JOC Article

3,3-Difluoro-1-iodocyclopropenes: A Simple Synthesis and Their Reactions

Wei Xu and Qing-Yun Chen*

Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, 200032 Shanghai, China

chenqy@pub.sioc.ac.cn

Received June 25, 2002

The [1 + 2] cycloaddition reaction of 1-iodoalkynes with difluorocarbene, generated from the decomposition of $FSO_2CF_2COOSiMe_3$ in diglyme in the presence of 10 mol % NaF at 120 °C, gives 3,3-difluoro-1-iodocyclopropenes in good yields. These new iodides can be trifluoromethylated and functionalized via the Heck reaction. The unusual hydrolytic reactions of the iodides under acidic conditions was also investigated.

Introduction

The cycloaddition reaction of difluorocarbene to carbon−carbon double or triple bonds is one of the most important methods for synthesizing organic fluorine compounds.[1] *gem*-Difluorocyclopropanes, formed by insertion of difluorocarbene to carbon−carbon double bonds, are versatile intermediates for preparing difluoromethylene-substituted compounds. For example, a key step for the synthesis of 24,24-difluoro-25-hydroxy-vitamin-D_3 was through anionic opening of the corresponding *gem*-difluorocyclopropane.[2] Some interesting difluoro methylene-containing compounds were obtained by the cationic ring opening of difluorocyclopropanes.[3] Radical induced ring opening of *gem*-difluorocyclopropanes was also reported to occur not only with good regioselectivity but also with high steroselectivity.[4] As compared with carbon−carbon double bonds, the addition of difluorocarbene to carbon−carbon triple bonds is rare because carbenes or carbenoids generated from diazoalkanes or haloforms undergo [1 + 2] cycloaddition reactions with alkynes much less readily than with alkenes.[5] As the smallest member of the cyclic organofluorine compounds, 3,3-difluorocyclopropene derivatives command much attention on account of their remarkable properties. They are of interest both for theoretical investigation and in synthetic applications. According to the relative ab initio calculation, small rings having double bonds would be stabilized by fluorine substitution, whereas fluorine substitution on cyclopropane leads to destabilization; this implies that it is possible to synthesize such highly strained compounds.[6] *gem*-Difluorocyclopropene derivatives have been obtained through Cl−F exchange of *gem*-dichlorocyclopropenes with SbF_3,[7] KF,[8] or AgF[9] or elimination of *gem*-difluorohalocyclopropanes with KOBu-t,[9] Zn,[10] or KOH.[11] However, a more convenient method is the addition of difluorocarbene to alkynes. Some difluorocarbene precursors under various reaction conditions (e.g. $(CH_3)_3SnCF_3$, 150 °C;[12] $(CF_3)_3PF_2$, 100 °C;[13] $ClCF_2COONa$, 160 °C;[14] $(C_6H_5)_3P^+CF_2BrBr^-$/ KF/18-crown-6, 25 °C;[5] $(CF_3)_2Cd$, −5 °C;[15] 1,2-epoxyhexafluoropropane, 185 °C [16]) have been used to synthesize *gem*-difluorocyclopropenes. But all of these direct methods suffered either from difficulties in preparing difluorocarbene reagents or in requiring harsh reaction conditions.

In connection with the recent finding that trimethylsilyl fluorosulfonyldifluoroacetate ($FSO_2CF_2COOSiMe_3$, TFDA) is a highly versatile source of difluorocarbene,[17] we envisioned that this reagent might be applicable to

(1) (a) *Chemistry of Organic Fluorine Compounds II*; Hudlický, M., Pavlath, A. E., Eds.; American Chemical Society: Washington, DC, 1995. (b) Brahams, D. L. S.; Dailey, W. P. *Chem. Rev.* **1996**, *96*, 1585−1632. (c) Gerstenberger, M. R. C.; Haas, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 647−667. (d) Tozer, M. J.; Herpin, T. F. *Tetrahedron* **1996**, *26*, 8619−8683.

(2) Kobayashi, Y.; Taguchi, T.; Terada, T.; Oschida, J.-I.; Morisaki, M.; Ikekawa, N. *J. Chem. Soc., Perkin Trans 1* **1982**, 85−91.

(3) Bessard, Y.; Kuhlmann, L.; Schlosser, M. *Tetrahedron* **1990**, *46*, 5230−5236.

(4) (a) Dolbier, W. R., Jr.; Al-Sader, B. H.; Sellers, S. F.; Koroniak, H. *J. Am. Chem. Soc.* **1981**, *103*, 2138−2139. (b) Moricawa, T.; Uejima, M.; Kobayashi, Y. *Chem. Lett.* **1988**, 1407−1410.

(5) Bessard, Y.; Schlosser, M. *Tetrahedron* **1991**, *47*, 7323−7328.

(6) Wiberg, K. B.; Marquez, M. *J. Am. Chem. Soc.* **1998**, *120*, 2932−2938.

(7) (a)Smart, B. E. *J. Org. Chem.* **1976**, *41*, 2377−2379. (b) Sepiol, J.; Soulen, R. L. *J. Org. Chem.* **1975**, *40*, 3791−3793. (c) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, 2481−2488. (d) Glück, C.; Poignée, V.; Schwager, H. *Synthesis* **1987**, 260−262.

(8) Law, D. C. F.; Tobey, S. W.; West, R. *J. Org. Chem.* **1973**, *38*, 768−733.

(9) Müller, P.; Etienne, R.; Pfyffer, J.; Pineda, N.; Schipoff, M. *Helv. Chim. Acta* **1978**, *61*, 2482−2487.

(10) (a) Cammagi, G.; Gozzo, F. *J. Chem. Soc. C* **1970**, 178−182. (b) Sargeant, P. B.; Krespan, C. G. *J. Am. Chem. Soc.* **1969**, *91*, 415−419. (c) Abdo, B. T.; Alberts, I. L.; Attfield, C. J.; Banks, R. E.; Blake, A., J. *J. Am. Chem. Soc.* **1996**, *118*, 209−216. (d) Smart, B. E. *J. Am. Chem. Soc.* **1974**, *96*, 927−928.

(11) Lee, C.-C.; Lin, S.-T. *Synthesis* **2000**, 496−498.

(12) Cullen, W. R.; Leeder, W. R. *Inorg. Chem.* **1966**, *5*, 1004−1008.

(13) Mahler, W. *J. Am. Chem. Soc.* **1962**, *84*, 4600−4601.

(14) Babin, D.; Pilorge, F.; Delbarre, L. M.; Demoute, J. P. *Tetrahedron* **1995**, *51*, 9603−9610.

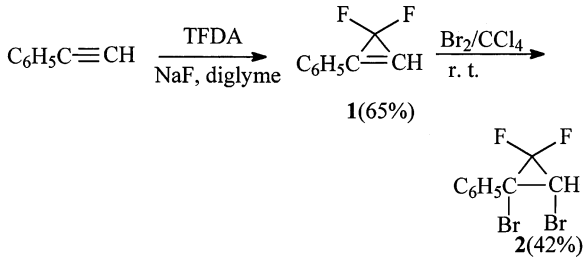
(15) Eujen, R.; Hoge, B. *J. Organomet. Chem.* **1995**, *503*, C51−C54.

(16) (a) Sargeant, P. B. *J. Am. Chem. Soc.* **1969**, *91*, 3061−3068. (b) Sargeant, P. B. *J. Org. Chem.* **1970**, *35*, 678−682.

(17) Tian, F.; Kruger, V. K.; Bautista, O.; Duan, J.-X.; Li, A.-R.; Dolbier, W. R., Jr.; Chen, Q.-Y. *Org. Lett.* **2000**, *2*, 563−564.

10.1021/jo020431v CCC: $22.00
Published on Web 11/27/2002

SCHEME 1



the preparation of *gem*-difluoropropenes through its reaction with alkynes. The results are, herein, presented.

Results and Discussion

(1) Synthesis of 3,3-Difluoro-1-iodocyclopropenes. To verify the report that *gem*-difluoropropenes are unstable (decompose slowly at 25 °C),[5] we first tried the [1 + 2] cycloaddition of phenylacetylene with difluorocarbene generated by $FSO_2CF_2COOSiMe_3$ (TFDA) in diglyme in the presence of 10 mol % sodium fluoride at 120 °C for 1 h. (Scheme 1).

The desired product **1** was obtained in 65% yield. It, however, turns black quickly and finally loses fluorine on standing when exposed to air at room temperature. Nevertheless, **1** could be trapped by bromine to give a rather stable compound **2**.

On the basis of the above results, we were interested in using 1-iodoalkynes as substrates, because *gem*-difluoroiodocyclopropenes, if formed, are expected to be more stable than compound **1**. Furthermore, the iodine atom can be readily functionalized, which might expand the chemistry of *gem*-difluorocyclopropenes. It was found indeed that iodoalkynes (**3**) can readily react with TFDA to give 3,3-difluoro-1-iodocyclopropenes (**4**) in good yields (Scheme 2). The results are listed in Table 1.

As expected, **4** was rather stable: they can be stored at room temperature without decomposition for several hours and much longer in a solvent in refrigerator. Morever, the products bearing an electron-withdrawing group on the benzene ring were shown to be more stable than those with an electron-donating group (entries 8−10 vs entries 1−3, Table 1).

Notably, our results show an interesting difference with previous reports,[13,18] that the noniodinated compounds can further react with CF_2: to produce bicyclobutane, whereas neither **3** undergoes a double cycloaddition of CF_2 by using excess TFDA (3 equiv) nor further TFDA adds to **4** (Scheme 2).

(2) Heck Reaction of 3,3-Difluoro-1-iodocyclopropenes. To functuionalize **4**, we first applied the Heck reaction to α,*β*-unsaturated compounds. Thus, when α,*β*-unsaturated aldehyde, ketone, or ester **5** was treated with **4** under Jeffery's reaction conditions,[19] i.e., $Pd(OAc)_2$ (0.05 equiv), K_2CO_3 (2.5 equiv), and Bu_4NBr (1 equiv), 12 h, both the conversation of **4** and the yield of products **6** were low. The yields were slightly improved if Lu's reaction conditions[20] were employed, i.e., $Pd(OAc)_2$ (0.05 equiv) and Ag_2CO_3 (1.5 equiv) at room temperature. Interestingly, the yields can be greatly improved by using acetonitrile as the solvent in the latter reaction conditions. Significantly, the cross-coupling Heck reaction of **4** with **5** showed a high sterospecificity (Scheme 3). The results are listed in Table 2.

The X-ray analysis of **6aa** (see Supporting Information) suggests that phenyl, 3,3-difluorocyclopropene, and the α,*β*-unsaturated ester group are coplanar. Furthermore, the double bond is in E-form. Notably, the length of the carbon−carbon double bond of cyclopropene is 1.328(3) Å, just like that of a normal carbon−carbon double bond (1.34 Å); this is, perhaps, due to its conjugation with the α,*β*-unsaturated ester.

(3) Trifluoromethylation of 3,3-Difluoro-1-iodocyclopropenes. Methyl fluorosulfonyldifluoroacetate (FSO_2CF_2COOMe) is a useful trifluoromethylation reagent for aryl, benzyl, vinyl, and allyl halides, which was discovered in our laboratory in 1989.[21] It was found that this reagent can be applied successfully to **4** in the presence of CuI at 80−85 °C for 6−12 h to give the corresponding trifluoromethylated compounds **7** in moderate yields (Scheme 4).

The results are listed in Table 3.

In likeness to **4**, **7** could not be converted to bicyclobutane derivatives when treated with TFDA. As anticipated, product **7** is very stable and can be stored at room temperature for several months without any damage.

(4) Hydrolysis of 3,3-Difluoro-1-iodocyclopropenes. It is known that *gem*-difluorocyclopropenes are susceptible both to basic[22] and acidic hydrolysis[23] to afford the corresponding cyclopropanones regardless of whether an alkyl group or hydrogen is present on the cyclopropene ring. However, in our case, **4a** and **4e** were demonstrated to be completely inert under basic conditions, such as 50% aqueous sodium hydroxide in methanol, acetone, diglyme, or ether (Bu_4NBr was added as a phase-transfer agent). On the other hand, **4** were readily hydrolyzed with 2 N hydrochloride acid under reflux for 6 h to give ring-opened products, *β*,*β*-alkyliodoacrylic acids (**8**) with only Z-configuration (Scheme 5). The results are listed in Table 4.

To our surprise, the iodine atom and R are located on the same carbon atom in the products, which is different from the starting materials, in which these two groups are placed on the neighboring carbons; in other words, a migration of the R group seems to have taken place. The structure of **8** was fully assigned by ^1H NMR, MS, and X-ray diffraction measurement for **8a-*Z*** (see Supporting Information).

$^1H-^{13}C$ (HMBC) analysis of **8f** indicates that in **8f** the hydrogen and alkyl group are on the neighboring carbons of the double bond (see Supporting Information). NOESY of **8f** demonstrates that the hydrogen and alkyl group are on the same side of the double bond. All the data show that the configuration of **8f** is also in Z-form.

(18) Cullen, W. R.; Waldman, M. C. *J. Fluorine Chem.* **1977**, *1*, 151−163.

(19) (a) Jeffery, T. *Tetrahedron Lett.* **1985**, *5*, 2667−2670. (b) Jeffery, T. *Synth. Commun.* **1988**, *18*, 77−84.

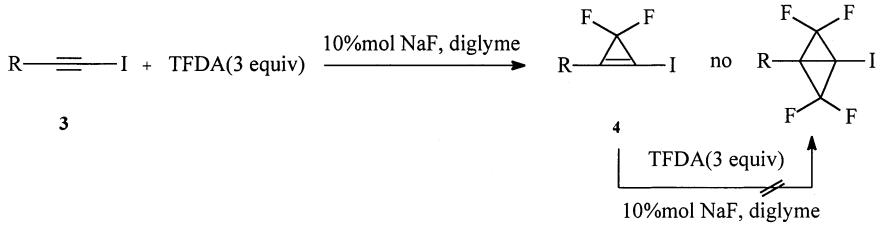
(20) Lu, X. Y.; Huang, X. l.; Ma, S. M. *Tetrahedron Lett.* **1992**, *5*, 2535−2538.

(21) Chen, Q.-Y.; Wu, S.-W. *J. Chem. Soc., Chem. Commun.* **1989**, 705−706.

(22) Dehmlow, E. V.; Winterfeldt, A. *Tetrohedron* **1989**, *45*, 2925−2936.

(23) Anderson, P.; Crabbé, P.; Cross, A. D.; Fried, J. H.; Knox, L. H.; Murphy, J.; Velarrde, E. *J. Am. Chem. Soc.* **1968**, *90*, 3888−3889.

SCHEME 2[a]



3 4

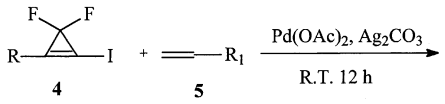
[a] R = C_6H_5(a), 4-$CH_3OC_6H_4$(b), 4-$CH_3C_6H_4$(c), 4-ClC_6H_4(d), $CH_3(CH_2)_4$(e), $CH_3(CH_2)_9$(f), $C_6H_5CH_2OCH_2$(g), 3-$CF_3C_6H_4$(h), 4-BrC_6H_4(i), 4-$O_2NC_6H_4$(j), $CH_3(CH_2)_5$(k).

TABLE 1. Results of Reaction of 3 with TFDA in Diglyme in the Presence of 10 mol % Sodium Fluoride[a]

entry	R	temp (°C)	time (h)	product	yield (%)
1	C_6H_5	118	1	**4a**	82
2	4-$CH_3OC_6H_4$	124	1	**4b**	74
3	4-$CH_3C_6H_4$	118	2	**4c**	73
4	4-ClC_6H_4	124	1.5	**4d**	79
5	$CH_3(CH_2)_4$	120	1	**4e**	77
6	$CH_3(CH_2)_9$	120	1	**4f**	75
7	$C_6H_5CH_2OCH_2$	120	1	**4g**	71
8	3-$CF_3C_6H_4$	122	0.5	**4h**	73
9	4-BrC_6H_4	112	1	**4i**	72
10	4-$O_2NC_6H_4$	110	1	**4j**	71
11	$CH_3(CH_2)_5$	117	1	**4k**	69

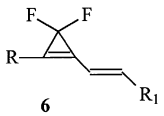
[a] Compound **3**: TFDA:NaF = 1:3:0.1.

SCHEME 3[a]



4 5

4a: R=C_6H_5 5a: R_1=$COOCH_3$
4e: R=$CH_3(CH_2)_4$ 5b: R_1=CHO
4i: R=4-BrC_6H_4 5c: R_1=$COCH_3$
4j: R=4-$O_2NC_6H_4$



6

[a] **4a**, R = C_6H_5; **4e**, R = $CH_3(CH_2)_4$; **4i**, R = 4-BrC_6H_4; **4j**, R = 4-$O_2NC_6H_4$; **5a**, R_1 = $COOCH_3$; **5b**, R_1 = CHO; **5c**, R_1 = $COCH_3$.

Even more surprisingly, when **4a** was exposed in air for 24 h, the E-form of **8a** [**8a′**] was exclusively formed instead of the above-mentioned Z-form. Its structure was assigned by X-ray analysis (see Supporting Information).

Our tentative rationalization is as follows: proton attack on the carbon−carbon double bond gives the carbonium intermediate, followed by the alkyl or aryl group shift and accompanied by the simultaneous collapse of the cyclopropenes ring and finally hydrolysis of the resultant difluoromethylcarbonium ion as shown path a in Scheme 6.

Alternatively,[24] initial protonation at the carbon bearing iodine followed by iodonium ion bridging and then rearrangement of the iodonium ion is also likely as shown in path b.

Because *E*-**8a** on heating in 2 N HCl for 6 h did not rearrange to *Z*-**8a** (the same conditions for the formation of *Z*-**8a** from **4a; Scheme 7**), the suggested mechanisms are unable to rationalize the fact that a large configuration difference resulted from acidic hydrolysis as compared to the results from a moisture attack of **4a**.

(24) We thank the reviewer for this suggestion.

TABLE 2. Heck Type Reaction of 3,3-Difluoro-1-iodocyclopropenes with α,β-Unsaturated Carbonyl Compounds

entry	**4**	**5**	**6**	E:Z[e]	yield (%)
1[a]	**4a**	**5a**	**6aa**		22
2[b]	**4a**	**5a**			48
3[c]	**4a**	**5a**		97:3	68
4[a]	**4a**	**5b**	**6ab**		11
5[b]	**4a**	**5b**			38
6[c]	**4a**	**5b**		95:5	66
7[b]	**4a**	**5c**	**6ac**		11
8[c]	**4a**	**5c**		92:8	38
9[b]	**4e**	**5a**	**6ea**		51
10[c]	**4e**	**5a**		94:6	60
11[b]	**4e**	**5b**	**6eb**		20
12[c]	**4e**	**5b**		100	43
13[c]	**4e**	**5c**	**6ec**	100	41
14[c]	**4i**	**5a**	**6ia**	100	80
15[c]	**4i**	**5b**	**6ib**	100	55
16[c]	**4i**	**5c**	**6ic**	100	74
17[c]	**4j**	**5a**	**6ja**	100	76
18[c]	**4j**	**5b**	**6jb**	91:9	53
19[c]	**4j**	**5c**	**6jc**	100	80

[a] Under Jeffery's reaction conditions. [b] Under Lu's reaction conditions. [c] Under Lu's reaction conditions, but adding acetonitrile as the solvent. [d] Determined by ^{19}F or ^{1}H NMR.

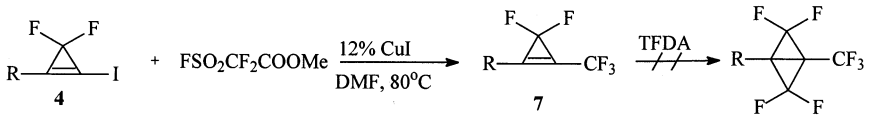
In conclusion, we have developed a simple method for the synthesis of relatively stable 3,3-difluoroiodocyclopropenes from the reactions of alkynes with an easily available difluorocarbene precursor, $FSO_2CF_2COOSiMe_3$. Trifluoromethylation and Heck type cross-coupling reaction with α,β-unsaturated compounds provide examples for further functionalization of these iodides. Acidic hydrolysis of these iodides led to some unexpected observations.

Experimental Section

^{1}H NMR spectra were recorded with trimethylsilane (TMS) as an internal standard (positive for upfield). ^{19}F NMR spectra were recorded with $CFCl_3$ as an external standard (negative for upfield). The solvent for NMR measurement was $CDCl_3$ or CD_3COCD_3. Diglyme was dried with sodium; $FSO_2CF_2COOSiMe_3$ (TFDA) was prepared according to literature.[17] Phenylacetylene, 1-octyne, and 1-hyptyne are commercially available, whereas all other alkynes used were prepared following published procedures.[25−27]

(1) Synthesis of 1-Iodoalkynes.[28] **Typical Experimental Procedure for the Preparation of 1-Iodoalkynes.** To a

SCHEME 4[a]

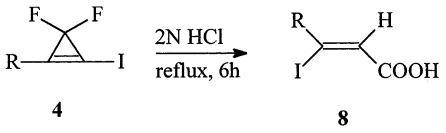


[a] R = C_6H_5 (a), 4-$CH_3OC_6H_4$ (b), 4-$CH_3C_6H_4$ (c), 4-ClC_6H_4 (d), $CH_3(CH_2)_4$ (e), $CH_3(CH_2)_9$ (f).

TABLE 3. Trifluoromethylation of 3,3-Difluoro-1-iodocyclopropenes

entry	R	time (h)	product	yield (%)
1	C_6H_5	6	**7a**	45
2	4-$CH_3OC_6H_4$	8	**7b**	71
3	4-$CH_3C_6H_4$	12	**7c**	64
4	4-ClC_6H_4	6	**7d**	59
5	$CH_3(CH_2)_4$	8	**7e**	55
6	$CH_3(CH_2)_9$	6	**7f**	64

SCHEME 5[a]



[a] R = C_6H_5 (a), $CH_3(CH_2)_4$ (e), $CH_3(CH_2)_9$ (f), 4-BrC_6H_4 (i), 4-$O_2NC_6H_4$ (j), $CH_3(CH_2)_5$ (k).

TABLE 4. Hydrolysis of Selected 3,3-Difluoro-1-iodocyclopropenes under Acidic Conditions[a]

entry	R	product	*Z* or *E*[c]	yield (%)
1	C_6H_5	**8a**	Z	26
2	$CH_3(CH_2)_4$	**8e**	Z	33
3	$CH_3(CH_2)_9$	**8f**	Z	37
4	4-BrC_6H_4	**8i**	Z	60
5	4-$O_2NC_6H_4$	**8j**	Z	34
6	$CH_3(CH_2)_5$	**8k**	Z	43
7*b*	C_6H_5	**8a**	E	31

[a] 2 N HCl reflux, 6 h. [b] Exposing **4a** to air for 24 h. [c] Determined by ^{1}H NMR.

methanol solution of CH_3ONa prepared by methanol (150 mL) and sodium (1.5 g, 65.2 mmol) was added phenylacetylene (6 g, 58.7 mmol) dropwise at room temperature. On stirring, to the mixture iodine (15 g, 59.0 mmol) was added slowly until the color of iodine did not fade. The content was then treated with sodium thiosulfate solution and extracted with dichloromethane (2 × 30 mL), and the organic layer was dried over Na_2SO_4. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on a silica gel column to give 1-iodophenylacetylene (10.5 g, 79%).

Yields: **3b**, 85%; **3c**, 80%; **3d**, 77%; **3e**, 75%; **3f**, 79%; **3g** , 83%; **3h**, 78%; **3i**, 81%; **3j**, 82%; **3k**, 75%.

(2) Synthesis of 2,2-Dibromo-1-phenyl-3,3-difluorocyclopropane (2). Under nitrogen atmosphere, in a 10 mL sidearmed Pyrex tube with a magnetic stirring bar and a pressure-equalized addition funnel, was placed phenylacetylene (0.67 g, 6.6 mmol), sodium fluoride (27 mg, 0.7 mmol), and diglyme (1 mL). After heating to about 120 °C (bath), $FSO_2CF_2COOSiMe_3$ (TFDA; 3.78 g, 15.1 mmol) was added dropwise. The content was stirred at this temperature for 2 h (traced by ^{19}F NMR), cooled to room temperature, and then directly purified by flash chromatography on a silica gel column to give 3,3-difluoro-1-phenylcyclopropene (**1**; 0.56 g, 65%) as a yellow liquid (eluent: petroleum ether).

To a solution of **1** in 20 mL of carbon tetrachloride, 0.25 mL of bromine in 5 mL of carbon tetrachloride was added dropwise at room temperature. After addition, the mixture was stirred for an additional 6 h and then washed with saturated aqueous $NaHCO_3$, brine. The organic layer was dried over Na_2SO_4. After removal of solvent, the residue was purified by flash chromatography on a silica gel column to give of 2,2-dibromo-1-phenyl-3,3-difluorocyclopropane (**2**) (0.51 g; overall yield is 25%) as a colorless liquid (eluent: petroleum ether).

IR (film; cm^{-1}): 3046, 1450, 1417, 1162, 1006. ^{1}H NMR (CD_3COCD_3): δ 4.56−4.59 (d, J = 10.7 Hz, 1H), 7.44−7.51(m, 5H). ^{19}F NMR (CD_3COCD_3): δ −124.24 (dd, J_{F-F} = 148.3 Hz, $^3J_{H-F}$ = 11 Hz, 2F). MS *m*/*z* (rel intens): 233 (35.94), 213 (22.10), 152 (23.23), 102 (16.75). Anal. Calcd for $C_9H_6Br_2F_2$: C, 34.65; H, 1.94; F, 12.18. Found: C, 34.56; H, 1.98; F, 12.43.

(3) Synthesis of 1-Iodo-3,3-difluorocyclopropenes. (a) Typical Experimental Procedure. Under nitrogen atmosphere, in a 10 mL sidearmed Pyrex tube with a magnetic stirring bar and a pressure-equalized addition funnel, was placed 1-iodophenylacetylene (3a; 1.15 g, 5.0 mmol), sodium fluoride (21 mg, 0.5 mmol), and diglyme (1 mL). After heating the mixture to about 120 °C (bath), TFDA (3.78 g, 15.1 mmol) was added dropwise. The mixture was stirred at this temperature for 2 h and traced by ^{19}F NMR. Then the reaction was cooled to room temperature and directly purified by flash chromatography on a silica gel column. 3,3-Difluoro-1-iodo-2-pehenylcyclopropene (**4a**; 1.15 g, 82%) was obtained as a pale yellow liquid (eluent: petroleum ether).

(b) Compound 4a. IR (film; cm^{-1}): 1752, 1611, 1472, 1309, 1296, 1073, 1021. ^{1}H NMR ($CDCl_3$): δ 7.49−7.54 (m, 3H), 7.64−7.67 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −105.31 (s, 2F). MS *m*/*z* (rel intens): 259 (M^+ − F, 0.59), 151 (100.00), 131 (4.71), 101 (7.85), 77 (6.84). Anal. Calcd for $C_9H_5F_2I$: C, 38.88; H, 1.81; F, 13.67. Found: C, 38.96; H, 1.84; F, 13.38.

(c) Compound 4b. Pale yellow liquid. IR (film; cm^{-1}): 1731, 1612, 1314, 1306, 1045. ^{1}H NMR ($CDCl_3$): δ 3.80(s, 3H), 6.82−6.85 (m, 2H), 7.37−7.40 (m, 2H). ^{19}F NMR($CDCl_3$): δ −103.39 (s, 2F). MS *m*/*z* (rel intens): 289 (M^+ − F, 63.01), 229 (6.86), 181 (100.00), 112 (0.75). Anal. Calcd for $C_{10}H_7F_2IO$: C, 38.99; H, 2.29; F,12.33. Found: C, 39.45; H, 2.38; F, 12.03.

(d) Compound 4c. Pale yellow liquid. IR (film; cm^{-1}): 3032, 2924, 1746, 1608, 1315, 1300, 1232, 1041. ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3H), 7.13−7.32 (m, 2H), 7.40−7.55 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −105.17 (s, 2F). MS *m*/*z* (rel intens): 292 (M^+, 1.50), 273 (2.57), 165 (100.00), 127 (14.47), 115 (25.38). Anal. Calcd for $C_{10}H_7F_2I$: C, 41.12; H, 2.42; F,13.01. Found: C, 40.80; H, 2.62; F, 12.65.

(e) Compound 4d. Pale yellow liquid. IR (film; cm^{-1}): 1748, 1589, 1487, 1312, 1295, 1234, 1093, 1047, 1016. ^{1}H NMR ($CDCl_3$): δ 7.47−7.494 (m, 2H), 7.50−7.61 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −105.13 (s, 2F). MS *m*/*z* (rel intens): 312 (M^+, 1.41), 293 (1.36), 185 (91.05), 183 (100.00), 150 (14.42), 120 (45.69). Anal. Calcd for $C_9H_4ClF_2I$: C, 34.59; H, 1.29; F, 12.16. Found: C, 35.63; H, 1.46; F, 12.20.

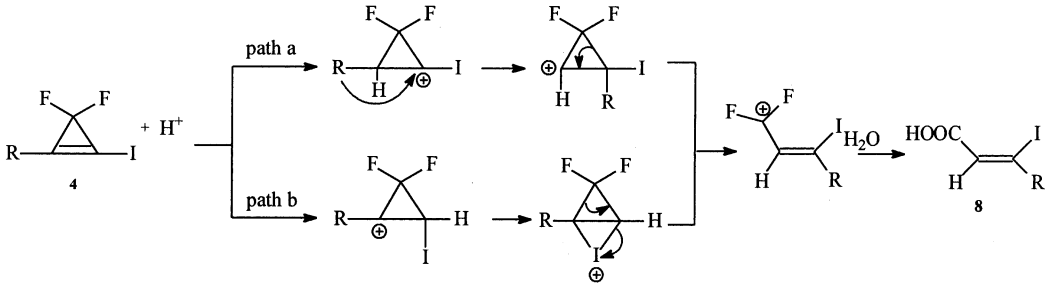
(25) 3-(Benzyloxy)propyne was prepared in 79% yield. Reaction condition: 2-propyn-1-ol (5 g, 89 mmol), 20% NaOH (20 mL), TBAC (2 mL), benzyl bromide (10 mL, 84 mmol), hexane (50 mL), room temperature, 6 h. ^{1}HNMR ($CDCl_3$): δ 2.48(s, 1H), 4.18(s, 2H), 4.62 (s, 2H), 7.26−7.39(m, 5H).

(26) (a) Klein, J.; Gurfinkel, E. *Tetrahedron* **1970**, *26*, 2127−2131. (b) Yoshikazu Kimura, Steven L. *J. Org. Chem*. **1982**, 2493−2494.

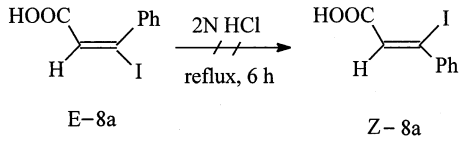
(27) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett*. **1972**, 3769−3772.

(28) Heasley, V. L.; Shellhamer, D. F.; Heasley, L. E; Yaeger, D. B. *J. Org. Chem*. **1980**, *45*, 4649−4652.

SCHEME 6. Possible Mechanisms of Hydrolysis of 4 under Acidic Conditions



SCHEME 7



(f) Compound 4e. Pale yellow liquid. IR (film; cm^{-1}): 2960, 2935, 2864, 1756, 1423, 1303, 1147, 1042. ^1H NMR ($CDCl_3$): δ 0.93 (t, J = 7.2 Hz, 3H), 1.30−1.39 (m, 4H), 1.61−1.68 (m, 2H), 2.47−2.54 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −103.11 (d, $^3J_{H-F}$ = 11 Hz, 2F). MS m/z (rel intens): 253 (M^+ − F, 80.78), 229 (0.99), 216 (15.81), 201 (6.10), 125 (38.64), 55 (95.974), 41 (100.00). Anal. Calcd for $C_8H_{11}F_2I$: C, 35.32; H, 4.08; F, 13.97. Found: C, 34.94; H, 3.95; F, 14.15.

(g) Compound 4f. Pale yellow liquid. IR (film; cm^{-1}): 2970, 2947, 1758, 1428, 1313, 1142, 1036. ^1H NMR ($CDCl_3$): δ 0.90−0.95 (m, 3H), 1.30−1.39 (m, 4H), 1.61−1.68 (m, 2H), 2.47−2.54 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −103.11 (d, $^3J_{H-F}$ = 11 Hz, 2F). MS m/z (rel intens): 342 (M^+, 0.37), 323 (100.00), 216 (8.77), 131 (35.04), 117 (41.08), 97 (29.70). HRMS. Calcd for $C_{13}H_{21}F_2I$: 342.0656. Found: 342.0671.

(h) Compound 4g. Pale yellow liquid. IR (film; cm^{-1}): 1753, 1605, 1466, 1458, 1310, 1293, 1080, 1031. ^1H NMR ($CDCl_3$): δ 4.49−4.51 (m, 2H), 4.61 (s, 2H), 7.32−7.38 (m, 5H), 2.47−2.54 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −102.27 (s, 2F). MS m/z (rel intens): 322 (M^+, 0.59), 292 (5.39), 215 (4.34), 195 (1.02), 165 (44.11), 91 (100.00). Anal. Calcd for $C_{11}H_9F_2IO$: C, 41.02; H, 2.82; F, 11.80. Found: C, 41.28; H, 2.68; F, 11.56.

(i) Compound 4h. Pale yellow liquid. IR (film; cm^{-1}): 1750, 1614, 1441, 1336, 1301, 1277, 1222, 1172, 1134, 1069. ^1H NMR ($CDCl_3$): δ 7.64−7.69 (m, 1H), 7.79−7.90 (m, 3H). ^{19}F NMR ($CDCl_3$): δ −106.88 (s, 2F), −64.86 (s, 3F). MS m/z (rel intens): 327 (M^+ − F, 7.52), 219 (100.00), 277 (1.01), 200 (6.97), 169 (16.40), 69 (1.71). Anal. Calcd for $C_{10}H_4F_5I$: C, 34.71; H, 1.17; F, 27.45. Found: C, 34.63; H, 1.25; F, 27.45.

(j) Compound 4i. Pale yellow solid. IR (film; cm^{-1}): 1749, 1582, 1482, 1311, 1297, 1231, 1068, 1025, 1012. ^1H NMR ($CDCl_3$): δ 7.51−7.55 (m, 2H), 7.63−7.67 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −106.47 (s, 2F). MS m/z (rel intens): 356 (M^+ + 2, 9.48), 354 (M^+, 9.35), 227 (100.00). Anal. Calcd for $C_9H_4BrF_2I$: C, 30.29; H, 1.13; F, 10.65. Found: C, 30.38; H, 1.34; F, 10.87.

(k) Compound 4j. Yellow solid. IR (film; cm^{-1}): 1743, 1602,1522, 1511, 1344, 1307, 1292, 1245, 1037. ^1H NMR ($CDCl_3$): δ 7.54−7.87 (m, 2H), 8.36−8.40 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −106.15 (s, 2F). MS m/z (rel intens): 304 (M^+ − F, 2.23), 196 (100.00), 150 (55.12). Anal. Calcd for $C_9H_4F_2INO_2$: C, 33.46; H, 1.25; N, 4.34; F, 11.76. Found: C, 33.75; H, 1.46; N, 4.27; F, 12.21.

(l) Compound 4k. Pale yellow liquid. IR (film; cm^{-1}): 2958, 2933, 1809, 1756, 1304, 1146, 1042. ^1H NMR ($CDCl_3$): δ 0.91 (t, J = 6.9 Hz, 3H), 1.29−1.42 (m, 6H), 1.61−1.70 (m, 2H), 2.47−2.54 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −106.15 (s, 2F). MS m/z (rel intens): 267 (M^+ − F, 5.63), 216 (14.21), 201 (4.09), 127 (10.17), 41 (100.00). Anal. Calcd for $C_9H_{13}F_2I$: C, 37.78; H, 4.58; F, 13.28. Found: C, 37.54; H, 4.50; F, 13.13.

(4) Heck Type Reaction of 3,3-Difluoro-1-iodocyclopropenes with α,β-Unsaturated Compounds. (a) Method A. Under nitrogen atmosphere, in a 10 mL three-neck flask with a magnetic stirring bar was placed Bu_4NBr (322 mg, 1.0 mmol), K_2CO_3 (206 mg, 1.5 mmol), and methyl 2-propenioate (1 mL). To the mixture, $Pd(OAc)_2$(6 mg) was first added, after 5 min, a solution of 3,3-difluoro-1-iodo-2-phenylcyclopropene (**4a**; 278 mg, 1.0 mmol) in 0.5 mL of methyl 2-propenioate was then added. The content was stirred at room temperature overnight, diluted with ether, and filtered. After removal of the solvent, the residue was purified by flash chromatography on a silica gel column. Compound **6aa** (56 mg, 22%) was obtained as a nearly colorless solid.

(b) Method B. Under nitrogen atmosphere, in a 10 mL Pyrex tube with a magnetic stirring bar was placed **4a** (0.65 g, 2.34 mmol), methyl 2-propenioate (2 mL), Ag_2CO_3 (0.99 g, 3.59 mmol), and $Pd(OAc)_2$ (26 mg, 0.12 mmol). The content was stirred at room temperature for about 12 h (traced by ^{19}F NMR). After the reaction was complete, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on a silica gel column. Compound **6aa** (0.27 g, 48%) was obtained as a nearly colorless solid.

(c) Method C. Under nitrogen atmosphere, a mixture of **4a** (0.711 g, 2.62 mmol), methyl 2-propenioate (2 mL), Ag_2CO_3 (1.081 g, 3.92 mmol), $Pd(OAc)_2$ (29 mg), and acetonitrile (2 mL) was stirred at room temperature for 3.5 h. The usual workup gave **6aa** (0.41 g, 68%).

(d) Compound 6aa. IR (film; cm^{-1}): 1848, 1720, 1684, 1495, 1438, 1421, 1312, 1255, 1204, 1172, 1137. ^1H NMR ($CDCl_3$): δ 3.84 (s, 3H), 6.54 (d d, J = 15.3, 0.9 Hz, 1H), 7.53 (d t, J = 15.3, 2.7 Hz, 1H), 7.50−7.54 (m, 3H), 7.66−7.69 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −111.84 (s, 2F). MS m/z (rel intens): 236 (M^+, 32.99), 221 (98.40), 205 (7.69), 176 (100.00), 77 (5.10). HRMS. Calcd for $C_{13}H_{10}F_2O_2$: 236.0649. Found: 236.0649. Anal. Calcd for $C_{13}H_{10}F_2O_2$: C, 66.10; H, 4.27; F, 16.09. Found: C, 66.11; H, 4.94; F, 16.18. X-ray crystallographic data: crystal system, orthorhombic; space group, $P2_12_1$; unit cell diamensions, a = 6.6919(6) Å, b = 11.6094(10) Å, c = 15.3509(13) Å, α = 90°, β = 90°, γ = 90°; Z = 4; F(000) = 488; R1 = 0.0391, wR2 = 0.0619.

(e) Compound 6ab. Pale yellow solid. IR (film; cm^{-1}): 2839, 1764, 1691, 1494, 1450, 1362, 1320, 1309, 1270, 1197, 1174, 1022. ^1H NMR ($CDCl_3$): δ 6.77 (m, 1H), 7.28−7.34 (m, 1H), 7.55−7.58 (m, 3H), 7.70−7.73 (m, 2H), 9.81 (d, J = 6.1 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ −112.79 (s, 2F). MS m/z (rel intens): 206 (M^+, 81.20), 177 (100.00), 151 (36.85), 127 (71.57), 102 (39.85), 77 (30.33). HRMS. Calcd for $C_{12}H_8F_2O$: 206.0543. Found: 206.0505. Anal. Calcd for $C_{12}H_8F_2O$: C, 69.90; H, 3.91; F, 18.43. Found: C, 69.75; H, 3.96; F, 18.21.

(f) Compound 6ac. Pale yellow solid. IR (film; cm^{-1}): 1765, 1676, 1650, 1494, 1452, 1367, 1312, 1274, 1240, 1115, 1003, 925. ^1H NMR ($CDCl_3$): δ 2.42 (s, 3H), 6.77(d, J = 15.9 Hz, 1H), 7.27 (d t, J = 15.9, 4.8 Hz, 1H), 7.51−7.53 (m, 3H), 7.67−7.70 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −112.79 (s, 2F). MS m/z (rel intens): 220 (M^+, 71.97), 205 (58.97), 177 (100.00), 151 (36.90), 43 (28.47). Anal. Calcd for $C_{13}H_{10}F_2O$: C, 70.90; H, 4.58; F, 17.25. Found: C, 70.99; H, 4.74; F, 17.31.

(g) Compound 6ea. Pale yellow liquid. IR (film; cm^{-1}): 2959, 2936, 1786, 1729, 1633, 1459, 1438, 1309, 1270, 1197, 1174, 1022. ^1H NMR ($CDCl_3$): δ 0.93 (t, J = 7.2 Hz, 3H), 1.34−1.43 (m, 4H), 1.76 (t, J = 7.1 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H), 3.84 (s, 3H), 6.67 (d, J = 8.8 Hz, 1H), 7.19 (d, J = 15.9 Hz, 1H)). ^{19}F NMR ($CDCl_3$): δ −110.30 (s, 2F). MS *m/z* (rel intens): 211 (17.47), 198 (7.53), 171 (26.61), 159 (100.00), 41 (97.31). Anal. Calcd for $C_{12}H_{16}F_2O_2$: C, 62.60; H, 7.00; F, 16.50. Found: C, 62.43; H, 7.15; F, 16.92.

(h) Compound 6eb. Pale yellow liquid. IR (film; cm^{-1}): 2961, 2935, 2865, 1782, 1721, 1695, 1468, 1421, 1318, 1280, 1222, 1118, 1023. ^1H NMR ($CDCl_3$): δ 0.90−0.95 (m, 3H), 1.36−1.41 (m, 4H), 1.68−1.72 (m, 2H), 2.59−2.65 (m, 2H), 6.57 (t, 1H), 7.03−7.09 (d d, 1H), 9.72 (d, 1H)). ^{19}F NMR ($CDCl_3$): δ −109.39 (s, 2F). MS *m/z* (rel intens): 200 (M^+, 5.40), 181 (7.39), 171 (5.68), 151 (10.37), 144 (100.00), 115 (70.31). Anal. Calcd for $C_{11}H_{14}F_2O$: C, 65.99; H, 7.05; F, 18.98. Found: C, 65.74; H, 6.98; F, 17.49.

(i) Compound 6ec. Pale yellow liquid. IR (film; cm^{-1}): 2961, 2935, 2865, 1784, 1699, 1681, 1607, 1423, 1363, 1318, 1250, 1180, 1041. ^1H NMR ($CDCl_3$): δ 0.91−0.93 (m, 3H), 1.32−1.41 (m, 4H), 1.63−1.73 (m, 2H), 2.37 (s, 3 H), 2.55−2.62 (m, 3H), 6.59 (d, J = 16.2 Hz, 1H), 7.03 (d t, J = 15.9, 2.7 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ −110.43 (s, 2F). MS *m/z* (rel intens): 214 (M^+, 1.83), 199 (1.25), 195 (6.44), 158 (21.43), 115 (11.76), 107 (15.16), 43 (100.00). 82). Anal. Calcd for $C_{12}H_{16}F_2O$: C, 67.27; H,7.53; F, 17.73. Found: C, 67.10; H, 6.98; F, 17.63.

(j) Compound 6ia. Yellow solid. IR (film; cm^{-1}): 2958, 1773, 1630, 1585, 1488, 1436, 1365, 1311, 1294, 1175, 1067, 1062. ^1H NMR ($CDCl_3$): δ 3.85 (s, 3H), 6.54 (d, J = 15.9 Hz, 1H), 7.47 (dt, J = 15.9, 2.4 Hz, 1H), 7.51−7.55 (m, 2H), 7.64−7.67 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −113.64 (s, 2F). MS *m/z* (rel intens): 316 (M^+ + 2, 20.21), 314 (M^+, 20.33), 299 (25.41), 255 (26.75), 235 (14.42), 220 (100.00), 192 (56.26), 155 (6.52). Anal. Calcd for $C_{13}H_9BrF_2O_2$: C, 49.55; H, 2.88; F, 12.06. Found: C, 49.76; H, 3.03; F, 12.17.

(k) Compound 6ib. Yellow solid. IR (film; cm^{-1}): 2994, 2826, 1767, 1721, 1690, 1583, 1487, 1365, 1313, 1282, 1228, 1012. ^1H NMR ($CDCl_3$): δ 6.69 (m, 1H), 7.28 (d t, J = 15.9, 2.1 Hz, 1H), 7.54−7.69 (m, 4H), 9.81 (d, J = 7.5 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ −112.47 (s, 2F). MS *m/z* (rel intens): 286 (M^+ + 2, 53.71), 284 (M^+, 56.37), 264 (9.88), 255 (29.90), 234 (25.50), 206 (40.52), 177 (100.00). Anal. Calcd for $C_{12}H_7BrF_2O$: C, 50.56; H, 2.47; F, 13.33. Found: C, 50.62; H, 2.69; F, 13.09.

(l) Compound 6ic. Yellow solid. IR (film; cm^{-1}): 3095, 3028, 1766, 1695, 1609, 1583, 1488, 1368, 1299, 1253,1173, 1067, 1024. ^1H NMR ($CDCl_3$): δ 2.42 (s, 3H), 6.76 (d, J = 15.9 Hz, 1H), 7.25 (d t, J = 15.9, 2.4 Hz, 1H), 7.52−7.56 (m, 2H), 7.64−7.68 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −113.64 (s, 2F). MS *m/z* (rel intens): 300 (M^+ + 2, 38.20), 298 (M^+, 38.65), 284 (20.96), 255 (30.60), 229 (3.41), 191 (9.99), 155 (14.11). Anal. Calcd for $C_{13}H_9BrF_2O$: C, 52.20; H, 3.03; F, 12.70. Found: C, 52.38; H, 3.09; F, 12.63.

(m) Compound 6ja. Pale brown solid. IR (film; cm^{-1}): 3087, 1717, 1631, 1517, 1442, 1340, 1312, 1262, 1201, 1180, 1041. ^1H NMR ($CDCl_3$): δ 3.87 (s, 3H), 6.62 (d, J = 15.9 Hz, 1H), 7.43 (dt, J = 15.6, 2.7 Hz, 1H), 7.82−7.87 (m, 2H), 8.35−8.40 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −109.48 (s, 2F). MS *m/z* (rel intens): 281 (M^+, 26.54), 266 (100.00), 249 (15.79), 222 (31.07), 192 (38.61). Anal. Calcd for $C_{13}H_9F_2NO_4$: C, 55.52; H, 3.23; N, 4.98; F, 13.51. Found: C, 55.53; H, 3.28; N, 4.87; F, 13.50.

(n) Compound 6jb. Pale brown solid. IR (film; cm^{-1}): 3109, 2832, 1764, 1682, 1601, 1519, 1347, 1278, 1136, 1047. ^1H NMR ($CDCl_3$): δ 6.77−6.84 (m,1H), 7.34 (d t, J = 15.9, 2.1 Hz, 1H), 7.87 (d, J = 8.7 Hz, 2H), 8.40 (d, J = 6.9 Hz, 2H), 9.85 (d, J = 7.2 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ −112.93 (s, 2F). MS *m/z* (rel intens): 251 (M^+, 34.76), 232 (2.17), 222 (6.14), 204 (11.72), 175 (28.05), 43 (100.00). Anal. Calcd for $C_{12}H_7F_2NO_3$: C, 57.38; H, 2.81; N, 5.58; F, 15.13. Found: C, 57.34; H, 3.19; N, 5.53; F, 15.31.

(o) Compound 6jc. Pale brown solid. IR (film; cm^{-1}): 3109, 3047, 1763, 1690, 1602, 1521, 1347, 1301, 1258, 1174, 1031. ^1H NMR ($CDCl_3$): δ 2.45 (s, 3H), 6.84 (d, J = 16.2 Hz, 1H), 7.31 (dt, J = 17.6 Hz, 2.7 Hz, 1H), 7.84−7.87 (m, 2H), 8.36−8.39 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −113.17 (s, 2F). MS *m/z* (rel intens): 265 (M^+, 32.86), 250 (2.93), 222 (22.02), 176 (39.43), 43 (100.00). Anal. Calcd for $C_{13}H_9F_2NO_3$: C, 58.87; H, 3.42; N, 5.28; F, 14.33. Found: C, 58.35; H, 3.65; N, 5.04; F, 14.37.

(5) Trifluoromethylation Reaction of 3,3-Difluoro-1-iodocyclopropenes. (a) Typical Experimental Procedure. Under nitrogen atmosphere, in a 10 mL side Pyrex tube with a magnetic stirring bar was placed **4a** (0.56 g, 2.0 mmol), CuI (46 mg, 0.24 mmol), dimethylformamide (DMF; 1 mL), and FSO_2CF_2COOMe (0.78 g, 4.0 mmol); the mixture was stirred and heated at about 80 °C for 6 h and traced by ^{19}F NMR. After the reaction was complete, the mixture was cooled to room temperature, poured into water (5 mL), and extracted with ether (2 × 10 mL). The organic layer was dried over Na_2SO_4. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on a silica gel column. 3,3-Difluoro-1-pehenyl-2-trifluoromethylcyclopropenes (**7a**; 0.20 g, 45%) was obtained as a colorless liquid (eluent: petroleum ether).

(b) Compound 7a. Colorless liquid. IR (film; cm^{-1}): 1803, 1609, 1513, 1367, 1334, 1170, 1066. ^1H NMR($CDCl_3$): δ 7.69−7.88 (m, 5H). ^{19}F NMR ($CDCl_3$): δ −103.49 (d, 2F), −55.14 (d, 3F). MS *m/z* (rel intens): 220 (M^+, 35.79), 201 (13.34), 169 (11.84), 151 (100.00), 69 (10.13). HRMS. Calcd for $C_9H_5F_5$: 220.0311. Found: 220.0264.

(c) Compound 7b. Colorless liquid. IR (film; cm^{-1}): 2934, 2849, 1799, 1606, 1515, 1333, 1303, 1266, 1163, 1060. ^1H NMR ($CDCl_3$): δ 3.90 (s, 3H), 7.01−7.05 (m, 2H), 7.65−7.69 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −107.80 (d, 2F), −59.01 (d, 3F). MS *m/z* (rel intens): 250 (M^+, 100.00), 231 (26.22), 200 (31.00), 181 (99.76), 69 (7.70). Anal. Calcd for $C_{10}H_7F_5O$: C, 52.81; H, 2.82; F, 37.97. Found: C, 51.93; H, 2.45; F, 38.19.

(d) Compound 7c. Colorless liquid. IR (film; cm^{-1}): 1801, 1609, 1513, 1367, 1334, 1305, 1170, 1066. ^1H NMR ($CDCl_3$): δ 2.56 (s, 3H), 7.26−7.36 (m, 2H), 7.60−7.65 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −105.92 (s, 2F), −59.20 (s, 3F). MS *m/z* (rel intens): 234 (M^+, 56.14), 215 (8.49), 200 (3.62), 165 (100.00), 115 (9.57), 69 (2.75). HRMS. Calcd for $C_{11}H_7F_5$: 234.0468. Found: 234.0460.

(e) Compound 7d. Colorless liquid. IR (film; cm^{-1}): 2964, 2935, 1806, 1595, 1492, 1332, 1171, 1095, 1072, 1017. ^1H NMR ($CDCl_3$): δ 7.53−7.57 (m, 2H), 7.65−7.69 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −105.13 (t, 2F), −55.73 (d, 3F). MS *m/z* (rel intens): 254 (M^+, 50.81), 235 (13.17), 219 (27.23), 185 (100.00), 150 (17.88), 69 (13.63). HRMS. Calcd for $C_{10}H_4ClF_5$: 253.9922. Found: 253.9952.

(f) Compound 7e. Colorless liquid. IR (film; cm^{-1}): 2965, 2839, 1815, 1452, 1336, 1159, 1067. ^1H NMR($CDCl_3$): δ 0.90−0.95 (m, 3H), 1.30−1.39 (m, 4H), 1.61−1.68 (m, 2H), 2.47−2.54 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −106.19 (s, 2F), −60.79 (s, 3F). MS *m/z* (rel intens): 195 (M^+ − F, 0.51), 171 (14.81), 158 (100.00), 145 (18.06), 69 (13.63), 41 (56.08). Anal. Calcd for $C_9H_{11}F_5$: C, 50.46; H, 5.19; F, 44.35. Found: C, 50.14; H, 5.33; F, 43.76.

(g) Compound 7f. Colorless liquid. IR (film; cm^{-1}): 2930, 2859, 1815, 1468, 1336, 1159, 1070. ^1H NMR ($CDCl_3$): δ 0.86−0.90 (m, 3H), 1.27 (s, 12H), 1.64−1.71 (m, 2H), 2.61−2.66 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −103.11 (s, 2F), −60.80 (s, 3F). MS *m/z* (rel intens): 265 (M^+ − F, 0.70), 241 (0.77), 158 (19.14), 69 (58.79), 43 (100.00). Anal. Calcd for $C_{14}H_{21}F_5$: C, 59.13; H,7.46; F, 33.41. Found: C, 58.98; H, 7.37; F, 33.38.

(6) Hydrolysis of 3,3-Difluoro-1-iodo-2-phenylcyclopropene (4a). (a) Typical Experimental Procedure for the Hydrolysis of 3,3-Difluoro-1-iodo-2-phenylcyclopropene under Acidic Conditions. A 10 mL flask with a water condenser and a magnetic stirring bar was charged with **4a** (0.76 g, 2.75 mmol) and 5 mL of 2 N HCl, and the mixture

was heated to reflux and stirred for 6 h. After being cooled to room temperature, the content was extracted with dichloromethane (2 × 10 mL). The organic layer was dried over Na_2SO_4. After removal of solvent under reduced pressure, the residue was purified by flash chromatography on a silica gel column. The title product (**8a**) (0.21 g, 28%) was obtained as a pale brown solid.

(b) Compound 8a. Mp, 188−189 °C. IR (film; cm^{-1}): 3057, 1690, 1598, 1490, 1443, 1403, 1302, 1277, 1229, 1205. ^1H NMR (CD_3COCD_3): δ 6.75 (s, 1H), 6.94 (a very small peak, impurities) 7.29−7.61 (m, 5H). MS *m*/*z* (rel intens): 274 (M^+, 6.15), 257 (1.52), 147 (100.00), 102 (36.51), 77 (35.77). HRMS. Calcd for $C_9H_7IO_2$: 273.94918. Found: 273.9475. X-ray crystallographic data: crystal system, monoclinic; space group, $P2_1/c$; unit cell diamensions, a = 7.8282(6) Å, b = 9.9520(7) Å, c = 11.6294(9) Å, α = 90°, β = 94.750(7)°, γ = 90°; Z = 4; F(000) = 520; R1 = 0.0474, wR2 = 0.1196.

(c) Compound 8e. Liquid. IR (film; cm^{-1}): 3080, 2958, 1694, 1607, 1589, 1411, 1293, 1235, 1127. ^1H NMR ($CDCl_3$): δ 0.90 (t, J = 7.2 Hz, 3H), 1.31−1.37 (m, 6H), 2.46−2.51 (m, 2H), 6.68 (s, 1H). MS *m*/*z* (rel intens): 268 (M^+, 16.66), 251 (4.04), 212 (61.61), 141 (23.15), 95 (100.00), 41 (70.36). HRMS. Calcd for $C_8H_{13}IO_2$: 267.9960. Found: 267.9911.

(d) Compound 8f. Liquid. IR (film; cm^{-1}): 2920, 2849, 1710, 1618, 1462, 1417, 1297, 1223. ^1H NMR ($CDCl_3$): δ 0.88 (t, J = 7.2 Hz, 1H), 1.27 (m, 14H), 1.61 (m, 2H), 2.73 (t, J = 7.8 Hz, 2H), 6.40 (s, 1H). ^{13}C NMR ($CDCl_3$): 14.1, 22.7, 28.2, 29.2, 29.3, 29.4, 29.5, 48.4, 124.2, 125.2, 168.8. MS *m*/*z* (rel intens): 338 (M^+, 3.00), 321 (0.93), 264 (0.81), 239 (0.92), 212 (65.79), 43 (100.00). HRMS. Calcd for $C_{13}H_{23}IO_2$: 338.0743. Found: 338.0740.

(e) Compound 8i. Liquid. IR (film; cm^{-1}): 3030, 2912, 2806, 1686, 1602, 1481, 1413, 1314, 1232, 1210, 1071. ^1H NMR ($CDCl_3$): δ 6.71 (s, 1H), 7.41−7.58 (m, 4H). MS *m*/*z* (rel intens): 354 (M^+ + 2, 5.93), 352 (M^+, 6.26), 306 (1.15), 254 (37.18), 225 (68.31), 209 (2.64), 182 (97.11), 180 (95.910, 155 (3.670, 127 (24.80). HRMS. Calcd for $C_9H_6BrIO_2$: 351.8596. Found: 351.8611.

(f) Compound 8j. Solid. IR (film; cm^{-1}): 1693, 1613, 1589, 1517, 1414, 1345, 11234. ^1H NMR ($CDCl_3$): δ 6.79 (s, 1H), 7.54−7.65 (m, 4H). MS *m*/*z* (rel intens): 319 (M^+, 18.54), 227 (M^+, 20.54), 192 (100.00), 102 (41.89). Anal. Calcd for $C_9H_6INO_4$: C, 33.88; H, 1.90; N, 4.39. Found: C, 34.02; H, 1.43; N, 4.31.

(g) Compound 8k. Colorless liquid. IR (film; cm^{-1}): 2957, 2931, 2859, 1696, 1618, 1466, 1407, 1282, 1220. ^1H NMR ($CDCl_3$): δ 0.89 (t, J = 6.9 Hz, 1H), 1.26−1.62 (m, 8H), 2.73 (t, J = 7.8 Hz, 2H), 6.40 (s, 1H). MS *m*/*z* (rel intens): 282 (M^+, 7.92), 212 (14.50), 155 (4.67), 41 (100.00). HRMS. Calcd for $C_9H_{15}IO_2$: 282.0117. Found: 282.0112.

(7) Hydrolysis of 3,3-Difluoro-1-iodocyclopropene (4a) in Air. In a 10 mL flask was placed **4a** (0.80 g, 2.88 mmol), the content was exposed to air for 24 h, and then the black residue was purified by flash chromatography on a silica gel column. The title product (**8a′**; (0.25 g, 31%) was obtained (eluent: ether).

(a) Compound 8a′. Solid. Mp: 189−190 °C. IR (film; cm^{-1}): 3063, 2989, 1695, 1594, 1487, 1442, 1408, 1306, 1232, 1200. ^1H NMR ($CDCl_3$): δ 6.72 (s, 1H), 7.33−7.56 (m, 5H). MS *m*/*z* (rel intens): 274 (M^+, 25.04), 215 (3.83), 147 (100.00), 127 (4.18), 102 (36.95), 77 (31.07). X-ray crystallographic data: crystal system, momoclinic; space group, $P2_1/n$; unit cell diamensions, a = 5.5629(9) Å, b = 23.988(4) Å, c = 7.3325(13) Å, α = 90°, β = 110.761(3)°, γ = 90°; Z = 4; F(000) = 520; R1 = 0.0478, wR2 = 0.1057.

(b) Attempt To Rearrange *E*-8a to *Z*-8a. A mixture of *E*-**8a** (50 mg) and 2 N hydrochloric acid (5 mL) was stirred under reflux for 6 h; after workup, 42 mg of *E*-**8a** was recovered. ^1H NMR showed no change.

Acknowledgment. We thank the Natural Science Foundation of China for support of this work.

Supporting Information Available: Figures showing ^1H NMR and ^{19}F NMR spectra of **2**, **4a**−**k**, **5**, **6aa**, **9ab**, **6ac**, **6ea**−**ec**, **6ia**−**ic**, **6ja**−**jc**, **7a**−**f**, **8a**,**e**,**f**,**i**−**k**, and **8a′**, HMBC of **8f,** and crystal packing diagrams for **6aa**, **8a**, and **8a′**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO020431V