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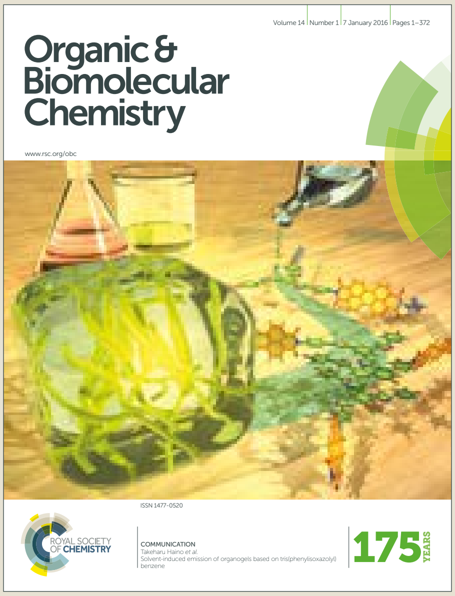

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COMMUNICATION

Sterically controlled C-H/C-H homocoupling of arenes via C-H borylation

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A mild one-pot protocol for the synthesis of symmetrical biaryls by sequential Ir-catalyzed C-H borylation and Cu-Catalyzed homocoupling of arenes is described. The regiochemistry of the biaryl formed is sterically controlled as dictated by the C-H borylation step. The methodology is also successfully extended to heteroarenes. Some of the products obtained by this approach are impossible to obtain via the Ullmann or the Suzuki coupling protocols. Finally, we have shown a one-pot sequence describing C-H borylation/Cu-catalyzed homocoupling/Pd-catalyzed Suzuki coupling to obtain π-extended arene framework.

C-C bond formation is considered to be a key transformation in organic synthesis due to its ability to construct organic molecules having utilities in a broad spectrum of fields[1]. Homocoupling of arenes is one such reaction which finds applications spanning areas from materials to medicines[2]. For example, symmetrical biaryls, the products of homocoupling of arenes are indispensable building blocks in various OLEDs[3a], graphene-based materials[3b], porous polymers[3c], ligands used in organic synthesis[3d], antibiotics[3e] and so on (Fig. 1). Recently, biaryl stapling of biologically active peptides has been shown to enhance the blood-brain barrier (BBB) crossing ability of those peptides[4]. Given the importance of these motifs, there is always a demand for new and improved methods to synthesize them.

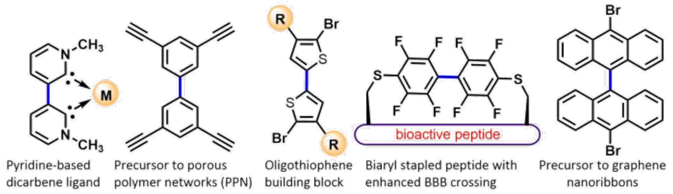
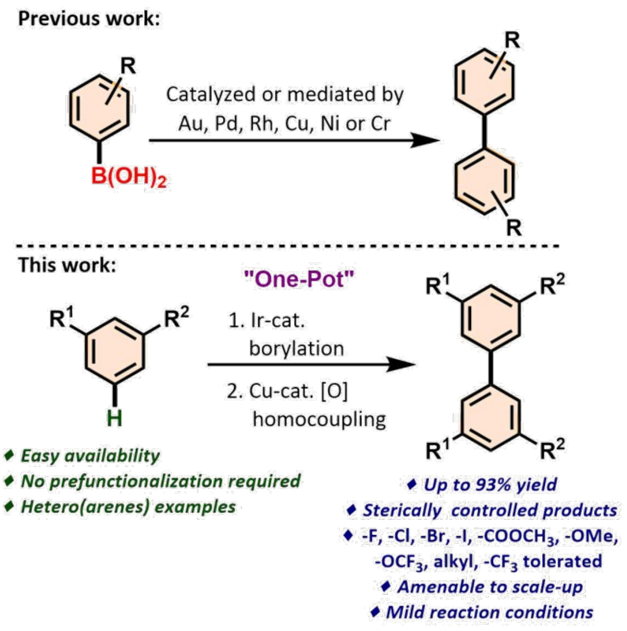


Fig. 1 Representative examples of symmetrical biaryls

Historically, copper-mediated Ullmann coupling of aryl halides has remained as a prominent reaction to make symmetrical biaryls[5].



Scheme 1 Comparison of the known methods to synthesis biaryls from aryl boronic acids with the present approach

More recently, a number of different methods have evolved to obtain symmetrical biaryls from arenes. However, these methods also require the presence of a prefunctionalized group such as -OTs, -B(OH)$_2$, -COOH, -MgX, -SnBu$_3$, etc. on the arene to effect the coupling[2,6, 11-17]. This severely limits the substrate scope of the reaction. It is either time consuming to prepare these starting materials or expensive if commercially available. Dehydrogenative homocoupling of arenes are also known, but the substrate scope of this method is limited to a very few sets of (hetero)arenes[7]. Hence, there is a necessity to develop a reliable method that could deliver a variety of symmetrical biaryl compounds with predictable regioselectivity from simple starting materials that are not prefunctionalized, Herein, we introduce one such method to prepare symmetrical biaryls in a regioselective fashion by sequential iridium-catalyzed C-H borylation of arene (ArH), followed by a newly developed copper-catalyzed oxidative homocoupling of the *in situ* formed aryl boronates (ArBpin) in a one-pot fashion (Scheme 1). The regioselectivity of the products formed are controlled by steric

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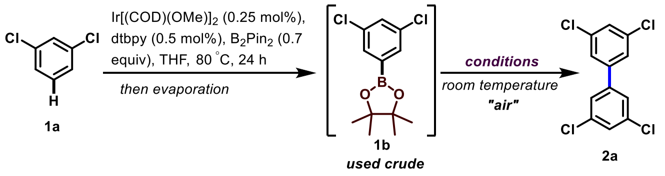
factors as dictated by the C-H borylation step. The methodology was also smoothly extended to heteroarenes. Further, it has been shown that the protocol is amenable for scale-up synthesis. Finally, it has also been demonstrated that the crude biaryl product (bearing –I substituents) formed in the reaction sequence can be further derivatized via Pd-catalyzed Suzuki coupling into π-extended compounds that are of great interest to materials chemists.

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst[b]	Ligand[c]	Solvent	Yield[d] (%)
1.	$Cu(OTf)_2$	bipyridine	CH_3CN	traces
2.	$Cu(OTf)_2$	bipyridine	THF	traces
3.	$Cu(OTf)_2$	bipyridine	*i*-PrOH	10
4.	$Cu(OTf)_2$	bipyridine	DMF	50
5.	$Cu(OTf)_2$	bipyridine	H_2O	0
6.	$Cu(OTf)_2$	bipyridine	EtOH:H_2O (1:1)	0
7.	$Cu(OTf)_2$	bipyridine	1,4-dioxane	0
8.	$Cu(OTf)_2$	bipyridine	CH_2Cl_2	0
9.	$Cu(OTf)_2$	phen	DMF	28
10.	CuCl	phen	DMF	30
11.	$Cu(NO_3)_2$	phen	DMF	25
12.	$Cu(OAc)_2$	phen	DMF	92
13.	$Cu(OAc)_2$	bipyridine	DMF	38
14.[e]	$Cu(OTf)_2$[e]	bipyridine[e]	DMF	90
15.	$Cu(OAc)_2$	phen	MeOH	15
16[f].	$Cu(OTf)_2$	bipyridine	DMF	38
17[f].	$Cu(OAc)_2$	phen	DMF	23
18[e].	$Cu(OTf)_2$	-	DMF	42
19.	$Cu(OAc)_2$	-	DMF	45
20.	-	bipyridine	DMF	0
21.	-	phen	DMF	0

[a] Reaction was performed on a 0.5 mmol scale. [b] 5 mol% of the catalyst was used. [c] 6 mol% of the ligand was used. [d] Yield recorded after purification by silica-chromatography. [e] 10 mol% of the catalyst and 12 mol% of the ligand were used. Reaction performed under O_2 atmosphere. [f] Reaction performed under N_2 atmosphere.

Iridium-catalyzed C-H borylation of arene enables the introduction of –Bpin functionality at the least hindered site on the arene[8]. The regiochemistry of the product formed is controlled more by steric effects than electronic or directing effects of the arene substituents. Hence, reactions of 1,3-disubstituted arenes selectively forms the corresponding *meta* borylated product irrespective of the electronics of the substituents. The reaction tolerates most of the common organic functional groups. The selectivity of the borylation step coupled with functional group tolerance has been utilized for the one-pot transformation of an aryl C-H to various useful functional groups such as phenol, aniline, nitrile, aryl (via Pd-catalyzed Suzuki coupling), halide, and so on.[9] We have also recently shown that C-H of arenes can be converted into 1,2,3-triazole[10a] and -NO_2[10b] via C-H borylation. However, this platform has never been utilized for the one-pot transformation of an arene C-H to symmetrical biaryl, a useful transformation, which we describe herein.

Arylboronic acids are known to undergo homocoupling reactions[2]. Pd-catalyzed homocoupling reactions of arylboronic acids have been well documented[2, 11]. Rh,[12] Ni,[13] and Cu-catalyzed[14b,14c] versions of this reaction are also been known. Other metals such as Au[15], Cr[16], and V[17] have been used to mediate this reaction[2]. Among these methods, the Cu-catalyzed version is more attractive because of the affordability of the metal catalyst as well as the simplicity of reaction conditions. This method does not require malodorous solvents such as pyridine or expensive metals such as silver to mediate the homocoupling. However, all these reported Cu-mediated[14a] and Cu-catalyzed[2, 14b-c,] methods use only arylboronic acid as substrates and not the aryl boronate esters (ArBpin). This can be possibly due to the less reactivity of the ArBpin when compared to that of the free arylboronic acid[18]. Hence, we sought to develop a one-pot method that integrate the Ir-catalyzed C-H borylation of arenes and Cu-catalyzed homocoupling of the crude ArBpin product. This method would enable access to sterically controlled symmetrical biaryl products, starting from simple arene (C-H) precursors.

1,3-dichlorobenzene was chosen as the model substrate for the optimization of reaction conditions. At first, iridium-catalyzed C-H borylation was performed on the substrate using Ir[(cod)OMe]$_2$/dtbpy and B_2Pin_2 system in THF at 80 °C for 24 hours. The solvent was evaporated and the crude ArBpin formed was used directly without any further purification for the optimization of the subsequent homocoupling reaction (Table 1). The desired product was observed only in traces when the reaction was carried out initially in CH_3CN with 5 mol% of $Cu(OTf)_2$ and 6 mol% of bipyridine as the catalytic system (Table 1, entry 1). In order to investigate the optimal solvent conditions, an array of solvents was screened employing the same catalytic system. All of these reactions were performed at room temperature in the presence of air as oxidant. The reaction in THF furnished only traces of the required product, whilst the yield in *i*-PrOH was slightly better (10%) (Table 1, entry 3). On the other hand, solvents such as 1,4-dioxane, H_2O, aq. EtOH, CH_2Cl_2 did not yield any desired product (Table 1, entries 5-8). Among the solvents screened, DMF was found to be the best furnishing the desired biaryl product in an isolated yield of 50% (Table 1, entry 4). After the solvent optimization, a number of copper sources were screened to further improve the yield of the reaction. Either phen or bipyridine was used as ligand (Table 1, entries 9-14). When used in combination with phen, the reaction catalyzed by $Cu(OAc)_2$ furnished an isolated yield of 92% of the biaryl product (Table 1, entry 12) outperforming other copper sources. It was found out in the further investigation that a 10 mol% of $Cu(OTf)_2$ /bipyridine system also gave a 90% yield of the desired product (Table 1, entry 14). In the absence of ligand, the yield of the reaction dropped from 92% to 45% when $Cu(OAc)_2$ was used as a catalyst (Table 1, entry 12 vs 18). Similarly, the yield dropped from 90% to 42% when $Cu(OTf)_2$ was used without a ligand (table 1 entry 14 vs 19). Demir and co-workers first postulated the mechanism of copper-mediated homocoupling of arylboronic acids[14a]. Until now this mechanism is not completely understood but 3 possible pathways have been proposed.[14] From our

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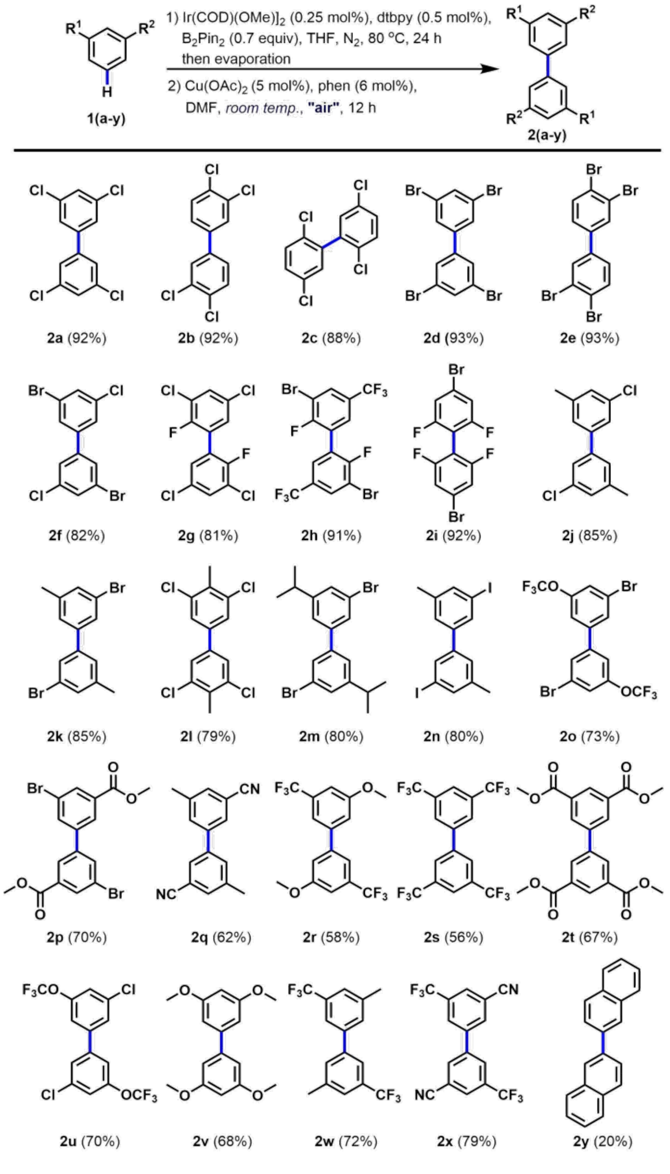
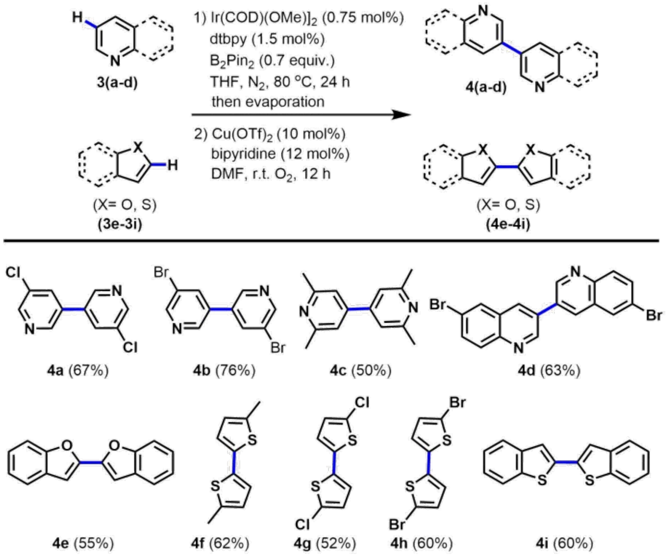
experimental evidence, we conclude the following: (1) In the absence of any copper source, the formation of biaryl was not observed, indicating the importance of copper (Table 1, entries 20 and 21). (2) Iridium does not have any role in the homocoupling of ArBpin intermediates (3) O_2 or air is necessary for the homocoupling step. When the reaction was performed in the absence of air or oxygen the yield dropped from 92 to 23% (Table 1, entry 12 vs 16 and 17). (4) Ligand enhances the yield of the homocoupling reaction.



Scheme 2 One-pot homocoupling of arenes. Reactions were performed on 1 mmol scale.

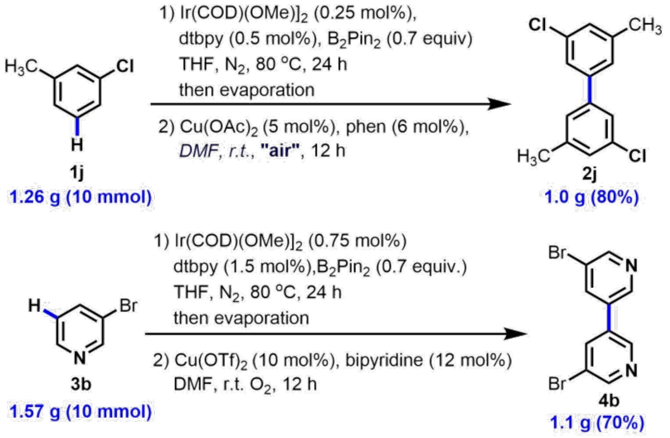
Having the optimized conditions ready (Table 1, entry 12), we then proceeded to evaluate the substrate scope of the one-pot C-H borylation/homocoupling reaction sequence (Scheme 2). At first, a panel of arenes was subjected to the Ir-catalyzed C-H borylation reaction. After the completion of the reaction, the solvent was removed *in vacuo* and the crude material was dissolved in DMF and subjected to the Cu-catalyzed homocoupling reaction using $Cu(OAc)_2$ (5 mol%) and phen (6 mol%). The reactions were performed at room temperature and in the presence of air as an oxidant. In general, arenes containing halogen substituents performed best with isolated product yields of up to 93%. It should be noted that most of these halogen substituted biaryl products can neither be synthesized via the classical Ullmann coupling conditions nor by the Pd-catalyzed Suzuki coupling protocol. In addition, it was surprising that 3-iodotoulene furnished an isolated yield of 80% of the biaryl product (compound **2n**), without the formation of any detectable amount of des-iodo byproduct. All these –Cl, -Br, and –I substituted products can further be used for Suzuki coupling to construct more π–extend aromatic systems. Arenes bearing alkyl substituents such as $–CH_3$ and –*i*Pr (**2j** to **2n**) tolerated the reaction sequence with product yields ranging from 80 to 85% whilst a drop in yield (58%) was observed with the arene bearing both $–CF_3$ and $–OCH_3$ groups (**2r**). It was observed that electron deficient arenes (**1s** and **1t**) furnished products (**2s** and **2t**) in the modest yields of 56% and 67% respectively. Highly electron-rich substrates such as 1,3-dimethoxybenzene furnished the biaryl **2v** in 68% yield. At the same time, arenes with two strong electron withdrawing groups such as 3-(trifluoromethyl)benzonitrile afforded the biaryl **2x** in 79% yield. Naphthalene selectively furnished less hindered 2,2-binapthyl **2y**, although only in 20%, mainly due to the formation of multiple products in the borylation step. Overall, arenes bearing –F, -Cl, -Br, -I, $-CH_3$, -*i*Pr, $-CF_3$, $-OCF_3$, -CN, $-COOCH_3$, underwent the reaction sequence smoothly as evident from the results shown in Scheme 2. In all cases, sterically less hindered biaryls and binaphthyl were obtained in a regioselective manner.



Scheme 3 One-pot homocoupling of heteroarenes. Reactions were performed on 1 mmol scale.

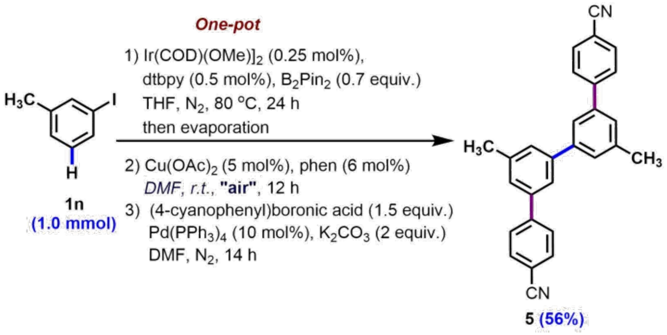
Having successfully synthesized various symmetrical biaryls, this methodology was then extended to the heteroarenes such as pyridines, quinoline, benzofuran, thiophenes and benzothiophene (Scheme 3). It is worth mentioning that all these scaffolds are important building blocks in medicines, materials and ligand design. We found that $Cu(OTf)_2$/bipyridine condition (Table 1, entry 14) worked better while dealing with the heteroarenes. 3-chloropyridine and 3-bromopyridine furnished the 3,3'-bipyridine derivatives **4a** and

4b in isolated yields of 67% and 76% respectively. 2,6-lutidine furnished 4,4'-bipyridine derivative in a modest yield of 50%. 3,3'-biquinoline derivative, **4d** was obtained in 63% yield from 3-bromoquinoline. Similarly, 2,2'-bi(hetero)arene derivatives of benzofuran, **4e** and thiophene **4f**, were obtained in 55 and 62% yields respectively. 2-chlorothiophene and 2-bromothiophene furnished the respective halogenated 2,2'-bi(hetero)arenes **4g** and **4h** in 52% and 60% yield respectively. Benzothiophene smoothly afforded the 2,2'-bi(benzothiophene) **4i** in 60% yield. These results successfully demonstrate the scope to obtain symmetrical biheteroaryl derivatives in a regioselective fashion as dictated by the C-H borylation reaction. It is also interesting to note that the starting materials used are simple heteroarenes without requiring any prefunctionalization.



Scheme 4 Evaluation of scale-up reactions

We then sought to assess the suitability of our method for scale-up reactions (Scheme 4). By employing the standard conditions outlined in Scheme 2, 10 mmol (1.26 g) of 3-chlorotoluene, **1j** furnished the biaryl product **2j** in 80% isolated yield. Similarly, 10 mmol (1.57 g) of 3-bromopyridine furnished the desired homocoupled product **4b** in 70% isolated yield by using the standard conditions outlined in Scheme 3. These results demonstrate that our method is amenable for scale-up reactions.



Scheme 5 One-pot borylation/homocoupling/cross-coupling sequence

Halogenated biaryl compounds are versatile intermediates for the synthesis of π-extended materials. The halogenated biaryls obtained by this approach could be used directly for further Suzuki cross-coupling reaction without the need for isolation or purification (Scheme 5). 3-iodotolune, **1n** was subjected to a one-pot C-H borylation/Cu-catalyzed homocoupling/Pd-catalyzed Suzuki cross-coupling (with 4-cyanophenylboronic acid) to afford the π-extended arene **5** in 56% isolated yield. This clearly demonstrate the potential of our method in accessing well-defined π-extended molecular frameworks from simple arenes.

Conclusions

In summary, a mild one-pot C-H borylation/copper-catalyzed homocoupling sequence was developed to access symmetrical biaryls with predictable regioselectivity from the respective arene (C-H) precursors in excellent yields. The method was further extended to several heteroarenes. The halogenated (-Br and –I) biaryls obtained by this method are not possible to access via the existing Ullmann or Suzuki coupling protocols, and can be used as building blocks for further cross-coupling reactions. We have also shown that the method is amenable for scale-up synthesis. Finally, we have demonstrated that the biaryl (with iodo-substituent) obtained by this strategy can be directly converted to the π-extended aromatic system via Suzuki coupling. Overall, we are optimistic that this method will simplify the ways to make useful biaryls in a regioselective manner from readily available precursors.

Conflicts of interest

The authors declare no conflict of interest.

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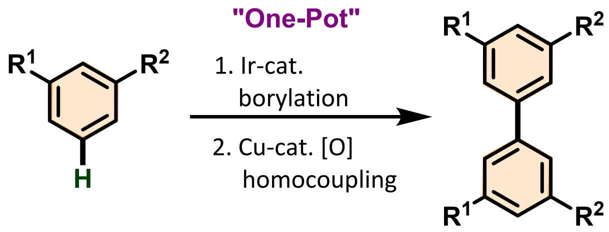

- ♦ *Easy availability*
- ♦ *No prefunctionalization required*
- ♦ *Hetero(arenes) examples*

- ♦ *Up to 93% yield*
- ♦ *Sterically controlled products*
- ♦ *Mild reaction conditions*
- ♦ *34 examples*

Sterically controlled synthesis of symmetrical biaryls from arenes by a one-pot sequential Ir-catalyzed C-H borylation and Cu-catalyzed homocoupling is described.