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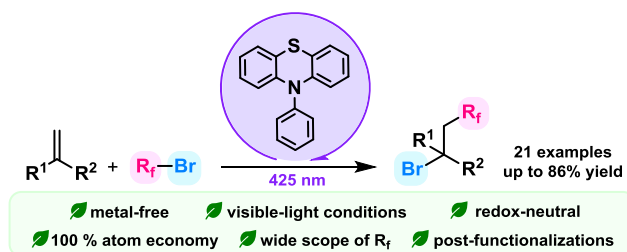
# 10-Phenylphenothiazine-Organophotocatalyzed Bromo-Perfluoroalkylation of Unactivated Olefins

*Koto Tagami,<sup>[1,2]</sup> Moeko Nakayama,<sup>[1]</sup> Tadashi Kanbara,<sup>[1]</sup> Dominique Cahard,<sup>\*[2]</sup> Tomoko Yajima<sup>\*[1]</sup>*

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KEYWORDS. perfluoroalkylation; bromination; difunctionalization, ATRA; photocatalysis; metal-free; visible-light; atom economy.



ABSTRACT. In this study, we have developed a smooth metal-free visible-light-induced bromo-perfluoroalkylation of unactivated olefins with the aid of 10-phenylphenothiazine (PTH) as an organic photoredox catalyst. The reaction is 100% atom-economic redox-neutral and proceeds with stoichiometric amounts of olefin and perfluoroalkyl bromide. To show the potential of these

unexplored motifs, we carried out various post-functionalizations taking advantage of the bromine atom, including gram-scale experiments.

## INTRODUCTION

The unique properties of fluorine atoms mean that fluorine-containing compounds are ubiquitous in pharmaceuticals, agrochemicals, and functional materials.<sup>1</sup> Among them, compounds containing both a perfluorocarbon segment and a hydrocarbon moiety have recently raised concerns regarding the "PFAS issue"; however, their extremely high value cannot be ignored. For instance, they have been used clinically in ophthalmic surgery,<sup>2a,b</sup> and their distinctive interfacial properties make them intriguing objects in microfluidics.<sup>2c</sup> In addition, the utility of perfluoroalkyl compounds as functional materials is significant and they are essential to our lives, making the synthesis of potentially valuable compounds a major challenge. Therefore, various research groups are actively engaged in the development of low-cost, direct, and straightforward methods for introducing perfluoroalkyl chains.<sup>3</sup> Atom Transfer Radical Addition (ATRA) reaction is an excellent atom-economical method for the simultaneous difunctionalization of olefin substrates.<sup>4</sup> In this context, most previous work has focused on perfluoroalkyl iodides, with only a few examples using perfluoroalkyl bromides.<sup>5</sup> This could be attributed to the inability of bromo-adducts to withstand harsh conditions, such as high temperatures or ultraviolet light conditions, required to cleave the more robust C-Br bond versus the C-I bond. Considering that radical reactions with perfluoroalkyl bromides as precursors have been already developed,<sup>6</sup> enhancing their utility in ATRA would be of significant importance. To achieve the synthesis of bromo-perfluoroalkyl derivatives by ATRA reaction, the use of photoredox catalyst and visible light appeared as an attractive approach, in particular from the perspective of green chemistry and the development of environmentally-friendly mild

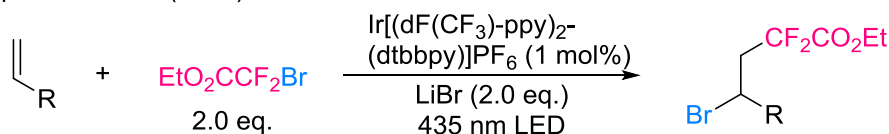
processes.<sup>7</sup> An early example of visible-light-induced reaction using ethyl bromodifluoroacetate was reported by Stephenson *et al* in the bromo-difluoroalkylation of olefins by means of an iridium catalyst and a light emitting diode (Scheme 1a).<sup>8</sup>

**Scheme 1.** (a-d) State-of-the-Art in Photocatalyzed Bromo-Perfluoroalkylation of Olefins, and (e) Our work

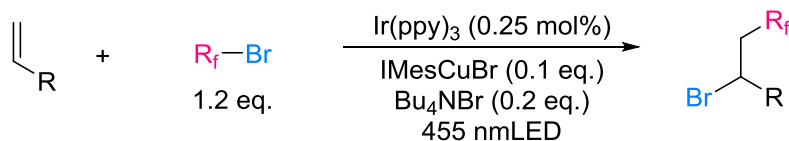
In b) change “Dilman *et al* “ by “Dilman *et al*”with *et al* in italics

In b) c) d) place a space between nm and LED

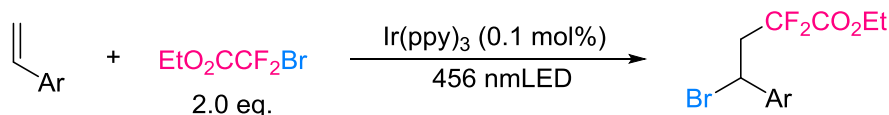
a) Stephenson *et al* (2011)



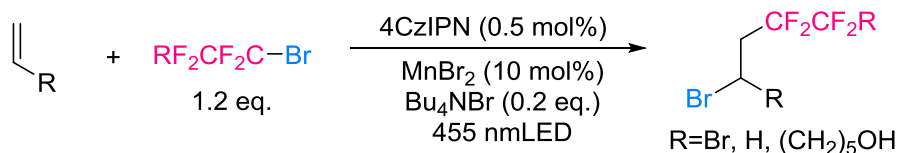
b) Dilman *et al* (2021)



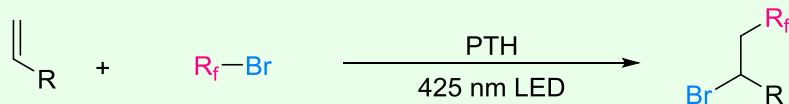
c) Molander *et al* (2022)



d) Dilman *et al* (2023)



e) This work.



- 🌿 metal-free
 🌿 visible-light conditions
 🌿 redox-neutral
- 🌿 100% atom economy
 🌿 wide scope of R<sub>f</sub>
🌿 post-functionalizations

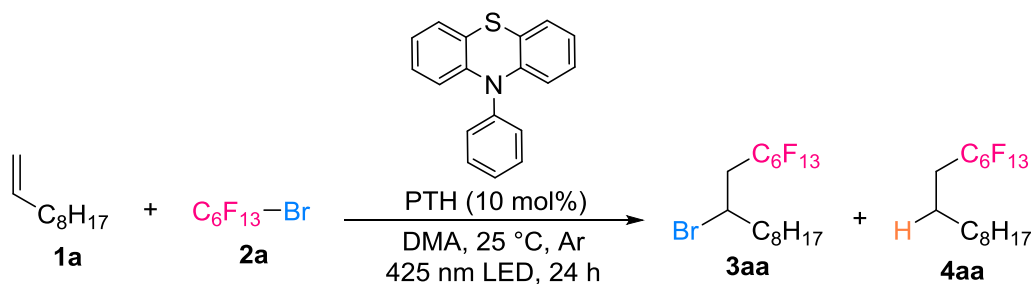
[Ir{dF(CF<sub>3</sub>)ppy}<sub>2</sub>(dtbpy)]PF<sub>6</sub>: [4,4'-bis(1,1-dimethylethyl)-2,2'-bipyridine-N1,N1']bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-N]phenyl-C]Iridium(III) hexafluorophosphate; LED: light emitting diode; Ir(ppy)<sub>3</sub>: tris(2-phenylpyridine)iridium; IMesCuBr: *N*-heterocyclic carbene ligated copper bromide; 4CzIPN: 1,2,3,5-tetrakis(carbazole-9-yl)-4,6-dicyanobenzene; PTH: 10-phenylphenothiazine.

In recent years, a similar ATRA reaction using an iridium catalyst has been reported by Dilman *et al.*<sup>9</sup> This reaction took place through the cooperative roles of Ir and *N*-heterocyclic carbene ligated copper bromide (IMesCuBr) in the presence of tetrabutylammonium bromide as an additive. In 2022, a bromo-difluoroalkylation was reported by Molander *et al* (Scheme 1c).<sup>10</sup> This reaction was carried out without the need for a reducing agent to recycle the iridium catalyst, with as low as 0.1 mol% Ir(ppy)<sub>3</sub>. However, iridium, which is a precious metal, is expensive and may present a potential risk to the human body. Therefore, exploring reactions under metal-free conditions is currently one of the most important concerns.<sup>11</sup> In this vein, during our own investigation, Dilman *et al* reported the bromo-perfluoroalkylation of olefins using 1,2,3,5-tetrakis(carbazole-9-yl)-4,6-dicyanobenzene (4CzIPN) as organic photoredox catalyst (Scheme 1d).<sup>12</sup> However, this reaction was accomplished using a dual catalytic system 4CzIPN and MnBr<sub>2</sub> in the presence of tetrabutylammonium bromide, and to our knowledge, a truly metal-free bromo-perfluoroalkylation reaction has not been reported to date. Previously, Hawker *et al* reported that the readily available and inexpensive organocatalyst 10-phenylphenothiazine (PTH) promoted Atom Transfer Radical Polymerization (ATRP) reactions of methyl methacrylate initiated by ethyl bromophenylacetate.<sup>13</sup> Inspired by this reaction, we hypothesized that PTH could act as a photocatalyst for bromo-perfluoroalkylation of olefins (Scheme 1e). We herein report the effectiveness of the reaction that affords an unprecedented access to novel amphiphilic scaffolds featuring a perfluoroalkyl chain and a bromine atom installed for further chemical transformations.

## RESULTS AND DISCUSSION

At the outset, we screened the reaction conditions using 1-decene (**1a**) and perfluorohexyl bromide (**2a**) as model reaction partners (Table 1). Alongside with the desired bromo-perfluoroalkylated product **3aa**, we could detect by  $^{19}\text{F}$  NMR the hydro-perfluoroalkylated by-product **4aa** in up to 14% as a result of a competitive hydrogen abstraction.

**Table 1.** Selected Results for the Optimization of the Reaction Conditions <sup>a</sup>



Entry	Deviation from standard conditions	Yield <sup>b</sup>	
		<b>3aa</b>	<b>4aa</b>
1	-	78	8
2	10 mol% eosin Y	0	0
3	380 nm LED	76	5
4	450 nm LED	6	2
5	White LED	0	0
6	In the dark at 100 °C without LED	0	0
7	3 mol% of PTH	63	9
8	15 mol% of PTH	77	6
9	3 h	73	5

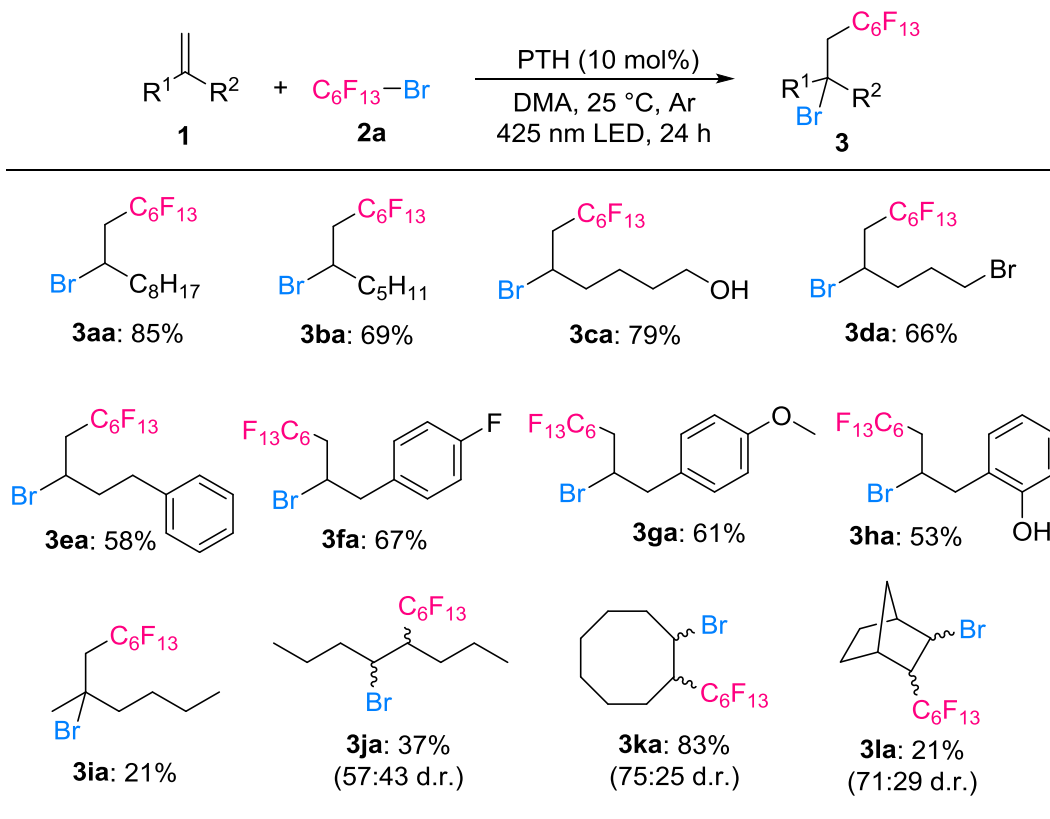
10	36 h	77	11
11	DMF (0.1 M)	70	3
12	DCE (0.1 M)	63	4
13	CH <sub>3</sub> CN (0.1 M)	40	7
14	No solvent	48	0
15	DMA (0.05 M)	66	14
16	DMA (1.0 M)	84	2
17	DMA (1.0 M), <b>2a</b> (1.0 eq.)	86 (85)	1

<sup>a</sup> Reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol, 3.0 equiv.), PTH (0.025 mmol, 10 mol %), DMA (0.1 M), at 25 °C, under argon atmosphere for 24 h, and under 425 nm LED irradiation. <sup>b</sup> Yields based on <sup>19</sup>F NMR spectroscopy using benzo-trifluoride as an internal standard; isolated yields are given in parentheses.

In the presence of 10 mol% of 10-phenylphenothiazine (PTH), 3 equiv. of **2a** were added to **1a** (0.25 mmol) in dimethylacetamide (DMA), and the mixture was irradiated with a 425 nm light emitting diode (LED) and stirred at an external temperature of 25 °C under an argon atmosphere for 24 hours. As a result, the bromo-perfluoroalkylated product **3aa** was obtained in 78% yield accompanied by 8% of hydro-perfluoroalkylated by-product **4aa** (entry 1). With this first experiment, we confirmed that this reaction is redox-neutral,<sup>14</sup> as it proceeds well without transition-metal nor any additive required in previous reports.<sup>8-12</sup> We examined other organophotocatalysts instead of PTH, including eosin Y, which was successful in our previous work on iodo-perfluoroalkylation of olefins (entry 2, see also Table S1).<sup>15</sup> However, the reaction did not proceed, suggesting that the ground state redox potential of PTH is higher than the reported value (+0.68 V vs SCE),<sup>11, 13</sup> exceeding that of Eosin Y (+0.76 V vs SCE).<sup>11, 16</sup> Next, the light wavelength was tuned. The reaction proceeded in 76% yield at a shorter wavelength of 380 nm LED while hardly any reaction proceeded at 450 nm LED or with a white LED (entries 3–5).

In addition, the reaction was carried out under purely thermal conditions at 100°C in the dark without irradiation, but the reaction did not proceed (entry 6). Therefore, we decided to continue our investigation using a 425 nm LED. The amount of PTH was then investigated, confirming that 3 mol% of PTH was insufficient but more than 10 mol% was not necessary (entries 7, 8). It was also revealed that reaction time had no significant effect on the yield of **3aa** (entries 9, 10); we have set the reaction time at 24 hours taking into account the lower reactivity of other substrates. Next, we screened other solvents in the hope of improving the yield of **3aa** and suppressing by-product **4aa** (entries 11–14); however, using dimethylformamide (DMF), 1,2-dichloroethane (DCE) or acetonitrile, the yield of **3aa** was not improved. DMA was found to be suitable due to its high solubility for PTH and fewer competing side reactions. We also carried out the reaction under neat conditions; however, **3aa** was obtained only in 48% yield albeit without the production of **4aa** (entry 14). This result suggested that the hydrogen in the by-product **4aa** originates from the solvent. The concentration of reactants in DMA was also examined and we observed that a more dilute 0.05 M solution enhanced the formation of by-product **4aa** to 14% (entry 15). On the other hand, the yield of **3aa** was improved to 84% in a 1.0 M concentrated solution together with a reduced yield of **4aa** (entry 16). Finally, we were fortunate to find that reducing the amount of **2a** to 1 equiv. still allowed the reaction and even improved the yield of **3aa** to 86% (entry 17). These later optimized conditions clearly demonstrate full atom-economy. Using the conditions of entry 17 as the optimal conditions, we next investigated the scope of unactivated olefins (Scheme 2).

**Scheme 2.** Scope of Unactivated Olefins <sup>a, b</sup>



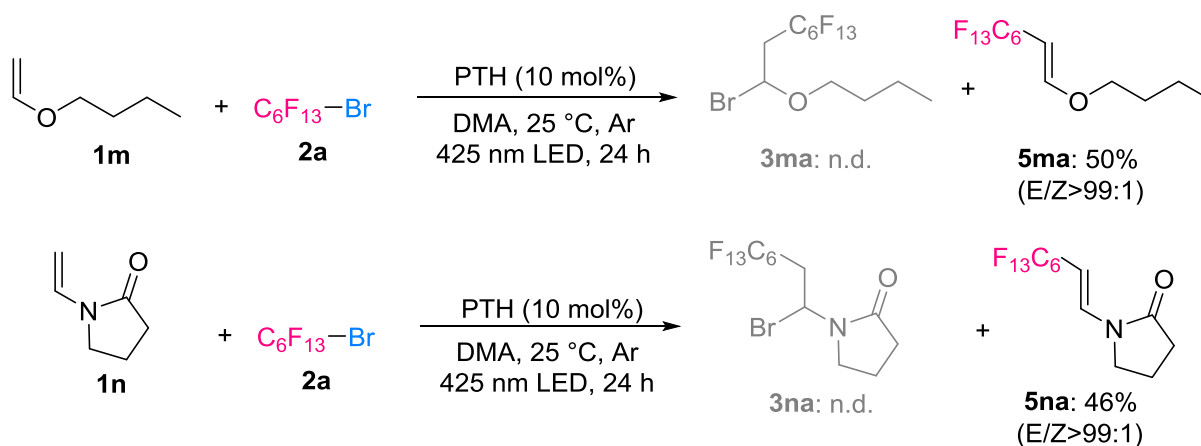
<sup>a</sup> Reaction conditions: **1** (0.25 mmol), **2a** (0.25 mmol, 1.0 equiv.), PTH (0.025 mmol, 10 mol %), DMA (1.0 M), at 25 °C, under argon atmosphere for 24 h, and under 425 nm LED irradiation. <sup>b</sup> Isolated yields.

Initially, 1-heptene (**1b**) with a shorter alkyl chain length, versus 1-decene (**1a**), was examined and gave compound **3ba** in 69% yield. Olefins **1c–1e** having a hydroxy function, a bromine atom, or a phenyl group at the terminal position, respectively, were also investigated, giving products **3ca–3ea** in yields ranging from 58 to 79%. Allyl aryls featuring fluorine, methoxy, and hydroxy substituents on the aromatic ring also gave the desired products **3fa–3ha** in 53–67% yield. After having investigated monosubstituted olefins, we examined disubstituted ones; for instance, from 1,1-disubstituted olefin **1i**, we could isolate the tertiary alkyl bromide **3ia** albeit in 21% yield. Internal disubstituted symmetrical olefins **1j–l** successfully gave the corresponding

bromo-perfluoroalkylated products **3ja–3la** in 21–83% yield as mixtures of diastereomers due to the creation of two contiguous stereogenic centers. The acyclic product **3ja** was obtained with a poor dr value, while cyclic products **3ka** and **3la** present moderate dr values (Scheme 2).

Subsequently, we applied the reaction conditions to heteroatom-substituted olefins such as the butyl vinyl ether (**1m**) and *N*-vinyl-2-pyrrolidone (**1n**) (Scheme 3).

**Scheme 3.** Reaction of Vinyl Ether / Vinylpyrrolidone <sup>a, b</sup>

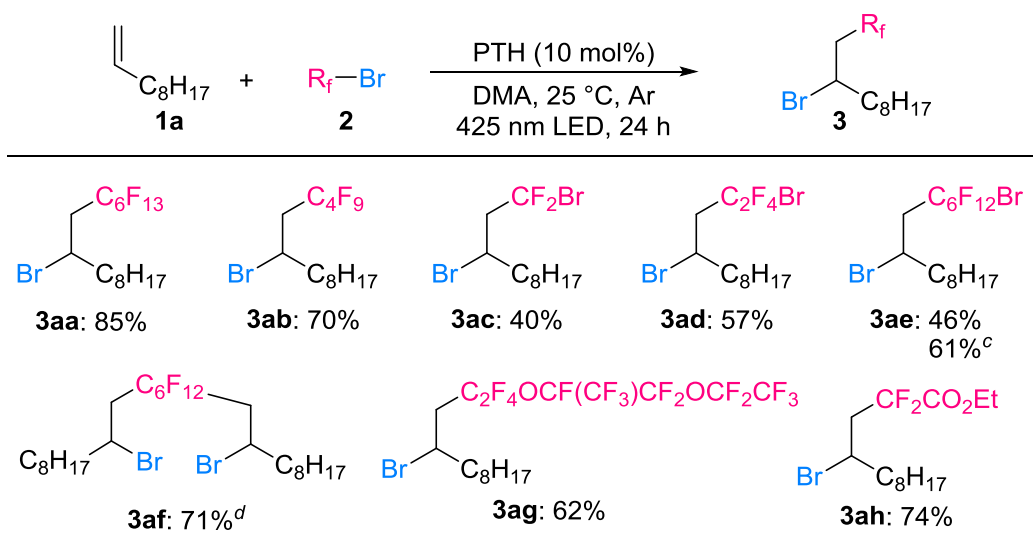


<sup>a</sup> Reaction conditions: **1** (0.25 mmol), **2a** (0.25 mmol, 1.0 equiv.), PTH (0.025 mmol, 10 mol %), DMA (1.0 M), at 25 °C, under argon atmosphere, for 24 h, and under 425 nm LED irradiation. <sup>b</sup> Isolated yields. N.d: not detected.

As a result, bromo-perfluoroalkylated products **3ma** and **3na** were not observed, and only olefin compounds **5ma** and **5na**, in which HBr was eliminated, were obtained in 50 and 46% yields, respectively with high stereoselectivity (E/Z > 99:1). These results suggest that if the bromo-perfluoroalkylated product is not stable, the elimination proceeds rapidly. We also screened this reaction with several conjugated olefins and alkynes, but in all cases the yield of the desired products was low or the products were not obtained due to the low reactivity of the substrates or the instability of the products (Tables S8, S9).

Next, we investigated the scope of perfluoroalkyl bromides, dibromides and functionalized derivatives (Scheme 4).

**Scheme 4.** Scope of Perfluoroalkyl Bromides <sup>a, b</sup>



<sup>a</sup> Reaction conditions: **1a** (0.25 mmol), **2** (0.25 mmol, 1.0 equiv.), PTH (0.025 mmol, 10 mol %), DMA (1.0 M), at 25 °C, under argon atmosphere, for 24 h, and under 425 nm LED irradiation. <sup>b</sup> Isolated yields. <sup>c</sup> 2.0 equiv. of **2e** was used. <sup>d</sup> 2.0 equiv. of **1a** was used.

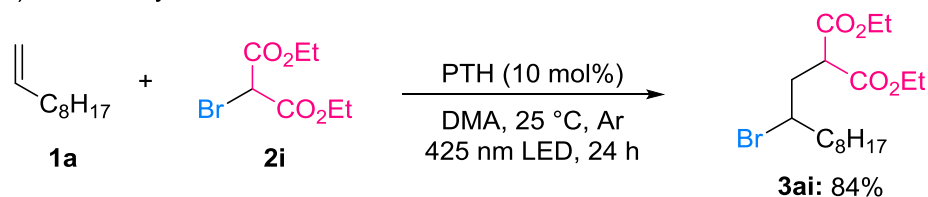
The short-chain perfluorobutyl bromide (**2b**) was engaged in the reaction and gave compound **3ab** in 70% yield. Subsequently, we examined dibromoperfluoroalkanes **2c–2e** with different chain lengths and obtained the products **3ac–3ae**, featuring one bromine atom being incorporated onto the olefin and one bromine atom remaining attached on the perfluoroalkyl chain, in 40–57% yield. We could increase the yield of **3ae** to 61% by adding 2 equiv. of **2e**. Utilization of 2 equiv. of **1a** gave preferentially the bis-adduct **3af** for which both bromine atoms reacted. We also found that this reaction enabled not only the introduction of perfluoroalkyl or

bromoperfluoroalkyl chains, but also long-chain fluoroethers **2g** and ethyl difluoroacetate **2h**, giving products **3ag** and **3ah** in 62 and 74% yield, respectively.

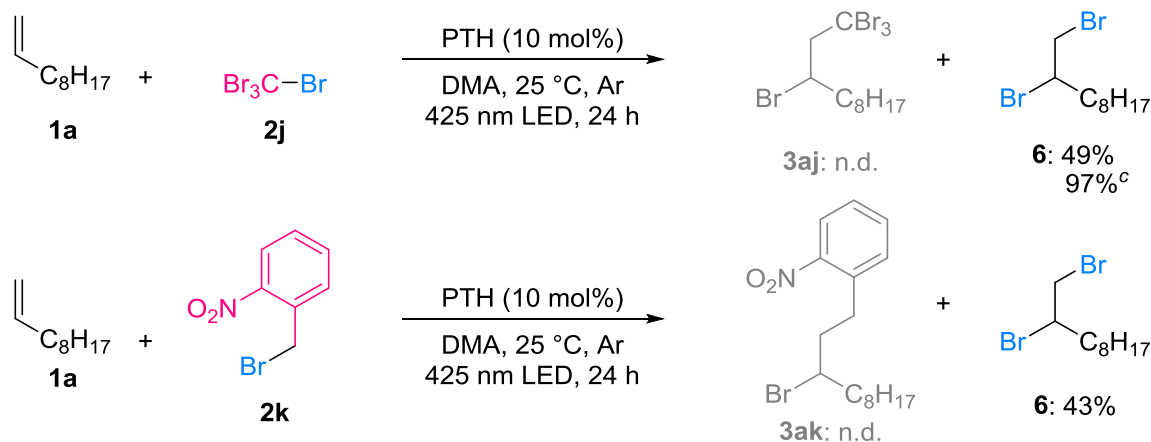
Outside of the scope of fluorine-containing bromides but with a view to enabling comparison with non-fluorinated reactants, we performed reactions using fluorine-free alkyl bromides. The versatility of the bromoalkylation procedure was demonstrated with electron-deficient diethyl bromomalonate (**2i**) (Scheme 5a, and Table S11) while carbon tetrabromide (**2j**) and 2-nitro benzyl bromide (**2k**) unexpectedly gave the dibrominated product **6** (Scheme 5b, and Scheme S2).<sup>17</sup> Interestingly, the addition of 2 equiv. of **2j** enhanced the yield of **6** to 97%, confirming the high efficiency of this reaction.

**Scheme 5.** Reactions Using Fluorine-Free Alkyl Bromides, (a) Bromo-alkylation, and (b) Dibromination <sup>a, b</sup>

a) Bromo-alkylation.



b) Dibromination



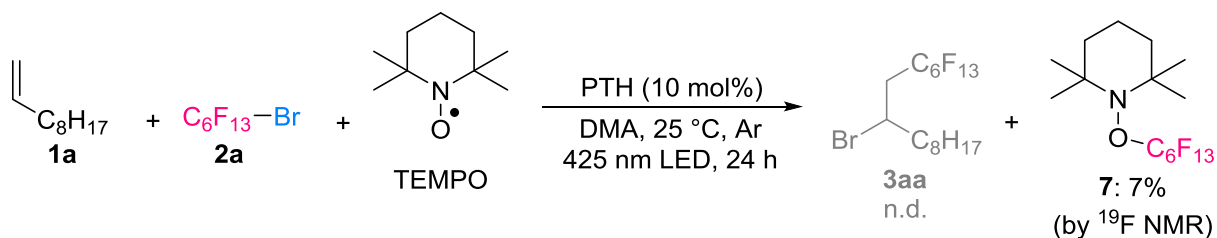
<sup>a</sup> Reaction conditions: **1a** (0.25 mmol), **2** (0.25 mmol, 1.0 equiv.), PTH (0.025 mmol, 10 mol %), DMA (1.0 M), at 25 °C, under argon atmosphere, for 24 h, and under 425 nm LED irradiation. <sup>b</sup> Isolated yields. <sup>c</sup> 2.0 equiv. of **2j** was used. N.d: not detected.

We hypothesized that the resulting CBr<sub>3</sub> and benzyl radicals were too stable to add to the olefin, and we suggest the involvement of bromine radicals in this reaction. Finally, we applied this reaction to other perfluoroalkyl halides (Scheme S3). In the reaction with perfluoroalkyl iodide, the iodo-adduct was subsequently reduced by PTH, leading to the formation of olefinic compounds and unidentified complex products. On the other hand, the reaction did not proceed with perfluoroalkyl chlorides, confirming the reaction specificity for bromo-perfluoroalkylation.<sup>18</sup>

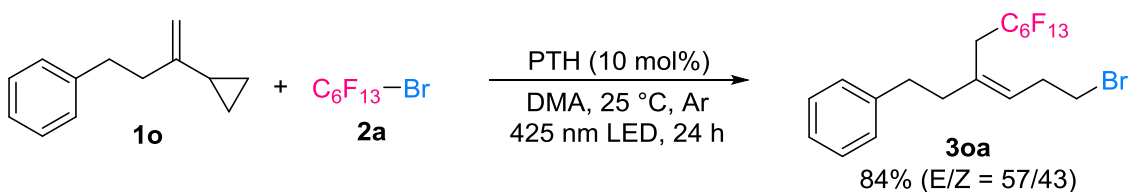
To get insights into the reaction mechanism, we carried out a series of experiments (Scheme 6).

**Scheme 6.** Mechanistic Studies, (a) Radical Trap Experiment, (b) Radical Clock Experiment, and (c) Cation Trap Experiment <sup>a, b</sup>

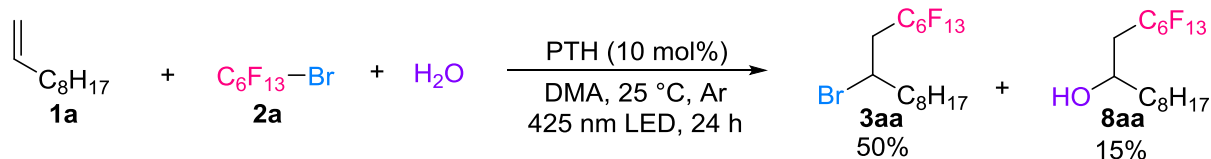
a) Radical trap experiment.



b) Radical clock experiment.



c) Cation trap experiment.

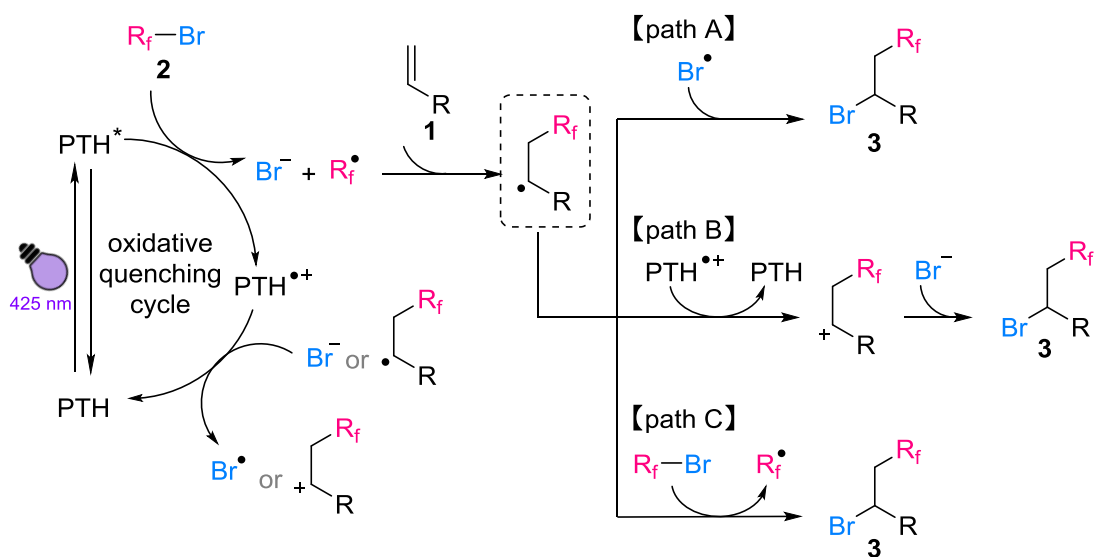


<sup>a</sup> Reaction conditions: **1** (0.25 mmol), **2a** (0.25 mmol, 1.0 equiv.), PTH (0.025 mmol, 10 mol %), TEMPO (0.25 mmol, 1.0 equiv. (a)), H<sub>2</sub>O (2.5 mmol, 10 equiv. (c)), DMA (1.0 M), at 25 °C, under argon atmosphere, for 24 h, and under 425 nm LED irradiation. <sup>b</sup> Isolated yields.

First, we performed a radical scavenging experiment using 1 equiv. of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) under the optimal reaction conditions. In this case, **3aa** was not obtained and only TEMPO adduct **7** was detected as evidenced by <sup>19</sup>F NMR (Scheme 6a). This result suggested the generation of perfluoroalkyl radicals. A radical clock experiment was then performed using olefin **1o** featuring a three-membered ring (Scheme 6b). As a result, the ring-opened product **3oa** was obtained in 84% yield, confirming the addition of a perfluoroalkyl radical to the olefin and subsequent ring-opening to afford the 1,5-addition product **3oa**. Finally, a cation trap experiment was conducted with 10 equiv. of water as a nucleophile under optimal reaction conditions, in order to evaluate whether a radical

intermediate, generated by the addition of the perfluoroalkyl radical to the olefin, was converted into a cation intermediate (Scheme 6c). The result of this experiment showed that the main product was still the bromine adduct **3aa**. However, the hydroxyl adduct **8aa** was also obtained in 15% yield, suggesting that the radical intermediate was partially converted into the corresponding cation intermediate. Furthermore, intermittent irradiation experiments were examined to investigate the possibility of radical chain reactions (Table S12, Figure S1). As a result, the yield increased only during light irradiation, but this result does not entirely rule out the radical chain mechanism.<sup>19</sup> Based on the results of these control experiments, we proposed a plausible reaction mechanism as follows (Scheme 7).

**Scheme 7.** Proposed Reaction Mechanism

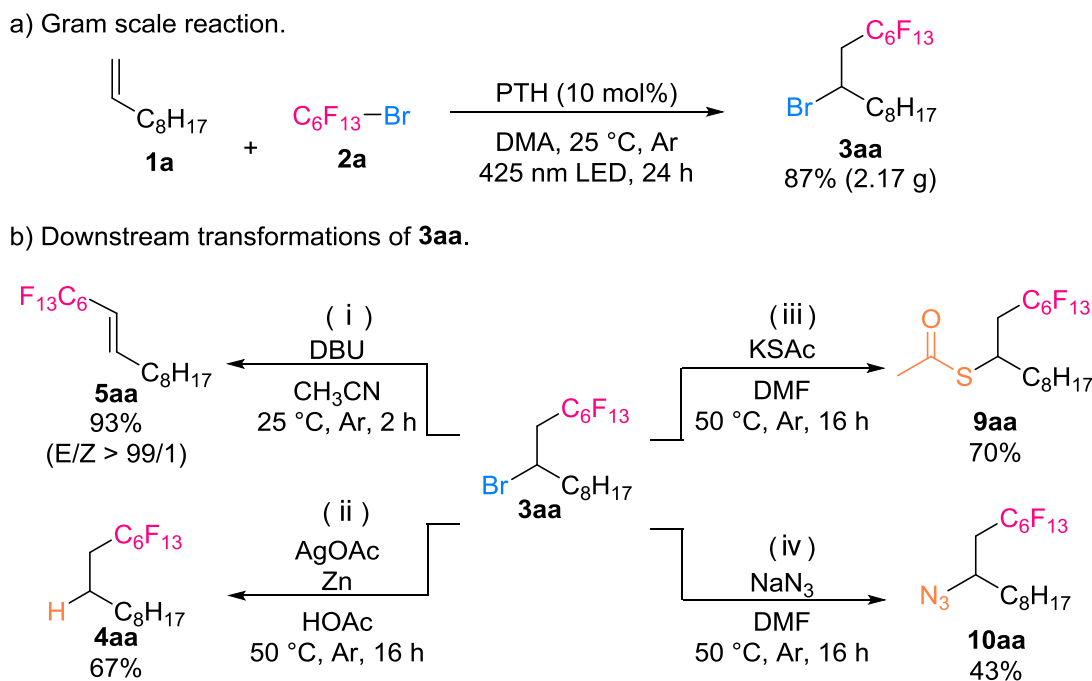


Initially, perfluoroalkyl radical and bromide anion are generated by single-electron-transfer from the excited state of PTH to perfluoroalkyl bromide **2**. The generated radical is next added to olefin **1** to generate a radical intermediate. At this stage, single-electron-transfer from the

bromide anion or the radical intermediate to PTH radical cation proceeds, returning PTH to the ground state. We then propose that the radical intermediate evolves in three ways: in path A, the desired bromo-perfluoroalkylated product **3** is obtained by radical coupling between the radical intermediate and the bromine radical; in path B, the radical intermediate is oxidized to a cation by the PTH radical cation, and then a bromide anion is added to the cation to yield product **3**; in path C, **3** is formed via a radical chain mechanism where the radical intermediate abstracts bromine from perfluoroalkyl bromide **2**.

Finally, we attempted scale-up experiments and post-modification reactions in the hope of developing this reaction in the medical and agrochemical industries (Scheme 8).

**Scheme 8.** (a) Gram Scale Reaction, and (b) Downstream Transformations of **3aa**<sup>a, b</sup>



<sup>a</sup> Reaction conditions: (a) **1** (4.0 mmol), **2a** (4.0 mmol, 1.0 equiv.), PTH (0.4 mmol, 10 mol %), DMA (1.0 M), at 25 °C, under argon atmosphere, for 24 h, and under 425 nm LED irradiation. (b)( i) **3aa** (0.1 mmol), DBU (0.1 mmol, 1.0 equiv.), CH<sub>3</sub>CN (1.0 M), at 25 °C, under argon atmosphere, for 2 h. ( ii) **3aa** (0.1 mmol), AgOAc (0.01 mmol, 10 mol%), Zn (0.4 mmol, 4.0

equiv.), HOAc (0.2 M), at 50 °C, under argon atmosphere, for 16 h. (iii) **3aa** (0.1 mmol), KSAc (0.2 mmol, 2.0 equiv.), DMF (0.2 M), at 50 °C, under argon atmosphere, for 16 h. (iv) **3aa** (0.1 mmol), NaN<sub>3</sub> (0.2 mmol, 2.0 equiv.), DMF (0.2 M), at 50 °C, under argon atmosphere, for 16 h. <sup>b</sup> Isolated yields. AgOAc: Silver acetate, HOAc: acetic acid, DBU: 1,8-diazabicyclo(5.4.0)undec-7-ene, KSAc: potassium thioacetate, NaN<sub>3</sub>: sodium azide.

As a result, the reaction performed under the optimized conditions on a 4 mmol scale gave 2.17 g of the desired product **3aa** in 87% yield (Scheme 8a). With this large amount of compound **3aa** in hand, we next attempted a range of different chemical transformations taking advantage of the presence of the bromine atom. First, HBr elimination using 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) proceeded well, giving *E*-selective olefin **5aa** in 93% yield (Scheme 8b(i)).<sup>15</sup> Reduction with silver acetate and zinc also proceeded well at 50 °C in acetic acid solution to give compound **4aa** in 67% yield (Scheme 8b(ii)).<sup>20</sup> We reacted potassium thioacetate with **3aa** in DMF solution and obtained the sulfur-containing product **9aa** in 70% yield (Scheme 8b(iii)).<sup>5a</sup> Finally, we observed that addition of sodium azide to **3aa** under same conditions afforded the azido perfluoroalkyl compound **10aa** in 43% yield (Scheme 8b(iv)).<sup>5a, 10a, 10b, 20</sup> From these results, we confirmed that the bromine atom in **3aa** can be converted into various functional groups, and we firmly believe there is room for further reactions.

## CONCLUSIONS

In this manuscript, we have demonstrated the visible-light induced radical bromo-perfluoroalkylation of unactivated olefins using PTH as an organophotoredox catalyst. This reaction requires only stoichiometric amounts of olefin and perfluoroalkyl bromide, without the necessity for a transition metal catalyst or an equivalent amount of a reductant as typically

demanded by previously reported methods. Under the optimized conditions, various terminal olefins, internal olefins, cyclic olefins, and perfluoroalkyl bromides with different structures were applicable. Furthermore, this atom-economical process can be carried out on a gram scale, and the bromine atom of the resulting compounds allows for subsequent post-reactions such as reduction, elimination, thiolation, and azidation.

## EXPERIMENTAL SECTION

**General information.** Unless otherwise noted, all reactions were performed under the argon atmosphere.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a JEOL GSX-400 spectrometer (400 MHz for  $^1\text{H}$ , 101 MHz for  $^{13}\text{C}$ , and 376 MHz for  $^{19}\text{F}$ ), or a BRUKER DPX 300 (300 MHz for  $^1\text{H}$ , 75 MHz for  $^{13}\text{C}$ , and 282 MHz for  $^{19}\text{F}$ ) with  $\text{CDCl}_3$  as the solvent, tetramethylsilane (TMS:  $\delta$  0 ppm for  $^1\text{H}$ ), chloroform-d ( $\text{CDCl}_3$ :  $\delta$  76.9 ppm for  $^{13}\text{C}$ ) and hexafluorobenzene ( $\text{C}_6\text{F}_6$ : -162.2 ppm for  $^{19}\text{F}$ ) as an internal standard. IR spectra were taken on SHIMADZU IRSpirit-T, or PerkinElmer Spectrum 100. HRMS were obtained with a BRUKER Compact with an ESI source, or a waters LCT Premier with EI or CI source. Precoated Merck Kieselgel 60 F254 and silica gel aluminum plates with F-254 were used for thin layer chromatography (TLC). Visualization was accomplished by UV light (254 nm). Kanto silica gel 60 (spherical neutral) were used for flash chromatography. All commercially available reagents and solvents (Sigma-Aldrich, Tokyo Chemical Industry, or Kanto Chemical) were used as received, without further purification. Compound **1o** was synthesized by reported literature<sup>21</sup> procedure and characterized by  $^1\text{H}$  NMR.<sup>21</sup> For irradiation, EvoluChem light-emitting diodes (SKU: HCK1012-XX-012,  $\lambda_d = 425$  nm, 33 mW/cm<sup>2</sup>, HepatoChem Inc.) was used without a filter and at a distance of 5 cm from the

light source to irradiation vessel (<https://www.hepatochem.com/product/hck1012-xx-012/>). For the heating reaction, an oil bath was used.

**General procedures.** To an oven-dried 20 ml two-necked flask equipped with a magnetic stirring bar and fitted with a septum was added 10-phenylphenothiazine (0.025 mmol, 10 mol%) and ultrasonic degassing was done in the presence of dry dimethylacetamide (0.25 ml). Then, olefin **1** (0.25 mmol), and perfluoroalkyl bromide **2** (0.25 mmol, 1.0 eq.) were added. The mixture was stirred for 24 hours at 25 °C under 425 nm LED irradiation. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give product **3**.

*8-Bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorohexadecane (3aa)*. The crude product was purified by column chromatography (hexane). Colorless oil, 118.1 mg, yield: 85%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 4.32–4.25 (1H, m), 2.88–2.59 (2H, m), 1.98–1.82 (2H, m), 1.61–1.52 (1H, m), 1.51–1.39 (1H, m), 1.36–1.28 (10H, m), 0.89 (3H, t, *J* = 6.9 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ: 120.1–110.8 (6C, m), 44.5, 40.0 (t, *J* = 21.0 Hz), 39.3 (d, *J* = 1.9 Hz), 32.0, 29.5, 29.4, 28.9, 27.3, 22.8, 14.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -81.2 (3F, s), -112.8 (1F, d, *J* = 289.0 Hz), -114.4 (1F, d, *J* = 289.0 Hz), -122.2 (2F, s), -123.3 (2F, s), -124.0 (2F, s), -126.6 (2F, s). IR (neat, cm<sup>-1</sup>) 2928, 2859, 1235, 1190, 1144, 812, 732, 716, 707, 699. HRMS (CI<sup>+</sup>) calcd for C<sub>16</sub>H<sub>19</sub>BrF<sub>13</sub> [M+H-H<sub>2</sub>]<sup>+</sup>: 537.0463, found 537.0443.

*6-Bromo-1,1,1,2,2,3,3,4,4-nonafluorotetradecane (3ab)*. The crude product was purified by column chromatography (hexane). Colorless oil, 77.0 mg, yield: 70%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 4.31–4.25 (1H, m), 2.87–2.59 (2H, m), 1.98–1.82 (2H, m), 1.63–1.52 (1H, m), 1.49–1.40 (1H, m), 1.39–1.28 (10H, m), 0.89 (3H, t, *J* = 6.6 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ: 120.0–108.6 (4C, m), 44.4, 39.9 (t, *J* = 21.1 Hz), 39.3, 32.0, 29.5, 29.3, 28.9, 27.3, 22.8, 14.2.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.5 (3F, s), -113.1 (1F, d,  $J = 292.9$  Hz), -114.7 (1F, d,  $J = 292.9$  Hz), -125.0 (2F, s), -126.4 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 2928, 1353, 1218, 1186, 1133, 1099, 1016, 879, 806, 722. HRMS ( $\text{CI}^+$ ) calcd for  $\text{C}_{14}\text{H}_{19}\text{BrF}_9$   $[\text{M}+\text{H}-\text{H}_2]^+$ : 437.0526, found 437.0530.

*1,3-Dibromo-1,1-difluoroundecane (3ac)* [CAS:98319-84-7]. The crude product was purified by column chromatography (petroleum ether). Colorless oil, 35.0 mg, yield: 40%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.27–4.20 (1H, m), 3.14–2.89 (2H, m), 1.96–1.78 (2H, m), 1.54–1.46 (2H, m), 1.29–1.26 (10H, m), 0.89 (3H, t,  $J = 8.0$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 120.8–110.4 (m), 52.8 (t,  $J = 21.2$  Hz), 47.1 (t,  $J = 2.5$  Hz), 38.7, 32.0, 29.5, 29.3, 28.9, 27.2, 22.8, 14.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -42.7 (2F, s). Data are in accordance with those described in the literature.<sup>22</sup>

*1,4-Dibromo-1,1,2,2-tetrafluorododecane (3ad)* [CAS:98319-92-7]. The crude product was purified by column chromatography (hexane). Colorless oil, 57.1 mg, yield: 57%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.31–4.25 (1H, m), 2.88–2.61 (2H, m), 1.98–1.81 (2H, m), 1.61–1.52 (1H, m), 1.49–1.40 (1H, m), 1.39–1.28 (10H, m), 0.89 (3H, t,  $J = 6.9$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 120.4–109.9 (2C, m), 45.2, 39.6 (t,  $J = 21.2$  Hz), 39.2 (d,  $J = 2.0$  Hz), 32.0, 29.5, 29.3, 28.9, 27.3, 22.8, 14.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -66.9 (2F, s), -110.5 (1F, dd,  $J = 254.3$ , 34.7 Hz), -112.3 (1F, dd,  $J = 254.3$ , 34.7 Hz). Data are in accordance with those described in the literature.<sup>22</sup>

*1,8-Dibromo-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexadecane (3ae)*. The crude product was purified by column chromatography (hexane). Colorless oil, 69.0 mg, yield: 46%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.32–4.25 (1H, m), 2.88–2.59 (2H, m), 1.98–1.82 (2H, m), 1.61–1.51 (1H, m), 1.49–1.40 (1H, m), 1.39–1.28 (10H, m), 0.89 (3H, t,  $J = 6.9$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 119.2–110.9 (6C, m), 44.6, 40.0 (t,  $J = 20.1$  Hz), 39.3, 32.0, 29.5, 29.3, 28.9, 27.3, 22.8,

14.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -63.9 (2F, s), -112.9 (1F, d,  $J = 289.0$  Hz), -114.5 (1F, d,  $J = 289.0$  Hz), -117.7 (2F, s), -121.6 (2F, s), -122.0 (2F, s), -124.1 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 2928, 2856, 1468, 1366, 1202, 1148, 1080, 743, 719, 699, 657. HRMS ( $\text{Cl}^+$ ) calcd for  $\text{C}_{16}\text{H}_{19}\text{Br}_2\text{F}_{12}$   $[\text{M}+\text{H}-\text{H}_2]^+$ : 596.9662, found 596.9666.

*9,18-Dibromo-11,11,12,12,13,13,14,14,15,15,16,16-dodecafluorohexacosane (3af)*. The crude product was purified by column chromatography (hexane). Colorless oil, 131.1 mg, yield: 71%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.41–4.25 (2H, m), 2.87–2.59 (4H, m), 1.96–1.83 (4H, m), 1.67–1.51 (2H, m), 1.49–1.40 (2H, m), 1.39–1.28 (20H, m), 0.89 (6H, t,  $J = 6.9$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 120.1–110.9 (6C, m), 44.7 (2C), 40.1 (2C, t,  $J = 21.0$  Hz), 39.3 (2C), 32.0 (2C), 29.5 (2C), 29.3 (2C), 28.9 (2C), 27.3 (2C), 22.8 (2C), 14.2 (2C).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -112.8 (2F, d,  $J = 277.4$  Hz), -114.5 (2F, d,  $J = 277.4$  Hz), -122.1 (4F, s), -124.2 (4F, s). IR (neat,  $\text{cm}^{-1}$ ) 2927, 2856, 1459, 1366, 1194, 1141, 1099, 720, 696, 659. HRMS ( $\text{ESI}^+$ ) calcd for  $\text{C}_{26}\text{H}_{40}\text{Br}_2\text{F}_{12}\text{Na}$   $[\text{M}+\text{Na}]^+$ : 761.1203, found 761.1212.

*4-Bromo-1,1,2,2-tetrafluoro-1-((1,1,1,2,3,3-hexafluoro-3-(1,1,2,2,2-pentafluoroethoxy)propan-2-yl)oxy)dodecane (3ag)*. The crude product was purified by column chromatography (hexane). Colorless oil, 96.3 mg, yield: 62%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.28–4.21 (1H, m), 2.79–2.52 (2H, m), 1.96–1.80 (2H, m), 1.60–1.51 (1H, m), 1.48–1.39 (1H, m), 1.36–1.28 (10H, m), 0.89 (3H, t,  $J = 6.9$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 120.2–113.8 (7C, m), 44.5, 39.7 (t,  $J = 21.0$  Hz), 39.2, 32.0, 29.5, 29.3, 28.9, 27.3, 22.8, 14.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -80.3 (3F, s), -83.5 (2F, s), -86.3 (2F, s), -87.2 (3F, s), -88.9 (2F, s), -116.0–118.5 (2F, m), -146.1 (1F, s). IR (neat,  $\text{cm}^{-1}$ ) 2930, 2859, 1308, 1231, 1189, 1135, 1098, 986, 713, 696. HRMS ( $\text{Cl}^+$ ) calcd for  $\text{C}_{17}\text{H}_{19}\text{BrF}_{15}\text{O}_2$   $[\text{M}+\text{H}-\text{H}_2]^+$ : 619.0329, found 619.0326.

*Ethyl 4-bromo-2,2-difluorododecanoate (3ah)* [CAS:1025955-87-6]. The crude product was purified by column chromatography (hexane/EtOAc = 20:1). Colorless oil, 63.4 mg, yield: 74%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.34 (2H, dd,  $J = 14.0, 8.0$  Hz), 4.19–4.11 (1H, m), 2.89–2.74 (1H, m), 2.70–2.58 (1H, m), 1.92–1.79 (2H, m), 1.56–1.49 (1H, m), 1.48–1.41 (1H, m), 1.37 (3H, t,  $J = 8.0$  Hz), 1.29–1.26 (10H, m), 0.88 (3H, t,  $J = 6.6$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 163.7 (t,  $J = 31.7$  Hz), 117.4–112.4 (m), 63.3, 46.5 (q,  $J = 1.9$  Hz), 43.8 (t,  $J = 23.0$  Hz), 39.3, 31.9, 29.5, 29.3, 28.9, 27.3, 22.8, 14.2, 14.0.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -102.9 (1F, d,  $J = 267.0$  Hz), -107.9 (1F, d,  $J = 267.0$  Hz). Data are in accordance with those described in the literature.<sup>23</sup>

*Diethyl (2-bromodecyl)propandioate (3ai)* [CAS:156001-85-3]. The crude product was purified by column chromatography (petroleum ether/EtOAc = 10:1). Colorless oil, 79.3 mg, yield: 84%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.27–4.15 (4H, m), 4.00–3.98 (1H, m), 3.78 (1H, dd,  $J = 9.0, 3.0$  Hz), 2.50–2.40 (1H, m), 2.28–2.18 (1H, m), 1.88–1.80 (2H, m), 1.51–1.43 (2H, m), 1.30–1.24 (16H, m), 0.87 (3H, t,  $J = 7.5$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 169.1, 168.9, 61.8, 61.7, 55.2, 50.7, 39.6, 38.0, 31.9, 29.5, 29.3, 29.1, 27.5, 22.8, 14.2, 14.2, 14.1. Data are in accordance with those described in the literature.<sup>5b</sup>

*8-Bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorotridecane (3ba)*. The crude product was purified by column chromatography (petroleum ether). Colorless oil, 85.7 mg, yield: 69%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.33–4.24 (1H, m), 2.91–2.57 (2H, m), 2.00–1.80 (2H, m), 1.61–1.33 (2H, m), 1.31–1.26 (4H, m), 0.91 (3H, t,  $J = 6.0$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 119.2–110.7 (6C, m), 44.5, 40.2 (t,  $J = 20.6$  Hz), 39.2, 31.0, 27.0, 22.6, 14.1.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.2 (3F, s), -112.8 (1F, d,  $J = 284.8$  Hz), -114.5 (1F, d,  $J = 284.8$  Hz), -122.2 (2F, s), -123.3 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 2935, 2864, 1236, 1196,

1145, 1124, 846, 812, 708, 733. HRMS (CI<sup>+</sup>) calcd for C<sub>13</sub>H<sub>13</sub>BrF<sub>13</sub> [M+H-H<sub>2</sub>]<sup>+</sup>: 494.9993, found 494.9965.

*5-Bromo-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluorododecan-1-ol (3ca)*. The crude product was purified by column chromatography (hexane/EtOAc = 2:1). Colorless oil, 98.5 mg, yield: 79%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 4.33–4.27 (1H, m), 3.67 (2H, t, *J* = 3.0 Hz), 2.89–2.61 (2H, m), 2.03–1.86 (2H, m), 1.70–1.52 (4H, m). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ: 120.1–110.8 (6C, m), 62.6, 44.2, 40.0 (t, *J* = 21.0 Hz), 39.0, 31.8, 23.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -81.2 (3F, s), -112.8 (1F, d, *J* = 277.4 Hz), -114.5 (1F, d, *J* = 277.4 Hz), -122.2 (2F, s), -123.3 (2F, s), -124.0 (2F, s), -126.6 (2F, s). IR (neat, cm<sup>-1</sup>) 2943, 1232, 1188, 1143, 1059, 812, 732, 707, 699, 656. HRMS (CI<sup>+</sup>) calcd for C<sub>12</sub>H<sub>11</sub>BrF<sub>13</sub>O [M+H-H<sub>2</sub>]<sup>+</sup>: 496.9786, found 496.9785.

*8,11-Dibromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoroundecane (3da)*. The crude product was purified by column chromatography (hexane). Colorless oil, 90.4 mg, yield: 66%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 4.33–4.27 (1H, m), 3.48–3.44 (2H, m), 2.92–2.61 (2H, m), 2.25–2.13 (2H, m), 2.11–1.95 (2H, m). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ: 118.9–110.8 (6C, m), 43.1, 40.1 (t, *J* = 21.1 Hz), 37.6, 32.3, 30.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -81.3 (3F, s), -112.7 (1F, d, *J* = 265.9 Hz), -114.5 (1F, d, *J* = 265.9 Hz), -122.2 (2F, s), -123.3 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm<sup>-1</sup>) 1232, 1188, 1142, 1122, 812, 733, 716, 707, 699, 656. HRMS (EI<sup>+</sup>) calcd for C<sub>11</sub>H<sub>9</sub>Br<sub>2</sub>F<sub>13</sub> [M]<sup>+</sup>: 545.8863, found 545.8866.

*(3-Bromo-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene (3ea)*. The crude product was purified by column chromatography (hexane). Colorless oil, 78.1 mg, yield: 58%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.33–7.20 (5H, m), 4.26–4.20 (1H, m), 2.98–2.61 (4H, m), 2.34–2.12 (2H, m). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ: 140.1, 128.8 (2C), 128.6 (2C), 126.5, 120.1–108.4 (6C, m), 43.7, 40.8, 40.0 (t, *J* = 21.0 Hz), 33.5. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -81.2 (3F, s), -112.5

(1F, d,  $J = 265.9$  Hz), -114.4 (1F, d,  $J = 265.9$  Hz), -122.2 (2F, s), -123.3 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 1233, 1189, 1143, 1122, 1074, 813, 732, 716, 707, 698. HRMS ( $\text{EI}^+$ ) calcd for  $\text{C}_{16}\text{H}_{12}\text{BrF}_{13}$  [ $\text{M}$ ] $^+$ : 529.9915, found 529.9903.

*1-(2-Bromo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)-4-fluorobenzene (3fa)*. The crude product was purified by column chromatography (petroleum ether). Colorless oil, 89.5 mg, yield: 67%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.22–7.18 (2H, m), 7.06–7.00 (2H, m), 4.44–4.38 (1H, m), 3.31 (1H, dd,  $J = 16.0, 8.0$  Hz), 3.15 (1H, dd,  $J = 16.0, 8.0$  Hz), 2.87–2.65 (2H, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 163.5, 161.1, 131.0, 131.0, 118.8–108.4 (6C, m), 115.8, 115.6, 44.6, 43.6, 39.2 (t,  $J = 21.2$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.2 (3F, s), -112.7 (1F, d,  $J = 267.0$  Hz), -113.8 (1F, d,  $J = 267.0$  Hz), 115.5 (1F, s), -122.2 (2F, s), -123.3 (2F, s), -124.0 (2F, s), -126.6 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 2934, 1512, 1230, 1190, 1161, 1143, 1121, 823, 707, 698. HRMS ( $\text{EI}^+$ ) calcd for  $\text{C}_{15}\text{H}_9\text{BrF}_{14}$  [ $\text{M}$ ] $^+$ : 533.9664, found 533.9673.

*1-(2-Bromo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)-4-methoxybenzene (3ga)*. The crude product was purified by column chromatography (petroleum ether/EtOAc = 3:1). Colorless oil, 83.4 mg, yield: 61%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.14 (2H, d,  $J = 8.0$  Hz), 6.88 (2H, d,  $J = 8.0$  Hz), 4.44–4.38 (1H, m), 3.81 (3H, s), 3.24 (1H, dd,  $J = 16.0, 8.0$  Hz), 3.15 (1H, dd,  $J = 16.0, 8.0$  Hz), 2.79–2.64 (2H, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.0, 130.5 (2C), 129.2, 119.8–111.1 (6C, m), 114.2 (2C), 55.4, 44.8, 43.9, 38.9 (t,  $J = 21.2$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.2 (3F, s), -113.3 (2F, s), -122.2 (2F, s), -123.3 (2F, s), -124.0 (2F, s), -126.5 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 2939, 2840, 1514, 1235, 1192, 1143, 1121, 1036, 811, 698. HRMS ( $\text{EI}^+$ ) calcd for  $\text{C}_{16}\text{H}_{12}\text{BrF}_{13}\text{O}$  [ $\text{M}$ ] $^+$ : 545.9864, found 545.9857.

*2-(2-Bromo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)phenol (3ha)*. The crude product was purified by column chromatography (petroleum ether/EtOAc = 5:1). Colorless oil, 69.2 mg,

yield: 53%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.19–7.11 (2H, m), 6.94–6.89 (1H, m), 6.76 (1H, d,  $J$  = 8.0 Hz), 4.91 (1H, s), 4.68–4.61 (1H, m), 3.36 (1H, dd,  $J$  = 16.0, 8.0 Hz), 3.20 (1H, dd,  $J$  = 16.0, 8.0 Hz), 2.84–2.70 (2H, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 153.7, 132.0, 128.9, 124.0, 121.2, 120.1–110.4 (6C, m), 115.7, 42.5, 41.0, 39.3 (t,  $J$  = 21.2 Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.2 (3F, s), -113.6 (2F, s), -122.2 (2F, s), -123.3 (2F, s), -124.0 (2F, s), -126.5 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 3522, 2933, 1458, 1234, 1194, 1144, 1122, 1071, 812, 753, 707. HRMS ( $\text{EI}^+$ ) calcd for  $\text{C}_{15}\text{H}_{10}\text{BrF}_{13}\text{O}$   $[\text{M}]^+$ : 531.9707, found 531.9718.

*8-Bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-methyldodecane (3ia)*. The crude product was purified by column chromatography (hexane). Colorless oil, 26.1 mg, yield: 21%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.94–2.73 (2H, m), 1.97–1.94 (3H, m), 1.61–1.44 (2H, m), 1.42–1.32 (2H, m), 1.29 (2H, s), 0.97 (3H, t,  $J$  = 7.1 Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 119.3–110.2 (6C, m), 44.4 (d,  $J$  = 1.9 Hz), 42.3 (t,  $J$  = 22.0 Hz), 31.8, 28.9, 27.4, 21.6, 13.1.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.3 (3F, s), -111.9 (1F, d,  $J$  = 277.4 Hz), -113.0 (1F, d,  $J$  = 277.4 Hz), -122.1 (2F, s), -123.3 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 1231, 1204, 1143, 845, 812, 732, 707, 699, 656. HRMS ( $\text{EI}^+$ ) calcd for  $\text{C}_{13}\text{H}_{13}\text{BrF}_{13}$   $[\text{M}+\text{H}-\text{H}_2]^+$ : 494.9993, found 497.9987.

*8-Bromo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-7-propylundecane (3ja)*. (57: 43 diastereomeric mixture, dr was measured by  $^1\text{H}$  NMR of the crude mixture.) The crude product was purified by column chromatography (hexane). Colorless oil, 47.2 mg, yield: 37%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.39 (major, 1H, dt,  $J$  = 11.1, 2.4 Hz), 4.34 (minor, 1H, dq,  $J$  = 9.5, 2.1 Hz), 2.83–2.73 (major, 1H, m), 2.50–2.40 (minor, 1H, m), 1.89–1.61 (major and minor, 4H, m), 1.56–1.29 (major and minor, 4H, m), 0.99–0.91 (major and minor, 6H, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 120.1–108.5 (major and minor, 6C, m), 52.7 (major), 51.2 (minor), 48.3 (major, t,  $J$  = 20.2 Hz), 46.3 (minor, t,  $J$  = 20.2 Hz), 39.9 (major), 29.2 (minor), 23.0 (major), 22.8

(minor), 21.7 (major), 21.3 (minor), 14.2, 14.1 (major), 13.9 (minor), 13.3 (major), 13.2 (minor).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , major and minor mixture)  $\delta$ : -81.2 (3F, s), -110.3–115.6 (2F, m), -120.8–122.3 (4F, m), -123.1 (2F, s), -126.5 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 2968, 1235, 1192, 1145, 1054, 839, 809, 735, 699, 654. HRMS ( $\text{CI}^+$ ) calcd for  $\text{C}_{14}\text{H}_{15}\text{BrF}_{13}$   $[\text{M}+\text{H}-\text{H}_2]^+$ : 509.0149, found 509.0137.

*1-Bromo-2-(tridecafluorohexyl)cyclooctane (3ka)*. (75: 25 diastereomeric mixture, dr was measured by  $^1\text{H}$  NMR of the crude mixture.) The crude product was purified by column chromatography (hexane). Colorless oil, 105.7 mg, yield: 83%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.60–4.58 (minor, 1H, m), 4.46–4.34 (major, 1H, m), 2.45–1.40 (major and minor, 13H, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 119.5–109.3 (major and minor, 6C, m), 55.4 (minor), 55.0 (major), 41.0 (minor, t,  $J = 20.1$  Hz), 40.7 (major, t,  $J = 20.1$  Hz), 37.3, 36.3, 33.7, 26.7, 25.4, 23.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , major and minor mixture)  $\delta$ : -81.3 (3F, s), -115.8–117.9 (2F, m), -120.3 (2F, s), -122.5 (2F, s), -123.2 (2F, s), -126.6 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 2930, 1449, 1232, 1191, 1143, 1119, 809, 735, 707, 694, 654. HRMS ( $\text{CI}^+$ ) calcd for  $\text{C}_{14}\text{H}_{13}\text{BrF}_{13}$   $[\text{M}+\text{H}-\text{H}_2]^+$ : 506.9993, found 506.9984.

*2-Bromo-3-(tridecafluorohexyl)bicyclo[2.2.1]heptane (3la)*. (71: 29 diastereomeric mixture, dr was measured by  $^1\text{H}$  NMR of the crude mixture.) The crude product was purified by column chromatography (hexane). Colorless oil, 26.1 mg, yield: 21%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.34 (major, 1H, t,  $J = 6.0$  Hz), 4.15 (minor, 1H, dd,  $J = 7.3, 2.3$  Hz), 2.70–2.66 (minor, 2H, m), 2.54–2.53 (major, 2H, m), 2.48–2.47 (minor, 1H, m), 2.38–2.28 (major, 1H, m), 2.14–2.11 (minor, 1H, m), 2.05–1.99 (major, 1H, m), 1.80–1.26 (major and minor, 5H, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , major)  $\delta$ : 119.3–108.4 (6C, m), 54.5 (t,  $J = 20.3$  Hz), 50.0 (t,  $J = 3.8$  Hz), 43.7, 38.3 (t,  $J = 3.0$  Hz), 36.3, 30.0, 23.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.1 (major and minor, 3F,

s), -107.8 (minor, 1F, d,  $J = 289.0$  Hz), -115.9 (minor, 1F, d,  $J = 289.0$  Hz), -116.3 (major, 1F, d,  $J = 277.3$  Hz), -118.0 (major, 1F, d,  $J = 277.3$  Hz), -119.2--123.1 (major and minor, 6F, m), -126.2--126.6 (major and minor, 2F, m). IR (neat,  $\text{cm}^{-1}$ ) 1363, 1197, 1143, 1119, 1063, 735, 719, 694, 674, 638. HRMS ( $\text{CI}^+$ ) calcd for  $\text{C}_{13}\text{H}_{19}\text{BrF}_{13}$  [ $\text{M}+\text{H}-\text{H}_2$ ] $^+$ : 490.9680, found 490.9678.

*(3-(3-Bromopropylidene)-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene (30a)*. (57:43 isomeric mixture, *E/Z* ratio was measured  $^{19}\text{F}$  NMR of the crude mixture.) The crude product was purified by column chromatography (petroleum ether). Colorless oil, 120.0 mg, yield: 84%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.32–7.27 (2H, m), 7.23–7.17 (3H, m), 5.57 (*Z*-isomer, 1H, t,  $J = 8.0$  Hz), 5.44 (*E*-isomer, 1H, t,  $J = 8.0$  Hz), 3.34 (1H, t,  $J = 8.0$  Hz), 3.20 (1H, t,  $J = 8.0$  Hz), 2.88–2.71 (4H, m), 2.63–2.46 (4H, m).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 141.32 (*Z*-isomer), 141.2 (*E*-isomer), 131.7, 130.3 (*E*-isomer), 130.1 (*Z*-isomer), 128.7, 128.6 (2C), 128.5, 126.4 (*E*-isomer), 126.2 (*Z*-isomer), 118.5–108.8 (6C, m), 39.9 (*Z*-isomer), 37.4 (t,  $J = 21.7$  Hz), 34.6 (*Z*-isomer), 34.2 (*E*-isomer), 33.1 (*E*-isomer), 32.0 (*E*-isomer), 31.9 (*Z*-isomer), 31.8 (*Z*-isomer), 31.6 (*E*-isomer).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.3 (3F, s), -112.5 (*Z*-isomer, 2F, s), -113.2 (*E*-isomer, 2F, s), -122.2 (2F, s), -123.3 (2F, s), -1237 (2F, d,  $J = 45.1$  Hz), -126.6 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 3030, 2963, 1455, 1233, 1190, 1143, 1120, 1096, 811, 744, 698. HRMS ( $\text{EI}^+$ ) calcd for  $\text{C}_{19}\text{H}_{16}\text{BrF}_{13}$  [ $\text{M}$ ] $^+$ : 570.0228, found 570.0231.

*1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorohexadecane (4aa)* [CAS:147492-59-9]. The crude product was purified by column chromatography (hexane). Yellow oil, 30.8 mg, yield: 67%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.11–1.98 (2H, m), 1.63–1.55 (2H, m), 1.39–1.27 (14H, m), 0.88 (3H, t,  $J = 6.5$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 120.2–106.0 (6C, m), 32.0, 30.8 (t,  $J = 21.9$  Hz), 29.7, 29.6, 29.5, 29.4, 29.2, 22.9, 20.1, 14.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.3 (3F,

s), -114.9 (2F, s), -122.5 (2F, s), -123.4 (2F, s), -124.1 (2F, s), -126.6 (2F, s). Data are in accordance with those described in the literature.<sup>6f</sup>

*1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorohexadec-7-ene (5aa)* [CAS:152128-75-1]. (*E*-isomer) The crude product was purified by column chromatography (petroleum ether). Yellow oil, 42.6 mg, yield: 93%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 6.46–6.36 (1H, m), 5.59 (1H, dd, *J* = 29.8, 11.8 Hz), 2.20 (2H, t, *J* = 3.0 Hz), 1.45 (2H, t, *J* = 6.0 Hz), 1.28 (10H, m), 0.88 (3H, t, *J* = 6.0 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ:143.5 (t, dd, *J* = 9.0 Hz), 119.3–110.0 (6C, m), 116.9 (t, *J* = 22.5 Hz), 32.2, 32.0, 29.4, 29.3, 29.1, 28.2, 22.8, 14.2. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ: -81.3 (3F, s), -111.6 (2F, s), -122.1 (2F, s), -123.4 (2F, s), -124.0 (2F, s), -126.6 (2F, s). Data are in accordance with those described in the literature.<sup>15</sup>

*1-Butoxy-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-ene (5ma)* [CAS: 126015-41-6]. (*E*-isomer) The crude product was purified by column chromatography (hexane). Yellow oil, 52.3 mg, yield: 50%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.01–6.97 (1H, m), 4.85 (1H, dd, *J* = 25.2, 12.5 Hz), 3.81 (2H, t, *J* = 6.6 Hz), 1.72–1.66 (2H, m), 1.47–1.40 (2H, m), 0.95 (3H, t, *J* = 7.3 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ:156.1 (t, *J* = 10.6 Hz), 119.4–108.4 (6C, m), 91.6 (t, *J* = 22.1 Hz), 70.6, 31.0, 19.1, 13.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -81.3 (3F, s), -108.2 (2F, s), -122.1 (2F, s), -123.4 (2F, s), -123.9 (2F, s), -126.6 (2F, s). Data are in accordance with those described in the literature.<sup>24</sup>

*1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooct-1-en-1-yl)pyrrolidin-2-one (5na)* [CAS:1796567-59-3]. (*E*-isomer) The crude product was purified by column chromatography (hexane/EtOAc = 1:1). Yellow oil, 49.4 mg, yield: 46%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.64–7.60 (1H, m), 4.93 (1H, dd, *J* = 26.0, 12.8 Hz), 3.57 (2H, t, *J* = 7.3 Hz), 2.57 (2H, t, *J* = 8.2 Hz), 2.24–2.16 (2H, m). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ:174.3, 132.6 (t, *J* = 11.1 Hz), 118.8–110.6 (6C, m), 96.4 (t,

$J = 24.1$  Hz), 45.0, 31.0, 17.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.3 (3F, s), -108.9 (2F, s), -122.0 (2F, s), -123.3 (2F, s), -123.6 (2F, s), -126.6 (2F, s). Data are in accordance with those described in the literature.<sup>25</sup>

*1,2-Dibromodecane (6)* [CAS:28467-71-2]. The crude product was purified by column chromatography (petroleum ether). Colorless oil, 37.5 mg, yield: 49%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.21–4.12 (1H, m), 3.85 (1H, dd,  $J = 10.5, 4.5$  Hz), 3.63 (1H, t,  $J = 10.5$  Hz), 2.19–2.07 (1H, m), 1.84–1.71 (1H, m), 1.44–1.27 (12H, m), 0.88 (3H, t,  $J = 6.0$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 53.3, 36.5, 36.2, 32.0, 29.5, 29.3, 29.0, 26.9, 22.8, 14.3. Data are in accordance with those described in the literature.<sup>26</sup>

*1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorohexadecan-8-ol (8aa)* [CAS:2956402-50-7]. The crude product was purified by column chromatography (hexane/EtOAc = 20:1). Yellow oil, 17.9 mg, yield: 15%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.19–4.13 (1H, m), 2.35–2.13 (2H, m), 1.89 (1H, s), 1.63–1.51 (2H, m), 1.50–1.43 (1H, m), 1.29 (11H, d,  $J = 6.0$  Hz), 0.88 (3H, t,  $J = 6.9$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$ : 120.5–108.4 (6C, m), 65.5, 38.1 (d,  $J = 15.1$  Hz), 37.8, 32.0, 29.6, 29.5, 29.4, 25.4, 22.8, 14.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.3 (3F, s), -113.0 (1F, d,  $J = 277.4$  Hz), -114.0 (1F, d,  $J = 277.4$  Hz), -122.3 (2F, s), -123.3 (2F, s), -124.1 (2F, s), -126.6 (2F, s). Data are in accordance with those described in the literature.<sup>27</sup>

*S-(1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorohexadecan-8-yl) ethanethioate (9aa)*. The crude product was purified by column chromatography (EtOAc). Colorless oil, 37.1 mg, yield: 70%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.90–3.84 (1H, m), 2.50–2.31 (2H, m), 2.33 (3H, s), 1.78–1.73 (1H, m), 1.70–1.61 (1H, m), 1.26 (12H, m), 0.87 (3H, t,  $J = 6.0$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.7, 118.8–108.8 (6C, m), 37.4, 35.8 (t,  $J = 21.2$  Hz), 34.6, 32.0, 30.8, 29.5, 29.3 (2C), 26.7, 22.8, 14.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.2 (3F, s), -112.2 (1F, d,  $J = 289.5$  Hz),

-114.3 (1F, d,  $J = 289.5$  Hz), -122.2 (2F, s), -123.3 (2F, s), -124.0 (2F, s), -126.5 (2F, s). IR (neat,  $\text{cm}^{-1}$ ) 2928, 2859, 1698, 1235, 1192, 1144, 1119, 812, 733, 706. HRMS ( $\text{EI}^+$ ) calcd for  $\text{C}_{18}\text{H}_{23}\text{F}_{13}\text{OS}$   $[\text{M}]^+$ : 534.1262, found 534.1272.

*8-Azido-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorohexadecane (10aa)* [CAS:149473-30-3]. The crude product was purified by column chromatography (petroleum ether). Yellow oil, 21.4 mg, yield: 43%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.77–3.71 (1H, m), 2.33–2.20 (2H, m), 1.66–1.60 (2H, m), 1.51–1.42 (2H, m), 1.30–1.28 (10H, m), 0.89 (3H, t,  $J = 8.0$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 120.2–108.4 (6C, m), 56.1, 35.8 (t,  $J = 21.2$  Hz), 35.6, 32.0, 29.5, 29.3, 29.2, 25.8, 22.8, 14.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -81.3 (3F, s), -113.8 (2F, s), -122.3 (2F, s), -123.4 (2F, s), -124.0 (2F, s), -126.7 (2F, s). Data are in accordance with those described in the literature.<sup>28</sup>

## ASSOCIATED CONTENT

**Data Availability.** The data underlying this study are available in the published article and its Supporting Information.

**Supporting Information.** The Supporting Information is available free of charge at. General information, general procedures, optimization studies, substrate scope studies, mechanistic studies, characterization of the products, copy of  $^1\text{H}$  NMR spectra of synthesized substrate **10**, and copies of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra of products.

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### **Notes**

The authors declare no competing financial interest.

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SYNOPSIS. A visible-light-induced metal-free radical bromo-perfluoroalkylation of unactivated olefins has been developed through the use of an organic photoredox catalyst, 10-phenylphenothiazine.