HOKKAIDO UNIVERSITY

Title	Solid-State Silver-Catalyzed Ring-Opening Fluorination of Cyclobutanols by Using Mechanochemistry
Author(s)	Isshiki, Ryota; Kubota, Koji; Ito, Hajime
Citation	Synlett, 34(12), 1419-1424 https://doi.org/10.1055/a-2021-9599
Issue Date	2023-05-03
Doc URL	https://hdl.handle.net/2115/92243
Type	journal article
File Information	20230125_Synlett_C-Cfluorination_Win_revise_Isshiki.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Solid-state Silver-catalyzed Ring-opening Fluorination of Cyclobutanols Using Mechanochemistry

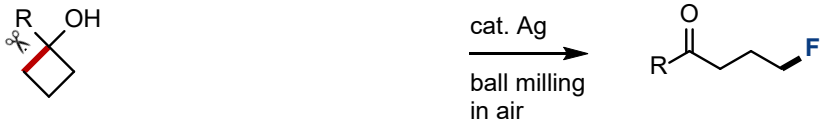
Ryota Isshiki*[a,b]
Koji Kubota*[a,b]
Hajime Ito*[a,b]

[a] Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

[b] Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

isshiki@icredd.hokudai.ac.jp
kbt@eng.hokudai.ac.jp
hajito@eng.hokudai.ac.jp

Published as part of the Special Issue
Honoring Masahiro Murakami's Contributions to Science

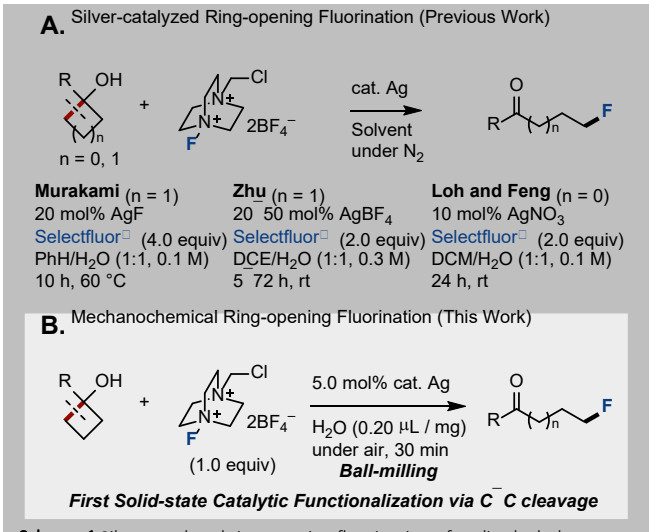


Received:
Accepted:
Published online:
DOI:

Abstract In this report, we demonstrate that a ball milling technique facilitates fast and efficient silver-catalyzed ring-opening fluorination of cyclobutanols. This is the first report of a catalytic C–C bond cleavage/functionalization reaction under solid-state mechanochemical conditions. The developed protocol affords a high yield of γ-fluorinated ketones within much shorter reaction times and requires less silver catalyst and Selectfluor® as compared to those under previous solution-based conditions. Notably, the process can be carried out in air. Considering the reduced use of chemicals and the simple, time-saving experimental procedures, this technique is an efficient and environmentally friendly way to access γ-fluorinated ketones.

Key words C–C bond cleavage, fluorination, mechanochemistry, ball-milling, solid-state, silver catalyst

In recent years, solvent-free solid-state organic transformations using ball milling, known as mechanochemical reactions, have been extensively studied as a new tool for organic chemistry.[1,2] Compared to conventional solution-based reactions, the advantages of these mechanochemical conditions include the avoidance of potentially harmful organic solvents, shorter reaction times, simple experimental operations, and the possibility of different reactivities from that in solution.[3] Owing to these advantages, a number of organic transformations have been attempted under mechanochemical conditions. Although the benefits of mechanochemistry for solid-state reactions of compounds with reactive bonds, such as organic halides, have been well-demonstrated, unactivated bond cleavage through mechanochemical transformation remains unexplored. Catalytic C–C bond cleavage/functionalization reactions have great synthetic utility in the preparation of complex valuable molecules and have been well-demonstrated under solution-based conditions, but these types of reactions under mechanochemical conditions have not been studied.



Scheme 1 Silver-catalyzed ring-opening fluorination of cyclic alcohols.

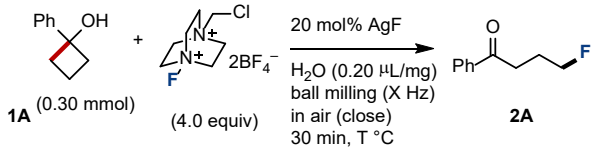
Fluorine-containing hydrocarbon compounds are often found in pharmaceuticals, agrochemicals, and materials.[4,5] Therefore, efficient methods to construct C(sp^3)–F bonds have been extensively researched over the past several decades.[6] Ring-opening fluorination of cyclic compounds has attracted attention as a valuable method for remote C(sp^3)–F bond formation.[7,8] In pioneering studies in 2015, the Murakami,[8b] Zhu,[8c] and Loh and Feng[8d] groups independently reported the silver-catalyzed ring-opening fluorination of cyclic alcohols

(Scheme 1A). Although these C–C bond cleavage/fluorination reactions can provide an efficient way to synthesize γ-fluorinated ketones, the solution-based conditions require high catalyst loading (>10 mol%), long reaction times, excessive amounts of Selectfluor®, an inert-gas atmosphere, and toxic organic solvents. These requirements greatly reduce the practical utility of the ring-opening fluorination of cyclic alcohols. As part of our ongoing studies into mechanochemical synthesis, we propose transferring this important reaction to a mechanochemical process.

Herein, we report a silver-catalyzed ring-opening fluorination reaction of cyclic alcohols under solid-state mechanochemical conditions (Scheme 1B).[9] The reaction proceeded efficiently to produce the desired γ-fluorinated ketones with high yield within a much shorter reaction time and requiring less silver catalyst and Selectfluor® than when using the established solution conditions. Notably, the entire newly developed solid-state protocol can be carried out under ambient conditions, *i.e.*, the chemicals, reagents, and catalysts can be added to the milling jar in air. Thus, this operationally simple protocol provides a more convenient and sustainable alternative to conventional solution-based ring-opening fluorination. Importantly, this study is the first example of catalytic C–C bond cleavage/functionalization reactions under mechanochemical conditions.

We began our study by exploring the milling conditions (milling jar, grinding ball, frequency, and internal temperature) of the solid-state ring-opening fluorination of 1-phenylcyclobutanol (**1A**) (Table 1). Reactions were conducted using a Retsch MM400 mill equipped with a temperature-controllable heat gun (see the Supporting Information for details).[2f] Using the solution-based conditions discovered by the Murakami group[8b] as a guideline, the mechanochemical reaction of **1A** was carried out in the presence of 20 mol% AgF catalyst and 4.0 equivalents (equiv) of Selectfluor®, with H_2O (0.20 μL of liquid per mg of solid reactant) as the liquid-assisted grinding material[10] in a stainless-steel jar (5 mL) with a stainless-steel grinding ball (10 mm) at 25 Hz for 30 min. The internal temperature was 110 °C, confirmed by thermography (preset temperature: 200 °C). Under these conditions, the desired γ-fluorinated ketone **2A** was obtained at a yield of only 5% (Table 1, entry 1). Although a small amount of **2A** was generated, the mechanochemical reaction under these preliminary conditions resulted in a complex mixture and poor mass balance. We hypothesized that high-temperature mechanochemical conditions were too harsh, due to the higher concentrations than those observed in solution reactions. To make the reaction conditions milder, we next examined the reaction under a lower internal temperature. As expected, the yield of **2A** was improved (43%) when the reaction was conducted at 55 °C (preset temperature: 80 °C) (Table 1, entry 2). Lowering the frequency from 25 Hz to 15 Hz gave a slightly better yield of **2A**. (46%, Table1, entry 3). A shorter reaction time (10 min) at 30 Hz provided poor results (10%, Table 1, entry 4). These results suggest that reaction temperature mainly affected the efficiency of this mechanochemical ring-opening fluorination reaction. In all cases, undesired decomposition of **1A** still occurred during the reaction, with insoluble and unidentified compounds observed in the crude mixture. When the reaction was performed at room temperature, it was still incomplete after 30 min. A low yield of **2A** was obtained (7%), and 49% of **1A** was recovered (Table 1, entry 5). Since decomposition of **1A** was still observed even under the milder conditions, we hypothesized that metallic residue from the stainless-steel milling jar or ball might interfere with the substrate, silver catalyst or Selectfluor®, leading to undesired side reactions.[11,12] To confirm this, AgF was excluded from the mixture (Table 1, entry 6). Surprisingly, the ring-opening fluorination reaction still proceeded and produced **2A** at 28% yield, with 30% of **1A** converted into unidentified side-products. This result suggested that the stainless-steel milling jar and ball caused the side reactions. Other types of jars and balls, made from different materials, were examined. It was found that a ZrO_2 jar (10 mL) and a ball (10 mm) resulted in a cleaner reaction mixture and produced **2A** at 52% yield (Table 1, entry 7). Teflon jar and ball, which has a low density of the material and allows for gentle mixing, also gave **2A** in good yield (51%, Table 1. Entry 8). Using a tungsten carbide jar (10 mL) and a ball (10 mm), the yield of **2A** decreased significantly to 16% (Table 1, entry 9). Based on these results, the optimal milling conditions were a 10 mL ZrO_2 jar with a 10 mm ZrO_2 ball at 15 Hz at 55 °C (Table 1, entry 7).

Table 1 Optimization of milling conditions[a]

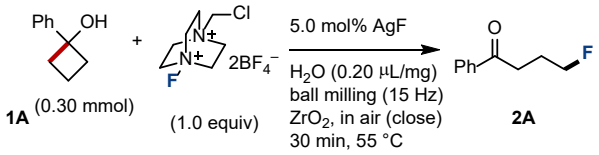


entry	jar / ball material	frequency X (Hz)	int. temperature T (°C)	Yield of **2A** (%)[b]
1	stainless-steel	25	110	5
2	stainless-steel	25	55	43
3	stainless-steel	15	55	46
4[c]	stainless-steel	30	55	10
5	stainless-steel	15	35	7
6[d]	stainless-steel	15	55	28
7	ZrO_2	15	55	52
8	Teflon	15	55	51
9	tungsten carbide	15	55	16

[a] Conditions: **1A** (0.30 mmol), AgF (20 mol%), Selectfluor® (4.0 equiv), H_2O (0.20 μL/mg) in a milling jar with a milling ball. [b] Yield was determined using ^1H NMR analysis with CH_2Br_2 as the internal standard. [c] Reaction time was 10 min. [d] Reaction conducted without AgF.

Further optimization of the conditions was subsequently carried out using the ZrO_2 milling jar and ball (Table 2). After extensive experimentation, the standard conditions were defined as follows: AgF (5.0 mol%) and Selectfluor® (1.0 equiv) with a small volume of H_2O (0.20 μL/mg) under the optimal milling conditions for 30 min. Using these conditions, **1A** was converted to **2A** at 68% yield (Table 2, entry 1). At a higher catalyst loading, **1A** was entirely consumed, but the yield of **2A** decreased (Table 2, entry 2). This result suggested that higher silver catalyst loading increases the concentration of reactive radical species and causes the undesired side reactions. Lower catalyst loading (2.5 mol%) and a shorter reaction time (15 min) yielded nearly identical results to the standard conditions (Table 2, entry 3). Other metal additives, such as manganese and iron salts, known to be effective catalysts under solution conditions, were not suitable for this solid-state reaction (Table 2, entries 4 and 5).[8d,h] When AgF was excluded from the standard conditions, the reaction did not proceed (Table 2, entry 6).

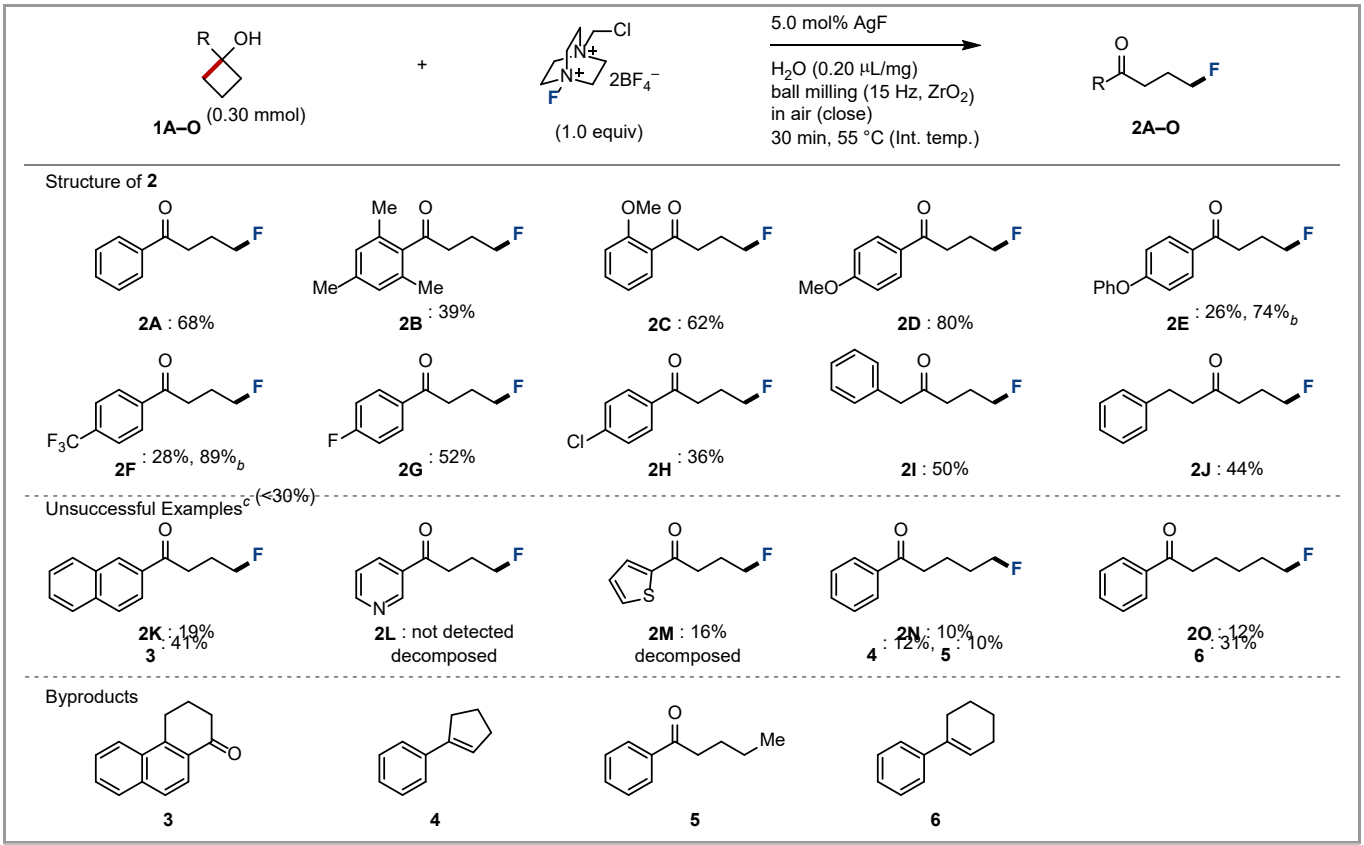
Table 2 Catalyst optimization using ZrO_2 milling jar and ball[a]



entry	deviation from the standard conditions	Yield of **2A** (%)[b]
1	none	68
2	20 mol% AgF	55
3	2.5 mol% AgF, 15 min	70
4	20 mol% $Mn(OAc)_2{\cdot}4H_2O$	27
5	20 mol% $Fe(acac)_2$	0
6	without AgF	0

[a] Conditions: **1A** (0.30 mmol), AgF (5.0 mol%), Selectfluor® (1.0 equiv), H_2O (0.20 μL/mg) at 55 °C (internal temperature) for 30 min in a ZrO_2 ball-milling jar (10 mL) with a ZrO_2 ball (10 mm) with ball-milling (15 Hz). [b] Yield was determined by ^1H NMR analysis using CH_2Br_2 as the internal standard.

With the optimized conditions determined, we then examined the substrate scope (Scheme 2). A simple phenyl-substituted cyclobutanol **1A** reacted well and produced the corresponding fluoroketone **2A** at 68% yield. Sterically hindered 1-mesitylcyclobutanol (**1B**) produced the ring-opening compound **2B** at 39% yield. Aromatic substituents with an electron-donating methoxy group showed a facile fluorination reaction, producing γ-fluorinated acetophenones (**2C** and **2D**) at a good to excellent yield. Phenoxy- and trifluoromethyl-substituents at the *para* position, as shown in **2E** and **2F**, diminished the reaction efficiency. In these cases, even in the presence of 10 mol% AgF catalyst, the reaction required a longer reaction time to produce the desired compounds with good yields (74% and 89% yield, respectively). Halogen functionalities such as fluoride and chloride were suitable for use under these conditions (**2G** and **2H**). The reaction also proceeded with alkyl-substituted cyclobutanols, producing the corresponding products **2I** and **2J** at 50% and 44% yield, respectively. In the case of naphthyl-substituted alcohol **1K**, a ring-opening intramolecular cyclization reaction occurred instead of the fluorination reaction to form **3** at 41% yield.[13] When heteroaromatic compounds such as pyridine **1L** and thiophene **1M** were subjected to these reaction conditions, the starting materials decomposed into complex mixtures. Less ring-strained cyclopentanol **1N** and cyclohexanol **1O** afforded the corresponding fluorinated ketones **2N** and **2O** in lower yield (10% and 12% yield, respectively), in contrast to the favorable results observed with these substrates under solution-based conditions.[8d] These low yields were primarily caused by an undesired dehydration or protonation reaction that formed alkenes **4** and **6,** and simple ketone **5**. In addition, a high concentration of the starting materials remained after the reactions of **2N** and **2O**.[14]

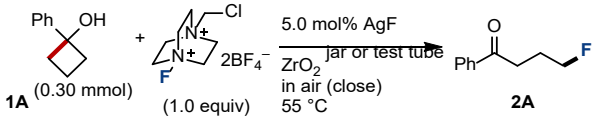


Scheme 2 Substrate scope for the solid-state ring-opening fluorination. [a] Conditions: **1A** (0.30 mmol), 5.0 mol% AgF, Selectfluor® (1.0 equiv), H_2O (0.20 mL/mg) at 55 °C (internal temperature) for 30 min in a ZrO_2 ball-milling jar (10 mL) with a ZrO_2 ball (10 mm) with ball-milling (15 Hz). [b] 10 mol% AgF for 1 h. [c] Yield was determined by ^1H NMR analysis using CH_2Br_2 as the internal standard.

To demonstrate the practical utility of the solid-state ball-milling reaction, solution and neat-stirring reactions were performed in screw cap tubes under conditions similar to the mechanochemical standard conditions (Table 3). The solution reaction of **1A** was conducted in the presence of AgF (5.0 mol%) and Selectfluor® (1.0 equiv) in a 1:1 water/benzene biphasic solvent (2.0 mL) at 55 °C under ambient atmosphere with magnetic stirring at 500 rpm. This solvent system was used by

the Murakami group in their work.[8b] Under these conditions, **2A** was obtained at very low yield after 30 min and 12 h (2% and 6% yield, respectively). The neat-stirring reaction progressed with low efficiency to yield the desired fluorinated ketone **2A** at 27% yield, suggesting that the strong mechanical agitation by ball milling is crucial for successful solid-state fluorination.

Table 3 Comparative studies with solution-state and neat conditions.



	ball-milling (15 Hz)	solution-state (500 rpm)	neat (500 rpm)
Yield of **2A** (%)[a]	68% (30 min)	2% (30min) 6% (12 h)	27% (30 min)

[a] Yield was determined by ^{1}H NMR analysis using CH_2Br_2 as the internal standard.

To investigate the reaction mechanisms in the solid-state, we performed radical trapping experiments (details in Supporting Information). It was found that the addition of 2,2,6,6-tetramethylpiperidinooxy (TEMPO) as a radical scavenger was completely inhibited the desired ring-opening fluorination. This result was consistent with the previously reported solution-state reactions. Therefore, we assume that this solid-state reaction is a radical-type reaction mechanism similar to solution-state conditions.

In summary, we have developed a method for silver-catalyzed solid-state ring-opening fluorination of cyclobutanols under ball-milling conditions. This is the first example of catalytic C–C bond cleavage/functionalization reactions under solid-state mechanochemical conditions. The developed mechanochemical conditions do not require potentially harmful organic solvents and use less silver catalyst and Selectfluor® than previously reported solution-state conditions. Notably, all synthetic operations can be carried out in air. Considering these practical utilities, the present solid-state ring-opening fluorination is an efficient and environmentally friendly strategy to access γ-fluorinated ketones. Further studies to expand the scope of cyclic alcohols and the development of unique C–C bond cleavage reactions in the solid-state are ongoing in our laboratory.

Funding Information

This work was financially supported by the Japan Society for the Promotion of Science (JSPS) via KAKENHI grants 22H00318, 21H01926 22K18333, 22H05328, and 22K20523, by the JST via the CREST grant JPMJCR19R1, by the FOREST grant PJ2521A02I, and by the Institute for Chemical Reaction Design and Discovery (ICReDD) established by the World Premier International Research Initiative (WPI), MEXT, Japan.

Acknowledgment

We thank Mr. Yuma Shiratori for his help in crosschecking the experiments.

Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

References and Notes

(1) For selected reviews on the use of ball-milling for organic synthesis, see: (a) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friščić, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. *Chem. Soc. Rev*. **2012**, *41*, 413. (b) Wang, G. W. *Chem. Soc. Rev*. **2013**, *42*, 7668. (c) Do, J. L.; Friščić, T. *ACS Cent. Sci*. **2017**, *3*, 13. (d) Hernández, J. G.; Bolm, C. *J. Org. Chem*. **2017**, *82*, 4007. (e) Métro, T.-X.; Martinez, J.; Lamaty, F. *ACS Sustainable Chem. Eng.* **2017**, *5*, 9599. (f) Achar, T. K.; Bose, A.; Mal, P. *Beilstein J. Org. Chem*. **2017**, *13*, 1907. (g) Eguaogie, O.; Vyle, J. S.; Conlon, P. F.; Gîlea, M. A.; Liang, Y. *Beilstein J. Org. Chem*. **2018**, *14*, 955. (h) Howard, J. L.; Cao, Q.; Browne, D. L. *Chem. Sci*. **2018**, *9*, 3080. (i) Andersen, J.; Mack, J. *Green Chem.* **2018**, *20*, 1435. (j) Bolm, C.; Hernández, J. G. *Angew. Chem., Int. Ed.* **2019**, *58*, 3320. (k) Friščić, T.; Mottillo, C.; Titi, H. M. *Angew. Chem., Int. Ed.* **2020**, *59*, 1030. (l) Kubota, K.; Ito, H. *Trends Chem.* **2020**, *2*, 1066. (m) Porcheddu, A.; Colacino, E.; De Luca, L.; Delogu, F. *ACS Catal.* **2020**, *10*, 8344. (n) Virieux, D.; Delogu, F.; Porcheddu, A.; García, F.; Colacino, E. *J. Org. Chem.* **2021**, *86*, 13885. (o) Cuccu, F.; De Luca, L.; Delogu, F.; Colacino, E.; Solin, N.; Mocci, R.; Porcheddu, A. *ChemSusChem* **2022**, *15*, e202200362. (p) Shaw, T. E.; Mathivathanan, L.; Jurca, T. *Organometallics* **2019**, *38*, 4066. (q) Hwang, S.; Grätz, S.; Borchardt, L. *Chem. Commun.* **2022**, *58*, 1661.

(2) For selected examples of solid-state organic transformations using ball-milling from our group, see: (a) Kubota, K.; Pang, Y.; Miura, A.; Ito, H. *Science* **2019**, *366*, 1500. (b) Kubota, K.; Takahashi, R.; Ito, H. *Chem. Sci.* **2019**, *10*, 5837. (c) Kubota, K.; Seo, T.; Koide, K.; Hasegawa, S.; Ito, H. *Nat. Commun.* **2019**, *10*, 111. (d) Pang, Y.; Lee, J. W.; Kubota, K.; Ito, H. *Angew. Chem., Int. Ed.* **2020**, *59*, 22570. (e) Seo, T. Kubota, K.; Ito, H. *J. Am. Chem. Soc.* **2020**, *142*, 9884. (f) Seo, T.; Toyoshima, T.; Kubota, K. Ito, H. *J. Am. Chem. Soc.* **2021**, *143*, 6165. (g) Kubota, K.; Toyoshima, N.; Miura, D.; Jiang, J.; Maeda, S.; Jin, M.; Ito, H. *Angew. Chem., Int. Ed*. **2021**, *60*, 16003. (h) Takahashi, R.; Hu, A.; Gao, P.; Gao, Y.; Pang, Y.; Seo, T.; Maeda, S.; Jiang, J.; Takaya, H.; Kubota, K. Ito, H. *Nat. Commun.*, **2021**, *12*, 6691. (i) Kubota, K.; Kondo, K.; Seo, T.; Ito, H. *Synlett*, **2022**, *33*, 898.

(3) (a) Colacino, E.; Isoni, V.; Crawford, D.; García, F. *Trends Chem.* **2021**, *3*, 335. (b) Ardila-Fierro, K. J.; Hernández, J. D. *ChemSusChem* **2021**, *14*, 2145. (c) Fantozzi, N.; Volle, J.-N.; Porcheddu, A.; Virieux, D.; García, F.; Colacino, E. *ChemRxiv Preprint* **2022**, DOI: 10.26434/chemrxiv-2022-b370p.

(4) (a) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881. (b) Hangmann, W. K. *J. Med. Chem.* **2008**, *51*, 4359. (c) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320. (d) Beger, R.; Resnati, G.; Metrangolo, P.; Weber. E.; Hulliger, J. *Chem. Soc. Rev.* **2011**, *40*, 3496. (e) Cametti, M.; Crousse, B.; Metrangolo, P.; Milani, R.; Resnati, G. *Chem. Soc. Rev.* **2012**, *41*, 31. (f) Jacobson, O.; Kiesewetter, D. O.; Chen, X. *Bioconjugate Chem.* **2015**, *26*, 1. (g) Gills, E. P.; Eastman, K. J.; Hill, M. D.; Donnelly, D. J.; Meanwell, N. A. *J. Med. Chem.* **2015**, *58*, 8315. (h) Yerien, D. E.; Bonesi, S.; Postigo, A. *Org. Biomol. Chem.* **2016**, *14*, 8398. (i) Meanwell, N. A. *J. Med. Chem.* **2018**, *61*, 5822. (j) Ogawa, Y.; Tokunaga, E.; Kobayashi, O.; Hirai, K.; Shibata, N. *iScience* **2020**, *23*, 101467. (k) Inoue, M.; Sumii, Y.; Shibata, N. *ACS Omega* **2020**, *5*, 10633.

(5) (a) Smart, B. E. *J. Fuluorine Chem.* **2001**, *109*, 3. (b) O'Hagan, D. *Chem. Soc. Rev.* **2008**, *37*, 308. (c) Han, J.; Kiss, L; Haibo, M. Remete, A. M.; Ponikvar-Svet, M.; Sedgwick, D. M.; Roman, R.; Fustero, S.; Moriwaki, H.; Soloshonok, V. A. *Chem. Rev.* **2021**, *121*, 4678.

(6) For selected reviews, see: (a) Lian, T.; Constanze, N. N.; Ritter, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 8214. (b) Brooks, A. F.; Topczewski, J. J.; Ichiishi, N.; Sanford, M. S.; Scott, P. J. H. *Chem. Sci.* **2014**, *5*, 4545. (c) Champagne, P. A.; Desroches, J.; Hamel, J.-D.; Vandamme, M.; Paquin, J.-F. *Chem. Rev.* **2015**, *115*, 9073. (d) Zhu, Yi.; Han, J.; Wang,

J.; Shibata, N.; Sodeoka, M.; Soloshonok, V. A.; Coelho, J. A. S.; Toste, F. D. *Chem. Rev.* **2018**, *118*, 3887. (e) Szpera, R.; Moseley, D. F. J.; Smith, L. B.; Sterling, A. J.; Gouverneur, V. *Angew. Chem., Int. Ed.* **2019**, *58*, 14824. (f) Bertrand, X.; Chabaud, L.; Paquin, J.-F. *Chem. Asian J.* **2021**, *16*, 563. (g) Suto, A.; Yamaguchi, J. *J. Synth. Org. Chem., Jpn.* **2021**, *79*, 910.

(7) For selected reviews of the ring-opening functionalization of cyclic alcohols, see: (a) Nikolaev, A.; Orellana, A. *Synthesis* **2016**, *48*, 1741. (b) Murakami, M.; Ishida, N. *Chem. Lett.* **2017**, *46*, 1692. (c) Liu, Y.; Wang, Q.-L.; Chen, Z.; Zhou, C.-S.; Xiong, B.-Q.; Zhang, P.-L.; Yang, C.-A.; Zhou, Q. *Beilstein J. Org. Chem.* **2019**, *15*, 256. (d) Wu, X.; Zhu, C. *Chem. Commun.* **2019**, *55*, 9747. (e) Tsui, E.; Wang, H.; Knowles, R. R. *Chem. Sci.* **2020**, *11*, 11124. (f) Murakami, M.; Ishida, N. *Chem. Rev.* **2021**, *121*, 264. (g) McDonald, T. R.; Mills, L. R.; West, M. S.; Rousseaux, S. A. L. *Chem. Rev.* **2021**, *121*, 3.

(8) For a review of ring-opening fluorination, see: (a) Remete, A. M.; Kiss, L. *Eur. J. Org. Chem.* **2019**, 5574. For selected examples of the ring-opening fluorination, see: (b) Ishida, N.; Okuma, S.; Nakanishi, Y.; Murakami, M. *Chem. Lett.* **2015**, *44*, 821. (c) Zhao, H.; Fan, X.; Yu, J.; Zhu, C. *J. Am. Chem. Soc.* **2015**, *137*, 3490. (d) Ren, S.; Feng, C.; Loh, T.-P. *Org. Biomol. Chem.* **2015**, *13*, 5105. (e) Bloom, S.; Bume, D. D.; Pitts, C. R.; Lectka, T. *Chem. Eur. J.* **2015**, *21*, 8060. (f) Deng, Y.; Kauser, N. I.; Islam, S. M.; Mohr, J. T. *Eur. J. Org. Chem.* **2017**, 5872. (g) Lu, Y.-C.; Jordan, H. M.; West, J. G. *Chem. Commun.* **2021**, *57*, 1871. (h) Lu, Y.-C.; West, J. G. *ACS Catal.* **2021**, *11*, 12721. (i) Wu, P.; Ma, S. *Org. Lett.* **2021**, *23*, 2533. (j) Pitts, C. R.; Ling, B.; Snyder, J. A.; Bragg, A. E.; Lectka, T. *J. Am. Chem. Soc.* **2016**, *138*, 6598. (k) Banik, S. M.; Mennie, K. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2017**, *139*, 9152. (l) Ilchenko, N. O.; Hedberg, M.; Szabó, K. J. *Chem. Sci.* **2017**, *8*, 1056. (m) Wang, M.-M.; Waser, J. *Angew. Chem., Int. Ed.* **2020**, *59*, 16420. (n) Pitts, C. R.; Bloom, M. S.; Bume, D. D.; Zhang, Q. A.; Lectka, T. *Chem. Sci.* **2015**, *6*, 5225. (o) Dauncey, E. M.; Morcillo, S. P.; Douglas, J. J.; Sheikh, N. S.; Leonori, D. *Angew. Chem., Int. Ed.* **2018**, *57*, 744. (p) Kim, D.; Lim, H. N. *Org. Lett.* **2020**, *22*, 7465. (q) Song, J. W.; Lim, H. N. *Org. Lett.* **2021**, *23*, 5394. (r) Roque, J. B.; Kuroda, Y.; Göttemann, L. T.; Sarapong, R. *Science* **2018**, *361*, 171. (s) Komatsuda, M.; Suto, A.; Kondo, H., Jr.; Hiroyuki, T.; Kato, K.; Saito, B.; Yamaguchi, J. *Chem. Sci.* **2022**, *13*, 665. (t) Komatsuda, M.; Ohki, H.; Kondo, H., Jr.; Suto, A.; Yamaguchi, J. *Org. Lett.* **2022**, *24*, 3270.

(9) For selected examples of solid-state C(sp_3)–F bond construction, see: (a) Wang, Y.; Wang, H.; Jiang, Y.; Zhang, C.; Shao, J.; Xu, D. *Green Chem.* **2017**, *19*, 1674. (b) Howard, J. L.; Sagatov, Y.; Repusseau, L.; Schotten, C.; Browne, D. L. *Green Chem.* **2017**, *19*, 2798. (c) Howard, J. L.; Sagatov, Y.; Browne, D. L. *Tetrahedron* **2018**, *74*, 3118.

(10) (a) Bowmaker, G. A. *Chem. Commun.* **2013**, *49*, 334. (b) Ying, P.; Yu, J.; Su, W. *Adv. Synth. Catal.* **2021**, *363*, 1246.

(11) Štefanić, G.; Krehula, S.; Štefanić, I. *Chem. Commun.* **2013**, *49*, 9245.

(12) For selected examples of reactions which milling ball and/or jar work as a metal catalyst, see: (a) Hwang, S.; Grätz, S.; Borchardt, L. *Chem. Commun.* **2022**, *58*, 1661. (b) Fulmer, D. A.; Shearouse, W. C.; Medonza, S. T.; Mack, J. *Green Chem.* **2009**, *11*, 1821. (c) Cook, T. L.; WalkerJr., J. A.; Mack, J. *Green Chem.* **2013**, *15*, 617. (d) Yu, J.; Li, Z.; Jia, K.; Jiang, Z.; Liu, M.; Su, W. *Tetrahedron Lett.* **2013**, *54*, 2006. (e) Sawama, Y.; Niikawa, M.; Yabe, Y.; Goto, R.; Kawajiri, T.; Marumoto, T.; Takahashi, T.; Itoh, M.; Kimura, Y.; Sasai, Y.; Yamauchi, Y.; Kondo, S.; Kuzuya, M.; Monguchi, Y.; Sajiki, H. *ACS Sustainabe Chem. Eng.* **2015**, *3*, 683. (f) Sawama, Y.; Kawajiri, T.; Niikawa, M.; Goto, R.; Yabe, Y.; Takahashi, T.; Marumoto, T.; Itoh, M.; Kimura, Y.; Monguchi, Y.; Kondo, S.; Sajiki, H. *ChemSusChem*, **2015**, *8*, 3773. (g) Haley, R. A.; Zellner, A. R.; Krause, J. A.; Guan, H.; Mack, J. *ACS Sustainable Chem. Eng.* **2016**, *4*, 2464. (h) Sawama, Y.; Yasukawa, N.; Bau, K.; Goto, R.; Niikawa, M.; Monoguchi, Y.; Itoh, M.; Sajiki, H. *Org. Lett.* **2018**, *20*, 2892. (i) Vogt, C. G.; Grätz, S.; Lukin, S.; Halasz, I.; Etter, M.; Evans, J. D.; Borchardt, L. *Angew. Chem., Int. Ed.* **2019**, *58*, 18942. (j) Pickhardt, W.; Beaković, C.; Mayer, M.; Wohlgemuth, M.; Kraus, F. J. L.; Etter, M.; Grätz, S.; Borchardt, L. *Angew. Chem., Int. Ed.* **2022**, e202205003.

(13) For silver-catalyzed ring expansion of cyclic alcohols, see: Yu, J.; Zhao, H.; Liang, S.; Bao, X.; Zhu, C. *Org. Biomol. Chem.* **2015**, *13*, 7924.

(14) For dehydration reaction of tertiary cycloalcohols using copper catalyst and Selectfluor®, see: Ren, S.; Zhang, J.; Zhang, J.; Wang, H.; Zhang, W.; Liu, Y.; Liu, M. *Eur. J. Org. Chem.* **2015**, 5381.

(15) **Representative Experimental Procedure for Solid-state Silver-catalyzed Ring-opening Fluorination of Cyclic Alcohols**

Cyclobutanol **1A** (44.3 mg, 0.30 mmol, 1.0 equiv), AgF (1.9 mg, 0.015 mmol, 5.0 mol%), and Selectfluor® (107.2 mg, 0.30 mmol, 1.0 equiv) were placed in a ball milling vessel (ZrO_2, 10 mL) loaded with one grinding ball (ZrO_2, diameter: 10 mm). Then H_2O (31 μL, 0.20 μL/mg) was added *via* syringe. After the vessel was closed in air without purging with inert gas, the vessel was placed in the ball mill (Retsch MM400, 30 min at 15 Hz). After 30 min, the mixture was added H_2O and Et_2O and extracted three times with Et_2O. The combined organic layer was dried over $MgSO_4$, filtrated, and then concentrated *in vacuo*. The crude mixture was then purified by flash column chromatography (SiO_2, hexane/ethyl acetate, 50:1) to give the corresponding ring-opening product **2A** as a colorless oil (33.8 mg, 0.20 mg, 68% yield)

Compound **2A**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.16 (dquint, *J* = 27.6, 6.4 Hz, 2H), 3.16 (t, *J* = 6.4 Hz, 2H), 4.57 (dt, *J* = 48.8, 6.4 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz $CDCl_3$, δ): 24.8 (d, J_{C-F} = 20.2 Hz, CH_2), 33.9 (d, J_{C-F} = 4.8 Hz, CH_2), 83.3 (d, J_{C-F} = 165.9 Hz, CH_2), 127.9 (*C*H), 128.6 (*C*H), 133.1 (*C*H), 136.7 (*C*), 199.0 (*C*). ^{19}F NMR (376 MHz $CDCl_3$, δ): −220.9 – −221.4 (m, 1F). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{10}H_{11}FO$, 166.07939; found, 166.07934.