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COMMUNICATION

$TMSCFX_2$ (X = Cl, Br) as halofluorocarbene sources for the synthesis of halofluorocyclopropanes

Dingben Chen[a,b], Zili Fan[a], Ling Huang[b], Kaili Gao[b], Pan Xiao[a,c], Chuanfa Ni[a] and Jinbo Hu[a,c*]

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$TMSCFX_2$ (X = Cl, Br; TMS = trimethylsilyl) have been developed as halofluorocarbene (:CFX, X = Cl, Br) precursors for [2+1] cyclopropanation with alkenes. Structurally diverse halofluorocyclopropanes were obtained in good to excellent yields. It was found that the reactivity order of three halofluorocarbene reagents ($TMSCF_2Br$, $TMSCFCl_2$, and $TMSCFBr_2$) in the halofluorocyclopropanation with 1,1-diphenylethylene can be very different under different reaction conditions.

Fluorocyclopropanes have found applications in a variety of biologically active molecules and bioisosteres of natural products that were developed over the past decades.[1] The introduction of fluorine atom(s) into constrained three-membered rings could affect the conformation and physicochemical property of the corresponding fluorocyclopropane molecules,[2] thus allowing the discovery of novel bioactive compounds. Some bioactive molecules containing halofluorocyclopropane moieties are shown in Figure 1. Ethyl 2-(4-(2-chloro-2-fluorocyclopropyl)phenoxy)-2-methylpropanoate (**A**) was known as a hypolipemic agent,[3] while other chlorofluoro- or bromofluorocyclopropanes (**B**–**D**) showed insecticidal or acaricidal activity.[4]

Halofluorocarbenes are reactive intermediates for several types of fluorohaloalkylation reactions, among which, the [2+1] cycloaddition reaction between a halofluorocarbene and an alkene has proved to be the most straightforward method to construct halofluorocyclopropanes.[5] Because of the interaction of the electron lone pairs of fluorine with the carbenoid carbon center, halofluorocarbene tends to be a relatively stabilized species with a singlet ground state.[5a] Among all the halofluorocarbenes ($:CF_2$, :CFCl, :CFBr, and :CFI), difluorocarbene ($:CF_2$) has been most widely studied.[5] In recent years, many convenient and efficient $:CF_2$ sources have been developed,[5] including $FSO_2CF_2CO_2R$ (R = $SiMe_3$, Me),[6] $BrCF_2CO_2Na$,[7] $TMSCF_2X$ (X = F, Cl, Br),[8] and $Ph_3P^+CF_2CO_2^-$

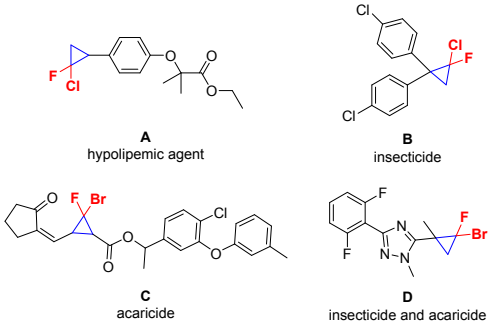


Figure 1 Some bioactive molecules containing halofluoro-cyclopropane moieties.

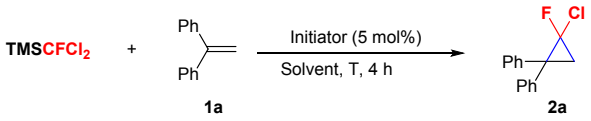
reagents.[9] By contrast, sources of :CFCl and :CFBr are limited,and most of the halofluorocarbene precursors including $CHFX_2$ (X = Cl, Br),[10] CFX_2CO_2R (X = Cl, Br, R = Me, Et),[11] as well as $CFCl_2C(O)CFCl_2$[12] required a strong base (e.g. NaOMe) to generate :CFX. Although some other reagents, such as $CFCl_3$,[13] $PhHgCFX_2$ (X= Cl, Br),[14] and $CFBr_2CO_2Na$,[13] could give access to halofluorocarbenes under base-free conditions, corrosive $TiCl_4$,[13] toxic organomercury reagent,[14] or transition metal catalyst (NHC)AgCl (NHC = *N*-heterocyclic carbene)[15] was needed in the related reaction system. In this context, it is highly desirable to develop new halofluorocarbene reagents which are able to release halofluorocarbenes in a mild and efficient way.

Fluoroalkytrimethylsilanes ($TMSR_f$) are commonly used as nucleophilic fluoroalkylating agents, among which the most well-known example is the Ruppert–Prakash reagent ($TMSCF_3$).[16] $TMSCF_3$ has been widely used for the direct trifluoromethylation of aldehydes, ketones, imines, esters, and amides, among others.[17] Fluoroalkylated organosilanes can also participate in radical reactions via fluoroalkyl radicals.[18] Recently, our group and others reported that fluoroalkylsilanes, such as $TMSCF_2Cl$ and $TMSCF_2Br$, can act as difluorocarbene reagents.[19] These reagents require only mild nucleophiles to achieve C–Si bond cleavage and generate the desired difluorocarbene intermediates. Inspired by the $TMSCF_2X$ reagents, we envisaged that $TMSCFX_2$ (X = Cl, Br) could also act as new halofluorocarbene reagents, in which the silicon center is attacked by a nucleophile to produce CFX_2^-, followed by α- elimination of X^- to give :CFCl or :CFBr species. Herein, we report the [2+1] cycloaddition reactions of

[a] *Key Laboratory of Organofluorine Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032, China. E-mail: jinbohu@sioc.ac.cn.*
[b] *School of Pharmaceutical and Materials Engineering, Taizhou University, Taizhou, Zhejiang, China.*
[c] *School of Physical Science and Technology, ShanghaiTech University, 100 Haike Road, Shanghai 201210, China.*
† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

$TMSCFX_2$ (X= Cl and Br) with alkenes to give halofluorocyclopropanes, and compare

Table 1 Optimization of the reaction conditions using $TMSCFCl_2$ and 1,1-diphenylethylene (**1a**).[a]



1a 2a

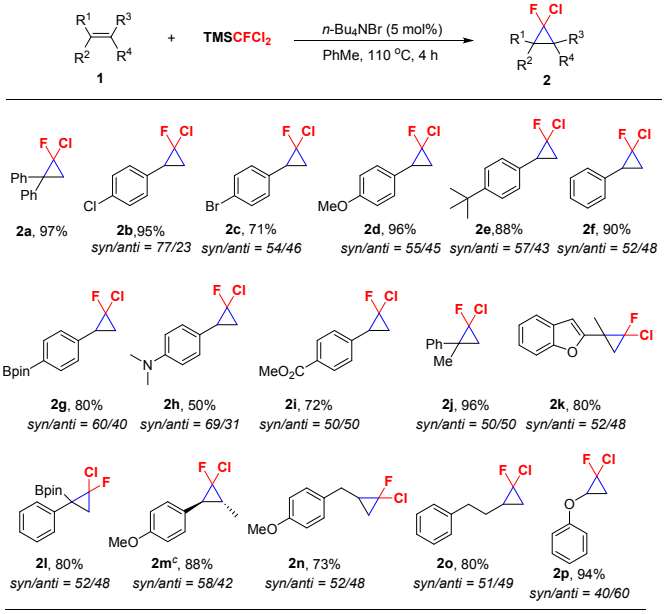
Entry	Solvent	T (°C)	Initiator(5 mol%)	Yield of **2a** (%)[c]
1	THF	110	*n*-Bu_4NBr	0
2	CH_3CN	110	*n*-Bu_4NBr	16
3	DMF	110	*n*-Bu_4NBr	trace
4	toluene	110	*n*-Bu_4NBr	98
5	toluene	110	*n*-Bu_4NCl	>99
6	toluene	110	*n*-Bu_4NF	93
7	toluene	110	Et_3BnNCl	91
8	toluene	110	*n*-$C_{18}H_{37}Me_3NBr$	89
9	toluene	80	*n*-Bu_4NBr	94
10	toluene	rt	*n*-Bu_4NBr	0
11	toluene	110	None	0

[a] $TMSCFCl_2$ (0.3 mmol, 1.5 equiv) and **1a** (0.2 mmol, 1.0 equiv) were used. [b] The amount of initiator was calculated on the basis of the amount of reactant **1a** used. [c] All yields were determined using ^{19}F NMR spectroscopy with $PhCF_3$ as an internal standard.

the reactivity difference among three fluorocarbene reagents ($TMSCF_2Br$, $TMSCFCl_2$, and $TMSCFBr_2$).

Our investigation began with the [2+1] chlorofluorocyclopropanation using fluorodichlorotrimethylsilane ($TMSCFCl_2$) as chlorofluorocarbene source and 1,1-diphenylethylene (**1a**) as model substrate. Reaction parameters including the solvent, initiator, and temperature were carefully screened, and the results are shown in Table 1. When the reaction was carried out in THF at 110 °C in the presence of 5 mol% of *n*-Bu_4NBr (TBAB) in a sealed pressure tube, no product **2a** was formed (Table 1, entry 1). Other polar solvents were also unfavorable to this transformation since very low yield of **2a** was obtained in the presence of CH_3CN or DMF (entries 2-3). The less polar solvent toluene proved to be the optimal solvent which allowed the formation of **2a** in 98% yield (entry 4). In addition to *n*-Bu_4NBr, *n*-Bu_4NCl (TBAC), *n*-Bu_4NF (TBAF), Et_3BnNCl, and *n*-$C_{18}H_{37}Me_3NBr$ were further examined as initiators, and in all cases product **2a** was formed in excellent yield (89–99%; entries 5-8). Decrease of reaction temperature to 80 °C gave a comparable yield, but no reaction occurred at room temperature (entries 9-10). It is worth noting that an initiator was critical for this chemistry because no desired product was formed in the absence of a quaternary ammonium salt (entry 11). Finally, the optimized reaction conditions were obtained as follows: **1a** (1.0 equiv), $TMSCFCl_2$ (1.5 equiv), *n*-Bu_4NBr or *n*-Bu_4NCl (5 mol%), 110 °C, 4 h (entry 4 or 5).

Next, we examined the substrate scope of the present [2+1] cyclopropanation between $TMSCFCl_2$ and various alkenes **1** using standard reaction conditions (as those in Table1, entry 9).[20] As shown in Scheme 1, the reactions with most of the examined substrates **1** provided the corresponding products **2** in good to excellent yields. Most Aryl-substituted alkenes bearing electron-donating or electron-withdrawing groups were able to smoothly proceed in the current chlorofluorocyclopropanation reaction (**2a**–**2g** and **2i**–**2m**)



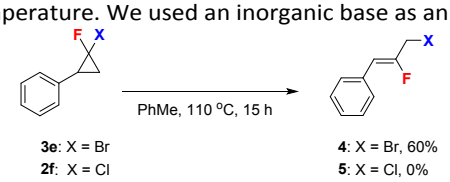
Scheme 1 [2+1] Cycloaddition reaction between $TMSCFCl_2$ and alkenes.[a,b] [a] $TMSCFCl_2$ (0.75 mmol, 1.5 equiv) and **1** (0.5 mmol, 1.0 equiv) were used. [b] Unless otherwise mentioned, isolated yields are given. [c] *E*-1-mehtyl-2-*p*-methoxyphenylethene (**1m**) was used, and the relative *anti*-configuration of the methyl and *p*-methoxyphenyl groups in product **2m** is shown.

except for N,N-dimethyl-4-vinylaniline (**2h**, only in 50% yield). Aryl-substituted alkenes containing Bpin group, reacted with $TMSCFCl_2$ to give **2g** and **2j** in 80% yield (in both cases). The reaction was also amenable to heterocycle-substituted alkene **1l**, and **2l** was formed in 80% yield. Furthermore, alkyl-substituted alkenes (such as **1n** and **1o**) are slightly less reactive than aryl-substituted ones, affording **2n** and **2o** in 73% and 80% yield, respectively. The reaction with (vinyloxy)benzene gave the product **2p** in 94% yield.

Encouraged by the success in chlorofluorocyclopropanation with $TMSCFCl_2$, we further explored the analogous bromofluorocyclopropanation with $TMSCFBr_2$ using 1,1-diphenylethylene (**1a**) as model substrate. After a quick screening of the reaction conditions [see Table S1 in electronic supplementary information (ESI)], we found that under the similar conditions used for $TMSCFCl_2$, a full conversion of alkene **1a** (8 hours) led to the desired product **3a** (2-bromo-2-fluorocyclopropane-1,1-diyl)dibenzene) in only 62% yield (determined by ^{19}F NMR). The ^{19}F NMR spectra of **3a** showed the presence of a by-product. Indeed, we found that when fluorobromocyclopropane **3e** was heated at 110 °C for 15 hours in toluene, it underwent isomerization to give the corresponding ring-opening product **4** in 60% yield (determined by ^{19}F NMR; Scheme 1), which explains part of the reason for the low efficiency of the desired fluorobromocyclopropanation reaction at high temperature (110 °C). Interestingly, we found that the fluorochlorocyclopropane product **2f** did not undergo similar isomerization upon heating at 110 °C (Scheme 2).

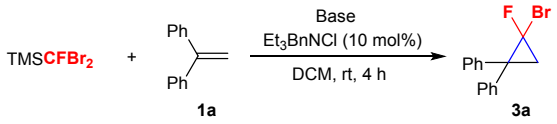
Owing to the undesired thermal isomerization of cyclopropanes upon heating, we further developed other reaction conditions to achieve efficient bromofluoro-

cyclopropanation reactions between $TMSCFBr_2$ and alkenes at room temperature. We used an inorganic base as an activator



Scheme 2 Ring-opening isomerization of the bromofluoro-cyclopropane **3e** upon heating.

Table 2 Optimization of the reaction conditions using $TMSCFBr_2$ and 1,1- diphenylethylene (**1a**) in an aqueous medium.[a]



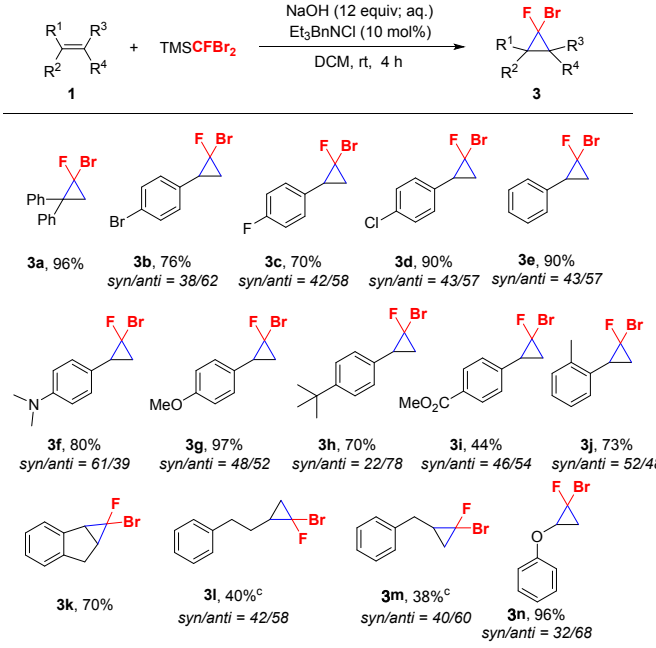
Entry	Base	Equivalents	Yield of **3a** (%)[c]
1	KOH (aq., 20 wt%)	12	66
2	KOH (aq., 50 wt%)	12	85
3	KOH (aq., 50 wt%)	24	75
4	NaOH (aq., 50 wt%)	12	94
5	NaOH (aq., 50 wt%)	24	69
6	NaOH (aq., 50 wt%)	6	85
7	Na_2CO_3 (aq., 20 wt%)	12	trace

[a] $TMSCFBr_2$ (0.50 mmol, 2.0 equiv) and **1a** (0.25 mmol, 1.0 equiv) were used. [b] The amount of base was calculated on the basis of the amount of alkene **1a**. [c] All yields were determined using ^{19}F NMR spectrosopy with $PhCF_3$ as an internal standard. Et_3BnNCl = benzyltriethylammonium chloride (TEBAC).

to optimize the conditions for the reaction between $TMSCFBr_2$ and 1,1-diphenylethylene (**1a**) in dicholoromethane (DCM)/water in the presence of phase-transfer catalyst Et_3BnNCl (Table 3). When 12 equivalents of KOH (aq., 20 wt%) was added dropwise to the reaction mixture, product **3a** was formed in 66% yield (Table 2, entry 1). By increasing the concentration of the KOH aqueous solution to 50 wt%, the yield of **3a** was increased to 85% (entry 2). However, 24 equivalents of KOH (aq., 50 wt%) did not improve the yield of **3a** (entry 3). The optimal yield (94%) of **3a** was obtained when 12 equivalents of NaOH (aq., 50 wt%) was used as an activator (entry 4). In contrast, the addition of weaker base Na_2CO_3 was ineffective to this reaction (entry 7).

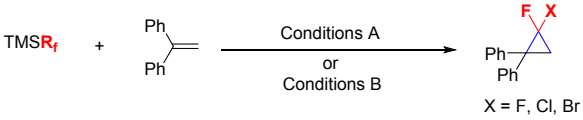
With the optimized reaction conditions in hand (Table 2, entry 4), we investigated the substrate scope of the bromofluorocyclopropanation reaction between $TMSCFBr_2$ and alkenes.[20] As shown in Scheme 3, most of the alkenes that we examined were able to undergo bromofluorocyclopropanation to provide the corresponding products in high yields. Aryl- substituted olefins bearing either electron-donating or electron-withdrawing groups were amenable to the reaction. In particular, some compounds, such as **3f** and **3k**, which were only formed in low yields using 5% TBAB in PhMe at 110 °C (as the conditions used in Scheme 1), could be obtained in good yields (85% and 70%, respectively) under the present NaOH-mediated conditions. The reaction with vinyl ether **1n** gave the product **3n** in 96% yield. However, we found that the reactions with alkyl-substituted alkenes gave the corresponding products in moderate yields (such as **3l** and **3m**), although the reaction time was prolonged to 12 h. It is worthy to note that product 3a could be readily debrominated to give 1-fluoro-2,2-diphenylcyclopropane in 75% yield (see S8 in ESI).

Subsequently, we conducted a comparative study on the reactivity of the different halofluorochlorocarbene reagents ($TMSCF_2Br$, $TMSCFCl_2$, and $TMSCFBr_2$) developed by our group. As shown in Table 3, under non-aqueous conditions A [TBAB (5 mol%), PhMe as solvent, 110 °C, 4 h], both the conversion of alkene and product yield increased in the following order: $TMSCF_2Br$ > $TMSCFCl_2$ > $TMSCFBr_2$. However, under the DCM/water biphasic conditions [NaOH (aqueous solution, 12 equiv), Et_3BnNCl (10 mol%), dichloromethane as solvent, rt, 4 h], the conversion of alkene and product yield increased in the following order: $TMSCF_2Br$ < $TMSCFCl_2$ < $TMSCFBr_2$. The different reactivity order of three halofluorocarbene reagents ($TMSCF_2Br$, $TMSCFCl_2$, and $TMSCFBr_2$) in the halofluorocyclopropanation with 1,1-diphenylethylene is mainly due to the different reaction mechanisms in the non-aqueous and aqueous medium (see S4-S5 In ESI).[22]



Scheme 3 [2+1] Cycloaddition reactions between $TMSCFBr_2$ and alkenes.[a,b] [a] $TMSCFBr_2$ (0.50 mmol, 2.0 equiv), **1** (0.25 mmol, 1.0 equiv) and NaOH (12 equiv; as 50 wt% aqueous solution) were used. [b] Isolated yields. [c] The reaction time was 12 h.

Table 3 The comparison of the reactions using different halofluoro-carbene reagents and 1,1-diphenylethylene.

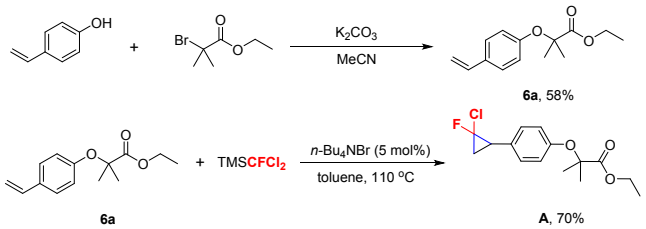


$TMSR_f$	Conditions A[a]		Conditions B[b]	
	Conversion[c]	Yield[d]	Conversion[c]	Yield[d]
$TMSCF_2Br$	100%	98%	0%	0%
$TMSCFCl_2$	95%	90%	90%	85%
$TMSCFBr_2$	70%	65%	100%	94%

[a]Conditions A: *n*-Bu_4NBr (5 mol%); toluene as solvent; 110 °C; 4 h. [b]Conditions B: NaOH (12 equiv; as 50 wt% aqueous solution); Et_3BnNCl (10 mol%); DCM as solvent; rt; 4 h. [c] Conversion of alkene was determined by ^1H NMR spectroscopy

analysis of the crude product using 1,3,5-triisopropylbenzene as an internal standard. [d]Yield of product was determined by ^{19}F NMR using $PhCF_3$ as an internal standard.

To demonstrate the synthetic application of the present haloflorocyclopropanation, we used $TMSCFCl_2$ to synthesize a compound **A** that was used as a hypolipemic agent[3] (Scheme 4). Vinyl phenol reacted with ethyl 2-bromo-2-methylpropionate to give ethyl 2-methyl-2-(4-vinylphenoxy) propanoate (**6a**). Intermediate **6a** was then treated with $TMSCFCl_2$ to give **A** in 70% yield.



Scheme 4 Synthesis of chlorofluorocyclopropane **A** used as a hypolipemic agent.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (a) K. L. Kirk, S. Yoshida and G. Haufe, in Fluorine and Health: Molecular Imaging, Biomedical Materials and Pharmaceuticals, ed. A. Tressaud and G. Haufe, Elsevier, Amsterdam, 2008, ch. 15, pp. 661–697; (b) E. David, G. Milanole, P. Ivashkin, S. Couve-Bonnaire, P. Jubault and X. Pannecoucke, *Chem. Eur. J.,* 2012, **18**, 14904; (c) A. Pons, T. Poisson, X. Pannecoucke, A. B. Charette and P. Jubault, *Synthesis,* 2016, **48**, 4060.

2 (a) H. Lebel, J. F. Marcoux, C. Molinaro and A. B. Charette, *Chem. Rev.,* 2003, **103**, 977; (b) H. Pelissier, *Tetrahedron*, 2008, **64**, 7041; (c) G. Bartoli, G. Bencivenni and R. Dalpozzo, *Synthesis*, 2014, **46**, 979.

3 D. K. Phillips, *Fr. Pat.*, FR2197586A1, 1974.

4 (a) P. A. Worthington, I. R. Matthews, D. Bartholomew, P. J. Crowley, D. R. Baker and K. J. Fisher, *Eur. Pat.*, EP436348A2, 1991; (b) G. Holan, *Nature*, 1969, **221**, 1025; (c) F. E. Tisdell, J. T. Pechacek, J. R. J. Schoonover, P. V. Ripa, L. P. Dintenfass, J. M. Gifford, T. P. Martin, M. Yap, D. H. Devries and M. L. Ash, *PCT Pat.*, WO2000024720A1, 2000; (d) K. T. Koho, *Jpn. Pat.*, JP58079909 A, 1983.

5 (a) R. A. Moss, *Acc. Chem. Res.* 1980, **13**, 58; (b) D. L. S. Brahms and W. P. Dailey, *Chem. Rev.*, 1996, **96**, 1585; (c) C. Ni and J. Hu, *Synthesis*, 2014, **46**, 842; (c) A. D. Dilman and V. V. Levin, *Acc. Chem. Res.*, 2018, **51**, 1272; (d) K. Fuchibe, R. Takayama, T. Aono, J. Hu, T. Hidano, H. Sasagawa, M. Fujiwara, S. Miyazaki, R. Nadano, J. Ichikawa, *Synthesis*, 2018, **50**, 514; (e) W. Zhang and Y. Wang, *Tetrahedron Lett.*, 2018, **59**, 1301; (f) M. Fedorynski, Chem. Rev. 2003, **103**, 1099; (h) W. Zhang and Y. Wang, Tetrahedron Lett., 2018, **59**, 1301; (g) Ref 10(b).

6 (a) S. Eusterwiemann, H. Martinez and W. R. Dolbier, Jr., *J. Org. Chem.,* 2012, **77**, 5461; (b) F. Tian, V. Kruger, O. Bautista, J. X. Duan, A. R. Li, W. R. Dolbier, Jr. and Q. Y. Chen, *Org. Lett.,* 2000, **2**, 563.

7 K. Oshiro, Y. Morimoto and H. Amii, *Synthesis*, 2010, 2080.

8 (a) F. Wang, W. Zhang, J. Zhu, H. Li, K. W. Huang and J. Hu, *Chem. Commun.*, 2011, **47**, 2411; (b F. Wang, T. Luo, J. Hu, Y. Wang, H. S. Krishnan, P. V. Jog, S. K. Ganesh, G. K. S. Prakash and G. A. Olah, *Angew. Chem. Int. Ed.,* 2011, **50**, 7153; (c) L. Li, F. Wang, C. Ni and J. Hu, *Angew. Chem. Int. Ed.*, 2013, **52**, 12390.

9 J. Zheng, J. H. Lin, J. Cai and J. C. Xiao, *Chem. Eur. J.,* 2013, **19**, 15261.

10 (a) T. Taguchi and M. Okada, *J. Fluorine Chem.,* 2000, **105**, 279; (b) W. R. Dolbier, Jr. and M. A. Battiste, *Chem. Rev.,* 2003, **103**, 1071; (c) M. Fedorynski, *Chem. Rev.,* 2003, **103**, 1099; (d) A. P. Thankachan, K. S. Sindhu, K. K. Krishnan and G. Anilkumar, *Org. Biomol. Chem.,* 2015, 13, 8780; (e) R. R. Kostikov, A. P. Molchanov and H. Hopf, *Top. Curr. Chem.,* 1990, **155**, 42; (f) A. P. Molchanov and R. R. Kostikov, *Zh. Org. Khim.,* 1993, **29**, 510; (g) N. V. Volchkov, M. A. Novikov, M. B. Lipkind and O. M. Nefedov, *Mendeleev Commun.*, 2013, **23**, 19; (h) M. A. Novikov, N.V. Volchkov, M. B. Lipkind and O. M. Nefedov, *J. Fluorine Chem.,* 2015, **180**, 131; (i) O. B. Bondarenko, A. A. Vinogradov, A. I. Komarov, A. S. Smirnov and N. V. Zyk, *J. Fluorine Chem.,* 2016, **185**, 201; (j) K. N. Sedenkova, E. B. Averina, Y. K. Grishin, A.G. Kutateladze, V. B. Rybakov, T. S. Kuznetsova and N. S. Zefirov, *J. Org. Chem.,* 2012, **77**, 9893.

11 (a) C. Aouf, and M. Santelli, *Tetrahedron Lett.,* 2011, **52**, 688; (b) T. Ando, T. Ishihara, E. Ohtani and H. Sawada, *J. Org. Chem.,* 1981, **46**, 4446; (c) T. Ando, H. Hosaka, H. Yamanaka and W. Funasaka, *Bull. Chem. Soc. Jpn.,* 1969, **42**, 2013.

12 L. Ghosez, G. Slinckx, M. Glineur, P. Hoet and P. Laroche, *Tetrahedron Lett.,* 1967, **8**, 2773.

13 W. R. Dolbier, Jr. and C. R. Burkholder, *J. Org. Chem.,* 1990, **55**, 589.

14 (a) D. Seyferth and K. V. Darragh, *J. Org. Chem.*, 1970, **35**, 1297; (b) D. Seyferth and S. P. Hopper, *J. Organomet. Chem.,* 1973, **51**, 77.

15 A. A. Andrianova, Y. D. Maslova, M. A. Novikov, S. E. Semenov and O. M. Nefedov, *J. Fluorine Chem.*, 2018, **209**, 49.

16 G. K. S. Prakash and A. K. Yudin, *Chem. Rev.,* 1997**, 97**, 757.

17 X. Liu, C. Xu, M. Wang and Q. Liu, *Chem. Rev.,* 2015**, 115**, 683.

18 (a) S.-Q. Zhu, X.-H. Xu and F.-L. Qing, *Org. Chem. Front.*, 2015, **2**, 1022; (b) S.-Q. Zhu, X.-H. Xu and F.-L. Qing, *Chem. Commun.*, 2017, **53**, 11484; (c) G. Ma, W. Wan, J. Li, Q. Hu, H. Jiang, S. Zhu, J. Wang and J. Hao, *Chem. Commun.*, 2014, **50**, 9749; (d) Y.-b. Wu, G.-p. Lu, T. Yuan, Z.-b. Xu, L. Wan and C. Cai, *Chem. Commun.*, 2016, **52**, 13668; (e) Q. Chen, J. Zhou, Y. Wang, C. Wang, X. Liu, Z. Xu, L. Lin and R. Wang, *Org. Lett.*, 2015, **17**, 4212; (f) Y.-F. Wang, G. H. Lonca and S. Chiba, *Angew. Chem. Int. Ed.*, 2014, **53**, 1067.

19 (1) F. Wang, W. Zhang, J. Zhu, H. Li, K.-W. Huang and J. Hu, *Chem. Commun.*, 2011, **47**, 2411; (2) F. Wang, L. Li, C. Ni and J. Hu, *Beilstein J. Org. Chem.*, 2014, **10**, 344; (3) F. Wang, T. Luo, J. Hu, Y. Wang, H. S. Krishnan, P. V. Jog, S. K. Ganesh, G. K. S. Prakash, G. A. Olah, Angew. Chem. Int. Ed. 2011, 50, 7153; (4) L. Li, F. Wang, C. Ni and J. Hu, , *Angew. Chem. Int. Ed.*, 2013, **52**, 12390; (5) Q. Xie, C. Ni, R. Zhang, L. Li, J. Rong and J. Hu, , *Angew. Chem. Int. Ed.*, 2017, **56**, 3206.

20 For the proposed reaction mechanism of halofluorocyclopropanation with $TMSCFCl_2$ and $TMSCFBr_2$, see Scheme S1 and S2 in electronic supplementary information (ESI).

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Graphical Abstract

The [2+1] cycloaddition reactions of novel halofluorocarbene reagents [Me_3SiCFX_2 (X = Cl, Br)] with alkenes have been disclosed.