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The stereoselective synthesis of (*E*)-octafluoro-1,3,5-hexatriene and (3*E*,5*E*,7*E*)-dodecafluoro-1,3,5,7,9-decapentaene

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(1*Z*,3*E*,5*Z*)-(1,2,3,4,5,6-Hexafluoro-1,3,5-hexenetriyl)bis[tributylstannane]
$Pd(PPh_3)_4$/CuI-catalyzed reactions

ABSTRACT

(*E*)-(1,2-Difluoro-1,2-ethenediyl)bis[tributylstannane], **3**, readily undergoes a $Pd(PPh_3)_4$/CuI-catalyzed cross-coupling reaction with iodotrifluoroethene to yield (*E*)-octafluoro-1,3,5-hexatriene, **4**, in high isomeric purity. (1*Z*,3*E*,5*Z*)-(1,2,3,4,5,6-Hexafluoro-1,3,5-hexenetriyl)bis[tributylstannane], **7**, was sequentially prepared from (1*Z*,3*E*,5*Z*)-(1,2,3,4,5,6-hexafluoro-1,3,5-hexenetriyl)bis[triethylsilane], **5**, which was prepared *via* a $Pd(PPh_3)_4$/CuI-catalyzed cross-coupling reaction of **3** with (*E*)-1,2-difluoro-1-iodo-2-triethylsilylethene, **6**. $Pd(PPh_3)_4$/CuI cross-coupling of **7** with iodotrifluoroethene gave (3*E*,5*E*,7*E*)-dodecafluoro-1,3,5,7,9-decapentaene, **8**.

1. Introduction

Conjugated perfluoropolyenes are both theoretically and synthetically interesting compounds. Although significant amount of work has been accomplished on diene analogs [1], limited reports of more extensively conjugated π-electron systems have appeared in the chemical literature. Recent computational calculation studies have focused on the torsional potentials of perfluoropolyenes and have compared ab initio self-consistent (SCF) field methods and several density functional theory (DFT) variants applying large basis sets and complete geometry optimizations [2]. In a related study MP2/6-31G level static longitudinal linear polarizability calculations have been reported for several perfluoropolyenes [3].

Perfluoro-1,3,5-hexatriene was first prepared by Dedek and Chvatal by dehalogenation of crude dibromotrichlorononafluorohexane, formed *via* photochemically initiated reaction of 1,2-dibromo-1-chlorotrifluoroethane with chlorotrifluoroethene, as illustrated in Eq. (1) [4]. Authentic samples of **1** and **2** were obtained by preparative GLPC. No structural assignment of **1** was made. Subsequent work by Lemal and Jing demonstrated that the dehalogenation reaction yielded a mixture of hexatrienes; the *cis* isomer was the major product, Eq. (2) [5].

$$BrCF_2CFClBr + F_2C{=}CFCl \xrightarrow{uv} \text{mixture of telomers}$$

$$\text{hexene fraction (of telomers)} \xrightarrow[EtOH]{Zn} \underset{\mathbf{1}}{F_2C{=}CFCF{=}CFCF{=}CF_2} + \underset{\mathbf{2}}{F_2C{=}CFCFClCF_2CF{=}CF_2} \quad (1)$$

$$65 : 35$$

$$BrCF_2CFClCF_2CFClCFClCF_2Br \xrightarrow[EtOH]{Zn} \underset{\text{major 85-90\%}}{F_8} + \underset{\text{minor 10-15\%}}{F_8} \quad (2)$$

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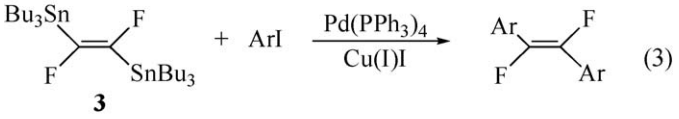
Recently we have described the preparation of a new synthon, (*E*)-(1,2-difluoro-1,2-ethenediyl)bis[tributylstannane], **3** [6]. This bis-synthon reacts stereospecifically with aryl iodides in a $Pd(PPh_3)_4$/CuI-catalyzed cross-coupling reaction to give high isolated yields of (*E*)-1,2-difluorostilbenes, Eq. (3) [6]. Synthon, **3**, is readily prepared in a one-pot sequence from the cheap olefin, chlorotrifluoroethene.



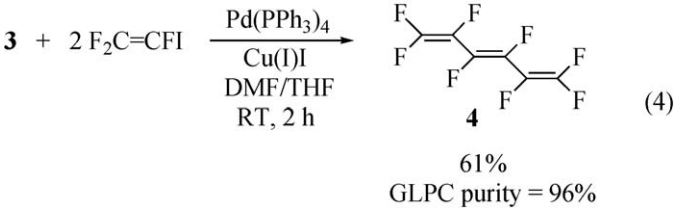
(3)

It is known that vinyl halides, similar to their sp^2 hybridized aryl halides, can undergo $Pd(Ph_3)_4$/CuI-catalyzed cross-coupling reactions with vinylstannanes. Thus, we were interested to determine if **3** could be cross-coupled with a perfluorovinyl iodide to provide a useful stereoselective synthetic entry to perfluoropolyenes with a *trans* (*E*)-configuration, thus complementing the previously described zinc dehalogenation, which gave predominantly the *cis* (*Z*)-configuration, cf. Eq. (2).

2. Results and discussion

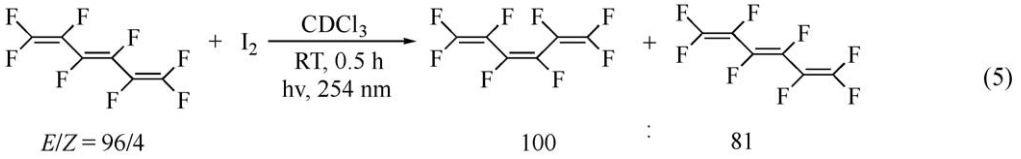
2.1. Preparation of (E)-octafluoro-1,3,5-hexatriene, 4

(*E*)-(1,2-Difluoro-1,2-ethenediyl)bis[tributylstannane], **3** can be readily prepared from chlorotrifluoroethene *via* a sequential series of reactions to provide an excellent isolated yield of **3**, as illustrated in Scheme 1 [6]. Subsequent $Pd(PPh_3)_4$/Cu(I)I catalyzed cross-coupling of **3** with iodotrifluoroethene provided a good yield predominantly of perfluoro-1,3,5-hexatriene, **4**, as illustrated in Eq. (4). The (*Z*)-isomer accounted for 4% of the isolated hexatrienes. This methodology provides a stereoselective preparative route to **4**.

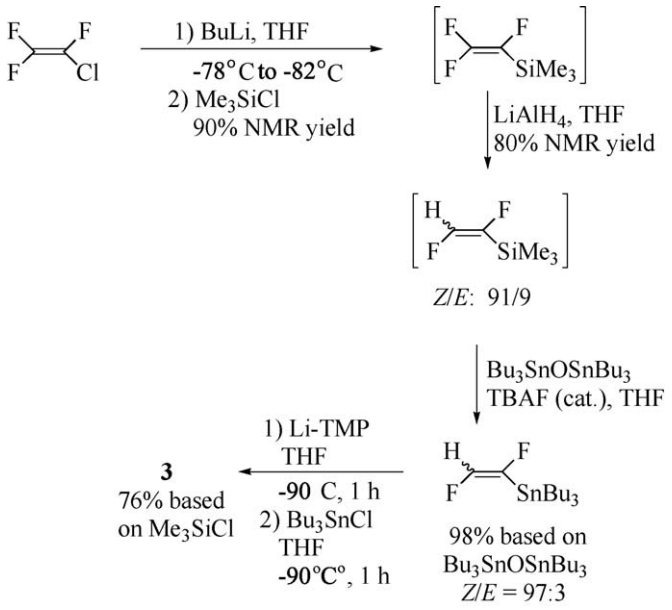


(4)

Irradiation of **4** with I_2 at 254 nm readily equilibrated the (*E*)- and (*Z*)-trienes, as previously observed [5] and illustrated in Eq. (5).



(5)



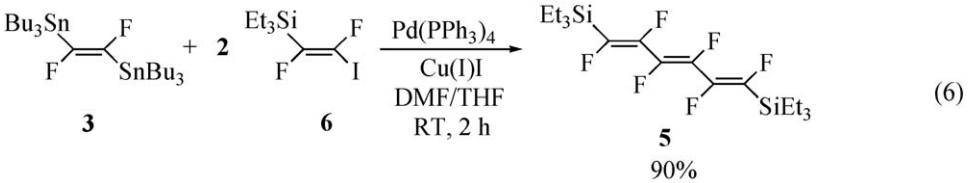
Scheme 1. Preparation of **3** from F_2C=CFCl.

A ratio of *Z*/*E*-hexatrienes similar to that observed by Lemal (*Z*/*E* = 100/83) was found [5]. Integration of the ^{19}F NMR peaks at δ-104.5 (*E*) and δ-106.0 (*Z*) was utilized to obtain the ratio of isomers described above [7].

Our success with cross-coupling of **3** to provide **4** encouraged us to attempt to prepare an analog of **3** that would permit the stereospecific introduction of three conjugated double bonds in one-step. Thus, we investigated an approach to (1*Z*,3*E*,5*Z*)-(1,2,3,4,5,6)-(hexafluoro-1,3,5-hexenetriyl)bis[tributylstannane], **7**, as illustrated below.

2.2. Preparation of (1Z,3E,5Z)-(1,2,3,4,5,6)-(hexafluoro-1,3,5-hexenetriyl)bis[triethylsilane], 5

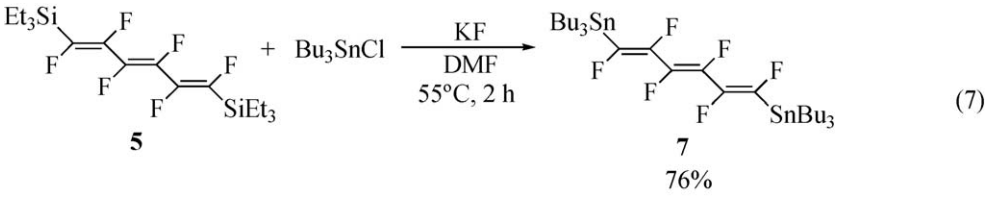
We and others have previously described the preparation of (*E*)-1,2-difluoro-1-iodo-2-triethylsilylethene **6** [8,9]. Successful $Pd(PPh_3)_4$/Cu(I)I cross-coupling of **6** with **3** would provide a conjugated triene system with predictable stereochemistry of the fluorinated π-bonds. To our satisfaction, we found that cross-coupling of **3** with **6** provided a high yield preparative route to **5**, as shown in Eq. (6).



(6)

2.3. Preparation of (1Z,3E,5Z)-(1,2,3,4,5,6)-(hexafluoro-1,3,5-hexenetriyl)-bis[tributylstannane], 7

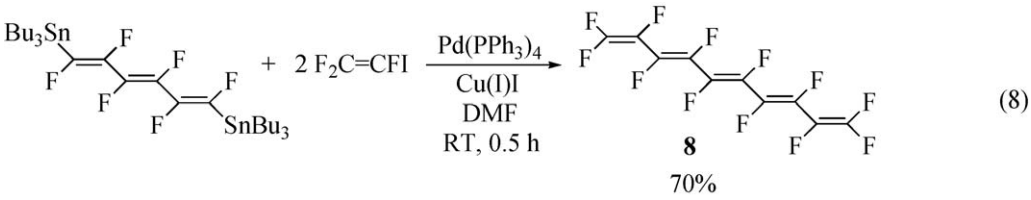
Previous work in our laboratory has demonstrated that trialkylsilyl groups in fluorine-containing vinylsilanes can be stereospecifically replaced by trialkylstannyl groups [10]. Thus, when **5** was reacted with chlorotributylstannane and potassium fluoride in DMF, exchange of the trialkylsilyl group by a trialkylstannyl group occurred stereospecifically to provide **7** in good yield, as illustrated in Eq. (7). Thus, the stereospecific preparation of a conjugated fluorine-containing bis-synthon containing three π-bonds was successfully accomplished.



(7)

2.4. Preparation of (3E,5E,7E)-dodecafluoro-1,3,5,7,9-decapentaene, 8

To test the utility of **7** to provide entry to additional perfluoropolyenes, we attempted the cross-coupling reaction of **7** with iodotrifluoroethene, as illustrated in Eq. (8). Iodorifluoroethene was used as the limiting agent to avoid separation problems in product isolation. Flash distillation of the product mixture, followed by simple distillation, gave a colorless liquid (GLPC = 96%). 19F NMR analysis of this liquid supported the assignment of **8** (six fluorine signals). Unfortunately, this liquid material rapidly decomposed before additional data could be collected.



(8)

Although **8** easily decomposed, other less reactive vinyl or aryl halide reactants which would give less reactive end groups in the product pentaene are most likely attainable by this methodology. Also, our approach to the preparation of **7** can likely be extended to polyfluoroheptaenes and beyond. Thus, the synthetic attainment of a wide variety of polyfluorinated polyenes are potentially possible by the methodology outlined in this manuscript.

3. Experimental

3.1. General experimental procedures

Routine ^{19}F NMR spectra were recorded on a JEOL FX90Q Spectrometer and high resolution data was obtained on a Bruker AC-300 Spectrometer. Chemical shifts have been reported in ppm upfield from internal $CFCl_3$ and were generally determined in $CDCl_3$ unless otherwise noted. Routine ^1H NMR spectra were recorded on a JEOL FX90Q Spectrometer and high resolution data was obtained on either a Bruker AC-300 or WM-360 Spectrometer. Chemical shifts have been reported in ppm relative to internal TMS. Unless otherwise noted, $CDCl_3$ was used as the solvent. High Resolution $\{^1H\}$ ^{13}C NMR spectra were recorded on either a Bruker AC-300 or WM-360 Spectrometer. Chemical shifts have been reported in ppm relative to internal TMS. Unless otherwise noted, $CDCl_3$ was used as the solvent. Low resolution mass spectra were obtained using a TRIO-1 GC–MS instrument operated at 70 eV in the electron impact mode using a DB-1 column (0.25 mm ID × 15 m). High resolution mass spectra (HRMS) were obtained by the University of Iowa High Resolution Mass Spectrometry Facility.

Infrared absorbance spectra were obtained using a Mattson Cygnus FTIR Spectrophotometer, as solutions in CCl_4. All FTIR values are reported in units of reciprocal centimeters. Analytical GLPC were performed on a Hewlett-Packard Model 5890, equipped with a TCD detector and 3393A integrator. The column was packed with 5% OV-101 on Chromosorb B. Column chromatography was carried out on silica gel (silica gel 60, 0.063–0.200 mm, 70–30 mesh). All boiling points were determined during fractional distillation using a partial immersion thermometer, and are uncorrected. DMF was dried by stirring over CaH_2 overnight, then distilled at reduced pressure. THF was dried by stirring overnight over sodium chips, then distilled from sodium benzophenome ketyl at atmospheric pressure prior to use. $Ph(PPh_3)_4$ was prepared by Coulson's procedure [11]. KF was dried by azeotropic distillation overnight using benzene and a Dean–Stark apparatus. Residual benzene was removed under reduced pressure at RT. All other chemicals used were obtained commercially, and used directly, or *via* methodology previously reported from this laboratory.

3.2. Preparation of iodotrifluoroethene [12]

A two-neck 10 ml flask, equipped with a stir bar, rubber septum and flash distillation apparatus attached to a vacuum line, was charged with 0.51 g (2 mmol) I_2. Then 1,1,2-trifluoroethenyltributylstannane [13] (0.74 g, 10 mmol) was gradually introduced into the flask *via* syringe. Flash distillation of the reaction mixture at RT/0.5 mm Hg yielded 0.38 g (91%) of iodotrifluoroethene, GLPC = 100%. ^{19}F NMR: δ −88.2 (dd, $^2J_{FF}$ = 65 Hz, $^3J_{FF}$ = 51 Hz), −113.4 (dd, $^3J_{FF}$ = 129 Hz, $^2J_{FF}$ = 65 Hz), −150.1 (dd, $^3J_{FF}$ = 129 Hz, $^3J_{FF}$ = 51 Hz). ^{13}C NMR: δ 154.2 (ddd, $^1J_{CF}$ = 298 Hz, $^1J_{CF}$ = 275 Hz, $^2J_{CF}$ = 39 Hz), 75.6 (ddd, $^1J_{CF}$ = 311 Hz, $^2J_{CF}$ = 65 Hz, $^2J_{CF}$ = 28 Hz), GC–MS, *m*/*z* (relative intensity): 208 (M^+, 100) 127 (56.3).

3.3. Preparation of (E)-1,2-difluoro-1-iodo-2-triethylsilylethene, 6

A modified procedure for the preparation of the titled compound is described below. An improved yield was obtained by minimizing distillation of the product silane. A three-necked 2 l flask, equipped with a stir bar, low temperature thermometer, nitrogen tee and rubber septum, was charged with (*E*)- and (*Z*)-1,2-difluorotriethylsilylethenes, *E*/*Z* = 95:5, (65.8 g, 329 mmol), 200 ml THF and 700 ml

Et_2O The mixture was cooled to −100 to −110 °C with liquid nitrogen/pentane slush bath. Then, 145 ml (365 mmol) of a 2.5 M n-BuLi solution was gradually added to the reaction mixture, maintaining the internal temperature at <−100 °C. After complete addition of the n-BuLi solution, the reaction mixture was stirred at −90 to −100 °C for 1 h. Then, a solution of I_2 [110 g I_2 (443 mmol) in 200 ml THF] was gradually added to the reaction mixture *via* a syringe, maintaining the temperature at −95 to −100 °C. After complete addition of the I_2 solution, the reaction mixture was stirred at −95 to −100 °C for 1 h, then slowly warmed to −30 °C over 3 h. Then, the reaction mixture was quenched with dilute HCl at −30 °C until pH <6. The solution was washed with saturated aqueous $Na_2S_2O_3$ until the color of the solution changed from dark brown to light yellow. The organic layer was extracted with Et_2O (3× 100 ml), washed with $NaHCO_3$ solution (5× 50 ml), water (5× 100 ml), then dried over $MgSO_4$. After removal of the $MgSO_4$ by gravity filtration, most of the solvent was removed by rotary evaporation. Removal of the remaining solvent by flash distillation at ~20 °C/1 mm Hg yielded 94.2 g (89%) of a colorless liquid, **6**, GLPC = 95%. The ^{19}F and ^1H NMR were identical to previously prepared material [8].

3.4. Preparation of (E)-octafluoro-1,3,5-hexatriene, 4

A one-neck 100 ml round bottom flask equipped with a Teflon-coated stir bar and attached to a nitrogen inlet tee was charged with 12.02 g (19 mmol) of **3**, 6.86 g (32.7 mmol, GLPC purity = 99%) iodotrifluoroethene, 30 ml DMF, 0.83 g (4.3 mmol), Cu(I)I and 1.1 g (3 mol%) $Pd(PPh_3)_4$. The reaction mixture was stirred at RT for 6 h; followed by flash distillation to give a crude liquid product. Fractional distillation of the crude product *via* a 8 cm Vigreux column yielded 2.32 g (61%) of a colorless liquid **4**, bp 67–68 °C/760 mm Hg, GLPC purity = 96%. ^{19}F NMR: δ −91.5 (dd, $^2J_{FF}$ = 40 Hz, $^3J_{FF}$ = 32 Hz), −104.6 (ddm, $^3J_{FF}$ = 115 Hz, $^2J_{FF}$ = 40 Hz), −150.9 (m), −185.2 (ddm, $^3J_{FF}$ = 115 Hz, $^3J_{FF}$ = 32 Hz). GC–MS, *m*/*z* (relative intensity): 224 (M^+, 37), 155 (100). HRMS: calculated for C_6F_8: 223.9872, observed 223.9856 [7].

3.5. Preparation of (1Z,3E,5Z)-(1,2,3,4,5,6-hexafluoro-1,3,5-hexeneyl)bis(triethylsilane), 5

A one-neck 50 ml flask, equipped with a stir bar, and attached to a nitrogen inlet tee was charged with 4.49 g (7 mmol) of **3**, 3.7 g (12.2 mmol) of **6**, 8 ml THF and 8 ml DMF, 0.1 g (0.5 mmol, 4 mol%) Cu(I)I and 0.25 g (3 mol%) $Pd(PPh_3)_4$. The reaction mixture was stirred at RT for 2 h. The dark reaction mixture was poured onto a silica gel column and eluted with pentane, R_f = 0.6. Removal of solvent at RT/1 mm Hg gave 2.28 g (90%) of a colorless liquid, **5**. ^{19}F NMR: δ −148.9 (dt, $^3J_{FF}$ = 133 Hz, $^3J_{FF}$ = 23 Hz), −150.8 (m, 2F), −161.8 (ddd, $^3J_{FF}$ = 133 Hz, $^4J_{FF}$ = 14 Hz, $^5J_{FF}$ = 6 Hz); ^1H NMR: δ 1.02 (t, $^3J_{HH}$ = 7.8 Hz), 0.80 (q, $^3J_{HH}$ = 7.8 Hz); ^{13}C NMR: δ 162.5 (ddd), $^1J_{CF}$ = 286 Hz, $^2J_{CF}$ = 72 Hz, $^3J_{CF}$ = 2 Hz), 150.5 (m), 104.4 (m), 6.98 (s), 2.21 (s). FTIR: 2959 (vs), 2939 (m), 2914 (s), 1458 (w), 1285 (m), 1181 (vs), 1006 (s). GC–MS, *m*/*z* (relative intensity) 416 (M^+, 2.7), 105 (40.6), 77 (100). HRMS: calculated for $C_{18}H_{30}Si_2F_6$: 416.1790, observed 416.1806.

3.6. Preparation of (1Z,3E,5Z)-(1,2,3,4,5,6-hexafluoro-1,3,5-hexenyltriyl)bis[tributylstannane], 7

A one-neck 50 ml flask, equipped with a stir bar, condenser, and attached to a nitrogen inlet tee, was charged with 0.45 g (1.08 mmol) of **5**, 0.74 g (2.2 mmol) of tributyltin chloride, 0.16 g (2.6 mmol) KF and 2 ml DMF. The reaction mixture was stirred at 55 °C for 2 h. The dark reaction mixture was poured onto a silica gel column and eluted with pentane. Removal of solvent at RT/1 mm Hg gave 0.63 g (76%) of a colorless liquid, **7**. ^{19}F NMR: δ −139.8 (dt, $^3J_{FF}$ = 124 Hz, $^3J_{FF}$ = 22 Hz, 2F), −151.7 (m, 2F), −163.4 (dm, $^3J_{FF}$ = 124 Hz, 2F). ^1H NMR: δ 1.6 (m), 1.34 (m), 1.2 (tm, $^3J_{HH}$ = 8 Hz), 0.9 (t, $^3J_{HH}$ = 7 Hz). ^{13}C NMR: δ 28.7 (m), 27.1 (m), 13.6 (m), 10.3 (n)-butyl group.

3.7. Preparation of (3E,5E,7E)-dodecafluoro-1,3,5,7,9-decapentaene, 8

A one-neck 50 ml flask, equipped with a stir bar and attached to a nitrogen inlet tee, was charged with 0.44 g (0.57 mmol) of **7**, 0.17 g (0.9 mmol) iodotrifluoroethene, 2 ml DMF, 0.03 g (3 mol%) $Pd(PPh_3)_4$ and 0.05 g (0.3 mmol) Cu(I)I. The reaction mixture was stirred at RT for 0.5 h. Flash distillation of the reaction mixture at RT/0.1 mm Hg gave a liquid, which on simple distillation gave 0.20 g (70%) of a colorless liquid **8**, GLPC = 96%. ^{19}F NMR: δ −90.7 (m), −103.5 (m), −148.4 (m), −151.8 (m), −155.2 (m), −186.3 (m). On storage in the freezer, this product underwent decomposition.

4. Conclusion

(*E*)-(1,2-Difluoro-1,2-ethenediyl)bis[tributylstannane] **3**, readily undergoes a $Pd(PPh_3)_4$/CuI-catalyzed coupling reaction with iodotrifluoroethene to give (*E*)-octafluoro-1,3,5-hexatriene in good isolated yield and high isomeric purity, (1*Z*,3*E*,5*Z*)-(1,2,3,4,5,6-hexafluoro-1,3,5-hexenetriyl)bis[tributylstannane], **7**, was prepared from (1*Z*,3*E*,5*Z*)-(1,2,3,4,5,6-hexafluoro-1,3,5-hexenetriyl)bis[triethylsilane], which was prepared *via* a $P(PPh_3)_4$/CuI-catalyzed cross-coupling reaction of **3** with (*E*)-1,2-difluoro-1-iodo-2-triethylsilylethene. $Pd(PPh_3)_4$/CuI-catalyzed cross-coupling of **7** with iodotrifluoroethene gave (3*E*,5*E*,7*E*)-dodecafluoro-1,3,5,7,9-decapentaene, **8**.

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