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Oxidative Cross-Coupling of Two Different Phenols: An Efficient Route to Unsymmetrical Biphenols

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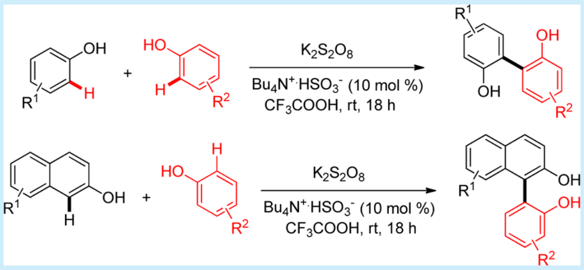
Supporting Information

ABSTRACT: An efficient synthesis of unsymmetrical biphenols via the oxidative cross-coupling of two different phenols in the presence of $K_2S_2O_8$ and $Bu_4N^+{\cdot}HSO_3^-$ (10 mol %) in CF_3COOH at ambient conditions is described. 1:1 Cross-coupling of substituted phenols with naphthols and 1:2 cross-coupling of naphthols with phenol are also disclosed. By using $Bu_4N^+{\cdot}HSO_3^-$, the homocoupling of phenols or naphthols was controlled. In these reactions, the *ortho* C−H bond of two different phenols and the *ortho* and *para* C−H bond of phenols were coupled together.



The development of a highly efficient, easily accessible, and environmentally friendly method for synthesizing biphenol molecules under mild reaction conditions in a highly atom economical manner is highly important in organic synthesis. Biphenol units are present in various natural products, drug molecules, and functional materials.[1] In addition, biphenol molecules are efficiently used as ligands in various organic transformations including enantioselective reactions.[2] Generally, nature prefers to synthesize phenolic ligands, biomaterials, isoquinoline alkaloids, and natural products via an oxidative phenol coupling in the presence of oxidative enzymes such as laccase, peroxidase, and cytochrome P450 (CYP) as catalysts.[3] Meanwhile, it is also believed that this coupling reaction is involved in the formation of humic materials in soils via enzymatic and abiotic routes.[4] Thus, to understand the reaction mechanism and to develop a practical route to synthesize biphenols has been a long time interest among organic chemists.[5−7] Symmetrical biphenols are prepared by the oxidative homocoupling of phenols in the presence of a stoichiometric amount of metal salts or metal catalysts along with a stoichiometric amount of oxidants or organic reagents such as hypervalent iodine(III) reagents, DDQ, NaOCl, and molecular oxygen as a terminal oxidant catalyzed by $NaNO_2$.[5−7]

Although the oxidative coupling of phenols has been known in the literature for several decades, the cross-coupling of two different phenols is not well studied and very challenging due to the formation of many competitive side products. While designing this type of oxidative coupling reaction, control of competitive side products such as homocoupling of phenols, Pummerer's ketones, C−O bond formation between two phenols, quinones, polymers, and dehydrotrimers is very important.[8a] Very recently, the cross-coupling of phenols has been successfully achieved by using a chromium salen catalyst or an electrochemical oxidation pathway.[8a−c] In the reaction, metal oxy or hydroxy or alkoxyl radicals are key intermediates, which abstract hydrogen from phenol and initiates the coupling reaction. The metal oxy radical was generated by the chromium catalyst, and hydroxyl or alkoxyl radicals were generated by BDP electrode.

A sulfate anion radical ($SO_4^{-\bullet}$) is efficiently used as a potential oxidant for the degradation of environmental pollutant.[9a] Due to the strong electron-accepting ability of $SO_4^{-\bullet}$, it has been efficiently used to destroy soil carbon pollutants. Although the oxidation potential of $SO_4^{-\bullet}$ is 2.6 V, the reactivity between organic compounds is considered to be slow but very selective.[9b,c] $K_2S_2O_8$, $Na_2S_2O_8$, and $(NH_4)_2S_2O_8$ are commonly used sources to generate $SO_4^{-\bullet}$. Interestingly, the sulfate anion radical can be generated very easily at rt without having any external reagents or sources. Our continuous interest in the $SO_4^{-\bullet}$ anion radical chemistry prompted us to explore the possibility of using $SO_4^{-\bullet}$ as an oxidant for the cross-coupling of two different phenols.[10a,b] Herein, we report an efficient synthesis of unsymmetrical biphenols via the oxidative cross-coupling of two different phenols in the presence of $K_2S_2O_8$ in CF_3COOH at ambient temperature under air. The cross-coupling reaction was also successfully extended into 1:1 cross-coupling of substituted phenols with naphthols and 1:2 cross-coupling of naphthols with phenol.

To accomplish the cross-coupling reaction, initially, a combination of phenol and 2-naphthol substrates such as 4-methoxyphenol (**1a**) and 2-naphthol (**2a**) were selected (Scheme 1). The cross-coupling reaction of **1a** with **2a** was tested in the presence of $K_2S_2O_8$ in CF_3COOH at rt for 18 h under air. In the reaction, the homocoupling of **1a** (product **3aa** in 23% yield), the homocoupling of **2a** (product **4aa** in 27% yield), and the expected cross-coupling product **5aa** in 21% yield were observed. In the reaction, $K_2S_2O_8$ generates the $SO_4^{-\bullet}$ anion radical at ambient temperature. It is believed that the $SO_4^{-\bullet}$ anion radical was stabilized by CF_3COOH solvent via

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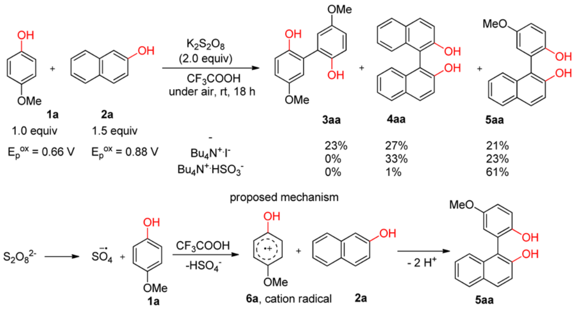
Scheme 1. Cross-Coupling of Phenol and Naphthol

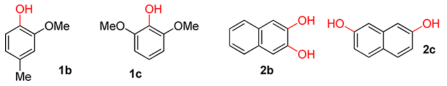


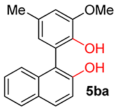
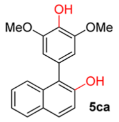
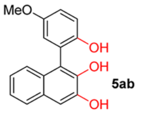
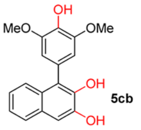
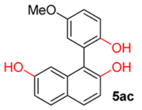
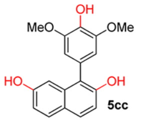
hydrogen bonding. Later, the $SO_4^{-\bullet}$ anion radical abstracts hydrogen from **1a** or **2a** in the presence of CF_3COOH, providing a cationic phenol or naphthol radical intermediate **6** and nontoxic HSO_4^- salt. To gain further insight into the radical formation, the oxidation potential of **1a** and **2a** was tested by using cyclic voltammetry (see Supporting Information). The oxidation potential of **1a** is SHE 0.66 V, and that of **2a** is SHE 0.88 V. It is expected that the $SO_4^{-\bullet}$ anion radical prefers to abstract hydrogen from **1a**, forming a cationic intermediate **6a** compared to **2a** due to the lower oxidation potential value. To support the formation of a cationic intermediate **6a**, a UV−vis spectroscopy study was done. An intense absorption band was observed in the visible region between 400 to 500 nm during the reaction of phenol **1a** with $K_2S_2O_8$ at rt. This study strongly supports that a cationic intermediate is formed during the reaction as previously observed by Kochi's group.[10c−e] Later, the nucleophilic addition of **2a** into cationic intermediate **6a** provides the cross-coupling product **5aa**.

It is clear that the coupling reaction proceeds via a cationic radical intermediate. We expected that if the reaction is done in the presence of an ionic salt, a negatively charged counterion could coordinate with a cationic phenol radical intermediate **6a** and stabilize it. Thus, the possibility is there to increase the yield of cross-coupling product **5aa**. With this idea, the reaction was tested with a catalytic amount of 10 mol % of salts such as $Bu_4N^+ \cdot I^-$, $Bu_4N^+ \cdot Br^-$, $Bu_4N^+ \cdot Cl^-$, $Bu_4N^+ \cdot F^-$, and $Bu_4N^+ \cdot HSO_3^-$. $Bu_4N^+ \cdot I^-$ provided homocoupling product **4aa** in 33% yield and cross-coupling product **5aa** in 23% yield, respectively. The other homocoupling product **3aa** was not observed (Scheme 1). Surprisingly, $Bu_4N^+ \cdot HSO_3^-$ afforded cross-coupling product **5aa** in 61% yield and homocoupling product **4aa** in a very minor 1% yield (for mass balance, see Supporting Information). Other salts were not active for the reaction. The same reaction was also done under a nitrogen atmosphere. In the reaction, product **5aa** was observed in 60% yield as in the case of under air. This result clearly reveals that the reaction is not air sensitive. $K_2S_2O_8$ is crucial for the reaction, and without that the reaction did not proceed. Meanwhile, 2.0 equiv of $K_2S_2O_8$ are also needed to raise the yield of cross-coupling product **5aa**. The reaction was also examined with 1.0 and 1.5 equiv of $K_2S_2O_8$. In these reactions, product **5aa** was observed only in 40% and 57% yields, respectively. The cross-coupling reaction was also examined with various solvents such as AcOH, MeOH, $ClCH_2Cl$, *tert*-amyl alcohol, *tert*-BuOH, and CF_3SO_3H. In acetic acid solvent, product **5aa** was observed in very low 5% yield and the remaining solvents were not effective. The reaction was also tried with $Na_2S_2O_8$ and $(NH_4)_2S_2O_8$. $(NH_4)_2S_2O_8$ was also equally effective, providing product **5aa** in 60% yield. But, $Na_2S_2O_8$ provided only product **5aa** in 40% yield. It is expected that the solubility of $Na_2S_2O_8$ is less in organic solvent.

In the presence of $Bu_4N^+ \cdot HSO_3^-$ (10 mol %), 2-naphthol (**2a**) underwent cross-coupling with 4-methyl-2-methoxy phenol (**1b**) or 2,6-dimethoxy phenol (**1c**), providing products **5ba** and **5ca** in 61% and 82% yields, respectively (Table 1, entries 1 and 2). In the reaction of **1c** with **2a**, the *para* C−H bond of **1c** was coupled with the *α* C−H bond of 2-naphthol (**2a**). The oxidation potential of **1b** is 0.7 V, and that of **1c** is 0.62 V. Thus, in these reactions, only phenols **1b−c** form the cationic radical species, and **2a** acts as a nucleophile. Similarly, naphthalene-2,3-diol (**2b**) reacted with **1a** or **1c**, affording the cross-coupling products **5ab** and **5cb** in 64% and 51% yields, respectively (entries 3 and 4). Further, naphthalene-2,7-diol (**2c**) reacted with **1a** or **1c**, providing coupling products **5ac** and **5cc** in 73% and 69% yields, respectively (entries 5 and 6). The mass balance of all these reactions was mentioned in the Supporting Information.

Table 1. Cross-Coupling of Phenols and Naphthols[a]



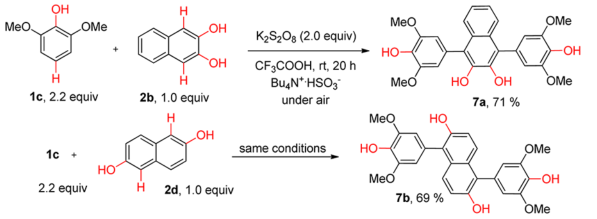
entry	phenol **1** (1.0 equiv)	**2** (1.5 equiv)	product **5**	yield (%)[b]
1	**1b**	**2a**	 **5ba**	61
2	**1c**	**2a**	 **5ca**	82
3	**1a**	**2b**	 **5ab**	64
4	**1c**	**2b**	 **5cb**	51
5	**1a**	**2c**	 **5ac**	73
6	**1c**	**2c**	 **5cc**	69

[a] All reactions were carried out using **1a−c** (1.0 equiv), **2a−c** (1.5 equiv), $Bu_4N^+ \cdot HSO_3^-$ (10 mol %), and $K_2S_2O_8$ (2.0 equiv) in CF_3COOH at ambient conditions for 18 h. [b] Isolated yield.

In the naphthols **2b** and **2d**, two OH groups are present on the aromatic moiety. We tried to incorporate two phenol moieties at the *α* C−H bond of the corresponding OH groups (Scheme 2). Thus, treatment of **2b** or **2d** with an excess amount of 2,6-dimethoxyphenol (**1c**) (2.2 equiv) gave polycyclic naphthol derivatives **7a** and **7b** in 71% and 75% yields, respectively (for mass balance, see Supporting Information).

Encouraged by the 1:1 and 2:1 cross-coupling of phenols with naphthols, the possibility of cross-coupling of two different phenols was tested (Scheme 3). The cross-coupling of two

Scheme 2. *bis*-Arylation of Naphthols 2b and 2d



Scheme 3. Cross-Coupling of Two Different Phenols

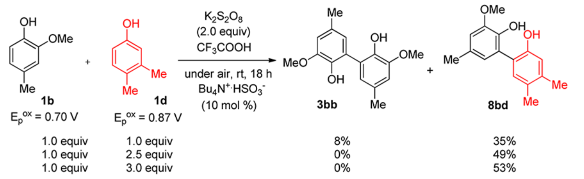
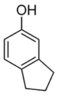
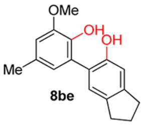
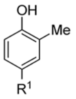
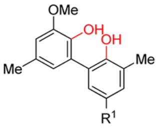
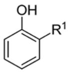
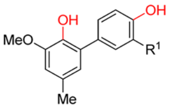
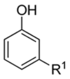
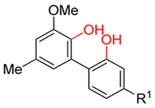
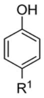
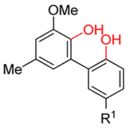
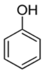
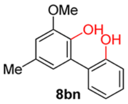


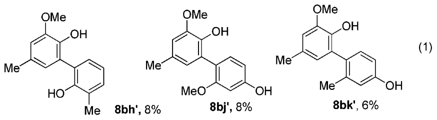
Table 2. Cross-Coupling of Two Different Phenols[a]

entry	phenol (3.0 equiv)	product **8**	yield (%)[b]
1	 **1e**	 **8be**	56
			
2	**1f**: R^1 = Me	**8bf**: R^1 = Me	57[c]
3	**1g**: R^1 = *t*-Bu	**8bg**: R^1 = *t*-Bu	43
			
4	**1h**: R^1 = Me	**8bh**: R^1 = Me	46[d]
5	**1i**: R^1 = OH	**8bi**: R^1 = OH	38
			
6	**1j**: R^1 = OMe	**8bj**: R^1 = OMe	26[d]
7	**1k**: R^1 = Me	**8bk**: R^1 = Me	49[d]
			61
8	**1l**: R^1 = Me	**8bl**: R^1 = Me	42
9	**1m**: R^1 = *t*-Bu	**8bm**: R^1 = *t*-Bu	38
10	 **1n**	 **8bn**	33

[a]All reactions were carried out using **1b** (1.0 equiv), **1e**−**n** (3.0 mmol), Bu$_4$N$^+$·HSO$_3^-$ (10 mol %), and K$_2$S$_2$O$_8$ (2.0 equiv) in CF$_3$COOH (0.5 mL) at rt for 18 h. [b]Isolated yield. [c]Homocoupling of **1f** was observed in 7% yield. [d]Other regioisomer was observed.

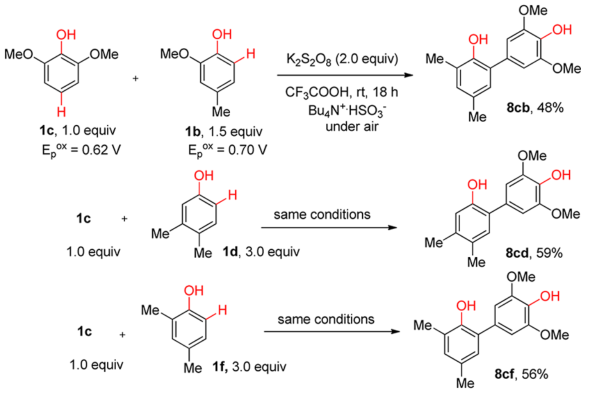
different phenols is difficult due to the similar oxidation potential values. Initially, 2-methoxy-4-methylphenol (**1b**) with 3,4-dimethylphenol (**1d**) were taken as model substrates for the reaction. The oxidation potential of **1b** is 0.7 V, and that of **1d** is 0.87 V. Thus, **1b** prefers to form a cationic radical intermediate in the presence of SO$_4^{-\bullet}$. The oxidation potential difference between **1b** and **1d** is very small; thus, homocoupling of these phenols would be expected more compared with the cross-coupling product. Treatment of **1b** (1.0 equiv) with **1d** (1.0 equiv) in the presence of Bu$_4$N$^+$·HSO$_3^-$ (10 mol %) in CF$_3$COOH at ambient temperature gave the cross-coupling product **8bd** in 35% yield along with the homocoupling product of **1b**, product **3bb**, in 8% yield. Surprisingly, the homocoupling product of **1d** was not observed, and the remaining starting material was recovered. To increase the yield of the cross-coupling product, the amount of **1d** was increased to 2.5 equiv to 3.0 equiv. Surprisingly, with 3.0 equiv, cross-coupling product **8bd** was observed in 53% yield, and no homocoupling product of **1b** was detected. In 2.5 equiv, product **8bd** was observed in 49% yield.

Next, the scope of the cross-coupling reaction was examined with various substituted phenols **1e**−**n** (Table 2). Trisubstituted phenols such as 2,3-dihydro-1*H*-inden-5-ol (**1e**), 2,4-dimethylphenol (**1f**), or 4-*tert*-butyl-2-methyl phenol (**1g**) reacted efficiently with **1b**, giving the corresponding biphenols **8be**−**bg** in 56%, 57%, and 43% yields (entries 1−3). In the reaction of **1b** with **1f**, the homocoupling product of **1f** was observed in 7% yield. Next, the cross-coupling reaction was examined with disubstituted phenols. Thus, treatment of 2-methyl phenol (**1h**) with **1b** gave a mixture of two regioisomeric products, 2,4′-biphenol **8bh** in 46% yield and 2,2′-biphenol **8bh′** in 8% yield (eq 1), respectively (entry 4). Interestingly, in the reaction of 2-hydroxy phenol (**1i**) with **1b**, only 2,4′-biphenol **8bi** was observed in 38% yield (entry 5). In the reaction of **1b** with **1i**, the *ortho* C−H bond of **1b** was coupled with the *para* C−H bond of **1i**. 1,3-Disubstituted phenols such as 3-methoxy (**1j**) or 3-methyl (**1k**) phenols reacted with **1b**, affording 2,2′-biphenols **8bj** and **8bk** in 26% and 49% yields, respectively (entries 6 and 7). In addition, the other regioisomers **8bj′** and **8bk′** were observed in 8% and 6% yields, respectively (eq 1). 1,4-Disubstituted phenols such as 4-methyl (**1l**) or 4-*tert*-butyl phenols (**1m**) were also involved in the reaction, giving the corresponding cross-coupling products **8bl** and **8bm** in 42% and 38% yields, respectively (entries 8 and 9). We have tried the cross-coupling of a less reactive unsubstituted phenol (**1n**) with **1b**. In the reaction, interestingly, 2,2′-biphenol (**8an**) was observed in 33% yield and the other regioisomeric 2,4′-biphenol was not observed (entry 10). In entry 5, *ortho*-*para* product **8bi** and, in entry 10, *ortho*-*ortho* product **8bn** were observed. The exact reason for the selectivity is not clear; it is possible that the *para* carbon electron density of **1i** and the *ortho* carbon electron density of **1n** could be more and favorable for the coupling reaction. Treatment of **1b** or **1d** or **1f** with 2,6-dimethoxy phenol (**1c**) under similar reaction conditions gave *ortho*-*para* cross-coupling products **8cb**−**8cf** in 48%, 59%, and 56% yields, respectively (Scheme 4). In most phenol cross-coupling reactions, only good to moderate yields were observed. It is important to note that, for the first time in the literature, this type of cross-coupling with various new phenols was demonstrated.



(1)

Scheme 4. ***ortho-para*** **Cross-Coupling of Phenols**



We have checked the oxidation potential value of several phenols and naphthols and compared them with the present reaction. This result clearly reveals that the oxidation potential of phenol up to 0.7 V satisfactorily reacts with $SO_4^{-\bullet}$, providing the corresponding cationic phenolic radical intermediate. If the oxidation potential is above 0.7 V, the substrate does not oxidize and participate in the reaction. For example, 4-*tert*-butyl-2-methyl phenol (**1g**) (E_p^{ox} = 0.81) or 2-naphthol (**2a**) (E_p^{ox} = 0.81) did not react with 3,4-dimethylphenol (**1d**) (E_p^{ox} = 0.87). In these reactions, not even the homocoupling product was observed. However, **1a** (E_p^{ox} = 0.66 V), **1b** (E_p^{ox} = 0.70 V), and **1c** (E_p^{ox} = 0.62 V) were nicely involved in the reaction.

In conclusion, we have demonstrated an efficient synthesis of unsymmetrical biphenols via the oxidative cross-coupling of two different phenols in the presence of $K_2S_2O_8$ and $Bu_4N^+ \cdot HSO_3^-$ (10 mol %) in CF_3COOH at ambient conditions. 1:1 Cross-coupling of substituted phenols with naphthols and 2:1 cross-coupling of substituted phenols with naphthols were also described. In these reactions, the *ortho* C–H bond of two different phenols and the *ortho* and *para* C–H bond of phenols were coupled together. By using $Bu_4N^+ \cdot HSO_3^-$, the homocoupling of phenols or naphthols and also overoxidation of the desired cross-coupling products were controlled.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental procedure and characterization details. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01324.

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Notes

The authors declare no competing financial interest.

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