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ARTICLE

Dibenzofuran and Dibenzothiophene based Palladium(II)/NHC Catalysts – Synthesis and Applications in C-C bond formation

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In the quest of new ligand system for Pd(II)/NHCs, we developed new dibenzofuran and dibenzothiophene based Palladium *N*-heterocyclic carbene catalysts **D1**-**D6** in good yields. All the catalysts were characterized by multinuclear NMR and HRMS. X-ray crystal structure of representative dibenzothiophene based Pd(II)/NHC **D4** was determined. Among the precatalysts, **D1** has been shown to be highly effective in the Suzuki-Miyaura cross-coupling reaction of heterocyclic bromides with boronic acids. Besides, **D1** affords diverse arylated benzoxazoles *via* direct C-H bond functionalization with substituted bromo derivatives.

Introduction

Dibenzofuran (DBF) and dibenzothiophene (DBTH) derivatives are valuable targets for synthetic, medicinal and material chemist owing to their splendid applications in biological,[1] pharmaceuticals,[2] polymers[3] and functional materials.[2d, 4] Undeniably, considerable efforts have been devoted to developing synthetic methodologies for functionalized dibenzofurans and dibenzothiophenes and conjugated them with various materials to realize the above-mentioned applications.[5] DBF and DBTH serve as the polyheterocyclic framework to construct multidentate ligand whose applications range from chemosensor,[6] extractant of *f*-block metal cations,[7] high-triplet energy host materials,[8] and organic field-effect transistors[9] and in organic electronics.[10] With suitable donor substituents on DBF and DBTH scaffold forms highly stable transition metal complexes *viz*. zinc,[11] ruthenium,[12] magnesium,[13] zirconium & hafnium[14] and rhodium[15] complexes which find application as a catalyst in lactide polymerization, transfer hydrogenation, ring-opening polymerization, propylene polymerization and desulfurization respectively. *N*-heterocylic carbenes (NHC) have garnered sufficient accolade both in academic and industry as a versatile ligand in view of its distinctive σ-donor ability with metal ions.[16] Besides, metal-NHC promotes facile oxidative-addition of unreactive aryl halides and sterics around the metal center favoring the reductive-elimination in cross-coupling chemistry.[16a] Among various

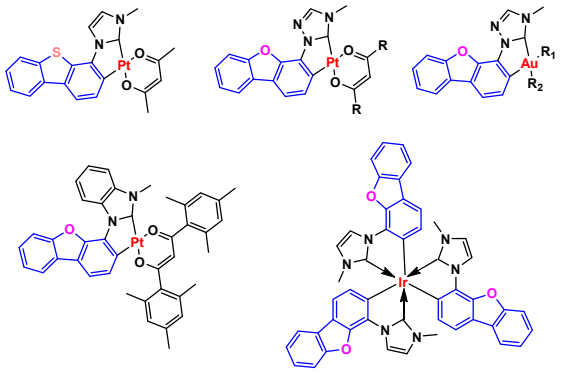

Fig.1 Representative examples of dibenzofuran and dibenzothiophene based metal-NHC complexes.

azolium salts, imidazolium-based metal-NHCs were prominent due to its robustness, high thermal stability, and affordability.[16d, 17] Strassner and co-workers have reported the cycloplatinated *N*-heterocyclic carbene complexes involving the DBF and DBTH framework, which exhibited interesting photophysical properties as phosphorescent emitters.[18] Kang and co-workers have shown the application of isomeric-homoleptic cycloiridated *N*-heterocyclic carbene complexes bearing dibenzofuran in deep-blue phosphorescent OLEDs.[19] Along the same line, Venkatesan and co-workers have reported the NHC-cycloaurated Au(III) complexes arising out of dibenzofuranyl unit showing deep blue to blue-green phosphorescence emission.[20] The above examples clearly show the rich photophysical properties originating from both metal and NHC ligand (Fig. 1). However, to the best of our knowledge, synthesis and catalytic studies on similar

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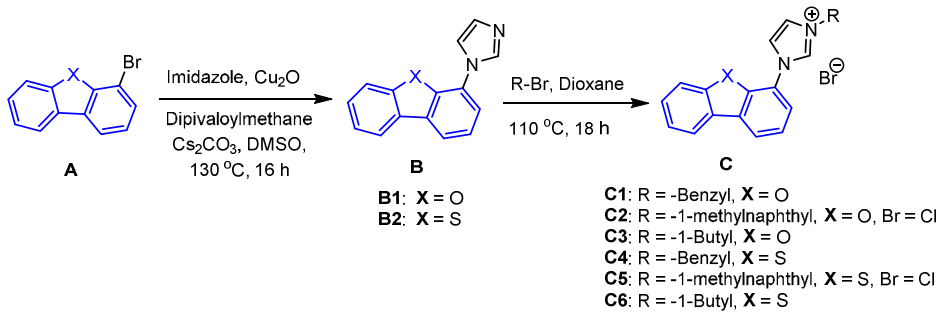
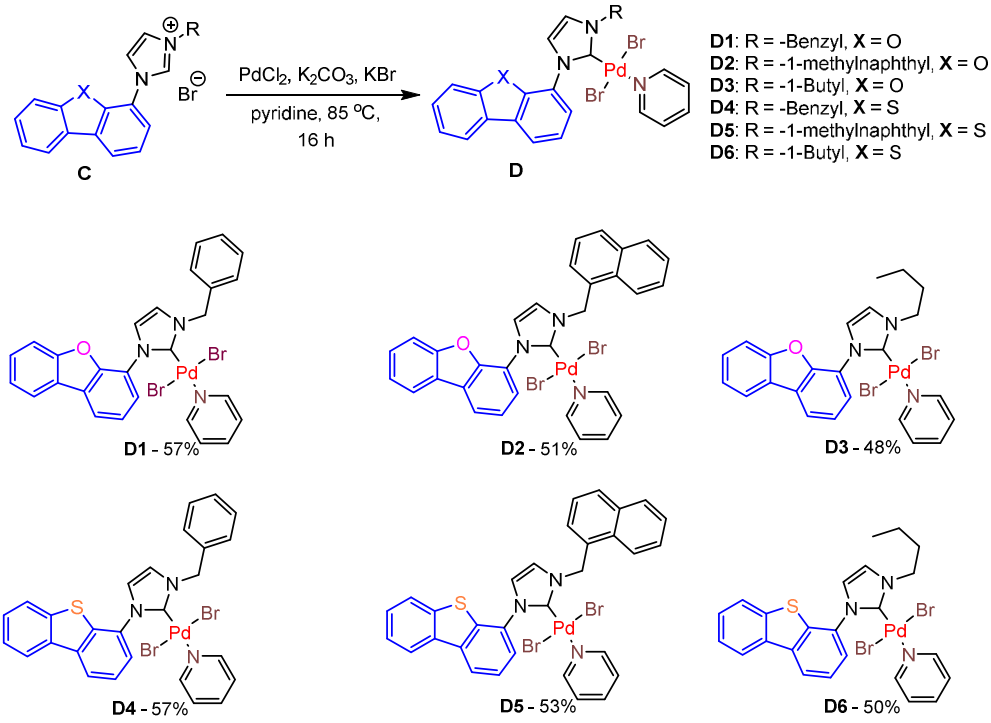
Metal/NHC complex (M = Pd, Rh, Ru etc) bearing DBF and DBTH scaffold have not been reported so far. Palladium-NHC complexes have been



Scheme 1 Synthesis of dibenzofuran and dibenzothiophene based imidazolium salts (**C1**-**C6**).



Scheme 2 Synthesis of dibenzofuran and dibenzothiophene based palladium NHC catalysts **D1**-**D6**. Yields are isolated.

profoundly studied in homogeneous catalysis especially in cross-coupling reactions and proven to be an ideal alternative to Pd/phosphine combination.[21] In carbon-carbon bond chemistry, Suzuki-Miyaura coupling[22] and direct C-H arylation of azoles[23] catalyzed by transition metal salts have significant contribution in the field of fine chemical synthesis and pharmaceuticals. Our group has recently reported the Pd/NHC-PEPPSI type catalysts decorated with naphthalimide and pyrene moiety in various catalytic organic transformations.[24] Thus, knowing the importance of DBF and DBTH core units, herein, we report 4-substituted dibenzofuran and dibenzothiophene based Pd(II)/*N*-heterocyclic carbene PEPPSI catalysts and its application in Suzuki-Miyaura coupling and direct C-H arylation reactions of benzoxazoles.

Results and discussion

Synthesis of DBF/DBTH functionalized imidazolium salts C1-C6

On implementing modest change in literature report,[18e] DBF and DBTH functionalized imidazoles **B1** & **B2** were synthesized by reacting corresponding bromides with imidazole with the catalytic amount of Cu_2O-dipivaloylmethane, Cs_2CO_3 as a base in DMSO solvent at 130 °C for 16 h. Expectedly, the

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synthesized imidazoles were obtained in relatively good yields as bench stable-yellow crystalline solids. Further, 4-substituted DBF and DBTH based imidazolium salts **C1**-**C6** were obtained in 30-80% of yield, by reacting various ar-alkyl and alkyl halides with imidazole in dioxane solvent at 110 °C for 16 h (Scheme 1). Apparently, the products are purified by filtration followed by reprecipitation with diethyl ether and hexane to furnish as off-white to grey color solids in high purity. All these compounds

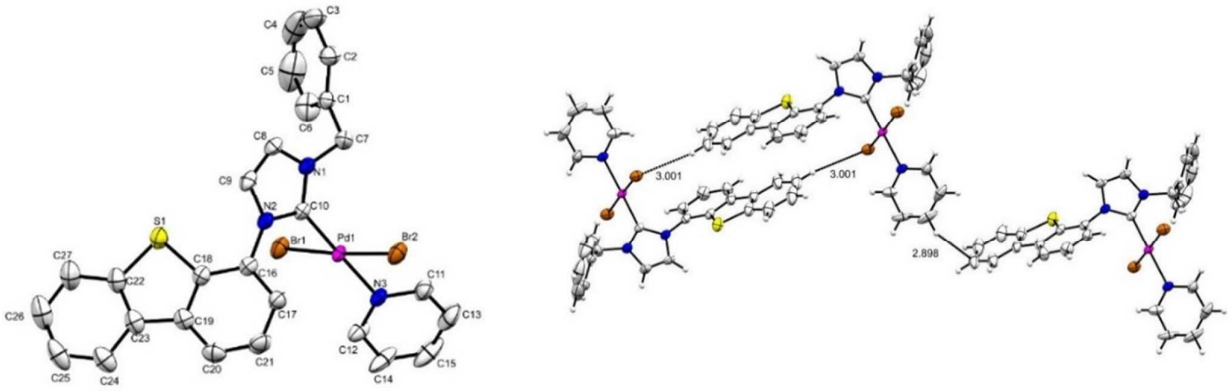

Fig. 2 (a) ORTEP representation of **D4** in the solid state with thermal ellipsoids depicted at 35% probability level. Hydrogen atoms are omitted for clarity (b) Crystal packing of **D4** showing CH···π interaction and CH···Br interaction. Selected interatomic distances (Å) and angles (deg) of **D4** are as follows: Pd(1)-C(10), 1.957(4); Pd(1)-N(3), 2.105(3); Pd(1)-Br(1), 2.4181(9); Pd(1)-Br(2), 2.4216(9); N(1)-C(10), 1.337(4); N(2)-C(10),1.360(5); N(3)-C(11),1.333(5); N(3)-C(12), 1.328(5); Br(1)-Pd(1)-N(3), 91.12(8); Br(2)-Pd(1)-N(3), 92.26(8); Br(2)-Pd(1)-C(10), 89.0(1); Br(1)-Pd(1)-C(10), 87.5(1); Br(1)-Pd-Br(2), 175.86(2); C10-Pd-N3, 177.7(1).

C1-**C6** were characterized by multinuclear NMR and HRMS. Comprehensibly, the peak resonates at δ 9.97-10.29 for single proton is congruous with -NC*H*N segment of imidazolium salts which in turn confirms its formation. The singlet peak resonates at δ 5.62-6.18 agrees with -CH_2 portion of benzyl and naphthyl substituents of **C1**, **C2**, **C4**, **C5** but this is split into a triplet for **C3** and **C6** and resonates at δ 4.36-4.43.

Synthesis of Pd-NHC catalysts D1-D6

Straightforwardly, a series of PEPPSI (Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation) type DBF and DBTH appended Pd-NHC catalysts **D1**-**D6** were synthesised by deprotonative metalation of imidazolium salts by reacting with $PdCl_2$ in the presence of K_2CO_3 as a base, KBr as an additive, in pyridine solvent at 85 °C for 16 h yielding moderate to good yields (48-57%) as yellow crystalline solids (Scheme 2 and ESI, S3). Notably, the synthesized **D1**-**D6** derivatives are freely soluble in dichloromethane and chloroform, yet having poor solubility in polar-protic solvents such as methanol, ethanol and non-polar solvents such as hexane and toluene. Prominently, the palladation of imidazolium salts is corroborated by multinuclear NMR spectrum and HRMS. As evident by the disappearance of downfield ^{1}H NMR signal for the acidic -NC*H*N proton of imidazolium group and the appearance of Pd-$C_{carbene}$ peak at δ 151-156 ppm in ^{13}C NMR.

X-ray crystallographic studies

The molecular structure of **D4** was unambiguously confirmed by single crystal X-ray analysis. Suitable crystals of **D4** were grown by slow evaporation of concentrated dichloromethane-diethyl ether solution at low temperature. The molecular structure ascertained by this analysis depicted in (Fig. 2a), shows the presence of triclinic crystal system (Table 1 and ESI, S4). The two trans anti oriented bromide ligands coordinate the Pd(II) centre along with carbene and pyridine ligands in a distorted-square planar geometry with shorter Pd-$C_{carbene}$ bond length of 1.957(4) Å. Yet the distance between Pd(1)-Br(1) and Pd(1)-Br(2) bond length is 2.4181(9) and 2.4216(9) Å respectively, which is much larger than the Pd(1)-N(3) bond distance of 2.105(3) Å. The dihedral angle between carbene carbon of imidazole unit and the two trans bromide ligands as in Br(2)-Pd(1)-C(10) and Br(1)-Pd(1)-C(10) are 89.0(1) and 87.5(1) Å respectively (Fig. 2b). But the angle observed in Br(1)-Pd(1)-N(3) and Br(2)-Pd(1)-N(3) are 91.12(8) and 92.26(8) Å respectively.

Table 1 Crystallographic data for Pd-NHC **D4**

Complex	**D4**
CCDC no	1845489
Empirical formula	C27 H21 Br2 N3 Pd S
Formula weight	685.75
Temperature	298K
Wavelength	0.71073 Å
Crystal system	triclinic

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Space group	P -1
a	8.903(5)
b	9.681(5)
c	16.055(5)
α	104.731(5)
β	95.807(5)
γ	102.598(5)
Volume	1288.0(11)
Z, calculated density	2, 1.768
Absorption coefficient	3.925
F (000)	672
Limiting indices	-11 ≤ h ≤ 11 -12 ≤ k ≤ 12 -21 ≤ l ≤ 21
Reflections collected /unique	33029/6395 [$R_{(int)}$ = 0.0447]
Data/restraint/parameters	6395/0/307
Goodness- of-fit on F^2	1.032
Final R indices [I> 2 sigma(I)]	R_1=0.0375 wR_2= 0.0694
R indices (all data)	R1 = 0.0743 wR2 = 0.0694

The crystals are arranged in head to tail pattern of dibenzofuran and pyridine ligand to effect CH···π interaction with the length of 2.898 Å. Besides, the presence of CH···Br interaction between dibenzofuran unit and twisted bromide ligands of Pd center is observed with their typical length of 3.001 Å. Both these interactions stabilized **D4** in its crystal lattice.

Photophysical properties

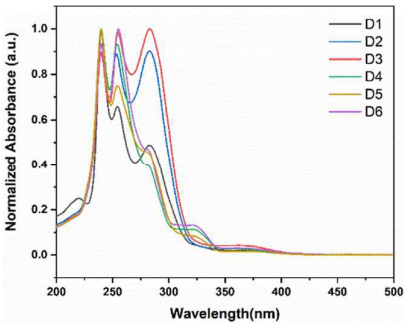

Fig. 3 Normalized UV-Vis absorption spectra of **D1**-**D6** in dichloromethane at room temperature.

The electronic spectra of **D1**-**D6** were recorded in dichloromethane at room temperature in the wavelength range of 200-800 nm are shown in Fig. 3. The complex nature of the spectra is due to the various possible transitions. Among these, the presence of intense absorption band at λ_{max} 200-300 nm and 300-350 nm responsible for ligand centered π–π* and n–π* transitions respectively. The weak metal-ligand charge transfer (MLCT) band shows an absorbance maximum in the range 350-400 nm.

Catalytic properties

The catalytic applicability of synthesized DBF and DBTH based *N*-heterocyclic carbene catalysts **D1**-**D6** in C-C bond formation were tested by choosing Suzuki-Miyaura coupling reaction. Aryl pyridines are important building blocks and ubiquitous in nature prevailing in biological, medicinal (altinicline, Nevirapine, atazanavir) and polymers and functional materials. The augmentation of effective methodologies providing easy access to those heteroaryl derivatives is very appreciable in synthetic organic chemistry.[25] Thus, the coupling of 2-bromopyridine with phenylboronic acid was taken as a standard substrate, K_2CO_3 as a base, Pd-NHC complex (3 mol%) as the catalyst, in toluene-water at 95 °C for 16 h. The solvent combination (toluene/water) is a common and effective solvent mixture for Suzuki-Miyaura reaction.[26] Among the catalysts studied, **D1** gave the coupled product 2-phenylpyridine **3a** with 76% of yield. Intriguingly, DBF and DBTH units having naphthyl and butyl wingtip substituents moderated the yield of **3a** to 72% and 60% respectively in correlation with benzyl surrogate. This is probably due to the non-covalent interaction of benzyl unit with the substrate, which is less favorable in case of naphthyl, where steric supersedes the non-covalent interaction.

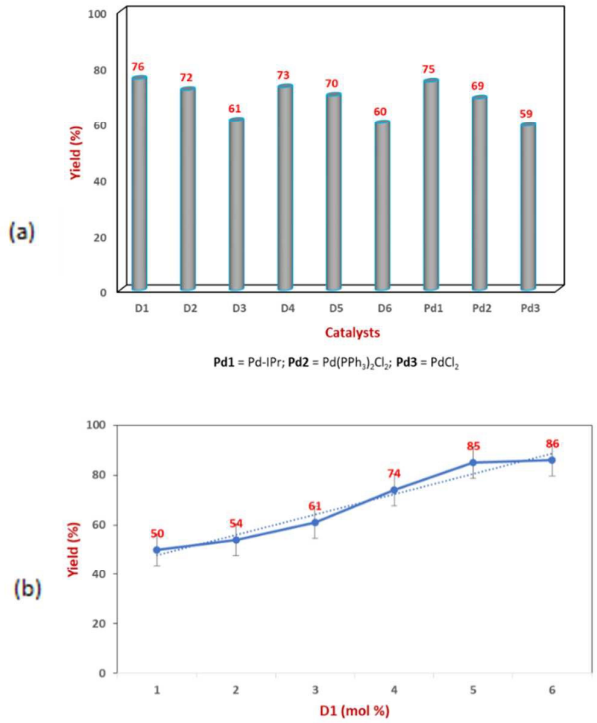

Fig. 4 (a) Reactivities of catalysts in Suzuki-Miyaura coupling of heteroaryl bromides (b) Effect of **D1** mol%.

Notably, DBF based Pd-NHC complex **D1** gave the maximum yield as compared with DBTH based Pd-NHC **D4**. We also compared our catalysts with other palladium catalysts such as $PdCl_2$, $Pd(PPh_3)Cl_2$ and Pd-PEPPSI-IPr, and observed the

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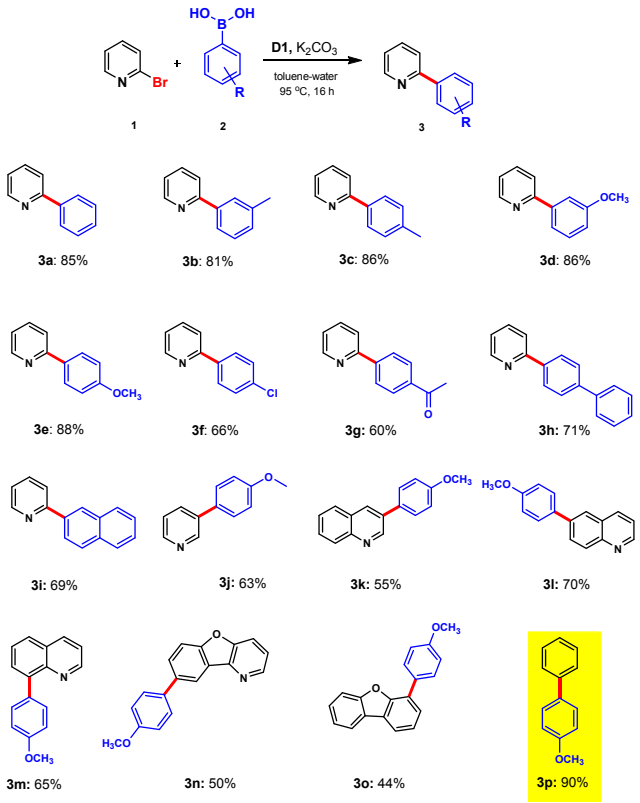
following order of reactivity: $PdCl_2$< $Pd(PPh_3)Cl_2$ < **D1** ≈ Pd-PEPPSI-IPr (Fig. 4a).

These results prompted us to evaluate mol% of added DBF-Pd-NHC complex **D1** in Suzuki-Miyaura coupling. Amazingly the loading of DBF-NHC to 5 mol% improves the yield of **3a** to 85%. No affordable changes in **3a** yield were observed in further increase in mol% of **D1** (Fig. 4b). Thus, the optimized conditions for this reaction is **1** (0.31 mmol), **2** (0.47 mmol), K_2CO_3 (0.63 mmol), **D1** (5 mol%), toluene-water, 95°C, 16 h. Having an optimum reaction protocol in hand, an investigation of the substrate scope for the Suzuki-Miyaura cross-coupling reaction was executed. Interestingly, boronic acids with methyl substituent in meta and para positions gave high yields of coupled products **3b** and **3c** in 81% and 86% respectively. Compelling results were obtained when a highly electron-donating group -OCH_3 were substituted in **3d** (86%) and **3e** (88%). Expectedly, electron-withdrawing substituents such as chloro and acetyl in **3f** and **3g** dwindle the yield of product to 66 and 60% respectively. 4-Biphenyl **3h** and 2-naphthylboronic acid **3i** particularly moderate the yield of coupling product to 71 and 69% respectively.

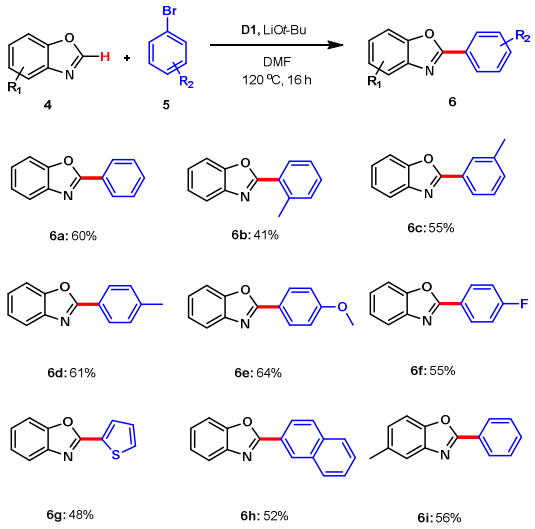
Table 2 Suzuki-Miyaura coupling of heteroaryl bromides with arylboronic acids using **D1**[1]



[1]Reaction conditions: **1** (0.31 mmol), **2** (0.47 mmol), K_2CO_3 (0.63 mmol), **D1** (5 mol%), toluene-water, 95 °C, 16 h. Isolated yields.

3-bromopyridine **3j**, 3-bromoquinoline **3k**, 6-bromo quinoline **3l** and 8-bromoquinoline **3m** reacts smoothly with 4-methoxyphenylboronic acid to afford the coupled products in the range of 55-70% yields. Besides, benzofuro[3,2-*b*]pyridine **3n** and dibenzo[*b*,*d*]furan **3o** derivatives were isolated with 50% and 68% of yields respectively. The applicability of this optimized condition was also verified with non-pyridine substrate such as bromobenzene with 4-methoxyphenyl boronic acid to afford 4-methoxy biphenyl **3p** in 90% yield. (Table 2 and ESI, S7). After successful accomplishment of Suzuki-Miyaura cross-coupling reaction using our catalyst inspired us to further explore its applicability in direct C-H bond functionalization of benzoxazole. The suitable reaction condition to carry out the reaction was benzoxazole (0.31 mmol), bromobenzene (0.47 mmol), LiO*t*-Bu (0.63 mmol) as a base and **D1** (5 mol%) as the catalyst, at 120 °C for 16 h. Methyl group at ortho **6b**, meta **6c**, and para **6d** arylated derivatives were obtained at the high yield of 41, 55 and 61% respectively. Highly electron-donating methoxy substituents in para position **6e** improve the yield of product to 64%. Acceptingly electron- withdrawing substituent fluoro at para position diminished the yield of **6f** to 55%. Heterocyclic **6g** (48%) and polycylicaromatic

Table 3 Direct C-H arylation of benzoxazoles with aryl



bromides using **D1**[1]

[1]Reaction conditions: **4** (0.42 mmol), **5** (0.58 mmol), LiO*t*-Bu (1.26 mmol), **D1** (5 mol%), DMF, 120 °C, 16 h. Isolated yields.

hydrocarbon **6h** (52%) unit impressively afford direct C-H functionalized products. Variation in the benzoxazole unit such as 5-methylbenzo[*d*]oxazole unit yield **6i** in a lower yield

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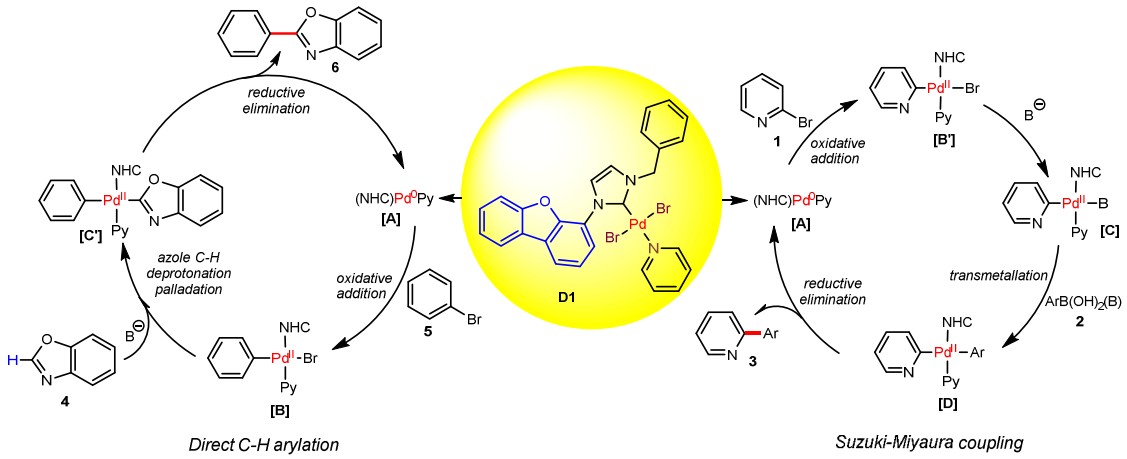
of 56% (Table 3 and ESI, S13). Based on previous reports,[22c] a plausible mechanism is depicted in (scheme 3). Initially, an active palladium species **A** undergoes oxidative addition with aromatic bromides to give **B** and **B'**. Further, **C'** is formed by sequential deprotonation and palladation of **4** with **B**, which was then transformed to arylated product **6** *via* reductive elimination (C-H arylation). Likewise, reaction **B'** with base followed by transmetalation of **2** furnishes the organopalladium intermediate **D**. Eventually, **3** is obtained by the reductive elimination of **D** and regenerates Pd^0 species **A** (Suzuki-Miyaura coupling).

Conclusions

In summary, dibenzofuran and dibenzothiophene based Pd-NHC catalysts **D1**-**D6** were synthesized in appreciable yields. These precatalysts were characterized by multinuclear NMR, HRMS and single crystal X-ray crystallography. The presence of CH···π and CH···Br interaction was observed and their photophysical properties were studied. The synthesised precatalysts were efficiently explored in Suzuki-Miyaura cross-coupling reaction with electron-donating, electron-withdrawing substitutents, isoquinolines, benzofuropyridines and dibenzofuran derivatives. The direct C-H functinalization of benzoxazoles using **D1** were examined with various aryl bromide including heterocyclic and polycyclic units at affordable conditions. These studies revealed that such precatalysts can be adequately applied in various cross-coupling reactions.



Scheme 3 Proposed reaction mechanism of Suzuki-Miyaura coupling and direct C-H arylation of benzoxazole using **D1.**

Experimental

General methods and materials

Unless otherwise mentioned all the reactions were carried out in screw capped reaction tubes, under an inert atmosphere of nitrogen. The reagents and solvents were purchased from commercial sources (Sigma-Aldrich, Alfa-Aesar, AVRA) and used without further purification. 4-bromodibenzo[*b,d*]furan and 4-bromodibenzo[*b,d*]thiophene was synthesised following a reported literature.[18a] Column chromatography purification was performed by using silica gel (100-200 mesh) as a stationary phase and chloroform or n-hexane-ethyl acetate mobile phase. ^{1}H NMR spectra were recorded on Bruker spectrometer (400 MHz) and are reported in units ppm (parts per million) relative to the signals for residual chloroform (7.26 ppm) and DMSO in (2.54 ppm) in the deuterated solvent. ^{13}C NMR spectra were recorded on Bruker spectrometer (100 MHz) and are reported ppm relative to deuterated chloroform (77.23 ppm) and DMSO (39.52 ppm) with tetramethylsilane (TMS) as an internal standard. Coupling constants (*J*) are reported in Hz; splitting patterns are assigned *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *br* = broad signal (ESI, S2)

General procedure for synthesis of dibenzofuran and dibenzothiophene imidazole derivatives (B1-B2)

A 50 mL round bottom flask equipped with a stir bar was charged with 4-bromodibenzo[*b,d*]furan (1000 mg, 4.08 mmol),
imidazole (555 mg, 8.16 mmol), Cs_2CO_3 (3316 mg, 10.20 mmol), Cu_2O (58 mg, 0.40 mmol), 2,2,6,6-Tetramethyl-3,5-heptanedione (Dipivaloylmethane) (150 mg, 0.81 mmol), DMSO (15 mL) was added with vigorous stirring at room temperature,
and then the reaction mixture was placed in a preheated oil bath at 130 °C and stirred for 16 h. After the indicated time, the

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reaction mixture was diluted with water (500 mL), extracted with ethyl acetate (200 mL x 2) and concentrated. The crude material was purified by column chromatography on silica gel with $CHCl_3$-MeOH as eluent and used for further reactions.

Procedure for synthesis of dibenzofuran and dibenzothiophene imidazolium derivatives (C1-C6)

An oven-dried vial equipped with a stir bar was charged with 1-(dibenzo[*b,d*]furan-4-yl)-1*H*-imidazole **B1** (100 mg, 0.42 mmol) and the corresponding benzyl bromide (219 mg, 1.28 mmol), were dissolved in dry Dioxane (3 mL) and then the reaction mixture was placed in a preheated oil bath at 110 °C and stirred for 18 h. After the indicated time, the precipitated solid was filtered and washed with Dioxane (3 mL) followed by diethyl ether and n-hexane (10 mL each) and dried under nitrogen.

3-benzyl-1-(dibenzo[*b,d*]furan-4-yl)-1*H*-imidazol-3-ium bromide C1

Off-white solid; (137 mg with 80% yield); ^{1}H NMR (400 MHz, DMSO-d^6): δ 10.20 (s, 1H), 8.51-8.50 (m, 1H), 8.41 (d, *J* = 7.6 Hz, 1H), 8.31 (d, *J* = 7.6 Hz, 1H), 8.18-8.17 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.69-7.59 (m, 4H), 7.55-7.44 (m, 4H), 5.65 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 155.65, 146.83, 136.95, 134.42, 129.03, 128.91, 128.57, 126.20, 124.17, 124.07, 123.22, 123.05, 122.76, 121.88, 119.69, 112.11, 52.48;

HRMS(EI) for calculated for $C_{22}H_{17}N_2O$ [M-Br]$^+$ 325.1335, found 325.1333.

1-(dibenzo[*b,d*]furan-4-yl)-3-(naphthalen-1-ylmethyl)-1*H*-imidazol-3-iumchloride C2

C2 was synthesised by a similar procedure to that used for **C1** but using 1-chloromethyl naphthalene (1.28 mmol) to give grey solid; (131 mg with 75% yield); ^{1}H NMR (400 MHz, DMSO-d^6): δ 10.29 (s, 1H), 8.50-8.49 (m, 1H), 8.39 (d, *J* = 7.6 Hz, 1H), 8.34-8.28 (m, 2H), 8.14-8.13 (m, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.73-7.60 (m, 6H), 7.52 (t, *J* = 7.6 Hz, 1H), 6.18 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 156.12, 147.35, 137.76, 133.94, 130.98, 130.26, 129.40, 128.45, 127.77, 126.95, 126.18, 124.65, 124.53, 123.81, 123.51, 123.26, 122.37, 120.18, 112.55, 50.90; HRMS (EI) calculated for $C_{26}H_{19}N_2O$ [M-Br]$^+$ 375.1492, found 375.1490.

3-butyl-1-(dibenzo[*b,d*]furan-4-yl)-1*H*-imidazol-3-ium bromide C3

C3 was synthesised by a similar procedure to that used for **C1** but using 1-bromo butane (4.27 mmol) to give Grey solid; (60 mg with 38% yield); ^{1}H NMR (400 MHz, DMSO-d^6): δ 10.09 (s, 1H), 8.52-8.51 (m, 1H), 8.39 (d, *J* = 7.6 Hz, 1H), 8.30 (d, *J* = 7.6 Hz, 1H),), 8.24-8.23 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.68-7.62 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 4.41 (t, *J* = 7.2 Hz, 2H), 1.98-1.90 (m, 2H), 1.43-1.33 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 156.14, 147.27, 137.23, 129.31, 126.68, 124.56, 123.65, 123.23, 120.18, 112.62, 49.70, 31.71, 19.36, 13.84; HRMS(EI) calculated for $C_{19}H_{19}N_2O$ [M-Br]$^+$ 291.1492, found 291.1490.

3-benzyl-1-(dibenzo[*b,d*]thiophen-4-yl)-1*H*-imidazol-3-ium bromide C4

C4 was synthesised by a similar procedure to that used for **C1** but using benzyl bromide (1.28 mmol) to give off-white solid; (117 mg with 76% yield); ^{1}H NMR (400 MHz, DMSO-d^6): δ 10.08 (s, 1H), 8.68 (d, *J* = 7.6 Hz, 1H), 8.55-8.53 (m, 1H), 8.43-8.42 (m, 1H), 8.21-8.20 (m, 1H), 8.16-8.13 (m, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.65-7.56 (m, 4H), 7.52-7.50 (m, 3H), 5.62 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 138.20, 137.69, 135.02, 134.26, 129.57, 129.42, 128.99, 128.85, 126.71, 126.18, 124.54, 124.02, 123.78, 123.39, 53.01; HRMS(EI) calculated for $C_{22}H_{17}N_2S$ [M-Br]$^+$ 341.1107, found 341.1105.

1-(dibenzo[*b,d*]thiophen-4-yl-3(napthalen-1-ylmethyl)-1*H*-imidazol-3-ium chloride C5

C5 was synthesised by a similar procedure to that used for **C1** but using 1-chloromethyl naphthalene (1.28 mmol) to give grey solid; (105 mg with 62% yield); ^{1}H NMR (400 MHz, DMSO-d^6): δ 10.20 (s, 1H), 8.66 (d, *J* = 7.6 Hz, 1H), 8.54-8.52 (m, 1H), 8.42-8.41 (m, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.18-8.17 (m, 1H), 8.14-8.12 (m, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.72-7.61 (m, 6H), 6.16 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 138.16, 138.00, 135.01, 134.34, 133.95, 130.96, 130.30, 129.42, 128.83, 128.45, 127.82, 126.69, 126.16, 124.60, 124.49, 124.27, 123.75, 123.39, 50.97; HRMS (EI) for $C_{26}H_{19}N_2S$ [M-Br]$^+$ 391.1263, found 391.1261.

3-butyl-1-(dibenzo[*b,d*]thiophen-4-yl)-1*H*-imidazol-3-ium bromide C6

C6 was synthesised by a similar procedure to that used for **C1** but using 1-bromo butane (4.2 mmol) to give grey solid; (46 mg with 30% yield); ^{1}H NMR (400 MHz, DMSO-d^6) δ 9.97 (s, 1H), 8.66 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.55-8.53 (m, 1H), 8.42-8.41 (m, 1H), 8.26-8.25 (m, 1H), 8.16-8.14 (m, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.64-7.62 (m, 2H), 4.38 (t, *J* = 7.2 Hz, 2H), 1.97-1.90 (m, 2H), 1.42-1.33 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 138.23, 138.08, 137.49, 135.02, 130.34, 128.83, 126.72, 126.15, 124.53, 123.79, 123.39, 49.74, 31.63, 19.34, 13.83; HRMS(EI) calculated for $C_{19}H_{19}N_2S$ [M-Br]$^+$ 307.1263, found 307.1260.

General procedure for synthesis of dibenzofuran and dibenzothiophene based palladium-NHC catalysts (D1-D6)

An oven-dried 20 mL reaction tube equipped with a stir bar was charged with 3-benzyl-1-(dibenzo[*b,d*]furan-4-yl)-1*H*-imidazol-3-ium bromide **C1** (200 mg, 0.49 mmol) potassium carbonate (204 mg, 1.48 mmol), potassium bromide (589 mg, 4.95 mmol), palladium(II)chloride (115 mg, 0.54 mmol) followed by pyridine 5mL. The reaction mixture was stirred at 85 °C for 16 h. After the indicated time, the solution was cooled to room temperature and 25 mL of dichloromethane was added and filtered through a short pad of celite and the filtrate was concentrated. The crude material was purified by

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column chromatography on silica gel with $CHCl_3$ as eluent to yield **D1** as yellow solid.

(190 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 7.6 Hz, 1H), 8.78 (d, *J* = 5.6 Hz, 2H), 8.01-7.92 (m, 2H), 7.62-7.46 (m, 6H),7.42-7.29 (m, 5H), 7.16 (d, *J* = 6.4 Hz, 2H), 6.87 (d, *J* = 2.0 Hz, 1H), 5.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.41, 152.56, 150.87, 149.33, 137.73, 134.83, 129.52, 129.07, 128.74, 127.81, 126.38, 125.85, 124.45, 123.35, 122.97, 121.49, 121.19, 120.95, 112.23,55.60; HRMS(EI) calculated for $C_{27}H_{21}Br_2N_3OPd$ $[M]^+$ 666.9086, found 666.9085.

Synthesis of D2

D2 was prepared by a similar procedure to that used for **D1**, but using 1-(dibenzo[*b*,*d*]furan-4-yl)-3-(naphthalen-1-ylmethyl)-1*H*-imidazol-3-iumchloride **C2** (0.48 mmol) to give yellow solid (180 mg, 51 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.0 Hz, 1H), 8.82 (d, *J* = 5.2 Hz, 2H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.93-7.85 (m, 3H), 7.68-7.47 (m, 8H), 7.41-7.28 (m, 3H), 7.17 (d, *J* = 6.8 Hz, 1H),6.61 (d, *J* = 2.0 Hz, 1H), 6.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.39, 152.60, 150.35, 149.28, 137.77, 133.96, 131.84, 130.03, 129.50, 128.71, 127.80, 127.47, 126.44, 125.50, 124.49, 123.91, 123.34, 122.98, 121.19, 120.94, 112.22, 53.59; HRMS(EI) calculated for $C_{31}H_{23}Br_2N_3OPd$ $[M]^+$ 716.9243, found 716.9244.

Synthesis of D3

D3 was prepared by a similar procedure to that used for **D1**, but using 3-butyl-1-(dibenzo[*b*,*d*]furan-4-yl)-1*H*-imidazol-3-ium bromide **C3** (0.54 mmol) to give yellow solid (165 mg, 48 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79-8.76 (m, 3H), 7.99-7.91 (m, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.53-7.48 (m, 3H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.16-7.12 (m, 3H), 4.63 (t, *J* = 7.6 Hz, 2H), 2.16-2.08 (m, 2H), 1.57-1.50 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.39, 152.53, 149.81, 149.35, 137.71, 127.78, 125.92, 124.43, 123.95, 123.32, 122.92, 121.85, 121.12, 120.95, 112.21, 51.61, 32.12, 20.11, 13.88. HRMS(EI) calculated for $C_{24}H_{23}Br_2N_3OPd$ $[M]^+$ 632.9243, found 632.9241.

Synthesis of D4

D4 was prepared by a similar procedure to that used for **D1**, but using 3-benzyl-1-(dibenzo[*b*,*d*]thiophen-4-yl)-1*H*-imidazol-3- ium bromide **C4** (0.47 mmol) to give yellow solid (188 mg, 57 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75-8.73 (m, 2H), 8.53 (d, *J* = 7.6 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.15-8.12 (m, 1H), 7.79-7.74 (m, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.59-7.56 (m, 3H), 7.43-7.35 (m, 6H), 7.16-7.13 (m, 2H), 6.86 (d, *J* = 2.0 Hz, 1H), 5.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.54, 151.58, 139.35, 137.67, 136.33, 135.41, 134.77, 134.18, 129.48, 129.09, 128.74, 127.35, 126.87, 125.07, 124.78, 124.38, 123.17, 122.91, 122.19, 121.88, 55.48, HRMS(EI) calculated for $C_{27}H_{21}Br_2N_3PdS$ $[M]^+$ 682.8858, found 682.8856.

Synthesis of D5

D5 was prepared by a similar procedure to that used for **D1**, but using 1-(dibenzo[*b*,*d*]thiophen-4-yl-3(napthalen-1-ylmethyl)-1*H*-imidazol-3-ium chloride **C5** (0.46 mmol) to give yellow solid (185 mg, 53 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80-8.78 (m, 2H), 8.56 (d, *J* = 7.6 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.14-8.12 (m, 1H), 7.88 (t, *J* = 9.2 Hz, 2H), 7.75-7.47 (m, 7H), 7.43-7.38 (m, 2H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.17-7.14 (m, 2H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.57, 139.36, 137.69, 136.37, 133.97, 131.84, 130.05, 129.50, 128.70, 127.48, 126.87, 126.44, 125.49, 125.07, 124.76, 124.40, 122.91, 122.57, 121.97, 121.76, 53.81; HRMS(EI) calculated for $C_{31}H_{23}Br_2N_3PdS$ $[M]^+$ 732.9014, found 732.9012.

Synthesis of D6

D6 was prepared by a similar procedure to that used for **D1**, but using 3-butyl-1-(dibenzo[*b*,*d*]thiophen-4-yl)-1*H*-imidazol-3-ium bromide **C6** (0.51 mmol) to give yellow solid (169 mg, 50 % yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73-8.71 (m, 2H), 8.49 (d, *J* = 7.6 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.13-8.11 (m, 1H), 7.75-7.33 (m, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.60-7.55 (m, 1H), 7.42-7.36 (m, 3H), 7.15-7.12 (m, 3H), 4.62 (t, *J* = 7.6 Hz, 2H), 2.16-2.08 (m, 2H), 1.56-1.47 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.52, 150.58, 139.35, 137.63, 136.36, 135.41, 134.33, 127.32, 126.88, 125.02, 124.75, 124.35, 122.89, 122.22, 121.97, 51.54, 32.04, 20.10, 13.85; HRMS(EI) calculated for $C_{24}H_{23}Br_2N_3PdS$ $[M]^+$ 648.9014, found 648.9016.

General procedure for Suzuki-Miyaura coupling using D1

An oven-dried vial equipped with a stir bar was charged with 2-bromo pyridine (0.31 mmol) and the corresponding phenyl boronic acid (0.47 mmol), potassium carbonate (0.63 mmol), **D1** (5 mol%), followed by toluene-water (4:1 mL). Then the reaction mixture was placed in a preheated oil bath at 95 °C and stirred for 16 h. After the indicated time, the reaction mixture was diluted with water (5 mL), extracted with ethyl acetate (5 mL x 2) and concentrated. The crude material was purified by column chromatography on silica gel with n-hexane - ethyl acetate as eluent, to yield the title compounds and their spectra was authenticated with reported literatures (ESI, S18).

General procedure direct C-H arylation of benzoxazoles with D1

An oven-dried vial equipped with a stir bar was charged with benzoxazole (0.42 mmol) and the corresponding bromobenzene (0.58 mmol), lithium tertiary butoxide (1.26 mmol), **D1** (5 mol%), followed by DMF (0.5 mL). Then the reaction mixture was placed in a preheated oil bath at 120 °C and stirred for 16 h. After the indicated time, the solvent was removed and purification by flash column chromatography on silica gel with n-hexane - ethyl acetate as eluent, to yield the title compound and their spectra was authenticated with reported literatures (ESI, S18).

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