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Efficient Anodic and Direct Phenol-Arene C,C Cross-Coupling: The Benign Role of Water or Methanol

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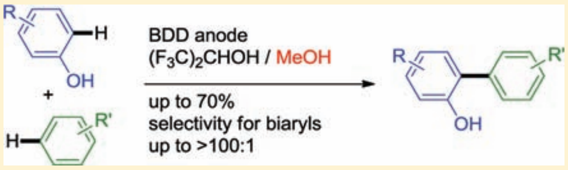
Ⓢ *Supporting Information*



ABSTRACT: C,C cross-coupling reactions for the synthesis of nonsymmetrical biaryls represent one of the most significant transformations in contemporary organic chemistry. A variety of useful synthetic methods have been developed in recent decades, since nonsymmetrical biaryls play an evident role in natural product synthesis, as ligand systems in homogeneous catalysis and materials science. Transformation of simple arenes by direct C,H activation belongs to the cutting-edge strategies for creating biaryls; in particular the 2-fold C,H activation is of significant interest. However, in most examples very costly noble metal catalysts, ligand systems, and significant amount of waste-producing oxidants are required. Electrochemical procedures are considered as inherently "green" methods, because only electrons are required and therefore, no reagent waste is produced. Here, we report a metal-free electrochemical method for cross-coupling between phenols and arenes using boron-doped diamond (BDD) anodes in fluorinated media. Our sustainable approach requires no leaving functionalities. Employing water or methanol as mediator represents the key improvement for achieving nonsymmetrical biaryls with superb selectivity and synthetic attractive yields.

INTRODUCTION

Nonsymmetrical biaryls play an important role in organic chemistry in natural product synthesis,[1] molecular catalysis,[2] and materials science.[3] C,C cross-coupling reactions represent highly versatile transformations for their synthesis.[4] Typically, such coupling reactions require leaving functionalities and complex catalysts often based on toxic transition metals, such as palladium.[5,6] Selective functionalization of arenes by direct C,H activation consequently belongs to the hot topics in contemporary organic synthesis. A variety of efficient protocols for this modern strategy were recently developed, allowing a catalytic approach to the active transition metal species in the presence of only one activated coupling partner.[7−10] C,H activation of one reaction partner can also be achieved by an organocatalytic pathway.[11] Considerably more atom economy results in the direct oxidative coupling of arenes.[12,13] The absence of leaving functionalities creates a cutting-edge concept. Unfortunately, most of the elaborated examples require costly catalyst systems and produce large quantities of reagent waste.

Electroorganic synthesis has turned out to be an attractive alternative in the preparation of organic compounds,[14] in particular when C,C coupling reactions are involved.[15,16] Since only electrons serve as reagent and carbon electrodes are reproduced sustainably, electrochemistry complies with the terms of "green chemistry".[17] Particular attention was given to the novel electrode material boron-doped diamond (BDD), which is easily available by chemical vapor deposition methods.[18] Due to their unique electrochemical properties,[19] BDD electrodes open up new synthetic pathways in electroorganic synthesis.[20] Because of the high overpotential for oxygen evolution in aqueous and alcoholic media, highly reactive hydroxyl or alkoxyl radicals[21] are directly and efficiently formed. These enormously aggressive spin centers are employed for wastewater treatment or constructive synthesis.[22] In general, the oxidative power usually leads to a complete electrochemical mineralization ending with CO_2. Fluorinated alcohols like 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) turned out to be the key for stabilizing these intermediates and minimizing mineralization of the substrates.[23,24] This particular solvent has experienced significant attention in organic synthesis since its use affected several improvements in organic synthesis.[25] Combining both materials, BDD and HFIP, we developed an anodic biphenol synthesis[26] to provide starting material for supercapacitor applications.[27] Although the yields were moderate to low, the first anodic phenol−arene cross-coupling was demonstrated.[28]

Here, we report the specific role of water or methanol being the key additive with respect to selectivity, scope, and minimizing overoxidation of the desired products.

EXPERIMENTAL DETAILS

An experimental setup is shown in Figure 2 in the Supporting Information. A solution of phenol component (0.005 mol), arene component (0.015 mol), and *N*-methyl-*N*,*N*,*N*-triethylammonium methylsulfate ($Et_3NMe \cdot O_3SOMe$, 0.68 g, 0.003 mol)

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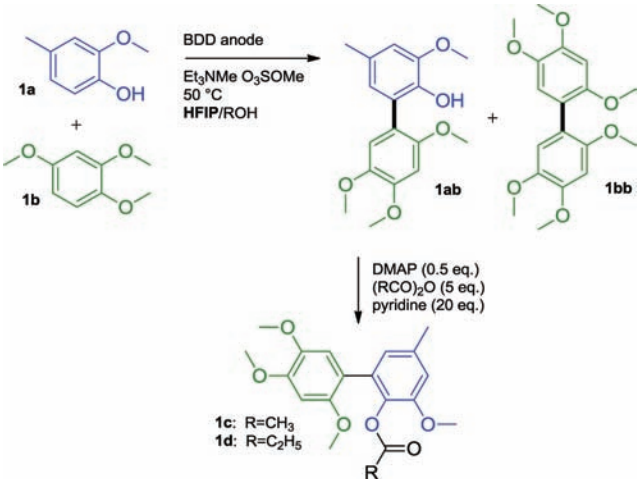
in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP, 27 mL) and methanol (6 mL) was transferred into an undivided electrolysis cell equipped with a BDD anode and a nickel cathode. At 50 °C, a constant current electrolysis with a current density of 2.8 mA/cm^2 was performed. After 965 C (2 F/mol of phenol), the electrolysis was stopped and the solvent mixture was recovered in vacuo (50 °C, 150 mbar). Nonconverted starting materials were recovered by short-path distillation (120−145 °C, 10^{-3} mbar), and purification of the crude products by column chromatography (SiO_2, ethyl acetate/cyclohexane) afforded the coupling products. They were washed with cold *n*-heptane (0 °C) and dried in high vacuum to afford the corresponding nonsymmetrical biaryls as almost colorless solids.

■ RESULTS

Since the mechanistic rationale for previous studies was not clear, the phenol−arene cross-coupling of phenol **1a** and arene **1b** on BDD anodes was carried out in highly pure HFIP. Surprisingly, the desired cross-coupling product **1ab** was only formed only as a minor product (Table 1, entry 1). Employment of recycled HFIP improved the situation tremendously. ^{1}H NMR data of such recycled HFIP indicated traces of water and methanol. Thus, a systematic variation with well-defined amounts of water or methanol in the electrolysis was carried out (Table 1, entries 2−12). For easier workup on a preparative scale, **1ab** was acylated. With water as the additive, best results were obtained in the presence of 9 vol % H_2O; the cross-coupling product **1ab** was formed with pronounced selectivity with a product ratio of 85:1 compared to homocoupling product **1bb**. The isolated yield for **1d** of 67% is synthetically attractive (Table 1, entry 4). For methanol as additive, the use of 18 vol % was superior and **1d** was isolated in 69% yield with a slightly improved selectivity up to 90:1 (Table 1, entry 10). It is noteworthy that this corresponds to almost the same molar amount of additive.

Table 1. Influence of Water and Methanol on the Anodic Phenol−Arene Cross-Coupling Reaction[a]



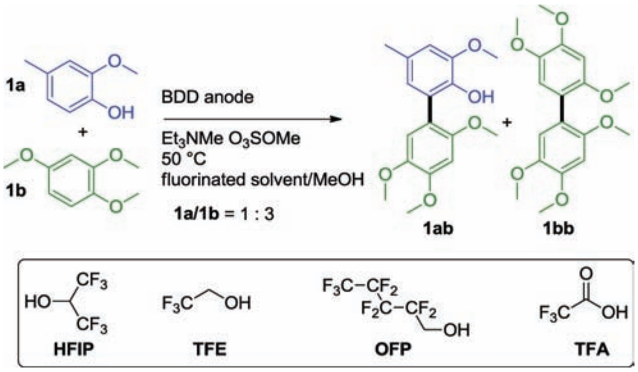
entry	ratio **1a**:**1b**	HFIP/ROH, mL/mL	yield,[b] %	ratio **1ab**: **1bb**[c]
1	1: 5	30/-	21 (**1d**)	1:3
2	1:5	32/1 (H_2O)	47 (**1d**)	1.5:1
3	1:5	31/2 (H_2O)	68 (**1d**)	8:1
4	1:5	30/3 (H_2O)	67 (**1d**)	85:1
5	1:5	28/5 (H_2O)	41 (**1ab**)	>100:1[d]
6	1:5	31/2 (MeOH)	56 (**1d**)	2:1
7	1:5	30/3 (MeOH)	66 (**1c**)	6:1
8	1:5	29/4 (MeOH)	64 (**1d**)	11:1
9	1:5	28/5 (MeOH)	66 (**1d**)	10:1
10	1:5	27/6 (MeOH)	69 (**1d**)	90:1
11	1:5	26/7 (MeOH)	55 (**1d**)	22:1
12	1:7	27/6 (MeOH)	58 (**1d**)	45:1
13	1:3	27/6 (MeOH)	69 (**1d**)	>100:1[d]
14	1:2	27/6 (MeOH)	55 (**1d**)	45:1

[a] Electrolysis conditions: 50 °C, constant current (j = 2.8 mA/cm^2), BDD anode, nickel cathode, undivided cell, 2 F/mol of phenol, 0.68 g Et_3NMe O_3SOMe. [b] Isolated yield of cross-coupling derivative. [c] Determined by GC. [d] Homocoupling product **1bb** was not detected.

In order to minimize the excess of arene component **1b**, the ratio of these substrates was studied. When 3 equiv of **1b** was subjected to electrolysis, the mixed biaryl **1d** was the only detectable dehydrodimer, which was obtained in almost 70% isolated yield (Table 1, entry 13). The use of these conditions also leads to decreased oligomer formation due to overoxidation.

The superior properties of HFIP on the anodic phenol−arene cross-coupling reaction is underscored by the comparison of other common fluorinated solvents like 1,1,1-trifluoroethanol (TFE), 2,2,3,3,4,4,5,5-octafluoropentanol (OFP), and trifluoroacetic acid (TFA, Table 2). The latter is known for its ability to stabilize radical cations.[23,24] Although TFE and OFP provided the cross-coupling product **1ab** with remarkable selectivity, the yields dropped dramatically (Table 2, entries 2 and 3). In the case of TFA, an inferior yield for **1ab** with no selectivity was observed.

Table 2. Solvent Effects in the Anodic Phenol−Arene Cross-Coupling Reaction[a]



entry	fluorinated solvent	yield, %	CE,[b] %	selectivity **1ab**:**1bb**
1	HFIP	69 (**1ab**)	69	>100:1[c]
2	TFE	33 (**1ab**)	33	85:1
3	OFP	23 (**1ab**)	23	>100:1[c]
4	TFA	49 (**1d**)	49	1:1

[a] Electrolysis conditions: 50 °C, BDD anode, constant current (j = 2.8 mA/cm^2), undivided cell, 2 F/mol of phenol, ratio phenol/arene = 1:3, 0.68 g of Et_3NMe O_3SOMe, 27 mL of fluorinated solvent, 6 mL of MeOH. [b] Current efficiency. [c] **1bb** was not detected by GC.

The properties of the fluorinated electrolyte, such as HFIP, turned out to be more essential than the nature of the electrode material. Usually, the electrode material represents one of the most important parameters in electrochemistry, since different reaction courses are often determined. Interestingly, the investigated reaction of phenol **1a** and arene **1b** gave congruent results when performed on different standard electrode materials like platinum, graphite, or glassy carbon (Table 3). However, BDD is the superior electrode material and provides by far the best results.

Table 3. Influence of Anode Material on the Phenol–Arene Cross-Coupling Reaction[a]

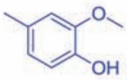
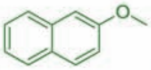
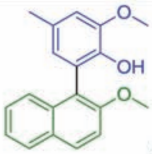
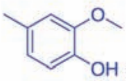
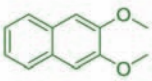
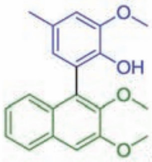
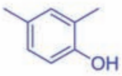
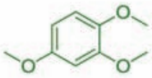
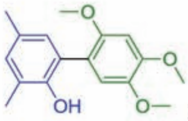
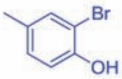
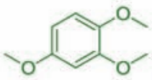
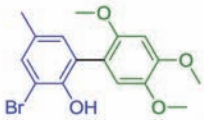
entry	anode material	yield,[b] %	CE, %	ratio **1ab**:**1bb**[c]
1	BDD	69	69	>100:1[d]
2	graphite	58	58	50:1
3	glassy carbon	59	59	100:1
4	platinum	57	57	>100:1[d]

[a] Electrolysis conditions: 50 °C, constant current (j = 2.8 mA/cm^2), nickel cathode, undivided cell, 2 F/mol of phenol, 0.68 g of $Et_3NMe\ O_3SOMe$. [b] Isolated yield of cross-coupling derivative. [c] Determined by GC. [d] Homocoupling product **1bb** was not detected.

To elucidate the scope of the electrolysis protocol, it was applied to the substrates shown in Table 4. Compared to the initial conditions of the electrosynthesis,[28] the mixed biaryls **6ab**, **7ab**, **13ab**, and **15ab** are formed with significantly improved selectivity with respect to the homocoupling products **1bb**, **6bb**, and **7bb**. For comparison, the previous data are given in parentheses. The isolated yields are the same or even better. Then the scope was broadened since several new substrates could be applied (Table 5). The transformation proceeded in most cases with high chemo- and regioselectivity. The competitive formation of homocoupling products **bb** was either prevented or strongly suppressed. In a few cases, regioisomers of mixed biaryls are found (**3ab**, **4ab**, **17ab**, and **18ab**). In these cases the coupling is not limited to the position ortho to the OH group (**11ab**) but also occurs in the position para to it (**12ab**). This is because the aromatic coupling partner should exhibit electron-releasing groups such as methoxy moieties. Therefore, coupling of such substrate combinations turned out to be favorable (**1ab**, **11ab**, and **12ab**). In addition, alkyl groups such as methyl, propyl (**9ab**), and ^{t}butyl (**10ab**) proved to be beneficial as well. Application of more electricity than 2 F/mol strongly promotes the formation of oligomers and a significant coloring of the electrolyte.[28]

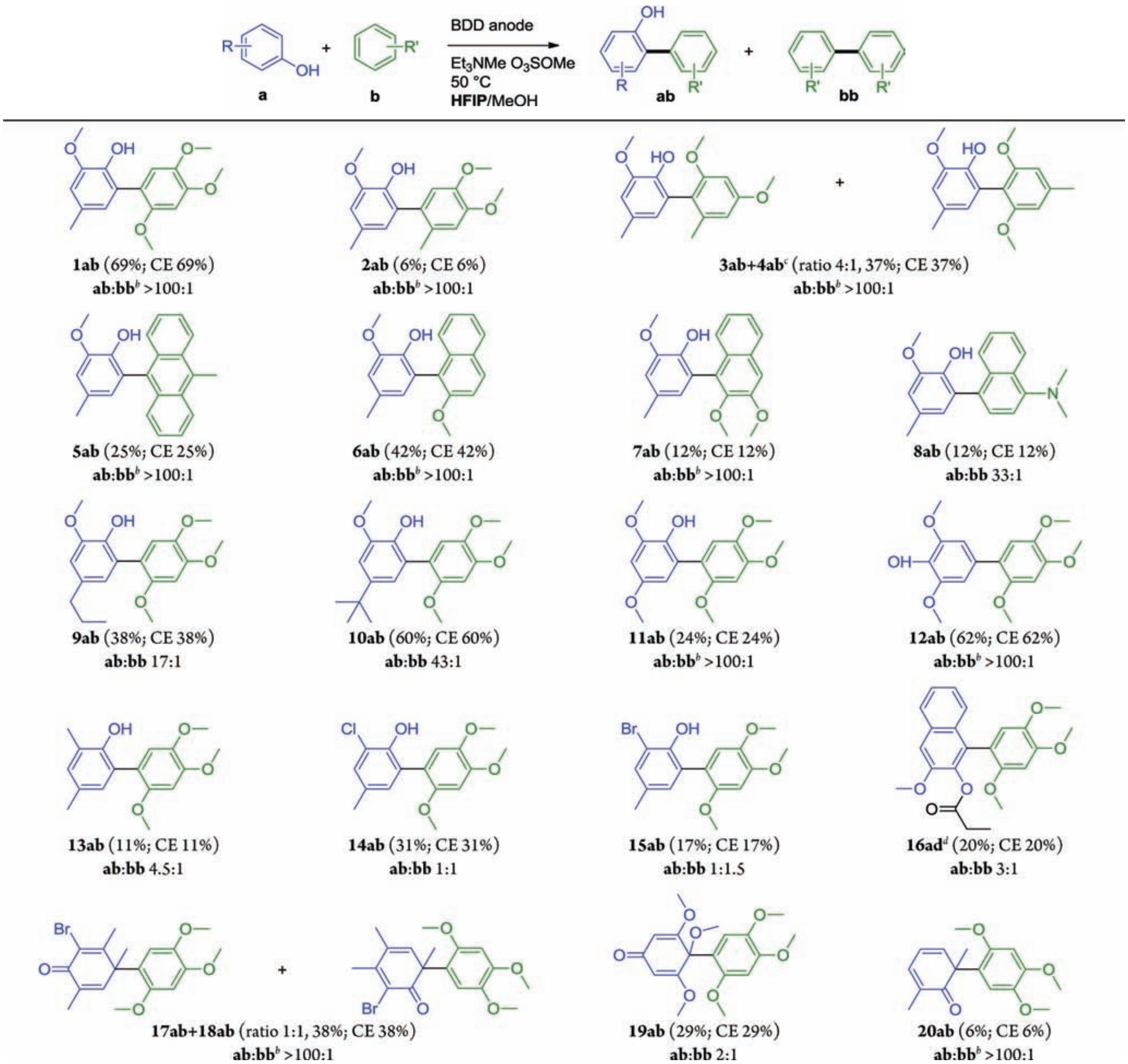
Polycyclic aromatic moieties that are prone to overoxidation, such as naphthalene (**6ab**, **7ab**, **8ab**, and **16d**) or anthracene (**5ab**) fragments, can also be incorporated. In contrast to other arene cross-coupling methods, wherein halogen[8−11] atoms or OH[13,29] groups were sacrificed, such moieties were conserved (**14ab**, **15ab**) since no leaving functionality is required. Remarkably, the scope of the anodic phenol–arene cross-coupling reaction, proceeding under acidic conditions due to the 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), was expanded to amino arenes (**8ab**). If phenolic components are subjected with activated positions being blocked, C,C-coupled aryl cyclohexadienones (**17ab**–**20ab**) are furnished. In fact, this demonstrates the formation of C(sp^2)–C(sp^3) cross-coupling products by anodic C,H activation. Their molecular structures were successfully confirmed by X-ray analysis of suitable single

Table 4. Application of Improved Protocol[a]

entry	phenol	arene	ab	yield (%)	CE[d] (%)	selectivity **ab** : **bb**
1	 **1a**	 **5b**	 **6ab**	42[a] (33)[b]	42 (33)	>100 : 1[c] (12 : 1)
2	 **1a**	 **6b**	 **7ab**	12[a] (11)[b]	12 (11)	>100 : 1[c] (2.5: 1)
3	 **6a**	 **1b**	 **13ab**	11[a] (15)[b]	11 (15)	4.5 : 1 (1 : 1)
4	 **8a**	 **1b**	 **15ab**	17[a] (5)[b]	17 (5)	1 : 1.5 (1 : 13)

[a] Electrolysis conditions: 50 °C, BDD anode, constant current (j = 2.8 mA/cm^2), undivided cell, 2 F/mol of phenol, ratio phenol/arene = 1:3, 0.68 g of $Et_3NMe\ O_3SOMe$, 27 mL of HFIP, 6 mL of MeOH. [b] Nonoptimized electrolysis conditions in pure HFIP; ratio phenol/arene = 1:10; values are taken from ref 3. [c] **bb** was not detected by GC. [d] Current efficiency.

Table 5. Anodic Cross-Coupling Reaction of Various Phenols with Different Arenes in the Presence of HFIP/MeOH[a]



1ab (69%; CE 69%)
ab:bb[b] >100:1

2ab (6%; CE 6%)
ab:bb[b] >100:1

3ab+4ab[c] (ratio 4:1, 37%; CE 37%)
ab:bb[b] >100:1

5ab (25%; CE 25%)
ab:bb[b] >100:1

6ab (42%; CE 42%)
ab:bb[b] >100:1

7ab (12%; CE 12%)
ab:bb[b] >100:1

8ab (12%; CE 12%)
ab:bb 33:1

9ab (38%; CE 38%)
ab:bb 17:1

10ab (60%; CE 60%)
ab:bb 43:1

11ab (24%; CE 24%)
ab:bb[b] >100:1

12ab (62%; CE 62%)
ab:bb[b] >100:1

13ab (11%; CE 11%)
ab:bb 4.5:1

14ab (31%; CE 31%)
ab:bb 1:1

15ab (17%; CE 17%)
ab:bb 1:1.5

16ad[d] (20%; CE 20%)
ab:bb 3:1

17ab+18ab (ratio 1:1, 38%; CE 38%)
ab:bb[b] >100:1

19ab (29%; CE 29%)
ab:bb 2:1

20ab (6%; CE 6%)
ab:bb[b] >100:1

[a] Electrolysis conditions: 50 °C, BDD anode, constant current ($j = 2.8\ mA/cm^2$), undivided cell, 2 F/mol of phenol, ratio phenol/arene = 1:3, 0.68 g of $Et_3NMe{\cdot}O_3SOMe$, 27 mL of HFIP, 6 mL of MeOH. CE, current efficiency. [b] **bb** was not detected by GC. [c] Isomers could not be separated by several techniques. [d] For a better separation, the crude product was derivatized.

crystals (see Figure 1 and Supporting Information). Thus, this electrolysis opens up access to an additional attractive substance family that plays an important role in natural product synthesis.[30]

DISCUSSION

Very recently, the first anodic phenol–arene cross-coupling reaction was reported. The key to avoid a statistical product distribution seemed to be the use of the fluorinated alcohol HFIP, which was expected to act as a typical mediator. Cyclovoltametric measurements of HFIP electrolyte on BDD electrodes revealed the largest electrochemical window for a protic system of approximately 5.0 V.

Since the oxidation potentials of the employed phenols and arenes were determined to about +1.0 V (vs Ag/AgCl), the anticipated role as mediator of HFIP was excluded. This was confirmed by the result displayed in Table 1, entry 1. The selectivity was reversed with far inferior yield. Obviously, by employment of water or methanol, a synthetically attractive access to cross-coupling product **1ab** was established. Almost identical oxidation potentials for **1a** and **1b**[28] exclude the control of selectivity by electrochemical potential. Thus, a chemoselectivity by stabilization of an oxyl intermediate is obvious. Consequently, water or methanol as mediator is proposed in the initial step of the transformation (Scheme 1). Anodic oxidation on BDD results in highly reactive hydroxyl or methoxyl radicals. In the presence of HFIP, the reactivity is decreased due to an enhanced lifetime[23,24] of these spin centers. The stabilizing mode of action might be based on oxyl–HFIP interactions. Because of its strong hydrogen-bond donor ability, HFIP forms in solid state a helically arranged supramolecular network.[31] In

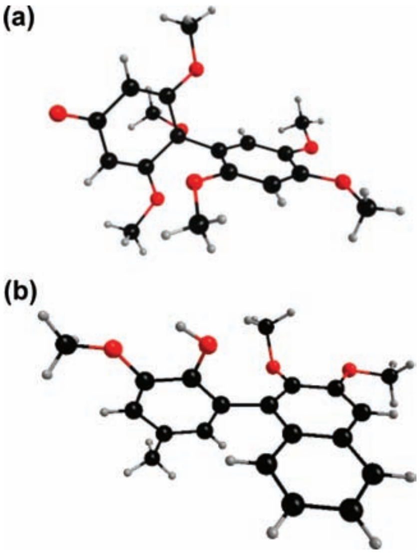


Figure 1. Molecular structures of (a) **19ab** and (b) **7ab** by X-ray analysis.

analogy, a HFIP cluster (**I**) via hydrogen bonding in liquid state is anticipated wherein oxyl intermediates are involved. This supramolecular caging provides the stabilizing effect. Subsequently, the encased spin centers attack the O−H group of the phenol chemoselectively and abstract the corresponding hydrogen atom, resulting in phenoxyl radicals **II**.

Such a reaction sequence is known as an electrochemical *Umpolung* reaction.[15,32] This indirect electrochemical formation of phenoxyl radicals cannot be directly achieved under potentiostatic control since phenol **A** and arene **B** exhibit very similar oxidation potentials.[28] Behaving as electrophiles, these radicals **II** are trapped by electron-rich arene **B**, which acts as nucleophile. The resulting tautomers **III** and **IV** undergo a second oxidation, accomplishing the mixed biaryls **AB** after rearomatization. Following this strategy, a statistical product mixture, which originally was expected according to the oxidation potentials of **A** and **B**, was successfully circumvented.

■ CONCLUSION

In summary, a novel and significantly improved electrochemical C,C cross-coupling was reported. Advantageously, various nonsymmetrical biaryls are available in a metal-free and highly selective transformation. Moreover, no additional leaving functionalities are required for this conversion, which allows the use of very simple starting materials. Since only electrons are used as oxidants, no reagent waste is produced, based on stoichiometric reagents. In addition to that, this new protocol represents the first example of supramolecular taming of oxyl species. This approach allows the synthetic use of highly reactive intermediates, which usually cause complete substrate degradation. Thus, this approach fulfills the requirements for "green chemistry". It represents a powerful and practicable method for direct arylation by C,H functionalization in present-day organic synthesis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional text, 13 figures, and two tables giving further results, preparation of substrates, electrochemical setup, and analytical data of products (PDF) and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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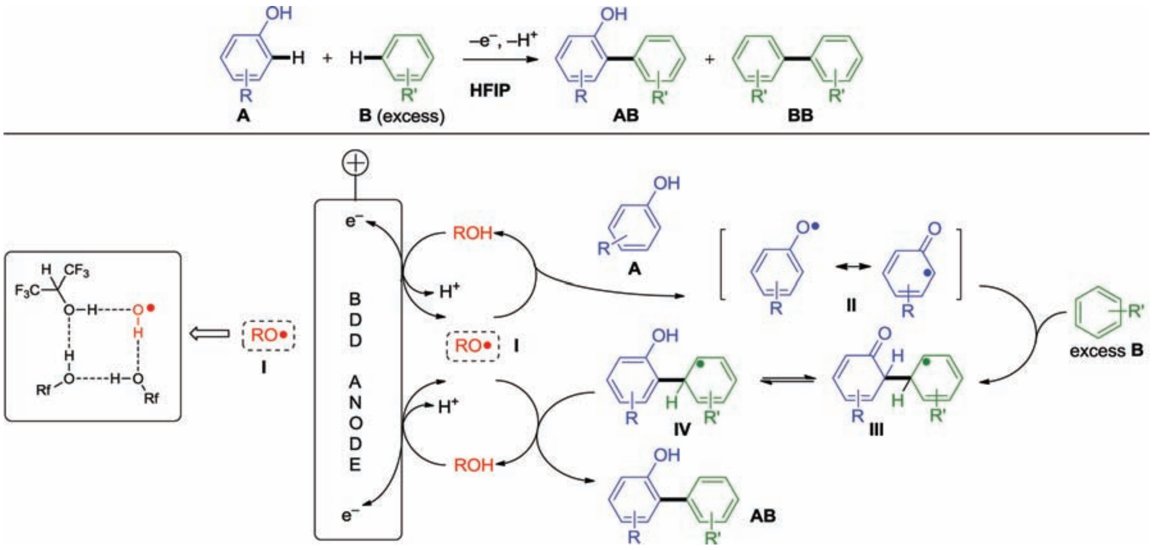
Scheme 1. Proposed Mechanism for Anodic Phenol−Arene C,C Cross-Coupling on Boron-Doped Diamond in the Presence of HFIP[a]



[a]Water or methanol is oxidized at the anode, forming highly reactive spin centers (**I**). Encased in a H-bonding solvent cluster of HFIP, their lifetime is dramatically enhanced. Chemoselective attack of phenol **A** furnishes phenoxyl radicals (**II**). Trapping them by excess arene **B** finally achieves cross-coupling product **AB** after a second oxidation step of intermediates **III** and **IV**.

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