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Gold-catalyzed direct oxidative coupling reactions of non-activated arenes

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ABSTRACT

A general gold-catalyzed oxidative homo- and hetero-coupling of arenes in mild conditions is described. This reaction gives moderate to excellent yield using $PhI(OAc)_2$ as an oxidant. The effects of temperature, solvent, oxidant and concentration of substrate in this process have also been studied in detail. The product identity and distribution as well as the substrate limitation give us insights into this type of gold catalysts. Depending upon the reaction conditions, the gold catalyst behaves as a simple Lewis acid, which produces amines from arenes using DIAD as an aminating reagent.

1. Introduction

In recent decades, transition metal-catalyzed coupling reactions to construct aromatic C–C and C–X (X = N, O, S) bonds have gained great attention of the scientific community and presently reached a highly advanced status [1]. The classical way to this type of transformation is the metal-mediated coupling reactions of the "pre-activated" compounds, such as halogenated arenes [2]. The most simple and convenient method to connect the electrophilic reagents (ArX) with the nucleophilic counter part, such as organometallic derivatives (ArM), or amines, alcohols and thiols, is undoubtedly the transition metal-catalyzed cross-coupling reactions [1,3]. The major drawback of these reactions is the necessity of an activating group on both or at least one of the coupling partners, which may not be always easily available. Also this "pre-activation", such as halogenation, sulfonate formation or preparation of organometallic reagents, normally refers to an extra step towards the final product.

Biaryls as well as aromatic amines constitute important structural motifs in natural products, pharmaceuticals, agrochemicals and materials. Owing to the numerous appealing applications, many efforts have been devoted to providing direct and efficient processes for their preparation. Organometallic reagents from elegant C–H bond functionalization methods save one synthetic step [4] and direct metal, such as Pd, Rh and Ru etc., catalyzed regioselective C–H bond activation with subsequent coupling reaction has better atom efficiency [5]. However, direct aromatic C–H functionalization has not been reached its optimum level as practical synthetic utility demands less expensive, highly efficient, environmentally friendly catalytic systems. Recently, significant advances have been made in the development of arylation of arenes, such as indole, benzofuran and naphthalene, with benzenes in metal-catalyzed reactions in the presence of oxidants [6]. Light mediated Ar–H substitution [7] and Lewis acid [8] mediated oxidative coupling of arenes are also impressive. On the other hand, metal-mediated direct aromatic C–H activation followed by coupling with amines [9] or Lewis acid-catalyzed amination of electron-rich arenes with electrophilic nitrogen source to produce aromatic amines has been well documented in the literature [10]. In general, use of inert atmosphere or drastic conditions and limited substrate scope often renders the practicability of industrial usage of these types of reactions. Therefore, the improvement of aromatic C–H bond transformations under practical and mild conditions is one of the priority tasks for modern organic chemists.

In recent years, gold has emerged as one of the most discussed topic of the catalysis community [11]. Gold catalysts are known to produce extraordinary results both in the fields of heterogeneous and homogeneous catalysis. Although in the last few years, there is a significant increase in scientific publication using gold as homogeneous catalysts, especially as a "soft" Lewis acid to perform C–C [12], C–N [13], C–O [14] and C–F [15] bond formation reactions with multiple bonds, heterogeneous gold catalysts are still dominant. Gold catalysts also have been employed in redox-type reactions such as reduction [16], oxidation [17], diboration [18], homo-coupling of boronic acids [19], cross-coupling reactions

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[20] and coupling of alkyl triflates with electron-rich arenes [21]. They have been used fruitfully for multi-component and cascade reactions to generate complex structures [22]. Mechanistically, there is still a concern associated with the role of protons in reactions catalyzed by gold and other Lewis acids [23].

Gold is known to react with arenes to produce stable aryl-gold complexes. In early landmark reports, these aryl complexes used to be synthesized from Au(I)/(III) complexes with Grignard reagents or organo-mercury compounds [24]. These Au(I) aryl complexes can be further oxidized to their Au(III) derivatives [24a,24b]. C–H bond activation of arenes with Au(III) complexes to produce gold aryl complexes has also been reported in the literature, which is often stabilized by *N*-donating ligands [25]. In stoichiometric reactions, this gold complex reacts with acetylenes to produce aryl acetylenes and Au(I) species [26]. However, when this reaction was performed in catalytic amount of gold in the presence of various oxidants, only hydroarylation of alkynes was observed [27]. It should be noted that C–H bond activation and homo-coupling of the coordinating ligand itself was determined [28]. On the basis of these observations it was thought for long times that switching over between two distinct oxidation states of gold in catalytic reaction conditions will be fruitful to the chemical enterprise. Very recently, it has been demonstrated that gold with a suitable ligand system can also perform Suzuki [29] as well as Cu-free Sonogashira [20a] coupling reactions. In our long term searching for efficient C–H functionalization of arenes [30] and oxidation reaction systems [31], we thought that gold can be a good candidate to act as catalyst for biaryl synthesis from arenes with a suitable oxidant [32].

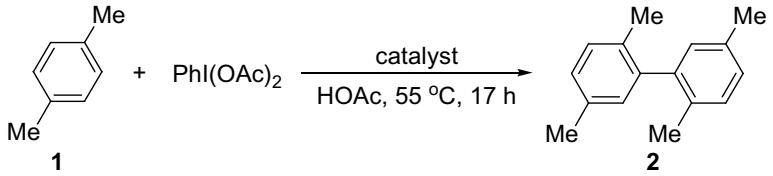
Herein we present more detailed studies of the homo- and hetero-coupling of non-activated arenes on the basis of aromatic C–H bond functionalization catalyzed by gold [33], and some initial experiments on aromatic electrophilic amination reaction. These results give us some insights on the diverse reaction mechanism.

Kozhevnikov et al. reported the oxidative homo-coupling of *p*-xylene using Pd *via* a one electron transfer mechanism [34]. We have chosen *p*-xylene as a model substrate to form 2,2′,5,5′-tetramethylbiphenyl using $PhI(OAc)_2$ as the oxidant (Table 1). Initially we started with 5 mol% of $HAuCl_4$ as catalyst with respect to the oxidant employed. This reaction went smoothly to yield the biphenyl in 65% at 55 °C (Table 1, entry 2) but remained unreactive in the absence of the catalyst (Table 1, entry 1). Control experiments without employing $PhI(OAc)_2$, using catalytic and substoichiometric amounts of $HAuCl_4$ gave no product (not shown in Table 1). As substantial amount of chlorination of *p*-xylene also observed with 5 mol% of $HAuCl_4$, reduction of the catalyst loading to 2 mol% slightly enhanced the product yield by decreasing the amount of chlorine source (Table 1, entry 3). Further experiments show that catalyst loading can be reduced down to 1 mol% with a slight decrement in yield but with accretion in TON and TOF of the reaction (Table 1, entry 4).

With 2 mol% of the catalyst loading, other gold catalysts such as $Au(OAc)_3$, $AuCl(PPh_3)$ and $Au(OAc)PPh_3$ also showed moderate activity, whereas AuCN remained completely inactive (Table 1, entries 5, 7, 8 and 6). Though Lewis acid mediated oxidative coupling of electron-rich arenes has been reported, low temperature (−78 °C), inert gas (N_2) and overstoichiometric amount of the Lewis acid ($BF_3 \cdot Et_2O$) are necessary [8]. Typical Lewis acids like $FeCl_3$ and $BF_3 \cdot OEt_2$ did not work under our catalytic reaction conditions (Table 1, entries 9 and 13). Catalysts like NH_4FeCl_4, $AgNO_3$, $CuCl_2$ also remained unreactive (Table 1, entries 10, 11 and 12). These results reveal that the reaction do not follow a simple electrophilic substitution reaction pathway through a non-stabilized cationic radical [8].

Solvent shows pivotal effects to this reaction and acetic acid appeared to be the best solvent. Acids activate the gold catalyst. Only small amounts of HOAc (56 μL) provided sufficient activity (66%) for the reaction (Table 2, entry 8). For a more practical reaction protocol for solid substrates, 1–2 mL of HOAc proved to be convenient. When strong acid (TFA) was used as the solvent, the reaction furnished rapidly but produced inferior results, possibly due to the formation of polymers (Table 2, entries 6). Catalytic amounts of TFA (5 mol%) with $HAuCl_4$ (2 mol%) showed moderate activity (Table 2, entry 9). On the other hand, when catalytic amounts of TFA

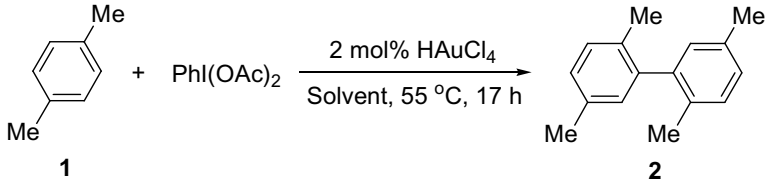
Table 1
Catalyst screening of oxidative homo-coupling of *p*-xylene.[a]



Entry	Catalyst	Yield (%)[b]	TON[c]	TOF (h^{-1})[d]
1	Nil	0	0	0
2[e]	$HAuCl_4$	65	13	0.8
3	$HAuCl_4$	**74**	37	2.2
4[f]	$HAuCl_4$	57	57	3.4
5	$Au(OAc)_3$	39	20	1.1
6	AuCN	0	0	0
7	$AuCl(PPh_3)$	**76**	38	2.2
8	$Au(OAc)PPh_3$	**75**	38	2.2
9	$FeCl_3$	0	0	0
10	NH_4FeCl_4	0	0	0
11	$AgNO_3$	0	0	0
12	$CuCl_2$	0	0	0
13	$BF_3 \cdot OEt_2$	0	0	0

[a] *Reaction conditions*: $PhI(OAc)_2$ (1.0 mmol), *p*-xylene (10.0 mmol), dodecane (55 μL, internal standard) and catalyst (0.02 mmol, 2.0 mol%) were heated in HOAc (1.0 mL) at 55 °C in air for 17 h.
[b] Calibrated GC yields were reported; % yield = (no. of moles of biaryl)/(no. of moles of oxidant) × 100%.
[c] Turnover number (TON) = (no. of moles of biaryl produced)/(no. of moles of catalyst).
[d] Turnover frequency (TOF) = (no. of moles of biaryl produced)/[(no. of moles of catalyst) × (reaction time in hour)].
[e] 5 mol% of catalyst used.
[f] 1 mol% of catalyst used.

Table 2
Solvent screening for oxidative homo-coupling of *p*-xylene.[a]



Entry	Solvent	Yield (%)[b]	TON[c]	TOF (h^{-1})[d]
1	*p*-Xylene	58	29	1.7
2	CH_3CN	0	0	0
3	CH_3NO_2	12	6	0.4
4	$ClCH_2CH_2Cl$	42	21	1.2
5	MeOH	3	2	0.1
6	TFA	<1	<1	<0.1
7	HOAc	**74**	37	2.2
8[e]	HOAc	66	33	2.0
9[f]	TFA	63	32	2.0
10	Ac_2O	71	36	2.1

[a] *Reaction conditions*: $PhI(OAc)_2$ (1.0 mmol), *p*-xylene (10.0 mmol), dodecane (55 μL, internal standard) and $HAuCl_4$ (3.2 mg, 0.02 mmol, 2.0 mol%) were heated in an appropriate solvent (2.0 mL) at 55 °C in air for 17 h.
[b] Calibrated GC yields were reported; % Yield = (no. of moles of biaryl)/(no. of moles of oxidant) × 100%.
[c] Turnover number (TON) = (no. of moles of biaryl produced)/(no. of moles of catalyst).
[d] Turnover frequency (TOF) = (no. of moles of biaryl produced)/[(no. of moles of catalyst) × (reaction time in hour)].
[e] 56 μL of HOAc used.
[f] 5 mol% TFA was used.

(5 mol%) was merely used without employing $HAuCl_4$, it did not give the desired product (no polymerization was observed in GC). Both acetic acid anhydride and HOAc produced the desired biaryl in comparable yields, when they were used as the solvent (Table 2, entry 7 and 10). These results imply that water in the reaction mixture does not affect our system very much. The reaction can also be carried out in the presence of non-coordinative solvents like 1,2-dichloroethane and the substrate, *p*-xylene itself but with comparatively lower yield (Table 2, entries 1 and 4). As HOAc was generated during the reaction, the reaction may activate itself. With strongly coordinative solvents like CH_3CN and $MeNO_2$ (Table 2, entries 2 and 3), either there was no reaction or the yield was very poor, suggesting that the reduced Lewis acidity may be the reason for this.

Amongst the oxidant used, $PhI(OAc)_2$ was found to be the best oxidant of this reaction (Table 3, entries 1). $PhI(OCOCF_3)_2$, a suitable reagent for Lewis acid mediated biaryl formation reactions, gave slightly lower productivity in our model reaction (Table 3, entry 2). Hypervalent iodine seems participating in the reaction as well. Indeed only very low yield of product was detected, PhI with peracetic acid, a formal *in situ* generation method for $PhI(OAc)_2$, gave 3% of the biphenyl while peracetic acid alone did not produce any coupling product. Other conventional oxidants such as $K_2S_2O_8$, Oxone® and $Cu(OAc)_2$ did not work at all (Table 3, entries 2–6).

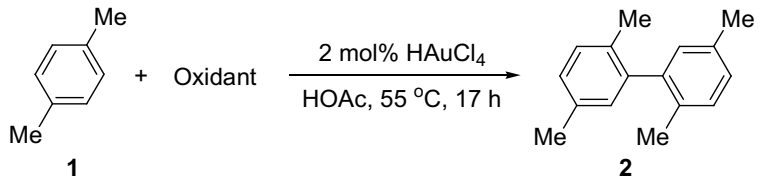
To improve the effectiveness of the gold catalytic system, the concentration effect was examined using the preliminary optimized reaction conditions (Table 4). The reaction is dependent on the concentration of substrate, mainly because of the formation of undesired oligomers observed by GC–MS (Table 4, entries 1, 4–6). When the concentration of the substrate such as *p*-xylene and benzene was increased to 20-fold compared to the oxidant, the yield of the corresponding homo-coupled product was also increased substantially especially in the latter case (Table 4, entries 6 and 9). While temperature effect is insignificant to electron-rich *p*-xylene (Table 4, entries 1–3), it is beneficial to non-activated benzene (Table 4, entries 7 and 8). With these reaction conditions, various non-activated arenes were coupled to test the effectiveness of the gold catalytic system.

While electron-rich substrates work well at 55 °C, neutral or electron deficient substrates need slightly higher temperature (95 °C). In general, the reaction works smoothly in good to excellent yield. Even though slightly higher concentration (10 equivalents to the oxidant) of arene is used to get optimized yield, the excess starting material can be recovered and reused. For example, 7.5 equivalents of 4-bromo-2-methylanisole with respect to $PhI(OAc)_2$ were recovered after the reaction (Table 5, entry 10). The regioselectivity of the reaction follows typical electrophilic aromatic substitution pattern. A range of arenes worked comparably well under our reaction conditions to give the corresponding biaryls in moderate to good yields (Table 5). Even difficult substrates such as 4-nitroanisole, which was reported to be unreactive in Lewis acid mediated oxidative coupling [35], produced the corresponding biaryl in moderate yield (Table 5, entry 12). Highly electron deficient substrates like 1,3-dicholorobenzene also reacted at elevated temperature (Table 5, entry 16).

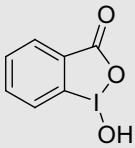
A wide range of functional groups has been tolerated by the present reaction protocol. All halogens survived and kept intact during the course of the reaction. To the best of our knowledge, neither palladium- nor Lewis acid-catalyzed reactions can maintain the reactivity tolerating all halogens (Table 5, entries 5–11). Some C–H functionalization reactions exhibit such high halogen group preservation [4a]. Methoxide and ester groups also survived and worked equally well in our reaction conditions (Table 5, entries 13 and 14). The electron-rich heterocycle, thiophene also coupled to the corresponding product in single regioisomeric form in moderate yield (Table 5, entry 15). One of the drawbacks for this protocol is the compatibility with strong coordinating groups. Substrates containing functionalization such as *N*,*N*-dimethylbenzyl amine, 2-phenyl pyridine, *N*-acetyl aniline, aliphatic aromatic ketones did not give any desired product. Although auration of 2-phenyl pyridine is reported in the literature [24c], it did not give any desired product. Electron-rich mesitylene did not produce the desired homo-coupled product possibly due to the increased steric bulk in the substrate.

Nevertheless, the present protocol is very easy to handle. It can be managed in ambient conditions and is not necessary to protect

Table 3
Oxidant screening of oxidative homo-coupling of *p*-xylene.[a]

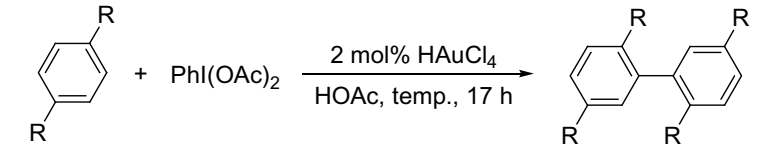


1 2

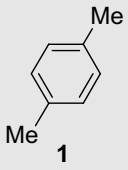
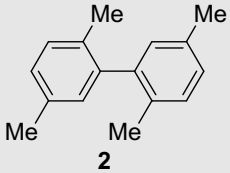
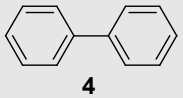
Entry	Oxidant	Yield (%)[b]	TON[c]	TOF (h^{-1})[d]
1	$PhI(OAc)_2$	**74**	37	2.2
2	$PhI(OCOCF_3)_2$	69	35	2.1
3		0	0	0
4	45% IBX	<1	<1	<0.1
5	Dess-Martin	1	<1	<0.1
6	35% CH_3CO_3H	0	0	0
7	PhI + 35% CH_3CO_3H	3	2	<0.1
8	DMSO	0	0	0
9	$K_2S_2O_8$	0	0	0
10	Oxone®	0	0	0
11	$Cu(OAc)_2$	0	0	0

[a] *Reaction conditions*: oxidant (1.0 mmol), *p*-xylene (10.0 mmol), dodecane (55 μL, internal standard) and $HAuCl_4$ (3.2 mg, 0.02 mmol, 2.0 mol%) were heated in HOAc (1.0 mL) at 55 °C in air for 17 h.
[b] Calibrated GC yields were reported; % yield = (no. of moles of biaryl)/(no. of moles of oxidant) × 100%.
[c] Turnover number (TON) = (no. of moles of biaryl produced)/(no. of moles of catalyst).
[d] Turnover frequency (TOF) = (no. of moles of biaryl produced)/[(no. of moles of catalyst) × (reaction time in hour)].

Table 4
Concentration effects on Au-catalyzed oxidative homo-coupling of arenes.[a]



R = H, Me

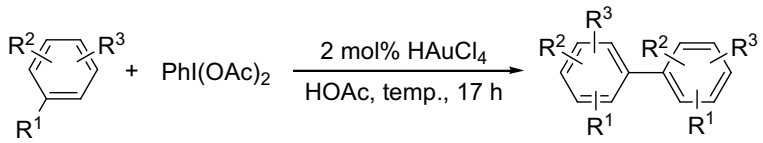
Entry	ArH	ArH:$PhI(OAc)_2$:HOAc[b]	Major product	Temperature (°C)	Yield (%)[c]
1	 **1**	10:1:17	 **2**	55	74
2	**1**	10:1:17	**2**	75	74
3	**1**	10:1:17	**2**	95	70
4	**1**	10:1:3	**2**	55	31
5	**1**	10:1:9	**2**	55	52
6	**1**	20:1:17	**2**	55	81
7	 **3**	10:1:17	 **4**	55	34
8	**3**	10:1:17	**4**	95	54
9	**3**	20:1:17	**4**	95	71

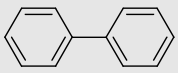
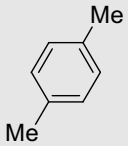
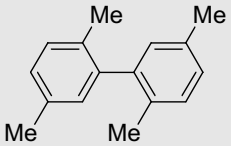
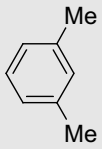
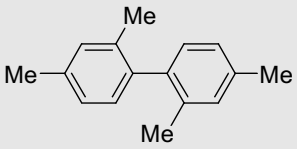
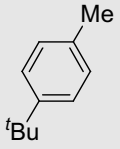
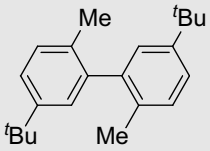
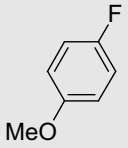
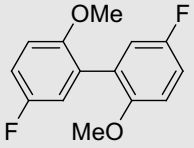
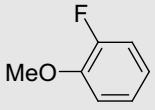
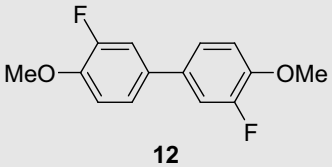
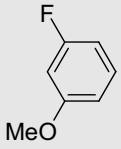
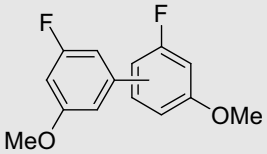
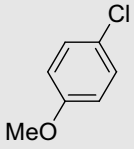
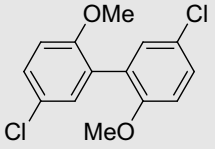
[a] *Reaction conditions*: oxidant (1.0 mmol), *p*-xylene, dodecane (55 μL, internal standard) and $HAuCl_4$ (0.02 mmol, 2.0 mol%) were heated in the appropriate solvent (1.0 mL) and temperature in air for 17 h.
[b] Molar ratio.
[c] GC yields.

the mixture under inert atmosphere or pre-treat of the solvent or substrate.

Exploration of oxidative hetero-coupling of arenes using our protocols showed interesting concentration effects. With equal

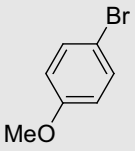
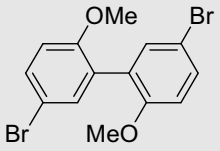
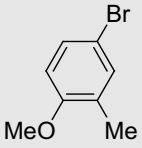
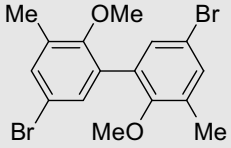
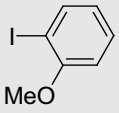
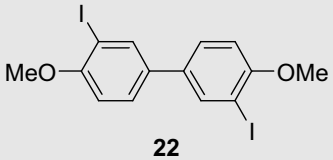
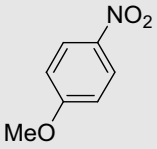
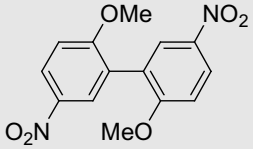
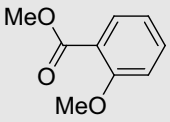
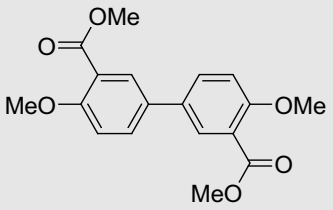
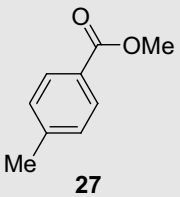
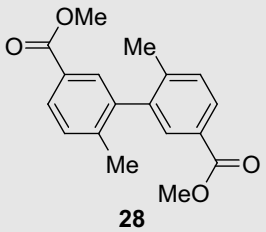
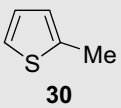
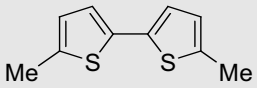
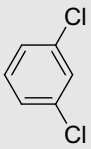
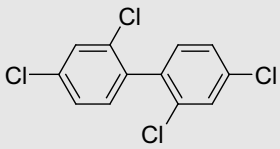
Table 5
Au-catalyzed oxidative homo-coupling of arenes.[a]



Entry	ArH	Major product	Temperature (°C)	Yield (%)[b]
1[c]	 **3**	 **4**	95	71[d]
2[c]	 **1**	 **2**	55	81[d]
3	 **5**	 **6**	55	75[e]
4	 **7**	 **8**	95	62
5	 **9**	 **10**	95	68[d]
6	 **11**	 **12**	55	63[f]
7	 **13**	 **14**	95	63[g]
8	 **15**	 **16**	95	68

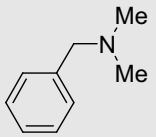
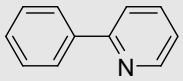
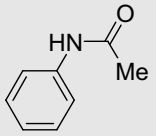
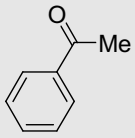
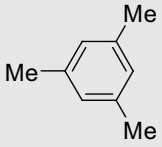
(*continued on next page*)

Table 5 (*continued*)

Entry	ArH	Major product	Temperature (°C)	Yield (%)[b]
9	 **17**	 **18**	95	56
10	 **19**	 **20**	95	56[h]
11	 **21**	 **22**	95	79[i]
12	 **23**	 **24**	95	38
13	 **25**	 **26**	95	86[j]
14	 **27**	 **28**	95	78
15	 **30**	 **31**	95	31
16	 **32**	 **33**	95	15[k]

(*continued on next page*)

Table 5 (*continued*)

Entry	ArH	Major product	Temperature (°C)	Yield (%)[b]
17	 **34**	–	95	0
18	 **35**	–	95	0
19	 **36**	–	95	0
20	 **37**	–	95	0
21	 **38**	–	95	0

[a] *Reaction conditions*: oxidant (1.0 mmol), arene (10.0 mmol), dodecane (55 μL, internal standard) and $HAuCl_4$ (0.02 mmol, 2.0 mol%) were heated in HOAc (1.0 mL) at appropriate temperature in air for 17 h.
[b] Isolated yields based on the oxidant used.
[c] GC yields.
[d] 20.0 mmol of arene was used.
[e] An isomer mixture was isolated; product ratio = 89:11 on GC-FID.
[f] 54% of *para–para* coupled product and 9% of *para–ortho* coupled product were isolated.
[g] An isomer mixture was isolated; product ratio = 24:49:27 on GC-FID.
[h] An isomer mixture was isolated; product ratio = 88:12 (^{1}H NMR).
[i] 69% of *para–para* coupled product and 10% of *para–ortho* coupled product were isolated.
[j] 74% of *para–para* coupled product was isolated and 12% of *para–ortho* coupled product were observed.
[k] An isomer mixture was isolated; product ratio = 94:6 on GC-FID.

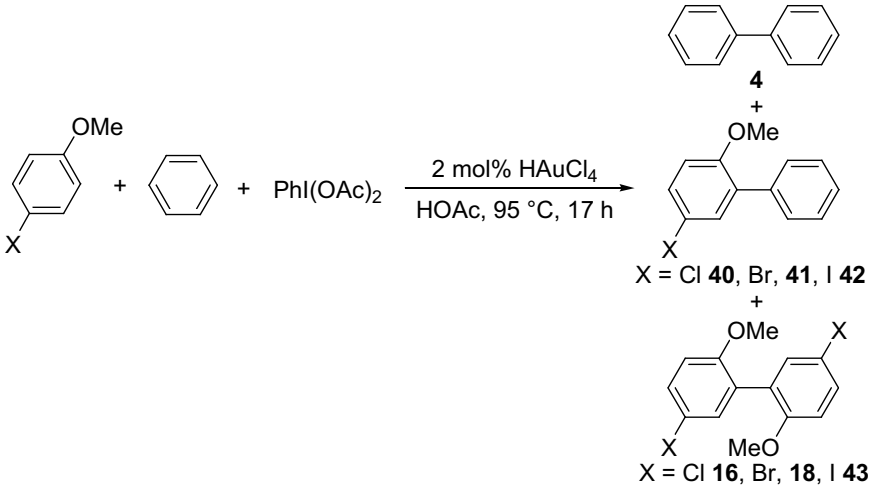
amounts of *para*-haloanisole and benzene, nearly equal amount of the homo-coupling product of biphenyl and the hetero-coupling product of phenylanisole was observed, whereas the yield of bisanisole was only in a few percent (Table 6, entries 3, 9, 15). Clearly it can be imagined that the activation of benzene occurs in the initial step and the reactive intermediate is then trapped by another arene. Hence the biphenyl to phenylanisole ratio is close to the concentration ratio of benzene and anisole. Increasing the amount of benzene from 1 to 10 equivalents to $PhI(OAc)_2$ caused increment of biphenyl, as expected (Table 6, entries 1–4).

Higher concentration of arenes resulted in a better total yield. The best result was obtained when a ratio of 15:6:1 of *para*-bromoanisole:benzene:$PhI(OAc)_2$ was performed, in which a total yield of 95% was attained with 55% of cross-coupling product (Table 6, entry 12). On the other hand, in the case of *para*-iodoanisole, *ortho*-acetoxylated product with respect to the methoxy goup, which was the major product in homocouplig reaction conditions, was not observed (according to GS–MS spectra of the crude reaction mixtures). The formation of such acetoxylated product with hypervalent iodine salt and a Lewis acid was already reported in the literature [36], which supports our observation during the homo-coupling experiments with *para*-iodoanisole. But surprisingly, the same substrate in hetero-coupling conditions produced different amount of homo- and hetero-coupling product of *para*-iodoanisole together with the formation of biphenyl (**4**) but not the acetoxylated product.

Gold catalysts can be extended to C–N bond formation [37]. The same type of C–N bond formation reaction of electron-rich arenes was reported in the literature promoted mainly with stoichiometric amount of Lewis acids [10]. In a model reaction C–N bond formation of *p*-xylene catalyzed by gold catalysts using diisopropylazodicarboxylate (DIAD) as a nitrogen source was performed (Table 7). To our delight, 5% $HAuCl_4$ catalyzed the reaction to yield the major product in 31% at 55 °C using $MeNO_2$ as solvent (Table 7, entry 1).

But in sharp contrast to the C–C bond formation reaction, C–N bond formation did not proceed when $Au(OAc)_3$, $AuCl(PPh_3)$ or AuCN were used as catalyst, whereas $AuCl_3$ showed comparable

Table 6
Au-catalyzed oxidative hetero-coupling of arenes.[a]



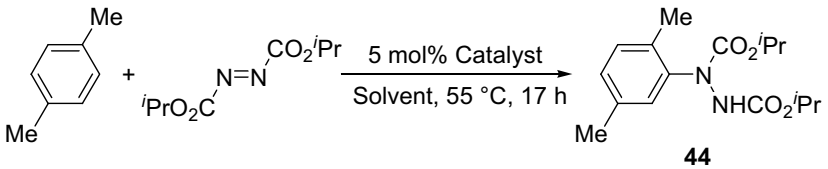
Entry	X	Halo-anisole:benzene[b]	Hetero-coupled product (**40**, **41** or **42**) (%)[c]	Homo-coupled product (**16**, **18** or **43**) (%)[c]	Biphenyl (**4**) (%)[c]	Hetero:homo:**4** (%)[d]
1	Cl	5:1	23	17	4	49:40:11
2	Cl	5:2	32	7	18	52:12:36
3	Cl	5:5	30	3	32	41:5:53
4	Cl	5:10	23	0	41	32:0:68
5	Cl	10:4	43	10	19	56:15:29
6	Cl	15:6	46	11	22	54:15:31
7	Br	5:1	27	15	9	45:37:18
8	Br	5:2	42	7	27	48:13:39
9	Br	5:5	37	3	43	38:4:58
10	Br	5:10	29	1	60	27:2:71
11	Br	10:4	50	8	30	50:13:37
12	Br	15:6	55	11	30	51:14:35
13	I	5:1	15	nd[e]	3	48:40:12
14	I	5:2	26	nd	16	51:16:33
15	I	5:5	25	nd	29	41:7:52
16	I	5:10	20	nd	54	25:2:73
17	I	10:4	36	nd	17	53:21:26
18	I	15:6	41	nd	15	48:13:39

[a] *Reaction conditions*: oxidant (1.0 mmol), appropriate amounts of arenes, dodecane (55 μL, internal standard) and $HAuCl_4$ (0.02 mmol, 2.0 mol%) were heated in HOAc (1.0 mL) at 95 °C in air for 17 h.
[b] No. of moles of anisole: no. of moles of benzene.
[c] Calibrated GC yields based on the oxidant used.
[d] GC peak area ratio of corresponding products.
[e] Not determined.

reactivity (Table 1, entries 2, 3, 4 and 5). Further solvent screening revealed that, $MeNO_2$ is the solvent of choice, whereas polar protic solvent like AcOH and MeOH, coordinative CH_3CN, and non-polar aprotic 1,2-dichloroethane gave inferior results (Table 1, entries 6–10). However, using 5 mol% of $BF_3 \cdot Et_2O$ instead of $HAuCl_4$, a similar yield was given (Table 1, entry 11), which suggests the present aromatic C–N bond formation passes through a Lewis acid-catalyzed reaction mechanism. This type of gold-catalyzed electrophilic aromatic C–H functionalization is mechanistically entirely different from the aforementioned oxidative homo-coupling of arenes.

Some mechanistic insights can be drawn from this diverse reactivity of gold catalysts. It should be noted that both $AuCl(PPh_3)$, $Au(OAc)PPh_3$ and $HAuCl_3$ worked with same efficiency under our oxidative conditions and this strongly supports the fact that Au itself but not Lewis acid is the exact C–H functionalization catalyst [14j,38]. Lewis acid mediated oxidative coupling reactions of electron-rich arenes using hypervalent iodine salts could perform at as low temperature as −78 °C and a cationic radical species has been proposed as the reaction intermediate [8b]. In the aromatic C–N bond formation process both $BF_3 \cdot OEt_2$ and $HAuCl_4$ worked equally well, establishing that it is likely a Lewis acid-catalyzed process, while no biaryl was observed with 2 mol% $BF_3 \cdot OEt_2$ in the present oxidative homo-coupling system. Moreover, nitro-substituted anisole did not work in the Lewis acid systems, while it worked moderately in our case. Hence, direct participation of cationic radicals is not very likely. But the regioselectivity in the present homo-coupling reaction protocol strictly follows typical electrophilic aromatic substitution pattern. During the screening process of homo-coupling of *p*-xylene, a trace amount of an unidentified compound with a molecular mass of 212, which corresponds to the not oxidized intermediate to bixylyl was observed. Participation of gold stabilized cationic radical species or electrophilic metalation like conventional Pd(II) or Pt(II) cannot be entirely ruled out. It has been recently reported that oxidative addition of aryliodides is possible with gold(I) complexes. But under our conditions, the substrate with the weakest carbon halogen bond (C–I) coupled smoothly with intact preservation of iodo-group in the product (Table 5, entry 11), which implies that high-valent gold is the major catalyst [14j,20,38]. Knowing the distinct difference of reactiv-

Table 7
Catalyst and solvent screening for electrophilic amination of *p*-xylene.[a]



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Entry	Catalyst	Solvent	Yield of major isomer (%)[b]	Major:minor (%)[c]
1	$HAuCl_4$	CH_3NO_2	31	85:15
2	$AuPPh_3Cl$	CH_3NO_2	0	0:0
3	$AuCl_3$	CH_3NO_2	30	85:15
4	$Au(OAc)_3$	CH_3NO_2	0	0:0
5	AuCN	CH_3NO_2	0	0:0
6	$HAuCl_4$	CH_3CN	14	80:20
7	$HAuCl_4$	*p*-Xylene	11	83:17
8	$HAuCl_4$	$ClCH_2CH_2Cl$	14	84:16
9	$HAuCl_4$	AcOH	22	84:16
10	$HAuCl_4$	MeOH	0	0:0
11	$BF_3.OEt_2$	CH_3NO_2	31	85:15

[a] *Reaction conditions*: DIAD (1.0 mmol), *p*-xylene (10.0 mmol), dodecane (55 μL, internal standard) and catalyst (0.05 mmol, 5.0 mol%) were heated in the appropriate solvent (1.0 mL) at 55 °C in air for 17 h.
[b] Calibrated GC yields.
[c] GC peak area ratio of corresponding products.

ity between the C–C bond formation and C–N bond formation process, it strongly suggests that rather than a simple aromatic electrophilic substitution, it follows a complicated pathway.

In summary, a new general gold-catalyzed oxidative coupling of arenes was reported. Hetero-coupling was shown for the first time possible. This reaction can be simply handled in air and no pre-treatment of substrate and solvent is necessary. Interestingly our reaction protocol activated by a suitable acidic solvent and does not require any Ag salt to enhance the reactivity.[39] Remarkable functional groups tolerance has been shown in our reaction conditions. The reaction proceeds via a double CH-functionalization, which is in principle the most efficient process for the synthesis of biaryls. From the reaction pattern showed by electrophilic C-N bond formation of *p*-xylene, the mechanism of gold-catalyzed CH-functionalization is still unclear and an interesting area. Studies of the reaction mechanism are undoubtedly a currently fruitful area for the next generation of gold catalysis.

2. Experimental

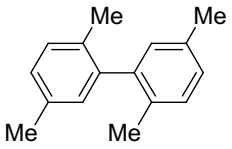
2.1. General

NMR spectra were recorded on a Bruker ARX 300 spectrometer, operating at 300 MHz for ^{1}H NMR, 75 MHz for ^{13}C NMR were reported downfield from $CDCl_3$ (δ: 7.27 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.0 ppm) used as an internal reference. Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector. Column chromatography was performed with silica gel Fluka 60 (70-230 mesh ASTM).

2.2. General procedure for $HAuCl_4$ catalyzed homo-coupling of arenes

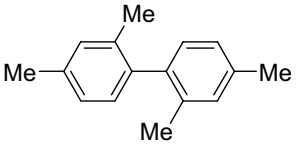
To a 10 mL vial arene (10 mmol), $PhI(OAc)_2$ (1 mmol), $HAuCl_4$ (0.02 mmol) and acetic acid (1 mL) were added. The mixture was stirred for 17 h at 55 °C and then quenched with water (10 mL). The reaction mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layer was washed with saturated $NaHCO_3$ (2 × 20 mL), brine (10 ml), dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography to afford the desired product.

2.2.1. 2,5,2′,5′-Tetramethylbiphenyl (**2**) [40]



R_f = 0.63 (hexane); white solid; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 2.04 (s, 6H), 2.35 (s, 6H), 6.90-7.00 (m, 2H), 7.05-7.2 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.30, 20.93, 127.70, 129.59, 129.94, 132.59, 134.82, 141.58; ATR-IR (cm^{-1}): 3017m, 2917m, 2859s, 1610m, 1501s, 1446w, 1376s, 1145s, 1037w, 890s, 882s, 812s, 754s, 7646s, 475m; MS (EI): *m/z* (rel. int.) 211 (11), 210 (66), 196 (15), 195 (100), 180 (33), 179 (23), 178 (21), 165 (31); HRMS calcd. for $C_{16}H_{18}$ *m/z* 210.1403, found *m/z* 210.1399.

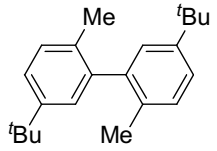
2.2.2. 2,4,2′,4′-Tetramethylbiphenyl (**6**) [41]



R_f = 0.60 (hexane); colorless oil; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 2.05 (s, 6H), 2.39 (s, 6H), 6.90-7.20 (m, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.79, 21.11, 126.19, 129.43, 130.52, 135.80, 136.51, 138.63; ATR-IR (cm^{-1}): 3013w, 2919w, 2858w, 1612s, 1487s, 1443w, 1377s, 1233s, 1035w, 1007s, 874s, 815s,

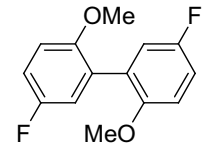
768s, 724s; MS (EI): *m/z* (rel. int.) 211 (15), 210 (90), 209 (7), 195 (100), 180 (39), 179 (27), 178 (22), 165 (35), 89 (11); HRMS calcd. for $C_{16}H_{18}$ *m/z* 210.1403, found *m/z* 210.1402.

*2.2.3. 5,5′-Di-tert-butyl-2,2′-dimethylbiphenyl (**8**) [42]*



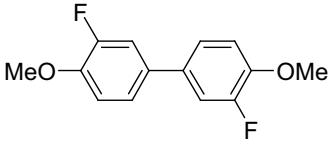
R_f = 0.64 (hexane); colorless oil; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 1.34 (s, 18H), 2.05 (s, 3H), 7.18–7.25 (m, 4H), 7.28–7.33 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.37, 31.45, 34.41, 123.83, 126.64, 129.44, 132.78, 141.50, 148.30; ATR-IR (cm^{-1}): 2960w, 2867s, 1607s, 1491s, 1463m, 1391w, 1260m, 1202s, 1151m, 1113s, 894s, 847s, 818s, 738m, 682m; MS (EI): *m/z* (rel. int.) 295 (5), 294 (22), 280 (23), 279 (100), 57 (11); HRMS calcd. for $C_{22}H_{30}$ *m/z* 294.2342, found *m/z* 294.2343.

*2.2.4. 5,5′-Difluoro-2,2′-dimethoxybiphenyl (**10**) [43]*



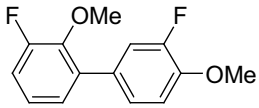
R_f = 0.14 (hexane:ethyl acetate = 100:3); white solid; m.p. = 123–124 °C (hexane); ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.73 (s, 6H), 6.88 (dd, *J* = 8.9, 4.6 Hz, 2H), 6.96 (dd, *J* = 8.9, 2.8 Hz, 2H), 7.00 (ddd, *J* = 8.8, 8.0, 3.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 56.29, 112.08 (d, $^3J_{CF}$ = 8.4 Hz), 114.81 (d, $^2J_{CF}$ = 22.6 Hz), 118.11 (d, $^2J_{CF}$ = 23.2 Hz), 127.77 (dd, J_{CF} = 8.0, 1.6 Hz), 153.034 (d, $^4J_{CF}$ = 1.9 Hz), 156.64 (d, $^1J_{CF}$ = 238.2 Hz); ATR-IR (cm^{-1}): 3126w, 3072w, 3020w, 2958w, 2940w, 2910w, 2837w, 1869w, 1592w, 1506m, 1486s, 1464m, 1441m, 1425m, 1406w, 1293m, 1271m, 1256m, 1245s, 1219m, 1180s, 1158s, 1136m, 1035s, 1023s, 947m, 937w, 868s, 844m, 818s, 749s, 722s, 696m; MS (EI): *m/z* (rel. int.) 251 (14), 250 (100), 235 (24), 220 (40), 204 (32), 164 (10); HRMS calcd. for $C_{14}H_{12}F_2O_2$ *m/z* 250.0800, found *m/z* 250.0798. Elemental Anal. Calc. for $C_{14}H_{12}F_2O_2$: C, 67.20; H, 4.83. Found: C, 67.02; H, 4.68%.

*2.2.5. 3,3′-difluoro-4,4′-dimethoxybiphenyl [major isomer] (**12**) [44]*



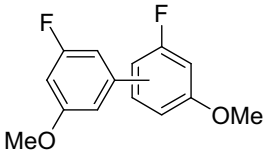
R_f = 0.11 (hexane); white solid; m.p. = 155–156 °C (hexane); ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.85 (s, 6H), 6.90–6.95 (m, 2H), 7.13–7.21 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 56.33, 113.67 (d, $^4J_{CF}$ = 2.6 Hz), 114.37 (d, $^2J_{CF}$ = 19.3 Hz), 122.17 (d, $^3J_{CF}$ = 3.3 Hz), 132.94 (dd, J_{CF} = 6.5, 2.0 Hz), 146.94 (d, $^2J_{CF}$ = 10.3 Hz), 152.54 (d, $^1J_{CF}$ = 245.9 Hz); ATR-IR (cm^{-1}): 3051w, 3030w, 2977w, 2950w, 2922w, 2845w, 2582w, 2031w, 1618m, 1575m, 1499s, 1463s, 1440s, 1404m, 1303s, 1260s, 1209s, 1179s, 1133s, 1043s, 1013s, 863s, 839s, 800s, 760s; MS (EI): *m/z* (rel. int.) 251 (13), 250 (73), 236 (15), 235 (100), 207 (14), 192 (17), 164 (17); HRMS calcd. for $C_{14}H_{12}F_2O_2$ *m/z* 250.0800, found *m/z* 250.0800. Elemental Anal. Calc. for $C_{14}H_{12}F_2O_2$: C, 67.20; H, 4.83. Found: C, 67.64; H, 4.67%.

2.2.6. 3,3′-Difluoro-2,4′-dimethoxybiphenyl (minor isomer)



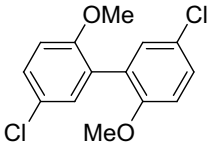
R_f = 0.21 (hexane); colorless oil; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.72 (d, $^5J_{HF}$ = 1.5 Hz, 3H), 3.92 (s, 3H), 6.97–67.10 (m, 4H), 7.24 (ddd, *J* = 8.4, 2.1, 1.1 Hz, 1H), 7.30 (dd, *J* = 12.5, 2.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 56.22, 61.17 (d, $^4J_{CF}$ = 4.4 Hz), 113.01 (d, $^4J_{CF}$ = 1.9 Hz), 115.86 (d, $^2J_{CF}$ = 19.4 Hz), 116.99 (d, $^2J_{CF}$ = 19.4 Hz), 123.76 (d, $^3J_{CF}$ = 8.4 Hz), 124.96 (d, $^3J_{CF}$ = 3.7 Hz), 125.48 (d, $^4J_{CF}$ = 2.6 Hz), 130.22 (dd, J_{CF} = 6.8, 3.0 Hz), 135.11 (unresolved dd), 145.04 (d, $^2J_{CF}$ = 10.8 Hz), 147.06 (d, $^2J_{CF}$ = 10.8 Hz), 151.93 (d, $^1J_{CF}$ = 245.2 Hz), 156.07 (d, $^1J_{CF}$ = 246.3 Hz); MS (EI): *m/z* (rel. int.) 251 (17), 250 (100), 235 (33), 220 (34), 204 (39), 175 (12), 164 (24); HRMS calcd. for $C_{14}H_{12}F_2O_2$ *m/z* 250.0800, found *m/z* 250.7976.

*2.2.7. Mixtures of homo-coupled isomers of 3-fluoroanisole (**14**)*



R_f = 0.17 (hexane); colorless oil of isomer mixture; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.68 (s, 6H, 1st isomer, 21%), 3.71 (s, 3H, 2nd isomer, 49%), 3.75 (s, 3H, 2nd isomer, 49%), 3.76 (s, 6H, 3rd isomer, 30%), 6.59–6.71 (m), 7.05–7.23 (m); GC–MS (40 °C, 2 min.; 15 °C $min.^{-1}$; 280 °C, 12 min.) [*m/z* (rel. int.)] t_r = 12.59 min. [251 (15), 250 (100), 235 (15), 220 (41), 204 (39), 175 (11), 164 (12)], 13.27 min. [251 (15), 250 (100), 235 (29), 220 (17), 207 (11), 204 (23), 175 (10), 164 (16)], 13.93 min. [251 (15), 250 (100), 236 (10), 235 (69), 207 (29), 192 (12), 164 (15)].

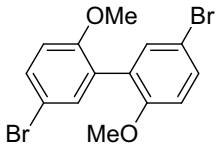
*2.2.8. 5,5′-Dichloro-2,2′-dimethoxybiphenyl (**16**) [43,45]*



R_f = 0.29 (ethyl acetate:hexane = 1:19); white solid; m.p. = 109–110 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.77 (s, 6H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 2.8 Hz, 2H), 7.30 (dd, *J* = 8.6, 2.8 Hz, 2H); *m/z* (rel. int.) = 286 (11), 285 (9), 284 (6), 283 (15), 282 (100), 232 (49), 217 (19), 189 (11); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.97, 112.23, 125.18, 127.94, 128.62, 131.01, 155.56; ATR-IR (cm^{-1}): 3004m, 2934m, 2835s, 1766w, 1729w, 1590, 1499w,

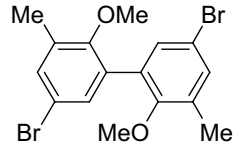
1487w, 1469m, 1443m, 1288w, 1271m, 1242b, 1230m, 1181s, 1147s, 1134s, 1096s, 1021s, 889s, 878, 865s, 810, 753s, 727m, 654s; HRMS calcd. for $C_{14}H_{12}Cl_2O_2$ *m/z* 282.0209, found *m/z* 282.0214.

*2.2.9. 5,5′-Dibromo-2,2′-dimethoxybiphenyl (**18**) [43,46]*



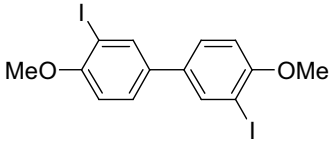
R_f = 0.28 (ethyl acetate:hexane = 1:19); white solid; m.p. = 105–107 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.78 (s, 6H), 6.85 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 2.6 Hz, 2H), 7.44 (dd, *J* = 8.8, 2.6 Hz, 2H); *m/z* (rel. int.) = 374 (49), 373 (16), 372 (100), 371 (9), 370 (51), 278 (41), 276 (41), 263 (25), 261 (27), 235 (16), 233 (15), 139 (20), 138 (12), 126 (27), 63 (12); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.91, 112.48, 112.71, 128.35, 131.62, 133.77, 156.09; ATR-IR (cm^{-1}): 3077s, 3017m, 2936w, 2835w, 1599w, 1584w, 1496w, 1479w, 1458m, 1435s, 1410w, 1377s, 1289s, 1257w, 1242w, 1221w, 1180w, 1148s, 1138s, 1082s, 1029w, 1018w, 883s, 868w, 842w, 815w, 806w, 742s, 724w, 670w; HRMS calcd. for $C_{14}H_{12}Br_2O_2$ *m/z* 369.9199, found *m/z* 369.9196.

*2.2.10. 5,5′-dibromo-2,2′-dimethoxy-3,3′-dimethylbiphenyl (major isomer) (**20**) [47]*



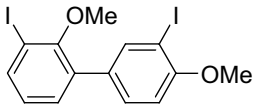
R_f = 0.13 (hexane); ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 2.30 (s, 6H), 3.40 (s, 6H), 7.25 (dd, *J* = 2.4, 0.6 Hz, 2H), 7.32 (dd, *J* = 2.6, 0.7 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.19, 60.34, 116.00, 131.31, 132.75, 133.55, 133.69, 155.32; MS (EI): *m/z* (rel. int.) 402 (50), 401 (17), 400 (100), 398 (52), 306 (35), 304 (35), 291 (20), 290 (11), 289 (24), 225 (12), 210 (14), 181 (11), 165 (11), 153 (11), 152 (14).

*2.2.11. 3,3′-Diiodo-4,4′-dimethoxybiphenyl [major isomer] (**22**) [43,48]*



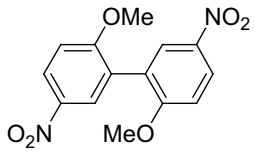
R_f = 0.20 (ethyl acetate:hexane = 1:19); white solid; m.p. = 150–152 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.92 (s, 6H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6, 2.3 Hz, 2H), 7.98 (d, *J* = 2.3 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.47, 87.41, 110.96, 127.73, 133.90, 137.57, 157.45; ATR-IR (cm^{-1}): 2963s, 2933m, 2833m, 1594s, 1565s, 1549s, 1474w, 1434m, 1404s, 1375w, 1269w, 1244s, 1183s, 1144w, 1049s, 1027w, 941s, 872w, 842s, 805w, 792w, 719s, 706s, 693s, 661s; MS (EI): *m/z* (rel. int.) 468 (3), 467 (16), 466 (100), 451 (42), 309 (149, 167 (12), 126 (18); HRMS calcd. for $C_{16}H_{16}I_2O_2$ *m/z* 465.8921, found *m/z* 465.8919.

2.2.12. 3,3′-Diiodo-2,4′-dimethoxybiphenyl [minor isomer]



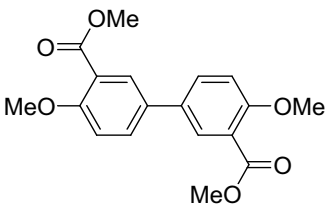
R_f = 0.31 (ethyl acetate:hexane = 1:19); viscous liquid; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.44 (s, 3H), 3.94 (s, 3H), 6.84-6.94 (m, 2H), 7.24–7.31 (m, 1H), 7.56 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.75 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 56.40, 60.29, 85.67, 93.15, 110.50, 126.19, 130.09, 131.11, 132.09, 133.83, 138.49, 139.61, 156.74, 157.62; ATR-IR (cm^{-1}): 3001w, 2929m, 2837s, 1724s, 1594s, 1546m, 1492s, 1455m, 1413s, 1373s, 1281m, 1249m, 1233m, 1180s, 1146m, 1074s, 1053s, 1016m, 999w, 888s, 814s, 781m, 755s, 731s, 664s; MS (EI): *m/z* (rel. int.) 468 (2), 467 (16), 466 (100), 324 (35), 309 (17), 139 (14), 126 (12); HRMS calcd. for $C_{16}H_{16}I_2O_2$ *m/z* 465.8921, found *m/z* 465.8921.

*2.2.13. 2,2′-Dimethoxy-5,5′-dinitrobiphenyl (**24**) [49]*



R_f = 0.16 (hexane:ethyl acetate = 8:2); yellow solid; m.p. = 266–268 °C (hexane); ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.90 (s, 6H), 7.07 (d, *J* = 9.2 Hz, 2H), 8.18 (d, *J* = 2.8 Hz, 2H), 8.32 (d, *J* = 9.2, 2.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 56.39, 110.63, 125.85, 125.89, 127.19, 141.15, 161.85; ATR-IR (cm^{-1}): 3129w, 2921w, 2847s, 1896s, 1611s, 1580w, 1510s, 1470m, 1453w, 1422w, 1335s, 1259s, 1182s, 1146, 1112w, 1097w, 1034s, 1013s, 900s, 863s, 823s, 786s, 747m, 713s; MS (EI): *m/z* (rel. int.) 305 (21), 304 (100), 245 (14), 228 (16), 73 (13), 44 (46), 32 (72).

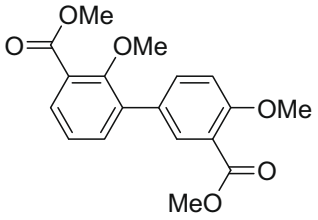
*2.2.14. 3,3′-Dicarbomethoxy-4,4′-dimethoxybiphenyl [major isomer] (**26**)*



R_f = 0.19 (hexane:ethyl acetate = 7:3); white solid; m.p. = 115–117 °C (hexane); ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.93 (s, 6H), 3.95 (s, 6H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.66 (dd, *J* = 8.8, 2.4 Hz, 2H), 8.00 (d, *J* = 2.4 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 52.13, 56.17, 112.49, 120.29, 129.79, 131.48, 131.86, 158.37, 166.60; ATR-IR (cm^{-1}): 3033s, 2925w, 2840s, 1704s, 1611s, 1567s, 1489s,

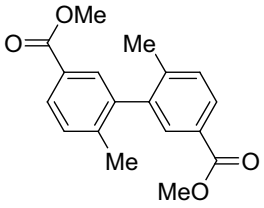
1433m, 1380s, 1313s, 1258s, 1236w, 1181s, 1154s, 1094s, 1059s, 1013s, 960s, 900s, 841s, 801s, 778s, 705s, 678s; MS (EI): *m/z* (rel. int.) 331 (20), 330 (100), 315 (12) 300 (7), 299 (36), 297 (15), 285 (10), 139 (9); HRMS calcd. for $C_{18}H_{18}O_6$ *m/z* 330.1098, found *m/z* 330.1103.

2.2.15. 3,3′-Dicarbomethoxy-2,4′-dimethoxybiphenyl [minor isomer]



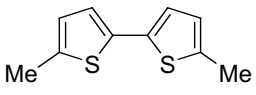
R_f = 0.27 (hexane:ethyl acetate = 7:3); colorless oil; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.50 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 3.98 (s, 3H), 7.05 (d, *J* = 8.7 Hz, 1H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.50 (dd, *J* = 5.7, 2.0 Hz, 1H), 7.71-7.78 (m, 2H), 8.01 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 52.08, 52.31, 56.11, 61.54, 111.92, 119.92, 124.04, 125.71, 129.43, 130.38, 132.27, 134.24, 134.60, 135.07, 157.14, 158.59, 166.45, 166.81; MS (EI): *m/z* (rel. int.) 331 (22), 330 (100), 299 (42), 297 (22), 256 (12), 239 (19), 238 (13), 209 (10), 139 (13), 126 (129, 44 (11), 32 (11).

*2.2.16. 5,5′-Dicarbomethoxy-2,2′-dimethylbiphenyl (**28**) [50]*



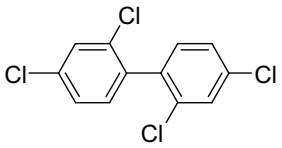
R_f = 0.36 (hexane:ethyl acetate = 9:1); white solid; m.p. = 134–136 °C (hexane); ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 2.11 (s, 6H), 3.90 (s, 6H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 1.8 Hz, 2H), 7.96 (dd, *J* = 8.0, 1.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.04, 52.01, 127.84, 128.78, 130.14, 130.42, 140.65, 141.41, 167.02; ATR-IR (cm^{-1}): 3429s, 3024s, 2954w, 1721s, 1606s, 1574s, 1433s, 1295m, 1254w, 1231w, 1189m, 1110w, 1045s, 997m, 966m, 912s, 853s, 834s, 790w, 761w; MS (EI): *m/z* (rel. int.) 299 (18), 298 (92), 283 (11), 268 (17), 267 (100), 239 (13), 180 (31), 179 (25), 178 (209, 165 (40), 118 (26), 103 (13), 89 (13); HRMS calcd. for $C_{18}H_{18}O_4$ *m/z* 298.1200, found *m/z* 298.1197.

*2.2.17. 5,5′-Dimethyl-2,2′-bithiophenyl (**31**) [6e,51]*



R_f = 0.63 (hexane); white solid; m.p. = 62–65 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 2.48 (d, *J* = 1.1 Hz, 6H), 6.65 (qd, *J* = 3.8, 1.1 Hz, 2H), 6.89 (d, *J* = 3.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.30, 122.84, 125.72, 135.49, 138.45; ATR-IR (cm^{-1}): 3066s, 2972w, 2914m, 2850m, 2736s, 1717s, 1570s, 1531s, 1450w, 1381m, 1202s, 1155m, 1051s, 1036w, 871s, 858s, 778w, 737s, 667s; MS (EI): *m/z* (rel. int.) 195 (18), 194 (100), 193 (73), 179 (10), 161 (33), 96 (8), 32 (30); HRMS calcd. for $C_{10}H_{10}S_2$ *m/z* 194.0218, found *m/z* 194.0222.

*2.2.18. 2,2′,4,4′-Tetrachlorobiphenyl (**33**) [52]*

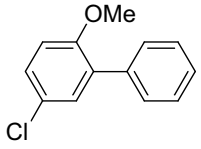


R_f = 0.67 (hexane); colorless liquid; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.2 Hz, 2H), 7.32 (dd, *J* = 8.2, 2.0 Hz, 2H), 7.52 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 127.03, 129.47, 131.93, 134.33, 134.83, 135.75; MS (EI): *m/z* (rel. int.) 294 (48), 293 (13), 292 (100), 291 (11), 290 (81), 257 (11), 255 (11), 222 (39), 220 (61), 184 (10), 150 (17), 111 (11), 110 (16), 92 (9); HRMS calcd. for $C_{12}H_6Cl_4$ *m/z* 289.9218, found *m/z* 289.9217.

2.3. General procedure for $HAuCl_4$ catalyzed hetero-coupling of arenes with benzene

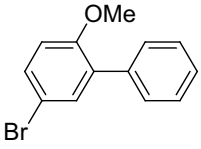
To a 10 mL vial arene (5–15 mmol), benzene (1–10 mmol), $PhI(OAc)_2$ (1 mmol), $HAuCl_4$ (0.02 mmol) and acetic acid (1 mL) were added. The mixture was stirred for 17 h at 95 °C and then quenched with water (10 mL). The reaction mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layer was washed with saturated $NaHCO_3$ (2 × 20 mL), brine (10 ml), dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography to afford the desired product. Analytically pure sample was obtained by thin layer chromatography of the purified product.

*2.3.1. 5-Chloro-2-methoxybiphenyl (**40**) [53]*



R_f = 0.18 (hexane); colorless liquid; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 6.92 (d, *J* = 8.7 Hz, 1H), 7.27–7.47 (m, 5H), 7.50–7.55 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.86, 112.45, 125.67, 127.41, 128.05, 128.08, 129.37, 130.54, 132.24, 137.21, 155.11; MS (EI): *m/z* (rel. int.) 220 (29), 219 (14), 218 (87), 205 (6), 202 (20), 169 (13), 168 (100), 167 (7), 140 (8), 139 (35).

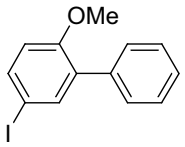
*2.3.2. 5-Bromo-2-methoxybiphenyl (**41**) [54]*



R_f = 0.17 (hexane); colorless liquid; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 6.88 (d, *J* = 8.6 Hz, 1H), 7.33–7.53 (m, 5H), 7.49–7.54 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.79,

112.93, 113.00, 127.42, 128.08, 129.38, 131.04, 132.71, 133.36, 137.10, 155.61; MS (EI): *m*/*z* (rel. int.) 265 (7), 264 (50), 263 (9), 262 (52), 168 (100), 169 (13), 152 (5), 140 (8), 139 (32).

2.3.3. 5-Iodo-2-methoxybiphenyl (**42**) [55]



R_f = 0.22 (hexane); colorless liquid; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 6.75 (d, J = 8.4 Hz, 1H), 7.34–7.47 (m, 5H), 7.60–7.65 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.66, 83.02, 113.50, 127.40, 128.06, 129.35, 133.20, 136.96, 137.15, 139.17, 156.41; MS (EI): *m*/*z* (rel. int.) 311 (14), 310 (100), 169 (9), 168 (68), 152 (5), 140 (8), 139 (30).

2.4. General procedure for catalytic amination of arenes

To a 10 mL vial arene (10 mmol), diisopropylazodicarboxylate (1 mmol), catalyst (0.05 mmol) and appropriate solvent (1 mL) were added. The mixture was stirred for 17 h at 55 °C, cooled and quenched with water (10 mL). The reaction mixture was added dodacane (internal standard, 55 μL), stirred for 15 min, extracted with EtOAc and the organic layer was to GC analysis to determine the yield. The analytically pure sample of **44** was prepared by known literature method [56] to calibrate the GC machine.

2.5. 1,2-Bis(isopropyloxycarbony)-1-(2,5-dimethylphenyl)hydrazine (**44**)

R_f = 0.32 (hexane:ethyl acetate = 8:2); white solid; m.p. = 104 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 1.25 (d, J = 6.2 Hz, 6H), 1.30 (d, J = 6.2 Hz, 6H), 2.26 (s, 3H), 2.32 (s, 3H), 4.96–5.06 (m, 2H), 6.78 (s, 1H), 7.00–7.04 (m, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.26 (bs, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.25, 20.71, 21.95, 21.99, 69.98, 70.55, 128.33, 128.83, 130.43, 132.27, 136.29, 140.50, 155.99; ATR-IR (cm^{-1}): 3429s, 3018w, 2980s, 2937w, 1747s, 1690s, 1617s, 1521s, 1506s, 1466s, 1449s, 1396s, 1381w, 1337s, 1322s, 1309s, 1239s, 1173s, 1108s, 1050s, 1028s, 942w, 895s, 856m, 815s, 768m, 729s, 677m; MS (EI): *m*/*z* (rel. int.) 308 (6), 223 (6), 222 (40), 207 (14), 181 (10), 180 (100), 164 (6), 147 (5), 146 (7), 136 (7), 135 (49), 133 (15), 121 (8), 120 (23), 119 (21), 118 (14), 108 (26), 106 (5), 105 (15), 93 (10), 91 (16), 79 (6), 77 (11), 43 (71), 41 (17), 27 (6); HRMS calcd. for $C_{16}H_{24}O_4N_2$ *m*/*z* 308.1736, found *m*/*z* 308.1738.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.016.

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