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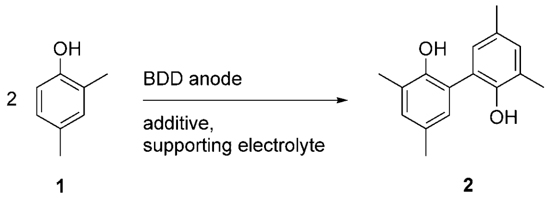
ortho-Selective Phenol-Coupling Reaction by Anodic Treatment on Boron-Doped Diamond Electrode Using Fluorinated Alcohols

Axel Kirste,[a] Martin Nieger,[b] Itamar M. Malkowsky,[c] Florian Stecker,[c]
Andreas Fischer,[c] and Siegfried R. Waldvogel*[a]

Biphenols are very common motifs in natural products[1] as well as in technical applications.[2] Recently, biphenols based on simple methyl-substituted phenols, for example, 2,4-dimethylphenol have drawn significant attention as components of highly potent ligand systems.[3–5] The sustainable synthesis of such biphenols is challenging despite their rather simple scaffolds. Methyl-substituted phenols are prone to side reactions and 2,4-dimethylphenol in particular results in predominantly polycyclic architectures upon anodic treatment.[6] To circumvent this challenge we developed a boron-based template strategy[7,8] that can be performed on larger scale.[9] A protocol for the conversion of neat phenol (**1**) on boron-doped diamond (BDD) electrodes was developed in our laboratory.[10] To prevent electrochemical incineration and to avoid by-products only partial conversion of about 30% is performed.[11] In such cases the electrochemical transformation is very clean. By using these particular conditions 2,4-dimethylphenol is converted to the biphenol (Scheme 1). Other tested phenols gave either no detectable products or ended up in decomposition, as for example, sesamol (**3**; see Scheme 4). BDD is a very appealing innovative electrode material that opens up novel synthetic pathways since alcoxyl or hydroxyl radicals are easily formed.[12] The free path length of oxyl radicals that are generated on BDD electrodes is in the nanometer range.[13] Especially, at high current densities overoxidation is a severe challenge when a specific product should be formed. Therefore, BDD electrodes are mostly used for disinfection purposes or waste water treatment.[14]



Scheme 1. Electrochemical oxidation of **1** on BDD anodes.

To overcome this limit and the restriction to the sole substrate **1**, studies in our group led to the application of mediators. Based on electrochemical incineration of waste water treatment, alcohols or water can be considered as mediators which react according to the proposed mechanism (Figure 1).[15] The synthetic utility of such mediators affords a high anodic stability and a stabilizing effect onto the oxygen spin center. We report a significantly enlarged scope and efficiency for the anodic coupling process of simple phenols on BDD electrodes by fluorinated mediators.

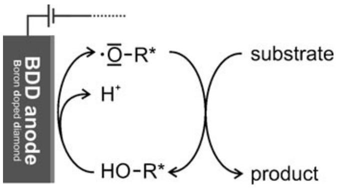


Figure 1. Common mechanism for the conversion on BDD anodes.

Methanol and other simple alcohols were applied in our initial studies on the anodic phenol coupling reaction of **1**.[10] This led to very moderate amounts of **2**; a significant amount of the starting material ended up in polymeric by-products. Moreover, a decent amount of methanol disappeared from the electrolysis cell despite cooling the electro-

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[a] A. Kirste, Prof. Dr. S. R. Waldvogel
Rheinische Friedrich-Wilhelms-Universität Bonn
Kekulé-Institut für Organische Chemie und Biochemie
Gerhard-Domagk-Strasse 1, 53121 Bonn (Germany)
Fax: (+49) 228-73-9608
E-mail: waldvogel@uni-bonn.de

[b] Dr. M. Nieger
Laboratory of Inorganic Chemistry, University of Helsinki
00014 Helsinki (Finland)

[c] Dr. I. M. Malkowsky, Dr. F. Stecker, Dr. A. Fischer
BASF SE, GCI/E-M311, 67056 Ludwigshafen (Germany)

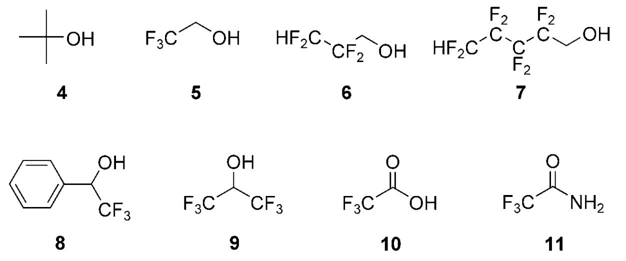
lyte. Most probably, oxidative degradation yielded more volatile carbonyl derivatives, which open up a non-desired reaction pathway. Consequently, more redox-stable mediators were investigated, leading to fluorinated alcohols. Previous studies ruled out simple acids for this transformation.[10] Typically, *tert*-butyl alcohol (**4**) is employed as the inert alcohol for oxidative transformations. When **4** was used in the conversion of **1** far less attractive yields were obtained (Table 1, entry 1).

Table 1. Anodic treatment of **1** using different mediators.[a]

Entry	Mediator	Supporting electrolyte	*T* [°C]	*j* [mA cm^{-2}]	**2** [%][b]	*CE* [%][c]
1	**4**	**12**	45	4.7	10	10
2	**5**	**12**	45	4.7	26	26
3	**6**	**12**	45	9.5	17	17
4	**7**	**12**	45	4.7	18	18
5	**9**	**12**	45	4.7	47	47
6	**8**	**12**	70	4.7	43	43
7	**10**	**14**	20	9.5	15	15
8	**11**	**14**	100	9.5	5	5

[a] Reaction conditions: 2.44 g **1**, 30 mL mediator, 0.68 g supporting electrolyte, BDD anode, nickel cathode, Q = 1.0 F per mol **1**. [b] Determined from crude product by GC using an internal standard. [c] Current efficiency.

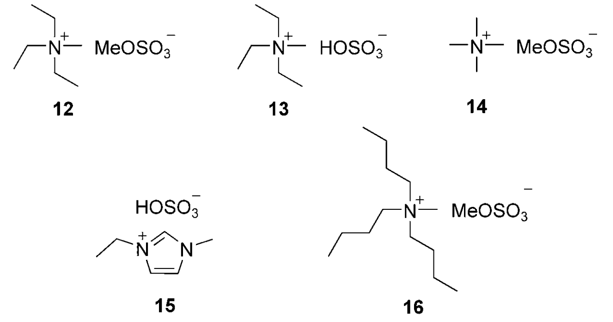
A variety of different fluorinated potential mediators were tested (Scheme 2). Primary alcohols with fluorous moieties in the β-position, such as 2,2,2-trifluoroethanol (**5**), 2,2,3,3-tetrafluoropraponol (**6**), or 2,2,3,3,4,4,5,5-octafluoropentanol (**7**), could be applied but gave only moderate yields of **2** (Table 1, entries 2–4). A doubling of the current density led to a decrease in the yield because of an enhanced concentration of oxyl spin centers close to the electrode that promotes overoxidations.



Scheme 2. Mediators for the oxidation of **1**.

Significantly better results were obtained when hexafluoroisopropanol (**9**) was employed as mediator. In a very clean conversion, 2,4-dimethylphenol (**1**) is transformed to **2** (Table 1, entry 5). Application of more electric current than 1 F per mole substrate did not improve the yield and quality of the product **2**. A trifluoromethyl group can be replaced by a phenyl moiety to stabilize the oxyl spin center. Thus, the fluorinated analogue of phenethyl alcohol **8** provided comparable results to **9**. Higher electrolysis temperatures were necessary to create sufficient ionic conductivity (Table 1, entry 6). Trifluoroacetic acid (**10**) and the carboxamide (**11**) gave under optimized conditions dramatically inferior results for those mediators, revealing that the Brønstedt behavior of **9** is not responsible for the good conversion of 2,4-dimethylphenol (Table 1, entries 7 and 8). The detailed molecular action of hexafluoroisopropanol (**9**) has still to be elucidated and explained, but the beneficial effect of this highly fluorinated alcohol is well documented in metal catalysis and oxidation reactions.[16]

Despite the acidic nature of the components, electrolysis of **1** in hexafluoroisopropanol (**9**) requires an unusually high applied voltage across the electrodes. By addition of a supporting electrolyte, the applied voltage can be tremendously decreased.[17] A collection of different tetraalkylammonium salts and an imidazolium derivative were employed as supporting electrolyte in the electrolysis of **1** in hexafluoroisopropanol (**9**) (Scheme 3); all gave similar results. Due to the longer alkyl chains, the cation of **16** modifies the lipophilicity of the anode by insertion in the Helmholtz double layer. This causes a slight decrease in yield (Table 2, entry 1). Neutral and more polar tetraalkylammonium salts gave the best results (Table 2, entries 2 and 3), whereas the acidic supporting electrolytes led to slightly inferior yields (Table 2, entries 4 and 5). Because of the reproducibility and practicability, the ionic liquid **12** was used for further studies.



Scheme 3. Tested supporting electrolytes in the anodic conversion of **1**.

The yields and the current efficiency were studied over the course of the electrolysis under optimized conditions for

Table 2. Anodic treatment of **1** with different supporting electrolytes.[a]

Entry	Supporting electrolyte	*T* [°C]	*j* [mA cm^{-2}]	**2** [%][b]	*CE* [%][c]
1	**16**	20	9.5	37	37
2	**12**	45	4.7	47	47
3	**15**	45	4.7	45	45
4	**14**	45	4.7	46	46
5	**13**	45	4.7	43	43

[a] Reaction conditions: 2.44 g **1**, 0.1 M supporting electrolyte in 30 mL HFIP, BDD anode, nickel cathode, Q = 1.0 F per mol **1**. [b] Determined from crude product by GC using an internal standard. [c] Current efficiency.

1 (Figure 2). The chemical yield reached a maximum (ca. 50%) when a current of 1 to 1.3 F was applied per mole **1**. The current efficiency decreases with increasing applied electric current, indicating that electrochemical decomposition might occur to some extent. Therefore, application of 1 F electric current per mole substrate represents a reasonable compromise between yield and current efficiency.

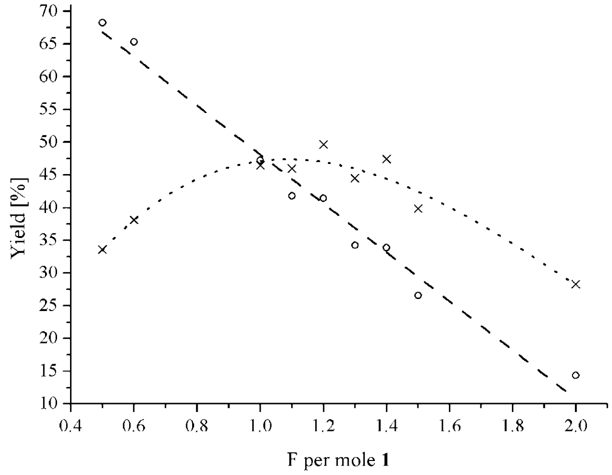
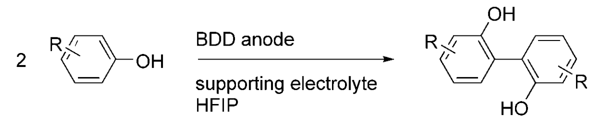


Figure 2. Progress of the conversion of **1** on BDD anode in respect to current efficiency; × Yield of **2**, ○ *CE*.



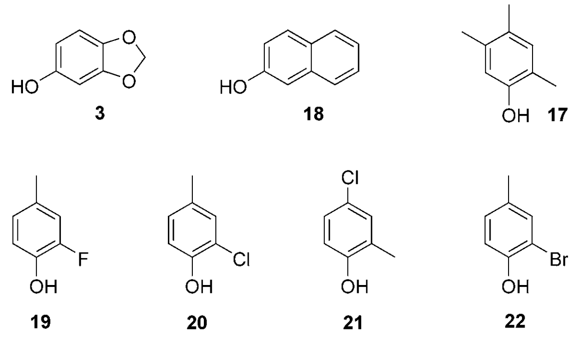
Scheme 5. General oxidation of substituted phenols on BDD anodes.

Table 3. Electrochemical synthesis of biphenols.[a]

Entry	Substrate	Supporting electrolyte	*j* [mA cm⁻]	Yield (Product) [%][b]	*CE* [%][c]
1	**17**[d]	**12**	4.7	22 (**23**)	22
2	**18**[e]	**15**	4.7	41 (**24**)	41
3	**3**[f]	**12**	2.8	74 (**25**)	74
4	**19**	**12**	4.7	13 (**26**)	13
5	**20**	**12**	4.7	30 (**27**)	30
6	**21**[g]	**12**	4.7	24 (**28**)	12
7	**22**	**12**	4.7	30 (**29**)	30

[a] Reaction conditions: 0.02 mol phenol, 0.1 M supporting electrolyte in 30 mL HFIP, BDD anode, nickel cathode, Q = 1.0 F per mol phenol. [b] Yield of isolated product. [c] Current efficiency. [d] 0.01 mol phenol. [e] 0.005 mol phenol. [f] 0.012 mol phenol. [g] 0.04 mol phenol, Q = 2.0 F per mol phenol.

To elucidate the scope of the elaborated protocol, a variety of differently substituted phenols were subjected to electrolysis (Scheme 4 and 5). The solubility of the phenolic substrate in the fluorous electrolyte is crucial for the conversion. Therefore, solid substrates (**3**, **17**, **18**) had to be electrolyzed at 45 °C and at lower concentrations (Table 3, entries 1–3). Sterically demanding phenol **17** could be converted in moderate yield (Table 3, entry 1), since alternative reaction pathways promote complete incineration.[18] Better results were obtained with 2-naphthol (**18**),which provided binol (**24**) as the sole product (Table 3, entry 2). Most remarkably, sesamol (**3**) was anodically coupled in very good yield (Table 3, entry 3). Without hexafluoroisopropanol (**9**), anodic conversion of **3** results in only tarry residues on the BDD electrodes. Furthermore, halogenated phenolic substrates were selectively coupled to the corresponding biphenol (Table 3, entries 4–7). The low yield is reflected by the electron-deficient nature of the substituents. Despite the low yield for the fluorinated biphenol **26**, it represents the first direct example for the oxidative coupling of such a fluorinated substrate. The chloro and bromo congeners, **20** and **22**, respectively, yielded significantly better results, which can be attributed to the less deactivating effect of these substituents. On switching the halogen moiety to position 4, only the 4-chlorocresol (**21**) is converted to the biphenol (Table 3, entry 6). The corresponding 4-fluorocresol is not converted on BDD electrodes and marks the limit of this method. Since free radicals are involved in this anodic transformation iodo phenols are not compatible with the protocol.



Scheme 4. Converted phenols on BDD anode using **8**.

A suitable single crystal of **26** was obtained and the structure elucidated by X-ray analysis (Figure 3). The molecular structure of the fluorinated biphenol is specific. Despite the rather large dipole moment created by the fluoro and hydroxyl moieties, the polar groups of both aryls point to the same side. This spatial arrangement is favored in the solid-state and dominated by the intramolecular hydrogen bond between the phenolic oxygen atoms. Since such a seven-

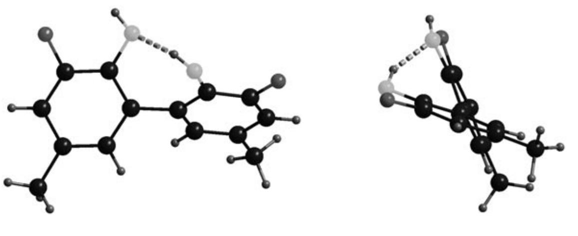


Figure 3. Molecular structure in the solid state of 3,3′-difluoro-5,5′-dimethyl-2,2′-biphenol (**26**); left: top view with indicated hydrogen bonding; right: side view along biaryl axis.

membered ring system is not comfortable in plane, the molecule is twisted around the biaryl axis about 46.5°. The monomers form stacks along the *a* axis, which are linked by intermolecular hydrogen bonds. Along the *b* axis, these stacks are also linked by intermolecular hydrogen bonding.

In conclusion, hexafluoroisopropanol (**9**) with supporting electrolytes creates a powerful electrolyte system for the anodic coupling reaction of phenols. The scope of BDD electrodes in organic synthesis has thereby been significantly enlarged. The protocol is easy to perform and practical. When only 1 F electric current is applied, a clean reaction mixture is obtained consisting of products, starting material, and electrolyte. The protocol is particularly useful for very electron-rich phenols as well as halogenated substrates. For the latter biphenols, the access is fast and provides interesting scaffolds for ligand design and catalyst development. This together with other BDD-generated oxyl spin centers will be studied with fluorous electrolytes and reported in due course.

Experimental Section

General remarks: All reagents were used in analytical grades. Solvents were desiccated if necessary by standard methods. BBD (CONDIAS GmbH, Itzehoe, Germany, 10 μm BDD on Si). Column chromatography was performed on silica gel (particle size 63–200 mm, Merck, Darmstadt, Germany) by using mixtures of cyclohexane with ethyl acetate as eluents. For thin-layer chromatography silica gel 60 sheets on glass (F_{254}, Merck, Darmstadt, Germany) were used. Melting points were determined with a Melting Point Apparatus SMP3 (Stuart Scientific, Watford Herts, UK) and were uncorrected. Microanalysis was performed with a Vario EL III (Elementar-Analysensysteme, Hanau, Germany). ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C by using a Bruker ARX 300, AMX 300, or AMX 400 instrument (Analytische Messtechnik, Karlsruhe, Germany). Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS as internal standard or to traces of $CHCl_3$, [D$_6$]acetone, or CD_3OD in the corresponding deuterated solvents. ^{19}F NMR spectra were recorded at 25 °C by using a Bruker AC200 spectrometer with external calibration relative to CCl_3F. Mass spectra were obtained by using a MAT8200, MAT95XL (Finnigan, Bremen, Germany), or MS50 (Kratos, Manchester, England) apparatus employing EI and by using a Quattro LC (Waters-Micromass), or Micro TOF (Bruker) apparatus employing ESI and HRMS (negative mode). Gas chromatography was performed with a Shimadzu GC-2010 (Shimadzu, Japan) using a HP 5 column (Agilent Technologies, USA; length: 30 m, inner diameter: 0.25 mm, film: 0.25 μm, carrier gas: hydrogen). GC calibration was accomplished with analytically pure biphenols (**2**, **23**–**29**) and pentadecane as internal standard. Single-crystal X-ray diffraction study was carried out on a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Direct methods (SHELXS-97)[19] were used for structure solution, and refinement was carried out using SHELXL-97 (full-matrix least-squares on F^2).[19] H atoms were localized by difference electron density determination and refined by using a riding model (H(O) free). The absolute structure could not be determined reliably by refinement of Flack's *x*-parameter ($x = 0.0(10)$).[20] Graphics DIAMOND 3.0d (Crystal Impact GbR, Bonn, Germany).

General procedure for the anodic oxidation of substituted phenols: A solution of the corresponding phenol (0.005–0.02 mol) and supporting electrolyte (0.003 mol) in hexafluoroisopropanol (**9**, 30 mL) was transferred into a non-divided electrolysis cell equipped with a BDD anode and a nickel cathode. At 50 °C, a galvanostatic electrolysis with a current density of 2.8–9.5 mA cm^{-2} was performed. After complete reaction (ca. 1 F per mol phenol), the electrolysis was stopped and hexafluorisopropanol was recovered in vacuo. The remaining crude product was fractioned by water (50 mL) and *tert*-butyl methyl ether (TBME, 50 mL), the layers were separated and the aqueous layer was extracted with TBME (2 × 30 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo to give a brown oil. Purification by column chromatography and drying under vacuum yielded the corresponding biphenol as a colorless solid.

3,3′,5,5′-Tetramethyl-2,2′-biphenol (2): 2,4-Dimethylphenol (**1**) (2.44 g, 0.02 mol), **12** (0.68 g, 3 mmol), purified by column chromatography (cyclohexane/ethyl acetate 98:2; $R_f = 0.10$), yielded **2** (1.15 g, 4.7 mmol, 47 %); m.p. 134–135 °C (cyclohexane, value in ref. [7]; m.p. 13 5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.29$ (s, 12 H; CH_3), 5.09 (s, 2 H; OH), 6.88 (s, 2 H, 4-H), 7.01 ppm (s, 2 H; 6-H).

3,3′,5,5′,6,6′-Hexamethyl-2,2′-biphenol (23): 2,4,5-Trimethylphenol (**17**) (1.36 g, 0.01 mol), **12** (0.68 g, 3 mmol), purified by column chromatography (cyclohexane/ethyl acetate 95:5; $R_f = 0.21$), yielded **23** (0.31 g, 1.2 mmol, 22 %); m.p. 171 °C (*n*-heptane, value in ref. [7]; m.p. 169 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.86$ (s, 6 H; CH_3), 2.24 (s, 12 H; CH_3), 4.03 (s, 2 H; OH), 7.01 ppm (s, 2 H; 4-H).

1,1′-Binaphthyl-2,2′-ol (24): 2-Naphthol (**18**) (0.72 g, 0.005 mol), **12** (0.68 g, 3 mmol), purified by vacuum sublimation (105 °C, 39 mbar), yielded **24** (0,30 g, 1.0 mmol, 41 %); analytical verification was accomplished by comparing to the commercial available substance.

5,5′-Dihydroxy[6,6′]bi(benzo[1,3]dioxolyl) (25): Sesamol (**3**) (1.66 g, 0.012 mol), **13** (0.62 g, 3 mmol), the crude product washed with cold methanol (2 × 10 mL), yielded **24** (1.23 g, 4.5 mmol, 74 %); m.p. 202–203 °C (cyclohexane, value in ref. [7]; m.p. 201 °C; ^{1}H NMR (400 MHz, CD_3OD): $\delta = 5.88$ (s, 4 H; 2-H), 6.46 (s, 2 H; 4-H), 6.65 (s, 2 H, 7-H), 8.87 ppm (brs, 2 H; OH).

3,3′-Difluoro-5,5′-dimethyl-2,2′-biphenol (26): 2-Fluoro-4-methylphenol (**19**) (2.52 g, 0.02 mol), **12** (0.68 g, 3 mmol), purified by column chromatography (cyclohexane/ethyl acetate 9:1; $R_f = 0.14$), yielded **25** (0.32 g, 1.3 mmol, 13 %); m.p. 152–153 °C (cyclohexane); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.32$ (s, 6 H; CH_3), 5.73 (s, 2 H; OH), 6.88 (s, 2 H, 6-H), 6.96 ppm (d, ^3J(H,F) = 11.1 Hz, 2 H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.66$ (CH_3), 116.07, 126.06, 126.73, 131.02, 138.48, 150.63 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -138.94$ ppm; HRMS: calcd for $C_{14}H_{12}F_2O_2$: 250.0805; found: 250.0805; elemental analysis calcd (%) for $C_{14}H_{12}F_2O_2$ (250.08): C 67.20, H 4.83; found: C 66.93, H 4.85.

Crystal data of 26: Colorless crystals, $C_{14}H_{12}F_2O_2$, $M = 250.24$, crystal size 0.30 × 0.12 × 0.06 mm, orthorhombic, $P2_12_12_1$ (no. 19): $a = 7.110(1)$, $b = 7.693(1)$, $c = 20.923(2)$ Å, $V = 1144.4(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.452$ Mg m^{-3}, $F(000) = 520$, $\mu = 0.118$ mm^{-1}, 11 199 reflections ($2\theta_{max} = 50°$), 2004 unique [$R_{int} = 0.0482$], 171 parameters, 2 restraints, $R1$ ($I > 2\sigma(I)$) = 0.0405, $wR2$ (all data) = 0.0830, $S = 1.073$, largest difference peak and hole 0.165 and −0.200 e Å^{-3}. CCDC-710803 (**26**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

3,3′-Dichloro-5,5′-dimethyl-2,2′-biphenol (27): 2-Chloro-4-methylphenol (**20**) (2.52 g, 0.02 mol), **12** (0.68 g, 3 mmol), purified by column chromatography (cyclohexane/ethyl acetate 9:1; $R_f = 0.20$), yielded **26** (0.84 g, 3.0 mmol, 30 %); m.p. 127–128 °C (cyclohexane); ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta = 2.28$ (s, 6 H; CH_3), 2.95 (s, 2 H; OH), 6.97 (s, 2 H, 6-H), 7.20 ppm (s, 2 H; 4-H); ^{13}C NMR (100 MHz, [D$_6$]acetone): $\delta = 21.21$ (CH_3), 122.74, 128.77, 131.32, 131.95, 132.56, 149.72 ppm; HRMS: calcd for $C_{14}H_{12}Cl_2O_2$: 282.0214; found: 282.0216; elemental analysis calcd (%) for $C_{14}H_{12}Cl_2O_2 \cdot 0.5H_2O$ (292.16): C 57.55, H 4.48; found: C 57.76, H 4.33.

5,5′-Dichloro-3,3′-dimethyl-2,2′-biphenol (28): 4-Chloro-2-methylphenol (**21**) (5.66 g, 0.04 mol), **12** (0.68 g, 3 mmol), 2.0 F per mole phenol, purified by column chromatography (cyclohexane/ethyl acetate 95:5; $R_f = 0.14$), yielded **27** (1.37 g, 4.8 mmol, 24 %); m.p. 160 °C (cyclohexane); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.29$ (s, 6 H; CH_3), 5.18 (s, 2 H; OH), 7.04 (s, 2 H, 6-H), 7.19 ppm (s, 2 H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 16.16$ (CH_3), 123.02, 125.67, 127.60, 127.95, 131.32, 149.89 ppm; HRMS: calcd for $C_{14}H_{12}Cl_2O_2$: 282.0214; found: 282.0214; elemental analysis calcd (%) for $C_{14}H_{12}Cl_2O_2$ (282.02): C 59.39, H 4.27; found: C 59.62, H 4.39.

3,3′-Dibromo-5,5′-dimethyl-2,2′-biphenol (29): 2-Bromo-4-methylphenol (**22**) (3.75 g, 0.02 mol), **12** (0.68 g, 3 mmol), purified by column chromatography (cyclohexane/ethyl acetate 95:5; $R_f = 0.10$), yielded **21** (1.12 g, 3.0 mmol, 30 %); m.p. 136–138 °C (cyclohexane); ^1H NMR (300 MHz, $[D_6]$acetone): $\delta = 2.27$ (s, 6H; CH_3), 3.05 (s, 2H; OH), 6.99 (s, 2H, 6-H), 7.35 ppm (s, 2H; 4-H); ^{13}C NMR (75 MHz, $[D_6]$acetone): $\delta = 21.07$ (CH_3), 112.67, 128.69, 132.57, 133.32, 134.53, 150.63 ppm; HRMS: calcd for $C_{14}H_{12}Br_2O_2$: 369.9210; found: 369.9204; elemental analysis calcd (%) for $C_{14}H_{12}Br_2O_2 \cdot 1\,H_2O$ (390.07): C 43.11, H 3.62; found: C 43.46, H 3.28.

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Keywords: C–C coupling · electrochemistry · fluorine · oxidation · phenols

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