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Copper-Catalyzed Selective Arylations of Benzoxazoles with Aryl Iodides

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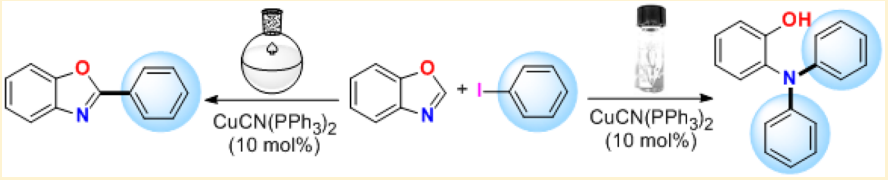
Supporting Information



ABSTRACT: A copper-catalyzed direct ring-opening double *N*-arylation of benzoxazoles with aryl iodides has been developed. The present system exhibits high selectivity despite competition from *C*-arylation. The selectivity between ring-opening *N*-arylation and *C*-arylation was controlled by the choice of reaction vessel. The nitrile bound bis(triphenylphosphine)copper cyanide was identified as the active catalytic species for both reactions, and when combined with a nitrile-containing solvent, enhanced the reaction efficiency.

Benzoxazole derivatives are important heterocyclic organic molecules in pharmaceutical research.[1] Various functionalizations of benzoxazole have been studied. In particular, the most acidic C−H bond, between the nitrogen and oxygen atom, can be easily activated allowing for the functionalization of the C-2 position. Arylation of the C-2 position has been explored using aryl halides in combination with palladium, nickel, or copper catalysts.[2−4] A stoichiometric amount of copper iodide was employed to functionalize the C−H bond in the C-2 position using an arylation reaction by Miura et al.[4a] On the other hand, the Daugulis group developed a copper-catalyzed arylation of the benzoxazole C-2 position with lithium *tert*-butoxide as the base.[4b] In addition to carbon−carbon bond formation at the C-2 position, carbon−nitrogen bond formation was also developed using transition metal-catalyzed conditions.[5]

Direct arylation of the C-2 position can be in competition with a ring-opening arylation reaction. In Miura's system, a small amount of triphenylamine derivative was detected which could be synthesized via a benzoxazole ring-opening reaction followed by *N*-arylation.[4a] Both the Ullmann and Buchwald-Hartwig aminations are well-known copper-catalyzed cross-coupling reactions between an aryl halide and an amine.[6] These reactions suggested that the benzoxazole was transformed into an aminophenol derivative first, followed by a Buchwald-Hartwig type *N*-arylation to form the triphenylamine product. In a complementary fashion, Han et al. also applied the benzoxazole ring-opening reaction to *O*-arylation reactions using copper nanoparticles.[7] In the proposed mechanism of this system, cesium carbonate was first employed to open the benzoxazole ring, and then a copper-catalyzed *O*-arylation of the *ortho*-aminophenol intermediate took place. Very little is known about the ring-opening *N*-arylation as there are no catalytic studies on this system to date, hence no way to optimize the transformation. Described herein is our study on the copper-catalyzed selective ring-opening *N*-arylation of benzoxazole with aryl iodides.

Using benzoxazole (**1a**) and iodobenzene (**2a**) as starting materials, optimization of the ring-opening *N*-arylation was undertaken (Table 1). While the C-2 arylated product (**4aa**) was the major product using Miura's condition,[4a] changing the reaction vessel from a round-bottomed flask to a screw-capped reaction vial shifts the preference from an arylation of the C-2 position to a ring-opening *N*-arylation. Additionally, changing the copper salt from copper(I) iodide to copper(I) cyanide increased catalytic efficiency of the ring-opening *N*-arylation (entry 2). It turns out that the counteranion in the copper catalyst and the solvent displayed significant effects on the catalytic activity as demonstrated in entry 3. Among the various polar solvents screened, the nitrile-containing solvents displayed improved reactivity and solubility. To circumvent the low boiling point of many nitrile containing solvents, pivalonitrile (2,2,-dimethylpropanenitrile, bp 105 °C) was used for the ring-opening *N*-arylation reaction. While the combination of both a nitrile-containing copper salt and solvent has good reactivity, modulating the base had a pronounced effect. Using cesium carbonate as a base accelerated the ring-

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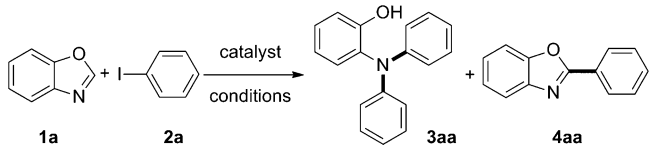
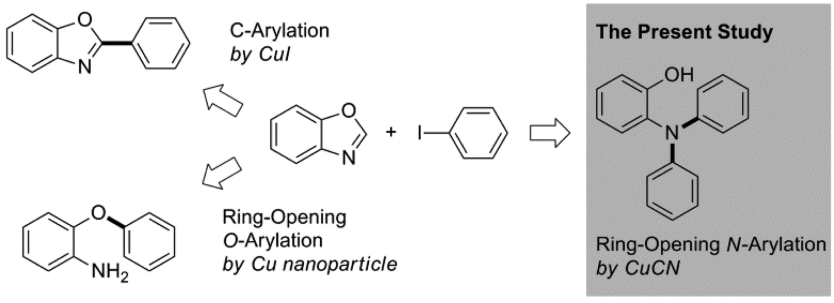
Table 1. Screening of Reaction Conditions for Copper-Catalyzed Selective Arylations[a]



entry	copper salt	PPh_3	base	solvent	temp	time	yield[b] (%) 3aa	yield[b] (%) 4aa
1	CuI (1 equiv)	20 mol %	Na_2CO_3	DMF	160	24	33	10
2	CuCN (1 equiv)	20 mol %	Na_2CO_3	DMF	160	24	28	-
3	CuCN (1 equiv)	20 mol %	Na_2CO_3	Pivalonitrile	140	24	-	14
4	CuCN (1 equiv)	20 mol %	Cs_2CO_3	Pivalonitrile	140	24	98	-
5	CuCN (10 mol %)	20 mol %	Cs_2CO_3	Pivalonitrile	120	24	92	-
6	CuCN (10 mol %)	30 mol %	Cs_2CO_3	Pivalonitrile	120	18	90	-
7	CuCN (10 mol %)	-	Cs_2CO_3	Pivalonitrile	120	18	44	-
8	$CuCN(PPh_3)_2$ (10 mol %)	-	Cs_2CO_3	Pivalonitrile	120	18	94	-
9	$CuCN(PPh_3)_2$ (10 mol %)	10 mol %	Cs_2CO_3	Pivalonitrile	120	24	96	-
10[c]	$CuCN(PPh_3)_2$ (10 mol %)	10 mol %	Cs_2CO_3	Pivalonitrile	105 *reflux*	24	-	85
11	$CuCN(PPh_3)_2$ (10 mol %)	10 mol %	Cs_2CO_3	DMF	150	24	59	16

[a]Reaction condition: A mixture of benzoxazole (0.15 mmol), iodobenzene (0.45 mmol), copper salt, triphenylphosphine, and base (0.45 mmol) in solvent (0.5 mL) was placed in a screw-capped vial, closed, and stirred for the indicated time and temperature. [b]Isolated yield of product reported as an average from at least two independent measurements. [c]A mixture of benzoxazole (0.6 mmol), iodobenzene (1.8 mmol), copper salt (10 mol %), triphenylphosphine (10 mol %), and cesium carbonate (1.8 mmol) in pivalonitrile (2 mL) was placed in round-bottomed flask and stirred for 24 h.

Scheme 1. Carbon−Carbon, Carbon−Oxygen, and Carbon−Nitrogen Bond Formations of Benzoxazole Using Transition Cu Catalysts



opening *N*-arylation to afford 2-(diphenylamino)phenol (**3aa**) in 98% isolated yield (entry 4). It has been suggested that the cesium carbonate plays a key role in the ring-opening of benzoxazole. Han and co-workers proposed a cesium carbonate-mediated benzoxazole ring-opening route for the first step of their reaction mechanism.[7] In fact, switching to cesium carbonate, from sodium carbonate, decreased the amount of copper salt required to obtain a similar yield (entry 5) from stoichiometric (1 equiv) to catalytic (10 mol %) amounts. However, the reaction time and quantity of phosphine ligand were inversely proportional. When the reaction time decreased from 24 to 18 h, the amount of phosphine required increased from 20 mol % to 30 mol % (entry 6). Entries 5−7 demonstrate that the amount of triphenylphosphine ligand has a significant effect on this particular system. Interestingly, the mono-*N*-arylation product was not obtained as the major product under any condition, even with only a single equivalent of aryl iodide present.

Since $CuCl(PPh_3)_3$ is a widely studied and common copper salt, the active catalytic species was expected to be $CuCN(PPh_3)_3$ in our optimized reaction condition. However, bis(triphenylphosphine)copper cyanide was only obtained and confirmed by the reaction of copper cyanide and triphenylphosphines.[8] A hexameric PPh_3-bounded copper cyanide species $[CuCN(PPh_3)_2]_6$ (**5**) could be synthesized and isolated by following a previous report[8a] (Scheme 2). It was originally reported as a red crystal; however, only colorless crystals were obtained and the structure was confirmed by single crystal X-ray diffraction (Scheme 2 and Supporting Information for detail). In the hexameric complex (**5**), the nitrile coordinates with two copper atoms by using each carbon and nitrogen atom. A decade ago, the polymeric structure of CuCN was intensively studied, and it has a similar oligomeric binding mode to $CuCN(PPh_3)_2$.[9] Interestingly, the reaction yield was improved by exchanging copper cyanide with the synthesized bis(triphenylphosphine)copper cyanide salt and reacting with external triphenylphosphines (entries 5, 7, and 8). The best condition for the ring-opening double *N*-arylation was achieved by using bis(triphenylphosphine)copper cyanide (**5**) salt with additional triphenylphosphine ligands (entry 9).

Finally, perfect selectivity of arylation was revealed by the simple choice of reaction vessel. In the optimized condition (entry 9 in Table 1), the reaction was performed in a screw-capped vial, and formed the ring-opened double-arylated product **3aa**, as the sole product. However, by changing the reaction vessel from a closed, and assuming pressured, screw-capped vial to an open round-bottomed flask, the *C*-arylated product **4aa** was the major product and isolated in high yields

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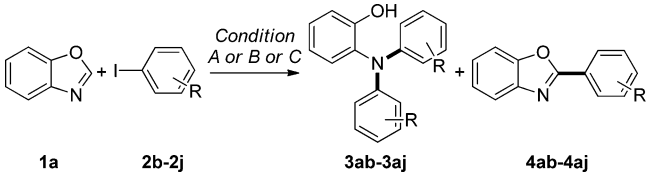
(85%, entry 10). Interestingly, the selectivity of arylation was not achieved using DMF as the solvent. Both **3aa** (59%) and **4aa** (16%) were obtained from condition B in DMF at 150 °C. Utilizing a nitrile-containing solvent and copper salt together can optimize this series of reactions to be performed as a selective one-pot synthesis (entries 9−11).

Under the optimized conditions using CuCN as a catalyst and PPh_3 as a ligand, substrate scope was subsequently investigated (Condition A, Table 2). In general, electronic variation on the aryl iodides, bearing different types of substituents, displayed substantial effects on the reaction efficiency. Aryl iodides containing electron donating groups showed moderate to good yields for all *ortho*-, *meta*-, and *para*-substituted substrates (entries 1−7). However, certain electron withdrawing groups (i.e., 4-nitroiodobenzene and methyl-4-iodobenzoate) demonstrate poor reactivity in the *N*-arylation reaction. The halides seemed to be exempt as 4-fluoroiodobenzene and 4-chloroiodobenzene showed moderate reactivity in condition A.

Due to the fact that the presynthesized bis(triphenylphosphine)copper cyanide has better reactivity in the ring-opening double *N*-arylation with iodobenzene (Table 1), we scrutinized the aryl iodide substrate scope again using complex **5** instead of CuCN (Condition B, in Table 2). We were pleased to observe improved yields under reaction condition B which employed the bis(triphenylphosphine) copper cyanide and an external triphenylphosphine. At the same time, the *C* arylated product **4a** series was successfully synthesized using condition C from same starting materials and catalysts.

Under the optimized condition B, we also explored the substrate scope of the benzoxazole component to the ring-opening double *N*-arylation using iodobenzene (Scheme 3).

Table 2. Copper-Catalyzed Ring-Opening Double *N*-Arylation of Benzoxazole with Aryl Iodides[a]

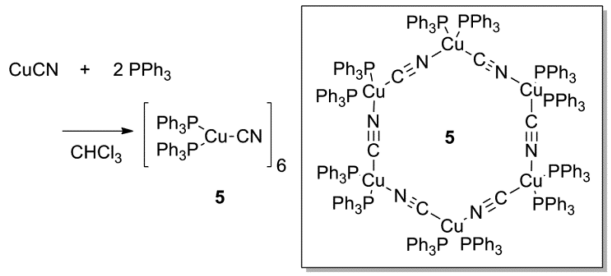


Condition A & B: in a screw-capped vial for **3a** synthesis
Condition C: in a round-bottomed flask for **4a** synthesis

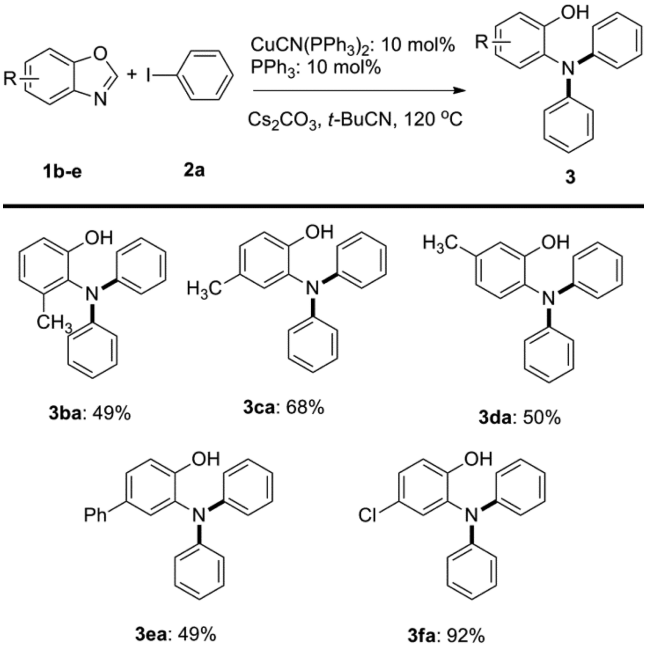
		yield[b] (%)		
entry	R	Condition A	Condition B	Condition C
1	4-Me	**3ab**, 61	**3ab**, 79	**4ab**, 96
2	3-Me	**3ac**, 82	-	**4ac**, 94
3	2-Me	**3ad**, 53	**3ad**, 79	**4ad**, 75
4	4-OMe	**3ae**, 58	**3ae**, 80	**4ae**, 93
5	3-OMe	**3af**, 95	-	**4af**, 87
6	2-OMe	**3ag**, 65	**3ag**, 78	**4ag**, 89
7	3,5-diMe	**3ah**, 64	**3ah**, 71	**4ah**, 82
8	4-F	**3ai**, 71	**3ai**, 77	**4ai**, 86
9	4-Cl	**3aj**, 30	**3aj**, 68	**4aj**, 55

[a]Reaction condition A: A mixture of benzoxazole (0.15 mmol), aryl iodide (0.45 mmol), copper cyanide (0.015 mmol), triphenylphosphine (0.045 mmol), and cesium carbonate (0.45 mmol) in pivalonitrile (0.5 mL) was placed in a screw-capped vial and stirred for 18 h at 120 °C. Reaction condition B: A mixture of benzoxazole (0.15 mmol), aryl iodide (0.45 mmol), bis(triphenylphosphine) copper cyanide (0.015 mmol), triphenylphosphine (0.015 mmol), and cesium carbonate (0.45 mmol) in pivalonitrile (0.5 mL) was placed in a screw-capped vial and stirred for 24 h at 120 °C. Reaction condition C: A mixture of benzoxazole (0.3 mmol), aryl iodide (0.9 mmol), bis(triphenylphosphine) copper cyanide (0.03 mmol), triphenylphosphine (0.03 mmol), and cesium carbonate (0.9 mmol) in pivalonitrile (1 mL) was placed in a round-bottomed flask and stirred for 24 h under reflux. [b]Isolated yield of product reported as an average from at least two independent measurements.

Scheme 2. Synthesis of $[CuCN(PPh_3)_2]_6$



Scheme 3. Ring-Opening Double *N*-Arylation with Various Benzoxazoles.[a]



[a]Reaction condition: A mixture of benzoxazole (0.15 mmol), aryl iodide (0.45 mmol), bis(triphenylphosphine) copper cyanide (0.015 mmol), triphenylphosphine (0.015 mmol), and cesium carbonate (0.45 mmol) in pivalonitrile (0.5 mL) was placed in screw-capped vial and stirred for 24 h at 120 °C. The yields of isolated products are reported as an average from at least two independent measurements.

Benzoxazoles bearing substituents with diverse electronic properties such as methyl (**1b**-**1d**), phenyl (**1e**), and chloro (**1f**) groups all underwent reactions with iodobenzene to provide the desired products in the moderate yields. In contrast to the effects seen when the substrate is on the aryl halide, benzoxazoles bearing an electron-withdrawing group, such as a chloro group (**1f**), showed the highest conversion in the reaction condition. The reaction with 4-methylbenzoxazole (**1b**) and 6-methylbenzoxazole (**1d**) afforded the correspond-

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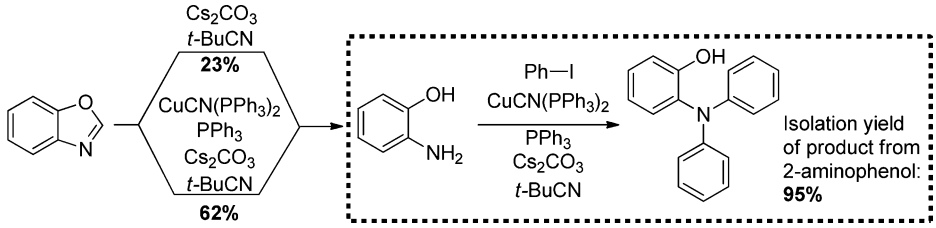
Scheme 4. Teasing Apart the Order of Reactions for the Transformation of Benzoxazole to 2-(Diphenylamino)phenol



ing product with a diminished yield. Both benzothiazole and benzimidazole exhibit no reactivity in the copper-catalyzed ring-opening double *N*-arylation even with elevated temperature, suggesting that the present copper system could discriminate between these types of intermediates and only perform the arylation on aminophenols.

To obtain any mechanistic insight into the present ring-opening double *N*-arylation, the reaction was performed in separated systems (Scheme 4). As discussed in ref 7, benzoxazole rings can be opened by cesium carbonate. By employing benzoxazole and cesium carbonate only, the ring-opened 2-aminophenol was obtained in 23% yield, with the remaining materials being unreacted benzoxazole. Interestingly, a mixture of copper salt, triphenylphosphine, and base converted benzoxazole to 2-aminophenol with higher yield (62%), indicating that the copper catalyst can also affect the ring-opening of benzoxazole. Using 2-aminophenol as the starting material for condition B, the final product was obtained in a 95% yield. Unsurprisingly, when the *C*-2 arylated product (**4aa**) was used as a starting material, no further reaction (ring-opening or arylation) was observed. These separate results led us to propose that the copper-catalyzed ring-opening double *N*-arylation is a sequential set of reactions. Ring-opening of benzoxazole occurs first, followed by the copper-catalyzed *N*-arylation to form the product.[10]

In summary, we have presented a copper-catalyzed direct arylation and ring-opening double *N*-arylation of benzoxazoles. A judicious choice of both the copper catalyst and reaction conditions was crucial for achieving selectivity and preference for the catalytic activity to follow a nontraditional route. The reaction pathway between *C*-arylation and ring-opening double *N*-arylation was perfectly controlled by the choice of reaction vessel with a nitrile-containing solvent. A wide range of substituted starting materials was examined using the developed copper-catalyzed arylation of benzoxazoles. In this system, the key parameters, such as the substituent placement on either the aryl halide or the benzoxazole, and the electronics of the substituent, can be teased apart leading to an improved understanding of the mechanism and optimization of the synthesis.

EXPERIMENTAL SECTION

All reagents were used as received unless otherwise noted. Flash column chromatography was performed on silica gel (400−630 mesh) using the indicated solvent system. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 400 or 500 MHz. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz). Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded at 100 or 125 MHz and was fully decoupled by broad band decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d* or the appropriate solvent peak. High-resolution mass spectra (HRMS) were acquired on a high resolution Q-TOF mass spectrometer (ionization mode: ESI).

$CuCN(PPh_3)_2$(**5**),[8a] 2-(diphenylamino)phenol (Table 1, **3aa**),[11] 2-phenylbenzoxazole (Table 1, **4aa**),[12] 2-(di-*p*-tolylamino)phenol (Table 2, entry 1, **3ab**),[10b] 2-(*p*-tolyl)benzo[*d*]oxazole (Table 2, entry 1, **4ab**),[13a] 2-(*m*-tolyl)benzo[*d*]oxazole (Table 2, entry 2, **4ac**),[13a] 2-(di-*o*-tolylamino)phenol (Table 2, entry 3, **3ad**),[10b] 2-(*o*-tolyl)benzo[*d*]-oxazole (Table 2, entry 3, **4ad**),[4b] 2-(bis(4-methoxyphenyl)amino)-phenol (Table 2, entry 4, **3ae**),[10b] 2-(4-methoxyphenyl)benzo[*d*]-oxazole (Table 2, entry 4, **4ae**),[4b] 2-(bis(3-methoxyphenyl)amino)-phenol (Table 2, entry 5, **3af**),[11] 2-(3-methoxyphenyl)benzo[*d*]oxazole (Table 2, entry 5, **4af**),[13a] 2-(2-methoxyphenyl)benzo[*d*]oxazole (Table 2, entry 6, **4ag**),[13b] 2-(bis(3,5-dimethylphenyl)amino)phenol (Table 2, entry 7, **3ah**),[11] 2-(3,5-dimethylphenyl)benzo[*d*]oxazole (Table 2, entry 7, **4ah**),[4b] 2-(4-fluorophenyl)benzo[*d*]oxazole (Table 2, entry 8, **4ai**),[4b] 2-(4-chlorophenyl)benzo[*d*]oxazole (Table 2, entry 9, **4aj**),[13a] 2-(diphenylamino)-4-methylphenol (Scheme 3, **3ca**),[10b] 4-chloro-2-(diphenylamino)phenol (Scheme 3, **3fa**)[10b] are known compounds.

Preparation of $CuCN(PPh_3)_2$(Scheme 2).[8a] Copper(I) cyanide (250 mg, 2.8 mmol), triphenylphosphine (2.89 g, 11 mmol) and chloroform (40 mL) were added to round-bottom flask. The mixture was vigorously stirred at room temperature for 4 h. The colorless solid was separated by filtration and washed with 20 mL diethyl ether (4 times). After washing, the solid was recrystallized in hot methanol. The colorless powder was separated by filtration again and solvent was removed in vacuo; the desired product was finally recrystallized in dichloromethane (1.12 g, 65%).

General Procedures for the Copper-Catalyzed Ring-Opening Double *N*-Arylation: Condition A (Tables 1 and 2). Benzoxazole (18 mg, 0.15 mmol), aryl iodide (0.45 mmol), cesium carbonate (147 mg, 0.45 mmol), copper(I) cyanide (1.3 mg, 0.015 mmol), triphenylphosphine (12 mg, 0.045 mmol), and pivalonitrile (0.5 mL) were added to an oven-dried screw-capped vial. The mixture was vigorously stirred at 120 °C for 18 h. After cooling to room temperature, the mixture was diluted with ethyl acetate (1 mL). Solvent was removed in vacuo, and the desired product was isolated by a silica gel column chromatography.

General Procedures for the Ring-Opening Double *N*-Arylation: Condition B (Tables 1, 2 and Scheme 3). Benzoxazole (18 mg, 0.15 mmol), aryl iodide (0.45 mmol), cesium carbonate (147 mg, 0.45 mmol), bis(triphenylphosphine)copper(I) cyanide (9 mg, 0.015 mmol), triphenylphosphine (4 mg, 0.015 mmol), and pivalonitrile (0.5 mL) were added to an oven-dried screw-capped vial. The mixture was vigorously stirred at 120 °C for 24 h. After cooling to room temperature, the mixture was diluted with ethyl acetate (1 mL). Solvent was removed in vacuo, and the desired product was isolated by a silica gel column chromatography.

Copper-Catalyzed Direct Arylation of Benzoxazole (Table 1, entry 10). Benzoxazole (71 mg, 0.6 mmol), iodobenzene (0.20 mL, 1.8 mmol), cesium carbonate (586 mg, 1.8 mmol), bis-(triphenylphosphine)copper(I) cyanide (37 mg, 0.06 mmol), triphenylphosphine (16 mg, 0.06 mmol), and pivalonitrile (2.0 mL) were added to a round-bottomed flask. The mixture was vigorously stirred under reflux for 24 h. After cooling to room temperature, the mixture was filtered through silica gel pad with ethyl acetate (10 mL) to remove insoluble solids. Solvent was removed in vacuo, and the desired product was isolated by a silica gel column chromatography.

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General Procedures for the Direct Arylation of Benzoxazole: Condition C (Table 2). Benzoxazole (36 mg, 0.3 mmol), aryl iodidie (0.9 mmol), cesium carbonate (293 mg, 0.9 mmol), bis-(triphenylphosphine)copper(I) cyanide (19 mg, 0.03 mmol), triphenylphosphine (8 mg, 0.03 mmol), and pivalonitrile (1 mL) were added to a round-bottomed flask. The mixture was vigorously stirred under reflux for 24 h. After cooling to room temperature, the mixture was filtered through silica gel pad with ethyl acetate (10 mL) to remove insoluble solids. Solvent was removed in vacuo, and the desired product was isolated by a silica gel column chromatography.

*2-(Diphenylamino)phenol(Table 1, **3aa**).*[11] Condition A: iodobenzene (0.050 mL, 0.45 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (36 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (s, 1H), 6.93−6.97 (m, 1H), 7.02−7.08 (m, 7H), 7.11−7.13 (q, 1H) 7.20−7.24(m, 1H), 7.26−7.31(m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.6, 121.5, 121.8, 122.8, 127.7, 129.4, 133.1, 146.8, 152.4.

*2-Phenylbenzoxazole (Table 1, **4aa**).*[12] Iodobenzene (0.20 mL, 1.8 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (ethyl acetate/*n*-hexane, 1:20) as a colorless solid (100 mg, 85%); ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.35−7.39 (m, 2H), 7.51−7.56 (m, 3H), 7.57−7.62 (m, 1H), 7.77−7.82 (m, 1H), 8.26−8.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.6, 120.0, 124.7, 125.2, 127.0, 127.7, 129.0, 131.7, 141.8, 150.7, 163.1.

*2-(Di-p-tolylamino)phenol (Table 2, entry 1, **3ab**).*[10b] Conditions A and B: 4-iodotoluene (98 mg, 0.45 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (34.4 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 6H), 5.57 (s, 1H), 6.89−6.95 (m, 5H), 7.01−7.10 (m, 6H), 7.15−7.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 116.4, 121.3, 121.8, 127.3, 129.0, 130.0, 132.2, 133.6, 144.6, 152.2.

*2-(p-Tolyl)benzo[d]oxazole (Table 2, entry 1, **4ab**).*[13a] Condition C: 4-iodotoluene (196 mg, 0.90 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (60.3 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.32−7.36 (m, 4H), 7.56−7.58 (m, 1H), 7.75−7.78 (m, 1H), 8.14−8.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 110.4, 119.8, 124.3, 124.4, 124.8, 127.5, 129.6, 142.0, 142.1, 150.6, 163.2.

*2-(Di-m-tolylamino)phenol (Table 2, entry 2, **3ac**).* Condition A: 3-iodotoluene (0.058 mL, 0.45 mmol) was used for the preparation of the title compound, and it was purified by silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (35.7 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (s, 1H), 6.82−6.84 (m, 6H), 6.89−6.93 (m, 1H), 7.01−7.04 (q, 1H), 7.08−7.20 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 116.5, 121.5, 121.7, 122.7, 127.7, 129.4, 133.1, 146.7, 152.4; HR-ESI-MS (Q-TOF) *m*/*z* calcd. for $C_{20}H_{19}NO$ $[M+H]^+$: 290.1545, found $[M+H]^+$: 290.1545.

*2-(m-Tolyl)benzo[d]oxazole (Table 2, entry 2, **4ac**).*[13a] Condition C: 3-iodotoluene (116 mL, 0.90 mmol) was used for the preparation of the title compound, and it was purified by silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a yellow solid (59.1 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.32−7.35 (m, 3H), 7.38−7.42 (t, 1H, *J* = 7.6 Hz), 7.56−7.58 (m, 1H), 7.76−7.79 (m, 1H), 8.04−8.06 (d, 1H, *J* = 7.7 Hz), 8.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 110.5, 119.9, 124.5, 124.7, 124.9, 126.9, 128.1, 128.7, 132.3, 138.6, 142.0, 150.7, 163.2.

*2-(Di-o-tolylamino)phenol (Table 2, entry **3ad**).*[10b] Condition A and B: 2-iodotoluene (0.057 mL, 0.45 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (34.4 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.96 (s, 6H), 5.19 (s, 1H), 6.77−6.86 (m, 4H), 6.95−6.97 (q, 1H), 7.05−7.14 (m, 5H), 7.18−7.20 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 100.0, 116.2, 120.9, 125.8, 126.2, 131.9, 134.8, 150.3.

*2-(o-Tolyl)benzo[d]oxazole (Table 2, entry 3, **4ad**).*[4b] Condition C: 2-iodotoluene (115 mL, 0.90 mmol)was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a yellow solid (47.4 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (s, 3H), 7.34−7.38 (m, 4H), 7.39−7.44 (m, 1H), 7.58−7.62 (m, 1H), 7.81−7.83 (m, 1H), 8.18−8.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 110.5, 120.1, 124.3, 125.0, 126.0, 126.2, 129.9, 130.9, 131.8, 138.8, 142.1, 150.3, 163.4.

*2-(Bis(4-methoxyphenyl)amino)phenol (Table 2, entry 4, **3ae**).*[10b] Condition A and B: 4-iodoanisole (105 mg, 0.45 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:2) as a yellow solid (39.2 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 6H), 5.61 (s, 1H), 6.81−6.84 (m, 4H), 6.89−6.92 (m, 1H), 6.94−6.97 (m, 4H), 7.01−7.06 (m, 2H), 7.13−7.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 114.7, 116.3, 121.1, 123.2, 126.8, 128.4, 134.2, 140.8, 151.9, 155.3.

*2-(4-Methoxyphenyl)benzo[d]oxazole (Table 2, entry 4, **4ae**).*[4b] Condition C: 4-iodoanisole (211 mg, 0.90 mmol)was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (62.7 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 7.02−7.05 (m, 2H), 7.30−7.35 (m, 2H), 7.55−7.57 (m, 1H), 7.73−7.76 (m, 1H), 8.19−8.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 110.4, 114.4, 119.7, 119.8, 124.4, 124.6, 129.4, 142.3, 150.7, 162.4, 163.2.

*2-(Bis(3-methoxyphenyl)amino)phenol(Table 2, entry 5, **3af**).*[11] Condition A: 3-iodoanisole (0.054 mL, 0.45 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:2) as a yellow solid (45.9 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.6−6.7 (m, 6H), 6.9 (m, 1H), 7.0 (q, 1H), 6.9 (m, 1H), 7.1−7.2 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 108.0, 108.1, 114.5, 116.7, 121.5, 127.9, 129.4, 130.1, 133.0, 147.9, 152.5, 160.6.

*2-(3-Methoxyphenyl)benzo[d]oxazole (Table 2, entry 5, **4af**).*[13a] Condition C: 3-iodoanisole (107 mL, 0.90 mmol)was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (58.8 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 7.07−7.10 (m, 1H), 7.34−7.38 (m, 2H), 7.41−7.44 (t, 1H, *J* = 6.4 Hz), 7.57−7.60 (m, 1H), 7.77−7.80 (m, 2H) 7.84−7.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 110.6, 111.8, 118.3, 120.0, 120.1, 124.6, 125.1, 128.3, 130.0, 142.0, 150.7, 159.9, 162.9.

*2-(Bis(2-methoxyphenyl)amino)phenol (Table 2, entry 6, **3ag**).* Conditions A and B: 2-iodoanisole (0.059 mL, 0.45 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:2) as a yellow solid (37.7 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 6H), 6.80−6.98 (m, 8H), 7.05−7.13 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 112.7, 115.4, 119.9, 121.0, 124.7, 124.9, 126.8, 127.6, 135.2, 137.1, 153.2, 153.5; HR-ESI-MS (Q-TOF) *m*/*z* calcd. for $C_{20}H_{19}NO_3$ $[M+H]^+$: 322.1443, found $[M+H]^+$: 322.1442.

*2-(2-Methoxyphenyl)benzo[d]oxazole (Table 2, entry 6, **4ag**).*[13b] Condition C: 2-iodoanisole (117 mL, 0.90 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a yellow solid (60.3 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 3H), 7.07−7.11 (m, 2H), 7.32−7.35 (m, 2H), 7.48−7.51 (m, 1H), 7.57−7.60 (m, 1H), 7.81−7.84 (m, 1H), 8.13−8.15 (dd, 1H, *J* = 1.4, 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1, 110.4, 112.0, 116.1, 120.2, 120.7, 124.2, 124.9, 131.3, 132.7, 142.1, 150.3, 158.4, 161.5.

*2-(Bis(3,5-dimethylphenyl)amino)phenol (Table 2, entry 7, **3ah**).*[11] Conditions A and B: 3,5-dimethyl-iodobenzene (0.065 mL, 0.45 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (34.0 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 12H), 5.56 (s, 1H), 5.65−5.67 (d, 6H), 6.90−6.94 (m, 1H), 7.02−7.04 (q, 1H), 7.08−7.11 (q, 1H), 7.16−7.20 (m,

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1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 99.9, 116.3, 119.8, 121.2, 124.5, 127.3, 129.3, 133.5, 139.0, 146.9, 152.3.

*2-(3,5-Dimethylphenyl)benzo[d]oxazole (Table 2, entry 7, **4ah**).*[4b] Condition C: 3,5-dimethyl iodobenzene (130 mL, 0.90 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a yellow solid (54.8 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 6H), 7.15 (s, 1H), 7.32−7.37 (m, 2H), 7.55−7.58 (m, 1H), 7.76−7.78 (m, 1H), 7.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 110.4, 119.8, 124.4, 124.9, 125.3, 126.8, 133.2, 138.5, 142.1, 150.6, 163.4.

*2-(Bis(4-fluorophenyl)amino)phenol (Table 2, entry 8, **3ai**).* Conditions A and B: 1-fluoro-4-iodobenzene (0.052 mL, 0.45 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:2) as a yellow solid (33.5 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85−6.96 (m, 8H), 7.01−7.04 (m, 2H), 7.16−7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 96.3, 118.1, 127.3, 129.1, 131.2, 133.5, 150.5; HR-ESI-MS (Q-TOF) *m*/*z* calcd. for $C_{18}H_{13}F_2NO$ $[M+H]^+$:298.1043, found $[M+H]^+$: 298.1039.

*2-(4-Fluorophenyl)benzo[d]oxazole (Table 2, entry 8, **4ai**).*[4b] Condition C: 1-fluoro-4-iodobenzene (104 mL, 0.90 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (55.0 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.21 (t, 2H, *J* = 8.6 Hz), 7.33−7.35 (m, 2H), 7.54−7.56 (m, 1H), 7.74−7.76 (m, 1H), 8.22−8.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.5, 116.0, 116.2, 119.9, 123.4, 123.4, 124.6, 125.1, 129.7, 129.8, 142.0, 150.7, 162.1, 163.5, 166.0.

*2-(Bis(4-chlorophenyl)amino)phenol (Table 2, entry 9, **3aj**).* Conditions A and B: 1-chloro-4-iodobenzene (107 mg, 0.45 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a yellow solid (33.5 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41(s, 1H), 6.92−6.97 (m, 5H), 7.02−7.06 (m, 2H), 7.19−7.23 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.0, 121.9, 122.9, 128.0, 128.3, 129.3, 132.4, 145.1, 152.2; HR-ESI-MS (Q-TOF) *m*/*z* calcd. for $C_{18}H_{13}Cl_2NO$ $[M+H]^+$: 330.0452, found $[M+H]^+$: 330.0447.

*2-(4-Chlorophenyl)benzo[d]oxazole (Table 2, entry 9, **4aj**).*[13a] Condition C: 1-chloro-4-iodobenzene (214 mg, 0.90 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (38.0 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.38 (m, 2H), 7.49−7.51 (d, 2H, *J* = 8.6 Hz), 7.57−7.59 (m, 1H), 7.76−7.78 (m, 1H), 8.18−8.20 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.6, 120.1, 124.7, 125.3, 125.7, 128.8, 129.3, 137.8, 142.0, 150.8, 162.1.

Experimental Procedures for Ring-Opening Double *N*-Arylation with Various Benzoxazoles (Scheme 3). *2-(Diphenylamino)-3-methylphenol (Scheme 3, **3ba**).* Condition B: 4-methylbenzoxazole (38.9 mg, 0.25 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (20.4 mg, 49%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 5.58 (s, 1H), 6.84−6.95 (m, 2H), 6.98−7.02 (m, 2H), 7.08−7.11 (m, 4H), 7.19−7.23 (t, 1H), 7.25−7.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 113.9, 120.0, 122.1, 123.1, 128.5, 129.4, 130.6, 138.9, 145.3, 153.7; HR-ESI-MS (Q-TOF) *m*/*z* calcd. for $C_{19}H_{17}NO$ $[M+H]^+$: 275.1310, found $[M+H]^+$: 275.1309.

*2-(Diphenylamino)-4-methylphenol (Scheme 3, **3ca**).*[10b] Condition B: 5-methylbenzoxazole (20 mg, 0.15 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a yellow solid (20.4 mg, 49%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 5.36 (s, 1H), 6.93−6.96 (m, 2H), 7.01−7.08 (m, 7H), 7.26−7.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 117.4, 121.3, 121.5, 128.4, 129.2, 129.3, 131.1, 132.8, 147.6, 152.3.

*2-(Diphenylamino)-5-methylphenol (Scheme 3, **3da**).* Condition B: 6-methylbenzoxazole (38.9 mg, 0.25 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a colorless solid (20.8 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 1H), 5.50 (s, 1H), 6.76−6.78 (q, 1H), 6.89−6.90 (d, 1H), 7.00−7.08 (m, 7H), 7.26−7.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 117.0, 121.6, 122.3, 122.6, 129.2, 129.4, 130.5, 138.1, 146.9, 152.2; HR-ESI-MS (Q-TOF) *m*/*z* calcd. for $C_{19}H_{17}NO$ $[M+H]^+$: 275.1310, found $[M+H]^+$: 275.1312.

*3-(Diphenylamino)-[1,1′-biphenyl]-4-ol (Scheme 3, **3ea**).* Condition B: 5-phenylbenzoxazole (38.9 mg, 0.25 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a yellow solid (24 mg, 47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 7.03−7.07 (m, 2H), 7.10−7.14 (m, 5H), 7.28−7.32 (m, 5H), 7.36−7.41 (m, 3H), 7.45−7.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.0, 121.8, 122.9, 126.3, 126.7, 126.9, 127.9, 128.7, 129.5, 133.4, 134.9, 140.3, 146.7, 151.8. HR-ESI-MS (Q-TOF) *m*/*z* calcd. for $C_{24}H_{19}NO$ $[M+H]^+$: 338.1545, found $[M+H]^+$: 338.1539.

*4-Chloro-2-(diphenylamino)phenol (Scheme 3, **3fa**).*[10b] Condition B: 5-chlorobenzoxazole (23 mg, 0.15 mmol) was used for the preparation of the title compound, and it was purified by a silica gel column chromatography (dichloromethane/*n*-hexane, 1:5) as a yellow solid (41 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (s, 1H), 6.98−7.01 (d, 1H), 7.05−7.09 (m, 5H), 7.10−7.12 (m, 1H), 7.16−7.19 (m, 1H), 7.28−7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.9, 121.7, 122.2, 123.2, 127.3, 129.5, 129.9, 134.6, 147.2, 153.6.

Experimental Procedure for the Synthesis of 2-Aminophenol from Benzoxazole (Scheme 4). Benzoxazole (18 mg, 0.15 mmol), cesium carbonate (147 mg, 0.45 mmol), and pivalonitrile (0.5 mL) were added to an oven-dried screw-capped vial. The mixture was vigorously stirred at 120 °C for 18 h. After cooling to room temperature, the mixture was purified and isolated by a silica gel column chromatography (ethyl acetate/*n*-hexane, 1:4) as a pale yellow solid (3.8 mg, 23%).

Experimental Procedure for the Synthesis of 2-(Diphenylamino)phenol from 2-Aminophenol (Scheme 4). Condition B: 2-aminophenol (16 mg, 0.15 mmol) was used for the preparation of 2-(diphenylamino)phenol, and it was purified by a silica gel column chromatography (ethyl acetate/*n*-hexane, 1:10) as a colorless solid (40 mg, 97%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C spectra for all obtained compounds. CIF file for complex **5**. 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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