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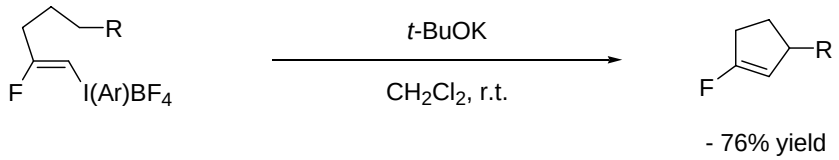
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An efficient synthesis of fluorocyclopentenes using fluoroalkylidenecarbenes

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Tong Guan, Kohei Takemura, Hisanori Senboku, Masanori Yoshida* and Shoji Hara



- 76% yield

Pergamon

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LETTERS

An efficient synthesis of fluorocyclopentenes using fluoroalkylidenecarbenes

Tong Guan, Kohei Takemura, Hisanori Senboku, Masanori Yoshida* and Shoji Hara

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Abstract—An efficient synthesis of fluorocyclopentenes is described. By treatment of (2-fluoroalkenyl)iodonium salts with potassium *tert*-butoxide, (α-fluoroalkylidene)carbenes were generated efficiently to give fluorocyclopentenes via 1,5-C–H insertion. Fluorocyclopentenes having a functionality, such as chlorine, acetoxy or ketone, and a spiro fluorocyclopentene were synthesized in good yields. © 2008 Elsevier Science. All rights reserved

Fluoroalkene synthesis has received considerable attention from biological and medicinal chemists because the introduction of a fluorine atom into the double bond of a biologically active compound can dramatically enhance its bioactivity.[1,2] Therefore, much attention has been paid for the fluoroalkene synthesis, and many successful methodologies of terminal and internal fluoroalkene synthesis have been developed.[3,4] However, only a few methods for the synthesis of fluorocycloalkenes, especially fluorocyclopentenes, have been reported so far.[5-8] Since a cyclopentene moiety is a common structure in natural organic molecules, it would be worthwhile developing an efficient method for synthesizing fluorocyclopentenes to develop fluorinated pharmaceuticals. In 1993, Ochiai and co-workers reported that a fluorocyclopentene could be synthesized by 1,5-C–H insertion of an (α-fluoroalkylidene)carbene, which was generated by α-elimination of (*Z*)-(2-fluorohexadec-1-enyl)(phenyl)iodonium tetrafluoroborate using tetrabutylammonium fluoride (TBAF) as a base. However, the fluorocyclopentene was obtained in only 17% yield and no other products were mentioned in their paper.[8] Moreover, there was no method for efficient synthesis of fluoroalkenyliodonium salts at that time.[9] Recently, we found that various (*Z*)-(2-fluoroalkenyl)iodonium salts **1** could be synthesized efficiently by the reaction of alkynyliodonium salts, which can be readily prepared from terminal alkynes,[10] with diluted aqueous HF.[11] In this context, we decided to investigate the synthesis of fluorocyclopentenes using **1**. First, we attempted to synthesize a fluorocyclopentene by the reaction of a fluoroalkenyliodonium salt with TBAF according to the reported procedure.[8] The results obtained by using (*Z*)-(11-acetoxy-2-fluoroundec-1-enyl)(phenyl)iodonium tetrafluoroborate (**1a**) as a starting material revealed that TBAF worked not only as a base but also as a fluoride source to afford a small amount of fluorocyclopentene, 3-(6-acetoxyhexyl)-1-fluorocyclopentene (**2a**, 9%), and a relatively large amount of 11-acetoxy-1,2,2-trifluoroundecane (**3**, 21%)[12] with many minor products (Scheme 1).[8,11,13]

[Scheme 1]

We therefore investigated the reaction conditions to obtain a fluorocyclopentene efficiently using a simple fluoroalkenyliodonium salt, (*Z*)-(2-fluorododec-1-enyl)(phenyl)iodonium tetrafluoroborate (**1b**), as a starting material (Table 1). A screening of bases showed that potassium *tert*-butoxide, *t*-BuOK, can dramatically increase the yield of fluorocyclopentene, and 3-heptyl-1-fluorocyclopentene (**2b**) was obtained in 66% yield (Table 1, Entry 1). Other bases, including KOH (42%), NaOEt (39%), LDA (17%) and DBU (16%), gave lower yields than that obtained by using *t*-BuOK (Table 1, Entries 2-5). The use of benzene, THF and chlorobenzene as solvents gave **2b** in a range of 26-37% yields, and CH_2Cl_2 was found to be a good solvent for this reaction (Table 1, Entries 1 and 6-8). Finally, the best result (**2b**, 74%) was obtained by the reaction of **1b** with *t*-BuOK (3 equiv.) in CH_2Cl_2 at a low substrate concentration (0.01 M) (Table 1, Entry 10).[14]

[Table 1]

Under the same reaction conditions, the fluoroalkenyliodonium salt **1a** was also successfully converted into fluorocyclopentene **2a** in 68% yield, while the treatment of **1a** with TBAF gave only 9% yield as shown in Scheme 1 (Table 2, Entry 1).

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Fluoroalkenyliodonium salts **1c** and **1d** having a functional group, e.g. Cl or *t*-BuCO, could be converted into fluorocyclopentenes **2c** and **2d**, respectively, in good yields (Table 2, Entries 2 and 3). The 1,5-C–H insertion of an (α-fluoroalkylidene)carbene into an acetal C–H bond also proceeded smoothly to afford a spiro product **2e** in 71% yield (Table 2, Entry 4).

[Table 2]

Next, we studied the effect of substituents of the aryliodanyl group of fluoroalkenyliodonium salts (Table 3, Entries 1 and 2). (*Z*)-(2-Fluorododec-1-enyl)(*p*-tolyl)iodonium tetrafluoroborate (**1f**) and (*Z*)-(2-fluorododec-1-enyl)(*p*-chlorophenyl)iodonium tetrafluoroborate (**1g**) were prepared and subjected to the reaction conditions.[11,15,16] By comparison with the reaction using **1b**, it was found that neither the chlorine nor the methyl group has a significant influence on the yield of **2b** (74% from **1f** and 70% from **1g**) or on the reaction rate. In addition, the stereoisomer of **1f**, (*E*)-(2-fluorododec-1-enyl)(*p*-tolyl)iodonium tetrafluoroborate (**1h**),[17] also gave **2b** in a similar yield (76%) under the same reaction conditions (Table 3, Entry 3). These results indicate that the 1,5-C–H insertion occurred via an (α-fluoroalkylidene)carbene, not an (α-fluoroalkylidene)carbenoide, as in the reaction using usual alkenyliodonium salts.[18]

[Table 3]

In summary, we found that (α-fluoroalkylidene)carbenes can be generated efficiently by the reaction of (2-fluoroalkenyl)iodonium salts with potassium *tert*-butoxide in dichloromethane. The 1,5-C–H insertion of (α-fluoroalkylidene)carbenes smoothly proceeded to give fluorocyclopentenes having a functional group, e.g., OAc, Cl or *t*-BuCO, in good yields. A spiro fluorocyclopentene was also obtained by the 1,5-C–H insertion of a fluoroalkylidenecarbene into an acetal C–H bond.

Acknowledgment

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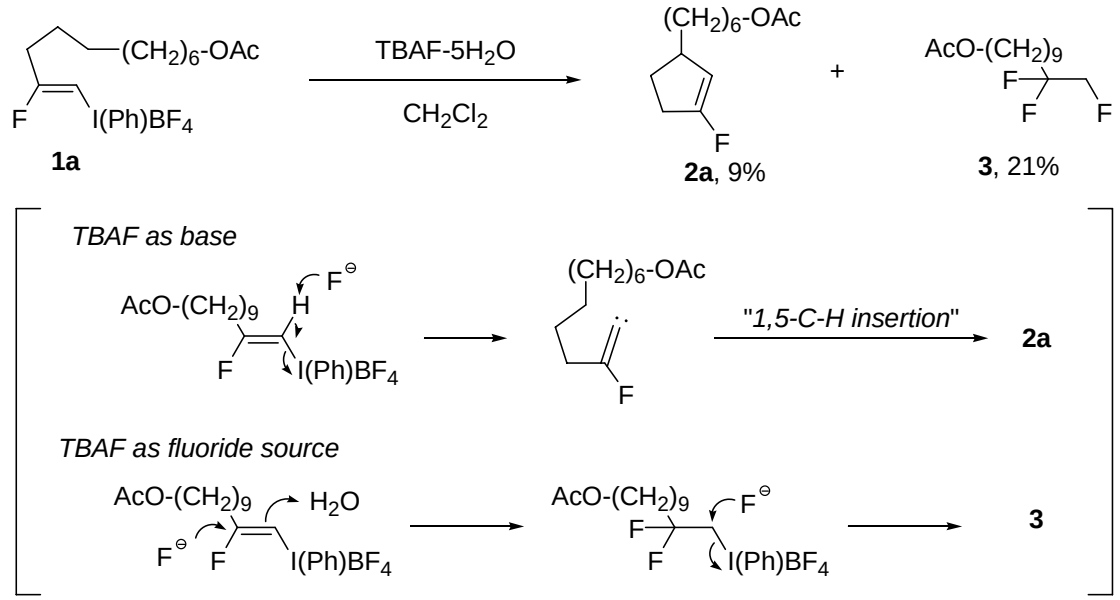
12 The compound **3** was obtained as a mixture with a small amount of impurities. Therefore the yield of **3** was determined by ^{1}H NMR using an internal standard. For spectral data of a 1,2,2-trifluoroalkane, see, reference 11.

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14 Experimental procedure and spectra data for the synthesis of **2b**: In a round bottomed flask were placed (Z)-(2-fluorododec-1-enyl)(phenyl)iodonium tetrafluoroborate (**1b**) (238 mg, 0.5 mmol), CH_2Cl_2 (50 mL), and potassium *tert*-butoxide (168 mg, 1.5 mmol) at room temperature, and the mixture was stirred for 24 h at room temperature. The reaction mixture was poured into a sat. aq. NH_4Cl (30 mL) and the organic phase was separated. The aqueous phase was extracted with Et_2O (20 mL) three times. The combined organic phase

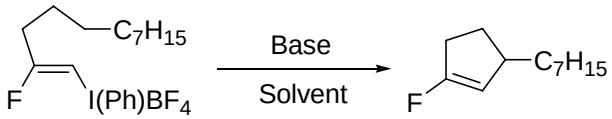
was dried over $MgSO_4$ and concentrated under reduced pressure. The product, 1-fluoro-3-heptylcyclopentene (**2b**) was isolated by column chromatography (silicagel; hexane) in 74% yield (68 mg, 0.37 mmol); $\delta_H(CDCl_3)$ 0.88 (3H, t, *J* 6.7 Hz), 1.22-1.56 (13H, m), 2.08-2.15 (1H, m), 2.36-2.44 (2H, m), 2.54-2.64 (1H, m), 4.94-4.98 (1H, m); $\delta_F(CDCl_3)$ –122.2 (1F, s); $\delta_C(CDCl_3)$ 14.1, 22.7, 27.4, 27.7 (d, *J* 7.7 Hz), 28.6 (d, *J* 21.8 Hz), 29.3, 29.8, 31.9, 36.9 (d, *J* 1.9 Hz), 40.0 (d, *J* 7.7 Hz), 106.5 (d, *J* 8.6 Hz), 162.0 (d, *J* 278.8 Hz); ν(KBr)/cm^{-1} 2954, 2925, 2855, 1679, 1460, 1350, 1164, 821, 723; [HR EI-MS: Calc. for $C_{12}H_{21}F$ (*M*): 184.1627. Found: M^+, 184.1629].

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(CH2)6-OAc
F
I(Ph)BF4
1a
TBAF-5H2O
CH2Cl2
(CH2)6-OAc
F
2a, 9%
+
AcO-(CH2)9
F
F
F
3, 21%
TBAF as base
AcO-(CH2)9
H
F⊖
F
I(Ph)BF4
(CH2)6-OAc
F
"1,5-C-H insertion"
2a
TBAF as fluoride source
AcO-(CH2)9
H2O
F⊖
F
I(Ph)BF4
AcO-(CH2)9
F⊖
F
F
I(Ph)BF4
3

Scheme 1.

Table 1. Optimization of reaction conditions[a]

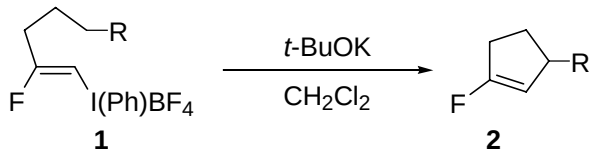


1b **2b**

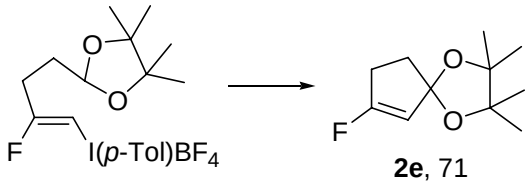
Entry	Base	Solvent	Yield (%)[b]
1	*t*-BuOK	CH_2Cl_2	66
2	KOH	CH_2Cl_2	42
3	NaOEt	CH_2Cl_2	39
4	LDA	CH_2Cl_2	17
5	DBU	CH_2Cl_2	16
6	*t*-BuOK	Benzene	27
7	*t*-BuOK	THF	26
8	*t*-BuOK	Chlorobenzene	37
9[c]	*t*-BuOK	CH_2Cl_2	70
10[d]	*t*-BuOK	CH_2Cl_2	74

[a] Unless otherwise mentioned, reactions were carried out with **1b** (0.5 mmol) and a base (0.75 mmol) in a solvent (10 mL, 0.05 M) at r.t. for 24 h. [b] Isolated yield of **2b**. [c] CH_2Cl_2 (50 mL, 0.01 M). [d] Base (1.5 mmol), CH_2Cl_2 (50 mL, 0.01 M).

Table 2. Synthesis of **2**[a]

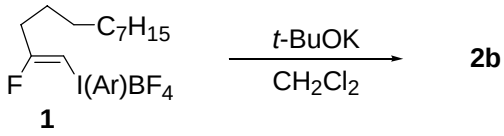


1 **2**

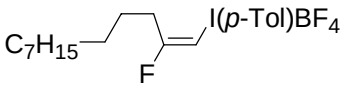
Entry	R	Yield (%)[b]
1	AcO-$(CH_2)_6$	**2a**, 68
2	Cl-$(CH_2)_6$	**2c**, 64
3	*t*-BuCO-$(CH_2)_5$	**2d**, 71
4		**2e**, 71

[a] Reagents and conditions: **1** (0.5 mmol), *t*-BuOK (1.5 mmol), CH_2Cl_2 (50 mL, 0.01 M), r.t., 24 h. [b] Isolated yield.

Table 3. Effect of substituents of the aryliodanyl group of fluoroalkenyl(aryl)iodonium salts on the synthesis of **2b**[a]



1

Entry	**1**	Yield (%)[b]
1	**1f**, Ar = *p*-Tol	74
2	**1g**, Ar = *p*-Cl-C_6H_4	70
3	 **1h, (*E*)-isomer of 1f**	76

[a] Reagents and conditions: **1** (0.5 mmol), *t*-BuOK (1.5 mmol), CH_2Cl_2 (50 mL, 0.01 M), r.t., 24 h. [b] Isolated yield.

An efficient synthesis of fluorocyclopentenes using fluoroalkylidenecarbenes

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Experimental Procedures and Spectral Data

General Information

The IR spectra were recorded using a JASCO FT/IR-410. The ^{1}H-NMR (400 MHz), ^{19}F-NMR (376 MHz) and ^{13}C-NMR (100 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, ^{13}C) and $CFCl_3$ (^{19}F). The EI low- and high-resolution mass spectra were measured on a JEOL JMS-700TZ, JMS-FABmate or JMS-HX110. Melting points are measured by Yanagimoto micro melting point apparatus and are uncorrected. (2-Fluoroalk-1-enyl)(aryl)iodonium tetrafluoroborates **1a-d**,[11,13] **1f-g**,[15] and **1h**[16] were prepared by literature procedures. The spectral data for **1b-d**,[11] and **1h**[16] were reported in the literatures.

(*Z*)-(11-Acetoxy-2-fluoroundec-1-enyl)(phenyl)iodonium tetrafluoroborate (1a).

Viscous oil, $\delta_H(CDCl_3)$ 1.18-1.38 (10H, m), 1.50-1.66 (4H, m), 2.05 (3H, s), 2.58 (2H, dt, *J* 7.7, 17.5 Hz), 4.04 (2H, t, *J* 6.8 Hz), 6.51 [1H, d, *J* 33.4 Hz, 1-H], 7.48 (2H, t, *J* 7.8 Hz), 7.64 (1H, t, *J* 7.5 Hz), 8.02 (2H, d, *J* 7.8 Hz); $\delta_F(CDCl_3)$ –63.9 [1F, dt, *J* 17.5, 33.4 Hz, 2-F]; $\delta_C(CDCl_3)$ 21.0, 25.4, 25.8, 28.5, 28.6, 28.9, 29.0, 29.1, 32.2 (d, *J* 24.0 Hz, 3-C), 64.6, 74.4 (d, *J* 22.0 Hz, 1-C), 111.5, 132.3 (2C), 132.6, 135.3 (2C), 171.3, 174.0 (d, *J* 280.7 Hz, 2-C); ν(KBr)/cm^{-1} 3100, 2931, 2857, 1735, 1647, 1471, 1443, 1367, 1246, 1065, 740; [HR FAB-MS: Calc. for $C_{19}H_{27}FIO_2$ (*M* –BF_4): 433.1040. Found: M^+ –BF_4, 433.1051].

(*Z*)-[2-Fluoro-4-(4,4,5,5-tetramethyl-[1,3]dioxylan-2-yl)but-1-enyl](*p*-tolyl)iodonium tetrafluoroborate (1e).

In a round bottomed flask, PCC (19.2 g, 90 mmol), silica gel (20 g) and CH_2Cl_2 (120 mL) were placed. A solution of pent-4-yn-1-ol (5.04 g, 60 mmol) in CH_2Cl_2 (40 mL) was poured into the flask at one portion with stirring, and the whole reaction mixture was stirred for 1.5 h at room temperature. Then, Et_2O (200 mL) was added to the reaction mixture, and the resulting black precipitate was filtered. The precipitate was washed twice with 100 mL of Et_2O. The combined ethereal solution was concentrated by an evaporator carefully under reduced pressure, and the residue was placed in a distillation flask. Under reduced pressure, almost pure pent-4-ynal was collected in a receiver cooled at -78 °C by gradually warming the distillation flask. After the obtained pent-4-ynal was dissolved in benzene (50 mL) in a round bottomed flask equipped with a Dien-Stark trap, pinacol (20g, 169 mmol) and *p*-toluenesulfonic acid (570 mg, 3 mmol) were added to the solution. After the mixture had refluxed for 1.5 h, the resulting solution was cooled to room temperature. Then, the mixture was poured into H_2O (300 mL), followed by the extraction with Et_2O (100 mL × 3). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Purification with column chromatography (Silica gel/hexane-Et_2O) gave pure 2-(but-3-ynyl)-4,4,5,5-tetramethyl-[1,3]dioxolane (38%, 4.2g, 23 mmol). The fluoroalkenyliodonium salt **1e** was synthesized by the literature procedure.[15]
Mp. 119- 120 ºC, $\delta_H(CDCl_3)$ 1.15 (12H, s), 1.82-1.87 (2H, m), 2.43 (3H, s), 2.67-2.76 (2H, m), 5.00 (1H, t, *J* 4.7 Hz), 6.46 [1H, d, *J* 33.1 Hz, 1-H], 7.26-7.29 (2H, m), 7.87-7.90 (2H, m); $\delta_F(CDCl_3)$ –64.3 [1F, dt, *J* 16.6, 33.1 Hz, 2-F]; $\delta_C(CDCl_3)$ 21.4, 22.0 (2C), 24.1 (2C), 27.1 (d, *J* 24.9 Hz, 3-C), 31.3, 74.6 (d, *J* 22.0 Hz, 1-C), 82.2 (2C), 98.7, 107.4, 133.2 (2C), 135.4 (2C), 143.8, 173.2 (d, *J* 279.8 Hz, 2-C); ν(KBr)/cm^{-1} 3069, 2980, 2869, 1730, 1650, 1485, 1445, 1402, 1386, 1244, 1137; [HR FAB-MS: Calc. for $C_{18}H_{25}FIO_2$ (*M* –BF_4): 419.0883. Found: M^+ –BF_4, 419.0885].

(*Z*)-(2-Fluorododec-1-enyl)(*p*-tolyl)iodonium tetrafluoroborate (1f).

Viscous oil, $\delta_H(CDCl_3)$ 0.88 (3H, t, *J* 7.1 Hz), 1.18-1.32 (14H, m), 1.52-1.62 (2H, m), 2.43 (3H, s), 2.57 (2H, dt, *J* 7.7, 17.4 Hz), 6.45 [1H, d, *J* 33.4 Hz, 1-H], 7.28 (2H, d, *J* 10.2 Hz), 7.89 (2H, d, *J* 8.5 Hz); $\delta_F(CDCl_3)$ –64.3 [1F, dt, *J* 17.4, 33.4 Hz, 2-F]; $\delta_C(CDCl_3)$ 14.0, 21.3, 22.6, 25.4, 28.6, 29.0, 29.2, 29.3, 29.4, 31.8, 32.1 (d, *J* 24.0 Hz, 3-C), 74.4 (d, *J* 22.0 Hz, 2-C), 107.5, 133.0 (2C), 135.3 (2C), 143.6, 173.8 (d, *J* 280.7 Hz, 1-C); ν(KBr)/cm^{-1} 3047, 2918, 2850, 1655, 1469, 1303, 1232, 1207, 1044, 871, 792; [HR APCI-MS: Calc. for $C_{19}H_{29}FI$ (*M* –BF_4): 403.1298. Found: M^+ –BF_4, 403.1307].

(*Z*)-(2-Fluorododec-1-enyl)(*p*-chlorophenyl)iodonium tetrafluoroborate (1g).

Viscous oil, $\delta_H(CDCl_3)$ 0.88 (3H, t, *J* 7.1 Hz), 1.18-1.34 (14H, m), 1.52-1.59 (2H, m), 2.57 (2H, dt, *J* 7.7, 17.5 Hz), 6.49 [1H, d, *J* 33.3 Hz, 1-H], 7.41-7.45 (2H, m), 7.94-7.97 (2H, m); $\delta_F(CDCl_3)$ –63.3 [1F, dt, *J* 17.5, 33.3 Hz, 2-F]; $\delta_C(CDCl_3)$ 14.1, 22.6, 25.4, 28.7, 29.0, 29.2, 29.3, 29.4, 31.8, 32.1 (d, *J* 23.7 Hz, 3-C), 74.7 (d, *J* 22.0 Hz, 2-C), 108.2, 132.3 (2C), 136.7 (2C), 139.6, 174.2 (d, *J* 281.9 Hz, 1-C); ν(KBr)/cm^{-1} 3060, 2921, 2852, 1726, 1645, 1467, 1384, 1069, 828, 807; [HR FAB-MS: Calc. for $C_{18}H_{26}ClFI$ (*M* –BF_4): 423.0752. Found: M^+ –BF_4, 423.0748].

3-(6-Acetoxyhexyl)-1-fluorocyclopentene (2a).

$\delta_H(CDCl_3)$ 1.19-1.70 (11H, m), 2.05-2.15 (4H, m), 2.38-2.41 (2H, m), 2.56-2.64 (1H, m), 4.05 (2H, t, *J* 6.8 Hz), 4.94-4.95 (1H, m); $\delta_F(CDCl_3)$ –122.0 (1F, s); $\delta_C(CDCl_3)$ 20.1, 25.9, 27.2, 27.6 (d, *J* 8.4 Hz), 28.528, 28.530 (d, *J* 21.8 Hz), 29.3, 36.8 (d, *J* 1.9 Hz), 39.9 (d, *J* 8.6 Hz), 64.6, 106.4 (d, *J* 9.6 Hz), 162.1 (d, *J* 278.8 Hz), 171.3; ν(KBr)/cm^{-1} 2928, 2856, 1740, 1679, 1462, 1365, 1242, 1163, 1039, 824; [HR EI-MS: Calc. for $C_{13}H_{22}FO_2$ (*M* +H): 229.1604. Found: M^+ +H, 229.1608].

3-(6-Chlorohexyl)-1-fluorocyclopentene (2c).
$\delta_H(CDCl_3)$ 1.22-1.66 (9H, m), 1.73-1.80 (2H, m), 2.07-2.16 (1H, m), 2.37-2.45 (2H, m), 2.55-2.64 (1H, m), 3.54 (2H, t, *J* 6.8 Hz), 4.94-4.96 (1H, m); $\delta_F(CDCl_3)$ –122.0 (1F, s); $\delta_C(CDCl_3)$ 26.8, 27.2, 27.6 (d, *J* 8.2 Hz), 28.5 (d, *J* 21.4 Hz), 28.9, 32.5, 36.7 (d, *J* 1.9 Hz), 39.8 (d, *J* 8.2 Hz), 45.1, 106.3 (d, *J* 8.4 Hz), 162.1 (d, *J* 277.5 Hz); ν(KBr)/cm^{-1} 2930, 2856, 1710, 1678, 1615, 1461, 1349, 1222, 1163, 825; [HR EI-MS: Calc. for $C_{11}H_{18}ClF$ (*M*): 204.1081. Found: M^+, 204.1088].

3-(7,7-Dimethyl-6-oxooctanyl)-1-fluorocyclopentene (2d).
$\delta_H(CDCl_3)$ 1.13 (9H, s), 1.21-1.41 (7H, m), 1.50-1.61 (2H, m), 2.06-2.15 (1H, m), 2.37-2.42 (2H, m), 2.47 (2H, t, *J* 7.3 Hz), 2.54-2.64 (1H, m), 4.93-4.95 (1H, m); $\delta_F(CDCl_3)$ –122.0 (1F, s); $\delta_C(CDCl_3)$ 23.9, 26.4 (3C), 27.3, 27.6 (d, *J* 7.8 Hz), 28.5 (d, *J* 21.1 Hz), 29.4, 36.3, 36.7 (d, *J* 2.2 Hz), 39.9 (d, *J* 8.2 Hz), 44.1, 106.3 (d, *J* 8.5 Hz), 162.1 (d, *J* 276.3 Hz), 216.0; ν(KBr)/cm^{-1} 2929, 2857, 1706, 1678, 1478, 1463, 1350, 1223, 1163, 1065, 822; [HR EI-MS: Calc. for $C_{15}H_{25}FO$ (*M*): 240.1889. Found: M^+, 240.1896].

1,4-Dioxa-7-fluoro-2,2,3,3-tetramethyl-spiro[4,4]non-6-ene (2e).
$\delta_H(CDCl_3)$ 1.20 (6H, s), 1.23 (6H, s), 2.28-2.31 (2H, m), 2.42-2.46 (2H, m), 5.08-5.09 (1H, m); $\delta_F(CDCl_3)$ –110.9 (1F, s); $\delta_C(CDCl_3)$ 23.0 (2C), 23.4 (2C), 26.7 (d, *J* 19.2 Hz), 37.4 (d, *J* 2.9 Hz), 82.5 (2C), 106.9 (d, *J* 7.0 Hz), 113.5 (d, *J* 15.3 Hz), 166.7 (d, *J* 285.5 Hz); ν(KBr)/cm^{-1} 2977, 2934, 1684, 1366, 1350, 1254, 1185, 1160, 1077, 1044, 955, 934, 922, 819; [HR EI-MS: Calc. for $C_{11}H_{17}FO_2$ (*M*): 200.1213. Found: M^+, 200.1204].