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Reaction of Perfluoroalkyl Iodides with Electron-Deficient Olefins under UV Irradiation

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The reaction of perfluoroalkyl iodides **1** with acrylates, acrylic acid, acrylamide, and acrylonitrile has been investigated. In the presence of a catalytic amount of palladium(0), the reaction of R_fI with ethyl acrylate produces mostly polymer. Under irradiation with 254 nm UV light, perfluoroalkyl iodides react with ethyl acrylate to give high yields of the 1:1 addition products (74−88% isolated yield, $C_nF_{(2n+1)}CH_2CHICO_2Et$) and small amounts of 1:2 adducts (<10% NMR yield) at ambient temperature. The functionalized iodide 5-iodo-3-oxaoctafluoropentanesulfonyl fluoride also reacts with ethyl acrylate to give the 1:1 adduct in 88% yield. However, it has been found that the reaction selectivity is related to the length of the perfluoroalkyl group in **1** when methyl acrylate is employed in the reaction under similar conditions. Both 1:1 (56−76%) and 1:2 adducts [$C_nF_{(2n+1)}$-$CH_2CH(CO_2Me)CH_2CHICO_2Me$, 24−34%] are formed when methyl acrylate reacts with short-chain perfluoroalkyl iodides [$C_nF_{(2n+1)}I$, $n \leqslant 4$], whereas the reaction of perfluorohexyl or longer chain perfluoroalkyl iodides [$C_nF_{(2n+1)}I$, $n \geqslant 6$] gives predominantly the 1:1 addition products (>85%). The formation of the 1:2 adduct can be efficiently suppressed by using excess R_fI in the reaction. The reaction of *N*,*N*-dimethylacrylamide with perfluoropropyl iodide (**1a**) produces exclusively the 1:1 adduct. Products from the further elimination, reduction, and decarboxylation of the 1:1 and 1:2 adducts are observed when **1a** reacts with methyl methacrylate under similar conditions. The reaction of **1a** with acrylonitrile produces the 1:1 and 1:2 adducts in 53% and 47% yields, respectively. An addition−reduction product, *n*-$C_3F_7CH_2CH_2CO_2H$ (68%), is obtained in the reaction of acrylic acid with **1a**.

Introduction

The reaction of perfluoroalkyl iodides with carbon−carbon multiple bonds is one of the most important and useful methods for the introduction of perfluoroalkyl groups into various organic substrates.[1] A radical intermediate is generally involved, and many practical and efficient initiators have been developed.[2] However, because the perfluoroalkyl radical is electrophilic, this reaction is mainly limited to electron-rich olefins. With electron-deficient olefins, low conversion to 1:1 adduct and the formation of the undesired dimeric, telomeric, or polymeric products is frequently observed.[3−9]

Photolysis is one of the classic methods for initiation of a radical reaction. Haszeldine reported the reaction of CF_3I with acrylonitrile via irradiation with >300 nm high-pressure Hg UV light, and a 72% yield of CF_3-$CH{=}CHCO_2H$ was reported after treatment with a base, followed by hydrolysis.[4,5] However, the reaction of CF_3I with methyl acrylate gave $CF_3CH_2CHICO_2Me$ in 25% conversion and 88% isolated yield.[6] Later, Brace attempted the reaction of $C_7F_{15}I$ with ethyl acrylate at high temperature[7] or in the presence of AIBN initiator.[8] In both cases the conversion and the yields of the desired products were low, and telomer products were formed. Recently, a variety of metals and their low-valent complexes have been found to be excellent electron donors, which efficiently initiates the radical reaction of R_fI via single electron transfer.[2b,10] However, the reaction of R_fI with ethyl acrylate gave only a nonvolatile solid in the presence of a catalytic amount of Cu^0, and the corresponding 1:1 adduct was obtained in 19% and 45% yields respectively when the reaction used excess of Cu^0 in diglyme or Ac_2O.[9]

Recently, we have developed general and efficient methods for the preparation of α,α-difluoro ketones, which exhibit excellent biological activity as enzyme inhibitors,[11] via the addition of iododifluoromethyl ketones and substituted alkenes.[12] A novel selectivity has been observed in the reaction of iododifluoromethyl phenyl ketone with methyl and ethyl, *n*-butyl, or *tert*-

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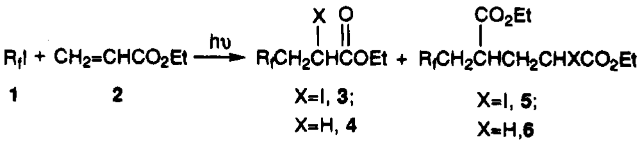
butyl acrylates under UV irradiation when this study was extended to electron-deficient olefins.[13] This result prompted us to systematically examine the reaction of perfluoroalkyl iodides with a series of electron-deficient olefins. Recently, zinc powder and a catalytic amount of bromo(pyridine)cobaloxime(III) have also been successfully employed for initiation of the reaction of perfluoroalkyl iodides with ethyl acrylate[14] and propiolate.[15] High yields of the corresponding addition–reduction products were reported. Here, we present the results of the UV-initiated addition reaction of perfluoroalkyl iodides with a series of electron-deficient olefins.

Results and Discussion

Palladium(0) has been found to be a highly efficient initiator for the reaction of perfluoroalkyl iodides[2b] and iododifluoromethyl ketones[12] with electron-rich alkenes under mild conditions. However, in the presence of a catalytic amount of Pd(0) (5–10 mol %), the reaction of R_fI with ethyl acrylate produced a transparent polymer in minutes, and <20% conversion of R_fI was observed. In hexane, similar polymerization occurred for this reaction either at 60 °C or at room temperature, although the conversion of R_fI increased to 30–45%.

Photolysis of R_fI is a classic method for the generation of $R_f^{\bullet}$ and has been widely applied for the introduction of perfluoroalkyl groups into organic substrates.[1] However, the previously reported photoreactions of R_fI with electron-deficient olefins were unsatisfactory.[5,6] Interestingly, we found that perfluoroalkyl iodides **1a–e** reacted smoothly with ethyl acrylate (**2**) under irradiation with 254 nm UV light, and high yields of the corresponding 1:1 addition adducts **3a–e** (74–88% isolated yield) were obtained. Small amounts of the addition–reduction product $R_fCH_2CH_2CO_2Et$ (**4**, <7%), 1:2 addition adducts [$R_fCH_2CH(CO_2Et)CH_2CHXCO_2Et$, X = I, **5**(<10%); X = H, **6** (<4%)], or 1-hydroperfluoroalkane (R_fH, **7**, <5%) were formed as byproducts.

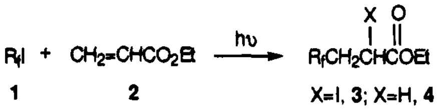
The products were isolated by direct distillation from the reaction mixture or via column chromatography. For example, when perfluoropropyl iodide (**1a**) and ethyl acrylate (**1a**:**2** = 3:1) were mixed in a quartz tube and irradiated at 254 nm in a Rayonet photoreactor for 24 h at ambient temperature, ethyl 2-iodo-4,4,5,5,6,6,6-heptafluorohexanoate (**3a**) was isolated in 83% yield by distillation. The functionalized perfluoroalkyl iodide $FSO_2CF_2CF_2OCF_2CF_2I$ (**1f**) was also reacted with ethyl acrylate and gave the corresponding 1:1 addition adduct **3f** in 94% NMR yield (88% isolated, entry 10). The detailed results for the reaction of perfluoroalkyl iodides with ethyl acrylate are summarized in Table 1.



$$\underset{\mathbf{1}}{R_fI} + \underset{\mathbf{2}}{CH_2{=}CHCO_2Et} \xrightarrow{h\nu} \underset{X=I,\ \mathbf{3};\ X=H,\ \mathbf{4}}{R_fCH_2\overset{X}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}OEt} + \underset{X=I,\ \mathbf{5};\ X=H,\mathbf{6}}{R_fCH_2\overset{CO_2Et}{\overset{|}{C}}HCH_2CHXCO_2Et}$$

R_f: $n\text{-}C_3F_7$ (**a**), $n\text{-}C_4F_9$ (**b**), $n\text{-}C_6F_{13}$ (**c**), $n\text{-}C_7F_{15}$ (**d**), $n\text{-}C_8F_{17}$ (**e**), $FSO_2CF_2CF_2OCF_2CF_2$ (**f**)

Table 1. Reaction of R_fI with Ethyl Acrylate under UV Irradiation[a]



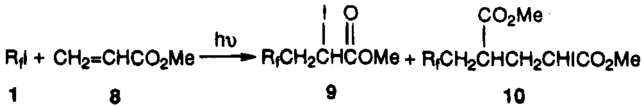
$$\underset{\mathbf{1}}{R_fI} + \underset{\mathbf{2}}{CH_2{=}CHCO_2Et} \xrightarrow{h\nu} \underset{X=I,\ \mathbf{3};\ X=H,\ \mathbf{4}}{R_fCH_2\overset{X}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}OEt}$$

					products (%)[b]		
entry	1	1:2	T (h)	convn (%)	3	4	5
1	**1a**	1:1.5	4	25	100		
2	**1a**	1:2	24	91	100		
3	**1a**	1:3	24	93	94 (83)		
4	**1b**	1:2.5	24	61	92 (85)		7
5	**1c**	1:3	48	79	96 (79)		3
6	**1c**	1:6.5	24	70[c]	66	26	2
7	**1d**	1:3	24	54	89 (74)	3	5
8	**1d**	1:8.5	28	100	18	72	10
9	**1e**	1:3	60	70	86 (82)	7	7
10	**1f**	1:2	24	68	94 (88)		6
11	**1f**	1:3	24	80	95		5

[a] Reaction at ambient temperature. The % conversion was determined by ^{19}F NMR analysis. Small amounts of R_fH [^{19}F NMR spectra (<5%)] and 1:3 adduct (GC-MS) were sometimes observed. [b] Analyzed by GLPC and GC-MS spectra. Isolated yield in parentheses based on consumed **1**. [c] 4% of **6c** was formed in the reaction.

After the reaction, some polymer, formed via the polymerization of ethyl acrylate, appeared on the wall of the quartz tube above the liquid surface. Therefore, excess ethyl acrylate was usually used in the reaction to ensure a high conversion of **1**. However, the addition of a large excess of ethyl acrylate resulted in the formation of more 1:1 addition–reduction products **4** (entries 6 and 8). For example, the reaction of **1d** with **2** in the ratio of 1:8 gave 72% of **4d** and small amounts of the 1:1 addition product **3d** (18%) (entry 8, Table 1).

Similarly, methyl acrylate (**8**) reacted with R_fI to afford the corresponding 1:1 adducts under UV irradiation. However, considerable amounts of the 1:2 adducts (**10**, 24–34%) and sometimes a small amount of the 1:3 adduct were also formed in the reactions with **1a** and **1b** under similar conditions. For example, the reaction of **1a** with methyl acrylate gave 70% of $n\text{-}C_3F_7CH_2CHICO_2Me$ (**9a**), 24% of $n\text{-}C_3F_7CH_2CH(CO_2Me)CH_2CHICO_2Me$ (**10a**), and 1–2% of the 1:3 adduct (identified by GC-MS) with a conversion of 93% after irradiation for 40 h. The 1:1 adduct was isolated by distillation from the reaction mixture, and the 1:2 adduct was obtained by chromatography of the distillation residue. More interestingly, the reaction of perfluorohexyl iodide (**1c**) or the longer perfluoroalkyl chain iodides (**1d** and **1e**) predominantly produced the 1:1 adducts in 85–90% yields with a small amount of 1:2 adducts under similar conditions (<10%) (Table 2).



$$\underset{\mathbf{1}}{R_fI} + \underset{\mathbf{8}}{CH_2{=}CHCO_2Me} \xrightarrow{h\nu} \underset{\mathbf{9}}{R_fCH_2\overset{I}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}OMe} + \underset{\mathbf{10}}{R_fCH_2\overset{CO_2Me}{\overset{|}{C}}HCH_2CHICO_2Me}$$

In order to suppress the formation of the 1:2 adduct, we used an excess of R_fI in the reaction of **1b**, instead of an excess of methyl acrylate. The yield of the 1:1 adduct was greatly improved (>95%) when 2 equiv of **1b** reacted with methyl acrylate, and the 1:2 adduct was decreased to <5% as illustrated in Table 2 (entry 15). The excess **1b** was recovered by distillation after the reaction. In the reaction of the longer chain $C_nF_{2n+1}I$, the use of excess **1c** (n = 6, **1c**:**8** = 2:1) resulted in the exclusive formation of the 1:1 adduct as shown by GLPC analysis (entry 17).

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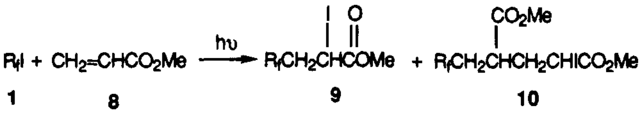
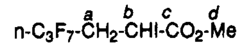
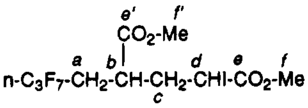
Table 2. Reaction of R_fI with Methyl Acrylate under UV Irradiation[a]



entry	1	1:8	T (h)	convn (%)	products (%)[b]	
					9	10
12	**1a**	1:2	20	54	56	34
13	**1a**	1:2.5	40	93	72 (62)	27 (21)
14	**1b**	1:3	36	87	76 (56)	24 (18)
15	**1b**	2:1	40	70[c]	95 (64)	5
16	**1c**	1:3.5	12	73	90	10
17	**1c**	2:1	48	67[c]	>98 (58)	
18	**1d**	1:1.4	24	50	95	5
19	**1d**	1:3.5	30	68	93 (79)	5
20	**1e**	1:3	24	50	89 (72)	11

[a] Reaction at ambient temperature. The conversions were determined by ^{19}F NMR analysis. Small amounts of 1:3 adducts were sometimes observed by GC-MS spectra (<3%). [b] Determined by GLPC or GC-MS. Isolated yield in parentheses based on consumed **1**. [c] Conversion and isolated yield based on **8**; ~65% of **1** was recovered after reaction.

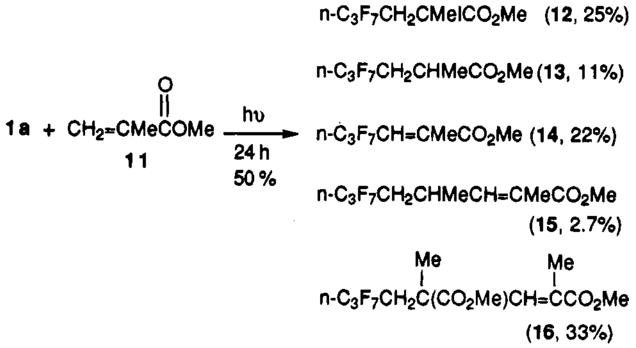
Table 3. Typical ^{13}C NMR Data of 9a and 10a (ppm)[a]

 $\overset{a}{C}H_2$ … n-C_3F_7-$\overset{a}{C}H_2$-$\overset{b}{C}HI$-$\overset{c}{C}O_2$-$\overset{d}{Me}$ **9a**	a: 38.5 (t, J = 21Hz) b: 4.45 c: 170.9 d: 53.47
 n-C_3F_7-$\overset{a}{C}H_2$-$\overset{b}{C}H(\overset{e'}{C}O_2\text{-}\overset{f'}{Me})$-$\underset{c}{C}H_2$-$\overset{d}{C}HI$-$\overset{e}{C}O_2$-$\overset{f}{Me}$ **10a**	a: 32.82 / 32.52 (t, J = 22Hz) b: 39.54 /38.64 c: 38.30 / 38.10 d: 17.11 / 14.09 e': 173.23 / 173.12 e: 171.39 / 170.85 f': 53.16 f: 52.63

[a] Solvent, $CDCl_3$; TMS standard.

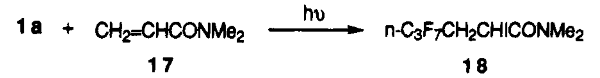
The 1:1 and 1:2 adducts exhibit different structural features apparent in the spectroscopic data. For example, only one peak appeared for the two stereoisomers of the 1:1 addition adduct in the GLPC and GC-MS spectra, whereas both the 1:2 and 1:3 adducts exhibited two peaks with a time difference of 0.2−0.3 min. However, both the 1:1 and 1:2 adducts displayed a strong molecular ion signal when analyzed by GC-MS spectroscopy. In the ^{19}F NMR spectrum, the two fluorines of the CF_2 group adjacent to CH_2 show a typical AB splitting pattern in the 1:1 adduct due to the adjacent chiral center. The coupling constant between the two fluorine atoms is ~272 Hz. However, only a singlet appeared for the same CF_2 group in the 1:2 adduct. Interestingly, all the chiral and adjacent carbons in the 1:2 adducts show two sets of ^{13}C NMR signals, but the chiral and adjacent carbons in the 1:1 adducts show only one set of ^{13}C NMR signals, as illustrated in Table 3 for **9a** and **10a**.

With methyl methacrylate (**11**), the reaction of perfluoropropyl iodide (**1a**) gave only ~50% conversion and a mixture of products after irradiation for 24 h. The main products were identified as **12−16**, which are formed by the subsequent reduction, elimination, or decarboxylation from the corresponding 1:1 and 1:2 adducts.



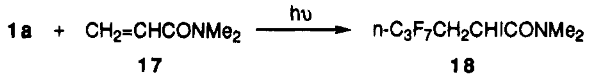
Perfluoroalkyl iodides, e.g. **1a**, also reacted with N,N-dimethylacrylamide (**17**) under similar conditions to form the corresponding 1:1 adduct **18** in high selectivity. However, the conversion was lower compared to the reactions with acrylate, although it could be increased via addition of excess **17** and increased reaction time as illustrated in Table 4.

Table 4. Reaction of 1a with N,N-Dimethylacrylamide (17) under UV Irradiation[a]

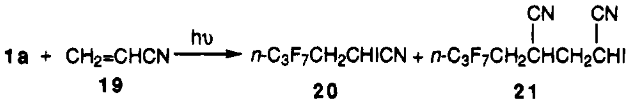


entry	1:17	T (h)	convn (%)	yield (%) of **18**
21	1:1	20	10	100
22	1:2	20	26	100
23	1:3	20	31	100
24	1:2.2	48	63	100 (81)

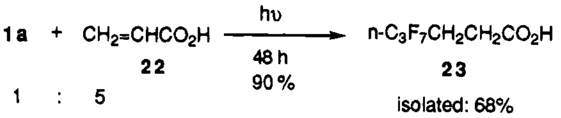
[a] Conversion and yield were determined by ^{19}F NMR. Isolated yield in parentheses based on consumed **1a**.



The reaction of **1a** with acrylonitrile (**19**) under UV irradiation was completed in 36 h. The 1:1 (**20**) and 1:2 (**21**) adducts were formed in 52% and 47% yields, respectively. Interestingly, the carbon signal of −CHI− in the adducts appears at much higher field than TMS, −20 ppm for the 1:1 adduct, −14 and −7 ppm for the 1:2 adduct *vs* TMS standard.



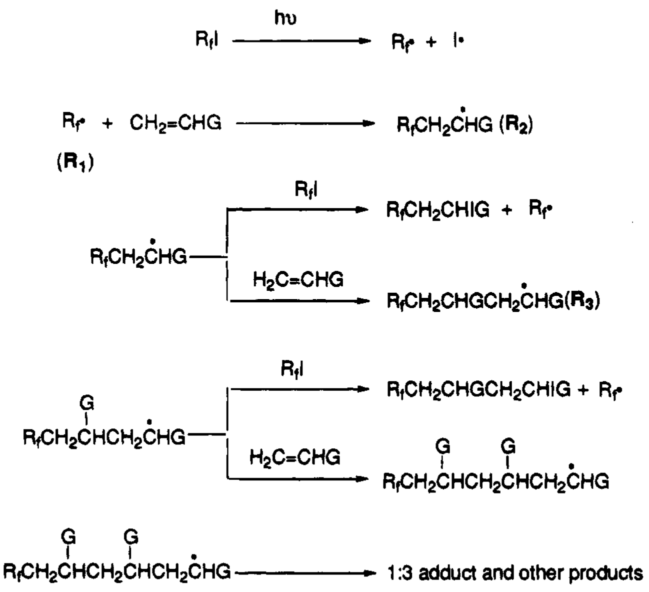
R_fI also reacted with acrylic acid (**22**) under similar conditions and gave an addition−reduction product in good yield. For example, when a mixture of **1a** and excess **22** (**1**:**22** = 1:5) was irradiated for 48 h, 90% of **1a** reacted and 4,4,5,5,6,6,6-heptafluorohexanoic acid (**23**) was isolated in 68% yield via column chromatography.



However, the reaction of R_fI with a nonterminal electron-deficient olefin was not successful. For example, the reaction of **1b** and 2-cyclohexenone produced a polymer, and <5% of **1b** was converted when the reaction mixture was irradiated for 24 h.

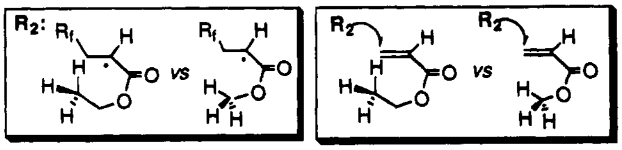
It has been well documented that the C−I bond in perfluoroalkyl iodide can be homolyticly cleaved to gener-

Scheme 1



(G: electron withdrawing group)

Scheme 2



(A) (B)

ate the corresponding $R_f^\bullet$ under photoirradiation.[1] Therefore, we propose a similar radical chain mechanism for the reaction in Scheme 1.

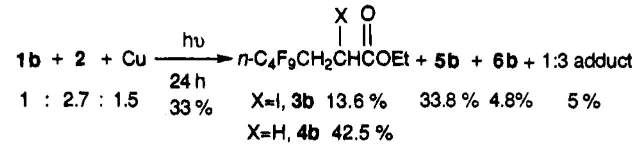
Radical inhibitors are useful probes for radical mechanisms.[9] In the presence of excess hydroquinone, the reaction of **1d** with methyl acrylate (**8**) was partially suppressed (**1d**:**8**:hydroquinone = 1:2:2), and the conversion of **1d** was decreased to 33%, compared with a conversion of 50% in the absence of hydroquinone (entry 16 in Table 2) after irradiation for 24 h. However, no inhibition was observed in the presence of 30 mol % of hydroquinone.

The reactions of **1a** and **1b** with ethyl and methyl acrylates exhibit quite different selectivity, which indicates that the ester groups from the acrylate can have an important effect on the reactions. From Scheme 1, the radical intermediate $\mathbf{R_2}$, produced by the addition of $R_f^\bullet$ to the alkene, can abstract an iodine atom from R_fI to give the corresponding 1:1 adduct and consequently regenerate the propagating radical $R_f^\bullet$. Another competing reaction for $\mathbf{R_2}$ is the addition to a second molecule of alkene to form the 1:2 or telomerized products via $\mathbf{R_3}$. The fact that the addition of excess of R_fI in the reaction favors the formation of the 1:1 adduct supports the proposal of these competitive processes in the reaction. The longer ethyl ester group in the acrylate can shield the terminal carbon of the double bond more efficiently via steric hindrance than the methyl group, which facilitates the abstraction of iodine atom by $\mathbf{R_2}$ (Scheme 2, **B**). At the same time, the steric hindrance should also result in the lower reactivity and increased selectivity of the ethyl-substituted $\mathbf{R_2}$ as compared with the methyl analog because of the better shielding effect of the ethyl group to the radical intermediate (Scheme 2, **A**), which could also partially suppress the reaction of $\mathbf{R_2}$(Et) with a second molecule of alkene to form $\mathbf{R_3}$.

The reaction of acrylonitrile with R_fI gave more 1:2 adduct, which can also be similarly attributed to less steric hindrance of the nitrile group on the terminal alkene carbon of acrylonitrile and the nitrile group substituted $\mathbf{R_2}$, similar to the reaction of methyl acrylate.

However, the ester group effect of the acrylate was diminished as the longer chain perfluoroalkyl iodides ($n \geqslant 6$) were employed in the reaction, which implies that the perfluoroalkyl chain also has an effect on the selectivity of $\mathbf{R_2}$, possibly by a similar steric effect. The formation of numerous products in the reaction of methyl methacrylate could be attributed to the instability of the initially formed tertiary iodides under the reaction conditions.

Considering the longer reaction time and incomplete conversion of the photoreaction of R_fI with electron-deficient alkenes, we tried to accelerate the reaction by addition of an electron donor to assist the cleavage the C–I bond of R_fI to generate $R_f^\bullet$ by formation of an electron donor–acceptor complex.[16] Therefore, excess copper powder was added to the reaction mixture of **1b** with ethyl acrylate, and some white solid (CuI) appeared after irradiation for 24 h.



However, the addition of copper neither facilitated the formation of the 1:1 adduct nor the conversion of the photoreaction based on the ^{19}F NMR analysis of the reaction mixture. Instead, the conversion was slightly decreased (from 61% to 53%) as compared with the reaction without addition of Cu (entry 4 in Table 1), and more 1:1 addition–reduction product **4b** and 1:2 (**5b**, **6b**) and 1:3 adducts were formed. One explanation for this result is the formation of a donor–acceptor complex between the iodide (**1b**) and Cu,[16] which decreased the concentration of free R_fI in the solution and made it more difficult for $\mathbf{R_2}$ to abstract an iodine atom from free R_fI to form the corresponding 1:1 addition adduct in the chain-transfer process. Consequently, more $\mathbf{R_2}$ reacted with **2** or abstracted a hydrogen to form the 1:2 and telomeric or addition–reduction products. This result also excludes the possibility of the generation of radical $R_f^\bullet$ in the initiation process as the rate-determing step in the reaction.

Conclusion

We have systematically studied the UV-initiated reaction of perfluoroalkyl iodides with a series of electron-deficient olefins. Perfluoroalkyl iodides react readily with ethyl acrylate, methyl acrylate, *N,N*-dimethylacrylamide, acrylonitrile, and acrylic acid under mild conditions

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[16] (a) Chen, Q. Y.; Qiu, Z. M. *J. Fluorine Chem.* **1987**, *35*, 79. (b) *International Symposium on Centenary of Discovery of Fluorine*, p 75, Paris, 1986. (c) Qiu, Z. M. Ph.D. Thesis, Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, 1987.

[17] (a) Yang, Z. Y.; Burton, D. J. *J. Org. Chem.* **1992**, *57*, 4676; **1991**, *56*, 5125.

[18] (a) Walborsky, H. M.; Baum, M.; Loncrini, D. F. *J. Am. Chem. Soc.* **1955**, *76*, 3637. (b) Walborsky, H. M.; Baum, M. *J. Org. Chem.* **1956**, *21*, 538.

under the UV irradiation of 254 nm light to give the corresponding 1:1 adducts in high yields, which provides a useful and practical method for the introduction of perfluoroalkyl groups into these functionalized electron-deficient olefins. However, the reaction with an internal electron-deficient olefin was unsuccessful under similar reaction conditions. An ester group effect from the acrylate has been observed, which can efficiently change the reaction selectivity and provide a simple and useful method for the control of the formation of the desired 1:1 addition products. Utilizing an excess of R_fI in the reaction provides another practical option for the selective synthesis of the 1:1 adducts.

Experimental Section

General. All perfluoroalkyl iodides and electron-deficient olefins were obtained from Aldrich Chemical Co. and used without further purification. Copper was prepared from $CuSO_4$ by the literature method.[19] All reactions were performed in a Rayonet photochemical reactor equipped with 254 nm UV bulbs. All boiling points were recorded during fractional distillation using a partial immersion thermometer and are uncorrected. The ^{19}F, ^{1}H, and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent. All chemical shifts are reported in parts per million downfield (positive) of the standard. ^{19}F NMR spectra are referenced against internal $CFCl_3$ and ^{1}H and ^{13}C NMR spectra against internal tetramethylsilane (TMS). FTIR spectra were recorded in CCl_4 solution in a cell with 0.1 cm path length. GC-MS were performed at 70 eV, in the electron impact mode with a DB-1 column. GLPC analyses were performed on a 5% OV-101 column with a thermal conductivity detector. High resolution mass spectra were measured by the University of Iowa High Resolution Mass Spectrometry Facility.

Pd(0)-Initiated Reaction of 1a with Ethyl Acrylate. A 25 mL two-neck flask was charged with 0.2 g (0.17 mmol) of $Pd(PPh_3)_4$ and 2.1 g (21 mmol) of ethyl acrylate under an atmosphere of N_2. Then, 1.9 g (6.4 mmol) of **1a** was added in one portion at room temperature while vigorously stirring. The reaction started in 10 s and produced a transparent polymer in 5 min. The polymer was dissolved in diethyl ether, and 17% of **1a** had been converted when the solution was checked by ^{19}F NMR.

Similarly, the reaction in hexane yielded a polymer both at room temperature and at 60 °C (oil bath temperature). The conversion of **1a** was increased to 30–45%.

Representative General Procedure for the Photoreaction of R_fI with Electron-Deficient Olefins. Ethyl 4,4,5,5,6,6,6-Heptafluoro-2-iodohexanoate (3a, *n*-$C_3F_7CH_2CHICO_2Et$). In a 50 mL quartz tube were combined 2.0 g (6.7 mmol) of perfluoropropyl iodide (**1a**) and 2.0 g (20 mmol) of ethyl acrylate. After sealing the tube, the reactants were mixed by shaking and then irradiated in a Rayonet photochemical reactor with 254 nm UV light at ambient temperature. The reaction was monitored by ^{19}F NMR analysis, and 93% of **1a** was converted after reaction for 24 h. **3a** (94%) and a small amount of 1:2 adduct **5a** were formed as shown by GLPC. The reaction mixture was distilled under vacuum and gave 2.05 g of **3a** with a boiling point of 60–60.5 °C/3.75 mmHg (isolated yield 83%; GLPC purity >98%): ^{19}F NMR δ −81.0 (t, J = 9.89 Hz, 3F), −128.33 (s), −114.55 (dm, J = 274.0 Hz, 1F), −116.51 (dm, J = 274.0 Hz, 1F); ^{1}H NMR δ 4.62 (dd, J = 10.5, 4.50 Hz, 1H), 4.25 (qd, J = 6.0 Hz, 1.5 Hz, 2H), 3.43–3.22 (m, 1H), 2.81–2.62 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 170.45, 117.99 (qt, J = 286.8 Hz, 33.6 Hz), 117.11 (tt, J = 256.6 Hz, 31.7 Hz), 108.73 (t-sextet, J = 264.9 Hz, 37.0 Hz), 62.73, 38.59 (t, J = 20.8 Hz), 13.69, 5.42; GC-MS 396 (M^+, 16.86), 351 (M^+ − OEt, 11.54), 323 (M^+ − CO_2Et, 28.55), 269 (M^+ − I, 37.43), 241 (17.98), 222 (21.71), 213 (26.54), 177 (30.70), 159 (15.79), 145 (10.36), 141 (17.76), 77 (19.08), 69 (22.99), 55 (100), 45 (26.10); HRMS obsd 395.9458, $C_8H_8O_2F_7I$, calcd 395.9457; FTIR 2985, 1744, 1378, 1353, 1261, 1228, 1202, 1196, 1186, 1128 cm^{-1}.

Diethyl 2-Iodo-4-(2,2,3,3,4,4,4-heptafluorobutyl)-1,5-pentanedioate (5a, *n*-$C_3F_7CH_2CH(CO_2Et)CH_2CHICO_2Et$]. A small amount of **5a** (0.03g, <1%) was isolated by column chromatography through a silica gel from the above distillation residue (GC-MS purity 95%): ^{19}F NMR δ −80.99 (m, 3F), −114.50 (m, 2F), −128.29 (m, 2F); ^{1}H NMR δ 4.39–4.17 (m, 1H), 4.28–4.17 (m, 4H), 3.09–2.83 (m, 1H), 2.73–2.67 (m, 1H), 2.55–2.42 (m, 1H), 2.39–2.09 (m, 2H), 1.34–1.26 (m, 6H); ^{13}C NMR δ 172.81, 172.70, 170.90, 170.82, 62.73, 61.76, 39.77, 38.67, 38.49, 38.31, 32.85 (t, J = 21.3 Hz), 32.66 (J = 21.37 Hz), 17.62, 14.83, 14.09, 13.78; GC-MS 496 (M^+, 1.14), 450 (15.71), 451 (12.50), 423 (M^+ − CO_2Et, 28.55), 369 (M^+ − I, 26.88), 341 (11.95), 313 (18.36), 295 (15.82), 268 (16,81), 267 (100), 227 (15.38), 199 (12.72), 99 (15.60), 73 (16.81), 59 (18.47), 55 (86.28), 45 (12.94); FTIR 2984, 2940, 1799, 1739, 1477, 1441, 1375, 1323, 1299, 1263, 1181, 1120, 1020 cm^{-1}.

Ethyl 4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptanoate (3b, *n*-$C_4F_9CH_2CHICO_2Et$). Similarly, 8.6 g (24.8 mmol) of **1b** and 6.3 g (63 mmol) ethyl acrylate were irradiated in a quatz tube for 24 h; 61% of **1b** was converted based on ^{19}F NMR analysis of the reaction mixture, and 92% of **3b**, 7% of **5b**, and a small amount of 1:3 adduct were formed. Distillation gave 5.7 g (85% isolated yield; GLPC purity 93.5%) of **3b** and 0.4 g (4.8%; GLPC purity 95.1%) of **5b**.

3b: bp 68 °C/2.5 mmHg; ^{19}F NMR δ −81.62 (m, 3F), −126.43 (s), −113.88 (dm, J = 272.4 Hz, 1F), −115.8 (d, J = 278.2 Hz, 1F), −124.97 (s, 2F); ^{1}H NMR δ 4.61 (dd, J = 10.5, 3.50 Hz, 1H), 4.25 (qm, J = 7.1 Hz, 2H), 3.44–3.24 (m, 1H), 2.81–2.62 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 170.38, 62.69, 38.73 (t, J = 21.3 Hz), 13.68, 5.34; GC-MS 446 (M^+, 38.56), 401 (M^+ − OEt, 16.37), 373 (M^+ − CO_2Et, 33.63), 319 (M^+ − I, 25.0), 291 (17.43), 272 (31.34), 263 (31.51), 227 (35.92), 159 (19.37), 141 (26.58), 127 (I^+, 25.0), 77 (15.32), 69 (28.17), 55 (100), 45 (33.45); HRMS obsd 445.9416, $C_9H_6O_2F_9I$, calcd 445.9425; FTIR 2986, 2969, 1744, 1354, 1335, 1254, 1237, 1222, 1203, 1137 cm^{-1}.

Diethyl 2-iodo-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,5-pentanedioate (5b, *n*-$C_4F_9CH_2CH(CO_2Et)CH_2CHICO_2Et$): bp 126–128 °C/2.5 mmHg; ^{19}F NMR δ −81.61 (m, 3F), −113.77 (m, 2F), −124.93 (m, 2F), −126.41 (s, 2F); ^{1}H NMR δ 4.38–4.30 (m, 1H), 4.27–4.17 (m, 4H), 3.06–2.83 (m, 1H), 2.76–2.60 (m, 1H), 2.57–2.45 (m, 1H), 2.39–2.09 (m, 2H), 1.32–1.29 (m, 6H); ^{13}C NMR δ 172.79, 172.68, 170.87, 170.79, 62.71, 61.74, 39.72, 38.62, 38.44, 38.27, 33.03 (t, J = 21.6 Hz), 32.83 (J = 21.3 Hz), 17.84, 14.72, 14.07, 13.78; GC-MS 546 (M^+, 3.86), 501 (M^+ − OEt, 33.33), 500 (28.79), 473 (M^+ − CO_2Et, 14.11), 419 (M^+ − I, 43.56), 420 (33.71), 391 (18.37), 365 (32.20), 345 (29.92), 318 (30.68), 317 (100), 227 (30.30), 199 (17.99), 127 (I^+, 7.48), 101 (14.30), 99 (21.78), 73 (20.08), 59 (18.84), 55 (86.36), 45 (18.75); HRMS obsd 547.0029, $C_{14}H_{17}O_4F_9I$, calcd 547.0028; FTIR 2985, 2940, 1739, 1701, 1440, 1375, 1325, 1255, 1223, 1136 cm^{-1}.

Diethyl 2-iodo-4-(ethoxycarbonyl)-6-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,7-heptanedioate (*n*-$C_4F_9CH_2CH(CO_2Et)CH_2CH(CO_2Et)CH_2CHICO_2Et$): GC-MS 601 ($M^+$ − OEt, 40.30), 573 (M^+ − CO_2Et, 6.62), 519 (M^+ − I, 100), 475 (14.18), 445 (67.50), 427 (29.10), 417 (15.39), 373 (15.95), 372 (25.75), 346 (76.49), 343 (32.46), 318 (15.49), 299 (38.43), 287 (25.00), 153 (41.04), 127 (I^+, 21.46), 114 (25.00), 101 (43.66), 97 (15.11), 85 (27.61), 81 (25.37), 73 (39.18), 69 (15.86), 55 (86.94), 45 (17.35).

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-2-iodononanoate (3c, *n*-$C_6F_{13}CH_2CHICO_2Et$). Similarly, after irradiation for 48 h, the reaction of 2.65 g (5.9 mmol) of **1c** with 1.78 g (17.8 mmol) of **2** gave 2.01 g (79%; GLPC purity 92%, conversion 79%) of **3c**, and small amounts of **4c**, **5c**, and **6c** were identified by GC-MS. **3c**: bp 86–90 °C/2.3 mmHg; ^{19}F NMR δ −81.49 (m, 3F), −113.62 (dm, J = 271.8 Hz, 1F), −115.53 (d, J = 273.0 Hz, 1F), −122.20 (s, 2F), −123.26 (s, 2F), −123.98 (s, 2F), −126.65 (s); ^{1}H NMR δ 4.62 (dd, J = 10.5, 3.50 Hz, 1H), 4.26 (qd, J = 7.2 Hz, 1.03 Hz, 2H), 3.45–3.24 (m, 1H), 2.81–2.60 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 170.96, 63.0, 39.0 (t, J = 21.2 Hz), 13.67, 5.34; GC-MS 546

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(19) Brewster, R.; Groening, T. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. 2, p 446.

(M^+, 18.90), 501 (M^+ − OEt, 15.26), 473 (M^+ − CO_2Et, 39.53), 419 (M^+ − I, 10.90), 391 (22.97), 372 (37.21), 363 (32.12), 327 (41.28), 159 (17.73), 141 (26.16), 131 (13.37), 127 (I^+, 19.48), 119 (14.24), 77 (23.11), 69 (38.95), 55 (100), 45 (23.55); HRMS obsd 545.9354, $C_{11}H_8O_2F_{13}I$, calcd 545.9361; FTIR 2986, 1742, 1369, 1336, 1297, 1242, 1213, 1135, 1110, 1028 cm^{-1}.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoate[14] (4c, n-$C_6F_{13}CH_2CH_2CO_2Et$): GC-MS 420 (M^+, 6.94), 493 (21.82), 375 (M^+ − OEt, 100), 373 (16.74), 327 (M^+ − CO_2Et − HF, 6.67), 131 (20.76), 123 (19.49), 119 (17.80), 103 (17.58), 100 (10.06), 77 (33.05), 73 (14.19), 69 (51.06), 65 (21.40), 55 (24.58), 51 (21.19), 45 (33.90).

Diethyl 2-iodo-4-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1,5-pentanedioate (5c, n-$C_6F_{13}CH_2CH(CO_2Et)CH_2CHICO_2Et$): GC-MS 646 ($M^+$, 1.07), 601 ($M^+$ − OEt, 17.40), 600 (9.44), 573 (M^+ − CO_2Et, 7.44), 513 (M^+ − I, 17.77), 463 (15.07), 445 (15.20), 417 (100), 418 (18.50), 227 (10.05), 199 (7.72), 127 (I^+, 5.21), 55 (39.71).

Diethyl 2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1,5-pentanedioate (6c, n-$C_6F_{13}CH_2CH(CO_2Et)CH_2CH_2CO_2Et$): GC-MS 475 ($M^+$ − OEt, 87.10), 447 (M^+ − CO_2Et, 34.14), 446 (39.52), 427 (10.55), 419 (43.01), 417 (78.49), 399 (28.49), 374 (9.88), 357 (11.22), 353 (16.94), 295 (18.55), 131 (17.20), 127 (28.33), 119 (22.85), 101 (77.42), 99 (25.92), 77 (20.45), 73 (38.71), 69 (50.54), 65 (15.39), 59 (26.34), 55 (100), 51 (12.34), 45 (31.99).

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-2-iododecanoate (3d, n-$C_7F_{15}CH_2CHICO_2Et$). Similarly, the reaction of 8.77 g (17.68 mmol) of **1d** with 5.3 g (53 mmol) of **2** gave 4.2 g (74%; GLPC purity 100%) of **3d** and 0.2 g of **5d** (3%; GLPC purity 100%). **3d**: bp 65 °C/0.25 mmHg; ^{19}F NMR δ −81.39 (t, J = 8.4 Hz, 3F), −113.68 (dd, J = 271.6 Hz, 13.4 Hz, 1F), −115.56 (d, J = 275.8 Hz, 1F), −122.08 (s, 2F), −122.51 (s, 2F), −123.21 (s, 2F), −124.0 (s, 2F), −126.66 (s, 2F); ^1H NMR δ 4.61 (dd, J = 10.5, 3.5 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.44−3.24 (m, 1H), 2.81−2.61 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 170.96, 63.0, 39.0 (t, J = 21.2 Hz), 13.67, 5.34; GC-MS 596 (M^+, 7.49), 551 (M^+ − OEt, 4.37), 573 (M^+ − CO_2Et, 8.43), 469 (M^+ − I, 1.64), 425 (11.36), 422 (11.51), 413 (11.56), 377 (13.89), 169 (8.23), 141 (12.65), 131 (25.0), 127 (I^+, 18.45), 119 (19.64), 100 (16.47), 95 (17.86), 77 (29.17), 69 (57.94), 55 (100), 51 (14.29), 45 (18.25); FTIR 2985, 1744, 1558, 1377, 1297, 1241, 1214, 1144, 1132, 1108, 1004 cm^{-1}.

Diethyl 2-iodo-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-1,5-pentanedioate (5d, n-$C_7F_{15}CH_2CH(CO_2Et)CH_2CHICO_2Et$): bp 105 °C/0.25 mmHg; ^{19}F NMR δ −81.41 (m, 3F), −113.53 (m, 2F), −122.06 (m, 2F), −122.50 (s, 2F), −123.20 (s, 2F), −123.96 (s, 2F), −126.65 (s, 2F); ^1H NMR δ 4.38−4.17 (m, 5H), 3.11−2.17 (m, 5H),1.32−1.26 (m, 6H); ^{13}C NMR δ 172.86, 172.76, 170.94, 170.85, 62.29, 61.78, 39.76, 38.64, 38.50, 38.33, 33.17 (t, J = 21.6 Hz), 32.96 (t, J = 21.4 Hz), 17.84, 14.68, 14.07, 13.79; GC-MS 696 (M^+, 6.14), 651 (M^+ − OEt, 30.75), 650 (14.85), 622 (M^+ − HCO_2Et, 7.86), 569 (M^+ − I, 54.59), 513 (15.94), 495 (14.19), 467 (100), 127 (I^+, 4.99), 55 (16.38), 45 (11.46); FTIR 2985, 1739, 1701, 1653, 1474, 1465, 1457, 1439, 1394, 1374, 1245, 1214, 1151, 1104 cm^{-1}.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-2-iodoundecanoate (3e, n-$C_8F_{17}CH_2CHICO_2Et$). Similarly, 5.62 g (10.3 mmol) of **1e** reacted with 3.1 g (31 mmol) of **2** to give 3.8 g (82%; GLPC purity 98%) of **3e**. Small amounts of **4e** and **5e** were identified by GC-MS spectrum. **3e**: bp 86 °C/0.20 mmHg; ^{19}F NMR δ −81.56 (t, J = 8.4 Hz, 3F), −113.58 (dm, J = 272.9 Hz, 1F), −115.45 (d, J = 272.9 Hz, 1F), −121.94 (s, 2F), −122.27 (s, 4F), −123.17 (s, 2F), −123.90 (s, 2F), −126.68 (s, 2F); ^1H NMR δ 4.63 (dd, J = 10.5, 3.5 Hz, 1H), 4.25 (qd, J = 7.1 Hz, 3.7 Hz, 2H), 3.45−3.25 (m, 1H), 2.82−2.65 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 170.47, 62.72, 38.91 (t, J = 21.3 Hz), 13.69, 4.52; GC-MS 646 (M^+, 3.76), 601 (M^+ − OEt, 4.69), 573 (M^+ − CO_2Et, 15.05), 491 (11.81), 472 (22.80), 463 (17.82), 427 (29.63), 169 (13.08), 159 (18.98), 141 (28.70), 131 (20.72), 127 (I^+, 19.79), 119 (22.22), 100 (11.34), 77 (29.63), 73 (10.76), 69 (52.78), 55 (100), 51 (12.73), 45 (26.85); FTIR 2987, 2909, 1743, 1428, 1377, 1318, 1241, 1147, 1135, 1109, 1074, 1032, 1019 cm^{-1}.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoate (4e, n-$C_8F_{17}CH_2CH_2CO_2Et$): GC-MS 520 (M^+, 5.59), 493 (15.20), 475 (M^+ − OEt, 71.37), 473 (18.39), 427 (M^+ − CO_2Et − HF, 3.83), 169 (19.05), 131 (46.26), 123 (29.52), 119 (39.21), 109 (19.16), 103 (21.59), 100 (17.40), 77 (51.54), 73 (24.56), 69 (100), 65 (36.56), 59 (13.11).

Diethyl 2-iodo-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-1,5-pentanedioate (5e, n-$C_8F_{17}CH_2CH(CO_2Et)CH_2CHICO_2Et$): GC-MS 746 ($M^+$, 1.00), 701 ($M^+$ − OEt, 13.76), 673 (M^+ − HCO_2Et), 4.89), 619 (M^+ − I, 25.70), 563 (11.14), 545 (12.05), 517 (100), 227 (11.55), 119 (6.63), 99 (13.35), 73 (11.35), 69 (14.56), 59 (10.64), 55 (40.96), 45 (10.04), 43 (11.14).

Ethyl 4,4,5,5,7,7,8,8-Octafluoro-2-iodo-6-oxa-8-(fluorosulfonyl)octanoate (3f, $FSO_2CF_2CF_2OCF_2CF_2CH_2CHICO_2Et$). Similarly, 3.8 g (8.9 mmol) of **1f** reacted with 1.8 g (18 mmol) of **2** to give 2.8 g (88%; GLPC purity 92.4%) of **3f**; <6% of **5f** was identified by GC-MS spectrum. **3f**: bp 105−109.5 °C/2.45 mmHg; ^{19}F NMR δ +35.66 (s, 1F), −82.58 (s, 2F), −88.0 (s, 2F), −112.67 (s, 2F), −117.39 (ddd, J = 264.3 Hz, 27.4 Hz, 9.7 Hz, 1F), −119.27 (ddd, J = 264.1 Hz, 26.7 Hz, 1F); ^1H NMR δ 4.59 (dd, J = 10.3, 3.7 Hz, 1H), 4.25 (qd, J = 7.1 Hz, 0.8 Hz, 2H), 3.39−3.17 (m, 1H), 2.77−2.58 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 170.37, 62.72, 38.35 (t, J = 21.1 Hz), 13.70, 5.08; GC-MS 526 (M^+, 17.16), 481 (M^+ − OEt, 13.58), 433 (M^+ − CO_2Me − HF, 47.45), 399 (17.09), 371 (63.01), 355 (12.88), 353 (97.96), 299 (17.35), 223 (18.88), 203 (23.47), 143 (21.43), 127 (I^+, 22.45), 119 (62.76), 100 (47.45), 84 (38.52), 77 (31.38), 69 (20.15), 67 (63.78), 66 (52.30), 55 (100), 45 (24.23), 43 (32.65); FTIR 2985, 2940, 2920, 1744, 1462, 1445, 1372, 1351, 1330, 1244, 1207, 1197, 1115, 1073 cm^{-1}.

Diethyl 2-iodo-4-(2,2,3,3,5,5,6,6-octafluoro-4-oxa-6-(fluorosulfonyl))-1,5-pentanedioate (5f, $FSO_2CF_2CF_2OCF_2CF_2CH_2CH(CO_2Et)CH_2CHICO_2Et$): GC-MS 581 ($M^+$ − OEt, 10.77), 580 (6.53), 553 (M^+ − CO_2Me, 4.25), 525 (3.69), 499 (M^+ − I, 22.10), 443 (10.77), 397 (100), 227 (13.26), 133 (11.88), 127 (I^+, 11.33), 119 (22.93), 100 (15.88), 73 (16.16), 67 (28.18), 55 (79.56), 45 (12.71).

Methyl 4,4,5,5,6,6,6-Heptafluoro-2-iodohexanoate (9a, n-$C_3F_7CH_2CHICO_2Me$). Similarly, the reaction of 4.2 g (14.9 mmol) of **1a** with 3.2 g (37.2 mmol) of **8** yields 3.28 g (62%; GLPC purity 100%) of **9a** and 1.36 g (22%; GLPC purity 92.3%) of **10a** by distillation in vacuum. A small amount of 1:3 adduct was also identified by GC-MS spectrum. **9a**: bp 77−78.5 °C/20 mmHg; ^{19}F NMR δ −81.0 (t, J = 26.3 Hz, 3F), −128.30 (s, 2F), −114.67(dm, J = 272.9 Hz, 1F), −116.60 (dm, J = 272.3 Hz, 1F); ^1H NMR δ 4.64 (dd, J = 10.4Hz, 3.7 Hz, 1H), 3.79 (s, 3H), 3.43−3.23 (m, 1H), 2.82−2.62 (m, 1H); ^{13}C NMR δ 170.90, 53.47, 38.51 (t, J = 21.3 Hz), 4.45; GC-MS 382 (M^+, 18.53), 351 (M^+ − OMe, 2.54), 323 (M^+ − CO_2Me, 13.83), 255 (M^+ − I, 16.50), 227 (11.93), 127 (I^+, 12.56), 77 (9.64), 69 (15.48), 59 (CO_2Me^+, 100), 55 (45.69); HRMS obsd 381.9288, $C_7H_6O_2F_7I$, calcd 381.9300; FTIR 2956, 1750, 1438, 1377, 1267, 1229, 1202, 1183, 1130, 1110 cm^{-1}.

Dimethyl 2-iodo-4-(2,2,3,3,4,4,4-heptafluorobutyl)-1,5-pentanedioate (10a, n-$C_3F_7CH_2CH(CO_2Me)CH_2CHICO_2Me$): bp 113−114.5 °C/1.8 mmHg; ^{19}F NMR δ −80.95 (t, J = 9.57 Hz, 3F), −114.68 (m, 2F), −128.25 (s, 2F); ^1H NMR δ 4.41−4.33 (m, 1H), 3.77 (d, J = 5.91 Hz, 3H), 3.74 (s, 3H), 3.08−2.11 (m, 5H); ^{13}C NMR δ 173.23, 173.12, 171.39, 170.85, 53.16, 52.63, 39.54, 38.64, 38.30, 38.10, 32.82 (t, J = 22.0 Hz), 32.52 (t, J = 22.0 Hz), 17.11, 14.09; GC-MS 468 (M^+, 1.16), 436 (31.25), 437 (19.21), 341 (M^+ − I, 100), 282 (20.22), 281 (39.71), 262 (19.49), 253 (15.26), 127 (I^+, 6.34), 69 (5.72), 59 (40.07), 55 (27.94); HRMS obsd 467.9696, $C_{11}H_{12}O_4F_7I$, calcd 467.9669; FTIR 2955, 1798, 1744, 1439, 1354, 1266, 1227, 1201, 1174, 1120 cm^{-1}.

Dimethyl 2-iodo-6-(2,2,3,3,4,4,4-heptafluorobutyl)-4-(methoxycarbonyl)-1,7-heptanedioate (n-$C_3F_7CH_2CH(CO_2Me)CH_2CH(CO_2Me)CH_2CHICO_2Me$): GC-MS 523 ($M^+$ − OMe, 15.37), 495 (M^+ − CO_2Me, 4.26), 427 (M^+ − I, 100), 363 (21.48), 308 (14.26), 282 (40.19), 249 (13.33), 237 (10.69), 139 (34.44), 127 (I^+, 16.67), 87 (16.48), 81 (11.62), 59 (CO_2Me^+, 70.37), 55 (51.11).

Methyl 4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptanoate (9b, n-$C_4F_9CH_2CHICO_2Me$). Similarly, the reaction of 7.65 g (22.1 mmol) of **1b** and 5.7 g (6.3 mmol) of **8** gives 4.65 g (56%;

GLPC purity 100%) of **9b** and 1.8 g (18%; GLPC purity: 98%) of **10b**. **9b**: bp 106−108 °C/60 mmHg; ^{19}F NMR δ −81.66 (m, 3F), −113.94 (dm, J = 273.0 Hz, 1F), −115.8 (d, J = 273.2 Hz, 1F), −124.88 (s, 2F), −126.38 (s, 2F); ^{1}H NMR δ 4.64 (dd, J = 10.4 Hz, 3.6 Hz, 1H), 3.79 (s, 3H), 3.44−3.24 (m, 1H), 2.83−2.64 (m, 1H); ^{13}C NMR δ 170.66, 53.13, 38.52 (t, J = 21.2 Hz), 4.16; GC-MS 432 (M$^+$, 41.57), 401 (M$^+$ − OMe, 7.06), 373 (M$^+$ − CO$_2$Me, 22.55), 305 (M$^+$ − I, 15.49), 277 (19.02), 165 (25.10), 141 (18.33), 127 (I$^+$, 25.10), 77 (16.08), 69 (CF$_3^+$, 20.49), 59 (CO$_2$Me$^+$, 100), 55 (78.82); HRMS obsd 431.9277, $C_8H_6O_2F_9I$, calcd 431.9269; FTIR 2956, 1750, 1438, 1378, 1298, 1235, 1223, 1209, 1185, 1137, 1109, 1072, 1043, 1023 cm^{-1}.

Dimethyl 2-iodo-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,5-pentanedioate (10b, n-$C_4F_9CH_2CH(CO_2Me)CH_2CHICO_2Me$): bp 99−115 °C/0.6−0.75 mmHg; ^{19}F NMR δ −81.59 (s, 3F), −113.91 (m, 2F), −124.90(s, 2F), −126.38 (m, 2F); ^{1}H NMR δ 4.28 (dt, J = 5.6 Hz, 8.7 Hz, 1H), 3.69 (dd, J = 5.9 Hz, 0.7 Hz, 3H), 3.66 (s, 3H), 3.00−2.03 (m, 5H); ^{13}C NMR δ 173.23, 173.12, 171.39, 171.34, 53.18, 52.64, 39.54, 38.62, 38.28, 38.10, 33.01 (t, J = 22.0 Hz), 32.28 (t, J = 22.1 Hz), 17.03, 13.96; GC-MS 518 (M$^+$, 3.25), 487 (M$^+$ − OMe, 18.11), 486 (23.62), 459 (M$^+$ − CO$_2$Et, 6.99), 391 (M$^+$ − I, 100), 359 (14.96), 332 (16.54), 331 (46.85), 312 (25.20), 303 (17.13), 127 (I$^+$, 9.35), 113 (17.13), 75 (16.34), 69 (14.17), 59 (91.34), 55 (54.33); HRMS obsd 517.9650, $C_{12}H_{12}O_4F_9I$, calcd 517.9637; FTIR 2954, 1744, 1438, 1356, 1259, 1237, 1203, 1185, 1136, 1021 cm^{-1}.

Methyl 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-2-iodononanoate (9c, n-$C_6F_{13}CH_2CHICO_2Me$). Similarly, the reaction of excess **1c** (21.7 g, 48.6 mmol) with 2.1 g (24.4 mmol) of **8** yields 7.5 g (58% yield based on **8**; GLPC purity 100%) of **9c** by distillation; 14.5 g of **1c** was recovered (67%) after reaction and ~1% of **10c** was identified by GC-MS spectrum. **9c**: bp 55−56 °C/0.18 mmHg; ^{19}F NMR δ −81.51 (t, J = 8.7 Hz, 3F), −113.74 (dd, J = 272.1 Hz, 13.2 Hz, 1F), −115.59 (dm, J = 272.2 Hz, 1F), −122.17 (m, 2F), −123.25 (s, 2F), −123.94 (s, 2F), −126.64 (s, 2F); ^{1}H NMR δ 4.65 (dd, J = 10.4 Hz, 3.6 Hz, 1H), 3.79 (s, 3H), 3.45−3.24 (m, 1H), 2.83−2.65 (m, 1H); ^{13}C NMR δ 170.76, 54.19, 38.62 (t, J = 21.2 Hz), 4.25; GC-MS 532 (M$^+$, 16.41), 501 (M$^+$ − OMe, 2.49), 473 (M$^+$ − CO$_2$Me, 7.79), 405 (M$^+$ − I, 2.56), 386 (11.27), 141 (9.72), 136 (8.05), 127 (9.85), 69 (18.18), 63 (10.48), 59 (100), 55 (36.36); HRMS obsd 531.9194, $C_{10}H_6O_2F_{13}I$, calcd 531.9205; FTIR 2956, 1750, 1438, 1344, 1241, 1146, 1109, 1074 cm^{-1}.

Dimethyl 2-iodo-4-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1,5-pentanedioate (10c, n-$C_6F_{13}CH_2CH(CO_2Me)CH_2CHICO_2Me$): GC-MS 618 (M$^+$, 4.25), 588 (2.04), 587 (M$^+$ − OMe, 22.75), 586 (16.57), 559 (M$^+$ − OMe, 7.16), 558 (4.99), 492 (11.80), 491 (M$^+$ − I, 100), 459 (9.34), 432 (16.36), 431 (35.96), 412 (16.92), 403 (12.64), 127 (I$^+$, 3.92), 69 (CF$_3^+$, 5.27), 59 (CO$_2$Me$^+$, 19.10), 55 (10.74).

Methyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-iodododecanoate (9d, n-$C_7F_{15}CH_2CHICO_2Me$). Similarly, the reaction of 7.6 g (15 mmol) of **1d** and 4.5 g (52 mmol) of **8** yields 4.7 g (79%; GLPC purity 93.4%) of **9d**. Small amounts of 1:2 addition adduct **10d** and addition−reduction product **9dH** were also identified by GC-MC spectrum. **9d**: bp 77−80.5 °C/1.5 mmHg; ^{19}F NMR δ −81.45 (t, J = 8.3 Hz, 3F), −113.78 (dd, J = 271.7 Hz, 13.2 Hz, 1F), −115.67 (d, J = 272.6 Hz, 1F), −122.05 (s, 2F), −122.48 (s, 2F), −123.20 (s, 2F), −124.0 (s, 2F), −126.66 (s, 2F); ^{1}H NMR δ 4.64 (dd, J = 10.4, 3.6 Hz, 1H), 3.80 (s, 3H), 3.44−3.24 (m, 1H), 2.82−2.64 (m, 1H); ^{13}C NMR δ 171.16, 53.58, 38.93 (t, J = 21.5 Hz), 4.51; GC-MS 582 (M$^+$, 24.12), 551 (M$^+$ − OMe, 4.53), 523 (M$^+$ − CO$_2$Me, 15.49), 455 (M$^+$ − I, 4.90), 436 (24.90), 427 (16.18), 169 (10.59), 141 (29.80), 136 (15.59), 131 (24.71), 127 (I$^+$, 25.88), 119 (24.80), 104 (18.73), 100 (14.51), 77 (27.84), 69 (52.94), 63 (30.98), 59 (100), 55 (85.45), 51 (13.33); FTIR 2956, 1750, 1438, 1242, 1214, 1150, 1132, 1109, 1092 cm^{-1}.

Methyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoate (9d, n-$C_7F_{15}CH_2CH_2CO_2Me$): GC-MS 473 (M$^+$ − F, 2.54), 425 (M$^+$ − OMe, 21.74), 169 (5.01), 137 (12.85), 131 (19.76), 119 (17.59), 100 (9.19), 89 (15.15), 77 (31.62), 69 (43.48), 65 (19.37), 59 (100), 55 (20.26), 51 (18.87), 42 (12.06).

Dimethyl 2-iodo-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-1,5-pentanedioate (10d, n-$C_7F_{15}CH_2CH(CO_2Me)CH_2CHICO_2Me$): GC-MS 668 (M$^+$, 3.37), 637 (M$^+$ − OEt, 21.45), 636 (13.65), 609 (M − CO$_2$Et, 7.76), 541 (M$^+$ − I, 100), 542 (14.18), 509 (11.17), 482 (23.23), 481 (40.78), 462 (16.67), 453 (14.72), 127 (I$^+$, 4.52), 113 (6.52), 69 (10.55), 59 (32.98), 55 (19.86).

Methyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-iodoundecanoate (9e, n-$C_8F_{17}CH_2CHICO_2Me$). Similarly, the reaction of 5.8 g (10.6 mmol) of **1e** and 2.7 g (31.4 mmol) of **8** yields 2.4 g (72%; GLPC purity 96%) of **9e**: bp 84−97 °C/0.45 mmHg; ^{19}F NMR δ −81.52 (t, J = 9.1 Hz, 3F), −113.77 (dm, J = 271.7 Hz, 1F), −115.65 (dm, J = 272.9 Hz, 1F), −121.98 (s, 2F), −122.32 (s, 4F), −123.17 (s, 2F), -123.91 (s, 2F), −126.67 (s, 2F); ^{1}H NMR δ 4.64 (dd, J = 10.4, 3.6 Hz, 1H), 3.79 (s, 3H), 3.44−3.24 (m, 1H), 2.82−2.62 (m, 1H); ^{13}C NMR δ 171.16, 53.57, 39.05 (t, J = 21.3 Hz), 4.55; GC-MS 632 (M$^+$, 48.11), 613 (M$^+$ − F, 1.75), 601 (M$^+$ − OEt, 7.90), 573 (M$^+$ − CO$_2$Me, 25.47), 505 (M$^+$ − I, 9.20), 486 (M$^+$ − I − F, 44.10), 477 (26.18), 131 (13.21), 127 (I$^+$, 12.15), 119 (14.15), 69 (22.88), 59 (100), 55 (33.25); HRMS obsd 631.9129, $C_{12}H_6O_2F_{17}I$, calcd 631.9141; FTIR 2956, 1750, 1718, 1653, 1559, 1541, 1438, 1340, 1216, 1183, 1135, 1110 cm^{-1}.

Dimethyl 2-iodo-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-1,5-pentanedioate (10e, n-$C_8F_{17}CH_2CH(CO_2Me)CH_2CHICO_2Me$). **10e** (0.19 g, 5%; GLPC purity 92%) was isolated by distillation from the above reaction mixture: bp 96−108 °C/0.45 mmHg; ^{13}C NMR δ 173.15, 173.06, 171.29, 171.24, 53.15, 52.63, 39.38, 38.44, 38.16, 38.00, 33.00 (t, J = 22.2 Hz), 32.72 (t, J = 22.3 Hz), 16.95, 13.77; GC-MS 718 (M$^+$, 3.22), 699 (M$^+$ − HF, 1.22), 687 (M$^+$ − MeOH, 20.83), 686 (M$^+$ − OEt, 12.05), 592 (M$^+$ − I, 15.13), 591 (100), 559 (10.69), 532 (19.93), 531 (39.49), 512 (15.13), 503 (14.31), 59 (17.30), 55 (9.06).

Reaction of 1a with methyl methacrylate. Similarly, 7.6 g (25.7 mmol) of **1a** was reacted with 3.6 g (35.9 mmol) of methyl methacrylate under UV irradiation in a quartz tube for 24 h; 48% of **1a** was converted as shown in ^{19}F NMR spectrum. The yields and structure of the main products **12**−**16** were identified by GC-MS.

Methyl 4,4,5,5,6,6,6-heptafluoro-2-methylhexanoate (12, n-$C_3F_7CH_2CHMeCO_2Me$, 11.3%): GC-MS 270 (M$^+$, 4.31), 250 (M$^+$ − HF, 0.99), 239 (M$^+$ − OMe, 17.93), 211 (M$^+$ − CO$_2$Me, 18.79), 145 (8.49), 127 (I$^+$, 4.70), 101 (7.46), 95 (5.69), 91 (9.66), 69 (CF$_3^+$, 20.17), 59 (CO$_2$Me$^+$, 100), 47 (64.83), 43 (39.31), 41 (17.76).

Methyl 4,4,5,5,6,6,6-heptafluoro-2-methyl-2-hexenoate (13, n-$C_3F_7CH{=}CMeCO_2Me$, 22.1%): GC-MS 268 (M$^+$, 2.79), 248 (M$^+$ − HF, 37.65), 237 (M$^+$ − OMe, 100), 189 (30.74), 169 (C$_3$F$_7^+$, 9.19), 163 (30.00), 145 (40.59), 139 (24.71), 119 (19.41), 101 (15.59), 99 (23.38), 95 (15.74), 90 (15.15), 89 (21.76), 77 (17.06), 69 (41.76), 59 (58.24), 54 (10.88), 51 (19.71), 43 (49.41).

Methyl 4,4,5,5,6,6,6-heptafluoro-2-iodo-2-methylhexanoate (14, n-$C_3F_7CH_2CIMeCO_2Me$, 24.8%): GC-MS 396 (M$^+$, 1.93), 365 (M$^+$ − OMe, 1.66), 337 (M$^+$ − CO$_2$Me, 12.02), 269 (M$^+$ − I, 61.88), 241 (100), 237 (8.11), 189 (12.85), 145 (12.15), 139 (9.25), 127 (I$^+$, 15.06), 77 (13.26), 69 (54.70), 59 (61.88), 43 (13.95), 41 (38.12).

Methyl 5,5,6,6,7,7,7-heptafluoro-2,3-dimethyl-2-heptenoate (15, n-$C_3F_7CH_2CMe{=}CMeCO_2Me$, 33.2%): GC-MS 310 (M$^+$, 4.10), 296 (4.82), 295 (42.99), 251 (7.47), 241 (2.02), 119 (1.54), 111 (2.93), 69 (8.31), 59 (9.38), 55 (5.79), 44 (2.84).

Dimethyl 4-(2,2,3,3,4,4,4-heptafluorobutyl)-2,4-dimethyl-2-pentene-1,5-dioate (16, n-$C_3F_7CH_2CMe(CO_2Me)CH{=}CMeCO_2Me$, 2.7%): GC-MS 368 (M$^+$, 2.16), 337 (17.47), 309 (41.35), 308 (74.36), 277 (19.71), 276 (12.02), 257 (17.23), 249 (58.65), 241 (10.98), 229 (27.24), 199 (14.34), 159 (9.13), 153 (18.59), 139 (39.10), 125 (14.02), 109 (14.90), 100 (25.64), 99 (31.73), 85 (20.83), 79 (25.32), 77 (25,32), 69 (81.09), 65 (20.11), 59 (100), 55 (19.79), 45 (11.70), 41 (45.19).

Reaction of 1a with *N,N*-Dimethylacrylamide (17) under UV Irradiation. Similarly, the reaction of 12.9 g (43.6 mmol) of **1a** with 9.5 g (95 mmol) of **17** resulted in a conversion of 63% after irradiated for 48 h; 8.78 g (81%) of **18a** was isolated by distillation in vacuum, with a boiling point of 85−87 °C/2.7 mmHg (GLPC purity 92.4%).

***N,N*-Dimethyl-4,4,5,5,6,6,6-heptafluoro-2-iodohexanamide (18a, *n*-$C_3F_7CH_2CHICONMe_2$):** ^{19}F NMR δ −80.96 (s, 3F), −114.14 (dd, J = 271.6 Hz, 20.5 Hz, 1F), −116.75 (dd, J = 269.8 Hz, 18.8 Hz, 1F), −128.35 (s, 2F); ^1H NMR δ 4.81 (dd, J = 9.4, 3.7 Hz, 1H), 3.66−3.46 (m, 1H), 3.07 (s, 3H), 2.99 (s, 3H), 2.84−2.61 (m, 1H); ^{13}C NMR δ 168.69, 37.93 (t, J = 20.5 Hz), 37.33, 36.42, 4.47; GC-MS 395 (M^+, 5.95), 323 (M^+ − $CONMe_2$, 2.12), 268 (M^+ − I, 50.61), 240 (20.73), 127 (I^+, 7.09), 72 ($CONMe_2^+$, 100), 44 (22.87), 42 (21.04); HRMS obsd 394.9624, $C_8H_9ONF_7I$, calcd 394.9617; FTIR 2937, 1667, 1541, 1490, 1460, 1414, 1404, 1353, 1251, 1226, 1201, 1184, 1104, 1057 cm^{-1}.

Reaction of 1a with Acrylonitrile (19) under UV Irradiation. Similarly, the reaction of 5.6 g (18.9 mmol) of **1a** with 3.0 g (56.7 mmol) of **19** gives 52% of **20a** and 47% of **21a** as shown in the ^{19}F NMR spectrum after irradiation for 36 h. Distillation gave 2.7 g of **20a** (41% isolated yield; GLPC purity 100%) and 2.4 g of **21a** (32%; GLPC purity 98%).

4,4,5,5,6,6,6-Heptafluoro-2-iodohexanenitrile (20a, *n*-$C_3F_7CH_2CHICN$): bp 82 °C/20 mmHg; ^{19}F NMR δ −80.94 (s, 3F), −114.80 (dm, J = 274.0 Hz, 1F), −116.32 (dm, J = 274.4 Hz, 1F), −128.15 (s, 2F); ^1H NMR δ 4.54 (dd, J = 10.4, 4.7 Hz, 1H), 3.19−2.93 (m, 1H), 2.96−2.86 (m, 1H); ^{13}C NMR δ 118.05 (CN), 39.90 (t, J = 21.5 Hz), −20.25 (−CHI−); GC-MS 349 (M^+, 63.21), 330 (M^+ − F, 1.99), 222 (M^+ − I, 41.01), 202 (12.67), 180 (40.55), 169 (34.56), 166 (27.07), 127 (I^+, 49.77), 119 (23.96), 102 (30.41), 100 (12.79), 69 (100), 51 (19.01); FTIR 2978, 2244, 1353, 1253, 1136, 1122, 1106, 1106 cm^{-1}.

2-Iodo-4-(2,2,3,3,4,4,4-heptafluorobutyl)pentanedinitrile (21a, *n*-$C_3F_7CH_2CHCNCH_2CHICN$): bp 135.5−140 °C/2.5 mmHg; ^{19}F NMR δ −80.93 (t, J = 9.0 Hz, 3F), −113.16 to −115.85 (m, 2F), −128.12 (s, 2F); ^1H NMR δ 4.58−4.45 (m, 1H), 3.34−3.24 (m, 1H), 2.70−2.33 (m, 4H); ^{13}C NMR δ 118.40, 118.15, 118.06, 117.84 (CN), 40.08, 38.67, 32.57 (t, J = 21.6 Hz), 32.49 (t, J = 21.6 Hz), 25.43 (t, J = 3.2 Hz), 25.25 (t, J = 3.1 Hz), −7.78, −20.78; GC-MS 402 (M^+, 38.08), 349 (30.38), 275 (M^+ − I, 37.15), 255 (21.35), 248 (13.02), 235 (13.89), 228 (31.77), 222 (12.50), 215 (8.72), 208 (12.50), 202 (26.39), 180 (87.50), 169 (16.67), 166 (16.15), 127 (79.86), 119 (25.35), 102 (30.03), 91 (24.31), 84 (27.43), 69 (100), 64 (24.65), 54 (61.11), 53 (30.03), 52 (41.15), 51 (28.82), 41 (13.72); FTIR 2961, 1717, 1439, 1386, 1354, 1269, 1229, 1124 cm^{-1}.

Reaction of 1a with Acrylic Acid (22) under UV Irradiation. Similarly, a mixture of 4.88 g of **1a** (16.2 mmol) and 5.83 g of **22** (81 mmol) was irradiated for 48 h, and 90% of **1a** was converted as shown in ^{19}F NMR spectroscopy; 2.67 g of **23a** was isolated by a column chromatography (68% isolated yield; GLPC purity 96%).

4,4,5,5,6,6,6-Heptafluorohexanoic acid (23a, *n*-$C_3F_7CH_2CH_2CO_2H$): ^{19}F NMR δ −81.15 (s, 3F), −116.24 (m, 2F), −128.28 (s, 2F); ^1H NMR δ 10.07 (s, br, 1H), 2.71 (t, J = 7.7 Hz, 2H), 2.47 (m, 2H); ^{13}C NMR δ 180.33, 28.72 (t, J = 22.3 Hz), 28.01 (t); GC-MS 243 (M^+ + 1, 0.09), 223 (M^+ − F, 0.15), 183 (M^+ − CH_2CO_2H, 0.04), 124 (8.16), 119 (0.15), 69 (0.93), 59 (4.72), 45 (8.10).

Reaction of 1b with 2-Cyclohexen-1-one. The mixture of 0.9 g (9.4 mmol) of 2-cyclohexen-1-one and 3.0 g (8.7 mmol) of **1b** was irradiated with 254 nm UV light for 24 h in a quartz tube. A viscous polymer was obtained, which was dissolved in acetone, and < 5% conversion of **1b** was observed when the solution was analyzed by ^{19}F NMR spectroscopy.

Photoreaction of 1d with Methyl Acrylate in the Presence of Hydroquinone. A quartz tube was charged with 1.3 g (2.7 mmol) of **1d**, 1.0 g (11.6 mmol) of methyl acrylate, and 0.63 g (5.7 mmol) of hydroquinone. The mixture was irradiated with 254 nm UV light for 24 h. ^{19}F NMR analysis showed that 32.8% of **1d** was converted, and 83% of 1:1 adduct **9d**, 3% of **9dH** and 5.8% of 1:2 adduct **10d** was formed based on GC-MS analysis.

When 30 mol % of hydroquinone was used in the reaction, the conversion of **1d** was 59%. No inhibition effect was observed compared to the reaction without hydroquinone.

Photoreaction of 1b with Ethyl Acrylate in the Presence of Cu. Similarly, 1.4 g (4 mmol) of *n*-perfluorobutyl iodide (**1b**) was reacted with 1.1 g (11 mmol) of ethyl acrylate in the presence of 0.4 g (6.3 mmol) of copper powder under UV irradiation. After reaction for 24 h, the conversion was 33% as shown in the ^{19}F NMR spectrum; 13.6% of 1:1 adduct **3b**, 42.5% of **4b**, 33.8% of 1:2 adduct **5b**, 4.8% of **6b**, and ~5% of 1:3 adduct was formed as analyzed and assigned by GLPC and GC-MS spectra.

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