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Fluoride-induced nucleophilic (phenylthio)difluoromethylation of carbonyl compounds with [difluoro(phenylthio)methyl]trimethylsilane (TMS–CF_2SPh)

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Dedicated to Professor Richard D. Chambers on the occasion of his 70th birthday.

Abstract

A fluoride-induced nucleophilic (phenylthio)difluoromethylation method using TMS–CF_2SPh has been achieved. This new methodology efficiently transfers ''$PhSCF_2$'' group into both enolizable and non-enolizable aldehydes and ketones to give corresponding (phenylthio)difluoromethylated alcohols in good to excellent yields. Diphenyldisulfide can also be (phenylthio)difluoromethylated into $PhSCF_2SPh$ in high yield. The reaction with methyl benzoate, however, gives only low yield of (phenylthio)difluoromethyl phenyl ketone. The above-obtained $PhSCF_2$-containing alcohols can be further transformed into difluoromethyl alcohols using an oxidation–desulfonylation procedure. This new type of nucleophilic (phenylthio)difluoromethylation methodology may have other potential applications in the medicinal and agrochemical fields.

Keywords: [Difluoro(phenylthio)methyl]trimethylsilane; (Phenylthio)difluoromethylation; Carbonyl compounds; Fluoride; Autocatalytic reaction

1. Introduction

Recently, the selective introduction of difluoro(arylthio)-methyl or difluoro(heteroarylthio)methyl group ($ArSCF_2$) into organic molecules has been found to be attractive, since these compounds have potential biological applications such as anti-HIV-1 reverse transcriptase inhibitors and other agrochemical intermediates [1,2]. The currently known methods to construct the $ArSCF_2$ moiety are based on the S_RN1 reactions between an aryl- or heteroarylthiolate (ArSNa) and a halodifluoromethyl-containing compound (halo = Br, Cl) [1,2]. To our best knowledge, there is no synthetic method available so far for the direct introduction of a difluoro(arylthio)methyl ($ArSCF_2$) building block into organic molecules.

In 1989, we developed the first general and efficient nucleophilic trifluoromethylation method using (trifluoromethyl)trimethylsilane (TMS–CF_3) [3–5]. With a similar protocol, fluoride-induced nucleophilic chlorodifluoromethylation with TMS–CF_2Cl, (trimethylsilyl)difluoromethylation with $TMSCF_2TMS$, and perfluorovinylation with TMS CF_2CF_2TMS have been developed in our laboratory [6]. Herein, we would like to disclose another nucleophilic fluoroalkylation methodology in this category, using [difluoro(phenylthio)methyl]trimethylsilane (TMS–CF_2SPh) as the nucleophilic (phenylthio)difluoromethylating reagent.

2. Results and discussion

[Difluoro(phenylthio)methyl]trimethylsilane (TMS–CF_2SPh) was prepared for the first time by us as a high-boiling and reasonably stable liquid (b.p. 86–87 °C/4 mmHg), using

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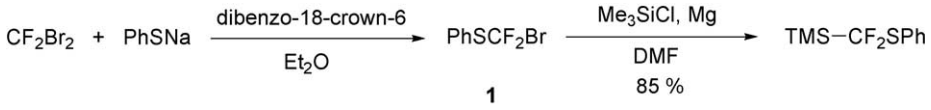


Scheme 1. Preparation of TMS–CF_2SPh.

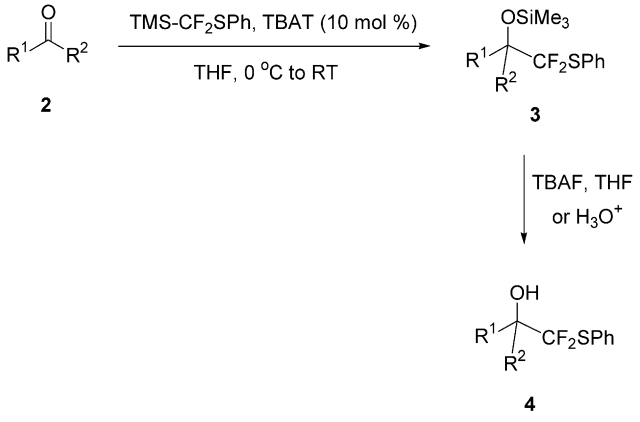
the Barbier coupling reaction of bromodifluoromethyl phenyl sulfide (**1**), magnesium metal and chlorotrimethylsilane (TMSCl) in 85% isolated yield (Scheme 1) [7]. Since compound **1** can be readily prepared from dibromodifluoromethane (Halon 1202) and sodium benzenethiolate [8], TMS–CF_2SPh is an inexpensive chemical and can be widely used.

The reaction conditions for the fluoride-induced nucleophilic (phenylthio)difluoromethylation reaction (Scheme 2) is similar to that of trifluoromethylation with TMS–CF_3 [3,4]. Catalytic amount (10 mol.%) of tetrabutylammonium triphenyldifluorosilicate (TBAT) was used as the anhydrous fluoride source. The results are summarized in Table 1.

As shown in Table 1, various aldehydes and ketones were (phenylthio)difluoromethylated in good to excellent yields with this method. Enolizable carbonyl compounds behave similarly as non-enolizable ones, with slightly lower yields (see entries 7 and 8). In the case of an α,β-unsaturated carbonyl compound, only 1,2-addition product was obtained (entry 5).

This new type of (phenylthio)difluoromethylation method was also applied to other systems such as disulfides and esters. For example, when excess potassium *tert*-butoxide was used as the promoter, diphenyl disulfide (**5**) reacted with TMS–CF_2SPh to give product **6** in 85% yield (Scheme 3, Eq. (1)). The reaction between methyl benzoate (**7**) and TMS–CF_2SPh was attempted several times using different solvents at −78 °C to room temperature, and the ketone product **8** was produced in 28–41% conversions (Scheme 3, Eq. (2)).

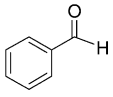
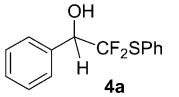
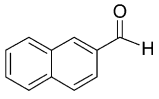
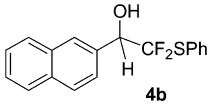
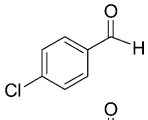
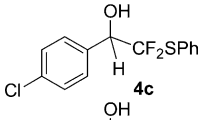
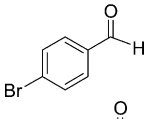
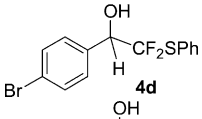
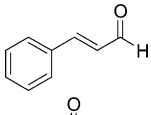
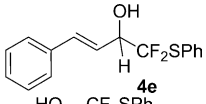
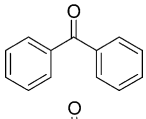
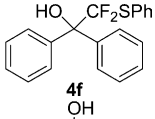
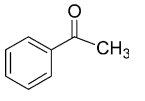
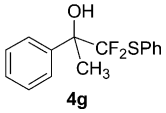
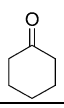
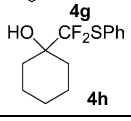
The above-obtained (phenylthio)difluoromethyl carbinols (**4**) can also be further transformed into difluoromethyl carbinols (**10**), using simple oxidation and reductive desulfonylation procedure (Scheme 4). Difluoromethyl alcohols are highly useful compounds for many applications [9].



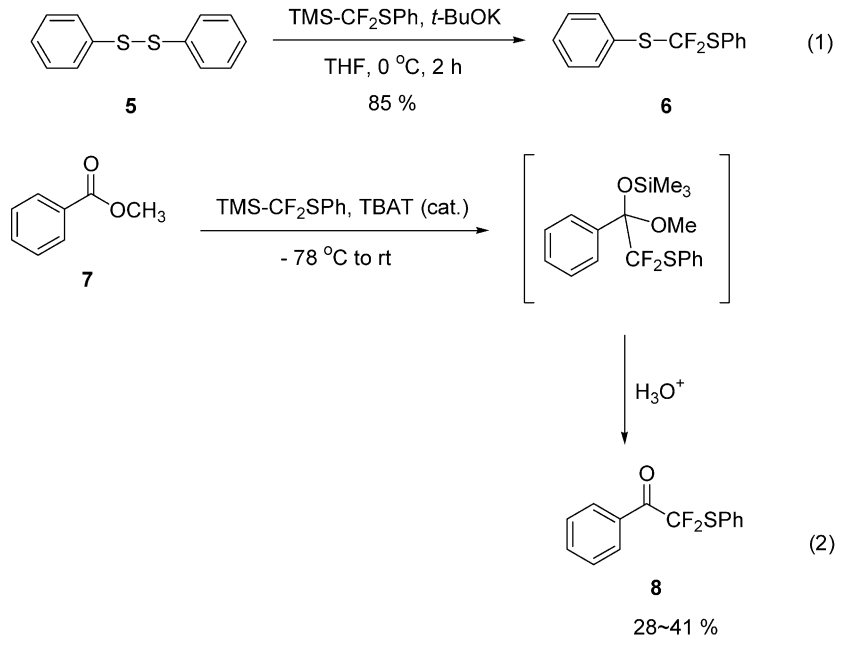
Scheme 2. Nucleophilic (phenylthio)difluoromethylation with TMS–CF_2SPh.

Concerning the mechanism of this fluoride-induced (phenylthio)difluoromethylation of carbonyl compounds (both aldehydes and ketones), we propose that a pentacovalent silicon anion species **11** is formed from TMS–CF_2SPh and TBAT (Scheme 5). Species **11** acts as a real (phenylthio)difluoromethylating agent, transferring the $PhSCF_2^-$ into the carbonyl compound **2** to give alkoxide **12**. Alkoxide **12** can further act as an initiator for TMS–CF_2SPh to form another pentacovalent silicon species **13** as a (phenylthio)difluoromethylating agent, thus giving the silylated carbinol product **3** from TMS–CF_2SPh and carbonyl compounds **2** in a catalytic cycle (Scheme 5). In principle, the reaction is a fluoride-induced autocatalytic process, and such a mechanism has been previously proposed by us in the case of TMS–CF_3 [3].

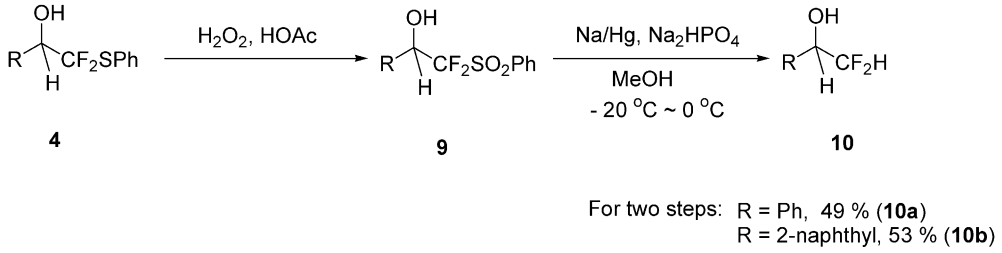
Table 1
Nucleophilic (phenylthio)difluoromethylation of carbonyl compounds with TMS–CF_2SPh (after desilylation)

Entry	Carbonyl compounds **2**	Product **4**	Yield (%)[a]
1		 **4a**	85
2		 **4b**	87
3		 **4c**	72
4		 **4d**	81
5		 **4e**	91
6		 **4f**	86
7		 **4g**	82
8		 **4h**	77

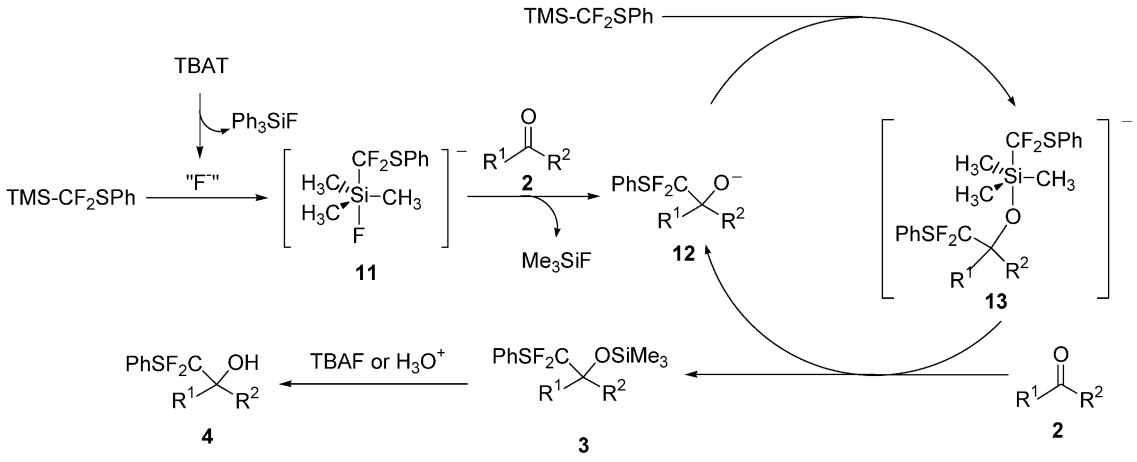
[a] Isolated yield.



Scheme 3. (Phenylthio)difluoromethylation of diphenyl disulfide and methyl benzoate.



Scheme 4. Preparation of difluoromethyl alcohols (**10**) from **4**.



Scheme 5. Proposed mechanism of the (phenylthio)difluoromethylation of carbonyl compounds with TMS–CF_2SPh.

3. Conclusion

In conclusion, a fluoride-induced nucleophilic (phenylthio)difluoromethylation method using TMS–CF_2SPh has been achieved. This new methodology efficiently transfers $PhSCF_2$ group into both enolizable and non-enolizable aldehydes and ketones to give the corresponding (phenylthio)difluoromethylated carbinols in good to excellent yields. Diphenyldisulfide can also be (phenylthio)-difluoromethylated into $PhSCF_2SPh$ in high yield. The

reaction with methyl benzoate, however, gives only low yield of (phenylthio)difluoromethyl phenyl ketone. The above-obtained $PhSCF_2$-containing alcohols can be further transformed into difluoromethyl alcohols using oxidation–desulfonylation procedure. This nucleophilic fluoroalkylation chemistry can also be extended to other (arylthio)-difluoromethylation, (heteroarylthio)difluoromethylation and (alkylthio)difluoromethylation using corresponding TMS–CF_2SR reagents, which are still under investigation in our laboratory.

4. Experimental

4.1. General

Unless otherwise mentioned, all reagents were purchased from commercial sources. TMS–CF_2SPh was prepared according to our previous procedures [7]. THF was distilled under nitrogen over sodium/benzophenone ketyl prior to use. Toluene was distilled over sodium. Column chromatography was carried out using silica gel (60–200 mesh).

^1H, ^{13}C, ^{19}F NMR spectra were recorded on Bruker AMX 500 and Varian Mercury-400 NMR spectrometers. $(CH_3)_4Si$ (TMS) was used as an internal standard for ^1H and ^{13}C NMR, $CFCl_3$ was used as internal standard for ^{19}F NMR. For some cases, $CDCl_3$ was used as the internal standard for ^1H NMR (7.26 ppm) and ^{13}C NMR (77 ppm). Mass spectra were obtained on a Hewlett Packard 5890 Gas Chromatograph equipped with a Hewlett Packard 5971 Mass Selective Detector at 70 eV. HRMS data were recorded on a VG 7070 high-resolution mass spectrometer. The purity of the isolated products (usually >97% purity) was examined by GC–MS and ^1H, ^{13}C, ^{19}F NMR spectroscopy.

4.2. Typical procedures for the nucleophilic (phenylthio)difluoromethylation with TMS–CF_2SPh

Under an argon atmosphere, into a Schlenk flask containing benzaldehyde (106 mg, 1.0 mmol) and TMS–CF_2SPh (278 mg, 1.2 mmol) in dry THF (5 mL) at 0 °C, was added dropwise a THF solution (3 mL) of TBAT (54 mg, 0.1 mmol). Then the reaction mixture was stirred at 0 °C for 1 h, followed by stirring at room temperature overnight. A wet THF solution (10 mL, containing 10% of water) of $TBAF{\cdot}3H_2O$ (315 mg, 1 mmol) was then added and the whole mixture was stirred for another 30 min. The THF solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (hexane:ethyl acetate (v/v) = 9:1, then 7:1) to give the 2,2-difluoro-2-phenylthio-1-phenylethanol (**4a**) as a colorless liquid, yield: 226 mg (85%).

4.2.1. 2,2-Difluoro-2-phenylthio-1-phenylethanol (*4a*)

Colorless liquid, 85 % yield. ^1H NMR ($CDCl_3$): δ 2.71 (d, $^3J_{H-H}$ = 4 Hz, 1H, O<u>H</u>), 4.92 (m, 1H, CF_2–C<u>H</u>), 7.21–7.51 (m, 10H, <u>Ph</u>). ^{13}C NMR ($CDCl_3$): δ 76.0 (t, $^2J_{C-F}$ = 28 Hz, CF_2<u>C</u>H), 125.7 (t, $^3J_{C-F}$ = 2.6 Hz, Ph), 127.7 (Ph), 128.3 (Ph), 128.8 (t, $^1J_{C-F}$ = 285 Hz, <u>C</u>F_2), 128.9 (Ph), 129.0 (Ph), 129.8 (Ph), 135.2 (Ph), 136.4 (Ph). ^{19}F NMR ($CDCl_3$): δ −81.7 (dd, $^2J_{F-F}$ = 210 Hz, $^3J_{F-H}$ = 8.2 Hz, 1F), −85.2 (dd, $^2J_{F-F}$ = 210 Hz, $^3J_{F-H}$ = 12 Hz, 1F). MS: 266 [M^+], 160, 107, 77. HRMS (EI): *m/z* calcd for $C_{14}H_{12}F_2OS$ [M^+] 266.0577, found 266.0575.

4.2.2. 2,2-Difluoro-2-phenylthio-1-(2-naphthyl)ethanol (*4b*)

Pale yellow solid, 87% yield. ^1H NMR ($CDCl_3$): δ 3.01 (d, $^3J_{H-H}$ = 3.5 Hz, 1H, O<u>H</u>), 5.20 (m, 1H, CF_2–C<u>H</u>), 7.28–8.00 (m, 12H, aryl). ^{13}C NMR ($CDCl_3$): δ 76.0 (t, $^2J_{C-F}$ = 27 Hz, CF_2<u>C</u>H), 124.9 (t, $^3J_{C-F}$ = 1.4 Hz, aryl), 125.8 (t, $^3J_{C-F}$ = 2.3 Hz, aryl), 126.2 (aryl), 126.5 (aryl), 127.5 (aryl), 127.6 (aryl), 128.0 (aryl), 128.2 (aryl), 129.0 (aryl), 129.0 (t, $^1J_{C-F}$ = 264 Hz, <u>C</u>F_2), 129.8 (aryl), 132.6 (aryl), 132.8 (aryl), 133.5 (aryl), 136.4 (aryl). ^{19}F NMR ($CDCl_3$): δ −81.3 (dd, $^2J_{F-F}$ = 210 Hz, $^3J_{F-H}$ = 8 Hz, 1F), −84.6 (dd, $^2J_{F-F}$ = 210 Hz, $^3J_{F-H}$ = 12 Hz, 1F). MS: 316 [M^+], 187, 157, 129, 77. HRMS (EI): *m/z* calcd for $C_{18}H_{14}F_2OS$ [M^+] 316.0733, found 316.0730.

4.2.3. 2,2-Difluoro-2-phenylthio-1-(4′-chlorophenyl)ethanol (*4c*)

White solid, 72% yield. ^1H NMR ($CDCl_3$): δ 3.08 (d, $^3J_{H-H}$ = 4.2 Hz, 1H, O<u>H</u>), 4.97 (m, 1H, CF_2–C<u>H</u>), 7.35–7.60 (m, 9H, aryl). ^{13}C NMR ($CDCl_3$): δ 75.4 (t, $^2J_{C-F}$ = 27.3 Hz, CF_2<u>C</u>H), 125.5 (t, $^3J_{C-F}$ = 2.2 Hz, aryl), 128.5 (aryl), 128.7 (t, $^1J_{C-F}$ = 285 Hz, CF_2), 129.1 (aryl), 129.2 (aryl), 130.0 (aryl), 133.6 (aryl), 135.0 (aryl), 136.4 (aryl). ^{19}F NMR ($CDCl_3$): δ −81.4 (dd, $^2J_{F-F}$ = 210 Hz, $^3J_{F-H}$ = 7.2 Hz, 1F), −85.2 (dd, $^2J_{F-F}$ = 210 Hz, $^3J_{F-H}$ = 11.5 Hz, 1F). HRMS (EI): *m/z* calcd for $C_{14}H_{11}ClF_2OS$ [M^+] 300.0187, found 300.0179.

4.2.4. 2,2-Difluoro-2-phenylthio-1-(4′-bromophenyl)ethanol (*4d*)

Pale yellow solid, 81% yield. ^1H NMR ($CDCl_3$): δ 2.84 (d, $^3J_{H-H}$ = 4 Hz, 1H, O<u>H</u>), 4.96 (m, 1H, CF_2–C<u>H</u>), 7.35–7.60 (m, 9 H, aryl). ^{13}C NMR ($CDCl_3$): δ 75.5 (t, $^2J_{C-F}$ = 27.3 Hz, CF_2<u>C</u>H), 123.3 (aryl), 125.4 (aryl), 128.6 (t, $^1J_{C-F}$ = 285 Hz, CF_2), 129.1 (aryl), 129.4 (aryl), 130.0 (aryl), 131.5 (aryl), 134.0 (aryl), 136.4 (aryl). ^{19}F NMR ($CDCl_3$): δ −81.6 (dd, $^2J_{F-F}$ = 211 Hz, $^3J_{F-H}$ = 7.3 Hz, 1F), −85.7 (dd, $^2J_{F-F}$ = 211 Hz, $^3J_{F-H}$ = 11.4 Hz, 1F). HRMS (EI): *m/z* calcd for $C_{14}H_{11}BrF_2OS$ [M^+] 343.9682, found 343.9681.

4.2.5. 1,1-Difluoro-1-phenylthio-4-phenyl-but-3-en-2-ol (*4e*)

Pale yellow liquid, 91% yield. ^1H NMR ($CDCl_3$): δ 3.13 (d, $^3J_{H-H}$ = 5.4 Hz, 1H, O<u>H</u>), 4.59 (m, 1H, CF_2–C<u>H</u>), 6.26 (dd, $^3J_{H-H}$ = 16.1 Hz, $^3J_{H-H}$ = 6.3 Hz, 1H, PhCH = C<u>H</u>–CH), 6.77 (d, $^3J_{H-H}$ = 16 Hz, 1H, PhCH = CH–CH), 7.31 (m, 8H, aryl), 7.60 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, aryl). ^{13}C NMR

($CDCl_3$): δ 75.0 (t, $^2J_{C-F}$ = 27 Hz), 122.4 (–CH=CH–), 125.7 (t, $^3J_{C-F}$ = 2.5 Hz, aryl), 126.8 (aryl), 128.3 (aryl), 128.5 (aryl), 128.9 (t, $^1J_{C-F}$ = 285 Hz, CF_2), 129.0 (aryl), 129.8 (aryl), 135.1 (–CH=CH–), 135.7 (aryl), 136.4 (aryl). ^{19}F NMR ($CDCl_3$): δ −83.0 (dd, $^2J_{F-F}$ = 207.6 Hz, $^3J_{F-H}$ = 9.2 Hz, 1F), −84.8 (dd, $^2J_{F-F}$ = 207.8 Hz, $^3J_{F-H}$ = 8.9 Hz, 1F). HRMS (EI): *m/z* calcd for $C_{16}H_{14}F_2OS$ [M^+] 292.0733, found 292.0728.

4.2.6. 2,2-Difluoro-2-phenylthio-1,1-diphenylethanol (**4f**)

White solid, 86% yield. ^{1}H NMR ($CDCl_3$): δ 3.16 (b, 1H, OH), 7.29–7.62 (m, 15H, aryl). ^{13}C NMR ($CDCl_3$): δ 81.5 (t, $^2J_{C-F}$ = 24 Hz, CF_2C–), 126.2 (t, $^3J_{C-F}$ = 2 Hz, aryl), 127.7 (t, $^3J_{C-F}$ = 2 Hz, aryl), 127.9 (aryl), 128.2 (aryl), 128.9 (aryl), 129.7 (aryl), 131.1 (t, $^1J_{C-F}$ = 293 Hz, CF_2), 136.6 (aryl), 140.2 (aryl). ^{19}F NMR ($CDCl_3$): δ −77.9 (s). MS: 342 [M^+], 213, 183, 165, 105, 77. HRMS (EI): *m/z* calcd for $C_{20}H_{16}F_2OS$ [M^+] 342.0890, found 342.0899.

4.2.7. 2,2-Difluoro-2-phenylthio-1-methyl-1-phenylethanol (**4g**)

Colorless liquid, 82% yield. ^{1}H NMR ($CDCl_3$): δ 1.83 (s, 3H, CH_3), 2.64 (b, 1H, OH), 7.32–7.68 (m, 10H, aryl). ^{13}C NMR ($CDCl_3$): δ 24.5 (t, $^3J_{C-F}$ = 2.4 Hz, CH_3), 77.9 (t, $^2J_{C-F}$ = 24.4 Hz, CF_2C–), 126.1 (t, $^3J_{C-F}$ = 2.2 Hz, aryl), 126.3 (aryl), 128.1 (aryl), 128.2 (aryl), 128.8 (aryl), 129.6 (aryl), 131.0 (t, $^1J_{C-F}$ = 290 Hz, CF_2), 136.5 (aryl), 140.0 (aryl). ^{19}F NMR ($CDCl_3$): δ −82.1 (d, $^2J_{F-F}$ = 204.5 Hz, 1F), −84.9 (d, $^2J_{F-F}$ = 204.5 Hz, 1F). HRMS (EI): *m/z* calcd for $C_{15}H_{14}F_2OS$ [M^+] 280.0733, found 280.0727.

4.2.8. 1-Difluoro(phenylthio)methylcyclohexanol (**4h**)

Colorless liquid, 77% yield. ^{1}H NMR ($CDCl_3$): δ 1.19–1.88 (m, 11H, $5CH_2$ and 1CH), 7.34–7.63 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 20.8 (CH_2), 25.3 (CH_2), 31.0 (t, $^3J_{C-F}$ = 2.2 Hz, CF_2–C–CH_2), 75.9 (t, $^2J_{C-F}$ = 23.3 Hz, CF_2–C), 126.2 (t, $^3J_{C-F}$ = 2.4 Hz, aryl), 128.9 (aryl), 129.6 (aryl), 132.1 (aryl), 136.7 (aryl). ^{19}F NMR ($CDCl_3$): δ −87.6 (s). HRMS (EI): *m/z* calcd for $C_{13}H_{16}F_2OS$ [M^+] 258.0890, found 258.0894.

4.3. Nucleophilic (phenylthio)difluoromethylation of diphenyl disulfide

Under an argon atmosphere, into a Schlenk flask containing diphenyl disulfide (218 mg, 1.0 mmol) and TMS–CF_2SPh (464 mg, 2.0 mmol) in dry THF (7 mL) at 0 °C, was added dropwise a THF solution (3 mL) of *t*-BuOK (336 mg, 3.0 mmol). Then the reaction mixture was stirred at 0 °C to room temperature for 2 h, followed by quenching with saturated NaCl aqueous solution (10 mL). The mixture was extracted with ether (15 mL × 3), and the combined organic phase was dried over $MgSO_4$. After the removal of volatile solvents, the residue was further purified by silica gel column chromatography (using hexane as eluent) to give $PhSCF_2SPh$ (**6**) as a colorless liquid, yield: 227 mg (85%). ^{1}H NMR ($CDCl_3$): δ 7.33 (tt, *J* = 7.3 Hz, 2.0 Hz, 4H, aryl), 7.39 (tt, *J* = 7.3 Hz, 2.0 Hz, 2H, aryl), 7.58 (d, *J* = 8.0 Hz, 4H, aryl). ^{13}C NMR ($CDCl_3$): δ 127.2 (t, $^3J_{C-F}$ = 14 Hz), 129.1 (aryl), 130.2 (aryl), 132.3 (t, $^1J_{C-F}$ = 315 Hz), 136.1 (aryl). ^{19}F NMR ($CDCl_3$): δ −49.5 (s). MS: 268 [M^+], 159, 109, 77.

4.4. Preparation of difluoromethylated alcohols (**10**) from (phenylthio)difluoromethylated alcohols (**4**)

Compound **4a** (or **4b**) (1 equiv.) was oxidized with 30% aqueous H_2O_2 (4 equiv.) in acetic acid at 50 °C overnight. After a standard workup, the neutralized crude product **9a** (or **9b**) was added into a mixture of Na(Hg) amalgam (5 wt.% Na in Hg, 5 equiv.) and MeOH at −20 °C, and the mixture was stirred at −20 °C to room temperature for 1 h. The liquid phase was decanted, and the solid residue was washed with ether for 3 times. After solvent removal of the combined organic phase, the residue was purified by silica gel column chromatography (hexane/ethyl acetate (v/v) = 5:1) to give product **10a** (or **10b**) in 49 and 53% yield, respectively. The characterization data of **10a** are consistent with the previous report [10]. For product **10b**: ^{1}H NMR ($CDCl_3$): δ 2.99 (b, 1H, OH), 4.98 (m, 1H, CF_2CH), 5.86 (td, *J* = 56 Hz, 4.7 Hz, 1H, CF_2H), 7.50 (m, 3H, aryl), 7.87 (m, 4H, aryl). ^{13}C NMR ($CDCl_3$): δ 73.7 (t, $^2J_{C-F}$ = 24.6 Hz, CF_2CH), 115.8 (t, $^1J_{C-F}$ = 246 Hz, CF_2), 124.3 (aryl), 126.4 (aryl), 126.5 (aryl), 126.6 (aryl), 127.7 (aryl), 128.1 (aryl), 128.4 (aryl), 133.0 (aryl), 133.2 (t, $^3J_{C-F}$ = 3.5 Hz, aryl), 133.5 (aryl). ^{19}F NMR ($CDCl_3$): δ −127.4 (ddd, $^2J_{F-F}$ = 284 Hz, $^2J_{F-H}$ = 56 Hz, $^3J_{F-H}$ = 9 Hz, 1F, CF_2H), −128.0 (ddd, $^2J_{F-F}$ = 284 Hz, $^2J_{F-H}$ = 56 Hz, $^3J_{F-H}$ = 10 Hz, 1F, CF_2H). MS: 208 [M^+].

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