EurJOC
European Journal of Organic Chemistry

DOI: 10.1002/ejoc.201201595

Cobalt(II)–Porphyrin-Catalyzed Aerobic Oxidation: Oxidative Coupling of Phenols

Qing Jiang,[a] Wenbing Sheng,[a] Mi Tian,[a] Jie Tang,[a] and Cancheng Guo*[a]

Keywords: Homogeneous catalysis / Oxidation / Metalloporphyrins / Cobalt / C–H functionalization / Biaryls

The first example of the cobalt–porphyrin-catalyzed aerobic oxidative coupling of phenols through oxidative C–H functionalization has been developed. In the presence of T(*p*-OMe)PPCo and Na_2CO_3, the oxidative coupling of phenols with different substituents proceeded smoothly with O_2 as a terminal oxidant to give the corresponding biaryl compounds in satisfactory yields. The biaryl derivatives are important in the area of pharmaceuticals and as ligands in metal catalysis. Preliminary mechanistic studies of this oxidative coupling reaction are also reported.

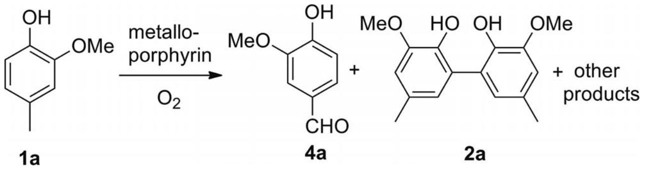
Introduction

The selective and efficient construction of C–C bonds is considered one of the most challenging goals in organic synthesis. Traditionally, coupling reactions for C–C bond formation has depended primarily on preactivated substrates for both reactivity and selectivity.[1] Although these reactions have found extensive use in the laboratory and in industry, the prefunctionalization of each coupling partner generally requires tedious procedures and causes environmental problems. For this reason, the transition-metal-catalyzed direct functionalization of C–H bonds has emerged as a powerful method for the construction of value-added molecules through C–C bond formation or carbon–heteroatom bond formation.[2] Among the efficient reactions available for the functionalization of C–H bonds, the oxidative coupling of phenols has received considerable attention,[3] because the resultant biaryl compounds are ubiquitous in natural and synthetic bioactive molecules,[4] in functional materials as structural motifs,[5] and in various ligand families.[6] Although various kinds of stoichiometric methods involving the use of Fe, Cu, Mn, and Ti salts as oxidative coupling reagents have been reported,[7] the reactions are often stoichiometric and require the use of hazardous and expensive materials and the products are difficult to remove from the reaction solution. Recently, some efficient catalytic methods involving the use of molecular oxygen as the sole oxidant for the above reaction have been developed.[8–10] However, these strategies suffer from one or more limitations, including complex preparations of the catalyst, high catalyst loading, or the need to employ harsh reaction conditions. Although significant progress has been made in this field, it is still highly desirable to develop novel approaches for the construction of biaryl compounds.

It is well known that metalloporphyrins are a class of versatile catalysts with the capability to catalytically convert hydrocarbons into value-added functional molecules through C–O, C–N, and C–C bond formation.[11] However, to the best of our knowledge, the metalloporphyrin-mediated aerobic oxidative C–H coupling of phenols has not been established. Herein, we report the first examples of the cobalt(II)–porphyrin-catalyzed aerobic oxidative C–H coupling of phenols to synthesize biphenols. This method uses non-noble metals and proceeds under mild reaction conditions with operational simplicity, which thus allows the expedient and atom-economical assembly of biphenols from readily available phenols. Furthermore, we provide preliminary mechanistic investigations of this oxidative coupling reaction.

Results and Discussion

During our investigations on the metalloporphyrin-catalyzed aerobic oxidation of 4-methylguaiacol (**1a**) to synthesize vanillin (**4a**), unexpected C–C coupling product **2a** was observed (Scheme 1).



Scheme 1. Aerobic oxidation of **1a** catalyzed by metalloporphyrins.

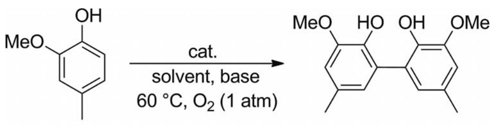
---

[a] College of Chemistry and Chemical Engineering, Hunan University,
Changsha 410082, China
Fax: +86-731-8821667
E-mail: ccguo@hnu.edu.cn
Homepage: http://www.hnu.edu.cn/

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201595.

This result prompted us to envisage that a metalloporphyrin-based strategy could be applied to construct C–C bonds from phenolic C–H bonds. To test our hypothesis, the oxidative coupling of 4-methylguaiacol (**1a**) was chosen as the model reaction (Table 1). To our delight, the oxidative coupling reaction gave desired product **2a** in 98% yield in the presence of *meso*-tetra(4-methoxyphenyl)porphyrincobalt(II) {T(*p*-OMe)PPCo} and Na_2CO_3 in CH_3OH at 60 °C under an atmosphere of O_2 (Table 1, entry 1). Notably, only trace amounts of desired product **2a** were observed when the reaction was carried out in the absence of either base or catalyst (Table 1, entries 2 and 3). Very little product was obtained when the procedure was preformed under a nitrogen atmosphere (Table 1, entry 4). Among the bases screened, KOH, $NaHCO_3$, K_2CO_3, and NaOH were found to be as effective as Na_2CO_3 (Table 1, entries 5–8). The use of an excess amount of Na_2CO_3 (2.0 equiv.) decreased the yield slightly, and the use of 0.2 equiv. of Na_2CO_3 led to an 82% yield of **2a** (Table 1, entries 9 and 10). Among the solvents examined, including methanol, ethanol, water, acetonitrile, acetonitrile/water (1:1), and methanol/water(4:1), the methanol/water (4:1) mixture was also found to be a suitable solvent system (Table 1, entries 11–15). Other cobalt(II)–porphyrin catalysts, including T(*p*-Cl)PPCo, T(*p*-Me)PPCo, and TPPCo, were also tested, and the results demonstrated that T(*p*-OMe)PPCo was the best choice (Table 1, entries 16–18). To achieve a reasonable reaction rate, heating was required (Table 1, entry 19). When distilled methanol was used as the solvent, the oxidative coupling was considerably less efficient (<10% yield), which indicates that water is essential for the reaction to proceed efficiently. Consequently, the optimal conditions were a combination of T(*p*-OMe)PPCo (0.2 mol-%), Na_2CO_3 (1 equiv.), and O_2 in methanol/water (4:1).

Table 1. Optimization of the reaction conditions.[a]



1a **2a**

Entry	Catalyst	Base	Solvent	Conv. [%][b]	Yield [%][b]
1	T(*p*-OMe)PPCo	Na_2CO_3	CH_3OH	>99	98
2	T(*p*-OMe)PPCo	none	CH_3OH	<5	<5
3	none	Na_2CO_3	CH_3OH	<5	<5
4[c]	T(*p*-OMe)PPCo	Na_2CO_3	CH_3OH	<5	<5
5	T(*p*-OMe)PPCo	KOH	CH_3OH	98	94
6	T(*p*-OMe)PPCo	$NaHCO_3$	CH_3OH	>99	95
7	T(*p*-OMe)PPCo	NaOH	CH_3OH	98	95
8	T(*p*-OMe)PPCo	K_2CO_3	CH_3OH	>99	96
9[d]	T(*p*-OMe)PPCo	Na_2CO_3	CH_3OH	98	94
10[e]	T(*p*-OMe)PPCo	Na_2CO_3	CH_3OH	85	82
11	T(*p*-OMe)PPCo	Na_2CO_3	CH_3CH_2OH	46	30
12	T(*p*-OMe)PPCo	Na_2CO_3	H_2O	90	52
13	T(*p*-OMe)PPCo	Na_2CO_3	CH_3CN	<5	<1
14	T(*p*-OMe)PPCo	Na_2CO_3	CH_3CN/H_2O	52	27
15	T(*p*-OMe)PPCo	Na_2CO_3	CH_3OH/H_2O	>99	97
16	TPPCo	Na_2CO_3	CH_3OH	85	82
17	T(*p*-Me)PPCo	Na_2CO_3	CH_3OH	89	87
18	T(*p*-Cl)PPCo	Na_2CO_3	CH_3OH	83	80
19[f]	T(*p*-OMe)PPCo	Na_2CO_3	CH_3OH	34	12

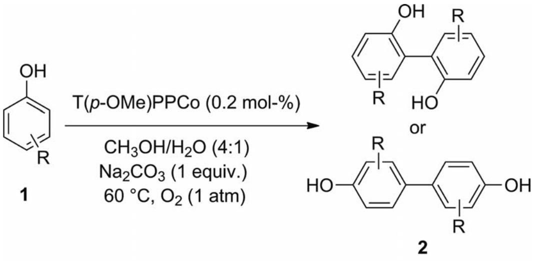
[a] Unless otherwise noted, the reaction was carried out with **1a** (1.0 mmol), catalyst (0.2 mol-%), solvent (5.0 mL), base (1.0 equiv.), 60 °C, 15 h, O_2 (1 atm). [b] Determined by HPLC with 1,4-dichlorobenzene as an internal standard and calculated on the basis of the amount of **1a**. [c] Under N_2 atmosphere. [d] 2 equiv. of Na_2CO_3 were used. [e] 0.2 equiv. of Na_2CO_3 was used. [f] At room temperature.

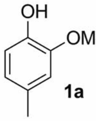
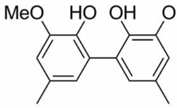
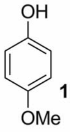
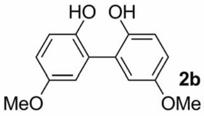
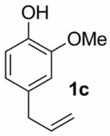
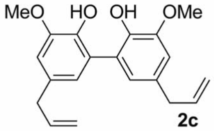
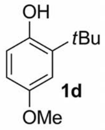
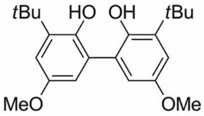
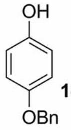
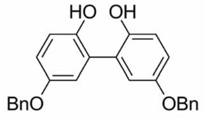
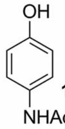
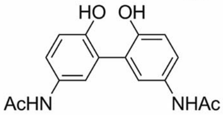
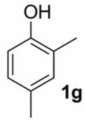
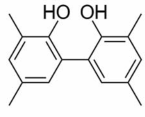
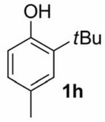
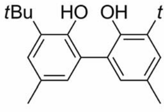
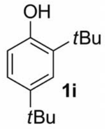
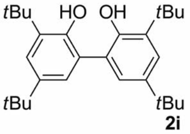
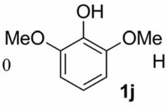
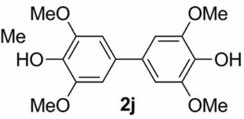
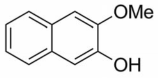
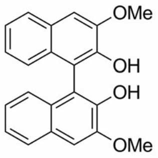
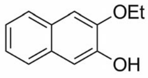
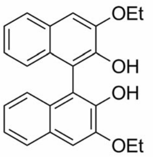
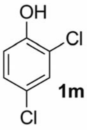
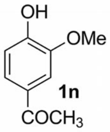
With the optimized conditions in hand, we then set out to explore the scope and limitations of the above method (Table 2). Phenols with various substituents were tested. The reaction efficiency depended on the nature of the substituents on the aromatic ring (Table 2, entries 1–9). Substrates bearing an alkoxy group furnished the product smoothly in 71–93% yield (Table 2, entries 1–5), whereas alkyl- and acetamido-substituted phenols provided lower yields of the products (46–56%; Table 2, entries 6–9). The *para–para* coupling product of **2j** was obtained in 73% yield when the oxidative C–C coupling reaction of 2,6-dimethoxyphenol (**1j**) was carried out under the same reaction conditions (Table 2, entry 10). The present methodology can be further extended to naphthols. Under the optimized reaction conditions, the oxidative coupling reaction of **1k** and **1l** furnished **2k** and **2l** in 41 and 42% yield, respectively (Table 2, entries 11 and 12).

Unlike phenols bearing electron-donating substituents, phenols with electron-withdrawing substituents failed to give any desired products under the above experimental conditions, and all of the starting material was recovered in each case. For example, no reaction occurred when 2,4-dichlorophenol and 4-hydroxy-3-methoxyacetophenone were subjected to the same reaction conditions (Table 2, entries 13 and 14).

Though the exact mechanism remains unclear, some information has been gathered. We found that an aromatic OH group was essential for the reaction, as no reaction occurred in its absence [Equations (1–3)]. When the oxidative coupling of **1a** was carried out in the presence of 1.5 equiv. of a radical inhibitor hydroquinone, desired product **2a** was not detected in an appreciable amount, which indicates the possible involvement of radical species in the reaction. To see whether radical insertion of an aryl into the C–H bond of another aryl molecule ($X^{\cdot} + Y$) was involved in the reaction, a competitive reaction of **1a** and **3a**[12] was conducted [Equation (4)]. This result demonstrated that the present oxidative coupling reaction proceeds through the homolytic coupling of two radical species. To understand the role of Na_2CO_3 in the reaction system, UV/Vis spectroscopy was performed. The UV/Vis spectra of a solution of T(*p*-OMe)PPCo and Na_2CO_3 in aqueous methanol in the presence of O_2 at room temperature are shown in Figure 1. It can also be seen from analysis of the spectra that the position of the peak is shifted to lower frequencies with the lapse of time. The redshift of the peak (Soret band: 414→429 nm, Q band: 531→543 nm)[13] indicated the formation of T(*p*-OMe)PPCo(OH) species **A** (Scheme 2, for more details see the Supporting Information). Similar results were also

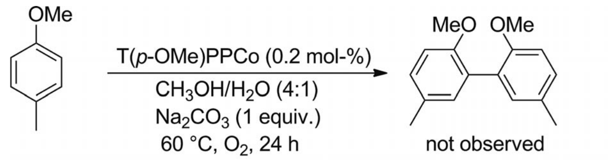
Table 2. Substrate scope in the cobalt(II)–porphyrin-catalyzed aerobic oxidative coupling of phenols.[a]



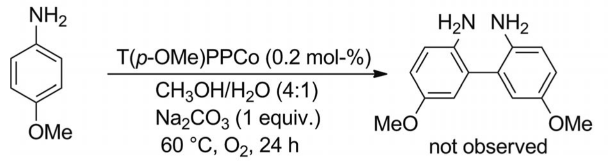
Entry	Substrate	Product	Time [h]	Conv. [%][b]	Yield [%][c]
1	 1a	 2a	15	>99	93
2	 1b	 2b	32	83	75
3	 1c	 2c	32	86	73
4	 1d	 2d	15	93	80
5	 1e	 2e	32	76	71
6	 1f	 2f	32	52	47
7	 1g	 2g	48	49	46
8	 1h	 2h	48	54	50
9	 1i	 2i	48	58	56
10	 1j	 2j	24	89	73
11	 1k	 2k	54	61	41
12	 1l	 2l	54	63	42
13	 1m	–	48	0	0
14	 1n	–	48	0	0

[a] Reaction conditions: 1 (1.0 mmol), Na_2CO_3 (1 equiv.), T(p-OMe)PPCo (0.2 mol-%), methanol/water (4:1 mL), 60 °C, O_2 (1 atm). [b] Determined by HPLC analyses of the crude reaction mixture and calculated on the basis of the amount of **1**. [c] Isolated yield calculated on the basis of the amount of **1**.

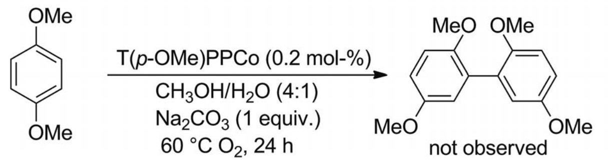
reported by Avlasevich in the study of the TPPCo/air/$NaHCO_3$ system.[14] According to the literature,[15] under the conditions used in this work, T(*p*-OMe)PPCo^{II} (noted for its instability)[16] is oxidized to T(*p*-OMe)PPCo^{III}. The nature of the axial ligand is determined by the reaction conditions and related reports.[13,14] After T(*p*-OMe)PPCo(OH) species **A** was generated in situ from T(*p*-OMe)PPCo, 4-methylguaiacol was added to the mixture under a nitrogen atmosphere. The reaction mixture was followed by UV/Vis spectroscopy (Figure 2). It was found that the position of the peak shifted to higher frequencies with a lapse of time



(1)

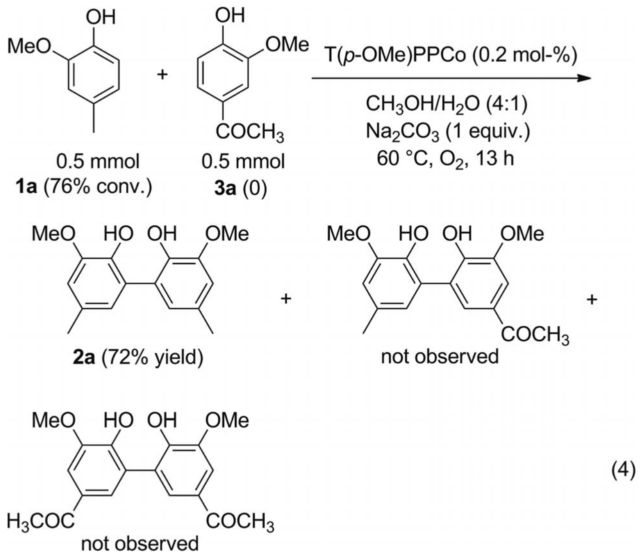


(2)



(3)

(Soret band: 429→415 nm, Q band: 543→532 nm). These results also support the present reaction mechanism (Scheme 2).



(4)

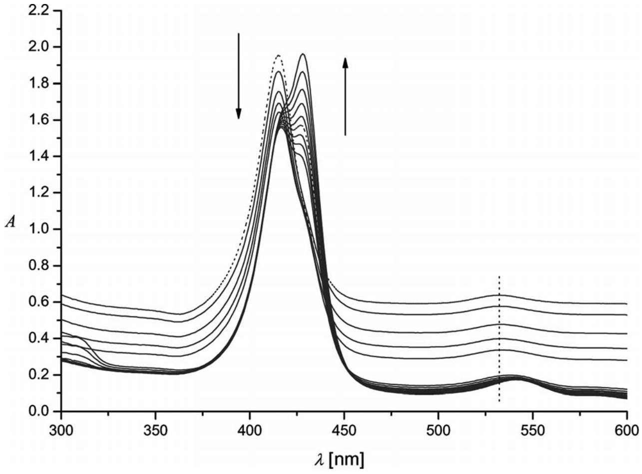


Figure 1. UV/Vis spectra of an aqueous methanol solution of T(*p*-OMe)PPCo (dashed curve) and that of a mixture of T(*p*-OMe)PPCo/Na_2CO_3 in aqueous methanol in the presence of O_2 at room temperature collected within 8.0 h (solid curve).

On the basis of these mechanistic insights and related reports,[8–10,17] a possible mechanism employing **1a** as the substrate is proposed to account for the present catalytic reaction (Scheme 2). Under the reaction conditions, active catalytic species **A** is generated in situ from T(*p*-OMe)PPCo. Active species **A** then reacts with **1a** by ligand exchange to form intermediate **B**, followed by a single-electron transfer process to afford intermediate **C**, which concertedly induces the regioselective intermolecular radical–radical coupling to give corresponding carbon–carbon coupling product **2a**.[18] The dissociated cobalt species is oxidized by oxygen to regenerate active species **A**.

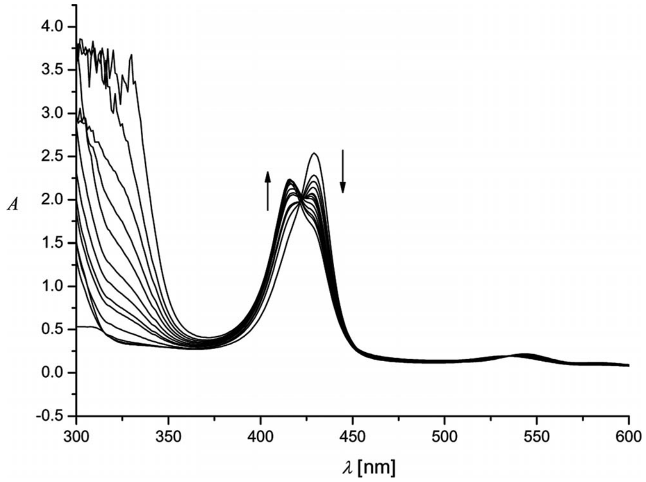
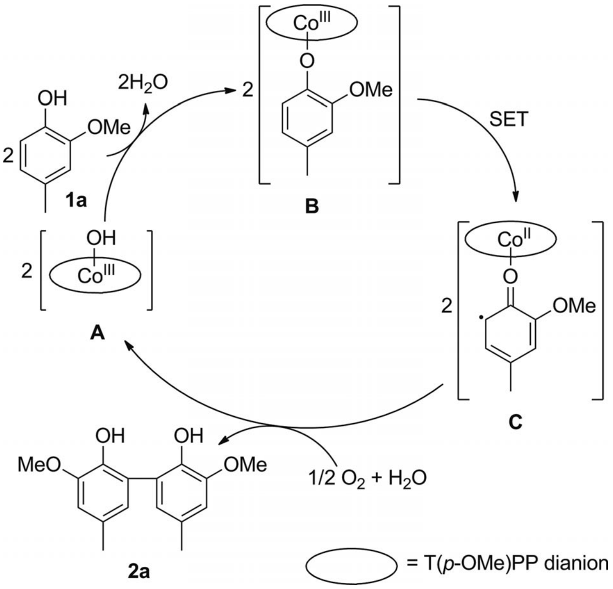


Figure 2. UV/Vis spectra of a mixture of T(*p*-OMe)PPCo(OH)/4-methylguaiacol/Na_2CO_3 in aqueous methanol in the presence of N_2 at room temperature collected within 12 h.



Scheme 2. Proposed reaction mechanism.

Conclusions

In summary, we have developed a mild cobalt(II)–porphyrin-catalyzed oxidative coupling of phenols. The reaction makes use of inexpensive cobalt as the catalyst and molecular oxygen as the oxidant and affords satisfactory yields of the products. This is a convenient protocol for the preparation of biphenols of interest in pharmaceuticals and in metal catalysis as ligands. More detailed mechanistic studies are presently being performed in our laboratory.

Experimental Section

General Procedure for the Aerobic Oxidative Coupling of Phenols Catalyzed by T(*p*-OMe)PPCo: T(*p*-OMe)PPCo (0.2 mol-%), phenol (1.0 mmol), Na_2CO_3 (1.0 mmol), methanol (4.0 mL), and water

(1.0 mL) were added to a 25 mL flame-dried Schlenk tube in air. The air was removed by vacuum, and O_2 (1 atm) was introduced. The Schlenk tube was then sealed, and the resulting mixture was stirred at 60 °C under an atmosphere of oxygen (1 atm). After stirring for the time indicated, the mixture was cooled to room temperature, carefully acidified with dilute aqueous HCl, diluted with ethyl acetate (10 mL), filtered through a plug of silica gel, and washed with ethyl acetate (20–30 mL). The combined organic extract was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel to afford the desired product.

Supporting Information (see footnote on the first page of this article): Experiment details, characterization data, and copies of the NMR spectra of products **2a**–**2l**.

Acknowledgments

This project was financially supported by the Chinese National Natural Science Fund.

---

[1] a) A. de Meijere, F. Diederich (Eds.), *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed., Wiley-VCH, Weinheim, Germany, **2004**, vol. 1 and 2; b) F. Diederich, P. J. Stang (Eds.), *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, Germany, **1998**.

[2] a) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315–1345; b) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215–1292; c) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740–4761; d) T. Newhouse, P. S. Baran, *Angew. Chem.* **2011**, *123*, 3422–3435; *Angew. Chem. Int. Ed.* **2011**, *50*, 3362–3374; e) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293–1314; f) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885–1898; g) W. R. Gutekunst, P. S. Baran, *Chem. Soc. Rev.* **2011**, *40*, 1976–1991; h) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147–1169; i) L.-M. Xu, Z. Yang, Z.-J. Shi, *Chem. Soc. Rev.* **2010**, *39*, 712–733; j) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, *46*, 677–685; k) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074–1086; l) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976–10011; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792–9826; m) W. Wu, W. Su, *J. Am. Chem. Soc.* **2011**, *133*, 11924–11927; n) W. Wu, J. Xu, S. Huang, W. Su, *Chem. Commun.* **2011**, *47*, 9660–9662.

[3] a) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem.* **2011**, 123, 11256–11283; *Angew. Chem. Int. Ed.* **2011**, *50*, 11062–11087; b) J. A. Ashenhurst, *Chem. Soc. Rev.* **2010**, *39*, 540–548; c) H. Wang, *Chirality* **2010**, *22*, 827–837; d) M. C. Kozlowski, B. J. Morgan, E. C. Linton, *Chem. Soc. Rev.* **2009**, *38*, 3193–3207; e) J. M. Brunel, *Chem. Rev.* **2005**, *105*, 857–898.

[4] a) S. K. Quideau, S. Feldman, *Chem. Rev.* **1996**, *96*, 475–504; b) D. J. Tweardy, X. Huang, M. M. Kasembeli, Patent WO 149192 A1, **2009**; c) G. Bringmann, C. Günther, M. Ochse, O. Schupp, S. Tasler, in: *Progress in the Chemistry of Organic Natural Products* (Eds.: W. Herz, H. Falk, G. W. Kirby, R. E. Moore), Springer, Vienna, **2001**, vol. 82, pp. 1–249.

[5] a) A. N. Carnrnidge, R. J. Bushby, in: *Handbook of Liquid Crystals* (Eds.: D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, Germany, **1998**, vol. 2B, pp. 693–748; b) K. J. Toyne in *Handbook of Liquid Crystals* (Eds.: D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, Germany, **1998**, vol. 2B, pp. 47–59; c) L. Pu, *Chem. Rev.* **1998**, *98*, 2405–2494.

[6] a) J. Wang, W. Wang, W. Li, X. Hu, K. Shen, C. Tan, X. Liu, X. Feng, *Chem. Eur. J.* **2009**, *15*, 11642–11659; b) C. Hawner, K. Li, V. Cirriez, A. Alexakis, *Angew. Chem.* **2008**, *120*, 8334–8337; *Angew. Chem. Int. Ed.* **2008**, *47*, 8211–8214; c) A. G. Cortez, R. R. Schrock, A. H. Hoveyda, *Angew. Chem.* **2007**, *119*, 4618–4622; *Angew. Chem. Int. Ed.* **2007**, *46*, 4534–4538; d) L. Palais, I. S. Mikhel, C. Bournaud, L. Micouin, C. A. Falciola, M. Vuagnoux-d'Augustin, S. Rosset, G. Bernardinelli, A. Alexakis, *Angew. Chem.* **2007**, *119*, 7606–7609; *Angew. Chem. Int. Ed.* **2007**, *46*, 7462–7465; e) J. Wang, X. Hu, J. Jiang, S. Gou, X. Huang, X. Liu, X. Feng, *Angew. Chem.* **2007**, *119*, 8620–8622; *Angew. Chem. Int. Ed.* **2007**, *46*, 8468–8470; f) Z. Hua, V. C. Vassar, H. Choi, I. Ojima, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5411–5416; g) A. Alexakis, C. Benhaim, S. Rosset, M. Humam, *J. Am. Chem. Soc.* **2002**, *124*, 5262–5263.

[7] a) J. Doussot, A. Guy, C. Ferroud, *Tetrahedron Lett.* **2000**, *41*, 2545–2547; b) K. Ding, Y. Wang, L. Zhang, Y. Wu, *Tetrahedron* **1996**, *52*, 1005–1010; c) H. Ishino, N. Itoh, M. Nagashima, K. Kurosawa, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 620–622; d) M. Hovorka, J. Günterová, J. Závada, *Tetrahedron Lett.* **1990**, *31*, 413–416; e) F. Toda, K. Tanaka, S. Iwata, *J. Org. Chem.* **1989**, *54*, 3007–3009; f) K. Yamamoto, H. Fukushima, Y. Okamoto, K. Hatada, M. Nakazaki, *J. Chem. Soc., Chem. Commun.* **1984**, 1111–1112; g) B. Feringa, H. Wynberg, *J. Org. Chem.* **1981**, *46*, 2547–2557; h) B. Feringa, H. Wynberg, *Tetrahedron Lett.* **1977**, *18*, 4447–4450; i) M. J. S. Dewar, T. Nakaya, *J. Am. Chem. Soc.* **1968**, *90*, 7134–7135.

[8] For selected reports on enantioselective oxidative biaryl coupling, see: a) H. Egami, K. Matsumoto, T. Oguma, T. Kunisu, T. Katsuki, *J. Am. Chem. Soc.* **2010**, *132*, 13633–13635; b) H. Egami, T. Katsuki, *J. Am. Chem. Soc.* **2009**, *131*, 6082–6083; c) S. Takizawa, *Chem. Pharm. Bull.* **2009**, *57*, 1179–1188; d) S. Takizawa, T. Katayama, C. Kameyama, K. Onitsuka, T. Suzuki, T. Yanagida, T. Kawai, H. Sasai, *Chem. Commun.* **2008**, 1810–1812; e) Q.-X. Guo, Z.-J. Wu, Z.-B. Luo, Q.-Z. Liu, J.-L. Ye, S.-W. Luo, L.-F. Cun, L.-Z. Gong, *J. Am. Chem. Soc.* **2007**, *129*, 13927–13938; f) M. Tada, N. Kojima, Y. Izumi, T. Taniike, Y. Iwasawa, *J. Phys. Chem. B* **2005**, *109*, 9905–9916; g) M. Tada, T. Taniike, L. M. Kantam, Y. Iwasawa, *Chem. Commun.* **2004**, 2542–2543; h) H. Somei, Y. Asano, T. Yoshida, S. Takizawa, H. Yamataka, H. Sasai, *Tetrahedron Lett.* **2004**, *45*, 1841–1844; i) J. Gao, J. H. Reibenspies, A. E. Martell, *Angew. Chem.* **2003**, *115*, 6190–6194; *Angew. Chem. Int. Ed.* **2003**, *42*, 6008–6012; j) X. Li, J. B. Hewglay, C. A. Mulrooney, J. Yang, M. C. Kozlowski, *J. Org. Chem.* **2003**, *68*, 5500–5511; k) Z. Luo, Q. Liu, L. Gong, X. Cui, A. Mi, Y. Jiang, *Angew. Chem.* **2002**, *114*, 4714–4717; *Angew. Chem. Int. Ed.* **2002**, *41*, 4532–4535; l) N. B. Barhate, C.-T. Chen, *Org. Lett.* **2002**, *4*, 2529–2532; m) S.-W. Hon, C.-H. Li, J.-H. Kuo, N.-B. Barhate, Y.-H. Liu, Y. Wang, C.-T. Chen, *Org. Lett.* **2001**, *3*, 869–872; n) X. Li, J. Yang, M. C. Kozlowski, *Org. Lett.* **2001**, *3*, 1137–1140.

[9] For selected reports on homogeneous catalytic aerobic oxidative biaryl coupling, see: a) B.-S. Liao, Y.-H. Liu, S.-M. Peng, S.-T. Liu, *Dalton Trans.* **2012**, *41*, 1158–1164; b) P. Yan, Y. Sugiyama, Y. Takahashi, H. Kinemuchi, T. Temma, S. Habaue, *Tetrahedron* **2008**, *64*, 4325–4331; c) S. Habaue, T. Temma, Y. Sugiyama, P. Yan, *Tetrahedron Lett.* **2007**, *48*, 8595–8598; d) J. K. Joseph, S. L. Jain, B. Sain, *Catal. Commun.* **2006**, *7*, 184–186; e) S.-Y. Zhang, J.-B. Lan, X.-Y. Su, S.-J. Guo, L. Chen, J.-S. You, R.-G. Xie, *J. Chem. Res.* **2005**, *7*, 418–419; f) P. S. Umare, G. L. Tembe, *React. Kinet. Catal. Lett.* **2004**, *82*, 173–178; g) V. B. Sharma, S. L. Jain, B. Sain, *Tetrahedron Lett.* **2003**, *44*, 2655–2656; h) J. S. Yadav, B. V. S. Reddy, K. U. Gayathri, A. R. Prasad, *New J. Chem.* **2003**, *27*, 1684–2686; i) R. Gupta, R. Mukherjee, *Tetrahedron Lett.* **2000**, *41*, 7763–7767; j) D.-R. Hwang, C.-P. Chen, B.-J. Uang, *Chem. Commun.* **1999**, 1207–1208; k) H. Nishino, H. Satoh, M. Yamashita, K. Kurosawa, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1919–1924.

[10] For selected reports on heterogeneous catalytic aerobic oxidative biaryl coupling, see: a) H. Eshghi, M. Bakavoli, H. Moradi, *Chin. Chem. Lett.* **2009**, *20*, 663–667; b) M. Matsushita, K. Kamata, K. Yamaguchi, N. Mizuno, *J. Am. Chem. Soc.* **2005**, *127*, 6632–6640; c) T. Ikeda, N. Misawa, Y. Ichihashi, S. Nishiyama, S. Tsuruya, *J. Mol. Catal. A* **2005**, *231*, 235–240; d) K. Iwai, T. Yamauchi, K. Hashimoto, T. Mizugaki, K. Ebitani,

K. Kaneda, *Chem. Lett.* **2003**, *32*, 58–59; e) M. R. Prasad, G. Kamalakar, S. J. Kulkarni, K. V. Raghavan, *J. Mol. Catal. A* **2002**, *180*, 109–123; f) P. Mastrorilli, F. Muscio, G. P. Suranna, C. F. Nobile, M. Latronico, *J. Mol. Catal. A* **2001**, *165*, 81–87; g) E. Armengol, A. Corma, H. García, J. Primo, *Eur. J. Org. Chem.* **1999**, 1915–1920; h) T. Sakamoto, H. Yonehara, C. Pac, *J. Org. Chem.* **1997**, *62*, 3194–3196.

[11] For reviews, see: a) H. Lu, X. P. Zhang, *Chem. Soc. Rev.* **2011**, *40*, 1899–1909; b) C.-M. Che, J.-S. Huang, *Chem. Commun.* **2009**, 3996–4015; c) S. Fantauzzi, A. Caselli, E. Gallo, *Dalton Trans.* **2009**, 5434–5443; d) C.-M. Che, V. K.-Y. Lo, C.-Y. Zhou, J.-S. Huang, *Chem. Soc. Rev.* **2011**, *40*, 1950–1975; e) Q. Liu, C.-C. Guo, *Sci. Sin.: Chim.* **2012**, *42*, 1399–1416.

[12] Compound **3a** is unreactive under the same reaction conditions.

[13] J. Huet, A. Gaudemer, C. Boucly-Goester, P. Boucly, *Inorg. Chem.* **1982**, *21*, 3413–3419.

[14] Y. S. Avlasevich, A. A. Rat'ko, V. V. Egorov, *J. Appl. Spectrosc.* **2002**, *69*, 554–559.

[15] H. Thiele, I. Behlke, W. Scheler, *Acta Biol. Med. German* **1963**, *11*, 767–785.

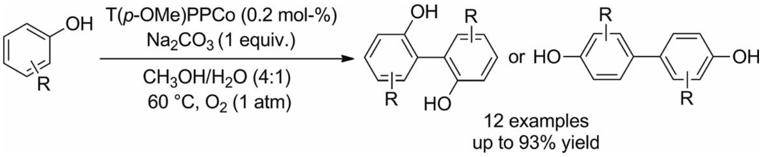
[16] a) K. M. Smith (Ed.), *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, **1975**; b) B. D. Berezin, *Coordination Compounds of Porphyrins and Phthalocyanine*, Nauka, Moscow, **1978**.

[17] a) M. Smrciná, Š. Vyskoci1, B. Máca, M. Polášek, T. A. Claxton, A. P. Abbott, P. Kocovský, *J. Org. Chem.* **1994**, *59*, 2156–2163; b) C. T. To, T. L. Chan, B. Z. Li, Y. Y. Hui, T. Y. Kwok, S. Y. Lam, K. S. Chan, *Tetrahedron Lett.* **2011**, *52*, 1023–1026; c) S. Murakami, Y. Akutsu, S. Habaue, O. Haba, H. Higashimura, *Nat. Sci.* **2010**, *2*, 803–808.

[18] H. Higashimura, K. Fujisawa, M. Kubota, S. Kobayashi, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1955–1962.

Received: November 27, 2012

Aerobic Oxidation



The T(*p*-OMe)PPCo-catalyzed oxidative coupling of phenols was developed for the synthesis of biphenols. This reaction features low catalyst loadings, mild reaction conditions, and operational simplicity. Preliminary mechanistic studies were conducted.

Q. Jiang, W. Sheng, M. Tian, J. Tang, C. Guo* **1–7**

Cobalt(II)–Porphyrin-Catalyzed Aerobic Oxidation: Oxidative Coupling of Phenols

Keywords: Homogeneous catalysis / Oxidation / Metalloporphyrins / Cobalt / C–H functionalization / Biaryls