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Photoredox catalyzed synthesis of organosulfur compounds from olefins

（フォトレドックス触媒によるオレフィン類からの有機硫黄化合物の合成法に関する研究）

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June 2016

Preface and Acknowledgements

The studies described in this thesis have been carried out under the direction of Professor Dr. Munetaka Akita and Assistant Professor Dr. Takashi Koike from 2013 to 2016 at Chemical Resources Laboratory, Tokyo Institute of Technology.

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Yanjie LI

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Chapter 1

General Introduction

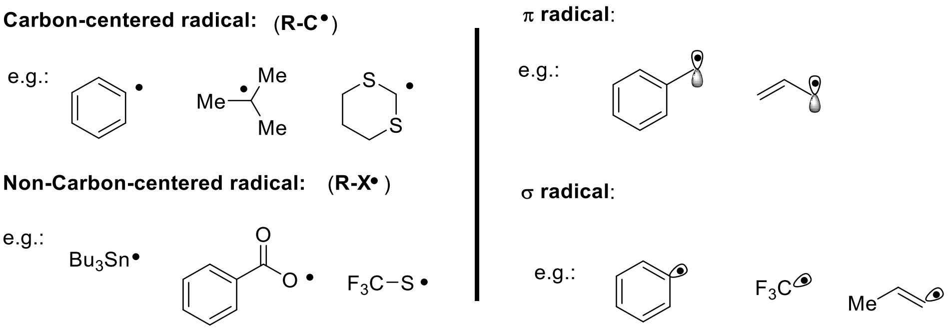
In organic chemistry, reactive species are usually classified into two types: compound with and without unpaired valence electron(s). Because radical species with unpaired valence electron(s) have many advantages such as mild reaction conditions, different behavior from that of non-radical species, and tolerance to functional groups, radical chemistry is regarded as an attractive research area. Radical generation by conventional methods, however, has many drawbacks such as requirement of toxic and explosive reagent, UV light, the use of a stoichiometric amount of a reductant or an oxidant, and so on. Visible-light-induced photoredox catalysis is regarded as an attractive approach for radical generation because the system is non-toxic and can be driven by the abundant energy source, sunlight. Thus, the author decided to develop new radical reactions by visible-light-induced photoredox catalysis.

Organosulfur compounds are valuable in medicinal and materials science because of their unique features. Many researchers have made great efforts to develop numerous synthetic reactions for organosulfur compounds. But green, simple, mild, and effective synthetic methods for them are still demanded. In addition, functionalization of alkenes, abundant feedstocks, is an efficient strategy for constructing carbon skeletons. In the present thesis, the author describes the results obtained to pursue development of new radical synthesis of organosulfur compounds from alkenes by photoredox catalysis.

1.1 Organic radical

In chemistry, atom, molecule, or ion which has unpaired valence electron(s) is regarded as radical or free radical [1]. Organic radical is one kind of radicals which contains one or more carbon atoms.

1.1.1 Types of organic radical

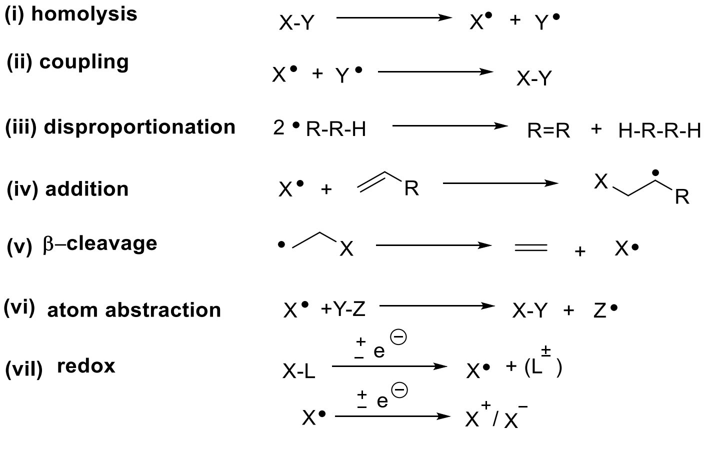


Scheme 1.1 Examples of diferent types of radicals

Organic radicals are classified into carbon-centered radical and non-carbon-centered radical. On the basis of the character of the orbital where the unpaired electron resides, organic radical also can be divided into π radical and σ radical. Generally, the π radicals such as benzyl, and allyl radicals are stabilized by hyperconjugation or π–conjugation. σ Radicals, however, are not stabilized, and thus σ radical are more reactive than π radical[2].

1.1.2 Elemental reactions of organic radical species

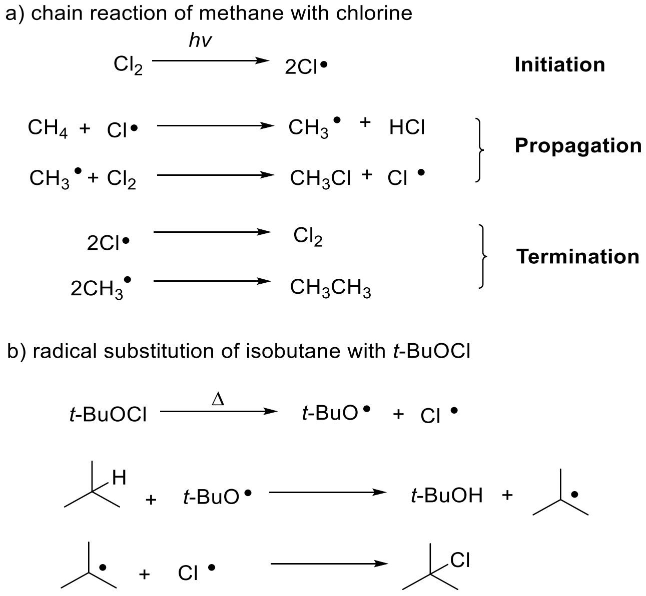
Elemental reactions of organic radical species can be classified according to Scheme 1.2 and are totally different from those of non-radical species without unpaired electron(s). Most of radical reactions have been interpreted by combinations of them.



Scheme 1.2. Elemental reactions of organic radical

Radical species can be generated by homolysis of a bond (i) and can undergo coupling with another radical species to form a new bond to quench the radical species (ii). Radicals can also be quenched by disproportionation to afford a mixture of the hydrogenated and dehydrogenated products (iii). Radicals can undergo addition to unsaturated bonds to form new radical species with extended organic skeletons (iv). A kind of reverse reaction of (iv) is β-cleavage to form a new radical with elimination of a fragment of the original organic skeleton (v). The radical center can be transfered to another molecule by atom abstraction accompanying bond cleavage (vi). Redox processes including photoredox catalysis (vii) play key roles in radical chemistry as described in detail below. Radical species can be generated by redox processes of neutral precursors frequently accompanying elimination of a fragment of the precursor and, on the contrary, redox processes can convert radical species into ionic species, which are susceptible to nucleophilic or electrophilic reactions.

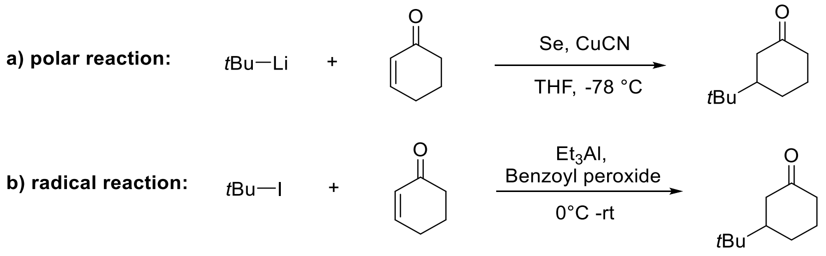
A combination of these elementary reactions leads either to a chain reaction (a) or to a stoichiometric reaction (b) as shown in Scheme 1.3. Chain reaction usually consists of three steps: initiation, propagation, and termination. Radical homo-coupling reaction occurs as a side reaction to terminate reaction. The stoichiometric substitution reaction is simpler and only includes two radical transfer process.



Scheme 1.3. Typical examples of chain reaction and stoichiometric redox reaction

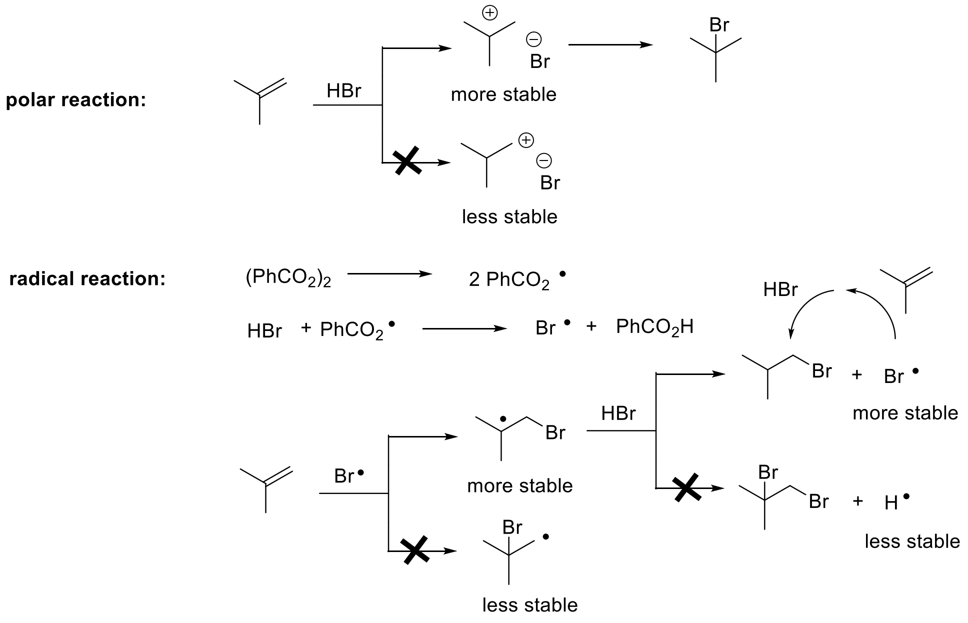
Radical reactions exhibit many advantages:

(1) Mild reaction conditions. Radicals are generated under mild conditions, i.e. without addition of acids or bases and at low to moderate temperatures. To take the alkylation of alkene for instance, both polar reaction and radical reaction can afford alkylated product, but the reaction conditions are different. In polar reaction, alkene is usually treated with strong base R-Li at low temperature (-78 ˚C) in the presence of CuCN and Se (Scheme 1.4a) [3], but radical reaction only needs radical initiators (Scheme 1.4b) [4]. In addition, the possibility of participation of radical process in the polar reaction (Scheme 1.4a) can not be excluded completely.



Scheme 1.4. Addition reactions of cyclohex-2-enone

(2) Many functional groups which the polar reaction can not be tolerant are stable during radical reactions. For example, hydroxyl group is stable in radical reactions due to the thermodynamically stable O-H bond. Radical species can not abstract proton from the OH group easily.



Scheme 1.5. Addition reactions of hydrogen bromide (HBr) to isobutene

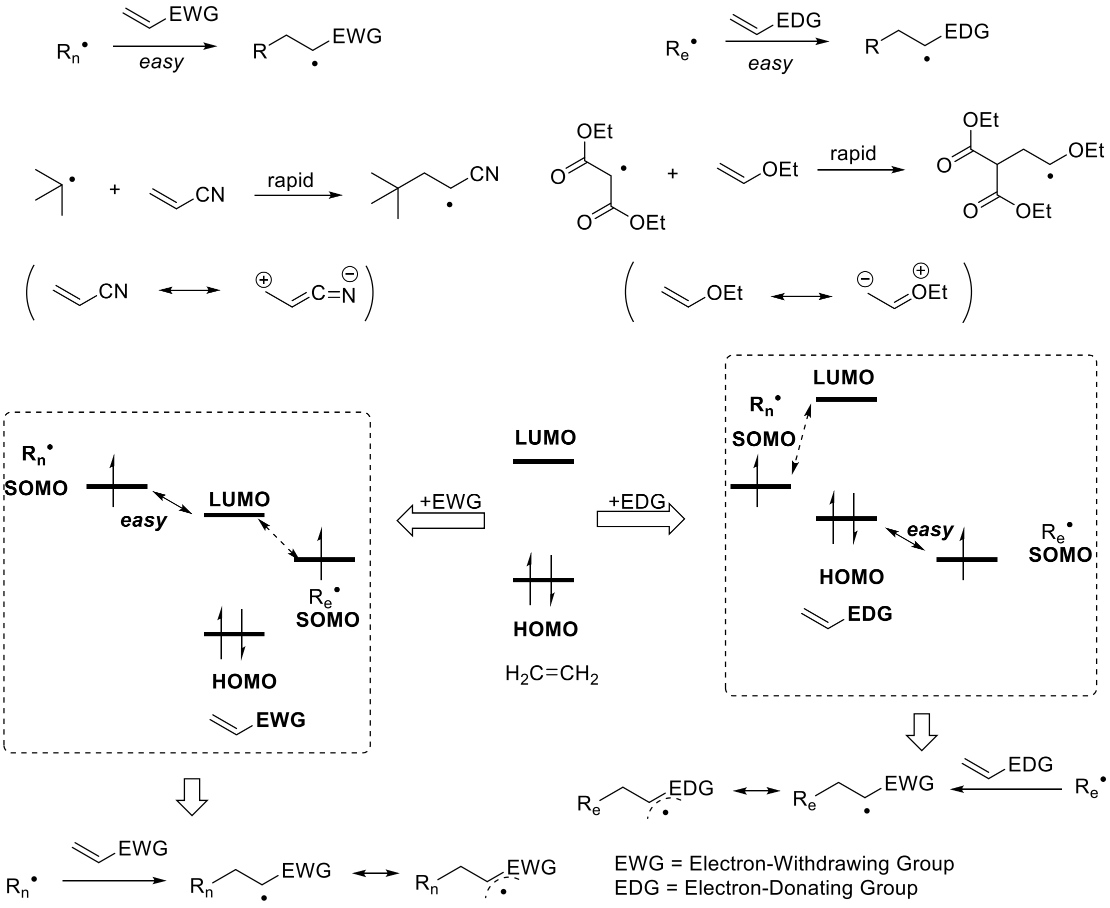
(3) Radical species has different regioselectivity in addition reactions. A typical

example is addition reaction of hydrogen bromide (HBr) to isobutene (Scheme 1.5). For the polar reaction, *t*-butyl cation is firstly produced from the addition of a proton of HBr to the terminal *sp*^{2} carbon atom of isobutene, then it reacts with the bromide anion to form *t*-butyl bromide as the product. For the radical reaction, however, the hydrogen atom of HBr is abstracted first by $PhCO_2\cdot$ radical which is generated from $(PhCO_2)_2$, then formed Br· radical adds to the terminal *sp*^{2} carbon atom of isobutene, to form 3-bromo-2-methylprop-2-yl-radical. The regiochemistry of the reaction is determined at the next stage, i.e. which of H· or Br· is abstracted by the radical. Because Br· radical is more stable than H· due to the size of Br atom being much larger than H atom, hydrogen is abstracted by the resultant radical from HBr to afford *i*-butyl bromide and more stable Br·, which continues to react with *i*-butene following the radical chain mechanism as discussed above.

1.1.3 Reactivity of radicals toward unsaturated bonds

Before discussion of the generation methods of radical species (section1.2), reactivity of radicals toward unsaturated bonds, which is the major subject of the present thesis, is discussed to follow the discussion on the reactivity of organic radicals in the this section.

Organic radicals are classified into two groups, i.e. nucleophilic ($R_n\cdot$) and electrophilic ones ($R_e\cdot$) (Scheme 1.6) [5]. *t*-Butyl radical and diethyl malonyl radical are typical examples of them, respectively. *t*-Butyl radical adds to acrylonitrile but not to vinyl ether. On the contrary, the malonyl radical adds to vinyl ether but not to acrylonitrile. The different reactivity can be interpreted taking into account the resonance contributors of the acceptors. Because the β-carbon atom of acrylonitrile is positively charged due to the electronegative nitrogen atom, nucleophilic radical adds to the β-carbon atom. On the other hand, because the β-carbon atom of vinyl ether is negatively charged due to the π-donating effect of the oxygen atom, electrophilic radical adds to the β-carbon atom. The different reactivity can be also interpreted in terms of MO consideration (Scheme 1.6). In the case of *t*-butyl radical, the energy level of the singly occupied molecular orbital (SOMO) is raised higher in energy owing to the inductive effect of the three electron-donating methyl groups so that it adds to electron-deficient olefins (e.g. acrylonitrile), the LUMO of which is, in energy, comparable to the SOMO of the *t*-butyl radical so as to couple with each other. Thus *t*-butyl radical is regarded as a nucleophilic radical (R_n•). On the contrary, the malonyl radical carrying the electron-withdrawing substitutents, which lower the SOMO energy level, usually adds to electron-rich olefins (*e.g.* vinyl ethers) with HOMO comparable in energy to the SOMO of the radical so as to couple with each other. Thus the malonyl radical is regarded as an electrophilic radical (R_e•).



Scheme 1.6. Reactivity of radical on addition reaction

The regiochemistry of the addition is determined by the factor of the stability of the radical intermediates formed by the addition. In both cases, the radical centers are generated at the positions, where the resultant radicals are stabilized by the resonace effects of the substituents, i.e. usually, α-position with respect to the substituents. In other words, radical adds to the β-carbon atoms. The regiochemistry can also be interpreted in terms of the resonance structures of the acceptors discussed above.

The radical intermediates thus generated further react with other organic species in the reaction mixture following the pathways shown in Scheme 1.2 to afford products. For example, *atom abstraction* affords the addition product and *chain reaction* with olefinic substrates leads to radical polymerization.

1.2 Photoredox catalysis

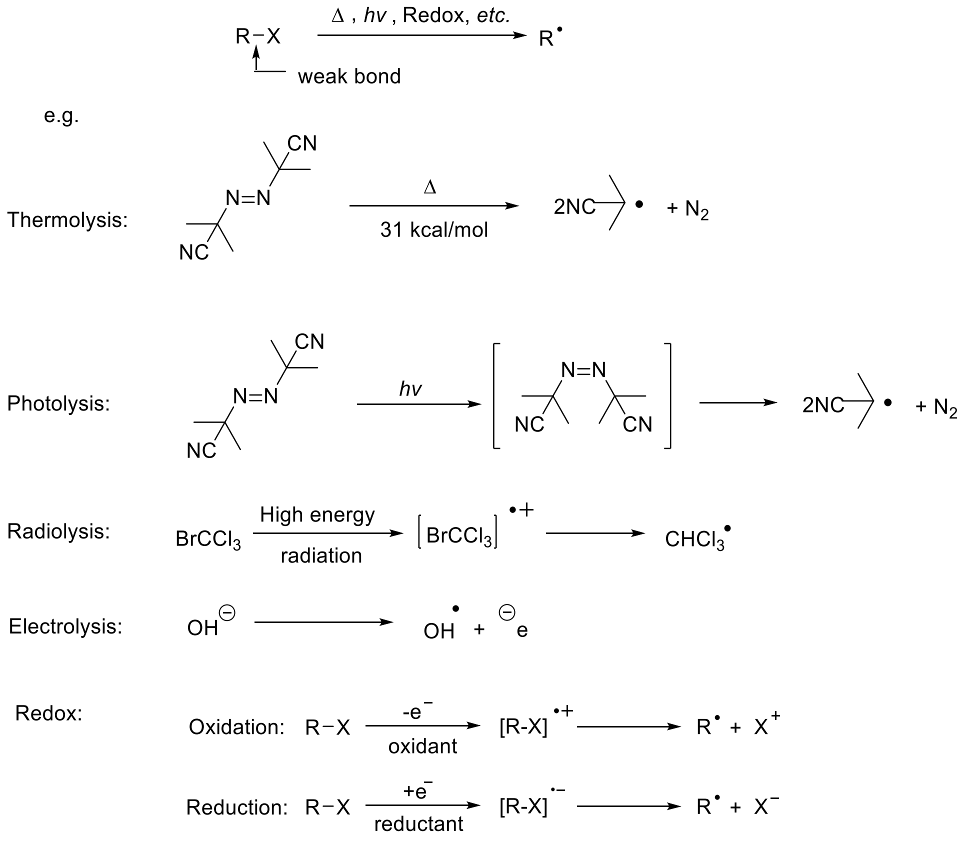
In this section features of photoredox catalysis will be summarized. In the present thesis, *photoredox catalysis* is regarded as organic radical reactions involving a series of redox (electron-transfer) processes induced by irradiation of visible light.

Generation of radicals is the first step of any radical reaction processes including photoredox catalysis. This section is initiated by comparison of the radical generation method by photoredox catalysis with the conventional methods and then characteristics of photoredox catalysis including reaction features and mechanisms will be summarized.

1.2.1 Conventional methods for radical generation

Organic radicals are usually generated by homolysis of a weak bond in a precursor or redox processes of a precursor (Scheme 1.7). [5]

The homolysis is induced by thermolysis, photolysis, radiolysis, or electrolysis and so on. Azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO) are typical initiators of radical polymerization and both of them decompose upon heating or UV irradiation. Bonds associated with a heavy element are, in general, so weak that compounds containing a heavy element are frequently involved in radical reactions, as typically exemplified by organotin reagents. These precursors are convenient but have some drawbacks. For example, AIBN and BPO are explosive and therefore must be kept in a refrigerator in the dark and handled with care. Furthermore, compounds containing a heavy element such as organotin reagents are frequently harmful so that their use must be limited as least as possible.



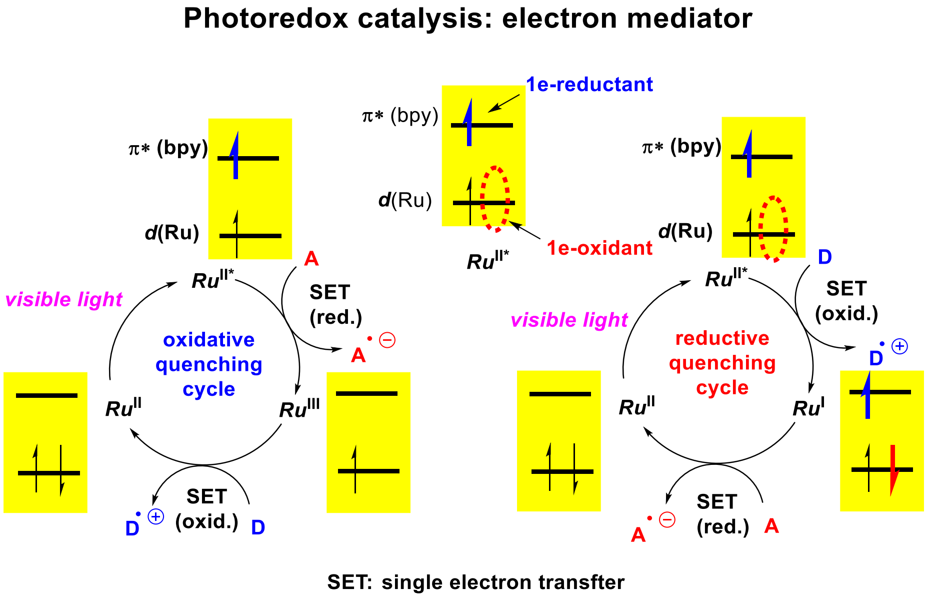
Scheme 1.7. Conventional methods for generation of organic radicals

Organic radicals, odd-electron species, can be generated also by redox processes. Bond homolysis can be induced by addition (reduction)/ removal (oxidation) of an electron to/ from an appropriate precursor with closed shells, i.e. either by the action of a stoichiometric amount of a reductant or an oxidant or by electrolysis. Although these methods are convenient, the stoichiometric use of the redox reagents causes formation of wastes and the electrolysis requires a special equipment.

1.2.2 Generation of organic radicals by means of photoredox catalysis

In recent years, the visible-light-induced photoredox catalysis has been regarded as useful and green processes because the drawbacks of the conventional methods can be overcome by this process as will be discussed later. As described above, one of the features of photoredox catalysis is *driving organic transformations by sunlight (visible light)*, which is abundant on the earth as supplied from the sun. Because most of organic compounds are colorless, they cannot absorb visible light. Some sensitizer, therefore, should be added to the reaction system so that the system absorbs the solar energy. The colored catalysts include organic dyes and coordination and organometallic compounds (e.g. ruthenium polypyridine complexes, cyclometalated iridium complexes, and relevant copper, platinum and gold complexes) [6].

The photochemical processes will be explained taking $[Ru(bpy)_3]^{2+}$ for instance. The ruthenium complex exhibits an intense absorption band around 450 nm, i.e. the higher energy component of the sunlight. Irradiation of the photocatalyst (***Ru^{II}***) with visible light leads to the singlet excited state via MLCT transition (from the frontier metal *d* orbital to the ligand π^* orbital), which is converted to the triplet excited species (***Ru^{II*}***) via intersystem crossing. The triplet excited species has a lifetime of μs order, which is long enough for most of chemical processes (ns - ps order).



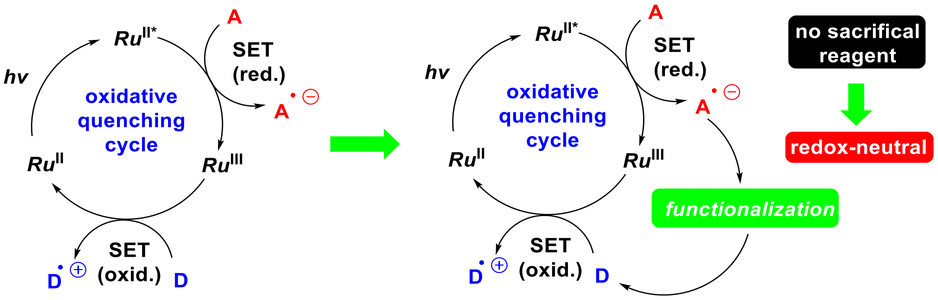
Scheme 1.8 Reductive quenching cycle and oxidative quenching cycle of $[Ru(bpy)_3]^{2+}$

The triplet excited species can be used in two ways. The electron in the higher SOMO and the hole in the lower SOMO may serve as a 1e-reductant or a 1e-oxidant, respectively. When the present photochemical system is combined with chemical reactions, which require the redox properties of the catalyst, the reactions will proceed by simply irradiating visible light (sunlight).

The photocatalytic reactions have been divided into two types, called *reductive quenching cycle* and *oxidative quenching cycle*, which are initiated by reduction and oxidation processes of the photoexcited species ($\boldsymbol{Ru}^{\mathbf{II}*}$), respectively (Scheme 1.8). In the *reductive quenching cycle*, the hole of $\boldsymbol{Ru}^{\mathbf{II}*}$ abstracts an electron from a donor ($\boldsymbol{D}$) nearby to form the cationic radical of the donor ($\boldsymbol{D}^{+\cdot}$) together with the reduced Ru species ($\boldsymbol{Ru}^{\mathbf{I}}$), which then may undergo 1e-transfer to an acceptor ($\boldsymbol{A}$) nearby to afford the anionic species ($\boldsymbol{A}^{-\cdot}$) together with the ground state metal catalyst ($\boldsymbol{Ru}^{\mathbf{II}}$). Thus simple irradiation of the reaction system containing the redox photocatalyst drives the reaction cycle to afford the oxidized and reduced radical species. The redox process can also be initiated by the oxidation processes, and the catalytic cycle is called *oxidative quenching cycle*, in which the photoexcited species interacts with the external reagents in the order of an acceptor ($\boldsymbol{Ru}^{\mathbf{II}*} + \boldsymbol{A} \rightarrow \boldsymbol{Ru}^{\mathbf{III}} + \boldsymbol{A}^{-\cdot}$) and a donor ($\boldsymbol{Ru}^{\mathbf{III}} + \boldsymbol{D} \rightarrow \boldsymbol{Ru}^{\mathbf{II}} + \boldsymbol{D}^{+\cdot}$). Thus the radical generation by the action of photredox catalysis turns out to be superior to the conventional methods in any aspects mentioned above, i.e. safe, harmless, no need for a special equipment, and no use of fossil fuel (just light), to make the catalystic system *green*.

1.2.3 Reaction features of photoredox catalysis

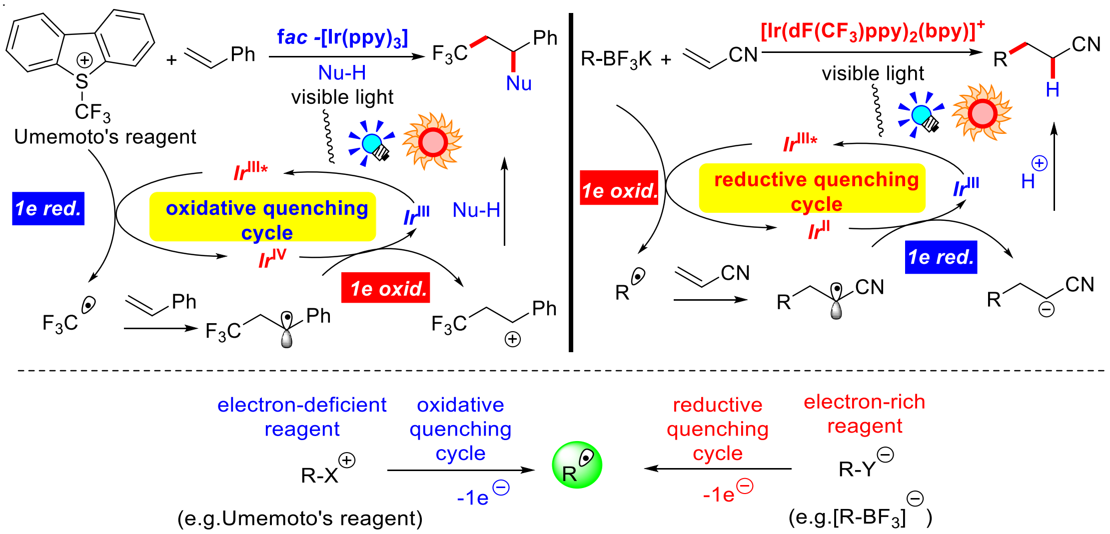
In the field of inorganic chemistry, the reductive quenching cycle has been utilized for reduction of small inorganic molecules such as CO_2 (to CO) and H^+ (to H_2). But in these cases, a sacrificial electron donor (usually tertiary amine) is needed and the donor is not included in the skeleton of the product but just serves as an electron source. This is not acceptable from the view point of *atom economy*. If the radical intermediate formed by the initial redox process is functionalized by a third molecule and then subjected to the second redox process, both donor and acceptor will be combined into the product together with the third component to make the system *atom-economic*. In addition, the electron transfered to or taken out of the catalyst in the first redox process is taken out of or transfered to the catalyst through the second redox process and thus the reaction system is regarded also as a *redox-neutral* system (Scheme 1.9). Although the author’s group regards the advanced combined system without addition of sacrificial redox reagents as *photoredox catalysis*, the separated systems are often called *photoredox catalysis* by other researchers.



Scheme 1.9 Ru photoredox catalysis is a redox-neutral system

It should be noted that the redox power of the catalyst is enhanced by the photo-excitation. When the oxidative quenching cycle is taken as an example, the reduction power of a species is roughly characterized by the energy level of the highest occupied orbital, which is HOMO for the ground state and the higher SOMO for the excited state (Scheme 1.8). Thus the reduction power of the photo-excited species is enhanced by the energy gap between the HOMO of the ground state catalyst of the excited species and the higher SOMO of the excited species. Similar consideration for the oxidation process points out that the oxidation power of the photo-excited species is enhanced by the energy gap between the LUMO of the ground state catalyst and the lower SOMO of the photo-excited species.

Typical examples of our previous results are summarized in Scheme 1.10, which shows oxy-trifluoromethylation of styrene derivatives [7] and Giese-type reaction of organotrifluoroborates [8]. In these reactions, trifluoromethyl radical and organyl radicals are generated by 1e-transfer from and to the the excited catalyst. Subsequent capture of the radical intermediates by olefinic substrates followed by reverse 1e-transfer affords the ground state catalyst and the carbo-cationic or -anionic intermediates, respectively, which are further functionalized by the action of the nucleophile or proton to furnish the products. It is notable that these two processes are *redox-neutral*, although the orders of the two redox processes are reversed.



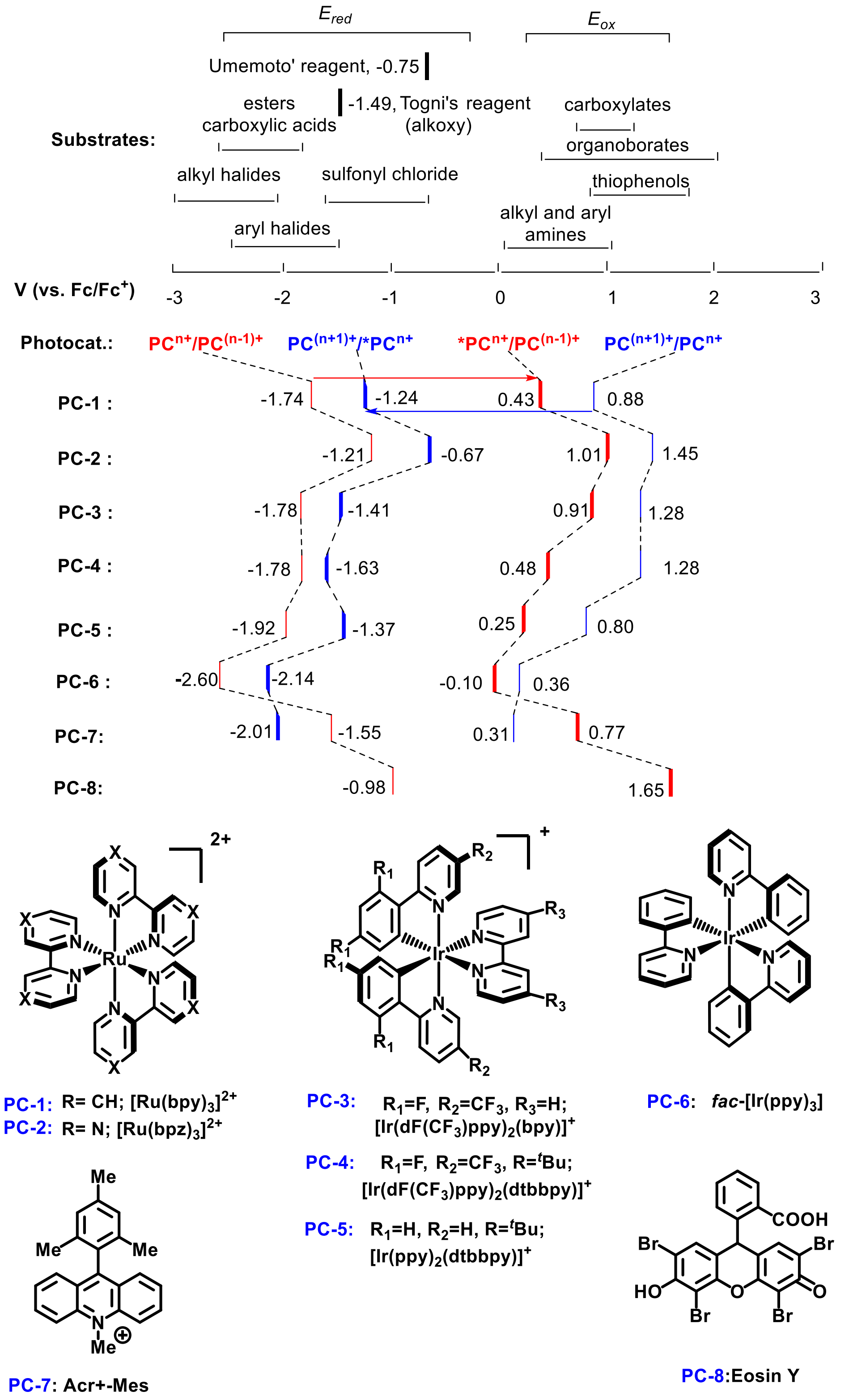
Scheme 1.10 Photoredox catalysis via oxidative and reductive quenching cycles

The concept included in the typical examples can be further generalized according to Scheme 1.10 (the lower scheme). Organic radicals may be generated either by 1e-oxidation of electron-rich precursors following the reductive quenching cycle or by 1e-reduction of electron-deficient precursors following the oxidative quenching cycle.

1.2.4 Physical properties of the photoredox catalysts

Because photoredox catalysis is regarded as a catalytic process involving redox processes, the redox potentials of the photo-excited species are the most important features of the catalysts. The redox potentials of the photo-excited catalyst are shown in Scheme 1.11 together with those of the ground state species [6h,i].

The potential $\mathbf{PC^{(n+1)+}/{*}PC^{n+}}$ stands for the oxidation potential for the photo-excited species $\mathbf{{*}PC^{n+}}$, which is comparable to the reduction power of the excited species, and the potential $\mathbf{{*}PC^{n+}/PC^{(n-1)+}}$ stands for the reduction potential for the photo-excited species $\mathbf{{*}PC^{n+}}$, which is comparable to the oxidizing power of the excited species. In contrast, the potential $\mathbf{PC^{n+}/PC^{(n-1)+}}$ stands for the reduction potential for the ground state species $\mathbf{PC^{n+}}$, which is comparable to the oxidizing power of the ground state, and the potential $\mathbf{PC^{(n+1)}/PC^{n+}}$ stands for the oxidation potential for the ground state species $\mathbf{PC^{n+}}$, which is comparable to the reduction power of the ground state.



Scheme 1.11. Redox potentials of photocatalyst and representative organic substrates

First of all, both of the oxidizing and reducing power of the metal catalyst is significantly enhanced by the photo-irradiation. For example, for $[Ru(bpy)_3]^{2+}$, the oxidizing and reducing power of enhanced by 2.17 V (-1.74 V → 0.43 V) and 2.12 V (0.88 V → -1.24 V), respectively, as indicated by the arrows and the difference would be roughly comparable to the HOMO-LUMO gap, as already discussed in section 1.2.3.

The redox potentials of the photoredox catalysts are dependent on several factors such as the kind of the central metal (Ru vs. Ir), the charge (neutral vs. cationic), the electron-donating property, and the charge of the chelating ligand. A catalyst appropriate for the purpose of the experiment should be chosen. For example, for an oxidative transformation via RQC, it may be better to choose a catalyst having a larger $\mathbf{{}^*PC^{n+}/PC^{(n-1)}}$ value. Other factors such as the multiplicity and the lifetime of the photoexcited species and solubility, however, should be taken into account.

When the redox potentials of the photo-excited species are compared with those of representative organic substances, the latter fall between the two potentials, $\mathbf{PC^{(n+1)}/{}^*PC^{n+}}$ and $\mathbf{{}^*PC^{n+}/PC^{(n-1)}}$, indicating that these substances can be oxidized or reduced by the excited photocatalyst.

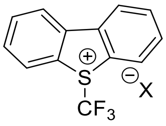
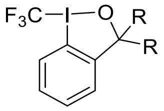
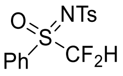
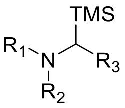
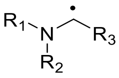
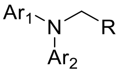
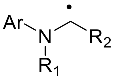
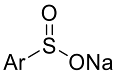
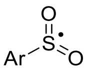
1.2.5 Photoredox catalyzed reactions

An increasing number of a variety of photoredox catalyzed reactions have been reported. For a brief survey, selected examples of the catalytic reactions involving carbon- and sulfur-centered radicals, which are relevant to the present thesis, are summarized together with the precursors, the catalysts, and resultant radicals in Table 1.1. The reactions are further divided into those following the oxidative quenching cycle (OQC) and the reductive quenching cycle (RQC).

As mentioned in the previous section, electron-deficient substrates, in general, follow oxidative quenching cycle, i.e. 1e-reduction, to generate the corresponding radicals with elimination of small fragments. Fluoromethyl radicals can be generated from the corresponding electrophilic fluoromethylating reagents. In addition, various aryl radicals can be generated from the arenediazonium salts or diaryliodonium salts.

On the other hand, electron-rich substrates follow reductive quenching cycle, i.e. 1e-oxidation to generate the corresponding radicals with elimination of small fragments. α-Hetero-substituted radicals can be rather easily generated due to the π-stabilization by the hetero atom. For the S-centered radicals, the fluoromethylthiyl radical also can be generated from the electrophilic reagent by OQC, and alkyl- or aryl-thiyl radical and arylsulfonyl radical can be afforded from electron-rich thiols and aryl sulfonates by RQC.

Table 1.1 the generation of typical organic radicals by photoredox catalysis

Types of radicals	Cycle	Precursor	Catalyst	Radical	Ref
Carbon-centered organic radicals	OQC	R-X	PC-1	R·	9
		ArN_2X or Ar_2IX	PC-1	Ar·	10, 11
		 or  Umemoto's reagent Togni's reagent	PC-6	$\cdot CF_3$	7
		 Hu's reagent	PC-6	$\cdot CF_2H$	12
	RQC	$R\text{-}BF_3K$	PC-3	R·	8
		RCOOH	PC-7	R·	13
			PC-5		14
			PC-5		15
Sulfur-centered organic radicals	OQC	$BrSCF_3$	PC-6	$\cdot SCF_3$	16
	RQC	RSH	PC-2	RS·	17
			PC-8		18

RQC: reductive quenching cycle; OQC: oxidative quenching cycle

1.3 Organosulfur compounds

Organosulfur compounds are defined as a molecule containing one or more sulfur atom(s). They are important and essential for human life. For example, of the twenty amino acids, two of them are organosulfur compounds, i.e. cysteine and methionine, and many antibiotics such as penicillin contain organosulfur unit.

1.3.1 Key features of sulfur and organosulfur compounds

In organosulfur compounds, the sulfur atom plays key roles in the character of the molecules. Sulfur, a group 6 element, lies below oxygen in the periodic table. Organosulfur compounds show similarities to the corresponding oxygen analogues yet there are some differences between them, of course. [19]

1. The atomic radius of sulfur (1.02 Å) is larger than that of oxygen (0.73 Å) because of the larger size of the valence orbitals (3*s*/3*p* for S vs. 2*s*/2*p* for O).
2. Due to the size effect and the more polarizable character of the 3*s*/3*p* electrons,
   (i) the electronegativity of sulfur (2.44) is significantly smaller than that of oxygen (3.5),
   (ii) sulfur is softer than oxygen, and thus organosulfur compounds are more nucleophilic toward electrophiles and better donors toward metal ions than the corresponding oxygen analogues,
   (iii) organosulfur compounds are susceptible to oxidation, and
   (iv) thiyl radicals (RS•) are much more stable than the corresponding oxyl radicals (RO•),
3. In contrast to oxygen atom, the vacant 3*d* orbitals of sulfur atom can participate in bonding to lead to hypervalent compounds such as those containing a SO_2 and SO_3 moiety. The SF_5 group, which will be dealt with in this thesis, is a member of hypervalent species.

Many features of organosulfur compounds can be interpreted in terms of these factors. For example, the weaker acidity of thiol, R-SH, can be ascribed to factor 2;

the negative charge is accommodated in the larger 3*s*/3*p* orbitals to make electrostatic interaction with H^+ weaker. Furthermore, thiolate (RS^-) and thiyl radical ($RS\cdot$) are frequently utilized as synthones for organosulfur compounds due to their stability (factors 2-ii and iii).

Typical S-functional organic compounds are listed in Scheme 1.12.

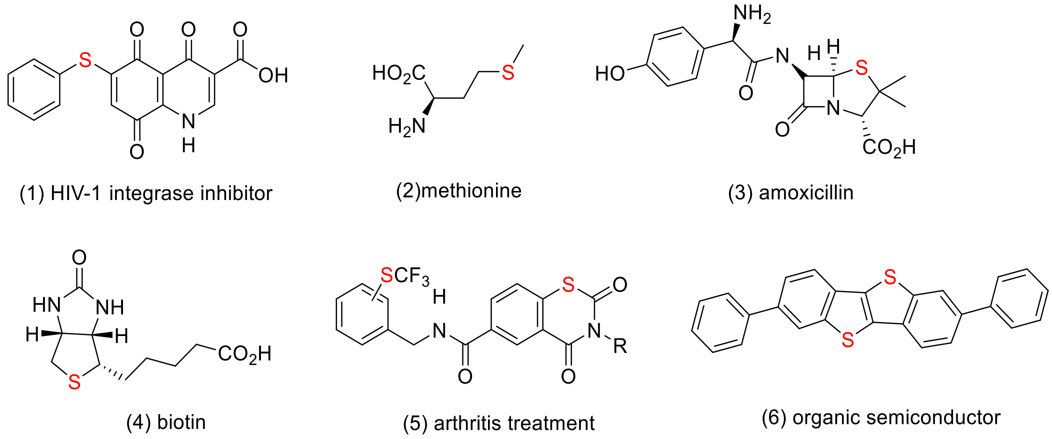
RS-H R-S-R R-S-S-R R-S(O)-R $R\text{-}S(O)_2\text{-}R$ $R_2S{=}NR'$ $F_5S\text{-}R$

RSX R-S-N=O RC(=S)R' RSOH $R\text{-}S(O)_2H$ $R\text{-}S(O)_3H$ $[R_3S]^+$ *etc.*

Scheme 1.12 Typical organosulfur compounds

Of the organosulfur compounds listed above, the present thesis deals with thioether (sulfide) and pentafluorosulfanylphenyl compounds. Furthermore, it is known that the S-functionalization of alkenes is an efficient strategy for constructing valuable organosulfur molecules. Thus, in this thesis the author describes results of the investigation on the synthetic reactions for organosulfur compounds from alkenes by the action of photoredox catalysis.

1.3.2 Thioether (Sulfide)



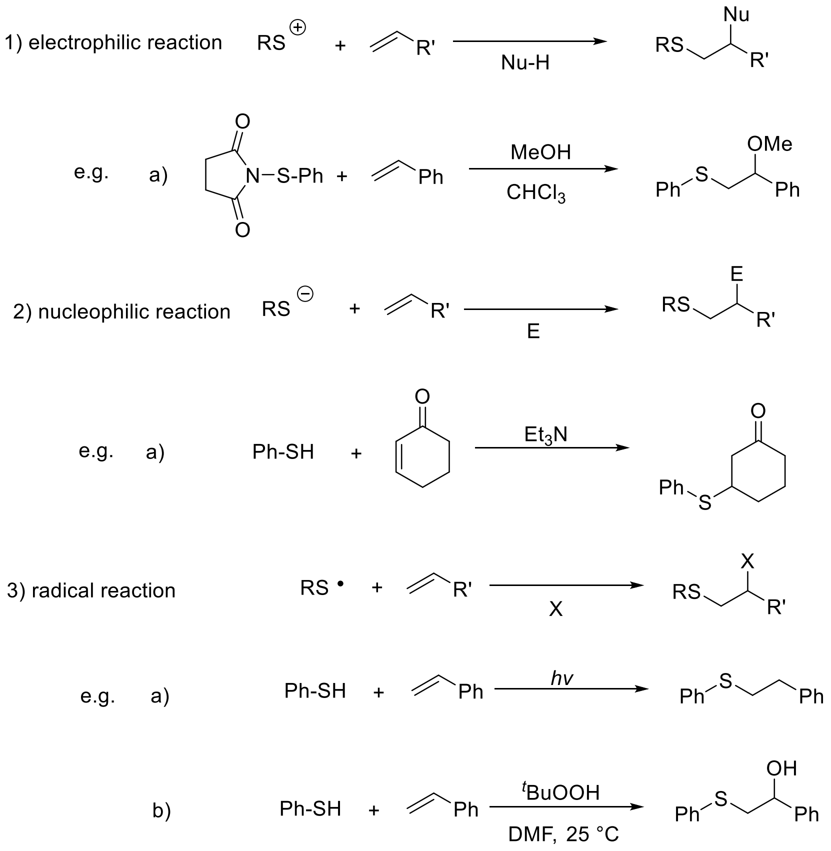
(1) HIV-1 integrase inhibitor (2)methionine (3) amoxicillin

(4) biotin (5) arthritis treatment (6) organic semiconductor

Scheme 1.13. Application of organosulfur compounds in medical and material field

Thioethers (sulfides) are widely found in medical and functional molecules [20]. For example, the organosulfur compounds (1) to (5) show excellent bioactivity, and (6) shows good performance as a semiconductor (Scheme 1.13).

Thioethers are usually prepared by constructing a new carbon-sulfur bond, via addition of sulfur cation or sulfur anion or sulfur radical. Thus, S-functionalization of alkenes can be classified into 3 types: a) electrophilic reaction; b) nucleophilic reaction; c) radical reaction. Because of different reactive species, the reactions could afford various products from the corresponding sulfur reagents (Scheme 1.14).



Scheme 1.14. Addition of the organosulfur fragments to olefins

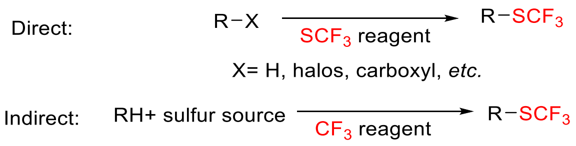
For the radical S-functionalization of alkenes, because RS· radical is electrophilic, it is different from RS^- but has some similarities with RS^+ on addition to alkene. For example, PhS· radical can easily react with electron-rich alkene like PhS^+ (Scheme 1.14 1a and 3a). In addition, RS· radical also can give hydroxyl addition products (Scheme 1.14 3b), thus it can afford more types of sulfides [21-23].

Organosulfur compounds are accessible by many other synthetic methods in addition to the C-S bond formation reactions (Scheme 1.14). In the following sections, the synthetic methods relevant to the contents of the present thesis will be summarized, i.e. synthesis of organosulfur compounds from alkenes via C-S bond formation and C-C bond formation of S-containing starting materials.

1.3.2.1 Trifluoromethylthiolation of alkene for synthesis of sulfides

SCF_3-containing sulfides are valuable in pharmaceutical and agrochemical fields, because the SCF_3 group is strongly electron-withdrawing ($\sigma_m = 0.40$, $\sigma_p = 0.50$) and highly lipophilic ($\pi = 1.44$) [24].

Two major strategies have been reported for synthesis of SCF_3-containing sulfides (Scheme 1.15). One is direct trifluoromethylthiolation by using SCF_3 reagents. The other is indirect formation using CF_3 reagents and sulfur sources.

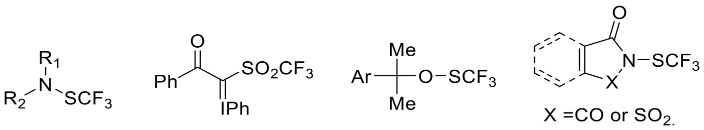


Scheme 1.15. Strategies for the synthesis of SCF_3-containing compound

In the strategy of the direct trifluoromethylthiolation, nucleophilic and electrophilic SCF_3 reagents are used (Table 1.2). Most of the nucleophilic reagents are metal trifluoromethylthiolate salts, which provide SCF_3 anion. Electrophilic reagents involve trifluoromethylsulfuryl halide, trifluoromethylsulfuryl acetate, and F_3CSSCF_3. Although they are active electrophilic reagents, they have many drawbacks such as gaseous, toxic, and highly corrosive nature and thus some shelf-stable trifluoromethylthiolating reagents have been developed in recent years as summarized in Table 1.2.

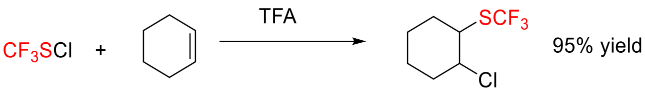
Herein, some seminal works on trifluromethylthiolation (SCF_3) of alkenes with related reagents are given below, and the reactions are classified according to the three types (Scheme 1.14).

Table 1.2. Two types of SCF_3 Reagents

Types	SCF_3 Reagents
Nucleophilic	$Hg(SCF_3)_2$, $AgSCF_3$, $CuSCF_3$, $[(bpy)CuSCF_3]$, $CsSCF_3$, Me_4NSCF_3, $HSCF_3$
Electrophilic	Hazardous reagents: $ClSCF_3$, $FSCF_3$, CF_3SOCOR, F_3CSSCF_3. Shelf-stable reagents:  X =CO or SO_2.

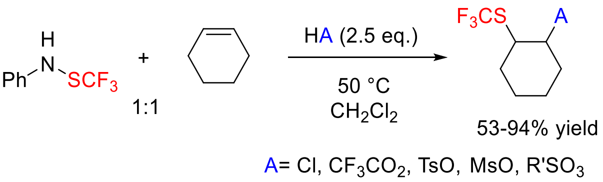
Electrophilic trifluromethylthiolation of alkenes

In 1985, Zhang developed the electrophilic SCF_3 addition to olefin with CF_3SCl by using trifluoroacetic acid (TFA)-catalysis (Scheme 1.16)[25].



Scheme 1.16. Electrophilic trifluromethylthiolation of alkenes

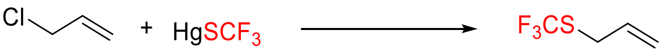
In 2009, Billard made a great progress on trifluoromethylthiolation of alkenes. His group first developed a stable SCF_3 cation precursor, trifluoromethanesulfanylamide, and reported the electrophilic trifluoromethylthiolation of alkenes with it via addition of the CF_3S^+ intermediate as shown in Scheme 1.17. A variety of SCF_3 adducts were obtained from the coressponding strong acids. In this case, the anionic part of the acids is incorponated into the products. But, only aliphatic alkenes were investigated in the reaction scope [26].



Scheme 1.17. Trifluoromethylthiolation of alkenes with trifluoromethanesulfanylamide

Nucleophilic trifluromethylthiolation of alkenes

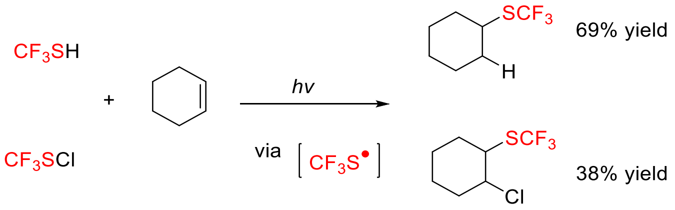
In nucleophilic trifluromethylthiolation of alkenes, most of examples are focused on nucleophilic substitution of allyl halide. For example, in 1959, Man reported the nucleophilic substitution of 3-chloroprop-1-ene by using $HgSCF_3$ (Scheme 1.18).[27]



Scheme 1.18. Nucleophilic SCF_3-substitution of allyl chloride

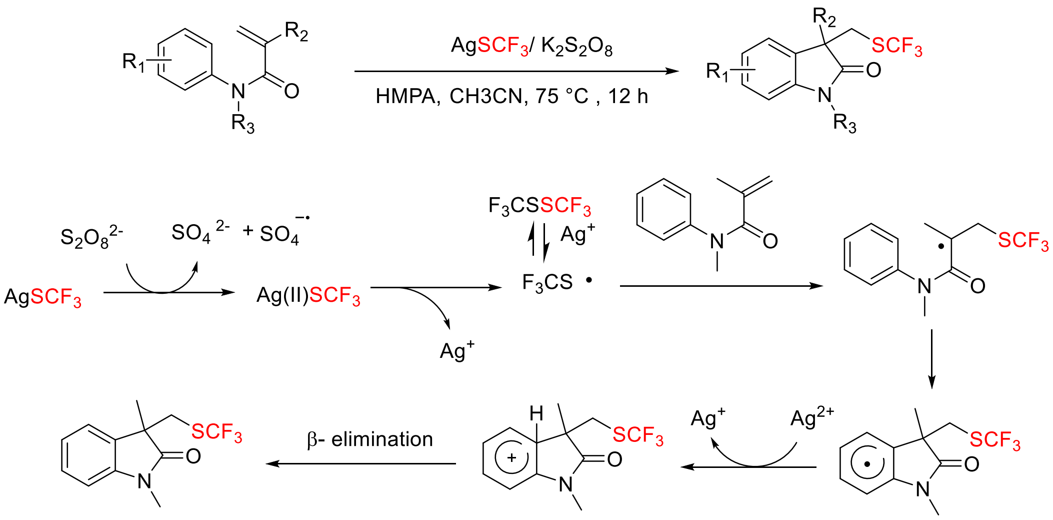
Radical triflurومethylthiolation of alkenes

Thiyl radcials (RS·) are interesting species due to their low sensitivity to oxygen and their high reactivity toward a wide range of alkenes. Generally, RS· radical can be easily generated from RSH and RSSR, because the S-H and S-S bonds are relatively weak. F_3CS· radical also can be generated from $HSCF_3$. For example, in 1960's, Harris successfully developed radical triflurومethylthiolation of alkenes using $HSCF_3$ and $ClSCF_3$ as the SCF_3 sources by UV irradiation [28-29].



Scheme 1.19. Radical triflurومethylthiolation of alkenes by $HSCF_3$ and $ClSCF_3$

AgSCF₃ works as an active radical reagent upon oxidation. For instance, in 2013, Wang developed aryltrifluoromethylthiolaton of activated alkenes by $AgSCF_3$ reagent via F_3CS·. A plausible mechanism is proposed as shown in Scheme 1.20. Firstly, the $AgSCF_3$ is oxidized by $K_2S_2O_8$ to afford Ag(II)SCF_3 species, which generates the F_3CS· radical via homolysis of the Ag-S bond. Then F_3CS· radical reacts with alkene to generate the corresponding alkyl radical intermediate. Subsequent cyclization affords the cyclohexadienyl radical intermediate. 1e-Oxidation followed by β-H elimination of the resultant cationic species affords the product [30].

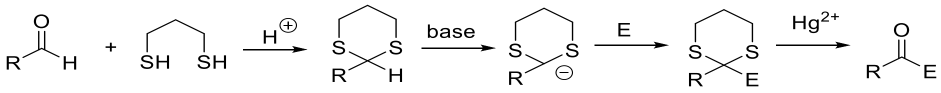


Scheme 1.20. Radical triflurومethylthiolation of alkenes by $AgSCF_3$

1.3.2.2 α-Thioalkylation of alkenes for synthesis of sulfides

Organic sulfides are also accessible through a C-C bond formation reaction with an S-containing precursor. Among them, α-thioalkylation of alkenes is one of important and efficient methods.

From synthetic point of view, dithiane has been used as a synthetic equivalent of *acyl anion*. Dithane are prepared by treatment of carbonyl compounds with 1,3-propandithiol. The hydrogen atoms attached to the methylene or methine carbon atoms adjacent to the two sulfur atoms are so acidic as to undergo deprotonation, and the resultant anionic species serve as nuclephiles in various transformations. After the series of the reactions, the carbonyl functional group can be recovered by deprotection, usually, by treatment with a Hg(II) salt (Scheme 1.21) [31].

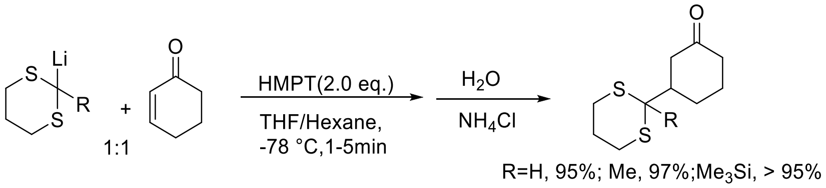


Scheme 1.21 1,3-Dithiane as an acyl anion equivalent.

α-Thioalkylation of alkenes also can be classified into three types like Scheme 1.14: a) nucleophilic addition; b) electrophilic addition; c) radical addition.

Nucleophilic α-thioalkylation of alkenes

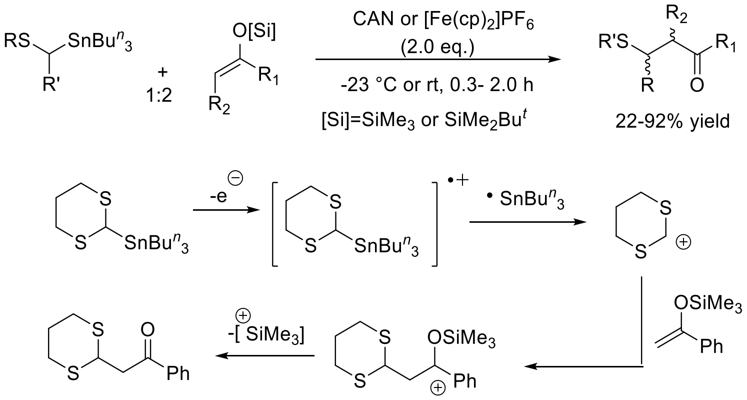
Substituted dithianes have been used as a masked acyl anion as mentioned above, and a variety of transformations have been studied. An example is shown in Scheme 1.22, where the lithiated intermediate underwent 1,4-addition to enones to furnish the β-substituted products. [32]



Scheme 1.22. Dithanylation of cyclohex-2-en-1-one

Electrophilic α-thioalkylation of alkenes

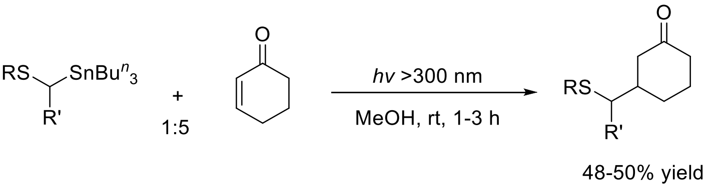
In 1993, Narasaka reported a coupling reaction between α-thioalkyltin compound and silyl enol ether by the action of an oxidant (ceric ammonium nitrate (CAN) or $[Fe(cp)_2]PF_6$) (Scheme 1.23). 1e-Oxidation of the tin reagent followed by elimination of the tin radical gives the cationic intermediate, which reacts with the silyl enol ether to afford the coupling product [33].



Scheme 1.23. Alkyl-and aryl-thioalkylation of alkenes via electrophilic addition

Radical α-Thioalkylation of alkenes

Later on, Narasaka reported an addtion reaction between the α-thioalkyltin compound and enone (Scheme 1.24). Judging from the regioselectivity of the addition, i.e. 1,4-addition, α-thioalkyl radical species should play a key role in this addition reaction[34].



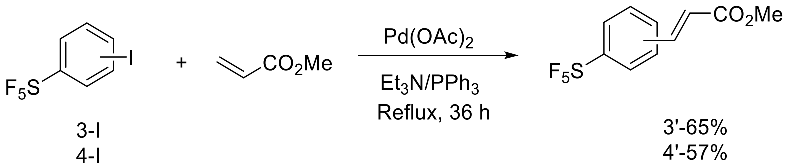
Scheme 1.24. Alkyl-and aryl-thioalkylation of cyclohexenone via radical intermediates

1.3.3 Pentafluorosulfanylphenyl group and Pentafluorosulfanyl-phenylation of alkenes

Pentafluorosulfanyl (SF_5) group has potentials of applications in the fields of medicinal and material science [35]. Because of the strong electron-withdrawing inductive effect, high lipophilicity and chemical stability, the SF_5 group has been regarded as an enhanced version of CF_3 group. In addition, it was reported that the SF_5 group can improve bioactivity of some compounds, when it replaces the CF_3

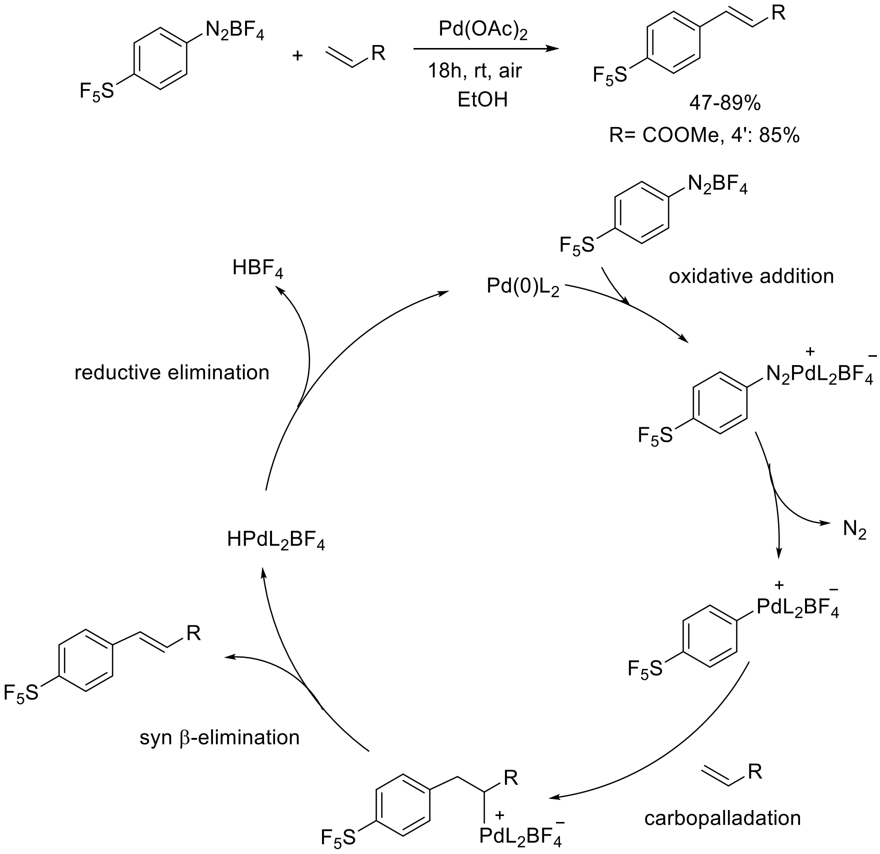
group on a benzene ring in the compound.[36] A useful and simple synthetic method for a variety of SF_5-arenes was developed by Umemoto' group in 2012.[37] In recent years, pentafluorosulfanylarylation (SF_5-arylation) of alkenes have been studied [38], but most of them were obtained by cross coupling reaction by transition metal catalysis.

For example, Philp gave the first example in SF_5-arylation of alkenes by Heck reaction in 2000. [38a]



Scheme 1.25. Heck-type pentafluorosulfanylphenylation of alkenes of alkenes

Laali synthesized 4-pentafluorosulfanylbenzenediazonium salt, and developed the cross coupling reaction in 2014[38g].



Scheme 1.26. Heck-Matsuda pentafluorosulfanylphenylation of alkenes

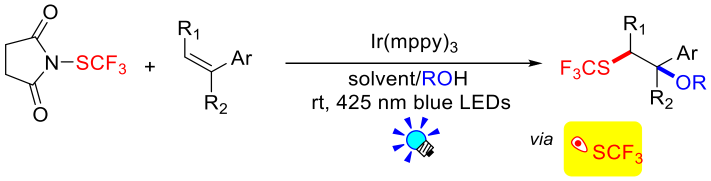
Under simple and mild reaction conditions, the SF_5Ph-diazonium salt afforded the *trans*-product in a high yield in a stereospecific manner. Furthermore, other alkenes also afford the products in 47-89% yield. As is shown in Scheme 1.26., the catalytic cycle includes 4 steps: oxidative addition, migratory insertion or carbopalladation, syn β-elimination and reductive elimination.

1.4 Survey of This Thesis

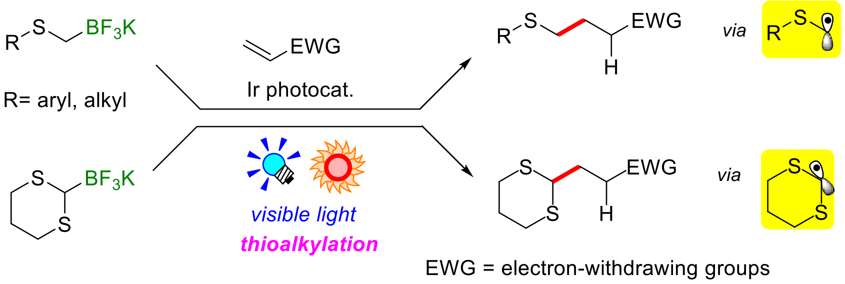
As the author has described, radical reaction and visible-light-induced photoredox catalysis have many advantages for organic synthesis and, therefore, coupling of the two concepts should lead to a new phase of organic synthesis. Thus, the author has made efforts to develop new synthetic routes of organosulfur compounds by photoredox catalysis.

The subjects detailed in the following Chapters are as follows:

In Chapter 2, the author shows radical oxy-trifluoromethylthiolation of styrenes with 1-trifluoromethylthio-pyrrolidine-2,5-dione as the SCF_3 radical source. In this reaction, water and a variety of alcohol can be used as the nucleophile.

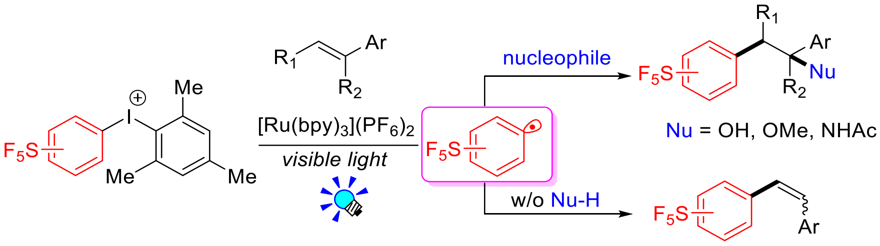


In Chapter 3, the author describes alkyl- and aryl-thioalkylation of olefins by the Ir photoredox catalysis. α-Thioalkyl radicals are generated from the coressponding thioalkyltrifluoroborates via deboronation, and react with electron-deficient olefins to provide the C-C coupling products in good yields.



Chapter 4 describes radical SF_5-phenylation of styrenes by photoredox catalysis.

Two different type of products are obtained depengding on the reaction conditions.



In the last chapter, summary and outlook are described.

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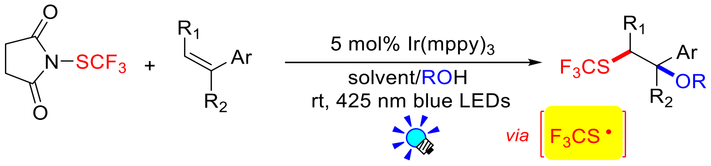
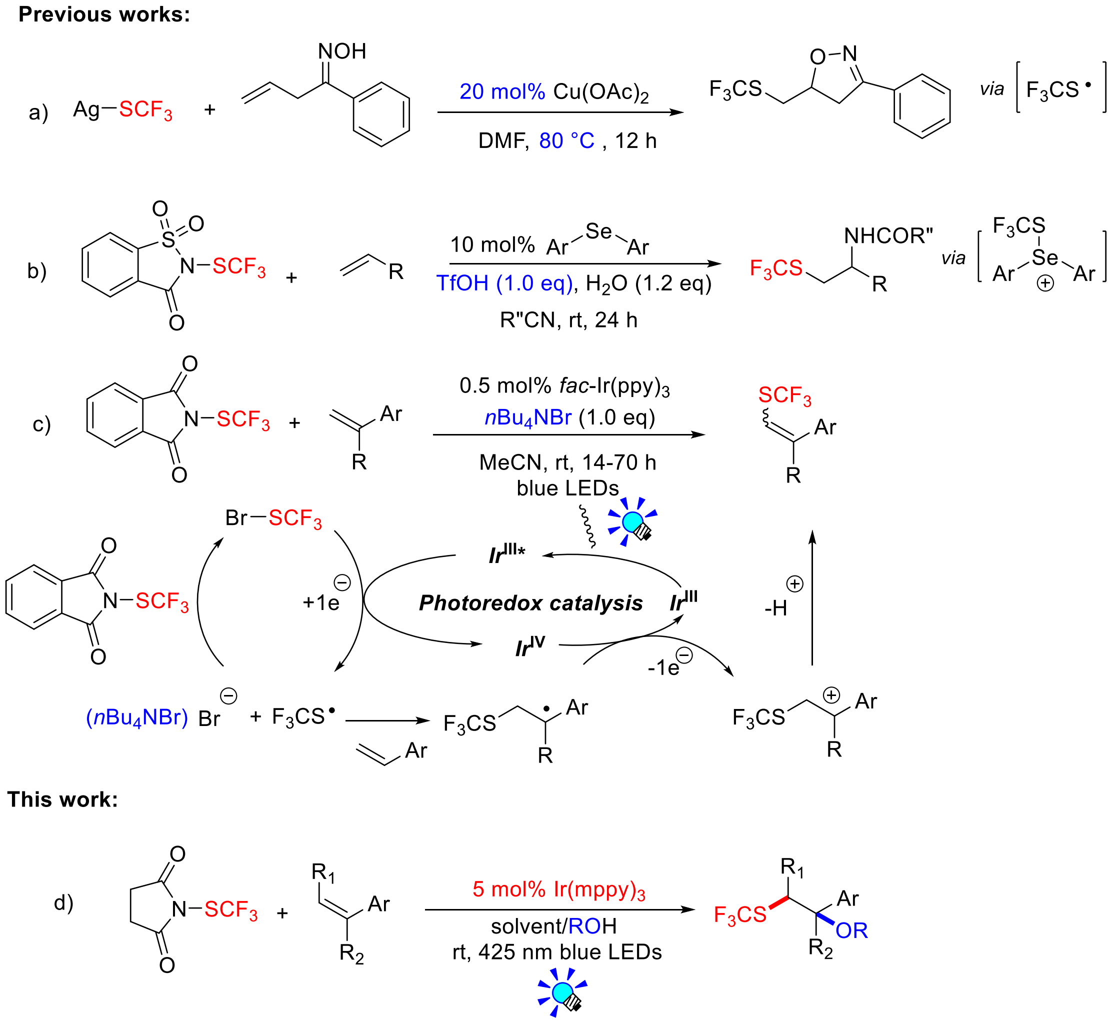
Chapter 2

Radical Oxy-trifluromethylthiolation of Styrenes by Photoredox Catalysis

ABSTRACT: A simple and novel oxy-trifluromethylthiolation of styrene derivatives by photoredox catalysis has been developed. The use of the Ir(mppy)3 (mppy = 2-(4-methoxyphenyl)-pyridyl) photocatalyst and 1-trifluoromethylthio-pyrrolidine-2,5-dione as the SCF_3 radical precursor is the key to success. The well-designed photoredox system achieves synthesis of not only β-SCF_3-substituted alcohols but also ethers from alkenes through solvolytic processes. The present method allows single-step and regioselective synthesis of the oxy-trifluromethylthiolated products from terminal and internal alkenes.



2.1 Introduction



Scheme 2.1 SCF$_3$-difunctionalization of alkenes

As the author described in Chapter 1, the SCF$_3$ group has great potentials in pesticide science and medical chemistry owing to its strongly electron-withdrawing effect and high lipophilicity. Therefore, a number of works have been devoted for incorporation of the CF$_3$S group into target organic molecules in the past years [1]. In these trifluromethylthiolations, the SCF$_3$-difunctionalization of alkenes is a simple and efficient strategy for synthesis of SCF$_3$ compounds, and has been developed in recent years [2]. For example, in 2014, Wang reported copper-catalyzed radical intramolecular oxy-trifluoromethylthiolation of unactivated alkenes by using AgSCF$_3$

reagent, and the reaction afforded a variety of SCF_3-isoxazolines (Scheme 2.1a) [2f]. The mechanism of this reaction is not clear, but participation of SCF_3 and oxime radical intermediates was proved from radical trapping experiments. In 2015, Zhao developed vicinal trifluoromethylthioamination of alkenes with *N*-trifluoromethylthio-saccharin by diaryl selenide catalysis (Scheme 2.1b). In this reaction, the SCF_3 reagent react with TfOH in the presence of diaryl selenide, and gave the highly active diaryl(trifluoromethylthio)selenonium intermediate, which reacts with alkenes to afford trifluoromethylthioaminated product. The wide scope of the substance was presented in this reaction, but a stoichiometric amount of superacid TfOH is needed [2h]. But, a simple, green and efficient strategy for SCF_3-difunctionalization of alkenes is still demanded.

On the other hand, Glorius recently developed dual photoredox/halide catalytic trifluoromethylthiolation of styrenes using *N*-trifluoromethylthio-phthalimide as the SCF_3 radical source, and the reaction afforded various vinyl-SCF_3 compounds as products (Scheme 2.1c) [2i]. In this reaction, the intermediate reagent $BrSCF_3$ was first formed from reaction of *N*-trifluoromethylthiophthalimide and *n*-Bu_4NBr. Then $BrSCF_3$ was reduced by the photoexcited *fac*-$[Ir(ppy)_3]$ species to generated $\cdot SCF_3$ radical, which added to styrene derivatives to afford the vinyl-SCF_3 compounds after deprotonation. Taking into account this situation, the author developed photoredox catalytic radical oxy-trifluromethylthiolation of styrenes with 1-trifluoromethylthio-pyrrolidine-2,5-dione (Scheme 2.1d).

When a photoredox-catalyzed transformation with addition of a CF_3S fragment is designed, OQC providing an electron at the first redox stage would be a better choice, because the CF_3S group is so electron-withdrawing that CF_3S-containing reagent should be susceptible to reduction rather than oxidation. For CF_3S-X type precursors, introduction of an electron-withdrawing X is essential to enhance the electrophilicity of reagents, and reagents containing NR_2, OR, SR groups and halides are available. Of shelf-stable reagents, CF_3S-NR_2 reagents and CF_3S-OR reagents have been well developed in the last few years. Expecially, the CF_3S-NR_2 reagents has many advantages: (1) simple synthesis, (2) stability in air, and (3) easy access from commerce. Therefore, the CF_3S-NR_2 reagents was the first choice for investigating this reaction.

2.2 Optimization

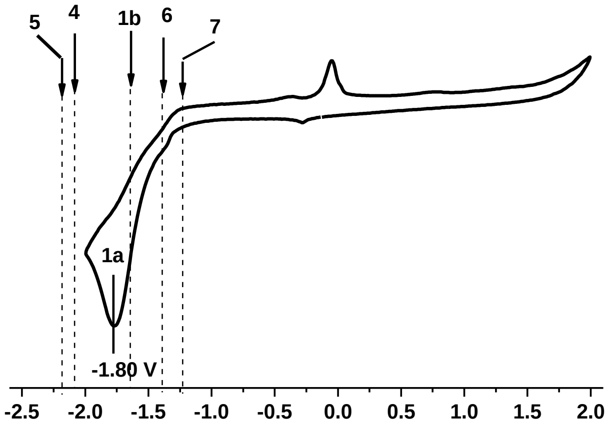
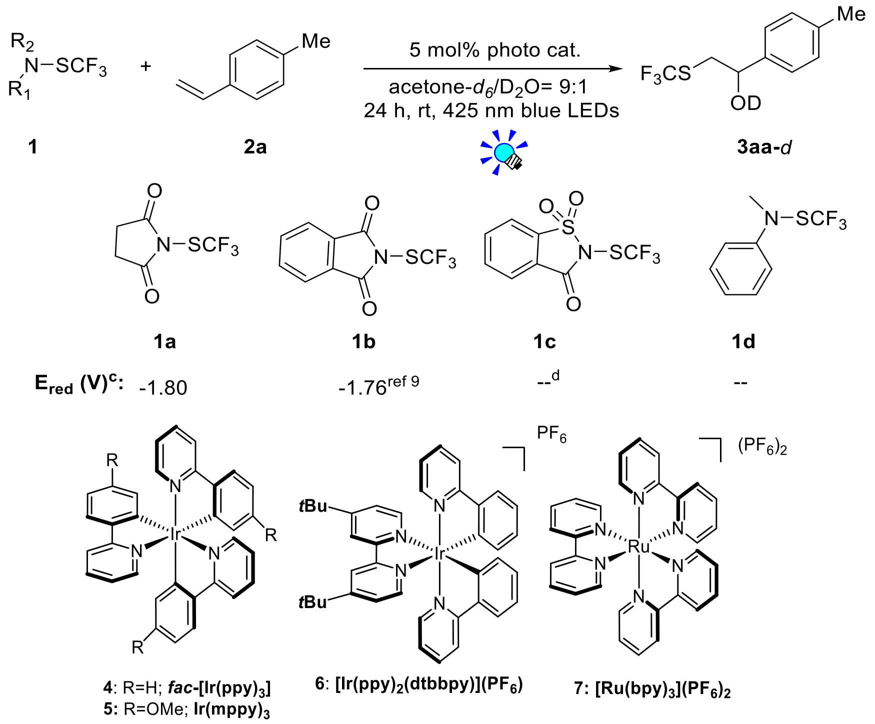


Figure 2.1 A CV trace for 1a. (Observed in 0.002 M MeCN; $[NBu_4][PF_6]$ = 0.1 M; reference electrode: $Ag/AgNO_3$; counter electrode: Pt; working electrode: Pt; reported with respect to the Fc/Fc^+).

The reaction system for optimization of the reaction conditions consisted of 4-methylstyrene (**2a**), a CF_3S-NR_2 reagent, and a photocatalyst dissolved in an acetone-water mixture.

Firstly, the optimization was conducted for the CF_3S-NR_2 reagents for the reaction with the *fac*-[Ir(ppy)$_3$] catalyst **4** (5 mol%), and the mixture was irradiated by blue LED lamps for 24 h. The key component is the CF_3S-NR_2 reagent **1**, and the four CF_3S-NR_2 reagents **1a-1d** were examined. A CV trace for **1a** is shown in Figure 2.1. The reduction potentials of **1a** and **1b** were determined to be -1.80 V and -1.76 V, which are large enough to be reduced by the Ir catalyst **4** (-2.14 V), but those for **1c**, **d** are not available. In particular, **1c** is so unstable in CH_3CN that its redox potentials can not be determined. As a result of the experiment, **1a** with the succinimide backbone gave the desired product **3aa-*d*** in an acceptable yield (55%, entry 1). The reagents **1c-d,** however, did not give the product at all, and most of styrene was unreacted and recovered (entries 2-4). The reagents **1b**, **d** were mostly recovered unreacted, although the reduction potential of **1b** was almost the same as that of **1a**. The saccharin derivative **1c** was consumed quickly presumably due to a decomposition process. The aniline derivative **1d** was not consumed at all presumably due to the redox potential.

Table 2.1. Optimization of photocatalytic hydroxytrifluoromethylthiolation



Entry	SCF_3 reagent **1** (**1**:**2a**)	Photocat.	**E**$_{\mathbf{red}}$[M^*/M^{n+1}](V)^c	NMR yields of **3aa-*d*** /%
1	**1a** (1:1.2)	**4**	-2.14	55
2	**1b** (1:1.2)	**4**		trace
3	**1c** (1:1.2)	**4**		0 (n.d.)[d]
4	**1d** (1:1.2)	**4**		0 (n.r.)
5	**1a** (1:1.2)	**5**	-2.21[7]	70
6	**1a** (1:1.2)	**6**	-1.37	0 (n.r.)
7	**1a** (1:1.2)	**7**	-1.24	0 (n.r.)
8	**1a** (1.2:1)	**5**		82
9	**1a** (1.5:1)	**5**		93
10[b]	**1a** (1:1.2)	**5**		0 (n.r.)
11	**1a** (1:1.2)	none		0 (n.r.)

[a] Reaction conditions: A reaction mixture containing **1** (0.017 mmol), **2a** (0.02 or 0.014 or 0.011 mmol), Photocat. (0.9 μ mol), $SiEt_4$ (internal standard), and solvent (0.4 mL) was irradiated by 3 W blue LEDs (λ = 425 ± 15 nm) under N_2. [b] The reaction was conducted in the dark. [c] **E**$_{\mathbf{red}}$ vs Fc/Fc$^+$ in CH_3CN. [d] Because **1d** is readily decomposed in CH_3CN, **E**$_{\mathbf{red}}$ can not be acquired.

Then the photocatalyst was screened. While the cationic catalysts **6** and **7** with the reduction potentials larger than -1.8 V were not effective (entries 6-7), the neutral Ir catalyst with the *p*-methoxy substituents on the phenyl rings **5** showed performance better than that of **4** to give the product in 70% yield (entry 5). By tuning the substance ratio, the yield of the product was finally improved up to 93% when a slight excess amount of **1a** (1.5:1) was used (entry 9).

Finally, the present photocatalytic reaction did not proceed at all either in the dark or in the absence of the photoredox catalyst (entry 10-11), indicating that a photo-activated species is involved in the present catalysis.

The reaction (entry 9) was monitor by ^{1}H NMR and ^{19}F NMR, and spetra before and after irradiation for 24 h are compared in Figure 2.2 and 2.3. All signals for the reactants are replaced by those of the products, indicating quantitative conversion to the product. In addition, from a ^{19}F NMR spectrum of entry 9, formation of a small amount of F_3CSSCF_3 (-46.7 ppm) was observed at an early stage of the reaction (1h), but disappeared after 24 h (Figure 2.3).

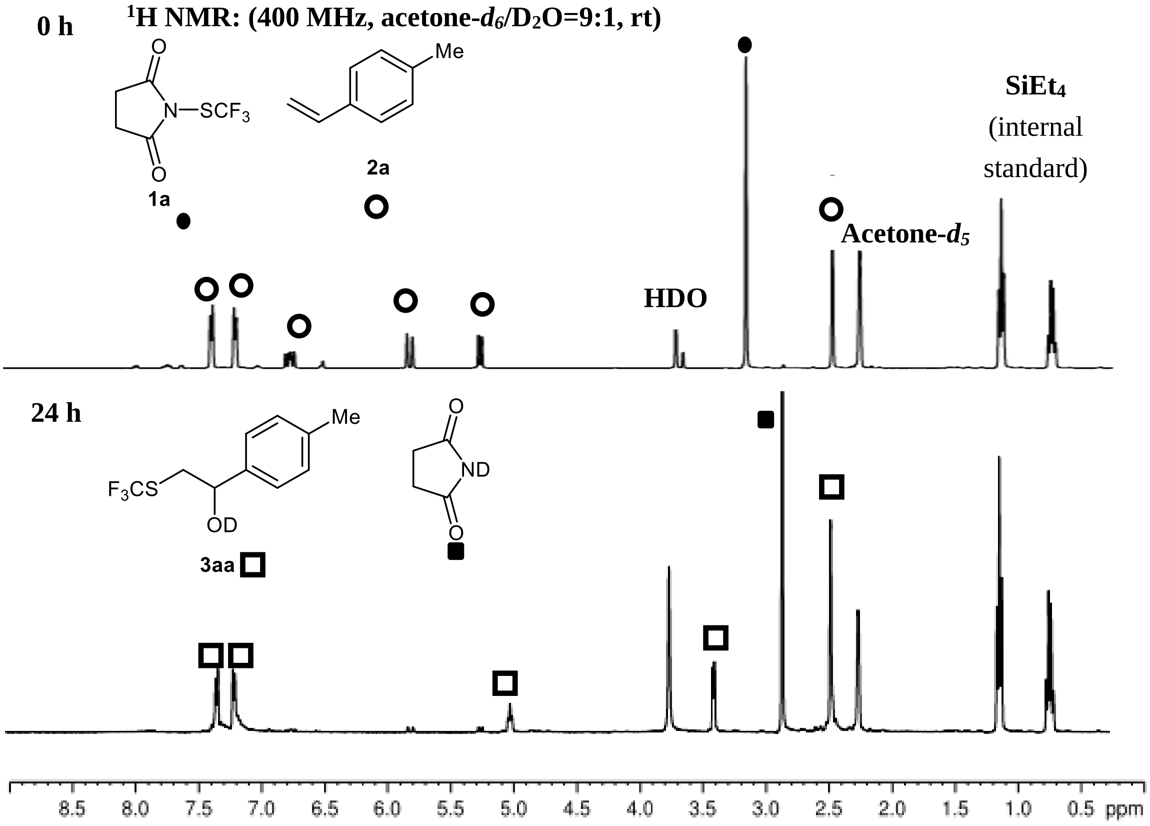


Figure 2.2 ^{1}H NMR spectra for the photocatalytic reaction of 1a with 2a.

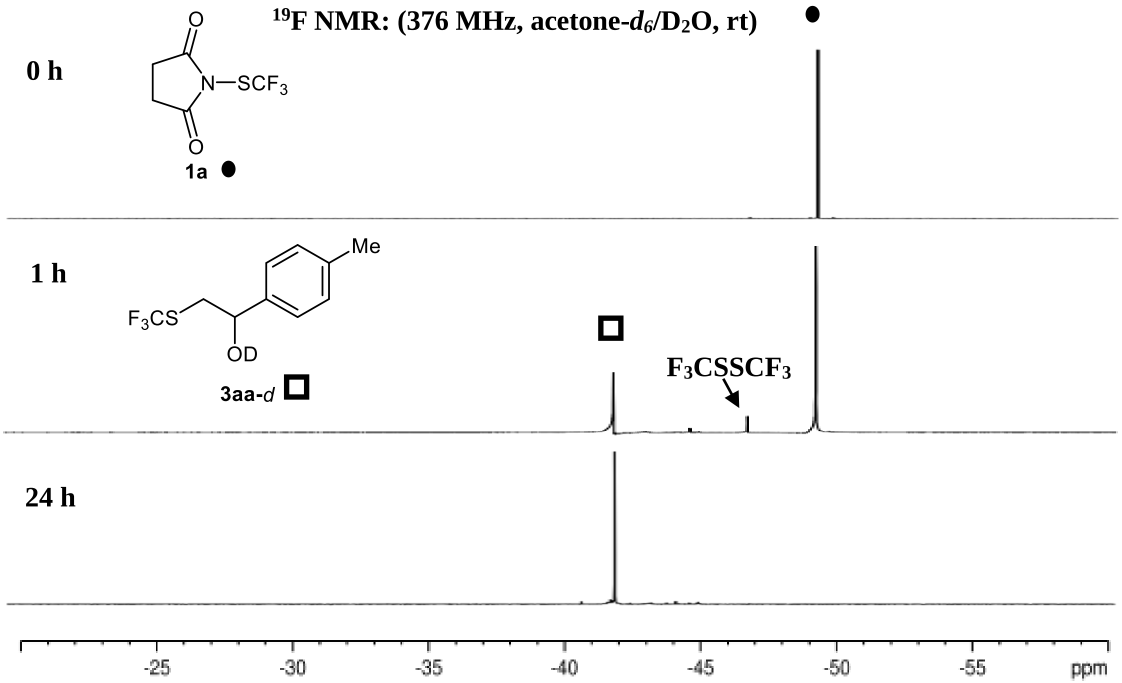
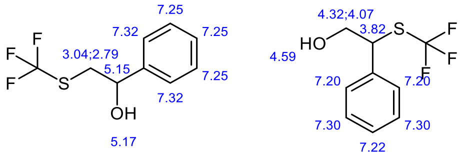


Figure 2.3 ^{19}F NMR spectra for the photocatalytic reaction of 1a with 2a

The regiochemistry of the reaction was characterized by ^{1}H NMR and ^{13}C NMR spectra (Figure 2.4 and 2.5). For example, a ^{1}H NMR spectrum of **3ab** contains three signals of an AA'B pattern (δ (H_A) = 3.13 ppm, δ ($H_{A'}$) = 3.23 ppm, δ (H_B) = 4.92 ppm,) in addition to the phenyl signals, indicating retention of the Ph-CH-CH_2 linkage. The presence of the OH and SCF_3 groups is also confirmed by the respective signals. For the regiochemistry, the ^{13}C NMR signal at δc 38.6 ppm assigned to the $H_2\boldsymbol{C}$-SCF_3 moiety appears as a quartet signal due to coupling with the F atoms on the CF_3 group ($^{3}J_{C\text{-}F}$ = 2 Hz), indicating that the SCF_3 group is attached to the $H_2\boldsymbol{C}$ atom in the Ph-CH-CH_2 linkage, i.e. the OH and SCF_3 groups are introduced to the α- and β-carbon atoms of styrene, respectively, to be consistent with their chemical shifts.



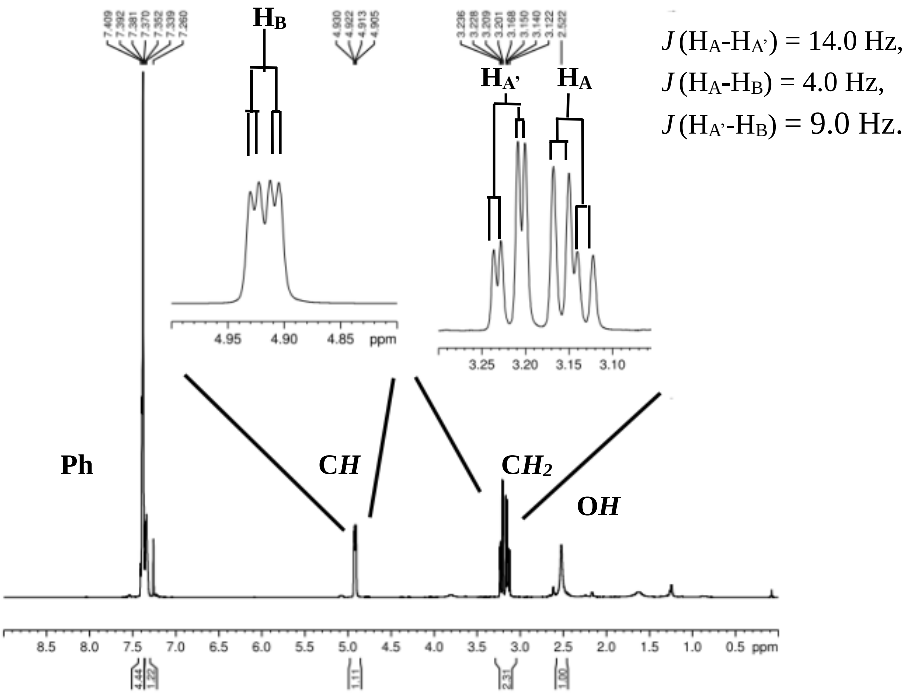
3ab

3ab'

Figure 2.4 Predicted chemical shifts of 3ab and 3ab' in ^{1}H NMR (ppm)

The assignment is also in accord with the calculated spectra (Fighre 2.4). Thus the product has been unequivocally assigned to **3ab**. Because the other isomer **3ab’** was not detected by NMR at all, the present catalystic transformation turned out to be *regiospecific*.

^{1}H NMR: (500 MHz, CDCl$_3$, rt)



^{13}C NMR (125 MHz, CDCl$_3$, rt)

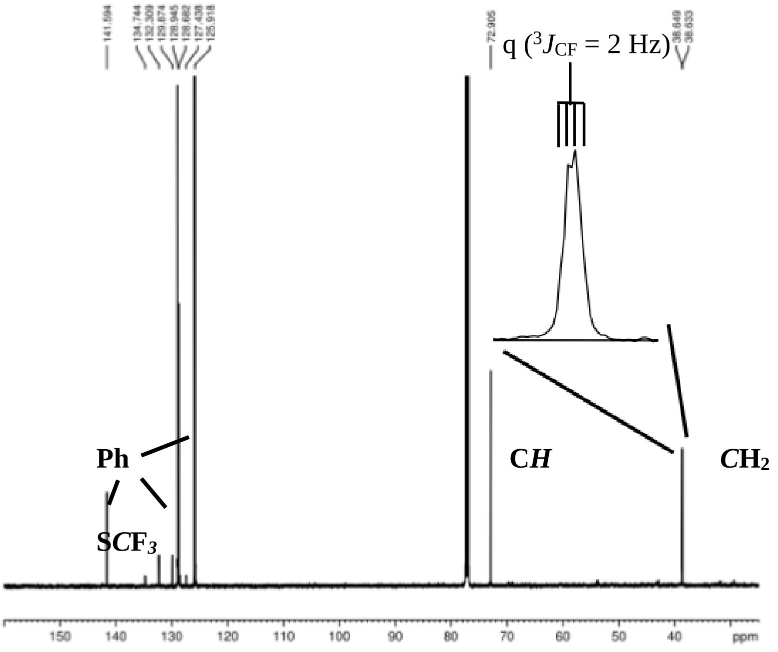
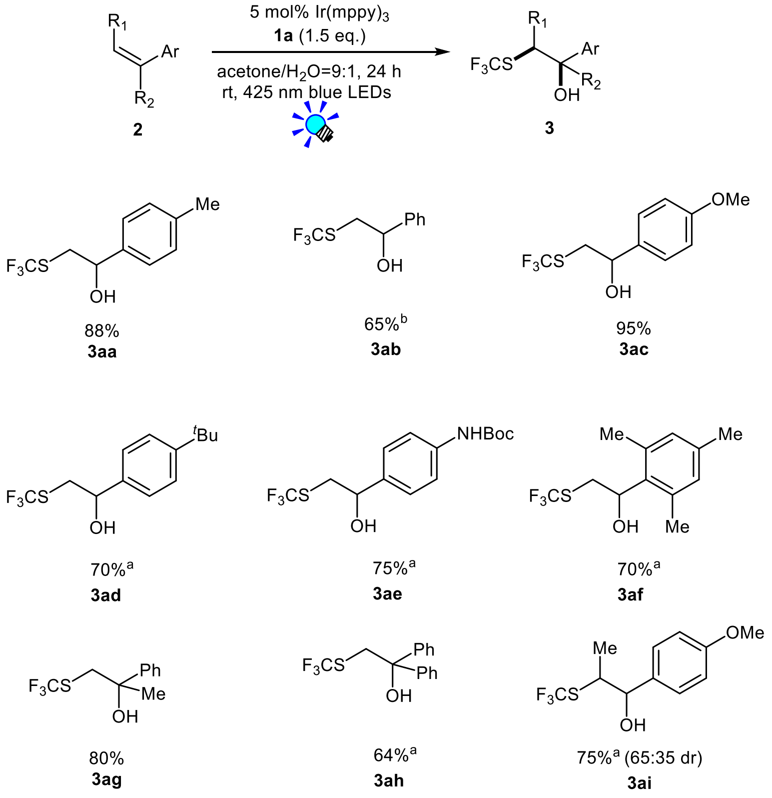


Figure 2.5 ^{1}H NMR and ^{13}C NMR spectra of 3ab

2.3 Scope and limitation



88% **3aa**

65%[b] **3ab**

95% **3ac**

70%[a] **3ad**

75%[a] **3ae**

70%[a] **3af**

80% **3ag**

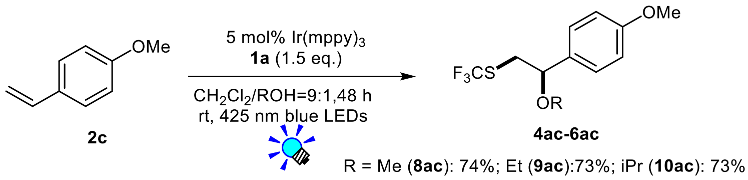
64%[a] **3ah**

75%[a] (65:35 dr) **3ai**

Scheme 2.2 Scope of the present photocatalytic hydroxy-SCF$_3$ of styrenes 2. Reaction conditions: A reaction mixture containing Ir(mppy)$_3$ (15.0 μmol), **1a** (0.30 mmol), dry acetone (6.3 mL), water (0.7 mL), and styrenes **2** (0.20 mmol) was irradiated by 3 W blue LED lamp ($\lambda = 425 \pm 15$ nm) under N_2 atmosphere. Yields were obtained after purification. Diastereomeric ratios (dr) were determined by ^{1}H NMR spectra of crude reaction mixtures. [a] the reaction time: 48 h. [b] the reaction time: 60 h.

The scope of the present photocatalytic hydroxyl-trifluoromethylthiolation of styrene derivatives is summarized in Scheme 2.2. Styrenes with various functional groups on the benzene ring such as alkyl (**2a**, **2d**, **2f**), Boc-protected amino (**2e**), and methoxy groups (**2c**) smoothly produced the corresponding SCF$_3$-containing alcohols (**3a**-**f**) in good yields (65-95%, 24-48 h). Compared with styrene (**2b**), the reaction of styrene with an electron-donating group on the benzene ring afforded the corresponding product in a good yield within a shorter reaction time, presumably because the F$_3$CS· radical is electrophilic. In addition, α-substituted styrene derivatives, such as α-methylstyrene (**2g**) and 1,1-diphenylethylene (**2h**) were also successfully applied to the present photocatalytic reaction, leading to the corresponding SCF_3 alcohols (**3ag**, **3ah**) in 80% and 64% yields, respectively. Furthermore, anethole (**2i**), a β-substituted styrene derivative, afforded the corresponding product as a mixture of diastereomers (**3ai**: 75%, 65:35 dr).

Next, the author investigated the reaction with alcohols (ROH), because the reaction may be a solvolytic reaction like the reaction shown in Scheme 1.10 (reaction in the left side). When the reactions with methanol, ethanol and isopropanol were conducted in dry CH_2Cl_2/ROH (9:1), alkoxy-trifluoromethylthiolation smoothly proceeded in a regiospecific manner to afford the corresponding ethers in good yields (Scheme 2.3)



Scheme 2.3 Oxytrifluoromethylthiolation of 4-methoxylstyrene (2c). Yields were obtained after purification.

2.4 Plausible reaction mechanism

To gain insight into the reaction mechanism, a couple of experiments were conducted.

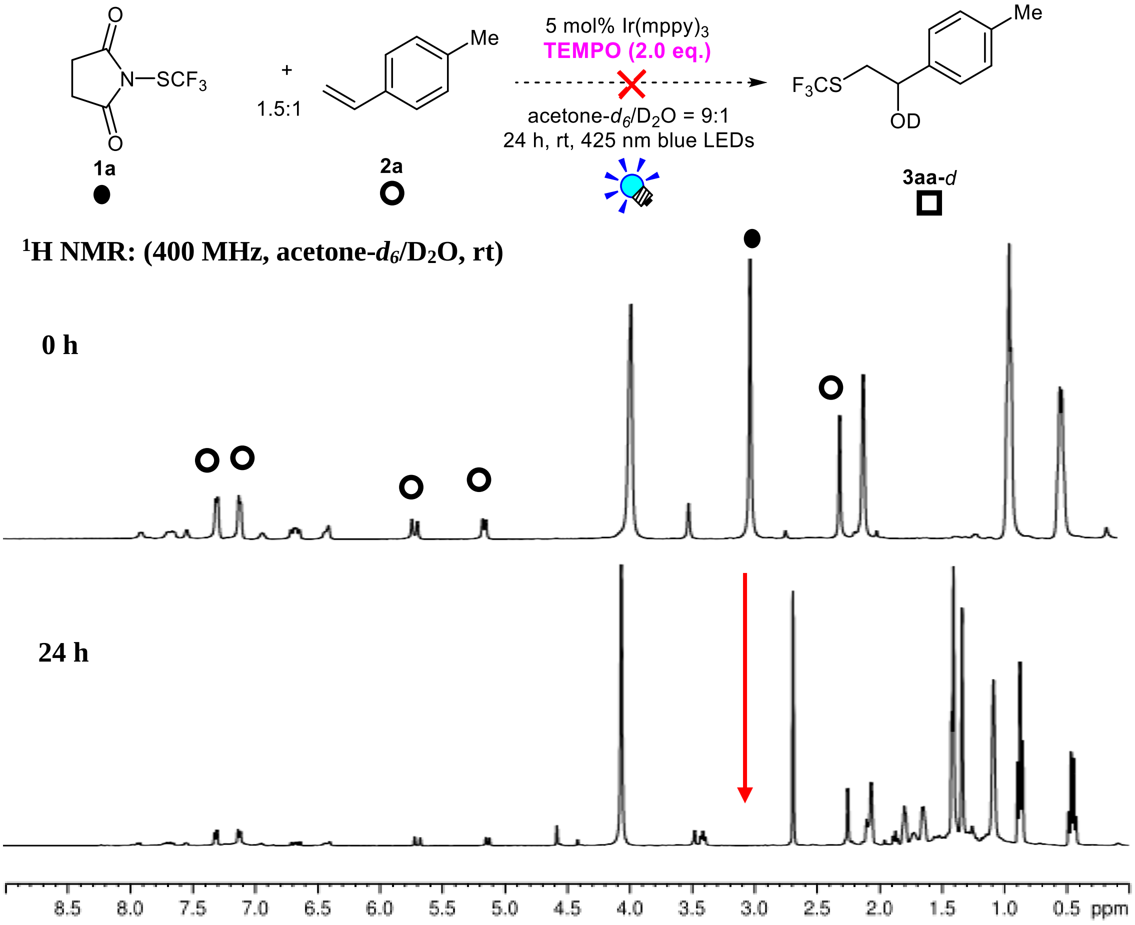


Figure 2.6 Photocatalytic reaction in the presence of TEMPO

The involvement of a radical inrermediate was checked by a trapping experiment with 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO), a radical scavenger (Figure 2.6). The ^{1}H NMR spectra obtained before and after the irradiation for 24 h reveal recovery of the starting compound **2a**, consumption of the F_3CS reagent **1a**, and no formation of the product **3aa-*d***, indicating that radical intermediates are trapped by TEMPO to retard the reaction, i.e. intermediates of the present reaction are radical species to be trapped by TEMPO.

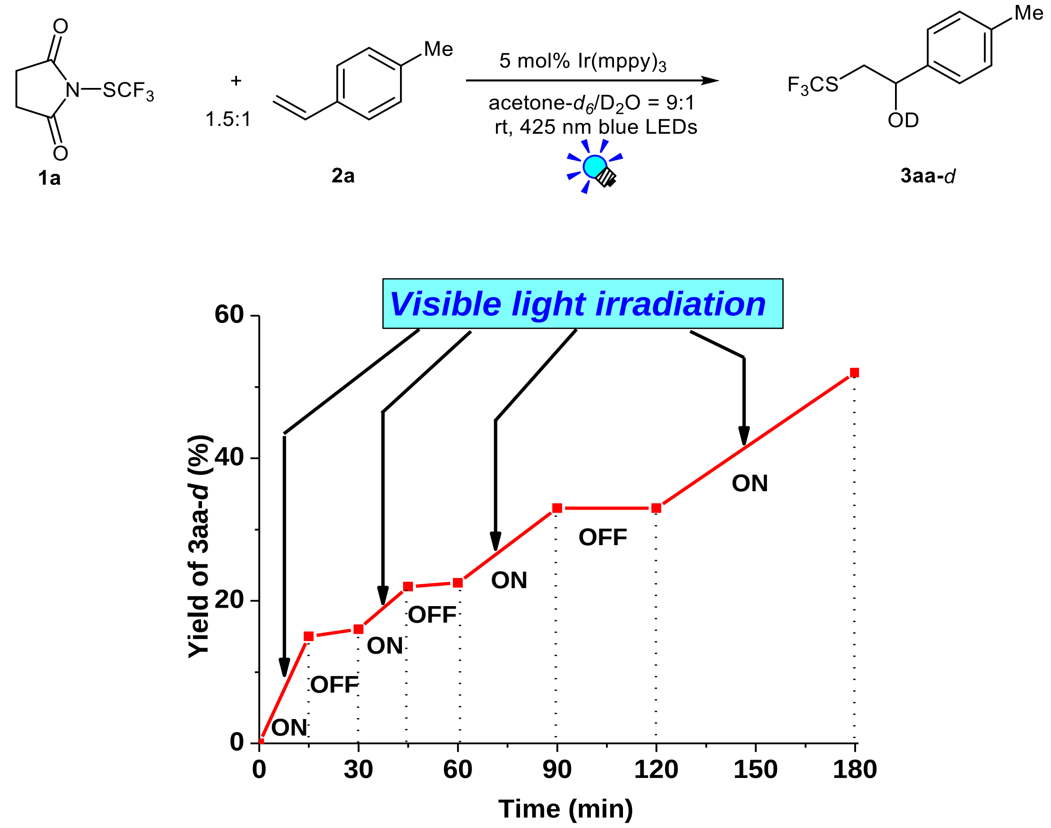
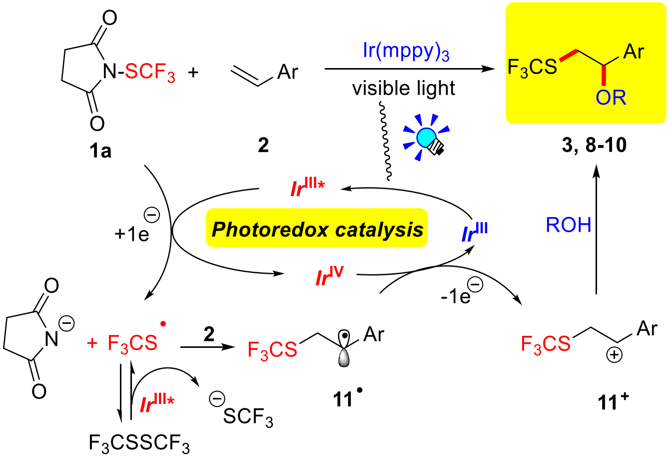


Figure 2.7. Time profile of the reaction of 2a with 1a.

Furthermore, to check participation of radical propagation as a main reaction pathway, the light control experiment was carried out. As a result, the present reaction required continuous irradiation of visible light to proceed steadily (see the Figure 2.7.), suggesting that the radical propagation process (Scheme 1.3) is not involved as the major reaction pathway.

On the basis of these results, a plausible reaction mechanism is outlined in Scheme 2.4. First, the photocatalyst ***Ir***$^{\mathrm{III}}$ is excited by visible-light irradiation with blue LED lamps to give the excited species ******Ir***$^{\mathrm{III}}$, which can serve as a strong 1e-reductant. The radical SCF_3· is generated from **1a** via 1e-reduction by ******Ir***$^{\mathrm{III}}$, and reacts with styrene **2** in a regioselective manner to give the benzyl-type radical intermediate **11·**. Then intermediate radical **11·** is oxidized by the strongly oxidizing species ***Ir***$^{\mathrm{IV}}$ to generate carbocationic intermediate **11**$^{+}$ together with the photocatalyst ***Ir***$^{\mathrm{III}}$ of the ground state. Lastly, the carbocationic intermediate **11**$^{+}$ undergoes solvolysis by ROH (water or alcohols) to produce oxy-trifluoromethylthiolated products **3** or **8-10**. The minor by-prduct F_3CSSCF_3 observed at an early stage of the reaction may be formed via homocouling of the SCF_3·radical. 1e-Reduction of F_3CSSCF_3 would regenerate the F_3CS· and F_3CS^- anion.



Scheme 2.4. A plausible reaction mechanism

2.5 Conclusion

The auther has developed a novel photoredox-catalyzed oxy-trifluoromethylthiolation of styrenes. The designed redox-neutral reaction system enables one step, economical synthesis of β-SCF_3-substituted alcohols and ethers under mild reaction conditions. It is remarkable that, the present photocatalytic oxy-trifluoromethylthiolation system exhibits good functional group compatibility.

2.6 Experimental

Materials and Methods

$[Ru(bpy)_3](PF_6)_2$[3a], *fac*-$[Ir(ppy)_3]$[3b], $[Ir(ppy)_2(dtbbpy)](PF_6)$[3c] and $Ir(mppy)_3$ were prepared according to the literature procedures [3d]. 1-(Trifluoromethylthio)pyrrolidine-2,5-dione (**1a**)[4a], *N*-trifluoromethyl-thiophthalimide (**1b**)[4b], and *N*-trifluoromethylthio saccharin (**1c**)[4c] were prepared according to the literatures. *N*-methyl-*N*-phenyl-S-(trifluoromethyl)thiohydroxylamine (**1d**) and styrenes **2a**, **2b**, **2c**, **2d**, **2g**, **2h** and **2f** were purchased from TCI. Styrene **2i** was purchased from Aldrich. *N*-tert-Butoxycarbonyl-4-vinylaniline (**2e**) were prepared according to the literature procedures [5]. Catalytic reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. Acetone was dried by K_2CO_3, distilled, and stored under N_2 atmosphere. Anhydrous methanol, ethanol, isopropanol were purchased from KANTO CHEMICAL CO., INC. and degassed with supersonic waves, and stored under N_2 atmosphere. Thin-layer chromatography was performed on a Merck TLC plate with 60 F_{254}.

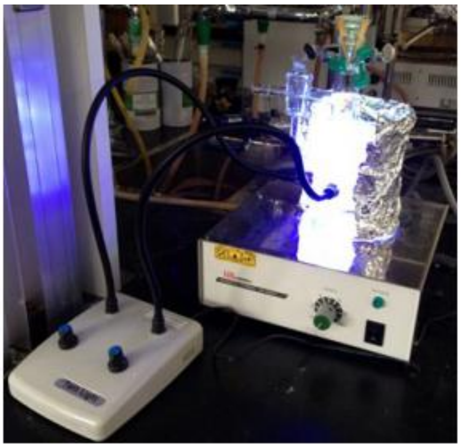
Visible light irradiation was performed with a Relyon LED lamp (3 W×2: $\lambda = 425 \pm 15$ nm). ^1H NMR spectra were acquired on a Bruker AVANCE-400 (400 MHz) and a Bruker AVANCE-HD500 (500 MHz).

Single-crystal X-ray measurement was made on a Bruker SMART APEX II ULTRA.

^1H NMR chemical shifts were referenced to the the residual protio impurities in the deuterated solvents. ^{19}F NMR chemical shifts were referenced to external $C_6H_5CF_3$ (–63.72 ppm), 1,4-difluorobenzene (-118.8 ppm in DMSO-d_6), and trifluoroacetic acid (-77.8 ppm in CD_3OD, -76.6 ppm in $CDCl_3$). All ^{11}B-NMR chemical shifts were referenced to external boron trifluoride diethyl etherate (0.0 ppm). UV-vis spectra and luminescence spectra were obtained on a JASCO V-670DS and HITACHI F-7000, respectively. GC-MS analyses were carried out using a GC-MS system (Shimadzu GC-MS Parvum 2, capillary column: Rxi®-5ms (30 m × 0.25 mm × 0.25 μm)). HRMS spectra were obtained on Bruker microTOF II (ESI-TOF Mass) and JEOL JMS-700 spectrometers (EI Mass) at Technical Department of Technical Department of Tokyo Institute of Technology. Elemental analysis was conducted with a J-SCIENCE JM10. Electrochemical measurements were recorded on Hokutodenkou HZ-5000 analyzer.

Reaction apparatus

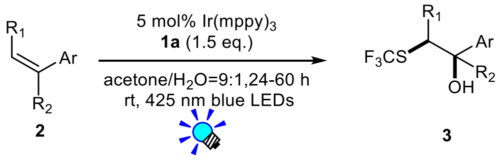
Irradiation of visible light was performed with a Relyon LED lamp (3 W × 2; $\lambda_{max} = 425 \pm 15$ nm)



Typical NMR experimental procedures (Table 2.1)

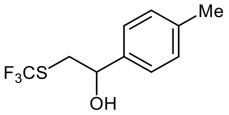
Under N_2 atmosphere, Ir(mppy)$_3$ (0.7 mg, 0.9 µmol), **1a** (3.4 mg, 0.017 mmol), tetraethylsilane ($SiEt_4$; as an internal standard), acetone-*d*$_6$ (0.36 mL), D_2O (0.04 mL), and 4-methylstyrene (**2a**) (1.4 mg, 0.011 mmol) were added to an NMR tube. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps).

General Procedures for the Photocatalytic Synthesis of Oxytrifluoromethylthiolated Products (Scheme 2.2)



A 20 mL Schlenk tube was charged with Ir(mppy)$_3$ (11.2 mg, 15.0 µmol), **1a** (59.7 mg, 0.30 mmol), dry acetone (6.3 mL), water (0.7 mL), and styrenes **2** (0.20 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps). After the reaction, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*. Purification by the column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) afforded **3** as a colorless oil.

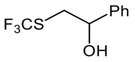
1-*p*-tolyl-2-trifluoromethylthioethanol (3aa)



The reaction of Ir(mppy)$_3$ (11.3 mg, 15.0 µmol), **1a** (59.6 mg, 0.30 mmol), and 4-methylstyrene (**2a**) (23.6 mg, 0.20 mmol) afforded **3aa** (41.5 mg, 88% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 1H; O*H*), 2.29 (s, 3H; *Me*), 3.09 (m, 2H; C*H$_2$*), 4.81 (dd, *J* = 8.6, 4.5 Hz, 1H; C*H*), 7.12 (d, J = 7.4 Hz, 2H; *phenyl*), 7.19 (d, J = 7.4 Hz, 2H; *phenyl*). The spectral data were identical with these reported in the literature [6].

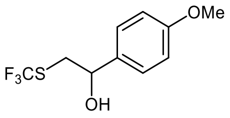
1-phenyl-2-trifluoromethylthioethanol (3ab)



The reaction of Ir(mppy) (22.4 mg, 30.0 µmol), **1a** (119.8 mg, 0.60 mmol), and styrene (**2b**) (41.6 mg, 0.40 mmol) afforded **3ab** (57.7 mg, 65% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 2.52 (s, 1H; O*H*), 3.13 (dd, *J* = 14 Hz, 9 Hz, 1H; CH*H*), 3.23 (dd, *J* = 14 Hz, 4 Hz, 1H; C*H*H), 4.91-4.93 (m, 1H; C*H*), 7.33-7.41 (m, 5H; *phenyl*). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ -42.2 (s, 3F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 38.6 (q, *J* =2 Hz, *C*H$_2$), 72.9 (*C*H), 125.9 (*phenyl*), 128.7 (*phenyl*), 128.9 (*phenyl*), 131.1 (q, *J* = 304.4 Hz; S*C*F$_3$), 141.6 (*phenyl*) **HRMS (ESI-TOF)**: calculated for $[C_9H_9F_3OSNa]^+$ requires 245.0218, found 245.0217.

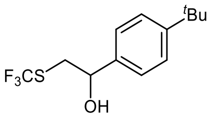
1-(4-methoxyphenyl)-2-trifluoromethylthioethanol (3ac)



The reaction of Ir(mppy)$_3$ (11.3 mg, 15.0 μmol), **1a** (59.7 mg, 0.30 mmol), and 4-methoxystyrene (**2c**) (26.8 mg, 0.20 mmol) afforded **3ac** (47.8 mg, 95% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}**H NMR** (500 MHz, $CDCl_3$, rt): δ 2.30 (s, 1H; O*H*), 3.12-3.20 (m, 2H; CH_2), 3.82 (s, 3H; OCH_3), 4.86-4.88 (m, 1H; C*H*), 6.91 (d, *J* = 10.0 Hz, 2H; *phenyl*), 7.30 (d, *J* = 10.0 Hz, 2H; *phenyl*). ^{19}**F NMR** (376 MHz, $CDCl_3$, rt): δ -42.1 (s, 3F). ^{13}**C NMR** (125 MHz, $CDCl_3$, rt): δ 39.5 (q, *J* =2 Hz, *C*H_2), 55.5 (O*C*H_3), 72.5 (*C*H), 114.3 (*phenyl*), 127.2 (*phenyl*), 131.1 (q, *J* = 304.3 Hz; S*C*F_3), 133.7 (*phenyl*), 159.9 (*phenyl*). **HRMS (ESI-TOF)**: calculated for $[C_{10}H_{11}F_3O_2SNa]^+$ requires 275.0324, found 275.0324.

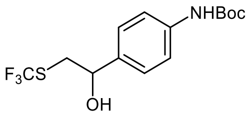
1-(4-tert-butylphenyl)-2-trifluoromethylthioethanol (3ad)



The reaction of Ir(mppy)$_3$ (11.3 mg, 15.0 μmol), **1a** (59.8 mg, 0.30 mmol), and 4-*t*-butylstyrene (**2d**) (32.1 mg, 0.20 mmol) afforded **3ad** (39.0 mg, 70% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 1.33 (s, 9H; 3*CH_3), 2.38(s, 1H; O*H*), 3.14-3.23 (m, 2H; CH_2), 4.89-4.91 (m, 1H; C*H*), 7.31 (d, *J* = 8.0 Hz, 2H; *phenyl*), 7.41 (d, *J* = 8.0 Hz, 2H; *phenyl*). ^{19}**F NMR** (376 MHz, $CDCl_3$, rt): δ -41.9 (s, 3F). ^{13}**C NMR** (125 MHz, $CDCl_3$, rt): δ 31.4 (*C*H_3), 34.7 (*C*$(CH_3)_3$) 38.5 (q, *J* =2 Hz, *C*H_2), 72.8 (*C*H), 125.7 (*phenyl*), 125.9 (*phenyl*), 131.2 (q, *J* = 304.3 Hz; S*C*F_3), 138.6 (*phenyl*), 151.8 (*phenyl*). **HRMS (ESI-TOF)**: calculated for $[C_{13}H_{17}F_3OSNa]^+$ requires 301.0844, found 301.0847.

t-Butyl 4-(1-hydroxy-2-trifluoromethylthioethyl)phenylcarbamate (3ae)

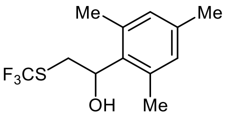


The reaction of Ir(mppy)$_3$ (11.1 mg, 15.0 μmol), **1a** (59.9 mg, 0.30 mmol), and *t*-butyl (4-vinylphenyl)carbamate (**2e**) (43.8 mg, 0.20 mmol) afforded **3ae** (50.5 mg, 75% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}**H NMR** (500 MHz, $CDCl_3$, rt): δ 1.52 (s, 9H; 3*CH_3), 2.17 (s, 1H; O*H*), 3.12 (dd, *J* = 15 Hz, 10 Hz, 1H; CH*H*), 3.17 (dd, *J* = 15 Hz, 5 Hz, 1H; C*H*H), 4.86-4.89 (m, 1H; C*H*), 6.49 (s, 1H; N*H*), 7.29 (d, *J* = 8.5 Hz, 2H; *phenyl*), 7.37 (d, *J* = 8.5 Hz, 2H; *phenyl*). ^{19}**F NMR** (376 MHz, $CDCl_3$, rt): δ -41.9 (s, 3F). ^{13}**C NMR** (125 MHz, $CDCl_3$, rt): δ 28.4 (*C*H_3), 38.5 (q, *J* =2 Hz, *C*H_2), 72.5 (*C*H), 80.9 (O*C*$(CH_3)_3$), 118.9 (*phenyl*), 126.7 (*phenyl*), 131.2 (q, *J* = 304.4 Hz; S*C*F_3), 136.2 (*C*=O), 138.6 (*phenyl*), 152.8 (*phenyl*). **HRMS (ESI-TOF)**: calculated for $[C_{14}H_{18}F_3NO_3SNa]^+$ requires

360.0852, found 360.0851.

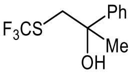
1-mesityl-2-trifluoromethylthioethanol (3af)



The reaction of Ir(mppy)$_3$ (11.3 mg, 15.0 µmol), **1a** (59.7 mg, 0.30 mmol), and 2,4,6-trimethylstyrene (**2f**) (29.3 mg, 0.20 mmol) afforded **3af** (40.0 mg, 70% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H NMR (500 MHz, CDCl$_3$, rt): δ 2.26 (s, 3H; *Me*(*mesityl*)), 2.40 (s, 6H; *Me*(*mesityl*)), 3.16 (dd, *J* = 15 Hz, 10 Hz, 1H; C*H*H), 3.36-3.42 (m, 1H; CH*H*), 5.32-5.35 (m, 1H; C*H*), 6.84 (s, 2H, *phenyl*(*mesityl*)). **^{19}F NMR** (376 MHz, CDCl$_3$, rt): δ -42.1 (s, 3F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 20.7 *Me*(*mesityl*), 20.9 *Me*(*mesityl*), 35.4 (*C*H$_2$), 70.4 (*C*H), 130.5 (*phenyl*(*mesityl*)), 131.3 (q, *J* = 304.5 Hz; S*C*F$_3$), 133.7 (*phenyl*), 136.3 (*phenyl*), 137.8 (*phenyl*). **HRMS (ESI-TOF)**: calculated for [$C_{12}H_{15}F_3OSNa$]$^+$ requires 287.0688, found 287.0683.

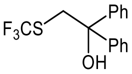
2-phenyl-1-trifluoromethylthiopropan-2-ol (3ag)



The reaction of Ir(mppy)$_3$ (11.3 mg, 15.0 µmol), **1a** (59.6 mg, 0.30 mmol), and α-methylstyrene (**2g**) (23.5 mg, 0.20 mmol) afforded **3ag** (37.7 mg, 80% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H NMR (500 MHz, CDCl$_3$, rt): δ 1.69 (s, 3H; *Me*), 2.34 (s, 1H; O*H*), 3.26 (d, *J* =13.0 Hz, 1H; C*H*H), 3.45 (d, *J* =13.0 Hz, 1H; CH*H*), 7.29-7.46 (m, 5H; *phenyl*). **^{19}F NMR** (376 MHz, CDCl$_3$, rt): δ -42.2 (s, 3*F*). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 29.1 (*C*H$_2$), 43.5 (q, *J* =2 Hz, *C*H$_2$), 73.4 (*C*H), 124.8 (*phenyl*), 127.8 (*phenyl*), 128.7 (*phenyl*), 131.10 (q, *J* = 304.4 Hz; S*C*F$_3$), 145.3 (*phenyl*). **HRMS (ESI-TOF)**: calculated for [$C_{10}H_{11}F_3OSNa$]$^+$ requires 259.0375, found 259.0374.

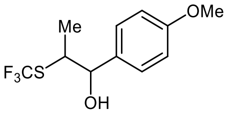
1,1-diphenyl-2-(trifluoromethylthio)ethanol (3ah)



According to the general procedure, Ir(mppy)$_3$ (11.2 mg, 15.0 µmol), **1a** (59.7 mg, 0.30 mmol), and 1,1-diphentlethylene (**2h**) (36.8 mg, 0.20 mmol) with 48h irradiation of blue LEDs afforded **3ah** (38.1 mg, 64% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 2.95 (br, 1H; O*H*), 3.81 (s, 2H; C*H$_2$*), 7.33-7.27 (m, 2H; *phenyl*), 7.39-7.33 (m, 4H; *phenyl*), 7.45-7.40 (m, 4H; *phenyl*). .The spectral data were identical with these reported in the literature [2i].

1-(4-methoxyphenyl)-2-trifluoromethylthiopropanol (3ai)



The reaction of Ir(mppy)$_3$ (22.6 mg, 30.0 µmol), **1a** (119.7 mg, 0.60 mmol), and *trans*- Anethole (**2i**) (59.3 mg, 0.40 mmol) afforded a mixture of isomers of **3ai** (79.8 mg, 75% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

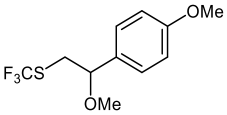
Major isomer: ^{1}H NMR (500 MHz, CDCl$_3$, rt): 1.27 (d, *J* = 7.0 Hz, 3H; *Me*CH), 3.55-3.58 (m, 1H; MeC*H*), 3.82 (s, 3H; O*Me*), 5.01-5.02 (m, 1H; HOC*H*), 6.90 (d, *J* = 8.5 Hz, 2H; *phenyl*), 7.28 (d, *J* = 8.5 Hz, 2H; *phenyl*). **^{19}F NMR** (376 MHz, CDCl$_3$, rt): δ -40.5 (s, 3F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 15.2 (*Me*CH), 47.8 (Me*C*H$_2$), 55.4 (O*Me*), 75.4 (HO*C*H), 113.9 (*phenyl*), 127.3 (*phenyl*), 131.2 (q, *J* = 304.3 Hz; S*C*F$_3$), 132.5 (*phenyl*), 159.5 (*phenyl*). **HRMS (ESI-TOF)**: calculated for $[C_{11}H_{13}F_3O_2SNa]^+$ requires 289.0481, found 289.0481.

Minor isomer: ^{1}H NMR (500 MHz, CDCl$_3$, rt): 1.33 (d, *J* = 7.0 Hz, 3H; *Me*CH), 3.47-3.48 (m, 1H; MeC*H*), 3.79 (s, 3H; O*Me*), 4.63-4.65 (m, 1H; HOC*H*), 6.90 (d, *J* = 8.5 Hz, 2H; *phenyl*), 7.28 (d, *J* = 8.5 Hz, 2H; *phenyl*). **^{19}F NMR** (376 MHz, CDCl$_3$, rt): δ -39.6 (s, 3F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 19.3 (*Me*CH), 48.8 (Me*C*H$_2$), 55.4 (O*Me*), 76.5 (HO*C*H), 114.0 (*phenyl*), 127.0 (*phenyl*), 131.2 (q, *J* = 304.3 Hz; S*C*F$_3$), 132.4 (*phenyl*), 159.8 (*phenyl*). **HRMS (ESI-TOF)**: calculated for $[C_{11}H_{13}F_3O_2SNa]^+$ requires 289.0481, found 289.0481.

General procedures for the photocatalytic alkoxytifluoromethylthiolation of 4-methoxystyrene (2c) (Scheme 2.3)

A 20 mL Schlenk tube was charged with Ir(mppy) (15.0 µmol), **1a** (0.30 mmol), dry CH_2Cl_2 (6.3 mL), alcohol (0.7 mL), and 4-methoxystyrene (**2c**) (0.20 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamp). After 48 h, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*. Purification by the column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) afforded product **8-10** as a colorless oil.

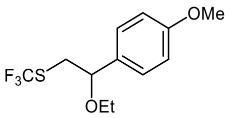
1-(4-methoxyphenyl)-2-trifluoromethylthioethanol (8ac)



The reaction of Ir(mppy)$_3$ (11.2 mg, 15.0 µmol), **1a** (60.0 mg, 0.30 mmol), dry CH_2Cl_2 (6.3 mL), MeOH (0.7 mL) and 4-methoxystyrene (**2c**) (26.9 mg, 0.20 mmol) afforded **8ac** (39.3 mg, 74% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H NMR (500 MHz, CDCl$_3$, rt): δ 3.04 (dd, *J* = 20 Hz, 5 Hz, 1H; C*H*H), 3.18-3.23 (m, 1H; C*H*H), 3.24 (s, 3H; CH-O*Me*), 3.82 (s, 3H; phenyl-O*Me*), 4.29-4.32 (m, 1H; C*H*), 6.91 (d, *J* = 8.5 Hz, 2H; *phenyl*) , 7.24 (d, *J* = 8.5 Hz, 2H; *phenyl*). **^{19}F NMR** (376 MHz, CDCl$_3$, rt): δ -42.7 (s, 3F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 37.1 (q, *J* =2 Hz, *C*H$_2$), 55.4 (CH-O*C*H$_3$), 57.0 (phenyl-O*C*H$_3$), 80.2 (*C*H), 114.3 (*phenyl*), 128.0 (*phenyl*), 131.1 (q, *J* = 304.3 Hz; S*C*F$_3$), 131.4 (*phenyl*), 159.9 (*phenyl*). **HRMS (ESI-TOF)**: calculated for $[C_{11}H_{13}F_3O_2SNa]^+$ requires 289.0481, found 289.0481.

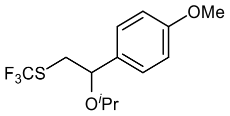
2-ethoxy-2-(4-methoxyphenyl)ethyl trifluoromethyl sulfide (9ac)



The reaction of Ir(mppy)$_3$ (11.3 mg, 15.0 µmol), **1a** (60.2 mg, 0.30 mmol), dry CH_2Cl_2 (6.3 mL), EtOH (0.7 mL)and 4-methoxystyrene (**2c**) (26.8 mg, 0.20 mmol) afforded **9ac** (40.9 mg, 73% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 1.18 (t, *J* = 7 Hz, 3H; *Et*), 3.02 (dd, *J* = 15 Hz, 5 Hz, 1H; C*H*H), 3.20 (dd, *J* = 15 Hz, 10 Hz, 1H; CH*H*), 3.34-3.43 (m, 2H; *Et*), 3.81 (s, 3H; phenyl-O*Me*), 4.40-4.42 (m, 1H; C*H*), 6.90 (d, *J* = 8.5 Hz, 2H; *phenyl*) , 7.25 (d, *J* = 8.5 Hz, 2H; *phenyl*). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ -42.4 (s, 3F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 15.2 (*Et*), 37.1 (q, *J* =2 Hz, *C*H$_2$), 55.4 (*Et*), 64.7 (phenyl-O*C*H$_3$), 82.0 (*C*H), 114.2 (*phenyl*), 127.9 (*phenyl*), 131.1 (q, *J* = 304.3 Hz; S*C*F$_3$), 132.6 (*phenyl*), 159.8 (*phenyl*). **HRMS (ESI-TOF)**: calculated for $[C_{12}H_{15}F_3O_2SNa]^+$ requires 303.0637, found 303.0637.

2-isopropoxy-2-(4-methoxyphenyl)ethyl trifluoromethyl sulfide (10ac)



The reaction of Ir(mppy)$_3$ (11.3 mg, 15.0 µmol), **1a** (59.9 mg, 0.30 mmol), dry CH_2Cl_2 (6.3 mL), ^{i}PrOH (0.7 mL)and 4-methoxystyrene (**2c**) (26.8 mg, 0.20 mmol) afforded **10ac** (42.9 mg, 73% yield) as a pale yellow oil after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 1.07 (d, *J* = 6.0 Hz, 3H; ^{i}*Pr*), 1.17 (d, *J* = 6.0 Hz, 3H; ^{i}*Pr*), 3.00 (dd, *J* = 15 Hz, 5 Hz, 1H; C*H*H), 3.13-3.17 (dd, *J* = 15 Hz, 10 Hz, 1H; CH*H*), 3.49-3.54 (m, 1H; ^{i}*Pr*), 3.81 (s, 3H; phenyl-O*Me*), 4.50-4.53 (m, 1H; C*H*), 6.90 (d, *J* = 8.5 Hz, 2H; *phenyl*) , 7.25 (d, *J* = 8.5 Hz, 2H; *phenyl*). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ -42.4 (s, 3F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 21.2 (^{i}*Pr*), 23.4 (^{i}*Pr*), 37.6 (q, *J* =2 Hz, *C*H$_2$), 55.4 (^{i}*Pr*), 69.8 (phenyl-O*C*H$_3$), 77.6 (*C*H), 114.1 (*phenyl*), 127.9 (*phenyl*), 131.1 (q, *J* = 304.3 Hz; S*C*F$_3$), 135.1 (*phenyl*), 159.7 (*phenyl*). **HRMS (ESI-TOF)**: calculated for $[C_{13}H_{17}F_3O_2SNa]^+$ requires 317.0794, found 317.0794.

Photocatalytic reaction in the presence of TEMPO (Figure 2.6)

Under N_2 atmosphere, Ir(mppy)$_3$ (0.7 mg, 0.9 µmol), **1a** (3.4 mg, 0.017 mmol), tetraethylsilane ($SiEt_4$) as an internal standard, acetone-d_6 (0.36 mL), D_2O (0.04 mL), 4-methylstyrene (**2a**) (1.4 mg, 0.011 mmol) and TEMPO (5.1 mg. 0.033 mmol) were added to an NMR tube. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps).

2.7 References

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[7] Calculation for reduction potential [8] of **Ir(mppy)$_3$**: λ_{max}(emission)=495 nm(298K)[1d], $E_{0.0}$= hc/λ_{max}(emission)= 2.51 V. Oxidative Quenching: $E_{red}[Ir^{III}*/$

$Ir^{IV}](298K)= E_{red}[Ir^{III}/ Ir^{IV}]- E_{0.0}= (0.30 – 2.51)\ V= -2.21\ V$

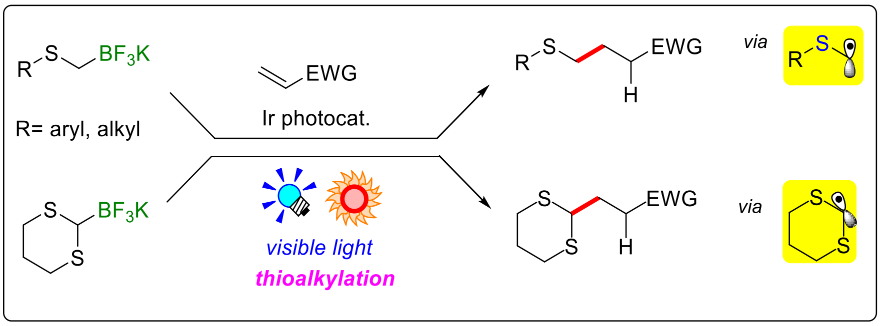
[8] J. W. Tucker and C. R. J. Stephenson, *J. Org. Chem.* **2012**, *77*, 1617.

[9] R. Pluta, P. Nikolaienko, M. Rueping, *Angew. Chem. Int. Ed.* **2014**, *53,* 1650.

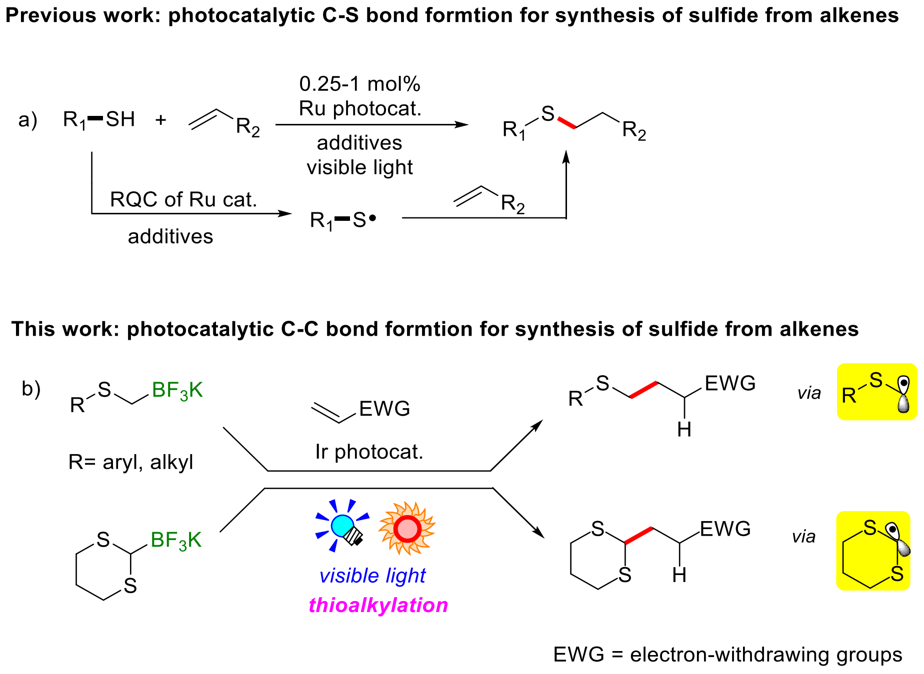
Chapter 3

Alkyl- and aryl-thioalkylation of olefins with organotrifluoroborates by photoredox catalysis

ABSTRACT: The author has developed a facile and environmentally benign protocol for alkyl- and aryl-thioalkylation of olefins. By photoredox catalysis with an Ir photocatalyst, $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$, α-thioalkyl radicals are generated from alkyl- and aryl-thioalkyltrifluoroborates via deboronation, and the resultant radicals smoothly react with electron-deficient olefins to afford addition products in good yields. Furthermore, a range of alkyl sulfides can be obtained by the present photocatalytic method under mild reaction conditions via a single step.

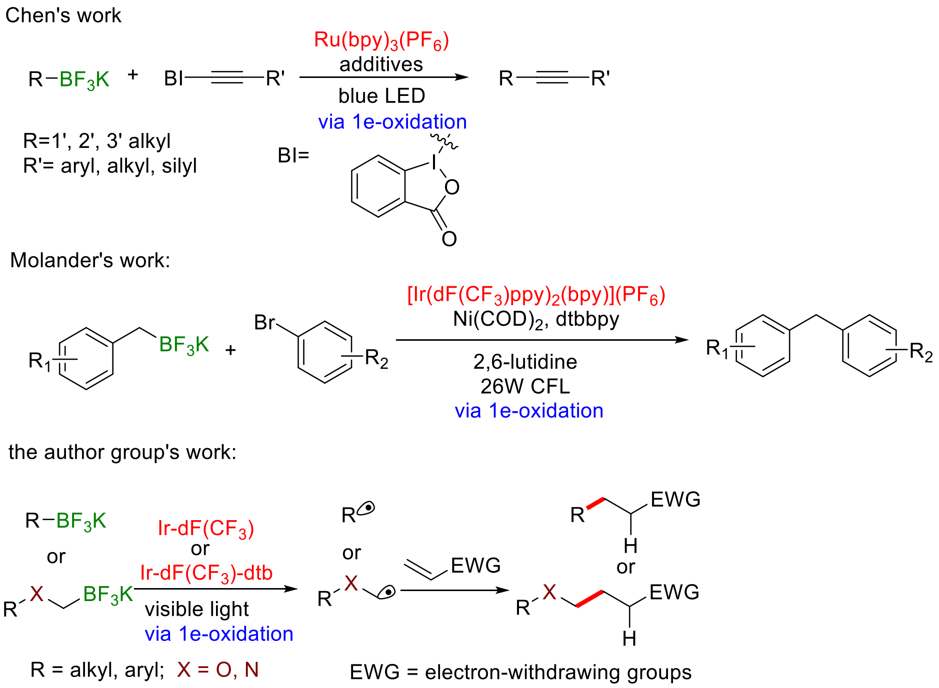


3.1 Introduction



Scheme 3.1 Synthesis of sulfide from alkenes by photoredox catalysis.

As the author introduced in Chapter 1, sulfide is an important functional group in medicine and material chemistry, and it can be easily constructed from alkenes via C-S bond formation and C-C bond formation of S-containing starting material, but conventional synthetic methods for sulfide are still limited. Photoredox catalysis has been recognized as a useful redox protocol from the viewpoint of radical chemistry and green chemistry, and some groups developed synthetic reactions for sulfides with the photoredox catalysis [1]. For example, in 2012, Yoon reported radical thiol-ene reactions involved the RQC of the $[Ru(bpz)_3]^{2+}$. Later, his group reported this reaction also can be initiated by RQC of the $[Ru(bpy)_3]^{2+}$ in the presence of *p*-toluidine which serves as a redox mediator. (Scheme 3.1(a))[1e,f]. All of these works, however, were focused on new C-S bonding formation, but reaction of S-substituted alkyl radicals, i.e. α-thioalkyl radicals, by photoredox catalysis has not been reported yet, though it can become a new strategy for the synthesis of organic sulphides. Herein the author describes the first example of photoredox-catalyzed thioalkylation of olefins through generation of α-thioalkyl radicals via oxidation of alkyl- and aryl-thioalkyltrifluoroborates (Scheme 3.1 (b)).

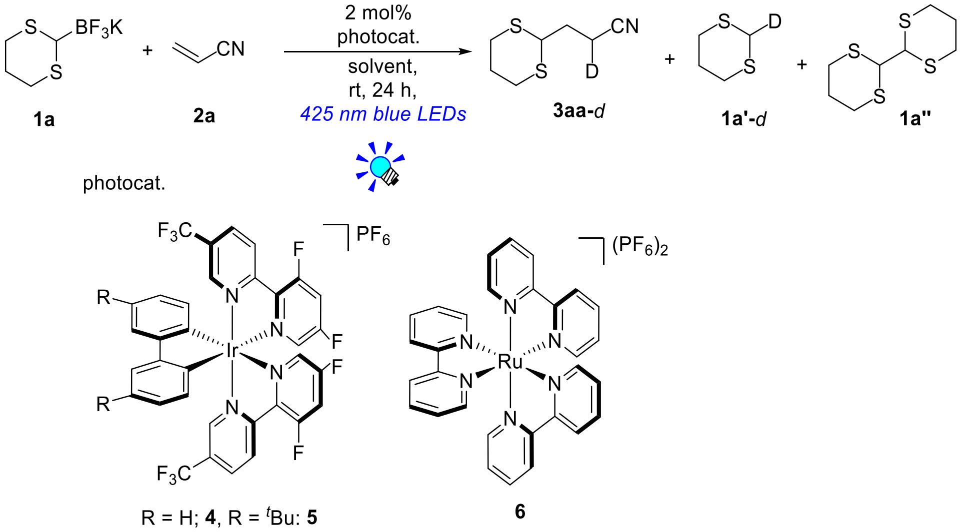


Scheme 3.2 Generation of radical from organobaorates by photoredox catalysis

Organoborates are widely used in synthetic chemistry (for example, Suzuki-Miyaura reaction) because of their easy-to-handle properties and compatibility with a variety of functional groups including sulfides [2]. In addition, generation of organic radicals by oxidation of organoborates has been well-documented so far [3]. Recently, the author's group and the groups of Chen and Molander reported on photocatalytic reactions using some organoborates (Scheme 3.2) [4,5]. In particular, the author's group has extensively developed redox-neutral, radical amino- and alkoxy-methylation of olefins using the corresponding organotrifluoroborates (i.e. R-OCH$_2$-BF$_3$K, R$_2$NCH$_2$-BF$_3$K) by RQC of the Ir photoredox catalysis [4b,4d] (Scheme 3.2). On the basis of these works, the author speculated thioalkylborates also can be applied to photoredox catalysis, and investigated thioalkylation of olefins with the corresponding organoborates. In addition, the reaction of potassium 1,3-dithian-2-yltrifluoroborate (**1a**) can be regarded as a synthetic equivalent of formylanion (Scheme 1.21). Thus, radical dithianylation can be connected to nucleophilic acylation [6].

3.2 Optimization

Table 3.1. Optimization of photocatalytic radical reaction of 1a with 2a[a]



Entry	**1a:2a**	Photocat.	Solvent	**3aa-*d***[b]	**1a'-*d***[b]	**1a"**[b]
1	1:1	**4**	Acetone-d_6/CD_3OD(1/1)	56%	10%	33%
2	1:2	**4**	Acetone-d_6/CD_3OD(1/1)	90%	3%	6%
3	1:2	**5**	Acetone-d_6/CD_3OD(1/1)	73%	2%	17%
4	1:2	**6**	Acetone-d_6/CD_3OD(1/1)	79%	1%	15%
5	**1:2**	**4**	**CD_3OD**	**93%**	**1%**	**5%**
6	1:2	**4**	Acetone-d_6	10%	1%	12%
7	1:2	**4**	CD_3CN	17%	0%	11%
8	1:2	**4**	DMSO-d_6	10%	5%	10%
9[c,d]	1:2	**4**	CD_3OD	0%	0%	0%
10[d]	1:2	**none**	CD_3OD	0%	0%	0%

[a] Reaction conditions: A reaction mixture containing **1a** (0.05 mmol), **2a** (0.05 or 0.10 mmol), photocatalyst (1.0 μmmol), $SiEt_4$ (an internal standard) and solvent (0.40 mL) was irradiated by using 3 W blue LEDs (λ = 425 ± 15 nm) at room temperature under N_2 atmosphere for 24 h. [b] NMR yields. [c] The reaction was conducted in the dark.[d] No reaction

The author firstly examined the reaction of potassium 1,3-dithian-2-yltrifluoroborate, because the possible intermediate 1,3-dithian-2-yl radical, is supposed to be more stable than monothiomethyl radical. The visible light reaction of potassium 1,3-dithian-2-yltrifluoroborate **1a** with 1.0 eq. of acrylonitrile **2a** in a mixture of acetone-d_6 and CD_3OD(1/1) proceeded in the presence of Ir photocatalyst **4**, $[Ir(dF(CF_3)\text{-}ppy)_2(bpy)](PF_6)(dF(CF_3)ppy$, which can serve as a strong oxidant (Ir^{II}/ $*Ir^{III}$ = +0.91 V vs Fc/Fc^+) when photochemically excited[7]. The catalyst **4** was chosen, because the present reaction was designed to proceed via a

RQC mechanism. As a result, hydrodithianylated product **3aa-*d*** was obtained in a 56% NMR yield together with 2-deuteratio-1,3-dithiacyclohexane **1a'-*d*** (33%) and 1,3-dithianyl dimer **1a"** (10%) (entry 1 in Table 3.1). The formation of these by-products suggests that the 1,3-dithian-2-yl radical is involved in the present photocatalytic reaction.

Next, the use of 2.0 eq. of acrylonitrile (**2a**) dramatically increased the yield of **3aa-*d*** up to 90% NMR yield and suppressed the side reactions (entry 2). In accord with the author's reaction design, other photocatalysts, [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) **5** (Ir^{II}/ $*Ir^{III}$ = +0.48 V vs Fc/Fc$^+$) and [Ru(bpy)$_3$](PF$_6$)$_2$ **6**[8] (Ru^{I}/ $*Ru^{II}$ = +0.43 V vs Fc/Fc$^+$), resulted in lower yields (entries 3 and 4) owing to their oxidizing ability being lower than that of photocatalyst **4**. CD$_3$OD and the mixed solvent system of acetone-d_6 and CD$_3$OD turned out to be appropriate solvent systems (entries 5-8). Furthermore, in the absence of visible-light irradiation and the photocatalyst no reaction took place (entries 9 and 10).

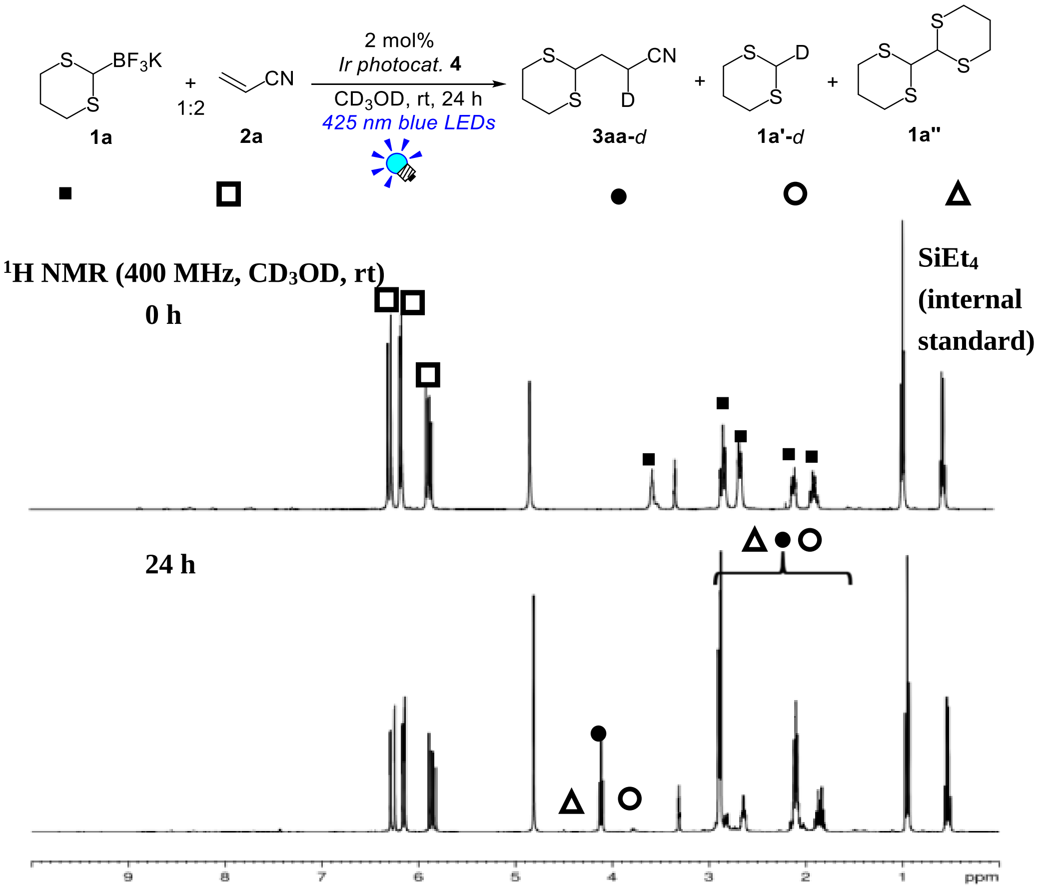
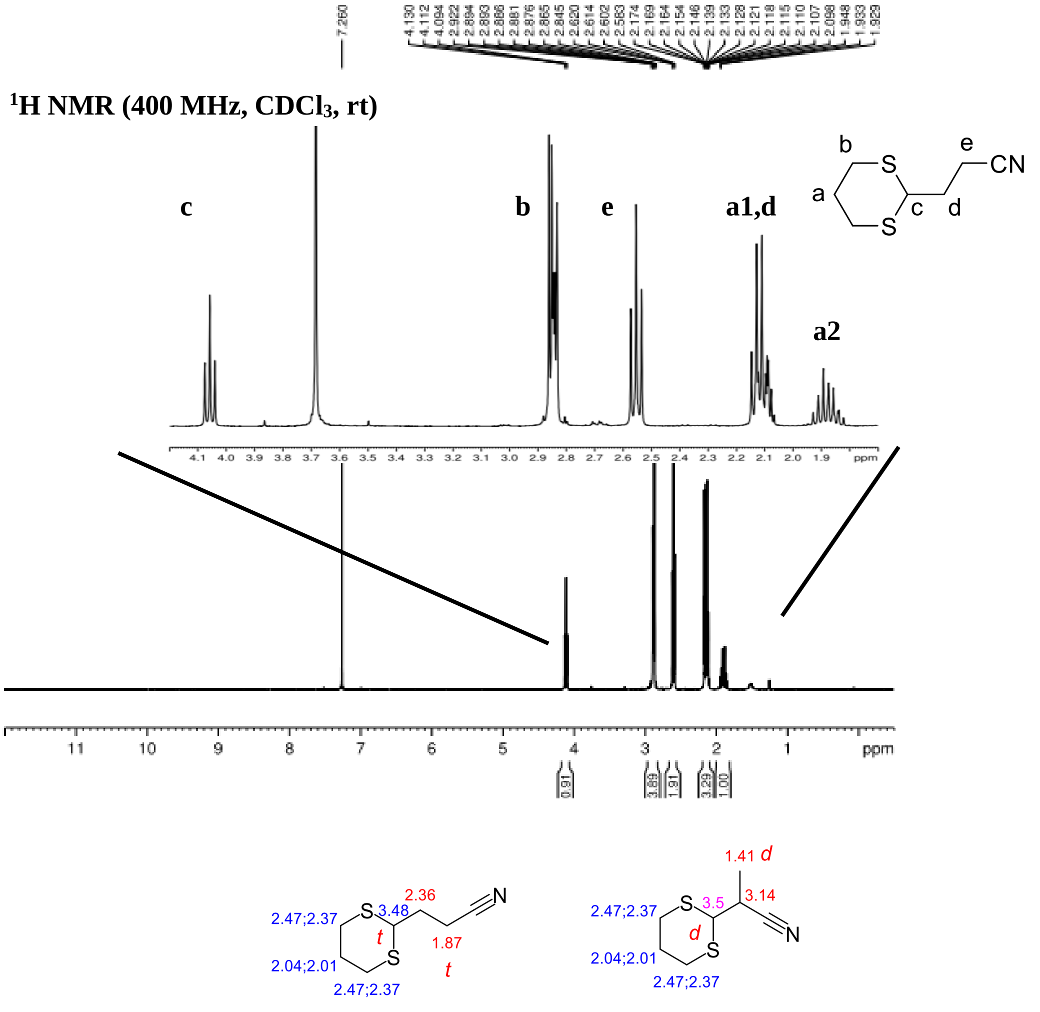


Figure 3.1 ^{1}H NMR spectra for the photocatalytic reaction of 1a with 2a (entry 5).

The reaction (entry 5) was monitored by ^{1}H NMR, and the spetra before and after irradiation for 24 h are compared in Figure 3.1. All signals for the reactants are replaced by those of the products, indicating quantitative conversion to the product and by-products (**1a'**-*d* and **1a"**).



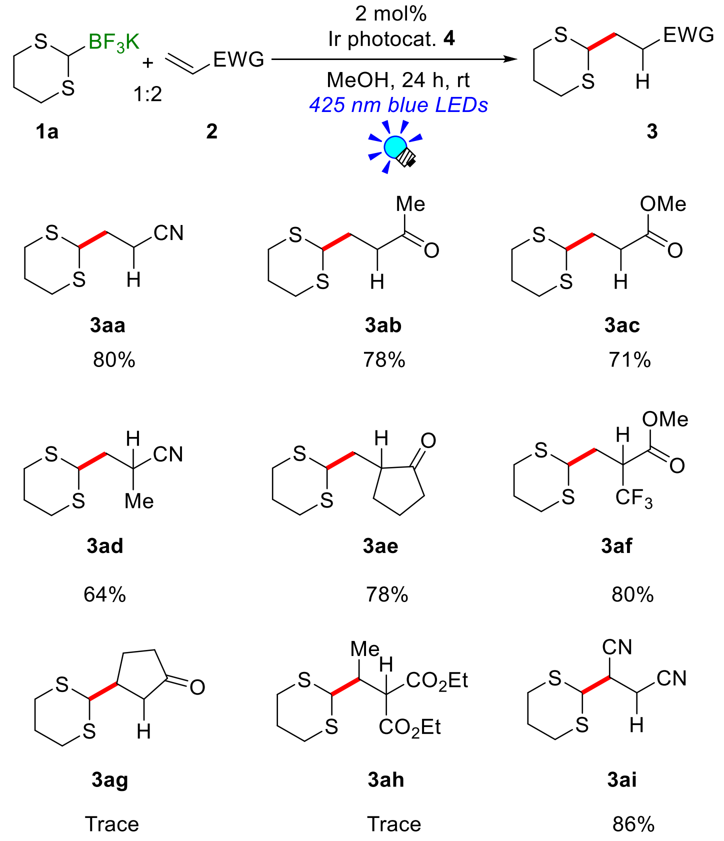
3aa

3aa'

Figure 3.2 ^{1}H NMR spectra of 3aa and predicted chemical shifts of 3aa and 3aa' in ^{1}H NMR

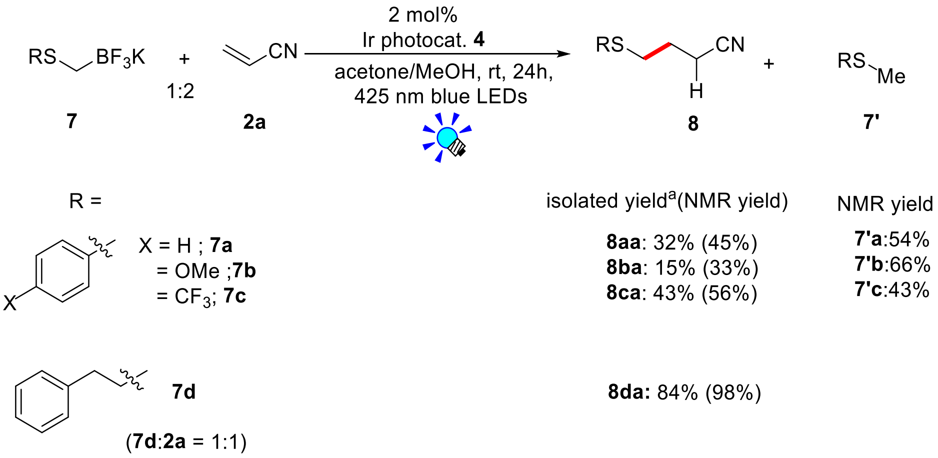
The regiochemistry of the reaction was characterized by ^{1}H NMR. To take the product **3aa** for instance (Figure 3.2), the disappearance of the olefin signals indicates conversion of the sp^2-carbon atoms into sp^3-carbon atoms, i.e. occurrence of some addition reaction to the olefinic part. The A_2B_2C pattern ((m, 2.10-2.17 ppm, 2H; CH_2-$C\mathit{H}_2$-CH), (t, 2.60 ppm, 2H; $C\mathit{H}_2$-CH_2-CH), and (t, 4.11 ppm, 1H; CH_2-CH_2-$C\mathit{H}$)) supports the presence of a CH_2-CH_2-CH skeleton, and the remaining signals have been assigned to the dithianyl part. These data reveal formation of the product **3aa** resulting from addition of the dithianyl radical to the β-carbon atom of acrylonitrile. The lack of a doublet signal for the methyl group in the other isomer **3aa’** clearly indicates that the present addition reaction, i.e. hydro-dithianylation, is *regiospecific*.

3.3 Scope and limitation



Scheme 3.3. The scope of the present photocatalytic hydrodithianylation. Reaction conditions: A reaction mixture containing photocatalyst **4** (5.0 μmol), **1a** (56.5 mg, 0.25 mmol), dry methanol (2.0 mL), and alkene **2** (0.50 mmol), was irradiated by using 3 W blue LEDs ($\lambda = 425 \pm 15$ nm) at room temperature under N_2 atmosphere. Yields were obtained after purification.

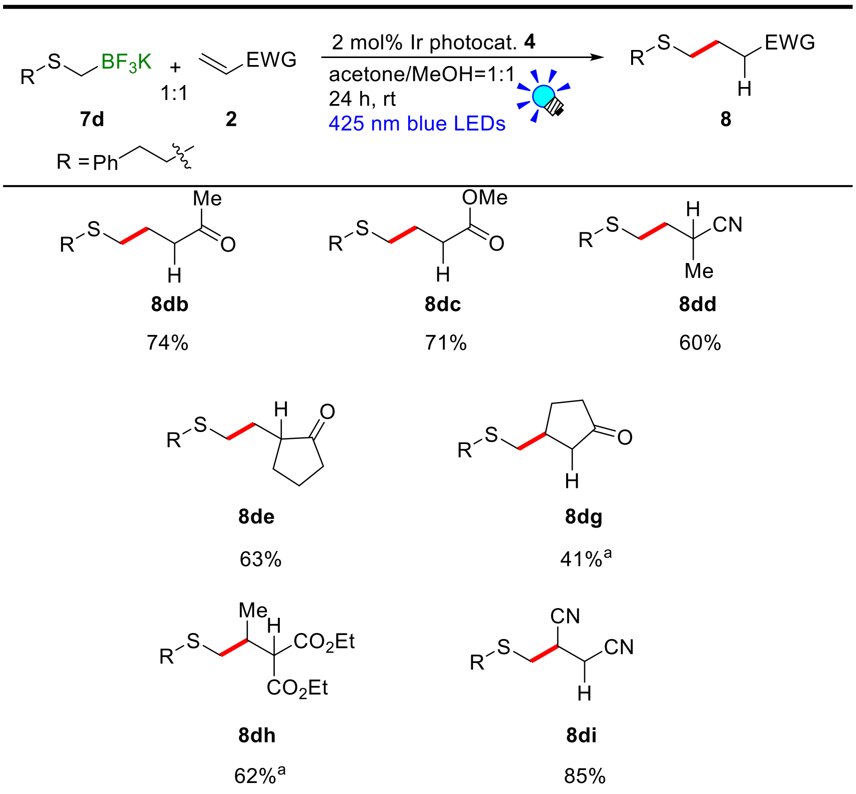
With the optimal reaction conditions in hand, the preparative scale hydrodithianylation of olefins was performed (Scheme 3.3). The reactions of typical electron-deficient alkenes, acrylonitrile **2a**, methyl vinyl ketone **2b** and methyl acrylate **2c** proceeded smoothly to give the corresponding products **3aa**-**3ac** in good yields (71-80%) (entries 1-3). 1,1-Disubstituted olefins such as methacrylonitrile **2d**, α-methylene-γ-butyro-lactone **2e,** and methyl 2-trifluoromethylacrylate **2f** could also be applied to the present reaction (**3ad**-**3af**: 64-80% yields). But olefins with a substituent at the reaction site, 2-cyclopenten-1-one **2g** and diethyl ethylidenemalonate **2h**, resulted in low conversions of the olefins and formation of a significant amount of deborohydrogenated by-product **1a’**. In contrast, the reaction of fumaronitrile **2i** afforded the hydrodithianylated product **3ai** in an 86% yield. These results suggest that the present photocatalytic dithianylation is effective for terminal olefins bearing electron-withdrawing groups and highly electron-deficient internal olefins.



Scheme 3.4. Examination of substituents on the sulfur atom in thiomethyltrifluoroborates. Reaction conditions: A reaction mixture containing photocatalyst **4** (5.0 μmol), **7** (0.25 mmol), degassed methanol (1.0 mL) and degassed acetone (1.0 mL) and alkene **2a** (0.50 mmol), was irradiated by using 3 W blue LEDs ($\lambda = 425 \pm 15$ nm) at room temperature under N_2 atmosphere. [a] Yields were obtained after purification.

Then, the optimized reaction conditions were applied to monothiomethyl derivatives, i.e. aryl- and alkyl-thiomethyltrifluoroborates (Scheme 3.4). The reactions of potassium phenylthiomethyltrifluoroborate **7a**, potassium 4-methoxyphenylthiomethyltrifluoroborate **7b**, and potassium 4-trifluoromethylphenylthiomethyltrifluoroborate **7c** with acrylonitrile **2a** afford the corresponding arylthiomethylated products (**8aa-ca**) in moderate yields (15-43%) due to the formation of a considerable amount of arylthiomethanes **7’** as by-products. The significant formation of the by-product **7’** compared to the reaction of 1,3-dithianyl compounds should result from the instability of the radical intermediate. In addition, the electron-withdrawing CF_3 group hinders the formation of the by-product **7’**. These results suggest that the electron-withdrawing group stabilizes the generated arylthiomethyl radical under these reaction conditions. In contrast, potassium phenethylthiomethyltrifluroborate **7d** gave the alkylthiomethylated product **8da** in an excellent yield (84% yield). In addition, the reaction of **7d** did not require an excess amount of olefin.

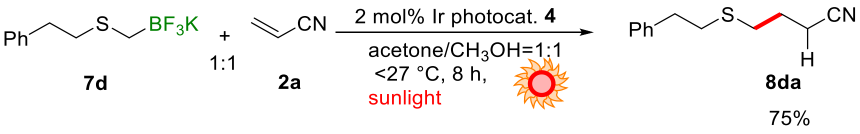
Table 3.2 Scope of the photocatalytic phenethylthiomethylation of alkenes[a,b]



[a] Reaction conditions: A reaction mixture containing **7d** (0.25 mmol), alkene **2** (0.25 mmol), photocatalyst **4** (5.0 μ mol), degassed acetone (1.0 mL) and MeOH (1.0 mL) was irradiated by using 3W blue LEDs (λ = 425 ±15 nm) at room temperature under N_2 atmosphere for 24 h.[b] Isolated yields. [c]**7d**:**2** = 2: 1, 5 mol% of photocatalyst **4** was used.

In the light of high reactivity and selectivity of potassium phenethylthiomethyltrifluoroborate **7d**, the scope of olefins was investigated (Table 3.2). Electron-deficient olefins **2b-e**, **2i** were also applicable to the present reaction. It should be noted that the reaction with **7d** led to alkylthiomethylation of olefins with a substituent at the reaction site such as 2-cyclopenten-1-one **2g** and diethyl ethylidenemalonate **2h**, which could not be applied to the reaction with **1a** (vide supra). The alkylthiomethylated products were obtained in 41% (**8dg**) and 62% (**8dh**) yields with the use of an excess amount of borate and 5 mol% of Ir catalyst **4**. These results suggest that the phenethylthiomethyl radical serves as a species more nucleophilic than the 1,3-dithian-2-yl radical and arylthiomethyl radicals presumably due to steric and electronic reasons.

Utilization of sunlight as the light source for photoreaction is promising in terms of green and sustainable chemistry. Thus, sunlight-driven photocatalytic alkylthiomethylation of **2a** with **7d** was performed. As a result, the reaction also proceeded efficiently to afford **8da** in a good yield under irradiation of sunlight for 8h (Scheme 3.5).



Scheme 3.5. Sunlight-driven photocatalytic alkylthiomethylation of 2a with 7d

3.4 Plausible reaction mechanism.

To gain an insight into the reaction mechanism, a few experiments were conducted.

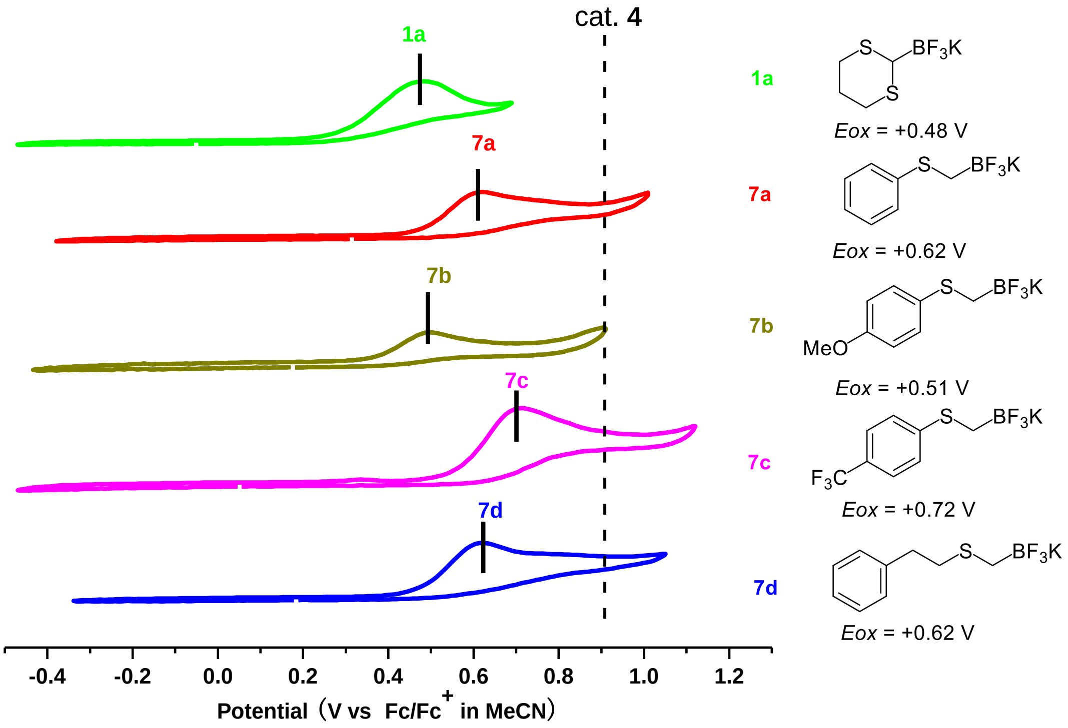


Figure 3.3 CV traces for 1a, 7a-7d. (Observed in 0.002 M MeCN; $[NBu_4][PF_6]$ = 0.1 M; reference electrode: $Ag/AgNO_3$; counter electrode: Pt; working electrode: Pt; reported with respect to the Fc/Fc^+).

As the electrochemical analysis of organoborates (Figure 3.3) shows, oxidation potentials for all of α-thioalkylborates (**1a, 7a-7d**) are less than +0.72 V vs. Fc/Fc^+, indicating that they can be easily oxidized by the photoactivated Ir catalyst **4** ($E_{1/2}$ = +0.91 V vs. Fc/Fc^+).

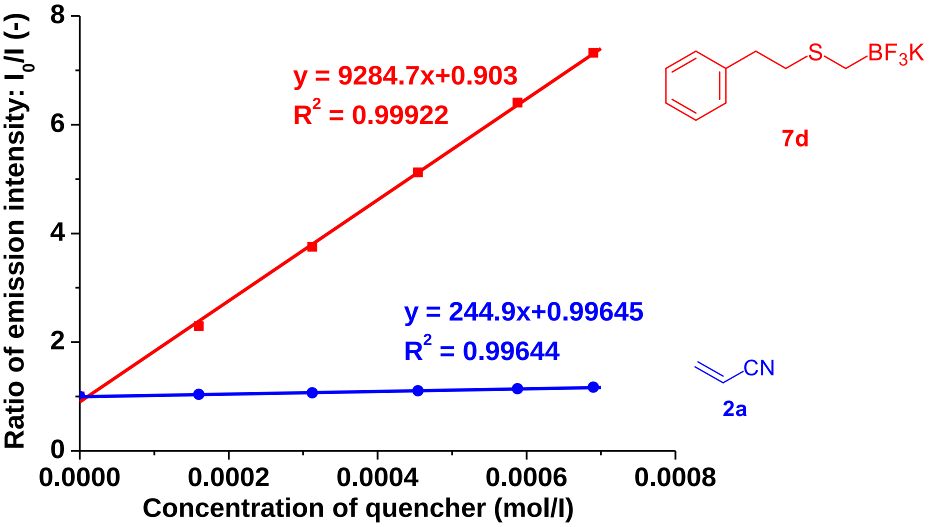
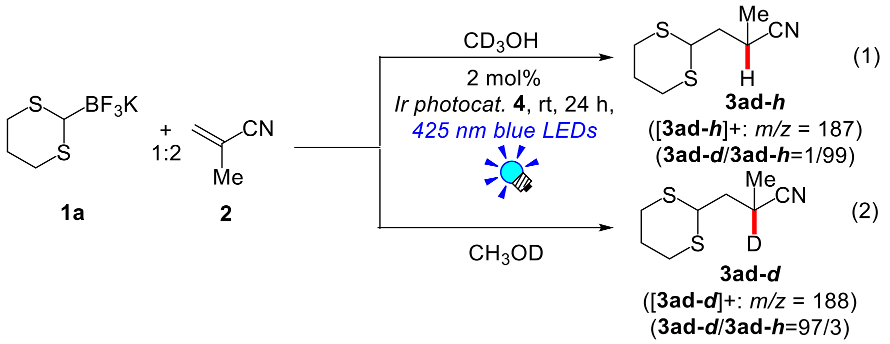


Figure 3.4 Stern-Volmer plots for 1e and 2a

Stern-Volmer plots were carried out to determine the species, which interacted with the photo-excited catalyst **4** (Figure 3.4). As a result, the phosphorescence from the triplet excited state of **4** was not quenched by **2a** but by the trifluoroborate **7d**, supporting that the first SET event occurs between the excited Ir photocatalyst **4** and **7d**.



Scheme 3.6. Isotope incorporation experiments

The isotope incorporation experiments in the deuterated methanols(Scheme 3.6) reveal that the H atom in the product **3** does not result from hydrogen abstraction from the CD_3 part of CD_3OH group but from protonation with the OD group of CH_3OD, indicating that the last intermediate is an anionic species.

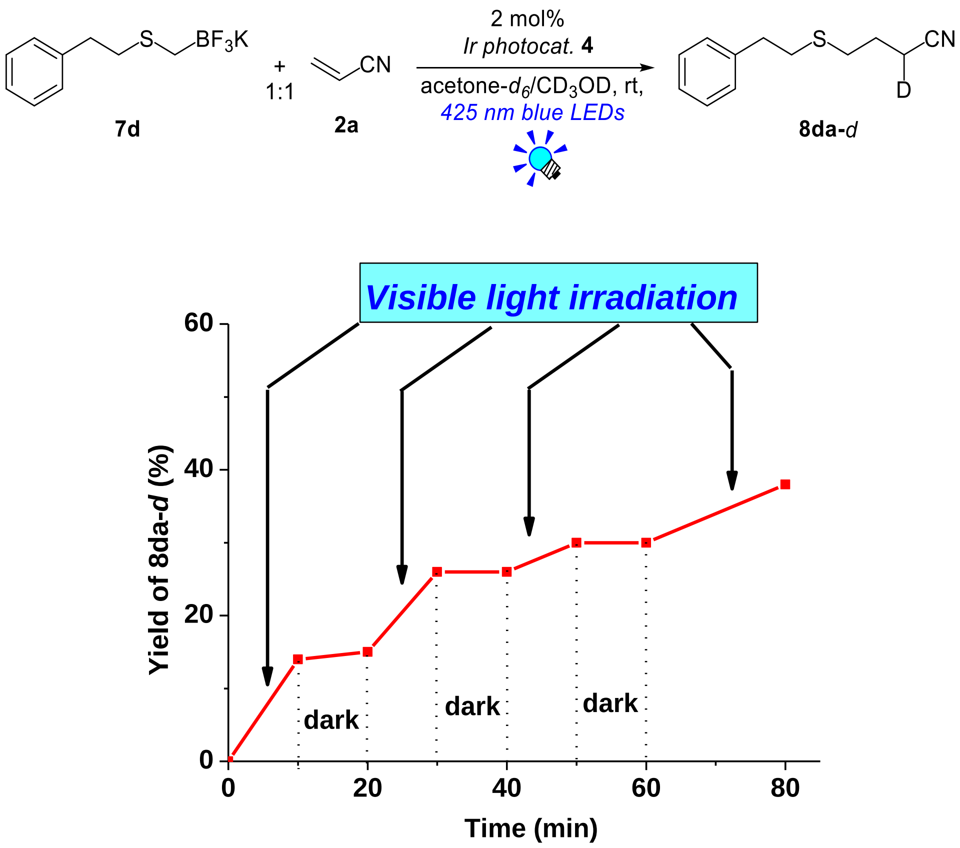
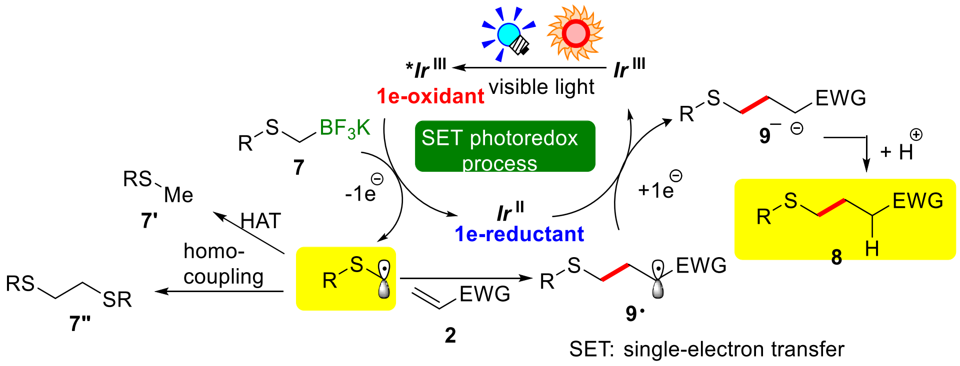


Figure 3.5. Dependence of thioalkylation on constant irradiation

Furthermore, to investigate participation of radical propagation as a main reaction pathway, the light control experiment was conducted (Figure 3.5). As a result, it can be seen the present reaction required continuous irradiation of visible light to proceed steadily. Therefore, the radical propagation process is not the major reaction pathway, if any.



Scheme 3.7 A plausible reaction mechanism

A plausible reaction mechanism for alkyl- and aryl-thioalkylation is illustrated in Scheme 3.7. Visible light irradiation induces the excitation of the Ir photocatalyst (***Ir*$^{\mathbf{III}}$**) to the photoactivated state (****Ir*$^{\mathbf{III}}$**), which serves as a strong oxidant. One-electron oxidation of alkyl- or aryl-thioalkylborate **7** by ****Ir*$^{\mathbf{III}}$** generates an α-thioalkyl radical via deboronation accompanying the formation of the highly reduced Ir species, ***Ir*$^{\mathbf{II}}$**. Subsequent addition of the α-thioalkyl radical to electron-deficient olefins **2** affords the radical intermediate **9·**, which undergoes a second SET event from ***Ir*$^{\mathbf{II}}$** to be converted into carboanionic intermediate **9**$^-$. Finally, protonation of **9**$^-$ by the protic solvent affords alkyl- or aryl-thioalkylated product **8**. In addition, by-products **7’** and **7”** are generated from HAT (hydrogen atom abstraction) and homo-coupling of the α-thioalkyl radical.

3.5 Conclusion

The author has developed alkyl- and aryl-thioalkylation of olefins using the corresponding organotrifluoroborates by visible-light-induced photoredox catalysis. The present photocatalytic protocol enables facile generation of α-thioalkyl radicals and access to a new range of alkylsulfides without any additives under mild reaction conditions: room temperature and visible light irradiation including natural sunlight.

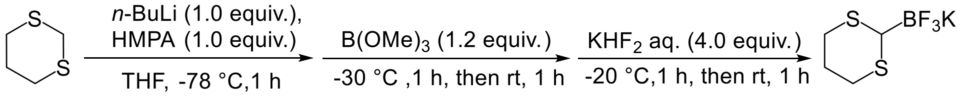
3.6 Experimental

Materials and methods

[Ir(dF(CF_3)ppy)$_2$(bpy)](PF_6) (**4**)[9a], [Ir(dF(CF_3)ppy)$_2$(dtbbpy)](PF_6) (**5**)[9b], [Ru(bpy)$_3$](PF_6)$_2$ (**6**)[9c], and potassium (1,3-dithian-2-yl)trifluoroborate (**1a**)[10] were prepared according to the reported literature procedures. Electron-deficient alkenes **2a**, **2b**, **2c**, **2e**, **2g**, and **2i** were purchased from TCI. **2d** was purchased from Wako. **2f** was purchased from SynQuest. **2h** was purchased from Aldrich. Recycled gel permeation chromatography (GPC) was performed by LC-9201 on Japan Analytical Industry Co. Ltd.

Procedures for the synthesis of organotrifluoroborates

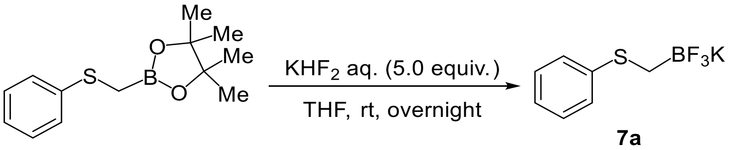
Potassium 1,3-dithian-2-yl trifluoroborate (1a)



1a

According to the literature [2], 1,3-dithiane (2.40 g, 20.0 mmol), dry THF (40.0 mL), a 1.55 M hexane solution of *n*-BuLi (13.0 mL, 20.0 mmol), HMPA (3.6 mL, 20.0 mmol), B(OMe)$_3$ (2.7 mL, 24.0 mmol), and a saturated KHF_2 aq. (6.24 g, 80.0 mmol, water = 20.0 mL) afforded **1a** as a white solid in 47% yield (2.11 g, 9.3 mmol). **^{1}H NMR** (500 MHz, CD_3OD) δ 3.49 (br, 1H; SC*H*S), 2.82 (m, 2H; SC*H*HCH_2), 2.65 (m, 2H; SCH*H*CH_2), 2.08 (m, 1H; SCH_2C*H*H), 1.88 (m, 1H; SCH_2CH*H*). **^{13}C NMR** (125 MHz, CD_3OD) δ 40.0 (S*C*HS), 31.5 (S*C*H_2CH_2), 28.2 (SCH_2*C*H_2). **^{11}B NMR** (160 MHz, CD_3OD) δ 3.14 (apparent q). **^{19}F NMR** (470 MHz, CD_3OD) δ -147.65 (apparent q). **HRMS (ESI-TOF):** calculated for $[C_4H_7BF_3S_2]^-$ requires 187.0041, found 187.0044.

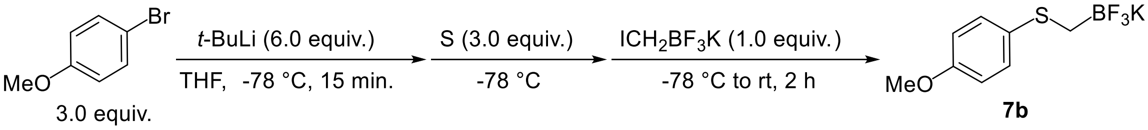
Potassium phenylthiomethyltrifluoroborate (7a)



7a

To a solution of 4,4,5,5,-tetramethyl-2-phenylsulfanylmethyl-1,3,2-dioxaborolane (1.00 g, 4.0 mmol) in THF (25.0 mL) at room temperature, then a saturated KHF_2 aq. (1.56 g, 20.0 mmol, water = 5.0 mL) was added. Then, the reaction mixture was stirred for 12 h. The suspension was concentrated and dried *in vacuo*. The residue was dissolved in dry acetone and filtered. After the solvent was removed, the residue was washed with Et_2O and dried *in vacuo*. The product was obtained as a white solid in 95% (0.88 g, 3.8 mmol). **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 7.17 (4H; *phenyl*), 6.97 (1H; *phenyl*), 1.62 (apparent d, SC*H*$_2$). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ 143.5 (*phenyl*), 128.3 (*phenyl*), 124.7 (*phenyl*), 122.8 (*phenyl*), 20.7 (S*C*H_2). **^{11}B NMR** (160 MHz, DMSO-*d*$_6$) δ 3.86 (apparent br.q). **^{19}F NMR** (470 MHz, DMSO-*d*$_6$) δ -135.6 (br). **HRMS (ESI-TOF):** calculated for $[C_7H_7BF_3S]^-$ requires 191.0320, found 191.0318. **Elemental Anal.:** calculated for $C_7H_7BF_3SK$: C 36.54, H 3.07. Found: C 36.28, H 3.04.

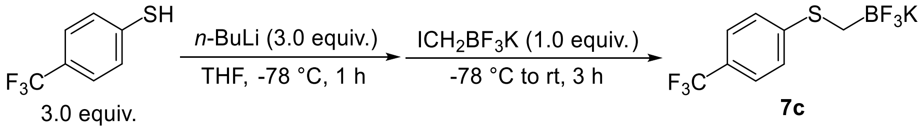
Potassium 4-methoxyphenylthiomethyltrifluoroborate (7b)



7b

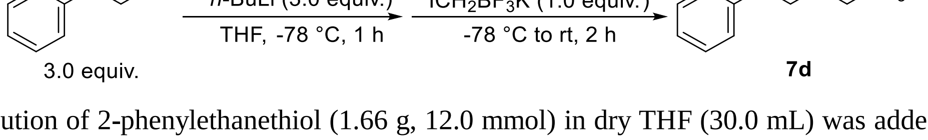
To a solution of 4-bromoanisole (0.45 g, 2.4 mmol) in dry THF (6.0 mL) was added a 1.61 M pentane solution of *t*-BuLi (3.0 ml, 4.8 mmol) at -78 ˚C for 15 min., and the mixture was stirred for 15 min. at -78 ˚C under N_2 atmosphere. Then, sulfur powder (0.08 g, 2.4 mmol) was added in one portion. After the reaction mixture changed to a yellow clear solution, a solution of potassium iodomethyltrifluoroborate (0.20 g, 0.8 mmol) in dry THF (6.0 mL) was slowly added and then the reaction mixture was gradually warmed up to room temperature for 2 h. After the reaction was completed, it was quenched with 1.5 M KHF_2 aq. (4.0 mL) and then the suspension was concentrated and dried *in vacuo*. The residue was dissolved in dry acetone and filtered. After the solvent was removed, the residue was washed with Et_2O and dried *in vacuo*. The product was obtained as a white solid in 59% yield (0.21 g, 0.5 mmol). **^{1}H NMR** (500 MHz, DMSO-*d$_6$*) δ 7.07 (d, *J* = 9.0 Hz, 2H; *phenyl*), 6.81 (d, *J* = 9.0 Hz, 2H; *phenyl*), 3.70 (s, 3H; OC*H*$_3$), 1.62 (apparent d, 2H; SC*H*$_2$). **^{13}C NMR** (125 MHz, DMSO-*d$_6$*) δ 156.5 (*phenyl*), 134.4 (*phenyl*), 127.2 (*phenyl*), 114.7 (*phenyl*), 55.5 (O*C*H$_3$), 22.8 (S*C*H$_2$). **^{11}B NMR** (160 MHz, DMSO-*d$_6$*) δ 3.75 (br). **^{19}F NMR** (470 MHz, DMSO-*d$_6$*) δ -135.8 (br). **HRMS (ESI-TOF):** calculated for $[C_8H_9BF_3OS]^-$ requires 221.0426, found 221.0426.

Potassium 4-trifluoromethylphenylthiomethyltrifluoroborate (7c)



To a solution of 4-trifluoromethyl benzenethiol (1.07 g, 6.0 mmol) in dry THF (15.0 mL) was added a 1.55 M hexane solution of *n*-BuLi (4.0 ml, 6.0 mmol) at -78 ˚C for 10 min., and the mixture was stirred for 1 h at -78 ˚C under N_2 atmosphere. A solution of potassium iodomethyltrifluoroborate (0.50 g, 2.0 mmol) in dry THF (15.0 mL) was gradually added and then the reaction mixture was slowly warmed up to room temperature for 3 h. After the reaction was completed, the mixture was quenched with 1.5 M KHF_2 aq. (10.0 mL) and then the suspension was concentrated and dried *in vacuo*. The residue was dissolved in dry acetone and filtered. After the solvent was removed, the residue was washed with Et_2O and dried *in vacuo*. The product was obtained as a white solid in 90% yield (0.54 g, 1.8 mmol). **^{1}H NMR** (500 MHz, DMSO-*d$_6$*) δ 7.51 (d, *J* = 8.5 Hz, 2H; *phenyl*), 7.32 (d, *J* = 8.5 Hz, 2H; *phenyl*), 1.68 (q, *J* = 5.5 Hz, 2H; SC*H*$_2$). **^{13}C NMR** (125 MHz, DMSO-*d$_6$*) δ 150.0 (*phenyl*), 124.8 (q, *J* = 269.4 Hz, *C*F$_3$), 125.0 (q, *J* = 3.6 Hz, *phenyl*), 124.8 (*phenyl*), 123.1 (q, *J* = 31.5 Hz, *phenyl*), 22.6 (S*C*H$_2$). **^{11}B NMR** (160 MHz, DMSO-*d$_6$*) δ 3.77 (br). **^{19}F NMR** (470 MHz, DMSO-*d$_6$*) δ -59.9 (s, C*F*$_3$), -135.8 (br, B*F*$_3$K). **HRMS (ESI-TOF):** calculated for $[C_8H_6BF_6S]^-$ requires 259.0194, found 259.0189.

Potassium phenethylthiomethyltrifluoroborate (7d)

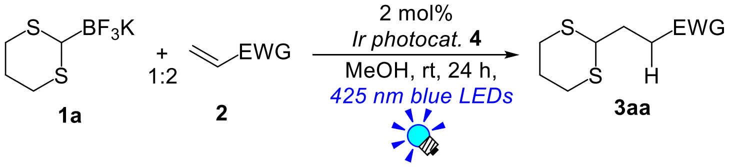


To a solution of 2-phenylethanethiol (1.66 g, 12.0 mmol) in dry THF (30.0 mL) was added a 1.55 M hexane solution of *n*-BuLi (8.0 ml, 12.0 mmol) at -78 ˚C for 20 min, and the mixture was stirred for 1 h at -78 ˚C under N_2 atmosphere. A solution of potassium iodomethyltrifluoroborate (0.99 g, 4.0 mmol) in dry THF (30.0 mL) was slowly added and then the reaction mixture was gradually warmed up to room temperature for 2 h. After the reaction was completed, the mixture was quenched with 1.5 M KHF_2 aq. (20.0 mL) and then the suspension was concentrated and dried *in vacuo*. The residue was dissolved in dry acetone and filtered. After the solvent was removed, the residue was washed with Et_2O and dried *in vacuo*. The product was obtained as a white solid in 92% yield (0.94 g, 3.7 mmol). **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 7.22 (2H; *phenyl*), 7.15 (3H; *phenyl*), 2.75 (m, 2H; phenyl-C*H*$_2$), 2.53 (m, 2H; phenyl-CH$_2$C*H*$_2$), 1.32 (q, *J* = 5.5 Hz, 2H; SC*H*$_2$BF$_3$K). **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ 141.5 (*phenyl*), 128.4 (*phenyl*), 128.2 (*phenyl*), 125.8 (*phenyl*), 36.0 (phenyl-*C*H$_2$), 35.6 (phenyl-CH$_2$*C*H$_2$), 22.3 (S*C*H$_2$). **^{11}B NMR** (160 MHz, DMSO-*d*$_6$) δ 3.94 (br). **^{19}F NMR** (470 MHz, DMSO-*d*$_6$) δ -135.7 (br). **HRMS (ESI-TOF):** calculated for $[C_9H_{11}BF_3S]^-$ requires 219.0634, found 219.0629.

Typical NMR experimental procedure (Table 3.1)

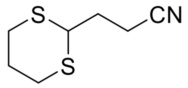
Under N_2 atmosphere, Ir photocatalyst **4** (1.0 mg, 1.0 μmol), potassium 1,3-dithian-2-yl trifluoroborate (**1a**) (11.3 mg, 0.05 mmol), tetraethylsilane ($SiEt_4$; an internal standard), CD_3OD (0.40 mL), and acrylonitrile (**2a**) (5.3 mg, 0.10 mmol) were added to an NMR tube. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps.

General procedure for the photocatalytic reaction of potassium 1,3-dithian-2-yl trifluoroborate (1a) with electron-deficient alkenes (Scheme 3.3.)



A 20 mL Schlenk tube was charged with Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium 1,3-dithian-2-yl trifluoroborate (**1a**) (56.5 mg, 0.25 mmol), dry methanol (2.0 mL), and electron-deficient alkene **2** (0.50 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps). After the reaction was completed, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by the recycled gel permeation chromatography (GPC).

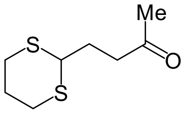
3-1,3-Dithian-2-ylpropanenitrile (3aa)



The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.4 mg, 0.25 mmol) and acrylonitrile (**2a**) (26.5 mg, 0.50 mmol) afforded **3aa** (34.6 mg, 80% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 4.11 (t, *J* = 7.2 Hz, 1H; SC*H*S), 2.89 (m, 4H; SC*H*$_2$CH$_2$), 2.60 (t, *J* = 7.2 Hz, 2H; CH$_2$C*H*$_2$CN), 2.14 (m, 3H; SCH$_2$C*H*H and C*H*$_2$CH$_2$CN), 1.94 (m, 1H; SCH$_2$CH*H*). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 118.7 (*C*N), 45.2 (S*C*HS), 31.1 (*C*H$_2$CH$_2$CN), 29.8 (S*C*H$_2$CH$_2$), 25.7 (SCH$_2$*C*H$_2$), 14.9 (*C*H$_2$CN). **HRMS (ESI-TOF):** calculated for $[C_7H_{11}NS_2+Na]^+$ requires 196.0225, found 196.0221.

4-(1,3-Dithian-2-yl)butan-2-one (3ab)

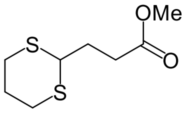


The reaction of Ir photocatalyst **4** (5.1 mg, 5.1 μmol), potassium

(1,3-dithian-2-yl)trifluoroborate (**1a**) (56.8 mg, 0.25 mmol) and 3-buten-2-one (**2b**) (35.4 mg, 0.50 mmol) afforded **3ab** (37.1 mg, 78% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 4.05 (t, *J* =7.2 Hz, 1H; SC*H*S), 2.84 (m, 4H; SC*H$_2$*CH$_2$), 2.68 (t, *J* = 7.2 Hz, 2H; CH$_2$C*H$_2$*C=O), 2.16 (s, 3H; C*H$_3$*C=O), 2.09 (m, 3H; SCH$_2$C*H*H and C*H$_2$*CH$_2$C=O), 1.89 (m, 1H; SCH$_2$CH*H*). **^{13}C NMR** (100 MHz, CDCl$_3$, rt) δ 207.5 (*C*=O), 46.5 (S*C*HS), 40.2 (CH$_2$*C*H$_2$C=O), 30.2 (*C*H$_3$C=O), 30.1 (S*C*H$_2$CH$_2$), 29.1 (*C*H$_2$CH$_2$C=O), 26.0 (SCH$_2$*C*H$_2$). **HRMS (ESI-TOF):** calculated for $[C_8H_{14}OS_2+Na]^+$ requires 213.0378, found 213.0372.

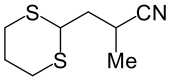
Methyl 3-(1,3-Dithian-2-yl)propanoate (3ac)



The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.5 mg, 0.25 mmol) and methyl acrylate (**2c**) (43.1 mg, 0.50 mmol) afforded **3ac** (36.6 mg, 71% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 4.06 (t, *J* = 7.2 Hz, 1H; SC*H*S), 3.69 (s, 3H; OC*H$_3$*), 2.85 (m, 4H; SC*H$_2$*CH$_2$), 2.56 (t, *J* = 7.2 Hz, 2H; CH$_2$C*H$_2$*C=O), 2.12 (m, 3H; SCH$_2$C*H*H and C*H$_2$*CH$_2$C=O), 1.88 (m, 1H; SCH$_2$CH*H*). **^{13}C NMR** (100 MHz, CDCl$_3$, rt) δ 173.2 (*C*=O), 51.9 (O*C*H$_3$), 46.3 (S*C*HS), 31.1 (CH$_2$*C*H$_2$C=O), 30.4 (*C*H$_2$CH$_2$C=O), 29.9 (S*C*H$_2$CH$_2$), 25.9 (SCH$_2$*C*H$_2$). **HRMS (ESI-TOF):** calculated for $[C_8H_{14}O_2S_2+Na]^+$ requires 229.0327, found 229.0322.

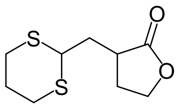
3-(1,3-Dithian-2-yl)-2-methylpropanenitrile (3ad)



The reaction of Ir photocatalyst **4** (5.1 mg, 5.1 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (57.3 mg, 0.25 mmol) and methacrylonitrile (**2d**) (34.0 mg, 0.50 mmol) afforded **3ad** (30.4 mg, 64% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 4.19 (dd, *J* = 9.9 Hz, *J* = 5.2 Hz, 1H; SC*H*S), 3.03 (m, 1H; C*H*CN), 2.90 (m, 4H; SC*H$_2$*CH$_2$), 2.12 (m, 2H; SCHC*H*H and SCH$_2$C*H*H), 1.91 (m, 2H; SCHCH*H* and SCH$_2$CH*H*), 1.36 (d, *J* = 6.4 Hz, 3H; CHC*H$_3$*). **^{13}C NMR** (100 MHz, CDCl$_3$, rt) δ 122.0 (*C*N), 44.4 (S*C*HS), 39.5 (*C*H$_2$CHCN), 30.1 (S*C*H$_2$CH$_2$), 30.0 (S*C*H$_2$CH$_2$), 25.8 (SCH$_2$*C*H$_2$), 23.2 (*C*HCN), 18.1 (CH*C*H$_3$). **HRMS (ESI-TOF):** calculated for $[C_8H_{13}NS_2+Na]^+$ requires 210.0382, found 210.0377.

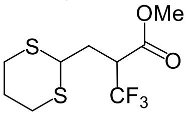
3-(1,3-Dithian-2-ylmethyl)dihydrofuran-2(3H)-one (3ae)



The reaction of Ir photocatalyst **4** (5.1 mg, 5.1 μmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.6 mg, 0.25 mmol) and α-methylene-γ-butyrolactone (**2e**) (49.2 mg, 0.50 mmol) afforded **3ae** (42.6 mg, 78% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (400 MHz, CDCl$_3$, rt) δ 4.32 (dt, *J* = 9.0 Hz, *J* = 2.0 Hz, 1H; OC*H*H), 4.19 (m, 2H; SC*H*S and OCH*H*), 2.88 (m, 5H; SC*H$_2$*CH$_2$ and C=OC*H*CH$_2$), 2.47 (m, 2H; SCHC*H$_2$*CH), 2.08 (m, 1H; SCH$_2$C*H*H), 1.92 (m, 3H; SCH$_2$CH*H* and OCH$_2$C*H$_2$*). **^{13}C NMR** (100 MHz, CDCl$_3$, rt) δ 178.6 (*C*=O), 66.5 (O*C*H$_2$), 44.9 (S*C*HS), 37.0 (SCHCH$_2$*C*H), 36.3 (SCH*C*H$_2$), 29.7(2C; S*C*H$_2$CH$_2$), 29.5 (OCH$_2$*C*H$_2$), 25.9 (SCH$_2$*C*H$_2$). **HRMS (ESI-TOF):** calculated for $[C_9H_{14}O_2S_2+Na]^+$ requires 241.0327, found 241.0322.

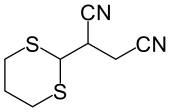
Methyl 2-(1,3-dithian-2-ylmethyl)-3,3,3-trifluoropropanoate (3af)



The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.5 mg, 0.25 mmol) and methyl 2-(trifluoromethyl) acrylate (**2f**) (77.2 mg, 0.50 mmol) afforded **3af** (54.6 mg, 80% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 3.93 (dd, *J* = 8.9 Hz, *J* = 6.3 Hz, 1H; SC*H*S), 3.81 (s, 3H; OC*H₃*), 3.52 (m, 1H; C*H*CF₃), 2.84 (m, 4H; SC*H₂*CH₂), 2.52 (m, 1H; SCHC*H*HCH), 2.26 (m, 1H; SCHCH*H*CH), 2.10 (m, 1H; SCH₂C*H*H), 1.94 (m, 1H; SCH₂CH*H*). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 167.4 (q, *J* = 3.1 Hz; *C*=O), 124.5 (q, *J* = 266.1 Hz; *C*F₃), 53.2 (O*C*H₃), 47.6 (q, *J* = 27.8 Hz; *C*HCF₃), 43.3 (S*C*HS), 31.6 (d, *J* = 1.8 Hz; SCH*C*H₂), 29.1 (S*C*H₂CH₂), 28.9 (S*C*H₂CH₂), 25.6 (SCH₂*C*H₂). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.0 (d, *J* = 8.5 Hz; C*F₃*). **HRMS (ESI-TOF):** calculated for $[C_9H_{13}F_3O_2S_2+Na]^+$ requires 297.0201, found 297.0197.

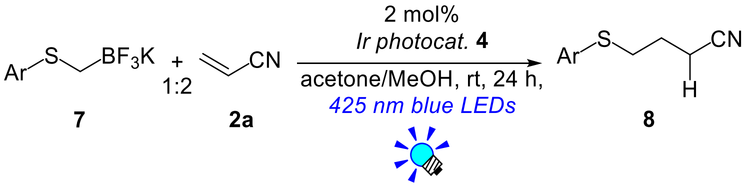
2-(1,3-Dithian-2-yl)succinonitrile (3ai)



The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium (1,3-dithian-2-yl)trifluoroborate (**1a**) (56.6 mg, 0.25 mmol) and fumaronitrile (**2i**) (39.0 mg, 0.50 mmol) afforded **3ai** (42.5 mg, 86% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

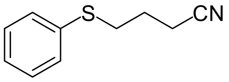
^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 4.15 (d, *J* = 7.2 Hz, 1H; SC*H*S), 3.44 (apparent q, 1H; CNC*H*), 3.02 (m, 4H; SC*H₂*CH₂ and CHC*H₂*CN), 2.87 (m, 2H; SC*H₂*CH₂), 2.14 (m, 1H; SCH₂C*H*H), 2.03 (m, 1H; SCH₂CH*H*). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 116.9 (*C*NCH), 115.3 (CH₂*C*N), 44.1 (S*C*HS), 34.8 (CN*C*H), 28.3 (S*C*H₂CH₂), 28.2 (S*C*H₂CH₂), 24.6 (SCH₂*C*H₂), 19.9 (CN*C*H₂). **HRMS (ESI-TOF):** calculated for $[C_8H_{10}N_2S_2+Na]^+$ requires 221.0178, found 221.0173.

General procedure for the photocatalytic reaction of arylthiomethyltrifluoroborates with acrylonitrile (2a) (Scheme 3.4)



A 20 mL Schlenk tube was charged with Ir photocatalyst **4** (5.0 mg, 5.0 µmol), arylthiomethyltrifluoroborate **7** (0.25 mmol), dry methanol (1.0 mL), dry acetone (1.0 mL) and acrylonitrile (**2a**) (26.5 mg, 0.50 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps). After the reaction was completed, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by the recycled gel permeation chromatography (GPC).

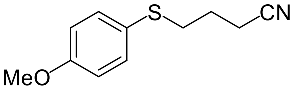
4-Phenylthiobutanenitrile (8aa)



The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenylthiomethyltrifluoroborate (**7a**) (57.5 mg, 0.25 mmol) and acrylonitrile (**2a**) (26.7 mg, 0.50 mmol) afforded **8aa** (14.2 mg, 32% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, CDCl$_3$, rt) δ 7.29 (5H; *phenyl*), 3.04 (t, *J* = 7.0 Hz, 2H; SC*H*$_2$), 2.52 (t, *J* = 7.0 Hz, 2H; C*H*$_2$CN), 1.96 (apparent quint, 2H; C*H*$_2$CH$_2$CN). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 134.8 (*phenyl*), 130.3 *(phenyl*), 129.3 (*phenyl*), 126.9 (*phenyl*), 119.2 (*C*N), 32.7 (S*C*H$_2$), 24.9 (*C*H$_2$CH$_2$CN), 16.0 (*C*H$_2$CN). **HRMS (ESI-TOF):** calculated for [C$_{10}$H$_{11}$NS+Na]$^+$ requires 200.0504, found 200.0510.

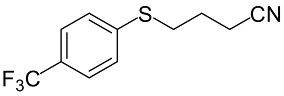
4-(4-Methoxyphenylthio)butanenitrile (8ba)



The reaction of Ir photocatalyst **4** (5.1 mg, 5.1 μmol), potassium 4-methoxyphenylthiomethyltrifluoroborate (**7b**) (65.0 mg, 0.25 mmol) and acrylonitrile (**2a**) (26.6 mg, 0.50 mmol) afforded **8ba** (8.0 mg, 15% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, CDCl$_3$, rt) δ 7.32 (d, *J* = 8.5 Hz, 2H; *phenyl*), 6.86 (d, *J* = 8.5 Hz, 2H; *phenyl*), 3.80 (s, 3H; C*H*$_3$O), 2.92 (t, *J* = 6.5 Hz, 2H; SC*H*$_2$), 2.51 (t, *J* = 6.5 Hz, 2H; C*H*$_2$CN), 1.90 (apparent quint, 2H; SCH$_2$C*H*$_2$). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 159.6 (*phenyl*), 134.1 (*phenyl*), 124.8 (*phenyl*), 119.3 (*C*N), 114.9 (*phenyl*), 55.5 (*C*H$_3$O), 34.7 (S*C*H$_2$), 25.0 (*C*H$_2$CH$_2$CN), 15.9 (*C*H$_2$CN). **HRMS (ESI-TOF):** calculated for [C$_{11}$H$_{13}$NOS+Na]$^+$ requires 230.0610, found 230.0607.

4-(4-Trifluoromethylphenylthio)butanenitrile (8ca)

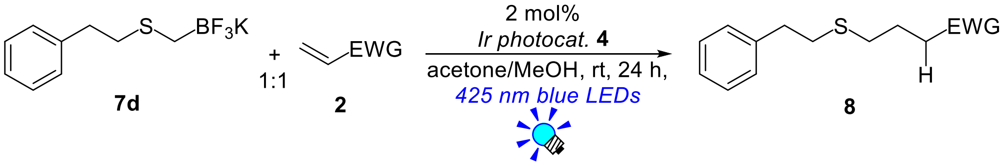


The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium 4-trifluoromethylphenylthiomethyltrifluoroborate (**7c**) (74.5 mg, 0.25 mmol) and acrylonitrile (**2a**) (26.6 mg, 0.50 mmol) afforded **8ca** (26.1 mg, 43% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

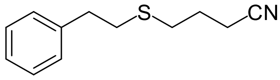
^{1}H NMR (500 MHz, CDCl$_3$, rt) δ 7.55 (d, *J* = 8.0 Hz, 2H; *phenyl*), 7.40 (d, *J* = 8.0 Hz, 2H; *phenyl*), 3.12 (t, *J*= 7.0 Hz, 2H; SC*H*$_2$), 2.53 (t, *J* = 7.0 Hz, 2H; C*H*$_2$CN), 2.02 (apparent quint, 2H; CH$_2$C*H*$_2$CN). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 140.5 (*phenyl*), 128.4 (*phenyl*), 126.1 (q, *J* = 3.6 Hz; *phenyl*), 124.1 (q, *J* = 270.1 Hz; *C*F$_3$), 123.1 (*phenyl*), 118.9 (*C*N), 31.4 (S*C*H$_2$), 24.7 (*C*H$_2$CH$_2$CN), 16.2 (*C*H$_2$CN). **^{19}F NMR** (500 MHz, CDCl$_3$) δ -62.5 (s; C*F*$_3$). **HRMS (ESI-TOF):** calculated for [C$_{11}$H$_{10}$F$_3$NS+Na]$^+$ requires 268.0378, found 268.0375.

General procedure for the photocatalytic reaction of potassium phenethylthiomethyltrifluoroborate (7d) with electron-deficient alkenes (Table 3.2)

A 20 mL Schlenk tube was charged with Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (64.5 mg, 0.25 mmol), dry methanol (1.0 mL), dry acetone (1.0 mL), and electron-deficient alkene **2** (0.25 mmol) under N$_2$ atmosphere.



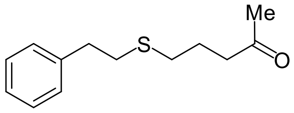
4-Phenethylthiobutanenitrile (8da)



The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 μmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (64.8 mg, 0.25 mmol) and acrylonitrile (**2a**) (13.8 mg, 0.25 mmol) afforded **8da** (43.1 mg, 84% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.27 (5H; *phenyl*), 2.89 (m, 2H; phenyl-$C\mathit{H_2}$), 2.78 (m, 2H; phenyl-$CH_2C\mathit{H_2}$), 2.65 (t, *J* = 7.2 Hz, 2H; $C\mathit{H_2}CH_2CH_2CN$), 2.48 (t, *J* = 7.2 Hz, 2H; $C\mathit{H_2}CN$), 1.92 (apparent quint, 2H; $CH_2C\mathit{H_2}CH_2CN$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 140.3 (*phenyl*), 128.7 (*phenyl*), 128.6 (*phenyl*), 126.6 (*phenyl*), 119.3 ($\mathit{C}N$), 36.3 (phenyl-$\mathit{C}H_2$), 33.8 (phenyl-$CH_2\mathit{C}H_2$), 30.9 ($\mathit{C}H_2CH_2CH_2CN$), 25.3 ($\mathit{C}H_2CH_2CN$), 16.1 ($\mathit{C}H_2CN$). **HRMS (ESI-TOF):** calculated for $[C_{12}H_{15}NS+Na]^+$ requires 228.0817, found 228.0816.

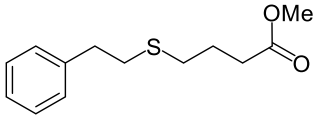
4-Phenethylthiobutan-2-one (8db)



The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (64.4 mg, 0.25 mmol) and 3-buten-2-one (**2b**) (17.4 mg, 0.25 mmol) afforded **8db** (41.1 mg, 74% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.26 (5H; *phenyl*), 2.89 (m, 2H; phenyl-$C\mathit{H_2}$), 2.77 (m, 2H; phenyl-$CH_2C\mathit{H_2}$), 2.55 (m, 4H; $C\mathit{H_2}CH_2C\mathit{H_2}C{=}O$), 2.14 (s, 3H; $C\mathit{H_3}C{=}O$), 1.88 (apparent quint, 2H; $SCH_2C\mathit{H_2}CH_2C{=}O$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 208.3 ($\mathit{C}{=}O$), 140.6 (*phenyl*), 128.6 (*phenyl*), 128.6 (*phenyl*), 126.5 (*phenyl*), 42.2 ($\mathit{C}H_2C{=}O$), 36.4 (phenyl-$\mathit{C}H_2$), 33.5 (phenyl-$CH_2\mathit{C}H_2$), 31.6 ($\mathit{C}H_2CH_2CH_2C{=}O$), 30.2 ($\mathit{C}H_3C{=}O$), 23.2 ($CH_2\mathit{C}H_2CH_2C{=}O$). **HRMS (ESI-TOF):** calculated for $[C_{13}H_{18}OS+Na]^+$ requires 245.0971, found 245.0967.

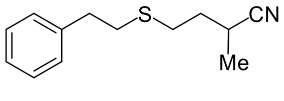
Methyl 4-phenethylthiobutanoate (8dc)



The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (64.6 mg, 0.25 mmol) and methyl acrylate (**2c**) (21.5 mg, 0.25 mmol) afforded **8dc** (42.3 mg, 71% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.26 (5H; *phenyl*), 3.68 (s, 3H; $OC\mathit{H_3}$), 2.89 (m, 2H; phenyl-$C\mathit{H_2}$), 2.77 (m, 2H; phenyl-$CH_2C\mathit{H_2}$), 2.57 (t, *J* = 7.2 Hz, 2H; $C\mathit{H_2}C{=}O$), 2.44 (t, *J* = 7.3 Hz, 2H; $C\mathit{H_2}CH_2CH_2C{=}O$), 1.92 (apparent quint, 2H; $C\mathit{H_2}CH_2C{=}O$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 173.7 ($\mathit{C}{=}O$), 140.7 (*phenyl*), 128.7 (*phenyl*), 128.6 (*phenyl*), 126.5 (*phenyl*), 51.7 ($O\mathit{C}H_3$), 36.5 (phenyl-$\mathit{C}H_2$), 33.6 (phenyl-$CH_2\mathit{C}H_2$), 33.0 ($\mathit{C}H_2CH_2CH_2C{=}O$), 31.7 ($\mathit{C}H_2C{=}O$), 24.9 ($\mathit{C}H_2CH_2C{=}O$). **HRMS (ESI-TOF):** calculated for $[C_{13}H_{18}O_2S+Na]^+$ requires 261.0920, found 261.0922.

2-Methyl-4-phenethylthiobutanenitrile (8dd)

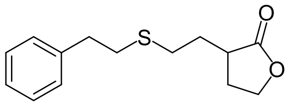


The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (65.1 mg, 0.25 mmol) and methacrylonitrile (**2d**) (17.0 mg, 0.25 mmol) afforded **8dd** (33.7 mg, 60% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, $CDCl_3$, rt) δ 7.26 (5H; *phenyl*), 2.90 (m, 2H; phenyl-$C\mathit{H_2}$), 2.82 (m, 3H; phenyl-$CH_2C\mathit{H_2}$ and $C\mathit{H}CN$), 2.67 (m, 2H; $C\mathit{H_2}CH_2CHCN$), 1.83 (m, 2H; $C\mathit{H_2}CHCN$), 1.33 (d, *J* = 7.0 Hz, 3H; $CHC\mathit{H_3}$). **^{13}C NMR** (125 MHz, $CDCl_3$, rt) δ 140.3 (*phenyl*), 128.6 (*phenyl*), 128.6 (*phenyl*), 126.6 (*phenyl*), 122.5 ($\mathit{C}N$), 36.3 (phenyl-$\mathit{C}H_2$), 33.9 (phenyl-$CH_2\mathit{C}H_2$), 33.9 ($\mathit{C}H_2CHCN$), 29.6 ($\mathit{C}H_2CH_2CHCN$), 24.5 ($\mathit{C}HCN$), 17.9 ($CH\mathit{C}H_3$). **HRMS (ESI-TOF):**

calculated for [C$_{13}$H$_{17}$NS +Na]$^+$ requires 242.0974, found 242.0976.

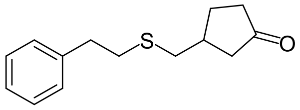
3-(2-Phenethylthioethyl)dihydrofuran-2(3H)-one (8de)



The reaction of Ir photocatalyst **4** (5.1 mg, 5.1 µmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (65.6 mg, 0.25 mmol) and α-methylene-γ-butyrolactone (**2e**) (25.0 mg, 0.25 mmol) afforded **8de** (40.1 mg, 63% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, CDCl$_3$, rt) δ 7.26 (5H; *phenyl*), 4.36 (m, 1H; OC*H*HCH$_2$), 4.19 (m, 1H; OCH*H*CH$_2$), 2.90 (m, 2H; phenyl-C*H*$_2$), 2.80 (m, 2H; phenyl-CH$_2$C*H*$_2$), 2.73 (m, 3H; C*H*C=O and SC*H*$_2$CH$_2$CH), 2.54 (m, 1H; OCH$_2$C*H*H), 2.17 (m, 1H; OCH$_2$CH*H*), 1.82 (m, 1H; SCH$_2$C*H*HCH), 1.72 (m, 1H; SCH$_2$CH*H*CH). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 179.2 (*C*=O), 140.5 (*phenyl*) 128.6 (*phenyl*), 128.6 (*phenyl*) 126.6 (*phenyl*), 66.6 (O*C*H$_2$CH$_2$), 38.0 (phenyl-*C*H$_2$), 36.3 (phenyl-CH$_2$*C*H$_2$), 33.4 (*C*HC=O), 30.1 (SCH$_2$*C*H$_2$CH), 29.8 (S*C*H$_2$CH$_2$CH), 28.8 (OCH$_2$*C*H$_2$). **HRMS (ESI-TOF):** calculated for [C$_{14}$H$_{18}$O$_2$S+Na]$^+$ requires 273.0920, found 273.0916.

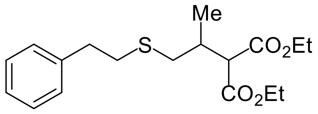
3-Phenethylthiomethylcyclopentanone (8dg)



The reaction of Ir photocatalyst **4** (12.0 mg, 12.0 µmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (129.0 mg, 0.50 mmol) and 2-cyclopenten-1-one (**2g**) (19.9 mg, 0.25 mmol) afforded **8dg** (23.6 mg, 41% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

^{1}H NMR (500 MHz, CDCl$_3$, rt) δ 7.26 (5H; *phenyl*), 2.90 (m, 2H; phenyl-C*H*$_2$), 2.80 (m, 2H; phenyl-CH$_2$C*H*$_2$), 2.63 (d, *J* = 8.5 Hz, 2H; SC*H*$_2$CH), 2.43 (m, 2H; CHC*H*HC=O, C*H*CH$_2$C=O), 2.33 (m, 1H; CH$_2$C*H*HC=O), 2.20 (m, 2H; C*H*HCH$_2$C=O and CH$_2$CH*H*C=O), 1.97 (m, 1H; CHC*H*HC=O), 1.65 (m, 1H; CH*H*CH$_2$C=O). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 218.6 (*C*=O), 140.5 (*phenyl*), 128.6 (*phenyl*), 128.6 (*phenyl*), 126.6 (*phenyl*), 44.7 (CH*C*H$_2$C=O), 38.4 (CHCH$_2$*C*H$_2$C=O), 37.8 (S*C*H$_2$CH), 37.2 (SCH$_2$*C*H), 36.6 (phenyl-*C*H$_2$), 34.5 (phenyl-CH$_2$*C*H$_2$), 28.9 (*C*H$_2$CH$_2$C=O)**.** **HRMS (ESI-TOF):** calculated for [C$_{14}$H$_{18}$OS+Na]$^+$ requires 257.0971, found 257.0976.

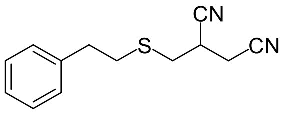
Diethyl 2-(1-phenethylthiopropan-2-yl)malonate (8dh)



The reaction of Ir photocatalyst **4** (12.5 mg, 12.5 µmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (129.1 mg, 0.50 mmol) and diethyl ethylidenemalonate (**2h**) (46.6 mg, 0.25 mmol) afforded **8dh** (52.5 mg, 62% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC).

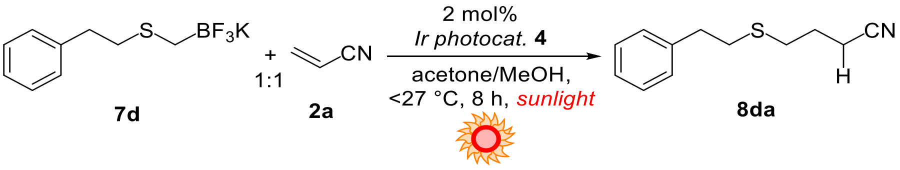
^{1}H NMR (500 MHz, CDCl$_3$, rt) δ 7.26 (5H; *phenyl*), 4.19 (m, 4H; OC*H*$_2$CH$_3$), 3.48 (d, *J* = 8.7 Hz, 1H; C=OC*H*), 2.88 (m, 2H; phenyl-C*H*$_2$), 2.79 (m, 3H; phenyl-CH$_2$C*H*$_2$ and CH$_3$C*H*), 2.46 (m, 2H; SC*H*$_2$CH), 1.268 (t, *J* = 8.9 Hz, 3H; OCH$_2$C*H*$_3$), 1.265 (t, *J* = 8.9 Hz, 3H; OCH$_2$C*H*$_3$), 1.11 (d, *J* = 8.2 Hz, 3H; CHC*H*$_3$). **^{13}C NMR** (125 MHz, CDCl$_3$, rt) δ 168.8 (*C*=O), 168.5 (*C*=O), 140.6 (*phenyl*) 128.6 (*phenyl*), 128.5(*phenyl*) 126.4 (*phenyl*), 61.5 (O*C*H$_2$CH$_3$), 61.4 (O*C*H$_2$CH$_3$), 56.0 (C=O*C*H), 37.1 (SCH$_2$*C*H), 36.4 (phenyl-*C*H$_2$), 34.0 (phenyl-CH$_2$*C*H$_2$), 33.7 (S*C*H$_2$CH), 16.9 (*C*H$_3$CH), 14.2 (OCH$_2$*C*H$_3$), 14.2 (OCH$_2$*C*H$_3$). **HRMS (ESI-TOF):** calculated for [C$_{18}$H$_{26}$O$_4$S+Na]$^+$ requires 361.1444, found 361.1450.

2-Phenethylthiomethylsuccinonitrile (8di)



The reaction of Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (64.5 mg, 0.25 mmol) and fumaronitrile (**2i**) (19.5 mg, 0.25 mmol) afforded **8di** (49.0 mg, 85% yield) as a pale yellow oil after purification with recycled gel permeation chromatography (GPC). ^{1}**H NMR** (500 MHz, CDCl$_3$, rt) δ 7.27 (5H; *phenyl*), 2.93 (m, 5H; phenyl-C*H*$_2$, phenyl-CH$_2$C*H*$_2$ and C*H*CN), 2.88 (m, 1H; SC*H*HCHCN), 2.82 (m, 3H; SCH*H*CHCN and CHC*H*$_2$CN). ^{13}**C NMR** (125 MHz, CDCl$_3$, rt) δ 139.7 (*phenyl*), 128.9 (*phenyl*), 128.8 (*phenyl*), 127.1 (*phenyl*), 118.2 (*C*NCH), 115.4 (CH$_2$*C*N), 36.4 (phenyl-*C*H$_2$), 34.9 (phenyl-CH$_2$*C*H$_2$), 33.7 (S*C*H$_2$CHCN), 29.5 (CN*C*H), 20.0 (*C*H$_2$CN). **HRMS (ESI-TOF):** calculated for [C$_{13}$H$_{14}$N$_2$S+Na]$^+$ requires 253.0770, found 253.0769.

Sunlight-driven reaction (Scheme 3.5)



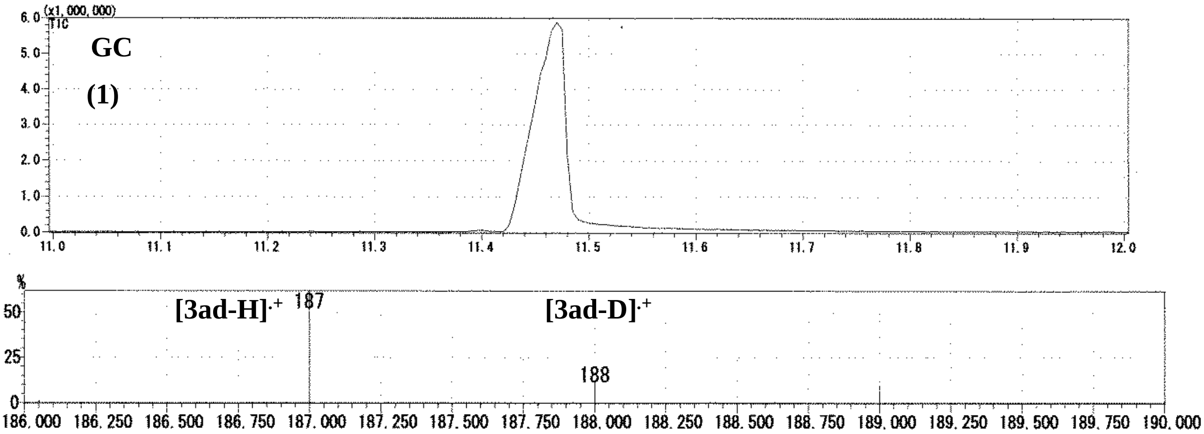
A cylindrical vessel was used for photocatalytic reaction under sunlight. Cylindrical vessel was charged with Ir photocatalyst **4** (5.0 mg, 5.0 µmol), potassium phenethylthiomethyltrifluoroborate (**7d**) (64.5 mg, 0.25 mmol), dry methanol (1.0 mL), dry acetone (1.0 mL) and acrylonitrile (**2a**) (13.4 mg, 0.25 mmol) under N$_2$ atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction mixture was exposed to sunlight for 8 h (in June 28th, 2014) below 27 ˚C. After workup, **8da** was obtained as pale yellow oil in 75％ yield (38.5 mg, 0.19 mmol).

Luminescence quenching experiments (Figure 3.4)

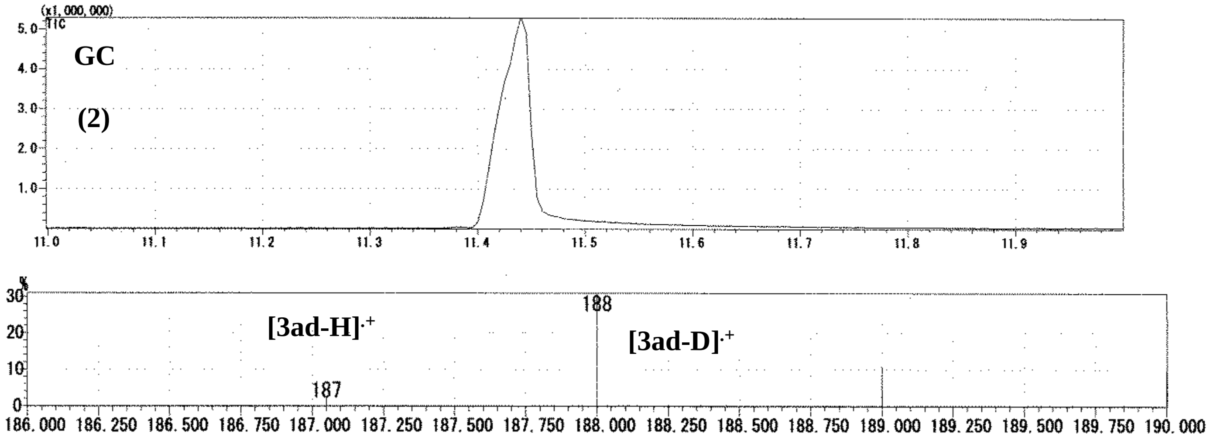
Emission spectra for the Ir photocatalyst **4** in a deaerated solution whose concentration was adjusted so as to show the absorbance of 0.1 at the excitation wavelength (at 379 nm) were recorded at room temperature. The excited Ir photocatalyst **4** in DMSO exhibited band at 479 nm. The solution of the Ir photocatalyst **4** was prepared and degassed three times via freeze-pump-thaw cycle in a 1 cm quartz cell equipped with a sphere moiety for freeze. The solution of quencher was added to the solution of the Ir photocatalyst **4** before measurement of emission intensities.

Isotope incorporation experiments (Scheme 3.6)

According to the typical NMR experimental procedure, the isotope incorporation experiments (1) and (2) were conducted by using CD$_3$OH and CD$_3$OD, respectively. The peaks of **3ad-*h*** and **3ad-*d*** were detected at 11.44 min. On the basis of absolute intensity of isotope peaks in MS spectra, the ratios of **3ad**-*d* /**3ad**-*h* were calculated.



Absolute intensity: 187(434775), 188(48164), 189(42506)



Absolute intensity: 187(12859), 188(414460), 189(56308)

Figure 3.6 GC-MS spetra of (1) and (2)

3.7 References

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[8] The photoexcited state of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) (**5**) and [Ru(bpy)$_3$](PF$_6$)$_2$ (**6**) are weaker oxidants ($E_{1/2}$ = +0.80 V and +0.36 V *vs*. Cp$_2$Fe, respectively) than that of **4**; see: 11(*a*) and K. Kalyanasundaram, *Coord. Chem. Rev.*, **1982**, *46*, 159.

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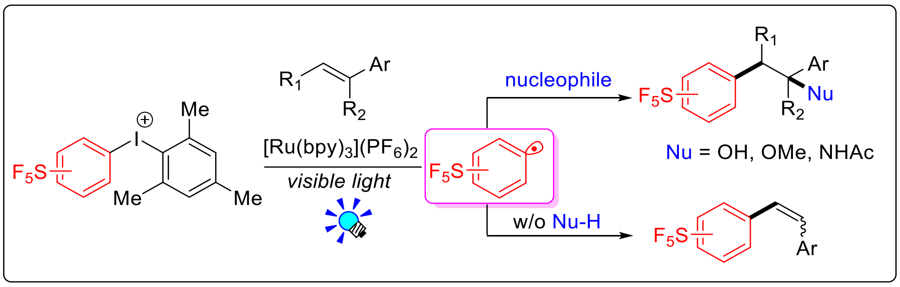
[10] A.S. Vieira, P. F. Fiorante, J. Z. Schpector, D. Alves, G. V. Botteselle and H. A. Stefani, *Tetrahedron*. **2008**, *64*, 7234.

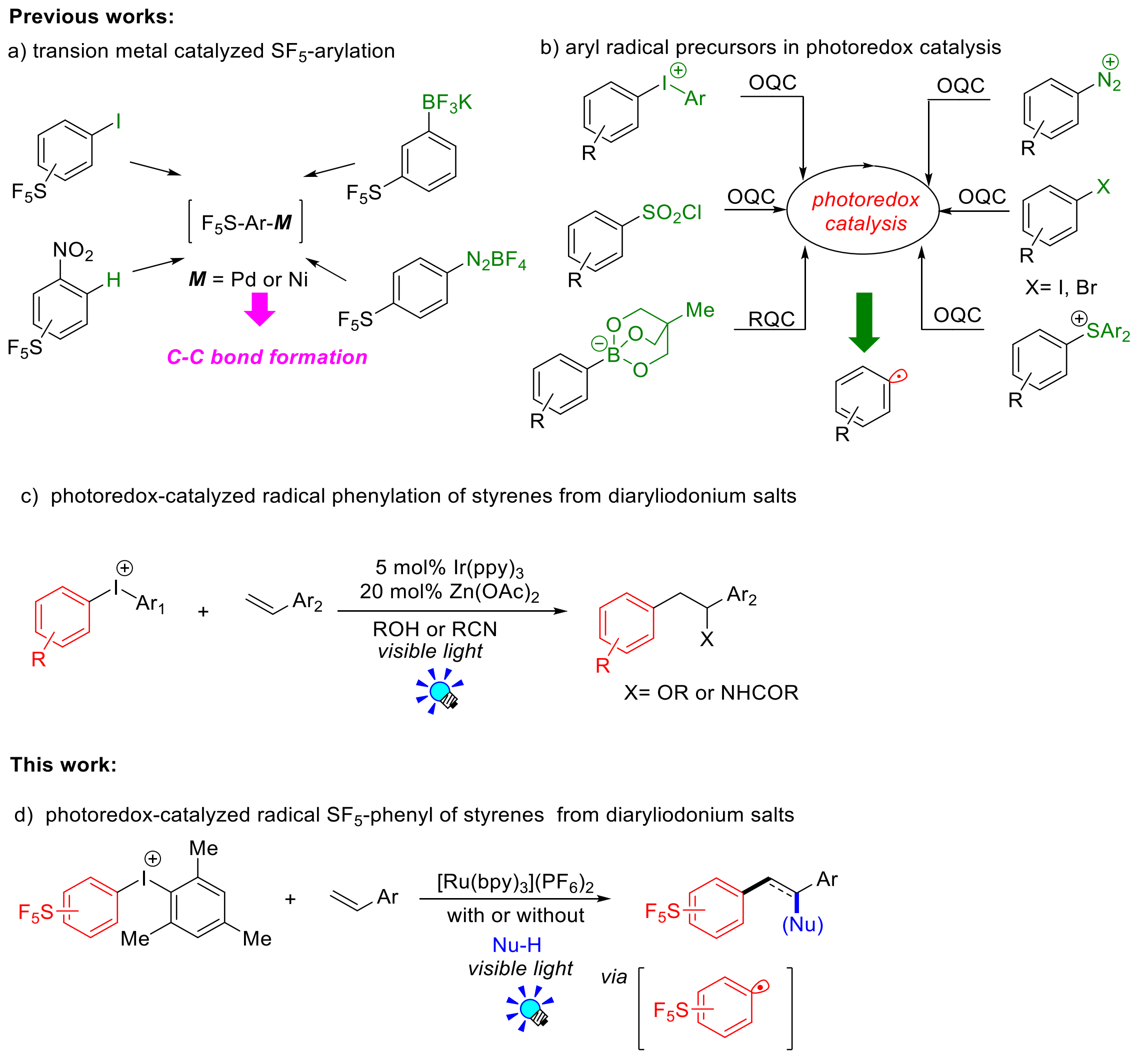
Chapter 4

Radical Pentafluorosulfanylphenylation of Styrenes by Photoredox Catalysis

ABSTRACT: The author has developed a simple and versatile pentafluorosulfanylphenylation (SF_5-phenylation) of styrenes by photoredox catalysis. Pentafluorosulfanyl-phenyliodnium salts (SF_5-phenyliodonium salts), which can be easily synthesized from the corresponding iodides, and generate SF_5-phenyl radicals by photocatalysis of a Ru catalyst, $[Ru(bpy)_3]^{2+}$. A variety of SF_5-phenyl-containing compounds are obtained by photocatalytic SF_5-phenylation of styrenes combined with solvolysis or deprotonation.



4.1 Introduction



Scheme 4.1 Arylation by transion metal catalysis and photoredox catalysis

As the author described in Chapter 1, pentafluorosulfanylphenyl group has a great potential in medicinal chemistry and material science. Therefore, many works have been devoted for pentafluorosulfanylarylation (SF_5-arylation) of organic molecules in the last few years [1]. A few catalytic strategies for C–C bond formation were reported by the groups of Philp,[1a] Zhang, [1d] Carreira, [1e] Weix, [1f] and Laali [1g] (Scheme 4.1, a). Novel catalytic strategy for simple and versatile SF_5-phenylation under mild reaction conditions, however, is still demanded.

In recent years, a great number of photoredox-catalyzed radical arylation reactions from various aryl radical precursors such as aryldiazonium salts [2], aryliodonium salts

[3], aryl halide [4], arylsulfonyl chlorides [5], arylsulfonium salts [6], and arylborates [7] have been reported (Scheme 4.1, b). The pentafluorosulfanyl-phenylation by photoredox catalysis however has not reported yet. The author envisaged that photoredox-catalyzed SF_5-phenylation of alkenes could be achieved by choice of an appropriate SF_5-phenyl source.

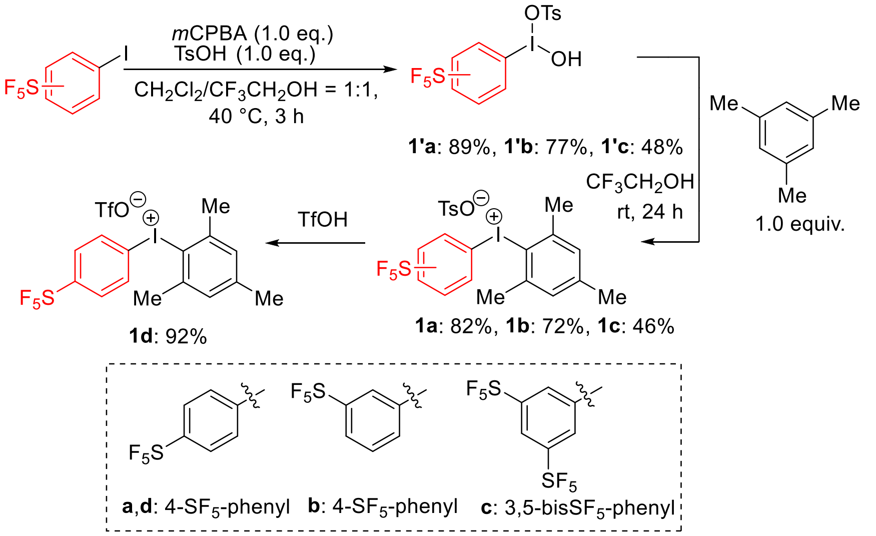
Diaryliodonium salts have gained attention as arylation agents which was easy to be synthesized form iodo-arene, and very stable on air or moisture. In addition, Greaney recently reported the oxyarylation and aminoarylation of styrenes with diaryliodonium salts using OQC of $Ir(ppy)_3$ in the presence of stoichiometric amount of $Zn(OAc)_2$ (Scheme 4.1, c). Symmetrical diaryliodonium salt has been well developed for arylation, but it is not suitable for SF_5-arylation, because expensive SF_5-aryl-I will be sacrificed on reaction. In addition, the previous report [8] has described reduction of unsymmetrical diaryliodonium reagents, leading to cleavage of the Ar–I bond carrying the more electron-withdrawing aryl group. Thus, the author chose the mesityl group as the electron-rich arene counterpart.

The author’s attention has been directed toward the use of SF_5-phenyliodonium salts because they could be easily prepared from commercially available SF_5-phenyl iodides. Herein, the results of the first example of radical pentafluorosulfanylphenylation (SF_5-phenylation) of styrenes by photoredox catalysis are described (Scheme 4.1, d). In addition, this versatile protocol offers us new SF_5-phenyl-containing compounds with a range of functionalities through reaction of SF_5 -phenyl radical.

4.2. Synthesis of SF_5-phenyliodonium salts 1

Recently, Shibata and co-workers reported on convenient one-pot synthesis of SF_5-aryliodonium triflate for reactions with nucleophiles [1h]. In this thesis, the author developed the synthesis of SF_5-phenyliodonium tosylates **1** following the method as shown in Scheme 4.2. The SF_5-phenyl ioides were first oxidized by *m*CPBA in the presence of TsOH to give isolable Koser-type reagents (**1′a**: 89%, **1′b**: 77%, **1′c**:

48%). Subsequent electrophilic aromatic substitution of mesitylene by **1′** afford the solid and bench-stable SF_5-phenyliodonium tosylates **1** in good yields (**1a**: 82%, **1b**: 72%, **1c**: 46%: two-step total yields). To improve the solubility of **1a**, the tosylate counteranion was exchanged by triflate anion through treatment with two equivalents of TfOH.



Scheme 4.2 Synthesis of SF_5-phenyliodonium salts 1

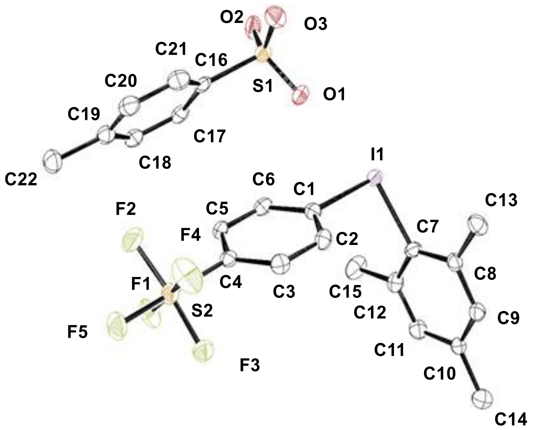


Figure 4.1. An ORTEP drawing of 4-SF_5-phenyliodonium salt 1a. The thermal ellipsoids are set at a 50% probability level

The SF_5-phenyliodonium tosylates **1** were characterized by NMR analyses as well as X-ray crystallography (Figure 4.1). ^{1}H NMR spectra of **1** contain the signals for the aryl groups, and their ^{19}F NMR spectra contain AX_4 pattern signals (J_{FF}= 148.1 Hz) consistent with octahedral Ar-SF_5 structures as typically shown for **1a** (Figure 4.2). The signals for the equatorial and axial fluorine atoms of **1a** are located at δ_F 60.1 and

78.9 ppm, respectively. The structure of the iodonium moiety was characterized by X-ray crystallography, which reveals the dicoordinated structure with the Ar-I-Ar angle being close to the right angle 91.82(10)° in addition to the octahedral geometry of the $ArSF_5$ moiety. Such a bent structure typical for dicoordinated hypervalent iodonium species, and structural features associated with the sulfur and iodine moieties are very similar to those of the related compounds [9].

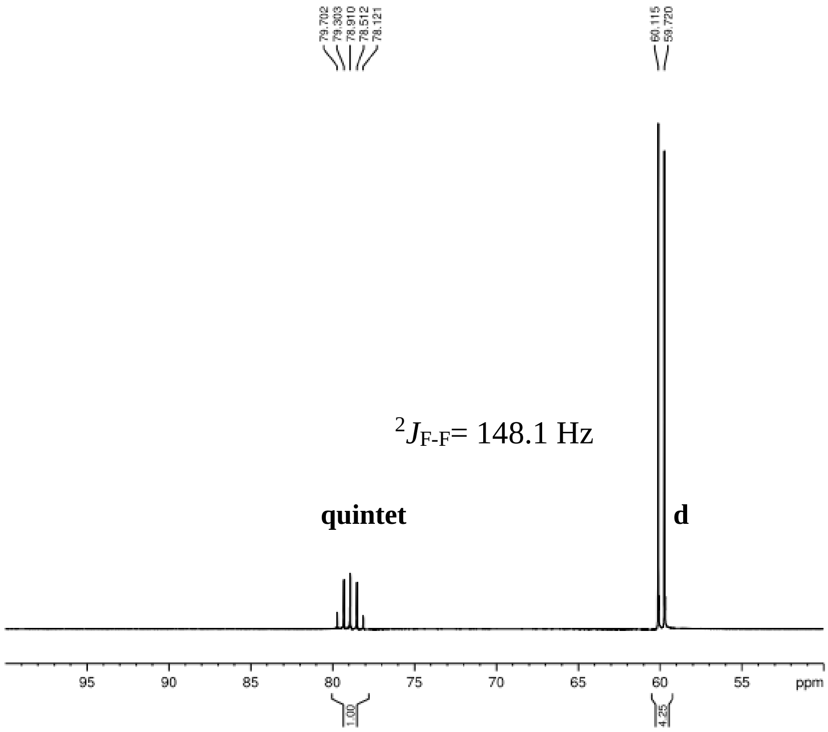
Table 4.1. Bond lengths (Å) for 1a. (part)

S1-O3	1.441(2)	S1-O1	1.456(2)
S1-O2	1.464(2)	S1-C16	1.777(3)
I1-C7	2.113(3)	I1-C1	2.113(3)
F1-S2	1.5806(19)	F2-S2	1.577(2)
F3-S2	1.5779(18)	F4-S2	1.579(2)
F5-S2	1.586(2)		

Table 4.2. Bond angles (°) for 1a. (part)

O3-S1-O1	113.70(13)	O3-S1-O2	113.43(13)
O1-S1-O2	110.67(13)	O3-S1-C16	107.21(13)
O1-S1-C16	106.55(12)	O2-S1-C16	104.55(12)
C7-I1-C1	91.82(10)	F2-S2-F4	90.21(14)
F2-S2-F3	174.89(11)	F4-S2-F3	89.75(13)
F2-S2-F1	89.90(12)	F4-S2-F1	174.99(12)
F3-S2-F1	89.69(11)	F2-S2-F5	87.70(12)
F4-S2-F5	87.55(12)	F3-S2-F5	87.19(11)
F1-S2-F5	87.46(11)	F2-S2-C4	92.60(12)
F4-S2-C4	92.27(13)	F3-S2-C4	92.51(11)
F1-S2-C4	92.73(11)	F5-S2-C4	179.65(14)

^{19}F NMR (CD_3OD, 376 MHz, rt)

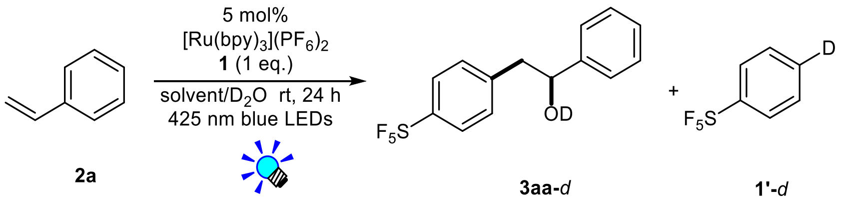


$^2J_{F\text{-}F}$= 148.1 Hz

Figure 4.2. The ^{19} F NMR spectrum of 1a

4.3. Optimization

Table 4.3. Optimization of the oxypentafluorosulfanylphenylation of styrene (2a)[a].



Entry	**SF_5-Aryl source (Aryl source:2a)**	Solvent	NMR yields /% **3aa-*d***	**1’-*d***
1	**4-SF_5-C_6H_4I** (1:1.2)	acetone-d_6/D_2O = 9/1	0(n.r.)	0
2[b]	**1a** (1:1.2)	acetone-d_6/D_2O = 9/1	60	35
3	**1a (**1:1.2)	CD_3CN/D_2O = 9/1	17	16
4	**1a** (1:1.2)	CD_3OD/D_2O = 9/1	16	47
5	**1a** (1:1.2)	$CDCl_2$/ D_2O = 9/1	33	14
6[b]	**1a** (1:2)	acetone-d_6/D_2O = 9/1	82	15
7[b]	**1a** (1:4)	acetone-d_6/D_2O = 9/1	92	6
8[c]	**1a** (1:1.2)	acetone-d_6/D_2O = 9/1	0(n.r.)	0
9[d]	**1a** (1:1.2)	acetone-d_6/D_2O = 9/1	0(n.r.)	0

[a] Reaction conditions: A reaction mixture containing **1** (0.017 mmol), **2a** (the designated amount), $[Ru(bpy)_3](PF_6)_2$ (0.9 μ mol), $SiEt_4$ (an internal standard), and solvent (0.4 mL) was irradiated by using 3 W blue LED lamps (λ = 425 ± 15 nm) at room temperature under N_2 atmosphere. [b] Reaction time = 1 h. [c] The reaction was conducted in the dark. [d] No catalyst.

The author firstly investigated hydoxy-pentafluorosulfanylphenylation of styrene (**2a**). The visible-light reaction of pentafluoro-4-iodophenyl-λ^6-sulfane (**4-SF_5-C_6H_4I**) with 1.2 equivalent of styrene (**2a**) in a mixed solvent system (acetone-d_6/D_2O) in the presence of $[Ru(bpy)_3](PF_6)_2$ photocatalyst was examined but no reaction took place after irradiation for 24 h (entry 1). Then diaryliodonium salt **1a** was used as the SF_5-aryl source. The reaction was completed within 1 h and **3aa-*d*** was formed in a 60% NMR yield together with **1’-*d*** (35%) (entry2). The deuterated compound **1’-*d*** might be formed through hydrogen atom abstraction of the SF_5-phenyl radical from acetone-d_6. Other mixed solvent systems such as CD_3CN/D_2O, CD_3OD/D_2O, and

CD_2Cl_2/D_2O systems resulted in lower yields (entries 3-5). The use of an excess amount of styrene (**2a**) resulted in an increase of the yield of **3aa**-*d* (entry 6 and 7). Furthermore, the present reaction required both visible-light irradiation and the photocatalyst (entries 8 and 9).

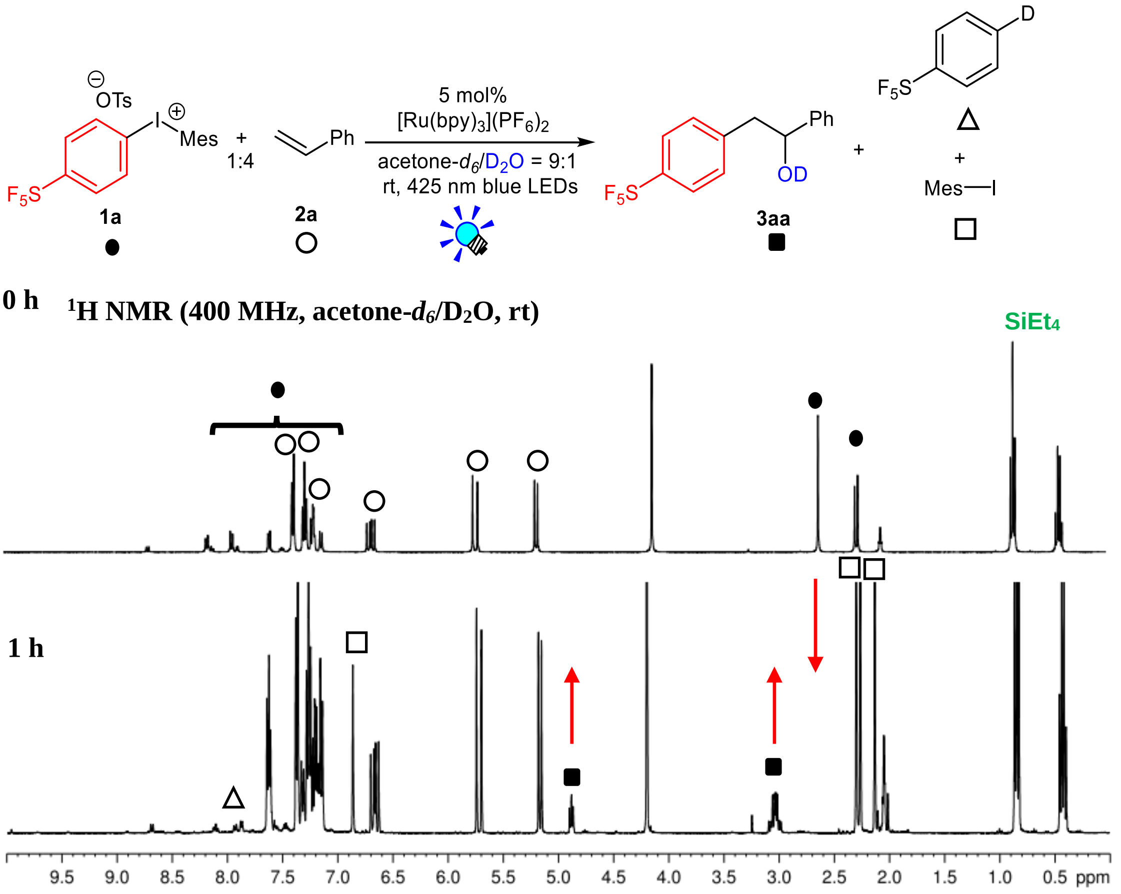
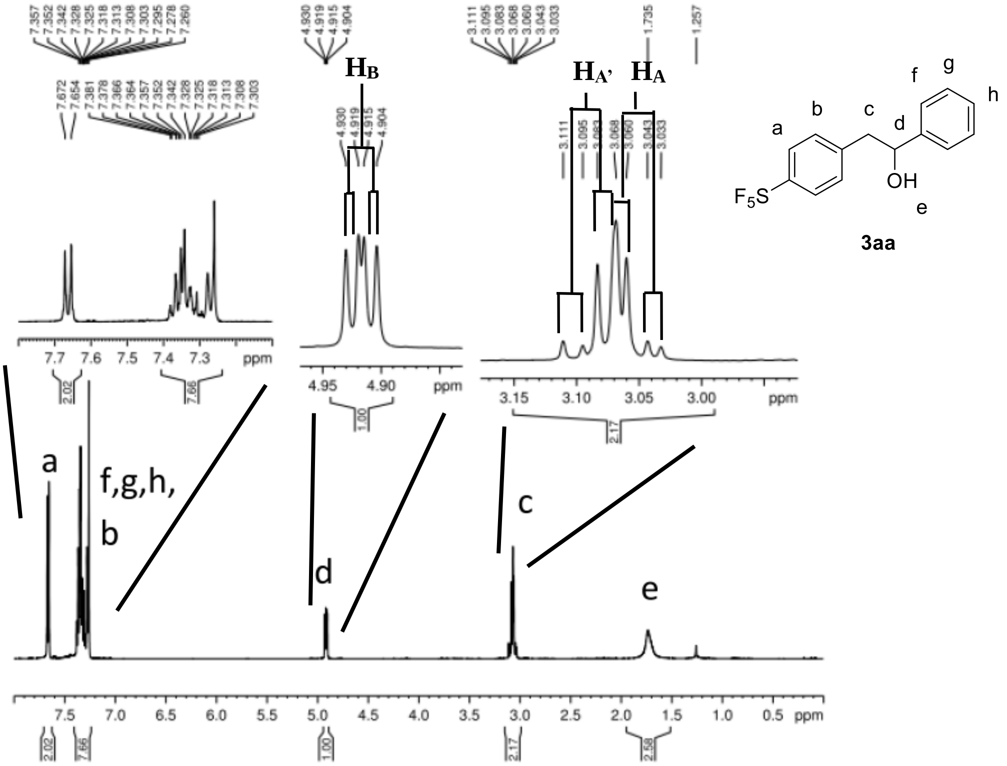


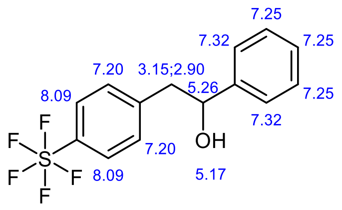
Figure 4.3 ^{1}H NMR spectra for the photocatalytic reaction of 1a with 2a

The reaction (entry 7) was monitored by ^{1}H NMR spectroscopy, and the spetra before and after irradiation for 1 h are compared in Figure 4.3. All signals for the **1a** are replaced by those of the products, indicating quantitative conversion of **1a**.

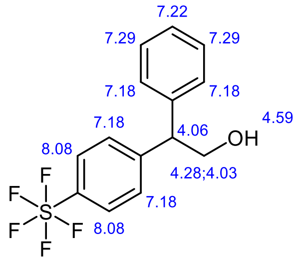
The product and its regiochemistry was characterized by ^{1}H NMR. To take the product **3aa** for instance, from the ^{1}H NMR spectrum (Figure 4.4), the AA'B pattern of the Ph-CH-CH_2 signals (δ (H_A) = 3.05 ppm, δ ($H_{A'}$) = 3.07 ppm, δ (H_B) = 4.92 ppm, $J_{AA'}$ = 15.0 Hz, J_{AB} = 8.0 Hz, $J_{A'B}$ = 10.0 Hz) indicates retention of the skeleton. Judging from the chemical shifts, the coupling pattern, and the intensity of the CH_n signal attached to the OH group, which appears in the highest field, it is concluded that the OH group is bonded to the methine carbon atom. The assignment is in accord with the calculated spectrum (Figure 4.4). Because no other isomer was detected by NMR, the present catalytic transformation turned out to be *regiospecific*.

^{1}H NMR: (500 MHz, CDCl$_3$, rt)





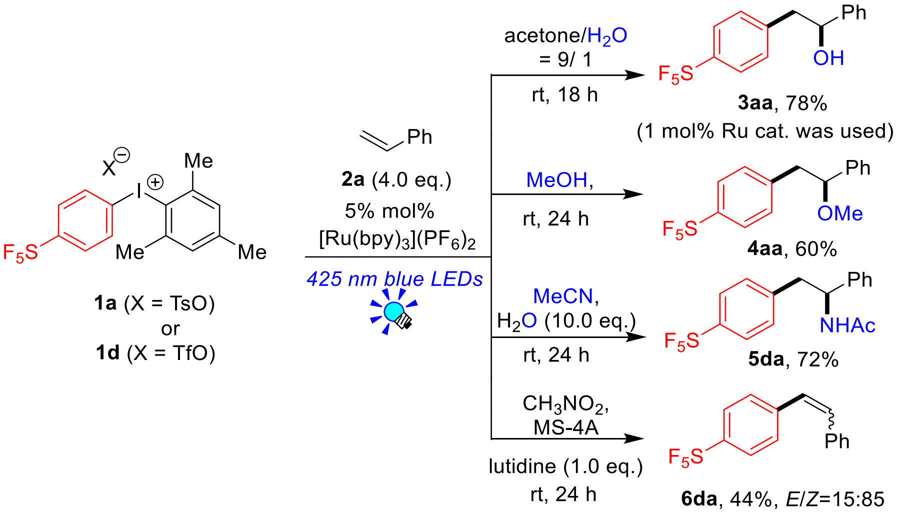
3aa



3aa'

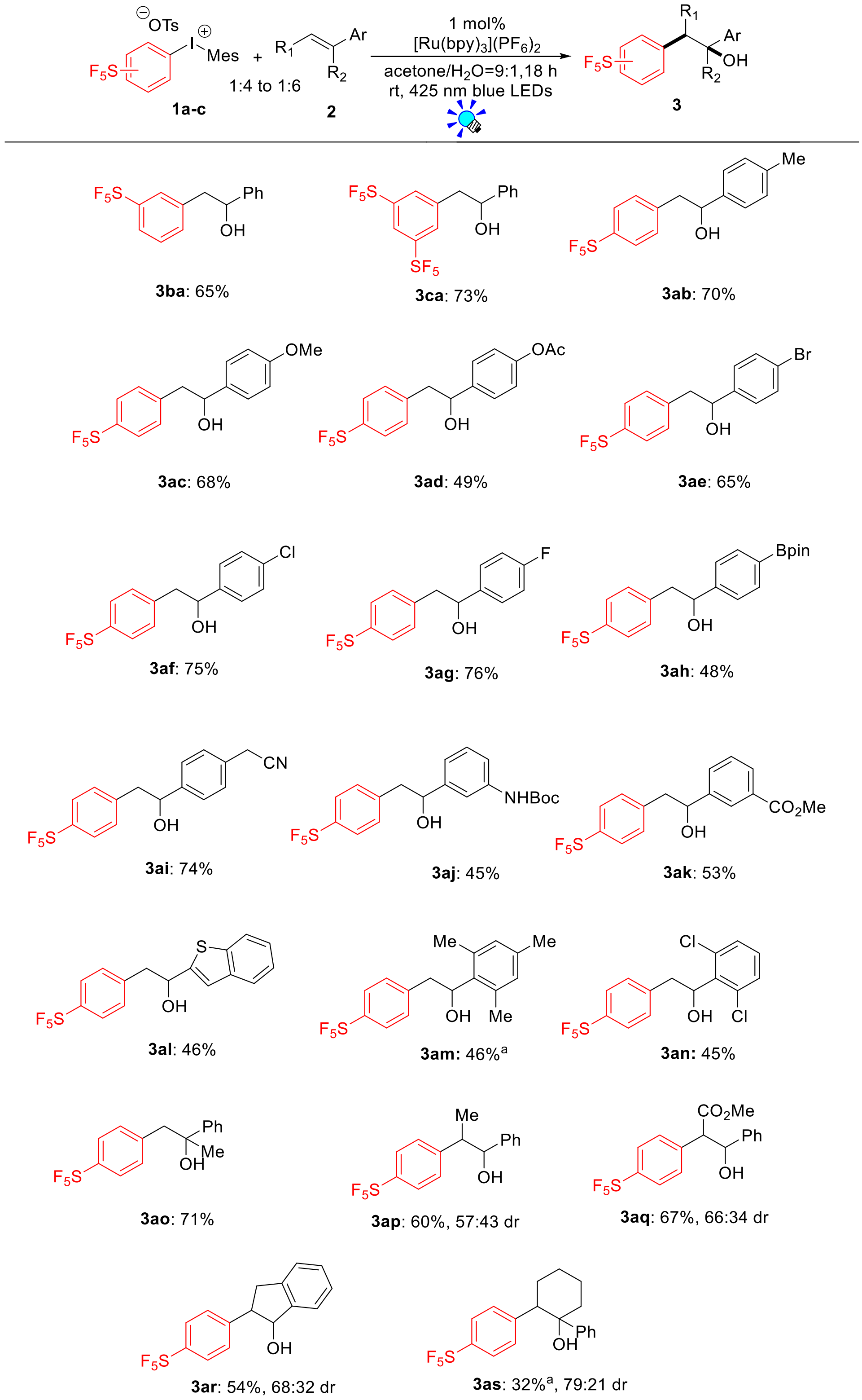
Figure 4.4 ^{1}H NMR spectrum of 3aa and predicted chemical shifts of 3aa and 3aa' (in ppm)

4.4. Scope and limitations



Scheme 4.3. SF_5-phenylation of styrene (2a) by photoredox catalysis. Yields were determined after purification.

The solvent system was found to induce dramatic changes of the products as shown in Scheme 4.3, as observed for solvolytic trifluoromethylative difunctionalization of alkenes (Scheme 1.10) [10]. The reaction in methanol produced methoxy-SF_5-phenylated product **4aa** in a 60% yield instead of **3aa**. In MeCN containing a small amount of H_2O, SF_5-phenylation concomitant with acetylamidation proceeded regioselectively to give amino-SF_5-phenylated product **5da** (72%). Furthermore, when the reaction was carried out in the presence of 2,6-lutidine a base in $MeNO_2$, Heck-type SF_5-phenylation rather than the solvolytic reaction occurred to give 4-SF_5-stilbene **6da** in a moderate yield (45%, *E*/*Z* = 15:85) together with a large amount of SF_5-benzene (**1'**-*d*). These results showed that the present photoredox-catalyzed SF_5 -phenylation is a versatile protocol for the synthesis of SF_5 -phenyl derivatives with various functionalities from styrene only by simply changing the solvent system.



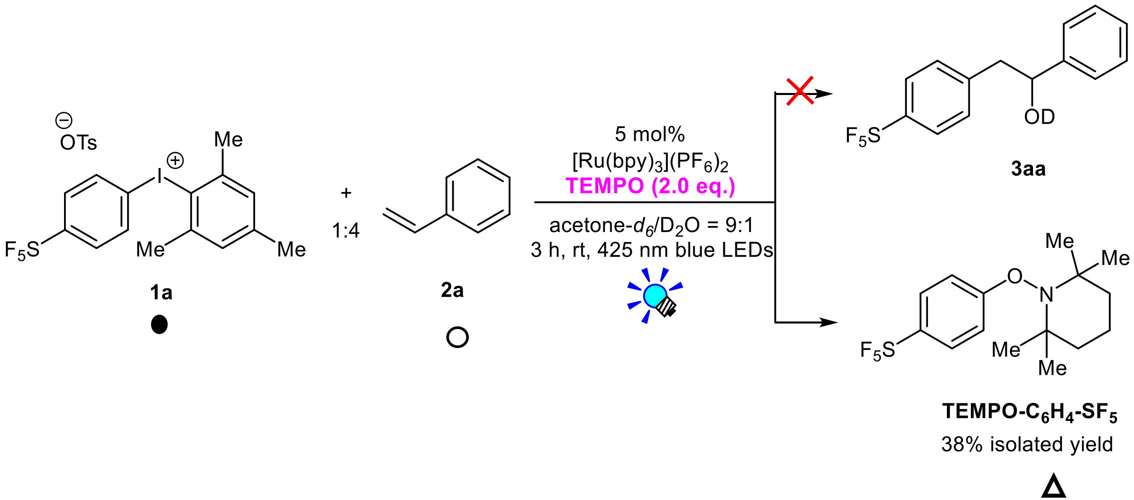
Scheme 4.4. Scope of the photocatalytic hydroxy-SF$_5$-phenylation of styrenes 2. Reaction conditions: A reaction mixture containing [Ru(bpy)$_3$](PF$_6$)$_2$ (1.7 µmol), **1** (0.17 mmol), dry acetone (1.8 mL), water (0.2 mL), and styrenes **2** (0.67 mmol) was irradiated by 425 nm blue LEDs under N$_2$ atmosphere. Yields were obtained after purification. Diastereomeric ratios (dr) were determined by ^{1}H NMR spectra of the crude reaction mixtures. ^{a} 6.0 equiv. of styrene derivative was used.

The scope of the present photocatalytic hydroxy-SF_5-phenylation was investigated (Scheme 4.4). First of all, 3-SF_5-phenylation and 3,5-bis-SF_5-phenylation of styrene **2a** also proceeded in a manner similar to the 4-SF_5-phenylation to give the corresponding products in 65% (**3ba**) and 73% (**3ca**) yields, respectively. Styrene derivatives bearing Me (**2b**), OMe (**2c**), OAc (**2d**), Br (**2e**), Cl (**2f**) and F (**2g**) groups on the benzene ring afforded the corresponding products (**3ab**–**3ag**) in 49–76% yields in a regioselective manner. It should be noted that Bpin (**2h**), cyanomethyl (**2i**), Boc-protected amino (**2j**), and ester (**2k**) and benzothiophene groups (**2l**) were tolerated with the present photocatalytic reaction (**3ah**: 48%, **3ai**: 74%, **3aj**: 45%, **3ak**: 53%, **3al**: 46%). In addition, styrene derivatives with a bulky benzene ring (**2m**, **n**) and α-methylstyrene (**2o**) were also applied to the present SF_5-phenylation (**3am**: 46%, **3an**: 45%, **3ao**: 71%).

Furthermore, β-substituted styrenes such as β-methylstyrene (**2p**), methyl cinnamate (**2q**), indene (**2r**) and 1-phenylcyclohexene (**2s**) afforded the corresponding difuctionalized products as mixtures of diastereomers (**3ap**: 60% 57:43 dr, **3aq**: 67% 66:34 dr, **3ar**: 54% 68:32 dr, **3as**: 32% 79:21 dr). These results suggest that the present photocatalytic hydroxy-SF_5-phenylation is regiospecific with respect to both terminal and internal olefins.

4.5. Plausible Reaction Mechanism

To gain insight into the reaction mechanism, a few control experiments were conducted.



^{1}H NMR (400 MHz, acetone-d_6/D_2O, rt)

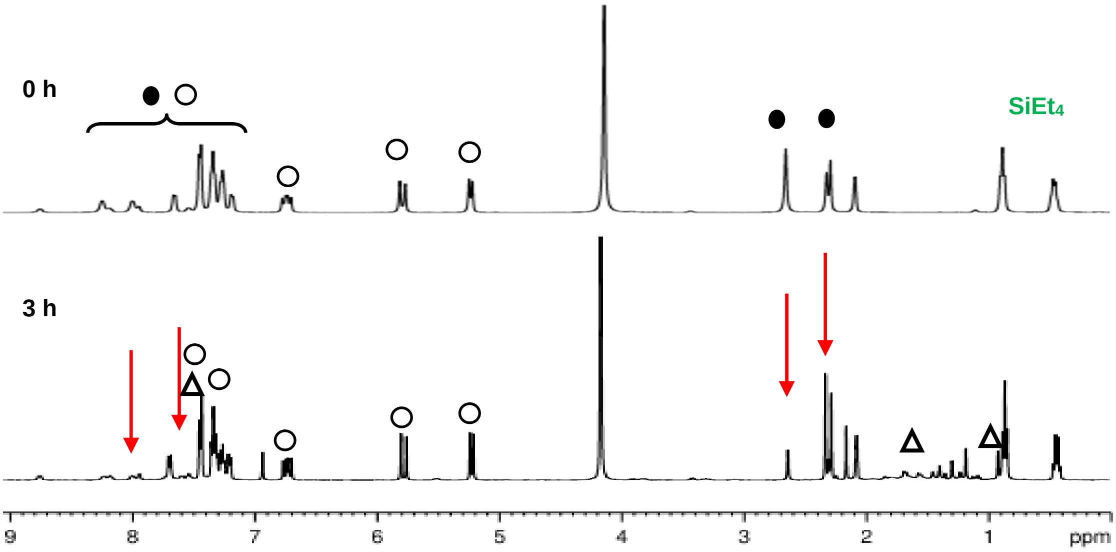


Figure 4.5 ^{1}H NMR spectra for the photocatalytic reaction in the presence of TEMPO

Participation of radical inrermediate was checked by a trapping for the reaction of **2a** by TEMPO under otherwise the optimized conditions. As a result, the hydroxyl-SF_5-phenylated product **3aa** was not formed at all. Instead, the isoable compound was the TEMPO adduct of the SF_5-phenyl radical (TEMPO-C_6H_4-SF_5, 38% isolated yield). This result suggests that the SF_5-phenyl radical is involved in the reaction.

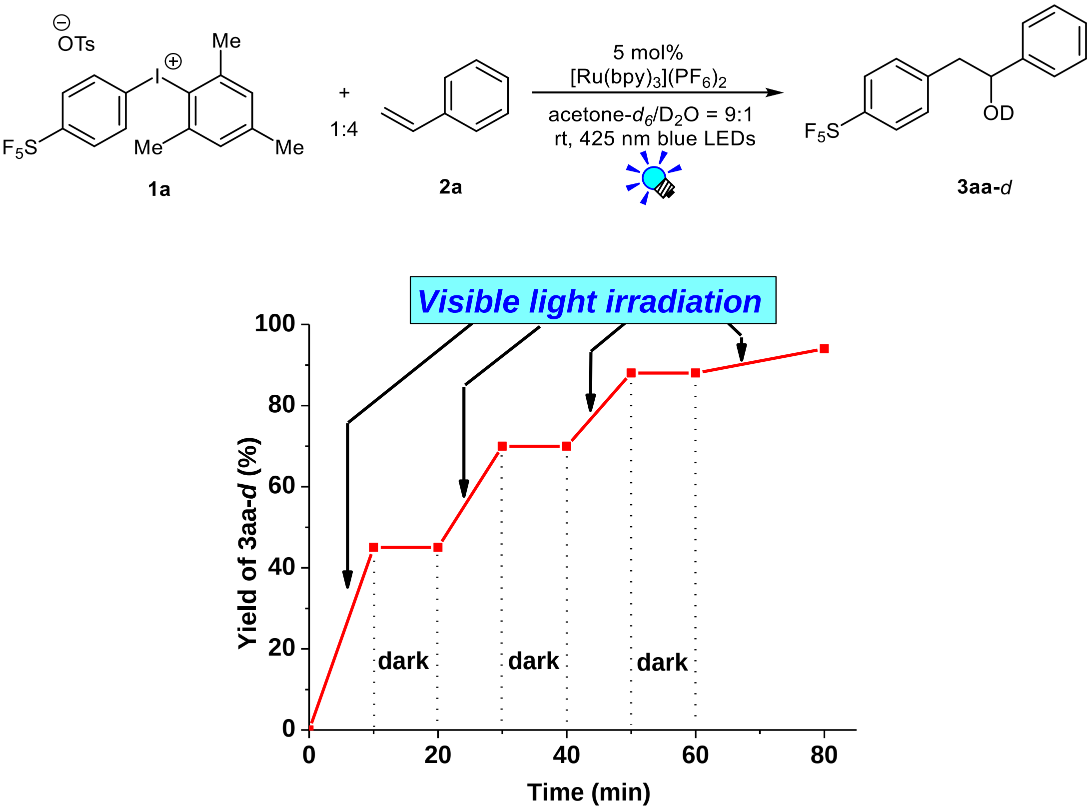
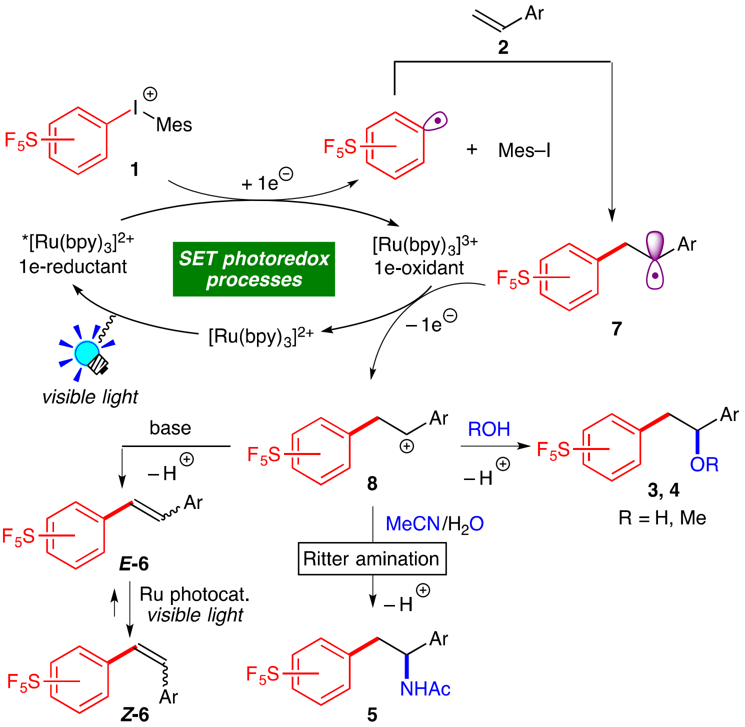


Figure 4.6 Switching on and off experiment of pentafluorosulfanylphenylation

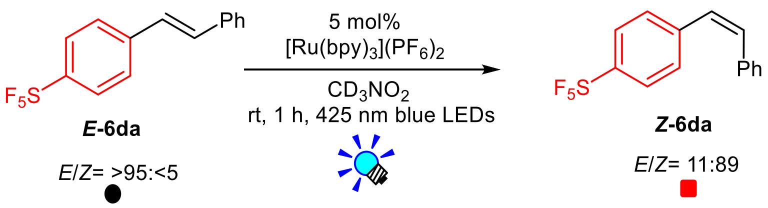
In addition, to check the possibility of a radical chain mechanism, switching experiment was carried out (Figure 4.6). As a result, product **3aa** was fromed only while the light was turned on, suggesting that a radical chain mechanism was not involved as a main reaction pathway.

On basis of the observation and the previous reports, a plausible reaction mechanism *via* SET processes is shown in Scheme 4.5. First, irradiation of visible light excites $[Ru(bpy)_3]^{2+}$ into $*[Ru(bpy)_3]^{2+}$, which serves as a 1e-reductant. SF_5-phenyliodonium reagent **1** is reduced by $*[Ru(bpy)_3]^{2+}$ to be converted into the SF_5-phenyl radical and mesityl iodide (Mes–I) together with formation of the highly oxidized Ru species, $[Ru(bpy)_3]^{3+}$. SF_5-phenyl radical reacts with styrenes **2** in a regioselective manner, leading to the radical intermediate **7**, which is followed by 1e-oxidation by $[Ru(bpy)_3]^{3+}$ to give the carbocationic intermediate **8**. Nucleophilic solvent such as H_2O, MeOH and MeCN captures the intermediate **8** to afford hydroxy-, methoxy- and amino-SF_5-phenylated products (**3**, **4** and **5**), respectively.

When a base is added in the absence of nucleophile, deprotonation from **8** produces stilbene derivative **6**. In the present photocatalytic reaction, ***Z*-6** was obtained as a major isomer. The author confirmed that an authentic sample of ***E*-6** isomerized into ***Z*-6** under the present photocatalytic conditions (see Figure 4.7). The isomerization should be induced by an energy transfer mechanism from the triplet excited state of the photocatalyst to ***E*-6** [11].



Scheme 4.5. A plausible reaction mechanism



^{1}H NMR (400 MHz, CD$_3$NO$_2$, rt)

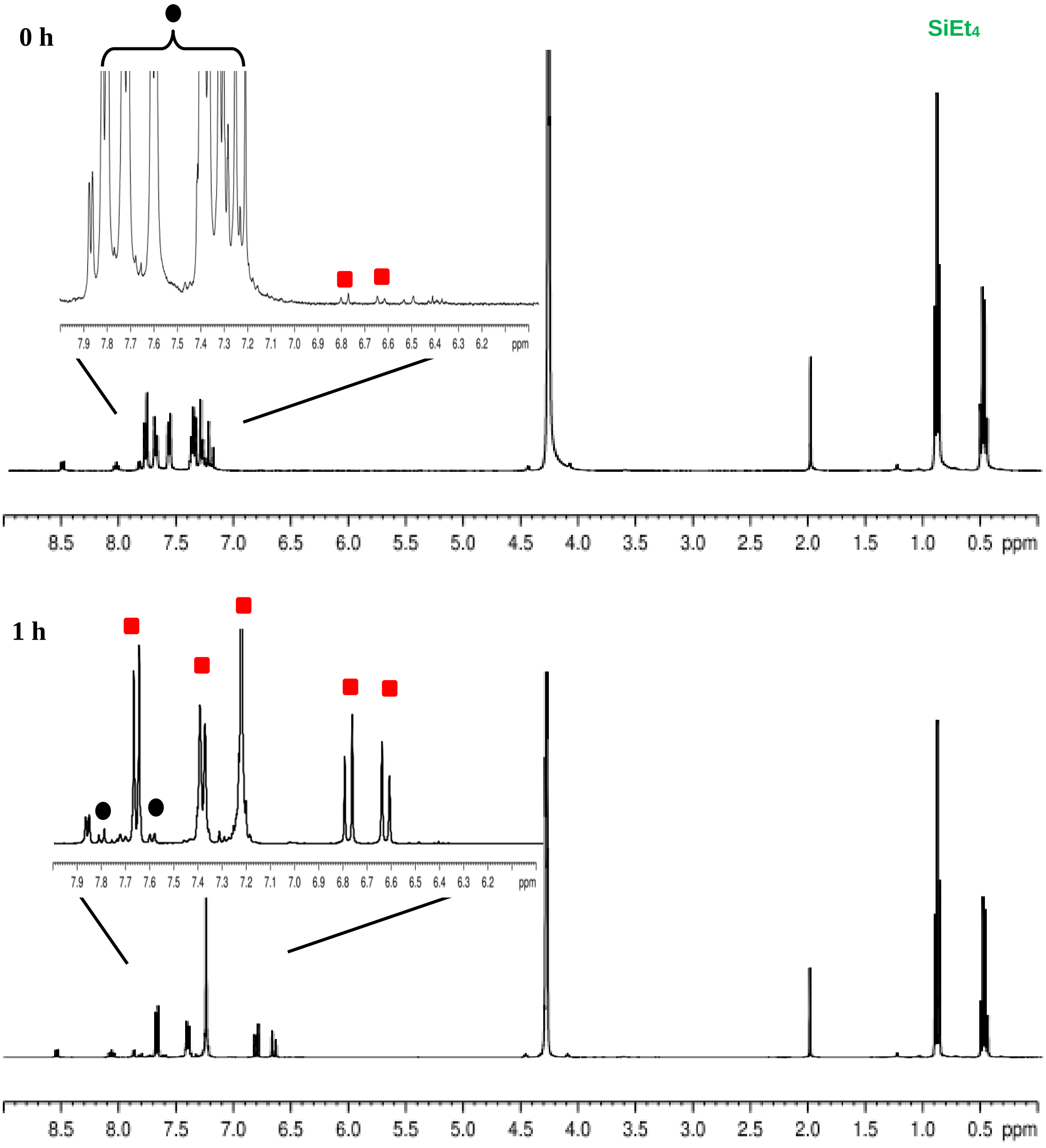


Figure 4.7 ^{1}H NMR spectra for isomerization of *E*-6da

4.6. Conclusion

A simple and versatile photoredox-catalyzed SF_5-phenylation of styrenes has been developed. Bench-stable SF_5-phenyliodonium salts are key compounds for the present photocatalytic generation of SF_5-phenyl radical species. In addition, it has been revealed that SF_5-phenyl radicals are capable of efficient and selective addition to the C=C bonds of various styrene derivatives. The present protocol allows us to access a variety of SF_5-phenylated compounds by simple operation under mild reaction conditions.

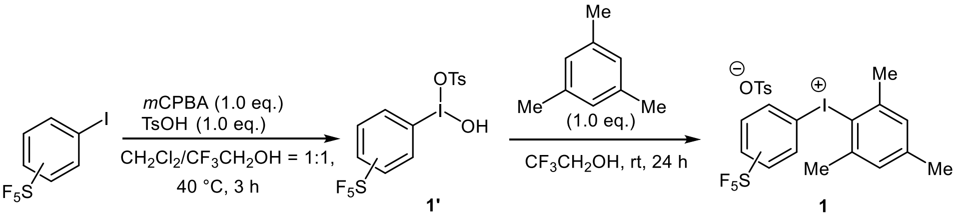
4.7. Experimental

Materials and methods

Styrenes **2a**, **2e**, **2f**, **2g**, **2m**, **2o**, **2p**, **2q**, and **2r** were purchased from TCI. Styrenes **2b**, **2c**, **2d**, **2n**, and **2s** were purchased from Aldrich. They were used without further purification. Pentafluoro(4-iodophenyl)-λ^6-sulfane and pentafluoro-3-iodophenyl-λ^6-sulfane were purchased from TCI or SynQuest Laboratories. 3,5-Bis(pentafluorothio)bromo- benzene was purchased from UBE Industries, LTD. 5-Iodo-1,3-phenylenebis- (pentafluoro-λ^6-sulfane) was prepared according to the reported literature[12]. Styrenes **2h**[13a], **2i**[13b], **2j**[13c], **2k**[13d], and **2l**[13e] were prepared according to the reported literatures. The crystallographic data was deposited at the Cambridge Crystallographic Data Centre: CCDC 1431812.

Synthesis and characterization of diaryliodonium salts 1 (Scheme 4.2)

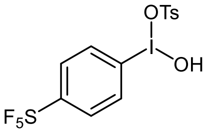
Diaryliodonium salts **1a-1c** were prepared according to the modified literature procedures [14].



1a : 4-SF$_5$; **1b**: 3- SF$_5$; **1c**: 3,5-bis(SF$_5$)

To a stirred solution of **SF$_5$-ArI** (1.0 mmol) in CH_2Cl_2/CF_3CH_2OH (v/v = 1:1, 10.0 mL) was added sequentially 69-75 wt% grade of *m*CPBA (1.0 mmol), and TsOH (1.0 mmol). The resulting solution was stirred at 40 ˚C for 3 h and concentrated under a stream of air, then diethyl ether was added to the remaining residue. The resulting precipitate was filtered off and dried *in vacuo* to afford compound **1’** as a solid. To a stirred solution of mesitylene (1.0 eq.) in CF_3CH_2OH (5.0 mL), **1’** (1.0 eq.) as obtained was added in one portion at room temperature under air, and the mixture was stirred for 24 h. The mixture was concentrated and the resulting crude product was precipitated by addition of diethyl ether. The precipitate was filtered and dried *in vacuo* to give pure product **1** as a white solid.

Hydroxy-4-pentafluoro-λ^6-sulfanylphenyl- λ^3-iodanyl 4-methylbenzenesulfonate (1’a)

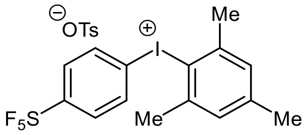


The reaction of pentafluoro-4-iodophenyl- λ^6-sulfane (331.0 mg, 1.0 mmol), CH_2Cl_2/ CF_3CH_2OH (v/v = 1:1, 10.0 mL), *m*CPBA (230.1 mg, 1.0 mmol), and TsOH (190.0 mg, 1.0 mmol) afforded **1’ a** (459.3 mg, 0.89 mmol, 89%).

^{1}H NMR (CD_3OD, 400 MHz, rt): δ 2.37 (s, 3H; *Me*(tosyl)), 7.22 (d, *J* = 8.0 Hz, 2H; *phenyl*(tosyl)), 7.68 (d, *J* = 8.0 Hz, 2H; *phenyl*(tosyl)), 8.16 (d, *J* = 9.2 Hz, 2H; SF$_5$-*phenyl*), 8.51 (d, *J* = 9.2 Hz, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CD_3OD, 376 MHz, rt): δ 59.8 (d, *J* = 147.5 Hz, 4F), 78.6 (quintet, *J* = 150.0 Hz, 1F). **^{13}C NMR** (CD_3OD, 125 MHz, rt): δ 21.2 (*Me*(tosyl)), 126.9 (*phenyl*(tosyl)), 129.8 (*phenyl*(tosyl)), 130.1 (m; SF$_5$-*phenyl*), 137.0 (SF$_5$-*phenyl*), 139.4 (*phenyl*(tosyl)), 142.1 (SF$_5$-*phenyl*),142.6 (*phenyl*(tosyl)), 157.7 (apparent triplet, *J* = 18.5 Hz; SF$_5$-*phenyl*). **Elemental Anal.**: calculated for $C_{13}H_{12}F_5IO_4S_2$: C, 30.13; H, 2.33; Found: C, 30.20;

H, 2.17.

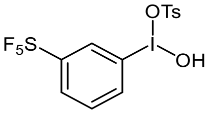
Mesityl-4-pentafluoro-λ^6-sulfanylphenyliodonium 4-methylbenzenesulfonate (1a)



According to the general procedure, **1'a** (459.3 mg, 0.89 mmol), CF_3CH_2OH (5.0 mL), and mesitylene (108.1 mg, 0.89 mmol) produced **1a** (509.1 mg, 0.82 mmol, 82% yield) as a white solid. Recrystallization from $MeOH/CH_2Cl_2$ afforded colorless crystals suitale for single-crystal X-ray measurement.

^{1}H NMR (CD_3OD, 500 MHz, rt): δ 2.37-2.38 (6H; *p-Me*(mesityl) and *Me*(tosyl)), 2.66 (s, 6H; *o-Me*(mesityl)), 7.22 (d, *J* = 7.5 Hz, 2H; *phenyl*(tosyl)), 7.29 (s, 2H; *phenyl*(mesityl)), 7.70 (d, *J* = 7.0 Hz, 2H; *phenyl*(tosyl)), 7.96 (d, *J* = 8.0 Hz, 2H; SF_5-*phenyl*), 8.05 (d, *J* = 8.0 Hz, 2H; SF_5-*phenyl*). **^{19}F NMR** (CD_3OD, 376 MHz, rt): δ 60.1 (d, *J* = 148.1 Hz, 4F), 78.9 (quintet, *J* = 149.5 Hz, 1F). **^{13}C NMR** (CD_3OD, 125 MHz, rt): δ 21.0 (*p-Me*(mesityl)), 21.3 (*Me*(tosyl)), 27.1 (*o-Me*(mesityl)), 117.5 (*phenyl*(mesityl)), 122.5 (*phenyl*(mesityl)), 126.9 (*phenyl*(tosyl)), 129.8 (*phenyl*(tosyl)), 130.5 (m; SF_5-*phenyl*), 131.5 (*phenyl*(mesityl)), 135.8 (SF_5-*phenyl*), 141.6 (*phenyl*(tosyl)), 143.6 (*phenyl*(tosyl)), 143.7 (SF_5-*phenyl*), 146.3 (*phenyl*(mesityl)), 157.1 (apparent triplet; *J* = 22.9 Hz; SF_5-*phenyl*).

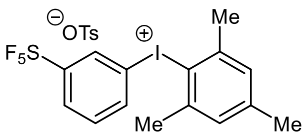
Hydroxy-4-pentafluoro-λ^6-sulfanylphenyl- λ^3-iodanyl 4-methylbenzenesulfonate (1'b)



The reaction of pentafluoro(3-iodophenyl)-λ^6-sulfane (330.1 mg, 1.0 mmol), CH_2Cl_2/CF_3CH_2OH (v/v = 1:1, 10.0 mL), *m*CPBA (231.1 mg, 1.0 mmol), and TsOH (190.1 mg, 1.0 mmol) afforded **1'b** (400.1 mg, 0.77 mmol, 77% yield).

^{1}H NMR (CD_3OD, 400 MHz, rt): δ 2.37 (s, 3H; *Me*(tosyl)), 7.23 (d, *J* = 8.0 Hz, 2H; *phenyl*(tosyl)), 7.69 (d, *J* = 8.0 Hz, 2H; *phenyl*(tosyl)), 7.86-7.90 (m, 1H; SF_5-*phenyl*), 8.23-8.25 (m, 1H; SF_5-*phenyl*), 8.51-8.56 (m, 1H; SF_5-*phenyl*), 8.84- 8.87 (m, 1H; SF_5-*phenyl*). **^{19}F NMR** (CD_3OD, 376 MHz, rt): δ 60.4 (d, *J* = 148.5 Hz, 4F), 78.7 (quintet, *J* = 148.5 Hz, 1F). **^{13}C NMR** (CD_3OD, 125 MHz, rt): δ 21.3 (*Me*(tosyl)), 122.1 (*phenyl*(tosyl)), 126.9 (*phenyl*(tosyl)), 129.9 (*phenyl*(tosyl)), 131.6 (SF_5-*phenyl*), 133.4 (SF_5-*phenyl*), 133.7 (SF_5-*phenyl*), 139.8 (SF_5-*phenyl*), 142.2 (SF_5-*phenyl*), 142.4 (*phenyl*(tosyl)), 155.6 (apparent triplet; *J* = 18.3 Hz; SF_5-*phenyl*). **Elemental Anal.**: calculated for $C_{13}H_{12}F_5IO_4S_2$: C, 30.13; H, 2.33; Found: C, 30.18; H, 2.19.

Mesityl-3-pentafluoro-λ^6-sulfanylphenyliodonium 4-methylbenzenesulfonate (1b)

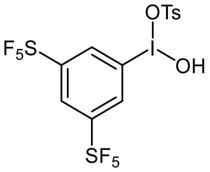


The reaction of **1'b** (400.1 mg, 0.77 mmol), CF_3CH_2OH (4.0 mL), and mesitylene (94.0 mg, 0.77 mmol) produced **1b** (477.1 mg, 0.72 mmol, 72% yield) as a white solid.

^{1}H NMR (CD_3OD, 500 MHz, rt): δ 2.37-2.38 (6H; *p-Me*(mesityl) and *Me*(tosyl)), 2.64 (s, 6H; *o-Me*(mesityl)), 7.20 (d, *J* = 8.0 Hz, 2H; *phenyl*(tosyl)), 7.26 (s, 2H; *phenyl*(mesityl)), 7.65-7.69

(m, 3H; *phenyl*(tosyl) and SF_5-*phenyl*), 7.99 (d, *J* = 8.0 Hz, 1H; SF_5-*phenyl*), 8.12 (d, *J* = 8.0 Hz, 1H; SF_5-*phenyl*), 8.43 (m, 1H; SF_5-*phenyl*). **^{19}F NMR** (CD_3OD, 376 MHz, rt): δ 60.2 (d, *J* = 148.2 Hz, 4F), 78.6 (quintet, *J* = 148.9 Hz, 1F). **^{13}C NMR** (CD_3OD, 125 MHz, rt): δ 21.1 (*p-Me*(mesityl)), 21.3 (*Me*(tosyl)), 27.0 (*o-Me*(mesityl)), 113.8 (*phenyl*(mesityl)), 122.7 (*phenyl*(mesityl)), 126.9 (*phenyl*(tosyl)), 129.8 (*phenyl*(tosyl)), 130.5 (apparent triplet, *J* = 4.1 Hz; SF_5-*phenyl*), 131.5 (*phenyl*(mesityl)), 132.4 (apparent triplet, *J* = 18.8 Hz; SF_5-*phenyl*), 134.0 (SF_5-*phenyl*), 138.2 (SF_5-*phenyl*), 141.7 (*phenyl*(tosyl)), 143.5 (*phenyl*(mesityl)), 143.6 (SF_5-*phenyl*), 146.3 (*phenyl*(tosyl)), 156.0 (apparent triplet, *J* = 18.8 Hz, SF_5-*phenyl*).

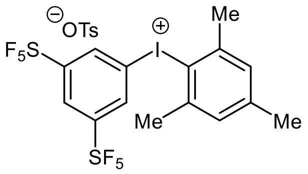
3,5-Bis(pentafluoro-λ^6-sulfanyl)phenylhydroxy-λ^3-iodanyl 4-methylbenzenesulfonate (1'c)



The reaction of (5-iodo-1,3-phenylene)bis(pentafluoro-λ^6-sulfane) (800.0 mg, 1.76 mmol), CH_2Cl_2/CF_3CH_2OH (v/v = 1:1, 20.0 mL), *m*CPBA (404.0 mg, 1.76 mmol), and TsOH (340.0 mg, 1.76 mmol) afforded **1'c** (0.539 g, 0.84 mmol, 48%).

^{1}H NMR (CD_3OD, 500 MHz, rt): δ 2.33 (s, 3H; *Me*(tosyl)), 7.17 (d, *J* = 8.0 Hz, 2H; *phenyl*(tosyl)), 7.55 (d, *J* = 8.0 Hz, 2H; *phenyl*(tosyl)), 8.53 (s, 1H; SF_5-*phenyl*), 9.01 (s, 2H; SF_5-*phenyl*). **^{19}F NMR** (CD_3OD, 376 MHz, rt): δ 62.0 (d, *J* = 149.3 Hz, 4F), 77.7 (quintet, *J* = 150.8 Hz, 1F). **^{13}C NMR** (CD_3OD, 125 MHz, rt): δ 21.2 (*Me*(tosyl)), 122.4 (*phenyl*(tosyl)), 126.8 (*phenyl*(tosyl)), 128.9 (SF_5-*phenyl*), 129.9 (*phenyl*(tosyl)), 136.9 (SF_5-*phenyl*), 141.8 (SF_5-*phenyl*), 142.4 (*phenyl*(tosyl)), 155.2 (apparent triplet, *J* = 20.6 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_6H_3F_{10}S_2I]^+$ requires 455.8555 found 455.8551.

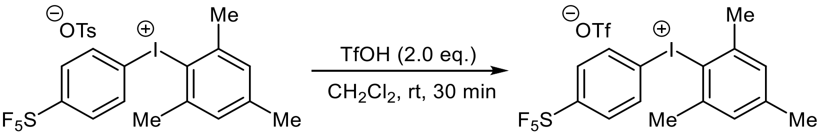
(3,5-Bis(pentafluoro-λ^6-sulfanyl)phenyl)(mesityl)iodonium 4-methylbenzenesulfonate (1c)



The reaction of **1'c** (0.539 g, 0.84 mmol), CF_3CH_2OH (8.0 mL), and mesitylene (104.5 mg, 0.84 mmol) produced **1c** (600.1 mg, 0.80 mmol, 46% yield) as a white solid.

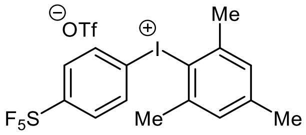
^{1}H NMR ($CDCl_3$, 500 MHz, rt): δ 2.28-2.31 (6H; *p-Me*(mesityl) and *Me*(tosyl)), 2.60 (s, 6H; *o-Me*(mesityl)) 6.93 (d, *J* = 8.0 Hz, 2H; *phenyl*(tosyl)), 7.01(s, 2H; *phenyl*(mesityl)), 7.20 (d, *J* = 8.0 Hz, 2H; *phenyl*(tosyl)), 8.01 (t, *J* = 2.0 Hz, 1H; SF_5-*phenyl*), 8.28 (d, *J* = 3.0 Hz, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 376 MHz, rt): δ 61.9 (d, *J* = 150.7 Hz, 4F), 78.3 (quintet, *J* = 149.6 Hz, 1F). **^{13}C NMR** ($CDCl_3$, 125 MHz, rt): δ 21.2 (*p-Me*(mesityl)), 21.3 (*Me*(tosyl)), 27.0 (*o-Me*(mesityl)), 114.9 (*phenyl*(mesityl)), 124.0 (*phenyl*(mesityl)), 125.7 (*phenyl*(tosyl)), 125.9 (SF_5-*phenyl*), 128.4 (*phenyl*(tosyl)), 130.1 (*phenyl*(mesityl)), 133.9 (m; SF_5-*phenyl*), 139.8 (*phenyl*(tosyl)), 141.8 (SF_5-*phenyl*), 142.3 (*phenyl*(mesityl)), 144.2 (*phenyl*(tosyl)), 154.5 (apparent triplet, *J* = 25.3 Hz; SF_5-*phenyl*). **Elemental Anal.**: calculated for $C_{22}H_{21}F_{10}IO_3S_3$: C, 35.40; H, 2.84; F, 25.45; Found: C, 35.21; H, 2.56; F, 25.41

Procedure for anion exchange from OTs to OTf for synthesis of diaryliodonium salt 1d



To a stirred solution of **1a** (328.6 mg, 0.53 mmol) in CH_2Cl_2 (5.0 mL) was dropwise added TfOH (0.1 mL, 1.06 mmol). The resulting solution was stirred at rt for 30 min. Then the solution was concentrated by aspirator, then water (10.0 mL) was added to the remaining residue. The resulting precipitate was filtered, and the residue was dissolved in CH_2Cl_2 and dried over molecule sieves 4A. After filtration, the solvent was removed under reduced pressure, and the residue was washed with pentane and dried *in vacuo*. The product **1d** was obtained in 92% yield (292.0 mg, 0.49 mmol) as a white solid.

Mesityl-4-pentafluoro-λ⁶-sulfanylphenyliodonium 4-methylbenzenesulfonate (1d)

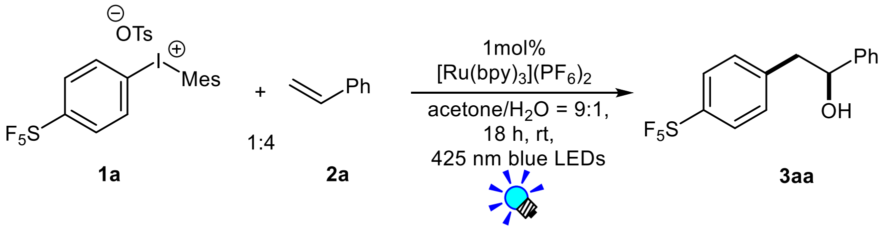


^{1}H NMR (($(CD_3)_2CO$, 400 MHz, rt): δ 2.38 (s, 3H; *p-Me*(mesityl)), 2.72 (s, 6H; *o-Me*(mesityl)), 7.32 (s, 2H; *phenyl*(mesityl)), 8.06 (d, *J* = 7.0 Hz, 2H; SF_5-*phenyl*), 8.27 (d, *J* = 7.0 Hz, 2H; SF_5-*phenyl*). **^{19}F NMR** (($(CD_3)_2$ CO, 282 MHz, rt): δ −77.8 (s, 3F), 63.1 (d, *J* = 148.5 Hz, 4F), 82.7 (quintet, *J* = 148.1 Hz, 1F).The spectral data were identical with those reported in the literature [2].

Typical NMR experimental procedures (Table 4.3)

Under N_2 atmosphere, $[Ru(bpy)_3](PF_6)_2$ (0.7 mg, 0.9 μmol), **1a** (10.5 mg, 0.017 mmol), tetraethylsilane ($SiEt_4$) as an internal standard, acetone-*d*$_6$ (0.36 mL), D_2O (0.04 mL), and styrene (**2a**) (0.067 mmol) were added to an NMR tube. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps).

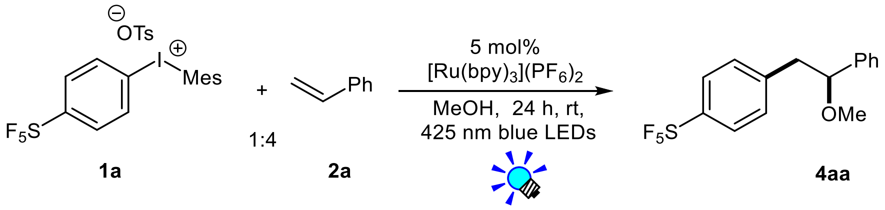
Synthesis and characterization of 2-(4-(Pentafluoro-λ⁶-sulfanyl)phenyl)- 1-phenylethan-1-ol (3aa) (Scheme 4.3)



A 20 mL Schlenk tube was charged with $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 μmol), **1a** (103.4 mg, 0.17 mmol), dry acetone (1.8 mL), water (0.2 mL), and styrene (**2a**) (69.7 mg, 0.67 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps). After the reaction, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*. Purification by the column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) afforded **3aa** (42.2 mg, 78% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 1.73 (s, 1H; O*H*), 3.03-3.11 (m, 2H; CH*H* and C*H*H), 4.92 (dd, *J* = 7.5 Hz, *J* = 5.5 Hz, 1H; C*H*), 7.26-7.38 (m, 7H; *phenyl* and SF_5-*phenyl*), 7.65-7.67 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 376 MHz, rt): δ 62.2 (d, *J* = 145.3 Hz, 4F), 84.0 (quintet, *J* = 151.8 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 45.3 (*C*H_2), 75.2 (*C*H-OH), 125.9 (*phenyl*), 126.0 (m; SF_5-*phenyl*), 128.2 (*phenyl*), 128.8 (*phenyl*), 129.9 (SF_5-*phenyl*), 142.4 (*phenyl*), 143.5 (SF_5-*phenyl*), 157.2 (apparent triplet, *J* = 16.9 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{14}H_{13}F_5OS+Na]^+$ requires 347.0499, found 347.0496. **Elemental Anal.**: calculated for $C_{14}H_{13}F_5OS$: C, 51.85; H, 4.04; Found: C, 51.98; H, 3.96.

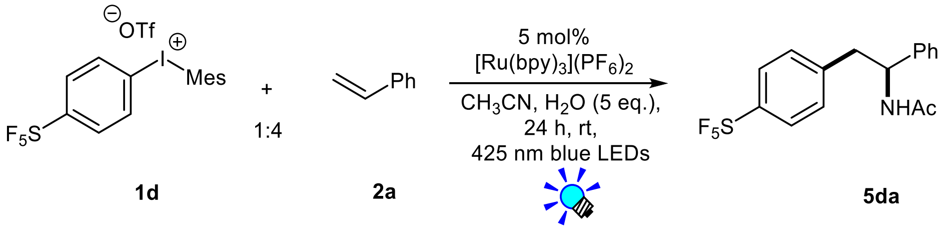
Synthesis and characterization of Pentafluoro-4-(2-methoxy-2- phenylethyl)phenyl-λ^6-sulfane (4aa) (Scheme4.3)



A 20 mL Schlenk tube was charged with $[Ru(bpy)_3](PF_6)_2$ (7.1 mg, 8.4 μmol), **1a** (103.6 mg, 0.17 mmol), dry MeOH (2.0 mL), and styrene (**2a**) (69.8 mg, 0.67 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps). After the reaction, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*. Purification by the column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC afforded **4aa** (33.9 mg, 60% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 2.91-2.96 (m, 1H; C*H*H), 3.09-3.16 (m, 1H; CH*H*), 3.18 (s, 3H; O*Me*), 4.31 (dd, *J* = 7.6 Hz, *J* = 4.8 Hz, 1H; C*H*), 7.19-7.26 (m, 4H; *phenyl* and SF_5-*phenyl*), 7.27-7.37 (m, 3H; *phenyl*), 7.60-7.63 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 470 MHz, rt): δ 62.1 (d, *J* = 149.9 Hz, 4F), 84.2 (quintet, *J* = 150.3 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 44.4 (*C*H_2), 57.0 (O*Me*), 84.4 (*C*H-OMe), 125.7 (m; SF_5-*phenyl*), 126.8 (*phenyl*), 128.1 (*phenyl*), 128.6 (*phenyl*), 129.8 (SF_5-*phenyl*), 141.1 (*phenyl*), 142.8 (SF_5-*phenyl*), 152.3 (apparent triplet, *J* = 16.9 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{15}H_{15}F_5OS+Na]^+$ requires 361.0656, found 361.0652.

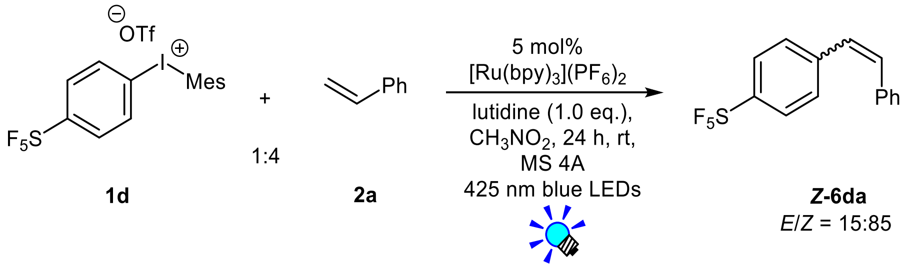
Synthesis and characterization of *N*-2-(4-pentafluoro-λ^6-sulfanylphenyl)-1-phenylethylacetamide (5da) (Scheme 4.3)



A 20 mL Schlenk tube was charged with $[Ru(bpy)_3](PF_6)_2$ (7.2 mg, 8.4 μmol), **1d** (100.0 mg, 0.17 mmol), dry CH_3CN (2.0 mL), H_2O (15 mg, 0.84 mmol), and styrene (**2a**) (69.8 mg, 0.67 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps). After the reaction, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*. Purification by the column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC afforded **5da** (43.8 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.97 (s, 3H; *Me*), 3.10-3.16 (m, 1H; C*H*H), 3.23-3.28 (m, 1H; CH*H*), 5.23-5.29 (m, 1H; C*H*), 5.70 (d, *J* = 7.6 Hz, 1H; N*H*), 7.11-7.19 (m, 2H; *phenyl*), 7.20-7.21 (m, 2H; SF_5-*phenyl*), 7.26-7.34 (m, 3H; *phenyl*), 7.57-7.60 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 376 MHz, rt): δ 61.8 (d, *J* = 150.0 Hz, 4F), 83.6 (quintet, *J* = 151.5 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 23.5 (*C*H_3), 41.9 (*C*H_2), 54.6 (*C*H-NH), 125.9 (m; SF_5-*phenyl*), 126.8 (*phenyl*), 128.0 (*phenyl*), 128.9 (*phenyl*), 129.6 (SF_5-*phenyl*), 140.6 (*phenyl*), 141.7 (SF_5-*phenyl*), 152.5 (apparent triplet, *J* = 17.1 Hz; SF_5-*phenyl*), 169.5 (*C*=O). **HRMS (ESI-TOF):** calculated for $[C_{16}H_{16}F_5NOS+Na]^+$ requires 388.0765, found 388.0763.

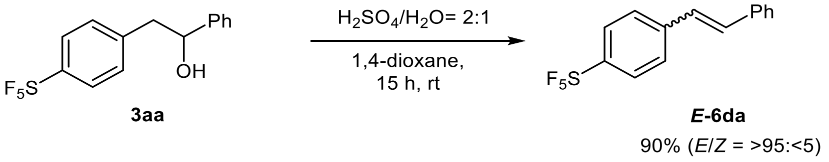
Synthesis and characterization of (*Z*)-Pentafluoro-4-styrylphenyl-λ^6-sulfane (*Z*-6da)



A 20 mL Schlenk tube was charged with molecule sieve 4A (300.1 mg), $[Ru(bpy)_3](PF_6)_2$ (14.1 mg, 16.5 μmol), **1d** (199.7 mg, 0.33 mmol), dry CH_3NO_2 (4.0 mL), 2,6-lutidine (36.0 mg, 0.33 mmol), and styrene (**2a**) (140.1 mg, 1.336 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps). After the reaction, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*. The residue contained **6da** as a mixture of *E*- and *Z*- isomer (*E*/*Z* = 15:85, determined by ^{19}F NMR spectrum of the crude reaction mixture). Purification by the column chromatography on silica gel (*n*-hexane) and GPC afforded ***Z*-6da** (22.0 mg, 45% yield) as a white solid.

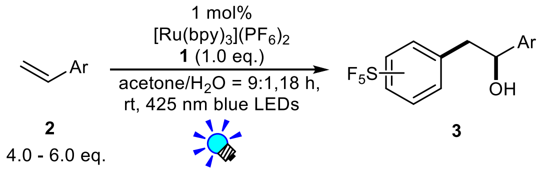
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (d, *J* = 12.4 Hz; 1H; phenyl-C*H*), 6.75 (d, *J* = 12.4 Hz, 1H; C*H*), 7.21-7.31 (m, 7H; SF_5-*phenyl* and *phenyl*), 7.58 (d, *J* = 8.8 Hz, 2H; SF_5-*phenyl*). **^{19}F NMR** (470 MHz, $CDCl_3$): δ 61.6 (d, *J* = 149.2 Hz, 4F), 83.7 (quintet, *J* = 145.9 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 126.0 (m, SF_5-*phenyl*), 127.9 (*phenyl*), 128.1 (phenyl-*C*H), 128.7 (SF_5-phenyl-*C*H), 128.9 (*phenyl*), 129.2 (SF_5-*phenyl*), 133.1 (*phenyl*), 136.5 (*phenyl*), 140.8 (SF_5-*phenyl*), 152.5 (apparent triplet, *J* = 17.1 Hz; SF_5-*phenyl*). **HRMS (EI):** calculated for $[C_{14}H_{11}F_5S]^+$ requires 306.0502, found 306.0502.

Dehydration of 3aa for synthesis of (*E*)-Pentafluoro4-styrylphenyl-λ^6-sulfane (*E*-6da)



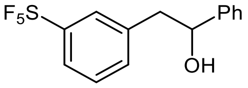
To a solution of the alcohol **3aa** (0.13 mmol, 42.2 mg) in 1,4-dioxane (0.20 mL), and H_2SO_4 aqueous solution (H_2SO_4/H_2O = 2:1) was added dropwise. Then the mixture was stirred at room temperature for 15h. Then the resulting mixture was extracted with CH_2Cl_2 (3 × 10.0 mL), dried over $MgSO_4$, and evaporated. Purification by the column chromatography on silica gel (*n*-hexane) afforded ***E*-6da** (35.8 mg, 90%, *E*/*Z* = >95:<5, determined by ^{19}F NMR spectrum) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.09 (d, *J* = 16.4 Hz, 1H; phenyl-C*H*), 7.19 (d, *J* = 16.4 Hz, 1H; C*H*), 7.31 (t, *J* = 7.4 Hz, 1H; *phenyl*), 7.39 (t, *J* = 7.4 Hz, 2H; *phenyl*), 7.53 (d, *J* = 7.4 Hz, 2H; *phenyl*), 7.56 (d, *J* = 8.5 Hz, 2H; SF_5-*phenyl*), 7.73 (d, *J* = 8.5 Hz, 2H; SF_5-*phenyl*). **^{19}F NMR** (470 MHz, $CDCl_3$): δ 89.9 (quint, *J* = 150.2 Hz, 1 F), 61.0 (d, *J* = 150.2 Hz, 4 F). The spectral data were identical with these reported in the literature [1g].

General procedures for the hydoxy-pentafluorosulfanylphenylation of styrenes 2 (Scheme 4.4)



A 20 mL Schlenk tube was charged with $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 µmol), **1** (0.17 mmol), dry acetone (1.8 mL), water (0.2 mL), and styrene derivative **2** (0.67 mmol) under N_2 atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at room temperature (in a water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamps). After the reaction, H_2O was added. The resulting mixture was extracted with CH_2Cl_2, washed with H_2O, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by the chromatography or GPC.

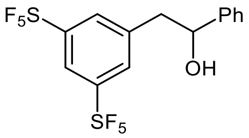
2-(3-Pentafluoro-λ^6-sulfanylphenyl)-1-phenylethanol (3ba)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 µmol), **1b** (103.6 mg, 0.17 mmol), and styrene (**2a**) (69.9 mg, 0.67 mmol) afforded **3ba** (35.4 mg, 65% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 1.95 (d, *J* = 3.0 Hz, 1H; O*H*), 3.04-3.12 (m, 2H; CH_2), 4.90-4.93 (m, 1H; C*H*), 7.29-7.39 (m, 6H; *phenyl* and SF_5-*phenyl*), 7.60 (s, 1H; SF_5-*phenyl*), 7.60-7.62 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 470 MHz, rt): δ 62.7 (d, *J* = 150.3 Hz, 4F), 84.8 (quintet, *J* = 149.5 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 45.6 (*C*H_2), 75.2 (*C*H-OH), 124.2 (m; SF_5-*phenyl*), 125.9 (*phenyl*), 127.2 (m, SF_5-*phenyl*), 128.1 (*phenyl*), 128.6 (*phenyl*), 128.7 (SF_5-*phenyl*), 132.9 (SF_5-*phenyl*), 139.4 (*phenyl*), 143.4 (SF_5-*phenyl*), 154.1 (apparent triplet, *J* = 16.5 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{14}H_{13}F_5OS+Na]^+$ requires 347.0499, found 347.0496. **Elemental Anal.**: calculated for $C_{14}H_{13}F_5OS$: C, 51.85; H, 4.04; Found: C, 51.68; H, 3.89.

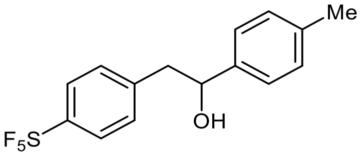
2-(3,5-Bis(pentafluoro-l6-sulfanyl)phenyl)-1-phenylethanol (3ca)



The reaction of [Ru(bpy)$_3$](PF$_6$)$_2$ (1.5 mg, 1.7 µmol), **1c** (124.9 mg, 0.17 mmol), and styrene (**2a**) (69.7 mg, 0.67 mmol) afforded **3ca** (54.8 mg, 73% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}**H NMR** (500 MHz, CDCl$_3$, rt): δ 1.84 (s, 1H; O*H*), 3.10-3.19 (m, 2H; C*H$_2$*), 4.93-4.95 (m, 1H; C*H*), 7.27-7.37 (m, 5H; *phenyl*), 7.67 (s, 2H; SF$_5$-*phenyl*) 7.99 (s, 1H; SF$_5$-*phenyl*). ^{19}**F NMR** (CDCl$_3$, 470 MHz, rt): δ 62.0 (d, *J* = 150.3 Hz, 4F), 81.2 (quintet, *J* = 150.8 Hz, 1F). ^{13}**C NMR** (125 MHz, CDCl$_3$, rt): δ 45.3 (*C*H$_2$), 74.6 (*C*H-OH), 122.3 (m; SF$_5$-*phenyl*), 125.8 (*phenyl*), 128.5 (*phenyl*), 128.9 (*phenyl*), 130.5 (m, SF$_5$-*phenyl*), 140.8 (SF$_5$-*phenyl*), 142.8 (*phenyl*), 153.3 (apparent triplet, *J* = 18.8 Hz; SF$_5$-*phenyl*). **HRMS (ESI-TOF):** calculated for [C$_{14}$H$_{12}$F$_{10}$OS$_2$+Na]$^+$ requires 473.0062, found 473.0062. **Elemental Anal.**: calculated for C$_{14}$H$_{12}$F$_{10}$OS$_2$: C, 37.34; H, 2.69; Found: C, 37.60; H, 2.60.

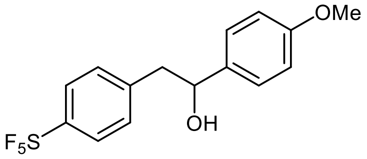
2-(4-Pentafluoro-λ^6-sulfanylphenyl)-1-*p*-tolylethanol (3ab)



The reaction of [Ru(bpy)$_3$](PF$_6$)$_2$ (1.4 mg, 1.7 µmol), **1a** (103.7 mg, 0.17 mmol), and 4-vinyltoluene (**2b**) (78.6 mg, 0.67 mmol) afforded **3ab** (39.5 mg, 70% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}**H NMR** (400 MHz, CDCl$_3$, rt): δ 1.87 (s, 1H; O*H*), 2.38 (s, 3H; *Me*), 3.03-3.13 (m, 2H; CH*H* and C*H*H), 4.91 (dd, *J* = 7.5 Hz, *J* = 5.5 Hz, 1H; C*H*), 7.18-7.30 (m, 6H; *phenyl* and SF$_5$-*phenyl*), 7.67-7.69 (m, 2H; SF$_5$-*phenyl*). ^{19}**F NMR** (CDCl$_3$, 376 MHz, rt): δ 61.8 (d, *J* = 149.6 Hz, 4F), 83.8 (quintet, *J* = 146.7 Hz, 1F). ^{13}**C NMR** (125 MHz, CDCl$_3$, rt): δ 21.3 (*C*H$_3$), 45.2 (*C*H$_2$), 75.0 (*C*H-OH), 125.9 (*phenyl*), 126.0 (m; SF$_5$-*phenyl*), 129.4 (*phenyl*), 129.9 (SF$_5$-*phenyl*), 137.9 (*phenyl*), 140.6 (*phenyl*), 142.6 (SF$_5$-*phenyl*), 152.5 (apparent triplet, *J* = 17.1 Hz; SF$_5$-*phenyl*). **HRMS (ESI-TOF):** calculated for [C$_{15}$H$_{15}$F$_5$OS+Na]$^+$ requires 361.0656, found 361.0655.

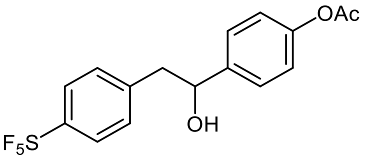
1-(4-Methoxyphenyl)-2-(4-(pentafluoro-λ^6-sulfanyl)phenyl)ethanol (3ac)



The reaction of [Ru(bpy)$_3$](PF$_6$)$_2$ (1.3 mg, 1.7 µmol), **1a** (103.4 mg, 0.17 mmol), and 4-methoxystyrene (**2c**) (90.0 mg, 0.67 mmol) afforded **3ac** (40.2 mg, 68% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}**H NMR** (400 MHz, CDCl$_3$, rt): δ 1.62 (s, 1H; O*H*), 3.03-3.08 (m, 2H; CH*H* and C*H*H), 3.82 (s, 3H; *Me*), 4.87 (dd, *J* = 7.5 Hz, *J* = 5.5 Hz, 1H; C*H*), 6.88-6.90 (m, 2H; *phenyl*), 7.24-7.26 (m, 4H; SF_5-*phenyl* and *phenyl*), 7.64-7.67 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 376 MHz, rt): δ 61.8 (d, *J* = 149.6 Hz, 4F), 83.7 (quintet, *J* = 150.7 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 45.3 (*C*H_3), 55.5 (*C*H_2), 74.8 (*C*H-OH), 114.1 (*phenyl*), 126.0 (m; SF_5-*phenyl*), 127.3 (*phenyl*), 129.9 (SF_5-*phenyl*), 135.6 (*phenyl*), 142.6 (SF_5-*phenyl*), 152.5 (apparent triplet, *J* = 17.1 Hz; SF_5-*phenyl*), 159.5 (*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{15}H_{15}F_5O_2S+Na]^+$ requires 377.0605, found 377.0605.

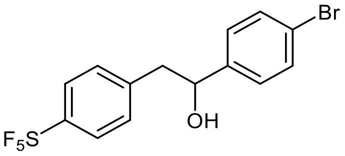
4-(1-Hydroxy-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethyl)phenyl acetate (3ad)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 μmol), **1a** (103.2 mg, 0.17 mmol), and 4-acetoxystyrene (**2d**) (108.7 mg, 0.67 mmol) afforded **3ad** (31.2 mg, 49% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 1.91 (s, 1H; O*H*), 2.31(s, 3H; C*H$_3$*), 3.04-3.06 (m, 2H; CH*H* and C*H*H), 4.91-4.94 (m, 1H; C*H*), 7.08-7.10 (m, 2H; *phenyl*), 7.26-7.29 (m, 2H; SF_5-*phenyl*), 7.35-7.38 (m, 2H; *phenyl*), 7.66-7.68 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 376 MHz, rt): δ 61.8 (d, *J* = 149.6 Hz, 4F), 83.7 (quintet, *J* = 150.8 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 21.3 (*C*H_3), 45.3 (*C*H_2), 74.6 (*C*H-OH), 121.9 (*phenyl*), 126.1 (m; SF_5-*phenyl*), 127.1 (*phenyl*), 129.9 (SF_5-*phenyl*), 141.1 (*phenyl*), 142.3 (SF_5-*phenyl*), 150.4 (*phenyl*), 152.6 (apparent triplet, *J* = 17.1 Hz; SF_5-*phenyl*), 169.6 (*C*=O). **HRMS (ESI-TOF):** calculated for $[C_{16}H_{15}F_5O_3S+Na]^+$ requires 405.0554, found 405.0550.

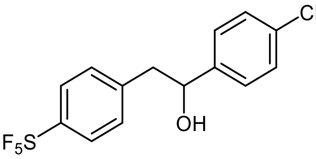
1-(4-Bromophenyl)-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethanol (3ae)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 μmol), **1a** (103.5 mg, 0.17 mmol), and 4-bromostyrene (**2e**) (122.6 mg, 0.67 mmol) afforded **3ae** (43.7 mg, 65% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 1.91 (d, *J* = 3.0 Hz, 1H; O*H*), 3.03-3.04 (m, 2H; CH*H* and C*H*H), 4.88-4.90 (m, 1H; C*H*), 7.20-7.25 (m, 4H; *phenyl* and SF_5-*phenyl*), 7.47-7.49 (m, 2H; *phenyl*), 7.66-7.68 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 470 MHz, rt): δ 62.1 (d, *J* = 149.5 Hz, 4F), 83.8 (quintet, *J* = 150.9 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 45.3 (*C*H_2), 74.5 (*C*H-OH), 121.9 (*phenyl*), 126.1 (m; SF_5-*phenyl*), 127.7 (*phenyl*), 129.9 (SF_5-*phenyl*), 131.8 (*phenyl*), 141.9 (*phenyl*), 142.4 (SF_5-*phenyl*), 152.6 (apparent triplet, *J* = 17.1 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{14}H_{12}BrF_5OS+Na]^+$ requires 424.9605, found 424.9601.

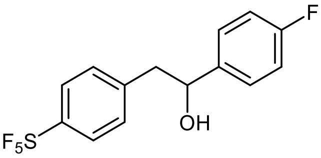
1-(4-Chlorophenyl)-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethanol (3af)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 μmol), **1a** (103.5 mg, 0.17 mmol), and 4-chlorostyrene (**2f**) (93.0 mg, 0.67 mmol) afforded **3af** (45.2 mg, 75% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.91 (s, 1H; O*H*), 3.03-3.05 (m, 2H; CH*H* and C*H*H), 4.89-4.92 (m, 1H; C*H*), 7.24-7.28 (m, 4H; SF_5-*phenyl* and *phenyl*), 7.31-7.35 (m, 2H; *phenyl*), 7.65-7.69 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 470 MHz, rt): δ 63.0 (d, *J* = 149.53 Hz, 4F), 84.8 (quintet, *J* = 150.9 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 45.3 (*C*H_2), 74.4 (*C*H-OH), 126.1 (m; SF_5-*phenyl*) 127.4 (*phenyl*), 128.9 (SF_5-*phenyl*), 129.9 (*phenyl*), 133.8 (*phenyl*), 141.9 (*phenyl*), 141.9 (SF_5-*phenyl*), 152.6 (apparent triplet, *J* = 16.9 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{14}H_{12}ClF_5OS+Na]^+$ requires 381.0110, found 381.0113.

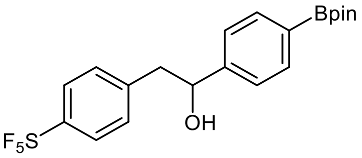
1-(4-Fluorophenyl)-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethanol (3ag)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.5 mg, 1.7 μmol), **1a** (103.6 mg, 0.17 mmol) and 4-fluorostyrene (**2g**) (82.9 mg, 0.67 mmol) afforded **3ag** (43.4 mg, 76% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.90 (s, 1H; O*H*), 3.00-3.10 (m, 2H; CH*H* and C*H*H), 4.89-4.93 (m, 1H; C*H*), 7.02-7.06 (m, 2H; *phenyl*), 7.24-7.32 (m, 4H; *phenyl* and SF_5-*phenyl*), 7.66-7.68 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 470 MHz, rt): δ -115.3 (d, *J* = 4.2 Hz, 1F), 62.1 (d, *J* = 150.2 Hz, 4F), 83.9 (quintet, *J* = 150.9 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 45.4 (*C*H_2), 74.5 (*C*H-OH), 115.6, (d, *J* = 21.3 Hz; *phenyl*)126.1 (m; SF_5-*phenyl*),127.6 (d, *J* = 8.0 Hz; *phenyl*), 129.9 (SF_5-*phenyl*), 139.2 (d, *J* = 4.0 Hz; *phenyl*), 142.1 (SF_5-*phenyl*), 152.6 (apparent triplet, *J* = 17.2 Hz; SF_5-*phenyl*), 162.5 (d, *J* = 244.4 Hz; *phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{14}H_{12}F_6OS+Na]^+$ requires 365.0405, found 365.0406.

2-(4-Pentafluoro-λ^6-sulfanylphenyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanol (3ah)

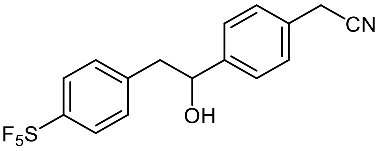


The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 μmol), **1a** (103.6 mg, 0.17 mmol), and 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (**2h**) (153.7 mg, 0.67 mmol) afforded

3ah (36.0 mg, 48% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 1.35 (s, 12H; *Me*), 1.56 (s, 1H; O*H*), 3.05-3.07 (m, 2H; CH*H* and C*H*H), 4.91-4.95 (m, 1H; C*H*), 7.25-7.27 (m, 2H; SF$_5$-*phenyl*), 7.33-7.35 (m, 2H; *phenyl*), 7.65-7.67 (m, 2H; SF$_5$-*phenyl*), 7.79-7.81 (m, 2H; *phenyl*). **^{19}F NMR** (CDCl$_3$, 376 MHz, rt): δ 61.9 (d, *J* = 149.6 Hz, 4F), 83.7 (quintet, *J* = 150.7 Hz, 1F).**^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 25.0 (*C*H$_3$), 45.3 (*C*H$_2$), 74.4 (*C*H-OH), 84.0 (*C*(CH$_3$)$_2$), 125.3 (*phenyl*), 126.0 (m; SF$_5$-*phenyl*), 129.9 (SF$_5$-*phenyl*), 135.2 (*phenyl*), 142.3 (SF$_5$-*phenyl*), 146.6 (*phenyl*), 152.5 (apparent triplet, *J* = 16.6 Hz; SF$_5$-*phenyl*). **HRMS (ESI-TOF):** calculated for [$C_{20}H_{24}BF_5O_3S$+Na]$^+$ requires 473.1355, found 473.1354.

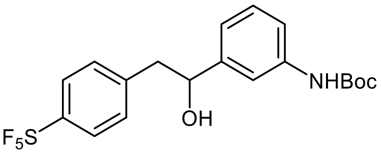
4-(1-Hydroxy-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethylphenyl)acetonitrile (3ai)



The reaction of [Ru(bpy)$_3$](PF$_6$)$_2$ (1.4 mg, 1.7 µmol), **1a** (103.4 mg, 0.17 mmol), and 4-vinyl-phenyl-acetonitrile (**2i**) (95.7 mg, 0.67 mmol) afforded **3ai** (44.8 mg, 74% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 1.91 (s, 1H; O*H*), 3.04-3.06 (m, 2H; CH*H* and C*H*H), 3.76 (s, 2H; CNC*H$_2$*), 4.92-4.95 (m, 1H; C*H*), 7.27-7.31 (m, 2H; SF$_5$-*phenyl*), 7.34-7.37(m, 4H; *phenyl*), 7.67-7.69 (m, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CDCl$_3$, 376 MHz, rt): δ 61.8 (d, *J* = 149.6 Hz, 4F), 83.6 (quintet, *J* = 151.5 Hz, 1F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 23.5 (CN*C*H$_2$), 45.3 (*C*H$_2$), 74.5 (*C*H-OH), 117.9 (*C*N), 126.0 (m; SF$_5$-*phenyl*), 126.8 (*phenyl*), 128.3 (*phenyl*), 129.6 (*phenyl*), 129.9 (SF$_5$-*phenyl*), 142.1 (SF$_5$-*phenyl*), 143.6 (*phenyl*), 152.5 (apparent triplet, *J* = 16.9 Hz; SF$_5$-*phenyl*). **HRMS (ESI-TOF):** calculated for [$C_{16}H_{14}F_5NOS$+Na]$^+$ requires 386.0608, found 386.0604.

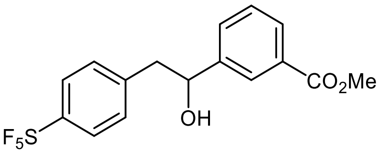
***t*-Butyl 3-(1-hydroxy-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethylphenyl)carbamate (3aj)**



The reaction of [Ru(bpy)$_3$](PF$_6$)$_2$ (1.4 mg, 1.7 µmol), **1a** (103.4 mg, 0.17 mmol), and *tert*-butyl 3-vinylphenylcarbamate (**2j**) (115.8 mg, 0.67 mmol) afforded **3aj** (33.1 mg, 45% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (500 MHz, CDCl$_3$, rt): δ 1.52 (s, 9H; *t-Bu*), 1.92 (s, 1H; O*H*), 3.03-3.05 (m, 2H; CH*H* and C*H*H), 4.86-4.88 (m, 1H; C*H*), 6.52 (s, 1H; N*H*), 6.99-7.00 (m, 1H; *phenyl*), 7.19-7.28 (m, 4H; *phenyl* and SF$_5$-*phenyl*), 7.46 (s, 1H; *phenyl*), 7.65-7.67 (m, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CDCl$_3$, 470 MHz, rt): δ 62.1 (d, *J* = 149.6 Hz, 4F), 84.0 (quintet, *J* = 150.5 Hz, 1F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 28.5 (*Me*), 45.2 (*C*H$_2$), 74.9 (*C*H-OH), 80.9 (*C*(CH$_3$)$_3$), 116.0 (*phenyl*), 118.1 (*phenyl*), 120.6 (*phenyl*), 126.0 (m; SF$_5$-*phenyl*), 129.3 (*phenyl*), 129.9 (SF$_5$-*phenyl*), 138.8 (*phenyl*), 142.4 (SF$_5$-*phenyl*), 144.7 (*phenyl*), 152.6 (apparent triplet, *J* = 16.9 Hz; SF$_5$-*phenyl*), 152.9 (*C*=O). **HRMS (ESI-TOF):** calculated for $[C_{19}H_{22}F_5NO_3S+Na]^+$ requires 462.1133, found 462.1133.

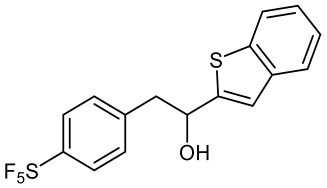
Methyl 3-(1-hydroxy-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethyl)benzoate (3ak)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 µmol), **1a** (103.4 mg, 0.17 mmol), and methyl 3-vinylbenzoate (**2k**) (108.5 mg, 0.67 mmol) afforded **3ak** (34.1 mg, 53% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.85 (s, 1H; O*H*), 3.06-3.08 (m, 2H; CH*H* and C*H*H), 3.93 (s, 3H; *Me*), 4.97-5.00 (m, 1H; C*H*), 7.26-7.29 (m, 2H; SF_5-*phenyl*), 7.42-7.45 (m, 1H; *phenyl*), 7.52-7.54 (m, 1H; *phenyl*), 7.66-7.69 (m, 2H; SF_5-*phenyl*), 7.97-8.01 (m, 2H; *phenyl*). **^{19}F NMR** ($CDCl_3$, 376 MHz, rt): δ 61.8 (d, *J* = 149.6 Hz, 4F), 83.6 (quintet, *J* = 150.4 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 45.3 (*C*H_2), 52.4 (O*Me*), 74.6 (*C*H-OH), 126.0 (m; SF_5-*phenyl*), 127.1 (*phenyl*), 128.8 (*phenyl*), 129.3 (SF_5-*phenyl*), 130.0 (*phenyl*), 130.5 (*phenyl*), 130.6 (*phenyl*), 142.0 (*phenyl*), 143.9 (SF_5-*phenyl*), 152.6 (apparent triplet, *J* = 17.1 Hz; SF_5-*phenyl*), 167.0 (*C*=O). **HRMS (ESI-TOF):** calculated for $[C_{16}H_{15}F_5O_3S+Na]^+$ requires 405.0554, found 405.0554.

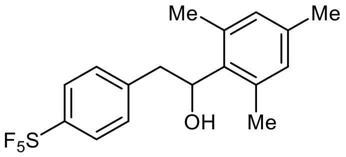
1-(Benzo[b]thiophen-2-yl)-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethanol (3al)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.5 mg, 1.7 µmol), **1a** (103.4 mg, 0.17 mmol), and 2-vinylbenzo[b]thiophene (**2l**) (106.9 mg, 0.67 mmol) afforded **3al** (29.0 mg, 46% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.62 (s, 1H; O*H*), 3.24 (apparent d, *J* = 6.8 Hz, 2H; C*H*H and CH*H*), 5.23-5.26 (m, 1H; C*H*), 7.16 (s, 1H; *benzothiophene*), 7.31-7.37 (m, 4H; SF_5-*phenyl* and *benzothiophene*), 7.66-7.72 (m, 3H; SF_5-*phenyl* and *benzothiophene*), 7.82-7.85 (m, 1H; *benzothiophene*) . **^{19}F NMR** ($CDCl_3$, 376 MHz, rt): δ 61.8 (d, *J* = 149.3 Hz, 4F), 83.6 (quintet, *J* = 151.5 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 45.0 (*C*H_2), 71.6 (*C*H-OH), 126.1 (m; SF_5-*phenyl*), 120.9 (2C; *benzothiophene*), 122.7 (*benzothiophene*), 123.8 (*benzothiophene benzothiophene*), 124.6 (*benzothiophene*), 126.2 (SF_5-*phenyl*), 129.9 (SF_5-*phenyl*), 139.4 (*benzothiophene*), 141.6 (SF_5-*phenyl*), 147.8 (2C; *benzothiophene*), 152.5 (apparent triplet, *J* = 16.9 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{16}H_{13}F_5OS_2+Na]^+$ requires 403.0220, found 403.0221.

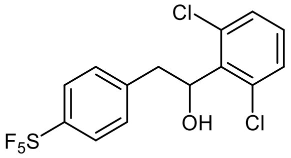
1-Mesityl-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethanol (3am)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (2.8 mg, 3.4 µmol), **1a** (207.2 mg, 0.33 mmol), and 2,4,6-trimethylstyrene (**2m**) (294.2 mg, 2.00 mmol) afforded **3am** (56.2 mg, 46% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.71 (s, 1H; O*H*), 2.27 (s, 3H; C*H*$_3$), 2.39 (s, 6H; C*H*$_3$), 2.98-3.03 (m, 1H; C*H*H), 3.27-3.33 (m, 1H; CH*H*), 5.29-5.32 (m, 1H; C*H*), 6.84 (s, 2H; *phenyl*), 7.26-7.32 (m, 2H; SF_5-*phenyl*), 7.66-7.70 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 376 MHz, rt): δ 61.9 (d, *J* = 149.6 Hz, 4F), 83.8 (quintet, *J* = 150.8 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 20.8 (*Me*), 20.9 (*Me*), 41.8 (*C*H$_2$), 72.4 (*C*H-OH), 126.1 (m; SF_5-*phenyl*), 129.8 (SF_5-*phenyl*), 130.4 (*phenyl*), 135.6 (*phenyl*), 136.1 (*phenyl*), 137.2 (*phenyl*), 143.3 (SF_5-*phenyl*), 152.5 (apparent triplet, *J* = 17.1 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{17}H_{19}F_5OS+Na]^+$ requires 389.0968, found 389.0968.

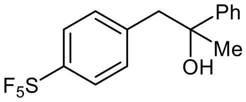
1-(2,6-Dichlorophenyl)-2-(4-pentafluoro-λ^6-sulfanylphenyl)ethanol (3an)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 µmol), **1a** (103.3 mg, 0.17 mmol), and 2,6-dichlorostyrene (**2n**) (115.8 mg, 0.67 mmol) afforded **3an** (29.5 mg, 45% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.55 (s, 1H; O*H*), 3.18-3.23 (m, 1H; C*H*H), 3.40-3.46 (m, 1H; CH*H*), 5.64-5.68 (m, 1H; C*H*), 7.15-7.19 (m, 1H; *phenyl*), 7.30-7.34 (m, 4H; *phenyl* and SF_5-*phenyl*), 7.65-7.69 (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 376 MHz, rt): δ 61.8 (d, *J* = 149.6 Hz, 4F), 83.6 (quintet, *J* = 150.5 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 41.3 (*C*H$_2$), 72.8 (*C*H-OH), 126.1 (m; SF_5-*phenyl*), 129.5 (*phenyl*), 129.6 (SF_5-*phenyl*), 129.8 (*phenyl*), 134.3 (*phenyl*), 136.7 (*phenyl*), 141.9 (SF_5-*phenyl*), 152.6 (apparent triplet, *J* = 17.9 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{14}H_{11}Cl_2F_5OS+Na]^+$ requires 414.9720, found 414.9720.

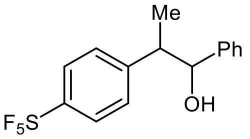
1-(4-Pentafluoro-λ^6-sulfanylphenyl)-2-phenylpropan-2-ol (3ao)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 µmol), **1a** (103.4 mg, 0.17 mmol), and α-methylstyrene (**2o**) (79.1 mg, 0.67 mmol) afforded **3ao** (40.3 mg, 71% yield) as a white solid after purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.59 (s, 3H; *Me*), 1.72 (s, 1H; O*H*), 3.06 (d, *J* = 13.6 Hz, 1H; C*H*H), 3.14 (d, *J* = 13.6 Hz, 1H; CH*H*), 7.06-7.08 (m, 2H; *phenyl*), 7.25-7.28 (m, 1H; *phenyl*), 7.32-7.39 (m, 4H; SF$_5$-*phenyl* and *phenyl*), 7.56-7.59 (m, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CDCl$_3$, 376 MHz, rt): δ 61.8 (d, *J* = 148.9 Hz, 4F), 83.8 (quintet, *J* = 151.9 Hz, 1F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 29.5 (*C*H$_3$), 50.0 (*C*H$_2$), 74.7 (*C*H-OH), 125.0 (*phenyl*), 125.5 (m, SF$_5$-*phenyl*), 127.2 (*phenyl*), 128.4 (*phenyl*), 130.9 (SF$_5$-*phenyl*), 141.3 (SF$_5$-*phenyl*), 147.0 (*phenyl*), 152.6 (apparent triplet, *J* = 13.9 Hz; SF$_5$-*phenyl*). **HRMS (ESI-TOF):** calculated for [C$_{15}$H$_{15}$F$_5$OS+Na]$^+$ requires 361.0656, found 361.0657.

2-(4-Pentafluoro-λ^6-sulfanylphenyl)-1-phenylpropanol (3ap)

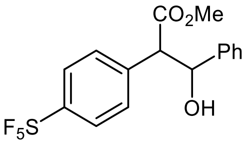


The reaction of [Ru(bpy)$_3$](PF$_6$)$_2$ (2.9 mg, 3.4 µmol), **1a** (207.6 mg, 0.33 mmol), and *trans*-β-methylstryene (**2p**) (158.3 mg, 0.67 mmol) afforded **3ap** as a mixture of isomers (57:43 dr, determined by ^{1}H NMR spectrum of the crude reaction mixture). Purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC gave major isomer (46.3 mg, 41% yield) and minor isomer (21.3 mg, 19% yield) as an each white solid.

Major isomer: ^{1}H NMR (500 MHz, CDCl$_3$, rt): δ 1.33 (d, *J* = 7.0 Hz, 3H; C*H$_3$*), 1.83 (s, 1H; O*H*), 3.14-3.19 (m, 1H; Me-C*H*), 4.80-4.81 (d, *J* = 7.0 Hz, 1H; C*H*), 7.17-7.30 (m, 7H; *phenyl* and SF$_5$-*phenyl*), 7.60-7.62 (m, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CDCl$_3$, 470 MHz, rt): δ 62.1 (d, *J* = 150.4 Hz, 4F), 84.1 (quintet, *J* = 149.9 Hz, 1F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 15.3 (*C*H$_3$), 47.0 (Me-*C*H), 78.5 (*C*H-OH), 125.8 (m, SF$_5$-*phenyl*), 126.4 (*phenyl*), 127.8 (*phenyl*), 128.3 (*phenyl*), 128.6 (SF$_5$-*phenyl*), 142.5 (SF$_5$-*phenyl*), 147.9 (*phenyl*), 152.3 (apparent triplet, *J* = 17.0 Hz; SF$_5$-*phenyl*). **HRMS (ESI-TOF):** calculated for [C$_{15}$H$_{15}$F$_5$OS+Na]$^+$ requires 361.0656, found 361.0658. **Elemental Anal.**: calculated for C$_{15}$H$_{15}$F$_5$OS: C, 57.13; H, 5.06. Found: C, 57.12; H, 5.09.

Minor isomer: ^{1}H NMR (500 MHz, CDCl$_3$, rt): δ 1.10 (d, *J* = 7.0 Hz, 3H; C*H$_3$*), 1.80 (s, 1H; O*H*), 3.09-3.12 (m, 1H; Me-C*H*), 4.71 (d, *J* = 7.0 Hz,1H; C*H*), 7.31-7.38 (m, 7H; *phenyl* and SF$_5$-*phenyl*), 7.70-7.72 (m, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CDCl$_3$, 376 MHz, rt): δ 62.2 (d, *J* = 148.9 Hz, 4F), 84.0 (quintet, *J* = 150.8 Hz, 1F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 18.5 (*C*H$_3$), 47.6 (Me-*C*H), 79.4 (*C*H-OH), 126.1 (m, SF$_5$-*phenyl*), 126.9 (*phenyl*), 128.3 (*phenyl*), 128.5 (*phenyl*), 128.6 (SF$_5$-*phenyl*), 142.4 (SF$_5$-*phenyl*), 147.9 (*phenyl*), 152.5 (apparent triplet, *J* = 16.9 Hz; SF$_5$-*phenyl*). **HRMS (ESI-TOF):** calculated for [C$_{15}$H$_{15}$F$_5$OS+Na]$^+$ requires 361.0656, found 361.0657.

Methyl 3-hydroxy-2-(4-pentafluoro-λ^6-sulfanylphenyl)-3-phenylpropanoate (3aq)

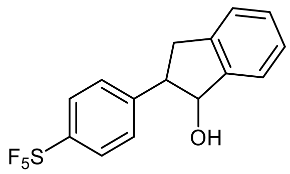


The reaction of [Ru(bpy)$_3$](PF$_6$)$_2$ (2.8 mg, 3.4 µmol), **1a** (206.8 mg, 0.33 mmol), and methyl cinnamate (**2q**) (216.7 mg, 1.34 mmol) afforded **3aq** as a mixture of isomers (66:34 dr, determined by ^{1}H NMR spectrum of the crude reaction mixture). Purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC gave major product (57.4 mg, 45% yield) and minor product (28.0 mg, 22% yield) an each white solid.

Major isomer: ^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 1.62 (s, 1H; O*H*), 3.75 (s, 3H; C*H*$_3$), 3.96 (d, *J* = 9.2 Hz, 1H; MeCOO-C*H*), 5.17 (d, *J* = 8.8 Hz, 1H; HO-C*H*), 7.10-7.12 (m, 2H; *phenyl*), 7.19-7.23 (m, 5H; SF$_5$-*phenyl* and *phenyl*), 7.56-7.58 (m, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CDCl$_3$, 470 MHz, rt): δ 61.8 (d, *J* = 150.0 Hz, 4F), 83.3 (quintet, *J* = 150.4 Hz, 1F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 52.7 (COO*Me*), 59.4 (COOMe-*C*H), 76.6 (*C*H-OH), 126.2 (m, SF$_5$-*phenyl*), 126.6 (*phenyl*), 128.4 (*phenyl*), 128.5 (*phenyl*), 129.1 (SF$_5$-*phenyl*), 139.2 (SF$_5$-*phenyl*), 140.2 (*phenyl*), 153.2 (apparent triplet, *J* = 17.4 Hz, SF$_5$-*phenyl*), 173.1 (*C*=O). **HRMS (ESI-TOF):** calculated for $[C_{16}H_{15}F_5O_3S+Na]^+$ requires 405.0554, found 405.0554.

Minor isomer: ^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 1.55 (s, 1H; O*H*), 3.59 (s, 3H; C*H*$_3$), 3.95 (d, *J* = 6.4 Hz, 1H; MeOOC-C*H*), 5.35 (d, *J* = 6.8 Hz, 1H; HO-C*H*), 7.24-7.40 (m, 7H; SF$_5$-*phenyl* and *phenyl*), 7.67-7.70 (m, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CDCl$_3$, 376 MHz, rt): δ 61.7 (d, *J* = 150.0 Hz, 4F), 83.1 (quintet, *J* = 150.8 Hz, 1F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 52.5 (COO*Me*), 58.9 (COOMe-*C*H), 74.8 (*C*H-OH), 126.1 (m; SF$_5$-*phenyl*), 126.5 (*phenyl*), 128.4 (*phenyl*), 128.6 (*phenyl*), 129.8 (SF$_5$-*phenyl*), 138.8 (SF$_5$-*phenyl*), 140.5 (*phenyl*), 153.4 (apparent triplet, *J* = 16.9 Hz; SF$_5$-*phenyl*), 172.3 (*C*=O). **HRMS (ESI-TOF):** calculated for $[C_{16}H_{15}F_5O_3S+Na]^+$ requires 405.0554, found 405.0553.

2-(4-Pentafluoro-λ^6-sulfanylphenyl)-2,3-dihydro-1H-indenol (3ar)

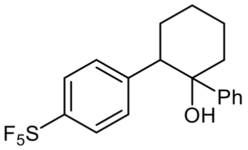


The reaction of [Ru(bpy)$_3$](PF$_6$)$_2$ (2.9 mg, 3.4 μmol), **1a** (207.5 mg, 0.33 mmol) and indene (**2r**) (155.2 mg, 1.33 mmol) afforded **3ar** as a mixture of isomers (68:32 dr, determined by ^{1}H NMR spectrum of the crude reaction mixture). Purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC gave major isomer (34.7 mg, 31% yield) and minor isomer (26.1 mg, 23% yield) an each white solid.

Major isomer: ^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 2.05 (s, 1H; O*H*), 3.02-3.08 (m, 1H; SF$_5$-phenyl-C*H*), 3.39-3.51 (m, 2H; C*H*H and CH*H*), 5.24-5.25 (m, 1H; HO-C*H*), 7.26-7.33 (m, 3H; *phenyl* and SF$_5$-*phenyl*), 7.42-7.46 (m, 3H; *phenyl*), 7.71-7.74 (m, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CDCl$_3$, 376 MHz, rt): δ 61.8 (d, *J* = 150.0 Hz, 4F), 83.6 (quintet, *J* = 148.9 Hz, 1F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 37.4 (*C*H$_2$), 55.9 (SF$_5$-phenyl-*C*H), 82.6 (*C*H-OH), 124.1 (*phenyl*), 124.9 (*phenyl*), 126.4 (m, SF$_5$-*phenyl*), 127.5 (*phenyl*), 127.9 (*phenyl*), 128.8 (SF$_5$-*phenyl*), 140.7 (*phenyl*), 143.7 (SF$_5$-*phenyl*), 146.6 (*phenyl*), 152.6 (apparent triplet, *J* = 17.1 Hz; SF$_5$-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{15}H_{13}F_5OS+Na]^+$ requires 359.0502, found 359.0499.

Minor isomer: ^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 1.40 (s, 1H; O*H*), 3.24-3.29 (m, 1H; C*H*H), 3.35-3.40 (m, 1H; CH*H*), 3.74-3.78 (m, 1H; SF$_5$-phenyl-C*H*), 5.30-5.31 (m, 1H; HO-C*H*), 7.26-7.46 (m, 6H; *phenyl* and SF$_5$-*phenyl*), 7.71-7.73 (m, 2H; SF$_5$-*phenyl*). **^{19}F NMR** (CDCl$_3$, 376 MHz, rt): δ 63.0 (d, *J* = 150.0 Hz, 4F), 84.8 (quintet, *J* = 150.7 Hz, 1F). **^{13}C NMR** (125 MHz, CDCl$_3$, rt): δ 36.1 (*C*H$_2$), 50.8 (SF$_5$-phenyl-*C*H), 77.5 (*C*H-OH), 125.0 (*phenyl*), 125.1 (*phenyl*), 126.2 (m, SF_5-*phenyl*), 127.5 (*phenyl*), 129.2 (*phenyl*), 129.3 (SF_5-*phenyl*), 142.7 (*phenyl*), 143.6 (SF_5-*phenyl*), 143.9 (*phenyl*), 152.8 (apparent triplet, *J* = 18.8 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{15}H_{13}F_5OS+Na]^+$ requires 359.0502, found 359.0498.

2-(4-Pentafluoro-λ⁶-sulfanylphenyl)-1-phenylcyclohexanol (3as)



The reaction of $[Ru(bpy)_3](PF_6)_2$ (2.8 mg, 3.4 µmol), **1a** (207.0 mg, 0.33 mmol) and 1-phenyl-cyclohexene (**2s**) (158.6 mg, 2.00 mmol) afforded **3as** as a mixture of isomers (79:21 dr, determined by ^{1}H NMR spectrum of the crude reaction mixture). Purification with column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and GPC gave a mixture of isomers (39.9mg, 32 % yield, 85:15 dr) as a white solid.

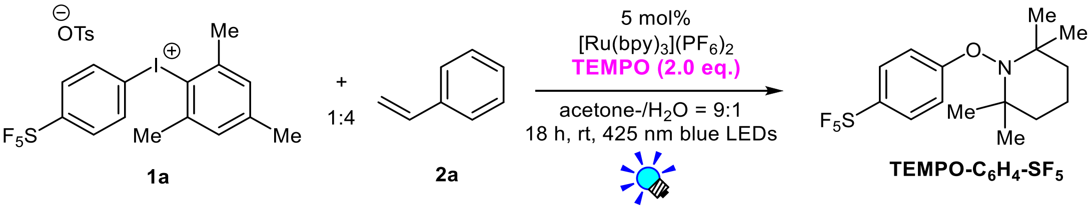
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 1.60-1.69 (m, 1H; $CH_2CH\mathit{H}CH_2CH_2COH$), 1.71 (s, 1H; O*H*), 1.75-1.90 (m, 1H; $CH_2C\mathit{H}HCH_2CH_2COH$), 1.90-2.05 (m, 5H; $C\mathit{H_2}CH_2C\mathit{H_2}CH\mathit{H}COH$), 2.43-2.47 (m, 1H; $C\mathit{H}HCOH$), 3.15-3.17 (m, 1H; C*H*), 7.01-7.03 (m, 2H; SF_5-*phenyl*), 7.13-7.21 (m, 5H; *phenyl*), 7.46-7.48, (m, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 470 MHz, rt): δ 62.1 (d, *J* = 150.0 Hz, 4F), 84.4 (quintet, *J* = 148.9 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 24.1 ($CH_2\mathit{C}H_2CH_2CH_2COH$), 24.6 ($CH_2CH_2\mathit{C}H_2CH_2COH$), 28.7 ($\mathit{C}H_2CH_2CH_2CH_2COH$), 39.2 ($\mathit{C}H_2COH$), 54.0 (*C*H), 75.7 (*C*OH), 124.9 (m; SF_5-*phenyl*), 127.0 (*phenyl*), 127.3 (*phenyl*), 128.1 (SF_5-*phenyl*), 129.9 (*phenyl*), 144.9 (SF_5-*phenyl*), 147.1 (*phenyl*), 152.8 (apparent triplet; *J* = 16.1 Hz; SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{18}H_{19}F_5OS+Na]^+$ requires 401.0969, found 401.0973. **Elemental Anal.**: calculated for $C_{18}H_{19}F_5OS$: C, 57.13; H, 5.06; Found: C, 57.12; H, 5.09

Photocatalytic reaction in the presence of TEMPO (Figure 4.5)

- **NMR experiment**

The reaction was carried out with $[Ru(bpy)_3](PF_6)_2$ (0.7 mg, 0.9 µmol), **1a** (10.5 mg, 0.017 mmol), tetraethylsilane ($SiEt_4$) as an internal standard, acetone-d_6 (0.36 mL), D_2O (0.04 mL), styrene (**2a**) (7.0 mg, 0.068 mmol), and TEMPO (5.1 mg. 0.033 mmol) were added to an NMR tube. As a result, the reaction could not afford the product **3aa**, but complete conversion of **1a** was observed.

- **Preparative experiment**



38%

The reaction was carried out with $[Ru(bpy)_3](PF_6)_2$ (1.4 mg, 1.7 µmol), **1a** (103.5mg, 0.17 mmol), dry acetone (1.8 mL), water (0.2 mL), and styrene **2a** (69.8 mg, 0.67 mmol) under N_2 atmosphere. Purification by the chromatography on silica gel (*n*-hexane) and GPC gave the TEMPO adduct (21.8 mg, 38 % yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 0.99 (s, 6H; 2*C*H₃*), 1.23 (s, 6H; 2*C*H₃*), 1.42-1.45 (m, 1H; $CH_2C\mathit{H}HCH_2$), 1.54-1.69 (m, 5H; $C\mathit{H_2}CH\mathit{H}C\mathit{H_2}$), 7.21 (br, 2H; SF_5-*phenyl*), 7.58-7.60 (d, *J* = 9.5

Hz, 2H; SF_5-*phenyl*). **^{19}F NMR** ($CDCl_3$, 470 MHz, rt): δ 64.5 (d, *J* = 149.5 Hz, 4F), 87.0 (quintet, *J* = 158.5 Hz, 1F). **^{13}C NMR** (125 MHz, $CDCl_3$, rt): δ 17.1 (*C*H_3), 20.6 (*C*H_3), 32.6 (CH_2*C*H_2CH_2), 39.8 (*C*H_2CH_2*C*H_2), 60.8.0 (N*C*), 113.7 (SF_5-*phenyl*), 127.1 (m, SF_5-*phenyl*), 146.2 (apparent triplet; *J* = 17.0 Hz; SF_5-*phenyl*), 165.4 (SF_5-*phenyl*). **HRMS (ESI-TOF):** calculated for $[C_{15}H_{22}F_5NOS+Na]^+$ requires 382.1234, found 382.1235. **Elemental Anal.**: calculated for $C_{15}H_{22}F_5NOS$: C, 50.13; H, 6.17; Found: C, 49.89; H, 6.14

Isomerization of *E*-6da under photocatalytic conditions (Figure 4.7)

Under N_2 atmosphere, $[Ru(bpy)_3](PF_6)_2$ (0.7 mg, 0.85 µmol), ***E*-6da** (*E*/*Z* = >95:<5, 5.1 mg, 0.017 mmol), tetraethylsilane ($SiEt_4$) as an internal standard, and CD_3NO_2 (0.40 mL) were added to an NMR tube. The mixture was degassed by three freeze-pump-thaw cycles. The reaction was monitored by 1H NMR spectroscopy.

Crystallographic data for diaryliodonium salt 1a

Table 4.4 Sample and crystal data for 1a

Identification code	1a	
Chemical formula	$C_{22}H_{22}F_5IO_3S_2$	
Formula weight	620.41	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal size	0.086 x 0.128 x 0.150 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 13.0701(19) Å	α = 90°
	b = 10.5646(15) Å	β = 109.670(2)°
	c = 17.897(3) Å	γ = 90°
Volume	2327.0(6) $Å^3$	
Z	4	
Density (calculated)	1.771 g/cm^3	
Absorption coefficient	1.618 mm^{-1}	
F(000)	1232	

Table 4.5. Data collection and structure refinement for 1a.

Theta range for data collection	1.69 to 25.03°
Index ranges	-15<=h<=13, -12<=k<=12, -14<=l<=21
Reflections collected	10302
Independent reflections	4101 [R(int) = 0.0313]
Coverage of independent reflections	99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.8730 and 0.7930
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)

Function minimized	Σ w(Fo^2 - Fc^2)^2	
Data / restraints / parameters	4101 / 0 / 302	
Goodness-of-fit on F^2	1.545	
Δ/σ_{max}	0.001	
Final R indices	3429 data; I>2σ(I)	R1 = 0.0264, wR2 = 0.0695
	all data	R1 = 0.0335, wR2 = 0.0727
Weighting scheme	w=1/[σ^2(F$_o^2$)]	
	where P=(F$_o^2$+2F$_c^2$)/3	
Largest diff. peak and hole	0.962 and -0.465 eÅ^{-3}	
R.M.S. deviation from mean	0.085 eÅ^{-3}	

Table 4.6. Bond lengths (Å) for 1a.

S1-O3	1.441(2)	S1-O1	1.456(2)
S1-O2	1.464(2)	S1-C16	1.777(3)
I1-C7	2.113(3)	I1-C1	2.113(3)
C1-C6	1.388(4)	C1-C2	1.392(4)
C2-C3	1.379(4)	C4-S2	1.807(3)
C3-C4	1.388(4)	C7-C12	1.395(4)
C4-C5	1.383(4)	C8-C9	1.391(4)
C5-C6	1.377(4)	C9-C10	1.391(4)
C7-C8	1.404(4)	C10-C11	1.392(4)
C8-C13	1.496(4)	C11-C12	1.380(4)
C10-C14	1.508(4)	C12-C15	1.508(4)
C16-C17	1.394(4)	C16-C21	1.382(4)
C17-C18	1.373(4)	C19-C20	1.393(5)
C18-C19	1.398(4)	C20-C21	1.390(5)
C19-C22	1.511(5)	F1-S2	1.5806(19)
F2-S2	1.577(2)	F3-S2	1.5779(18)
F4-S2	1.579(2)	F5-S2	1.586(2)

Table 4.7. Bond angles (°) for 1a.

O3-S1-O1	113.70(13)	O3-S1-O2	113.43(13)
O1-S1-O2	110.67(13)	O3-S1-C16	107.21(13)
O1-S1-C16	106.55(12)	O2-S1-C16	104.55(12)
C7-I1-C1	91.82(10)	C6-C1-C2	121.4(3)
C6-C1-I1	119.6(2)	C2-C1-I1	118.9(2)
C3-C2-C1	119.3(3)	C2-C3-C4	118.9(3)
C5-C4-C3	121.8(3)	C5-C4-S2	119.3(2)
C3-C4-S2	118.9(2)	C4-C5-C6	119.5(3)
C1-C6-C5	119.1(3)	C12-C7-C8	123.7(3)
C12-C7-I1	117.1(2)	C8-C7-I1	119.2(2)
C9-C8-C7	116.2(2)	C9-C8-C13	119.4(3)

C7-C8-C13	124.3(3)	C10-C9-C8	122.5(3)
C9-C10-C11	118.2(3)	C9-C10-C14	121.5(3)
C11-C10-C14	120.3(3)	C12-C11-C10	122.6(3)
C11-C12-C7	116.7(3)	C11-C12-C15	119.8(3)
C7-C12-C15	123.5(3)	C21-C16-C17	119.6(3)
C21-C16-S1	121.3(2)	C17-C16-S1	119.1(2)
C18-C17-C16	120.8(3)	C17-C18-C19	120.7(3)
C20-C19-C18	117.8(3)	C20-C19-C22	121.7(3)
C18-C19-C22	120.6(3)	C19-C20-C21	121.9(3)
C16-C21-C20	119.2(3)	F2-S2-F4	90.21(14)
F2-S2-F3	174.89(11)	F4-S2-F3	89.75(13)
F2-S2-F1	89.90(12)	F4-S2-F1	174.99(12)
F3-S2-F1	89.69(11)	F2-S2-F5	87.70(12)
F4-S2-F5	87.55(12)	F3-S2-F5	87.19(11)
F1-S2-F5	87.46(11)	F2-S2-C4	92.60(12)
F4-S2-C4	92.27(13)	F3-S2-C4	92.51(11)
F1-S2-C4	92.73(11)	F5-S2-C4	179.65(14)

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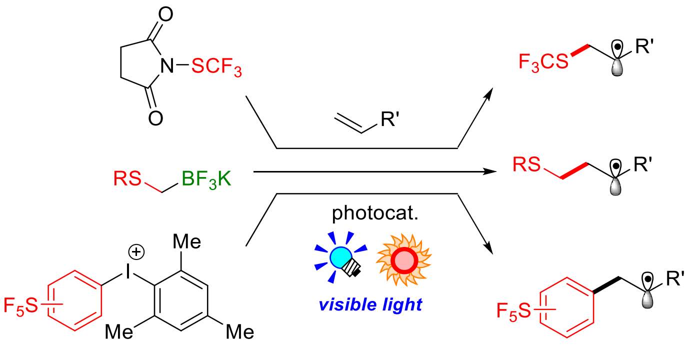
Chapter 5

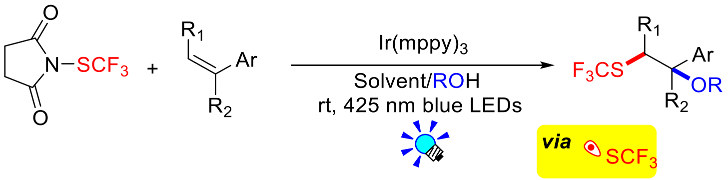
Summary and Outlook

In this thesis, the author has developed three kinds of novel radical reactions for synthesis of organosulfur compounds from alkenes by photoredox-catalysis. The overview is given below.

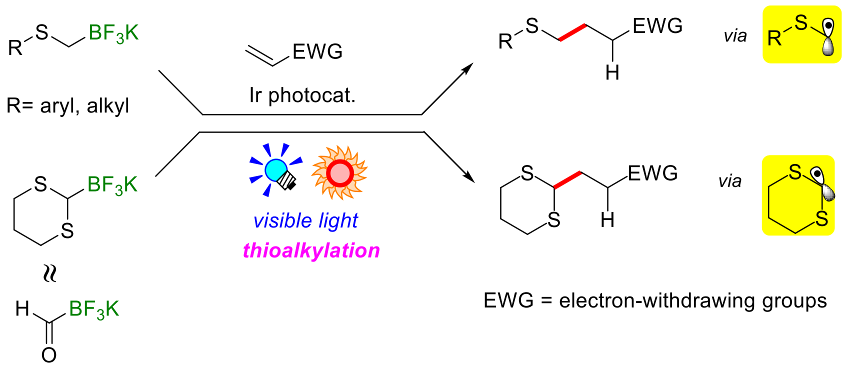


Scheme 5.1 Radical reactions for synthesis of organosulfur compounds from alkenes by photoredox-catalysis

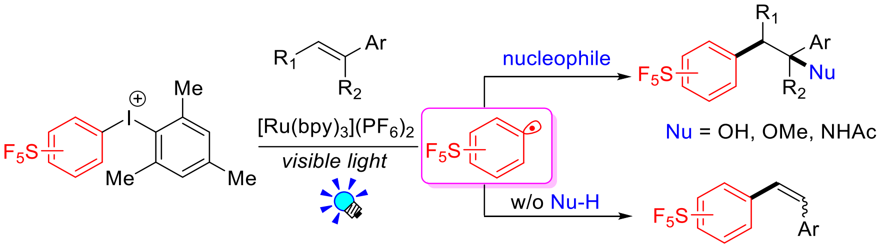
In Chapter 2, the author has developed radical oxy-trifluromethylthiolation of styrenes following the oxidative quenching cycle of the photocatalysis of Ir(mppy)$_3$, the use of which is the key to success. 1-Trifluoromethylthio-pyrrolidine-2,5-dione turns out to be the best SCF$_3$ radical source among the reagents examined. The present reaction affords various β-SCF$_3$-substituted alcohols and ethers from styrene derivatives through solvolytic processes. In addition, not only terminal but also internal olefins also can afford oxy-trifluromethylthiolated products.



In Chapter 3, the author has developed radical alkyl- and aryl-thioalkylation of olefins with Ir photocatalysis. The photocatalytic reaction of aryl- and alkyl-thioalkyltrifluoroborates follows the reductive quenching cycle to generate the coressponding α-thioalkyl radicals via deboronation, the resultant α-thioalkyl radicals can smoothly react with electron-deficient olefins to afford addition products in good yields. In particular, the dithianyl group, an acyl anion equivalent, can also be indroduced to electron- deficient alkenes by means of photoredox catalysis.



In Chapter 4, the author has developed radical SF_5-phenylation of styrenes with the photocatalysis (oxidative quenching cycle) of $[Ru(bpy)_3]^{2+}$. SF_5-phenyliodonium salts, which are easily accessible from SF_5-phenyl iodides, serve as precursors of the SF_5-phenyl radicals. A variety of SF_5-phenyl-containing compounds are obtained by photocatalytic SF_5-phenylation of styrenes combined with solvolysis or deprotonation.



The author has developed a series of new synthetic reactions for organosulfur compounds with photoredox catalysis. In particular, a few useful moieties, such as SCF_3, α-thioalkyl, SF_5-Phenyl can be easily incorporated into target molecule under mild reaction conditions. In addition, these photocatalytic reactions afford a variety of compounds which is a useful and promising structural motif in biologically active molecules and organic functional materials.

In the fields of synthetic reactions for organosulfur compounds with photoredox catalysis, there are still few challenging problems to be solved.

(1) Redox power of photocatalyst is still not enough for reaction. For example, in chapter 2, the reaction rate of oxy-trifluromethylthiolation is still not high, the main reason is probably the reducing power of photocatalyst is still not enough. Thus, the

author hopes to design and synthesize high redox power photocatalyst. As the author introduced in chapter 1, the redox power of photocatalyst is due to the ligand and central metal. On the case of same central metal, the electron-donating group on the ligand can improve the reducing power of photocatalyst, and electron withdrawing group can improve the oxidizing power of photocatalyst (see the Scheme 1.11.). On the basis of this knowledge, the author expect to synthesize a higher reducing power or higher oxidizing power photocatalyst.

(2) Novel stable and active radical reagent is still limited. For example, the gasous and highly toxic SF_5Cl is still used as a SF_5 radical precursor. To solve this problem, based on the knowledge of SCF_3 reagent, the author hopes to design and synthesize R_1R_2N-SF_5 reagent.

The author believes that further study of photoredox-catalyzed reactions developed in this thesis would contribute to efficient construction of useful organic organosulfur compounds.

List of Publications

Chapter 3

Alkyl- and aryl-thioalkylation of olefins with organotrifluoroborates by photoredox catalysis

Y. Li, K. Miyazawa, T. Koike, M. Akita, *Org. Chem, Front.*, **2015**, *2*, 319.

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Chapter 4

Radical Pentafluorosulfanylphenylation of Styrenes by Photoredox Catalysis

Y. Li, T. Koike, M. Akita, *Synlett,* **2016***, 27*, 736.

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