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Catalyst-free Geminal Aminofluorination of *ortho*-Sulfonamide-Tethered Alkylidenecyclopropanes *via* Wagner-Meerwein Rearrangement†

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A catalyst-free intramolecular geminal aminofluorination of *ortho*-sulfonamide-tethered alkylidenecyclopropanes has been developed. The reaction proceeded through twice SET processes with Selectfluor to give the fluorinated cyclopropylcarbinyl cation and the further Wagner-Meerwein rearrangement to generate cyclobutyl carbocation, which undergoes intramolecular nucleophilic capture by amide to forge fluorinated cyclobuta[*b*]indoline derivatives. A polycyclic multi-fluorinated byproduct was also formed through a Ritter-type reaction in some cases.

Introducing a fluorine atom into organic scaffolds can significantly improve their physical and chemical properties such as higher thermal stability, higher stability to metabolic degradation, increased lipophilicity and lower polarity as well as weaker intermolecular interactions, which are of great significance in pharmaceuticals,[1a] agrochemicals,[1b] material sciences,[1d] and biochemical imaging.[1c] Therefore, the synthetic methods on fluorofunctionalizations of small molecules to access various substances containing fluorine atom have attracted a substantial amount of attention from organic chemists. Thus far, although great progress has been made in the fluorofunctionalization of small molecules at vicinal carbon atoms,[2] introducing a fluorine atom together with another functional group at the geminal carbon atom remains challenging.[3-5]

Among the reported examples in the geminal fluorofunctionalization, the use of diazo compounds as substrates has been extensively investigated so far.[3] Pioneering studies on hydrofluorination and halofluorination of diazoalkanes and diazoketones were provided by Olah and co-workers,[3a,b] in which pyridinium polyhydrogen fluoride solution was used as the fluorination source in the presence of N-bromosuccinimide (NBS) as oxidant. After that, numerous studies were reported with different fluorine sources, including the use of trifluoro(fluor-oxy)methane (CF_3OF) discovered by Wakselman's group[3c] and hypervalent iodine reagents developed by the groups of Murphy,[3d] Szabó,[3e] and Wang,[3f] respectively. Moreover, the use of Selectfluor, NFSI and HF·Py was reported by the groups of Katzenellenbogen,[3g] Huang,[3h] Szabó[3i] and Gouverneur's group[3j] (Scheme 1a, eq 1). In 2013, Chen and co-workers demonstrated the first visible-light-promoted selective C-H *gem*-difluorination of benzylic hydrogens using Selectfluor as a fluorine source.[4a] One year later, Tang's group reported a method to form difluoromethylated arenes by the activation of benzylic C-H bonds utilizing $AgNO_3$ as catalyst and Selectfluor as a fluorination reagent.[4b] Subsequently, Huang and co-workers conducted the first streamlined strategy for asymmetric α-alkynylation-α-fluorination of ynones with the assistance of chiral phosphoric acid and a recyclable chiral amine auxiliary using Selectfluor as a fluorine source[4c] (Scheme 1a, eq 2). Besides, the *gem*-fluorofunctionalization of alkenes has also emerged as an attractive strategy in introducing fluorine atom into small molecules.[5] In 2014, Szabó's group reported that treatment of hypervalent fluoroiodane with $AgBF_4$ could induce geminal difluorination of styrenes *via* phenonium ion intermediates.[5a,b] In the next year, Oyamada's group developed difluorination of styrenes with $PhI(OCOCF_3)_2$ and pyridine·HF under oxidation conditions.[5c] Furthermore, with regard to unactivated amino alkenes, Toste and co-workers achieved a palladium-catalyzed enantioselective *gem*-fluoroarylation through an oxidative Heck reaction using Selectfluor as the fluorination reagent[5d] (Scheme 1a, eq 3).

Our group has reported a fluorination of methylenecyclopropanes (MCPs) and alkylidenecyclopropanes (ACPs) with NFSI in 2009, affording ring-opened fluorination products in good yields.[6a] Later, Ji's group also developed a similar fluorination process with NFSI or Selectfluor (Scheme 1b, eq 4).[6b] These two reports indicated that the ring-opening of MCPs or ACPs can also provide driving force for introducing fluorine atom into

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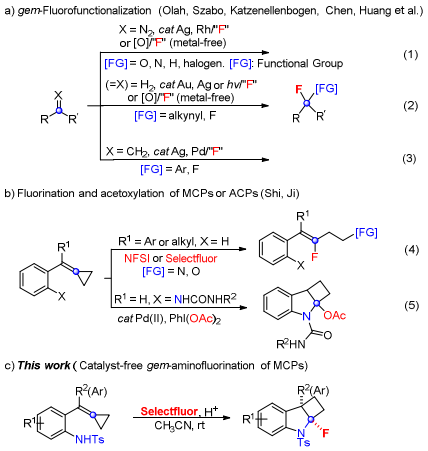
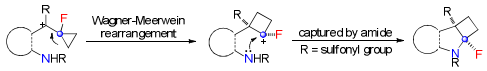
small molecules. More recently, we also presented a Pd(II)-catalyzed *gem*-oxyamination of urea-tethered ACPs through a ring expansion of ACP along with the nucleophilic attack of nitrogen atom onto the *in situ* generated palladium carbenoid species, giving the corresponding cyclobuta[*b*]indolines[6c] (Scheme 1b, eq 5). Herein, we wish to report a novel strategy for the *gem*-aminofluorination of *ortho*-sulfonamide-tethered alkylidenecyclopropanes (ACPs) upon treatment with Selectfluor under catalyst-free condition (Scheme 1c, this work).



Scheme 1. Strategies for *gem*-Fluorofunctionalization Reactions and Fluorination and Acetoxylation of MCPs or ACPs and This Work.

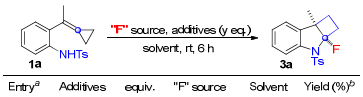


Scheme 2. Our Strategies for *gem*-Aminofluorination of *ortho*-Sulfonamide-tethered Alkylidenecyclopropanes.

To the best of our knowledge, *gem*-aminofluorination is a much less explored area in synthetic organofluorine chemistry.[3i,k] We envisaged that fluorinated cyclopropylcarbinyl cation formed from the oxidation of ACPs with Selectfluor could go through a Wagner-Meerwein rearrangement along with the intramolecular nucleophilic capture by the amide in sequence, affording the corresponding fluorinated cyclobuta[*b*]indoline derivatives[7] (Scheme 2).

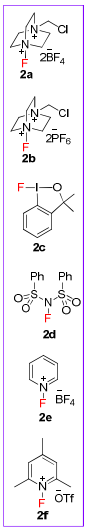
We initiated the investigation by examining the *gem*-aminofluorination of **1a** with Selectfluor **2a** and found that using 3.0 equivalents of **2a** in CH_3CN afforded the desired product **3a** in 68% yield (Table 1, entry 1). The use of Selectfluor **2b** gave **3a** in 41% yield (Table 1, entry 2). The examination of other fluorination reagents **2c**-**2f** revealed that they are totally ineffective in this transformation (Table 1, entry 3). Carrying out the reaction in $MeNO_2$ gave **3a** in 32% yield (Table 1, entry 4) and the other solvents are not suitable for this reaction (Table 1, entry 5). To improve the yield of **3a**, we next examined additives such as InF_3,[8a] bases[1k] and acids[8b] and realized that adding 10 equivalents of acetic acid in CH_3CN produced **3a** in 89% NMR yield and 81% isolated yield under otherwise identical conditions (Table 1, entries 6-18). Further increasing the amount of acetic acid to 100 equivalents did not give the better result[8c] (Table 1, entry 19) (see Supporting Information for more details).

Table 1. Optimization of Conditions[a,b,c,d].



Entry[a]	Additives	equiv.	"F" source	Solvent	Yield (%)[b]
1	none	0	**2a**	MeCN	68
2	none	0	**2b**	MeCN	41
3	none	0	**2c-2f**	MeCN	<5
4	none	0	**2a**	$MeNO_2$	32
5	none	0	**2a**	Others[c]	<5
6	InF_3	0.2	**2a**	MeCN	46
7	$NaHCO_3$	2	**2a**	MeCN	36
8	DABCO	2	**2a**	MeCN	17
9	2,6-lutidine	2	**2a**	MeCN	31
10	PhOH	2	**2a**	MeCN	46
11	PivOH	2	**2a**	MeCN	68
12	PhCOCOOH	2	**2a**	MeCN	74
13	PhCOOH	2	**2a**	MeCN	78
14	CH_3COOH	2	**2a**	MeCN	79
15	CF_3COOH	2	**2a**	MeCN	trace
16	citric acid	2	**2a**	MeCN	66
17	CH_3COOH	5	**2a**	MeCN	82
18	CH_3COOH	10	**2a**	MeCN	89 (81[d])
19	CH_3COOH	100	**2a**	MeCN	65

[a] All reactions were carried out with **1a** (0.1 mmol) and "F" source (0.3 mmol) in solvent (1.0 mL) at ambient temperature for 6 h. [b] ^{19}F NMR yields using 1-fluoronaphthalene as an internal standard. [c] Others including PhCN, EtCN, toluene, DCM, acetone, DCE, ether, MeOH, THF and EtOAc. [d] Isolated yields.



With the optimized conditions in hand, we next investigated the substrate scope and its limitations, and the results are summarized in Scheme 3. Overall, most of the reactions proceeded smoothly under the optimal conditions, giving the desired products in moderate to good yields except for substrates **1f** and **1u**. At first, substrates **1b** to **1e**, having different sulfonyl protecting groups, were examined, yielding the desired products **3b** to **3e** in 32-69% yields. Substrate **1f**, bearing a methyl group, did not give the desired product under the optimal conditions. In all these cases, **3a** was obtained in higher yield. Therefore, tosyl group was used as the protecting group to the other substrates. Substrates **1g**-**1i** with different alkyl substituents afforded the corresponding products **3g**-**3i** in good yields ranging from 71-90% yields. Introducing halogen atoms on the aromatic ring produced the corresponding products **3j**-**3q** in moderate to high yields ranging from 39%-98%. It should be noted that the yield of **3** decreased along with the increasing in the carbon number of alkyl chain in the cases of substrates **1j** *vs* **1k**, **1l** *vs* **1m** *vs* **1n** and **1o** *vs* **1p** *vs* **1q**. Moreover, phenyl substituent is also tolerated, furnishing the desired products **3r**-**3t** in moderate yields. The structure of **3t** was confirmed by X-ray diffraction (see Supporting Information). However, for these substrates bearing electron-rich aromatic rings, the reactions did not proceed effectively as those of electron-poor ones. For example, in the case of substrate **1u** bearing a methoxyl group at the benzene ring, the desired product was observed in less than 5% yield under identical conditions although the starting materials were completely consumed. For substrate **1v**, the reaction gave the desired product **3v** in 36% yield within 5 h. Furthermore, in the case of substrate **1w**, difluorinated product **3w'** was yielded in 23% yield along with the desired product **3w** in 6% yield under the standard reaction conditions, suggesting that strong oxidation conditions are not beneficial to the electron-rich substrates. The structure of **3w'** was

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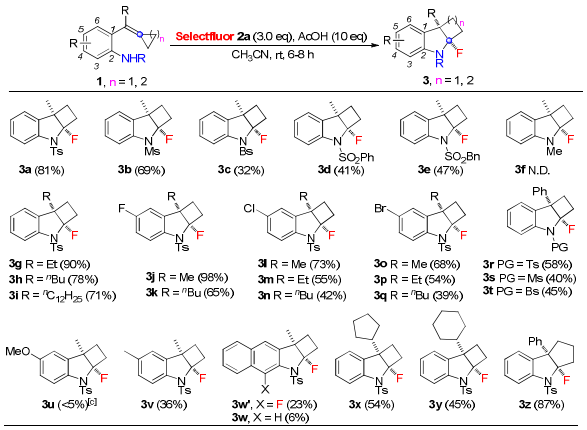
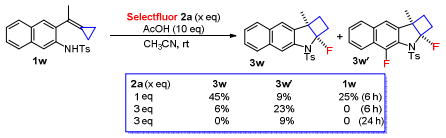
confirmed by X-ray diffraction (see Scheme 4 and Supporting Information for more information). Substrates **1x** and **1y** having cyclopentyl and cyclohexyl groups also afforded the desired products **3x** and **3y** in 54% and 45% yields, respectively. Additionally, tosylamide-tethered alkylidenecyclobutane **1z** was compatible in this reaction, giving the corresponding product **3z** in 87% yield.



[a] All reactions were carried out with **1** (0.2 mmol), **Selectfluor 2a** (0.6 mmol), **AcOH** (2.0 mmol) in 2.0 mL CH_3CN at ambient temperature for 6-8 h. [b] Isolated yields. [c] **3u** could not be isolated.

Scheme 3. Substrate Scope for Synthesis of **3**[a,b,c].

The lower yields of electron-rich substrates **3u**-**3w** and the formation of difluorinated product **3w'** warned us that the strong oxidation property of Selecfluor may be harmful to this reaction. Therefore, we reduced the amount of Selectfluor in the reaction with **1w** and the results are summarized in Scheme 4. The use of 1.0 eq of Selecfluor **2a** afforded the desired product **3w** in 45% yield along with **3w'** in 9% yield and 25% of substrate **1w**. Using 3.0 eq of **2a** gave the desired product **3w** in 6% yield along with 23% of **3w'** within 6 h. Product **3w** decomposed and the yield of difluorinated product **3w'** decreased after prolonging the reaction time to 24 h. Thus, it is obvious that both electron-rich substrates and products were instable under the oxidation conditions.[9]

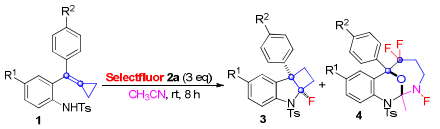


2a (x eq)	3w	3w'	1w
1 eq	45%	9%	25% (6 h)
3 eq	6%	23%	0 (6 h)
3 eq	0%	9%	0 (24 h)

[a] All reactions were carried out with **1w** (0.2 mmol), **Selectfluor 2a** (0.6 mmol), **AcOH** (2.0 mmol) in 2.0 mL CH_3CN at ambient temperature. [b] Isolated yields.

Scheme 4. The Strong Oxidation Property of **Selectfluor 2a**[a,b].

To clarify the reaction mechanism and identify the intermediacy of fluorinated cyclopropylcarbinyl cation,[10] we performed the further exploration using two aromatic rings substituted substrates such as **1aa**-**1ac**, which would enable to stabilize the *in situ* generated benzyl carbocation (Scheme 5).[10e] The crude products have been checked by ^1H and ^{19}F NMR spectroscopy, and we identified a new product for the use of substrates **1ab** and **1ac**. The structure of this new fluorinated product **4ac** was determined by X-ray diffraction,[6ab,10,11] suggesting the existence of fluorinated cyclopropylcarbinyl cation (see Scheme 6 and Supporting Information for more information). Interestingly, the addition of acetic acid could slightly raise the yield of desired product **3ab** from 42% to 45% but impair the formation of **4ab** (entries 2 and 3).

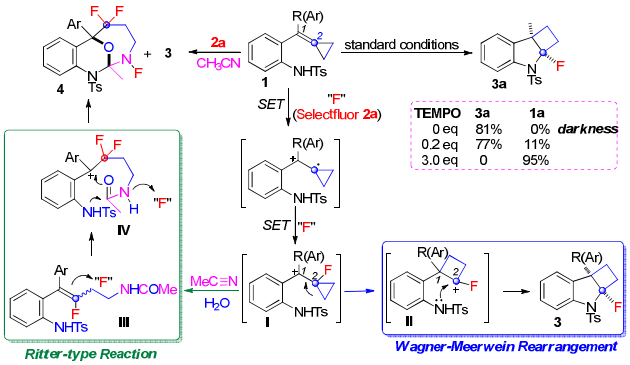


Entry[a]	Substrates	R^1	R^2	3 (%)[b]	4 (%)[b]
1	**1aa**	F	H	**3aa**, 39	**4aa**, trace
2	**1ab**	Cl	H	**3ab**, 42	**4ab**, 8
3[c]	**1ab**	Cl	H	**3ab**, 45	**4ab**, trace
4	**1ac**	H	Br	**3ac**, 39	**4ac**, 9
5[d]	**1ac**	H	Br	**3ac**, 30	**4ac**, 4

[a] All reactions were carried out with **1** (0.2 mmol), **Selectfluor 2a** (0.6 mmol) in 2.0 mL CH_3CN without AcOH for 8 h. [b] Isolated yields. [c] 10 eq of AcOH was added. [d] **1ac** (454.4 mg, 1.0 mmol) and **Selectfluor 2a** (1.06 g, 3.0 mmol) was used.

Scheme 5. Substrate Scope of the Reaction[a,b,c,d].

To obtain more insights into the reaction mechanism, the reaction of **1a** with Selectfluor **2a** was conducted in the presence of 2,2,6,6-tetramethylpiperidinooxy (TEMPO) under the standard conditions. We found that the use of catalytic amount of TEMPO (0.2 eq) reduced the yield of **3a** from 81% to 77% along with the recovery of **1a** in 11%, while, the use of 3.0 eq of TEMPO prohibited the reaction proceeding and **1a** was recovered in 95% yield along with the decomposition of Selectfluor, which has been confirmed by HRMS (see Supporting Information at S96). In addition, the reaction proceeded very well under darkness, suggesting that photo-irradiation does not accelerate the reaction proceeding (see Supporting Information for more details).[12]



Scheme 6. Control Experiments and Proposed Mechanism.

A plausible mechanism for this geminal aminofluorination of functionalized ACPs is outlined in Scheme 6. The reaction is initiated by Selectfluor **2a** through twice SET processes[12b,c] to generate the fluorinated cyclopropylcarbinyl cation **I**, which undergoes a Wagner-Meerwein rearrangement to forge intermediate **II** along with a cascade ring closure process by the intramolecular capture of the amide to afford the product **3** (blue frame). Alternatively, the intermediate **I** can undertake a Ritter-type reaction process to give intermediate **III**,[6a,13] which generates a benzylic cation **IV** upon treating with Selectfluor. Trapping the formed cation by the acetamido group and addition of the sulfonamide group on the formed ring along with fluorination of nitrogen atom[14] afford the

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multi-fluorinated polycyclic product **4** (green frame).

In summary, we have disclosed a novel intramolecular cascade *gem*-aminofluorination of *ortho*-sulfonamide-tethered alkylidenecyclopropanes, proceeding through twice SET processes to form the fluorinated cyclopropylcarbinyl cation using Selectfluor as a fluorination reagent under catalyst-free conditions. The further Wagner-Meerwein rearrangement gives a cyclobutyl carbocation, which can be captured by the amide in an intramolecular manner to produce a variety of fluorinated cyclobuta[*b*]indolines in moderate to good yields. The mechanistic investigations suggested that this reaction proceeds through twice SET processes and the side reaction could afford the Ritter-type polycyclic multi-fluorinated product. Further investigations on the application of this methodology to synthesize more interesting fluorinated compounds are underway in our laboratory.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgment

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15 The structures of **3t**, **3w'** and **4ac** have been confirmed by X-ray diffraction and their CIF data are shown in the Supporting Information.

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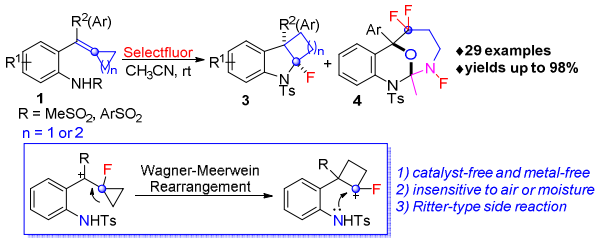
Catalyst-free Geminal Aminofluorination of *ortho*-Sulfonamide-Tethered Alkylidenecyclopropanes *via* Wagner-Meerwein Rearrangement



A catalyst-free intramolecular geminal aminofluorination of *ortho*-sulfonamide-tethered alkylidenecyclopropanes has been developed to forge fluorinated cyclobuta[*b*]indoline derivatives. A polycyclic multi-fluorinated byproduct was also formed through a Ritter-type reaction in some cases.

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