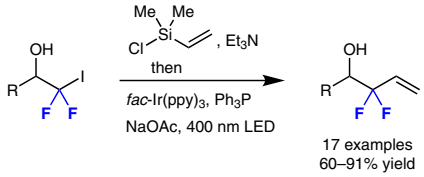
Synthesis L. I. Panferova et al. Feature

Vinylation of Iododifluoromethylated Alcohols via a Light-Promoted Intramolecular Atom-Transfer Reaction

Liubov I. Panferova
Marina I. Struchkova
Alexander D. Dilman*

N. D. Zelinsky Institute of Organic Chemistry, Leninsky prosp. 47, 119991 Moscow, Russian Federation
adil25@mail.ru



Received: 16.05.2017
Accepted after revision: 06.07.2017
Published online: 07.08.2017
DOI: 10.1055/s-0036-1590855; Art ID: ss-2017-z0331-fa

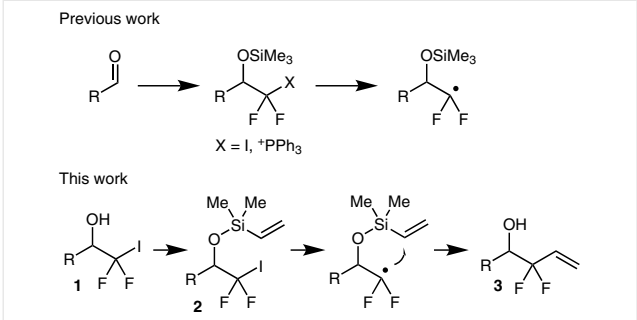
Abstract A method for the synthesis of *gem*-difluorohomoallylic alcohols by the substitution of iodine in the iododifluoromethyl group by a vinyl fragment is described. The reaction proceeds via an intramolecular iodine atom transfer followed by β-elimination. The reaction is performed in the presence of an iridium photocatalyst, *fac*-Ir(ppy)$_3$, and triphenylphosphine under irradiation with light-emitting diodes.

Key words organofluorine compounds, photocatalysis, silicon reagents, radical reaction, atom transfer

The synthesis of organofluorine compounds has become an intensively investigated area in recent years,[1] apparently, owing to the importance of such compounds in medicinal chemistry[2] and materials science.[3] Though diverse approaches for the preparation of fluorinated molecules can be envisaged,[1] classical ionic reactions[4] and transition-metal-catalyzed cross-couplings[5] have dominated the field for a long time. In contrast, reactions involving fluorinated radicals have come to the fore within the last decade.[6] The advent of photoredox catalysis with visible light[7] has further advanced the scope of methods for the generation of fluorinated radicals.[8]

Because of a strong electron-withdrawing effect, fluorine atoms facilitate the reductive generation of radical species from perfluorinated substrates.[9] In this regard, electron-deficient sulfonium salts (e.g., Umemoto's reagents)[10] or Togni's iodanes[11] are the most easily reducible reagents, which are typically used as sources of the trifluoromethyl radical.[12] At the same time, radical processes involving partially fluorinated substrates have been less elaborated,[13] which may be associated with difficult access to the corresponding precursors (e.g., partially fluorinated iodides).

Recently, we reported the fluoroalkylation of carbonyl compounds and iminium ions with iododifluoromethyl[14] and phosphinyldifluoromethyl[15] nucleophilic reagents, and demonstrated that the primary addition products of these reactions can serve as sources of radicals under photoredox conditions[16] (Scheme 1). Herein, we apply this concept for reactions of compounds **2** containing a double bond as a part of the silyl fragment. The silicon tether makes the radical attack intramolecular, thereby alleviating the regioselectivity problem.[17] At the same time, facile C–Si bond cleavage reinstates the double bond affording alcohols **3**, with the overall sequence corresponding to the substitution of iodine in substrates **1**[18] by the vinyl group.[19]



Scheme 1 Applications of difluorinated radicals

Silyl ether **2a**, obtained from iododifluoromethyl-substituted alcohol **1a** (R = 4-ClC$_6$H$_4$) and chloro(dimethyl)vinylsilane, was evaluated under various conditions upon irradiation with a strip of either blue or 400 nm light-emitting diodes for 2 hours (Table 1). There was virtually no reaction until a combination of sodium acetate with a substoichiometric amount (0.2 equiv) of triphenylphosphine was used (entry 6). The application of 400 nm light was also important, allowing for about 90% conversion of substrate **2a** after 2 hours, as there was no reaction with blue light without a photocatalyst (entry 7). Further addition of 0.25 mol% *fac*-Ir(ppy)$_3$ provided a significant rate acceleration, and complete conversion was observed within 15 minutes! However, for generality, the reactions were typically performed

for 2 hours (entry 10). Based on ^{1}H and ^{19}F NMR analysis, the product is formed as a mixture of several compounds of general structure **4** differing in the silicon substituent Y, presumably acetate or siloxane.

To obviate the prior isolation of silyl ethers **2**, the whole sequence involving silylation/radical vinylation/desilylation was performed in a one-pot manner. Thus, alcohols **1** were treated with chloro(dimethyl)vinylsilane and triethylamine, followed by addition to the same flask of sodium acetate, triphenylphosphine, and the photocatalyst under irradiation (400 nm). Then, the mixture was treated with ammonium fluoride, and worked up. A series of alcohols was subjected to this radical vinylation of the iododifluoromethyl group (Table 2). Various aromatic and heteroaromatic substrates provided good yields of products. The reaction tolerates ester and nitrile groups, and works well with electron-donating and electron-withdrawing substituents, as well as substituents at the *ortho*-position. The substrate **1q** obtained from an enolizable aliphatic aldehyde also provided product **3q**, although in a decreased yield of 60%. However, the iododifluoromethylated alcohol derived from acetophenone gave a complex mixture of products.

Concerning the mechanism, we believe that the reaction proceeds via an atom transfer/radical addition (ATRA) process.[20,21] The reaction presumably starts with the formation of a halogen-bonded complex[22] between the iododifluoromethyl group and the phosphine[23] (Scheme 2). This complex can lead to radical **5** either with assistance of light or by reduction with the photoexcited iridium(III) complex. Subsequent *exo-dig* cyclization with the formation of a five-membered ring proceeds rapidly, leading to radical **6**. Though oxidation of the primary radical with iridium(IV) is, in principle, possible, a chain process seems more likely. Thus, transfer of the iodine atom from the starting iodide **2** can regenerate radical **5** along with formation of iodide **7**. The latter species undergoes rapid fragmentation with con-

Biographical Sketches

Liubov Panferova studied at the Higher Chemical College of the Russian Academy of Sciences, and performed undergraduate work in the group of Prof. Vladimir Grushin at the Institute of Chemical Research of Catalonia, Spain. In 2015 she joined the group of A. D. Dilman as a graduate student at the Zelinsky Institute of Organic Chemistry. She is interested in organoelement and organofluorine compounds.

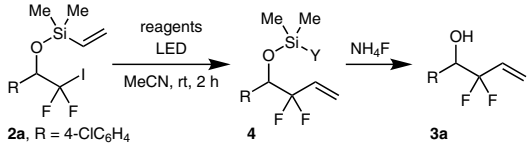
Marina Struchkova graduated from Moscow State University in 1968, and obtained her Ph.D. in 1977 from the Moscow University of Chemical Technology. Then, she joined the NMR laboratory of the Zelinsky Institute of Organic Chemistry. Her major interests involve NMR spectroscopy.

Alexander Dilman received his Ph.D. from the Zelinsky Institute of Organic Chemistry in 2001 (with Prof. S. L. Ioffe). Then, he spent one year as a postdoc in the group of Prof. H. B. Kagan at the Université Paris-Sud, France. In 2003 he returned to the Zelinsky Institute and started independent work. In 2008 he completed his habilitation studies (Dr. Sci. in Russia), and in 2011 he became a Head of Laboratory. His current interests include the chemistry of organofluorine compounds.

certed breaking of carbon–iodine and carbon–silicon bonds.[24] This β-elimination may be facilitated by acetate anion, which can coordinate to the silicon atom.

In summary, a convenient method for the formal substitution of iodine in iododifluoromethylated alcohols by the vinyl group is described. The reaction process involves a sequence of transformations, such as silylation, light-mediated atom transfer, and desilylation, which are performed in a one-pot manner by consecutive addition of the required reagents. A combination of sodium acetate, triphenylphosphine, and 400 nm light irradiation is a key feature responsible for the reaction efficiency.

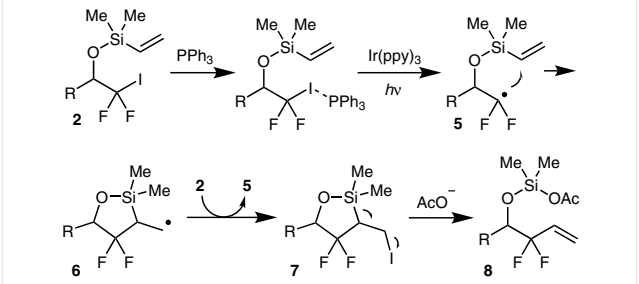
Table 1 Optimization Studies



2a, R = 4-ClC$_6$H$_4$ **4** **3a**

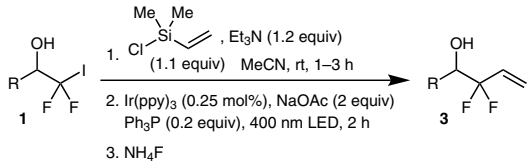
Entry	Reagents (equiv)	LED	Yield (%) of **4**[a]
1	–	400 nm	0
2	NaOAc (2)	400 nm	0
3	NaOAc (2), Eosin Y-Na$_2$ (0.02)	blue	0
4	NaOAc (2), Ru(bipy)$_3$(BF$_4$)$_2$ (0.005)	blue	0
5	NaOAc (2), Ir(ppy)$_3$ (0.005)	400 nm	0
6	NaOAca (2), Ph$_3$P (0.2)	400 nm	85[b]
7	NaOAc (2), Ph$_3$P (0.2)	blue	0
8	Ph$_3$P (0.2)	400 nm	<3
9	NaOAc (2), Ph$_3$P (0.2), Ru(bipy)$_3$(BF$_4$)$_2$ (0.005)	blue	52
10	NaOAc (2), Ph$_3$P (0.2), Ir(ppy)$_3$ (0.0025)	400 nm	91 (91)[c]

[a] Determined by NMR analysis of the reaction mixture.
[b] Incomplete conversion; 5% of starting **2a**.
[c] Isolated yield of **3a**.



Scheme 2 Proposed mechanism

Table 2 Synthesis of Alcohols **3**



1 **3**

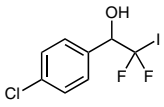
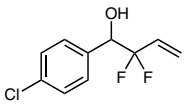
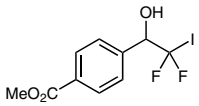
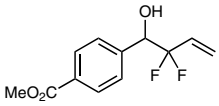
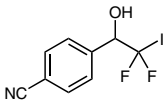
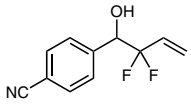
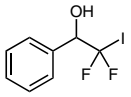
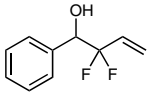
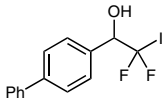
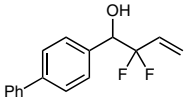
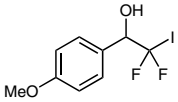
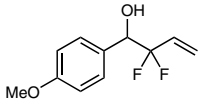
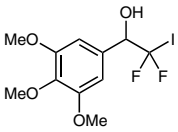
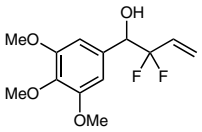
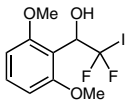
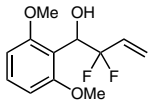
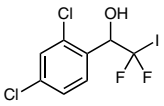
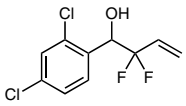
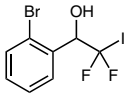
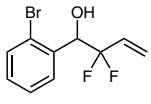
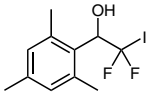
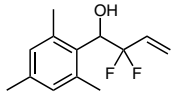
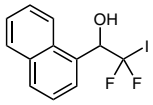
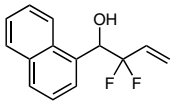
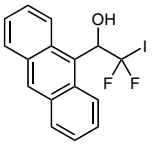
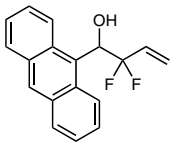
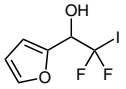
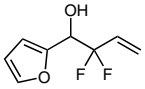
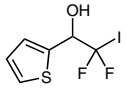
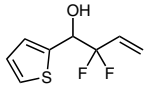
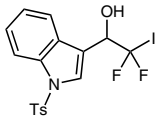
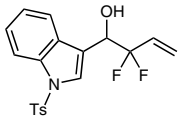
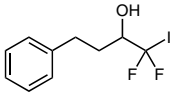
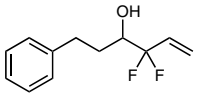
Substrate	Product		Yield (%) of **3**[a]
		**3a**	79
		**3b**	91
		**3c**	73
		**3d**	79
		**3e**	91
		**3f**	79
		**3g**	87
		**3h**	80
		**3i**	85
		**3j**	85
		**3k**	81

Table 2 (continued)

Substrate	Product		Yield (%) of **3**[a]
		**3l**	83
		**3m**[b]	80
		**3n**	89
		**3o**	79
		**3p**[b]	64
		**3q**[b]	60

[a] Isolated yield.
[b] Irradiation reaction time: for **3m**, 6 h; for **3p**, 5 h; for **3q**, 15 h.

All reactions were performed under an argon atmosphere. Acetonitrile was distilled twice, from P_2O_5 and CaH_2 successively, and stored over 3 Å molecular sieves. 1,2-Dimethoxyethane was distilled from $LiAlH_4$. Column chromatography was carried out employing silica gel (230–400 mesh). Precoated silica gel plates F-254 were used for analytical TLC; visualization was with UV light and/or acidic aqueous $KMnO_4$ solution. NMR spectra were recorded in $CDCl_3$ using residual solvent signal as internal standard on a Bruker AM 300 MHz spectrometer. IR spectra were recorded on a Bruker alpha-T spectrophotometer. High-resolution mass spectra were measured on a Bruker micrOTOF II spectrometer using electrospray ionization (ESI) and a time-of-flight mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage: 4500 V) or in a negative ion mode (3200 V), with a mass range from *m*/*z* 50 to *m*/*z* 3000. For 400 nm light irradiation, a strip of diodes 2x smd 3528 (Arlight RT 2-5000 12V UV400 2X) was used. Starting compounds **1a–d**, **f**, **j**, **k**, **n**, **p**[14c] and **1q**[18a] have been described previously.

Starting Iododifluoromethylated Alcohols 1e, g–i, l, m, o; General Procedure

A mixture of NaI (750 mg, 5 mmol) and LiBr (57 mg, 0.66 mmol) was dried for 3 min under reduced pressure (0.5 mmHg) using a heat gun. After the mixture was cooled to room temperature, 1,2-dimethoxyethane (2 mL), Me_3SiCF_2Br[25] (609 mg, 3 mmol), and aldehyde (2 mmol) were added, and the mixture was stirred at 80 °C for 2–7 h and then cooled to room temperature. For the workup, for compounds **1e**,**g–i**,**l**,**m**, concentrated hydrochloric acid (500 µL) was added [for **1o**, trifluoroacetic acid (0.36 mL, 4.8 mmol) and KHF_2 (187 mg, 2.4 mmol) were added], and the mixture was stirred for 2 h. Then, EtOAc (5.0 mL), saturated aqueous Na_2CO_3 (2.0 mL), and sodium thiosulfate pentahydrate (333 mg, 1.33 mmol) were added, and stirring was continued for 5 min. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 3 mL). The combined organic layers were filtered through Na_2SO_4 and concentrated, and the residue was purified by column chromatography.

1-(1,1′-Biphenyl-4-yl)-2,2-difluoro-2-iodoethanol (1e)

Reaction time: 2 h.

Yield: 691 mg (96%); white crystals; mp 106–107 °C.

R_f = 0.33 (hexanes/EtOAc, 6:1).

IR (KBr): 3344, 1486, 1168, 1102, 941, 753, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.34 (m, 9 H), 4.84–4.70 (m, 1 H), 2.78 (d, *J* = 4.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 142.5, 140.5, 133.6 (d, *J* = 2.9 Hz), 129.0, 128.5, 127.8, 127.3, 127.2, 107.9 (dd, *J* = 318.9, 316.7 Hz), 80.1 (t, *J* = 23.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –48.7 (dd, *J* = 181.2, 7.5 Hz, 1 F), –53.8 (dd, *J* = 180.9, 11.0 Hz, 1 F).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{11}F_2IONa$: 382.9715; found: 382.9697.

2,2-Difluoro-2-iodo-1-(3,4,5-trimethoxyphenyl)ethanol (1g)

Reaction time: 7 h.

Yield: 598 mg (80%); white crystals; mp 174–175 °C.

R_f = 0.36 (hexanes/EtOAc, 1:1).

IR (KBr): 3419, 1597, 1514, 1460, 1420, 1334, 1235, 1131, 966, 644 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.70 (s, 2 H), 4.63 (ddd, *J* = 11.2, 7.2, 4.2 Hz, 1 H), 3.88 (s, 6 H), 3.87 (s, 3 H), 2.91 (d, *J* = 4.2 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 153.3, 139.0, 130.0, 107.7 (dd, *J* = 320.1, 317.2 Hz), 105.4, 80.2 (t, *J* = 22.9 Hz), 61.0, 56.4.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –48.4 (dd, *J* = 181.1, 7.2 Hz, 1 F), –53.5 (dd, *J* = 181.0, 11.2 Hz, 1 F).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{14}F_2IO$: 374.9909; found: 374.9899; *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{13}F_2IONa$: 396.9724; found: 396.9719.

1-(2,6-Dimethoxyphenyl)-2,2-difluoro-2-iodoethanol (1h)

Reaction time: 3 h.

Yield: 612 mg (89%); white crystals; mp 58–59 °C.

R_f = 0.21 (hexanes/EtOAc, 6:1).

IR (KBr): 3411, 1505, 1463, 1216, 1100, 1039, 985, 708, 545 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.01 (d, *J* = 2.9 Hz, 1 H), 6.90 (dd, *J* = 9.0, 2.9 Hz, 1 H), 6.85 (d, *J* = 9.0 Hz, 1 H), 5.17–5.00 (m, 1 H), 4.16 (d, *J* = 7.3 Hz, 1 H), 3.81 (s, 3 H), 3.78 (s, 3 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 153.6, 151.8, 123.4, 115.5, 115.4, 112.6, 106.5 (dd, *J* = 322.0, 318.9 Hz), 76.9 (dd, *J* = 24.5, 23.0 Hz), 56.4, 55.9.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –48.8 (dd, *J* = 177.0, 7.4 Hz, 1 F), –52.8 (dd, *J* = 177.0, 13.3 Hz, 1 F).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{11}F_2IO_3Na$: 366.9613; found: 366.9614.

1-(2,4-Dichlorophenyl)-2,2-difluoro-2-iodoethanol (1i)

Reaction time: 2 h.

Yield: 600 mg (85%); colorless oil.

R_f = 0.34 (hexanes/EtOAc, 7:1).

IR (film): 3426, 1591, 1476, 1382, 1165, 1105, 1083, 937, 856, 795, 595 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.5 Hz, 1 H), 7.42 (d, *J* = 2.2 Hz, 1 H), 7.31 (dd, *J* = 8.5, 2.2 Hz, 1 H), 5.32 (ddd, *J* = 10.6, 7.6, 4.9 Hz, 1 H), 3.66 (d, *J* = 4.9 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 136.2, 134.9, 131.0 (d, *J* = 2.1 Hz), 130.8, 129.6, 127.6, 105.9 (dd, *J* = 322.0, 319.4 Hz), 75.9 (dd, *J* = 25.0, 22.9 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –50.4 (br d, *J* = 182.3 Hz, 1 F), –53.5 (dd, *J* = 182.3, 10.6 Hz, 1 F).

Anal. Calcd for $C_8H_5Cl_2F_2IO$: C, 27.22; H, 1.43. Found: C, 27.25; H, 1.27.

2,2-Difluoro-2-iodo-1-(naphthalen-1-yl)ethanol (1l)

Reaction time: 4 h.

Yield: 581 mg (87%); yellow oil.

R_f = 0.21 (hexanes/EtOAc, 20:1).

IR (film): 3436, 1167, 1091, 1010, 931, 781 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.2 Hz, 1 H), 8.00–7.87 (m, 3 H), 7.68–7.49 (m, 3 H), 5.61 (ddd, *J* = 11.2, 6.7, 4.5 Hz, 1 H), 2.93 (d, *J* = 4.5 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 133.8, 131.4, 130.5 (d, *J* = 2.3 Hz), 130.3, 129.1, 126.8, 126.7, 126.0, 125.2, 123.2, 108.1 (t, *J* = 321.0 Hz), 76.3 (t, *J* = 23.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –46.5 (dd, *J* = 180.0, 6.7 Hz, 1 F), –51.2 (dd, *J* = 180.0, 11.2 Hz, 1 F).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_9F_2IONa$: 356.9558; found: 356.9569.

1-(Anthracen-9-yl)-2,2-difluoro-2-iodoethanol (1m)

Reaction time: 4 h.

Yield: 691 mg (90%); yellow crystals; mp 119–121 °C.

R_f = 0.28 (hexanes/EtOAc, 6:1).

IR (KBr): 3523, 1167, 1078, 912, 860, 730, 692, 580 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.91 (br, 1 H), 8.56 (s, 1 H), 8.14 (br, 1 H), 8.04 (d, *J* = 8.3 Hz, 2 H), 7.70–7.42 (m, 4 H), 6.69 (ddd, *J* = 18.3, 9.0, 4.5 Hz, 1 H), 3.21 (d, *J* = 4.5 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 142.0 (d, *J* = 2.4 Hz), 132.3 (d, *J* = 1.8 Hz), 132.2 (d, *J* = 1.9 Hz), 131.3, 130.7, 128.6, 127.6, 122.9 (dd, *J* = 249.9, 246.5 Hz), 118.7, 112.4, 73.7 (dd, *J* = 31.0, 27.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –46.4 (dd, *J* = 176.0, 9.0 Hz, 1 F), –47.1 (dd, *J* = 176.0, 18.3 Hz, 1 F).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{11}F_2IONa$: 406.9715; found: 406.9719.

2,2-Difluoro-2-iodo-1-(thien-2-yl)ethanol (1o)

Reaction time: 4 h.

Yield: 348 mg (60%); yellow oil.

R_f = 0.20 (hexanes/EtOAc, 6:1).

IR (film): 3423, 1419, 1161, 1097, 983, 924, 708, 600 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 5.5 Hz, 1 H), 7.22 (d, *J* = 3.5 Hz, 1 H), 7.07 (dd, *J* = 5.1, 3.4 Hz, 1 H), 4.92 (td, *J* = 8.6, 5.1 Hz, 1 H), 3.10 (d, *J* = 5.3 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 137.2 (d, *J* = 3.4 Hz), 127.8, 127.1, 106.2 (t, *J* = 318.9 Hz), 77.2 (t, *J* = 25.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –50.3 (dd, *J* = 182.1, 8.3 Hz, 1 F), –53.9 (dd, *J* = 182.2, 9.4 Hz, 1 F).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_6H_5F_2IOSNa$: 312.8960; found: 312.8966.

[1-(4-Chlorophenyl)-2,2-difluoro-2-iodoethoxy](dimethyl)vinylsilane (2a)

Chloro(dimethyl)vinylsilane (342 μL, 2.2 mmol) and triethylamine (344 μL, 2.4 mmol) were added to a solution of alcohol **1a** (R = 4-ClC_6H_4; 636 mg, 2 mmol) in dichloromethane (2 mL) at room temperature. The mixture was stirred for 1 h. Then, water (5 mL) was added, and the mixture was extracted with hexane (3 × 10 mL). The combined extracts were filtered through Na_2SO_4 and concentrated under reduced pressure, and the residue was purified by column chromatography (hexane/EtOAc, 20:1).

Yield: 707 mg (88%); colorless oil.

R_f = 0.60 (hexanes/EtOAc, 20:1).

IR (film): 1491, 1408, 1256, 1155, 1129, 1093, 1003, 860, 841, 791 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.5 Hz, 2 H), 7.38 (d, *J* = 8.5 Hz, 2 H), 6.20–6.03 (m, 2 H), 5.90–5.76 (m, 1 H), 4.57 (dd, *J* = 9.9, 7.4 Hz, 1 H), 0.31 (s, 3 H), 0.24 (s, 3 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 136.1, 135.2, 134.8 (d, *J* = 3.6 Hz), 134.8, 129.7, 128.5, 108.0 (t, *J* = 318.1 Hz), 79.9 (t, *J* = 24.3 Hz), –1.5.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –48.2 (dd, *J* = 179.7, 7.4 Hz, 1 F), –53.9 (dd, *J* = 179.7, 9.9 Hz, 1 F).

Anal. Calcd for $C_{12}H_{14}ClF_2IOSi$: C, 35.79; H, 3.50. Found: C, 35.74; H, 3.43.

Vinylation Reaction; General Procedure

Chloro(dimethyl)vinylsilane (171 μL, 1.1 mmol) and triethylamine (172 μL, 1.2 mmol) were added to a solution of an alcohol **1** (1 mmol) in acetonitrile (1.5 mL) at room temperature, and the mixture was stirred for 2 h. Then, AcONa (164 mg, 2 mmol), triphenylphosphine (52.4 mg, 0.2 mmol), and *fac*-Ir(ppy)$_3$ (1.6 mg, 0.0025 mmol) were added. The reaction vessel was irradiated with 400 nm LEDs (for **3a–l**,**n**,**o**, 2 h; for **3m**, 6 h; for **3p**, 5 h; for **3q**, 15 h); during irradiation the mixture was cooled with room temperature water. Ammonium fluoride (370 mg, 10 mmol) was added, and the mixture was stirred at room temperature (for **3a–d**, 2 h; for **3e–j**,**l**,**m**,**p**,**q**, 6 h; for **3k**,**n**,**o**, 15 h). For the workup, the mixture was diluted with water (5 mL) and extracted with hexane/EtOAc (2:1, 3 × 10 mL). The combined extracts were filtered through Na_2SO_4 and concentrated under reduced pressure, and the residue was purified by column chromatography.

1-(4-Chlorophenyl)-2,2-difluorobut-3-en-1-ol (3a)[26]

Yield: 173 mg (79%); light-yellow oil.

R_f = 0.36 (hexanes/EtOAc, 2:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.29 (m, 4 H), 5.93–5.75 (m, 1 H), 5.58 (d, *J* = 17.1 Hz, 1 H), 5.48 (d, *J* = 10.9 Hz, 1 H), 4.88 (dt, *J* = 10.5, 3.7 Hz, 1 H), 2.69 (d, *J* = 3.7 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 134.7, 134.2, 129.2 (t, *J* = 26.3 Hz), 129.1, 128.5, 122.1 (t, *J* = 9.4 Hz), 119.5 (t, *J* = 244.2 Hz), 75.4 (t, *J* = 30.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –108.3 (dt, *J* = 246.6, 10.5 Hz, 1 F), –110.4 (dt, *J* = 246.6, 10.5 Hz, 1 F).

Methyl 4-(2,2-Difluoro-1-hydroxybut-3-en-1-yl)benzoate (3b)[27]

Yield: 220 mg (91%); white crystals; mp 53–54 °C.

R_f = 0.23 (hexanes/EtOAc, 4:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.2 Hz, 2 H), 7.46 (d, *J* = 6 Hz, 2 H), 5.94–5.75 (m, 1 H), 5.52 (d, *J* = 17.4 Hz, 1 H), 5.42 (d, *J* = 11.0 Hz, 1 H), 4.97–4.90 (m, 1 H), 3.94 (d, *J* = 4.3 Hz, 1 H), 3.85 (s, 3 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 167.2, 141.7 (d, *J* = 3.4 Hz), 130.0, 129.2 (t, *J* = 25.3 Hz), 129.2, 127.8, 121.8 (t, *J* = 9.2 Hz), 119.4 (t, *J* = 245.5 Hz), 75.3 (t, *J* = 29.8 Hz), 52.2.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –107.2 (dt, *J* = 247.8, 10.5 Hz, 1 F), –110.3 (dt, *J* = 247.8, 10.5 Hz, 1 F).

4-(2,2-Difluoro-1-hydroxybut-3-en-1-yl)benzonitrile (3c)[28]

Yield: 153 mg (73%); white crystals; mp 66–67 °C.

R_f = 0.28 (hexanes/EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.3 Hz, 2 H), 7.56 (d, *J* = 8.3 Hz, 2 H), 5.93–5.76 (m, 1 H), 5.61–5.55 (m, 1 H), 5.51 (d, *J* = 11.0 Hz, 1 H), 5.00 (dt, *J* = 8.8, 3.7 Hz, 1 H), 2.69 (d, *J* = 3.7 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 141.3 (d, *J* = 4.2 Hz), 132.0, 128.8 (t, *J* = 26.4 Hz), 128.5, 122.5 (t, *J* = 9.2 Hz), 119.3 (t, *J* = 246.5 Hz), 118.6, 112.6, 75.2 (t, *J* = 29.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –107.1 (dt, *J* = 249.3, 8.8 Hz, 1 F), –110.6 (dt, *J* = 249.3, 8.8 Hz, 1 F).

2,2-Difluoro-1-phenylbut-3-en-1-ol (3d)[26]

Yield: 145 mg (79%); colorless oil.

R_f = 0.33 (hexanes/EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.30 (m, 5 H), 5.97–5.80 (m, 1 H), 5.62 (dt, *J* = 17.3, 2.4 Hz, 1 H), 5.48 (d, *J* = 11.5 Hz, 1 H), 4.88 (td, *J* = 10.1, 3.8 Hz, 1 H), 3.00 (d, *J* = 3.8 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 136.2, 129.5 (t, *J* = 25.4 Hz), 128.7, 128.2, 127.7, 121.6 (t, *J* = 9.2 Hz), 119.7 (t, *J* = 244.4 Hz), 75.9 (t, *J* = 28.7 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –108.4 (dt, *J* = 246.7, 10.1 Hz, 1 F), –110.1 (dt, *J* = 246.7, 10.1 Hz, 1 F).

1-(1,1′-Biphenyl-4-yl)-2,2-difluorobut-3-en-1-ol (3e)

Yield: 236 mg (91%); white crystals; mp 78–79 °C.

R_f = 0.35 (hexanes/EtOAc, 5:1).

IR (KBr): 3375, 1213, 1194, 1155, 1074, 996, 957, 804, 761, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.57 (m, 4 H), 7.55–7.32 (m, 5 H), 5.90 (dq, *J* = 17.4, 11.0 Hz, 1 H), 5.65 (d, *J* = 17.4 Hz, 1 H), 5.52 (d, *J* = 11.0 Hz, 1 H), 4.98 (td, *J* = 9.6, 4.0 Hz, 1 H), 2.50 (d, *J* = 4.0 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 141.8, 140.8, 135.2, 129.6 (t, *J* = 25.8 Hz), 128.8, 128.2, 127.7, 127.3, 127.1, 121.7 (t, *J* = 9.2 Hz), 119.8 (t, *J* = 244.2 Hz), 75.9 (t, *J* = 30.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –108.2 (dt, *J* = 247.0, 9.6 Hz, 1 F), –110.0 (dt, *J* = 247.0, 9.6 Hz, 1 F).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{14}F_2ONa$: 283.0913; found: 283.0905; *m*/*z* [M + K]$^+$ calcd for $C_{16}H_{14}F_2OK$: 299.0652; found: 299.0644.

2,2-Difluoro-1-(4-methoxyphenyl)but-3-en-1-ol (3f)[29]

Yield: 169 mg (79%); colorless oil.

R_f = 0.31 (hexanes/EtOAc, 4:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.6 Hz, 2 H), 6.90 (d, *J* = 8.6 Hz, 2 H), 5.96–5.78 (m, 1 H), 5.61 (d, *J* = 16.9 Hz, 1 H), 5.47 (d, *J* = 11.0 Hz, 1 H), 4.86 (td, *J* = 9.6, 3.2 Hz, 1 H), 3.82 (s, 3 H), 2.48 (d, *J* = 3.7 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 159.8, 129.7 (t, *J* = 25.8 Hz), 128.9, 128.5, 121.3 (t, *J* = 9.2 Hz), 119.7 (t, *J* = 244.2 Hz), 113.6, 75.5 (t, *J* = 28.7 Hz), 55.2.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –106.7 (dt, *J* = 245.8, 9.6 Hz, 1 F), –108.7 (dt, *J* = 245.8, 9.6 Hz, 1 F).

2,2-Difluoro-1-(3,4,5-trimethoxyphenyl)but-3-en-1-ol (3g)

Yield: 238 mg (87%); white crystals; mp 56–57 °C.

R_f = 0.40 (hexanes/EtOAc, 1:1).

IR (KBr): 3463, 2937, 1594, 1422, 1327, 1234, 1129, 1070, 997 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.58 (s, 2 H), 5.94–5.77 (m, 1 H), 5.59 (d, *J* = 17.4 Hz, 1 H), 5.43 (d, *J* = 11.0 Hz, 1 H), 4.76 (td, *J* = 9.7, 3.6 Hz, 1 H), 3.79 (s, 6 H), 3.78 (s, 3 H), 3.28 (d, *J* = 3.8 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 152.8, 138.0, 132.1, 129.7 (t, *J* = 25.7 Hz), 121.3 (t, *J* = 9.3 Hz), 119.6 (t, *J* = 244.4 Hz), 104.9, 75.8 (t, *J* = 30.0 Hz), 60.8, 56.1.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –107.9 (dt, *J* = 247.0, 9.7 Hz, 1 F), –110.2 (dt, *J* = 247.0, 9.7 Hz, 1 F).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}F_2O_4Na$: 297.0904; found: 297.0909; *m*/*z* [M + K]$^+$ calcd for $C_{13}H_{16}F_2O_4K$: 313.0648; found: 313.0648.

1-(2,6-Dimethoxyphenyl)-2,2-difluorobut-3-en-1-ol (3h)

Yield: 195 mg (80%); colorless oil.

R_f = 0.23 (hexanes/EtOAc, 5:1).

IR (film): 3449, 2947, 1503, 1421, 1221, 1047, 994, 820, 717 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.98 (br, 1 H), 6.86 (d, *J* = 1.5 Hz, 2 H), 5.97 (dq, *J* = 17.4, 11.2 Hz, 1 H), 5.63 (d, *J* = 17.4 Hz, 1 H), 5.46 (d, *J* = 11.2 Hz, 1 H), 5.18 (td, *J* = 11.0, 6.7 Hz, 1 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 3.62 (d, *J* = 6.7 Hz, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 153.6, 151.7, 130.4 (t, *J* = 25.4 Hz), 125.4, 120.7 (t, *J* = 10.0 Hz), 119.8 (t, *J* = 245.5 Hz), 115.1, 114.7, 112.4, 71.8 (t, *J* = 29.9 Hz), 56.3, 55.8.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –110.3 (m, 2 F).

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{12}H_{18}F_2O_3N$: 262.1251; found: 262.1249; *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{14}F_2O_3Na$: 267.0802; found: 267.0803; *m*/*z* [M + K]$^+$ calcd for $C_{12}H_{14}F_2O_3K$: 283.0537; found: 283.0543.

1-(2,4-Dichlorophenyl)-2,2-difluorobut-3-en-1-ol (3i)

Yield: 215 mg (85%); colorless oil.

R_f = 0.27 (hexanes/EtOAc, 5:1).

IR (film): 3402, 1592, 1476, 1420, 1384, 1192, 1144, 1106, 1075, 1044, 995, 859, 805 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.5 Hz, 1 H), 7.41 (d, *J* = 2.1 Hz, 1 H), 7.31 (dd, *J* = 8.5, 2.1 Hz, 1 H), 5.95 (dq, *J* = 17.5, 11.4 Hz, 1 H), 5.63 (d, *J* = 17.5 Hz, 1 H), 5.53 (d, *J* = 11.1 Hz, 1 H), 5.44 (td, *J* = 10.0, 4.1 Hz, 1 H), 2.76 (d, *J* = 4.1 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 135.2, 134.4, 132.7, 130.5 (d, *J* = 2.2 Hz), 129.4 (t, *J* = 25.2 Hz), 129.2, 122.1 (t, *J* = 9.3 Hz), 119.5 (t, *J* = 246.9 Hz), 71.2 (t, *J* = 29.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –110.5 (m, 2 F).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_8Cl_2F_2ONa$: 274.9809; found: 274.9812.

1-(2-Bromophenyl)-2,2-difluorobut-3-en-1-ol (3j)[29]

Yield: 224 mg (85%); colorless oil.

R_f = 0.27 (hexanes/EtOAc, 6:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.7 Hz, 1 H), 7.57 (dd, *J* = 7.7, 1.5 Hz, 1 H), 7.36 (td, *J* = 7.7, 1.5 Hz, 1 H), 7.21 (td, *J* = 7.7, 1.5 Hz, 1 H), 5.96 (ddd, *J* = 22.9, 17.4, 11.5 Hz, 1 H), 5.65–5.58 (m, 1 H), 5.55–5.36 (m, 2 H), 2.80 (d, *J* = 4.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 135.7, 132.8, 130.3, 129.8, 129.7 (t, *J* = 25.2 Hz), 127.6, 124.2, 121.9 (t, *J* = 9.2 Hz), 119.7 (t, *J* = 245.5 Hz), 74.0 (t, *J* = 29.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –110.4 (m, 2 F).

2,2-Difluoro-1-mesitylbut-3-en-1-ol (3k)

Yield: 183 mg (81%); light-yellow oil.

R_f = 0.38 (hexanes/EtOAc, 5:1).

IR (film): 3437, 1167, 1142, 1091, 1010, 980, 931, 781, 590 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.87 (s, 2 H), 6.10–5.92 (m, 1 H), 5.72 (d, *J* = 16.8 Hz, 1 H), 5.49 (d, *J* = 11.0 Hz, 1 H), 5.36 (td, *J* = 13.9, 4.4 Hz, 1 H), 2.42 (br, 6 H), 2.31 (s, 3 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 137.8, 131.0 (t, *J* = 26.1 Hz), 130.3 (br), 129.0 (d, *J* = 2.4 Hz), 120.8 (dd, *J* = 244.3, 246.9 Hz), 120.6 (t, *J* = 10.3 Hz), 73.6 (t, *J* = 29.8 Hz), 21.4 (br), 20.8.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –105.5 (dt, *J* = 243.9, 13.9 Hz, 1 F), –109.3 (dt, *J* = 243.9, 13.9 Hz, 1 F).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{16}F_2ONa$: 249.1072; found: 249.1061; calcd for $C_{13}H_{16}F_2OK$: 265.0812; found: 265.0801.

2,2-Difluoro-1-(naphthalen-1-yl)but-3-en-1-ol (3l)

Yield: 194 mg (83%); yellow oil.

R_f = 0.25 (hexanes/EtOAc, 5:1).

IR (film): 3419, 1421, 1209, 1168, 1073, 988, 954, 787 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.0 Hz, 1 H), 7.89 (m, 2 H), 7.77 (d, *J* = 7.3 Hz, 1 H), 7.54 (m, 3 H), 6.04–5.87 (m, 1 H), 5.80 (br t, *J* = 9.2 Hz, 1 H), 5.68–5.60 (m, 1 H), 5.47 (d, *J* = 11.0 Hz, 1 H), 2.76 (s, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 133.7, 132.4 (d, *J* = 4.6 Hz), 131.6, 129.7 (t, *J* = 25.2 Hz), 129.5, 129.0, 126.5, 126.1, 125.8, 125.2, 123.6, 121.6 (t, *J* = 9.2 Hz), 120.3 (t, *J* = 245.5 Hz), 71.7 (t, *J* = 31.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –106.1 (dt, *J* = 245.9, 9.2 Hz, 1 F), –108.8 (dt, *J* = 245.9, 9.2 Hz, 1 F).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{12}F_2ONa$: 257.0754; found: 257.0748.

1-(Anthracen-9-yl)-2,2-difluorobut-3-en-1-ol (3m)

Yield: 227 mg (80%); yellow oil.

R_f = 0.23 (hexanes/EtOAc, 5:1).

IR (film): 3430, 1420, 1159, 1073, 991, 853, 732 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.06 (br, 1 H), 8.49 (s, 1 H), 8.18 (br, 1 H), 8.02 (d, *J* = 7.3 Hz, 2 H), 7.73–7.40 (m, 4 H), 6.49 (dt, *J* = 12.6, 3.7 Hz, 1 H), 6.04–5.87 (m, 1 H), 5.75 (d, *J* = 17.4 Hz, 1 H), 5.43 (d, *J* = 10.8 Hz, 1 H), 2.87 (d, *J* = 3.7 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 134.0, 130.93, 130.88 (t, *J* = 25.7 Hz), 130.1, 129.3 (br), 128.2 (br), 126.4 (br), 125.7 (br), 124.9 (br), 121.0 (t, *J* = 9.5 Hz), 120.8 (t, *J* = 246.7 Hz), 73.4 (t, *J* = 30.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –104.9 (dt, *J* = 243.5, 12.6 Hz, 1 F), –106.1 (dt, *J* = 243.5, 12.6 Hz, 1 F).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{15}F_2O$: 285.1094; found: 285.1085; *m*/*z* $[M + NH_4]^+$ calcd for $C_{18}H_{18}F_2NO$: 302.1355; found: 302.1351; *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{14}F_2ONa$: 307.0912; found: 307.0905; *m*/*z* $[M + K]^+$ calcd for $C_{18}H_{14}F_2OK$: 323.0651; found: 323.0644.

2,2-Difluoro-1-(furan-2-yl)but-3-en-1-ol (3n)[30]

Yield: 155 mg (89%); yellow oil.

R_f = 0.25 (hexanes/EtOAc, 6:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.44 (s, 1 H), 6.42 (d, *J* = 9.6 Hz, 2 H), 6.07–5.90 (m, 1 H), 5.75–5.69 (m, 1 H), 5.54 (d, *J* = 11.3 Hz, 1 H), 5.06–4.80 (m, 1 H), 2.97 (d, *J* = 5.8 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 149.6, 143.0, 129.6 (t, *J* = 25.0 Hz), 121.8 (t, *J* = 9.4 Hz), 118.6 (t, *J* = 244.3 Hz), 110.7, 109.6, 70.3 (t, *J* = 31.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –109.6 (m, 2 F).

2,2-Difluoro-1-(thien-2-yl)but-3-en-1-ol (3o)[27]

Yield: 150 mg (79%); yellow oil.

R_f = 0.33 (hexanes/EtOAc, 5:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.5 Hz, 1 H), 7.39 (d, *J* = 2.1 Hz, 1 H), 7.27 (dd, *J* = 8.5, 2.1 Hz, 1 H), 5.92 (dq, *J* = 17.3, 11.3 Hz, 1 H), 5.60 (dt, *J* = 17.3, 2.5 Hz, 1 H), 5.49 (d, *J* = 11.3 Hz, 1 H), 5.40 (td, *J* = 10.0, 4.4 Hz, 1 H), 3.20 (d, *J* = 4.4 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 138.8, 129.3 (t, *J* = 25.3 Hz), 127.0, 126.9, 126.4, 122.2 (t, *J* = 9.2 Hz), 119.1 (t, *J* = 244.5 Hz), 72.6 (t, *J* = 32.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –108.8 (dt, *J* = 247.6, 10.0 Hz, 1 F), –110.4 (dt, *J* = 247.6, 10.0 Hz, 1 F).

2,2-Difluoro-1-(1-tosyl-1*H*-indol-3-yl)but-3-en-1-ol (3p)

Yield: 241 mg (64%); colorless oil.

R_f = 0.17 (hexanes/EtOAc, 4:1).

IR (film): 3525, 1448, 1370, 1175, 1123, 1086, 972, 749, 679, 577, 538 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.2 Hz, 2 H), 7.72–7.64 (m, 2 H), 7.35 (td, *J* = 9.9, 1.1 Hz, 1 H), 7.30–7.22 (m, 3 H), 6.02–5.85 (m, 1 H), 5.63 (d, *J* = 17.4 Hz, 1 H), 5.49 (d, *J* = 11 Hz, 1 H), 5.18 (td, *J* = 9.2, 4.6 Hz, 1 H), 2.52 (d, *J* = 4.6 Hz, 1 H), 2.37 (s, 3 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 145.3, 135.2 (d, *J* = 4.4 Hz), 130.1, 129.5 (t, *J* = 25.2 Hz), 129.2, 127.0, 125.7, 125.1, 123.6, 122.0 (t, *J* = 9.2 Hz), 121.0, 118.2 (d, *J* = 122.8 Hz), 113.7, 70.4 (t, *J* = 31.9 Hz), 21.7.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –108.1 (dt, *J* = 247.9, 9.2 Hz, 1 F), –109.8 (dt, *J* = 247.9, 9.2 Hz, 1 F).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}F_2NO_3S$: 378.0965; found: 378.0970; *m*/*z* [M + NH_4]$^+$ calcd for $C_{19}H_{21}F_2N_2O_3S$: 395.1232; found: 395.1235; *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{17}F_2NO_3SNa$: 400.0786; found: 400.0789; *m*/*z* [M + K]$^+$ calcd for $C_{19}H_{17}F_2NO_3SK$: 416.0529; found: 416.0529.

4,4-Difluoro-1-phenylhex-5-en-3-ol (3q)[26]

Yield: 127 mg (60%); colorless oil.

R_f = 0.32 (hexanes/EtOAc, 4:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.34 (m, 2 H), 7.35–7.23 (m, 3 H), 6.17–5.94 (m, 1 H), 5.85–5.73 (m, 1 H), 5.61 (d, *J* = 11.3 Hz, 1 H), 3.96–3.76 (m, 1 H), 3.09–2.94 (m, 1 H), 2.86–2.72 (m, 1 H), 2.43 (br, 1 H), 2.10–1.95 (m, 1 H), 1.95–1.78 (m, 1 H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 141.3, 129.8 (t, *J* = 26.0 Hz), 128.6, 126.2, 121.4 (t, *J* = 9.4 Hz), 120.4 (t, *J* = 242.8 Hz), 72.7 (dd, *J* = 30.2, 28.4 Hz), 31.8 (t, *J* = 2.5 Hz), 31.6.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –109.2 (dt, *J* = 249.0, 10.6 Hz, 1 F), –112.8 (dt, *J* = 249.0, 10.6 Hz, 1 F).

Funding Information

This work was supported by the Russian Science Foundation (project 17-13-01041).

Acknowledgment

We are grateful to Mr. R. Larkovich for experimental assistance.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1590855.

References

(1) (a) Liang, T.; Neumann, C. N.; Ritter, T. *Angew. Chem. Int. Ed.* **2013**, *52*, 8214. (b) *Modern Synthesis Processes and Reactivity of Fluorinated Compounds*; Groult, H.; Leroux, F. R.; Tressaud, A., Eds.; Elsevier: Amsterdam, **2017**. (c) For a special issue of *Chemical Reviews* devoted to fluorine chemistry, see: *Chem. Rev.* **2015**, *115*, 563.

(2) (a) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881. (b) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320. (c) Kirk, K. L. *Org. Process Res. Dev.* **2008**, *12*, 305. (d) Wang, J.; Sanchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H. *Chem. Rev.* **2014**, *114*, 2432. (e) Zhou, Y.; Wang, J.; Gu, Z.; Wang, S.; Zhu, W.; Aceña, J. L.; Soloshonok, V. A.; Izawa, K.; Liu, H. *Chem. Rev.* **2016**, *116*, 422. (f) *Fluorine in Medicinal Chemistry and Chemical Biology*; Ojima, I., Ed.; John Wiley & Sons: Chichester, **2009**. (g) Bégué, J.-P.; Bonnet-Delpon, D. *Bioorganic and Medicinal Chemistry of Fluorine*; Wiley-VCH: Weinheim, **2008**.

(3) (a) Kirsch, P. *Modern Fluoroorganic Chemistry*; Wiley-VCH: Weinheim, **2004**. (b) Babudri, F.; Farinola, G. M.; Naso, F.; Ragni, R. *Chem. Commun.* **2007**, 1003. (c) Hird, M. *Chem. Soc. Rev.* **2007**, *36*, 2070.

(4) (a) Prakash, G. K. S.; Yudin, A. K. *Chem. Rev.* **1997**, *97*, 757. (b) Ma, J.-A.; Cahard, D. *J. Fluorine Chem.* **2007**, *128*, 975. (c) Shimizu, M.; Hiyama, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 214. (d) Dilman, A. D.; Levin, V. V. *Mendeleev Commun.* **2015**, *25*, 239. (e) Uneyama, K. *Organofluorine Chemistry*; Blackwell: Oxford, **2006**. (f) *Chemistry of Organic Fluorine Compounds II: A Critical Review, ACS Monograph Series 187*; Hudlicky, M.; Pavlath, A. E., Eds.; American Chemical Society: Washington D.C., **1995**.

(5) (a) Liu, T.; Shen, Q. *Eur. J. Org. Chem.* **2012**, 6679. (b) Wang, H.; Vicic, D. A. *Synlett* **2013**, *24*, 1887. (c) Chu, L.; Qing, F.-L. *Acc. Chem. Res.* **2014**, *47*, 1513. (d) Tomashenko, O. A.; Grushin, V. V. *Chem. Rev.* **2011**, *111*, 4475.

(6) Studer, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 8950.

(7) (a) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322. (b) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898.

(8) (a) Koike, T.; Akita, M. *Acc. Chem. Res.* **2016**, *49*, 1937. (b) Chatterjee, T.; Iqbal, N.; You, Y.; Cho, E. J. *Acc. Chem. Res.* **2016**, *49*, 2284. (c) Koike, T.; Akita, M. *Top. Catal.* **2014**, *57*, 967. (d) Barata-Vallejo, S.; Bonesi, S. M.; Postigo, A. *Org. Biomol. Chem.* **2015**, *13*, 11153.

(9) Andrieux, C. P.; Gelis, L.; Medebielle, M.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 3509.

(10) Zhang, C. *Org. Biomol. Chem.* **2014**, *12*, 6580.

(11) Charpentier, J.; Früh, N.; Togni, A. *Chem. Rev.* **2015**, *115*, 650.

(12) For the generation of various fluorinated radicals from sulfur reagents, see: (a) Nagib, D. A.; MacMillan, D. W. C. *Nature* **2011**, *480*, 224. (b) Ji, Y.; Brueckl, T.; Baxter, R. D.; Fujiwara, Y.; Seiple, I. B.; Su, S.; Blackmond, D. G.; Baran, P. S. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 14411. (c) Daniel, M.; Dagousset, G.; Diter, P.; Klein, P.-A.; Tuccio, B.; Goncalves, A.-M.; Masson, G.; Magnier, E. *Angew. Chem. Int. Ed.* **2017**, *56*, 3997.

(13) (a) Zhou, Q.; Ruffoni, A.; Gianatassio, R.; Fujiwara, Y.; Sella, E.; Shabat, D.; Baran, P. S. *Angew. Chem. Int. Ed.* **2013**, *52*, 3949. (b) Rong, J.; Deng, L.; Tan, P.; Ni, C.; Gu, Y.; Hu, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 2743.

(14) (a) Kosobokov, M. D.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *Org. Lett.* **2014**, *16*, 3784. (b) Tsymbal, A. V.; Kosobokov, M. D.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *J. Org. Chem.* **2014**, *79*, 7831. (c) Levin, V. V.; Smirnov, V. O.; Struchkova, M. I.; Dilman, A. D. *J. Org. Chem.* **2015**, *80*, 9349.

(15) (a) Levin, V. V.; Trifonov, A. L.; Zemtsov, A. A.; Struchkova, M. I.; Arkhipov, D. E.; Dilman, A. D. *Org. Lett.* **2014**, *16*, 6256. (b) Trifonov, A. L.; Zemtsov, A. A.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *Org. Lett.* **2016**, *18*, 3458.

(16) (a) Panferova, L. I.; Tsymbal, A. V.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *Org. Lett.* **2016**, *18*, 996. (b) Panferova, L. I.; Smirnov, V. O.; Levin, V. V.; Kokorekin, V. A.; Struchkova, M. I.; Dilman, A. D. *J. Org. Chem.* **2017**, *82*, 745. For recent work on light-mediated reactions from our group, see: (c) Chernov, G. N.; Levin, V. V.; Kokorekin, V. A.; Struchkova, M. I.; Dilman, A. D. *Adv. Synth. Catal.* **2017**, in press; DOI: 10.1002/adsc.201700423. (d) Supranovich, V. I.; Levin, V. V.; Struchkova, M. I.; Korlyukov, A. A.; Dilman, A. D. *Org. Lett.* **2017**, *19*, 3215.

(17) (a) Bols, M.; Skrydstrup, T. *Chem. Rev.* **1995**, *95*, 1253. (b) Fensterbank, L.; Malacria, M.; Sieburth, S. M. *Synthesis* **1997**, 813.

(18) For alternative methods for the synthesis of the starting iododifluoromethyl-substituted alcohols **1**, see: (a) Miao, W.; Ni, C.; Zhao, Y.; Hu, J. *Org. Lett.* **2016**, *18*, 2766. (b) Zhao, Y.; Gao, B.; Hu, J. *J. Am. Chem. Soc.* **2012**, *134*, 5790.

(19) For alternative methods for the synthesis of alcohols **3**, see: (a) Kirihara, M.; Takuwa, T.; Takizawa, S.; Momose, T.; Nemoto, H. *Tetrahedron* **2000**, *56*, 8275. (b) Fujita, M.; Obayashi, M.; Hiyama, T. *Tetrahedron* **1988**, *44*, 4135. (c) Ramachandran, P. V.; Tafelska-Kaczmarek, A.; Chatterjee, A. *J. Org. Chem.* **2012**, *77*, 9329.

(20) (a) Wallentin, C.-J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875. (b) Zhang, C.-P.; Chen, Q.-Y.; Guo, Y.; Xiao, J.-C.; Gu, Y.-C. *Chem. Soc. Rev.* **2012**, *41*, 4536.

(21) For recent reports on photoredox-mediated atom-transfer reactions, see: (a) Tang, X.-J.; Dolbier, W. R. *Angew. Chem. Int. Ed.* **2015**, *54*, 4246. (b) Beniazza, R.; Atkinson, R.; Absalon, C.; Castet, F.; Denisov, S. A.; McClenaghan, N. D.; Lastécouères, D.; Vincent, J.-M. *Adv. Synth. Catal.* **2016**, *358*, 2949. (c) Li, G.; Cao, Y.-X.; Luo, C.-G.; Su, Y.-M.; Li, Y.; Lan, Q.; Wang, X.-S. *Org. Lett.* **2016**, *18*, 4806.

(22) (a) Beale, T. M.; Chudzinski, M. G.; Sarwar, M. G.; Taylor, M. S. *Chem. Soc. Rev.* **2013**, *42*, 1667. (b) Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. *Chem. Rev.* **2016**, *116*, 2478.

(23) For the activation of halogen-bonded complexes with light, see: (a) Sun, X.; Wang, W.; Li, Y.; Ma, J.; Yu, S. *Org. Lett.* **2016**, *18*, 4638. (b) Wang, Y.; Wang, J.; Li, G.-X.; He, G.; Chen, G. *Org. Lett.* **2017**, *19*, 1442.

(24) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X. Y.; So, J. H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183.

(25) Kosobokov, M. D.; Dilman, A. D.; Levin, V. V.; Struchkova, M. I. *J. Org. Chem.* **2012**, *77*, 5850.

(26) Zhang, H.; Lin, J.-H.; Xiao, J.-C.; Gu, Y.-C. *Org. Biomol. Chem.* **2014**, *12*, 581.

(27) Lin, X.; Qing, F.-L. *Org. Lett.* **2013**, *15*, 4478.

(28) Kirihara, M.; Kawasaki, M.; Katsumata, H.; Kakuda, H.; Shiro, M.; Kawabata, S. *Tetrahedron: Asymmetry* **2002**, *13*, 2283.

(29) Qing, F.-L.; Wan, D.-P. *Tetrahedron* **1998**, *54*, 14189.

(30) Audouard, C.; Fawcett, J.; Griffiths, G. A.; Percy, J. M.; Pintat, S.; Smith, C. A. *Org. Biomol. Chem.* **2004**, *2*, 528.