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Synthesis of 1,1-difluoroethylsilanes and their application for the introduction of the 1,1-difluoroethyl group

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Dedicated to Professor Kenji Uneyama on the occasion of receiving the 2007 ACS Award for Creative Work in Fluorine Chemistry.

Abstract

1,1-Difluoroethysilanes ($R_3SiCF_2CH_3$, R = Me or Et) were synthesized from 1,1-difluoroethyl phenyl sulfone and chlorosilanes using magnesium metal *via* reductive 1,1-difluoroethylation. It was confirmed that 1,1-difluoroethylsilanes were effective 1,1-difluoroethylating reagents for carbonyl compounds.

Keywords: 1,1-Difluoroethylation; 1,1-Difluoroethylsilane; 1,1-Difluoroethyl phenyl sulfone; Magnesium

1. Introduction

Introduction of 1,1-difluoroethyl group ($–CF_2CH_3$) into organic molecules is very attractive, because $–CF_2CH_3$ is isopolar and isometric with $–OCH_3$ and expected to play an important role in biological and medicinal chemistry [1]. Preparation of compounds with difluoromethylene group have been reported, however, most of them are through electrophilic fluorination methods, such as deoxofluorination of ketones by SF_4 [2], diethylaminosulfur trifluoride (DAST) or its derivatives [3], SeF_4 [4], IF [5]. Fluorination of ketoximes [6] or 1,3-dithiolane [7] by $NO^+BF_4^-$ and hydrofluorinations of multiple bonds by Et_3N/HF [8] have also been disclosed.

$TMSR_f$ is well known as an effective perfluoroalkylating reagent, and has been widely used in organofluorine chemistry [9]. Therefore, $R_3SiCF_2CH_3$ would be a good synthon to introduce $–CF_2CH_3$ group into organic molecules, however, there is no report on the direct synthesis of $R_3SiCF_2CH_3$ synthon, although it has been invoked in a kinetic study of the gas-phase photochemical reaction [10]. Hagiwara and Fuchikami reported synthesis of (1,1-difluoroalkyl)silane derivatives and their 1,1-difluoroalkylation abilities [11]. They succeeded in introducing 1,1-difluoroalkyl group into carbonyl compounds using $PhMe_2SiCF_2R$ (R = H, Et, *iso*-Pr, *cyclo*-Hexyl), but 1,1-difluoroethyl (R = Me) was not included. Recently, we reported a unique method to synthesize $TMSCF_2X$ (X = F, H, Br) from $PhSO_2CF_2X$ and TMSCl with magnesium metal [12]. Furthermore, we have earlier developed a convenient route to $PhSO_2CF_2R$ from $PhSO_2CF_2H$ and alkyl halides [13]. From these results it is evident that R_3SiCF_2R' can be prepared from the key compound $PhSO_2CF_2H$. Herein we report a useful method for the synthesis of 1,1-diluoroethylsilanes and introduction of $–CF_2CH_3$ group into carbonyl compounds employing them.

2. Results and discussion

2.1. Synthesis of 1,1-difluoroethylsilanes $R_3SiCF_2CH_3$

1,1-Difluoroethyl phenyl sulfone $PhSO_2CF_2CH_3$ (**6**) was prepared as shown in Scheme 1. The reaction between benzenethiol (**1**) and $CHClF_2$ (**2**) was carried out in a similar fashion as was carried out in a previously reported method [14]. $PhSCF_2H$ (**3**) was oxidized by H_2O_2 to $PhSO_2CF_2H$ (**4**),

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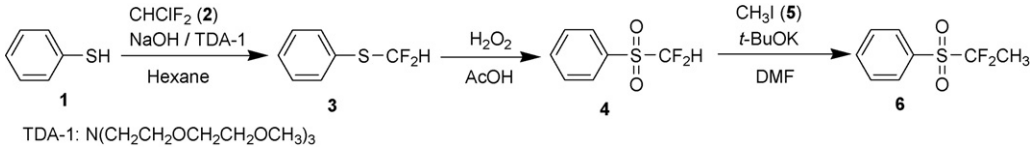
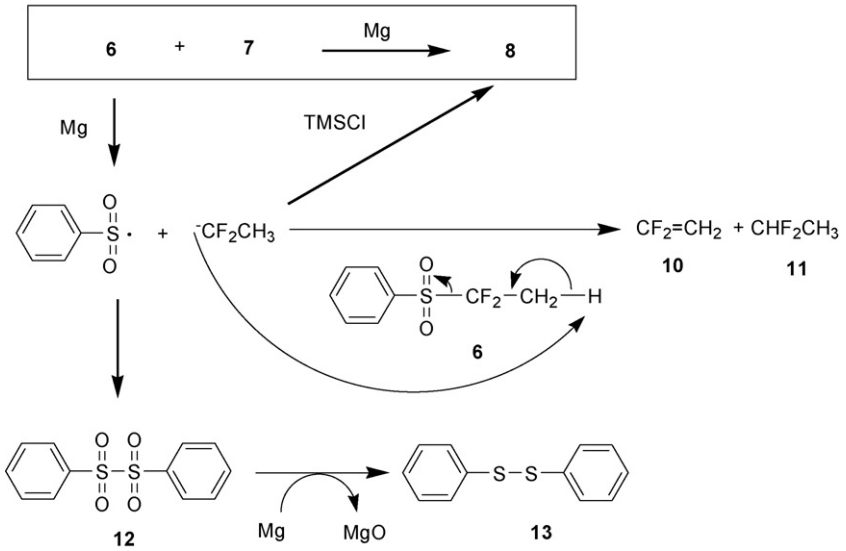


Scheme 1. Preparation of 1,1-difluoroethyl phenyl sulfone **6**.

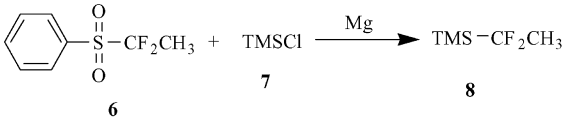


Scheme 2. Mechanism for the reaction of $PhSO_2CF_2CH_3$ (**6**) and TMSCl (**7**) with Mg.

followed by the reaction with CH_3I (**5**) using *t*-BuOK, to give (**6**) [12].

The reaction between (**6**) and TMSCl (**7**) with magnesium metal was carried out in DMF at room temperature. The signals for the starting material disappeared completely after 1 h in ^1H and ^{19}F NMR, and the signals due to $TMSCF_2CH_3$ (**8**) and TMS–O–TMS (**9**) appeared and the latter was generated by the hydrolysis of excess of TMSCl (**7**) during aqueous quench. However, the estimated yield from the ratio of (**8**) and (**9**) as analyzed by ^1H NMR was only 50% (Table 1, entry 1). In this reaction, $CH_3CF_2^-$ anion is generated by reductive decomposition of $PhSO_2CF_2CH_3$ (**6**) by magnesium involving single electron transfer. This basic anion abstracts the acidic methyl proton of (**6**), leading to elimination products as shown in Scheme 2, resulting low boiling gaseous compounds, $CF_2=CH_2$ (**10**) and CF_2HCH_3 (**11**), which are not detected in the NMR of the reaction mixture. This decomposition is accelerated, when the reductive cleavage of (**6**) by magnesium is slow, and when the basic $CH_3CF_2^-$ anion and (**6**) are simultaneously present in the reaction media. However, such decomposition could be suppressed if the reaction rate between (**6**) and magnesium can be enhanced. Actually, the yield of (**8**) improved to more than 90%, when magnesium granule was used instead of the turnings (Table 1, entry 2). Nature of solvent is also an important factor in this reaction, and THF was found to give no reaction (Table 1, entry 3).

Table 1
Synthesis of $TMSCF_2CH_3$ (**8**)



	Mg	Solvent	Conversion (%)	Yield of **8** (%)[a]
1	Turnings	DMF	100	50
2	Granule	DMF	100	>90
3	Granule	THF	0	–

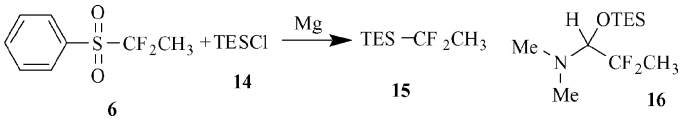
The reactions were carried out using $PhSO_2CF_2CH_3$ (**6**) 1.0 equiv., TMSCl (**7**) 4.0 equiv. and Mg 12.0 equiv. at r.t.

[a] Yields were estimated from the ratio compared with TMS–O–TMS (**9**) in ^1H NMR.

The excess of (**7**) is transformed to (**9**) by aqueous hydrolysis as mentioned earlier. In addition, it was also confirmed that MgO promote the formation of (**9**) from (**7**) without H_2O present. MgO is generated *in situ* by the deep-seated reduction of by-product $PhSO_2SO_2Ph$ (**12**), which is formed from coupling of two $PhSO_2$ radical species, to PhSSPh (**13**) [12]. The boiling points of (**9**) and (**8**) are comparable (~100 °C), and hence it was difficult to separate (**8**) from the reaction mixture even by careful distillation. Washing away (**9**) by conc. H_2SO_4 was attempted, but led to significant product loss. Washing by 1N HCl showed no effect.

To overcome the problem of close boiling points of (**8**) and (**9**), we performed the reaction of (**6**) with triethylsilyl chloride (TESCl, **14**) under similar reaction conditions. The conversion of (**6**) after 1.2 h was 100%, but the yield of $TESCF_2CH_3$ (**15**) as estimated by NMR, was quite low, due to the formation of a hemiaminal adduct (**16**) with DMF (Table 2, entry 1). The reactivity of (**14**), because of the steric bulk, appears to be lower than that of (**7**), resulting in reaction of the $CH_3CF_2^-$ with the

Table 2
Synthesis of $TESCF_2CH_3$ (**15**)



6 **14** **15** **16**

	Solvent	Conversion (%)	Yield of products (%)[a]	
			15	**16**
1	DMF	100	39	40
2	THF/DMF (1:1)	25	4	0
3	THF/sulfolane (1:1)	0	–	–
4	CH_3CN	0	–	–
5	DMSO	0	–	–
6	NMP	96	26	–
7	THF/HMPA (3:1)	79	20	–
8	THF/HMPA (1:1)	100	67	–
9	THF/HMPA (1:3)	90	57	–
10	HMPA	74	28	–

The reactions were carried out using $PhSO_2CF_2CH_3$ (**6**) 1.0 equiv., TESCl (**14**) 4.0 equiv. and Mg granule 12.0 equiv. at r.t.
[a] Yields were estimated from the ratio compared with TES–O–TES (**17**) + TESOH (**18**) in ^1H NMR.

solvent DMF. Such a hemiaminal adduct of DMF with trifluoromethyl anion is known [15] and has been utilized for the nucleophilic trifluoromethylation of nonenolizable carbonyl compounds [16].

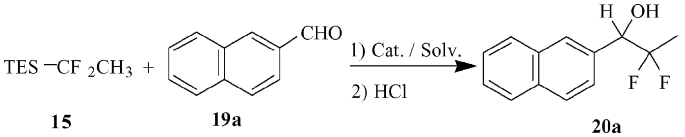
In the present study, we aimed at suppressing DMF adduct formation and isolate $TESCF_2CH_3$ (**15**) by changing the nature of the solvent. DMF adduct was not formed in THF/DMF mixtures, but the conversion was very low and a small amount of (**15**) was detected (Table 2, entry 2). The reaction did not proceed at all in THF/sulfolane, CH_3CN, and $(CH_3)_2SO$ (Table 2, entries 3–5). The conversion was nearly 100%, but the yield was quite low in NMP (Table 2, entry 6). The reaction rate between (**6**) and magnesium is not fast enough to prevent the decomposition of (**6**) by beta elimination to 1,1-diluroethylene, which is aided by the proton abstraction by the $CH_3CF_2^-$ anion as shown in Scheme 2. Finally, it was found that THF/HMPA mixed solvent system was particularly efficient for this reaction, and especially 1:1 solvent ratio gave the best result (Table 2, entry 8). When HMPA was used without THF, the yield was not good because of high viscosity of the reaction mixture (Table 2, entry 10).

By-products obtained from the use of (**14**) were TES–O–TES (**17**) and TESOH (**18**). The high boiling point (233–236 °C) of (**17**) permitted easy separation of (**15**) from (**17**) by vacuum distillation. However, (**18**), which has a boiling point of 158 °C, could not be separated from (**15**) by vacuum distillation, it still remained even after washing the mixture with 5% aq NaOH solution. On the other hand, (**18**) could be removed only by a flash silica gel column chromatography (hexane). The $TESCF_2CH_3$ (**15**) is not very stable on silica gel and the purification should be carried out rapidly.

2.2. Introduction of $–CF_2CH_3$

Table 3 shows the results of the reactions between (**15**) and 2-naphthaldehyde (**19a**) to effect the addition of the $–CF_2CH_3$

Table 3
Introduction of $–CF_2CH_3$ into 2-naphtaldehyde (**19a**) by $TESCF_2CH_3$ (**15**)



15 **19a** **20a**

	Catalyst (equiv.)	Conversion (%)	Yield of **20a** (%)[a]
1	Me_4NF (0.1)	42	25
2	$Bu_4NSiF_2Ph_3$ (0.1)	60	29
3	KF (0.1)	100	41
4	KF (0.5)	100	44
5	KF (1.0)	100	43
6	CsF (0.1)	100	71
7	CsF (1.0)	100	67

The reactions were carried out using **19a** 1.0 equiv. and **15** 1.2 equiv. with fluoride catalyst in DMF at 110 °C for 18 h.
[a] Yields were estimated from ^1H NMR of reaction mixtures.

Table 4
Effect of solvent on the reaction between 2-naphtaldehyde (**19a**) and $TESCF_2CH_3$ (**15**)

	Solvent	Conversion (%)	Yield of **20a** (%)[a]
1	DMF-d_7	52	47
2	CD_2Cl_2	0	–
3	THF-d_8	0	–
4	Toluene-d_8	0	–

The reactions were carried out using **19a** 1.0 equiv. and **15** 1.2 equiv. with Me_4NF 0.1 equiv. in NMR tube at r.t.
[a] Yields were estimated from ^1H NMR of reaction mixtures.

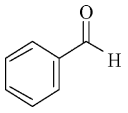
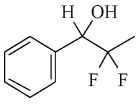
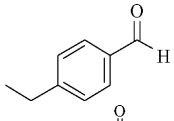
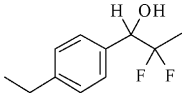
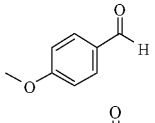
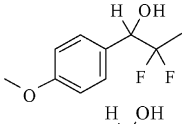
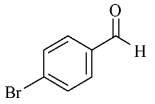
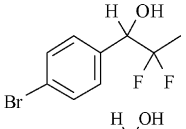
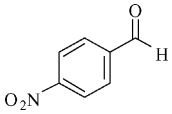
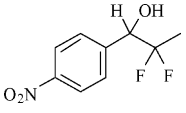
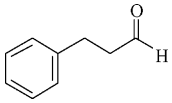
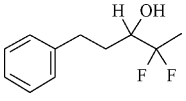
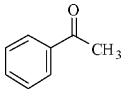
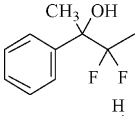
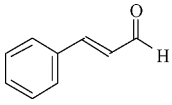
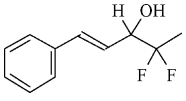
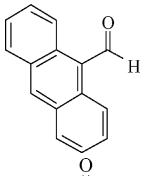
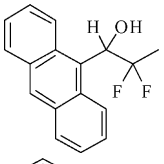
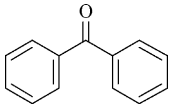
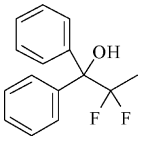
group. It was earlier reported that high temperature was needed for the reaction of 1,1-difluoroalkylsilanes to introduce the 1,1-difluoroalkyl group into the carbonyl compounds, because the Si–CF_2R bond is relatively stronger than the Si–CF_3 bond [11]. Therefore, all reactions in Table 3 were carried out in DMF at 110 °C for 18 h. Ammonium salts, such as Me_4NF (TMAF) and $Bu_4NPh_3SnF_2$ (TBAT), did not work well as fluoride sources, and $TESCF_2CH_3$ (**15**) remained unreacted (entries 1 and 2). In the case of KF, conversion was 100%, but yield of the product (**20a**) was around 40% (entry 3). The yield did not improve even when the amount of KF was increased to 1.0 equiv. (entries 4 and 5). CsF gave the best result, and yield of the product (**20a**) was about 70% (entries 6 and 7). Subsequently, the reactions were also attempted in deuteriated solvents at room temperature and the reactions monitored by NMR in order to check the effect of solvents (Table 4). It was confirmed that no reaction occurred in CD_2Cl_2, THF-d_8 and toluene-d_8.

Table 5 shows the results of the addition of the $–CF_2CH_3$ into various carbonyl compounds (**19**). Aromatic aldehydes gave moderate to high yields (entries b–e), except for the 4-nitrobenzaldehyde (entry f). 4-Nitrobenzaldehyde (**19f**) gave a complex mixture, because reactions could occur both at –CHO and the *ipso* nitro group bearing carbon of the aromatic ring. Enolizable aldehydes and ketones were not suitable for this reaction, because of deprotonation by $CH_3CF_2^-$ anion (entries g and h). Cinnamaldehyde (**19i**), a non-enolizable aldehyde, gave low yield, since 1,4-addition or polymerization would prevent the desired reaction. 9-Anthraldehyde (**19j**) and benzophenone (**19k**) are non-enolizable, but gave trace amount of products as a consequence of steric effects.

When the reaction was carried out with 4-fluorobenzaldehyde (**19l**), a unique product (**21l**) was formed in addition to the normal adduct (**20l**) (Table 6, entry 1). This by-product is formed in the following way; i.e. $CH_3CF_2^-$ anion attacks the carbonyl of the aldehyde, and $–O^-$ of intermediate attacks the 4-position of another molecule of 4-fluorobenzaldehyde substituting fluorine in a typical nucleophlic aromatic substitution pathway. Such a by-product has not been observed in the case of trifluoromethylation of aldehydes with $TMSCF_3$ and fluoride ion. Such reactivity may be due to higher reaction temperature (110 °C) employed for the reaction. When the reaction was performed with large excess of (**15**), formation of the by-product (**21l**) was suppressed and 100% of normal adduct (**20l**) was observed.

In conclusion, 1,1-difluoroethylsilanes were synthesized from $PhSO_2CF_2CH_3$ (**6**) and trialkylsilyl chlorides using magnesium metal. We have demonstrated the use of (**15**) as a promising reagent for introduction of $–CF_2CH_3$ moiety into carbonyl compounds.

Table 5
Introduction of $–CF_2CH_3$ into carbonyl compounds (**19**) by $TESCF_2CH_3$ (**15**)

	Substrate **19**	Product **20**	Yield (%)[a]
b			77
c			50
d			57
e			55
f			tr.
g			tr.
h			tr.
i			27
j			tr.
k			tr.

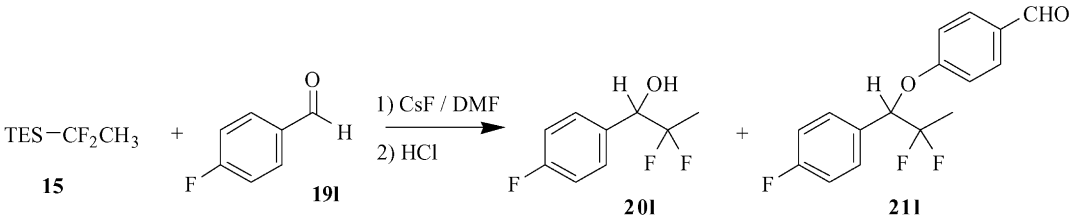
The reactions were carried out using **19** 1.0 equiv. and **15** 1.2 equiv. with CsF 0.1 equiv. in DMF at 110 °C for 18 h.
[a] Yields were estimated from ^1H NMR of reaction mixtures.

3. Experimental

3.1. General

1,1-Difluoroethyl phenyl sulfone was prepared as mentioned above. All other chemicals were purchased from commercial sources. DMF was distilled over calcium hydride and stored over activated molecular sieve. THF was freshly distilled over sodium. Other solvents were used as received. Column chromatography was carried out using silica gel (63–200 μm)

Table 6
The reaction between 4-fluorobenzaldehyde (**19l**) and $TESCF_2CH_3$ (**15**)



	15	19l	Selectivity (%)[a]	
			20l	21l
1	1.2 equiv.	1.0 equiv.	60	40
2	2.2 equiv.	1.0 equiv.	100	0

The reactions were carried out using **19l** 1.0 equiv. and **15** with CsF 0.1 equiv. in DMF at 110 °C for 18 h.
[a] Selectivities were estimated from ^{1}H NMR of reaction mixtures.

from Solvent Technologies. NMR spectra were obtained on a Varian AS-400 spectrometer using $CDCl_3$ as a solvent, TMS as an internal standard for ^{1}H and ^{13}C, and $CFCl_3$ as an internal standard for ^{19}F. GCMS data were recorded on a Thermo Finnigan TRACE GC/DSQ spectrometer at 70 eV.

3.2. Typical procedure for preparation of 1,1-difluoroethylsilanes

Into a flame-dried Schlenk flask containing 2.92 g (120 mmol) of magnesium granule and 20 ml of THF/HMPA (1:1 volume) mixture under nitrogen was added 12.06 g (80 mmol) of triethylsilyl chloride **14**. The mixture was stirred in an ice bath and a solution of 4.12 g (20 mmol) of 1,1-difluoroethyl phenyl sulfone **6** in 40 ml of THF/HMPA (1:1 volume) was added drop-wise through a dropping funnel. After 1 h, 120 ml of cold satd. $NaHCO_3$ aq was added, and the solution was extracted with ether (3 × 120 ml). The ether phase was washed with 120 ml of water, and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum, 11.22 g of white oil was obtained. The crude product contained TES–O–TES **17** and TESOH **18**, and purified by silica gel column chromatography (hexane). Resulting colorless oil still contained TES–O–TES **17**, and was purified by vacuum distillation to give 1.22 g (35% yield) of (1,1-difluoroethyl)-triethylsilane **15**, bp = 30–32 °C/10 Torr. ^{1}H NMR ($CDCl_3$): δ 0.71 (q, J = 8.1 Hz, 6H), 1.02 (t, J = 8.1 Hz, 9H), 1.55 (t, J = 24.4 Hz, 3H). ^{19}F NMR ($CDCl_3$): δ −99.9 (q, J = 24.4 Hz). ^{13}C NMR ($CDCl_3$): δ 1.0 (s), 7.0 (s), 23.8 (t, J = 22.9 Hz), 130.5 (t, J = 256.3 Hz). MS (*m/z*): 115 ($M^+ - CF_2CH_3$), 87.

(1,1-Difluoroethyl)trimethylsilane (**8**): Its formation was only confirmed by analyzing the NMR spectra of reaction mixture. ^{1}H NMR ($CDCl_3$): δ 0.16 (s, 9H), 1.53 (t, J = 24.0 Hz, 3H). ^{19}F NMR ($CDCl_3$): δ −106.2 (q, J = 24.4 Hz).

3.3. Typical procedure for the introduction of 1,1-difluoroethyl group into carbonyl compounds

Into a flame-dried round bottom flask containing 3 mg (0.02 mmol) of cesium fluoride and 0.5 ml of DMF under argon was added 26 mg (0.17 mmol) of 2-naphthaldehyde **19a**. To the reaction mixture under stirring was added, 36 mg (0.2 mmol) of (1,1-difluoroethyl)triethylsilane **15** through a syringe at room temperature followed by heating at 110 °C for 18 h. The reaction mixture was analyzed by NMR, and confirmed that 2,2-difluoro-1-(naphthalen-7-yl)propan-1-ol **20a** was formed. The yield based on ^{1}H NMR analyses was 71%. ^{1}H NMR ($CDCl_3$): δ 1.54 (dd, J = 18.9, 18.9 Hz, 3H), 5.03 (dd, J = 9.4, 9.4 Hz, 1H), 7.48–7.56 (m), 7.83–7.93 (m). ^{19}F NMR ($CDCl_3$): δ −101.1 (dqd, J = 246, 19.8, 9.2 Hz, 1F), −100.2 (dqd, J = 246, 19.8, 9.2 Hz, 1F). MS (*m/z*): 222 (M^+), 157 ($M^+ - CF_2CH_3$), 129, 128, 127, 65 ($C_2F_5^+$).

2,2-Difluoro-1-phenylpropan-1-ol **20b**. ^{1}H NMR ($CDCl_3$): δ 1.51 (dd, J = 18.9, 18.9 Hz, 3H), 4.86 (dd, J = 9.5, 9.5 Hz, 1H), 7.34–7.40 (m, 3H), 7.44–7.48 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −101.6 (dqd, J = 247, 18.3, 9.2 Hz, 1F), −100.6 (dqd, J = 247, 18.3, 9.2 Hz, 1F). MS (*m/z*): 172 (M^+), 107 ($M^+ - CF_2CH_3$), 77.

2,2-Difluoro-1-(4-ethylphenyl)propan-1-ol **20c**. ^{1}H NMR ($CDCl_3$): δ 1.24 (t, J = 7.6 Hz, 3H), 1.52 (dd, J = 19.0, 19.0 Hz, 3H), 2.65 (q, J = 7.6 Hz, 2H), 4.82 (dd, J = 9.7, 9.7 Hz, 1H), 7.20 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H). ^{19}F NMR ($CDCl_3$): δ −101.7 (dqd, J = 246, 18.3, 9.2 Hz, 1F), −100.7 (dqd, J = 246, 18.3, 9.2 Hz, 1F). MS (*m/z*) 200 (M^+), 135 ($M^+ - CF_2CH_3$), 79.

2,2-Difluoro-1-(4-methoxyphenyl)propan-1-ol **20d**. ^{1}H NMR ($CDCl_3$): δ 1.51 (dd, J = 18.9, 18.9 Hz, 3H), 3.81 (s, 3H), 4.80 (dd, J = 9.7, 9.7 Hz, 1H), 6.91 (m, 2H), 7.37 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −101.8 (dqd, J = 246, 18.3, 9.2 Hz, 1F), −101.1 (dqd, J = 246, 18.3, 9.2 Hz, 1F). MS (*m/z*): 202 (M^+), 137 ($M^+ - CF_2CH_3$), 109, 94, 77.

2,2-Difluoro-1-(4-bromophenyl)propan-1-ol **20e**. ^{1}H NMR ($CDCl_3$): δ 1.50 (dd, J = 18.9, 18.9 Hz, 3H), 4.82 (dd, J = 9.2, 9.2 Hz, 1H), 7.34 (m, 2H), 7.50 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −101.7 (dqd, J = 249, 18.3, 9.2 Hz, 1F), −100.2 (dqd, J = 249, 18.3, 9.2 Hz, 1F). MS (*m/z*): 252, 250 (M^+), 187, 185 ($M^+ - CF_2CH_3$), 159, 105, 77.

4,4-Difluoro-1-phenylpent-1-en-3-ol **20i**. ^{1}H NMR ($CDCl_3$): δ 1.64 (dd, J = 18.9, 18.9 Hz, 3H), 4.45 (ddd, J = 9.3, 9.3,

6.0 Hz, 1H), 6.24 (dd, $J = 15.9$, 6.0 Hz, 1H), 6.80 (d, $J = 15.7$ Hz, 1H), 7.20–7.36 (m). ^{19}F NMR ($CDCl_3$): δ −103.2 (dqd, $J = 247$, 18.3, 9.2 Hz, 1F), −100.7 (dqd, $J = 247$, 18.3, 9.2 Hz, 1F).

2,2-Difluoro-1-(4-fluorophenyl)propan-1-ol **20l**. ^{1}H NMR ($CDCl_3$): δ 1.50 (dd, $J = 18.9$, 18.9 Hz, 3H), 4.84 (dd, $J = 9.3$, 9.3 Hz, 1H), 7.06 (m, 2H), 7.44 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −114.1 (m, 1F), −101.9 (dqd, $J = 247$, 18.3, 9.2 Hz, 1F), −100.6 (dqd, $J = 247$, 18.3, 9.2 Hz, 1F). MS (*m/z*): 190 (M^+), 125 ($M^+ - CF_2CH_3$), 97, 77.

4-(2,2-Difluoro-1-(4-fluorophenyl)propoxy)benzaldehyde **21l**. ^{1}H NMR ($CDCl_3$): δ 1.71 (dd, $J = 18.7$, 18.7 Hz, 3H), 5.32 (dd, $J = 10.4$, 7.7 Hz, 1H), 6.97 (m, 2H), 7.06 (m, 2H), 7.43 (m, 2H), 7.77 (m, 2H), 9.85 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −112.5 (m, 1F), −101.7 (dqd, $J = 252$, 18.3, 10.7 Hz, 1F), −97.9 (dqd, $J = 252$, 18.3, 7.6 Hz, 1F). MS (*m/z*): 294 (M^+), 229 ($M^+ - CF_2CH_3$), 173 ($M^+ - OC_6H_4CHO$), 145, 133, 127, 123, 109.

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