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Visible Light-Induced Selective Generation of Radicals from Organoborates by Photoredox Catalysis

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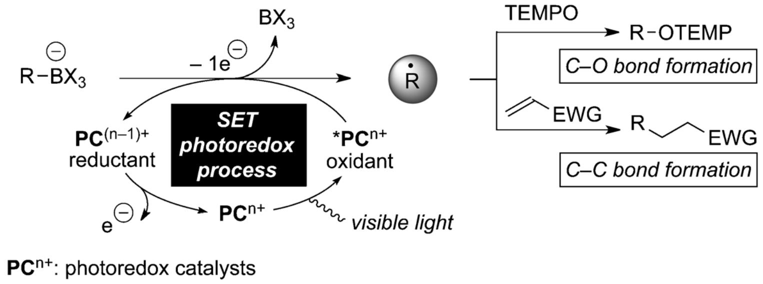
Abstract: A new strategy for the generation of carbon-centered radicals *via* oxidation of alkyl-, allyl-, benzyl- and arylborates by visible-light-driven single electron transfer (SET) photoredox catalysis has been established. The generated radicals smoothly react with TEMPO and electron-deficient alkenes to afford C−O and C−C coupling products, respectively. In this radical initiating system, cyclic organo(triol)borates turn out to be useful radical precursors.

Keywords: borates; green chemistry; photooxidation; photoredox catalysis; radical reactions

Radical chemistry is still rapidly advancing and has provided many kinds of versatile methodologies for organic synthesis, which are associated with the development of efficient radical initiating systems.[1] It is essential for selective and efficient radical reactions to choose a suitable radical initiator and/or reagent. In particular, tin reagents have been utilized as effective synthetic reagents for radical reactions including C−C coupling reaction but their toxicity limits their use in modern organic synthesis. Organoborates have lately attracted attention as alternatives to tin-mediated systems, because (i) they can generate organic radicals upon oxidation,[2] (ii) they are stable towards air and moisture and tolerant with a wide range of functional groups in contrast to the conventional Grignard and lithium reagents, and (iii) they are not so harmful as tin reagents. So far, oxidative generation of carbon-centered radicals from organoborate derivatives has been carried out by electrochemical methods,[2a] PET based on high-energy UV light,[2b,c] and a stoichiometric or excess amount of oxidants.[2e,f] However, there are some drawbacks of the above-mentioned methods, i.e., the requirement of special equipment and formation of large amounts of metallic wastes. As for the last aspect, Baran and co-workers recently reported that radical reactions could be induced by a combination of a catalytic amount of $AgNO_3$ with an excess amount of potassium persulfate as a co-oxidant.[2g,h]

For the past few years, photoredox catalysis with well-defined ruthenium(II) polypyridine derivatives {e.g., $[Ru(bpy)_3]^{2+}$} and the relevant cyclometalated iridium(III) complexes has been regarded as an efficient tool for redox reactions of organic compounds, because they can undergo *photoinitiated single electron transfer (SET)*.[3–7] In addition, this strategy of photoredox catalysis leads us to an efficient use of solar energy (visible light) for organic synthesis, which has received considerable interest for the development of green and sustainable chemistry.[8] We previously reported the photocatalytic transformation of enamines involving radical intermediates generated from the 1*e*-oxidation of enamines.[7a,b] The *visible-light-driven SET photoredox process* prompted us to examine generation of radical species from organoborate derivatives such as trifluoroborates, $M[RBF_3]$, and cyclic triolborates, $M[RB(OCH_2)_3CMe]$,[9] as shown in Scheme 1. A recent study by Jørgensen, Xiao and co-workers demonstrated the aerobic oxidative hydroxylation of arylboronic acids using the superoxide radical anion generated from a photoredox process.[5] In contrast, our concept is the direct oxidation of organoborates by photoredox catalysis.

In this communication, we wish to report the first photocatalytic generation of alkyl, allyl, benzyl, and aryl radicals from the corresponding organoborates. This protocol provides us with a greener and practical synthetic approach from the viewpoint of *environmentally benign catalytic radical reactions under low-energy visible light at room temperature*. The protocol has been applied to catalytic C−O and C−C bond formation, i.e., oxidative coupling of organoborates with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and alkenes bearing electron-withdrawing groups (EWG),

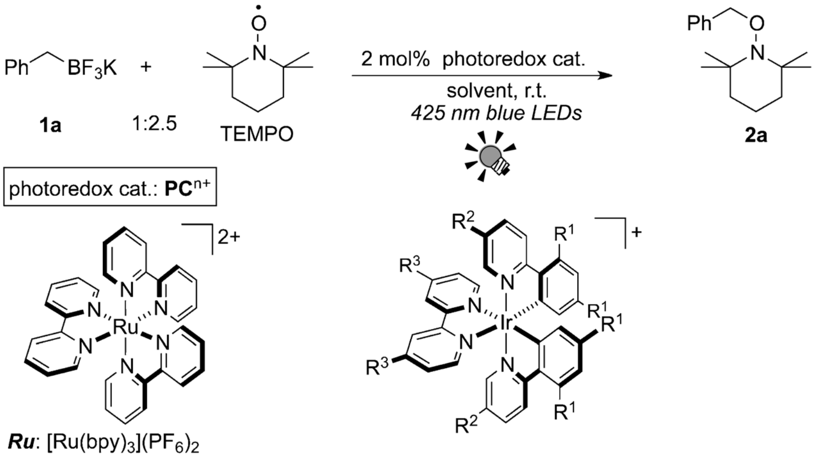


Scheme 1. Concept for radical reactions *via* generation of carbon-centered radicals from organoborates induced by the SET photoredox catalysis.

mediated by photoredox catalysts (**PC**$^{n+}$) under visible light irradiation (blue LEDs and the natural sunlight).

We initially examined the photocatalytic C–O bond formation of potassium benzyltrifluoroborate **1a** with TEMPO as a radical scavenger in the presence of typical photoredox catalysts (**PC**$^{n+}$) under visible light irradiation (blue LEDs: $\lambda = 425 \pm 15$ nm) (Table 1). As a result, the formation of oxyaminated product **2a** was observed by ^{1}H NMR spectroscopy but the choice of the photoredox catalyst turned out to be crucial for the reaction efficiency (entries 1–4). The Ir cyclometalated catalyst [***Ir-dF(CF$_3$)***], which has the highest oxidation potential at the photoexcited state (+0.91 V *vs.* Cp$_2$Fe) among the catalysts used,[10] afforded product **2a** with the highest efficiency in 99% NMR yield (entry 3). Addition of 2.5 equivalents of TEMPO was required to complete the reaction (*cf.* entry 5). The reaction in CH$_3$CN was slower than that in acetone (entry 6). Notably, this photocatalytic C–O

Table 1. Optimization of photocatalytic C–O bond formation of **1a** with TEMPO.[a]

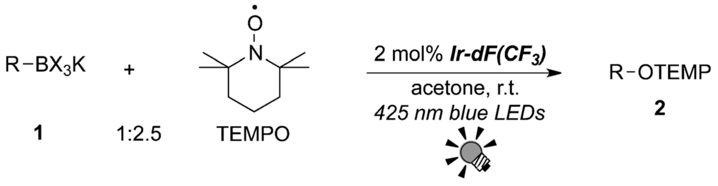


Ru: [Ru(bpy)$_3$](PF$_6$)$_2$
Ir-dtb: [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (R^1, R^2 = H, R^3 = *t*-Bu)
Ir-dF(CF$_3$): [Ir(dF(CF$_3$)ppy)$_2$(bpy)](PF$_6$) (R^1 = F, R^2 = CF$_3$, R^3 = H)
Ir-dF(CF$_3$)-dtb: [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) (R^1 = F, R^2 = CF$_3$, R^3 = *t*-Bu)

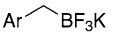
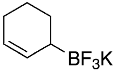
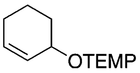
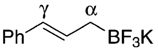
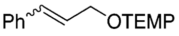
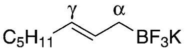
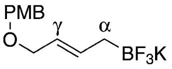
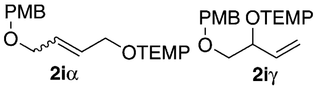
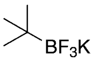
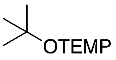
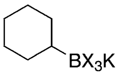
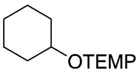
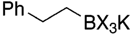
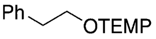
Entry	Photoredox cat.	Deuteration solvent	Reaction time [h]	Yield of **2a** [%][b]
1	***Ru***	acetone	21	12
2	***Ir-dtb***	acetone	21	36
3	***Ir-dF(CF$_3$)***	acetone	8	99
4	***Ir-dF(CF$_3$)-dtb***	acetone	18	99
5[c]	***Ir-dF(CF$_3$)***	acetone	21	53
6	***Ir-dF(CF$_3$)***	CH$_3$CN	21	55
7	none	acetone	21	0
8[d]	***Ir-dF(CF$_3$)***	acetone	21	0

[a] *Reaction conditions:* see Experimental Section.
[b] Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.
[c] One equivalent of TEMPO was used.
[d] Reaction was carried out in the dark.

Table 2. The scope and limitations of the present photocatalytic C–O bond formation.[a]



Ir-dF(CF$_3$): [Ir(dF(CF$_3$)ppy)$_2$(bpy)](PF$_6$)

Entry	Organoborate **1**		Product **2**: Yield [%], time [h]	
				
1	**1a**	Ar = Ph	**2a**: 97%, 12 h	
2	**1b**	Ar = p-C_6H_4Me	**2b**: 84%, 6 h	
3	**1c**	Ar = p-$C_6H_4(OMe)$	**2c**: quant., 2 h	
4	**1d**	Ar = p-C_6H_4Cl	**2d**: 99%, 13 h	
5	**1e**	Ar = p-C_6H_4CN	**2e**: 90%,[b] 48 h	
6	**1f**		**2f**: 81%, 8 h	
7	**1g**		**2gα** (*trans*:*cis* = 5:4), 97%, 8 h	
8	**1h**		**2hα** (*trans*:*cis* = 7:1), **2hγ** 95% (**2hα**:**2hγ** = 1:2), 10 h	
9[c]	**1i** (*trans*: *cis* = 9:1)		**2iα** (*trans*:*cis* = 4:1), **2iγ** 97% (**2iα**:**2iγ** = 1:4), 5 h	
10	**1j**		**2j**: 47%, 72 h	
				
11	**1k**	$X_3 = F_3$	**2k**: trace, 24 h	
12[d]	**1k′**	$X_3 = (OCH_2)_3CMe$	**2k**: 67%, 11 h	
				
13	**1l**	$X_3 = F_3$	**2l**: 0%, 24 h	
14[d]	**1l′**	$X_3 = (OCH_2)_3CMe$	**2l**: 40%, 36 h	

[a] *Reaction conditions:* see Experimental Section.

[b] Yield was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

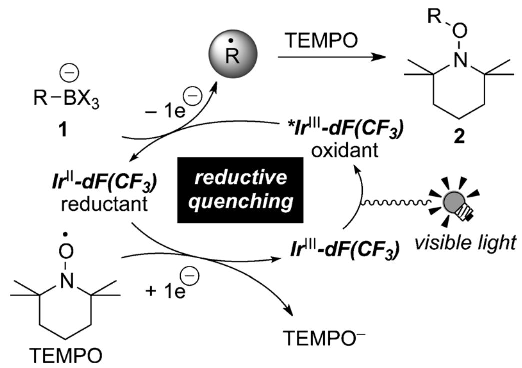
[c] PMB = p-MeOC$_6$H$_4$CH$_2$.

[d] The reaction was conducted in a mixture of acetone and H$_2$O (5:1) as solvent.

bond formation did not proceed either in the dark or in the absence of the Ir catalyst (entries 7 and 8), strongly supporting that the photoexcited species of the Ir catalyst are involved in the reaction.

The scope and limitations of this photocatalytic C–O bond formation are summarized in Table 2. Benzyltrifluoroborates with electron-donating substituents on the benzene ring (**1b**, **c**) smoothly produced the corresponding C–O coupled products (**2b**, **c**) in 84% and quantitative yields, respectively (entries 2 and 3). On the other hand, substrates with electron-withdrawing groups on the benzene ring (**1d**, **e**) resulted in slow conversion but in good yields (entries 4 and 5).

Next, to expand the scope and to gain insight into the reaction mechanism, γ-substituted allyltrifluoroborates were examined. While 2-cyclohexenylborate **1f** and (*E*)-3-phenyl-2-propenylborate **1g** gave **2f** (81%) and **2gα** (97%) as sole products (entries 6 and 7), respectively, (*E*)-2-octenylborate **1h** and (*E*)-4-*p*-methoxybenzyloxy-2-butenylborate **1i** gave mixtures of α- and γ-adducts with preference for the α-adduct (entries 8 and 9). Under the present photocatalytic conditions, deprotection of a PMB group was not observed at all.[11] In addition, the reactions of the linear allylic substrate were accompanied by geometrical isomerization of the C=C bonds. We cannot exclude the reaction mechanism involving the nucleophilic attack of organoborates to an *N*-oxoammonium cation derived from oxidation of TEMPO promoted by the photoredox catalyst because of the preferential



Scheme 2. A plausible reaction mechanism for the C–O bond formation.[13]

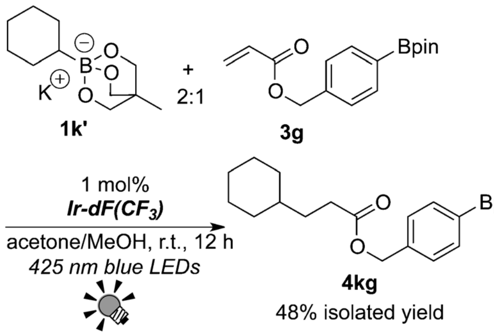
formation of **2hγ** and **2iγ**. However, the selective formation of **2gα** and the certain formation of **2hα** and **2iα** in the reaction of γ-allylborates supports involvement of allyl radical species *via* oxidation of organoborates.

Furthermore, tertiary alkylborate **1j** afforded the corresponding coupling product **2j** (entry 10). Secondary (**1k**) and primary (**1l**) alkyltrifluoroborates turned out to be sluggish (entries 11 and 13). It is remarkable, however, that secondary (**1k′**) and primary (**1l′**) alkylborates bearing the alkyltriol auxiliary gave the corresponding products **2k** and **2l** in 67% and 40% yields, respectively (entries 12 and 14), indicating that the efficiency of the radical generation depends on the borate auxiliary. Cyclic voltammograms for **1k** and **1k′** exhibited a broad irreversible oxidation wave around +1.10 V and +0.75 V (*vs.* Cp$_2$Fe), respectively (*cf.* oxidation potential of ****Ir-dF(CF$_3$)*** = +0.91 V *vs.* Cp$_2$Fe[10]).[12] These data indicate that cyclic alkyl(triol)borates are oxidized more easily than alkyltrifluoroborates. Importantly, this photoredox catalysis can be applied to a variety of organoborates including benzyl-, allyl-, and even secondary and primary alkylborates, and thus is regarded as a promising radical initiating system for selective radical generation by changing the auxiliary on the boron atom (*vide infra*).

A plausible reaction mechanism for the C–O bond formation is illustrated in Scheme 2. ***Ir^{III}-dF(CF$_3$)*** is first excited by visible light irradiation to generate ****Ir^{III}-dF(CF$_3$)***, which undergoes 1*e*-transfer (SET) from organoborate **1** to form the carbon-centered radical (˙R) and ***Ir^{II}-dF(CF$_3$)***. The generated radicals are captured by TEMPO to afford the C–O coupling products **2**. A sacrificial equivalent of TEMPO can serve as an oxidant, regenerating the ground state ***Ir^{III}-dF(CF$_3$)***.[7d]

We next attempted the extension of this photoredox catalysis to C–C bond formation, i.e., Giese-type reactions. Photocatalytic reactions of potassium benzyltrifluoroborate **1c** with methyl vinyl ketone **3a** in the presence of the Ir cyclometalated catalyst, ***Ir-dF(CF$_3$)***, under visible light irradiation gave adducts **4ca** in 81% yield (entry 1 in Table 3). Typical electron-deficient alkenes (**3a–c**) gave the corresponding products (**4ca–cc**) in good yields (entries 1–3). A less electron-deficient alkene, diethyl vinylphosphonate **3d**, did not react well under these reaction conditions (entry 4). A cyclic alkene, cyclohexenone **3e**, gave the C–C coupled product **4ce** (53% NMR yield) (entry 5). The reaction of methyl crotonate **3f** resulted in low conversion (entry 6). Furthermore, reactions of cyclic alkyl(triol)borates (**1k′**, **l′**) with methyl acrylate **3b** and acrylonitrile **3c** resulted in alkylation at the β-carbon atom of **3b** and **3c** to give the corresponding alkyl adducts **4kb**, **4lb**, **4kc** and **4lc** in moderate yields, respectively (entries 7–10). Finally, the reaction of arylborates, potassium *p*-tolyl(triol)borate **1m′**, lithium 2-pyridyl(triol)borate **1n′** and sodium 2-thienyl(triol)borate **1o′**, with **3b** produced the corresponding aryl adducts **4mb** (35%), **4nb** (24%) and **4ob** (27%), respectively (entries 11–13).[14] Importantly, this photoredox catalysis can be applied to a variety of organoborates including benzyl(allyl)-, alkyl-, and arylborates.

Interestingly, we have found that regiospecific C–C bond formation can be achieved on the basis of the selective generation of radicals from cyclic organo(triol)borates. In the reaction of cyclic alkyl(triol)borates **1k′** with methyl acrylate derivative **3g** bearing a boronic acid ester moiety (Bpin), the C–C coupling product **4kg** with the Bpin unit was obtained in 48% isolated yield [Eq. (1)]. The above-mentioned Baran's catalytic system can be applied to alkyl- and arylboronic acid derivatives as well as arylborates, however, it is non-selective with respect to the auxiliary on the boron atom. Selective generation of radicals from cyclic organo(triol)borates is a feature of our photocatalytic system.

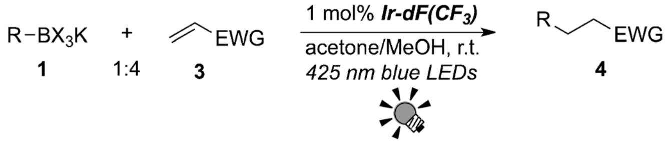


(1)

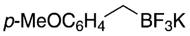
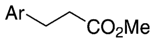
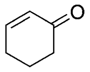
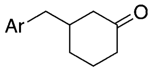
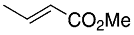
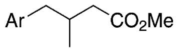
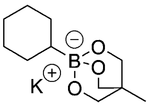
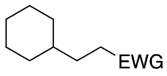
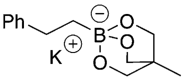
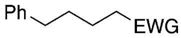
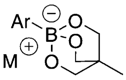
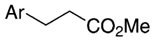
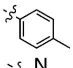
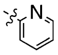
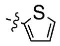
It should be noted that the sunlight efficiently induced the present C–C bond formation in a manner similar to irradiation with blue LEDs [Eq. (2)].

A plausible reaction mechanism for the C–C bond formation is illustrated in Scheme 3. The same mechanism as for the C–O bond formation in Scheme 2 pro-

Table 3. Photocatalytic C–C bond formation.[a]



Ir-dF(CF$_3$): [Ir(dF(CF$_3$)ppy)$_2$(bpy)](PF$_6$)

Entry	Organoborate 1		Alkene 3		Product 4: Yield [%], time [h]	
						
1	**1c**		**3a**	EWG = COMe	**4ca**: 81%, 8 h	
2	**1c**		**3b**	EWG = CO$_2$Me	**4cb**: 73%, 22 h	
3	**1c**		**3c**	EWG = CN	**4cc**: 85%, 10 h	
4[b]	**1c**		**3d**	EWG = PO(OEt)$_2$	**4cd**: 14%,[c] 24 h	
5[b]	**1c**		**3e**		**4ce**: 53%,[c] 8 h	
6[b]	**1c**		**3f**		**4cf**: trace, 24 h	
						
7[d]	**1k′**		**3b**		**4kb**: 69%, 11 h	
8[d]	**1k′**		**3c**		**4kc**: 62%, 12 h	
						
9[d]	**1l′**		**3b**		**4lb**: 45%, 24 h	
10[d]	**1l′**		**3c**		**4lc**: 60%, 24 h	
						
11[d]	**1m′**	M = K, Ar = 	**3b**		**4mb**: 35%, 24 h	
12[d]	**1n′**	M = Li, Ar = 	**3b**		**4nb**: 24%, 24 h	
13[d]	**1o′**	M = Na, Ar = 	**3b**		**4ob**: 27%, 24 h	

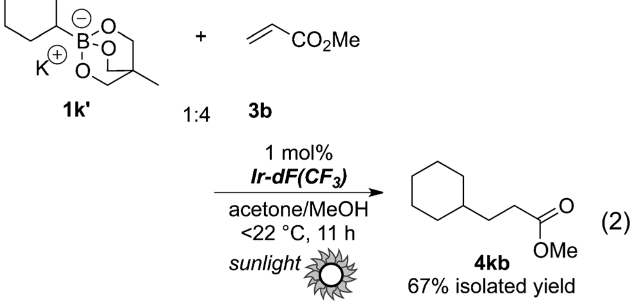
[a] *Reaction conditions:* see Experimental Section.

[b] Loading of Ir cat: 2 mol%.

[c] Yields were determined by ^{1}H NMR spectroscopy using tetraethylsilane as an internal standard.

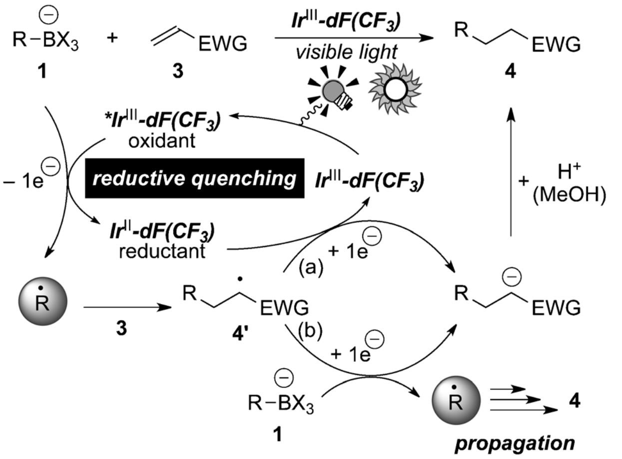
[d] The reaction was conducted in a mixture of acetone (2.5 mL) and MeOH (0.5 mL) as solvent.

duces $R^{\bullet}$ from organoborates under visible light irradiation (blue LEDs and the sunlight). Addition of $R^{\bullet}$ to the alkene **3** gives the alkyl radical intermediate **4′**, which reduced by the ***Ir***^{II}***-dF(CF$_3$)*** formed by the SET process (path a in Scheme 3). Subsequent protonation with MeOH solvent produces the C–C coupling product **4**. We cannot rule out radical chain propagation mechanism (path b), but the present transformation requires continuous irradiation of visible light (see Figure S8 in the Supporting Information), thus suggesting that chain propagation is not a main mechanistic component.



(2)

In conclusion, *visible-light-driven SET photoredox catalysis* provides a facile and efficient access to carbon-centered radicals *via* oxidation of organoborates. We have also developed radical reactions using alkyl-, allyl-, benzyl- and arylborates as radical precursors. Furthermore, it is revealed that cyclic organo-



Scheme 3. A plausible reaction mechanism for the C−C bond formation.[13]

(triol)borates are more effective as radical precursors than organotrifluoroborates, especially in the generation of *sec.*-, and *prim.*-alkyl and aryl radicals. This effect of borate auxiliary can be promising for selective radical generation and reaction. In addition, the sunlight is successfully used for the present photoreaction. This new strategy for generation of radical intermediates can provide us with a greener and more practical radical initiating system from the viewpoint of tin-free catalytic systems and use of low-energy visible light under ambient temperature. Further development of synthetically valuable photocatalytic radical transformations is a continuing effort in our laboratory.

Experimental Section

General Procedure for NMR Experiments: Reaction of Benzyltrifluoroborate 1a with TEMPO

TEMPO (19.5 mg, 125 μmol) was weighted in an NMR tube under N_2 atmosphere. Benzyltrifluoroborate **1a** (9.9 mg, 50 μmol), $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ (1.0 mg, 1.0 μmol), 1,3,5-trimethoxybenzene (2.0 mg) as an internal standard, and acetone-d_6 (0.50 mL) were added to the NMR tube. The reaction mixture was degassed by a freeze-pump-thaw cycle. The reaction was carried out at room temperature (water bath) under visible light irradiation (placed at a distance of <3 cm from the blue LED lamp: $\lambda = 425 \pm 15$ nm).

General Procedure for Iridium-Photocatalyzed C−O Bond Formation

A 20-mL Schlenk tube was charged with TEMPO (98 mg, 0.625 mmol), organoborate **1** (0.25 mmol), $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ (5.0 mg, 5.0 μmol), and acetone (2.5 mL) under N_2. Then, water (0.5 mL) was added to the mixture when triolborates was used. The reaction mixture was degassed by a freeze-pump-thaw cycle. The tube was placed at a distance of 2–3 cm from 3-W blue LED lamp. The yellow solution was stirred at room temperature under visible light irradiation. After completion of the reaction, the reaction mixture was poured into saturated aqueous K_2CO_3 and stirred for another 1 h. The resulting mixture was extracted with CH_2Cl_2, and combined organic layers were dried (Na_2SO_4), and filtered. The filtrate was concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel. The residue was dried under reduced pressure for 5–8 h to afford oxyaminated product **2**.

General Procedure for Iridium-Photocatalyzed C−C Bond Formation with Blue LEDs

A 20-mL Schlenk tube was charged with organoborate **1** (0.25 mmol) and $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ (5.0 mg, 0.005 mmol), then acetone (2.5 mL), MeOH (0.25 mL) and electron-deficient alkene **3** (1.0 mmol) were added under N_2. The tube was degassed by a freeze-pump-thaw cycle, and stirred at room temperature under visible light irradiation (blue LEDs, $\lambda = 425 \pm 15$ nm). The resulting mixture was extracted with CH_2Cl_2, and combined organic layers were dried (Na_2SO_4), filtered. The filtrate was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel to afford the corresponding C−C coupled product **4**.

Procedure for Iridium-Photocatalyzed C−C Bond Formation with Sunlight

A cylindrical vessel (see the Supporting Information) was charged with organoborate **1k′** (0.25 mmol) and $[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ (2.5 mg, 0.0025 mmol), then acetone (2.5 mL), MeOH (0.5 mL) and methyl acrylate **3b** (1.0 mmol) were added under N_2. The vessel was degassed by a freeze-pump-thaw cycle, and exposed to sunlight for 11 h (May 11th and 13th, 2012) below 22 °C. The resulting mixture was extracted with CH_2Cl_2, and combined organic layers were dried (Na_2SO_4), filtered. The filtrate was concentrated under vacuum and the residue was purified by flash column chromatography on silica gel to afford **4kb**; yield: 67%.

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[12] Cyclic voltammograms for benzyltrifluoroborate **1a** showed a broad irreversible oxidation wave around +0.67 V. Electrochemical data are shown in the Supporting Information. Generation of a radical from the precursor is strongly connected with their redox potentials.

[13] Luminescent quenching experiments are summarized in the Supporting Information. **1a** and TEMPO quenched efficiently emission of the Ir photoexcited state *___Ir-dF(CF$_3$)___. However luminescence from *___Ir-dF(CF$_3$)___ was not quenched by **3a**.

[14] Monitoring the reaction mixture by ^{1}H NMR revealed that the reaction stopped on the way, presumably due to deactivation of the Ir catalyst. In the reaction of **1m′** with **3b**, further addition of the Ir catalyst after 12 h increased the yield up to 50%.