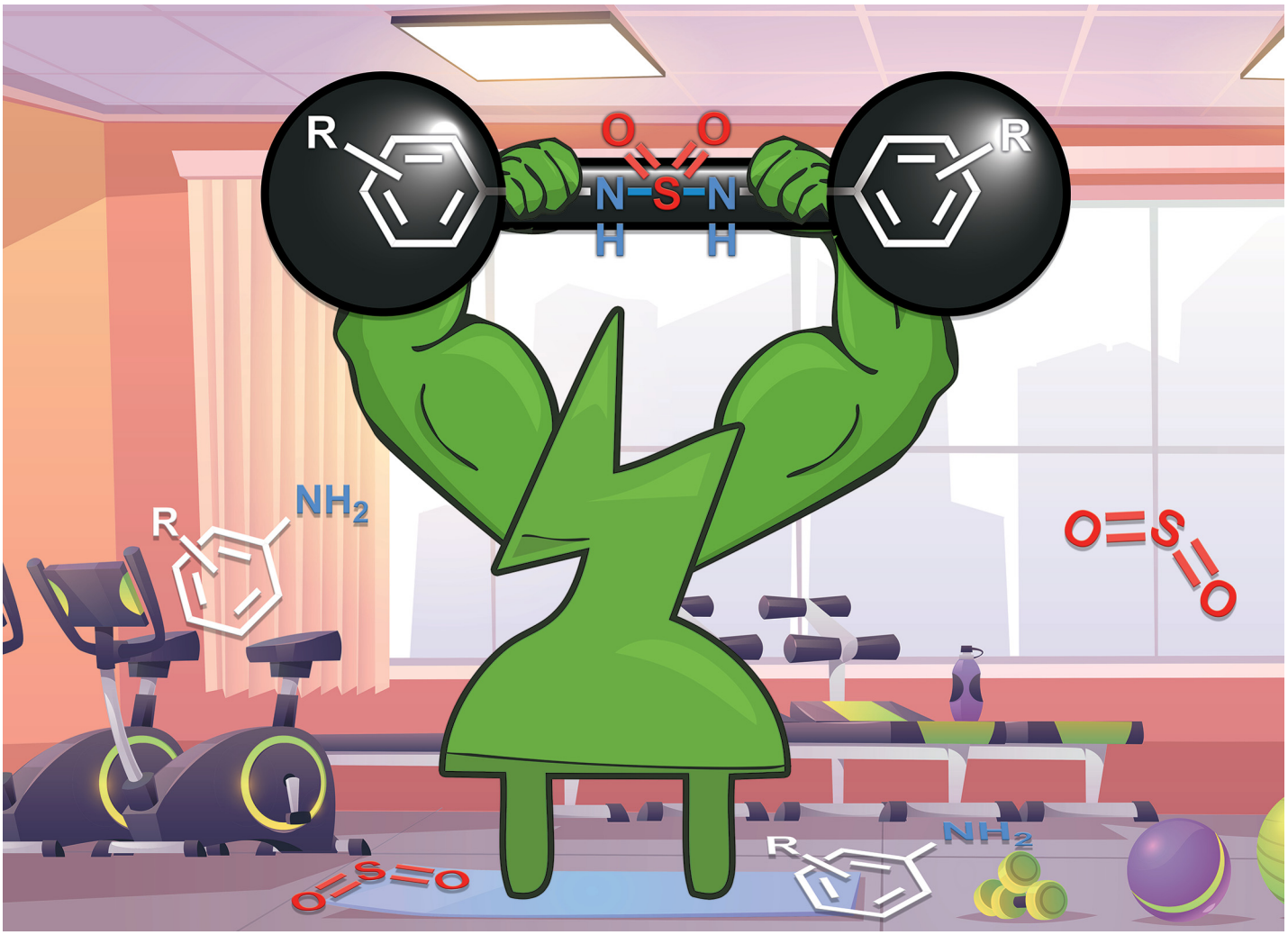


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Electrochemical synthesis of sulfamides

Organic electrosynthesis enables the powerful formation of symmetrical sulfamides directly from anilines and $SO_2$ in a divided cell mediated by iodide. The direct use of $SO_2$ from a stock solution and no requirement for an additional supporting electrolyte significantly increases the atom economy. Sulfamides are an emerging functional group in medicinal chemistry.

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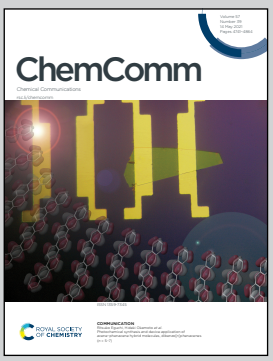


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# Electrochemical synthesis of sulfamides†

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**Herein we demonstrate the first electrochemical synthesis protocol of symmetrical sulfamides directly from anilines and $SO_2$ mediated by iodide. Sulfamides are an emerging functional group in drug design. Highlights are the direct use of $SO_2$ from a stock solution and no necessity of any supporting electrolyte. Overall, the reaction has been demonstrated for 15 examples with yields up to 93%.**

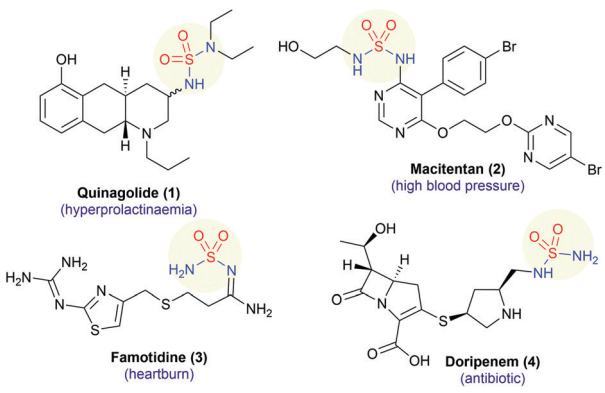
Molecules containing sulfamide functionalities slowly found their way into medicinal chemistry, which is attributed to their versatile biological activities.[1,2] Sulfamides are electron-rich, powerful hydrogen bonding donors/acceptors, and their tetrahedral configuration is conformationally-rich in regard to their target protein interaction.[2,3] They comprise bioisosteric replacements to sulfamates, sulfonamides, urea, carbamates, and amides.[2,4,5]

According to DrugBank database, there are currently four approved drugs containing sulfamide groups and 19 in experimental or investigational phase,[6] which is evidence for the emerging importance and application of this functionality in drug design. For example, the drug Quinagolide (**1**, Scheme 1) is used to lower elevated blood levels of prolactin (hyperprolactinaemia).[6,7] Macitentan (**2**) is applied to regulate high blood pressure.[6,8] Famotidine (**3**) can medicate heartburn.[6,9] The antibiotic Doripenem (**4**) is used to treat infectious diseases.[6,10]

In recent years, methodologies for sulfamide syntheses and functionalization have been reported increasingly.[2,4,5,11–13] Traditional strategies rely on hazardous and highly corrosive sulfuryl chloride with anilines (Schemes 2 and 3),[4,14] whereas sulfuryl chloride is chemically derived from sulfur dioxide and chlorine gas.[15] Further drawbacks are rather poor conversion and complex product mixtures resulting from side reactions, such as aromatic chlorination.[12,16] Rudkevich and coworkers reported the synthesis of symmetrical sulfamides by using stoichiometric amounts of iodine with excess $SO_2$ (~100 equiv.) resulting in the *in situ* formation of highly reactive sulfuryl iodide.[12] Alternatively, $SO_2$ surrogates can be utilized in this approach.[13,17]

Organic electrosynthesis currently experiences a renaissance,[18] which is attributed to numerous assets, such as inherent safety,[19] limited reagent waste, short cut of many synthetic steps,[20–22] unique reactivity[23,24] and the fact that electric current can be generated from renewable energy. Moreover, "green" electricity is inexpensive in comparison to hazardous and polluting chemical redox reagents and therefore electrifying organic synthesis to value-added products can pay off.[23,25,26] In summary, many principles of Green Chemistry are applied,[27] which is crucial for future applications in order to overcome global challenges such as climate change.[28]

In this work, the use of light-sensitive iodine can be elegantly avoided by using electricity to generate $I_2$ from catalytic amounts of iodide,[29] which drastically enhances the atom economy. The *in situ* generated iodine is considered to catalyze the formation of symmetrical sulfamides directly from anilines and $SO_2$. The pollutant and waste product of many industrial processes sulfur dioxide[30] is incorporated into the molecule by an atom economical way.[21,22] This circumvents the use of




Scheme 1 Approved drugs containing sulfamide functionalities.

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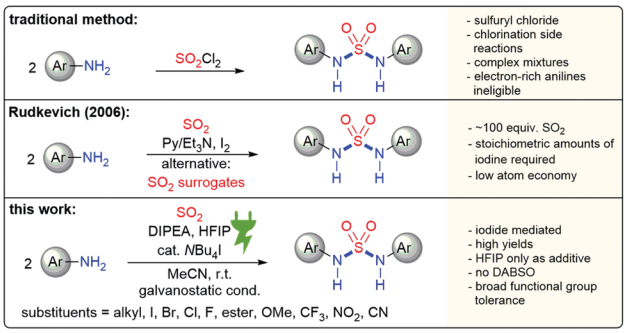
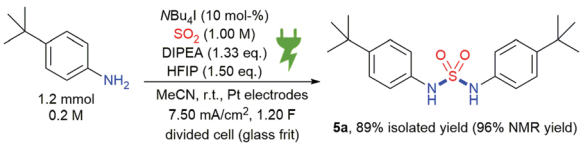



Scheme 2 Synthetic methodologies for symmetrical sulfamide synthesis; DIPEA = *N*,*N*-diisopropylethylamine; DABSO = 1,4-diazabicyclo[2.2.2]octane-bis(sulfur dioxide) adduct; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol; py = pyridine.




Scheme 3 Optimized reaction conditions.

expensive $SO_2$ surrogates with high molecular mass, which generate waste in course of application.[21,22] Additionally, unprotected anilines are hardly used as substrates in electrochemical synthesis due to their low oxidation potentials[31] leading to facile anodic oxidation, followed by polymerization (aniline black).[32]

Therefore, mostly protection as acylanilides was employed.[33] Herein, the issues with over-oxidation and additional protection/deblocking sequence was avoided by the presence of iodide salts, as these have even lower oxidation potentials than the free anilines.

Our electrosynthetic screening and optimization experiments were conducted in a device which is commercially available[34] and allows to obtain all relevant data.[25] We began our reaction optimization by using 4-*tert*-butylaniline as test substrate in an 1,1,1,3,3,3-hexafluoroisopropanol (HFIP)/MeCN (1 : 1) solvent mixture with BDD (boron-doped diamond) electrodes,[35] which resulted in 72% NMR yield (Table 1, entry 2). Higher HFIP content (entry 3) as well as no HFIP (entry 4) resulted only in traces or no sulfamide formation. Noteworthy, HFIP is very stable under these electrolytic conditions. It can be almost quantitatively recovered and reused. Stoichiometric amounts of HFIP (3.00 equiv., entry 5) significantly improved the yield to 80% and 1.50 equiv. (entry 6) even resulted in 88% yield. The application of glassy carbon electrodes showed similar results (89%, entry 7) and platinum electrodes gave 96% with 89% isolated yield (**5a**, entry 1). Higher current density slightly lowered the sulfamide formation (entry 8) and pyridine instead of DIPEA distinctively reduced the NMR yield to 52% (entry 9). The use of undivided cells gave 69% (entry 10). Omitting of the iodide salt (entry 11) as well as the substitution of $N$Bu$_4$I by $N$Bu$_4$Br (entry 12) or $N$Bu$_4$Cl (entry 13) resulted in no product formation. An organic base is necessary as omitting was also rendered in no sulfamide formation (entry 14, $N$Bu$_4$BF$_4$ was added for better electrical conductivity). No electricity resulted in no product formation (entry 15). Further information can be retrieved from the ESI.†

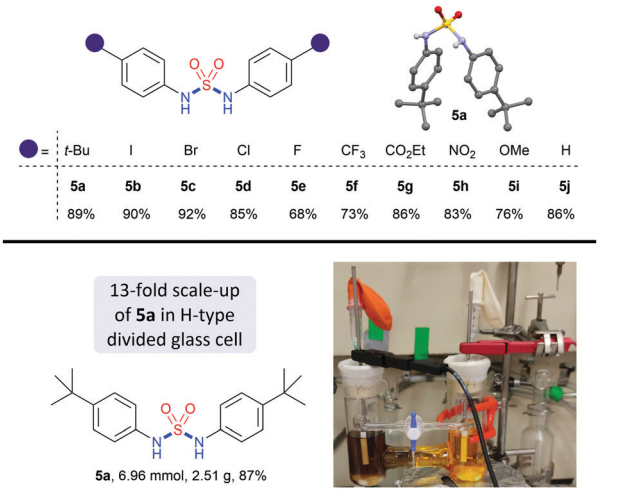
Thereupon, we examined the scope by testing various 4-substituted anilines as depicted in Scheme 4: halogen-substituted anilines resulted in excellent yields (**5b**, 90%; **5c**, 92%; **5d**; 85%), whereas the less nucleophilic 4-fluoroaniline gave **5e** with only 68% isolated yield and **5f** gave 73% with a $CF_3$ substituent. Sulfamide **5g** (86%) is derived from Benzocaine, which is a well-known local anesthetic agent.[36] Nitro- and methoxy-substituted sulfamides gave similar yields (**5h**, 83%; **5i**, 76%). Finally, aniline derived sulfamide **5j** was obtained in 86% yield. Impressively, 3-bromoaniline gave **6** with 93% yield (Scheme 5). It is noteworthy that sulfamide **7** (86%) bears two different halogen substituents (bromo and chloro). Anilines with increased steric hindrance are also eligible for this protocol (**8**, 73%; **10**, 52%), and 3-cyano substituted aniline gave **9** in 81% yield. A 13-fold scale-up of the reaction by employing 16.0 mmol aniline substrate gave 2.51 g of **5a**

Table 1 Optimization reactions of the test substrate

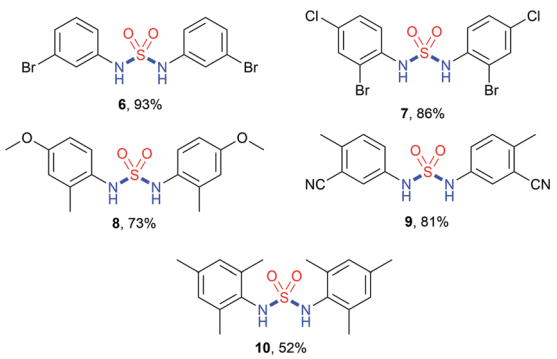
| Entry | Deviation from the standard conditions[a] | Yield[b] [%] |
|---|---|---|
| 1 | None | 96 (89% isolated yield) |
| 2 | BDD electrodes, HFIP/MeCN = 1 : 1 | 72 |
| 3 | BDD electrodes, HFIP/MeCN = 10 : 1.5 | Traces |
| 4 | BDD electrodes, no HFIP | 0 |
| 5 | BDD electrodes, HFIP (3.00 equiv.) | 80 |
| 6 | BDD electrodes | 88 |
| 7 | Glassy carbon electrodes | 89 |
| 8 | 12.0 mA cm$^{-2}$ | 86 |
| 9 | Pyridine instead of DIPEA | 52 |
| 10 | Undivided cell | 69 |
| 11 | No iodide source | 0 |
| 12 | $N$Bu$_4$Br instead of $N$Bu$_4$I | 0 |
| 13 | Glassy carbon electrodes, $N$Bu$_4$Cl instead of $N$Bu$_4$I | 0 |
| 14 | No DIPEA, instead: $N$Bu$_4$BF$_4$ (0.10 M) | 0 |
| 15 | No electricity | 0 |

[a] Standard conditions shown in Scheme 3. [b] Yield of **5a** determined by internal NMR standard (1,3,5-trimethoxybenzene).



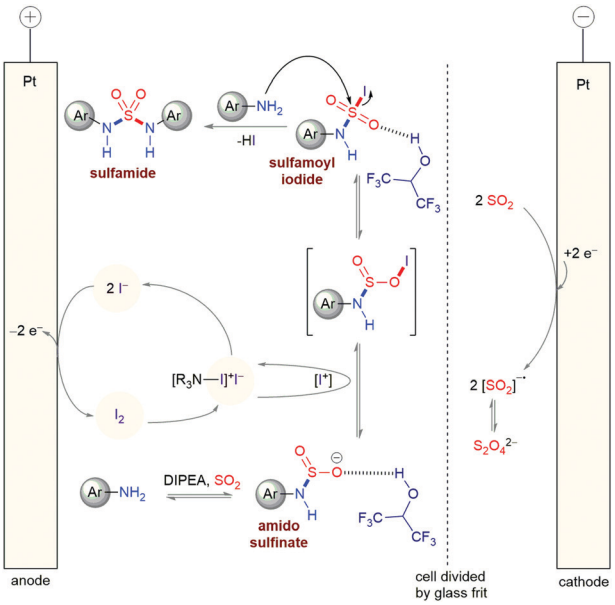

Scheme 4 Scope starting from 4-substituted anilines with isolated yields. Molecular structure of **5a** determined by X-ray analysis. Scale-up reaction of **5a** (lower part of the scheme).




Scheme 5 Substrate scope of further anilines with isolated yields.

(6.96 mmol, 87%), which is comparable to the results obtained in usual scale with 89% yield by using 1.20 mmol substrate.

Finally, the reaction mechanism was considered (Scheme 6). Cyclic voltammetry experiments (ESI†) indicate the initial anodic oxidation of iodide resulting in the formation of iodine, which is supposed to form extraordinarily strong Lewis acid–base adducts with amine bases, such as DIPEA, triethylamine or pyridine. These species have to some extent ionic character also leading to the iodonium ion.[37–39] Possibly, HFIP could further stabilize and promote the formation of those ionic species ($[R_3NI^+]I^-$ or $[(R_3N)_2I^+]I^-$)[38,39] *via* hydrogen bonding and therefore explain the necessity of HFIP and DIPEA in this protocol. Additionally, HFIP is considered to disperse or alter the charge transfer complex between DIPEA and $SO_2$ in MeCN, as a color change of the solution from black to orange was observed upon addition of HFIP (ESI†). Rudkevich and coworkers proposed the formation of sulfuryl iodide as intermediate upon reaction of iodine with $SO_2$ by activation with triethylamine or pyridine.[12] However, we consider the reaction to proceed *via* amidosulfinates generated from anilines, $SO_2$ and DIPEA, which could also be one of the conductible species in the electrolyte. The




Scheme 6 Postulated reaction mechanism.

*in situ* generated iodonium ion is considered to react with the amidosulfinate resulting in the formation of sulfamoyl iodide in an equilibrium reaction. This transformation could possibly be favored by hydrogen bonding stabilization of the intermediates from stoichiometric amounts of HFIP. Subsequent nucleophilic displacement with another equivalent of aniline provides the symmetrical aromatic sulfamide. As shown in the optimization table (Table 1, entry 2), excess HFIP proved to be unsuitable, which could be due to full protonation of DIPEA diminishing the reactivity of iodonium ion generation.

As cathodic reaction, $SO_2$ reduction was identified by cyclic voltammetry measurements (ESI†). The $SO_2$ anion radical is considered to dimerize to dithionite during the course of the electrolysis. Therefore, divided cells give improved yields as the reduced $SO_2$ species could be reoxidized anodically leading to lower overall current efficiency.

In conclusion, we have developed the first electrochemical synthesis protocol for symmetrical sulfamides. The use of a $SO_2$ stock solution significantly increases the atom economy in comparison to expensive $SO_2$ surrogates, such as DABSO. Moreover, no additional supporting electrolyte is required, and inexpensive electricity serves as oxidant for the *in situ* generation of iodine from catalytic amounts of iodide. DIPEA and HFIP are crucial for the success of this reaction due to the formation of the iodonium ion and stabilization of intermediates. Scalability has been proven in a 13-fold scale-up reaction. The broad functional group tolerance in combination with excellent yields up to 93% make this protocol a competitive and attractive alternative to the existing methodologies.

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## Conflicts of interest

There are no conflicts of interest to declare.

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