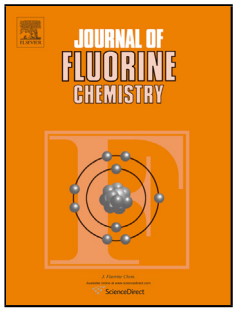

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An improved method for the fluorination of arylsulfurchlorotetrafluorides to arylsulfurpentafluorides

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Abstract

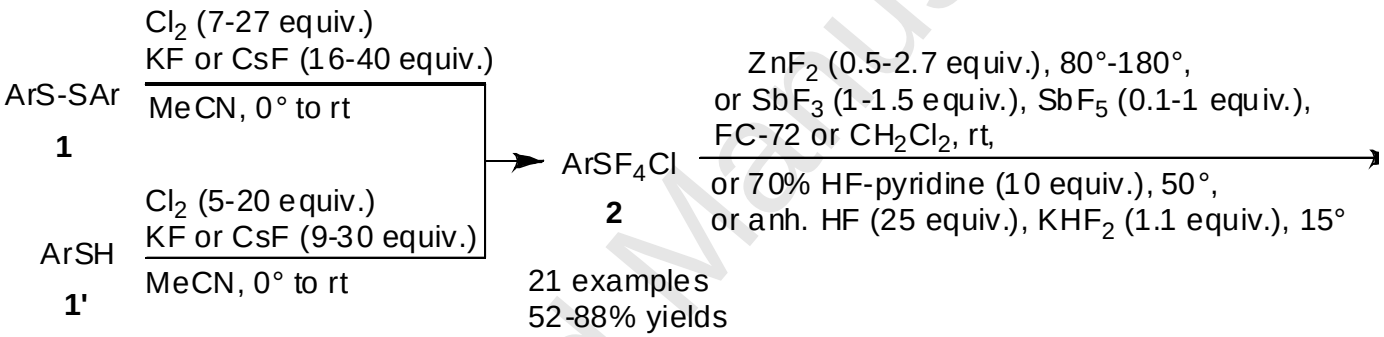
A new method for the fluorination of arylsulfurchlorotetrafluorides to arylsulfurpentafluorides is described. The reaction is promoted by hydrogen fluoride generated from potassium hydrogen fluoride and trifluoroacetic acid which also serves as a solvent. The reaction is performed under mild conditions and uses substochiometric amounts of potassium hydrogen fluorides in certain cases. Recovery and reuse of trifluoroacetic acid was successfully demonstrated which makes this method safe, simple to use, and atom- and cost-effective.

1. Introduction

The pentafluorosulfanyl group (SF_5) is a functionality that has received much attention in recent years, mainly in material, medicinal, and agrochemical research [1]. The incorporation of strongly electron-withdrawing pentafluorosulfanyl group into organic molecules can dramatically modify a variety of properties including lipophilicity, solubility, metabolic, thermal and chemical stability, bioavailability, bioactivity, or p*K*a [**Error! Bookmark not defined.**,2]. This functional group is starting to appear in compounds in development for various applications including pharmaceuticals, agrochemicals, energetic materials, liquid crystals, ionic liquids, and others [3]. Recently, the electron-acceptor and steric properties of the SF_5 group were also exploited in catalysis [4].

There is a limited number of commercially available compounds with the SF_5 group (compared to, for example, the CF_3-containing compounds), although, in recent years, many new products (mostly SF_5-aromatics) became available. In case of aromatic SF_5 compounds, there are two main methods for their practical synthesis available. The first one was developed in the 1990's and is based on direct fluorination of electron-deficient bis(aryl) disulfides (such as bis(*m*- or *p*-nitrophenyl) disulfides) with F_2/N_2 [5]. Building upon earlier studies of Sharp [6], Shreeve [7] and Janzen [8], the second method by

Umemoto is based on a two-step process of conversion of diaryl disulfides (**1**) or aryl thiols to aromatic sulfur chlorotetrafluorides (**2**) using chlorine in the presence of alkali metal fluorides in acetonitrile [9]. Arylsulfurtrifluorides [10] were identified as intermediates in these reactions. In the second step, arylsulfurchlorotetrafluorides were fluorinated to arylsulfurpentafluorides (**3**) using either ZnF_2 under elevated temperature, $SbF_3/SbF_5(SbCl_5)$ in a halocarbon solvent, excess of 70% HF-pyridine complex, or excess of anhydrous hydrogen fluoride (Scheme 1) [**Error! Bookmark not defined.**]. A fluoropolymer reactor or reaction flask is required for all of the methods. These methods havesome drawbacks: the zinc fluoride method uses high temperature, HF-pyridine and anhydrous hydrogen fluoride methods use large excess of very toxic and corrosive chemicals. Despite this, the last method seems to be the most suitable for bigger scale production.



Scheme 1: Umemoto'stwo-step synthesisofarylsulfurpentafluorides [**Error! Bookmark not defined.**].

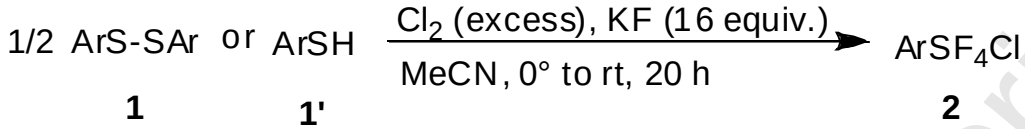
Umemoto's synthesis represents a significant development for economical production of arylsulfurpentafluorides. Importantly, various substitutions on the phenyl ring are tolerated including fluoro, chloro, bromo, nitro, alkyl, and methylsulfonyl. A weak point of this process is the second step which calls for improvements. Safe, inexpensive and atom-economic fluorination method would be highly desirable.

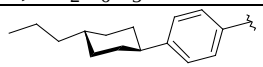
2. Results and discussion

First, a range of substituted phenylsulfurchlorotetrafluorides (**2**) were synthesized in good to high yields using Umemoto's conditions. The reliability of the method was validated on a multi-gram scale. Commercial spray-dried potassium fluoride further dried by heating *in vacuo* for several hours was used, and the reaction was performed in dry acetonitrile at ambient temperature using excess of chlorine (Table 1). Compounds **2a-d**were synthesized previously [**Error! Bookmark not defined.**] while compounds **2e** and **2f** are new. Compound **2d** could be prepared from *p*-*t*-butylthiophenol; however, we found that this method is not suitable for thiophenols substituted with electron-withdrawing group (4-F, 4-Cl or 2,4-F_2), and for these compounds, it was necessary to start from the corresponding diaryl

disulfides. The products were purified either by distillation under reduced pressure (**2a-c** and **2e**) or by crystallization (**2d**) and were found to be stable in a perfluoropolymer container but they decomposed over the course of hours or days on contact with glass.

Table 1: Preparation of arylsulfurchlorotetrafluorides (**2**).



Entry	**1** or **1'**	Ar	Product and yield (%)[a]
1	**1a**	Ph	**2a**, 84
2	**1b**	4-FC_6H_4	**2b**, 85
3	**1c**	4-ClC_6H_4	**2c**, 81
4	**1d'**	4-*t*-BuC_6H_4	**2d**, 55
5	**1e**	2,4-$F_2C_6H_3$	**2e**, 63
6	**1f**		**2f**, 84

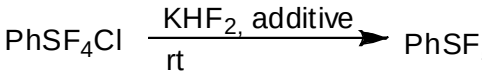
[a] Isolated yield.

The fluorine for chlorine exchange in arylsulfurchlorotetrafluorides (**2**) to arylsulfurpentafluorides (**3**) was previously achieved with Lewis acidic fluorides (BF_3, SnF_4, TiF_4 in low yields, or SbF_3/SbF_5, CuF_2 or ZnF_2) in good yields [**Error! Bookmark not defined.**]. We confirmed that with alkali metal fluorides (excess spray-dried KF or CsF) in THF under ambient temperature with ultrasound activation for 1 h, no fluorination of **2a** took place. An alternative fluorination reagent to Lewis acidic fluorides is hydrogen fluoride. Safety hazards associated with anhydrous HF, the necessity to use special equipment for handling it and cost of disposal of large excess of the reagent prompted us to think about modification of reaction conditions which would deliver the required minimum amount of HF in the solution of $ArSF_4Cl$. During the exchange reaction, the side product HCl,which is a more volatile acid than HF (bp?85 °C HCl; 19.5 °C HF), could react with KHF_2 to provide more HF or partially escape the reaction mixture to drive the reaction to completion.

We initiated investigations in fluorination of **2a** using excess 48% aqueous solution of HF and excess potassium hydrogen fluoride in dichloromethane (Table 2, entry 1). However, no product **3a** was observed. It is known that trifluoroacetic acid (TFA, pK_a?0.25) or triflic acid (pK_a ~ ?14) react with KHF_2 to form HF. This combination of reagents was used previously for the formation of highly electrophilic iminium fluorides from enamines [11]. Nevertheless, we did not observe any product **3a** with excess KHF_2 and catalytic TFA in dichloromethane (Table 2, entry 2). In acetic acid, hydrolysis to phenylsulfonylchoride and some phenylsulfonyl fluoride took place (Table 2, entry 3). Application of strong methanesulfonic acid (pK_a?2.6) as the solvent in combination with KHF_2 also did not give any

expected product. With even stronger triflic acid, however, small amount of $PhSF_5$ formed in addition to products of hydrolysis and diphenylsulfone. Similar result was observed using conc. sulfuric acid (pK_a?3). The key to success turned out to be the use of TFA as a solvent. With a two-fold excess of KHF_2, full conversion of **2a** to **3a** was observed (entry 7). The amount of KHF_2 could be reduced down to 0.6 equivalents (providing 1.2 equivalents of HF in the reaction with TFA) albeit in longer reaction time. The amount of TFA is critical; under essentially solvent free conditions the reaction mixture solidified and only low yield of **3a** was isolated (entry 11). Application of optimized conditions on multi-gram scale ? 0.6 equiv. of KHF_2 (preferably added in two portions to control the amount of HF and to release the formed HCl) and 1M solution of **2a** in TFA ? provided high isolated yield of **3a** (entry 12). All reactions in Table 2 were conducted in a closed fluoropolymer flask under ambient temperature.

Table 2: Optimization of fluorination of phenylsulfurchlorotetrafluride (**2a**) to phenylsulfurpentafluoride (**3a**).



2a **3a**

Entry	**2a** (mmol)	KHF_2 (equiv.) + additive (equiv.)	Solvent (mL)	Time (h)	Products	Yields (%)[a]
1	0.7	13 + 48% HF (11)	CH_2Cl_2 (3.5)	16	**3a**	0
2	0.6	5 + TFA (0.5)	CH_2Cl_2 (2)	16	**3a**	0
3	2.8	2 + TFA (2)	AcOH (4.7)	3.5	**3a** $PhSO_2Cl$ $PhSO_2F$	0 91 9
4	2.2	1	$MeSO_3H$ (2.2)	1	**3a**	0
5	1.8	1	CF_3SO_3H (2.25)	1.5	**3a** $PhSO_2Cl$ $PhSO_2F$ $PhSO_2Ph$	5 15 14 9

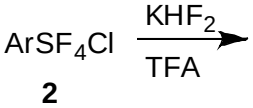
6	2	2	H_2SO_4 (3)	0.5	**3a** $PhSO_2Cl$ $PhSO_2F$ $PhSO_2Ph$	14 44 36 6
7	6	2[b]	TFA (6)	4	**3a**	100 (59)
8	2	1	TFA (2)	1.5	**3a**	100
9	2	0.6	TFA (2)	1	**3a**	65
10	2	0.6	TFA (2)	68	**3a**	100
11	30	1 + TFA (1)	?	16	**3a**	(8)
12	19	0.6[b]	TFA (19)	20	**3a**	**(82)**

[a] Determined by GCMS, in brackets isolated yields.

[b] KHF_2 was added in two portions every 15 min.

Our fluorination protocol was applied to substituted phenylsulfurchlorotetrafluorides (**2**) (Table 3). Compounds **2a-d** (entries 1?4) participated in the reaction effectively while **2e** showed some resistance towards fluorination. Excess of potassium hydrogenfluoride and elevated temperature had to be used; however, under these conditions, considerable hydrolysis to phenylsulfonyl chloride and fluoride took place and moderate yield of **3e** was obtained (entry 5). The 4-(propylcyclohexyl)benzenesulfurpentafluoride (**3f**) which was previously synthesized in three steps from 4-(pentafluorosulfanyl)aniline in overall 6.3% yield and investigated as a novel ionic liquid material [12] was prepared in good yield from **2f** using excess KHF_2.

Table 3: Fluorination of arylsulfurchlorotetrafluorides (**2**) to arylsulfurpentafluorides (**3**).



2 **3**

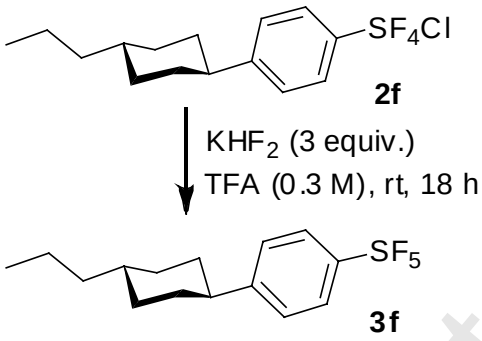
Entry	**2** (mmol)	Ar	KHF_2 (equiv.)	TFA (mL)	Temp (°)	Time (h)	Product and yield (%)[a]
1	**2a**, 19	Ph	0.6[b]	19	rt	20	**3a**, 82
2	**2b**, 14	4-FC_6H_4	0.6[b]	14	rt	18	**3b**, 69
3	**2c**, 33	4-ClC_6H_4	0.66[c]	30	rt	12	**3c**, 75
4	**2d**, 19	4-*t*-BuC_6H_4	0.66[c]	25	rt	12	**3d**, 54
5	**2e**, 3.8	2,4-$F_2C_6H_3$	3[d]	12.7	50	12	**3e**, 34
6	**2f**, 1.9		3[d]	9	rt	18	**3f**, 79
7	**2f**, 6.3		3[d]	21	rt	18	**3f**, 71

[a] Isolated yield.

[b] KHF_2 was added in two portions every 15 min.
[c] KHF_2 was added in two portions every 30 min.
[d] KHF_2 (1 equiv.) was added followed by 2 equiv. after 1 h.

The methodology uses very inexpensive fluorination reagent (KHF_2) and even sub-stochiometric amounts are sufficient for full conversion of certain substrates. The most expensive constituent is the solvent (TFA) and on multi-gram laboratory and larger scales it might be favorable to recover and reuse it. A brief study on the recovery of TFA by distillation under normal pressure (in glass apparatus) and its reuse in the synthesis of **3f** showed that the cost of the process and the amount of corrosive waste can be further reduced (Table 4).

Table 4: Recovery and reuse of trifluoroacetic acid in the synthesis of **3f**.



Entry	**2f** (mmol)	**3f**, yield (%)[a]
1	6.3	71
2[b]	2.2	63
3[b]	1.7	70

[a] Isolated yield.
[b] Using recovered TFA by distillation from reaction in entry 1.

3. Conclusion

In conclusion, we have described an improved methodology for the fluorination of arylsulfurchlorotetrafluorides to arylsulfurpentafluorides under mild conditions based on a controlled release of anhydrous hydrogen fluoride by the reaction of potassium hydrogenfluoride in trifluoroacetic acid. The process is safe, operationally simple, atom-economic, and high yielding for most tested substrates.

4. Experimental part

NMR spectra were recorded in $CDCl_3$ at ambient temperature. Chemical shifts (δ) are reported in ppm relative to Me_4Si (0 ppm for ^1H NMR), residual $CHCl_3$ (7.26 ppm for ^1H NMR), $CDCl_3$ (77.0 ppm for ^{13}C NMR), and internal $CFCl_3$ (0 ppm for ^{19}F NMR). GCMS spectra were recorded using quadrupole mass selective electron impact (EI) detector (70 eV). High resolution mass spectra (HRMS) were recorded on an Agilent 7890A gas chromatograph coupled with a Waters GCT Premier orthogonal acceleration time-of-flight detector using chemical (CI) ionization. Elemental analyses were performed using an automatic PE 2400 Series II CHNS/O analyzer. Acetonitrile was dried by distillation from CaH_2 and spray-dried potassium fluoride was dried by heating *in vacuo*for several hours.

*4.1. General procedure for the preparation of compounds **2***

*Note: The synthesis, distillation or crystallization of compounds **2** was performed in ordinary borosilicate glassware; however, purified compounds **2** were stored in fluoropolymer containers.*To a solution of **1a-f** (21?89 mmol) in dry acetonitrile (7.5-32 mL) spray-dried KF (16 equiv.) was added. The mixture was cooled with an ice bath and chlorine was introduced into the solution. After several hours the temperature of the reaction mixture was allowed to reach room temperature and the color of the mixture changed from yellow to white. After 8 h of passing chlorine the mixture was yellow again. At this point the chloride bubbling was stopped and the mixture was stirred for another 12 h. The solid was removed by filtration, washed with hexane, solvent was removed under reduced pressure, and the product was distilled under reduced pressure (**2a-c** and **2e**), recrystallized form hexane (**2d**), or used without further purification (**2f**), and stored in a fluoropolymer container at 2?8 °C.

*4.1.1. Phenylsulfurchlorotetrafluoride (**2a**)*[**Error! Bookmark not defined.**]

Pale yellow liquid (84% yield, 29.9 g from 17.6 g of **1a**).^1H NMR (400 MHz) δ_H 7.75?7.72 (m, 2H), 7.49?7.42 (m, 3H); ^{19}F NMR (376 MHz) δ_F 137.3 (s).

*4.1.2. 4-Fluorophenylsulfur chlorotetrafluoride (**2b**)*[**Error! Bookmark not defined.**]

Pale yellow liquid (85% yield, 14.87 g from 9.27 g of **1b**).^1H NMR (400 MHz) δ_H 7.74 (m, 2H), 7.11 (m, 2H); ^{19}F NMR (376 MHz) δ_F 138.3 (s, 4F), ?107.0 (s, 1F).

*4.1.3. 4-Chlorophenylsulfur chlorotetrafluoride (**2c**)*[**Error! Bookmark not defined.**]

Pale yellow liquid (81% yield, 14.31 g from 10.0 g of **1c**).^1H NMR (400 MHz) δ_H 7.67 (dm, 2H, J = 9.2 Hz), 7.42 (d, 2H, J = 9.2 Hz); ^{19}F NMR (376 MHz) δ_F 137.4 (s).

*4.1.4. 4-(tert-Butyl)phenylsulfurchlorotetrafluoride (**2d**)*[**Error! Bookmark not defined.**]

Blue solid (55% yield, 13.62 g from 14.84 g of **1d'**). ^1H NMR (400 MHz) δ_H 7.65 (dm, 2H, J = 8.7 Hz), 7.43 (d, 2H, J = 8.7 Hz), 1.32 (s, 9H); ^{19}F NMR (376 MHz) δ_F 138.3 (s).

*4.1.5. 2,4-Difluorophenylsulfur chlorotetrafluoride (**2e**)*

Pale yellow liquid (63% yield, 14.0 g from 12.6 g of **1e**). ^1H NMR (400 MHz) δ_H 7.78?7.70 (m, 1H), 6.97?6.87 (m, 2H); ^{19}F NMR (376 MHz) δ_F 141.4 (m, 4F), ?102.1 to ?102.5 (m, 1F), ?102.5 to ?102.7 (m, 1F); ^{13}C NMR (100 MHz)δ_C164.4 (dd, J = 258.8, 12.5 Hz), 156.8 (dd, J = 263.6, 12.5 Hz), 137.8 (quintdd, J = 11.5, 4.2 Hz), 130.0 (m), 111.4 (d, J = 22.0 Hz), 105.7 (t, J = 26.8 Hz); Anal. Calcd for $C_6H_3ClF_6S$: C, 28.08; H, 1.18. Found: C, 28.17; H, 1.35.

*4.1.6. 4-(4-Propylcyclohexyl)phenylsulfurchlorotetrafluoride (**2f**)*

Colorless viscous oil (84% yield, 12.41 g from 10.0 g of **1f**).^{1}H NMR (400 MHz) δ_H7.64 (d, 2H, *J* = 8.2 Hz), 7.26 (d, 2H, *J* = 8.2 Hz), 2.52 (tm, 1H, *J* = 11.9 Hz), 1.88 (d, 4H, *J* = 11.0 Hz), 1.51?1.19 (m, 7H), 1.11?1.01 (m, 2H), 0.91 (t, 3H, *J* = 7.3 Hz); ^{19}F NMR (376 MHz) δ_F 138.4 (s); ^{13}C NMR (100 MHz) δ_C 153.3 (quint, *J* = 17.3 Hz), 152.0, 127.1, 125.7, 44.4, 39.7, 37.1, 34.0, 33.4, 20.1, 14.5; Anal. Calcd for $C_{15}H_{21}ClF_4S$: C, 52.24; H, 6.15. Found: C, 52.43; H, 6.28.

*4.2. General procedure for the preparation of compounds **3***

To a stirred solution of **2a**?**f** (1.9?33 mmol, 0.21?1.1 M in TFA) in a fluoropolymer screw-cap flask, KHF_2 was added (0.6 equiv. in two portions every 15 min for **2a** and **2b**; 0.66 equiv. in two portions every 30 min for **2c** and **2d**; 1 equiv. followed by 2 equiv. after 1 h for **2e** and **2f**). The reaction mixture was stirred at room temperature (or at 50 °C for **2e**) for 12?20 h, and then poured into water. Extraction into dichloromethane, drying (Na_2SO_4), and solvent removal provided the crude product which was purified by chromatography on silica gel using hexane or pentane as eluent giving pure **3**.

*4.2.1. Phenylsulfurpentafluoride (**3a**)*[**Error! Bookmark not defined.**]

Colorless liquid (82% yield, 3.18 g, from 4.19 g of **2a**). ^{1}H NMR (400 MHz) δ_H 7.78?7.74 (m, 2H), 7.53?7.44 (m, 3H); ^{19}F NMR (376 MHz) δ_F 85.5?83.8 (m, 1F), 62.7 (d, 4F, *J* = 150.3 Hz).

*4.2.2. 4-Fluorophenylsulfur pentafluoride (**3b**)*[**Error! Bookmark not defined.**]

Colorless liquid (69% yield, 2.14 g, from 3.34 g of **2b**). ^{1}H NMR (400 MHz) δ_H 7.76 (m, 2H), 7.13 (t, 2H, *J* = 8.4 Hz); ^{19}F NMR (376 MHz) δ_F 85.1?83.5 (m, 1F), 63.8 (d, 4F, *J* = 150.3 Hz), ?107.1 (m).

*4.2.3. 4-Chlorophenylsulfur pentafluoride (**3c**)*[**Error! Bookmark not defined.**]

Colorless liquid (75% yield, 5.91 g, from 8.42 g of **2c**). ^{1}H NMR (400 MHz) δ_H 7.69 (dm, 2H, *J* = 8.8 Hz), 7.43 (d, 2H,*J* = 8.8 Hz); ^{19}F NMR (376 MHz) δ_F 84.5?82.9 (m, 1F), 63.3 (d, 4F, *J* = 150.3 Hz).

*4.2.4. 4-(tert-Butyl)phenylsulfurpentafluoride (**3d**)*

Colorless liquid (54% yield, 2.67 g, from 5.26 g of **2d**). ^{1}H NMR (400 MHz) δ_H 7.70 (dm, 2H, *J* = 8.7 Hz), 7.48 (dm, 2H, *J* = 8.7 Hz), 1.34 (s, 9H); ^{19}F NMR (376 MHz) δ_F 86.3?84.7 (m, 1F), 63.3 (d, 4F, *J* = 150.3 Hz).^{13}C NMR (100 MHz) δ_C 155.1, 151.5 (quint, *J* = 16.3 Hz), 125.7, 35.0, 31.1; HRMS (CI) *m/z*calcd for $C_{10}H_{13}F_5S$ $[M]^+$ 260.0658, found 260.0650.

*4.2.5. 2,4-Difluorophenylsulfur pentafluoride (**3e**)*

Colorless liquid (34% yield, 319 mg, from 990 mg of **2e**). ^{1}H NMR (400 MHz) δ_H 7.77 (ddd, 1H, *J* = 9.2, 7.8, 5.7 Hz), 7.01?6.97 (m, 1H), 6.97?6.93 (m, 1H); ^{19}F NMR (376 MHz) δ_F 81.9?80.3 (m, 1F), 68.6 (dd, 4F, *J* = 151.4, 25.3 Hz),?102.8 to ?102.9 (m, 1F), ?102.9 to ?103.2 (m, 1F); ^{13}C NMR (100 MHz) δ_C 164.4 (dd, *J* = 244.5, 13.6 Hz), 157.1 (ddquint, *J* = 262.5, 11.7, 1.6 Hz), 136.5 (quintdd, *J* = 15.9, 4.5, 1.2 Hz), 130.2 (m), 111.6 (dd, *J* = 22.5, 3.7 Hz), 105.8 (t, *J* = 26.5 Hz). HRMS (CI) *m/z*calcd for $C_6H_3F_7S$ $[M]^+$ 239.9844, found 239.9842.

*4.2.6. 4-(4-Propylcyclohexyl)phenylsulfurpentafluoride (**3f**)*[**Error! Bookmark not defined.**]

Colorless liquid (79% yield, 493 mg, from 655 mg of **2f**). ^{1}H NMR (400 MHz) δ_H 7.64 (dm, 2H, *J* = 8.7 Hz), 7.26 (dm, 2H, *J* = 8.7 Hz), 2.51 (t, 1H, *J* = 12.3 Hz), 1.87 (m, 4H), 1.48?1.16 (m, 7H), 1.10?0.98 (m, 2H), 0.89 (t, 3H, J = 7.3 Hz); ^{19}F NMR (376 MHz) δ_F 86.4?84.8 (m, 1F), 63.0 (d, 4F, *J* = 150.3 Hz).

*4.3. Recovery and reuse of TFA in the synthesis of **3f***

KHF_2 (492 mg, 6.3 mmol) was added to a solution of **2f** (2.17 g, 6.3 mmol) in TFA (21 mL) in a fluoropolymer flask. The mixture was stirred at room temperature and after 1 h, KHF_2 (984 mg, 12.6 mmol) was added. The mixture was stirred for further 17 h and then transferred to a glass round bottom flask. The solvent was distilled under normal pressure (90 °C bath temperature). Water was added to the residue and the product was worked-up as described in section 4.2. giving **3f** (71% yield, 1.47 g). To a solution of **2f** (0.76 g, 2.2 mmol) in recovered TFA (7.4 mL), KHF_2 (172 mg, 2.2 mmol) was added. The mixture was stirred at room temperature for 1 h followed by addition of KHF_2 (343 mg, 4.4 mmol). The mixture was stirred for further 17 h, followed by addition of water and work-up as described in section 4.2. giving **3f** (63% yield, 455 mg). To a solution of **2f** (0.59 g, 1.7 mmol) in recovered TFA (5.8 mL), KHF_2 (134 mg, 1.7 mmol) was added. The mixture was stirred at room temperature for 1 h followed by addition of KHF_2 (268 mg, 3.4 mmol). The mixture was stirred for further 17 h, followed by addition of water and work-up as described in section 4.2. giving **3f** (70% yield, 391 mg).

Acknowledgments

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References[1] (a) S. Altomonte, M. Zanda, J. FluorineChem. 143 (2012)57–93;

[2] B. Stump, C. Eberle, W.B.Schweizer, M. Kaiser, R. Brun, R.L.Krauth-Siegel, D. Lentz, F. Diederich, ChemBioChem 10 (2009) 79?83.

[3] (a) P. Kirsch, ModernFluoroorganicChemistry, Wiley-VCH, Weinheim, 2004, pp.

[4] (a) Y.-D.Yang, X. Lu, E. Tokunaga, N. Shibata, JournalofFluorineChem. 143 (2012) 204?209;

[5] (a) R.D.Bowden, M.P.Greenhall, J.S. Moilliet, J. Thomson, WO 9705106 (1997);

[6] J.I.Darragh, D.W.A.Sharp, J. Chem. Soc. Chem. Commun. (1969) 864?865.

[7] T. Abe, J.M. Shreeve, J. Fluorine Chem. 3 (1973) 187?196.

[8] X. Ou, G.M. Bernard, A.F.Janzen, Can. J. Chem. 75 (1997) 1878?1884.

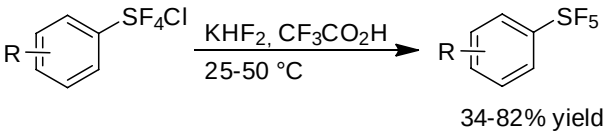
[9] T. Umemoto, L.M.Garrick, N.Saito, Beilstein J. Org. Chem. 8 (2012) 461–471 and patents by T. Umemotocitedtherein.

[10] T. Umemoto, R.P.Singh, Y. Xu, N. Saito, J. Am. Chem. Soc. 132 (2010) 18199?18205.

[11] (a) V.V.Levin, A.D. Dilman, P.A Belyakov, M.I. Struchkova, V.A.Tartakovsky, Eur. J. Org. Chem. (2008) 5226?5230;

[12] P. Kirsch, M. Bremer, M. Heckmeier, K. Tarumi, Angew. Chem. Int. Ed. 38 (1999) 1989?1992.

Graphical Abstract - pictogram



34-82% yield

Graphical Abstract – synopsis

An improved method for the fluorination of arylsulfur chlorotetrafluorides to arylsulfur pentafluorides

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Highlights

Fluorination $ArSF_4Cl$ to $ArSF_5$ takes place with KHF_2 in trifluoroacetic acid.

The solvent (trifluoroacetic acid) could be recovered by distillation and reused.

The reaction is performed under mild conditions.

The reaction does not require handling anhydrous HF