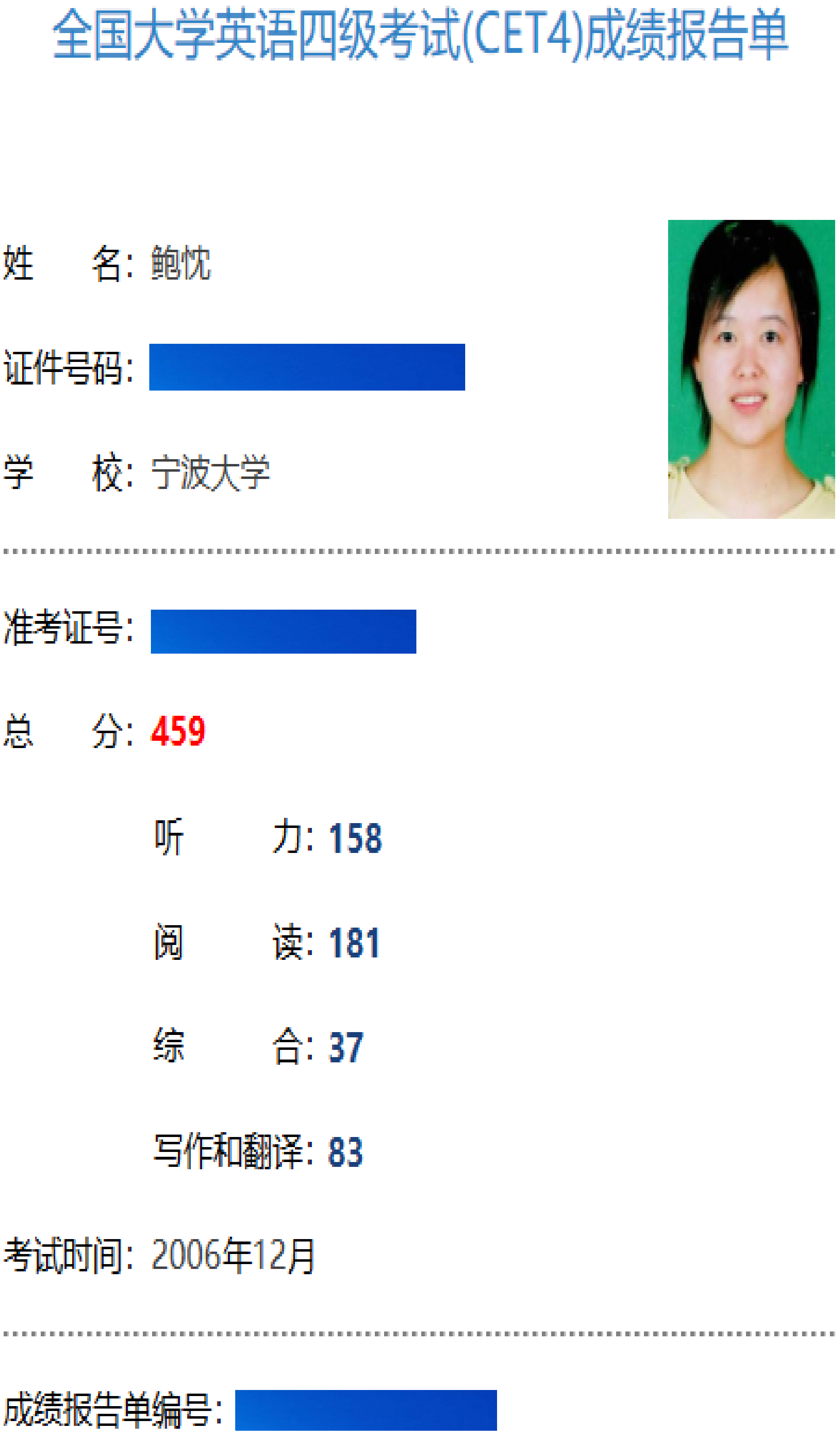
4、 外语能力证书



全国大学英语四级考试(CET4)成绩报告单

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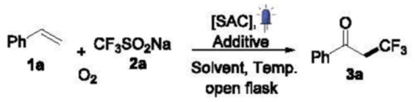
5、 学术能力证明材料

Umemoto reagent, Langlois reagent, CF_3I, $ROSO_2CF_3$, etc., were employed to produce the trifluoromethyl radical under metal catalysis,[12b,c] photocatalysis,[12d,e] and electrocatalysis.[12f] Notably, a trifluoromethyl sulfonylpyridinium salt could be reduced into CF_3• under photocatalysis to react with alkene toward various α-trifluoromethylketones.[12g]

Inspired by what is mentioned above, in this paper we disclose an MPHI-catalyzed oxytrifluoromethylation of alkenes for the synthesis of α-trifluoromethylketones (Scheme 1, eq d). In the process, it is hypothesized that photoexcited MPHI* facilitated the formation of singlet $^1O_2$ and a photoexcited alkene through an energy transfer (EnT) process. Then, we assumed that the resulting singlet $^1O_2$ could oxidize the photoexcited olefins to alkene radical cation **A** (−0.66 V (vs SCE) (see the Supporting Information)) by an oxidative SET process, while Langlois reagent **2** (−0.59 V (vs SCE) (see the Supporting Information)) was oxidized into CF_3• species **B.**[13] The catalytic cycle would be finalized by difunctionalization of alkene radical cation **A** and sequential H-abstraction of peroxo radical E (Scheme 1b). For the whole process, it seems the singlet $^1O_2$ is a highly crucial species, and the previous findings concluded that ionic PHI catalysis under photoirradiation could lead to the formation of key intermediate $^1O_2$.[4−10] It is believed that this projected transformation represents the first protocol toward α-trifluoromethyl ketones **3** under ionic PHI-based single-atom catalysis.

Table 1. Optimization of the Reaction Conditions[a]



entry	[SAC]	additive	solvent	Yields of 3a (%)[b]
1	$FeCl_3$	–	1,4-dioxane	trace
2	NaPHI	–	1,4-dioxane	34
3	KPHI	–	1,4-dioxane	30
4	FePHI	–	1,4-dioxane	25[c]
5	IrPHI	–	1,4-dioxane	16
6	RuPHI	–	1,4-dioxane	12
7	NaPHI	–	THF	26
8	NaPHI	–	toluene	30
9	NaPHI	–	MeOH	complex
10	NaPHI	–	DMSO	73
11	NaPHI	TBAB	DMSO	67
12	NaPHI	DMAP	DMSO	47
13	NaPHI	HOAc	DMSO	trace
14	NaPHI	PhSPh	DMSO	51
15[d]	NaPHI	–	DMSO	76
16[e]	NaPHI	–	DMSO	55
17[f]	NaPHI	–	DMSO	NR[i]
18[g]	NaPHI	–	DMSO	NR[i]
19[h]	NaPHI	–	DMSO	NR[i]

[a] Standard conditions: styrene **1a** (0.45 mmol), **2a** (0.3 mmol), [SAC] (15.0 mg), an additive (2.0 equiv), 10 W blue LED, 50 °C, air, 12 h. [b] Isolated yield based on **1a**. [c] Benzaldehyde (3%) was observed. [d] With 20 mg of NaPHI. [e] With a 5 W LED. [f] No LED was used. [g] With 2.0 equiv of TEMPO as an additive. [h] N_2 atmosphere. [i] No reaction.

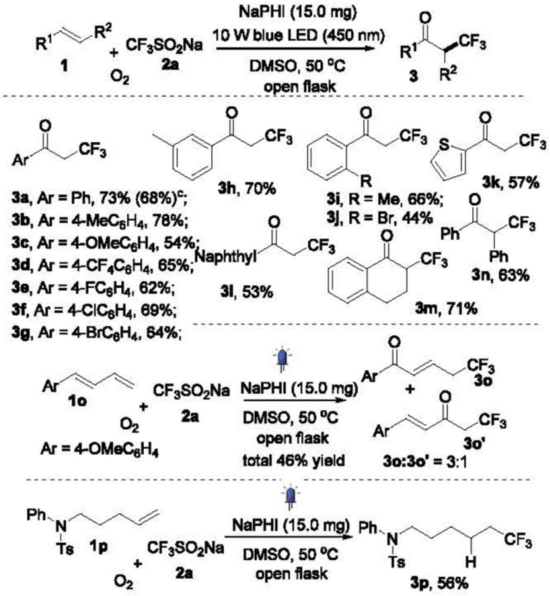
RESULTS AND DISCUSSION

To verify this projected transformation, we start to optimize the reaction condition. Initially, the model reaction mixture of styrene **1a** and Langlois reagent **2a** in 1,4-dioxane under an open flask was irradiated with a 10 W blue LED (450 nm) when a series of single-atom catalysts were employed as photocatalysts. To our delight, NaPHI (sodium poly(heptazine imide))[14] was the best choice, leading to the desired product **3a** in 34% isolated yield (entry 2, Table 1), while the use of other SACs such as KPHI, FePHI, RuPHI, and IrPHI did not give better yields (entries 3−6, respectively, Table 1). It is noteworthy that the use of FePHI made the formation of a byproduct benzaldehyde in 3% yield (entry 4, Table 1). Besides, iron/photo dual catalysis, which proved to be an efficient catalytic system in our previous study,[15] failed to produce the desired α-trifluoromethylketone **3a** (entry 1, Table 1). Encouraged by this promising result, other result-affecting factors were screened accordingly. Pleasingly, the use of dimethyl sulfoxide (DMSO) greatly improved the reaction efficiency, resulting in the desired product **3a** in 73% isolated yield (entry 10, Table 1). Inferior outcomes were observed when either tetrahydrofuran (THF) or toluene was used as the solvent (entry 7 or 8, respectively, Table 1). Notably, the reaction became complex when the reaction solvent was MeOH (entry 9, Table 1). It is reasoned that under photoirradiation MeOH was a reactive synthon to produce methoxyl radical and hydroxylmethyl radical species,[15a] thus increasing reaction diversities toward various byproducts.

The additive effect was also explored, and surprisingly, the additives, including tetrabutylammonium bromide (TBAB), 4-(*N*,*N*-dimethylamino)pyridine (DMAP), and PhSPh, were unfavorable for the model reaction, without yielding better outcomes (entries 11, 12, and 14, respectively, Table 1). The reaction was shut down in the presence of 2.0 equiv of acetic acid (HOAc) (entry 13, Table 1). An increase in NaPHI loading from 15.0 to 20.0 mg made a slight impact on the reaction, with the formation of the desired product **3a** in a similar yield (entry 15, Table 1). Decreasing the LED power from 10 to 5 W suppressed the reaction efficiency to 55% (entry 16, Table 1). The blank experiments without a LED, with 2.0 equiv of TEMPO as a radical scavenger, and under a N_2 atmosphere did not afford **3a** (entries 17−19, respectively, Table 1). It is worth noting that substrate styrene **1a** was oxidized into benzaldehyde in the presence of TEMPO (entry 18, Table 1).

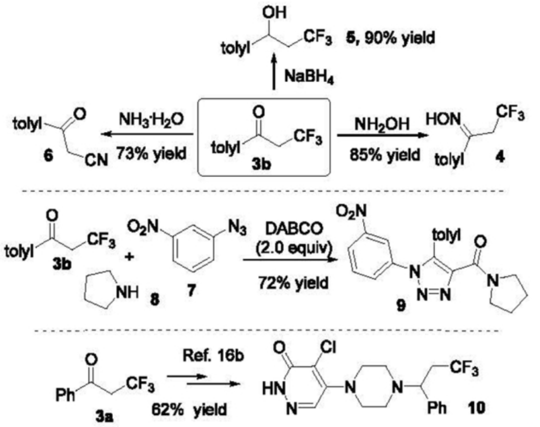
With the optimal reaction conditions in hand, the reaction generality was next explored. As presented in Scheme 2, various styrene **1** was suitable to afford a series of α-trifluoromethylketones **3a−3n** in moderate to good yields. In particular, a 1 mmol scale reaction of styrene **1a** worked well under the standard conditions to isolate the desired product **3a** in 68% yield.

For example, the reaction of 4-methylstyrene **1b** gave rise to product **3b** in 78% yield, while the reaction of 4-methoxyl-connected substrate **1c** offered final product **3c** in 54% yield. Substrate **1d** with a 4-fluoro group was a good reaction partner, leading to final α-trifluoromethylketone **3d** in 65% isolated yield. Interestingly, the bromo atom survived in the reaction to produce product **3g** in moderate yield. Subsequently, the *ortho* substituent effect of aryl in styrene was also examined. For instance, 2-methylphenylethene **1i** was compatible for the reaction, leading to product **3i** in 66% isolated yield. However, the reaction of 2-bromophenylethene **1j** was greatly retarded, with the formation of the desired product **3j** in 44% yield. Other styrenes such as naphthyl-linked and heteroatom-aryl-substituted ethenes also served as efficient reaction partners, and products **3k** and **3l** were afforded in 57% and 53% yields, Scheme 2. Scope for the Synthesis of α-Trifluoromethylketones[a,b]



[a]Standard conditions: styrene **1** (0.45 mmol), **2a** (0.3 mmol), NaPHI (15.0 mg), 10 W blue LED (450 nm), 50 °C, 2 mL of DMSO, stirred for 12 h under an air atmosphere. [b]Isolated yield based on **1**. [c]A 1 mmol scale reaction was conducted.

Scheme 3. Synthetic Applications



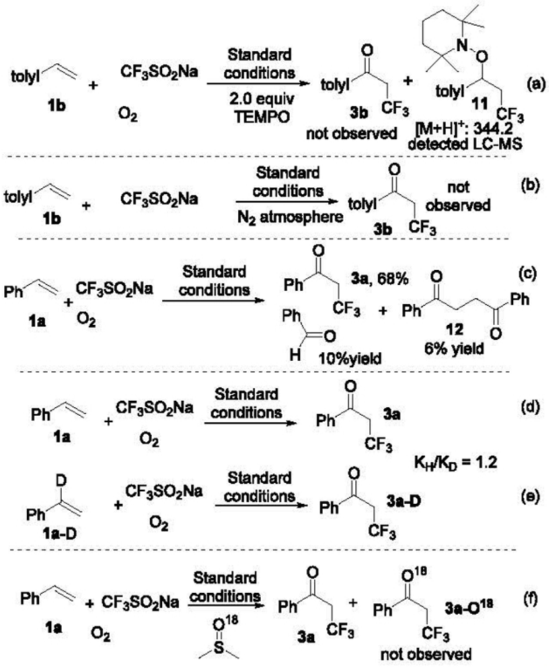
respectively. 1,2-Disubstituted alkenes were also compatible. For example, the reaction of 1,2,3,4-tetrahydronaphthalene **1m** worked well, and the desired product **3m** was afforded in 71% yield. The reaction of 1,2-diphenylethene **1n** also proceeded smoothly toward product **3n** in 63% yield, which was not synthesized by the previous procedures.[12]

Notably, a mixture of **3o** and **3o′** (3:1 **3o**:**3o′**) was isolated when 1-(4-methoxylphenyl)buta-1,3-diene **1o** was used as the substrate. It is convincible that the formation of this mixture was ascribed to the p−π conjugated effect of the resulting α-CF$_3$ allylic radical. Due to the higher stability of the 3-phenyl allylic radical, benzylic C−H carbonylated product **3o** is much more stable than **3o′**. Interestingly, distinctive trifluoromethyl hydrogenating product **3p** was observed when pent-4-en-1-amine **1p** was used as a substrate under the standard conditions, and the expected oxytrifluoromethylated product was not observed. Other alkyl-connected alkenes did not provide the corresponding α-trifluoromethylketones under the standard conditions (data not shown in Scheme 2).

To demonstrate the synthetic versatility, structural elaboration of α-trifluoromethylketone **3b** was conducted accordingly. As illustrated in Scheme 3, the carbonyl group in **3b** could be condensed with hydroxylamine to prepare oxime **4** and also reduced by NaBH$_4$ into alcohol **5**. Upon treatment with an ammonia solution, the trifluoromethyl group in **3b** served as an efficient precursor to construct a cyano group for the synthesis of α-cyanoketone **6** in 73% isolated yield. Notably, a DABCO-promoted three-component reaction of α-trifluoromethylketone **3b**, 3-nitrophenyl azide **7**, and pyrrolidine **8** worked well, isolating biologically interesting scaffold 1,4,5-trisubstituted triazole **9** in 72% yield.[16a] Besides, α-trifluoromethylketone **3a** proved to be a powerful building block to form potential TRPC5 inhibitor **10**.[16b]

As presented in Scheme 4, several control experiments were carried out with the aim of gaining insights into the mechanism. The reaction with TEMPO as an additive provided a negative result, failing to observe the desired product **3b**. TEMPO-adducted species **11** was detected by LC-MS analysis (Scheme 4, eq a), indicating the reaction undergoes a radical pathway. The absence of an air atmosphere totally suppressed the reaction, without detecting the desired product **3b**, which showed the requirement of an air atmosphere (Scheme 4, eq b). The 1 mmol scale reaction of **1a** afforded byproduct 1,4-diketone **12** in 6% yield when giving rise to another byproduct benzaldehyde in 10% yield (Scheme

Scheme 4. Control Experiments



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4, eq c). The formation of byproduct **12** might be ascribed to dimerization of resulting vinyl radical cation **A** (see Scheme 1b). The KIE data ($K_H/K_D = 1.2$) suggested H abstraction of intermediate E (See Scheme 1b) was not the rate-determining step in the whole process (Scheme 4, eqs d and e). The light off−on reaction indicated that the blue LED was required in the reaction (see the Supporting Information). The use of DMSO-^{18}O as a solvent replacement did not afford the formation of ^{18}O-labeled α-trifluoromethylketone **3a-^{18}O** by LC-MS analysis and GC-MS analysis (Scheme 4, eq f), excluding the possibility that the oxygen of the carbonyl in product **3a** came from solvent DMSO.[12g]

CONCLUSION

We developed a NaPHI-catalyzed oxytrifluoromethylation of styrenes. The reaction was applicable for the synthesis of α-trifluoromethylketones under photoirradiation. It is worth noting that building block α-trifluoromethylketones could be structurally elaborated into various useful molecules. Besides, synthetic applications toward biologically interesting scaffolds such as a potential TRPC5 inhibitor were also realized. Mechanistic investigations show photoexcited NaPHI* facilitates the formation of singlet $^1O_2$ and enables an oxidative SET process of styrene to radical cation species. The products α-trifluoromethylketones were ascribed to difunctionalization of styrene radical cation **A** with trifluoromethyl radical **B** and oxygen radical anion **C**. More ionic PHI-based single-atom photocatalyst-promoted transformations are being developed in our lab, and the results will be reported in due course.

EXPERIMENTAL SECTION

Experimental procedures and compound characterization data are given in the Supporting Information.

ASSOCIATED CONTENT

Data Availability Statement

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

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.5c00117.

Experimental procedures, mechanistic investigation, and compound characterization data (PDF)

FAIR data, including the primary NMR FID files, for compounds **3**−**6**, **9**, and **10** (ZIP)

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Author Contributions

$^\nabla$C.B. and X.Z. contributed to this work.

Notes

The authors declare no competing financial interest.

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Sodium Poly(heptazine imide)-Enabled Oxytrifluoromethylation of Alkenes for the Synthesis of α-CF_3 Ketones

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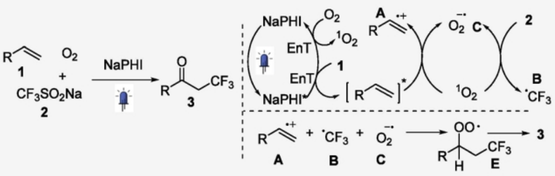
ABSTRACT: This paper describes a NaPHI-catalyzed oxytrifluoromethylation of olefins under photoirradiation. The reaction is applicable for the synthesis of α-trifluoromethyl ketones, which could be structurally elaborated into an array of useful scaffolds. Mechanistic studies suggested that photoexcited NaPHI* could facilitate the formation of singlet $^1O_2$ through an EnT process, thus enabling difunctionalization with trifluoromethyl radical and oxygen radical anion species.

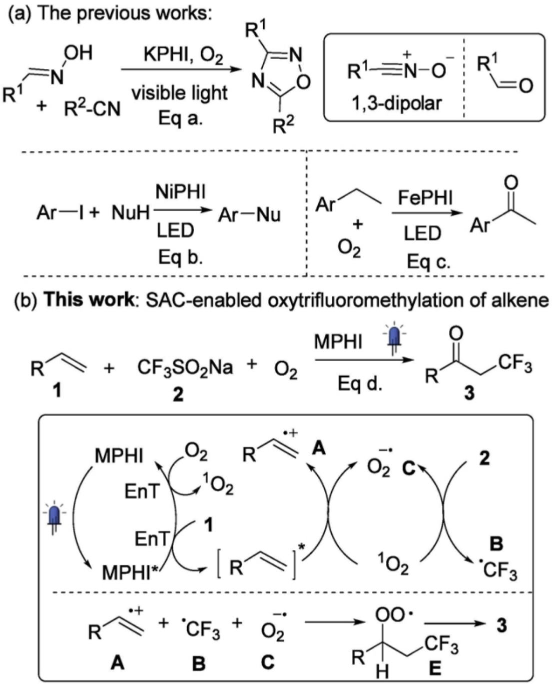


■ INTRODUCTION

Heterogeneous single-atom catalysis (SAC) had a significant impact on improving chemical synthesis, probably since it enhanced the catalytic turnover frequency and recyclability.[1] As such, a series of single-atom catalysts have been developed for enabling nitrogen fixation, CO_2 reduction, and H_2O_2 production.[2] Very recently, ionic poly(heptazine imides) (PHIs) have emerged as an efficient photocatalyst for SAC in a field of organic synthetic chemistry.[3] The previous results concluded that various metal PHIs exhibited high photocatalytic reactivity in oxidation, cross-coupling, and cycloaddition. It is clear that the reaction efficiency is subjected to the PHI's well-defined two-dimensional structure with a more positive valence band potential.[4] In 2020, Savateev and coworkers suggested potassium poly(heptazine imide) (KPHI) was a powerful single-atom photocatalyst to make oximes cyclize with nitrile for producing 1,2,4-oxadiazoles[5] (Scheme 1, eq a). Mechanistic investigations indicated KPHI was easily excited by visible light to initiate the formation of singlet $^1O_2$, which oxidized oximes to 1,3-diploars[5] and aldehydes.[6] Interestingly, the photoexcited KPHI* was capable of triggering single-electron transfer (SET) of $CHCl_3$ and Cl^- to the dichloromethyl radical ($\bullet CHCl_2$) for radical Michael-type addition[7] and the chloro radical ($\bullet Cl$) for coupling with aryl thioacetates,[8] respectively. The synthetic versatility of PHI-based chemistry is also highlighted by NiPHI-catalyzed cross-coupling of aryl iodides[9] (Scheme 1, eq b) and FePHI-promoted carbonylation of benzylic C−H bonds[10] (Scheme 1, eq c).

On the other hand, α-trifluoromethylketone was a powerful building block,[11] thus attracting more attention from synthetic chemists. In this field, one of the main trends tended to develop new types of catalytic systems.[12] Generally, electrophilic substitution[12a] and radical addition represent two types of trifluoromethylation reactions. Considering the high efficiency of radical trifluoromethylation, Togni's reagent,

Scheme 1. MPHI-Enabled Oxytrifluoromethylation of Alkenes for α-CF_3 Ketones



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