HOKKAIDO UNIVERSITY

Title	An Efficient Stereoselective Synthesis of (E)-β-Fluoroalkenyliodonium Salts
Author(s)	Yoshida, Masanori; Kawakami, Keiji; Hara, Shoji
Citation	Synthesis, (17), 2821-2824 https://doi.org/10.1055/s-2004-834857
Issue Date	2004-12-01
Doc URL	https://hdl.handle.net/2115/15818
Type	journal article
File Information	SYN-S17.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

An Efficient Stereoselective Synthesis of (*E*)-β-Fluoroalkenyliodonium Salts

Masanori Yoshida,* Keiji Kawakami, Shoji Hara*

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, 060-8628, Japan

Fax: +81(11)7066557

E-mail: myoshida@org-mc.eng.hokudai.ac.jp (Yoshida, M)

Received: The date will be inserted once the manuscript is accepted.

Abstract: Stereoselective synthesis of (*E*)-β-fluoroalkenyliodonium salts was performed by the treatment of alk-1-ynes with *p*-iodotoluene difluoride in the presence of HBF_4-Et_2O. The reaction immediately completed at -78 °C to give the fluoroalkenyliodonium salts in good yields with high stereoselectivity. The Pd-catalyzed carbomethoxylation of the fluoroalkenyliodonium salt was also carried out to obtain an (*E*)-β-fluoro-α,β-unsaturated ester.

Key words: iodonium salt, fluoroalkene, *p*-iodotoluene difluoride, stereoselective synthesis, fluorination reaction

Fluorine-containing organic compounds are widely used in medicinal and agricultural chemicals, since the fluorinated analogue of a biologically active compound often shows greater bioactivity than the original compound.[1] In a synthesis of a bioactive compound having a fluoroalkene moiety, the regio- and stereoselective introduction of the fluorine atom is important because the biological activity strongly depends on the position and stereochemistry of the fluorine atom.[2] Therefore, much effort has been made for development of a regio- and stereospecific fluoroalkene synthesis.[3,4,5] The most popular approach to the stereoselective synthesis of fluoroalkenes is via the Horner-Wadsworth-Emmons reaction using fluorine-containing organophosphonate; however, in this methodology, a mixture of stereoisomers generally formed.[4] Recently, Mestdagh *et al*. reported the stereoselective synthesis of (*E*)-2-fluoro-1-iodoalk-1-enes by iodofluorination of alk-1-ynes with bis(pyridinium)iodonium salt and pyridinium poly(hydrogen fluoride).[5] Although they prepared only two simple fluoroiodoalkenes from hept-1-yne and phenylacetylene, they demonstrated the stereoselective fluoroalkene synthesis by the Pd-catalyzed cross-coupling reactions using the fluoroiodoalkenes. In our recent study, we reported that the reaction of alk-1-ynes with *p*-iodotoluene difluoride (**1**)[6] in Et_3N-5HF proceeded at 0 °C to give (*E*)-β-fluoroalkenyliodonium salts (**2**, X=F) stereoselectively.[7] Moreover, the Pd-catalyzed cross-coupling reactions using the (*E*)-β-fluoroalkenyliodonium salts smoothly occurred at room temperature to afford a variety of (*E*)-2-fluoroalk-1-ene derivatives stereoselectively.[8] Since both the preparation of **2** (X=F) and its cross-coupling reactions can be carried out under mild reaction conditions, various functional groups are tolerated in the course of the fluoroalkene synthesis. Thus, the fluoroalkenyliodonium salt was found to be a good synthon for the stereoselective synthesis of fluoroalkenes; however, we have to handle a highly toxic reagent, anhydrous hydrogen fluoride, in the preparation of Et_3N-5HF which was necessary for the synthesis of fluoroalkenyliodonium salts. In this short paper, we present the preparation of **2** (X=BF_4) by the reaction of alk-1-ynes with **1** using HBF_4-Et_2O, which is a commercially available and relatively low toxic reagent. The Pd-catalyzed carbomethoxylation of **2** (X=BF_4) is also described.

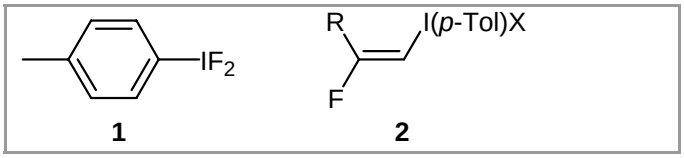
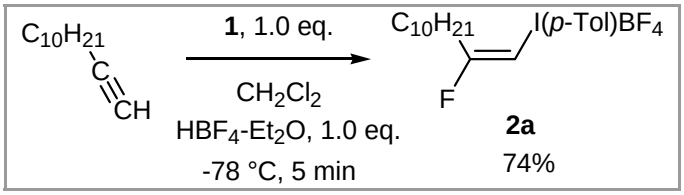


Figure 1

Initially, a simple terminal alkyne, dodec-1-yne, was employed as the starting material (Scheme 1). To the CH_2Cl_2 solution of **1** was added HBF_4-Et_2O at -78 °C to give a deep green-colored reaction mixture. Then dodecyne was added to the reaction mixture at -78 °C, and the green color quickly changed into light yellow. The reaction completed in 5 min and dodecyne was transformed into (*E*)-β-fluorododec-1-enyl(4-methylphenyl)iodonium tetrafluoroborate (**2a**) in 74% yield with high stereoselectivity (*E* / *Z* > 98 / 2).[9]



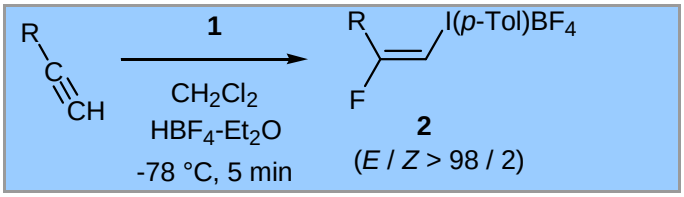
Scheme 1

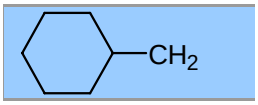
A variety of alk-1-ynes were subjected to the reaction to synthesize (*E*)-β-fluoroalkenyliodonium salts (**2b-f**) as shown in Table 1. Although a little excess amount of **1** and HBF_4-Et_2O were required to consume the alkynes completely, various functional groups, e.g., AcO, Cl, COOMe and ^{t}BuCO, are tolerated in the reactions (Entries 1-4). Unfortunately, the terminal acetylene bearing an electron-withdrawing group adjacent to the triple bond was found to be inert in the reaction conditions (Entry 6).

In order to show the usefulness of the fluoroalkenyliodonium salts, the Pd-catalyzed carbomethoxylation using **2a** was performed (Scheme 2).[8a] The carbomethoxylation smoothly proceeded at room temperature in 1.0 h to give methyl (*E*)-3-fluorotridec-2-enoate (**3a**) in 91% yield with retention of the stereochemistry (*E* / *Z* > 98 / 2). It was found that the coupling reaction selectively

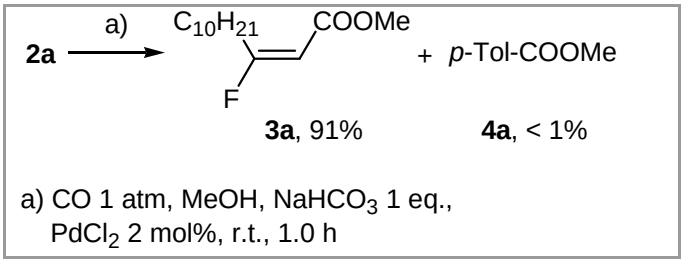
took place at the alkenyl part of **2a**, since only a trace amount of methyl 4-methylbenzoate (**4a**), which was formed by the carbomethoxylation of the 4-methylphenyl part in **2a**, was detected after the reaction.

Table 1 Stereoselective synthesis of (*E*)-β-fluoroalkenyliodonium salts[a]



Entry	R	Product	Yield (%)[b]
1	AcO-$(CH_2)_9$	**2b**	76
2[c]	Cl-$(CH_2)_9$	**2c**	85
3	MeOOC-$(CH_2)_8$	**2d**	84
4	^{t}Bu-CO-$(CH_2)_8$	**2e**	84
5		**2f**	83
6	EtOOC	--	N.R.[d]

[a] Reactions were carried out on a 1 mmol scale unless noted otherwise using 1.3 eq. of **1** and 1.2 eq. of HBF_4-Et_2O.
[b] Isolated yield based on alk-1-yne.
[c] Reaction was carried out with 1.2 eq.of **1** and 1.1 eq.of HBF_4-Et_2O.
[d] No reaction.



Scheme 2

In summary, the stereoselective synthesis of (*E*)-β-fluoroalkenyliodonium salts has been achieved by the addition of *p*-iodotoluene difluoride to alk-1-ynes in the presence of HBF_4-Et_2O. The addition reaction immediately completed at -78 °C to give the fluoroalkenyliodonium salts in good yields.

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 FAB-low and high-resolution mass spectra were measured on a JEOL JMS-700TZ, JMS-FABmate or JMS-HX110. The melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. Dodec-1-yne[10a] and 3-cyclohexylprop-1-yne[10b] was prepared according to the literature. Methyl undec-10-ynoate was obtained by esterification of undec-10-ynoic acid[10c] prepared from undec-10-enoic acid. 11-Acetoxyundec-1-yne[10d] and 11-chloroundec-1-yne[10b] were obtained from 11-hydroxyundec-1-yne prepared from 11-hydroxyundec-1-ene. Undec-10-enoic acid, 11-hydroxyundec-1-ene and propiolic acid ethyl ester were purchased from Tokyo Kasei Co., Ltd., and used without further purification. HBF_4-Et_2O was purchased from Fluka Co., Ltd..

Stereoselective synthesis of (*E*)-β-fluoroalkenyliodonium salts; (*E*)-2-Fluorododec-1-enyl(4-methylphenyl)iodonium tetrafluoroborate (2a); Typical Procedure

To a CH_2Cl_2 solution (5 mL) of *p*-iodotoluene difluoride (**1**, 256 mg, 1.0 mmol) was added HBF_4-Et_2O (162 mg, 1.0 mmol) at -78 °C. After stirring the reaction mixture for 5 min at -78 °C, dodec-1-yne (166 mg, 1 mmol) was added to the reaction mixture and the whole reaction mixture was stirred for 5 min at -78 °C. The resulting solution was poured into 5% aq. $NaBF_4$ (20 mL) and extracted with CH_2Cl_2 (10 mL × 4). 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 precipitate was washed with hexane (5 mL) again, separated from hexane by decantation. Finally, the solvent was removed in vacuo to give pure **2a** (74%, 363 mg, 0.74 mmol, *E*/*Z* > 98/2); M.p. 69.7-70.5 ºC.

^{1}H NMR: δ = 0.88 (t, *J* = 7.1 Hz, 3 H), 1.22-1.29 (m, 14 H), 1.45-1.53 (m, 2 H), 2.41 (s, 3 H), 2.78 (dt, $^3J_{H\text{-}F}$ = 22.2, *J* = 7.6 Hz, 2 H), 6.70 [d, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 H], 7.26 (d, *J* = 8.3 Hz, 2 H), 7.84 (d, *J* = 8.5 Hz, 2 H).

^{19}F NMR: δ = -66.71 [dt, $^3J_{H\text{-}F}$ = 22.2, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 F].

^{13}C NMR: δ = 14.09, 21.35, 22.65, 25.79, 28.90, 29.22, 29.27, 29.35, 29.47, 31.84, 32.13 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 78.33 (d, $^2J_{C\text{-}F}$ = 47.1 Hz), 108.19, 133.10 (2 C), 134.60, (2 C), 143.76, 175.91 (d, $^1J_{C\text{-}F}$ = 285.8 Hz).

IR ν(KBr)/cm^{-1} 3040, 2926, 2854, 1643, 1084.

MS: *m/z* = 403 (M^+ - BF_4 100 %), 307 (31), 289 (16), 155, (20), 154 (82), 138 (22), 137 (41), 136 (54), 107 (17), 91 (15), 90 (12), 89 (20), 78 (11), 77 (22), 55 (16), 43 (11), 41 (17), 39 (18).

HR FAB-MS: Calc. for $C_{19}H_{29}FI$ (*M* - BF_4): 403.1293. Found: M^+ - BF_4, 403.1292.

(*E*)-11-Acetoxy-2-fluoroundec-1-enyl(4-methylphenyl)iodonium tetrafluoroborate (2b)

Yield 76% (*E*/*Z* > 98/2); M.p. 50.2-51.0 ºC

^{1}H NMR: δ = 1.26-1.65 (m, 14 H), 2.05 (s, 3 H), 2.43 (s, 3 H), 2.80 (dt, $^3J_{H\text{-}F}$ = 21.9, *J* = 7.1 Hz, 2 H), 4.05 (t, *J* = 6.6 Hz, 2 H), 6.65 [d, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 H], 7.29 (d, *J* = 8.0 Hz, 2 H), 7.83 (d, *J* = 8.3 Hz, 2 H).

^{19}F NMR: δ = -65.92 [dt, $^3J_{H\text{-}F}$ = 21.9, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 F].

^{13}C NMR: δ = 20.99, 21.35, 25.75, 25.77, 28.49, 28.78, 29.03, 29.04, 29.23, 32.07 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 64.64, 78.32 (d, $^2J_{C\text{-}F}$ = 47.1 Hz), 108.16, 133.13 (2 C), 134.62, (2 C), 143.82, 171.50, 175.85 (d, $^1J_{C\text{-}F}$ = 286.5 Hz).

IR ν(KBr)/cm^{-1} 3083, 2930, 2855, 1737, 1703, 1638, 1433, 1369, 1244, 1065, 802.

MS: *m/z* = 447 (M^+ - BF_4 100 %), 307 (27), 289 (15), 155, (22), 154 (84), 138 (24), 137 (43), 136 (56), 107 (18), 91 (16), 90 (11), 89 (17), 77 (17), 69 (12), 57 (10), 55 (20), 43 (12), 41 (14), 39 (12).

HR FAB-MS: Calc. for $C_{20}H_{29}FIO_2$ (*M* - BF_4): 447.1191. Found: M^+ - BF_4, 447.1182.

(*E*)-11-Chloro-2-fluoroundec-1-enyl(4-methylphenyl)iodonium tetrafluoroborate (2c)

Yield 85% (*E*/*Z* > 98/2); M.p. 68.0-69.0 ºC

^{1}H NMR: δ = 1.24-1.54 (m, 12 H), 1.72-1.79 (m, 2 H), 2.41 (s, 3 H), 2.78 (dt, $^3J_{H\text{-}F}$ = 22.2, *J* = 7.6 Hz, 2 H), 3.53 (t, *J* = 6.6 Hz, 2 H), 6.70 [d, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 H], 7.27 (d, *J* = 8.3 Hz, 2 H), 7.84 (d, *J* = 8.5 Hz, 2 H).

^{19}F NMR: δ = -66.82 [dt, $^3J_{H\text{-}F}$ = 22.2, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 F].

^{13}C NMR: δ = 21.36, 25.75, 26.77, 28.70, 28.78, 29.04, 29.11, 32.07 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 32.52, 45.16, 78.37 (d, $^2J_{C\text{-}F}$ = 47.1 Hz), 108.16, 133.10 (2 C), 134.62, (2 C), 143.79, 175.82 (d, $^1J_{C\text{-}F}$ = 286.5 Hz).

IR ν(KBr)/cm^{-1} 3038, 2931, 2857, 1645, 1459, 1301, 1084.

MS: *m/z* = 423 (M^+ - BF_4 41 %), 307 (45), 289 (24), 155, (22), 154 (100), 139 (11), 138 (26), 137 (49), 136 (67), 107 (22), 91 (13), 90 (15), 89 (24), 78 (13), 77 (26), 63 (11), 51 (10), 39 (11).

HR FAB-MS: Calc. for $C_{18}H_{26}ClFI$ (*M* - BF_4): 423.0746. Found: M^+ - BF_4, 423.0733.

(*E*)-10-Methoxycarbonyl-2-fluorodec-1-enyl(4-methylphenyl)iodonium tetrafluoroborate (2d)

Yield 84% (*E*/*Z* > 98/2); Oil

^{1}H NMR: δ = 1.25-1.29 (m, 8 H), 1.48-1.64 (m, 4 H), 2.30 (t, *J* = 7.6 Hz, 2 H), 2.42 (s, 3 H), 2.79 (dt, $^3J_{H\text{-}F}$ = 22.2, *J* = 7.8 Hz, 2 H), 3.67 (s, 3 H), 6.68 [d, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 H], 7.28 (d, *J* = 8.0 Hz, 2 H), 7.84 (d, *J* = 8.6 Hz, 2 H).

^{19}F NMR: δ = -66.43 [dt, $^3J_{H\text{-}F}$ = 22.2, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 F].

^{13}C NMR: δ = 21.32, 24.79, 25.70, 28.69, 28.86, 28.89 (2C), 32.02 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 33.97, 51.48, 78.46 (d, $^2J_{C\text{-}F}$ = 47.1 Hz), 108.19, 133.08 (2 C), 134.64, (2 C), 143.76, 174.39, 175.75 (d, $^1J_{C\text{-}F}$ = 286.5 Hz).

IR ν(Film)/cm^{-1} 3090, 2932, 2858, 1734, 1638, 1444, 1075.

MS: *m/z* = 433 (M^+ - BF_4 100 %), 154 (23), 137 (11), 136 (17).

HR FAB-MS: Calc. for $C_{19}H_{27}FIO_2$ (*M* - BF_4): 433.1034. Found: M^+ - BF_4, 433.1031.

(*E*)-12,12-Dimethyl-2-fluoro-11-oxotridec-1-enyl(4-methylphenyl)iodonium tetrafluoroborate (2e)

Yield 84% (*E*/*Z* > 98/2); M.p. 54.5-55.2 ºC

^{1}H NMR: δ = 1.13-1.30 (m, 17 H), 1.49-1.57 (m, 4 H), 2.43 (s, 3H), 2.48 (t, *J* = 7.3 Hz, 2 H), 2.80 (dt, $^3J_{H\text{-}F}$ = 22.2, *J* = 7.8 Hz, 2 H), 6.65 [d, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 H], 7.30 (d, *J* = 8.0 Hz, 2 H), 7.83 (d, *J* = 8.6 Hz, 2 H).

^{19}F NMR: δ = -65.85 [dt, $^3J_{H\text{-}F}$ = 22.2, $^3J_{H\text{-}F(olefin)}$ = 14.4 Hz, 1 F].

^{13}C NMR: δ = 21.37, 23.81, 25.74, 26.38 (3C), 28.72, 28.91, 29.08, 29.13, 32.05 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 36.41, 44.11, 78.27 (d, $^2J_{C\text{-}F}$ = 47.2 Hz), 108.11, 133.17 (2 C), 134.62, (2 C), 143.89, 175.89 (d, $^1J_{C\text{-}F}$ = 286.6 Hz), 216.63.

IR ν(KBr)/cm^{-1} 3087, 2932, 2858, 1703, 1639, 1478, 1366, 1066.

MS: *m/z* = 459 (M^+ - BF_4 100 %), 307 (19), 289 (10), 155 (14), 154 (56), 138 (16), 137 (28), 136 (36), 107 (11), 91 (11), 89 (11), 77 (14), 57 (27), 55 (14), 41 (14).

HR FAB-MS: Calc. for $C_{22}H_{33}FIO$ (*M* - BF_4): 459.1555. Found: M^+ - BF_4, 459.1551.

(*E*)-3-Cyclohexyl-2-fluoroprop-1-enyl(4-methylphenyl)iodonium tetrafluoroborate (2f)

Yield 83% (*E*/*Z* > 98/2); M.p. 132.0-132.8 ºC

^{1}H NMR: δ = 0.88-1.25 (m, 5 H), 1.62-1.68 (m, 6 H), 2.41 (s, 3H), 2.67 (dd, $^3J_{H\text{-}F}$ = 22.9, *J* = 6.6 Hz, 2 H), 6.73 [d, $^3J_{H\text{-}F(olefin)}$ = 14.6 Hz, 1 H], 7.27 (d, *J* = 7.3 Hz, 2 H), 7.84 (d, *J* = 8.5 Hz, 2 H).

^{19}F NMR: δ = -63.94 [dt, $^3J_{H\text{-}F}$ = 22.9, $^3J_{H\text{-}F(olefin)}$ = 14.6 Hz, 1 F].

^{13}C NMR: δ = 21.38, 25.80, 25.92, 32.61 (2C), 35.52, 39.35 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 79.07 (d, $^2J_{C\text{-}F}$ = 47.1 Hz),

108.31, 133.18 (2 C), 134.61, (2 C), 143.89, 175.11 (d, $^1J_{C\text{-}F}$ = 287.4 Hz).

IR ν(KBr)/cm^{-1} 3094, 2931, 2857, 1738, 1640, 1459, 1083.

MS: *m/z* = 359 (M^+ - BF_4 100 %), 307 (22), 289 (10), 155 (11), 154 (48), 138 (11), 137 (24), 136 (33), 107 (10), 89 (12), 77 (13).

HR FAB-MS: Calc. for $C_{16}H_{21}FI$ (*M* - BF_4): 359.0667. Found: M^+ - BF_4, 359.0674.

Synthesis of methyl (*E*)-3-fluorotridec-2-enoate (3a)

In a 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 the complete replacement of the atmosphere in the flask with CO, the balloon was filled with CO. Then a solution of **2a** (238 mg, 0.5 mmol) in MeOH (1 mL) was added. After stirring for 1 h at room temperature, the reaction mixture was poured into 15% aq. NH_4Cl (15 mL), and extracted with diethyl ether (10 mL × 3). The combined organic phase was dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane-diethyl ether) gave **3a** in 91% yield (99 mg, 0.46 mmol, *E* / *Z* > 98 / 2). For the spectrum information of **3a**, see Ref. 8a.

References

(1) (a) Welch, J. T.; Eswarakrishnan, S. *Fluorine in Bioorganic Chemistry*; Wiley: New York, 1991. (b) Welch, J. T. *Tetrahedron* **1987**, *43*, 3123. (c) Ismail, F. M. D. *J. Fluorine Chem.* **2002**, *118*, 27. (d) Smart, B. E. *J. Fluorine Chem.* **2001**, *109*, 3.

(2) (a) Kim, B. T.; Min, Y. K.; Asami, T.; Park, N. K.; Kwon, O. Y.; Cho, K. Y.; Yoshida, S. *Tetrahedron Lett.* **1997**, *38*, 1797. (b) Masnyl, M.; Fried, J. *Tetrahedron Lett*. **1989**, *30*, 3243. (c) Grieco, P. A.; Takigawa, T.; Vedananda, T. R. *J. Org. Chem.* **1985**, *50*, 3111. (d) Grieco, P. A.; Schillinger, W. J.; Yokoyama, Y. *J. Med. Chem.* **1980**, *23*, 1077.

(3) (a) Okada, M.; Nakamura, Y.; Saito, A.; Sato, A.; Horikawa, H., Taguchi, T. *Tetrahedron Lett*. **2002**, *43*, 5845. (b) Otaka, A.; Watanabe, H.; Yukimasa, A.; Oishi, S.; Tamamura, H.; Fujii, N. *Tetrahedron Lett*. **2001**, *42*, 5443. (c) Peng, S.; Qing, F.-L.; Li, Y.-Q.; Hu, C.-M. *J. Org. Chem.* **2000**, *65*, 694. (d) Huang, X.-H.; He, P.-Y.; Shi, G.-Q. *J. Org. Chem.* **2000**, *65*, 627. (e) Brown, S. J.; Corr, S.; Percy, J. M. *Tetrahedron Lett*. **2000**, *41*, 5269. (f) Chevrie, D.; Lequeux, T.; Pommelet, J.-C. *Org. Lett*. **1999**, *1*, 1539. (g) Percy, J. M.; Prime, M. E. *J. Fluorine Chem*. **1999**, *100*, 147. (h) Lin, J.; Welch, J. T. *Tetrahedron Lett.* **1998**, *39*, 9613. (i) Percy, J. M.; Wilkes, R. D. *Tetrahedron* **1997**, *53*, 14749. (j) Hossain, M. A. *Tetrahedron Lett.* **1997**, *38*, 49. (k) Kuroboshi, M.; Yamada, N.; Takebe, Y.; Hiyama, T. *Tetrahedron Lett*. **1995**, *36*, 6271. (l) Clemenceau, D.; Cousseau, J. *Tetrahedron Lett*. **1993**, *34*, 6903. (m) Gillet, J. P.; Sauvêtre, R.; Normant, J. F. *Synthesis*, **1982**, 297.

(4) (a) Zhang, X.; Burton, D. J. *J. Fluorine Chem.* **2001**, *112*, 317. (b) Chen, C.; Wilcoxen, K.; Zhu, Y.-F.; Kim, K.-I.; McCarthy, J. R. *J. Org. Chem*. **1999**, *64*, 3476. (c) Burton, D. J. *J. Fluorine Chem.* **1999**, *100*, 177. (d) Chen, C.; Wilcoxen, K.; Strack, N.; McCarthy, J. R. *Tetrahedron Lett.* **1999**, *40*, 827. (e) Percy, E.; Singh, M.; Takahashi, T.; Takeuchi, Y.; Kirk, K. L. *J. Fluorine Chem.* **1998**, *91*, 5. (f) McCarthy, J. R.; Huber, E. W.; Le, T.-B.; Laskovics, F. M.; Matthews, D. P. *Tetrahedron* **1996**, *52*, 45. (g) Patrick, T. B.; Lanahan, M. V.; Yang, C.; Walker, J. K.; Hutchinson, C. L.; Neal, B. E. *J. Org. Chem*. **1994**, *59*, 1210. (h) Pirrung, M. C.; Rowley, E. G.; Holmes, C. P. *J. Org. Chem.* **1993**, *58*, 5683. (i) McCarthy, J. R.; Matthews, D. P.; Stemerick, D. M.; Huber, E. W.; Bey, P.; Lippert, B. J.; Snyder, R. D.; Sunkara, P. S. *J. Am. Chem. Soc*. **1991**, *113*, 7539. (j) Burton, D. J. *J. Fluorine Chem.* **1983**, *23*, 339. (k) Moghadam, G. E.; Penne, J. S. *Bull. Soc. Chim. Fr.*, **1985**, 448.

(5) (a) Eddarir, S.; Francesch, C.; Mestdagh, H.; Rolando, C. *Bull. Soc. Chim. Fr*. **1997**, *134*, 741. (b) Eddarir, S.; Mestdagh, H.; Rolando, C. *Tetrahedron Lett*. **1991**, *32*, 69.

(6) Carpenter, W. *J. Org. Chem*. **1966**, *31*, 2688. Recent study; Sawaguchi, M.; Ayuba, S.; Hara, S. *Synthesis* **2002**, 1802.

(7) Hara S.; Yoshida M.; Fukuhara T.; Yoneda N. *Chem. Commun.* **1998**, 965.

(8) (a) Hara, S.; Yamamoto, K.; Yoshida, M.; Fukuhara, T.; Yoneda, N. *Tetrahedron Lett.* **1999**, *40*, 7815. (b) Yoshida, M.; Hara, S.; Fukuhara, T.; Yoneda, N. *Tetrahedron Lett.* **2000**, *41*, 3887. (c) Yoshida, M.; Nagahara, D.; Fukuhara, T.; Yoneda, N.; Hara, S. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2283.

(9) The stereochemistry was determined by ^{1}H-NMR. A vinylic hydrogen of **2a** appeared at 6.70 ppm as a doublet ($^3J_{H\text{-}F}$ = 14.4 Hz), which was in good agreement with the reported data of an (*E*)-β-fluoroalkenyliodonium salt; See, Ref. 7. A larger coupling constant ($^3J_{H\text{-}F}$ = 33.2 Hz) was observed from (*Z*)-2-fluorododecenyliodonium tetrafluoroborate; Yoshida, M.; Hara, S. *Org. Lett.* **2003**, *5*, 573.

(10) (a) Dehmlow, E. V.; Lissel, M. *Liebigs Ann. Chem.* **1980**, *1*, 1. (b) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1971. (c) Khan, N. A. *Organic Synthesis Coll. Vol. IV*, **1963**, 969. (d) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981.

Please place the graphical abstract and short title of the article here. The short title will be used as a running header.

(*E*)-β-Fluoroalkenyliodonium Salts