Journal of Fluorine Chemistry 140 (2012) 17–27

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Arylsulfur chlorotetrafluorides as useful fluorinating agents: Deoxo- and dethioxo-fluorinations☆

Teruo Umemoto *, Rajendra P. Singh [1]

IM&T Research, Inc.[2], 6860 N. Broadway, Suite B, Denver, CO 80221, USA

ARTICLE INFO

Article history:
Received 3 January 2012
Received in revised form 2 March 2012
Accepted 7 March 2012
Available online 5 April 2012

Keywords:
Arylsulfur chloroterafluoride
Arylsulfur trifluoride
Fluorinating agent
Deoxofluorination
Dethioxofluorination
Disproportionation

ABSTRACT

Usage of arylsulfur chlorotetrafluorides **1** as versatile deoxo- and dethioxo-fluorinating agents is described. There have been developed two convenient methods for the *in situ* preparation of reactive arylsulfur trifluorides **2** from **1**. The one is reduction of **1** with a reducer such as pyridine to **2**, and the other is disproportionation of **1** with a diaryl disulfide to **2** with evolution of chlorine gas. The latter method is a convenient way to get neat **2** from **1**. The *in situ* prepared **2** fluorinates many kinds of substrates such as alcohols, aldehydes, ketones, diketones, and carboxylic acids to give the corresponding CF, CF_2, CF_2CF_2, and CF_3 compounds in high yields. **2** also fluorinates various sulfur compounds including C=S groups to give CF_2, OCF_2, CF_3, and OCF_3 compounds in high yields. Reactions of **2** with diols or bis(trimethylsilyl) derivatives of diols or amino alcohols provided the corresponding deoxofluoro-arylsulfinylation products in high yields. In addition, it has been found that chlorotetrafluorides **1** directly and effectively react with the sulfur compounds to give the corresponding fluoro compounds in high yields. Since they are the intermediates for the production of industrially useful arylsulfur pentafluorides, arylsulfur chlorotetrafluorides **1**, in particular, phenylsulfur chlorotetrafluoride (**1a**) are expected to find use as inexpensive and versatile deoxo- and dethioxo-fluorinating agents for the preparation of many organofluoro compounds.

1. Introduction

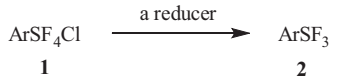
Fluorine has the highest electronegativity and the smallest atomic radius after the hydrogen atom, and the carbon–fluorine bond is one of the strongest. Accordingly, introducing fluorine to an organic molecule brings about remarkable changes in the original properties of the molecule. Therefore, fluorine has been attracting many researchers particularly in medicinal, agrochemical, and new-material chemistries to seek more novel chemicals in their fields [1]. Among fluorination strategies, deoxo- and dethioxo-fluorination methods have been chosen as among the most effective. Therefore, many deoxo- or dethioxo-fluorinating agents have been developed. Gaseous sulfur tetrafluoride (SF_4) [2], liquid dialkylaminosulfur trifluorides such as Et_2NSF_3 (DAST) [3] and $(MeOCH_2CH_2)_2NSF_3$ (Deoxo-Fluor) [3c,4], α,α-difluoroalkylamines such as $CHFClCF_2NEt_2$ (Yarovenko reagent) [5], $CF_3CHFCF_2NEt_2$ (Ishikawa reagent) [6], $CHF_2CF_2NMe_2$ [7], 2,2-difluoro-1,3-dimethylimidazolidine (DFI) [8], and *N*,*N*-diethyl-α,α-difluoro-(*m*-methylbenzyl)amine [9] have been developed. However, these reagents have significant drawbacks such as toxic gas, explosive nature, or limited scope due to narrow reactivity. In response to these, the authors have recently reported reactive and crystalline 4-*tert*-butyl-2,6-dimethylphenylsulfur trifluoride (Fluolead) which has high thermal stability, ease of handling due to its relative moisture and water insensitivity, and wide applications including conversions of COOH and OC(S)SMe to CF_3 and OCF_3, and new deoxofluoro-arylsulfinylation [10]. Dialkylamidodifluorosulfinium tetrafluoroborates such as XtalFluor-E and -M have also been developed as improved version of DAST recently [11].

We have recently discovered the first practical production method for arylsulfur pentafluorides ($ArSF_5$) [12], which have long been desired in academic and industrial fields because $ArSF_5$ has been considered to be "super-trifluoromethyl" arenes as the SF_5 group has the peculiarity of additional fluorine beyond the trifluoromethyl (CF_3) group [13]. The trifluoromethyl arenes have already grown up into a significant large chemistry and industry [1,14] since their production method was developed in 1930s–1940s [15]. The unusual properties of SF_5 group have been attracting many chemists in medicinal, agrochemical, and new material chemistries [13,16,17]. The practical production method for the $ArSF_5$ developed by us [12] consists of two steps, (step 1) treatment of a diaryl disulfide or aryl thiol with chlorine and potassium fluoride [18], and (step 2) treatment of the resulting

☆ This was presented at 242nd ACS National Meeting at Denver, Colorado, in August 28–September 1, 2011.

* Corresponding author. Tel.: +1 303 412 5650.
E-mail address: teruoumemoto@comcast.net (T. Umemoto).
[1] Current address: Boulder Ionics Corporation, Colorado, USA.
[2] Currently at: Ube America Inc.

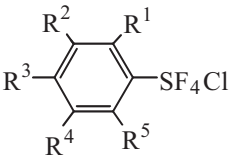
0022-1139/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2012.03.008



Scheme 1. Reduction of $ArSF_4Cl$ **1** to $ArSF_3$ **2**.

arylsulfur chlorotetrafluorides ($ArSF_4Cl$) with ZnF_2, HF, or Sb(III/V) fluorides. By means of this, the $ArSF_5$ can be produced in a commercially practical scale. This means that the intermediate $ArSF_4Cl$ will be produced in a large amount and at low cost in industry. This article describes the usefulness of the intermediate chemicals, $ArSF_4Cl$, as new, inexpensive, and versatile deoxo- and dethioxo-fluorinating agents.

2. Results and discussion



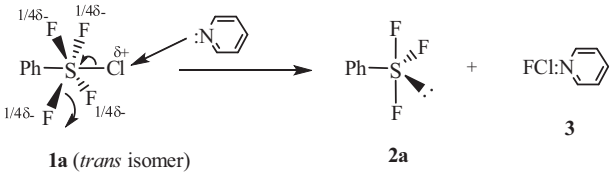
1

1a: $R^{1\text{-}5}$=H
1b: R^3=CH_3, $R^{1,2,4,5}$=H
1c: R^3=*tert*-Bu, $R^{1,2,4,5}$=H
1d: R^3=F, $R^{1,2,4,5}$=H
1e: R^3=Cl, $R^{1,2,4,5}$=H
1f: R^2=Br, $R^{1,3\text{-}5}$=H
1g: R^3=Br, $R^{1,2,4,5}$=H
1h: R^3=NO_2, $R^{1,2,4,5}$=H

2.1. Reduction of arylsulfur chlorotetrafluoride 1 to arylsulfur trifluoride 2

Phenylsulfur chlorotetrafluoride (**1a**) did not react with *n*-dodecanol, benzaldehyde, or benzoic acid in dichloromethane at room temperature for 24 h. Thus, we investigated the possibility of the *in situ* generation of reactive arylsulfur(IV) trifluorides **2** from arylsulfur(VI) chlorotetrafluorides **1** by reduction with a reducing compound (Scheme 1).

As phenylsulfur trifluoride (**2a**) which is extremely moisture-sensitive readily reacted with a carboxylic acid to produce a carbonyl fluoride quantitatively, we sought a suitable reducer by allowing **1a** to react with a reducer in the presence of benzoic acid in dichloromethane as seen in Table 1. We found that **1a** was readily reduced to **2a** under very mild conditions with various kinds of organic compounds or a combination of metals and a tetrabutylammonium iodide. The reaction of the metals was very slow without the ammonium iodide. The organics used (runs 2–4,6,7 Table 1) provided a quantitative yield of benzoyl fluoride, indicating that **2a** was quantitatively formed from **1a** by the reaction with the organics. Actually, **2a** was isolated in 88% yield by treatment of **1a** with an equimolar amount of pyridine in dichloromethane at room temperature for 1.5 h, followed by careful distillation at reduced pressure in dry atmosphere.



1a (*trans* isomer) **2a** **3**

Scheme 2. Formation of **2a** and possible pyridine ClF complex **3** from **1a** and pyridine.

With anthracene (run 4, Table 1), we observed the formation of 9-chloro- and 9,10-dichloroanthracenes by GC–Mass of the reaction mixture, which resulted from the electrophilic chlorination of anthracene. This indicates that **1a** reacted with anthracene (*C*-nucleophile) to give the chlorinated anthracenes and **2a**, which reacted with benzoic acid to give benzoyl fluoride.

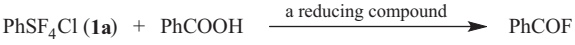
With pyridine which is *N*-nucleophile (run 2, Table 1), it is most likely that **1a** reacted with pyridine to give Py·ClF complex **3** (Py = pyridine) along with **2a** as shown in Scheme 2. It is well known that interhalogen compounds form complexes with *N*-nucleophiles such as pyridine [19]. Recent theoretical studies have revealed the structure and nature of the Py·ClF as a stable complex [20].

The reaction of **1a** with an equimolar amount of pyridine in dichloromethane without benzoic acid was traced by ^{19}F NMR. The NMR measured after 1 h showed two peaks of 2:1 integral ratio at 57.2 and −39.6 ppm and a broad peak at −168 ppm. The former two peaks were assigned to **2a**. The latter might be assigned to complex **3**. Benzoic acid was then added to the reaction solution and the ^{19}F NMR measured after 30 min showed that benzoyl fluoride was formed and that the broad peak at −168 ppm remained intact. Although we did not examine the complex **3** more, it may thus be regarded that extremely reactive ClF [21] is deactivated by the *N*-nucleophile.

2.2. Fluorination of various substrates with arylsulfur trifluoride 2 in situ prepared from arylsulfur chlorotetrafluoride 1 and pyridine

Next, we examined the fluorinations of various substrates using the arylsulfur trifluorides **2** *in situ* prepared from **1** with a reducer.

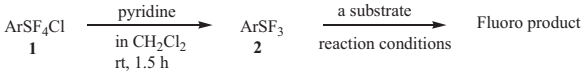
Table 1
Reactions of $PhSF_4Cl$ (**1a**) with reducers in the presence of benzoic acid.



Run[a]	**1a** (mmol)[b]	Reducing compound (mmol)[c]	Reaction conditions[d]	Yield (%) of PhCOF[e]
1	1.0	Non	DCM (2 mL), rt, 1.5 h	No reaction[f]
2	1.0	Pyridine (1.0)	DCM (2 mL), rt, 1.5 h	quant.
3	1.1	$Et_3N(HF)_3$ (1.1)	DCM (2 mL), rt, 6 h	quant.
4	1.0	Anthracene (1.0)	DCM (2 mL), rt, 5 h	quant.
5	1.0	Aniline (1.0)	DCM (2 mL), rt, 5 h	95
6	1.0	2,3-Dimethyl-2-butene (1.0)	DCM (2 mL), rt, 1.5 h	quant.
7	1.0	PhSPh (1.0)	DCM (2 mL), rt, 1.5 h	quant.
8	2.53	Mg (2.52), TBAI (cat)	THF (4 mL), rt, 3 h	93 (82)
9	1.75	Sn (1.75), TBAI (cat)	THF (4 mL), rt, 2 h	84

[a] An equimolar amount of benzoic acid to **1a** was used except for run 3 in which 0.91 equimolar amounts of benzoic acid to **1a** was used.
[b] The amounts (mmol) of **1a** used.
[c] The numbers in parentheses are amounts (mmol) of reducing compounds used. cat = catalytic amount.
[d] DCM = dichloromethane. rt = room temperature. The amounts (mL) of the solvents used are shown in parentheses.
[e] Yields were determined by ^{19}F NMR and calculated based on the amount of benzoic acid used. quant. = quantitative yield. The number in parentheses is an isolated yield.
[f] A small amount of PhCOF was detected, which was formed by the reaction of PhCOOH with a small amount of $PhSF_3$ (**2a**) containing as an impurity in **1a**.

Table 2
Fluorinations with $ArSF_3$ *in situ* prepared from $ArSF_4Cl$ and pyridine.



Run[a]	**1** (mmol)[b]	Substrate (mmol)[c]	Reaction conditions[d]	Fluoro product	Yield (%)[e]
1	**1a** (2.22)	PhCOOH (1.8)	DCM (2 mL), rt, 0.5 h	PhCOF	quant.[f]
2	**1a** (3.84)	n-$C_{12}H_{25}OH$ (2.6)	DCM (2 mL), rt, 20 h HF–Py (0.9 mL)	n-$C_{12}H_{25}F$	86[f]
3	**1a** (3.19)	PhCHO (1.2)	DCM (2 mL), rt, 2 h HF–Py (0.7 mL)	$PhCF_2H$	87[f]
4	**1a** (3.30)	$PhCOCH_3$ (1.32)	DCM (3 mL), rt, 20 h HF–Py (0.8 mL)	$PhCF_2CH_3$	75[f]
5	**1a** (4.2)	n-$C_{10}H_{21}COCH_3$ (1.32)	DCM (2 mL), rt, 20 h HF–Py (0.8 mL)	n-$C_{10}H_{21}CF_2CH_3$	86[f]
6	**1a** (3.5)	Cyclohexanone (1.4)	DCM (2 mL), rt, 2 h HF–Py (0.8 mL)	1,1-diF-cyclohexane	94[f]
7	**1a** (6.0)	PhCOCOPh (1.5)	DCM (3 mL), rt, 25 h HF–Py (1.15 mL)	$PhCF_2CF_2Ph$[h]	95[f]
8	**1a** (2.04)	$(Me_3SiOCH_2)_2$ (2.0)	DCM (6 mL), rt, 2 h	$FCH_2CH_2OS(O)Ph$ (**4**)	80[g]
9	**1b** (5.27)	$(Me_3SiOCH_2)_2$ (5.2)	DCM (6 mL), rt, 2 h	$FCH_2CH_2OS(O)Ar$ (**5**) (Ar = 4-tolyl)	72[g]
10	**1e** (4.44)	$(Me_3SiOCH_2)_2$ (4.3)	DCM (6 mL), rt, 2 h	$FCH_2CH_2OS(O)Ar$ (**6**) (Ar = 4-chlorophenyl)	76[g]

[a] For runs 1–7, pyridine was used in an equimolar amount to $ArSF_4Cl$. For runs 8–10, pyridine was used in two equimolar amounts to $ArSF_4Cl$.
[b] The numbers in parentheses are amounts (mmol) of $ArSF_4Cl$ used.
[c] The numbers in parentheses are the amounts (mmol) of substrates used.
[d] DCM = dichloromethane. HF–Py = 70 wt% HF–pyridine.
[e] Yields were calculated based on substrates. quant. = quantitative yield.
[f] Determined by ^{19}F NMR.
[g] Isolated yields.
[h] See Ref. [2].

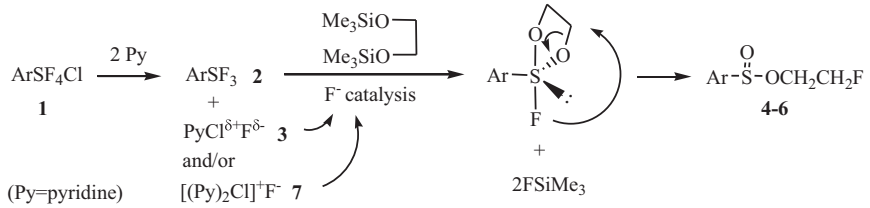
Among the reducers, pyridine was most suitable for actual fluorination reactions from the viewpoint of its availability and the easy removal of the reducer-derived product, probably Py·ClF, in the post-treatment washing with water. After **1** was treated with an equivalent amount of pyridine in dichloromethane at room temperature for 1.5 h, a substrate was added into the dichloromethane solution with an additive if necessary. As shown in Table 2, various substrates were fluorinated in high yields in this manner. Alcohols, aldehydes, ketones, and diketones were fluorinated with addition of a small amount of 70 wt% HF–pyridine to give the corresponding fluorinated compounds in high yields (runs 2–7, Table 2).

1,2-Bis(trimethylsiloxy)ethane was readily fluorinated without any additive to give 2-fluoroethyl arylsulfinates **4**–**6** in high yields (runs 8–10), in which $ArSF_3$ was *in situ* generated from $ArSF_4Cl$ with two equimolar amounts of pyridine. Pure $ArSF_3$ did not react with the bis(trimethylsiloxy)ethane without a fluoride anion catalyst. Thus, it is most likely that the bis(trimethylsiloxy)ethane reacted with $ArSF_3$ by activation of a fluoride anion from the complex $Py{\cdot}Cl^{\delta+}F^{\delta-}$ **3** and/or bis(pyridine)chloronium fluoride **7** to give products **4**–**6** through a cyclic intermediate followed by fluoride rearrangement [10a], as shown in Scheme 3. As the Cl^+ cation may have two-coordination with *N*-nucleophile [22], the latter **7** might be formed by the action of two molecules of pyridine to **1** or one molecule of pyridine to **3**.

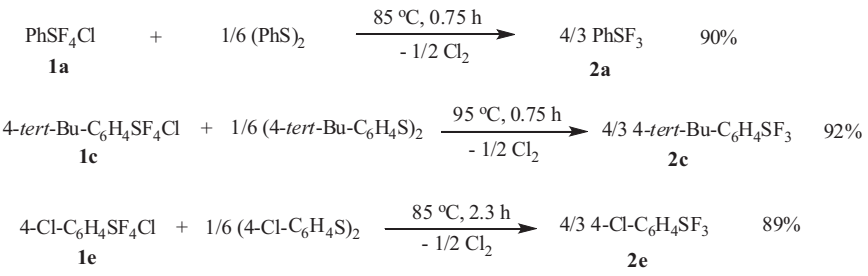
2.3. Preparation of neat arylsulfur trifluoride 2 by disproportionation of arylsulfur chlorotetrafluoride 1 with 1/6 diaryl disulfide

The *in situ* preparation mentioned above provides a mixture of $ArSF_3$ **2** and the other product which results from the reducer. The separation and purification of **2** from the reducer-derived product is another problem because **2** is extremely moisture-sensitive. Our studies on the reactivity of **2** have revealed that *neat* **2** has a strong fluorination capability including direct conversion of a COOH to a CF_3 group. Therefore, if neat **2** is *in situ* prepared in a direct manner from $ArSF_4Cl$ **1**, its applicability would be greatly expanded. Thus, according to the following equation (Eq. (1)), we attempted a disproportionation reaction to get neat **2**. As the co-product Cl_2 is gaseous, it can easily be removed from liquid **2**.

$$ArSF_4Cl\ \mathbf{1} + 1/6\ ArSSAr \rightarrow 4/3\ ArSF_3\ \mathbf{2} + 1/2\ Cl_2 \uparrow \quad (1)$$



Scheme 3. Proposed mechanism for the formation of 2-fluoroethyl arylsulfinates **4**–**6**.



Scheme 4. Preparation of $ArSF_3$ **2** from $ArSF_4Cl$ **1** by disproportionation.

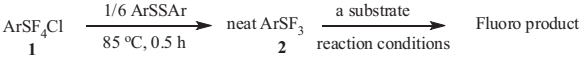
Fortunately the expected reaction cleanly took place around 85 °C to produce $ArSF_3$ **2** and chlorine gas. A concentrated solution of a sixth equimolar amount of diphenyl disulfide in a small amount of dry dichloromethane was added to neat **1a** in a fluoropolymer reactor heated at 85 °C. The reaction soon occurred to evolve chlorine gas. The flow of nitrogen served to remove the chlorine gas and dichloromethane, leaving neat and almost pure **2a** in the reactor.

As seen in Scheme 4, product **2a** was actually isolated after distillation in 90% yield based on the theoretical amount (4/3 times mol). 4-*tert*-Butyl- and 4-chlorophenylsulfur trifluorides **2c** and **2e** were also isolated in excellent yields in the same way. The evolution of chlorine gas was confirmed by passing it through a solution of stilbene in dichloromethane at ice bath temperature to give two isomers of 1,2-dichloro-1,2-diphenylethane in 80% yield, which agreed with an authentic sample produced by reaction of stilbene with chlorine gas. In addition to this simple process to generate neat **2**, this disproportionation method has a significant advantage in that the increased amount (4/3 times mol) of **2** is obtained. In contrast, the reduction method with a reducer gives an equimolar amount of **2** to **1**.

2.4. Fluorinations with various substrates with neat arylsulfur trifluoride 2 in situ prepared by disproportionation

The disproportionation method for neat $ArSF_3$ **2** was successfully applied to fluorination reactions of many kinds of substrates as shown in Table 3. Neat $PhSF_3$ (**2a**) fluorinated alcohols satisfactorily in dichloromethane solvent without 70 wt% HF–pyridine (runs 1 and 2) and carbonyl compounds with a catalytic amount of HF which was generated from the addition of a small amount of ethanol (runs 3 and 4). Aromatic and aliphatic carboxyl groups were converted to the corresponding CF_3 groups in excellent yields by heating a mixture of neat **2a** and 70 wt% HF–pyridine at 50 °C (runs 6 and 10).

Table 3
Fluorinations with $ArSF_3$ *in situ* prepared from $ArSF_4Cl$ and 1/6ArSSAr.

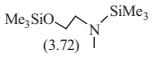
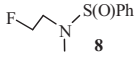
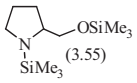
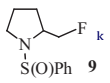


Run	**1** (mmol)[a]	Substrate (mmol)[b]	Reaction conditions[c]	Fluoro product	Yield (%)[d]
1	**1a** (3.95)	*n*-$C_{12}H_{25}OH$ (2.63)	DCM (3 mL), rt, 24 h	*n*-$C_{12}H_{25}F$	80
2	**1a** (2.1)	*n*-$C_{10}H_{21}CH(OH)CH_3$ (1.39)	DCM (3 mL), rt, 24 h	*n*-$C_{10}H_{21}CHFCH_3$	71
3	**1a** (2.72)	PhCHO (1.08)	DCM (2 mL), rt, 2 h EtOH (0.04 mL)	$PhCF_2H$	90
4	**1a** (3.82)	Cyclohexanone (1.5)	DCM (3 mL), rt, 24 h EtOH (0.05 mL)	1,1-diF-cyclohexane	80
5	**1a** (3.68)	PhCOOH (1.22)	DCM (3 mL), rt, 2 h	PhCOF	quant.
6	**1a** (2.63)	PhCOOH (0.87)	No solvent, 50 °C, 24 h, HF–Py (0.6 mL)	$PhCF_3$	90
7	**1b** (4.62)	PhCOOH (1.54)	No solvent, 50 °C, 24 h, HF–Py (1.1 mL)	$PhCF_3$	77
8	**1e** (4.95)	PhCOOH (1.63)	No solvent, 50 °C, 24 h, HF–Py (1.3 mL)	$PhCF_3$	98
9	**1a** (4.65)	PhCOCl (1.55)	No solvent, 50 °C, 24 h, HF–Py (1.2 mL)	$PhCF_3$	90
10	**1a** (3.94)	*n*-$C_{11}H_{23}COOH$ (1.30)	No solvent, 50 °C, 24 h, HF–Py (0.9 mL)	*n*-$C_{11}H_{23}CF_3$	96
11	**1a** (3.38)	PhCH[–$S(CH_2)_3S$–] (2.25)	DCM (4 mL), rt, 2 h	$PhCF_2H$	99
12	**1a** (2.43)	PhC(=S)OCH_3 (0.97)	DCM (2 mL), rt, 3 h	$PhCF_2OCH_3$[e]	98
13	**1a** (4.35)	*n*-$C_{10}H_{21}OC(=S)SCH_3$ (1.45)	DCM (4 mL), rt, 3 h	*n*-$C_{10}H_{21}OCF_3$[f]	90

[a] The numbers in parentheses are amounts (mmol) of $ArSF_4Cl$ used.
[b] The numbers in parentheses are amounts (mmol) of substrates used.
[c] DCM = dichloromethane. EtOH = ethanol. HF–Py = 70 wt% HF–pyridine.
[d] Yields were calculated based on substrates and determined by ^{19}F NMR. quant. = quantitative yield.
[e] See Ref. [26].
[f] See Ref. [29e].

Table 4
Fluorinations of various substrates with $PhSF_3$ (**2a**).

$PhSF_3$ (**2a**) + substrate → (reaction conditions) Fluoro product

Run	**2a**[a] (mmol)	Substrate (mmol)[b]	Reaction conditions[c]	Fluoro product[d]	Yield (%)[e]
1	2.7	PhCOOH (1.08)	No solvent, 100 °C, 2 h (sealed reactor)	$PhCF_3$	90[f]
2	1.8	PhCOOH (0.72)	No solvent, 100 °C, 2 h (open reactor)	$PhCF_3$	28[f]
3	6.4	PhCOOH (2.1)	No solvent, 100 °C, 24 h (open reactor)	$PhCF_3$	49[f]
4	2.0	PhCOF (0.80)	No solvent, 100 °C, 2 h (sealed reactor)	$PhCF_3$	~1[f,h]
5	1.92	*n*-$C_{11}H_{23}COOH$ (0.77)	No solvent, 100 °C, 2 h (sealed reactor)	*n*-$C_{11}H_{23}CF_3$	83[f]
6	3.19	1,3-$Ph(COOH)_2$ (0.70)	No solvent, 100 °C, 2 h (sealed reactor)	1,3-$Ph(CF_3)_2$	93[f]
7	4.10	PhC(=S)Ph (1.64)	DCM (1 mL), rt, 2 h	$PhCF_2Ph$	quant.[f]
8	2.55	*n*-$C_7H_{15}C(=S)OCH_3$ (1.66)	DCM (3 mL), rt, 20 h	*n*-$C_7H_{15}CF_2OCH_3$[i]	80[f]
9	1.59	PhC(=S)SCH_3 (0.31)	No solvent, 70 °C, 22 h (sealed reactor)	$PhCF_3$	85[f]
10	3.16	2-Py–$N(CH_3)C(=S)SCH_3$ (1.26)	No solvent, rt, 24 h	2-Py–$N(CH_3)CF_3$[j]	98[f]
11	2.49	$HOCH_2CH_2OH$ (2.49)	DCM (5 mL), −78 °C → rt, 3 h	$FCH_2CH_2OS(O)Ph$ (**4**)	80[g]
12	2.98	$Me_3SiOCH_2CH_2OSiMe_3$ (2.98)	DCM (4 mL), rt, 2 h, Bu_4NF (cat)	**4**	84[g]
13	3.72	 (3.72)	DCM (5 mL), rt, 1 h	 **8**	91[g]
14	3.55	 (3.55)	DCM (5 mL), rt, 3 h	 **9**	78[g]

[a] $PhSF_3$ (**2a**) which was purified by distillation, was used in these runs. The numbers are amounts (mmol) of $PhSF_3$ used.
[b] The numbers in parentheses are amounts (mmol) of substrates used.
[c] DCM = dichloromethane. cat = catalytic amount.
[d] Py = pyridyl.
[e] Yields were calculated based on the substrates used. quant. = quantitative yield.
[f] Determined by ^{19}F NMR.
[g] Isolated yields.
[h] 95% of PhCOF (a starting material) remained unreacted.
[i] See Ref. [26].
[j] Methyl(2-pyridyl)(trifluoromethyl)amine: see Ref. [29c].
[k] Product **9** was assigned a 86:14 mixture of two diastereomers.

Neat 4-methyl **2b** and 4-chloro **2e** generated *in situ* from **1b** and **1e**, respectively, similarly converted carboxyl groups to CF_3 groups in high yields (runs 7 and 8). A carbonyl chloride was also converted to a CF_3 compound in an excellent yield (run 9). **2a** fluorinated various sulfur compounds in dichloromethane solvent at room temperature to give the corresponding desulfur fluoro compounds in excellent yields (runs 11–13). The reaction of **2a** with *O*-alkyl *S*-methyl dithiocarbonate proceeded well at room temperature without any catalyst (run 13), while Fluolead needed $SbCl_3$ as a catalyst for the smooth reaction [10a].

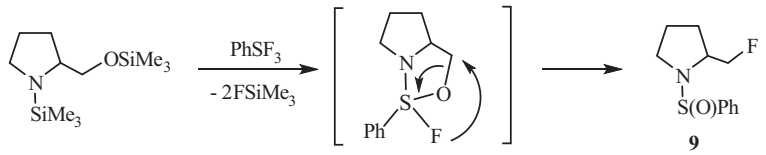
2.5. Additional examination on reactivity of phenylsulfur trifluoride (2a)

Table 4 shows the results of our further investigation on the reactivity of $PhSF_3$ (**2a**). When a mixture of **2a** and benzoic acid was heated without solvent or additives in a sealed reactor at 100 °C for 2 h, benzotrifluoride was obtained in 90% yield (run 1). However, when it was conducted in an open reactor, the yield was only 28% (run 2). The reaction was continued for 24 h, but the yield was still low (49%, run 3). Thus, the reaction was very slow in the open reactor for this case.

The conversion of COOH to CF_3 consists of two steps as shown in Scheme 5. The first reaction readily occurs at room temperature, giving benzoyl fluoride and HF, and the second reaction requires elevated temperature. The open reactor at elevated temperature allowed HF to exit from the reaction solution because of its low boiling point. Thus, the above results suggested that HF generated at the first step acts as an important catalyst for the second fluorination. As shown in run 4, the reaction of benzoyl fluoride with **2a** in which there is no HF did not provide the product, but the starting material mostly remained unreacted. This clearly demonstrated that HF is essential for the second fluorination. The sealing method was thus successfully applied to an alkyl carboxylic acid and an aryl dicarboxylic acid, and the respective corresponding trifluoromethyl compounds were obtained in high yields, as seen in runs 5 and 6, Table 4.

PhCOOH —(step 1: $ArSF_3$, - ArS(O)F)→ PhCOF + HF —(step 2: $ArSF_3$, - ArS(O)F)→ $PhCF_3$

Scheme 5. Stepwise fluorination of carboxylic acids with $ArSF_3$ **2**.



Scheme 6. Proposed mechanism for exclusive formation of product **9**.

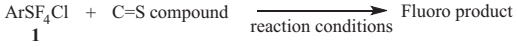
2a fluorinated thiocarbonyl compounds under mild conditions to give CF_2 compounds in high yields (runs 7 and 8). A *C*-dithioester was fluorinated by **2a** at 70 °C without solvent to give a CF_3 compound in high yield (run 9). A *N*-dithioester was fluorinated at room temperature to give a *N*-CF_3 compound in excellent yield (run 10). **2a** reacted with ethylene glycol to give 2-fluoroethyl benzenesulfinate (**4**) in high yield (run 11). The reaction of **2a** with 1,2-bis(trimethylsiloxy)ethane proceeded in the presence of a catalytic amount of fluoride anion to give **4** in high yield (run 12).

With bis(trimethylsilyl) derivative of an amino alcohol, the reaction of **2a** readily proceeded without the catalyst to give a fluoroalkyl benzenesulfinamide derivative **8** in 91% yield (run 13). Bis(trimethylsilyl) derivative of 2-(hydroxymethyl)pyrrolidine reacted with **2a** to exclusively give 2-fluoromethyl-*N*-benzenesulfinylpyrrolidine (**9**) in 78% yield (run 14). A 3-fluoropiperidine derivative was not formed in this reaction. The ^{19}F NMR showed two triplet-doublet signals corresponding to CH_2F at C-2 position in a 86:14 ratio. We assigned the product **9** as a mixture of two diastereomers based on two asymmetric centers at C-2 carbon and the sulfur atom, because our detailed studies have demonstrated that a mixture of two diastereomers is formed when an arylsulfur trifluoride reacts with an amino alcohol having an asymmetric center such as 3-hydroxypyrrolidine [10a].

All the reported fluorinations of 2-(hydroxymethyl)pyrrolidine derivatives were accompanied with the formation of the ring expansion products, 3-fluoropiperidine derivatives, which was explained to be formed *via* an azirinium intermediate [23]. To our knowledge, our reaction with **2a** is the first case which exclusively provided the non-ring expansion product **9**. This exclusive formation can clearly be explained by a cyclic intermediate [10a] as shown in Scheme 6. Interestingly, Fluolead did not react with the bis(trimethylsilyl) derivative of 2-(hydroxymethyl)pyrrolidine under the same reaction conditions, presumably due to its steric hindrance by the 2,6-dimethyl groups of Fluolead.

According to the paper reported by Sheppard in 1962 [24], the fluorination capability of phenylsulfur trifluoride (**2a**) was poor. Probably, in addition to the humid climate of the east coast, the reason was that no solvent or no effective catalyst was used for the fluorination of aldehydes and ketones and an unsuitable open reactor probably was used for the fluorination of carboxylic acids at high temperature. As discussed above, sealing a reactor is a significant factor to retain HF as a catalyst for the second step fluorination. Fluorination of alcohols might not be attempted, probably as it was thought at that time that $PhSF_3$ could not work well like SF_4 [25].

Table 5
Fluorinations of various thiocarbonyl compounds with $ArSF_4Cl$.



Run	**1** (mmol)[a]	C=S compound (mmol)[b]	Reaction conditions[c]	Product[d]	Yield (%)[e]
1	**1a** (2.0)	*n*-$C_{10}H_{21}OC(=S)SCH_3$ (2.0)	DCM (3 mL) rt, 5 h	*n*-$C_{10}H_{21}OCF_3$	99 (90)
2	**1b** (2.96)	*n*-$C_{10}H_{21}OC(=S)SCH_3$ (2.96)	DCM (3 mL) rt, 5 h	*n*-$C_{10}H_{21}OCF_3$	73
3	**1b** (3.21)	*n*-$C_{10}H_{21}OC(=S)SCH_3$ (2.24)	DCM (3 mL) rt, 4h	*n*-$C_{10}H_{21}OCF_3$	quant. (87)
4	**1d** (2.77)	*n*-$C_{10}H_{21}OC(=S)SCH_3$ (2.77)	DCM (3 mL) rt, 5 h	*n*-$C_{10}H_{21}OCF_3$	quant. (89)
5	**1e** (2.65)	*n*-$C_{10}H_{21}OC(=S)SCH_3$ (2.65)	DCM (3 mL) rt, 5 h	*n*-$C_{10}H_{21}OCF_3$	quant. (91)
6	**1f** (2.0)	*n*-$C_{10}H_{21}OC(=S)SCH_3$ (2.0)	DCM (3 mL) rt, 5 h	*n*-$C_{10}H_{21}OCF_3$	quant. (89)
7	**1g** (2.93)	*n*-$C_{10}H_{21}OC(=S)SCH_3$ (2.93)	DCM (3 mL) rt, 5 h	*n*-$C_{10}H_{21}OCF_3$	quant. (90)
8	**1h** (2.31)	*n*-$C_{10}H_{21}OC(=S)SCH_3$ (2.31)	DCM (2 mL) rt, 5 h	*n*-$C_{10}H_{21}OCF_3$	quant. (92)
9	**1a** (7.5)	PhC(=S)Ph (5.0)	DCM (10 mL) rt, 5 h	$PhCF_2Ph$	quant. (90)
10	**1a** (15)	Cyclohexyl-C(=S)OCH_3 (10)	DCM (10 mL) rt, 5 h	Cyclohexyl-CF_2OCH_3[f]	95 (81)
11	**1a** (1.34)	$PhC(=S)SCH_3$ (0.53)	DCM (3 mL) rt, 20 h	$PhCF_3$	99
12	**1a** (7.5)	2-Py–$N(CH_3)C(=S)SCH_3$ (5.0)	DCM (10 mL) rt, 48 h	2-Py–$N(CH_3)(CF_3)$[g]	90 (80)

[a] The numbers in parentheses are amounts (mmol) of $ArSF_4Cl$ used.
[b] The numbers in parentheses are amounts (mmol) of C=S compounds used.
[c] DCM = dichloromethane.
[d] Py = pyridyl.
[e] Determined by ^{19}F NMR. The numbers in parentheses are isolated yields. Yields were calculated based on C=S compounds. quant. = quantitative yield.
[f] See Ref. [26].
[g] Methyl(2-pyridyl)(trifluoromethyl)amine: see Ref. [29c].

As seen in Tables 2–4, our extensive studies on the reactivity of **2a** have revealed that **2a** has an excellent fluorinating capability for many kinds of substrates, though **2a** is an extremely moisture-sensitive liquid and has a somewhat unpleasant odor. The *in situ* preparation methods reported here work very well as the corresponding chlorotetrafluoride **1a** is much more easily prepared and handled and the moisture-sensitive **2a** is not exposed to air.

2.6. Fluorinations of various thiocarbonyl compounds with arylsulfur chlorotetrafluorides 1

Besides DAST [26], Deoxo-fluor [4c], and Fluolead [10a], BrF_3 [27], difluoroiodotoluene [28], and *N*-halo imide/HF–pyridine [29] have been known as dethioxofluorinating agents for thioketones, thioesters, or dithiocarbonates. Anodic *gem*-difluorination of thioacetals has also been reported [30]. The dethioxofluorination with DAST or Deoxo-fluor requires a catalyst such as $SbCl_3$.

As seen in Table 5, we have found that arylsulfur chlorotetrafluorides **1** themselves are excellent dethioxofluorinating agents for various thiocarbonyl compounds without any catalyst. A dithiocarbonate was treated with an equimolar amount of **1a** to give a CF_3O compound almost quantitatively (run 1, Table 5). It was remarkable that the one equimol of **1a** was enough to give the product quantitatively, while $PhSF_3$ (**2a**) required its 3 equimol for the high yield fluorination (run 13, Table 3). This is due to higher sulfur valency (VI) of $ArS^{VI}F_4Cl$ than $ArS^{IV}F_3$.

However, with *p*-methyl derivative **1b**, one equimol amount was not enough and 1.4 equimol was needed to get a quantitative yield of the product (runs 2 and 3, Table 5). Thus, the electron-donating methyl substituent of **1b** decreases the fluorination capability compared to unsubstituted **1a**. Halogenated derivatives **1d**–**g** and nitro **1h** provided quantitative yields with one equimolar amount of each of them (runs 4–8).

1a quantitatively converted a thioketone to the corresponding CF_2 compound (run 9) under mild conditions. A thioester was similarly converted to the OCF_2 compound in high yield (run 10). **1a** converted a *C*-dithioester to a *C*-CF_3 compound almost quantitatively at room temperature (run 11), while $PhSF_3$ (**2a**) needed 70 °C without solvent for the conversion (run 9, Table 4). A *N*-dithioester was similarly converted by **1a** to a *N*-CF_3 compound in high yield (run 12). Thus, the successful fluorination reactions of various thiocarbonyl compounds at mild conditions have demonstrated the excellent dethioxofluorination capability of $ArSF_4Cl$ **1**. However, as **1** has a considerable oxidation power, oxidation process other than the dethioxofluorination may precede in the reaction of **1** with a sulfur compound having a more oxidizable group than the sulfur group.

3. Conclusion

We have demonstrated the useful deployment of arylsulfur chlorotetrafluorides **1** as versatile deoxo- and dethioxo-fluorinating agents. There have been developed two methods to *in situ* prepare reactive arylsulfur trifluorides **2** from **1**. The one is the reduction method and the other is the disproportionation method. The former is a convenient process to generate **2**, though the reducer-derived product is formed together. The latter is a convenient process to give neat **2** because the side product, Cl_2, is easily removed as a gas. The arylsulfur trifluorides **2** successfully fluorinated many kinds of oxygen compounds such as alcohols, aldehydes, ketones, diketones, carboxylic acids, diols, and aminoalcohols, and sulfur compounds such as thioacetals, thioketones, thioesters, dithioesters, and dithiocarbonates. In addition, it has been shown that the chlorotetrafluorides **1** directly and effectively react the sulfur compounds to give the corresponding fluoro compounds in high yields. Since they are the intermediates for the production of industrially useful arylsulfur pentafluorides ($ArSF_5$), arylsulfur chlorotetrafluorides **1**, in particular, phenylsulfur chlorotetrafluoride (**1a**), will be available as inexpensive and useful deoxo- and dethioxo-fluorinating agents for the commercial production of many organofluoro compounds as the $ArSF_5$ industry develops.

4. Experimental

4.1. General

All the fluorination reactions were performed under anhydrous conditions in an atmosphere of N_2 with oven-dried fluoropolymer vessels. As arylsulfur trifluorides especially are very sensitive to moisture, their preparation and reactions must be conducted under very dry atmosphere. It is noted that Denver, Colorado has a very dry climate, and at the seasons when experiments were carried out its humidity is less than ca. 20% inside building (the lowest is ~6% in winter). Dichloromethane as a solvent for the fluorination reactions was dried over calcium hydride and distilled before use. THF was dried by distillation over lithium aluminum hydride. Arylsulfur chlorotetrafluorides (*trans*-isomers) **1** were prepared from diaryl disulfides by the method reported by us [12]. The thiocarbonyl compounds were prepared by literature procedures [26,29c–e]. Chemicals were purchased and used without prior purification unless otherwise noted. ^1H, ^{19}F and ^{13}C NMR spectra were recorded on a JEOL using a deuterium solvent at 300.52, 282.78, and 75.56 MHz, respectively. Chemical shifts are reported in ppm with TMS as internal standard ($\delta = 0.00$); ^{19}F, $CFCl_3$ ($\delta = 0.00$). IR spectra were recorded on a Perkin Elmer Spectrum™ RX FT-IR spectrometer. GC–MS analysis was performed on Agilent GC 6890 N and MS 5973 N with SPB™-1 Capillary Column 60 m × 0.25 mm × 0.25 mm film thickness and column condition: 80 °C. Keep 2 min, then 10 °C/min to 250 °C, keep 21 min.

4.2. Treatment of $ArSF_4Cl$ 1 with a reducing compound in the presence of benzoic acid

A typical procedure: 79 mg (1 mmol) of pyridine was added to a stirred solution of 221 mg (1 mmol) of phenylsulfur chlorotetrafluoride (**1a**) and 122 mg (1 mmol) of benzoic acid in 2 mL of dry dichloromethane (CH_2Cl_2) in a fluoropolymer (PFA) vessel at room temperature. The reaction mixture was stirred for 1.5 h at room temperature and analyzed by ^{19}F NMR. The fluorination with a different reducing compound was conducted in the same manner. Table 1 shows reducing compounds, reaction conditions, and results. The product, benzoyl fluoride, was identified with an authentic sample.

4.3. Isolation of $PhSF_3$ (2a) from reaction of $PhSF_4Cl$ (1a) with pyridine

Pyridine (0.79 g, 10 mmol) was added to a stirred solution of 2.21 g (10 mmol) of **1a** in 5 mL of dry CH_2Cl_2 in a fluoropolymer vessel at room temperature. The reaction mixture was stirred at room temperature for 1.5 h. After that, the reaction solvent was removed under vacuum and the residue was distilled under reduced pressure to give 1.46 g (88%) of **2a**; bp 70 °C/10 mmHg; ^{19}F NMR (CD_3CN) δ 57.84 (br.s, 2F), −41.99 (br.s, 1F). *Note*: As arylsulfur trifluorides **2** are extremely moisture-sensitive, the whole process for the isolation of **2** was conducted with minimum contact with air using N_2 flow in a dry atmosphere (humidity is less than 20%). Glassware (Pyrex) was used for distillation of **2**. Fluoropolymer grease, not silicon grease, had to be used for sealing at joints.

4.4. Fluorination of substrates with $ArSF_3$ 2 in situ prepared from $ArSF_4Cl$ 1 and pyridine

A typical procedure: 303 mg (3.84 mmol) of pyridine was added to a stirred solution of 847 mg (3.84 mmol) of **1a** in 2 mL of dry CH_2Cl_2 in a fluoropolymer vessel at room temperature. The reaction mixture was stirred for 1.5 h at room temperature. At this point, ^{19}F NMR of the reaction mixture showed that **2a** was formed. To the reaction mixture, was added 484 mg (2.6 mmol) of *n*-dodecanol and 0.9 mL of 70 wt% HF–pyridine (available from Sigma–Aldrich). The reaction mixture was then stirred for 20 h at room temperature and the ^{19}F NMR analysis showed *n*-dodecyl fluoride was produced in 86% yield. The product was identified with an authentic sample. The fluorination of a different substrate was carried out in a similar way. Table 2 shows substrates, reaction conditions, and results. The known fluorinated compounds were identified by spectral analysis or comparison with authentic samples (runs 1–7).

In run 8, after the reaction, an aq Na_2CO_3 solution was added to the reaction mixture. The mixture was then extracted with CH_2Cl_2 and the organic layer separated was washed with water, dried over anhydrous $MgSO_4$, and filtered. Removal of solvent at reduced pressure gave the product, which was further purified by thin-layered chromatography on silica gel to give pure **4**, yield: 80%, product **4** gradually decomposed on standing at room temperature.

2-Fluoroethyl benzenesulfinate (**4**): oil; ^1H NMR ($CDCl_3$) δ 3.5–3.9 (m, 1H), 4.05–4.30 (m, 1H), 4.3–4.65 (dm, J = 50 Hz, 2H), 7.4–7.55 (m, 3H), 7.6–7.7 (m, 2H); ^{19}F NMR ($CDCl_3$) δ −224.33 (m); ^{13}C NMR ($CDCl_3$) δ 63.0 (d, J = 20.0 Hz), 81.9 (d, J = 172.0 Hz), 125.3, 129.2, 132.5, 144.2.

In runs 9 and 10, the post-treatment was carried out in a similar way as in run 8 to give products **5** and **6**. Their spectral data are shown in the following.

2-Fluoroethyl 4-toluenesulfinate (**5**): yield 72%; oil; ^1H NMR ($CDCl_3$) δ 2.38 (s, 3H), 3.75 (m, 1H), 4.18 (m, 1H), 4.50 (dm, J = 47.5 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H); ^{19}F NMR ($CDCl_3$) δ −224.16 (tt, J = 47.6 Hz, 28.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.6, 62.6 (d, J = 20.2 Hz), 81.9 (d, J = 171.9 Hz), 125.4, 129.9, 142.2, 143.2.

2-Fluoroethyl 4-chlorobenzenesulfinate (**6**): yield 76%; oil; ^1H NMR ($CDCl_3$) δ 3.75 (m, 1H), 4.17 (m, 1H), 4.48 (dm, J = 47.0 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H); ^{19}F NMR ($CDCl_3$) δ −224.07 (tt, J = 47.6 Hz, 28.1 Hz); ^{13}C NMR ($CDCl_3$) δ 63.4 (d, J = 20.2 Hz), 81.8 (d, J = 171.0 Hz), 126.9, 129.5, 138.8, 142.8.

For the final identification, each of the products **4**–**6** of runs 8–10 was derivatized to a known and stable 2-fluoroethyl arylsulfonate by oxidation. A typical procedure: 3-chloroperbenzoic acid (77%) (829 mg, 3.7 mmol) was added to a stirred solution of 684 mg (3.64 mmol) of **4** in 10 mL of CH_2Cl_2. The mixture was stirred at room temperature for 3 h. During the reaction, insoluble 3-chlorobenzoic acid was formed. After that, 5 mL of CH_2Cl_2 was added to the reaction mixture to dissolve the acid and then a satd Na_2CO_3 solution was added. After the mixture was stirred for 20 min, the organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, and filtered. Removal of solvent under reduced pressure gave 2-fluoroethyl benzenesulfonate [31] in 87% yield. ^1H NMR ($CDCl_3$) δ 4.29 (dt, J = 16.0 Hz, 2.4 Hz, 2H), 5.58 (dt, J = 47.0 Hz, 2.4 Hz, 2H), 7.5–7.75 (m, 3H), 7.85–8.0 (m, 2H); ^{19}F NMR ($CDCl_3$) δ −224.52 (tt, J = 45.0 Hz, 28.0 Hz); ^{13}C NMR ($CDCl_3$) δ 68.8 (d, J = 21.0), 80.6 (d, J = 174.0 Hz), 128.0, 129.4, 134.2, 135.7.

2-Fluoroethyl 4-toluenesulfonate [31]: yield 88%; ^1H NMR ($CDCl_3$) δ 3.36 (s, 3H), 4.18 (dm, 2H), 4.52 (dt, J = 47.1 Hz, 4.1 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H); ^{19}F NMR ($CDCl_3$) δ −224.49 (tt, J = 47.7 Hz, 28.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.6, 68.9 (d, J = 20.2 Hz), 80.7 (d, J = 173.4 Hz), 127.9, 130.1, 132.5, 145.4.

2-Fluoroethyl 4-chlorobenzenesulfonate [32]: yield 90%; ^1H NMR ($CDCl_3$) δ 4.27 (dt, J = 24.9 Hz, 4.1 Hz, 2H), 4.55 (dt, J = 47.1 Hz, 4.1 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.81 (d, J = 8.6 Hz, 2H); ^{19}F NMR ($CDCl_3$) δ −224.36 (tt, J = 47.6 Hz, 28.1 Hz); ^{13}C NMR ($CDCl_3$) δ 69.3 (d, J = 20.2 Hz), 80.7 (d, J = 173.0 Hz), 129.2, 129.9, 134.2, 140.9.

4.5. Preparation of $ArSF_3$ 2 by disproportionation of $ArSF_4Cl$ 1 with 1/6 diaryl disulfide

4.5.1. Preparation of $PhSF_3$ (2a) and detection of chlorine (Cl_2) generated

1a (2.18 g, 9.87 mmol) was placed in a fluoropolymer reactor equipped with a condenser made of fluoropolymer, a gas inlet and outlet, and a magnetic stirrer. The reactor was heated on an oil bath of 85 °C, and a solution of 0.359 g (1.64 mmol) of diphenyl disulfide in 1 mL of dry CH_2Cl_2 was added dropwise to a stirred liquid of **1a** for 10 min. Evolution of chlorine gas started after about 15 min. Heating at 85 °C was continued till the evolution of chlorine ceased. It took 0.75 h. After the reaction, the reaction product was distilled under reduced pressure to give 1.96 g (11.8 mmol) of **2a**; bp 70 °C/10 mmHg. Yield was 90% based on the theoretical yield (9.87 × 4/3 = 13.16 mmol). See *Note* in Section 4.3.

The gas evolved during the reaction was passed with a flow of N_2 through a solution of *trans*-stilbene (1.44 g, 8 mmol) in 10 mL of CH_2Cl_2 at ice water temperature. After that, the reaction solution was evaporated up to dryness to give a solid (1.72 g). ^1H NMR and GC–Mass analysis of the solid showed that an about 1.5:1 mixture of two isomers of 1,2-dichloro-1,2-diphenylethane was produced. The NMR and GC–Mass data agreed with the authentic sample which was prepared by reaction of *trans*-stilbene with chlorine gas in a separate experiment. The weight increase of the product (1.72 g) from the starting material (*trans*-stilbene, 1.44 g) was 280 mg (3.94 mmol as Cl_2) which corresponded to the amount of chlorine gas generated. The amount of Cl_2 generated was thus calculated to be at least 80% yield based on the theoretical amount (9.87 × ½ = 4.94 mmol). This experiment confirmed that chlorine (Cl_2) was generated from the disproportionation reaction of **1a** with 1/6 equimolar amount of diphenyl disulfide.

4.5.2. Preparation of 4-tert-butylphenylsulfur trifluoride (2c)

1c (2.77 g, 10 mmol) was reacted with 0.584 g (1.66 mmol) of bis(4-*tert*-butylphenyl) disulfide at 95 °C for 0.75 h in the same way as for **2a** from **1a** and diphenyl disulfide as shown above (Section 4.5.1). Chlorine evolved was removed out of the reactor with a flow of N_2. Evolution of chlorine gas was detected by checking with a paper soaked with an aq KI solution. After the reaction, the reaction product was distilled under reduced pressure to give 2.71 g (12.2 mmol) (92% yield) of **2c**; bp 76 °C/1 mmHg. ^{19}F NMR ($CDCl_3$–Et_2O) δ 55.91 (d, J = 54.5 Hz, 2F), −37.01 (t, J = 54.5 Hz, 1F). See *Note* in Section 4.3.

4.5.3. Preparation of 4-chlorophenylsulfur trifluoride (2e)

1e (2.55 g, 10 mmol) was reacted with 0.477 g (1.67 mmol) of bis(4-chlorophenyl) disulfide at 85 °C for 2.25 h in the same way as for **2a** from **1a** and diphenyl disulfide as shown in Section 4.5.1. Chlorine evolved was removed out of the reactor with a flow of N_2. Evolution of chlorine gas was detected by checking with a paper soaked with an aq KI solution. After the reaction, the reaction product was distilled under reduced pressure to give 2.38 g (11.9 mmol) (89% yield) of **2e**; bp 56 °C/1 mmHg. ^{19}F NMR (CD_3CN) δ 55.59 (br.s, 2F), −40.60 (br.s. 1F). See *Note* in Section 4.3.

4.6. Fluorination of substrates with neat $ArSF_3$ 2 in situ prepared from $ArSF_4Cl$ 1 and 1/6 Ar_2S_2

A typical procedure: a solution of 142 mg (0.65 mmol) of diphenyl disulfide in 0.6 mL of dry CH_2Cl_2 was added dropwise to a stirred liquid of 871 mg (3.95 mol) of **1a** in a fluoropolymer reactor

heated on an oil bath of 85 °C. After the addition, the reaction mixture was stirred for 0.5 h at 85 °C. CH_2Cl_2 (bp 40 °C) and chlorine gas (Cl_2) evolved were removed out of the reactor with help of a flow of nitrogen during the reaction. After the reaction, the reactor was cooled to room temperature. A solution of 489 mg (2.63 mmol) of *n*-dodecanol in 3 mL of dry CH_2Cl_2 was added to the reactor in which neat **1a** left. The reaction mixture was stirred at room temperature for 24 h. ^{19}F NMR analysis of the reaction mixture showed that *n*-dodecyl fluoride was produced in 80% yield. By means of this, many substrates were fluorinated with the neat $ArSF_3$. Table 3 shows substrates, reaction conditions, and results. Products were identified by spectral analysis or comparison with authentic samples.

4.7. Fluorination of substrates with $PhSF_3$ (2a) (isolated)

4.7.1. Fluorination of carboxylic acids in a sealed reactor

A typical procedure: 132 mg (1.08 mmol) of benzoic acid was added portion by portion to 448 g (2.7 mmol) of **2a** in a fluoropolymer (PTFE or FEP) tube (i.d. 5/16″; o.d. 3/8″), the end of which was sealed, at room temperature. Immediately after the addition, the other end of the tube was sealed. When the two reactants were mixed, a mild exothermic reaction occurred. The sealed tube was heated for 2 h in an oil bath of 100 °C. After that, the tube was cooled to room temperature and opened. ^{19}F NMR analysis of the reaction mixture showed that benzotrifluoride was produced in 90% yield. *n*-Dodecanoic acid and isophthalic acid were reacted with **2a** in the same way. Table 4 summarizes substrates, reaction conditions, and results (runs 1,5,6). Products were identified by comparison with authentic samples.

4.7.2. Fluorination of thiocarbonyl compounds

A typical procedure: 264 mg (1.59 mmol) of **2a** and 53.5 mg (0.31 mmol) of methyl dithiobenzoate were put in a fluoropolymer tube, an end of which was sealed, at room temperature, and then the other end of the tube was sealed. The tube was heated in an oil bath of 70 °C for 22 h. After that, the tube was cooled to room temperature and opened. ^{19}F NMR analysis of the reaction mixture showed that benzotrifluoride was produced in 85% yield. Table 4 summarizes substrates, reaction conditions, and results (runs 7–10). Products were identified by comparison with authentic samples or spectral analysis.

4.7.3. Fluorination of ethylene glycol

A solution of 155 mg (2.49 mmol) of ethylene glycol in 2.5 mL of dry CH_2Cl_2 was slowly added to a stirred solution of 414 mg (2.49 mmol) of **2a** in 2.5 mL of dry CH_2Cl_2 cooled at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 3 h. An aq Na_2CO_3 solution was added to the reaction mixture and the mixture was extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, and filtered. Removal of solvent at reduced pressure gave the product, which was further purified by thin-layered chromatography on silica gel to give pure 2-fluoroethyl benzenesulfinate (**4**) as an oil, yield: 80%. The spectral data of **4** are shown in Section 4.4.

4.7.4. Fluorination of 1,2-bis(trimethylsiloxy)ethane

A typical procedure: 495 mg (2.98 mmol) of 1,2-bis(trimethylsiloxy)ethane was added to a solution of 615 mg (2.98 mmol) of **2a** in 6 mL of dry CH_2Cl_2 at room temperature. Into the solution, was added 0.1 mL of 1 M solution of 1 M tetrabutylammonium fluoride in THF (available from Sigma–Aldrich). The reaction mixture was stirred at room temperature for 2 h. The same post-treatment as for the reaction of **2a** with ethylene glycol as shown above (Section 4.7.3) was carried out to give 470 mg (84%) of **4** as an oil. The spectral data of **4** are shown in Section 4.4.

4.7.5. Fluorination of N-methyl-N-trimethylsilyl-[2-(trimethylsiloxy)ethyl]amine

N-Methyl-*N*-trimethylsilyl-[2-(trimethylsiloxy)ethyl]amine (815 mg, 3.72 mmol) was slowly added to a stirred solution of 618 mg (3.72 mmol) of **2a** in 5 mL of dry CH_2Cl_2 in a fluoropolymer vessel at room temperature. The reaction mixture was stirred at room temperature for 1 h, and the reaction mixture was poured into an aq Na_2CO_3 solution and extracted with CH_2Cl_2. The organic layer separated was washed with water, dried over anhydrous $MgSO_4$, and filtered. Removal of solvent at reduced pressure gave 680 mg (91%) of pure *N*-(2-fluoroethyl)-*N*-methyl-benzenesulfinamide (**8**): oil; ^1H NMR ($CDCl_3$) δ 2.54 (s, 3H), 3.2–3.4 (m, 2H), 4.40 (dm, J = 44.0 Hz, 2H), 7.2–7.6 (m, 5H); ^{19}F NMR ($CDCl_3$) δ −220.91 (tt, J = 45.0 Hz, 26.0 Hz); ^{13}C NMR ($CDCl_3$) δ 33.8, 52.8 (d, J = 21.0 Hz), 81.8 (d, J = 170.5 Hz), 126.1, 128.9, 131.0, 143.6.

For the final identification, product **8** was derivatized to known and stable *N*-(2-fluoroethyl)-*N*-methylbenzenesulfonamide (**10**) [33] by oxidation. Oxidation of **8**: 3-chloroperbenzoic acid (77%) (822 mg, 3.67 mmol) was added to a stirred solution of 718 mg (3.57 mmol) of **8** in 10 mL of CH_2Cl_2. The mixture was stirred at room temperature for 3 h. During the reaction, insoluble 3-chlorobenzoic acid was formed. After the reaction, some CH_2Cl_2 was added to dissolve the acid. The reaction mixture was mixed with a satd Na_2CO_3 solution and stirred for 20 min. The organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, and filtered. Removal of solvent at reduced pressure gave 697 mg (90%) of **10**: ^1H NMR ($CDCl_3$) δ 2.74 (s, 3H), 3.25 (dt, J = 25.8 Hz, 24.8 Hz, 2H), 4.45 (dt, J = 47.1 Hz, 4.8 Hz, 2H), 7.30–7.78 (m, 5H); ^{19}F NMR ($CDCl_3$) δ −220.75 (tt, J = 47.7 Hz, 24 Hz); ^{13}C NMR ($CDCl_3$) δ 36.3, 50.3 (d, J = 21.0 Hz), 82.6 (d, J = 170.4 Hz), 127.3, 129.3, 132.9, 137.4.

4.7.6. Fluorination of N-trimethylsilyl-2-(trimethylsiloxymethyl)pyrrolidine

A solution of 858 mg (3.5 mmol) of *N*-trimethylsilyl-2-(trimethylsiloxymethyl)pyrrolidine [34] in 2.5 mL of dry CH_2Cl_2 was slowly added to a stirred solution of 590 mg (3.55 mmol) of **2a** in 2.5 mL of dry CH_2Cl_2 in a fluoropolymer vessel at room temperature. The reaction mixture was stirred at room temperature for 3 h and poured into an aq Na_2CO_3 solution. The mixture was extracted with CH_2Cl_2 and the organic layer separated was washed with water, dried over anhydrous $MgSO_4$, and filtered. Removal of solvent at reduced pressure gave 2-fluoromethyl-*N*-(benzenesulfinyl)pyrrolidine (**9**) in 78% yield. The product was assigned a 86:14 mixture of two diastereomers by its ^{19}F NMR in which two signals were observed at −224.01 and −224.81 as triplet of doublet. The major isomer was isolated in pure form by thin-layered chromatography on silica gel, but we failed in isolating the minor isomer in pure form. The major isomer: oil; ^1H NMR ($CDCl_3$) δ 1.7–2.2 (m, 4H, 3-H and 4-H), 2.51 (m, 1H, 5-H), 3.38 (m, 1H, 5-H), 4.12 (m, 1H, 2-H), 4.44 (dm, J = 47.1 Hz, 2H, $C\underline{H_2}F$), 7.35–7.75 (m, 5H, aromatic protons); ^{19}F NMR ($CDCl_3$) δ −224.01 (td, J = 47.5 Hz, 17.3 Hz, $CH_2\underline{F}$); ^{13}C NMR ($CDCl_3$) δ 25.0, 28.4, 42.1, 60.5 (d, J = 20.2 Hz), 84.8 (d, J = 174.1 Hz), 125.8, 128.9, 130.7, 144.4. The minor isomer: ^{19}F NMR ($CDCl_3$) δ −224.81 (td, J = 47.5 Hz, 19.9 Hz, $CH_2\underline{F}$).

For the final identification, **9** (major isomer) was derivatized to a stable salt of known 2-(fluoromethyl)pyrrolidine [35] by treatment with CF_3COOH/methanol as follows: 4 mL (53 mmol) of trifluoroacetic acid was added to a stirred solution of 1.50 g (6.60 mmol) of **9** in 12 mL of methanol and the mixture was stirred at room temperature for 1 h. After that, all the volatiles were removed at reduced pressure (by vacuum pump) and the obtained

residue was filtered through a short column of silica gel using 30% ethyl acetate/hexane mixture and finally the product was eluted with methanol. Removal of methanol gave a residue, which was then extracted with CH_2Cl_2 and the extract was filtered to remove any silica gel which came with methanol from the silica gel column. Removal of solvent gave 1.26 g (88%) of 2-(fluoromethyl)-pyrrolidinium trifluoroacetate (**12**) as an oil. **12**: ^{1}H NMR ($CDCl_3$) δ 1.5–2.2 (m, 4H, 3-H, 4-H), 3.23 (m, 2H, 5-H), 3.79 (m, 1H, 2H), 4.3–3.8 (m, 2H, C$\underline{H}_2$F), 9.7 (br.s, 2H, N$\underline{H}_2^+$); ^{19}F NMR ($CDCl_3$) δ −75.70 (s, 3F, CF_3), −223.47 (dt, J = 22.0 Hz, 44.0 Hz, 1F, $CH_2\underline{F}$); ^{13}C NMR ($CDCl_3$) δ 23.7 (4-C), 25.5 (d, J = 5.8 Hz, 3-C), 45.7 (5-C), 58.9 (d, J = 18.8 Hz, 2-C), 81.5 (d, J = 176.6 Hz, $\underline{C}H_2F$), 116.7 (quartet, J = 292.6 Hz, CF_3), 162.1 (quartet, J = 34.7 Hz, CO); IR (neat, KBr) 2987, 2780, 1674, 1430, 1202, 1134, 1034, 837, 799, 722, 614 cm^{-1}.

4.8. Fluorination of thiocarbonyl compounds with $ArSF_4Cl$ 1

A typical procedure: a solution of 496 mg (2.0 mmol) of *O*-*n*-decyl *S*-methyl dithiocarbonate in 1 mL of dry CH_2Cl_2 was added slowly to a stirred solution of 441 mg (2.0 mmol) of **1a** in 2 mL of dry CH_2Cl_2 in a fluoropolymer vessel at room temperature. The mixture was stirred at room temperature for 5 h and poured to a satd Na_2CO_3 solution. The mixture was extracted with CH_2Cl_2 and the organic layer separated was washed with water, dried over anhydrous $MgSO_4$, and filtered. Solvent was removed and the residue was distilled at reduced pressure to give 407 mg (90%) of *n*-decyl trifluoromethyl ether. ^{19}F NMR ($CDCl_3$) δ −60.5. Table 5 shows fluorination of various thiocarbonyl compounds with **1** and their reaction conditions and results. Products were identified by spectral analysis or comparison with authentic samples.

Acknowledgement

The authors thank Ube Industries Ltd. for research funding.

References

[1] (a) P. Kirsch, Modern Fluoroorganic Chemistry, Synthesis, Reactivity, Applications, Wiley-VCH, Weinheim, 2004;
(b) K. Uneyama, Organofluorine Chemistry, Blackwell Publishing, Oxford, 2006;
(c) J.-P. Bégué, D. Bonnet-Delpon, Bioorganic and Medicinal Chemistry of Fluorine, John Wiley & Sons, Inc., New York, 2008;
(d) A. Tressaud, G. Haufe, Fluorine and Health: Molecular Imaging, Biomedical Materials and Pharmaceuticals, Elsevier, Amsterdam, 2008;
(e) I. Ojima (Ed.), Fluorine in Medicinal Chemistry and Chemical Biology, Wiley-Blackwell, New York, 2009.
[2] W.R. Hasek, W.C. Smith, V.A. Engelhardt, Journal of the American Chemical Society 82 (1960) 543–551.
[3] (a) W.J. Middleton, Journal of Organic Chemistry 40 (1975) 574–578;
(b) L.N. Markovskii, V.E. Pashinnik, A.V. Kirsanov, Synthesis (1973) 787–789;
(c) For recent review: R.P. Singh, D.T. Meshri, J.M. Shreeve, in: Atta-UrRahman, K.K. Laali (Eds.), Advances in Organic Synthesis, Modern Organofluorine Chemistry–Synthetic Aspects, vol. 2, Bentham Science Publishers Ltd., Hilversum, Netherlands, 2006, pp. 291–326.
[4] (a) G.S. Lal, G.P. Pez, R.J. Pesaresi, F.M. Prozonic, Chemical Communications (1999) 215–216;
(b) G.S. Lal, G.P. Pez, R.J. Pesaresi, F.M. Prozonic, H. Cheng, Journal of Organic Chemistry 64 (1999) 7048–7054;
(c) G.S. Lal, E. Lobach, A. Evans, Journal of Organic Chemistry 65 (2000) 4830–4832.
[5] N.N. Yarovenko, M.A. Raksha, V.N. Shemanina, A.S. Vasileva, Journal of General Chemistry – USSR 27 (1957) 2246.
[6] A. Takaoka, H. Iwakiri, N. Ishikawa, Bulletin of the Chemical Society of Japan 52 (1979) 3377–3380.
[7] V.A. Petrov, S. Swearingen, W. Hong, W.C. Petersen, Journal of Fluorine Chemistry 109 (2001) 25–31.
[8] H. Hayashi, H. Sonoda, K. Fukumura, T. Nagata, Chemical Communications (2002) 1618–1619.
[9] S. Kobayashi, A. Yoneda, T. Fukuhara, S. Hara, Tetrahedron 60 (2004) 6923–6930.
[10] (a) T. Umemoto, R.S. Singh, Y. Xu, N. Saito, Journal of the American Chemical Society 132 (2010) 18199–18205;
(b) R.P. Rajendra, T. Umemoto, Journal of Organic Chemistry 76 (2011) 3113–3121;
(c) Regarding in situ preparation of Fluolead: see W. Xu, H. Martinez, W.R. Dolbier Jr., Journal of Fluorine Chemistry, 132 (2011) 482–488.
[11] (a) F. Beaulieu, L.-P. Beauregard, G. Courchesne, M. Couturier, F. LaFlamme, A. L'Heureux, Organic Letters 11 (2009) 5050–5053;
(b) A. L'Heureux, F. Beaulieu, C. Bennett, D.R. Bill, S. Clayton, F. LaFlamme, M. Mirmehrabi, S. Tadayon, D. Tovell, M. Couturier, Journal of Organic Chemistry 75 (2010) 3401–3411.
[12] (a) T. Umemoto, Presentation at the Joint International Conference of the 19th International Symposium on Fluorine Chemistry and International Symposium on Fluorous Technologies, Wyoming, August 2009.
(b) T. Umemoto, L.M. Garrick, N. Saito, Beilstein Journal of Organic Chemistry 8 (2012) 461–471.
[13] P. Kirsch, Modern Fluoroorganic Chemistry, Synthesis, Reactivity, Applications, Wiley-VCH, Weinheim, 2004, pp. 146–156.
[14] (a) R.E. Banks (Ed.), Organofluorine Chemicals and their Industrial Applications, Ellis Horwood Ltd., Chichester, 1979;
(b) R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry, Principles and Commercial Applications, Plenum Press, New York, 1994;
(c) T. Hiyama, in: H. Yamamoto (Ed.), Organofluorine Compounds, Chemistry and Applications, Springer, Heidelberg, 2000.
[15] (a) J.H. Simons, C.J. Lewis, Journal of the American Chemical Society 60 (1938) 92;
(b) E. Pouterman, A. Giradet, Helvetica Chimica Acta 30 (1947) 107;
(c) E.T. McBee, H.B. Haas, P.E. Weiner, G.M. Rothrock, W.E. Burt, R.M. Robb, A.R. Van Dyken, Industrial and Engineering Chemistry 39 (1947) 298.
[16] A review: R.W. Winter, R.A. Dodean, G.L. Gard, in: V.A. Soloshonok (Ed.), Fluorine-containing Synthons – ACS Symposium Series, vol. 911, American Chemical Society, Washington, DC, 2005, pp. 87–118 (Chapter 4).
[17] Recent papers: (a) Y. Huang, G.L. Gard, J. Shreeve. Tetrahedron Letters, 51 (2010) 6951-6954
(b) T. Mo, X. Mi, E.E. Milner, G.S. Dow, P. Wipf, Tetrahedron Letters 51 (2010) 5137–5140;
(c) W.R. Dolbier Jr., Z. Zheng, Journal of Fluorine Chemistry 132 (2011) 389–393;
(d) R. Gujjar, F.E. Mazouni, K.L. White, J. White, S. Creason, D.M. Shackleford, X. Deng, W.N. Charman, I. Bathurst, J. Burrows, D.M. Floyd, D. Matthews, F.S. Buckner, S.A. Charman, M.A. Phillips, P.K. Rathod, Journal of Medicinal Chemistry 54 (2011) 3935–3949;
(e) J.M. Coteron, M. Marco, J. Esquivias, X. Deng, K.L. White, J. White, M. Koltun, F.E. Mazouni, S. Kokkonda, K. Katneni, R. Bhamidipati, D.M. Shackleford, I. Angulo Barturen, S.B. Ferrer, M.B. Jiménez-Díaz, F.-J. Gamo, E.J. Goldsmith, W.N. Charman, I. Bathurst, D. Floyd, D. Matthews, J.N. Burrows, P.K. Rathod, S.A. Charman, M.A. Phillips, Journal of Medicinal Chemistry 54 (2011) 5540–5561.
[18] V.E. Pashinnik, E.G. Martyniuk, M.R. Tabachuk, Yu. G. Shermolovich, L.M. Yagupolskii, Synthetic Communications 33 (2003) 2505–2509.
[19] (a) A.J. Downs, C.J. Adams, in: J.C. Bailar, H.J. Elemeleus, S.R. Nyholm, A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, vol. 2, Pergamon Press, Oxford, 1973, pp. 1515–1516;
(b) T. Surles, A.I. Popov, Inorganic Chemistry 8 (1969) 2049–2052.
[20] Z. Wang, B. Zheng, X. Yu, X. Li, P. Yi, Journal of Chemical Physics 132 (2010) 164104-1–164104-5.
[21] (a) W.K.R. Musgrave, in: M. Stacey, J.C. Tatlow, A.G. Sharpe (Eds.), Advances in Fluorine Chemistry, vol. 1, Butterworths Scientific Publications, London, 1960 pp. 1–28;
(b) D.D. DesMarteau, Journal of the American Chemical Society 100 (1978) 340.
[22] A.J. Downs, C.J. Adams, in: J.C. Bailar, H.J. Elemeleus, S.R. Nyholm, A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, vol. 2, Pergamon Press, Oxford, 1973, pp. 1346–1347.
[23] (a) I. Déchamps, D.G. Pardo, J. Cossy, European Journal of Organic Chemistry (2007) 4224–4234;
(b) V. Hugenberg, R. Fröhlich, G. Haufe, Organic Biomolecular Chemistry (2010), doi:10.1039/c0ob00560f.
[24] W.A. Sheppard, Journal of the American Chemical Society 84 (1962) 3058–3063.
[25] G.A. Boswell Jr., W.C. Ripka, R.M. Scribner, C.W. Tullock, Organic Reactions 21 (1974) 12–20.
[26] W.H. Bunnelle, B.R. McKinnis, B.A. Narayanan, Journal of Organic Chemistry 55 (1990) 768–770.
[27] (a) Y. Hagooly, J. Gatenyo, A. Hagooly, S. Rozen, Journal of Organic Chemistry 74 (2009) 8578–8582;
(b) I. Ben-David, D. Rechavi, E. Mishani, S. Rozen, Journal of Fluorine Chemistry 97 (1999) 75–78;
(c) S. Rozen, E. Mishani, Journal of the Chemical Society, Chemical Communications (1993) 1761–1762;
(d) S. Rozen, E. Mishani, Journal of the Chemical Society, Chemical Communications (1994) 2081;
(e) A. Hagooly, I. Ben-David, S. Rozen, Journal of Organic Chemistry 67 (2002) 8430–8434.
[28] (a) W.B. Motherwell, J.A. Wilkinson, Synlett (1991) 191–192;
(b) M.J. Koen, F.L. Guyader, W.B. Motherwell, Journal of the Chemical Society, Chemical Communications (1995) 1241–1242.
[29] (a) G.A. Olah, J.T. Welch, Synthesis (1974) 652;
(b) A.R. Katrizky, Tetrahedron 36 (1980) 679–699;
(c) K. Kanie, K. Mizuno, M. Kuroboshi, T. Hiyama, Bulletin of the Chemical Society of Japan 71 (1998) 1973–1991;
(d) S. Furuta, M. Kuroboshi, T. Hiyama, Bulletin of the Chemical Society of Japan 72 (1999) 805–819;
(e) K. Kanie, Y. Tanaka, K. Suzuki, M. Kuroboshi, T. Hiyama, Bulletin of the Chemical Society of Japan 73 (2000) 471–484.

[30] (a) T. Fuchigami, K. Mitomo, H. Ishii, A. Konno, Journal of Electroanalytical Chemistry 507 (2001) 30–33;
(b) S. Inagi, S. Hayashi, T. Fuchigami, Chemical Communications (2009) 1718–1720;
(c) M.R. Shaabon, S. Inagi, T. Fuchigami, Electrochimica Acta (2009) 2635–2639.
[31] J.L. Musachio, J. Shan, V.W. Pike, Journal of Labelled Compounds and Radiopharmaceuticals 48 (2005) 735–747.
[32] K. Szabo, E. Oswald, Magyar Kemiai Folyoirat 60 (1954) 99–101, From: Hung. Tech. Abstr. 7(1), 7 (1955).
[33] K. Mori, T. Komata, R. Tamai, K. Murakami, O. Tada, H. Koyasu, S. Matsubuchi, T. Fujisawa, Japanese Kokai Tokkyo Koho (1991) 068550.
[34] The *N*-trimethylsilyl-2-(trimethylsiloxymethyl)pyrrolidine was prepared in 90% yield by reaction of (S)-(+)-2-prrolidinemethanol (100 mmol) with *n*-butyl lithium (1.6 M in hexane) (203 mmol) in dry hexane at reflux temperature for 2 h, followed by addition of a solution of chlorotrimethylsilane (203 mmol) in dry hexane and then refluxing for 2 h. Physical and spectral data of the product are as follows: bp 85 °C/8 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H), 0.08 (s, 9H), 1.69 (m, 4H), 2.90 (m, 2H), 3.09 (t, J = 11.0 Hz, 1H), 3.28 (m, 2H); ^{13}C NMR (CDC_{l3}) δ −0.62, −0.42, 25.2, 29.3, 46.9, 59.7, 66.4.
[35] R.J. Altenbach, L.A. Black, S.-J. Chang, M.D. Cowart, R. Faghih, G.A. Gfesser, Y.-y. Ku, H. Liu, K.A. Lukin, D.L. Nersesian, Y.-m. Pu, P.N. Sharma, Y.L. Bennani, US Patent Application, 20040092521.