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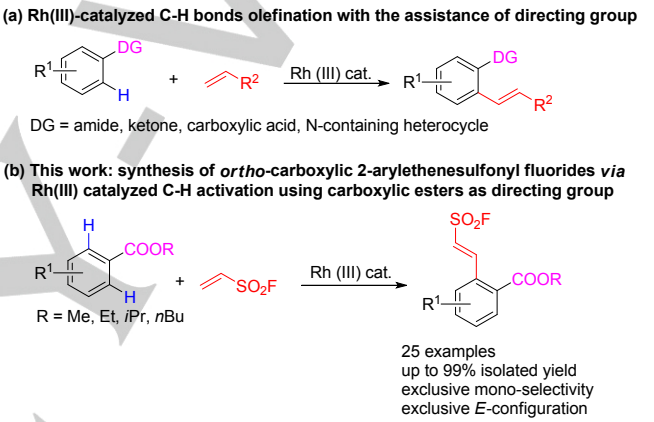
Rh-Catalyzed Carboxylates Directed C-H Activation for Synthesis of *ortho*-Carboxylic 2-Arylethenesulfonyl Fluorides: Access to Unique Electrophiles for SuFEx Click Chemistry

Shi-Meng Wang,[a] Balakrishna Moku,[a] Jing Leng[a] and Hua-Li Qin*[a]

Dedication ((optional))

Abstract: The first Rh(III)-catalyzed activation of *ortho*-C-H bonds of arylcarboxylic esters for monoselective coupling with ethenesulfonyl fluoride (ESF) was developed. This protocol provides a convenient procedure to synthesize a class of otherwise difficult to access 2-arylethenesulfonyl fluorides possessing *ortho*-carboxylic esters functionality. The 25 examples and up to 99% isolated yields of 2-arylethenesulfonyl fluorides bearing versatile carboxylic groups make this method remarkably applicable in developing of biological and pharmacological active ethenesulfonyl fluoride type of covalent drug candidates.

Sulfur (VI) fluoride exchange (SuFEx), a class of rapidly developing click reactions for introducing diversity-oriented sulfur (VI)-based functional groups and connectivity have been utilized in a variety of research fields.[1] 2-Arylethenesulfonyl fluorides, a family of irreplaceable unique scaffolds of SuFEx chemistry, a series of selectively addressable bifunctional electrophiles and potential covalent pharmacophores have recently been synthesized *via* Pd catalyzed Heck-type of reactions.[2] However, to introduce 2-arylethenesulfonyl fluoride into biological systems for the development of new covalent drugs or enzyme inhibitors is still a great challenge, because when both of the two electrophilic sites (the olefinic site and a latent S-F) are essential for targeted molecules, a third versatile building block is required for the preparation of diverse compound libraries to increase the chance of identifying drug candidates as well as lead compounds optimization.[3] Carboxylic acids and esters are important chemicals presented in pharmaceuticals, polymers, agrochemicals, natural products and biological systems and also have wide application as versatile building blocks in organic synthesis and drug discovery.[4] Therefore, the installation of carboxylic group adjacent to the olefinic site of 2-arylethenesulfonyl fluoride will significantly accelerate 2-arylethenesulfonyl fluoride based covalent drugs discovery and development. Unfortunately, there were no accomplished examples on accessing *ortho*-carboxylic 2-arylethenesulfonyl fluorides using the present established Pd-catalysed Heck-type of reactions,[2] which may be attributed to the steric hindrance and the passivation effect of the *ortho* carboxylic group, accordingly the development of reliable methods for the preparation of carboxylic groups functionalized 2-arylethenesulfonyl fluorides remains a major challenge for evolving of SuFEx chemistry and thus is highly desirable.



Scheme 1. Strategies for accessing to ortho-carboxylic 2-arylethenesulfonyl fluorides.

Transition-metal-catalyzed direct C−H bond functionalizations have emerged as a powerful tool for the diverse C-C and C-X bond formations in a step and atom-economical fashion,[5] among which Rh has been particularly recognized as one of the most powerful metals for the activation of aromatic C-H bonds to react with olefins with the assistance of various directing group.[6] In particular, amides, ketones, carboxylic acids and N-containing heterocycles are frequently employed as directing groups in the Rh-catalysed olefination.[7] However, carboxylic esters, one of the most versatile moieties, has gained very limited exploration as directing group for Rh catalyzed C-H bonds functionalization because of their much weaker coordination to metals for triggering the desired reactions.[8] Herein, we report the first Rh catalyzed activation of *ortho* C-H bonds of arylcarboxylic esters for monoselective coupling with ethenesulfonyl fluoride to synthesize the otherwise very difficult to access *ortho* carboxylic esters functionalized 2-arylethenesulfonyl fluorides as a part of our ongoing research on SuFEx chemistry (Scheme 1, b).[1n, 2a-c, 2e]

Initially, we investigated the reaction of ethyl 4-methoxybenzoate (**1a**) and ESF (**2**) using reported conditions employing silver and copper as oxidants.[8] The reaction was found to proceed in low yield with only 12% desired product **3a**

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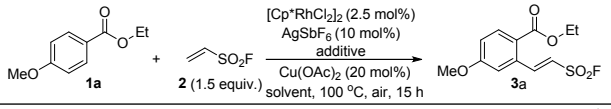
obtained (Table 1, entry 1). Various solvents were subsequently tested, both 1,2-dichloroethane and benzo trifluoride gave improved yields while benzo trifluoride gave a cleaner reaction product (Table 1, entry 1-6). The screening of many other silver salts, copper salts and different reaction temperatures failed to further improve the yields. Fortunately, when 1.0 equivalent of AcOH was added to the reaction, the yield of product was elevated to 92%. Subsequently, the equivalent of AcOH were examined and 5.0 equivalent AcOH gave a satisfying yield of 96% and thus was used as the condition of choice (Table 1, entry 12). The stronger acids of TfOH or CF_3COOH promoted this reaction in a very low yield (Table 1, entry 13, 14).

Table 1. Optimization of Reaction Conditions [a]

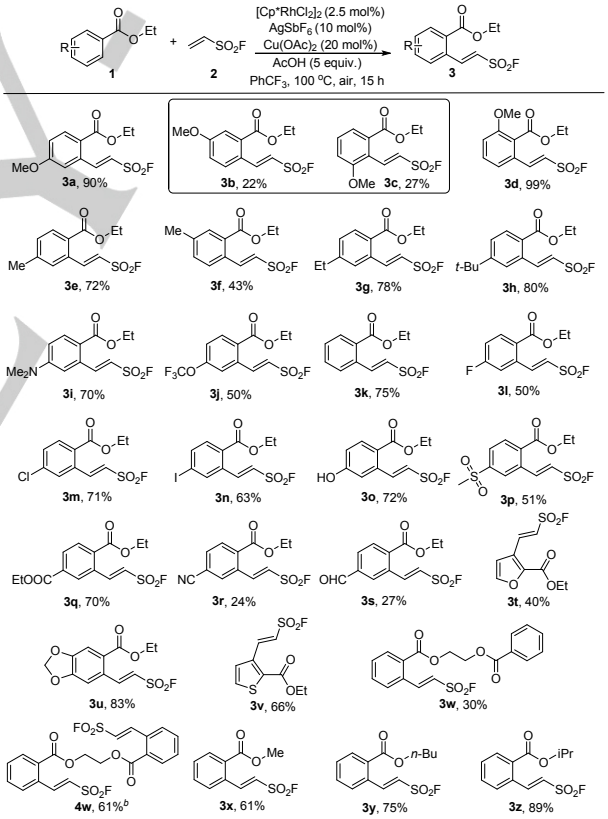


Entry	solvent	additive (equiv.)	Yield (%)[b]
1	dioxane	–	12
2	DCE	–	67
3	THF	–	8
4	HFIP	–	28
5	AcOH	–	36
6	$PhCF_3$	–	68
7[c]	$PhCF_3$	–	20
8[d]	$PhCF_3$	–	9
9	$PhCF_3$	AcOH (1.0)	92
10	$PhCF_3$	AcOH (0.5)	90
11	$PhCF_3$	AcOH(2.0)	93
12	$PhCF_3$	AcOH(5.0)	96
13	$PhCF_3$	TFA (1.0)	7
14	$PhCF_3$	TfOH (1.0)	trace

[a] Reaction conditions: a mixture of **1a** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (20 mol%), additive and solvents (2 mL) reacted under an air atmosphere at 100 °C for 15 h. [b] The yield was determined by HPLC using **3a** (t_R = 6.401 min, λ_{max} = 241.7 nm, water / methanol = 25 : 75 (v / v)) as the external standard. [c] $Cu(OAc)_2$ (2.0 equiv.) was used. [d] $AgSbF_6$ (1.0 equiv.) was used.

With the optimized conditions in hands, we next investigated the substrate scope of arylcarboxylic esters **1**. To our delight, a variety of substituted esters was alkenylated smoothly with ESF **2** to provide the fluorosulfonylvinylation products **3** in modest to excellent yield (up to 99%, Table 2). Both electron-donating groups, such as OMe, Me and NMe_2, and electron-withdrawing groups, such as cyano, formyl and ester on the aryl rings, were well tolerated. When the catalytic system was applied to *meta*-substituted phenyl esters (*ortho*, *meta*, or *para* refers substituted positions to carboxylic ester groups for all the examples), it was noteworthy to find that the methyl-substituted substrate (**1f**) afford the less sterically hindered products **3f** as the only regio isomer, while methoxy-substituted substrate (**1b**) gave a mixture of both mono-*ortho*-alkenylated products **3b** and **3c** with almost no regioselectivity. It was also notable that *ortho*-methyl, chloro, and bromo substituted substrates afforded mixtures of several unidentified compounds rather than the desired pure products under the standard conditions, while *ortho*-methoxy-substituted substrate **1d** gave the corresponding pure product **3d** in 99% yield. The reason that *ortho*-methyl, chloro, and bromo substituted substrates generated unidentified mixtures could be attributed to the conjugate addition between *ortho* C−H bonds of the arylcarboxylic ester and Michael acceptor ESF.[9] Trifluoromethoxy substituted substrate (**1j**) was also smoothly transformed into its corresponding product **3j**. Halide substrates **1l**-**1n**, which offered an opportunity for further chemical manipulation, were also tolerated in this transformation. Excellent efficacy was also observed in transforming of phenolic hydroxy substrate **1o** to **3o**, even though phenolic hydroxy is reactive to sulfonyl fluoride group. In addition, heterocyclic carboxylic esters **1t** and **1v** were also compatible with this catalytic system, giving good yields of desired products **3t** and **3v** respectively. For ethane-1,2-diyl dibenzoate **1w**, mono-fluorosulfonylvinylation product **3w** was obtained in 30% yield under the standard conditions. Interestingly, when the amount of ESF was increased to 10.0 equivalent, 61% bis-fluorosulfonylvinylation product **4w** was obtained instead while only a trace amount of mono-fluorosulfonylvinylation product **3w** was observed.

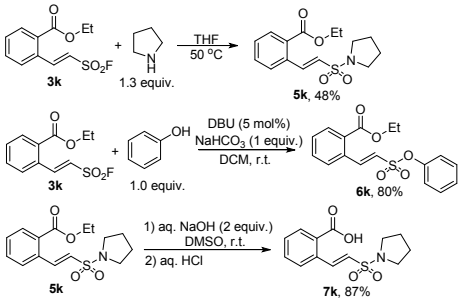
Table 2. Scope of arylcarboxylic esters **1** [a]



[a] Reaction conditions: **1** (1.0 mmol, 1.0 equiv.), **2** (1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (1.0 equiv), $Cu(OAc)_2$ (20 mol%), AcOH (5 equiv.), $PhCF_3$ (5.0 mL), 100 °C, 15 h. [b] **2** (10.0 equiv.) was used and reacted for 48 h.

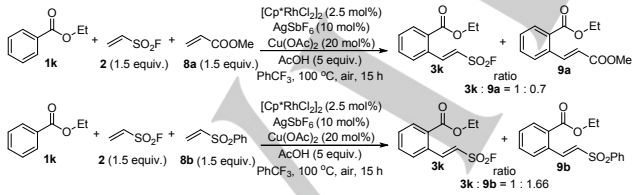
The effect of directing groups of carboxylic esters were also screened, it is worthy of note that in addition to ethyl esters, methyl ester **1x**, *n*-butyl ester **1y** and *i*-propyl ester **1z** provided their corresponding products **3x**, **3y**, **3z** in good yields as well. Isopropyl benzoate provided relatively higher yield of alkenylation product, while methyl, ethyl and butyl benzoates showed similar efficacy in the reaction with ESF. Whereas, the directing groups of *tert*-Butyl, phenyl and benzyl benzoates were found to be nonreactive under these conditions.

Considering that the carboxylic esters are versatile building blocks and the 2-arylethenesulfonyl fluorides can serve as excellent SuFEx coupling partners,[1a, 2a] the synthetic utility of *ortho* carboxylic ester functionalized 2-arylethenesulfonyl fluorides was demonstrated in Scheme 2. **3k** reacted with pyrrolidine in THF at 50 °C to provide sulfonamide **5k** in 48% yield. On the other hand, in the presence of 5 mol % of 1,8-diazabicycloundec-7-ene (DBU) and 1 equivalent of $NaHCO_3$, **3k** reacted with phenol in dichloromethane to afford the sulfonate **6k** in 80% isolated yield, which demonstrated **3k** can proceed selective substitution at the S^{VI}-F bond position with the adjacent olefin moiety unaffected. In addition, in aqueous NaOH solution, the ester group of **5k** was successfully hydrolyzed into the corresponding carboxylic acid **7k** while the sulfonyl amide was not hydrolyzed, the carboxylic acid can further be used as versatile building block to synthesized various useful moieties in drug discovery.



Scheme 2. Diverse derivations of **3k**.

In addition, a competitive reaction of ESF and other conjugated olefins with **1k** under the condition of Scheme 3 was performed to evaluate the general reactivity of ESF in the Rh(III)-catalyzed C-H coupling reaction (scheme 3). It was very interesting to find that methyl acrylate was a little less reactive than ESF while phenyl vinyl sulfone was more reactive than ESF. The result was just opposite to the palladium catalyzed Heck type of reactions, where the ESF was just about 1% as reactive as methyl acrylate but more reactive than phenyl vinyl sulfone.[2b]



Scheme 3. The competition reactions between ESF and other conjugated olefins as coupling partners in the Rh(III)-catalyzed C-H coupling reaction.

In conclusion, the synthesis of a class of the previous not accessible but very useful *ortho*-carboxylic esters functionalized 2-arylethenesulfonyl fluorides was achieved through Rh catalyzed activation of *ortho*-sp^2 C-H bonds for monoselective coupling with ethenesulfonyl fluoride using arylcarboxylic esters as directing group. This method featured a wide scope capacity and good to excellent yields. The successful introducing of carboxylic group adjacent to the olefinic site of 2-arylethenesulfonyl fluoride will significantly accelerate 2-arylethenesulfonyl fluoride based SuFEx reactions as well as covalent drugs discovery and development. Further studies on the applications of these *ortho* carboxylic ester functionalized 2-arylethenesulfonyl fluorides are undergoing in our laboratory.

Experimental Section

Procedures for the synthesis of **3**

An oven-dried screw cap test tube was charged with arylcarboxylic ester (**1**, 1.0 mmol), ethenesulfonyl fluoride (ESF, **2**, 1.5 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (20 mol%), AcOH (5.0 mmol, 5.0 equiv.) and $PhCF_3$ (5 mL) under an air atomosphere. The resulting mixture was stirred at 100 °C for 15 h before concentrating under vacuum. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product **3**.

Acknowledgements

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Keywords: C-H activation • arylcarboxylic esters • ethenesulfonyl fluoride • arylethenesulfonyl fluorides • sulfur (VI) fluoride exchange (SuFEx)

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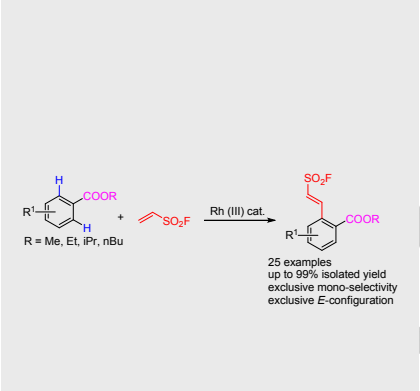

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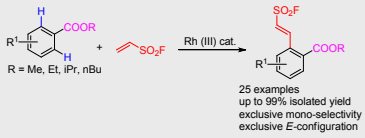

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Rh-Catalyzed Carboxylates Directed Activation of *sp²* C-H Bonds for the Synthesis of *ortho*-Carboxylic 2-Arylethenesulfonyl Fluorides: Access to a New Class of Unique Electrophiles for SuFEx Click Chemistry

A carboxylic ester directed monoselective coupling of sp^2 C-H bonds with ethenesulfonyl fluoride (ESF) was achieved using Rh(III) catalyst. This protocol allows, for the first time, the access to a class of *ortho*-carboxylic group functionalized 2-arylethenesulfonyl fluorides. The versatile and unique properties of carboxylic groups will significantly improve the capability of using 2-arylethenesulfonyl fluorides as covalent probes and in drug discovery.