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Stereoselective synthesis of fluoroalkenes via (*Z*)-2-fluoroalkenyliodonium salts

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Abstract—Stereoselective synthesis of fluoroalkenes is described. (*Z*)-2-Fluoro-1-alkenyl(phenyl)iodonium tetrafluoroborates (**1**) were synthesized stereoselectively in good yields by Michael-type addition of HF to 1-alkynyl(phenyl)iodonium tetrafluoroborates (**2**) with a commercially available HF reagent, hydrofluoric acid or Et_3N–3HF. Pd-catalyzed cross-coupling reactions using **1** gave (*Z*)-2-fluoro-1-alkene derivatives in moderate yields. The treatment of **1** with KI in the presence of a catalytic amount of CuI gave (*Z*)-2-fluoro-1-iodo-1-alkenes (**3**). Pd-catalyzed cross-coupling reactions of **3** gave better results than that of **1**, and a variety of (*Z*)-2-fluoro-1-alkene derivatives were synthesized in good yields.

1. Introduction

Fluorinated analogues of natural compounds have attracted the interest of biological and medicinal chemists, because the introduction of a fluorine atom into a natural product can dramatically enhance the biological activity.[1] However, organofluorine compounds are scarce in nature; therefore, they have to be synthesized by fluorination of organic compounds or by using building-block methodology with readily available fluorine-containing substrates.[2] When a fluorine atom is introduced into a carbon–carbon double bond of a biologically active compound, the regio- and stereoselective introduction of the fluorine atom is important because the bioactivity is strongly dependent on the position and stereochemistry of the fluorine atom.[3] The most popular approach to the stereoselective preparation of fluoroalkenes[4] is the Horner–Wadsworth–Emmons reaction using fluoroorganophosphonates with carbonyl compounds; however, a mixture of stereoisomers is generally formed.[5] On the other hand, Pd-catalyzed cross-coupling reaction using alkenyl halides or metals is often employed as a powerful tool to obtain further complex alkenes stereoselectively. Therefore, a cross-coupling reaction using fluoroalkenyl halides or metals would be a versatile method for the stereoselective synthesis of fluoroalkenes. However, the cross-coupling method has been adequately developed because the stereoselective synthesis of fluoroalkenyl halides or metals is difficult. Recently, we reported the stereoselective syntheses of various (*E*)-2-fluoro-1-alkene derivatives by Pd-catalyzed cross-coupling reactions using (*E*)-2-fluoro-1-alkenyl-(*p*-tolyl)iodonium salts, which were prepared from terminal alkynes and *p*-iodotoluene difluoride.[6] Hence, we turned our attention into the stereoselective synthesis of (*Z*)-2-fluoro-1-alkene derivatives. Ochiai et al. reported that (*Z*)-2-fluoro-1-alkenyl(phenyl)iodonium salts (**1**)[7] were stereoselectively prepared by Michael-type addition of a fluoride anion to the corresponding 1-alkynyl(phenyl)iodonium salts (**2**)[8] with CsF; however, the yields were only 15–20% due to the low nucleophilicity of the fluoride anion. Although the simplest reagent for an HF addition is hydrogen fluoride, it requires special equipment, technique, and know-how to use for organic synthesis due to the high toxicity and explosive reactivity to organic compounds. In ordinary laboratories, amine–*n*HF[9] and hydrofluoric acid are commonly used as convenient HF reagents instead of hydrogen fluoride. We found that the HF addition of **2** with these HF reagents smoothly proceeded to afford **1** effectively.[10] In this report, we would like to present the details of the stereoselective synthesis of **1** and their utilization to the synthesis of (*Z*)-2-fluoro-1-alkene derivatives by Pd-catalyzed cross-coupling reactions.

2. Results and discussions

2.1. Stereoselective synthesis of (*Z*)-2-fluoroalkenyliodonium salts (1)

Initially, we employed 1-dodecynyl(phenyl)iodonium tetrafluoroborate (**2a**) as a simple starting material and attempted an HF addition using Et_3N–*n*HF (Table 1). Although

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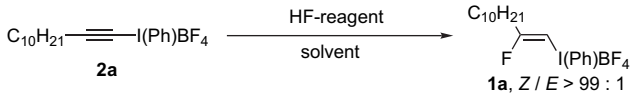
Table 1. HF addition of **2a** with Et_3N–*n*HF or aq HF

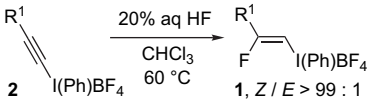


Entry	HF reagent	Solvent	Temp (°C)	Time (h)	Yield (%)
1	Et_3N–5HF	CH_2Cl_2	rt	24	0[a]
2	Et_3N–3HF	CH_2Cl_2	rt	96	71
3	Et_3N–2HF	CH_2Cl_2	rt	44	32[b]
4	Et_3N–3HF	Neat	rt	78	71
5	Et_3N–3HF	Neat	40	8	72
6	Et_3N–3HF	Neat	60	0.75	67[c]
7	46% aq HF	$CHCl_3$	60	84	81
8	30% aq HF	$CHCl_3$	60	8	82
9	20% aq HF	$CHCl_3$	60	6	84
10	10% aq HF	$CHCl_3$	60	5	71[c]

[a] Starting material **2a** was recovered unchanged.
[b] Tri-fluorinated compound, 1,2,2-trifluorododecane (**4**), was obtained in 26% yield.
[c] Small amount of **4** was observed after the reaction.

Et_3N–5HF was inert to **2a** in dichloromethane at room temperature (entry 1), a more nucleophilic fluorinating reagent, Et_3N–3HF, reacted slowly with **2a** to give (*Z*)-2-fluoro-1-dodecenyl(phenyl)iodonium tetrafluoroborate (**1a**) in 71% yield after 96 h (entry 2). The ^1H NMR of the crude reaction mixture indicated that the HF addition proceeded with excellent stereoselectivity (*Z*/*E*>99:1). When **2a** was treated with a more nucleophilic reagent, Et_3N–2HF, further Michael addition of fluoride anion to **1a** occurred to produce 1,2,2-trifluorododecane (**4**) in 26% yield, and the yield of **1a** was reduced to 32% (entry 3). When fluorination of **2a** was carried out with Et_3N–3HF without dichloromethane, the reaction time was reduced to 78 h (entry 4). The HF addition reaction proceeded more effectively at 40 °C (entry 5), but the formation of a small amount of tri-fluorinated compound **4** was observed at 60 °C (entry 6). Next, we attempted the HF addition using hydrofluoric acid, which is commonly used in a laboratory as a simple and cost effective HF reagent. Although commercially available 46% hydrofluoric acid required 84 h at 60 °C to consume **2a** completely, the desired product **1a** was obtained in high yield (entry 7).

Table 2. Synthesis of **1**



1	R^1	Time (h)	Yield (%)
b	Ph	8	43
c	*t*-Bu	12	84
d	(*cyclo*-C_6H_{11})-CH_2	12	74
e	Cl-$(CH_2)_9$	6	80
f	*t*-Bu-CO-$(CH_2)_8$	6	72
g	*i*-PrO_2C-$(CH_2)_8$	6	76

We found that the HF addition reaction was more effectively carried out with diluted hydrofluoric acid (entries 8–10).[11] Finally, the best result was obtained by using 20% hydrofluoric acid, and **1a** was synthesized in 84% yield with excellent stereoselectivity (*Z*/*E*>99:1) (entry 9).[12]

Under the same reaction conditions, 1-alkynyl(phenyl)iodonium salts **2**, which have a *n*-alkyl or a sterically hindered alkyl group, were converted into the corresponding (*Z*)-2-fluoro-1-alkenyliodonium salts **1** in good yields (Table 2). Unfortunately, 2-phenylethynyl(phenyl)iodonium tetrafluoroborate (**2b**) gave the desired product **1b** in lower yield because the starting material **2b** was somewhat labile under the reaction conditions, although **1b** was isolated as a stable white solid.

2.2. Stereoselective synthesis of (*Z*)-2-fluoro-1-alkene derivatives by Pd-catalyzed cross-coupling reaction using (*Z*)-2-fluoroalkenyliodonium salts (1)

First of all, we tried the methoxycarbonylation of **1a** in the presence of $PdCl_2$ with CO in methanol.[6b,13,14] The methoxycarbonylation completed in 2 h at room temperature to give the desired product, methyl (*Z*)-3-fluoro-2-tridecenoate (**5a**) in 73% yield; however, methyl benzoate (**6**, 8%) and (*Z*)-2-fluoro-1-iodo-1-dodecene (**3a**, 9%) were also formed by the methoxycarbonylation of the phenyl group instead of the fluoroalkenyl group on the starting material (Fig. 1).

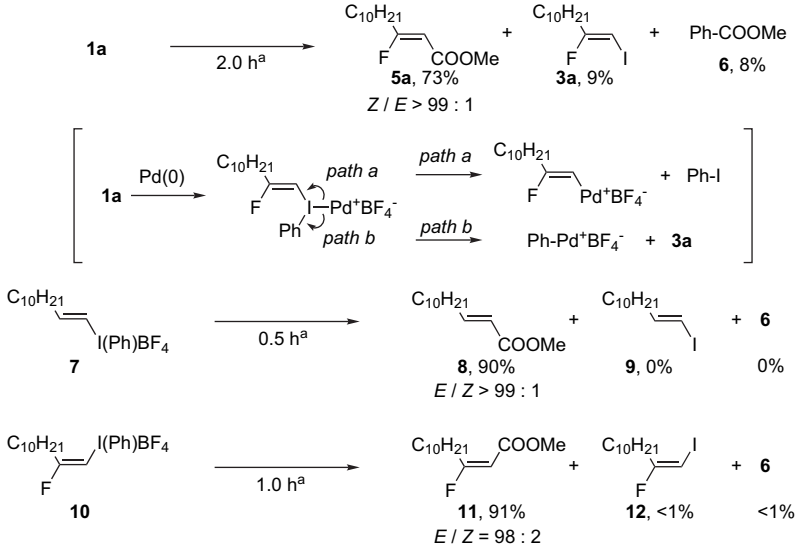
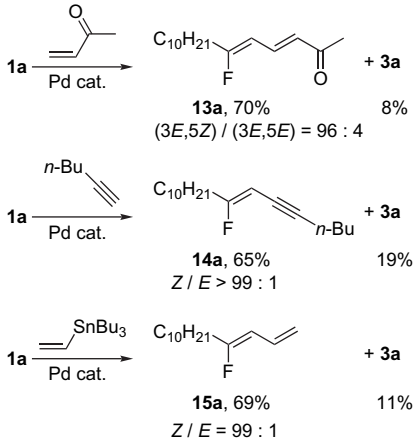


Figure 1. Methoxycarbonylation of **1a**, **7**, and **10**. [a]Reagents and conditions: $PdCl_2$ 2 mol %, CO 1 atm, $NaHCO_3$ 1 equiv, MeOH, rt.

When a nonfluorinated starting material, (*E*)-1-dodecenyl-(phenyl)iodonium tetrafluoroborate (**7**), was subjected to the reaction conditions, the methoxycarbonylation proceeded much faster than that of **1a** to give methyl (*E*)-2-tridecenoate (**8**, 90%) without the formation of (*E*)-1-iodo-1-dodecene (**9**) and **6**.[14] Interestingly, the methoxycarbonylation of (*E*)-2-fluoro-1-dodecenyl(phenyl)iodonium tetrafluoroborate (**10**), which has an alkyl group on the cis-position to the iodonio group, proceeded faster than that of **1a** to give methyl (*E*)-3-fluoro-2-tridecenoate (**11**, 91%) with only a trace amount of (*E*)-2-fluoro-1-iodo-1-dodecene (**12**) and **6**.[6b] Generally, the Pd-catalyzed methoxycarbonylation of an (*E*)-alkenyliodide proceeds faster than that of the (*Z*)-isomer.[15] Hence, we found that the cis-bonded vinylic fluorine atom to the iodonio group disturbed '*path a*', which gave (*Z*)-fluoroalkenylpalladium intermediate, and it caused to produce the phenylpalladium intermediate by '*path b*'; however, the effect of the fluorine atom is unclear now.[14,16,17]

Similarly, Heck reaction,[6c,d,16] Sonogashira reaction,[4k,6f,17] and Stille reaction[6d,18] of **1a** gave the desired (*Z*)-2-fluoro-1-alkene derivatives **13a**–**15a** in moderate yields, but the formation of **3a** was observed in all cases (Scheme 1). Unfortunately, we couldn't suppress the formation of **3a** by modification of the reaction conditions; therefore, we decided to use (*Z*)-2-fluoro-1-iodo-1-alkenes **3** to the Pd-catalyzed cross-coupling reactions instead of (*Z*)-2-fluoro-1-alkenyliodonium salts **1**.

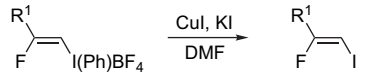


Scheme 1. Pd-catalyzed cross-coupling reactions using **1a**.

2.3. Synthesis of (*Z*)-2-fluoro-1-iodo-1-alkenes (3) from (*Z*)-2-fluoroalkenyliodonium salts (1)

The transformation of alkenyliodonium salts to iodoalkenes with CuI and KI was first reported by Ochiai et al.[7,14b] They proposed that the substitution reaction of iodine for iodonio group can be catalyzed by CuI; however, excess amount of CuI and KI were used in their procedure. We tried the synthesis of **3a** from **1a** with a catalytic amount of CuI and a stoichiometric amount of KI, and confirmed that the reaction well proceeded with 5 mol % of CuI to give **3a** in good yield (Table 3, entry 2), although no reaction occurred without CuI (entry 3). Under the reaction conditions listed in entry 2, a variety of (*Z*)-fluoroiodoalkenes **3** were synthesized from **1** in good yields with retention of the stereochemistry (entries 4–8).

Table 3. Synthesis of **3** from **1**[a]



Entry	3	R^1	Time (h)	Yield (%)
1[b]	**a**	$C_{10}H_{21}$	12	87
2	**a**	$C_{10}H_{21}$	36	89
3[c]	**a**	$C_{10}H_{21}$	24	0
4	**b**	Ph	3	87
5	**d**	(*cyclo*-C_6H_{11})-CH_2	36	88
6	**e**	Cl-$(CH_2)_9$	36	92
7	**f**	*t*-Bu-CO-$(CH_2)_8$	36	91
8	**g**	*i*-PrO_2C-$(CH_2)_8$	36	91

[a] Unless otherwise mentioned, reactions were carried out with 0.5 mmol of **1**, 5 mol % of CuI, and 0.5 mmol of KI in DMF (0.125 M) at rt.
[b] CuI (0.5 mmol) was used.
[c] KI (0.75 mmol) was used in the absence of CuI.

2.4. Pd-catalyzed cross-coupling reaction using (*Z*)-2-fluoro-1-iodo-1-alkene (3)

Then, we attempted the Pd-catalyzed cross-coupling reactions using (*Z*)-2-fluoro-1-iodo-1-dodecene (**3a**) and (*Z*)-α-fluoro-β-iodostyrene (**3b**). By Pd-catalyzed cross-coupling reactions, such as methoxycarbonylation, Heck reaction, Stille reaction, Sonogashira reaction, and Suzuki–Miyaura reaction[19] using (*Z*)-2-fluoro-1-iodoalkenes **3**, a variety of (*Z*)-2-fluoro-1-alkene derivatives (**5** and **13**–**17**) were synthesized stereoselectively in good yields (Table 4). By using our methodology for the fluoroalkenes synthesis, we have succeeded in the stereoselective synthesis of the fluorinated analogues of insect sex pheromones and reported in a recent paper.[20]

3. Conclusions

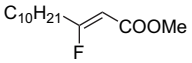
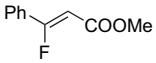
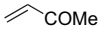
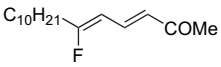
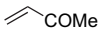
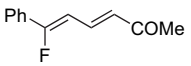
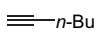
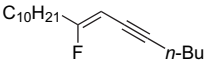
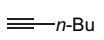
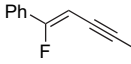
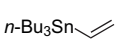
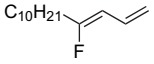
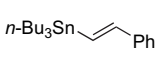
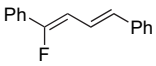
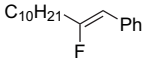
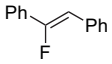
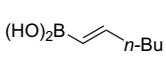
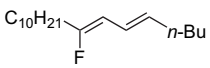
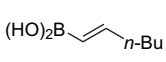
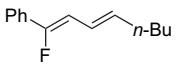
(*Z*)-2-Fluoro-1-alkenyl(phenyl)iodonium salts **1** were stereoselectively synthesized in good yields by an HF addition to 1-alkynyl(phenyl)iodonium salts **2** with diluted hydrofluoric acid or Et_3N–3HF. Pd-catalyzed cross-coupling reactions using **1** gave (*Z*)-2-fluoro-1-alkene derivatives in fair yields. The transformation of **1** to (*Z*)-2-fluoro-1-iodo-1-alkenes **3** was performed with a catalytic amount of CuI and a stoichiometric amount of KI. By Pd-catalyzed cross-coupling reactions of **3**, various (*Z*)-2-fluoro-1-alkene derivatives were stereoselectively synthesized in good yields. We previously reported that (*E*)-2-fluoro-1-alkenyliodonium salts were stereoselectively synthesized by the reaction of terminal alkynes with *p*-iodotoluene difluoride and their application to the stereoselective synthesis of (*E*)-2-fluoro-1-alkenes. Hence, we developed an efficient methodology for the highly stereoselective synthesis of (*E*)- and (*Z*)-2-fluoro-1-alkene derivatives from terminal alkynes via the fluoroalkenyliodonium salts.

4. Experimental

4.1. General

The chemical shifts, δ, of ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), and ^{13}C NMR (100 MHz) spectra were referred

Table 4. Pd-catalyzed cross-coupling reactions **3a** and **3b**

Substrate	Coupling reagent	Product		Yield (%)	*Z*/*E*
3a	CO, MeOH		**5a**	88	>99:1
3b	CO, MeOH		**5b**	77	>99:1
3a			**13a**	77	98:2 (3*E*,5*Z*)/(3*E*,5*E*)
3b			**13b**	76	96:4 (3*E*,5*Z*)/(3*E*,5*E*)
3a			**14a**	88	>99:1
3b			**14b**	83	>99:1
3a			**15a**	86	>99:1
3b			**15b**	83	>99:1(1*Z*,3*E*)/(1*E*,3*E*)
3a	Ph-B(OH)$_2$		**16a**	88	>99:1
3b	Ph-B(OH)$_2$		**16b**	85	>99:1
3a			**17a**	81	>99:1 (5*E*,7*Z*)/(5*E*,7*E*)
3b			**17b**	72	>99:1(1*Z*,3*E*)/(1*E*,3*E*)

to TMS (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F). Et_3N–2HF was prepared as CH_2Cl_2 solution by the addition of Et_3N to Et_3N–3HF in CH_2Cl_2 before use. Commercial $CHCl_3$ was distilled before use. $Pd(PPh_3)_4$,[21] (*E*)-1-dodecenyl(phenyl)iodonium tetrafluoroborate (**7**),[14b] Et_3N–5HF,[22] tributylvinylstannane,[23] tributylstyrylstannane,[24] and (*E*)-1-hexenylboronic acid[25] were prepared according to the literatures. 1-Alkynyl(phenyl)-iodonium tetrafluoroborates (**2**) were prepared from the corresponding terminal alkynes by our method.[8c] The spectral data for **1a**,[10] **1c–g**,[10] **2b**,[26] **3a**,[10] **5a**,[10] **11**,[6b] **12**,[6a] and **14a**[10] were reported in the literatures.

4.2. Synthesis of (*Z*)-2-fluoro-1-dodecenyl(phenyl)iodonium tetrafluoroborate (1a) by the reaction of 2a with Et_3N–3HF

In a Teflon™ PFA vessel were placed 1-dodecynyl(phenyl)-iodonium tetrafluoroborate (**2a**) (228 mg, 0.5 mmol) and Et_3N–3HF (805 mg, 5 mmol) at room temperature, and the mixture was stirred at 40 °C for 8 h. The reaction mixture was poured into water (100 ml) and extracted with CH_2Cl_2 (10 ml) four times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting viscous oil was dissolved in CH_2Cl_2 (1 ml) and a white suspension was formed by the addition of hexane (40 ml). The white suspension was left in a refrigerator for 2 h and clear upper liquid was removed by decantation. The remained white solid was washed with hexane (5 ml) again, separated by decantation, and dried in vacuo to give (*Z*)-2-fluoro-1-dodecenyl(phenyl)iodonium tetrafluoroborate (**1a**)[10] (72%, 171 mg, 0.36 mmol, *Z*/*E*>99:1).

4.3. Synthesis of 1a by the reaction of 2a with hydrofluoric acid

In a Teflon™ PFA vessel were placed **2a** (228 mg, 0.5 mmol), $CHCl_3$ (2 ml), and a 20% hydrofluoric acid (500 mg, 5 mmol) at room temperature, and the mixture was vigorously stirred at 60 °C for 6 h. The reaction mixture was poured into a 0.5 M aq $NaBF_4$ (20 ml) and extracted with CH_2Cl_2 (10 ml) four times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting viscous oil was dissolved in CH_2Cl_2 (1 ml) and a white suspension was formed by the addition of hexane (40 ml). The white suspension was left in a refrigerator for 2 h and the clear upper liquid was removed by decantation. The remained precipitate was washed with hexane (40 ml) again, separated from hexane by decantation, and dried in vacuo to give pure **1a** (84%, 200 mg, 0.42 mmol, *Z*/*E*>99:1).

4.4. (*Z*)-2-Fluoro-2-phenylethenyl(phenyl)iodonium tetrafluoroborate (1b)

Mp 136.5–137.0 °C, δ_H (DMSO-d_6) 7.53–7.77 (8H, m), 7.94 [1H, d, $^3J_{H-F(olefin)}$ 37.5 Hz, 1-H], 8.17 (2H, d, *J* 8.03 Hz); δ_F (DMSO-d_6) −83.80 [1F, d, $^3J_{H-F(olefin)}$ 37.5 Hz, 2-F]; δ_C (DMSO-d_6) 80.4 (d, $^2J_{C-F}$ 21.5 Hz, 1-C), 115.4, 125.9 (2C, d, $^3J_{C-F}$ 7.4 Hz, *ortho*), 127.4 (d, $^2J_{C-F}$ 28.0 Hz, *ipso*), 129.3 (2C), 131.8 (2C), 132.0, 132.5, 135.0 (2C), 164.6 (d, $^1J_{C-F}$ 261.8 Hz, 2-C); ν (KBr)/cm^{-1} 3113, 1625, 1575, 1496, 1470, 1445, 1290, 1084, 1037, 987, 796, 768, 740, 677, 651, 634, 603, 521; [HR FABMS Calcd for $C_{14}H_{11}FI$ (M−BF_4): 324.9890. Found: M^+−BF_4, 324.9868]. Found: C, 40.63; H, 2.67%. Calcd for $C_{14}H_{11}BF_5I$: C, 40.82; H, 2.69%.

4.5. 1-Dodecynyl(phenyl)iodonium tetrafluoroborate (2a)

Mp 41.5–42.2 °C, δ_H ($CDCl_3$) 0.88 (3H, t, *J* 7.1 Hz, 12-H), 1.19–1.39 (14H, m), 1.55–1.63 (2H, m, 4-H), 2.65 (2H, t, *J* 7.1 Hz, 3-H), 7.53–8.07 (5H, m, Ph); δ_C ($CDCl_3$) 14.1, 16.0, 20.8, 22.6, 27.6, 28.7, 28.9, 29.2, 29.3, 29.5, 31.8, 114.1, 114.6, 132.7 (2C), 132.9, 133.8 (2C); ν (KBr)/cm^{-1} 3051, 2924, 2853, 2168, 1470, 1441, 1069, 1038, 987, 738, 678, 650; [HR FABMS Calcd for $C_{18}H_{26}I$ (M−BF_4): 369.1079. Found: M^+−BF_4, 369.1096]. Found: C, 47.42; H, 5.81%. Calcd for $C_{18}H_{26}BF_4I$: C, 47.40; H, 5.75%.

4.6. 3,3-Dimethyl-1-butynyl(phenyl)iodonium tetrafluoroborate (2c)

Mp 189.6–190.5 °C, δ_H ($CDCl_3$) 1.33 (9H, s, ^{t}Bu), 7.55–8.05 (5H, m, Ph); δ_C ($CDCl_3$) 15.7, 29.9 (3C), 30.2, 114.8, 121.4, 132.77 (2C), 132.83, 133.5 (2C); ν (KBr)/cm^{-1} 3097, 2977, 2932, 2871, 2192, 2155, 1560, 1470, 1446, 1366, 1286, 1253, 1051, 921, 743, 675, 645; [HR FABMS Calcd for $C_{12}H_{14}I$ (M−BF_4): 285.0140. Found: M^+−BF_4, 285.0146]. Found: C, 38.55; H, 3.74%. Calcd for $C_{12}H_{14}BF_4I$: C, 38.75; H, 3.79%.

4.7. 3-Cyclohexyl-1-propynyl(phenyl)iodonium tetrafluoroborate (2d)

Mp 86.2–87.2 °C, δ_H ($CDCl_3$) 0.94–1.30 (5H, m), 1.56–1.77 (6H, m), 2.57 (2H, d, *J* 6.6 Hz, 3-H), 7.54–8.07 (5H, m, Ph); δ_C ($CDCl_3$) 16.4, 25.8 (2C), 25.8, 28.5, 32.6 (2C), 36.9, 113.6, 114.8, 132.8 (2C), 132.9, 133.7 (2C); ν (KBr)/cm^{-1} 3086, 2928, 2849, 2185, 1562, 1473, 1446, 1417, 1327, 1275, 1070, 891, 765, 738, 676, 650; [HR FABMS Calcd for $C_{15}H_{18}I$ (M−BF_4): 325.0453. Found: M^+−BF_4, 325.0470]. Found: C, 43.83; H, 4.42%. Calcd for $C_{15}H_{18}BF_4I$: C, 43.73; H, 4.40%.

4.8. 11-Chloro-1-undecynyl(phenyl)iodonium tetrafluoroborate (2e)

Mp 47.7–48.4 °C, δ_H ($CDCl_3$) 1.21–1.44 (10H, m), 1.55–1.63 (2H, m, 4-H), 1.72–1.79 (2H, m, 10-H), 2.64 (2H, t, *J* 7.3 Hz, 3-H), 3.53 (2H, t, *J* 6.8 Hz, 11-H), 7.52–8.07 (5H, m, Ph); δ_C ($CDCl_3$) 15.9, 20.9, 26.8, 27.6, 28.69, 28.73, 28.8, 29.2, 32.6, 45.2, 114.2, 114.6, 132.8 (2C), 132.9, 133.8 (2C); ν (KBr)/cm^{-1} 3050, 2992, 2925, 2854, 2166, 1562, 1470, 1441, 1305, 1051, 988, 740, 679, 650; [HR FABMS Calcd for $C_{17}H_{23}ClI$ (M−BF_4): 389.0533. Found: M^+−BF_4, 389.0545]. Found: C, 42.91; H, 4.76%. Calcd for $C_{17}H_{23}BClF_4I$: C, 42.85; H, 4.86%.

4.9. 2-(10,10-Dimethyl-9-oxoundecanyl)ethynyl-(phenyl)iodonium tetrafluoroborate (2f)

Oil, δ_H ($CDCl_3$) 1.13–1.37 (17H, m), 1.51–1.63 (4H, m), 2.47 (2H, t, *J* 7.1 Hz, 10-H), 2.65 (2H, t, *J* 7.1 Hz, 3-H), 7.53–8.07 (5H, m, Ph); δ_C ($CDCl_3$) 16.0, 20.8, 23.7, 26.4 (3C), 27.5, 28.5, 28.6, 29.0, 29.1, 36.4, 44.1, 114.0, 114.6, 132.7 (2C), 132.9, 133.8 (2C), 216.4; ν (neat)/cm^{-1} 3093, 2930, 2857, 2182, 1702, 1469, 1445, 1366, 1067, 985, 740, 676; [HR FABMS Calcd for $C_{21}H_{30}IO$ (M−BF_4): 425.1341. Found: M^+−BF_4, 425.1344]. Found: C, 49.19; H, 5.91%. Calcd for $C_{21}H_{30}BF_4IO$: C, 49.25; H, 5.90%.

4.10. 10-Isopropoxycarbonyl-1-decynyl(phenyl)-iodonium tetrafluoroborate (2g)

Oil, δ_H ($CDCl_3$) 1.20–1.39 (14H, m), 1.56–1.61 (4H, m), 2.25 (2H, t, *J* 7.3 Hz, 10-H), 2.65 (2H, t, *J* 7.1 Hz, 3-H), 4.97–5.03 (1H, m, ^{i}Pr), 7.54–8.07 (5H, m, Ph); δ_C ($CDCl_3$) 16.3, 20.5, 21.6 (2C), 24.6, 27.2, 28.3, 28.4, 28.61, 28.64, 34.4, 67.3, 113.1, 114.3, 132.4 (2C), 132.7, 133.8 (2C), 173.4; ν (neat)/cm^{-1} 3090, 3062, 2980, 2932, 2857, 2182, 1726, 1691, 1469, 1445, 1375, 1182, 1107, 985, 741, 676; [HR FABMS Calcd for $C_{20}H_{28}IO_2$ (M−BF_4): 427.1134. Found: M^+−BF_4, 427.1134]. Found: C, 46.50; H, 5.43%. Calcd for $C_{20}H_{28}BF_4IO_2$: C, 46.72; H, 5.49%.

4.11. Synthesis of (*Z*)-2-fluoro-1-iodo-1-dodecene (3a) from 1a

To a DMF solution (4 ml) of **1a** (238 mg, 0.5 mmol) were added CuI (4.8 mg, 0.025 mmol) and KI (83 mg, 0.5 mmol), and the mixture was stirred at room temperature for 36 h. The reaction mixture was poured into 3 M aq NH_4Cl (15 ml) and extracted with ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. In order to remove the generated iodobenzene, the reaction mixture was kept at 40 °C and 0.01 mmHg for 1 h. The product **3a**[10] was isolated by column chromatography (silica gel, hexane) in 89% yield (139 mg, *Z*/*E*>99:1).

4.12. (*Z*)-2-Fluoro-1-iodo-2-phenylethene (3b)

Oil, δ_H ($CDCl_3$) 6.08 [1H, d, $^3J_{H-F(olefin)}$ 34.4 Hz, 1-H], 7.36–7.52 (5H, m, Ph); δ_F ($CDCl_3$) −90.62 [1F, d, $^3J_{H-F(olefin)}$ 34.4 Hz]; δ_C ($CDCl_3$) 53.4 (d, $^2J_{C-F}$ 28.8 Hz, 1-C), 124.6 (2C, d, $^3J_{C-F}$ 5.8 Hz, *ortho*), 128.7 (2C, d, $^4J_{C-F}$ 1.7 Hz, *meta*), 129.8, 130.9 (d, $^2J_{C-F}$ 28.9 Hz, *ipso*), 163.1 (d, $^1J_{C-F}$ 251.9 Hz, 2-C); ν (neat)/cm^{-1} 3095, 3058, 1629, 1574, 1495, 1445, 1281, 1187, 1034, 1015, 791, 768, 741, 687, 606; [HR EIMS Calcd for C_8H_6FI (M): 247.9498. Found: M^+, 247.9480]. Found: C, 38.78; H, 2.48%. Calcd for C_8H_6FI: C, 38.74; H, 2.44%.

4.13. (*Z*)-3-Cyclohexyl-2-fluoro-1-iodo-1-propene (3d)

Oil, δ_H ($CDCl_3$) 0.85–1.30 (5H, m), 1.52–1.62 (6H, m), 2.22 (2H, dd, $^3J_{H-F}$ 20.0, *J* 7.0 Hz, 3-H), 5.14 [1H, d, $^3J_{H-F(olefin)}$

34.6 Hz, 1-H]; δ_F ($CDCl_3$) −79.22 [1F, d, $^3J_{H-F(olefin)}$ 34.6 Hz]; δ_C ($CDCl_3$) 26.0 (2C), 26.2, 32.7 (2C), 34.9, 40.6 (d, $^2J_{C-F}$ 26.4 Hz, 3-C), 51.3 (d, $^2J_{C-F}$ 26.4 Hz, 1-C), 165.5 (d, $^1J_{C-F}$ 261.0 Hz, 2-C); ν (neat)/cm^{-1} 3091, 2924, 2851, 1655, 1448, 1425, 1285, 1242, 1193, 1119, 962, 939, 896, 871, 746; [HR EIMS Calcd for $C_9H_{14}FI$ (M): 268.0124. Found: M^+, 268.0136].

4.14. (*Z*)-11-Chloro-2-fluoro-1-iodo-1-undecene (3e)

Oil, δ_H ($CDCl_3$) 1.30–1.54 (12H, m), 1.73–1.80 (2H, m, 4-H), 2.33 (2H, dt, $^3J_{H-F}$ 16.6, *J* 7.3 Hz, 3-H), 3.53 (2H, t, *J* 6.8 Hz, 11-H), 5.17 [1H, d, $^3J_{H-F(olefin)}$ 34.7 Hz, 1-H]; δ_F ($CDCl_3$) −79.87 [1F, dt, $^3J_{H-F}$ 16.6, $^3J_{H-F(olefin)}$ 34.7 Hz]; δ_C ($CDCl_3$) 25.8, 26.8, 28.6, 28.8, 29.0, 29.2, 32.6, 32.7 (d, $^2J_{C-F}$ 27.2 Hz, 3-C), 45.1, 50.6 (d, $^2J_{C-F}$ 27.2 Hz, 1-C), 166.6 (d, $^1J_{C-F}$ 261.0 Hz, 2-C); ν (neat)/cm^{-1} 3092, 2929, 2855, 1656, 1464, 1429, 1257, 1116, 875, 748, 724, 650; [HR EIMS Calcd for $C_{11}H_{19}ClFI$ (M): 332.0204. Found: M^+, 332.0178].

4.15. (*Z*)-12,12-Dimethyl-2-fluoro-1-iodo-11-oxo-1-tridecene (3f)

Oil, δ_H ($CDCl_3$) 1.13 (9H, s), 1.20–1.36 (8H, m), 1.48–1.58 (4H, m), 2.33 (2H, dt, $^3J_{H-F}$ 16.8, *J* 7.3 Hz, 3-H), 2.47 (2H, t, *J* 7.3 Hz, 10-H), 5.17 [1H, d, $^3J_{H-F(olefin)}$ 34.6 Hz, 1-H]; δ_F ($CDCl_3$) −79.85 [1F, dt, $^3J_{H-F}$ 16.8, $^3J_{H-F(olefin)}$ 34.6 Hz]; δ_C ($CDCl_3$) 23.8, 25.8, 26.4 (3C), 28.6, 29.0, 29.2, 29.3, 32.7 (d, $^2J_{C-F}$ 26.4 Hz, 3-C), 36.4, 44.1, 50.6 (d, $^2J_{C-F}$ 26.4 Hz, 1-C), 166.6 (d, $^1J_{C-F}$ 261.8 Hz, 2-C), 216.0; ν (neat)/cm^{-1} 3092, 2930, 2855, 1704, 1656, 1476, 1464, 1365, 1259, 1117, 1067, 988, 875, 747; [HR EIMS Calcd for $C_{15}H_{26}FIO$ (M): 368.1012. Found: M^+, 368.1039].

4.16. (*Z*)-10-Isopropoxycarbonyl-2-fluoro-1-iodo-1-decene (3g)

Oil, δ_H ($CDCl_3$) 1.22–1.30 (14H, m), 1.48–1.64 (4H, m), 2.26 (2H, t, *J* 7.8 Hz, 10-H), 2.33 (2H, dt, $^3J_{H-F}$ 16.6, *J* 7.6 Hz, 3-H), 4.96–5.05 (1H, m), 5.17 [1H, d, $^3J_{H-F(olefin)}$ 34.6 Hz, 1-H]; δ_F ($CDCl_3$) −79.93 [1F, dt, $^3J_{H-F}$ 16.6, $^3J_{H-F(olefin)}$ 34.6 Hz]; δ_C ($CDCl_3$) 21.8 (2C), 24.9, 25.8, 28.6, 28.97 (2C), 29.03, 32.7 (d, $^2J_{C-F}$ 27.3 Hz, 3-C), 34.6, 50.7 (d, $^2J_{C-F}$ 27.2 Hz, 1-C), 67.3, 166.6 (d, $^1J_{C-F}$ 261.0 Hz, 2-C), 173.3; ν (neat)/cm^{-1} 3092, 2979, 2931, 2856, 1730, 1657, 1467, 1373, 1252, 1181, 1146, 1111, 962, 876, 824, 748; [HR EIMS Calcd for $C_{14}H_{24}FIO_2$ (M): 370.0805. Found: M^+, 370.0818].

4.17. 1,2,2-Trifluorododecane (4)

Oil, δ_H ($CDCl_3$) 0.88 (3H, t, *J* 6.8 Hz, 12-H), 1.27–1.56 (16H, m), 1.87–2.00 (2H, m, 3-H), 4.42 (2H, dt, $^3J_{H-F}$ 11.4, $^2J_{H-F}$ 46.6 Hz, 1-H); δ_F ($CDCl_3$) −234.95 to −235.29 (1F, m), −109.44 to −109.64 (2F, m); δ_C ($CDCl_3$) 14.1, 21.5 (t, $^3J_{C-F}$ 4.1 Hz, 4-C), 22.7, 29.3 (3C), 29.4, 29.6, 31.9, 33.0 (t, $^2J_{C-F}$ 23.9 Hz, 3-C), 81.5 (dt, $^2J_{C-F}$ 37.1, $^1J_{C-F}$ 177.6 Hz, 1-C), 121.1 (dt, $^2J_{C-F}$ 22.3, $^1J_{C-F}$ 241.2 Hz, 2-C); ν (neat)/cm^{-1} 2960, 2926, 2856, 1466, 1381, 1280, 1196, 1137, 1060, 928; [HR EIMS Calcd for $C_{12}H_{23}F_3$ (M): 224.1752. Found: M^+, 224.1768].

4.18. Synthesis of methyl (*Z*)-3-fluoro-2-tridecenoate (5a) from 1a

In a glass round-bottom flask fitted with a balloon (3 L) were placed $PdCl_2$ (1.8 mg, 0.01 mmol), $NaHCO_3$ (42 mg, 0.5 mmol), and MeOH (4 ml). After complete replacement of the atmosphere in the flask with CO, the balloon was filled with CO. Then a MeOH solution (1 ml) of **1a** (238 mg, 0.5 mmol) was added and the mixture was stirred at room temperature for 2 h. The reaction mixture was poured into 3 M aq NH_4Cl (15 ml) and extracted with ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **5a**[10] was isolated by column chromatography (silica gel, hexane–diethyl ether) in 73% yield (89 mg, *Z*/*E*>99:1). Oil, δ_H ($CDCl_3$) 0.88 (3H, t, *J* 7.1 Hz, 13-H), 1.21–1.37 (14H, m), 1.52–1.59 (2H, m, 5-H), 2.26 (2H, dt, $^3J_{H-F}$ 17.3, *J* 7.6 Hz, 4-H), 3.72 (3H, s, OMe), 5.18 [1H, d, $^3J_{H-F(olefin)}$ 33.1 Hz, 2-H]; δ_F ($CDCl_3$) −79.53 [1F, dt, $^3J_{H-F}$ 17.3, $^3J_{H-F(olefin)}$ 33.1 Hz]; δ_C ($CDCl_3$) 14.1, 22.7, 25.5, 28.8, 29.2, 29.3, 29.4, 29.5, 31.9, 33.0 (d, $^2J_{C-F}$ 24.1 Hz, 4-C), 51.3, 98.4 (d, $^2J_{C-F}$ 6.0 Hz, 2-C), 164.3, 172.4 (d, $^1J_{C-F}$ 281.1 Hz, 3-C); ν (neat)/cm^{-1} 2951, 2926, 2855, 1736, 1685, 1466, 1436, 1349, 1278, 1217, 1137, 1033, 889, 833, 722; [HR EIMS Calcd for $C_{13}H_{22}FO$ (M−OMe): 213.1655. Found: M^+−OMe, 213.1648]. Found: C, 68.78; H, 10.42%. Calcd for $C_{14}H_{25}FO_2$: C, 68.82; H, 10.31%.

Under the same reaction conditions, methyl (*E*)-2-tridecenoate (**8**) (90%, *E*/*Z*>99:1) and methyl (*E*)-3-fluoro-2-tridecenoate (**11**) (91%, *Z*/*E*=2:98) were prepared from (*E*)-1-dodecenyl(phenyl)iodonium tetrafluoroborate (**7**) and (*E*)-2-fluoro-1-dodecenyl(phenyl)iodonium tetrafluoroborate (**10**), respectively.

4.19. Synthesis of 5a from 3a

In a round-glass flask fitted with a balloon (3 L) were placed $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol), Et_3N (50 mg, 0.5 mmol), and MeOH (5 ml). After complete replacement of the atmosphere in the flask with CO, the balloon was filled with CO, and **3a** (156 mg, 0.5 mmol) was added into the flask. After stirring at 60 °C for 48 h, the reaction mixture was poured into 3 M aq NH_4Cl (15 ml) and extracted with ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **5a** was isolated by column chromatography (silica gel, hexane–ether) in 88% yield (107 mg, *Z*/*E*>99:1).

The methoxycarbonylations of **9** and **12** were carried out under the same reaction conditions.

4.20. Methyl (*Z*)-3-fluoro-3-phenyl-2-propenoate (5b)

Prepared from **3b** as described for **5a** in 77% yield (*Z*/*E*>99:1). Oil, δ_H ($CDCl_3$) 3.80 (3H, s, COOMe), 5.92 [1H, d, $^3J_{H-F(olefin)}$ 33.4 Hz, 2-H], 7.42–7.68 (5H, m, Ph); δ_F ($CDCl_3$) −96.25 [1F, d, $^3J_{H-F(olefin)}$ 33.4 Hz]; δ_C ($CDCl_3$) 51.6, 96.8 (d, $^2J_{C-F}$ 7.4 Hz, 2-C), 125.6 (2C, $^3J_{C-F}$ 8.2 Hz, *ortho*), 128.9 (2C), 130.5 (d, $^2J_{C-F}$ 25.60 Hz, *ipso*), 131.6, 164.5, 166.4 (d, $^1J_{C-F}$ 277.6 Hz, 3-C); ν (neat)/cm^{-1} 3090, 2997, 2952, 2844, 1727, 1662, 1496, 1450, 1435, 1339,

1285, 1192, 1167, 1057, 1004, 828, 770, 688; [HR EIMS Calcd for $C_{10}H_9FO_2$ (M): 180.0586. Found: M^+, 180.0586].

4.21. (*E*)-1-Dodecenyl(phenyl)iodonium tetrafluoroborate (7)

Mp 36.0–36.5 °C, δ_H ($CDCl_3$) 0.88 (3H, t, *J* 7.1 Hz, 12-H), 1.19–1.32 (14H, m), 1.41–1.48 (2H, m, 4-H), 2.31–2.36 (2H, m, 3-H), 6.79 (1H, d, *J* 13.7 Hz, 1-H), 6.99 (1H, dt, *J* 7.3, 13.7 Hz, 2-H), 7.48–8.02 (5H, m, Ph); δ_C ($CDCl_3$) 14.1, 22.6, 27.6, 28.9, 29.2, 29.3, 29.4, 29.5, 31.8, 35.3, 96.5, 109.6, 132.4 (2C), 132.7, 135.6 (2C), 155.4; ν (KBr)/cm^{-1} 3052, 3002, 2918, 2850, 1469, 1444, 1067, 988, 739; [HR FABMS Calcd for $C_{18}H_{28}I$ ($M-BF_4$): 371.1236. Found: M^+-BF_4, 371.1220]. Found: C, 46.84; H, 6.03%. Calcd for $C_{18}H_{28}BF_4I$: C, 47.19; H, 6.16%.

4.22. Synthesis of (*E*)-2-fluoro-1-dodecenyl(phenyl)-iodonium tetrafluoroborate (10)

To a CH_2Cl_2 solution (6 ml) of 1-dodecyne (332 mg, 2 mmol) was added an Et_3N–5HF solution (22 ml) of *p*-iodotoluene difluoride (768 mg, 3 mmol) at 0 °C and the mixture was stirred at 0 °C for 2 h. The reaction mixture was poured into water (30 ml) and extracted with CH_2Cl_2 (20 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude (*E*)-2-fluoro-1-dodecenyl(phenyl)iodonium fluoride was dissolved in acetonitrile (10 ml) with $AgBF_4$ (779 mg, 4 mmol) and the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water (30 ml) and extracted with CH_2Cl_2 (20 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting viscous oil was dissolved in CH_2Cl_2 (1 ml) and a white suspension was formed by the addition of hexane (40 ml). The white suspension was left in a refrigerator for 2 h and clear upper liquid was removed by decantation. The remained white solid was washed with hexane (5 ml) again, separated by decantation, and dried in vacuo to give pure compound **10** (43%, 400 mg, 0.84 mmol, *E*/*Z*>99:1). Mp 71.8–72.4 °C, δ_H ($CDCl_3$) 0.88 (3H, t, *J* 6.8 Hz, 12-H), 1.17–1.30 (14H, m), 1.47–1.54 (2H, m, 4-H), 2.79 (2H, dt, *J* 7.6, $^3J_{H-F}$ 22.2 Hz, 3-H), 6.72 [1H, d, $^3J_{H-F(olefin)}$ 14.4 Hz, 1-H], 7.46–7.98 (5H, m, Ph); δ_F ($CDCl_3$) −65.89 [1F, dt, $^3J_{H-F(olefin)}$ 14.4, $^3J_{H-F}$ 22.2 Hz]; δ_C ($CDCl_3$) 14.1, 22.6, 25.8, 28.9, 29.2, 29.26, 29.32, 29.5, 31.8, 32.2 (d, $^2J_{C-F}$ 23.9 Hz, 3-C), 78.3 (d, $^2J_{C-F}$ 47.9 Hz, 1-C), 112.1, 132.3 (2C), 132.5, 134.5 (2C), 176.2 (d, $^1J_{C-F}$ 286.5 Hz, 2-C); ν (KBr)/cm^{-1} 3045, 2925, 2854, 1638, 1467, 1440, 1303, 1071, 993, 877, 797, 736, 684; [HR FABMS Calcd for $C_{18}H_{27}FI$ ($M-BF_4$): 389.1142. Found: M^+-BF_4, 389.1154]. Found: C, 45.47; H, 5.57%. Calcd for $C_{18}H_{27}BF_5I$: C, 45.41; H, 5.72%.

4.23. Synthesis of (3*E*,5*Z*)-6-fluoro-3,5-hexadecadien-2-one (13a) from 1a

To a mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) and KI (4.2 mg, 0.025 mmol) in DMF (1.5 ml) were added 1.2 M aq $NaHCO_3$ (0.5 ml, 0.60 mmol) and methyl vinyl ketone (88 mg, 1.25 mmol) at room temperature. The reaction mixture was then cooled to −20 °C and a DMF solution (1 ml) of **1a** (238 mg, 0.5 mmol) was added. After stirring for 12 h at −20 °C, the reaction mixture was poured into 3 M aq NH_4Cl (15 ml), and extracted with ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **13a** was isolated by column chromatography (silica gel, hexane–diethyl ether) in 70% yield [89 mg, (3*E*,5*Z*)/(3*E*,5*E*)=96:4]. Oil, δ_H ($CDCl_3$) 0.88 (3H, t, *J* 7.1 Hz, 16-H), 1.23–1.35 (14H, m), 1.54–1.57 (2H, m, 8-H), 2.25–2.33 (5H, m), 5.44 [1H, dd, *J* 11.2, $^3J_{H-F(olefin)}$ 33.4 Hz, 5-H], 6.04 (1H, d, *J* 15.9 Hz, 3-H), 7.42 (1H, dd, *J* 11.2, 15.9 Hz, 4-H); δ_F ($CDCl_3$) −92.13 [1F, dt, $^3J_{H-F}$ 17.7, $^3J_{H-F(olefin)}$ 33.4 Hz]; δ_C ($CDCl_3$) 14.1, 22.6, 25.9, 26.7, 28.9, 29.2, 29.3, 29.4, 29.5, 31.9, 32.5 (d, $^2J_{C-F}$ 24.0 Hz, 7-C), 105.5 (d, $^2J_{C-F}$ 11.5 Hz, 5-C), 128.8 (d, $^4J_{C-F}$ 3.2 Hz, 3-C), 135.5 (d, $^3J_{C-F}$ 6.6 Hz, 4-C), 167.4 (d, $^1J_{H-F}$ 274.2 Hz, 6-C), 198.7; ν (neat)/cm^{-1} 3057, 2951, 2926, 2855, 1695, 1659, 1599, 1466, 1361, 1254, 1134, 982, 866, 722; [HR FABMS Calcd for $C_{16}H_{27}FO$ ($M-BF_4$): 254.2046. Found: M^+-BF_4, 254.2037].

4.24. Synthesis of 13a from 3a

To a DMF solution (2.5 ml) of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol) were added Et_3N (505 mg, 5 mmol), methyl vinyl ketone (88 mg, 1.25 mmol), and **3a** (156 mg, 0.5 mmol) at room temperature and the mixture was stirred at 60 °C for 4 h. The reaction mixture was poured into 3 M aq NH_4Cl (15 ml) and extracted with ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **13a** was isolated by column chromatography (silica gel, hexane–diethyl ether) in 77% yield (98 mg, *Z*/*E*=98:2).

4.25. (3*E*,5*Z*)-6-Fluoro-6-phenyl-3,5-hexadien-2-one (13b)

Prepared from **3b** as described for **13a** in 76% yield (*Z*/*E*=96:4). Mp 89.2–90.0 °C, δ_H ($CDCl_3$) 2.35 (3H, s, Me), 6.24 (1H, d, *J* 15.9 Hz, 3-H), 6.27 [1H, dd, *J* 11.2, $^3J_{H-F(olefin)}$ 33.2 Hz, 5-H], 7.42–7.65 (6H, m); δ_F ($CDCl_3$) −108.44 [1F, d, $^3J_{H-F(olefin)}$ 33.2 Hz]; δ_C ($CDCl_3$) 27.0, 104.8 (d, $^2J_{C-F}$ 13.3 Hz, 5-C), 124.9 (2C, d, $^3J_{C-F}$ 7.4 Hz, *ortho*), 128.8 (2C, d, $^4J_{C-F}$ 2.5 Hz, *meta*), 130.3 (d, $^3J_{C-F}$ 4.1 Hz, 3-C), 130.5, 130.7 (d, $^2J_{C-F}$ 26.4 Hz, *ipso*), 135.3 (d, $^3J_{C-F}$ 5.8 Hz, 4-C), 161.8 (d, $^1J_{C-F}$ 265.1 Hz, 6-C), 198.4; ν (KBr)/cm^{-1} 1658, 1631, 1363, 1292, 1257, 1008, 976, 768, 692; [HR FABMS Calcd for $C_{12}H_{11}FO$ (M): 190.0794. Found: M^+, 190.0808].

4.26. Synthesis of (*Z*)-8-fluoro-7-octadecen-5-yne (14a) from 1a

A DMF solution (5 ml) of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) and PPh_3 (13.1 mg, 0.05 mmol) was stirred at room temperature for 10 min and then CuI (15.2 mg, 0.08 mmol), hex-1-yne (49 mg, 0.6 mmol), Et_3N (76 mg, 0.75 mmol), and a DMF solution (1 ml) of **1a** (238 mg, 0.5 mmol) were added. After stirring for 15 min at room temperature, the reaction mixture was poured into 3 M aq NH_4Cl (15 ml), and extracted with ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **14a**[10] was isolated by

column chromatography (silica gel, hexane) in 65% yield (86 mg, *Z*/*E*>99:1).

4.27. Synthesis of 14a from 3a

A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) and PPh_3 (13 mg, 0.05 mmol) in DMF (5 ml) was stirred at room temperature for 10 min and then CuI (15 mg, 0.08 mmol), hex-1-yne (62 mg, 0.75 mmol), Et_3N (150 mg, 1.5 mmol), and **3a** (156 mg, 0.5 mmol) were added. After stirring at 30 °C for 2 h, the reaction mixture was poured into 3 M aq NH_4Cl (15 ml), and extracted with ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **14a** was isolated by column chromatography (silica gel, hexane) in 88% yield (117 mg, *Z*/*E*>99:1).

4.28. (*Z*)-1-Fluoro-1-phenyl-1-octen-3-yne (14b)

Prepared from **3b** as described for **14a** in 83% yield (*Z*/*E*> 99:1). Oil, δ_H ($CDCl_3$) 0.94 (3H, t, *J* 7.3 Hz, 8-H), 1.44–1.61 (4H, m), 2.40–2.44 (2H, m, 5-H), 5.57 [1H, dt, $^5J_{H-H}$ 2.4, $^3J_{H-F(olefin)}$ 33.4 Hz, 2-H], 7.34–7.54 (5H, m, Ph); δ_F ($CDCl_3$) −106.77 [1F, d, $^3J_{H-F(olefin)}$ 33.4 Hz]; δ_C ($CDCl_3$) 13.6, 19.5, 22.0, 30.8, 73.1 (d, $^4J_{C-F}$ 3.3 Hz, 4-C), 87.6 (d, $^2J_{C-F}$ 16.6 Hz, 2-C), 97.8 (d, $^3J_{C-F}$ 5.8 Hz, 3-C), 123.9 (2C, d, $^3J_{C-F}$ 7.4 Hz, *ortho*), 128.6 (2C, d, $^4J_{C-F}$ 1.6 Hz, *meta*), 129.6, 131.3 (d, $^2J_{C-F}$ 26.4 Hz, *ipso*), 164.2 (d, $^1J_{C-F}$ 258.6 Hz, 1-C); ν (neat)/cm^{-1} 3058, 2958, 2932, 2872, 2221, 1643, 1496, 1448, 1326, 1286, 1038, 1018, 830, 760, 688; [HR EIMS Calcd for $C_{14}H_{15}F$ (M): 202.1158. Found: M^+, 202.1148].

4.29. Synthesis of (*Z*)-4-fluoro-1,3-tetradecadiene (15a) from 1a

To a DMF solution (2 ml) of $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol) were added a DMF solution (1 ml) of **1a** (238 mg, 0.5 mmol) and tributylvinylstannane (174 mg, 0.55 mmol) at room temperature. After stirring at room temperature for 96 h, the reaction mixture was poured into 3 M aq NH_4Cl (15 ml), and extracted with ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **15a** was isolated by column chromatography (silica gel, hexane) in 69% yield (73 mg, *Z*/*E*=99:1). Oil, δ_H ($CDCl_3$) 0.88 (3H, t, *J* 7.1 Hz, 14-C), 1.23–1.35 (14H, m), 1.47–1.54 (2H, m, 6-H), 2.19 (2H, dt, *J* 7.6, $^3J_{H-F}$ 17.5 Hz, 5-H), 4.95 (1H, d, *J* 10.5 Hz, 1-H), 5.10 (1H, dd, *J* 1.7, 17.1 Hz, 1-H), 5.25 [1H, dd, *J* 10.5, $^3J_{H-F(olefin)}$ 35.6 Hz, 3-H], 6.59 (1H, dt, *J* 10.5, 17.1 Hz, 2-H); δ_F ($CDCl_3$) −103.74 [1F, dt, $^3J_{H-F}$ 17.5, $^3J_{H-F(olefin)}$ 35.6 Hz]; δ_C ($CDCl_3$) 14.1, 22.7, 26.1, 29.0, 29.3 (2C), 29.5, 29.6, 31.9, 32.0 (d, $^2J_{C-F}$ 25.6 Hz, 5-C), 106.9 (d, $^2J_{C-F}$ 11.5 Hz, 3-C), 114.6 (d, $^4J_{C-F}$ 3.3 Hz, 1-C), 128.7 (d, $^3J_{C-F}$ 6.6 Hz, 2-C), 161.1 (d, $^1J_{C-F}$ 266.6 Hz, 4-C); ν (neat)/cm^{-1} 3088, 2955, 2926, 2855, 1684, 1467, 1418, 1133, 994, 899, 861; [HR EIMS Calcd for $C_{14}H_{25}F$ (M): 212.1940. Found: M^+, 212.1933].

4.30. Synthesis of 15a from 3a

To a DMF solution (3 ml) of $PdCl_2(PPh_3)_2$ (25 mg, 0.035 mmol) were added **3a** (156 mg, 0.5 mmol) and tributylvinylstannane (270 mg, 0.85 mmol) at room temperature. The reaction mixture was stirred at 60 °C for 0.5 h, then poured into 3 M aq NH_4Cl (15 ml), and extracted with ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **15a** was isolated by column chromatography (silica gel, hexane) in 86% yield (91 mg, *Z*/*E*>99:1).

4.31. (1*Z*,3*E*)-1-Fluoro-1,4-diphenyl-1,3-butadiene (15b)

Prepared from **3b** with tributylstyryltin as described for **15a** in 83% yield (*Z*/*E*>99:1). Mp 132.5–133.0 °C, δ_H ($CDCl_3$) 6.29 [1H, dd, *J* 11.0, $^3J_{H-F(olefin)}$ 34.8 Hz, 2-H], 6.66 (1H, d, *J* 15.8 Hz, 4-H), 7.21–7.60 (11H, m); δ_F ($CDCl_3$) −118.26 [1F, d, $^3J_{H-F(olefin)}$ 34.8 Hz]; δ_C ($CDCl_3$) 106.9 (d, $^2J_{C-F}$ 13.3 Hz, 2-C), 120.9 (d, $^3J_{C-F}$ 5.0 Hz, 3-C), 123.9 (2C, d, $^3J_{C-F}$ 7.4 Hz, *ortho*), 126.5 (2C), 127.7, 128.6 (2C), 128.7 (2C), 128.9, 132.0 (d, $^3J_{C-F}$ 26.4 Hz, *ipso*), 132.3 (d, $^4J_{C-F}$ 3.3 Hz, 4-C), 137.3, 157.0 (d, $^1J_{C-F}$ 255.3 Hz, 1-C); ν (KBr)/cm^{-1} 3060, 3033, 3020, 2997, 1634, 1488, 1444, 1320, 1280, 994, 965, 863, 748, 687, 653, 617; [HR EIMS Calcd for $C_{16}H_{13}F$ (M): 224.1001. Found: M^+, 224.1005].

4.32. Synthesis of (*Z*)-2-fluoro-1-phenyl-1-dodecene (16a) from 3a

To a mixture of $PdCl_2(PPh_3)_2$ (18 mg, 0.025 mmol) and phenylboronic acid (73 mg, 0.6 mmol) in benzene (5 ml) were added 2 M aq K_2CO_3 (0.3 ml, 0.6 mmol) and **3a** (156 mg, 0.5 mmol) at room temperature. After stirring at 80 °C for 1.5 h, the reaction mixture was poured into 3 M aq NH_4Cl (15 ml), and extracted with diethyl ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **16a** was isolated by column chromatography (silica gel, hexane) in 88% yield (112 mg, *Z*/*E*>99:1). Oil, δ_H ($CDCl_3$) 0.88 (3H, t, *J* 6.7 Hz, 12-H), 1.21–1.63 (16H, m), 2.31 (2H, dt, *J* 7.6, $^3J_{H-F}$ 18.3 Hz, 3-H), 5.45 [1H, d, $^3J_{H-F(olefin)}$ 39.5 Hz], 7.17–7.47 (5H, m, Ph); δ_F ($CDCl_3$) −101.25 [1F, dt, $^3J_{H-F}$ 18.3, $^3J_{H-F(olefin)}$ 39.5 Hz]; δ_C ($CDCl_3$) 14.1, 22.7, 26.4, 28.8, 29.1, 29.2, 29.3, 29.5, 29.6, 31.9, 108.0 (d, $^2J_{C-F}$ 28.9 Hz, 1-C), 126.6 (2C), 128.4 (3C), 134.4 (d, $^3J_{C-F}$ 14.1 Hz, *ipso*), 162.8 (d, $^1J_{C-F}$ 253.1 Hz, 2-C); ν (neat)/cm^{-1} 3059, 3026, 2926, 2854, 1691, 1496, 1466, 1346, 1149, 912, 882, 831, 751, 693; [HR EIMS Calcd for $C_{18}H_{27}F$ (M): 262.2097. Found: M^+, 262.2094].

4.33. (*Z*)-2-Fluoro-1,2-diphenylethene (16b)

Prepared from **3b** as described for **16a** in 85% yield (*Z*/*E*>99:1). Mp 92.5–93.2 °C, δ_H ($CDCl_3$) 6.31 [1H, d, $^3J_{H-F(olefin)}$ 39.5 Hz, 2-H], 7.23–7.65 (10H, m); δ_F ($CDCl_3$) −114.78 [1F, d, $^3J_{H-F(olefin)}$ 39.5 Hz]; δ_C ($CDCl_3$) 105.8 (d, $^2J_{C-F}$ 9.9 Hz, 2-C), 124.3 (2C, d, $^3J_{C-F}$ 7.4 Hz, *ortho*), 127.3 (2C, d, $^4J_{C-F}$ 2.5 Hz, *meta*), 128.6 (3C), 128.9, 129.0 (2C), 132.9 (d, $^2J_{C-F}$ 28.1 Hz, *ipso*), 133.7 (d, $^3J_{C-F}$ 3.3 Hz, *ipso*), 157.2 (d, $^1J_{C-F}$ 258.5 Hz, 1-C); ν (KBr)/cm^{-1} 3089, 3054, 3020, 1653, 1494, 1449, 1333, 1282, 1199, 1077, 1033, 1011, 913, 830, 762, 687, 626; [HR EIMS Calcd for $C_{14}H_{11}F$ (M): 198.0845. Found: M^+, 198.0845].

4.34. Synthesis of (5*E*,7*Z*)-8-fluoro-5,7-octadecadiene (17a) from 3a

To a mixture of $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) and (*E*)-hex-1-enylboronic acid (77 mg, 0.6 mmol) in benzene (5 ml) was added an EtOH solution (0.5 ml) of KOH (56 mg, 1 mmol) and **3a** (156 mg, 0.5 mmol) at room temperature. After stirring for 1 h at 80 °C, the reaction mixture was poured into 3 M aq NH_4Cl (15 ml), and extracted with diethyl ether (10 ml) three times. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **17a** was isolated by column chromatography (silica gel, hexane) in 83% yield (111 mg, (5*Z*,7*E*)/(5*E*,7*E*)>99:1). Oil, δ_H ($CDCl_3$) 0.86–0.91 (6H, m), 1.21–1.51 (20H, m), 2.05–2.21 (4H, m), 5.17 [1H, dd, *J* 10.7, $^3J_{H-F(olefin)}$ 36.3 Hz, 7-H], 5.57 (1H, dt, *J* 6.8, 15.6 Hz, 5-H), 6.22–6.29 (1H, m, 6-H); δ_F ($CDCl_3$) −106.88 [1F, dt, $^3J_{H-F}$ 17.7, $^3J_{H-F(olefin)}$ 36.3 Hz]; δ_C ($CDCl_3$) 13.9, 14.1, 22.2, 22.7, 26.2, 29.0, 29.3, 29.4, 29.5, 29.6, 31.9, 32.0 (d, $^2J_{C-F}$ 26.4 Hz, 9-C), 32.2, 32.5, 106.3 (d, $^2J_{C-F}$ 12.3 Hz, 7-C), 121.7 (d, $^3J_{C-F}$ 5.8 Hz, 6-C), 132.3, 159.2 (d, $^1J_{C-F}$ 260.2 Hz, 8-C); ν (neat)/cm^{-1} 3039, 2956, 2925, 2855, 1685, 1635, 1466, 1137, 969, 850, 722; [HR EIMS Calcd for $C_{18}H_{33}F$ (M): 268.2566. Found: M^+, 268.2561].

4.35. (1*Z*,3*E*)-1-Fluoro-1-phenyl-1,3-octadiene (17b)

Prepared from **3b** as described for **17a** in 72% yield [(1*Z*,3*E*)/(1*E*,3*E*)>99:1]. Oil, δ_H ($CDCl_3$) 0.92 (3H, t, *J* 7.1 Hz, 8-H), 1.30–1.46 (4H, m), 2.17 (2H, dt, *J* 7.1, 7.1 Hz, 5-H), 5.83 (1H, dt, *J* 7.1, 15.3 Hz, 4-H), 6.05 [1H, dd, *J* 10.7, $^3J_{H-F(olefin)}$ 35.6 Hz, 2-H], 6.48 (1H, dd, *J* 10.7, 15.3 Hz, 3-H), 7.27–7.55 (5H, m, Ph); δ_F ($CDCl_3$) −121.19 [1F, d, $^3J_{H-F(olefin)}$ 35.6 Hz]; δ_C ($CDCl_3$) 13.9, 22.3, 31.4, 32.8, 106.7 (d, $^2J_{C-F}$ 14.1 Hz, 2-C), 122.1 (d, $^3J_{C-F}$ 5.8 Hz, 3-C), 123.7 (2C, d, $^3J_{C-F}$ 7.4 Hz, *ortho*), 128.4 (2C), 128.5, 132.4 (d, $^2J_{C-F}$ 27.2 Hz, *ipso*), 135.7 (d, $^4J_{C-F}$ 3.3 Hz, 4-C), 155.1 (d, $^1J_{C-F}$ 251.9 Hz, 1-C); ν (neat)/cm^{-1} 3036, 2957, 2927, 2858, 1653, 1627, 1599, 1495, 1448, 1322, 1281, 994, 969, 761, 688; [HR EIMS Calcd for $C_{14}H_{17}F$ (M): 204.1314. Found: M^+ 204.1313].

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