Journal of Fluorine Chemistry 135 (2012) 45–58

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

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

Difluoro(phenylchalcogen)methylation of aldehydes, ketones, and imines with S-, Se-, and Te-containing reagents $PhXCF_2H$ (X = S, Se, Te)

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ARTICLE INFO

Article history:
Received 24 June 2011
Received in revised form 9 August 2011
Accepted 10 August 2011
Available online 13 September 2011

Dedicated to Professor Wei-Yuan Huang on the occasion of his 90th birthday.

Keywords:
(Phenylchalcogen)difluoromethylation
Fluorine
Difluoromethylation
Nucleophilic fluoroalkylation
Diastereoselectivity

ABSTRACT

A series of sulfur-, selenium- and tellurium-containing (phenylchalcogen)difluoromethylation reagents $PhSCF_2H$ (**1a**), $PhSeCF_2H$ (**1b**), and $PhTeCF_2H$ (**1c**) were prepared, and their relative reactivity towards aldehydes, ketones, and imines was investigated. Compared to the former developed (phenylchalcogen)difluoromethylation reagents, these reagents are relatively easily available and more atom-economical in fluoroalkylation reactions. It was found that the efficient nucleophilic (phenylchalcogen)difluoromethylation of aldehydes, ketones, and imines could be achieved with **1a**–**1c**. Reagents **1a** and **1b** showed better reactivity than **1c** toward carbonyl compounds and imines, and $PhOCF_2H$ (**1d**) was found to be unable to undergo similar fluoroalkylation reactions.

1. Introduction

Nucleophilic fluoroalkylation with (fluoroalkyl)silanes R_fSiR_3 (such as the Ruppert-Prakash reagent, $TMSCF_3$) has become one of the widely used methods for the synthesis of fluorinated organic compounds (Eq. (1)) [1,2]. Another class of nucleophilic fluoroalkylation agents are hydrofluorocarbons (R_fH), which, under the treatment of a proper base, generate the fluoroalkyl anions R_f^- that act as real nucleophilic fluoroalkylating species (Eq. (2)) [3,4]. The hydrofluorocarbon reagents include trifluoromethane (CF_3H) and other polyfluoroalkanes [5], diethyl difluoromethanephosphonate [6], difluoromethyl phenyl sulfone ($PhSO_2CF_2H$) [7], fluoromethyl phenyl sulfone ($PhSO_2CH_2F$) [8], and fluorobis(phenylsulfonyl)-methane [9], among others. The advantage of using R_fH as fluoroalkylating agents lies in the fact that the functionalization of C–H bond is the most atom-economical way in organic synthesis [10].

$$R_f-SiR_3 \xrightarrow[\text{activator}]{E^+} R_f-E \quad (1)$$

$$R_f-H \xrightarrow[\text{base}]{E^+} R_f-E \quad (2)$$

Recently, inspired by the importance of introducing a (phenylthio)difluoromethyl [11], (phenylseleno)difluoromethyl [12], or (phenyltelluro)difluoromethyl group [13] into organic molecules, we were interested in developing $PhSCF_2H$ (**1a**), $PhSeCF_2H$ (**1b**), and $PhTeCF_2H$ (**1c**) as efficient nucleophilic (phenylchalcogen)difluoromethylation reagents. It should be mentioned that, both (phenylthio)difluoromethylation and (phenylseleno)difluoromethylation with $PhSCF_2SiMe_3$ and $PhSeCF_2SiMe_3$ have been previously described [11,12], while the similar (phenyltelluro)difluoromethylation has never been reported. Furthermore, to the best of our knowledge, the nucleophilic (phenylchalcogen)difluoromethylation with $PhXCF_2H$ (X = S, Se, Te) reagents (**1a**–**c**) has never been reported, although compounds **1a**–**c** have been known for decades [13,14]. In this paper, we wish to disclose the efficient nucleophilic (phenylthio)-, (phenylseleno)-, and (phenyltelluro)-difluoromethylation of aldehydes, ketones, and imines with S-, Se-, and Te-containing reagents $PhXCF_2H$ (X = S, Se, Te).

2. Results and discussion

A series of difluoromethylation reagents $PhSCF_2H$ (**1a**), $PhSeCF_2H$ (**1b**) and $PhTeCF_2H$ (**1c**) were prepared by using previously known methods [13,14]. Then, we carried out the (phenylseleno)difuoromethylation reactions by using benzaldehyde (**2a**) as a model compound with $PhSeCF_2H$ (**1b**). The reaction conditions were initially based on the previously reported ones

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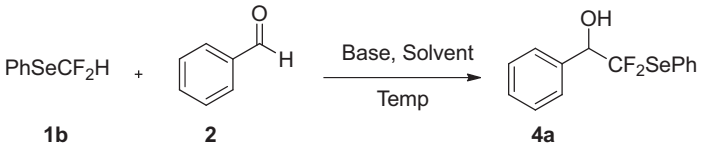
doi:10.1016/j.jfluchem.2011.08.007

Table 1
(Phenylseleno)difuoromethylation of benzaldehyde (**2a**) with reagent **1b**.



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Entry	Base	Solvent	Temp (°C)	Time (h)	**1b**:**2**:base	Yield (%)[a]
1	LiHMDS	THF	−78	0.5	1:1:2	0[b]
2	*n*-BuLi	THF	−78	0.5	1:1:2	0[b]
3	*t*-BuOK	DMF	−50	1	1:1:2	57[c]
4	*t*-BuOK	DMF	−50	3	1:1:2	57[c]
5	*t*-BuOK	THF	−78	0.5	1:1:2	0
6	*t*-BuOK	DMF	−30	2	1:1.5:2	21
7	*t*-BuOK	DMF	0–5	2	1:1.5:2	20
8	*t*-BuOK	DMF	rt	2	1:1.5:2	3
g	*t*-BuOK	THF	0–5	2	1:1.5:2	37
10	*t*-BuOK	DMSO	rt	2	1:1.5:2	3
11	***t*-BuOK**	**DMF**	**−50**	**2**	**1:1.5:2**	**86**[c]
12	*t*-BuOK	DMF	−50	2	1:1:4	58[c]

[a] Yield was based on ^{19}F NMR of a sample from the crude reaction mixture using $PhCF_3$ as an internal standard.
[b] When the temperature up to room temperature, there was still no product monitored.
[c] Isolated yield.

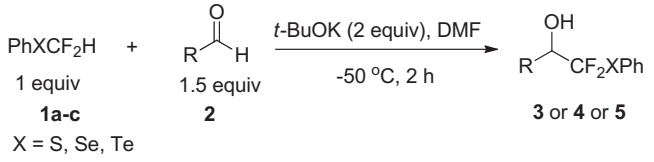
with $PhSO_2CF_2H$ reagent [15]. When we used *n*-BuLi and LiHMDS ($LiN(SiMe_3)_2$) as bases at −78 °C (or room temperature) in THF, the reaction failed to give the desired product, as monitored by ^{19}F NMR (Table 1, entry 1–2). When *t*-BuOK was employed, we found that the reaction took place at −50 °C, and further optimization revealed that DMF was the best solvent at −50 °C (Table 1, entries 3–12). The reaction typically completed within 2 h.

With the optimized condition, a variety of aldehydes as substrates have been investigated, and the results are summarized in Table 2. For those aldehydes with electron-donating substituents on the aromatic ring (such as 4-methoxy and 4-dimethylamino benzaldehyde), the yields were generally high (Table 2, entries 2 and 3). But for the alkyl substituted benzaldehyde, the yield was much lower since a significant amount of starting materials were unreacted (Table 2, entry 9). For electron-withdrawing substituents on the aromatic ring, the yields were relatively low due to the serious side reaction (Cannizzaro reaction) of the aldehydes (Table 2, entries 4 and 5), which was consistent with the previous report [16]. For reagent **1c**, the anion intermediate is unstable to some extent, and much lower yields were obtained (entries 1, 3, 5–7, 9 and 10).

Encouraged by the aforementioned results, we examined the reaction of these reagents with ketones, and the results were listed in Table 3. As ketones possess relatively lower reactivity than aldehydes, the yields dropped sharply with the decrease of the anion stability ($PhSCF_2^- > PhSeCF_2^- > PhTeCF_2^-$). However, in most cases when reagents **1a** and **1b** were used, the corresponding products were obtained in satisfactory yields regardless of the electronic nature of the substituents on the aromatic ring (Table 3).

It is worth noting that although reagents **1a**–**c** could react with non-enolizable aldehydes and ketones, they did not react efficiently with enolizable carbonyl compounds under the aforementioned conditions. Therfore, we chose acetone as a model substrate to further optimize the reaction conditions. It was found that, when LiHMDS and *n*-BuLi were employed as bases, no matter what the temperature and solvent were, there were no target products observed (Table 4, entries 3–6 and 11). However, when KHMDS was used, the product was observed in 30% yield (monitored by ^{19}F NMR), whereas in the case of NaHMDS, only 6% yield of product was formed (Table 4, entries 7–10). These results indicated that the metal counterion of the base may play an important role in the reaction. When the base was changed to potassium hydroxide (KOH), and the temperature was increased from 0 °C to room temperature, the reaction (in DMF) gave the product **11a** in 71% isolated yield (Table 4, entry 14). Encouraged by this result, we further investigated the substrate scope of

Table 2
(Phenylchalcogen)difluoromethylation of different aldehydes with reagents **1a**–**c**.



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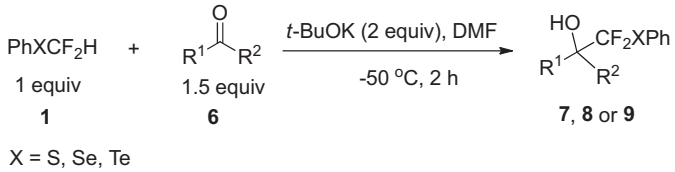
Entry	Substrate	Product	Yield (%)[a]
1	R = Ph (**2a**)	**3a** X=S	94
		4a X=Se	86
		5a X=Te	76
2	R = 4-(Me_2N)C_6H_4 (**2b**)	**3b** X=S	91
		4b X=Se	92
3	R = 4-(MeO)C_6H_4 (**2c**)	**3c** X=S	79
		4c X=Se	91
		5b X=Te	72
4	R = 2-BrC_6H_4 (**2d**)	**3d** X=S	28
		4d X=Se	91
5	R = 4-ClC_6H_4 (**2e**)	**3e** X=S	72
		4e X=Se	75
		5c X=Te	54
6	R = 4-BrC_6H_4 (**2f**)	**3f** X=S	94
		5d X=Te	73
7	R = 2-Naphthyl (**2g**)	**3g** X=S	91
		4f X=Se	75
		5e X=Te	35
8	R = 2,5-$(MeO)_2C_6H_3$ (**2h**)	**3h** X=S	68
		4g X=Se	83
9	R = 4-MeC_6H_4 (**2i**)	**3i** X=S	61
		4h X=Se	34[b]
		5f X=Te	47
10	R = *t*-Butyl (**2k**)	**3j** X=S	94
		4j X=Se	94
		5g X=Te	49

[a] Isolated yield.
[b] There were still lots of starting materials left.

Table 3
(Phenylchalcogen)difluoromethylation of different ketones with reagents **1**.



Entry	Substrate	R^1	R^2	Product	Yield (%)[a]
1	**6a**	Ph	Ph	**7a** X=S	96
				8a X=Se	88
2	**6b**	C_6H_4	C_6H_4	**7b** X=S	96
				8b X=Se	82
3	**6c**	Ph	4-ClC_6H_4	**7c** X=S	79
				8c X=Se	79
				9a X=Te	66
4	**6d**	Ph	4-BrC_6H_4	**7d** X=S	92
				8d X=Se	79
				9b X=Te	36
5	**6e**	Ph	4-FC_6H_4	**8e** X=Se	94
				9c X=Te	60
6	**6f**	Ph	4-$MeOC_6H_4$	**7e** X=S	89
				8f X=Se	91
				9d X=Te	28
7	**6g**	Ph	4-PhC_6H_4	**7f** X=S	82
				8g X=Se	91

[a] Isolated yeild.

(phenylchalcogen)difluoromethylation of enolizable ketones, and the results are summarized in Table 5. It was found that both acyclic and cyclic enolizable ketones could react with $PhSCF_2H$ (**1a**) and $PhSeCF_2H$ (**1b**) in moderate to excellent yields. It should be mentioned that when we tried the similar KOH-mediated reaction between ketones and $PhTeCF_2H$ (**1c**), no desired product was observed.

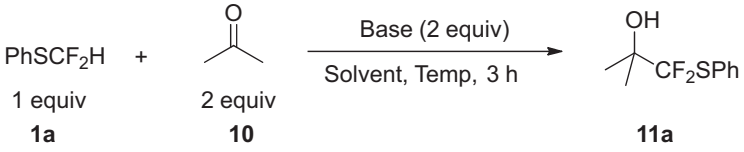
To probe the relative acidity of **1a–c**, we conducted the H/D excange experiments of **1a–c** in KOH/D_2O/DMF. The data are shown in Table 6, which suggest that the $PhSCF_2H$ (**1a**) is less acidic than $PhSeCF_2H$ (**1b**) and $PhTeCF_2H$ (**1c**). This is in consistent with the previous report that for α-substituted methyl carbanions XCH_2^-, the higher period substituents X substantially decrease the proton affinity (PA) of XCH_2^-, whereas lower period substituents are less effective in reducing the basicity of XCH_2^- [17]. It should be noted that we found that all of three carbanions $PhXCF_2^-$ (X = S, Se, Te) tend to undergo decomposition (presumably via α-elimination) (Table 6).

Furthermore, we extended the present nucleophilic (phenylchalcogen)difluoromethylation reactions to imines. At the outset, we utilized *N*-benzylidene-4-methylbenzenesulfonamide (PhCH=NTs) as a model substrate and *t*-BuOK as a base, to react with $PhSeCF_2H$ (**1b**) at −50 °C in DMF. However, no desired product was observed by ^{19}F NMR. Thereafter, we chose *N*-*tert*-butylsulfinyl imine (PhCH=NSO*t*-Bu) (**13a**) as a model substrate, and trace amount of product **15a** was observed by ^{19}F NMR. When we increased the temperature to −30 °C, the reaction proceeded smoothly to give the product **15b** in 80% isolated yield and with 98:2 diastereomeric ratio (Table 7, entry 2). Further investigation disclosed that the temperature scope could be ranged from −40 to −30 °C, and with this reaction condition, we examined the reaction with a variety of structurally diverse *N*-*tert*-butylsulfinyl imines (Table 7). It was found that, while both $PhSCF_2H$ (**1a**) and $PhSeCF_2H$ (**1b**) were able to efficiently undergo nucleophilic addition to sulfinimines **13** to afford corresponding $PhSCF_2$- and $PhSeCF_2$-containing chiral imines **14** (or **15**) in good yields and with high diastereoselectivity, the similar reactions with $PhTeCF_2H$ (**1c**) were not successful. It is worth noting that we found that $PhOCF_2H$ (**1d**) could not undergo similar (phenyloxo) difluoromethylation reaction with aldehydes, ketones and imines under similar aforementioned conditions.

3. Conclusions

In conclusion, we have developed efficient nucleophilic (phenylchalcogen)difluoromethylation of aldehydes, ketones, and imines with $PhSCF_2H$ (**1a**), $PhSeCF_2H$ (**1b**), and $PhTeCF_2H$ (**1c**). It was found that reagents **1a** and **1b** showed better reactivity

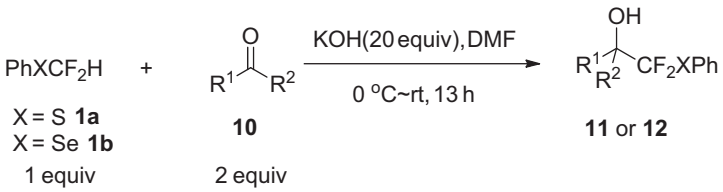
Table 4
The reaction between **1a** and enolizable ketones.

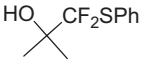
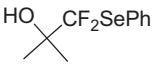
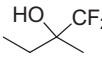
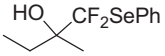
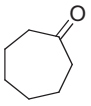
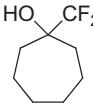
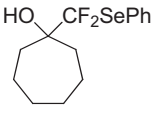
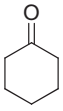
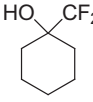
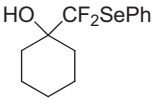


Entry	Base	Solvent	Temp (°C)	Yield (%)[a]
1	*t*-BuOK	DMF	−50	0[b]
2	*t*-BuOK	DMF	25	Trace
3	LiHMDS	THF/HMPA	−78	0[b]
4	LiHMDS	THF/HMPA	0	0[b]
5	LiHMDS	THF/HMPA	25	0[b]
6	LiHMDS	DMF	0	0[b]
7	KHMDS	THF	−50 to rt	0[b]
8	KHMDS	DMF	−50 to rt	30
9	NaHMDS	THF	−50 to rt	0[b]
10	NaHMDS	DMF	−50 to rt	6
11	*n*-BuLi	THF/HMPA	−78	0[b]
12	K_2CO_3	DMF	−50 to rt	0[b]
13	KOH	DMF	−50 to rt	27
14	KOH	DMF	0 to rt	71[c]

[a] Yield were determinded by ^{19}F NMR using $PhCF_3$ as an internal standard.
[b] No desired product was formed.
[c] Isolated yield after the reaction mixture was stirred for 13 h.

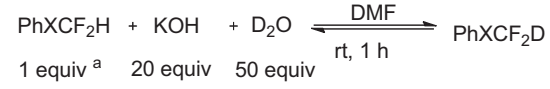
Table 5
The reaction of **1a** (or **1b**) with enolizable ketones.



Entry	Substrate	Reagent	Product	Yield (%)[a]
1	 **10a**	**1a**	 **11a**	71
2		**1b**	 **12a**	83
3	 **10b**	**1a**	 **11b**	97
4		**1b**	 **12b**	60
5	 **10c**	**1a**	 **11c**	94
6		**1b**	 **12c**	55
7	 **10d**	**1a**	 **11d**	53
8		**1b**	 **12d**	29

[a] Isolated yeild.

Table 6
The deuterium-labeling experiments with reagents **1a**–**1c**.

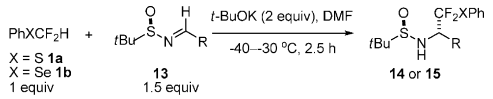


(X = S, Se, Te)

X	Result[b]		
	$PhXCF_2H$ (%)	$PhXCF_2D$ (%)	Decomposed (%)
S	36	23	41
Se	6	50	44
Te	7	35	58

[a] The starting material was employed on 0.2 mmol scale.
[b] Determined by ^{19}F NMR $PhCF_3$ as an internal standard. All reactants were added in one portion.

Table 7
The reaction of **1a** (or **1b**) with *N*-*tert*-butylsulfinyl imines.



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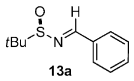
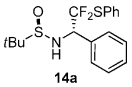
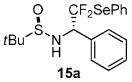
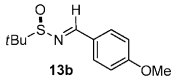
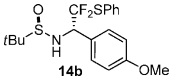
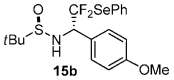
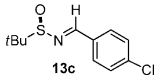
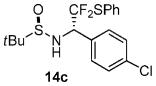
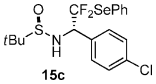
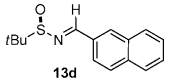
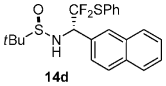
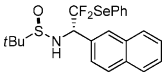
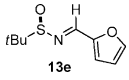
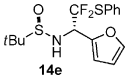
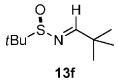
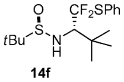
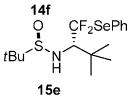
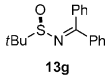
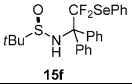
Entry	Reagent	Substrate	Product	Yield (%)[a]	dr[b]
1	**1a**	 **13a**	 **14a**	58	≥87:13
2	**1b**		 **15a**	80	≥98:2
3	**1a**	 **13b**	 **14b**	76	≥94:6
4	**1b**		 **15b**	73	≥94:6
5	**1a**	 **13c**	 **14c**	33	≥91:9
6	**1b**		 **15c**	52	≥99:1
7	**1a**	 **13d**	 **14d**	72	≥95:5
8	**1b**		 **15d**	71	≥91:1
9	**1a**	 **13e**	 **14e**	43	≥78:22
10	**1a**	 **13f**	 **14f**	72	≥97:3
11	**1b**		 **15e**	63	≥96:4
12	**1b**	 **13g**	 **15f**	52	–

[a] Isolated yield based on the main isomer.
[b] Determined by ^{19}F NMR.

than **1c** toward carbonyl compounds and imines, and $PhOCF_2H$ (**1d**) was unable to undergo similar fluoroalkylation reactions.

4. Experimental

All reactions and manipulations were performed using standard Schlenk techniques. Unless otherwise mentioned, solvents were purchased from commercial sources and purified before using. THF was distilled from sodium benzophenone ketyl. DMF, DMSO and HMPA were distilled over CaH_2 under nitrogen atmosphere. Other reagents were purchased from commercial sources and used as received. ^1H NMR spectra were recorded on Bruker 300 or Mercury 300 spectrometers with Me_4Si as internal standard. ^{19}F NMR spectra were recorded on Bruker 300 or Mercury 300 spectrometers with $CFCl_3$ as external standard. ^{13}C NMR spectra were recorded on Avance 500 or DPX-400 spectrometers. Mass spectra were obtained on a spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI, ESI or MALDI mode.

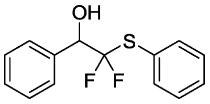
4.1. Typical procedure for preparation of reagents 1

The reagents **1** were prepared following reported methods [13].

4.2. General procedure for reaction of 1 (PhXCF2H, X = S, Se, Te) with 2 and 6

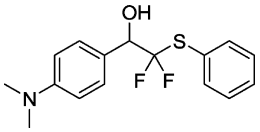
Under a nitrogen atmosphere, to a stirred solution of $PhSeCF_2H$ (**1b**) (414 mg, 2.0 mmol) and benzaldehyde (**2a)** (318 mg, 3.0 mmol) with 3 mL DMF in a Schlenk tube, *t*-BuOK (448 mg, 4.0 mmol) (dissolved in 2 mL DMF) was added dropwise at −50 °C. The mixture was stirred at this temperature for 2 h. Then quenched with saturated aqueous ammonium chloride or brine, the reaction mixture was extracted with Et_2O (3 × 10 mL). The combined organic layer was washed with H_2O (2 × 10 mL), followed by brine (10 mL), dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography with ethyl acetate/petroleum ether (1:10) as eluent to give 520 mg **4a** as a colorless oil. Yield 86%.

*4.2.1. 2,2-Difluoro-1-phenyl-2-(phenylthio)ethanol (**3a**)*



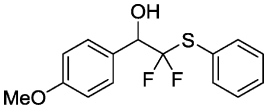
Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (d, J = 7.0 Hz, 2H), 7.47–7.31 (m, 8H), 4.98 (m, 1H), 2.82 (d, J = 4.0 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.1 (dd, J = 209.5 Hz, J = 8.1 Hz, 1F), −84.8 (dd, J = 209.5 Hz, J = 11.0 Hz, 1F). The characterization data were consistent with the previous report [18].

*4.2.2. 1-(4-(Dimethylamino)phenyl)-2,2-difluoro-2-(phenylthio)ethanol (**3b**)*



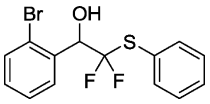
Yellow oil; IR (film): 3420, 3060, 2890, 2805, 1615, 1526, 1475, 1441, 1356, 1230, 1189, 1159, 1054, 981, 819, 787, 751, 691 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (d, J = 7.1 Hz, 2H), 7.41–7.31 (m, 5H), 6.70 (d, J = 6.7 Hz, 2H), 4.89 (t, J = 9.6 Hz, 1H), 2.95 (s, 6H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −82.1 (dd, J = 207.2 Hz, J = 9.1 Hz, 1F), −84.1 (dd, J = 207.3 Hz, J = 11.1 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.1, 136.4, 132.1, 129.7, 129.3, 129.0, 128.8, 126.4, 122.8, 112.1, 76.3 (t, J = 26.4 Hz), 40.4. MS (EI, m/z, %): 309 (M^+, 12.44), 150 (100.00). HRMS (EI): Calcd. for $C_{16}H_{17}F_2ONS$: 309.0999; found: 309.0990.

*4.2.3. 2,2-Difluoro-1-(4-methoxyphenyl)-2-(phenylthio)ethanol (**3c**)*



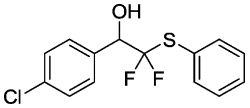
Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (d, J = 7.1 Hz, 2H), 7.41–7.31 (m, 5H), 6.90 (d, J = 8.6 Hz, 2H), 4.94 (m, 1H), 3.80 (s, 3H), 2.80 (d, J = 4.1 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.7 (dd, J = 208.4 Hz, J = 8.2 Hz, 1F), −84.6 (dd, J = 208.5 Hz, J = 10.6 Hz, 1F). The characterization data were consistent with the previous report [19].

*4.2.4. 1-(2-Bromophenyl)-2,2-difluoro-2-(phenylthio)ethanol (**3d**)*



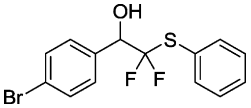
Yellow oil; IR (film): 3417, 3063, 1591, 1570, 1474, 1440, 1157, 1125, 1062, 984, 845, 749, 691 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72–7.54 (m, 4H), 7.45–7.35 (m, 4H), 7.25–7.15 (m, 1H), 5.53 (m, 1H), 2.77 (d, J = 4.4 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.8 (dd, J = 212.7 Hz, J = 5.1 Hz, 1F), −87.1 (dd, J = 212.7 Hz, J = 13.4 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.5, 134.9, 132.9, 131.7, 130.5, 130.0, 129.9, 129.2, 127.6, 125.8, 124.3, 74.1 (t, J = 26.4 Hz), 40.4. MS (EI, m/z, %): 345 (M^+, 2.06), 185 (100.00), 187 (98.79). HRMS (EI): Calcd. for $C_{14}H_{11}F_2BrOS$: 343.9682; found: 343.9686.

*4.2.5. 1-(4-Chlorophenyl)-2,2-difluoro-2-(phenylthio)ethanol (**3e**)*



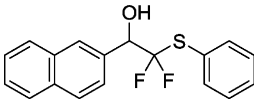
White solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58(m, 2H), 7.41–7.37 (m, 7H), 4.97 (m, 1H), 2.71 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.2 (d, J = 210.3 Hz, 1F), −85.3 (dd, J = 211.5 Hz, J = 11.5 Hz, 1F). The characterization data were consistent with the previous report [11a].

*4.2.6. 1-(4-Bromophenyl)-2,2-difluoro-2-(phenylthio)ethanol (**3f**)*



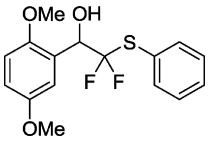
Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57–7.25 (m, 9H), 4.95 (m, 1H), 2.79 (d, J = 3.1 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.1 (dd, J = 211.3 Hz, J = 7.1 Hz, 1F), −85.2 (dd, J = 210.4 Hz, J = 10.2 Hz, 1F). The characterization data were consistent with the previous report [11a].

*4.2.7. 2,2-Difluoro-1-(naphthalen-2-yl)-2-(phenylthio)ethanol (**3g**)*



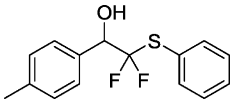
White solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.96 (s, 1H), 7.87–7.85 (m, 3H), 7.60–7.32 (m, 8H), 5.17 (m, 1H), 2.83 (d, J = 3.7 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.8 (dd, J = 209.5 Hz, J = 7.3 Hz, 1F), −84.2 (dd, J = 210.3 Hz, J = 11.1 Hz, 1F). The characterization data were consistent with the previous report [11a].

*4.2.8. 1-(2,5-Dimethoxyphenyl)-2,2-difluoro-2-(phenylthio)ethanol (**3h**)*



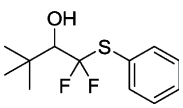
Yellow oil; IR (film): 3448, 3061, 3001, 2945, 2836, 1590, 1502, 1465, 1441, 1220, 1179, 1157, 1046, 989, 815, 751, 692 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, J = 7.7 Hz, 2H), 7.42–7.32 (m, 3H), 6.96 (s, 1H), 6.86 (m, 2H), 5.24 (m, 1H), 3.87 (m, 1H), 3.82 (s, 1H), 3.77 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.0 (dd, J = 205.5 Hz, J = 8.4 Hz, 1F), −84.8 (dd, J = 205.3 Hz, J = 13.4 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.7, 152.0, 136.4, 132.7, 129.7, 129.2, 129.0, 126.4, 124.4, 115.3, 115.1, 112.6, 73.4 (t, J = 26.6 Hz), 56.4, 55.8. MS (EI, m/z, %): 326 (M^+, 21.49), 167 (100.00). HRMS (EI): Calcd. for $C_{16}H_{16}F_2O_3S$: 326.0788; found: 326.0793.

*4.2.9. 2,2-Difluoro-2-(phenylthio)-1-p-tolylethanol (**3i**)*



Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (d, J = 7.1 Hz, 2H), 7.41–7.11 (m, 7H), 4.95 (m, 1H), 3.00 (m, 1H), 2.36 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.5 (dd, J = 209.6 Hz, J = 8.0 Hz, 1F), −84.6 (dd, J = 208.3 Hz, J = 11.3 Hz, 1F). The characterization data were consistent with the previous report [19].

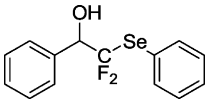
*4.2.10. 1,1-Difluoro-3,3-dimethyl-1-(phenylthio)butan-2-ol (**3j**)*



Colorless oil; IR (film): 3474, 3062, 2961, 2913, 2876, 1475, 1441, 1168, 1063, 1023, 977, 932, 875, 747, 705, 691 cm^{-1}. ^{1}H NMR

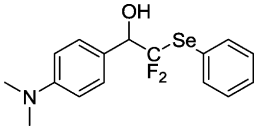
($CDCl_3$, 300 MHz): δ 7.55 (d, J = 7.3 Hz, 2H), 7.38–7.27 (m, 3H), 3.52 (m, 1H), 2.24 (d, J = 7.3 Hz, 1H), 1.00 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.4 (d, J = 208.9 Hz, 1F), −83.5 (dd, J = 209.2 Hz, J = 18.6 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.6, 134.2, 131.4, 129.8, 129.0, 126.4 (t, J = 2.3 Hz), 80.2 (t, J = 25.2 Hz), 35.1, 26.8. MS (EI, m/z, %): 246 (M^+, 37.01), 57 (100.00). HRMS (EI): Calcd. for $C_{12}H_{16}F_2OS$: 246.0890; found: 246.0894.

*4.2.11. 2,2-Difluoro-1-phenyl-2-(phenylselanyl)ethanol (**4a**)*



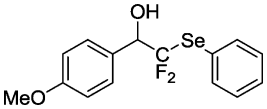
Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.52 (d, J = 7.3 Hz, 2H), 7.32–7.15 (m, 8H), 4.81 (m, 1H), 3.01 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −78.2 (dd, J = 208.5 Hz, J = 8.3 Hz, 1F), −82.2 (dd, J = 208.4 Hz, J = 12.4 Hz, 1F). The characterization data were consistent with the previous report [12].

*4.2.12. 1-(4-(Dimethylamino)phenyl)-2,2-difluoro-2-(phenylselanyl)ethanol (**4b**)*



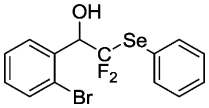
Yellow solid; m.p. 48–50 °C; IR (film): 3425, 3057, 2889, 2805, 1615, 1579, 1477, 1439, 1357, 1189, 1159, 1059, 966, 742, 692, 600 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.65 (d, J = 6.9 Hz, 2H), 7.38–7.30 (m, 5H), 6.70 (d, J = 9.2 Hz, 2H), 4.87 (t, J = 11.5 Hz, 1H), 2.96 (s, 6H), 2.64 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.0 (dd, J = 204.6 Hz, J = 9.5 Hz, 1F), −81.2 (dd, J = 205.6 Hz, J = 11.6 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.1, 137.2, 130.1, 129.3, 129.1, 128.7, 127.1, 124.3, 124.1, 122.7, 112.1, 77.0 (t, J = 25.3 Hz), 40.4. MS (EI, m/z, %): 357 (M^+, 5.20), 150 (100.00). HRMS (EI): Calcd. for $C_{16}H_{17}F_2NOSe$: 357.0443; found: 357.0438.

*4.2.13. 2,2-Difluoro-1-(4-methoxyphenyl)-2-(phenylselanyl)ethanol (**4c**)*



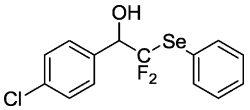
Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.64 (d, J = 7.3 Hz, 2H), 7.38–7.24 (m, 5H), 6.89 (d, J = 8.9 Hz, 2H), 4.90 (m, 1H), 3.80 (s, 3H), 2.76 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −78.9 (dd, J = 207.4 Hz, J = 8.1 Hz, 1F), −82.3 (dd, J = 208.9 Hz, J = 12.9 Hz, 1F). The characterization data were consistent with the previous report [20].

*4.2.14. 1-(2-Bromophenyl)-2,2-difluoro-2-(phenylselanyl)ethanol (**4d**)*



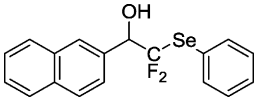
Colorless oil; IR (film): 3418, 3060, 1591, 1569, 1475, 1439, 1392, 1154, 1063, 968, 742, 691, 598 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.69 (d, J = 6.4 Hz, 3H), 7.53 (d, J = 8.2 Hz, 1H), 7.43–7.33 (m, 4H), 7.25–7.18 (m, 1H), 5.48 (m, 1H), 2.83 (d, J = 4.4 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −77.1 (dd, J = 212.7 Hz, J = 6.5 Hz, 1F), −84.7 (dd, J = 211.7 Hz, J = 14.8 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.3, 134.8, 132.9, 130.5, 129.9, 129.7, 129.4, 129.3, 129.2, 127.6, 126.40, 126.37, 124.3, 123.82, 123.78, 123.4, 74.8 (t, J = 25.1 Hz). MS (EI, m/z, %): 391 (M^+, 5.10), 187 (100.00). HRMS (EI): Calcd. for $C_{14}H_{11}BrF_2OSe$: 391.9127; found: 391.9131.

*4.2.15. 1-(4-Chlorophenyl)-2,2-difluoro-2-(phenylselanyl)ethanol (**4e**)*



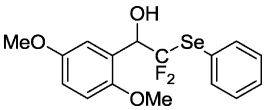
White solid; m.p. 80–81 °C; IR (film): 3573, 3089, 3069, 3046, 2897, 1592, 1578, 1485, 1475, 1438, 1407, 1196, 1051, 969, 743, 691, 606 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.63 (d, J = 6.9 Hz, 2H), 7.43–7.30 (m, 7H), 4.92 (m, 1H), 2.70 (d, J = 3.9 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −78.3 (dd, J = 211.6 Hz, J = 8.3 Hz, 1F), −83.2 (dd, J = 210.8 Hz, J = 12.4 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.2, 135.1, 133.5, 129.6, 129.4, 129.3, 129.2, 128.6, 126.4, 123.6, 76.2 (t, J = 24.1 Hz). MS (EI, m/z, %): 347 (M^+, 10.76), 141 (100.00). HRMS (EI): Calcd. for $C_{14}H_{11}ClF_2OSe$: 347.9632; found: 347.9634.

*4.2.16. 2,2-Difluoro-1-(naphthalen-2-yl)-2-(phenylselanyl)ethanol (**4f**)*



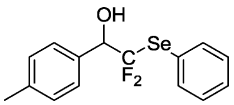
White solid; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.83 (s, 1H), 7.75–7.67 (m, 3H), 7.55–7.38 (m, 5H), 7.30–7.16 (m, 3H), 5.02 (m, 1H), 2.85 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): −78.1 (dd, J = 209.7 Hz, J = 8.4 Hz, 1F), −81.9 (dd, J = 209.6 Hz, J = 11.3 Hz, 1F). The characterization data were consistent with the previous report [20].

*4.2.17. 1-(2,5-Dimethoxyphenyl)-2,2-difluoro-2-(phenylselanyl)ethanol (**4 g**)*



Yellow oil; IR (film): 3448, 3058, 3001, 2941, 2836, 1613, 1578, 1500, 1439, 1278, 1179, 1156, 1045, 978, 813, 742, 591 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.68 (d, J = 6.8 Hz, 2H), 7.41–7.25 (m, 5H), 6.94 (s, 1H), 6.85 (s, 1H), 5.22 (m, 1H), 3.88 (m, 1H), 3.81 (s, 1H), 3.76 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −78.3 (dd, J = 204.5 Hz, J = 8.2 Hz, 1F), −82.0 (dd, J = 203.9 Hz, J = 14.5 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.7, 151.9, 137.2, 130.0, 129.3, 129.1, 127.0, 124.4, 124.3, 124.0, 115.22, 115.15, 112.6, 74.0 (t, J = 26.0 Hz), 56.3, 55.8. MS (EI, m/z, %): 374 (M^+, 10.90), 167 (100.00). HRMS (EI): Calcd. for $C_{16}H_{16}F_2O_3Se$: 374.0233; found: 374.0237.

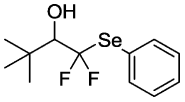
*4.2.18. 2,2-Difluoro-2-(phenylselanyl)-1-p-tolylethanol (**4h**)*



Yellow oil; IR (film): 3436, 3058, 3031, 2921, 1614, 1578, 1477, 1439, 1381, 1157, 1061, 967, 741, 691, 601 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.63 (d, J = 7.3 Hz, 2H), 7.37–7.26 (m, 5H), 7.16 (d, J = 7.6 Hz, 2H), 4.88 (m, 1H), 2.81 (d, J = 3.1 Hz, 1H), 2.34 (s, 1H). ^{19}F

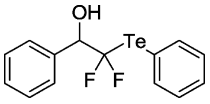
NMR ($CDCl_3$, 282 MHz): δ −78.6 (dd, J = 208.7 Hz, J = 9.3 Hz, 1F), −82.3 (dd, J = 208.3 Hz, J = 12.3 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.1, 137.3, 132.3, 129.8, 129.5, 129.3, 129.2, 129.1, 127.7, 126.8, 123.9, 123.8, 76.9 (t, J = 24.0 Hz), 21.3. MS (EI, m/z, %): 328 (M^+, 6.71), 121 (100.00). HRMS (EI): Calcd. for $C_{15}H_{14}F_2OSe$: 328.0174; found: 328.0176.

*4.2.19. 1,1-Difluoro-3,3-dimethyl-1-(phenylselanyl)butan-2-ol (**4i**)*



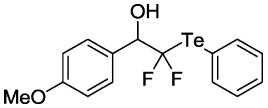
Yellow oil; IR (film): 3479, 3060, 2961, 2912, 2876, 1580, 1478, 1439, 1370, 1165, 1063, 971, 868, 739, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, J = 6.9 Hz, 2H), 7.44–7.32 (m, 3H), 3.60 (m, 1H), 2.33 (d, J = 7.7 Hz, 1H), 1.06 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −68.7 (d, J = 205.4 Hz, 1F), −81.6 (dd, J = 205.4 Hz, J = 20.4 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.3, 132.7, 129.74, 129.71, 129.4, 129.1, 126.7, 124.5, 81.2, 35.3, 26.7 (t, J = 2.9 Hz). MS (EI, m/z, %): 294 (M^+, 6.87), 57 (100.00). HRMS (EI): Calcd. for $C_{12}H_{16}F_2OSe$: 294.0334; found: 294.0333.

*4.2.20. 2,2-Difluoro-1-phenyl-2-(phenyltellanyl)ethanol (**5a**)*



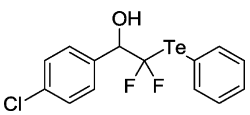
Yellow oil; IR (film): 3434, 3065, 1574, 1474, 1454, 1434, 1141, 1019, 997, 958, 843, 735, 692, 587 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.83 (d, J = 6.7 Hz, 2H), 7.44–7.21 (m, 8H), 4.85 (m, 1H), 2.75 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.1 (dd, J = 224.9 Hz, J = 9.0 Hz, 1F), −77.1 (dd, J = 225.0 Hz, J = 12.5 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.4, 135.5, 129.3, 129.2, 129.1, 128.4, 127.7, 110.7, 78.5 (t, J = 23.8 Hz). MS (EI, m/z, %): 364 (M^+, 50.00), 77 (100.00). HRMS (EI): Calcd. for $C_{14}H_{12}F_2OTe$: 363.9919; found: 363.9922.

*4.2.21. 2,2-Difluoro-1-(4-methoxyphenyl)-2-(phenyltellanyl)ethanol (**5b**)*



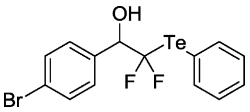
Yellow oil; IR (film): 3438, 3054, 2837, 1612, 1574, 1513, 1473, 1435, 1251, 1177, 1033, 997, 957, 832, 785, 736, 692, 586 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.84 (d, J = 7.3 Hz, 2H), 7.38–7.21 (m, 5H), 6.88 (d, J = 8.7 Hz, 2H), 4.85 (m, 1H), 3.80 (s, 1H), 2.73 (d, J = 4.1 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.8 (dd, J = 222.9 Hz, J = 8.8 Hz, 1F), −76.8 (dd, J = 223.7 Hz, J = 12.3 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3, 141.3, 129.3, 129.2, 129.0, 127.6, 110.8, 78.2 (t, J = 23.6 Hz). MS (EI, m/z, %): 394 (M^+, 11.71), 137 (100.00). HRMS (EI): Calcd. for $C_{15}H_{14}F_2O_2Te$: 394.0024; found: 394.0022.

*4.2.22. 1-(4-Chlorophenyl)-2,2-difluoro-2-(phenyltellanyl)ethanol (**5c**)*



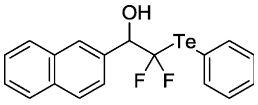
White solid; m.p. 66–68 °C; IR (film): 3566, 3064, 1594, 1573, 1486, 1471, 1433, 1406, 1217, 1132, 1075, 1036, 963, 821, 763, 736, 691, 645 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.82 (d, J = 6.9 Hz, 2H), 7.39–7.22 (m, 7H), 4.83 (m, 1H), 2.73 (d, J = 3.6 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ–73.2 (dd, J = 228.1 Hz, J = 9.1 Hz, 1F), −77.8 (dd, J = 227.6 Hz, J = 11.3 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.4, 135.1, 133.8, 129.4, 129.3, 129.1, 128.5, 120.4, 117.3, 110.4, 77.9 (t, J = 23.6 Hz). MS (EI, m/z, %): 396 (M^+, 37.27), 77 (100.00). HRMS (EI): Calcd. for $C_{14}H_{11}F_2OClTe$: 396.9525; found: 396.9528.

*4.2.23. 1-(4-Bromophenyl)-2,2-difluoro-2-(phenyltellanyl)ethanol (**5d**)*



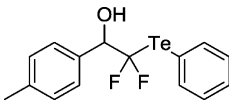
White solid; m.p. 92–94 °C; IR (film): 3565, 3081, 1693, 1587, 1484, 1471, 1433, 1402, 1220, 1132, 1099, 1074, 1036, 962, 816, 759, 737, 692, 647 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.81 (d, J = 7.4 Hz, 2H), 7.49–7.22 (m, 7H), 4.81 (m, 2H), 2.73 (d, J = 3.2 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ–72.9 (dd, J = 229.1 Hz, J = 4.5 Hz, 1F), −77.5 (dd, J = 229.1 Hz, J = 11.2 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.4, 134.3, 131.5, 129.4, 129.3, 123.3, 110.4, 77.9 (t, J = 23.4 Hz). MS (EI, m/z, %): 441 (M^+, 40.93), 77 (100.00). HRMS (EI): Calcd. for $C_{14}H_{11}F_2OBrTe$: 441.9024; found: 441.9022.

*4.2.24. 2,2-Difluoro-1-(naphthalen-2-yl)-2-(phenyltellanyl)ethanol (**5e**)*



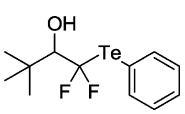
Yellow solid; m.p. 69–71 °C; IR (film): 3418, 3051, 1573, 1472, 1433, 1362, 1298, 1138, 1086, 1038, 994, 954, 867, 777, 729, 689, 560 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.93 (s, 1H), 7.82–7.79 (m, 5H), 7.51–7.16 (m, 7H), 5.02 (m, 1H), 2.84 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.8 (dd, J = 224.8 Hz, J = 9.2 Hz, 1F), −76.4 (dd, J = 225.9 Hz, J = 12.4 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 133.7, 132.9, 129.3, 129.2, 128.3, 128.2, 127.8, 127.3, 126.6, 126.4, 124.9, 110.7, 78.7 (t, J = 23.6 Hz). MS (EI, m/z, %): 414 (M^+, 38.44), 157 (100.00). HRMS (EI): Calcd. for $C_{18}H_{14}F_2OTe$: 414.0075; found: 414.0078.

*4.2.25. 2,2-Difluoro-2-(phenyltellanyl)-1-p-tolylethanol (**5f**)*



White solid; m.p. 63–65 °C; IR (film): 3527, 3067, 2897, 1512, 1473, 1433, 1376, 1238, 1143, 1074, 1040, 969, 953, 814, 734, 725, 689, 554 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.84 (d, J = 7.2 Hz, 2H), 7.39–7.14 (m, 7H), 4.83 (m, 1H), 2.75 (d, J = 2.5 Hz, 1H), 2.35 (s, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.4 (dd, J = 224.0 Hz, J = 9.1 Hz, 1F), −76.9 (dd, J = 223.7 Hz, J = 12.1 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.4, 139.1, 132.5, 129.3, 129.1, 127.6, 117.9 (t, J = 210.7 Hz), 110.7, 78.5 (t, J = 22.8 Hz), 21.3. MS (EI, m/z, %): 378 (M^+, 40.54), 121 (100.00). HRMS (EI): Calcd. for $C_{15}H_{14}F_2OTe$: 378.0075; found: 378.0077.

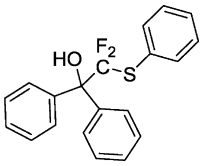
*4.2.26. 1,1-Difluoro-3,3-dimethyl-1-(phenyltellanyl)butan-2-ol (**5g**)*



Yellow oil; IR (film): 3459, 3055, 2956, 2875, 1574, 1475, 1435, 1369, 1155, 1058, 1018, 999, 864, 731, 691 cm^{-1}. ^1H NMR ($CDCl_3$,

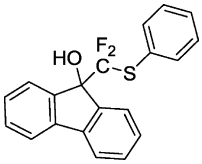
300 MHz): δ 7.94 (d, J = 7.1 Hz, 2H), 7.42–7.24 (m, 3H), 3.63 (m, 1H), 2.40 (d, J = 8.3 Hz, 1H), 1.05 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −62.6 (d, J = 218.2 Hz, 1F), −76.7 (dd, J = 218.7 Hz, J = 23.6 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 129.2, 129.1, 111.9, 83.3 (t, J = 23.4 Hz), 35.4, 26.6. MS (EI, m/z, %): 344 (M^+, 12.00), 57 (100.00). HRMS (EI): Calcd. for $C_{12}H_{16}F_2OTe$: 344.0232; found: 344.0227.

*4.2.27. 2,2-Difluoro-1,1-diphenyl-2-(phenylthio)ethanol (**7a**)*



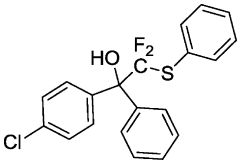
White solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62–7.54 (m, 6H), 7.42–7.28 (m, 9H), 2.90 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −77.4 (s, 2F). The characterization data were consistent with the previous report [11a].

*4.2.28. 9-(Difluoro(phenylthio)methyl)-9H-fluoren-9-ol (**7b**)*



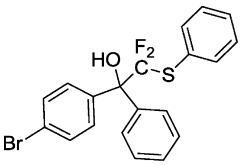
Colorless oil; IR (film): 3431, 3061, 1607, 1475, 1451, 1441, 1344, 1155, 1054, 994, 890, 838, 824, 769, 748, 732, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69 (t, J = 7.7 Hz, 4H), 7.46 (t, J = 6.9 Hz, 2H), 7.38–7.22 (m, 7H), 2.90 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −83.2 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.8, 141.2, 136.6, 132.4, 130.5, 129.8, 129.5, 128.8, 128.3, 126.1, 125.8, 120.2, 84.9 (t, J = 23.5 Hz). MS (EI, m/z, %): 340 (M^+, 4.72), 181 (100.00). HRMS (EI): Calcd. for $C_{20}H_{14}F_2OS$: 340.0733; found: 340.0735.

*4.2.29. 1-(4-Chlorophenyl)-2,2-difluoro-1-phenyl-2-(phenylthio)ethanol (**7c**)*



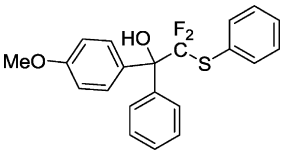
White solid; m.p. 58–59 °C; IR (film): 3571, 3450, 3056, 1592, 1491, 1474, 1447, 1439, 1404, 1173, 1093, 1062, 1039, 1019, 896, 807, 750, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59–7.51 (m, 6H), 7.40–7.28 (m, 8H), 3.13 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −77.5 (s, 1F), −77.6 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.0, 138.8, 136.7, 134.4, 131.0, 129.9, 129.4, 129.2, 129.1, 128.5, 128.20, 128.18, 128.0, 127.8, 127.7, 126.1, 81.4 (t, J = 24.2 Hz). MS (ESI, m/z, %): 399.0 ([M+Na]$^+$). HRMS (ESI): Calcd. for [$C_{20}H_{15}ClF_2OS$]: 399.0388; found: 399.0392.

*4.2.30. 1-(4-Bromophenyl)-2,2-difluoro-1-phenyl-2-(phenylthio)ethanol (**7d**)*



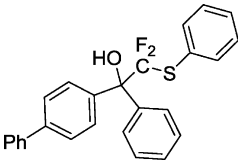
Colorless oil; IR (film): 3542, 3060, 1588, 1488, 1475, 1448, 1441, 1397, 1337, 1148, 1053, 1020, 901, 801, 751, 691 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59–7.33 (m, 14H), 3.11 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −77.5 (s, 1F), −77.6 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.2, 139.9, 139.2, 136.8, 131.1, 129.9, 129.6 (t, J = 2.1 Hz), 129.0, 128.5, 128.2, 127.6 (t, J = 2.4 Hz), 122.6, 98.7, 81.4 (t, J = 24.0 Hz). MS (EI, m/z, %): 294 ([M−PhSOH]$^+$, 0.83), 261 (100.00). HRMS (EI): Calcd. for [$C_{20}H_{15}BrF_2OS$–$PhSCF_2$]: 260.9915; found: 260.9916.

*4.2.31. 2,2-Difluoro-1-(4-methoxyphenyl)-1-phenyl-2-(phenylthio)ethanol (**7e**)*



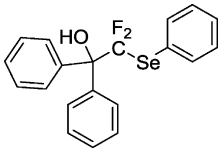
White solid; m.p. 70–71 °C; IR (film): 3421, 3074, 3001, 2841, 1605, 1509, 1474, 1450, 1375, 1247, 1177, 1089, 1058, 1035, 905, 837, 817, 742, 691, 597 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61–7.51 (m, 6H), 7.39–7.31 (m, 6H), 6.87–6.84 (m, 2H), 3.78 (s, 1H), 3.11 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −77.3 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 140.5, 136.7, 134.2, 132.5, 131.3, 129.8, 129.2, 129.1, 129.0, 128.2, 128.0, 127.8, 126.5, 113.3, 81.5 (t, J = 23.5 Hz), 52.2. MS (EI, m/z, %): 246 ([M−PhSOH]$^+$, 1.42), 213 (100.00). HRMS (EI): Calcd. for $C_{21}H_{18}F_2O_2S$: 372.0996; found: 372.1002.

*4.2.32. 1-(Biphenyl-4-yl)-2,2-difluoro-1-phenyl-2-(phenylthio)ethanol (**7f**)*



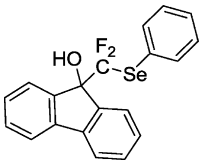
White solid; m.p. 86–87 °C; IR (film): 3538, 3059, 3031, 1600, 1487, 1448, 1405, 1334, 1149, 1053, 1018, 903, 815, 764, 698, 637 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69–7.55 (m, 10H), 7.45–7.31 (m, 9H), 3.14 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −77.3 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.2, 141.0, 140.4, 140.2, 139.2, 136.7, 139.8, 129.8, 129.0, 128.8, 128.3, 128.2 (t, J = 2.1 Hz), 128.1, 127.8 (t, J = 2.2 Hz), 127.5, 127.1, 126.7, 98.7, 81.5 (t, J = 24.8 Hz). MS (EI, m/z, %): 259 ([M−$PhSCF_2$]$^+$, 100.00). HRMS (EI): Calcd. for $C_{26}H_{20}F_2OS$: 418.1203; found: 418.1206.

*4.2.33. 2,2-Difluoro-1,1-diphenyl-2-(phenylselanyl)ethanol (**8a**)*



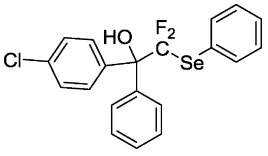
White solid; m.p. 122 °C; IR (film): 3434, 3073, 3056, 1598, 1582, 1491, 1448, 1341, 1169, 1150, 1053, 1038, 1012, 897, 810, 741, 634, 615 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (m, 6H), 7.38–7.32 (m, 9H), 3.12 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.5 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.2, 137.5, 132.3, 129.4, 129.19, 129.15, 129.0, 128.3, 128.2, 128.1, 127.9, 127.70, 127.68, 127.66, 126.1, 124.5, 82.0 (t, J = 22.1 Hz). MS (EI, m/z, %): 390 (M^+, 1.14), 183 (100.00). HRMS (EI): Calcd. for $C_{20}H_{16}F_2OSe$: 390.0334; found: 390.0331.

*4.2.34. 9-(Difluoro(phenylselanyl)methyl)-9H-fluoren-9-ol (**8b**)*



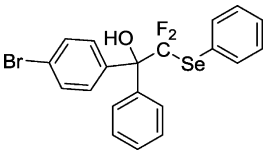
White solid; m.p. 58 °C; IR (film): 3436, 3060, 1608, 1477, 1451, 1439, 1336, 1150, 1063, 1022, 990, 907, 875, 824, 768, 744, 620 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.67 (t, J = 8.0 Hz, 4H), 7.46 (t, J = 6.8 Hz, 2H), 7.38–7.17 (m, 7H), 2.90 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.1 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.7, 141.3, 137.3, 130.5, 129.2, 129.1, 128.8, 128.3, 126.2, 125.8, 125.7, 124.2, 123.1, 120.22, 120.15, 85.5 (t, J = 22.1 Hz). MS (EI, m/z, %): 388 (M^+, 2.95), 181 (100.00). HRMS (EI): Calcd. for $C_{20}H_{14}F_2OSe$: 388.0178; found: 388.0170.

*4.2.35. 1-(4-Dhlorophenyl)-2,2-difluoro-1-phenyl-2-(phenylselanyl)ethanol (**8c**)*



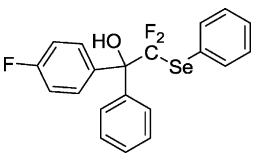
White solid; m.p. 63 °C; IR (film): 3535, 3060, 1594, 1578, 1492, 1448, 1402, 1333, 1147, 1093, 1016, 901, 793, 742, 691, 643 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.62–7.50 (m, 6H), 7.40–7.25 (m, 8H), 3.12 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.9 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.2, 139.8, 138.5, 137.4, 134.4, 129.5, 129.2 (t, J = 2.1 Hz), 129.1, 128.5, 128.2, 127.5 (t, J = 2.1 Hz), 124.2, 81.7 (t, J = 21.5 Hz). MS (EI, m/z, %): 423 (M^+, 0.94), 217 (100.00). HRMS (EI): Calcd. for $C_{20}H_{15}ClF_2OSe$: 423.9945; found: 423.9944.

*4.2.36. 1-(4-Bromophenyl)-2,2-difluoro-1-phenyl-2-(phenylselanyl)ethanol (**8d**)*



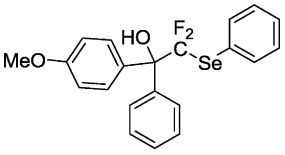
Colorless oil; IR (film): 3535, 3059, 1579, 1488, 1448, 1397, 1333, 1147, 1055, 1013, 900, 791, 741, 691, 639 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.51 (t, J = 8.5 Hz, 4H), 7.37 (s, 4H), 7.32–7.18 (m, 6H), 3.06 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.7 (d, J = 22.8 Hz, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.8, 139.1, 137.4, 137.4, 131.1, 129.5 (t, J = 3.1 Hz), 129.1, 128.5, 128.2, 127.5 (t, J = 2.1 Hz), 124.2, 122.7, 81.7 (t, J = 21.6 Hz). MS (EI, m/z, %): 467 (M^+, 1.11), 263 (100.00). HRMS (EI): Calcd. for $C_{20}H_{15}BrF_2OSe$: 467.9440; found: 467.9445.

*4.2.37. 2,2-Difluoro-1-(4-fluorophenyl)-1-phenyl-2-(phenylselanyl)ethanol (**8e**)*



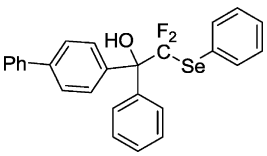
White solid; m.p. 64–65 °C; IR (film): 3434, 3055, 1604, 1511, 1493, 1438, 1339, 1245, 1169, 1058, 1012, 902, 794, 756, 692, 676, 614 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.62–7.53 (m, 6H), 7.38–7.27 (m, 6H), 6.99 (t, J = 9.0 Hz, 2H), 3.14 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.7 (d, 2F), −113.8 (m, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6 (d, J = 248.3 Hz), 140.1, 137.5, 135.9, 129.8, 129.7, 129.5, 129.1, 128.5, 128.2, 127.6, 115.0, 114.8, 81.7 (t, J = 22.7 Hz). MS (EI, m/z, %): 407 (M^+, 1.08), 201 (100.00). HRMS (EI): Calcd. for $C_{20}H_{15}F_3OSe$: 408.0240; found: 408.0240.

*4.2.38. 2,2-Difluoro-1-(4-methoxyphenyl)-1-phenyl-2-(phenylselanyl)ethanol (**8f**)*



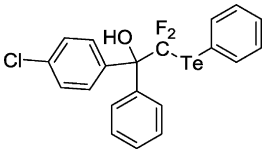
White solid; m.p. 83 °C; IR (film): 3401, 3071, 1605, 1508, 1475, 1451, 1378, 1294, 1246, 1178, 1153, 1072, 1057, 907, 838, 815, 738, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.67–7.52 (m, 6H), 7.44–7.28 (m, 6H), 6.88 (d, J = 9.6 Hz, 2H), 3.82 (s, 3H), 3.14 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.4 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 140.4, 137.4, 132.5, 132.3, 129.40, 129.35, 129.0, 128.9, 128.3, 128.0, 127.7, 127.6, 126.3, 124.6, 113.4, 81.8 (t, J = 22.6 Hz), 52.2. MS (EI, m/z, %): 246 ([M−PhSeOH]$^+$, 2.08), 213 (100.00). HRMS (EI): Calcd. for $C_{21}H_{18}F_2O_2Se$: 420.0440; found: 420.0441.

*4.2.39. 1-(Biphenyl-4-yl)-2,2-difluoro-1-phenyl-2-(phenylselanyl)ethanol (**8g**)*



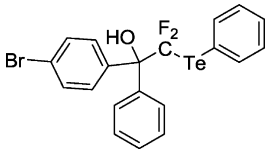
Brown oil; IR (film): 3537, 3058, 3031, 1599, 1579, 1487, 1448, 1405, 1334, 1147, 1055, 1009, 903, 804, 763, 697, 631 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.67–7.53 (m, 10H), 7.44–7.23 (m, 9H), 3.17 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.5 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.1, 140.5, 140.2, 139.2, 137.5, 132.3, 129.4, 129.3, 129.1, 128.9, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 127.2, 126.8, 124.6, 82.0 (t, J = 22.8 Hz). MS (EI, m/z, %): 312 ([M−(4-Ph)Ph]$^+$, 0.32), 259 (100.00). HRMS (EI): Calcd. for [$C_{26}H_{20}F_2OSe$–$PhSeCF_2$]: 259.1123; found: 259.1127.

*4.2.40. 1-(4-Chlorophenyl)-2,2-difluoro-1-phenyl-2-(phenyltellanyl)ethanol (**9a**)*



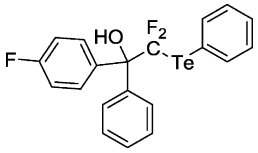
Yellow oil; IR (film): 3522, 3054, 1491, 1474, 1435, 1337, 1162, 1137, 1054, 1016, 997, 899, 828, 783, 735, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.82 (d, J = 7.3 Hz, 2H), 7.55–7.47 (m, 4H), 7.40–7.21 (m, 8H), 3.16 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −70.7 (s, 1F), −70.8 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.6, 139.8, 138.5, 134.4, 129.3, 129.23, 129.21, 128.6, 128.33, 128.28, 127.5, 121.0 (t, J = 320.6 Hz), 111.8, 81.4 (t, J = 20.6 Hz). MS (EI, m/z, %): 473 (M, 7.89), 217 (100.00). HRMS (EI): Calcd. for $C_{20}H_{15}ClF_2OTe$: 473.9842; found: 473.9840.

*4.2.41. 1-(4-Bromophenyl)-2,2-difluoro-1-phenyl-2-(phenyltellanyl)ethanol (**9b**)*



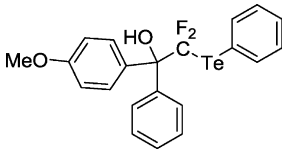
White solid; m.p. 62–63 °C; IR (film): 3380, 3054, 1487, 1433, 1393, 1136, 1154, 1011, 901, 821, 781, 735, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.81 (d, J = 7.3 Hz, 2H), 7.55–7.22 (m, 12H), 3.14 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −70.8 (s, 1F), −70.9 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.6, 139.7, 139.0, 131.2, 129.54, 129.51, 129.32, 129.29, 128.6, 128.3, 127.5, 122.7, 120.8 (t, J = 318.1 Hz), 111.8, 82.2 (t, J = 19.0 Hz). MS (EI, m/z, %): 517 (M, 8.90), 263 (100.00). HRMS (EI): Calcd. for $C_{20}H_{15}BrF_2OTe$: 517.9337; found: 517.9331.

*4.2.42. 2,2-Difluoro-1-(4-fluorophenyl)-1-phenyl-2-(phenyltellanyl)ethanol (**9c**)*



Yellow solid; m.p. 125–126 °C; IR (film): 3444, 3058, 1651, 1602, 1508, 1474, 1448, 1235, 1163, 1136, 1054, 902, 837, 736, 693 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.82 (d, J = 6.8 Hz, 2H), 7.55–7.23 (m, 10H), 6.97 (t, J = 8.7 Hz, 2H), 3.22 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −70.5 (s, 1F), −70.7 (s, 1F), −113.6 (m, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.5 (d, J = 247.2 Hz), 141.6, 140.0, 135.8, 132.7, 132.5, 130.0, 129.8, 129.7, 129.31, 129.27, 128.5, 128.4, 128.3, 127.5, 121.3 (t, J = 321.6 Hz), 115.1, 114.9, 111.9, 82.1 (t, J = 20.7 Hz). MS (EI, m/z, %): 458 (M, 1.92), 201 (100.00). HRMS (EI): Calcd. for $C_{20}H_{15}F_3OTe$: 458.0137; found: 458.0139.

*4.2.43. 2,2-Difluoro-1-(4-methoxyphenyl)-1-phenyl-2-(phenyltellanyl)ethanol (**9d**)*

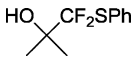


Yellow solid; m.p. 100 °C; IR (film): 3389, 3064, 2839, 1603, 1506, 1473, 1450, 1376, 1294, 1244, 1177, 1141, 947, 904, 807, 733, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.84 (d, J = 7.3 Hz, 2H), 7.56–7.22 (m, 10H), 6.84 (d, J = 9.2 Hz, 2H), 3.79 (s, 3H), 3.09 (s, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −70.5 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 141.5, 140.2, 132.6, 132.2, 129.8, 129.2, 129.1, 129.0, 128.3, 128.1, 127.7, 121.7, 113.5, 82.2 (t, J = 20.4 Hz), 55.2. MS (EI, m/z, %): 470 (M, 0.82), 213 (100.00). HRMS (EI): Calcd. for $C_{21}H_{18}F_2O_2Te$: 470.0337; found: 470.0332.

*4.3. General procedure for reaction of **1** ($PhXCF_2H$, X = S, Se) with **10***

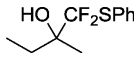
Under a nitrogen atmosphere, to a stirred solution of $PhSCF_2H$ (**1a**) (80 mg, 0.5 mmol) and acetone (**10a**) (56 mg, 1.0 mmol) with 5 mL DMF in a Schlenk tube, KOH (82%) (560 mg, 10.0 mmol) was added in one portion at 0 °C. The mixture was stirred at this temperature for 1 h, then gradually warm to room temperature. After 13 h, the reaction was quenched with saturated aqueous ammonium chloride or brine, extracted with Et_2O (3 × 10 mL). The combined organic layer was washed with H_2O (2 × 10 mL), followed by brine (10 mL), dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography with ethyl acetate/petroleum ether (1:20) as eluent to give 77 mg **11a** as a colorless oil. Yield 71%.

*4.3.1. 1,1-Difluoro-2-methyl-1-(phenylthio)propan-2-ol (**11a**)*



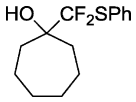
Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.62 (d, J = 7.5 Hz, 2H), 7.43–7.35 (m, 3H), 2.17 (s, 1H), 1.45 (s, 6H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −85.9 (s, 2F). The characterization data were consistent with the previous report [19].

*4.3.2. 1,1-Difluoro-2-methyl-1-(phenylthio)butan-2-ol (**11b**)*



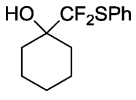
Yellow oil; IR (film): 3445, 3062, 2981, 2944, 2885, 1475, 1441, 1384, 1278, 1146, 1097, 1061, 1015, 967, 927, 749, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.55 (d, J = 6.4 Hz, 2H), 7.35–7.27 (m, 3H), 1.93 (s, 1H), 1.72 (m, 2H), 1.31 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −84.7 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.7, 132.3 (t, J = 287.7 Hz), 129.7, 129.0, 126.2, 77.1 (t, J = 22.8 Hz), 29.1, 20.4, 7.4. MS (EI, m/z, %): 232 (M, 12.01), 73 (100.00). HRMS (EI): Calcd. for $C_{11}H_{14}F_2OS$: 232.0733; found: 232.0736.

*4.3.3. 1-(Difluoro(phenylthio)methyl)cycloheptanol (**11c**)*



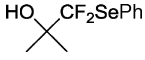
White solid; m.p. 42–43 °C; IR (film): 3440, 3061, 2929, 2860, 1474, 1462, 1441, 1199, 1138, 1045, 987, 941, 919, 748, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.62 (d, J = 7.2 Hz, 2H), 7.42–7.37 (m, 3H), 2.09–1.61 (m, 13H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −85.4 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.7, 132.9 (t, J = 293.4 Hz), 129.7, 129.0, 128.9, 126.4, 79.5 (t, J = 22.2 Hz), 39.6, 29.6, 22.1. MS (EI, m/z, %): 272 (M, 5.82), 113 (100.00). HRMS (EI): Calcd. for $C_{14}H_{18}F_2OS$: 272.1046; found: 272.1040.

*4.3.4. 1-(Difluoro(phenylthio)methyl)cyclohexanol (**11d**)*



Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.55 (d, J = 6.2 Hz, 2H), 7.31–7.28 (m, 3H), 1.77–1.10 (m, 11H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −87.6 (s, 2F). The characterization data were consistent with the previous report [11a].

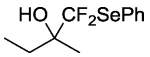
*4.3.5. 1,1-Difluoro-2-methyl-1-(phenylselanyl)propan-2-ol (**12a**)*



Yellow oil; IR (film): 3400, 3060, 2986, 2958, 2870, 1651, 1477, 1439, 1200, 1092, 1058, 1022, 979, 942, 825, 742, 692 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, J = 6.2 Hz, 2H), 7.41–7.31 (m,

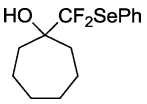
3H), 2.35 (s, 1H), 1.43 (s, 6H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.7 (s, 2F). MS (EI, *m*/*z*, %): 266 (M, 11.81), 82 (100.00). HRMS (EI): Calcd. for $C_{10}H_{12}F_2OSe$: 266.0021; found: 266.0023.

4.3.6. 1,1-Difluoro-2-methyl-1-(phenylselanyl)butan-2-ol (**12b**)



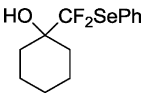
Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, *J* = 6.4 Hz, 2H), 7.40–7.33 (m, 3H), 2.05 (s, 1H), 1.75 (m, 2H), 1.35 (s, 3H), 1.01 (t, *J* = 6.7 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.5 (s, 1F), −80.7 (s, 1F). The characterization data were consistent with the previous report [12].

4.3.7. 1-(Difluoro(phenylselanyl)methyl)cycloheptanol (**12c**)



Yellow oil; IR (film): 3440, 3059, 2928, 2858, 1579, 1477, 1439, 1198, 1130, 1046, 1022, 989, 932, 826, 739, 691 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, *J* = 6.8 Hz, 2H), 7.42–7.30 (m, 3H), 2.06–1.98 (m, 3H), 1.87–1.52 (m, 10H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ–81.3 (s, 2F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.5, 131.7 (t, *J* = 255.6 Hz), 129.3, 129.0, 124.2, 80.0 (t, *J* = 20.7 Hz), 35.7, 29.6, 22.1. MS (EI, *m*/*z*, %): 320 (M, 13.41), 113 (100.00). HRMS (EI): Calcd. for $C_{14}H_{18}F_2OSe$: 320.0491; found: 320.0492.

4.3.8. 1-(Difluoro(phenylselanyl)methyl)cyclohexanol (**12d**)

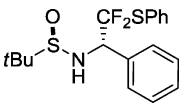


Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.35–7.23 (m, 3H), 1.83–1.76 (m, 3H), 1.64–1.01 (m, 8H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −83.1 (s, 2F). The characterization data were consistent with the previous report [12].

4.4. General procedure for reaction of 1 ($PhXCF_2H$, X = S, Se) with 13

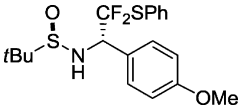
Under a nitrogen atmosphere, to a stirred solution of $PhSeCF_2H$ (**1b**) (104 mg, 0.5 mmol) and PhCH=NSO*t*-Bu (**13a**) (165 mg, 0.75 mmol) with 3 mL DMF in a Schlenk tube, *t*-BuOK (112 mg, 1.0 mmol) (dissolved in 2 mL DMF) was added dropwise at −30 °C. The mixture was stirred at −40 to −30 °C for 2 h, then quenched with saturated aqueous ammonium chloride or brine, extracted with Et_2O (3 × 10 mL). The combined organic layer was washed with H_2O (2 × 10 mL), followed by brine (10 mL), dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography with ethyl acetate/petroleum ether (1:5) as eluent to give 168 mg **15a** as a white solid (the product was the main isomer, and the other isomer was not obtained). Yield 80% (based on the main isomer).

4.4.1. (Rs)-N-[(S)-2,2-difluoro-1-phenyl-2-(phenylthio)ethyl]-2-methylpropane-2-sulfinamide (**14a**)



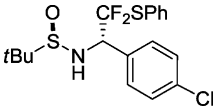
White solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51–7.54 (m, 2H), 7.31–7.45 (m, 8H), 4.83 (td, *J* = 10.8 Hz, *J* = 7.8 Hz, 1H), 3.79 (d, *J* = 7.2 Hz, 1H), 1.27 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −78.5 (dd, *J* = 205.0 Hz, *J* = 10.2 Hz, 1F), −79.8 (dd, *J* = 205.0 Hz, *J* = 11.0 Hz, 1F). The characterization data were consistent with the previous report [11b].

4.4.2. (Rs)-N-[(S)-2,2-difluoro-1-(4-methoxyphenyl)-2-(phenylthio)ethyl]-2-methylpropane-2-sulfinamide (**14b**)



White solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53 (d, *J* = 6.6 Hz, 2H), 7.32–7.43 (m, 5H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.79 (td, *J* = 9.9 Hz, *J* = 7.2 Hz, 1H), 7.80 (s, 3H), 3.71 (d, *J* = 7.2 Hz, 1H), 1.25 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −78.0 (dd, *J* = 205.2 Hz, *J* = 10.7 Hz, 1F), −80.6 (dd, *J* = 205.2 Hz, *J* = 10.4 Hz, 1F). The characterization data were consistent with the previous report [11b].

4.4.3. (Rs)-N-[(S)-1-(4-chlorophenyl)-2,2-difluoro-2-(phenylthio)ethyl]-2-methylpropane-2-sulfinamide (**14c**)

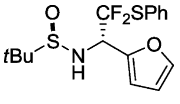


White solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53 (dd, *J* = 8.1 Hz, *J* = 1.5 Hz, 2H), 7.33–7.42 (m, 7H), 7.81 (td, *J* = 10.8 Hz, *J* = 7.8 Hz, 1H), 3.80 (d, *J* = 7.8 Hz, 1H), 1.26 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.0 (dd, *J* = 207.8 Hz, *J* = 9.3 Hz, 1F), −79.7 (dd, *J* = 207.8 Hz, *J* = 11.2 Hz, 1F). The characterization data were consistent with the previous report [11b].

4.4.4. (Rs)-N-[(S)-2,2-difluoro-1-(naphthalene-2-yl)-2-(phenylthio)ethyl]-2-methylpropane-2-sulfinamide (**14d**)

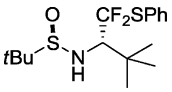
White solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.81–7.91 (m, 4H), 7.48–7.54 (m, 5H), 7.31–7.43 (m, 3H), 5.00 (td, *J* = 10.8 Hz, *J* = 7.5 Hz, 1H), 3.91 (d, *J* = 7.5 Hz, 1H), 1.27 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −77.9 (dd, *J* = 206.4 Hz, *J* = 10.1 Hz, 1F), −79.5 (dd, *J* = 206.4 Hz, *J* = 11.3 Hz, 1F). The characterization data were consistent with the previous report [11b].

4.4.5. (Rs)-N-[(S)-2,2-difluoro-1-(furan-2-yl)-2-(phenylthio)ethyl]-2-methylpropane-2-sulfinamide (**14e**)



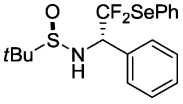
White solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 2H), 7.53–7.46 (m, 4H), 6.48 (d, *J* = 3.3 Hz, 1H), 6.39 (dd, *J* = 3.0, 1.8 Hz, 1H), 4.85–4.94 (m, 1H), 3.95 (s, 1H), 1.27 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.2 (dd, *J* = 206.4 Hz, *J* = 10.7 Hz, 1F), −80.1 (dd, *J* = 206.4 Hz, *J* = 10.4 Hz, 1F). The characterization data were consistent with the previous report [11b].

*4.4.6. (Rs)-N-[(S)-1,1-difluoro-3,3-dimethyl-1-(phenylthio)butan-2-yl]-2-methylpropane-2-sulfinamide (**14f**)*



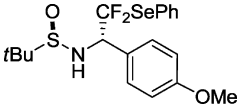
White solid; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55–7.59 (m, 2H), 7.34–7.45 (m, 3H), 3.61 (d, J = 8.4 Hz, 1H), 3.45–3.55 (m, 1H), 1.33 (s, 9H), 1.15 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −67.0 (dd, J = 204.1 Hz, J = 6.2 Hz, 1F), −76.6 (dd, J = 204.1 Hz, J = 14.7 Hz, 1F). The characterization data were consistent with the previous report [11b].

*4.4.7. (Rs)-N-[(S)-2,2-difluoro-1-phenyl-2-(phenyselanyl)ethyl]-2-methylpropane-2-sulfinamide (**15a**)*



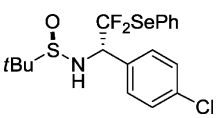
White solid; m.p. 132–134 °C; IR (film): 3179, 1578, 1475, 1439, 1096, 1064, 996 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, J = 6.9 Hz, 2H), 7.25–7.40 (m, 8H), 4.80–4.90 (m, 1H), 3.86 (d, J = 7.5 Hz), 1.26 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −76.3 (dd, J = 206.3 Hz, J = 11.8 Hz, 1F), −77.4 (dd, J = 206.9 Hz, J = 12.1 Hz, 1F); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.0, 135.1, 129.4, 129.2, 129.1, 128.8, 128.3, 125.8 (t, J = 298.0 Hz), 124.0, 66.3 (t, J = 22.3 Hz), 57.0, 22.4; MS (ESI, m/z): 474 (M^++Na). EA calcd. for $C_{18}H_{21}F_2NOSSe$: C, 51.92; H, 5.08; N, 3.36; found: C, 51.96; H, 4.92; N, 3.18.

*4.4.8. (Rs)-N-[(S)-N-(2,2-difluoro-1-(4-methoxyphenyl)-2-(phenylselanyl)ethyl)]-2-methylpropane-2-sulfinamide (**15b**)*



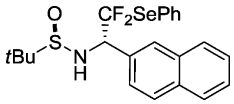
Yellow solid; m.p. 105–107 °C; IR (film): 3445, 3321, 3000, 2958, 2835, 1612, 1516, 1471, 1307, 1255, 1184, 1069, 972, 741 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (d, J = 6.7 Hz, 2H), 7.44–7.30 (m, 5H), 6.90 (d, J = 8.6 Hz, 2H), 4.81 (m, 1H), 3.81 (s, 3H), 3.76 (d, J = 6.9 Hz, 1H), 1.27 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −75.1 (dd, J = 204.4 Hz, J = 11.3 Hz, 1F), −77.7 (dd, J = 204.4 Hz, J = 12.2 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3, 137.1, 129.7, 129.5, 129.2, 127.3, 124.3, 114.3, 65.9 (t, J = 22.6 Hz), 57.0, 55.3, 22.5. MS (MALDI, m/z, %): 447 (M^+). HRMS (ESI): calcd. for $C_{19}H_{24}F_2NO_2SSe$: 442.07151; found: 442.07048.

*4.4.9. (Rs)-N-[(S)-N-(1-(4-chlorophenyl)-2,2-difluoro-2-(phenylselanyl)ethyl)]-2-methylpropane-2-sulfinamide (**15c**)*



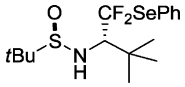
Yellow solid; m.p. 94–96 °C; IR (film): 3324, 3058, 2987, 2958, 1596, 1495, 1477, 1437, 1086, 1014, 974, 741 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, J = 7.6 Hz, 2H), 7.44–7.30 (m, 7H), 4.81 (m, 1H), 3.83 (d, J = 7.8 Hz, 1H), 1.26 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −76.8 (dd, J = 208.3 Hz, J = 12.1 Hz, 1F), −77.7 (dd, J = 206.3 Hz, J = 12.0 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.1, 135.4, 133.7, 129.8, 129.6, 129.3, 129.1, 65.9 (t, J = 23.9 Hz), 57.2, 22.5. MS (ESI, m/z, %): 474 (M^++Na). HRMS (ESI): calcd. for $C_{18}H_{20}ClF_2NO_2SSeNa$: 468.00392; found: 468.00399.

*4.4.10. (Rs)-N-[(S)-N-(2,2-difluoro-1-(naphthalen-2-yl)-2-(phenylselanyl)ethyl)]-2-methylpropane-2-sulfinamide (**15d**)*



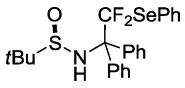
Yellow solid; m.p. 155 °C; IR (film): 3445, 3318, 3054, 2953, 2923, 1466, 1438, 1367, 1071, 1015, 969, 861, 747 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.89 (m, 4H), 7.62 (d, J = 6.7 Hz, 2H), 7.54–7.27 (m, 6H), 5.02 (m, 1H), 3.96 (d, J = 7.8 Hz, 1H), 1.30 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.8 (dd, J = 205.0 Hz, J = 10.9 Hz, 1F), −77.2 (dd, J = 205.0 Hz, 12.5 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.2, 133.1, 129.5, 129.2, 128.9, 128.4, 127.7, 126.9, 126.6, 125.3, 66.6 (t, J = 23.9 Hz), 57.2, 22.6. MS (ESI, m/z, %): 490 (M^++Na). HRMS (ESI): calcd. for $C_{22}H_{23}ClF_2NOSSeNa$: 484.05854; found: 484.05884.

*4.4.11. (Rs)-N-[(S)-N-(1,1-difluoro-3,3-dimethyl-1-(phenylselanyl)butan-2-yl)]-2-methylpropane-2-sulfinamide (**15e**)*



White solid; m.p. 87 °C; IR (film): 3352, 3060, 2964, 1471, 1371, 1233, 1159, 1097, 1071, 968, 877, 746 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.67 (m, J = 6.8 Hz, 2H), 7.44–7.32 (m, 3H), 3.66 (d, J = 8.5 Hz, 1H), 3.52 (m, 1H), 1.35 (s, 9H), 1.13 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −62.5 (d, J = 202.3 Hz, 1F), −74.3 (dd, J = 202.7 Hz, J = 17.8 Hz, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.4, 129.4, 129.1, 124.8, 70.5 (t, J = 22.9 Hz), 57.6, 34.8, 28.1 (t, J = 2.9 Hz), 23.1. MS (ESI, m/z, %): 420 (M^++Na). HRMS (ESI): calcd. for $C_{16}H_{25}F_2NOSSeNa$: 414.07419; found: 414.07383.

*4.4.12. (S)-N-(2,2-difluoro-1,1-diphenyl-2-(phenylselanyl)ethyl)-2-methylpropane-2-sulfinamide (**15f**)*



White solid; m.p. 117–118 °C; IR (film): 3319, 3049, 2966, 1446, 1369, 1143, 1075, 1061, 911, 850, 743 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62–7.56 (m, 4H), 7.45–7.23 (m, 11H), 4.79 (s, 1H), 1.24 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −70.4 (s, 1F), −70.5 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.1, 137.9, 137.3, 130.4, 130.0, 129.5, 129.1, 128.8, 128.1, 128.0, 57.2, 22.9. MS (ESI, m/z, %): 516 (M^++Na). HRMS (ESI): calcd. for $C_{24}H_{25}F_2NOSSeNa$: 510.07419; found: 510.07495.

Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (20772144, 20825209, 20832008) and the Chinese Academy of Sciences for financial support.

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