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Direct C−H Bond Arylation of (Benzo)oxazoles with Aryl Chlorides Catalyzed by *N*-Heterocyclic Carbene−Palladium(II)−1-Methylimidazole Complex

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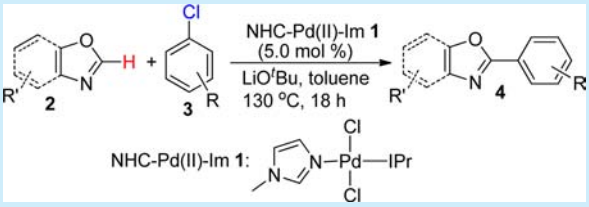
Supporting Information

ABSTRACT: The direct C−H bond arylation of (benzo)oxazoles with aryl chlorides was achieved catalyzed by a well-defined NHC−Pd(II)−Im complex. Under the optimal conditions, various aryl chlorides were successfully applied as the arylating reagents to achieve the 2-aryl (benzo)oxazoles in acceptable to high yields, providing a convenient and alternative method for the direct C−H bond arylation of (benzo)oxazoles and enriching the chemistry of the NHC−Pd(II) complex in organic synthesis.



2-Aryl substituted (benzo)oxazoles are very important moieties due to their biological or physical properties and are also important backbones for the synthesis of natural products, pharmaceutically active compounds, and functional materials.[1] Recently, the direct C−H bond arylation of (benzo)oxazoles, which represents an environmental, economical, and potential alternative method, has proven to be one of the most versatile methods.[2,3] Among the arylating reagents such as aryl halides,[4] phenol derivatives,[5] sodium arylsulfinates,[6] aryl organometallic reagents,[7] etc.,[8] aryl halides possess the advantages of easy availability, being economical, and easy operation. However, in the successful direct C−H bond arylation of (benzo)oxazoles using aryl halides as the arylating reagents, only the more activated aryl iodides and bromides were fully developed. In addition, in most cases, free tertiary phosphines were used as ligands with transition metal salts, thus usually excessive ligands were necessary compared to transition metal salts. Besides air-, thermal-, and moisture-sensitive tertiary phosphine ligands and metal salts systems, Arslan and co-workers reported a mixed halide *N*-heterocyclic carbene (NHC)−Pd complex, which has a strict 2:1 NHC/Pd ratio, and have examined its catalytic activity toward the direct C−H bond arylation of benzoxazoles.[9] However, only aryl bromides were examined as the arylating reagents and only moderate yields were obtained. Due to the economy and easy availability of aryl chlorides,[10] development of the phosphine-free, highly efficient direct C−H bond arylation of (benzo)oxazoles using aryl chlorides as the arylating reagents is still in great demand.

Recently, we have developed a well-defined *N*-heterocyclic carbene−palladium(II)−1-methylimidazole [NHC−Pd(II)−Im] complex **1** and have shown it to be a good catalyst in traditional coupling reactions using aryl chlorides as the substrates.[11] These results thus prompted us to further investigate its application toward the direct C−H bond arylation of (benzo)oxazoles using aryl chlorides as the arylating reagents. Herein, we report these results in detail.

At the outset of our investigations, the screening reactions were performed with respect to the bases and the solvents with benzoxazole **2a** (1.0 mmol) and chlorobenzene **3a** (0.5 mmol) as the model substrates in the presence of NHC−Pd(II)−Im complex **1** (5.0 mol %) at 130 °C for 12 h, and some representative results are shown in Table 1. For example, in the first round, dioxane was chosen as the solvent to find the most suitable base (Table 1, entries 1−6). It seems that LiO^{t}Bu was the best base to give the desired arylated product **4a** in 16% yield (Table 1, entry 3). In the presence of other bases such as KO^{t}Bu, NaO^{t}Bu, KOH, Li_2CO_3, $NaHCO_3$, Cs_2CO_3, $K_3PO_4 \cdot 3H_2O$, NaF, and CH_3COONa, very low yields (<5%) of product **4a** were obtained. In the second round, using LiO^{t}Bu as the base, the solvent effects were then investigated and toluene was the best choice (58%) over DMSO (<5%), DMF (11%), THF (<5%), and CH_3CN (8%). By increasing the amounts of LiO^{t}Bu to 4.0 and 5.0 equiv, the yields can be increased to 69% and 75%, respectively (Table 1, entries 12 and 13). Further studies showed that the yield can be increased to 82% when the reaction time was prolonged to 18 h in the presence of 5.0 equiv of LiO^{t}Bu (Table 1, entry 14), which was not disturbed when the reaction time was prolonged to 24 h (Table 1, entry 15). In addition, no reaction occurred in the

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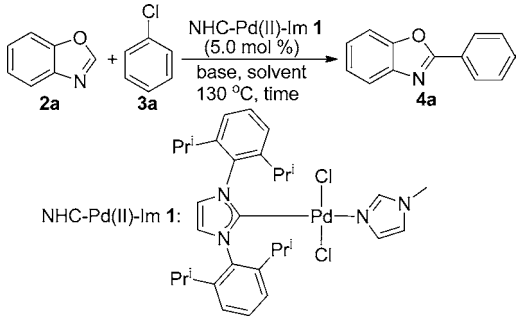
Table 1. Optimization for the Complex 1 Catalyzed Reaction of Benzoxazole 2a with Chlorobenzene 3a



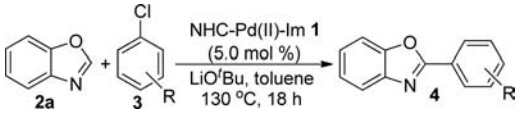
entry[a]	solvent	base (equiv)	time (h)	yield (%)[b]
1	dioxane	KO^{t}Bu (3.0)	12	<5
2	dioxane	NaO^{t}Bu (3.0)	12	<5
3	dioxane	LiO^{t}Bu (3.0)	12	16
4	dioxane	KOH (3.0)	12	<5
5	dioxane	Li_2CO_3 (3.0)	12	<5
6	dioxane	$NaHCO_3$ (3.0)	12	<5
7	DMSO	LiO^{t}Bu (3.0)	12	<5
8	DMF	LiO^{t}Bu (3.0)	12	11
9	toluene	LiO^{t}Bu (3.0)	12	58
10	THF	LiO^{t}Bu (3.0)	12	<5
11	CH_3CN	LiO^{t}Bu (3.0)	12	8
12	toluene	LiO^{t}Bu (4.0)	12	69
13	toluene	LiO^{t}Bu (5.0)	12	75
14	toluene	LiO^{t}Bu (5.0)	18	82
15	toluene	LiO^{t}Bu (5.0)	24	83
16[c]	toluene	LiO^{t}Bu (5.0)	24	NR

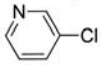
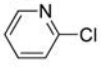
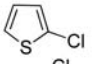
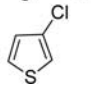
[a]Otherwise specified, all reactions were carried out using **2a** (1.0 mmol), **3a** (0.5 mmol), **1** (5.0 mol %), and base (3.0−5.0 equiv) in the solvent (2.0 mL) at 130 °C. [b]Isolated yields. [c]No catalyst was added.

absence of NHC−Pd(II)−Im complex **1** (Table 1, entry 16), implying that the introduction of the palladium catalyst was essential for such a transformation, although a metal-free system for direct C−H bond arylation has been well-defined during the past years.[12]

Having established the optimal reaction conditions, we then first carried out the reaction between benzoxazole **2a** and a variety of aryl chlorides **3** to test the generality (Table 2). As can be seen from Table 2, benzoxazole **2a** can be smoothly arylated using this methodology. Substituents on the aryl chlorides **3** affected the reaction to some extent. For instance, aryl chlorides **3** with an electron-donating group such as a methyl group on the *para*- or *meta*-position of the phenyl ring only gave the corresponding products **4b** and **4c** in 53 and 58% yields, respectively (Table 2, entries 1 and 2). However, when the electron-donating groups such as methyl and methoxy groups were attached on the *ortho*-position of aryl chlorides **3**, good and high yields of products **4d** and **4g** can be achieved (Table 2, entries 3 and 6). Sterically hindered substituents on the aryl chlorides **3** have less effect on the reaction to afford products **4d**, **4e**, and **4g** in good to high yields, respectively (Table 2, entries 3, 4, and 6). Electron-withdrawing substituents on the aryl chlorides are tolerant in these reactions to provide products **4e** and **4f** in good yields, respectively (Table 2, entries 4 and 5). Heteroaryl chlorides such as 3-chloropyridine **3h**, 2-chloropyridine **3i**, 2-chlorothiophene **3j**, and 3-chlorothiophene **3k** were also good reaction partners to

Table 2. NHC−Pd(II)−Im Complex 1 Catalyzed Reactions of Benzoxazole 2a with Aryl Chlorides 3



entry[a]	3 (R)	yield (%)[b]
1	**3b** (4-Me)	**4b**, 53
2	**3c** (3-Me)	**4c**, 58
3	**3d** (2-Me)	**4d**, 78
4	**3e** (2-CN)	**4e**, 81
5	**3f** (4-CN)	**4f**, 83
6	**3g** (2-MeO)	**4g**, 93
7	**3h** 	**4h**, 94
8	**3i** 	**4i**, 91
9	**3j** 	**4j**, 80
10	**3k** 	**4k**, 86

[a]All reactions were carried out using **2a** (1.0 mmol), **3** (0.5 mmol), **1** (5.0 mol %), and LiO^{t}Bu (5.0 equiv) in toluene (2.0 mL) at 130 °C for 18 h. [b]Isolated yields.

give products **4h**−**4k** in good to high yields, respectively (Table 2, entries 7−10).

Encouraged by these results, various other benzoxazoles **2** were then subjected to the reactions with aryl chlorides **3** under identical conditions (Table 3). As can be seen from Table 3, all reactions took place smoothly to give the desired arylated products **4** in good to high yields. Substituents on the benzoxazoles **2** and aryl chlorides **3** almost have no effect on the reactions investigated. For example, good to high yields of products **4l**, **4m**, **4o**, **4p**, **4t**, and **4z** can be achieved when aryl chlorides **3** possessing sterically hindered *ortho*-substituents were used as the substrates. Heteroaryl chlorides such as 2-chlorothiophene, 3-chloropyridine, and 2-chloropyridine were also suitable substrates in these reactions to afford products **4q**−**4s** and **4v**−**4x** in good to high yields, respectively.

Finally, 5-aryloxazoles **2** were also tested with aryl chlorides **3** under the optimal conditions. As can be seen from Table 4, all reactions performed smoothly to give the desired C2-arylated products **4** in good to high yields. Electron-rich, -withdrawing, and -poor substituents on the phenyl rings of 5-aryloxazoles **2** did not affect the reactions. It seems that such substituents on the aryl chlorides **3** also did not affect the reactions. Heteroaryl chlorides such as 2-chloropyridine and 3-chloropyridine also worked very well to give the corresponding arylated products **4al**−**4aq** in high yields.

In conclusion, to the best of our knowledge, we report herein the first example of a phosphine-free, NHC−Pd(II) complex catalyzed direct C−H bond arylation of (benzo)oxazoles using aryl chlorides as the arylating reagents. By using the readily available NHC−Pd(II)−Im complex **1** as the catalyst, a variety of (benzo)oxazoles can be arylated with aryl chlorides under the optimal reaction conditions. The reaction can tolerate various substrates. For example, aryl chlorides with electron-donating, -neutral, -withdrawing, and -sterically hindered substituents are all proven to be suitable substrates. The results

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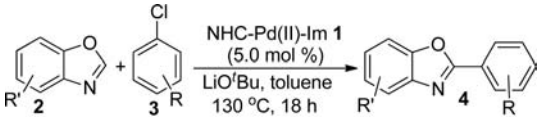
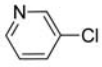
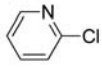
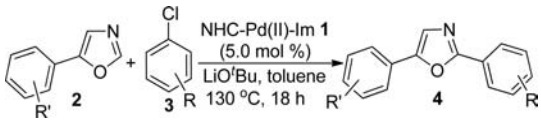
Table 3. NHC−Pd(II)−Im Complex 1 Catalyzed Reactions of Benzoxazoles 2 with Aryl Chlorides 3



entry[a]	2 (R')	3 (R)	yield (%)[b]
1	**2b** (5-Me)	**3d** (2-Me)	**4l**, 91
2	**2b**	**3e** (2-CN)	**4m**, 87
3	**2b**	**3f** (4-CN)	**4n**, 89
4	**2b**	**3l** (2,6-Me$_2$)	**4o**, 84
5	**2b**	**3g** (2-MeO)	**4p**, 85
6	**2b**	**3j** 	**4q**, 78
7	**2b**	**3h** 	**4r**, 88
8	**2b**	**3i** 	**4s**, 97
9	**2c** (5-^{t}Bu)	**3d**	**4t**, 81
10	**2c**	**3f**	**4u**, 79
11	**2c**	**3h**	**4v**, 96
12	**2c**	**3i**	**4w**, 93
13	**2c**	**3j**	**4x**, 83
14	**2d** (5-F)	**3a** (H)	**4y**, 78
15	**2d**	**3g**	**4z**, 80
16	**2d**	**3f**	**4aa**, 79

[a]All reactions were carried out using **2** (1.0 mmol), **3** (0.5 mmol), **1** (5.0 mol %), and LiO^{t}Bu (5.0 equiv) in toluene (2.0 mL) at 130 °C for 18 h. [b]Isolated yields.

Table 4. NHC−Pd(II)−Im Complex 1 Catalyzed Reactions of 5-Aryloxazoles 2 with Aryl Chlorides 3



entry[a]	2 (R')	3 (R)	yield (%)[b]
1	**2e** (H)	**3a** (H)	**4ab**, 81
2	**2e**	**3d** (2-Me)	**4ac**, 97
3	**2e**	**3m** (4-F)	**4ad**, 89
4	**2f** (4-F)	**3a**	**4ae**, 87
5	**2f**	**3d**	**4af**, 88
6	**2f**	**3m**	**4ag**, 83
7	**2g** (4-Me)	**3a**	**4ah**, 79
8	**2g**	**3d**	**4ai**, 90
9	**2h** (4-MeO)	**3a**	**4aj**, 77
10	**2h**	**3d**	**4ak**, 90
11	**2e**	**3i** 	**4al**, 92
12	**2f**	**3i**	**4am**, 92
13	**2g**	**3i**	**4an**, 86
14	**2h**	**3i**	**4ao**, 86
15	**2g**	**3h** 	**4ap**, 91
16	**2h**	**3h**	**4aq**, 89

[a]All reactions were carried out using **2** (1.0 mmol), **3** (0.5 mmol), **1** (5.0 mol %), and LiO^{t}Bu (5.0 equiv) in toluene (2.0 mL) at 130 °C for 18 h. [b]Isolated yields.

reported in this paper provide an economical, convenient, and alternative method for the direct C−H bond arylation of (benzo)oxazoles and will also enrich the chemistry of the NHC−Pd(II) complexes in organic synthesis.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details, spectra data, and copy of ^{1}H and ^{13}C NMR spectra of compounds **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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