Regio- and stereoselective synthesis of fluoroalkadienes using β-fluoroalkenyliodonium salt

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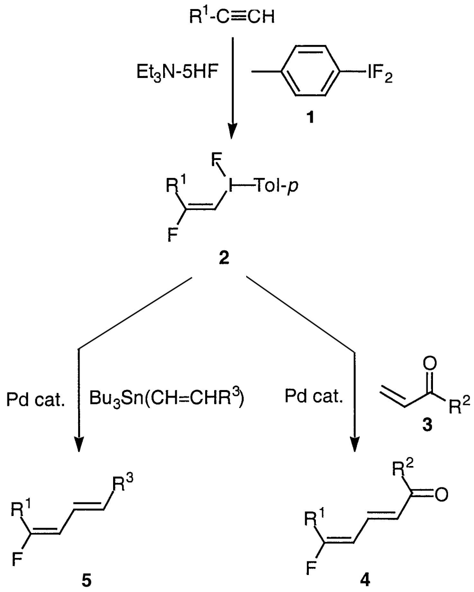
(*E*,*E*)-δ-Fluoro-α,β,γ,δ-unsaturated carbonyl compounds and (3*E*)-4-fluoro-1,3-dienes were stereoselectively synthesized by the palladium-catalyzed coupling reaction of (2-fluoroalkenyl)(*p*-tolyl)iodonium fluorides with α,β-unsaturated carbonyl compounds and tributylvinyltin, respectively.

Introduction

A fluorine atom on a conjugated double bond has been intensively used as a label for obtaining structural information and mechanistic details of natural compounds from ^{19}F NMR measurements.[1] Moreover, the introduction of a fluorine atom onto the conjugated double bonds of bioactive compounds was found to be effective for increasing the stability and bioactivities of these compounds.[2] Therefore, much effort has been made towards the stereoselective synthesis of fluorinated polyenes, and some successful studies have been reported.[3] However, in order to introduce a fluorine atom into any position on the conjugated double bonds of natural compounds, new methodologies for stereoselective fluoropolyene synthesis are required.

Recently, we found that (*E*)-(2-fluoroalk-1-enyl)(*p*-tolyl)iodonium fluorides **2** can be regio- and stereoselectively prepared by the reaction of alk-1-ynes with iodotoluene difluoride **1** and Et_3N–5HF.[4] On the other hand, Moriarty *et al.* reported that hypervalent iodine compounds showed unusually high reactivities in the transition metal-catalyzed Heck-type reaction[5] and in cross-coupling reactions with alkenyltin reagents.[6] We examined the Heck-type coupling reaction and the cross-coupling reaction of **2** for the development of new methodology applicable to the stereoselective synthesis of natural compound analogs having a fluorine atom on their polyene functions (Scheme 1). We have previously reported our preliminary findings[7] and now provide a full account of the work.



Scheme 1

Results and discussion

Heck-type reaction

(*E*)-(2-Fluorodec-1-enyl)(*p*-tolyl)iodonium fluoride **2a** was prepared by the reaction of dec-1-yne with **1**, which had been electrochemically prepared from iodotoluene, in the presence of Et_3N–5HF. In the ^{1}H-NMR spectrum of the crude reaction mixture, the characteristic signal of the olefin hydrogen was observed at δ 6.7 with a 15.1 Hz coupling constant which showed that the H and F on the double bond had *cis*(*Z*)-stereochemistry.[8] The crude **2a** was used for the Heck-type reaction with ethyl acrylate **3a** in the presence of $NaHCO_3$ and a catalytic amount of $Pd(OAc)_2$ in DMF.[5] The reaction was complete at room temperature after 2 h, and the desired fluorinated alkadienyl ester **4a** was obtained in 55% yield based on the decyne. The coupling constant between F and H on C-4 was 18.3 Hz which showed that the double bond at the γ,δ position had *E*-stereochemistry. This assignment was also supported by an NOE experiment; an NOE was observed between H on C-6 and C-3 while no NOE was observed between H on C-6 and C-4. The coupling constant between H on C-2 and H on C-3 was 14.9 Hz which showed that the newly formed double bond also had *E*-stereochemistry. Consequently, ethyl (2*E*,4*E*)-4-fluorotrideca-2,4-dienoate **4a** was obtained with more than 95% stereoselectivity. Various alk-1-ynes having functional groups such as an ester, ketone, and chloride were subjected to the reaction with **1**, and the resulting iodonium salts **2a**–**e** were used for the reaction with ethyl acrylate **3a**, acrolein **3b**, and α,β-unsaturated ketones **3c**, **3d** (Table 1). The expected δ-fluoro-α,β,γ,δ-unsaturated carbonyl compounds **4a**–**r** could be obtained in 51–68% yield with high stereoselectivity (>95%) based on the alkynes. The yields were not high because they are the overall yields of two steps.[9] As by-products, β-tolyl-α,β-unsaturated carbonyl compounds, formed by the Heck-type reaction between **3** and the *p*-tolyl group on **2**, were obtained in 2–5% yield with the starting alkynes formed by the decomposition of **2**. As the reaction proceeded under mild conditions, the functional groups in the substrates remained unchanged under the stated reaction conditions, and consequently the polyfunctionalized fluoroalkadienes could be synthesized in few steps with high selectivity.

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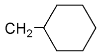
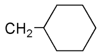
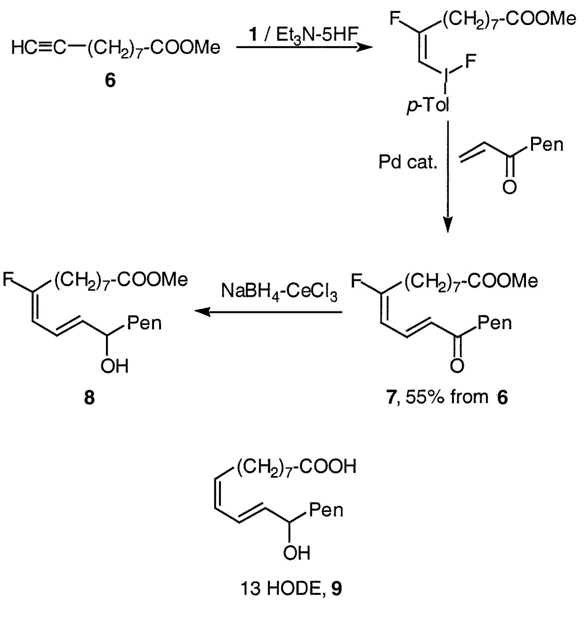
Table 1 Heck-type coupling reaction using (*E*)-(2-fluoroalkenyl)-iodonium salts **2**[a]

Product	R^1	R^2	Yield/%[b]
4a[c]	Oct	OEt	55
4b[c]	Oct	H	54
4c[c]	Oct	Me	53
4d[c]	Oct	Ph	57
4e[d]	$(CH_2)_8COOMe$	OEt	56
4f[d]	$(CH_2)_8COOMe$	H	55
4g[d]	$(CH_2)_8COOMe$	Me	60
4h[d]	$(CH_2)_8COOMe$	Ph	68
4i[d]	$(CH_2)_9Cl$	OEt	61
4j[d]	$(CH_2)_9Cl$	H	56
4k[d]	$(CH_2)_9Cl$	Me	65
4l[d]	$(CH_2)_9Cl$	Ph	54
4m[e]		Me	51
4n[e]		Ph	51
4o[f]	$(CH_2)_8CO\text{-}^tBu$	OEt	57
4p[f]	$(CH_2)_8CO\text{-}^tBu$	H	53
4q[f]	$(CH_2)_8CO\text{-}^tBu$	Me	61
4r[f]	$(CH_2)_8CO\text{-}^tBu$	Ph	66

[a] The reaction conditions are described in the Experimental section. [b] Isolated yield based on alkyne used. [c] It took 2 h to make **2**. [d] It took 8 h to make **2**. [e] It took 12 h to make **2**. [f] It took 14 h to make **2**.

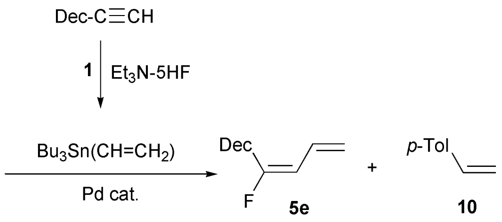
Application to the synthesis of the fluorinated analog of a natural compound

(9*Z*,11*E*)-13-Hydroxyoctadeca-9,11-dienoic acid (13-HODE, **9**) is known to have interesting bioactive properties[10] and its fluorinated analogs have been attractive targets for organic chemists.[11] We attempted to synthesize the methyl ester of 9-fluoro-13-HODE (**8**) which has a fluorine atom on the conjugated double bond of **9**. Methyl dec-9-ynoate (**6**) was allowed to react with **1** in the presence of Et_3N–5HF at 0 °C and the resulting (fluoroalkenyl)iodonium salt was used for the reaction with oct-1-en-3-one to give methyl (9*E*,11*E*)-9-fluoro-13-oxoocta-9,11-dienoate (**7**) in 55% yield from **6**. The desired methyl ester of 9-fluoro-13-HODE, compound **8**, was quantitatively obtained from **7** by reduction of the keto function (Scheme 2).



Scheme 2 Pen = C_5H_{11}-*n*.

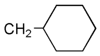
Table 2 Influence of Pd catalyst in the synthesis of **5e**[a]



Entry	Pd cat.	CuL (mol%)	**5e** : **10**[b]	Yield of **5e**/%[c]
1	$PdCl_2(CH_3CN)_2$		80 : 20	51
2	$Pd(PPh_3)_4$	8	80 : 20	32
3	$PdCl_2$	8	80 : 20	45
4	$BnPdCl(PPh_3)_2$	8	80 : 20	49
5	$PdCl_2(CH_3CN)_2$	8	80 : 20	52
6	$PdCl_2$	8	80 : 20	44
7	$BnPdCl(PPh_3)_2$		90 : 10	61

[a] The reaction conditions are described in the Experimental section. [b] Determined by GC analysis. [c] Isolated yield based on dodecyne used.

Table 3 Synthesis of fluorodienes **5**[a]

Entry	Product	R^1	R^3	Yield/%[b]
1	**5a**	$(CH_2)_8COOMe$	H	63(15)
2	**5b**	$(CH_2)_9Cl$	H	65(16)
3	**5c**		H	62(13)
4	**5d**	$(CH_2)_8CO\text{-}^tBu$	H	59(14)
5	**5e**	Dec	H	61(7)
6	**5f**	Dec	Ph	30(3)

[a] The reaction conditions are described in the Experimental section. [b] Isolated yield based on alkyne used. In parentheses, yield of tolylated products.

Vinylation reaction using tributylvinyltin reagent

The cross-coupling reaction of (*E*)-(2-fluorododec-1-enyl)(*p*-tolyl)iodonium fluoride with tributylvinyltin was carried out as reported[6] and the desired (*E*)-4-fluorotetradeca-1,3-diene (**5e**) was obtained in 51% yield based on the dodec-1-yne (Entry 1 in Table 2). As a by-product, *p*-vinyltoluene (*p*-methylstyrene) **10**, formed by the reaction of tributylvinyltin with the tolyl group on **2**, was obtained in 10% yield. As the formation of no identifiable by-products was reported for the reaction of the tributylvinyltin with alkenyl(phenyl)iodonium salts,[6] the *cis*-substituted alkyl group to iodine[12] or a strongly electronegative fluorine substituent in **2** retarded the oxidative addition of the palladium catalyst to the iodine–alkenyl bond[3d–g,13] and the selective formation of the dienyl product **5e** was disturbed. Various kinds of Pd catalysts with or without CuI were used in an attempt to improve the result, but the formation of **10** could not be suppressed. The best result was obtained when $Bn(PPh_3)_2$-PdCl was used without CuI and **5e** was obtained in 61% yield based on dodec-1-yne, with 7% of **10**. Various (fluoroalkenyl)-iodonium salts **2** were used for the cross-coupling reaction with the vinyltin reagent and the corresponding fluoroalkadienes (**5a**–**e**) could be obtained in 59–65% yields with high stereoselectivity (Table 3). The reaction proceeded at room temperature and the various functional groups remained unchanged under the given reaction conditions (Entries 1, 2, 4, Table 3). However, the application of **2** to the cross-coupling reaction with tributyl(β-styryl)tin resulted in a poor yield of **5f** (Entry 6).

Conclusions

(*E*,*E*)-δ-Fluoro-α,β,γ,δ-unsaturated carbonyl compounds **4** and (*E*)-4-fluoro-1,3-dienes **5**, were stereoselectively obtained using the Heck-type reaction or cross-coupling reaction with (2-fluoroalk-1-enyl)iodonium salts **2** obtained from the corresponding alk-1-ynes and **1**. The reaction proceeded at room temperature and many functional groups in the substrate could tolerate the reaction conditions. Consequently, various kinds of fluoroalkadienes having functional groups could be synthesized, and the reaction was used for the synthesis of a fluorinated analog of a natural compound. Further studies on the stereoselective synthesis of fluorinated alkenes using **2** are currently under investigation.

Experimental

General

The IR spectra were recorded using a JASCO FT/IR-410. The ^{1}H-NMR (400 MHz) and ^{19}F-NMR (376 MHz) spectra were recorded in $CDCl_3$ on a JEOL JNM-A400II FT NMR and the chemical shifts, δ, are referred to TMS (^{1}H) and $CFCl_3$ (^{19}F), respectively. The EI low- and high-resolution mass spectra were measured on a JEOL JMS-700TZ, JMS-FABmate or JMS-HX110. The elemental microanalyses were done using a Yanagimoto CHN Corder MT-5. For column chromatography, Merck silica gel 7734 was used, and for analytical thin-layer chromatography, Merck silica gel 5715 was used. Et_3N–5HF was prepared by the addition of freshly distilled Et_3N to anhydrous HF at 0 °C. Dec-1-yne, dodec-1-yne, undec-10-ynoic acid, undec-10-yn-1-ol, $PdCl_2$, $PdCl_2(CH_3CN)_2$, $Pd(PPh_3)_4$ and $Pd(OAc)_2$ were purchased from Tokyo Kasei Co., Ltd., and used without further purification. 11-Chloroundec-1-yne and methyl dec-9-ynoate were prepared from undec-10-yn-1-ol and dec-9-enoic acid, respectively. 3-Cyclohexylprop-1-yne,[14] tributylvinyltin[15] and tributyl[(*E*)-β-styryl]tin[16] were prepared according to the literature. 2,2-Dimethyltridec-12-yn-3-one was prepared from undec-10-yn-1-ol by the PCC oxidation reaction with ^{t}BuMgBr, and the PCC oxidation sequences.

Preparation of *p*-iodotoluene difluoride 1

p-Iodotoluene difluoride was prepared from iodotoluene by an electrochemical method in a divided cell made of Teflon™ PFA (25 mL × 2) with a Nafion™ 117 cation-exchange membrane. Each cell was equipped with a smooth platinum electrode (20 mm × 20 mm) and a magnetic stirrer bar. Et_3N–5HF (22 mL) was introduced into both cells, and *p*-iodotoluene (654 mg, 3 mmol) was added to the anodic cell. By passing 2 F mol^{-1} of electricity at a constant current (50 mA h^{-1}) and room temperature, iodotoluene could be completely converted to **1**. The resulting Et_3N–5HF solution of **1** was used for the further reactions.

General procedure for (*E*,*E*)-δ-fluoro-α,β,γ,δ-unsaturated carbonyl compounds 4 and 7

To a CH_2Cl_2 solution (6 mL) of an alk-1-yne (2 mmol) was added, at 0 °C, an Et_3N–5HF solution (22 mL) of *p*-iodotoluene difluoride prepared from *p*-iodotoluene (654 mg, 3 mmol). After stirring at 0 °C for 2–14 h, the reaction mixture was poured into water and the separated aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The remaining viscous yellow oil was washed with hexane (10 mL) and the hexane layer was removed by decantation. The residue was dissolved in DMF (10 mL), and $NaHCO_3$ (504 mg, 6 mmol), $Pd(OAc)_2$ (31 mg, 0.14 mmol), and an α,β-unsaturated carbonyl compound (5 mmol) were added. The reaction mixture was stirred at room temperature for 2 h and saturated aq. NH_4Cl was added. After extraction with diethyl ether, the organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The product **4** was isolated by column chromatography (silica gel/hexane–diethyl ether). When acrolein was used as the carbonyl compound, 6 equivalents of $NaHCO_3$ to the alk-1-yne were necessary.

Ethyl (2*E*,4*E*)-5-fluorotrideca-2,4-dienoate 4a. R_f 0.60 (hexane–diethyl ether 10 : 1); $\delta_H(CDCl_3)$ 0.88 (3H, t, *J* 7.1 Hz), 1.28–1.33 (13H, m), 1.53–1.61 (2H, m), 2.48 (2H, dt, *J* 7.6, $^3J_{H-F}$ 20.4 Hz), 4.21 (2H, q, *J* 7.1 Hz), 5.84 (1H, d, *J* 14.9 Hz), 5.86 (1H, dd, *J* 11.9, $^3J_{H-F(olefin)}$ 18.3 Hz), 7.31 (1H, dd, *J* 11.9, 14.9 Hz); $\delta_F(CDCl_3)$ −87.95 (1F, dt, $^3J_{H-F(olefin)}$ 18.3, $^3J_{H-F}$ 20.4 Hz); $\delta_C(CDCl_3)$ 14.09, 14.32, 22.63, 26.33, 28.83 (d, $^2J_{C-F}$ 25.9 Hz), 28.94, 29.12, 29.24, 31.80, 60.31, 107.06 (d, $^2J_{C-F}$ 28.9 Hz), 120.10 (d, $^4J_{C-F}$ 9.9 Hz), 138.48 (d, $^3J_{C-F}$ 14.1 Hz), 166.94, 169.50 (d, $^1J_{C-F}$ 266.0 Hz); ν(neat)/cm^{-1} 1718 [Calc. for $C_{15}H_{25}FO_2$ (*M*): 256.1832. Found: M^+, 256.1853] (Calc. for $C_{15}H_{25}FO_2$: C, 70.28; H, 9.83; F, 7.41. Found: C, 70.37; H, 9.79; F, 7.71%).

(2*E*,4*E*)-5-Fluorotrideca-2,4-dienal 4b. R_f 0.38 (hexane–diethyl ether 5 : 1); $\delta_H(CDCl_3)$ 0.88 (3H, t, *J* 7.4 Hz), 1.32–1.34 (10H, m), 1.58–1.65 (2H, m), 2.50 (2H, dt, *J* 7.3, $^3J_{H-F}$ 23.4 Hz), 6.01 (1H, dd, *J* 11.9, $^3J_{H-F(olefin)}$ 18.0 Hz), 6.14 (1H, dd, *J* 7.8, 15.1 Hz), 7.16 (1H, dd, *J* 11.9, 15.1 Hz), 9.55 (1H, d, *J* 7.8 Hz); $\delta_F(CDCl_3)$ −82.58 (1F, dt, $^3J_{H-F}$ 18.0, $^3J_{H-F(olefin)}$ 23.4 Hz); $\delta_C(CDCl_3)$ 14.02, 22.57, 26.21, 28.90, 28.93 (d, $^2J_{C-F}$ 24.7 Hz), 29.05, 29.15, 31.73, 107.68 (d, $^2J_{C-F}$ 29.7 Hz), 130.96 (d, $^4J_{C-F}$ 9.9 Hz), 145.99 (d, $^3J_{C-F}$ 14.0 Hz), 170.63 (d, $^1J_{C-F}$ 270.9 Hz), 192.85; ν(neat)/cm^{-1} 1689 [Calc. for $C_{13}H_{21}FO$ (*M*): 212.1576. Found: M^+, 212.1585].

(3*E*,5*E*)-6-Fluorotetradeca-3,5-dien-2-one 4c. R_f 0.36 (hexane–diethyl ether 5 : 1); $\delta_H(CDCl_3)$ 0.88 (3H, t, *J* 7.1 Hz), 1.27–1.30 (10H, m), 1.55–1.60 (2H, m), 2.26 (3H, s), 2.47 (2H, dt, *J* 7.6, $^3J_{H-F}$ 23.7 Hz), 5.87 (1H, dd, *J* 11.7, $^3J_{H-F(olefin)}$ 18.5 Hz), 6.16 (1H, d, *J* 15.3 Hz), 7.19 (1H, dd, *J* 11.7, 15.3 Hz); $\delta_F(CDCl_3)$ −85.62 (1F, dt, $^3J_{H-F(olefin)}$ 18.5, $^3J_{H-F}$ 23.7 Hz); $\delta_C(CDCl_3)$ 14.06, 22.61, 26.28, 28.09, 28.89 (d, $^2J_{C-F}$ 25.6 Hz), 28.91, 29.09, 29.21, 31.78, 107.43 (d, $^2J_{C-F}$ 28.9 Hz), 128.93 (d, $^4J_{C-F}$ 10.7 Hz), 136.93 (d, $^3J_{C-F}$ 13.2 Hz), 170.18 (d, $^1J_{C-F}$ 267.6 Hz), 197.59; ν(neat)/cm^{-1} 1653 [Calc. for $C_{14}H_{23}FO$ (*M*): 226.1733. Found: M^+, 226.1736].

(2*E*,4*E*)-5-Fluoro-1-phenyltrideca-2,4-dien-1-one 4d. R_f 0.56 (hexane–diethyl ether 5 : 1); $\delta_H(CDCl_3)$ 0.88 (3H, t, *J* 7.1 Hz), 1.27–1.31 (10H, m), 1.56–1.63 (2H, m), 2.52 (2H, dt, *J* 7.6, $^3J_{H-F}$ 23.7 Hz), 6.02 (1H, dd, *J* 12.2, $^3J_{H-F(olefin)}$ 18.3 Hz), 6.99 (1H, d, *J* 14.9 Hz), 7.46–7.58 (4H, m), 7.96 (2H, d, *J* 7.1 Hz); $\delta_F(CDCl_3)$ −85.22 (1F, dt, $^3J_{H-F(olefin)}$ 18.3, $^3J_{H-F}$ 23.7 Hz); $\delta_C(CDCl_3)$ 14.06, 22.61, 26.40, 28.96, 29.00 (d, $^2J_{C-F}$ 24.3 Hz), 29.10, 29.23, 31.77, 107.91 (d, $^2J_{C-F}$ 28.9 Hz), 124.01 (d, $^4J_{C-F}$ 10.7 Hz), 128.31 (2C), 128.57 (2C), 132.71, 138.05, 138.73 (d, $^3J_{C-F}$ 13.3 Hz), 171.01 (d, $^1J_{C-F}$ 268.5 Hz), 189.75; ν(neat)/cm^{-1} 1675 [Calc. for $C_{19}H_{25}FO$ (*M*): 288.1883. Found: M^+, 288.1916] (Calc. for $C_{19}H_{25}FO$: C, 79.13; H, 8.74; F, 6.59. Found: C, 79.04; H, 8.90; F, 6.58%).

1-Ethyl 14-methyl (2*E*,4*E*)-5-fluorotetradeca-2,4-dienedioate 4e. R_f 0.47 (hexane–diethyl ether 2 : 1); $\delta_H(CDCl_3)$ 1.27–1.31 (11H, m), 1.53–1.64 (4H, m), 2.30 (2H, t, *J* 7.6 Hz), 2.45 (2H, dt, *J* 7.6, $^3J_{H-F}$ 23.4 Hz), 3.67 (3H, s), 4.21 (2H, q, *J* 7.1 Hz), 5.85 (1H, d, *J* 14.9 Hz), 5.87 (1H, dd, *J* 12.2, $^3J_{H-F(olefin)}$ 18.5 Hz), 7.31 (1H, dd, *J* 12.2, 14.9 Hz); $\delta_F(CDCl_3)$ −88.03 (1F, dt, $^3J_{H-F(olefin)}$ 18.5, $^3J_{H-F}$ 23.4Hz); $\delta_C(CDCl_3)$ 14.29, 24.87, 26.26, 28.78 (d, $^2J_{C-F}$ 25.6 Hz), 28.81, 29.03 (2C), 29.05, 34.05, 51.43, 60.28, 107.07 (d, $^2J_{C-F}$ 28.9 Hz), 120.12 (d, $^4J_{C-F}$ 9.9 Hz), 138.40 (d, $^3J_{C-F}$ 14.1 Hz), 166.89, 172.47 (d, $^1J_{C-F}$ 266.0 Hz), 174.26; ν(neat)/cm^{-1} 1739, 1716 [Calc. for $C_{17}H_{27}FO_4$ (*M*): 314.1886. Found: M^+, 314.1915] (Calc. for $C_{17}H_{27}FO_4$: C, 64.94; H, 8.66. Found: C, 64.97, H, 8.75%).

Methyl (10*E*,12*E*)-10-fluoro-13-formyltindeca-10,12- dienoate 4f. R_f 0.53 (hexane–diethyl ether 1 : 1); $\delta_H(CDCl_3)$ 1.26–1.38 (8H, m), 1.60–1.63 (4H, m), 2.30 (2H, t, *J* 7.6 Hz), 2.49 (2H, dt,

J 7.3, $^3J_{\text{H-F}}$ 23.4 Hz), 3.67 (3H, s), 6.01 (1H, dd, J 11.7, $^3J_{\text{H-F(olefin)}}$ 18.1 Hz), 6.15 (1H, dd, J 7.8, 15.1 Hz), 7.15 (1H, dd, J 11.7, 15.1 Hz), 9.56 (1H, d, J 7.8 Hz); δ_{F}(CDCl$_3$) −82.68 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.1, $^3J_{\text{H-F}}$ 23.4 Hz); δ_{C}(CDCl$_3$) 24.82, 26.19, 28.83, 28.94 (d, $^2J_{\text{C-F}}$ 24.7 Hz), 29.00 (3C), 34.00, 51.45, 107.73 (d, $^2J_{\text{C-F}}$ 28.9 Hz), 131.01 (d, $^4J_{\text{C-F}}$ 9.8 Hz), 145.97 (d, $^3J_{\text{C-F}}$ 14.9 Hz), 170.53 (d, $^1J_{\text{C-F}}$ 270.9 Hz), 174.21, 192.89; ν(neat)/cm^{-1} 1738, 1686 [Calc. for $\text{C}_{15}\text{H}_{23}\text{FO}_3$ (M): 270.1631. Found: M$^+$, 270.1636].

Methyl (10*E*,12*E*)-10-fluoro-14-oxopentadeca-10,12-dienoate 4g. R_f 0.51 (hexane–diethyl ether 1 : 1); δ_{H}(CDCl$_3$) 1.26–1.37 (8H, m), 1.54–1.64 (4H, m), 2.26 (3H, s), 2.30 (2H, t, J 7.3 Hz), 2.47 (2H, dt, J 7.6, $^3J_{\text{H-F}}$ 23.4 Hz), 3.67 (3H, s), 5.87 (1H, dd, J 11.9, $^3J_{\text{H-F(olefin)}}$ 18.5 Hz), 6.17 (1H, d, J 15.4 Hz), 7.18 (1H, dd, J 11.9, 15.4 Hz); δ_{F}(CDCl$_3$) −85.71 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.5, $^3J_{\text{H-F}}$ 23.4 Hz); δ_{C}(CDCl$_3$) 24.84, 26.22, 28.11, 28.81, 28.86 (d, $^2J_{\text{C-F}}$ 28.1 Hz), 29.00 (3C), 34.01, 51.41, 107.44 (d, $^2J_{\text{C-F}}$ 28.9 Hz), 128.93 (d, $^4J_{\text{C-F}}$ 9.9 Hz), 136.84 (d, $^3J_{\text{C-F}}$ 14.1 Hz), 170.06 (d, $^1J_{\text{C-F}}$ 268.5 Hz), 174.21, 197.55; ν(neat)/cm^{-1} 1738, 1654 [Calc. for $\text{C}_{16}\text{H}_{25}\text{FO}_3$ (M): 284.1788. Found: M$^+$, 284.1809].

Methyl (10*E*,12*E*)-13-benzoyl-10-fluorotrideca-10,12-dienoate 4h. R_f 0.49 (hexane–diethyl ether 1 : 1); δ_{H}(CDCl$_3$) 1.26–1.37 (8H, m), 1.58–1.61 (4H, m), 2.30 (2H, t, J 7.6 Hz), 2.52 (2H, dt, J 7.6, $^3J_{\text{H-F}}$ 23.4 Hz), 3.66 (3H, s), 6.02 (1H, dd, J 11.9, $^3J_{\text{H-F(olefin)}}$ 18.3 Hz), 6.99 (1H, d, J 14.9 Hz), 7.46–7.58 (4H, m), 7.96 (2H, d, J 7.3 Hz); δ_{F}(CDCl$_3$) −85.34 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.3, $^3J_{\text{H-F}}$ 23.4 Hz); δ_{C}(CDCl$_3$) 24.87, 26.33, 28.84, 28.96 (d, $^2J_{\text{C-F}}$ 24.0 Hz), 29.01 (2C), 29.04, 34.03, 51.41, 107.94 (d, $^2J_{\text{C-F}}$ 28.1 Hz), 124.03 (d, $^4J_{\text{C-F}}$ 10.7 Hz), 128.30 (2C), 128.56 (2C), 132.71, 138.01, 138.64 (d, $^3J_{\text{C-F}}$ 14.1 Hz), 170.88 (d, $^1J_{\text{C-F}}$ 268.5 Hz), 174.24, 189.70; ν(neat)/cm^{-1} 1736, 1675 [Calc. for $\text{C}_{21}\text{H}_{27}\text{FO}_3$ (M): 346.1937. Found: M$^+$, 346.1966] (Calc. for $\text{C}_{21}\text{H}_{27}\text{FO}_3$: C, 72.81; H, 7.86; F, 5.48. Found: C, 72.75; H, 7.96; F, 5.48%).

Ethyl (2*E*,4*E*)-14-chloro-5-fluorotetradeca-2,4-dienoate 4i. R_f 0.36 (hexane–diethyl ether 10 : 1); δ_{H}(CDCl$_3$) 1.28–1.43 (13H, m), 1.54–1.60 (2H, m), 1.73–1.80 (2H, m), 2.46 (2H, dt, J 7.6, $^3J_{\text{H-F}}$ 23.4 Hz), 3.53 (2H, t, J 6.8 Hz), 4.21 (2H, q, J 7.1 Hz), 5.85 (1H, d, J 14.9 Hz), 5.87 (1H, dd, J 12.2, $^3J_{\text{H-F(olefin)}}$ 18.5 Hz), 7.31 (1H, dd, J 12.2, 14.9 Hz); δ_{F}(CDCl$_3$) −88.04 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.5, $^3J_{\text{H-F}}$ 23.4 Hz); δ_{C}(CDCl$_3$) 14.29, 26.25, 26.81, 28.76 (d, $^2J_{\text{C-F}}$ 25.6 Hz), 28.76, 28.81, 29.12, 29.23, 32.58, 45.11, 60.27, 107.07 (d, $^2J_{\text{C-F}}$ 29.7 Hz), 120.11 (d, $^4J_{\text{C-F}}$ 9.8 Hz), 138.40 (d, $^3J_{\text{C-F}}$ 14.1 Hz), 166.88, 169.36 (d, $^1J_{\text{C-F}}$ 266.0 Hz); ν(neat)/cm^{-1} 1716 [Calc. for $\text{C}_{16}\text{H}_{26}\text{ClFO}_2$ (M): 304.1599. Found: M$^+$, 304.1622].

(2*E*,4*E*)-14-Chloro-5-fluorotetradeca-2,4-dienal 4j. R_f 0.27 (hexane–diethyl ether 5 : 1); δ_{H}(CDCl$_3$) 1.31–1.44 (10H, m), 1.58–1.64 (2H, m), 1.73–1.80 (2H, m), 2.52 (2H, dt, J 7.5, $^3J_{\text{H-F}}$ 22.9 Hz), 3.53 (2H, t, J 11.2 Hz), 6.02 (1H, dd, J 12.0, $^3J_{\text{H-F(olefin)}}$ 18.2 Hz), 6.15 (1H, dd, J 7.8, 15.3 Hz), 7.15 (1H, dd, J 12.0, 15.3 Hz), 9.56 (1H, d, J 8.1 Hz); δ_{F}(CDCl$_3$) −85.69 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.2, $^3J_{\text{H-F}}$ 22.9 Hz); δ_{C}(CDCl$_3$) 26.21, 26.77, 28.76, 28.86, 28.94 (d, $^2J_{\text{C-F}}$ 25.6 Hz), 29.09, 29.21, 32.54, 45.10, 107.73 (d, $^2J_{\text{C-F}}$ 29.7 Hz), 131.00 (d, $^4J_{\text{C-F}}$ 9.9 Hz), 145.92 (d, $^3J_{\text{C-F}}$ 14.1 Hz), 170.54 (d, $^1J_{\text{C-F}}$ 271.0 Hz), 192.84; ν(neat)/cm^{-1} 1687 [Calc. for $\text{C}_{14}\text{H}_{22}\text{ClFO}$ (M): 260.1343. Found: M$^+$, 260.1339].

(3*E*,5*E*)-15-Chloro-6-fluoropentadeca-3,5-dien-2-one 4k. R_f 0.24 (hexane–diethyl ether 5 : 1); δ_{H}(CDCl$_3$) 1.26–1.38 (8H, m), 1.39–1.44 (2H, m), 1.55–1.60 (2H, m), 1.73–1.80 (2H, m), 2.26 (3H, s), 2.47 (2H, dt, J 7.6, $^3J_{\text{H-F}}$ 23.4 Hz), 3.53 (2H, t, J 6.8 Hz), 5.87 (1H, dd, J 11.9, $^3J_{\text{H-F(olefin)}}$ 18.5 Hz), 6.17 (1H, d, J 15.4 Hz), 7.19 (1H, dd, J 11.9, 15.4 Hz); δ_{F}(CDCl$_3$) −82.65 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.5, $^3J_{\text{H-F}}$ 23.4 Hz); δ_{C}(CDCl$_3$) 26.23, 26.78, 28.15, 28.76, 28.82, 28.85 (d, $^2J_{\text{C-F}}$ 25.6 Hz), 29.10, 29.21, 32.56, 45.10, 107.44 (d, $^2J_{\text{C-F}}$ 28.9 Hz), 128.90 (d, $^4J_{\text{C-F}}$ 9.9 Hz), 136.82 (d, $^3J_{\text{C-F}}$ 14.0 Hz), 170.08 (d, $^1J_{\text{C-F}}$ 267.6 Hz), 197.54; ν(neat)/cm^{-1} 1652 [Calc. for $\text{C}_{15}\text{H}_{24}\text{ClFO}$ (M): 274.1500. Found: M$^+$, 274.1523].

(2*E*,4*E*)-14-Chloro-5-fluoro-1-phenyltetradeca-2,4-dien-1-one 4l. R_f 0.62 (hexane–AcOEt 5 : 1); δ_{H}(CDCl$_3$) 1.30–1.42 (10H, m), 1.54–1.62 (2H, m), 1.73–1.80 (2H, m), 2.52 (2H, dt, J 7.6, $^3J_{\text{H-F}}$ 23.4 Hz), 3.52 (2H, t, J 6.6 Hz), 6.02 (1H, dd, J 11.9, $^3J_{\text{H-F(olefin)}}$ 18.3 Hz), 6.99 (1H, d, J 14.9 Hz), 7.46–7.59 (4H, m), 7.96 (2H, d, J 7.3 Hz); δ_{F}(CDCl$_3$) −85.36 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.3, $^3J_{\text{H-F}}$ 23.4 Hz); δ_{C}(CDCl$_3$) 26.33, 26.81, 28.76, 28.85, 28.95 (d, $^2J_{\text{C-F}}$ 24.4 Hz), 29.12, 29.23, 32.58, 45.12, 107.96 (d, $^2J_{\text{C-F}}$ 28.9 Hz), 124.02 (d, $^4J_{\text{C-F}}$ 10.7 Hz), 128.30 (2C), 128.57 (2C), 132.72, 138.01, 138.64 (d, $^3J_{\text{C-F}}$ 14.1 Hz), 170.89 (d, $^1J_{\text{C-F}}$ 268.5 Hz), 189.69; ν(neat)/cm^{-1} 1666 [Calc. for $\text{C}_{20}\text{H}_{26}\text{ClFO}$ (M): 336.1656. Found: M$^+$, 336.1676] (Calc. for $\text{C}_{20}\text{H}_{26}\text{ClFO}$: C, 71.31; H, 7.78; Cl, 10.52; F, 5.64. Found: C, 71.31; H, 7.89; Cl, 10.46; F, 5.62%).

(3*E*,5*E*)-7-Cyclohexyl-6-fluorohepta-3,5-dien-2-one 4m. R_f 0.31 (hexane–diethyl ether 5 : 1); δ_{H}(CDCl$_3$) 0.93–1.02 (2H, m), 1.10–1.31 (3H, m), 1.60–1.75 (6H, m), 2.26 (3H, s), 2.34 (2H, dd, J 7.1, $^3J_{\text{H-F}}$ 24.6 Hz), 5.92 (1H, dd, J 11.9, $^3J_{\text{H-F(olefin)}}$ 18.5 Hz), 6.16 (1H, d, J 15.4 Hz), 7.16 (1H, dd, J 11.9, 15.4 Hz); δ_{F}(CDCl$_3$) −82.88 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.5, $^3J_{\text{H-F}}$ 24.6 Hz); δ_{C}(CDCl$_3$) 26.03 (2C), 26.11, 28.11, 32.89 (2C), 35.54, 36.59 (d, $^2J_{\text{C-F}}$ 24.8 Hz), 108.40 (d, $^2J_{\text{C-F}}$ 28.9 Hz), 128.91 (d, $^4J_{\text{C-F}}$ 9.8 Hz), 137.10 (d, $^3J_{\text{C-F}}$ 13.3 Hz), 169.19 (d, $^1J_{\text{C-F}}$ 267.7 Hz), 197.54; ν(neat)/cm^{-1} 1651 [Calc. for $\text{C}_{13}\text{H}_{19}\text{FO}$ (M): 210.1420. Found: M$^+$, 210.1409].

(2*E*,4*E*)-6-Cyclohexyl-5-fluoro-1-phenyl-2,4-hexadien-1-one 4n. R_f 0.51 (hexane–AcOEt 5 : 1); δ_{H}(CDCl$_3$) 0.95–1.04 (2H, m), 1.10–1.30 (3H, m), 1.63–1.76 (6H, m), 2.40 (2H, dd, J 7.1, $^3J_{\text{H-F}}$ 24.9 Hz), 6.07 (1H, dd, J 11.9, $^3J_{\text{H-F(olefin)}}$ 18.5 Hz), 6.98 (1H, d, J 14.9 Hz), 7.46–7.58 (4H, m), 7.96 (2H, d, J 7.1 Hz); δ_{F}(CDCl$_3$) −82.47 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.5, $^3J_{\text{H-F}}$ 24.9 Hz); δ_{C}(CDCl$_3$) 26.08 (2C), 26.15, 32.92 (2C), 35.67, 36.68 (d, $^2J_{\text{C-F}}$ 24.8 Hz), 108.94 (d, $^2J_{\text{C-F}}$ 28.1 Hz), 124.04 (d, $^4J_{\text{C-F}}$ 10.7 Hz), 128.35 (2C), 128.59 (2C), 132.73, 138.08, 138.95 (d, $^3J_{\text{C-F}}$ 13.3 Hz), 170.06 (d, $^1J_{\text{C-F}}$ 268.5 Hz), 189.75; ν(neat)/cm^{-1} 1666 [Calc. for $\text{C}_{18}\text{H}_{21}\text{FO}$ (M): 272.1571. Found: M$^+$, 272.1577].

Ethyl (2*E*,4*E*)-5-fluoro-15,15-dimethyl-14-oxohexadeca-2,4-dienoate 4o. R_f 0.38 (hexane–diethyl ether 5 : 1); δ_{H}(CDCl$_3$) 1.13 (9H, s), 1.28–1.31 (11H, m), 1.50–1.58 (4H, m), 2.40–2.50 (4H, m), 4.20 (2H, q, J 7.3 Hz), 5.85 (1H, d, J 15.1 Hz), 5.86 (1H, dd, J 11.9, $^3J_{\text{H-F(olefin)}}$ 18.3 Hz), 7.31 (1H, dd, J 11.9, 15.1 Hz); δ_{F}(CDCl$_3$) −87.97 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.3, $^3J_{\text{H-F}}$ 23.3 Hz); δ_{C}(CDCl$_3$) 14.32, 23.89, 26.30, 26.43 (3C), 28.82 (d, $^2J_{\text{C-F}}$ 25.6 Hz), 28.89, 29.16, 29.25, 29.32, 36.41, 44.11, 60.32, 107.09 (d, $^2J_{\text{C-F}}$ 28.9 Hz), 120.11 (d, $^4J_{\text{C-F}}$ 10.7 Hz), 138.48 (d, $^3J_{\text{C-F}}$ 13.3 Hz), 166.96, 169.44 (d, $^1J_{\text{C-F}}$ 266.0 Hz), 216.17; ν(neat)/cm^{-1} 1708, 1661 [Calc. for $\text{C}_{20}\text{H}_{33}\text{FO}_3$ (M): 340.2405. Found: M$^+$, 340.2408] (Calc. for $\text{C}_{20}\text{H}_{33}\text{FO}_3$: C, 70.55; H, 9.77. Found: C, 70.47; H, 9.70%).

(2*E*,4*E*)-5-Fluoro-15,15-dimethyl-14-oxohexadeca-2,4-dienal 4p. R_f 0.60 (hexane–diethyl ether 1 : 1); δ_{H}(CDCl$_3$) 1.13 (9H, s), 1.30–1.33 (8H, m), 1.51–1.65 (4H, m), 2.42–2.55 (4H, m), 6.01 (1H, dd, J 11.9, $^3J_{\text{H-F(olefin)}}$ 18.1 Hz), 6.15 (1H, dd, J 7.8, 15.1 Hz), 7.17 (1H, dd, J 11.9, 15.1 Hz), 9.56 (1H, d, J 7.8 Hz); δ_{F}(CDCl$_3$) −82.64 (1F, dt, $^3J_{\text{H-F(olefin)}}$ 18.1, $^3J_{\text{H-F}}$ 24.8 Hz); δ_{C}(CDCl$_3$) 23.80, 26.20, 26.38 (3C), 28.86, 28.92 (d, $^2J_{\text{C-F}}$ 24.0 Hz), 29.04, 29.18, 29.28, 36.33, 44.06, 107.72 (d, $^2J_{\text{C-F}}$ 28.9 Hz), 130.99 (d, $^4J_{\text{C-F}}$ 9.9 Hz), 145.97 (d, $^3J_{\text{C-F}}$ 14.1 Hz), 170.58 (d, $^1J_{\text{C-F}}$ 271.0 Hz), 192.88, 216.03; ν(neat)/cm^{-1} 1703, 1653 [Calc. for $\text{C}_{18}\text{H}_{29}\text{FO}_2$ (M): 296.2151. Found: M$^+$, 296.2140].

(3*E*,5*E*)-6-Fluoro-16,16-dimethylheptadeca-3,5-diene-2,15-dione 4q. R_f 0.58 (hexane–diethyl ether 1 : 1); δ_H(CDCl$_3$) 1.13 (9H, s), 1.29–1.31 (8H, m), 1.50–1.60 (4H, m), 2.26 (3H, s), 2.42–2.51 (4H, m), 5.87 (1H, dd, *J* 11.9, $^3J_{H\text{-}F(olefin)}$ 18.5 Hz), 6.17 (1H, d, *J* 15.3 Hz), 7.19 (1H, dd, *J* 11.9, 15.3 Hz); δ_F(CDCl$_3$) −85.64 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 18.5, $^3J_{H\text{-}F}$ 24.1 Hz); δ_C(CDCl$_3$) 23.82, 26.24, 26.38 (3C), 28.10, 28.84, 28.85 (d, $^2J_{C\text{-}F}$ 25.6 Hz), 29.08, 29.19, 29.27, 36.34, 44.05, 107.42 (d, $^2J_{C\text{-}F}$ 28.9 Hz), 128.93 (d, $^4J_{C\text{-}F}$ 10.7 Hz), 136.87 (d, $^3J_{C\text{-}F}$ 13.3 Hz), 170.09 (d, $^1J_{C\text{-}F}$ 267.7 Hz), 197.56, 216.02; ν(neat)/cm^{-1} 1704, 1652 [Calc. for C$_{19}$H$_{31}$FO$_2$ (*M*): 310.2308. Found: M$^+$, 310.2306].

(2*E*,4*E*)-5-Fluoro-15,15-dimethyl-1-phenylhexadecadiene-1,14-dione 4r. R_f 0.62 (hexane–diethyl ether 1 : 1); δ_H(CDCl$_3$) 1.13 (9H, s), 1.29–1.32 (8H, m), 1.50–1.61 (4H, m), 2.44–2.57 (4H, m), 6.02 (1H, dd, *J* 11.9, $^3J_{H\text{-}F(olefin)}$ 18.3 Hz), 6.99 (1H, d, *J* 14.9 Hz), 7.46–7.59 (4H, m), 7.96 (2H, d, *J* 7.1 Hz); δ_F(CDCl$_3$) −85.31 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 18.3, $^3J_{H\text{-}F}$ 23.3 Hz); δ_C(CDCl$_3$) 23.89, 26.38, 26.42 (3C), 28.92, 29.00 (d, $^2J_{C\text{-}F}$ 25.5 Hz), 29.16, 29.24, 29.32, 36.40, 44.09, 107.97 (d, $^2J_{C\text{-}F}$ 28.9 Hz), 124.05 (d, $^4J_{C\text{-}F}$ 10.7 Hz), 128.34 (2C), 128.60 (2C), 132.75, 138.07, 138.71 (d, $^3J_{C\text{-}F}$ 13.3 Hz), 170.96 (d, $^1J_{C\text{-}F}$ 268.5 Hz), 189.75, 216.09; ν(neat)/cm^{-1} 1698, 1670 [Calc. for C$_{24}$H$_{33}$FO$_2$ (*M*): 372.2456. Found: M$^+$, 372.2452] (Calc. for C$_{24}$H$_{33}$FO$_2$: C, 77.38; H, 8.93; F, 5.10. Found: C, 77.34; H, 8.85; F, 5.34%).

Methyl (9*E*,11*E*)-9-fluoro-13-oxooctadeca-9,11-dienoate 7. δ_H(CDCl$_3$) 0.90 (3H, t, *J* 7.1 Hz), 1.27–1.34 (10H, m), 1.54–1.66 (6H, m), 2.30 (2H, t, *J* 7.6 Hz), 2.46 (2H, dt, *J* 7.6, $^3J_{H\text{-}F}$ 23.4 Hz), 2.51 (2H, t, *J* 7.6 Hz), 3.67 (3H, s), 5.86 (1H, dd, *J* 11.9, $^3J_{H\text{-}F(olefin)}$ 18.5 Hz), 6.19 (1H, d, *J* 15.1 Hz), 7.22 (1H, dd, *J* 11.9, 15.1 Hz); δ_F(CDCl$_3$) −86.35 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 18.5, $^3J_{H\text{-}F}$ 23.4 Hz); ν(neat)/cm^{-} 1739, 1691 [Calc. for C$_{19}$H$_{31}$FO$_3$ (*M*): 326.2249. Found: M$^+$, 326.2272].

Methyl ester of 9-fluoro 13-HODE, Compound 8. To a stirred MeOH solution (2.5 mL) of **7** (326 mg, 1 mmol) and CeCl$_3$·7H$_2$O (372 mg, 1 mmol) was added NaBH$_4$ (38 mg, 1 mmol) at room temperature. After 3 min, the reaction mixture was poured into water (10 mL) and extracted with diethyl ether. The organic phase was dried over MgSO$_4$ and concentrated under reduced pressure. The desired methyl ester **8** of 9-fluoro-13-HODE (328 mg, quant.) was obtained without further purification, δ_H(CDCl$_3$) 0.89 (3H, t, *J* 6.8 Hz), 1.30–1.32 (14H, m), 1.49–1.64 (5H, m), 2.30 (2H, t, *J* 7.6 Hz), 2.34 (2H, dt, *J* 7.1, $^3J_{H\text{-}F}$ 23.9 Hz), 3.67 (3H, s), 4.11–4.16 (1H, m), 5.61 (1H, dd, *J* 6.8, 15.1 Hz), 5.72 (1H, dd, *J* 11.2, $^3J_{H\text{-}F(olefin)}$ 19.7 Hz), 6.13 (1H, dd, *J* 11.2, 15.1 Hz); δ_F(CDCl$_3$) −101.18 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 19.7, $^3J_{H\text{-}F}$ 23.9 Hz) [Calc. for C$_{19}$H$_{33}$FO$_3$ (*M*): 328.2414. Found: M$^+$, 328.2432].

General procedure for (*E*)-4-fluoro-1,3-dienes 5

To a DMF solution (20 mL) of Bn(PPh$_3$)$_2$PdCl, prepared *in situ* by the addition of benzyl chloride (12.6 mg, 0.1 mmol) to a DMF solution (20 mL) of Pd(PPh$_3$)$_4$ (116 mg, 0.1 mmol),[17] was added a DMF solution (4 mL) of the alkenyliodonium salt **2**, prepared as already described, at room temperature. After the addition of tributylvinyltin (695 mg, 2.2 mmol), the reaction mixture was stirred at room temperature for 18 h and then poured into saturated aq. NH$_4$Cl. After extraction with diethyl ether, the organic phase was dried over MgSO$_4$ and concentrated under reduced pressure. The (*E*)-4-fluoro-1,3-dienes **5** and *p*-vinyltoluene (*p*-methylstyrene) **10** were isolated by column chromatography (silica gel/hexane–diethyl ether).

Methyl (10*E*)-10-fluorotrideca-10,12-dienoate 5a. δ_H(CDCl$_3$) 1.30 (8H, s), 1.50–1.63 (4H, m), 2.30 (2H, t, *J* 7.8 Hz), 2.33 (2H, dt, *J* 7.3, $^3J_{H\text{-}F}$ 23.9 Hz), 3.67 (3H, s), 4.99 (1H, d, *J* 10.2 Hz), 5.13 (1H, d, *J* 16.8 Hz), 5.75 (1H, dd, *J* 11.2, $^3J_{H\text{-}F(olefin)}$ 20.0 Hz), 6.26 (1H, dd, *J* 11.2, 16.8 Hz); δ_F(CDCl$_3$) −101.05 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 20.0, $^3J_{H\text{-}F}$ 23.9 Hz); ν(neat)/cm^{-1} 1740 [Calc. for C$_{14}$H$_{23}$FO$_2$ (*M*): 242.1683. Found: M$^+$, 242.1697].

(*E*)-13-Chloro-4-fluorotrideca-1,3-diene 5b. δ_H(CDCl$_3$) 1.30 (8H, s), 1.40–1.44 (2H, m), 1.50–1.56 (2H, m), 1.71–1.80 (2H, m), 2.34 (2H, dt, *J* 7.3, $^3J_{H\text{-}F}$ 23.7 Hz), 3.53 (2H, t, *J* 6.8 Hz), 5.00 (1H, d, *J* 10.2 Hz), 5.14 (1H, d, *J* 16.6 Hz), 5.78 (1H, dd, *J* 11.2, $^3J_{H\text{-}F(olefin)}$ 19.7 Hz), 6.27 (1H, dt, *J* 11.2, *J* 16.6 Hz); δ_F(CDCl$_3$) −101.05 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 19.7, $^3J_{H\text{-}F}$ 23.7 Hz) [Calc. for C$_{13}$H$_{22}$ClF (*M*): 232.1396. Found: M$^+$, 232.1382].

(*E*)-5-Cyclohexyl-4-fluoropenta-1,3-diene 5c. δ_H(CDCl$_3$) 0.87–0.99 (2H, m), 1.09–1.30 (3H, m), 1.54–1.75 (6H, m), 2.22 (2H, dd, *J* 7.2, $^3J_{H\text{-}F}$ 24.4 Hz), 4.98 (1H, d, *J* 10.4 Hz), 5.12 (1H, d, *J* 16.8 Hz), 5.80 (1H, dd, *J* 11.2, $^3J_{H\text{-}F(olefin)}$ 20.0 Hz), 6.25 (1H, dt, *J* 11.2, 16.8 Hz); δ_F(CDCl$_3$) −98.09 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 20.0, $^3J_{H\text{-}F}$ 24.4 Hz); [Calc. for C$_{11}$H$_{17}$F (*M*): 168.1315. Found: M$^+$, 168.1314].

(*E*)-2,2-Dimethyl-12-fluoropentadeca-12,14-dien-3-one 5d. δ_H(CDCl$_3$) 1.13 (9H, s), 1.29 (8H, s), 1.54–1.58 (4H, m), 2.32 (2H, dt, *J* 7.3, $^3J_{H\text{-}F}$ 23.7 Hz), 2.46 (2H, t, *J* 7.3 Hz), 4.99 (1H, d, *J* 10.3 Hz), 5.13 (1H, d, *J* 16.5 Hz), 5.75 (1H, dd, *J* 11.2, $^3J_{H\text{-}F(olefin)}$ 20.0 Hz), 6.27 (1H, dt, *J* 11.2, 16.5 Hz); δ_F(CDCl$_3$) −101.02 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 20.0, $^3J_{H\text{-}F}$ 23.7 Hz) ν(neat)/cm^{-1} 1706 [Calc. for C$_{17}$H$_{29}$FO (*M*): 268.2204. Found: M$^+$, 268.2185].

(*E*)-4-Fluorotetradeca-1,3-diene 5e. δ_H(CDCl$_3$) 0.88 (3H, t, *J* 7.3 Hz), 1.26 (14H, s), 1.50–1.58 (2H, m), 2.34 (2H, dt, *J* 7.6, $^3J_{H\text{-}F}$ 23.6 Hz), 4.99 (1H, d, *J* 10.2 Hz), 5.13 (1H, d, *J* 16.8 Hz), 5.75 (1H, dd, *J* 11.2, $^3J_{H\text{-}F(olefin)}$ 20.0 Hz), 6.27 (1H, dt, *J* 11.2, 16.8 Hz); δ_F(CDCl$_3$) −101.02 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 20.0, $^3J_{H\text{-}F}$ 23.6 Hz) [Calc. for C$_{14}$H$_{25}$F (*M*): 212.1942. Found: M$^+$, 212.1938].

(1*E*,3*E*)-4-Fluoro-1-phenyltetradeca-1,3-diene 5f. δ_H(CDCl$_3$) 0.87 (3H, t, *J* 7.1 Hz), 1.26 (14H, s), 1.57–1.62 (2H, m), 2.44 (2H, dt, *J* 7.3, $^3J_{H\text{-}F}$ 23.4 Hz), 5.88 (1H, dd, *J* 11.2, $^3J_{H\text{-}F(olefin)}$ 19.7 Hz), 6.46 (1H, d, *J* 15.6 Hz), 6.65 (1H, dd, *J* 11.2, 15.6 Hz), 7.19–7.38 (5H, m); δ_F(CDCl$_3$) −99.49 (1F, dt, $^3J_{H\text{-}F(olefin)}$ 19.7, $^3J_{H\text{-}F}$ 23.4 Hz) [Calc. for C$_{20}$H$_{29}$F, (*M*): 288.2320. Found: M$^+$, 288.2248].

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