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Deprotonated Salicylaldehyde as Visible Light Photocatalyst

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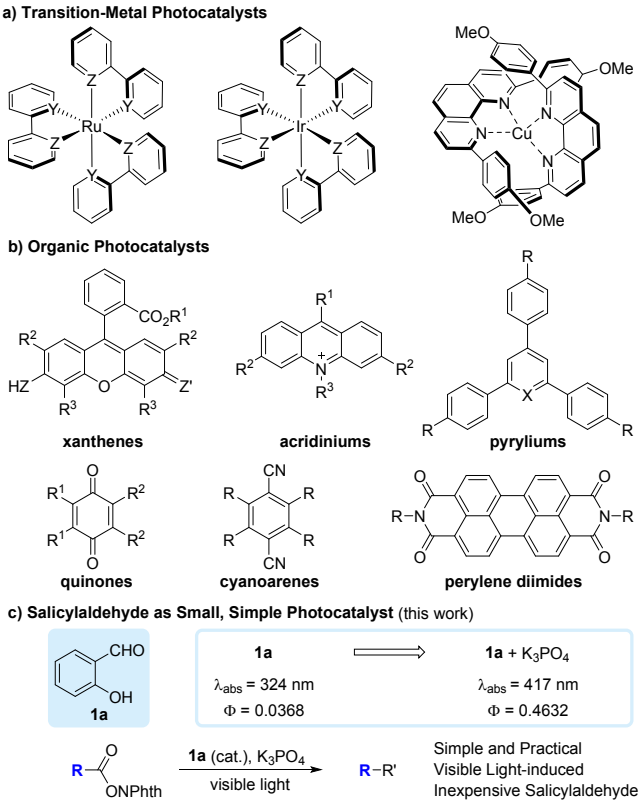
ABSTRACT: Salicylaldehyde is established as an efficient visible light photocatalyst for the first time. Compared to other simple aldehyde analogies, salicylaldehyde has a unique deprotonative red-shift from 324 nm to 417 nm and gives rise to the remarkable increase of fluorescence quantum from 0.0368 to 0.4632, thus enables salicylaldehyde as a visible light (> 400 nm) photocatalyst. The experimental investigations suggest that the reactive radical species are generated by sensitization of the substrates by the deprotonated salicylaldehyde through an energy-transfer pathway. Consequently, the C-C cleaving alkylation reactions of *N*-hydroxyphthalimide esters proceed smoothly in the presence of as low as 1 mol % of salicylaldehyde under the visible-light irradiation affording desired alkylation products with up to 99% yields. Application in visible-light induced aerobic oxidation of *N*-alkylpyridinium salts is also reported.

INTRODUCTION

Photochemical reaction has been considered as an attractive and powerful tool for the chemical syntheses, as it could develop unique reaction patterns that is generally unavailable by conventional pathways. It generally requires the utilization of high-energy irradiation, such as ultraviolet (UV) light sources because of the inability of simple organic molecules to absorb visible light. Over the past decade, visible light-driven photo catalysis has emerged as a promising approach that can produce unique value-added molecules.[1-3] It enables the generation of molecules which are sensitive toward UV photodegradation under mild conditions and therefore has attracted attentions from a large group of researchers including not only chemists but also researchers from materials science, pharmacology, as well as chemical biology. Relatively expensive transition metal complexes[4-6] or organic dyes[7] are generally used as photosensitizers in visible-light photocatalysis (Scheme 1a and 1b). Considering the environmental sustainability, the development of a green, efficient and practical visible-light photocatalysis process avoiding expensive transition-metal compounds or toxic reagents is therefore highly desired.

Substituted aromatic aldehydes or ketones are inexpensive and easily available organic compounds. Some of them, such as *p*-anisaldehyde (λ_{max} = 344 nm) display strong absorption in the UVA region. It has been utilized as an effective photosensitizer to absorb photons and then to activate substrates with the near UV part of the CFL emission spectrum in an atom-transfer radical addition (ATRA) via energy-transfer pathway.[8] In another case, stoichiometric benzaldehyde (λ_{max} = 340 nm) has been used in an α-heteroarylation of amides in the presence of peroxides, where the near UV part of the CFL emission spectrum again rather than visible light take effect.[9] Acetone was used as photosensitizer to perform cross-coupling under UV light.[10] However, to the best of our knowledge, applications of substituted aromatic aldehydes in the visible light-induced (> 400 nm) photocatalysis have never been reported.

Scheme 1. Photocatalyst for Visible-Light Induced Reactions



Salicylaldehyde **1a**, known as 2-hydroxybenzaldehyde, is a simple and naturally occurred compound. It is also commercially available low-cost (341 USD/10 Kg from Sigma Aldrich) reagent. Salicylaldehyde exhibits weak fluorescence because it contains a very small π-conjugated benzene ring system. As part of our research interest on pursuing green and

inexpensive organic synthesis process without the involvement of transition-metal compounds or toxic reagents, we started a project towards practical process using inexpensive reagents or catalysts. We found that the salicylaldehyde solution in DMSO displays much stronger fluorescence after deprotonation at room temperature. The strong red-shifted absorption and the high fluorescence quantum yield of deprotonated salicylaldehyde were also observed. We envision that the deprotonated salicylaldehyde could be used as an alternative for the traditional organic dye catalysts in photo-induced reactions and thus investigated the potential of **1a** as a photocatalyst. We found that salicylaldehyde could be utilized as a promising and efficient photocatalyst for the visible light-mediated decarboxylative alkylations (Scheme 1c). Further studies indicate that the red-shifted absorption of the deprotonated salicylaldehyde **1a** may result in its high catalytic efficiency. Herein we report our recent results in details.

RESULTS AND DISCUSSION

Establishing deprotonated salicylaldehyde as photocatalyst. As shown in Figure 1, the colour of **1a** solution changed from colourless to yellow after deprotonation, and the fluorescence also enhanced.

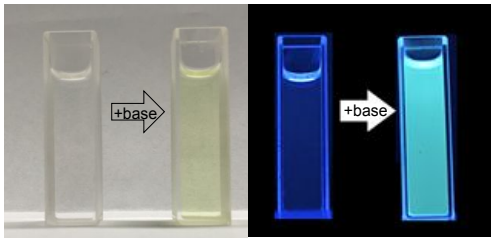


Figure 1. Photographs (left under sunlight, right under 360 nm UV light) of salicylaldehyde **1a** and deprotonated **1a** (base = K_3PO_4) in DMSO (0.05 mM).

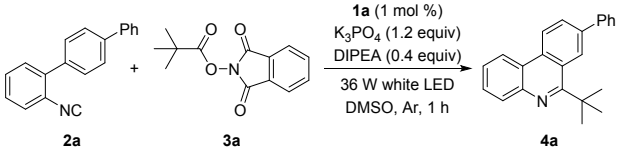
UV/visible absorption experiment shows the absorption maxima (λ_{abs}) of **1a** is at 324 nm with a molar extinction coefficient (ε) of 4.7 x 10^3 L•mol^{-1}•cm^{-1}, whereas the deprotonated **1a** exhibits a stronger red-shifted absorption band of λ_{abs} at 417 nm and ε of 7.9 x 10^3 L•mol^{-1}•cm^{-1}. The emission intensity of deprotonated salicylaldehyde increased dramatically compared to the non-deprotonated one. We also measured the fluorescence quantum yield (Φ) of salicylaldehyde and deprotonated one using quinine sulfate (Φ = 0.55, quinine in 0.05 M sulfuric acid) as a standard.[11] The Φ of salicylaldehyde in DMSO is 0.0368 comparable to its weak emission intensity. However, the Φ of deprotonated salicylaldehyde increased to 0.4632.

N-hydroxyphthalimide esters generate alkyl radicals under the irradiation of light, but normally toxic organic dyes,[12-13] expensive transition metal catalyst,[14-18] substoichiometric amounts reagents,[19-20] or even excess amounts of base[21] cannot be avoided. Using cheap salicylaldehyde as photosensitizer for the visible light catalyses may provide a practical and environment friendly alternative for the tradition ways. Therefore, the activity of **1a** as a photosensitizer was investigated using a model reaction of the decarboxylative cyclization of isocyanides **2a** and *N*-hydroxyphthalimide esters **3a**, which has been established as a typical photocatalytic reaction by various photocatalysts.

Initial experiment was performed in a quartz Schlenk tube containing **1a** (2.5 μmol), isocyanide **2a** (0.25 mmol), *N*-hydroxyphthalimide ester **3a** (0.5 mmol), DIPEA (0.1 mmol), K_3PO_4 (0.3 mmol), and DMSO (2.5 mL). After evacuating by three freeze−pump−thaw cycles, the reaction mixture was backfilled with argon and then stirred under irradiation of a 36 W white LED for 1 hour (Table 1, and details see ESI).

Under the standard conditions, the desired decarboxylative cyclization product **4a** was obtained in 86% yield (Table 1, entry 1). The involvement of light is necessary because no reaction proceeds in dark, indicating it is not a simple thermal radical reaction (entry 2). Other control experiments were also performed to prove that the involvement of **1a** and K_3PO_4 (to generate **1a**-**K**) is necessary (entries 2-4). For example, when the reaction was conducted without **1a**, only trace of **4a** could be detected, which confirms the necessity of **1a** in this photo induced reaction (entry 3). No reaction proceeded when the reaction was performed in the absence of K_3PO_4 (entry 4). DIPEA is NOT necessarily involved in the activation of **3a** and 9% of yield was obtained in the absence of DIPEA (entry 5). The reaction in the *absence* of DIPEA with 15 mol % of **1a** with prolonged reaction time afforded **4a** in 75% (entry 7). The direct promotion by DIPEA via electron donor-acceptor model is thus ruled out. *The involvement of UV light has been ruled out by a control reaction using a filter at λ ≥ 420 nm* (entry 6). Reactions carried out in glass Schlenk tube gave similar results.

Table 1. Control Experiments



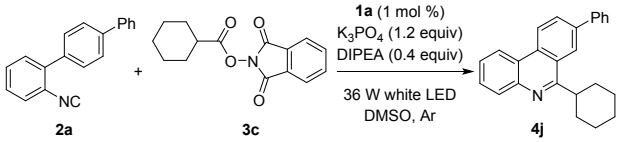
entry[a]	conditions	**4a**(%)[b]
1	standard conditions	86
2	no light	0
3	no **1a**	trace
4	no K_3PO_4	trace
5	no DIPEA	9
6	420 nm light instead of White LED[c]	84
7	15 mol% of **1a** without DIPEA[d]	75

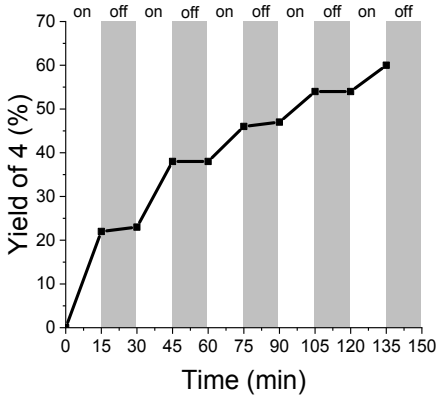
[a] Standard conditions: **2a** (0.25 mmol), **3a** (0.5 mmol), **1a** (0.0025 mmol, 1 mol %), DIPEA (0.1 mmol), K_3PO_4 (0.3 mmol), DMSO (2.5 mL), ambient temperature (about 40 °C) for 1 h under argon, 36 W white LEDs. [b] Yields were determined by ^{1}H NMR analysis using mesitylene and nitromethane as internal standards. [c] Using a 36 W White LED equipped with a filter at λ ≥ 420 nm. [d] 3 h.

To further investigate the effect of light, a mixture of **1a**, isocyanide **2a**, substituted *N*-hydroxyphthalimide ester **3c**, DIPEA, K_3PO_4, and DMSO was stirred for 135 min, alternating between 15 min periods of white LED irradiation and 15 min periods of complete lack of white LED irradiation (Scheme 2).

It was observed that the reaction progressed smoothly upon irradiation with light, but consumption of the isocyanide **2a** and *N*-hydroxyphthalimide ester **3c** abruptly stalled when the light source was removed. This result confirms that continuous light irradiation is a necessary component for the reaction.

Scheme 2. Time Profile of Alkylation of 2a[a]



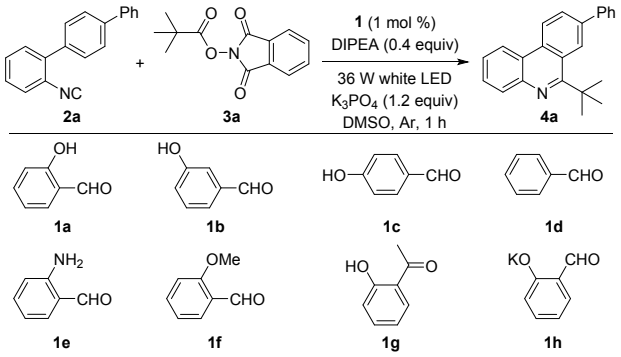


[a]Using standard reaction conditions for reaction of **2a** and **3a** demonstrated in Table 1, entry 1 with the light off/on over time. Yields of **4j** were determined by ^{1}H NMR analysis using mesitylene and nitromethane as internal standards.

Reaction conditions. Since salicylaldehyde **1a** works as a photocatalyst, we assumed that its derivatives could also display photocatalytic activities and then studied various salicylaldehyde derivatives (Table 2). 3-Hydroxybenzaldehyde (**1b**), 4-hydroxybenzaldehyde (**1c**), and benzaldehyde (**1d**) show much lower catalytic activity (entries 2-4 vs entry 1). This indicates the ortho-substituted hydroxyl group of salicylaldehyde (**1a**) is essential for the red-shift because in later study it was found that neither **1b** nor **1c** gave large red-shift over 400 nm. It is further supported by the fact that the replacement of hydroxyl group by an amino group (**1e**, entry 5) or a methoxy group (**1f**, entry 6) gives rise to decreasing yields. The formyl group is also necessary for the high catalytic reactivity of the photocatalyst, as the yield of **4a** drops to 43%, when an acetyl group is used instead of formyl group (**1g**, entry 7). Potassium 2-formylphenolate (**1h**) was also subjected to the standard reaction conditions, and it displays similar photocatalytic activities (entry 8).

Due to the low cost and high activity of salicylaldehyde **1a**, it was chosen for further investigation of reaction conditions. Reactions in DMAc or DMF afforded the desired compound **4a** in moderate yields (Table 3, entries 2-3 vs entry 1). No target products were obtained in MeCN, THF, toluene, DCE, or EtOH (entries 4−8). With the optimized solvent identified, we next screened different bases. Na_3PO_4 and K_2CO_3 provided similar yields (entries 9 and 10). Utilization of $KHCO_3$ or KF results in the low yields (entries 11 and 12). No reaction occurs in the presence of KO^{t}Bu (entry 13).

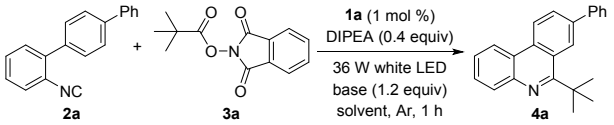
Table 2. Comparison of Aldehyde Catalysts



entry[a]	conditions	**4a**(%)[b]
1	Salicylaldehyde (**1a**)	86
2	3-Hydroxybenzaldehyde (**1b**)	31
3	4-Hydroxybenzaldehyde (**1c**)	17
4	Benzaldehyde (**1d**)	20
5	2-Aminobenzaldehyde (**1e**)	21
6	*o*-Anisaldehyde (**1f**)	15
7	2'-Hydroxyacetophenone (**1g**)	43
8[c]	**1a-K** (**1h**)	84

[a]**2a** (0.25 mmol), **3a** (0.5 mmol), catalyst **1** (0.0025 mmol, 1 mol %), DIPEA (0.1 mmol), K_3PO_4 (0.3 mmol), DMSO (2.5 mL), ambient temperature (about 40 °C) for 1 h under argon, 36 W white LEDs. bDetermined by ^{1}H NMR. [c]**1a-K** refers to the potassium salt of salicylaldehyde.

Table 3. Effect of Solvents



entry[a]	base	solvent	**4a**(%)[b]
1	K_3PO_4	DMSO	86
2	K_3PO_4	DMAc	48
3	K_3PO_4	DMF	35
4	K_3PO_4	MeCN	0
5	K_3PO_4	THF	0
6	K_3PO_4	Toluene	0
7	K_3PO_4	DCE	0
8	K_3PO_4	EtOH	0
9	Na_3PO_4	DMSO	84
10	K_2CO_3	DMSO	83
11	$KHCO_3$	DMSO	67
12	KF	DMSO	62
13	KO^{t}Bu	DMSO	0

[a] Conditions: **2a** (0.25 mmol), **3a** (0.5 mmol), catalyst **1a** (0.0025 mmol, 1 mol %), DIPEA (0.1 mmol), K_3PO_4 (0.3 mmol), DMSO (2.5 mL), ambient temperature (about 40 °C) for 1 h under argon, 36 W white LEDs. [b] Determined by ^{1}H NMR.

The independence of yield on the amount of DIPEA. It is known that photocatalysts can activate substrates through single-electron transfer (SET), direct hydrogen atom transfer (HAT), or energy transfer (ET) processes. Considering tertiary amines can form electron donor−acceptor complexes to activate *N*-hydroxyphthalimide esters,[19-22] we performed control

experiments using 0.2-0.5 equiv of DIPEA, and we found that the yield of **4a** is NOT dependent on the amount of DIPEA (Figure 2). Therefore, this reaction is NOT promoted by DIPEA via electron donor−acceptor complexes.

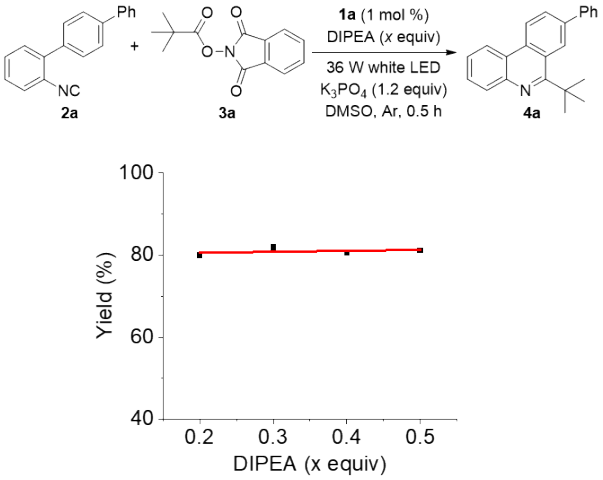


Figure 2. Effects of DIPEA. Reaction conditions: **2a** (0.25 mmol), **3a** (0.5 mmol), **1a** (0.0025 mmol, 1 mol %), DIPEA (x equivalent), K_3PO_4 (0.3 mmol), DMSO (2.5 mL), ambient temperature (about 40 °C), 0.5 h, 36 W white LEDs.

The photocatalytic role of salicylaldehyde 1a. The dependence of yield on salicylaldehyde **1a** is established in Figure 3. When the loading of salicylaldehyde **1a** increased to 15 mol % in the absence of DIPEA, yield of **4a** could also be as high as 77% (x = 15 in Figure 3). In the mechanism we consider DIPEA as an electron transfer reagent, and when DIPEA was missed, the deprotonated salicylaldehyde maybe employed both catalyst and electron transfer reagent (ion-radical-ion). These experiments further exclude the possibility of an electron pathway that undergoes an electron donor−acceptor complexes. Therefore, **1a** is identified as the photocatalyst in the reaction of **2a** and **3a**.

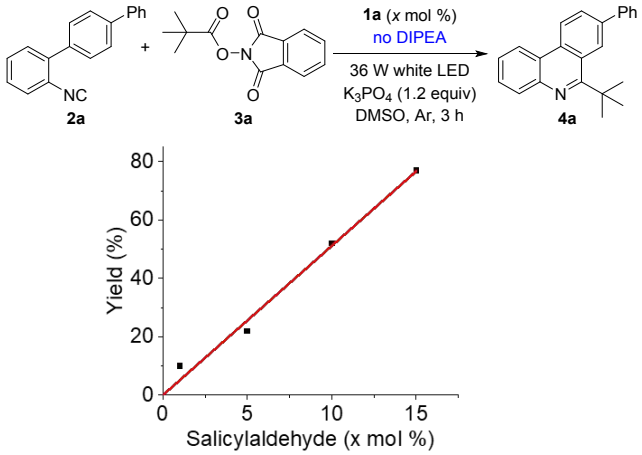


Figure 3. Effects of salicylaldehyde **1a** in the absence of DIPEA. Reaction conditions: **2a** (0.25 mmol), **3a** (0.5 mmol), **1a** (x mol %), K_3PO_4 (0.3 mmol), DMSO (2.5 mL), ambient temperature (about 40 °C) for 3 h under argon, 36 W white LEDs.

The possibility of salicylaldehyde working as an HAT catalyst is also excluded because the hydrogen atom on hydroxyl group of **1a** has been removed in the reaction (see the ^{1}H NMR spectra, Figure 4, upper and middle), and there is no active proton for the HAT process. Thus, the catalytically active species working in this reaction is the potassium salt (**1a**-K) of **1a** without hydroxyl proton. We also performed the reaction in the presence of potassium salt of salicylaldehyde (**1a**-K or **1h**, Table 2, entry 8) instead of salicylaldehyde **1a** and it afforded the comparable results with **1a**-K_3PO_4 system (Table 2, entry 1). A bit of shift of the peaks of **1a**-K might be due to the H-bond between **1a**-K and K_2HPO_4.

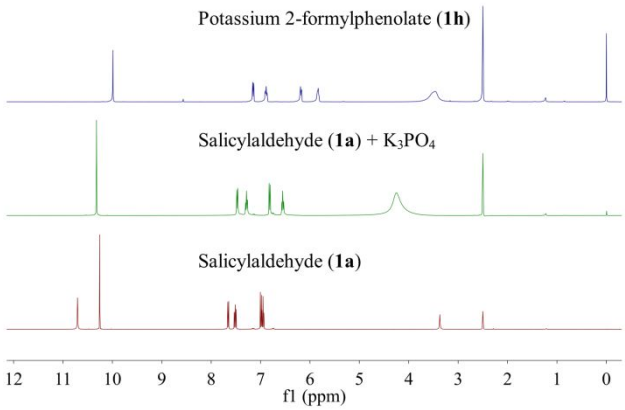


Figure 4. ^{1}H NMR of salicylaldehyde **1a**, **1a** + K_3PO_4, and **1h** in $(CD_3)_2SO$.

Time profile of the decarboxylative alkylation in different amount of salicylaldehyde **1a** was summarized in Figure 5. When the loading of **1a** increased, more **4j** was observed at the same reaction time.

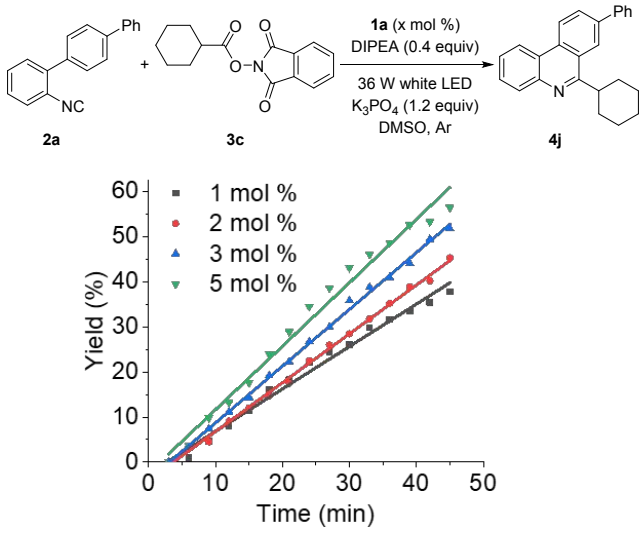


Figure 5. Time profile of the decarboxylative alkylation in different amount of salicylaldehyde **1a**. Reaction conditions: **2a** (0.25 mmol), **3c** (0.5 mmol), **1a** (x mol %), DIPEA (0.1 mmol), K_3PO_4 (0.3 mmol), DMSO (2.5 mL), ambient temperature (about 40 °C), 36 W white LEDs.

Kinetic study shows that the initial rate is first-order dependent on the concentration of salicylaldehyde **1a**, indicating that the deprotonated salicylaldehyde **1a** is catalytically active species in the reaction which involves the rate-determining step (Figure 6).

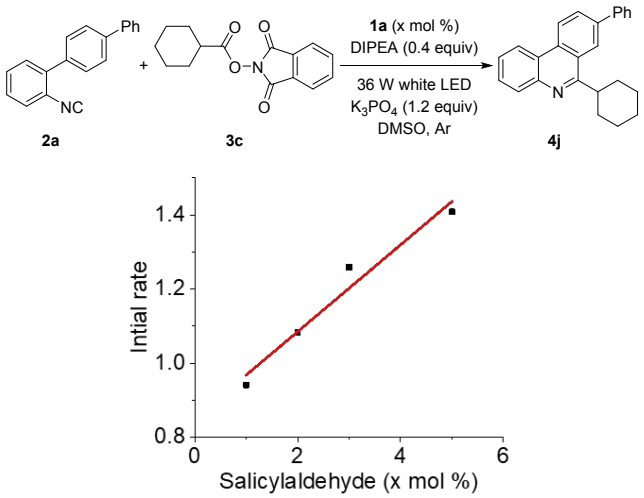


Figure 6. Kinetic study. Reaction conditions: **2a** (0.25 mmol), **3c** (0.5 mmol), **1a** (x mol %), DIPEA (0.1 mmol), K_3PO_4 (0.3 mmol), DMSO (2.5 mL), ambient temperature (about 40 °C), 36 W white LEDs.

Salicylaldehyde (**1a**) has a strong absorption band in the ultraviolet-visible range between 350-480 nm after deprotonation. The wavelength dependence experiment demonstrated the optimal wavelength and effective visible range for the decarboxylation alkylation reaction (Figure 7a). The apparent quantum efficiencies at 405, 430 and 450 nm were calculated to be between 40-50% (the calculation details see SI). The yields for **4a** under 405, 430 and 450 nm light irradiation were remained at a similar high level. Nevertheless, when the wavelength of light irradiation was longer than 520 nm, yields for **4a** decreased dramatically. The effective wavelength range is consistent with the absorption spectrum of deprotonated **1a**, further indicating that deprotonated **1a** was a good photosensitizer for the visible light induced decarboxylative reaction.

UV/visible absorption measurement was also performed (Figure 7b). The yield of **4a** decreases sharply when the wavelength is more than 450 nm. It is consistent with the UV/visible absorption spectra, indicating **1a** is an active catalyst in this reaction. Moreover, no absorption in the visible region was observed for **3a** or the combination of **3a** and DIPEA, proving the non-involvement of an EDA complex.

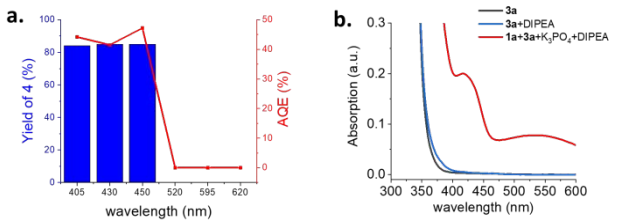


Figure 7. (a) Dependence of yields of **4a** (blue columns, left axis) on apparent quantum efficiency (AQE) (redline and hexagon symbol, right axis). Using standard reaction conditions for reaction of **2a** and **3a** stated in Table 1, entry 1 with wavelength indicated in the chart. Yields of **4a** were determined by ^{1}H NMR. (b) UV-Vis absorption spectra.

To provide further understanding of the effects of salicylaldehyde **1a**, we measured UV/visible absorption spectra of the other substituted sensitizers **1a-1h** (Figure 8). We performed the UV/Vis absorption measurement using a solution of the same concentration as the real reaction mixture. 4-Hydroxybenzaldehyde (**1c**), benzaldehyde (**1d**), 2-aminobenzaldehyde (**1e**), and *o*-anisaldehyde (**1f**) showed absorption features mostly in the region of less than 400 nm, even after deprotonation. This could explain the low reactivates in the presence of such aldehydes. In contrast, 3-hydroxybenzaldehyde (**1b**) and 2'-hydroxyacetophenone (**1g**) showed an obvious red-shifted absorption after deprotonation with K_3PO_4. An improvement in the yields was also observed (Table 2, entries 2, 7 vs 3-6). Therefore, both deprotonated α-hydroxyl group and formyl group in salicylaldehyde **1a** are essential for acting as a photosensitizer to harvest resonant photons from visible light.

We also measured the fluorescence quantum yield (Φ) of salicylaldehyde **1** and deprotonated **1** using quinine sulfate (Φ=0.55, quinine in 0.05 M sulfuric acid) as a standard (Table 4). The quantum yield for **1b-1g** is much less than that of **1a**. It further suggests that both α-hydroxyl group and formyl group in salicylaldehyde **1a** are essential for enabling it to work as a sensitizer in this reaction.

To evaluate the interaction between catalyst and reactant, we performed the fluorescence quenching experiment of deprotonated salicylaldehyde by NHPI ester **3a** (Figure 9a). The Stern-Volmer plot indicates that the excited state of the sensitizer was quenched by **3a** and the quenching effect of **3a** increased with its concentration. The same quenching effect was also observed using DMAc as solvent (Figure 9b). However, the excited state of the sensitizer could not be quenched by isonitrile **2a** (Figure 9c) (see the ESI for details). The reaction under UV irradiation via energy transfer suggests that the reaction occurs through the excited state (Scheme 3). All these results suggest that the reaction should be an energy transfer process.[23-25]

Catalytic model. Based on the experimental investigations discussed above, a tentative mechanism is proposed in Scheme 4. Initially salicylaldehyde **1a** is deprotonated by base, then it is activated by visible light to excited-state **1a*,** then energy transfer occurs to produce electronically excited NHPI ester **I** while simultaneously regenerating the ground state of 2-formylphenolate. After that, **I** is reduced by DIPEA to produce RCOOPht radical anion **II**. Then $NPhth^-$ and CO_2 are then released to provide alkyl radical **III**. **III** undergoes intermolecular addition with radical acceptor **3** to form radical intermediate **IV**, which attacks the phenyl group intramolecularly to give radical intermediate **V**. **V** can be oxidized to form cation **VI**. Ultimately, deprotonation of **VI** in the presence of base leads to the formation of target product **4**. We assume DIPEA works as an electron transfer reagent. When the reaction was performed in the absence of DIPEA, the deprotonated salicylaldehyde **1a** may be employed both a photo catalyst and an electron transfer reagent.

Evaluation of salicylaldehyde as photoredox catalyst in other reactions. The catalytic activity of **1a** was evaluated by comparing with the other known photosensitizers as demonstrated in Table 5. Transition metal complexes such as $Ru(bpy)_3Cl_2{\cdot}6H_2O$, $Ir(dtbpy)(ppy)_2PF_6$ or organic dye such as Rhodamine B or Eosin Y displayed similar catalytic reactivity, whereas a slightly higher yield was obtained by using **1a** (entries 2-5 vs entry 1). Simple ketones such as 2,3-butanedione and benzophenone are less effective catalyst (entries 6-7 vs

entry 1). A prolonged reaction improved the yield of **4a** to 95% (entry 8).

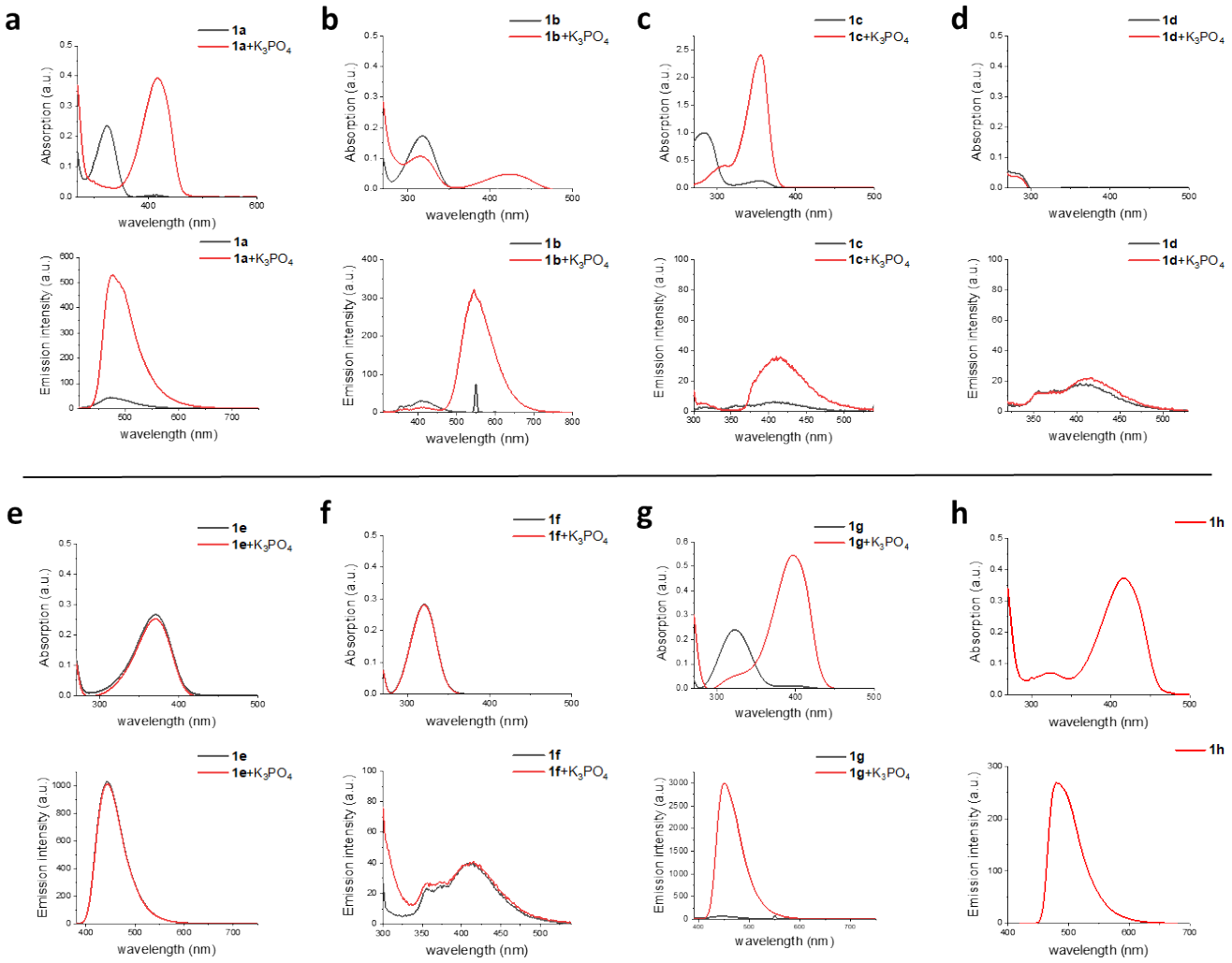


Figure 8. Absorption (up) and emission (below) spectra of aldehyde **1** and deprotonated **1** using K_3PO_4 as a base in DMSO (0.05 mM).

Table 4. Fluorescence Quantum Yield of 1a

1	Protonated			Deprotonated[a]		
	λ_{abs}/nm (ε)	λ_{em}/nm	Φ	λ_{abs}/nm (ε)	λ_{em}/nm	Φ
1a	325 (4320) 411 (540)	472	0.036822	417 (8600)	472	0.463201
1b	317 (3460)	411	0.026446	317 (2140) 424 (980)	516	0.036421
1c	284 (19860) 354 (2400)	403	0.025867	355 (47800)	411	0.039707
1d	–	406	0.040038	–	416	0.003980
1e	370 (5320)	443	0.196368	370 (5040)	444	0.194481
1f	320 (5660)	413	0.030045	320 (5580)	415	0.039567
1g	323 (4800)	–	0.033156	397 (10900)	487	0.008330
1h	–	–	–	417 (7460)	481	0.548555

[a] The measurement were done after the addition of K_3PO_4. The structure of **1** have been demonstrated in Table 2. ε refers to ε/dm^3 mol^{-1} cm^{-1}.

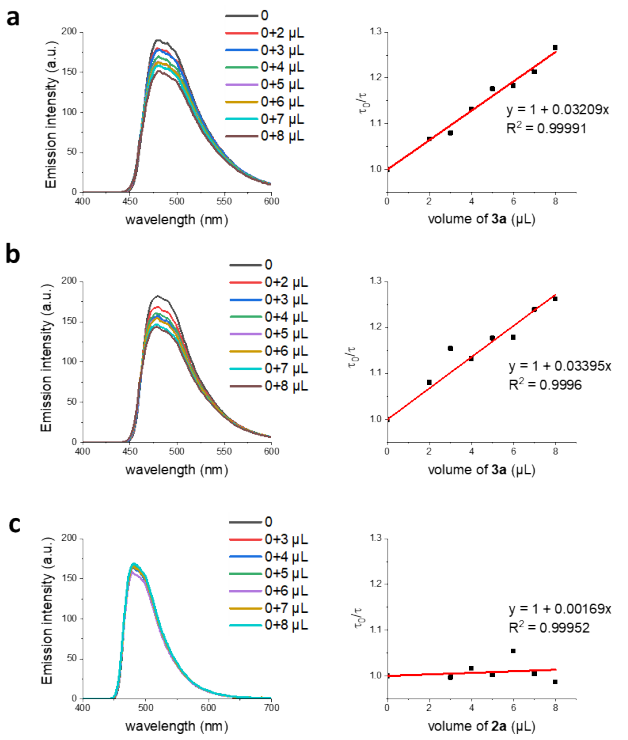
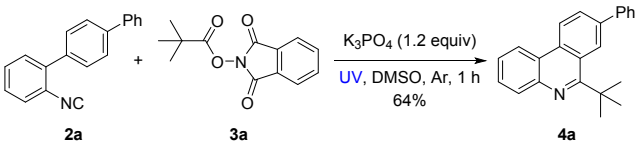


Figure 9. Stern-Volmer plot of catalyst and reactant. (a) Fluorescence quenching effect of catalyst by **3a** in DMSO. (b) Fluorescence quenching effect of catalyst by **3a** in DMAc. (c) Fluorescence quenching effect of catalyst by **2a** in DMSO.

Scheme 3. Reaction of 2a and 3a Directly under UV Irradiation



Applications of salicylaldehyde as photocatalyst. The synthetic potential of the salicylaldehyde catalyzed reaction was then studied. With the optimized conditions in hand, we first investigated the scope of **1a** catalyzed decarboxylative alkylations of substituted isocyanides **2**. As shown in Scheme 5, different substituted isocyanides were first subjected to the standard reaction conditions to react with *N*-hydroxyphthalimide ester **3a**. Both electron-donating and electron-withdrawing groups on the phenyl ring of isocyanides were well tolerated, and up to 99% isolated yields were obtained. Isocyanides bearing methyl and fluoro groups also produced the products (**4b** and **4i**) in good yields. 1-Adamantyl substituted *N*-hydroxyphthalimide ester **3b** was also employed to react with substituted isocyanides bearing either electron-donating or electron-withdrawing groups affording the desired products **4f-4i** in 77-89% yield. The reaction of 1-cyclohexyl substituted *N*-hydroxyphthalimide ester **3c** or 2-pyrrolidinyl substituted *N*-hydroxyphthalimide ester **3d** was also investigated.

Scheme 4. Proposed Mechanism

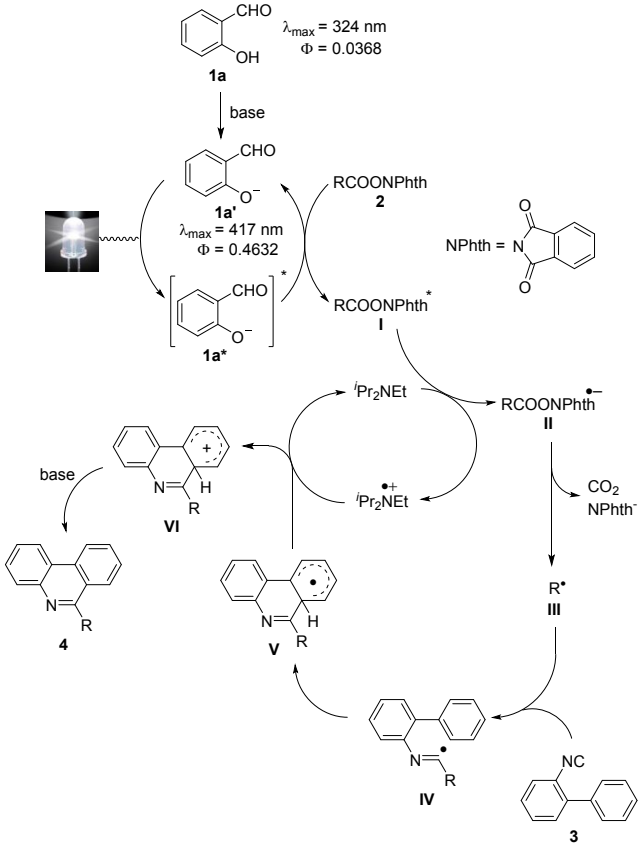
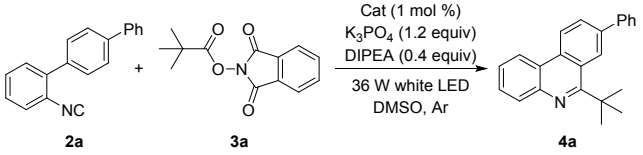


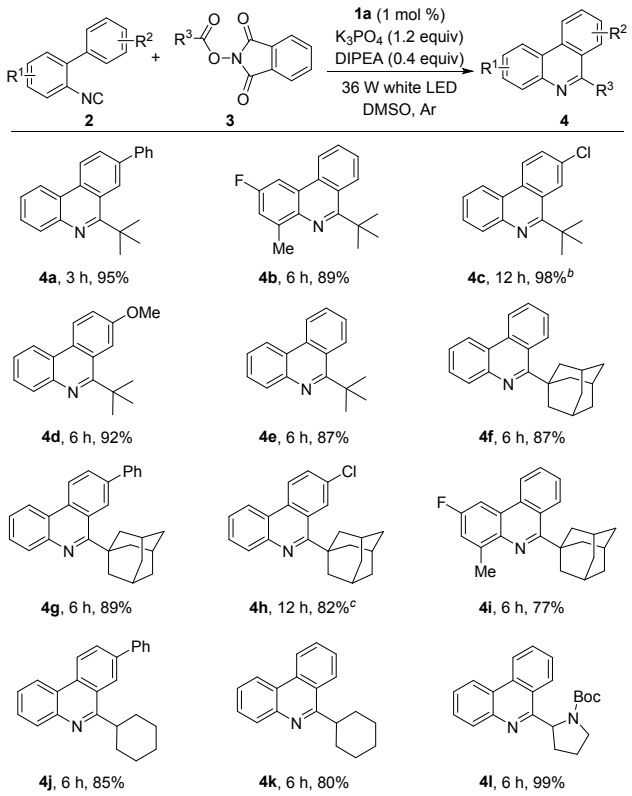
Table 5. Comparison of Common Photocatalysts



entry[a]	catalyst	yield(%)
1	Salicylaldehyde (**1a**)	86
2	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	79
3	$Ir(dtbpy)(ppy)_2PF_6$	78
4	Rhodamine B	62
5	Eosin Y	81
6	2,3-Butanedione	17
7	Benzophenone	15
8	Salicylaldehyde (**1a**)	95[b]

[a] Conditions: isocyanide **2a** (0.25 mmol), *N*-hydroxyphthalimide ester **3a** (0.5 mmol), catalyst (0.0025 mmol, 1 mol %), DIPEA (0.1 mmol), K_3PO_4 (0.3 mmol), DMSO (2.5 mL) for 1 h under argon; yields were determined by ^1H NMR. [b] Reaction was running for 3 h, isolated yield.

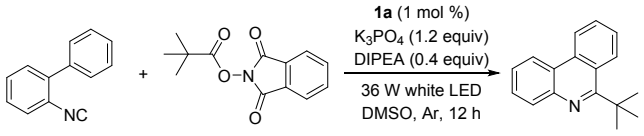
Scheme 5. Substrates Scope for Synthesis of 4[a]



[a] Reaction conditions: **2** (0.25 mmol), **3** (0.5 mmol), **1a** (0.0025 mmol, 1 mol %), DIPEA (0.1 mmol), K_3PO_4 (0.3 mmol), DMSO (2.5 mL), ambient temperature (about 40 °C) under argon, 36 W white LEDs, isolated yields. [b] 5 mol % catalyst. [c] 10 mol % catalyst.

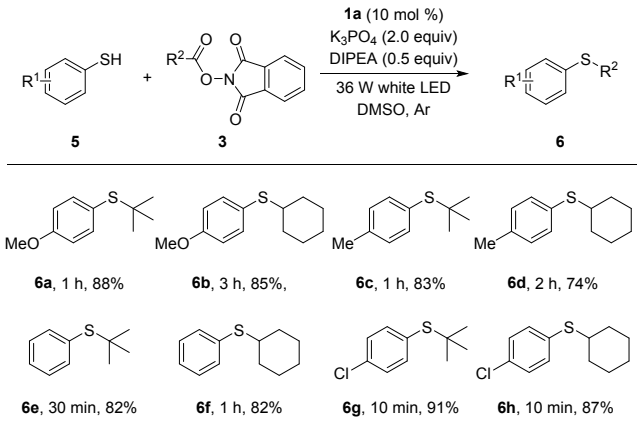
A gram-scale synthetic application with reaction of **2e** and **3a** was performed to demonstrate the potential utility of the salicylaldehyde catalyzed photo decarboxylative alkylation giving 1.64 g of alkylation product **4e** in 99% yield (Scheme 6).

Scheme 6. Gram scale Reaction



To further test the photocatalytic ability of **1a** in other transformations such as etherification reaction.[26-27] We first utilized **1a** to catalyze the photo-decarboxylative alkylations of substituted thiophenol derivatives **5** (Scheme 7). The light-induced alkylation of **5** with **3** catalyzed by **1a** proceeded smoothly. The reactions completed in 10 min to 2 h affording the desired alkylation products **6a-6i** in 74-91% yields. 10 mol % of **1a** is necessary in this reaction due to the decomposition of **1a** resulted from the acidity of thiophenol derivatives **5**.

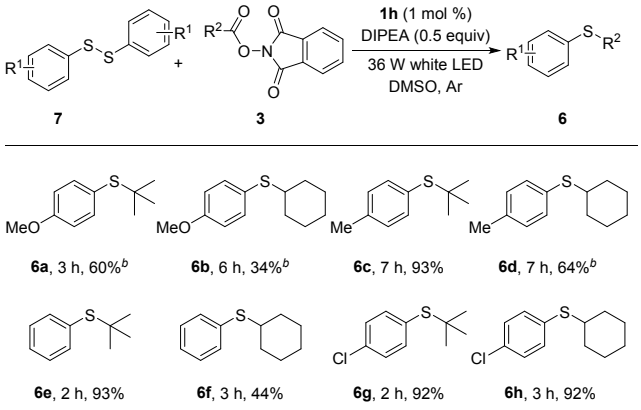
Scheme 7. Alkylations of Substituted Thiophenol Derivatives[a]



[a]Conditions: **5** (0.2 mmol), **3** (0.4 mmol), **1a** (0.02 mmol), DIPEA (0.1 mmol), K_3PO_4 (0.4 mmol), DMSO (2 mL), ambient temperature (about 40 °C) under argon, 36 W white LEDs.

On the other hand, the photocatalytic decarboxylative alkylations between disulfanes and *N*-hydroxyphthalimide esters remain unexplored.[21] Using 1 mol % of **1h** (deprotonated **1a**) as a photosensitizer, disulfanes **7** reacted with *N*-hydroxyphthalimide esters **3** under the irradiation of 36 W LED and the desired alkylation products **6a-6i** could be obtained in 34-93% yields (Scheme 8).

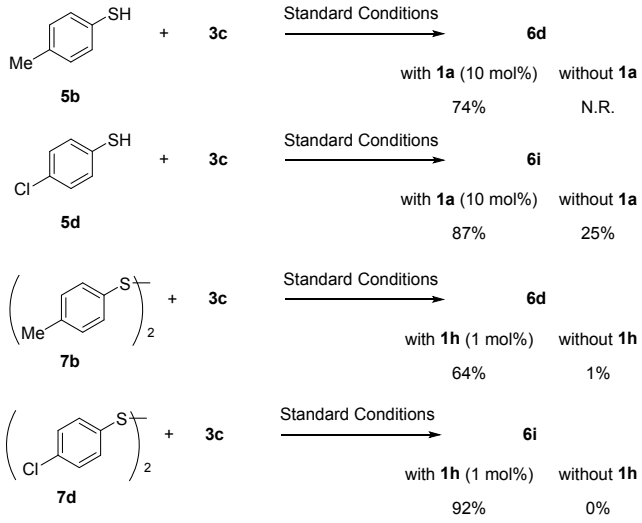
Scheme 8. Alkylations of Substituted Disulfane Derivatives[a]



[a]Conditions: **7** (0.3 mmol), **3** (0.2 mmol), **1h** (2 μmol), DIPEA (0.1 mmol), K_3PO_4 (0.4 mmol), DMSO (2 mL), ambient temperature (about 40 °C) under argon, 36 W white LEDs. [b]10 mol % catalyst.

Control experiments of reactions in the presence or absence of salicylaldehyde were also performed to investigate whether salicylaldehyde works as a photocatalyst in the above-mentioned decarboxylative alkylations (Schemes 7-8). As shown in Scheme 9, when the reaction was performed in the absence of **1a-K**, low conversion even no reaction were observed in both decarboxylative alkylations of substituted thiophenol derivatives and decarboxylative alkylations of substituted disulfane derivatives. Control experiments together with the results demonstrated above further demonstrates that deprotonated salicylaldehyde could work as an efficient visible light photocatalyst for decarboxylative alkylations in Schemes 7-8.

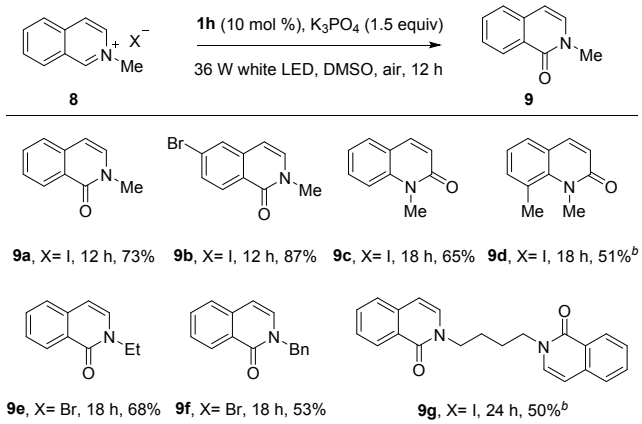
Scheme 9. Control Reactions[a]



[a]Conditions: **5** (0.2 mmol), **3** (0.4 mmol), **1a** (0.02 mmol), DIPEA (0.1 mmol), K_3PO_4 (0.4 mmol), DMSO (2 mL) or **7** (0.3 mmol), **3** (0.2 mmol), **1h** (2 μmol), DIPEA (0.1 mmol), K_3PO_4 (0.4 mmol), DMSO (2 mL), ambient temperature (about 40 °C) under argon, 36 W white LEDs.

Isoquinolones are important scaffolds exhibiting diverse biological and pharmaceutical activities. Preparation of isoquinolones from *N*-alkylpyridinium salts via visible light-mediated aerobic oxidation has been reported by used of Eosin Y as the organic photocatalyst.[28] Deprotonated salicylaldehyde **1h** was also applied in visible-light induced aerobic oxidation of *N*-alkylpyridinium salts to evaluate its catalytic activity (Scheme 10). The reaction proceeds smoothly under mild conditions and the desired isoquinolones **9** were obtained in good yields. This indicate that deprotonated salicylaldehyde could work as an efficient visible light photocatalyst in oxidation reactions as well.

Scheme 10. Aerobic Oxidation of *N*-Alkylpyridinium Salts[a]



[a] Conditions: **8** (0.2 mmol), **1h** (0.02 mmol), K_3PO_4 (0.3 mmol), DMSO (2 mL), ambient temperature (about 40 °C) under air, 36 W white LEDs. [b] 20 mol % catalyst.

CONCLUSION

Salicylaldehyde has been utilized as a low-cost and efficient photosensitizer for the visible light-mediated reactions for the first time. The decarboxylative alkylation reactions of *N*-hydroxyphthalimide esters proceed smoothly in the presence of catalytic salicylaldehyde under the visible-light irradiation affording desired alkylation products with up to 99% yields. Initial investigations suggest that the reactive radical species are generated by sensitization of the N-hydroxyphthalimide ester by deprotonated salicylaldehyde through an energy-transfer pathway. The strong red-shift absorption of deprotonated salicylaldehyde in UV-visible spectrum was observed, and this may explain the excellent photocatalytic activity of salicylaldehyde. The catalytic activity of deprotonated salicylaldehyde in visible-light photo catalysis has also been demonstrated by its application in the decarboxylative alkylations of substituted thiophenol derivatives or disulfane derivatives and aerobic oxidation *N*-alkylpyridinium salts.

EXPERIMENTAL SECTION

General Information. Solvents were predried by refluxing and distilling over CaH_2 (MeCN, DMF, DMSO, DMAc, toluene and DCE) or sodium (THF) or Mg/I_2 (EtOH) under argon atmosphere. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. UV-Vis spectrum was measured by UV-3600. Fluorescence emission spectrum was measured by F-4600 FL Spectrophotometer. The light source uses nine LED light bars that each have 4 W white LED beads. The bars were pasted on the inner wall of an aluminum hollow cylinder with an inner diameter of 9.5 cm. A fan was under the cylinder to control the temperature at 40 ± 2 °C. Photo of the device is available in the SI.

General procedures for NHPI ester. The alkyl carboxylic acid (10 mmol, 1.0 equiv), *N*-hydroxyphthalimide (10 mmol, 1.0 equiv) and DCC (10 mmol, 1.0 equiv) were mixed in a round-bottle with a magnetic stirring bar. EA (50 mL) was added. Then the mixture was stirred at room temperature. The reaction mixture was monitored by TLC. After completed, the white precipitate was filtered off and the solution was concentrated under vacuum. The product was purified by column chromatography on silica gel (petroleum ester/ethyl acetate as eluent).

General procedures for isonitrile. The amine (10 mmol, 1 equiv) and THF (20 mL) were added to a flask and the solution was cooled to 0 °C. Acetic formic anhydride (prepared from acetic anhydride (20 mmol, 2 equiv) with formic acid (20 mmol, 2 equiv) at r.t. for 1 h) was added dropwise to the reaction. After the addition was complete, the mixture was warmed to room temperature and stirred for 3 h. After that, the reaction was quenched with sat. aqueous $NaHCO_3$, and the mixture was extracted with EA (3 x 20 mL). The organic extract was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to give the formamide as a yellow powder. The material was used for next step without further purification.

THF (20 mL), Et_3N (60 mmol, 6 equiv) and the formamide were added to a flask and the solution was cooled to 0 °C. $POCl_3$ (15 mmol, 1.5 equiv) was added dropwise, and the mixture was stirred at room temperature after the addition was complete. The reaction mixture was monitored by TLC. After completed, the reaction was quenched with sat. aqueous Na_2CO_3, and the mixture was stirred for 1 h. The mixture was extracted with EA (3 x 20 mL). The organic extract was washed with brine, dried over Na_2SO_4 and the solvent was evaporated under reduced

pressure. The residue was purified by column chromatography on silica gel (petroleum ester/ethyl acetate as eluent).

General procedure 1. *N*-hydroxyphthalimide ester (0.5 mmol, 2 equiv), isocyanide (0.25 mmol, 1 equiv), DIPEA (0.1 mmol, 0.4 equiv), K_3PO_4 (0.3 mmol, 1.2 equiv) were weighed directly into a Schlenk tube (quartz) and then the solution of photocatalyst in DMSO (2.5 μmol in 2.5 mL, 1 mol %) was added. The mixture was degassed via three freeze-pump-thaw cycles, then stirred at room temperature under 36 W white LED for 3-24 hours. Upon completion, the product was purified by silica gel column (EtOAc/CH_2Cl_2/petroleum ester as eluent).

General procedure 2. *N*-hydroxyphthalimide ester (0.4 mmol, 2 equiv), benzenethiol (0.2 mmol, 1 equiv), DIPEA (0.1 mmol, 0.5 equiv), K_3PO_4 (0.4 mmol, 2 equiv) were weighed directly into a Schlenk tube (quartz) and then the solution of photocatalyst in DMSO (0.02 mmol in 2.0 mL, 10 mol %) was added. The mixture was degassed via three freeze-pump-thaw cycles, then stirred at room temperature under white LED for 10 minutes to 3 hours. Upon completion, the product was purified by silica gel column (petroleum ester as eluent).

General procedure 3. *N*-hydroxyphthalimide ester (0.2 mmol, 1 equiv), disulfane (0.3 mmol, 1.5 equiv), DIPEA (0.1 mmol, 0.5 equiv) were weighed directly into a Schlenk tube (quartz) and then the solution of photocatalyst in DMSO (2.0 μmol in 2.0 mL, 1 mol %) was added. The mixture was degassed via three freeze-pump-thaw cycles, then stirred at room temperature under white LED for 2-7 hours. Upon completion, the product was purified by silica gel column (petroleum ester as eluent).

General procedure 4. *N*-hydroxyphthalimide ester (0.2 mmol, 1 equiv), K_3PO_4 (0.3 mmol, 1.5 equiv) were weighted directly into a Schlenk tube and then the solution of photocatalyst in DMSO (0.02 mmol in 2.0 mL, 10 mol %) was added under air. The mixture was stirred at room temperature under white LED for 12-24 hours. Upon completion, the product was purified by silica gel column (EtOAc/CH_2Cl_2/petroleum ester as eluent).

*6-(tert-Butyl)-8-phenylphenanthridine **(4a)***. This compound was prepared by the general procedure 1, 74.1 mg, 95%, 3 h, white solid, m.p. 129-130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.85 (brs, 1H), 8.74 (d, J = 8.6 Hz, 1H), 8.55 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 1H), 8.16 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 1H), 8.03 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1H), 7.77-7.74 (m, 2H), 7.73-7.70 (m, 1H), 7.65-7.61 (m, 1H), 7.58-7.54 (m, 2H), 7.47-7.43 (m, 1H), 1.80 (s, 9H); ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ 166.9, 143.1, 141.0, 138.8, 133.2, 130.4, 129.3, 128.6, 128.5, 127.9, 127.6, 126.7, 124.8, 123.7, 123.4, 121.8, 40.4, 31.5. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{23}H_{22}N$ 312.1752, found 312.1752.[29]

*6-(tert-Butyl)-2-fluoro-4-methylphenanthridine **(4b)***. This compound was prepared by the general procedure 1, 59.4 mg, 89%, 6 h, white solid, m.p. 82-83 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (dd, J_1 = 8.5 Hz, J_2 = 0.6 Hz, 1H), 8.54 (dd, J_1 = 8.2 Hz, J_2 = 0.6 Hz, 1H), 7.97 (dd, J_1 = 10.3 Hz, J_2 = 2.8 Hz, 1H), 7.77 (ddd, J_1 = 8.3 Hz, J_2 = 7.0 Hz, J_3 = 1.3 Hz, 1H), 7.66 (ddd, J_1 = 8.4 Hz, J_2 = 7.0 Hz, J_3 = 1.4 Hz, 1H), 7.33-7.30 (m, 1H), 2.86 (s, 3H), 1.72 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.2 (d, J = 2.5 Hz), 162.0, 159.6, 141.5 (d, J = 2.5 Hz), 138.4, 134.0 (d, J = 4.3 Hz), 129.2, 128.2, 126.5, 124.5 (d, J = 9.5 Hz), 124.4, 123.5, 117.7 (d, J = 23.8 Hz), 104.2 (d, J = 22.9 Hz), 40.9, 31.2, 18.5. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{18}H_{19}NF$ 268.1502, found 268.1502.

*6-(tert-Butyl)-8-chlorophenanthridine **(4c)***. This compound was prepared by the general procedure 1, 66.2 mg, 98%, 12 h, 5 mol % catalyst, light yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60-8.58 (m, 2H), 8.45 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 1H), 8.13 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.74-7.69 (m, 2H), 7.62 (ddd, J_1 = 8.3 Hz, J_2 = 7.0 Hz, J_3 = 1.4 Hz, 1H), 1.73 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 165.7, 142.9, 132.5, 131.9, 130.5, 129.9, 128.8, 127.7, 127.0, 125.2, 124.8, 122.9, 121.6, 40.3, 31.2. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{17}H_{17}NCl$ 270.1050, found 270.1049.[29]

*6-(tert-Butyl)-8-methoxyphenanthridine **(4d)***. This compound was prepared by the general procedure 1, 60.9 mg, 92%, 6 h, light yellow solid, m.p. 155-156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59 (d, J = 9.1 Hz, 1H), 8.44 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 1H), 8.12 (dd, J_1 = 8.1 Hz, J_2 = 1.2 Hz, 1H), 8.0 (d, J = 2.6 Hz, 1H), 7.65 (ddd, J_1 = 8.3 Hz, J_2 = 7.0 Hz, J_3 = 1.4 Hz, 1H), 7.59 (ddd, J_1 = 8.3 Hz, J_2 = 6.9 Hz, J_3 = 1.4 Hz, 1H), 7.43 (dd, J_1 = 9.1 Hz, J_2 = 2.6 Hz, 1H), 4.00 (s, 3H), 1.75 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 165.8, 157.4, 142.2, 130.3, 128.3, 127.5, 126.6, 125.6, 124.6, 123.6, 21.2, 119.2, 109.8, 55.6, 40.2, 31.1. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{18}H_{20}NO$ 266.1545, found 266.1540.[29]

*6-(tert-Butyl)phenanthridine **(4e)***. This compound was prepared by the general procedure 1, 51.1 mg, 87%, 6 h, yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.70 (d, J = 7.9 Hz, 1H), 8.66 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 8.2 Hz, 1H), 8.17 (dd, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 1H), 7.81-7.77 (m, 1H), 7.75-7.70 (m, 1H), 7.68-7.61 (m, 2H), 1.77 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 166.7, 143.0, 134.1, 130.4, 129.4, 128.5, 128.4, 126.6, 126.1, 124.4, 123.5, 123.1, 121.7, 40.3, 31.3. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{17}H_{18}N$ 236.1439, found 236.1441.[29]

*6-Adamantanylphenanthridine **(4f)***. This compound was prepared by the general procedure 1, 68.2 mg, 87%, 6 h, white solid, m.p. 163-164 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.86 (d, J = 8.6 Hz, 1H), 8.69 (dd, J_1 = 8.3 Hz, J_2 = 1.3 Hz, 1H), 8.52 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 1H), 8.11 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H), 7.79-7.75 (m, 1H), 7.71-7.67 (m, 1H), 7.65-7.62 (m, 1H), 7.62-7.58 (m, 1H), 2.49 (d, J = 2.7 Hz, 6H), 2.23 (s, 3H), 1.96-1.87 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 166.1, 143.2, 134.1, 130.6, 129.2, 128.3, 128.0, 126.5, 125.7, 124.5, 123.3, 123.1, 121.7, 43.1, 42.1, 37.3, 29.4. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{23}H_{24}N$ 314.1909, found 314.1908.[30]

*6-Adamantanyl-8-phenylphenanthridine **(4g)***. This compound was prepared by the general procedure 1, 86.8 mg, 89%, 6 h, white solid, m.p. 214-215 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.10 (d, J = 1.5 Hz, 1H), 8.75 (d, J = 8.7 Hz, 1H), 8.55-8.53 (m, 1H), 8.13 (d, J = 7.4 Hz, 1H), 8.03 (dd, J_1 = 8.6 Hz, J_2 = 1.7 Hz, 1H), 7.78-7.76 (m, 2H), 7.72-7.68 (m, 1H), 7.64-7.60 (m, 1H), 7.58-7.55 (m, 2H), 7.47-7.43 (m, 1H), 2.54 (d, J = 2.5 Hz, 6H), 2.25 (brs, 3H), 1.92 (m, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 166.3, 143.3, 141.1, 138.4, 133.2, 130.4, 129.4, 128.5, 128.5, 127.8, 127.4, 126.7, 126.5, 124.9, 123.8, 123.3, 121.8, 43.2, 42.4, 37.4, 29.4. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{29}H_{28}N$ 390.2222, found 390.2210.

*6-Adamantanyl-8-chlorophenanthridine **(4h)***. This compound was prepared by the general procedure 1, 71.3 mg, 82%, 12 h, 10 mol % catalyst, white solid, m.p. 190-192 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.81 (d, J = 2 Hz, 1H), 8.60 (d, J = 8.9 Hz, 1H) 8.45 (d, J = 8.1 Hz, 1H), 8.12 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.73-7.69 (m, 2H), 7.63-7.59 (m, 1H), 2.45 (d, J = 2.6 Hz, 6H), 2.25 (brs, 3H), 1.96-1.88 (m, 6H); ^{13}C{^{1}H} NMR

($CDCl_3$, 100 MHz) δ 165.1, 143.1, 132.6, 131.7, 130.5, 129.8, 128.8, 127.5, 127.0, 125.3, 124.9, 122.8, 121.6, 43.1, 42.1, 37.2, 29.3. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{23}H_{23}NCl$ 348.1519, found 348.1512.

*6-Adamantanyl-2-fluoro-4-methylphenanthridine **(4i)***. This compound was prepared by the general procedure 1, 66.5 mg, 77%, 6 h, white solid, m.p. 214-216 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.84 (d, J = 8.5 Hz, 1H), 8.54 (d, J = 8.5 Hz, 1H), 7.96 (dd, J_1 = 10.3 Hz, J_2 = 2.4 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.31 (dd, J_1 = 9.1 Hz, J_2 = 1.9 Hz, 1H), 2.86 (s, 3H), 2.47 (m, 6H), 2.23 (brs, 3H), 1.95-1.87 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 163.6 (d, J = 3.0 Hz), 162.0, 159.6, 161.6 (d, J = 8.8 Hz), 138.5, 134.0 (d, J = 4.4 Hz), 129.1, 128.0, 126.2, 124.5, 124.3 (d, J = 9.5 Hz), 123.7, 117.7 (d, J = 23.3 Hz), 104.1 (d, J = 22.6 Hz), 43.7, 42.2, 37.4, 29.4, 18.5. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{24}H_{25}NF$ 346.1971, found 346.1969.

*6-Cyclohexyl-8-phenylphenanthridine **(4j)***. This compound was prepared by the general procedure 1, 71.6 mg, 85%, 6 h, white solid, m.p. 100-101 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.62 (d, J = 8.6 Hz, 1H), 8.48 (d, J = 7.5 Hz, 1H), 8.44 (d, J = 1.6 Hz, 1H), 8.13 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz 1H), 7.98 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1H), 7.72-7.71 (m, 2H), 7.70-7.66 (m, 1H), 7.59-7.55 (m, 1H), 7.54-7.50 (m, 2H), 7.44-7.40 (m, 1H), 3.66 (tt, J_1 = 11.4 Hz, J_2 = 3.1 Hz, 1H), 2.11-2.08 (m, 2H), 1.97-1.95 (m, 4H), 1.85-1.82 (m, 1H), 1.62-1.52 (m, 2H),1.47-1.41 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 165.5, 143.9, 140.9, 140.0, 132.1, 130.0, 129.3, 129.2, 128.5, 127.9, 127.6, 126.3, 125.1, 123.8, 123.3, 123.3, 122.0, 42.1, 32.4, 27.0, 126.4. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{25}H_{24}N$ 338.1909, found 338.1901.

*6-Cyclohexylphenanthridine **(4k)***. This compound was prepared by the general procedure 1, 52.3 mg, 80%, 6 h, yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.64 (d, J = 8.2 Hz, 1H), 8.53 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 1H), 8.32 (d, J = 8.3 Hz, 1H), 8.18 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H) 7.82-7.78 (m, 1H), 7.74-7.66 (m, 2H), 7.63-7.59 (m, 1H), 3.64 (tt, J_1 = 11.4 Hz, J_2 = 3.3 Hz, 1H), 2.13-2.10 (m, 2H), 2.03-1.86 (m, 5H), 1.65-1.55 (m, 2H), 1.52-1.45 (m, 1H);$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 165.4, 144.0, 133.1, 130.0, 130.0, 128.5, 127.1, 126.2, 125.7, 124.8, 123.4, 122.6, 121.9, 42.1, 32.4, 27.0, 26.4. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{19}H_{20}N$ 262.1596, found 262.1593.[30]

*tert-Butyl 2-(phenanthridin-6-yl)pyrrolidine-1-carboxylate **(4l)***. This compound was prepared by the general procedure 1, 86.1 mg, 99%, 6 h, white solid, m.p. 135-136 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.69-8.63 (m ,1H), 8.56-8.82 (m, 1H), 8.28-8.24 (m, 1H), 8.11-8.06 (m, 1H), 7.86-7.79 (m, 1H), 7.70-7.63 (m, 3H), 5.90-5.70 (m, 1H), 3.99-3.93 (m, 1H), 3.76-3.61 (m, 1H), 2.57-2.50 (m, 1H), 2.16-1.92 (m, 3H), 1.47 (s, 3H), 0.93 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 161.3, 154.8, 143.5, 133.2, 130.5 and 130.4, 130.3 and 130.2, 128.7 and 128.4, 127.3 and 127.2, 126.6 and 126.4, 125.4 and 125.1, 124.0 and 123.7, 122.8 and 122.7, 121.9, 79.1 and 78.9, 60.2 and 59.5, 47.2 and 47.1, 33.4 and 32.3, 28.7 and 28.1, 23.8 and 23.6. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{22}H_{25}N_2O_2$ 349.1916, found 349.1919.[18]

*tert-Butyl(4-methoxyphenyl)sulfane **(6a)***. This compound was prepared by the general procedure 2, 34.6mg, 88%, 1 h, colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.42 (m, 2H), 6.87-6.84 (m, 2H), 3.81 (s, 3H), 1.26 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 160.3, 139.0, 123.7, 114.1, 55.4, 45.6, 30.9.[31]

*Cyclohexyl(4-methoxyphenyl)sulfane **(6b)***. This compound was prepared by the general procedure 2, 37.8mg, 85%, 3 h, 15.1 mg, 34%, 6 h, colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.37 (m, 2H), 6.85-6.83 (m, 2H), 3.80 (s, 3H), 2.93-2.87 (m, 1H), 1.94-1.92 (m, 2H), 1.76-1.74 (m, 2H), 1.60-1.57 (m, 1H), 1.35-1.20 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 159.4, 135.7, 125.1, 114.4, 55.4, 48.0, 33.5, 26.2, 25.9.[32]

*tert-Butyl(p-tolyl)sulfane **(6c)***. This compound was prepared by the general procedure 2, 29.9mg, 83%, 1 h; This compound was prepared by the general procedure 3, 33.5 mg, 93%, 7 h, colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.41 (m, 2H), 7.15-7.13 (m, 2H), 2.36 (s, 3H), 1.28 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 138.9, 137.6, 129.4, 129.3, 45.7, 31.0, 21.4.[31]

*Cyclohexyl(p-tolyl)sulfane **(6d)***. This compound was prepared by the general procedure 2, 30.5mg, 74%, 2 h, colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.31 (m, 2H), 7.12-7.09 (m, 2H), 3.05-2.99 (m, 1H), 2.33 (s, 3H), 1.98-1.95 (m, 2H), 1.78-1.75 (m, 2H), 1.63-1.60 (m, 1H), 1.40-1.21 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 137.0, 132.9, 131.3, 129.6, 47.2, 33.5, 26.2, 25.9, 21.2.[32]

*tert-Butyl(phenyl)sulfane **(6e)***. This compound was prepared by the general procedure 2, 27.2mg, 82%, 0.5 h; This compound was prepared by the general procedure 3, 30.9 mg, 93%, 2 h, colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.55-7.53 (m, 2H), 7.37-7.33 (m, 3H), 1.29 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 137.6, 132.8, 128.8, 128.6, 46.0, 31.1.[32]

*Cyclohexyl(phenyl)sulfane **(6f)***. This compound was prepared by the general procedure 2, 31.6mg, 82%, 1 h, colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.38 (m, 2H), 7.29-7.25 (m, 2H), 7.25-7.18(m, 1H), 3.14-3.06 (M, 1h), 2.00-1.97 (m, 2H), 1.78-1.76 (m, 2H), 1.63-1.60 (m, 1H), 1.39-1.25 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 135.3, 132.0, 128.9, 126.7, 46.7, 33.5, 26.2, 25.9.[32]

*tert-Butyl(4-chlorophenyl)sulfane **(6g)***. This compound was prepared by the general procedure 2, 36.5mg, 91%, 10 min; This compound was prepared by the general procedure 3, 36.9 mg, 92%, 2 h, colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.44 (m, 2H), 7.31-7.29 (m, 2H), 1.27 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 138.8, 135.3, 131.4, 128.8, 46.3, 31.0.[33]

*(4-Chlorophenyl)(cyclohexyl)sulfane **(6h)***. This compound was prepared by the general procedure 2, 39.5mg, 87%, 10 min; This compound was prepared by the general procedure 3, 41.7 mg, 92%, 3 h, colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.31 (m, 2H), 7.26-7.24 (m, 2H), 3.06-3.05 (m, 1H), 1.97-1.94 (m, 2H), 1.78-1.76 (m, 2H), 1.63-1.59 (m, 1H), 1.34-1.29 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 133.8, 133.4, 132.8, 129.0, 47.0, 33.4, 26.1, 25.8.[32]

*2-Methylisoquinolin-1(2H)-one **(9a)***. This compound was prepared by the general procedure 4, 23.3 mg, 73%, 12 h, light yellow oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.43 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.51-7.46 (m, 2H), 7.07 (d, J = 7.3 Hz, 1H), 6.48 (d, J = 7.3 Hz, 1H), 3.61 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 162.7, 137.2, 132.5, 132.1, 127.7, 126.9, 126.2, 126.0, 106.1, 37.1.[24]

*6-Bromo-2-methylisoquinolin-1(2H)-one **(9b)***. This compound was prepared by the general procedure 4, 41.6 mg, 87%, 12 h, white solid, m.p. 152-154 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 28 (d, J = 8.6 Hz, 1H), 7.67 (d, J = 1.9 Hz, 1H), 7.57 (dd, J_1 = 8.6 Hz, J_2 = 1.9 Hz, 1H), 7.09 (d, J = 7.4 Hz, 1H), 6.39 (d, J = 7.3 Hz, 1H), 3.59 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100

MHz) δ 162.2, 138.6, 133.9, 130.1, 129.6, 128.3, 127.2, 124.8, 104.9, 37.2.[24]

*1-Methylquinolin-2(1H)-one (**9c**)*. This compound was prepared by the general procedure 4, 20.8 mg, 65%, 18 h, light yellow solid, m.p. 71-72 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65 (d, J = 9.5 Hz, 1H), 7.57-7.53 (m, 2H), 7.35-7.34 (m, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 9.5 Hz, 1H), 3.70 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 162.4, 140.1, 139.0, 130.7, 128.8, 122.2, 121.8, 120.7, 114.2, 29.5.[24]

*1,8-Dimethylquinolin-2(1H)-one (**9d**)*. This compound was prepared by the general procedure 4, 17.6 mg, 51%, 18 h, 20 mol % catalyst, light yellow solid, m.p. 70-71 °C; ^{1}H NMR ($CDCl_3$ 400 MHz) δ 7.61 (d, J = 9.4 Hz, 1H), 7.37-7.33 (m, 2H), 7.11 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 9.4 Hz, 1H), 3.83 (s, 3H), 2.72 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.6, 141.3, 140.0, 135.2, 127.4, 125.1, 122.6, 122.4, 121.1, 36.6, 24.1.[28]

*2-Ethylisoquinolin-1(2H)-one (**9e**)*. This compound was prepared by the general procedure 4, 23.6 mg, 68%, 18 h, light yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.44 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.51-7.46 (m, 2H), 7.07 (d, J = 7.1 Hz, 1H), 6.50 (d, J = 7.3 Hz, 1H), 4.01 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 162.0, 137.1, 132.1, 131.3, 127.8, 126.8, 126.4, 125.9, 106.3, 44.4, 14.7.[34]

*2-Benzylisoquinolin-1(2H)-one (**9f**)*. This compound was prepared by the general procedure 4, 24.9 mg, 53%, 18 h, light yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48-8.46 (m, 1H), 7.65-7.61 (m, 2H), 7.51-7.47 (m, 5H), 7.09 (d, J = 7.4 Hz, 1H), 6.48 (d, J = 7.4 Hz, 1H), 5.23 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 162.3, 137.1, 137.0, 132.3, 131.4, 128.9, 128.2, 128.1, 127.9, 127.0, 126.4, 126.0, 106.5, 51.8.[28]

*2,2'-(Butane-1,4-diyl)bis(isoquinolin-1(2H)-one) (**9g**)*. This compound was prepared by the general procedure 4, 34.5 mg, 50%, 24 h, 20 mol % catalyst, white solid, m.p. 201-203 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (d, J = 8.0 Hz, 2H), 7.63 (td, J_1 = 8.1 Hz, J_2 = 1.2 Hz, 2H), 7.51-7.46 (m, 4H), 7.08 (d, J = 7.3 Hz, 2H), 6.49 (d, J = 7.3 Hz, 2H), 4.09-4.06 (m, 4H), 1.89-1.85 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 162.3, 137.1, 132.2, 131.8, 127.9, 126.9, 126.3, 126.0, 106.4, 48.8, 26.4.[28]

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

Photo of the lamp and the reaction, Measurement of fluorescence quantum yield, Fluorescence quenching experiment, Calculation of apparent quantum efficiency (A. Q. E.), NMR spectra (PDF).

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Notes

The authors declare no competing financial interest.

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