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Copper-Catalyzed Hydroxylation of Aryl Halides: Efficient Synthesis of Phenols, Alkyl Aryl Ethers and Benzofuran Derivatives in Neat Water

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Abstract

A thorough study of environmentally friendly hydroxylation of aryl halides is presented. The best protocol consists of hydroxylation of different aryl bromides and electron-deficient aryl chlorides by water solution of tetrabutylammonium hydroxide catalyzed by Cu_2O/4,7-dihydroxy-1,10-phenantroline. Various phenol derivatives can be obtained in excellent selectivity and great functional group tolerance. This methodology also provides a direct pathway for the formation of alkyl aryl ethers and benzofuran derivatives in one-pot tandem reaction.

Keywords: copper, C-O coupling, hydroxylation, green chemistry, water

Introduction

Phenols are very important intermediates in chemical, pharmaceutical and material industries.[1,2] The classical method for preparation of phenols is based on the decomposition of cumene hydroperoxide with sulfuric acid (Hock process) or the pyrolysis of sodium salt of benzene sulfonic acid (Dow process). However, both the protocols suffer from low yield and inefficiency in energy use. Several alternative methods have been developed for the synthesis of functionalized phenols, such as nucleophilic aromatic substitution of activated aryl halides, benzyne protocol, as well as copper-mediated transformation of arene diazonium salts and arylboronic acids,[3-7] but these methods are limited in practical applications because of harsh reaction conditions, narrow substrate scopes and difficulties in obtaining starting materials. Recently, some research groups reported the iridium- or palladium-based catalytic systems for preparing phenols from aryl halides, providing a milder and more applicable access to phenols.[8-15] However, high price and source scarcity of noble metals restricts wide use of these catalytic protocols. More recently, it was reported that phenols could be also synthesized through direct cross-coupling of hydroxide salts and aryl halides catalyzed by copper salts cooperated with organic ligands.[16, 17] The cheaper copper catalysts appear to potential candidates for replacing noble metal catalysts in the efficient synthesis of phenols.

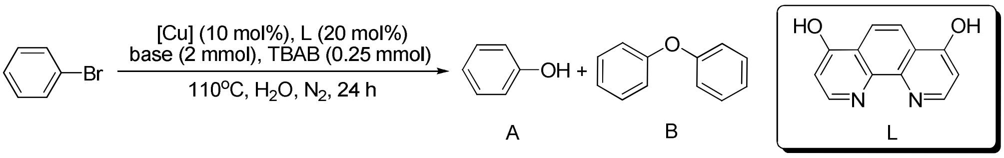
Although the reported copper-catalyzed hydroxylation protocols have provided decent strategies to synthesize phenols, there is still much room to broaden their applications. For the most reported copper catalytic systems, a well-defined ratio of water/organic solvent is usually required, and the use of water alone will result in unsatisfactory results.[16-24] It is well known that water is a cheap and readily available reaction medium, and the utilization of water-soluble catalytic systems may help simplify separation, recovery and recycling of the catalysts, especially for the separation of water-insoluble products.[25] However, organic reactions in neat water breed the additional challenge of water tolerance for the catalyst/ligand systems and the associated problems of the substrate solubility and reactivity. Recently, microwave heating has been employed to realize direct conversion of aryl halides to phenols catalyzed by copper complexes in neat water, but high temperature has been required and the yields of target products are not satisfactory when aryl bromides were used as starting materials.[26-28] In other established protocols of copper-catalyzed direct hydroxylation of aryl halides for preparing phenols in water, significant limitations, such as long reaction time, high catalyst loading and insufficient conversion of electron-rich aryl bromides, are encountered.[29-32] As a result, it is highly desirable to develop new copper-catalyzed strategies for synthesizing phenols under mild conditions in neat water, especially when inexpensive aryl chlorides are used as substrates.

It is well known that organic ligands play crucial roles in transition metal-catalyzed organic reactions. They not only may stabilize metal ions during reaction and separation, but also can exert important effects on activity and selectivity of the catalytic systems through their steric and electronic characters as well as coordination properties to metal ions. In the context, 1,10-phenanthroline and its derivatives have been extensively employed in copper-catalyzed cross-coupling reactions owing to their strong electron-donating ability and ready availability.[33-35] The modification of their catalytic performances were achieved through the deliberate variation of substituents, but the catalytic applications are mainly focused on their utilization in organic solvents. The potential utility in neat water is largely limited owing to their poor solubility in water. Generally, the implementation of catalytic reactions in water requires the presence of water-soluble or water-dispersed ligands and catalyst complexes. It is a common strategy to increase hydrophilicity by attaching ionic groups, such as sulfonate, carboxylate and ammonium, to hydrophobic ligands. In our previous study, 4,7-dihydroxy-1,10-phenanthroline has been demonstrated to be a representative candidate, which may serve as an efficient ligand in the copper-catalyzed Ullmann reaction between aryl bromides and imidazoles in water.[36] The superior promoting effect of 4,7-dihydroxy-1,10-phenanthroline was attributed to its water solubility under basic conditions. Herein, we extend the application scope of 4,7-dihydroxy-1,10-phenanthroline, and report a simple and efficient copper-catalyzed system for direct synthesis of phenols through hydroxylation of aryl bromides and electron-deficient chlorides under mild conditions in neat water.

Results and Discussion

The copper-catalyzed hydroxylation reaction was initially evaluated using bromobenzene as a substrate and 0.2 equivalent of 4,7-dihydroxy-1,10-phenanthroline (L) as a ligand for optimization of reaction conditions. When the reaction was performed using 0.1 equivalent of CuI as a copper salt and 0.4 equivalent of CsOH as a nucleophile in neat water at 110 ^{o}C for 24 h, 66% bromobenzene was converted and phenol was obtained in a 56% GC yield. Meanwhile, a 10% GC yield of biphenyl ether was detected as a byproduct (Table 1, entry 1). When the reaction was conducted in the presence of 0.5 equivalent of tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst (PTC), bromobenzene afforded a total conversion with the formation of phenol and biphenyl ether in 80 and 20% GC yields, respectively (entry 2), indicating that PTC is beneficial for this aqueous phase reaction. A total conversion of bromobenzene was also achieved when KOH was used as a nucleophile instead of CsOH, but the selectivity of phenol decreased to 63% (entry 3), suggesting that strong base was favorable for the formation of phenol, which was consistent with the previous reports.[37] To further confirm selectivity-dependent on base, much weaker base K_3PO_4 was utilized. As expected, the product is almost totally biphenyl ether, though only 39% bromobenzene was transformed (entry 4). Different copper salts were also screened. When Cu_2O was used, 93% conversion of bromobenzene and 80% selectivity of phenol were obtained (entry 5), CuO and $CuSO_4 \cdot 5H_2O$ gave quantitative conversion and 82% selectivity of phenol (entries 6 and 7), while CuBr was inferior to others with a moderate conversion of the substrate (entry 8). In order to pursue a high conversion along with a high selectivity, the reaction temperature was raised to 130 °C in the presence of Cu_2O. Unfortunately, the selectivity of phenol decreased though a full conversion of bromobenzene was observed (entry 9). However, when the amount of L decreased to 0.1 equivalent, a total conversion of bromobenzene was achieved and 90% GC yield of phenol was observed by using Cu_2O at 110 °C (entry 10). Other copper salts were all inferior to Cu_2O under the identical reaction conditions (entries 11~13). When sodium dodecyl sulfate (SDS) was tested as PTC instead of TBAB, 85% conversion of bromobenzene was obtained (entry 14). It was known that tetrabutylammonium hydroxide (TBAOH) may act as both PTC and nucleophile, so 25% and 55% (w/w) aqueous TBAOH were examined, respectively. To our delight, total conversion of bromobenzene was detected in both cases, 96% and 98% selectivity of phenol were acquired, respectively (entries 15 and 16). At this stage, a further decrement of the amount of L led to only 36% GC yield of phenol (entry 17). When the reaction temperature was decreased to 100 °C, only 88% bromobenzene was converted, indicating that temperature has an important effect on hydroxyalation of aryl halides (entry 18). However, no product was detected when the reaction was performed in air or in the absence of L (entries 19 and 20), implying that both inert atmosphere and L ligand are necessary in this catalytic system. Thus, after these attempts, the optimal conditions were 5 mol% Cu_2O, 10 mol% L, 1 mL 55% aqueous TBAOH at 110 °C in N_2 atmosphere.

Table 1. Screening of reaction conditions for hydroxylation of aryl bromides.[a]



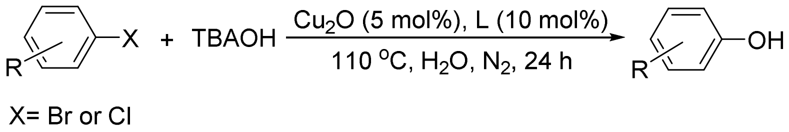
Entry	[Cu]	Base	PTC	T	Conversion	Yield[%][b]	
				(°C)	[%]	A	B

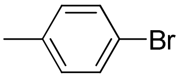
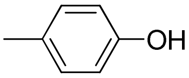
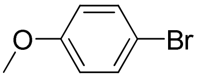
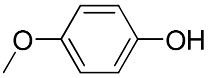
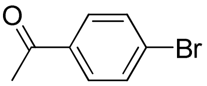
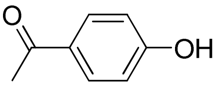
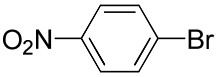
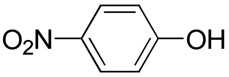
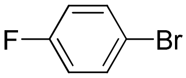
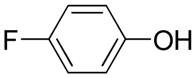
1[c]	CuI	CsOH	---	110	66	56	10
2	CuI	CsOH	TBAB	110	100	80	20
3	CuI	KOH	TBAB	110	100	63	37
4	CuI	K_3PO_4	TBAB	110	39	<2	37
5	Cu_2O	CsOH	TBAB	110	93	80	13
6	CuO	CsOH	TBAB	110	100	82	18
7	$CuSO_4\cdot 5H_2O$	CsOH	TBAB	110	100	82	18
8	CuBr	CsOH	TBAB	110	68	53	15
9	Cu_2O	CsOH	TBAB	130	100	67	33
10[d]	Cu_2O	CsOH	TBAB	110	100	90	10
11[d]	CuI	CsOH	TBAB	110	100	82	18
12[d]	CuO	CsOH	TBAB	110	39	35	4
13[d]	$CuSO_4\cdot 5H_2O$	CsOH	TBAB	110	45	41	4
14[d]	Cu_2O	CsOH	SDS	110	85	70	15
15[d,e]	Cu_2O	TBAOH	---	110	100	96	4
16[d,f]	Cu_2O	TBAOH	---	110	100	98	2
17[g]	Cu_2O	TBAOH	---	110	100	36	64
18[d,f,h]	Cu_2O	TBAOH	---	100	88	86	<2
19[d,f,i]	Cu_2O	TBAOH	---	110	0	0	0
20[j]	Cu_2O	TBAOH	---	110	0	0	0

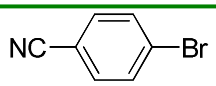
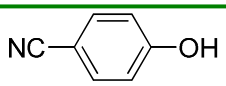
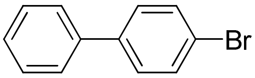
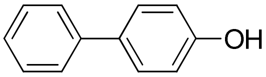
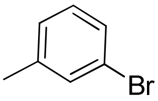
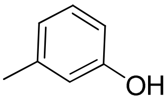
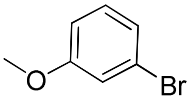
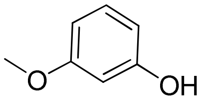
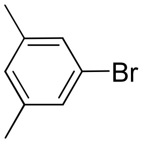
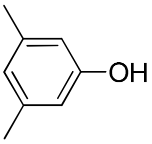
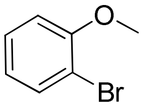
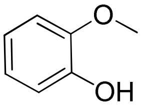
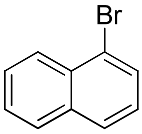
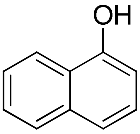
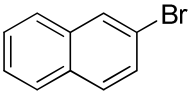
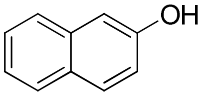
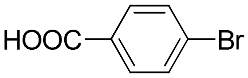
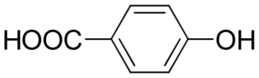
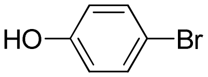
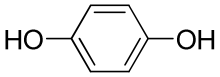
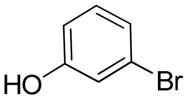
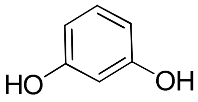
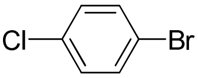
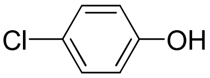
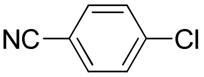
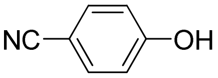
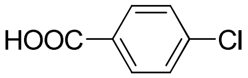
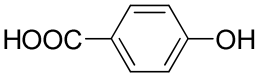
[a] Reaction conditions: Bromobenzene (0.5 mmol), Base (2.0 mmol), [Cu] (0.025 mmol Cu_2O, 0.05mmol for others), L (0.1 mmol), TBAB (0.25 mmol), H_2O (1.0 mL), 110 °C, N_2; [b] GC yields; [c] No PTC was added; [d] L (0.05 mmol); [e] 25% aqueous TBAOH solution (2.1 mL/ 4.0 eq); [f] 55% aqueous TBAOH solution (1.0 mL/ 4.0 eq) as base; [g] L (0.025 mmol); [h] the reaction temperature was 100 °C; [i] the reaction was performed in air; [j] In the absence of L.

With the optimized conditions in hand, the scope and generality of aryl halides were then investigated, and the results were summarized in Table 2. The *para*-substituted electron-rich and electron-deficient aryl bromides afforded the desirable products in excellent yields (entries 1~7). It seems that the electronic nature in *para*-positioned substituents of aryl bromides have no obvious effect on hydroxylation reaction under the optimized conditions. Excellent yields can be also achieved when electron-rich *meta*-methylbromobenzene, *meta*-methoxybromobenzene and 3,5-dimetylbromobenzene were used, the corresponding target products were obtained in 87, 96 and 85% isolated yields, respectively (entries 8~10). However, only 48% isolated yield was obtained when *orth*-methoxybromobenzene was employed as a substrate, which was probably attributed to bulkier steric hindrance (entry 11). Interestingly, high yields can be achieved when both bulky 1-bromonaphthalene and 2-bromonaphthalene were used (entries 12 and 13). Moreover, carboxyl and hydroxy can be well tolerated in this catalytic system, the use of *para*-bromobenzoic acid, *para*-bromophenol and *meta*-bromophenol gave target products in 99, 75 and 86% isolated yields, respectively (entries 14~16). The use of 1-bromo-4-chlorobenzene gave rise to 4-chlorophenol in an 88% isolated yield, indicating good chemoselectivity between aryl bromide and chloride (entry 17). It is noteworthy that the catalytic system is also effective for aryl chlorides bearing electron-withdrawing groups, the use of *para*-chlorobenzonitrile and *para*-chlorobenzoic acid gave the target products in 88 and 99% GC yields, respectively (entries 18 and 19).

Table 2. Synthesis of phenols by copper-catalyzed hydroxylation of arylbromides and chlorides.[a]



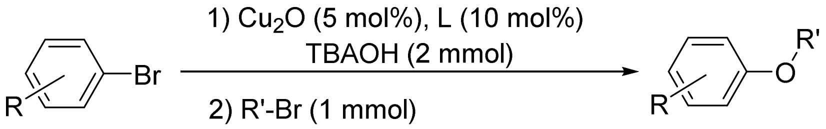
Entry	Ar-X	Product	Yield[b] (%)
1			94
2			99
3			95
4			94
5			86

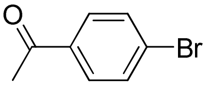
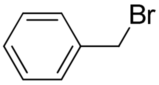
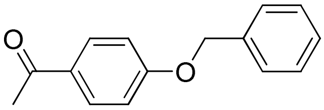
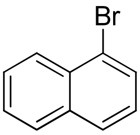
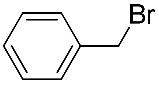
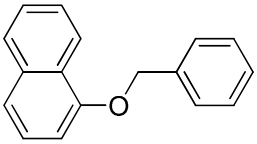
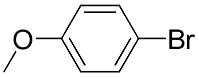
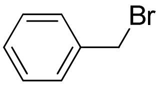
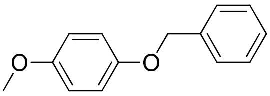
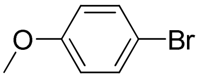
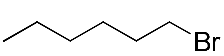
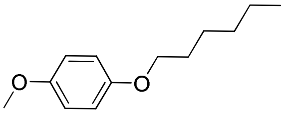
6			86
7			92
8			87
9			96
10			85
11			48
12			94
13			99
14			99
15			75
16			86
17			88
18			88
19			99

[a] Reaction conditions: Aryl halides (0.5 mmol), Cu_2O (0.025 mmol), L (0.05 mmol), 55% aqueous TBAOH (1.0 mL), 110 ^{o}C, N_2, 24 h; [b] isolated yields.

By combining with Williamson ether synthesis, the generality of this hydroxylation methodology was extended for one-pot synthesis of alkyl aryl ethers (Table 3). Compared to previous works by others,[15, 17] no more PTC and bases were added in the second step of the one-pot reaction. To our delight, both electron-deficient and electron-rich aryl bromides provided good to excellent yields to corresponding alkyl aryl ethers. This procedure offers a straightforward strategy for the synthesis of alkyl aryl ethers based on two electrophilic components.

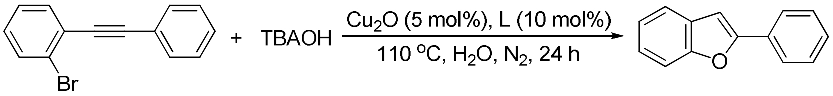
Table 3. One-pot synthesis of alkyl aryl ethers from aryl bromides[a]



Entry	Ar-Br	R′-X	Product	Yield[b] (%)
1				89
2				84
3				95
4				98

[a] Reactions were carried out using Cu_2O (5 mol%), L (10 mol%), and aryl bromides (0.5 mmol) in 1 mL aqueous 55% TBAOH at 110 °C for 24 h. After the reaction mixture was cooled down to ambient temperature, R′-X (1 mmol) was added and the reaction system was kept at 110 °C for the additional 24 h. [b] isolated yields.

We also explored application of this catalytic system for the preparation of substituted benzofuran because benzofuran frameworks are frequently found in a variety of biologically active compounds.[38,39] When 1-bromo-2-(phenylethynyl)benzene is submitted to our catalytic protocol (Scheme 1), 2-phenylbenzofuran was obtained in an 80% isolated yield through a sequential one-pot tandem reaction involving hydroxylation coupling and subsequent intramolecular hydroalkoxylation.



Scheme 1. Synthesis of 2-phenylbenzofuran from 2-bromoaryl alkyne.

Conclusion

We have presented a highly efficient method for direct preparation of phenols in neat water through hydroxylation of aryl bromides and chlorides. Excellent selectivity and great functional groups tolerance are achieved in the catalytic system. This protocol also provides a one-pot procedure for the synthesis of alkyl aryl ethers based on two electrophilic components. Moreover, this methodology is applicable in preparing benzofuran derivatives through hydroxylation of 1-bromo-2-(phenylethynyl) benzene and subsequent intramolecular hydroalkoxylation. These promising catalytic performances may be ascribed to solubility of 4,7-dihydroxy-1,10-phenanthroline under catalytic conditions in water. In summary, this study not only extends the scope of copper-catalyzed coupling reaction in water, but also paves a new pathway for the development of eco-friendly non-precious metal catalytic systems.

Experimental section

4,7-dihydroxy-1,10-phenanthroline[33] and 1-bromo-2-(phenylethynyl)benzene[40] were synthesized according to literature methods, other chemicals were purchased from commercial suppliers and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III NMR spectrometer at 400 and 100 MHz, respectively, by using deuterated $CDCl_3$ as locking solvent except otherwise indicated. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-5, 30×0.25 μm) by using a flame ionization detector.

General procedures for screening reaction conditions in hydroxylation of

bromobenzene

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with copper salts (0.05 mmol), 4,7-dihydroxy-1,10-phenanthroline (0.1 mmol), base (2 mmol) and phase-transfer catalyst (0.25 mmol). The tube was evacuated and back-filled with nitrogen, and this procedure was repeated for three times. After that, bromobenzene (0.5 mmol) and deionized water (1 mL) was added at a stream of nitrogen, the tube was sealed and stirred in a preheated oil bath (110 ^{o}C). After 24 h, the reaction mixture was cooled to ambient temperature, carefully acidified with dilute aqueous HCl, and extracted with ethyl acetate. The combined organic phase was analyzed with GC to determine conversion and selectivity. The identity of products was confirmed by comparison with GC retention times of commercial materials.

General procedures for hydroxylation of aryl halides

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with Cu_2O (0.025 mmol), 4,7-dihydroxy-1,10-phenanthroline (0.05 mmol) and aryl halides (0.5 mmol). For solid aryl halides, the tube was evacuated and back-filled with nitrogen, and this procedure was repeated three times, while for liquid aryl halides, the reaction components were added after removal of air. After that, 55% aqueous solution of TBAOH (2 mmol, 1 mL) was added at a stream of nitrogen and the tube was sealed and stirred in a preheated oil bath (110 ^{o}C). After 24 h, the mixture was cooled to ambient temperature, carefully acidified with dilute aqueous HCl, and extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude products were purified by flash column chromatography on silica gel to afford the desired product. The identity of the products was confirmed by comparison with literature spectroscopic data.

General procedure for one-pot synthesis of alkyl aryl ethers

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with Cu_2O (0.025 mmol), 4,7-dihydroxy-1,10-phenanthroline (0.05 mmol), and aryl halides (0.5 mmol). For solid aryl halides, the tube was evacuated and back-filled with nitrogen, and this procedure was repeated three times, while for liquid aryl halides, the reaction components were added after removal of air. After that, 55% aqueous solution of

TBAOH (2 mmol, 1 mL) was added at a stream of nitrogen, the tube was sealed and stirred in a preheated oil bath (110 ^{o}C) for 24 h. After the mixture was cooled to ambient temperature, alkyl bromide (1.0 mmol) was added. The reaction mixture was heated at 110 ^{o}C for another 24 h, then cooled to ambient temperature, diluted with water and extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude products were purified by flash column chromatography on silica gel to afford the desired product. The identity of the products was confirmed by comparison with literature spectroscopic data.

Synthesis of 2-phenylbenzofuran

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with Cu_2O (0.025 mmol), 4,7-dihydroxy-1,10-phenanthroline (0.05 mmol). The tube was evacuated and back-filled with nitrogen, and this procedure was repeated three times. After that, 1-bromo-2-(phenylethynyl)benzene (0.5 mmol) and 55% aqueous solution of TBAOH (2 mmol, 1 mL) were added at a stream of nitrogen, the tube was sealed and stirred in a preheated oil bath (110 ^{o}C) for 24 h. Then reaction mixture was cooled to ambient temperature, diluted with water and extracted with ethyl acetate (3×5 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude products were purified by flash column chromatography on silica gel to afford the desired product. The identity of the products was confirmed by comparison with literature spectroscopic data.

Acknowledgements

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Supporting information

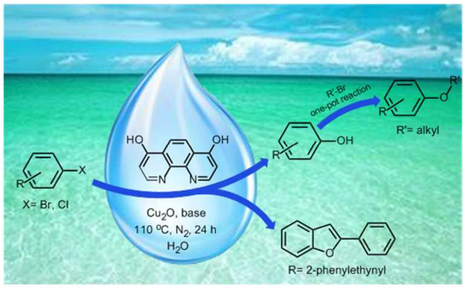
Electronic Supplementary Information (ESI) available: [NMR data and spectra for the catalytic products]. See DOI: 10.1039/x0xx00000x

References

1. J. H. P. Tyman, *Synthetic and Natural Phenols*, Elsevier: New York, 1996.
2. Z. Rappoport, *The Chemistry of Phenols*, Wiley-VCH, Weinheim, 2003.
3. C. Hoarau and T. R. R. Pettus, *Synlett*, 2003, **1**, 127-137.
4. T. George, R. Mabon, G. Sweeney, J. B. Sweeney and A. Tavassoli, *J. Chem. Soc., Perkin Trans.,* 2000, **1**, 2529-2574.
5. P. Hanson, J. R. Jones, A. B. Taylor, P. H. Walton and A. W. Timms, *J. Chem. Soc., Perkin Trans.,* 2002, **2**, 1135-1150.
6. J. Xu, X. Wang, C. Shao, D. Su, G. Cheng and Y. Hu, *Org. Lett.*, 2010, **12**, 1964-1967.
7. K. Inamoto, K. Nozawa, M. Yonemoto and Y. Kondo, *Chem. Commun.*, 2011, **47**, 11775-11777.
8. R. E. Maleczka, F. Shi, D. Holmes and M. R. Smith, *J. Am. Chem. Soc.*, 2003, **125**, 7792-7793.
9. K. W. Anderson, T. Ikawa, R. E. Tundel and S. L. Buchwald, *J. Am. Chem. Soc.*, 2006, **128**, 10694-10695.
10. M. C. Willis, *Angew. Chem. Int. Edit.*, 2007, **46**, 3402-3404.
11. G. Chen, A. S. C. Chan and F. Y. Kwong, *Tetrahedron Lett.*, 2007, **48**, 473-476.
12. B. J. Gallon, R. W. Kojima, R. B. Kaner and P. L. Diaconescu, *Angew. Chem. Int. Edit.*, 2007, **46**, 7251-7254.
13. A. G. Sergeev, T. Schulz, C. Torborg, A. Spannenberg, H. Neumann and M. Beller, *Angew. Chem. Int. Edit.*, 2009, **48**, 7595-7599.
14. T. Schulz, C. Torborg, B. Schaffner, J. Huang, A. Zapf, R. Kadyrov, A. Borner and M. Beller, *Angew. Chem. Int. Edit.*, 2009, **48**, 918-921.
15. C. Yu, G. S. Chen, C. Huang and J. Chern, *Org. Lett.*, 2012, **14**, 3688-3691.
16. A. Tlili, N. Xia, F. Monnier and M. Taillefer, *Angew. Chem. Int. Edit.*, 2009, **48**, 8725-8728.
17. D. Zhao, N. Wu, S. Zhang, P. Xi, X. Su, J. Lan and J. You, *Angew. Chem. Int. Edit.*, 2009, **48**, 8729-8732.
18. K. G. Thakur and G. Sekar, *Chem. Comm.*, 2011, **47**, 6692-6694.
19. K. YANG, Z. Li, Z. Wang, Z. Yao and S. Jiang, *Org. Lett.*, 2011, **13**, 4340-4343.

20. Y. Xiao, Y. Xu, H. S. Cheon and J. Chae, *J. Org. Chem.*, 2013, **78**, 5804-5809.
21. R. Paul, M. A. Ali and T. Punniyamurthy, *Synthesis*, 2010, **24**, 4268-4272.
22. P. J. A. Joseph, S. Priyadarshini, M. L. Kantam and H. Maheswaran, *Catal. Sci. Technol.*, 2011, **1**, 582-585.
23. J. Chen, T. Yuan, W. Hao and M. Cai, *Catal. Commun.*, 2011, **12**, 1463-1465.
24. G. Ding, H. Han, T. Jiang, T. Wu and B. Han, *Chem. Commun.*, 2014, **50**, 9072-9075.
25. K. H. Shaughnessy, *Chem. Rev.*, 2009, **109**, 643-710.
26. C. M. Kormos and N. E. Leadbeater, *Tetrahedron*, 2006, **62**, 4728-4732.
27. A. Mehmood and N. E. Leadbeater, *Catal. Commun.*, 2010, **12**, 64-66.
28. F. Ke, X. Chen, Z. Li, H. Xiang and X. Zhou, *RSC Adv.*, 2013, **3**, 22837.
29. L. H. Jing, J. T. Wei, L. Zhou, Z. Y. Huang, Z. K. Li and X. G. Zhou, *Chem. Commun.*, 2010, **46**, 4767-4769.
30. H. J. Xu, Y. F. Liang, Z. Y. Cai, H. X. Qi, C. Y. Yang and Y. S. Feng, *J. Org. Chem.*, 2011, **76**, 2296-2300.
31. D. Yang and H. Fu, *Chem. Eur. J.*, 2010, **16**, 2366-2370.
32. D. Wang, D. Kuang, F, Zhang, S. Tang and W. Jiang, *Eur. J. Org. Chem.*, 2014, 315-318.
33. R. A. Altman and S. L. Buchwald, *Org. Lett.*, 2006, **8**, 2779-2782.
34. R. A. Altman, E. D. Koval and S. L. Buchwald, *J. Org. Chem.*, 2007, **72**, 6190-6199.
35. R. K. Gujadhur, C. G. Bates and D. Venkataraman, *Org. Lett.*, 2001, **3**, 4315-4317.
36. R. Lv, Y. Wang, C. Zhou, L. Li and R. Wang, *ChemCatChem*, 2013, **5**, 2978-2982.
37. G. Lefevre, A. Tlili, M. Taillefer, C. Adamo, I. Ciofini and A. Jutand, *Dalton Trans.*, 2013, **42**, 5348-5354.
38. G. A. Kraus and I. Kim, *Org. Lett.*, 2003, **5**, 1191-1192.
39. S. M. Bakunova, S. A. Bakunov, T. Wenzler, T. Barszcz, K. A. Werbovetz, R. Brun, J. E. Hall and R. R. Tidwell, J. Med. Chem., 2007, **50**, 5807-5823.
40. N. Ototake, Y. Morimoto, A. Mokuya, H. Fukaya, Y. Shida and O. Kitagawa, *Chem. Eur. J.*, 2010, **16**, 6752-6755.

Table of Contents



An efficient catalytic protocol for hydroxylation of aryl halides in water is proposed to prepare phenols, ethers and benzofuran derivatives.