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Ring-Opening Functionalization of Simple *gem*-Difluorocyclopropanes by Single Electron Oxidants

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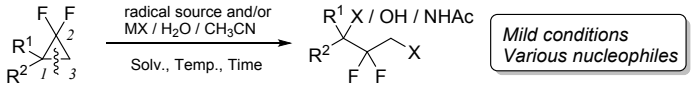
KEYWORDS gem-Difluorocyclopropane, ring-opening, 1,3-difunctionalization



ABSTRACT: It was reported for the first time that single electron oxidants such as CAN or $K_2S_2O_8$ affected facile ring-opening of simple *gem*-difluorocyclopropanes to afford 1,3-dibromo-2,2-difluoropropanes in good yields by the action of KBr, and appropriate choice of conditions allowed to incorporate not only second halogen atoms but also hydroxy or acetamido groups at the C^1 position in the difluoropropane structures in a regiospecific fashion after initiation of the reaction by introduction of the first bromine atom at the C^3.

INTRODUCTION

gem-Difluorocyclopropanes (F_2CPs) constitute one of the most attractive components in organic syntheses,[1] and their ring-opening readily afforded the corresponding difluoromethylenated compounds some of which have been paid special attention because of their actual application as biologically active substances[2] shown in Figure 1.[3,4] This would at least in part attribute to their unique structural characteristics which nicely bring about metabolic stability enhancement[5] and biological similarity to phosphoric ester oxygen (bioisosteres).[6]

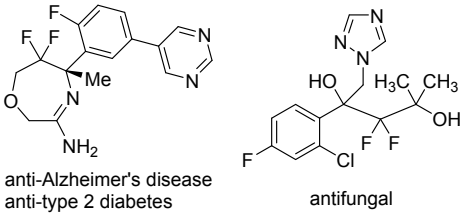
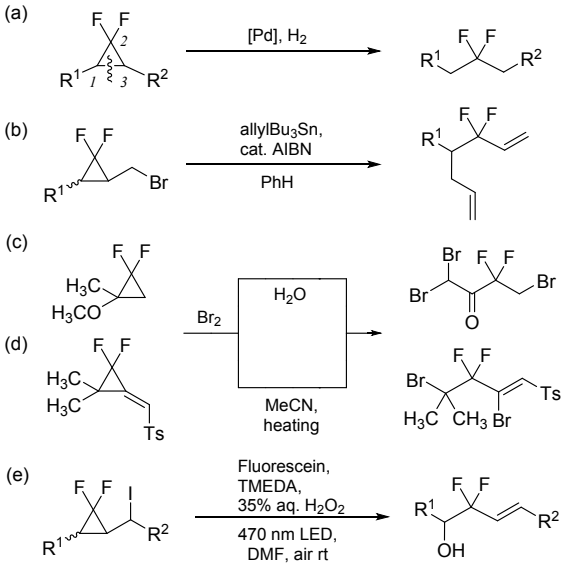


Figure 1. Biologically active compounds with a difluoromethylene moiety.

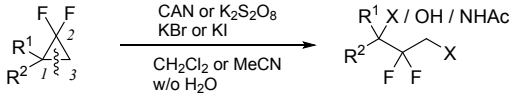
One of the most convenient and promising routes to get access to this framework would be the utilization of ring-opening reactions of *gem*-F_2CPs, and various protocols have been developed for this purpose since 1980s: they are, for example, by way of Pd-catalyzed hydrogenation (a),[7] radical-type ring-opening allylation (b)[8] and bromination (c and d),[9,10] with other type of radical-based ring opening protocols[11,12] (Scheme 1). Very recently, the Itoh group achieved the synthesis of cycloalkenes with *gem*-difluoromethylene moiety as the extension of (b),[13] and also developed the convenient route to 2,2-difluoro homoallylic alcohols *via* the photo-irradiative aerobic oxidation (Scheme 1 (e)).[14] However, problems occurred in most of such transformations were the general requirement of special structural features in substrates whose preparation should be involved multi-step syntheses. To the best of our knowledge, since there is no transformation methods applicable to simple F_2CPs except for the one in Scheme 1 (a), it is significantly important to exploit an

Scheme 1. Ring-opening functionalization of cyclopropanes



adequate pathway from such simple substrates to efficiently construct various compounds with difluoromethylene units by way of the ready and straightforward direct ring-opening technique. Additional advantage would be the inclusion of plural functionalities in this ring-opening products which would be nicely employed as versatile building blocks for installation of a CF_2 group. Because we have recently found out a more convenient preparation method of F_2CPs starting from methyl 2,2-difluoro-2-(fluorosulfonyl)acetate and styrene derivatives by slight modification[15] of the Dolbier's procedure,[16] utilization of these products[17] was explored at the next step for demonstration of their synthetic importance as potent building blocks. With reference to the reported method on the Br radical-promoted (di)bromination of alkenes[18] as well as non-fluorinated cyclopropanes,[19] our own modification led to a facile and mild protocol which was affected by a mixture of KBr and CAN. This transformation realized not only 1,3-dibromination but also 1,3-bromohydroxylation as well as 1,3-bromoamidation just from simple F_2CPs without any special structural devices (Scheme 2). Results along this line are reported in detail in this article.

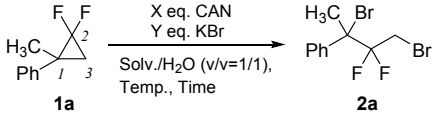
Scheme 2. The present ring-opening functionalization of simple F_2CPs (*this work*)



RESULTS AND DISCUSSION

First of all, for optimization of the reaction conditions of CAN and KBr-mediated dibromination, we employed (2,2-difluoro-1-methylcycloprop-1-yl)benzene **1a** as the model substrate which was readily prepared from the reaction of 1-methylstyrene and methyl 2,2-difluoro-2-(fluorosulfonyl)acetate.[12] Entries 1-4 in Table 1 clearly demonstrated that 9 h was the adequate reaction time for the conversion of **1a** to **2a**. This protocol furnished not only the desired 1,3-dibromobutane **2a** but also (1,2,4-tribromo-3,3-difluorobutan-2-yl)benzene **3a** as a byproduct in 2-18% yields. In our system, the regiospecific cleavage of the C^1-C^3 bond was realized without formation of any other compounds stemmed from the C^1-C^2 and/or C^2-C^3 bond disconnection. The amounts of CAN of 2.3 eq. and KBr of 2.2 eq. were the best among tested (entries 3 vs 5-6), and room temperature was found to be the most appropriate in terms of the yield of **2a** (entries 3 vs 7-8). In this system, dichloromethane (DCM) was suitable and other solvents did not give any fruitful outcome (entries 3 vs 9-11) although decolorization of the reaction mixture was noticed in tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) or methanol (MeOH) solvents which clearly indicated the consumption of CAN. Because the substrate **1a** was recovered in a larger amount in these instances, we assumed that these solvents would disturb the generation or presence of Br• species. Aqueous acetonitrile (MeCN) (entry 12) afforded a different byproduct in 28% yield which was identified as 4-bromo-3,3-difluoro-2-phenylbutan-2-ol (**4a**). This result unambiguously manifested the possible plural routes related to the C^1-C^3 bond cleavage of the

Table 1. Optimization of dibrominative ring opening conditions[a]



1a **2a**

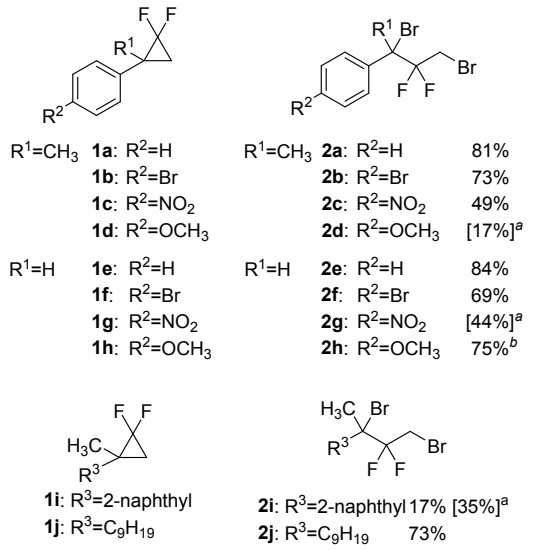
entry	X (eq.)	Y (eq.)	Solv.	Temp. (°C)	Time (h)	Yield[b] (%)
1	2.3	2.2	DCM	25	3	61
2	2.3	2.2	DCM	25	6	74
3	2.3	2.2	DCM	25	9	[81]
4	2.3	2.2	DCM	25	12	76
5	1.0	1.0	DCM	25	9	17
6	3.0	3.0	DCM	25	9	53
7	2.3	2.2	DCM	0	9	43
8	2.3	2.2	DCM	40	9	50
9	2.3	2.2	THF	25	9	0
10	2.3	2.2	DME	25	9	0
11	2.3	2.2	MeOH	25	9	18
12	2.3	2.2	MeCN	25	9	(28)
13	2.3[c]	2.2	DCM	25	9	27
14	2.3	2.2[d]	DCM	25	9	77
15	2.3	2.2[d]	DCM	25	9	73

[a]Reactions were performed in a 0.5 mmol scale with 5 mL each of H_2O and an appropriate solvent. [b]Yields of **2a** were determined by ^{19}F NMR analyses. The numbers in bracket (entry 3) and parenthesis (entry 12) were the yields of the isolated **2a** and 4-bromo-3,3-difluoro-2-phenylbutan-2-ol **4a**, respectively. [c]$Ce(SO_4)_2{\cdot}4H_2O$ was employed instead of CAN. [d] NaBr (entry 14) and LiBr (entry 15) were employed instead of KBr.

F_2CPs. Lower efficiency of $Ce(SO_4)_2{\cdot}4H_2O$ was noticed when compared with CAN (entry 13), and the almost equal potency was exerted by NaBr and LiBr to KBr (entries 3 vs 14-15). Finally, the condition of entry 3 was determined as the best of all.

The scope and limitation of the present dibrominative ring-opening were shown in Figure 2. (2,2-Difluorocycloprop-1-yl)benzenes **1a** or **1e** with or without a methyl substituent at the benzylic position led to efficient formation of the 1,3-dibromoalkanes **2a** or **2e** in excellent

yields, respectively. Smooth C-C bond cleavage was also noticed for substrates with Br as R^2 (**1b** and **1f**), while the



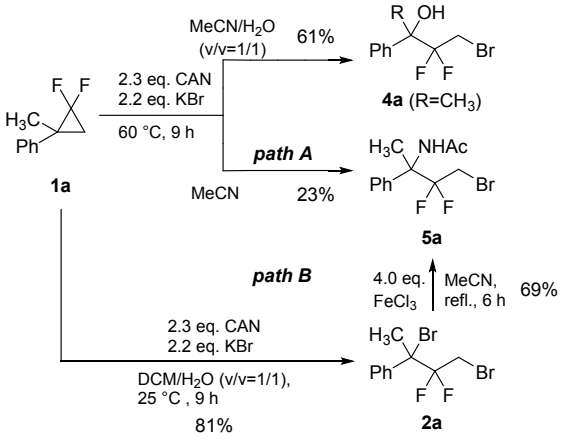
[a] The numbers in brackets were determined by ^{19}F NMR analyses.
[b] The reaction was performed at 70 °C in DCE.

Figure 2. Dibromination of various substrates.

strongly electron-withdrawing nitro moiety at the same position (**1c** and **1g**) did not allow full conversion with recovery of substrates to some extent. On the other hand, a complicated reaction was occurred for **1d** possessing the electron-donating methoxy group as R^2, which recorded a quite low material balance because of significant decomposition of the substrate and/or product under the conditions employed. The fact that substitution of a Me group as R^1 for H led to a decent production of the desired **2h** in 75% yield would be due to the different stability of the resultant intermediate (*vide infra*). 2-(2,2-Difluoro-1-methylcyclo-prop-1-yl)-naphthalene **1i** was not a good candidate for this reaction with 50% recovery of **1i** but the alkyl substituent instead of the naphthalene ring worked nicely for construction of the corresponding product **2j** in 71% yield.

Under the condition of entry 12 in Table 1, 4-bromo-3,3-difluoro-2-phenylbutan-2-ol (**4a**) was obtained in 28% yield possibly as the consequence of ring opening of **1a**, followed by acceptance of the H_2O attack at the benzylic position. After briefly checking the reaction conditions, raising the reaction temperature from 25 °C to 60 °C allowed to increase its isolated yield to the acceptable level of 61% (Scheme 3). This transformation is interesting because only two precedented methods were available at present to get access to this type of brominated alcohols: they are 1) 2,2,3,3-tetrafluorooxetane opening by Grignard reagents (R=aryl)[20] and 2) reduction of the corresponding 3-bromo-2,2-difluoropropan-1-one (R=H).[21] The most significant advantage of our method is to perform the reaction under open-air in aqueous solvents using easily available F_2CPs. Furthermore, it was found out that the absence of H_2O conveniently modified this process to form *N*-(4-bromo-3,3-difluoro-2-phenylbutan-2-yl)acetamide **5a** in 23% yield (path A) via the Ritter-type pathway. In spite of difficulty in improvement of this process even after the detailed reaction condition search, this unprecedented product **5a** was nicely isolated in 67% yield as a white solid by the alternative stepwise reactions of dibrominative

Scheme 3. Bromohydroxylation and bromoamidation

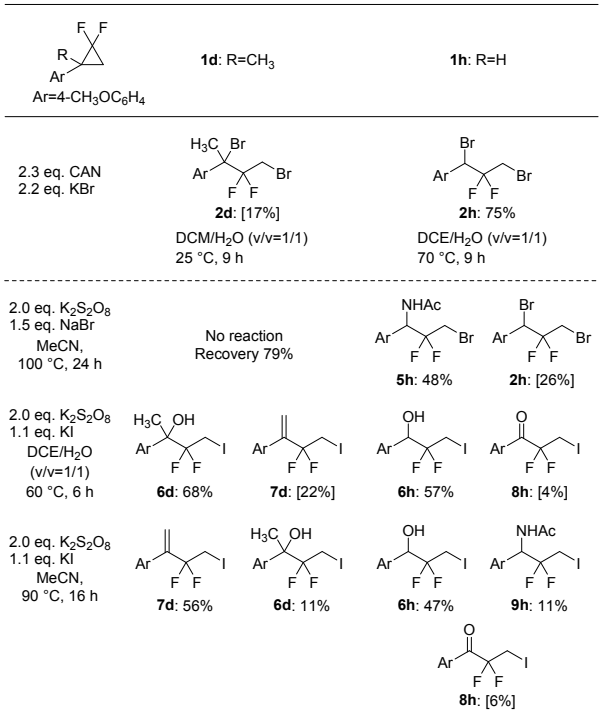


The numbers in brackets were determined by ^{19}F NMR analyses.
The isolated yield of **5a** was the figure after recrystalization.

ring-opening, followed by treatment with $FeCl_3$ under reflux in MeCN (path B).[22]

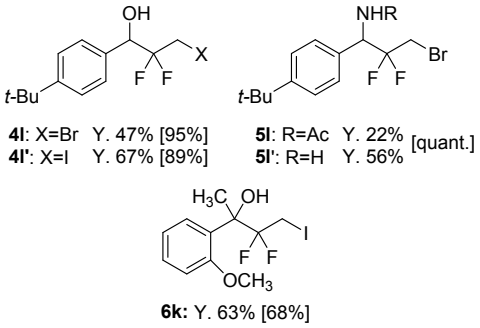
As described in Figure 2, success of this dibromination was highly dependent on the presence of the benzylic methyl group in the case of substrates with the 4-methoxyphenyl group, i.e. **1d** and **1h**. In Table 2 was shown their direct reactivity comparison when potassium persulfate ($K_2S_2O_8$) was used because CAN affected about 40% decomposition

Table 2. Reactivity difference between 1d and 1h



The numbers in brackets were determined by ^{19}F NMR analyses.

of **1d** and/or **2d**. KBr (17% yield) and NaBr (79% recovery) were proved to be ineffective as a Br source for **1d**, in sharp contrast to the structurally similar compound **1h** which was transformed to the difluoroamide **5h** in moderate yield by treatment with NaBr. Iodohydroxylation of **1d** and **1h** was also achieved by use of KI to nicely provide **6d** and **6h**, respectively. In the case of **1d**, exchange of the solvent to MeCN altered the main route to furnish the difluoroalkene **7d** with the benzylic alcohol **6d** as a byproduct. On the other hand, iodohydroxylation of **1h** was realized by $K_2S_2O_8$ and the difluoropropanol **6h** was obtained as the main product along with the corresponding ketone **8h** and/or acetamide **9h** as byproducts in DCE/H_2O and MeCN solvents, respectively. Furthermore, halohydroxylation and bromoamidation of different substrates were also performed (Figure 3). Based on the procedure for the conversion of **1a** to **4a** in Scheme 3, 2,2-difluoro-3-bromo-1-(4-*tert*-butylphenyl)propan-2-ol **4l** was obtained by increasing the reaction temperature to 80 °C. When KI was employed instead of KBr, formation of the corresponding iodopropanol **4l'** was realized in high yield. Dibromopropane and other unidentified byproducts were also observed by ^{19}F NMR measurement. In the case of bromoamidation, it was interesting to note that the corresponding deacetylated 3-bromopropyl-amine **5l'** was isolated along with the desired *N*-[3-bromo-2,2-difluoro-1-(4-*tert*-butylphenyl)prop-1-yl]acetamide **5l** in favor of the former. Iodohydroxylation by $K_2S_2O_8$ was also applicable to 1-(2,2-difluoro-1-methylcyclo-propyl)-2-methoxy-benzene (**1k**), leading to formation of the desired product in good yield.



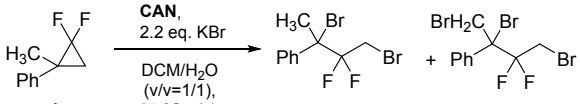
The numbers in brackets were conversion yields determined by ^{19}F NMR analyses.

Figure 3. Halohydroxylation and bromoamidation.

For obtaining further information on the reaction mechanism, the present dibromination was performed in the dark (Scheme 4a) which allowed to decrease the yield of the dibrominated butane **2a** from 86% under the standard conditions to 45% with a larger amount of the side product, tribrominated **3a** in 26% yields. In spite of great suppression of the formation of **2a** (40% yield) under an argon atmosphere with irradiation of light, usage of 1.5 times of CAN under such conditions accomplished the similar level of the yield of **2a** (73%) to the one under the original conditions (Table 1, entry 3). These results led to a clear conclusion that both light and oxygen worked at least in a supportive manner and thus, it is strongly considered that the radical mechanism is involved in the present reaction. In this system, the construction of **3a** expected us the in situ generation of molecular bromine,

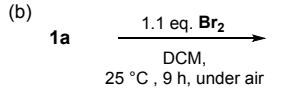
Scheme 4. Investigations on the reaction mechanism (1)

(a)



CAN (eq.)	light	atmosphere	^{19}F NMR yield (%)	
2.3 (Table 1, entry 3)	O	air	86%	6%
2.3	X	air	45%	26%
2.3	O	Ar	40%	trace
2.3	X	Ar	30%	17%
3.5	O	Ar	73%	0%

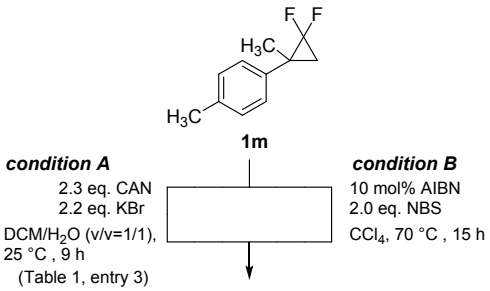
(b)



1.1 eq. TEMPO	light	^{19}F NMR yield (%)	
X	O	54%	30%
O	O	0% (Recovery of **1a**; 98%)	0%
X	X	54%	11%
X	12W white LED	77%	20%

and **2a** was actually obtained in 54% yield by the action of Br_2 in DCM[23] instead of a combination of CAN and KBr (Scheme 4b). In spite of known procedures for non-fluorinated cyclopropane ring opening affected by the direct submission of Br_2, the grad- ual generation of Br•/Br_2 by the present CAN/KBr system seemed to be superior in terms of the suppressed formation of the undesired tribromide **3a**. It is quite interesting to note that this reaction didn't proceed at all in the presence of 1.1 eq. of TEMPO with 98% recovery of the substrate **1a**. In spite of the fact that dibromination by Br_2 in the dark actually occurred, almost complete inhibition of the reaction by the addition of TEMPO strongly suggested the radical character of this reaction course.

Scheme 5. Investigations on the reaction mechanism (2)



condition A	Y. [89%]	Y. [11%]
condition B	Y. [47%]	Y. [11%]

Yields were determined by ^{19}F NMR analyses.

Scheme 5 demonstrated an exceptional example where 1-(2,2-difluoro-1-methylcycloprop-1-yl)-4-methylbenzene **1m** preferentially experienced bromination at the benzylic position to yield **10m** under the original conditions (Table 1, entry 3). A similar trend was observed by the Whol-Ziegler bromination conditions by *N*-bromosuccinimide (NBS) in the presence of a catalytic amount of AIBN in CCl_4, which again assumed the radical mechanism.

For obtaining further information, computation was performed whose results were summarized in Table 3.[24] On the basis of the orbital energies, the Br radical SOMO and the occupied orbital of **1a** should be responsible for this reaction because of their least energy gap, and the present reaction was considered to be initiated by the bond forma- tion of Br• and the C^3 atom at least in a regioselective manner because 1) the occupied lobe by two electrons on the C^1-C^3 bond is the energetically highest of all the cyclo-propane-related lobes and thus should be responsible for the ring opening, and 2) the attack at C^3 should be facile due to its lower steric hindrance, and afford the thermodynamically more favorable benzylic radical species. It is interesting to note that the regioselective ring-opening of the same type of F_2CPs was also realized at the other C-C bonds by emnploying totally different reaction conditions and/or substrate substituent patterns.[17b,25] After ring opening, further one electron oxidation of the resultant radical intermediate seemed to be the next step and further reaction with Br_2 (or Br^- ion), H_2O, or acetonitrile readily furnished the corresponding adducts **2**, **4a**, and **5a**, respectively. Formation of the tribromide **3a** was also ex plained by the proton elimination from the intermediary benzyl cation, where the addition of Br_2 was occurred. In the case of **1m**, the lobe at the benzylic C-H bond was calculated to be at the energy level of –10.549 eV which is 0.466 eV higher than the case of the one at the C^1-

Table 3. Computational results for 1a and Br_2 or Br•

	Energy level (eV)			
	Singlet		Triplet	
	Occupied	Unoccupied	Occupied	Unoccupied
C^1-C^2	–14.796	0.739		0.544 (α)
				0.559 (β)
C^1-C^3	–12.710	0.413	–12.495 (α)	0.433 (α)
			–12.626 (β)	0.433 (β)
C^2-C^3	–13.838	0.610		0.735 (α)
				0.734 (β)
Br_2	–7.982	–4.238		
Br•			–8.898 (α)	0.114 (α)
			–8.519 (β)	–6.535(β)

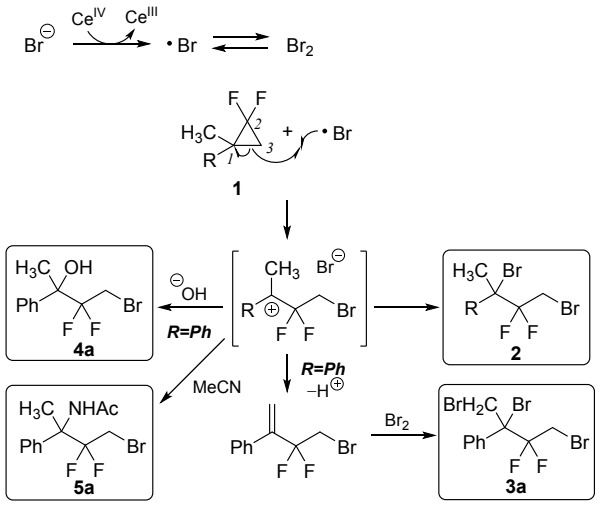


Figure 4. Proposed reaction mechanism.

C^3 bond (–11.015 eV) which unambiguously explained the preferential bromination at the benzylic position as shown in Scheme 5.

On the bases of the experimental as well as computational results described above, the following reaction mechanism was considered to be plausible (Figure 4). At first, Br radical was produced by ready oxidation of the corresponding anion by CAN. After attack of this active species at the sterically least hindered C^3 atom in the electronically highest occupied molecular orbital at the cyclopropane ring, following one electron oxidation of the resultant radical intermediate seemed to occur and the resultant benzylic cation would react with such nucleophiles as Br^- (or Br• before one electron oxidation), H_2O, or MeCN. Alternative pathway is to lose proton from the benzylic methyl group to afford the styrene type intermediate whose fate would react with Br_2 to give the corresponding tribromide.

The electron-withdrawing nature of fluorine affected the inherently lower stability of the neighboring carbocation when compared with the case of the corresponding non-fluorinated counterparts. The impact of the methoxy group in **1d** on a benzene ring should be in a dual manner, thus causing stabilization of the benzylic radical (or cation) as well as activation of the benzene ring toward electrophilic attack by the in situ generated Br_2 molecule. However, this is not the case for 1-(2,2-difluorocycloprop-1-yl)-4-methoxybenzene **1h** (substitution of a CH_3 group in **1d** for hydrogen) which was nicely transformed into the desired **2h** at the elevated temperature of 70 °C in a 1,2-dichloroethane (DCE) solvent. These phenomena would be understood as the consequence of the "adequately unstable" secondary radical formation from **1h** which might permit the promotion of the selective second bromination at this site. Relatively lower yields of the products with a 4-nitrophenyl group (**2c** and **2g**) on the benzene ring would be stemmed from the less stable benzylic cation because of the presence of the strongly electron-withdrawing NO_2 substituent.

CONCLUSION

In summary, we have successfully demonstrated hitherto unknown and easy-to-use methods for regiospecific ring opening of the simple *gem*-difluorocyclopropanes without installation of any specific functions in the presence of single electron oxidants such as CAN (IV) or $K_2S_2O_8$. This process readily furnished 1,3-dibromo-2,2-difluoropropane derivatives in good yields when KBr was employed in a DCM/H_2O (v/v=1/1) mixed solvent. Characteristic feature of the present reaction was noticed for the realization of bromohydroxylation and -amidation just by changing the solvent system. These products with a difluoromethylene moiety are considered as excellent building blocks for pharmaceuticals and functional materials. Further functionalization of these products are ongoing in our laboratory whose results would be presented in due course.

EXPERIMENTAL SECTION

Unless otherwise mentioned, the NMR spectra for ^{1}H, ^{13}C, and ^{19}F were recorded at 300, 75.5, and 282 MHz, respectively in $CDCl_3$ unless otherwise noted on JEOL JMN AL-300, with chemical shifts being reported in ppm downfield from internal TMS (δ: 0.00) for ^{1}H, $CDCl_3$ (δ: 77.0) for $^{13}C\{^1H\}$ NMR, and BTF (δ: –64.00) or C_6F_6 (δ: –163.00) for ^{19}F NMR spectra. Data were tabulated in the following order: a number of protons or fluorines, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad peak), and coupling constants in Hertz. IR spectra were reported in wave numbers (cm^{-1}) on JASCO FTIR-6100. High resolution mass spectra were obtained by double-focusing mass spectrometer in the FAB mode by using JEOL JMS-700. Elemental analyses were recorded on Perkin Elmer CHNS/O Analyzer 2400.

Preparation of *gem*-difluorinated cyclopropanes 1. Method A[16]**:** To a mixture of KI (2.0 or 4.0 equiv.) and an alkene (1.0 equiv.) in EtCN (1.0 *M* to alkene), methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (MDFA, 2.0 or 4.0 equiv.) was added at room temperature and the resultant solution was stirred at 50 °C (oil bath temperature) for 24 h. After cooling to room temperature, the reaction mixture was quenched by water and extracted by hexane three times. The combined hexane layer was successively washed with water, sat. aq. $NaHCO_3$ and brine. After drying over anhydrous Na_2SO_4, followed by concentration under reduced pressure, the crude product was purified by silica gel column chromatography. **Method B**[26]**:** To a mixture of NaI (0.2 equiv.) and an alkene (1.0 equiv.) in anhydrous THF (3.4 *M* to alkene) under argon atmosphere was added $TMSCF_3$ (2.5 equiv.) and the resultant solution was stirred at 65 °C (oil bath temperature) until the starting material was disappeared (judged by TLC). After cooling to room temperature and evaporation to dryness under reduced pressure, water (20 mL) was added to the residue which was extracted by Et_2O three times. The combined extract was washed with water, sat. aq. $Na_2S_2O_3$ and brine. After drying over anhydrous Na_2SO_4 and concentration, the crude product was purified by silica gel column chromatography.

*(2,2-Difluoro-1-methylcyclopropyl)benzene (**1a**)*.[16] Method A, 2.0 equiv. of KI and MDFA, 5.31 g (31.6 mmol, yield 79%), colorless oil. Rf = 0.42 (hexane). ^{1}H NMR δ 7.37-7.26 (5H, m), 1.68 (1H, ddd, *J* = 13.7, 7.7, 3.6 Hz), 1.52 (3H, dd, *J* = 2.7, 1.8 Hz), 1.40 (1H, ddd, J = 12.3, 7.7, 4.5 Hz) ppm. $^{13}C\{^1H\}$ NMR δ 139.1 (t, *J* = 2.5 Hz), 128.5, 128.3 (d, *J* = 2.4 Hz), 127.2, 114.5 (dd, *J* = 288.7, 286.9 Hz), 31.2 (dd, *J* = 11.2, 9.3 Hz), 22.5 (t, *J* = 9.9 Hz), 21.4 (dd, *J* = 6.2, 1.8 Hz) ppm. ^{19}F NMR δ –133.49 ~ –134.06 (1F, m), –138.50 ~ –139.08 (1F, m) ppm. The NMR data are agreement with previously reported.

*1-Bromo-4-(2,2-difluoro-1-methylcyclopropyl)benzene (**1b**)*. Method A, 4.0 equiv. of KI and MDFA, 1.15 g (4.66 mmol, yield 93%, colorless oil. Rf = 0.26 (hexane). 1H NMR δ 7.51-7.45 (2H, m), 7.26-7.17 (2H, m), 1.64 (1H, ddd, *J* = 13.5, 7.8, 3.6 Hz), 1.49 (3H, dd, *J* = 3.0, 2.1 Hz), 1.42 (1H, ddd, *J* = 12.3, 7.5, 4.5 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 138.1 (t, *J* = 1.9 Hz), 131.7, 130.1 (d, *J* = 2.5 Hz), 121.2, 114.1 (dd, *J* = 289.0, 285.4 Hz), 30.6 (dd, *J* = 11.2, 9.3 Hz), 22.5 (t, *J* = 9.9 Hz), 21.1 (dd, *J* = 6.2, 2.5 Hz) ppm. ^{19}F NMR: δ –133.70 (1F, dd, *J* = 150.5, 11.4 Hz), –138.87 (1F, dd, *J* = 150.5, 11.4 Hz) ppm. IR ($CHCl_3$) ν 3019, 2984, 1492, 1470, 1370, 1216, 1173, 1094, 1005, 759 cm^{-1}. HRMS (FAB+, m/z) $[M]^+$ calcd for $C_{10}H_9F_2Br$, 245.9856; Found, 245.9885.

*1-(2,2-Difluoro-1-methylcyclopropyl)-4-nitrobenzene (**1c**)*. Method A, 4.0 equiv. of KI and MDFA, 0.828 g (2.22 mmol, yield 89%), white solid. mp: 53.6-53.9 °C. Rf = 0.20 (hexane:Et_2O = 25:1). ^{1}H NMR: δ 8.11 (2H, d, *J* = 8.7 Hz), 7.41 (2H, d, *J* = 8.7 Hz), 1.70-1.62 (1H, m), 1.50-1.42 (4H, m) ppm. $^{13}C\{^1H\}$ NMR: δ 147.0, 146.4 (dd, *J* = 2.5, 1.9 Hz), 129.4 (dd, *J* = 1.9, 0.6 Hz), 123.8, 113.6 (dd, *J* = 290.3, 286.6 Hz), 30.8 (dd, *J* = 11.5, 9.6 Hz), 22.8 (t, *J* = 9.9 Hz), 20.8 (dd, *J* = 6.2, 1.8 Hz) ppm. ^{19}F NMR: δ –133.07 ~ –138.81 (1F, m), –138.24 ~ –138.81 (1F, m) ppm. IR (KBr) ν 3117, 3085, 2976, 1599, 1517, 1347, 1222, 1005, 856, 725 cm^{-1}. HRMS (FAB+, m/z) $[M+H]^+$ calcd for $C_{10}H_{10}F_2NO_2$, 214.0680; Found, 214.0702.

*1-(2,2-Difluoro-1-methylcyclopropyl)-4-methoxybenzene (**1d**)*.[16] Method A, 4.0 equiv. of KI and MDFA, 2.35 g (11.9 mmol, yield 99%), pale yellow oil. Rf = 0.57 (hexane:CH_2Cl_2 = 1:1). ^{1}H NMR: δ 7.26-7.22 (2H, m), 6.90-6.85 (2H, m), 3.80 (3H, s), 1.63(1H, ddd, *J* = 13.5, 7.5, 3.6 Hz), 1.49 (3H, dd, *J* = 2.7, 1.8 Hz), 1.36 (1H, ddd, *J* = 12.3, 7.5, 4.2 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 158.6, 131.2, 129.4, 114.8 (dd, *J* = 288.7, 286.3 Hz), 113.9, 55.2, 30.5 (dd, *J* = 10.6, 10.0 Hz), 22.5 (dd, *J* = 10.0, 9.9 Hz), 21.5 (d, *J* = 6.2 Hz) ppm. ^{19}F NMR: δ –133.72 ~ –134.29 (1F, m), –138.67 ~ –139.25 (1F, m) ppm. The NMR data are agreement with previously reported.

*(2,2-Difluoro-1-cyclopropyl)benzene (**1e**)*.[26] Method B, 1.36 g (8.81 mmol, yield 88%), pale yellow oil. Rf = 0.75 (hexane). ^{1}H NMR: δ 7.34-7.20 (5H, m), 2.79-2.68 (1H, m), 1.86-1.73 (1H, m), 1.66-1.55 (1H, m) ppm. $^{13}C\{^1H\}$ NMR: δ 133.7, 128.4, 128.0 (dd, *J* = 1.9, 1.2 Hz), 127.1, 112.6 (dd, *J* = 285.9, 283.4 Hz), 27.2 (t, *J* = 11.2 Hz), 17.0 (t, *J* = 10.1 Hz) ppm. ^{19}F NMR: δ –126.84 ~ –127.47 (1F, m), –143.39 ~ –144.00 (1F, m) ppm. The NMR data are agreement with previously reported.

*1-Bromo-4-(2,2-difluorocyclopropyl)benzene (**1f**)*.[26] Method A, 4.0 equiv. of KI and MDFA, 1.85 g (7.93 mmol, yield 82%), colorless oil. Rf = 0.57 (hexane). ^{1}H NMR: δ 7.44 (2H, d, *J* = 8.1 Hz), 7.09 (2H, d, *J* = 8.4 Hz), 2.75-2.64 (1H, m), 1.90-1.76 (1H, m), 1.64-1.35 (1H, m) ppm. $^{13}C\{^1H\}$ NMR: δ 132.7, 131.6, 129.7, 121.0, 112.2 (dd, *J* = 286.6, 283.4 Hz), 26.6 (dd, *J* = 11.7, 11.2 Hz), 17.1 (dd, *J* = 10.6, 10.5 Hz) ppm. ^{19}F NMR: δ –127.09 ~ –127.72 (1F, m), –143.27 ~ –143.89 (1F, m) ppm. The NMR data are agreement with previously reported.

*1-(2,2-Difluorocyclopropyl)-4-nitrobenzene (**1g**)*.[27] Method B, 0.880 g (4.42 mmol, yield 88%), yellow oil. Rf = 0.28 (hexane:AcOEt = 10:1). ^{1}H NMR: δ 8.18 (2H, d, *J* = 8.7 Hz), 7.38 (2H, d, *J* = 8.7 Hz), 2.91-2.80 (1H, m), 2.05-1.93 (1H, m), 1.80-1.69 (1H, m) ppm. ^{13}C{^{1}H} NMR: δ 147.0, 141.4, 128.7 (t, *J* = 1.9 Hz), 123.6, 111.9 (dd, *J* = 287.7, 283.5 Hz), 27.0 (dd, *J* = 12.4, 11.2 Hz), 17.9 (t, *J* = 10.6 Hz) ppm. ^{19}F NMR: δ –126.40 ~ –127.04 (1F, m), –142.83 ~ –143.44 (1F, m) ppm. The NMR data are agreement with previously reported.

*1-(2,2-Difluorocyclopropyl)-4-methoxybenzene (**1h**)*.[26] Method A, 4.0 equiv. of KI and MDFA, 1.36 g (8.81 mmol, yield 88%), colorless oil. Rf = 0.31 (hexane:Et_2O = 25:1). ^{1}H NMR: δ 7.16 (2H, d, *J* = 8.3 Hz), 6.87 (2H, d, *J* = 8.3 Hz), 3.80 (3H, s), 2.77-2.66 (1H, m), 1.85-1.72 (1H, m), 1.61-1.50 (1H, m) ppm. ^{13}C{^{1}H} NMR: δ 158.7, 129.2, 125.6, 113.9, 112.7 (dd, *J* = 286.3, 283.2 Hz), 55.2, 26.4 (t, *J* = 11.2 Hz), 16.9 (dd, *J* = 10.8, 10.2 Hz) ppm. ^{19}F NMR: δ –127.30 ~ –127.93 (1F, m), –141.66 ~ –142.25 (1F, m) ppm. The NMR data are agreement with previously reported.

*2-(2,2-Difluoro-1-methylcyclopropyl)naphthalene (**1i**)*. Method A, 4.0 equiv. of KI and MDFA, 1.09 g (4.97 mmol, yield 99%), colorless oil. Rf = 0.30 (hexane). ^{1}H NMR: δ 7.85-7.71 (4H, m), 7.51-7.43 (3H, m), 1.80 (1H, ddd, *J* = 13.5, 7.5, 3.6 Hz), 1.60 (3H, dd, *J* = 2.7, 1.8 Hz), 1.48 (1H, ddd, *J* = 12.0, 7.5, 4.2 Hz) ppm. ^{13}C{^{1}H} NMR: δ 136.5 (dd, *J* = 2.5, 1.8 Hz), 133.3, 132.5, 128.3, 127.7, 127.6, 127.0 (d, *J* = 2.5 Hz), 126.5 (d, *J* = 1.9 Hz), 126.2, 126.0, 114.7 (dd, *J* = 289.7, 286.6 Hz), 31.3 (dd, *J* = 10.9, 9.7 Hz), 22.5 (t, *J* = 10.0 Hz), 21.2 (dd, *J* = 6.8, 5.0 Hz) ppm. ^{19}F NMR: δ –133.72 (1F, dd, *J* = 150.7, 13.9 Hz), –138.61 (1F, dd, *J* = 150.4, 11.6 Hz) ppm. IR ($CHCl_3$) ν 3019, 1477, 1466, 1216, 1006, 904, 859, 820, 759, 670 cm^{-1}. HRMS (FAB+, m/z): [M+H]$^+$ calcd for $C_{14}H_{13}F_2$, 219.0985, Found, 219.1010.

*1-(2,2-Difluoro-1-methylcyclopropyl)nonane (**1j**)*. Method A, 4.0 equiv. of KI and MDFA, 0.993 g (4.55 mmol, yield 91%), colorless oil. Rf = 0.60 (hexane). ^{1}H NMR: δ 1.42-1.37 (4H, m), 1.31-1.21 (12H, m), 1.16-1.15 (3H, m), 1.02-0.91 (2H, m), 0.90-0.86 (3H, m) ppm. ^{13}C{^{1}H} NMR: δ 116.9 (dd, *J* = 288.4, 287.8 Hz), 32.7 (dd, *J* = 4.9, 1.2 Hz), 31.9, 29.6, 29.6, 29.5, 29.3, 26.3 (d, *J* = 4.1 Hz), 26.1 (t, *J* = 9.9 Hz), 22.7, 22.3 (t, *J* = 10.0 Hz), 16.1 (dd, *J* = 6.8, 1.3 Hz), 14.1 ppm. ^{19}F NMR: δ –138.84 ~ –139.42 (1F, m), –140.38 ~ –140.97 (1F, m) ppm. IR ($CHCl_3$) ν 2959, 2928, 2857, 1479, 1460, 1190, 1009, 902, 710, 5 76 cm^{-1}. HRMS (FAB+, m/z) [M]$^+$ calcd for $C_{13}H_{24}F_2$, 218.1846; Found, 218.1850.

*1-(2,2-Difluoro-1-methylcyclopropyl)-2-methoxybenzene (**1k**)*. Method A, 4 eq. of KI and MDFA, 1.54 g (7.77 mmol, yield 78%), colorless oil. Rf = 0.71 (hexane:AcOEt = 4:1). ^{1}H NMR: δ 7.20-7.26 (2H, m), 6.91 (1H, dt, *J* = 7.2, 1.2 Hz), 6.89 (1H, d, *J* = 8.1 Hz), 3.87 (3H, s), 1.53(1H, ddd, *J* = 13.5, 7.8, 3.9 Hz), 1.44 (3H, dd, *J* = 2.7, 1.8 Hz), 1.36 (1H, ddd, *J* = 12.3, 7.8, 4.8 Hz) ppm. ^{13}C{^{1}H} NMR: δ 158.5, 129.7, 128.7, 127.5, 120.4, 114.9 (t, *J* = 286.0 Hz), 110.7, 55.4, 28.4 (t, *J* = 10.6 Hz), 22.4 (t, *J* = 10.0 Hz), 19.4 (d, *J* = 5.6 Hz) ppm. ^{19}F NMR: δ –134.78 (1F, dd, *J* = 150.7, 11.6 Hz), –140.3 (1F, dd, *J* = 150.7, 11.6 Hz) ppm. IR (neat) ν 2972, 2940, 2839, 1498, 1468, 1275, 1245, 1211, 1007, 756 cm^{-1}. HRMS (FAB+, m/z): [M+H]$^+$ calcd for $C_{11}H_{13}F_2O$, 199.0934, Found, 199.0961.

*1-(2,2-Difluorocyclopropyl)-4-tert-butylbenzene (**1l**)*.[28] Method B, 1.04 g (4.95 mmol, yield 99%), colorless oil. Rf = 0.50 (hexane). ^{1}H NMR: δ 7.35 (2H, d, *J* = 8.4 Hz), 7.16 (2H, d, *J* = 7.8 Hz), 2.72 (1H, m), 1.79 (1H, ddd, *J* = 12.0, 7.2, 4.5 Hz), 1.60 (1H, ddd, *J* = 12.3, 8.1, 3.9 Hz), 1.31 (9H, s) ppm. ^{13}C{^{1}H} NMR: δ 150.1, 130.7, 127.7, 125.4, 112.7 (t, *J* = 286.6 Hz), 34.5, 31.3, 26.8 (t, *J* = 11.2 Hz), 17.0 (d, *J* = 10.6 Hz) ppm. ^{19}F NMR: δ –127.16 (1F, dtd, *J* = 152.9, 13.8, 4.8 Hz), –143.53 (1F, ddd, *J* = 152.6, 12.8, 4.5 Hz) ppm. The NMR data are agreement with previously reported.

*1-(2,2-Difluoro-1-methylcyclopropyl)-4-methylbenzene (**1m**)*. Method A, 4 eq. of KI and MDFA, 0.702 g (3.85 mmol, yield 77%), colorless oil. Rf = 0.45 (hexane). ^{1}H NMR: δ 7.20 (2H, d, *J* = 8.4 Hz), 7.14 (2H, d, *J* = 8.4 Hz), 2.32 (3H, s), 1.63(1H, ddd, *J* = 13.5, 7.5, 3.6 Hz), 1.47 (3H, dd, *J* = 2.7, 1.5 Hz), 1.35 (1H, ddd, *J* = 12.3, 7.5, 4.5 Hz) ppm. ^{13}C{^{1}H} NMR: δ 136.9, 136.1, 129.2, 128.2 (d, *J* = 1.9 Hz), 114.7 (dd, *J* = 289.0, 286.6 Hz), 30.9 (dd, *J* = 11.2, 10.0 Hz), 22.4 (t, *J* = 9.9 Hz), 21.4 (dd, *J* = 6.8, 2.5 Hz), 21.0 ppm. ^{19}F NMR: δ –133.81 (1F, dd, *J* = 148.1, 13.5 Hz), –138.9 (1F, dd, *J* = 148.1, 12.5 Hz) ppm. IR ($CHCl_3$) ν 3019, 2981, 2927, 1518, 1472, 1371, 1217, 1007, 821, 759 cm^{-1}. HRMS (FAB+, m/z): [M]$^+$ calcd for $C_{11}H_{12}F_2$, 182.0907, Found, 182.0915.

General procedure of dibromination: *(2,4-Dibromo-3,3-difluorobut-2-yl)benzene (**2a**)*. To a mixture of (2,2-difluoro-1-methylcycloprop-1-yl)benzene 0.0841 g (0.50 mmol) and KBr 0.1309 g (1.10 mmol) in CH_2Cl_2 5.0 mL, aqueous solution of $Ce(NH_4)_2(NO_3)_6$ 0.6304 g (1.15 mmol) in H_2O 5.0 mL was added at room temperature. After stirring for 9 h, the reaction mixture was extracted with CH_2Cl_2 three times and the organic layer was washed with brine. After dried over anhydrous Na_2SO_4, the crude product was evaporated and purified by silica gel column chromatography by using hexane as an eluent. 0.1325 g (0.40 mmol), yield 81%, colorless oil. Rf = 0.29 (hexane). ^{1}H NMR: δ 7.69-7.66 (2H, m), 7.40-7.35 (3H, m), 3.82 (1H, ddd, *J* = 27.6, 12.0, 3.3 Hz), 3.57 (1H, ddd, *J* = 27.3, 12.0, 3.3 Hz), 2.33 (3H, s) ppm. ^{13}C{^{1}H} NMR: δ 138.3, 129.0, 128.7 (t, *J* = 1.5 Hz), 128.3, 118.6 (dd, *J* = 252.4, 250.6 Hz), 65.9 (t, *J* = 26.0 Hz), 30.3 (t, *J* = 27.3 Hz), 27.4 (dd, *J* = 3.8, 2.5 Hz) ppm. ^{19}F NMR: δ –104.38 (1F, dd, *J* = 237.1, 27.4 Hz), –106.72 (1F, dd, *J* = 237.1, 27.4 Hz) ppm. IR ($CHCl_3$) ν 3014, 1496, 1446, 1422, 1384, 1275, 1216, 1038, 1016, 750 cm^{-1}. Anal. Calcd for $C_{10}H_{10}Br_2F_2$: C, 36.63; H, 3.07. Found: C, 36.76; H, 2.94.

*(1,2,4-Tribromo-3,3-difluorobut-2-yl)benzene (**3a**)*. Several bathes were gathered and purified. White solid. mp: 64.0-64.4 °C. Rf = 0.15 (hexane). ^{1}H NMR: δ 7.65-7.62 (2H, m), 7.44-7.40 (3H, m), 4.54 (1H, d, *J* = 12.0 Hz), 4.26 (1H, d, *J* = 11.7 Hz), 4.08 (1H, ddd, *J* = 29.4, 12.3, 2.4 Hz), 3.35 (1H, ddd, *J* = 27.9, 12.3, 3.3 Hz) ppm. ^{13}C{^{1}H} NMR: δ 134.2 (d, *J* = 1.8 Hz), 129.5, 129.1 (dd, *J* = 2.5, 1.2 Hz), 128.7, 118.6 (dd, *J* = 255.5, 251.8 Hz), 71.7 (t, *J* = 24.1 Hz), 37.5 (dd, *J* = 4.3, 3.1 Hz), 30.8 (t, *J* = 26.0 Hz) ppm. ^{19}F NMR: δ –103.17 (1F, dd, *J* = 237.1, 22.9 Hz), –106.51 (1F, dd, *J* = 237.1, 28.3 Hz) ppm. IR (KBr) ν 3050, 2991, 1493, 1443, 1432, 1420, 1274, 1258, 1220, 1190 cm^{-1}. Anal. Calcd for $C_{10}H_9Br_3F_2$: C, 29.52; H, 2.23. Found: C, 29.73; H, 2.08.

*1-Bromo-4-(2,4-dibromo-3,3-difluorobut-2-yl)benzene (**2b**)*. 0.148 g (0.365 mmol, yield 73%), colorless oil. Rf = 0.17 (hexane). ^{1}H NMR: δ 7.58-7.49 (4H, m), 3.83 (1H, ddd, *J* = 26.7, 12.3, 3.9 Hz), 3.61 (1H, ddd, *J* = 26.7, 12.0, 4.2 Hz), 2.31 (3H, dd, *J* = 1.2, 0.9 Hz) ppm. ^{13}C{^{1}H} NMR: δ 137.4, 131.5, 130.4 (t, *J* = 1.8 Hz), 123.6, 118.4 (dd, *J* = 252.5, 251.2 Hz), 64.8 (t, *J* = 26.0 Hz), 30.0 (t, *J* = 27.6 Hz), 27.5 (t, *J* = 3.1 Hz) ppm. ^{19}F NMR: δ –104.63 (dd, *J* = 240.5, 27.1 Hz) ppm, –106.52 (dd, *J* =

240.5, 27.4 Hz) ppm. IR ($CHCl_3$) ν 3019, 1589, 1490, 1397, 1215, 1084, 1040, 1010, 758, 670 cm^{-1}. Anal. Calcd for $C_{10}H_9Br_3F_2$: C, 29.52; H, 2.23. Found: C, 29.31; H, 1.96.

1-(2,4-Dibromo-3,3-difluorobut-2-yl)-4-nitrobenzene ***(2c)***. 0.091 g, (0.245 mmom, yield 49%), pale yellow oil. Rf = 0.32 (hexane:Et_2O = 4:1). ^1H NMR: δ 8.26-8.21 (2H, m), 7.90 (2H, d, *J* = 9.3 Hz), 3.94-3.66 (2H, m), 2.38 (3H, s) ppm. $^{13}C\{^1H\}$ NMR: δ 147.8, 144.9, 130.2 (t, *J* = 1.9 Hz), 123.2, 118.4 (t, *J* = 251.9 Hz), 63.8 (t, *J* = 26.7 Hz), 29.8 (t, *J* = 27.2 Hz), 27.7 (t, *J* = 3.1 Hz) ppm. ^{19}F NMR: δ –104.56 (1F, ddd, *J* = 241.7, 22.9, 6.8 Hz), –105.71 (1F, ddd, *J* = 241.7, 22.9, 6.8 Hz) ppm. IR ($CHCl_3$) ν 3020, 1526, 1352, 1216, 1063, 1043, 1016, 862, 763, 472 cm^{-1}. HRMS (FAB+, m/z) $[M+H]^+$ calcd for $C_{10}H_{10}Br_2F_2NO_2$, 371.9046; Found, 371.9062.

1-(2,4-Dibromo-3,3-difluorobut-2-yl)-4-methoxybenzene ***(2d)***. Only ^{19}F NMR data were shown due to impossible isolation of this compound. Yield 17% (by ^{19}F NMR). ^{19}F NMR: δ –104.25 (dd, *J* = 237.1, 27.1 Hz), –106.67 (dd, *J* = 237.1, 27.4 Hz) ppm.

(1,3-dibromo-2,2-difluoropropyl)benzene ***(2e)***. 0.131 g, (0.419 mmol, yield 84%), colorless oil. Rf = 0.29 (hexane). ^1H NMR: δ 7.54-7.50 (2H, m), 7.39-7.36 (3H, m), 5.36 (1H, dd, *J* = 13.8, 12.3 Hz), 3.73 (1H, q, *J* = 12.0 Hz), 3.45 (1H, dt, *J* = 14.1, 12.0 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 134.1 (d, *J* = 3.1 Hz), 129.7, 129.3 (dd, *J* = 1.9, 1.3 Hz), 128.8, 118.2 (t, *J* = 248.0 Hz), 50.1 (t, *J* = 26.7 Hz), 29.7 (t, *J* = 32.2 Hz) ppm. ^{19}F NMR: δ –102.35 (dq, *J* = 246.2, 11.3 Hz), –103.71 (dq, *J* = 246.2, 11.3 Hz) ppm. IR ($CHCl_3$) ν 3109, 1455, 1421, 1264, 1216, 1103, 1026, 754, 700, 671 cm^{-1}. HRMS (FAB+, m/z) $[M]^+$ calcd for $C_9H_8Br_2F_2$, 311.8961, Found, 311.8971.

1-Bromo-4-(1,3-dibromo-2,2-difluoropropyl)benzene ***(2f)***. 0.136 g, (0.346 mmol, yield 69%), colorless oil. Rf = 0.26 (hexane). ^1H NMR (acetone-d_6) δ 7.53 (2H, m), 7.41 (2H, m), 5.33 (1H, t, *J* = 12.8 Hz), 3.78 (1H, dq, *J* = 24.3, 12.0 Hz), 3.48 (1H, dq, *J* = 24.6, 12.0 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 133.1 (dd, *J* = 1.9, 1.3 Hz), 132.0, 131.0 (t, *J* = 1.2 Hz), 124.0, 118.1 (t, *J* = 248.7 Hz), 49.0 (t, *J* = 27.3 Hz), 29.6 (t, *J* = 32.8 Hz) ppm. ^{19}F NMR: δ –103.31 ~ –103.44 ppm (m) . IR ($CHCl_3$) ν 3015, 1591, 1490, 1421, 1408, 1264, 1216, 1100, 1076, 1026 cm^{-1}. HRMS (FAB+, m/z) $[M]^+$ calcd for $C_9H_7Br_3F_2$, 389.8066, Found, 389.8075.

1-(1,3-Dibromo-2,2-difluoropropyl)-4-nitrobenzene ***(2g)***. Only ^1H, ^{13}C and ^{19}F NMR data and HRMS were shown due to impossible isolation of this compound. Yield 44% (by ^{19}F NMR). ^1H NMR: δ 8.25 (2H, d, *J* = 8.4 Hz), 7.73 (2H, d, *J* = 8.4 Hz), 5.46 (1H, dd, J = 15.3, 10.2 Hz), 3.88 (1H, ddd, *J* = 16.8, 11.1, 9.9 Hz), 3.56 (1H, q, *J* = 11.7 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 148.4, 140.7, 130.6, 123.8, 118.2 (t, *J* = 249.3 Hz), 47.8 (t, *J* = 27.5 Hz), 29.5 (t, *J* = 32.6 Hz) ppm. ^{19}F NMR: δ –100.98 ~ –102.62 (1F, m) ppm, –103.77 ~ –105.58 (1F, m) ppm. HRMS (FAB+, m/z) $[M+H]^+$ calcd for $C_9H_8Br_2F_2NO_2$, 357.8890, Found, 357.8874.

1-(2,4-Dibromo-3,3-difluorobut-2-yl)-4-methoxybenzene ***(2h)***. 0.130 g (0.377 mmol, yield 75%), pale yellow oil. Rf = 0.20 (hexane:Et_2O = 20:1). ^1H NMR: δ 7.44 (2H, d, *J* = 7.8 Hz), 6.88 (2H, d, *J* = 7.2 Hz), 5.35 (1H, dd, *J* = 14.1, 11.4 Hz), 3.80 (3H, s), 3.71 (1H, dd, *J* = 23.7, 11.7 Hz), 3.44 (1H, dd, *J* = 26.1, 12.0 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 160.4, 130.6, 126.1 (d, *J* = 3.8 Hz), 118.2 (dd, *J* = 248.8, 247.4 Hz), 114.1, 55.3, 50.2 (t, *J* = 26.6 Hz), 29.7 (dd, *J* = 33.5, 32.2 Hz) ppm. ^{19}F NMR: δ –102.20 (1F, dq, *J* = 246.2, 11.3 Hz), –103.99 (1F, dq, *J* = 246.2, 11.3 Hz) ppm. IR ($CHCl_3$) ν 3013, 2840, 1610, 1514, 1297, 1256, 1180, 1100, 1027, 757 cm^{-1}. HRMS (FAB+, m/z) $[M+H]^+$ calcd for $C_{10}H_{11}Br_2F_2O$, 342.9139, Found, 342.9150.

2-(2,4-Dibromo-3,3-difluorobut-2-yl)naphthalene ***(2i)***. 0.032 g (0.085 mmol, yield 17%), white solid. mp: 62.9-63.8 °C. Rf = 0.14 (hexane). ^1H NMR: δ 8.11-8.06 (1H, m), 7.88-7.81 (4H, m), 7.55-7.52 (2H, m), 3.87-3.74 (1H, m), 3.68-3.53 (1H, m), 2.44 (3H, s) ppm. $^{13}C\{^1H\}$ NMR: δ 135.6, 133.0, 132.4, 128.5, 128.2, 127.8 (dd, *J* = 1.8, 1.2 Hz), 127.4 (d, *J* = 0.6 Hz), 127.3, 126.8, 126.3 (t, *J* = 2.5 Hz), 118.7 (dd, *J* = 252.4, 250.1 Hz), 65.9 (t, *J* = 25.4 Hz), 30.3 (t, *J* = 27.2 Hz), 27.5 (dd, *J* = 3.7, 2.4 Hz). ^{19}F NMR: δ –102.93 ~ –103.86 (1F, m), –105.56 ~ –106.52 (1F, m) ppm. IR ($CHCl_3$) ν 3052, 2991, 2943, 1596, 1273, 1384, 1273, 1013, 796, 756 cm^{-1}. HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{14}H_{12}Br_2F_2$, 375.9274, Found, 375.9291.

1,3-Dibromo-2,2-difluoro-3-methyldodecane ***(2j)***. 0.134 g (0.364 mmol, yield 73%), colorless oil. Rf = 0.48 (hexane). ^1H NMR: δ 4.09-4.01 (1H, m), 3.98-3.90 (1H, m), 2.00-1.81 (2H, m), 1.78 (3H, s), 1.65-1.41 (2H, m), 1.32-1.28 (12H, m), 0.89 (3H, t, *J* = 6.3 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 119.4 (t, *J* = 250.0 Hz), 66.7 (t, *J* = 25.5 Hz), 38.9 (dd, *J* = 2.5, 1.8 Hz), 31.8, 30.8 (t, *J* = 27.3 Hz), 29.54, 29.48, 29.4, 29.3, 25.1, 24.7 (t, *J* = 3.1 Hz), 22.7, 14.1 ppm. ^{19}F NMR: δ –106.68 ~ –107.65 (1F, m), –108.64 ~ –109.61 (1F, m) ppm. IR ($CHCl_3$) ν 2927, 2855, 1466, 1422, 1382, 1216, 1052, 1031, 761, 652 cm^{-1}. HRMS (FAB+, m/z) $[M+Na]^+$ calcd for $C_{13}H_{24}Br_2F_2Na$, 399.0111, Found, 399.0137.

Procedure of bromohydroxylation by CAN: *4-Bromo-3,3-difluoro-2-phenylbutan-2-ol* ***(4a)***. To a mixture of (2,2-difluoro-1-methylcycloprop-1-yl)benzene 0.0841 g (0.50 mmol) and KBr 0.1309 g (1.10 mmol) in MeCN 5.0 mL, $Ce(NH_4)_2(NO_3)_6$ 0.6304 g (1.15 mmol) in H_2O 5.0 mL was added at room temperature. After stirring at 60 °C (oil bath temperature) for 9 h, the reaction mixture was extracted with CH_2Cl_2 three times, washed with brine, and dried over anhydrous Na_2SO_4. After evaporation, the crude product was purified by silica gel coumn chromatography (hexane:CH_2Cl_2=1:1) to yield 4-bromo-3,3-difluoro-2-phenylbutan-2-ol 0.081 g (0.306 mmol, yield 61%) as a colorless oil. Rf = 0.30 (hexane: CH_2Cl_2 = 1:1). ^1H NMR: δ 7.54 (2H, d, *J* = 7.8 Hz), 7.41-7.33 (3H, m), 3.79 (1H, ddd, *J* = 30.0, 12.0, 2.4 Hz), 3.46 (1H, ddd, *J* = 28.5, 12.3, 3.3 Hz), 2.38 (1H, br s), 1.77 (3H, s) ppm. $^{13}C\{^1H\}$ NMR: δ 139.8 (d, *J* = 4.3 Hz), 128.4, 128.2, 125.7 (dd, *J* = 2.5, 1.2 Hz), 119.7 (dd, *J* = 251.8, 250.0 Hz), 75.9 (dd, *J* = 27.3, 25.4 Hz), 30.2 (t, *J* = 26.7 Hz), 24.1 (dd, *J* = 3.1, 2.5 Hz) ppm. ^{19}F NMR: δ –112.14 (1F, dd, *J* = 241.9, 31.7 Hz), –115.47 (1F, dd, *J* = 243.9, 27.4 Hz). IR ($CHCl_3$) ν 3601, 3459, 3017, 1449, 1216, 1141, 1073, 1037, 761, 703 cm^{-1}. Anal. Calcd for $C_{10}H_{11}BrF_2O$: C, 45.31; H, 4.18. Found: C, 45.53; H, 4.31.

3-Bromo-1-(4-tert-butylphenyl)-2,2-difluoropropan-2-ol ***(4l)***. The reaction was conducted at 80 °C (oil bath temperature) for 9 h. 0.072 g (0.234 mmol, yield 47%) as a colorless oil. Rf = 0.40 (hexane:AcOEt = 4:1). ^1H NMR: δ 7.40 (4H, m), 5.12 (1H, ddd, *J* = 11.7, 9.0, 4.2 Hz), 3.75 (1H, dt, *J* = 18.0, 12.0 Hz), 3.46 (1H, ddd, *J* = 18.3, 12.0, 8.7 Hz), 2.44 (1H, br d, *J* = 4.2 Hz), 1.33 (9H, s) ppm. $^{13}C\{^1H\}$ NMR: δ 152.2, 132.5, 127.1, 125.5, 119.2 (t, *J* = 246.9 Hz), 73.4 (t, *J* = 27.9 Hz), 34.6, 31.2, 29.2 (t, *J* = 30.4 Hz) ppm. ^{19}F NMR: δ –104.87 (1F, m), –106.14 (1F, m) ppm. IR (KBr) ν 3415, 2965, 2905, 2870, 1108, 1036, 735, 588, 478,

470 cm^{-1}. HRMS (FAB+, m/z) $[M+Na]^+$ calcd for $C_{13}H_{17}BrF_2NaO$, 329.0329, Found, 329.0304.

*1-(4-tert-Butylphenyl)-2,2-difluoro-3-iodopropan-2-ol (**4l'**).* KI 0.1829 g (1.10 mmol) was employed instead of KBr. The reaction was conducted at 80 °C (oil bath temperature) for 9 h. 0.103 g (0.335 mmol, yield 67%) as a white solid. mp: 83.0-84.0 °C. Rf = 0.46 (hexane:AcOEt = 4:1). ^{1}H NMR: δ 7.40 (4H, m), 5.09 (1H, td, *J* = 9.0, 3.9 Hz), 3.59 (1H, ddd, *J* = 24.0, 11.7, 8.4 Hz), 3.29 (1H, ddd, *J* = 23.6, 11.7, 7.5 Hz), 2.46 (1H, br d, *J* = 4.2 Hz), 1.32 (9H, s) ppm. ^{13}C{^{1}H} NMR: δ 152.2, 132.7 (d, *J* = 1.9 Hz), 126.9, 125.5, 119.3 (t, *J* = 246.3 Hz), 73.6 (t, *J* = 28.5 Hz), 34.6, 31.2, 1.44 (t, *J* = 28.6 Hz) ppm. ^{19}F NMR: δ –104.20 (1F, ddt, *J* = 244.2, 18.4, 9.0 Hz), –106.25 (1F, ddt, *J* = 243.9, 18.4, 9.0 Hz) ppm. IR (KBr) ν 3557, 2962, 2870, 1509, 1214, 1141, 1075, 1015, 846, 863 cm^{-1}. HRMS (FAB+, m/z) $[M+Na]^+$ calcd for $C_{13}H_{17}F_2NaIO$, 377.0190, Found, 377.0210.

Procedure of bromoamidation by CAN: *N-(4-Bromo-3,3-difluoro-2-phenylbut-2-yl)acetamide (**5a**)*. To a mixture of (2,2-difluoro-1-methylcycloprop-1-yl)benzene 0.0838 g (0.50 mmol) and KBr 0.1308 g (1.10 mmol) in MeCN 5.0 mL, $Ce(NH_4)_2(NO_3)_6$ 0.6311 g (1.15 mmol) was added at room temperature. After stirring at 60 °C (oil bath temperature) for 9 h, the reaction mixture was quenched by water 5.0 mL. The usual work-up and recrystallization from chloroform yielded *N*-(4-bromo-3,3-difluoro-2-phenylbut-2-yl)acetamide 0.035 g (0.114 mmol, yield 23%) as a white solid. mp: 178.2-179.0 °C. Rf = 0.10 (CH_2Cl_2). ^{1}H NMR (DMSO-d_6) δ 8.41 (1H, s), 7.34-7.27 (5H, m), 4.05 (1H, ddd, *J* = 29.4, 12.0, 3.6 Hz), 3.87 (1H, ddd, *J* = 29.4, 12.3, 3.0 Hz), 1.93 (3H, s), 1.88 (3H, s) ppm. ^{13}C{^{1}H} NMR (DMSO-d_6) δ 169.1, 139.0, 127.9, 127.3, 127.1, 119.6 (t, *J* = 250.0 Hz), 62.5 (t, *J* = 23.5 Hz), 31.5 (t, *J* = 25.4 Hz), 23.5, 20.4 (dd, *J* = 3.1, 2.5 Hz) ppm. ^{19}F NMR: δ –109.9 (1F, dd, *J* = 241.6, 27.4 Hz), –112.6 (1F, ddd, *J* = 239.4, 27.4, 4.5 Hz) ppm. IR (KBr) ν 3274, 3082, 2992, 1649, 1563, 1372, 1308, 1228, 1206, 1057 cm^{-1}. HRMS (FAB+, m/z) $[M+H]^+$ calcd for $C_{12}H_{15}BrF_2NO$, 306.0305, Found, 306.0293.

Procedure of bromoamidation by $FeCl_3$: *N-(4-Bromo-3,3-difluoro-2-phenylbut-2-yl)acetamide (**5a**)*. To a mixture of (2,4-dibromo-3,3-difluorobut-2-yl)benzene (**2a**) 0.1402 g (0.43 mmol) in MeCN (1.1 mL), anhydrous $FeCl_3$ 0.2774g (1.71 mmol) was added at room temperature. The reaction mixture was stirred at reflux for 6 h in an oil bath. After cooling to room temperature the reaction mixture was quenched by water 2.0 mL and extracted with Et_2O three times. The organic layer was successively washed with 1 *M* HCl aq., water, and brine, and dried over anhydrous Na_2SO_4. Then the crude product was recrystallized from chloroform to yield *N*-(4-bromo-3,3-difluoro-2-phenylbut-2-yl)acetamide (**5a**) 0.090 g (0.294 mmol, yield 67%) as a white solid.

Procedure of bromoamidation by $K_2S_2O_8$: *N-[3-Bromo-2,2-difluoro-1-(4-methoxyphenyl)prop-1-yl]acetamide (**5h**)*. A mixture of (2,2-difluorocycloprop-1-yl)-4-methoxybenzene 0.0921 g (0.50 mmol), NaBr 0.0771 g (0.75 mmol), $K_2S_2O_8$ 0.2307 g (1.00 mmol) in MeCN 1.50 mL in a pressure tight glass tube was stirred at 100 °C (oil bath temperature) for 24 h, and the usual work-up and recrystallization from chloroform yielded *N*-[3-bromo-2,2-difluoro-1-(4-methoxyphenyl)prop-1-yl]acetamide 0.0773 g (0.240 mmol, yield 48%) as a white solid. mp: 147.7-149.0 °C. Rf = 0.50 ($CHCl_3$:MeOH = 10:1). ^{1}H NMR: δ 7.33 (2H, d, *J* = 8.6 Hz), 6.91 (2H, d, *J* = 8.6 Hz), 6.15 (1H, br s), 5.61 (1H, ddd, *J* = 15.3, 12.9, 9.3 Hz), 3.81 (3H, s), 3.57-3.32 (2H, m), 2.05 (3H, s) ppm. ^{13}C{^{1}H} NMR: δ 169.5, 159.9, 129.4, 126.5 (d, *J* = 3.8 Hz), 119.7 (dd, *J* = 250.6, 247.5 Hz), 114.3, 55.3, 54.5 (t, *J* = 23.5 Hz), 30.0 (t, *J* = 30.4 Hz), 23.3 ppm. ^{19}F NMR: δ –107.77 ~ –108.79 (1F, m), –108.93 ~ –109.94 (1F, m) ppm. IR (KBr) ν 3292, 3045, 2840, 1901, 1664, 1516, 1369, 1188, 1041, 809 cm^{-1}. HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{12}H_{15}BrF_2NO_2$, 322.0254; Found, 322.0224.

*N-[3-Bromo-1-(4-tert-butylphenyl)-2,2-difluoroprop-1-yl]acetamide (**5l**)*. 0.0384 g (0.110 mmol, yield 22%) as a yellow solid. mp: 132.0 – 133.0 °C. Rf = 0.15 (hexane:AcOEt = 4:1). ^{1}H NMR: δ 7.40 (2H, dt, *J* = 8.4, 2.1 Hz), 7.32 (2H, d, *J* = 8.4 Hz), 6.22 (1H, br s), 5.64 (1H, ddd, *J* = 14.7, 12.6, 9.3 Hz), 3.46 (2H, m), 2.05 (3H, s), 1.32 (9H, s) ppm. ^{13}C{^{1}H} NMR: δ 169.6, 152.0, 131.5 (d, *J* = 3.2 Hz), 127.8, 125.9, 119.5 (dd, *J* = 247.5, 250.0 Hz), 54.8 (t, *J* = 23.6 Hz), 34.6, 31.2, 30.1 (t, *J* = 29.8 Hz), 23.2 ppm. ^{19}F NMR: δ –108.13 (1F, dq, *J* = 244.2, 14.4 Hz), –109.27 (1F, dq, *J* = 246.2, 13.6 Hz) ppm. IR (KBr) ν 3361, 2968, 2866, 1928, 1660, 1534, 1286, 1044, 849, 591 cm^{-1}. HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{15}H_{21}BrF_2NO_2$, 348.0774; Found, 348.0779.

*3-Bromo-1-(4-tert-butylphenyl)-2,2-difluoropropan-2-amine (**5l'**).* 0.0852 g (0.278 mmol, yield 56%) as a yellow solid. mp: 44.0 – 45.0 °C. Rf = 0.68 (hexane:AcOEt = 4:1). ^{1}H NMR: δ 7.44 (2H, d, *J* = 8.4 Hz), 7.38 (2H, d, *J* = 8.4 Hz), 5.35 (1H, dd, *J* = 14.1, 11.1 Hz), 3.73 (1H, q, *J* = 12.0 Hz), 3.46 (1H, dt, *J* = 14.1, 11.7 Hz), 1.32 (9H, s) ppm. ^{13}C{^{1}H} NMR: δ 152.9, 131.1 (d, *J* = 3.1 Hz), 129.0, 125.8, 118.2 (t, *J* = 248.2 Hz), 50.2 (t, *J* = 26.7 Hz), 34.7, 31.2, 29.8 (t, *J* = 32.3 Hz) ppm. ^{19}F NMR: δ –101.99 (1F, dq, *J* = 246.5, 11.3 Hz), –103.91 (1F, dq, *J* = 246.2, 11.5 Hz) ppm. IR (KBr) ν 3042, 2962, 2867, 1918, 1798, 1685, 1612, 1196, 1035, 608 cm^{-1}. HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{13}H_{19}BrF_2N$, 306.0663; Found, 306.0683.

General procedure of iodohydroxylation by $K_2S_2O_8$: *3,3-difluoro-4-iodo-2-(4-methoxyphenyl)butan-2-ol (**6d**)*. A mixture of (2,2-difluoro-1-methylcycloprop-1-yl)benzene 0.0841 g (0.50 mmol), KI 0.0830 g (0.55 mmol), $K_2S_2O_8$ 0.2307 g (1.00 mmol) in DCE 0.75 mL and water 0.75 mL in a pressure tight glass tube was stirred at 60 °C (oil bath temperature) for 6 h, and the reaction mixture was extracted CH_2Cl_2 three times. After the usual work-up and chromatography on silica gel (hexane:CH_2Cl_2=1:1 v:v) yielded 3,3-difluoro-4-iodo-2-(4-methoxyphenyl)butan-2-ol 0.1163 g (0.340 mmol, yield 68%.) as a white solid. mp: 63.5-64.0 °C. Rf = 0.20 (hexane:CH_2Cl_2 = 1:1). ^{1}H NMR: δ 7.48-7.42 (2H, m), 6.92-6.87 (2H, m), 3.81 (3H, s), 3.65 (1H, ddd, *J* = 32.7, 12.0, 2.4 Hz), 3.03 (1H, ddd, *J* = 31.2, 12.0, 3.2 Hz), 2.34 (1H, s), 1.74 (3H, dd, *J* = 1.5, 1.2 Hz) ppm. ^{13}C{^{1}H} NMR: δ 159.3, 132.2 (dd, *J* = 3.7, 1.2 Hz), 127.0 (dd, *J* =2.5, 1.3 Hz), 120.2 (t, *J* = 250.3 Hz), 113.6, 75.0 (dd, *J* = 27.9 Hz), 55.2, 24.3 (t, *J* = 2.5 Hz), 2.9 (t, *J* = 28.5 Hz) ppm. ^{19}F NMR: δ –105.97 (1F, dd, *J* = 239.4, 31.9 Hz), –108.35 (1F, dd, *J* = 239.4, 31.7 Hz) ppm. IR (KBr) ν 3518, 2952, 2933, 1515, 1257, 1207, 1171, 1025, 1001, 819 cm^{-1}. HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{11}H_{13}F_2IO_2$, 341.9928, Found, 341.9904.

*2,2-Difluoro-3-iodo-1-(4-methoxyphenyl)propan-2-ol (**6h**)*. 0.094 g (0.285 mmol, yield 57%). Colorless oil. Rf = 0.32 (hexane:CH_2Cl_2 = 1:2). ^{1}H NMR: δ 7.37 (2H, d, *J* = 8.4 Hz), 6.91 (2H, d, *J* = 9.0 Hz), 5.05 (1H, ddd, *J* = 9.9, 8.1, 3.6 Hz), 3.81 (3H, s), 3.56 (1H, ddd, *J* = 23.7, 12.0, 9.0 Hz), 3.28 (1H, ddd, *J* = 23.1,

12.0, 7.8 Hz), 2.64 (1H, s) ppm. $^{13}C\{^1H\}$ NMR: δ 160.1, 128.6, 127.8, 119.3 (dd, *J* = 253.7, 249.4 Hz), 73.4 (t, *J* = 27.9 Hz), 55.3, 1.4 (t, *J* = 28.5 Hz) ppm. ^{19}F NMR: δ –104.56 (1F, ddt, *J* = 244.2, 22.9, 9.0 Hz), –106.53 (1F, ddt, *J* = 243.9, 22.8, 9.0 Hz) ppm. IR (KBr) ν 3598, 3453, 3008, 2840, 1613, 1515, 1253, 1176, 1085, 1013 cm^{-1}. HRMS (FAB+, m/z): $[M]^+$ calcd for $C_{10}H_{11}F_2IO_2$, 327.9772, Found, 327.9774.

*2,2-difluoro-3-iodo-1-(4-methoxyphenyl)propan-1-one (**8h**)*.[21] Yield 4% (by ^{19}F NMR). White solid. Rf = 0.43 (hexane:CH_2Cl_2 = 1:1). ^1H NMR: δ 8.11 (2H, d, *J* = 9.3 Hz), 6.98 (2H, d, *J* = 9.3 Hz), 3.91 (3H, s), 3.76 (1H, t, *J* = 16.2 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ185.1 (t, *J* = 31.0 Hz), 164.8, 132.8 (t, *J* = 3.1 Hz), 124.1 (t, *J* = 3.2 Hz), 115.7 (t, *J* = 254.3 Hz), 114.1, 55.6, 1.3 (t, *J* = 27.2 Hz) ppm. ^{19}F NMR : δ –95.32 (t, *J* = 16.1 Hz) ppm.

*3,3-Difluoro-4-iodo-2-(2-methoxyphenyl)butan-2-ol (**6k**)*. The reaction was performed with KI 0.1826 g (1.10 mmol), $K_2S_2O_8$ 0.5406 g (2.00 mmol) in DCE 1.00 mL and water 3.00 mL in a pressure tight glass tube and stirred at 60 °C (oil bath temperature) for 24 h. 0.108 g (0.317 mmol, yield 63%) as a white solid. mp: 60.5-61.0 °C. Rf = 0.46 (hexane:AcOEt = 4:1). ^1H NMR: δ 7.36-7.28 (2H, m), 7.04-6.96 (2H, m), 3.93 (3H, s), 3.78-3.57 (2H,m), 1.73(3H, s) ppm. $^{13}C\{^1H\}$ NMR: δ 157.7, 129.7 (d, *J* = 6.3 Hz), 127.3, 121.5, 120.4 (t, *J* = 251.9 Hz), 112.4, 77.2 (t, *J* = 26.0 Hz), 56.2, 23.9, 3.1 (t, *J* = 28.6 Hz) ppm. ^{19}F NMR: δ –104.87 (1F, dm, *J* = 239.4 Hz), –106.14 (1F, dm, *J* = 239.4 Hz) ppm. IR (KBr) ν 3432, 3041, 2986, 2954, 1601, 1583, 1466, 1014, 762, 525 cm^{-1}. HRMS (FAB+, m/z): $[M+Na]^+$ calcd for $C_{11}H_{13}F_2NaIO_2$, 364.9826, Found, 364.9837.

Procedure of iodoalkenylation by $K_2S_2O_8$: *1-(3,3-Difluoro-4-iodobut-1-en-2-yl)-4-methoxybenzene (**7d**)*. A mixture of (2,2-difluoro-1-methylcycloprop-1-yl)benzene 0.0995 g (0.50 mmol), KI 0.0827 g (0.55 mmol), $K_2S_2O_8$ 0.2302 g (1.00 mmol) in MeCN 1.50 mL in a pressure tight glass tube was stirred at 90 °C (oil bath temperature) for 16 h. The usual work-up and chromatography on silica gel (hexane:CH_2Cl_2=1:1 v:v) afforded 1-(3,3-difluoro-4-iodobut-1-en-2-yl)-4-methoxybenzene 0.091 g (0.281 mmol, yield 56%) as a pale yellow oil and **6d** as a byproduct. Colorless oil. Rf = 0.64 (hexane:CH_2Cl_2 = 1:1). ^1H NMR: δ 7.36 (2H, d, *J* = 8.7 Hz), 6.88 (2H, d, *J* = 8.7 Hz), 5.78 (1H, s), 5.50, (1H, s), 3.82 (3H, s), 3.43 (2H, t, *J* = 14.8 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 159.8, 141.5 (t, *J* = 22.9 Hz), 129.4, 128.3, 119.0 (t, *J* = 8.1 Hz), 118.6 (t, *J* = 243.8 Hz), 113.9, 55.2, 4.8 (t, *J* = 32.9 Hz) ppm. ^{19}F NMR: δ –94.31 (t, *J* = 13.7 Hz) ppm. IR (neat) ν 2959, 2935, 2837, 1609, 1514, 1251, 1180, 1034, 1009, 837 cm^{-1}. HRMS (FAB+, m/z): $[M]^+$ calcd. for $C_{11}H_{11}F_2IO$, 323.9823, Found, 323.9818.

*N-[2,2-difluoro-3-iodo-1-(4-methoxyphenyl)prop-1-yl]acetamide (**9h**)*. When **1h** was employed as a substrate, the product **6h** was yielded mainly with **8h** and **9h** as byproducts. 0.021 g (0.057 mmol, yield 11%, white solid. mp: 155.0-156.0 °C. Rf = 0.19 (CH_2Cl_2). ^1H NMR: δ 7.32 (2H, d, *J* = 8.4 Hz), 6.90 (2H, d, *J* = 9.0 Hz), 6.32 (1H, d, *J* = 9.0 Hz), 5.60 (1H, ddd, *J* = 15.3, 12.6, 9.6 Hz), 3.81 (3H, s), 3.34 (2H, m), 2.04 (3H, s) ppm. $^{13}C\{^1H\}$ NMR: δ 169.5, 160.0, 129.3, 126.9 (d, *J* = 3.8 Hz), 119.7 (t, *J* = 247.5 Hz), 114.8, 55.3, 54.8 (t, *J* = 24.1 Hz), 23.3, 2.4 (t, *J* = 29.1 Hz) ppm. ^{19}F NMR: δ –102.06 ~ –103.08 (1F, m), –103.80 ~ –104.81 (1F, m) ppm. IR (KBr) ν 3291, 3038, 2966, 1662, 1515, 1367, 1257, 1186, 1022, 809 cm^{-1}. HRMS (FAB+, m/z): $[M+H]^+$ calcd for $C_{12}H_{15}F_2INO_2$, 370.0116; Found, 370.0142.

*1-(Bromomethyl)-4-(2,2-difluoro-1-methylcycloprop-1-yl)benzene (**10m**)*. By using general procedure of dibromination, **10m** was obtained with unidentified byproducts. Yield 89% (by ^{19}F NMR). Rf = 0.33 (hexane). ^1H NMR: δ 7.38 (2H, d, *J* = 8.1 Hz), 7.29 (2H, d, *J* = 8.1 Hz), 4.49 (2H, s), 1.67 (1H, ddd, *J* = 13.5, 7.8, 3.6 Hz), 1.51 (3H, dd, *J* = 2.7, 1.8 Hz), 1.42 (1H, ddd, *J* = 12.6, 7.8, 4.8 Hz) ppm. $^{13}C\{^1H\}$ NMR: δ 139.4, 136.7, 129.2, 128.8, 114.3 (dd, *J* = 289.0, 286.6 Hz), 33.0, 30.8 (t, *J* = 9.9 Hz), 22.5 (t, *J* = 9.9 Hz), 21.1 (d, *J* = 6.2 Hz). ^{19}F NMR: δ –133.79 (1F, dd, *J* = 150.4, 13.6 Hz), –138.77 (1F, dd, *J* = 150.7, 11.3 Hz) ppm. HRMS (FAB+, m/z) $[M+H]^+$ calcd for $C_{11}H_{12}BrF_2$, 261.0090, Found, 261.0090.

Procedure of bromination by NBS and AIBN: *1-(Bromomethyl)-4-(2,2-difluoro-1-methylcycloprop-1-yl)benzene (**10m**)*. A mixture of 1-(2,2-difluoro-1-methylcyclopropyl)-4-methylbenzene 0.0906 g (0.5 mmol), *N*-bromosuccinimide 0.1779 g (1.0 mmol) and azobis(isobutyronitrile) 0.0164 g (0.1 mmol) in carbontetrachloride 5 mL was stirred at 70 °C for 15 h. After usual workup and chromatography on silica gel (hexane) to obtain 1-(bromomethyl)-4-(2,2-difluoro-1-methylcycloprop-1-yl)benzene (**10m**) with unidentified byproducts. Yield 47% (by ^{19}F NMR).

ASSOCIATED CONTENT

Supporting Information. Spectroscopic data of new compounds and computational details were shown. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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