Benzotriazol-1-ylmethanol: An excellent bidentate ligand for the copper/palladium-catalyzed C-N and C-C coupling reaction

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Dedicated to Professor Richard R. Schmidt on the occasion of his 78th anniversary

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Abstract

An efficient benzotriazole based N,O bidentate ligands for the Cu-catalyzed N-arylation of π-excessive nitrogen heterocycles is described. This ligand accomplishes C-N coupling of N-heterocycles and C-C coupling of boronic acids with a variety of hindered, functionalized aryl/heteroaryl halides under mild reaction conditions in good to excellent yields. Using his ligand C-N and C-C (Suzuki) couplings with bromoarenes could be conducted with less catalyst loading. A wide array of deactivated and hindered aryl halides react cleanly to afford the functionalized biaryl derivatives in high yields.

Keywords: *N*-Heterocycles, Cu-catalysis, *N*-arylation, benzotriazol-1-ylmethanol

Introduction

The classical copper-mediated Ullmann reaction has strengthened the research community with the functionalities such as diaryl ethers, diaryl amines and diaryl thio-ethers, owing to their importance as structural motif in a wide range of molecules. However, the harsh reaction conditions and moderate yields give rise to increased demand for new methods to facilitate the synthesis of such compounds.[1,2] Among such compounds, *N*-aryl heterocycles are an important class of compounds because of their significant pharmacological, biological and chemical activities.[3] Accordingly, during the last decade, significant advances have been reported in the development of cross-coupling methodology.[2] Traditionally, these moieties have been prepared with nucleophilic aromatic substitution or by Ullman type coupling.[1,4] However, for *N*-aryl

heterocycles, other methodologies need additional steps to convert aryl halides into the corresponding reagents such as aryllead triacetate,[5a-c] arylboronic acids,[5d-f] aryl stannanes,[5g-j] triphenylbismuths,[5h] diaryliodonium salts,[5k] aryl siloxanes,[5l] and which are limited by the high costs and poor availability of the substrate. Also, in addition, the synthesis of some of these reagents may involve the use of highly toxic materials and unstable reagents.[3c] Although, there are lot of development in palladium-catalyzed C-N bond forming reactions[6] but the copper catalyzed *N*-arylations of *N*-heterocycles with aryl halides promoted by ligands attracted much attention due to its economy and efficiency.[2,6] So far, many efficient ligands have been used with copper such as (S)-pyrrolidinylmethylimidazoles,[7] diazabutadiene,[8] 2-aminopyrimidine-4, 6-diol,[9] 1,10-phenanthroline derivatives,[10] diamines,[11] aminoarenethiol,[12] amino acid derivatives,[13] 8-hydroxyquinoline,[14] pyrrolidine-2-phosphate,[15] oxime-phosphine oxides,[16] phosphoramidite,[17] *N*-hydroxymaleimide,[18a] acylhydrazone[18b] and L-histidine,[19] while various phosphine ligands have been explored in the case of palladium-catalyzed reactions.[2f] The Pd-catalyzed C-C coupling reaction (Suzuki-Miyuara) also represents one of the most synthetically valuable methods for the synthesis of biaryl derivatives.[20] These catalytic systems using different derivatives of indole, benzimidazole, pyrrole and imidazole have been reported. However, very few examples of coupling of aryl halides with different nitrogen heterocycles have been disclosed. The majority of aryl halides investigated to date, already limited in examples, were aryl iodides. All of these methods are useful in their own right, though each suffers a lack of generality. With these requirements in mind, we considered that steric hindrance and strong electron-donation property of the benzotriazole derivatives could create practical catalyst system for the coupling reactions. The benzotriazole moiety has been much explored by the Katritzky group[21] as a synthetic auxiliary in a number of transformations due to its interesting properties.

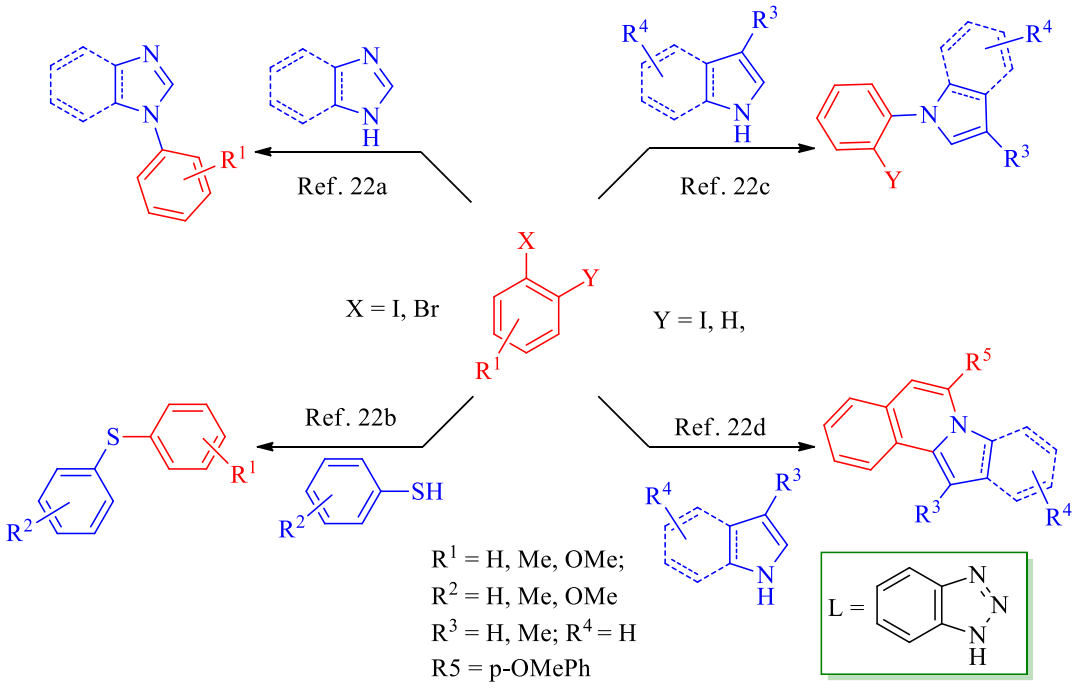


Figure 1. Coupling reactions using benzotriazole as a ligand.

Our group has also been utilizing benzotriazole as a catalyst for various transformations.[22] Thus, as a part of our ongoing research, we noticed that this air and moisture stable molecule have excellent coordination capability which could be favourable for stabilizing catalytic species and assisting the catalytic cycle (Figure 1).

Using benzotriazole (**L1)** as ligand, C-N, C-S and C-C coupling with different derivatives of indole, benzimidazole, pyrrole and imidazole and substituted aryl halides have been reported.[22a-c] Recently, we reported the use of benzotriazole (**L1**) and benzotriazol-1-yl-methanol (**L3**) ($BtCH_2OH$) as a ligand in the tandem synthesis of indolo- and pyrrolo-[2,1-*a*]isoquinolines by the addition of *N*-heterocycles onto *ortho*-haloarylalkynes, followed by intramolecular arylation.[22d]

In continuation of our ongoing work using benzotriazole as a ligand, herein we are reporting benzotriazol-1-yl-methanol (**L3)** as a robust and inexpensive ligand for the copper-catalyzed C–N coupling and palladium-catalyzed C–C (Suzuki) coupling reactions.

Results and Discussion

In our initial communication, with utilizing benzotriazole as ligands for copper-catalysis, a number of *N*-heterocycles were reported to undergo coupling with aryl halide in DMSO as a solvent. In a subsequent, more detailed exploration of the coupling of aryl halides with indoles became apparent that derivatives of benzotriazole were superior to the parent ligand (Figure 2).[22b-c, e]

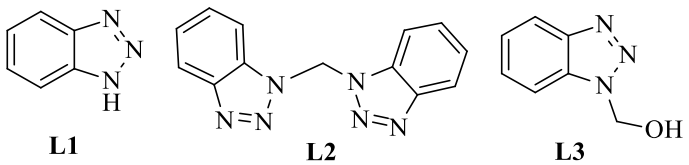
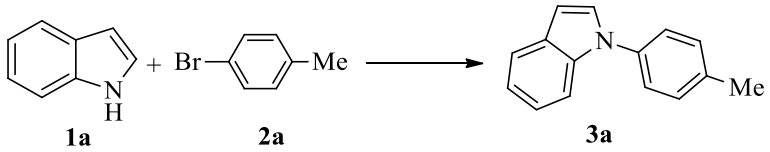


Figure 2. Benzotriazole based designed ligands.

To search for most optimal catalysts system for the *N*-arylation, we initiated our investigation with 1.0 mmol indole (**1a**) and 1.2 equiv of *p*-bromotoluene (**2a)** using 5.0 mol % of CuI, 10 mol % of ligand **L1** and 2.0 equiv of K-O-*t*Bu in 2.0 mL of DMSO at 25 °C for 12 h, the coupling product **3a** was observed in poor yield (Table 1, entry 1). With increasing temperature upto 80 °C, product **3a** was obtained in 32% yield (Table 1, entry 2). On further increasing the temperature upto 120 °C, coupling product **3a** was obtained in 40% (after 12 h) and 48% yields (after 18 h) respectively (Table 1, entry 3–4). Increasing the catalyst loading from 5 to 10 mol % affprded the coupling product **3a** in 58% yield (Table 1, entry 5).

Table 1. Optimization of the reaction condition for the *N*-arylation[a]



1a **2a** **3a**

Entry	Cat. (mol %)	**L** (mol %)	Solvent	T(h) / T(°C)	Yield (%)[b]
1	CuI (5)	**L1** (10)	DMSO	12 / 25	8
2	CuI (5)	**L1** (10)	DMSO	12 / 80	32
3	CuI (5)	**L1**(10)	DMSO	12 / 120	40
4	CuI (5)	**L1** (10)	DMSO	18 / 120	48
5	CuI (10)	**L1** (20)	DMSO	18 / 120	58
6	CuI (10)	**L1** (20)	DMSO	24 / 120	60
7	CuI (5)	**L2** (5)	DMSO	12 / 120	54
8	CuI (5)	**L2** (5)	DMSO	18 / 120	65
9	CuI (10)	**L2** (10)	DMSO	18 / 120	74
10	**CuI (10)**	**L3 (10)**	**DMSO**	**18/ 120**	**90**
11	CuI (5)	**L3** (5)	DMSO	18/ 120	62
12	CuI (10)	**L3** (10)	DMSO	18 / 120	70[c]
13	CuI (10)	**L3** (10)	DMSO	18 / 120	76[d]
14	CuI (10)	**L3** (10)	DMSO	18 / 120	61[e]
15	CuI (10)	**L3** (10)	DMF	18 / 120	83
16	CuI (10)	**L3** (10)	DMA	18/ 120	80
17	CuI (10)	**L3** (10)	Dioxane	18 / 120	78
18	CuI (10)	**L3** (10)	Toluene	18 / 110	71
19	CuCl (10)	**L3** (10)	DMSO	18 / 120	81
20	CuBr (10)	**L3** (10)	DMSO	18/120	85
21	Cu_2O(10)	**L3** (10)	DMSO	18 / 120	58
22	$Cu(OAc)_2$(10)	**L3** (10)	DMSO	18 / 120	63

[a] All the reactions were performed using 1.0 mmol of indole **1a**, 1.2 equiv of **2a**, 2.0 equiv of KO-*t*Bu, catalyst and ligand (**L)** in 2.0 mL of solvent under nitrogen atmosphere unless otherwise noted. [b] Isolated yields. [c] using 2.0 equiv of NaOEt. [d] Using 2.0 equiv of K_3PO_4. [e] Using 2.0 equiv of NaOH.

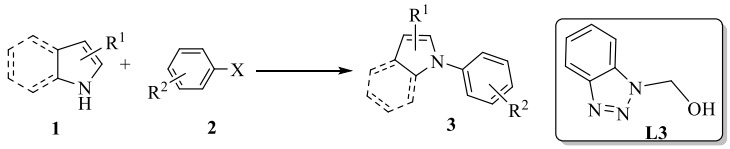
When the same reaction was continued for a longer time, no significant effect on the yield of the product was observed (Table 1, entry 6). In order to increase the yields and make reaction conditions mild, we investigated some designed *N*,*N*- and *N*,*O*-bidentate ligands having more donating sites with bulkiness which could create practical catalyst system for the coupling reactions. The use of *N*,*N*-bidentate ligand **L2** made no considerable improvement on the yield of the coupling product (Table 1, entries 7–8). The use of 10 mol % of the ligand **L2** could afford

the coupling product in 74% yield (Table 1, entry 9). After obtaining the slight improvement in the yield of the coupling product with *N*, *N*-bidentate ligand, we next employed the *N*, *O*-bidentate ligand **L3** , and it was found that ligand **L3** afforded the desired coupling product in 90% at 120 °C after 18 h (Table 1, entry 10). When the same reaction was carried out with 5 mol % ligand-catalyst system, thedesired product was obtained in 62% yield (Table 1, entry 11). Other strong bases like NaOEt, K_3PO_4, and NaOH, gave inferior results under the same conditions (Table 1, entries 12-14). Amongst different solvents, polar solvents like DMSO, DMF and DMA were found suitable for the reaction and afforded the coupling product in high yield in comparison to the non polar solvents like dioxane and toluene (Table 1, entries 15–18).

Other copper sources like CuCl, CuBr afforded the desired product in comparable yield (Table1, entries 19–20) while Cu_2O and $Cu(OAc)_2$ were found to be less effective (Table1, entries 21–22). The commercially available ligand **L3** can be readily prepared in a straight-forward fashion from the inexpensive starting material benzotriazole and formaldehyde, in a single step with excellent yield, in multigram-scale.

After optimizing the reaction condition for *N*-arylation, we extend the methodology to more challenging substrate combinations (Table 2). We were delighted to find that the *N*-arylation of indole and substituted indoles such as 3-methyl and 2-methyl indole with a variety of aryl bromides containing electron-rich *o*- and *p*-substituents proceeded smoothly to give the corresponding products in good to excellent yields (Table 2, entries 1-14). When aryl halide bearing electron–withdrawing substituents were reacted with indoles, coupling-products were obtained in comparative yields (Table 2, entries 4, 9–10). Having attained results on the coupling of indoles, we further extended the scope of the reaction on other π-electron-rich nitrogen heterocycles with functionalized aryl bromides. The coupling proceeded smoothly with imidazole, substituted imidazoles and pyrroles and afforded the corresponding N-arylated products in 72–90% yields (Table 2, entries 15–25). In case of carbazoles, significant yields of the products were obtained with substituted aryl halides (Table 2, entries 26–29). We were pleased to find that our catalytic system could tolerate a variety of functional groups such as nitrile and nitro functionality (Table 2, entries 4, 9–10, 20). Besides these arylhalides, *N*-heterocycles were also coupled with heteroaryl halide **2c** efficiently (Table 2, entries 3, 7, 15, 21). The results indicated that the developed protocol worked well with a wide range of *N*-heterocycles (Table 2). Gratifyingly, the hindered substrate also underwent *N*-arylation smoothly in good yields.

Table 2. Coupling of aryl and heteroaryl bromides with *N*-heterocycles using CuI and ligand **L3**[a]



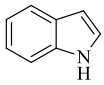
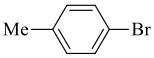
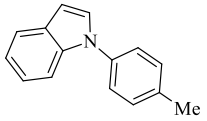
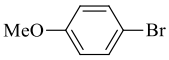
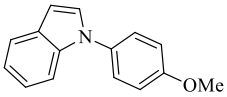
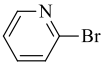
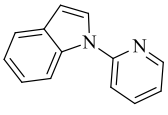
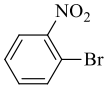
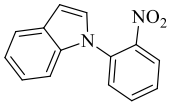
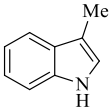
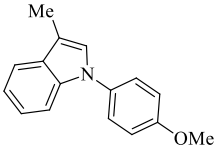
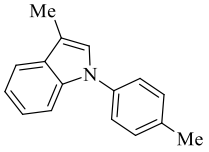
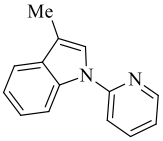
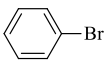
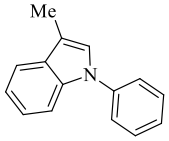
Entry	Indole	Halide	Product	Yield (%)[b]
1	 **1a**	 **2a**	 **3a**	90
2	**1a**	 **2b**	 **3b**	86
3	**1a**	 **2c**	 **3c**	85
4	**1a**	 **2d**	 **3d**	89
5	 **1b**	**2b**	 **3e**	88
6	**1b**	**2a**	 **3f**	87
7	**1b**	**2c**	 **3g**	82
8	**1b**	 **2e**	 **3h**	83

Table 2 (continued)

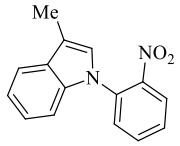
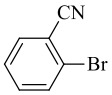
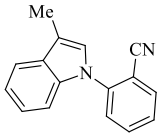
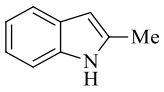
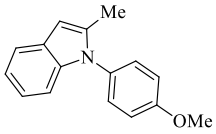
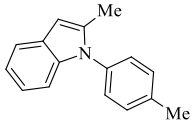
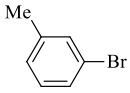
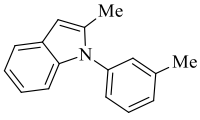
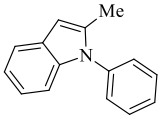
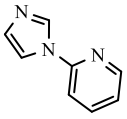
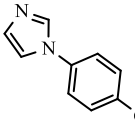
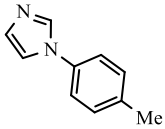
Entry	Indole	Halide	Product	Yield (%)[b]
9	**1b**	**2d**	 **3i**	89
10	**1b**	 **2f**	 **3j**	87
11	 **1c**	**2b**	 **3k**	82
12	**1c**	**2a**	 **3l**	80
13	**1c**	 **2g**	 **3 m**	89
14	**1c**	**2e**	 **3n**	82
15	 **1d**	**2c**	 **3o**	81
16	**1d**	**2b**	 **3p**	89
17	**1d**	**2a**	 **3q**	90

Table 2 (continued)

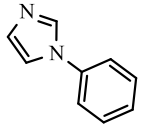
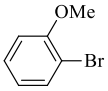
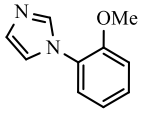
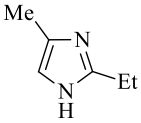
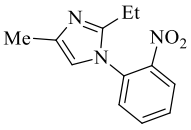
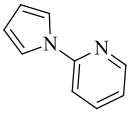
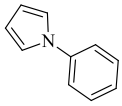
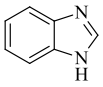
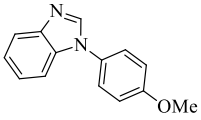
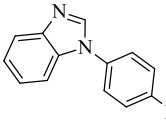
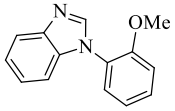
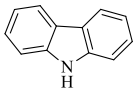
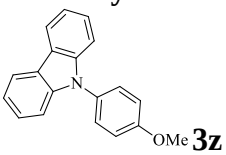
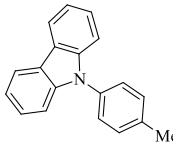
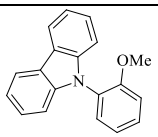
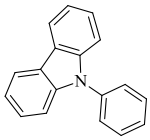
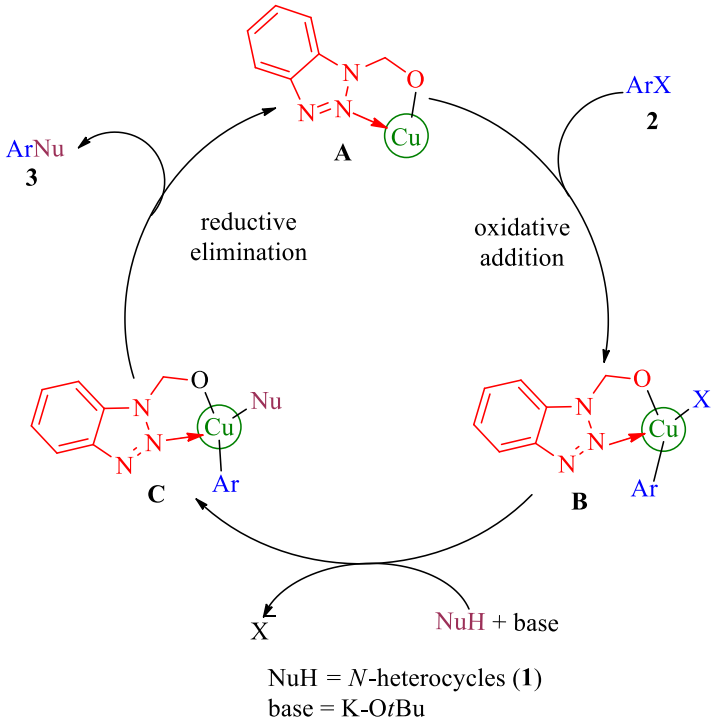
Entry	Indole	Halide	Product	Yield (%)[b]
18	**1d**	**2e**	 **3r**	88
19	**1d**	 **2h**	 **3s**	86
20	 **1e**	**2d**	 **3t**	82
21	 **1f**	**2c**	 **3u**	84
22	**1f**	**2e**	 **3v**	72
23	 **1g**	**2b**	 **3w**	81
24	**1g**	**2a**	 **3x**	80
25	**1g**	**2h**	 **3y**	88
26	 **1h**	**2b**	 **3z**	78
27	**1h**	**2a**	 **3aa**	90

Table 2 (continued)

Entry	Indole	Halide	Product	Yield (%)[b]
28	**1h**	**2h**	 **3ab**	83
29	**1h**	**2e**	 **3ac**	86

[a] The reactions were performed using 1.0 mmol of *N*-heterocycle **1**, 1.2 mmol of ary/heteroaryl halide **2**, 2.0 equiv of K-O-*t*Bu, 10 mol % of CuI, 10 mol % of **L3** in 2.0 mL of DMSO at 120 ºC for 18 h under nitrogen atmosphere. [b] Isolated yields.

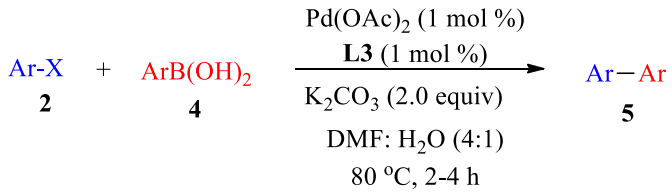
A plausible catalytic cycle for the formation of *N*-aryl heterocycles based on the previously reported mechanism is shown in Scheme 1.[2,4] Presumably, CuI and ligand **L3** ($BtCH_2OH$) generates the copper (I) complex **A**, which upon oxidative addition with aryl halides results in the formation of intermediate **B**. Copper complex **C** is formed by the attack of nucleophile (*N*-heterocycle) in the presence of base. Reductive elimination of **C** affords *N*-arylated product **3** and regenerates copper complex **A**. Study of the accuracy of this mechanism is in progress.



Scheme 1. Plausible mechanism.

The reaction conditions and effectiveness of the ligand **L3** was further extended for the Suzuki coupling reaction.[20] We optimized the reaction condition for the Suzuki reaction by using 1.0 mmol of *p*-bromotoluene (**2a**) and *p*-methoxyphenyl boronic acid (**4a**) , and it was found that 1.0 mol % $Pd(OAc)_2$ and 1.0 mol % of Ligand **L3** in 2.0 mL of DMF:H_2O (4:1) at 80 °C for 2 h was best among various reaction condition.[23] The scope of the reaction was examined by using various aryl/heteroaryl halides **2** with a variety of boronic acid **4a**–**j** (Table 3, entries 1–17). The reaction proceeded well with hindered boronic acid **4b** and provided coupling product **5b** in 88% yield (Table 3, entry 2). Reaction of 5-bromo-1*H*-indole (**2i**) with (1*H*-indol-5-yl)boronic acid (**4c**) under the same reaction conditions afforded the 1*H*,1′*H*-5,5′-biindole (**5c**) selectively in 86% yield without any *N*-arylated product (Table 3, entry 4). Coupling of 4-(4-bromophenyl)pyrrolo [1,2-*a*]quinoxaline (**2j)** with boronic acids **4a** and **4e** afforded the Suzuki coupling products **5e**–**f** in 92 and 90% yields respectively (Table 3, entries 6–7). When the [1,1′-biphenyl]-2-ylboronic acid (**4f**) was used with aryl halides bearing electron-withdrawing, as well as electron-donating group, the coupling products **5g–h** were obtained in 85 and 80% yields respectively (Table 3, entries 8–9). Reaction of (4-((4-fluorobenzyl)oxy)phenyl)boronic acid (**4g**) with aryl halides **2k** and **2a** afforded the coupling products **5j–k** in excellent yields (Table 3, entries 11–12). Coupling of 1,4-dibromo-2,5-diiodobenzene (**2n**), with *p*-tolylboronic acid (**4j**) selectively afforded the diarylated product **5o** in 83% yield (Entry 16). Reaction of tetrabromothiophene (**2o**) with 4.0 equiv of *p*-methoxyphenyl boronic acid provided the 2,3,4,5-tetraarylated thiophene **5p** in 79 % yields (Table 3, entry 17).

Table 3. Suzuki reaction with different boronic acids[a]



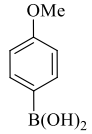
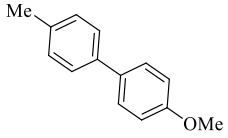
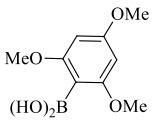
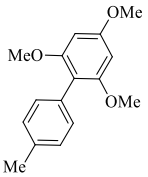
Entry	Aryl Halide	Boronic Acids	Product	Yield (%)[b]
1	**2a**	 **4a**	 **5a**	92
2	**2a**	 **4b**	 **5b**	88

Table 3 (continued)

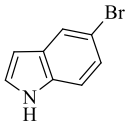
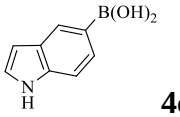
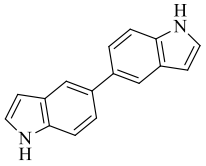
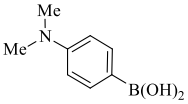
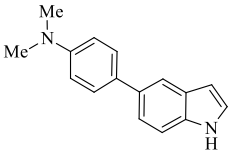
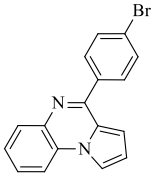
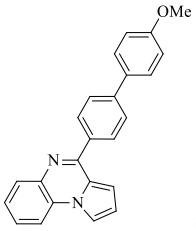
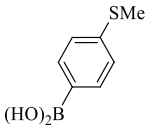
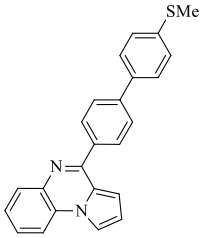
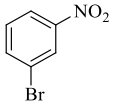
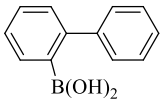
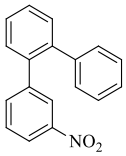
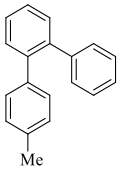
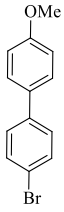
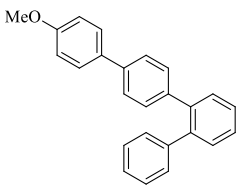
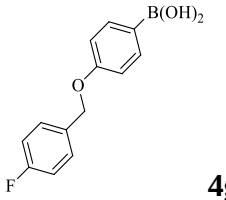
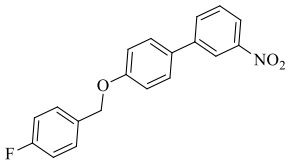
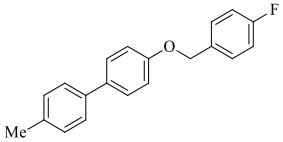
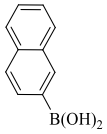
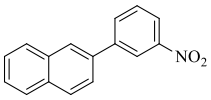
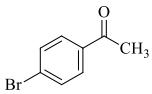
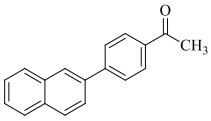
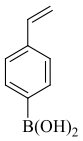
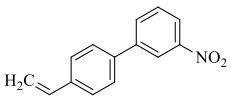
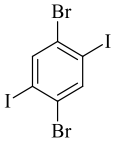
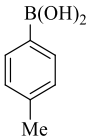
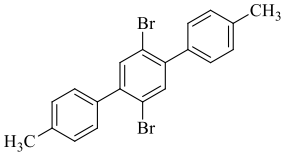
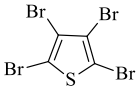
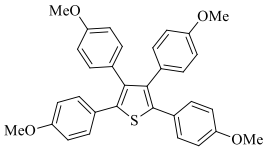
Entry	Aryl Halide	Boronic Acids	Product	Yield (%)[b]
4	 **2i**	 **4c**	 **5c**	86
5	**2i**	 **4d**	 **5d**	84
6	 **2j**	**4a**	 **5e**	92
7	**2j**	 **4e**	 **5f**	90
8	 **2k**	 **4f**	 **5g**	85
9	**2a**	**4f**	 **5h**	80
10	 **2l**	**4f**	 **5i**	84

Table 3 (continued)

Entry	Aryl Halide	Boronic Acids	Product	Yield (%)[b]
11	**2k**	 **4g**	 **5j**	89
12	**2a**	**4g**	 **5k**	90
13	**2k**	 **4h**	 **5l**	83
14	 **2m**	**4h**	 **5m**	89
15	**2k**	 **4i**	 **5n**	87
16	 **2n**	 **4j**	 **5o**	83[c]
17	 **2o**	**4a**	 **5p**	79[d]

[a] Reactions were performed using arylhalide **1** (1.0 mmol), boronic acids **2** (1.2 equiv), $Pd(OAc)_2$ (1.0 mol %), **L3** (1.0 mol %), and K_2CO_3 (2.0 equiv) in DMF/ H_2O at 80 °C for 2-4 h unless otherwise noted. [b] Isolated. yields. [c] Boronic acid **4j** (2.0 equiv), $Pd(OAc)_2$ (3.0 mol %), **L4** (3.0 mol %), and K_2CO_3 (4.0 equiv) in DMF/Water (4:1) at 80 °C for 3 h. [d] boronic acid **4a** (4.0 equiv) and K_2CO_3 (8.0 equiv).

Conclusions

In summary, we have described benzotriazol-1-yl-methanol (**L3)** as an efficient N, O-bidentate ligand for the C-N and Suzuki coupling reaction. The ligand efficiently catalyzed the coupling of π-excessive nitrogen heterocycles with variety of aryl halides under copper-catalysis. Efficasy of the ligand was sucessfully extended for the palladium-catalyzed Suzuki coupling reaction. The C-C coupling of variety of boronic acids with various aryl halides has been accomplished under mild reaction conditions using low catalyst loading. The designed catalyst for the C-N and C-C coupling reaction tolerates variety of functional groups and afforded the coupling products in good to excellent yield. Mild reaction conditions, low cost of the catalyst and high yield of the coupling products, increasing the overall utility of this process. The catalytic system is expected to find application in general, and in the synthesis of various biologically important heterocyclic compounds.

Experimental Section

General. All reagents used were AR grade. Melting points were determined using a Buchi B-540 melting point apparatus. ^{1}H (300 MHz), and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker 300 NMR spectrometer and ^{1}H (400 MHz), and ^{13}C NMR (100 MHz) was recorded on Jeol 400 NMR spectrometer in $CDCl_3$ (with TMS for ^{1}H and chloroform-*d* for ^{13}C as internal references) unless otherwise stated. Column chromatography was performed on silica gel (100–200 mesh). The reactions were monitored by thin-layer chromatography (TLC) using aluminum sheets with silica gel 60 F254 (Merck). High resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer.

General procedure for the synthesis of BtCH_2Bt, L2. The CuI (1.0 mol %) was added to a 50 mL round bottom flask containing the BtCH_2Cl (1.00 mmol), benzotriazole (1.0 mmol) and potassium *tert*-butoxide (1.6 equiv) in 5 mL of DMSO. The flask was sealed with a cap containing a PTFE septum. The mixture was then heated at 110 ˚C for 1 h. The reaction mixture was washed with ethyl acetate and water. The organic layer was then washed with brine and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate as eluent.

1-[(1*H*-Benzotriazol-1-yl)methyl]-1*H*-benzotriazole (**L2**)**.** The product was obtained as a white solid – mp 78–80 °C, yield - 86% : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06 (d, *J* 8.4 Hz, 1H), 7.95 (d, *J* 8.4 Hz, 1H), 7.87–7.83 (m, 2H), 7.56 (dt, *J* 6.3 and 0.9 Hz, 1H), 7.42–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 146.3, 145.0, 132.6, 128.6, 127.5, 124.6, 120.2, 118.5, 109.9, 64.8. HRMS (ESI) Calcd for $C_{13}H_{10}N_6$ ($M+H^+$): 250.0967, found 250.0969.

General procedure for the synthesis of *N*-aryl heterocycles (**3a-3ac**). The CuI (10 mol %) and ligand L3 (10 mol %), was added to a 5ml round bottom flask containing the aryl halide 2 (1.0

mmol), *N*- heterocycles 1 (1.0 mmol) and potassium *tert*-butoxide (2.0 equiv.) in 1.5 ml of DMSO. The flask was sealed with a cap containing a PTFE septum. The mixture was then heated at 120 °C until the aryl halides were consumed, as determined by TLC. The reaction mixture was washed with ethyl acetate and water. The organic layer was then washed with brine and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the crude residue was purified by column chromatography on silica gel using hexanes or a mixture of hexane and ethylacetate as eluent. *N*-arylheterocycles were isolated in the yields reported in Table 2.

1-(4-Methoxyphenyl)-1*H*-indole (**3b**)**.** The product was obtained as a white solid– mp 68–70 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.72 (d, *J* 7.5 Hz, 1H), 7.49–7.41 (m, 3H), 7.30 (d, *J* 3.3 Hz, 1H), 7.26–7.15 (m, 2H), 7.06–7.03 (m, 2H), 6.68 (d, *J* 3.0 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.2, 136.3, 132.8, 128.9, 128.3, 125.9, 122.1, 120.9, 120.0, 114.7, 110.3, 102.8, 55.6. HRMS (ESI) Calcd for $C_{15}H_{13}NO$ ($M+H^+$): 223.0997, found 223.1002.

1-Pyridin-2-yl-1*H*-indole (**3c**)**.** The product was obtained as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.58–8.57 (m, 1H), 8.21 (d, *J* 8.1 Hz, 1H), 7.82 (d, *J* 3.0 Hz, 1H), 7.73 (d, *J* 3.0 Hz, 1H), 7.67 (d, *J* 7.5 Hz, 1H), 7.57–7.50 (m, 1H), 7.32–7.09 (m, 3H), 6.72 (d, *J* 3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.5, 149.0, 138.4, 135.0, 130.4, 123.1, 122.6, 121.2, 121.1, 120.1, 114.6, 112.9, 105.5. HRMS (ESI) Calcd for $C_{13}H_{10}N_2$($M+H^+$): 194.0844, found 194.0847.

1-(2-Nitrophenyl)-1*H*-indole (**3d**)**.** The product was obtained as a yellow solid – mp 80–83 °C, : ^{1}H NMR (300 MHz, $CDCl_3$)δ: 8.03 (dd, *J* 6.9 and 1.2 Hz, 1H), 7.77–7.64 (m, 2H), 7.60–7.54 (m, 2H), 7.23–7.11 (m, 4H), 6.73 (d, *J* 3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 136.6, 133.6, 132.9, 129.7, 128.9, 128.3, 127.9, 125.5, 122.9, 121.3, 120.9, 109.4, 105.0. HRMS (ESI) Calcd for $C_{14}H_{10}N_2O_2$ ($M+H^+$): 238.0742, found 238.0746.

1-(4-Methoxyphenyl)-3-methyl-1*H*-indole (**3e**)**.** The product was obtained as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.69–7.57 (m, 1H), 7.46 (s, 1H), 7.36 (d, *J* 6.3 Hz, 1H), 7.18–7.09 (m, 3H), 7.08–7.05 (m, 3H), 3.78 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$)δ: 154.3, 136.9, 128.9, 128.4, 128.1, 127.9, 126.7, 121.8, 121.8, 119.2, 118.8, 112.4, 111.7, 110.7, 55.7, 9.7. HRMS (ESI) Calcd for $C_{16}H_{15}NO$ ($M+H^+$): 237.1154, found 237.1159.

3-Methyl-1-(pyridin-2-yl)-1*H*-indole (**3g**)**.** The product was obtained as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.55–8.53 (m, 1H), 8.22 (d, *J* 8.4 Hz, 1H), 7.82–7.76 (m, 1H), 7.60 (d, *J* 7.2 Hz, 1H), 7.52 (s, 1H), 7.45 (dd, *J* 7.8 and 0.6 Hz, 1H), 7.33–7.19 (m, 2H), 7.14–7.09 (m, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.6, 148.8, 138.2, 135.3, 131.0, 123.2, 120.7, 119.4, 119.0, 114.8, 114.0, 113.0, 9.7. HRMS (ESI) Calcd for $C_{14}H_{12}N_2$ ($M+H^+$): 208.1000, found 208.1005.

3-Methyl-1-phenyl-1*H*-indole (**3h**)**.** The product was obtained as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64–7.62 (m, 1H), 7.58–7.56 (m, 1H), 7.52–7.47 (m, 3H), 7.37–7.30 (m, 2H), 7.27–7.15 (m, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 131.0, 129.5, 129.2, 125.8, 125.5, 123.9, 122.3, 119.7, 119.2, 112.8, 110.3, 9.6. HRMS (ESI) Calcd for $C_{15}H_{13}N$ ($M+H^+$): 207.1048, found 207.1054.

3-Methyl-1-(2-nitrophenyl)-1*H*-indole (**3i**)**.** The product was obtained as a yellow solid – mp 73–74 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.01 (dd, *J* 1.3 and 6.9 Hz, 1H), 7.74 (dt, *J* 1.5 and

6.5 Hz, 1H), 7.66–7.12 (m, 3H), 7.25–7.14 (m, 3H), 6.95 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 146.0, 136.7, 133.5, 133.1, 129.6, 129.4, 127.7, 125.5, 125.2, 122.9, 120.4, 119.4, 114.4, 119.3, 9.6. HRMS (ESI) Calcd for $C_{15}H_{12}N_2O_2$ ($M+H^+$): 252.0899, found 252.0902.

2-(3-Methylindol-1-yl)benzonitrile (**3j**)**.** The product was obtained as a white solid – mp 127–129 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76–7.64 (m, 2H), 7.62–7.59 (m, 1H), 7.46 (dt, *J* 1.2 and 6.6 Hz, 1H), 7.35(dd, *J* 1.5 and 6.3 Hz, 1H), 7.33 (dd, *J* 2.7 and 3.9 Hz, 1H), 7.31–7.22 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.2, 136.3, 134.5, 133.8, 129.9, 127.0, 126.8, 125.5, 122.8, 120.6, 119.4, 114.2, 110.2, 109.3, 9.6. HRMS (ESI) Calcd for $C_{16}H_{12}N_2$ ($M+H^+$): 232.1000, found 232.1006.

1-(4-Methoxyphenyl)-2-methyl-1*H*-indole (**3k**)**.** The product was obtained as a white solid – mp 63–65 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58–7.54 (m, 1H), 7.28–7.23 (m, 2H), 7.12–7.05 (m, 4H), 7.02 (d, *J* 2.1 Hz, 1H), 6.37 (s, 1H), 3.89 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.0, 138.5, 137.4, 130.6, 129.2, 128.0, 120.8, 119.8, 119.4, 114.5, 109.9, 100.7, 55.5, 13.2. HRMS (ESI) Calcd for $C_{16}H_{15}NO$ ($M+H^+$): 237.1154, found 237.1157.

2-Methyl-1-*p*-tolyl-1*H*-indole (**3l**)**.** The product was obtained as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57–7.54 (m, 1H), 7.33 (d, *J* 8.1 Hz, 2H), 7.26–7.22 (m, 2H), 7.13–7.06 (m, 3H), 6.39 (s, 1H), 2.46 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.2, 137.6, 137.1, 135.3, 130.0, 128.5, 127.8, 121.0, 120.3, 119.8, 110.0, 100.9, 21.2, 13.3. HRMS (ESI) Calcd for $C_{16}H_{15}N$ ($M+H^+$): 221.1204, found 221.1209.

2-Methyl-1-*m*-tolyl-1*H*-indole (**3m**)**.** The product was obtained as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58–7.54 (m, 1H), 7.39 (t, *J* 7.5 Hz, 1H), 7.25–7.19 (m, 1H), 7.15–7.04 (m, 5H), 6.38 (s, 1H), 2.42 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.4, 138.1, 137.8, 137.0, 129.1, 128.5, 128.4, 128.1, 124.9, 120.9, 119.8, 119.5, 110.0, 101.1, 21.3, 13.4. HRMS (ESI) Calcd for $C_{16}H_{15}N$ ($M+H^+$): 221.1204, found 221.1208.

1-(4-Methoxyphenyl)-1*H*-imidazole (**3p**)**.** The product was obtained as a white solid – mp 64–66 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.33–7.28 (m, 2H), 7.20 (d, *J* 6.6 Hz, 2H), 7.03–6.97 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.8, 135.8, 130.7, 130.0, 123.2, 118.7, 114.8, 55.6. HRMS (ESI) Calcd for $C_{10}H_{10}N_2O$ ($M+H^+$): 174.0793, found 174.0796.

1-(4-Tolyl)-1*H*-imidazole (**3q**)**.** The product was obtained as a white solid – mp 93–95 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.82 (s, 1H), 7.27 (s, 4H), 7.25 (s, 1H), 7.19 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.4, 135.6, 134.9, 130.3, 130.1, 121.4, 118.3, 20.9. HRMS (ESI) Calcd for $C_{10}H_{10}N_2$ ($M+H^+$): 158.0844, found 158.0847.

1-Phenyl-1*H*-imidazole (**3r**)**.** The product was obtained as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.74 (s, 1H), 7.34–7.39 (m, 2H), 7.21–7.25 (m, 3H), 7.14 (s, 1H), 7.12 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.1, 135.4, 130.3, 129.8, 127.2, 121.4, 118.2. HRMS (ESI) Calcd for $C_9H_8N_2$ ($M+H^+$): 144.0687, found 144.0689.

1-(2-Methoxyphenyl)-1*H*-imidazole (**3s**)**.** The product was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.79 (s, 1H), 7.38–7.33 (m, 1H), 7.27(d, *J* 7.5 Hz, 1H), 7.20–7.17(m, 2H),

7.07–7.01(m, 2H), 3.84(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.4, 137.1, 128.9, 128.6, 126.3, 125.4, 120.9, 120.2, 112.2, 55.7. HRMS (ESI) Calcd for $C_{10}H_{10}N_2O$ ($M+H^+$): 174.0793, found 174.0795.

2-Ethyl-4-methyl-1-(2-nitrophenyl)-1*H*-imidazole (**3t**)**.** The product was obtained as a yellow solid – mp 58–60 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.03 (dd, *J* 1.6 and 6.3 Hz, 1H), 7.74 (dt, *J* 1.5 and 6.0 Hz, 1H), 7.66 (dt, *J* 1.5 and 6.3 Hz, 1H), 7.43 (dd, *J* 1.5 and 6.3 Hz, 1H), 6.60 (s, 1H), 2.46 (q, *J* 7.5 Hz, 2H), 2.24 (s, 3H), 1.19 (t, *J* 3.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.5, 146.4, 137.4, 133.5, 131.1, 130.1, 129.8, 125.0, 116.6, 20.2, 13.4, 12.0. HRMS (ESI) Calcd for $C_{12}H_{13}N_3O_2$ ($M+H^+$): 231.1008, found 231.1011.

2-(Pyrrol-1-yl)pyridine (**3u**)**.** The product was obtained as a dark brown oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.46 (dd, *J* 0.9 and 3.0 Hz, 1H), 7.78–7.72 (m, 1H), 7.54 (t, *J* 2.2 Hz, 2H), 7.35–7.29 (m, 1H), 7.14–7.09 (m, 1H), 6.39 (t, *J* 2.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.4, 148.7, 138.4, 120.1, 118.0, 111.4, 111.3, 109.6. HRMS (ESI) Calcd for $C_9H_8N_2$ ($M+H^+$): 144.0687, found 144.0691.

1-(4-Methoxyphenyl)-1*H*-benzoimidazole (**3w**)**.** The product was obtained as a white solid – mp 93–95 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06 (s, 1H), 7.88–7.86 (m, 1H), 7.48–7.38 (m, 3H), 7.35–7.31 (m, 2H), 7.09–7.06 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.3, 143.8, 142.5, 134.2, 129.1, 125.7, 123.5, 122.5, 120.5, 115.1, 110.3, 55.6. HRMS (ESI) Calcd for $C_{14}H_{12}N_2O$ ($M+H^+$): 224.0950, found 224.0956.

1-*p*-Tolyl-1*H*-benzoimidazole (**3x**)**.** The product was obtained as a white solid – mp 87–89 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.08 (s, 1H), 7.89–7.83 (m, 1H), 7.53–7.45 (m, 1H), 7.37–7.36 (m, 3H), 7.33–7.29 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 143.9, 142.4, 138.1, 133.9, 133.8, 130.6, 124.0, 123.6, 122.7, 120.5, 110.5, 21.1. HRMS (ESI) Calcd for $C_{14}H_{12}N_2$ ($M+H^+$): 208.1000, found 208.1004.

1-(2-Methoxyphenyl)-1*H*-benzoimidazole (**3y**)**.** The product was obtained as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.09 (s, 1H), 7.88–7.85 (m, 1H), 7.49–7.41 (m, 2H), 7.33–7.26 (m, 3H), 7.14–7.09 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.9, 143.8, 143.2, 134.4, 129.7, 127.2, 124.7, 123.2, 122.3, 120.9, 120.2, 112.4, 110.7, 55.7. HRMS (ESI) Calcd for $C_{14}H_{12}N_2O$ ($M+H^+$): 224.0950, found 224.0954.

9-(4-Methoxyphenyl)-9*H*-carbazole (**3z**)**.** The product was obtained as a white solid – mp 145–147 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.14 (d, *J* 7.8 Hz, 2H), 7.47–7.42 (m, 2H), 7.39–7.36 (m, 2H), 7.33–7.20 (m, 4H), 7.12–7.07 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.8, 141.3, 130.2, 128.5, 125.8, 123.0, 120.2, 119.6, 115.0, 109.6, 55.6. HRMS (ESI) Calcd for $C_{19}H_{15}NO$ ($M+H^+$): 273.1154, found 273.1157.

9-*p*-Tolyl-9*H*-carbazole (**3aa**)**.** The product was obtained as a white solid – mp 108–110 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.14 (d, *J* 7.5 Hz, 2H), 7.45–7.36 (m, 8H), 7.32–7.25 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 141.1, 137.4, 135.0, 130.5, 127.0, 125.8, 123.2, 120.2, 119.7, 109.8, 109.9, 21.2. HRMS (ESI) Calcd for $C_{19}H_{15}N$ ($M+H^+$): 257.1204, found 257.1207.

9-Phenyl-9*H*-carbazole (**3ac**)**.** The product was obtained as a white solid – mp 84–86 °C : ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.16 (t, *J* 0.9 Hz, 1H), 8.13 (t, *J* 0.9 Hz, 1H), 7.59–7.53 (m, 4H),

7.47–7.42 (m, 1H), 7.41–7.39 (m, 4H), 7.32–7.26 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.9, 137.7, 129.9, 127.5, 127.2, 126.0, 123.4, 120.3, 119.9, 109.8. HRMS (ESI) Calcd for $C_{18}H_{13}N$ ($M+H^+$): 243.1048, found 243.1052.

General procedure for the synthesis of compounds 5a-5p. To a vial was added the aryl halide (1.0 mmol), the boronic acid (1.2 equiv), 1 mol % $Pd(OAc)_2$, 1 mol % of ligand (**L3**) and K_2CO_3 (2.0 equiv) in DMF:H_2O (4:1, 2.0 ml). The solution was flushed with nitrogen, and then stirred at 80 °C until TLC revealed complete conversion of the starting material. The solution was allowed to cool and diluted with H_2O and then extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, concentrated in rotary evaporator, and purified by column chromatography to afford the corresponding product.

2,4,6-Trimethoxy-4′-methylbiphenyl (**5b**)**.** The product was obtained as a white solid – mp: 48–50 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45 (d, *J* 7.8 Hz, 2H), 7.23 (d, *J* 7.8 Hz, 2H), 6.76 (s, 2H), 3.91 (s, 6H), 3.88 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 153.5, 138.5, 137.4, 137.2, 137.1, 129.5, 126.9, 104.2, 60.9, 56.2, 21.1. HRMS (ESI) Calcd for $C_{16}H_{18}O_3$ ($M+H^+$): 258.1256, found 259.1254.

1*H*,1′*H*-5,5′-Biindole (**5c**)**.** The product was obtained as a red oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.13 (brs, 2H), 7.89 (s, 2H), 7.54–7.44 (m, 4H), 6.61 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 134.9, 134.8, 128.4, 124.6, 122.5, 119.3, 111.0, 102.9. HRMS (ESI) calcd for $C_{16}H_{12}N_2$ ($M+H^+$): 232.2799, found 232.4591.

4-(1*H*-Indol-5-yl)-*N*,*N*-dimethylaniline (**5d**)**.** The product was obtained as a white solid – mp: 134–136 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07 (brs, 1H), 7.80 (s, 1H), 7.54 (d, *J* 8.7 Hz, 2H), 7.41 (dd, *J* 8.7 and 2.7 Hz, 2H), 7.23–7.17 (m, 1H), 6.82 (d, *J* 8.7 Hz, 2H), 6.57 (s, 1H), 2.98 (s, 6H); ^{13}C NMR: 149.5, 134.8, 133.6, 131.1, 128.4, 127.9, 124.6, 121.6, 118.3, 113.1, 111.1, 102.9, 40.8. HRMS Calcd for $C_{16}H_{16}N_2$ ($M+H^+$): 236.1313, found 236.1318.

4-(4′-Methoxybiphenyl-4-yl)pyrrolo[1,2-*a*]quinoxaline (**5e**)**.** The product was obtained as a white solid – mp: 187–190 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06 (d, *J* 7.5 Hz, 4H), 7.90 (d, *J* 8.1 Hz, 1H), 7.73 (d, *J* 7.8 Hz, 2H), 7.60 (d, *J* 8.4 Hz, 2H), 7.50–7.40 (m, 2H), 7.07–7.01 (m, 3H), 6.90 (s, 1H), 3.90 (s, 3H); ^{13}C (75 MHz, $CDCl_3$): 159.3, 154.0, 142.2, 136.7, 136.2, 133.0, 130.1, 129.0, 128.2, 127.0, 126.8, 125.3, 125.2, 114.6, 114.3, 114.0, 113.6, 108.6, 55.3. HRMS (ESI) Calcd for $C_{24}H_{18}N_2O$ ($M+H^+$): 350.1419, found 350.1421.

4-(4′-(Methylthio)biphenyl-4-yl)pyrrolo[1,2-*a*]quinoxaline (**5f**)**.** The product was obtained as a pale white solid – mp: 173–175 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10–8.00 (m, 3H), 7.99–7.98 (m, 1H), 7.88–7.86 (m, 1H), 7.73 (d, *J* 8.0 Hz, 2H), 7.60 (d, *J* 8.0 Hz, 2H), 7.51–7.45 (m, 2H), 7.34 (d, *J* 8.8 Hz, 2H), 7.04 (m, 1H), 6.90 (t, *J* 3.3 Hz, 1H), 2.53 (s, 3H); ^{13}C (100 MHz, $CDCl_3$): 153.8, 141.8, 138.1, 137.2, 136.2, 130.2, 129.1, 127.4, 127.1, 127.0, 126.9, 126.8, 125.2, 114.6, 113.9, 113.6, 108.5, 15.7. HRMS (ESI) Calcd for $C_{24}H_{18}N_2S$ ($M+H^+$): 366.1190, found 366.1193.

2-(3-Nitrophenyl)biphenyl (**5g**)**.** The product was obtained as a white solid – mp: 60–62 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.00–7.96 (m, 2H), 7.39 (s, 4H), 7.32–7.22 (m, 2H), 7.14 (s, 3H), 7.04–7.03 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.1, 143.3, 141.0, 140.5, 138.0, 136.1,

130.8, 130.3, 129.9, 128.7, 128.6, 128.2, 127.9, 127.0, 124.6, 121.5. HRMS (ESI) Calcd for $C_{18}H_{13}NO_2$ ($M+H^+$): 275.0946, found 275.0952.

2-(4-Methylphenyl)biphenyl (**5h**)**.** The product was obtained as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.33–7.25 (m, 4H), 7.23–7.18, (m, 1H), 7.13–7.07(m, 4H), 6.95–6.89(m, 3H), 6.54 (d, *J* 7.2 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 141.7, 140.5, 138.5, 137.1, 131.7, 130.6, 129.8, 129.7, 128.6, 127.8, 127.4, 127.2, 127.0, 126.4, 21.1. HRMS (ESI) Calcd for $C_{19}H_{16}$ ($M+H^+$): 244.1252, found 244.1257.

4‴-Methoxy-1,1′:2′,1″:4″,1‴-quaterphenyl (**5i**). The product was obtained as a yellow solid: mp: 140–142 °C :^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57–7.53 (m, 4H), 7.44–7.41 (m, 5H), 7.33–7.29 (m, 1H), 7.24–7.22 (m, 3H), 7.15–7.13 (m, 1H), 6.99–6.98 (m, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 141.4, 140.8, 140.5, 140.2, 139.6, 133.7, 130.5, 130.4, 129.8, 129.4, 128.6, 128.1, 127.8, 127.4, 126.7, 126.6, 126.4, 114.2, 55.3. HRMS (ESI) Calcd for $C_{25}H_{20}O$ ($M+H^+$): 336.1514, found 336.1510.

4′-(4-Fluorobenzyloxy)-3-nitrophenyl (**5j**)**.** The product was obtained as a yellow solid – mp: 65–68 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.31–8.30 (m, 1H), 8.07–8.03 (m, 1H), 7.78 (d, *J* 7.8 Hz, 1H), 7.50–7.45 (m, 3H), 7.37 (q, *J* 5.7 Hz, 2H), 7.03–6.97 (m, 4H), 4.99 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.2, 160.9, 159.1, 148.7, 142.3, 132.5, 132.4, 131.5, 129.7, 129.4, 129.3, 128.3, 121.5, 121.4, 115.8, 115.5, 69.5. HRMS (ESI) Calcd for $C_{19}H_{14}NO_3F$ ($M+H^+$): 323.0958, found 323.0960.

4′-(4-Fluorobenzyloxy)-4-methylbiphenyl (**5k**)**.** The product was obtained as a white solid – mp: 100–105 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44–7.31 (m, 6H), 7.15 (d, *J* 7.8, 2H), 7.02–6.91 (m, 4H), 4.96 (s, 2H), 2.29(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.1, 160.9, 157.9, 137.8, 136.4, 134.1, 132.7, 129.4, 129.3, 129.2, 127.9, 126.6, 115.6, 115.3, 115.0, 69.4, 21.0. HRMS (ESI) Calcd for $C_{20}H_{17}FO$ ($M+H^+$): 292.1263, found 292.1266.

1-(3-Nitrophenyl)naphthalene (**5l**). The product was obtained as a pale yellow solid – mp: 55–57 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.37 (s, 1H), 8.30 (d, *J* 8.4 Hz, 1H), 7.94–7.91(m, 2H), 7.83 (d, *J* 7.5 Hz, 1H), 7.77 (d, *J* 8.1 Hz, 1H), 7.65 (t, *J* 9.3 Hz, 1H), 7.57–7.49 (m, 2H),7.44 (t, *J* 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.3, 142.4, 137.5, 136.1, 133.8, 131.1, 129.2, 128.8, 127.2, 126.7, 126.2, 125.3, 125.0, 124.8, 122.2. HRMS (ESI) Calcd for $C_{16}H_{11}NO_2$ ($M+H^+$): 249.0790, found 249.0794.

1-(4-(Naphthalen-1-yl)phenyl)ethanone (**5m**)**.** The product was obtained as a white solid – mp: 90–91 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.00 (d, *J* 7.8 Hz, , 2H), 7.83–7.74 (m, 3H), 7.51–7.46 (m, 2H), 7.43–7.36 (m, 2H), 7.33–7.31 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.8, 145.7, 138.9, 135.9, 133.7, 131.1, 130.3, 128.3, 126.9, 126.3, 125.9, 125.3, 26.7. HRMS (ESI) Calcd for $C_{18}H_{14}O$ ($M+H^+$): 246.1045, found 246.1048.

3-Nitro-4′-vinylbiphenyl (**5n**)**.** The product was obtained as a white solid – mp: 68–70 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.36(s, 1H), 8.11 (d, *J* 7.2 Hz, 1H), 7.84 (d, *J* 7.1 Hz, 1H), 7.54–7.37 (m, 5H), 6.73 (q, *J* = 10.8 Hz, 1H), 5.78 (d, *J* 17.7 Hz, 1H), 5.26 (d, *J* 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.7, 142.3, 137.8, 136.3, 135.9, 132.7, 129.7, 127.2, 126.9, 126.6, 121.9, 121.6, 114.8. HRMS (ESI) Calcd for $C_{14}H_{11}NO_2$ ($M+H^+$): 225.0790, found 225.0794.

2′,5′-Dibromo-4,4′′-dimethyl-1,1′:4′,1′′-terphenyl (**5o**)**.** The product was obtained as a white solid – mp: 162–164 °C: ^{1}H NMR (400 MHz, $CDCl_3$)δ: 7.60(s, 2H), 7.32 (d, *J* 8.0 Hz, 4H), 7.24 (d, *J* 6.4 Hz, 4H), 2.4 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 137.9, 136.6, 135.2, 129.1, 128.8, 121.4, 21.3. HRMS (ESI) Calcd for $C_{20}H_{16}Br_2$ ($M+H^+$): 413.9619, found 413.9617.

2,3,4,5-Tetrakis-(4-methoxyphenyl)thiophene (**5p**)**.** The product was obtained as a yellow solid – mp: 178–180 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13(d, *J* 8.8 Hz, 4H), 6.84 (d, *J* 8.8 Hz, 4H), 6.74 (d, *J* 8.8 Hz, 4H), 6.65 (d, *J* 8.8 Hz, 4H), 3.75 (s, 6H), 3.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 158.0, 138.3, 137.2, 131.9, 130.3, 129.1, 127.0, 113.7, 113.3, 55.2, 55.0. HRMS (ESI) Calcd for $C_{32}H_{28}O_4S$ ($M+H^+$): 508.1708, found 508.1705.

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