solid; 37 mg (25% yield); mp 102–103°C (MeOH); [Found: C 73.75; H 5.12; N 4.74. $C_{18}H_{15}NO_3$ requires C, 73.71; H, 5.15; N, 4.78%]; R$_f$ (petroleum ether/Et$_2$O 9:1) 0.25; ν_{max} (neat) 2965, 1555, 1505, 1429, 1336, 1214, 1180, 1044, 836, 800, 718 cm^{-1}; δ_H (600 MHz, CDCl$_3$) 8.35 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 2H), 7.43–7.42 (m, 1H), 7.38–7.33 (m, 3H), 7.16–7.13 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 4H), 1.26 (t, *J* = 7.2 Hz, 3H); δ_C (150 MHz, CDCl$_3$) 153.1, 147.0, 144.3, 134.8, 132.3, 130.4, 129.5, 127.7, 127.0, 126.8, 124.0, 123.6, 123.4, 114.9, 63.5, 14.9; MS (EI): *m/z* 293 (100, M$^+$), 265 (80), 218 (45), 189 (65).

*4.3.30. Methyl 3-(2-methylphenyl)thiophene-2-carboxylate (**6a**).*

6a was obtained as a white solid; 68 mg (59% yield); mp 103–104°C (MeOH; lit.[41] mp 102–104 °C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.35; δ_H (600 MHz, CDCl$_3$) 7.51 (d, *J* = 4.8 Hz, 1H), 7.32–7.20 (m, 4H), 6.97 (d, *J* = 5.4 Hz, 1H), 3.71 (s, 3H), 2.13 (s, 3H); δ_C (150 MHz, CDCl$_3$) 162.3, 148.5, 136.1, 131.4, 130.6, 130.3, 129.8, 129.0, 128.0, 127.9, 125.3, 51.9, 20.0; MS (EI): *m/z* 232 (25, M$^+$).

*4.3.31. Methyl 3-phenylthiophene-2-carboxylate (**6b**).*

6b was obtained as a pale orange solid; 99 mg (91% yield); mp 115–116°C (MeOH; lit.[42] mp 117–118 °C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.38; δ_H (600 MHz, CDCl$_3$) 7.51 (d, *J* = 4.8 Hz, 1H), 7.46–7.40 (m, 2H), 7.38–7.37 (m, 3H), 7.07 (d, *J* = 4.8 Hz, 1H), 3.77 (s, 3H); δ_C (150 MHz, CDCl$_3$) 162.5, 148.8, 135.7, 131.7, 130.4, 129.3, 128.0, 127.9, 126.9, 51.8; MS (EI): *m/z* 218 (85, M$^+$).

*4.3.32. Methyl 3-(4-chlorophenyl)thiophene-2-carboxylate (**6c**).*

6c was obtained as a pale grey solid; 106 mg (84% yield); mp 98–99°C (MeOH; lit.[43] mp 98–99 °C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.40; δ_H (600 MHz, CDCl$_3$): δ = 7.49 (d, *J* = 5.4 Hz, 1H), 7.39–7.35 (m, 4H), 7.03 (d, *J* = 5.4 Hz, 1H), 3.77 (s, 3H); δ_C (150 MHz, CDCl$_3$) 162.4, 147.5, 134.1, 134.0, 131.4, 130.7, 130.6, 128.1, 127.2, 52.1; MS (EI): *m/z* 252 (55, M$^+$).

*4.3.33. 3-(3-Nitrophenyl)pyridine (**6d**).*

6d was obtained as a pale yellow solid; 81 mg (81% yield); mp 95–96°C (MeOH; lit.[44] mp 93–95 °C); R$_f$ (petroleum ether/Et$_2$O 9:1) 0.35; δ_H (600 MHz, CDCl$_3$) 8.82 (s, 1H), 8.59–8.57 (m, 2H), 8.25 (d, *J* = 7.2 Hz, 1H), 7.99 (t, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H); δ_C (150

MHz, $CDCl_3$) 149.3, 148.7, 147.7, 140.2, 135.9, 134.4, 131.1, 128.8, 125.5, 124.6, 122.5; MS (EI): *m/z* 200 (85, M^+).

*4.3.34. 4-(3-Pyridinyl)benzaldehyde (**6e**).*

6e was obtained as a pale grey solid; 72 mg (78% yield); mp 128–130°C (MeOH; lit.[44] mp 127–129 °C); R_f (petroleum ether/Et_2O 9:1) 0.42; δ_H (600 MHz, $CDCl_3$) 9.92 (s, 1H), 8.82 (s, 1H), 8.57 (d, *J* = 6.6 Hz, 1H), 7.98–7.97 (m, 3H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H); δ_C (150 MHz, $CDCl_3$) 191.9, 148.9, 147.9, 142.9, 137.4, 136.4, 131.4, 131.3, 128.9, 125.4; MS (EI): *m/z* 183 (55, M^+).

*4.3.35. 2-(2-Methylphenyl)benzo[d]thiazole (**6f**).*

6f was obtained as a pale orange solid; 54 mg (48% yield); mp 53–54°C (MeOH; lit.[45] mp 52 °C); R_f (petroleum ether/Et_2O 9:1) 0.45; δ_H (600 MHz, $CDCl_3$) 8.05–8.03 (m, 1H), 8.00–7.98 (m, 1H), 7.62–7.61 (m, 1H), 7.48–7.46 (m, 2H), 7.32–7.29 (m, 3H), 2.46 (s, 3H); δ_C (150 MHz, $CDCl_3$) 168.1, 152.5, 136.5, 136.3, 135.4, 131.2, 130.7, 128.4, 127.4, 126.9, 125.5, 123.7, 122.2, 20.3; MS (EI): *m/z* 225 (40, M^+).

*4.3.36. 2-(4-Chlorophenyl)benzo[d]thiazole (**6g**).*

6g was obtained as a white solid; 86 mg (70% yield); mp 113–114°C (MeOH; lit.[46] mp 115–116 °C); R_f (petroleum ether/Et_2O 9:1) 0.50; δ_H (600 MHz, $CDCl_3$) 8.05–8.03 (m, 1H), 8.00–7.98 (m, 1H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.48–7.44 (m, 4H); δ_C (150 MHz, $CDCl_3$) 162.1, 152.5, 137.8, 136.3, 136.1, 129.2, 128.3, 126.9, 125.3, 123.6, 122.7; MS (EI): *m/z* 245 (50, M^+).

*4.3.37. 3-(4-Methoxyphenyl)quinoline (**6h**).*

6h was obtained as a grey solid; 93 mg (79% yield); mp 85–86°C (MeOH; lit.[47] mp 83–85 °C); R_f (petroleum ether/Et_2O 9:1) 0.30; δ_H (600 MHz, $CDCl_3$) 8.93 (s, 1H), 8.38 (s, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.61–7.57 (m, 3H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H); δ_C (150 MHz, $CDCl_3$) 158.5, 148.7, 148.4, 135.2, 135.1, 132.1, 129.9, 129.5, 129.2, 129.0, 128.7, 126.4, 114.5, 56.0; MS (EI): *m/z* 235 (65, M^+).

*4.3.38. 3-Phenylquinoline (**6i**).*

6i was obtained as a grey solid; 79 mg (77% yield); mp 50–51°C (MeOH; lit.[47] mp 49–51 °C); R_f (petroleum ether/Et_2O 9:1) 0.38; δ_H (600 MHz, $CDCl_3$) 8.97 (s, 1H), 8.41 (s, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.64–7.58 (m, 3H), 7.48–7.42 (m, 3H), 7.36–7.34 (m, 1H); δ_C (150 MHz, $CDCl_3$): δ = 148.7, 148.4, 138.1, 135.2, 135.1, 132.1, 129.9, 129.2, 129.0, 128.7, 128.4, 126.8 126.4; MS (EI): *m/z* 205 (70, M^+).

4.4. Control experiments

4.4.1 In a oven-dried flask and under nitrogen flow, benzenediazonium *o*-benzenedisulfonimide (**1a**, 161 mg, 0.5 mmol) was added to a suspension of 4-methoxyphenylboronic acid (**3a**, 91 mg, 0.6

mmol), [bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold(I) (2:1) toluene adduct (39 mg, 0.025 mmol, 5mol%), Cs_2CO_3 (325 mg, 1 mmol) and toluene (55 mg, 0.6 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature for 2 h; the completion of the reaction was confirmed by the absence of azo coupling with 2-naphthol. Then, the reaction mixture was poured into diethyl ether/water (100 mL, 1:1). The aqueous layer was separated and extracted with diethyl ether (50 mL). The combined organic extracts were washed with water (50 mL), dried with Na_2SO_4 and evaporated under reduced pressure. GC analyses of the crude residue, beside target **4a** and other by-products, showed the precence of *o, m, p*-methylbiphenyl, each with MS (EI): *m/z* 168 (M^+), in a 4.08:1:0.61 ratio. The structure of these three isomers was confirmed by comparison with authentic and commercial samples (Sigma-Aldrich)

4.4.2. In a oven-dried flask and under nitrogen flow, 4-methoxyphenylboronic acid (**3a**, 91 mg, 0.6 mmol) was added to a suspension of Cs_2CO_3 (325 mg, 1 mmol) and [bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold(I) (2:1) toluene adduct (942 mg, 0.6 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature for about 1 h until TLC, (petroleum ether/acetone 1:1) GC and GC-MS analyses showed the complete disappearance of **3a**. Moreover, ^{31}PNMR spectrum of a reaction sample showed a peak at 43.0 ppm, in accordance to the data reported in the literature for Ph_3PAuPh.[1h,8a]

At this point, benzenediazonium *o*-benzenedisulfonimide (**1a**, 161 mg, 0.5 mmol) was added. The mixture was stirred at room temperature for about 1.5 h; the completion of the reaction was confirmed by the absence of azo coupling with 2-naphthol. The above described work-up furnished **4a** (65 mg, 71% yield).

The same reaction was carried out using chloro(triphenylphosphine)gold (297 mg, 0.6 mmol). Even after 8 h, TLC, GC and GC-MS analyses showed the presence of unreacted **3a.** Anyhow, benzenediazonium *o*-benzenedisulfonimide (**1a**, 161 mg, 0.5 mmol) was added. The mixture was stirred at room temperature for about 5 h and interrupted (though azo coupling with 2-naphthol was still positive). The usual work-up furnished **4a** (32 mg, 35% yield).

4.3.3. In a oven-dried flask and under nitrogen flow, benzenediazonium o-benzenedisulfonimide (**1a**, 193 mg, 0.6 mmol) was added to a solution of [bis(trifluoromethanesulfonyl)imidate](triphenylphosphine)gold(I) (2:1) toluene adduct (942 mg, 0.6 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature for about 4 h; however, unreacted **1a** was still present as confirmed by azo coupling with 2-naphthol. At this point, 4-methoxyphenylboronic acid (**3a**, 76 mg, 0.5 mmol) and Cs_2CO_3 (325 mg, 1 mmol) were added. The mixture was stirred at room temperature for about 8 h and interrupted (though azo coupling with 2-naphthol was still positive). GC-MS analyses of the crude residue showed a complex mixture of products among which 4-methoxybiphenyl (**4a**), MS (EI): *m/z* 184 (M^+) was recognized.

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References

1. (a) Garcia P, Malacria M, Aubert C, Gandon V, Fensterbank L. *ChemCatChem* 2010; 2: 493;
   (b) Wegner HA, Auzias M. *Angew. Chem., Int. Ed.* 2011; 50:8236;
   (c) Hopkinson MN, Gee AD, Gouverneur V. *Chem. Eur. J.* 2011; 17:8248;
   (d) Livendahl M, Echavarren AM. *Chim. Oggi-Chem. Today,* 2012; 30:19;
   (e) Nieto Faza O, Silva Lopez C. *J. Org. Chem.* 2013; 78:4929;
   (f) Joost M, Amgoune A, Bourissou D. *Angew. Chem., Int. Ed.* 2015; 54:15022;
   (g) Zhang M, Zhu C, Ye LW. *Synthesis* 2017; 49:1150;
   (h).Akram MO, Shinde SS, Chintawar CC, Patil, NT. *Org. Biomol. Chem.* 2018; 16:2865.
2. (a) González-Arellano C, Corma A, Iglesias M, Sánchez F. *J. Catal.* 2006; 238:497;
   (b) Han J, Liu Y, Guo R. *J. Am. Chem. Soc.* 2009; 131:2060;
   (c) Levin MD, Toste FD. *Angew. Chem., Int. Ed.* 2014; 53:6211;
   (d) García-Calvo J, García-Calvo V, Vallejos S, García FC, Avella M, García JM, Torroba T. *Appl. Mater. Interfaces* 2016; 8: 24999;
   (e) Thomas M, Sheikh MUD, Ahirwar D, Bano M, Khan F. *J. Colloid Interface Sci.* 2017; 505:115;
   (f) Hofer M, Genoux A, Kumar R, Nevado C. *Angew. Chem., Int. Ed.* 2017; 56:1021;
   (g) Dwadnia N, Roger J, Pirio N, Cattey H, Ben Salem R, Hierso JC. *Chem. Asian J.* 2017; 12:459;
   (h) Sauer C, Liu,Y, De Nisi A, Protti S, Fagnoni M, Bandini M. *ChemCatChem* 2017; 9:4456.

3. (a) Lauterbach T, Livendahl M, Rosellon A, Espinet P, Echavarren AM. *Org. Lett.* 2010; 12:3006;

   (b) Corma A, Juarez R, Boronat M, Sanchez F, Iglesias M, Garcia, H. *Chem. Commun*. 2011 47:1446;

   (c) Li G, Jiang D, Liu C, Yu C, Jin R. *J. Catal*. 2013; 306:177:

   (d) Lin J, Abroshan H, Liu C, Zhu M, Li G, Haruta M. *J. Catal.* 2015; 330:354;

   (e) Nielsen MB. *Synthesis* 2016; 48:2732;
4. delPozo J, Carrasco D, Perez-Temprano MH, Garcia-Melchor M, Alvarez R, Casares JA, Espinet P. *Angew. Chem., Int. Ed.* 2013; 52:2189;
5. (a) Brenzovich WE, Brazeau JF, Dean Toste F. *Org. Lett.* 2010; 12:4728;

   (b) Shah D, Kaur H. *Curr. Catal.* 2015; 4:224.
6. (a) Jadhav AM, Bhunia S, Liao HY, Liu RS. *J. Am. Chem. Soc.* 2011; 133:1769;

   (b) Qian D, Zhang J. *Chem. Commun*. 2011; 47:11152;

   (c) Pawar SK, Wang CD, Bhunia S, Jadhav AM, Liu RS. *Angew. Chem., Int. Ed*. 2013; 52:7559;

   (d) Shu C, Li L, Yu YF, Jiang S, Ye LW. *Chem. Commun.* 2014; 50:2522;

   (e) Santos MD, Davies PW. *Chem. Commun*. 2014; 50:6001;

   (f) Ji K, Liu X, Du B, Yang F, Gao J. *Chem. Commun.* 2015; 51:10318;

   (g) Chen M, Chen Y, Sun N, Zhao J, Liu Y, Li, Y *Angew. Chem. Int. Ed.* 2015; 54:1200;

   (h) Leyva-Pérez A, Doménech-Carbó, A, Corma A. *Nat. Commun.,*2015; 6:6703;

   (i) Shaikh AC, Ranade DS, Rajamohanan PR, Kulkarni PP, Patil NT. *Angew. Chem., Int. Ed.* 2017; 56:757.
7. (a) Sahoo B, Hopkinson MN, Glorius F. *J. Am. Chem. Soc*. 2013; 135:5505;

   (b) Sahoo B, Hopkinson MN, Glorius F. *Chem. Eur. J.* 2016; 22:5909;

   (c) Shu XZ, Zhang M, He Y, Frei H, Toste FD. *J. Am. Chem. Soc*. 2014; 136:5844;

   (d) Kim S, Rojas-Martin J, Toste FD. *Chem. Sci.* 2016; 7:85;

   (e) Huang L, Rudolph M, Rominger F, Hashmi ASK. *Angew. Chem., Int. Ed*. 2016; 55:4808;

   (f) Huang L, Rominger F, Rudolph M, Hashmi ASK. *Chem. Commun*. 2016; 52:6435;

   (g) Alcaide B, Almendros P, Busto E, Lázaro-Milla C. *J. Org. Chem*. 2017; 82:2177.
8. (a) Cornilleau T, Hermange P, Fouquet E. *Chem. Commun.* 2016;52:10040;

   (b) Gauchot V, Lee AL. *Chem. Commun.* 2016;52:10163;

   (c) Witzel S, Xie J, Rudolph M, Hashmi ASK. *Adv. Synth. Catal.* 2017; 359:1522.
9. (a) Barbero M, Crisma M, Degani I, Fochi R, Perracino, P. *Synthesis* 1998; 1171;

   (b) Artuso E, Barbero M, Degani I, Dughera S, Fochi R. *Tetrahedron* 2006; 62:3146;

(c) Dughera S. *Synthesis,* 2006; 1117;
(d) Barbero M, Cadamuro S, Dughera S, Giaveno C. *Eur. J. Org. Chem.* 2006; 4884
(e) Barbero M, Cadamuro S, Dughera S. *Synthesis* 2008, 474;
(f) Barbero M, Cadamuro S, Dughera S, Ghigo G. *Eur. J. Org. Chem.* 2008, 862.
(g) Barbero M, Cadamuro S, Dughera S. *Eur. J. Org. Chem.* 2014, 598;
(h) Barbero M, Cadamuro S, Dughera, S. *Tetrahedron,* 2014; 70:8010.

10. Miyaura N, Suzuki A. *Chem. Rev.* 1995; 95:2457.
11. (a) Barbero M, Dughera S. *Org. Biomol. Chem.* 2018; 16:295;
    (b) Barbero M, Degani I, Dughera S, Fochi R. *J. Org. Chem.* 1999; 64:3448;
    (c) Barbero M, Cadamuro S, Dughera, S. *Org. Biomol. Chem.* 2016; 14:1437.
12. (a) Burri P, Zollinger H. *Helv. Chim. Acta* 1973; 56:2204;
    (b) Williams GH, in *Homolytic Aromatic Substitution*; Pergamon: New York, 1960; p 68.
13. Jia M, Bandini M. *ACS Catal*. 2015; 5:1638.
14. Ajdačić V, Nikolić A, Simić S, Manojlović D, Stojanović Z, Nikodinovic-Runic J, Opsenica, I M. *Synthesis* 2018; 50:119.
15. Schimler SD, Sanford MS. *Synlett* 2016; 27:2279.
16. Xu C, Yin L, Huang B, Liu H, Cai M. *Tetrahedron* 2016; 72:2065.
17. Toummini D, Ouazzani F, Taillefer M. *Org. Lett.* 2013;*15*:4690.
18. Xu H, Ekoue-Kovi K, Wolf C. *J. Org. Chem*. 2008; *73*:7638.
19. Haihua K, Xiaofeng C, Gang Z. *J. Org. Chem.* 2014; 79:7132.
20. Benkeser RA, Hickner RA, Hoke DJ. *J. Am. Chem. Soc.* 1958; 80:2279.
21. Prastaro A, Ceci P, Chiancone E, Boffi A, Cirilli R, Colone M, Fabrizi G, Stringaro A, Cacchi S. *Green Chem.*2009; 11:1929.
22. Tang J, Biafora A, Goossen LJ. *Angew. Chem., Int. Ed.* 2015; 54:13130.
23. Felpin FX, Fouquet E. *Adv. Synth. Catal.* 2008; 350:863.
24. Contreras-Celedón CA, Mendoza-Rayo D, Rincón-Medina JA, Chacón-García L. *Beilstein J. Org. Chem*. 2014; 10:2821.
25. Ortgies DH, Barthelme A, Aly S, Desharnais B, Rioux S, Forgione P. *Synthesis* 2013; 45:694.
26. Rahil R, Sengmany S, Le Gall E, Léonel E. *Synthesis* 2018; 50:146.
27. Kutonova KV, Jung N, Trusova ME, Filimonov VD, Postnikov PS, Bräse S. *Synthesis* 2017; 49:1680.
28. Liu JB, Yan H, Chen HX, Luo Y, Weng J, Lu G. *Chem. Commun*. 2013; 49:5268.
29. Isfahani AL, Mohammadpoor-Baltork I, Mirkhani V, Khosropour AR, Moghadam M, Tangestaninejad S, Kia R. *Adv. Synth. Catal.* 2013; 355:957.

30. Abe T, Mino T, Watanabe K, Yagishita F, Sakamoto M. *Eur. J. Org. Chem.* 2014; 3909.
31. He Y, Zhang XY, Cui LY, Fan XS. *Chem. Asian J.* 2013; 8:717.
32. Tan X, Zhou ZJ, Zhang, JX, Duan XH. *Eur. J. Org. Chem.* 2014; 5153.
33. Clemens AH, Hartshorn MP, Richards KE, Wright GJ. *Aust. J. Chem.*1977; 30:103.
34. Cacchi S, Caponetti E, Casadei MA, Di Giulio A, Fabrizi G, Forte G, Goggiamani A, Moreno S, Paolicelli P, Petrucci F, Prastaro A, Saladino ML. *Green Chem.* 2012; 14:317.
35. Wu Z, An Z, Chen X, Chen P. *Org. Lett*. 2013; 15:1456.
36. Wagner AM, Hickman AJ, Sanford, MS. *J. Am. Chem. Soc.* 2013; 135:15710.
37. Rao MLN, Banerjee D, Dhanorkar RJ. *Tetrahedron Lett.* 2010; 51:6101.
38. Yasamut K, Jongcharoenkamol J, Ruchirawat S, Ploypradith P. *Tetrahedron* 2016; 72:5994.
39. Al-Amin M, Akimoto M, Tameno T, Ohki Y, Takahashi N, Hoshiya N, Shuto S, Arisawa M. *Green Chem.* 2013; 15:1142.
40. Qin C, Lu, W. *J. Org. Chem.* 2008; 73:7424
41. Raduan M, Padrosa J, Pla-Quintana A, Parella T, Roglans A. *Adv. Synth. Catal.* 2011; 353:2003.
42. Huang L, Weix, DJ. *Org. Lett.* 2016; 18:5432.
43. Hauptmann W. *J. Prakt. Chem.* 1972; 314:499.
44. Fu XL, Wu LL, Fu HY, Chen H, Li, RX. *Eur. J. Org. Chem.* 2009; 2051.
45. Shrestha B, Thapa S, Gurung SK, Pike RAS, Giri R. *J. Org. Chem.* 2016; 81:787.
46. Huang Y, Yan D, Wang X, Zhou P, Wu W, Jiang H. *Chem. Commun.* 2018; 54:1742.
47. Tiwari VK, Pawar GG, Das R, Adhikary A, Kapur M. *Org. Lett.* 2013; 15:3310.