Photoinduced Electron-transfer Reaction of Pentafluoroiodobenzene with Alkenes

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Abstract: Irradiation of pentafluoroiodobenzene and alkenes gave the corresponding adducts. The presence of single electron-transfer scavengers, (p-dinitrobenzene and t-Bu$_2$NO) and the free radical inhibitor (hydroquinone) suppressed the reaction. A photoinduced electron-transfer mechanism is proposed.

Keywords: Photochemistry, pentafluoroiodobenzene, alkene, single electron-transfer, free radical inhibitor.

Introduction

The investigation of pentafluoroiodobenzene, C$_6$F$_5$I (**1**), previously, has been concentrated mainly on its radical generation and reaction with aromatic compounds [1], besides the formation of pentafluorophenyl organometallic compounds [2]. The pentafluorophenyl radical was formed *in situ* by oxidation of pentafluorophenyl-hydrazine [3], by photochemical decomposition of **1** [2a] or pyrolysis of pentafluorobenzenesulphonyl chlorides [4]. The introduction of the pentafluorophenyl moiety to toluene with [C$_6$F$_5$Xe]$^+$[AsF$_6$]$^-$ was also assumed to be through the pentafluorophenyl radical [5].

Very recently, we found that this radical can be photolytically generated from both pentafluorophenyl per-(poly)fluoroalkanesulphonates (R$_F$SO$_3$C$_6$F$_5$) and C$_6$F$_5$I (**1**) [2d, 6]. Using this method, the pentafluorophenyl group can be smoothly introduced into benzenes, anilines, pyrroles, indoles, imidazoles, aromatic ethers or phenols. Furthermore

a photo-induced electron-transfer (PET) rather than a simple radical mechanism has been proposed. Surprisingly, to our knowledge, there is no report of the reaction of **1** with alkenes in spite of the fact that a palladium catalyzed addition of **1** with alkyne has already been described [7]. Herein, we present the results of irradiation of **1** with simple olefins as well as allyl ethers.
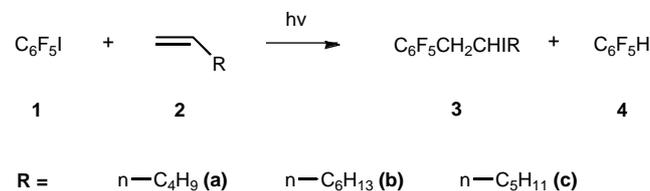
Scheme 1.

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$$C_6F_5I + {=\!\!=}_R \xrightarrow{h\nu} C_6F_5CH_2CHIR + C_6F_5H$$

1   **5**   **6**   **4**

5a : ⟋⟍O⟍

5b : ⟋⟍O^Ac

6a :

6b :
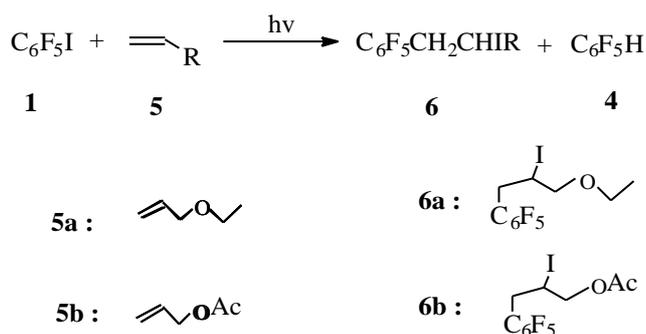
Scheme 2.

Results and Discussion

Irradiation of **1** with alkenes **2** (**1:2**=1:10) for 12h gave the 1:1 adducts in moderate yields in addition to a small amount of pentafluorobenzene (**4**) (Scheme 1).

The reaction temperature, ca. 80°C, was a result of the irradiation, however, at this temperature without irradiation no reaction took place, an indication that irradiation was essential.

Similarly, the reaction of **1** with excess ethyl allyl ether and allyl acetate gave the corresponding adducts in high yields (Scheme 2).

The reaction results are listed in Table 1.

All the reactions proceeded without extra solvent; when using CH_3CN or CH_3OH as a solvent the yield of **4** was increased (see Table 1, Entry 16-18).

Under similar conditions **1** did not react with electron-deficient alkenes such as $CH_2=CHCN$. When **1** reacted with arylallylethers (**7**) in CH_3CN, both the pentafluorinated biphenyl products **8** and the 1:1 adducts **9** were obtained. (see, Entry 8-10, Table 1). Compound **4** was not detected by ^{19}F NMR spectroscopy in these reactions. The total yield of **8** and **9** was remarkably dependent upon the ratio of **1** and **7** used. For example, when **1:7a** was 1:3, the total yield of (**8**+**9**) reached 66%, whereas 1:1 only 37%. It was also found that the para substitute (X) in **7** has some influence on the yield of **8** and **9**. For example, the reactant with an electron-donating group, e.g. **7b**, seemed to give more favorable substitu-

Table 1. *Irradiation reaction of **1** with alkenes[a].*

Entry	Olefin[a]	Solvent	Conv.%[b]	Products	Yield%[c]	C_6F_5H%[b]
1	2a	-	60	3a	30	10
2	2b	-	70	3b	80	10
3	2c	-	70	3c	60	5
4[d]	2a	-	26	3a	-	10
5[e]	2a	-	30	3a	-	10
6[f]	2a	-	35	3a	-	10
7	5b	-	60	6b	60	trace
8	7a	CH_3CN	50	8a	36	-
				9a	24	
9	7b	CH_3CN	79	8b	40	-
				9b	26	
10	7c	CH_3CN	46	8c	21	-
				9c	42	
11	10	-	70	11	52	8
				12	6	-
12	5a	-	82	6a	70	9
13[d]	5a	-	46	6a	34	10
14[e]	5a	-	53	6a	40	9
15[f]	5a	-	56	6a	46	9
16[g]	5a	n-C_6H_{14}	82	6a	54	25
17[g]	5a	CH_3CN	86	6a	40	36
18[g]	5a	CH_3OH	100	6a	50	30

(a) **1**: Alkenes=1:10, for 10-12h; (b) Determined by ^{19}F NMR; (c) Isolated yields based on **1** consumed; (d) 20mol% p-DNB was added; (e) 20mol% t-Bu$_2$NO was added; (f) 20mol% HQ was added; (g) **1**: **5a**=1:3.
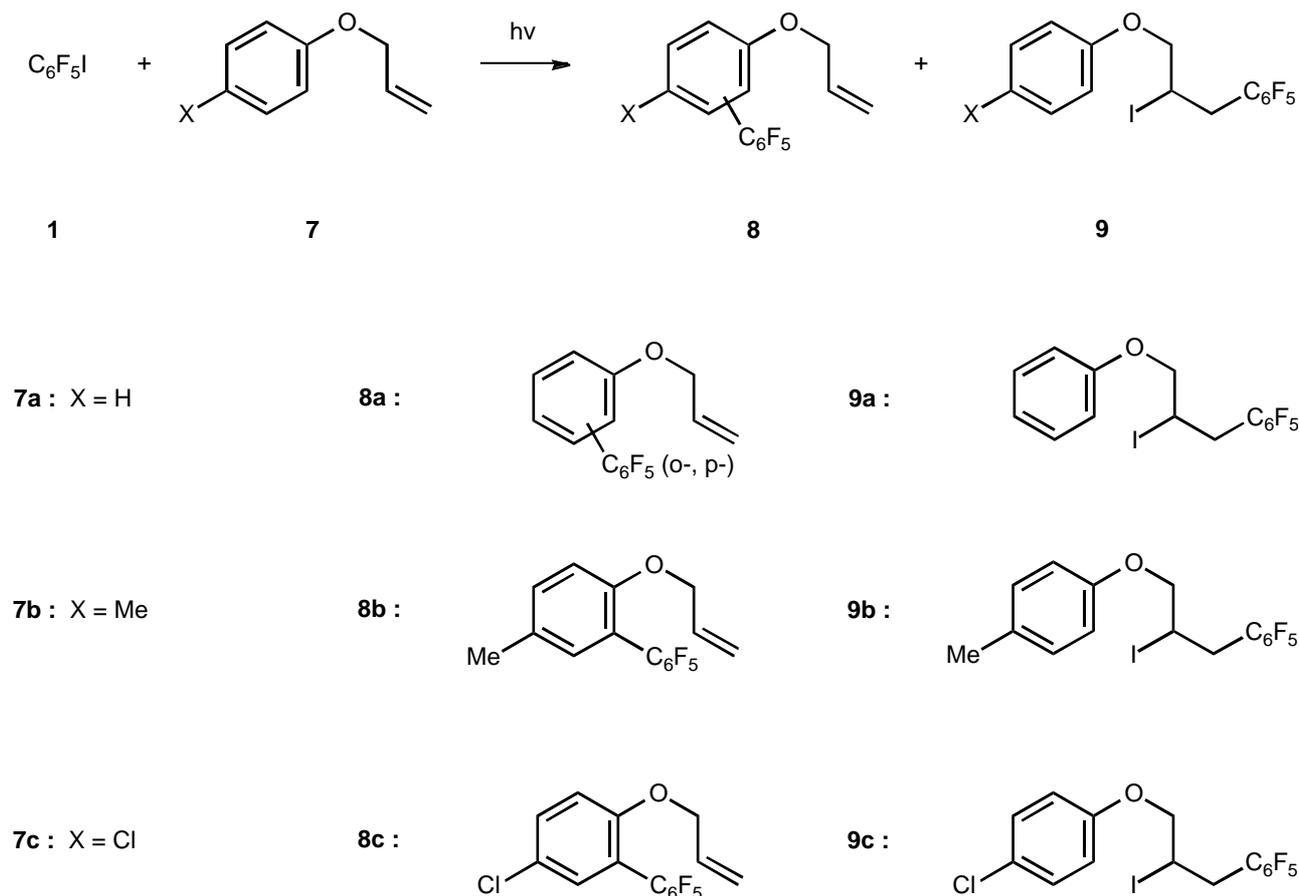
Scheme 3.

tion in the benzene ring than addition to the alkene, whereas the reverse result for **7c** was observed (Scheme 3).

Noteworthy, for **7a**, only ortho- and para- (**8a**) (1:2), for **7b** and **7c** merely ortho-(related to allyoxy group) **8b** or **8c** were isolated and none of the other regioisomers were detected.

Usually diallyether (DAE, **10**) can trap efficiently the poly or perfluoroalkyl radicals resulting in the formation of tetrahydrofuran derivatives (Clock reaction) [8]. However, in this case, besides the major product, **11**, a small amount of 1:1 adduct (**12**) was also obtained (Scheme 4).

In order to elucidate the reaction mechanism, inhibition studies were carried out. For example, the presence of single electron transfer (SET) scavengers, p-dinitrobenzene (p-DNB) and t-Bu$_2$NO or a free radical inhibitor hydroquinone (HQ), in the reaction system significantly suppressed the reaction of **1** and **2a** or **5a** (see Entry 4-6, 13-15).

All the results, in addition to our previous work [2d, 6], seem to show that the mechanism may involve a photoinduced electron-transfer cation diradical coupling process, described using **7a** as an example, as shown in Scheme 5.

The radical cation of **7a** and pentafluorophenyl radical are generated through an electron-transfer under UV irradiation. The resulting C$_6$F$_5$• either adds to the alkene giving the
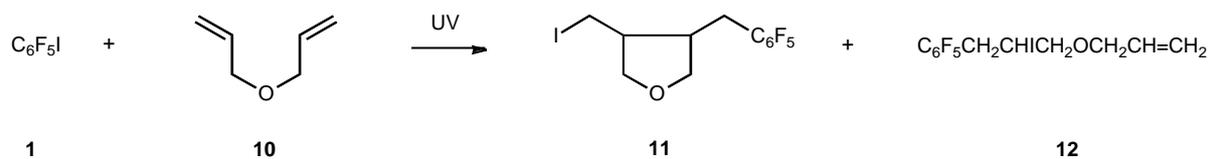
Scheme 4.
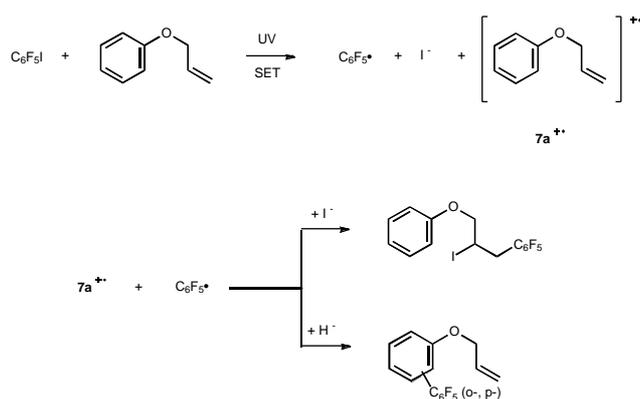
Scheme 5.

adduct or attacks the benzene ring producing the corresponding o- and p-biphenyl mixture.

It is interesting to note that both cyclized (**11**) and uncyclized (**12**) products were obtained in the reaction of **1** and **10**, indicating that, as very recently reported by Ashby et al, the uncyclized, like cyclized, product, can still be formed via SET pathway [9]. On the other hand, for the formation of the cyclized product **11**, the cation diradical coupling may proceed either stepwise or by first transfering DAE$^{+\cdot}$ to the distonic radical cation [10] (Scheme 6).

Experimental

M.P.s are uncorrected. IR spectra were obtained on a Schimadzu-440 instrument in potassium bromide pellets for all solid samples and in films for all liquid samples. ^{1}H NMR spectra were recorded on a Jeol FX-90Q instrument using tetramethylsilane as an internal standard. ^{19}F NMR spectra were recorded on a Varian EM-360 instrument at 56.4 MHz using trifluoroacetic acid as an external standard with chemical shifts in ppm positive upfield. Mass spectra was obtained on a Finnigan-4021 instrument. Silica gel (10-40μ) was used for column chromatography.

Typical procedure of the reaction of pentafluoroiodoben-zene (1) with alkene (2) and (5)

Under a N_2 atmosphere, a stirred mixture of **1** (2.94g, 10mmol) and 1-hexene (8.4g, 100mmol) in a quartz flask,

distonic radical cation
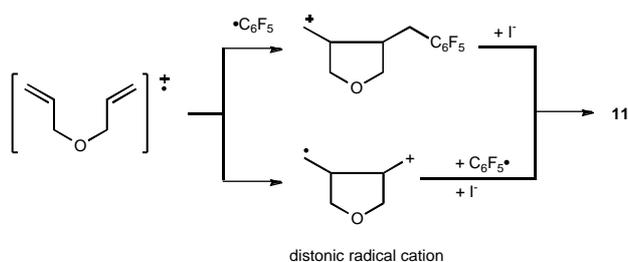
Scheme 6.

connected to a condenser, was exposed to a high pressure mercury lamp (300W) at a distance of 8cm for 12h. ^{19}F NMR, showed that 10% of pentafluorobenzene (**4**) was formed. The mixture was concentrated under reduced pressure and was subjected to column chromatography, using light petroleumether as eluent to give the product **3a** (0.68g, 30%).

2-Iodo-1-pentafluorophenyl hexane (**3a**)

max/cm^{-1}: 2890, 1530, 1510, 1130, 950-1020; $_H$ (CDCl$_3$): 4.20 (m, 1H), 3.30 (d, 2H, J=6), 1.63 (m, 2H), 1.33 (m, 4H) and 0.88 (s, 3H)ppm; $_F$(CDCl$_3$): 64.3 (m, 2F), 78.9 (t, 1F), 84.3 (m, 2F) ppm; m/z: 251 (M$^+$-I, 31%), 181(C$_6$F$_5$CH$_2$$^+$, 100%), 127 (2.7%), 57 (30%); Found: C, 38.18; H, 3.36; F, 25.25%; Calc. for C$_{12}$H$_{12}$F$_5$I: C, 38.10; H, 3.17; F, 25.13%.

2-Iodo-1-pentafluorophenyl octane (**3b**)

max/cm^{-1}: 2890, 1530, 1510, 1120; $_H$ (CDCl$_3$): 4.27 (m, 1H), 3.33 (d, 2H, J=6), 0.90-2.0 (m, 13H) ppm; $_F$(CDCl$_3$): 66.0 (m, 2F), 80.0 (t, 1F), 86.2 (m, 2F) ppm; m/z: 279 (M$^+$-I, 12.4%), 278 (M$^+$-HI, 46.1%), 194 (M$^+$-I-C$_6$H$_{13}$, 56.8%), 181 (C$_6$F$_5$CH$_2$$^+$, 100%), 167 (5.4%); Found: C, 41.38; H, 3.94; F, 23.40%; Calc. for C$_{12}$H$_{12}$F$_5$I: C, 41.39; H, 3.97; F, 23.38%.

2-Iodo-1-pentafluorophenyl heptane (**3c**)

max/cm^{-1}: 2890, 1530, 1500, 1120; $_H$ (CDCl$_3$): 4.27 (m, 1H), 3.33 (d, 2H, J=6), 0.90-2.20 (m, 11H) ppm; $_F$(CDCl3): 65.0 (m, 2F), 79.0 (t, 1F), 85.2 (m, 2F) ppm; m/z: 265 (M$^+$-I, 2.4%), 264 (M$^+$-HI, 16.1%), 194 (M$^+$-I-C$_5$H$_{11}$, 100%), 181 (C$_6$F$_5$CH$_2$$^+$, 35.2%), 167 (7.4%); HRMS (for C$_{13}$F$_5$H$_{13}$, M$^+$-HI), Calc: 264.0937, Found: 264.0922.

C$_6$F$_5$CH$_2$CH(I)CH$_2$OC$_2$H$_5$ (**6a**)

max/cm^{-1}: 2900, 1740, 1500, 1220; $_H$(CDCl$_3$): 3.10-4.24 (m, 7H), 1.80 (t, 3H)ppm; $_F$(CDCl$_3$): 65.7 (m, 2F), 79.5 (t, 1F), 85.3 (m, 2F) ppm; m/z: 353 (M$^+$-I, 34.0%), 224 (M$^+$-I-C$_2$H$_5$, 29%), 181 (C$_6$F$_5$CH$_2$$^+$, 100%), Found: C, 34.70; H, 2.56; F, 24.50%; Calc. for C$_{11}$H$_{10}$F$_5$IO: C, 34.74; H, 2.62; F, 25.00%.

C$_6$F$_5$CH$_2$CHICH$_2$OAc (**6b**)

max/cm^{-1}: 2900, 1740, 1500, 1220; $_H$(CDCl$_3$): 4.37 (m, 3H), 3.37 (m, 2H), 2.13 (s, 3H)ppm; $_F$(CDCl$_3$): 66.7 (m, 2F), 80.3 (t, 1F), 86.7 (m, 2F) ppm; m/z: 395 (M$^+$+1, 0.77%), 335 (M$^+$-AcO, 29%), 267 (M$^+$-I, 100%), 207 (M$^+$-AcO-HI, 67%), 181 (C$_6$F$_5$CH$_2$$^+$, 49%), 43 (AcO$^+$, 84%), Found: C, 33.56; H, 1.99; F, 24.52%; Calc. for C$_{11}$H$_8$F$_5$IO$_2$: C, 33.50; H, 2.03; F, 24.52%.

*Typical procedure of the reaction of pentafluoroiodoben-zene (**1**) with aryl allyl ether **7***

Under a N_2 atmosphere, the mixture of **1** (2.94g, 10mmol), **7a** (10g, 0.1mol) and CH_3CN(20ml) was irradiated for 12h as above. After work-up, the excess of **7a** was then distilled off in vacuum, the oily residue was subject to column chromatography using petroleum ether as eluent to give product **8a** (0.6g, 36%) and **9a** (0.4g, 24%).

8a (Formula see Scheme 7)

max/cm^{-1}: 1640, 1520, 1480, 1280, 1060, 860, 820; $_H$(CDCl$_3$): 7.0 (m, 4H), 5.9 (m, 1H), 5.25 (m, 2H), 4.5 (m, 2H) ppm; $_F$(CDCl$_3$): 63.7 (m, 2F, p-), 65.7 (m, 2F, o-), 78.7 (t, 1F), 85.0 (m, 2F) ppm; m/z: 300 (M$^+$, 100%), 260 (M$^+$-C$_3$H$_4$, 18%), 231 (M$^+$-CO-C$_3$H$_5$, 46%), 205 (M$^+$-C$_3$H$_5$-C$_2$H$_2$, 24%), 181 (C$_6$F$_5$CH$_2^+$, 70%), HRMS (for C$_{15}$H$_9$F$_5$O): Calc: 300.2220, Found: 300.1599.

9a (Formula see Scheme 7)

max/cm^{-1}: 1580, 1500, 1230, 980, 750, 680; $_H$(CDCl$_3$): 7.10 (m, 5H), 4.42 (m, 1H), 4.20 (m, 2H), 3.40 (m, 2H) ppm; $_F$(CDCl$_3$): 66.3 (m, 2F), 78.7 (t, 1F), 85.0 (m, 2F) ppm; m/z: 427 (M$^+$, 18.0%), 300 (M$^+$-I, 100%), 181 (C$_6$F$_5$CH$_2^+$, 70%), 94 (C$_6$H$_5$OH$^+$, 25.0%), Found: C, 42.32; H, 2.39; Calc. for C$_{15}$H$_{10}$F$_5$IO: C, 42.08; H, 2.35.

8b (Formula see Scheme 7)

max/cm^{-1}: 1640, 1600, 1580, 1500, 1280, 1220, 1120, 980, 910, 800; $_H$(CDCl$_3$): 6.95 (m, 3H), 5.9 (m, 1H), 5.20 (m, 2H), 4.40 (d, 2H), 2.21 (s, 3H) ppm; $_F$(CDCl$_3$): 63.0 (m, 2F), 79.0 (t, 1F), 85.3 (m, 2F) ppm; m/z: 314 (M$^+$, 100%), 299 (M$^+$-CH$_3$, 36%), 273 (M$^+$-C$_3$H$_5$, 12%), 245 (M$^+$-CO-

C$_3$H$_5$, 16%). HRMS (for C$_{16}$H$_{11}$F$_5$O): Calc: 314.2543, Found: 314.0768.

9b (Formula see Scheme 7)

M.p.: 71-73°C. max/cm^{-1}: 2860, 1520, 1500, 1370, 1220, 1120, 980, 960; $_H$(CDCl$_3$): 6.90 (AA'BB', 4H), 4.4 (m, 1H), 4.20 (s, 2H), 3.40 (m, 2H), 2.23 (s, 3H) ppm; $_F$(CDCl$_3$): 65.0 (m, 2F), 78.0 (t, 1F), 85.3 (m, 2F) ppm; m/z: 442 (M$^+$, 26%), 315 (M$^+$-CH$_3$, 36%), 181 (C$_6$F$_5$CH$_2^+$, 82%), 108 (p-MeC$_6$H$_4$OH$^+$, 100%). Found: C, 43.32; H, 2.39; Calc. for C$_{16}$H$_{12}$F$_5$IO: C, 43.44; H, 2.71.

8c (Formula see Scheme 7)

max/cm^{-1}: 2960, 1640, 1590, 1580, 1520, 1480 1280, 1220, 1010, 980; $_H$(CDCl$_3$): 7.17-6.83 (m, 3H), 5.90 (m, 1H), 5.30 (m, 2H), 4.62 (s, 2H) ppm; $_F$(CDCl$_3$): 63.0 (m, 2F), 78.3 (t, 1F), 86.0 (m, 2F) ppm; m/z: 334 (M$^+$, 100%), 293 (M$^+$-C$_3$H$_5$, 32%), 265 (M$^+$-CO-C$_3$H$_5$, 45%). HRMS (for C$_{15}$H$_8$ClF$_5$O): Calc: 334.6640, Found: 334.6216.

9c (Formula see Scheme 7)

M.p.: 59-60°C. max/cm^{-1}: 1600, 1540, 1510, 1498, 1240, 1000; $_H$(CDCl$_3$): 7.27 (AA'BB', 4H), 4.40 (m, 2H), 4.25(d, 1H, J=4Hz), 3.43 (m, 2H) ppm; $_F$(CDCl$_3$): 65.0 (m, 2F), 78.3 (t, 1F), 84.7 (m, 2F) ppm; m/z: 462 (M$^+$, 50%), 335 (M$^+$-I, 25%), 181 (C$_6$F$_5$CH$_2^+$, 100%), 128 (p-ClC$_6$H$_4$OH+, 25%), Found: C, 39.25; H, 1.81; F, 20.40%; Calc. for C$_{15}$H$_9$ClF$_5$IO: C, 38.96; H, 1.94; F, 20.56%.

11 (Formula see Scheme 7)

M.p.: 42-44°C. max/cm^{-1}: 1520, 1500, 1120, 980; $_H$(CDCl$_3$): 4.00 (d, 2H, J=6Hz), 3.70 (m, 4H), 3.26 (m, 2H),
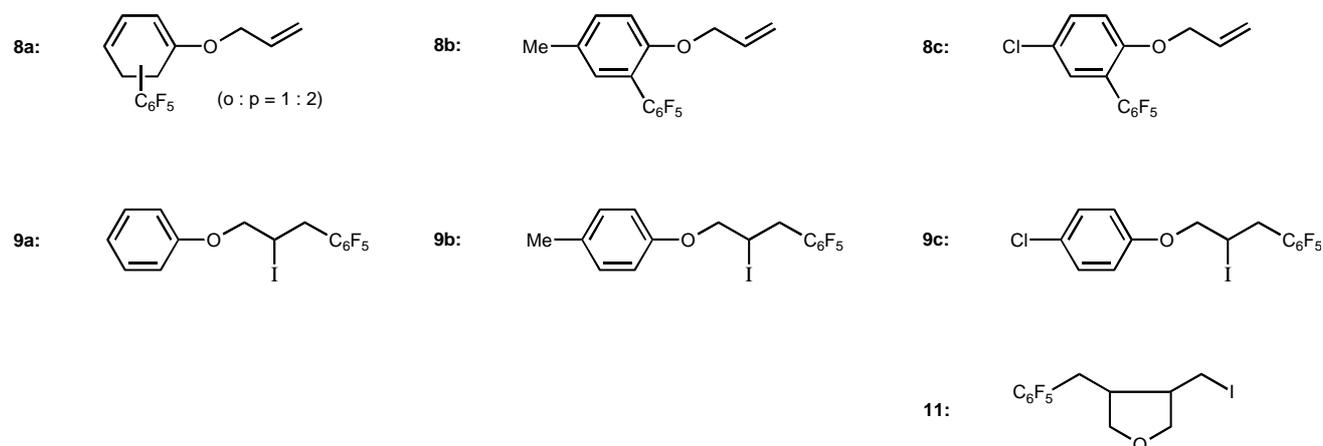
Scheme 7.

2.80 (m, 2H) ppm; $_F$(CDCl$_3$): 66.0 (m, 2F), 79.7 (t, 1F), 85.3 (m, 2F) ppm; m/z: 392 (M$^+$, 19%), 265 (M$^+$-I, 60%), 235 (M$^+$-I-CH$_2$O, 22%), 181 (C$_6$F$_5$CH$_2^+$, 100%), Found: C, 37.51; H, 2.57; F, 24.45%; Calc. for C$_{12}$H$_{10}$F$_5$IO: C, 37.42; H, 2.55; F, 24.23%.

C$_6$F$_5$CH$_2$CHIOCH$_2$CH=CH$_2$ (**12**)

max/cm^{-1}: 2800, 1650,1500, 1110, 980; $_H$(CDCl$_3$): 5.80 (m, 1H), 5.23 (m, 2H), 4.32 (m, 1H), 4.00 (d, 2H, J=4Hz) ppm; $_F$(CDCl$_3$): 65.0 (m, 2F), 79.0 (t, 1F), 85.0 (m, 2F) ppm; m/z: 392 (M$^+$, 0.68%), 335 (M$^+$-C$_3$H$_5$O, 63%), 181 (C$_6$F$_5$CH$_2^+$, 100%), 127 (I$^+$, 4.5%), Found: C, 37.74; H, 2.55; F, 24.23%; Calc. for C$_{12}$H$_{10}$F$_5$IO: C, 37.42; H, 2.55; F, 24.23%.

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Sample Availability: Samples available from the author.