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Reagent- and Metal-Free Anodic C–C Cross-Coupling of Aniline Derivatives

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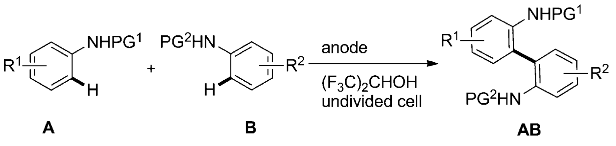
Abstract: *The dehydrogenative cross-coupling of aniline derivatives to 2,2′-diaminobiaryls is reported. The oxidation is carried out electrochemically, which avoids the use of metals and reagents. A large variety of biphenyldiamines were thus prepared. The best results were obtained when glassy carbon was used as the anode material. The electrosynthetic reaction is easily performed in an undivided cell at slightly elevated temperature. In addition, common amine protecting groups based on carboxylic acids were employed that can be selectively removed under mild conditions after the cross-coupling, which provides quick and efficient access to important building blocks featuring free amine moieties.*

Nonsymmetric biaryls are very important structural motifs in natural products and in catalysis.[1] In particular, 1,1′-binaphthyl-2,2′-diamine (BINAM) is a promising ligand system and has already been studied in detail. Asymmetric Michael additions,[2] indole N arylation reactions,[3] as well as hydrogenations of ketones and olefins[4] have been realized using BINAM or derivatives thereof as a ligand in transition-metal catalysis. Moreover, new ligands for contrast agents in magnetic resonance imaging also feature 2,2′-diaminobiaryls as structural motifs.[5] However, access to these substrates by classical synthetic means is limited because anilines easily undergo oxidative polymerization to polyaniline, which is also known as aniline black.[6] Symmetric 2,2′-diaminobiaryls are accessible by copper-catalyzed Ullmann reactions, for example.[7] Direct oxidative cross-couplings with stoichiometric amounts of inorganic reagents such as Cu^{II} salts have only been reported for naphthylamines and provided the desired compounds in rather poor yields.[8] Sigmatropic rearrangements of diaryl hydrazines in the presence of catalytic amounts of an acid provide symmetric 2,2′-diaminobiaryls in good yields while the synthesis of nonsymmetric derivatives is still challenging.[9] Furthermore, several steps are required for synthesizing those starting materials.[9,10] Applying these strategies requires much effort and complicated reaction conditions. Such approaches often lead to complex reaction mixtures and low yields of the desired products. In contrast, oxidative coupling reactions by direct C–H activation are of great interest as a sustainable method.[11,12] Recently, an oxidative conversion of diaryl amines in the presence of a highly fluorinated iron phthalocyanine catalyst was reported that enabled C–C as well as N–N bond formation.[13]

In particular, electrochemical techniques are remarkably advanced in terms of avoiding the formation of waste products because no leaving groups or oxidants are required.[14] The generation of reactive intermediates by electrochemical means is a highly attractive pathway in terms of atom economy and cost efficiency.[15] In our group, anodic phenol–phenol[12,16,17] and phenol–arene cross-couplings have been developed.[18] The best results for the direct oxidative cross-coupling of aryl compounds were attained in stabilizing media such as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), which is frequently used in reactions that involve hypervalent iodine.[19,20] This unique solvent can form strong hydrogen bonds,[21] which results in a significantly different solvation of the individual coupling partners, and the oxidation potential is thus decoupled from its nucleophilicity.[22]

Herein, we present a selective method for the synthesis of nonsymmetric 2,2′-diaminobiaryls by anodic cross-coupling (Scheme 1). The electrochemical synthesis of nonsymmetric 2,2′-diaminobiaryls is very easy to conduct as only a simple two-electrode arrangement in an undivided beaker-type cell is required. In addition, the electrolysis is performed in a constant-current mode, which immensely simplifies the equipment needed. To efficiently find suitable coupling partners, several screening experiments were performed.[23] Usually, component **A** has a lower oxidation potential than aniline **B**, and is therefore preferentially oxidized at the anode. To statistically favor the cross-coupling over the homocoupling product, the aniline with the higher oxidation potential, that



Scheme 1. Direct anodic C–C cross-coupling of protected aniline derivatives. PG = protecting group.

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is, **B**, was applied in slight excess. It was essential to stabilize the reactive radical intermediates during the electrolysis to avoid undesired oligomerization or even mineralization. The favorable effects of HFIP and protic additives such as methanol or water on yield and selectivity were recently described.[12,18,22] Unfortunately, simple aniline derivatives are prone to overoxidation because of their electron-rich nature and the resulting low oxidation potentials. Polymerization is a serious problem in anodic reactions of anilines.[24] Organocatalytic reactions currently use nitrogen protecting groups to prevent the formation of undesired side products.[19] N-Mesyl-protected anilines were converted in good yields in a hypervalent iodine mediated coupling but the desired aminobiphenyls were only obtained after waste-intensive and time-consuming deprotection.[19] Recently, Muñiz and co-workers used a hypervalent iodine reagent in a diamination reaction generating tosyl-protected diamines.[25] However, in our work, various easily removable protecting groups were used for the aniline derivatives (Figure 1).

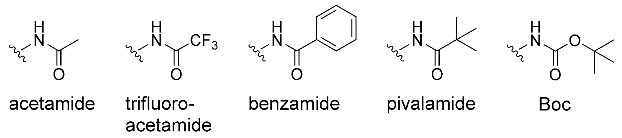


Figure 1. Common and easily removable carbonyl-based protecting groups for anilines.

Amides and carbamates proved to be suitable groups for N protection and exhibited sufficient stability during the electrolysis. In addition, cyclic voltammetry (CV) studies indicated that the protecting groups have a significant influence on the oxidation potential (which correlates with the pK_a values of the anilides)[26] as well as on the potential interaction between substrate and solvent by hydrogen bonding (Figure 2).

Electron-rich anilines, such as 3,4-dimethoxyaniline, have low oxidation potentials (832 mV in pure HFIP; $\mathrm{p}K_{\mathrm{a(anilinium)}} = 4.6$ in DMSO)[26] and are therefore prone to anodic overoxidation. The oxidation potential can be increased to 1.39 V or even 1.57 V, respectively, through the installation of an acetyl or trifluoroacetyl group ($\mathrm{p}K_{\mathrm{a(acetanilide)}} = 18.8$, $\mathrm{p}K_{\mathrm{a(trifluoroacetanilide)}} = 12.6$ in DMSO).[26] Owing to the ability of the amide functional group to participate in hydrogen bonding as a donor as well as an acceptor, the protected anilines experience strong solvation by HFIP. CV investigations of differently protected 3,4-dimethoxyanilines revealed a clear shift of the oxidation potentials to lower values with an increasing concentration of methanol in HFIP. Methanol acts as a weak base when added to the electrolyte and thus weakens the solvation of the amides. The oxidation potentials of anilines can be adjusted to some extent by using different protecting groups (Figure 2). This benefits the anodic cross-coupling of anilides as there seems to be an ideal difference for the oxidation potentials of the coupling partners.[22] In general, CV helps to indicate the correct stoichiometry for the anodic cross-coupling as component **A** should exhibit a lower oxidation potential than component **B** and thus be preferably oxidized at the anode to initiate the cross-coupling sequence (Scheme 1).

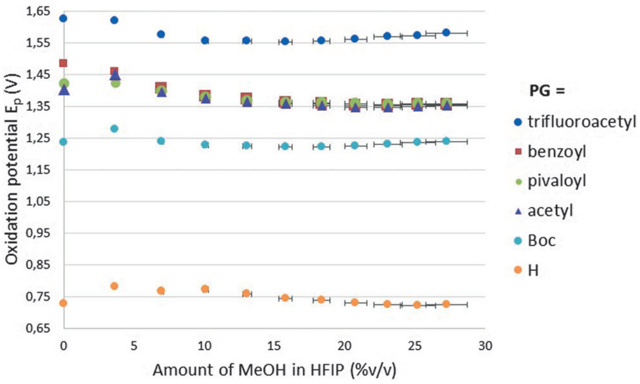
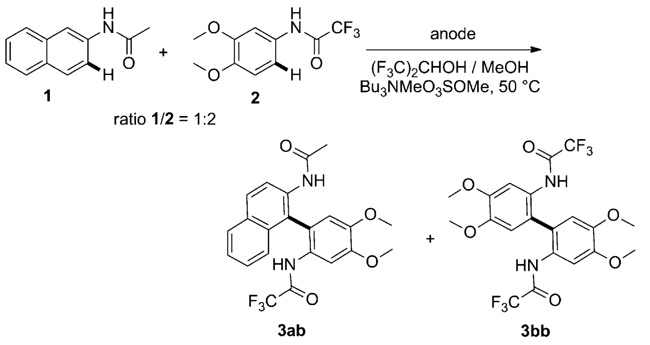


Figure 2. Changes in the oxidation potentials of various protected 3,4-dimethoxyanilines with increasing MeOH concentration in HFIP. WE: glassy carbon electrode tip, 2 mm diameter; CE: glassy carbon rod; RE: Ag/AgCl in saturated LiCl/EtOH; solvent: HFIP with 0–27 % v/v MeOH; supporting electrolyte: 0.09 M Bu_3NMeO_3SOMe.

Usually, the electrode material has a crucial influence on electrochemical conversions as different reaction pathways and adsorption characteristics often result. However, in this system, the electrolyte system was found to be the key. Interestingly, the investigated reaction of anilides **1** and **2** (Scheme 2) gave consistent results when performed at different electrode materials, such as platinum, boron-doped diamond, graphite, or glassy carbon (Table 1).



Scheme 2. The influence of methanol and different electrode materials on the anodic cross-coupling of anilines. 2-Acetamidonaphthalene (**1**) was used as component **A**, compound **2** as component **B**.

Considering the selectivity in HFIP, all electrode materials gave similar results but the best yields were achieved on graphite and platinum. The addition of methanol to the solvent led to significantly improved selectivity, and the cross-coupling product was exclusively obtained on glassy carbon (Table 1, entry 2). In addition, significantly less oligomerization was observed on glassy carbon than on the other electrode materials. This is important for two reasons: First, it simplifies the work-up tremendously, and second, non-converted starting materials can be easily recovered. Furthermore, glassy carbon shows excellent chemical stability even after long-term use whereas graphite undergoes signifi-

Table 1: Influence of the electrode material on the aniline–aniline cross-coupling.[a]

Entry[b]	Electrode material	Additive	Yield [%][c]	**3 ab/3 bb**[c]
1	glassy carbon	–	51	6:1
2	glassy carbon	MeOH	20	>100:1[d]
3	boron-doped diamond	–	48	3:1
4	boron-doped diamond	MeOH	34	34:1
5	graphite	–	60[e]	6:1
6	graphite	MeOH	28[e]	28:1
7	platinum	–	60[e]	7:1
8	platinum	MeOH	29[e]	29:1

[a] 2-Acetamidonaphthalene **1** was used as component **A**, compound **2** as component **B**. [b] Electrolysis conditions: 50 °C, constant current ($j = 5.2$ mA cm^{-2}), undivided screening cell, $Q = 2$ F (aniline **A**), solvent: HFIP or HFIP/MeOH (18% v/v), supporting electrolyte: 0.09 M Bu_3NMeO_3SOMe, **A**/**B** = 1:2. [c] Determined by GC analysis. [d] The homocoupling product **3 bb** was not detected. [e] Increased formation of oligomeric side products.

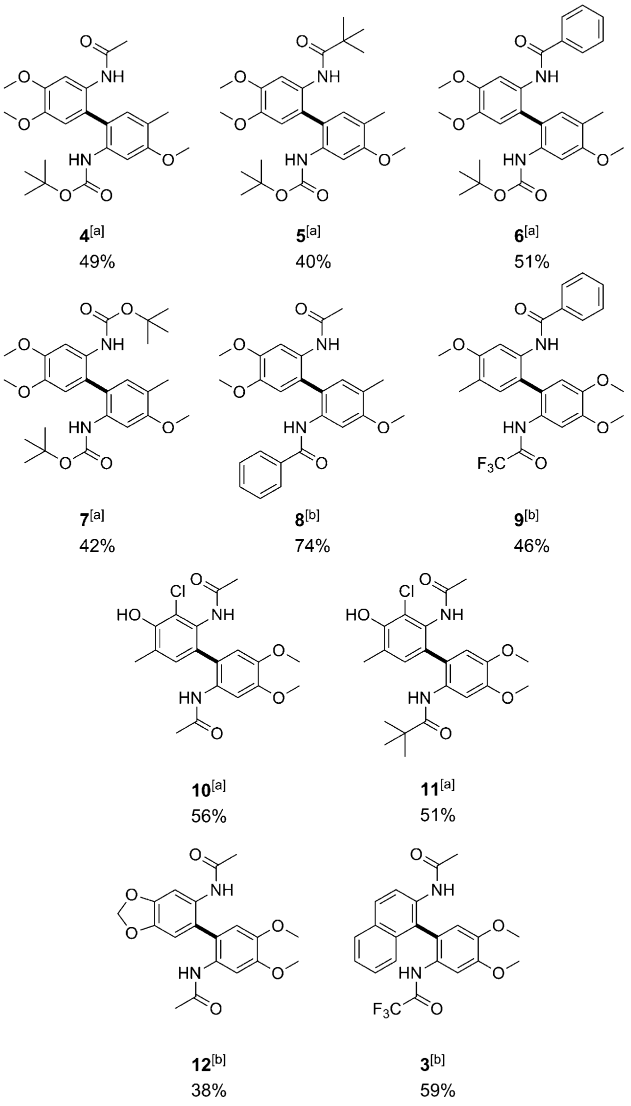


Figure 3. Scope of protected nonsymmetric 2,2′-diaminobiaryls. Yields of isolated products are given. [a] Electrolysis conditions: 50 °C, constant current ($j = 5.2$ mA cm^{-2}), glassy carbon anode, glassy carbon cathode, undivided beaker-type cell, $Q = 2$ F (aniline **A**), solvent: HFIP/MeOH (18% v/v), supporting electrolyte: 0.09 M Bu_3NMeO_3SOMe, **A**/**B** = 1:2. [b] Electrolysis conditions as in [a], solvent: HFIP.

cant erosion. When taking into account the selectivity, electrochemical stability, and cost, glassy carbon is the electrode material of choice.

During this aniline cross-coupling, the new C–C bond is formed exclusively *ortho* to the amine moiety, and 2,2′-diaminobiaryl derivatives are obtained. Aniline derivatives with electron-releasing moieties such as methoxy groups in the *para* position to the newly formed C–C bond seem to particularly favor the coupling reaction. The scope of protected, nonsymmetric 2,2′-diaminobiaryl derivatives obtained by electrolysis is shown in Figure 3. It should be noted that none of the protecting groups was removed during electrolysis.

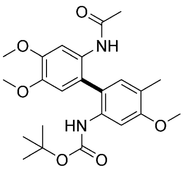
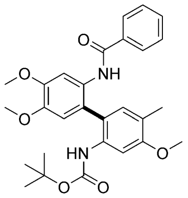
Oligomerization is still the predominant side reaction decreasing the yields of the cross-coupling products. Nevertheless, N-Boc-protected 3-methoxy-4-methylaniline provided the mixed 2,2′-diaminobiaryl derivatives **4**, **5**, **6**, and **7** in good yields of 40 to 51%. The highest yield of 74% was achieved for the coupling of *N*-(3,4-dimethoxyphenyl)acetamide with *N*-(3-methoxy-4-methylphenyl)benzamide (**8**). In the cross-coupling of *N*-(3,4-dimethoxyphenyl)acetamide with a benzodioxole derivative, the yield was slightly inferior (38%, **12**). 2-Acetamidonaphthalene (**1**) was also cross-coupled with trifluoroacetamide **2** to provide **3** in 59% yield. Accordingly, anilines with electron-releasing or alkyl moieties in the 3- and 4-position turned out to be suitable coupling partners. The coupling of anilines with chloro substituents was also possible (56%, **10** and 51%, **11**). The amount of unconverted component **A** was about 2–24%. Increasing the applied charge could, in some cases, improve the yields.

During the initial optimization of the electrolysis conditions, the influence of temperature on the yields of the cross-coupling products was evaluated (Table 2). These studies revealed that an electrolysis temperature of 30 °C seems to be advantageous (entries 3 and 6).

To enable the later use of such protected 2,2′-diaminobiaryls in organocatalysts, ligands, or functionalized materials,[27] it is vital to efficiently deprotect the amino moiety. The applied protecting groups are based on common carboxylic acids and are thus easily removed by standard procedures.[28] By employing orthogonal protecting groups, the two amino groups can be independently deprotected, which allows for further chemo- and regioselective transformations (Table 3). These partially protected cross-coupling products had previously not been described and can be considered as congeners to the recently reported partially protected biphenol derivatives.[16]

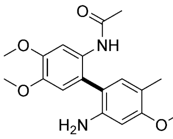
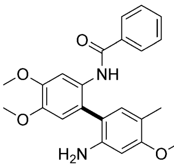
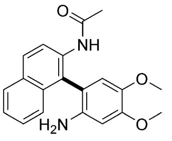
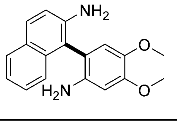
A Boc group could be selectively removed with water without the need for additional acid,[29] whereas the acetyl and benzoyl groups in substrates **4** and **6**, respectively, remained unaffected (Table 3, entries 1 and 2). A trifluoroacetyl group could be selectively removed with potassium carbonate in the presence of an acetamide (entry 3). Both protecting groups in **3**, an acetyl and a trifluoroacetyl moiety, could be simulta-

Table 2: Temperature dependence of the anodic cross-coupling of aniline derivatives.[a]

Entry	Product	T [°C]	Yield [%][b]
1	 **4**[c]	50	49
2		40	46
3		*30*	*59*
4		20	49
5	 **6**[c]	50	51
6		*30*	*59*
7		20	54

[a] Electrolysis conditions: 20–50 °C, constant current ($j = 5.2\ \mathrm{mA\,cm^{-2}}$), glassy carbon anode, glassy carbon cathode, undivided beaker-type cell, $Q = 2$ F (aniline **A**), HFIP/MeOH (18% v/v), supporting electrolyte: 0.09 M Bu_3NMeO_3SOMe, **A**/**B** = 1:2. [b] Yields of isolated products. [c] Acetyl- and benzoyl-protected 3,4-dimethoxyaniline was used as component **A** for the synthesis of **4** and **6**, respectively.

Table 3: Partial and complete deprotection of differently protected 2,2′-diaminobiaryl derivatives.

Entry	Substrate	Removed PG	Product	Yield [%]
1	**4**	Boc[a]	 **4'**	98[d]
2	**6**	Boc[a]	 **6'**	99
3	**3**	trifluoroacetyl[b]	 **3'**	99
4	**3**	acetyl and trifluoroacetyl[c]	 **3''**	98

[a] Reaction conditions: Substrate (0.20 mmol), 100 °C, H_2O/MeOH (2:1 v/v), 24 h. [b] Substrate (1.50 mmol), 20 °C, MeOH/H_2O (2:1 v/v), K_2CO_3 (10 equiv), 4 days. [c] Substrate (0.7 mmol), 120 °C, hydrazine hydrate (80% in H_2O), 4 days. [d] Migration of the remaining acetyl moiety can occur after work-up (see the Supporting Information).

neously cleaved with hydrazine hydrate (entry 4). These facile and efficient methods for deprotecting the cross-coupling products highlight once more the effectiveness of our method in generating precursors for relevant building blocks.

In conclusion, an innovative and facile method to obtain 2,2′-diaminobiaryls by electrochemical C–C cross-coupling has been established. The scope includes differently substituted and protected aniline derivatives. The HFIP solvent effect is essential for the high selectivity while no leaving groups are required. This highly fluorinated alcohol allows the oxidation potential to be decoupled from the nucleophilicity of the coupling partners. The protecting groups are based on common carboxylic acids and therefore easily removable. When a set of different protecting groups is applied, they can be selectively removed, and thus liberate the respective amino groups, with different nucleophiles. The use of electric current to drive this conversion leads to an exceptionally sustainable metal- and reagent-free reaction sequence. Moreover, the electrolysis protocol is very easy to conduct because an undivided cell and a two-electrode arrangement are employed.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: biaryls · C–H activation · cross-coupling · electrochemistry · protecting groups

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Communications

Electrosynthesis

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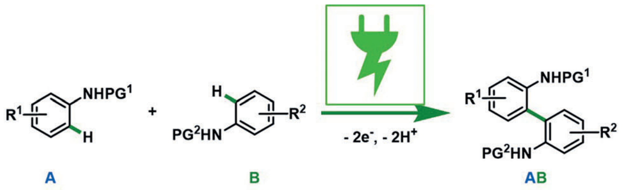
S. R. Waldvogel* ________ ■■■■–■■■■

Reagent- and Metal-Free Anodic C–C Cross-Coupling of Aniline Derivatives



- up to 74% yield
- highly selective
- selective and mild removal of protecting groups

Cross-couplings under electrochemical conditions selectively provide protected 2,2′-diaminobiaryl derivatives. For clean conversion, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and glassy carbon should be used as the electrolyte and anode material, respectively. Easily removable protecting groups enable the stepwise and selective liberation of the amine functional groups.