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2-Carbomethoxy-3-hydroxyquinoxaline-di-*N*-oxide as a novel ligand for the copper-catalyzed coupling reaction of phenols and aryl halides†

Cite this: *Org. Biomol. Chem.*, 2013, **11**, 1502

Received 9th May 2012,
Accepted 21st December 2012

DOI: 10.1039/c2ob26556g

www.rsc.org/obc

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2-Carbomethoxy-3-hydroxyquinoxaline-di-*N*-oxide was identified as an efficient novel ligand for the copper-catalyzed coupling of aryl halides with various phenols under mild conditions. The catalytic system shows great functional-group tolerance and excellent reactive selectivity.

Introduction

The diaryl ether motif is commonly found in many natural products, polymers, and pharmaceutically active compounds.[1,2] Because the classic Ullmann ether synthesis is carried out under relatively harsh conditions, such as high temperatures (125–220 °C) and stoichiometric amounts of the catalyst, namely copper (Cu), with only low to moderate yields, much effort has been devoted to finding direct and efficient processes for preparation of biaryl ethers.[3] Using transition-metal catalysts, such as palladium (Pd), copper (Cu), and iron (Fe), has achieved extraordinary improvement in the formation of the C–O bond.[4–6] Because Pd catalysts are expensive, the application of Pd-catalyzed methods has thus far been limited to small-scale production. Cu-catalyzed Ullmann coupling between an aryl halide and phenol/alcohols is a viable alternative to Pd-catalyzed diaryl ether synthesis. Recently, a major progress has been made in modifying the Cu-catalyzed Ullmann coupling reaction by using several special ligands, such as 1-naphthoic acid, 1,10-phenanthroline, neocuproine, triphenylphosphine, 2,6,6-tetramethylheptane-3,5-dione, tetraethyl orthosilicate, *N*,*N*-dimethylglycine, diimine ligands, β-keto esters, tripod ligands and bipyridyl complexes.[3] However, only a few ligands were reported for the copper catalyzed coupling of aryl chlorides with phenols.[5j,o,s] It is essential to search for other new, less costly, and versatile ligands that can be used in this Cu-catalyzed protocol. Herein, we report 2-carbomethoxy-3-hydroxyquinoxaline-di-*N*-oxide as an efficient novel ligand for the formation of diaryl ethers.

Results and discussion

By analyzing the structural features of previously reported ligands of the Cu-catalyzed Ullman reaction, we found that most of them contained bidentate chelating centers consisting of coordinating atoms such as oxygen and/or nitrogen atoms, which might coordinate with a Cu ion to form a transitional 5- or 6-membered ring. The ligands that coordinate with the metal center constitute the most important factor in determining the efficiency of the catalytic system. Based on this survey, 2-carbomethoxy-3-hydroxyquinoxaline-di-*N*-oxide (**L1**), in which the oxygen atom of nitrogen oxide (1), the oxygen atom of the carbomethoxy group (2), another oxygen atom (3), and the oxygen atom of the second nitrogen oxide (4; Fig. 1) might form transitional 6-membered and 5-membered rings with the Cu ion, was designed as a novel potential tetradentate ligand to improve Cu-catalyzed cross-couplings.

To evaluate the catalytic activity of the thus-designed ligand, we first chose iodobenzene as the model substrate to react with phenol, and the results are summarized in Table 1. Clearly, 2-carbomethoxy-3-hydroxyquinoxaline-di-*N*-oxide (**L1**) can successfully promote the Cu-catalyzed coupling reaction and produce high yield (90%). Interestingly, due to the

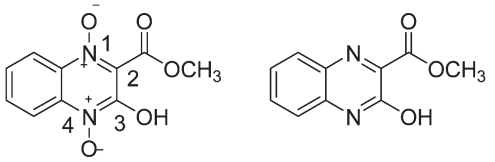

Fig. 1 Structure of the ligands designed in this study.

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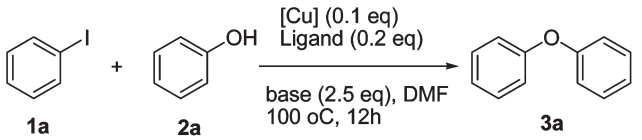
†Electronic supplementary information (ESI) available: ^{1}H NMR and ^{13}C NMR spectra of all compounds. See DOI: 10.1039/c2ob26556g

‡These authors contributed equally to the work.

Table 1 Copper-catalyzed *O*-arylation of phenol with iodobenzene: optimization of the reaction conditions[a]



Entry	[Cu]	Ligand	Base	Yield[b] (%)
1	CuI	**L1**	Cs_2CO_3	90
2	CuI	**L2**	Cs_2CO_3	33
3	CuBr	**L1**	Cs_2CO_3	82
4	CuI	**L1**	K_2CO_3	39
5	CuI	**L1**	K_3PO_4	5

[a] Reaction conditions: [Cu] (0.01 mmol), ligand (0.02 mmol), iodobenzene (0.1 mmol), phenol (0.11 mmol), Cs_2CO_3 (0.25 mmol), 100 °C. [b] Isolated yield.

absence of an oxygen atom, **L2** (1,1,1-trifluoro-3-(pyridin-2-yl)-propan-2-one) showed much lower efficiency (entries 1 and 2). After evaluation of the catalytic efficiency of **L1** and **L2**, the conditions for catalysis, including the source of Cu and the base, were also optimized. The experimental results showed that CuI was more efficient than CuBr (entries 1 and 3), whereas cesium carbonate (Cs_2CO_3) was the best among the various bases tested (entries 1, 4, and 5). Thus, the optimized reaction conditions were as follows: 10 mol% of Cu(I), 20 mol % of **L1**, and 2.5 equiv. of Cs_2CO_3 in 0.5 M DMF (as a solvent) reacting at a temperature of 100 °C under a nitrogen atmosphere.

To define the scope of the CuI-catalyzed *O*-arylation reaction, we applied this process to several different aryl iodides and phenols or 2-naphthol. As shown in Table 2, both electron-rich (**3e–3i**) and electron-deficient (**3j–3m**) aryl iodides are suitable substrates for this reaction, which provide the corresponding diaryl ethers in good to excellent yields. A variety of functional groups, which include methyl, alkoxyl, nitro, and carbonyl groups, of aryl iodides are tolerant to these reaction conditions well. The reactivity of phenols containing various electron-withdrawing and electron-donating substrates was compared using iodobenzene as an arylating agent (**3a–3d**). We also observed that the coupling was favored by electron-donating groups (**3d**). To our delight, the steric hindrance of phenols is also favorable for this reaction. For example, when 2,4-di-*tert*-butylphenol was used as the substrate, the reaction gave excellent yields (96%) in comparison with that of less-hindered phenols (compare **3j** and **3l**). To the best of our knowledge, the examples for Pd- or Cu-catalyzed diaryl ether synthesis with substrates bearing a *o-tert*-butyl group were relatively rare. In addition, we also tested reactions of alkyl alcohols with aryl iodides, and good yields were obtained (**3n–3p**).

The proposed catalytic system was further applied to the coupling reaction of aryl bromides and phenols with good results. As shown in Table 3, high yields were obtained for aryl bromides with electron-withdrawing (**5b–5d**) and electron-donating (**5e**) groups. However, the sterically hindered phenols are slightly disfavored in this reaction. For example, when 2,4-di-*tert*-butylphenol was used as the substrate, the reaction gave considerably lower yield in comparison with that of less-hindered phenols (compare **5f**, **5g**, and **5h**). Additionally, the relatively lower yield for phenol in comparison with the electron-donating group of phenol implies that the electron-donating group of phenol is favored for the coupling reaction (compare **5i** and **5j**). The poor yield for the reaction of phenyl bromide with phenol resulted from low conversion (**5a**). We also tested the coupling reaction of alkyl alcohols such as ethanol, *n*-butanol and isopropanol with aryl bromides. However the yield is very low.

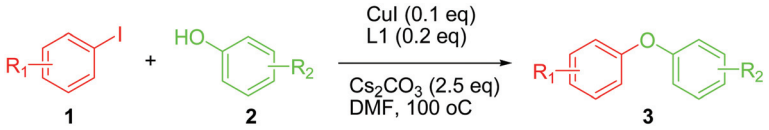
Due to their low cost and ready availability, aryl chlorides are attractive substrates for both industrial production and laboratory preparation of diaryl ethers. Therefore, we further investigated the potential catalytic efficiency of the present catalytic system for the coupling reaction of aryl chlorides and phenols. As shown in Table 4, electron-deficient (**7a–7i**) aryl chlorides are suitable substrates for this reaction, and they produce the corresponding diaryl ethers in good to excellent yields. In the aryl iodide component, the substituent position of the nitro group slightly influences the yield of the coupling reaction (**7a** *versus* **7b**, and **7d–7f** *versus* **7g–7i**). For example, when 1-chloro-4-nitrobenzene reacted with phenol, the yield was 84%. The yield improved to 97% when 1-chloro-2-nitrobenzene reacted with phenol (**7a** and **7b**). It is noteworthy that the reaction of 1-chloro-2-nitrobenzene or 1-chloro-4-nitrobenzene with sterically hindered phenols, such as 2,4-di-*tert*-butylphenol, which are difficult cases for the classical Ullmann coupling method, gave the product of the coupling reaction at 89% and 91% yields, respectively (**7e** and **7i**). Additionally, high yields were also obtained for other substrates, such as 2-naphthol, 8-hydroxyquinoline and *N*-(4-hydroxyphenyl)acetamide, when aryl chlorides with electron-withdrawing groups were used (**7c**, **7d**, and **7f–7i**). In addition, very lower yields were obtained after 20 h when 1-chloro-2-nitrobenzene was reacted with phenol at 110 °C when the copper catalyst or the ligand was absent.

As described in Fig. 2, we have formulated a possible mechanism for the copper-catalyzed coupling of aryl halides with various phenols, which is based on the previously proposed mechanism.[1–3] The chelating CuI with 2-carbomethoxy-3-hydroxyquinoxaline-di-*N*-oxide (**L1**) formed a six-membered and five-membered reactive species **8**, and the subsequent oxidative addition of the chelating species with aryl halides led to the intermediate **9**. In the presence of a base, various phenols reacted with intermediate **8** readily to afford intermediate **11**, followed by reductive elimination to provide the desired product and regenerate active Cu(I) species **8**.

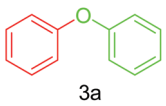
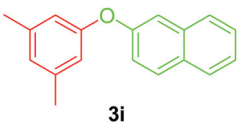
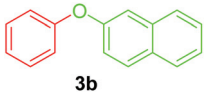
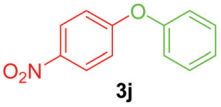
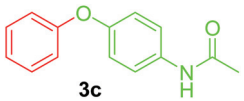
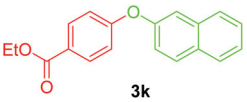
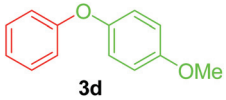
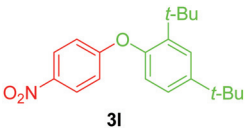
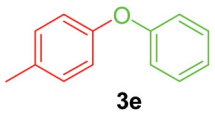
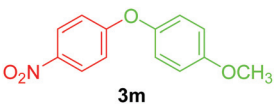
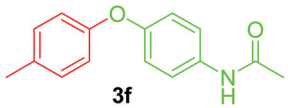
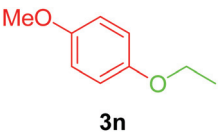
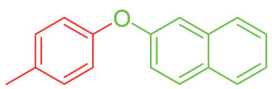
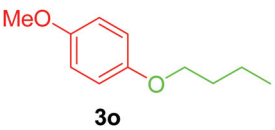
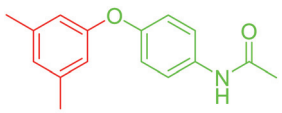
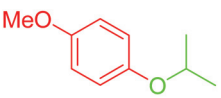
Conclusion

In summary, we have developed an efficient, experimentally simple, and economically attractive method for the

Table 2 CuI-catalyzed coupling reaction of aryl iodides with phenols or 2-naphthol[a]



1 2 3

Product	T (h)	Y^b (%)	Product	T (h)	Y^b (%)
 3a	12	90	 3i	5	95
 3b	12	83	 3j	12	89
 3c	15	74	 3k	7	75
 3d	15	99	 3l	12	96
 3e	12	72	 3m	6	71
 3f	9	70	 3n	24	63
 3g	10	60	 3o	24	73
 3h	20	60	 3p	24	71

[a] Reaction conditions: CuI (0.10 mmol), **L1** (0.20 mmol), ArI (1.0 mmol), phenol (1.2 mmol), Cs_2CO_3 (2.5 mmol), DMF (1.5 mL), 100 °C. [b] Isolated yield.

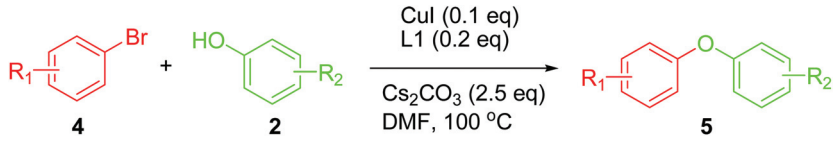
Cu-catalyzed synthesis of diaryl ethers from various aromatic iodides, bromides, and chlorides using 2-carbomethoxy-3-hydroxyquinoxaline-di-*N*-oxide as the ligand. This method shows broad functional-group tolerance and high selectivity in the presence of multiple potentially reactive groups at moderate temperatures. This report provides an attractive method for the synthesis of more complex diaryl ethers. Efforts to extend the applications of these ligands to other types of Cu-catalyzed coupling reactions are currently underway in our laboratory and will be reported in due course.

Experimental

General procedure A

A flask was charged with CuI (19.1 mg, 0.1 mmol, 10 mol%), **L1** (47.2 mg, 0.2 mmol, 20 mol%), Cs_2CO_3 (812.5 mg, 2.5 mmol), and any remaining solids (phenol and/or aryl halide). The flask was evacuated and backfilled with argon. Aryl iodide (1.0 mmol, if liquid), phenol (1.5 mmol, if liquid), and DMF (1.5 mL) were added to the flask under an argon atmosphere. Then the mixture was stirred at 100 °C until complete consumption of starting material was monitored by TLC.

Table 3 CuI-catalyzed coupling reaction of aryl bromide with phenols or 2-naphthol[a]



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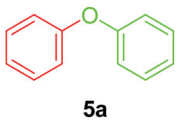
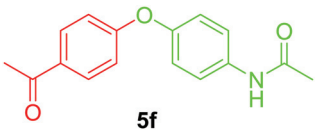
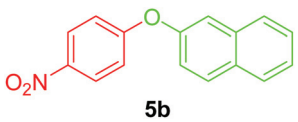
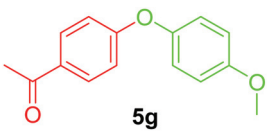
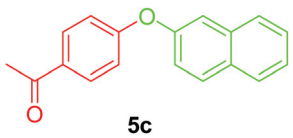
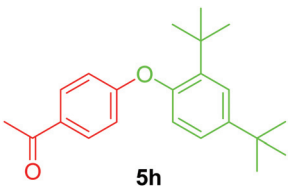
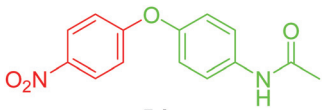
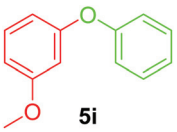
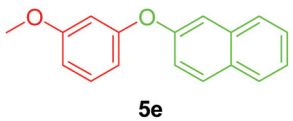
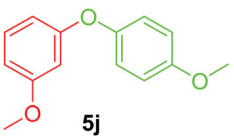
 5a	20[a]	44	 5f	20[d]	71
 5b	12[a]	93	 5g	20[d]	87
 5c	15[a]	92	 5h	20[d]	54
 5d	11[c]	98	 5i	20[c]	55
 5e	16[a]	92	 5j	20[c]	77

[a] Reaction conditions: CuI (0.10 mmol), **L1** (0.20 mmol), ArBr (1.0 mmol), phenol (1.2 mmol), Cs_2CO_3 (2.5 mmol), DMF (1.5 mL), 100 °C. [b] Isolated yield. [c] Reaction was carried out at 110 °C. [d] Reaction was carried out at 100 °C for 12 h and 110 °C for 8 h.

After completion of the reaction, the mixture was diluted with ethyl acetate, passed through a fritted glass filter to remove the inorganic salts and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to provide the desired product.

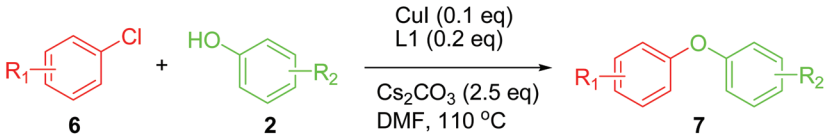
Diphenyl ether (3a). Following procedure A, iodobenzene (0.112 mL, 1.0 mmol) was allowed to react with phenol (0.134 mL, 1.5 mmol) for 12 h. The crude brown oil was purified by flash chromatography on silica gel to provide 90% yield of the desired product as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.32 (m, 4H), 7.12–7.08 (m, 2H), 7.02–7.00 (m, 4H) ppm. MS (EI, *m*/*z*): 171 (M^+ + 1).

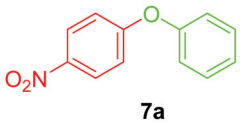
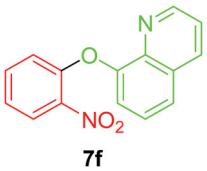
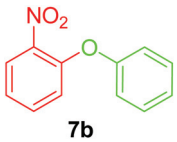
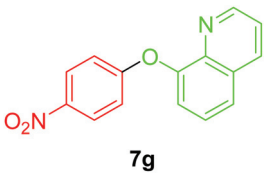
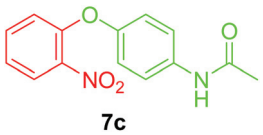
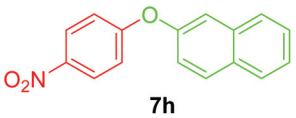
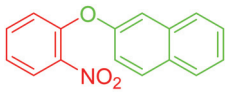
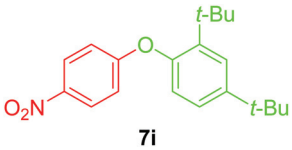
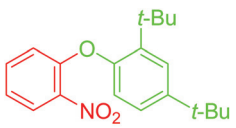
2-Phenoxynaphthalene (3b). Following procedure A, iodobenzene (0.112 mL, 1.0 mmol) was allowed to react with naphthalen-2-ol (216.3 mg, 1.5 mmol) for 12 h. The crude brown oil was purified by flash chromatography on silica gel to provide 83% yield of the desired product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.82 (m, 2H), 7.72–7.70 (m, 1H), 7.48–7.26 (m, 6H), 7.17–7.14 (m, 1H), 7.10–7.08 (m, 2H) ppm. MS (EI, *m*/*z*): 221 (M^+ + 1).

***N*-(4-Phenoxyphenyl)acetamide (3c).** Following procedure A, iodobenzene (0.112 mL, 1.0 mmol) was allowed to react with *N*-(4-hydroxyphenyl)acetamide (226.7 mg, 1.5 mmol) for 15 h. The crude brown oil was purified by flash chromatography on silica gel to provide 74% yield of the desired product as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (br s, 1H), 7.48–7.45 (m, 2H), 7.32–7.28 (m, 2H), 7.08–7.07 (m, 1H), 6.97–6.94 (m, 4H), 2.15 (s, 3H) ppm. MS (EI, *m*/*z*): 228 (M^+ + 1).

1-Methoxy-4-phenoxybenzene (3d). Following procedure A, iodobenzene (0.112 mL, 1.0 mmol) was allowed to react with 4-methoxyphenol (186.2 mg, 1.5 mmol) for 15 h. The crude brown oil was purified by flash chromatography on silica gel to provide 99% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.30 (m, 2H), 7.09–7.05 (m, 1H), 7.03–6.97 (m, 4H), 6.93–6.90 (m, 2H), 3.82 (s, 3H) ppm. MS (EI, *m*/*z*): 201 (M^+ + 1).

Table 4 CuI-catalyzed coupling reaction of aryl chloride with phenols or 2-naphthol[a]



Product	*T* (h)	*Y*[b] (%)	Product	*T* (h)	*Y*[b] (%)
 **7a**	5	84	 **7f**	12	72
 **7b**	8	97	 **7g**	12	99
 **7c**	12	95	 **7h**	12	87
 **7d**	12	94	 **7i**	12	91
 **7e**	12	89			

[a] Reaction conditions: CuI (0.10 mmol), **L1** (0.20 mmol), ArCl (1.0 mmol), phenol (1.2 mmol), Cs_2CO_3 (2.5 mmol), DMF (1.5 mL), 110 °C. [b] Isolated yield.

1-Methyl-4-phenoxybenzene (3e). Following procedure A, 1-iodo-4-methylbenzene (141.2 mg, 1.0 mmol) was allowed to react with phenol (0.134 mL, 1.5 mmol) for 12 h. The crude brown oil was purified by flash chromatography on silica gel to provide 72% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 2H), 7.17–7.15 (m, 2H), 7.10–7.07 (m, 1H), 7.01–6.99 (m, 2H), 6.95–6.93 (m, 2H), 2.35 (s, 3H) ppm. MS (EI, *m*/*z*): 185 (M^+ + 1).

***N*-(4-(*p*-Tolyloxy)phenyl)acetamide (3f).** Following procedure A, 1-iodo-4-methylbenzene (141.2 mg, 1.0 mmol) was allowed to react with *N*-(4-hydroxyphenyl)acetamide (226.7 mg, 1.5 mmol) for 9 h. The crude brown oil was purified by flash chromatography on silica gel to provide 70% yield of the desired product as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (br s, 1H), 7.42 (dt, J = 7.2, 2.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.93 (dt, J = 7.2, 2.0 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 2.32 (s, 3H), 2.15 (s, 3H) ppm. MS (EI, *m*/*z*): 242 (M^+ + 1).

2-(*p*-Tolyloxy)naphthalene (3g). Following procedure A, 1-iodo-4-methylbenzene (141.2 mg, 1.0 mmol) was allowed to react with naphthalen-2-ol (216.3 mg, 1.5 mmol) for 10 h. The crude brown oil was purified by flash chromatography on silica gel to provide 60% yield of the desired product as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.81 (m, 2H), 7.70–7.68 (m, 1H), 7.47–7.39 (m, 2H), 7.28–7.25 (m, 2H), 7.20–7.17 (m, 2H), 7.01–6.98 (m, 2H), 2.37 (s, 3H) ppm. MS (EI, *m*/*z*): 235 (M^+ + 1).

***N*-(4-(3,5-Dimethylphenoxy)phenyl)acetamide (3h).** Following procedure A, 1-iodo-3,5-dimethylbenzene (0.145 mL, 1.0 mmol) was allowed to react with *N*-(4-hydroxyphenyl)acetamide (226.7 mg, 1.5 mmol) for 20 h. The crude brown oil was purified by flash chromatography on silica gel to provide 60% yield of the desired product as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.72 (s, 1H), 6.59 (s, 2H), 2.27 (s, 6H), 2.17 (s, 3H) ppm.

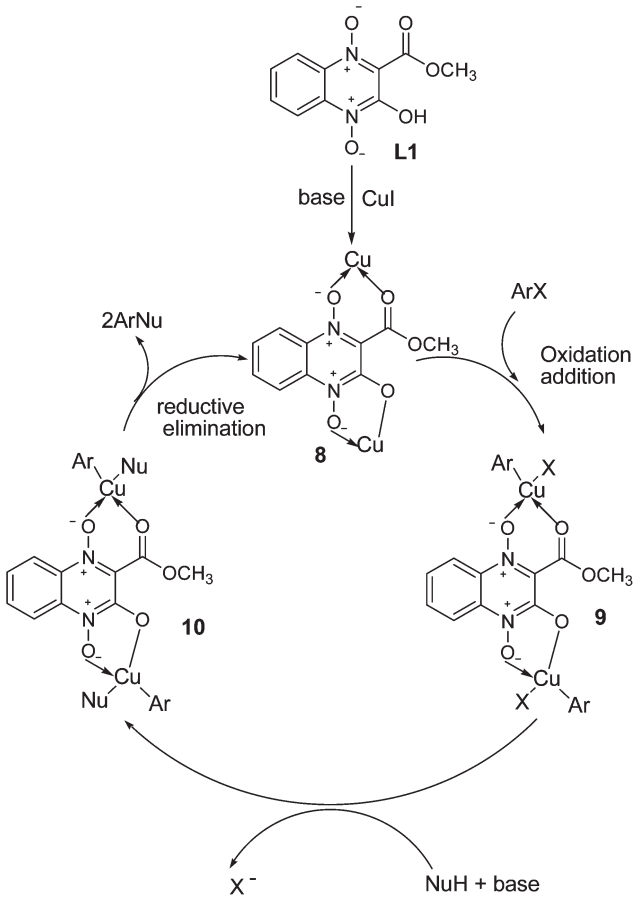


Fig. 2 Proposed mechanism.

MS (EI, *m*/*z*): 256 (M^+ + 1). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 157.5, 153.7, 139.6, 133.1, 124.8, 121.7, 119.6, 116.1, 24.4, 21.3 ppm. HRMS (ESI): calcd for $C_{16}H_{17}NO_2Na$ [MNa^+] 278.1157, found 278.1153.

2-(3,5-Dimethylphenoxy)naphthalene (3i). Following procedure A, 1-iodo-3,5-dimethylbenzene (0.145 mL, 1.0 mmol) was allowed to react with naphthalen-2-ol (216.3 mg, 1.5 mmol) for 5 h. The crude brown oil was purified by flash chromatography on silica gel to provide 95% yield of the desired product as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (dt, J = 9.2, 2.8 Hz, 2H), 7.73–7.65 (m, 4H), 7.38 (d, J = 3.6 Hz, 1H), 7.33–7.29 (m, 1H), 7.27–7.23 (m, 1H), 6.78 (dd, J = 3.4, 0.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.3, 155.5, 139.7, 134.5, 130.2, 129.8, 127.8, 127.2, 126.5, 125.3, 124.6, 120.2, 116.9, 114.2, 21.3 ppm. MS (EI, *m*/*z*): 249 (M^+ + 1). HRMS (ESI): calcd for $C_{18}H_{17}O$ [MH^+] 249.1279, found 249. 1272.

1-Nitro-4-phenoxybenzene (3j). Following procedure A, 1-iodo-4-nitrobenzene (249 mg, 1.0 mmol) was allowed to react with phenol (0.134 mL, 1.5 mmol) for 12 h. The crude brown oil was purified by flash chromatography on silica gel to provide 89% yield of the desired product as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 9.2 Hz, 2H), 7.46–7.42 (m, 2H), 7.28–7.24 (m, 1H), 7.09 (m, 2H), 7.01 (d, J = 9.2 Hz, 2H) ppm. MS (EI, *m*/*z*): 216 (M^+ + 1).

Ethyl 4-(naphthalen-2-yloxy)benzoate (3k). Following procedure A, ethyl 4-iodobenzoate (276.0 mg, 1.0 mmol) was allowed to react with naphthalen-2-ol (216.3 mg, 1.5 mmol) for 7 h. The crude brown oil was purified by flash chromatography on silica gel to provide 75% yield of the desired product as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.03 (m, 2H), 7.89–7.85 (m, 2H), 7.76–7.74 (m, 1H), 7.51–7.44 (m, 3H), 7.27–7.25 (m, 1H), 7.06–7.04 (m, 2H), 4.37 (q, J = 14.4 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H) ppm. MS (EI, *m*/*z*): 293 (M^+ + 1).

2,4-Di-*tert*-butyl-1-(4-nitrophenoxy)benzene (3l). Following procedure A, 1-iodo-4-nitrobenzene (249 mg, 1.0 mmol) was allowed to react with 2,4-di-*tert*-butylphenol (206.3 mg, 1.5 mmol) for 12 h. The crude brown oil was purified by flash chromatography on silica gel to provide 96% yield of the desired product as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–8.18 (m, 2H), 7.47–7.46 (m, 1H), 7.24–7.21 (m, 1H), 7.03–6.99 (m, 2H), 6.82–6.80 (m, 1H), 1.36 (s, 9H), 1.35 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 151.1, 148.0, 142.5, 140.9, 125.9, 124.7, 124.3, 121.1, 117.2, 34.9, 34.7, 31.5, 30.4 ppm. MS (EI, *m*/*z*): 328 (M^+ + 1). HRMS (ESI): calcd for $C_{20}H_{25}NO_3Na$ [MNa^+] 350.1732, found 350.1729.

1-Methoxy-4-(4-nitrophenoxy)benzene (3m). Following procedure A, 1-iodo-4-nitrobenzene (249 mg, 1.0 mmol) was allowed to react with 4-methoxyphenol (186.2 mg, 1.5 mmol) for 6 h. The crude brown oil was purified by flash chromatography on silica gel to provide 71% yield of the desired product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 9.2 Hz, 2H), 7.02 (d, J = 9.2 Hz, 2H), 6.97–6.94 (m, 4H), 3.83 (s, 3H) ppm. MS (EI, *m*/*z*): 246 (M^+ + 1).

4-Ethoxyanisole (3n). Following procedure A, 4-iodoanisole (234.0 mg, 1.0 mmol) was allowed to react with ethanol (0.087 mL, 1.5 mmol) for 24 h. The crude brown oil was purified by flash chromatography on silica gel to provide 63% yield of the desired product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67–6.65 (m, 4H), 3.98 (q, J = 7.2 Hz, 2H), 3.75 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 153.5, 115.4, 114.6, 64.7, 55.7, 15.8 ppm.

4-*n*-Butoxyanisole (3o). Following procedure A, 4-iodoanisole (234.0 mg, 1.0 mmol) was allowed to react with *n*-butanol (0.137 mL, 1.5 mmol) for 24 h. The crude brown oil was purified by flash chromatography on silica gel to provide 73% yield of the desired product as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.68–6.65 (m, 4H), 3.93 (t, J = 6.8 Hz, 2H), 3.76 (s, 3H), 1.78–1.70 (m, 2H), 1.62–1.52 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 153.5, 115.4, 114.6, 68.6, 55.3, 34.9, 18.9, 13.8 ppm.

4-Isopropyloxyanisole (3p). Following procedure A, 4-iodoanisole (234.0 mg, 1.0 mmol) was allowed to react with isopropanol (0.115 mL, 1.5 mmol) for 24 h. The crude brown oil was purified by flash chromatography on silica gel to provide 71% yield of the desired product as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88–6.84 (m, 4H), 4.44–4.35 (m, 1H), 3.75 (s, 3H), 1.38 (d, J = 6.4 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 153.3, 115.4, 114.6, 64.9, 55.3, 25.3 ppm.

General procedure B

An oven-dried Schlenk tube equipped with a Teflon valve (Kontes) was charged with a magnetic stir bar, CuI (19.1 mg, 0.1 mmol, 10 mol%), the **L1** (47.2 mg, 0.2 mmol, 20 mol%) and the inorganic base (2.5 mmol): Cs_2CO_3 (812.5 mg). Any remaining solids (phenol and/or aryl bromide) were added at this point. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counterflow of argon, phenol (if liquid), aryl bromide (if liquid) and DMF (1.5 mL) were added using a syringe. Finally, the tube was sealed and the mixture was heated at the indicated temperature (100 °C–110 °C) for the indicated period of time. Upon completion of the reaction, the mixture was allowed to cool to room temperature and then was diluted with ethyl acetate, passed through a fritted glass filter to remove the inorganic salts and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel and the product was dried under vacuum for at least 1 h.

Diphenyl ether (5a/3a). Following procedure B, bromobenzene (0.105 mL, 1.0 mmol) was allowed to react with phenol (0.134 mL, 1.5 mmol) for 20 h at 100 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 44% yield of the desired product as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.32 (m, 4H), 7.12–7.08 (m, 2H), 7.02–7.00 (m, 4H) ppm. MS (EI, *m*/*z*): 171 (M^+ + 1).

2-(4-Nitrophenoxy)naphthalene (5b). Following procedure B, 1-bromo-4-nitrobenzene (202.0 mg, 1.0 mmol) was allowed to react with naphthalen-2-ol (216.3 mg, 1.5 mmol) for 12 h at 100 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 93% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24–8.20 (m, 2H), 7.94–7.88 (m, 2H), 7.81–7.78 (m, 1H), 7.56–7.48 (m, 3H), 7.27–7.24 (m, 1H), 7.09–7.05 (m, 2H) ppm. MS (EI, *m*/*z*): 266 (M^+ + 1).

1-(4-(Naphthalen-2-yloxy)phenyl)ethanone (5c). Following procedure B, 1-(4-bromophenyl)ethanone (199.0 mg, 1.0 mmol) was allowed to react with naphthalen-2-ol (216.3 mg, 1.5 mmol) for 15 h at 100 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 92% yield of the desired product as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.95 (m, 2H), 7.90–7.86 (m, 2H), 7.77–7.75 (m, 1H), 7.53–7.45 (m, 3H), 7.28–7.25 (m, 1H), 7.08–7.05 (m, 2H), 2.59 (s, 3H) ppm. MS (EI, *m*/*z*): 263 (M^+ + 1).

***N*-(4-(4-Nitrophenoxy)phenyl)acetamide (5d).** Following procedure B, 1-bromo-4-nitrobenzene (202.0 mg, 1.0 mmol) was allowed to react with *N*-(4-hydroxyphenyl)acetamide (226.7 mg, 1.5 mmol) for 11 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 98% yield of the desired product as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 9.2 Hz, 2H), 7.69 (br s, 1H), 7.57 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 9.2 Hz, 2H), 2.20 (s, 3H) ppm. MS (EI, *m*/*z*): 273 (M^+ + 1).

2-(3-Methoxyphenoxy)naphthalene (5e). Following procedure B, 1-bromo-3-methoxybenzene (0.126 mL, 1.0 mmol) was allowed to react with naphthalen-2-ol (216.3 mg, 1.5 mmol) for 16 h at 100 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 92% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.83 (m, 2H), 7.74–7.71 (m, 1H), 7.49–7.40 (m, 2H), 7.36–7.35 (m, 1H), 7.29–7.24 (m, 2H), 6.72–6.65 (m, 3H), 3.79 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 158.6, 155.0, 134.5, 130.4, 130.2, 129.9, 127.8, 127.2, 126.6, 124.8, 120.1, 114.5, 111.3, 109.3, 105.2, 55.4 ppm. MS (EI, *m*/*z*): 251 (M^+ + 1). HRMS (ESI): calcd for $C_{17}H_{15}O_2$ [MH^+] 251.1072, found 251.1070.

***N*-(4-(4-Acetylphenoxy)phenyl)acetamide (5f).** Following procedure B, 1-(4-bromophenyl)ethanone (199.0 mg, 1.0 mmol) was allowed to react with *N*-(4-hydroxyphenyl)acetamide (226.7 mg, 1.5 mmol) at 100 °C for 12 h and 110 °C for 8 h. The crude brown oil was purified by flash chromatography on silica gel to provide 71% yield of the desired product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (br s, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 9.2 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 2.56 (s, 3H), 2.17 (s, 3H) ppm. MS (EI, *m*/*z*): 270 (M^+ + 1).

1-(4-(4-Methoxyphenoxy)phenyl)ethanone (5g). Following procedure B, 1-(4-bromophenyl)ethanone (199.0 mg, 1.0 mmol) was allowed to react with 4-methoxyphenol (186.2 mg, 1.5 mmol) at 100 °C for 12 h and 110 °C for 8 h. The crude brown oil was purified by flash chromatography on silica gel to provide 87% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.90 (m, 2H), 7.02–7.00 (m, 2H), 6.95–6.91 (m, 4H) ppm. MS (EI, *m*/*z*): 243 (M^+ + 1).

1-(4-(2,4-Di-*tert*-butylphenoxy)phenyl)ethanone (5h). Following procedure B, 1-(4-bromophenyl)ethanone (199.0 mg, 1.0 mmol) was allowed to react with 2,4-di-*tert*-butylphenol (206.3 mg, 1.5 mmol) at 100 °C for 12 h and 110 °C for 8 h. The crude brown oil was purified by flash chromatography on silica gel to provide 54% yield of the desired product as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 2.4 Hz, 1H), 7.18 (d, J = 2.4 Hz, 1H), 6.99 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.4 Hz, 1H), 2.57 (s, 3H), 1.38 (s, 9H), 1.34 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5, 151.7, 147.1, 140.7, 130.5, 124.5, 124.1, 120.9, 117.2, 34.9, 34.6, 31.6, 31.5, 30.3, 29.7, 26.3 ppm. MS (EI, *m*/*z*): 325 (M^+ + 1). HRMS (ESI): calcd for $C_{22}H_{28}O_2Na$ [MNa^+] 347.1987, found 347.1984.

1-Methoxy-3-phenoxybenzene (5i). Following procedure B, 1-bromo-3-methoxybenzene (0.126 mL, 1.0 mmol) was allowed to react with phenol (0.134 mL, 1.5 mmol) for 20 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 55% yield of the desired product as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.34 (m, 2H), 7.28–7.22 (m, 1H), 7.15–7.11 (m, 1H), 7.06–7.04 (m, 2H), 6.69–6.67 (m, 1H), 6.62–6.60 (m, 2H), 3.80 (s, 3H) ppm. MS (EI, *m*/*z*): 201 (M^+ + 1).

1-Methoxy-3-phenoxybenzene (5j). Following procedure B, 1-bromo-3-methoxybenzene (0.126 mL, 1.0 mmol) was allowed to react with phenol (4-methoxyphenol; 186.2 mg, 1.5 mmol)

for 20 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 77% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.17 (m, 1H), 7.01–6.99 (m, 2H), 6.90–6.88 (m, 2H), 6.61–6.59 (m, 1H), 6.53–6.52 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H) ppm. MS (EI, *m*/*z*): 231 (M^+ + 1).

General procedure C

An oven-dried Schlenk tube equipped with a Teflon valve (Kontes) was charged with a magnetic stir bar, CuI (19.1 mg, 0.1 mmol, 10 mol%), the **L1** (47.2 mg, 0.2 mmol, 20 mol%) and the inorganic base (2.5 mmol): Cs_2CO_3 (812.5 mg). Any remaining solids (phenol and/or aryl chloride) were added at this point. The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counterflow of argon, phenol (if liquid), aryl chloride (if liquid) and DMF (1.5 mL) were added using a syringe. Finally, the tube was sealed and the mixture was heated at the indicated temperature (110 °C) for the indicated period of time. Upon completion of the reaction, the mixture was allowed to cool to room temperature and then was diluted with ethyl acetate, passed through a fritted glass filter to remove the inorganic salts and the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel and the product was dried under vacuum for at least 1 h.

1-Nitro-2-phenoxybenzene (7b). Following procedure C, 1-chloro-2-nitrobenzene (236.3 mg, 1.0 mmol) was allowed to react with phenol (0.134 mL, 1.5 mmol) for 8 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 97% yield of the desired product as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.93 (m, 1H), 7.52–7.48 (m, 1H), 7.40–7.36 (m, 2H), 7.21–7.17 (m, 2H), 7.06–6.99 (m, 3H) ppm. MS (EI, *m*/*z*): 216 (M^+ + 1).

***N*-(4-(2-Nitrophenoxy)phenyl)acetamide (7c).** Following procedure C, 1-chloro-2-nitrobenzene (236.3 mg, 1.0 mmol) was allowed to react with *N*-(4-hydroxyphenyl)acetamide (226.7 mg, 1.5 mmol) for 12 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 95% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.91 (m, 1H), 7.76 (m, 1H), 7.51–7.45 (m, 3H), 7.19–7.15 (m, 1H), 6.98–6.94 (m, 3H), 2.16 (s, 3H) ppm. MS (EI, *m*/*z*): 273 (M^+ + 1).

2-(2-Nitrophenoxy)naphthalene (7d). Following procedure C, 1-chloro-2-nitrobenzene (236.3 mg, 1.0 mmol) was allowed to react with naphthalen-2-ol (216.3 mg, 1.5 mmol) for 12 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 94% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01–7.99 (m, 1H), 7.90–7.84 (m, 2H), 7.75–7.73 (m, 1H), 7.54–7.44 (m, 3H), 7.38 (m, 1H), 7.30–7.21 (m, 2H), 7.08–7.06 (m, 1H) ppm. MS (EI, *m*/*z*): 266 (M^+ + 1).

2,4-Di-*tert*-butyl-1-(2-nitrophenoxy)benzene (7e). Following procedure C, 1-chloro-2-nitrobenzene (236.3 mg, 1.0 mmol) was allowed to react with 2,4-di-*tert*-butylphenol (206.3 mg, 1.5 mmol) for 12 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 89% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.93 (m, 1H), 7.47–7.43 (m, 2H), 7.21–7.18 (m, 1H), 7.14–7.11 (m, 1H), 6.96–6.94 (m, 1H), 6.77–6.75 (m, 1H), 1.42 (s, 9H), 1.35 (s, 9H) ppm. MS (EI, *m*/*z*): 328 (M^+ + 1).

8-(2-Nitrophenoxy)quinoline (7f). Following procedure C, 1-chloro-2-nitrobenzene (236.3 mg, 1.0 mmol) was allowed to react with quinolin-8-ol (217.8 mg, 1.5 mmol) for 12 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 72% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (d, J = 4.0 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.48–7.42 (m, 3H), 7.22–7.16 (m, 2H), 6.97 (d, J = 8.4 Hz, 1H) ppm. MS (EI, *m*/*z*): 267 (M^+ + 1).

8-(4-Nitrophenoxy)quinoline (7g). Following procedure C, 1-chloro-4-nitrobenzene (236.3 mg, 1.0 mmol) was allowed to react with quinolin-8-ol (217.8 mg, 1.5 mmol) for 12 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 99% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89–8.88 (m, 1H), 8.26–8.24 (m, 1H), 8.17 (d, J = 8.8 Hz, 2H), 7.77–7.75 (m, 1H), 7.59–7.55 (m, 1H), 7.49–7.46 (m, 1H), 7.44–7.42 (m, 1H), 7.02 (d, J = 9.2 Hz, 2H) ppm. MS (EI, *m*/*z*): 267 (M^+ + 1).

2-(4-Nitrophenoxy)naphthalene (7h/5b). Following procedure C, 1-chloro-4-nitrobenzene (236.3 mg, 1.0 mmol) was allowed to react with naphthalen-2-ol (216.3 mg, 1.5 mmol) for 12 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 87% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24–8.20 (m, 2H), 7.94–7.88 (m, 2H), 7.81–7.78 (m, 1H), 7.56–7.48 (m, 3H), 7.27–7.24 (m, 1H), 7.09–7.05 (m, 2H) ppm. MS (EI, *m*/*z*): 266 (M^+ + 1).

2,4-Di-*tert*-butyl-1-(4-nitrophenoxy)benzene (7i). Following procedure C, 1-chloro-4-nitrobenzene (236.3 mg, 1.0 mmol) was allowed to react with 2,4-di-*tert*-butylphenol (206.3 mg, 1.5 mmol) for 12 h at 110 °C. The crude brown oil was purified by flash chromatography on silica gel to provide 91% yield of the desired product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22–8.18 (m, 2H), 7.47–7.46 (m, 1H), 7.24–7.21 (m, 1H), 7.03–6.99 (m, 2H), 6.82–6.80 (m, 1H), 1.36 (s, 9H), 1.35 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 151.1, 148.0, 142.5, 140.9, 125.9, 124.7, 124.3, 121.1, 117.2, 34.9, 34.7, 31.5, 30.4 ppm. MS (EI, *m*/*z*): 328 (M^+ + 1). HRMS (ESI): calcd for $C_{20}H_{25}NO_3Na$ [MNa^+] 350.1732, found 350.1729.

Acknowledgements

We thank the National Natural Science Foundation (Grant No. 20972160 and 21172220), the National Basic Research Program of China (Grant No. 2009CB940900), and CSA-Guangdong Joint Foundation (Grant No. 2011B090300069) for their financial support.

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