Synthesis of Difluoroalkenes from Thiocarbonyl Compounds via Difluorothiiranes: Electrophilic Counterpart to Wittig-Type Difluoromethylidenation

Kohei Fuchibe,[1] Atsushi Yamada,[1] Kosei Hachinohe,[1] Kana Matsumoto,[1] Ryo Takayama,[1] and Junji Ichikawa*[1]

[1] Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571 (Japan)

E-mail: junji@chem.tsukuba.ac.jp

Kohei Fuchibe

Kohei Fuchibe was born in Fukui, Japan in 1974. He received his B.Sc. in 1999 and Ph.D. in 2002 from the University of Tokyo (Prof. K. Narasaka). He joined Gakushuin University as a Research Associate in 2002 and was shifted to an Assistant Professor in 2007. He moved to University of Tsukuba as a Lecturer in 2007 and was promoted to an Associate Professor in 2011. His research interests involve synthetic reactions catalyzed by transition metals or organic small molecules.

Junji Ichikawa

Junji Ichikawa was born in Tokyo, Japan in 1958. He received his B.Sc. in 1981 and Ph.D. in 1986 from the University of Tokyo (Prof. T. Mukaiyama). He joined Kyushu University as an Assistant Professor in 1985. In 1989, he was a research associate at Harvard University (Prof. E. J. Corey) and then worked at Kyushu Institute of Technology as a Lecturer and an Associate Professor. In 1999, he moved to the University of Tokyo as an Associate Professor. He was appointed Professor at University of Tsukuba in 2007. His research interests lie in the area of synthetic methodology based on the properties of metals and fluorine.

Abstract

The synthesis of 1,1-difluoro-1-alkenes was achieved by the treatment of dithioesters and thioketones with trimethylsilyl 2-fluorosulfonyl-2,2-difluoroacetate in the presence of a proton sponge catalyst, namely, 1,8-bis(dimethylamino)naphthalene. The generated electrophilic difluorocarbene (:CF_2) reacted with the thiocarbonyl functionalities to form 2,2-difluorothiirane intermediates, desulfurization of which afforded the products in a Barton–Kellogg-type difluoromethylidenation. The reaction described herein is an electrophilic counterpart to the Wittig-type (nucleophilic) difluoroalkene synthesis starting from carbonyl compounds. The electrophilic difluoromethylidenation facilitated the synthesis of sulfanylated and diarylated 1,1-difluoroalkenes, including sterically hindered ones, which are inaccessible by nucleophilic difluoromethylidenation.

Keywords: Carbene, Fluorine, Thiirane

1. Introduction

The utility of 1,1-difluoro-1-alkenes has been increasingly recognized in various fields. For instance, due to their characteristics,[1] such as small atom size and high electronegativity, fluorine substituents can alter and enhance the biological activities of the parent molecules.[2] Thus, the potential of fluoroalkenes including 1,1-difluoroalkenes and monofluoroalkenes as high performance pharmaceuticals and agrochemicals has been extensively investigated.[3,4] Recently, the utility of 1,1-difluoroalkenes as synthetic intermediates has attracted particular attention.[5] At present, the synthesis of monofluoroalkenes[6] typically involves nucleophilic vinylic substitution (S_NV) reactions of 1,1-difluoroalkenes.[5a,7,8] Moreover, the α-cation-stabilizing effect of fluorine substituents[1] has been shown to facilitate cationic cyclizations of 1,1-difluoroalkenes, leading to the synthesis of pinpoint-fluorinated polycyclic aromatic hydrocarbons (PAHs),[9] fluorine-free PAHs,[10] and fluorinated hetero-PAHs.[11] 1,1-Difluoroalkenes have also been widely used as acceptors in reactions of organometallics[5d,f] and radicals.[5e,12]

Among 1,1-difluoro-1-alkenes, we were particularly interested in sulfanylated and diarylated difluoroalkenes (Figure 1). Sulfanylated difluoroalkenes act as intermediates for the synthesis of (2,2-difluorovinyl)stannanes, which afford diarylated 1,1-difluoroethenes via a cross-coupling reaction (Scheme 1, top).[13] Furthermore, diaryldifluoroethenes bearing biaryl moieties readily produce dibenzo[*g*,*p*]chrysenes through cationic domino cyclization (bottom).[14] In addition to their synthetic applications, diarylated 1,1-difluoroethene scaffolds can be found in the structures of various therapeutics or drug

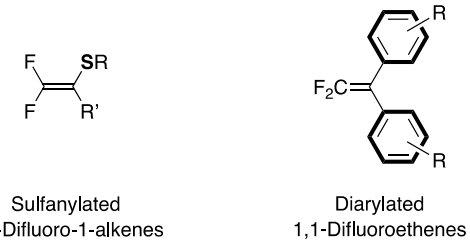
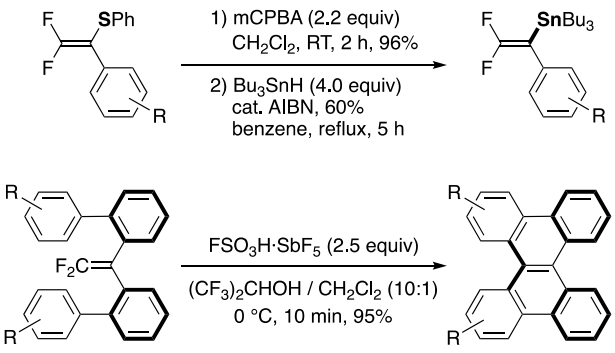


Figure 1. Sulfanylated and diarylated 1,1-difluoro-1-alkenes.



Scheme 1. 1,1-Difluoro-1-alkenes as synthetic intermediates.l

candidates, such as antitubulin agents (*e.g.*, phenstatin analogues)[15] and ligands for the retinoic acid receptor (RAR),[16] as well as functional materials, including photoreceptors (Figure 2).[17] However, despite their utilities, the synthetic methods for the preparation of sulfanylated and diarylated 1,1-difluoroalkenes require further development.

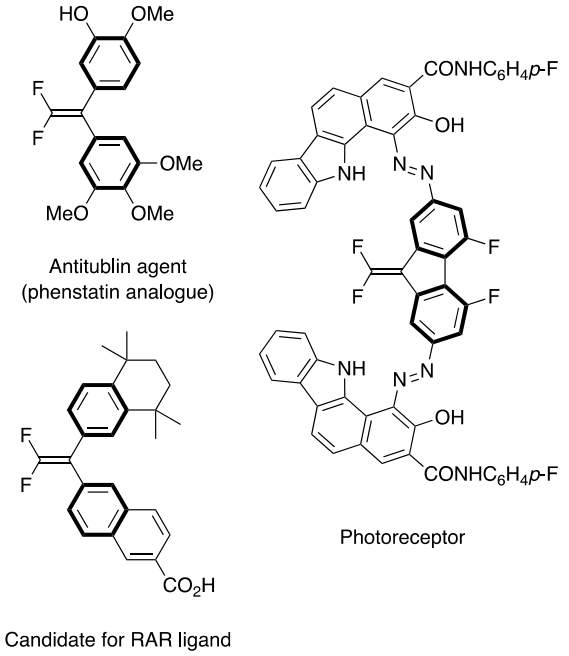
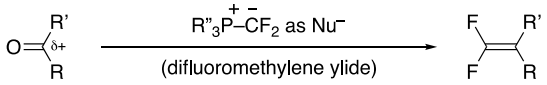


Figure 2. Examples of diarylated 1,1-difluoroethene scaffolds.

One of the most frequently employed approaches for the synthesis of 1,1-difluoroalkenes is the Wittig-type difluoromethylidenation, which involves treatment of carbonyl compounds with difluoromethylene ylides typically generated from $CClF_2CO_2Na/PPh_3$ or $CBr_2CF_2/P(NMe_2)_3$ (Scheme 2).[18] Although commonly used for the preparation of monosubstituted 1,1-difluoroalkenes from aldehydes (R′ = H), the Wittig-type synthesis is hardly applicable for the production of sulfanylated and diarylated 1,1-difluoroalkenes.



Scheme 2. The Wittig-type difluoroalkene synthesis (nucleophilic approach).

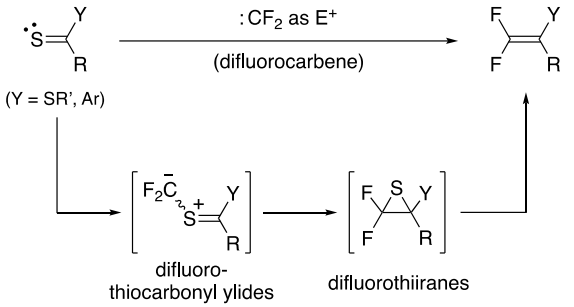
Because the reaction proceeds via a nucleophilic attack of the ylide onto the carbonyl carbon atom, its efficiency is significantly affected by the electronic and steric nature of the substituents on the carbonyl moiety. Hence, nucleophilic difluoromethylidenation is rarely applied in the case of less electrophilic carbonyl compounds, such as thioesters (R′ = S–alkyl/S–aryl, Scheme 2), to produce sulfanylated 1,1-difluoroalkenes.[19] To address the issue of the moderate reactivity toward ketones, Horner–Wadsworth–Emmons (HWE)[20] and Julia-type difluoromethylidenation[21] reactions have been developed. Nevertheless, there have been no successful reports on the synthesis of sterically hindered diaryldifluoroethenes using these nucleophilic methods.[22]

In this work, we report the synthesis of sulfanylated and diarylated 1,1-difluoroalkenes by difluorothiirane-mediated difluoromethylidenation (*i.e.*, Barton–Kellogg-type difluoromethylidenation) of thiocarbonyl compounds. The described reaction is an electrophilic counterpart to the Wittig-type difluoromethylidenation and addresses the challenges associated with poor substrate reactivity. Theoretical investigation on enhanced reactivity of the difluorothiirane intermediates is also described.

2. Results and Discussion

Strategy. Generally, the Barton–Kellogg reaction[23] is a powerful tool for the synthesis of substituted alkenes. Thiirane intermediates[24] are typically prepared from carbonyl compounds in the presence of hydrazine, hydrogen sulfide, and Pb(IV) or from thiocarbonyl and diazo group-containing compounds. Reductive treatment of the resulting thiiranes with phosphines affords the corresponding alkenes and phosphine sulfides. Notably, due to its applicability to sterically hindered systems, the Barton–Kellogg reaction has been utilized for the construction of alkene moieties, *e.g.*, tetrasubstituted alkenes, in natural products[25] and molecular machines.[26]

Because nucleophilic difluoromethylidenation suffers from the electron-donating property and steric hindrance of the substituents on the carbonyl group, in the present study, we adopted a strategy involving thiirane-based electrophilic difluoromethylidenation of dithioesters and thioketones using difluorocarbene (*i.e.*, Barton–Kellogg-type difluoromethylidenation, Scheme 3). We speculated that treatment of the substrates with difluorocarbene would afford the key difluorothiirane intermediates. Subsequently, desulfurization reaction would yield the desired sulfanylated and diarylated 1,1-difluoroalkenes. We envisioned that the Barton–Kellogg-type difluoromethylidenation would be advantageous because dithioesters are more electron-rich than ketones; therefore, they would react readily with electrophilic difluorocarbene. Moreover, the formation of thiirane begins with the attack of difluorocarbene onto a sulfur atom (vide infra), not a carbonyl carbon atom; thus, the reaction would be less sensitive to steric hinderance of the substituents on the thiocarbonyl moieties.

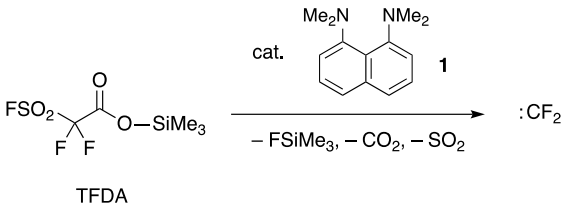


Scheme 3. Barton–Kellogg-type difluoroalkene synthesis (electrophilic approach used in this study).

To the best of our knowledge, Barton–Kellogg-type difluoromethylidenation of dithioesters has never been reported. Mloston described that thioketones, specifically diphenyl thioketone and di(*p*-methoxyphenyl) thioketone, reacted with difluorocarbene generated from $PhHgCF_3$ and NaI to form the corresponding difluorothiiranes, which underwent facile desulfurization in the absence of phosphines to afford the corresponding diarylated 1,1-difluoroethenes.[27] However, the utility of difluorothiiranes as synthetic intermediates has not been fully revealed.

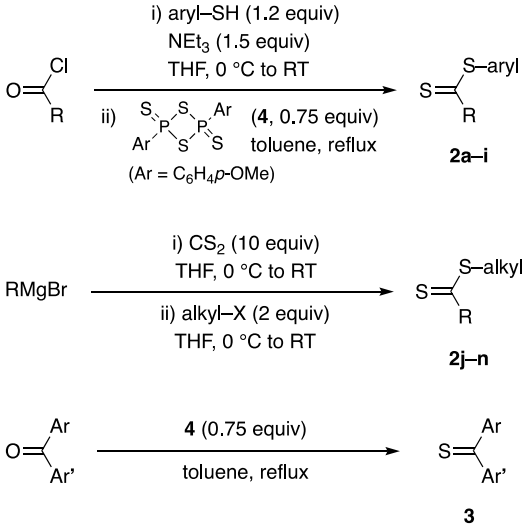
A significant issue associated with the Barton–Kellogg-type difluoromethylidenation is the generation of

difluorocarbene. The species has been extensively described in the literature;[28] however, vigorous reaction conditions required for the formation of difluorocarbene are known to cause undesired side reactions, overreactions, and carbene dimerization. We recently reported facile generation of difluorocarbene using organocatalysts.[29] It was found that treatment of trimethylsilyl 2-fluorosulfonyl-2,2-difluoroacetate (TFDA)[30] with proton sponge, namely, 1,8-bis(dimethylamino)naphthalene (**1**) (Scheme 4), or *N*-heterocyclic carbenes (NHCs) resulted in the fragmentation of the compound at temperatures as low as 60 °C to produce difluorocarbene. Hence, we expected that the organocatalytic generation of difluorocarbene would facilitate the synthesis of sulfanylated and diarylated 1,1-difluoroalkenes under nontoxic and mild conditions.



Scheme 4. Proton sponge-catalyzed generation of difluorocarbene.

Preparation of dithioesters and thioketones. The substrates, *i.e.*, dithioesters **2** and thioketones **3**, were prepared as follows. Aryl dithioates **2a**–**i** were synthesized by sulfurization of *S*-aryl thiocarboxylates, prepared from acid chlorides and thiophenols, with 2,4-di(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (**4**, Lawesson's reagent, Scheme 5, top). Alkyl dithiocarboxylates **2j**–**n** were obtained by alkylation of dithiocarboxylate ions generated from Grignard reagents and carbon disulfide (middle). Dithioesters were stable under air at ambient temperature and could be purified by silica gel column chromatography. Thioketones **3** were synthesized by the treatment of the corresponding ketones with **4** (bottom) and were purified by silica gel column chromatography at −10 °C to prevent hydrolysis.



Scheme 5. Preparation of thiocarbonyl compounds.

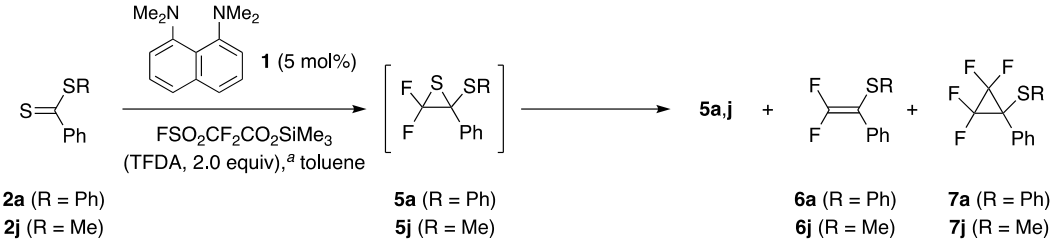
Electrophilic difluoromethylidenation of dithioesters. As reported in our preliminary communication,[31] we attempted the electrophilic difluoromethylidenation of dithioesters using phenyl (**2a**) and methyl (**2j**) benzenedithioates as model substrates (Table 1).[31] Phenyl dithioate **2a** was treated with TFDA (2.0 equiv over 5 min) in toluene in the presence of 5 mol% of proton sponge (**1**) at 40 °C (Table 1, Entry 1). Visible gas evolution was observed, indicating the decomposition of TFDA. The expected thiirane intermediate **5a** was generated, albeit in a low yield of 7% (determined by ^{19}F NMR analysis). According to the thin layer chromatography (TLC) analysis, a considerable amount of dithioate **2a** remained unreacted. Pleasingly, performing the reaction at 60 °C led to complete conversion of **2a**, affording **5a** and the desired difluoroalkene **6a** in 40% and 46% yields, respectively (Entry 2). In contrast, when **2a** was treated with TFDA at room temperature and then warmed to 60 °C, **5a** was obtained in just a 6% yield. On the basis of the TLC analysis, **2a** was recovered in spite of substantial consumption of TFDA. It was speculated that at temperatures below 60 °C, the dimerization of difluorocarbene might proceed more readily than the formation of thiirane. Thus, upon raising the temperature to 60 °C, difluorocarbene was not available for the desired reaction.

As summarized in Table 1, reactions at higher temperatures (*e.g.*, at 90 °C, Entry 3, or reflux, Entry 4) resulted in complete conversion of **5a** to **6a** in 84% or 90% yields, along with the formation of the undesired difluorocyclopropanation product **7a** in 2% or 5% yields. To prevent the overreaction to **7a**, **2a** was treated with TFDA at 60 °C for 30 min before increasing the reaction temperature. After confirming that **2a** was completely consumed by TLC analysis and that difluorocarbene generation reached completion by monitoring gas evolution, the reaction mixture comprising **5a** and **6a** was heated at 100 °C for 30 min. Consequently, sulfanylated difluoroalkene **6a** was isolated in an 87% yield without accompanying **7a** (Entry 5, Method A).

We hypothesized that electron-donating *methyl* dithioate **2j** was more reactive than *phenyl* dithioate **2a** due to the electron-deficient nature of difluorocarbene. Unexpectedly, **2j** was found to be less reactive. Specifically, as shown in Entry 6, the reaction of **2j** at 60 °C led to the formation of thiirane in a lower yield of 46% (**5j** + **6j**) compared with 86% (**5a** + **6a**) in the case of Entry 2. Thiocarbonyl compounds react with carbenes to form the corresponding thiocarbonyl ylides,[24b,32] whose electrocyclic ring closure[33] affords thiiranes. The observed reactivity difference between **2a** and **2j** was rationalized by the assumption that the electrocyclization was rate-determining and retained nucleophilic character. Thus, the cyclization was retarded by the electron-donating property of the methylsulfanyl group (**2j**). When the reaction was performed at reflux (Entry 7), thiirane was obtained in an increased 81% yield (**6j** + **7j**), along with the undesired cyclopropane **7j** (14% yield). To reduce the contact time between difluoroalkene **6j** and difluorocarbene, the addition of TFDA was completed within 1 min, which improved the yield of **6j** up to 82% (Entry 8, Method B).

It is noteworthy that dithioester-derived difluorothiirane **5a** was isolated by silica gel column chromatography. To the best of our knowledge, the preparation of just nine 2,2-difluorothiiranes (**8**,[34] **9**,[35] **10**,[27] and **11**[27]) has been previously described (Figure 3). The reported products were derived from thioaldehydes or thioketones, and spectroscopic characterization was only conducted for 2,2-difluorothiiranes **10**. In our preliminary communication,[31] the structure of the sulfanylated, *dithioester*-derived thiirane **5a** was firstly characterized by spectroscopic methods (^{1}H, ^{13}C, and ^{19}F NMR; and IR). Difluorothiirane **5a** showed characteristic ^{13}C and ^{19}F NMR signals that are similar to those of **10** in the literature,[27] whereas the HRMS of **5a** did not give a parent peak because of the rapid desulfurization under ionization conditions.

Table 1. Optimization of reaction conditions.[a)]



2a (R = Ph)
2j (R = Me)

5a (R = Ph)
5j (R = Me)

6a (R = Ph)
6j (R = Me)

7a (R = Ph)
7j (R = Me)

Entry	**2**	R	Conditions	**5** (%)[b,c]	**6** (%)[b,c)]	**7** (%)[b,c)]
1	**2a**	Ph	40 °C, 0.5 h	7, **5a**	trace, **6a**	– , **7a**
2	**2a**	Ph	60 °C, 0.5 h	40, **5a**	46 , **6a**	– , **7a**
3	**2a**	Ph	90 °C, 0.5 h	2, **5a**	84, **6a**	2, **7a**
4	**2a**	Ph	reflux, 0.5 h	–, **5a**	90, **6a**	5, **7a**
5[d)]	**2a**	Ph	60 °C, 0.5 h, then 100 °C, 0.5 h	–, **5a**	90 (87),[e)] **6a**	– , **7a**
6	**2j**	Me	60 °C, 0.5 h	5, **5j**	41, **6j**	trace, **7j**
7	**2j**	Me	reflux, 0.5 h	–, **5j**	67, **6j**	14, **7j**
8[f,g)]	**2j**	Me	reflux, 0.5 h	–, **5j**	82, **6j**	6 , **7j**

a) Unless otherwise noted, TFDA was added over 5 min. b) ^{19}F NMR yield based on the internal $(CF_3)_2C(C_6H_4p\text{-}Me)_2$ standard. c) – : Not detected by ^{19}F NMR analysis. d) Method A. e) Isolated yield is indicated in parentheses. f) TFDA was added over 1 min. g) Method B.

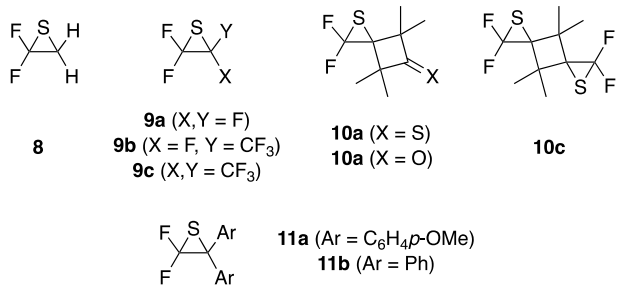


Figure 3. Previously reported 2,2-difluorothiiranes.

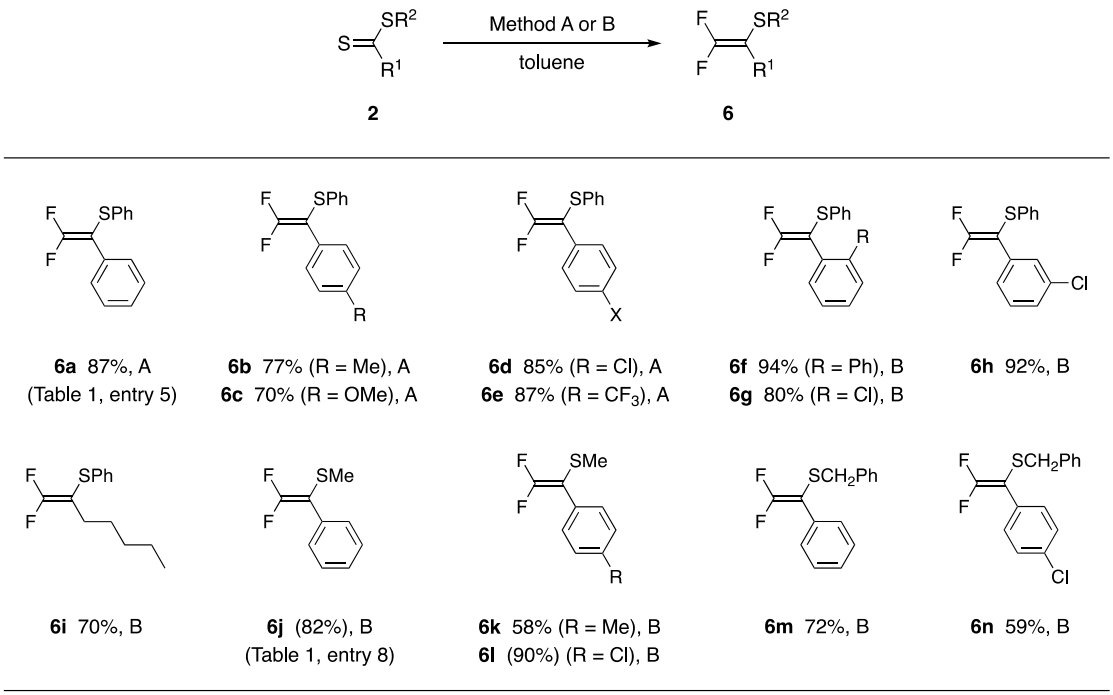
Furthermore, we synthesized various sulfanylated 1,1-difluoro-1-alkenes **6** by electrophilic difluoromethylidenation of dithioesters (Figure 4).[31] Phenyl arenedithioates **2a**–**e** underwent difluoromethylidenation by Method A to give the corresponding products **6a**–**e** in 70–87% yields. Sterically demanding thiiranes **2f**,**g** were treated according to Method B to provide the corresponding **6f**,**g** in 94% and 80% yields, respectively. Dithioate **2h** containing a *meta*-chloro-substituted phenyl group, also afforded the corresponding product **6h** by Method B in a 92% yield. Using the same approach, phenyl alkanedithioate **2i** and alkyl arenedithioates **2j**–**n** gave products **6i** and **6j**–**n** in 58–90% yields.

On the basis of these results, it was concluded that for relatively electron-deficient (*i.e.*, *S*-arylated) and sterically less demanding dithioates (**2a**–**e**), Method A worked well because of the high reactivity of the compounds. In contrast, electron-rich (*i.e.*, *S*-alkylated, **2j**–**n**) or sterically demanding (**2f**,**g**) dithioates were less reactive; therefore, Method B was more suitable.

Over the last decade, the difluoromethyl moiety (CHF_2) has attracted considerable interest[36] not only as a nonnucleophilic proton donor for hydrogen bonding[37] but also as a functional group for increasing the lipophilicity of compounds[38] used for the preparation of pharmaceuticals and agrochemicals. Among the CHF_2-containing compounds, difluoromethyl sulfides are particularly promising.[39] We found that difluorocarbene generated from TFDA in the presence of **1** readily promoted difluoromethylation of dithiocarboxylic acid **12** to afford difluoromethyl dithioate **2o** in a 71% yield (Scheme 6).[40] Upon treatment with additional TFDA (2.0 equiv.), dithioate **2o** underwent difluoromethylidenation in a one-pot operation, producing difluoromethyl difluorovinyl sulfide **6o** in a 65% yield from **12**. This is the first example of the difluoromethylation of dithiocarboxylic acids.[41]

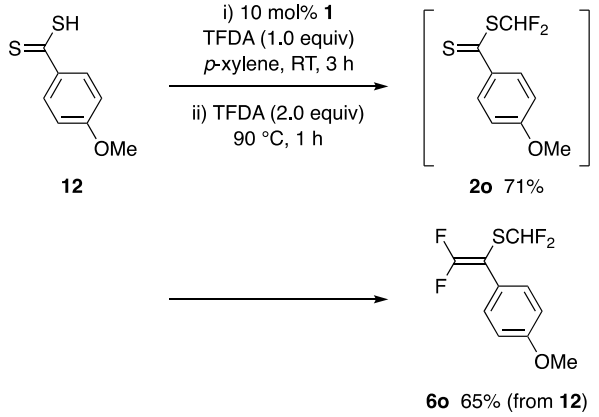
Sodium chlorodifluoroacetate and bromodifluoroacetate were also examined as difluorocarbene sources (Scheme 7).[31] Notably, dithioate **2j** underwent difluoromethylidenation with these sodium salts at 160 °C to give difluoroalkene **6j** in moderate 41% ($ClCF_2CO_2Na$) and 31% ($BrCF_2CO_2Na$) yields, along with 48% ($ClCF_2CO_2Na$) and 57% ($BrCF_2CO_2Na$) recovery of **2j**. It was speculated that the high temperature (160 °C) required for the generation of difluorocarbene caused unfavorable dimerization of difluorocarbene, leading to the recovery of the substrate. Hence, the formation of difluorocarbene from TFDA by an organocatalyst proved to be more effective for the synthesis of sulfanylated 1,1-difluoroalkenes than the classical :CF_2 generations with sodium halodifluoroacetates.

Electrophilic Barton–Kellogg-type difluoromethylidenation is complementary to the nucleophilic Wittig-type difluoromethylidenation as confirmed by Scheme 8.[31]. Although the nucleophilic difluoromethylidenation failed to produce the sulfanylated difluoroalkene **6a** from dithioate **2a** (0% yield, Scheme 8B), the electrophilic method afforded **6a** in an 87% yield (A).[42] Conversely, electrophilic difluoromethylidenation was not suitable for *o*-phenylbenzaldehyde (0% yield, C). Instead, the compound was subjected to nucleophilic difluoromethylidenation to give the corresponding difluorostyrene **13** in an 87% yield (D).[9b]



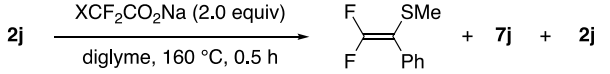
Isolated yields [^{19}F NMR yield based on the internal $(CF_3)_2C(C_6H_4p\text{-}Me)_2$ standard in parentheses].
Method A: 5 mol% **1**, TFDA (2 equiv) over 5 min, 60 °C for 0.5 h, then 100 °C for 0.5 h.
Method B: 5 mol% **1**, TFDA (2 equiv) over 1 min, reflux, 0.5 h.

Figure 4. Synthesis of sulfanylated 1,1-difluoro-1-alkenes from dithioesters.



^{19}F NMR yields based on the internal $(CF_3)_2C(C_6H_4p\text{-}Me)_2$ standard.

Scheme 6. Successive difluoromethylation/ difluoromethylidenation of dithiocarboxylic acids.

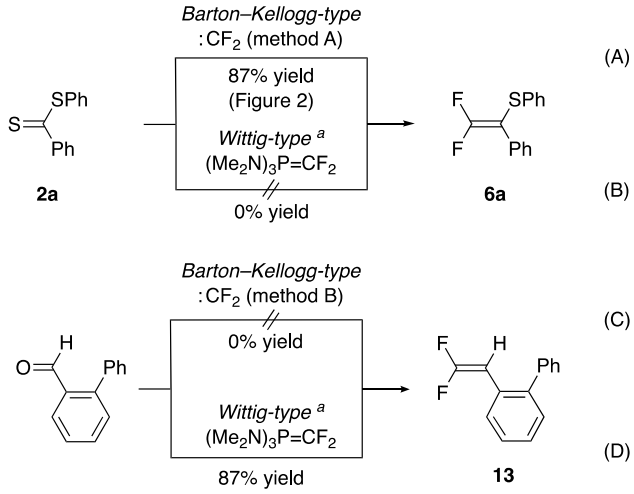


X = Cl	**6j** 41%	trace	48%
X = Br	**6j** 31%	–	57%

^{19}F NMR yields based on the internal $(CF_3)_2C(C_6H_4p\text{-}Me)_2$ standard.

Scheme 7. Difluoromethylidenation of dithioesters with sodium halodifluoroacetates.

Mechanistic investigation on desulfurization: experimental approach. In a standard Barton–Kellogg reaction involving fluorine-free substrates, external reducing agents such as phosphines are required to remove sulfur in the form of



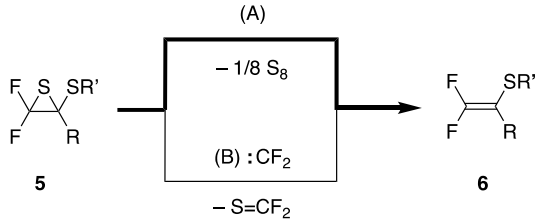
[a] $(Me_2N)_3P{=}CF_2$: CBr_2F_2 (2 equiv), $P(NMe_2)_3$ (4 equiv)
THF, –78 °C to RT.

Scheme 8. Comparative study on difluoromethylidenation.

phosphine sulfides ($S{=}PR_3$). In contrast, desulfurization of difluorothiiranes **5** proceeded in the absence of phosphines. Although it has been established that the elimination of sulfur from difluorothiirane proceeds without reducing agents,[27] experimental details for the phosphine-free desulfurization have not been fully elucidated. Hence, in this study, we examined the desulfurization pathway of this system.

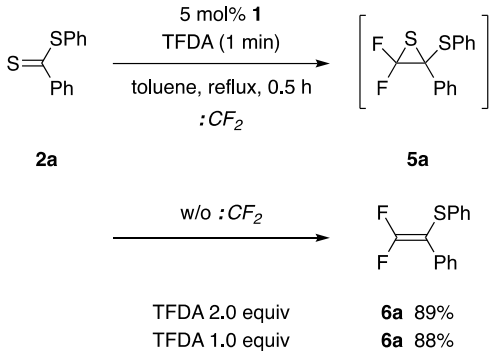
The two possible pathways for the desulfurization reaction are demonstrated in Scheme 9. Pathway (A) involves spontaneous elimination of the sulfur atom in the form of S_8, which is supported by the report that dichlorothiiranes underwent thermal desulfurization to form elemental sulfur.[43] In

route B, a second molecule of difluorocarbene eliminates the sulfur atom from thiirane to generate S=CF_2. This is supported by the report that electron-deficient carbenoids or carbenes, such as N_2=C(CO_2Me)$_2$[44] and :CF_2,[45] work as desulfurization or deoxygenation agents, forming S=C(CO_2Me)$_2$ and O=CF_2, respectively.[46] To distinguish between these pathways (A) and (B), we investigated the stoichiometry of the desulfurization reaction.



Scheme 9. Possible desulfurization pathways.

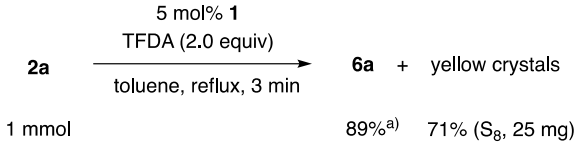
Dithiobenzoate **2a** was treated with 1.0 or 2.0 equiv. of TFDA (Scheme 10).[31] It was found that the yield of **6a** remained nearly the same, regardless of the TFDA loading, indicating that the desulfurization reaction proceeded spontaneously in the absence of difluorocarbene (Scheme 9A).



^{19}F NMR yields based on the internal $(CF_3)_2C(C_6H_4p\text{-Me})_2$ standard.

Scheme 10. Effect of TFDA loading on desulfurization.

We subsequently attempted to isolate elemental sulfur (S_8) from the fluorinated system as reported in our preliminary communication (Scheme 11).[31] Dithioate **2a** (1.0 mmol) was treated with TFDA (2.0 equiv) in the presence of **1** (5 mol%) at reflux for 3 min. Difluoroalkene **6a** was obtained in an 89% yield, and 25 mg of yellow crystalline material was successfully isolated. Elemental analysis of the product suggested that the sulfur content in the sample was 91.63 wt% (0.71 mmol). This implied that the isolated sample was essentially elemental sulfur (S_8) and the yield (71%) was nearly consistent with that of **6a** (89%). Thus, the elimination of elemental sulfur was confirmed.[47]



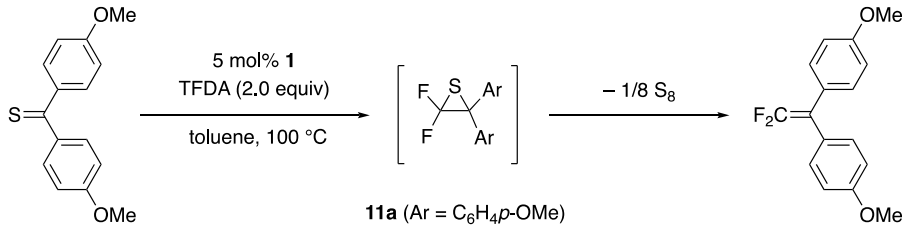
a) ^{19}F NMR yields based on the internal $PhCF_3$ standard.

Scheme 11. Isolation of elemental sulfur.

Electrophilic difluoromethylidenation of thioketones. Similarly to sulfanylated 1,1-difluoroalkenes, disubstituted 1,1-difluoroethenes are not easily accessible from ketones by the nucleophilic Wittig-type difluoromethylidenation due to electronic and steric reasons. Thus, the transformation has been typically conducted with activated ketones, such as α-oxygenated ketones[48] and α-haloketones,[49] predominantly trifluoromethyl ketones.

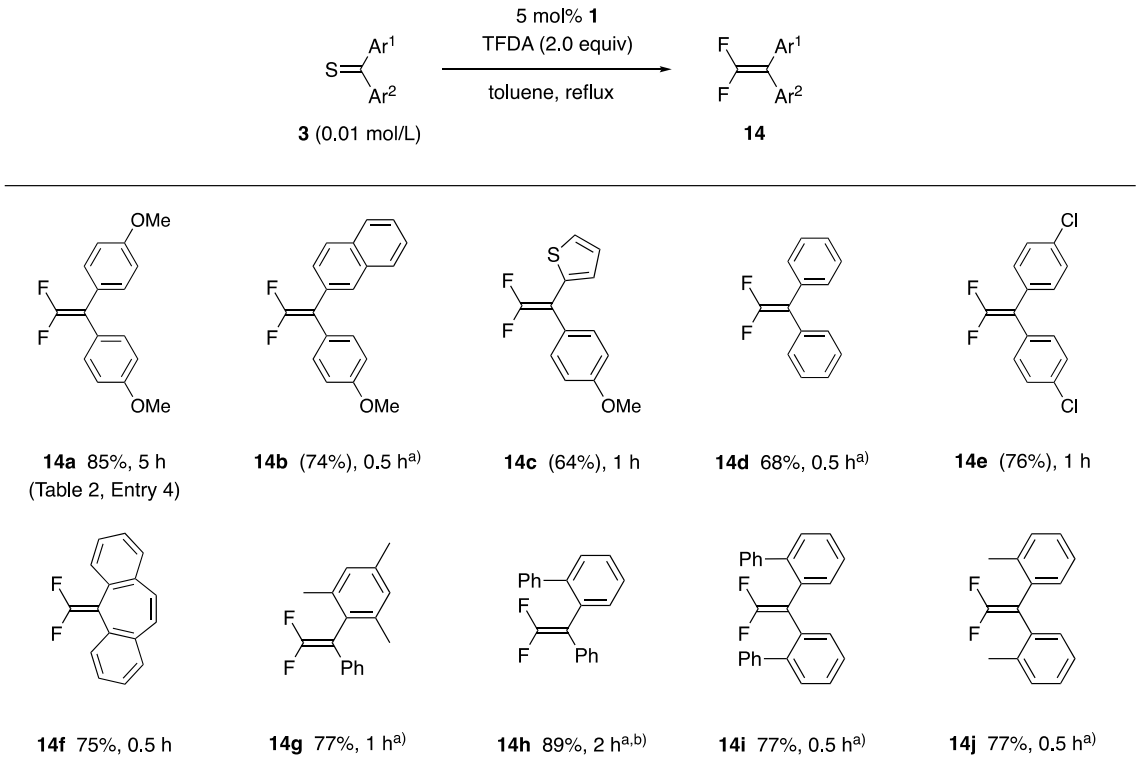
When di(*p*-methoxyphenyl) thioketone **3a** (0.1 mol/L) was treated with TFDA in the presence of 5 mol% of proton sponge (**1**) at 100 °C, the desired 1,1-difluoroethene **14a** was obtained in a 75% yield (Table 2, Entry 1). Notably, the mass balance was improved under diluted conditions. When the reaction was conducted at a substrate concentration of 0.05 mol/L (Entry 2), ^{19}F NMR analysis indicated the formation of two compounds, namely, difluoroethene **14a** and difluorothiirane intermediate **11a**, of which the latter was not isolated (**11a** + **14a** = 87% yield). Thus, difluorothiirane **11a** generated from thioketone **3a** was much less stable than **5a** and could not be fully characterized (^{19}F NMR: δ 63.2 vs. C_6F_6).

Table 2. Synthesis of diarylated 1,1-difluoroethenes from thioketones.[a)]



Entry	*c* (**3a**) (mol/L)	*t* (h)	**11a** (%)	**14a** (%)[b)]	**11a** + **14a** (%)
1	0.1	0.5	–	75	75
2	0.05	0.5	10	77	87
3	0.01	0.5	53	38	91
4	0.01	5	–	90 (85)	90

a) ^{19}F NMR yield based on the internal $(CF_3)_2C(C_6H_4p\text{-Me})_2$ standard. B) Isolated yield is indicated in parentheses.



Isolated yields [^{19}F NMR yields based on the internal $(p\text{-Tol})_2C(CF_3)_2$ standard in parentheses]. a) 0.1 mol/L **3**. b) TFDA (3 equiv).

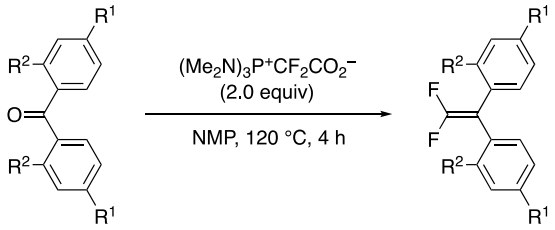
Figure 5. Synthesis of diarylated 1,1-difluoroethenes.

The mass balance was further improved at a **3a** concentration of 0.01 mol/L. In this case, the desired products were obtained in a 91% yield (**11a** + **14a**, Entry 3). Finally, extending the reaction time resulted in full conversion of difluorothiirane to afford 1,1-difluoroethene **14a** in a 90% yield (85% isolated yield, Entry 4).

Furthermore, various diarylated 1,1-difluoroethenes were synthesized from thioketones by the Barton–Kellogg-type difluoromethylidenation (Figure 5). Similarly to **14a**, difluoroethene **14b**–**d** were obtained from **3b**–**d** in 74%, 64%, and 68% yields, respectively.[50] As well as electron-rich difluoroethenes, electron-deficient difluoroethene **14e** was synthesized in a 76% yield. The synthesis of tricyclic difluoroethene **14f** was also achieved in a 75% yield.

Importantly, as mentioned above, electrophilic difluoromethylidenation was expected to be advantageous for the synthesis of sterically hindered thioketones. Indeed, mesitylated thioketone **3g** readily reacted with the *in situ* generated difluorocarbene and the corresponding difluoroethene **14g** was isolated in a 77% yield. Difluoroethenes **14h**,**i**, bearing one or two *o*-phenylphenyl groups, were prepared in 89% and 77% yields. Difluoroditolylethene **14j** was synthesized from di(*o*-tolyl) thioketone **3j** in a 77% yield. Thus, the Barton–Kellogg-type, thioketone-based method provides an easy access to sterically hindered difluoroethenes. As demonstrated in Scheme 1, bis(biaryl)difluoroethenes such as **14i** act as useful precursors for the synthesis of PAHs via a Brønsted acid-promoted domino cyclization.[14]

It is noteworthy that treatment of electron-rich di(*p*-methoxyphenyl) *ketone* and sterically hindered di(*o*-phenylphenyl) *ketone* with a Wittig-type reagent, [tris(dimethylamino)phosphonio]difluoroacetate[51] resulted in the formation of the corresponding 1,1-difluoroethenes **14a** and **14i** in poor yields (Scheme 12). Hence, we determined that electrophilic difluoromethylidenation (Figure 5) could be used as a complementary method for substrates, for which the nucleophilic reaction is not suitable.[52]



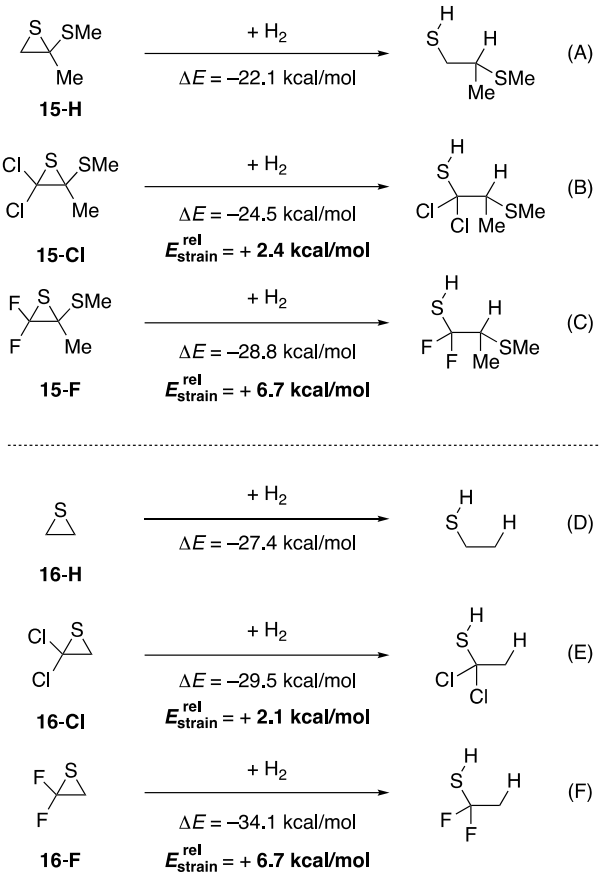
Scheme 12. Wittig-type reactions for the synthesis of electron-rich or sterically hindered 1,1-difluoroethenes.

Mechanistic investigation on desulfurization: theoretical approach. Fluorine-free thiiranes are thermally stable and require phosphines for their desulfurization. In contrast, difluorothiirane was found to be unstable and readily underwent elimination of elemental sulfur to give the corresponding 1,1-difluoroalkenes. Interestingly, it was reported that the reactivity of dichlorothiirane was moderate and that spontaneous desulfurization occurred after a few months of storage.[32,53]

The aforementioned successful isolation of eliminated S_8 encouraged us to investigate the origin of the enhanced reactivity of chlorinated and fluorinated thiiranes. Mosquera previously calculated the energies of fluorinated thiiranes and reported that their calculated ring strains correlated with the calculated reaction energies.[54] Nonetheless, no comparison of ring strains of (dihalo)thiiranes with their observed reactivities toward desulfurization has not been performed to date.

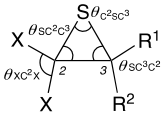
In this study, we estimated the energy change during hydrogenolysis of the S–C bond of fluorine-free thiirane **15-H** (Scheme 13A, −22.1 kcal/mol, DFT, B3LYP/6-31G*).[53] In the case of dichlorothiirane **15-Cl**, the energy change during the hydrogenolysis of the S–C bond distal to the CCl_2 moiety was determined at −24.5 kcal/mol (B), which indicated that **15-Cl** was less stable than **15-H** by 2.4 kcal/mol (relative strain, E_{strain}^{rel}). Moreover, the relative strain for difluorothiirane **15-F** was considerably higher at 6.7 kcal/mol (C). Additionally, the relative strains of dichlorothiirane **16-Cl** and difluorothiirane **16-F** were estimated in a similar manner.[55] It was found that the relative strains of the dichlorothiirane and the difluorothiirane were 2.1 (E) and 6.7 kcal/mol (F), respectively. We concluded that the relative strains of the halogenated thiiranes rationalized their desulfurization reactivities.

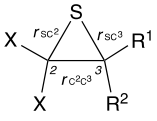
It was determined that the introduction of halogens caused distortion in the structures of thiiranes (Table 3). The DFT calculation suggested that the bond angles for the H–C–H (θ_{HC^2H}) and S–C–C ($\theta_{SC^2C^3}$) bonds in thiirane **15-H** were 114.9° and 67.2°, respectively. Furthermore, the bond length of the S–C bond (r_{SC^3}) was established at 1.86 Å (Entry 1). In **15-F**, the F–C–F bond angle (θ_{FC^2F}) was calculated at 107.0°, which was 7.9° narrower than in the case of **15-H** (Entry 3). In addition, the S–CF_2–C bond angle ($\theta_{SC^2C^3}$) in **15-F** was 71.4°, which was wider than the same bond angle in **15-H** by 4.2°. The bond length of the S–C bond distal to the CF_2 moiety (r_{SC^3}) in **15-F** was determined at 1.93 Å; therefore, it was 0.07 Å longer than the corresponding bond in **15-H** (Entry 3). The distortion of dichlorothiirane **15-Cl** was intermediary between **15-H** and **15-F** (Entry 2). The same trend was observed in derivatives **16**. Thus, the S–CCl_2–C (**16-Cl**) bond angle ($\theta_{SC^2C^3}$) increased only marginally, whereas the S–CF_2–C (**16-F**) bond angle was significantly larger. The bond lengths of the S–C bonds distal to the CCl_2 and CF_2 moieties (r_{SC^3}) were also slightly and significantly increased, respectively (Entries 4–6). The calculated parameters for **16-H** were in agreement with the previously reported experimental values (Entries 4 and 7).



Scheme 13. Calculated relative strain energies of thiiranes.

Table 3. Calculated structural parameters of thiiranes.[a)]





	R^1 = SMe, R^2 = Me (dithioester-derived)	R^1 = R^2 = H (thioketone-derived)
X = H	**15-H**	**16-H**
X = Cl	**15-Cl**	**16-Cl**
X = F	**15-F**	**16-F**

Entry	**15/16**	θ_{XC^2X} (°)	$\theta_{SC^2C^3}$ (°)	$\theta_{SC^3C^2}$ (°)	$\theta_{C^2SC^3}$ (°)	r_{SC^3} (Å)	r_{SC^2} (Å)	$r_{C^2C^3}$ (Å)
1	**15-H**	114.9	67.2	65.4	47.4	1.86	1.84	1.49
2	**15-Cl**	108.7 (–6.2)	69.1 (+1.9)	62.9 (–2.5)	47.9 (+0.5)	1.89 (+0.03)	1.80 (–0.04)	1.50 (+0.01)
3	**15-F**	107.0 (–7.9)	71.4 (+4.2)	61.7 (–3.7)	46.8 (–0.6)	1.93 (+0.07)	1.79 (–0.05)	1.48 (–0.01)
4	**16-H**	114.7	66.2	66.2	47.5	1.84	1.84	1.48
5	**16-Cl**	111.1 (–3.6)	67.5 (+1.3)	64.7 (–1.5)	47.8 (+0.3)	1.85 (+0.01)	1.81 (–0.03)	1.48 (+0.00)
6	**16-F**	108.7 (–6.0)	68.7 (+1.5)	64.4 (–1.8)	47.0 (–0.5)	1.87 (+0.03)	1.81 (–0.03)	1.47 (–0.01)
7	**16-H**	116.0,[b)] 115.83[c)]	65.80,[b)] 65.87[c)]	65.80,[b)] 65.87[c)]	48.43,[b)] 48.27[c)]	1.819,[b)] 1.815[c)]	1.819,[b)] 1.815[c)]	1.492,[b)] 1.484[c)]

a) Differences from **15-H** or **16-H** are shown in parentheses. b) The experimental values reported by Le Van.[56] c) The experimental values reported by Sheridan.[57]

According to Bent's rule, these distortions were attributed to the strongly electron-withdrawing inductive effect of the fluorine substituents. Because the *p* character-rich C–F bonds exhibit a smaller interelectronic repulsion around the CF_2 carbon atom than the *s* character-rich C–S/C–C bonds, the F–C–F bond angle became narrower, while the S–CF_2–C bond angle became wider, leading to distortions and instability of difluorothiiranes.

3. Conclusion

A facile method for the synthesis of sulfanylated and sterically demanding diarylated 1,1-difluoroalkenes via difluorothiiranes was developed herein. TFDA was treated with a proton sponge catalyst to generate difluorocarbene ($:CF_2$), which reacted with dithioesters and diaryl thioketones to form difluorothiirane intermediates. Spontaneous desulfurization (*i.e.*, elimination of elemental sulfur) of difluorothiiranes afforded the desired difluoroalkenes. The utilized Barton–Kellogg-type reaction is an electrophilic counterpart to the Wittig-type reaction of aldehydes or ketones. The two approaches are complementary and can be used for the preparation of diverse 1,1-difluoro-1-alkenes. Theoretical calculation indicated that the distortion caused by the electron-withdrawing fluorine substituents is the origin of the enhanced reactivity of the difluorothiirane intermediates.

4. Experimental

THF and toluene were dried by passing through a column of activated alumina followed by a column of Q-5 scavenger (Engelhard). *p*-Xylene was distilled with azeotropic removal of water and stored over molecular sieves 4A. Nitromethane was distilled form calcium hydride and stored under nitrogen.

Trimethylsilyl 2,2-difluoro-2-fluorosulfonylacetate (TFDA) was purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. and distilled under reduced pressure (62 °C/15 mmHg). TFDA can be prepared according to the literature.[30b] 1,8-Bis(dimethylamino)naphthalene (proton sponge, **1**) was purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. and recrystallized from methanol/ water. Sodium bromodifluoroacetate was prepared by our method.[58] The sodium salts were hygroscopic and handled in a glove box. Carbodithioic acid **12** was prepared by the procedure in literature.[59] α,α,α-Trifluorotoluene ($PhCF_3$) and 1,1,1,3,3,3-hexafluoro-2,2-di(4-methylphenyl)propane [$(CF_3)_2C(C_6H_4$*p*-$Me)_2$] as internal standards for determination of ^{19}F NMR yields was purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. and used as received. All reactions were performed under an argon atmosphere.

Column chromatography was conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography). Purification was also performed by preparative HPLC (GPC), using a JAI LC-908 instrument (Jaigel-2H, $CHCl_3$).

IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR method). NMR spectra were recorded on Bruker Avance 500 or Jeol JNM ECS-400 spectrometers in $CDCl_3$ at 500 or 400 MHz (^1H NMR), at 126 or 101 MHz (^{13}C NMR), and at 470 or 376 MHz (^{19}F NMR). Chemical shifts were given in ppm relative to internal Me_4Si (for ^1H NMR: δ = 0.00), $CDCl_3$ (for ^{13}C NMR: δ = 77.0) and C_6F_6 (for ^{19}F NMR: δ = 0.0; C_6F_6 exhibits a ^{19}F NMR signal at –162.9 ppm vs. $CFCl_3$). High-resolution mass spectroscopy (HRMS) was conducted with a Jeol JMS-T100GCV (EI/TOF) spectrometer. Elemental analyses (EA) were performed with a Yanako MT-3 CHN Corder apparatus or an Elementar Vario Micro Cube apparatus.

Preparation and spectral data of dithioesters **2a**–**n** were described in our previous publication.[31] Thioketones **3** were prepared from the corresponding ketones using Lawesson's reagent **4** in a similar manner to **2a**–**i**.

Difluoromethyl 4-methoxybenzenecarbodithioate (2o): ^1H NMR (500 MHz, $CDCl_3$): δ 3.88 (s, 3H), 6.90 (d, *J* = 9.0 Hz, 2H), 7.54 (t, J_{HF} = 54.8 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.7, 113.9, 123.2 (t, J_{CF} = 272 Hz), 129.3, 137.2, 164.8, 218.5; ^{19}F NMR (471 MHz, $CDCl_3$): δ 61.3 (d, J_{FH} = 55 Hz); IR (neat): ν 2841, 1593, 1244, 1173, 904, 725 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_9H_8F_2OS_2$ $[M]^+$: 233.9985; found: 233.9988.

Di(4-methoxyphenyl)methanethione (3a): ^1H NMR (500 MHz, $CDCl_3$): δ 3.88 (s, 6H), 6.88 (d, *J* = 8.5 Hz, 4H), 7.73 (d, *J* = 8.5 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.5, 113.2, 132.1, 140.8, 163.1, 233.4; IR (neat): ν 2974, 1589, 1502, 1250, 837 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{15}H_{14}SO_2$ $[M]^+$: 258.0715; found: 258.0717.

(4-Methoxyphenyl)(2-naphthyl)methanethione (3b): ^1H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.85 (d, *J* = 8.9 Hz, 2H), 7.47 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.53 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.75–7.84 (m, 6H), 8.05 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.5, 113.3, 126.7, 127.1, 127.5, 127.6, 127.8, 129.2, 129.4, 132.1, 132.3, 134.6, 140.5, 145.0, 163.5, 235.0; IR (neat): ν 2920, 1724, 1234, 756, 694 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{18}H_{14}OS$ $[M]^+$: 278.0765; found: 278.0769.

(4-Methoxyphenyl)(2-thienyl)methanethione (3c): ^1H NMR (500 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.12 (dd, *J* = 5.0, 4.2 Hz, 1H), 7.36 (dd, *J* = 4.2 Hz, 1H), 7.71 (d, *J* = 5.0 Hz, 1H), 7.73 (dd, *J* = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.4, 113.2, 128.5, 130.8, 131,3. 137.3, 140.0, 154.8, 162.8, 221.2; IR (neat): ν 2929, 1595, 1350, 1255, 1167, 1024 cm^{-1}; HRMS (EI, TOF): *m/z* calcd. for $C_{12}H_{10}OS_2$ $[M]^+$: 234.0173; found: 234.0165.

Diphenylmethanethione (3d): ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 7.8, 7.8 Hz, 4H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.71 (dd, *J* = 7.8, 0.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 128.0, 129.6, 132.0, 147.3, 238.5; IR (neat): ν 3057, 1441, 1265, 1219, 756, 688 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{13}H_{10}S$ $[M]^+$: 198.0503; found: 198.0499.

Di(4-chlorophenyl)methanethione (3e): ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (ddd, *J* = 8.7, 2.3, 2.3 Hz, 4H), 7.64 (ddd, *J* = 8.7, 2.3, 2.3 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 128.4, 130.7, 138.9, 145.2, 234.4; IR (neat): ν 1662, 1585, 1092, 771 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{13}H_8Cl_2S$ $[M]^+$: 265.9724; found: 265.9730.

5*H*-Dibenzo[*a*,*d*][7]annulene-5-thione (3f): ^1H NMR (500 MHz, $CDCl_3$): δ 7.00 (s, 2H), 7.36 (dd, *J* = 7.6, 1.1 Hz, 2H), 7.40 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 2H), 7.51 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 2H), 8.03 (dd, *J* = 7.6, 1.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 128.5, 128.6, 129.4, 130.5, 130.7, 131.4, 149.2, 239.8; IR (neat): ν 3057, 1282, 1196, 802, 766, 712 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{15}H_{10}S$ $[M]^+$: 222.0503; found: 222.0512.

Mesityl(phenyl)methanethione (3g): ^1H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 6H), 2.33 (s, 3H), 6.90 (s, 2H), 7.35 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.3, 21.7, 128.6, 129.2, 129.4, 133.2, 134.2, 137.9, 144.5, 146.9, 243.9; IR (neat): ν 2916, 1446, 1219, 1047, 687 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{16}H_{16}S$ $[M]^+$: 240.0973; found: 240.0965.

Phenyl(2-phenylphenyl)methanethione (3h): ^1H NMR (400 MHz, $CDCl_3$): δ 7.06–7.14 (m, 5H), 7.16–7.20 (m, 2H), 7.30–7.43 (m, 3H), 7.49–7.57 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 126.88, 126.92, 127.7, 127.8, 128.7, 129.2, 129.9, 130.0, 130.1, 132.3, 139.3, 140.6, 146.3, 148.7, 241.8; IR (neat):

ν 2916, 1400, 1348, 1242, 1049, 717 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{19}H_{14}S$ $[M]^+$: 274.0816; found: 274.0828.

Di(2-phenylphenyl)methanethione (3i): ^1H NMR (500 MHz, $CDCl_3$): δ 6.82–6.87(m, 4H), 6.92–6.94 (m, 4H), 7.04–7.10 (m, 6H), 7.14 (dd, *J* = 7.7, 7.7 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 126.2, 126.7, 127.7, 128.6, 129.3, 129.5, 132.4, 137.9, 141.2, 149.4, 248.5; IR (neat): ν 3057, 1466, 1279, 754, 698 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{25}H_{18}S$ $[M]^+$: 350.1129; found: 350.1127.

Di(2-methyphenyl)methanethione (3j): ^1H NMR (400 MHz, $CDCl_3$): δ 2.12 (s, 6H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.18 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 2H), 7.32 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 2H), 7.44 (dd, *J* = 7.5, 1.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.1, 125.8, 129.6, 130.4, 131.1, 134.6, 150.0, 245.6; IR (neat): ν 3060, 1595, 1454, 1290, 1227, 752 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{15}H_{14}S$ $[M]^+$: 226.0816; found: 226.0817.

Synthesis of sulfanylated difluoroalkenes 6 (difluoromethylidenation of dithioesters 2, method A; for electron-deficient and sterically less hindered substrates). Synthesis of difluoroalkene **6a** is described as a typical procedure. To a toluene solution (4 mL, 60 °C) of phenyl benzenecarbodithioate (**2a**, 115 mg, 0.499 mmol) and proton sponge (**1**, 5.6 mg, 0.030 mmol) was added TFDA (200 μL, 1.06 mmol) dropwise over 5 min. Gas evolution was observed and the solution was stirred for 30 min. After the solution was heated up to 100 °C and stirred for 30 min, saturated aqueous sodium hydrogen carbonate (10 mL) was added to quench the reaction at room temperature. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give difluoroalkene **6a** (109 mg, 87% yield) as a colorless liquid.

Synthesis of sulfanylated difluoroalkenes 6 (difluoromethylidenation of dithioesters 2, method B; for electron-rich or sterically hindered substrates). Synthesis of difluoroalkene **6j** is described as a typical procedure. To a refluxing toluene solution (2 mL) of methyl benzenecarbodithioate (**2j**, 43 mg, 0.26 mmol), proton sponge (**1**, 2.8 mg, 0.013 mmol), and 1,1,1,3,3,3-hexafluoro-2,2-di(4-methylphenyl)propane (14 mg, 0.042 mmol) was added TFDA (100 μL, 0.531 mmol) dropwise over 1 min. The solution was stirred for 30 min. ^{19}F NMR analysis based on an internal standard, 1,1,1,3,3,3-hexafluoro-2,2-di(4-methylphenyl)propane indicated that difluoroalkene **6j** was obtained in 82% yield.

2,2-Difluoro-3-phenyl-3-(phenylsulfanyl)thiirane (5a): A sample after purification by column chromatography (hexane), which contained a small amount of **14a**, was used for analysis. ^1H NMR (500 MHz, $CDCl_3$): δ 7.19–7.31 (m); ^{13}C NMR (126 MHz, $CDCl_3$): δ 63.4 (dd, J_{CF} = 11, 10 Hz), 120.5 (dd, J_{CF} = 310, 310 Hz), 127.9, 128.6, 129.0, 129.1, 129.5, 130.5, 135.0, 135.3 (d, J_{CF} = 4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 63.0 (d, *J* = 106 Hz, 1F), 65.6 (d, *J* = 106 Hz, 1F); IR (neat): ν 1323, 1234, 1140, 933, 737 cm^{-1}.

Spectral data of difluoroalkene **6a**[19b] were in complete agreement with those in literature.

1,1-Difluoro-2-phenylsulfanyl-2-(4-methylphenyl)ethene (6b): ^1H NMR (500 MHz, $CDCl_3$): δ 2.30 (s, 3H), 7.10–7.13 (m, 3H), 7.19 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.22–7.24 (m, 2H), 7.42 (dd, *J* = 8.1, 1.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.1, 88.7 (dd, J_{CF} = 21, 21 Hz), 126.3, 128.0, 128.5 (dd, J_{CF} = 4, 4 Hz), 128.9, 129.1, 129.3 (d, J_{CF} = 4 Hz), 134.6 (dd, J_{CF} = 2, 2 Hz), 137.9, 156.9 (dd, J_{CF} = 305, 290 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 85.2 (d, *J* = 14 Hz, 1F), 87.2 (d, *J* = 14 Hz, 1F); IR (neat): ν 3076, 3028, 1684, 1265, 1009, 814, 735, 687 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{15}H_{12}F_2S$ $[M]^+$: 262.0628; found: 262.0627.

1,1-Difluoro-2-(4-methoxyphenyl)-2-(phenylsulfanyl)ethene (6c): ^1H NMR (500 MHz, $CDCl_3$): δ 3.78 (s, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.12 (t, *J* = 6.8 Hz, 1H), 7.15–7.24 (m, 4H), 7.46 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.2, 88.5 (dd, J_{CF} = 21, 21 Hz), 113.8, 124.3 (d, J_{CF} = 4 Hz), 126.3, 128.0, 129.0, 129.9 (dd, J_{CF} = 4, 4 Hz), 134.5, 156.7 (dd, J_{CF} = 304, 290 Hz), 159.2; ^{19}F NMR (471 MHz, $CDCl_3$): δ = 83.1 (d, *J* = 16 Hz, 1F), 85.2 (d, *J* = 16 Hz, 1F); IR (neat): ν 3060, 2836, 1684, 1606, 1510, 1242, 912, 744 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{15}H_{12}F_2OS$ $[M]^+$: 278.0577; found: 278.0576.

1-(4-Chlorophenyl)-2,2-difluoro-1-(phenylsulfanyl)ethene (6d): ^1H NMR (500 MHz, $CDCl_3$): δ 7.12 (tt, *J* = 6.9, 1.8 Hz, 1H), 7.17–7.26 (m, 6H), 7.45 (dd, *J* = 8.6, 1.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 88.4 (dd, J_{CF} = 22, 20 Hz), 126.6, 128.3, 128.6, 129.1, 130.0 (dd, J_{CF} = 4, 4 Hz), 130.8 (d, J_{CF} = 4 Hz), 133.8–133.9 (m), 157.0 (dd, J_{CF} = 306, 291 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 86.1 (d, *J* = 11 Hz, 1F), 88.2 (d, *J* = 11 Hz, 1F); IR (neat): ν 3074, 1682, 1477, 1279, 1009, 933, 737, 688 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{14}H_9ClF_2S$ $[M]^+$: 282.0082; found: 282.0087.

1,1-Difluoro-2-phenylsulfanyl-2-[4-(trifluoromethyl)phenyl]ethene (6e): ^1H NMR (500 MHz, $CDCl_3$): δ 7.15–7.19 (m, 1H), 7.21–7.25 (m, 4H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 88.6 (dd, J_{CF} = 22, 20 Hz), 123.9 (q, J_{CF} = 272 Hz), 125.4 (q, J_{CF} = 4 Hz), 126.8, 128.4, 129.0 (dd, J_{CF} = 4, 4 Hz), 129.2, 130.0 (q, J_{CF} = 33 Hz), 133.7 (dd, J_{CF} = 2, 2 Hz), 136.2 (d, J_{CF} = 5 Hz), 157.5 (dd, J_{CF} = 307, 292 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 87.4 (d, *J* = 8 Hz, 1F), 89.8 (d, *J* = 8 Hz, 1F), 100.1 (s, 3F); IR (neat): ν 3066, 1682, 1319, 1273, 1119, 1068, 1011, 841, 741 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{15}H_9F_5S$ $[M]^+$: 316.0345; found: 316.0341.

1-(Biphenyl-2-yl)-2,2-difluoro-1-(phenylsulfanyl)ethene (6f): ^1H NMR (500 MHz, $CDCl_3$): δ 7.19–7.26 (m, 9H), 7.29–7.39 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 88.9 (dd, J_{CF} = 24 Hz), 127.1, 127.2, 127.4, 128.1, 128.6, 128.7, 128.9, 130.4, 130.7, 131.2, 131.3, 133.4 (dd, J_{CF} = 2 Hz), 140.8, 142.2 (d, J_{CF} = 2 Hz), 156.0 (dd, J_{CF} = 300, 292 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 83.3 (d, *J* = 15 Hz, 1F), 86.2 (d, *J* = 15 Hz, 1F); IR (neat): ν 3060, 1697, 1475, 1277, 1219, 1007, 914, 748 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{20}H_{14}F_2S$ $[M]^+$: 324.0784; found: 324.0796.

1-(2-Chlorophenyl)-2,2-difluoro-1-(phenylsulfanyl)ethene (6g): ^1H NMR (500 MHz, $CDCl_3$): δ 7.13–7.25 (m, 6H), 7.33–7.35 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 86.8 (dd, J_{CF} = 25, 25 Hz), 126.6, 127.4, 128.9, 129.69, 129.72, 130.7, 131.5 (d, J_{CF} = 3 Hz), 131.6, 132.9 (dd, J_{CF} = 2, 2 Hz), 134.2, 156.2 (dd, J_{CF} = 302, 292 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 84.5 (d, *J* = 10 Hz, 1F), 89.3 (d, *J* = 10 Hz, 1F); IR (neat): ν 1697, 1471, 1275, 1065, 1011, 750, 688 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{14}H_9ClF_2S$ $[M]^+$: 282.0082; found: 282.0081.

1-(3-Chlorophenyl)-2,2-difluoro-1-(phenylsulfanyl)ethene (6h): ^1H NMR (500 MHz, $CDCl_3$): δ 7.13 (tt, *J* = 7.0, 1.8 Hz, 1H), 7.19–7.24 (m, 6H), 7.39–7.41 (m, 1H), 7.53 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 88.4 (dd, J_{CF} = 21, 21 Hz), 126.7, 126.9 (dd, J_{CF} = 4, 4 Hz), 128.1, 128.3, 128.7 (dd, J_{CF} = 4, 4 Hz), 129.1, 129.6, 133.8 (dd, J_{CF} = 2, 2 Hz), 134.2 (d, J_{CF} = 4 Hz), 134.3, 157.2 (dd, J_{CF} = 307, 291 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 86.9 (d, *J* = 10 Hz, 1F), 89.1 (d, *J* = 10 Hz, 1F); IR (neat): ν 1683, 1475,

1282, 1217, 1012, 908, 732, 688 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{14}H_9ClF_2S$ $[M]^+$: 282.0082; found: 282.0081.

1,1-Difluoro-2-(phenylsulfanyl)hept-1-ene (6i): ^1H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.19–1.31 (m, 4H), 1.49 (dt, *J* = 7.4, 7.4 Hz, 2H), 2.14 (tt, *J* = 7.4, 2.5 Hz, 2H), 7.18–7.22 (m, 1H), 7.28–7.29 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.9, 22.3, 27.0 (dd, J_{CF} = 2, 2 Hz), 28.1, 30.9, 86.7 (dd, J_{CF} = 26, 16 Hz), 126.5, 128.8, 129.0, 134.2 (dd, J_{CF} = 2, 2 Hz), 156.9 (dd, J_{CF} = 297, 288 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 80.6 (d, *J* = 27 Hz, 1F), 81.4 (d, *J* = 27 Hz, 1F); IR (neat): ν 2929, 1709, 1477, 1259, 1126, 771, 739, 688 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{13}H_{16}F_2S$ $[M]^+$: 242.0941; found: 242.0941.

1,1-Difluoro-2-methylsulfanyl-2-phenylethene (6j): ^1H NMR (500 MHz, $CDCl_3$): δ 2.07 (s, 3H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 16.4, 91.0 (dd, J_{CF} = 22, 21 Hz), 128.0, 128.5, 129.0 (dd, J_{CF} = 3, 3 Hz), 131.9 (dd, J_{CF} = 3, 1 Hz), 154.7 (dd, J_{CF} = 301, 288 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 81.8 (d, *J* = 24 Hz, 1F), 84.0 (d, *J* = 24 Hz, 1F); IR (neat): ν 2925, 1695, 1265, 1236, 1007, 912, 748, 741 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_9H_8F_2S$ $[M]^+$: 186.0315; found: 186.0317.

1,1-Difluoro-2-methylsulfanyl-2-(4-methylphenyl)ethene (6k): ^1H NMR (500 MHz, $CDCl_3$): δ 2.06 (s, 3H), 2.36 (s, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 16.3 (dd, J_{CF} = 2 Hz), 21.2, 90.8 (dd, J_{CF} = 22, 21 Hz), 154.5 (dd, J_{CF} = 300, 288 Hz), 137.9, 129.2, 128.9 (dd, J_{CF} = 3 Hz), 128.8 (d, J_{CF} = 4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 81.4 (d, *J* = 26 Hz, 1F), 83.3 (d, *J* = 26 Hz, 1F); IR (neat): ν 2924, 1691, 1510, 1265, 1234, 1011, 931, 816 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{10}H_{10}F_2S$ $[M]^+$: 200.0471; found: 200.0480.

1-(4-Chlorophenyl)-2,2-difluoro-1-(methylsulfanyl)ethene (6l): ^1H NMR (500 MHz, $CDCl_3$): δ 2.07 (s, 3H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 16.4, 90.3 (dd, J_{CF} = 23, 20 Hz), 128.8, 130.3 (dd, J_{CF} = 3, 3 Hz), 130.4 (dd, J_{CF} = 4, 2 Hz), 133.9, 154.9 (dd, J_{CF} = 302, 289 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 82.8 (d, *J* = 22 Hz, 1F), 85.0 (d, *J* = 22 Hz, 1F); IR (neat): ν 2925, 1685, 1488,1274, 1009, 912, 827, 742 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_9H_7ClF_2S$ $[M]^+$: 219.9925; found: 219.9930.

1-Benzylsulfanyl-2,2-difluoro-1-phenylethene (6m): ^1H NMR (500 MHz, $CDCl_3$): δ 3.62 (s, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.20–7.26 (m, 3H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.36 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 37.2 (dd, J_{CF} = 2, 2 Hz), 89.1 (dd, J_{CF} = 23, 21 Hz), 127.2, 127.9, 128.38, 128.43, 128.9, 129.1 (dd, J_{CF} = 3, 3 Hz), 132.2 (d, J_{CF} = 3 Hz), 137.3, 155.9 (dd, J_{CF} = 303, 289 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 83.1 (d, *J* = 19 Hz, 1F), 85.4 (d, *J* = 19 Hz, 1F); IR (neat): ν 2925, 1689, 1491, 1265, 1234, 1007, 694 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{15}H_{12}F_2S$ $[M]^+$: 262.0628; found: 262.0628.

1-Benzylsulfanyl-1-(4-chlorophenyl)-2,2-difluoroethene (6n): ^1H NMR (500 MHz, $CDCl_3$): δ 3.63 (s, 2H), 7.11–7.13 (m, 2H), 7.21–7.28 (m, 3H), 7.31–7.36 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 37.3 (dd, J_{CF} = 2, 2 Hz), 88.3 (dd, J_{CF} = 23, 20 Hz), 127.3, 128.4, 128.7, 128.9, 130.3 (dd, J_{CF} = 4, 4 Hz), 130.8 (d, J_{CF} = 3 Hz), 133.8, 137.1, 156.0 (dd, J_{CF} = 304, 290 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 84.1 (d, *J* = 17 Hz, 1F), 86.4 (d, *J* = 17 Hz, 1F); IR (neat): ν 3032, 1685, 1491, 1275, 1090, 1010, 827 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{15}H_{11}F_2S$ $[M]^+$: 296.0238; found: 296.0238.

2,2-Difluoro-1-difluoromethylsulfanyl-1-(4-methoxyphenyl)ethene (6o): ^1H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.63 (t, J_{HF} = 56.8 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.2, 90.6–91.0 (m), 114.0, 119.5 (t, J_{CF} = 271 Hz), 123.7 (d, J_{CF} = 4 Hz), 129.9 (dd, J_{CF} = 2, 2 Hz), 157.0 (dd, J_{CF} = 291, 291 Hz), 159.5; ^{19}F NMR (471 MHz, $CDCl_3$): δ 69.4 (td, *J* = 57, 3 Hz, 2F), 87.5 (br d, *J* = 57 Hz, 1F), 88.9 (dt, *J* = 57, 3 Hz, 1F); IR (neat): ν 2836, 1683, 912, 744 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{10}H_8F_4OS$ $[M]^+$: 252.0232; found: 252.0237.

1,1,2,2-Tetrafluoro-3-methylsulfanyl-3-phenylcyclopropane (7j): the sample was obtained using 8 equiv of TFDA. ^1H NMR (500 MHz, $CDCl_3$): δ 2.08 (s, 3H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.36–7.44 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 13.8, 45.5 (dddd, J_{CF} = 13, 13, 11, 11 Hz), 106.0 (dddd, J_{CF} = 313, 313, 12, 12 Hz), 128.7, 129.0, 130.1; ^{19}F NMR (471 MHz, $CDCl_3$): δ 18.7 (dm, *J* = 165 Hz, 2F), 23.5 (dm, *J* = 165 Hz, 2F); IR (neat): ν 2927, 1489, 1217, 1157, 810, 748, 696, 565 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{10}H_8F_4S$ $[M]^+$: 236.0283; found: 236.0278.

Synthesis of diarylated difluoroethenes 14 (difluoromethylidenation of thioketones 3). Synthesis of difluoroethene **14g** is described as a typical procedure. To a toluene solution (6 mL) of mesityl(phenyl)methanethione (**3g**, 144 mg, 0.60 mmol) and proton sponge (**1**, 6.8 mg, 0.030 mmol) was added TFDA (240 μL, 1.20 mmol) dropwise. The solution was stirred under reflux for 30 min. Saturated aqueous sodium hydrogen carbonate (10 mL) was added to quench the reaction at room temperature. Organic materials were extracted with ethyl acetate three times. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give difluoroethene **14g** (119 mg, 77% yield) as a colorless liquid.

1,1-Difluoro-2,2-di(4-methoxyphenyl)ethene (14a): ^1H NMR (500 MHz, $CDCl_3$): δ 3.80 (s, 6H), 6.87 (d, *J* = 8.8 Hz, 4H), 7.18 (d, *J* = 8.8 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.2, 95.2 (t, J_{CF} = 19 Hz), 113.8, 126.8, 130.7 (t, J_{CF} = 3 Hz), 153.4 (t, J_{CF} = 292 Hz), 158.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ 73.1 (s); IR (neat): ν 2937, 1701, 1512, 1244, 1028, 831 cm^{-1}; HRMS (EI, TOF): *m/z* calcd for $C_{16}H_{14}F_2O_2$ $[M]^+$: 276.0962; found: 276.0960.

1,1-Difluoro-2-(4-methoxyphenyl)-2-(2-naphthyl)-ethene (14b): ^1H NMR (500 MHz, $CDCl_3$): 3.80 (s, 3H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.44–7.49 (m, 2H), 7.72–7.84 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.2, 95.9 (dd, J_{CF} = 18, 18 Hz), 113.9, 126.2, 126.5 (dd, J_{CF} = 3, 3 Hz), 127.2 (dd, J_{CF} = 3, 3 Hz), 127.6, 127.9, 128.0, 128.8 (dd, J_{CF} = 3, 3 Hz), 130.8 (dd, J_{CF} = 3, 3 Hz), 132.0 (dd, J_{CF} = 4, 4 Hz), 132.5, 133.2, 153.8 (dd, J_{CF} = 293, 293 Hz), 159.0; ^{19}F NMR (471 MHz, $CDCl_3$): δ 74.0 (d, *J* = 35 Hz, 1F), 74.1 (d, *J* = 35 Hz, 1F); IR (neat): ν 2837, 1701, 1512, 1236, 1176, 816 cm^{-1}; *m/z* calcd for $C_{19}H_{14}F_2O$ $[M]^+$: 296.1013; found: 296.1020.

1,1-Difluoro-2-(4-methoxyphenyl)2-(2-thienyl)ethene (14c): ^1H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.90 (dd, *J* = 4.0, 1.0 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.99 (dd, *J* = 4.0, 4.0 Hz, 1H), 7.26–7.30 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.3, 91.6 (dd, J_{CF} = 25, 18 Hz), 113.9, 125.2 (dd, J_{CF} = 3, 3 Hz), 125.6 (dd, J_{CF} = 6, 3 Hz), 126.9, 127.0 (dd, J_{CF} = 4, 4 Hz), 131.0 (dd, J_{CF} = 3, 3 Hz), 136.9 (dd, J_{CF} = 7, 2 Hz), 153.3 (dd, J_{CF} = 298, 291 Hz), 159.5; ^{19}F NMR (471 MHz, $CDCl_3$): δ 73.9 (d, *J* = 28 Hz, 1F), 78.5 (d, *J* = 28 Hz, 1F); IR (neat): ν 2837, 1699, 1510, 1244, 1173, 827 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{13}H_{10}F_2OS$ $[M]^+$: 252.0420; found: 252.0426.

1,1-Difluoro-2,2-diphenylethene (14d): ^1H NMR (500 MHz, $CDCl_3$): δ 7.25–7.31 (m, 6H), 7.34 (dd, *J* = 7.5 Hz, 7.5 Hz,

4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 96.2 (t, J_{CF} = 18 Hz), 127.5, 128.4, 129.6 (t, J_{CF} = 3 Hz), 134.3, 153.8 (t, J_{CF} = 294 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 75.1 (s); IR (neat): ν 3060, 1703, 1242, 1211, 984, 760, 694 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{14}H_{10}F_2$ $[M]^+$: 216.0751; found: 216.0741.

1,1-Di(4-chlorophenyl)-2,2-difluoroethene (14e): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.5 Hz, 4H), 7.33 (d, *J* = 8.5, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 94.7 (t, J_{CF} = 19 Hz), 128.8, 130.8 (t, J_{CF} = 3 Hz), 132.3, 133.8, 153.7 (t, J_{CF} = 295 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 76.5 (s); IR (neat): ν 1705, 1495, 1250, 1093, 989, 825 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{14}H_8Cl_2F_2$ $[M]^+$: 283.9971; found: 283.9958.

5-Difluoromethylidene-5*H*-dibenzo[*a*,*d*][7]annulene (14f): ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (s, 2H), 7.29–7.31 (m, 4H), 7.33–7.39 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 95.1 (t, J_{CF} = 21 Hz), 127.8, 128.5, 129.0 (t, J_{CF} = 2 Hz), 129.1, 131.0, 131.7, 135.6, 152.3 (t, J_{CF} = 292 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 69.4 (s); IR (neat): ν 3024, 1720, 1244, 985, 802, 760 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{16}H_{10}F_2$ $[M]^+$: 240.0751; found: 240.0754.

1,1-Difluoro-2-mesityl-2-phenylethene (14g): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 6H), 2.32 (s, 3H), 6.94 (s, 2H), 7.20–7.23 (m, 3H), 7.27–7.31 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.8, 21.1, 92.6 (dd, J_{CF} = 24, 13 Hz), 127.0, 127.5 (dd, J_{CF} = 6, 4 Hz), 128.5, 128.6, 129.2 (d, J_{CF} = 4 Hz), 133.2 (dd, J_{CF} = 6, 4 Hz), 137.6 (d, J_{CF} = 2 Hz), 137.8, 152.8 (dd, J_{CF} = 301, 286 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 74.1 (d, *J* = 32 Hz, 1F), 79.6 (d, *J* = 32 Hz, 1F); IR (neat): ν 2918, 1240, 1209, 982, 764 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{17}H_{16}F_2OS$ $[M]^+$: 258.1220; found: 258.1218.

1,1-Difluoro-2-phenyl-2-(2-phenylphenyl)ethene (14h): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04–7.08 (m, 2H), 7.12–7.24 (m, 8H), 7.33–7.44 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 95.3 (dd, J_{CF} = 16, 16 Hz), 126.8, 126.9, 127.4, 127.8, 128.0, 128.4, 128.50, 128.53, 130.4, 131.5 (dd, J_{CF} = 2, 2 Hz), 132.3 (dd, J_{CF} = 2, 2 Hz), 134.5 (dd, J_{CF} = 4, 4 Hz), 140.9, 142.9, 153.2 (dd, J_{CF} = 290, 289 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 73.4 (d, *J* = 30 Hz, 1F), 78.8 (d, *J* = 30 Hz, 1F); IR (neat): *v* = 3060, 1707, 1238, 984, 694 cm^{-1}; m/z calcd for $C_{20}H_{14}F_2$ $[M]^+$: 292.1064; found: 292.1079.

1,1-Difluoro-2,2-di(2-phenylphenyl)ethene (14i): ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.57 (d, *J* = 7.6 Hz, 2H), 6.89 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 2H), 7.01–7.03 (m, 2H), 7.07 (dd, *J* = 7.6, 0.9 Hz, 2H), 7.12 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2H), 7.19–7.23 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 95.0 (t, J_{CF} = 20 Hz), 126.5, 126.8, 127.2, 127.8, 128.6, 129.8, 131.4, 132.4, 141.6, 142.1, 153.5 (t, J_{CF} = 292 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 74.5 (s); IR (neat): ν 3059, 3024, 1712, 1477, 1244, 984, 760, 698 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{17}H_{16}F_2$ $[M]^+$: 368.1377; found: 368.1364.

1,1-Difluoro-2,2-di(2-methyphenyl)ethene (14j): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.26 (s, 6H), 7.11–7.16 (m, 4H), 7.17–7.23 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.9, 93.6 (t, J_{CF} = 21 Hz), 125.7, 127.8, 130.5 (t, J_{CF} = 3 Hz), 130.6, 133.6, 136.9, 152.2 (t, J_{CF} = 292 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ 75.8 (s); IR (neat): ν 3064, 1714, 1489, 1244, 982 cm^{-1}; HRMS (EI, TOF): *m*/*z* calcd for $C_{16}H_{14}F_2$ $[M]^+$: 244.1064; found: 244.1064.

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Graphical Abstract

Synthesis of Difluoroalkenes from Thiocarbonyl Compounds via Difluorothiiranes: Electrophilic Counterpart to Wittig-Type Difluoromethylidenation

Kohei Fuchibe,[1] Atsushi Yamada,[1] Kosei Hachinohe,[1] Kana Matsumoto,[1] Ryo Takayama,[1] and Junji Ichikawa*[1]

The synthesis of 1,1-difluoro-1-alkenes was achieved by the treatment of dithioesters and thioketones with trimethylsilyl 2-fluorosulfonyl-2,2-difluoroacetate in the presence of a proton sponge catalyst. Sulfanylated and sterically hindered diarylated difluoroalkenes were obtained. In the reaction, the generated difluorocarbene reacted with the thiocarbonyl moiety to form 2,2-difluorothiirane intermediates, whose desulfurization afforded the products (Barton–Kellogg-type difluoromethylidenation).