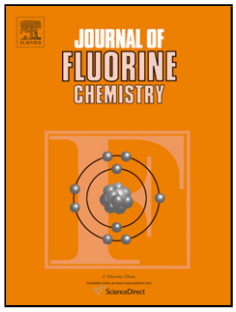

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Visible Light Promoted Iodofluoroalkylation of Alkenes with Iodo-3-oxaperfluoroalkanesulphonates

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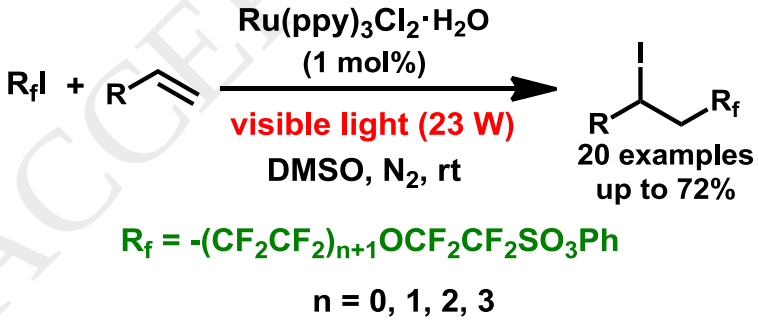
Graphical abstract



Highlight

- Visible light promoted radical fluoroalkylation was researched.

- The amount of ruthenim catalyst is 1 mol%.
- The fluoroalkylating reagent was iodo-3-oxa-perfluoroalkanesulfonate.

Abstract

Iodo-3-oxa-perfluoroalkanesulfonyl fluorides ($I(CF_2CF_2)_{n+1}OCF_2CF_2SO_2F$, n = 0, 1, 2, 3) was functionalized by phenol to provide phenyl fluoroalkanesulfonate. The ATRA reaction of $I(CF_2CF_2)_{n+1}OCF_2CF_2SO_3Ph$ with alkenes was realized by visible light phototcatalysis with $Ru(ppy)_3Cl_2$.

Keywords

ATRA; iodo-3-oxa-perfluoroalkanesulfonate; fluoroalkylation; visible light; alkene

Introduction

The increasing demand of new fluorinated compounds in agrochemicals, pharmaceuticals, and materials attracted widespread attention in the methodology for the introduction of fluorinated groups into organic molecules [1]. Iodo-3-oxa-perfluoroalkanesulfonyl fluorides (namely, $I(CF_2CF_2)_{n+1}OCF_2CF_2SO_2F$, **1**, n = 0, 1, 2, 3) are widely used fluoroalkylation reagents, which can incorporate fluorous tags into organic compounds [2]. **1** bearing with both sulfonyl fluoride and halo groups, it behaves as bi-functional fluoroalkylation reagents. Sulfonyl fluoride group ($-SO_2F$) can be functionalized by K_2SO_3 [3a], NaOH [3b, 3c], and phenols [3d] to provide fluoroalkanesulfite, fluoroalkanesulfonic acid salts, and fluoroalkanesulfonic acid esters respectively. Perfluoroalkyl iodides (R_fI) are very different from their corresponding alkyl iodides (RI). **1** is reactive in a radical [4-8] and single electron transfer [9-13] processes, and a fluoralkyl radical generated from **1** reacted with alkenes, alkynes and arenes to provide fluoroalkylated products. Visible

light promoted fluoroalkylation are widely researched [14-22] (Scheme 1). Photosensitive transition metal complexes are usual photocatalysts, allowing atom transfer radical addition (ATRA) of perfluoroalkyl halides to alkenes under the visible light irradiation [23-26]. The visible light-promoted reaction has the advantages of greenness, mildness, and high efficiency. Therefore, we researched the visible light promoted fluoralkylation with iodo-3-oxa-perfluoroalkanesulfonates.

Previous work:

2. Results and discussion

Inspired by the above literatures, we initially selected $I(CF_2CF_2)_2OCF_2CF_2SO_2F$ (**1b**) as the fluorine-containing starting material and reacted with hex-5-en-1-yl benzoate (**3a**) under the irradiation of 23 W fluorescent lamp with $Ru(bpy)_3Cl_2$ as a photocatalyst, conducting a preliminary investigation. As a result, it was found that no signal of the target product was observed at all by ^{19}F NMR monitoring. In contrast, the ^{19}F NMR signal of the $-SO_2F$ of the starting material disappeared. Later, in order to carry out the experiment as originally assumed, we transferred sulfonyl fluoride to sulfonate by reacting with phenol (Scheme 2), and the obtained products (**2a-d**) was subjected to ATRA with the alkenes.

The protocol was investigated with alkene **3a** as a model substrate; it was reacted with 1.5 – 6 equivalents of **2b** (Table 1, entries 1 – 6) and 1 mol% of $Ru(bpy)_3Cl_2$ in dimethyl sulfoxide (DMSO) under visible light irradiation with a 23 W fluorescent lamp at room temperature under nitrogen atmosphere for 24 hours. When 6 equivalents of **2b** were employed, the yield reached 91% (Table 1, entry 6; detected by ^{19}F NMR spectroscopy). Among the common solvents tested including DCM, acetonitrile, DMF, NMP, DMPU, THF, and DMSO (Table 1, entry 6-12), all of them promoted the reaction and DCM was the best, giving product **4b** in 98% yield (Table 1, entry 7). However, considering that the solvent contains chlorine, we chose DMSO with the second highest yield (91%) as solvent (Table 1, entry 6). And we increased the solvent from 1 mL to 3 mL of solvent and found that the 2 mL is the best. (Table 1, entries 6, 13 and 14). A blue LED was applied, and gave the product in 74% yield (Table 1, entry 15). By increasing the reaction time to 48 h and the best yield (99%) of

the product was obtained (Table 1, entries 16, 17). While continue to extend the reaction time to 60 h, the yield instead declined (Table 1, entry 18). When we reduced the amount of $Ru(bpy)_3Cl_2$ to 0.5 mol%, the yield decreased to 76% (Table 1, entry 19). Notably, **4b** could not be obtained in the dark or in the absence of photocatalyst (Table 1, entries 20 and 21). To our delight, employing Eosin Y as a photocatalyst provided **4b** in 56% yield (Table 1, entry 22).

With the optimized conditions identified (Table 1, entry 17), we began to explore the substrate scope of alkenes and the results were summarized in Table 2. Inspiringly, a wide array of alkenes were subjected to the protocol. And numerous functional groups were tolerated, including esters (**4a - o**), halogens (**4e, 4h - j**), ethers (**4p, 4r, 4s**), phthalimide (**4q**), heterocycles (**4m, 4n**), ketones (**4s**), nitro (**4g**), hydroxyl (**4t**). In addition, terminal alkenes derived from relatively complex molecules 4-methylumbelliferone (**4o**) and estrone (**4s**) were compatible with the reaction conditions and yielded the desired products in moderate yields, which demonstrated the potential of the reaction in late-stage functionalization. The products of **2** (n=1, 2, 3) could gave the corresponding products (**4b - d**) in moderate yields. However, the **4a** (n=0) only give a 13% yield. Notably, styrenes and electron-poor alkenes are not good candidates for this atom-transfer radical addition (ATRA), thus suggesting a profound effect of electronic properties of the alkenes.

Table 2 Substrate scope

To gain more insights into the reaction mechanism, inhibition experiments were conducted on **3a** (Scheme 3). The yield of the target product (**4b**) was reduced from 91% to 24% when the reaction was conducted under the optimized conditions in the presence of 1,4-dinitrobenzene. This demonstrated that the reaction may proceed through a single electron transfer process. However, there is no effect when using hydroquinone.

3. Conclusion

In summary, we developed a fluoroalkylation reaction of alkenes with iodo-3-oxa-perfluoroalkanesulfonates under visible light irradiation. The reaction was

catalyzed by 1 mol% $Ru(ppy)_3Cl_2$ and ATRA products were obtained. Various alkenes undergo the reaction to afford the corresponding products in moderate to good yields.

4. Experimental section

4.1. General information

NMR spectra were obtained on a 400 MHz spectrometer using $CDCl_3$ as deuterated solvents, with proton, carbon and fluorine resonances at 400 MHz, 100 MHz and 376 MHz, respectively. ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relatived to $CFCl_3$ as inter standard. Carbons in the perfluorinated carbon chains are not reported due to their multiple couplings with fluorine atoms. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The NMR yield was determined by ^{19}F NMR using benzotrifluoride (^{19}F NMR: δ -63.0 ppm) as an internal standard before working up the reaction. GC-MS (EI) data were determined on an Agilent 5975C. HRMS (ESI) data were tested on a Water Micromass GCT Premier. Unless otherwise noted, solvents were freshly dried and degassed according to the purification handbook Purification of Laboratory Chemicals before using. Flash column chromatography was carried out using 300 - 400 mesh silica gel.

4.2. Preparation of $I(CF_2CF_2)_{n+1}OCF_2CF_2SO_3Ph$

Synthesis of phenyl 1,1,2,2-tetrafluoro-2-(1,1,2,2,3,3,4,4-octafluoro-4-iodobutoxy)ethane-1-sulfonate (2a)

To a 100 mL flask containing a magnetic stirring bar were added triethylamine (40 mL), $I(CF_2)_2OCF_2CF_2SO_2F$ (**1a**, 20 mmol, 8.52 g) and phenol (30 mmol, 2.82 g). The mixture was stirred vigorously at room temperature for 4 hours. After removal of the solvent under reduced pressure with a rotary evaporator, water (20 mL) was added. The aqueous phase was extracted with DCM (20 × 3 mL). The organic layers were combined, washed with H_2O (50 mL × 2) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel

column chromatography (EA/PE = 1:50 v/v) to give a colorless liquid (8.54 g, 85% yield).

phenyl 1,1,2,2-tetrafluoro-2-(1,1,2,2,3,3,4,4-octafluoro-4-iodobutoxy)ethane-1-sulfonate (2a) [3d]**:** Obtained as colorless liquid in 85% yield by silica gel flash column chromatography eluted with EA/PE = 1:50 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -65.1 (t, *J* = 5.8 Hz, 2F), -81.8 – -82.0 (m, 2F), -85.4 – -85.5 (m, 2F), -113.0 (s, 2F). **HRMS** (ESI): calcd. for [$C_{10}H_5F_8IO_4S + Na^+$] 522.8718, found 522.8717.

The following substrates were prepared according to the procedure described for **2a**.

phenyl 2-((1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-6-iodohexyl)oxy)-1,1,2,2-tetrafluoroethane -1-sulfonate (2b) [3d]**:** Obtained as colorless liquid in 85% yield by silica gel flash column chromatography eluted with EA/PE = 1:50 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.5 (t, *J* = 14.0 Hz, 2F), -81.5 – -81.6 (m, 2F), -83.1 – -83.2 (m, 2F), -113.1 (s, 2F), -113.4 – -113.5 (m, 2F), -124.4 – -124.5 (m, 2F). **HRMS** (ESI): calcd. for [$C_{12}H_5F_{12}IO_4S + NH_4^+$] 617.9100, found 617.9091.

phenyl 2-((1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-6-iodohexyl)oxy)-1,1,2,2-tetrafluoroethane -1-sulfonate (2c) [3d]**:** Obtained as colorless liquid in 85% yield by silica gel flash column chromatography eluted with EA/PE = 1:50 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.2 – -59.4 (m, 2F), -81.5 – -81.6 (m, 2F), -82.8 – -83.0 (m, 2F), -113.1 – -113.3 (m, 4F), -121.0 – -121.3 (m, *J* = 11.3 Hz, 2F), -122.1 (s, 2F), -125.3 (m, 2F). **HRMS** (ESI): calcd. for [$C_{14}H_5F_{16}IO_4S + Na^+$] 722.8590, found 722.8589.

phenyl 1,1,2,2-tetrafluoro-2-((1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluoro-8-iodooctyl)ox

y)ethane-1-sulfonate (2d) [3d]**:** Obtained as colorless liquid in 85% yield by silica gel flash column chromatography eluted with EA/PE = 1:50 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.2 – -59.4 (m, 2F), -81.6 – -81.7 (m, 2F), -82.8 – -83.0 (m, 2F), -113.1 – -113.4 (m, 4F), -121.1 (s, 2F), -121.7 – -122.4 (m, 6F), -125.4 (s, 2F). **HRMS** (ESI): calcd. for [$C_{16}H_5F_{20}IO_4S + Na^+$] 822.8526, found 822.8523.

4.3. Preparation of various alkenes starting material

Synthesis of hex-5-en-1-yl benzoate (3a)

To a flame-dried 250 mL two-neck flask containing a magnetic stirring bar were added 4-dimethylaminopyridine (DMAP, 488 mg, 4 mmol), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI, 7.67 g, 40 mmol), benzoic acid (2.74 g, 24 mmol) and 5-hexen-1-ol (2.00 g, 20 mmol) in 100 mL CH_2Cl_2 under N_2 atmosphere at 0 ℃. The reaction mixture was stirred at room temperature for 24 h. After that, the organic phase was filtered through a pad of celite and concentrated. The resulting residue was purified by silica gel column chromatography (EA/PE = 1:20 v/v) to give a colorless liquid. (4.08 g, yield 87%)

hex-5-en-1-yl benzoate (3a) [27]**:** Obtained as colorless liquid in 87% yield by silica gel flash column chromatography eluted with EA/PE = 1:20 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H), 7.59 – 7.52 (m, 1H), 7.44 (dd, *J* = 10.6, 4.7 Hz, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.08 – 4.95 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 2.18 – 2.10 (m, 2H), 1.83 – 1.75 (m, 2H), 1.61 – 1.51 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 138.3, 132.8, 130.4, 129.5, 128.3, 114.8, 64.8, 33.3, 28.1, 25.3. **GC-MS** (EI): *m/z* = 204.0 (M^+).

The following substrates were prepared according to the procedure described for **3a**.

hex-5-en-1-yl 2-fluorobenzoate (3e) [27]**: ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (td, *J* = 7.6, 1.8 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.23 – 7.09 (m, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07 – 4.95 (m, 2H), 4.34 (t, *J* = 6.6 Hz, 2H), 2.17 – 2.09 (m, 2H), 1.83 – 1.73 (m, 2H), 1.60 – 1.51 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.50 – -109.61 (m, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5 (d, *J* = 3.6 Hz), 161.9 (d, *J* = 259.0 Hz), 138.3, 134.3 (d, *J* = 8.9 Hz), 132.0, 123.8 (d, *J* = 3.9 Hz), 119.0 (d, *J* = 9.9 Hz), 116.9

(d, *J* = 22.0 Hz), 114.8, 65.2, 33.2, 28.0, 25.2.

hex-5-en-1-yl 3-methylbenzoate (3f) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.27 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07 – 4.93 (m, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H), 2.15 – 2.08 (m, 2H), 1.81 – 1.72 (m, 2H), 1.58 – 1.49 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 138.3, 138.0, 133.5, 130.3, 130.0, 128.2, 126.6, 114.8, 64.7, 33.3, 28.1, 25.3, 21.2.

hex-5-en-1-yl 3-nitrobenzoate (3g) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 – 8.81 (m, 1H), 8.45 – 8.35 (m, 2H), 7.68 (t, *J* = 8.0 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09 – 4.96 (m, 2H), 4.40 (t, *J* = 6.7 Hz, 2H), 2.19 – 2.11 (m, 2H), 1.88 – 1.79 (m, 2H), 1.62 – 1.53 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 148.2, 138.0, 135.1, 132.1, 129.5, 127.2, 124.4, 114.9, 65.7, 33.1, 27.9, 25.1.

hex-5-en-1-yl 4-fluorobenzoate (3h) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.15 – 7.07 (m, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07 – 4.96 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.17 – 2.10 (m, 2H), 1.83 – 1.71 (m, 2H), 1.60 – 1.50 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.70 – -106.25 (m, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 252.0 Hz), 165.6, 138.2, 132.0 (d, *J* = 10.0 Hz), 126.7 (d, *J* = 3.0 Hz), 115.4 (d, *J* = 22.0 Hz), 114.9, 65.0, 33.3, 28.1, 25.2.

hex-5-en-1-yl 4-iodobenzoate (3i) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 4H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.16 – 2.10 (m, 2H), 1.82 – 1.72 (m, 2H), 1.58 – 1.49 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 138.1, 137.6, 130.9, 129.8, 114.9, 100.5, 65.1, 33.2, 28.0, 25.2.

but-3-en-1-yl 4-chlorobenzoate (3j) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.42 – 7.37 (m, 2H), 5.86 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.21 – 5.08 (m, 2H), 4.37 (t, *J* = 6.7 Hz, 2H), 2.55 – 2.48 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 139.2, 133.8, 130.9, 128.7, 128.6, 117.3, 64.1, 33.0.

but-3-en-1-yl 4-(tert-butyl)benzoate (3k) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.42 (m, 2H), 5.87 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.20 – 5.07 (m, 2H), 4.36 (t, *J* = 6.7 Hz, 2H), 2.55 – 2.47 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 156.3, 134.0, 129.3, 127.5, 125.2, 117.1, 63.6, 34.9, 33.1,

31.0.

pent-4-en-1-yl 4-methoxybenzoate (3l) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 6.91 – 6.86 (m, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.08 – 4.95 (m, 2H), 4.27 (t, *J* = 6.6 Hz, 2H), 3.81 (s, 3H), 2.22 – 2.15 (m, 2H), 1.87 – 1.79 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 163.2, 137.4, 131.4, 122.7, 115.2, 113.5, 63.9, 55.3, 30.1, 27.9.

hex-5-en-1-yl thiophene-2-carboxylate (3m) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 1H), 7.55 – 7.50 (m, 1H), 7.10 – 7.05 (m, 1H), 5.86 – 5.74 (m, 1H), 5.06 – 4.94 (m, 2H), 4.31 – 4.25 (m, 2H), 2.15 – 2.06 (m, 2H), 1.79 – 1.70 (m, 2H), 1.57 – 1.47 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.1, 138.2, 133.9, 133.1, 132.1, 127.6, 114.8, 64.9, 33.1, 28.0, 25.1.

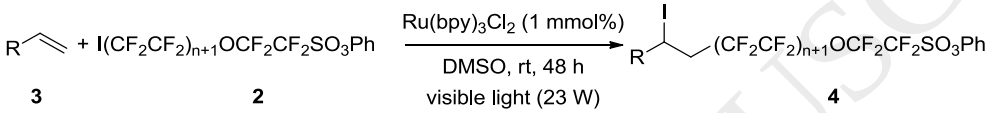
hex-5-en-1-yl 1-methyl-1H-pyrrole-2-carboxylate (3n) [27]**:** Obtained as colorless liquid in 85% yield by silica gel flash column chromatography eluted with EA/PE = 1:20 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 3.7, 1.6 Hz, 1H), 6.77 (s, 1H), 6.10 (m, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07 – 4.93 (m, 2H), 4.22 (t, *J* = 6.6 Hz, 2H), 3.92 (s, 3H), 2.15 – 2.07 (m, 2H), 1.78 – 1.66 (m, 2H), 1.57 – 1.47 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3, 138.3, 129.3, 122.6, 117.6, 114.7, 107.7, 63.6, 36.7, 33.3, 28.2, 25.3. **GC-MS** (EI): *m/z* = 207.1 (M^+).

4-methyl-2-oxo-2H-chromen-7-yl pent-4-enoate (3o) [27]**:** Obtained as colorless liquid in 89% yield by silica gel flash column chromatography eluted with EA/PE = 1:3 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 7.08 – 7.03 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.26 (s, 1H), 5.90 (ddt, *J* = 16.8, 10.3, 6.5 Hz, 1H), 5.20 – 5.07 (m, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.56 – 2.48 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 160.5, 154.2, 153.1, 151.9, 136.0, 125.3, 118.1, 117.8, 116.2, 114.5, 110.4, 33.6, 28.7, 18.7. **GC-MS** (EI): *m/z* = 258.1 (M^+).

2-(pent-4-en-1-yl)-1H-indene-1,3(2H)-dione (3q) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 4.96 (m, 2H), 3.70 (t, *J* = 8.0 Hz, 2H), 2.16 – 2.09 (m, 2H), 1.84 – 1.74 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 137.2, 133.8, 132.1, 123.1, 115.2, 37.5, 30.9, 27.6.

(8S,9R,13R,14R)-3-(hex-5-en-1-yloxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3s) [27]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.08 – 4.93 (m, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.92 – 2.86 (m, 2H), 2.55 – 2.46 (m, 1H), 2.43 – 2.36 (m, 1H), 2.29 – 2.21 (m, 1H), 2.18 – 1.93 (m, 6H), 1.83 – 1.74 (m, 2H), 1.65 – 1.40 (m, 8H), 0.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.9, 157.1, 138.6, 137.7, 131.8, 126.3, 114.7, 114.5, 112.1, 67.6, 50.4, 48.0, 44.0, 38.4, 35.8, 33.4, 31.6, 29.6, 28.7, 26.5 25.9, 25.3, 21.6, 13.8.

4.4. General procedures for the reactions of fluorinated alkyl iodides with various alkenes



3 **2** **4**

To an oven-dried Schlenk tube equipped with a magnetic stir bar were added in turn $Ru(bpy)_3Cl_2·6H_2O$ (1 mol%, 1.5 mg), alkene substrate (0.2 mmol), $I(CF_2CF_2)_{n+1}OCF_2CF_2SO_3Ar$ (1.2 mmol) and freshly-distilled DMSO (2.0 mL) under N_2 atmosphere. The mixture was stirred at room temperature and irradiated by a 23W compact fluorescent lamp for 48 h. Benzotrifluoride (0.2 mmol, 24 uL) was then added into the reaction mixture as an internal standard, and the yield of the desired product was measured by ^{19}F NMR before working up. Water (15 mL) was added and the resulting mixture was extracted with DCM (20 mL × 3). The organic layers were combined, washed with H_2O (50 mL × 2) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography to give the desired product.

7,7,8,8-tetrafluoro-5-iodo-8-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)octyl benzoate (4a): Obtained as yellow liquid in yield 13% by silica gel flash column chromatography eluted with EA/PE = 1:15 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.41 – 7.35 (m, 1H), 7.30 – 7.24 (m, 2H), 4.37 – 4.30 (m, 3H), 2.96 – 2.69 (m, 2H), 1.92 – 1.67 (m, 5H), 1.64 – 1.56 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.9 – -82.1 (m, 2F), -87.7 – -89.1 (ABm, *J* = 142 Hz, 2F), -113.2 (s, 2F), -118.4 – -118.9 (AB, *J* = 260 Hz, 2F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 149.8, 132.9, 130.3, 130.2, 129.5, 128.4, 128.3, 121.4, 64.5, 41.2 (tm, *J* = 21.0 Hz), 39.8, 27.7, 26.2, 20.0. **IR** (film) ν_{max}: 2954, 1720, 1602, 1585, 1488, 1422, 1276, 881, 773, 713 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{23}H_{21}F_8IO_6S + Na^+$] 726.9868, found 726.9865.

7,7,8,8,9,9,10,10-octafluoro-5-iodo-10-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)decyl benzoate (4b): Obtained as yellow liquid in yield 71% by silica gel flash column chromatography eluted with EA/PE = 1:15 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.56 (tt, *J* = 16.0, 7.4 Hz, 1H), 7.51 – 7.35 (m, 5H), 7.31 – 7.25 (m, 2H), 4.38 – 4.29 (m, 3H), 3.01 – 2.69 (m, 2H), 1.97 – 1.68 (m, 5H), 1.65 – 1.57 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.9 (s, 2F), -124.9 – -125.1 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 149.8, 132.9, 130.3, 130.2, 129.6, 128.4, 128.3, 121.4, 64.4, 41.5 (tm, *J* = 21.0 Hz), 39.7, 27.7, 26.3, 20.2. **IR** (film) ν_{max}: 3382, 2974, 1718, 1603, 1488, 1425, 1208, 1050, 881, 713 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{25}H_{21}F_{12}IO_6S + H^+$] 804.9985, found 804.9993.

7,7,8,8,9,9,10,10,11,11,12,12-dodecafluoro-5-iodo-12-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)dodecyl benzoate (4c): Obtained as yellow liquid in yield 69% by silica gel flash column chromatography eluted with EA/PE = 1:15 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (dt, *J* = 7.8, 1.9 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.24 (m, 2H), 4.39 – 4.29 (m, 3H), 3.01 – 2.69 (m, 2H), 3.02 – 1.69 (m, 5H), 1.66 – 1.53 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -121.8 (s, 2F), -122.2 (s, 2F), -123.7 (s, 2F), -125.2 – -125.4 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 149.8, 132.9, 130.3, 130.2, 129.5, 128.4, 128.3, 121.3, 64.4, 41.6 (tm, *J* = 21.0 Hz), 39.8, 27.7, 26.3, 20.2. **IR** (film) ν_{max}: 2956, 1712, 1488, 1421, 1358, 1262, 1208, 1145, 882, 734 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{27}H_{21}F_{16}IO_6S + Na^+$] 926.9740, found 926.9743.

7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-hexadecafluoro-5-iodo-14-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)tetradecyl benzoate (4d): Obtained as yellow liquid in yield 66% by silica gel flash column chromatography eluted with EA/PE =

1:20 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.24 (m, 2H), 4.35 (t, *J* = 5.8 Hz, 3H), 3.02 – 2.70 (m, 2H), 1.97 – 1.70 (m, 5H), 1.66 – 1.54 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -121.9 (m, 8F), -123.7 (s, 2F), -125.3 (s, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 149.8, 132.9, 130.3, 130.2, 129.5, 128.4, 128.3, 121.3, 64.4, 41.7 (tm, *J* = 21.0 Hz), 39.8, 27.7, 26.3, 20.1. **IR** (film) ν_{max}: 1953, 1720, 1488, 1427, 1276, 1220, 1150, 882, 713 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{29}H_{21}F_{20}IO_6S$ + Na^+] 1026.9676, found 1026.9681.

7,7,8,8,9,9,10,10-octafluoro-5-iodo-10-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)decyl 2-fluorobenzoate (4e): Obtained as yellow liquid in yield 64% by silica gel flash column chromatography eluted with EA/PE = 1:15 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (td, *J* = 7.6, 1.7 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.47 – 7.41 (m, 2H), 7.41 – 7.35 (m, 1H), 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 1H), 7.16 – 7.09 (m, 1H), 4.38 – 4.29 (m, 3H), 3.00 – 2.69 (m, 2H), 1.95 – 1.68 (m, 5H), 1.65 – 1.53 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -109.4 – -109.5 (m, 1F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.9 (s, 2F), -124.9 – -125.1 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5 (d, *J* = 3.6 Hz), 161.9 (d, *J* = 260 Hz), 149.8, 134.4 (d, *J* = 9.0 Hz), 132.1, 130.2, 128.3, 123.9 (d, *J* = 3.9 Hz), 121.4, 118.8 (d, *J* = 9.8 Hz)116.9 (d, *J* = 22.0 Hz), 64.8, 41.5 (tm, *J* = 21.0 Hz), 39.7, 27.6, 26.2, 20.1. **IR** (film) ν_{max}: 2955, 1728, 1614, 1488, 1425, 1300, 1208, 1143, 882, 759 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{25}H_{20}F_{13}IO_6S$ + Na^+] 844.9710, found 844.9714.

7,7,8,8,9,9,10,10-octafluoro-5-iodo-10-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)decyl 3-methylbenzoate (4f): Obtained as yellow liquid in yield 59% by silica gel flash column chromatography eluted with EA/PE = 1:15 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 11.1 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.41 – 7.25 (m, 5H), 4.38 – 4.29 (m, 3H), 3.02 – 2.69 (m, 2H), 2.40 (s, 3H), 1.94 – 1.70 (m, 5H), 1.65 – 1.52 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.9 (s, 2F), -124.9 – -125.1

(m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 149.8, 138.2, 133.7, 130.3, 130.2, 130.1, 128.3, 128.2, 126.7, 121.4, 64.4, 41.5 (tm, *J* = 21.0 Hz), 39.8, 27.7, 26.3, 21.2, 20.3. **IR** (film) ν_{max}: 2953, 1720, 1587, 1488, 1424, 1208, 1143, 1009, 881, 754 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{26}H_{23}F_{12}IO_6S + H^+$] 819.0141, found 819.0152.

7,7,8,8,9,9,10,10-octafluoro-5-iodo-10-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)decyl 3-nitrobenzoate (4g): Obtained as yellow liquid in yield 47% by silica gel flash column chromatography eluted with EA/PE = 1:30 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.36 – 8.44 (m, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.44 – 4.30 (m, 3H), 3.02 – 2.70 (m, 2H), 1.97 – 1.70 (m, 5H), 1.69 – 1.54 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.8 (s, 2F), -124.9 – -125.1 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 149.9, 148.4, 135.4, 132.2, 130.4, 129.8, 128.5, 127.5, 124.7, 121.5, 65.5, 41.5 (tm, *J* = 21.0 Hz), 39.7, 27.7, 26.4, 20.3. **IR** (film) ν_{max}: 2953, 1728, 1618, 1585, 1537, 1488, 1425, 1352, 1143, 882, 720 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{25}H_{20}F_{12}INO_8S + Na^+$] 871.9655, found 871.9654.

7,7,8,8,9,9,10,10-octafluoro-5-iodo-10-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)decyl 4-fluorobenzoate (4h): Obtained as yellow liquid in yield 70% by silica gel flash column chromatography eluted with EA/PE = 1:20 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 4.39 – 4.28 (m, 3H), 3.01 – 2.68 (m, 2H), 1.96 – 1.67 (m, 5H), 1.64 – 1.52 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -105.8 (m, 1F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.9 (s, 2F), -124.9 – -125.1 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8 (d, *J* = 252 Hz), 165.6, 149.8, 132.1 (d, *J* = 9.2 Hz), 130.2, 128.3, 126.5 (d, *J* = 3.0 Hz), 121.4, 115.5 (d, *J* = 21.9 Hz), 64.6, 41.6 (tm, *J* = 21.0 Hz), 39.7, 27.7, 26.3, 20.2. **IR** (film) ν_{max}: 3393, 2973, 1718, 1605, 1508, 1425, 1208, 1146, 881, 770 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{25}H_{20}F_{13}IO_6S + H^+$] 822.9890, found 822.9896.

7,7,8,8,9,9,10,10-octafluoro-5-iodo-10-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)decyl 4-iodobenzoate (4i): Obtained as yellow liquid in yield 72% by silica gel

flash column chromatography eluted with EA/PE = 1:15 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.77 – 7.72 (m, 2H), 7.49 – 7.41 (m, 2H), 7.41 – 7.36 (m, 1H), 7.30 – 7.26 (m, 2H), 4.37 – 4.30 (m, 3H), 3.01 – 2.68 (m, 2H), 1.94 – 1.67 (m, 5H), 1.63 – 1.51 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.8 (s, 2F), -125.0 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 149.8, 137.7, 131.0, 130.2, 129.7, 128.3, 121.4, 100.7, 64.7, 41.6 (tm, *J* = 21.0 Hz), 39.7, 27.6, 26.2, 20.2. **IR** (film) ν_{max}: 2954, 1718, 1488, 1425, 1280, 1201, 1146, 881, 747 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{25}H_{20}F_{12}I_2O_6S + Na^+$] 952.8771, found 952.8763.

5,5,6,6,7,7,8,8-octafluoro-3-iodo-8-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)octyl 4-chlorobenzoate (4j): Obtained as yellow liquid in yield 66% by silica gel flash column chromatography eluted with EA/PE = 1:25 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.49 – 7.35 (m, 5H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.61 – 4.52 (m, 1H), 4.51 – 4.38 (m, 2H), 3.09 – 2.79 (m, 2H), 2.40 – 2.18 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.8 (s, 2F), -125.1 – -124.9 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 150.0, 139.7, 131.0, 130.2, 128.8, 128.3, 128.2, 121.3, 64.8, 41.8 (tm, *J* = 21.0 Hz), 38.8, 15.0. **IR** (film) ν_{max}: 1725, 1596, 1488, 1425, 1273, 1205, 1144, 1016, 882, 760 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{23}H_{16}ClF_{12}IO_6S + Na^+$] 832.9101, found 832.9100.

5,5,6,6,7,7,8,8-octafluoro-3-iodo-8-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)octyl 4-(tert-butyl)benzoate (4k): Obtained as yellow liquid in yield 59% by silica gel flash column chromatography eluted with EA/PE = 1:35 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.41 (m, 4H), 7.41 – 7.35 (m, 1H), 7.27 (d, *J* = 7.9 Hz, 2H), 4.58 – 4.37 (m, 3H), 3.07 – 2.80 (m, 2H), 2.39 – 2.16 (m, 2H), 1.34 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.8 (s, 2F), -125.1 – -124.9 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 156.9, 149.8, 130.2, 129.4, 128.3, 127.0, 125.4, 121.3, 64.3, 41.8 (tm, *J* = 21.0 Hz), 39.0, 35.1, 31.1, 15.3. **IR** (film) ν_{max}: 2966, 1721, 1610, 1488, 1425, 1275, 1190, 1144, 1018, 881, 774 cm^{-1}. **HRMS** (ESI):

calcd. for [$C_{27}H_{25}F_{12}IO_6S + Na^+$] 855.0117, found 855.0115.

6,6,7,7,8,8,9,9-octafluoro-4-iodo-9-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)nonyl 4-methoxybenzoate (4l): Obtained as yellow liquid in yield 57% by silica gel flash column chromatography eluted with EA/PE = 1:10 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 9.2 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.43 – 4.31 (m, 3H), 3.86 (s, 3H), 3.03 – 2.70 (m, 2H), 2.07 – 1.86 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.8 (s, 2F), -124.9 – -125.1 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 163.4, 149.8, 131.6, 130.2, 128.3, 122.5, 121.4, 113.6, 63.2, 55.4, 41.6 (tm, *J* = 21.0 Hz), 36.9, 29.0, 19.6. **IR** (film) ν_{max}: 3355, 2974, 2896, 1716, 1608, 1425, 1260, 1090, 1050, 881 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{25}H_{21}F_{12}IO_7S + H^+$] 820.9934, found 820.9936.

7,7,8,8,9,9,10,10-octafluoro-5-iodo-10-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)eth oxy)decyl thiophene-2-carboxylate (4m): Obtained as yellow liquid in yield 70% by silica gel flash column chromatography eluted with EA/PE = 1:15 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.56 (dd, *J* = 6.0, 5.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.12 (t, *J* = 4.0 Hz, 1H), 4.36 – 4.28 (m, 3H), 2.99 – 2.69 (m, 2H), 1.78 – 1.69 (m, 5H), 1.63 – 1.53 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.9 (s, 2F), -124.9 – -125.1 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 149.8, 133.8, 133.4, 132.3, 130.2, 128.3, 127.7, 121.4, 64.6, 41.5 (tm, *J* = 21.0 Hz), 39.7, 27.6, 26.2, 20.2. **IR** (film) ν_{max}: 2954, 1720, 1586, 1488, 1426, 1276, 1220, 1147, 1071, 882, 713 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{23}H_{19}F_{12}IO_6S_2 + Na^+$] 832.9368, found 832.9373.

7,7,8,8,9,9,10,10-octafluoro-5-iodo-10-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)eth oxy)decyl 1-methyl-1H-pyrrole-2-carboxylate (4n): Obtained as yellow liquid in yield 43% by silica gel flash column chromatography eluted with EA/PE = 1:15 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.25 (m, 2H), 6.97 – 6.93 (m, 1H), 6.78 (s, 1H), 6.13 – 6.09 (m, 1H), 4.38 – 4.28 (m,

1H), 4.24 (t, *J* = 6.1 Hz, 2H), 3.92 (s, 3H), 2.99 – 2.70 (m, 2H), 1.92 – 1.64 (m, 5H), 1.60 – 1.52 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.8 (s, 2F), -125.1 – -124.9 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3, 149.8, 130.2, 129.5, 128.3, 122.5, 121.4, 117.8, 107.8, 63.2, 41.5 (tm, *J* = 21.0 Hz), 39.8, 36.8, 27.8, 26.3, 20.3. **IR** (film) ν_{max}: 2923, 1702, 1488, 1417, 1321, 1208, 1146, 881, 738 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{24}H_{22}F_{12}INO_6S + Na^+$] 829.9913, found 829.9910.

4-methyl-2-oxo-2H-chromen-7-yl 6,6,7,7,8,8,9,9-octafluoro-4-iodo-9-(1,1,2,2-tetrafluoro-2-(phenoxysulfonyl)ethoxy)nonanoate (4o): Obtained as yellow liquid in yield 43% by silica gel flash column chromatography eluted with EA/PE = 1:2 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.6 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.10 (td, *J* = 11, 4 Hz, 2H), 6.27 (s, 1H), 4.48 – 4.40 (m, 1H), 3.07 – 2.74 (m, 4H), 2.43 (s, 3H), 2.35 – 2.14 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.8 (s, 2F), -125.1 – -124.9 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 160.4, 154.1, 152.8, 151.9, 149.8, 130.2, 128.3, 125.4, 121.3, 118.0, 117.9, 114.5, 110.3, 41.7 (tm, *J* = 21.0 Hz), 34.9, 34.7, 18.6, 18.5. **IR** (film) ν_{max}: 1732, 1615, 1488, 1421, 1388, 1208, 1135, 881, 774 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{27}H_{19}F_{12}IO_8S + Na^+$] 880.9546, found 880.9543.

phenyl 2-((7-(3,4-dimethoxyphenyl)-1,1,2,2,3,3,4,4-octafluoro-6-iodoheptyl)oxy)-1,1,2,2-tetrafluoroethane-1-sulfonate (4p): Obtained as yellow liquid in yield 51% by silica gel flash column chromatography eluted with EA/PE = 1:8 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.41 – 7.35 (m, 1H), 7.31 – 7.25 (m, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.77 – 6.69 (m, 2H), 4.49 – 4.39 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), , 3.26 – 3.09 (m, 2H), 2.95 – 2.75 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.9 (s, 2F), -125.0 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.8, 148.9, 148.2, 131.0, 130.2, 128.3, 121.3, 121.2, 112.1, 111.1, 55.84, 55.81, 46.6, 40.5 (tm, *J*

= 21.0 Hz) 20.0. **IR** (film) ν_{max}: 2938, 1518, 1424, 1488, 1208, 1144, 1029, 882, 772 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{23}H_{19}F_{12}IO_6S + Na^+$] 800.9648, found 800.9651.

phenyl 2-((9-(1,3-dioxoisoindolin-2-yl)-1,1,2,2,3,3,4,4-octafluoro-6-iodononyl)oxy)-1,1,2,2-tetrafluoroethane-1-sulfonate (4q): Obtained as yellow liquid in yield 52% by silica gel flash column chromatography eluted with EA/PE = 1:5 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.75 – 7.69 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.25 (m, 2H), 4.37 – 4.29 (m, 1H), 3.80 – 3.70 (m, 2H), 2.97 – 2.64 (m, 2H), 2.04 – 1.92 (m, 1H), 1.92 – 1.75 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.9 (s, 2F), -125.0 – -125.1 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 149.8, 134.0, 132.0, 130.2, 128.3, 123.3, 121.4, 41.4 (tm, *J* = 21 Hz), 37.3, 36.7, 28.9, 19.1. **IR** (film) ν_{max}: 2954, 1720, 1488, 1426, 1276, 1220, 1150, 882, 713 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{25}H_{18}F_{12}INO_6S + Na^+$] 837.9600, found 837.9603.

phenyl 2-((1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-8-iodo-9-(4-phenoxyphenyl)nonyl)oxy)-1,1,2,2-tetrafluoroethane-1-sulfonate (4r): Obtained as yellow liquid in yield 48% by silica gel flash column chromatography eluted with EA/PE = 1:30 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.30 – 7.24 (m, 2H), 7.18 – 7.08 (m, 3H), 6.99 (q, *J* = 8.2 Hz, 4H), 4.47 – 4.38 (m, 1H), 3.26 (dd, *J* = 14.6, 5.6 Hz, 1H), 3.12 – 3.20 (m, 1H), 2.97 – 2.78 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB system, *J* = 263.0 Hz, 2F), -113.0 (s, 2F), -121.7 (s, 2F), -122.2 (s, 2F), -123.6 (s, 2F), -125.2 (s, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 156.5, 149.8, 133.3, 130.3, 130.2, 129.8, 128.3, 123.4, 121.4, 119.0, 118.8, 46.4, 41.8 (tm, *J* = 21.0 Hz), 20.0. **IR** (film) ν_{max}: 1590, 1507, 1488, 1426, 1224, 1146, 881, 773 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{29}H_{19}F_{16}IO_5S + Na^+$] 932.9635, found 932.9649.

phenyl 1,1,2,2-tetrafluoro-2-((1,1,2,2,3,3,4,4-octafluoro-6-iodo-10-(((8S,9R,13R,14R)-13-

methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)decyl)oxy)ethane-1-sulfonate (4s): Obtained as yellow liquid in yield 58% by silica gel flash column chromatography eluted with EA/PE = 1:5 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.64 (s, 1H), 4.37 – 4.29 (m, 1H), 3.95 (t, *J* = 5.9 Hz, 2H), 2.98 – 2.70 (m, 4H), 2.56 – 2.44 (m, 1H), 2.43 – 2.37 (m, 1H), 2.31 – 2.18 (m, 1H), 2.17 – 1.93 (m, 4H), 1.89 – 1.72 (m, 4H), 1.66 – 1.41 (m, 8H), 0.90 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.8 (s, 2F), -124.9 – -125.1 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 221.0, 156.9, 149.8, 137.7, 132.1, 130.2, 128.3, 126.3, 121.3, 114.6, 112.1, 67.4, 50.4, 48.0, 44.0, 41.5 (tm, *J* = 21.0 Hz), 40.0, 38.4, 35.8, 31.6, 29.6, 28.2, 26.5, 26.4, 25.9, 21.6, 20.3, 13.9. **IR** (film) ν_{max}: 2930, 1739, 1609, 1488, 1424, 1201, 1146, 881, 774, 524 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{36}H_{37}F_{12}IO_6S + Na^+$] 975.1056, found 975.1061.

phenyl 1,1,2,2-tetrafluoro-2-((1,1,2,2,3,3,4,4-octafluoro-10-hydroxy-6-iododecyl)oxy)ethane-1-sulfonate (4t): Obtained as yellow liquid in yield 66% by silica gel flash column chromatography eluted with EA/PE = 1:2 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.42 – 7.36 (m, 1H), 7.31 – 7.25 (m, 2H), 4.37 – 4.29 (m, 1H), 3.67 (t, *J* = 6.5 Hz, 2H), 3.00 – 2.68 (m, 2H), 1.89 – 1.77 (m, 2H), 1.68 – 1.41 (m, 5H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.5 – -81.6 (m, 2F), -83.0 – -83.2 (m, 2F), -111.4 – -115.2 (AB, *J* = 263 Hz, 2F), -113.0 (s, 2F), -123.9 (s, 2F), -125.0 – -125.1 (m, 2F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.8, 130.2, 128.3, 121.4, 62.4, 41.5 (tm, *J* = 21.0 Hz), 40.0, 31.5, 26.0, 20.5. **IR** (film) ν_{max}: 3365, 2939, 1723, 1586, 1488, 1424, 1318, 1143, 882, 773 cm^{-1}. **HRMS** (ESI): calcd. for [$C_{18}H_{17}F_{12}IO_5S + Na^+$] 722.9542, found 722.9547.

Supporting Information

The Supporting Information is available free of charge on the website at DOI: Copies

of NMR spectra (PDF)

Acknowledgements

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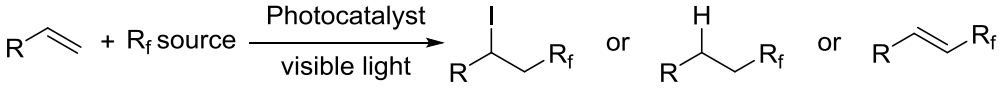
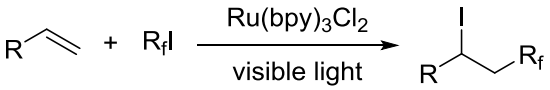


Rf source:	Umemoto's reagent
	Togni's reagent
	R_fSO_2Cl
	R_fI

For examples

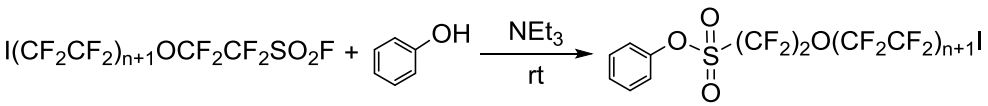
This work:



$R_f = (CF_2CF_2)_{n+1}OCF_2CF_2SO_3Ph$

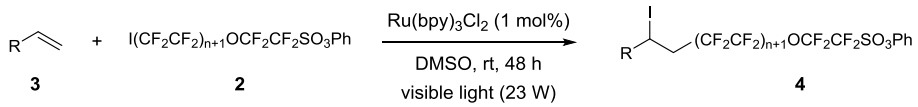
n = 0, 1, 2, 3

Scheme 1 Fluoroalkylation of terminal alkenes under visible light promotion

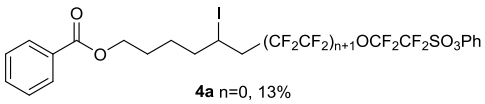


1a, n=0 **2a**, n=0
1b, n=1 **2b**, n=1
1c, n=2 **2c**, n=2
1d, n=3 **2d**, n=3

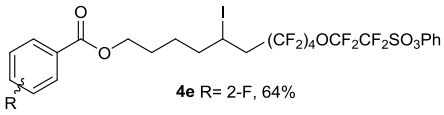
Scheme 2 Synthesis of sulfonates



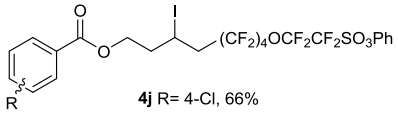
3 **2** **4**



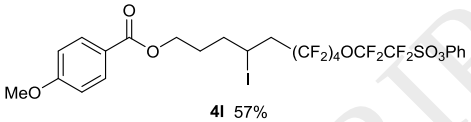
4a n=0, 13%
4b n=1, 71%
4c n=2, 69%
4d n=3, 68%



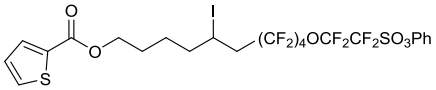
4e R= 2-F, 64%
4f R= 3-Me, 59%
4g R= 3-NO_2, 47%
4h R= 4-F, 70%
4i R= 4-I, 72%



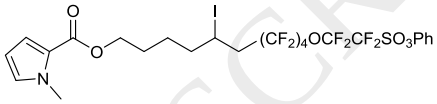
4j R= 4-Cl, 66%
4k R= 4-*t*-Bu, 59%



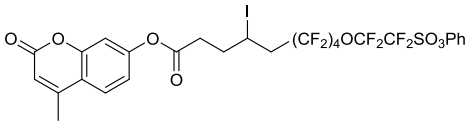
4l 57%



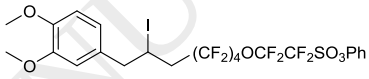
4m 70%



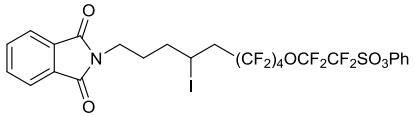
4n 43%



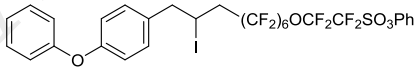
4o 43%



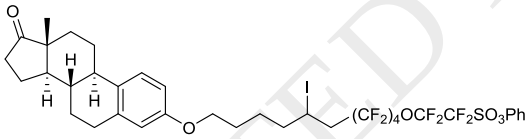
4p 51%



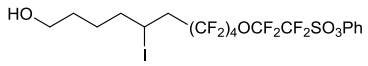
4q 52%



4r 48%

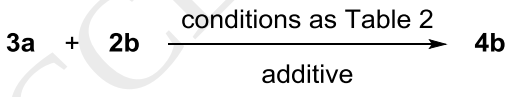


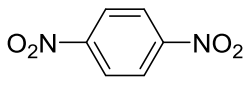
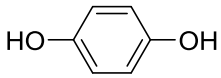
4s 58%



4t 66%

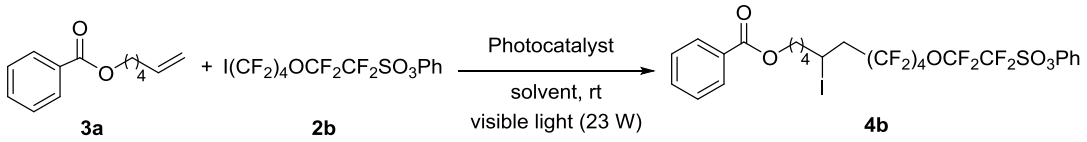
[a] Reaction conditions: **2** (1.2 mmol), **3** (0.2 mmol), DMSO (2.0 mL), visible light, 48 h, under N_2.
[b] Isolated yields.



additive		yield (%)
20 mol%		24
20 mol%		99

Scheme 3 Inhibition experiments

Table 1 Screening of reaction conditions



3a **2b** **4b**

Table 1 Screening of reaction conditions

Entry[a]	ratio (**3a:2b**)	solvent	Photocatalyst	light	t (h)	yield (%)[e]
1	1:1.5	DMSO	$Ru(bpy)_3Cl_2$	white light	24	31
2	1:2	DMSO	$Ru(bpy)_3Cl_2$	white light	24	35
3	1:3	DMSO	$Ru(bpy)_3Cl_2$	white light	24	45
4	1:4	DMSO	$Ru(bpy)_3Cl_2$	white light	24	56
5	1:5	DMSO	$Ru(bpy)_3Cl_2$	white light	24	77
6	1:6	DMSO	$Ru(bpy)_3Cl_2$	white light	24	91
7	1:6	DCM	$Ru(bpy)_3Cl_2$	white light	24	98
8	1:6	MeCN	$Ru(bpy)_3Cl_2$	white light	24	51
9	1:6	DMF	$Ru(bpy)_3Cl_2$	white light	24	56
10	1:6	NMP	$Ru(bpy)_3Cl_2$	white light	24	53
11	1:6	DMPU	$Ru(bpy)_3Cl_2$	white light	24	83
12	1:6	THF	$Ru(bpy)_3Cl_2$	white light	24	79
13	1:6	DMSO[b]	$Ru(bpy)_3Cl_2$	white light	24	86
14	1:6	DMSO[c]	$Ru(bpy)_3Cl_2$	white light	24	76
15	1:6	DMSO	$Ru(bpy)_3Cl_2$	blue LED	24	74
16	1:6	DMSO	$Ru(bpy)_3Cl_2$	white light	36	94
17	1:6	DMSO	$Ru(bpy)_3Cl_2$	white light	48	99
18	1:6	DMSO	$Ru(bpy)_3Cl_2$	white light	60	78
19	1:6	DMSO	$Ru(bpy)_3Cl_2$[d]	white light	48	76
20	1:6	DMSO	$Ru(bpy)_3Cl_2$	dark	48	0
21	1:6	DMSO	-	white light	48	0
22	1:6	DMSO	Eosin Y	white light	48	56

[a]Reaction conditions: **3a** (0.2 mmol), solvent (2.0 mL), Photocatalyst (1 mol%), visible light, under N_2.

[b]DMSO (1.0 mL), [c]DMSO (3.0 mL), [d]Photocatalyst (0.5 mol%).

[e]Yields were determined by ^{19}F NMR spectroscopy using benzotrifluoride as the internal standard.