

Regio- and stereoselective synthesis of fluoroalkenes and fluoroalkadienes

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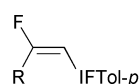
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(*E*)-Fluoroalkenes and (*E,E*)-fluoroalkadienes are synthesized stereoselectively from (*E*)-2-fluoro-1-iodoalk-1-enes by Pd-catalyzed cross-coupling reaction with organoboranes.

Introduction

Organofluorine compounds often show unique biological properties originating from the high electronegativity of the fluorine atom.¹ However, organofluorine compounds are scarce in Nature, and, in order to obtain the desired organofluorine compound, the building-block methodology using readily available fluorine-substituted molecules has been employed.² Recently, we found (*E*)-(2-fluoroalk-1-enyl)(*p*-tolyl)iodonium fluorides **1** could be synthesized stereo- and regioselectively by the reaction of alk-1-yne with *p*-iodotoluene difluoride.³ Furthermore, we succeeded in obtaining (*E*)-2-fluoro-1-iodoalk-1-enes **2**,³ (*E,E*)- δ -fluoro- $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compounds⁴ and (*E*)- β -fluoro- α,β -unsaturated esters⁵ by using **1** as a building block. Our next interest was directed to the stereoselective synthesis of fluoroalkenes and fluoroalkadienes by the coupling reaction with organoboranes using a Pd catalyst.⁶ Many natural products have double bonds or conjugated dienes in their structures, and the coupling reactions of organoboranes with aryl or alkenyl halides using a Pd catalyst are known as the Suzuki–Miyaura reaction,⁷ which has been used for the stereoselective synthesis of alkenes and alkadienes. Therefore, we examined the Pd-catalyzed cross-coupling reaction of **1** with organoboranes.⁸

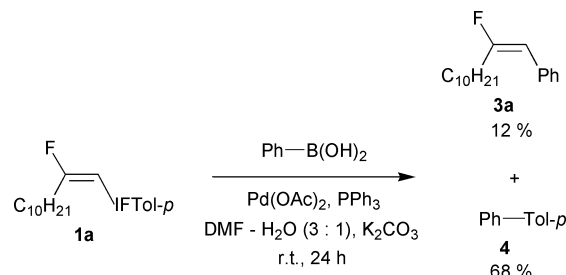


1 R = C₁₀H₂₁, MeOOC-(CH₂)₈, t-Bu-CO-(CH₂)₈, AcO-(CH₂)₉, HO-(CH₂)₉, Cl-(CH₂)₉

Results and discussion

Cross-coupling reaction using (*E*)-(2-fluoroalk-1-enyl)(*p*-tolyl)-iodonium fluorides **1**

The cross-coupling reaction of **1a**, prepared from dodec-1-yne, with phenylboronic acid was carried out in the presence of Pd(OAc)₂, PPh₃ and K₂CO₃ in DMF–water (3 : 1). After stirring of the mixture for 24 h at room temperature, the desired (*E*)-2-fluoro-1-phenyldodec-1-ene **3a** was obtained only in 12% isolated yield along with a significant amount of 4-phenyl-toluene **4** (68% yield) (Scheme 1).⁹ In order to improve the result, some bases and solvents were examined, but the formation of by-product **4** could not be suppressed. It was reported that stilbene was selectively obtained without formation of a significant amount of biphenyl in the cross-coupling reaction of phenylboronic acid with (*E*)- β -styryl(phenyl)iodonium salt.^{8b,c} Therefore, in the reaction of **1a** with phenylboronic acid,



Scheme 1 Cross-coupling reaction of **1a** with phenylboronic acid.

the alkyl group at a *cis*-position to iodine¹⁰ or strongly electronegative fluorine atom on the double bond retarded the oxidative addition of the palladium catalyst to the iodine–alkenyl bond and the selective formation of **3a** was disturbed.¹¹ Consequently, we gave up our attempts at the selective synthesis of fluoroalkenes using **1**, and examined the coupling reaction of (*E*)-2-fluoro-1-iodoalk-1-enes **2** which can be prepared from **1**.³

Cross-coupling reaction of (*E*)-2-fluoro-1-iodoalk-1-enes **2** with arylboronic acids

The cross-coupling reaction of (*E*)-2-fluoro-1-iodododec-1-ene **2a** with phenylboronic acid was examined to find a suitable catalyst (Table 1). When Pd(PPh₃)₄ or Pd(PPh₃)₂Cl₂, a common catalyst in the Suzuki–Miyaura reaction,⁷ was used in benzene and aq. K₂CO₃ under reflux, it took about 12 h to consume **2a** completely and the desired **3a** was obtained in moderate yield (Entries 1 and 2). As **2a** is not stable under the reaction conditions, a more effective catalyst was necessary to obtain **3a** in good yield. Fortunately, the reaction was found to be accelerated by using Pd(OAc)₂ with bidentate ligands and completed in 5 h (Entries 3–5).¹² Finally, we found that **3a** could be obtained in 85% yield by using 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) as ligand (Entry 5). Under these reaction conditions, the cross-coupling reaction between a variety of (*E*)-2-fluoro-1-iodoalk-1-enes **2** and arylboronic acids was carried out, and various types of (*E*)-fluoroalkenes were obtained in 74–94% yield and more than 98% stereoselectivity (Table 2).

Cross-coupling reaction of (*E*)-2-fluoro-1-iodoalk-1-enes **2** with (*E*)-alk-1-enylboronic acids or -boronates

The coupling reaction of **2** with (*E*)-alk-1-enylboronic acids or boronates was also examined to obtain the fluorinated conjugated dienes. When the coupling reaction between **2a** and (*E*)-hex-1-enylboronic acid was carried out under the same

conditions as optimized in Table 1, the desired (5*E*,7*E*)-8-fluorooctadeca-5,7-diene **5a** was obtained in 73% yield along with 9% of its regioisomer **6** (Table 3). Owing to the low nucleophilicity of an alkenylboronic acid compared with aryl derivative, the transmetalation step on the Pd catalyst slowly proceeded and a Heck-type side reaction took place competitively to give the regioisomer **6**.¹³ In order to accelerate the transmetalation step and suppress the formation of **6**, a stronger base, KOH, was used instead of K₂CO₃. As expected, the reaction went to completion in a shorter reaction time and the yield of **6** decreased. Finally, we succeeded in synthesizing **5a** in 87% yield without the formation of **6** by using Pd(OAc)₂,

BINAP and KOH. Under these reaction conditions, various types of fluoroalkadienes could be prepared from **2** and (*E*)-alk-1-enylborane derivatives with more than 98% stereoselectivity in 67–87% yield (Table 4). When diisopropyl (*E*)-but-1-enylboronate was used, the reaction proceeded slowly and the yield of **5** decreased due to the high solubility of diisopropyl (*E*)-but-1-enylboronate in water. This problem was overcome by using dioxane as solvent instead of benzene (Entries 2 and 5).

Conclusion

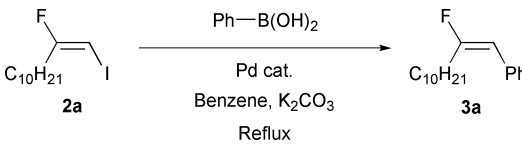
(*E*)-Fluoroalkenes and (*E,E*)-fluoroalkadienes having various types of functionalities were synthesized stereoselectively by the cross-coupling reaction between (*E*)-2-fluoro-1-iodoalk-1-enes and organoboranes.

Experimental

General

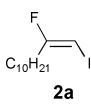
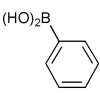
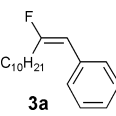
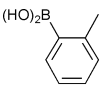
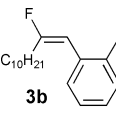
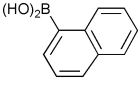
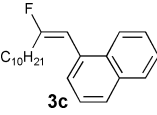
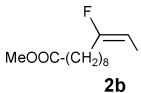
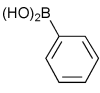
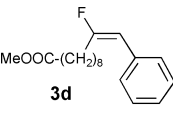
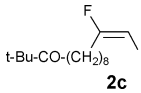
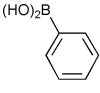
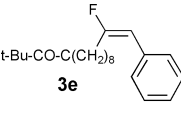
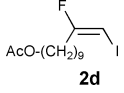
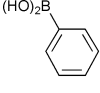
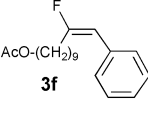
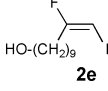
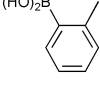
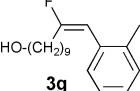
IR spectra were recorded using a JASCO FT/IR-410. ¹H NMR (400 MHz), ¹⁹F NMR (376 MHz) and ¹³C-NMR (100 MHz) spectra were recorded in CDCl₃ on a JEOL JNM-A400II FT NMR and chemical shifts, δ , are referred to TMS (¹H, ¹³C) and CFC₃ (¹⁹F). EI low- and high-resolution mass spectra were measured on a JEOL JMS-700TZ, JMS-FABmate or JMS-HX110. Elemental microanalyses were done using a Yanagimoto CHN Corder MT-5. For column chromatography, Merck silica gel 7734 was used, and, for analytical TLC, Merck silica gel 5715 was used. Et₃N–5HF was prepared by the addition of freshly distilled Et₃N to anhydrous HF at 0 °C.¹⁴ PdCl₂, Pd(PPh₃)₄, Pd(OAc)₂, PPh₃, phenylboronic acid and

Table 1 Cross-coupling reaction of **2a** with phenylboronic acid^a

			
Entry	Catalyst	Time (t/h)	Yield/% ^b
1	Pd(PPh ₃) ₄	12	65
2	Pd(PPh ₃) ₂ Cl ₂	12	56
3	Pd(OAc) ₂ + DPPP	5	48
4	Pd(OAc) ₂ + DPPF	5	70
5	Pd(OAc) ₂ + BINAP	5	85

^a The reaction was carried out using **2a** (0.5 mmol), phenylboronic acid (1 mmol), Pd cat. (5 mol%), ligand (5 mol%), aq. 2 M K₂CO₃ (0.5 mL), and benzene (5 mL). ^b Isolated yield based on **2a**.

Table 2 Cross-coupling reaction of **2** with arylboronic acids

Entry	Fluoroiodoalkene 2	Arylboronic acid	Product	Yield/% ^a
1				85
2	2a			92
3	2a			94
4				93
5				77
6				90
7				74

^a Isolated yield based on **2**.

dodec-1-yne were purchased from Tokyo Kasei Co., Ltd., and used without further purification. 1,3-Bis(diphenylphosphino)propane (DPPP), 1,1'-bis(diphenylphosphino)ferrocene (DPPF) and BINAP were purchased from Kanto Kagaku Co., Ltd., and used without further purification. 11-Acetoxyundec-1-yne¹⁵ and 11-chloroundec-1-yne¹⁶ were prepared from undec-10-yn-1-ol which was in turn prepared from undec-10-en-1-ol.¹⁶ Methyl dec-9-ynoate¹⁷ was prepared from dec-9-enoic acid. 2,2-Dimethyltridec-12-yn-3-one was prepared from undec-10-yn-1-ol by PCC oxidation, reaction with ^tBuMgBr, and PCC oxidation sequences. *o*-Tolylboronic acid,¹⁸ 1-naphthylboronic acid,¹⁸ (*E*)-hex-1-enylboronic acid,¹⁹ diisopropyl (*E*)-but-1-enylboronate²⁰ and diethyl [(*E*)-4-ethoxycarbonyl-4-methylpent-1-enyl]boronate²⁰ were prepared according to the literature. The procedures for the preparation of **1** and **2** have been already reported.^{3,21}

Cross-coupling reaction of (*E*)-(2-fluorododec-1-enyl)(*p*-tolyl)-iodonium salt **1a** with phenylboronic acid

(*E*)-(2-Fluorododec-1-enyl)(*p*-tolyl)iodonium salt **1a**, prepared from dodec-1-yne (83 mg, 0.5 mmol),³ was dissolved in a 3 : 1

Table 3 Cross-coupling reaction of **2a** with (*E*)-hex-1-enylboronic acid.

				Yield/% ^a	
Entry	Catalyst	Base	Time (t/h)	5a	6
1	Pd(OAc) ₂ + BINAP	K ₂ CO ₃	3.5	73	9
2	Pd(OAc) ₂ + BINAP	KOH	2	89	1
3	Pd(OAc) ₂ + 2BINAP	KOH	2	87	trace

^a Isolated yield. The ratio of **5a** and **6** was determined by ¹H-NMR.

Table 4 Stereoselective synthesis of fluoroalkadienes

Entry	Fluoroiodoalkene 2	Alkenylboronic acid or ester	Product	Yield/% ^a
1				87
2	2a			67 ^b
3	2a			82
4				85
5				67 ^b
6				80

^a Isolated yield based on **2**. ^b The reaction was carried out in 1,4-dioxane at 70 °C.

mixture of DMF and water (5 mL). To this solution were added, K₂CO₃ (346 mg, 2.5 mmol), PPh₃ (262 mg, 0.1 mmol), Pd(OAc)₂ (225 mg, 0.1 mmol) and phenylboronic acid (91 mg, 0.75 mmol) sequentially. Then the reaction mixture was stirred for 24 h at room temperature. The resulting solution was poured into saturated aq. NH₄Cl (30 mL) and the separated aqueous phase was extracted with diethyl ether. The combined organic phase was washed with water and dried over MgSO₄. After the MgSO₄ was removed by filtration, the solvent was removed by evaporation. The desired product **3a** was isolated in 12% yield by column chromatography (silica gel; hexane–diethyl ether). 4-Phenyltoluene **4** was obtained as a mixture with biphenyl, which is the homo-coupled product of phenylboronic acid, and the yield of **4** was determined by gas chromatography.

General procedure for (*E*)-fluoroalkenes **3**

To a mixture of benzene (5 mL) and 0.5 mL of 2 M aq. K₂CO₃ (1.0 mmol) were added Pd(OAc)₂ (5.6 mg, 0.025 mmol) and (*S*)-(–)-BINAP (15.6 mg, 0.025 mmol). After the complete replacement of atmosphere in the flask with N₂, an (*E*)-2-fluoro-1-iodoalk-1-ene **2** (0.5 mmol) and arylboronic acid (1.0 mmol) were added. Then the reaction mixture was stirred under reflux for 5 h and then cooled to room temperature. The resulting mixture was poured into saturated aq. NaHCO₃ (30 mL) and the separated aqueous phase was extracted with diethyl ether. The combined organic phase was dried over MgSO₄ and concentrated under reduced pressure. The product **3** was isolated by column chromatography (silica gel; hexane–diethyl ether).

General procedure for (*E,E*)-fluoroalkadienes **5**

To a mixture of benzene (5 mL) and 0.5 mL of 2 M aq. KOH (1.0 mmol) were added Pd(OAc)₂ (5.6 mg, 0.025 mmol) and (*S*)-(–)-BINAP (31.2 mg, 0.05 mmol). After the complete replacement of atmosphere in the flask with N₂, an (*E*)-2-fluoro-1-iodoalk-1-ene **2** (0.5 mmol) and alkenylborane (1.0 mmol) were added. Then the reaction mixture was stirred under reflux for 2 h and then cooled to room temperature. The

resulting solution was poured into saturated aq. NaHCO_3 (30 mL) and the separated aqueous phase was extracted with diethyl ether. The combined organic phase was dried over MgSO_4 and concentrated under reduced pressure. The product **5** was isolated by column chromatography (silica gel; hexane–diethyl ether). When diisopropyl (*E*)-but-1-enylboronate was used as alkenylborane, the coupling reaction was carried out in 1,4-dioxane instead of benzene at 70 °C for 2 h.

(E)-2-Fluoro-1-iodododec-1-ene 2a. $\delta_{\text{H}}(\text{CDCl}_3)$ 0.85 (3H, t, J 6.5 Hz, 12- H_3), 1.20–1.32 (14H, m), 1.44–1.56 (2H, m, 4- H_2), 2.46 (2H, dt, $^3J_{\text{H-F}}$ 23.0, J 7.6 Hz, 3- H_2), 5.63 [1H, d, $^3J_{\text{H-F(olefin)}}$ 17.7 Hz, 1-H]; $\delta_{\text{F}}(\text{CDCl}_3)$ –82.25 [1F, dt, $^3J_{\text{H-F}}$ 23.0, $^3J_{\text{H-F(olefin)}}$ 17.7 Hz]; $\delta_{\text{C}}(\text{CDCl}_3)$ 14.11, 22.69, 25.72, 28.75, 29.27, 29.31, 29.47, 29.56, 30.94 (d, $^2J_{\text{C-F}}$ 25.6 Hz, 3-C), 31.88, 54.65 (d, $^2J_{\text{C-F}}$ 39.7 Hz, 1-C), 164.22 (d, $^1J_{\text{C-F}}$ 264.4 Hz, 2-C); $\nu(\text{neat})/\text{cm}^{-1}$ 3080, 2920, 2845, 1645, 1465, 1430, 1380, 1125, 1085, 875, 770, 720; m/z 312 (M^+ , 18%), 185 (11), 165 (6), 123 (8), 109 (35), 95 (51), 83 (42), 69 (52), 55 (53), 43 (100) [Calc. for $\text{C}_{12}\text{H}_{22}\text{FI}$ (*M*): 312.0750. Found: M^+ , 312.0742].

Methyl (E)-10-fluoro-11-iodoundec-10-enoate 2b. $\delta_{\text{H}}(\text{CDCl}_3)$ 1.28–1.39 (8H, br s), 1.51–1.64 (4H, m), 2.31 (2H, t, J 7.3 Hz, 2- H_2), 2.50 (2H, dt, $^3J_{\text{H-F}}$ 22.5, J 7.3 Hz, 9- H_2), 3.67 (3H, s, OMe), 5.67 [1H, d, $^3J_{\text{H-F(olefin)}}$ 17.8 Hz, 11-H]; $\delta_{\text{F}}(\text{CDCl}_3)$ –82.36 [1F, dt, $^3J_{\text{H-F}}$ 22.5, $^3J_{\text{H-F(olefin)}}$ 17.8 Hz]; $\delta_{\text{C}}(\text{CDCl}_3)$ 24.92, 25.68, 28.63, 29.07 (3C), 30.91 (d, $^2J_{\text{C-F}}$ 26.4 Hz, 9-C), 34.09, 51.46, 54.75 (d, $^2J_{\text{C-F}}$ 40.5 Hz, 11-C), 164.14 (d, $^1J_{\text{C-F}}$ 264.4 Hz, 10-C), 174.28; $\nu(\text{neat})/\text{cm}^{-1}$ 3080, 2930, 2855, 1735, 1645, 1460, 1440, 1365, 1255, 1205, 1175, 1140, 1105, 1075, 880, 775, 720; m/z 311 (M^+ – OMe, 20%), 215 (14), 195 (28), 180 (20), 163 (78), 155 (7), 145 (27), 135 (33), 121 (100), 111 (9), 95 (28), 87 (37), 81 (56), 74 (77), 67 (27), 55 (78), 41 (52) [Calc. for $\text{C}_{11}\text{H}_{17}\text{FIO}$ (*M* – OMe): 311.0308. Found: M^+ – OMe, 311.0321].

(E)-12-Fluoro-13-iodo-2,2-dimethyltridec-12-en-3-one 2c. $\delta_{\text{H}}(\text{CDCl}_3)$ 1.13 (9H, s, tBu), 1.23–1.39 (8H, m), 1.51–1.58 (4H, m), 2.45–2.54 (4H, m), 5.66 [1H, d, $^3J_{\text{H-F(olefin)}}$ 17.8 Hz, 13-H]; $\delta_{\text{F}}(\text{CDCl}_3)$ –82.48 [1F, dt, $^3J_{\text{H-F}}$ 23.3, $^3J_{\text{H-F(olefin)}}$ 17.7 Hz]; $\delta_{\text{C}}(\text{CDCl}_3)$ 23.88, 25.68, 26.41 (3C), 28.66, 29.12, 29.25, 29.33, 30.90 (d, $^2J_{\text{C-F}}$ 26.5 Hz, 11-C), 36.40, 44.08, 54.72 (d, $^2J_{\text{C-F}}$ 40.5 Hz, 13-C), 164.15 (d, $^1J_{\text{C-F}}$ 264.4 Hz, 12-C), 216.10; $\nu(\text{neat})/\text{cm}^{-1}$ 3069, 2963, 2930, 2856, 1707, 1649, 1478, 1462, 1365, 1112, 1066, 771; m/z 368 (M^+ , 0.2%), 311 (41), 241 (17), 185 (6), 135 (11), 121 (10), 99 (16), 93 (10), 85 (18), 67 (11), 57 (100), 41 (34) [Calc. for $\text{C}_{15}\text{H}_{26}\text{FIO}$ (*M*): 368.1012. Found: M^+ , 368.1014].

(E)-11-Acetoxy-2-fluoro-1-iodoundec-1-ene 2d. $\delta_{\text{H}}(\text{CDCl}_3)$ 1.28–1.39 (10H, m), 1.53–1.64 (4H, m), 2.05 (3H, s, MeCO), 2.50 (2H, dt, $^3J_{\text{H-F}}$ 22.7, J 7.3 Hz, 3- H_2), 4.05 (2H, t, J 6.8 Hz, 11- H_2), 5.67 [1H, d, $^3J_{\text{H-F(olefin)}}$ 17.8 Hz, 1-H]; $\delta_{\text{C}}(\text{CDCl}_3)$ 21.03, 25.69, 25.88, 28.59, 28.67, 29.28 (2C), 29.31, 30.92 (d, $^2J_{\text{C-F}}$ 26.4 Hz, 3-C), 54.73 (d, $^2J_{\text{C-F}}$ 39.7 Hz, 1-C), 64.62, 164.16 (d, $^1J_{\text{C-F}}$ 264.4 Hz, 2-C), 171.22; $\delta_{\text{F}}(\text{CDCl}_3)$ –82.48 [1F, dt, $^3J_{\text{H-F}}$ 22.7, $^3J_{\text{H-F(olefin)}}$ 17.8 Hz]; $\nu(\text{neat})/\text{cm}^{-1}$ 3077, 2929, 2856, 1740, 1650, 1464, 1430, 1388, 1365, 1240, 1125, 1079, 1038, 871, 772, 714; m/z 337 (M^+ – F, 3%), 324 (3), 311 (2), 254 (10), 229 (14), 221 (7), 209 (4), 198 (79), 185 (14), 169 (3), 149 (66), 121 (10), 107 (25), 93 (31), 69 (44), 55 (67), 43 (100) [Calc. for $\text{C}_{13}\text{H}_{22}\text{IO}_2$ (*M* – F): 337.0649. Found: M^+ – F, 337.0665].

(E)-10-Fluoro-11-iodoundec-10-en-1-ol 2e. Mp 30 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.27–1.40 (11H, m), 1.51–1.61 (4H, m), 2.50 (2H, dt, $^3J_{\text{H-F}}$ 22.4, J 7.6 Hz, 9- H_2), 3.64 (2H, t, J 6.6 Hz, 1- H_2), 5.67 [1H, d, $^3J_{\text{H-F(olefin)}}$ 17.8 Hz, 11-H]; $\delta_{\text{F}}(\text{CDCl}_3)$ –82.50 [1F, dt, $^3J_{\text{H-F}}$ 22.4, $^3J_{\text{H-F(olefin)}}$ 17.8 Hz]; $\delta_{\text{C}}(\text{CDCl}_3)$ 25.66 (2C), 28.65, 29.14, 29.31, 29.36, 30.88 (d, $^2J_{\text{C-F}}$ 26.4 Hz, 9-C), 32.74, 54.67 (d, $^2J_{\text{C-F}}$ 39.7 Hz, 11-C), 63.03, 164.63 (d, $^1J_{\text{C-F}}$ 264.4 Hz, 10-C); $\nu(\text{neat})/\text{cm}^{-1}$ 3330br, 3074, 2927, 2854, 1649, 1463, 1429, 1119,

1077, 1051, 870, 771, 714; m/z 314 (M^+ , 0.1%), 277 (3), 235 (1), 221 (2), 212 (1), 198 (64), 185 (18), 167 (12), 159 (3), 149 (76), 121 (14), 107 (36), 99 (46), 81 (66), 69 (75), 55 (100), 41 (82) [Calc. for $\text{C}_{11}\text{H}_{20}\text{FIO}$ (*M*): 314.0543. Found: M^+ , 314.0534].

(E)-11-Chloro-2-fluoro-1-iodoundec-1-ene 2f. $\delta_{\text{H}}(\text{CDCl}_3)$ 1.30–1.44 (10H, m), 1.52–1.59 (2H, m, 4- H_2), 1.73–1.81 (2H, m, 10- H_2), 2.50 (2H, dt, $^3J_{\text{H-F}}$ 22.4, J 7.3 Hz, 3- H_2), 3.53 (2H, t, J 6.6 Hz, 11- H_2), 5.67 [1H, d, $^3J_{\text{H-F(olefin)}}$ 17.8 Hz, 1-H]; $\delta_{\text{F}}(\text{CDCl}_3)$ –82.35 [1F, dt, $^3J_{\text{H-F}}$ 22.4, $^3J_{\text{H-F(olefin)}}$ 17.8 Hz]; $\delta_{\text{C}}(\text{CDCl}_3)$ 25.66, 26.83, 28.64, 28.80, 29.12, 29.25, 30.90 (d, $^2J_{\text{C-F}}$ 26.4 Hz, 3-C), 32.60, 45.15, 54.73 (d, $^2J_{\text{C-F}}$ 40.5 Hz, 1-C), 164.13 (d, $^1J_{\text{C-F}}$ 264.4 Hz, 2-C); $\nu(\text{neat})/\text{cm}^{-1}$ 3074, 2929, 2855, 1649, 1463, 1430, 1309, 1131, 1107, 1073, 875, 772, 726; m/z 332 (M^+ , 33%), 273 (3), 198 (4), 185 (20), 169 (4), 143 (13), 128 (9), 109 (35), 95 (40), 81 (90), 69 (81), 55 (100), 41 (75) [Calc. for $\text{C}_{11}\text{H}_{19}\text{ClFI}$ (*M*): 332.0204. Found: M^+ , 332.0204].

(E)-2-Fluoro-1-phenyldodec-1-ene 3a. $\delta_{\text{H}}(\text{CDCl}_3)$ 0.88 (3H, t, J 7.0 Hz, 12- H_3), 1.25–1.33 (14H, m), 1.57–1.65 (2H, m, 4- H_2), 2.43 (2H, dt, $^3J_{\text{H-F}}$ 23.4, J 7.6 Hz, 3- H_2), 6.18 [1H, d, $^3J_{\text{H-F(olefin)}}$ 21.9 Hz, 1-H], 7.18–7.34 (5H, m, Ph); $\delta_{\text{F}}(\text{CDCl}_3)$ –99.03 (1F, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.11, 22.67, 26.37, 28.96 (d, $^2J_{\text{C-F}}$ 26.4 Hz, 3-C), 29.14, 29.31 (2C), 29.50, 29.56, 31.88, 108.02 (d, $^2J_{\text{C-F}}$ 28.9 Hz, 1-C), 126.53 (2C), 128.40 (3C), 134.41 (d, $^3J_{\text{C-F}}$ 14.1 Hz, *ipso*-Ph), 162.77 (d, $^1J_{\text{C-F}}$ 252.7 Hz, 2-C); $\nu(\text{neat})/\text{cm}^{-1}$ 3084, 3059, 3027, 2955, 2926, 2854, 1682, 1601, 1496, 1466, 1377, 1225, 1142, 1095, 913, 885, 844, 747, 697; m/z 262 (M^+ , 100%), 135 (53), 122 (18), 115 (18), 104 (8), 91 (12), 57 (7), 43 (13) [Calc. for $\text{C}_{18}\text{H}_{27}\text{F}$ (*M*): 262.2097. Found: M^+ , 262.2093] (Calc. for $\text{C}_{18}\text{H}_{27}\text{F}$: C, 82.39; H, 10.37. Found: C, 82.58; H, 10.53%).

(E)-2-Fluoro-1-(2-methylphenyl)dodec-1-ene 3b. $\delta_{\text{H}}(\text{CDCl}_3)$ 0.88 (3H, t, J 6.9 Hz, 12- H_3), 1.28–1.33 (14H, m), 1.52–1.60 (2H, m, 4- H_2), 2.25 (3H, s, $\text{C}_6\text{H}_4\text{Me}$), 2.30 (2H, dt, $^3J_{\text{H-F}}$ 22.9, J 7.6 Hz, 3- H_2), 6.14 [1H, d, $^3J_{\text{H-F(olefin)}}$ 21.2 Hz, 1-H], 7.10–7.18 (4H, m, ArH); $\delta_{\text{F}}(\text{CDCl}_3)$ –101.46 (1F, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.11, 20.07, 22.68, 26.29, 28.56 (d, $^2J_{\text{C-F}}$ 27.2 Hz, 3-C), 29.02, 29.27, 29.31, 29.52, 29.57, 31.90, 106.62 (d, $^2J_{\text{C-F}}$ 27.2 Hz, 1-C), 125.71, 127.07, 129.03, 129.78, 133.45 (d, $^3J_{\text{C-F}}$ 13.3 Hz, *ipso*-Ar), 136.85, 162.36 (d, $^1J_{\text{C-F}}$ 252.8 Hz, 2-C); $\nu(\text{neat})/\text{cm}^{-1}$ 3106, 3066, 3021, 2956, 2925, 2854, 1684, 1603, 1484, 1459, 1379, 1233, 1195, 1143, 1095, 885, 845, 788, 746, 721; m/z 276 (M^+ , 100%), 149 (93), 134 (20), 129 (31), 115 (18), 105 (23), 55 (8), 43 (26) [Calc. for $\text{C}_{19}\text{H}_{29}\text{F}$ (*M*): 276.2253. Found: M^+ , 276.2251].

(E)-2-Fluoro-1-(1-naphthyl)dodec-1-ene 3c. $\delta_{\text{H}}(\text{CDCl}_3)$ 0.87 (3H, t, J 7.0 Hz, 12- H_3), 1.15–1.30 (14H, m), 1.53–1.60 (2H, m, 4- H_2), 2.31 (2H, dt, $^3J_{\text{H-F}}$ 22.7, J 7.6 Hz, 3- H_2), 6.57 [1H, d, $^3J_{\text{H-F(olefin)}}$ 20.5 Hz, 1-H], 7.30–7.53 (4H, m), 7.42–8.00 (3H, m); $\delta_{\text{F}}(\text{CDCl}_3)$ –103.32 (1F, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 14.12, 22.67, 26.31, 28.74 (d, $^2J_{\text{C-F}}$ 26.4 Hz, 3-C), 28.97, 29.22, 29.28, 29.46, 29.52, 31.88, 105.56 (d, $^2J_{\text{C-F}}$ 27.3 Hz, 1-C), 124.92, 125.37, 125.93, 126.03, 126.67, 127.56, 128.34, 131.54 (d, $^3J_{\text{C-F}}$ 13.2 Hz, *ipso*-naphthyl), 132.29, 133.52, 163.29 (d, $^1J_{\text{C-F}}$ 254.4 Hz, 2-C); $\nu(\text{neat})/\text{cm}^{-1}$ 3062, 3046, 2955, 2925, 2854, 1683, 1596, 1515, 1466, 1174, 1143, 1095, 892, 842, 798, 780, 651, 626; m/z 312 (M^+ , 100%), 185 (42), 165 (17), 141 (10), 43 (3) [Calc. for $\text{C}_{22}\text{H}_{29}\text{F}$ (*M*): 312.2253. Found: M^+ , 312.2240] (Calc. for $\text{C}_{22}\text{H}_{29}\text{F}$: C, 84.57; H, 9.35. Found: C, 84.84; H, 9.58%).

Methyl (E)-10-fluoro-11-phenylundecenoate 3d. $\delta_{\text{H}}(\text{CDCl}_3)$ 1.27–1.36 (8H, br s), 1.57–1.65 (4H, m), 2.29 (2H, t, J 7.6 Hz, 2- H_2), 2.43 (2H, dt, $^3J_{\text{H-F}}$ 23.4, J 7.6 Hz, 9- H_2), 3.66 (3H, s, OMe), 6.18 [1H, d, $^3J_{\text{H-F(olefin)}}$ 21.9 Hz, 11-H], 7.17–7.34 (5H, m, Ph); $\delta_{\text{F}}(\text{CDCl}_3)$ –99.09 (1F, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 24.91, 26.32, 28.91 (d, $^2J_{\text{C-F}}$ 24.8 Hz, 9-C), 29.07, 29.09 (3C), 34.08, 51.44, 108.09, (d, $^2J_{\text{C-F}}$ 28.9 Hz, 11-C), 126.56 (2C), 128.42 (3C), 134.34 (d, $^3J_{\text{C-F}}$ 14.1 Hz, *ipso*-Ph), 162.67 (d, $^1J_{\text{C-F}}$ 251.9 Hz, 10-C), 174.28; $\nu(\text{neat})/\text{cm}^{-1}$ 3085, 3058, 3026, 2930, 2856, 1739, 1682,

1601, 1495, 1436, 1363, 1196, 1171, 1119, 1075, 1029, 915, 885, 749, 698; m/z 292 (M^+ , 8%), 261 (5), 149 (6), 135 (17), 130 (100), 115 (12), 91 (7), 55 (6), 41 (3) [Calc. for $C_{18}H_{25}FO_2$ (M): 292.1838. Found: M^+ , 292.1838].

(*E*)-12-Fluoro-2,2-dimethyl-13-phenyltridec-12-en-3-one 3e. δ_H (CDCl₃) 1.13 (9H, s, ¹Bu), 1.25–1.36 (8H, m), 1.49–1.64 (4H, m), 2.38–2.48 (4H, m), 6.18 [1H, d, ³ $J_{H-F(olefin)}$ 21.9 Hz, 13-H], 7.17–7.34 (5H, m, Ph); δ_F (CDCl₃) –99.06 (1F, m); δ_C (CDCl₃) 23.90, 26.35, 26.42 (3C), 28.95 (d, ² J_{C-F} 28.2 Hz, 11-C), 29.09, 29.18, 29.26, 29.36, 36.41, 44.10, 108.07 (d, ² J_{C-F} 28.0 Hz, 13-C), 126.55 (2C), 128.42 (3C), 134.39 (d, ³ J_{C-F} 14.1 Hz, *ipso*-Ph), 162.70 (d, ¹ J_{C-F} 251.9 Hz, 12-C), 216.11; ν (neat)/cm^{–1} 3088, 3059, 3027, 2971, 2930, 2856, 1706, 1684, 1601, 1477, 1465, 1393, 1365, 1223, 1148, 1124, 1070, 987, 914, 885, 842, 749, 698; m/z 318 (M^+ , 26%), 261 (23), 223 (7), 157 (12), 135 (30), 130 (100), 117 (23), 109 (8), 91 (52), 57 (58), 41 (17) [Calc. for $C_{21}H_{31}FO$ (M): 318.2359. Found: M^+ , 318.2347] (Calc. for $C_{21}H_{31}FO$: C, 79.20; H, 9.81. Found: C, 79.36, H, 9.96%).

(*E*)-11-Acetoxy-2-fluoro-1-phenylundec-1-ene 3f. δ_H (CDCl₃) 1.27–1.36 (10H, m), 1.57–1.65 (4H, m), 2.05 (3H, s, MeCO), 2.43 (2H, dt, ³ J_{H-F} 23.4, J 7.6 Hz, 3-H₂), 4.05 (2H, t, J 6.7 Hz), 6.18 [1H, d, ³ $J_{H-F(olefin)}$ 21.9 Hz, 1-H], 7.17–7.34 (5H, m, Ph); δ_F (CDCl₃) –99.12 (1F, m); δ_C (CDCl₃) 21.03, 25.87, 26.34, 28.59, 28.94 (d, ² J_{C-F} 28.1 Hz, 3-C), 29.08, 29.21 (2C), 29.35, 64.63, 108.09 (d, ² J_{C-F} 28.9 Hz, 1-C), 126.57 (2C), 128.42 (3C), 134.40 (d, ³ J_{C-F} 14.1 Hz, *ipso*-Ph), 162.69 (d, ¹ J_{C-F} 252.7 Hz, 2-C), 171.26; ν (neat)/cm^{–1} 3085, 3059, 3027, 2930, 2856, 1739, 1683, 1601, 1496, 1447, 1365, 1241, 1135, 1037, 915, 883, 749, 699; m/z 306 (M^+ , 12%), 246 (6), 148 (51), 130 (100), 122 (8), 115 (17), 91 (9), 69 (6), 55 (7), 43 (18) [Calc. for $C_{19}H_{27}FO_2$ (M): 306.1995. Found: M^+ , 306.1984] (Calc. for $C_{19}H_{27}FO_2$: C, 74.48; H, 8.88. Found: C, 74.59, H, 8.84%).

(*E*)-10-Fluoro-11-(2-methylphenyl)undec-10-en-1-ol 3g. δ_H (CDCl₃) 1.20–1.40 (11H, m), 1.51–1.58 (4H, m), 2.25–2.34 (5H, m), 3.62 (2H, t, J 6.6 Hz, 1-H₂), 6.14 [1H, d, ³ $J_{H-F(olefin)}$ 21.2 Hz, 11-H], 7.10–7.16 (4H, m, ArH); δ_F (CDCl₃) –101.45 (1F, m); δ_C (CDCl₃) 20.07, 25.69, 26.25, 28.54 (d, ² J_{C-F} 27.3 Hz, 9-C), 28.96, 29.17, 29.35, 29.42, 32.79, 63.06, 106.65 (d, ² J_{C-F} 27.2 Hz, 11-C), 125.71, 127.08, 129.03, 129.78, 133.43 (d, ³ J_{C-F} 13.2 Hz, *ipso*-Ph), 136.85, 162.30 (d, ¹ J_{C-F} 252.7 Hz, 10-C); ν (neat)/cm^{–1} 3346br, 3061, 3020, 2928, 2855, 1683, 1603, 1484, 1459, 1232, 1194, 1153, 1084, 1056, 883, 846, 788, 747, 724; m/z 278 (M^+ , 43%), 260 (17), 161 (28), 149 (100), 144 (84), 136 (21), 129 (78), 118 (19), 105 (36), 93 (7), 81 (8), 69 (14), 55 (21), 41 (9) [Calc. for $C_{18}H_{27}FO$ (M): 278.2046. Found: M^+ , 278.2046].

(*E,E*)-8-Fluorooctadeca-5,7-diene 5a. δ_H (CDCl₃) 0.86–0.92 (6H, m), 1.25–1.37 (18H, m), 1.49–1.56 (2H, m, 10-H₂), 2.05–2.10 (2H, m, 4-H₂), 2.31 (2H, dt, ³ J_{H-F} 23.4, J 7.3 Hz, 9-H₂), 5.57 (1H, dt, J 7.1, 14.9 Hz, 5-H), 5.69 [1H, dd, ³ $J_{H-F(olefin)}$ 20.3, J 11.0 Hz, 7-H], 5.87–5.94 (1H, m, 6-H); δ_F (CDCl₃) –104.73 (1F, m); δ_C (CDCl₃) 13.94, 14.13, 22.25, 22.71, 26.39, 28.42 (d, ² J_{C-F} 27.2 Hz, 9-C), 28.97, 29.35 (2C), 29.56, 29.62, 31.59, 31.93, 32.70, 108.01 (d, ² J_{C-F} 26.4 Hz, 7-C), 122.84 (d, ³ J_{C-F} 10.7 Hz, 6-C), 133.31 (d, ⁴ J_{C-F} 9.9 Hz, 5-C), 161.47 (d, ¹ J_{C-F} 251.1 Hz, 8-C); ν (neat)/cm^{–1} 3033, 2957, 2926, 2855, 1681, 1632, 1466, 1434, 1377, 1272, 1141, 1094, 960, 867, 722; m/z 268 (M^+ , 100%), 225 (22), 135 (12), 127 (20), 107 (15), 95 (29), 82 (97), 67 (42), 55 (29), 43 (35) [Calc. for $C_{18}H_{33}F$ (M): 268.2566. Found: M^+ , 268.2564].

(*E,E*)-6-Fluorohexadeca-3,5-diene 5b. δ_H (CDCl₃) 0.88 (3H, t, J 6.8 Hz, 16-H₃), 1.01 (3H, t, J 7.5 Hz, 1-H₃), 1.23–1.36 (14H, br s), 1.48–1.56 (2H, m, 8-H₂), 2.06–2.13 (2H, m, 2-H₂), 2.32 (2H, dt, ³ J_{H-F} 23.7, J 7.3 Hz, 7-H₂), 5.58–5.73 (2H, m), 5.87–

5.97 (1H, m, 4-H); δ_F (CDCl₃) –104.70 (1F, m); δ_C (CDCl₃) 13.69, 14.13, 22.70, 26.01, 26.38, 28.41 (d, ² J_{C-F} 27.2 Hz, 7-C), 28.97, 29.34, 29.36, 29.55, 29.61, 31.91, 107.96 (d, ² J_{C-F} 26.4 Hz, 5-C), 121.95 (d, ³ J_{C-F} 10.7 Hz, 4-C), 134.77 (d, ⁴ J_{C-F} 9.1 Hz, 3-C), 161.51 (d, ¹ J_{C-F} 251.9 Hz, 6-C); ν (neat)/cm^{–1} 3033, 2960, 2926, 2854, 1681, 1631, 1463, 1376, 1319, 1242, 1173, 1141, 1092, 1013, 959, 867, 775, 721; m/z 240 (M^+ , 100%), 149 (6), 135 (11), 127 (8), 121 (13), 113 (40), 107 (14), 99 (77), 85 (42), 81 (33), 67 (38), 59 (12), 55 (38), 43 (57) [Calc. for $C_{16}H_{29}F$ (M): 240.2253. Found: M^+ , 240.2253].

Ethyl (*E,E*)-7-fluoro-2,2-dimethylheptadeca-4,6-dienoate 5c. δ_H (CDCl₃) 0.88 (3H, t, J 7.1 Hz, 17-H₃), 1.16 (6H, s, Me \times 2), 1.22–1.34 (17H, m), 1.48–1.53 (2H, m, 9-H₂), 2.26–2.35 (4H, m), 4.11 (2H, q, J 7.1 Hz, OCH₂CH₃), 5.46–5.53 (1H, m, 4-H), 5.69 [1H, dd, ³ $J_{H-F(olefin)}$ 20.2, J 11.0 Hz, 6-H], 5.90–5.97 (1H, m, 5-H); δ_F (CDCl₃) –99.92 (1F, m); δ_C (CDCl₃) 14.13, 14.28, 22.69, 24.85 (2C), 26.38, 28.45 (d, ² J_{C-F} 27.2 Hz, 8-C), 28.96, 29.33, 29.35, 29.54, 29.59, 31.91, 42.59, 43.90, 60.32, 107.83 (d, ² J_{C-F} 27.3 Hz, 6-C), 126.12 (d, ³ J_{C-F} 11.5 Hz, 5-C), 128.02 (d, ⁴ J_{C-F} 9.9 Hz, 4-C), 162.17 (d, ¹ J_{C-F} 253.6 Hz, 7-C), 177.42; ν (neat)/cm^{–1} 3032, 2957, 2927, 2855, 1731, 1679, 1631, 1469, 1386, 1365, 1303, 1242, 1196, 1147, 1095, 1029, 964, 865, 768, 722; m/z 340 (M^+ , 23%), 266 (18), 225 (100), 205 (6), 149 (5), 135 (12), 121 (21), 107 (14), 93 (23), 79 (22), 67 (32), 55 (22), 43 (27) [Calc. for $C_{21}H_{37}FO_2$ (M): 340.2777. Found: M^+ , 340.2791] (Calc. for $C_{21}H_{37}FO_2$: C, 74.07; H, 10.95. Found: C, 74.03; H, 10.98%).

Methyl (*E,E*)-10-fluoroheptadeca-10,12-dienoate 5d. δ_H (CDCl₃) 0.90 (3H, t, J 7.1 Hz, 17-H₃), 1.27–1.38 (12H, m), 1.48–1.65 (4H, m), 2.05–2.10 (2H, m, 14-H₂), 2.26–2.36 (4H, m), 3.67 (3H, s, OMe), 5.54–5.61 (1H, m, 13-H), 5.69 [1H, dd, ³ $J_{H-F(olefin)}$ 20.5, J 11.0 Hz, 11-H], 5.86–5.93 (1H, m, 12-H); δ_F (CDCl₃) –104.53 (1F, m); δ_C (CDCl₃) 13.94, 22.24, 24.94, 26.35, 28.40 (d, ² J_{C-F} 27.3 Hz, 9-C), 28.87, 29.11, 29.13 (2C), 31.58, 32.69, 34.09, 51.44, 108.04 (d, ² J_{C-F} 27.2 Hz, 11-C), 122.79 (d, ³ J_{C-F} 10.7 Hz, 12-C), 133.38 (d, ⁴ J_{C-F} 9.8 Hz, 13-C), 161.36 (d, ¹ J_{C-F} 251.9 Hz, 10-C), 174.29; ν (neat)/cm^{–1} 3029, 2955, 2929, 2857, 1741, 1680, 1631, 1459, 1436, 1364, 1197, 1171, 1119, 1077, 1027, 962, 868, 721; m/z 298 (M^+ , 76%), 278 (11), 267 (23), 238 (6), 224 (5), 208 (12), 177 (8), 161 (20), 149 (17), 136 (88), 127 (11), 121 (38), 107 (48), 93 (78), 85 (72), 79 (94), 67 (75), 59 (38), 55 (100), 41 (80) [Calc. for $C_{18}H_{31}FO_2$ (M): 298.2308. Found: M^+ , 298.2308] (Calc. for $C_{18}H_{31}FO_2$: C, 72.44; H, 10.47. Found: C, 72.35; H, 10.36%).

(*E,E*)-10-Fluoropentadeca-10,12-dien-1-ol 5e. δ_H (CDCl₃) 1.01 (3H, t, J 7.6 Hz, 15-H₃), 1.22–1.38 (11H, m), 1.51–1.58 (4H, m), 2.06–2.13 (2H, m, 14-H₂), 2.32 (2H, dt, ³ J_{H-F} 23.4, J 7.3 Hz, 9-H₂), 3.64 (2H, t, J 6.6 Hz, 1-H₂), 5.59–5.74 (2H, m), 5.87–5.93 (1H, m, 12-H); δ_F (CDCl₃) –104.73 (1F, m); δ_C (CDCl₃) 13.70, 25.72, 26.00, 26.36, 28.39 (d, ² J_{C-F} 27.2 Hz, 9-C), 28.92, 29.26, 29.38, 29.46, 32.79, 63.08, 107.99 (d, ² J_{C-F} 27.3 Hz, 11-C), 121.90 (d, ³ J_{C-F} 10.7 Hz, 12-C), 134.82 (d, ⁴ J_{C-F} 9.9 Hz, 13-C), 161.45 (d, ¹ J_{C-F} 252.0 Hz, 10-C); ν (neat)/cm^{–1} 3313br, 3033, 2963, 2929, 2855, 1680, 1631, 1461, 1434, 1371, 1320, 1150, 1128, 1077, 1057, 960, 867, 722; m/z 242 (M^+ , 45%), 224 (5), 153 (16), 135 (14), 125 (34), 112 (62), 97 (100), 79 (71), 67 (68), 55 (94), 41 (83) [Calc. for $C_{15}H_{27}FO$ (M): 242.2046. Found: M^+ , 242.2050].

(*E,E*)-17-Chloro-8-fluoroheptadeca-5,7-diene 5f. δ_H (CDCl₃) 0.90 (3H, t, J 7.6 Hz, 1-H₃), 1.28–1.46 (14H, m), 1.48–1.57 (2H, m), 1.73–1.80 (2H, m, 10-H₂), 2.05–2.08 (2H, m, 4-H₂), 2.34 (2H, dt, ³ J_{H-F} 23.4, J 7.3 Hz, 9-H₂), 3.52 (2H, t, J 6.6 Hz, 17-H₂), 5.54–5.61 (1H, m, 5-H), 5.69 [1H, dd, ³ $J_{H-F(olefin)}$ 20.2, J 11.0 Hz, 7-H], 5.87–5.93 (1H, m, 6-H); δ_F (CDCl₃) –104.85 (1F, m); δ_C (CDCl₃) 13.95, 22.23, 26.34, 26.87, 28.39 (d, ² J_{C-F} 27.2 Hz, 9-C), 28.85, 28.88, 29.23, 29.33, 31.58, 32.64,

32.69, 45.17, 108.04 (d, $^2J_{\text{C-F}}$ 27.2 Hz, 7-C), 122.78 (d, $^3J_{\text{C-F}}$ 10.7 Hz, 6-C), 133.38 (d, $^4J_{\text{C-F}}$ 9.0 Hz, 5-C), 161.36 (d, $^1J_{\text{C-F}}$ 251.9 Hz, 8-C); $\nu(\text{neat})/\text{cm}^{-1}$ 3029, 2959, 2928, 2856, 1680, 1631, 1465, 1375, 1147, 1075, 962, 868, 726, 653; m/z 288 (M^+ , 50%), 245 (17), 232 (5), 135 (6), 127 (22), 121 (16), 107 (16), 95 (27), 82 (100), 67 (53), 55 (48), 41 (51) [Calc. for $\text{C}_{17}\text{H}_{30}\text{ClF}$ (M): 288.2020. Found: M^+ , 288.2027] (Calc. for $\text{C}_{17}\text{H}_{30}\text{ClF}$: C, 70.68; H, 10.47. Found: C, 70.48; H, 10.25%).

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