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Organocatalysis

Anodic Oxidation and Organocatalysis: Direct Regio- and Stereoselective Access to *meta*-Substituted Anilines by α-Arylation of Aldehydes**

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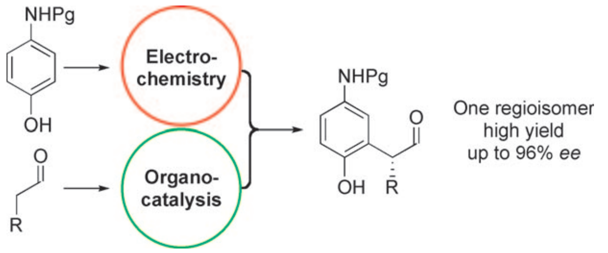
During the last decades chemists have witnessed the development of thousands of new catalytic reactions driven by need and interest from both industrial and academic settings. Asymmetric catalysis has been one of the focus areas as a result of the increased need for optically active compounds in life science. Many catalytic asymmetric processes are based on metal complexes and rely on activation modes such as Lewis acid catalysis, atom-transfer catalysis, as well as σ- and π-bond insertions. Recently, organocatalysis[1] has emerged as a powerful source of enantioselective transformations and has led to the development of α-,[2] β-,[3] γ-,[4] and SOMO-activations,[5] as well as cascade, domino, and tandem reactions.[6]

Aromatic compounds are ubiquitous as medicines and functionalized materials, and are often formed by electrophilic substitution reactions.[7] Friedel–Crafts alkylations, in particular of highly nucleophilic aromatic compounds such as phenols and anilines, are difficult owing to the regioselectivity and the competitive nucleophilic heteroatoms, which lead to undesired alkylation products. The application of copper catalysis to direct the substitution *meta* to an amido group through dearomatizing oxy-cupration[8] provides a recent example of where selectivity has been circumvented. Additionally, it has been shown by Gaunt and co-workers that *para*-substituted phenols can be converted into highly functionalized chiral molecules through oxidative dearomatization and intramolecular enamine catalysis.[9] Breaking aromaticity changes the reactivity from nucleophilic to electrophilic,[10] and thus makes it susceptible to addition of systems such as enamines.

Electrochemical reactions often follow environmentally friendly protocols because electrons, as reagents, are inherently pollution free. The ability of electrochemistry to reverse the polarity of a functional group—by selective removal or addition of electrons—makes it thus possible to induce reactions of otherwise nonreactive molecules.[11] Successful combinations of electrochemistry and metal catalysis or mediated electron-transfer processes have been reported in numerous cases,[11] although the risk of having electrode fouling is always present. For example, palladium metal deposition on the cathode has been observed from the reduction of palladium(II), which is generated at the anode, in an undivided cell.[12] Organocatalysts are stable organic molecules and many stereoselective organocatalytic reactions are performed under conditions not possible for metal-catalyzed reactions. We thus anticipated that it might be possible to combine organocatalysis with anodic molecular transformations.[11b,13]

Herein, the combination of electrochemistry and asymmetric organocatalysis is presented. This new concept is demonstrated by a direct intermolecular α-arylation[14] of aldehydes using electron-rich aromatic compounds providing *meta*-alkylated anilines—a transformation not possible by Friedel–Crafts reactions of anilines (Scheme 1). We show the potential of the electrochemical/organocatalytic method and demonstrate its applications by the synthesis of optically active dihydrobenzofurans.[15]



Scheme 1. Regio- and stereoselective anodic oxidation/organocatalytic α-arylation of aldehydes and formal *meta*-addition to anilines. Pg = protecting group.

The regio- and stereoselective anodic oxidation/organocatalytic formation of *meta*-alkylated anilines **5** is anticipated to take place by two combined sequences (Figure 1). The first sequence involves the electrochemical activation of the aromatic compound **1** leading to the formation of an umpoled electrophilic intermediate **7**. In the second sequence, an electron-rich enamine **A**, generated by condensation of aldehyde **2** and organocatalyst **3**, undergoes a nucleophilic addition to electrophile **7** to give intermediate **B**. Hydrolysis of **B**, followed by a series of proton transfers regenerates the catalyst and forms the product **5**.

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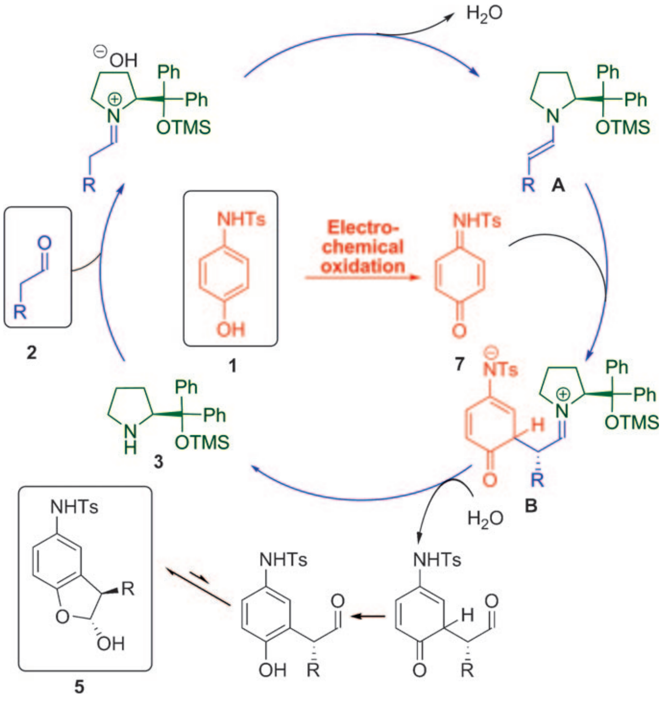
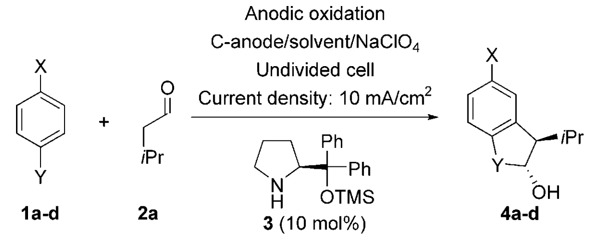


Figure 1. Proposed mechanism for the electrochemical/organocatalytic sequence. TMS = trimethylsilyl, Ts = 4-toluenesulfonyl.

Table 1: Representative screening examples of the anodic oxidation/organocatalytic α-arylation of some aromatic compounds.[a]



1a: X = OH, Y = OH
1b: X = NHBoc, Y = OH
1c: X = NHTs, Y = OH
1d: X = NHTs, Y = NHTs

Entry	Solvent	Elec	Yield of **4** [%][b]	*ee* [%][c]
1	CH_3CN/H_2O(1:1)	**1a**	30	n.d.
2	CH_3CN/H_2O(1:1)	**1b**	< 30 of **4a**	n.d.
3	CH_3CN/H_2O(1:1)	**1c**	75	96
4	CH_3CN/H_2O(1:1)	**1d**	n.r.	–
5	CH_3CN[d]	**1c**	< 20	n.d.
6	CH_3CN/H_2O(1:1)[e]	**1c**	77	94
7	CH_3CN/H_2O(1:1)[f]	**1c**	n.r.	–
8	CH_3CN/H_2O(1:1)[g]	**1c**	n.r.	–

[a] Performed with **2a** (2.80 mmol), **1a–d** (0.56 mmol), and **3** (0.056 mmol) in a 0.1 M $NaClO_4$ solvent mixture (2 mL) (carbon rod anode: applied current 25 mA and current density 10 mA cm^{-2}) at room temperature. [b] Isolated by flash chromatography. [c] Determined by HPLC on a chiral stationary phase of the corresponding alcohols **6**. [d] 5 equivalents of H_2O relative to **1c**. [e] Performed at 0.375 M of **1c**. [f] No current applied. [g] Performed with (*S*)-2-[bis(3,5-bistrifluoromethylphenyl)trimethylsilanyloxymethyl]pyrrolidine as catalyst. Boc = *tert*-butoxycarbonyl, n.d. = not determined, n.r. = no reaction, Elec = electrophile.

We started the investigations by treating 3-methylbutanal (**2a**) with 1,4-hydroquinone (**1a**) in the presence of (*S*)-2-[diphenyl(trimethylsilyloxy)methyl]pyrrolidine (**3**) as the catalyst in a simple electrochemical setup consisting of an undivided cell equipped with carbon-rod and platinum-net electrodes. The reaction was performed using galvanostatic electrolysis (applied current: 25 mA, current density: 10 mA cm^{-2}) with $NaClO_4$ as the supporting electrolyte in a CH_3CN/H_2O mixture for 24 hours, and gave **4a** in less than 30% yield (Table 1, entry 1).

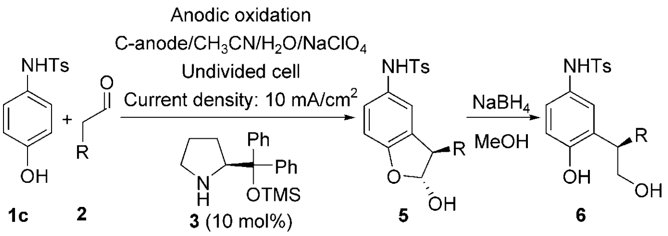
We then tried the reaction with *N*-Boc-4-aminophenol **1b**, but the oxidized intermediate was not stable to hydrolysis and **4a** was obtained with less than 30% conversion (Table 1, entry 2). To our delight, by changing the N-protecting group to tosyl (**1c**) gave **4c** after 5 hours in 75% yield and excellent enantioselectivity 96% *ee* (Table 1, entry 3). The product was isolated as the diastereomerically pure dihydrobenzofuran. The enantiomeric excess was determined after reduction to the corresponding alcohol. To assess the influence of H_2O we performed the reaction in CH_3CN with only 5 equivalents of H_2O relative to **1c** (Table 1, entry 5). These conditions lowered the conversion dramatically, thus indicating that H_2O is important for the reaction—most likely in the proton transfers leading to product **5** shown in the mechanism (Figure 1). Increasing the concentration did not affect the yield, although the enantioselectivity dropped to 94% *ee* (Table 1, entry 6). The reaction was also tested without the current applied to confirm that $NaClO_4$ was not acting as an oxidation reagent, and no reaction was observed (Table 1, entry 7). When (*S*)-2-[bis(3,5-bistrifluoromethylphenyl)trimethylsilanyloxymethyl]-pyrrolidine was applied as the catalyst no reaction was observed (Table 1, entry 8).

Pleasingly, the reaction worked under such simple reaction conditions. Undivided cells are highly desirable owing to the simplicity of the setup, but can be difficult to use if specific electrode potentials are needed to avoid uncontrolled oxidation and reduction taking place in the same medium. However, the present results show that the organocatalyst and the catalytic cycle are robust under these conditions, which might allow new developments by combining electrochemistry and organocatalysis.

After having found the optimal reaction conditions the generality of the reaction was explored for *N*-tosyl-4-aminophenol **1c** with a series of aldehydes (Table 2). The alkylation reaction gave exclusively **5**, which is the *meta*-product relative to the amino substituent. The β-branched aldehyde **2a** gave the product in good yield (75%) and an excellent enantioselectivity of 96% *ee* (Table 2, entry 1). Linear aliphatic substrates **2b,c** and the nonconjugated unsaturated system **2d** were also well tolerated and gave the products in 71–83% yield and 89–94% *ee* (Table 2, entrie 2–4). Hydrocinnamaldehyde **2e** gave **5e** in good yield and moderate selectivity (87%, 81% *ee*; Table 2, entry 5). The reaction also worked well with 5 mol% of catalyst **3** and on a gram scale (Table 2, entries 6 and 7).

We have further investigated the anodic oxidation/organocatalytic sequence to obtain information about the electrochemistry involved. The current yields for the results obtained

Table 2: Scope of the enantioselective anodic oxidation/organocatalytic reaction.[a]

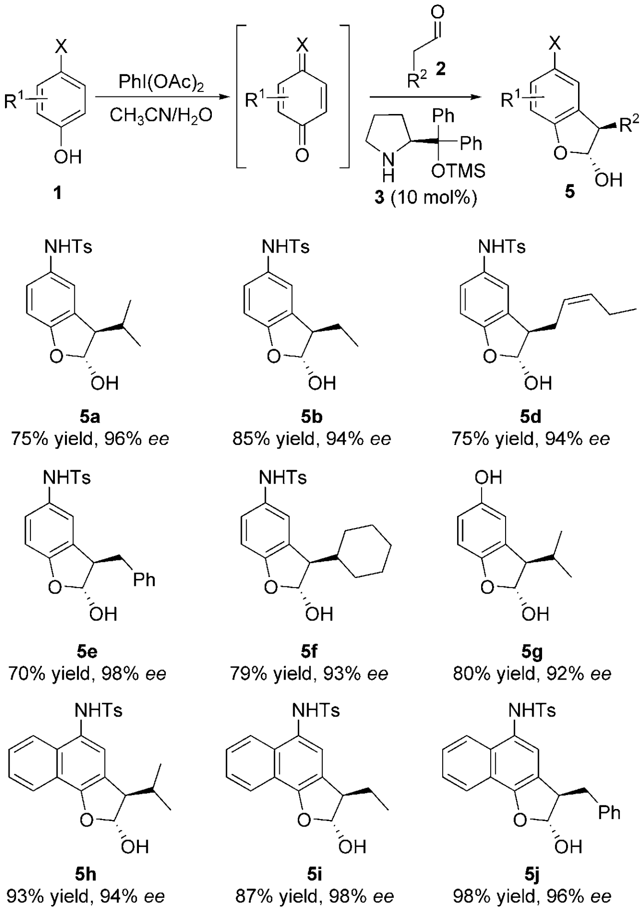


Entry	R	Yield of **5** [%][b]	Yield of **6** [%][b]	*ee* [%][c]
1	*i*Pr (**2a**)	75	75	96
2	Et (**2b**)	83	65	94
3	hexyl (**2c**)	83	72	92
4	cis-2-pentenyl (**2d**)	71	69	89
5	Bn (**2e**)	87	61	81
6[d]	*i*Pr (**2a**)	69	70	92
7[e]	*i*Pr (**2a**)	–	54	94

[a] Performed with **2** (2.80 mmol), **1c** (0.56 mmol), and **3** (0.056 mmol) in CH_3CN/H_2O (1:1) at constant current (25 mA) and current density (10 $mA\,cm^{-2}$) at room temperature for 5 h. [b] Isolated by flash chromatography. [c] Determined by HPLC on a chiral stationary phase of the corresponding alcohols **6** (see the Supporting Information). [d] Performed with 5 mol% catalyst. [e] Performed on a 4 mmol scale relative to **1c** and the yield given is the overall yield of **6a**. Bn = benzyl.

in Table 2 are approximately 15%. However, these results were obtained under a standard protocol of 5 hours of galvanostatic electrolysis. The reaction of hydrocinnamaldehyde **2e** with *N*-tosyl-4-aminophenol **1c** that led to **5e** was studied as a function of electrolysis time to determine the current yield. This showed that the 2 $F\,mol^{-1}$ process after 1 hour (corresponding to 100% current yield for complete conversion), 2 hours, and 5 hours, resulted in 80%, 83% and 88% conversion, respectively (as determined by ^1H NMR spectroscopy). These results corresponds to current yields of 80%, 42% and 18%, respectively, thereby showing that the current yield can be improved considerably at the expense of a minor reduction in conversion. It should also be noted that hydrogen evolution was observed at the platinum cathode resulting from the reduction of water. For further details concerning the electrochemistry see the Supporting Information.

To broaden the scope of our reaction sequence we decided to explore this reaction further using a chemical oxidation procedure. The reaction was performed using chemical in situ oxidation with iodobenzene diacetate, $PhI(OAc)_2$, and gave similar results to those obtained by the electrochemical approach. As shown in Scheme 2, the reactions of *N*-tosyl-4-aminophenol **1c** worked well with both linear aliphatic and nonconjugated unsaturated systems, and gave products **5a–f** in good yields (70–85%) and in excellent enantioselectivity (93–98% *ee*). Moreover, the procedure allowed us to perform the reaction on 1,4-hydroquinone (**1a**) and *N*-tosyl-4-aminonaphthalen-1-ol **1e** (Scheme 2). For various aldehydes, we obtained products **5g–j** in 80–98% yield and > 92% *ee*. These results show the scope of the chemical oxidation/organocatalytic addition of various aldehydes to various electron-rich aromatic compounds.



5a 75% yield, 96% *ee*
5b 85% yield, 94% *ee*
5d 75% yield, 94% *ee*
5e 70% yield, 98% *ee*
5f 79% yield, 93% *ee*
5g 80% yield, 92% *ee*
5h 93% yield, 94% *ee*
5i 87% yield, 98% *ee*
5j 98% yield, 96% *ee*

Scheme 2. Scope for the chemical oxidation approach. Performed with $PhI(OAc)_2$ (0.56 mmol), **2** (2.80 mmol), **1** (0.56 mmol), and **3** (0.056 mmol) in CH_3CN/H_2O (1:1); see the Supporting Information.

The absolute configuration of the product was assigned by single-crystal X-ray analysis of compound **6a** as shown in Figure 2.[16] The structure led to the *R* assignment of the stereogenic center created, which indicates that the addition takes place to the *Si* face of the enamine **A** in Figure 1.

The 2,3-dihydrobenzofuran skeleton is widespread in many natural products and biologically active molecules.[15] The application of the anodic oxidation/organocatalytic methodology is demonstrated in Scheme 3—where the synthesis of an optically active 5-amino-2,3-disubstituted dihydrobenzofuran is presented. Wittig reaction of lactol **5a** and

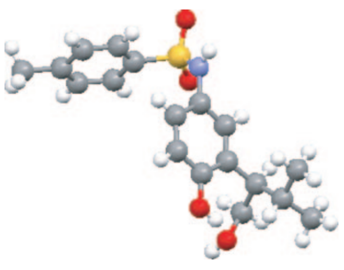
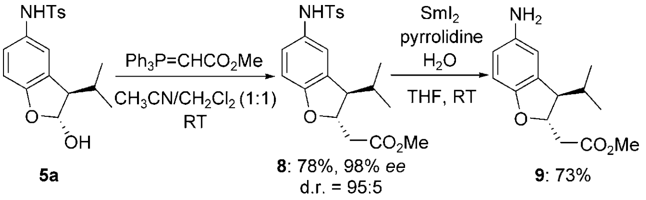


Figure 2. X-ray crystal structure of **6a**. C gray, H white, O red, N blue, S yellow.



Scheme 3. Synthesis of optically active 5-amino-2,3-disubstituted dihydrobenzofurans. THF = tetrahydrofuran.

subsequent spontaneous intramolecular cyclization led to the formation of *trans*-2,3-disubstituted dihydrobenzofuran **8** in 78% yield with excellent diastereoselectivity (95:5) and maintained the enantiomeric excess at 98% *ee*. The relative configuration was assigned by ^{1}H NMR spectroscopy through the relatively small coupling constant observed between the two hydrogen atoms in the furan ring.[17] Initial attempts to remove the tosyl group using Mg in CH$_3$OH under sonication gave a low yield. Removal of the *N*-tosyl group was successfully achieved using SmI$_2$ as the reductant and the target molecule **9** was obtained in 73% yield.[18] Anilines are of particular interest because of their ability to participate in important reactions such as the Buchwald–Hartwig coupling, the Sandmeyer reaction, hydroamination, and reductive amination. The Sandmeyer reaction allows for the introduction of many different groups making product **9** a versatile building block in the synthesis of more elaborate products.

In summary, we have developed an anodic oxidation/organocatalytic protocol for the α-arylation of aldehydes using substituted electron-rich aromatic compounds, thus giving access to *meta*-substituted anilines in good yields and excellent enantiomeric excesses. This method is an example of a new concept combining asymmetric organocatalysis with electrochemistry.

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