A Facile Synthesis of 1,1-Difluoroallenes from Commercially Available 1,1,1-Trifluoro-2-iodoethane

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Abstract: 1,1-Difluoroallenes are synthesized in good yield via zinc-promoted 1,2-elimination of 3,3-difluoro-2-iodoallylic acetates, which are prepared by the reaction of aldehydes or ketones with 1-iodo-2,2-difluorovinyllithium, generated from commercially available 1,1,1-trifluoro-2-iodoethane.

Key words: fluorinated allenes, metalation, carbanions, elimination, difluorovinylidenation

1,1-Difluoroallenes have attracted much attention because of their unusual reactivities, entailing them to be used as synthetic building blocks for fluorinated molecules. The Diels–Alder and [3+2]-cycloaddition reactions of 1,1-difluoroallenes with 1,3-dienes and 1,3-dipoles readily take place on the internal, nonfluorinated alkene moiety to give the corresponding *exo*-difluoromethylene compounds.[1] For example, 1,1-difluoroallene ($F_2C=C=CH_2$), with a low LUMO energy level, gives an excellent yield (>99%) of the cyclized product with cyclopentadiene under very mild conditions (–20 °C, 1 min), while the nonfluorinated counterpart allene ($H_2C=C=CH_2$) requires vigorous conditions (200–230 °C) to give the product in a modest yield (49%).[1a,f] The [2+2]-cycloaddition reactions with alkenes and alkynes occur on the terminal, fluorinated alkene moiety to give ring fluorinated cyclobutane[2a] and cyclobutene[2b] derivatives. 1,1-Difluoroallenes also react with various nucleophiles to afford CF_2-terminal or internal addition products selectively, depending on the character of the nucleophile.[3]

Although the parent 1,1-difluoroallene has been known since the 1950s,[4] very few synthetic methods for the 3-substituted 1,1-difluoroallenes have been reported.[3a,5] Recently, we have developed a versatile synthetic method for 3-substituted 1,1-difluoroallenes **1** using two steps: (i) lithiation of 1,1-dibromo-2,2-difluoroethene with butyllithium generates 1-bromo-2,2-difluorovinyllithium ($F_2C=CBrLi$), which in turn, reacts with aldehydes or ketones to form 2-bromo-3,3-difluoroallylic acetates, and (ii) treatment of the bromoacetates with butyllithium gives 1,1-difluoroallenes via the 1,2-elimination of lithium acetate.[6]

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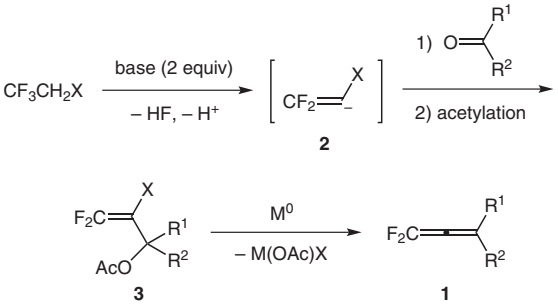
However, there are two factors that limit the scope of this method: (a) the starting material, $F_2C=CBr_2$, is a high-cost, potential ozone-depleting substance, and is now unavailable because of the ban on its industrial manufacture, and (b) highly nucleophilic alkyllithiums are required in the preparation of 1,1-difluoroallenes, which restricts the choice of substrate. Here, we report an improved synthetic method for 1,1-difluoroallenes to overcome these issues using 1) an environmentally friendly and commercially available compound as the starting material, and 2) an effective process for carrying out a 1,2-elimination reaction under mild and tolerant reaction conditions.

First, we considered that the key intermediate, a 1-halogenated 2,2-difluorovinyl anion **2** (Scheme 1), would be generated by the addition of two equivalents of a strong base to 1,1,1-trifluoro-2-haloethanes,[7–9] which bear two hydrogen atoms and are recognized to have much lower ozone depletion potential (ODP). These compounds are manufactured industrially for use as refrigerants or as fluorinated intermediates. Second, we proposed a different route to access the desired 1,1-difluoroallenes **1** from 3,3-difluoro-2-haloallylic acetates **3** (Scheme 1) on treatment with a zerovalent metal instead of highly reactive alkyllithiums, which would promote the 1,2-elimination from acetates **3** to form one more double bond under mild conditions. This sequence would expand the scope of the substrates.



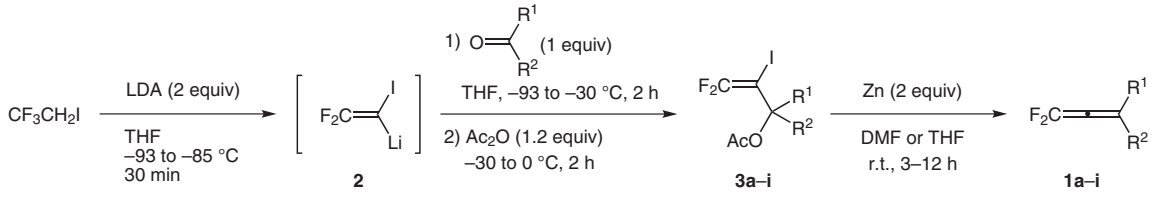
Scheme 1 A synthetic plan for 1,1-difluoroallenes from a 1,1,1-trifluoro-2-haloethane

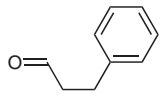
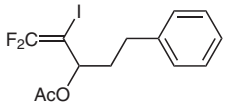
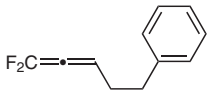
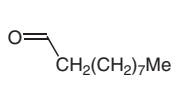
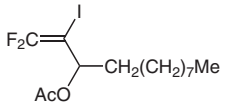
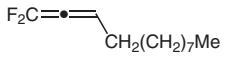
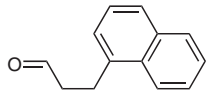
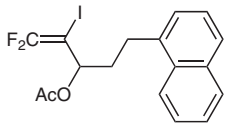
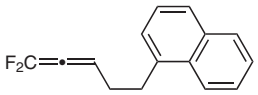
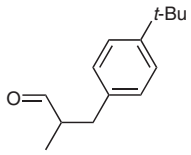
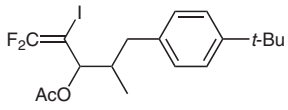
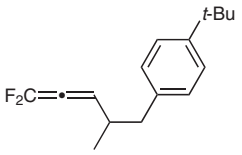
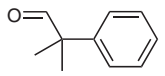
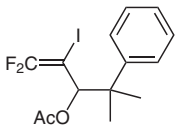
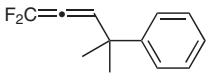
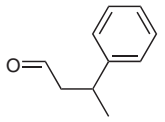
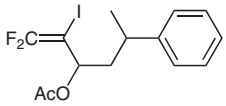
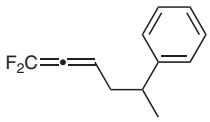
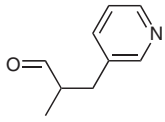
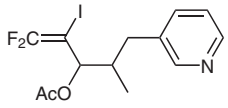
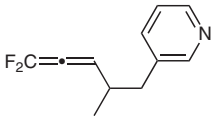
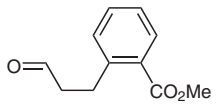
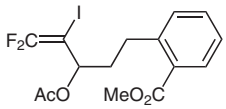
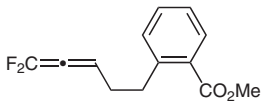
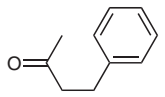
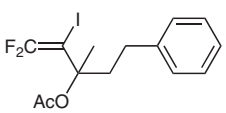
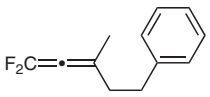
1,1,1-Trifluoro-2-iodoethane was selected as the starting material because of its ease of handling (bp 55–56 °C/760 Torr). The lithiation of 1,1,1-trifluoro-2-iodoethane with two equivalents of lithium diisopropylamide at low temperatures (–93 to –85 °C) successfully gave 2,2-difluoro-1-iodovinyllithium (**2**, Table 1).[10] Lithium species **2** then

reacted with one equivalent of either an aldehyde or a ketone, and was subsequently acetylated with acetic anhydride (Table 1, entries 1–8) or with isopropenyl acetate and *p*-toluenesulfonic acid (entry 9) to afford 3,3-difluoro-2-iodoallylic acetates **3** in good yield.

Then, a facile and effective route by the zinc-promoted 1,2-elimination of acetates **3** under mild and tolerant reaction conditions (e.g., at room temperature for several hours) was found compared with the previously used *n*-butyllithium-promoted 1,2-elimination.[6,11,12] The conditions of the zinc-promoted 1,2-elimination were optimized, as shown in Table 2. In most cases, 1,1-difluoroallenes **1** were obtained in good yield on treatment of acetates **3** with two equivalents of zinc, either in *N*,*N*-dimethylformamide or in tetrahydrofuran, at room temperature for 3–12 hours (Table 2, entries 1–6). However, 1,1-difluoroallene **1g** was only formed in *N*,*N*-dimethylformamide, and not in tetrahydrofuran (Table 2, entries 7

Table 1 Synthesis of 1,1-Difluoroallenes **1** via Difluorovinylidenation of Carbonyl Compounds



Entry	Carbonyl compound	3,3-Difluoro-2-iodoallylic acetate **3**	Yield of **3** (%)	1,1-Difluoroallene **1**	Yield of **1** (%) (time)
1			**3a**: 82		**1a**: 86 (3 h)
2			**3b**: 84		**1b**: 87 (6 h)
3			**3c**: 83		**1c**: 82 (6 h)
4			**3d**: 87		**1d**: 92 (6 h)
5			**3e**: 83		**1e**: 93 (12 h)
6			**3f**: 81		**1f**: 95 (6 h)
7			**3g**: 73		**1g**: 71 (12 h)
8			**3h**: 82		**1h**: 74 (6 h)
9			**3i**: 80[a]		**1i**: 86 (8 h)

[a] Acetylation was performed with isopropenyl acetate and TsOH.[6]

and 8), although the reason for this is not clear at present.[13] 3-Substituted 1,1-difluoroallenes with a primary alkyl group were produced readily using this method, while the yield decreased when the reaction period was extended by several hours (Table 2, entries 1 and 2). In contrast, the yield of 1,1-difluoroallenes with a secondary or tertiary alkyl group at the 3-position remained steady, even after an extended reaction time (Table 2, entries 3–5). This may be the result of the stability of 1,1-difluoroallenes.

Table 2 Optimization of the Zinc-Promoted 1,2-Elimination

Entry	Acetate **3**	Zn (equiv)	Solvent	Time (h)	Yield of **1** (%)
1	**3a**	2	DMF	3	**1a**: 86
2	**3a**	2	DMF	6	**1a**: 72[a]
3	**3d**	2	DMF	3	**1d**: 83
4	**3d**	2	DMF	6	**1d**: 92
5	**3d**	2	DMF	12	**1d**: 90
6	**3d**	2	THF	6	**1d**: 88
7	**3g**	2	DMF	8	**1g**: 71
8	**3g**	4	THF	12	**1g**: trace[b]

[a] Allene **1a** partly decomposed to a complex mixture.
[b] Acetate **3g** was recovered quantitatively.

Owing to the mild conditions of the zinc-promoted 1,2-elimination, 1,1-difluoroallenes bearing a pyridine ring or an ester functionality were synthesized in good yield (Table 1, entries 7 and 8). A 3,3-disubstituted 1,1-difluoroallene was obtained in high yield from a 1,1-disubstituted 2-iodo-3,3-difluoroallylic acetate, which was prepared from the corresponding ketone (Table 1, entry 9).

In summary, we have developed a general and efficient method for the synthesis of 1,1-difluoroallenes from commercially available and environmentally friendly 1,1,1-trifluoro-2-iodoethane under mild reaction conditions. This facile and low-cost synthesis allows 1,1-difluoroallenes to be used as practical building blocks for the synthesis of a various useful fluorinated molecules. Their application is in progress in our laboratory and will be reported in due course.

NMR spectra were recorded on a Bruker Avance 500 or a Bruker Avance 400 spectrometer in $CDCl_3$. Chemical shift values were given in ppm relative to internal $SiMe_4$ (for ^1H NMR: $\delta = 0.00$), $CDCl_3$ (for ^{13}C NMR: $\delta = 77.0$), and C_6F_6 (for ^{19}F NMR: $\delta = 0.0$). Mass spectra (EI-TOF or ESI-TOF) were recorded on Jeol JMS-T100GCv or JMS-T100CS mass spectrometer. IR spectra were recorded by ATR (attenuated total reflectance) method on a Horiba FT-720 spectrometer. Column chromatography and preparative TLC were conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography and Wakogel B-5F, Wako Pure Chemical Industries for PTLC, respectively). All reactions were conducted under argon. THF and DMF were dried by passing over a column of activated alumina followed by a column of Q-5 scavenger (Engelhard). 1,1,1-Trifluoro-2-iodoethane was obtained from Tosoh F-tech, Inc., and distilled from activated 4 Å molecular sieves. This compound can also be purchased from Tokyo Chemical Industry Co., Ltd. or Sigma-Aldrich Co. NMR and IR Spectra of compounds **1a**, **1c**, **1d**, and **1f** are in agreement with the published data.[6]

1,1-Difluoro-2-iodo-5-phenylpent-1-en-3-yl Acetate (3a); Typical Procedure

To a THF (10 mL) solution of $(i\text{-Pr})_2NH$ (2.8 mL, 20 mmol) was added BuLi (12.0 mL, 1.67 M in hexane, 20.0 mmol) over 10 min at 0 °C under argon. The resulting solution was allowed to stir for an additional 15 min, and then cooled to –93 °C using a cold hexane bath. To this cold LDA solution was added a THF (5 mL) solution of CF_3CH_2I (2.10 g, 10.0 mmol) over 10 min, keeping the temperature between –93 and –85 °C. After stirring for 20 min at the same temperature, a THF (5 mL) solution of 3-phenylpropanal (1.34 g, 10.0 mmol) was added over 5 min, keeping the temperature between –93 and –85 °C. The mixture was stirred for an additional 30 min, then warmed to –30 °C over 90 min. After the addition of Ac_2O (1.23 g, 12.0 mmol), the mixture was allowed to warm to 0 °C over 2 h. The reaction was quenched with sat. aq NH_4Cl (20 mL), and the product was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (20 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane–EtOAc, 20:1). The acetate **3a** was obtained as a colorless liquid (3.01 g, 82%).

IR (ATR): 3028, 2954, 1743, 1716, 1267, 1219, 1024, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.87–1.93 (m, 1 H), 2.05–2.17 (m, 1 H), 2.07 (s, 3 H), 2.58 (t, J = 7.2 Hz, 2 H), 4.98 (t, J = 7.2 Hz, 1 H), 7.17–7.22 (m, 3 H), 7.29 (dd, J = 7.3, 7.6 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.9, 30.9, 36.0, 53.8 (dd, $J_{C,F}$ = 25, 26 Hz), 68.9 (d, $J_{C,F}$ = 3 Hz), 126.2, 128.2, 128.5, 140.2, 154.0 (dd, $J_{C,F}$ = 286, 286 Hz), 169.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 89.2 (d, $J_{F,F}$ = 22 Hz, 1 F), 90.2 (d, $J_{F,F}$ = 22 Hz, 1 F).

HRMS (ESI^+): m/z calcd for $C_{13}H_{13}F_2IO_2$ + Na $[M + Na]^+$: 388.9826; found: 388.9830.

1,1-Difluoro-2-iodododec-1-en-3-yl Acetate (3b)

Prepared from 1,1,1-trifluoro-2-iodoethane (840 mg, 4.00 mmol); yield: 84%; colorless liquid.

IR (ATR): 2925, 2856, 1749, 1716, 1458, 1371, 1269, 1225, 1024, 962, 604 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3 H), 1.19–1.35 (br, 14 H), 1.52–1.61 (m, 1 H), 1.65–1.74 (m, 1 H), 2.07 (s, 3 H), 4.94 (t, J = 7.2 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.0, 20.9, 22.6, 24.5, 28.9, 29.2, 29.30, 29.34, 31.8, 34.2, 54.1 (dd, $J_{C,F}$ = 24, 26 Hz), 69.3 (d, $J_{C,F}$ = 3 Hz), 153.9 (dd, $J_{C,F}$ = 286, 299 Hz), 169.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 88.3 (d, $J_{F,F}$ = 24 Hz, 1 F), 89.6 (d, $J_{F,F}$ = 24 Hz, 1 F).

HRMS (EI): m/z calcd for $C_{12}H_{19}F_2I$ [M AcOH]$^+$: 328.0500; found: 328.0478.

1,1-Difluoro-2-iodo-5-(1-naphthyl)pent-1-en-3-yl Acetate (3c)

Prepared from 1,1,1-trifluoro-2-iodoethane (840 mg, 4.00 mmol); yield: 83%; pale yellow liquid.

IR (ATR): 3047, 2939, 1743, 1716, 1371, 1269, 1225, 1026, 966, 798 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.87–1.96 (m, 1 H), 1.97 (s, 3 H), 2.04–2.13 (m, 1 H), 2.92 (t, J = 8.1 Hz, 2 H), 5.00 (tdd, J = 6.4, 2.2, 1.4 Hz, 1 H), 7.19 (d, J = 6.9 Hz, 1 H), 7.28 (dd, J = 7.1, 7.1 Hz, 1

H), 7.39 (d, J = 8.0 Hz, 1 H), 7.41 (d, J = 7.0 Hz, 1 H), 7.61 (d, J = 8.2 Hz, 1 H), 7.74 (d, J = 8.8 Hz, 1 H), 7.90 (d, J = 8.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.9, 28.1, 35.4, 53.8 (t, $J_{C,F}$ = 25 Hz), 69.2 (d, $J_{C,F}$ = 3 Hz), 123.4, 125.5, 126.0 (2 C), 127.1, 128.9, 131.5, 133.9, 136.3, 154.1 (dd, $J_{C,F}$ = 299, 286 Hz), 169.6.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 89.4 (d, $J_{F,F}$ = 22 Hz, 1 F), 90.3 (d, $J_{F,F}$ = 22 Hz, 1 F).

HRMS (EI): m/z calcd for $C_{17}H_{15}F_2IO_2$ $[M]^+$: 416.0085; found: 416.0059.

5-(4-*tert*-Butylphenyl)-1,1-difluoro-2-iodo-4-methylpent-1-en-3-yl Acetate (3d)

Prepared from 1,1,1-trifluoro-2-iodoethane (840 mg, 4.00 mmol); yield: 87% (diastereomer ratio = 1:1); pale yellow liquid.

IR (ATR): 2962, 2871, 1741, 1716, 1510, 1462, 1369, 1269, 1225, 1020, 968, 606, 573 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.74 (d, J = 6.4 Hz, 1.5 H), 0.91 (d, J = 6.2 Hz, 1.5 H), 1.15–1.45 (m, 1 H), 1.31 (s, 9 H), 2.06 (s, 1.5 H), 2.09 (s, 1.5 H), 2.05–2.13 (m, 0.5 H), 2.34 (dd, J = 13.5, 9.5 Hz, 0.5 H), 2.67 (d, J = 12.2 Hz, 0.5 H), 2.92 (d, J = 13.5 Hz, 0.5 H), 4.70 (d, J = 10.0 Hz, 0.5 H), 4.75 (d, J = 9.5 Hz, 0.5 H), 7.08 (d, J = 8.4 Hz, 1 H), 7.09 (d, J = 8.3 Hz, 1 H), 7.30 (d, J = 8.4 Hz, 1 H), 7.31 (d, J = 8.3 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.5, 14.8, 20.8, 31.4, 34.3, 37.6, 38.0, 38.4, 39.1, 53.3 (dd, $J_{C,F}$ = 26, 26 Hz), 73.3 (d, $J_{C,F}$ = 3 Hz), 73.4 (d, $J_{C,F}$ = 3 Hz), 125.2, 128.7, 128.8, 136.0, 136.4, 148.9, 149.0, 154.3 (dd, $J_{C,F}$ = 298, 286 Hz), 154.4 (dd, $J_{C,F}$ = 297, 286 Hz), 169.7, 169.8.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 88.5 (d, $J_{F,F}$ = 23 Hz, 0.5 F), 89.1 (d, $J_{F,F}$ = 22 Hz, 0.5 F), 89.8 (d, $J_{F,F}$ = 23 Hz, 0.5 F), 90.6 (d, $J_{F,F}$ = 22 Hz, 0.5 F).

HRMS (ESI$^+$): m/z calcd for $C_{18}H_{23}F_2IO_2$ + Na $[M + Na]^+$: 459.0608; found: 459.0610.

1,1-Difluoro-2-iodo-4-methyl-4-phenylpent-1-en-3-yl Acetate (3e)

Prepared from 1,1,1-trifluoro-2-iodoethane (840 mg, 4.00 mmol); yield: 83%; colorless liquid.

IR (ATR): 2976, 1745, 1709, 1498, 1442, 1369, 1265, 1219, 1030, 980, 768, 698, 609 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.46 (s, 3 H), 1.48 (s, 3 H), 2.05 (s, 3 H), 5.14 (dd, J = 1.9, 1.0 Hz, 1 H), 7.24 (t, J = 7.7 Hz, 1 H), 7.32 (dd, J = 7.7, 7.7 Hz, 2 H), 7.40 (d, J = 7.7 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.8, 24.9, 25.0 (d, $J_{C,F}$ = 9 Hz), 42.8, 48.0 (dd, $J_{C,F}$ = 25, 25 Hz), 74.5 (d, $J_{C,F}$ = 2 Hz), 126.7, 127.0, 128.0, 144.4, 153.8 (dd, $J_{C,F}$ = 298, 286 Hz), 169.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 91.1 (d, $J_{F,F}$ = 23 Hz, 1 F), 91.3 (d, $J_{F,F}$ = 23 Hz, 1 F).

HRMS (ESI$^+$): m/z calcd for $C_{14}H_{15}F_2IO_2$ + Na $[M + Na]^+$: 402.9982; found: 403.0012.

1,1-Difluoro-2-iodo-5-phenylhex-1-en-3-yl Acetate (3f)

Prepared from 1,1,1-trifluoro-2-iodoethane (840 mg, 4.00 mmol); yield: 81% (diastereomer ratio = 6:4); colorless liquid.

IR (ATR): 3028, 2962, 1747, 1716, 1495, 1452, 1371, 1269, 1225, 1020, 978, 700 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.28 (d, J = 7.0 Hz, 1.8 H), 1.29 (d, J = 7.0 Hz, 1.2 H), 1.80–1.88 (m, 1 H), 1.95 (s, 1.8 H), 1.98–2.05 (m, 0.4 H), 2.06 (s, 1.2 H), 2.06–2.12 (m, 0.6 H), 2.62–2.69 (m, 0.6 H), 2.70–2.78 (ddq, J = 7.0, 7.0, 7.0 Hz, 0.4 H), 4.78 (dd, J = 6.5, 6.5 Hz, 0.6 H), 4.84 (dd, J = 7.5, 7.5 Hz, 0.4 H,), 7.16 (dd, J = 7.0, 5.0 Hz, 1.8 H), 7.20 (dd, J = 7.5, 7.5 Hz, 1.2 H), 7.28 (t, J = 7.5 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.8, 20.9, 21.7, 23.1, 35.8, 36.0, 42.3, 42.7, 54.0 (dd, $J_{C,F}$ = 25, 25 Hz), 54.2 (dd, $J_{C,F}$ = 26, 26 Hz), 68.0 (d, $J_{C,F}$ = 3 Hz), 126.5, 126.7, 126.8, 128.58, 128.61, 145.2, 145.5, 153.7 (d, $J_{C,F}$ = 299, 286 Hz), 153.9 (d, $J_{C,F}$ = 300, 286 Hz), 169.4, 169.5.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 88.8 (d, $J_{F,F}$ = 23 Hz, 0.4 F), 89.6 (d, $J_{F,F}$ = 21 Hz, 0.6 F), 89.7 (d, $J_{F,F}$ = 23 Hz, 0.4 F), 90.2 (d, $J_{F,F}$ = 21 Hz, 0.6 F).

HRMS (ESI$^+$): m/z calcd for $C_{14}H_{15}F_2IO_2$ + Na $[M + Na]^+$: 402.9982; found: 403.0000.

1,1-Difluoro-2-iodo-4-methyl-5-(3-pyridyl)pent-1-en-3-yl Acetate (3g)

Prepared from 1,1,1-trifluoro-2-iodoethane (840 mg, 4.00 mmol); yield: 73% (diastereomer ratio = 6:4); colorless liquid.

IR (ATR): 2968, 2933, 1736, 1714, 1425, 1371, 1265, 1221, 1024, 968, 793, 715 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.75 (d, J = 7.0 Hz, 1.6 H), 0.92 (d, J = 6.0 Hz, 1.4 H), 2.10–2.11 (m, 4.4 H), 2.40 (dd, J = 13.5, 9.5 Hz, 0.6 H), 2.72 (d, J = 10.0 Hz, 0.4 H), 2.99 (dd, J = 13.5, 4.5 Hz, 0.6 H), 4.72 (d, J = 10.0 Hz, 0.6 H), 4.78 (d, J = 9.5 Hz, 0.4 H), 7.28 (dd, J = 8.0, 4.0 Hz, 1 H), 7.53 (d, J = 8.0 Hz, 1 H), 8.45 (s, 1 H), 8.49 (d, J = 4.5 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3, 14.6, 20.79, 20.83, 35.3, 35.6, 38.3, 39.0, 52.7 (dd, $J_{C,F}$ = 25, 25 Hz), 72.9 (d, $J_{C,F}$ = 3.5 Hz), 73.2 (d, $J_{C,F}$ = 3.2 Hz), 123.4, 134.8, 135.2, 136.8, 136.9, 147.3, 147.5, 150.0, 150.1, 154.4 (dd, $J_{C,F}$ = 299, 286 Hz), 154.5, (dd, $J_{C,F}$ = 299, 286 Hz), 169.59, 169.62.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 89.0 (d, $J_{F,F}$ = 22 Hz, 0.6 F), 89.5 (d, $J_{F,F}$ = 21 Hz, 0.4 F), 90.3 (d, $J_{F,F}$ = 22 Hz, 0.6 F), 91.2 (d, $J_{F,F}$ = 21 Hz, 0.4 F).

HRMS (ESI$^+$): m/z calcd for $C_{13}H_{15}F_2INO_2$ $[M + H]^+$: 382.0116; found: 382.0117.

Methyl 2-(3-Acetoxy-5,5-difluoro-4-iodopent-4-en-1-yl)benzoate (3h)

Prepared from 1,1,1-trifluoro-2-iodoethane (840 mg, 4.00 mmol); yield: 82%; pale yellow liquid.

IR (ATR): 3068, 2952, 1747, 1716, 1435, 1373, 1259, 1228, 1088, 1026, 966, 712 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.86–1.92 (m, 1 H), 2.04–2.13 (m, 1 H), 2.08 (s, 3 H), 2.90 (ddd, J = 15.5, 10.0, 5.5 Hz, 1 H), 2.98 (ddd, J = 15.5, 10.0, 5.5 Hz, 1 H), 3.91 (s, 3 H), 5.02 (ddt, J = 7.0, 2.0, 2.0 Hz, 1 H), 7.24 (d, J = 7.5 Hz, 1 H), 7.28 (dd, J = 7.5, 1.0 Hz, 1 H), 7.44 (td, J = 7.5, 1.5 Hz, 1 H), 7.91 (dd, J = 7.5, 1.4 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.9, 29.7, 36.2, 52.0, 53.9 (t, $J_{C,F}$ = 26 Hz), 69.2 (d, $J_{C,F}$ = 4 Hz), 126.4, 129.4, 130.9, 131.0, 132.2, 142.3, 154.0 (dd, $J_{C,F}$ = 299, 286 Hz), 167.7, 169.7.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 89.1 (d, $J_{F,F}$ = 23 Hz, 1 F), 89.9 (d, $J_{F,F}$ = 23 Hz, 1 F).

HRMS (ESI$^+$): m/z calcd for $C_{15}H_{15}F_2IO_4$ + Na $[M + Na]^+$: 446.9881; found: 446.9879.

1,1-Difluoro-2-iodo-3-methyl-5-phenylpent-1-en-3-yl Acetate (3i)

To a THF (5 mL) solution of (*i*-Pr)$_2$NH (1.1 mL, 8.00 mmol) was added BuLi (4.8 mL, 1.67 M in hexane, 8.0 mmol) over 10 min at 0 °C under argon. The resulting solution was allowed to stir for an additional 15 min, then cooled to –93 °C using a cold hexane bath. To this cold LDA solution was added a THF (2 mL) solution of

CF_3CH_2I (840 mg, 4.00 mmol) over 10 min, keeping the temperature between –93 and –85 °C. After stirring for 20 min at the same temperature, a THF (2 mL) solution of 4-phenylbutan-2-one (593 mg, 4.00 mmol) was added over 5 min, keeping the temperature between –93 and –85 °C. The mixture was stirred for an additional 30 min, then warmed to –30 °C over 90 min. The reaction was quenched with sat. aq NH_4Cl (15 mL), and the product was extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with brine (15 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane–EtOAc, 10:1). This alcohol was used in the next step without further purification. To a solution of the alcohol in isopropenyl acetate (3 mL) was added 4-methylbenzenesulfonic acid monohydrate (5 mg, 0.03 mmol). After refluxing for 4 h, the reaction was quenched with sat. aq $NaHCO_3$ (15 mL). The products were extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with brine (15 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane–EtOAc, 30:1). Acetate **3i** was obtained as a colorless liquid (1.22 g, 80%, two steps).

IR (ATR): 3028, 2931, 2862, 1790, 1741, 1712, 1496, 1454, 1369, 1238, 1196, 1068, 1020, 700 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.87 (d, J = 4.6 Hz, 1 H), 2.04 (s, 3 H), 2.11–2.23 (m, 2 H), 2.58 (t, J = 8.6 Hz, 2 H), 7.18–7.20 (m, 3 H), 7.29 (dd, J = 7.0, 7.0 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.8, 22.9 (d, $J_{C,F}$ = 7 Hz), 30.0, 42.8 (dd, $J_{C,F}$ = 2 Hz), 59.7 (dd, $J_{C,F}$ = 26, 22 Hz), 80.6 (d, $J_{C,F}$ = 3 Hz), 126.1, 128.3, 128.5, 140.8, 152.5 (dd, $J_{C,F}$ = 301, 281 Hz), 169.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ = 89.0 (dq, $J_{F,F}$ = 33 Hz, $J_{F,H}$ = 5 Hz, 1 F), 97.3 (d, $J_{F,F}$ = 33 Hz, 1 F).

HRMS (ESI+): m/z calcd for $C_{14}H_{15}F_2IO_2$ + Na $[M + Na]^+$: 402.9982; found: 402.9979.

1,1-Difluoro-5-phenylpenta-1,2-diene (1a); Typical Procedure

To a suspension of Zn powder (131 mg, 2.00 mmol) in DMF (3 mL) was added a DMF (2 mL) solution of **3a** (366 mg, 1.00 mmol) at r.t. under argon. After stirring for 3 h, the resulting reaction mixture was filtered to remove the excess Zn and then diluted with Et_2O (20 mL) and brine (15 mL). The products were extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with brine (15 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue was purified by column chromatography (pentane). Allene **1a** was obtained as a colorless liquid (155 mg, 86%).

IR (ATR): 3030, 2929, 2362, 2013, 1462, 1196, 744, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.53–2.61 (m, 2 H), 2.81 (t, J = 7.5 Hz, 2 H), 6.47 (tt, J = 6.1 Hz, $J_{H,F}$ = 2.4 Hz, 1 H), 7.17–7.22 (m, 3 H), 7.30 (dd, J = 7.3, 7.3 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 33.76, 33.77, 121.4 (t, $J_{C,F}$ = 6 Hz), 126.2, 128.4, 128.5, 140.6, 152.8 (t, $J_{C,F}$ = 261 Hz), 170.1 (t, $J_{C,F}$ = 36 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 60.0 (td, $J_{F,H}$ = 5, 2 Hz, 2 F).

HRMS (EI): m/z calcd for $C_{11}H_{10}F_2$ $[M]^+$: 180.0751; found: 180.0749.

1,1-Difluorododeca-1,2-diene (1b)

Prepared from **3b** (388 mg, 1.00 mmol); yield: 87%; colorless liquid.

IR (ATR): 2925, 2856, 2011, 1462, 1246, 1194, 721 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3 H), 1.27–1.30 (m, 12 H), 1.49 (tq, J = 7.5, 7.0 Hz, 2 H), 2.23 (ttd, J = 7.0, 6.3, 6.0 Hz, 2 H), 6.42 (tt, J = 6.3 Hz, $J_{H,F}$ = 2.3 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 22.7, 27.6, 28.9, 29.3, 29.4, 29.5, 31.9, 32.3 (t, $J_{C,F}$ = 2 Hz), 122.5 (t, $J_{C,F}$ = 6 Hz), 152.5 (t, $J_{C,F}$ = 261 Hz), 169.3 (t, $J_{C,F}$ = 36 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 59.4 (td, $J_{F,H}$ = 6, 3 Hz, 2 F).

HRMS (EI): m/z calcd for $C_{12}H_{20}F_2$ $[M]^+$: 202.1533; found: 202.1516.

1,1-Difluoro-5-(1-naphthyl)penta-1,2-diene (1c)

Prepared from **3c** (416 mg, 1.00 mmol); yield: 82%; colorless liquid.

IR (ATR): 3062, 2941, 2009, 1745, 1458, 1186, 791 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.48–2.54 (m, 2 H), 3.09 (t, J = 7.4 Hz, 2 H), 6.36 (tt, J = 6.1 Hz, $J_{H,F}$ = 2.4 Hz, 1 H), 7.16 (d, J = 6.6 Hz, 1 H), 7.25 (dd, J = 7.6 Hz, 1 H), 7.32–7.39 (m, 2 H), 7.59 (d, J = 7.5 Hz, 1 H), 7.72 (d, J = 8.0 Hz, 1 H), 7.83 (d, J = 7.5 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 30.8, 33.0, 121.6 (t, $J_{C,F}$ = 5.5 Hz), 123.4, 125.5, 125.6, 126.0, 126.1, 127.1, 128.9, 131.6, 133.9, 136.6, 152.9 (t, $J_{C,F}$ = 261 Hz), 170.0 (t, $J_{C,F}$ = 36 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 60.4 (dt, $J_{F,H}$ = 2, 5 Hz, 2 F).

HRMS (EI): m/z calcd for $C_{15}H_{12}F_2$ $[M]^+$: 230.0907; found: 230.0906.

5-(4-*tert*-Butylphenyl)-1,1-difluoro-4-methylpenta-1,2-diene (1d)

Prepared from **3d** (436 mg, 1.00 mmol); yield: 92%; colorless liquid.

IR (ATR): 2964, 2870, 2009, 1446, 1238, 1190, 937, 858 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.05 (d, J = 6.6 Hz, 3 H), 1.30 (s, 9 H), 2.57 (dd, J = 13.0, 6.6 Hz, 1 H), 2.59–2.68 (m, 1 H), 2.75 (dd, J = 13.0, 7.6 Hz, 1 H), 6.41 (ddd, J = 5.0 Hz, $J_{H,F}$ = 2.5, 2.5 Hz, 1 H), 7.08 (d, J = 8.0 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.5, 31.4, 34.3, 38.4, 41.6 (d, $J_{C,F}$ = 2 Hz), 125.2, 127.1 (dd, $J_{C,F}$ = 6, 6 Hz), 128.8, 136.4, 149.1, 153.5 (dd, $J_{C,F}$ = 261, 261 Hz), 168.6 (dd, $J_{C,F}$ = 36, 36 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 60.0 (ddd, $J_{F,F}$ = 127 Hz, $J_{F,H}$ = 3, 3 Hz, 1 F), 60.3 (ddd, $J_{F,F}$ = 127 Hz, $J_{F,H}$ = 3, 3 Hz, 1 F).

HRMS (EI): m/z calcd for $C_{16}H_{20}F_2$ $[M]^+$: 250.1533; found: 250.1532.

1,1-Difluoro-4-methyl-4-phenylpenta-1,2-diene (1e)

Prepared from **3e** (380 mg, 1.00 mmol); yield: 93%; colorless liquid.

IR (ATR): 2972, 2931, 2873, 2009, 1601, 1495, 1435, 1192, 958, 854, 760, 696 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.47 (s, 6 H), 6.55 (t, $J_{H,F}$ = 2.8 Hz, 1 H), 7.23–7.25 (m, 1 H), 7.31–7.36 (m, 4 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 28.0, 42.4 (dd, $J_{C,F}$ = 2 Hz), 125.9, 126.6, 128.5, 131.0 (t, $J_{C,F}$ = 6 Hz), 146.2 (d, $J_{C,F}$ = 2 Hz), 153.3 (dd, $J_{C,F}$ = 262, 262 Hz), 167.1 (dd, $J_{C,F}$ = 36, 36 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 61.1 (d, $J_{H,F}$ = 2 Hz, 2 F).

HRMS (EI): m/z calcd for $C_{12}H_{12}F_2$ $[M]^+$: 194.0907; found: 194.0903.

1,1-Difluoro-5-phenylhexa-1,2-diene (1f)

Prepared from **3f** (380 mg, 1.00 mmol); yield: 95%; colorless liquid.

IR (ATR): 3030, 2964, 2009, 1726, 1603, 1495, 1458, 1240, 1190, 760, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (d, J = 7.0 Hz, 3 H), 2.44–2.60 (m, 2 H), 2.95 (qdd, J = 7.1, 7.1, 7.1 Hz, 1 H), 6.28 (dddd, J = 6.9, 6.9 Hz, $J_{H,F}$ = 2.4, 2.4 Hz, 1 H), 7.18–7.23 (m, 3 H), 7.30 (t, J = 6.5 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6, 38.8, 40.7, 120.4 (dd, $J_{C,F}$ = 6, 6 Hz), 126.4, 126.9, 128.5, 145.7, 152.4 (dd, $J_{C,F}$ = 260, 260 Hz), 170.9 (dd, $J_{C,F}$ = 36, 36 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 59.1 (br ddd, $J_{F,F}$ = 122 Hz, $J_{F,H}$ = 6, 4 Hz, 1 F), 59.6 (br ddd, $J_{F,F}$ = 122 Hz, $J_{F,H}$ = 7, 4 Hz, 1 F).

HRMS (EI): m/z calcd for $C_{12}H_{12}F_2$ $[M]^+$: 194.0907; found: 194.0906.

3-(5,5-Difluoro-2-methylpenta-3,4-dien-1-yl)pyridine (1g)
Prepared from **3g** (381 mg, 1.00 mmol); yield: 71%; colorless liquid.

IR (ATR): 2970, 2931, 2009, 1576, 1446, 1188, 1026, 939, 856, 796, 714 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, J = 8.0 Hz, 3 H), 2.60–2.72 (m, 2 H), 2.81 (dd, J = 12.7, 6.0 Hz, 1 H), 6.42 (dt, J = 8.0 Hz, $J_{H,F}$ = 2.6 Hz, 1 H), 7.23 (ddd, J = 7.8, 4.8, 0.6 Hz, 1 H), 7.49 (ddd, J = 7.8, 2.1, 1.9 Hz, 1 H), 8.45 (d, J = 1.9 Hz, 1 H), 8.48 (dd, J = 4.8, 1.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.5, 38.0 (t, $J_{C,F}$ = 2 Hz), 38.9 (t, $J_{C,F}$ = 2 Hz), 123.3, 126.0 (t, $J_{C,F}$ = 6 Hz), 134.8, 136.5, 147.7, 150.3, 153.4 (t, $J_{C,F}$ = 262 Hz), 169.4 (t, $J_{C,F}$ = 36 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = 60.5 (d, J = 120 Hz, 1 F), 60.7 (d, J = 120 Hz, 1 F).

HRMS (ESI$^+$): m/z calcd for $C_{11}H_{12}F_2N$ $[M + H]^+$: 196.0938; found: 196.0947.

Methyl 2-(5,5-Difluoropenta-3,4-dien-1-yl)benzoate (1h)
Prepared from **3h** (424 mg, 1.00 mmol); yield: 74%; colorless liquid.

IR (ATR): 2952, 2009, 1716, 1460, 1254, 1186, 1130, 1082, 962, 748, 708 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.54–2.59 (m, 2 H), 3.13 (t, J = 7.5 Hz, 2 H), 3.88 (s, 3 H), 6.49 (tt, J = 6.0 Hz, $J_{H,F}$ = 2.5 Hz, 1 H), 7.24 (d, J = 7.5 Hz, 1 H), 7.27 (dt, J = 7.5, 1.0 Hz, 1 H), 7.42 (td, J = 7.5, 1.5 Hz, 1 H), 7.92 (dd, J = 7.5, 1.5 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 32.6, 33.9, 51.9, 121.6 (t, $J_{C,F}$ = 6 Hz), 126.3, 129.3, 130.9, 131.1, 132.1, 142.6, 152.6 (t, $J_{C,F}$ = 261 Hz), 167.7, 169.7 (t, $J_{C,F}$ = 36 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 60.0 (s, 2 F).

HRMS (EI): m/z calcd for $C_{13}H_{12}F_2O_2$ $[M]^+$: 238.0805; found: 238.0805.

1,1-Difluoro-3-methyl-5-phenylpenta-1,2-diene (1i)
Prepared from **3i** (380 mg, 1.00 mmol); yield: 86%; colorless liquid.

IR (ATR): 3064, 2922, 2360, 2004, 1801, 1604, 1481, 1173, 1043, 995, 696 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.91 (t, J = 5.0 Hz, 3 H), 2.40–2.48 (m, 2 H), 2.74 (t, J = 8.2 Hz, 2 H), 7.13–7.18 (m, 3 H), 7.25 (t, J = 7.6 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.8, 33.4, 38.6, 126.1, 128.3, 128.4, 132.3 (t, $J_{C,F}$ = 6 Hz), 141.0, 150.4 (t, $J_{C,F}$ = 260 Hz), 163.0 (t, $J_{C,F}$ = 35 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ = 61.5 (tq, J = 5, 5 Hz, 2 F).

HRMS (EI): m/z calcd for $C_{12}H_{12}F_2$ $[M]^+$: 194.0907; found: 194.0909.

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(10) The lithiation of CF_3CH_2I with BuLi instead of LDA at –93 to –85 °C led to a low yield of 2,2-difluoro-1-iodovinyllithium, probably due to I–Li exchange reaction.

(11) For 2-bromo-3,3-difluoroallylic acetates, zinc-promoted 1,2-elimination also took place readily at r.t. and led to the formation of the corresponding 1,1-difluoroallenes.

(12) Mg was employed in THF to promote the 1,2-elimination of acetate **3d** in vain.

(13) When THF was used as a solvent, only a trace amount of **1g** was observed by the ^{19}F NMR measurement in spite of a large excess amount of Zn and an extended reaction time. A similar behavior was exhibited by some other acetates **3** without a heteroaromatic ring.