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Research Article

Simple nucleophile/H_2O promoted defluorinative ring-opening of *gem*-difluorocyclopropenes

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ABSTRACT

A novel defluorinative ring-opening of *gem*-difluorocyclopropenes is presented, providing a concise and efficient method for accessing 2-fluoropropenals and 2-fluorobuta-1,3-dienes in moderate to good yields with excellent regio- and stereoselectivities. The reaction is performed under mild conditions with no need of using an excess amount of nucleophilic reagents. Water plays a crucial role in this transformation.

1. Introduction

As favourable peptide bond isosteres, monofluoroalkenes have attracted significant attention in drug discovery due to their superior physicochemical and bioactivity characteristics imparted by the fluorine atom [1–5]. Despite their great potential, previous methods toward these scaffolds usually suffer from low regio- or stereoselectivity and poor functional group tolerance, because of the employment of sensitive reagents [6–10]. The C–F bond functionalization of *gem*-difluoroalkenes provides an alternative strategy for accessing monofluoroalkenes with good stereoselectivity [11–30]. Nevertheless, the high bond dissociation energy of the C–F bond (DH_{298} CH_3–F = 115 kcal/mol) [31] makes β-F elimination difficult, forcing the reactions to conduct under harsh conditions, in which transition metal catalysts or dangerous bases are inevitably needed (Scheme 1a). Moreover, functional groups have limitations in these transformations, as the incorporation of some valuable ones, such as carbonyl groups, into the alkenes, being still pending. In 2011, Rolando reported a palladium-catalyzed stereoconvergent formylation of β-bromo-β-fluorostyrenes with carbon monoxide and sodium formate towards (*Z*)-α-fluorocinnamic aldehydes (Scheme 1b) [32]. However, the reaction predictably suffered from the use of a noble palladium catalyst, especially a high pressure of CO. Therefore, the development of a green, the concise and efficient protocol that enables expanding the scope of introducible functional groups is highly desired.

gem-Difluorocyclopropenes can be concisely and efficiently prepared from simple alkynes with many difluorocarbene sources [33–35]. Nevertheless, their applications in organic transformations are still rare. Sporadic examples include: utilizing 3,3-difluoro-1,2-diarylcyclopropenes (CpFluors) as reactivity-tunable fluorination reagents, Hu and coworkers realized the deoxyfluorination of alcohols and carboxylic acids (Scheme 1c) [36,37]; the group of Chen demonstrated the hydrolysis of *gem*-Difluorocyclopropenes to produce unsaturated acids under acidic conditions (Scheme 1d) [38–40]; highly regio- and stereoselective hydrostannylation, hydroborylation and hydrosilylation of *gem*-difluorocyclopropenes were achieved by Konno's group and Cao's group (Scheme 1e) [41,42]; through a [3 + 2]/[2 + 1] cycloaddition sequence, highly functionalized 5-fluoropyridazines and 4-fluoropyridines were conveniently accessed (Scheme 1f) [43–46]; the group of Yi and ours developed a Cp*Rh(III)-catalyzed [4 + 3] annulation between *N*-methoxyamides and *gem*-Difluorocyclopropenes for the direct assembly of seven-numbered 2*H*-azepin-2-one frameworks (Scheme 1f) [47–52]. Inspired by these results, we envisaged that *gem*-difluorocyclopropenes first conducted a hydrofunctionalization reaction, and if the attached functional groups were electron-rich, it was likely to further provoke a defluorinative ring-opening process and finally formed fluoroolefins [53]. In this process, the release of tough ternary ring tension somewhat counteracted the high C–F bonding energy, facilitating the reaction to proceed under milder conditions.

In continuation of our interest in the transformations of *gem*-difluorocyclopropenes [7k,7m], we herein report a novel defluorinative ring-opening of *gem*-difluorocyclopropenes. The reaction allows a facile and

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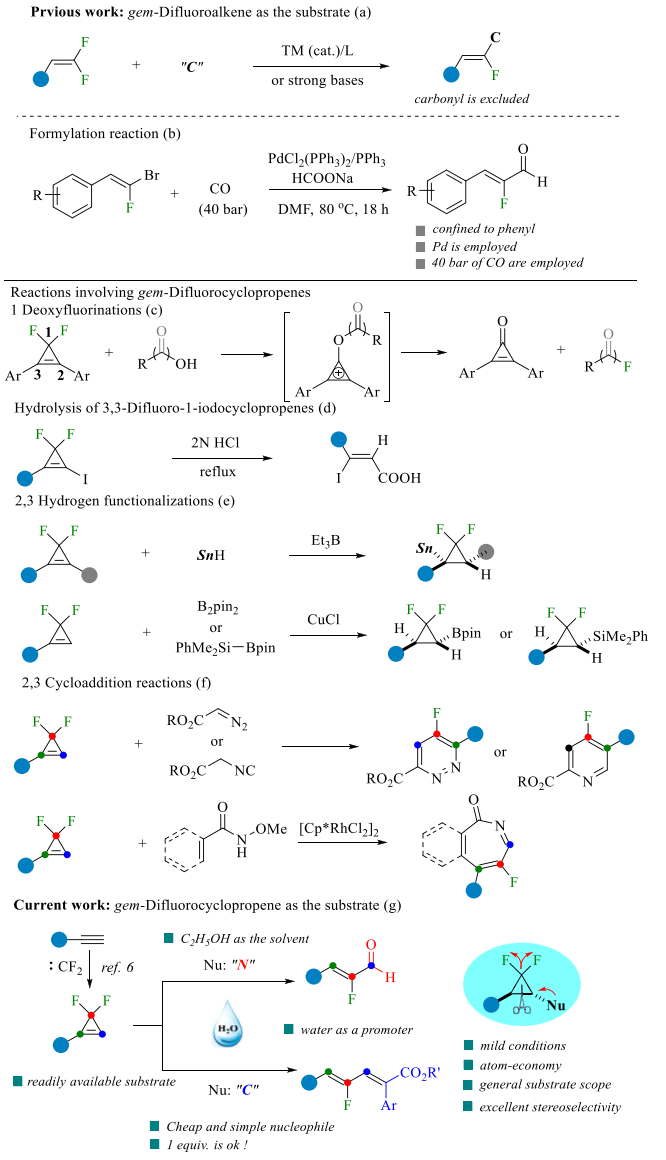


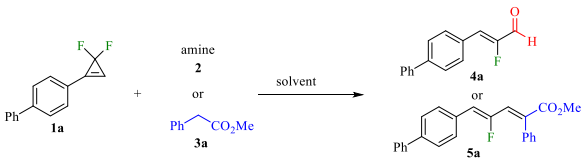
Scheme 1. Preparation of monofluoroalkenes.

stereoselective construction of 2-fluoropropenals [54,55] and 2-fluorobuta-1,3-dienes [56–59] in moderate to good yields (Scheme 1g). Both types of approaches toward monofluorinated olefins are performed under mild and airy conditions, wherein readily available substrates, cheap and simple nucleophiles and bases are employed in 1 equiv. amount. Water not merely promoted the hydrolysis of imines in the synthesis of 2-fluoropropenals, but also facilitated the dissolution of inorganic bases in the preparation of 2-fluorobuta-1,3-dienes, thus playing a crucial role in both transformations. The smooth performance of one-pot reactions, gram-scale experiments and derivatizations proved the practicality of this method.

2. Results and discussion

The reaction was initially screened using *gem*-difluorocyclopropene **1a** as the model substrate, pyrrolidine (**2a**) as the nucleophile, H_2O as the additive, and C_2H_5OH as the solvent at room temperature. To our delight, the desired product **4a** obtained in 76% yield (Table 1, entry 1). Other cyclic secondary amines such as azetidine (**2b**) and morpholine (**2c**) made the conversion of **1a** sparkly reduced (entries 2 and 3), and the reaction could not even proceed in the presence of acyclic secondary amines (entries 4 and 5). The solvents were also detected, other solvents,

Table 1
Optimization of reaction conditions [a,b].



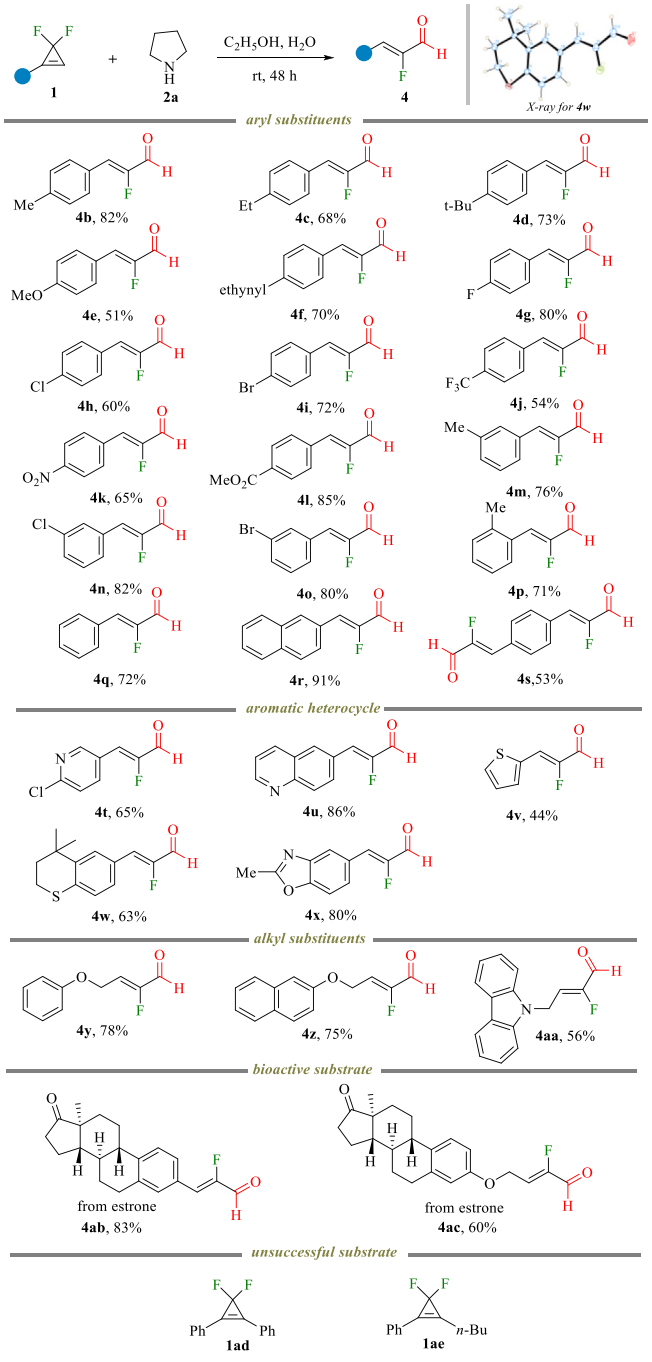
Entry	Nuclephile	Solvent	Yield of 4a [%][b]	Yield of 5a [%][b]
1 [c]	**2a**	C_2H_5OH	76%	
2 [c]	**2b**	C_2H_5OH	71%	
3 [c]	**2c**	C_2H_5OH	42%	
4 [c]	**2d**	C_2H_5OH	N.D.	
5 [c]	**2e**	C_2H_5OH	N.D.	
6	**2a**	DCE	66%	
7	**2a**	toluene	43%	
8	**2a**	CH_3CN	35%	
9	**2a**	DCM	75%	
10 [d]	**2a**	C_2H_5OH	<5%	
11 [e]	**3a**	DMF		81%
12 [f]	**3a**	DMF		75%
13 [g]	**3a**	DMF		71%
14 [d]	**3a**	DMF		27%

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.0 equiv.), H_2O (2.0 equiv.), solvent (1.0 mL, dry), r.t., in air, 48 h.
[b] Isolated yields.
[c] **2a**, pyrrolidine; **2b**, azetidine; **2c**, morpholine; **2d**, diethylamine; **2e**, *N*-methylaniline.
[d] Without H_2O.
[e] **1a** (0.2 mmol), **3a** (1.0 equiv.), Cs_2CO_3 (1.0 equiv.), DMF/H_2O = 1.0 mL/0.1 mL, r.t., in air, 48 h.
[f] Cs_2CO_3 is replaced by K_2CO_3.
[g] Cs_2CO_3 is replaced by Na_2CO_3.

including DCE, toluene, CH_3CN, and DCM, did not present better conversion than C_2H_5OH (entries 6–9). The reaction could hardly take place in the absence of water (entry 10). Then, the reaction was conducted between *gem*-difluorocyclopropene **1a** and methyl phenylacetate **3a** in the presence of Cs_2CO_3 as the base, DMF and H_2O as the solvents, and the desired product **5a** was released in 81% yield. Other bases (entries 11–13) and solvents could not promote the reaction further. The yield of **5a** sharply decreased to 27% without water (entry 14).

With optimized conditions in hand, the reaction between *gem*-difluorocyclopropenes **1a**-**1ac** and pyrrolidine **2a** was next investigated. As shown in Scheme 2, substrates bearing electron-donating substituents such as Me, Et, *t*-Bu and OMe in opposite positions of the phenyl ring worked well, and gave the products **4a**-**4e** in moderate to good yields. Specifically, the substrate with 4-ethynyl substituent was also tolerant and led to the ring-opening product **4f** in 70% yield, which could provide a convenient handle for further conversion. Substrates with electron-withdrawing groups such as F, Cl, Br, CF_3, NO_2 and CO_2Me were subsequently prepared and used in the reaction, and the corresponding products **4g**-**4l** were isolated in 54%–85% yields.

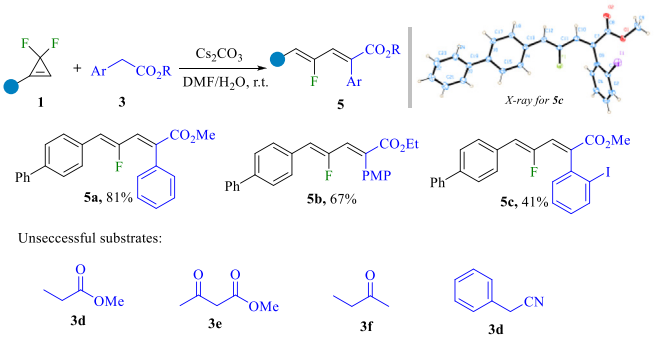
Notably, the results indicated that little influence was exhibited by the steric effect. For example, a 2-methyl-substituted substrate gave product **4p** in 71% yield. Other aromatic heterocycles, such as pyridine **4t**, quinolone **4u**, thiophene **4v**, thiochromane **4w** (CCDC: 2120300) and benzoxazole **4x** were also tolerated well, albeit with slightly lower yields. Moreover, di-2-fluoropropenal product **4s** was easily accessed, with 53% yield under standard conditions, thus offering a practical approach for the construction of complex fluorine-containing conjugated molecules. Then, alkyl-substituted difluorocyclopropenes were evaluated. Methylene groups with oxygen-centred linkages such as phenol or naphthol gave products **4y** and **4z** in 78% and 75% yields, respectively, and nitrogen-centred linkages such as carbazole afforded product **4aa** in 56% yields. To further highlight the synthetic versatility of our method, bioactive estriol derivatives **1 ab** and **1ac** were subjected to the reaction,



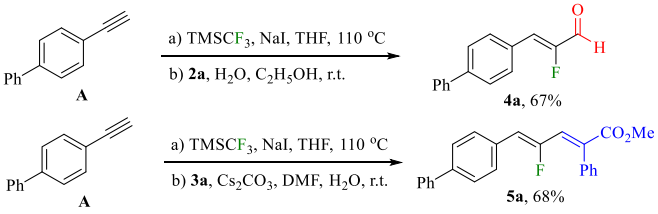
Scheme 2. Substrate scope for the synthesis of 2-fluoropropenals. Reaction conditions: **1** (0.2 mmol), **2a** (0.2 mmol), H_2O (2.0 equiv.), C_2H_5OH (1.0 mL) at room temperature for 48 h in air. Isolated yields.

and the corresponding products **4 ab** and **4ac** were isolated in 83% and 60% yields, respectively. However, disubstituted *gem*-difluorocyclopropenes such as **1ad** and **1ae** were not suitable substrates for the reaction, probably due to steric reasons.

A regioselective hydrocarbonization of *gem*-difluorocyclopropene **1a** with methyl phenylacetate **3a** was screened (Scheme 3), in which 2-fluorobuta-1,3-diene **5a** was generated in 81% yield with excellent stereoselectivity. Phenylacetate with electron-donating groups such as a methoxy moiety was compatible with the reaction and gave product **5b** in 67% yield. Notably, *ortho*-iodide substrate **3c** did not retard the reaction, although the yield of **5c** (CCDC: 2110572) was reduced. Nevertheless, the attempt to use other carbon-based nucleophiles such as **3d**-**3g**



Scheme 3. Substrate scope for 2-fluorobuta-1,3-dienes. Reaction conditions: **1a** (0.2 mmol), **3** (0.2 mmol), Cs_2CO_3 (0.2 mmol), DMF (1.0 mL), H_2O (0.1 mL) at room temperature for 48 h in air. Isolated yields.



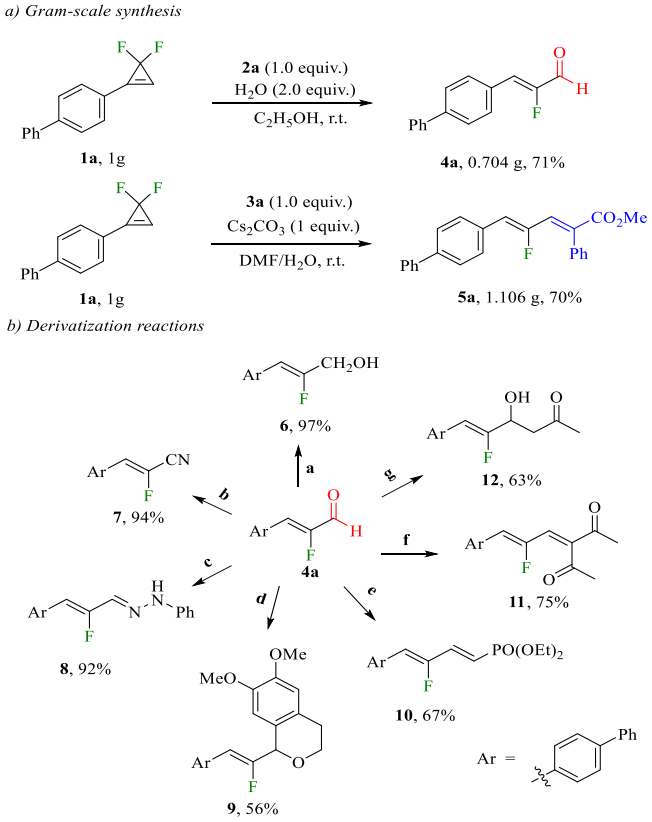
Scheme 4. Two-step and one-pot reactions.

failed as no main product could be identified.

Furthermore, a "one-pot" synthetic method for accessing 2-fluoropropenals or 2-fluorobuta-1,3-dienes originating from terminal alkyne was developed (Scheme 4). The alkyne **A** first performed a [2 + 1] cycloaddition procedure to release *gem*-difluorocyclopropene intermediate **1a**, which subsequently proceeded a regioselective addition, ring-opening and defluorination sequence to finally obtain target products **4a** and **5a** in 67% and 68% yields, respectively.

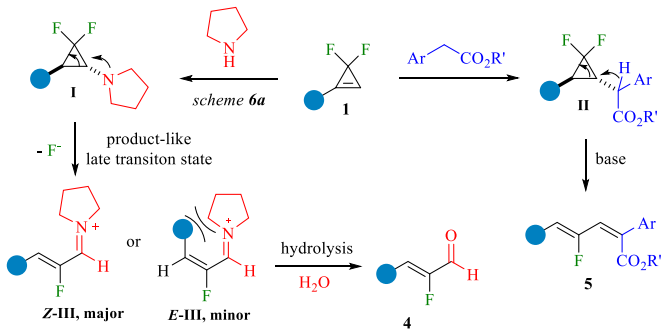
To further demonstrate synthetic applications, gram-scale reactions of *gem*-difluorocyclopropene **1a** with pyrrolidine **2a** or methyl phenylacetate **3a** were conducted, and the products **4a** and **5a** were isolated in 71% and 70% yields, respectively (Scheme 5a). The aldehydes are a versatile class of functional groups, so subsequent derivatization revolves around the 2-fluoropropenals (Scheme 5b). $NaBH_4$ reduction of the carbonyl group in **4a** led to a single configuration of alcohol **6** in 97% yield (path a) [60]. Nitrile **7** was synthesized from **4a** with ammonium acetate as the nitrogen source *via* an I_2-catalyzed oxidative pathway (path b) [61]. Treatment of **4a** with hydrazine afforded hydrazone product **8** in 92% yield (path c) [62]. By coupling aldehyde **3a** with β-arylethanol under catalytic $Fe(OTf)_2$, isochroman **9** was isolated in 56% yield (path d) [63]. A Horner-Wadsworth-Emmons olefination of aldehyde **4a** with tetraethyl methylenebisphosphonate in the presence of solid potassium carbonate afforded (1*E*,3*Z*)-dienylphosphonate **10** in 67% yield (path e) [64]. The reaction of the acetylacetone with **4a** catalyzed by $CeCl_3$ and NaI gave the dehydration product **11** in 75% yield [65], and the aldol addition product **12** was obtained when using NaOMe as the base.

To explore the reaction mechanism for the defluorinative ring-opening of *gem*-difluorocyclopropenes, several control experiments were designed (Scheme 6). In the presence of catalytic K_2CO_3, a hydroamination process of *gem*-difluorocyclopropene **1a** with *N*-methoxybenzamide **13** was conducted, and the targeted product **14** was generated in 49% yield (Scheme 6a). The deuterated tetrahydropyrrole **2a-D** reacted with **1a** for 48 h, then 2 equiv. of H_2O were added to the reaction and reacted for another 6 h (Scheme 6b), which obtained **4a-D** as a major product. This result indicated that a regioselective hydroamination process was possible. When H_2O^{18} was used in the model reaction under air conditions, almost **4a-O^{18}** was obtained (Scheme 6c),



Scheme 5. Synthetic application. Reaction conditions: a) **4a** (0.2 mmol), $NaBH_4$ (0.26 mmol), MeOH (0.5 mL), THF (0.5 mL) at room temperature. for 2 h; b) **4a** (0.2 mmol), NH_4OAc (0.3 mmol), I_2 (2.5 mol%), TBHP (0.22 mmol), ethanol (1 mL), 50 °C; c) **4a** (0.2 mmol), phenylhydrazine (0.2 mmol), ethanol (1 mL), r.t.; d) **4a** (0.2 mmol), phenylethanol (0.2 mmol), $Fe(OTf)_2$ (1 mol%), toluene (1 mL), 70 °C; e) **4a** (0.2 mmol), tetraethyl methylenebisphosphonate (0.24 mmol), K_2CO_3 (0.6 mmol), DMF (1 mL), 165 °C; f) **4a** (0.2 mmol), acetylacetone (0.24 mmol), $CeCl_3.7H_2O$ (20 mol%), NaI (10 mol%), r.t.; g) **4a** (0.2 mmol), acetylacetone (0.24 mmol), NaOMe (10 mol%), TBAB (10 mol%), CH_3OH (1 mL), r.t.

which suggested that the oxygen of the aldehyde group in the substrate was likely to originate from water instead of the air. Furthermore, *gem*-difluorocyclopropene **1r** with 60% deuterium was prepared and pitched into the reaction (Scheme 6d), and 60% of the hydrogen on the aldehyde in product **4r** was deuterated.



Scheme 7. Possible reaction mechanism.

On the basis of related works [66,67] and our preliminary studies, a plausible mechanism is proposed in Scheme 7. A regioselective addition of pyrrolidine **2a** or phenylacetate **3** to *gem*-difluorocyclopropene **1** gave intermediates **I** and **II**. The synergistic effect of *gem*-difluorine and the nucleophile promoted the ring-opening defluorination process of intermediates **I** and **II**. The high *E/Z* ratios could be a result of a late (more product-like) transition state, as the ***E*-III** intermediate would experience significant steric repulsion. The hydrolysis of intermediate **III** finally produces 2-fluoropropenals **4**.

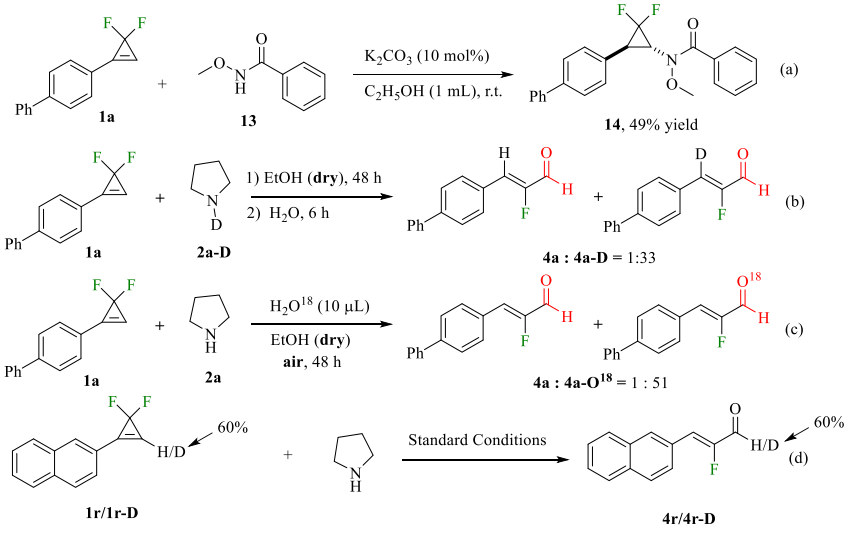
3. Conclusion

In summary, we have developed a novel defluorinative ring-opening of *gem*-difluorocyclopropenes, providing a concise and efficient approach for accessing 2-fluoropropenals and 2-fluorobuta-1,3-dienes in moderate to good yields with high *Z*-selectivity. The reaction occurs under mild conditions, and water plays an important role in the transformation. Multiple synthetic applications, including two-step and one-pot reactions, gram-scale reactions, modification of bioactive molecules and derivatization reactions, are also elaborated.

4. Experimental

4.1. General procedure for the synthesis of 4

A 15 mL schlenk tube was charged with a mixture of **1** (0.2 mmol), **2a** (0.2 mmol), H_2O (0.4 mmol) in C_2H_5OH (1.0 mL) and was stirred at room temperature for 48 h. The solvent was removed on a rotary evaporator under reduced pressure. The resultant residue was purified by silica gel column chromatography to afford the desired product **4**.



Scheme 6. Preliminary mechanistic studies.

4.2. General procedure for the synthesis of **5**

A 15 mL schlenk tube was charged with a mixture of **1** (0.2 mmol), **3** (0.2 mmol) and Cs_2CO_3 (0.2 mmol) in DMF/H_2O (1.0 mL/0.1 mL) and was stirred at room temperature for 48 h. The solvent was removed on a rotary evaporator under reduced pressure. The resultant residue was purified by silica gel column chromatography to afford the desired product **5**.

4.3. Two-step and one-pot synthesis of ***4a***

Alkyne (0.2 mmol), $TMSCF_3$ (0.4 mmol), NaI (0.44 mmol), and THF (1 mL) were mixed into a pressure tube at room temperature. Then the reaction mixture was heated at 110 °C for 2 h, and completion of the reaction was assessed by TLC. The reaction mixture was allowed to cool down to room temperature, to which **2a** (0.2 mmol) and H_2O (0.4 mmol) in C_2H_5OH (1.0 mL) was added. The reaction was stirred for another 48 h. The solvent was removed on a rotary evaporator under reduced pressure. The resultant residue was purified by silica gel column chromatography to afford the desired product **4a**.

4.4. Two-step and one-pot synthesis of ***5a***

Alkyne (0.2 mmol), $TMSCF_3$ (0.4 mmol), NaI (0.44 mmol), and THF (1 mL) were mixed into a pressure tube at room temperature. Then the reaction mixture was heated at 110 °C for 2 h, and completion of the reaction was assessed by TLC. The reaction mixture was allowed to cool down to room temperature, to which **3a** (0.2 mmol) and Cs_2CO_3 (0.2 mmol) in DMF/H_2O (1.0 mL/0.1 mL) was added. The reaction was stirred for another 48 h. The solvent was removed on a rotary evaporator under reduced pressure. The resultant residue was purified by silica gel column chromatography to afford the desired product **5a**.

4.5. Gram scale experiment

A 25 mL dry round bottom flask was charged with a mixture of **1a** (1g, 4.39 mmol), **2a** (4.39 mmol), H_2O (8.78 mmol) in C_2H_5OH (5 mL) and was stirred at room temperature for 48 h. The solvent was removed on a rotary evaporator under reduced pressure. The resultant residue was purified by silica gel column chromatography to afford the desired product **4a**.

A 25 mL dry round bottom flask was charged with a mixture of **1a** (1g, 4.39 mmol), **3a** (4.39 mmol) and Cs_2CO_3 (4.39 mmol) in DMF/H_2O (5.0 mL/0.5 mL) and was stirred at room temperature for 48 h. The solvent was removed on a rotary evaporator under reduced pressure. The resultant residue was purified by silica gel column chromatography to afford the desired product **5a**.

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.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gresc.2023.01.003.

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