JOC Article

An Efficient Photoinduced Iodoperfluoroalkylation of Carbon−Carbon Unsaturated Compounds with Perfluoroalkyl Iodides

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Dependent on the selection of the light sources employed, the photoinduced iodoperfluoroalkylation of a variety of unsaturated compounds takes place efficiently via a radical mechanism. Upon irradiation with a xenon lamp through Pyrex ($h\nu$ >300 nm), terminal alkenes ($R-CH=CH_2$) and alkynes ($R-C\equiv CH$) undergo iodoperfluoroalkylation with perfluoroalkyl iodides (R_F-I) regioselectively, providing $R-CH(I)-CH_2-R_F$ and $R-C(I)=CH-R_F$, respectively. In the case of terminal allenes ($R-CH=C=CH_2$), the photoinduced iodoperfluoroalkylation occurs selectively at the terminal double bond, giving the corresponding β-perfluoroalkylated vinylic iodides ($R-CH=C(I)-CH_2-R_F$) in good yields. The photoinitiated reaction of vinylcyclopropanes (c-$C_3H_5-C(R)=CH_2$) with R_F-I proceeds via the rearrangement of cyclopropylcarbinyl radical intermediates to the homoallylic radical intermediates, and the corresponding 1,5-iodoperfluoroalkylated products ($I-(CH_2)_2CH=C(R)-CH_2-R_F$) are obtained in high yields. Isocyanides ($R-NC$), as C−N unsaturated compounds, also undergo the xenon-lamp-irradiated iodoperfluoroalkylation to provide the corresponding 1,1-adducts ($R-N=C(I)-R_F$) in good yields. Furthermore, the present photoinitiation procedure can be applied to the iodotrifluoromethylation of unsaturated compounds, when the xenon-lamp-irradiated reactions are conducted under the refluxing conditions of excess CF_3-I.

Introduction

In view of the growing interest in fluorinated organic compounds in material science, medicinal chemistry, and organic synthesis,[1] the development of efficient and selective methods for synthesis of fluorinated organic compounds is of great importance. In particular, recent advance in fluorous combinatorial technique requires convenient methods for selective introduction of fluorous tags containing perfluoroalkyl groups into various organic compounds.[2] Perfluoroalkyl iodides (R_F-I) are representative perfluoroalkylating reagents for various organic molecules and can work not only as electrophiles toward various carbon nucleophiles but also as perfluoroalkyl radical precursors in the presence of radical initiators.[1,3]

Because perfluoroalkyl iodides exhibit their absorption in UV and near-UV regions (Figure 1), the photoinitiation based on the homolytic dissociation of R_F-I (eq 1) is also applicable for the iodoperfluoroalkylation of unsaturated compounds with R_F-I. Although several kinetic studies of the addition of R_F-I to alkenes and alkynes have been conducted by using the photoinitiation technique,[1] highly efficient photoinduced methods for the introduction of fluorous groups into a wide range of unsaturated compounds have remained largely undeveloped.[4] Contrary

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(3) (a) Brace, N. O.; Van Elswyk, J. E. *J. Org. Chem.* **1976**, *41*, 766. (b) Dolbier, W. R., Jr. *Chem. Rev.* **1996**, *96*, 1557. (c) Dolbier, W. R., Jr. In *Organofluorine Chemistry−Fluorinated Alkenes and Reactive Intermediates*; Chambers, R. D., Ed.; Springer-Verlag: Berlin, 1997; pp 97−163. (d) Brace, N. O. *J. Fluorine Chem.* **1999**, *93*, 1.

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10.1021/jo0495889 CCC: \$27.50

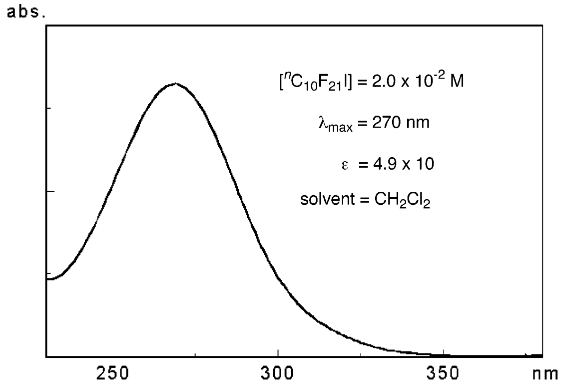
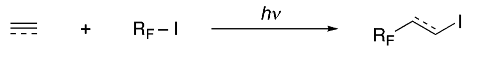


FIGURE 1. UV–vis spectrum of $^nC_{10}F_{21}I$.

to this, we here report novel findings that the xenon-lamp irradiation successfully induces highly efficient iodoperfluoroalkylation of a wide variety of unsaturated compounds with R_F-I (eq 2).[5]

$$R_F-I \xrightarrow{h\nu,\ \Delta,\ \text{or radical initiator}} R_F\bullet + I\bullet \qquad (1)$$



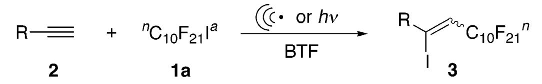
(2)

Results and Discussion

Perfluoroalkylation of Alkynes and Alkenes. We initiated the radical addition reaction of perfluoroalkyl iodides to alkynes such as 1-octyne and phenylacetylene under sonication or photoirradiation conditions by using benzotrifluoride (BTF)[6] as the solvent, and the results are summarized in Table 1. Since the homolytic cleavage of organic halides is well-known to take place by sonication,[7] the sonication of heneicosafluoro-*n*-decyl iodide (**1a**) in the presence of 5 equiv of 1-octyne (**2a**) or phenylacetylene (**2b**) in BTF was examined. As can be seen from entries 1, 2, 5, and 6, however, sonication was inefficient for the desired iodoperfluoroalkylation of **2a** or **2b**. On the other hand, the attempted iodoperfluoroalkylation of **2a** or **2b** upon irradiation with a tungsten lamp through Pyrex resulted in the formation of the desired iodoperfluoroalkylated products in very low yields (entries 3 and 7). This is because the light intensity of the tungsten lamp is very weak in the region of wavelength between 300 and 350 nm. In contrast, the xenon-lamp irradiation successfully causes the desired radical addition of R_F-I to **2** (entries 4 and 8).[8]

A possible mechanistic pathway may include the following (see Scheme 1): (i) upon irradiation with near-UV light, $^nC_{10}F_{21}I$ undergoes homolytic dissociation to generate $^nC_{10}F_{21}{}^\bullet$ and $I^\bullet$, and the former radical ($^nC_{10}F_{21}{}^\bullet$) attacks the terminal carbon of alkynes regioselectively, forming a vinylic radical intermediate (**4**); (ii) the vinylic radical (**4**) abstracts an iodide atom from $^nC_{10}F_{21}I$ to produce the iodoperfluoroalkylated product (**3**) with regeneration of $^nC_{10}F_{21}{}^\bullet$.

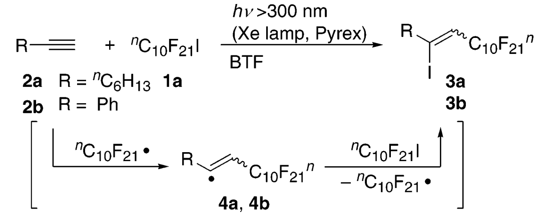
TABLE 1. Iodoperfluoroalkylation under Sonication or Photoirradiation



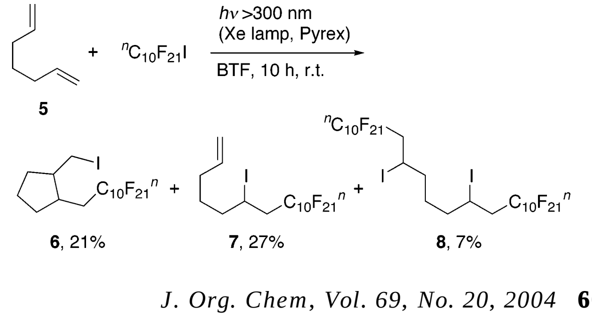
entry	R		substrate	conditions	yield, %^{d}
1	$^nC_6H_{13}$	**2a**	1 equiv	))), 55 °C, 4 h	no reaction
2	$^nC_6H_{13}$	**2a**	5 equiv	))), 55 °C, 4 h	25
3	$^nC_6H_{13}$	**2a**	3 equiv	$h\nu$,^{b} 45 °C, 10 h	27
4	$^nC_6H_{13}$	**2a**	3 equiv	$h\nu$,^{c} 45 °C, 10 h	99^e
5	Ph	**2b**	5 equiv	))), 55 °C, 4 h	no reaction
6	Ph	**2b**	5 equiv	))), 55 °C, 8 h	12
7	Ph	**2b**	3 equiv	$h\nu$,^{b} 45 °C, 10 h	7
8	Ph	**2b**	3 equiv	$h\nu$,^{c} 45 °C, 10 h	38^f

[a] $^nC_{10}F_{21}I$ (1 mmol, 1 M). [b] Tungsten lamp (500 W), Pyrex (>300 nm). [c] Xe lamp (500 W), Pyrex (>300 nm). [d] Attempted isolation of each stereoisomers is commented on in ref 9. [e] *E*/*Z* = 85/15. [f] *E*/*Z* = 72/28.

SCHEME 1



In this mechanism, it is important to know the rate for the iodine atom abstraction by alkyl radical from $^nC_{10}F_{21}I$. We thus estimated the rate for the iodine transfer by employing the 5-hexenyl radical clock system.[10] The reaction of 1,6-heptadiene (**5**, 1 M) with $^nC_{10}F_{21}I$ in BTF upon irradiation with visible light afforded the cyclic and acyclic adducts (**6**, **7**, and **8**) with the ratio of 21/27/7 (eq 3). Since the rate constant (k_c) for cyclization of 5-hexenyl radical is 2.0×10^5 s^{-1},[10,11] the rate constant for the iodine abstraction by radical intermediates from $^nC_{10}F_{21}I$ is roughly estimated to be 2.6×10^5 M^{-1} s^{-1}. This radical capturing ability is lower compared with those of $^nBu_3SnH$ or $(PhSe)_2$ and higher than those of $(Me_3Si)_3SiH$ or $^nBu_3GeH$.[12]



(3)

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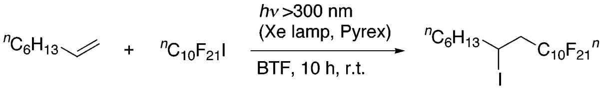
[5] Recently, we have reported preliminary results concerning the photoinduced iodoperfluoroalkylation of substituted allenes; see: Ogawa, A.; Imura, M.; Kamada, N.; Hirao, T. *Tetrahedron Lett.* **2001**, *42*, 2489.

[6] (a) Ogawa, A.; Curran, D. P. *J. Org. Chem.* **1997**, *62*, 450. (b) Maul, J. J.; Ostrowski, P. J.; Ublacker, G. A.; Linclau, B.; Curran, D. P. In *Modern Solvents in Organic Synthesis*; Knochel, P., Ed.; Springer: Berlin, 1999; Vol. 206, pp 79–105.

[7] (a) Dunogues, J.; Boileau, S. *Tetrahedron Lett.* **1995**, *36*, 1843. (b) Petrier, C.; Luche, J.-L. In *Synthetic Organic Sonochemistry*; Luche, J.-L., Ed.; Plenum Press: New York, 1998; Chapter 2, pp 51–90.

[8] Compared with a tungsten lamp, a xenon lamp has satisfactory light intensity in the region of wavelength of 300–350 nm (see Supporting Information: S1, Figure 2).

With these kinetic considerations in mind, we next examined the reaction of perfluoroalkyl iodide with alkenes (eq 4). The photoinduced reaction of 1-octene (**9**) with heneicosafluoro-*n*-decyl iodide (**1a**) took place successfully to give the desired iodoperfluoroalkylated product (**10**) in 61% yield. Similarly, iodoperfluoroalkylation of allyl alcohol and 5-hexen-2-one afforded the desired products in 28% and 34% yields, respectively. Prolonged reaction time (18 h) improved the yields of the iodoperfluoroalkylated products (allyl alcohol, 45%; 5-hexen-2-one, 56%). In the case of aromatic alkenes such as styrene, however, the reaction did not proceed efficiently, most probably because of the instability of the benzylic iodide under the photoirradiation conditions.[13] On the other hand, the attempted iodoperfluoroalkylation of electron-deficient alkenes such as acrylonitrile or ethyl acrylate resulted in the polymerization of the alkenes.



(4)

9, 3 equiv **1a** **10**, 61%

Perfluoroalkylation of 1,2- and 1,3-Dienes. Except for one example of gas-phase reaction of $\mathrm{CF_3I}$ with allene itself,[14] the radical addition reaction of $\mathrm{R_F}$-I to allenes is not reported hitherto.[5] When the reaction of *tert*-butylallene (**11a**) with $^{n}\mathrm{C}_{10}\mathrm{F}_{21}\mathrm{I}$ (**1a**) was conducted upon irradiation with the light of wavelength over 300 nm, the corresponding iodoperfluoroalkylated product (**12a**) was obtained in 88% yield, in which perfluoroalkyl and iodo groups were regioselectively introduced into the terminal and central carbons of **11a**, respectively (Scheme 2). The *E*/*Z* ratios of these products (**12a**) were determined on the basis of the measurement of NOE difference spectra.[15] With some other monosubstituted allenes (**11b**−**d**), the iodoperfluoroalkylation also took place selectively at the terminal carbon−carbon double bond of the allenes to give the corresponding *β*-iodoallylic perfluoroalkanes (**12b**−**d**) in good yields. In these reactions, irradiation with near-UV light causes homolytic dissociation to generate $^{n}\mathrm{C}_{10}\mathrm{F}_{21}{}^{\bullet}$ and $\mathrm{I}^{\bullet}$, the formed $^{n}\mathrm{C}_{10}\mathrm{F}_{21}{}^{\bullet}$ attacks the kinetically favorable terminal carbon of allenes regioselectively, forming a vinylic radical intermediate (**13**), and then the vinylic radical (**13**) abstracts an iodide atom from $^{n}\mathrm{C}_{10}\mathrm{F}_{21}\mathrm{I}$ to produce the iodoperfluoroalkylated products (**12**) with regeneration of $^{n}\mathrm{C}_{10}\mathrm{F}_{21}{}^{\bullet}$. Compared with monosubstituted allenes, the iodoperfluoroalkylation of disubstituted allenes (**11e**−**g**) proceeded inefficiently, as shown in Table 2. 1,1-Disubstituted allene (**11e**) provided the corresponding iodoperfluoroalkylated product (**12e**) in 32% (*E*/*Z* = 21/79) yield regioselectively, whereas the iodoperfluoroalkylation of internal allene (**11f**) afforded

SCHEME 2

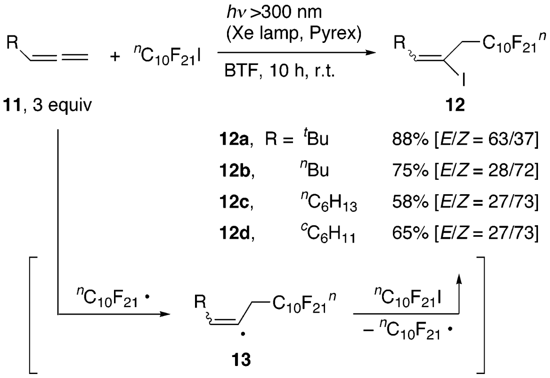
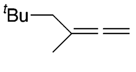
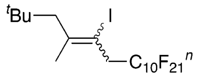
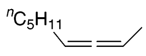
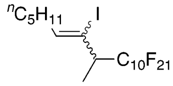
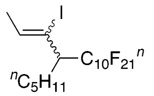
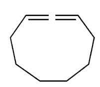
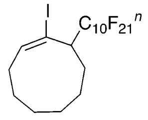
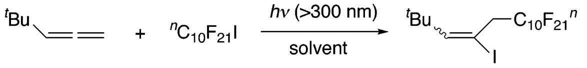


TABLE 2. Iodoperfluoroalkylation of Disubstituted Allenes[a]

substrate	product (yield, %, [*E*/*Z*])
 **11e**	 **12e** (32, [21/79])
 **11f**	 **12f** (12, [20/80])  **12f'** (3, [49/51])
 **11g**	 **12g** (7, [27/73])

[a] Reaction conditions: 0.9 mmol of allenes and 0.3 mmol of $^{n}\mathrm{C}_{10}\mathrm{F}_{21}\mathrm{I}$ were used in the precence of BTF (0.2 mL).

TABLE 3. Iodoperfluoroalkylation of *tert*-Butylallene in Several Solvents[a]



11a **12a**

entry	solvent	$E_{\mathrm{T}}^{\mathrm{N}}$ [b]	NMR yield, %	*E*/*Z*
1	$\mathrm{PhCH_3}$	0.099	78	69/31
2	$\mathrm{C_6F_6}$	0.108	75	67/33
3	$\mathrm{Et_2O}$	0.117	54	70/30
4	THF	0.207	39	72/28
5	BTF	0.241	85	71/29
6	$\mathrm{CHCl_3}$	0.259	80	77/23
7	DMF	0.404	47	78/22
8	DMSO	0.444	13	77/23
9	$\mathrm{CH_3CN}$	0.460	49	78/31
10	neat		73	66/34

[a] Reaction conditions: $^{n}\mathrm{C}_{10}\mathrm{F}_{21}\mathrm{I}$ (0.3 mmol), *tert*-butylallene (0.9 mmol), solvent (0.2 mL), Xe lamp (Pyrex), r.t., 10 h. [b] Normalized empirical parameter of solvent polarity, based on the intramolecular CT absorption of a pyridinium-*N*-phenoxide betaine dye.[16]

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(9) Although much effort has been made for the separation of stereoisomers (*E*- and *Z*-isomers), in the case of the iodoperfluoroalkylation of 1-octyne, the separation was difficult probably because the similar polarities between *E*- and *Z*-isomers.

(10) (a) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 2. (b) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(11) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

(12) Some representative rate constants for the hydrogen atom transfer reactions are as follows: $^{n}\mathrm{Bu_3SnH}$, $2.4 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$; $\mathrm{(Me_3Si)_3SiH}$, $3.8 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$; $^{n}\mathrm{Bu_3GeH}$, $1.0 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$. See: Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Wiley: New York, 1995.

(13) In general, allyl and benzylic iodides are unstable thermally or photochemically; see: *The Merck Index*, 13th ed.; Budavari, S., Ed.; Merck & Co., Inc.: Whitehouse Station, New Jersey, 2001; p 291.

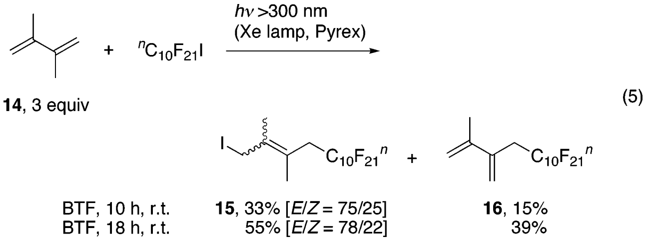
(14) Meunier, H. G.; Abell, P. I. *J. Phys. Chem.* **1967**, *71*, 1430.

(15) In the case of (*Z*)-**12a**, for example, irradiation of the vinylic singlet at δ 6.21 resulted in an enhancement of the signal at δ 3.40 (allylic triplet), whereas irradiation of the vinylic singlet of (*E*)-**12a** at δ 6.69 indicated no enhancement of the signal at δ 3.57 (allylic triplet).

a regioisomeric mixture, i.e., **12f** (12%, $E/Z = 20/80$) and **12f′** (3%, $E/Z = 49/51$). Cyclic allene (**11g**) also underwent iodoperfluoroalkylation inefficiently.

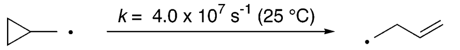
Table 3 represents influences of solvents on this iodoperfluoroalkylation of *tert*-butylallene (**11a**). These results strongly suggest that nonpolar solvents such as toluene or halogen-containing solvents such as C_6F_6, BTF, and $CHCl_3$ are effective for this iodoperfluoroalkylation (entries 1, 2, 5, and 6). Even in the absence of solvents, the photoinitiated iodoperfluoroalkylation of **11a** gave rise to 73% of **12a** (entry 10).

We next examined the iodoperfluoroalkylation of 2,3-dimethyl-1,3-butadiene (**14**) (eq 5). When the iodoperfluoroalkylation of **14** was conducted under the same reaction conditions, a 1,4-adduct (**15**) was obtained in 33% yield along with a small amount of a byproduct (**16**). Prolonged reaction time (18 h) led to increase in the yield of **15** (55%). Although conjugate dienes are generally subject to polymerization under radical conditions, no formation of polymerized product in this reaction is of interest.



(5)

Perfluoroalkylation of Vinylcyclopropanes. Because the ring-opening process of cyclopropylcarbinyl radical (eq 6)[17] is much faster than the iodine abstraction process by the radical intermediates from $^nC_{10}F_{21}I$ (2.6×10^5 M^{-1} s^{-1}), the iodoperfluoroalkylation of vinylcyclopropanes is predicted to proceed via ring-opening process of cyclopropane ring (Scheme 3).[18]



(6)

As expected, the photoinduced reaction of 1-cyclopropylstyrene (**17a**) with $^nC_{10}F_{21}I$ provided 1,5-iodoperfluoroalkylated product (**18a**) selectively in almost quantitative yield (Table 4, entry 1). Compared with the iodoperfluoroalkylation of alkynes or alkenes, the present reaction of vinylcyclopropanes proceeds efficiently even for only 0.5 h (entry 5) or even in the absence of the solvent (entry 7). In addition, this iodoperfluoroalkylation of vinylcyclopropanes gradually took place upon irradiation with room light (entry 8). On the other hand, in the dark and/or under sonication conditions, no reaction took place at all (entries 9 and 10).

SCHEME 3

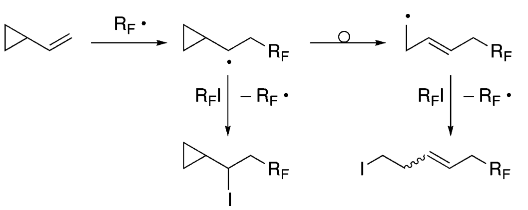


TABLE 4. Iodoperfluoroalkylation of Vinylcyclopropanes[a]

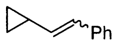
17a

18a

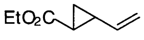
entry	equiv	time, h	conditions	yield, %[b] [E/Z]
1	3	4	Xe lamp, r.t.	>99 [88/12]
2	3	2	Xe lamp, r.t.	>99 [91/9]
3	1.5	2	Xe lamp, r.t.	>99 [88/12]
4	1.2	2	Xe lamp, r.t.	95 [92/8]
5	3	0.5	Xe lamp, r.t.	>99 [88/12]
6[c]	3	10	Xe lamp, r.t.	>99 [88/12]
7	3	2	neat, r.t.	86 [88/12]
8	3	100	fluorescent lamp, r.t.	57 [95/5]
9	3	10	dark, 60 °C	no reaction
10	3	5	(((•, dark, 20 °C	no reaction

[a] Reaction conditions: $^nC_{10}F_{21}I$ (0.3 mmol), BTF (0.2 mL), Xe lamp (500 W, Pyrex), r.t. [b] NMR yield. [c] Hexane (0.2 mL) was used as the solvent.

Similar conditions can be employed with a variety of vinylcyclopropanes, and the results are summarized in Table 5. Interestingly, inner vinylcyclopropanes also underwent selective iodoperfluoroalkylation effectively (entries 2, 3, and 5). On the other hand, iodoperfluoroalkylation of 2-cyclopropylstyrene (**17f**) proceeded inefficiently and most of the starting materials were recovered. In the case of a vinylcyclopropane bearing an ethoxycarbonyl group (**17g**), no reaction took place at all. The reason these substrates do not undergo iodoperfluoroalkylation efficiently is unclear at the present.



17f



17g

Moreover, when aryl-substituted methylenecyclopropane (**17h**, R = Ph) was used as a substrate, the iodoperfluoroalkylation took place via the ring opening of the cyclopropane, to give the 1,3-adduct (**18h**) in good yield (Scheme 4). The fact that the same reaction did not

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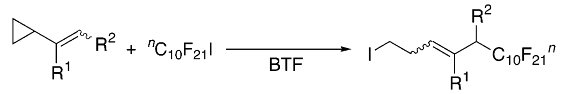
(16) (a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988; Chapter 7 and Appendix, pp 339–410. (b) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319. (c) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Wiley-VCH: Weinheim, 2003; Chapter 7 and Appendix, pp 389–475.

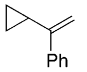
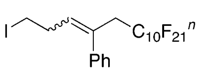
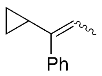
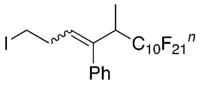
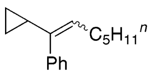
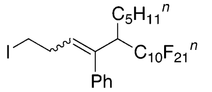
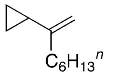
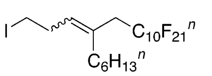
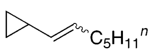
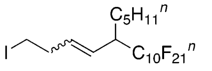
(17) (a) Beckwith, A. L. J.; Bowry, V. W. *J. Org. Chem.* **1989**, *54*, 2681. (b) Newcomb, M.; Manek, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 9662. (c) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687. (d) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5699. (e) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151. (f) Beckwith, A. L. J.; Bowry, V. W. *J. Am. Chem. Soc.* **1994**, *116*, 2710.

(18) One example has been reported for iodoperfluoroalkylation of α-(trimethylsilyloxy)vinylcyclopropane with $^iC_3F_7I$. See, for example: Miura, K.; Taniguchi, M.; Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 6391.

TABLE 5. Photoinitiated Iodoperfluoroalkylation of Vinylcyclopropanes[a]

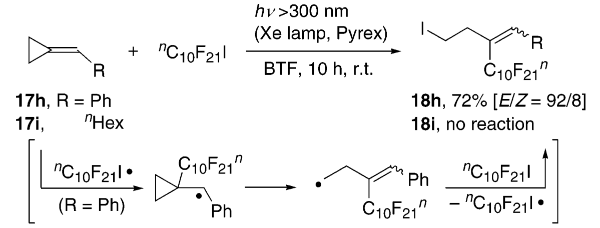


17 18

entry	substrate	product	yield, %[b] [*E*/*Z*]
1	 **17a**	 **18a**	92 [89/11]
2	 **17b**	 **18b**	98 [79/21]
3	 **17c**	 **18c**	87 [34/66]
4	 **17d**	 **18d**	98 [40/60]
5	 **17e**	 **18e**	97 [89/11]

[a] Reaction conditions: ${}^{n}C_{10}F_{21}I$ (0.3 mmol), vinylcyclopropane (0.9 mmol), BTF (0.2 mL), Xe lamp (500 W, Pyrex), r.t., 10 h. [b] Isolated yield.

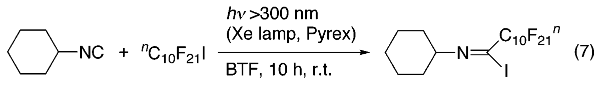
SCHEME 4



17h, R = Ph
17i, nHex
18h, 72% [*E*/*Z* = 92/8]
18i, no reaction

occur at all with alkyl-substituted methylenecyclopropane (**17i**, R = ^{n}Hex) suggests the formation of benzylic radical intermediate is important for controlling the reaction course.

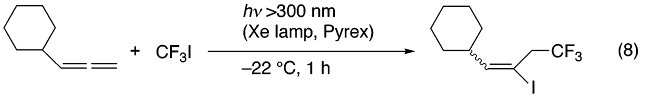
Perfluoroalkylation of Isocyanide. Isocyanides have isoelectronic structures with carbon monoxide[19] and react with various radical species to provide imidoyl radicals.[20] Although the radical addition reactions of R_F-I to isocyanides by using copper reagent or radical initiators are reported by Wakselman,[21] the photoinitiated radical reaction is not reported. Thus, we next examined the photoinduced iodoperfluoroalkylated reaction of isocyanides (eq 7). When the reaction of cyclohexyl isocyanide (**19**) with ${}^{n}C_{10}F_{21}I$ was conducted upon irradiation, 1-iodo-1-perfluoroalkylated product (**20**) was obtained in 92% yield.



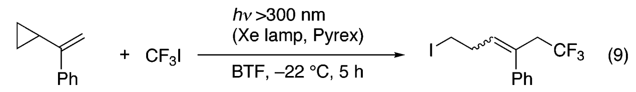
19, 3 equiv **20**, 92%

The obtained imidoyl iodides, which have several heteroatom functions, are expected to work as a promising building block for the synthesis of useful heterocyclic compounds or amino acid including fluorous tags.[22]

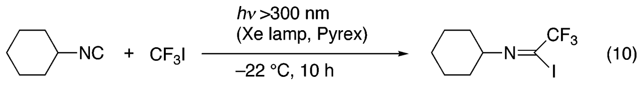
Application to Iodotrifluoromethylation. In view of fluorinated drug synthesis, the iodotrifluoromethylation of several unsaturated compounds was attempted as follows.[23] The photoinduced iodotrifluoromethylation of cyclohexylallene (**11d**) with CF_3I (**1b**, bp −22.5 °C) at −22 °C led to the regioselective formation of the corresponding iodotrifluoromethylated product (**21**) in 26% yield (the reaction conditions were not optimized) (eq 8). Moreover, the reaction of vinylcyclopropane (**17a**) with CF_3I at −22 °C successfully afforded 1,5-iodotrifluoromethylated product (**22**) in 81% yield via the ring opening of the cyclopropane (eq 9). In the case of cyclohexyl isocyanide (**19**), 1-iodo-1-trifluoromethylated product (**23**) was obtained in 68% yield (eq 10).



11d, 0.9 mmol excess **21**, 26% [*E*/*Z* = 29/71]



17a, 0.9 mmol excess **22**, 81% [*E*/*Z* = 90/10]



19, 0.9 mmol excess **23**, 68%

These results clearly indicate that the photoinitiation is effective for the trifluoromethylation of unsaturated compounds even at low temperature.

Conclusion

Upon irradiation through Pyrex with a xenon lamp, the radical addition of R_F-I to a variety of unsaturated compounds has been revealed to proceed efficiently:

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(19) (a) Ryu, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1050. (b) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev.* **1999**, *99*, 1991.

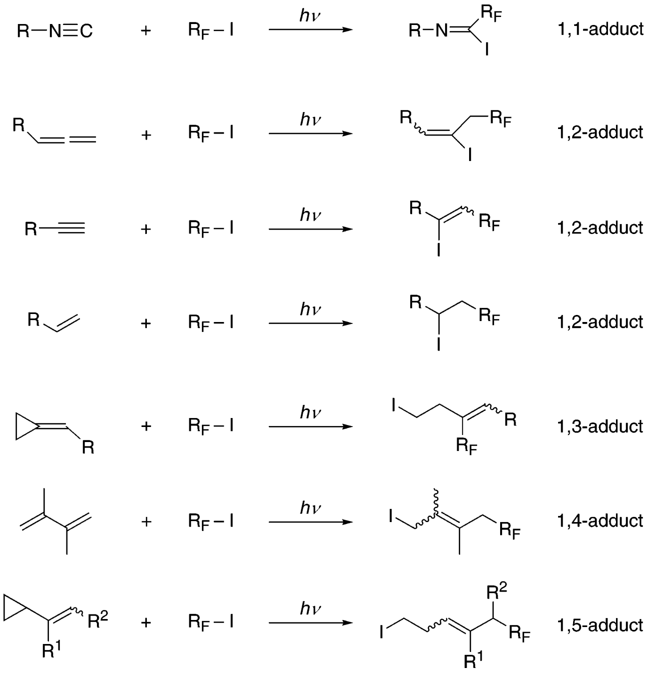
(20) For radical reactions of isocyanides, see for example: (a) Saegusa, T.; Kobayashi, S.; Ito, Y.; Yasuda, N. *J. Am. Chem. Soc.* **1968**, *90*, 4182. (b) Saegusa, T.; Kobayashi, S.; Ito, Y. *J. Org. Chem.* **1970**, *35*, 2118. (c) Barton, D. H. R.; Ozbalik, N.; Vacher, B. *Tetrahedron* **1988**, *44*, 3501. (d) Chatgilialoglu, C.; Giese, B.; Kopping, B. *Tetrahedron Lett.* **1990**, *31*, 6013. (e) Curran, D. P.; Liu, H. *J. Am. Chem. Soc.* **1991**, *113*, 2127. (f) Curran, D. P.; Liu, H. *J. Am. Chem. Soc.* **1992**, *114*, 5863. (g) Fukuyama, T.; Chen, X.; Peng, G. *J. Am. Chem. Soc.* **1994**, *116*, 3127. (h) Bachi, M. D.; Balanov, A.; Bar-Ner, N. *J. Org. Chem.* **1994**, *59*, 7752. (i) Nanni, D.; Pareschi, P.; Rizzoli, C.; Sgarabotto, P.; Tundo, A. *Tetrahedron* **1995**, *51*, 9045. (j) Yamago, S.; Miyazoe, H.; Goto, R.; Yoshida, J. *Tetrahedron Lett.* **1999**, *40*, 2347. (k) Leardini, R.; Nanni, D.; Zanardi, G. *J. Org. Chem.* **2000**, *65*, 2763. (l) Daniele, N. *Radicals in Organic Synthesis*; Wiley-VCH: Weinhein, 2001; Vol. 2, pp 44−61. (m) Ogawa, A.; Doi, M.; Tsuchii, K.; Hirao, T. *Tetrahedron Lett.* **2001**, *42*, 2317. (n) Yamago, S.; Miyazoe, H.; Goto, R.; Hashidume, M.; Sawazaki T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 3697.

(21) Tordeux, M.; Wakselman, C. *Tetrahedron* **1981**, *37*, 315.

(22) (a) Uneyama, K.; Sugimoto, K. *J. Org. Chem.* **1992**, *57*, 6014. (b) Uneyama, K. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 43. (c) Uneyama, K. *J. Synth. Org. Chem. Jpn.* **1997**, *55*, 1081. (d) Hudlicky, M. *Fluorine Chemistry for Organic Chemists*; Oxford: New York, 2002.

(23) (a) Uneyama, K. *J. Synth. Org. Chem. Jpn.* **1991**, *49*, 612. (b) Umemoto, T.; Ishihara, S. *J. Am. Chem. Soc.* **1993**, *115*, 2156.

SCHEME 5



isocyanides, allenes, alkynes, alkenes, methylenecyclopropanes, conjugated dienes, and vinylcyclopropanes undergo regioselective iodoperfluoroalkylation, providing the corresponding 1,1-, 1,2-, 1,3-, 1,4-, and 1,5-adducts, respectively (Scheme 5). Thus, a variety of iodoperfluoroalkylated products can be synthesized conveniently by using the present xenon lamp-irradiated procedure without the formation of any polymerized byproducts from unsaturated compounds.

Experimental Section

General Comments. ^{1}H, ^{13}C, and ^{19}F NMR spectra (300, 75, and 282 MHz, respectively) were determined by using $CDCl_3$ as the solvent with Me_4Si as the internal standard. Chemical shifts in ^{1}H and ^{13}C NMR were measured relative to $CDCl_3$ and converted to δ (Me_4Si) value by using δ ($CDCl_3$) = 7.26 and 77.0 ppm, respectively. Chemical shifts in ^{19}F NMR were measured relative to the CF_3 group of $^nC_{10}F_{22}$ and converted to δ $CFCl_3$ value by using δ $CFCl_3 = -81.4$ ppm. IR spectra were recorded on a FT-IR instrument. Mass spectra were run by EI ionization (70 eV).

General Procedure for Iodoperfluoroalkylation: 2-Iodo-1-perfluoro-*n*-decyl-1-octene (3a). In a Pyrex glass tube (10 mm × 75 mm) under N_2 atmosphere were placed 1-octyne (**2a**, 0.9 mmol, 99.17 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent, yielding 99% (224.6 mg) of 2-iodo-1-perfluoro-*n*-decyl-1-octene (**3a**) as a stereoisomeric mixture (E/Z = 85/15). The E/Z ratio was determined by ^{1}H NMR at the vinylic proton of the product (**3a**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): [E-isomer] δ 0.89 (t, J = 6.8 Hz, 3 H), 1.30−1.35 (m, 6 H), 1.53−1.63 (m, 2 H), 2.63 (t, J = 7.4 Hz, 2 H), 6.32 (t, J_{H-F} = 14.6 Hz, 1 H); [Z-isomer] δ 0.89 (t, J = 6.8 Hz, 3 H), 1.30−1.38 (m, 6 H), 1.53−1.63 (m, 2 H), 2.64−2.69 (m, 2 H), 6.23 (t, J = 13.2 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): [E-isomer] δ 14.0, 22.6, 28.2, 30.1, 31.6, 41.2, 123.0, 126.3 (t, J_{C-F} = 23.6 Hz); [Z-isomer] δ 14.0, 22.6, 27.8, 29.1, 31.6, 48.5, 119.0, 121.6 (t, J_{C-F} = 23.6 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): [E-isomer] δ −81.4 (3 F), −105.9 (2 F), −122.3 (10 F), −123.2 (2 F), −123.7 (2 F) −126.6 (2 F); [Z-isomer] δ −81.4 (3 F), −109.0 (2 F), −122.0 (10 F), −123.4 (2 F), −123.7 (2 F), −126.6 (2 F). IR (KBr): 2930, 2860, 2370, 1636, 1246, 1221, 1153, 1103, 893, 656 cm^{-1}. MS (EI) m/z: 756 (M$^+$, 25). Anal. Calcd for $C_{18}H_{14}F_{21}I$: C, 28.59; H, 1.87. Found: C, 28.67; H, 2.23.

2-Iodo-1-perfluoro-*n*-decyl-1-octane (10). In a Pyrex glass tube (10 mm × 75 mm) under N_2 atmosphere were placed 1-octene (**9**, 0.9 mmol, 101.0 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent, yielding 61% (138.7 mg) of **10**: white solid; mp 54.6−55.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, J = 6.8 Hz, 3 H), 1.31−1.46 (m, 6 H), 1.48−1.62 (m, 2 H), 1.70−1.90 (m, 2 H), 2.68−3.02 (m, 2 H), 4.29−4.38 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 21.0, 22.7, 28.3, 29.6, 31.7, 40.4, 41.8 (t, J_{C-F} = 20.6 Hz). IR (KBr): 2934, 2862, 2349, 1371, 1205, 1150, 1095, 648, 555 cm^{-1}. MS (EI) m/z: 758 (M$^+$, 1). Anal. Calcd for $C_{18}H_{16}F_{21}I$: C, 28.51; H, 2.13. Found: C, 28.43; H, 2.15.

2-Iodo-1-perfluoro-*n*-decyl-2-heptene (12b). In a Pyrex glass tube (10 mm × 75 mm) under N_2 atmosphere were placed *n*-butylallene (**11b**, 0.9 mmol, 86.55 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent, yielding 75% (167.0 mg) of **12b** as a stereoisomeric mixture (E/Z = 28/72). The E/Z ratio was determined by ^{1}H NMR at the vinylic proton of the product (**12b**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): [E-isomer] δ 0.90 (t, J = 6.6 Hz, 3 H), 1.25−1.50 (m, 4 H), 2.04 (dt, J = 7.2, 7.2 Hz, 2 H), 3.39 (t, J_{H-F} = 17.6 Hz, 2 H), 6.50 (t, J = 7.2 Hz, 1 H); [Z-isomer] δ 0.92 (t, J = 6.6 Hz, 3 H), 1.25−1.50 (m, 4 H), 2.18 (dt, J = 7.0, 7.0 Hz, 2 H), 3.39 (t, J_{H-F} = 17.6 Hz, 2 H), 5.82 (t, J = 7.0 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): [E-isomer] δ 13.8, 22.2, 30.7, 31.5, 39.5 (t, J_{C-F} = 21.3 Hz), 78.2, 150.5; [Z-isomer] δ 14.0, 22.3, 30.1, 36.8, 45.3 (t, J_{C-F} = 21.3 Hz), 86.1, 145.3. ^{19}F NMR (282 MHz, $CDCl_3$): [E-isomer] δ −81.4 (3 F), −113.7 (2 F), −122.3 (10 F), −123.3 (2 F), −124.0 (2 F), −126.7 (2 F); [Z-isomer] δ −81.4 (3 F), −114.2 (2 F), −122.3 (10 F), −123.3 (2 F), −123.8 (2 F), −126.7 (2 F). IR (NaCl): 2961, 2932, 2860, 2353, 1636, 1456, 1339, 667 cm^{-1}. MS (EI) m/z: 742 (M$^+$, 55). Anal. Calcd for $C_{17}H_{12}F_{21}I$: C, 27.51; H, 1.63. Found: C, 27.08; H, 1.67.

2-Iodo-1-perfluoro-*n*-decyl-2-nonene (12c). In a Pyrex glass tube (10 mm × 75 mm) under N_2 atmosphere were placed *n*-hexylallene (**11c**, 0.9 mmol, 124.2 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent, yielding 58% (134.0 mg) of **12c** as a stereoisomeric mixture (E/Z = 27/73). The E/Z ratio was determined by ^{1}H NMR in the methylene signal at the α-position of R_F group of the product (**12c**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): [E-isomer] δ 0.89 (t, J = 6.6 Hz, 3 H), 1.33−1.64 (m, 8 H), 2.04 (q, J = 7.2, 7.2 Hz, 2 H), 3.39 (t, J_{H-F} = 17.4 Hz, 2 H), 6.66 (t, J = 7.2 Hz, 1 H); [Z-isomer] δ 0.89 (t, J = 6.6 Hz, 3 H), 1.33−1.64 (m, 8 H), 2.17 (dt, J = 7.2, 7.2 Hz, 2 H), 3.39 (t, J_{H-F} = 17.4 Hz, 2 H), 5.82 (t, J = 7.2 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): [E-isomer] δ 14.1, 22.6, 27.9, 28.6, 30.2, 30.6, 39.5 (t, $J_{\text{C−F}} = 21.5$ Hz), 78.2, 150.5; [*Z*-isomer] δ 14.1, 22.7, 28.5, 29.0, 31.7, 37.1, 45.3 (t, $J_{\text{C−F}} = 21.3$ Hz), 86.1, 145.4. ^{19}F NMR (282 MHz, CDCl$_3$): [*E*-isomer] δ −81.4 (3 F), −113.6 (2 F), −122.0 (10 F), −123.5 (2 F) −124.0 (2 F), −126.7 (2 F); [*Z*-isomer] δ −81.4 (3 F), −114.1 (2 F), −122.3 (10 F), −123.2 (2 F), −123.7 (2 F), −126.7 (2 F). IR (NaCl): 2930, 2858, 1726, 1636, 1468, 1207, 1149, 662 cm^{-1}. MS (EI) *m*/*z*: 770 (M$^+$, 36). Anal. Calcd for $C_{19}H_{16}F_{21}I$: C, 29.63; H, 2.09. Found: C, 29.92; H, 2.21.

1-Cyclohexyl-2-iodo-3-perfluoro-*n*-decyl-prop-1-ene (12d). In a Pyrex glass tube (10 mm × 75 mm) under N$_2$ atmosphere were placed *c*-hexylallene (**11d**, 0.9 mmol, 122.2 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using CHCl$_3$ as an eluent, yielding 65% (149.8 mg) of **12d** as a stereoisomeric mixture (*E*/*Z* = 27/73). The *E*/*Z* ratio was determined by ^{1}H NMR at the vinylic proton of the product (**12d**): white solid; mp 46.7−47.9 °C. ^{1}H NMR (300 MHz, CDCl$_3$): [*E*-isomer] δ 1.24−1.40 (m, 5 H), 1.65−1.74 (m, 5 H), 2.04−2.17 (m, 1 H), 3.39 (t, $J_{\text{H−F}} = 17.7$ Hz, 2 H), 6.49 (d, $J = 10.2$ Hz, 1 H); [*Z*-isomer] δ 1.08−1.27 (m, 5 H), 1.65−1.74 (m, 5 H), 2.19−2.31 (m, 1 H), 3.36 (t, $J_{\text{H−F}} = 17.4$ Hz, 2 H), 5.62 (d, $J = 8.1$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$): [*E*-isomer] δ 25.9, 32.1, 39.5 (t, $J_{\text{C−F}} = 21.3$ Hz), 41.5, 76.2, 155.5; [*Z*-isomer] δ 25.6, 31.2, 45.3 (t, $J_{\text{C−F}} = 21.3$ Hz), 46.1, 83.5, 150.0. ^{19}F NMR (282 MHz, CDCl$_3$): [*E*-isomer] δ −81.4 (3 F), −113.9 (2 F), −122.3 (10 F), −123.3 (2 F), −124.0 (2 F), −126.7 (2 F); [*Z*-isomer] δ −81.4 (3 F), −114.1 (2 F), −122.3 (10 F), −123.3 (2 F), −123.7 (2 F), −126.7 (2 F). IR (NaCl): 2922, 2850, 1639, 1448, 1211, 1151, 906, 735, 650 cm^{-1}. MS (EI) *m*/*z*: 768 (M$^+$, 11). Anal. Calcd for $C_{19}H_{14}F_{21}I$: C, 29.71; H, 1.84. Found: C, 29.95; H, 1.97.

1-Iodo-2,3-dimethyl-4-perfluoro-*n*-decyl-2-butene (15). In a Pyrex glass tube (10 mm × 75 mm) under N$_2$ atmosphere were placed 2,3-dimethly-1,3-butadiene (**14**, 0.9 mmol, 85.15 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using CHCl$_3$ as an eluent, yielding 18% (39.3 mg) of **15** as a stereoisomeric mixture (*E*/*Z* = 75/25) (33% yield of **15** in the text was NMR yield.). The *E*/*Z* ratio was determined by ^{1}H NMR in the methylene signal at the α-position of R$_\text{F}$ group of the product (**15**): white solid; mp 53.5−53.9 °C. ^{1}H NMR (300 MHz, CDCl$_3$): [*E*-isomer] δ 1.76 (s, 3 H), 1.85 (s, 3 H), 2.82 (t, $J_{\text{H−F}} = 19.2$ Hz, 2 H), 3.95 (s, 2 H); [*Z*-isomer] δ 1.75 (s, 3 H), 1.89 (s, 3 H), 2.85 (t, $J_{\text{H−F}} = 19.4$ Hz, 2 H), 3.89 (s, 2 H). ^{13}C NMR (75 MHz, CDCl$_3$): [*E*-isomer] δ 9.3, 18.0, 20.1, 36.1 (t, $J_{\text{C−F}} = 21.6$ Hz), 122.9, 134.6; [*Z*-isomer] δ 9.6, 18.5, 21.5, 34.1 (t, $J_{\text{C−F}} = 21.6$ Hz), 122.4 134.3. ^{19}F NMR (282 MHz, CDCl$_3$): [*E*-isomer] δ −81.4 (3 F), −105.9 (2 F), −122.3 (10 F), −123.2 (2 F), −123.7 (2 F), −126.7 (2 F); [*Z*-isomer] δ −81.4 (3 F), −109.0 (2 F), −122.0 (10 F), −123.2 (2 F), −123.7 (2 F), −126.7 (2 F). IR (NaCl): 2964, 2360, 1211, 1151, 1091, 1049, 804, 647, 559 cm^{-1}. MS (EI) *m*/*z*: 728 (M$^+$ − I, 100). Elemental analysis of **15** was failed, because **15** has an allylic iodide structure and is extremely unstable.

5-Iodo-1-perfluoro-*n*-decyl-2-phenyl-2-pentene (18a). In a Pyrex glass tube (10 mm × 75 mm) under N$_2$ atmosphere were placed **17a** (0.9 mmol, 130.0 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using CHCl$_3$ as an eluent, yielding 92% (218.1 mg) of **18a** as a stereoisomeric mixture (*E*/*Z* = 89/11). The *E*/*Z* ratio was determined by ^{1}H NMR at the vinylic proton of the product (**18a**): white solid; mp 64.2−65.5 °C. ^{1}H NMR (300 MHz, CDCl$_3$): [*E*-isomer] δ 2.83 (dt, $J = 6.9$, 7.2 Hz, 2 H), 3.26 (t, $J = 6.9$ Hz, 2 H), 3.32 (t, $J_{\text{H−F}} = 18.9$ Hz, 2 H), 5.98 (t, $J = 7.2$ Hz, 1 H), 7.16−7.42 (m, 5 H); [*Z*-isomer] δ 2.60 (dt, $J = 7.2$, 7.2 Hz, 2 H), 3.11 (t, $J = 7.2$ Hz, 2 H), 3.15 (t, $J_{\text{H−F}} = 18.0$ Hz, 2 H), 5.72 (t, $J = 7.2$ Hz, 1 H), 7.16−7.42 (m, 5 H). ^{13}C NMR (75 MHz, CDCl$_3$): [*E*-isomer] δ 4.2, 31.6 (t, $J_{\text{C−F}} = 22.2$ Hz), 33.1, 126.3, 127.5, 128.4, 130.6, 134.8, 141.9. ^{19}F NMR (282 MHz, CDCl$_3$): [*E*-isomer] δ −81.4 (3 F), −111.9 (2 F), −122.4 (10 F), −123.3 (2 F), −123.7 (2 F), −126.7 (2 F); [*Z*-isomer] δ −81.4 (3 F), −112.8 (2 F), −122.4 (10 F), −123.3 (2 F), −123.7 (2 F), 126.7 (2 F). IR (NaCl): 3083, 3057, 3032, 2957, 1600, 1574, 1238, 1202, 1148, 748, 694 cm^{-1}. MS (EI) *m*/*z*: 790 (M$^+$, 40). Anal. Calcd for $C_{21}H_{12}F_{21}I$: C, 31.92; H, 1.53. Found: C, 31.48; H, 1.63.

1-Iodo-4-(perfluoro-*n*-decyl-methyl)-3-decene (18d). In a Pyrex glass tube (10 mm × 75 mm) under N$_2$ atmosphere were placed **17d** (0.9 mmol, 137.0 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using CHCl$_3$ as an eluent, yielding 98% (234.7 mg) of **18d** as a stereoisomeric mixture (*E*/*Z* = 40/60). The *E*/*Z* ratio was determined by ^{1}H NMR at the vinylic proton of the product (**18d**): white solid; mp 41.0−42.8 °C. ^{1}H NMR (300 MHz, CDCl$_3$): [*E*-isomer] δ 0.89 (d, $J = 6.6$ Hz, 3 H), 1.25−1.48 (m, 8 H), 2.13 (t, $J = 7.5$ Hz, 2 H), 2.61 (dt, $J = 7.2$, 7.2 Hz, 2 H), 2.81 (t, $J_{\text{H−F}} = 19.8$ Hz, 2 H), 3.15 (t, $J = 7.2$ Hz, 2 H), 5.50 (t, $J = 7.2$ Hz, 1 H); [*Z*-isomer] δ 0.89 (d, $J = 6.6$ Hz, 3 H), 1.25−1.48 (m, 8 H), 2.13 (t, $J = 7.5$ Hz, 2 H), 2.68 (dt, $J = 7.2$, 7.2 Hz, 2 H), 2.75 (t, $J_{\text{H−F}} = 18.6$ Hz, 2 H), 3.14 (t, $J = 7.2$ Hz, 2 H), 5.35 (t, $J = 7.2$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$): [*E*-isomer] δ 5.0, 14.2, 22.7, 27.8, 28.9, 31.0 (t, $J_{\text{C−F}} = 22.2$ Hz), 31.7, 32.3, 38.1, 130.4, 132.8; [*Z*-isomer] δ 4.5, 14.2, 22.7, 28.0, 29.3, 31.0, 31.7, 32.2, 37.2 (t, $J_{\text{C−F}} = 21.6$ Hz), 131.0, 132.1. ^{19}F NMR (282 MHz, CDCl$_3$): [*E*-isomer] δ −81.4 (3 F), −112.7 (2 F), −122.4 (10 F), −123.3 (2 F), −123.9 (2 F), −126.7 (2 F); [*Z*-isomer] δ −81.4 (3 F), −113.4 (2 F), −122.4 (10 F), −123.3 (2 F), −123.7 (2 F), −126.7 (2 F). IR (NaCl): 2956, 2928, 2858, 1466, 1243, 1207, 1150, 761 cm^{-1}. MS (EI) *m*/*z*: 798 (M$^+$, 2). Anal. Calcd for $C_{21}H_{20}F_{21}I$: C, 31.60; H, 2.53. Found: C, 31.27; H, 2.49.

1-Iodo-5-perfluoro-*n*-decyl-3-decene (18e). In a Pyrex glass tube (10 mm × 75 mm) under N$_2$ atmosphere were placed **17e** (0.9 mmol, 124.4 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using CHCl$_3$ as an eluent, yielding 97% (228.2 mg) of **18e** as a stereoisomeric mixture (*E*/*Z* = 89/11). The *E*/*Z* ratio was determined by ^{1}H NMR at the vinylic proton of the product (**18e**): colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$): [*E*-isomer] δ 0.89 (t, $J = 6.9$ Hz, 3 H), 1.15−1.35 (m, 6 H), 1.38−1.48 (m, 2 H), 2.55−2.87 (m, 1 H), 2.63 (t, $J = 7.5$ Hz, 2 H) 3.10−3.20 (m, 2 H), 5.31 (dd, $J = 9.6$, 15.4 Hz, 1 H), 5.56 (dt, $J = 15.4$, 6.8 Hz, 1 H); [*Z*-isomer] δ 0.89 (t, $J = 6.9$ Hz, 3 H), 1.15−1.35 (m, 6 H), 1.38−1.48 (m, 2 H), 1.70−1.82 (m, 2 H), 2.55−2.87 (m, 1 H), 3.10−3.23 (m, 2 H), 5.26−5.37 (m, 1 H), 5.54−5.68 (m, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$): [*E*-isomer] δ 4.5, 14.1, 22.6, 26.2, 31.4, 36.4, 46.2, (t, $J_{\text{C−F}} = 21.2$ Hz), 126.0, 134.7; [*Z*-isomer] δ 3.4, 13.8, 26.2, 29.8, 30.7, 31.6, 31.9, 45.3, 133.9. IR (NaCl): 2956, 2928, 2871, 2859, 1244, 1207, 1151, 972 cm^{-1}. MS (EI) *m*/*z*: 784 (M$^+$, 1). Anal. Calcd for $C_{20}H_{18}F_{21}I$: C, 30.63; H, 2.31. Found: C, 30.57; H, 2.37.

4-Iodo-2-perfluoro-*n*-decyl-1-styrene (18h). In a Pyrex glass tube (10 mm × 75 mm) under N_2 atmosphere were placed **17h** (0.9 mmol, 117.2 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent, yielding 72% (167.7 mg) of **18h** as a stereoisomeric mixture (E/Z = 92/8). The E/Z ratio was determined by ^{1}H NMR at the vinylic proton of the product (**18h**): white solid; mp 72.5−73.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): [*E*-isomer] δ 3.02 (t like, $J = 8.3$ Hz, 2 H), 3.19 (t like, $J = 8.3$ Hz, 2 H), 7.14 (s, 1 H), 7.32−7.48 (m, 5 H); [*Z*-isomer] δ 3.10 (t like, 2 H), 6.96 (s, 1 H), 7.32−7.48 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): [*E*-isomer] δ 0.3, 32.1, 128.5, 128.9, 129.1, 129.3, 133.7, 138.1 (t, $J_{C-F} =$ 9.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): [*E*-isomer] δ −81.4 (3 F), −111.4 (2 F), −122.0 (2 F), −122.3 (10 F), −123.3 (2 F), −126.7 (2 F); [*Z*-isomer] δ −81.4 (3 F), −114.0 (2 F), −122.0 (2 F), −122.3 (10 F), −123.3 (2 F), −126.7 (2 F). IR (NaCl): 3086, 3055, 3024, 2974, 2953, 1576, 1252, 1207, 1145, 1123, 759, 694 cm^{-1}. MS (EI) *m*/*z*: 776 (M^+, 17). Anal. Calcd for $C_{20}H_{10}F_{21}I$: C, 30.95; H, 1.30. Found: C, 31.19; H, 1.38.

***N*-(Cyclohexyl)-perfluoro-*n*-decylimidoyl Iodide (20).** In a Pyrex glass tube (10 mm × 75 mm) under N_2 atmosphere were placed cyclohexyl isocyanide (**19**, 0.9 mmol, 98.25 mg) and heneicosafluoro-*n*-decyl iodide (**1a**, 0.3 mmol, 193.8 mg) in BTF (0.2 mL). The mixture was irradiated with a xenon lamp (500 W) at room temperature for 10 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent, yielding 92% (208.4 mg) of **20**: colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25−1.85 (m, 10 H), 3.15−3.24, (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.7, 25.4, 31.2, 74.3, 112.4 (t, $J_{C-F} = 36.0$ Hz). IR (NaCl): 2938, 2862, 1697, 1453, 1366, 1244, 1215, 1153, 720, 644 cm^{-1}. MS (EI) *m*/*z*: 754 (M^+, 1). Anal. Calcd for $C_{17}H_{11}F_{21}IN$: C, 27.04; H, 1.47; N, 1.85. Found: C, 27.01; H, 1.56; N, 2.09.

General Procedure for Iodotrifluoromethylation of Vinylcyclopropanes: 6-Iodo-1,1,1-trifluoro-3-phenyl-3-hexene (22). In a 20-mL two-neck flask equipped with a dry ice condenser were placed 1-cyclopropylstyrene (**17a**, 0.9 mmol, 130.0 mg) and BTF (0.2 mL) under N_2 atmosphere. Then, gaseous trifluoromethyl iodide (**1b**) was introduced into the reaction vessel and liquified at the dry ice cooler, to reside in the vessel as liquid solution (ca. 0.2−0.5 mL). The mixture was irradiated with a xenon lamp (500 W) at −22 °C for 5 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent, yielding 81% (247.9 mg) of 6-iodo-1,1,1-trifluoro-3-phenyl-3-hexene (**22**) as a stereoisomeric mixture (E/Z = 90/10). The E/Z ratio was determined by ^{1}H NMR at the vinylic proton of the product (**22**): colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): [*E*-isomer] δ 2.87 (dt, $J = 7.2$, 7.0 Hz, 2 H), 3.26 (t, $J = 7.0$ Hz, 2 H), 3.34 (q, $J_{H-F} = 10.7$ Hz, 2 H), 5.94 (t, $J = 7.2$ Hz, 1 H), 7.27−7.40 (m, 5 H); [*Z*-isomer] δ 2.59 (dt, $J = 7.2$, 7.0 Hz, 2 H), 3.12 (t, $J = 7.0$ Hz, 2 H), 3.17 (q, $J_{H-F} = 9.4$ Hz, 2 H), 5.72 (t, $J = 6.9$ Hz, 1 H), 7.30−7.54 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): [*E*-isomer] δ 4.2, 33.0, 35.0 (q, $J_{C-F} = 29.5$ Hz), 125.6 (q, $J_{C-F} = 276$ Hz), 126.3, 127.5, 128.4, 131.5, 133.9, 141.4; [*Z*-isomer] δ 4.7, 32.0, 34.4 (q, $J_{C-F} = 29.5$ Hz), 123.8, 127.5, 128.1, 131.1, 133.2. ^{19}F NMR (282 MHz, $CDCl_3$): [*E*-isomer] δ −64.2 (t, $J_{H-F} = 10.3$ Hz, 3 F); [*Z*-isomer] δ −65.0 (t, $J_{H-F} = 10.3$ Hz, 3 F). IR (NaCl): 3081, 3057, 3026, 2959, 1598, 1574, 1252, 1134, 1105, 755, 698 cm^{-1}. MS (EI) *m*/*z*: 340 (M^+, 52). Anal. Calcd for $C_{12}H_{12}F_3I$: C, 42.38; H, 3.56. Found: C, 42.07; H, 3.61.

***N*-(Cyclohexyl)-2,2,2-trifluoro-acetimidoyl Iodide (23):** In a 20-mL two-neck flask equipped with a dry ice condenser were placed cyclohexyl isocyanide (**19**, 0.9 mmol, 98.25 mg) and BTF (0.2 mL) under N_2 atmosphere. Then, gaseous trifluoromethyl iodide (**1b**) was introduced into the reaction vessel and liquified at the dry ice cooler, to reside in the vessel as liquid solution (ca. 0.2−0.5 mL). The mixture was irradiated with a xenon lamp (500 W) at −22 °C for 5 h. After the reaction was complete, unreacted materials were evaporated, and the purification of the products was performed on a recycling preparative HPLC, equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent, yielding 68% (178.5 mg) of **23**: colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25−1.85 (m, 10 H), 3.13 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.9, 25.3, 31.3, 73.7, 110.9 (q, $J_{C-F} = 41.7$ Hz), 114.3 (q, $J_{C-F} = 275$ Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −70.27 (s, 3 F). IR (NaCl): 2935, 2859, 1692, 1451, 1365, 1270, 1256, 1200, 1157, 1058, 956, 904, 875, 709 cm^{-1}. MS (EI) *m*/*z*: 305 (M^+, 2). Anal. Calcd for $C_8H_{11}F_3IN$: C, 31.50; H, 3.63; N, 4.59. Found: C, 31.37; H, 3.71; N, 4.58.

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Supporting Information Available: ^{1}H, ^{13}C, and ^{19}F NMR spectral data; IR, mass, and analytical data for compounds **3b**, **12a**, **18b**, and **18c**; and ^{19}F NMR spectral data for compounds **10**, **18e**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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