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Complete List of Authors:	Mulla, Shafeek; Nationa Chemical Laboratory, Chemical Engineering and Process Development Division Chavan, Santosh; National Chemical Laboratory, Chemical Engineering and Process Development Division Pathan, Mohsinkhan; National Chemical Laboratory, Chemical Engineering and Process Development Division Inamdar, Suleman; National Chemical laboratory, Chemical Engineering & Process Development Division Shaikh, Taufeekaslam; National Chemical Laboratory, Chemical Engineering and Process Development Division

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ARTICLE TYPE

Ligand-, base-, co-catalyst-free copper fluorapatite (CuFAP) as a versatile, ecofriendly, heterogeneous and reusable catalyst for an efficient homocoupling of arylboronic acid at ambient reaction condition

Shafeek A. R. Mulla,* Santosh S. Chavan, Mohsinkhan Y. Pathan, Suleman M. Inamdar and Taufeekaslam M. Y. Shaikh

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This paper describes the first report, in which copper species containing copper fluorapatite (CuFAP) act as a versatile, eco-friendly, recyclable, heterogeneous catalyst for an efficient synthesis of symmetric biaryls from homo-coupling of arylboronic acids in methanol solvent at ambient reaction condition. The developed protocol is ligand-, base-, and co-catalyst-free, sustainable, mild, inexpensive, and compatible with a wide range of aromatic/heterocyclic boronic acids and provides corresponding product in excellent yields without purification. The catalyst was easily recovered from the reaction mixture and reused several times without loss of activity.

Introduction

The biaryl linkages act as building block not only in polymer[3] and ligand synthesis[4] but also in variety of synthetic/ natural occurring biologically active molecules, which posses wide range of bioactivities such as antiviral,[1] antibacterial (Crisamicin A and Biphenomycin B), [2] etc. Owing to the potent importance of biaryl moieties in life sciences, pharmaceuticals, polymers and catalysis, synthesis of their structural units have immense attraction among the researchers and developed various methods such as metal catalyzed coupling of aryl halides,[5] Grignard reagents, arenediazonium salts and 1, 2-diarylditellanes etc.,[6] and name reactions for their synthesis.[7] However, copper catalyzed Ullmann coupling reaction of arylhalide is well known conventional method for the synthesis of biaryls.[8]

Arylboronic acids being easily available, more stable, non-toxic, and compatible with different functional groups compared to arylhalide/organometallic reagents, hence their utilization has become centre of interest among the chemists/biologists to introduce the phenyl ring in various biologically active molecules[9] and/ or to synthesize biaryl motifs by homo-coupling arylboronic acids. Because of these novel features of arylboronic acids, homo-coupling of arylboronic acids for the synthesis of symmetrical biaryl using various catalysts such as $CuSO_4$,[10a] $Cu(OAc)_2$,[10b] RhCl $(PPh_3)_3$,[10c] Au (III) Schiff base-complexes,[10d] AuNP,[10e] $Pd(OAc)_2$/N,O-ligands,[10f] [{(1,10-phenanthroline)Cu(ω-OH)}$_2Cl_2$]·$3H_2O$,[10g] CuCl,[10h] $Ag_2O/CrCl_2$,[10i] $Pd(PPh_3)_2Cl_2$,[10j] $PdCl_2$,[10k] $Pd(OAc)_2$,[10l] $Pd(OAc)_2$/$AgNO_3$,[10m] $NaAuCl_4 2H_2O$,[10n] AuNP/In_2O_3[10o] I_2,[10p] have been well reported in the literature. Nonetheless, so far only four papers,[10a-b,10g-h] have been reported in which copper species act as catalyst for the synthesis of biaryls from homo-coupling of arylboronic acids. Moreover, all these approaches reported so far using either costly transition metals or moisture sensitive, toxic, corrosive homogeneous catalysts in excess or stoichiometric quantity with the requirements of oxidants, high concentration of base, highly expensive ligands/co-catalyst in the presence/absence of hazardous/malodorous solvents, which leads to the problems of toxic waste disposal besides long reaction time, high temperature and low yield for the desired product. Hence, all these approaches lack generalization to implements the commercial scale production of biaryls from homo-coupling of aryboronic acids.

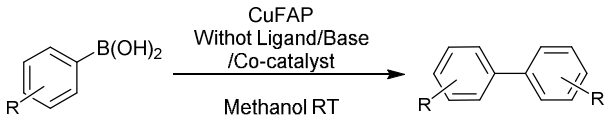
Diaryl motifs being a key constituent of the structural backbone of many bioactive natural/pharmaceutical compounds, the construction of their structural units by developing more general, ligand, base, co-catalyst free, straightforward, environment friendly, and cost effective protocol using non-toxic, environmentally benign solvents, cost effective recyclable catalysts at milder reaction condition is still challenging and the subject of intense investigation. To the best of our knowledge, so far no report on the biaryls synthesis from homocoupling of arylboronic acids using copper species as heterogeneous, reusable catalyst has been published in the literature. As we were stimulated from our research work for the organic transformation over recyclable, heterogeneous copper fluorapatite (CuFAP) catalyst[11a-c] as well as use of copper in the classical Ullmann coupling reaction of arylhalide for the synthesis of biaryls, fascinated us to investigate the application of copper fluorapatite (CuFAP) catalyst for the homo-coupling of arylboronic acid, and therefore this paper describes the first report in which copper species containing CuFAP act as a

Chemical Engineering & Process Development Division, CSIR-National Chemical Laboratory. Dr. Homi Bhaba Road, Pune-411008, Maharashtra, India.
Tel +91-20-25902316
Fax: +91-20-25902676
E-mail: sa.mulla@ncl.res.in

† Electronic Supplementary Information (ESI) available
Experimental details and spectral data of all the new compounds.

versatile, recyclable, heterogeneous catalyst for the homo coupling reaction of arylboronic acids.

As part of our ongoing program to develop general, green, ecofriendly, and cost effective approaches for organic transformation using recyclable catalysts,[11a-h] we herein report ligand-, base-, co-catalyst-free, environment friendly, cost effective, and mild protocol for an efficient synthesis of biaryls from homo-coupling of arylboronic acids over ecofriendly, heterogeneous reusable CuFAP catalyst in methanol solvent at ambient temperature (Scheme 1).

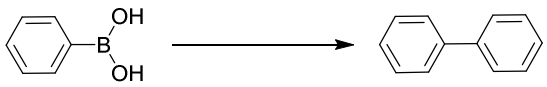


Scheme 1 CuFAP catalyzed homo coupling of arylboronic acid.

Results and Discussion

To develop protocol for the synthesis of biaryl from the homo coupling of arylboronic acid, phenyl boronic acid (1 mmol) catalyzed by a 100 mg of CuFAP catalyst in a 5 mL solvent was selected as model reaction to optimized reaction conditions. Initially, the screening of different solvents such as MeOH, n-PrOH, THF, i-PrOH, EtOH, 1, 4-dioxane, PhMe, DMSO, DMF, $CHCl_3$, DCM, and MeCN were carried out at room temperature (Table 1, entries 1-12). However, MeOH solvent gives a 92% yield to the desired product in 2 h, whereas EtOH, *n*-PrOH, *i*-PrOH, THF, and 1,4-dioxane solvent gives 91%, 80%, 84%, 71%, and 74% yields, respectively in 8 h (Table 1, entries 2-6).

Table 1 Optimisation of reaction conditions for biaryl synthesis from phenyl boronic acid.[a]



1a **2a**

Entry	Catalyst	Solvent	Temp (^{0}C)	Time (h)	Yield (%)[b]
Effect of solvent					
1	**CuFAP**	**MeOH**	**rt**	**2**	**92**
2	CuFAP	EtOH	rt	8	91
3	CuFAP	n-PrOH	rt	8	80
4	CuFAP	iPrOH	rt	8	84
5	CuFAP	THF	rt	8	71
6	CuFAP	Dioxane	rt	8	74
7	CuFAP	PhMe	rt	12	N.R.[c]
8	CuFAP	DMSO	rt	12	N.R.[c]
9	CuFAP	DMF	rt	12	N.R.[c]
10	CuFAP	$CHCl_3$	rt	12	N.R.[c]
11	CuFAP	DCM	rt	12	N.R.[c]
12	CuFAP	MeCN	rt	12	N.R.[c]
Catalyst screening					
13	PdFAP	MeOH	rt	5	88
14	RhFAP	MeOH	70	24	N.R.[c]
15	DTP/SiO_2	MeOH	70	24	N.R.[c]
Effect of catalyst loading					
16	CuFAP (50 mg)	MeOH	rt	2	57
17	CuFAP (75 mg)	MeOH	rt	2	80
18	CuFAP (125 mg)	MeOH	rt	2	93

[a] Reaction conditions: Phenyl boronic acid (1 mmol), solvent (5 mL), catalyst (100 mg). [b] Isolated yield after chromatographic purification. [c] No reaction.

The formation of desired product was not observed in PhMe, DMSO, DMF, $CHCl_3$, DCM, and MeCN solvents even after 12 h (Table 1, entries 7-12).

The excited results using MeOH as a solvent over ligand-, base-, and co-catalyst free CuFAP catalyst, made us keen to design, develop, and explore the scope of various catalysts for the homo-coupling of arylboronic acid. The various catalysts such as CuFAP, rhodium fluorapatite (RhFAP), palladium fluorapatite (PdFAP), and silica supported dodecatungstophosphoric acid (DTP/SiO_2) were screened for the synthesis of biaryl from homo-coupling of phenylboronic acid in a 5 mL methanol solvent at room temperature. However, CuFAP catalyst provided the desired product in excellent yield in a short reaction time (Table 1, entry 1) as compared to PdFAP catalyst (Table 1, entry 13). The RhFAP, and DTP/SiO_2 catalysts does not show any sign of desired product formation even though the reaction was heated at 70^{o}C for 24 h (Table 1, entry 14, 15).

The excellent results on CuFAP catalyst made us to further optimized catalyst loading. Interestingly, increasing the catalyst loading from 50 mg to 100 mg resulted in a dramatic enhancement in the yield from 57% to 92% (Table 1, entry 16, 17, 1). However, no progress in the yield was observed by further increasing 125 mg catalyst loading (Table 1, entry 18).

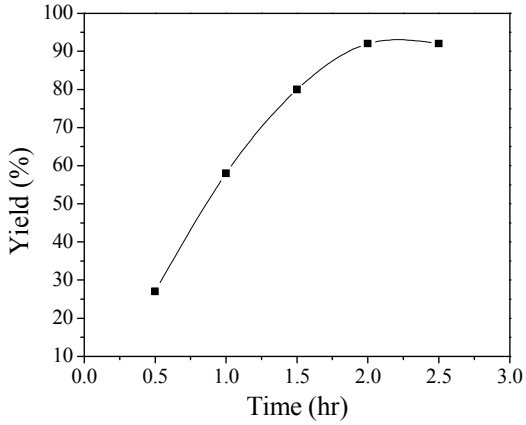


Fig. 1 Effect of reaction time: Phenylboronic acid (1 mmol), CuFAP (100 mg) in MeOH (5 mL) at room temperature.

We optimized the reaction time as shown in the Figure 1. The yield of desired product was increased with increasing reaction time from 0.5 h to 2 h and remains unchanged by further increasing the reaction time to 2.5 h. These optimization results reveals that CuFAP catalyst with 100 mg loading in Methanol solvent shows excellent catalytic activity at room temperature in 2 h (Table 1, entries 1-18 and Figure 1). The formation biaryl was not observed in the absence of CuFAP catalyst.

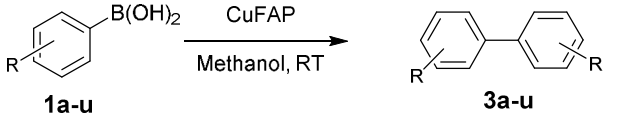
The promising performance of ligand-, base-, co-catalyst-free CuFAP catalyst at optimized reaction conditions, encourage us to ascertain general compatibility of CuFAP catalyst with various arylboronic acids, hence, homo-couling reaction of various arylboronic acids have been examined and results are shown in Table 2. Surprisingly, homo-coupling reaction of various substituted aylboronic acid in the presence of ligand-, base-, co-catalyst-free CuFAP catalyst under optimized reaction conditions provided the corresponding biaryl product in very good to excellent yield (Table 2, entries 1-21). Initially, homo-coupling reaction of various para substituted phenylboronic acid were carried out under the optimized reaction condition, the

electron donating/ withdrawing groups such as Me, OMe, $C(Me)_3$, F, Cl at para position on the aryl ring provided an excellent yield (Table 2, entry 2-6). Moreover, phenylboronic acid bearing a sensitive functional groups such as -CHO and -$CH=CH_2$ were successfully reacted to afford the desired homo-coupling compounds in a 85% and 92% yield, respectively (Table 2, entries 7 and 8), whereas phenyl boronic acid bearing OMe, and -Cl group at ortho and meta position, respectively, afforded the corresponding homo-coupling product in excellent yield (Table 1, entry 9, 10).

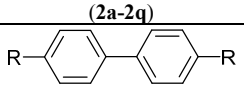
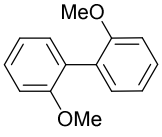
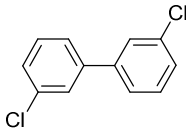
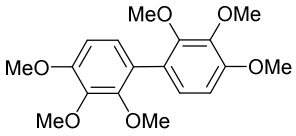
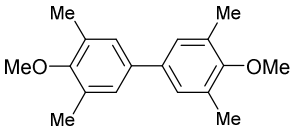
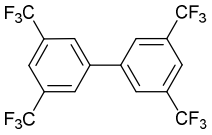
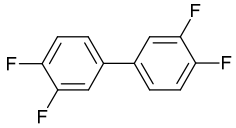
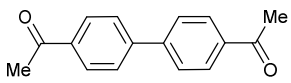
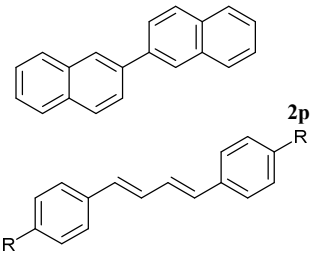
Encouraging results on various mono substituted phenylboronic acids create a keen interest to further elaborate the scope to various di and tri-substituted phenyl boronic acid. Interestingly, 2, 3, 4-trimethoxy phenylboronic acid, (4-methoxy-3,5-dimethylphenyl)boronic acid, (3,5-bis(trifluoromethyl)phenyl)boronic acid, 3, 4 fluoro phenyboronic acid, acetylphenyboronic acid, and 2-naphthylboronic acid were reacted without any problem under optimized reaction condition and afforded the corresponding biaryl product in good to excellent (88-98%) yield (Table 2, entries 11-16). Amazing results on homo-coupling of mono-, di-, tri- arylboronic acid as well as 2- naphthylboronic acid, passionate us to investigate homo-coupling reaction of substituted trans-2-phenylvinylboronic acid, to our surprise, homo-coupling reaction of various electronically rich and poor trans-2-phenylvinylboronc acids was amenable to precede the anticipated product in excellent yield (Table, entries 17-21).

Incredible performance of ligand-, base-, co-catalyst-free CuFAP catalyst on various substituted arylboronicacid/2-napthyleneboronic acid/phenylvinylboronic acids (Table 2, entries 1-21), made us aflame to check the feasibility of this protocol to hetrocyclicboronic acid. Hence, various hetrocyclicboronic acid such as 2-thiopheneboronic acid, 3-thiopheneboronic acid, 2-benzothiopheneboronic acid, 3-benzothiopheneboronic acid, and 2-furanylboronic acid were

Table 2 Substrate scope of CuFAP catalyzed homocoupling of arylboronic acid.[a, b]

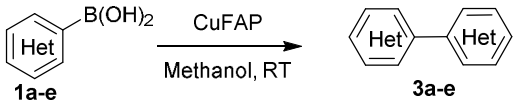


1a-u **3a-u**

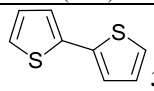
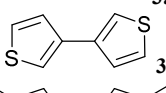
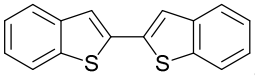
Entry	Product (**2a-2q**)	Yield (%)[b]
		
1	**2a,** R = H	92
2	**2b,** R = Me	94
3	**2c,** R = OMe	93
4	**2d,** R = $C(Me)_3$	96
5	**2e,** R = F	90
6	**2f,** R = Cl	93
7	**2g,** R = CHO	85
8	**2h,** R = $CH=CH_2$	92
9	 **2i**	95
10	 **2j**	95
11	 **2k**	98
12	 **2l**	97
13	 **2m**	97
14	 **2n**	93
15	 **2o**	88
16	 **2p**	90
17	**2q,** R = H	96
18	**2r,** R = F	93
19	**2s,** R = CF_3	90
20	**2t,** R = Cl	94
21	**2u,** R = Ph	96

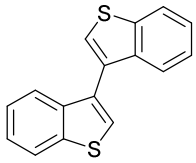
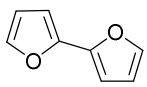
[a] Reaction conditions: Arylboroni acid/ (1 mmol), CuFAP (100 mg) in MeOH (5 mL) at room temperature for 2 h. [b] Isolated yield without chromatographic purification.

Table 3 CuFAP catalyzed homo coupling of hetrocyclicboronic acid.[a, b]



1a-e **3a-e**

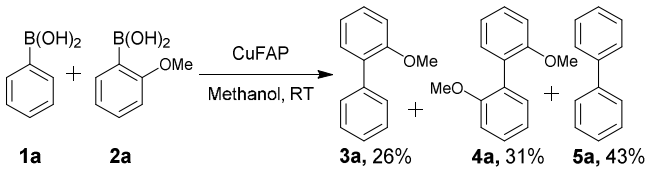
Entry	Product (**3a-e**)	Yield (%)[b]
1	 **3a**	95
2	 **3b**	96
3	 **3c**	93

4		**3d**	95
5		**3e**	87

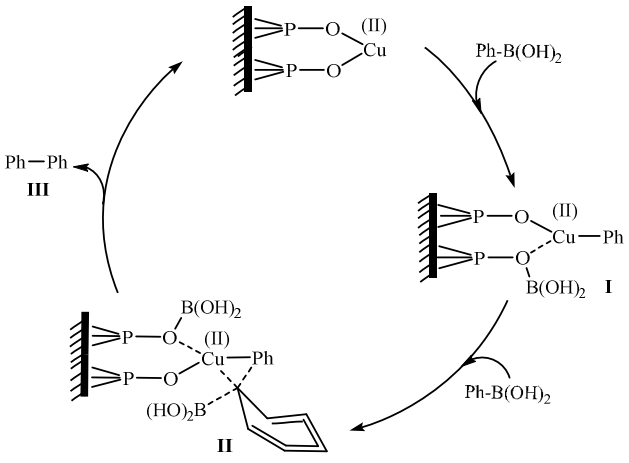
[a] Reaction conditions: Heterocyclic boroni acid (1 mmol), CuFAP (100 mg) in MeOH (5 mL) at room temperature for 2 h. [b] Isolated yield without chromatographic purification.

subjected to homo-coupling reaction under the optimized reaction condition. Miraculously, all hetrocyclicboronic acid provided desired coupling products in an excellent yield (Table 3, entries 1-4) except 2-furanylboronic acid, which afforded 87% yield (Table 3, entry 5). The results in the Table 2 and 3 reveals that a novel ligand-, base-, co-catalyst-free protocol over a versatile, eco-friendly, recyclable, heterogeneous copper fluorapatite catalyst is well tolerated to homo-coupling reaction of various aryl/hetrocyclicboronic acids having different functional groups. However, yield obtained does not depend on the nature of substituents on aryl/hetrocyclicboronic acids and provided excellent yield except Table 2 entry 7 (85% yield), 15 (88% yield), Table 3 entry 5 (87% yield).

Delighted with the performance of ligand-, base- and co-catalyst-free CuFAP catalyst for homo-coupling reaction of the aromatic, hetrocyclicboronic acid, made us inquisitiveness to investigate the coupling of two different arylboronic acids (Scheme 2).



Scheme 2 CuFAP catalyzed the coupling reaction of phenylboronic and 2-methoxyboronic acids.



Scheme 3 Plausible mechanism for homo coupling over CuFAP

Therefore, phenylboronic acid and 2-methoxy phenylboronic acid was coupled under the optimized reaction condition, provided homo-coupling and cross coupling products in 31% (4a), 43% (5a) and 26% (3a) yield, respectively, as predicted in the Scheme-2. The yield is based on GC analysis

As per our[11a-c,] and previous[12a-b] research work reported in the literature, the probable mechanism proposed for the synthesis of biaryl from the homo coupling reaction of arylboronic acid over ligand-, base-, co-catalyst-free CuFAP catalyst is shown in Scheme 3. Initially phenylboronic acid reacts with the CuFAP catalyst to generate the intermediate complex I. Subsequently complex I react with another mole of phenylboronic acid to form intermediate complex II, which instantaneously undergoes formation of C-C coupling to eliminate the biaryl product as well as CuFAP catalyst to reuse.

Recyclability of CuFAP catalyst

Today's environmental concern demands to develop "Green Chemical Processes" hence, recovery, recyclability of catalyst is the choice to achieve environmental sustainable and economical viable processes. Therefore, the recyclability and recovery of ligant-, base-, co-catalyst-free CuFAP catalyst was investigated for the synthesis of symmetrical biaryl by homo-coupling reaction of phenylboronic acid at optimized reaction condition. The results are shown in Table 4. The catalyst was recovered and recycled several times without loss of catalytic activity (Table 4, entries 2-5). The isolated yield obtained at the end of 4th recycle (Table 4, entry 5) is very much consistent as of fresh catalyst (Table 4, entry 1). The consistent performance of reused catalyst clearly indicate that no loss or leaching of copper species during the course of reaction, which was confirmed by ICP analysis as well.

Table 4 Recoverability and reusability of CuFAP catalyst.[a]

Entry	Run	Yield[b] (%)
1	Fresh	92
2	Run-1	92
3	Run-2	90
4	Run-3	92
5	Run-4	91

[a] Reaction conditions: Phenylboronic acid (1 mmol), CuFAP (100 mg) in MeOH (5 mL) at RT for 2 h. [b] Isolated yield without chromatographic purification.

Conclusions

In conclusion, a novel, general, ligand-, base-, co-catalyst-free, sustainable, mild, and inexpensive protocol has been developed over a versatile, eco-friendly, recyclable, heterogeneous copper fluorapatite catalyst for an efficient synthesis of symmetric biaryls in good to excellent yield from homo-coupling of aryl/hetrocylicboronic acids in methanol solvent at ambient reaction condition in a short reaction time. The CuFAP catalyst was recovered by simple filtration from the reaction mixture and reused several times without the loss of catalytic activity. The described protocol is very much compatible with wide range of sensitive functional groups and may be applicable for the synthesis of various bioactive and natural products containing biaryls; hence further studies are in progress in this direction.

Experimental Section

All chemicals and reagents were procured from Sigma Aldrich, S.D. Fine chemical and commercial suppliers and used without further purification. The products were characterized using ^{1}H NMR, ^{13}C NMR spectra. NMR spectrums of product were obtained using Bruker AC-200 MHz spectrometer with TMS as the internal standard. Column chromatography was performed on silica gel, Merck grade 60-120 mesh size. TLC was performed on 0.25mm E. Merck precoated silica gel plates (60 F_{254}).

General experimental procedure for synthesis of biaryl over the CuFAP:

Arylboronic acid (1 mmol) in a 5 mL methanol solvent was stirred at room temperature for 2 h in the presence of 100 mg of CuFAP catalyst. The completion of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with 10 ml methanol followed by filtration to recover the catalyst. The filtrate was dried under vacuum, thereafter added 10 ml water and 10 ml ethyl acetate to separate out the organic layer. The organic layer is dried over anhydrous Na_2SO_4 and concentrate in vacuum to gives the pure product. All the isolated reaction products were characterized and confirmed by NMR.

Acknowledgments

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Ligand-, base-, co-catalyst-free copper fluorapatite (CuFAP) as a versatile, ecofriendly, heterogeneous and reusable catalyst for an efficient homocoupling of arylboronic acid at ambient reaction condition

Shafeek A. R. Mulla,* Santosh S. Chavan, Mohsinkhan Y. Pathan, Suleman M. Inamdar and Taufeekaslam M. Y. Shaikh

This paper describes the first report, in which copper species containing copper fluorapatite (CuFAP) act as ligand-, base-, co-catalyst-free, a versatile, eco-friendly, recyclable, heterogeneous catalyst for an efficient synthesis of symmetric biaryls in excellent yield from homocoupling of arylboronic acids in methanol solvent at ambient reaction conditions.