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Ring-Opening Diarylation of Siloxydifluorocyclopropanes by Ag(I) Catalysis: Stereoselective Construction of 2-Fluoroallylic Scaffold

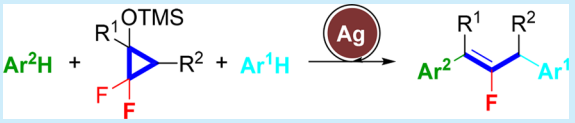
Xiaoning Song,[†] Cong Xu,[†] Dongxu Du,[†] Ziming Zhao,[†] Dongsheng Zhu,*[,†] and Mang Wang*[,†,‡]

[†]Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis, Faculty of Chemistry, Northeast Normal University, Changchun 130024, China

[‡]State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China

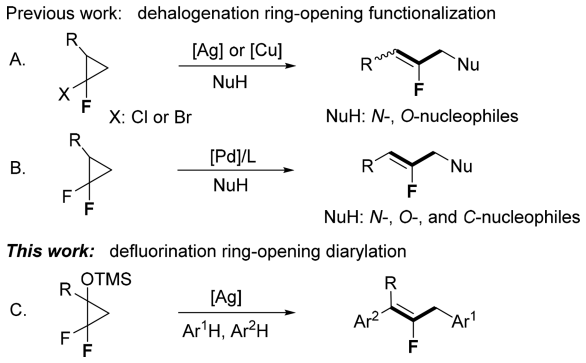
Supporting Information

ABSTRACT: A silver-catalyzed, defluorination ring-opening diarylation of siloxy 2,2-difluorocyclopropanes, with two arenes, to directly prepare polysubstituted 2-fluoroallylic compounds, is described. This multicomponent reaction proceeds smoothly in good stereoselectivity, which is due to a chelation-controlled addition of arenes to α-fluorinated ketone intermediate.



2-Fluoropropene is present as a privileged motif in a wide range of medicinal and bioactive molecules.[1,2] This substructure also has relevance to material science.[3] The striking features of these compounds have encouraged many efforts for their preparation,[4] among which dehalogenation ring-opening functionalizations of *gem*-halofluorocyclopropanes provide a general access to 2-fluoroallylic scaffold (Scheme 1A).[5] However, the processes generally lack satisfactory stereochemical control of the olefin configuration. The reaction partners are limited to heteroatom-based nucleophiles, such as amines or alcohols. In addition, miscellaneous methods have also been used to synthesize 2-fluoropropenes, for example, classical olefination reactions of carbonyl compounds with a proper fluorine-containing precursor,[6] nucleophilic additions of fluoro-olefin substrates with aldehydes,[7] and hydrofluorination of alkynes.[8] Current investigations have emphasized efficient and stereoselective routes to fluoroalkenes[9] in which metal-catalyzed C−F bond cleavage and allylic substitution of α,α-difluoroalkenes with nucleophiles have been recognized as an alternative representative to 2-fluoropropene target.[9d,10] However, available examples still suffer from restricted substrate scope or limited reaction mode. Reliable and facile methods for stereoselective construction of the 2-fluoroallylic scaffold with diverse substituents are highly desired.

Scheme 1. Metal-Catalyzed Dehalogenation Ring-Opening Functionalizations of *gem*-Difluorocyclopropanes



gem-Difluorocyclopropanes are important fluoroorganics.[11] Most research interests to date have focused on their distinguished biological and physical properties as well as their preparations.[5a,12] However, their synthetic utilities have hardly been explored, although they are expected to be readily available fluorine-containing three-carbon synthons.[13,14] Generally, simple *gem*-difluorocyclopropane derivatives undergo thermodynamic ring-cleavage rearrangements at high temperature.[15] Catalytic ring-opening reaction provides an opportunity for their applications.[13,16] For instance, a new synthesis of 2-fluoropropenes via Pd-catalyzed dehalogenation ring-opening functionalization of *gem*-difluorocyclopropanes was recently reported by Fu (Scheme 1B).[16c] The reactions proceeded in stereoselectivity and could be extended to the nucleophilic trap of Pd-intermediate with *N*-, *O*-, and *C*-nucleophiles.

In comparison, *gem*-difluorocyclopropanes bearing an *O*- or *N*-based substituent on the three-numbered ring usually lack stability.[13] For example, the ring-opening of *gem*-difluorocyclopropanes derived from enol acetate easily occurred, affording the homologous fluoroenones.[17] This background reaction has hampered practical applications of *gem*-difluorocyclopropanes containing *O*- or *N*-substituents in synthesis.[13] As part of our ongoing interest in this field,[18] we here report a preliminary finding on stereoselectively Ag-catalyzed defluorination ring-opening diarylations of *gem*-difluorocyclopropanes (Scheme 1C). The new chemistry of this work includes the following. (a) First dehalogenation ring-opening difunctionalization of *gem*-difluorocyclopropanes. The use of arenes expands the reaction partners from heteroatom-based nucleophiles to carbon-based ones. (b) This tandem process includes a chelation-controlled

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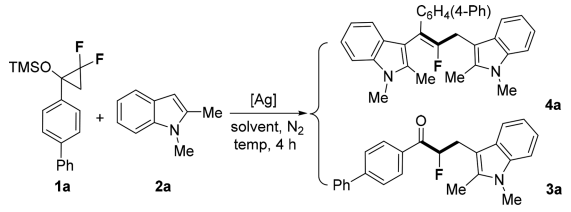
addition of arenes to α-halo carbonyls which provides a stereoselective method for the synthesis of monfluoroalkenes. To the best of our knowledge, the stereoselective addition of C-based nucleophiles to α-halo carbonyls under the chelation-controlled conditions still challenges this field.[19] (c) The transformation broadens the application of *gem*-difluorocyclopropanes for general fluorine-containing three-carbon synthons and provides a direct route to polysubstituted 2-fluoroallylic compounds, which are expected to be used for the screening of potential bio/pharmacological compounds.

Siloxy *gem*-difluorocyclopropane **1a** was synthesized in situ by the difluorocyclopropanation of 4-acetobiphenyl with $TMSCF_2Br$ according to our previous work.[18] Initially, we investigated the defluorination ring-opening reaction of **1a** with 1,2-dimethylindole **2a** by the use of silver salt as the catalyst. After 4 h of reaction at room temperature, α-fluoroketone **3a** was obtained in 59% yield under the catalysis of 10 mol % $AgBF_4$ in DCM (Table 1, entry 1). Interestingly, the reaction

Table 1. Survey of Reaction Conditions[a]



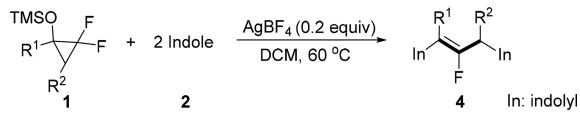
entry	catalyst (equiv)	ratio (**1a**:**2a**)	solvent	temp (°C)	yield (%)[b] **3a**, **4a** (*Z*/*E*)[c]
1	$AgBF_4$ (0.1)	1:1	DCM	rt	59, 12
2	$AgBF_4$ (0.1)	1:1	DCM	60	43, 24
3	$AgBF_4$ (0.1)	1:2	DCM	60	22, 76
4	$AgBF_4$ (0.2)	1:2	DCM	rt	64, 32
5	$AgBF_4$ (0.2)	1:2	DCM	40	30, 64
6	$AgBF_4$ (0.2)	1:2	DCM	60	6, 89 (12:1)
7	$AgBF_4$ (0.3)	1:2	DCM	60	5, 85 (11:1)
8	$AgBF_4$ (0.2)	1:2	DCM	80	4, 50 (3:1)
9	AgF (0.2)	1:2	DCM	60	27, 23[d]
10	AgOTf (0.2)	1:2	DCM	60	-, 84[d] (8:1)
11	Ag_2CO_3 (0.2)	1:2	DCM	60	-, 19[d]
12	$AgNO_3$ (0.2)	1:2	DCM	60	44, 52[d]
13	$AgBF_4$ (0.2)	1:2	THF	60	48, 45
14	$AgBF_4$ (0.2)	1:2	MeCN	60	43, 31
15	$AgBF_4$ (0.2)	1:2	DMF	60	-, -[e]

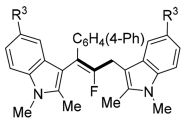
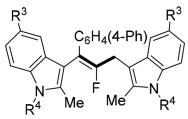
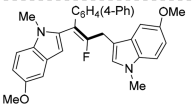
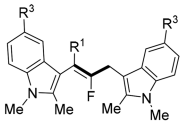
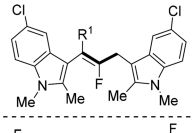
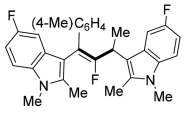
[a]Conditions: **1a** which was synthesized in situ from 4-acetobiphenyl (0.5 mmol), solvent (4 mL), in a sealed tube. [b]Isolated yields based on **2a**. [c]The ratio of *Z*-**4a** and *E*-**4a** was determined by ^{19}F NMR spectroscopy of crude **4a**. [d]Yields were determined by ^{19}F NMR analysis using benzotrifluoride as an internal standard. [e]Fluoro enone was obtained.[18c]

also gave an unprecedented product, 2-fluoropropene **4a**, likely resulting from further nucleophilic addition and dehydration of indole **2a** with **3a**. Considering that the addition of **2a** to **3a** may involve a scarce chelation-controlled addition of arenes to α-halo carbonyls[19] and the 2-fluoropropene derivatives are useful compounds,[1,2] we systematically screened the reaction conditions for the formation of **4a** from **1a** and **2a**. As described in Table 1, the efficiency of the conversion from **3a** to **4a** is higher at 60 °C than at lower temperature (entries 1−7). With the ratio of **1a** to **2a** as 1:2 at 60 °C, the reaction afforded **4a** in 76% yield (entry 3). When the amount of $AgBF_4$ was increased, the yield of **4a** could be reached to 89% (entry 6). Notably, the transformation proceeded with stereoselectivity delivering *Z*-**4a** as major product (entry 6). However, further heightening temperature resulted in low yield and poor stereoselectivity (entry 8). We then turned to screen the silver catalysts, including AgF, AgOTf, Ag_2CO_3, and $AgNO_3$ (entries 9−12). It was found that all the reaction could give desired **4a** in 19% to 84% yields while $AgBF_4$ was the best one. In addition, a screen of other solvent revealed that the reactions also worked in THF and MeCN (entries 13 and 14), but DMF was an ineffective solvent. Fluoroenone was obtained via a background reaction[17] in this case (entry 15).

With the optimized reaction conditions (Table 1, entry 6), we then investigated the substrate scope of both **1** and **2**. As presented in Table 2, most tested conversions are efficient; for example, the reactions of **1a** with indoles **2** bearing different substituents on the indole ring were well tolerated to provide a set of 2-fluoroallylic compounds **4b−g** in 63−91% yields (entries 2−7). When 2,3-unsubstituted indole **1h** was used as

Table 2. Substrate Scope of Both 1 and 2[a]



entry	product *Z*-**4**	yield[b] (*Z*/*E*)[c]
1		**4a**, R^3 = H, 89% (12:1)
2		**4b**, R^3 = Me, 91% (17:1)
3		**4c**, R^3 = MeO, 63% (10:1)
4		**4d**, R^3 = F, 84% (16:1)
5		**4e**, R^3 = Cl, 85% (15:1)
6		**4f**, R^3 = H, R^4 = H, 73% (13:1)
7		**4g**, R^3 = Cl, R^4 = Et, 85% (> 20:1)
8		**4h**, 57% (17:1)
9		**4i**, R^1 = 4-$MeOC_6H_4$, R^3 = H, 90% (10:1)
10		**4j**, R^1 = 4-$AcOC_6H_4$, R^3 = Cl, 89% (> 20:1)
11		**4k**, R^1 = 4-BrC_6H_4, R^3 = H, 81% (> 20:1)
12		**4l**, R^1 = 4-IC_6H_4, R^3 = Cl, 66% (> 20:1)
13		**4m**, R^1 = 4-$NO_2C_6H_4$, R^3 = Cl, 89% (15:1)
14		**4n**, R^1 = 3-$NO_2C_6H_4$, R^3 = Cl, 82% (14:1)
15[c]		**4o**, R^1 = 3-CNC_6H_4, R^3 = F, 89% (8:1)
16		**4p**, R^1 = 3-CO_2Et-4-$EtOC_6H_3$, R^3 = Cl, 68% (15:1)
17		**4q**, R^1 = 3,4-$(OCH_2O)C_6H_3$, R^3 = Cl, 77% (> 20:1)
18		**4r**, R^1 = 2-naphthyl, 83% (> 20:1)
19		**4s**, R^1 = 3-thienyl, 44% (17:1)
20		**4t**, R^1 = $PhCH_2CH_2$, 36% (> 20:1)
21		**4u**, 54% (> 20:1)

[a]Conditions: **1** was synthesized in situ from corresponding ketones (0.5 mmol), **2** (0.8 mmol), $AgBF_4$ (0.08 mmol), DCM (4 mL), 60 °C, 4−6.5 h. [b]Isolated yields based on **2**. [c]The ratio of *Z*- and *E*-isomer was determined by ^{19}F NMR spectroscopy of crude **4**.

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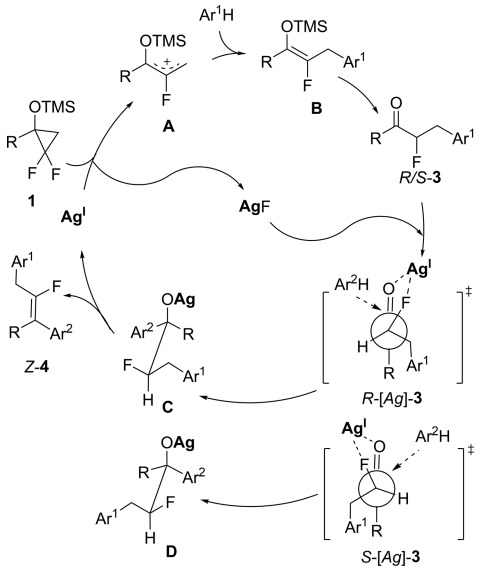
the substrate, the reaction afforded **4h** in 57% yield (entry 8). The formation of this 2′,3-cross-substituted product **4h** likely resulted from a C3 to C2 migration of the alkenyl substituent of the usual 3′,3-substituted product under the present reaction conditions.[20] On the other hand, a range of diverse *gem*-difluorocyclopropanes, including those with electron-donating or electron-deficient substituents at different positions of the phenyl ring, were also found to be suitable to afford the desire **4i**–**q** in 66–90% isolated yields (entries 9–17). In addition, 2-naphthylated substrate **1r** gave **4r** in 83% yield (entry 18), while 3-thienylated **1s** furnished **4s** in moderate yield (entry 19). In the case of **1t** containing an alkylic R^1 substituent, the reaction had a complex results, in which product **4t** was isolated in 36% yield (entry 20). Furthermore, *gem*-difluorocyclopropane **1u** having two substituents on the three-membered ring could also lead to the desired 2-fluoropropene product **4u** in moderate yield (entry 21). It is noteworthy that all the above reactions produced 2-fluoroallylic compounds **4** in good to excellent stereoselectivity.

On the basis of reports of both ring-opening of *gem*-halofluorocyclopropanes[5] and chelation-controlled additions of nucleophiles to α-halo carbonyl derivatives,[19] a plausible mechanism is tentatively proposed as described in Scheme 2.

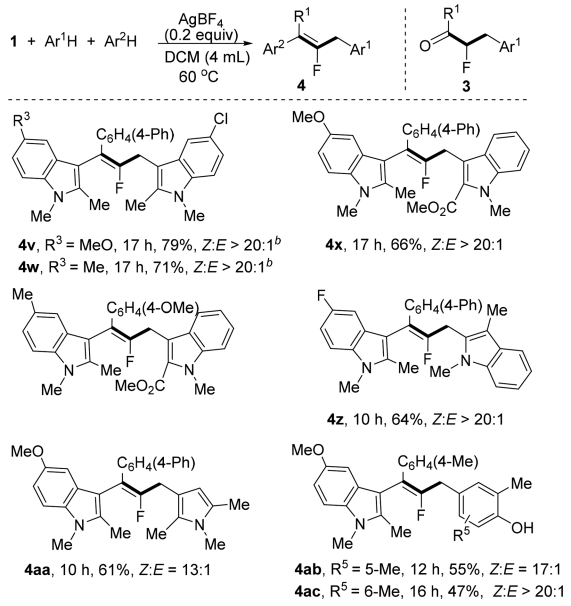
Scheme 2. Plausible Reaction Mechanism



At first, Ag(I)-mediated defluorination ring-opening of **1** furnishes allylic cations **A**, which undergo a sequential Friedel–Crafts reaction with arenes and a desilylation to give **3** via monofluoroalkene intermediates **B**. Next, Ag(I) salt acts as chelating agent to coordinate with the fluorine and oxygen atoms of the **3** to form a highly ordered transition state *R*- and *S*-[*Ag*]-**3**, respectively. Sequential nucleophilic additions of arenes to carbonyl group of *R*/*S*-[*Ag*]-**3** obey Cram's rule to deliver adducts **C** and **D** in high diastereoselectivity.[21] Finally, either **C** or **D** can afford *Z*-**4** as main product via E2-elimination of AgOH, which will be for the next catalytic cycle. To the best of our knowledge, C-based nucleophiles are rarely utilized in dehalogenation ring-opening functionalizations of *gem*-halofluorocyclopropanes.[5] Stereoselective addition of C-based nucleophiles to α-halo carbonyls under the chelation-controlled conditions has still a challenge compared to addition of hydride nucleophile.[19] By comparison, we realized a well trap of carbocation with eletron-rich arenes in the ring-opening of *gem*-difluorocyclopropanes and found a stereoselective addition of arenes to α-fluoroketones for the first time by using Ag(I) as chelating catalyst.

Following the success in three-component reactions of **1** and two identical indoles, we turned our attention to the reactions between **1** and two different arenes. We found that mixed products **4** were always obtained if two different indoles **2** were added in one pot at 60 °C. Reactions could be controlled to furnish **3** at room temperature in a shorter time. In the case of *N*-methyl-2-(methoxycarbonyl)indole as the substrate, only **3** was obtained even when reacting at 60 °C. Thus, we hoped to add two indoles step by step under different conditions. For example, we carried out the reaction of **1a** with indole **2e** at room temperature for generating α-fluoroketone **3** and then added the second indole **2c** to this reaction system for further addition at 60 °C. As a result, cross-substituted **4v** was isolated in 79% yields (Scheme 3). Other tested reactions also afforded

Scheme 3. Reactions of 1 with Two Different Arenes[a]



[a]Isolated yields based on Ar^1H. [b]Reaction with Ar^1H at rt and with Ar^2H at 60 °C.

Z-**4w**–**z** in good yields (Scheme 3 and SI). Additionally, pyrrole and phenol were proved to be suitable trapping reagents for intermediate **A** (Scheme 2) in the ring-opening of **1**, delivering **3** which could be detected by ^1H NMR. But they were inefficient nucleophiles for further addtion to **3**, while indoles could be used for this Ag-chelation-controlled addition procedure leading to **4aa**–**ac** in good yields. Delightfully, all reactions in Scheme 3 afforded *Z*-**4** as main products.

In conclusion, a tandem Ag-catalyzed defluorination ring-opening diarylation reaction of siloxy 2,2-difluorocyclopropanes for the synthesis of 2-fluoroallylic compounds, which are of interesting importance in medicines and materials, is described. The transformations efficiently proceed with high stereoselectivity, which is consistent with the transition state being under chelation control. Arenes proved to be extended to alkenes as nucleophilic partners. To the best of our knowledge, this work provides the first example of ring-opening difunctionalization of *gem*-difluorinated cyclopropanes, which

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involves a chelation-controlled addition of arenes to α-fluoroketones. In addition, it also represents general application of *gem*-difluorocyclopropanes for fluorine-containing three-carbon synthons in organic synthesis. Further work focused on the extension of this synthetic strategy is in progress in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03254.

Experimental procedures, analytical data for new compounds, and crystallographic data for **4e** (PDF)

Accession Codes

CCDC 1576220 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhuds206@nenu.edu.cn.
*E-mail: wangm452@nenu.edu.cn.

ORCID

Xiaoning Song: 0000-0001-5507-8073
Cong Xu: 0000-0001-9817-7186
Mang Wang: 0000-0001-8006-4626

Notes

The authors declare no competing financial interest.

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