Doctoral Dissertation

Studies on Defluorinative Transformation of Perfluoroalkyl Compounds by Merging Photoredox Catalysis and Lewis Acid Activation

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Preface and Acknowledements

The study of this doctoral dissertation was carried out under the guidance of Prof. Dr. Makoto Yasuda at the Department of Applied Chemistry, Graduated School of Engineering, Osaka University from April 2018 to March 2024. The thesis describes the development of defluorinative transformation of perfluoroalkyl compounds by merging photoredox catalysis and Lewis acid activation.

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Contents

General introduction

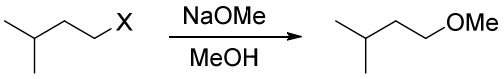
Fluorine has attractive characters such as high electronegativity and small atomic radius.[1] A fluorine atom forms a quite robust bond with a carbon atom as shown in Table 1. The bond dissociation energy of a C–F bond is much higher than other single bonds such as C–H, C–O, and C–C bonds.[2]

Table 1. Bond dissociation energy

Bond type	C−F	C−H	C−O	C−C
Bond dissociation energy (kJ/mol)	485	411	358	346

In addition, a fluorine in organofluorides is a quite poor leaving group in organic chemistry, especially in S_N2 type reactions. For example, the rate of reaction of alkyl halides with methoxide in methanol are shown in Table 2.[3] Fluoride is substituted more slowly than chloride, bromide, and iodide. The electrostatic effect sufficiently stabilizes a C–F bond so the elimination of fluoride is unfavored even though the carbon of C–F is polarized positively.[4] Therefore direct C–F substitution is difficult.

Table 2. Relative rates of S_N2 reaction of alkyl halides.

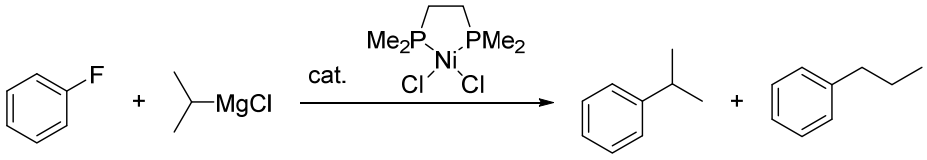


X^-	Relative reaction rate
F^-	1
Cl^-	71
Br^-	3500
I^-	4500

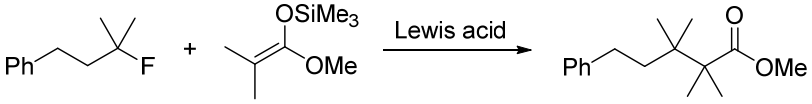
Transformation of inert C–F bonds is a challenging issue in organic chemistry and many chemists have been tackling the issue. Many reactions for direct C–F bond transformation have been reported.[5] Some examples are shown in Scheme 1. Tamao and Kumada reported the nickel-catalyzed cross coupling reaction of aryl fluorides with Grignard reagents (Scheme 1A).[6] Oxidative addition of C(sp^2)–F bond to a Ni complex is a key in this coupling reaction. Lewis acids such as $AlMe_3$ and $BF_3 \bullet OEt_2$ catalyze defluorinative transformation, in which these strong Lewis acids abstract F anion from alkyl fluorides (Scheme 1B).[7] Traditional nucleophilic aromatic substitutions were also reported (Scheme 1C).[8]

Scheme 1. Defluorinative transformation of organofluorine compounds (A) Nickel-catalyzed cross coupling reaction of aryl fluorides with Grignard reagents (B) Lewis acid-catalyzed defluoroalkylation of alkylfluorides (C) Nucleophilic aromatic substitution of aryl fluorides.

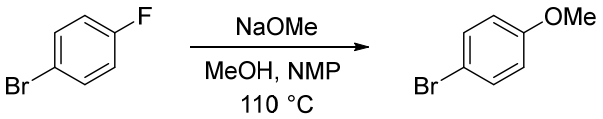
(A) Nickel-catalyzed cross coupling reaction of aryl fluorides



(B) Defluoroalkylation of alkylfluorides by Lewis acid catalysis

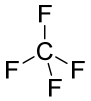
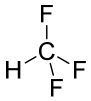
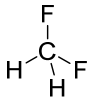
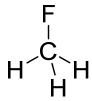


(C) Nucleophilic aromatic substitution of aryl fluorides



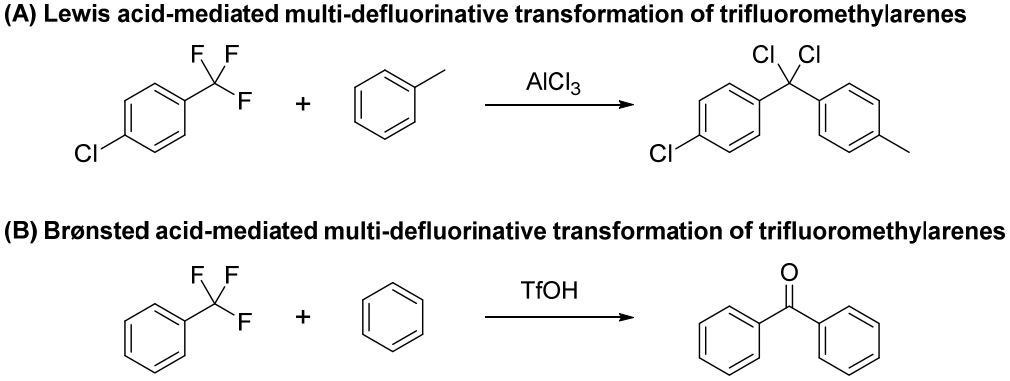
Perfluoroalkyl compounds have attracted much attention and are widely used in pharmaceuticals, agrochemicals, and organic electronic materials.[9] Introduction of perfluoroalkyl substituents changes the properties of the parent compounds, such as binding ability, metabolic stability, and membrane permeability in medicinal chemistry.[9b,9f] Installation of perfluoroalkyl moieties can improve thermal stability and surface tension of lubricants and surfactants.[10] Therefore, various reactions for introduction of perfluoroalkyl substituents were well-established to synthesize perfluoroalkylated compounds.[11] The site-selective C–F bond transformation of perfluoroalkyl compounds enables to synthesize functionalized multi-fluorinated compounds, which have more valuable potentials. The selective C–F bond transformations, however, remains a challenging issue because unselective transformations or multi-defluorinative transformations readily proceed. For example, as the number of fluorine substituents in fluorinated methanes decreases, the C–F bond energy decreases (Table 3). That is, as a transformation of a C–F bond in perfluoroalkyl group is conducted, the bond energy of residual C–F bond is decreased, which cause multi-transfromation.[12]

Table 3. Bond strength of fluoromethanes

compound				
bond dissociation energy (kcal/mol)	130	128	122	109
bond distance (C–F) (Å)	1.317	1.332	1.358	1.385

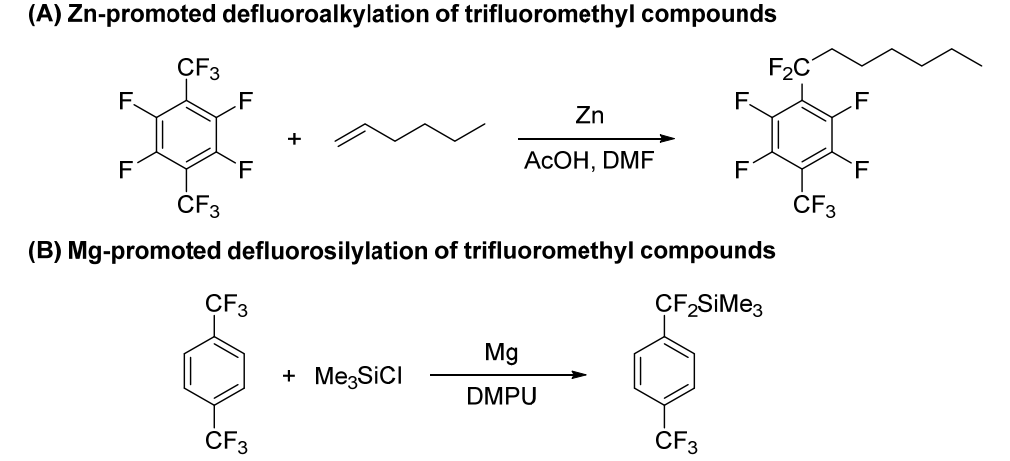
Actually, the transformation of trifluoromethyl compounds with toluene in the presence of $AlCl_3$ afforded fully-defluorinated products (Scheme 2A).[13] The Brønsted acid mediated substitution of trifluoromethylarenes gave ketones, in which all fluorine atoms were eliminated (Scheme 2B).[14]

Scheme 2. (A) Lewis acid-mediated multi-defluorinative transformation of trifluoromethylarenes (B) Brønsted acid-mediated multi-defluorinative transformation of trifluoromethylarenes



On the other hand, reductive defluorination is a promising method for selective defluorination. Reductive defluoroalkylation of trifluoromethylarenes with alkenes and defluorosilylation with Me_3SiCl were reported, in which low valent metals such as Zn or Mg were used and selective mono-defluorinated products were obtained (Scheme 3).[15] In the reductive method, The key for selective mono-defluorination is that the reductant reduces the starting material more rapidly than the product because of higher redox potential.

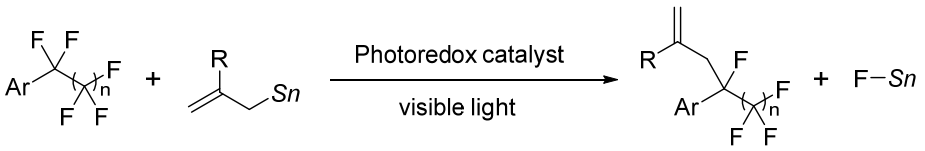
Scheme 3. Reductive defluorination of perfluoroalkyl compounds (A) Zn-promoted defluoroalkylation of trifluoromethyl compounds (B) Mg-promoted defluorosilylation of trifluoromethyl compounds



In this context, I envisioned that reductive defluorination systems using reductants with appropriate redox potential have much potential for selective defluorinated transformation of perfluoroalkyl compounds. In this study, merging photoredox catalysis and Lewis acid systems were investigated for selective C–F bond transformation of perfluoroalkyl compounds.

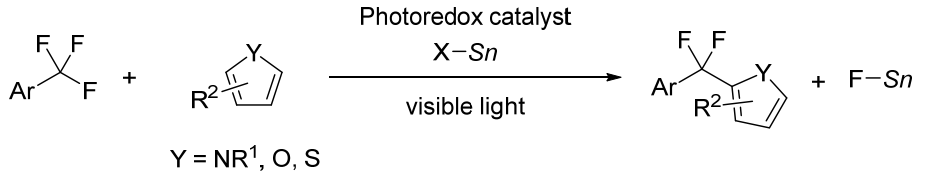
In chapter 1, defluoroallylation of perfluoroalkylarenes with allylic stannanes by photoredox catalysis was accomplished (Scheme 4). Benzylic C–F bond is selectively activated by single-electron reduction of perfluoroalkylarenes to afford benzylic radical after defluorination. Allylic stannanes are suitable for radical accepters. DFT calculations revealed tin fluoride which is generated as a by-product works as a fluoride scavenger and promotes the reaction progress.

Scheme 4. Defluoroallylation of perfluoroalkylarenes with allylic stannanes by photoredox catalysis



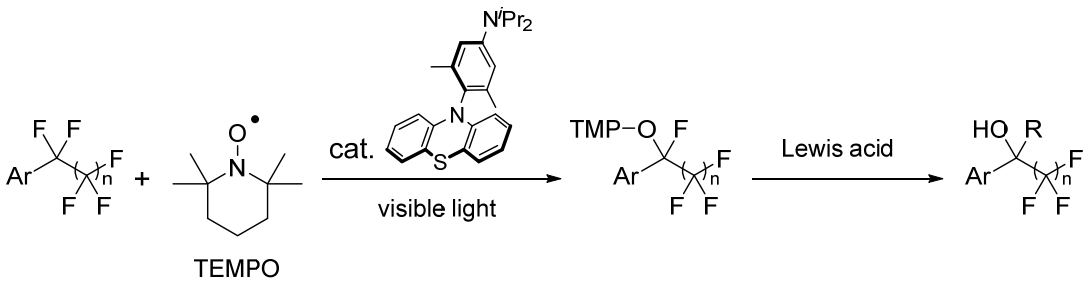
In chapter 2, defluoroarylation of trifluoromethylarenes with heteroarenes by photoredox catalysis is described (Scheme 5). In this reaction, Bu_3SnI serves as a reductant to produce Ir(II) species, which has sufficiently high reduction potential to reduce trifluoromethylarenes by single electron transfer. Bu_3SnI also works as a fluoride ion scavenger to form stable tin fluoride.

Scheme 5. Defluoroarylation of trifluoromethylarenes with heteroarenes by photoredox catalysis



In chapter 3, sequential defluorinative transformation of CF_2 unit in perfluoroalkyl groups was achieved by combination of photoredox catalysis and Lewis acid activation (Scheme 6). Newly developed phenothiazine derivative efficiently catalyzed defluoroaminoxylation of perfluoroalkylarenes with 2,2,6,6-tetramethylpiperidine (TEMPO) for 1st C–F bond transformation. $AlCl_3$ mediated defluorinative transformation of the defluoroaminoxylated compounds proceeded, which allowed 2nd C–F bond transformation to afford perfluoroalkyl alcohols.

Scheme 6. Sequential defluorinative transformation of CF_2 unit in perfluoroalkyl groups



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Chapter 1: Photoredox-Catalyzed C-F Bond Allylation of Perfluoroalkylarenes at the Benzylic Position

1-1. Introduction

The importance of organic fluorides is well established in the production of pharmaceutical, agrochemical, and organic electronic materials.[1] In particular, polyfluoroalkyl substances have attracted great interest because polyfluoroalkyl moieties dramatically enhance thermal stability and exert a unique surface effect on surfactants and lubricants.[2] The most practical synthetic method is the installation of perfluoroalkyl groups ($–C_nF_{2n+1}$) to organic compounds, and fully fluorinated alkyl group-substituted compounds ($R–C_nF_{2n+1}$) can be easily prepared by many well-established methods (Figure 1A).[3] Further functionalization of perfluoroalkyl units is rare, however, despite the fact that the C-F bond activation of readily available $R–C_nF_{2n+1}$ has shown huge potential for access to functionalized perfluoroalkyl compounds. The transformation of C–F bonds has intrinsic problems with site-selectivity due to the harsh conditions and/or highly reactive reagents that are needed to activate the robust C-F bonds.[4] These factors lead to undesired non- site-selective transformations and multi-activations of C–F bonds.[5]

1-2. Results and Discussion

Many groups have reported single C-F bond transformations of the CF_3 group in which the issue of site-selectivity is not included (Figure 1B, n = 1). Hosoya and Yoshida reported the transformation of $ArCF_3$ bearing a hydrosilyl group.[6] Young reported a frustrated Lewis-pair-mediated transformation.[7] Following a report by Mattay that described a photoinduced C-F bond activation,[8] many methodologies involving a single-electron transfer (SET) mechanism have been developed.[9] Recently, photoredox catalysis has become a significant protocol; König[10] and Jui[11] independently reported efficient C–F bond transformations of $ArCF_3$ with alkenes. In contrast to the CF_3 group, the single C–F bond activation of longer perfluoroalkyl groups is rare, and only two reports are known to have described a transformation of the CF_2CF_3 group (Figure 1B, n = 2). The two-electron reduction of $ArCF_2CF_3$ via either an electrochemical method or Mg metal generates $[ArCFCF_3]^-$ species as key intermediates and accomplishes either a nucleophilic addition to CO_2[12] or a nucleophilic substitution with Me_3SiCl[13], respectively. Additionally, as far as double C-F activation of CF_2CF_3 group, Ichikawa reported Ni-mediated [3+2] cycloaddition of 2-pentafluoroethyl-1-alkene with 4-octyne.[14] These methods, however, have never been applied to longer perfluoroalkyl compounds most likely due to steric hindrance and the electron-withdrawing effect of perfluoroalkyl groups that decrease the nucleophilicity of the corresponding carbanions (Figure 1B, $n \geq 3$). Instead of a two-electron reduction, we focused on a mechanism via SET (Figure 1C) wherein the reduction of perfluoroalkylarene **1** by an excited photoredox catalyst (PC*) followed by F^- elimination from radical anion **A** selectively gives benzylic carbon radical **B**.[10,11] Even in this case, the perfluoroalkyl groups cause serious problems such as destabilization of the generated radical **B**[14] and inhibition of a sequential bond-forming reaction via large steric hindrance.[16] As a result, a retro process that includes back-electron transfer (BET) and F^- addition returns the reaction to its starting point.[17] We speculated that the utilization of organometallic reagents (R-M) would overcome

these problems. The efficient reactivity of R-M toward a radical intermediate and the trapping of F^- by M^+ kinetically and thermodynamically favored the progress of the reaction. Herein, we report a photoredox-catalyzed, selective, C-F bond allylation of perfluoroalkyl-substituted arenes by using allylic stannanes (Figure 1D). This is the first achievement of a selective C–F bond transformation in long perfluoroalkyl groups ($n \geq 3$).

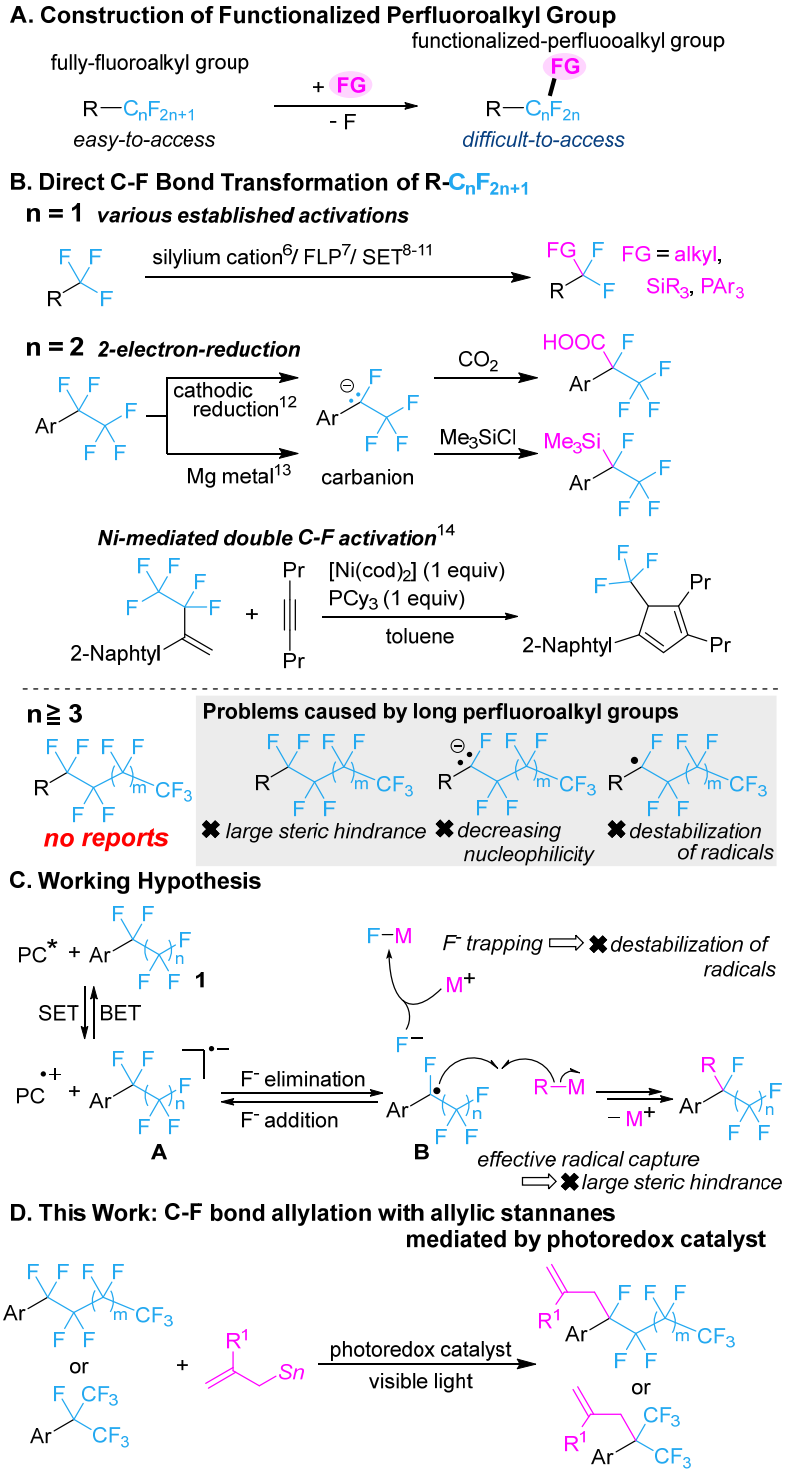
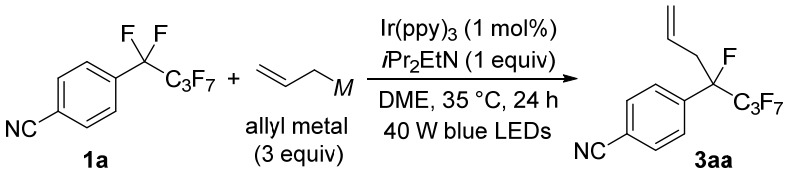


Figure 1. Site-selective C-F bond transformation of perfluoroalkyl compounds

We chose allylmetal reagents that possess an efficient level of reactivity to carbon radical species[18] in the reaction of nonafluorobutyl arene **1a** with $Ir(ppy)_3$ (1 mol%) and $^iPr_2EtN$ (1 equiv) under irradiation from 40 W blue LEDs (Table 1). The use of allyltrimethylsilane (Entry 1), allylboronic ester (Entry 2), or allyltrifluoroborate salt (Entry 3) resulted in no reaction. On the other hand, allyltributylstannane **2a** gave the desired allylated compound **3aa** in 52% yield (Entry 4). In this reaction, allylation occurred exclusively at the benzylic position without the formation of multi-allylated products because the reduction of defluoroallylated product **3aa** would be difficult than starting material **1a** due to its high reduction potential.[19] Both $Ir(ppy)_3$ and photo-irradiation were essential to the reaction progress (Entries 5 and 6).

Table 1. Optimization of photoredox-catalyzed defluoroallylation of nonafluorobutyl arene **1a** with allyl metal reagents[a]



Entry	Allyl Metal	Yield of **3aa**
1	$SiMe_3$	0%
2	Bpin	0%
3	BF_3K	0%
4	$SnBu_3$ (**2a**)	52%
5[b]	**2a**	0%
6[c]	**2a**	0%
7[d]	**2a**	38%

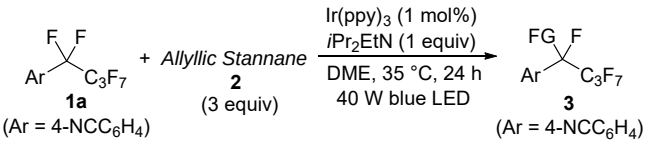
[a]**1a** (0.4 mmol), allyl metal (1.2 mmol), $Ir(ppy)_3$ (0.004 mmol), $^iPr_2EtN$ (0.4 mmol), DME (2 mL), irradiation with 40 W blue LEDs at 35 °C. Yields were determined by ^1H NMR spectroscopy using 1,1,1,2-tetrachloroethane as an internal standard. [b]No irradiation with 40 W blue LEDs. [c]Without $Ir(ppy)_3$. [d]Without $^iPr_2EtN$.

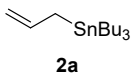
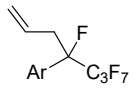
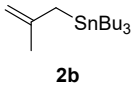
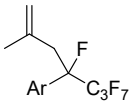
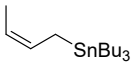
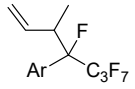
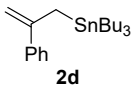
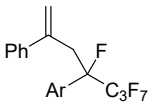
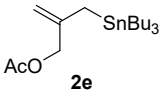
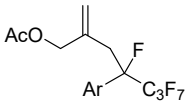
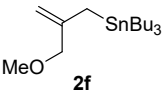
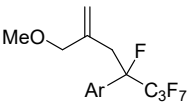
Under the conditions without $^iPr_2EtN$, the yield of **3aa** was decreased and a large consumption of **2a** was observed (entry 7).[20] As described above, we discovered that allylstannane **2a** showed outstanding efficiency toward defluoroalkylation of perfluoroalkylarene because control experiments in our hand based on either the König[10] or the Jui[11] systems were not applicable to perfluoroalkylarene **1a** (Schemes S1 and S2).

Table 2 shows the scope of the allylic stannanes **2** in the reaction of **1a** with the optimized reaction conditions (Table 1, Entry 4). Methallylstannane **2b** afforded the defluoroallylated product **3ab** in a higher yield than that of **2a** (Entries 1 and 2). Crotylstannane **2c** was not suitable due to steric hindrance (Entry 3). Allylic stannanes bearing substituents at the β-position of a Sn atom were applicable substrates. Ph-,

$AcOCH_2$-, and $MeOCH_2$-substituted substrates (**2d**, **2e**, and **2f**) afforded the corresponding products (Entries 4-6).

Table 2. Scope of allylic stannanes in defluoroallylation of **1a**



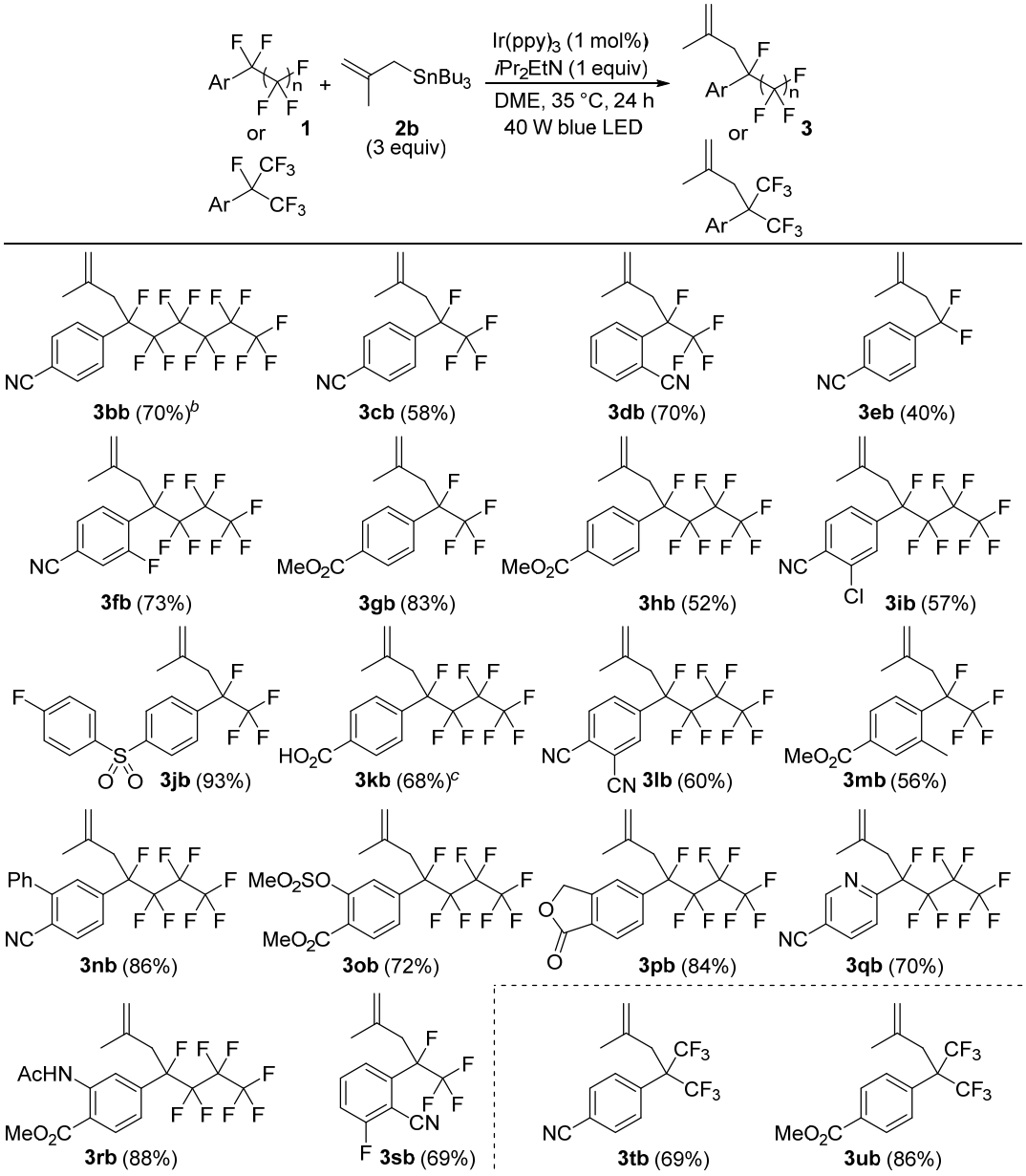
Entry	*Allyllic Stannane* **2**	Product **3**		Yield
1	 **2a**		**3aa**	52%
2	 **2b**		**3ab**	85%
3	 **2c**		**3ac**	0%
4	 **2d**		**3ad**	51%
5	 **2e**		**3ae**	47%
6	 **2f**		**3af**	69%

[a] **1a** (0.4 mmol), **2** (1.2 mmol), $^{i}Pr_2EtN$ (0.4 mmol), and $Ir(ppy)_3$ (0.004 mmol), DME (2 mL), irradiation with blue LEDs at 35 °C for 24 h. Isolated yields are shown.

The scope of perfluoroalkyl arenes was investigated using methallylstannane **2b** (Table 3). Selective allylation of the benzylic C–F bonds of C_6F_{13} and C_2F_5 groups other than the C_4F_9 group smoothly proceeded (**3bb**, **3cb**, **3db**, and **3gb**). The CF_3 group was also applicable to the present allylation (**3eb**). C(sp^2)–F and C(sp^2)–Cl bonds were tolerated and a benzylic F group was selectively substituted (**3fb**, **3jb**, **3sb**, and **3ib**). An electron-withdrawing group on the benzene ring decreases the reduction potential of substrate **1** to accelerate SET from excited $Ir(ppy)_3$ to **1**, and CN, CO_2Me, CO_2H, and SO_2Ar groups were suitable substituents (e.g. **3bb**, **3gb**, **3kb**, **3jb**). On the other hand, perfluoroalkylarenes **1** without electron-withdrawing groups were not available due to their higher reduction potential.[21] Functional groups such as methanesulfonyloxy, methyl, phenyl, and acetylamino groups were compatible with this reaction system (**3ob**, **3mb**, **3nb**, **3rb**). The structure of **3ob** was determined by X-ray diffraction analysis (Figure S8). Perfluoroalkyl-substituted pyridine smoothly gave the desired allylated product **3qb**. The present reaction

system was applicable to a heptafluoroisopropyl ($CF(CF_3)_2$) group regardless of the large steric hindrance, and the benzylic C-F bond selectively underwent allylation (**3tb** and **3ub**).

Table 3. Defluoroallylation of various perfluoroalkylarenes **1** using methallylstannane **2b**[a]



[a]**1** (0.4 mmol), **2b** (1.2 mmol), $^{i}Pr_2EtN$ (0.4 mmol), and $Ir(ppy)_3$ (0.004 mmol), DME (2 mL), irradiation with blue LEDs at 35 °C for 24 h. Isolated yields are shown. [b]48 h. [c]The yield of **3kb** was determined by ^1H NMR spectroscopy using 1,1,1,2-tetrachloroethane as an internal standard.

The Stern–Volmer luminescence quenching experiments provided the information for electron transfer involving an Ir catalyst and reagents (Figure 2). The experiments using perfluoroalkylarene **1a**, $^{i}Pr_2EtN$, and

allylic stannane **2b** revealed that the principal interaction with the excited state of $Ir(ppy)_3$ was performed by **1a**, and by comparison, $^{i}Pr_2EtN$ and **2b** exhibited a much less efficient quenching effect.

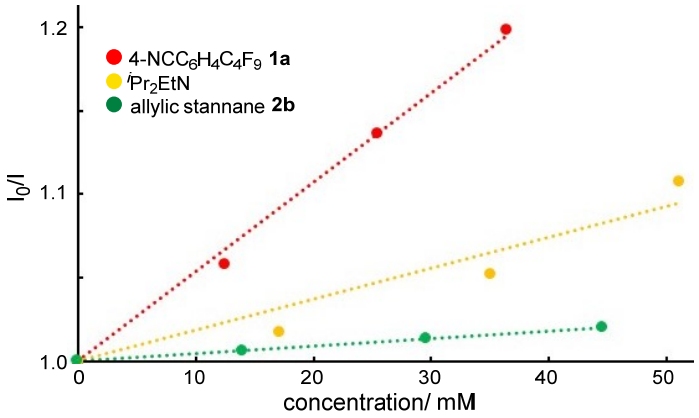


Figure 2. Stern–Volmer luminescence quenching studies of photocatalyst $Ir(ppy)_3$ (excitation 380 nm, emission 514 nm)

Based on the above results, a plausible mechanism for the reaction of **1c** with **2a** is illustrated in Figure 3A. The blue-light-excited $Ir(ppy)_3$ (E_{red} = –1.73 V vs. SCE)[22] reduces **1c** (E_{red} = –1.84 V vs. SCE)[23] via SET, affording the Ir(IV) species and radical anion **A**, although this step is an uphill reaction with respect to the redox potential. The elimination of F^- from the benzylic position of **A** affords radical **B**. Bu_3SnF, which is generated as a by-product, complexes with F^- to give $Bu_3SnF_2^-$ and avoid the retro-reaction step.[24] Then, **B** adds to **2a** to give radical **C**. Reduction of the Ir(IV) species by $^{i}Pr_2EtN$ regenerates Ir(III) with radical cation $^{i}Pr_2EtN^{\cdot+}$.[25] $^{i}Pr_2EtN^{\cdot+}$ oxidizes **C**, which generates $^{i}Pr_2EtN$ and cation **D**. $Bu_3SnF_2^-$ assists in the elimination of the stannyl cation, which leads to product **E** and Bu_3SnF. Light ON/OFF experiments suggested that the contribution of the radical chain mechanism to this reaction was small.[26] Density functional theory by means of the (U)ω97XD/6-31+G(d) method (Figure 3B) revealed the details of the key process from **A** to **C**, in which Bu_3SnF participated (Me groups on a Sn atom instead of Bu groups were adopted for DFT calculation).[27] Elimination of the F^- from radical anion **A** exergonically proceeds, and the activation energy for this step is 4.4 kcal/mol. The addition of **B** to allyl stannane **2g** occurs via **TS2** with a much higher activation barrier (19.6 kcal/mol) than in a retro-reaction from **INT1** to **A** (11.8 kcal/mol). Therefore, the retro-process including a back electron transfer from **A** to the Ir(IV) species easily occurs in the absence of Me_3SnF. In the presence of Me_3SnF, however, F^- coordinates to Me_3SnF to generate $Me_3SnF_2^-$, and this complexation creates thermodynamical stabilization (ΔG = 13.3 kcal/mol) in the system (**INT3**). Thus, Bu_3SnF suppresses the retro reaction and allows the desired reaction to proceed effectively.[28] In the use of simple alkenes like König's[10] and Jui's[11] systems (Schemes S1 and S2), the addition of perfluoroalkyl radicals to alkenes is slow due to their larger steric hindrance than that of difluoromethyl radicals derived from CF_3 groups so the retro reaction preferentially occurs. On the other hand, the high reactivity of allylic stannanes accelerates the capture of perfluoroalkyl radicals, and Bu_3SnF traps F^- to disturb the retro reaction. Thus, the use of allylic stannanes is the most important key to accomplish the C-F bond activation of perfluoroalkyl groups. The SOMO of radical anion **A** is displayed in Figure 3C. **1c** receives an electron from

the excited Ir(III) that delocalizes in an π orbital on the benzene ring and also in the σ* orbitals of two benzylic C–F bonds (C^1–F^1 and C^1–F^2), and these C–F bonds of **A** are lengthened by comparison with those of neutral **1c** (from 1.365 Å to 1.402 Å). Therefore, the separation of a benzylic F atom exclusively occurs to give benzylic radical **B**, which accomplishes the site-selective defluoroallylation.

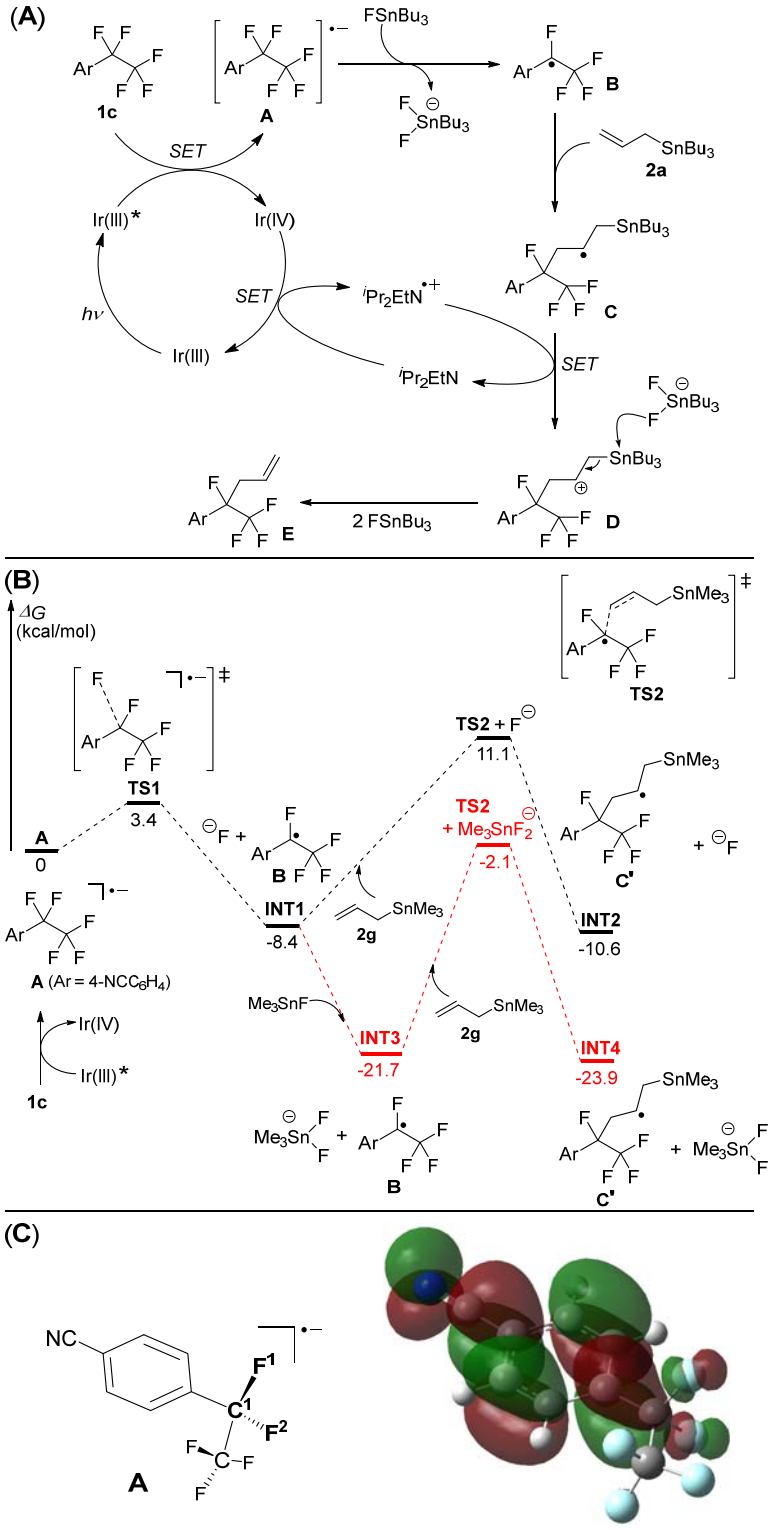
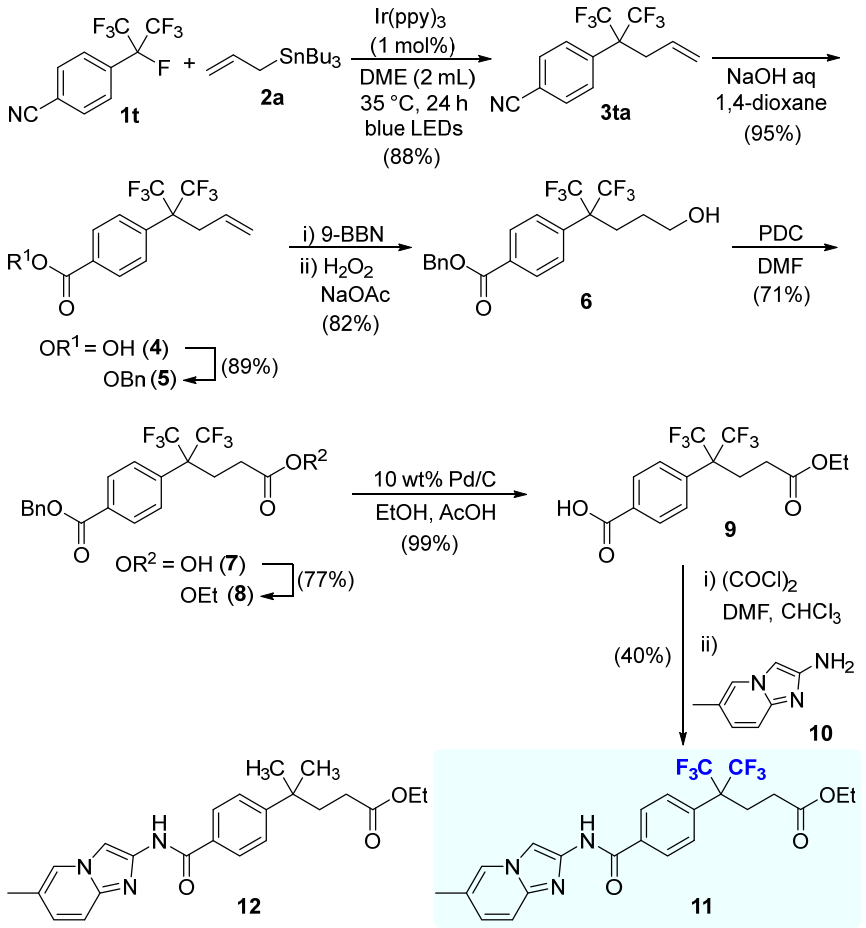


Figure 3. (A) Plausible mechanism for photoredox-catalyzed defluoroallylation of 1c with 2a. (B) Free energy profile for tin fluoride-accelerated defluoroallylation. (C) SOMO of radical anion A.

In pharmaceutical compounds, the replacement of alkyl groups by perfluoroalkyl groups is an important issue because significant changes are often found in the biological properties. Therefore, we targeted compound **11**, which is bis(trifluoromethyl)-analogue of compound **12** with ASK1 inhibitory action that is useful for the prophylaxis or treatment of diabetes and inflammatory diseases (Scheme 1).[29] Substrate **1t** was employed in the defluoroallylation system using **2a** under standard conditions to give bis(trifluoromethyl) compound **3ta** in 88% yield. Hydrolysis of the CN group followed by esterification of the carboxyl group of **4** afforded benzyl ester **5**. The vinyl group in **5** was transformed to a terminal hydroxyl moiety via hydroboration-oxidation, giving **6**. The subsequent oxidation of **6** with pyridinium dichromate (PDC) in DMF was followed by esterification to provide diester **8**. After deprotection of the benzyl ester moiety, the amidation of carboxylic acid **9** with amine **10** gave the targeted compound **11**.

Scheme 1. Synthesis of bis(trifluoromethyl)methylene-unit-containing-compound **11** to be an analog being useful as a pharmaceutical agent[30]



1-3. Conclusion

In conclusion, a direct and site-selective C(sp^3)–F bond allylation in perfluoroalkylarenes with allylic stannanes was accomplished via the use of $Ir(ppy)_3$. The present defluoroallylation proceeds exclusively at the benzylic position through perfluoroalkyl radicals generated by SET between excited $Ir(ppy)_3$ and perfluoroalkylarenes. The mild conditions promoted compatibility among various functional groups. DFT calculation studies showed that when Bu_3SnF is generated as a by-product, it traps F^- and prevents the retro reaction from an unstable perfluoroalkyl-substituted carbon radical, which allows the reaction of the radical intermediate with allylic stannanes to proceed. The synthesis of a bis(trifluoromethyl)methylene unit containing compound **11** demonstrated significance of the present reaction to medicinal chemistry.

1-4. Experimental Section

General

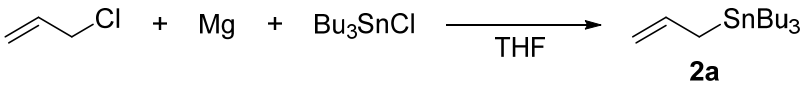
NMR spectra were recorded on a JEOL-AL400 and a JEOL-ECS400 spectrometers (400 MHz for ^1H, 100 MHz for ^{13}C, and 372 MHz for ^{19}F NMR) and a Bruker AVANCE III spectrometer (600 MHz for ^1H, 150 MHz for ^{13}C, and 558 MHz for ^{19}F NMR). Chemical shifts were reported in ppm on the δ scale relative to tetramethylsilane (δ = 0 for ^1H NMR) and residual $CHCl_3$ (δ = 77.0 for ^{13}C NMR) as an internal reference. Chemical shifts were reported in ppm on the δ scale relative to $BF_3{\cdot}Et_2O$ (δ = -153 for ^{19}F NMR) and Me_4Sn in $CDCl_3$ (0 ppm) as an external reference. Coupling constants were quoted in Hz (*J*). ^1H NMR spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), and sextet (sext). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). New compounds were characterized by ^1H, ^{13}C, ^{13}C off-resonance techniques, COSY, HMQC, and HMBC. Infrared (IR) spectra were recorded on a JASCO FT/IR-6200 Fourier transform infrared spectrophotometer. Column chromatographies were performed with silica gel. Purification by recycle HPLC was performed on SHIMADZU recycle HPLC system (SPD-20A, RID-10A, DGU-20A, LC-6AD, and FCV-20H2) and Japan Analytical Industry Co. (NEXT recycling preparative HPLC). Reactions were carried out in dry solvents under nitrogen atmosphere, unless otherwise stated. Reagents were purchased from Aldrich or Tokyo Chemical Industry Co., Ltd. (TCI), FUJIFILM Wako Pure Co., Ltd., and used after purification by distillation or used without purification for solid substrates. Light irradiation was performed by using a blue LED (Kessil A 160WE TUNA Blue). X-ray diffraction analysis was carried out by Rigaku XtaLAB Synergy with Hypix-6000HE.

Materials

Dehydrated solvents were purchased from FUJIFILM Wako Pure Co., Ltd. and used as obtained. Perfluoroalkylarene **1e** is commercially available. Allylstannanes and perfluoroalkylarenes were synthesized and used. The synthetic procedures and characterization data for allylstannanes **2a**, **2e**, and **2f** were described below. Other allylstannanes were synthesized according to reported procedures and the well characterization data were reported (**2b**: Preparation, N. Yoshinori, N. Yutaka, M. Kazuhiro, *Chem. Lett.* **1986**, *15*, 1857. Characterization data K. Komeyama, Y. Itai, K. Takaki, *Chem. Eur. J.* **2016**, *22*, 9130. **2c**: Preparation and

Characterization data, I. Suzuki, K. Kiyokawa, M. Yasuda, A. Baba, *Org. Lett.* **2013**, *15*, 1728. **2d**: Preparation and Characterization data: K. Miura, H. Saito, D. Itoh, T. Matsuda, N. Fujisawa, D. Wang, A. Hosomi, *J. Org. Chem.* **2001**, *66*, 10, 3348.). The synthetic procedures and characterization data for perfluoroalkylarenes **1d**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, **1s**, **1t**, and **1u** were described below. Other perfluoroalkylarenes were synthesized according to reported procedures and the well characterization data were reported (**1a**: Preparation: J. Kvíčala, M. Schindler, V. Kelbichová, M. Babuněk, M. Rybáčková, M. Kvíčalová, J. Cvačka, A Březinová, *J. Fluorine Chem.* **2013**, *153*, 12. Spectra: D. F. Jiang, C. Liu, Y. Guo, J. C. Xiao, Q. Y. Chen, *Eur. J. Org. Chem.* **2014**, 6303. **1b**: Preparation: J. Kvíčala, M. Schindler, V. Kelbichová, M. Babuněk, M. Rybáčková, M. Kvíčalová, J. Cvačka, A Březinová, *J. Fluorine Chem.* **2013**, *153*, 12. Spectra: M. Khrizanforov, V. Khrizanforova, V. Mamedov, N. Zhukova, S. Strekalova, V. Grinenko, T. Gryaznova, O. Sinyashin, Y. Budnikova, *J. Organomet. Chem.* **2016**, *820*, 82. **1c**: Preparation and Characterization data, Q. Xie, L. Li, Z. Zhu, R. Zhang, C. Ni, and J. Hu, *Angew. Chem. Int. Ed.*, **2018**, *57*,13211.).

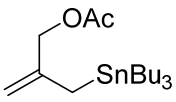
allyltributyltin (2a)



2a

A three-necked flask with Mg (355 mmol, 8.63 g) was flame-dried, and then THF (300 mL), Bu_3SnCl (326 mmol, 106.3 g), and allyl chloride (365 mmol, 27.9 g) were added to the flask. The reaction mixture was sonicated at 0 °C for 3 h, and then was stirred at room temperature for 2 h. H_2O (100 mL) was added to stop the reaction, and the resulting solution was filtrated by Celite. 15 wt% of NH_4F aq (100 mL) was added to the filtrate, and then the extraction with hexane was carried out. The corrected organic layers were washed with H_2O, dried over $MgSO_4$, and concentrated. The residual oil was distillated under reduced pressure (0.2 mmHg, 92-98 °C) to obtain the targeted compound **2a** (84% yield, 90.5 g). This compound was characterized by NMR (Reported NMR data: D.-Yu, Wang, C. Wang, M. Uchiyama, *J. Am. Chem. Soc.* **2015**, *137*, 10488.)

tributyl{2-(acetoxymethyl)allyl}stannane (2e)

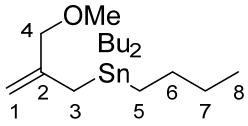


Allylic stannane **2e** was synthesized according to the reported procedure (B. M. Trost, P. J. Bonk, *J. Am. Chem. Soc.* **1985**, *107*, 1778.). To a solution of *n*BuLi (1.6 M in hexane, 44 mL) and TMEDA (84.0 mmol, 12.5 mL) in Et_2O (3 mL) at 0 °C was added dropwise 2-methyl-1-propen-3-ol (30.0 mmol, 2.16 g) in THF (13 mL) and stirred overnight at room temperature. The reaction mixture was cooled to 0 °C, and then *n*Bu_3SnCl (33.0 mmol, 10.7 g) was added. The resulting clear solution was stirred at room temperature for 15 minutes. The reaction mixture was added to Et_2O (20 mL), washed with saturated $CuSO_4$ aq, 15% NH_4F aq, and brine. The organic layer was dried over $MgSO_4$ and evaporated, and then the crude tributyl{2-(hydroxymethyl)allyl}stannane (8.25 g, 22.8 mmol) was obtained. The crude tributyl{2-(hydroxymethyl)allyl}stannane was used without further purification. The crude tributyl{2-(hydroxymethyl)allyl}stannane (8.44 mmol, 3.11 g) and DMAP (0.844 mmol, 0.103 g) were solved in dichloromethane (50 mL) and added acetic anhydride (16.9 mmol, 1.72 g) and NEt_3 (42.2 mmol,

4.27 g) at 0 °C. The reaction mixture was stirred for 20 minutes at room temperature. Then the reaction was quenched with sat. NH_4Cl aq and extracted with dichloromethane (10 mL x 3). The organic layers were dried over $MgSO_4$. The volatiles were removed under reduced pressure and purified by column chromatography (hexane/ethyl acetate = 9:1, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 2.23 g, 73%).

IR: (neat) 1745 (C=O) cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 4.76-4.68 (m, 2H), 4.42 (s, 2H), 2.09 (s, 3H), 1.78 (s, d by J_{Sn-H} = 58.2 Hz, 2H), 1.47 (m, 6H), 1.31 (m, 6H), 0.89 (m, 15H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 170.6, 144.1, 107.4, 68.2, 29.0 (s, d by J_{Sn-C} = 20.4 Hz), 27.3 (s, d by J_{Sn-C} = 55.8 Hz), 20.9, 15.3 (s, d by J_{Sn-C} = 222.8 Hz, J_{Sn-C} = 233.5 Hz), 13.6, 9.4 (s, d by J_{Sn-C} = 305.6 Hz, J_{Sn-C} = 320.3 Hz); **^{119}Sn NMR**: (150 MHz, in $CDCl_3$) -14.2 ; **HRMS**: (DART+) Calculated ($C_{18}H_{37}O_2Sn$) 405.18100 ($[M+H]^+$) Found: 405.17956

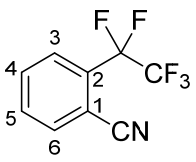
tributyl{2-(methoxymethyl)allyl}stannane (2f)



To a solution of *n*BuLi (1.6 M in hexane, 44 mL) and TMEDA (84.0 mmol, 12.5 mL) in Et_2O (3 mL) at 0 °C was added dropwise 2-methyl-1-propen-3-ol (30.0 mmol, 2.16 g) in THF (13 mL) and stirred overnight at room temperature. The reaction mixture was cooled to 0 °C, and then *n*Bu_3SnCl (33.0 mmol, 10.7 g) was added. The resulting clear solution was stirred at room temperature for 15 minutes. The reaction mixture was added to Et_2O (20 ml), washed with saturated $CuSO_4$ aq., 15% NH_4F aq., and brine. The organic phase was dried over $MgSO_4$ and evaporated, and then the crude tributyl{2-(hydroxymethyl)allyl}stannane (8.25 g, 22.8 mmol) was obtained and used without further purification. The crude tributyl{2-(hydroxymethyl)allyl}stannane (5.00 mmol, 1.80 g) was solved in THF (9 mL). Then, NaH (60% oil, 7.5 mmol, 0.300 g) and MeI (10.0 mmol, 1.41 g) were added to the reaction mixture at 0 °C. The reaction mixture was stirred overnight at 70 °C. Then the reaction was quenched with water, extracted with ether (10 mL x 3). The organic layers were washed with sat. $Na_2S_2O_3$ aq. and brine and dried over $MgSO_4$. The volatiles were removed under reduced pressure and purified by distillation under reduced pressure (0.20 Torr) with Kugelrohr to afford the product (colorless oil, 3.07 g, 82%).

IR: (neat) 2957, 2921, 2870, 2852 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 4.73-4.64 (m, 2H, 1-H_2), 3.76 (s, 2H, 4-H_2), 3.31 (s, 3H, MeO), 1.77 (s, d by $^1J_{Sn-H}$ = 59.9 Hz, 2H, 3-H_2), 1.48 (m, 6H, 6-H_2 x 3), 1.31 (m, 6H, 7-H_2 x 3), 0.94-0.82 (m, 15H, 5-H_2 x 3, 8-H_3 x 3); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 146.4 (s, d by $^2J_{Sn-C}$ = 20.1 Hz, C-2), 106.7 (t, d by $^3J_{Sn-C}$ = 38.6 Hz, C-1), 77.0 (t, C-4), 57.9 (q, MeO), 29.0 (t, d by $^1J_{Sn-C}$ = 19.6 Hz, C-3), 27.4 (m, C-6), 15.3 (m, C-7), 13.7 (m, C-8), 9.5 (m, C-5); **^{119}Sn NMR**: (150 MHz, in $CDCl_3$) -15.5 ; **HRMS**: (EI, 70 eV) Calculated ($C_{17}H_{37}OSn$) 377.1866 ($[M]^+$) Found: 377.1861

2-(pentafluoroethyl)benzonitrile (1d)

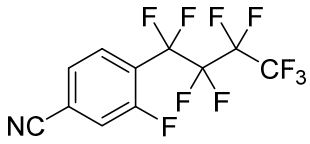


To a three-necked flask were added CuCl (22.3 mmol, 2.36 g) and KF (16.9 mmol, 0.983 g,). Then DMF (30 mL), $TMSCF_3$ (17.6 mmol, 2.51 g) and pyridine (30 mL) were successively added under N_2 atmosphere. After stirred at room temperature for 5 minutes, the reaction mixture was stirred at 80 °C for 10 hours. Then the reaction mixture was

cooled to room temperature and 2-iodobenzonitrile (4.21 mmol, 0.964 g) was added to the solution. The reaction mixture was again heated at 80 °C for 10 h. After the solution was cooled to room temperature, the reaction mixture was quenched with 3.0 M HCl aq (150 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with brine (30 mL x 2), dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm, diameter 21 mm silica gel) and GPC to give the product (yellow oil, 0.609 g, 65%).

IR: (neat) 2236 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.89 (d, J = 6.8 Hz, 1H, 6-H), 7.82-7.72 (m, 3H) **^{13}C NMR**: (150 MHz, in $CDCl_3$) 135.3 (d, C-6), 132.9 (d), 132.4 (d), 130.8 (s, t, $^2J_{C\text{-}F}$ = 23.7 Hz, C-2), 128.7 (d, t, $^3J_{C\text{-}F}$ = 6.9 Hz, C-3), 118.8 (s, qt, $^1J_{C\text{-}F}$ = 286.7 Hz, $^2J_{C\text{-}F}$ = 38.1 Hz, CF_3), 115.7 (s, CN), 112.5 (s, tq, $^1J_{C\text{-}F}$ = 256.9 Hz, $^2J_{C\text{-}F}$ = 39.3 Hz, CF_2), 111.3 (s, t, $^3J_{C\text{-}F}$ = 3.5 Hz, C-1); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -84.1 (s, 3F), -112.8 (s, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_9H_4F_5N$) 221.0264 ($[M]^+$) Found: 221.0262

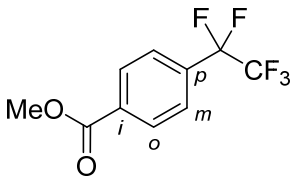
3-fluoro-4-(perfluorobutyl)benzonitrile (1f)



To a solution of copper powder (11.1 mmol, 0.705 g), 2,2'-bipyridine (0.424 mmol, g) and 2-fluoro-6-iodobenzonitrile (5.39 mmol. 1.33 g) in DMSO (8 mL) were added nonafluorobutyliodide (6.39 mmol, 2.21 g). The mixture was stirred at 80 °C for 72 hours. After cooling to room temperature, the reaction mixture was extracted with chloroform (10 mL x 3) and the combined organic layer was washed with NH_3 aq. (20 mL x 2) and brine (20 mL). The organic layer dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 1.30 g, 71%).

IR: (neat) 2242 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.73 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 10.0 Hz, 1H); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 160.0 (dt, $J_{C\text{-}F}$ = 262.4, 3.2 Hz), 130.4 (t, $J_{C\text{-}F}$ = 7.5 Hz), 128.1 (d, $J_{C\text{-}F}$ = 4.6 Hz), 121.3 (td, $J_{C\text{-}F}$ = 25.1, 10.8 Hz), 121.0 (d, $J_{C\text{-}F}$ = 25.4 Hz), 118.3 (d, $J_{C\text{-}F}$ = 9.8 Hz), 117.3 (qt, $J_{C\text{-}F}$ = 288.4, 33.2 Hz) 116.1 (d, $J_{C\text{-}F}$ = 2.3 Hz), 114.6 (tt, $J_{C\text{-}F}$ = 259.5, 33.5 Hz), 110.2 (m), 108.5 (m); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -81.2 (t, J = 9.2 Hz, 3F), -108.0 (m, 1F), -110.3 (t, J = 22.9 Hz, 2F), -122.9 (s, 2F), -126.1 (t, J = 13.7 Hz, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{11}H_3F_{10}N$) 339.0106 ($[M]^+$) Found: 339.0105

methyl-4-(pentafluoroethyl)benzoate (1g)

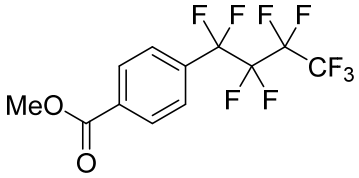


To a three-necked flask were added CuCl (22.5 mmol, 2.23 g) and KF (16.8 mmol, 0.979 g,). Then DMF (30 mL), $TMSCF_3$ (17.0 mmol, 2.43 g) and pyridine (30 mL) were successively added under N_2 atmosphere. After stirred at room temperature for 5 minutes, the reaction mixture was stirred at 80 °C for 10 hours. Then the reaction mixture was cooled to room temperature and methyl-4-iodobenzoate (4.21 mmol, 0.964 g) was added to the solution. The reaction mixture was again heated at 80 °C for 10 h. After the solution was cooled to room temperature, the reaction mixture was quenched with 3.0 M HCl aq. (150 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with brine (30 mL x 2), dried over

$MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm, diameter 21 mm silica gel) and GPC to give the product (yellow oil, 0.555 g, 48%).

IR: (neat) 1734 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.17 (d, J = 8.5 Hz, 2H, *o*), 7.69 (d, J = 8.5 Hz, 2H, *m*), 3.96 (s, 3H, MeO); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 165.8 (s, C=O), 133.5 (s, *i*), 132.8 (s, t, $^5J_{C\text{-}F}$ = 24.0 Hz, *p*), 129.9 (d, *o*), 126.6 (d, t, $^3J_{C\text{-}F}$ = 6.1 Hz, *m*), 118.9 (s, qt, $^1J_{C\text{-}F}$ = 286.1 Hz, $^2J_{C\text{-}F}$ =38.7 Hz, CF_3), 113.1 (s, tq, $^1J_{C\text{-}F}$ = 254.6 Hz, $^2J_{C\text{-}F}$ = 38.5 Hz, CF_2), 52.5 (q, MeO); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -84.7 (s, 3F), -115.4 (s, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{10}H_7F_5O_2$) 254.0366 ($[M]^+$) Found: 254.0369

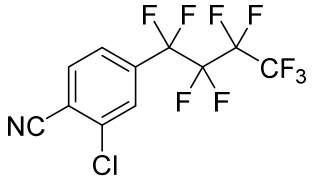
methyl 4-(nonafluorobutyl)benzoate (1h)



To a solution of copper powder (11.3 mmol, 0.721 g), 2,2'-bipyridine (0.434 mmol, 0.0678 g) and methyl 4-iodobenzoate (5.15 mmol, 1.35 g) in DMSO (8 mL) were added nonafluorobutyl iodide (6.12 mmol, 2.12 g). The mixture was stirred at 80 °C for 48 hours. After cooling to room temperature, the reaction mixture was extracted with chloroform (10 mL x 3) and the combined organic layers were washed with NH_3 aq. (20 mL x 2) and brine (20 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 1.45 g, 80%).

IR: (neat) 1735 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.18 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 3.96 (s, 3H) **^{13}C NMR**: (150 MHz, in $CDCl_3$) 165.8, 133.6, 132.9 (t, $J_{C\text{-}F}$ = 24.3 Hz), 129.8, 127.0 (t, $J_{C\text{-}F}$ = 6.4 Hz), 117.4 (qt, $J_{C\text{-}F}$ = 288.4, 33.4 Hz), 115.5 (tt, $J_{C\text{-}F}$ = 257.2, 31.5 Hz), 110.3 (tquintet, $J_{C\text{-}F}$ = 265.3, 34.1 Hz), 108.9 (tsextet, $J_{C\text{-}F}$ = 270.2, 36.4 Hz), 52.4; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -81.3 (s, 3F), -111.7 (s, 2F), -122.9 (s, 2F), -125.8 (s, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{12}H_7F_9O_2$) 354.0302 ($[M]^+$) Found: 354.0301

2-chloro-4-(perfluorobutyl)benzonitrile (1i)

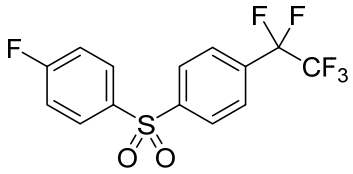


To a solution of copper powder (11.3 mmol, 0.718 g), 2,2'-bipyridine (0.416 mmol, 0.0649 g) and 4-bromo-2-chlorobenzonitrile (5.35 mmol. 1.16 g) in DMSO (8 mL) was added nonafluorobutyliodide (6.33 mmol, 3.68 g). The mixture was stirred at 80 °C for 72 hours. After cooling to room temperature, the reaction mixture was extracted with chloroform (10 mL x 3) and the combined organic layers were washed with NH_3 aq. (20 mL x 2) and brine (20 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 1.59 g, 84%).

IR: (neat) 2238 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.89 (d, J = 8.2 Hz, 1H), 7.78 (s, 1H), 7.66 (d, J = 8.2 Hz, 1H); **^{13}C NMR**: (150 MHz, in $CDCl_3$); 137.7, 134.4 (t, J = 25.1 Hz), 134.3, 128.5 (t, J = 6.9 Hz), 125.7 (t, J = 6.4 Hz), 117.3, 117.2 (qt, J = 287.8, 33.2 Hz), 114.6, 114.4 (m), 110.0 (m), 108.7 (m); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (s, 3F), -111.8 (s, 2F), -122.3 (s, 2F), -125.5 (s, 2F)

HRMS: (EI, 70 eV) Calculated ($C_{11}H_3ClF_9N$) 354.9810 ($[M]^+$) Found: 354.9807

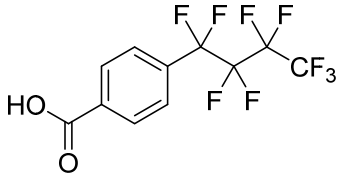
1-fluoro-4-((4-(perfluoroethyl)phenyl)sulfonyl)benzene (1j)



To a three-necked flask were added CuCl (24.1 mmol, 2.39 g) and KF (17.2 mmol, 1.12 g,). Then DMF (30 mL), $TMSCF_3$ (17.2 mmol, 2.44 g) and pyridine (30 mL) were successively added under N_2 atmosphere. After stirred at room temperature for 5 minutes, the reaction mixture was stirred at 80 °C for 10 hours. Then the reaction mixture was cooled to room temperature and 1-fluoro-4-((4-iodophenyl)sulfonyl)benzene (4.05 mmol, 1.46 g) was added to the solution. The reaction mixture was again heated at 80 °C for 15 h. After the solution was cooled to room temperature, the reaction mixture was quenched with 3 M HCl aq. (150 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with brine (30 mL x 2), dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 75:25, column length 11 cm, diameter 21 mm silica gel) and GPC to give the product (yellow solid, 1.04 g, 73%).

^{1}H NMR: (600 MHz, in $CDCl_3$) 8.07 (d, J = 7.9 Hz, 2H), 8.00 (dd, J = 7.6, 5.1 Hz, 2H), 7.76 (d, J = 7.9 Hz, 2H), 7.23 (t, J = 8.2 Hz, 2H); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 165.8 (d, J = 257.2 Hz), 145.3, 136.5 (d, J = 2.9 Hz), 133.4 (t, J = 24.3 Hz), 130.8 (d, J = 9.8 Hz), 128.0, 127.8 (t, J = 6.1 Hz), 118.7 (qt, J = 286.5, 38.1 Hz), 116.9 (d, J = 23.1 Hz), 112.6 (tq, J = 254.7, 38.6 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -84.4 (s, 3F), -102.8 (s, 1F), -115.4 (s, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{14}H_8F_6O_2S$) 354.0149 ($[M]^+$) Found: 354.0151

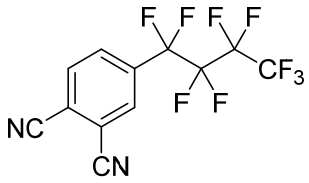
4-(nonafluorobutyl)benzoic acid (1k)



To a solution of methyl 4-(nonafluorobutyl)benzoate (0.993 mmol, 0.352 g), in THF/methanol/water (4:1:1) mixture (6 ml) was added lithium hydroxide (0.0714 g). The mixture was stirred at 70 °C for 24 hours. After cooling to room temperature, diluted with water (20 ml), followed by evaporation of THF and methanol under reduced pressure. Then, the water phase residue was washed with ethyl acetate (20 ml x 2), acidified with 1 M HCl (10 mL), and extracted with chloroform (10 mL x 3). The organic layer was dried over $MgSO_4$ and the solvent was removed under vacuum, yielding the product (white solid, 0.322 g, 95%).

mp: 158-160 °C; **IR**: (KBr) 1686 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in acetone-d_6) 8.28 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H); **^{13}C NMR**: (150 MHz, in acetone-d_6) 165.6, 134.6, 132.0 (t, $J_{C\text{-}F}$ = 24.0 Hz), 130.1, 127.2 (t, $J_{C\text{-}F}$ = 6.6 Hz), 117.4 (qt, $J_{C\text{-}F}$ = 286.5, 33.2 Hz), 115.7 (m), 110.3 (m), 108.7 (m); **^{19}F NMR**: (376 MHz, in acetone-d_6) -81.9 (t, J = 9.2 Hz, 3F), -111.6 (m, 2F), -123.3 (m, 2F), -126.3 (m, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{11}H_5F_9O_2$) 340.0146 ($[M]^+$) Found: 340.0140

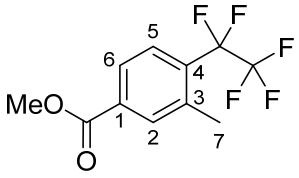
4-(nonafluorobutyl)phthalonitrile (1l)



To a solution of copper powder (11.7 mmol, 0.749 g), 2,2'-bipyridine (0.437 mmol, 0.0684 g) and 6-bromonicotinonitrile (5.70 mmol. 1.18 g) in DMSO (8 mL) was added nonafluorobutyliodide (6.30 mmol, 2.18 g). The mixture was stirred at 80 °C for 48 hours. After cooling to room temperature, the reaction mixture was extracted with chloroform (10 mL x 3) and the combined organic layers were washed with NH_3 aq. (20 mL x 2) and brine (20 mL). The organic layer dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 92:8, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 1.26 g, 74%).

mp: 51-52 °C; **IR**: (KBr) 2240 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$); 8.06-7.99 (m, 3H); **^{13}C NMR**: (150 MHz, in $CDCl_3$); 134.1 (t, $J_{C\text{-}F}$ = 25.4 Hz), 131.9 (t, $J_{C\text{-}F}$ = 6.4 Hz), 131.6 (t, $J_{C\text{-}F}$ = 6.4 Hz), 119.6, 117.2 (qt, $J_{C\text{-}F}$ = 288.3, 33.2 Hz), 117.0, 114.2 (tt, $J_{C\text{-}F}$ = 258.9, 32.4 Hz), 114.15, 114.07, 109.9 (m), 108.8 (m); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.8 (t, J = 9.9 Hz, 3F), -112.0 (t, J = 13.4 Hz, 2F), -122.2 (m, 2F), -125.4 (m, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{12}H_3F_9N_2$) 346.0153 ($[M]^+$) Found: 346.0155

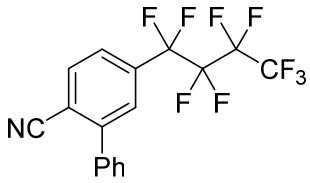
methyl 3-methyl-4-(pentafluoroethyl)benzoate (1m)



To a three-necked flask were added CuCl (24.4 mmol, 2.37 g) and KF (17.0 mmol, 0.990 g,). Then DMF (30 mL), $TMSCF_3$ (17.6 mmol, 2.50 g) and pyridine (30 mL) were successively added under N_2 atmosphere. After stirred at room temperature for 5 minutes, the reaction mixture was stirred at 80 °C for 10 hours. Then the reaction mixture was cooled to room temperature and methyl 3-methyl-4-iodobenzoate (4.00 mmol, 1.10 g) was added to the solution. The reaction mixture was again heated at 80 °C for 15 h. After the solution was cooled to room temperature, the reaction mixture was quenched with 3.0 M HCl aq. (150 mL) and the solution was diluted with Et_2O. The solution was divided into three layers. The middle layer was picked up and the solid was removed away through centrifugation. The residual solution was extracted with Et_2O (20 mL x 3) and the combined organic layer was washed with brine (30 mL x 2). The organic layer dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm, diameter 21 mm silica gel) and GPC to give the product (yellow oil, 0.558 g, 52%).

IR: (neat) 1731 (C=O) cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.95 (s, 1H, 2-H), 7.93 (d, J = 7.7 Hz, 1H, 6-H), 7.59 (d, J = 7.7 Hz, 1H, 5-H), 3.94 (s, 3H, MeO), 2.53 (t, $^5J_{H\text{-}F}$ = 3.1 Hz, 3H, 7-H_3); **^{13}C NMR**: (100 MHz, in $CDCl_3$) 165.9 (s, C=O), 138.2 (s, C-3), 133.4 (d, C-2), 133.1 (s, C-1), 130.7 (s, t, $^2J_{C\text{–}F}$ = 21.9 Hz, C-4), 128.2 (d, t, $^3J_{C\text{–}F}$ = 8.7 Hz, C-5), 126.9 (d, C-6), 119.3 (s, qt, $^1J_{C\text{–}F}$ =286.6 Hz, $^2J_{C\text{–}F}$ =38.8 Hz, CF_3), 114.5 (s, tq, $^1J_{C\text{–}F}$ =255.5 Hz, $^2J_{C\text{–}F}$ =38.6 Hz, CF_2), 52.3 (q, MeO), 20.1 (q, m, C-7); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -84.4 (s, 3F), -111.1 (s, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{11}H_9F_5O_2$) 268.0523 ($[M]^+$) Found: 268.0523

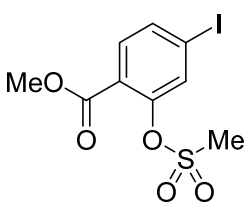
5-(perfluorobutyl)-[1,1'-biphenyl]-2-carbonitrile (1n)



To a solution of 2-chloro-4-(nonafluorobutyl)-benzonitrile (1.70 mmol, 0.604 g) and phenylboronic acid (2.42 mmol, 0.296 g) in toluene/dioxane/2 N Na_2CO_3 aq. (2:1:1) solution (12 mL) were added $Pd(PPh_3)_4$ (0.190 mmol, 0.220 g) and dppf (0.404 mmol, 0.224 g). The solution was degassed by N_2 bubbling for 10 min. Then it was refluxed at 100 °C under N_2 atmosphere for 12 h. After cooled down to ambient temperature, the reaction mixture was filtered over celite and extracted with ethyl acetate (15 mL x 3). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 1.54 g, 91%).

mp: 46-47 °C; **IR**: (KBr) 2228 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.92 (d, J = 8.2 Hz, 1H), 7.75 (s, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 7.5 Hz, 2H), 7.54-7.50 (m, 3H); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 146.2, 136.7, 134.1, 133.2 (t, $J_{C\text{-}F}$ = 24.6 Hz), 129.5, 129.0, 128.7, 128.5 (t, $J_{C\text{-}F}$ = 6.4 Hz), 125.8 (t, $J_{C\text{-}F}$ = 6.6 Hz), 117.3, 117.3 (qt, $J_{C\text{-}F}$ = 288.2, 33.1 Hz), 115.1 (t, $J_{C\text{-}F}$ = 1.4 Hz), 115.0 (tt, $J_{C\text{-}F}$ = 259.5, 32.1 Hz), 110.2 (m), 108.5 (m); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (t, J = 9.2 Hz, 3F), -111.7 (t, J = 13.7 Hz, 2F), -122.4 (m, 2F), -125.5 (m, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{17}H_8F_9N$) 397.0513 ($[M]^+$) Found: 397.0514

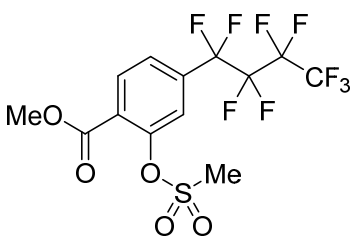
precursor of 1o: methyl 4-iodo-2-((methylsulfonyl)oxy)benzoate



Methyl 4-iodosalicylate (2.78 g, 10.0 mmol) and mesyl chloride (1.71 g, 15.0 mmol) were dissolved in CH_2Cl_2 (40 mL) at 0 °C. Et_3N (3.30 g, 30.0 mmol) was slowly added and the reaction was allowed to warm up to room temperature and left stirring for 1 hour. Sat. $NaHCO_3$ aq. (20 mL) was added and the water phase was extracted with CH_2CH_2 (30 mL x 3). The combined organic phases were washed with water (30 mL x 2), brine (30 mL x 2) and dried over $MgSO_4$. After concentration *in vacuo* the crude product was washed with hexane to give the product (brown solid, 3.49 g, 98 %).

mp: 112-113 °C; **IR**: (KBr) 1723 (C=O) cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.80 (s, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 3.91 (s, 3H), 3.31 (s, 3H); **^{13}C NMR**: (100 MHz, in $CDCl_3$) 164.1, 147.4, 136.5, 133.1, 132.8, 123.8, 99.4, 52.6, 38.6; **HRMS**: (EI, 70 eV) Calculated ($C_9H_9O_5SI$) 355.9215 ($[M]^+$) Found: 355.9208

methyl 2-((methylsulfonyl)oxy)-4-(perfluorobutyl)benzoate (1o)

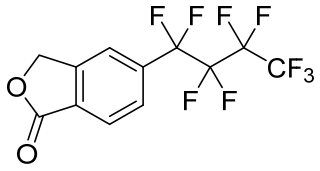


To a solution of copper powder (11.4 mmol, 0.723 g), 2,2'-bipyridine (0.437 mmol, 0.0683 g) and methyl 4-iodo-2-((methylsulfonyl)oxy)benzoate (5.00 mmol, 1.78 g) in DMSO (8 mL) were added nonafluorobutyliodide (6.13 mmol, 2.12 g).The mixture was stirred at 80 °C for 48 hours. After cooling to room temperature, the reaction mixture was extracted with chloroform (10 mL x 3) and the

combined organic layers were washed with NH_3 aq. (20 mL x 2) and brine (20 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 1.15 g, 51%).

mp: 44-45 °C; **IR**: (KBr) 1716 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.11 (d, J = 8.2 Hz, 1H), 7.66 (s, 1H), 7.62 (d, J = 8.2 Hz, 1H), 3.97 (s, 3H), 3.32 (s, 3H); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 163.7, 147.5, 133.9 (t, $J_{C\text{-}F}$ = 25.1 Hz), 132.4, 128.1 (d, $J_{C\text{-}F}$ = 1.7 Hz), 125.5 (t, $J_{C\text{-}F}$ = 6.4 Hz), 123.1 (t, $J_{C\text{-}F}$ = 6.6 Hz), 117.3 (qt, $J_{C\text{-}F}$ = 288.4, 33.4 Hz), 114.6 (tt, $J_{C\text{-}F}$ = 258.1, 32.1 Hz), 110.1 (m), 108.8 (m), 52.8, 38.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -81.0 (s, 3F), -111.5 (t, J = 12.2 Hz, 2F), -122.5 (s, 2F), -125.6 (t, J = 12.2 Hz, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{13}H_9F_9O_5S$) 448.0027 ($[M]^+$) Found: 448.0030

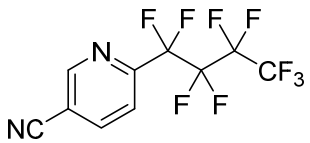
5-(perfluorobutyl)isobenzofuran-1(3H)-one (1p)



To a solution of copper powder (11.6 mmol, 0.736 g), 2,2'-bipyridine (0.438 mmol, 0.0684 g) and 5-bromoisobenzofuran-1(3H)-one (5.28 mmol. 1.12 g) in DMSO (8 mL) were added nonafluorobutyliodide (6.10 mmol, 2.11 g). The mixture was stirred at 80 °C for 48 hours. After cooling to room temperature, the reaction mixture was extracted with chloroform (10 mL x 3) and the combined organic layer was washed with NH_3 aq. (20 mL x 2) and brine (20 mL). The organic layer dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 1.30 g, 87%).

mp: 63-64 °C; **IR**: (KBr) 1770 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.08 (d, J = 8.4 Hz, 1H), 7.80 (m, 2H), 5.44 (s, 2H); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 169.4, 146.7, 134.4 (t, $J_{C\text{-}F}$ = 24.3 Hz), 129.3 (t, $J_{C\text{-}F}$ = 1.4 Hz), 127.9 (t, $J_{C\text{-}F}$ = 6.4 Hz), 126.2, 121.3 (t, $J_{C\text{-}F}$ = 6.9 Hz), 117.3 (qt, $J_{C\text{-}F}$ = 288.2, 33.4 Hz), 115.3 (tt, $J_{C\text{-}F}$ = 258.4, 32.1 Hz), 110.1 (m), 108.8 (m), 69.5; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -81.1 (t, J = 10.7 Hz, 3F), -110.9 (t, J = 13.7 Hz, 2F), -122.5 (m,2F), -125.7 (t, J = 12.2 Hz, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{12}H_5F_9O_2$) 352.0146 ($[M]^+$) Found: 352.0149

6-(nonafluorobutyl)nicotinonitrile (1q)

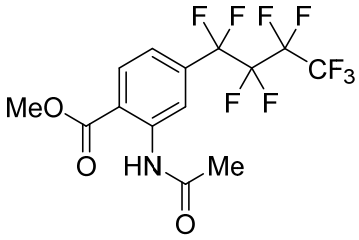


To a solution of copper powder (15.5 mmol, 0.985 g), 2,2'-bipyridine (0.528 mmol, 0.0825 g) and 6-bromonicotinonitrile (7.06 mmol. 1.29 g) in DMSO (8 mL) was added nonafluorobutyl iodide (10.6 mmol, 3.68 g). The mixture was stirred at 80 °C for 72 hours. After cooling to room temperature, the reaction mixture was extracted with chloroform (10 mL x 3) and the combined organic layers were washed with NH_3 aq. (20 mL x 2) and brine (20 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 90:10, column length 11 cm, diameter 21 mm silica gel) to give the product (white solid, 1.09 g, 48%).

mp: 67-68 °C; **IR**: (neat) 2240 (CN) cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 9.05 (d, J = 1.5 Hz, 1H), 8.23 (dd, J = 8.2, 1.5 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H); **^{13}C NMR**: (100 MHz, in $CDCl_3$) 152.3, 151.0 (t, $J_{C\text{-}F}$ =

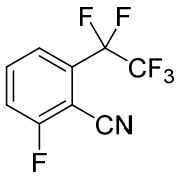
26.3 Hz), 140.8, 122.4 (t, $J_{C\text{-}F}$ = 4.6 Hz), 117.3 (qt, $J_{C\text{-}F}$ = 288.2, 33.2 Hz), 115.2, 112.9, 112.7 (tt, $J_{C\text{-}F}$ = 258.9, 32.1 Hz), 110.6 (m), 108.7 (m); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.8 (s, 3F), -114.5 (s, 2F), -122.5 (s, 2F), -125.5 (s, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{10}H_3F_9N_2$) 322.0153 ($[M]^+$)
Found: 322.0156

methyl 2-acetamido-4-(nonafluorobutyl)benzoate (1r)



To a solution of copper powder (11.1 mmol, 0.705 g), 2,2'-bipyridine (0.424 mmol, g) and methyl 2-amino-4-bromobenzoate (5.39 mmol, 1.33 g) in DMSO (8 mL) were added nonafluorobutyl iodide (6.39 mmol, 2.21 g).The mixture was stirred at 80 °C for 48 hours. After cooling to room temperature, the reaction mixture was extracted with chloroform (10 mL x 3) and the combined organic layers were washed with NH_3 aq. (20 mL x 2) and brine (20 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 9:1, column length 10 cm, diameter 26 mm silica gel) to give methyl 2-amino-4-(nonafluorobutyl)benzoate (white solid, 1.51 g, 76%). To a solution of methyl 2-amino-4-(nonafluorobutyl)benzoate (1.02 mmol, 0.393 g) in 1,2-dichloroethane (2.5 mL) were added acetic anhydride (1.29 mmol, 0.132 g) and trimethylamine (2.78 mmol, 0.281 g). The mixture was stirred at 85 °C for 72 hours. After cooling to room temperature, the reaction mixture was quenched with sat. $NaHCO_3$ aq. (10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 85:15, column length 10 cm, diameter 26 mm silica gel) to give the compound (white solid, 0.216 g, 52%).
mp: 59-60 °C; **IR**: (neat) 1706, 1592 cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 11.09 (s, 1H), 9.07 (s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.4Hz, 1H), 3.97 (s, 3H), 2.26 (s, 3H); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 169.2, 167.8, 141.8, 134.4 (t, J = 24.3 Hz), 131.1, 120.3 (t, J = 6.4 Hz), 119.0 (t, J = 7.2 Hz), 117.4 (qt, J = 288.4, 33.5 Hz), 117.4, 115.1 (tt, J = 258.1, 31.8 Hz), 110.2 (m), 108.9 (m), 52.8, 25.4; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (s, 3F), -111.7 (s, 2F), -122.5 (s, 2F), -125.5 (s, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_{14}H_{10}F_9NO_3$) 411.0517 ($[M]^+$) Found: 411.0519

2-fluoro-6-(perfluoroethyl)benzonitrile (1s)

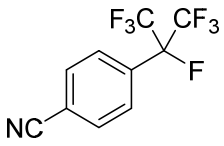


To a three-necked flask were added CuCl (24.5 mmol, 2.42 g) and KF (15.7 mmol, 0.911 g). Then DMF (30 mL), $TMSCF_3$ (16.3 mmol, 2.33 g) and pyridine (30 mL) were successively added under N_2 atmosphere. After stirred at room temperature for 5 minutes, the reaction mixture was stirred at 80 °C for 10 hours. Then the reaction mixture was cooled to room temperature and 2-fluoro-6-iodobenzonitrile (5.46 mmol, 1.35 g) was added to the solution. The reaction mixture was again heated at 80 °C for 10 h. After the solution was cooled to room temperature, the reaction mixture was quenched with 3.0 M HCl aq. (150 mL) and extracted with Et_2O (20 mL x 3). The combined organic layer was washed with brine (30 mL x 2), dried over $MgSO_4$ and concentrated under

vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) and GPC to give the product (yellow oil, 0.628 g, 48%).

IR: (neat) 2241 cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.83 (td, J = 8.2, 5.4 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.54 (t, J = 8.2 Hz, 1H); **^{13}C NMR**: (150 MHz, in $CDCl_3$); 164.5 (d, $J_{C\text{-}F}$ = 261.2 Hz), 135.0 (d, $J_{C\text{-}F}$ = 9.2 Hz), 132.3 (t, $J_{C\text{-}F}$ = 24.3 Hz), 124.5 (td, $J_{C\text{-}F}$ J = 7.2, 3.3 Hz), 120.3 (d, $J_{C\text{-}F}$ = 20.8 Hz), 118.6 (qt, $J_{C\text{-}F}$ = 286.7, 37.9 Hz), 112.0 (tq, $J_{C\text{-}F}$ = 257.7, 39.7 Hz), 110.3, 100.7 (dt, $J_{C\text{-}F}$ = 18.5, 3.5 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -84.1 (s, 3F), -102.3 (s, 1F), -112.5 (s, 2F); **HRMS**: (EI, 70 eV) Calculated ($C_9H_3F_6N$) 239.0170 ($[M]^+$) Found: 239.0168

4-(perfluoropropan-2-yl)benzonitrile (1t)

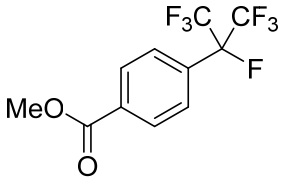


To an oven-dried 50 mL two-neck round-bottomed flask equipped with a magnetic stir bar were added dichloromethane (12 mL) and DMF (0.94 mL, 12 mmol) under nitrogen atmosphere. The solution was cooled at -78 °C. Heptafluoroisopropyl iodide (4.43 g, 15.0 mmol) was added to the solution. Diethyl zinc solution (1.0 M in Hexane, 6 mL, 6 mmol) was added dropwise at -78 °C. After stiring at 0 °C for 3 h, unreacted heptafluoroisopropyl iodide and dichrorometane were removed in vacuo. The slurry compound obtained was washed with cyclohexane (10 mL) three times and hexane (10 mL) two times and dried under vacuum to give Zn(*i*-$C_3F_7)_2(dmf)_2$ as a white solid (3.03 g, 92% yield).

To an oven-dried vial 4-iodobenzonitrile (2.00 mmol, 0.458 g), copper(I) 2-thiophenecarboxylate (3.11 mmol, 0.592 g), Zn(*i*-$C_3F_7)_2(dmf)_2$ (2.00 mmol. 1.10 g) and DMF (4 mL) was added under nitrogen atmosphere. The mixture was stirred at 90 °C for 7 hours. After cooling to room temperature, the reaction mixture was filtrated by celite. The filtrate was extracted with ether (10 mL x 3) and the combined organic layers were washed with 1 M HCl aq. (10 mL x 2) and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow liquid, 0.468 g, 82%).

IR: (neat) 2237 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.84 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 132.6 (d, J = 2.3 Hz), 131.3 (d, J = 20.8 Hz), 126.7 (d, J = 11.0 Hz), 120.2 (qd, $J_{C\text{-}F}$ = 287.8, 27.7 Hz), 117.3, 115.6, 91.1 (dsept, $J_{C\text{-}F}$ = 204.6, 33.4 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$); -75.3 (d, J = 9.2 Hz, 6F), -182.6 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{10}H_4F_7N$) 271.0232 ($[M]^+$) Found: 271.0228

methyl 4-(perfluoropropan-2-yl)benzoate (1u)



To an oven-dried 50 mL two-neck round-bottomed flask equipped with a magnetic stir bar were added dichloromethane (12 mL) and DMF (0.94 mL, 12 mmol) under nitrogen atmosphere. The solution was cooled at -78 °C. Heptafluoroisopropyl iodide (4.43 g, 15.0 mmol) was added to the solution. Diethyl zinc solution (1.0 M in Hexane, 6 mL, 6 mmol) was

added dropwise at -78 °C. After stiring at 0 °C for 3 h, unreacted heptafluoroisopropyl iodide and dichrorometane were removed in vacuo. The slurry compound obtained was washed with cyclohexane (10 mL) three times and hexane (10 mL) two times and dried under vacuum to give $Zn(i\text{-}C_3F_7)_2(dmf)_2$ as a white solid (3.03 g, 92% yield).

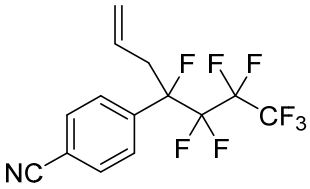
To an oven-dried vial methyl 4-iodobenzoate (2.10 mmol, 0.550 g), copper(I) 2-thiophenecarboxylate (3.15 mmol, 0.600 g), $Zn(iC_3F_7)_2(dmf)_2$ (2.10 mmol. 1.18 g) and DMF (6.3 mL) was added under nitrogen atmosphere. The mixture was stirred at 90 °C for 7 hours. After cooling to room temperature, the reaction mixture was filtrated by celite. The filtrate was extracted with ether (10 mL x 3) and the combined organic layers were washed with 1 M HCl aq. (20 mL x 2) and brine (20 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow liquid, 0.448 g, 70%).

IR: (neat) 1734 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.17 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 3.96 (s, 3H); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 165.9, 132.8 (d, J = 1.2 Hz), 131.1 (d, J = 20.8 Hz), 130.0 (d, J = 2.3 Hz), 125.9 (dt, J = 10.6, 1.4 Hz), 120.4 (qd, J = 287.3, 27.7 Hz), 92.7-90.1 (m), 52.4 (d, J = 1.2 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -75.6 (d, J = 6.1 Hz, 6F), -182.6 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{11}H_7F_7O_2$) 304.0334 ($[M]^+$) Found: 304.0332

Products

The preparation and characterization of new compounds were described below.

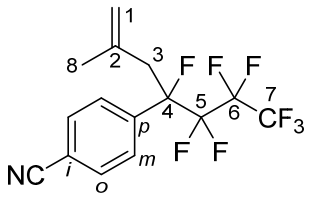
4-(4,5,5,6,6,7,7,7-octafluorohept-1-en-4-yl)benzonitrile (3aa)



To a solution of *fac*-$Ir(ppy)_3$ (0.0042 mmol, 2.8 mg) and 4-(nonafluorobutyl)benzonitrile (0.401 mmol, 0.129 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.402 mmol, 0.0520 g) and methallyltributyltin (1.26 mmol, 0.436 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.0724 g, 52%).

IR: (neat) 2233 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.73 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 5.37 (m, 1H), 5.10 (d, J = 16.0 Hz, 1H), 5.08 (d, J = 9.8 Hz, 1H), 3.18 (d, J = 6.3 Hz, 1H), 2.95 (m); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 138.4 (d, $J_{C\text{-}F}$ = 21.7 Hz), 132.2 (d, $J_{C\text{-}F}$ = 2.3 Hz), 127.6 (d, $J_{C\text{-}F}$ = 3.5 Hz), 126.7 (d, $J_{C\text{-}F}$ = 11.0 Hz), 121.7, 118.0, 117.4 (m), 113.4 (d, $J_{C\text{-}F}$ = 1.2 Hz), 111.7 (m), 109.6 (m), 96.2 (dt, $J_{C\text{-}F}$ = 193.0, 26.4 Hz), 37.6 (d, $J_{C\text{-}F}$ = 21.4 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (t, J = 10.7 Hz, 3F), -119.3 (m, 2F), -123.7 (m, 2F), -174.2 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{14}H_9F_8N$) 343.0607 ($[M]^+$) Found: 343.0603

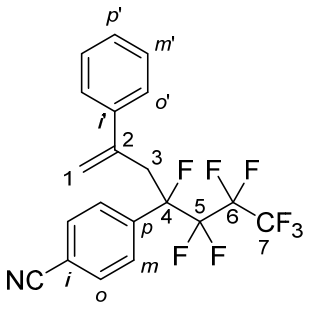
4-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)benzonitrile (3ab)



To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.7 mg) and 4-(nonafluorobutyl)benzonitrile (0.401 mmol, 0.128 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.397 mmol, 0.0514 g) and methallyltributyltin (1.26 mmol, 0.436 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm, diameter 21 mm silica gel) to give the product (colorless oil, 0.121 g, 85%).

IR: (neat) 2233 (CN) cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.72 (d, J = 8.5 Hz, 2H, *o*), 7.56 (d, J = 8.5 Hz, 2H, *m*), 4.78 (s, 1H, 1-H^A), 4.59 (s, 1H, 1-H^B), 3.14 (dd, $^3J_{H\text{-}F}$ = 14.4 Hz, J = 14.4 Hz, 1H, 3-H^A), 2.91 (dd, $^3J_{H\text{-}F}$ = 41.8 Hz, J = 14.4 Hz, 1H, 3-H^B), 1.53 (s, 3H, 8-H$_3$); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 138.2 (s, d, $^2J_{C\text{-}F}$ = 22.0 Hz, *p*), 136.5 (s, C-2), 131.8 (d, d, $^4J_{C\text{-}F}$ = 2.3 Hz, *o*), 126.8 (d, d, $^3J_{C\text{-}F}$ = 10.4 Hz, *m*), 118.3 (t, C-1), 117.9 (s, CN), 117.4 (s, qt, $^1J_{C\text{-}F}$ = 288.4 Hz, $^2J_{C\text{-}F}$ = 33.5 Hz, C-7), 113.6 (s, tq, $^1J_{C\text{-}F}$ = 263.0 Hz, $^2J_{C\text{-}F}$ = 30.2 Hz, C-5), 113.3 (s, *i*), 109.6 (s, tsext, $^1J_{C\text{-}F}$ = 268.2 Hz, $^2J_{C\text{-}F}$ = 37.4 Hz, C-6), 97.0 (s, dt, $^1J_{C\text{-}F}$ = 194.0 Hz, $^2J_{C\text{-}F}$ = 26.0 Hz, C-4), 40.5 (t, d, $^2J_{C\text{-}F}$ = 20.2 Hz, C-3), 23.3 (q, d, $^4J_{C\text{-}F}$ = 2.3 Hz, C-8); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (t, J = 11.5 Hz, 3F), -117.6 – -120.4 (m, 2F), -121.5 – -125.2 (m, 2F), -172.0 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{15}H_{11}F_8N$) 357.0764 ([M]$^+$) Found: 357.0769

4-(4,5,5,6,6,7,7,7-octafluoro-2-phenylhept-1-en-4-yl)benzonitrile (3ad)

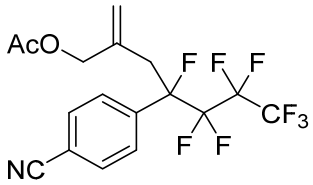


To a solution of *fac*-Ir(ppy)$_3$ (0.0042 mmol, 2.8 mg) and 4-(nonafluorobutyl)benzonitrile (0.409 mmol, 0.131 g) in DME (2 mL) was added *N,N*-diisopropylethylamine (0.403 mmol, 0.0521 g) and 2-phenylallyltributyltin (1.20 mmol, 0.489 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) and GPC to give the product (colorless oil, 0.0879 g, 51%).

IR: (neat) 2233 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.47 (d, J = 8.2 Hz, 2H, *o*), 7.32 (d, J = 8.2 Hz, 2H, *m*), 7.20-7.15 (m, 3H, *p*', *m*'), 6.95 (d, J = 7.0 Hz, 2H, *o*'), 5.20 (s, 1H, 1-H^A), 5.01 (s, 1H, 1-H^B), 3.66 (dd, J = 14.7 Hz, $^3J_{H\text{-}F}$ = 13.6 Hz, 1H, 3-H^A), 3.33 (dd, $^3J_{H\text{-}F}$ = 38.7 Hz, J = 14.7 Hz, 1H, 3-H^B); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 141.2 (s, *i*'), 140.0 (s, C-2), 137.8 (s, d, $^2J_{C\text{-}F}$ = 20.8 Hz, *p*), 131.5 (d, d, $^4J_{C\text{-}F}$ = 2.3 Hz, *o*), 128.1 (d, *p*'), 127.5 (d, *o*'), 126.7 (d, d, $^3J_{C\text{-}F}$ = 11.0 Hz, *m*), 126.2 (d, *m*'), 120.5 (t, C-1), 118.0 (s, CN), 117.4 (s, qt, $^1J_{C\text{-}F}$ = 288.3 Hz, $^2J_{C\text{-}F}$ = 33.5 Hz, C-7), 113.7 (s, tq, $^1J_{C\text{-}F}$ = 265.0 Hz, $^2J_{C\text{-}F}$ = 30.3 Hz, C-5), 113.0 (s, *i*), 109.6 (s, tsext, $^1J_{C\text{-}F}$ = 268.1 Hz, $^2J_{C\text{-}F}$ = 37.0 Hz, C-6), 96.4 (s, dt, $^1J_{C\text{-}F}$ = 194.8, $^2J_{C\text{-}F}$ = 26.0 Hz, C-4), 38.6 (t, d, $^2J_{C\text{-}F}$ = 20.8 Hz, C-3); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (t, J = 9.2 Hz, 3H), -117.6 – -

120.3 (m, 2F), -121.5 – -125.4 (m, 2F), -172.4 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{20}H_{13}F_8N$) 419.0920 ($[M]^+$) Found: 419.0918

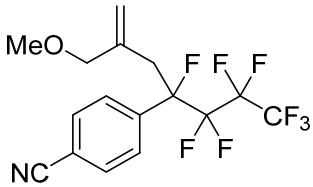
4-(4-cyanophenyl)-4,5,5,6,6,7,7,7-octafluoro-2-methyleneheptyl acetate (3ae)



To a solution of *fac*-Ir(ppy)$_3$ (0.0042 mmol, 2.8 mg) and 2-chloro-4-(nonafluorobutyl)benzonitrile (0.400 mmol, 0.128 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.394 mmol, 0.0510 g) and 2-((tributylstannyl)methyl)allyl acetate 2-(acetoxymethyl)-3-allyltributyltin (1.20 mmol, 0.486 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.0789 g, 47%).

IR: (neat) 2234 (CN), 1742 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.73 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 5.10 (s, 1H), 4.83 (s, 1H), 4.31 (d, J = 13.8 Hz, 1H), 4.22 (d, J = 13.6 Hz, 1H), 3.27 (dd, J = 15.0, 12.1 Hz, 1H), 2.95 (dd, J = 41.4, 15.0 Hz, 1H), 2.06 (s, 3H); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 170.3, 137.9 (d, $J_{C\text{-}F}$ = 22.0 Hz), 134.9, 132.1 (d, $J_{C\text{-}F}$ = 2.3 Hz), 126.7 (d, $J_{C\text{-}F}$ = 11.0 Hz), 120.4, 117.9, 117.4 (qt, $J_{C\text{-}F}$ = 289.2, 33.5 Hz), 113.7, 113.5 (m), 109.6 (m), 96.8 (dt, $J_{C\text{-}F}$ = 194.8, 26.2 Hz), 66.4 (d, $J_{C\text{-}F}$ = 3.5 Hz), 36.6 (d, $J_{C\text{-}F}$ = 20.8 Hz), 20.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -81.0 (t, J = 9.2 Hz, 3F), -119.0 (m, 2F), -123.5 (m, 2F), -172.5 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{17}H_{13}F_8NO_2$) 415.0819 ($[M]^+$) Found: 415.0811

4-(4,5,5,6,6,7,7,7-octafluoro-2-(methoxymethyl)hept-1-en-4-yl)benzonitrile (3af)

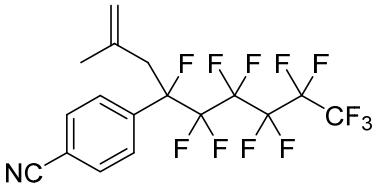


To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.7 mg) and 4-(nonafluorobutyl)benzonitrile (0.400 mmol, 0.129 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.402 mmol, 0.0520 g) and tributyl{2-(methoxymethyl)allyl}stannane (1.25 mmol, 0.470 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.106 g, 69%).

IR: (neat) 2233 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.72 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H), 5.09 (s, 1H), 4.85 (s, 1H), 3.62 (d, J = 12.8 Hz, 1H), 3.40 (d, J = 12.8 Hz, 1H), 3.21 (dd, $J_{H\text{-}F}$ = 13.5 Hz, J = 13.5 Hz, 1H), 3.18 (s, 3H), 2.99 (dd, $J_{H\text{-}F}$ = 41.7 Hz, J = 14.9 Hz, 1H); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 138.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 136.8, 131.9 (d, $J_{C\text{-}F}$ = 1.7 Hz), 126.8 (d, $J_{C\text{-}F}$ = 10.4 Hz), 119.4, 117.9, 117.4 (qt, $J_{C\text{-}F}$ = 287.8, 33.2 Hz), 113.5 (tq, $J_{C\text{-}F}$ = 264.1, 36.4 Hz), 113.4, 109.6 (tsext, $J_{C\text{-}F}$ = 268.7, 35.8 Hz), 96.6 (dt, $J_{C\text{-}F}$ = 194.2, 26.0 Hz), 75.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 57.8, 35.4 (d, $J_{C\text{-}F}$ = 20.2 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.8 (m, 3F), -119.1 (m, 2F), -123.5 (m, 2F), -172.2 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{16}H_{13}F_8NO$)

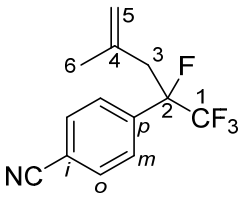
387.0869 ([M]$^+$) Found: 387.0864

4-(4,5,5,6,6,7,7,8,8,9,9,9-dodecafluoro-2-methylnon-1-en-4-yl)benzonitrile (3bb)



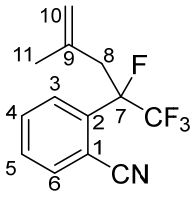
To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.7 mg) and 4-(perfluorohexyl)benzonitrile (0.401 mmol, 0.169 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.392 mmol, 0.0507 g) and methallyltributyltin (1.20mmol, 0.416 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 48 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.128 g, 70%). **IR**: (neat) 2233 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.71 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 4.78 (s, 1H), 4.60 (s, 1H), 3.15 (dd, J = 13.8 Hz, $J_{H\text{-}F}$ = 13.8 Hz, 1H), 2.92 (dd, $J_{H\text{-}F}$ = 41.5, J = 14.7 Hz, 1H), 1.53 (s, 3H); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 138.4 (d, $J_{C\text{-}F}$ = 22.0 Hz), 136.6, 131.9 (d, $J_{C\text{-}F}$ = 1.7 Hz), 126.8 (d, $J_{C\text{-}F}$ = 11.0 Hz), 118.4, 118.0, 117.2 (qt, $J_{C\text{-}F}$ = 288.2, 33.1 Hz), 114.2 (m), 113.3, 112.0 (m), 110.2 (m), 108.4 (m), 97.2 (dt, $J_{C\text{-}F}$ = 195.4, 26.0 Hz), 40.7 (d, $J_{C\text{-}F}$ = 20.2 Hz), 23.4 (d, $J_{C\text{-}F}$ = 2.9 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.8 (t, J = 10.7 Hz, 3F), -118.9 (m, 4F), -122.7 (m, 2F), -126.2 (m, 2F), -172.1 (m, 1F); **HRMS**: (EI, 70 eV); Calculated ($C_{17}H_{11}F_{12}N$) 457.0700 ([M]$^+$) Found: 457.0698

4-(1,1,1,2-tetrafluoro-4-methylpent-4-en-2-yl)benzonitrile (3cb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0042 mmol, 2.7 mg) and 4-(pentafluoroethyl)benzonitrile (0.395 mmol, 0.0875 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.399 mmol, 0.0516 g) and methallyltributyltin (1.22 mmol, 0.424 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm, diameter 21 mm silica gel) and GPC to give the product (colorless oil, 0.588 g, 58%). **IR**: (neat) 2234 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.72 (d, J = 8.5 Hz, 2H, *o*), 7.56 (d, J = 8.5 Hz, 2H, *m*), 4.78 (s, 1H, 5-H^A), 4.59 (s, 1H, 5-H^B), 3.14 (dd, $^3J_{H\text{-}F}$ = 14.4 Hz, J = 14.4 Hz, 1H, 3-H^A), 2.91 (dd, $^3J_{H\text{-}F}$ = 41.8 Hz, J = 14.4 Hz, 1H, 3-H^B), 1.53 (s, 3H, 6-H$_3$); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 138.3 (s, d, $^2J_{C\text{-}F}$ = 22.0 Hz, *p*), 136.8 (s, C-4), 132.0 (d, d, $^4J_{C\text{-}F}$ = 2.3 Hz, *o*), 126.8 (d, d, $^3J_{C\text{-}F}$ = 10.4 Hz, *m*), 122.8 (s, qd, $^1J_{C\text{-}F}$ = 285.2, $^2J_{C\text{-}F}$ = 30.1 Hz, C-1), 118.0 (s, CN), 117.9 (t, C-5), 113.4 (s, *i*), 95.6 (s, dq, $^1J_{C\text{-}F}$ = 192.3 Hz, $^2J_{C\text{-}F}$ = 30.7 Hz, C-2), 40.5 (t, d, $^2J_{C\text{-}F}$ = 20.2 Hz, C-3), 23.4 (q, d, $^4J_{C\text{-}F}$ = 2.9 Hz, C-6); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.0 (d, J = 9.2 Hz, 3F), -172.6 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{13}H_{11}F_4N$) 257.0828 ([M]$^+$) Found: 257.0824

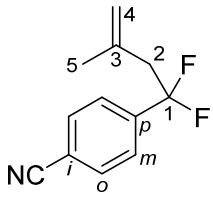
2-(1,1,1,2-tetrafluoro-4-methylpent-4-en-2-yl)benzonitrile (3db)



To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.7 mg) and 2-(pentafluoroethyl)benzonitrile (0.393 mmol, 0.871 g) in DME (2 mL) were added *N*,*N*-diisopropylethylamine (0.400 mmol, 0.0517 g) and methallyltributyltin (1.21 mmol, 0.418 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm, diameter 21 mm silica gel) to give the product (yellow oil, 0.0707 g, 70%).

IR: (neat) 2230 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.78 (d, J = 7.6 Hz, 1H), 7.69-7.64 (m, 2H), 7.53 (t, J = 8.1 Hz, 1H), 4.85 (s, 2H, 10-H$_2$), 3.54-3.33 (br m, 1H, 8-H^A), 3.06 (dd, J = 16.0, $^3J_{H\text{-}F}$ = 16.0 Hz, 1H, 8-H^B), 1.64 (s, 3H, 11-H$_3$); **^{13}C NMR**: (150 MHz, in $CDCl_3$) 136.7 (s, C-9), 135.8 (s, d, $^2J_{C\text{-}F}$ = 21.4 Hz, C-2), 135.5 (d), 132.5 (d), 129.7 (d), 128.1 (d, d, $^3J_{C\text{-}F}$ = 13.3 Hz, C-3), 122.8 (s, qd, $^1J_{C\text{-}F}$ = 286.1 Hz, $^2J_{C\text{-}F}$ = 29.8 Hz, CF_3), 117.9 (t, C-10), 114.6 (s, CN), 110.8 (s, d, $^3J_{C\text{-}F}$ = 4.6 Hz, C-1), 96.0 (s, dq, $^1J_{C\text{-}F}$ = 192.8 Hz, $^2J_{C\text{-}F}$ = 31.5 Hz, C-7), 39.4 (t, d, $^2J_{C\text{-}F}$ = 19.7 Hz, C-8), 23.3 (q, d, $^4J_{C\text{-}F}$ = 2.9 Hz, C-11); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -79.5 (m, 3F), -164.8 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{13}H_{11}F_4N$) 257.0828 ([M]$^+$) Found: 257.0826

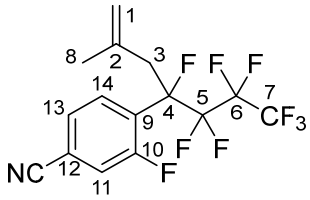
4-(1,1-difluoro-3-methylbut-3-en-1-yl)benzonitrile (3eb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and 4-(trifluoromethyl)benzonitrile (0.406 mmol, 0.0695 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.399 mmol, 0.0516 g) and methallyltributyltin (1.21 mmol, 0.418 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.0337 g, 40%).

IR: (neat) 2233 (CN) cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.73 (d, J = 8.7 Hz, 2H, *o*), 7.58 (d, J = 8.2 Hz, 2H, *m*), 4.91 (s, 1H, 4-H^A), 4.69 (s, 1H, 4-H^B), 2.84 (t, $^3J_{H\text{-}F}$ = 16.4 Hz, 2H, 2-H$_2$), 1.73 (s, 3H, 5-H$_3$); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 141.4 (s, t, $^2J_{C\text{-}F}$ = 27.0 Hz, *p*), 136.5 (s, t, $^3J_{C\text{-}F}$ = 3.7 Hz, C-3), 132.1 (d, *o*), 125.9 (d, t, $^3J_{C\text{-}F}$ = 6.1 Hz, *m*), 121.3 (s, t, $^1J_{C\text{-}F}$ = 245.4 Hz, C-1), 118.0 (s, CN), 117.7 (t, C-4), 113.6 (s, *i*), 46.7 (t, t, $^2J_{C\text{-}F}$ = 27.0 Hz, C-2), 23.3 (q, C-5); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -94.6 (t, J = 15.3 Hz); **HRMS**: (EI, 70 eV) Calculated ($C_{12}H_{11}F_2N$) 257.0860 ([M]$^+$) Found: 207.0859

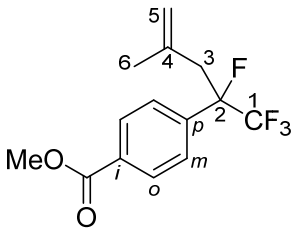
3-fluoro-4-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)benzonitrile (3fb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0042 mmol, 2.8 mg) and 3-fluoro-4-(nonafluorobutyl)benzonitrile (0.490 mmol, 0.166 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.398 mmol, 0.0515 g) and methallyltributyltin (1.46 mmol, 0.504 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.133 g, 73%).

IR: (neat) 2239 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.70 (dd, J = 7.7 Hz, $^4J_{H\text{-}F}$ = 7.7 Hz, 1H, 14-H), 7.54 (dd, J = 8.2 Hz, $^5J_{H\text{-}F}$ = 1.5 Hz, 1H, 13-H), 7.40 (d, $^3J_{H\text{-}F}$ = 10.7 Hz, 1H, 11-H), 4.77 (s, 2H, 1-H$_2$), 3.28 (dd, $^3J_{H\text{-}F}$ = 45.4 Hz, J = 15.4 Hz, 1H, 3-H^A), 3.01 (dd, J = 15.4 Hz, $^3J_{H\text{-}F}$ = 15.4 Hz, 1H, 3-H^B), 1.58 (s, 3H, 8-H$_3$); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 158.3 (s, dd, $^1J_{C\text{-}F}$ = 254.0, $^3J_{C\text{-}F}$ 5.5 Hz, C-10), 137.0 (s, C-2), 129.7 (d, dd, $J_{C\text{-}F}$ = 17.9, 3.5 Hz, C-14), 128.0 (d, t, $J_{C\text{-}F}$ = 3.5 Hz, C-13), 126.2 (s, dd, $J_{C\text{-}F}$ = 23.7, 12.7 Hz, C-9), 120.1 (d, dd, $J_{C\text{-}F}$ = 27.5, 2.0 Hz, C-11), 117.7 (t, C-1), 117.5 (s, qt, $^1J_{C\text{-}F}$ = 289.0 Hz, $^2J_{C\text{-}F}$ = 33.8 Hz, C-7), 116.7 (s, d, $^4J_{C\text{-}F}$ = 2.9 Hz, CN), 115.5 (s, dd, $J_{C\text{-}F}$ = 9.8, 1.2 Hz, C-12), 113.3 (s, tq, $^1J_{C\text{-}F}$ = 266.4 Hz, $^2J_{C\text{-}F}$ = 30.6 Hz, C-5), 109.7 (s, tsext, $^1J_{C\text{-}F}$ = 268.2 Hz, $^2J_{C\text{-}F}$ = 37.4 Hz, C-6), 97.0 (s, dt, $^1J_{C\text{-}F}$ = 196.3 Hz, $^2J_{C\text{-}F}$ = 28.0 Hz, C-4), 39.0 (t, dd, $^2J_{C\text{-}F}$ = 19.9, $^4J_{C\text{-}F}$ = 3.2 Hz, C-3), 23.2 (q, d, $^4J_{C\text{-}F}$ = 2.9 Hz, C-8); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (t, J = 10.7 Hz, 3F), -105.1 (s, 1F), -117.9--120.5 (m, 2F), -122.9--125.7 (m, 2F), -165.0 (s, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{15}H_{10}F_9N$) 375.0670 ([M]$^+$) Found: 375.0668

methyl 4-(1,1,1,2-tetrafluoro-4-methylpent-4-en-2-yl)benzoate (3gb)

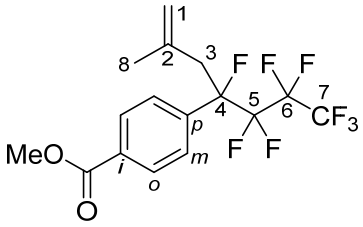


To a solution of *fac*-Ir(ppy)$_3$ (0.0042 mmol, 2.8 mg) and methyl 4-(pentafluoroethyl)benzoate (0.338 mmol, 0.0860 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.393 mmol, 0.0509 g) and methallyltributyltin (1.11 mmol, 0.385 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 48 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm, diameter 21 mm silica gel) and GPC to give the product (colorless oil, 0.0811 g, 83%).

IR: (neat) 1729 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.08 (d, J = 8.7 Hz, 2H, *o*), 7.53 (d, J = 8.7 Hz, 2H, *m*), 4.79 (s, 1H, 5-H^A), 4.67 (s, 1H, 5-H^B), 3.93 (s, 3H, MeO), 3.03 (dd, $^3J_{H\text{-}F}$ = 15.0 Hz, J = 15.0 Hz, 1H, 3-H^A), 2.92 (dd, $^3J_{H\text{-}F}$ = 39.5 Hz, J = 15.0 Hz, 1H, 3-H^B), 1.55 (s, 1H, 6-H$_3$); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 166.4 (s, C=O), 138.1 (s, d, $^2J_{C\text{-}F}$ = 21.4 Hz, *p*), 137.1 (s, C-4), 130.9 (s, *i*), 129.4 (d, d, $^4J_{C\text{-}F}$ = 1.7 Hz, *o*), 126.0 (d, d, $^3J_{C\text{-}F}$ = 10.4 Hz, *m*), 123.0 (s, qd, $^1J_{C\text{-}F}$ = 285.5 Hz, $^2J_{C\text{-}F}$ = 30.1 Hz, C-1), 117.6 (t, C-5), 95.8 (s, dq, $^1J_{C\text{-}F}$ = 191.0 Hz, $^2J_{C\text{-}F}$ = 30.4 Hz, C-2), 52.2 (q, MeO), 40.6 (t, d, $^2J_{C\text{-}F}$ = 20.2 Hz, C-3), 23.5 (q,

d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, C-6); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.1 (d, *J* = 6.1 Hz, 3F), -172.6 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{14}H_{14}F_4O_2$) 290.0930 ($[M]^+$) Found: 290.0934

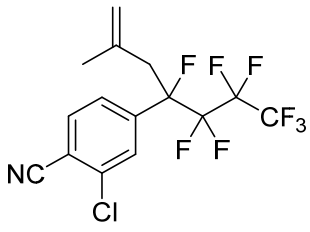
methyl 4-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)benzoate (3hb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and methyl 4-(nonafluorobutyl)benzoate (0.408 mmol, 0.144 g) in DME (2 mL) was added *N,N*-diisopropylethylamine (0.397 mmol, 0.0514 g) and methallyltributyltin (1.22 mmol, 0.422 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 48 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm, diameter 21 mm silica gel) and GPC to give the product (colorless oil, 0.0825 g, 52%).

IR: (neat) 1731 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.07 (d, *J* = 8.3 Hz, 2H, *o*), 7.51 (d, J = 8.3 Hz, 2H, *m*), 4.75 (s, 1H, 1-H^{A}), 4.60 (s, 1H, 1-H^{B}), 3.93 (s, 3H, MeO), 3.13 (dd, *J* = 14.7 Hz, $^{3}J_{H\text{-}F}$ = 14.7 Hz, 1H, 3-H^{A}), 2.92 (dd, $^{3}J_{H\text{-}F}$ = 41.3 Hz, *J* = 14.7 Hz, 1H, 3-H^{B}), 1.51 (s, 3H, 8-H$_3$); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 166.4 (s, C=O), 138.0 (s, d, $^{2}J_{C\text{-}F}$ = 21.4 Hz, *p*), 136.9 (s, C-2), 130.8 (s, *i*), 129.3 (d, d, $^{4}J_{C\text{-}F}$ = 2.3 Hz, *o*), 126.1 (d, d, $^{3}J_{C\text{-}F}$ = 10.4 Hz, *m*), 118.1 (t, C-1), 117.5 (s, qt, $^{1}J_{C\text{-}F}$ = 289.0 Hz, $^{2}J_{C\text{-}F}$ = 33.8 Hz, C-7), 113.7 (s, tq, $^{1}J_{C\text{-}F}$ = 263.9 Hz, $^{2}J_{C\text{-}F}$ = 30.1 Hz, C-5), 109.7 (s, tsext, $^{1}J_{C\text{-}F}$ = 267.9 Hz, $^{2}J_{C\text{-}F}$ = 36.8 Hz, C-6), 97.2 (s, dt, $^{1}J_{C\text{-}F}$ = 193.0, $^{2}J_{C\text{-}F}$ 25.7 Hz, C-4), 52.2 (q, MeO), 40.8 (t, d, $^{2}J_{C\text{-}F}$ = 20.2 Hz, C-3), 23.6 (q, d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, C-8); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -81.0 (t, *J* = 9.2 Hz, 3F), -119.2 (m, 2F), -123.6 (m, 2F), -172.3 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{16}H_{14}F_8O_2$) 390.0866 ($[M]^+$) Found: 390.0865

2-chloro-4-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)benzonitrile (3ib)

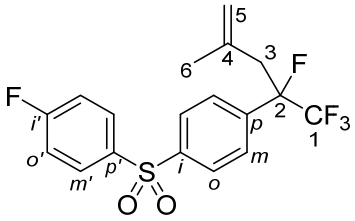


To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and 2-chloro-4-(nonafluorobutyl)benzonitrile (0.352 mmol, 0.125 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.402 mmol, 0.0520 g) and methallyltributyltin (1.26 mmol, 0.436 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.0792 g, 57%).

IR: (neat) 2236 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.72 (d, *J* = 8.2 Hz, 1H), 7.59 (s, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 4.82 (s, 1H), 4.61 (s, 1H), 3.14 (dd, *J* = 13.9 Hz, $J_{H\text{-}F}$ = 13.9 Hz, 1H), 2.88 (dd, $J_{H\text{-}F}$ = 41.7 Hz, *J* = 13.9 Hz, 1H), 1.56 (s, 3H); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 139.9 (d, $J_{C\text{-}F}$ = 22.0 Hz), 137.1 (d, $J_{C\text{-}F}$ = 2.3 Hz), 136.2, 133.6, 127.7 (d, $J_{C\text{-}F}$ = 11.6 Hz), 124.9 (d, $J_{C\text{-}F}$ = 9.8 Hz), 118.8, 117.4 (qt, $J_{C\text{-}F}$ = 289.4, 33.2 Hz), 115.2, 114.2, 113.4 (m), 109.6 (m), 96.7 (dt, $J_{C\text{-}F}$ = 195.9, 26.3 Hz), 40.6 (d, $J_{C\text{-}F}$ = 20.2 Hz), 23.6

(d, $J_{C\text{-}F}$ = 2.3 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (t, J = 10.7 Hz, 3F), -119.0 (m, 2F), -123.4 (m, 2F), -171.5 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{15}H_{10}ClF_8N$) 391.0374 ($[M]^+$) Found: 391.0373

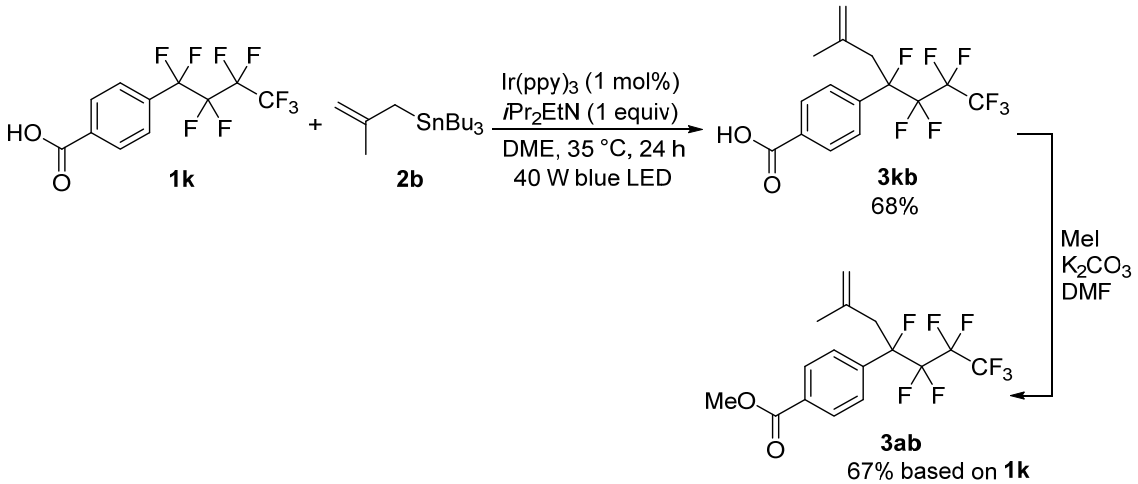
1-fluoro-4-((4-(1,1,1,2-tetrafluoro-4-methylpent-4-en-2-yl)phenyl)sulfonyl)benzene (3jb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0042 mmol, 2.8 mg) and 1-fluoro-4-((4-(perfluoroethyl)phenyl)sulfonyl)benzene (0.405 mmol, 0.143 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.403 mmol, 0.0521 g) and methallyltributyltin (1.21 mmol, 0.419 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 85:15, column length 10 cm, diameter 26 mm silica gel) and GPC to give the product (colorless oil, 0.147 g, 93%).

IR: (neat) 1180 cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.99 (m, 4H), 7.61 (d, J = 8.4 Hz, 2H, *m*), 7.20 (m, 2H, *o*'), 4.78 (s, 1H, 5-H^A), 4.65 (s, 1H, 5-H^B), 3.03 (dd, J = 15.0 Hz, $^3J_{H\text{-}F}$ = 15.0 Hz, 1H, 3-H^A), 2.91 (dd, J = 39.5 Hz, $^3J_{H\text{-}F}$ =15.0 Hz, 1H, 3-H^B), 1.54 (s, 3H, 6-H$_3$); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 165.6 (s, d, $^1J_{C\text{-}F}$ = 256.6 Hz, *i*'), 142.4 (s, *i*), 138.8 (s, d, $^2J_{C\text{-}F}$ = 22.0 Hz, *p*), 137.0 (s, d, $^4J_{C\text{-}F}$ = 3.5 Hz, *p*'), 136.6 (s, C-4), 130.6 (d, d, $^3J_{C\text{-}F}$ = 9.8 Hz, *m*'), 127.4 (d, d, $^4J_{C\text{-}F}$ = 1.7 Hz, *o*), 127.0 (d, d, $^3J_{C\text{-}F}$ = 10.4 Hz, *m*), 122.7 (s, qd, $^1J_{C\text{-}F}$ = 285.8, $^2J_{C\text{-}F}$ = 29.5 Hz, C-2), 117.9 (s, C-5), 116.7 (d, d, $^2J_{C\text{-}F}$ = 22.5 Hz, *o*'), 95.6 (s, dq, $^1J_{C\text{-}F}$ = 191.9, $^2J_{C\text{-}F}$ = 30.6 Hz, C-2), 40.5 (t, d, $^2J_{C\text{-}F}$ = 20.2 Hz, C-3), 23.4 (q, d, $^4J_{C\text{-}F}$ = 2.3 Hz, C-6); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.0 (d, J = 6.1 Hz, 3F), -103.5 (d, J = 6.1 Hz, 1F), -172.2 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{18}H_{15}F_4O_2S$) 390.0713 ($[M]^+$) Found: 390.0713

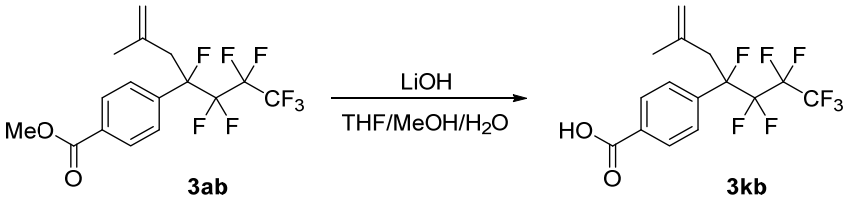
4-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)benzoic acid (3kb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0042 mmol, 2.8 mg) and 4-(nonafluorobutyl)benzoic acid **1k** (0.402 mmol, 0.137 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.403 mmol, 0.0521 g) and methallyltributyltin (1.20 mmol, 0.415 g). After degassing by freeze-pump-thaw process for three cycles, the

mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 48 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure to give carboxylic acid **3kb** (68% yield measured by NMR). The isolation of this carboxylic acid by silica gel column chromatography was difficult because of it high polarity. Therefore, carboxylic acid **3kb** was transformed to ester **3ab**. The crude product including **3kb** was dissolved in DMF (1 mL), and MeI (1.20 mmol, 0.170 g) and K_2CO_3 (0.400 mmol, 0.0552 g) were added. The mixture was stirred for 4 hours at 80 °C. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (10 mL x 3) and the combined organic layers were washed with brine (10 mL x 2). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give esterificated product **3ab** (yellow liquid, 0.105 g, 67% based on **1k**).

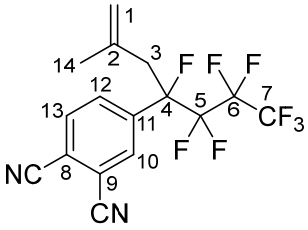
As shown below, pure carboxylic acid **3kb** was synthesized by the hydrolysis of purified esterificated product **3ab**.



To a solution of methyl 4-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)benzoate (0.190 mmol, 0.0742 g), in THF/methanol/water (4:1:1) mixture (3 mL) were added lithium hydroxide (0.0242 g). The mixture was stirred at 70 °C for 24 hours. After cooling to room temperature, diluted with water (10 mL). Then, the water phase residue was washed with chloroform (10 mL x 2), acidified with 1 M HCl (10 mL), and extracted with chloroform (10 mL x 3). The organic layer was dried over $MgSO_4$ and the solvent was removed under vacuum, yielding the product (white solid, 0.0586 g, 82%).

mp: 93-94 °C; **IR**: (KBr) 1697 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.15 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 4.77 (s, 1H), 4.61 (s, 1H), 3.14 (dd, J = 13.7, $J_{H\text{-}F}$ = 13.7 Hz, 1H), 2.93 (dd, $J_{H\text{-}F}$ = 41.1 Hz, J = 13.7 Hz, 1H), 1.53 (s, 3H); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 171.1, 139.0 (d, $J_{C\text{-}F}$ = 20.8 Hz), 136.8, 130.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 129.9, 126.3 (d, $J_{C\text{-}F}$ = 10.4 Hz), 118.2, 117.5 (m), 113.6 (m), 109.4 (m), 97.2 (dt, $J_{C\text{-}F}$ = 192.7, 26.2 Hz), 40.8 (d, $J_{C\text{-}F}$ = 19.7 Hz), 23.6 (d, $J_{C\text{-}F}$ = 2.3 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.8 (m, 3F), -119.1 (m, 2F), -123.5 (m, 2F), -172.2 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{15}H_{12}F_8O_2$) 376.0710 ($[M]^+$) Found: 376.0709

4-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)phthalonitrile (3lb)

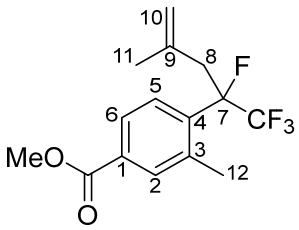


To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and 4-(nonafluorobutyl)phthalonitrile (0.406 mmol, 0.140 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.408 mmol, 0.0528 g) and methallyltributyltin (1.21 mmol, 0.419 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W

blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.0928 g, 60%).

IR: (neat) 2238 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.89 (d, J = 8.4 Hz, 1H, 13-H), 7.87 (s, 1H, 10-H), 7.80 (d, J = 8.4 Hz, 1H, 12-H), 4.82 (s, 1H, 1-H^A), 4.61 (s, 1H, 1-H^B), 3.19 (dd, J = 14.2 Hz, $^{3}J_{H\text{-}F}$ = 14.2 Hz, 1H, 3-H^A), 2.93 (dd, $^{3}J_{H\text{-}F}$ = 42.2 Hz, J = 14.2 Hz, 1H, 3-H^B), 1.56 (s, 3H, 14-H_3); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 139.5 (s, d, J = 22.5 Hz, C-11), 136.0 (s, C-2), 133.3 (d, d, $^{4}J_{C\text{-}F}$ = 2.3 Hz, C-13), 131.0 (d, d, $^{3}J_{C\text{-}F}$ = 11.6 Hz, C-10), 130.7 (d, d, $^{3}J_{C\text{-}F}$ = 10.4 Hz, C-12), 119.3 (t, C-1), 117.3 (s, t, $^{1}J_{C\text{-}F}$ = 288.0 Hz, $^{2}J_{C\text{-}F}$ = 33.1 Hz, C-7), 116.7 (s, d, $^{5}J_{C\text{-}F}$ = 1.2 Hz, C-8), 116.2 (s, d, $^{4}J_{C\text{-}F}$ = 2.3 Hz, C-9), 114.7 (s, 8-CN), 114.6 (s, 9-CN), 113.2 (s, tq, $^{1}J_{C\text{-}F}$ = 264.1 Hz, $^{2}J_{C\text{-}F}$ = 30.6 Hz, C-5), 109.6 (s, tsext, $^{1}J_{C\text{-}F}$ = 266.2 Hz, $^{2}J_{C\text{-}F}$ = 38.0 Hz, C-6), 96.8 (s, dt, $^{1}J_{C\text{-}F}$ = 196.1 Hz, $^{2}J_{C\text{-}F}$ = 26.2 Hz, C-4), 40.5 (t, d, $^{2}J_{C\text{-}F}$ = 19.7 Hz, C-3), 23.5 (q, d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, C-14); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (t, J = 10.7 Hz, 3F), -119.0 (m, 2F), -123.3 (m, 2F), -171.5 (t, J = 29.0 Hz, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{16}H_{10}F_8N_2$) 382.0716 ($[M]^+$) Found: 382.0718

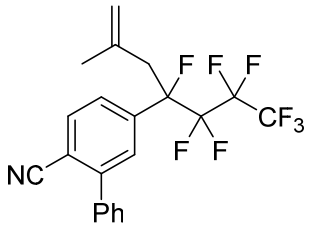
methyl 3-methyl-4-(1,1,1,2-tetrafluoro-4-methylpent-4-en-2-yl)benzoate (3mb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.7 mg) and methyl 3-methyl-4-(pentafluoroethyl)benzoate (0.388 mmol, 0.104 g) in DME (2 mL) was added *N,N*-diisopropylethylamine (0.392 mmol, 0.0507 g) and methallyltributyltin (1.20 mmol, 0.417 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 48 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) and GPC to give the product (yellow liquid, 0.0669 g, 56%).

IR: (neat) 1728 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.87 (s, 1H, 2-H), 7.84 (d, J = 8.4 Hz, 1H, 6-H), 7.34 (br, 1H, 5-H), 4.81 (s, 1H, 10-H^A), 4.73 (s, 1H, 10-H^B), 3.91 (s, 3H, MeO), 3.08 (dd, $^{3}J_{H\text{-}F}$ = 40.1 Hz, J = 15.6 Hz, 1H, 8-H^A), 3.00 (dd, $^{3}J_{H\text{-}F}$ = 16.7 Hz, J = 15.6 Hz, 1H, 8-H^B), 2.55 (d, J = 7.5 Hz, 3H, 12-H_3), 1.58 (s, 3H, 11-H_3); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 166.5 (s, C=O), 138.2 (br, C-3), 137.5 (s, C-9), 135.5 (s, d, $^{2}J_{C\text{-}F}$ = 20.2 Hz, C-4), 134.0 (d, C-2), 130.7 (s, C-1), 128.2 (d, dd, $^{3}J_{C\text{-}F}$ = 9.2, J = 1.2 Hz, C-5), 126.4 (d, C-6), 123.4 (s, dd, $^{1}J_{C\text{-}F}$ = 286.1, $^{2}J_{C\text{-}F}$ = 30.1 Hz, CF_3), 117.1 (t, C-10), 98.2 (s, dq, $^{1}J_{C\text{-}F}$ = 190.4, $^{2}J_{C\text{-}F}$ = 30.0 Hz, C-7), 52.2 (q, MeO), 41.0 (t, d, $^{2}J_{C\text{-}F}$ = 20.8 Hz, C-8), 23.3 (q, d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, C-11), 22.2 (q, d, J = 13.3 Hz, C-12); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -79.9 (d, J = 10.7 Hz, 3F), -167.8 (br, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{15}H_{16}F_4O_2$) 304.1086 ($[M]^+$) Found: 304.1087

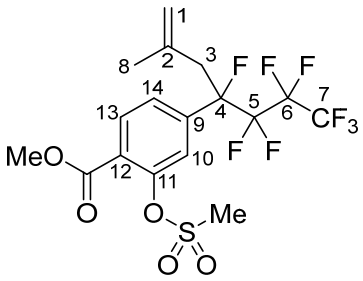
5-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)-[1,1'-biphenyl]-2-carbonitrile (3nb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.7 mg) and 5-(nonafluorobutyl)-[1,1'-biphenyl]-2-carbonitrile (0.400 mmol, 0.158 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.397 mmol, 0.0513 g) and methallyltributyltin (1.20 mmol, 0.414 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.149 g, 86%).

IR: (neat) 2229 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.79 (d, J = 8.2 Hz, 1H), 7.59 (s, 1H), 7.55 (d, J = 7.0 Hz, 2H), 7.51 (m, 3H), 7.47 (t, J = 7.2 Hz, 1H), 4.82 (s, 1H), 4.65 (s, 1H), 3.16 (dd, J = 14.0 Hz, $J_{H\text{-}F}$ = 14.0 Hz, 1H), 2.96 (dd, $J_{H\text{-}F}$ = 41.6, J = 14.0 Hz, 1H), 1.57 (s, 3H); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 145.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 138.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 137.5, 136.7, 133.4 (d, $J_{C\text{-}F}$ = 2.3 Hz), 129.1, 128.8, 128.7, 127.7 (d, $J_{C\text{-}F}$ = 10.4 Hz), 125.2 (d, $J_{C\text{-}F}$ = 11.0 Hz), 118.4, 117.9, 117.5 (m), 113.6 (m), 112.1 (s), 109.7 (m), 97.0 (dt, $J_{C\text{-}F}$ = 194.0, 25.9 Hz), 40.6 (d, $J_{C\text{-}F}$ = 20.8 Hz), 23.5 (d, $J_{C\text{-}F}$ = 2.9 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -81.0 (s, 3F), -119.0 (m, 2F), -123.4 (m, 2F), -171.7 (s, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{21}H_{15}F_8N$) 433.1077 ([M]$^+$) Found: 433.1082

methyl 2-((methylsulfonyloxy)-4-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)benzoate (3ob)

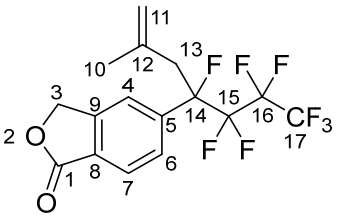


To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.7 mg) and methyl 2-(methylsulfonyloxy)-4-(nonafluorobutyl)benzoate (0.394 mmol, 0.177 g) in DME (2 mL) was added *N,N*-diisopropylethylamine (0.393 mmol, 0.0508 g) and methallyltributyltin (1.21 mmol, 0.418 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 48 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 9:1, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow solid, 0.137 g, 72%). The structure was determined by X ray analysis (CCDC: 2070966).

mp: 66-67 °C; **IR**: (KBr) 1725 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.01 (d, J = 8.4 Hz, 1H, 13-H), 7.48 (s, 1H, 10-H), 7.46 (d, J = 8.4 Hz, 1H, 14-H), 4.79 (s, 1H, 1-H^A), 4.65 (s, 1H, 1-H^B), 3.94 (s, 3H, MeO), 3.27 (s, 3H, $MeSO_2$), 3.13 (dd, J = 14.7 Hz, $^3J_{H\text{-}F}$ = 13.8 Hz, 1H, 3-H^A), 2.91 (dd, $^3J_{H\text{-}F}$ = 41.8, J = 14.7 Hz, 1H, 3-H^B), 1.55 (s, 3H, 8-H$_3$); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 164.1 (s, C=O), 147.4 (s, d, $^4J_{C\text{-}F}$ = 2.3 Hz, C-11), 139.4 (s, d, $^2J_{C\text{-}F}$ = 22.0 Hz, C-9), 136.4 (s, C-2), 131.8 (d, d, $^4J_{C\text{-}F}$ = 1.7 Hz, C-13), 125.0 (s, C-12), 124.6 (d, d, $^3J_{C\text{-}F}$ = 11.0 Hz, C-14), 122.2 (d, d, $^3J_{C\text{-}F}$ = 10.4 Hz, C-10), 118.7 (s, C-1), 117.4 (s, qt, $^1J_{C\text{-}F}$ = 288.7 Hz, $^2J_{C\text{-}F}$ = 33.3 Hz, C-7), 113.5 (s, tq, $^1J_{C\text{-}F}$ = 265.2 Hz, $^2J_{C\text{-}F}$ = 30.4 Hz, C-5), 109.6 (s, tsext, $^1J_{C\text{-}F}$ = 270.2 Hz, $^2J_{C\text{-}F}$ = 37.8 Hz, C-6), 96.8 (s, dt, $^1J_{C\text{-}F}$ = 194.6, $^2J_{C\text{-}F}$ = 26.2 Hz, C-4), 52.6 (s, MeO), 40.7 (d, $^2J_{C\text{-}}$

$_F$ = 20.2 Hz, C-3), 38.4 (s, $MeSO_2$), 23.5 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, C-8); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (t, *J* = 10.7 Hz, 3F), -117.6 – -120.5 (m, 2F), -121.7 – -125.2 (m, 2F), -171.5 (m, 1F); **HRMS**: (CI, 70 eV) Calculated ($C_{17}H_{17}F_8O_5S$) 485.0669 ($[M+H]^+$) Found: 485.0677

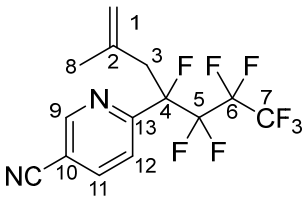
5-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)isobenzofuran-1(3H)-one (3pb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.7 mg) and 5-(nonafluorobutyl)isobenzofuran-1(3H)-one (0.399 mmol, 0.141 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.395 mmol, 0.0510 g) and methallyltributyltin (1.20 mmol, 0.414 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.130 g, 84%).

IR: (neat) 1771 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.96 (d, *J* = 8.1 Hz, 1H, 7-H), 7.63 (s, 1H, 4-H), 7.61 (d, *J* = 8.2 Hz, 1H, 6-H), 5.38 (s, 2H, 3-H_2), 4.78 (s, 1H, 11-H^A), 4.62 (s, 1H, 11-H^B), 3.18 (dd, *J* = 13.8 Hz, $^3J_{H\text{-}F}$ = 13.8 Hz, 1H, 13-H^A), 2.98 (dd, $^3J_{H\text{-}F}$ = 41.7 Hz, *J* = 13.8 Hz, 1H, 13-H^B), 1.54 (s, 3H, 10-H_3); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 170.1 (s, C-1), 146.5 (s, d, $^4J_{C\text{-}F}$ = 2.3 Hz, C-9), 139.7 (s, d, $^2J_{C\text{-}F}$ = 21.4 Hz, C-5), 136.6 (s, C-12), 127.1 (d, d, $^3J_{C\text{-}F}$ = 9.8 Hz, C-6), 126.6 (s, C-8), 125.4 (d, d, $^4J_{C\text{-}F}$ = 2.3 Hz, C-7), 120.0 (d, d, $^3J_{C\text{-}F}$ = 12.1 Hz, C-4), 118.4 (t, C-11), 117.4 (qt, $^1J_{C\text{-}F}$ = 287.3 Hz, $^2J_{C\text{-}F}$ = 34.2 Hz, C-17), 113.6 (tq, $^1J_{C\text{-}F}$ = 288.6 Hz, $^2J_{C\text{-}F}$ = 30.5 Hz, C-15), 109.7 (tsext, $^1J_{C\text{-}F}$ = 268.5 Hz, $^2J_{C\text{-}F}$ = 38.0 Hz, C-16), 97.4 (dt, *J* = 194.4 Hz, 26.0 Hz, C-14), 69.5 (t, C-3), 40.8 (t, d, $^2J_{C\text{-}F}$ = 20.2 Hz, C-13), 23.5 (q, d, $^4J_{C\text{-}F}$ = 2.9 Hz, C-10); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -81.0 (t, *J* = 9.2 Hz, 3F), -119.0 (m, 2F), -123.5 (m, 2F), -170.9 (s, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{16}H_{12}F_8O_2$) 388.0710 ($[M]^+$) Found: 388.0713

6-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)nicotinonitrile (3qb)

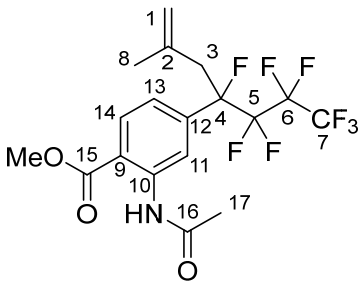


To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and 6-(nonafluorobutyl)nicotinonitrile (0.401 mmol, 0.129 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.394mmol, 0.0509 g) and methallyltributyltin (1.20 mmol, 0.414 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 9:1 column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.100 g, 70%).

IR: (neat) 2237 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.91 (s, 1H, 9-H), 8.07 (dd, *J* = 8.3 Hz, $^5J_{H\text{-}F}$ = 2.1 Hz, 1H, 11-H), 7.75 (dd, *J* = 8.3 Hz, $^4J_{H\text{-}F}$ = 1.8 Hz, 1H, 12-H), 4.73 (m, 1H, 1-H^A), 4.53 (s, 1H, 1-H^B), 3.32 (dd, $^3J_{H\text{-}F}$ = 41.7 Hz, *J* = 14.3 Hz, 1H, 3-H^A), 3.06 (dd, *J* = 14.3 Hz, $^3J_{H\text{-}F}$ = 10.3 Hz, 1H, 3-H^B), 1.56 (s,

3H, 8-H_3); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 157.7 (dd, $^2J_{C\text{-}F}$ = 27.5 Hz, J = 2.6 Hz, C-13), 151.3 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, C-9), 140.0 (d, $^4J_{C\text{-}F}$ = 2.3 Hz, C-11), 136.7 (C-2), 121.4 (d, $^3J_{C\text{-}F}$ = 11.6 Hz, C-12), 117.9 (C-1), 117.4 (qt, $^1J_{C\text{-}F}$ = 288.4 Hz, $^2J_{C\text{-}F}$ = 33.8 Hz, C-7), 115.9 (s, CN), 113.3 (tq, $^1J_{C\text{-}F}$ = 266.7 Hz, $^2J_{C\text{-}F}$ = 30.1 Hz, C-5), 110.1 (C-10), 109.6 (tsext, $^1J_{C\text{-}F}$ = 267.9 Hz, $^2J_{C\text{-}F}$ = 38.1 Hz, C-6), 97.7 (dt, $^1J_{C\text{-}F}$ = 193.6, $^2J_{C\text{-}F}$ = 24.9 Hz, C-4), 39.3 (d, $^2J_{C\text{-}F}$ = 19.1 Hz, C-3), 23.9 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, C-8); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.8 (t, J = 10.7 Hz, 3F), -118.4 (m, 2F), -123.9 (m, 2F), -176.0 (t, J = 25.9 Hz, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{14}H_{10}F_8N_2$) 358.0716 ([M]$^+$) Found: 358.0710

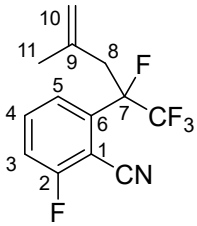
methyl 2-acetamido-4-(4,5,5,6,6,7,7,7-octafluoro-2-methylhept-1-en-4-yl)benzoate (3rb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and methyl 2-acetamido-4-(nonafluorobutyl)benzoate (0.394 mmol, 0.0978 g) in DME (2 mL) was added *N,N*-diisopropylethylamine (0.397 mmol, 0.0514 g) and methallyltributyltin (1.22 mmol, 0.424 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 90:10, column length 10 cm, diameter 26 mm silica gel) and GPC to give the product (yellow liquid, 0.156 g, 88%).

IR: (neat) 1700 (C=O), 1617 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 11.06 (s, 1H, NH), 8.89 (s, 1H, 11-H), 8.06 (d, J = 8.4 Hz, 1H, 14-H), 7.19 (d, J = 8.4 Hz, 1H, 13-H), 4.77 (s, 1H, 1-H^A), 4.69 (s, 1H, 1-H^B), 3.94 (s, 3H, MeO), 3.11 (dd, J = 13.8 Hz, $^3J_{H\text{-}F}$ = 13.8 Hz, 1H, 3-H^A), 2.99 (dd, $^3J_{H\text{-}F}$ = 41.4 Hz, J = 14.7 Hz, 1H, 3-H^B), 2.24 (s, 3H, 17-H_3), 1.57 (s, 3H, 8-H_3); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 169.1 (s, C-16), 168.1 (s, C-15), 141.2 (s, d, $^4J_{C\text{-}F}$ = 2.3 Hz, C-10), 139.8 (s, d, $^2J_{C\text{-}F}$ = 20.8 Hz, C-12), 136.9 (s, C-2), 130.5 (s, d, $^4J_{C\text{-}F}$ = 1.7 Hz, C-14), 119.8 (d, d, $^3J_{C\text{-}F}$ = 12.1 Hz, C-13), 118.3 (s, d, $^3J_{C\text{-}F}$ = 8.7 Hz, C-11), 118.2 (t, C-1), 117.5 (s, qt, $^1J_{C\text{-}F}$ = 288.4 Hz, $^2J_{C\text{-}F}$ = 33.8 Hz, C-7), 115.1 (s, C-9), 113.6 (tq, $^1J_{C\text{-}F}$ = 264.4 Hz, $^2J_{C\text{-}F}$ = 28.9 Hz, C-5), 109.7 (s, tsext, $^1J_{C\text{-}F}$ = 269.3 Hz, $^2J_{C\text{-}F}$ = 38.1 Hz, C-6), 97.2 (s, dt, $^1J_{C\text{-}F}$ = 193.6 Hz, $^2J_{C\text{-}F}$ = 26.0 Hz, C-4), 52.4 (q, MeO), 40.5 (t, d, $^2J_{C\text{-}F}$ = 20.2 Hz, C-3), 25.4 (q, d, J = 1.7 Hz, C-17), 23.6 (q, d, $^4J_{C\text{-}F}$ = 2.9 Hz, C-8); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (m, 3F), -119.0 (m, 2F), -123.6 (m, 2F), -172.0 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{18}H_{17}F_8NO_3$) 447.1081 ([M]$^+$) Found: 447.1077

2-fluoro-6-(1,1,1,2-tetrafluoro-4-methylpent-4-en-2-yl)benzonitrile (3sb)

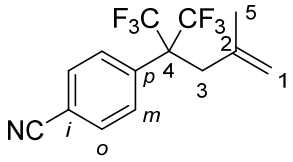


To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and 2-fluoro-6-(perfluoroethyl)benzonitrile (0.408 mmol, 0.0978 g) in DME (2 mL) was added *N,N*-diisopropylethylamine (0.397 mmol, 0.0514 g) and methallyltributyltin (1.34 mmol, 0.463 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 4 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil

was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) and GPC to give the product (yellow liquid, 0.0776 g, 69%).

IR: (neat) 2237 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.68 (td, J = 8.2 Hz, $^4J_{H\text{-}F}$ = 5.8 Hz, 1H, 4-H), 7.47 (d, J = 8.2 Hz, 1H, 5-H), 7.32 (t, J = 8.2 Hz, 1H, 3-H), 4.88 (s, 1H, 10-H^A), 4.85 (s, 1H, 10-H^B), 3.40 (br, 1H, 8-H^A), 3.06 (dd, J = 16.0 Hz, $J_{H\text{-}F}$ = 16.0 Hz, 1H, 8-H^B), 1.66 (s, 3H, 11-H_3); **^{13}C NMR**: (150 Hz, in $CDCl_3$); 164.7 (d, $^1J_{C\text{-}F}$ = 259.5 Hz, C-2), 137.8 (d, $^2J_{C\text{-}F}$ = 21.4 Hz, C-6), 136.5 (C-9), 134.3 (d, $^3J_{C\text{-}F}$ = 8.7 Hz, C-4), 123.8 (dd, $^3J_{C\text{-}F}$ = 13.6 Hz, $^4J_{C\text{-}F}$ = 2.0 Hz, C-5), 122.6 (dd, $^1J_{C\text{-}F}$ = 286.1 Hz, $^2J_{C\text{-}F}$ = 29.5 Hz, CF_3), 118.3 (d, $^4J_{C\text{-}F}$ = 31.8 Hz, C-10), 117.3 (d, $^2J_{C\text{-}F}$ = 20.2 Hz, C-3), 112.3 (CN), 100.5 (d, $^2J_{C\text{-}F}$ = 17.9 Hz, C-1), 95.9 (dq, $^1J_{C\text{-}F}$ = 194.1 Hz, $^2J_{C\text{-}F}$ = 31.4 Hz, C-7), 39.3 (d, $^2J_{C\text{-}F}$ = 17.3 Hz, C-8), 23.3 (d, $^4J_{C\text{-}F}$ = 2.3 Hz, C-11); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -79.4 (d, J = 6.1 Hz, 3F), -103.1 (m, 1F); **HRMS**: (EI, 70 eV) Calculated ($C_{13}H_{10}F_5N$) 275.0733 ($[M]^+$) Found: 275.0728

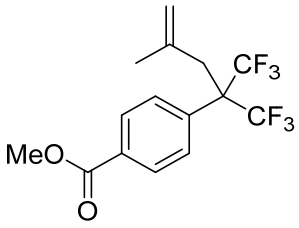
4-(1,1,1-trifluoro-4-methyl-2-(trifluoromethyl)pent-4-en-2-yl)benzonitrile (3tb)



To a solution of *fac*-Ir(ppy)$_3$ (0.0042 mmol, 2.8 mg) and 4-(heptafluoropropan-2-yl)benzonitrile (0.380 mmol, 0.108 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.394 mmol, 0.0510 g) and methallyltributyltin (1.20 mmol, 0.417 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.0804 g, 69%).

IR: (neat) 2234 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.76 (d, J = 8.8 Hz, 2H, *m*), 7.74 (d, J = 8.8 Hz, 2H, *o*), 4.90 (s, 1H, 1-H^A), 4.81 (s, 1H, 1-H^B), 3.14 (s, 2H, 3-H_2), 1.33 (s, 3H, 5-H_3); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 137.1 (s, C-2), 135.0 (s, *p*), 132.1 (d, *m*), 129.6 (d, *o*), 124.0 (q, $^1J_{C\text{-}F}$ = 287.3 Hz, CF_3), 118.5 (t, C-1), 117.7 (s, CN), 113.4 (s, *i*), 59.2 (s, sep, $^2J_{C\text{-}F}$ = 24.6 Hz, C-4), 37.3 (t, C-3), 23.6 (s, C-5); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -66.1 (s); **HRMS**: (EI, 70 eV) Calculated ($C_{14}H_{11}F_6N$) 307.0796 ($[M]^+$) Found: 307.0795

methyl 4-(1,1,1-trifluoro-4-methyl-2-(trifluoromethyl)pent-4-en-2-yl)benzoate (3ub)

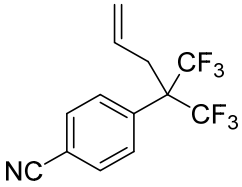


To a solution of *fac*-Ir(ppy)$_3$ (0.0042 mmol, 2.8 mg) and methyl 4-(perfluoropropan-2-yl)benzoate (0.401 mmol, 0.122 g) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.403 mmol, 0.0521 g) and methallyltributyltin (1.20 mmol, 0.417 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.118 g, 86%).

IR: (neat) 1730 (C=O) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 8.09 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.5 Hz,

2H), 4.87 (s, 1H), 4.82 (s, 1H), 3.94 (s, 3H), 3.15 (s, 2H), 1.31 (s, 3H); **^{13}C NMR**: (150 Hz, in $CDCl_3$); 166.2, 137.7, 134.7, 130.9, 129.5, 128.8 (m), 124.3 (q, $J_{C\text{-}F}$ = 288.0 Hz), 118.1, 59.2 (sep, $J_{C\text{-}F}$ = 24.3 Hz), 52.3, 37.5 (m), 23.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -66.1 (s); **HRMS**: (EI, 70 eV) Calculated ($C_{15}H_{14}F_6O_2$) 340.0898 ($[M]^+$) Found: 340.0892

4-(1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)benzonitrile (3ta)

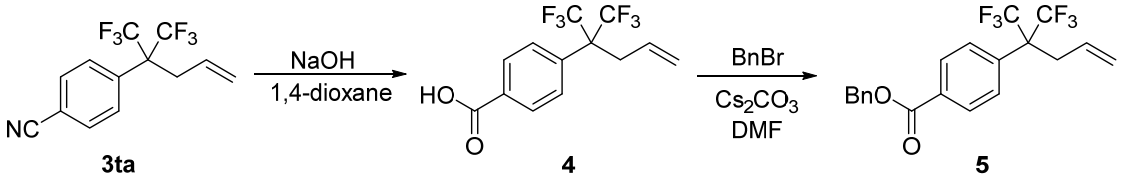


To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.7 mg) and 4-(perfluoropropan-2-yl)benzonitrile (0.402 mmol, 0.109 g) in DME (2 mL) were added allyltributyltin (1.20 mmol, 0.399 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.104 g, 88%).

IR: (neat) 2234 (CN) cm^{-1}; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 7.75 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H), 5.55 (m, 1H), 5.30 (dd, J = 17.0, 1.4 Hz, 1H), 5.18 (dd, J = 10.3, 1.3 Hz, 1H), 3.20 (d, J = 7.0 Hz, 2H); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 134.0, 132.3, 130.0 (m), 128.8, 124.0 (m), 121.0, 117.7, 113.6, 58.4 (sep, $J_{C\text{-}F}$ = 24.9 Hz), 32.9 (sep, $J_{C\text{-}F}$ = 2.0 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -66.1 (s)

HRMS: (EI, 70 eV) Calculated ($C_{13}H_9F_6N$) 293.0639 ($[M]^+$) Found: 293.0637

benzyl 4-(1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)benzoate (5)

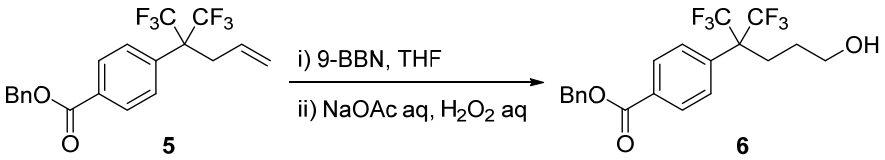


To a solution of 4-{1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl}benzonitrile **3ta** (1.11 mmol, 0.327 g) in 1,4-dioxane (3 mL) was added 2 M NaOH aq (3 mL). The mixture was stirred at 95 °C for 60 h. The reaction mixture was quenched with 1 M HCl aq (10 mL) and extracted with ethyl acetate (10 mL x 3). The volatiles were removed under reduced pressure, and then the crude 4-{1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl}benzoic acid **4** (white solid, 0.332 g, 1.06 mmol, 95%) was obtained and used without further purification. To a solution of 4-(1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)benzoic acid (0.298 mmol, 0.0932 g) **4** in DMF (0.5 mL) were added Cs_2CO_3 (0.371 mmol, 0.121 g) and benzyl bromide (0.347 mmol, 0.0594 g). The mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (30 mL) and brine (20 mL x 2). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give compound **5** (colorless oil, 0.266 mmol, 0.107 g, 89%).

^{1}H NMR: (400 MHz, in $CDCl_3$); 8.13 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.45 (dd, J = 8.2, 1.4 Hz, 2H), 7.42-7.33 (m, 3H), 5.57 (m, 1H), 5.38 (s, 2H), 5.28 (m, 1H), 5.14 (m, 1H), 3.20 (d, J = 7.0 Hz, 2H);

^{13}C NMR: (100 Hz, in $CDCl_3$) 165.5, 135.7, 133.7, 130.9, 129.8, 129.3, 129.2, 128.6, 128.3, 128.2, 124.2 (q, $J_{C\text{-}F}$ = 289.2 Hz), 120.5, 66.9, 58.3 (m), 33.0; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -66.1 (s); **HRMS**: (EI) Calculated ($C_{20}H_{16}F_6O_2$) 402.1054 ($[M]^+$) Found: 402.1053

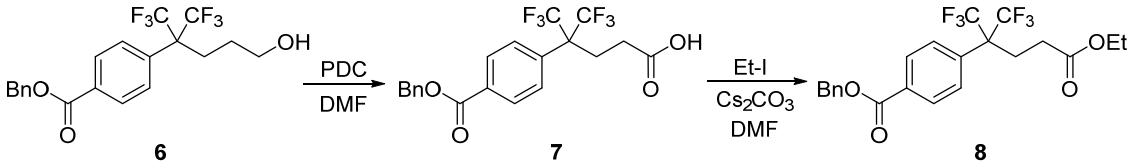
benzyl 4-(1,1,1-trifluoro-5-hydroxy-2-(trifluoromethyl)pentan-2-yl)benzoate (6)



To a solution of benzyl 4-(1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)benzoate **5** (0.248 mmol, 0.100 g) in THF (1 mL) was added 9-BBN (0.5 M in THF, 1 mL) at 0 °C. The mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with 3 M NaOAc aq (0.5 mL) and 30% H_2O_2 aq (0.5 mL) at 0 °C and stirred at room temperature for 1 h. The reaction mixture was diluted with ether (50 mL) and washed with brine (20 mL) and sat. $Na_2S_2O_3$ aq (20 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 6:4, column length 10 cm, diameter 26 mm silica gel) to give compound **6** (colorless oil, 0.204 mmol, 0.0856 g, 82%).

^{1}H NMR: (400 MHz, in $CDCl_3$) 8.12 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.41-7.32 (m, 3H), 5.37 (s, 2H), 3.69 (t, J = 5.9 Hz, 2H), 2.52 (t, J = 8.3 Hz, 2H), 1.56 (m, 2H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 165.6, 135.6, 133.8, 130.8, 129.8, 129.1, 128.6, 128.3, 128.2, 124.4 (d, $J_{C\text{-}F}$ = 289.2 Hz), 67.0, 61.8, 58.1 (m), 26.2, 25.0; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -66.3 (s); **HRMS**: (EI) Calculated ($C_{20}H_{18}F_6O_3$) 420.1160 ($[M]^+$) Found: 420.1156

benzyl 4-(5-ethoxy-1,1,1-trifluoro-5-oxo-2-(trifluoromethyl)pentan-2-yl)benzoate (8)

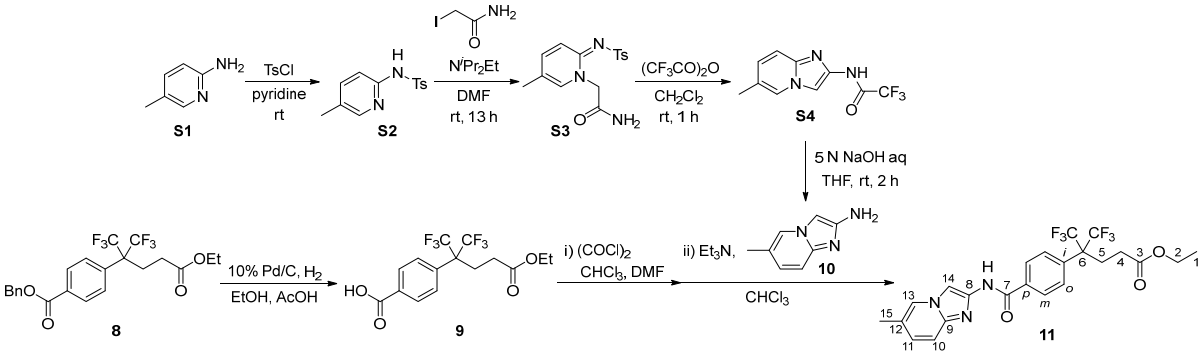


To a solution of benzyl 4-(1,1,1-trifluoro-5-hydroxy-2-(trifluoromethyl)pentan-2-yl)benzoate **6** (0.203 mmol, 0.0856 g) in DMF (1.2 mL) was added pyridinium dichromate (0.723 mmol, 0.272 g). The mixture was stirred at room temperature for 11 h. The reaction mixture was diluted with ether (10 mL) and quenched with water (10 mL) at 0 °C. The mixture was extracted with ethyl acetate (10 mL x 3). The organic layers were washed with brine (20 mL x 2), dried over Na_2SO_4, and concentrated under reduced pressure to give the crude product **7** (yelow oil, 0.145 mmol, 71%). To a solution of crude 4-(4-((benzyloxy)carbonyl)phenyl)-5,5,5-trifluoro-4-(trifluoromethyl)pentanoic acid **7** (0.149 mmol, 0.0651 g) in DMF (0.6 mL) were added Cs_2CO_3 (0.371 mmol, 0.0715 g) and iodoethane (0.653 mmol, 0.102 g). The mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (30 mL) and brine (10 mL x 5). The organic layer was dried over Na_2SO_4 and concentrated under reduced

pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 8:2, column length 10 cm, diameter 26 mm silica gel) to give compound **8** (colorless oil, 0.116 mmol, 0.0536 g, 77%).

^{1}H NMR: (400 MHz, in $CDCl_3$) 8.14 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 6.8 Hz, 2H), 7.42-7.33 (m, 3H), 5.38 (s, 2H), 4.16 (q, J = 7.2 Hz, 2H), 2.77 (t, J = 8.3 Hz, 2H), 2.32 (t, J = 8.3 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 171.7, 165.4, 135.7, 133.1, 131.1, 130.1, 128.9, 128.6, 128.4, 128.2, 124.2 (q, $J_{C\text{-}F}$ = 285.9 Hz), 67.0, 61.1, 57.9 (m), 28.4, 23.6, 14.1; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -66.3 (s); **HRMS**: (EI) Calculated ($C_{22}H_{20}F_6O_4$) 462.1266 ($[M]^+$) Found: 462.1260

_N_-(6-methylimidazo[1,2-_a_]pyridin-2-yl)-4-(1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)benzamide (11)



The synthesis of **S4** from **S1** was carried out according to the reported method (reference: Y. Terao *et. al*., *Bioorg. Med. Chem. Lett.* **2012**, *22*, 7326.). To a solution of 5-methylpyridin-2-amine **S1** (10.9 g, 100 mmol) in pyridine was added TsCl (22.8 g, 120 mmol) and the mixture was stirred at room temperature for 15 h. The solvent was evaporated and the residue was washed with methanol to give the crude product **S2** as a white solid (26.2 g, 100%) and used without further purification. To a suspension of the crude **S2** (15.7 g, 60.0 mmol) and *N,N*-diisopropylethylamine (8.55 g, 66.1 mmol) in DMF (200 mL) was added 2-iodoacetamide (12.4 g, 67.0 mmol). The reaction mixture was stirred at room temperature overnight. The mixture was then concentrated and the residue was washed with CH_2Cl_2 and ethyl acetate to give the crude **S3** as a white solid (15.5 g, 81%) and carried through to the next step without further purification. To a suspension of the crude **S3** (6.38 g, 20.0 mmol) in CH_2Cl_2 (55 mL) was added trifluoroacetic anhydride (5.5 mL, 40 mmol). The reaction mixture was stirred at room temperature for 2 h. The mixture was then concentrated. The residue was extracted with ethyl acetate and washed with aq $NaHCO_3$. Then organic layer was dried over $MgSO_4$ and concentrated to give the crude **S4** as a white solid (4.38 g, 84%). The crude **S4** was used without further purification. The synthesis of **10** from **S4** was carried out according to the reported method (reference: N. Masurier *et. al*., *J. Org. Chem.* **2012**, *77*, 3679.). To a suspension of the crude **S4** (0.486 g, 2.00 mmol) in 5 M NaOH aq (4 mL) was added THF (0.4 mL). The solution was stirred at 50 °C for 4 h. The solution was extracted with ethyl acetate (10 mL x 3). The organic layers were dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure to give the crude 6-methylimidazo[1,2-*a*]pyridin-2-amine **10** (0.294 g, 100%).

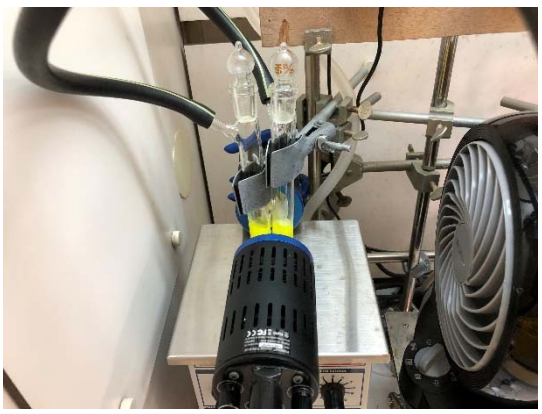
To a solution of benzyl 4-(5-ethoxy-1,1,1-trifluoro-5-oxo-2-(trifluoromethyl)pentan-2-yl)benzoate **8** (0.094 mmol, 0.0433 g) in EtOH (1 mL) and AcOH (0.15 mL) was added 10% Pd/C (0.0104 g). The reaction mixture was hydrogenated under H_2 gas (1 bar) for 4 h. The suspension was diluted by ethyl acetate and filtered. The filtration was washed with water (10 mL x 5), dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product **9** (0.0940 mmol, 99%) The crude product **9** was used without further purification. To a solution of **9** (0.0500 mmol, 0.0186 g) in 0.2% (v/v) solution of DMF in chloroform (0.33 mL) was added oxalyl chloride (0.0953 mmol, 0.0121 g). The reaction mixture was stirred at room temperature for 4 h and then concentrated under reduced pressure. The resulting residue was dissolved in chloroform (0.1 mL). To the solution were added triethylamine (0.074 mmol, 0.0075 g) and a solution of amine **10** (0.067 mmol, 0.0098 g) in chloroform (0.3 mL). The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with diethyl ether and quenched with water. The mixture was extracted with ethyl acetate (10 mL x 3) and washed with sat. $NaHCO_3$ aq (10 mL x 2). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, chloroform/EtOH = 95:5, Rf = 0.63) to give the target product **11** (white solid, 0.0199 mmol, 0.0100 g, 40%).

mp: 164-165 °C; **^{1}H NMR**: (600 MHz, in $CDCl_3$) 11.31 (s, 1H, NH), 8.22 (s, 1H, 14-H), 8.06 (d, *J* = 8.2 Hz, 2H, *m*), 7.90 (s, 1H, 13-H), 7.58 (d, *J* = 8.2 Hz, 2H, *o*), 6.85 (d, *J* = 9.1 Hz, 1H, 11-H), 6.70 (d, *J* = 9.1 Hz, 1H, 10-H), 4.16 (q, *J* = 7.1 Hz, 2H, 2-H_2), 2.74 (t, *J* = 8.5 Hz, 2H, 5-H_2), 2.31 (t, *J* = 8.5 Hz, 2H, 4-H_2), 2.30 (s, 3H, 15-H_3), 1.26 (t, *J* = 7.1 Hz, 3H, 1-H_3); **^{13}C NMR**: (150 Hz, in $CDCl_3$) 171.7 (C, C-3), 164.4 (C, C-7), 141.4 (C, C-8), 140.6 (C, C-9), 135.2 (C, *p*), 131.8 (C, *i*), 129.1 (CH, *o*), 128.3 (CH, *m*), 127.9 (CH, C-11), 124.3 (C, q, $J_{C\text{-}F}$ = 288.1 Hz, CF_3), 123.6 (CH, C-13), 122.1 (C, C-12), 114.9 (CH, C-10), 101.6 (CH, C-14), 61.1 (CH_2, C-2), 57.8 (C, m, C-6), 28.5 (CH_2, C-4), 23.6 (CH_2, C-5), 18.0 (CH_3, C-15), 14.1 (CH_3, C-1); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -66.3 (s); **HRMS**: (DART+) Calculated ($C_{23}H_{22}F_6N_3O_3$) 502.15599 ($[M+H]^+$) Found: 502.15824

General Procedures

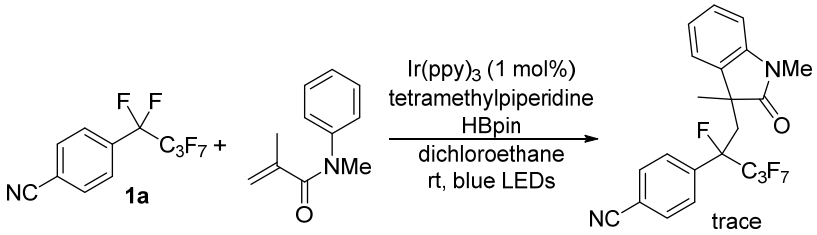
Defluoroalkylation of 1a with allyl metal reagents using $Ir(ppy)_3$ and ^{i}PrEtN (Table 1, Entries 1-4)

To a solution of *fac*-$Ir(ppy)_3$ (0.004 mmol) and 4-(pentafluoroethyl)benzonitrile (0.4 mmol) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.4 mmol) and methallyltributyltin (1.2 mmol). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while was cooled by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The yields of **3aa** was determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.



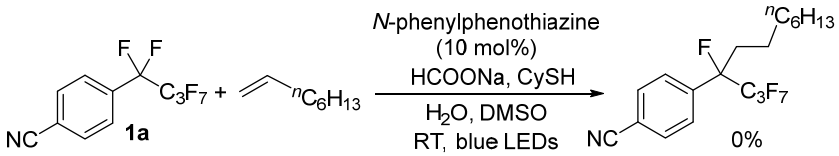
Comparison of Allylstannane with Alkenes in Defluoroalkylation of Perfluoroalkylarene 1a (Schemes S1 and S2)

(with electron-deficient alkene) The defluoroalkylation of perfluoroalkylarene **1a** with an electron-deficient alkene was examined according to the reported conditions for that of trifluoromethylarenes (ref. Chen, K.; Berg, N.; Gschwind, R.; König, B. *J. Am. Chem. Soc.* **2017**, *139*, 18444.). To a solution of $Ir(ppy)_3$ (0.0020 mmol, 0.0013 g) in 1,2-dichloroethane (2 mL) were added 4-(nonafluorobutyl)benzonitrile **1a** (0.202 mmol, 0.649 g), *N*-methyl-*N*-phenylmethacrylamide (0.409 mmol, 0.717 g), tetramethylpiperidine (0.400 mmol, 0.0565 g) and HBpin (0.600 mmol, 0.0767 g). After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated by blue LED at 35 °C for 24 h. Then the reaction mixture was concentrated under reduced pressure. The crude residues were analyzed by ^{1}H NMR spectroscopy with 1,1,1,2-tetrachloroethane as an internal standard and GC-MS.



Scheme S1

(with electron-rich alkene) The defluoroalkylation of perfluoroalkylarene **1a** with an electron-rich alkene was examined according to the reported conditions for that of trifluoromethylarenes (ref. Wang, H.; Jui, N. T. *J. Am. Chem. Soc.* **2018**, *140*, 163.). To a solution of *N*-phenylphenothiazine (0.040 mmol, 0.0011 g) and sodium formate (1.23 mmol, 0.0839 g) in 5% (v/v) solution of H_2O in DMSO (4 mL) were added 4-(nonafluorobutyl)benzonitrile **1a** (0.400 mmol, 0.128 g), 1-octene (1.26 mmol, 0.141 g) and cyclohexanethiol (0.040 mmol, 0.0046 g). After degassing by freeze-pump-thaw process for three cycles, the reaction mixture was irradiated by blue LED at 35 °C for 24 h. Then the reactions were concentrated under reduced pressure. The crude residues were analyzed by ^{1}H NMR spectroscopy with 1,1,1,2-tetrachloroethane as an internal standard and GC-MS.



Scheme S2

Stern–Volmer Luminescence Quenching Studies of Photo-catalyst Ir(ppy)$_3$ (Figure S1)

Fluorescence quenching studies were performed using a JACSO FP-6600 spectro fluorometer. In each experiment, Ir(ppy)$_3$ and various concentrations of **1a**, ^{i}Pr$_2$EtN, or **2b** were combined in 1,2-dimethoxyethane (DME) in screw-top 1.0 cm quartz cuvettes. The emission quenching of the Ir(ppy)$_3$ was achieved using a concentration of 5.0 x 10^{-6} M under excitation at 380 nm. The emission intensity was observed at 514 nm. Plots were constructed according to the Stern–Volmer equation $I0/I = 1 + k_q\tau_0[Q]$

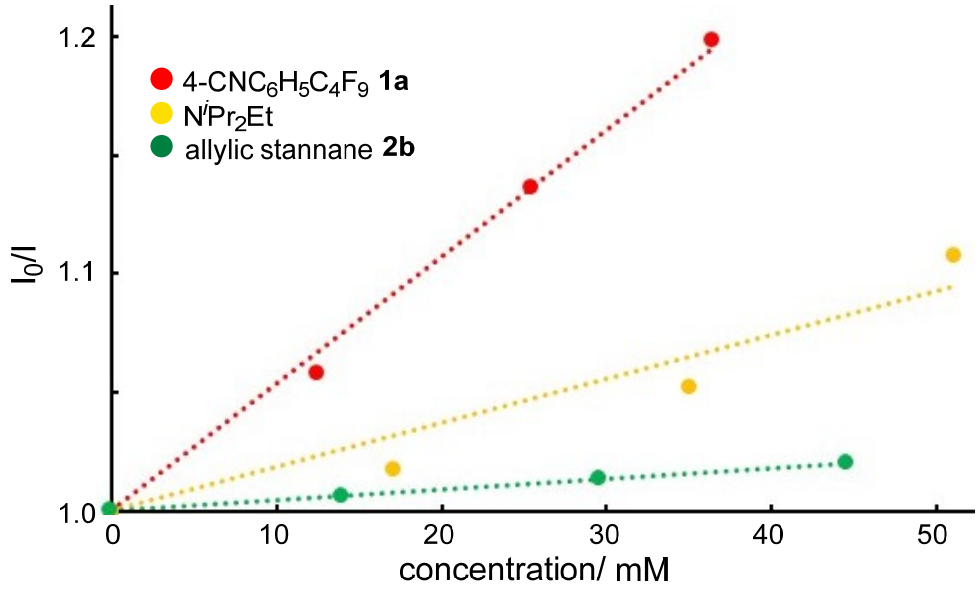


Figure S1

Light ON/OFF Experiments (Figure S2)

The reaction of **1a** with **2b** was performed with or without visible light irradiation. The time profile of the reaction is shown in Figure S2. The yield of **3ab** was determined by GC using *n*-dodecane as an internal standard. These results indicated that continuous irradiation with blue LED was essential for promoting the reaction, and the contribution of the radical chain mechanism to this reaction was small.

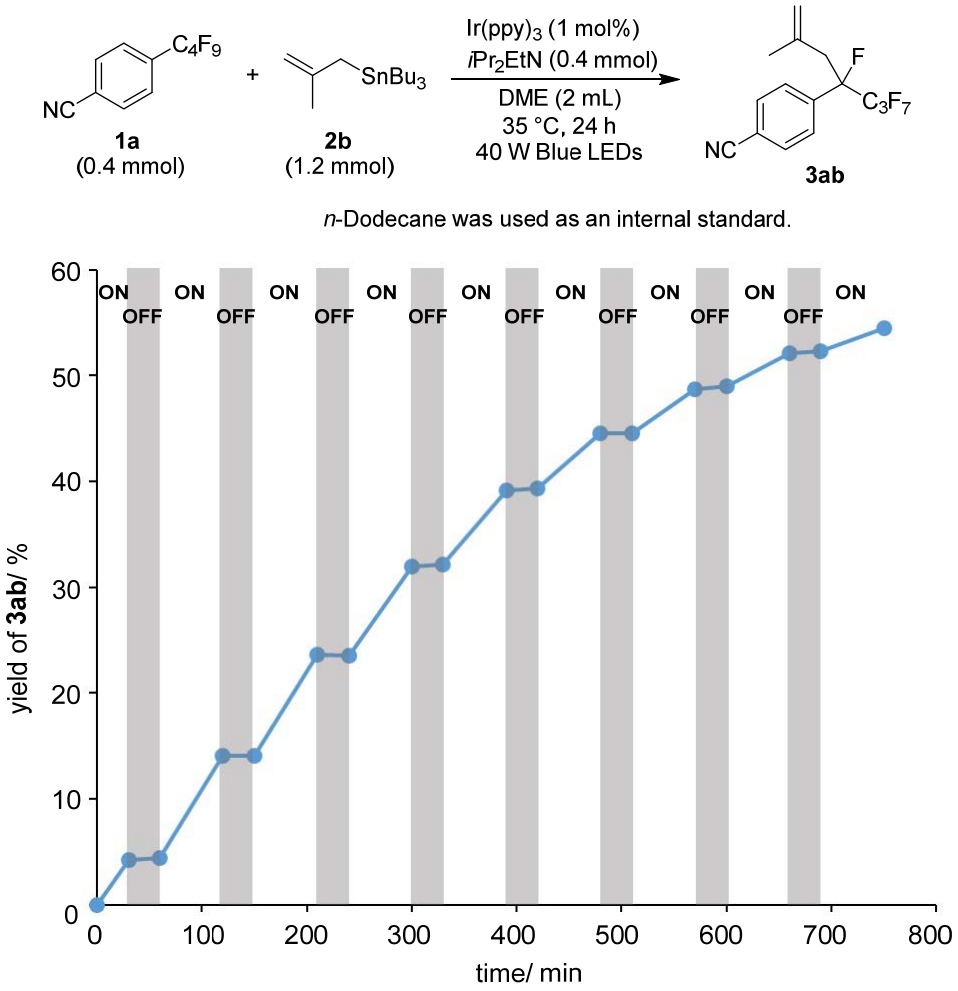


Figure S2

Cyclic Voltammetry Measurement (Figure S3)

Cyclic voltammetric measurements were performed with an ALS-600C electrochemical analyzer (BAS Inc.) using a glassy carbon working electrode, a Pt counter electrode, and an $Ag/AgNO_3$ reference electrode at room temperature in MeCN containing 0.1 M Et_4NBF_4 as the supporting electrolyte. The cyclic voltammogram was measured starting from 0 V towards negative potential at scan rate of 20 mV/s at room temperature. Potentials vs. SCE were reported according to $E_{SCE} = E\ (Fc/Fc^+) + 0.38$ V (reference: Pavlishchuk, V. V.; Addison, A. W. *Inorg. Chim. Acta.* **2000**, *298,* 97−102.).

1a

E_{red} = –1.79 V vs. SCE

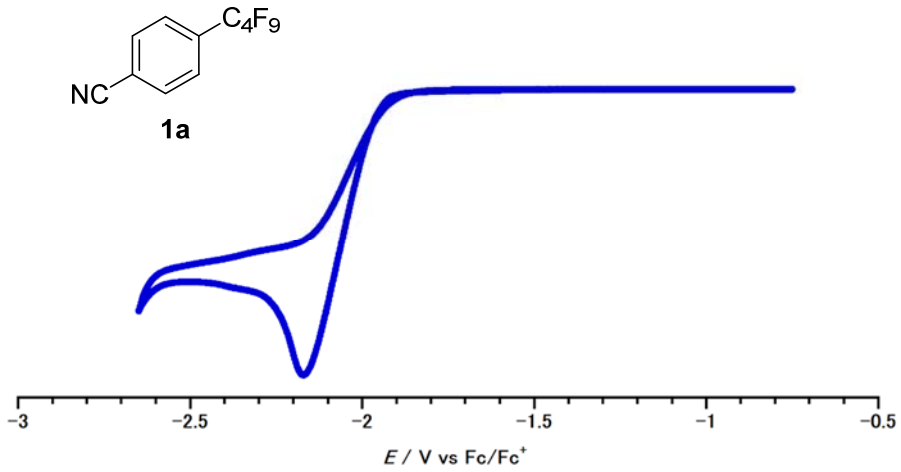
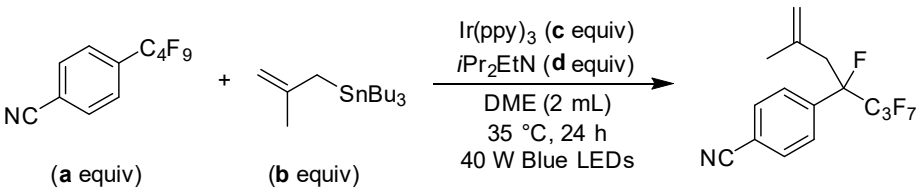


Figure S3. Cyclic voltammograms of **1a** (V vs. Fc/Fc^+, in 0.1M Et_4NBF_4/MeCN, scan rate = 20 mV/s, room temperature).

Further Optimization of Reaction Conditions (Tables S1, S2, and S3)

Screening of amount of reagents, $Ir(ppy)_3$, and iPr_2NEt were shown below.

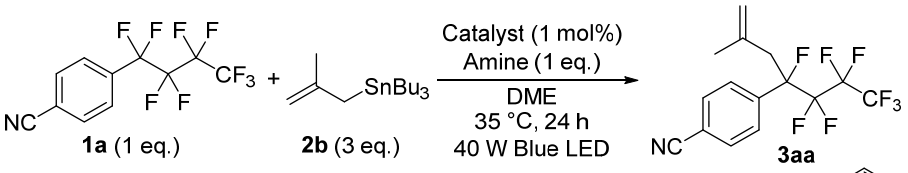
Table S1



Entry	**a** (equiv)	**b** (equiv)	**c** (equiv)	**d** (equiv)	Yield (%)
1	1	3	0.01	1	84
2	1	3	0.005	1	58
3	3	1	0.01	1	43
4	1	3	0.01	2	63
5	1	3	0.01	0.8	76
6	1	3	0.01	0.5	70
7	1	3	0.01	0	56

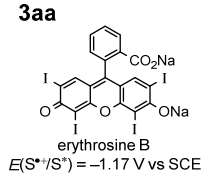
Different types of photoredox catalysts and amines were examined and the results were shown below.

Table S2

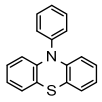


Entry	Catalyst	Amine	Yield (%)
1[a]	erythrosine B	none	0
2[a]	PTH	none	21
3	$Ir(ppy)_3$	none	56
4	$Ir(ppy)_3$	NEt_3	78
5	$Ir(ppy)_3$	pentamethylpiperidine	63
6	$Ir(ppy)_3$	N^iPr_2Et	84

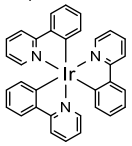
[a]Catalyst (10 mol%)



erythrosine B
$E(S^{\bullet+}/S^*) = -1.17$ V vs SCE



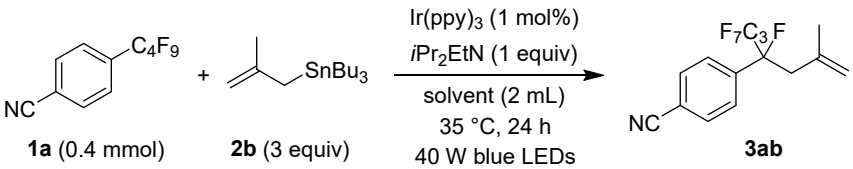
PTH
(phenylphenothiazine)
$E(S^{\bullet+}/S^*) = -2.10$ V vs SCE



$Ir(ppy)_3$
$E(Ir^{4+}/Ir^{3+*}) = -1.73$ V vs SCE

Effects of solvents were shown below.

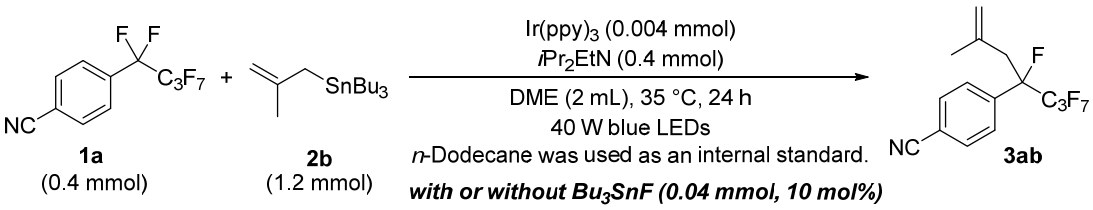
Table S3



entry	solvent	yield of **3ab**
1	DME	84
2	DMSO	39
3	DMF	60
4	1,4-dioxane	57
5	$CHCl_3$	6
6	MeCN	46
7	hexane	31
8	toluene	6
9	Et_2O	24
10	$ClCH_2CH_2Cl$	48
11	acetone	56
12	THF	79

Reaction Profile with or without Bu_3SnF: Effect of Bu_3SnF (Figure S4)

To a solution of *fac*-Ir(ppy)$_3$ (0.004 mmol) and 4-(pentafluoroethyl)benzonitrile (0.4 mmol) in DME (2 mL) were added *N,N*-diisopropylethylamine (0.4 mmol) and methallyltributyltin (1.2 mmol). In the case of the conditions with Bu_3SnF, Bu_3SnF (0.04 mmol, 10 mol%) was added. *n*-Dodecane was added as an internal standard for the determination of yield of **3aa** by GC. After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation. The yields of **3aa** was determined by GC. The reaction rate in the case of adding Bu_3SnF was faster than that in the case of not adding.



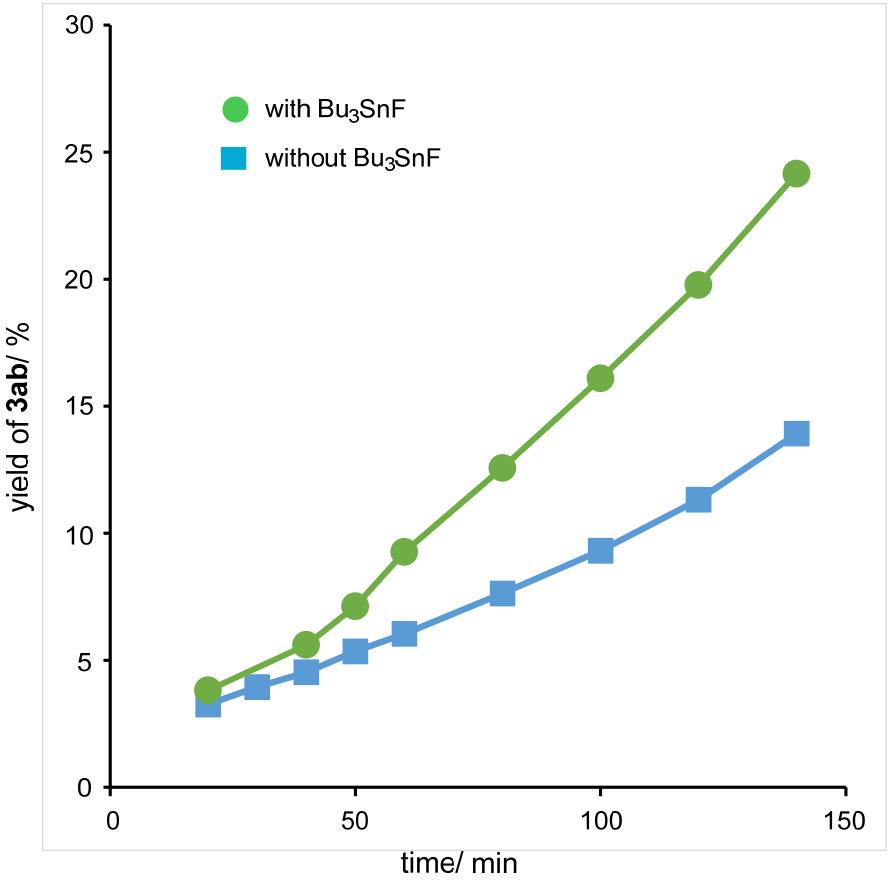


Figure S4

1-5. References

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(19) An electron transferred from an excited Ir catalyst to **1a** is localized on the arene ring. Therefore, the electron-withdrawing effect of C_4F_9 group decreases the reduction potential of **1a** to accelerate the single electron transfer. The electron-withdrawing effect of a monoallylated-perfluoroalkyl group is lower than that of a perfluoroalkyl group, so defluoroallylated product **3aa** have a higher reduction potential than **1a**.
(20) The extensive screening of photoredox catalysts, solvents, reaction time, temperature, and equivalents of components was conducted in Supporting Information (Tables S1, S2, and S3).
(21) Scheme S3 in Supporting Information shows perfluoroalkylarenes **1** that were not available in this reaction systems.
(22) Nguyen, J. D.; D'Amato, E. M.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nat. Chem.* **2012**, *4*, 854–859.
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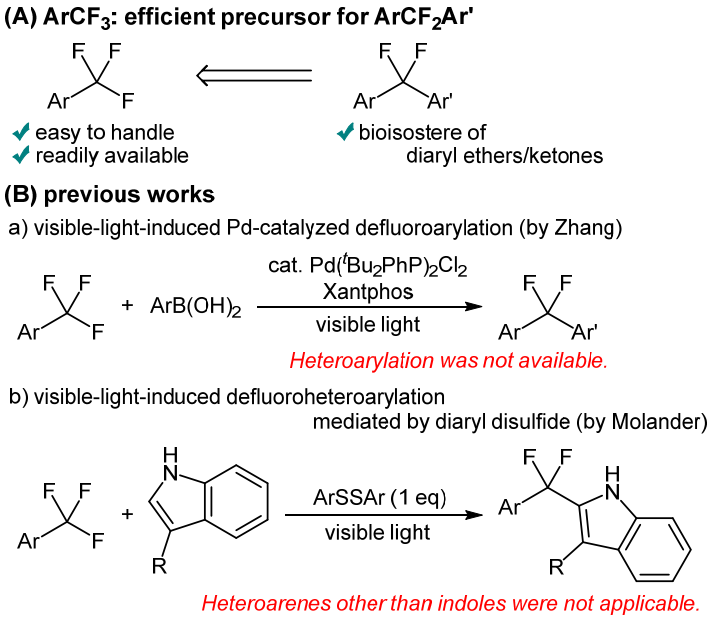
(25) An excess amount of *i*Pr_2EtN would be needed to effective regeneration of Ir(III) catalyst to disturb a back electron from **A** to Ir(IV) species.
(26) The results of light ON/OFF experiments are shown in Figure S2.
(27) The complete description of energy profiles for the defluoroallylation without or with Me_3SnF are shown in Figures S6 and S7.
(28) We observed that the addition of Bu_3SnF accelerated the defluoroallylation of **1a** with **2b** (Figure S4).
(29) Uchikawa, O.; Sakai, N.; Terao, Y.; Suzuki, H. Fused Heterocyclic Compound. U.S. Patent WO 2008016131(A1), May 13, 2009.
(30) Details of experimental procedures for each steps were described in the Supporting Information.

Chapter 2: Photo-catalyzed C–F Bond Heteroarylation of Trifluoromethylarenes with Heteroarenes: Two Roles of Bu_3SnI as Fluoride Ion Scavenger and Activator for Photo-catalyst

2-1. Introduction

Diaryldifluoromethane structures are important in organic chemistry in view of their function as bioisosteres of diaryl ether and diaryl ketone structures.[1,2] A CF_2 unit leads to advantageous changes in the physical and biological properties of CF_2-containing molecules.[3] Trifluoromethylarenes ($ArCF_3$) would be efficient precursors for diaryldifluoromethanes ($ArCF_2Ar'$) because of their ready availability via well-established synthetic methods such as cross-coupling reactions and photoredox catalytic reactions (Figure 1A).[4] Recently, various C–F bond transformations of $ArCF_3$ have been reported despite the difficulty of activating the inactive C–F bond;[5,6] however, arylation reactions remain a challenge. Although Zang and coworkers developed a visible-light-induced Pd-catalyzed defluoroarylation of $ArCF_3$ with $Ar'B(OH)$, heteroarylation was not reported (Figure 1B-a).[7] For heteroarylation, Molander reported visible-light-induced defluoroheteroarylation of $ArCF_3$ with indoles using a stoichiometric amount of diaryl disulfide (Figure 1B-b).[8] However, heteroaromatic compounds other than indoles were not applicable. Therefore, a novel reaction system is critical for diversifying and varying C–F bond heteroarylation. We herein report the photocatalyzed C–F bond heteroarylation of $ArCF_3$ with pyrrole, furan, and thiophene derivatives using an Ir photocatalyst and Bu_3SnI as an additive (Figure 1C). Mechanistic studies revealed two roles of Bu_3SnI: as a fluoride ion scavenger to suppress a retro-reaction including undesired C–F bond reformation, and as a single electron source to generate Ir(II) species that reduce $ArCF_3$.



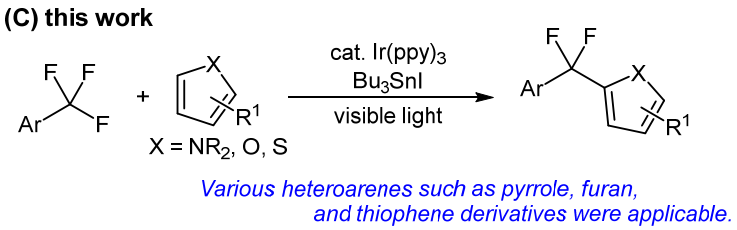
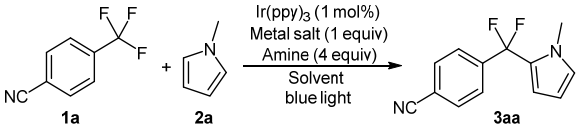


Figure 1. Synthesis of diaryldifluoromethanes by C–F bond arylation of trifluoromethylarenes

2-2. Results and Discussion

Initially, we optimized the reaction of 4-(trifluoromethyl)benzonitrile (**1a**) with *N*-methylpyrrole (**2a**) in the presence of $Ir(ppy)_3$ (1 mol%) as a photocatalyst and 1,2,2,6,6-pentamethylpiperidine (PMP) as a base in THF under blue LED irradiation for 24 h (Table 1). In the absence of a metal salt additive, the desired product **3aa** was obtained in only 28% yield (Entry 1). We previously reported the defluorinative allylation of perfluoroalkylarenes with allylic stannanes, in which tributyltin halides worked as a fluoride ion scavenger to accelerate the defluorination step.[9] Thus, several stannanes were investigated as additives. The addition of Bu_3SnI promoted C–F bond heteroarylation to give **3aa** in 62% yield (Entry 2), in which the C–C bond formation exclusively occurred at the 2-position of *N*-methylpyrrole. Bu_3SnBr and Bu_3SnCl were not effective (Entries 3 and 4). Bu_3SnOTf, being a higher Lewis acid, resulted in a lower yield (Entry 5). Bu_3SnNEt_2 did not accelerate the heteroarylation at all (Entry 6). Bulkier tin iodides such as Cy_3SnI and Ph_3SnI led to lower yields than Bu_3SnI (Entries 7 and 8). Other typical Lewis acids such as Me_3SiI, Me_3SiOTf, and $BF_3{\cdot}OEt_2$ led to lower yields compared with that achieved with Bu_3SnI (Entries 9, 10, and 11). After surveying amines, we found that PMP was the most suitable (Entries 4, 12–15). The investigation of the solvent effect revealed that moderate polar solvents such as THF, acetone, and 1,2-dimethoxyethane (DME) were suitable for the present reaction (Entries 4, 17, and 18) and that the use of highly polar solvents such as CH_3CN, DMF, DMSO, and DMA gave poor results (Entries 19–22).

Table 1. Optimization of reaction conditions for heteroarylation of a C–F bond of trifluoromethylarene **1a** with *N*-methylpyrrole **2a**[a]



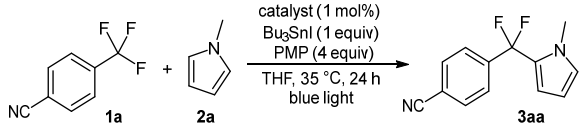
Entry	Metal salt	Amine	Solvent	Yield
1	none	PMP	THF	28%
2	Bu_3SnI	PMP	THF	62%
3	Bu_3SnBr	PMP	THF	27%
4	Bu_3SnCl	PMP	THF	30%
5	Bu_3SnOTf	PMP	THF	33%
6	Bu_3SnNEt_2	PMP	THF	0%
7	Cy_3SnI	PMP	THF	8%

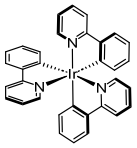
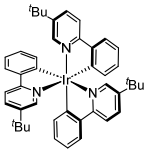
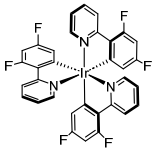
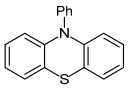
8	Ph_3SnI	PMP	THF	19%
9	Me_3SiI	PMP	THF	12%
10	Me_3SiOTf	PMP	THF	40%
11	$BF_3{\cdot}OEt_2$	PMP	THF	36%
12	Bu_3SnI	N*i*Pr_2Et	THF	29%
13	Bu_3SnI	NEt_3	THF	13%
14	Bu_3SnI	NBu_3	THF	30%
15	Bu_3SnI	DABCO	THF	12%
16	Bu_3SnI	none	THF	6%
17	Bu_3SnI	PMP	acetone	43%
18	Bu_3SnI	PMP	DME	51%
19	Bu_3SnI	PMP	CH_3CN	24%
20	Bu_3SnI	PMP	DMF	13%
21	Bu_3SnI	PMP	DMSO	0%
22	Bu_3SnI	PMP	DMA	16%

[a] **1a** (0.4 mmol), **2a** (4 mmol), $Ir(ppy)_3$ (0.004 mmol), metal salt (0.4 mmol), amine (1.6 mmol), solvent (4 mL), blue LED, 24 h, cooling by fan. NMR yields of **3aa** determined by ^1H NMR using an internal standard were shown.

In the survey of photocatalysts (Table 2), the C–F bond transformation with $Ir(ppy)_3$[10] gave the best result (Entry 1). Ir(*t*Bu-ppy)$_3$[10] exhibited the same catalytic ability as $Ir(ppy)_3$ (Entry 2). The use of Ir(dF-ppy)$_3$, which exhibits slightly lower reduction ability[11] than $Ir(ppy)_3$ and Ir(*t*Bu-ppy)$_3$, resulted in a low yield (Entry 3). *N*-Phenylphenothiazine did not work well, likely because of a short lifetime of its excited species (Entry 4).[12]

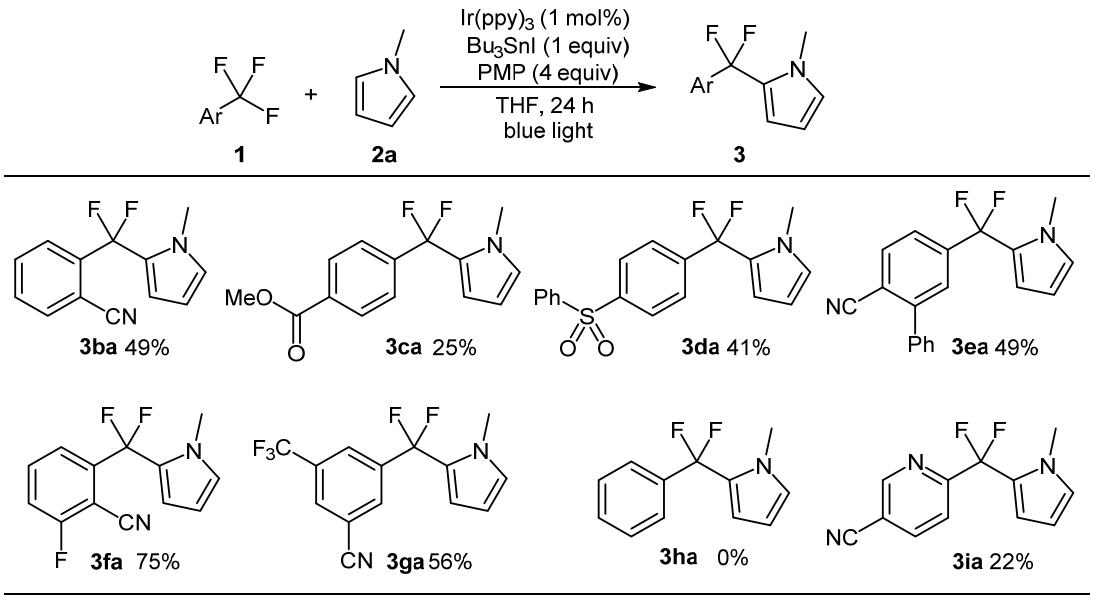
Table 2. Survey of photocatalysts in C–F bond transformation of trifluoromethylarene **1a** with *N*-methylpyrrole **2a**[a]



Entry	Catalyst		Yield
1		$Ir(ppy)_3$ $E(Ir^{IV}/Ir^{III*}) = -1.81$ V vs SCE $E(Ir^{III}/Ir^{II}) = -2.19$ V vs SCE	62%
2		$Ir(t\text{Bu-ppy})_3$ $E(Ir^{IV}/Ir^{III*}) = -1.81$ V vs SCE $E(Ir^{III}/Ir^{II}) = -2.30$ V vs SCE	60%
3		$Ir(dF\text{-ppy})_3$ $E(Ir^{IV}/Ir^{III*}) = -1.48$ V vs SCE $E(Ir^{III}/Ir^{II}) = -2.11$ V vs SCE	27%
4		*N*-Phenylphenothiazine (PTH) $E(PTH^{+}/PTH^{*}) = -2.49$	15%

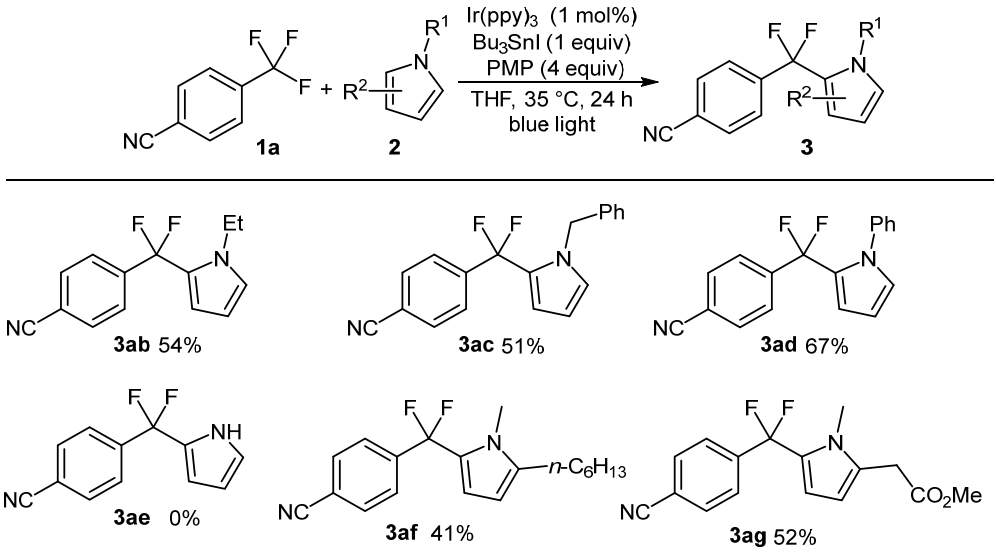
[a] **1a** (0.4 mmol), **2a** (4 mmol), catalyst (0.004 mmol), Bu_3SnI (0.4 mmol), PMP (1.6 mmol), THF (4 mL), blue LED, 24 h, cooling by fan. NMR yields of **3aa** determined by ^1H NMR using an internal standard were shown.

With the optimal reaction conditions in hand, we investigated the scope of trifluoromethylarenes (Scheme 1). Electron-deficient substrates were appropriate for the present reaction system. The electron-withdrawing effect of cyano, methoxycarbonyl, and $PhSO_2$ groups effectively promoted the reaction (**3ba**, **3ca**, **3da**, and **3ea**). A C(sp^2)–F bond was tolerant to the present reaction conditions (**3fa**). A substrate with two CF_3 groups underwent single C–F bond transformation to give product **3ga** because the reduction potential of product **3ga** is lower than that of starting material **1g**. The reaction using trifluorotoluene gave no product (**3ha**), suggesting that an electron-withdrawing group on a benzene ring was critical to the reaction progress. A trifluoromethyl-substituted pyridine gave product **3ia** in 19% yield.



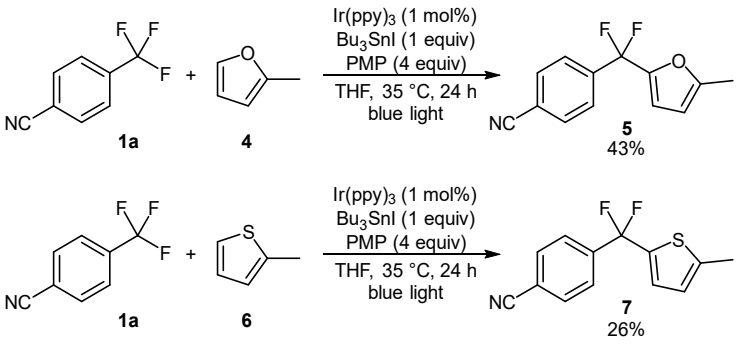
Scheme 1. Scope and limitation of trifluoromethylarenes: **1** (0.4 mmol), **2a** (4 mmol), $Ir(ppy)_3$ (0.004 mmol), Bu_3SnI (0.4 mmol), PMP (1.6 mmol), THF (4 mL), blue LED, 24 h, cooling by fan. NMR yields of **3** determined by ^1H NMR using an internal standard were shown.

Various pyrroles were available in this reaction system (Scheme 2). *N*-Alkylpyrroles other than *N*-methylpyrrole were also applicable, and *N*-ethyl- and *N*-benzylpyrroles afforded the desired products **3ab** and **3ac** in 54% and 51% yield, respectively. The reaction using *N*-phenylpyrrole proceeded to give **3ad** in 67% yield. An unprotected pyrrole was not available (**3ae**). An alkyl substituent at the 2-position did not disturb the reaction to give the corresponding product **3af**. An ester moiety attached to a pyrrole structure was tolerated (**3ag**).



Scheme 2. Scope and limitation of pyrroles: **1a** (0.4 mmol), **2** (4 mmol), $Ir(ppy)_3$ (0.004 mmol), Bu_3SnI (0.4 mmol), PMP (1.6 mmol), THF (4 mL), blue LED, 24 h, cooling by fan. NMR yields of **3** determined by ^1H NMR using an internal standard were shown.

The present reaction conditions also support C–F bond transformation using other classes of heteroarenes (Scheme 3). The reactions proceeded with 1-methylfuran (**4**) and 1-methylthiophene (**6**), which provided aryl(furyl)- and aryl(thiophenyl)difluoromethane compounds **5** and **7**, respectively. These heteroarenes exhibited lower reactivity than pyrroles because of the electron-deficient character of their aromatic rings.



Scheme 3. Heteroarylation with furan and thiophene derivatives. NMR yields of **5** and **7** determined by ^{1}H NMR using an internal standard were shown.

A light on–off interval experiment of the reaction of $ArCF_3$ **1a** with **2a** in the presence of $Ir(ppy)_3$ was conducted, and no product formation was observed during the dark periods (Figure 2). Thus, the contribution of an effective radical chain mechanism was ruled out.

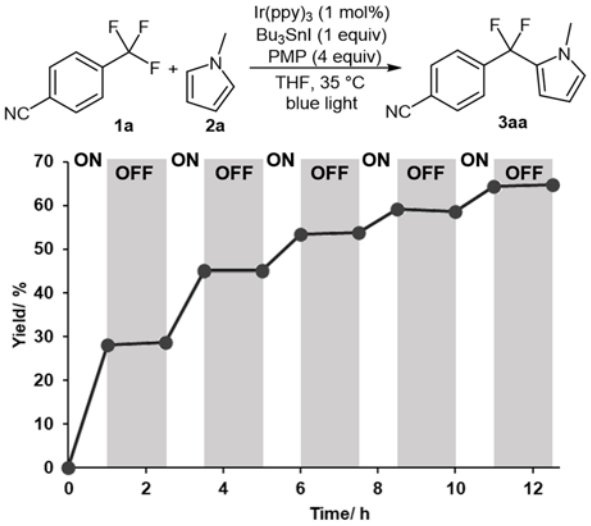


Figure 2 Visible-light-irradiation on–off interval experiment.

To reveal the role of excited $Ir(ppy)_3$, Stern–Volmer quenching experiments were performed (Figure 3). Compound **2a** and PMP hardly quenched the luminescence of $Ir(ppy)_3$. To our surprise, effective quenching by Bu_3SnI was observed, and the slope for Bu_3SnI was much larger than that for **1a**. This result differs from that in our previous report on the defluoronative allylation of perfluoroalkylarenes (ArC_nF_{2n+1}, $n > 2$), where $Ir(ppy)_3$* was found to directly reduce perfluoroalkylarenes. The quenching study suggests that single electron transfer (SET) from Bu_3SnI to the excited $Ir(ppy)_3$* occurs to generate an Ir(II) complex, which is a critical reductant to reduce $ArCF_3$ **1**. König reported that $ArCF_3$ **1a** was effectively reduced not by $Ir(ppy)_3$*

but by the Ir(II) species generated via the photoinduced reduction of $Ir(ppy)_3$ with a dialkylamine.[5h] Thus, in our case, Bu_3SnI would act as a single electron source for the reduction of $Ir(ppy)_3$* to generate Ir(II) species.

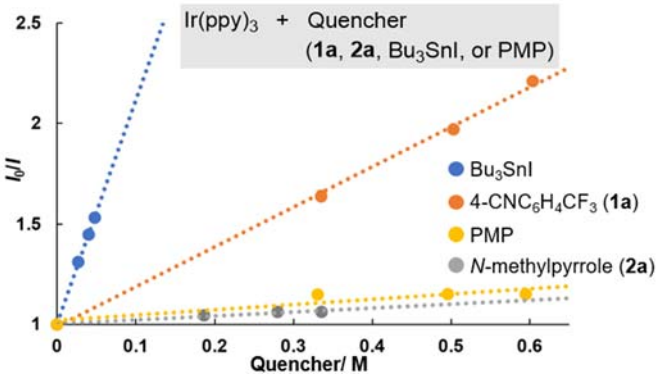
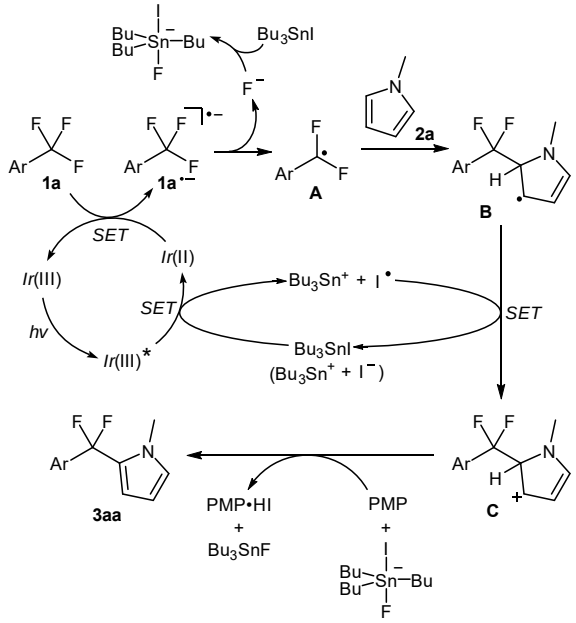


Figure 3 Stern–Volmer luminescence-quenching measurements of $Ir(ppy)_3$: excitation 380 nm, emission 514 nm.

A plausible reaction mechanism between **1a** and **2a** is illustrated in Scheme 4. $Ir(ppy)_3$ (*Ir*(III)) is excited by blue light. Then, *Ir*(III)* (E(*Ir*(III)*/*Ir*(II)) = 0.35 V vs SCE) is reduced by Bu_3SnI (E($Bu_3SnI^{\bullet+}$/Bu_3SnI) = 0.89 V vs SCE)[13] to give *Ir*(II), I$^\bullet$, and Bu_3Sn^+. This SET is an uphill process in terms of redox potential; however, Stern–Volmer quenching experiments support the progress of this SET. Iodide ion (I^-) likely functions as an actual reductant (E($I^\bullet$/I^-) = 0.27 V vs SCE)[14] because I^- is often used as a redox mediator in dye sensitized solar cell technology.[15] $ArCF_3$ **1a** (E(**1a**/**1a**$^{\bullet-}$) = –1.94 V vs SCE)[5h] undergoes single electron reduction by *Ir*(II) (E(*Ir*(III)/*Ir*(II)) = –2.19 V vs SCE)[10], generating radical anion **1a**$^{\bullet-}$ and *Ir*(III). Mesolysis of the C–F bond in **1a**$^{\bullet-}$ gives benzylic radical **A** and F^-. Bu_3SnI then captures F^- to suppress the retro reaction involving C–F bond reformation, giving $Bu_3Sn(F)I^-$. The addition of **A** to **2a** affords radical intermediate **B**, which is oxidized by I$^\bullet$ to give carbocation **C** and Bu_3SnI. Rearomatization of **C** via deprotonation by PMP leads to final product **3aa** and PMP•HI.



Scheme 4. Plausible reaction mechanism of $Ir(ppy)_3$-catalyzed C–F bond transformation of **1a** with **2a**

To clarify the role of Bu_3SnI as a F^- ion scavenger, density functional theory (DFT) calculation studies were carried out (Figure 4) for the mesolysis of the C–F bond and the addition of radical **A** to pyrrole **2a** (Figure 4A).[16] The corresponding energy profile is illustrated in Figure 4B (Et groups on a Sn atom instead of Bu groups were adopted for the DFT calculation). Mesolysis of the C–F bond of radical anion $\mathbf{1a}^{\bullet-}$ is an uphill step to give radical **A**, although the activation barrier is moderate ($\Delta G^{\ddagger}$ = 11.0 kcal/mol). The reaction between Et_3SnI and F^- to give $Bu_3Sn(F)I^-$ provides large thermodynamic stability ($\Delta G^{\ddagger}$ = −17.2 kcal/mol) for the reaction system because of the formation of a stable Sn–F bond. In the addition of radical **A** to **2a**, the activation barrier is 15.6 kcal/mol.[17] If Et_3SnI is not involved in this reaction, transition state TS **E** becomes less thermodynamically stable than TS **D** and the retro reaction between **A** and F^- proceeds prior to the addition reaction between **A** and the pyrrole **2a**. Therefore, the role of Bu_3SnI as a F^- ion scavenger is critical to the progress of the present C–F bond heteroarylation.

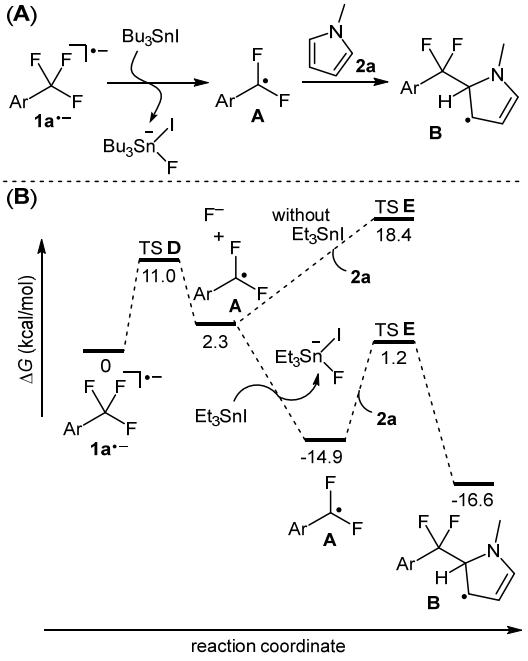
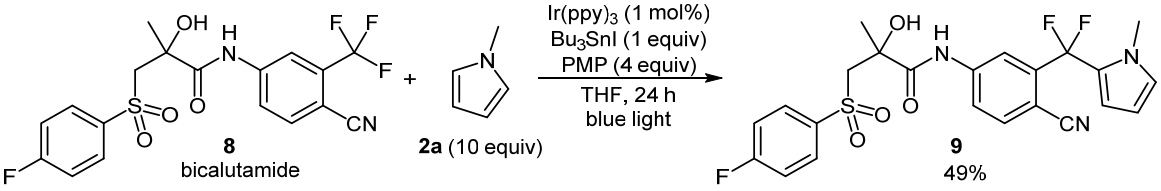


Figure 4. (A) Reaction scheme of the mesolysis of a C–F bond and the addition of radical **A** to pyrrole **2a**. (B) The corresponding energy profile at 298.15 K.

The late-stage C–F bond transformation is one of the most important issues in the development of F-containing drugs and agrochemicals. We demonstrated the heteroarylation of a C–F bond in bicalutamide (**8**), which is an antiandrogen used to treat prostate cancer.[18] The structure of **8** includes various functionalities such as CN and OH groups, amide and sulfone moieties, and C(sp^2)–F bonds; however, a C–F bond of the CF_3 group was selectively transformed to a pyrrolyl group (Scheme 5).



Scheme 5. Late-stage C–F bond heteroarylation of bicalutamide (**8**)

2-3. Conclusion

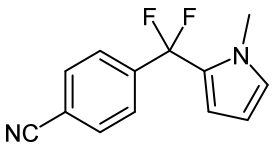
In summary, we achieved C–F bond heteroarylation of trifluoromethylarenes with heteroarenes by using $Ir(ppy)_3$ catalyst and Bu_3SnI under visible-light irradiation. The present heteroarylation proceeds under mild reaction conditions and enables transformation of various functionalized trifluoromethylarenes and heteroarenes. Notably, the examination of **8** was a study of a representative highly chemoselective transformation. Mechanistic studies clarified vital roles of Bu_3SnI for the effective progress of the present photocatalytic reaction. Bu_3SnI functions as a F^- ion scavenger to suppress retro-reactions including the undesired C–F bond reformation. In addition, Bu_3SnI can act as a single electron source for the reduction of photoexcited $Ir(ppy)_3$* to generate Ir(II) species for the effective reduction of $ArCF_3$.

2-4. Experimental Section

NMR spectra were recorded on a JEOL ECS400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C and 377 MHz for ^{19}F). Chemical shifts are reported in ppm on the δ scale relative to tetramethylsilane ($\delta = 0$ ppm for ^1H NMR) or the middle peak of the triplet of $CDCl_3$ ($\delta = 77$ ppm for ^{13}C NMR) as an internal reference and relative to $BF_3{\cdot}OEt$ in $CDCl_3$ ($\delta = -153$ ppm for ^{19}F NMR) as an external reference. Coupling constants were quoted in Hz (J). ^1H NMR spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). Cyclic voltammetry and differential pulse voltammetry measurements were performed with an ALS-600C electrochemical analyzer using a glassy carbon working electrode, a Pt counter electrode, and an $Ag/AgNO_3$ reference electrode at room temperature in THF containing 0.1 M $n Bu_4NBF_4$ as a supporting electrolyte. Infrared (IR) spectra were recorded on a JASCO FT/IR-6200 Fourier transform infrared spectrophotometer. Purification by flash chromatography system was performed on EPCLC-AI-580S (Yamazen Corporation) with Biotage Sfär Amino D (Biotage Japan Ltd.). Purification of all diaryldifluoromethan products by silica gel column chromatography required the use of amino-silica gel to avoid the hydrolysis of the products. Purification by recycle GPC was performed on a LaboACE LC-5060 preparative HPLC system with JAIGEL-2HR Plus (Japan Analytical Industry). High-resolution mass spectra were recorded on a JEOL JMS-700 and JMS-T100LP (time-of-flight analyzer with electrospray ionization (ESI) or direct analysis in real time (DART) ionization sources). All calculations were performed with Gaussian 16, Revision C.01 (The details are described in the Supporting Information). Reactions were carried out in dry solvents under a N_2 atmosphere, unless otherwise stated. Reactions were carried out in dry solvents under nitrogen atmosphere, unless otherwise stated. Reagents were purchased from Aldrich or Tokyo Chemical Industry Co., Ltd. (TCI), FUJIFILM Wako Pure Co., Ltd.. Light irradiation was performed by using a blue LED (Kessil A 160WE TUNA Blue). Starting materials **1d**,[19] **1e**,[20] and **2f**[21] are known compounds and were synthesized according to the literatures and the spectral data are in agreement with the reports. Other starting compounds are commercially available. All products **3**, **5**, **7**, and **9** are new compounds, and the preparation and characterization of them were described below.

Products

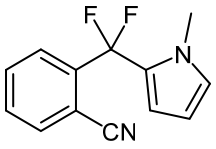
4-(difluoro(1-methyl-1*H*-pyrrol-2-yl)methyl)benzonitrile (3aa)



To a solution of *fac*-Ir(ppy)$_3$ (0.00397 mmol, 2.60 mg) and *para*-trifluoromethylbenzonitrile (0.413 mmol, 0.0707 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.71 mmol, 0.265 g), tributyltin iodide (0.388 mmol, 0.162 g), and 1-methylpyrrole (4.17 mmol, 0.338 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 62%). The residual oil was purified by amino-silica column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (yellow oil, 0.0539 g, 58%).

IR: (neat) 2233 cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 7.76 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 6.73 (m, 1H), 5.98 (m, 1H), 5.71 (m, 1H), 3.80 (s, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 140.7 (t, J = 27.2 Hz), 132.0, 127.0 (two signals overlap), 126.2 (t, J = 29.1 Hz), 118.1, 117.5 (t, J = 237 Hz), 114.1 (t, J = 1.7 Hz), 113.8 (t, J = 5.8 Hz), 106.6, 35.5 (t, J = 3.2 Hz); **^{19}F NMR**: (376 MHz, $CDCl_3$) -85.3; **HRMS**: (DART+) Calculated ($C_{13}H_{11}F_2N_2$) 233.0884 ([M+H]$^+$), Found: 233.0891

2-(difluoro(1-methyl-1*H*-pyrrol-2-yl)methyl)benzonitrile (3ba)

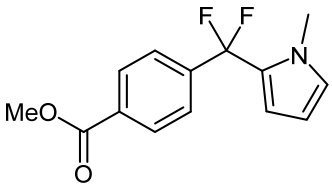


To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and 2-(trifluoromethyl)benzonitrile (0.399 mmol, 0.0683 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.6 mmol, 0.249 g), tributyltin iodide (0.400 mmol, 0.167 g), and 1-methylpyrrole (4.00 mmol, 0.324 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at room temperature under 40 W blue LED light irradiation for 24 h. The reaction mixture was diluted with ether (30 mL) and the volatiles removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 49%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (yellow solid, 0.0372 g, 40%).

mp 75-76 °C

IR: (KBr) 2232 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.81 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.70 (m, 1H), 7.61 (t, J = 7.6 Hz, 1H), 6.74 (m, 1H), 5.98 (m, 1H), 5.69 (m, 1H), 3.86 (s, 3H); **^{13}C NMR**: (100 MHz, in $CDCl_3$) 138.9 (t, J = 26.8 Hz), 134.2, 132.3, 130.5, 127.4 (t, J = 5.7 Hz), 127.3, 125.4 (t, J = 28.0 Hz), 117.0 (t, J = 236.6 Hz), 116.6, 114.2 (t, J = 5.7 Hz), 111.0 (t, J = 2.2 Hz), 106.8, 35.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -83.9; **HRMS**: (EI) (*m*/*z*) Calculated ($C_{13}H_{10}F_2N_2$) 232.0812 (M$^+$), Found: 232.0809

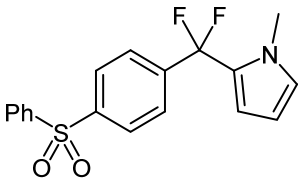
methyl 2-(5-((4-cyanophenyl)difluoromethyl)-1-methyl-1*H*-pyrrol-2-yl)acetate (3ca)



To a solution of *fac*-Ir(ppy)$_3$ (0.00397 mmol, 2.70 mg) and methyl 4-(trifluoromethyl)benzoate (0.416 mmol, 0.0850 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.48 mmol, 0.230 g), tributyltin iodide (0.412 mmol, 0.172 g), and *N*-methylpyrrole (4.11 mmol, 0.334 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 25%). The residual oil was purified by amino-silica column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (dark yellow oil, 0.0200 g, 19%).

IR: (neat) 1730 (CO) cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 8.10 (d, J = 9 Hz, 2H), 7.64 (d, J = 9 Hz, 2H), 6.70 (m, 1H), 5.96 (m, 1H), 5.73 (m, 1H), 3.95 (s, 3H), 3.78 (s, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 166.6, 141.0 (t, J = 29 Hz), 131.9, 129.6, 127.2 (t, J = 32 Hz), 126.9, 126.6 (t, J = 5 Hz), 118.2 (t, J = 232 Hz), 113.8 (t, J = 6 Hz), 106.8, 52.4, 35.4 (t, J = 4 Hz); **^{19}F NMR**: (376 MHz, $CDCl_3$) -85.1; **HRMS**: (DART+) Calculated ($C_{14}H_{14}F_2NO_2$) 266.0987 ([M+H]$^+$), Found: 266.0975

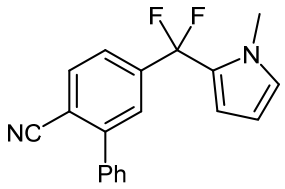
2-(difluoro(4-(phenylsulfonyl)phenyl)methyl)-1-methyl-1*H*-pyrrole (3da)



To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and 1-(phenylsulfonyl)-4-(trifluoromethyl)benzene (0.405 mmol, 0.116 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.6 mmol, 0.249 g), tributyltin iodide (0.400 mmol, 0.167 g), and 1-methylpyrrole (4.00 mmol, 0.324 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at room temperature under 40 W blue LED light irradiation for 24 h. The reaction mixture was diluted with ether (30 mL) and the volatiles removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 41%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 80:20) and GPC to give the product (yellow oil, 0.0448 g, 32%).

IR: (neat) 2972, 1629, 1543, 1447 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 8.04 (d, J = 8.6 Hz, 2H), 7.99 (m, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.63-7.52 (m, 3H), 6.71 (m, 1H), 5.95 (m, 1H), 5.69 (m, 1H), 3.77 (s, 3H); **^{13}C NMR**: (100 MHz, in $CDCl_3$) 143.3, 141.1 (t, J = 27.2 Hz), 140.8, 133.5, 129.4, 127.8, 127.5, 127.3 (t, J = 4.8 Hz), 127.0, 126.2 (t, J = 28.9 Hz), 117.5 (t, J = 235.7 Hz), 113.8 (t, J = 5.5 Hz), 106.7, 35.4; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -86.2 (s); **HRMS**: (EI) (*m*/*z*) Calculated ($C_{18}H_{15}F_2NO_2S$) 347.0792 (M$^+$), Found: 347.0797

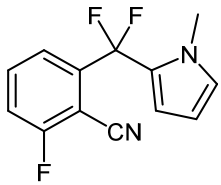
5-(difluoro(1-methyl-1*H*-pyrrol-2-yl)methyl)-[1,1'-biphenyl]-2-carbonitrile (3ea)



To a solution of *fac*-Ir(ppy)$_3$ (0.00397 mmol, 2.60 mg) and 5-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (0.399 mmol, 0.0987 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.60 mmol, 0.245 g), tributyltin iodide (0.401 mmol, 0.167 g), and 1-methylpyrrole (3.99 mmol, 0.324 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 49%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (white solid, 0.0431 g, 35%).

mp: 85-86 °C; **IR:** (neat) 2226 cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 7.86 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 1.4 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.61-7.46 (m, 5H), 6.75-6.73 (m, 1H), 6.00-5.98 (m, 1H), 5.81-5.78 (m, 1H), 3.82 (s, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 145.6, 140.8 (t, *J* = 29.3 Hz), 137.2 , 133.6, 129.1, 128.8, 128.7, 127.9 (t, *J* = 4.4 Hz), 127.1, 126.3 (t, *J* = 28.4 Hz), 125.3 (t, *J* = 4.3 Hz), 118.0, 117.5 (t, *J* = 235 Hz), 113.9 (t, *J* = 5.6 Hz), 112.8, 106.7, 35.5; **^{19}F NMR**: (376 MHz, $CDCl_3$) -86.4 (s); **HRMS**: (EI) Calculated ($C_{19}H_{14}F_2N_2$) 308.1125 ([M]$^+$), Found: 308.1123

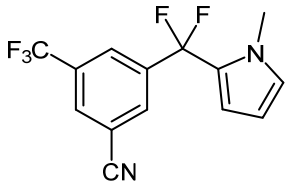
2-(difluoro(1-methyl-1*H*-pyrrol-2-yl)methyl)-6-fluorobenzonitrile (3fa)



To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.6 mg) and 2-fluoro-6-(trifluoromethyl)benzonitrile (0.400 mmol, 0.0757 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.6 mmol, 0.249 g), tributyltin iodide (0.400 mmol, 0.167 g), and 1-methylpyrrole (4.00 mmol, 0.324 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at room temperature under 40 W blue LED light irradiation for 24 h. The reaction mixture was diluted with ether (30 mL) and the volatiles removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 75%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (white solid, 0.0697 g, 70%).

mp: 110-111 °C; **IR:** (KBr) 2226 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.70 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.38 (m, 1H), 6.75 (m, 1H), 5.99 (m, 1H), 5.74 (m, 1H), 3.84 (s, 3H); **^{13}C NMR**: (100 MHz, in $CDCl_3$) 163.9 (d, *J* = 260.0 Hz), 140.7 (t, *J* = 27.2 Hz), 134.2 (d, *J* = 8.6 Hz), 127.5, 124.7 (t, *J* = 27.7 Hz), 123.1 (d, *J* = 3.8 Hz), 118.1 (d, *J* = 20.1 Hz), 116.5 (td, *J* = 237.3, 2.4 Hz), 114.2 (t, *J* = 5.7 Hz), 111.3, 107.0, 100.4 (d, *J* = 17.2 Hz), 35.5; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -83.5 (s, 2F), -105.6 (m, 1F); **HRMS**: (EI) *m*/*z* Calculated ($C_{13}H_9F_3N_2$) 250.0718 (M$^+$), Found: 250.0716

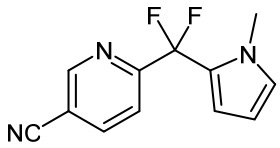
3-(difluoro(1-methyl-1*H*-pyrrol-2-yl)methyl)-5-(trifluoromethyl)benzonitrile (3ga)



To a solution of *fac*-Ir(ppy)$_3$ (0.00443 mmol, 2.90 mg) and 3,5-bis(trifluoromethyl)benzonitrile (0.401 mmol, 0.0960 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.65 mmol, 0.256 g), tributyltin iodide (0.393 mmol, 0.164 g), and 1-methylpyrrole (4.07 mmol, 0.330 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 56%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (yellow oil, 0.0587 g, 49%).

IR: (neat) 2242 cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 8.09 - 8.06 (m, 3H), 6.77 (m, 1H), 6.00 (m, 1H), 5.64 (m, 1H), 3.84 (s, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 139.2 (t, *J* = 29 Hz), 133.1 (t, *J* = 4 Hz), 132.2 (q, *J* = 35 Hz), 130.6, 127.6, 127.3 (m), 125.4 (t, *J* = 28 Hz), 122.5 (q, *J* = 274 Hz), 116.7 (t, *J* = 237 Hz), 116.6, 114.2 (t, *J* = 6 Hz), 113.7, 107.0, 35.6 (t, *J* = 3 Hz); **^{19}F NMR**: (376 MHz, $CDCl_3$) -63.0 (3F), -84.6 (2F); **HRMS**: (DART+) Calculated ($C_{14}H_{10}F_5N_2$) 301.0759 ($[M+H]^+$) Found: 301.0761

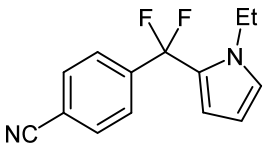
6-(difluoro(1-methyl-1*H*-pyrrol-2-yl)methyl)nicotinonitrile (3ia)



To a solution of *fac*-Ir(ppy)$_3$ (0.0041 mmol, 2.9 mg) and 6-(trifluoromethyl)nicotinonitrile (0.417 mmol, 0.0718 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.60 mmol, 0.242 g), tributyltin iodide (0.408 mmol, 0.170 g), and *N*-methylpyrrole (4.12 mmol, 0.334 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 22%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (yellow oil, 0.0500 g, 20%).

IR: (neat) 2234 cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 8.96 (d, *J* = 2 Hz, 1H), 8.12 (dd, *J* = 8 and 2 Hz, 1H), 7.84 (d, *J* = 8 Hz, 1H), 6.71 (m, 1H), 6.00 (m, 1H), 5.82 (m, 1H), 3.81 (s, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 157.7 (t, *J* = 31 Hz), 151.9, 140.5, 127.0, 125.1 (t, *J* = 29 Hz), 121.1 (t, *J* = 4 Hz), 115.9 (t, *J* = 240 Hz, overlapped), 115.9(overlapped), 113.2 (t, *J* = 6 Hz), 111.2, 107.1, 35.7 (t, *J* = 30 Hz); **^{19}F NMR**: (376 MHz, $CDCl_3$) -89.4; **HRMS**: (DART+) Calculated ($C_{12}H_9F_2N_3$) 233.0759 ($[M]^+$), Found: 233.0757

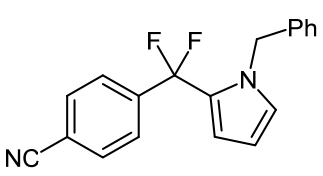
4-((1-ethyl-1*H*-pyrrol-2-yl)difluoromethyl)benzonitrile (3ab)



To a solution of *fac*-Ir(ppy)$_3$ (0.00458 mmol, 3.00 mg) and *para*-trifluoromethylbenzonitrile (0.414 mmol, 0.0708 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.64 mmol, 0.254 g), tributyltin iodide (0.412 mmol, 0.172 g), and 1-ethylpyrrole (4.10 mmol, 0.390 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 54%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (pale yellow oil, 0.0500g, 51%).

IR: (neat) 2233 cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 7.76 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 6.84 (m, 1H), 6.02 (m, 1H), 5.66 (m, 1H), 4.16 (q, J = 7.3 Hz, 2H), 1.45 (t, J = 7.3 Hz, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 141.0 (t, $^2J_{C\text{-}F}$ = 27.4 Hz), 132.0, 127.1 (t, J = 4.8 Hz), 125.7 (t, J = 29.1 Hz), 124.9, 118.1, 117.5 (t, J = 237 Hz), 114.1 (J = 1.7 Hz), 113.5 (t, J = 5.5 Hz), 107.1, 43.0 (t, J = 2.9 Hz), 16.8; **^{19}F NMR**: (376 MHz, $CDCl_3$) -84.6; **HRMS**: (DART+) Calculated ($C_{14}H_{13}F_2N_2$) 247.1041 ([M+H]$^+$), Found: 247.1036

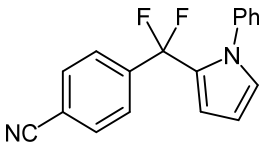
4-((1-benzyl-1*H*-pyrrol-2-yl)difluoromethyl)benzonitrile (3ac)



To a solution of *fac*-Ir(ppy)$_3$ (0.00411 mmol, 2.69 mg) and *para*-trifluoromethylbenzonitrile (0.411 mmol, 0.0703 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.62 mmol, 0.252 g), tributyltin iodide (0.410 mmol, 0.171 g), and 1-benzyl-1*H*-pyrrole (4.08 mmol, 0.641 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 51%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (pale yellow oil, 0.0115 g, 9%).

IR: (neat) 2232 (CN) cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 7.72 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.34–7.28 (m, 3H), 7.10 (m, 2H), 6.74 (m, 1H), 6.06 (m, 1H), 5.80 (m, 1H), 5.29 (s, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) 140.8 (t, J = 27.4 Hz), 137.4, 131.9, 128.6, 127.7, 127.1 (t, J = 4.6 Hz), 127.0, 126.5 (t, J = 29.6 Hz), 126.3, 118.1, 117.5 (t, J = 238 Hz), 114.1 (t, J = 2.0 Hz), 113.7 (t, J = 5.6 Hz), 107.5, 51.7 (t, J = 2.9 Hz); **^{19}F NMR**: (376 MHz, $CDCl_3$) -84.0; **HRMS**: (DART+) Calculated ($C_{19}H_{15}F_2N_2$) 309.1198 ([M+H]$^+$), Found: 309.1206

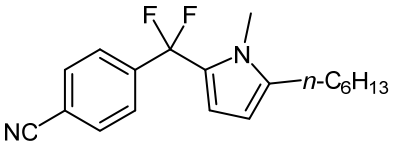
4-(difluoro(1-phenyl-1*H*-pyrrol-2-yl)methyl)benzonitrile (3ad)



To a solution of *fac*-Ir(ppy)$_3$ (0.0040 mmol, 2.7 mg) and 4-(trifluoromethyl)benzonitrile (0.394 mmol, 0.0675 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.68 mmol, 0.262 g), tributyltin iodide (0.420 mmol, 0.175 g), and methyl 2-(1-phenyl-1*H*-pyrrol-2-yl)acetate (3.93 mmol, 0.688 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 67%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (yellow oil, 0.0298 g, 23%).

IR: (neat) 2232 cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 7.56 (d, J = 8 Hz, 2H), 7.39 (d, J = 8 Hz, 2H), 7.35-7.29 (m, 3H), 7.19 (d, J = 7 Hz, 2H), 6.83 (m, 1H), 6.27 (m, 1H), 6.21 (m, 1H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 141.3 (t, J = 27 Hz), 139.6, 131.9, 128.7, 128.4, 128.0 (t, J = 34 Hz), 127.4, 126.9 (t, J = 5 Hz), 126.9 (overlapped), 118.2 , 117.0 (t, J = 239 Hz), 113.7, 113.3 (t, J = 5 Hz), 107.9; **^{19}F NMR**: (376 MHz, $CDCl_3$) -83.5; **HRMS**: (DART+) Calculated ($C_{18}H_{13}F_2N_2$) 295.1041 ([M]$^+$), Found: 295.1046

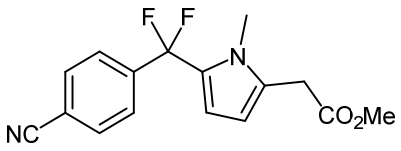
4-(difluoro(5-hexyl-1-methyl-1*H*-pyrrol-2-yl)methyl)benzonitrile (3af)



To a solution of *fac*-Ir(ppy)$_3$ (0.00489 mmol, 3.20 mg) and methyl *para*-trifluoromethylbenzonitrile (0.400 mmol, 0.0850 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.60 mmol, 0.248 g), tributyltin iodide (0.406 mmol, 0.169 g), and 2-hexyl-1-methyl-1*H*-pyrrole (4.22 mmol, 0.342 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 41%). The residual oil was dissolved in hexane and the precipitation was removed. Further The purification was carried out by GPC to give the product (yellow oil, 0.0070g, 5%).

IR: (neat) 2233 (CN) cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 7.75 (d, J = 8 Hz, 2H), 7.70 (d, J = 8 Hz, 2H), 5.75 (m, 1H), 5.55 (m, 1H), 3.69 (s, 3H), 2.54 (t, 2H), 1.62 (m, 2H), 1.41-1.21 (m, 6H), 0.90 (m, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 141.1 (t, J = 27 Hz), 139.1, 131.9, 127.2 (t, J = 5 Hz), 125.4 (t, J = 8 Hz), 118.2, 117.8 (t, J = 236 Hz), 114.0, 112.8 (t, J = 6 Hz), 104.5, 31.7 (t, J = 4 Hz), 31.6, 29.1, 28.3, 26.4, 22.6, 14.1; **^{19}F NMR**: (376 MHz, $CDCl_3$) -84.9; **HRMS**: (DART+) Calculated ($C_{19}H_{22}F_2N_2$) 316.1746 ([M]$^+$), Found: 316.1756

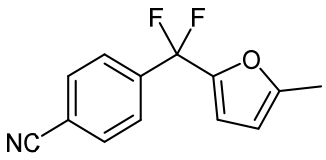
methyl 2-(5-((4-cyanophenyl)difluoromethyl)-1-methyl-1*H*-pyrrol-2-yl)acetate (3ag)



To a solution of *fac*-Ir(ppy)$_3$ (0.00397 mmol, 2.60 mg) and 4-(trifluoromethyl)benzonitrile (0.403 mmol, 0.0689 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.68 mmol, 0.261 g), tributyltin iodide (0.40 mmol, 0.168 g), and methyl 2-(1-methyl-1*H*-pyrrol-2-yl)acetate (3.81 mmol, 0.584 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 52%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (yellow oil, 0.0087 g, 7%).

IR: (neat) 2232 (CN) cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 7.75 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 5.89 (d, J = 5.0 Hz, 1H), 5.61-5.59 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.65 (s, 2H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 170.4, 140.9 (t, J = 31 Hz), 132.1, 130.2, 127.3 (t, J = 5.4 Hz), 127.0 (t, J = 116 Hz), 118.2, 117.6 (t, J = 235.9 Hz), 114.3, 113.1 (t, J = 5.7 Hz), 107.9, 52.5, 32.6, 32.4 (t, J = 3.5 Hz); **^{19}F NMR**: (376 MHz, $CDCl_3$) -85.5 (s); **HRMS**: (DART+) Calculated ($C_{16}H_{15}F_2N_2O_2$) 305.1096 ([M+H]$^+$) Found: 305.1108

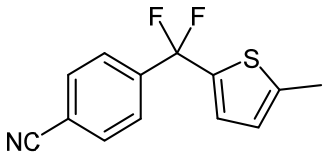
4-(difluoro(5-methylfuran-2-yl)methyl)benzonitrile (5)



To a solution of *fac*-Ir(ppy)$_3$ (0.00443 mmol, 2.90 mg) and *para*-trifluoromethylbenzonitrile (0.408 mmol, 0.0698 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.66 mmol, 0.258 g), tributyltin iodide (0.398 mmol, 0.166 g), and 2-methylfuran (3.95 mmol, 0.324 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 43%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (brown oil, 0.0294 g, 32%).

IR: (neat) 2238 cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 7.76 (d, J = 8 Hz, 2H), 7.71 (d, J = 8 Hz, 2H), 7.47 (m, 1H), 7.03 (m, 1H), 2.31 (s, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 155.1 (t, J = 2 Hz), 145.6 (t, J = 36 Hz), 139.9 (t, J = 28 Hz), 132.2 (*m*), 126.7 (t, J = 5 Hz), 118.0, 114.9 (t, J = 239 Hz), 114.3 (t, J = 2 Hz), 117.9 (t, J = 4 Hz), 106.6, 13.57; **^{19}F NMR**: (376 MHz, $CDCl_3$) -91.7; **HRMS**: (DART+) Calculated ($C_{13}H_{10}F_2NO$) 234.0725 ([M+H]$^+$), Found: 234.0729

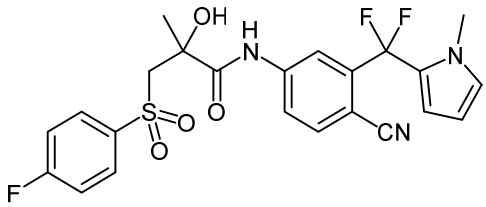
4-(difluoro(5-methylthiophen-2-yl)methyl)benzonitrile (7)



To a solution of *fac*-Ir(ppy)$_3$ (0.00443 mmol, 2.90 mg) and *para*-trifluoromethylbenzonitrile (0.400 mmol, 0.0684 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.64 mmol, 0.255 g), tributyltin iodide (0.415mol, 0.173 g), and 2-methylthiophene (4.13 mmol, 0.405 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 26%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 95:5) and GPC to give the product (yellow oil, 0.010 g, 10%).

IR: (neat) 2233 (CN) cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 7.76 (d, J = 9 Hz, 2H), 7.71 (d, J = 9 Hz, 2H), 6.79 (m, 1H), 6.66 (m, 1H), 2.49 (m, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 143.9, 141.4 (t, J = 29 Hz), 136.1 (t, J = 33 Hz), 132.3, 128.4 (t, J = 6 Hz), 126.6 (t, J = 5 Hz), 125.0, 118.0, 117.9 (t, J = 241 Hz), 114.2 (t, J = 2 Hz), 15.3; **^{19}F NMR**: (376 MHz, $CDCl_3$) -79.9; **HRMS**: (DART+) Calculated ($C_{13}H_{10}F_2NS$) 250.0497 ($[M+H]^+$), Found: 250.0509

Compound 9



To a solution of *fac*-Ir(ppy)$_3$ (0.00443 mmol, 2.90 mg) and Bicalutamide (0.400 mmol, 0.172 g) in THF (4 mL) were added 1,2,2,6,6-pentamethylpiperidine (1.60 mmol, 0.249 g), tributyltin iodide (0.417 mmol, 0.174 g), and 1-methylpyrrole (4.14 mmol, 0.336 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 40 W blue LED lights irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (7 mL) and the volatiles were removed under reduced pressure. The crude yield was confirmed by ^{1}H NMR using 1,1,1,2-tetrachloroethane as an internal standard (NMR yield: 49%). The residual oil was purified by amino-silica gel column chromatography (hexane/ethyl acetate = 50:50) and GPC to give the product (yellow oil, 0.0179 g, 9%).

IR: (neat) 2230 cm^{-1}; **^{1}H NMR**: (400 MHz, $CDCl_3$) 9.06 (s, 1H), 7.91-7.83 (m, 3H), 7.78-7.74 (m, 2H), 7.17-7.12 (m, 2H), 6.75 (m, 1H), 5.99 (m, 1H), 5.72 (m, 1H), 5.05 (s, 1H), 4.01 (d, 1H, J = 14.6 Hz), 3.50 (d, 1H, J = 14.6 Hz), 3.87 (s, 3H), 1.60 (s, 3H); **^{13}C NMR**: (100 MHz, $CDCl_3$) 171.5, 166.2 (d, J = 260 Hz), 140.7, 140.4 (t, J = 26.9 Hz), 135.5, 135.2 (d, J = 3.4 Hz), 131.0 (d, J = 9.6 Hz), 127.6, 125.2 (t, J = 27.9 Hz), 120.6, 118.2 (t, J = 6.5 Hz), 116.9 (t, J = 243 Hz), 116.8 (d, J = 22.6 Hz), 116.6, 114.4 (t, J = 5.8 Hz), 107.1, 106.3, 74.3, 61.8, 35.6 (t, J = 3.1 Hz), 27.7; **^{19}F NMR**: (376 MHz, $CDCl_3$) -82.8 (2F), -101.3 (1F); **HRMS**: (EI) Calculated ($C_{23}H_{20}F_3N_3O_4S$) 491.1127 ($[M]^+$), Found: 491.1121

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(17) DFT calculation studies suggested that the oxidation of **C′** by I˙ and aromatization of cation **D′** by deprotonation with PMP are highly exergonic paths to give the final product **3aa**. See the Supporting Information.

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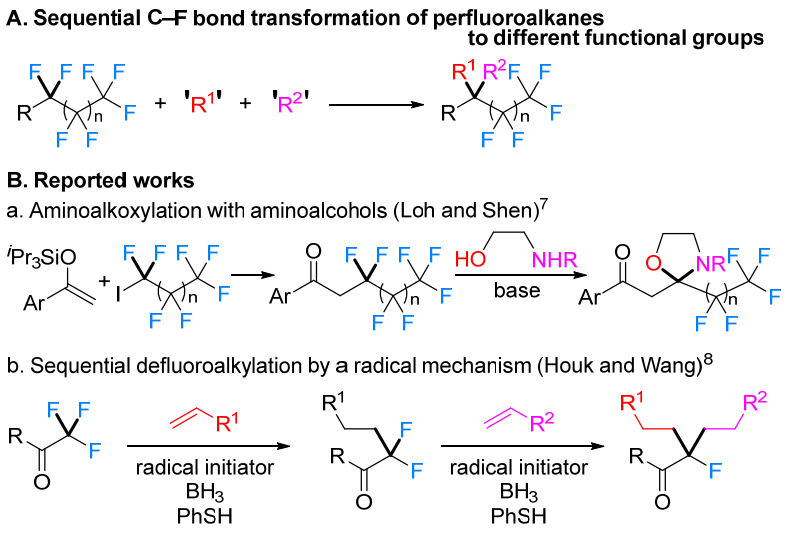
Chapter 3: Sequential C–F Bond Transformation of the Difluoromethylene Unit in Perfluoroalkyl Groups: A Combination of Fine-Tuned Phenothiazine Photoredox Catalyst and Lewis Acid

3-1. Introduction

The carbon–fluorine (C–F) bond transformation in perfluoroalkyl compounds not only is an important synthetic method in organic chemistry,[1] but also is an urgent issue to solve PFAS (polyfluoroalkyl substances) environmental problems.[2] Numerous C–F bond activation protocols have been reported for single C–F bond transformations of perfluoroalkyl group.[3,4] However, a sequential C–F bond transformation of a difluoromethylene unit (–CF_2–) into two different functional groups remains underdeveloped (Figure 1A) despite being an important clue to the solution of PFAS problems. This is because the harsh reaction conditions needed to cleave robust C–F bonds cause the undesired installation of the same functional group. In fact, dialkoxylation,[5] dimethylation[6] and dichlorination[6] of a CF_2 moiety have been reported. To avoid installing the same groups, amino alcohols were used in the aminoalkoxylation of *α*-perfluoroalkyl ketones in a three-component tandem reaction (Figure 1B, a).[7] Recently, two distinguished reactions were reported: a sequential defluorinative alkylation of trifluoroacetyl compounds by a radical mechanism (Figure 1B, b)[8] and a coupling reaction of 1,1-difluoroalkyl compounds (RCF_2R') with Grignard reagents and chlorosilanes or alkyl tosylates by $CrCl_2$ catalysis via chromium carbenoid species (Figure 1B, c).[9] Neither method is applicable to the transformation of longer perfluoroalkyl compounds ($RCF_2(CF_2)_nR'$). Herein we propose a reaction design based on a sequential process via radical and ionic paths (Figure 1C). The primary substitution of F with RO groups involves C–F bond activation by photocatalysis[4g] and capture of the perfluoroalkyl radical by an oxyl radical.[10] Then the second transformation employs a Lewis acid and nucleophiles. Because the reaction mechanism includes an oxonium intermediate, diverse nucleophiles can be introduced. Based on our proposed design using a dual activation system, in this study we achieved a sequential C–F bond transformation of perfluoroalkylarenes via aminoxylation with a fine-tuned phenothiazine photocatalyst and aminoxyl radical reagent followed by $AlCl_3$-mediated nucleophilic substitution with organosilicon reagents (Figure 1D).



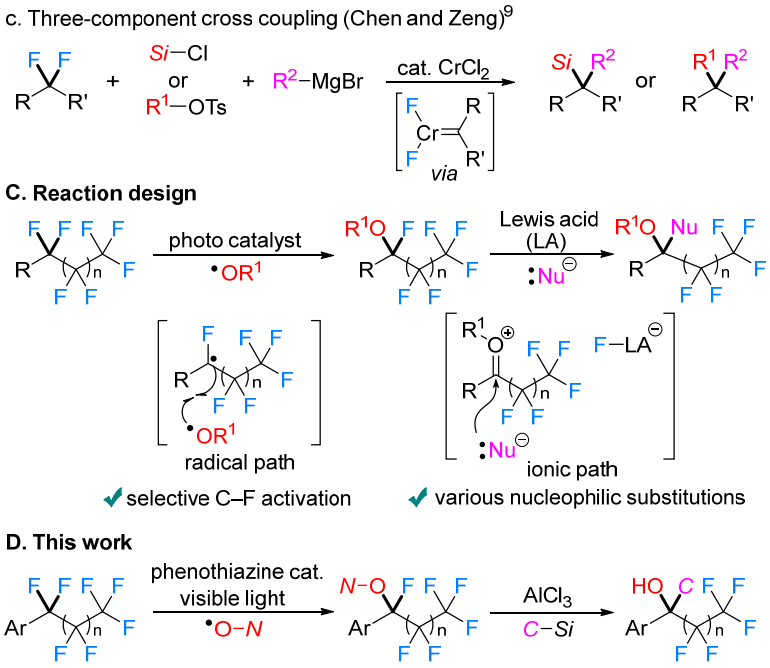
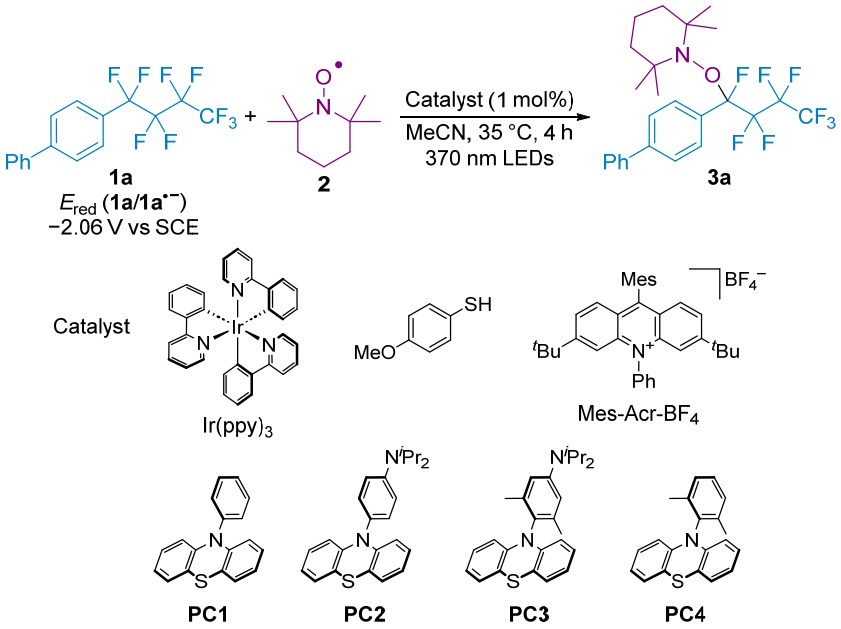


Figure 1. Sequential C–F bond transformation of perfluoroalkyl compounds

3-2. Results and Discussion

Firstly, we investigated reaction conditions for the photo-catalyzed aminoxylation using 4-phenyl(perfluorobutyl)benzene **1a** (E_{red} = –2.06 V vs SCE) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (**2**) under visible light irradiation (370 nm) (Table 1). The use of $Ir(ppy)_3$ resulted in no reaction due to the low reducing ability of excited $Ir(ppy)_3$ (Entry 1).[4g] We focused on phenothiazines exhibiting higher reducing abilities than $Ir(ppy)_3$. Their photocatalytic activities can be tuned by a substituent effect.[11] *N*-Phenylphenothiazine **PC1** exhibited a catalytic activity to mediate the aminoxylation, giving product **3a** (Entry 2). To access more negative redox potentials, phenothiazine **PC2** was used, leading to an improved yield (Entry 3). It should be noted that newly developed phenothiazine **PC3** bearing diisopropylamino and two methyl groups showed the best catalytic activity (Entry 4), suggesting the effect of the two Me groups is crucial to the aminoxylation. *N*-Dimethylphenylphenothiazine **PC4** was less effective, which indicates the increase of reducing ability by an amino group is significant (Entry 5). Next, to utilize much lower reduction potential of photocatalysts, we applied thiolate catalysis[12] and consecutive photo-induced electron transfer (conPET) system[13] to this reaction. Thiolate catalysis resulted in no reaction, and **1a** was hardly converted (Entry 6). In the conPET system, **1a** was completely consumed, but only a trace amount of **3a** was obtained according to complicated products (Entry 7). In this case, the high reducing ability of the active catalytic species generated by conPET would cause the undesired overreduction or side-reactions. Both photocatalyst and photo-irradiation were essential for the reaction progress (Entries 8 and 9). Finally, under the optimized conditions using the 5 mol% amount of **PC3**, **3a** was obtained in 82 % yield (Entry 10). Further optimization for addition amount of TEMPO **2** and solvent screening is described in the supporting information.[14]

Table 1. Optimization of Photo-catalyzed Aminoxylation of Perfluoroalkylarene 1a with TEMPO 2



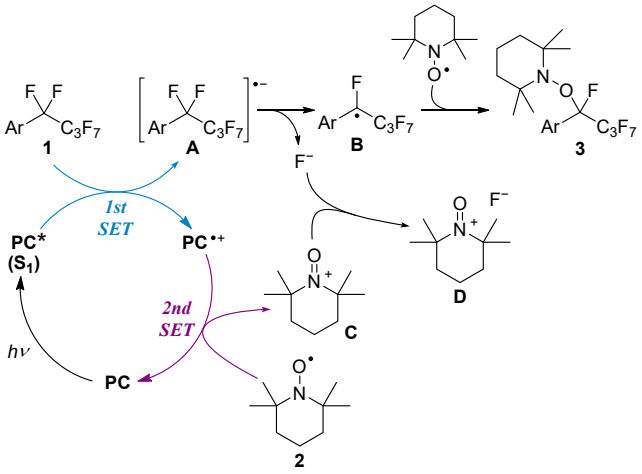
entry	catalyst	E_{ox}* (V vs SCE)	yield
1	$Ir(ppy)_3$	–1.73	0%
2	**PC1**	–2.45	35%
3	**PC2**	–2.68	42%
4	**PC3**	–2.57	60%
5	**PC4**	–2.47	38%
6[b]	4-$MeOC_6H_4SH$	–3.31	0%
7[c]	Mes-Acr-BF_4	–3.36	trace
8[d]	**PC3**	–2.57	0%
9	none	-	0%
10[e]	**PC3**	–2.57	82% (71%)[f]

[a]**1a** (0.4 mmol), **2** (0.8 mmol), catalyst (0.004 mmol), MeCN (2 mL), irradiation with 370 nm LEDs at 35 °C for 4 h. Yields were determined by ^{1}H NMR spectroscopy using an internal standard. [b]4-$MeOC_6H_4SH$ (0.08 mmol), HCO_2Cs (0.8 mmol), DMSO (2 mL) irradiation with 427 nm LEDs at 35 °C for 24 h. [c]Mes-Acr-BF_4 (0.04 mmol), N^{i}Pr$_2$Et (1.2 mmol), MeCN (1.3 mL), irradiation with 390 nm LEDs at 35 °C for 24 h. [d]No irradiation. [e]**PC3** (0.02 mmol), 24 h. [f]Isolated yield.

Scheme 1 depicts a plausible mechanism for the aminoxylation of **1** with TEMPO **2** catalyzed by phenothiazine **PC**. The photoexcited **PC*** reduces **1** via single electron transfer (SET), affording radical anion **A** and radical cation **PC**$^{\bullet+}$. Mesolysis of a C–F bond affords benzyl radical **B**.[4g] Then, **B** associates

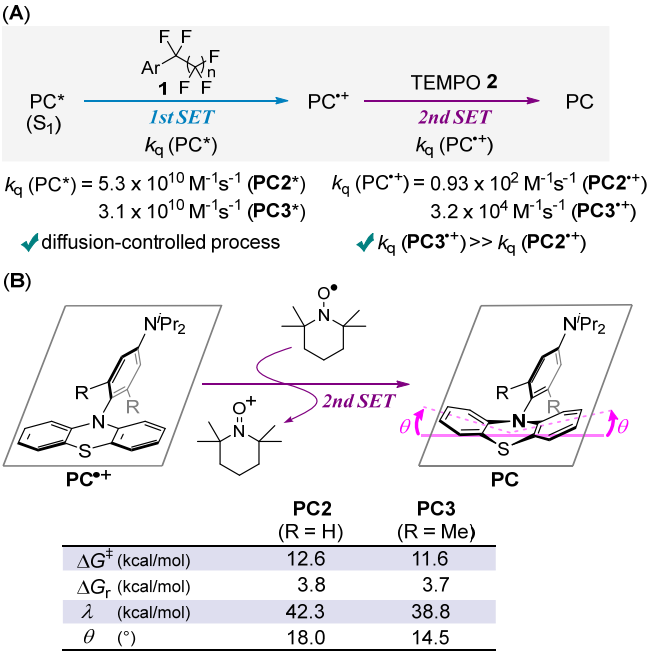
with **2** to give product **3**. **PC** (E(**PC3**$^{\bullet+}$/**PC3**) = 0.61 V vs SCE) is regenerated by single electron reduction with **2** (E(**2**$^{+}$/**2**) = 0.62 V vs SCE).[15] A by-product, *N*-oxoammonium cation **C** captures F^{-}, suppressing the retro-reaction from **B** to **A**.[16] HRMS and ^{19}F NMR confirmed *N*-oxoammonium fluoride **D** was generated.[17] The appropriate reduction potential of **PC3*** achieves selective reduction of starting material **1** and not product **3**, realizing a single C–F bond transformation without overreduction and side-reactions.[18]

Scheme 1. Proposed Mechanism for Photo-catalyzed Aminoxylation of Perfluoroalkylarenes



We focus on the fact that our developed **PC3** exhibited a more efficient catalytic activity than **PC2** despite the lower reducing ability of **PC3*** than **PC2*** (Table 1).[19] We conducted mechanistic studies to understand the origin of the high activity of **PC3**. First, the fluorescence quenching experiments of PC* with 4-trifluoromethyl(perfluorohexyl)benzene **1e** were performed. Stern-Volmer plots determined that the rate constants of the dynamic quenching of excited singlet species **PC2*** and **PC3*** were 5.3 x 10^{10} $M^{-1}s^{-1}$ and 3.1 x 10^{10} $M^{-1}s^{-1}$, respectively (Figures S2 and S4).[20,21] The 1st SET between **1e** and PC* is a diffusion-controlled process,[22] which indicates that the catalytic turnover is independent of the reducing ability of PC*.[23] We then considered the 2nd SET between PC$^{\bullet+}$ and TEMPO for the catalyst regeneration. The sub-microsecond transient absorption spectroscopy using laser flash photolysis method at 355 nm (4 mJ/pulse, 4 ns pulse-width) was conducted for a mixture of PC, 4-phenyl(perfluoroethyl)benzene **1n**, and TEMPO to monitor the generation and quenching of PC$^{\bullet+}$.[24] The quenching rate constant of **PC3**$^{\bullet+}$ (3.2 x 10^{4} $M^{-1}s^{-1}$) was found to be much larger than that of **PC2**$^{\bullet+}$ (0.93 x 10^{2} $M^{-1}s^{-1}$) (Figures S19 and S20).[25] Thus, the fast regeneration of **PC3** dominates the catalytic turnover (Figure 2A). Next, Gibbs free energy changes (ΔG_r) and reorganization energies (λ) in the 2nd SET were obtained by DFT calculation to estimate activation energies ($\Delta G^{\ddagger}$) according to Marcus-Hush theory (Figure 2B).[26,27] While two ΔG_r values are almost identical (3.8 and 3.7 kcal/mol), λ value for **PC3** (38.8 kcal/mol) is lower than that for **PC2** (42.3 kcal/mol). Finally, $\Delta G^{\ddagger}$ for **PC3** (11.6 kcal/mol) is lower than that for **PC2** (12.6 kcal/mol). This trend in $\Delta G^{\ddagger}$ is consistent with that in the catalyst regeneration rate. Thus, we focused on the geometry change of PC because a smaller λ value leads to the decrease of $\Delta G^{\ddagger}$ for SET. The planar structure of phenothiazine backbone in PC$^{\bullet+}$ changes to the bent one upon reduction (Figure 2B). This bending is the dominant geometry change and would be deeply related to λ values. We adopted the bent angle (θ) in Figure 2B right to represent the extent of a bent

structure of PC. The smaller value of θ in **PC3** (θ = 14.5°) shows the smaller geometry change in the reduction of **PC3**$^{\bullet+}$ compared to **PC2** (θ = 18.0°). The steric repulsion of Me groups of **PC3** suppresses bending of a phenothiazine backbone, eventually decreasing $\Delta G^{\ddagger}$. A catalyst design including both fast catalyst regeneration and effective photo-excited reduction potential is achieved by the rigidity of molecular structure and the introduction of an electron-donating group.

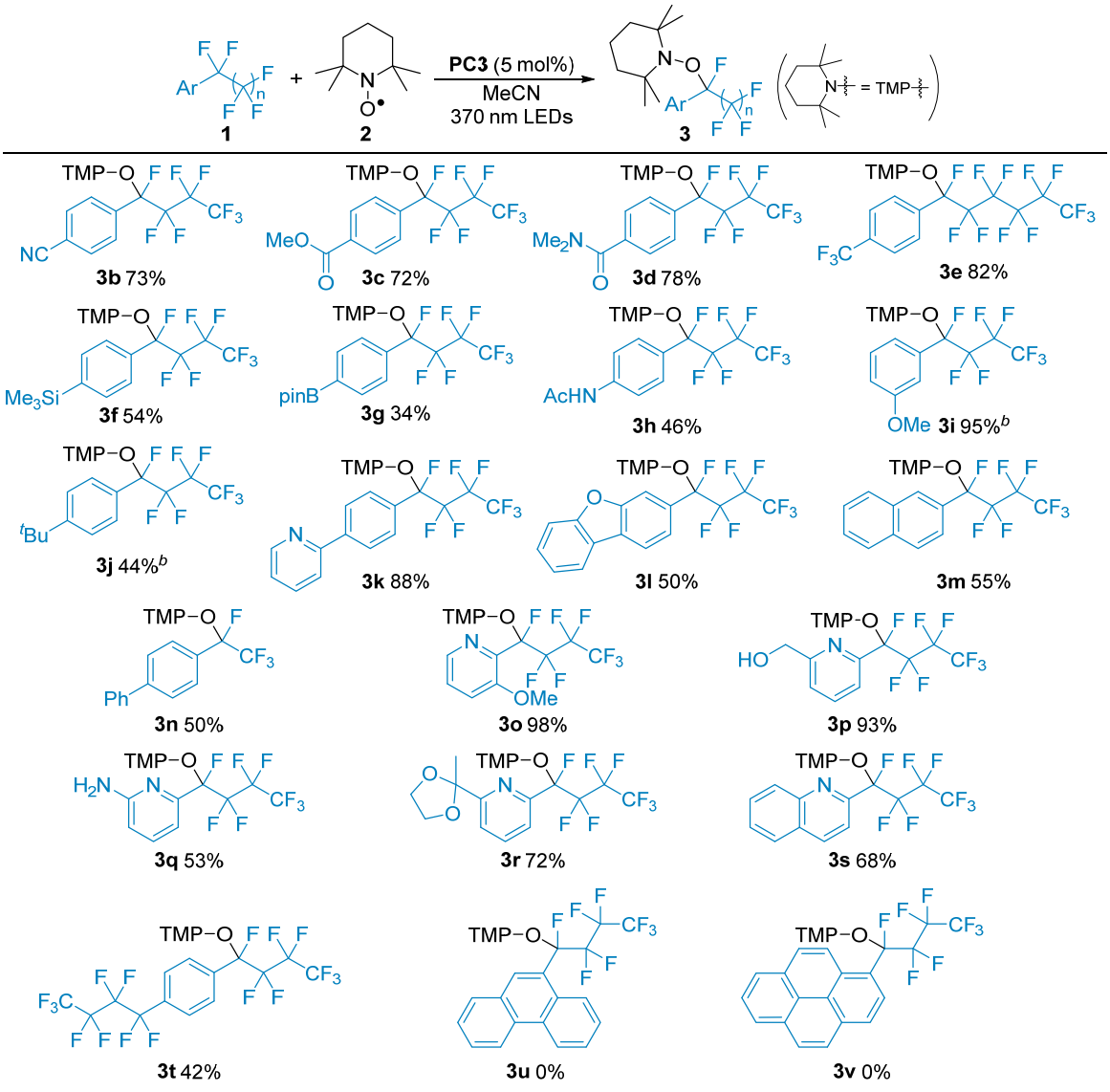


	PC2 (R = H)	PC3 (R = Me)
$\Delta G^{\ddagger}$ (kcal/mol)	12.6	11.6
ΔG_r (kcal/mol)	3.8	3.7
λ (kcal/mol)	42.3	38.8
θ (°)	18.0	14.5

Figure 2. (A) Quenching rate constants of PC* and PC$^{\bullet+}$. (B) Activation energies ($\Delta G^{\ddagger}$), Gibbs free energy changes (ΔG_r), reorganization energies (λ), and bent angles (θ) in the 2nd SET by DFT calculation studies ((U)ωB97XD/6-31+G(d,p)/SMD(acetonitrile)).

Using the determined optimal reaction conditions, we explored the substrate scope of this aminoxylation (Scheme 2). Electron withdrawing groups such as CN, CO_2Me, and $CONMe_2$ were available for the transformation (**3b**, **3c**, **3d**). The CF_3-substituted perfluoroalkylarene selectively underwent the aminoxylation in the perfluoroalkyl group (**3e**).[28] Silyl and boryl substituents were also tolerated (**3f** and **3g**). It is noted that perfluoroalkylarenes with electron-donating groups smoothly underwent aminoxylation (**3h**, **3i**, and **3j**). The development of **PC3** with high reducing ability overcame the limitation of the substrate scope in our previous report for defluoroallylation.[4g] Substrates including pyridine, benzofuran, or naphthalene moieties efficiently gave the corresponding products (**3k**, **3l**, and **3m**). The reaction of perfluoroethylarene also gave **3n** in a moderate yield. Perfluoroalkyl-substituted pyridines were feasible substrates, and various functional groups such as OMe, OH, NH_2, and acetal groups were compatible with the present reaction (**3o**, **3p**, **3q**, and **3r**). A quinoline-based substrate afforded desired product **3s** in 68% yield. The substrate with two C_4F_9 groups underwent single aminoxylation to give product **3t**. Reactions of perfluoroalkylphenanthrene and -pyrene gave no products (**3u** and **3v**).[29]

Scheme 2. Substrate Scope of Perfluoroalkylarenes in the Aminoxylation with TEMPO

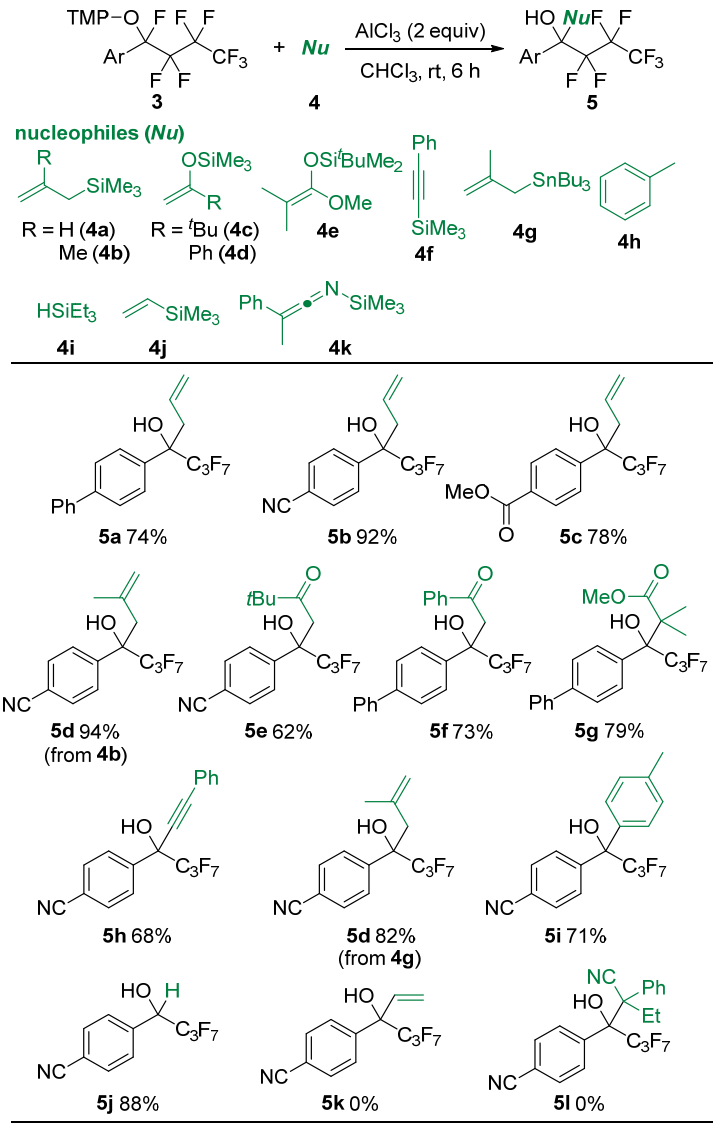


[a]**1a** (0.4 mmol), **2** (0.8 mmol), **PC3** (0.02 mmol), MeCN (2 mL), irradiation with 370 nm LEDs at 35 °C for 24 h. Isolated yields are shown. [b]**2a** (1.2 mmol) and **PC3** (0.04 mmol).

Next, Lewis acid mediators and nucleophilic coupling partners were surveyed for the selective C–F bond transformation of aminoxylated compounds **3** via an ionic path[30] (Tables S3 and S4). The combination of $AlCl_3$ and organosilicon reagents was found to be appropriate in the transformation (Scheme 3). After isolation of **3a**, which was provided by aminoxylation between **1a** and **2** (Table 1, Entry 10), **3a** was treated with allyltrimethylsilane (**4a**) in the presence of $AlCl_3$. The reaction gave allylated alcohol **5a** in 74% yield, in which the amino group was removed on the O atom (*vide infra*). The CN and CO_2Me groups were tolerated in this allylation (**5b** and **5c**). Various organosilicon nucleophiles were applicable to this C–F bond transformation. Methallylsilane **4b**, silyl enol ethers **4c** and **4d**, silyl ketene acetal **4e**, and alkynylsilane **4f** provided functionalized perfluoroalkyl alcohols **5d**, **5e**, **5f**, **5g**, and **5h**, respectively. An organotin reagent, methallyltributyltin (**4g**) also acted well as a nucleophile. Toluene (**4h**) was a suitable nucleophile for the

Friedel-Crafts reaction to give product **5i**. The reduction with $HSiEt_3$ smoothly proceeded to yield defluorinated product **5j**. On the other hand, vinylsilane **4j** and silyl ketene imine **4k** were not applicable.

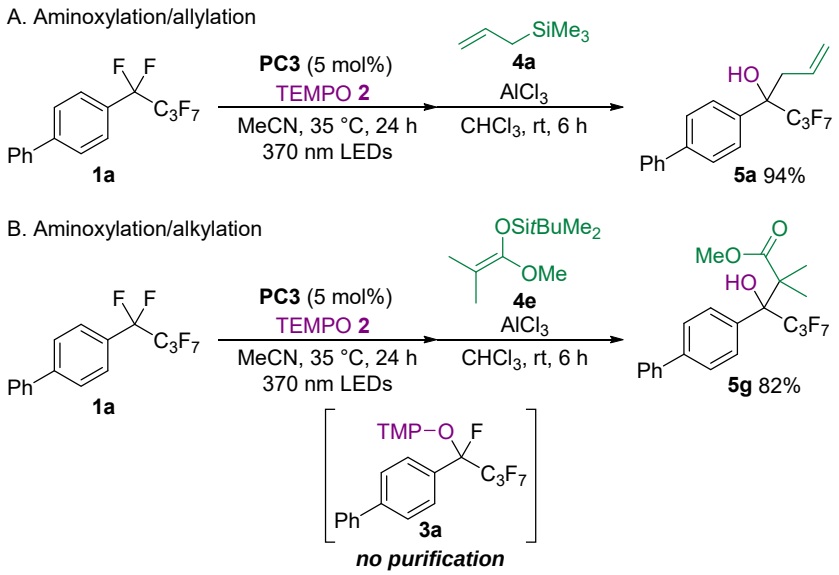
Scheme 3. Second Defluorinative Transformation Mediated by a Lewis Acid



[a]**3** (0.2 mmol), **4** (1.0 mmol), and $AlCl_3$ (0.4 mmol) in $CHCl_3$ (2 mL) at room temperature for 6 h. Isolated yields are shown. [b]**4h** (1 mL).

Using the radical and ionic methods to realize two types of C–F bond activation, we demonstrated a one-pot transformation of a CF_2 unit via aminoxylation and allylation reactions (Scheme 4A). After aminoxylation of perfluoroalkylarene **1a** with **2** using **PC3** and 370 nm LED light, the crude product was treated with **4a** and $AlCl_3$ to give product **5a** in high yield. The one-pot aminoxylation/alkylation was also successful using silyl ketene acetal **4e** (Scheme 4B).

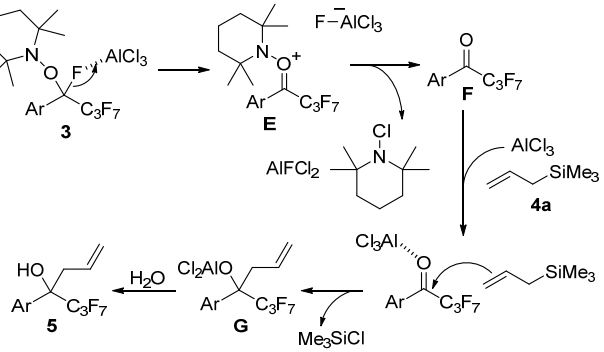
Scheme 4. One-pot Sequential C–F Bond Transformation of CF_2 Unit



[a]**1a** (0.4 mmol), **2** (0.8 mmol), **PC3** (0.02 mmol), MeCN (2 mL). Then, **4** (2.0 mmol), $AlCl_3$ (1.2 mmol), $CHCl_3$ (4 mL). Yields were determined by ^1H NMR spectroscopy using an internal standard.

Scheme 5 illustrates a proposed mechanism for $AlCl_3$-mediated C–F bond allylation of **3** with allylsilane **4a**. $AlCl_3$ abstracts F^- to give oxonium intermediate **E**. Then *N*-chloroamine and $AlFCl_2$ are eliminated to give ketone **F**. $AlCl_3$ activates **F**, and **4a** adds to a carbonyl group, affording **G**.[31] Finally, hydrolysis of **G** yields product **5**. The generation of **F** was confirmed when **3** was treated with $AlCl_3$ in the absence of nucleophiles (Scheme S4). Other typical Lewis acids[30] were not effective (Table S3). $AlCl_3$ can mediate abstraction of fluoride ion of **3** and activation of a less basic carbonyl group of **F** due to high Lewis acidity. In terms of the intermediacy of ketone **F**, our procedure has an impact on the synthesis of perfluoroalkyl ketones from PFAS via defluorination. Traditional methods such as defluorination of fully-perfluorinated alkylbenzenes,[32] perfluoroalkyl-substituted anilines[33] and -enamines,[34] and α-hydroperfluoroalkanoic acid esters[5,35] have problems such as narrow substrate scopes. Especially for the synthesis of aryl ketones **F**, available substrates were extremely limited. In this report, compounds **3** can be synthesized and used as synthetic equivalents for **F** with the wide substrate scope and the high compatibility of functional groups. Our process is an efficient synthetic method of functionalized perfluoroalkyl alcohols like **5** from PFAS.

Scheme 5. Proposed Mechanism for C–F Bond Transformation Mediated by $AlCl_3$



3-3. Conclusion

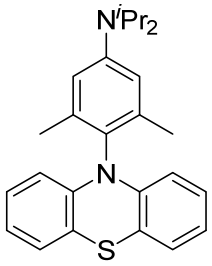
In summary, a combination of photoredox catalysis and Lewis acid activation realizes sequential C–F bond transformation of a CF_2 unit in perfluoroalkylarenes. Functionalized perfluoroalkyl alcohols were synthesized by phenothiazine-catalyzed photo-induced defluoroaminoxylation with TEMPO and subsequent $AlCl_3$ mediated substitution of a F atom with various carbon nucleophiles. Mechanistic studies revealed that the rigidity of molecular structure and the introduction of an electron-donating group is important in catalyst design to achieve fast catalyst regeneration and effective photo-excited reduction potential.

3-4. Experimental Section

NMR spectra were recorded on JEOL JNM-ECZL400S spectrometers (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 376 MHz for ^{19}F NMR). Chemical shifts were reported in ppm on the δ scale relative to tetramethylsilane (δ = 0 for ^{1}H NMR) and $CDCl_3$ (δ = 77.0 for ^{13}C NMR) as an internal reference. Chemical shifts were reported in ppm on the δ scale relative to $CF_3C_6H_5$ (δ = -63.7 for ^{19}F NMR) as an external reference. Coupling constants were quoted in Hz (J). ^{1}H NMR spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), sextet (sext), and septet (sep). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). New compounds were characterized by ^{1}H, ^{13}C, ^{13}C off-resonance techniques, COSY, HSQC, and HMBC. Infrared (IR) spectra were recorded on a JASCO FT/IR-6200 Fourier transform infrared spectrophotometer. A column chromatography was performed with silica gel. Purification by recycle HPLC was performed on SHIMADZU recycle HPLC system (SPD-20A, RID-10A, DGU-20A, LC-6AD, and FCV-20H2) and Japan Analytical Industry Co. (NEXT recycling preparative HPLC). UV-vis spectra were recorded on JASCO V-670 and V-770 spectrophotometers. Fluorescence lifetime measurements were performed on Hamamatsu Photonics K.K. Quantaurus-Tau. Cyclic voltammetry and differential pulse voltammetry measurements were performed with an ALS-600C electrochemical analyzer using a glassy carbon working electrode, a Pt counter electrode, and an $Ag/AgNO_3$ reference electrode at room temperature in MeCN containing 0.1 M nBu_4NBF_4 as the supporting electrolyte. Sub-micro second laser flash photolysis was performed with a tunable YAG-OPO laser at 355 nm. The monitoring system consists of a 150 W Xenon arc lamp as light source, a Unisoku MD200 monochromator detection and a photomultiplier. Sub-nano second laser flash photolysis was performed with Unisoku picoTAS. Pulse radiolysis experiments were performed using an electron pulse (27 MeV, 8 ns, 0.87 kGy per pulse) from a linear accelerator at Osaka University. Details of the detection system for transient absorption have been described elsewhere.[1] Reactions were carried out in dry solvents under nitrogen atmosphere, unless otherwise stated. Reagents were purchased from Sigma-Aldrich or Tokyo Chemical Industry Co., Ltd. (TCI), FUJIFILM Wako Pure Co., Ltd., and used after purification by distillation or used without purification for solid substrates. Light irradiation was performed by using a 370 nm LED (Kessil PR160L-370). X-ray diffraction analysis was carried out by Rigaku XtaLAB Synergy with Hypix-6000HE.

Materials

***N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine (PC3)**



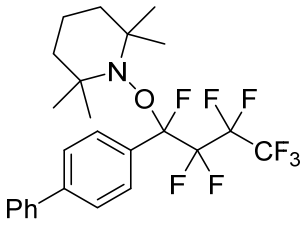
To a solution of $Pd(dppf)_2{\cdot}CH_2Cl_2$ (0.600 mmol, 0.703 g), and KO^{t}Bu (24.0 mmol, 0.0630 g) in DMSO (16 mL) were added 1-bromo-3,5-dimethylbenzene (12 mmol, 2.22 g) and diisopropylamine (24.0 mmol, 2.43 g). The mixture was stirred at 150 °C for 48 hours. After cooling to room temperature, the reaction mixture was extracted with ether (20 mL x 3) and the combined organic layers were washed with brine (20 mL x 3). The organic layer was filtrated through a pad of silica, the solvent was removed under reduced pressure, the residue was diluted hexane (15 mL). The products were extracted with 3 M HCl aq (20 mL x 4) then, 50 w/w% NaOH aq (10 mL) was added and the products were extracted with ether (10 mL x 4). The organic layers were dried over $MgSO_4$ and concentrated under vacuum to afford *N*,*N*-diisopropyl-3,5-dimethylaniline (16% yield measured by ^{1}H NMR) with regioisomer. To a solution of crude *N*,*N*-diisopropyl-3,5-dimethylaniline (1.87 mmol) in MeCN (12 mL) was dropped NBS (1.86 mmol, 0.331 g) in MeCN (6 mL) at 0 °C. Then the mixture was stirred at room temperature for 12 h. The volatile solvent was removed under reduced pressure and the residue was filtrated a pad of silica with ether. The solvent was removed under vacuum to give crude 4-bromo-*N*,*N*-diisopropyl-3,5-dimethylaniline (1.45 mmol measured by ^{1}H NMR). To a solution of $Pd_2(dba)_3$ (0.200 mmol, 0.183 g), tri-*tert*-butylphosphonium tetrafluoroborate (0.2 mmol, 0.0580g), and phenothiazine (2.30 mmol, 0.458 g) in toluene (6 mL) were added crude 4-bromo-*N*,*N*-diisopropyl-3,5-dimethylaniline (1.45 mmol) and potassium KO^{t}Bu (3.00 mmol, 0.337 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 125 °C for 48 h. the mixture was extracted with ethyl acetate (10 mL x 3) and the combined organic layers were washed with brine (20 mL x 2). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 20 cm, diameter 26 mm silica gel) and recrystallization (ether/MeOH) to give the product (white solid, 0.520 g, 65%).

mp: 134-135 °C; **IR**: (KBr) 3437, 2965, 1600 cm^{-1}; **^{1}H NMR**: (400 MHz, in acetone-d_6) 6.88 (dd, J = 7.5, 1.6 Hz, 2H), 6.84 (m, 2H), 6.80 (s, 2H), 6.73 (m, 2H), 5.98 (dd, J = 8.3, 1.2 Hz, 2H), 3.92 (sep, J = 6.8 Hz, 2H), 2.09 (s, 6H), 1.30 (s, 6H), 1.28 (s, 6H); **^{13}C NMR**: (100 MHz, in acetone-d_6) 149.0, 142.8, 138.2, 128.1, 127.4, 126.9, 122.8, 118.8, 118.2, 114.9, 48.0, 21.5, 18.5; **HRMS**: (DART+) Calculated: ($C_{26}H_{31}N_2S$) 403.2203 ($[M+H]^+$) Found: 403.2199

Products

The preparation and characterization of new compounds were described below.

1-(1-([1,1'-biphenyl]-4-yl)-1,2,2,3,3,4,4,4-octafluorobutoxy)-2,2,6,6-tetramethylpiperidine (3a)

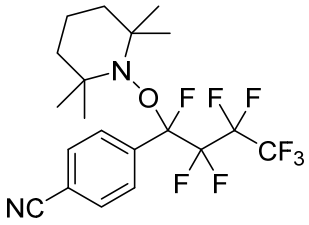


To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 4-(nonafluorobutyl)biphenyl **1a** (0.400 mmol, 0.149 g) in MeCN (2 mL) was added TEMPO **2** (0.813 mmol, 0.127 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 370 nm LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.144 g, 71%).

IR: (neat) 2984, 2931, 1468 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.79 (d, *J* = 8.2 Hz, 2H), 7.64-7.59 (m, 4H), 7.46-7.42 (m, 2H), 7.38-7.34 (m, 1H), 1.58-1.25 (m, 6H), 1.23 (s, 3H), 1.20 (s, 3H), 1.11 (d, *J* = 1.1 Hz, 3H), 0.99 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 142.4, 140.0, 130.0-129.8 (m), 128.8, 127.8, 127.1, 125.5, 118.0 (m), 113.9 (m), 112.9 (m), 109.6 (m), 62.0 (d, *J* = 1.4 Hz), 61.2, 41.2, 40.5, 33.6 (d, *J* = 11.0 Hz), 33.2 (d, *J* = 1.4 Hz), 20.8, 20.7, 16.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.8 (td, *J* = 9.6, 5.5 Hz, 3F), -97.8 (d, *J* = 5.5 Hz, 1F), -114.7 (dd, *J* = 284.5, 3.8 Hz, 1F), -116.2--117.1 (m, 1F), -123.1 (d, *J* = 14.3 Hz, 2F); **HRMS**: (DART+) Calculated: ($C_{25}H_{28}NOF_8$) 510.2038 ($[M+H]^+$)

Found: 510.2047

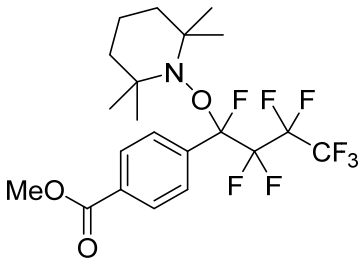
4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzonitrile (3b)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 4-(perfluorobutyl)benzonitrile **1b** (0.404 mmol, 0.134 g) in MeCN (2 mL) was added TEMPO **2** (0.812 mmol, 0.127 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 0.133 g, 73%).

mp: 80-81 °C; **IR**: (KBr) 2234 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.87 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 1.59-1.20 (m, 12H), 1.04 (s, 3H), 0.94 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 135.7 (d, *J* = 29.6 Hz), 130.8, 130.2 (dd, *J* = 9.1, 2.9 Hz), 118.1, 117.7 (m), 114.0, 112.9 (m), 112.6 (m), 109.3 (m), 62.3 (d, *J* = 1.4 Hz), 61.5, 41.1, 40.4, 33.5 (d, *J* = 11.0 Hz), 33.0, 20.7, 20.6, 16.5; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.3 (m, 3F), -99.6 (s, 1F), -116.3 (m, 1F), -118.0 (m, 1F), -124.7 (m, 2F); **HRMS**: (DART+) Calculated: ($C_{20}H_{23}N_2OF_8$) 459.1677 ($[M+H]^+$) Found: 459.1695

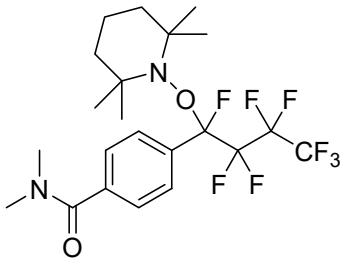
methyl 4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzoate (3c)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and methyl 4-(perfluorobutyl)benzoate **1c** (0.400 mmol, 0.142 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 370 nm LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.141 g, 72%).

IR: (neat) 1729 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 8.05 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 3.94 (s, 3H), 1.58-1.19 (m, 12H), 1.06 (s, 3H), 0.94 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 166.5, 135.5 (dd, *J* = 29.2, 1.4 Hz), 131.4, 129.5 (dd, *J* = 8.6, 2.9 Hz), 128.1, 117.8 (m), 113.4 (m), 112.7 (m), 109.5 (m), 62.2 (d, *J* = 1.4 Hz), 61.3, 52.3, 41.1, 40.5, 33.5 (d, *J* = 11.0 Hz), 33.1, 20.8, 20.7, 16.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.3 (m, 3F), -99.5 (m, 1F), -116.3 (m, 1F), -118.0 (m, 1F), -124.7 (m, 2F); **HRMS**: (DART+) Calculated: ($C_{21}H_{26}NO_3F_8$) 492.1780 ($[M+H]^+$) Found: 492.1795

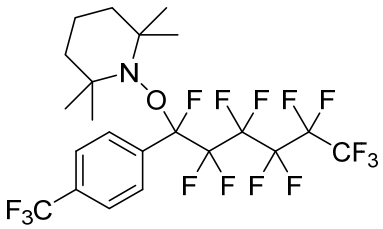
***N*,*N*-dimethyl-4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzamide (3d)**



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and *N*,*N*-dimethyl-4-(perfluorobutyl)benzamide **1d** (0.400 mmol, 0.147 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.156 g, 78%).

IR: (neat) 1640 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.78 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 3.13 (s, 3H), 2.98 (s, 3H), 1.58-1.20 (m, 12H), 1.07 (s, 3H), 0.97 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 170.7, 137.6, 132.1 (d, *J* = 27.7 Hz), 129.4 (dd, *J* = 8.6, 2.9 Hz), 125.7, 117.8 (m), 113.4 (m), 112.7 (m), 109.4 (m), 62.0, 61.2, 41.0, 40.4, 39.4, 35.2, 33.4 (d, *J* = 10.5 Hz), 33.0, 20.7, 20.6, 16.5; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.3 (m, 3F), -99.6 (s, 1F), -116.3 (m, 1F), -118.2 (m, 1F), -124.7 (m, 2F); **HRMS**: (DART+) Calculated: ($C_{22}H_{29}N_2O_2F_8$) 505.2096 ($[M+H]^+$) Found: 505.2119

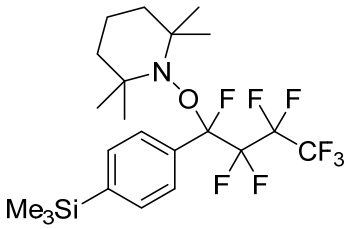
2,2,6,6-tetramethyl-1-(1,2,2,3,3,4,4,4-octafluoro-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butoxy)piperidine (3e)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.040 mmol, 16.2 mg) and 1-(perfluorohexyl)-4-(trifluoromethyl)benzene **1e** (0.403 mmol, 0.187 g) in MeCN (2 mL) was added TEMPO **2** (0.819 mmol, 0.128 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane only, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.199 g, 82%).

IR: (neat) 2941, 1471, 1326 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.87 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 1.59-1.21 (m, 12H), 1.05 (s, 3H), 0.97 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 134.8 (d, J = 29.2 Hz), 132.1 (q, J = 32.7 Hz), 130.1 (m), 124.0 (m), 123.8 (q, J = 272.3 Hz), 117.4 (m), 113.5 (m), 113.3 (m), 111.8 (m), 110.7 (m), 108.7 (m), 62.3 (d, J = 1.4 Hz), 61.5, 41.2, 40.6, 33.6 (d, J = 11.0 Hz), 33.1, 20.8, 20.7, 16.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -64.4 (s, 3F), -82.4 (s, 3F), -99.7 (m, 1F), -115.6 (m, 1F), -116.9 (m, 1F), -120.1 (m, 1F), -121.2 (m, 1F), -123.5 (m, 1F), -124.7 (m, 1F), -126.8 (m, 1F), -128.0 (m, 1F); **HRMS**: (DART+) Calculated: ($C_{22}H_{23}NOF_{15}$) 602.1535 ($[M+H]^+$) Found: 602.1556

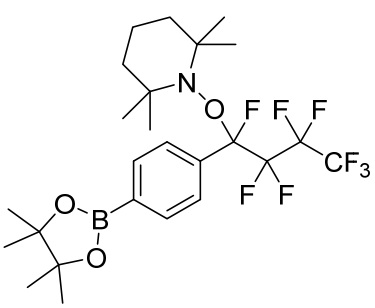
2,2,6,6-tetramethyl-1-(1,2,2,3,3,4,4,4-octafluoro-1-(4-(trimethylsilyl)phenyl)butoxy)piperidine (3f)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and trimethyl(4-(perfluorobutyl)phenyl)silane **1f** (0.397 mmol, 0.146 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane only, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.108 g, 54%).

IR: (neat) 2941, 1468, 1385 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.68 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 1.59-1.19 (m, 12H), 1.07 (s, 3H), 0.94 (s, 3H), 0.28 (9H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 142.7, 131.9, 131.2 (dd, J = 28.7, 1.4 Hz), 128.5 (dd, J = 8.6, 2.9 Hz), 118.0 (m), 114.0 (m), 113.0 (m), 109.7 (m), 62.0 (d, J = 1.4 Hz), 61.1, 41.2, 40.5, 33.6 (d, J = 11.0 Hz), 33.1, 33.0, 20.8, 20.7, 16.7, -1.2; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (m, 3F), -99.6 (s, 1F), -116.1 (m, 1F), -118.1 (m, 1F), -124.6 (m, 2F); **HRMS**: (DART+) Calculated: ($C_{22}H_{32}NOF_8Si$) 506.2120 ($[M+H]^+$) Found: 506.2134

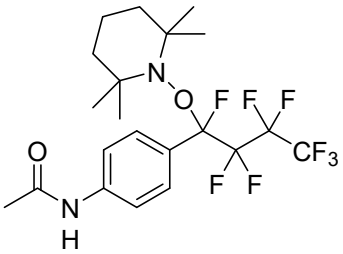
2,2,6,6-tetramethyl-1-(1,2,2,3,3,4,4,4-octafluoro-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butoxy)piperidine (3g)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 4,4,5,5-tetramethyl-2-(4-(perfluorobutyl)phenyl)-1,3,2-dioxaborolane **1g** (0.405 mmol, 0.171 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.0770 g, 34%).

IR: (neat) 2941, 1616, 1519 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.80 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 1.57-1.22 (m, 18H), 1.20 (s, 3H), 1.19 (s, 3H), 1.05 (s, 3H), 0.97 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 133.5 (d, *J* = 28.7 Hz), 133.2, 128.6 (dd, *J* = 8.6, 2.4 Hz), 117.9 (m), 113.7 (m), 112.8 (m), 109.6 (m), 84.0, 62.0 (d, *J* = 1.4 Hz), 61.1, 41.2, 40.5, 33.6 (d, *J* = 11.0 Hz), 33.1, 24.9, 24.8, 20.8, 20.7, 16.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (dd, *J* = 14.3, 9.9 Hz, 3F), -98.9 (d, *J* = 6.6 Hz, 1F), -114.5--115.3 (m, 1F), -116.5--117.3 (m, 1F), -123.2 (d, *J* = 15.3 Hz, 2F); **HRMS**: (DART+) Calculated: ($C_{25}H_{35}BNO_3F_8$) 560.2577 ($[M+H]^+$) Found: 560.2592

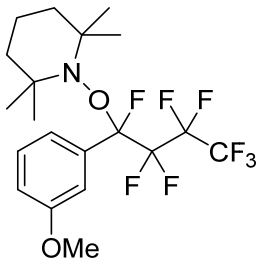
***N*-(4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)phenyl)acetamide (3h)**



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and *N*-(4-(perfluorobutyl)phenyl)acetamide **1h** (0.402 mmol, 0.142 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 65:35, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 0.0905 g, 46%).

mp: 138-139 °C; **IR**: (KBr) 1670, 1606, 1540 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 8.15 (s, 0.4H, AcNH), 8.06 (s, 0.6H, AcNH), 7.66 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 2.19 (s, 3H), 1.57-1.18 (m, 12H), 1.04 (s, 3H), 0.96 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$); 169.0 (d, *J* = 6.7 Hz), 139.4, 130.3 (m), 126.5, 126.2, 118.5 (m), 117.7, 116.9 (m), 113.6 (m), 112.8 (m), 61.9 (d, *J* = 1.4 Hz), 61.1, 41.1, 40.5, 33.5 (d, *J* = 10.5 Hz), 33.1, 24.6, 20.7, 20.6, 16.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.3 (m, 3F), -99.1 (m, 1F), -116.2 (m, 1F), -118.2 (m, 1F), -124.6 (m, 2F); **HRMS**: (CI) Calculated: ($C_{21}H_{27}N_2O_2F_8$) 491.1945 ($[M+H]^+$) Found: 491.1937

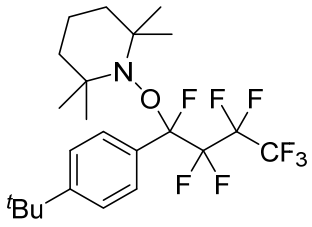
2,2,6,6-tetramethyl-1-(1,2,2,3,3,4,4,4-octafluoro-1-(3-methoxyphenyl)butoxy)piperidine (3i)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 1-methoxy-3-(perfluorobutyl)benzene **1i** (0.400 mmol, 0.130 g) in MeCN (2 mL) was added TEMPO **2** (1.20 mmol, 0.188 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow solid, 0.176 g, 95%).

mp: 74-75 °C; **IR**: (KBr) 2941, 1589, 1468, 1346 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.32-7.24 (m, 3H), 6.97 (m, 1H), 3.81 (s, 3H), 1.62-1.24 (m, 6H), 1.21 (s, 3H), 1.19 (s, 3H), 1.09 (s, 3H), 0.99 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 158.3 (d, J = 1.0 Hz), 132.2 (dd, J = 28.7, 1.9 Hz), 127.9, 121.7 (dd, J = 9.1, 2.9 Hz), 117.9 (m), 115.6 (d, J = 2.9 Hz), 115.5, 113.6 (m), 112.8 (m), 109.6 (m), 62.0 (d, J = 1.4 Hz), 61.1, 55.3, 41.2, 40.6, 33.6 (d, J = 10.5 Hz), 33.1 (d, J = 1.4 Hz), 20.8, 20.7, 16.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (s, 3F), -99.0 (m, 1F), -116.3 (m, 1F), -118.2 (m, 1F), -124.6 (m, 2F); **HRMS**: (DART+) Calculated: ($C_{24}H_{27}N_2OF_8$) 511.1990 ($[M+H]^+$) Found: 511.1993

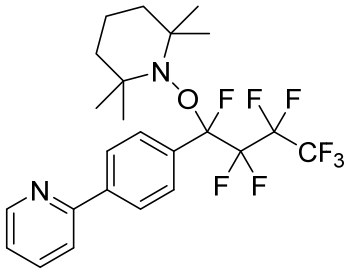
1-(1-(4-(tert-butyl)phenyl)-1,2,2,3,3,4,4,4-octafluorobutoxy)-2,2,6,6-tetramethylpiperidine (3j)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 1-(tert-butyl)-4-(perfluorobutyl)benzene **1j** (0.400 mmol, 0.141 g) in MeCN (2 mL) was added TEMPO **2** (1.20 mmol, 0.188 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane only, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.0860 g, 44%).

IR: (neat) 2951, 1615, 1468, 1367, 1344, 1232 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.63 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 1.61-1.24 (m, 15H), 1.20 (s, 3H), 1.18 (s, 3H), 1.08 (d, J = 1.5 Hz, 3H), 0.89 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 152.9, 129.1 (m), 127.9 (m), 123.8, 118.0 (m), 114.0 (m), 112.9 (m), 109.6 (m), 61.8 (d, J = 1.9 Hz), 61.0, 41.1, 40.5, 34.6, 33.6 (d, J = 11.0 Hz), 33.0 (d, J = 1.4 Hz), 31.2, 20.8, 20.7, 16.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (td, J = 9.6, 5.5 Hz, 3F), -98.7 (m, 1F), -116.1 (m, 1F), -118.0 (m, 1F), -124.6 (m, 2F); **HRMS**: (DART+) Calculated: ($C_{23}H_{32}NOF_8$) 490.2351 ($[M+H]^+$) Found: 490.2370

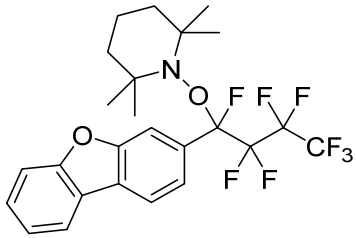
2-(4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)phenyl)pyridine (3k)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 2-(4-(perfluorobutyl)phenyl)pyridine **1k** (0.400 mmol, 0.149 g) in MeCN (2 mL) was added TEMPO **2** (0.806 mmol, 0.126 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.179 g, 88%).

IR: (neat) 2941, 1589, 1468, 1346 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 8.71 (m, 1H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.75 (br, 2H), 7.24 (br, 1H), 1.56-1.20 (m, 12H), 1.10 (s, 3H), 1.02 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 156.3, 149.7, 140.6, 136.8, 131.4 (d, *J* = 29.2 Hz), 129.9 (m), 125.4, 122.5, 120.7, 117.9 (m), 113.8 (m), 112.8 (m), 109.5 (m), 62.0 (d, *J* = 1.4 Hz), 61.1, 41.1, 40.4, 33.5 (d, *J* = 10.5 Hz), 33.1, 20.7, 20.6, 16.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (s, 3F), -99.5 (s, 1F), -116.2 (m, 1F), -118.2 (m, 1F), -124.6 (m, 2F); **HRMS**: (DART+) Calculated: ($C_{24}H_{27}N_2OF_8$) 511.1990 ($[M+H]^+$) Found: 511.1993

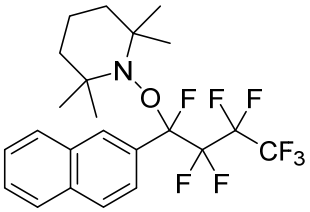
1-(1-(dibenzo[*b*,*d*]furan-3-yl)-1,2,2,3,3,4,4,4-octafluorobutoxy)-2,2,6,6-tetramethylpiperidine (3l)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 3-(perfluorobutyl)dibenzo[*b*,*d*]furan **1l** (0.400 mmol, 0.154 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.104 g, 50%).

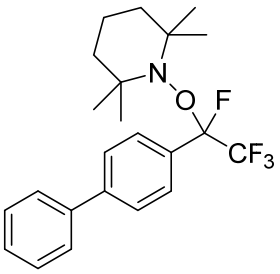
IR: (neat) 2936, 1457, 1346 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.99-7.91 (m, 3H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.48 (m, 1H), 7.34 (m, 1H), 1.56-1.22 (m, 12H), 1.08 (s, 3H), 1.05 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 156.9, 154.9, 129.9, 129.6, 128.0, 125.6, 124.0 (dd, *J* = 9.1, 2.9 Hz), 123.5, 122.9, 121.1, 119.0, 117.9 (m), 113.9 (m), 113.4 (dd, *J* = 9.6, 2.9 Hz), 112.9 (m), 111.8, 109.6 (m), 62.1, 61.2, 41.2, 40.5, 33.6, 33.3, 20.8 (d, *J* = 13.9 Hz), 16.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (t, *J* = 12.6 Hz, 3F), -98.2 (s, 1F), -116.0 (m, 1F), -118.0 (m, 1F), -124.5 (m, 2F); **HRMS**: (DART+) Calculated: ($C_{25}H_{26}NO_2F_8$) 524.1830 ($[M+H]^+$) Found: 524.1837

2,2,6,6-tetramethyl-1-(1,2,2,3,3,4,4,4-octafluoro-1-(naphthalen-2-yl)butoxy)piperidine (3m)



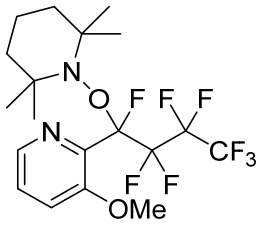
To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 2-(nonafluorobutyl)naphthalene **1m** (0.400 mmol, 0.139 g) in MeCN (2 mL) was added TEMPO **2** (0.819 mmol, 0.128 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.106 g, 55%). **IR**: (neat) 2936, 1471, 1343 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 8.23 (s, 1H), 7.89-7.82 (m, 4H), 7.56-7.48 (m, 2H), 1.60-1.15 (m, 12H), 1.10 (s, 3H), 1.03 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 133.6, 131.9, 129.9 (dd, J = 9.8, 2.2 Hz), 129.0, 128.5, 128.4 (d, J = 28.7 Hz), 127.43, 127.37, 126.4, 126.1 (d, J = 3.3 Hz), 118.0 (m), 114.0 (m), 113.0 (m), 109.7 (m), 62.1 (d, J = 1.4 Hz), 61.3, 41.2, 40.5, 33.7 (d, J = 10.5 Hz), 33.3 (d, J = 1.9 Hz), 20.9, 20.7, 16.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.8 (td, J = 9.9, 5.5 Hz, 3F), -98.0 (s, 1F), -114.1--114.9 (m, 1F), -116.1--117.0 (m, 1F), -123.1 (d, J = 15.3 Hz, 2F); **HRMS**: (DART+) Calculated: ($C_{23}H_{26}NOF_8$) 484.1881 ($[M+H]^+$) Found: 484.1897

1-(1-([1,1'-biphenyl]-4-yl)-1,2,2,2-tetrafluoroethoxy)-2,2,6,6-tetramethylpiperidine (3n)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 4-(perfluoroethyl)-1,1'-biphenyl **1n** (0.400 mmol, 0.109 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane only, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.0816 g, 50%).
IR: (neat) 2937, 1471, 1249, 1193 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.75 (d, J = 8.0 Hz, 2H), 7.64-7.59 (m, 4H), 7.47-7.43 (m, 2H), 7.36 (m, 1H), 1.58-1.25 (m, 12H), 1.16 (s, 3H), 0.69 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 142.4, 140.0, 130.5 (d, J = 29.6 Hz), 129.1 (d, J = 7.2 Hz), 128.8, 127.8, 127.1, 125.7, 121.5 (qd, J = 287.8, 40.2 Hz), 110.7 (dq, J = 229.9, 32.5 Hz), 61.5 (d, J = 1.4 Hz), 61.1, 41.0, 40.3, 33.7 (d, J = 11.0 Hz), 33.3, 20.8, 20.7, 16.8; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -79.4 (s, 3F), -103.2 (s, 1F); **HRMS**: (DART+) Calculated: ($C_{23}H_{28}NOF_4$) 410.2102 ($[M+H]^+$) Found: 410.2106

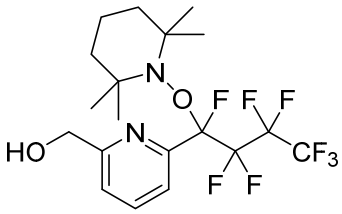
3-methoxy-2-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)pyridine (3o)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 3-methoxy-2-(nonafluorobutyl)pyridine **1o** (0.409 mmol, 0.134 g) in MeCN (2 mL) was added TEMPO **2** (0.812 mmol, 0.127 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 90:10, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.186 g, 98%).

IR: (neat) 2938, 1584, 1468, 1432 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 8.18 (dd, *J* = 3.6, 1.9 Hz, 1H), 7.30-7.27 (m, 2H), 3.84 (s, 3H), 1.63-1.06 (m, 15H), 0.18 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 156.2 (d, *J* = 3.3 Hz), 140.7 (dt, *J* = 37.3, 2.9 Hz), 138.6 (d, *J* = 2.9 Hz), 125.7, 119.8, 118.2 (m), 113.4 (m), 113.3 (m), 110.0 (m), 61.6 (d, *J* = 1.4 Hz), 61.3 (d, *J* = 1.4 Hz), 55.1, 40.9, 40.4, 33.3, 33.2, 21.3, 20.5, 16.9; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.9 (t, *J* = 10.4 Hz, 3F), -105.9 (m, 1F), -113.5 (dd, *J* = 283.4, 9.3 Hz, 1F), -115.7 (d, *J* = 283.9 Hz, 1F), -121.0 (ddd, *J* = 283.9, 28.5, 9.9 Hz, 1F), -123.1 (d, *J* = 285.0 Hz, 1F); **HRMS**: (DART+) Calculated: ($C_{19}H_{25}N_2O_2F_8$) 465.1783 ($[M+H]^+$) Found: 465.1789

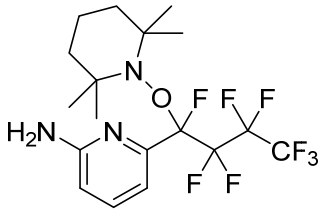
(6-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)pyridin-2-yl)methanol (3p)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and (6-(perfluorobutyl)pyridin-2-yl)methanol **1p** (0.403 mmol, 0.132 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 60:40, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.174 g, 93%)

IR: (neat) 3412, 2936, 1460 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.76 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 4.75 (s, 2H), 3.93 (s, 1H), 1.56-1.08 (m, 15H), 0.54 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 150.5 (dt, *J* = 39.0, 2.3 Hz), 150.3, 136.1, 124.0 (d, *J* = 4.8 Hz), 121.0, 117.9 (m), 113.0 (m), 111.9 (m), 109.6 (m), 63.4, 61.9 (d, *J* = 1.4 Hz), 61.1, 41.0, 40.3, 33.6 (d, *J* = 12.9 Hz), 32.9, 20.8, 20.5, 16.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (m, 3F), -101.3 (d, *J* = 25.2 Hz, 1F), -117.1 (m, 2F), -123.8 (ddd, *J* = 286.9, 26.0, 5.8 Hz, 1F), -125.4 (m, 1F); **HRMS**: (DART+) Calculated: ($C_{19}H_{25}N_2O_2F_8$) 465.1783 ($[M+H]^+$) Found: 465.1786

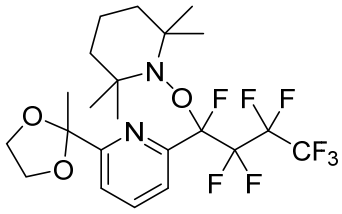
6-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)pyridin-2-amine (3q)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 6-amino-2-(perfluorobutyl)pyridine **1q** (0.404 mmol, 0.125 g) in MeCN (2 mL) was added TEMPO **2** (0.819 mmol, 0.128 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 80:20, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.0953 g, 53%).

IR: (neat) 3400, 2938, 1613, 1466, 1345 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.45 (t, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 4.40 (s, 2H), 1.57-1.20 (m, 12H), 1.15 (s, 3H), 0.80 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 156.2 (d, *J* = 3.8 Hz), 149.9 (d, *J* = 37.3 Hz), 136.8, 118.0 (m), 115.5 (d, *J* = 6.2 Hz), 113.0 (m), 112.0 (m), 109.6 (m), 109.0, 61.8 (d, *J* = 1.9 Hz), 60.9, 41.1, 40.5, 33.7 (d, *J* = 12.9 Hz), 33.2, 20.8, 20.7, 16.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (m, 3F), -102.9 (m, 1F), -117.3 (m, 2F), -123.6 (m, 1F), -125.5 (m, 1F); **HRMS**: (CI) Calculated: ($C_{18}H_{24}N_3OF_8$) 450.1792 ($[M+H]^+$) Found: 450.1789

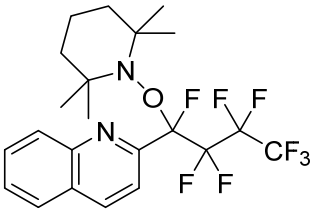
2-(2-methyl-1,3-dioxolan-2-yl)-6-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)pyridine (3r)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 2-(2-methyl-1,3-dioxolan-2-yl)-6-(perfluorobutyl)pyridine **1r** (0.401 mmol, 0.154 g) in MeCN (2 mL) was added TEMPO **2** (0.825 mmol, 0.129 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 370 nm LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane/ethyl acetate = 9:1, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.288 g, 72%).

mp: 64-65 °C; **IR**: (KBr) 2941, 1232, 1200 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.74 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 4.12-4.05 (m, 2H), 3.98-3.93 (m, 1H), 3.89-3.84 (m, 1H), 1.72 (s, 3H), 1.57-1.07 (m, 15H), 0.43 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 158.2 (d, *J* = 3.1 Hz), 151.3 (dt, *J* = 39.2, 2.4 Hz), 135.5, 124.5 (d, *J* = 4.1 Hz), 120.1, 117.9 (m), 112.8 (m), 111.9 (m), 109.5 (m), 108.5, 64.9, 64.7, 61.6 (d, *J* = 1.7 Hz), 60.9 (d, *J* = 1.0 Hz), 40.8, 40.1, 33.5 (d, *J* = 12.9 Hz), 32.7, 24.0, 20.7, 20.4, 16.5; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (td, *J* = 9.8, 4.6 Hz, 3F), -100.2 (d, *J* = 25.6 Hz, 1F), -116.8 (m, 1F), -117.8 (m, 1F), -123.6 (m, 1F), -125.2 (dt, *J* = 286.7, 7.7 Hz, 1F); **HRMS**: (CI) Calculated: ($C_{22}H_{29}N_2O_3F_8$) 521.2050 ($[M+H]^+$) Found: 521.2058

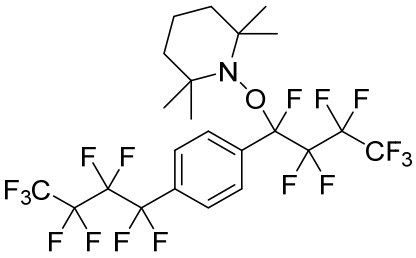
2-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)quinoline (3s)



To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 2-(perfluorobutyl)quinoline **1s** (0.400 mmol, 0.139 g) in MeCN (2 mL) was added TEMPO **2** (0.806 mmol, 0.126 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 370 nm LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane , column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.131 g, 68%).

IR: (neat) 2976, 2936, 1351 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 8.16 (d, *J* = 8.7 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.84-7.82(m, 2H), 7.71 (m, 1H), 7.59 (m, 1H), 1.58-1.01 (m, 15H), 0.52 (3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 152.0 (dt, *J* = 38.9, 2.3 Hz), 145.8 (d, *J* = 3.3 Hz), 134.8, 130.2, 129.5, 127.72, 127.70, 127.4, 121.9 (d, *J* = 4.3 Hz), 118.1 (m), 113.1 (m), 112.3 (m), 109.8 (m), 62.0 (d, *J* = 1.4 Hz), 61.2, 41.0, 40.3, 33.7 (d, *J* = 12.4 Hz), 32.9, 20.9, 20.6, 16.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -83.5 (td, *J* = 9.9, 4.4 Hz, 3F), -101.8 (d, *J* = 25.2 Hz, 1F), -117.4--119.2 (m, 2F), -124.8 (m, 1F), -126.3 (m, 1F); **HRMS**: (DART+) Calculated: ($C_{22}H_{25}N_2OF_8$) 485.1834 ($[M+H]^+$) Found: 485.1846

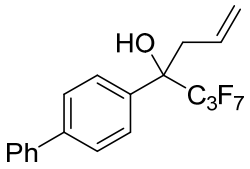
2,2,6,6-tetramethyl-1-(1,2,2,3,3,4,4,4-octafluoro-1-(4-(perfluorobutyl)phenyl)butoxy)piperidine (3t)



To a solution of *N*,*N*-diisopropyl-3,5-dimethyl-4-(10*H*-phenothiazin-10-yl)aniline **PC3** (0.020 mmol, 8.2 mg) and 1,4-bis(perfluorobutyl)benzene **1t** (0.401 mmol, 0.206 g) in MeCN (2 mL) was added TEMPO **2** (0.801 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 370 nm LED irradiation for 24 h. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) and GPC to give the product (colorless oil, 0.109 g, 42%).

IR: (neat) 2940, 1393, 1241, 1202 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.89 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 1.59-1.25 (m, 6H), 1.22 (s, 3H), 1.20 (s, 3H), 1.06 (s, 3H), 0.89 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 135.1 (d, *J* = 29.6 Hz), 130.4 (t, *J* = 24.4 Hz), 129.9 (dd, *J* = 8.8, 3.1 Hz), 125.5 (t, *J* = 6.0 Hz), 117.9 (m), 117.4 (m), 115.5 (m), 113.2 (m), 112.8 (m), 110.3 (m), 109.5 (m), 108.9 (m), 62.3 (d, *J* = 1.4 Hz), 61.4, 41.2, 40.5, 33.5 (d, *J* = 10.5 Hz), 33.0, 20.8, 20.7, 16.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.3--82.5 (m, 6F), -99.1 (s, 1F), -112.9 (m, 2F), -116.3 (m, 1F), -118.0 (m, 1F), -124.3 (s, 2F), -124.7--124.8 (m, 2F), -127.0 (s, 2F); **HRMS**: (DART+) Calculated: ($C_{23}H_{23}NOF_{17}$) 652.1503 ($[M+H]^+$) Found: 652.1522

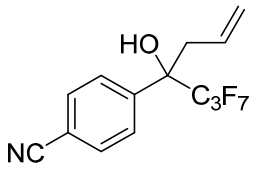
4-([1,1'-biphenyl]-4-yl)-5,5,6,6,7,7,7-heptafluorohept-1-en-4-ol (5a)



To a solution of 1-(1-([1,1'-biphenyl]-4-yl)-1,2,2,3,3,4,4,4-octafluorobutoxy)-2,2,6,6-tetramethylpiperidine **1a** (0.200 mmol, 0.102 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.402 mmol, 0.0536 g) and allyltrimethylsilane **4a** (1.03 mmol, 0.117 g). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography (hexane/$CHCl_3$ = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.0579 g, 74%).

IR: (neat) 3553, 3080, 3035, 1487 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.62-7.60 (m, 6H), 7.46-7.42 (m, 2H), 7.37-7.33 (m, 1H), 5.51-5.40 (m, 1H), 5.29-5.21 (m, 2H), 3.07 (dd, J = 14.1, 5.8 Hz, 1H), 2.91 (dd, J = 14.1, 8.5 Hz, 1H), 2.68 (s, 1H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 141.1, 140.2, 135.7, 130.2, 128.8, 127.6, 127.1, 127.0, 126.8, 122.5, 117.8 (m), 115.8 (m), 110.1 (m), 76.7 (m), 40.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.1 (t, J = 11.0 Hz, 3F), -118.4 (m, 1F), -119.8 (m, 1F), -122.6 (m, 1F), -125.4 (m, 1F); **HRMS**: (EI) Calculated: ($C_{19}H_{15}OF_7$) 392.1011 (M^+) Found: 392.1012

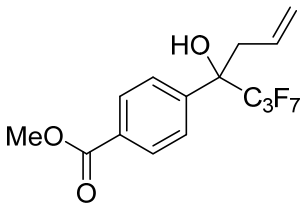
4-(5,5,6,6,7,7,7-heptafluoro-4-hydroxyhept-1-en-4-yl)benzonitrile (5b)



To a solution of 4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzonitrile **3b** (0.200 mmol, 0.0917 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.403 mmol, 0.0537 g) and allyltrimethylsilane **4a** (1.02 mmol, 0.116 g). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography (hexane/$CHCl_3$ = 30:70, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 0.0628 g, 92%).

mp: 74-75 °C; **IR**: (KBr) 3393, 2244, 1221 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.73-7.68 (m, 4H), 5.38 (m, 1H), 5.28-5.22 (m, 2H), 3.02-2.96 (m, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 142.1, 132.0, 129.1, 127.5, 123.0, 118.3, 117.5 (m), 115.6 (m), 112.4, 109.9 (m), 76.7 (m), 40.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (t, J = 11.0 Hz, 3F), -118.3 (m, 1F), -119.8 (m, 1F), -122.8 (m, 1F), -125.1 (m, 1F); **HRMS**: (DART+) Calculated: ($C_{14}H_{11}NOF_7$) 342.0723 ($[M+H]^+$) Found: 342.0732

methyl 4-(5,5,6,6,7,7,7-heptafluoro-4-hydroxyhept-1-en-4-yl)benzoate (5c)

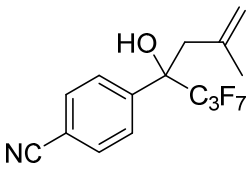


To a solution of methyl 4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzoate **3c** (0.200 mmol, 0.0982 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.400 mmol, 0.0533 g) and allyltrimethylsilane **4a** (1.05 mmol, 0.120 g). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was

collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography ($CHCl_3$ only, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.0582 g, 78%).

IR: (neat) 3450, 1710 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 8.06 (m, 2H), 7.66 (m, 2H), 5.39 (m, 1H), 5.26-5.20 (m, 2H), 3.93 (s, 3H), 3.06-2.91 (m, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 166.7, 141.8 (d, J = 1.9 Hz), 130.1, 129.6, 129.4, 126.7, 122.6, 117.6 (m), 115.7 (m), 110.0 (m), 76.9 (t, J = 23.7 Hz), 52.2, 40.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (t, J = 10.4 Hz, 3F), -118.3 (m, 1F), -119.9 (m, 1F), -122.8 (m, 1F), -125.3 (m, 1F); **HRMS**: (EI) Calculated: ($C_{15}H_{13}O_3F_7$) 374.0753 (M^+) Found: 374.0759

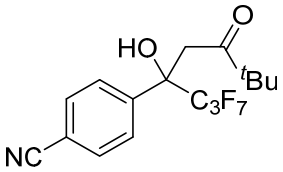
4-(5,5,6,6,7,7,7-heptafluoro-4-hydroxy-2-methylhept-1-en-4-yl)benzonitrile (5d)



To a solution of 4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzonitrile **3b** (0.200 mmol, 0.0917 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.400 mmol, 0.0533 g) and methallyltrimethylsilane **4b** (1.00 mmol, 0.128 g). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography (hexane/$CHCl_3$ = 20:80, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 0.0663 g, 94%).

mp: 69-70 °C; **IR**: (KBr) 3376, 2243 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.76 (d, J = 8.4 Hz, 2H), 7.69 (m, 2H), 5.02 (m, 1H), 4.86 (s, 1H), 3.18 (m, 1H), 3.00 (d, J = 13.9 Hz, 1H), 2.93 (d, J = 13.9 Hz, 1H), 1.29 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 142.7, 138.6, 131.9, 127.5, 119.3, 118.3, 117.6 (m), 115.5 (m), 112.4, 109.9 (m), 75.9 (t, J = 24.4 Hz), 43.6 (t, J = 2.9 Hz), 23.7; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.3 (t, J = 10.4 Hz, 3F), -118.4 (m, 1F), -119.9 (m, 1F), -122.2 (m, 1F), -125.3 (m, 1F); **HRMS**: (EI) Calculated: ($C_{15}H_{12}NOF_7$) 355.0807 (M^+) Found: 355.0802

4-(1,1,1,2,2,3,3-heptafluoro-4-hydroxy-7,7-dimethyl-6-oxooctan-4-yl)benzonitrile (5e)

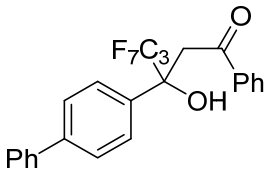


To a solution of 4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzonitrile **3b** (0.200 mmol, 0.0917 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.400 mmol, 0.0533 g) and ((3,3-dimethylbut-1-en-2-yl)oxy)trimethylsilane **4c** (1.00 mmol, 0.172 g). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography ($CHCl_3$/MeOH = 90:10, column length 10 cm, diameter 26 mm silica gel) to give the product (yellow oil, 0.0475 g, 62%).

mp: 80-81 °C; **IR**: (neat) 2232, 1692 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.72 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H), 6.34 (s, 1H), 3.34 (d, J = 17.6 Hz, 1H), 3.29 (d, J = 17.6 Hz, 1H), 1.08 (s, 9H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 216.8, 143.2, 132.0, 127.1, 118.2, 117.5 (m), 115.1 (m), 112.7, 109.8 (m), 77.7

(t, J = 24.1 Hz), 45.3, 39.0, 25.6; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -80.8 (t, J = 10.7 Hz, 3F), -116.7 (m, 1F), -117.6 (m, 1F), -121.8 (m, 1F), -123.4 (m, 1F); **HRMS**: (DART+) Calculated: ($C_{17}H_{17}NO_2F_7$) 400.1142 ($[M+H]^+$) Found: 400.1159

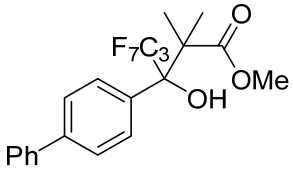
3-([1,1'-biphenyl]-4-yl)-4,4,5,5,6,6,6-heptafluoro-3-hydroxy-1-phenylhexan-1-one (5f)



To a solution of 1-(1-([1,1'-biphenyl]-4-yl)-1,2,2,3,3,4,4,4-octafluorobutoxy)-2,2,6,6-tetramethylpiperidine **3a** (0.200 mmol, 0.102 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.400 mmol, 0.0533 g). The resulting mixture was stirred at room temperature for 1h. Then, trimethyl((1-phenylvinyl)oxy)silane **4d** (1.00 mmol, 0.192 g) was added and stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography (hexane/$CHCl_3$ = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 0.0686 g, 73%).

mp: 81-82 °C; **IR**: (KBr) 3487, 1657 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.91 (d, J = 7.4 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.62-7.54 (m, 5H), 7.46 (t, J = 8.1 Hz, 2H), 7.40 (t, J = 8.1 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 6.01 (s, 1H), 4.03 (d, J = 17.1 Hz, 1H), 3.71 (d, J = 17.1 Hz, 1H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 200.2, 141.3, 140.1, 136.7, 136.3, 134.4, 128.9, 128.7, 128.2, 127.5, 127.0, 126.9, 126.8, 117.8 (m), 115.2 (m), 110.1 (m), 78.2 (t, J = 23.9 Hz), 40.5; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.0 (t, J = 11.0 Hz, 3F), -118.3 (m, 1F), -119.2 (m, 1F), -122.9 (m, 1F), -124.9 (m, 1F); **HRMS**: (DART+) Calculated: ($C_{24}H_{18}O_2F_7$) 471.1190 ($[M+H]^+$) Found: 471.1174

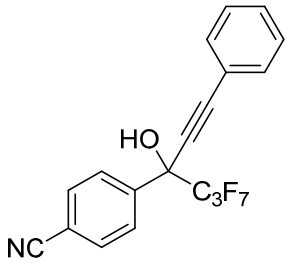
5-([1,1'-biphenyl]-4-yl)-6,6,7,7,8,8,8-heptafluoro-5-hydroxy-2,2,4,4-tetramethyloctan-3-one (5g)



To a solution of 1-(1-([1,1'-biphenyl]-4-yl)-1,2,2,3,3,4,4,4-octafluorobutoxy)-2,2,6,6-tetramethylpiperidine **3a** (0.200 mmol, 0.102 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.400 mmol, 0.0533 g). The resulting mixture was stirred at room temperature for 1h. Then ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **4e** (1.00 mmol, 0.202 g) was added and stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography (hexane/$CHCl_3$ = 80:20, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 0.0712 g, 79%).

mp: 116-117 °C; **IR**: (KBr) 3292, 1693, 1289 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 8.10-7.51 (m, 6H), 7.45 (m, 2H), 7.35 (m, 1H), 6.66 (s, 1H), 3.83 (s, 3H), 1.47 (d, J = 3.4 Hz, 3H), 0.97 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 179.8, 141.0, 140.1, 133.0, 128.8, 127.6, 127.0, 126.4, 125.6, 118.6 (m), 117.8 (m), 110.0 (m), 80.8 (t, J = 21.8 Hz), 53.3, 46.9, 24.2, 19.7 (d, J = 7.2 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (m, 3F), -108.5 (m, 1F), -113.6 (m, 1F), -119.6 (m, 1F), -124.4 (m, 1F); **HRMS**: (EI) Calculated: ($C_{21}H_{19}O_3F_7$) 452.1222 (M^+) Found: 452.1218

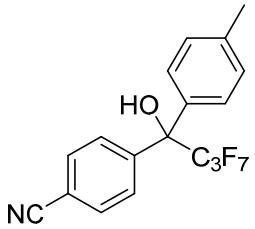
4-(4,4,5,5,6,6,6-heptafluoro-3-hydroxy-1-phenylhex-1-yn-3-yl)benzonitrile (5h)



To a solution of 4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzonitrile **3b** (0.200 mmol, 0.0917 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.400 mmol, 0.0533 g) and trimethyl(phenylethynyl)silane **4f** (1.04 mmol, 0.181 g). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography (hexane/$CHCl_3$ = 20:80, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.0548g, 68%).

mp: 80-81 °C; **IR**: (neat) 3359, 2240, 1335, 1243, 1216 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.93 (d, *J* = 8.7 Hz, 2H), 7.71 (m, 2H), 7.51 (m, 2H), 7.43 (m, 1H), 7.37 (m, 2H), 3.70 (s, 1H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 140.7, 132.0, 131.9, 129.9, 128.6, 128.5, 120.3, 118.2, 117.6 (m), 113.5 (m), 113.2, 110.0 (m), 90.0, 83.2 (d, *J* = 4.3 Hz), 73.4 (t, *J* = 26.8 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.2 (t, *J* = 11.0 Hz, 3F), -116.1 (m, 1F), -119.3 (m, 1F), -123.6 (s, 2F); **HRMS**: (DART+) Calculated: ($C_{17}H_{17}NO_2F_7$) 402.0723 ($[M+H]^+$) Found: 402.0743

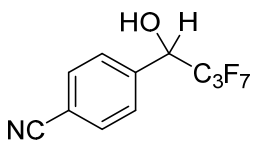
4-(2,2,3,3,4,4,4-heptafluoro-1-hydroxy-1-(p-tolyl)butyl)benzonitrile (5i)



To a solution of 4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzonitrile **3b** (0.200 mmol, 0.0917 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.400 mmol, 0.0533 g) and toluene **4h** (1 mL). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography (hexane/$CHCl_3$ = 50:50, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.0556 g, 71%).

IR: (neat) 2231, 1610, 1515, 1507, 1348 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.65-7.62 (dt, *J* = 8.4, 1.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.68 (t, *J* = 17.6 Hz 1H), 2.33 (s, 3H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 140.5, 140.5, 138.5, 132.5, 131.0, 130.6, 130.0, 129.7, 129.1, 118.3, 117.7, 116.8, 112.0, 109.3, 52.9 (t, *J* = 21.3 Hz), 21.0; **^{19}F NMR**: (376 MHz, in $CDCl_3$) -81.7 (t, *J* = 10.9 Hz, 3F), -112.0 (m, 1F), -113.2 (m, 1F), -124.4 (m, 2F); **HRMS**: (DART-) Calculated: ($C_{18}H_{11}NOF_7$) 390.0734 ($[M-H]^-$) Found: 390.0715

4-(2,2,3,3,4,4,4-heptafluoro-1-hydroxybutyl)benzonitrile (5j)



To a solution of 4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzonitrile **3b** (0.200 mmol, 0.0917 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.407 mmol, 0.0542 g) and triethylsilane **4i** (1.03 mmol, 0.116 g). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was

quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography ($CHCl_3$/MeOH = 98:2, column length 10 cm, diameter 26 mm silica gel) to give the product (colorless oil, 0.0530 g, 88%).

IR: (neat) 3403, 2238, 1412 cm^{-1}; **^{1}H NMR**: (400 MHz, in $CDCl_3$) 7.70 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 5.30 (dd, *J* = 17.1, 5.4 Hz, 1H), 3.27 (s, 1H); **^{13}C NMR**: (100 Hz, in $CDCl_3$) 139.1, 132.2, 128.8, 118.2, 117.6 (m) , 114.2 (m), 113.1, 109.4 (m), 71.2 (dd, *J* = 28.7, 22.5 Hz); **^{19}F NMR**: (376 MHz, in $CDCl_3$) -82.1 (m, 3F), -119.1 (m, 1F), -125.8 (m, 1F), -126.9--127.9 (m, 2F); **HRMS**: (EI) Calculated: ($C_{11}H_6NOF_7$) 301.0338 (M^+) Found: 301.0334

General Procedures

Defluoroaminoxylation of Perfluoroalkylarene 1 with TEMPO 2 (Table 1)

Entry 1

To a solution of $Ir(ppy)_3$ (0.004 mmol, 2.6 mg) and 4-(nonafluorobutyl)biphenyl **1a** (0.400 mmol, 0.149 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 4 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The yield of **3a** was determined by ^{1}H NMR analysis in $CDCl_3$ with 1,1,2,2-tetrachloroethane as an internal standard.

Entries 2-5, 8, and 9

To a solution of **PC** (0.004 mmol) and 4-(nonafluorobutyl)biphenyl **1a** (0.400 mmol, 0.149 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 370 nm LED irradiation for 4 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. 1,1,2,2- tetrachloroethane was added as an internal standard to the crude reaction mixture, and an aliquot was taken for ^{1}H NMR analysis in $CDCl_3$.

Entry 6

To a solution of 3,6-di-*tert*-butyl-9-(2,4,6-trimethylphenyl)-10-phenylacridinium tetrafluoroborate (0.040 mmol, 0.0229 g) and 4-(nonafluorobutyl)biphenyl **1a** (0.400 mmol, 0.149 g) in MeCN (1.3 mL) were added TEMPO **2** (0.800 mmol, 0.125 g) and NEt_3 (4.0 mmol, 0.405 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 390 nm LED irradiation for 24 h while cooling by a fan. The solvent was removed under reduced pressure. 1,1,2,2- tetrachloroethane was added as an internal standard to the crude reaction mixture, and an aliquot was taken for ^{1}H NMR analysis in $CDCl_3$.

Entry 7

To a solution of cesium formate (0.800 mmol, 0.142 g) and 4-(nonafluorobutyl)biphenyl **1a** (0.400 mmol,

0.149 g) in DMSO (2 mL) TEMPO **2** (0.800 mmol, 0.125 g) and 4-methoxybenzenethiol (0.080 mmol, 0.0112 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 390 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with ethyl acetate (30 mL) and washed with water, and the organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. 1,1,2,2- tetrachloroethane was added as an internal standard to the crude reaction mixture, and an aliquot was taken for ^1H NMR analysis in $CDCl_3$.

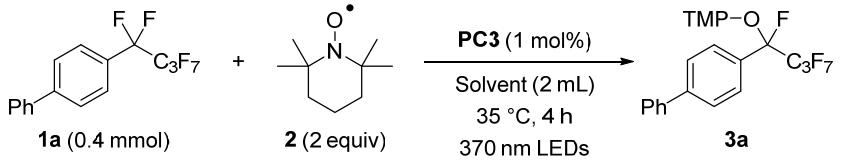
Entry 10

To a solution of *N*-(4-*N*,*N*-diisopropylamino-2,6-dimethylphenyl)phenothiazine **PC3** (0.020 mmol, 8.1 mg) and 4-(nonafluorobutyl)biphenyl **1a** (0.400 mmol, 0.149 g) in MeCN (2 mL) was added TEMPO **2** (0.813 mmol, 0.127 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred under 370 nm LED irradiation for 24 h while cooling by a fan. The reaction mixture was diluted with chloroform (30 mL) and the volatiles were removed under reduced pressure. The residual oil was purified by silica gel column chromatography (hexane, column length 10 cm, diameter 26 mm silica gel) to give **3a** (colorless oil, 0.144 g, 71%).

*The reaction temperature increased to 35 °C under light irradiation while cooling by a fan.

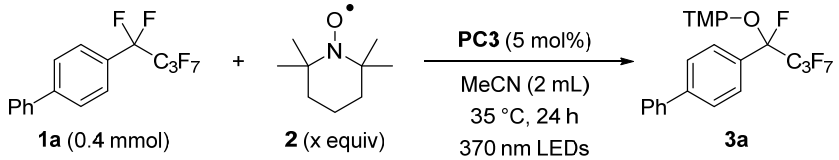
Further Optimization (Tables S1 and S2)

Table S1. Solvent Screening



Entry	Solvent	Yield of **3a** / %	Recovery of **1a** / %
1	MeCN	60	30
2	THF	0	98
3	Acetone	40	43
4	Hexane	0	87
5	Et_2O	0	89
6	DMSO	21	79
7	DMF	12	88
8	$CHCl_3$	0	95
9	Toluene	0	95
10	DME	0	80
11	1,4-dioxane	0	86

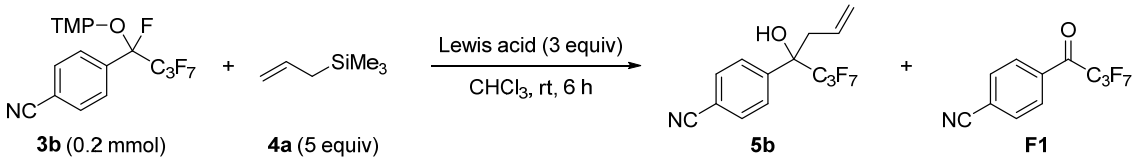
Table S2. Screening of the Amount of TEMPO 2



Entry	x / equiv	Yield of **3a** / %	Recovery of **1a** / %
1	1.0	31	29
2	1.5	53	15
3	2.0	82	0
4	3.0	68	0

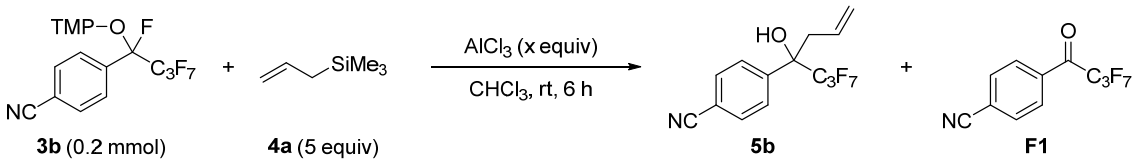
Optimization of Lewis Acid Mediated Defluorinative Transformation (Tables S3 and S4)

Table S3. Screening of Lewis Acid



Entry	Lewis acid	Yield of **5b** / %	Yield of **F1** / %	Recovery of **1a** / %
1	$AlCl_3$	99	0	0
2	$BF_3 \cdot Et_2O$	0	99	0
3	$B(C_6F_5)_3$	0	0	99
4	$ZnCl_2$	0	0	99
5	$FeCl_3$	18	0	0

Table S4. Optimization of the Amount of $AlCl_3$

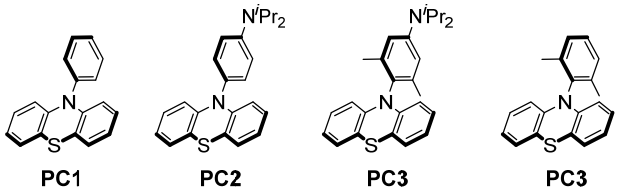


Entry	x / equiv	Yield of **5b** / %	Yield of **F1** / %	Recovery of **1a** / %
1	3.0	99	0	0
2	2.0	99	0	0
3	1.5	78	22	0
4	1.0	45	32	28

Photoluminescence Quantum Yields of PC (Table S5)

Photoluminescence quantum yield measurements were conducted by a Hamamatsu PMA12 spectrofluorometer equipped with an integrating sphere.

Table S5. Photoluminescence quantum yield of PCs



PC1 PC2 PC3 PC3

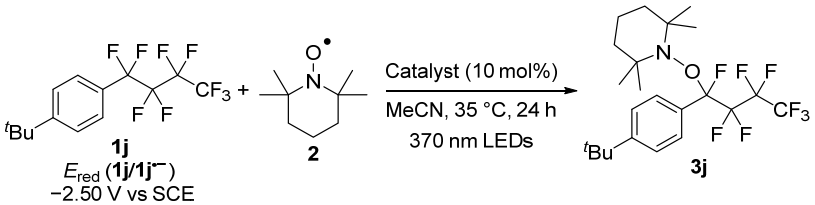
organic dye	PC1	PC2	PC3	PC4
photoluminescence quantum yield (PLQY)[a]	0.01	0.01	0.01	0.01

[a] in MeCN

Comparison of Catalytic Activity in Aminoxylation of Substrate Possessing Low Reduction Potential (Table S6 and S7)

The results about the aminoxyation of substrate **1j**, which exhibited a lower reduction potential than **1a**, are shown in Table S6 to prove lower reducing abilities of **PC1*** and **PC4*** compared to **PC2*** and **PC3***. **PC1** and **PC4** did not work in the aminoxylation of **1j** in contrast to **PC2** and **PC3**. In contrast, the aminoxylation of **1a** was mediated by **PC1** and **PC4** as well as **PC2** and **PC3** (Table S7). The lower catalytic activities of **PC1** and **PC4** are due to the slow reduction of perfluoroalkylarenes **1** caused by lower reducing abilities of **PC1*** and **PC4*** than **PC2*** and **PC3***.

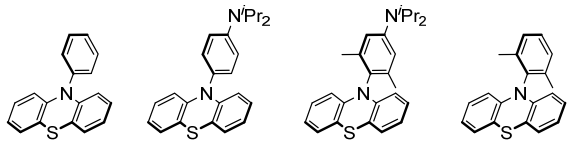
Table S6. Screening of catalysts for aminoxylation of **1j**



1j **2** **3j**

E_{red} (**1j**/**1j**$^{\bullet-}$) −2.50 V vs SCE

catalyst

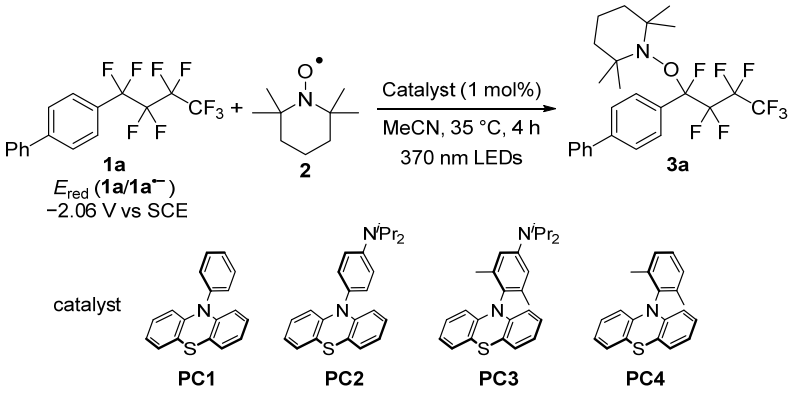


PC1 PC2 PC3 PC4

Entry	Catalyst	E_{ox}* (V vs SCE)	Yield
1	**PC1**	−2.45	0%
2	**PC2**	−2.68	14%
3	**PC3**	−2.57	52% (42%)[a]
4	**PC4**	−2.47	0%

[a](isolated yield)

Table S7. Screening of catalysts for aminoxylation of **1a**



Entry	Catalyst	E_{ox}* (V vs SCE)	Yield
1	**PC1**	−2.45	35%
2	**PC2**	−2.68	42%
3	**PC3**	−2.57	60%
4	**PC4**	−2.47	38%

Stern-Volmer Luminescene Quenching Studies of Photocatalyst PC2 and PC3 (Figures S1 and S2)

Fluorescence quenching studies were performed by using a JACSO FP-6600 spectrofluorometer. In each experiment, **PC2** or **PC3** with various concentrations of **1e** were combined in MeCN in screw-top 1.0 cm quartz cuvettes. The emission quenching of the **PC2** and **PC3** was achieved using a concentration of 2.0 x 10^{-5} M under excitation at 320 nm. The emission intensity was observed at 446 nm. Plots were constructed according to the Stern–Volmer equation $I_0/I = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q]$

τ_0 was determined by transient absorption spectroscopy (τ_0(**PC2**) = 2.43 ns, τ_0(**PC3**) = 2.48 ns; See Figures S6 and S8).

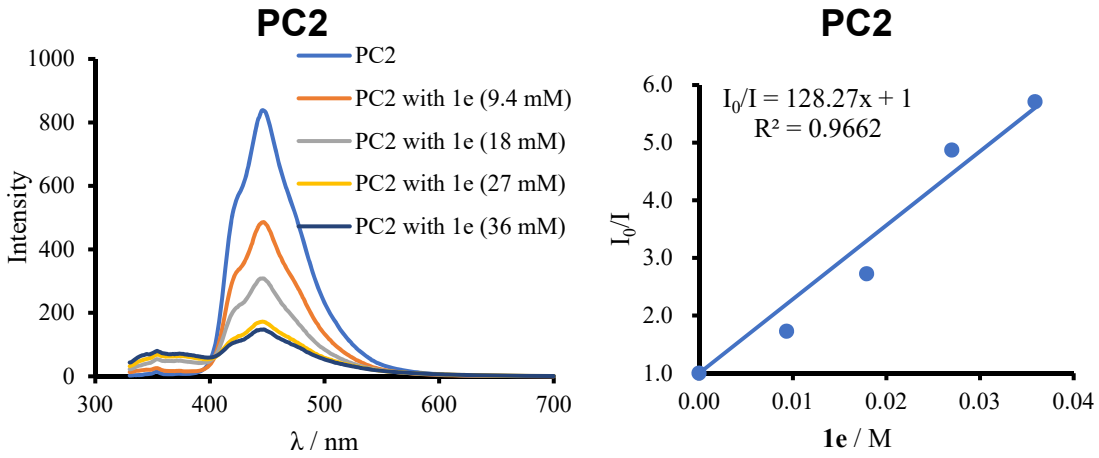


Figure S1. Stern-Volmer plots of changes in fluorescence intensity of **PC2** versus the concentration of **1e**

*K*sv (**PC2**) = 1.28 x 10^2 M^{-1}

k_q (**PC2**) = 4.72 x 10^{10} $M^{-1}s^{-1}$

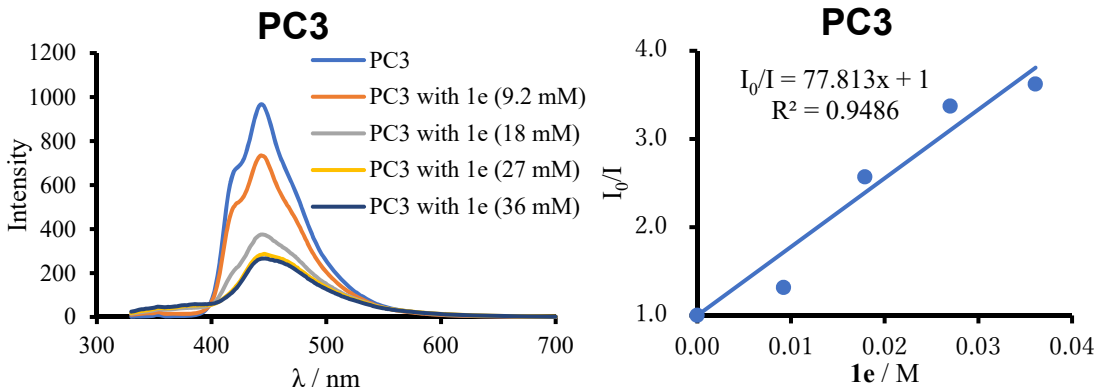


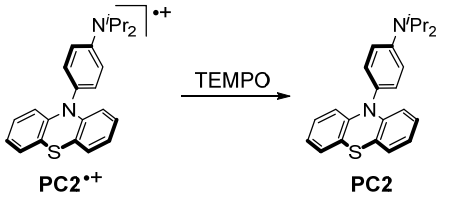
Figure S2. Stern-Volmer plots of changes in fluorescence intensity of **PC3** versus the concentration of **1e**

*K*sv (**PC3**) = 7.78 x 10 M^{-1}

k_q (**PC3**) = 2.95 x 10^{10} $M^{-1}s^{-1}$

Stern-Volmer Quenching Studies of Radical Cation of PC2 and PC3 (Figures S3 and S4)

Plots were constructed according to the Stern–Volmer equation $1/\tau = 1/\tau_0 + k_q[Q]$ by using lifetime of **PC2**$^{\bullet+}$ and **PC3**$^{\bullet+}$ obtained in transient absorption spectra of **PC2** and **PC3** with **1n** and TEMPO **2** by sub-micro second laser flash photolysis.



entry	TEMPO (M)	τ (ms)	k_q (s^{-1})
1	0.0897	83.6	12.0
2	0.217	42.2	23.7
3	0.275	34.1	29.3

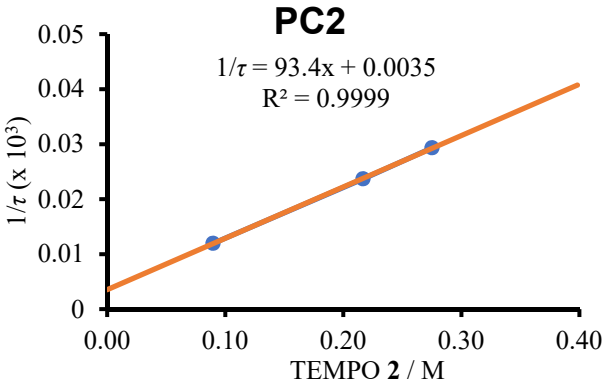
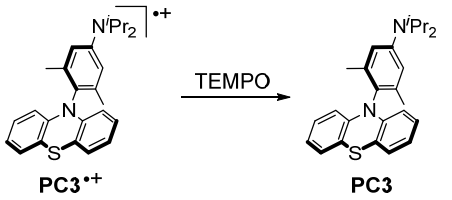


Figure S3. Stern-Volmer plots of lifetime of radical cation of **PC2** versus the concentration of TEMPO **2** in MeCN

$k_q = 9.34 \times 10\ M^{-1}s^{-1}$



entry	TEMPO (M)	τ (ms)	k_q (s^{-1})
1	0.121	0.201	4.98×10^3
2	0.241	0.118	8.48×10^3
3	0.309	0.0902	1.11×10^4

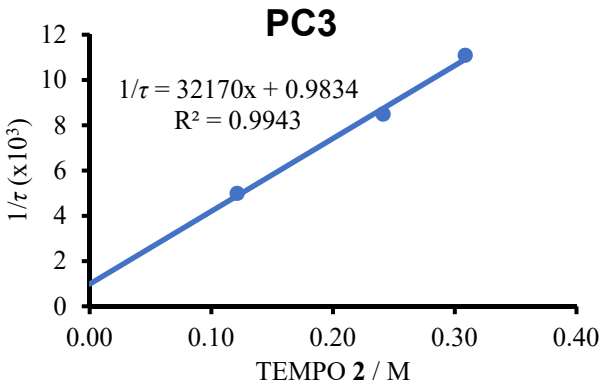


Figure S4. Stern-Volmer plots of lifetime of radical cation of **PC3** versus the concentration of TEMPO **2** in MeCN

$k_q = 3.21 \times 10^4\ M^{-1}s^{-1}$

Estimation of Rate Constant of Inter System Crossing by Transient Absorption Spectroscopy (Figures S5–S8)

Sub-nano second laser flash photolysis was conducted by the Unisoku picoTAS to determine the rise rates of T_1 (k_{T1rise}) and the decay rates of S_1 (k_0) in **PC2** and **PC3**.

The values of k_0 and k_{T1rise} are nearly identical, implying a direct transformation from S_1 species to T_1 species.

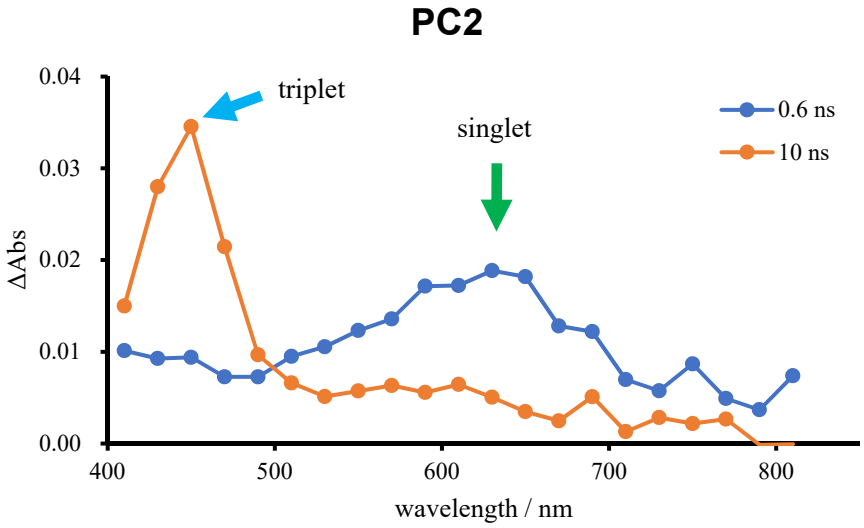
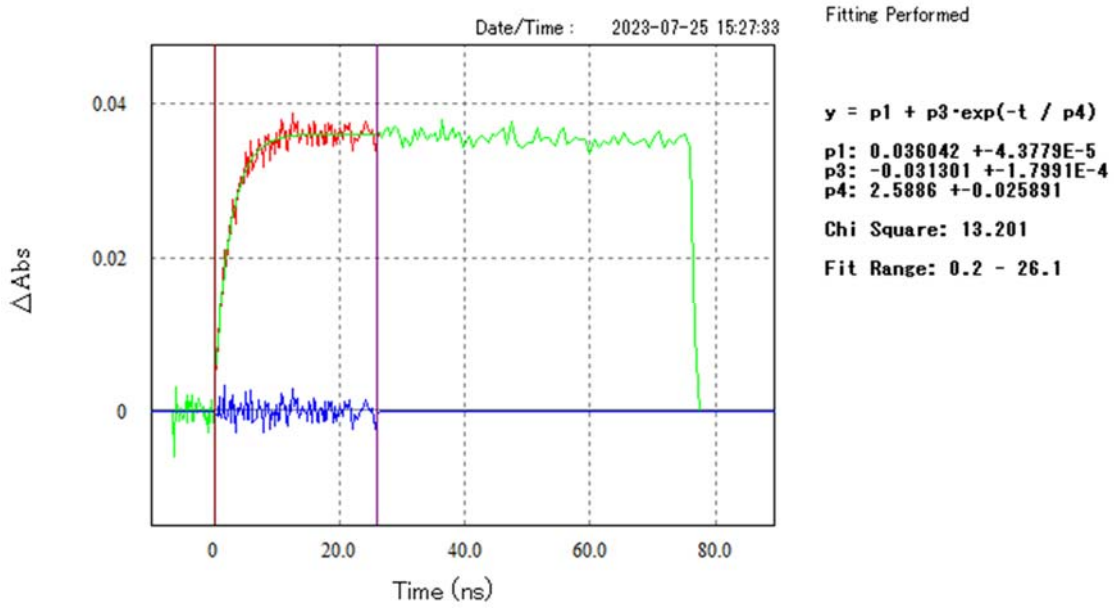


Figure S5. Transient absorption spectra of **PC2** (2 mM) in MeCN excited by 355 nm pulsed laser

(A) Time profile monitored at 450 nm



(B) Time profile monitored at 610 nm

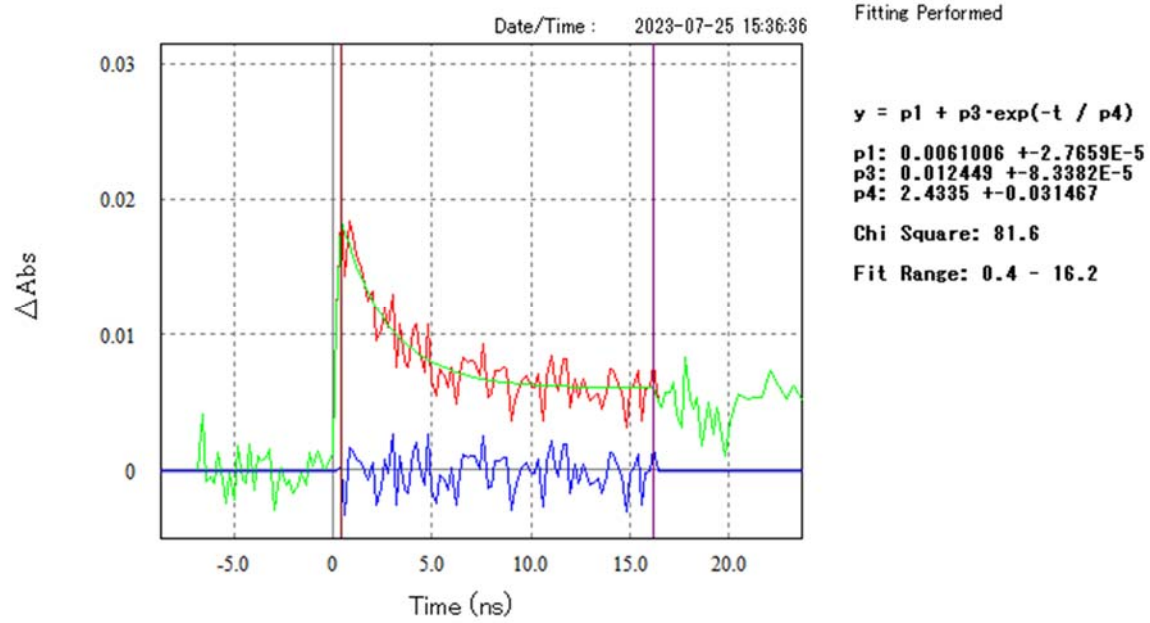


Figure S6. Time profile of **PC2** (2 mM) in MeCN excited by 355 nm pulsed laser (A) monitored at 450 nm (B) monitored at 610 nm

k_{T1rise} = 3.86 x 10^8 s^{-1}

k_0 = 4.11 x 10^8 s^{-1} ($^1\tau_0$ = 2.43 ns)

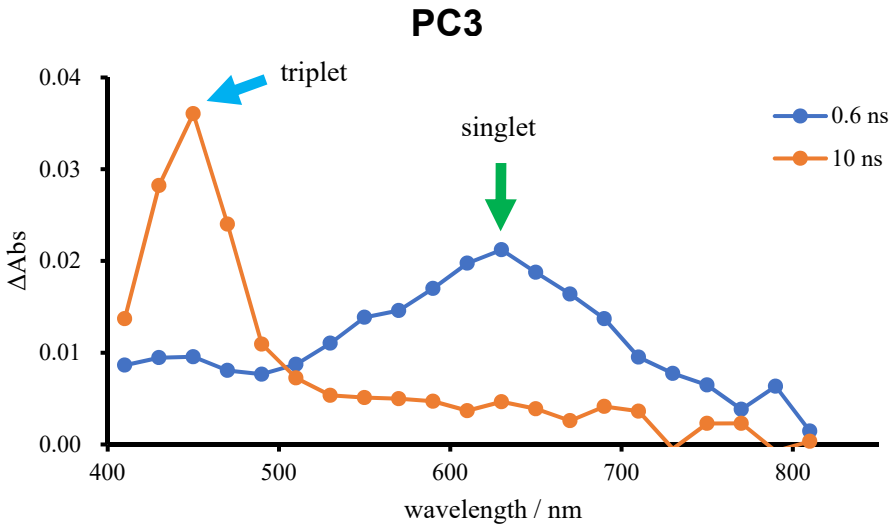
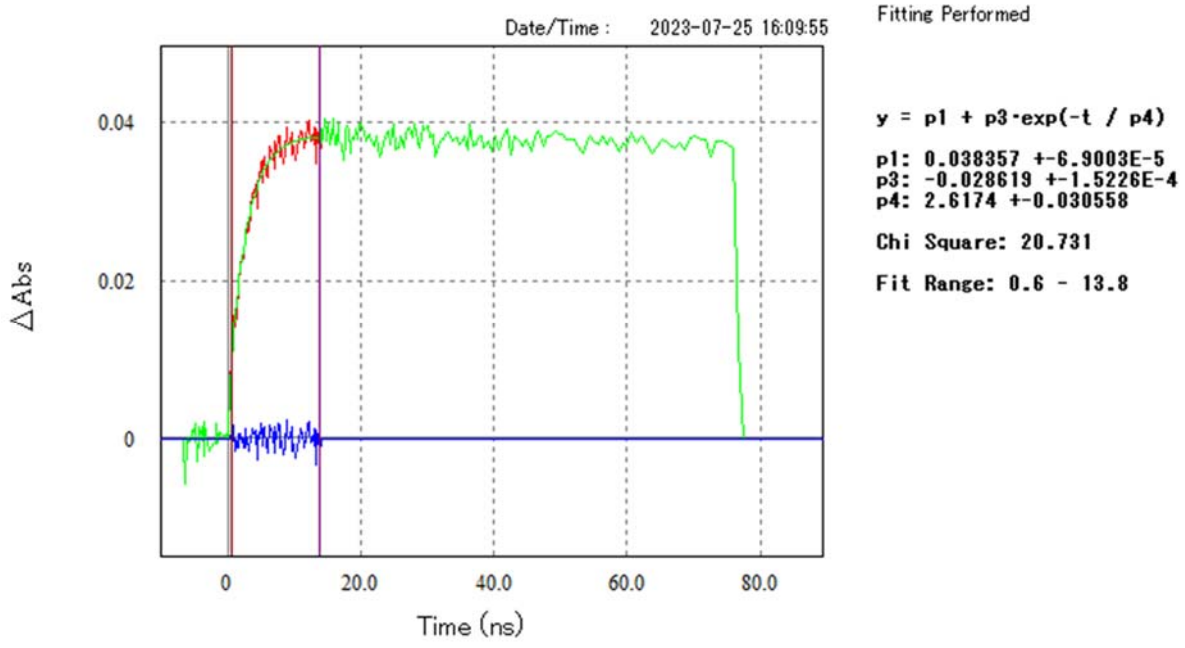


Figure S7. Transient absorption spectra of **PC3** (2 mM) in MeCN excited by 355 nm pulsed laser

(A) Time profile monitored at 450 nm



(B) Time profile monitored at 610 nm

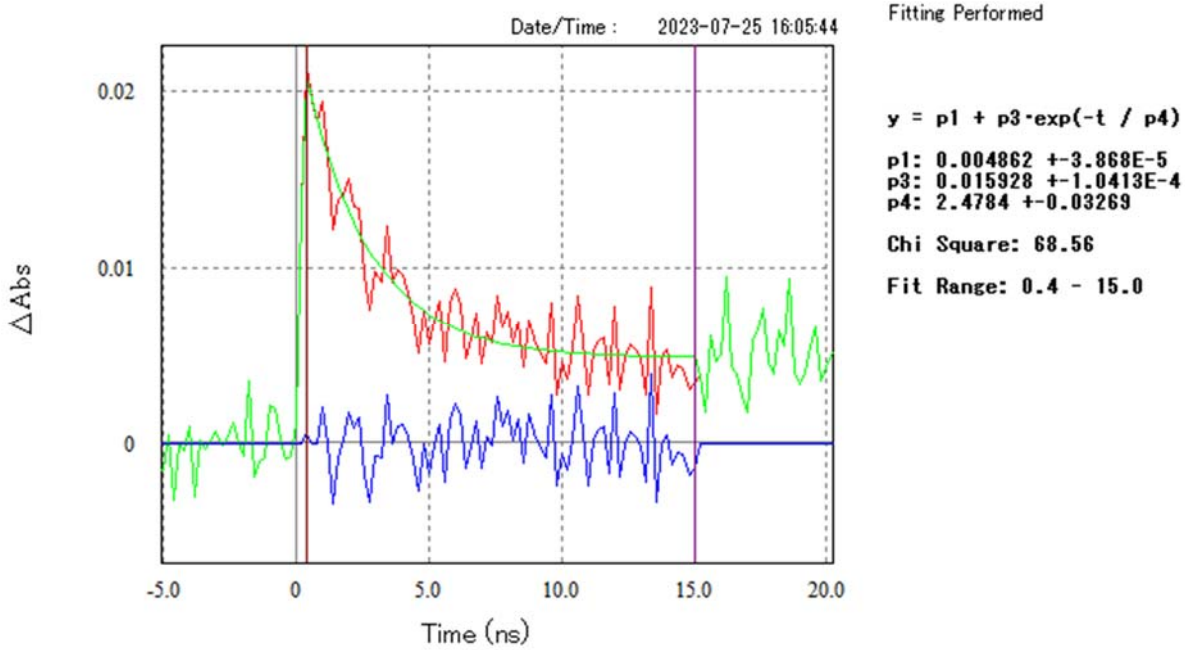
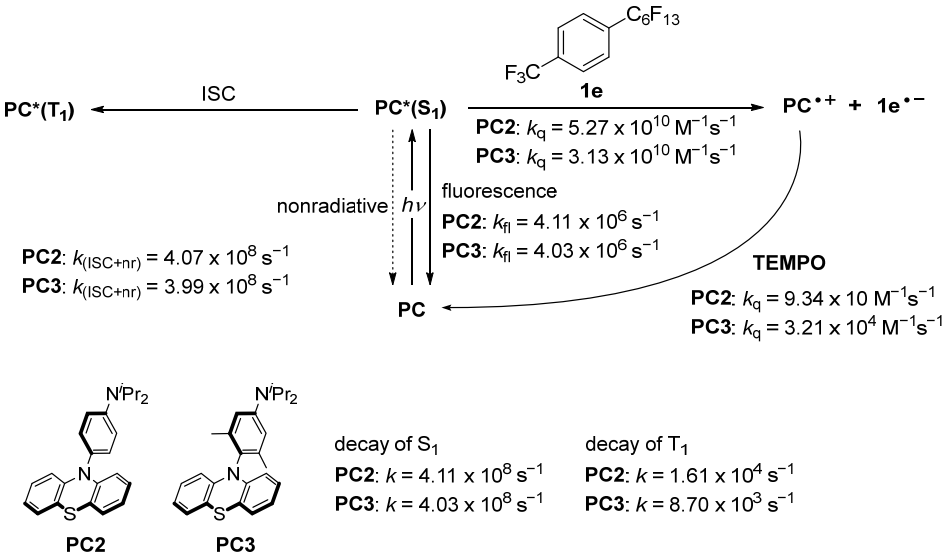


Figure S8. Time profile of **PC3** (2 mM) in MeCN excited by 355 nm pulsed laser (A) monitored at 450 nm (B) monitored at 610 nm

k_{T1rise} = 3.83 x 10^8 s^{-1}

k_0 = 4.03 x 10^8 s^{-1} ($^1\tau_0$ = 2.48 ns)

Summary of Kinetic Constants of PC (Scheme S1)



Scheme S1. Kinetic constants of **PC2** and **PC3**

Cyclic Voltammetry Measurements (Figures S9)

The cyclic voltammogram was measured at scan rate of 100 mV/s at room temperature. Potentials vs. SCE were reported according to $E_{SCE} = E\ (Fc/Fc^{+}) + 0.38$ V.[36]

Redox potentials of excited state were calculated according to $E_{ox}^{*}\ (PC^{\bullet+}/PC^{*}) = E_{ox}\ (PC^{\bullet+}/PC) - E_{0\text{-}0}$.[37]

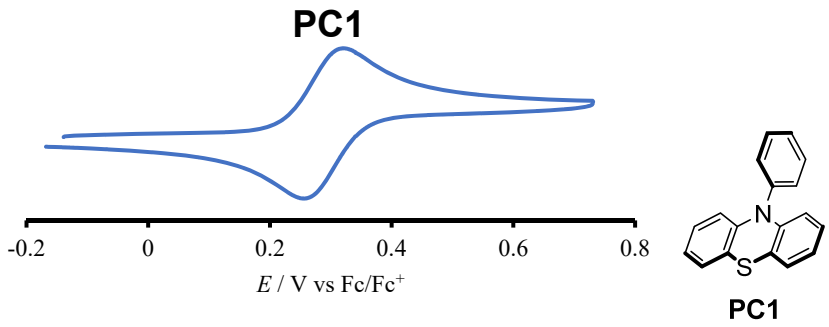


Figure S9a. Cyclic voltammogram of **PC1** (V vs. Fc/Fc^{+}, in 0.1 M Bu_4NBF_4/MeCN, scan rate = 100 mV/s, room temperature).

E_{ox} = 0.67 V vs SCE

E_{ox}^{*} = -2.45 V vs SCE

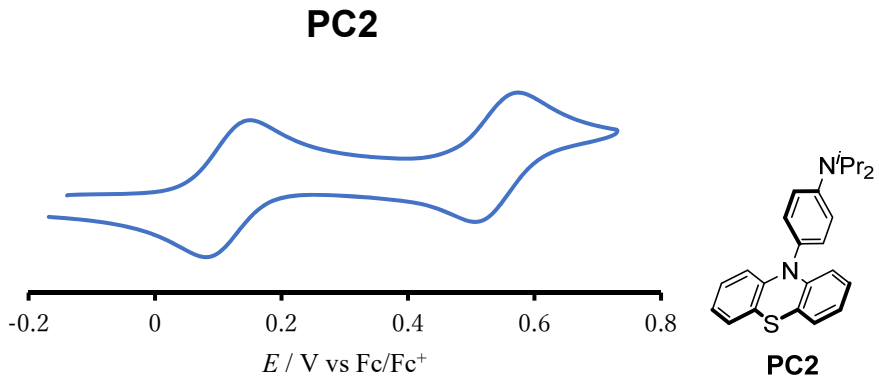


Figure S9b. Cyclic voltammogram of **PC2** (V vs. Fc/Fc^+, in 0.1 M Bu_4NBF_4/MeCN, scan rate = 100 mV/s, room temperature).

E_{ox} = 0.50 V vs SCE, E_{ox}* = -2.68 V vs SCE

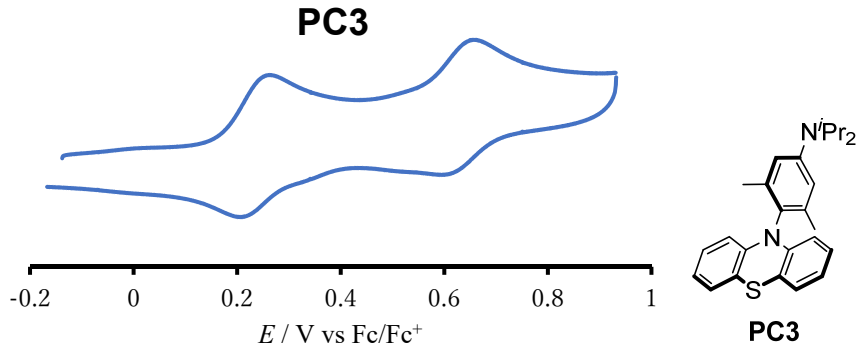


Figure S9c. Cyclic voltammogram of **PC3** (V vs. Fc/Fc^+, in 0.1 M Bu_4NBF_4/MeCN, scan rate = 100 mV/s, room temperature).

E_{ox} = 0.61 V vs SCE, E_{ox}* = -2.57 V vs SCE

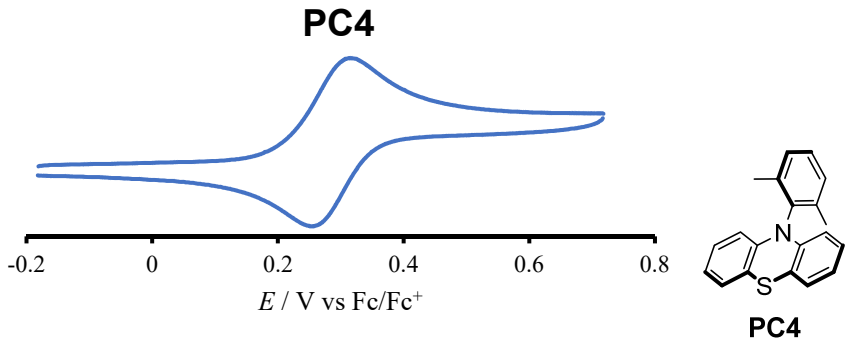


Figure S9d. Cyclic voltammogram of **PC4** (V vs. Fc/Fc^+, in 0.1 M Bu_4NBF_4/MeCN, scan rate = 100 mV/s, room temperature).

E_{ox} = 0.67 V vs SCE, E_{ox}* = -2.47 V vs SCE

Differential Pulse Voltammetry (Figure S10)

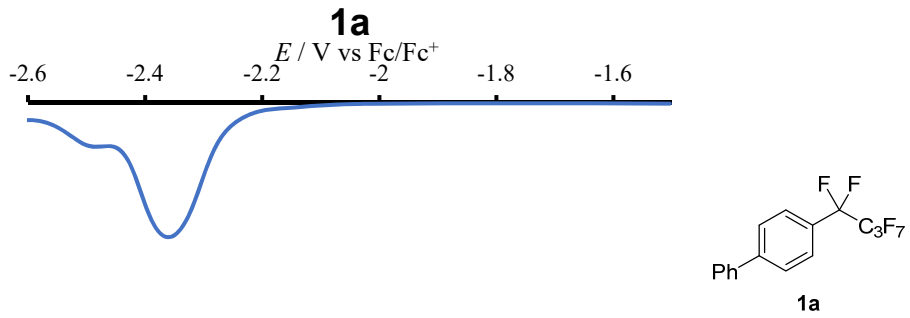


Figure S10a. Difference pulse voltammograms of **1a** (V vs. Fc/Fc^+, in 0.1 M Bu_4NBF_4/MeCN, pulse width = 0.05 s, sample width = 0.0167 s, pulse period = 0.2 s scan rate = 100 mV/s, room temperature).

E_{red} (**1a**) = -2.44 V vs Fc/Fc^+ = -2.06 V vs SCE

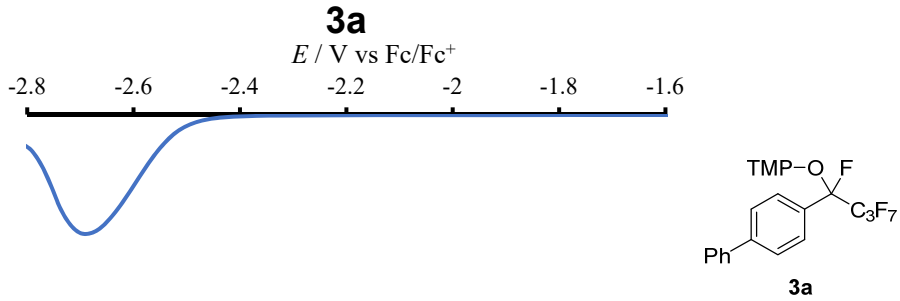


Figure S10b. Difference pulse voltammograms of 3**a** (V vs. Fc/Fc^+, in 0.1 M Bu_4NBF_4/MeCN, pulse width = 0.05 s, sample width = 0.0167 s, pulse period = 0.2 s, room temperature).

E_{red} (3**a**) = -2.69 V vs Fc/Fc^+ = -2.31 V vs SCE

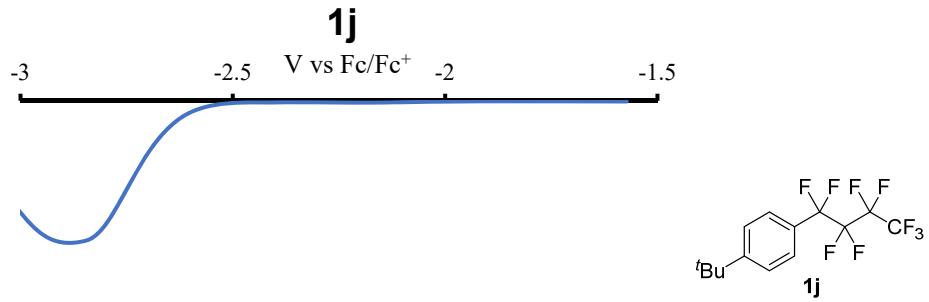


Figure S10c. Difference pulse voltammograms of **1j** (V vs. Fc/Fc^+, in 0.1 M Bu_4NBF_4/MeCN, pulse width = 0.05 s, sample width = 0.0167 s, pulse period = 0.2 s, room temperature).

E_{red} (**1j**) = -2.88 V vs Fc/Fc^+ = -2.50 V vs SCE

Light On/Off Experiments (Figure S11)

The reaction of **1a** with **2** was performed with or without 370 nm LEDs irradiation. The time profile of the yield of **3a** is shown in Figure S11. The yield of **3a** was determined by ^{19}F NMR using fluorobenzene as an internal standard. These results indicated that continuous irradiation with 370 nm LEDs was essential for promoting the reaction, and the contribution of the radical chain mechanism to this reaction was small.

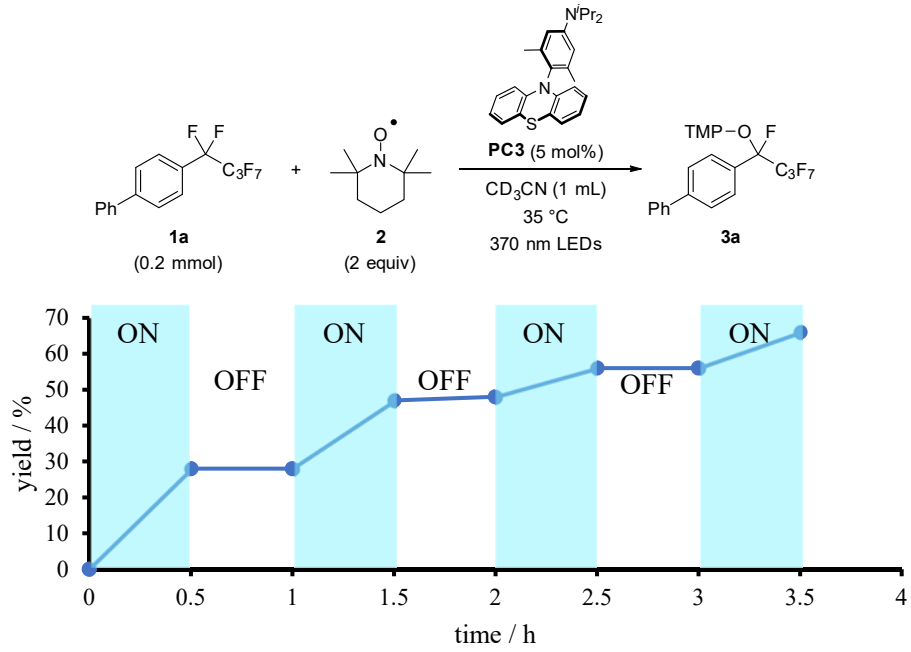
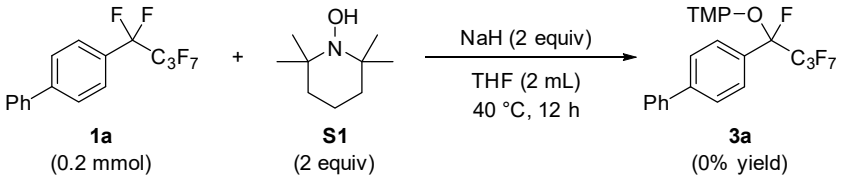


Figure S11. ON/OFF experiment for reaction progress

Examination of Aminoxylation via Ionic Reaction (Scheme S2)

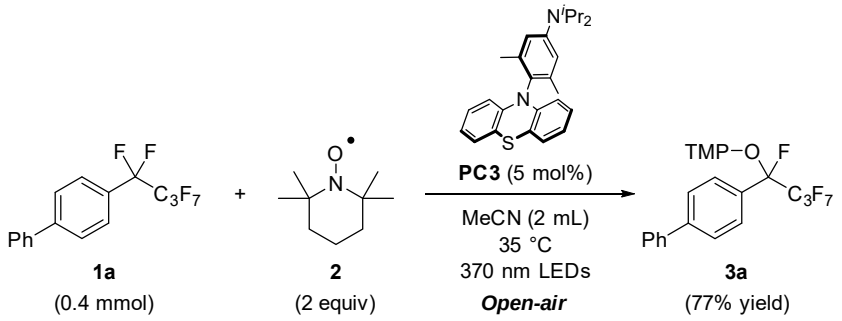
The reaction of **1a** with **S1** was performed in the presence of NaH. The product **3a** was not obtained. This result suggest that the reaction didn't proceed via S_N2 process after reduction of TEMPO **2** by PC.



Scheme S2. Examination of aminoxylation via ionic reaction

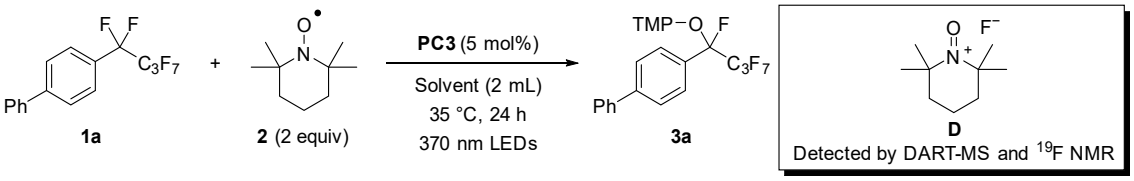
Open-air Experiment (Scheme S3)

The reaction of **1a** with **2** was performed under open-air conditions. The reaction proceeded to afford product **3a** in 77% yield. This result suggests that an excited singlet state of **PC3** works as a reductant and the triplet state has low contribution to the reaction progress.



Scheme S3. Open-air experiment for defluoroaminoxylation

Detection of *N*-Oxoammonium Fluoride D (Figures S12 and S13)



To a solution of *N*,*N*-diisopropyl-3,5-dimethyl-4-(10*H*-phenothiazin-10-yl)aniline (0.020 mmol, 8.1 mg) and 4-(nonafluorobutyl)biphenyl (0.400 mmol, 0.149 g) in MeCN (2 mL) was added TEMPO **2** (0.800 mmol, 0.125 g). After degassing by freeze-pump-thaw process for three cycles, the mixture was stirred at 35 °C under 370 nm LED irradiation for 24 h. The volatiles of reaction mixture were removed under reduced pressure. The residual solid was washed by hexane and ether. A white solid was collected. DART-MS and ^{19}F NMR analysis of the white solid were conducted.

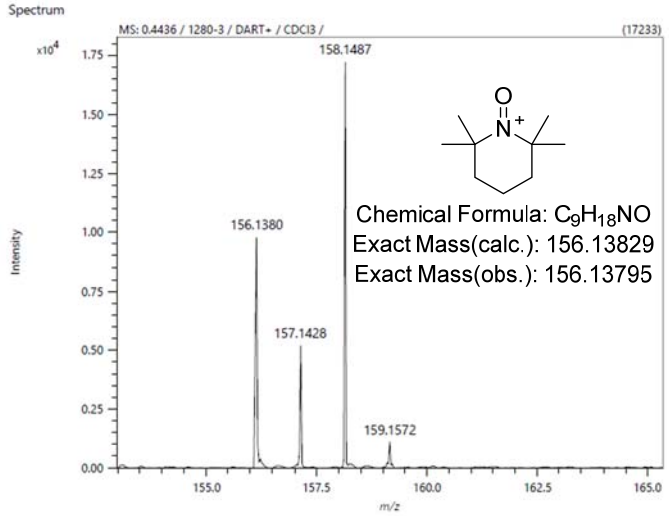


Figure S12. DART-MS analysis of *N*-oxoammonium fluoride **D**

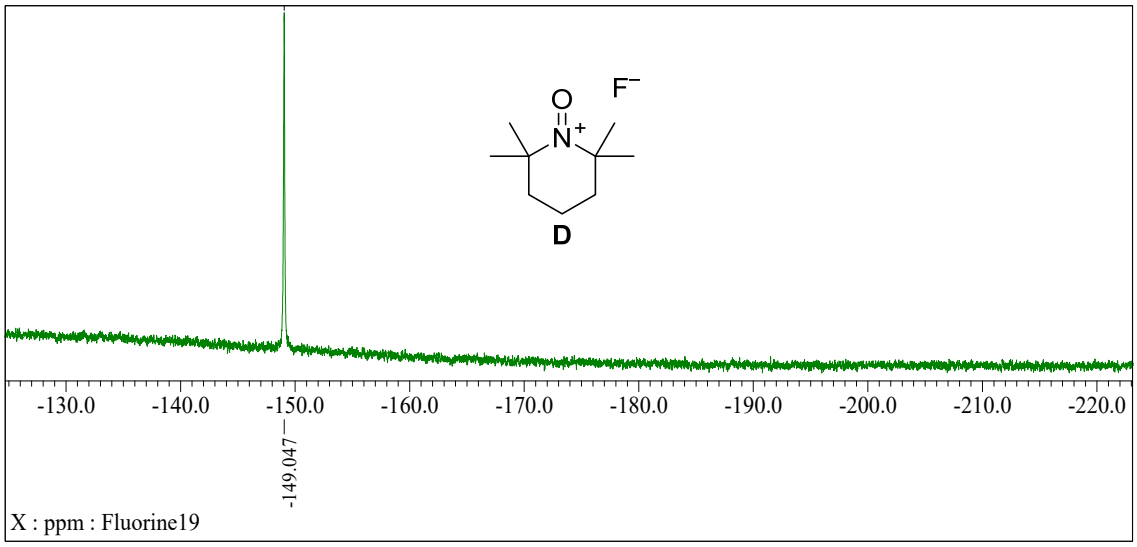
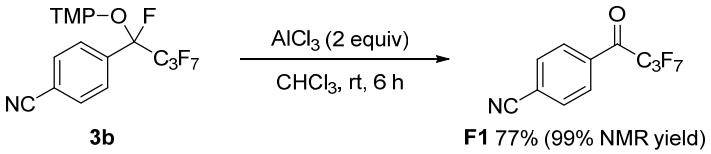


Figure S13. ^{19}F NMR spectrum of *N*-oxoammonium fluoride **D** in $CDCl_3$

Isolation of Intermediate F (Scheme S4)

Intermediate **F** was isolated to confirm the reaction mechanism.



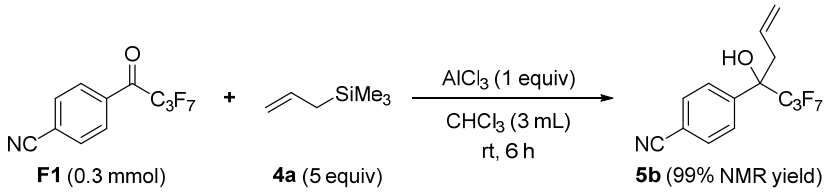
Scheme S4. Isolation of intermediate **F**

To a solution of 4-(1,2,2,3,3,4,4,4-octafluoro-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)benzonitrile **3b** (0.200 mmol, 0.0917 g) in $CHCl_3$ (2 mL) was added $AlCl_3$ (0.400 mmol, 0.0533 g). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with water and the product was extracted with chloroform. The organic layer was dried over $MgSO_4$. The solution was collected by filtration and the solvents were removed under vacuum. The residual oil was purified by silica gel column chromatography (hexane/EtOAc = 95:5, column length 10 cm, diameter 26 mm silica gel) to give the product (white solid, 0.0463 g, 77%).

mp: 44-45 °C; **IR:** (KBr) 2236, 1608 cm^{-1}; **^{1}H NMR: (400 MHz, in $CDCl_3$)** 8.18 (d, J = 8.6 Hz, 2H), 7.88 (m, 2H); **^{13}C NMR: (100 Hz, in $CDCl_3$)** 182.3 (t, J = 27.0 Hz), 134.2 (t, J = 1.8 Hz), 132.7, 130.5 (t, J = 3.3 Hz), 118.6, 117.3 (m), 117.2, 110.2 (m), 108.4 (m); **^{19}F NMR: (376 MHz, in $CDCl_3$)** -81.4 (t, J = 8.8 Hz, 3F), -115.2 (m, 2F), -126.8 (t, J = 9.3 Hz, 2F); **HRMS: (DART+)**: Calculated ($C_{11}H_5NOF_7$) 300.0254 ($[M+H]^+$) Found: 300.0264

Allylation from Intermediate F (Scheme S5)

Isolated intermediate **F1** was treated with $AlCl_3$ and allyltrimethylsilane **4a** to afford **5b** in 99% yield (confirmed by ^{1}H NMR). This result supports the intermediate **F** is an intermediate in allylation from **3**. $AlCl_3$ is crucial for activation of the ketone **F** while $BF_3 \cdot OEt_2$ produced **F1** from **3b** (Table S3).



Scheme S5. Allylation from intermediate **F1**

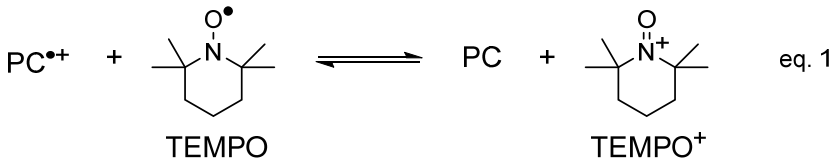
DFT Calculation Studies

All calculations were performed with Gaussian 16, Revision C.01.[38] Quantum chemical calculations were performed under vacuum at 298 K and 1 bar. The geometry optimizations were carried out at ωB97X-D level of theory with a mixed basis set; 6-31+G(d,p). SMD (acetonitrile) was used as a solvent effect. Gibbs free energies including contribution of vibrational entropy at an appropriate temperature were described in energy profiles. Stationary points were identified by vibrational analysis. Gibbs free energies were calculated as a sum of the single-point electronic energy and thermal correction to the Gibbs free energy.

Estimation of Activation Energy for the Electron Transfer Process

We used the Marcus-Hush theory to estimate the activation energies for the 2nd single electron transfer (SET) process in Scheme 1 and Figure 2. The DFT calculations were performed at the (U)ωB97XD/6-31+G(d,p) level of theory in acetonitrile (SMD). In the calculation of TEMPO and $TEMPO^+$, we set cavity type to 'alpha=1.03' which specified the electrostatic scaling factor in SCRF because these compounds could not be optimized in the default value (alpha=1.00). All PC and $PC^{\bullet+}$ structures were optimized in the default value (alpha=1.00).

The single-electron transfer between $PC^{\bullet+}$ and TEMPO is shown as:



The activation energy for an SET process was estimated using Marcus-Hush theory.[39-45] The expression for the activation energy of an SET process is given by,

$$\Delta G^{\ddagger} = \frac{(\Delta G_r + \lambda)^2}{4\lambda} \qquad \text{eq. 2}$$

$$\lambda = \lambda_{inner} + \lambda_{outer} \qquad \text{eq. 3}$$

$\Delta G^{\ddagger}$ = Activation energy for the SET process

ΔG_r = Free energy change for the SET process

λ = Total reorganization energy for the SET process

λ_{inner} = Total inner-sphere contribution

λ_{outer} = Total outer-sphere contribution

ΔG_r is the free energy change of eq. 1 obtained from DFT calculations. The total reorganization energy (λ) is the sum of total inner-sphere (λ_{inner}) and total outer-sphere (λ_{outer}) contributions by eq. 3.

Calculation of ΔG_r

ΔG_r is the Gibbs free energy change of eq. 1 obtained from DFT calculations.

Calculation of Total Inner-sphere Contributions (λ_{inner})

The total inner-sphere contribution (λ_{inner}) was calculated by López-Estrada and Amador-Bedolla's reported method[46] (eq. 4) according to the Four-Point Approach to the Electron-Transfer Marcus-Hush Theory.

$$\lambda_{inner} = (\lambda_1 \lambda_2)^{1/2} \qquad \text{eq. 4}$$

λ_1 and λ_2 denote the reorganization energies of the forward and backward reactions in eq. 1. Nelsen's four-point method was used to estimate the reaction energy (ΔG_r) and the internal reorganization energies (λ_1 and λ_2).[47,48] The method is as follows,

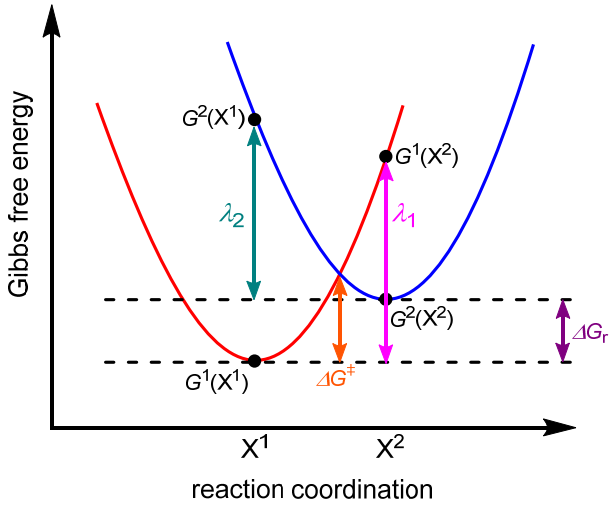


Figure S14. Nelsen's four-point method

$G^1(X^1)$ = Sum of Gibbs free energies of reactants in equilibrium geometries.
$G^2(X^2)$ = Sum of Gibbs free energies of products in equilibrium geometries.
$G^1(X^2)$ = Sum of Gibbs free energies of reactants in products geometries.
$G^2(X^1)$ = Sum of Gibbs free energies of products in reactants geometries.

$\Delta G_r = G^2(X^2) - G^1(X^1)$ eq. 5
$G^2(X^1) - G^1(X^1) = \lambda_2 + \Delta G_r$ eq. 6
$G^1(X^2) - G^2(X^2) = \lambda_1 - \Delta G_r$ eq. 7

To obtain the relevant parameters of the left parabola, we conducted the structural optimization of $PC^{\bullet+}$ (radical cation state, **PC1**$^{\bullet+}$, **PC2**$^{\bullet+}$, **PC3**$^{\bullet+}$, or **PC4**$^{\bullet+}$) and TEMPO (neutral state, **TEMPO**) to obtain $G^1(X^1)$, following Figure S37, and then performed a single-point calculation with these coordinates but changing the charge to get PC (neutral state, **PC1'**, **PC2'**, **PC3'**, or **PC4'**) and $TEMPO^+$ (cation state, **TEMPO**$^+$**'**) to compute $G^2(X^1)$. For the right parabola, by an analogous procedure we obtain $G^2(X^2)$ and $G^1(X^2)$. That is, we conducted the structural optimization of PC (neutral state, **PC1**, **PC2**, **PC3**, or **PC4**) and $TEMPO^+$ (cation state, **TEMPO**$^+$) to obtain $G^2(X^2)$, and then performed a single-point calculation with these coordinates but changing the charge to get $PC^{\bullet+}$ (radical cation state, **PC1**$^{\bullet+}$**'**, **PC2**$^{\bullet+}$**'**, **PC3**$^{\bullet+}$**'**, or **PC4**$^{\bullet+}$**'**) and TEMPO (neutral state, **TEMPO'**) to compute $G^1(X^2)$.

For **PC1**;
$G^1(X^1)$ = Sum of Gibbs free energies of reactants (**PC1**$^{\bullet+}$ and **TEMPO**) in equilibrium geometries.
$G^2(X^2)$ = Sum of Gibbs free energies of products (**PC1** and **TEMPO**$^+$) in equilibrium geometries.
$G^1(X^2)$ = Sum of Gibbs free energies of reactants (**PC1**$^{\bullet+}$**'** and **TEMPO'**) in products geometries.

$G^2(X^1)$ = Sum of Gibbs free energies of products (**PC1'** and **TEMPO^{+}'**) in reactants geometries.

For **PC2**;

$G^1(X^1)$ = Sum of Gibbs free energies of reactants (**PC2$^{\bullet+}$** and **TEMPO**) in equilibrium geometries.

$G^2(X^2)$ = Sum of Gibbs free energies of products (**PC2** and **TEMPO^{+}**) in equilibrium geometries.

$G^1(X^2)$ = Sum of Gibbs free energies of reactants (**PC2$^{\bullet+}$'** and **TEMPO'**) in products geometries.

$G^2(X^1)$ = Sum of Gibbs free energies of products (**PC2'** and **TEMPO^{+}'**) in reactants geometries.

For **PC3**;

$G^1(X^1)$ = Sum of Gibbs free energies of reactants (**PC3$^{\bullet+}$** and **TEMPO**) in equilibrium geometries.

$G^2(X^2)$ = Sum of Gibbs free energies of products (**PC3** and **TEMPO^{+}**) in equilibrium geometries.

$G^1(X^2)$ = Sum of Gibbs free energies of reactants (**PC3$^{\bullet+}$'** and **TEMPO'**) in products geometries.

$G^2(X^1)$ = Sum of Gibbs free energies of products (**PC3'** and **TEMPO^{+}'**) in reactants geometries.

For **PC4**;

$G^1(X^1)$ = Sum of Gibbs free energies of reactants (**PC4$^{\bullet+}$** and **TEMPO**) in equilibrium geometries.

$G^2(X^2)$ = Sum of Gibbs free energies of products (**PC4** and **TEMPO^{+}**) in equilibrium geometries.

$G^1(X^2)$ = Sum of Gibbs free energies of reactants (**PC4$^{\bullet+}$'** and **TEMPO'**) in products geometries.

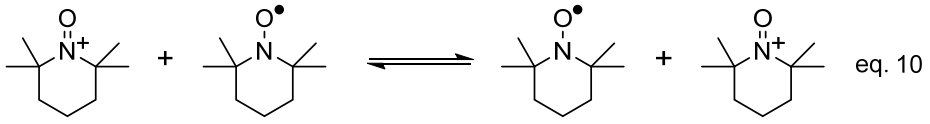
$G^2(X^1)$ = Sum of Gibbs free energies of products (**PC4'** and **TEMPO^{+}'**) in reactants geometries.

Calculation of Total Outer-sphere Contributions (λ_{outer})

The total outer-sphere contribution (λ_{outer}) in eq. 3 was obtained through eq. 8, where $\lambda_{(PC)outer}$ and $\lambda_{(TEMPO)outer}$ are outer-sphere contributions of the reorganization energies associated with the self-exchange electron transfer reactions, eqs. 9 and 10, respectively.

$$\lambda_{outer} = \frac{\lambda_{(PC)outer} + \lambda_{(TEMPO)outer}}{2} \qquad \text{eq. 8}$$

eq. 9



eq. 10

$\lambda_{(PC)outer}$ and $\lambda_{(TEMPO)outer}$ are derived from the solvent reorganization energy of the Born model for the solvation of charged species in a dielectric continuum.[49] Here, r_1 and r_2 are the effective radii (Å) of PC and PC$^{\bullet+}$, respectively. r_3 and r_4 are the effective radii (Å) of TEMPO and TEMPO^{+}, respectively. ε_{op} and ε_s are the optical and static dielectric constant of the solvent (MeCN: $\varepsilon_{op} = 1.81$[50] and $\varepsilon_s = 35.88$[51]).

$$\lambda_{(PC)outer\ (kcal/mol)} = N_A \frac{(ze_0)^2}{4\pi\varepsilon_0}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_1 + r_2}\right)$$

$$= 332.2\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_1 + r_2}\right) \qquad \text{eq. 11}$$

$$\lambda_{(TEMPO)outer\ (kcal/mol)} = N_A \frac{(ze_0)^2}{4\pi\varepsilon_0}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{2r_3} + \frac{1}{2r_4} - \frac{1}{r_3 + r_4}\right)$$

$$= 332.2\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{2r_3} + \frac{1}{2r_4} - \frac{1}{r_3 + r_4}\right) \qquad \text{eq. 12}$$

ε_{op} = the optical constant of the solvent (MeCN: ε_{op} = 1.81)

ε_s = the static dielectric constant of the solvent (MeCN: ε_s = 35.88)

r_1 = the effective radii (Å) of PC

r_2 = the effective radii (Å) of $PC^{\bullet+}$

r_3 = the effective radii (Å) of TEMPO

r_4 = the effective radii (Å) of $TEMPO^{\bullet+}$

N_A = Avogadro constant (6.02×10^{23} mol^{-1})

z = the number of electrons transferred in the electron transfer step (z = 1 in eqs. 9 and 10)

e_0 = elementary charge (1.60×10^{-19} C)

ε_0 = electric constant (8.85×10^{-12} F•m^{-1})

In this case, $r_1 = r_2$ and $r_3 = r_4$ are approximated.

The effective radius ($r = r_1$ and r_3) were approximated by the following method.

The van der Waals volumes (V_{vdW}) of PC and TEMPO were calculated by Abraham's reported method.[52]

Table S8. Summary of van der Waals volumes

	PC1 (Å^3)	**PC2** (Å^3)	**PC3** (Å^3)	**PC4** (Å^3)	**TEMPO** (Å^3)
V_{vdW}	243.54	358.31	392.90	278.13	170.33

Then, according to Miyamoto's reported method,[53] the effective radii were derived using the following equation:

$$V_{vdW} = \frac{4}{3}\pi r^3 \qquad \text{eq. 13}$$

where the effective radii r (r_1 and r_3) is the radii of a sphere with the V_{vdW}.

Summary of The Values of λ_1, λ_2, λ_{inner}, V_{vdW}, r_1, r_3, λ_{outer}, λ, ΔG_r, and $\Delta G^{\ddagger}$

The total inner-sphere contributions (λ_{inner}) were obtained through eqs. 4, 6, and 7. The total outer-sphere contributions (λ_{outer}) were obtained through eqs. 8-13. The total reorganization energies (λ) were obtained through eq. 3. In addition to the reaction driving force (ΔG_r) obtained by eq. 5, the corresponding activation energy ($\Delta G^{\ddagger}$) was obtained by using eq. 2.

Table S9. Summary of values of λ_1, λ_2, λ_{inner}, V_{vdW}, r_1, r_3, λ_{outer}, λ, ΔG_r, and $\Delta G^{\ddagger}$

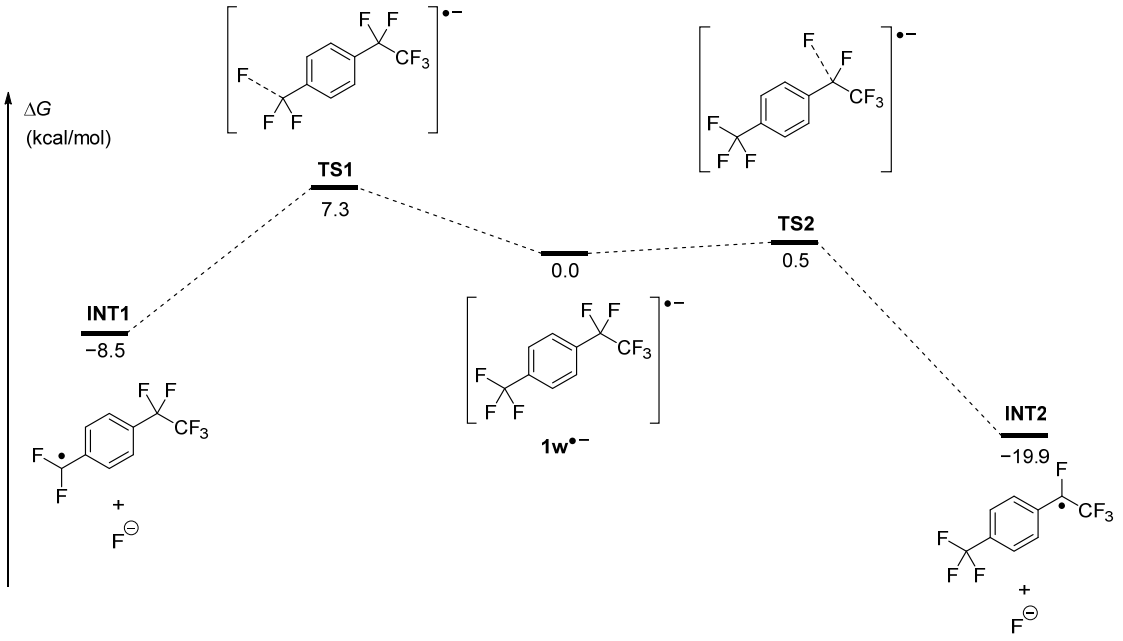
PC	λ_1 (kcal/mol)	λ_2 (kcal/mol)	λ_{inner} (kcal/mol)	r_1 (= r_2) (Å)	r_3 (= r_4) (Å)	$\lambda_{(PC)outer}$ (kcal/mol)	$\lambda_{(TEMPO)outer}$ (kcal/mol)	λ_{outer} (kcal/mol)
PC1	18.63	19.12	18.88	3.875	3.439	22.49	25.34	23.91
PC2	20.52	19.07	19.78	4.407	3.439	19.77	25.34	22.55
PC3	15.83	17.23	16.51	4.544	3.439	19.18	25.34	22.26
PC4	18.10	17.21	17.65	4.050	3.439	21.52	25.34	23.43

Table S9. Summary of values of λ_1, λ_2, λ_{inner}, V_{vdW}, r_1, r_3, λ_{outer}, λ, ΔG_r, and $\Delta G^{\ddagger}$ (Continued)

PC	λ (kcal/mol)	ΔG_r (kcal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)
PC1	42.79	2.04	11.75
PC2	42.34	3.84	12.59
PC3	38.77	3.68	11.62
PC4	41.08	3.17	11.91

Origin of Site-selectivity in Transformation of 1e (Scheme S6)

DFT calculations were conducted to clarify the site-selectivity in the transformation of **1e** possessing both CF_3 and C_6F_{13} groups (Scheme 2, product **3e**). To simplify the calculations, perfluoroalkylarene **1w** possessing CF_3 and C_2F_5 groups instead of **1e** was used as a model substrate. The energy profile of defluorination from radical anion of **1w** is shown in Scheme S6. Mesolysis of C–F bond in the C_2F_5 group preferentially proceeds compared to that in the CF_3 group due to a lower activation energy, giving a more stable radical intermediate **INT2** than **INT1**. Therefore, the aminoxylation of **1e** proceeded with a high site-selectivity to give **3e**.



Scheme S6. Energy profile of mesolysis of C–F bond of **1w** radical anion

3-5. References

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(17) See Figures S12 and S13.

(18) Excited **PC3*** selectively reduces starting material **1** in prior to product **3** in terms of reduction potential. For example, E(**1a**/**1a**$^{\bullet-}$) = −2.06 V vs SCE, E(**3a**/**3a**$^{\bullet-}$) = −2.31 V vs SCE.

(19) In contarast to **PC2** and **PC3**, **PC1** and **PC4** did not work in the aminoxylation of **1j**, which exhibited lower reduction potential than **1a**, due to the lower reducing abilities of **PC1*** and **PC4*** (Tables S6 and S7). This is because that the 1st SET is slower due to lower reducing abilities of **PC1*** and **PC4*** caused by the lack of N^{i}Pr$_2$ group. Thus, the catalytic activities of **PC1** and **PC4** are lower than those of **PC2** and **PC3**. The Marcus analysis of **PC1** and **PC4** as well as **PC2** and **PC3** is shown in the Supporting Information.

(20) Figures S1 and S2 show the Stern-Volmer fluorescence quenching studies of **PC2** and **PC3** with **1e**.

(21) Sub-nano second laser flash photolysis was conducted to determine the lifetimes of singlet states of **PC2** and **PC3**. The singlet lifetime of **PC2** was $^1\tau_0$ = 2.4 ns ($1/^1\tau = k_d$ = 4.1 x 10^8 s^{-1}) and that of **PC3** was $^1\tau_0$ = 2.5 ns ($1/^1\tau_0 = k_0$ = 4.0 x 10^8 s^{-1}) (see Figures S6 and S8).

(22) The diffusion-controlled rate constant of acetonitrile is k_{diff} = 1.9 x 10^{10} L mol^{-1}s^{-1}. M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Handbook of Photochemistry, 3rd ed.*; CRC Press, **2006**.

(23) The quenching rate constants of excited singlet species of PC (^1k_q) with **1e** is much larger than the inter-

system-crossing rates of PC (Scheme S1). Thus, the triplet species has a negligible contribution to this reaction. In fact, open air conditions gave the target product in high yield (Scheme S3).

(24) The absorption of radical anion **A** was not observed due to being out of the monitoring range.

(25) Figures S3 and S4 show the Stern-Volmer plots for $1/\tau$ of $PC^{\bullet+}$ versus [TEMPO **2**].

(26) Recently, in several papers, activation energies for single electron transfer processes, in organic reactions were estimated by Marcus-Hush theory. See selected papers: (a) López-Estrada, O.; Laguna, H. G.; Barrueta-Flores, C.; Amador-Bedolla, C. *ACS Omega* **2018**, *3*, 2130–2140. (b) Fu, M.-C.; Shang, R.; Zhao, B.; Wang, B.; Fu, Y. *Science* **2019**, *363*, 1429–1434. (c) Paulisch, T. O.; Strieth-Kalthoff, F.; Henkel, C.; Pitzer, L.; Guldi, D. M.; Glorius, F. *Chem. Sci.* **2020**, *11*, 731–736. (d) Matsumoto, K.; Nakajima, M.; Nemoto, T. *J. Org. Chem.* **2020**, *85*, 11802–11811. (e) Sil, S.; Bhaskaran, A. S.; Chakraborty, S.; Singh, B.; Kuniyil, R.; Mandal, S. K. *J. Am. Chem. Soc.* **2022**, *144*, 22611–22621. (f) Ma, C.; Shen, J.; Qu, C.; Shao, T.; Cao, S.; Yin, Y.; Zhao, X.; Jiang, Z. *J. Am. Chem. Soc.* **2023**, *145*, 20141–20148. (g) Wang, M.; Rowshanpour, R.; Guan, L.; Ruskin, J.; Nguyen, P. M.; Wang, Y.; Zhang, Q. A.; Liu, R.; Ling, B.; Woltornist, R.; Stephens, A. M.; Prasad, A.; Dudding, T.; Lectka, T.; Pitts, C. R. *J. Am. Chem. Soc.* **2023**, *145*, 22442–22455.

(27) See Table S9 for the derivation of ΔG_r, λ, and $\Delta G^{\ddagger}$

(28) DFT calculation study revealed that the alkyl radical intermediate generated via C–F bond mesolysis at perfluoroalkyl group was more stable than one generated via the mesolysis at CF_3 group and that the activation energy for perfluoroalkyl group is lower than that for CF_3 group (Scheme S6).

(29) The elimination of fluoride ion from the corresponding radical anion intermediate would be very slow because a negative charge in the radical anion is effectively delocalized in a large π-conjugation system.

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Conclusion

In this study, the synthetic methodologies for the selective C–F bond transformation of perfluoroalkyl compounds have been developed by merging photoredox catalysis and Lewis acid activation.

Firstly, photoredox-catalyzed C–F bond allylation of perfluoroalkylarenes at the benzylic position was described in Chapter 1. Allylic stannanes worked as effective radical acceptors and tin fluoride, which is produced as a by-product, captured fluoride ion and improved the reaction efficienecy. Selective transformation of a C–F bond in long perfluoroalkyl groups was accomplished. The synthesis of fluorine-substituted analogue of ASK1 inhibitor was successful using present reaction system.

Secondly, photo-catalyzed C–F bond heteroarylation of trifluoromethylarenes with heteroarenes was described in Chapter 2. Bu_3SnI worked as a fluoride ion scavenger to improve reaction efficiency. Furthermore, it worked as a reductant to produce Ir(II) species, which has higher reduction ability than photoexcited Ir(III)* species. This reaction system has high functional group tolerance and was able to be used for late-stage functionalization of medicines.

Thirdly, sequential C–F bond transformation of the difluoromethylene unit in perfluoroalkyl groups was accomplished. Newly developed phenothiazine-based photoredox catalyst which has amino and dimethyl groups was an efficient catalyst in the defluoroaminoxylation of perfluoroalkylarenes. Spectroscopic measurements revealed the catalyst has not only high reduction ability to reduce various perfluoroalkyl compounds but also appropriate oxidation potential and the radical cation is smoothly reduced by TEMPO. A further transformation of the defluoroaminoxylated products was achieved by $AlCl_3$ and nucleophiles. $AlCl_3$ was suitable for not only abstraction of fluoride ion but also activation of ketone intermediates. Totally sequential transformation of CF_2 unit in perfluoroalkyl groups was conducted.

Knowledges obtained from chapter 1 and 2 is that a combination of photoredox catalysis and Lewis acid activation shows selective activation of inert C–F bond. Formation of tin fluoride is a driving force for defluorinative transformation by photoredox catalysis. This strategy will be more suitable for further work to be aimed at other inert bonds transformation. Chapter 3 gives us an important knowledge that photoredox catalytic system and Lewis acid activation possess distinct strengths. Their combination facilitates selective sequential transformation of C–F bonds in difluoromethylene unit. This fact is significant not only in organofluorine chemistry, but also in photochemistry.

The obtained knowledge provides an unprecedent strategy to transform inert bonds as well as a C–F bond by combination of photoredox catalysis and Lewis acid activation. The insights obtained from the present works are expected to contribute to radical chemistry.

List of Publications

1) **Photoredox-Catalyzed C–F Bond Allylation of Perfluoroalkylarenes at the Benzylic Position**
   N. Sugihara, K. Suzuki, Y. Nishimoto, M. Yasuda
   J. Am. Chem. Soc. **2021**, *143*, 9308-9313.

2) **Photo-catalyzed C–F Bond Heteroarylation of Trifluoromethylarenes with Heteroarenes: Two Roles of Bu_3SnI as Fluoride Ion Scavenger and Activator for Photo-catalyst**
   N. Sugihara, M. Abe, Y. Nishimoto, M. Yasuda
   Synthesis DOI: 10.1055/a-2235-1380

3) **Sequential C–F Bond Transformation of the Difluoromethylene Unit in Perfluoroalkyl Groups: A Combination of Fine-Tuned Phenothiazine and Lewis Acid Catalysis**
   N. Sugihara, Y. Nishimoto, Y. Osakada, M. Fujitsuka, M. Abe, M. Yasuda
   Angew. Chem. Int. Ed. **2024**, *63*, e202401117.

<Supplementary Publications>

1) **C(sp^3)–F Bond Transformation of Perfluoroalkyl Compounds Mediated by Visible-Light Photocatalysis: Spin-Center Shift and Radical/Polar Crossover Process via Anionic Intermediates**
   Y. Nishimoto, N. Sugihara, M. Yasuda
   Synthesis **2022***, 54,* 2765-2777.

2) ***anti*-Selective Borylstannylation of Alkynes with (*o*-Phenylenediaminato)borylstannanes by a Radical Mechanism**
   K. Suzuki, N. Sugihara, Y. Nishimoto, M. Yasuda
   Angew. Chem. Int. Ed. **2022**, *61*, e202201883.