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Synthesis and functionalization of (*Z*)-1,2-difluoro-1-tri-*n*-butylstannyl-1,4-pentadiene^{\approx}

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Dedicated to Professor Véronique Gouverneur.

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ABSTRACT

The Zn reagent prepared from (*E*)-1,2-difluoro-1-iodo-2-triethylsilylethene followed by reaction with allyl bromide gave (*Z*)-1,2-difluoro-1-triethylsilyl-1,4-pentadiene. Further reaction of (*Z*)-1,2-difluoro-1-triethylsilyl-1,4-pentadiene with KF, *n*-Bu₃SnCl, in DMF at 70 °C gave (*Z*)-1,2-difluoro-1-tri-*n*-butylstannyl-1,4-pentadiene. Coupling of (*Z*)-1,2-difluoro-1-tri-*n*-butylstannyl-1,4-pentadiene with substituted aryl iodides under Stille–Libeskind (Pd(PPh₃)₄/Cu(I)I) conditions gave the arylated product. Similar coupling of perfluorovinyl iodides stereospecifically gave the corresponding trienes. Hydroboration/oxidation with 9-BBN and H₂O₂ of (*Z*)-1,2-difluoro-1-tri-*n*-butylstannyl-1,4-pentadiene gave (*Z*)-4,5-difluoro-5-tri-*n*-butylstannyl-4-penten-1-ol. Additional couplings of (*Z*)-4,5-difluoro-5-tri-*n*-butylstannyl-4-penten-1-ol. Stille–Libeskind conditions gave the corresponding difunctionalized molecule.

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1. Introduction

Recently, we have reported the synthesis of (E)- and (Z)-2chloro-1,2-difluoro-1-iodoethene and (E)- and (Z)-2-bromo-1,2difluoro-1-iodoethene [1]. Subsequently we developed the stereospecific synthesis of (E)- and (Z)-1-chloro-1,2-difluorostryenes from (E)- and (Z)-2-chloro-1,2-difluoro-1-iodoethene [2]. The selectivity and the formation of the styrenes depended on the difference in reactivity of the two halogens. It occurred to us that another system would also potentially exhibit selectivity depending on the reactivity of two functional groups. For example, 1,1,2trifluoro-1,4-pentadiene (CF₂=CFCH₂CH=CH₂) has two olefinic bonds with significant reactivity differences. The trifluorovinyl group reacts readily with nucleophiles whereas the vinyl group (CH=CH₂) reacts readily with electrophiles. Hexafluoropropene reacts with F⁻ and water to add HF via a carbanion intermediate (Eq. (1)) [3]. The regiochemistry of the F⁻ induced reactions with fluoroolefins can be predicted by the stability of the intermediate

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http://dx.doi.org/10.1016/j.jfluchem.2014.12.006 0022-1139/© 2014 Elsevier B.V. All rights reserved. carbanions. The stability of the carbanions is tertiary $(^{-}C(CF_3)_3) >$ secondary $(^{-}CF(CF_3)_2) >$ primary $(^{-}CF_2R_F)$). In contrast to the fluoroolefin the allyl group of 1,1,2-trifluoro-1,4-pentadiene will react selectively with electrophiles to generate the more stable carbocation $(3^{\circ}>2^{\circ}>1^{\circ})$.

Stannanes are useful intermediates in Pd(0) cross-coupling reactions. Pedersen utilized (*Z*)-1-tri-*n*-butylstannyl-1,2,3,4,4-pentafluoro-1,3-butadiene to develop the stereospecific preparation of (*E*)-1-aryl-F-1,3-butadienes (Eq. (2)) [4]. Liu and Burton utilized a *bis*-stannane to achieve the high yield synthesis of symmetrical stilbenes (Eq. (3)) [5]. Wesolowski and coworkers developed an approach to (*Z*)-1,2-difluorostilbenes (Eq. (4)) [6].

$$F \xrightarrow{F}_{F} CF_{3} + F^{-} \xrightarrow{F}_{F} \left[\begin{array}{c} F \\ F \xrightarrow{F}_{F} CF_{3} \end{array} \right]^{-} \xrightarrow{H_{2}O} F_{3}C \xrightarrow{F}_{C}F_{3}$$

$$(1)$$



 $^{^{\}ast}$ Abstracted in part from Sandra Lukaszewski-Rose thesis, University of Iowa, 2000.

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2. Results and discussion

1,1,2-Trifluoro-1,4-pentadiene reacts with simple nucleophiles to undergo addition and elimination reactions. However, we were more interested in aryl or vinyl derivatives, so we needed a substituent in place of vinyl fluorine to allow for the stereospecific introduction of aryl or vinyl groups. We have previously shown that fluorinated vinyl silanes can be stereospecifically converted to vinyl stannanes [7]. Therefore we attempted to prepare (*Z*)-1,2-difluoro-1-triethylsilyl-1,4-pentadiene (1). We investigated two pathways to attain 1. The first method utilized (*E*)-1,2-difluoro-1-iodo-2-triethylsilylethene as the precursor to produce 1 in 62% yield (Eq. (5)). The second method utilized 1,2-difluoro-1-triethylsilylethene to produce 1 in 75% yield (Eq. (6)).



1 can be converted to (*Z*)-1,2-difluoro-1-tri-*n*-butylstannyl-1,4pentadiene (**2**) with KF, *n*-Bu₃SnCl, and DMF at 70 °C (Eq. (7)). Although **2** was formed, the reaction times depended on concentration of **1** in DMF. When the concentration was kept between 0.60 M and 0.77 M, the reaction was completed overnight at 65–70 °C. When the concentration was approximately 1.0 M, the reaction took 72–96 h for completion at 65–70 °C. Burton reported that *n*-Bu₃SnOSn(*n*-Bu)₃ and catalytic KF gives a higher yield of the stannane than the reaction that required stoichiometric KF [7]. However, this method was not employed in this case due to the high boiling point of the Et₃SiOSiEt₃ by-product, which would cause difficulty in purification.

The thermal stability of **2** was determined by heating **2** in an NMR tubes with DMF and α, α, α -trifluorotoluene standard. **2** showed good thermal stability at the range of temperatures needed for the coupling reactions with only slight decomposition at 85–90 °C. Therefore, **2** can be used in Stille coupling reactions to introduce aryl and vinyl groups.

An alternative route to coupled products would utilize the zinc reagent from (*Z*)-1,2-difluoro-1-iodo-1,4-pentadiene (**3**), which can be readily prepared from **1** or **2** (Eq. (8)). When this iodide was reacted with Zn in DMF, (*Z*)-CH₂=CHCH₂CF=CFZnI and,

unfortunately, significant amounts of the reduced product (*E*)-CH₂=CHCH₂CF=CFH were obtained (Eq. (9)).



2.1. Palladium catalyzed cross-coupling of **2** with aryl iodides and fluorinated vinyl iodides

1.0:0.35 by NMR

When **2** was reacted with aryl iodides, $Pd(PPh_3)_4$, and Cu(1)I [8] at room temperature good yields of the aryl coupled products were obtained (Table 1). Similarly, when 1-iodo-perfluoroalkenes were used as substrates good yields of the coupled products were obtained (Table 2).

When **2** was coupled with an aryl iodide, the major by-product was tri-*n*-butylstannyliodide which needed to be removed from the final product in the workup. Washing with aqueous KF did not completely remove this by-product and when the *n*-Bu₃SnI/crosscoupled product mixture was purified by column chromatography, the *n*-Bu₃SnI streaked throughout the column and contaminated the final product. During the workup, $Cu(OAc)_2$ or $Co(OAc)_2$ was added and stirred with the reaction mixture to convert the n-Bu₃SnI to *n*-Bu₃SnOAc, which remained on the column when elution was performed with hexanes. However, the $Cu(OAc)_2$ also homo-coupled any remaining 2 to (E,E)-H₂C=CHCH₂CF=CFCF= CFCH₂CH=CH₂ [9]. The homo-coupled product was detected in small amounts in the reaction mixture of some of the crosscoupled products before workup. This homo-coupled product has a similar retention time to the cross-coupled product and is difficult to remove from the purified cross-coupled product. When $Co(OAc)_2$ was used to remove *n*-Bu₃SnI, it did not homo-couple 2. Therefore, if any 2 remained in the reaction mixture, it was best to use $Co(OAc)_2$ in the workup.

Table 1

Q

Reaction of $\mathbf{2}$ with aryl iodides, $Pd(PPh_3)_4$, and Cu(I)I in DMF.

F Sn(<i>n</i> -Bu) ₃ +	↓ ↓ ↓	Pd(PPh ₃) ₄ Cu(l)I DMF, RT //	F
Х	<i>T</i> (°C)	Time (h)	Yield ^a
<i>m</i> -(1)-CF ₃ 4	RT	12	82%
m-NO ₂ 5	RT	12	74%
-H 6	RT	12	65%
<i>p</i> -СН ₃ 7	RT	12	64%
p-OMe 8	RT	96	67%
0-CF ₃ 9	65	240	31%

^a Isolated yield.

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Table 2

Reaction of ${\bf 2}$ with fluorinated vinyl iodides, $\text{Pd}(\text{PPh}_3)_{4},$ and Cu(I)I in DMF.

F F +	F R _F	Pd(PPh ₃) ₄ Cu(I)I DMF, RT	F F F
2			10, 11
Iodide	<i>T</i> (°C)	Time (h)	Yield ^a
IFC=CF2 10	RT	12	75%
(Z)-IFC=CFCF ₃ 11	RT	12	54%
^a Isolated vield			

^a Isolated yield.

2.2. Functionalization of the vinyl group ($H_2C=CH-$)

For functionalization of the vinyl group, we needed a method that did not cause isomerization and was regiospecific for the terminal methylene group. Our reagent of choice was 9-BBN (9-borabicyclo[3.3.1]nonane), which adds to the terminal carbon of a 1-alkene with a selectivity of 99.9% [10]. Oxidation with hydrogen peroxide and hydroxide base cleanly gives the alcohols. Organoboranes with a tri-*n*-butyltin functionality have been prepared previously and there are also reports where the tri-*n*-butyltin group survives the oxidation step (Eq. (10)) [11]. We cannot predict what effect the difluorovinyl group that is attached to the tri-*n*-butyltin will have on the hydroboration/oxidation.

However, when **2** was treated with 1.5 equivalents of 9-BBN followed by 3 M sodium hydroxide and 30% hydrogen peroxide, 65% of the stannyl alcohol **12** was isolated (Eq. (11)). When **1** was reacted under the same conditions 74% of the silyl alcohol **13** was obtained (Eq. (12)). However, when the silyl alcohol **13** was treated with KF, *n*-Bu₃SnCl, and DMF at 55 °C we got a mixture of six products (Eq. (13)); this method was investigated no further.



Our initial intention was to functionalize the *n*-Bu₃Sn- group of **2** followed by hydroboration/oxidation of the $H_2C=CH-$ group. However, we needed to reverse the two processes to accomplish our overall goal of functionalizing both groups (Table 3).

When **12** was treated with neat I_2 we successfully created a difunctionalized molecule synthon **19** that would be amenable for further derivatization (Eq. (14)). Protection of the alcohol was accomplished with acetic anhydride (Eq. (15)). Further conversion of the alcohol group was carried out with dibromotriphenylphosphorane (Eqs. (16) and (17)). The brominated product potentially

Table 3

Reaction of $\boldsymbol{12}$ with aryl iodides, $Pd(PPh_3)_4$, and Cu(I)I in DMF.



^a Isolated yield.

allows for the bromine to be displaced by other nucleophiles to elaborate the carbon chain.



3. Experimental

3.1. General experimental procedures

Routine ¹⁹F NMR spectra were recorded on a JEOL FX90Q Spectrometer (83.81 MHz) and high-resolution data was obtained on a Bruker AC-300 Spectrometer (282.41 MHz). Chemical shifts have been reported in ppm relative to internal CFCl₃. Spectra of reaction mixtures were obtained in the ⁷Li external lock mode. Quantitative determinations were carried out by integration relative to internal benzotrifluoride. Routine ¹H NMR (300.17 MHz) spectra and high-resolution data were generally obtained on a Bruker AC-300 Spectrometer. Unless noted otherwise, CDCl₃ was used as the NMR lock solvent. Chemical shifts have been reported in ppm relative to internal TMS. High-resolution {¹H} ¹³C NMR spectra were recorded on a Bruker AC-300 Spectrometer (75.48 MHz). Chemical shifts have been reported in ppm relative to internal TMS. High-resolution for the spectra were obtained by the University of Iowa

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High Resolution Mass Spectrometry Facility. Analytical GLPC were performed on a Hewlett-Packard Model 5890 equipped with a thermal conductivity detector and 3393A integrator. The column was packed with 5% OV-101 on chromo-sorb P. All boiling points were determined during fractional distillation using a partial immersion thermometer and are uncorrected. THF was dried by distillation from sodium benzophenone ketyl at ambient pressure. 4 Å molecular sieves (Fisher) were activated by heating under vacuum (300 °C at 0.5 mm Hg) overnight. DMF was dried overnight over CaH₂ and then distilled at reduced pressure. Pd(PPh₃)₄ was prepared by Coulson's procedure [12]. Potassium fluoride was dried by azeotropic distillation with benzene solvent and a Dean-Stark apparatus. Residual benzene was removed under reduced pressure. Silica gel was purchased from EM Science (silica gel 60, particle sized 0.063-0.200 µm, 70-230 Mesh, ASTM). CuI (Aldrich) was purified according to Kauffman and Fang's procedure [13]. Allyl bromide was distilled under N₂ at atmospheric pressure. (E)-IFC=CFSiEt₃ was prepared by Davis et al.'s method [14]. (Z)-HFC=CFSiEt₃ was also prepared via a method developed by Davis et al. [14]. IFC=CF₂ was prepared by a method developed by Heinze and Burton [15]. Additionally, (Z)-IFC=CFCF₃ was synthesized via a method published by Heinze et al. [16]. ZnI₂ was prepared by published methods [17]. Cu(OAc)₂ was prepared by Blumenthal and Burton's method [9]. Bromotrifluoroethylene (Halocarbon), 9-BBN (Aldrich), ClSnBu₃ (Aldrich), any lithium reagents (Aldrich), trithethylsilyl chloride (Farchan), substituted aryl iodides, Br₂, PPh₃, and chlorotrifluoroethylene were obtained from commercial sources and used without further purification.

3.2. Preparation of (Z)-1,2-difluoro-1-triethylsilyl-1,4-pentadiene, (Z)- H_2C =CHCH₂CF=CFSiEt₃ (**1**) from (E)-1,2-difluoro-1-iodo-2-triethylsilylethene, (E)-IFC=CFSiEt₃

A 250 mL three-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, internal thermometer, and a rubber septum port was charged with zinc (5.50 g, 84.6 mmol), activated according to Knochel and Normant's method [18]. Then 70 mL of anhydrous DMF was added to the flask. Next, (E)-1,2-difluoro-1-iodo-2-triethylsilylethene (20.70 g, 67.70 mmol) was slowly added to the stirred mixture via syringe so as not to exceed 50 °C. After 1 h, the ¹⁹F NMR spectrum of the reaction mixture showed that all the (E)-IFC=CFSiEt₃ had been converted to the zinc reagent. (76% ¹⁹F NMR yield); ¹⁹F NMR (DMF) -153 ppm (d, 1F) -173 ppm, (d, 1F). A clean 250 mL two necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged via syringe with the solution of the zinc reagent. Next, allyl bromide (9.40 mL, 108 mmol) was slowly added via syringe. Cu(I)Br (3-5 mol%) was added in one portion to the flask after the allyl bromide addition had been completed. An exotherm resulted. The reaction mixture was stirred for 1 h until it returned to room temperature. 1 was isolated by the slow addition of 100 mL of a saturated aqueous solution of NaHCO₃ (foams) to the flask. Then ether (100 mL) was added and the solution was vacuum filtered to remove any solids. The filtrate was added to a separatory funnel and washed with ether (2×50 mL), and the combined ether layers washed with water (2×25 mL). The organic layer was dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by fractional distillation on a 6 cm Vigreux column to give 1 (9.10 g, 62% isolated yield, purity by ¹H NMR = 92%): bp 86–88°/15 mmHg; ¹⁹F NMR (CDCl₃): -145.8 ppm (dt, 1F, ${}^{3}J_{FF} = 124.8$ Hz, ${}^{3}J_{FH} = 21.9$ Hz), -172 ppm (dt, 1F, ${}^{3}J_{FF} = 124.8$ Hz, ${}^{4}J_{FH} = 6.4$ Hz); ${}^{1}H$ NMR (CDCl₃): 5.8 ppm (ddt, 1H, ${}^{3}J_{HH} = 17.0$ Hz, ${}^{3}J_{HH} = 10.4$ Hz, ${}^{3}J_{HH} = 6.2$ Hz), 5.2 ppm (ddt, 1H, ${}^{3}J_{HH} = 17.2$ Hz, ${}^{2}J_{HH} = 0.8$ Hz, ${}^{4}J_{HH} = 0.7$ Hz), 5.1 ppm (ddt, 1H, ${}^{3}J_{HH} = 10.1$ Hz, ${}^{2}J_{HH} = 1.5$ Hz, ${}^{4}J_{HH} =$ 1.3 Hz), 3.2 ppm (dddd, 2H, ${}^{3}J_{HF} = 22.6$ Hz, ${}^{3}J_{HH} = 6.2$ Hz, ${}^{4}J_{HF} = 6.2$ Hz, ${}^{4}J_{HH} = 1.5$ Hz, ${}^{4}J_{HH} = 1.5$ Hz), 1.0 ppm (t, 9H, ${}^{3}J_{HH} = 7.8$ Hz), 0.7 ppm (q, 6H, ${}^{3}J_{HH} = 8.0$ Hz); 13 C NMR (CDCl₃): 163.74 ppm (dd, ${}^{1}J_{CF} = 238.9$ Hz, ${}^{2}J_{CF} = 42.1$ Hz), 154.70 ppm (dd, ${}^{1}J_{CF} = 258.4$ Hz, ${}^{2}J_{CF} = 74.3$ Hz), 131.79 ppm (dd, ${}^{3}J_{CF} = 2.4$ Hz, ${}^{4}J_{CF} = 1.8$ Hz), 117.9 ppm (s), 31.35 ppm (dd, ${}^{3}J_{CF} = 2.6$ Hz, ${}^{3}J_{CF} = 3.3$ Hz), 7.11 ppm (s), 2.48 ppm (dd, ${}^{3}J_{CF} = 1.3$ Hz, ${}^{4}J_{CF} = 1.3$ Hz); GC–MS, *m/z* (relative intensity): 218 (M⁺, 15.60), 105 (87.86), 95 (85.70), 77 (100.00), 67 (73.04), 65 (80.03); HRMS: C₁₁H₂₀F₂Si (calculated: 218.1302, observed: 218.1314).

3.3. Preparation of (Z)-1,2-difluoro-1-triethylsilyl-1,4-pentadiene (Z)-CH₂=CHCH₂CF=CFSiEt₃ (**1**) from (Z)-1,2-difluoro-1-triethylsilylethene, (Z)-HFC=CFSiEt₃

A 250 mL three-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, internal low temperature thermometer, Teflon coated magnetic stir bar, and a rubber septum port was charged with 60 mL of dry THF and 30 mL of anhydrous diethyl ether. Next, (Z)-1,2-difluoro-1-triethylsilylethene (17.80 g, 100.0 mmol) was added via syringe and the reaction mixture was cooled to -100 °C using a pentane/liquid N₂ bath. Then, a solution of n-BuLi in hexanes (48.0 mL, 120 mmol, 2.5 M) was slowly added *via* syringe maintaining the temperature below -90 °C. After the addition was complete, the reaction mixture was stirred an additional 20 min at -100 °C. A solution of ZnI₂ [17] (41.47 g, 130.0 mmol) in THF was slowly added via syringe maintaining the temperature below -90 °C. The solution was cooled to -100 °C, then warmed to room temperature overnight. To form the coupled product, the reaction mixture was cooled to 0 °C and allyl bromide (18.15 g, 150.0 mmol) was added via syringe. Cu(I)Br (5 mol%) was added in one portion to the flask after the allyl bromide addition had been completed. The reaction mixture was stirred at 0-5 °C for 1 h, warmed to room temperature, and stirred for an additional 30 min at room temperature. Ether (100 mL) and water (100 mL) were added to the reaction mixture and then the solution was vacuum filtered to remove any solids. The filtered solids were rinsed with 15 mL ether. The filtrate was added to a separatory funnel and washed with ether ($2 \times 100 \text{ mL}$); the combined ether layers were washed with water (2×50 mL). The organic layer was dried over MgSO₄, filtered, and concentrated by simple distillation. The crude product was purified by fractional distillation on a 6 cm Vigreux column to give **1** (16.42 g, 75% isolated yield, purity by ¹H NMR = 92%): bp 86-88 °C/15 mmHg. The spectroscopic data are identical to the data reported in Section 3.2.

3.4. Preparation of (Z)-1,2-difluoro-1-tri-n-butylstannyl-1,4-pentadiene, (Z)- $H_2C=CHCH_2CF=CFSnBu_3-n$ (2)

A 250 mL two-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with anhydrous KF (5.19 g, 89.4 mmol), 100 mL of dry DMF, 1 (14.30 g, 65.60 mmol), and ClSnBu₃-n (24.60 g, 75.69 mmol). The reaction mixture was stirred at 70 °C overnight. The reaction mixture was extracted with ether $(2 \times 100 \text{ mL})$ and the combined ether layers were washed with water (2×100 mL). The organic layer was dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using hexanes as eluent to give 2 (20.90 g, 81% isolated yield, $R_{\rm f}$ (hexanes) = 0.50, purity by GLPC analysis = 98%): bp $88-90 \degree C/$ 1 mm Hg; small satellite peaks due to couplings to natural abundances of 7.68% ¹¹⁷Sn and 8.58% ¹¹⁹Sn isotopomers where excluded for clarity; ¹⁹F NMR (CDCl₃): -148.7 ppm (dt, 1F, ${}^{3}J_{FF} = 116.7$ Hz, ${}^{3}J_{FH} = 21$ 8 Hz), -164.7 ppm (dt, 1F, ${}^{3}J_{FF} = 117.2 \text{ Hz}, {}^{4}J_{FH} = 6.4 \text{ Hz}); {}^{1}\text{H} \text{ NMR} (\text{CDCl}_{3}): 5.8 \text{ ppm} (ddt, 1\text{H}, 1\text{H})$

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 ${}^{3}J_{\rm HH} = 17.0 \ {\rm Hz}, \ {}^{3}J_{\rm HH} = 10.2 \ {\rm Hz}, \ {}^{3}J_{\rm HH} = 6.3 \ {\rm Hz}), \ 5.2 \ {\rm ppm} \ ({\rm ddt}, \ 1{\rm H}, \ {}^{3}J_{\rm HH} = 17.1 \ {\rm Hz}, \ {}^{2}J_{\rm HH} = 1.5 \ {\rm Hz}, \ {}^{4}J_{\rm HH} = 1.5 \ {\rm Hz}), \ 5.1 \ {\rm ppm} \ ({\rm ddt}, \ 1{\rm H}, \ {}^{3}J_{\rm HH} = 10.0 \ {\rm Hz}, \ {}^{2}J_{\rm HH} = 1.5 \ {\rm Hz}, \ {}^{4}J_{\rm HH} = 1.5 \ {\rm Hz}), \ 5.1 \ {\rm ppm} \ ({\rm ddd}, \ 2{\rm H}, \ {}^{3}J_{\rm HH} = 10.0 \ {\rm Hz}, \ {}^{2}J_{\rm HH} = 1.4 \ {\rm Hz}, \ {}^{4}J_{\rm HH} = 1.3 \ {\rm Hz}), \ 3.2 \ {\rm ppm} \ ({\rm dddd}, \ 2{\rm H}, \ {}^{3}J_{\rm HH} = 22.0 \ {\rm Hz}, \ {}^{3}J_{\rm HH} = 6.1 \ {\rm Hz}, \ {}^{4}J_{\rm HH} = 1.5 \ {\rm Hz}, \ {}^{4}J_{\rm HH} = 7.2 \ {\rm Hz}), \ 1.1 \ {\rm ppm} \ ({\rm n}, \ 6{\rm H}), \ 0.9 \ {\rm ppm} \ ({\rm t}, \ 9{\rm H}, \ {}^{3}J_{\rm HH} = 7.3 \ {\rm Hz}); \ {}^{13}{\rm C} \ {\rm NMR} \ ({\rm CDCl}_3): \ 162.80 \ {\rm ppm} \ ({\rm dd}, \ {}^{1}J_{\rm CF} = 228.5 \ {\rm Hz}, \ {}^{2}J_{\rm CF} = 34.1 \ {\rm Hz}), \ 159.07 \ {\rm ppm} \ ({\rm dd}, \ {}^{1}J_{\rm CF} = 296.3 \ {\rm Hz}, \ {}^{2}J_{\rm CF} = 96.9 \ {\rm Hz}), \ 132.22 \ {\rm ppm} \ ({\rm dd}, \ {}^{3}J_{\rm CF} = 2.6 \ {\rm Hz}, \ {}^{4}J_{\rm CF} = 1.2 \ {\rm Hz}), \ 117.18 \ {\rm ppm} \ ({\rm s}), \ 30.97 \ {\rm ppm} \ ({\rm dd}, \ {}^{2}J_{\rm CF} = 28.0 \ {\rm Hz}, \ {}^{3}J_{\rm CF} = 3.5 \ {\rm Hz}), \ 28.85 \ {\rm ppm} \ ({\rm s}), \ 27.14 \ {\rm ppm} \ ({\rm s}), \ 13.66 \ {\rm ppm} \ ({\rm s}), \ 9.89 \ {\rm ppm} \ ({\rm dd}, \ {}^{2}J_{\rm CF} = 2.4 \ {\rm Hz}, \ {}^{4}J_{\rm CF} = 1.9 \ {\rm Hz}); \ {\rm GC-MS}, \ {}m/z \ ({\rm relative intensity}): \ 335 \ ({\rm M}^+-{\rm C}_4{\rm H_9}, 26.74), \ 253 \ (100.00), \ 252 \ (59.29), \ 251 \ (99.65), \ 250 \ (61.02), \ 249 \ (99.76), \ 177 \ (89.61), \ 175 \ (74.26), \ 139 \ (63.53), 57 \ (69.84); \ {\rm HRMS}: \ {\rm C}_{13}H_{23}F_{2}^{118} {\rm Sn} \ ({\rm M}^+-{\rm C}_4{\rm H_9}) \ ({\rm calculated:} \ 335.0784, \ observed: \ 335.0790).$

3.5. Thermal stability of 2

The thermal stability was determined by heating **2** in an NMR tube with DMF and α , α , α -trifluorotoluene standard. The mixture in the NMR tube was heated and the ¹⁹F NMR spectrum was taken at varying time and temperature intervals. The ratio of **2** to the standard was recorded. At 25 °C, **2** showed no decomposition. At 65–70 °C, **2** showed no significant decomposition after 48 h. After **2** was held at 85–90 °C for 3 h, a small peak grew in the ¹⁹F NMR spectra. Since most of the Pd(0) coupling reactions can be conducted at room temperature to 70 °C, **2** was considered a useful synthon for the stereospecific introduction of aryl groups.

3.6. Preparation of (Z)-1,2-difluoro-1-iodo-1,4-pentadiene, (Z)-CH₂=CHCH₂CF=CFI ($\mathbf{3}$)

A 50 mL two-necked, round bottomed flask equipped with a nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with iodine (1.36 g, 5.34 mmol). Next, 2 (2.10 g, 5.34 mmol) was slowly added to maintain the temperature of the reaction mixture below 50 °C. The reaction mixture was flash distilled after a color change from dark brown to clear. Flash distillation removed **3** from the tri-*n*-butyltin iodide (1.16 g, 94% isolated yield, purity by ¹H NMR = 99%); ¹⁹F NMR (CDCl₃): -127.2 ppm (dt, 1F, ${}^{3}J_{FF} = 141.6 \text{ Hz}$, ${}^{4}J_{FH} = 5.3 \text{ Hz}$), -130.0 ppm(dt, 1F, ${}^{3}J_{FF} = 142.1 \text{ Hz}$, ${}^{3}J_{FH} = 21.1 \text{ Hz}$); ${}^{19}F\{H\}$ NMR (CDCl₃): -127.2 ppm (d, 1F, ${}^{3}J_{FF} = 140.9 \text{ Hz}$), -130.0 ppm (d, 1F ${}^{3}J_{FF}$ = 141.5 Hz); ¹H NMR (CDCl₃): 5.8 ppm (ddt, 1H, ${}^{3}J_{HH}$ = 17.0 Hz, ${}^{3}J_{HH}$ = 10.3 Hz, ${}^{3}J_{HH}$ = 6.3 Hz), 5.2 ppm (dm, 1H, ${}^{3}J_{HH}$ = 17.1 Hz), 5.2 ppm (ddt, 1H, ${}^{3}J_{HH} = 10.1$ Hz, ${}^{2}J_{HH} = 1.3$ Hz, ${}^{4}J_{HH} = 1.3$ Hz), 3.3 ppm (ddddd, 2H, ${}^{3}J_{HF}$ = 21.1 Hz, ${}^{3}J_{HH}$ = 6.5 Hz, ${}^{4}J_{HF}$ = 5.7 Hz, ${}^{4}J_{HH}$ = 1.4 Hz, ${}^{4}J_{HH}$ = 1.4 Hz); ${}^{13}C$ NMR (CDCl₃): 155.01 ppm (dd, ${}^{1}J_{CF}$ = 244.2 Hz, ${}^{2}J_{CF}$ = 41.9 Hz), 130.31 ppm (dd, ${}^{3}J_{CF}$ = 3.4 Hz, ${}^{4}J_{CF}$ = 2.2 Hz), 118.62 ppm (s), 96.94 ppm (dd, ${}^{1}J_{CF}$ = 308.7 Hz, ²J_{CF} = 66.1 Hz), 31.73 ppm (d, ²J_{CF} = 23.9 Hz); GC–MS, *m*/*z* (relative intensity): 230 (M⁺, 29.0), 103 (46.0), 74 (64.0), 59 (100.00); HRMS: C₅H₅F₂I (calculated: 229.9404, observed: 229.9395).

3.7. Preparation of (E)-1,2-difluoro-1-(meta-trifluoromethylphenyl)-1,4-pentadiene, (E)- CH_2 = $CHCH_2CF$ = $CFC_6H_4CF_3$ -m (**4**)

General procedure: A 25 mL two-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with Pd(PPh₃)₄ (0.48 g, 3–5 mol%), Cu(1)I (0.87 g, 4.6 mmol), and 10 mL of dry DMF. Next, 3-iodobenzotrifluorine (2.28 g, 8.30 mmol) was added to the solution *via* syringe. Then, **2** (3.93 g, 9.22 mmol) was slowly added to this solution by syringe. The reaction mixture was stirred 12 h at room temperature. To remove the ISnBu₃-*n*, the reaction mixture was stirred with Cu(OAc)₂ (3.36 g, 18.4 mmol)

and 5 mL of extra DMF for 2 h. Alternately, dry KF (0.58 g, 9.9 mmol) was added to the reaction flask and the mixture was stirred overnight. The reaction mixture was then poured over water (25 mL) in a separatory funnel and extracted with ether ($3 \times$ 25 mL). The combined ether layers were washed with water ($2 \times$ 25 mL). The organic layer was dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using hexanes as eluent to give **4** (2.90 g, 82% isolated yield, $R_{\rm f}$ (hexanes) = 0.36. purity by GLPC analysis = 98%): 19 F NMR (CDCl₃) -63.4 ppm (s, 3F), pullity by oth c analysis – 50%). If HMR (CDCI₃) – 03.4 ppin (0, 51), –143.3 ppm (dt, 1F, ${}^{3}J_{FF} = 122.6$ Hz, ${}^{3}J_{FH} = 23.9$ Hz), –159.8 ppm (dt, 1F, ${}^{3}J_{FF} = 123.7$ Hz, ${}^{4}J_{FH} = 4.6$ Hz); ${}^{19}F{H}$ NMR (CDCI₃): –63.4 ppm (s, 3F), –143.3 ppm (d, 1F, ${}^{3}J_{FF} = 122.9$ Hz), –159.8 ppm (d, 1F, ${}^{3}J_{FF} = 123.4$); 1 H NMR (CDCI₃): 7.9 ppm (s, 1H), 7.8 ppm (d, 1H, ${}^{3}J_{HH} = 7.9$ Hz), 7.6 ppm (dd, 1H, ${}^{3}J_{HH} = 9.0$ Hz, ${}^{3}J_{FF} = 123.4$ Hz), ${}^{3}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 122.9$ Hz), ${}^{2}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 122.9$ Hz), ${}^{2}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 122.9$ Hz, ${}^{3}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 122.9$ Hz, ${}^{3}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 122.9$ Hz, ${}^{3}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 123.4$ Hz, ${}^{3}J_{FF} = 122.9$ Hz, ${}^{3}J_{FF} = 123.4$ Hz, 1H), 7.8 ppm (d, 1H, ${}^{3}J_{HH} = 7.9$ Hz), 7.6 ppm (dd, 1H, ${}^{3}J_{HH} = 9.0$ Hz, ${}^{3}J_{HH} = 7.8$ Hz), 7.5 ppm (d, 1H, ${}^{3}J_{HH} = 7.7$ Hz), 5.9 ppm (ddt, 1H, ${}^{3}J_{HH} = 17.0$ Hz, ${}^{3}J_{HH} = 10.2$ Hz, ${}^{3}J_{HH} = 6.4$ Hz), 5.3 ppm (dm, 1H, ${}^{3}J_{HH} = 17.1$ Hz), 5.2 ppm (dd, 1H, ${}^{3}J_{HH} = 10.1$ Hz, ${}^{2}J_{HH} = 1.3$ Hz), 3.3 ppm (ddddd, 2H, ${}^{3}J_{HF} = 23.3$ Hz, ${}^{3}J_{HH} = 6.5$ Hz, ${}^{4}J_{HH} = 5.3$ Hz, ${}^{4}J_{HH} = 1.4$ Hz, ${}^{4}J_{HH} = 1.3$ Hz); ${}^{13}C$ NMR (CDCl₃): 151.51 ppm (dd, ${}^{1}J_{CF} = 251.6$ Hz, ${}^{2}J_{CF} = 55.9$ Hz), 146.00 ppm (dd, ${}^{1}J_{CF} = 225.2$ Hz, ${}^{2}J_{CF} = 43.3$ Hz), 131.11 ppm (qd, ${}^{2}J_{CF} = 32.0$ Hz, ${}^{4}J_{CF} = 2.7$ Hz), 120.06 ppm (dd) ${}^{3}I_{H} = 1.9$ Hz, ${}^{4}I_{HT} = 1.8$ Hz) 120.64 ppm (dd) 130.96 ppm (dd, ${}^{3}J_{CF} = 1.9$ Hz, ${}^{4}J_{CF} = 1.8$ Hz), 130.64 ppm (dd, ${}^{2}J_{CF} = 25.8$ Hz, ${}^{3}J_{CF} = 6.6$ Hz), 129.03 ppm (d, ${}^{4}J_{CF} = 2.0$ Hz), 128.35 ppm (ddm, ${}^{3}J_{CF}$ = 8.5 Hz, ${}^{4}J_{CF}$ = 1.4 Hz), 125.16 ppm (m), 124.04 ppm (q, ${}^{1}J_{CF}$ = 272.3 Hz), 122.11 ppm (m), 118.43 ppm (s), 32.13 ppm (d, ²*J*_{CF} = 22.8 Hz); GC–MS, *m*/*z* (relative intensity): 248 (M⁺, 100.00), 213 (62.76), 201 (62.15), 179 (85.05), 177 (57.02) 164 (92.70), 159 (70.96), 151 (98.55); HRMS: C₁₂H₉F₅ (calculated: 248.0624, observed: 248.0620).

3.8. Preparation of (E)-1,2-difluoro-1-(meta-nitrophenyl)-1,4pentadiene, (E)-CH₂=CHCH₂CF=CFC₆H₄NO₂-m (**5**)

Similar to the procedure described in Section 3.7. 1-Iodo-3nitrobenzene (1.58 g 6.40 mmol) was reacted with 2 (3.00 g, 7.60 mmol), $Pd(PPh_3)_4$ (0.37 g, 3–5 mol%), Cu(I)I (0.61 g, 3.2 mmol), and 8 mL of dry DMF. The reaction mixture was stirred 12 h at room temperature. After standard workup, the crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give 5 (1.06 g, 74%, *R*_f (88% hexanes, 12% EtOAc) 0.46, purity by ¹H NMR = 99%): ¹⁹F NMR (CDCl₃): -141.4 ppm (dt, 1F, ³ $J_{FF} = 124.1 \text{ Hz}$, ${}^{3}J_{FH}$ = 22.9 Hz), -160.0 ppm (dt, 1F, ${}^{3}J_{FF}$ = 124.0 Hz, ${}^{4}J_{FH}$ = 5.5 Hz); ¹H NMR (CDCl₃): 8.5 ppm (dd, 1H, ${}^{4}J_{HF}$ = 2.0 Hz, ${}^{5}J_{HF}$ = 2.0 Hz), 8.2 ppm (dd, 1H, ${}^{3}J_{HH}$ = 8.2 Hz, ${}^{4}J_{HF}$ = 2.2 Hz), 7.9 ppm (d, 1H, ${}^{3}J_{HH} = 8.0 \text{ Hz}$), 7.6 ppm (dd, 1H, ${}^{3}J_{HH} = 8.1 \text{ Hz}$, ${}^{3}J_{HH} = 8.0 \text{ Hz}$), 5.9 ppm (ddt, 1H, ${}^{3}J_{HH} = 17.0 \text{ Hz}$, ${}^{3}J_{HH} = 10.1 \text{ Hz}$, ${}^{3}J_{HH} = 6.4 \text{ Hz}$), 5.3 ppm (dm, 1H, ${}^{3}J_{HH}$ = 17.1 Hz), 5.2 ppm (dd, 1H, ${}^{3}J_{HH}$ = 10.0 Hz, ${}^{2}J_{\text{HH}}$ = 1.3 Hz), 3.4 ppm (ddddd, 2H, ${}^{3}J_{\text{HF}}$ = 23.4 Hz, ${}^{3}J_{\text{HH}}$ = 6.5 Hz, ${}^{4}J_{HF}$ = 6.5 Hz, ${}^{4}J_{HH}$ = 1.3 Hz); 13 C NMR (CDCl₃): 152.24 ppm (dd, ${}^{1}J_{CF}$ = 253.5 Hz, ${}^{2}J_{CF}$ = 54.7 Hz), 145.11 ppm (dd, ${}^{1}J_{CF}$ = 226.1 Hz, ${}^{2}J_{CF}$ 42.7 Hz), 148.44 ppm (s), 131.37 ppm (dd, ${}^{2}J_{CF} = 25.7$ Hz, ${}^{3}J_{CF} = 6.4$ Hz), 130.72 ppm (dd, ${}^{3}J_{CF} = 9.5$ Hz, ${}^{4}J_{CF} = 6.9$ Hz), 122.50 $J_{CF} = 0.4 \text{ Hz}$, 130.72 ppm (dd, $J_{CF} = 3.5 \text{ Hz}$, $J_{CF} = 6.9 \text{ Hz}$), 130.58 ppm (dd, ${}^{3}J_{CF} = 3.42 \text{ Hz}$, ${}^{4}J_{CF} = 3.42 \text{ Hz}$), 129.57 ppm (d, ${}^{5}J_{CF} = 1.9 \text{ Hz}$), 123.10 ppm (d, ${}^{4}J_{CF} = 2.7 \text{ Hz}$), 120.11 ppm (dd, ${}^{3}J_{CF} = 9.8 \text{ Hz}$, ${}^{4}J_{CF} = 8.1 \text{ Hz}$), 118.69 ppm (s), 32.11 ppm (d, ${}^{2}J_{CF} = 23.3 \text{ Hz}$); GC-MS, m/z (relative intensity): 225 (M⁺, 52.76), 177 (50.10), 164 (84.97), 151 (100.00), 133 (63.18); HRMS: C₁₁H₉F₂NO₂ (calculated: 225.0601, observed: 225.0604).

3.9. Preparation of (E)-1,2-difluoro-1-phenyl-1,4-pentadiene, (E)- CH_2 =CHCH₂CF=CFC₆H₅ (**6**)

Similar to the procedure described in Section 3.7. Iodobenzene (0.65 g, 3.2 mmol) was reacted with **2** (1.50 g, 3.80 mmol),

Pd(PPh₃)₄ (0.18 g, 3–5 mol%), Cu(1)I (0.31 g, 1.6 mmol), and 4 mL of dry DMF. The reaction mixture was stirred 12 h at room temperature. After standard workup, the crude product was purified by silica gel column chromatography using hexanes as eluent to give **6** (0.37 g, 65% isolated yield, $R_{\rm f}$ (hexanes) = 0.38, purity by ¹⁹F NMR = 92%): ¹⁹F NMR (CDCl₃): -146.0 ppm (dt, 1F, $^{3}J_{\rm FF}$ = 122.8 Hz, $^{3}J_{\rm FH}$ = 23.3 Hz), -159.0 ppm (dt, 1F, $^{3}J_{\rm FF}$ = 122.8 Hz, $^{3}J_{\rm FH}$ = 23.3 Hz), -159.0 ppm (dt, 2H, $^{3}J_{\rm HH}$ 7.2 Hz, $^{4}J_{\rm FH}$ = 1.6 Hz, $^{5}J_{\rm HF}$ = 1.1 Hz), 7.4 ppm (dddd, 2H, $^{3}J_{\rm HH}$ = 8.3 Hz, $^{3}J_{\rm HH}$ = 7.1 Hz, $^{5}J_{\rm HF}$ = 1.2 Hz, $^{6}J_{\rm HF}$ = 0.8 Hz), 7.3 ppm (m, 1H), 5.9 ppm (ddt, 1H, $^{3}J_{\rm HH}$ = 16.6 Hz, $^{3}J_{\rm HH}$ = 10.2 Hz, $^{3}J_{\rm HH}$ = 6.4 Hz), 5.3 ppm (dm, 1H, $^{3}J_{\rm HH}$ = 17.1 Hz), 5.2 ppm (ddt, 1H, $^{3}J_{\rm HH}$ = 10.0 Hz, $^{2}J_{\rm HH}$ = 1.5 Hz, $^{4}J_{\rm HH}$ = 1.3 Hz), 3.3 ppm (ddtdd, 2H, $^{3}J_{\rm HF}$ = 23.1 Hz, $^{3}J_{\rm HH}$ = 6.4, $^{4}J_{\rm HF}$ = 5.3 Hz, $^{4}J_{\rm HH}$ = 1.5 Hz, $^{4}J_{\rm HH}$ = 1.5 Hz, ^{13}C NMR (CDCl₃): 150.14 ppm (dd, $^{1}J_{\rm CF}$ = 248.6 Hz, $^{2}J_{\rm CF}$ = 57.2 Hz), 146.92 ppm (dd, $^{1}J_{\rm CF}$ = 244.4 Hz, $^{2}J_{\rm CF}$ = 43.1 Hz), 131.42 ppm (dd, $^{3}J_{\rm CF}$ = 0.9 Hz), 129.74 ppm (dd, $^{2}J_{\rm CF}$ = 2.7 Hz), 125.28 ppm (d, $^{1}J_{\rm CF}$ = 7.4 Hz), 125.16 ppm (d, $^{3}J_{\rm CF}$ = 7.8 Hz), 117.95 ppm(s), 32.06 ppm(d, $^{2}J_{\rm CF}$ = 23.9 Hz); GC–MS, *m/z* (relative intensity): 180 (M⁺, 81.27), 165 (100.00), 133 (68.99); HRMS: C_{11}H_{10}F_{2} (calculated: 180.0751, observed: 180.0776).

3.10. Preparation of (E)-1,2-difluoro-1-(para-tolyl)-1,4-pentadiene, (E)-CH₂=CHCH₂CF=CFC₆H₄CH₃-p (**7**)

Similar to the procedure described in Section 3.7. 4-Iodotoluene (1.28 g, 5.90 mmol) was reacted with 2 (2.77 g, 7.05 mmol), Pd(PPh₃)₄ (0.34 g, 3–5 mol%), Cu(1)I (0.50 g, 2.9 mmol), and 8 mL of dry DMF. The reaction mixture was stirred 12 h at room temperature. After standard workup, the crude product was purified by silica gel column chromatography using hexanes as eluent to give **7** (0.70 g, 64% isolated yield, R_f (hexanes) = 0.40, purity by ¹H NMR = 94%); ¹⁹F NMR (CDCl₃): -147.0 ppm (dt, 1F, ${}^{3}J_{FF}$ = 122.7 Hz, ${}^{3}J_{FH}$ = 23.4 Hz), -158.7 ppm (dt, 1F, ${}^{3}J_{FF}$ = 122.7 Hz, ${}^{4}J_{\text{FH}}$ = 4.8 Hz); ¹H NMR (CDCl₃): 7.5 ppm (dd, 2H, ${}^{3}J_{\text{HH}}$ = 8.4 Hz, ${}^{4}J_{HF} = 1.8 \text{ Hz}), 7.2 \text{ ppm} (dd, 2H, {}^{3}J_{HH} = 8.0 \text{ Hz}, {}^{5}J_{HF} = 0.6 \text{ Hz}), 5.9 \text{ ppm} (ddt, 1H, {}^{3}J_{HH} = 17.0 \text{ Hz}, {}^{3}J_{HH} = 10.1 \text{ Hz}, {}^{3}J_{HH} = 6.4 \text{ Hz}),$ 5.3 ppm (dm, 1H, ${}^{3}J_{HH}$ = 17.1 Hz), 5.2 ppm (ddt, 1H, ${}^{3}J_{HH}$ = 10.0 Hz, ${}^{2}J_{HH}$ = 1.4 Hz, ${}^{4}J_{HH}$ = 1.4 Hz), 3.3 ppm (ddddd, 2H, ${}^{3}J_{HF}$ = 23.3 Hz, ${}^{3}J_{HH}$ = 6.4 Hz, ${}^{4}J_{HF}$ = 5.3 Hz, ${}^{4}J_{HH}$ = 1.4 Hz, ${}^{4}J_{HH}$ = 1.4 Hz), 2.4 ppm (s, 3H); ¹³C NMR (CDCl₃): 149.66 ppm, (dd, ${}^{1}J_{CF}$ = 246.7 Hz, ${}^{2}J_{CF}$ = 56.8 Hz), 147.24 ppm (dd, ${}^{1}J_{CF}$ = 225.3 Hz, ${}^{2}J_{CF}$ = 43.5 Hz), 138.62 ppm (d, ${}^{5}J_{CF} = 2.2 \text{ Hz}$), 131.70 ppm (dd, ${}^{3}J_{CF} = 1.5 \text{ Hz}$, ${}^{4}J_{CF} = 1.5 \text{ Hz}$), 129.18 ppm (d, ${}^{4}J_{CF} = 2.5 \text{ Hz}$), 127.03 ppm (dd, ${}^{2}J_{CF} = 25.2 \text{ Hz}, {}^{3}J_{CF} = 6.0 \text{ Hz}), 125.27 \text{ ppm} (dd, {}^{3}J_{CF} = 8.2 \text{ Hz}, {}^{4}J_{CF} = 7.2 \text{ Hz}), 117.94 \text{ ppm} (s), 32.14 \text{ ppm} (d, {}^{2}J_{CF} = 23.5 \text{ Hz}),$ 21.42 ppm (s); GC-MS, *m*/*z* (relative intensity): 194 (M⁺, 100.00, 179 (82.75), 164 (56.75); HRMS: C₁₂H₁₂F₂ (calculated: 194.0907, observed: 194.0914).

3.11. Preparation of (E)-1,2-difluoro-1-(para-methoxyphenyl)-1,4-pentadiene, (E)-CH₂=CHCH₂CF=CFC₆H₄OCH₃-p (**8**)

Similar to the procedure described in Section 3.7. 4-Iodoanisole (0.74 g, 3.2 mmol) was reacted with **2** (1.50 g, 3.80 mmol), Pd(PPh₃)₄ (0.18 g, 3–5 mol%), Cu(I)I (0.31 g, 1.6 mmol), and 4 mL of dry DMF. The reaction mixture was stirred 96 h at room temperature. After standard workup, the crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give **8** (0.44 g, 67% isolated yield, $R_{\rm f}$ (88% hexanes, 12% EtOAc) = 0.50, purity by ¹H NMR = 99%); ¹⁹F NMR (CDCl₃): -148.8 ppm (dt, 1F, ³ $J_{\rm FF}$ = 123.5 Hz, ³ $J_{\rm FH}$ = 22.7 Hz), -158.2 ppm (dt, 1F, ³ $J_{\rm FF}$ = 123.7 Hz, ⁴ $J_{\rm FH}$ = 5.3 Hz); ¹H NMR (CDCl₃): 7.5 ppm (dz, 2H, ³ $J_{\rm HH}$ = 9.1 Hz), 6.8 ppm (dz, 2H, ³ $J_{\rm HH}$ = 8.9 Hz), 5.8 ppm (ddt, 1H, ³ $J_{\rm HH}$ = 17.1 Hz, ³ $J_{\rm HH}$ = 10.3 Hz,

 ${}^{3}J_{HH} = 6.3 \text{ Hz}$), 5.2 ppm (dm, 1H, ${}^{3}J_{HH} = 17.1 \text{ Hz}$), 5.1 ppm (dd, 1H, ${}^{3}J_{HH} = 9.9 \text{ Hz}$, ${}^{2}J_{HH} = 1.2 \text{ Hz}$), 3.7 ppm (s, 3H), 3.2 ppm (dddd, 2H, ${}^{3}J_{HF} = 23.2 \text{ Hz}$, ${}^{3}J_{HH} = 5.1 \text{ Hz}$, ${}^{4}J_{HF} = 5.1 \text{ Hz}$, ${}^{4}J_{HH} = 1.4 \text{ Hz}$, ${}^{4}J_{HH} = 1.4 \text{ Hz}$, ${}^{4}J_{HH} = 1.4 \text{ Hz}$, ${}^{1}J_{CF} = 245.2 \text{ Hz}$, ${}^{1}J_{CF} = 5.7 \text{ Hz}$, ${}^{4}J_{CF} = 2.3 \text{ Hz}$, 147.80 (dd, ${}^{1}J_{CF} = 245.2 \text{ Hz}$, ${}^{2}J_{CF} = 56.7 \text{ Hz}$), 145.97 (dd, ${}^{1}J_{CF} = 224.0 \text{ Hz}$, ${}^{2}J_{CF} = 43.9 \text{ Hz}$), 130.66 (dd, ${}^{3}J_{CF} = 2.3 \text{ Hz}$, ${}^{4}J_{CF} = 2.3 \text{ Hz}$), 125.74 (dd, ${}^{3}J_{CF} = 7.3 \text{ Hz}$, ${}^{4}J_{CF} = 7.3 \text{ Hz}$, 121.31 (dd, ${}^{2}J_{CF} = 25.8 \text{ Hz}$, ${}^{3}J_{CF} = 6.2 \text{ Hz}$), 116.70 (s), 112.76 (d, ${}^{4}J_{CF} = 1.9 \text{ Hz}$), 54.21 (s), 30.93 (d, ${}^{2}J_{CF} = 24.0 \text{ Hz}$). GC-MS, m/z (relative intensity): 210 (M⁺, 100.00); HRMS: C₁₂H₁₂F₂O (calculated: 210.0856, observed: 210.0857).

3.12. Preparation of (E)-1,2-difluoro-1-(orthotrifluoromethylphenyl)-1,4-pentadiene, (E)- CH_2 =CHCH₂CF=CFC₆H₄CF₃-0 (**9**)

Similar to the procedure described in Section 3.7. 2-Iodobenzotrifluoride (0.44 g, 1.6 mmol) was reacted with **2** (0.77 g, 1.6 mmol)2.0 mmol), Pd(PPh₃)₄ (0.09 g, 3–5 mmol%), Cu(I)I (0.15 g, 0.78 mmol), and 2 mL of dry DMF. The reaction mixture was stirred 240 h at 65 °C. After standard workup, the crude product was purified by silica gel column chromatography using hexanes as eluent to give **9** (0.15 g, 31% isolated yield, R_f (hexanes) = 0.38, purity by ¹H NMR = 99%); ¹⁹F NMR (CDCl₃): -61.5 ppm (dd, 3F, ${}^{5}J_{FF}$ = 12.1 Hz, ${}^{6}J_{FF}$ = 2.2 Hz), -141.4 ppm (dqt, 1F, ${}^{3}J_{FF}$ = 133.8 Hz, ${}^{5}J_{FF} = 12.7$ Hz, ${}^{4}J_{FH} = 6.5$ Hz), -146.5 ppm (dt, 1F, ${}^{3}J_{FF} = 134.2$ Hz, ${}^{3}J_{FH} = 22.1 \text{ Hz}$; ${}^{19}F{H}$ NMR (CDCl₃): -61.5 ppm (dd, 3F, ${}^{5}J_{FF} = 12.3 \text{ Hz}, {}^{6}J_{FF} = 2.2 \text{ Hz}, -141.4 \text{ ppm} (dq, 1F, {}^{3}J_{FF} = 133.4 \text{ Hz},$ ${}^{5}J_{FF}$ = 12.2 Hz), -146.5 ppm (dq, 1F, ${}^{3}J_{FF}$ = 132.9 Hz, ${}^{6}J_{FF}$ = 3.1 Hz); ¹H NMR (CDCl₃): 7.8 ppm (d, 1H, ${}^{3}J_{HH}$ = 7.2 Hz), 7.6 ppm (m, 3H), 5.9 ppm (ddt, 1H, ${}^{3}J_{HH}$ = 16.8 Hz, ${}^{3}J_{HH}$ = 10.3 Hz, ${}^{3}J_{HH}$ = 6.3 Hz), 5.3 ppm (dm, 1H, ${}^{3}J_{HH}$ = 17.1 Hz), 5.2 ppm (dm, 1H, ${}^{3}J_{HH}$ = 10.1 Hz), 3.3 ppm (ddd, 2H, ${}^{3}J_{HF}$ = 22.5 Hz, ${}^{3}J_{HH}$ = 5.2 Hz, ${}^{4}J_{HF}$ = 5.2 Hz); ${}^{13}C$ NMR (CDCl₃): 149.83 ppm (dd, ${}^{1}J_{CF}$ = 243.2 Hz, ${}^{2}J_{CF}$ = 52.9 Hz), 145.52 ppm (dd, ${}^{1}J_{CF} = 233.9 \text{ Hz}, {}^{2}J_{CF} = 49.9 \text{ Hz}$), 132.17 ppm (dd, ${}^{3}J_{CF} = 4.6 \text{ Hz}, {}^{4}J_{CF} = 3.1 \text{ Hz}$, 131.71 ppm (s), 130.96 ppm (dd, ${}^{3}J_{CF} = 2.3 \text{ Hz}, \quad {}^{4}J_{CF} = 2.0 \text{ Hz}), \quad 130.14 \text{ ppm}, \quad (d, \quad {}^{4}J_{CF} = 2.0 \text{ Hz}),$ 129.53 ppm (q, ${}^{2}J_{CF}$ = 31.4 Hz), 126.71 ppm (qd, ${}^{3}J_{CF}$ = 5.0 Hz, ${}^{4}J_{CF}$ = 1.6 Hz), 127.18 ppm (dm, ${}^{2}J_{CF}$ = 24.8 Hz), 123.56 ppm (q, ${}^{1}J_{CF}$ = 274.1 Hz), 118.17 ppm (s), 31.28 ppm (d, ${}^{2}J_{CF}$ = 23.7 Hz); GC– MS, *m*/*z* (relative intensity): 248 (M⁺, 42.00), 179 (78.42), 164 (76.44), 159 (69.96), 151 (100.00); HRMS: C₁₂H₉F₅ (calculated: 248.0624, observed: 248.0616).

3.13. Preparation of (E)-1,1,2,3,4-pentafluoro-1,3,6-heptatriene, (E)- CH_2 =CHCH₂CF=CFCF=CF₂ (**10**)

A 50 mL two-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with $Pd(PPh_3)_4$ (0.62 g, 3-5 mol%), Cu(I)I (1.00 g, 5.40 mmol), and 13 mL of dry DMF. Next, trifluoroiodoethene (2.26 g, 10.8 mmol) was added to the solution. Then, 2 (5.13 g, 13.0 mmol) was slowly added to this solution by syringe. The reaction mixture was stirred 12 h at room temperature. The product was flash distilled from the reaction mixture. The crude product was purified by fractional distillation on a 6 cm Vigreuxcolumn to give **10** (1.49 g, 75% isolated yield, purity by ¹H NMR = 98%): bp 78-80 °C; ¹⁹F NMR (CDCl₃): -96.0 ppm (dddd, 1F, ${}^{3}J_{FF} = 29.6 \text{ Hz}, \quad {}^{4}J_{FF} = 5.0 \text{ Hz}, \quad {}^{5}J_{FF} = 5.0 \text{ Hz}),$ ${}^{2}J_{\rm FF}$ = 52.5 Hz, $-108.6 \text{ ppm} (\text{ddd}, 1\text{F}, {}^{3}J_{FF} = 116.4 \text{ Hz}, {}^{2}J_{FF} = 52.3 \text{ Hz}, {}^{5}J_{FF} = 17.6 \text{ Hz},$ ${}^{4}J_{FF} = 12.6 \text{ Hz}, -134.8 \text{ ppm} (\text{dtddd}, 1\text{F}, {}^{3}J_{FF} = 134.3 \text{ Hz}, {}^{3}J_{FH} =$ 22.6 Hz, ${}^{5}J_{FF} = 17.0$ Hz, ${}^{4}J_{FF} = 10.5$ Hz, ${}^{5}J_{FF} = 5.1$ Hz), -164.5 ppm (ddtd, 1F, ${}^{3}J_{FF} = 134.9$ Hz, ${}^{3}J_{FF} = 32.6$ Hz, ${}^{4}J_{FF} = 12.6$ Hz, ${}^{4}J_{FH} =$ 4.7 Hz, ${}^{4}J_{FF} = 3.6$ Hz), -181.2 ppm (ddddt, 1F, ${}^{3}J_{FF} = 116.4$ Hz, ${}^{3}J_{FF} = 32.2$ Hz, ${}^{3}J_{FF} = 30.0$ Hz, ${}^{4}J_{FF} = 10.3$ Hz, ${}^{5}J_{FH} = 3.0$ Hz); ${}^{19}F$ {H} NMR (CDCl₃): -96.0 ppm (dddd, 1F, ${}^{2}J_{FF} = 52.3 \text{ Hz}$, ${}^{3}J_{FF} = 29.6 \text{ Hz}$,

3.14. Preparation of (E,E)-4,5,6,7,8,8,8-heptafluoro-1,4,6-octatriene, (E,E)-CH₂=CHCH₂CF=CFCF=CFCF₃ (**11**)

A 50 mL two-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar and a rubber septum port was charged with Pd(PPh₃)₄ (0.26 g, 3-5 mol%), Cu(I)I (0.43 g, 2.3 mmol), and 8 mL of dry DMF. Next, (Z)pentafluoro-1-iodo-1-propene (1.10 g, 4.50 mmol) was added to the solution. Then, 2 (2.30 g, 5.80 mmol) was slowly added to this solution by syringe. The reaction mixture was stirred 12 h at room temperature. The product was flash distilled from the reaction mixture. The crude product was purified by fractional distillation on a 6 cm Vigreux column to give 11 (0.54 g, 54% isolated yield, purity by ¹H NMR = 98%): bp $43-44 \degree C/50 \text{ mm Hg}$; ¹⁹F NMR (CDCl₃): -68.4 ppm (dd, 3F, ${}^{4}J_{FF} = 20.7 \text{ Hz}$, ${}^{3}J_{FF} = 10.9 \text{ Hz}$), $-130.5 \text{ ppm} (\text{ddtd}, 1F, {}^{3}J_{\text{FF}} = 131.7 \text{ Hz}, {}^{5}J_{\text{FF}} = 29.8 \text{ Hz}, {}^{3}J_{\text{FH}} = 22.3 \text{ Hz},$ ${}^{4}J_{FF} = 14.1$ Hz), -153.0 ppm (ddqdt, 1F, ${}^{3}J_{FF} = 137.7$ Hz, ${}^{3}J_{FF} = 32.0$ Hz, ${}^{4}J_{FF} = 21.5$ Hz, ${}^{4}J_{FF} = 13.6$ Hz, ${}^{5}J_{FH} = 1.8$ Hz), -158.7 ppm $(dddq, 1F, {}^{3}J_{FF} = 138.9 \text{ Hz}, {}^{5}J_{FF} = 30.0 \text{ Hz},$ $^{4}I_{\text{FF}} = 13.4 \text{ Hz},$ ${}^{3}J_{FF}$ = 10.5 Hz), -169.4 ppm (dddtq, 1F, ${}^{3}J_{FF}$ = 131.7 Hz, ${}^{3}J_{FF}$ = 32.8 Hz, ${}^{4}J_{FF} = 14.2$ Hz, ${}^{4}J_{FH} = 7.3$ Hz, ${}^{5}J_{FF} = 2.1$ Hz); ${}^{19}F{H}$ NMR (CDCl₃): -68.4 ppm (dd, 1F, ${}^{4}J_{FF} = 20.8 \text{ Hz}$, ${}^{3}J_{FF} = 10.9 \text{ Hz}$), -130.5 ppm (ddd, 1F, ${}^{3}J_{FF}$ = 131.4 Hz, ${}^{5}J_{FF}$ = 29.9 Hz, ${}^{4}J_{FF}$ = 13.8 Hz), -153.0 ppm (ddqd, 1F, ${}^{3}J_{FF}$ = 138.7 Hz, ${}^{3}J_{FF}$ = 32.0 Hz, ${}^{4}J_{FF}$ = 21.5 Hz, ${}^{4}J_{FF}$ = 13.6 Hz), -158.7 ppm (dddq, 1F, ${}^{3}J_{FF}$ = 137.7 Hz, ${}^{5}J_{FF}$ = 30.0 Hz, ${}^{4}J_{FF}$ = 13.4 Hz, ${}^{3}J_{FF}$ = 10.5 Hz), -169.3 ppm (dddq, 1F, ${}^{3}J_{FF} = 131.8$ Hz, ${}^{3}J_{FF} = 32.8$ Hz, ${}^{4}J_{FF} = 14.2$ Hz, ${}^{5}J_{FF} = 2.1$ Hz); 1 H NMR (CDCl₃): 5.8 ppm (ddt, 1H, ${}^{3}J_{HH} = 17.1$ Hz, ${}^{3}J_{HH} = 10.2$ Hz, ${}^{3}J_{HH} = 6.3$ Hz), 5.2 ppm (dm, 1H, ${}^{3}J_{HH} = 17.1$ Hz, ${}^{3}J_{HH} = 0.7$ Hz), 5.2 ppm (dd, 1H, ${}^{3}J_{HH} = 10.0$ Hz, ${}^{3}J_{HH} = 1.3$ Hz), 3.2 ppm (dm, 2H, ${}^{3}J_{HH} = 22.2$ Hz); ${}^{13}C$ NMR (CDCl₃): 155.62 ppm (dddd, ${}^{1}J_{CF} =$ $^{1}_{J_{CF}}$ 2212 H2, $^{2}_{J_{CF}}$ 47.0 Hz, $^{3}_{J_{CF}}$ = 3.6 Hz, $^{4}_{J_{CF}}$ = 3.3 Hz), 142.42 ppm (ddm, $^{1}_{J_{CF}}$ = 254.3 Hz, $^{2}_{J_{CF}}$ = 41.4 Hz, $^{3}_{J_{CF}}$ = 28.5 Hz), 139.41 ppm (ddm, $^{1}_{J_{CF}}$ = 257.7 Hz, $^{2}_{J_{CF}}$ = 41.1 Hz, $^{2}_{J_{CF}}$ = 41.1 Hz), 136.13 ppm (ddd, $^{1}_{J_{CF}}$ = 29.9 Hz, $^{2}_{J_{CF}}$ = 48.9 Hz, $^{2}_{J_{CF}}$ = 26.8 Hz, $^{3}_{J_{CF}}$ = 5.8 Hz), 120.07 EV 129.07 ppm (s), 119.63 ppm (s), 118.41 ppm (qdd, ${}^{1}J_{CF}$ = 272.5 Hz, $^{2}J_{CF}$ = 35.3 Hz, $^{3}J_{CF}$ = 4.9 Hz), 31.63 ppm (d, $^{2}J_{CF}$ = 21.7 Hz); GC–MS, *m*/*z* (relative intensity): 234 (M⁺, 2.7), 74 (95.7), 59 (100.0); HRMS: C₈H₅F₇ (calculated: 234.0279, observed: 234.0285).

3.15. Preparation of (Z)-4,5-difluoro-5-tri-n-butylstannyl-4-penten-1-ol (Z)-HOCH_2CH_2CF=CFSnBu_3-n (**12**)

A 50 mL three-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with a 0.5 M solution of 9-BBN in THF (15.0 mL, 7.50 mmol). Next, **2** (1.97 g, 5.01 mmol)

was slowly added at room temperature. The reaction mixture was stirred 16 h at room temperature. The oxidation was performed by cooling the reaction mixture to 0 °C; then 3 M NaOH (1.6 mL, 5.0 mmol) and 30% H₂O₂ (2.80 g, 25.0 mmol) were slowly added simultaneously via syringe. The reaction mixture was allowed to warm to room temperature with stirring overnight. A saturated aqueous solution of Na₂CO₃ (25 mL) was added to the reaction mixture and the mixture was extracted with ether $(3 \times 25 \text{ mL})$ in a separatory funnel. Then the combined ether layers were washed with water $(3 \times 15 \text{ mL})$. The organic layer was dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give 12 $(1.29 \text{ g}, 65\% \text{ isolated yield}, R_f (88\% \text{ hexanes}, 12\% \text{ EtOAc}) = 0.20,$ purity by ¹H NMR = 89%); ¹⁹F NMR (CDCl₃): -149.0 ppm (dt, 1F, ${}^{3}J_{\text{FF}}$ = 117.0 Hz, ${}^{3}J_{\text{FH}}$ = 23.0 Hz), -165.1 ppm (dt, 1F, ${}^{3}J_{\text{FF}}$ = 116.4 Hz, ${}^{4}J_{\text{FH}} = 6.1 \text{ Hz}, {}^{2}J_{\text{FSn}} = 83.3 \text{ Hz} \text{ satellite peaks}); {}^{1}\text{H} \text{ NMR} (\text{CDCl}_3):$ 3.7 ppm (t, 2H, ${}^{3}J_{HH} = 6.4$ Hz), 2.5 ppm (dtd, 2H, ${}^{3}J_{HF} = 22.8$ Hz, ${}^{3}J_{HH} = 7.1$ Hz, ${}^{4}J_{HF} = 6.5$ Hz), 1.8 ppm (pent, 2H, ${}^{3}J_{HH} = 6.8$ Hz), 1.5 ppm (m, 6H), 1.5 ppm (s), 1.3 ppm (sext, 6H, ${}^{3}J_{HH} = 6.7$ Hz), 1.1 ppm (t, 6H, ${}^{3}J_{HH}$ = 7.9 Hz), 0.9 ppm, t, 9H, ${}^{3}J_{HH}$ = 7.2 Hz); ${}^{13}C$ NMR (CDCl₃): 164.78 ppm (dd, ${}^{1}J_{CF}$ = 226.8 Hz, ${}^{2}J_{CF}$ = 35.1 Hz), (c) $^{1}J_{CF} = 294.8 \text{ Hz}, ^{2}J_{CF} = 22.08 \text{ Hz}, ^{2}J_{CF} = 53.1 \text{ Hz}, ^{2}$ 159.19 ppm (dd, $^{3}J_{CF} = 2.94.8 \text{ Hz}, ^{2}J_{CF} = 98.1 \text{ Hz}), 61.76 ppm (s), 28.95 ppm (dd, <math>^{3}J_{CF} = 2.2 \text{ Hz}, ^{4}J_{CF} = 2.2 \text{ Hz}), 28.89 ppm (s, <math>^{3}J_{CSn} = 10.7 \text{ Hz}$ satellite peaks), 27.15 ppm (s, $^{2}J_{CSn} = 29.8 \text{ Hz}$ satellite peaks), 13.67 ppm (s), 22.72 ppm (dd, $^{2}J_{CF} = 27.3 \text{ Hz}, ^{2}J_{CSn} = 10.7 \text{ Hz}$ satellite peaks), 13.67 ppm (s), 22.72 ppm (dd, $^{2}J_{CF} = 27.3 \text{ Hz}, ^{2}J_{CSn} = 20.0 \text{ Hz}, ^{2}J_{CSn} = 20.0 \text{ Hz}, ^{2}J_{CSn} = 10.7 \text{ Hz}$ satellite peaks), 13.67 ppm (s), 22.72 ppm (dd, $^{2}J_{CF} = 27.3 \text{ Hz}, ^{2}J_{CSn} = 20.0 \text{ Hz}, ^{2}J_{CSn} = 2$ ${}^{2}J_{CF}$ = 2.5 Hz), 9.90 ppm (dd, ${}^{3}J_{CF}$ = 1.8 Hz, ${}^{4}J_{CF}$ = 1.8 Hz, ${}^{1}J_{CSn}$ = 172.0 Hz satellite peaks); GC-MS, m/z (relative intensity): 353 (M⁺-C₄H₉, 19.64), 253 (100.00), 251 (93.71), 249 (57.28); HRMS: $C_{13}H_{25}F_2O^{118}Sn$ (M⁺-C₄H₉) (calculated: 353.0890, observed: 353.0888).

3.16. Preparation of (Z)-4,5-difluoro-5-triethsilyl-4-penten-1-ol, (Z)-HOCH₂CH₂CF₌CFSiEt₃ (**13**)

A 50 mL three-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with 0.5 M solution of 9-BBN in THF (13.8 mL, 6.90 mmol). Next, 1 (1.00 g, 4.59 mmol) was slowly added at room temperature. The reaction was stirred overnight. The oxidation was performed by cooling the reaction mixture to 0 °C and adding 3 M NaOH (1.6 mL, 4.6 mmol) and 30% H₂O₂ (2.80 g, 23.0 mmol) slowly and simultaneously via syringe. The reaction mixture was allowed to warm to room temperature with stirring overnight. A saturated aqueous solution of Na₂CO₃ (25 mL) was added to the reaction mixture and the mixture was extracted with ether (3× 15 mL) in a separatory funnel. Then the combined layers were washed with water $(3 \times 15 \text{ mL})$. The organic layer was dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give 13 (0.80 g, 74% isolated yield, R_f (88% hexanes, 12% (EtOAc) = 0.11, purity by ¹H NMR = 97%); ¹⁹F NMR (CDCl₃): -146.0 ppm (dt, 1F, ${}^{3}J_{FF} = 125.5 \text{ Hz}$, ${}^{3}J_{FH} = 23.2 \text{ Hz}$), -172.6 ppm (dt, 1F, ${}^{3}J_{FF} = 125.0 \text{ Hz}$, ${}^{4}J_{FH} = 6.2 \text{ Hz}$); ${}^{1}\text{H} \text{ NMR}$ (CDCl₃): 3.7 ppm (t, 2H, ${}^{3}J_{HH}$ = 6.4 Hz), 2.5 ppm (dtd, 2H, ${}^{3}J_{HF}$ = 23.2 Hz, ${}^{3}J_{HH}$ = 7.3 Hz, ${}^{4}J_{HF}$ = 6.4 Hz), 1.9 ppm (s, 1H), 1.8 ppm (pent, 2H, ${}^{3}J_{\rm HH}$ = 6.9 Hz), 1.0 ppm (t, 9H, ${}^{3}J_{\rm HH}$ = 7.5 Hz), 0.7 ppm (q, 6H, ${}^{3}J_{HH} = 6.9$ Hz), 1.0 ppin (t, 9ri, $J_{HH} = 7.5$ Hz), 0.7 ppin (t, 9ri, ${}^{3}J_{HH} = 7.9$ Hz); 1³C NMR (CDCl₃): 165.55 ppm (dd, ${}^{1}J_{CF} = 237.3$ Hz, ${}^{2}J_{CF} = 41.7$ Hz), 154.77 ppm (dd, ${}^{1}J_{CF} = 256.5$ Hz, ${}^{2}J_{CF} = 76.2$ Hz), 61.63 ppm (s), 28.67 ppm (t, ${}^{3}J_{CF} = 1.8$ Hz), 23.01 ppm (dd, ${}^{2}J_{CF} = 25.4$ Hz, ${}^{3}J_{CF} = 2.1$ Hz), 7.03 ppm (s), 2.36 ppm (dd, ${}^{3}J_{CF} = 2.0$ Hz, ${}^{4}J_{CF} = 2.0$ Hz); CC-MS m/z (relative intensity): 207 ${}^{3}J_{CF} = 2.0 \text{ Hz}, {}^{4}J_{CF} = 2.0 \text{ Hz}$; GC–MS, m/z (relative intensity): 207 $(M^{+}-C_{2}H_{5}, 31.81), 105 (74.81), 95 (50.76), 93 (53.75), 77 (100.00);$ HRMS: $C_9H_{17}F_2OSi$ (M⁺– C_2H_5) (calculated: 207.1017, observed: 207.1014).

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3.17. Preparation of (E)-4,5-difluoro-5-(meta-trifluoromethyphenyl)-4-penten-1-ol, (E)-HOCH₂CH₂CH₂CF=CFC₆H₄CF₃-m (**14**)

General procedure: A 50 mL two-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with $Pd(PPh_3)_4$ (0.15 g, 3–5 mol%), copper (I) iodide (0.19 g, 1.0 mmol), 5 mL of dry DMF, 3-iodobenzotrifluoride (0.72 g, 2.6 mmol), and 12 (1.00 g, 2.40 mmol). The reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was stirred with Co(OAc)₂ (0.86 g 4.8 mmol) and 3 mL of extra DMF for 2 h. Then, the reaction mixture was poured over water (15 mL) in a separatory funnel and extracted with ether (2×15 mL). The combined ether layers were washed with water (15 mL). The organic layer was dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using a mixture of 80% hexanes and 20% EtOAc as eluent to give 14 (0.40 g, 62% isolated yield, $R_{\rm f}$ (80% hexanes, 20% EtOAc) = 0.11, purity by ¹H NMR = 99%); ¹⁹F NMR (CDCl₃): -63.4 ppm (s, 3F), -143.6 ppm (dt, 1F, ${}^{3}J_{FF}$ = 122.8 Hz, ${}^{3}J_{FH}$ = 23.7 Hz), -160.0 ppm (dt, 1F, ${}^{3}J_{FF}$ = 122.8 Hz, ${}^{4}J_{FH}$ = 5.4 Hz); 1 H NMR (CDCl₃): 7.9 ppm (s, 1H), 7.8 ppm (d, 1H, $J_{\rm HH}$ = 7.6 Hz), 7.6 ppm (d, 1H, $^{3}J_{\rm HH}$ = 7.9 Hz), 7.5 ppm (dd, 1H, ${}^{3}J_{\text{HH}}$ = 7.8 Hz, ${}^{3}J_{\text{HH}}$ = 7.6 Hz), 3.8 ppm (t, 2H, ${}^{3}J_{\text{HH}}$ = 6.3 Hz), 2.7 ppm $(dtd, 2H, {}^{3}J_{HF} = 23.7 \text{ Hz}, {}^{3}J_{HH} = 7.4 \text{ Hz}, {}^{4}J_{HF} = 5.6 \text{ Hz}), 1.9 \text{ ppm} (pent, 1.9 \text{ ppm})$ 2H, ${}^{3}J_{HH}$ = 6.4 Hz), 1.7 ppm (s, 1H); ${}^{13}C$ NMR (CDCl₃): 153.32 ppm (dd, ${}^{1}J_{CF}$ = 250.3 Hz, ${}^{2}J_{CF}$ = 55.9 Hz), 145.94 ppm (dd, ${}^{1}J_{CF}$ = 224.2 Hz, ${}^{2}J_{CF} = 43.5$ Hz), 131.00 ppm (qd, ${}^{2}J_{CF} = 33.5$ Hz, ${}^{4}J_{CF} = 2.3$ Hz), 130.60 ppm (dd, ${}^{2}J_{CF} = 25.7$ Hz, ${}^{3}J_{CF} = 6.5$ Hz), 128.98 ppm (d, ${}^{4}J_{CF}$ = 2.3 Hz), 128.22 ppm (dd, ${}^{3}J_{CF}$ = 8.6 Hz, ${}^{4}J_{CF}$ = 8.1 Hz), 125.00 ppm (m), 123.97 ppm (q, ${}^{1}J_{CF}$ = 272.0 Hz), 121.96 ppm (m), 61.74 ppm (s), 28.77 ppm (d, ${}^{3}J_{CF}$ = 1.9 Hz), 24.06 ppm (d, ${}^{2}I_{CF}$ = 24.3 Hz); GC–MS, m/z (relative intensity): 266 (M⁺, 29.58), 248 (81.25), 233 (65.74), 213 (54.09), 201 (71.65), 179 (100.00), 164 (61.63), 151 (60.12); HRMS: C₁₂H₁₁F₅O (calculated: 266.0730, observed: 266.0729).

3.18. Preparation of (E)-4,5-difluoro-5-(meta-nitrophenyl)-4penten-1-ol, (E)-HOCH₂CH₂CH₂CF=CFC₆H₄NO₂-m (**15**)

Similar to the procedure described in Section 3.17. 1-Iodo-3nitrobenzene (0.55 g 2.2 mmol), 12 (0.82 g, 2.0 mmol), Pd(PPh₃)₄ (0.13 g, 3-5 mol%), Cu(I)I (0.19 g, 1.1 mmol), and 5 mL of dry DMF. The reaction mixture was stirred 12 h at room temperature. After standard workup, the crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give **15** (0.25 g, 52% isolated yield, R_f (88%) hexanes, 12% EtOAc) = 0.04, purity by 1 H NMR = 97%); 19 F NMR $(\text{CDCl}_3): -141.6 \text{ ppm}$ (dt, 1F, ${}^{3}J_{\text{FF}} = 123.7 \text{ Hz}$, ${}^{3}J_{\text{FH}} = 23.3 \text{ Hz}$), -160.0 ppm (dt, 1F, ${}^{3}J_{\text{FF}} = 123.2 \text{ Hz}$, ${}^{4}J_{\text{FH}} = 5.4 \text{ Hz}$); 1H NMR (CDCl₃): - 160.0 ppm (dt, 1F, ${}^{7}_{JFF}$ = 123.2 Hz, ${}^{7}_{FH}$ = 5.4 Hz); ${}^{7}_{H}$ MMR (CDCl₃): 8.5 ppm (m, 1H), 8.2 ppm (dm, 1H, ${}^{3}_{J_{HH}}$ = 8.3 Hz), 7.9 ppm (dm, 1H, ${}^{3}_{J_{HH}}$ = 8.0 Hz), 7.6 ppm (dd, 1H, ${}^{3}_{J_{HH}}$ = 8.1 Hz, ${}^{3}_{J_{HH}}$ = 8.0 Hz), 3.8 ppm (t, 2H, ${}^{3}_{J_{HH}}$ = 6.1 Hz), 2.7 ppm (ddt, 2H, ${}^{3}_{J_{HF}}$ = 23.7 Hz, ${}^{4}_{J_{HF}}$ = 7.5 Hz, ${}^{3}_{J_{HH}}$ = 5.7 Hz), 1.9 ppm (pent, 2H, ${}^{3}_{J_{HH}}$ = 7.3 Hz), 1.7 ppm (s, 1H); 13 C NMR (CDCl₃): 154.17 ppm (dd, ${}^{1}_{J_{CF}}$ = 252.0 Hz, ${}^{2}_{J_{CF}}$ = 54.8 Hz), 145.17 ppm (dd, ${}^{1}_{J_{CF}}$ = 224.81 Hz, ${}^{2}_{J_{CF}}$ = 43.8 Hz), 148.38 ppm (s), 131.42 ppm (dd, ${}^{2}_{J_{CF}}$ = 26.4 Hz, ${}^{3}_{J_{CF}}$ = 6.5 Hz), 130.64 ppm (dd, ${}^{3}J_{CF} = 9.7$ Hz, ${}^{4}J_{CF} = 6.7$ Hz), 129.54 ppm (d, $J_{CF} = 2.9 \text{ Hz}$), 122.95 ppm (d, $J_{CF} = 2.0 \text{ Hz}$), 120.02 ppm (dd, ${}^{3}J_{CF}$ = 10.7 Hz, ${}^{4}J_{CF}$ = 7.8 Hz), 61.67 ppm (s), 28.67 ppm (dd, ${}^{3}J_{CF}$ = 2.3 Hz, ${}^{4}J_{CF}$ = 2.3 Hz), 24.14 ppm (d, ${}^{2}J_{CF}$ = 23.4 Hz); GC– MS, *m*/*z* (relative intensity): 243 (M⁺, 8.65), 164 (87.60), 151 (100.00); HRMS: C₁₁H₁₁F₂NO₃ (calculated: 243.07070, observed: 243.07074).

3.19. Preparation of (E)-4,5-difluoro-5-phenyl-4-penten-1-ol, (E)-HOCH₂CH₂CH₂CF=CFC₆H₅ (**16**)

Similar to the procedure described in Section 3.17. 1lodobenzene (0.45 g, 2.2 mmol), **12** (0.71 g, 1.7 mmol), Pd(PPh₃)₄ (0.13 g, 3–5 mol%), Cu(1)I (0.19 g, 1.1 mmol), and 5 mL of dry DMF. The reaction mixture was stirred 36 h at room temperature. After standard workup, the crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give **16** (0.24 g, 71% isolated yield, R_f (88% hexanes, 12% EtOAc) = 0.12, purity by ¹H NMR = 99%); ¹⁹F NMR (CDCl₃): -146.2 ppm (dt, 1F, ³J_{FF} = 121.7 Hz, ³J_{FH} = 23.9 Hz), -159.2 ppm (dt, 1F, ³J_{FF} = 122.6 Hz, ⁴J_{FH} = 6.0 Hz); ¹H NMR (CDCl₃): 7.6 ppm (dm, 2H, ³J_{HH} = 7.3 Hz), 7.4 ppm (t, 2H, ³J_{HH} = 7.9 Hz), 7.3 ppm (m, 1H), 3.7 ppm (t, 2H, ³J_{HH} = 6.4 Hz), 2.7 ppm (dtd, 2H, ³J_{HH} = 6.8 Hz), 1.6 ppm (s, 1H); ¹³C NMR (CDCl₃): 151.99 ppm (dd ¹J_{CF} = 247.6 Hz, ²J_{CF} = 57.0 Hz), 147.04 ppm (dd, ¹J_{CF} = 224.8 Hz, ²J_{CF} = 44.2 Hz), 129.78 ppm (dd, ²J_{CF} = 7.2 Hz), 61.80 ppm (s), 28.89 ppm (dd, ³J_{CF} = 2.1 Hz, ⁴J_{CF} = 1.9 Hz), 23.97 ppm (d, ²J_{CF} = 23.9 Hz); GC–MS, *m*/z (relative intensity): 198 (M⁺, 26.10), 165 (100.00), 133 (84.70); HRMS: C₁₁H₁₂F₂O (calculated:198.0856, observed 198.0850).

3.20. Preparation of (E)-4,5-difluoro-5-(para-tolyl)-4-penten-1-ol, (E)-HOCH₂CH₂CH₂CF=CFC₆H₄CH₃-p (**17**)

Similar to the procedure described in Section 3.17. 4-Iodotoluene (0.06 g, 0.3 mmol), **12** (0.10 g, 0.24 mmol), Pd(PPh₃)₄ (0.02 g (3-5 mol%), Cu(I)I (0.02 g, 0.1 mmol), and 1 mL of dry DMF. The reaction mixture was stirred 36 h at room temperature. After standard workup, the crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give **17** (0.03 g, 60% isolated yield, $R_{\rm f}$ (88% hexanes, 12% EtOAc) = 0.10, purity by ¹H NMR = 85%); ¹⁹F NMR $(CDCl_3)$: -147.4 ppm (dt, 1F, ${}^{3}J_{FF} = 122.3$ Hz, ${}^{3}J_{FH} = 23.2$ Hz), $-159.1 \text{ ppm} (\text{dt}, 1\text{F}, {}^{3}J_{\text{FF}} = 122.3 \text{ Hz}, {}^{4}J_{\text{FH}} = 5.6 \text{ Hz}); {}^{1}\text{H} \text{NMR} (\text{CDCl}_{3}):$ 7.5 ppm (d, 2H, ${}^{3}J_{HH} = 8.4 \text{ Hz}$), 7.2 ppm (d, 2H, ${}^{3}J_{HH} = 8.0 \text{ Hz}$), 3.7 ppm (m, 2H), 2.7 ppm (dtd, 2H, ${}^{3}J_{HF}$ = 23.7 Hz, ${}^{3}J_{HH}$ = 7.4 Hz, ${}^{4}J_{\rm HF}$ = 5.6 Hz), 2.4 ppm (s, 3H), 1.9 ppm (pent, 2H, ${}^{3}J_{\rm HH}$ = 6.9 Hz), 1.7 ppm (s, 1H); 13 C NMR (CDCl₃): 151.36 ppm (dd, ${}^{1}J_{CF}$ = 246.3 Hz, ${}^{2}J_{CF}$ = 56.7 Hz), 147.24 ppm (dd, ${}^{1}J_{CF}$ = 223.9 Hz, ${}^{2}J_{CF}$ = 43.9 Hz), 138.42 ppm (d, ${}^{5}J_{CF}$ = 2.3 Hz), 129.07 ppm (d, ${}^{4}J_{CF}$ = 1.63 Hz), 126.96 ppm (dd, ${}^{2}J_{CF}$ = 24.8 Hz, ${}^{3}J_{CF}$ = 6.2 Hz), 125.09 ppm (dd, ${}^{3}J_{CF}$ = 8.6 Hz, ${}^{4}J_{CF}$ = 7.1 Hz), 61.82 ppm (s), 28.93 ppm (dd, ${}^{3}J_{CF}$ = 2.2 Hz, ${}^{4}J_{CF}$ = 1.6 Hz), 23.90 ppm (d, ${}^{2}J_{CF}$ = 24.0 Hz), 21.30 ppm (s); GC-MS, *m*/*z* (relative intensity): 212 (M⁺, 39.61), 179 (100.00), 164 (56.91), 147 (72.09), 136 (62.63); HRMS: C₁₂H₁₄F₂O (calculated: 212.1013, observed: 212.1015).

3.21. Preparation of (E)-4,5-difluoro-5-(para-methoxyphenyl)-4penten-1-ol, (E)-HOCH₂CH₂CH₂CF=CFC₆H₄OCH₃-p (**18**)

Similar to the procedure described in Section 3.17. 3-Iodoanisole (0.93 g, 40 mmol), **12** (1.48 g, 3.60 mmol), Pd(PPh₃)₄ (0.23, 3–5 mol%), Cu(1)I (0.34 g, 1.8 mmol), and 6 mL of dry DMF. The reaction mixture was stirred 36 h at room temperature. After standard workup, the crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give **18** (0.60 g, 73% isolated yield, R_f (88% hexanes, 12% EtOAc) = 0.07, purity by ¹H NMR = 99%); ¹⁹F NMR (CDCl₃): -149.0 ppm (dt, 1F, ³ J_{FF} = 122.6 Hz, ³ J_{FH} = 23.9 Hz), -158.4 ppm (dt, 1F, ³ J_{FF} = 122.8 Hz, ⁴ J_{FH} = 4.8 Hz); ¹H NMR (CDCl₃): 7.5 ppm (dm, 2H, ³ J_{HH} = 9.1 Hz), 6.9 ppm (dd, 2H, ³ J_{IHH} = 9.1 Hz,

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⁴*J*_{HF} = 0.7 Hz), 3.8 ppm (s, 3H), 3.7 ppm (t, 2H, ³*J*_{HH} = 6.4 Hz), 2.7 ppm (dtd, 2H, ³*J*_{HF} = 23.7 Hz, ³*J*_{HH} = 7.3 Hz, ⁴*J*_{HF} = 5.6 Hz), 1.9 ppm (pent, 2H, ³*J*_{HH} = 6.9 Hz), 2.4–1.5 ppm (s, 1H); ¹³C NMR (CDCl₃): 159.37 ppm (d, ⁵*J*_{CF} = 2.5 Hz), 150.63 ppm (dd, ¹*J*_{CF} = 245.0 Hz, ²*J*_{CF} = 57.2 Hz), 146.94 ppm (dd, ¹*J*_{CF} = 223.9 Hz, ²*J*_{CF} = 45.4 Hz), 126.56 ppm (dd, ³*J*_{CF} = 8.6 Hz, ⁴*J*_{CF} = 7.2 Hz), 122.32 ppm (dd, ²*J*_{CF} = 25.6 Hz, ³*J*_{CF} = 5.5 Hz), 113.68 ppm (d, ⁴*J*_{CF} = 1.8 Hz), 61.57 ppm (s), 55.11 ppm (s), 28.83 ppm (dd, ³*J*_{CF} = 2.0 Hz, ⁴*J*_{CF} = 1.6 Hz), 23.74 ppm (d, ²*J*_{CF} = 23.6 Hz); GC–MS, *m/z* (relative intensity): 228 (M⁺, 59.45), 183 (100,00), 152 (83.11), 139 (65.79); HRMS: C₁₂H₁₄F₂O₂ (calculated: 228.0962, observed 228.0957).

3.22. Preparation of (Z)-4,5-difluoro-5-iodo-4-penten-1-ol, (Z)-HOCH₂CH₂CH₂CF=CFI (**19**)

A 50 mL two necked, round bottomed flask equipped with a nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with of iodine (0.50 g, 2.0 mmol). Next, **12** (0.82 g, 2.0 mmol) was added. The solution turned dark very slowly and was exothermic. Eventually, the reaction mixture changed colors from a dark brown to clear. 19 did not flash distil, so the mixture was added to ether (15 mL) and washed with saturated aqueous KF (2×15 mL) in a separatory funnel to remove ISnBu₃-*n*. The mixture was washed with water $(1 \times 15 \text{ mL})$ and dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation. Since ISnBu₃-n remained, 15 mL of DMF and Co(OAc)₂ (0.36 g 4.0 mmol) was added and stirred for 1 h. The product was added directly onto a silica gel column and eluted with hexanes: EtOAc (80:20) to give **19** (0.31 g, 63% isolated yield, $R_{\rm f}$ (80% hexanes, 20% EtOAc) = 0.12, purity by ¹H NMR = 98%); ¹⁹F NMR (CDCl₃): -127.6 ppm (dt, 1F, ${}^{3}J_{FF} = 141.3$ Hz, ${}^{4}J_{FH} = 5.7$ Hz), -130.4 ppm (dt, 1F, ${}^{3}J_{FF} = 141.3 \text{ Hz}$, ${}^{3}J_{FH} = 21.5 \text{ Hz}$); ${}^{1}\text{H}$ NMR (CDCl₃): 3.6 ppm (t, 2H, ${}^{3}J_{HH} = 6.2$ Hz), 2.6 ppm (dtd, 2H, ${}^{3}J_{HF} = 21.5$ Hz, ${}^{3}J_{HH} = 7.3$ Hz, ${}^{4}J_{HF} = 6.0$ Hz), 1.9 ppm (s, 1H), 1.7 (pent, 2H, ${}^{3}J_{HH} = 6.8 \text{ Hz}$); ${}^{13}C$ NMR (CDCl₃): 155.83 ppm (dd, $^{1}J_{CF} = 243.9$ Hz, $^{2}J_{CF} = 40.6$ Hz), 95.65 ppm (dd, $^{1}J_{CF} = 306.0$ Hz, ${}^{2}J_{CF} = 66.4 \text{ Hz}$), 60.31 ppm (s), 27.48 ppm (dd, ${}^{3}J_{CF} = 2.1 \text{ Hz}$, ${}^{4}J_{CF}$ = 2.1 Hz), 22.80 ppm (d, ${}^{2}J_{CF}$ = 23.9 Hz); GC–MS, m/z (relative intensity): 248 (M⁺, 8.55), 230 (81.22), 103 (100.00), 83 (61.82); HRMS: C₅H₇F₂IO (calculated: 247.9510, observed: 247.9526).

3.23. Preparation of (E)-4,5-difluoro-5-(metatrifluoromethyphenyl)-4-penten-1-acetate, (E)-CH₃C(0)OCH₂CH₂CH₂CF=CFC₆H₄CF₃-m (**20**)

A 15 mL two-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with 1.1 mL of pyridine, 14 (0.10 g, 0.38 mmol), and acetic anhydride (0.15 g, 1.5 mmol). The reaction was stirred at room temperature for 5 h. Next, 5 mL of water was added and the reaction was stirred overnight at room temperature. The reaction mixture was added to ether (25 mL) in a separatory funnel and washed with water (2×15 mL). The organic layer was dried over MgSO₄, filtered and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give **20** (0.09 g, 77% isolated yield, $R_{\rm f}$ (88% hexanes, 12% EtOAc) = 0.37, purity by ¹H NMR = 99%); ¹⁹F NMR $(CDCl_3)$: -63.4 ppm (s, 3F), -144.3 ppm (dt, 1F, ${}^{3}J_{FF}$ =122.3 Hz, ^(c) ${}^{3}J_{HF} = 23.2 \text{ Hz}, {}^{3}J_{HH} = 7.3 \text{ Hz}, {}^{4}J_{HF} = 5.6 \text{ Hz}), 2.1 \text{ ppm } (s, 3H), 2.0 \text{ ppm}$ (pent, 2H, ${}^{3}J_{HH} = 7.3 \text{ Hz}); {}^{13}C \text{ NMR} (CDCl_3): 171.06 \text{ ppm } (s),$ 152.60 ppm (dd, ${}^{1}J_{CF}$ = 250.1 Hz, ${}^{2}J_{CF}$ = 56.0 Hz), 146.04 ppm, dd, ${}^{1}J_{CF}$ = 225.2 Hz, ${}^{2}J_{CF}$ = 42.8 Hz), 130.99 ppm (qd, ${}^{2}J_{CF}$ = 32.5 Hz, ${}^{4}J_{CF}$ = 2.3 Hz), 130.44 ppm (dd, ${}^{2}J_{CF}$ = 25.8 Hz, ${}^{3}J_{CF}$ = 6.0 Hz), 128.98 ppm (d, ${}^{4}J_{CF}$ = 2.8 Hz), 128.23 ppm (dd, ${}^{3}J_{CF}$ = 95 Hz, ${}^{4}J_{CF}$ = 7.7 Hz), 123.91 ppm (q, ${}^{1}J_{CF}$ = 272.2 Hz), 125.09 ppm (m), 122.00 ppm (m), 63.24 ppm (s), 24.94 ppm (s), 24.30 ppm (d, ${}^{2}J_{CF}$ = 22.9 Hz), 20.89 ppm (s); GC–MS, *m/z* (relative intensity): 308 (M⁺, 0.29), 289 (7.97), 248 (82.62), 179 (100.00); HRMS: C₁₄H₁₃F₅O₂ (calculated: 308.0836, observed: 308.0854, (M⁺-F) calculated: 289.0852, observed: 289.0844).

3.24. Preparation of (E)-1,2-difluoro-1-(metatrifluoromethylphenyl)-5-bromo-1-pentene, (E)- $BrCH_2CH_2CH_2CF=CFC_6H_4CF_3-m$ (**21**)

A 15 mL two necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with PPh_3 (0.10 g, 0.40 mmol) and 14 (0.10 g 0.37 mmol). Next, 1 mL of DMF was added and the mixture was stirred to dissolve the solids. Then, Br₂ was added dropwise until the orange color persisted. The reaction mixture was stirred overnight. The reaction mixture was added to water (15 mL) in a separatory funnel and washed with ether ($2 \times$ 20 mL). The combined ether layers were washed with water (2 \times 15 mL), dried over MgSO₄, filtered and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give **21** (0.10 g, 83% isolated yield, $R_{\rm f}$ (88% hexanes, 12% EtAcO) = 0.51, purity by ¹H NMR = 97%); ¹⁹F NMR $(CDCl_3)$: -63.4 ppm (s, 3F), -144.3 ppm (dt, 1F, ${}^{3}J_{FF}$ = 123.6 Hz, ${}^{3}J_{FH}$ = 23.4 Hz), -159.1 ppm (dt, ${}^{3}J_{FF}$ = 123.7 Hz, ${}^{4}J_{FH}$ = 5.3 Hz); ¹H NMR (CDCl₃): 7.9 ppm (s, 1H), 7.8 ppm (d, 1H, ${}^{3}J_{HH}$ = 7.8 Hz), 7.6 ppm (d, 1H, ${}^{3}J_{HH}$ = 7.9 Hz), 7.6 ppm (dd, 1H, ${}^{3}J_{HH}$ = 7.8 Hz, ${}^{3}J_{\text{HH}}$ = 7.6 Hz), 3.5 ppm (t, 2H, ${}^{3}J_{\text{HH}}$ = 6.7 Hz), 2.8 ppm (dtd, 2H, ${}^{3}J_{\rm HF} = 23.2$ Hz, ${}^{3}J_{\rm HH} = 7.5$ Hz, ${}^{4}J_{\rm HF} = 5.4$ Hz), 2.2 ppm (pent, 2H, ${}^{3}J_{\text{HH}}$ = 6.9 Hz); 13 C NMR (CDCl₃): 152.17 ppm (dd, ${}^{1}J_{\text{CF}}$ = 250.4 Hz, $^{2}J_{CF} = 55.6 \text{ Hz}$, 146.29 ppm (dd, $^{1}J_{CF} = 225.8 \text{ Hz}$, $^{2}J_{CF} = 43.6 \text{ Hz}$), 131.04 ppm (qd, $^{2}J_{CF} = 32.6 \text{ Hz}$, $^{4}J_{CF} = 2.8 \text{ Hz}$), 130.38 ppm (dd, ${}^{2}J_{CF} = 25.7 \text{ Hz}, \quad {}^{3}J_{CF} = 5.8 \text{ Hz}), \quad 129.02 \text{ ppm} \quad (d, \quad {}^{4}J_{CF} = 2.2 \text{ Hz}),$ 128.29 ppm (dd, ${}^{3}J_{CF} = 8.6$ Hz, ${}^{4}J_{CF} = 8.6$ Hz), 125.20 ppm (m), 123.92 ppm (q, ${}^{1}J_{CF}$ = 272.1 Hz), 122.06 ppm (m), 32.05 ppm (s), 28.95 ppm (dd, ${}^{3}J_{CF}$ = 1.8 Hz, ${}^{4}J_{CF}$ = 1.8 Hz), 26.28 ppm (d, ${}^{2}J_{CF}$ = 23.9 Hz), GC-MS, *m*/*z* (relative intensity): 328 (M⁺, 68.47) 330 (M²⁺, 66.84), 221 (88.33), 201 (100.00), 151 (81.33); HRMS: C₁₂H₁₀⁷⁹BrF₅ (calculated: 327.9886, observed: 327.9893).

3.25. (E)-1,2-Difluoro-1-(meta-nitrophenyl)-5-bromo-1-pentene, (E)-BrCH₂CH₂CH₂CF=CFC₆H₄NO₂-m (**22**)

A 15 mL two-necked, round bottomed flask equipped with a water condenser, nitrogen gas inlet, Teflon coated magnetic stir bar, and a rubber septum port was charged with PPh_3 (0.14 g, 0.54 mmol) and 15 (0.12 g, 0.50 mmol). Next, 1.5 mL of DMF was added and the mixture was stirred to dissolve the solids. Then, Br₂ was added dropwise until the orange color persisted. The reaction mixture was stirred overnight at room temperature. The reaction mixture was added to water (15 mL) in a separatory funnel and washed with ether (2×20 mL). The combined ether layers were washed with water $(2 \times 15 \text{ mL})$ dried over MgSO₄, filtered and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using a mixture of 88% hexanes and 12% EtOAc as eluent to give 22 (0.10 g, 67% isolated yield, R_f (88% hexanes, 12% EtOAc) = 0.30, purity by ¹H NMR = 97%); ¹⁹F NMR (CDCl₃): -142.4 ppm (dt, 1F, ³ J_{FF} = 123.2 Hz, ${}^{3}J_{FH} = 22.8 \text{ Hz}$, -159.0 ppm (dt, 1F, ${}^{3}J_{FF} = 123.1 \text{ Hz}$, ${}^{4}J_{FH} = 5.6 \text{ Hz}$); ${}^{1}\text{H}$ NMR (CDCl₃): 8.5 ppm (dd, 1H, ${}^{3}J_{HF} = 2.0 \text{ Hz}$, ${}^{4}J_{HF} = 1.9 \text{ Hz}$), 8.2 ppm (ddd, 1H, ${}^{3}J_{HH} = 8.1 \text{ Hz}$, ${}^{5}J_{HF} = 2.3 \text{ Hz}$, ${}^{6}J_{HF} = 1.1 \text{ Hz}$),

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7.9 ppm (ddd, 1H, ${}^{3}J_{HH} = 8.0$ Hz, ${}^{3}J_{HF} = 1.5$, ${}^{4}J_{HF} = 1.1$ Hz), 7.6 ppm (dd, 1H, ${}^{3}J_{HH} = 8.1$ Hz, ${}^{3}J_{HH} = 8.0$ Hz), 3.5 ppm (t, 2H, ${}^{3}J_{HH} = 6.6$ Hz), 2.8 ppm (dtd, 2H, ${}^{3}J_{HF} = 23.2$ Hz, ${}^{3}J_{HH} = 7.0$ Hz, ${}^{4}J_{HF} = 5.6$ Hz), 2.2 ppm (pent, 2H, ${}^{3}J_{HH} = 6.9$ Hz); ${}^{13}C$ NMR (CDCl₃): 152.96 ppm (dd, ${}^{1}J_{CF} = 251.4$ Hz, ${}^{2}J_{CF} = 55.2$ Hz), 145.57 ppm (dd, ${}^{1}J_{CF} = 26.3$ Hz, ${}^{2}J_{CF} = 43.3$ Hz), 148.42 ppm (s), 131.19 ppm (dd, ${}^{2}J_{CF} = 26.7$ Hz, ${}^{3}J_{CF} = 7.0$ Hz), 130.68 ppm (dd, ${}^{3}J_{CF} = 9.9$ Hz, ${}^{4}J_{CF} = 7.7$ Hz), 129.58 ppm (d, ${}^{3}J_{CF} = 9.4$ Hz, ${}^{4}J_{CF} = 7.6$ Hz) 31.98 ppm (s), 28.80 ppm (s), 26.31 ppm (d, ${}^{2}J_{CF} = 23.1$ Hz), GC–MS, m/z (relative intensity): 305 (M⁺, 43.11), 307 (M²⁺, 46.17), 198 (55.78), 152 (82.52), 151 (100.00); HRMS: C₁₁H₁₀⁷⁹BrF₂NO₂ (calculated: 304.9863, observed: 304.9855, (M²⁺) calculated: 306.9843, observed: 306.9834).

4. Conclusions

(Z)-H₂C=CHCH₂CF=CFSnBu₃ (**2**) can be readily prepared from **1**, KF, and ClSn(*n*-Bu)₃ in DMF. **2** was coupled with substituted aryl iodides under Stille–Liebeskind conditions to afford good yields to the corresponding 1,2-difluoro-1-aryl-1,4-pentadiene (**4–9**). Both electron withdrawing groups and electron releasing groups worked equally well during the coupling procedure. Hydroboration/oxidation of **2** with 9-BBN in THF produced the corresponding (*Z*)-HOCH₂CH₂CF=CFSn(*n*-Bu)₃ (**12**). Coupling of (*Z*)-HOCH₂ CH₂CH₂CF=CFSn(*n*-Bu)₃ (**12**) with substituted aryl iodides under Stille–Liebeskind conditions gave the corresponding (*E*)-4,5difluoro-5-aryl-4-penten-1-ol (**14–18**). Reaction of (*Z*)-HOCH₂ CH₂CH₂CF=CFSn(*n*-Bu)₃ (**12**) with I₂ (neat) gave (*Z*)-HOCH₂CH₂ CH₂CF=CFI (**19**).

References

- [1] C. Lim, C.A. Wesolowski, D.J. Burton, J. Fluorine Chem. 159 (2014) 21-28.
- [2] C. Lim, D.J. Burton, J. Fluorine Chem. 167 (2014) 61–73.
- [3] For a general survey of F-induced reactions with fluoroolefins: R.D. Chambers, Fluorine in Organic Chemistry, second ed., Wiley Blackwell, Oxford, UK, 2004, pp. 185–191.
- [4] S.D. Pedersen, D.J. Burton, J. Fluorine Chem. 155 (2013) 39–44.
- [5] Q. Liu, D.J. Burton, Org. Lett. 4 (2002) 1483–1485.
- [6] D.J. Burton, C.A. Wesolowski, Q. Liu, C.R. Davis, J. Fluorine Chem. 131 (2010) 989–995.
- [7] L. Xue, L. Lu, S.D. Pederson, Q. Liu, R.M. Narske, D.J. Burton, J. Org. Chem. 62 (1997) 1064–1071.
- [8] L.S. Liebeskind, R.W. Fengl, J. Org. Chem. 55 (1990) 5359–5364.
- [9] E.J. Blumenthal, D.J. Burton, Isr. J. Chem. 39 (1999) 109–115.
- [10] H.C. Brown, Organic Synthesis via Boranes, John Wiley & Sons, New York, 1975, pp. 40–41.
- [11] J.A. Akers, T.A. Bryson, Synth. Commun. 20 (1990) 3453–3458.
- [12] D.R. Coulson, Inorg. Synth. 13 (1972) 121-124.
- [13] G.B. Kauffman, L.Y. Fang, Inorg. Synth. 22 (1983) 101–103.
- [14] S.A. Fontana, C.R. Davis, Y.-B. He, D.J. Burton, Tetrahedron 52 (1996) 37-44.
- [15] P.L. Heinze, D.J. Burton, J. Org. Chem. 53 (1988) 2714–2720.
 [16] P.L. Heinze, T.D. Spawn, D.J. Burton, S. Shin-Ya, J. Fluorine Chem. 38 (1988)
- 101 La Tichick, T.D. Spawn, D.J. Burton, S. Shin-Td, J. Fluotine Chefil. 38 (1988) 131-134. 1171 D.I. Burton T.D. Snawn, P.I. Hainza, A.P. Bailay, S. Shin, Va. J. Eluorine, Chem. 44
- [17] D.J. Burton, T.D. Spawn, P.L. Heinze, A.R. Bailey, S. Shin-Ya, J. Fluorine Chem. 44 (1989) 167–174.
- [18] P. Knochel, J.F. Normant, Tetrahedron Lett. 25 (1984) 1475–1478.

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