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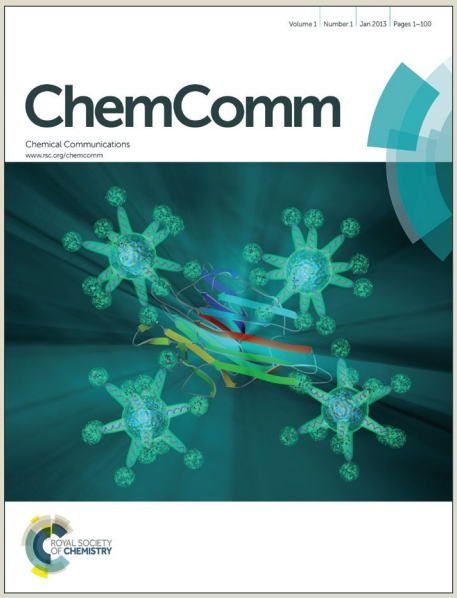

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Synthesis of 2,2′-biphenols through direct C(sp^2)–H hydroxylation of [1,1'-biphenyl]-2-ols

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A novel synthesis of diversely substituted 2,2′-biphenols through Pd(II)-catalyzed, ^{t}BuOOH-oxidized, and hydroxyl-directed C(sp^2)–H hydroxylation of [1,1'-biphenyl]-2-ols have been developed. Notably, this finding is distinct from previous reports in which [1,1'-biphenyl]-2-ols underwent an intramolecular C–H activation and C–O bond formation to afford dibenzofurans under the promotion of Pd(II) but in the absence of ^{t}BuOOH.

The 2,2′-biphenol framework is a substructure frequently found in natural products, pharmaceuticals and functional materials.[1,2] Moreover, 2,2′-biphenol and its derivatives are also acting as efficient ligands in numerous metal-catalyzed organic transformations and asymmetric synthesis.[3]

Due to their importance, tremendous efforts have been made in developing efficient methods for the preparation of 2,2′-biphenols. So far, the most frequently used approach toward 2,2′-biphenols is the oxidative homo- and cross-coupling of phenols.[4-6] Besides, other elegant strategies such as radical cyclization,[7] Ullmann-type coupling,[8] and Suzuki-Miyaura coupling[9] have also been well established. While these literature methods are generally efficient and reliable, there are some challenging issues remained: (1) the couplings of the electron-deficient substrates were much less efficient, which restricted the scope of this synthetic strategy; (2) the frequently required harsh reaction conditions could affect the functional group compatibility; (3) in many cases, the poor regio-selectivity led to the formation of side products, and the expensive reagents and toxic heavy metal oxidants employed therein compromised the sustainability. In view of the increasing importance of 2,2′-biphenols and the need for greener chemistry, more efficient, higher atom-economy and more environmentally friendly synthetic approaches toward 2,2′-biphenols are still highly desirable.

In recent years, C–H bond activation has been developed as a powerful tool for the formation of C–C and C–heteroatom bonds.[10] In particular, direct C(sp^2)–H hydroxylation of arenes is emerging as a new tactics for the synthesis of phenol derivatives.[11] Compared with other methods, this strategy is arguably the most straightforward, sustainable and atom-economy since it does not need pre-functionalization of substrates, and thus holds advantages such as reduced reaction steps, lower costs and less wastes. Generally, the hydroxylation of arenes occurred under the assistance of a directing group (DG), such as a ketone,[12] aldehyde,[13] ester,[14] carboxyl acid,[15] amide,[16,17] oxime ether,[18] anilide,[19] carbamate,[20] sulfide,[21] 2-pyridyl,[22] or 2-benzoxazol-2-yl unit,[23] and took place regio-selectively at the *ortho*-position(s) of the DG to afford substituted phenols. Moreover, recent studies demonstrated that the C(sp^2)–H hydroxylation could also be realized onto functionalized biphenyls such as [1,1'-biphenyl]-2-carboxylic acid and [1,1'-biphenyl]-2-yl phosphonate to give 2'-hydroxy-[1,1'-biphenyl]-2-carboxylic acid,[24] and 2'-hydroxy-[1,1'-biphenyl]-2-yl phosphonate,[25] respectively. Inspired by those pioneering studies and as a continuation of our recent interest in the synthesis and synthetic applications of 2-arylphenols,[26] we have studied the reaction of [1,1'-biphenyl]-2-ol under the promotion of Pd(II) in the presence of *tert*-butyl hydroperoxide (TBHP). We were pleased to find that under these conditions, the hydroxyl group attached on one of the two phenyl rings in [1,1'-biphenyl]-2-ol could act as a DG to introduce a new hydroxyl group regio-selectively onto the 2'-position of the other phenyl ring, thus resulting in a highly convenient and efficient synthetic pathway toward 2,2′-biphenol derivatives (Scheme 1, eq. 3). Notably, this finding is distinct from previous reports in which 2-arylphenols underwent an intramolecular C–H bond activation and C–O bond formation to afford dibenzofuran derivatives under the promotion of Pd(II) and the assistance of some specific additives by using air (Scheme 1, eq. 1)[27a] or *tert*-butyl peroxybenzoate (Scheme 1, eq. 2)[27b] as the oxidant.[28] Herein we wish to report our results on this regard.

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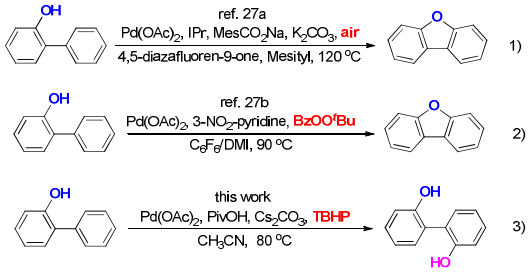
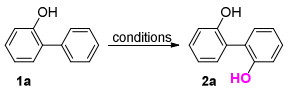


Scheme 1. Transformations of [1,1'-biphenyl]-2-ol under different conditions

Our study was initiated by treating 2-phenylphenol (**1a**) with $Pd(OAc)_2$, TBHP (70% aqueous solution) and K_2CO_3 in CH_3CN at 80 °C for 18 h. From this reaction, [1,1'-biphenyl]-2,2'-diol (**2a**) was obtained in 25% yield (Table 1, entry 1). Optimizations were then carried out by varying the reaction parameters. First, the effect of different bases including Na_2CO_3, Cs_2CO_3, and DABCO was tested. Among them, Cs_2CO_3 was the most effective (entries 1–4). In a control experiment, the formation of **2a** was not observed in the absence of a base (entry 5). To our delight, using PivOH as a ligand could improve the reaction significantly (entries 6-9). Next, replacing PivOH with AcOH resulted in a decreased yield of **2a** (entry 10). To check the effect of different Pd catalysts, $PdCl_2$, $Pd_2(dba)_3$, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ and $Pd(TFA)_2$ were tried. However, they were found to be less effective than $Pd(OAc)_2$ in promoting this reaction (entries 11-15 *vs* 8). Other oxidants such as $K_2S_2O_8$, oxone, *m*-CPBA, H_2O_2 and air were ineffective for this reaction (entries 16-20). Further study showed that changing the reaction atmosphere from air to nitrogen did not affect the yield of **2a** obviously (entry 21 vs 8). Finally, when 70% aqueous solution of TBHP was replaced by TBHP in decane (5.5 mol/L), **2a** could be obtained in a yield of 75% (entry 22). These results revealed that TBHP, rather than air or water, is the oxygen source of the newly introduced hydroxyl group.

With the optimized reaction conditions in hands (Table 1, entry 8), the scope and generality of this hydroxylation was explored. Initially, [1,1'-biphenyl]-2-ols bearing various functional groups (R^2) on the phenyl unit onto which the new hydroxyl group was going to be introduced were tried, and the results were included in Table 2. First, substrates bearing a halide, alkyl, trifluoromethyl, phenyl, alkoxyl, trifluoromethoxy, phenoxy, or acetyl group on the 4'-position of the biphenyl-2-ols underwent this reaction smoothly to afford the corresponding products (**2b**–**2n**) in good yields. Notably, different kinds of functional groups were well tolerated, and the electronic nature of the substituents did not show obvious effect. Second, biphenyl-2-ols bearing a fluoro, chloro, or methyl group on the 3'-position were found to be also able to participate in this reaction to give **2o**–**2q** with good efficiency. Meanwhile, for these 3'-substituted substrates, only one of the two possible regio-isomers was obtained, indicating that the hydroxylation proceeded regio-selectively at the less sterically hindered position. Third, [1,1'-biphenyl]-2-ols with a substituent attached on the 2'-position were tested. It turned out that 2'-fluoro-, 2'-chloro-, and 2'-methyl-[1,1'-biphenyl]-2-ols could also take part in this transformation to afford **2r**, **2s**, and **2t**, respectively, albeit in lower yields compared with their 4'- or 3'-substituted counterparts.

Table 1. Optimization studies on the formation of **2a** [a]



Entry	Catalyst	Oxidant	Ligand (eq.)	Base	Yield (%) [b]
1	$Pd(OAc)_2$	TBHP	-	K_2CO_3	25
2	$Pd(OAc)_2$	TBHP	-	Na_2CO_3	22
3	$Pd(OAc)_2$	TBHP	-	Cs_2CO_3	34
4	$Pd(OAc)_2$	TBHP	-	DABCO	33
5	$Pd(OAc)_2$	TBHP	-	-	-
6	$Pd(OAc)_2$	TBHP	PivOH (0.1)	Cs_2CO_3	45
7	$Pd(OAc)_2$	TBHP	PivOH (0.5)	Cs_2CO_3	64
8	$Pd(OAc)_2$	TBHP	PivOH (1)	Cs_2CO_3	76
9	$Pd(OAc)_2$	TBHP	PivOH (1.5)	Cs_2CO_3	74
10	$Pd(OAc)_2$	TBHP	AcOH (1)	Cs_2CO_3	51
11	$PdCl_2$	TBHP	PivOH (1)	Cs_2CO_3	57
12	$Pd_2(dba)_3$	TBHP	PivOH (1)	Cs_2CO_3	55
13	$Pd(PPh_3)_4$	TBHP	PivOH (1)	Cs_2CO_3	50
14	$Pd(PPh_3)_2Cl_2$	TBHP	PivOH (1)	Cs_2CO_3	72
15	$Pd(TFA)_2$	TBHP	PivOH (1)	Cs_2CO_3	50
16	$Pd(OAc)_2$	$K_2S_2O_8$	PivOH (1)	Cs_2CO_3	trace
17	$Pd(OAc)_2$	oxone	PivOH (1)	Cs_2CO_3	trace
18	$Pd(OAc)_2$	*m*-CPBA	PivOH (1)	Cs_2CO_3	trace
19	$Pd(OAc)_2$	H_2O_2	PivOH (1)	Cs_2CO_3	trace
20	$Pd(OAc)_2$	-	PivOH (1)	Cs_2CO_3	-
21[c]	$Pd(OAc)_2$	TBHP	PivOH (1)	Cs_2CO_3	70
22	$Pd(OAc)_2$	TBHP [d]	PivOH (1)	Cs_2CO_3	75

[a] Reaction conditions: **1a** (0.5 mmol), catalyst (0.025 mmol), oxidant (4 eq.), base (1.2 eq.), CH_3CN (2 mL), 80 °C, air, 18 h. [b] Isolated yields. [c] Under N_2. [d] 5.5 mol/L in decane (dried over 4Å molecular sieve).

Next, the reaction of [1,1'-biphenyl]-2-ols with different R^1 were tried. The results listed in Table 3 showed such substrates bearing a fluoro, chloro, or methoxy group on the 4-position, or a chloro, methyl, or methoxy group on the 3-position were all suitable for this hydroxylation process to give the corresponding products in yields ranging from 75% to 85%. Interestingly, 3-(2-hydroxy phenyl)naphthalene-2-ol (**2v**) was obtained in 58% yield from 2-(naphthalen-2-yl)phenol. Finally, 4-fluoro-4'-methoxy-[1,1'-bi phenyl]-2-ol, bearing substituents on both of the two phenyl units, took part in this reaction smoothly to give **2w** in a yield of 77%. Interestingly, as demonstrated by the synthesis of **2b**, **2c**, **2j**, **2p** and **2q**, this novel method could afford the same 2,2'-biphenol from different [1,1'-biphenyl]-2-ol substrates (see Table 2 and Table 3), thus resulting in a highly versatile method toward 2,2'-biphenol derivatives.

[1,1'-Binaphthalen]-2-ol (**1x**) was also tried as a possible substrate for this oxidative hydroxylation with the aim to

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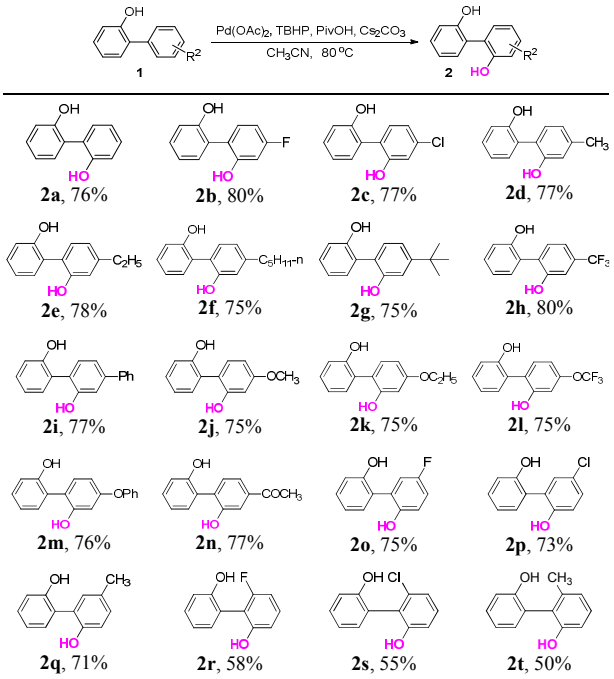
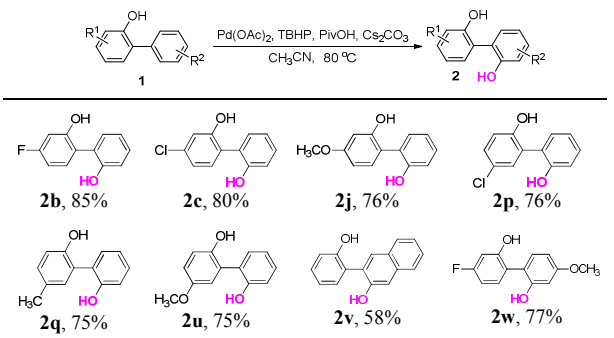
Table 2. Synthesis of 2,2′-biphenols (I) [a,b]



[a] Reaction conditions: **1** (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), TBHP (2 mmol), PivOH (0.5 mmol), Cs_2CO_3 (0.6 mmol), CH_3CN (2 mL), 80 °C, air, 18 h. [b] Isolated yields.

Table 3. Synthesis of 2,2′-biphenols (II) [a,b]



[a] Reaction conditions: **1** (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), TBHP (2 mmol), PivOH (0.5 mmol), Cs_2CO_3 (0.6 mmol), CH_3CN (2 mL), 80 °C, air, 18 h. [b] Isolated yields.

develop an alternative synthetic approach toward [1,1'-bi naphthalene]-2,2'-diol and its derivatives. However, treatment of **1x** under the optimized reaction conditions for 18 h afforded 1-hydroxy-[1,1'-binaphthalen]-2(1*H*)-one[29] (**3**, Scheme 2), rather than the desired [1,1'-binaphthalene]-2,2'-diol. This result might be attributed to the strong steric hindrance between the two naphthyl units of the required complex intermediate for the formation of [1,1'-binaphthalene] -2,2'-diol.[30]

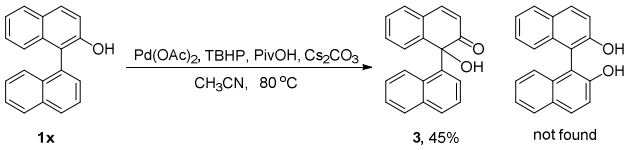
In order to clarify the reaction mechanism, some control experiments were carried out. First, 2 equiv of 2,2,6,6-tetramethylpiperidine oxide (TEMPO) were added as a radical scavenger in the reaction of **1a**. In this case, the yield of **2a** decreased to 35%. When the amount of TEMPO increased to 4 equiv, the formation of **2a** was completely suppressed. The obvious inhibitory effect shown by TEMPO indicated that this hydroxylation reaction might involve a single electron transfer process.

In a second control experiment, 2-methoxy-1,1'-biphenyl (**A**) was found to be intact after being subjected to the standard reaction conditions for 18 h. This result indicated that removal of the proton in the hydroxyl group of [1,1'-biphenyl]-2-ol should have been involved in the hydroxylation process.

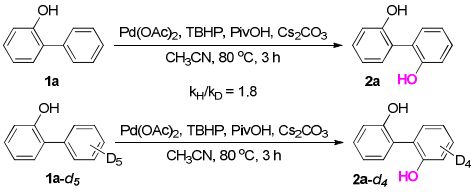
Third, an intermolecular kinetic isotope effect was studied by two side-by-side reactions of **1a** and **1a-*d*$_5$** under standard reaction conditions. From these reactions, a k_H/k_D value of 1.8 was observed (Scheme 3).

Fourth, an intramolecular KIE experiment was conducted by using **1a-*d*$_1$** as the substrate to give a k_H/k_D value of 3.0 (Scheme 4). These results indicated that a C–H cleavage might be involved in the rate-limiting step of this C(sp^2)–H hydroxylation process.

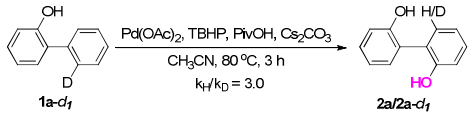
Based on the above results and related reports,[22] a tentative mechanism for the formation of **2a** from **1a** is illustrated in Scheme 5. Initially, **1a** is transformed into an anion (**I**) under the promotion of a base. Next, the phenoxide ion-directed, ligand (**L**)-assisted and Pd(II)-catalyzed C–H activation of **I** affords intermediate **III** and releases LH *via* a possible intermediate **II**. Meanwhile, homolysis of ^{t}BuOOH gives HO• and ^{t}BuO•. The later then abstracts a hydrogen radical from LH to release L•. The following oxidative addition of HO• and L• to **III** affords a Pd(IV) intermediate **IV**. Then, a reductive elimination occurs with **IV** to give a Pd(II)



Scheme 2. The reaction of [1,1'-binaphthalen]-2-ol (**1x**)



Scheme 3. Intermolecular KIE experiment



Scheme 4. Intramolecular KIE experiment

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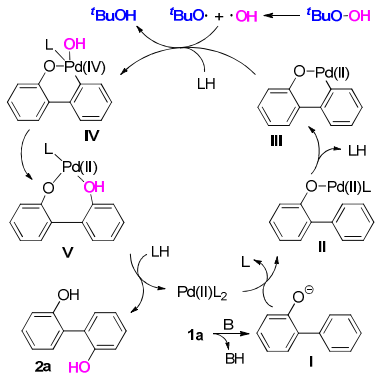

Scheme 5. Proposed reaction mechanism for the formation of **2a**

intermediate **V**, which is then protonated to generate **2a** and release the Pd(II) species.

In conclusion, we have developed a novel synthesis of 2,2′-biphenols *via* direct C(sp^2)–H hydroxylation of [1,1'-biphenyl]-2-ols. To our knowledge, this is the first example in which the hydroxyl group is used as a DG to introduce another hydroxyl group onto [1,1'-biphenyl]-2-ols. Generally, this new protocol showed unique features such as broad substrate scope, good functional group tolerance, sustainable oxidant, and excellent regio-selectivity. Therefore, it is well complementary to the existing methods for the synthesis of 2,2′-biphenols, and is thus expected to find wide applications in related areas.

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Notes and references

1 (a) V. Rempel, A. Fuchs, S. Hinz, T. Karcz, M. Lehr, U. Koetter and C. E. Müller, *ACS Med. Chem. Lett.*, 2013, **4**, 41; (b) R. Francke, R. Reingruber, D. Schollmeyer and S. R. Waldvogel, *J. Agric. Food Chem.*, 2013, **61**, 4709; (c) J. M. Lin, A. S. P. Gowda, A. K. Sharma and S. Amin, *Bioorg. Med. Chem.*, 2012, **20**, 3202.

2 (a) G. Bringmann, T. Gulder, T. M. Gulder and M. Breuning, *Chem. Rev.*, 2011, **111**, 563; (b) S. E. Allen, R. R. Walvoord, R. Padilla-Salians and M. C. Kozlowski, *Chem. Rev.*, 2013, **113**, 6234.

3 (a) Y. Chen, S. Yekta and A. K. Yudin, *Chem. Rev.*, 2003, **103**, 3155; (b) M. C. Kozlowski, B. J. Morgan and E. C. Linton, *Chem. Soc. Rev.*, 2009, **38**, 3193.

4 G. Lessene, K. S. Feldman, In *Modern Arene Chemistry*; D. Astruc, Eds.; Wiley-VCH: Weinheim, 2002; Chapter 14.

5 (a) K. V. N. Esguerra, Y. Fall, L. Petitjean and J.-P. Lumb, *J. Am. Chem. Soc.*, 2014, **136**, 7662; (b) Q. Jiang, W. Sheng, M. Tian, J. Tang and C. Guo, *Eur. J. Org. Chem.*, 2013, 1861; (c) J. Feng, X.-B. Yang, S. Liang, J. Zhang and X.-Q. Yu, *Tetrahedron Lett.*, 2013, **54**, 355; (d) B.-S. Liao, Y.-H. Liu, S.-M. Peng and S.-T. Liu, *Dalton Trans.*, 2012, **41**, 1158; (e) A. Kirste, G. Schnakenburg and S. R. Waldvogel, *Org. Lett.*, 2011, **13**, 3126.

6 (a) Y. E. Lee, T. Cao, C. Torruellas and M. C. Kozlowski, *J. Am. Chem. Soc.*, 2014, **136**, 6782; (b) B. Elsler, B. Schollmeyer, K. M. Dyballa, R. Franke and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2014, **53**, 5210; (c) A. Kirste, B. Elsler, G. Schnakenburg and S. R. Waldvogel, *J. Am. Chem. Soc.*, 2012, **134**, 3571; (d) N. Y. More and M. Jeganmohan, *Org. Lett.*, 2015, **17**, 3042; (e) K. Morimoto, K. Sakamoto, Y. Ohnishi, T. Miyamoto, M. Ito, T. Dohi and Y. Kita, *Chem. Eur. J.*, 2013, **19**, 8726; (f) N. Michihata, Y. Kaneko, Y. Kasai, K. Tanigawa, T. Hirokane, S. Higasa and H. Yamada, *J. Org. Chem.*, 2013, **78**, 4319.

7 K.-S. Masters and S. Bräse, *Angew. Chem., Int. Ed.*, 2013, **52**, 866.

8 R. Francke, G. Schnakenburg and S. R. Waldvogel, *Org. Lett.*, 2010, **12**, 4288.

9 (a) T. Konakahara, Y. B. Kiran, Y. Okuno, R. Ikeda and N. Sakai, *Tetrahedron Lett.*, 2010, **51**, 2335; (b) B. Schmidt, M. Riemer and M. Karras, *J. Org. Chem.*, 2013, **78**, 8680.

10 (a) G. Song, F. Wang and X. Li, *Chem. Soc. Rev.*, 2012, **41**, 3651; (b) J. Wencel-Delord and F. Glorius, *Nat. Chem.*, 2013, **5**, 369; (c) M. Zhang, Y. Zhang, X. Jie, H. Zhao, G. Li and W. Su, *Org. Chem. Front.*, 2014, **1**, 843; (d) L. Zhou and W. Lu, *Chem.-Eur. J.*, 2014, **20**, 634; (e) S. A. Girard, T. Knauber and C.-J. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 74; (f) L. Ackermann, *Acc. Chem. Res.*, 2014, **47**, 281; (g) H. Huang, X. Ji, W. Wu and H. Jiang, *Chem. Soc. Rev.*, 2015, **44**, 1155; (h) K. Shin, H. Kim and S. Chang, *Acc. Chem. Res.*, 2015, **48**, 1040; (i) G. Song and X. Li, *Acc. Chem. Res.*, 2015, **48**, 1007.

11 (a) D. A. Alonso, C. Nájera, I. M. Pastor and M. Yus, *Chem. Eur. J.*, 2010, **16**, 5274; (b) S. Enthaler and A. Company, *Chem. Soc. Rev.*, 2011, **40**, 4912; (c) Y. Rao, *Synlett*, 2013, **24**, 2472; (d) G. Shan, X. Yang, L. Ma and Y. Rao, *Angew. Chem., Int. Ed.*, 2012, **51**, 13070.

12 (a) F. Mo, L. J. Trzepkowski and G. Dong, *Angew. Chem., Int. Ed.*, 2012, **51**, 13075; (b) V. S. Thirunavukkarasu and L. Ackermann, *Org. Lett.*, 2012, **14**, 6206; (c) P. Y. Choy and F. Y. Kwong, *Org. Lett.*, 2013, **15**, 270; (d) G. Shan, X. Han, Y. Lin, S. Yu and Y. Rao, *Org. Biomol. Chem.*, 2013, **11**, 2318.

13 F. Z. Yang, K. Rauch, K. Kettelhoit and L. Ackermann, *Angew. Chem., Int. Ed.*, 2014, **53**, 11285.

14 Y. Q. Yang, Y. Lin and Y. Rao, *Org. Lett.*, 2012, **14**, 2874.

15 Y.-H. Zhang and J.-Q. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 14654.

16 V. S. Thirunavukkarasu, J. Hubrich and L. Ackermann, *Org. Lett.*, 2012, **14**, 4210.

17 F. Z. Yang and L. Ackermann, *Org. Lett.*, 2013, **15**, 718.

18 Y.-F. Liang, X. Wang, Y. Yuan, Y. Liang, X. Li and N. Jiao, *ACS Catal.*, 2015, **5**, 6148.

19 X. Yang, G. Shan and Y. Rao, *Org. Lett.*, 2013, **15**, 2334.

20 W. Liu and L. Ackermann, *Org. Lett.*, 2013, **15**, 3484.

21 R. Xu, J.-P. Wan, H. Mao and Y. Pan, *J. Am. Chem. Soc.*, 2010, **132**, 15531.

22 (a) S. Guin, S. K. Rout, A. Banerjee, S. Nandi and B. K. Patel, *Org. Lett.*, 2012, **14**, 5294; (b) Y. P. Yan, P. Feng, Q. Z. Zheng, Y. F. Liang, J. F. Lu, Y. X. Cui and N. Jiao, *Angew. Chem., Int. Ed.*, 2013, **52**, 5827; (c) J. Dong, P. Liu and P. Sun, *J. Org. Chem.*, 2015, **80**, 2925.

23 K. Seth, M. Nautiyal, P. Purohit, N. Parikh and A. K. Chakraborti, *Chem. Commun.*, 2015, **51**, 191.

24 J. Gallardo-Donaire and R. Martin, *J. Am. Chem. Soc.*, 2013, **135**, 9350.

25 H.-Y. Zhang, H.-M. Yi, G.-W. Wang, B. Yang and S.-D. Yang, *Org. Lett.*, 2013, **15**, 6186.

26 (a) Y. He, X. Zhang and X. Fan, *Chem. Commun.*, 2014, **50**, 14968; (b) Y. He, S. Guo, X. Zhang, C. Guo and X. Fan, *Tetrahedron Lett.*, 2015, **56**, 1513.

27 (a) B. Xiao, T.-J. Gong, Z.-J. Liu, J.-H. Liu, D.-F. Luo, J. Xu and L. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 9250; (b) Y. Wei and N. Yoshikai, *Org. Lett.*, 2011, **13**, 5504.

28 For a Cu(I) catalyzed formation of dibenzofurans from 2-aryl-phenols, see: J. Zhao, Y. Wang, Y. He, L. Liu and Q. Zhu, *Org. Lett.*, 2012, **14**, 1078.

29 K. Krohn and G. Zimmermann, *J. Org. Chem.*, 1998, **63**, 4140.

30 F. W. Patureau and F. Glorius, *J. Am. Chem. Soc.*, 2010, **132**, 9982.

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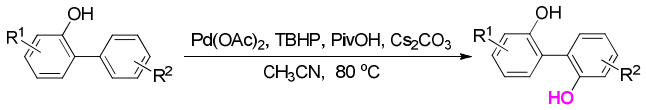

A novel synthesis of diversely substituted 2,2′-biphenols through Pd(II)-catalyzed, ^{t}BuOOH -oxidized, and hydroxyl-directed C(sp^2)–H hydroxylation of [1,1'-biphenyl]-2-ols have been developed.