

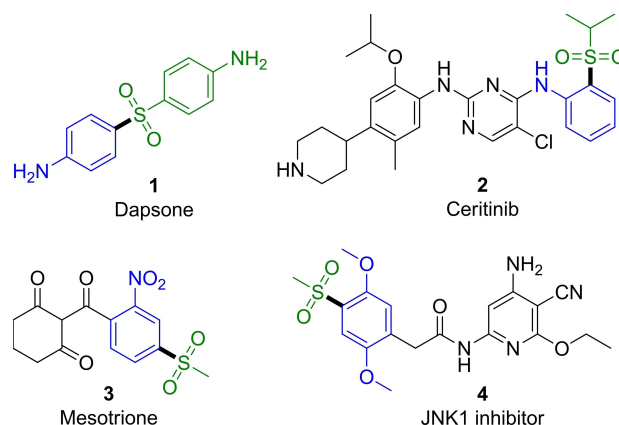
Straightforward Electrochemical Sulfonylation of Arenes and Aniline Derivatives using Sodium Sulfonates

Joachim Nikl,^[a] Davide Ravelli,^[a, b] Dieter Schollmeyer,^[a] and Siegfried R. Waldvogel^{*,[a]}

We present a general electrochemical synthesis of sulfones from arenes and aniline derivatives with sodium sulfonates. A wide range of C–S cross-coupling products is available by this oxidant- and transition metal-free method. Both aryl and diaryl sulfones can be readily obtained, using this scalable and inherently safe one-step protocol. Since the synthesis excludes the need for additional supporting electrolyte and occurs in an aqueous electrolyte system that is easily recovered and recycled, this strategy represents a sustainable and green alternative to existing sulfonylation reactions.

Sulfonylated aromatics are widely applicable biologically active substances, for example in medicine and agriculture (Scheme 1).^[1] In particular, sulfones are the most important drugs used in the treatment of leprosy.^[2] The most prominent example is Dapsone (1), which is also used as a malaria treatment agent.^[3] An example of a sulfonylated *N*-functionalized aniline derivative is the prescription-only drug Ceritinib (2), which is used to treat non-small cell lung carcinoma (NSCLC).^[4] Mesotrione (3) is a herbicide, belonging to the class of 4-hydroxyphenylpyruvate dioxygenase (HPPD) inhibitors and is especially used for maize cultivation.^[5] A further derivative showing biological activity is the *c*-Jun N-terminal kinase 1 (JNK1) inhibitor 4, whereby these kinases are associated with a number of different diseases such as asthma, Alzheimer and type 2 diabetes mellitus.^[6]

In addition, sulfones are commonly used as reagents in organic synthesis,^[7] as well as for high temperature plastics and fuel cell membranes.^[8] Over the past years, the synthesis of sulfonyl containing architectures has increasingly attracted interest, as demonstrated by the numerous reports in the field.^[9]



Scheme 1. Sulfone containing examples of bioactive ingredients and technically relevant compounds.

Overcoming the conventional Friedel-Crafts reactions or the employment of transition metal-catalysts,^[12] the use of sulfonates as direct C–S bond coupling components experienced significant interest.^[13] For example, the group of Willis described a direct photoinduced sulfonylation of *N*-alkylated anilines using an iridium catalyst (Scheme 2).^[10] This procedure allows to obtain good overall yields. However, harmful and expensive transition metals, ligands and mediators are needed. Manolikas and co-workers reported the first example of a purely manganese-promoted coupling of sulfonates (Scheme 2) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP).^[11] While the reaction tolerates various functional groups and provides a broad scope, over-stoichiometric amounts of transition metals are utilized, resulting in additional reagent waste. Nevertheless, the fundamental role of HFIP was outlined in this synthesis, describing a radical stabilizing effect. Furthermore, a metal-free preparation of sulfonylated *N,N*-dimethylanilines has been recently reported.^[14] The process makes use of DABCO·(SO₂)₂ and arenediazonium salts, albeit it only works at high temperatures and under inert gas atmosphere, leading to further disadvantages.

At variance with existing conventional reactions, electro-organic synthesis offers safer, sustainable and precisely controlled methods for direct C–H activation processes.^[15,16] Since, electrons are used as reagents, pre-functionalized substrates and oxidizing agents can be avoided.^[16]

So far, only a few precedents describing the electrochemical sulfonylation of arenes are present in the literature. Only 5 examples were reported in up to 59% yield and, importantly, the preparation of sulfonyl hydrazide reagents is essential, also requiring the use of an additional supporting electrolyte.^[17]

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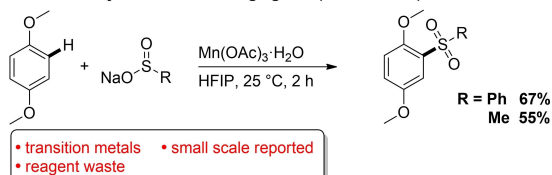
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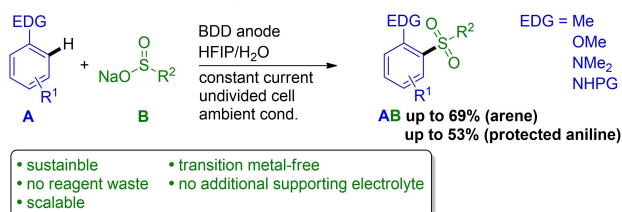
Photoinduced metal-catalyzed sulfonation of protected anilines (Willis)



Arene sulfonation via oxidizing agents (Manolikakes)



Direct electrochemical sulfonation of arenes and aniline derivatives (this work)

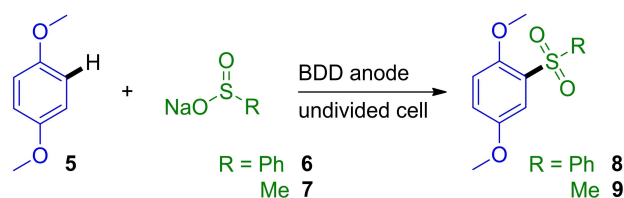


Scheme 2. Reported strategies for sulfinate-arene/aniline cross-coupling reactions and combining concept of this work.^[10,11]

Recently, an elegant method for the anodic sulfonation of *N,N*-disubstituted anilines was reported by Li and co-workers.^[18] In this case, ⁿBu₄NBF₄ had to be used as supporting electrolyte and the reaction was only described for *N,N*-disubstituted anilines. In contrast to that, sulfonation of *N,N*-dimethylanilines and anilides are performed and compared in this work.

Previously, we reported a direct method for the electrochemical sulfonation of phenols by using sodium sulfinate.^[19] In this work, an extension to arene and aniline derivative sulfonation is described, applying an undivided electrolysis cell by using a constant current mode of operation, ensuring scalability and an easy implementation.^[20] The utilization of additional supporting electrolyte is redundant, since the sulfinate acts both as the coupling substrate and the supporting electrolyte. The use of an aqueous solvent system and the efficient depletion of chemicals guarantees this protocol with attributes coinciding with a green chemistry methodology.^[20,21] Previously, the direct electrochemical, oxidative coupling of aromatic systems involving phenols,^[22] anilides,^[23] and arenes^[24] has been successfully established. The resulting products are of particular interest, since they offer access to unique substitution patterns,^[25] and can be used for example as ligand systems.^[26] A general challenge in these reactions is to minimize formation of poly- and oligomeric substances via over-oxidation in which aniline derivatives are particularly at risk.^[27] A central part in solving this shortcoming is provided by the utilization of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), enabling a solvent-controlled reaction process.^[28] Due to its remarkable solvation abilities, HFIP is able to stabilize radical and cationic intermediates by forming strong hydrogen bonds,^[29] and can lead to the

decoupling of oxidation potential and nucleophilicity, triggering distinctive cross-coupling reactions.^[21,28,30] Furthermore, sulfones are susceptible to electrochemical reduction,^[31] which makes constant current electrolysis under simple, scalable conditions particularly difficult. We have overcome these challenges by adapting the electrolysis conditions and reaction parameters reported in the past.^[19] A key concept is the addition of water to the solvent system enabling the use of sodium sulfinate as supporting electrolyte, due to improved solubility.^[19,32] By intensive optimization through an electrochemical screening set-up (see Supporting Information),^[33] electrolysis parameters were determined and applied in scale-up experiments, whereby the respective product was isolated (Scheme 3 and Table 1). For



Scheme 3. Test reaction under optimized conditions for electro-organic synthesis of 2,5-dimethoxydiphenylsulfone (8) and 2,5-dimethoxyphenylmethylsulfone (9).

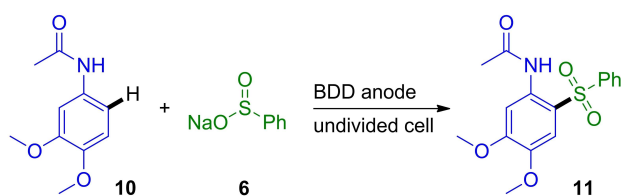
Table 1. Influence of water amount and current density onto the test reaction (Scheme 3).^[a]

Entry	R	H ₂ O in HFIP [vol.%]	<i>j</i> [mA cm ⁻²]	Yield ^[b] [%]
1	Ph	15	18	60
2	Ph	30	18	53
3	Ph	15	26	67
4	Ph	15	52	51
5 ^[c]	Me	15	12	40
6	Me	15	26	60
7 ^[d]	Ph	15	26	60

[a] BDD electrodes, r.t., *Q* = 2.5 F (ref. 5), 5/6 and 5/7 = 1:1.3. [b] Isolated yield. [c] *Q* = 5.0 F (ref. 5), 5/7 = 1:1.5. [d] Graphite electrodes.

validating the optimization, both sodium benzenesulfinate 6 and sodium methanesulfinate 7 were used to investigate whether the conditions identified as optimal were equally valid for both substrates.

In analogy to the sulfonation of phenols,^[19] the best results for arene sulfonation were consistently obtained with a water content of 15 vol.%. For the conversion of both reagents, high current densities of 26 mA cm⁻² were yield promoting, which considerably shortens the electrolysis time from approximately 3 h (for 12 mA cm⁻²) to 1.5 h. The highest conversions referring to arene sulfonation were achieved by applying 2.5 F at boron-doped diamond electrodes (BDD) with a HFIP-water mixture of 15 vol.% and a current density of 26 mA cm⁻² (Table 1, entries 3 and 6). Due to the small sulfinate excess of only 1.3 equivalents, this protocol also prevents the formation of significant amounts of waste. This advantage is attributed to the ambivalent solvent properties of HFIP. Due to its polar (hydroxyl) and non-polar (fluorinated) groups, microheteroge-



Scheme 4. Test reaction under optimized conditions for electro-organic synthesis of 2-acetamido-4,5-dimethoxydiphenylsulfone (**11**).

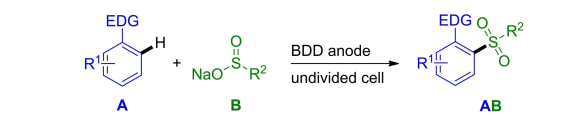
Table 2. Influence of charge quantity and current density onto the test reaction (Scheme 4).^[a]

Entry	Q [F ref. 10]	<i>j</i> [mA cm ⁻²]	Yield ^[b] [%]
1	3.5	12	30
2	2.5	6	24
3	3.5	26	18
4 ^[c]	3.5	12	27

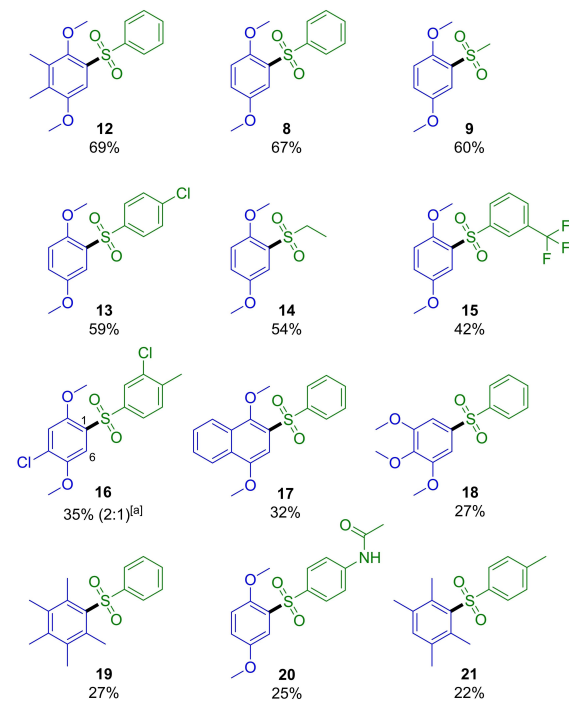
^[a] BDD electrodes, r.t., 15 vol.% water in HFIP, 10/6 = 1:1.5. ^[b] Isolated yield. ^[c] Glassy carbon electrodes.

neous domains are formed, which allow polar and non-polar reagents to be separated from each other,^[34] explaining the non-necessity of a high sulfinate excess. Another advantage of HFIP as a solvent is its low boiling point, which makes the complete recovery easy upon electrolysis.^[35] A variation of the electrode material does not lead to any yield improvement. Boron-doped diamond electrodes (BDD) have proven to be unsurpassed for these sulfonylation processes. Thus, when the reaction was carried out on graphite electrodes under optimized reaction conditions, **8** was obtained in 60% isolated yield (Table 1, entry 7). The results obtained by using BDD can be explained by its high robustness in electrochemical reactions.^[36] The extraordinary properties of BDD as an electrode material for electro-organic synthesis have already been manifold described, as well as the superior combination of BDD electrodes and HFIP in anodic coupling reactions.^[37] Besides arene sulfonylation, the protocol was also extended to anilides and *N,N*-dimethylanilines to demonstrate the great diversity of tolerable substrates for this approach. Therefore, the test substrate **10** was converted to the sulfonylated anilide **11** in the presence of sulfinate **6** (Scheme 4).

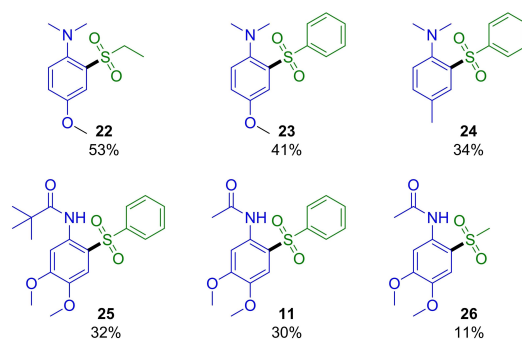
Screening results revealed different optimal parameter values, as opposed to the arene coupling. Lowering the current density from 26 mA cm⁻² resulted in increasing conversions (Table 2, entry 3). Best results were obtained with the application of 3.5 F on BDD electrodes in a HFIP-water mixture of 15 vol.% and a current density of 12 mA cm⁻² (Table 2, entry 1). However, during the optimization it was observed that the sulfonylation of substrate **10** leads to lower yields than in case of substrate **5**. Cyclic voltammetry measurements show a similar oxidation potential for both substrates (see Supporting Information). Therefore, it is assumed that a partial decomposition of the starting material takes place in the case of **10**, possibly leading to unprotected anilines and to easily occurring over-oxidation, which makes the anilide coupling in general challenging. Referring to the previously reported anodic anilide



Sulfonylated arenes



Sulfonylated aniline derivatives



Scheme 5. Scope of aryl sulfones. Conditions for arene sulfonylation: BDD electrodes, r.t., 15 vol.% water in HFIP, *j* = 26 mA cm⁻², *Q* = 2.5 F (ref. A), A/B = 1:1.3. Conditions for aniline sulfonylation: BDD electrodes, r.t., 15 vol.% water in HFIP, *j* = 12 mA cm⁻², *Q* = 3.5 F (ref. A), A/B = 1:1.5. [a] yield ratio between regioisomers **16a** (C1-coupling) and **16b** (C6-coupling).

coupling,^[23] also glassy carbon electrodes were tested (Table 2, entry 4). Here, a minor decreasing effect was observed, delivering **11** in 27% yield.

By applying the optimized conditions for arene sulfonylation (Table 1, entry 3 and 6), a collection of examples was produced (Scheme 5). The described protocol allows the conversion of different substituted arenes with a variety of functionalized sulfonates resulting in isolated yields up to 69%. As demonstrated by the examples **13**, **15** and **16**, halogen-containing sulfonates and arenes are tolerated as well as non-

methoxy-substituted arenes (e.g. **19**, **21**). Due to the variation of component **B**, monoarylsulfones (e.g. **9**, **14**) or diarylsulfones can be synthesized, opening a large accessible product scope. In order to demonstrate the broad applicability of this protocol, anilides and *N,N*-dimethylanilines were utilized as well. Overall, the isolated yields of the dimethylanilines **22**, **23** and **24** are higher than for the anilides **11**, **25** and **26**, after application of the same electrochemical protocol. This fact can be explained by two major assumptions. First, the amino moiety induces selectivity via the initial oxidation of the dimethylanilines prior to the sulfonates, due to their fundamentally lower oxidation potentials (see Supporting Information).

Second, after generation of the sulfones, a hydrogen bond between the sulfinate oxygen and the amide hydrogen can be formed, keeping the nitrogen lone pair in π -contact with the aromatic ring (Figure 1). Due to the persistent higher electron

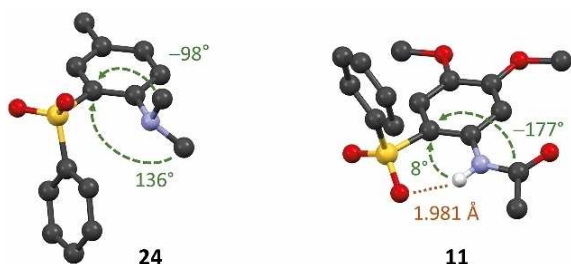


Figure 1. Molecular structures by X-ray analysis of **11** and **24** with indicated hydrogen bond for **11** (1.981 Å, dotted orange line). The remaining hydrogen atoms are omitted for clarity. Torsion angles for **11** are 8° and -177°, and for **24**, 136° and -98° (dashed green arrows).

density the products are prone to over-oxidation. As opposed to this, the sulfonylated *N,N*-dimethylanilines presumed to have a twist in the amino *N*-Ar bond due to the steric hindrance with the sulfone moiety, causing diminished conjugation of the nitrogen lone pair with the π -system of the aromatic ring (Figure 1). Therefore, less over-oxidation of these products is concluded.^[22b]

In general, diversification of the substrates was turned out to be challenging for the sulfonylation of aniline derivatives. By using the most promising reaction conditions, a few examples could be isolated, demonstrating concurrently the first electrochemically generated sulfonylation products of anilides (Scheme 5). As a general remark due to anodic oxidation reactions, a great decrease of yield is attributed to the formation of over-oxidation products, which remain on the silica as a dark residue during column chromatographic purification. In cases of the anilide conversions certain amounts of starting material were recovered after work-up, confirming a possible competing effect due to the oxidation of the sulfonates. To demonstrate the high scalability of this protocol, the reaction shown in Scheme 3 was performed in a 8-times magnified approach (Figure 2). The scale-up was performed from a 5 mmol batch scale (ref. 5, 25 mL electrolysis cell) to a 40 mmol batch scale (ref. 5, 200 mL electrolysis cell). Here **8** was obtained in a comparable yield of 55% (6.10 g). Further

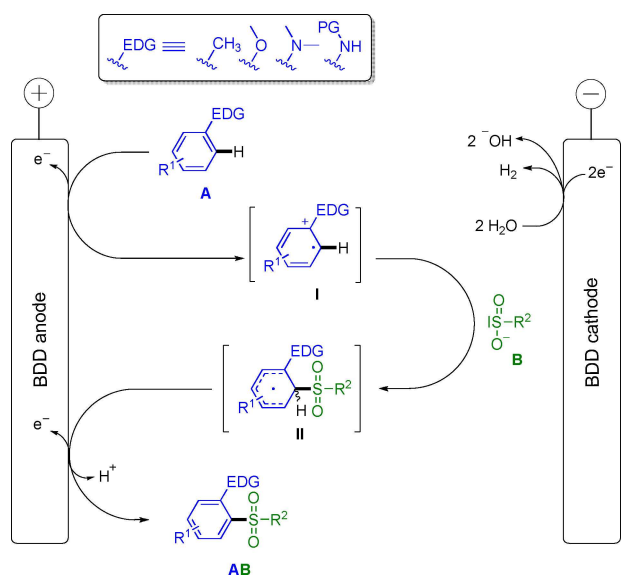


Figure 2. Scale-up from a 5 mmol to a 40 mmol batch. For size comparison of the beaker-type cells a 2 € coin is placed in front (diameter 25.75 mm \approx 1.01 in).

experimental details can be obtained in the Supporting Information.

For mechanistic considerations regarding the reaction, cyclic voltammetry measurements of the substrates were performed (see Supporting Information). The postulated sulfinate oxidation by Li and co-workers, which leads to sulfone formation,^[18] cannot be completely excluded. However, for both cases (arenes and aniline derivatives), it is apparent that an initial oxidation step of the **A** component is likely, due to the lower oxidation potentials. Stabilization of the positive charge is obtained through the electron donating properties of the functionalities. The following C-S bond formation occurs via a nucleophilic attack of the sulfinate to the formed radical cation **I**. Finally, a second oxidation step of the HFIP-stabilized intermediate **II** to the sulfone **AB** is assumed (Scheme 6). These results also refer to the previously described mechanism for the oxidative phenol sulfonylation^[19] and the anodic C,C cross-coupling reactions.^[22a-c] As counter reaction, an electro-reduction of water leading to hydrogen evolution is probable, since a visible gas evolution at the cathode surface occurs. A pH value determination via universal indicator paper before and after electrolysis shows an increase from a pH of 3–4 to 9–10, revealing a consumption of the co-solvent H₂O.

In conclusion, a unifying, direct, safe, and sustainable method for the electrochemical sulfonylation of arenes and aniline derivatives has been established. The presented protocol takes inspiration from the previously reported sulfonylation of phenols and leads to the preparation of aryl and diaryl sulfones in good yields, up to 69%. The use of the sulfonates as coupling component and supporting electrolyte prevents additional



Scheme 6. Postulated mechanism for the anodic arene/aniline sulfonation. The functionalities are depicted as EDG (Electron Donating Group).

additives and reagent waste. This transition-metal- and oxidant-free protocol is based on a constant current electrolysis in an undivided cell, whereby an easy performance, a high scalability and an efficient utilization of starting materials under green chemistry attributes is ensured.

Experimental Section

Detailed information on general procedures, electrolytic conversions and product characterization can be found in the Supporting Information.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: C–H activation • cross-coupling • electrochemistry • oxidation • sustainable chemistry

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