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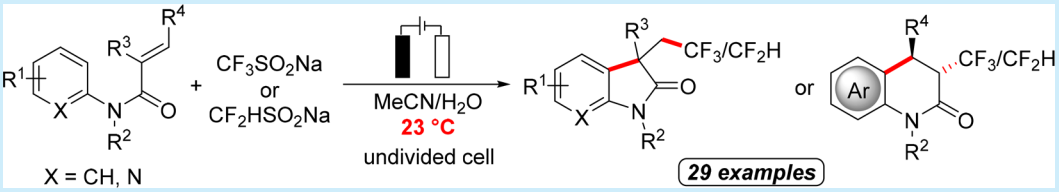
Catalyst-Free, Direct Electrochemical Tri- and Difluoroalkylation/Cyclization: Access to Functionalized Oxindoles and Quinolinones

Zhixiong Ruan,*[,†] Zhixing Huang,[†] Zhongnan Xu,[†] Guangquan Mo,[†] Xu Tian,[†] Xi-Yong Yu,[†] and Lutz Ackermann*[,‡]

[†]Key Laboratory of Molecular Target & Clinical Pharmacology and the State Key Laboratory of Respiratory Disease, School of Pharmaceutical Sciences & the Fifth Affiliated Hospital, Guangzhou Medical University, Guangzhou 511436, P.R. China

[‡]Institut für Organische und Biomolekulare Chemie, Georg-August-Universität, Tammannstraße 2, 37077 Göttingen, Germany

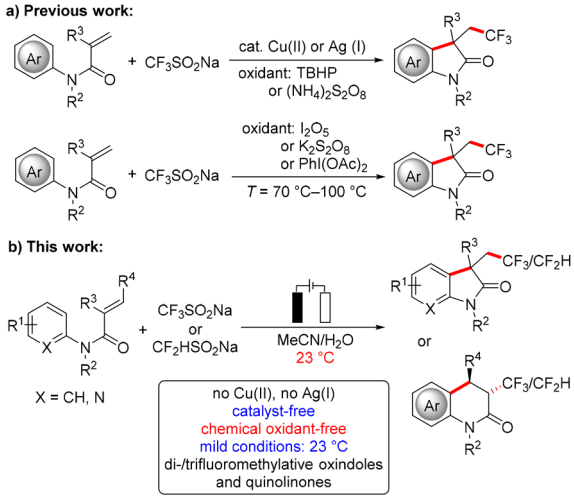
Supporting Information



ABSTRACT: The catalyst-free electrochemical di- and trifluoromethylation/cyclization of N-substituted acrylamides was realized under external oxidant-free conditions. The strategy provides expedient access to fluoroalkylated oxindoles and 3,4-dihydroquinolin-2(1*H*)-ones with ample scope and broad functional group tolerance by mild, direct electrolysis of sodium sulfinates in an undivided cell. Detailed mechanistic studies provided strong support for a SET-based reaction manifold.

The installation of fluorinated substituents into organic compounds uniquely affects their lipophilicity, electronegativity, solubility, metabolic stability, and bioavailability, among others.[1] For instance, fluorine can be found in approximately 20% of all marketed drugs and 30% of all agrochemicals.[2] As a consequence, methodologies for the facile synthesis of fluorinated molecules continue to be in strong demand.[3] Oxindoles and quinolinones are privileged heterocyclic scaffolds found in diverse bioactive natural products and pharmaceuticals.[4] Thus, extensive research efforts have been devoted to the development of methods that provide access to functionalized oxindoles and quinolinones.[5] Among these strategies, oxidative trifluoromethylation of alkenes in *N*-arylacrylamides through trifluoromethyl radical cyclization is one of the most attractive synthetic routes for the construction of fluoroalkylated oxindoles or quinolinones,[5d,6] featuring the inexpensive, solid, and stable Langlois's reagent CF_3SO_2Na.[7] However, despite these indisputable advances, the radical trifluoromethylation largely require transition-metal catalysts,[3l,8] primarily stoichiometric quantities of toxic and cost-intensive copper(II) or silver(I) salts,[9] and strong chemical oxidants, such as reactive hypervalent iodine ($PhI(OAc)_2$),[5f,6c,g] *tert*-butyl peroxide (TBHP),[6b,f] $(NH_4)_2S_2O_8$, or $K_2S_2O_8$,[6a,e] that lead to undesired side products (Scheme 1a). In recent years, electrochemistry has been established as an increasingly powerful tool for molecular synthesis.[10] In this context, Baran and co-workers have recently developed a metal-free radical C−H trifluoromethylation of heteroarenes under electrochemical condition.[11] Moreover, very recently, Zeng reported a bromide-catalyzed indirect electrolysis of CF_3SO_2Na to trifluoromethylated oxindoles.[12] In sharp contrast, within our program on electrochemical transformation,[13] we have now uncovered robust and mild reaction conditions for direct, catalyst-free electrochemical fluoroalkylation/cyclization of alkenes, on which we report herein (Scheme 1b). Notable features of our findings include (a) catalyst-free, direct electrolysis of sulfinate salts for radical formation, (b) effective tandem fluoroalkylation/cyclization being devoid of (photo)redox or metal catalyst and chemical oxidants, (c) exceedingly mild reactions at 23 °C

Scheme 1. Electrochemical Fluoroalkylation/Cyclization



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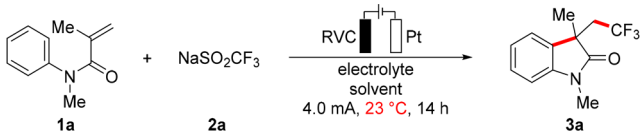
under ambient air, and (d) ample scope toward di- and trifluoromethylated oxindoles and 3,4-dihydroquinolin-2(1*H*)-ones.

Our studies were initiated by probing various reaction conditions for the envisioned electrochemical trifluoromethylation/cyclization of *N*-arylacrylamide **1a** with CF_3SO_2Na (**2a**) under constant current electrolysis conditions (see Table 1).

Table 1. Optimization of Reaction Conditions[a]



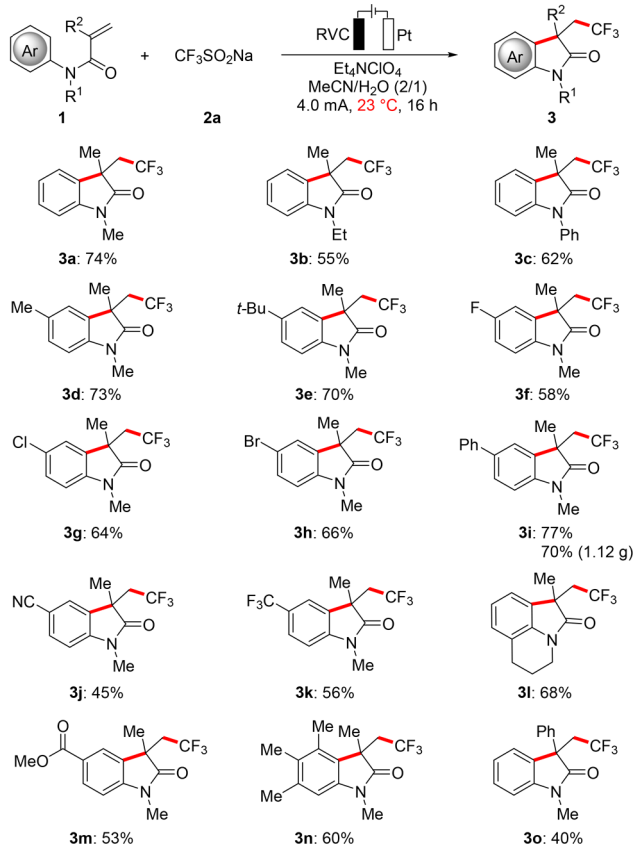
entry	solvent	electrolyte	yield (%)[b]
1	EtOH		19
2	H_2O		<5
3	MeCN		54
4	MeCN/H_2O (1/1)		44
5	MeCN/H_2O (1/2)		43
6	MeCN/H_2O (2/1)		67
7	**MeCN/H_2O (2/1)**	**Et_4NClO_4**	**74**
8	MeCN/H_2O (2/1)	*n*-Bu_4NBF_4	63
9	MeCN/H_2O (2/1)	*n*-Bu_4NOAc	53
10	MeCN/H_2O (2/1)	*n*-Bu_4NClO_4	54
11	MeCN/H_2O (2/1)	*n*-Bu_4NI	0
12	MeCN/H_2O (2/1)	*n*-Bu_4NHSO_4	70
13[c]	MeCN/H_2O (2/1)	Et_4NClO_4	68
14[d]	MeCN/H_2O (2/1)	Et_4NClO_4	0

[a]Reaction conditions: undivided cell, RVC anode, Pt cathode, constant current = 4.0 mA, **1a** (0.5 mmol), **2a** (1.5 mmol), electrolyte (1.0 mmol), solvent (5.0 mL), under air, 23 °C, 14 h. [b]Yield of isolated products. [c]$Zn(SO_2CF_3)_2$ (0.75 mmol) instead of $NaSO_2CF_3$. [d]No electricity.

Preliminary experimentation highlighted a mixture of CH_3CN and H_2O (v/v 2:1) as the optimal solvent for the trifluoromethylation/cyclization of alkene **1a** (entries 1−6). Among a set of representative electrolytes (entries 7−12), Et_4NClO_4 salt provided the optimal results and the desired product **3a** was obtained in 74% yield (entry 7); however, other salts such as *n*-Bu_4NI failed to deliver the functionalized oxindole (entry 11). Notably, $Zn(SO_2CF_3)_2$ as the trifluoromethylation source gave a comparable efficacy (entry 13). The robustness of the scalable electrocatalysis was reflected by the outstanding performance under an atmosphere of ambient air. Control experiments verified the essential nature of the electricity (entry 14).

With the optimal reaction conditions in hand, we next explored its versatility with a set of representative *N*-arylacrylamides **1** (Scheme 2). Thus, the electrochemical trifluoromethylation/cyclization manifold proved amenable to both electron-rich and electron-deficient substituents. Therefore, a variety of synthetically useful electrophilic functional groups were fully tolerated, including chloro, bromo, cyano, and ester substituents, which should prove invaluable for further late-stage manipulation. The electrochemical difunctionalization of acrylamides **1** smoothly proceeded with various N-substituents. The use of α-phenyl-substituted acrylamide slightly decreased the yield of **3o**. Furthermore, the reaction could also be performed in the presence of a tetrahydroquinoline moiety **1l**, affording tricyclic oxindole **3l** in 68% yield.

Scheme 2. Catalyst-Free Electrochemical Trifluoromethylation



The difluoromethyl group represents a key structural motif as lipophilic hydrogen-bond donor as well as an isostere for OH or SH groups.[14] Therefore, we turned our attention to the electrochemical difluoromethylation with differently substituted *N*-arylacrylamides **1** and sodium difluoromethanesulfinate (**2b**) (Scheme 3). Hence, the catalyst-free electrochemical difluoromethylation/cyclization of activated alkenes was tolerant of various electrophilic functional substituents, such as chloro, bromo, and ester groups. It is noteworthy that the azaindole **1k** was also fully tolerated and furnished the desired difluoromethylated oxindole **4k**.

The electrochemical fluoroalkylation/cyclization regime was not restricted to *N*-arylacrylamides **1**. Indeed, *N*-arylcinnamamides **5** were successfully converted into 3,4-dihydroquinolin-2(1*H*)-ones **6** under slightly modified reaction conditions (Scheme 4).[15]

In consideration of the remarkable performance of the catalyst-free electro-oxidative fluoroalkylation, we became intrigued to delineate its mode of action. To this end, cyclic voltammetry experiments were performed. Cyclic voltammetric analysis revealed key mechanistic insights into the electrochemical functionalization (Figure 1).[15] The voltammogram disclosed that anodic oxidation of the sulfonate anions **2a** or **2b**, followed by an irreversible reaction, occurred at a potential of ca. 1.4 or 1.1 V (vs Ag/AgCl), respectively, well below the oxidation potential of the substrate **1a** (1.8 V), indicating a direct oxidation of the *N*-arylacrylamide unlikely to be operative.

In addition, BHT (**7**, 2,4-di-*tert*-butyl-4-methylphenol) was selected as a typical radical trapping agent because its oxidation occurred at lower potential than for the substrate **1a** but at a

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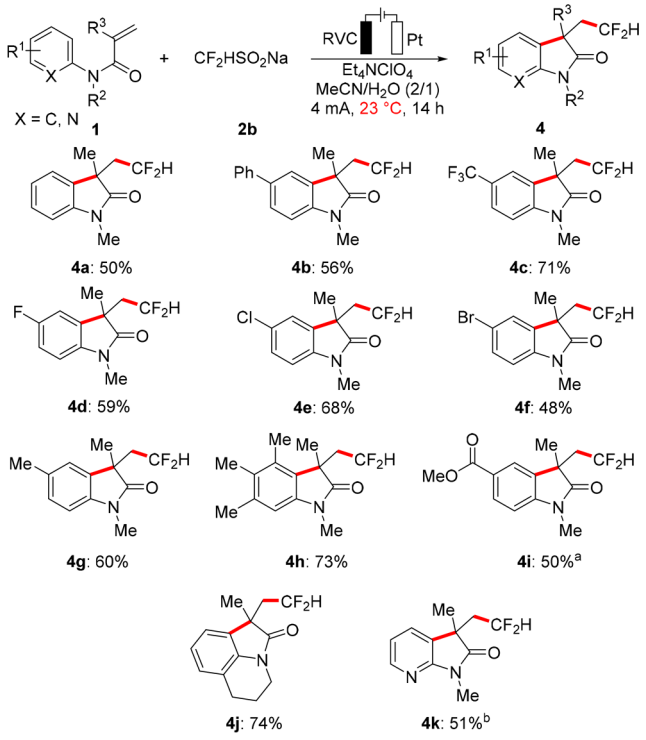
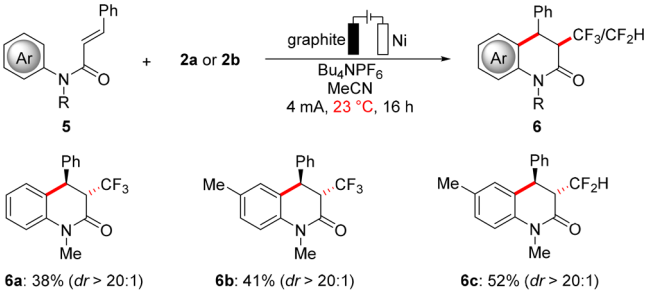
Scheme 3. Direct Electrochemical Difluoromethylation



[a]MeCN (5 mL). [b]MeCN (5 mL), 2 mA, 50 °C, 6 h.

Scheme 4. Catalyst-Free Electrochemical Di- and Trifluoromethylation of *N*-Arylcinnamamides 5



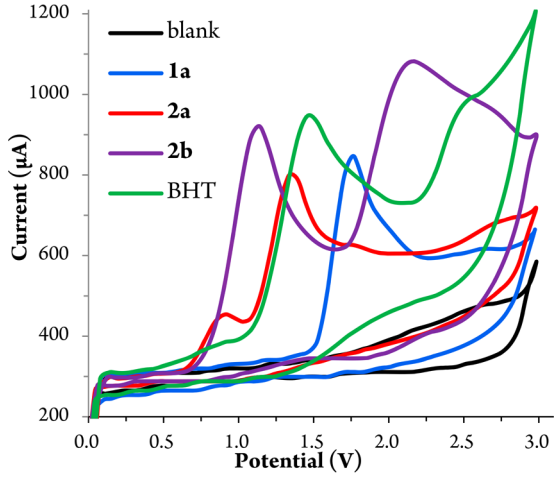
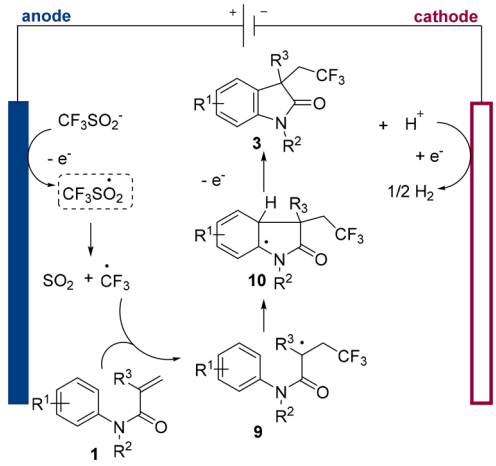


Figure 1. Cyclic voltammetry studies.

considerably higher potential than for the triflinate **2a**. Thus, the trifluoromethylation/cyclization of substrate **1a** was fully suppressed upon the addition of the radical scavenger BHT with a trace of desired product formed, suggestive of a single-electron transfer (SET) process. Gratifyingly, evidence for the radical intermediate **9** (Scheme 5) could be provided by the isolation and full characterization of the BHT adduct **8**.[15]

Scheme 5. Proposed Mechanism



Based on our studies, a plausible mechanistic scenario was proposed for the catalyst-free, electrochemical fluoroalkylation/cyclization in Scheme 5. The anodic oxidation of the sulfinate anion produces the corresponding radical that decomposes to the CF_3 radical in a desulfurative manner.[16] Attack of the CF_3 radical to the alkene, in the vicinity of the anode, results in intermediate **9**, which is further intramolecularly cyclized to the intermediate **10**. Finally, further aromatization affords the corresponding product **3** under anodic oxidation conditions. Hydrogen cations are concurrently reduced on the cathode, releasing molecular hydrogen.

In summary, we have developed a mild and efficient method for the preparation of biologically meaningful functionalized oxindoles or 3,4-dihydroquinolin-2(1*H*)-ones by user-friendly, electrochemical fluoroalkylation/cyclization of N-substituted acrylamides under catalyst- and chemical-oxidant-free conditions. The robust catalyst-free electrochemical di/trifluoromethylation/cyclization proved broadly applicable toward various *N*-aryacrylamides as well as N-heterocyclic acrylamides. Detailed mechanistic studies provided strong support for a SET-based reaction manifold in the direct electrosynthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00361.

Experimental procedures, characterization data, and ^1H and ^{13}C NMR spectra for all products (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zruan@gzhmu.edu.cn.
*E-mail: lutz.ackermann@chemie.uni-goettingen.de.

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ORCID

Lutz Ackermann: 0000-0001-7034-8772

Notes

The authors declare no competing financial interest.

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(15) For detailed information, see the Supporting Information.

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