FLUORINE-CONTAINING ALLENYLPALLADIUM COMPLEXES. SYNTHESIS OF OPTICALLY ACTIVE FLUOROALKYLATED ALLENES AND FURAN DERIVATIVES

Tsutomu KONNO[1,*], Mitsuru TANIKAWA, Takashi ISHIHARA[2] and Hiroki YAMANAKA[3]

Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Sakyo-ku, Matsugasaki, Kyoto 606-8585, Japan; e-mail: [1] konno@chem.kit.ac.jp, [2] ishihara@ipc.kit.ac.jp, [3] yamanaka@ipc.kit.ac.jp

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Dedicated to the memory of Professor Miloš Hudlický.

The reaction of fluoroalkylated propargyl mesylates with various nucleophiles, such as zinc reagents and enolates derived from 1,3-dicarbonyl compounds, in the presence of a palladium catalyst was investigated in detail. Various zinc reagents participated in the coupling reaction to give the corresponding fluoroalkylated allenes in good yields. When chiral mesylates were employed, the corresponding optically active allenes were obtained without any loss of enantiomeric purity in the reaction. On the other hand, treatment of trifluoromethylated propargyl mesylate with stabilized carbanions derived from methyl acetoacetate, acetylacetone, and diethyl malonate afforded fluorine-containing furan derivatives in moderate to high yields.

Keywords: Fluorine-containing allenylpalladium complexes; Allenes; Alkynes; Propargyl esters; Furanes; Fluorinated compounds; Palladium catalysis; Enantioselective synthesis; Cross-coupling reactions.

Transition metals are able to catalyze a wide range of synthetically useful organic reactions, very often with high levels of chemo- and stereoselectivity[1]. In particular, palladium-catalyzed reactions have been employed with success in a number of important chemical processes, such as Stille coupling[2], Suzuki coupling[3], Negishi coupling[4], Heck reactions[5], and allylic substitution[6].

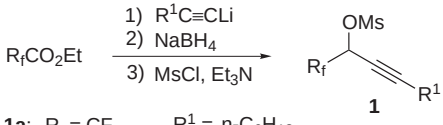
Palladium-catalyzed reactions of propargylic compounds have also been investigated in considerable detail over the last twenty years, and are considered as some of the most valuable synthetic reactions[7]. In sharp contrast to these investigations, palladium-catalyzed transformations of fluorine-

containing propargylic compounds have never been reported thus far, despite their potentially high synthetic value. Herein, we wish to describe the first examples of the palladium-catalyzed reactions of fluoroalkylated propargylic mesylates with various nucleophiles leading to optically active fluorine-containing allenes as well as furan derivatives.

RESULTS AND DISCUSSION

*The Reaction of Fluoroalkylated Mesylates **1** with Various Zinc Reagents in the Presence of Pd(0) Catalyst*

The fluoroalkylated mesylates **1**, used as the starting materials in this study, were readily prepared from ethyl polyfluoroalkanoate and lithium acetylides in three steps (Scheme 1).



1a: $R_f = CF_3$ $R^1 = n\text{-}C_6H_{13}$
1b: $R_f = CF_3$ $R^1 = CH_2OTBS$
1c: $R_f = CF_3$ $R^1 = CH_2OBn$
1d: $R_f = CF_3$ $R^1 = t\text{-}Bu$
1e: $R_f = CF_3$ $R^1 = TMS$
1f: $R_f = CF_2H$ $R^1 = n\text{-}C_6H_{13}$
1g: $R_f = CF_3CF_2$ $R^1 = n\text{-}C_6H_{13}$

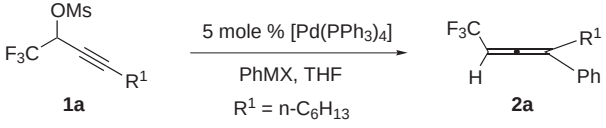
SCHEME 1

Initially, ester **1a** was treated with 5 mole % of $[Pd(PPh_3)_4]$ at room temperature for 10 min, followed by the addition of 2 equivalents of PhMgBr and stirring at that temperature for 24 h, but many unidentified products were produced and the starting ester was recovered in 37% yield (Table I; entry 1). Even the use of 3 equivalents of PhMgBr provided only a trace amount of product **2a** (7%), along with a lower recovery of the starting ester (8%) (entry 2). On the other hand, organozinc reagents were found to participate more efficiently in the reaction than the Grignard reagents did. Two equivalents of a zinc reagent, prepared from PhMgBr and $ZnCl_2$, were allowed to react with **1a** under the influence of the Pd(0) catalyst to produce **2a** in 47% yield, even though a part of the starting ester **1a** (17%) remained unchanged (entry 3). Three equivalents of the zinc reagent were sufficient for the completion of the reaction, in which **2a** was obtained in 63% yield (entry 4). $ZnCl_2$·TMEDA complex was then employed in place of $ZnCl_2$ for the preparation of the organozinc reagent, in view of its very

easy handling due to a low moisture-sensitivity. On treating **1a** with PhZnCl prepared from PhMgBr and $ZnCl_2$·TMEDA complex in the presence of the Pd(0) catalyst, the reaction proceeded smoothly to afford **2a** in good yields (entries 5–8). Eventually, the use of 2 equivalents of the zinc reagent led to the best result (77% yield), as shown in entry 7. Similarly, the reactions of propargyl esters **1** having various fluoroalkyl groups with a variety of organozinc reagents were carried out and the results are summarized in Table II.

In the case of arylzinc reagents (entries 1–4), the desired allenes **2a**–**2d** were obtained in excellent yields. With (*E*)-styrylzinc chloride, however, the yield of **2e** decreased due to the instability of the product (entry 5). The reaction of a 1-alkynylzinc reagent, prepared from the corresponding lithium acetylide and $ZnCl_2$·TMEDA, gave the desired allene in less than 10% yield. Even the use of 3 equivalents of the zinc reagent did not lead to a significant improvement. However, 3 equivalents of the zinc reagent prepared

TABLE I
Investigation of the reaction conditions



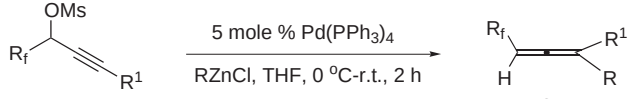
Entry[a]	PhMX (equivalents)	Time, h	Yield of **2a**, %[b]	Recovery of **1a**, %[c]
1	PhMgBr (2.0)	24	0	37
2	PhMgBr (3.0)	24	7	8
3	PhMgBr/$ZnCl_2$ (2.0)	24	47	17
4	PhMgBr/$ZnCl_2$ (3.0)	24	63	0
5	PhMgBr/$ZnCl_2$·TMEDA (1.5)	6	67	0
6[d]	PhMgBr/$ZnCl_2$·TMEDA (1.5)	6	70	0
7[d]	PhMgBr/$ZnCl_2$·TMEDA (2.0)	2	77	0
8[d]	PhMgBr/$ZnCl_2$·TMEDA (3.0)	1	76	0

[a] All reactions were carried out at room temperature, unless otherwise noted. [b] Isolated yields. [c] Determined by ^{19}F NMR. [d] Zinc reagent was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature.

from lithium acetylide and anhydrous $ZnCl_2$ allowed a smooth reaction of **1a**, giving the desired allene **2f** in 78% yield, when the reaction time was prolonged to 24 h (entry 6). As shown in entries 1, 7, and 8, propargyl mesylates **1** carrying a linear side chain R^1 participated readily in the reaction, while those having a bulky side chain such as a *t*-Bu or TMS group did not (entries 9 and 10).

Very interestingly, it was found that the pentafluoroethyl mesylate **1g** underwent the reaction as effectively as the trifluoromethyl mesylate **1a** (entries 13 and 14), while the difluoromethyl mesylate **1f** did not react at all; no trace of the desired product could be observed and the starting material was recovered almost quantitatively (entries 11 and 12).

TABLE II
Palladium-catalyzed reaction of various types of mesylates **1** with organozinc reagents



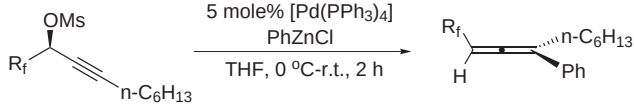
1 **2**

Entry	R_f	R^1	RZnCl	Product	Yield of **2**, %[a]
1	CF_3	n-C_6H_{13}	PhZnCl	**2a**	83 (77)
2	CF_3	n-C_6H_{13}	4-MeC_6H_4ZnCl	**2b**	89 (81)
3	CF_3	n-C_6H_{13}	4-MeOC_6H_4ZnCl	**2c**	86
4	CF_3	n-C_6H_{13}	1-$C_{10}H_7$ZnCl	**2d**	80
5[b]	CF_3	n-C_6H_{13}	PhCH=CHZnCl	**2e**	50 (50)
6[c]	CF_3	n-C_6H_{13}	n-C_6H_{13}C≡CZnCl	**2f**	78
7	CF_3	CH_2OTBS	PhZnCl	**2g**	(86)
8	CF_3	CH_2OBn	PhZnCl	**2h**	73
9	CF_3	*t*-Bu	PhZnCl	–	tr
10	CF_3	TMS	PhZnCl	–	tr
11	CF_2H	n-C_6H_{13}	PhZnCl	–	0
12	CF_2H	n-C_6H_{13}	4-MeC_6H_4ZnCl	–	0
13	CF_3CF_2	n-C_6H_{13}	PhZnCl	**2i**	(70)
14	CF_3CF_2	n-C_6H_{13}	4-MeC_6H_4ZnCl	**2j**	(79)

[a] Determined by ^{19}F NMR. Isolated yields are shown in parentheses. [b] Carried out for 4 h. [c] The reaction was performed at room temperature for 24 h by using 3 equivalents of a zinc reagent which was prepared from the corresponding lithium acetylide and anhydrous $ZnCl_2$.

Synthesis of Optically Active Fluorine-Containing Allenes

Our attention was then directed to the preparation of optically active fluorine-containing allenes, as described in Scheme 2.



(*S*)-1a :
$R_f = CF_3$ (96% ee)

(*S*)-1g :
$R_f = CF_3CF_2$ (94% ee)

(*S*)-2a :
$R_f = CF_3$ (77%; 96% ee)

(*S*)-2i :
$R_f = CF_3CF_2$ (70%; 96% ee)

SCHEME 2

The starting optically active mesylate esters (*S*)-**1a** and (*S*)-**1g** were easily prepared according to a literature method[8]. Their enantiomeric purities were determined to be 96 and 94% ee, respectively, by gas chromatography after the conversion to MTPA esters[9]. When these nonracemic mesylates (*S*)-**1a** and (*S*)-**1g** were allowed to react with PhZnCl in the presence of 5 mole % of [$Pd(PPh_3)_4$], the corresponding allenes (*S*)-**2a** and (*S*)-**2i** were obtained in 77 and 70% yields, respectively, with high enantiomeric excess (96% ee), as determined by HPLC using a chiral column (DAICEL, CHIRAL-CEL OD)[10]. It is of great synthetic value that no loss of enantiomeric purity was observed. This indicates that the reaction proceeds in a highly stereoselective manner.

The Reaction of Fluorine-Containing Mesylates with Various Carbanions Derived from Dicarbonyl Compounds in the Presence of Pd(0) Catalyst

Next we examined the reaction of **1a** with various stabilized carbanions derived from 1,3-dicarbonyl compounds, as shown in Table III.

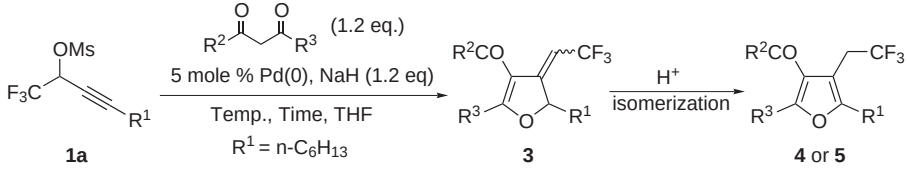
Ester **1a** was treated with sodium enolate derived from methyl acetoacetate in the presence of 5 mole % of [$Pd(PPh_3)_4$] (entry 1). After stirring the reaction mixture for 24 h, dihydrofuran **3a** was obtained in 80% yield as a sole product. In this case, no isomerization product, like **4** or **5**, was detected. When 1,2-bis(diphenylphosphino)ethane (dppe) was used as a ligand on Pd(0), the starting material was completely consumed in only 3 h, and **3a** was obtained in 84% isolated yield (entry 2). Similarly, these reaction conditions were also used for the reaction of **1a** with the sodium enolate of acetylacetone (entries 3 and 4). ^{19}F NMR analysis of the reaction

mixture indicated that the corresponding compound **3** was produced in good yield as a single isomer, but subsequent purification by silica gel column chromatography caused easy isomerization to afford **4a** in 61% isolated yield. When the reaction mixture was heated at reflux for 2 h, the yield of **4a** was improved (71%). As listed in entries 5 and 6, dppe was not a suitable ligand for the reaction with diethyl malonate. The employment of PPh_3 as a ligand led to a more satisfactory result (43% yield), as shown in entry 7.

Mechanism for the Formation of Allenes

To clarify the mechanism, the reaction of mesylate **1a** with PhZnCl in the presence of an equimolar amount of $[Pd(PPh_3)_4]$ was monitored by ^{19}F NMR (Fig. 1). Thus, **1a** was added to a solution of an equimolar amount of $[Pd(PPh_3)_4]$ in THF at 0 °C, and the mixture was stirred at this temperature for 10 min. ^{19}F NMR analysis of the reaction mixture indicated that the starting ester (^{19}F NMR δ 86.5 (d), referred C_6F_6) was completely consumed

TABLE III
Synthesis of furan derivatives



Entry	Pd(0)	R^2	R^3	Temp.	Time	Yield of **3** %[b]	Yield of **4** or **5** %[b]	Recovery of **1a** %[b]
1	$Pd(PPh_3)_4$	OMe	Me	r.t.	24	80 (**3a**)	0	0
2	$0.5[Pd_2(dba)_3]$/2dppe	OMe	Me	r.t	3	84 (**3a**)	0	0
3	$0.5[Pd_2(dba)_3]$/2dppe	Me	Me	r.t	24	[c]	61[a] (**4a**)	27
4	$0.5[Pd_2(dba)_3]$/2dppe	Me	Me	reflux	2	[c]	71[a] (**4a**)	0
5	$0.5[Pd_2(dba)_3]$/2dppe	OEt	OEt	r.t.	24	[c]	8 (**5a**)	27
6	$0.5[Pd_2(dba)_3]$/2dppe	OEt	OEt	reflux	6	[c]	25 (**5a**)	0
7	$[Pd(PPh_3)_4]$	OEt	OEt	r.t.	24	[c]	43 (**5a**)	0

[a] Isolated yields. [b] Determined by ^{19}F NMR, unless otherwise noted. [c] Not determined.

and intermediate **6a** was produced (^{19}F NMR δ 105 (d), Fig. 1b). PhZnCl (2 equivalents) was added to the reaction mixture at 0 °C, and the resultant solution was allowed to warm to room temperature. After stirring the reaction mixture for 3 h, the above peak in ^{19}F NMR disappeared completely and the fluorinated allene **2a** was formed (^{19}F NMR δ 103 (d), Fig. 1c). The chemical shift of **6a** is apparently very close to that of the allene and very different from that of the starting ester **1a**. This observation strongly suggests that the reaction proceeds *via* an allenylpalladium intermediate.

Although the absolute configurations of the above-obtained chiral allenes were not established conclusively, the origin of the *anti*-substitution products (*S*)-**2a** and (*S*)-**2i** is conceivable by assuming the reaction sequence depicted in Scheme 3 [11]. Thus, the oxidative insertion of the Pd(0) catalyst into mesylate **1** gives rise to the allenylpalladium intermediate **6** (inversion), which is in turn transformed into **7** (retention) *via* nucleophilic displacement of the mesylate ligand by the organozinc reagent. The resulting intermediate **7** undergoes reductive elimination to produce the allenic compound **2** (retention), along with the regeneration of the Pd(0) species. For the nonfluorinated series, it is proposed that depending on the starting propargyl ester used, an intermediate allenylpalladium complex **6**, is in equilibrium with a propargyl palladium intermediate **8** [12]. The latter intermediate may be displaced directly by a nucleophile to afford the *syn*-substitution product, which results in a decrease of the stereoselectivity of the reaction, *i.e.*, enantiomeric purity of the product. The extremely high

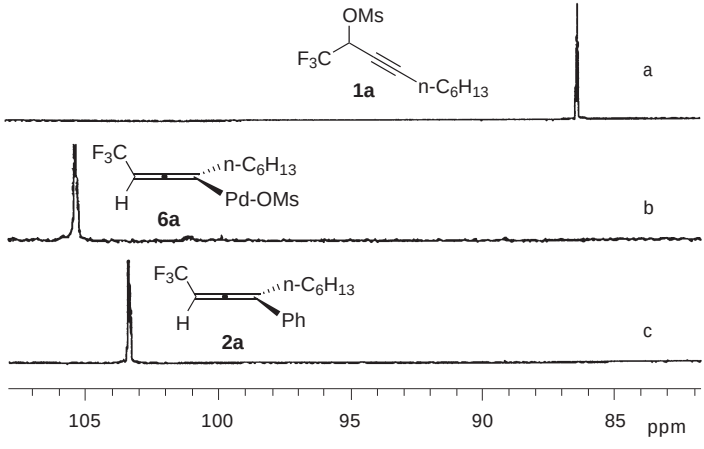
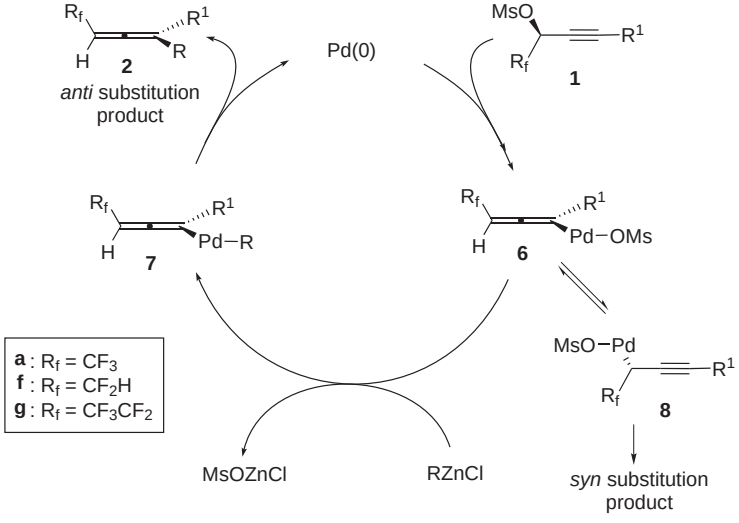


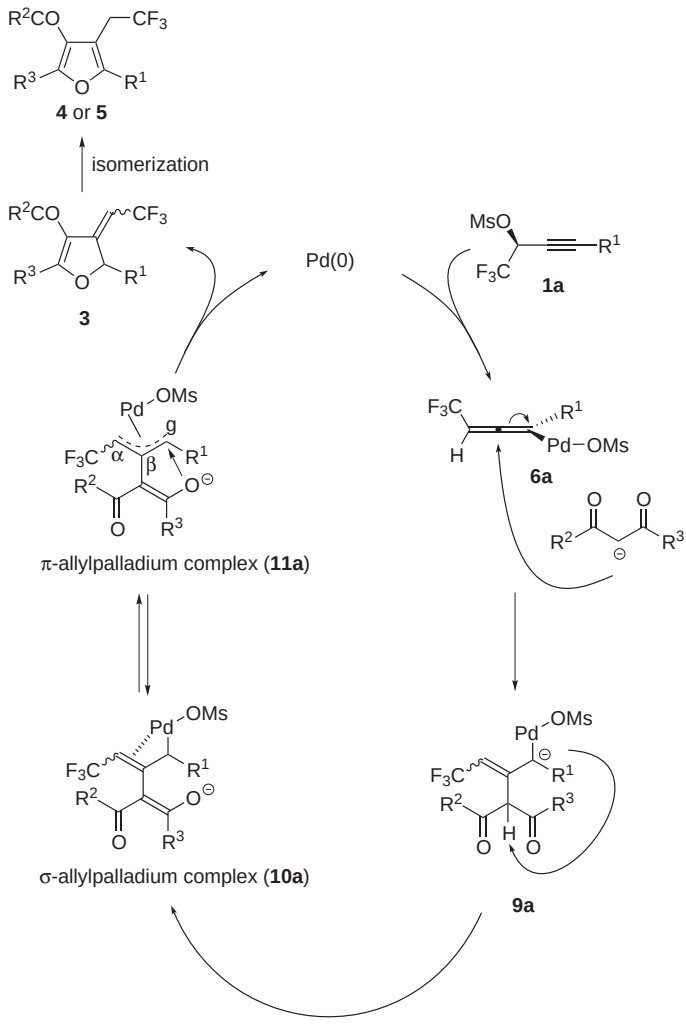
FIG. 1
^{19}F NMR monitoring

stereoselectivity observed in this study enables us to conclude that no isomerization of **6** to **8** occurs in the reaction of **1a** and **1g**. The difficulty in this isomerization can be ascribed primarily to a large steric bulk of the perfluoroalkyl group[13]. It is also possible that the allenylpalladium complex **6f** generated initially from the difluoromethyl ester **1f** isomerizes more readily to the propargylpalladium intermediate **8f** than complexes **1a** and **1g**, because the CF_2H group is not so bulky as the CF_3 and C_2F_5 groups. The resulting propargylpalladium intermediate **8f** seems to be stabilized by the electronegative CF_2H group[14] so that the catalytic cycle is entirely prohibited leaving the starting ester **1f** intact.



SCHEME 3

The mechanism for the formation of furans **4** or **5** is as follows (Scheme 4)[15]. The stabilized carbanion can attack the sp-hybridized carbon of allenylpalladium intermediate **6a** (*vide supra*) to furnish intermediate **9a**. Intramolecular proton abstraction then results in the formation of both enolate and σ-allylpalladium parts, leading to intermediates **10a** and **11a**. In the intermediate **11a**, the Pd moiety might be closer to the CF_3 group than to R^1 due to the electron-withdrawing effect of CF_3. Therefore, oxygen attacks preferentially the less hindered γ-carbon of **11a** to give furan derivatives following the reductive elimination of Pd. In the case of acetylacetone and diethyl malonate, treatment of **3** with aqueous HCl caused isomerization to give furan derivatives **4** and **5**.



SCHEME 4

Conclusion

In summary, we have developed the palladium(0)-catalyzed coupling reaction of fluoroalkyl propargyl mesylates **1** with organozinc reagents and stabilized carbanions derived from 1,3-dicarbonyl compounds, leading to the fluorinated allenic compounds **2** and furan derivatives **3a**, **4a**, and **5a** in high yields. More significantly, it has also been demonstrated that utilization of chiral starting mesylates **1** leads to the formation of chiral fluorinated allenes with an excellent level of stereoselectivity.

EXPERIMENTAL

General Methods

Infrared spectra (wavenumbers in cm^{-1}) were taken on a Shimadzu FTIR-8200(PC) spectrometer as film on a NaCl plate. ^1H NMR spectra were measured on a General Electric QE-300 and/or Bruker DRX-500 NMR spectrometer in a $CDCl_3$ solution with tetramethylsilane as an internal reference. ^{13}C NMR spectra were recorded on a Bruker DRX-500 (125.75 MHz) NMR spectrometer in a $CDCl_3$ solution with Me_4Si as an internal standard. A JEOL JNM-EX90A (84.21 MHz) FT-NMR spectrometer was used for recording ^{19}F NMR spectra in a $CDCl_3$ solution with the internal standard of trichlorofluoromethane. Chemical shifts (δ) are given in ppm, coupling constants (*J*) in Hz. High-resolution mass spectra (HRMS) were taken on a Hitachi M-80B mass spectrometer by electron impact (EI) or chemical ionization (CI) method. Elemental analyses were performed on a Yanaco CHN recorder MT-5 instrument. Gas-liquid chromatography (GLC) was performed on a Shimadzu GC-7AG chromatograph equipped with a flame ionization detector, using nitrogen as the carrier gas and a Shimadzu capillary column HiCap CBP-5-M25-025 (25 m × 0.2 mm). Thin-layer chromatography was performed on aluminium sheets coated with silica gel (Merck 60 F_{254}), and column chromatography was carried out using silica gel (Wacogel C-200) as an adsorbent. Optical rotations were taken on a HORIBA SEPA-200 instrument; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium/benzophenone ketyl under argon. Other solvents were dried by conventional methods before use. Butyllithium (1.6 M hexane solution) was commercially available from Kanto Chemical Co. Amines were distilled over calcium hydride and stored under argon. All chemicals were of reagent grade and, if necessary, they were purified in a usual manner prior to use.

Typical Procedure for the Preparation of Fluorine-Containing Propargyl Mesylates

BuLi (1.6 M hexane solution, 7.5 ml, 12 mmol) was added to a solution of oct-1-yne (1.5 ml, 10 mmol) in THF (20 ml) at –78 °C, and the reaction mixture was stirred at that temperature for 0.5 h. A solution of ethyl trifluoroacetate (1.8 ml, 15 mmol) in THF (10 ml) was added to this mixture at –78 °C. After stirring the reaction mixture for 1 h, sodium borohydride (0.253 g, 0.75 mmol) was added to the reaction mixture, and the mixture was warmed to room temperature after stirring for 0.5 h. After stirring the solution for 24 h, the reaction was quenched with saturated aqueous ammonium chloride, then extracted with ethyl acetate, washed with brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give the corresponding propargyl alcohol (1.47 g, 7.1 mmol).

Methanesulfonyl chloride (0.66 ml, 8.5 mmol) and triethylamine (1.18 ml, 8.5 mmol) were added to a solution of this propargyl alcohol (1.47 g, 7.1 mmol) in CH_2Cl_2 (35 ml) at –50 °C, and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous sodium hydrogencarbonate. The mixture was warmed to room temperature and extracted with CH_2Cl_2 (3 ×). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by silica gel column chromatography to give the desired propargyl mesylate.

1,1,1-Trifluorodec-3-yn-2-yl methanesulfonate (**1a**). ^1H NMR ($CDCl_3$): 5.45–5.49 m, 1 H (H-2′); 3.17 s, 3 H (CH_3SO_3); 2.30 td, 2 H, *J*(5′,6′ and 2′,5′) = 7.3, 2.0 (H-4′); 1.56 tt, 2 H, *J*(6′,5′ and 6′,7′) = 7.3, 7.3 (H-6′), 1.26–1.42 m, 6 H (H-7′, 8′, 9′); 0.89 t, 3 H, *J*(9′,10′) = 6.5

(H-10′). ^{13}C NMR ($CDCl_3$): 120.95 q, *J* = 280.8 (CF_3); 93.44; 67.99 d, *J* = 2.1 (CF_3CHC); 67.64 q, *J* = 38.8 (CF_3CH); 39.52; 31.11; 28.33; 27.66; 22.43; 18.62; 13.93. ^{19}F NMR ($CDCl_3$): –77.54 d, 3 F, *J* = 6.6 (CF_3). IR (neat): 2 936, 2 862, 2 245, 1 466, 1 377. For $C_{11}H_{17}F_3O_3S$ (286.3) calculated: 46.14% C, 5.98% H; found: 45.75% C, 5.77% H.

(2S)-1,1,1-Trifluorodec-3-yn-2-yl methanesulfonate (**1a**). $[\alpha]_D^{21}$ +71.5 (*c* 0.815, $CHCl_3$, 96% ee). All other data were identical with those of racemic **1a**.

1-tert-Butyldimethylsilyloxy-5,5,5-trifluoropent-2-yn-4-yl methanesulfonate (**1b**). ^{1}H NMR ($CDCl_3$): 5.52 q, 1 H, *J*(4′,F) = 5.0 (H-4′); 4.40 s, 2 H (H-1′); 3.18 s, 3 H (CH_3SO_3); 0.90 s, 9 H (*t*-Bu); 0.11 s, 6 H (*t*-Bu(CH_3)$_2$Si). ^{13}C NMR ($CDCl_3$): 120.81 q, *J* = 281.0 (CF_3); 90.51; 72.19; 67.13 q, *J* = 38.8 (CF_3CH); 51.32; 39.55; 25.60; 18.14; 5.37. ^{19}F NMR ($CDCl_3$): –77.07 d, 3 F, *J* = 6.6 (CF_3). IR (neat): 2 955, 2 936, 2 862, 2 361, 2 241, 1 474, 1 377, 1 273.

1-Benzyloxy-5,5,5-trifluoropent-2-yn-4-yl methanesulfonate (**1c**). ^{1}H NMR ($CDCl_3$): 7.30–7.38 m, 5 H (Ph); 5.56 tq, 1 H, *J*(1′,4′ and 4′,F) = 5.5, 1.5 (H-4′); 4.59 s, 2 H ($PhCH_2O$); 4.25 d, 2 H, *J*(1′,4′) = 1.5 (H-1′); 3.16 s, 3 H (CH_3SO_3). ^{13}C NMR ($CDCl_3$): 136.59; 128.54; 128.16; 128.14; 120.80 q, *J* = 281.1 (CF_3); 74.02 d, *J* = 2.0 (CF_3CHC); 72.02; 66.86 q, *J* = 38.8 (CF_3CH); 56.70; 39.47. ^{19}F NMR ($CDCl_3$): –77.20 d, 3 F, *J* = 4.4 (CF_3). IR (neat): 3 032, 2 943, 2 866, 2 237, 1 377, 1 273. For $C_{13}H_{13}F_3O_4S$ (322.3) calculated: 48.45% C, 4.07% H; found: 48.18% C, 4.02% H.

1,1,1-Trifluoro-5,5-dimethylhex-3-yn-2-yl methanesulfonate (**1d**). ^{1}H NMR ($CDCl_3$): 6.17 d, 1 H, *J*(4′,5′) = 15.50 (H-4′); 5.45 dd, 1 H, *J*(2′,3′ and 3′,4′) = 8.00, 15.50 (H-3′); 5.24 dq, 1 H, *J*(2′,3′ and 2′,F) = 8.00, 6.00 (H-2′); 3.07 s, 3 H (CH_3SO_3); 1.07 s, 9 H (*t*-Bu). ^{13}C NMR ($CDCl_3$): 154.28; 122.35 q, *J* = 280.73 (CF_3); 113.31; 78.21 q, *J* = 34.19 (CF_3CH); 39.55; 33.70; 28.72.

1,1,1-Trifluoro-4-trimethylsilyl-but-3-yn-2-yl methanesulfonate (**1e**). ^{1}H NMR ($CDCl_3$): 5.47 q, 1 H, *J*(2′,F) = 5.0 (H-2′); 3.20 s, 3 H (CH_3SO_3); 0.24 s, 9 H (TMS). ^{13}C NMR ($CDCl_3$): 116.21 q, *J* = 281.1 (CF_3); 98.63; 91.21; 67.41 q, *J* = 38.8 (CF_3CH); 39.58; –0.84. ^{19}F NMR ($CDCl_3$): –77.05 d, 3 F, *J* = 4.4 (CF_3). IR (neat): 3 036, 2 963, 1 736, 1 371.

1,1-Difluorodec-3-yn-2-yl methanesulfonate (**1f**). ^{1}H NMR ($CDCl_3$): 5.83 td, 1 H, *J*(1′,F and 1′,2′) = 55.0, 2.0 (H-1′); 5.26–5.31 m, 1 H (H-2′); 3.15 s, 3 H (CH_3SO_3); 2.29 td, 2 H, *J*(5′,6′ and 2′,5′) = 7.0, 2.0 (H-5′); 1.55 tt, 2 H, *J*(5′,6′ and 6′,7′) = 7.5, 7.5 (H-6′); 1.24–1.41 m, 6 H (H-7′, 8′, 9′); 0.89 t, *J*(9′,10′) = 6.5, 3 H (H-10′). ^{13}C NMR ($CDCl_3$): 111.56 t, *J* = 248.5 (CF_2H); 93.34; 69.28; 69.22 t, *J* = 29.6 (CF_2HCH); 39.34; 31.10; 28.34; 27.79; 22.40; 18.62; 13.90. ^{19}F NMR ($CDCl_3$): –128.43 ddd, 1 F, *J* = 286.2, 55.1, 8.8 (CF_2H); –125.67 ddd, 1 F, *J* = 286.2, 55.1, 8.8 (CF_2H). IR (neat): 2 936, 2 862, 2 241, 1 466, 1 373. For $C_{11}H_{18}F_2O_3S$ (268.3) calculated: 49.24% C, 6.76% H; found: 49.09% C, 6.62% H.

1,1,1,2,2-Pentafluoroundec-4-yn-3-yl methanesulfonate (**1g**). ^{1}H NMR ($CDCl_3$): 5.58 t, 1 H, *J*(3′,F) = 9.0 (H-3′); 3.17 s, 3 H (CH_3SO_3); 2.31 td, 2 H, *J*(3′,6′ and 6′,7′) = 7.0, 2.0 (H-6′); 1.55 tt, 2 H, *J*(6′,7′ and 7′,8′) = 7.5, 7.5 (H-7′); 1.27–1.42 m, 6 H (H-8′, 9′, 10′); 0.89 t, 3 H, *J*(10′,11′) = 7.0 (H-11′). ^{13}C NMR ($CDCl_3$): 118.17 qt, *J* = 287.1, 34.2 (CF_3); 110.52 tq, *J* = 261.6, 37.4 (CF_3CF_2); 94.56; 67.50 t, *J* = 2.9 (CF_3CF_2CH); 67.25; 39.56; 31.10; 28.29; 27.63; 22.41; 18.62; 13.87. ^{19}F NMR ($CDCl_3$): –122.95 dd, 2 F, *J* = 26.4, 8.8 (CF_3CF_2); –81.40 s, 3 F (CF_3). IR (neat): 2 936, 2 862, 2 245, 1 466, 1 377, 1 335. For $C_{12}H_{17}F_5O_3S$ (336.3) calculated: 42.86% C, 5.09% H; found: 42.93% C, 4.96% H.

(3S)-1,1,1,2,2-Pentafluoroundec-4-yn-3-yl methanesulfonate (**1g**). $[\alpha]_D^{21}$ +61.9 (*c* 0.825, $CHCl_3$, 94% ee). All other data were identical with those of racemic **1g**.

Typical Procedure for the Synthesis of Allenes

Propargyl mesylate **1a** (100 mg, 0.350 mmol) was added to a solution of $[Pd(PPh_3)_4]$ (20 mg, 5 mole %) in THF (2 ml) at room temperature, and the mixture was stirred for 10 min. After the reaction mixture was cooled to 0 °C, phenylzinc chloride (0.696 mmol, prepared from PhMgBr and $ZnCl_2$·TMEDA) was added, and the mixture was allowed to warm to room temperature. After stirring the reaction mixture for 2 h, the reaction was quenched with saturated aqueous ammonium chloride, and the resultant mixture was extracted with ethyl acetate (3 ×). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give the title compound.

1,1,1-Trifluoro-4-(phenyl)deca-2,3-diene (**2a**). ^{1}H NMR ($CDCl_3$): 7.27–7.39 m, 5 H (Ph); 5.75–5.79 m, 1 H (H-2′); 2.50–2.54 m, 2 H (H-5′); 1.26–1.57 m, 8 H (H-6′, 7′, 8′, 9′); 0.89 t, 3 H, *J*(9′,10′) = 7.0 (H-10′). ^{13}C NMR ($CDCl_3$): 205.62 q, *J* = 6.0 (CF_3CH=**C**=C); 133.88; 128.69; 128.15; 126.45; 122.79 q, *J* = 271.1 (CF_3); 113.76; 88.55 q, *J* = 38.8 (CF_3**C**H=C=C); 31.57; 29.80; 28.84; 27.39; 22.59; 14.03. ^{19}F NMR ($CDCl_3$): –60.61 d, 3 F, *J* = 6.6 (CF_3). IR (neat): 2 932, 2 858, 1 963, 1 454, 1 412. HRMS (EI): calculated for $C_{16}H_{19}F_3$ 268.1439; found: 268.1445.

(3S)-1,1,1-Trifluoro-4-(phenyl)deca-2,3-diene (**2a**). $[\alpha]_D^{21}$ +19.0 (*c* 0.915, $CHCl_3$, 96% ee). All other data were identical with those of racemic **2a**.

1,1,1-Trifluoro-4-(4′-methylphenyl)deca-2,3-diene (**2b**). ^{1}H NMR ($CDCl_3$): 7.26 d, 2 H, *J* = 7.5 (4-CH_3C_6**H**$_4$); 7.16 d, 2 H, *J* = 8.0 (4-CH_3C_6**H**$_4$); 5.73–5.75 m, 1 H (H-2′); 2.47–2.51 m, 2 H (H-5′), 2.34 s, 3 H (4-C**H**$_3C_6H_4$); 1.30–1.56 m, 8 H (H-6′, 7′, 8′, 9′); 0.89 t, 3 H, *J*(9′,10′) = 5.5 (H-10′). ^{13}C NMR ($CDCl_3$): 205.55 q, *J* = 5.9 (CF_3CH=**C**=C); 138.10; 130.84; 129.41; 126.34; 122.83 q, *J* = 270.6 (**C**F_3CH=C=C); 113.60; 88.38 q, *J* = 38.8 (CF_3**C**H=C=C); 31.59; 29.82; 28.86; 27.42; 22.61; 21.12; 14.02. ^{19}F NMR ($CDCl_3$): –60.64 d, 3 F, *J* = 6.6 (CF_3). IR (neat): 2 932, 2 858, 1 959, 1 512, 1 423. HRMS (EI): calculated for $C_{17}H_{21}F_3$ 282.1595; found: 282.1589.

1,1,1-Trifluoro-4-(4′-methoxyphenyl)deca-2,3-diene (**2c**). ^{1}H NMR ($CDCl_3$): 7.30 d, 2 H, *J* = 9.0 (4-CH_3OC_6**H**$_4$); 6.89 d, 2 H, *J* = 9.0 (4-CH_3OC_6**H**$_4$); 5.73–5.76 m, 1 H (H-2′); 3.81 s, 3 H (4-C**H**$_3OC_6H_4$); 2.46–2.50 m, 2 H (H-5′); 1.26–1.56 m, 8 H (H-6′, 7′, 8′, 9′); 0.89 t, 3 H, *J*(9′,10′) = 6.5 (H-10′). ^{13}C NMR ($CDCl_3$): 205.43 q, *J* = 5.3 (CF_3CH=**C**=C); 159.56; 127.63; 125.87; 122.80 q, *J* = 271.0 (CF_3); 114.12; 113.27; 88.38 q, *J* = 38.6 (CF_3**C**H=C=C); 55.29; 31.57; 29.87; 28.84; 27.39; 22.59; 14.02. ^{19}F NMR ($CDCl_3$): –60.65 d, 3 F, *J* = 4.5 (CF_3). IR (neat): 2 932, 2 858, 1 960, 1 609, 1 512. HRMS (EI): calculated for $C_{17}H_{21}F_3O$ 298.1544; found: 298.1527.

1,1,1-Trifluoro-4-(1′-naphthyl)deca-2,3-diene (**2d**). ^{1}H NMR ($CDCl_3$): 7.79–7.86 m, 3 H (naphthyl); 7.43–7.53 m, 4 H (naphthyl); 5.52–5.57 m, 1 H (H-2′); 2.51–2.55 m, 2 H (H-5′); 1.24–1.56 m, 8 H (H-6′, 7′, 8′, 9′); 0.87 t, 3 H, *J*(9′,10′) = 6.5 (H-10′). ^{13}C NMR ($CDCl_3$): 203.41 q, *J* = 6.0 (CF_3CH=**C**=C); 133.83; 128.46; 128.37; 126.36; 126.04; 125.60; 125.34; 124.99; 123.04 q, *J* = 270.5 (CF_3); 112.29; 85.71 q, *J* = 38.7 (CF_3**C**H=C=C); 34.44; 31.56; 28.74; 27.45; 22.57; 14.02. ^{19}F NMR ($CDCl_3$): –60.50 d, 3 F, *J* = 6.6 (CF_3). IR (neat): 2 932, 2 858, 1 975, 1 416. HRMS (EI): calculated for $C_{20}H_{21}F_3$ 318.1595; found: 318.1598.

(1E)-6,6,6-Trifluoro-3-hexyl-1-(phenyl)hepta-1,3,4-triene (**2e**). ^{1}H NMR ($CDCl_3$): 7.11–7.42 m, 5 H (Ph); 6.64 d, 1 H, *J* = 16.0 (H-2′); 6.60 d, 1 H, *J* = 16.0 (H-1′); 5.66–5.68 m, 1 H (H-5′); 2.26–2.40 m, 2 H (C**H**$_2(CH_2)_4)CH_3$); 1.26–1.57 m, 8 H (CH_2(C**H**$_2)_4$)CH_3); 0.90 t, 3 H, *J* = 6.5 ($CH_2(CH_2)_4$)C**H**$_3$). ^{13}C NMR ($CDCl_3$): 208.45 q, *J* = 6.3 (CF_3CH=**C**=C); 136.6; 130.6; 128.7;

128.5; 128.0; 127.6; 126.5; 126.1; 123.2; 122.5 q, *J* = 276.7 (CF_3); 87.10 q, *J* = 39.0 (CF_3**C**H=C=C); 31.60; 28.91; 28.32; 27.26; 22.60; 14.04. ^{19}F NMR ($CDCl_3$): –60.77 d, 3 F, *J* = 6.6 (CF_3). IR (neat): 2 932, 2 858, 1 956, 1 416. HRMS (EI): calculated for $C_{18}H_{21}F_3$ 294.1595; found: 294.1595.

1,1,1-Trifluoro-4-hexyldodeca-2,3-dien-5-yne (**2f**). ^{1}H NMR ($CDCl_3$): 5.55–5.56 m, 1 H (H-2′); 2.33 t, 2 H, *J*(7′,8′) = 7.0 (H-7′); 2.18 dq, 2 H, *J* = 7.5, 2.5 (CH_2(C**H**$_2$)$_4$$CH_3$); 1.26–1.57 m, 16 H (H-8′, 9′, 10′, 11′, CH_2(C**H**$_2$)$_4$$CH_3$); 0.87–0.91 m, 6 H (H-12′, CH_2(CH_2)$_4$C**H**$_3$). ^{13}C NMR ($CDCl_3$): 210.67 q, *J* = 5.5 (CF_3CH=**C**=C); 122.09 q, *J* = 270.6 (**C**F_3CH=C=C); 98.64; 96.65; 86.38 q, *J* = 39.0 (CF_3**C**H=C=C); 72.64; 33.67; 31.50; 31.29; 28.52; 28.43; 28.33; 27.23; 22.53; 22.52; 19.59; 14.00; 13.99. ^{19}F NMR ($CDCl_3$): –61.03 d, 3 F, *J* = 6.6. IR (neat): 2 932, 2 858, 2 226, 1 963, 1 416, 1 265. HRMS (EI): calculated for $C_{18}H_{27}F_3$ 300.2065; found: 300.2075.

1-tert-Butyldimethylsilyloxy-5,5,5-trifluoro-2-(phenyl)penta-2,3-diene (**2g**). ^{1}H NMR ($CDCl_3$): 7.31–7.48 m, 5 H (Ph); 5.88–5.91 m, 1 H (H-4′); 4.68 s, 2 H (H-1′); 0.92 s, 9 H (*t*-Bu); 0.11 s, 6 H (Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): 205.23 q, *J* = 5.5; 141.24; 128.70; 128.41; 127.16; 126.71; 122.60 q, *J* = 271.3; 114.29; 89.87 q, *J* = 39.2; 61.51; 25.71; 18.23; –5.44. ^{19}F NMR ($CDCl_3$): –60.49 d, 3 F, *J* = 4.5. IR (neat): 2 955, 2 932, 2 858, 1 963, 1 720, 1 454. HRMS (EI): calculated for $C_{17}H_{23}F_3OSi$ 328.1470; found: 328.1458.

5-(Benzyloxy)-1,1,1-trifluoro-4-phenylpenta-2,3-diene (**2h**). ^{1}H NMR ($CDCl_3$): 7.26–7.47 m, 10 H (Ph); 5.85–5.88 m, 1 H (H-2′); 4.49–4.59 m, 4 H (PhC**H**$_2$OC**H**$_2$). ^{13}C NMR ($CDCl_3$): 206.02 q, *J* = 5.2 (CF_3CH=**C**=C); 141.21; 137.50; 131.56; 128.79; 128.41; 127.87; 127.22; 127.13; 122.48 q, *J* = 271.3 (CF_3); 110.33, 88.88 q, *J* = 38.9 (CF_3**C**H=C=C); 71.77; 57.63. ^{19}F NMR ($CDCl_3$): –59.87 d, 3 F, *J* = 6.6 (CF_3). IR (neat): 3 032, 2 928, 2 862, 1 963, 1 720. HRMS (EI): calculated for $C_{18}H_{15}F_3O$ 304.1075; found: 304.1071.

1,1,1,2,2-Pentafluoro-5-(phenyl)undeca-3,4-diene (**2i**). ^{1}H NMR ($CDCl_3$): 7.27–7.39 m, 5 H (Ph); 5.71 tt, 1 H, *J* = 10.0, 3.0 (H-3′); 2.47–2.57 m, 2 H (H-6′); 1.26–1.57 m, 8 H (H-7′, 8′, 9′, 10′); 0.89 t, 3 H, *J* = 7.0 (H-11′). ^{13}C NMR ($CDCl_3$): 207.11 t, *J* = 7.8 (CF_3CF_2CH=**C**=C); 133.63; 128.70; 128.19; 126.41; 120.17 qt, *J* = 285.8, 38.6 (**C**F_3CF_2); 113.76; 111.62 tq, *J* = 251.0, 37.8 (CF_3**C**F_2); 86.57 t, *J* = 28.2 (CF_3CF_2**C**H=C=C); 31.56; 29.81; 28.92; 27.36; 22.57; 14.00. ^{19}F NMR ($CDCl_3$): –111.65 d, 2 F, *J* = 11.0 (CF_3C**F**$_2$); –85.53 s, 3 F (C**F**$_3CF_2$). IR (neat): 2 932, 2 862, 1 960, 1 454. HRMS (EI): calculated for $C_{17}H_{19}F_5$ 318.1407; found: 318.1412.

(4S)-1,1,1,2,2-Pentafluoro-5-(phenyl)undeca-3,4-diene (**2i**). $[\alpha]_D^{21}$ +43.9 (*c* 0.835, $CHCl_3$, 96% ee). All other data were identical with those of racemic **2i**.

1,1,1,2,2-Pentafluoro-5-(4′-methylphenyl)dodeca-3,4-diene (**2j**). ^{1}H NMR ($CDCl_3$): 7.26 d, 2 H, *J* = 8.0 (Ar); 7.16 d, 2 H, *J* = 8.0 (Ar); 5.69 tt, 1 H, *J*(3′,F and 3′,6′) = 10.0, 2.5 (H-3′); 2.44–2.55 m, 2 H (H-6′); 2.34 s, 3 H (4-C**H**$_3$$C_6H_4$); 1.26–1.56 m, 8 H (H-7′, 8′, 9′, 10′); 0.89 t, 3 H, *J* = 7.0 (H-11′). ^{13}C NMR ($CDCl_3$): 207.07 t, *J* = 7.6 (CF_3CF_2CH=**C**=C); 138.14; 130.57; 129.42; 120.19 qt, *J* = 285.7, 38.0 (**C**F_3CF_2); 113.59; 126.29; 111.64 tq, *J* = 250.9, 37.9 (CF_3**C**F_2); 86.40 t, *J* = 28.1 (CF_3CF_2**C**H=C=C); 31.57; 29.82; 28.9; 27.38; 22.58; 21.12; 14.01. ^{19}F NMR ($CDCl_3$): –85.50 s, 3 F (C**F**$_3CF_2$); –111.62 d, 2 F, *J* = 8.8 (CF_3C**F**$_2$). IR (neat): 2 932, 2 862, 1 960, 1 512, 1 458. HRMS (EI): calculated for $C_{18}H_{21}F_5$ 332.1563; found: 332.1554.

Typical Procedure for the Synthesis of Furan Derivatives

A solution of [Pd_2(dba)$_3$·$CHCl_3$] (5 mg, 2.5 mole %) and 1,2-bis(diphenylphosphino)ethane (60 mg, 10 mole %) in THF (2 ml) was stirred at room temperature for 10 min. Propargyl mesylate **1a** (51 mg, 0.178 mmol), methyl acetoacetate (61 mg, 0.526 mmol), and sodium hydride (14 mg, 0.588 mmol) were added to the solution in this order. After stirring the re-

action mixture at room temperature for 3 h, the reaction was quenched with water, and the resultant mixture was extracted with ethyl acetate (3 ×). The combined organic layers were washed with saturated aqueous ammonium chloride, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give the corresponding furan derivatives.

In the case of acetylacetone and diethyl malonate, the organic layer was treated with 3 M aqueous HCl in the extraction step.

Methyl 2-hexyl-5-methyl-3-(2,2,2-trifluoroethylidene)-2,3-dihydrofuran-4-carboxylate (**3a**). ^{1}H NMR ($CDCl_3$): 5.04–5.07 m, 1 H ($CH_3(CH_2)_4CH_2CHO$); 4.98 qd, 1 H, *J* = 9.5, 2.5 (CF_3CH); 3.76 s, 3 H (CH_3OCO); 2.25 s, 3 H (CH_3); 1.26–1.87 m, 10 H ($CH_2(CH_2)_4CH_3$); 0.89 t, 3 H, *J* = 6.5 ($CH_2(CH_2)_4CH_3$). ^{13}C NMR ($CDCl_3$): 177.71; 164.98; 150.32 q, *J* = 5.4 (CF_3CH=C); 123.54 q, *J* = 268.0 (CF_3); 106.98; 99.5 q, *J* = 37.5 (CF_3CH=C); 87.80; 51.25; 36.01; 31.56; 29.69; 28.95; 25.60; 24.04; 22.54; 14.81; 14.01. ^{19}F NMR ($CDCl_3$): –57.56 d, 3 F, *J* = 8.8 (CF_3). IR (neat): 2 959 (m), 2 932, 2 858, 1 720, 1 659, 1 605, 1 443, 1 416. HRMS (EI): calculated for $C_{15}H_{21}F_3O_3$ 306.1443; found: 306.1425.

3-Acetyl-5-hexyl-2-methyl-4-(2,2,2-trifluoroethyl)furan (**4a**). ^{1}H NMR ($CDCl_3$): 3.55 q, 2 H, *J* = 10.5 (CH_2CF_3); 2.56 s, 3 H (CH_3); 2.43 s, 3 H (CH_3CO); 1.60 q, 2 H, *J* = 7.5 ($CH_2(CH_2)_4CH_3$); 1.26–1.35 m, 8 H ($CH_2(CH_2)_4CH_3$); 0.89 t, 3 H, *J* = 6.5 ($(CH_2)_4CH_2CH_3$). ^{19}F NMR ($CDCl_3$): –66.61 t, 3 F, *J* = 11.0 (CF_3). IR (neat): 2 932, 2 858, 1 670, 1 570, 1 420, 1 354. HRMS (EI): calculated for $C_{15}H_{21}F_3O_2$ 290.1494; found: 290.1502.

Ethyl 2-ethoxy-5-hexyl-4-(2,2,2-trifluoroethyl)furan-3-carboxylate (**5a**). ^{1}H NMR ($CDCl_3$): 4.40 q, 2 H, *J* = 7.0 (CH_3CH_2O); 4.26 q, 2 H, *J* = 7.0 (CH_3CH_2OCO); 3.47 q, 2 H, *J* = 11.0 (CF_3CH_2); 2.50 t, 2 H, *J* = 7.3 ($CH_3(CH_2)_4CH_2$); 1.27–1.35 m, 12 H ($CH_3(CH_2)_3CH_2$, CH_3CH_2O); 1.55–1.59 m, 2 H ($CH_3(CH_2)_3CH_2$); 0.89 t, 3 H, *J* = 6.5 (CH_3CH_2OCO). ^{19}F NMR (CD_2Cl_2, standard TFA): 9.89 t, 3 F, *J* = 10.9 (CF_3CH_2). IR (neat): 2 959, 2 932, 2 862, 1 709, 1 605. HRMS (EI): calculated for $C_{17}H_{25}F_3O_4$ 350.1705; found: 350.1686.

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10. The retention time in HPLC (hexane–propan-2-ol 99.5 : 0.5, 0.7 ml/min) is as follows: compound **2a**: *R* isomer, 6.1 min, *S* isomer, 7.1 min; compound **2c**: *R* isomer, 5.9 min, *S* isomer, 6.5 min.
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14. Mesylate **1f** was treated with an equimolar amount of $[Pd(PPh_3)_4]$ at 0 °C in THF-d_8 for 10 min, and ^{19}F and ^{1}H NMR analysis of the reaction mixture was carried out. The formation of a single product was detected by ^{19}F NMR. Furthermore, only two peaks were observed (δ 4.0 (br s, 1 H, CF_2HCH); 4.78 (dt, J = 6.7, 57.1, 1 H, CF_2H)) in the range 4–7 ppm in ^{1}H NMR, and no olefinic proton peaks were found. This strongly suggests that the propargylpalladium complex **8** was formed exclusively, not the allenylpalladium complex **6**.
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