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The stereospecific preparation of (*E*)-1,2-difluoro-1,2-disubstituted alkenes

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ABSTRACT

(*Z*)-1,2-difluoro-2-substituted vinyl silanes were prepared stereospecifically from chlorotrifluoroethene, chlorotrimethylsilane and alkyl or aryllithium reagents. Subsequent exchange of the trimethylsilyl group *via* reaction of the vinylsilane with KF/*n*-Bu_3SnCl/DMF stereospecifically afforded the corresponding (*Z*)-1,2-difluoro-2-substituted vinyl stannanes. $Pd(PPh_3)_4$/Cu(I)I/DMF coupling of the vinyl stannanes with substituted aromatic iodides stereospecifically provided the (*E*)-1,2-difluoro-1-substituted aryl-alkenes in excellent yield.

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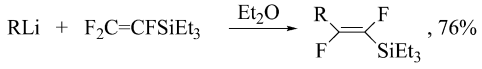
1. Introduction

The unique properties of fluoroorganic compounds, which contain one or more fluorines at strategic positions in the molecule, continue to attract the interest of polymer chemists, pharmaceutical chemists and agrochemists [1]. In most cases, only an isolated saturated hydrogen or one vinyl hydrogen was replaced by fluorine. Recent reports from our laboratory have demonstrated the utility of fluorine-containing vinyl stannanes as useful synthons for the preparation of fluoroolefin derivatives [2–13]. Although the introduction of the (*E*)-1,2-difluoroethene unit into organic compounds has been investigated by Normant and co-workers [14], a stereospecific entry into 1,2-disubstituted-1,2-difluoroolefins had not been described. Our work with 1,2-difluorostannanes suggested a useful synthetic methodology into this class of compounds, and this work outlines a stereospecific route to (*E*)-1,2-difluoro-1,2-disubstituted olefins [13].

2. Results and discussion

2.1. Preparation of (*Z*)-1,2-difluoro-2-substituted vinyl silanes and vinyl stannanes

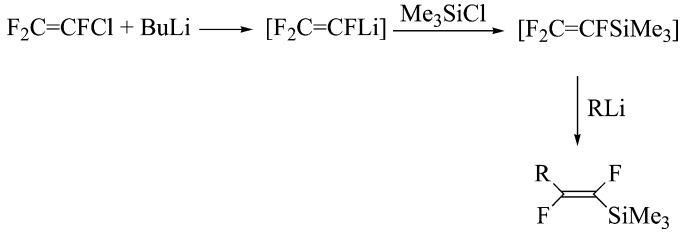
Seyferth and Wada reacted several organolithium reagents or Grignard reagents with $F_2C{=}CFSiEt_3$ and obtained only the monosubstituted (*Z*)-1,2-difluorovinylsilane [15], Eq. (1).



(1)

R = *n*-Bu, C_6H_5, vinyl, allyl

The corresponding perfluorovinyltin gave only an exchange reaction with organolithium reagents to form the unstable perfluorovinyllithium [15,16]. Subsequently, Normant and co-workers demonstrated that the corresponding trifluorovinyltrimethylsilane could be generated *in situ* from chlorotrifluoroethene and reacted with an equivalent of a different organolithium reagent to provide the corresponding Seyferth vinylsilane in one step, [17,18], Eq. (2). The Normant



(2)

methodology works very well and we have utilized this methodology to prepare a variety of (*Z*)-(2-substituted-1,2-difluoroethenylsilanes (both trimethylsilyl and triethylsilyl analogs) [19] either *via* a one-step or two-step process. We discovered

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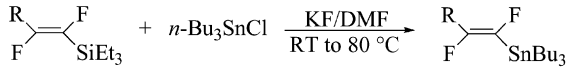
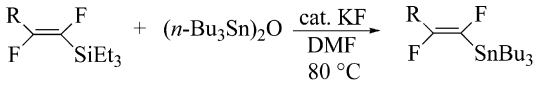
that the monosubstituted-1,2-difluorosilanes could be stereospecifically converted to the corresponding stannanes *via* reaction of the vinylsilane with *n*-Bu_3SnCl and KF in DMF at RT-80 °C or with $Bu_3Sn–O–SnBu_3$ and catalytic KF in DMF at 80 °C [19], Eqs. (3) and (4). This simple 2-step methodology provided a convenient entry



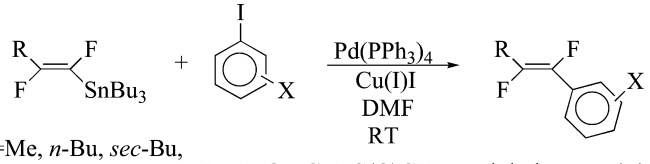
R = H, I, *n*-Bu, *tert*-Bu, Me, *sec*-Bu, Ph (3)



R = Me, *n*-Bu, *sec*-Bu, *tert*-Bu_3, Ph (4)

to the (*Z*)-monosubstituted vinylstannane (*Z*)-(RCF=CFSnBu_3). Although both the trimethyl and triethylsilanes work well in the reactions described in Eqs. (3) and (4), the trimethylsilane is less hindered and is more reactive in the Si–Sn exchange process and is the preferred vinylsilane.

As we have demonstrated several times [2–13], fluorine-containing vinylstannanes readily undergo Stille–Liebeskind coupling with aryl iodides. The preferred conditions utilize $Pd(PPh_3)_4$/Cu(I)I/DMF. $Pd(PPh_3)_4$ or Cu(I) alone do not catalyze the coupling reaction or give low yields of the cross-coupled product. Under the Liebeskind conditions, the (*Z*)-RCF=CFSnBu_3 coupled easily at RT with aryl iodides, Eq. (5).



R=Me, *n*-Bu, *sec*-Bu, *tert*-Bu, C_6H_5 X = NO_2, CN, C(O)CH_3, naphthyl (5)

Table 1 illustrates twelve examples of this methodology.

3. Conclusions

(*E*)-1,2-disubstituted-1-substituted aryl-alkenes were stereospecifically prepared *via* $Pd(PPh_3)_4$/Cu(I)I/DMF coupling at RT of (*Z*)-1,2-difluoro-2-substituted vinyl stannanes with substituted aryl iodides. The requisite (*Z*)-1,2-difluoro-2-substituted vinyl stannanes were prepared by stereospecific Si/Sn exchange from the corresponding (*Z*)-1,2-difluoro-2-substituted vinyl silanes *via* reaction with KF/*n*-Bu_3SnCl/DMF at 80 °C. The (*Z*)-1,2-disubstituted vinylsilanes were prepared from F_2C=CFCl. The (*Z*)-1,2-difluoro-2-substituted vinyl stannanes could also be readily coupled with vinyl halides to stereospecifically prepare fluorine-containing dienes [9], and coupled *via* Cu(II)$(OAc)_2$ to stereospecifically afford symmetrical dienes [12]. The aryl vinyl stannanes, when coupled with substituted aryl iodides, also provide a useful route to unsymmetrical (*E*)-1,2-difluorostilbenes.

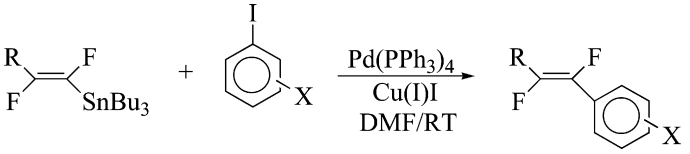
4. Experimental

4.1. General experimental procedures

^{19}F NMR (282.44 MHz), ^{1}H NMR (300.17 MHz), ^{13}C NMR (75.48 MHz) spectra were recorded on an AC-300-MHz multinuclear spectrometer. All samples were taken in $CDCl_3$ solvent and all chemical shifts were recorded in parts per million downfield of the standards. ^{19}F NMR spectra are referenced against internal $CFCl_3$, ^{1}H NMR and ^{13}C NMR spectra against internal TMS. FT-IR spectra were recorded as CCl_4 solutions on a Mattson Cygnus 100-FT-IR using a solution cell with a 0.1 cm path length and absorbance frequencies are reported in cm^{-1}. Low resolution GC–MS spectra were obtained at 70 eV in the electron-impact mode on a TRIO-1 GC–MS instrument. High resolution mass spectra determinations were made at the University of Iowa High Resolution Mass Spectrometry Facility. GLPC analysis was performed on a 5% OV-101 column with a thermal conductivity detector.

All melting points were determined in a 1.2 mm capillary tube in a Thomas-Hoover Unimelt apparatus and are uncorrected.

Table 1
Pd(0) catalyzed coupling of (*Z*)-1,2-difluoroalkenylstannanes with aryl iodides.[a]



Entry	R	X	Yield (%)[b]
1	CH_3	3-NO_2	85
2	CH_3	1-iodonaphthalene	86
3	*n*-Bu	4-CN	90
4	*n*-Bu	3-NO_2	87
5	*sec*-Bu	3-NO_2	83
6	*sec*-Bu	4-CN	86
7	*sec*-Bu	4-NO_2	87
8	*tert*-Bu	2-NO_2	82
9	*tert*-Bu	4-NO_2	92
10	Ph	4-C(O)CH_3	85
11	Ph	4-NO_2	92
12	Ph	4-CN	87

[a] All reactions were performed in DMF at RT on a 1 mmol scale using 3-mol% of $Pd(PPh_3)_4$ and 50 mol% Cu(I)I as catalysts.
[b] Isolated yields based on aryl iodides.

4.2. Materials

Alkyl and aryl lithium reagents were obtained from the Aldrich Chemical Co. and used directly. Bromotrifluoroethene and chlorotrifluoroethene were obtained from PCR Specialty Chemicals. Most aromatic iodides were purchased from Aldrich. 4-iodobenzonitrile was obtained from Kodak. Tributyltin chloride and chlorotrimethylsilane were obtained from Aldrich and used without further purification. KF was dried by refluxing with benzene prior to use. DMF was dried by distillation from CaH_2 and stored under nitrogen. Tetrakis (triphenylphosphine) palladium was prepared by Coulson's procedure [20]. Cu(I)I was purified by the reported procedure [21]. THF was dried by distillation from sodium benzophenone ketyl at ambient pressure. Silica gel was purchased from EM Science (Silica Gel 60, particle size 0.063–0200 μm, 70–230 Mesh, ASTM). All boiling points were determined during fractional distillation using a partial immersion thermometer and are uncorrected.

(*Z*)-1,2-difluoro-1-(trimethylsilyl)-1-propene ($CH_3CF{=}CFSiMe_3$), $CFSiMe_3$), (*Z*)-1,2-difluoro-1-(trimethylsilyl)-1-hexene (*n*-BuCF=$CFSiMe_3$), (*Z*)-1,2-difluoro-3-methyl-1-(trimethylsilyl)-1-pentene (*sec*-BuCF=$CFSiMe_3$), (*Z*)-1,2-difluoro-3, 3-dimethyl-1-(trimethylsilyl)-1-butene (*tert*-BuCF=$CFSiMe_3$), and (*Z*)-1,2-difluoro-1-(trimethylsilyl)-styrene (PhCF=$CFSiMe_3$) were prepared by the literature procedure [19]. (*Z*)-1,2-difluoro-1-(tributylstannyl)-1-propene ($CH_3CF{=}CFSnBu_3$), (*Z*)-1,2-difluoro-1-(tributylstannyl)-1-hexene (*n*-BuCF=$CFSnBu_3$), (*Z*)-1,2-difluoro-3-methyl-1-(tributylstannyl)-1-pentene (*sec*-BuCF=$CFSnBu_3$), (*Z*)-1,2-difluoro-3,3-dimethyl-1-(tributylstannyl)-1-butene (*tert*-BuCF=$CFSnBu_3$), and (*Z*)-1,2-difluoro-1-(tributylstannyl)styrene (PhCF=$CFSnBu_3$) were prepared by the literature procedure [19].

4.3. General procedure for the palladium (0) catalyzed coupling reactions of (Z)-RCF=CFSnBu$_3$ with aryl iodides

4.3.1. Reaction of (Z)-CH$_3$CF=CFSnBu$_3$ with 3-iodonitrobenzene

A 25 ml flask was charged with $Pd(PPh_3)_4$ (0.05 g, 0.043 mmol) Cu(I)I (0.1 g, 0.52 mmol), 3-iodonitrobenzene (0.25 g, 1.0 mmol) and dry DMF (5 ml). Then (*Z*)-$CH_3CF{=}CFSnBu_3$ (0.45 g, 1.2 mmol) was added at RT with stirring. The reaction mixture was stirred for 10 h at RT. Complete disappearance of the vinyl stannane was confirmed by ^{19}F NMR analysis of the reaction mixture. The reaction mixture was then diluted with ether (100 ml) and washed with aqueous KF solution (15%, 50 ml). The ethereal layer was separated, dried over anhydrous $MgSO_4$ and concentrated. The residue was chomatographed on a silica gel column using a mixture of ethyl acetate and hexane (1:20) as eluent to afford 0.17 g (85%) of (*E*)-1,2-difluoro-1-(3-nitrophenyl)-propene as yellow crystals, mp 52–53 °C. ^{19}F NMR: δ −134.5 (dq, $^3J_{FF}$ = 123.3 Hz, $^3J_{HF}$ = 18.5 Hz, 1F), −160.0 (dq, $^3J_{FF}$ = 123.3 Hz, $^4J_{HF}$ = 5.8 Hz, 1F). ^1H NMR: δ 8.42 (t, $^4J_{HH}$ = 1.9 Hz, 1H), 8.15 (ddd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.90 (dt, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz, 1H), 7.57 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 2.25 (dd, $^3J_{HF}$ = 18.0 Hz, $^4J_{HF}$ = 5.2 Hz, 3H); ^{13}C NMR: δ 151.4 (dd, $^1J_{CF}$ = 250.3 Hz, $^2J_{CF}$ = 56.8 Hz), 148.3 (s), 145.0 (dd, $^1J_{CF}$ = 224.0 Hz, $^2J_{CF}$ = 42.7 Hz), 131.4 (dd, $^2J_{CF}$ = 26.2 Hz, $^3J_{CF}$ = 6.7 Hz), 130.4 (dd, $^3J_{CF}$ = 9.8 Hz, $^4J_{CF}$ = 7.3 Hz), 129.4 (d, $^4J_{CF}$ = 2.4 Hz), 122.7 (d, $^5J_{CF}$ = 1.8 Hz), 119.7 (dd, $^4J_{CF}$ = 9.8 Hz, $^5J_{CF}$ = 8.5 Hz), 13.59 (d, $^2J_{CF}$ = 24.4 Hz). GC–MS, *m*/*z* (relative intensity): 199 (M^+, 100), 183 (3), 133 (91). FTIR: 1709.55 (C=C), 1577.42 (NO_2) cm^{-1}; HRMS: calcd for $C_9H_7NF_2O_2$, 199.0445; obsvd 199.0431.

4.3.2. Reaction of (Z)-CH$_3$CF=CFSnBu$_3$ with 1-iodonaphthalene

Similar to *4.3.1*, reaction of (*Z*)-$CH_3CF{=}CFSnBu_3$ (0.92 g, 2.5 mmol) with 1-iodonaphthalene (0.51 g, 2.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.10 g, 0.087 mmol) and Cu(I)I (0.19 g, 1.0 mmol) in dry DMF (10 ml) at RT for 24 h gave 0.35 g (86%) of (*E*)-1,2-difluoro-1-naphthyl-propene as a colorless oil (after chromatography) using hexane as the eluent. ^{19}F NMR: δ −139.7 (dq, $^3J_{FF}$ = 133.5 Hz, $^3J_{HF}$ = 17.2 Hz, 1F), −142.6 (d, $^3J_{FF}$ = 133.5 Hz, 1F); ^1H NMR: δ 8.01 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.79 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 7.57 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.45 (m, 3H), 2.22 (dd, $^3J_{HF}$ = 17.2 Hz, $^4J_{HF}$ = 5.2 Hz, 3H); ^{13}C NMR: δ 149.0 (dd, $^1J_{CF}$ = 237.5 Hz, $^2J_{CF}$ = 54.3 Hz), 147.3 (dd, $^1J_{CF}$ = 227.5 Hz, $^2J_{CF}$ = 48.8 Hz), 133.6 (s), 131.0 (s), 130.3 (s), 128.5 (d, $^3J_{CF}$ = 3.6 Hz), 128.4 (s), 126.6 (s), 126.5 (dd, $^2J_{CF}$ = 22.5 Hz, $^3J_{CF}$ = 2.0 Hz), 126.1 (s), 125.5 (d, $^4J_{CF}$ = 2.4 Hz), 124.9 (s), 12.97 (d, $^2J_{CF}$ = 5.1 Hz). GC–MS, *m*/*z* (relative intensity): 204 (M^+, 100), 189 (M^+-CH_3, 86). FTIR: 1727.70 (C=C) cm^{-1}. HRMS: calcd for $C_{13}H_{10}F_2$, 204.0751, obsvd 204.0747.

4.3.3. Reaction of (Z)-n-BuCF=CFSnBu$_3$ with 4-iodobenzonitrile

Similar to *4.3.1*, reaction of (*Z*)-*n*-BuCF=$CFSnBu_3$ (0.49 g, 1.2 mmol) with 4-iodobenzonitrile (0.23 g, 1.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.05 g, 0.043 mmol), Cu(I)I (0.10 g, 0.52 mmol), in dry DMF (5 ml) at RT for 10 h afforded 0.20 g (90%) of (*E*)-1,2-difluoro-1-(4-cyanophenyl)-1-hexene as a colorless oil (after chromatography) using a mixture of ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: −139.3 (dt, $^3J_{HF}$ = 121.5 Hz, $^3J_{HF}$ = 24.1 Hz, 1F), −161.2 (dt, $^3J_{FF}$ = 121.5 Hz, $^4J_{HF}$ = 5.7 Hz, 1F); ^1H NMR: δ 7.68(AB pattern, 4H), 2.58 (m, 2H), 1.62 (m, 2H), 1.42 (m, 2H), 0.96 (t, $^3J_{HH}$ = 7.3 Hz, 3H); ^{13}C NMR: δ 155.4 (dd, $^1J_{CF}$ = 254.5 Hz, $^2J_{CF}$ = 56.1 Hz), 145.2 (dd, $^1J_{CF}$ = 224.0 Hz, $^2J_{CF}$ = 43.3 Hz), 134.1 (dd, $^2J_{CF}$ = 25.0 Hz, $^3J_{CF}$ = 6.7 Hz), 132.1 (d, $^3J_{CF}$ = 2.4 Hz), 125.2 (dd, $^3J_{CF}$ = 10.4 Hz, $^4J_{CF}$ = 7.9 Hz), 118.5 (s), 111.4 (d, $^5J_{CF}$ = 3.1 Hz), 27.71 (s), 27.3 (d, $^2J_{CF}$ = 22.6 Hz), 21.99 (s), 13.58 (s). GC–MS, *m*/*z* (relative intensity): 221 (M^+, 47), 178 ($M^+-C_3H_7$, 100), 165 ($M^+-C_4H_8$, 69). FTIR: 2231.21 (CN), 1695.32 (C=C), 1609.16 (Ar)cm^{-1}. HRMS: calcd for $C_{13}H_{13}NF_2$, 221.1016; obsvd 221.1034.

4.3.4. Reaction of (Z)-n-BuCF=CFSnBu$_3$ with 3-iodonitrobenzene

Similar to *4.3.1*, reaction of (*Z*)-*n*-BuCF-$CFSnBu_3$ (0.49 g, 1.2 mmol) with 3-iodonitrobenzene (0.25 g, 1.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.05 g, 0.043 mmol), Cu(I)I (0.10 g, 0.52 mmol) in dry DMF (5 ml) at RT for 10 h gave 0.21 g (87%) of (*E*)-1,2-difluoro-1-(3-nitrophenyl)-1-hexene as a yellow oil (after chromatography) using a mixture of ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: δ −141.3 (dt, $^3J_{FF}$ = 122.7 Hz, $^3J_{HF}$ = 24.1 Hz, 1F), −160.7 (dt, $^3J_{FF}$ = 122.7 Hz, $^4J_{HF}$ = 5.7 Hz, 1F); ^1H NMR: δ 8.45 (t, $^4J_{HH}$ = 1.8 Hz, 1H), 8.15 (dm, $^3J_{HH}$ = 7.4 Hz, 1H), 7.9 (dd, $^2J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 0.9 Hz, 1H), 7.57 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 2.60 (m, 2H), 1.65 (m, 2H), 1.44 (m, 2H), 0.97 (t, $^3J_{HH}$ = 7.3 Hz, 3H); ^{13}C NMR: δ 154.8 (dd, $^1J_{CF}$ = 252.7 Hz, $^2J_{CF}$ = 55.5 Hz), 148.4 (s), 144.9 (dd, $^1J_{CF}$ = 224.0 Hz, $^2J_{CF}$ = 44.0 Hz), 131.6 (dd, $^2J_{CF}$ = 25.7 Hz, $^3J_{CF}$ = 6.1 Hz), 130.5 (dd, $^3J_{CF}$ = 9.8 Hz, $^4J_{CF}$ = 7.3 Hz), 129.4 (d, $^4J_{CF}$ = 2.5 Hz), 122.7 (d, $^5J_{CF}$ = 1.8 Hz), 119.9 (dd, $^3J_{CF}$ = 9.8 Hz, $^4J_{CF}$ = 8.6 Hz), 27.75 (s), 27.16 (d, $^2J_{CF}$ = 23.2 Hz), 22.03 (s), 13.61 (s). GC–MS, *m*/z (relative intensity): 241 (M^+, 29), 198 ($M^+-C_3H_7$, 18), 185 ($M^+-C_4H_8$, 57), 151 (100). FTIR: 1699.93 (C=C), 1534.86 (NO_2), 1350.77 (NO_2) cm^{-1}. HRMS: calcd for $C_{12}H_{13}NF_2O_2$, 241.0914, obsvd 241.0898.

4.3.5. Reaction of (Z)-sec-BuCF=CFSnBu$_3$ with 3-iodonitrobenzene

Similar to *4.3.1*, reaction of *sec*-BuCF=$CFSnBu_3$ (0.49 g, 1.2 mmol) with 3-iodonitrobenzene (0.25 g, 1.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.05 g, 0.043 mmol) and Cu(I)I (0.10 g, 0.52 mmol) in dry DMF (5 ml) at RT for 10 h gave 0.20 g (83%) of (*E*)-1,2-difluoro-3-methyl-1-(3-nitrophenyl)-1-pentene as a colorless oil (after chromatography) using ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: δ −154.2 (dd, $^3J_{FF}$ = 122.1 Hz, $^3J_{HF}$ = 33.1 Hz, 1F), −161.4 (dd, $^3J_{FF}$ = 122.1 Hz, $^4J_{HF}$ = 5.1 Hz, 1F); ^1H NMR: δ 8.47 (t, $^4J_{HH}$ = 1.9 Hz,

1H), 8.16 (m. 1H), 7.93 (m, 1H), 7.58 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 2.93 (m, 1H), 1.60 (m, 2H), 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H); ^{13}C NMR: δ 157.2 (dd, $^1J_{CF}$ = 255.4 Hz, $^2J_{CF}$ = 53.4 Hz), 148.3 (m), 144.5 (dd, $^1J_{CF}$ = 223.1 Hz, $^2J_{CF}$ = 43.9 Hz), 131.7 (dd, $^2J_{CF}$ = 26.3 Hz, $^3J_{CF}$ = 6.4 Hz), 130.6 (dd, $^3J_{CF}$ = 9.8 Hz, $^4J_{CF}$ = 7.0 Hz), 129.4 (d, $^4J_{CF}$ = 2.5 Hz), 122.7 (d, $^5J_{CF}$ = 2.1 Hz), 120.0 (dd, $^3J_{CF}$ = 10.1 Hz, $^4J_{CF}$ = 8.2 Hz), 33.87 (d, $^2J_{CF}$ = 22.3 Hz), 26.22 (d, $^3J_{CF}$ = 2.1 Hz), 16.68 (t, $^{3,4}J_{CF}$ = 1.5 Hz), 11.84 (s). GC–MS, *m*/*z* (relative intensity): 241 (M^+, 31), 212 ($M^+-C_2H_5$, 100). FTIR: 1695.44 (C=C), 1537.84 (NO_2), 1351.68 (NO_2) cm^{-1}, HRMS: calcd for $C_{12}H_{13}NF_2O_2$, 241.0914; obsvd 241.0892.

4.3.6. Reaction of (Z)-sec-BuCF=CFSnBu$_3$ with 4-iodobenzonitrile

Similar to *4.3.1*, reaction of (*Z*)-*sec*-BuCF=CFSnBu$_3$ (0.49 g, 1.2 mmol) with 4-iodobenzonitrile (0.23 g, 1.0 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.05 g, 0043 mmol), and Cu(I)I (0.10 g, 0.52 mmol) in dry DMF (5 ml) at RT for 10 h gave 0.19 g (86%) of (*E*)-1,2-difluoro-3-methyl-1-(4-cyanophenyl)-1-pentene as a yellow oil (after chromatography) using a mixture of ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: δ −152.2 (dd, $^3J_{FF}$ = 120.8 Hz, $^3J_{HF}$ = 33.01 Hz, 1F), −161.9 (dd, $^3J_{FF}$ = 120.8 Hz, $^4J_{HF}$ = 5.1 Hz, 1F); ^{1}H NMR: δ 7.70 (AB Pattern, 4H), 2.92 (m, 1H), 1.59 (m, 2H), 1.22 (d, $^3J_{HH}$ = 7.0 Hz, 3H), 0.96 (t, $^3J_{HH}$ = 7.4 Hz, 3H). ^{13}C NMR: δ 157.7 (dd, $^1J_{CF}$ = 257.0 Hz, $^2J_{CF}$ = 54.0 Hz), 144.8 (dd, $^1J_{CF}$ = 223.4 Hz, $^2J_{CF}$ = 43.6 Hz), 134.1 (dd, $^2J_{CF}$ = 25.3 Hz, $^3J_{CF}$ = 6.1 Hz), 132.0 (d, $^3J_{CF}$ = 2.4 Hz), 125.3 (dd, $^3J_{CF}$ = 10.0 Hz, $^4J_{CF}$ = 7.6 Hz), 118.4 (s), 111.4 (d, $^5J_{CF}$ = 3.1 Hz), 33.86 ($^2J_{CF}$ = 22.3 Hz), 26.15 (d, $^3J_{CF}$ = 2.1 Hz), 16.56 (s), 11.75 (s). GC–MS, *m*/*z* (relative intensity): 221 (M^+, 23), 192 ($M^+-C_2H_5$, 100). FTIR: 2230.76 (CN), 1690.54 (C=C), 1608.45 (Ar) cm^{-1}. HRMS: calcd for $C_{13}H_{13}NF_2$: 221.1026; obsvd 221.0990.

4.3.7. Reaction of (Z)-sec-BuCF=CFSnBu$_3$ with 4-iodonitrobenzene

Similar to *4.3.1*, reaction of (*Z*)-*sec*-BuCF=CFSnBu$_3$ (0.49 g, 1.2 mmol) with 4-iodonitrobenzene (0.25 g, 1.0 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.05 g, 0.043 mmol) and Cu(I)I (0.10 g, 0.52 mmol) in dry DMF (5 ml) at RT for 10 h give 0.21 g (87%) of (*E*)-1,2-difluoro-3-methyl-1-(4-nitrophenyl)-1-pentene as a yellow oil (after chromatography) using a mixture of ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: δ −150.9 (dd, $^3J_{FF}$ = 120.8 Hz, $^3J_{HF}$ = 33.1 Hz, 1F), δ −161.1 (dd, $^3J_{FF}$ = 120.8 Hz, $^4J_{HF}$ = 5.1 Hz, 1F). ^{1}H NMR: δ 8.25 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.78 (dm, $^3J_{HH}$ = 9.0 Hz, 2H), 2.94 (m, 1H), 1.60 (m, 2H), 1.23 (d, $^3J_{HH}$ = 7.0 Hz, 3H), 0.97 (t, $^3J_{HH}$ = 7.5 Hz, 3H); ^{13}C NMR: δ 158.3 (dd, $^1J_{CF}$ = 258.1 Hz, $^2J_{CF}$ = 53.7 Hz), 146.9 (d, $^5J_{CF}$ = 3.1 Hz), 144.8 (dd, $^1J_{CF}$ = 223.4 Hz, $^2J_{CF}$ = 43.7 Hz), 136.0 (dd, $^2J_{CF}$ = 25.0 Hz), $^3J_{CF}$ = 6.4 Hz), 125.6 (dd, $^3J_{CF}$ = 10.3 Hz, $^4J_{CF}$ = 7.6 Hz), 123.6 (d, $^4J_{CF}$ = 2.4 Hz), 34.01 (d, $^2J_{CF}$ = 2.0 Hz), 26.25 (d, $^3J_{CF}$ = 2.2 Hz), 16.64 (s), 11.84 (s). GC–MS, *m*/*z* (relative intensity): 241 (M^+, 50), 212 ($M^+-C_2H_5$, 100). FTIR: 1687.32 (C=C), 1600.12 (Ar), 1524.29 (NO_2) cm^{-1}. HRMS: calcd for $C_{12}H_{13}NF_2O_2$, 241.0914 obsvd 241.0918.

4.3.8. Reaction of (Z)-tert-BuCF=CFSnBu$_3$ with 2-iodonitrobenzene

Similar to *4.3.1*, reaction of (*Z*)-*tert*-BuCF=CFSnBu$_3$ (0.49 g, 1.2 mmol) with 2-iodonitrobenzene (0.25 g, 1.0 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.05 g, 0.043 mmol) and Cu(I)I (0.10 g, 0.52 mmol) in dry DMF (5 ml) at RT for 10 h gave 0.20 (82%) of (*E*)-1,2-difluoro-3,3-dimethyl-1-butene as a yellow oil (after chromatography) using a mixture of ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: δ −147.1 (d, $^3J_{FF}$ = 132.2 Hz, 1F), −148.0 (d, $^3J_{FF}$ = 132.2 Hz, 1F); ^{1}H NMR: δ 7.95 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.6 Hz, 1H), 7.58 m (3H), 1.31 (t, $^{4/5}J_{CF}$ = 2.0 Hz 9H); ^{13}C NMR: δ 157.0 (dd, $^1J_{CF}$ = 227.7 Hz, $^2J_{CF}$ = 26.9 Hz), 147.6 (s), 143.5 (dd, $^1J_{CF}$ = 212.4 Hz, $^2J_{CF}$ = 36.7 Hz), 132.7 (s), 131.4 (dd, $^3J_{CF}$ = 4.3 Hz, $^4J_{CF}$ = 3.0 Hz), 130.2 (s), 125.0 (dd, $^2J_{CF}$ = 23.8 Hz, $^3J_{CF}$ = 1.8 Hz), 124.4 (s), 34.90 (dd, $^2J_{CF}$ = 20.7 Hz, $^3J_{CF}$ = 3.0 Hz), 27.06 (t, $^{3,4}J_{CF}$ = 4.3 Hz). GC–MS, *m*/*z* (relative intensity): 241 (M^+, 1), 220 (2), 109 (100). FTIR: 1704.25 (C=C), 1535.91 (NO_2), 1353.10 (NO_2) cm^{-1}. HRMS: calcd for $C_{12}H_{13}NF_2O_2$, 241.0914, obsvd 241.0925.

4.3.9. Reaction of (Z)-PhCF=CFSnBu$_3$ with 4-iodoacetophenone

Similar to *4.3.1*, reaction of (*Z*)-PhCF=CFSnBu$_3$ (0.52 g, 1.21 mmol) with 4-iodoacetophenone (0.25 g, 1.0 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.5 g, 0.043 mmol) and Cu(I)I (0.10 g, 0.52 mmol) in dry DMF (5 ml) at RT for 10 h gave 0.22 g (85%) of (*E*)-1,2-difluoro-2-phenyl-1-(p-acetylphenyl)-ethene, mp = 128–129 °C, as colorless crystals (after chromatography) using a mixture of ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: δ−148.2 (d, $^3J_{FF}$ = 119.5 Hz, 1F), −153.5 (d, $^3J_{FF}$ = 119.5 Hz, 1F); ^{1}H NMR: δ 7.98 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.80 (m, 4H), 7.43 (m, 3H), 2.58 (s, 3H); ^{13}C NMR: δ 197.1 (s), 150.1 (dd, $^1J_{CF}$ = 183.1 Hz, $^2J_{CF}$ = 47.3 Hz), 146.9 (dd, $^1J_{CF}$ = 178.9 Hz, $^2J_{CF}$ = 47.6 Hz), 136.6 (d, $^5J_{CF}$ = 2.5 Hz), 134.4 (dd, $^2J_{CF}$ = 22.1 Hz, $^3J_{CF}$ = 6.4 Hz), 129.8 (d, $^3J_{CF}$ = 6.1 Hz), 129.5 (d, $^4J_{CF}$ = 1.9 Hz), 128.5 (d, $^3J_{CF}$ = 2.4 Hz), 128.3 (d, $^3J_{CF}$ = 2.4 Hz), 126.0 (dd, $^2J_{CF}$ = 9.4 Hz, $^3J_{CF}$ = 8.2 Hz), 125.6 (dd, $^3J_{CF}$ = 9.2 Hz, $^4J_{CF}$ = 7.9 Hz), 26.48 (s). GC–MS, *m*/*z* (relative intensity): 258 (M^+, 61), 243 (M^+-CH_3,100), 214 (38). FTIR: 1689.85 (C=C), 1606.21 (Ar), cm^{-1}. HRMS: calcd for $C_{16}H_{12}F_2O$, 258.0856; obsvd 258.0859.

4.3.10. Reaction of (Z)-PhCF=CFSnBu$_3$ with 4-iodonitrobenzene

Similar to *4.3.1*, reaction of (*Z*)-PhCF=CFSnBu$_3$ (0.52 g, 1.21 mmol) with 4-iodonitrobenzene (0.25 g, 1.0 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.05 g, 0043 mmol) and Cu(I)I (0.10 g, 0.52 mmol) in dry DMF (5 ml) at RT for 10 h gave 0.24 g (92%) of (*E*)-1,2-difluoro-2-phenyl-1-(4-nitrophenyl)ethene as yellow crystals, mp = 121–123 °C (after chromatography) using ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: δ −145.7 (d, $^3J_{FF}$ = 119.6 Hz, 1F), −153.8 (d, $^3J_{FF}$ = 119.6 Hz, 1F); ^{1}H NMR: δ 8.26 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.89 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.77 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.46 (m, 3H); ^{13}C NMR: δ 150.7 (dd, $^1J_{CF}$ = 242.9 Hz, $^2J_{CF}$ = 47.0 Hz), 147.2 (d, $^5J_{CF}$ = 2.8 Hz), 146.4 (dd, $^1J_{CF}$ = 235.9 Hz, $^2J_{CF}$ = 47.3 Hz), 136.2 (dd, $^2J_{CF}$ = 24.0 Hz, $^3J_{CF}$ = 6.7 Hz), 130.0 (d, $^4J_{CF}$ = 2.1 Hz), 129.2 (dd, $^2J_{CF}$ = 24.1 Hz, $^3J_{CF}$ = 6.7 Hz), 128.6 (d, $^4J_{CF}$ = 2.1 Hz), 126.3 (dd, $^3J_{CF}$ = 8.2 Hz, $^4J_{CF}$ = 1.2 Hz), 126.1 (dd, $^3J_{CF}$ = 8.2 Hz, $^4J_{CF}$ = 2.7 Hz), 123.7 (d, $^5J_{CF}$ = 2.4 Hz). GC–MS, *m*/*z* (relative intensity): 261 (M^+, 100), 231 (19), 214 (70). FTIR: 1651.67 (C=C), 1599.07 (Ar), 1525.79 (NO_2), 1344.51 (NO_2) cm^{-1}. HRMS: calcd for $C_{14}H_9NF_2O_2$, 261.0601; obsvd 261.0619.

4.3.11. Reaction of (Z)-tert-BuCF=CFSnBu$_3$ with 4-iodonitrobenzene

Similar to *4.3.1*, reaction of (*Z*)-*tert*-BuCF=CFSnBu$_3$ (0.49 g, 1.2 mmol) with 4-iodonitrobenzene (0.25 g, 1.0 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.05 g, 0.043 mmol), and Cu(I)I (0.10 g, 0.52 mmol) in dry DMF (5 ml) at RT for 10 h gave 0.22 g (92%) of colorless crystals (after chromatography), mp = 63–64 °C, using a mixture of ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: δ −141.3 (d, $^3J_{FF}$ = 120.4 Hz, 1F), −157.7 (d, $^3J_{FF}$ = 120.4 Hz, 1F; ^{1}H NMR: δ 8.30 (d, $^{4/5}J_{HF}$ = 9.2 Hz, 2H), 7.6 (dm, $^{4/5}J_{HF}$ = 9.2 Hz, 2H), 1.35 (m, 9H); ^{13}C NMR: δ 160.3 (dd, $^1J_{CF}$ = 256.3 Hz, $^2J_{CF}$ = 48.8 Hz), 146.9 (d, $^5J_{CF}$ = 2.4 Hz), 145.2 (dd, $^1J_{CF}$ = 229.3 Hz, $^2J_{CF}$ = 50.0 Hz), 136.9 (dd, $^2J_{CF}$ = 25.0 Hz, $^3J_{CF}$ = 6.7 Hz), 126.1 (dd, $^3J_{CF}$ = 11.0 Hz, $^4J_{CF}$ = 8.0 Hz), 123.5 (d, $^4J_{CF}$ = 1.8 Hz), 35.81 (dd, $^2J_{CF}$ = 21.4 Hz, $^3J_{CF}$ = 3.7 Hz), 27.41 (t, $^{3/4}J_{CF}$ = 4.5 Hz). GC–MS, *m*/*z* (relative intensity): 241 (M^+, 36), 226 (M^+-CH_3, 100). FTIR: 1673.99 (C=C), 1524.16 (NO_2), 1342.06 (NO_2) cm^{-1}. HRMS: calcd for $C_{12}H_{13}NF_2O_2$, 241.0914; obsvd 241.0889.

4.3.12. Reaction of (Z)-PhCF=CFSnBu$_3$ with 4-iodobenzonitrile

Similar to *4.3.1*, reaction of (*Z*)-PhCF=CFSnBu$_3$ (0.52 g, 1.21 mmol) with 4-iodobenzonitrile (0.23 g, 1.0 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.05 g, 0.043 mmol) and Cu(I)I (0.10 g, 0.52 mmol) in dry DMF (5 ml) at RT for 10 h gave 0.21 g (87%) of

(*E*)-1,2-difluoro-3-phenyl-1-(4-cyanophenyl)-ethene as white crystals, m.p. = 98–100 °C (after chromatography) using ethyl acetate and hexane (1:20) as the eluent. ^{19}F NMR: δ −146.7 (d, $^{3}J_{FF}$ = 119.5 Hz, 1F), −154.5 (d, $^{3}J_{FF}$ = 119.5 Hz, 1F); ^{1}H NMR: δ 7.84 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 7.76 (dd, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H), 7.71 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 7.46 (m, 3H); ^{13}C NMR: δ 150.4 (dd, $^{1}J_{CF}$ = 241.7 Hz, $^{2}J_{CF}$ = 47.0 Hz), 146.5 (dd, $^{1}J_{CF}$ = 235.6 Hz, $^{2}J_{CF}$ = 47.6 Hz), 134.4 (dd, $^{2}J_{CF}$ = 24.4 Hz, $^{3}J_{CF}$ = 6.4 Hz), 132.2 (d, $^{4}J_{CF}$ = 2.4 Hz), 129.9 (d, $^{5}J_{CF}$ = 1.8 Hz), 129.3 (dd, $^{2}J_{CF}$ = 24.1 Hz, $^{3}J_{CF}$ = 6.4 Hz), 128.6 (d, $^{4}J_{CF}$ = 2.2 Hz), 126.6 (dd, $^{3}J_{CF}$ = 9.4 Hz, $^{4}J_{CF}$ = 8.2 Hz), 125.9 (dd, $^{3}J_{CF}$ = 10.9 Hz, $^{4}J_{CF}$ = 8.2 Hz), 118.4 (s), 112.0 (d, J = 3.0 Hz). GC–MS, m/z (relative intensity): 241 (M^{+}, 100). FTIR: 2231.04 (CN), 1650.43 (C=C), 1606.97 (Ar) cm^{-1}. HRMS: calcd for $C_{15}H_9NF_2$, 241.0703; obsvd 241.0716.

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