



Full Communication

# Electrochemical *O*-trifluoromethylation of electron-deficient phenols

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## ABSTRACT

A simple and sustainable one-step strategy for the preparation of electron-deficient aryl trifluoromethyl ethers (ArOCF<sub>3</sub>) from the corresponding phenols by electrochemical synthesis is presented. Anodic oxidation of trifluoromethane sulfinate (Langlois reagent) leads to direct *O*-trifluoromethylation of phenol-derivatives bearing fluorine, chlorine, bromine and nitrile substituents under mild conditions in yields up to 75% and in gram-scale. This electrochemical protocol provides an economic and green synthesis for an otherwise inaccessible class of molecules without the need for expensive or toxic reagents, oxidants or metal catalysts.

## 1. Introduction

Fluorine-containing organic molecules are of great interest in the modern pharmaceutical and agrochemical industries as well as in materials science. Due to their intrinsic properties, fluorine atoms and fluorinated functional groups (e.g. CF<sub>3</sub>, OCF<sub>3</sub>, SCF<sub>3</sub>) strongly affect the biological and physical properties of organic molecules, in particular their polarity, lipophilicity and metabolic stability [1–4]. Currently, about 20% of all commercial pharmaceuticals registered globally since 1991 and 35% of all agrochemicals contain at least one fluorine atom per molecule [5,6]. In recent years, much progress has been made in terms of the introduction of fluorine atoms, CF<sub>3</sub> or SCF<sub>3</sub> groups into aromatic systems [7]. In contrast, the available synthetic routes for the preparation of aryl trifluoromethyl ethers (ArOCF<sub>3</sub>) are limited. Existing methods require harsh reaction conditions, multiple-step reactions or expensive and unstable reagents [8–15]. These strategies have a common feature in that their application is mainly limited to electron-rich arenes. An approach for *O*-trifluoromethylation of electron-poor pentafluorophenol was presented by Buxton et al. [16] in 1973, but only low yields were obtained and use of toxic reagents under high pressure and temperature was necessary (Scheme 1). While the preparation of electron-deficient aryl trifluoromethyl ethers is difficult to accomplish, the properties of this class of molecules are highly interesting, particularly due to the higher electronegativity of the trifluoromethoxy substituent compared to trifluoromethyl groups [17]. This is especially true in the field of molecular electronics, where fluorinated and trifluoromethyl-substituted aromatic systems already play an outstanding role [18–20], and the implementation of trifluoromethoxy

groups could lead to new n-type semiconducting materials. A fine tuning of orbital energies can be achieved by preparation of aromatic molecules bearing both fluorine atoms and trifluoromethoxy moieties. Consequently, simpler and more efficient reactions for the introduction of OCF<sub>3</sub> groups into fluorinated aromatic hydrocarbons are required.

In recent years, the application of electrochemical methods in organic chemistry has experienced a renaissance. Conventional chemical oxidizing and reducing agents as well as metal catalysts can be replaced by using electrical current as a cheap, sustainable and inherently safe reagent. Insertion or removal of an electron can be achieved under mild conditions and large amounts of reagent waste can be avoided, which results in high atom efficiency. Hence, electrochemical synthesis has become a powerful, versatile and green alternative to conventional organic chemistry [21–24].

Recently, a few methods for the electrochemical introduction of trifluoromethyl groups into aromatic compounds by anodic oxidation of trifluoromethane sulfinate (Langlois reagent) have been reported [25–29]. So far, these strategies have only been applied to the preparation of C-CF<sub>3</sub> and S-CF<sub>3</sub> bonds, but electrochemical *O*-trifluoromethylation has not yet been reported. Considering the difficult preparation of the *O*-CF<sub>3</sub> moiety by conventional methods, particularly for electron-deficient aromatic systems, an electrochemical strategy would be desirable.

Here, we present a simple and inexpensive one-step reaction for the direct *O*-trifluoromethylation of electron-deficient phenols by electrochemical synthesis using Langlois reagent. The electrolysis was conducted in an undivided cell equipped with a two-electrode arrangement under constant current conditions. To optimize the reaction parameters,

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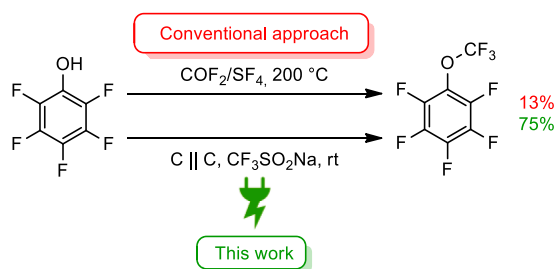
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**Scheme 1.** Conventional approach [16] vs. electrochemical synthesis (this work) of octafluoroanisole from pentafluorophenol.

pentafluorophenol **1a** was selected as a model substrate (Table 1). The yields of octafluoroanisole **3a** were determined by  $^{19}\text{F}$  NMR spectroscopy using fluorobenzene as an internal standard, as **3a** is highly volatile and very difficult to isolate.

## 2. Materials and methods

### 2.1. General information

All commercially acquired reagents were of analytical grade and were used without further purification. HPLC grade acetonitrile and methanol were used. The phenols **1b,g,h** could not be purchased and were synthesized as described in the Supporting Information. GC–MS data were recorded by a combination of a ThermoScientific Trace GC Ultra and a ITQ900 mass spectrometer. A Macherey Nagel OPTIMA 210 Fused-Silica capillary column was used for all measurements. The MALDI high-resolution mass spectra (HRMS) were acquired with a ThermoScientific LTQ Orbitrap XL.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a 300 MHz (AV300), 400 MHz (AV400 HD) and 500 MHz (AV500 HD) Bruker NMR spectrometer at room temperature. The  $^1\text{H}$  NMR shifts were determined relative to  $\text{CDCl}_3$  (7.26 ppm),  $\text{C}_6\text{D}_6$  (7.16 ppm) or  $\text{CD}_2\text{Cl}_2$  (5.32 ppm), the  $^{13}\text{C}$  NMR shifts relative to  $\text{CDCl}_3$  (77.16 ppm) and the  $^{19}\text{F}$  NMR shifts relative to the internal standard  $\text{CCl}_3\text{F}$  (0.00 ppm). Purification by HPLC was performed using a Cosmosil Bucky Prep Semi-Prep column (20 × 250 mm), a Waters 600 Controller and a Waters 2487 Dual  $\lambda$  Absorbance Detector with a flow rate of 16 mL  $\text{min}^{-1}$  at 30 °C. Graphite rods ( $l = 30.5$  cm,  $\phi = 0.64$  cm, PYROID® pyrolytic graphite) were obtained from Pine Research, Durham, USA. All electrochemical reactions were performed with a Vertex potentiostat (Ivium Technologies) in constant current mode with a two-electrode arrangement using IviumSoft (version 4.952). Custom-built undivided glass cells were used for all reactions. Half of the cylindrical surface area of the immersed part of the electrode was used to define the active electrode surface. All measurements by cyclic voltammetry were performed in a three-electrode arrangement with a Vertex potentiostat (Ivium Technologies) using IviumSoft (version 4.952). Samples were prepared with 0.01 mol  $\text{L}^{-1}$  substrate and 0.30 mol  $\text{L}^{-1}$   $\text{NaClO}_4$  in degassed  $\text{MeCN}/\text{H}_2\text{O}$  4:1. Electrode configuration: graphite disc working electrode, platinum wire counter electrode,  $\text{Ag}/\text{AgCl}$  reference electrode. Measurement parameters: scan rate = 100  $\text{mV s}^{-1}$ ,  $E_{\text{step}} = 1$  mV. 10 cycles were measured and the sixth cycle was plotted.

### 2.2. General procedure

In an undivided beaker-type cell equipped with a stirring bar, phenol **1a-i** (1.25 mmol),  $\text{NaSO}_2\text{CF}_3$  (0.78 g, 5.00 mmol) and  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (0.70 g, 5.00 mmol) were dissolved in  $\text{MeCN}/\text{H}_2\text{O}$  4:1 (25 mL). After degassing the solution by purging with Ar for 5 min, the cell was equipped with two parallel graphite rods (electrode gap 1.5 cm) serving as anode and cathode. The electrolysis was performed under constant current conditions ( $j = 10$   $\text{mA cm}^{-2}$ , active surface area 1.4  $\text{cm}^2$ , electric current 14 mA) until a charge of 8  $\text{F mol}^{-1}$  phenol **1a-i** was consumed.

After electrolysis, the reaction solution was diluted with  $\text{H}_2\text{O}$  and extracted with dichloromethane (4 × 20 mL). The combined organic phases were washed with aqueous  $\text{Na}_2\text{CO}_3$  solution (1 mol  $\text{L}^{-1}$ , 3 × 30 mL) and dried over  $\text{Na}_2\text{SO}_4$ . The solvents were evaporated under reduced pressure. The crude product was purified by HPLC. Experimental and characterization data for the trifluoromethyl ethers **3a-i** can be found in the Supporting Information.

## 3. Results and discussion

### 3.1. Optimization of reaction conditions

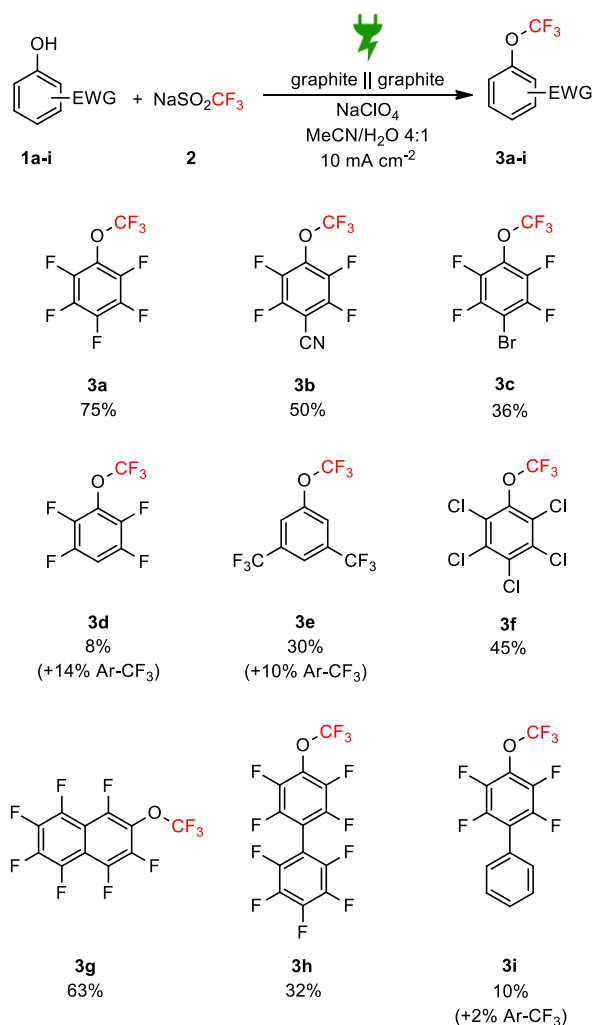
The best result for the preparation of **3a** (75% yield, Table 1, entry 1) was obtained by using two parallel graphite rods as anode and cathode, an acetonitrile/ $\text{H}_2\text{O}$  4:1 mixture as solvent and sodium perchlorate as supporting electrolyte. A constant current density of 10  $\text{mA cm}^{-2}$  (referred to the active surface, see Supporting Information) was applied until a charge of 8.0  $\text{F mol}^{-1}$  with respect to **1a** was consumed. At this current density, the initial terminal voltage was about 2.5 V, which increased slightly towards the end of the reaction. Decreasing (5  $\text{mA cm}^{-2}$ ) and increasing (20  $\text{mA cm}^{-2}$ ) the current density both led to lower yields (70% and 50%, entries 2 and 3). Reducing the amount of charge passed through the electrolyte and therefore shortening the reaction time resulted in slightly decreased yields. On applying charges of 4.0 and 6.0  $\text{F mol}^{-1}$ , only 60% and 67% product could be obtained, respectively (entries 4 and 5). Moreover, the influence of the solvent was explored. Experiments in pure acetonitrile were not successful due to the low solubility of sodium trifluoromethane sulfinate **2**. Using DMSO or hexafluoroisopropanol (HFIP)/acetonitrile mixtures as solvents led to decreased yields compared to acetonitrile/ $\text{H}_2\text{O}$  4:1 (entries 7, 8 and 9). Sodium perchlorate turned out to be the best supporting electrolyte due to its high electrochemical stability and its ability to increase the potential window of organic and aqueous solvents. When  $\text{NaClO}_4$  was substituted by  $n\text{Bu}_4\text{NPF}_6$  as supporting electrolyte, less of product **3a** could be obtained (60%, entry 10). Using perchloric acid instead also

**Table 1**  
Optimization of reaction conditions with pentafluorophenol **1a**.<sup>a</sup>

<b>1a</b>	<b>2</b>	<b>3a</b>
Entry	Variation from optimized reaction conditions <sup>a</sup>	Yield <sup>b</sup> of <b>3a</b> /%
1	None	75
2	5 $\text{mA cm}^{-2}$	70
3	20 $\text{mA cm}^{-2}$	50
4	4.0 $\text{F mol}^{-1}$	60
5	6.0 $\text{F mol}^{-1}$	67
6	$\text{MeCN}$	0
7	$\text{MeCN}/\text{HFIP}$ 1:2	56
8	$\text{MeCN}/\text{HFIP}$ 2:1	52
9	DMSO	15
10	$n\text{Bu}_4\text{NPF}_6$	60
11	$\text{HClO}_4$	67
12	2.50 mmol <b>1a</b>	71
13	Glassy carbon anode	traces
14	$\text{Pt} \parallel \text{Pt}$	8
15	Without degassing	57
16	Without electric current	0

<sup>a</sup> Optimized reaction conditions: undivided cell, graphite rod anode and cathode, constant current (10  $\text{mA cm}^{-2}$ ), 8.0  $\text{F mol}^{-1}$  phenol **1a** (1.25 mmol),  $\text{CF}_3\text{SO}_2\text{Na}$  **2** (5.00 mmol),  $\text{NaClO}_4$  (5.00 mmol), acetonitrile/ $\text{H}_2\text{O}$  4:1 (25 mL), degassed with Ar, rt.

<sup>b</sup> The yields were determined by  $^{19}\text{F}$  NMR spectroscopy using fluorobenzene as internal standard.

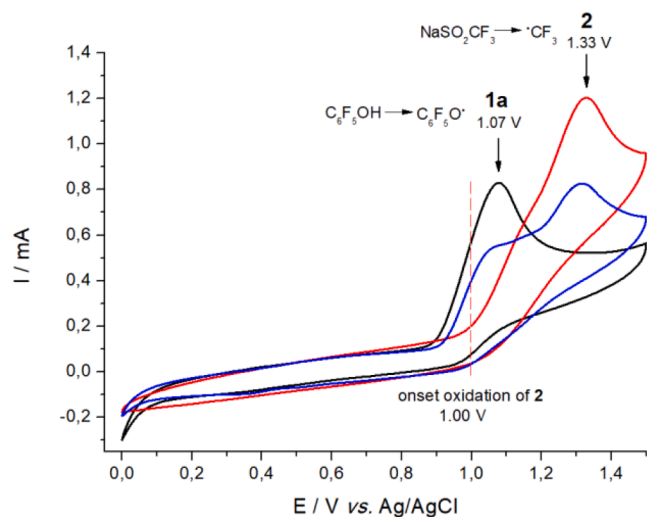


**Scheme 2.** Substrate scope of the electrochemical *O*-trifluoromethylation of electron-deficient phenols.

decreased the yield (67%, entry 11). Doubling the concentration of phenol **1a** to 2.50 mmol (0.1 mol L<sup>-1</sup>) led to the formation of a slightly lower amount of product **3a** (71%, entry 12). Furthermore, the electrode materials had a huge impact on the reaction. When the graphite rod anode was replaced by a glassy carbon rod, only traces of **3a** were found (entry 13). Conducting the electrolysis with two parallel platinum plates serving as anode and cathode led to only 8% yield (entry 14). When the electrolyte was not degassed, the yield decreased to 57% (entry 15). Control experiments showed that no reaction occurred without an electrical current (entry 16).

### 3.2. Investigation of scope and scale

With the optimized reaction conditions, we explored the scope of the electrochemical *O*-trifluoromethylation of electron-deficient phenols. Reactions with derivatives of phenol, naphthol and biphenylol with electron-withdrawing fluorine, chlorine, bromine and nitrile substituents were investigated. The desired trifluoromethyl-ethers **3a-i** could be obtained in low to good yields (see **Scheme 2**). Under optimized conditions, the benchmark substrate **1a** gave octafluoroanisole **3a** in 75% yield (<sup>19</sup>F NMR). Due to its high fugacity, separation of **3a** from the solvent was not possible. By substituting the *para* fluorine atom of **1a** by



**Fig. 1.** Cyclic voltammograms showing the oxidation potentials of pentafluorophenol **1a** (black), Langlois reagent **2** (red) and the reaction solution (**1a** + **2**, blue). Sample concentrations were 0.01 mol L<sup>-1</sup> in 0.30 mol L<sup>-1</sup> NaClO<sub>4</sub> in degassed MeCN/H<sub>2</sub>O 4:1. Electrode configuration: graphite disc working electrode, platinum wire counter electrode, Ag/AgCl reference electrode. Measurement parameters: scan rate = 100 mV s<sup>-1</sup>, E<sub>step</sub> = 1 mV. The sixth cycle of each measurement is displayed.

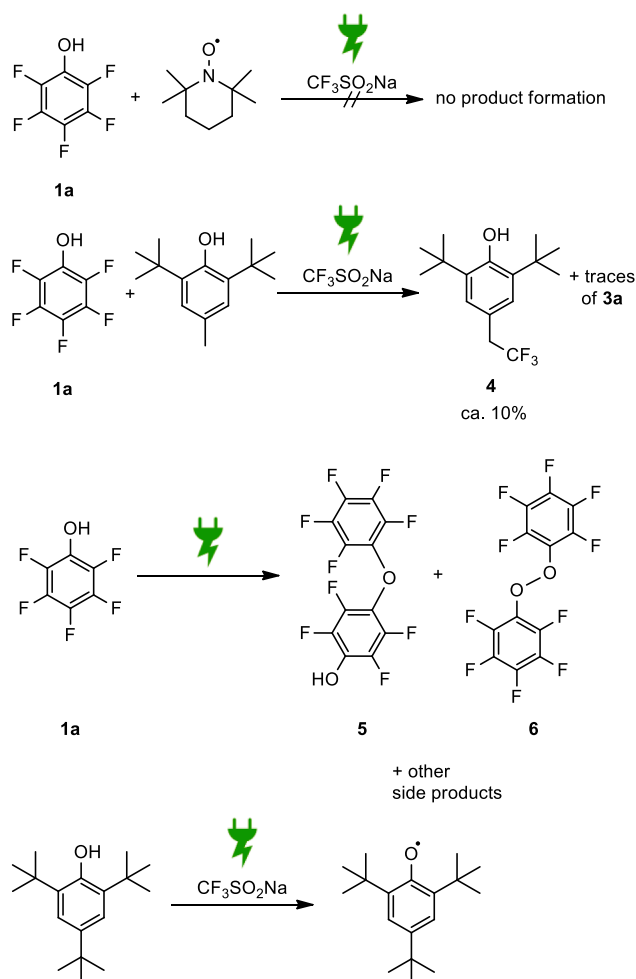
a bromine atom, a nitrile group or a hydrogen atom (**1b-d**), the desired products **3b-d** could be obtained in yields between 8% and 50%. By application of phenols with an aromatic C-H bond (**1d,e,i**), trifluoromethylation at the aromatic system was observed as a side reaction. Due to formation of those byproducts, the target molecules **3d,e,i** could be obtained only in low yields (between 10% and 30%). In contrast, when using persubstituted phenols, the trifluoromethylation reaction was highly selective, because only the desired substitution at the oxygen atom occurred. Pentachlorophenol **1f** gave **3f** in 45% yield. A Cl/CF<sub>3</sub> exchange could be observed only as a minor side reaction. We also investigated the scope of the reaction with larger fluorinated phenols **1g-i**. The corresponding trifluoromethyl ethers **3g-i** were isolated in yields between 10% and 63%. In the case of **3i**, the low yields were a result of incomplete conversion of the starting materials and side reactions. However, increasing the applied amount of charge did not lead to a better conversion.

To demonstrate the scalability of our method, a gram-scale *O*-trifluoromethylation of **1a** and **1g** was performed. The gram-scale reactions proceeded well to form the desired trifluoromethyl ethers **3a** in 74% yield (<sup>19</sup>F NMR) and **3g** in 55% isolated yield.

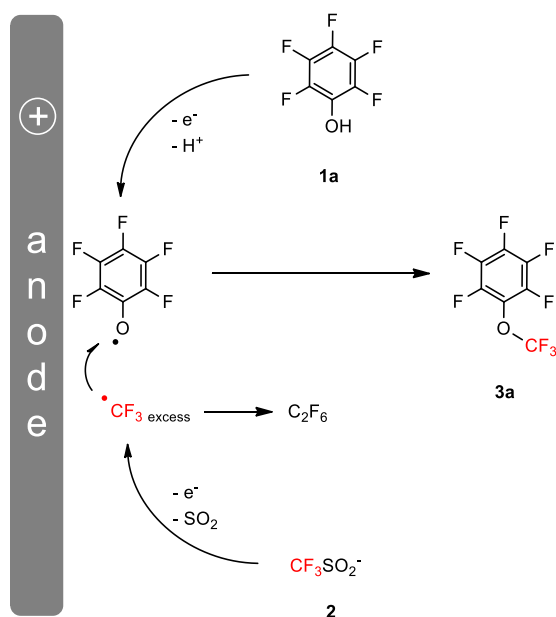
### 3.3. Mechanistic studies

A series of experiments was carried out to gain insights about the mechanism of the reaction. When pentafluorophenol **1a** and trifluoromethane sulfinate **2** were electrolyzed in the presence of an excess of radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), the formation of trifluoromethyl ether **3a** was suppressed, but no trapping product was detected. In contrast, when using 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a radical scavenger, the trapping product BHT-CF<sub>3</sub> **4** was detected in 10% yield together with small amounts of **3a**. These observations indicate the involvement of CF<sub>3</sub> radicals in the reaction, in accordance with previous reports [30].

To gain further information about the mechanism, cyclic voltammetry experiments were conducted with only pentafluorophenol **1a** and Langlois reagent **2** (**Fig. 1**).



**Scheme 3.** Control experiments with radical scavengers TEMPO and BHT (first and second rows), experiments without trifluoromethane sulfinate **2** (third row), and attempted trifluoromethylation of an electron-rich phenol.



**Scheme 4.** Proposed mechanism for the electrochemical O-trifluoromethylation of pentafluorophenol **1a** with trifluoromethane sulfinate **2**.

We found that the oxidation potential of **1a** (1.07 V) is lower than the potential of sulfinate **2** oxidation (1.33 V), which implies that **1a** is oxidized first during the electrolysis, forming pentafluorophenoxy radicals. The presence of those radicals was demonstrated by constant current electrolysis of **1a** without trifluoromethyl source **2** and detection of the dimerization product **5** as the main product by GC-MS, which according to the literature [31] is formed via the phenoxy radical (Scheme 3, third row). Also, the simple recombination product of the phenoxy radicals, the peroxide **6**, could be detected by HRMS. Similarly, the recombination product of the  $\text{CF}_3$  radicals,  $\text{C}_2\text{F}_6$ , could be detected by  $^{19}\text{F}$  NMR in the electrolysis solutions of **2**. The oxidation potentials for **1a** and **2** remained unchanged when the reaction solution containing both **1a** and **2** was characterized by cyclic voltammetry (Fig. 1, blue). Nevertheless, the onset potential (Fig. 1, dotted line) for the oxidation of **2**, where the generation of  $\text{CF}_3$  radicals begins (1.00 V), is lower than the peak potential of phenol oxidation. These observations lead to the conclusion that phenol oxidation and the formation of  $\text{CF}_3$  radicals proceed at the same time. The importance of this co-evolution becomes clear when an electron-rich phenol was employed as the substrate: 2,4,6-tri-*tert*-butylphenol did not yield any trifluoromethylation product, but only the intensely blue phenoxy radical [32]. Based on the results of all these experiments, a plausible mechanism is proposed in Scheme 4. Both phenol **1a** and Langlois reagent **2** are oxidized simultaneously at the anode generating the corresponding radicals, which recombine to form the desired trifluoromethyl ether **3a**. Under these conditions, the  $\text{CF}_3$  radical seems to be the excess species, which suppresses the formation of side products of the phenoxy radical, while some recombination of  $\text{CF}_3^{\bullet}$  to  $\text{C}_2\text{F}_6$  occurs, as confirmed by  $^{19}\text{F}$  NMR.

This mechanism, in which both reactive species have to be generated at the same time, also explains the difference in the yields of compounds **3a-i**, as the oxidation potentials of the corresponding phenols **1a-i** vary slightly with respect to that of the Langlois reagent, resulting in more or less efficient co-evolution of the reactive species.

#### 4. Conclusion

In conclusion, we have developed a simple and sustainable strategy for the preparation of electron-deficient aryl trifluoromethyl ethers by using an electrical current as a green oxidant. No chemical oxidants or metal catalysts were necessary for the reaction. Various phenols, naphthols and biphenyls bearing fluorine, chlorine, bromine and nitrile substituents were successfully transformed to the corresponding  $\text{CF}_3$  ethers by anodic oxidation with Langlois reagent under mild conditions in a single-step reaction. The scalability of the reaction up to gram-scale was also demonstrated. This simple and inexpensive protocol provides easy access to a class of molecules, which is difficult to prepare by conventional organic synthesis.

#### CRediT authorship contribution statement

**Johannes Bernd:** Methodology, Conceptualization, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Philipp Werner:** Investigation. **Marc Zeplichal:** Investigation. **Andreas Terfort:** Supervision, Project administration, Conceptualization, Resources, Validation, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2021.107165>.

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