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Silver-Catalyzed Ring-Opening Strategy for the Synthesis of β- and γ-Fluorinated Ketones

Huijun Zhao,[†,§] Xuefeng Fan,[†,§] Jiajia Yu,[†] and Chen Zhu*[,†,‡]

[†]Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People's Republic of China

[‡]Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

Supporting Information

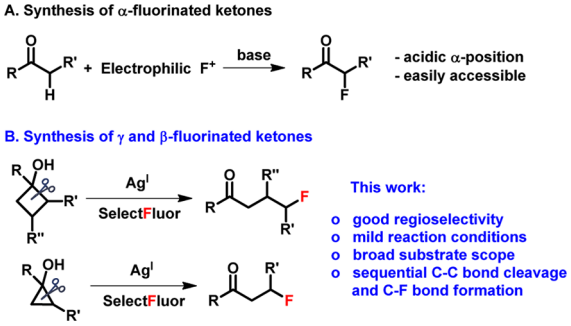
ABSTRACT: A regioselective synthesis of β- and γ-fluorinated ketones via silver-catalyzed ring opening is described. A variety of β- and γ-fluorinated ketones are efficiently prepared, respectively, from tertiary cyclopropanol and cyclobutanol precursors, providing a straightforward approach for the introduction of a fluorine atom into complex molecules. Preliminary mechanistic studies suggest that a radical-mediated sequential C−C bond cleavage and C−F bond formation pathway is involved.

The introduction of a fluorine atom into molecules frequently renders remarkable changes in their physical, chemical, and biological properties.[1] Thus, the development of mild and efficient fluorination methods is of considerable significance in pharmaceuticals, agrochemicals, and material sciences.[2] Recently, great progress has been made in the field of fluorination of arenes to form C_{sp^2}−F bonds via transition-metal catalyzed transformations, in particular, cross-coupling[3] and C−H activation.[4] In contrast, direct fluorination on alkyl groups to generate C_{sp^3}−F bonds is relatively less investigated. This type of fluorination successfully occurs at special positions, for instance benzylic fluorination[5] and allylic fluorination,[6] or via alkene fluorination.[7] The fluorination at nonspecific positions remains a challenging issue due to the poor regioselectivity.[8]

The synthesis of fluorinated ketones provides an efficient and straightforward approach for the introduction of a fluorine atom into complex molecules. α-Fluorinated ketones are easily accessed, since the acidic α-H of the ketone can be conveniently converted to fluorine by use of many electrophilic fluorinating agents (Scheme 1A).[9] However, the practically direct fluorination to regioselectively synthesize distal (β, γ, δ, etc.) fluorinated ketones is rarely reported.[10] Herein, we report an efficient synthesis of β- and γ-fluorinated ketones relying on a silver-catalyzed ring opening strategy (Scheme 1B). The transformation undergoes a sequence of C−C bond cleavage and C−F bond formation and affords a wide range of fluoro-ketones with good regioselectivities under mild reaction conditions.

Radical-mediated ring openings with strained cyclic compounds have been long established as a radical clock to determine the kinetics of free-radical reactions.[11,12] We envisioned that this strategy might be viable for the synthesis of distal fluorinated ketones from tertiary cycloalkanols. With this idea in mind, we set out to investigate the project by use of 1-phenylcyclobutanol **1a**, which was readily prepared from the addition of aryl Grignard reagent to cyclobutanone. After thoroughly surveying reaction conditions (fluorinating agent, solvent, concentration, etc.), we found that the combination of silver salt and SelectFluor gave the best fluorination yields at room temperature. In particular,[13] (a) $AgBF_4$ exhibited a better catalytic ability than other silver salts, such as $AgNO_3$, AgF, and AgOTf; (b) Fluorinating agents other than SelectFluor significantly decreased the chemical yields; and (c) a concentrated biphasic solution (0.3 M in DCE/H_2O 1:1) facilitated the transformation.

Scheme 1. Synthesis of Fluorinated Ketones



With the optimized reaction conditions in hand, we turned to evaluate the generality of this protocol. The transformation has wide functional group tolerance; both electron-rich and -deficient tertiary cyclobutanols were compatible, furnishing a variety of γ-fluorinated ketones (Scheme 2). The model substrate **1a** gave the corresponding product **2a** in satisfactory isolated yield. The linear phenylpropyl ketone without fluorination was identified as the principal byproduct.

Substrates with electron-donating groups, regardless of the arene substitution (*o*-, *m*-, *p*-), gave rise to the γ-fluoroketones **2b**−**2f** in good yields. Acceptable yields of products **2g** and **2h** were achieved when strong electron-withdrawing groups were present, e.g., OCF_3 and CF_3. However, the transformation generally required an increase of silver catalyst and fluorinating agent, or prolonged reaction times. An unintelligible trend was observed in the cases of haloaryl substrates **1i**−**1k**; while **1i** readily led to product **2i** in a few hours, the conversion of **1j** and

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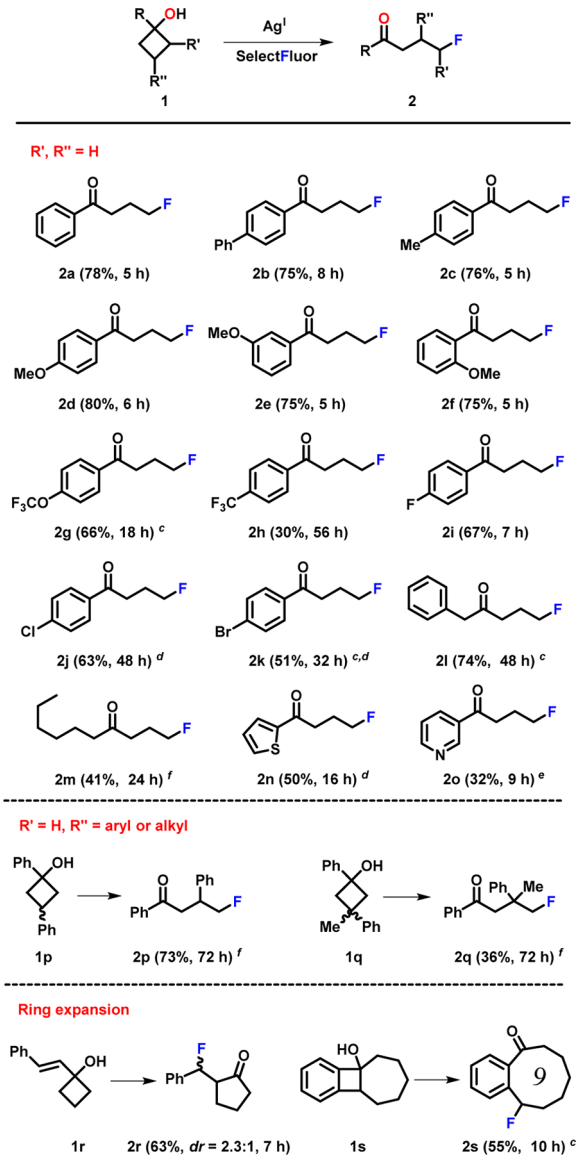
Scheme 2. Synthesis of γ-Fluorinated Ketones from Cyclobutanols[a,b]

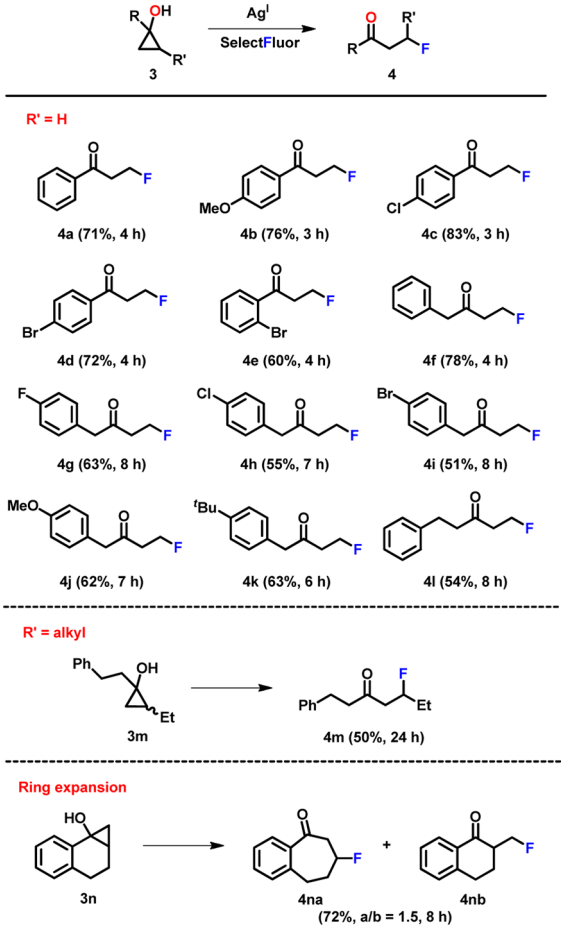


[a]**1** (0.3 mmol), $AgBF_4$ (0.06 mmol, 20 mol %), and SelectFluor (0.6 mmol, 2 equiv) in DCE/H2O (0.5/0.5 mL, 0.3 M) at rt. [b]Yields of isolated products. [c]30 mol % $AgBF_4$ and 3 equiv of SelectFluor. [d]60 °C. [e]2.5 equiv of SelectFluor. [f]50 mol % $AgBF_4$ and 3 equiv of SelectFluor.

1k took a few days even at elevated temperature. Though less reactive, aliphatic examples such as benzyl cyclobutanol **1l** and *n*-hexyl cyclobutanol **1m** were also suitable substrates. Remarkably, heteroaryl cyclobutanols were also tolerated in the reaction, yielding fluorinated thienyl ketone **2n** and pyridyl ketone **2o**. The reaction with 3-substituted cyclobutanol **1p** and **1q** was sluggish (72 h) which might be attributed to the increased steric hindrance from the additional substituent. Ring expansion is always an intriguing chemical transformation. When alkenyl substituted cyclobutanol **1r** was examined, two isomeric cyclopentanone **2r** were readily obtained. Another interesting example was the reaction of fused bicyclic **1s** which led regioselectively to the corresponding nine-membered γ-fluoroketone **2s** in useful yield.

Encouraged by the results, the ring-opening strategy was subsequently applied to the fluorination of cyclopropanols. After a survey of independent reaction parameters, the previously optimized conditions were slightly modified:[14] (a) $AgNO_3$ gave a better outcome than $AgBF_4$; (b) Chloroform/H_2O (0.2 M) was used instead of DCE/H_2O (0.3 M). A variety of cyclopropanols were assessed (Scheme 3). In general, cyclopropanol demonstrated a higher reactivity than cyclobutanol in terms of reaction rate. Under the current reaction conditions, both electron-rich and -deficient 1-arylcyclopropanols smoothly afforded the β-fluorinated products **4a**−**4e** in good yields within a few hours. In addition, 1-alkylcyclopropanols with different substituents gave rise to the corresponding products **4f**−**4l** in useful yields. The examples of dialkyl substituted cyclopropanol **3m** was noteworthy, as the fluorination product **4m** at the tertiary rather than the secondary carbon was exclusively generated albeit a prolonged reaction time was used. The fluorination of **3n** was notable because the seven-membered cyclic product **4na** via ring expansion was predominantly formed.

Scheme 3. Synthesis of β-Fluorinated Ketones from Cyclopropanols[a,b]



[a]**3** (0.2 mmol), $AgNO_3$ (0.04 mmol, 20 mol %), and SelectFluor (0.4 mmol, 2 equiv) in $CHCl_3/H_2O$ (0.5/0.5 mL, 0.2 M) at rt. [b]Yields of isolated products.

Regarding the possible mechanism, three pathways can be involved (Figure 1). First, in the presence of an electrophilic fluorinating agent, the four-membered ring might be directly opened via an anion without a silver catalyst (Path A). An

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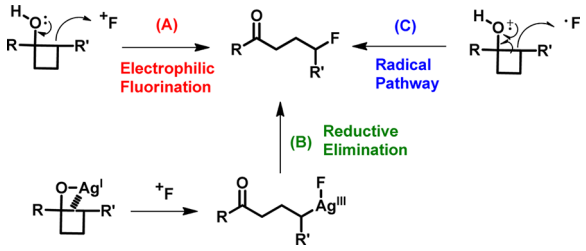
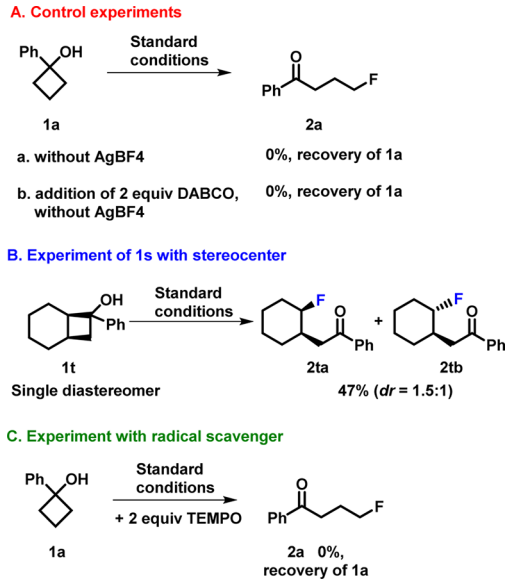


Figure 1. Possible mechanistic pathways.

alternative pathway is silver-assisted ring opening (Path B). Similarly to Rh^{I}-catalyzed ring opening of benzocyclobutenol,[15] Ag^{I} is incorporated with hydroxyl group and inserts into the proximal C−C bond, forming a C−Ag bond. Simultaneously, Ag^{I} reacts with SelectFluor to generate a Ag^{III} species. The resulting C−Ag^{III}−F complex undergoes reductive elimination to generate the product. The other route is a silver-catalyzed radical pathway (Path C).

To elucidate the mechanism, some control experiments were performed. In the absence of a silver catalyst, the reaction of **1a** did not furnish the expected fluorination product **2a** with or without the help of DABCO (Scheme 4A).[16] This might rule out

Scheme 4. Experiments for Mechanistic Elucidation



the possibility of Path A. If the reaction goes through Path B via the sequence of C−C bond insertion/reductive elimination, the configuration of the fluorinated C-center should be retained. Otherwise, the preformed configuration at the C-center should racemize through Path C, the radical pathway. A single diastereomer of **1t** was synthesized and subjected to the standard reaction conditions (Scheme 4B). It was found that the reaction did not proceed with retention of configuration, and instead, a couple of isomers **2ta** and **2tb** were generated in a 1.5:1 ratio, which might suggest that a radical pathway was more likely to be involved in the transformation. To verify the hypothesis, 2 equiv of TEMPO were added to the reaction (Scheme 4C). The resulting suppression of **2a** formation supports Path C.

Based on the above observations, a plausible mechanism is outlined in Figure 2. Initially, cyclobutanol **1** incorporates a silver salt to generate complex **a**, which interacts with SelectFluor to

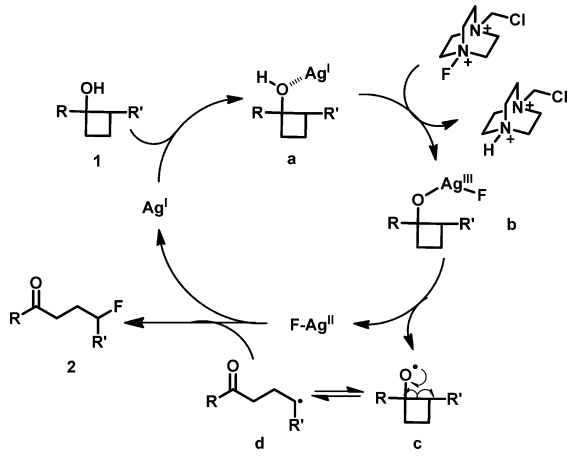


Figure 2. Plausible mechanism.

generate F−Ag^{III} complex **b**. Homolysis of **b** gives rise to a F−Ag^{II} species and cyclobutyloxy radical **c**. The alkyl radical **d**, an open chain tautomer of **c**, reacts with the F−Ag^{II} species, eventually forming the product γ-fluoroketone.

In summary, we have developed an efficient synthesis of fluoroketones via a silver-catalyzed ring-opening strategy. The transformation exhibits good tolerance for diverse functional groups. A variety of β- and γ-fluorinated ketones are prepared in good regioselectivities, respectively, from tertiary cyclopropanols and cyclobutanols, thus offering versatile building blocks for the construction of complexly fluorine-incorporated molecules. Preliminary mechanistic studies suggest a radical-mediated pathway might be involved. Further applications of the reaction are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, compound characterization data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*chzhu@suda.edu.cn

Author Contributions

§H.Z. and X.F. contributed equally.

Notes

The authors declare no competing financial interest.

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(10) A few examples of fluorinated ketones generated by benzylic fluorination were included in ref 5b−d, 5f, and g; a few examples of poor regioselectivities via alkyl fluorination were included in ref 8g−i.
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(13) For experimental details, see Supporting Information.
(14) For experimental details, see Supporting Information. For an example of **4f**, **4f** was generated in 78% yield under the modified conditions and in 60% yield under the previous conditions.
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(16) DABCO might be generated in the reaction as the byproduct of SelectFluor.

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