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2-Fluoro-3-phenyl-allyltrimethylsilane: A new fluorinated reagent for Hosomi–Sakurai reaction

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ABSTRACT

2-Fluoro-3-phenyl-allyltrimethylsilane, prepared from β-fluorinated allylic acetate via a π-allylpalladium intermediate, reacted with various aldehydes and acetals in the presence of $TiCl_4$ to afford the corresponding homoallyl alcohols and homoallyl ethers, respectively, in good to moderate yields.

1. Introduction

Allylation of carbonyl compounds using various allylic metals is a well-established methodology for the stereoselective construction of C–C bonds to provide homoallylic alcohols [1]. Lewis acid-promoted allylation of carbonyl compounds with allyltrimethylsilane is referred to as the Hosomi–Sakurai reaction [2]. Much attention has been focused on syntheses and applications of allylsilanes to synthetic reagents. However, a literature survey revealed only a small number of reports on fluorine-containing allylsilanes (α,α-difluoro [3], γ,γ-difluoro-β-benzyloxy [4], γ,γ-difluoro-β-carbamoyl [5] and β-trifluoromethyl [6]). β-Fluoroallylsilane derivatives have not been reported, although they would afford useful fluorinated homoallyl alcohol derivatives. Furthermore, despite its electron-withdrawing inductive effect, fluorine has a stabilizing effect on α-carbocations through donation of its unshared electron pair to the vacant π-orbital of the α-carbon [7]. Since the former mesomeric effect is operative for α-sp^2 carbons, carbocations are stabilized by α-fluorine. The α-carbocation-stabilizing effect is well exemplified in biomimetic polyene cyclization [8], where fluoroalkene moieties served as terminators. Herein, we report the synthesis and reactivity of 2-fluoro-3-phenyl-allyltrimethylsilane (**1**).

2. Results and discussion

We struggled to find milder and more efficient reaction conditions for the preparation of **1**. After several attempts, we found that treatment of 2-fluoro-3-phenylprop-2-enyl acetate [9] (*E*:*Z* = 45:1) with hexamethyl disilane (3 equiv.) in the presence of 1 mol% of $Pd(PPh_3)_4$ at 160 °C in a sealed tube afforded **1** (*E*:*Z* = 1:10) in 75% yield (Scheme 1).

Attention was next directed to the Lewis acid-promoted addition reaction of **1** to aldehydes. We first surveyed several Lewis acids [$SnCl_4$, $TiCl_4$, $BF_3{\cdot}OEt_2$, $Ti(OiPr)_4$] and a Brønsted acid (CF_3SO_3H) in the reaction of **1** with benzaldehyde in dichloromethane at −78 °C. The results are summarized in Table 1. In the presence of 1.0 equiv. of either $SnCl_4$ or $Ti(OiPr)_4$, the reaction did not yield the expected homoallyl alcohol. With 1.0 equiv. of $TiCl_4$, the reaction occurred in 80% yield affording the expected product **2a** regioselectively as a single diastereomer (entry 4). The dr of **2a** was determined by ^{19}F NMR spectroscopy. The reaction presumably goes through an open transition state [10] to afford the corresponding *syn*-diastereomer, which was confirmed by X-ray crystallography (Fig. 1).

We then investigated other aldehydes with **1** in the allylation reaction under optimized conditions. The results are summarized in Table 2. The reaction proceeded with both aromatic and aliphatic aldehydes diastereoselectively to afford the corresponding homoallyl alcohols in moderate to good yields. *p*-Nitrobenzaldehyde was converted into **2d** in 77% yield, however the dr was decreased to 83:17 (entry 3). When the allylation was carried out with *p*-methoxybenzaldehyde or 2-furylaldehyde, no desired reaction occurred (not shown in Table 2). These results could be explained by the electron-rich carbonyl group. While aliphatic aldehydes had a slightly lower reactivity in comparison with aromatic ones, these reactions were successfully performed with high diastereoselectivity.

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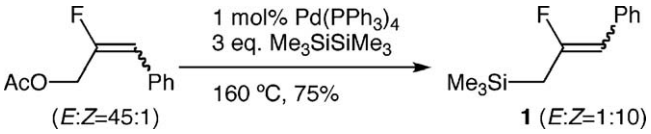
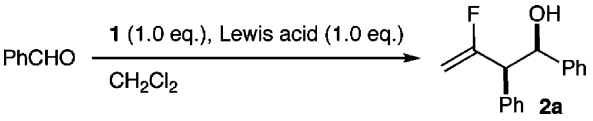


Scheme 1. Preparation of 2-fluoro-3-phenyl-allyltrimethylsilane **1**.

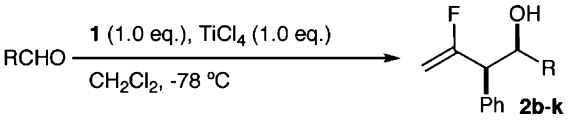
Table 1
Allylation of benzaldehyde with **1**.



	Lewis acid	Temp.	Time/h	Yield/%	dr[a]
1	$SnCl_4$	−78 °C → rt	24	0	–
2	$Ti(OiPr)_4$	−78 °C → rt	5	0	–
3	$BF_3{\cdot}OEt_2$	−78 °C → rt	24	4	sd[b]
4	$TiCl_4$	−78 °C	1	80	sd[b]
5	CF_3SO_3H	−78 °C → rt	5	2	sd[b]

[a] Diastereomeric ratio determined by ^{19}F NMR.
[b] Single diastereomer.

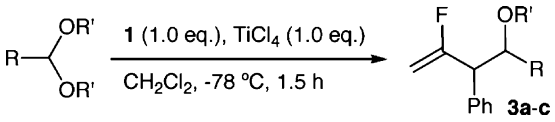
Table 2
Allylation of other aldehydes with **1**.



	R	Time/h	Product	Yield/%	dr[a]
1	p-$CH_3C_6H_4$	3	**2b**	40	sd[b]
2	p-$CF_3C_6H_4$	1	**2c**	54	sd[b]
3	p-$NO_2C_6H_4$	1	**2d**	77	83:17
4	*n*Pr	1	**2e**	58	sd[b]
5	Me	1.5	**2f**	58	sd[b]
6	*i*Pr	1.5	**2g**	44	sd[b]
7	$BnOCH_2$	1.5	**2h**	72	sd[b]
8	$CH_3(CH_2)_2CH(CH_3)$	1	**2i**	52	83:17
9	$PhCH(CH_3)$	1	**2j**	66	sd[b]
10	*n*BuOC=O	1	**2k**	36	sd[b]

[a] Diastereomeric ratio determined by ^{19}F NMR.
[b] Single diastereomer.

Table 3
Allylation of dialkyl acetals with **1**.



	R	R′	Product	Yield/%	dr[a]
1	$PhCH_2$	Me	**3a**	61	83:17
2	$BrCH_2$	Et	**3b**	44	74:26
3	Ph	Me	**3c**	78	63:37

[a] Diastereomeric ratio determined by ^{19}F NMR.

Allylations of dialkyl acetals with **1** afforded the corresponding homoallyl ethers **3** in moderate to good yields with moderate diastereoselectivity as shown in Table 3. The reaction took place regioselectively at the γ-position of allylsilane **1** similar to the previously reported results [11]. The relative configuration of the product has not been assigned yet.

3. Conclusion

In summary, we have developed a new synthesis of β-fluoroallylsilane derivative via a Pd-catalyzed process. This fluorine-containing allylsilane reacts with various aldehydes and acetals to provide the corresponding homoallyl alcohol derivatives in moderate to good yields. Work to apply the present protocol in fluorinated biomimetics is currently underway in our laboratory.

4. Experimental

All air- and moisture-sensitive reactions were carried out in flame-dried, argon-flushed, two-necked flasks sealed with rubber septa, and the dry solvents and reagents were introduced using a syringe. Tetrahydrofuran (THF) was freshly distilled under an argon atmosphere from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) was freshly distilled from phosphoric pentaoxide (P_2O_5). Flash column chromatography was carried out on a Kanto Chemical silica gel 60 N (spherical, neutral, 40–50 μm), and pre-coated Merck silica gel plates (Art5715 Kieselgel $60F_{254}$, 0.25 mm) were used for thin-layer chromatography (TLC). Unless mentioned otherwise, ^1H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on a JEOL JNM-LA400, JEOL JNM-LA300 or BRUKER AV-300. Chemical shifts of ^{19}F NMR were given by δ relative to that of an external trifluoroacetic acid (TFA). Mass

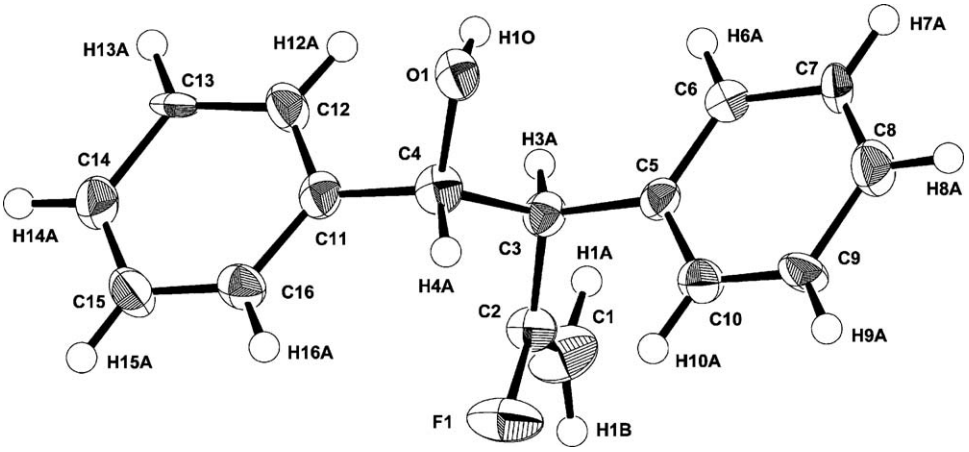


Fig. 1. X-ray structure of **2a**.

spectra were obtained on a JEOL JMS-700T or JEOL JMS-AX500 spectrometer.

4.1. Trimethyl(2-fluoro-3-phenyl-2-propenyl)silane 1

2-Fluoro-3-phenylprop-2-enyl acetate (0.638 g, 3.29 mmol) was placed in a Pyrex tube. After the atmosphere was replaced with argon, tatrakis(triphenylphosphine)palladium (0.038 g, 0.033 mmol) and hexamethyl disilane (1.443 g, 2.0 mL, 9.86 mmol) were added. Then the tube was sealed and heated at 160 °C for 3 h. After cooling to room temperature, the crude product was purified by a flash column chromatography (hexane) to give **1** (0.518 g, 2.48 mmol, yield 75%, *E*:*Z* = 1:10)

(*Z*)-**1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.10 (s, 9H), 1.78 (d, $^3J_{HF}$ = 25.4 Hz, 2H), 5.27 (d, $^3J_{HF}$ = 39.8 Hz, 1H), 7.11–7.19 (m, 1H), 7.24–7.29 (m, 2H), 7.39–7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.55, 23.96 (d, $^2J_{CF}$ = 29.7 Hz, C-3), 103.84 (d, $^2J_{CF}$ = 10.7 Hz, C-1), 125.96, 127.81, 128.32, 134.64 (d, $^3J_{CF}$ = 2.5 Hz), 160.68 (d, $^1J_{CF}$ = 262.7 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −90.83 (dt, $^3J_{HF}$ = 39.8, 25.4 Hz). MS (CI) *m*/*z* 209 $[M+H]^+$; HRMS (CI) Calcd. for $C_{12}H_{18}FSi$: 209.1162, Found: 209.1143.

(*E*)-**1** (selected date): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 9H), 1.97 (d, $^3J_{HF}$ = 28.0 Hz, 2H), 6.05 (d, $^3J_{HF}$ = 22.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.15, 20.12 (d, $^2J_{CF}$ = 32.2 Hz, C-3), 105.55 (d, $^2J_{CF}$ = 30.5 Hz, C-1); ^{19}F NMR (283 MHz, $CDCl_3$) δ −86.33 (dt, $^3J_{HF}$ = 22.3, 28.0 Hz).

4.2. Typical procedure for the reaction of aldehydes with 1

To a solution of benzaldehyde (0.17 mmol) in dry dichloromethane (0.28 mL) at −78 °C under an argon atmosphere was added $TiCl_4$ (1.0 M solution in dichloromethane; 0.17 mL, 0.17 mmol) dropwise with a syringe. After stirring at this temperature for 5 min, to the mixture was added dropwise a solution of **1** (0.035 g, 0.17 mmol) in dichloromethane (0.28 mL). The reaction mixture was stirred for 1 h at −78 °C. The resulting mixture was quenched with water (5 mL), and the aqueous layer was extracted with ether. The combined organic layers were washed with sat aq $NaHCO_3$, brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. The residue was purified by preparative thin-layer chromatography to afford **2a** in 80% yield as a single diastereomer.

4.2.1. 2-Fluoro-3,4-diphenyl-but-1-en-4-ol (2a)

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92 (s, 1H), 3.68 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HF}$ = 24.0 Hz, 1H), 4.22 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 50.0 Hz, 1H), 4.44 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 17.6 Hz, 1H), 5.19 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.26–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.85 (d, $^2J_{CF}$ = 23.1 Hz, C-3), 74.44 (d, $^3J_{CF}$ = 1.6 Hz, C-4), 92.68 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 126.54, 127.74, 127.99, 128.26, 128.76, 128.89 (d, $^3J_{CF}$ = 1.6 Hz), 137.13, 141.55, 164.76 (d, $^1J_{CF}$ = 260.2 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −100.82 (ddd, $^3J_{HF}$ = 17.6, 24.0, 50.0 Hz). MS (CI) *m*/*z* 225 $[M-H_2O+H]^+$; HRMS (CI) Calcd. for $C_{16}H_{14}F$: 225.1080, Found: 225.1077.

4.2.2. 2-Fluoro-3-phenyl-4-p-tolyl-but-1-en-4-ol (2b)

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85 (s, 1H), 2.34 (s, 3H), 3.68 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HF}$ = 24.0 Hz, 1H), 4.23 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 50.0 Hz, 1H), 4.44 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 17.9 Hz, 1H), 5.15 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.14 (d, $^3J_{HH}$ = 7.9 Hz, 2H), 7.25 (d, $^3J_{HH}$ = 7.9 Hz, 2H), 7.30–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.17, 57.74 (d, $^2J_{CF}$ = 23.1 Hz, C-3), 74.33 (d, $^3J_{CF}$ = 1.6 Hz, C-4), 92.60 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 126.48, 127.69, 128.74, 128.87 (d, $^3J_{CF}$ = 1.6 Hz), 128.97, 137.34, 137.67, 138.60, 164.89 (d, $^1J_{CF}$ = 260.2 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −100.67 (ddd, $^3J_{HF}$ = 17.9, 24.0, 50.0 Hz). MS (CI) *m*/*z* 239 $[M-H_2O+H]^+$; HRMS (CI) Calcd. for $C_{17}H_{16}F$: 239.1236, Found: 239.1237.

4.2.3. 2-Fluoro-3-phenyl-4-(4-trifluoromethyl-phenyl)-but-1-en-4-ol (2c)

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 3.63 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HF}$ = 24.0 Hz, 1H), 4.22 (dd, $^2J_{HH}$ = 3.3 Hz, $^3J_{HF}$ = 50.0 Hz, 1H), 4.48 (dd, $^2J_{HH}$ = 3.3 Hz, $^3J_{HF}$ = 17.9 Hz, 1H), 5.26 (dd, $^3J_{HH}$ = 2.0 Hz, 8.3 Hz, 1H), 7.32–7.38 (m, 5H), 7.48 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.59 (d, $^3J_{HH}$ = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.91 (d, $^2J_{CF}$ = 23.9 Hz, C-3), 74.33, 93.21 (d, $^2J_{CF}$ = 19.0 Hz, C-1), 124.08 (q, $^1J_{CF}$ = 271.7 Hz), 125.18 (q, $^3J_{CF}$ = 4.1 Hz), 126.88, 128.01, 128.88 (d, $^4J_{CF}$ = 1.6 Hz), 128.92, 130.09 (q, $^2J_{CF}$ = 32.2 Hz), 136.49, 145.39, 164.23 (d, $^1J_{CF}$ = 259.4 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −63.08 (s, 3F), -101.21 (ddd, $^3J_{HF}$ = 17.9, 24.0, 50.0 Hz, 1F). MS (CI) *m*/*z* 293 $[M-H_2O+H]^+$; HRMS (CI) Calcd. for $C_{17}H_{13}F_4$: 293.0953, Found: 293.0952.

4.2.4. 2-Fluoro-3-phenyl-4-(4-nitrophenyl)-but-1-en-4-ol (2d)

Major: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (d, $^3J_{HH}$ = 2.9 Hz, 1H), 3.62 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HF}$ = 23.3 Hz, 1H), 4.23 (dd, $^2J_{HH}$ = 3.2 Hz, $^3J_{HF}$ = 50.0 Hz, 1H), 4.52 (dd, $^2J_{HH}$ = 3.2 Hz, $^3J_{HF}$ = 18.0 Hz, 1H), 5.17 (dd, $^3J_{HH}$ = 2.9, 8.2 Hz, 1H), 7.29–7.37 (m, 5H), 7.56 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 8.19 (d, $^3J_{HH}$ = 8.8 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 57.94 (d, $^2J_{CF}$ = 23.4 Hz, C-3), 73.54 (d, $^3J_{CF}$ = 0.9 Hz, C-4), 93.53 (d, $^2J_{CF}$ = 19.3 Hz, C-1), 123.42, 127.37, 128.17, 128.91 (d, $^4J_{CF}$ = 1.6 Hz, C-2), 129.00, 136.04, 147.57, 148.68, 164.00 (d, $^1J_{CF}$ = 259.9 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −101.23 (ddd, $^3J_{HF}$ = 18.0, 23.3, 50.0 Hz). MS (CI) *m*/*z* 288 $[M+H]^+$; HRMS (CI) Calcd. for $C_{16}H_{15}FNO_3$: 288.1036, Found: 288.1036.

Minor (selected data): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 4.65 (dd, $^2J_{HH}$ = 3.3 Hz, $^3J_{HF}$ = 49.9 Hz, 1H), 4.85 (dd, $^2J_{HH}$ = 3.3 Hz, $^3J_{HF}$ = 17.8 Hz, 1H), 5.17 (dd, $^3J_{HH}$ = 3.0, 9.2 Hz, 1H), 8.04 (d, $^3J_{HH}$ = 8.8 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 57.86 (d, $^2J_{CF}$ = 23.7 Hz, C-3), 74.21 (d, $^3J_{CF}$ = 2.9 Hz, C-4), 93.93 (d, $^2J_{CF}$ = 19.5 Hz, C-1), 123.18, 127.52, 127.80, 128.39 (d, $^4J_{CF}$ = 1.9 Hz), 128.72, 136.27, 147.38, 148.47, 164.07 (d, $^1J_{CF}$ = 261.7 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −101.58 (ddd, $^3J_{HF}$ = 17.8, 24.0, 50.0 Hz).

4.2.5. 2-Fluoro-3-phenyl-hept-1-en-4-ol (2e)

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, $^3J_{HH}$ = 7.0 Hz, 3H), 1.39–1.63 (m, 4H), 3.40 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HF}$ = 21.4 Hz, 1H), 4.12 (br t, 1H), 4.44 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 50.4 Hz, 1H), 4.65 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 18.1 Hz, 1H), 7.28–7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.95, 18.93, 37.05, 55.73 (d, $^2J_{CF}$ = 23.1 Hz, C-3), 71.19 (d, $^3J_{CF}$ = 2.5 Hz, C-4), 92.26 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 127.58, 128.75, 128.96, 137.46, 165.86 (d, $^1J_{CF}$ = 259.4 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −100.10 (ddd, $^3J_{HF}$ = 18.1, 21.4, 50.4 Hz). MS (CI) *m*/*z* 191 $[M-H_2O+H]^+$; HRMS (CI) Calcd. for $C_{13}H_{16}F$: 191.1236, Found: 191.1239.

4.2.6. 2-Fluoro-3-phenyl-pent-1-en-4-ol (2f)

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (d, $^3J_{HH}$ = 6.2 Hz, 3H), 1.50 (br s, 1H), 3.33 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HF}$ = 22.9 Hz, 1H), 4.30 (dd, $^3J_{HH}$ = 6.2, 7.8 Hz, 1H), 4.45 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 50.2 Hz, 1H), 4.64 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 18.0 Hz, 1H), 7.27–7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.14, 57.35 (d, $^2J_{CF}$ = 23.1 Hz, C-3), 67.88 (d, $^3J_{CF}$ = 2.5 Hz, C-4), 92.20 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 127.67, 128.80 (d, $^3J_{CF}$ = 1.6 Hz), 128.83, 137.47, 165.75 (d, $^1J_{CF}$ = 260.2 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −100.55 (ddd, $^3J_{HF}$ = 18.0, 22.9, 50.2 Hz). MS (EI) *m*/*z* 180 $[M]^+$; HRMS (EI) Calcd. for $C_{11}H_{13}FO$: 180.0950, Found: 180.0952.

4.2.7. 2-Fluoro-5-methyl-3-phenyl-hex-1-en-4-ol (2g)

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (d, $^3J_{HH}$ = 13.0 Hz, 3H), 1.01 (d, $^3J_{HH}$ = 13.2 Hz, 3H), 1.36 (br s, 1H), 1.82–1.92 (m, 1H), 3.56 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HF}$ = 22.2 Hz, 1H), 3.91–3.96 (m, 1H), 4.41 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 50.4 Hz, 1H), 4.63 (dd, $^2J_{HH}$ = 3.1 Hz,

$^3J_{HF}$ = 18.0 Hz, 1H), 7.25–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.61, 20.13, 30.40, 53.08 (d, $^2J_{CF}$ = 24.0 Hz, C-3), 75.69, 92.22 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 127.54, 128.74, 129.01, 137.75, 166.00 (d, $^1J_{CF}$ = 260.2 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −101.00 (ddd, $^3J_{HF}$ = 18.0, 22.2, 50.4 Hz). MS (CI) *m/z* 191 $[M-H_2O+H]^+$; HRMS (CI) Calcd. for $C_{13}H_{16}F$: 191.1236, Found: 191.1234.

*4.2.8. 5-Benzyloxy-2-fluoro-3-phenyl-pent-1-en-4-ol (**2h**)*

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.60 (d, $^3J_{HH}$ = 4.5 Hz, 1H), 3.22 (dd, $^3J_{HH}$ = 5.5 Hz, $^2J_{HH}$ = 9.7 Hz, 1H), 3.38 (dd, $^3J_{HH}$ = 2.8 Hz, $^2J_{HH}$ = 9.7 Hz, 1H), 3.62 (dd, $^3J_{HH}$ = 9.5 Hz, $^3J_{HF}$ = 24.2 Hz, 1H), 4.22 (ddd, $^3J_{HH}$ = 2.8, 5.5, 9.5 Hz, 1H), 4.39 (d, A of AB, $^2J_{HH}$ = 11.7 Hz, 1H), 4.47 (dd, B of AB, $^2J_{HH}$ = 11.7 Hz, 1H), 4.54 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 50.0 Hz, 1H), 4.70 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 17.8 Hz, 1H), 7.24–7.35 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.45 (d, $^2J_{CF}$ = 24.7 Hz, C-3), 70.74 (d, $^3J_{CF}$ = 3.3 Hz, C-4), 71.47, 73.38, 92.38 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 127.48, 127.74, 127.80, 128.13 (d, $^3J_{CF}$ = 1.6 Hz), 128.40, 128.74, 137.66, 137.97, 165.14 (d, $^1J_{CF}$ = 260.2 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −101.91 (ddd, $^3J_{HF}$ = 17.8, 24.2, 50.0 Hz). MS (EI) *m/z* 286 $[M]^+$; HRMS (EI) Calcd. for $C_{18}H_{19}FO_2$: 286.1369, Found: 286.1364.

*4.2.9. 2-Fluoro-5-methyl-3-phenyl-oct-1-en-4-ol (**2i**)*

Major: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, $^3J_{HH}$ = 6.8 Hz, 3H), 0.96 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 1.21–1.55 (m, 5H), 1.81 (br s, 1H), 3.55 (dd, $^3J_{HH}$ = 9.3 Hz, $^3J_{HF}$ = 25.9 Hz, 1H), 4.08 (dt, $^3J_{HH}$ = 9.3, 2.9 Hz, 1H), 4.42 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 50.0 Hz, 1H), 4.61 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 18.0 Hz, 1H), 7.28–7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.44, 14.20, 34.74, 36.66, 53.47 (d, $^2J_{CF}$ = 23.1 Hz, C-3), 73.80 (C-4), 92.05 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 127.57, 128.72, 128.84, 138.30, 165.69 (d, $^1J_{CF}$ = 260.2 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −101.99 (ddd, $^3J_{HF}$ = 18.0, 25.9, 50.0 Hz). MS (CI) *m/z* 237 $[M+H]^+$; HRMS (CI) Calcd. for $C_{15}H_{22}FO$: 237.1654, Found: 237.1660.

Minor (selected data): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (m, 1H), 4.40 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 50.6 Hz, 1H), 4.64 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.37, 16.84, 20.27, 32.25, 35.24, 52.69 (d, $^2J_{CF}$ = 23.1 Hz, C-3), 75.75 (C-4), 92.35 (d, $^2J_{CF}$ = 19.8 Hz, C-1); ^{19}F NMR (283 MHz, $CDCl_3$) δ −100.66 (ddd, $^3J_{HF}$ = 18.1, 20.6, 50.6 Hz).

*4.2.10. 3,5-Diphenyl-2-fluoro-hex-1-en-4-ol (**2j**)*

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.52 (br s, 1H), 2.92 (quint, $^3J_{HH}$ = 6.6 Hz, 1H), 3.49 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HF}$ = 19.8 Hz, 1H), 4.30 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 4.42 (dd, $^2J_{HH}$ = 3.0 Hz, $^3J_{HF}$ = 50.6 Hz, 1H), 4.69 (dd, $^2J_{HH}$ = 3.0 Hz, $^3J_{HF}$ = 19.8 Hz, 1H), 7.18–7.35 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.25, 42.50, 36.66, 52.50 (d, $^2J_{CF}$ = 24.0 Hz, C-3), 75.35 (d, $^3J_{CF}$ = 1.5 Hz, C-4), 92.47 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 126.56, 127.53, 128.54, 128.57, 129.32, 137.20, 144.67, 166.19 (d, $^1J_{CF}$ = 260.4 Hz, C-2); ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.70 (dt, $^3J_{HF}$ = 19.8, 50.6 Hz). MS (CI) *m/z* 253 $[M-H_2O+H]^+$; HRMS (CI) Calcd. for $C_{18}H_{18}F$: 253.1393, Found: 253.1396.

*4.2.11. 4-Fluoro-2-hydroxy-3-phenyl-pent-4-enoic acid butyl ester (**2k**)*

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 1.24–1.36 (m, 2H), 1.49–1.59 (m, 2H), 3.02 (d, $^3J_{HH}$ = 6.2 Hz, 1H), 3.96 (dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HF}$ = 14.0 Hz, 1H), 4.13 (t, $^3J_{HH}$ = 6.6 Hz, 2H), 4.39 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 50.8 Hz, 1H), 4.77 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 18.5 Hz, 1H), 7.29–7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.56, 18.93, 30.35, 52.46 (d, $^2J_{CF}$ = 25.6 Hz, C-3), 65.93, 71.96 (d, $^3J_{CF}$ = 2.5 Hz, C-2), 93.97 (d, $^2J_{CF}$ = 18.1 Hz, C-5), 127.73, 128.61, 128.76, 136.87 (d, $^3J_{CF}$ = 2.5 Hz), 164.12 (d, $^1J_{CF}$ = 260.2 Hz, C-4), 173.33; ^{19}F NMR (283 MHz, $CDCl_3$) δ −97.33 (ddd, $^3J_{HF}$ = 14.0, 18.5, 50.8 Hz). MS (EI) *m/z* 248 $[M-H_2O]^+$; HRMS (EI) Calcd. for $C_{15}H_{17}FO_2$: 248.1213, Found: 248.1218.

4.3. Typical procedure for the reaction of dialkylacetals with **1**

To a solution of phenylacetoaldehyde dimethyl acetal (0.17 mmol) in dry dichloromethane (0.25 mL) at −78 °C under an argon atmosphere was added $TiCl_4$ (1.0 M solution in dichloromethane; 0.17 mL, 0.17 mmol) dropwise with a syringe. After stirring at this temperature for 5 min, to the mixture was added dropwise a solution of **1** (0.035 g, 0.17 mmol) in dichloromethane (0.28 mL). The reaction mixture was stirred for 1.5 h at −78 °C. The resulting mixture was quenched with water (5 mL), and the aqueous layer was extracted with ether (3×). The combined organic layers were washed with sat aq $NaHCO_3$, brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. The residue was purified by preparative thin-layer chromatography to afford **3a** in 61% yield as a 83:17 mixture of diastereomers.

*4.3.1. 2-Fluoro-4-methoxy-3,5-diphenylpent-1-ene (**3a**)*

Major: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.77 (dd, $^3J_{HH}$ = 7.1 Hz, $^2J_{HH}$ = 14.0 Hz, 1H), 2.84 (dd, $^3J_{HH}$ = 5.3 Hz, $^2J_{HH}$ = 14.0 Hz, 1H), 3.09 (s, 3H), 3.47 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HF}$ = 18.4 Hz, 1H), 3.90–3.96 (m, 1H), 4.31 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 50.6 Hz, 1H), 4.66 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 18.4 Hz, 1H), 7.18–7.39 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.85, 53.11 (d, $^2J_{CF}$ = 24.7 Hz, C-3), 59.01, 82.73, 92.63 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 126.23, 127.17, 128.27, 128.29, 129.43, 129.49, 137.84 (d, $^3J_{CF}$ = 1.6 Hz), 138.68, 166.48 (d, $^1J_{CF}$ = 259.4 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −100.11 (dt, $^3J_{HF}$ = 18.4, 50.6 Hz). MS (EI) *m/z* 270 $[M]^+$; HRMS (EI) Calcd. for $C_{18}H_{19}FO$: 270.1420, Found: 270.1412.

Minor (selected data): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (dd, $^3J_{HH}$ = 7.5 Hz, $^2J_{HH}$ = 14.0 Hz, 1H), 2.78 (dd, $^3J_{HH}$ = 3.7 Hz, $^2J_{HH}$ = 14.0 Hz, 1H), 3.27 (s, 3H), 3.44 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HF}$ = 26.0 Hz, 1H), 3.85–3.92 (m, 1H), 4.47 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 50.2 Hz, 1H), 4.63 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 17.6 Hz, 1H), 7.09–7.36 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.30, 53.93 (d, $^2J_{CF}$ = 24.7 Hz, C-3), 58.94, 82.75 (d, $^4J_{CF}$ = 1.6 Hz, C-5), 92.09 (d, $^2J_{CF}$ = 20.6 Hz, C-1), 126.19, 127.37, 128.18, 128.46 (d, $^3J_{CF}$ = 1.6 Hz), 128.71, 129.55, 138.54; ^{19}F NMR (283 MHz, $CDCl_3$) δ −102.21 (ddd, $^3J_{HF}$ = 17.6, 26.0, 50.2 Hz).

*4.3.2. 5-Bromo-4-ethoxy-2-fluoro-3-phenylpent-1-ene (**3b**)*

Major: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 3.34 (dq, $^3J_{HH}$ = 7.1 Hz, $^2J_{HH}$ = 9.1 Hz, 1H), 3.35 (dd, $^3J_{HH}$ = 5.7 Hz, $^2J_{HH}$ = 11.0 Hz, 1H), 3.45 (dd, $^3J_{HH}$ = 5.1 Hz, $^2J_{HH}$ = 11.0 Hz, 1H), 3.63 (dq, $^3J_{HH}$ = 7.1 Hz, $^2J_{HH}$ = 9.1 Hz, 1H), 3.82 (dd, $^3J_{HH}$ = 6.4 Hz, $^3J_{HF}$ = 18.4 Hz, 1H), 3.98–4.04 (m, 1H), 4.39 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 50.4 Hz, 1H), 4.69 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 18.4 Hz, 1H), 7.25–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.24, 33.37, 51.75 (d, $^2J_{CF}$ = 24.7 Hz, C-3), 67.04, 78.65 (d, $^3J_{CF}$ = 1.6 Hz, C-4), 93.09 (d, $^2J_{CF}$ = 19.0 Hz, C-1), 127.45, 128.32, 129.48 (d, $^4J_{CF}$ = 1.6 Hz), 136.51 (d, $^3J_{CF}$ = 1.6 Hz), 165.39 (d, $^1J_{CF}$ = 260.2 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −100.89 (dt, $^3J_{HF}$ = 18.4, 50.4 Hz). MS (EI) *m/z* 286 $[M]^+$; HRMS (EI) Calcd. for $C_{13}H_{16}{}^{79}BrFO$: 286.0369, Found: 286.0370.

Minor (selected data): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (t, $^3J_{HH}$ = 7.0 Hz, 3H), 3.03 (dd, $^3J_{HH}$ = 4.2 Hz, $^2J_{HH}$ = 11.1 Hz, 1H), 3.44 (dd, $^3J_{HH}$ = 3.5 Hz, $^2J_{HH}$ = 11.1 Hz, 1H), 3.49 (dq, $^3J_{HH}$ = 7.0 Hz, $^2J_{HH}$ = 9.0 Hz, 1H), 3.66 (dd, $^3J_{HH}$ = 9.3 Hz, $^3J_{HF}$ = 25.7 Hz, 1H), 3.68 (dq, $^3J_{HH}$ = 7.0 Hz, $^2J_{HH}$ = 9.0 Hz, 1H), 3.84 (dt, $^3J_{HH}$ = 3.8 Hz, $^3J_{HH}$ = 9.3 Hz, 1H), 4.46 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 50.0 Hz, 1H), 4.58 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 17.2 Hz, 1H), 7.21–7.27 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.27, 34.35, 52.81 (d, $^2J_{CF}$ = 24.0 Hz, C-3), 66.41, 78.09, 92.57 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 127.71, 128.27, 128.89, 164.58 (d, $^1J_{CF}$ = 261.0 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −102.95 (ddd, $^3J_{HF}$ = 17.2, 25.7, 50.0 Hz).

Table 4
Crystal data and experimental details for **2a**.

Formula	$C_{16}H_{15}FO$	
Formula weight	242.28	
Temperature	150(2) K	
Wavelength	0.71070 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	$a = 11.353(3)$ Å	$\alpha = 90^\circ$
	$b = 5.5834(13)$ Å	$\beta = 95.905(6)^\circ$
	$c = 20.232(5)$ Å	$\gamma = 90^\circ$
Cell volume	1275.6(5) Å^3	
Z	4	
Density (calculated)	1.262 Mg m^{-3}	
Absorption coefficient	0.087 mm^{-1}	
$F(000)$	512	
Crystal size	0.35 mm × 0.25 mm × 0.22 mm	
Theta range for data collection	4.05–27.48°	
Reflections collected/unique	11,692/2886 [$R_{int} = 0.0447$]	
Data/restraints/parameters	2886/0/276	
Goodness of fit on F^2	1.245	
R_1 ($I > 2\sigma(I)$)	0.0873	
wR_2 (all data)	0.1716	
Largest diff. peak and hole	0.316/−0.306 eÅ^{-3}	

*4.3.3. 2-Fluoro-4-methoxy-3,4-diphenylbut-1-ene (**3c**)*

Major: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.13 (s, 3H), 3.67 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HF}$ = 23.8 Hz, 1H), 4.16 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 50.0 Hz, 1H), 4.38 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HF}$ = 17.8 Hz, 1H), 4.69 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.15–7.34 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.84 (d, $^2J_{CF}$ = 24.0 Hz, C-3), 57.13, 83.39, 92.36 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 127.10, 127.30, 127.90, 128.16, 128.22, 128.78, 137.90, 139.69, 165.06 (d, $^1J_{CF}$ = 260.2 Hz, C-2); ^{19}F NMR (283 MHz, $CDCl_3$) δ −104.11 (ddd, $^3J_{HF}$ = 17.8, 23.8, 50.0 Hz). MS (CI) m/z 225 $[M-MeOH+H]^+$; HRMS (CI) Calcd. for $C_{16}H_{14}F$: 225.1080, Found: 225.1077.

Minor (selected data): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.26 (s, 3H), 3.68 (dd, $^3J_{HH}$ = 9.9 Hz, $^3J_{HF}$ = 24.8 Hz, 1H), 4.51 (d, $^3J_{HH}$ = 9.9 Hz, 1H), 4.53 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 50.2 Hz, 1H), 4.72 (dd, $^2J_{HH}$ = 3.1 Hz, $^3J_{HF}$ = 17.8 Hz, 1H), 7.04–7.16 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.82 (d, $^2J_{CF}$ = 24.0 Hz, C-3), 56.96, 84.11 (d, $^3J_{CF}$ = 3.3 Hz, C-4), 91.84 (d, $^2J_{CF}$ = 19.8 Hz, C-1), 127.02, 127.49, 127.72, 127.96, 128.22, 128.46 (d, $^3J_{CF}$ = 1.6 Hz), 137.74, 139.05, 165.49 (d, $^1J_{CF}$ = 261.0 Hz, C-2): ^{19}F NMR (283 MHz, $CDCl_3$) δ −105.59 (ddd, $^3J_{HF}$ = 17.8, 24.8, 50.2 Hz).

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Appendix A. X-ray crystallographic study on 2a

The diffraction experiments were carried out at 150(2) K on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα (λ = 0.71070 Å) radiation. Crystal data and collection details for **2a** are summarized in Table 4. The structure was solved by direct Methods (SIR97) [12] and refined on F^2 by full-matrix least-squares methods, using SHELXL-97 [13]. CCDC 768953 contains the supplementary crystallographic data for **2a**. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB12 1EZ, UK; fax: +44 1223 366 033, e-mail: deposit@ccdc.cam.ac.uk.

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