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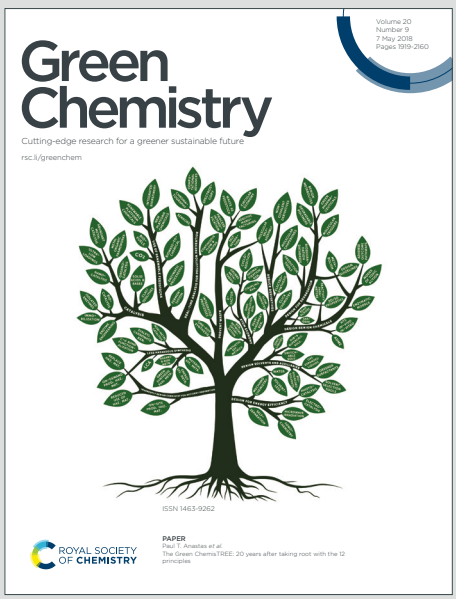

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ARTICLE

Hofmann reaction-involving annulation of *o*-(pyridin-2-yl)aryl amides selectively and rapidly leads to potential potocatalytic active 6*H*-pyrido[1,2-*c*]quinazolin-6-one derivatives

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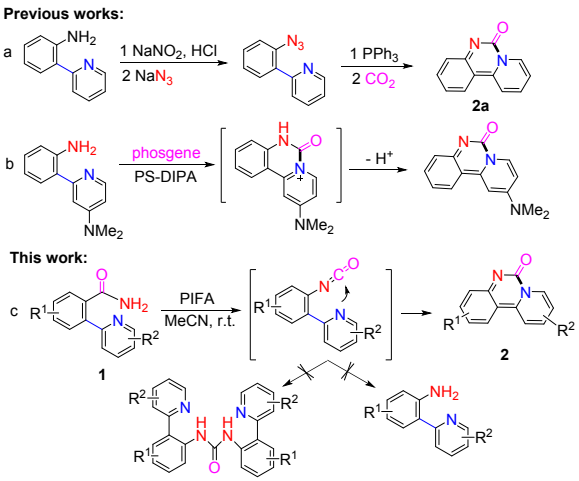
A highly efficient PIFA-mediated Hofmann reaction of *o*-(pyridin-2-yl)aryl amides has been developed to selectively and rapidly construct various potential potocatalytic active 6*H*-pyrido[1,2-*c*]quinazolin-6-ones. The use of nontoxic and eco-friendly organoiodine reagent, operationally simplicity, short reaction time and mild reaction conditions, broad substrate scope and high functional group tolerance, and excellent yields make this protocol very simple, practical, and easy to handle. It provides a feasible platform for developing novel organic fluorophore structures. Preliminary research for this purpose shows that the N^5-methylated pyridoquinazolinone **3a** could be used as a photocatalyst in several organic transformations, indicating it is a very promising lead fluorophore for developing new superior photocatalysts.

Introduction

Organic fluorophores are of great interest in diverse scientific fields like photocatalytic chemistry, materials science, and chemical biology due to their high sensitivity, structural versatility, high chemical stability, good specificity, and synthetic accessibility.[1] Photocatalysis, which utilizes light as a clean energy source, has attracted considerable attention from green and synthetic chemists and gained prominence in orchestrating challenging organic transformations under mild reaction conditions.[1f-k] The conjugated organic dyes as cyanoarenes, xanthenes, and acridiniums have been utilized for metal-free photocatalysis,[2] which has demonstrated a high photocatalytic efficiency for both oxidation[3] and reduction reactions.[4] However, certain disadvantages of organic photocatalysts including low redox capacity, photobleaching, and limited light-responsive nature restrict their broad range of applications. Therefore, the discovery of new photocatalytic active organic fluorophores is still highly desirable for development of new class of organic photocatalysts.

6*H*-Pyrido[1,2-*c*]quinazolin-6-one (**2a**, Scheme 1) containing dentate *N* atom and rigid structure with *N*-embedded extended conjugated π-systems is a promising privileged skeleton for organic semiconductors and potential catalyst backbone. Pyridoquinazolinone **2a** was firstly synthesized by Molina in 1992 from *o*-(2-pyridinyl)aniline via sequential diazo-reaction, azidation, Staudinger reaction, and subsequent pyrido annelation with CO_2 (Scheme 1a).[5] Since then, the sole alternative method was proposed through an one-step reaction of toxic phosgene with *o*-(2-pyridinyl)aniline in the presence of polymersupported diisopropylamine (PS-DIA) (Scheme 2b).[6] Besides the environmentally unfriendly and health risks associated with use of phosgene, there are also major problems associated with its production and storage. To date, there are not convenient and practical approaches to diverse pyridoquinazolinone derivatives.



Scheme 1. Synthetic routes to pyrido[1,2-*c*]quinazolin-6-ones.

The discovery of new photocatlyst candidates belonging to this class is seriously restricted to the lack of readily available structurally diverse pyridoquinazolinoniun derivatives. So far, the structural improvements of pyridoquinazolinoniun and applications in photocatalysis have not been reported.

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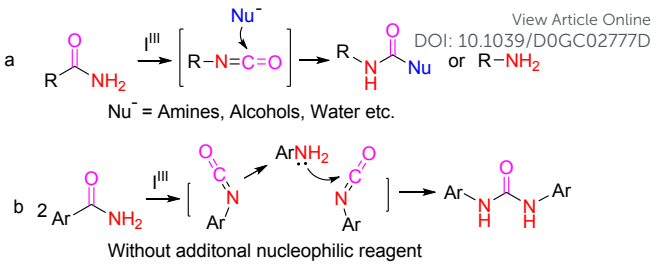
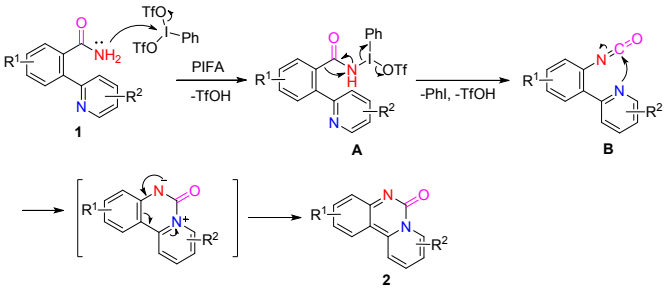
Practical and efficient methods of general synthetic applicability are therefore highly desirable. We report herein an efficient and straightforward method to rapid construct the diverse 6*H*-pyrido[1,2-*c*]quinazolin-6-one structures via a novel intramolecular Hofmann rearrangement reaction of readily available primary *o*-(pyridin-2-yl)aryl carboxamide mediated by a hypervalent organoiodine reagent bis-(trifluoroacetoxy) iodobenzene (PIFA) in mild conditions (Scheme 1c). These reactions were simply conducted by stirring a solution of amides and PIFA in CH_3CN at room temperature within 1 h to selectively produce a wide variety of 6*H*-Pyrido[1,2-*c*]quinazolin-6-one derivatives in excellent yields. The simple procedure, high chemoselectivity and excellent yields, short reaction time, mild reaction condition, and the use of nontoxic and environmentally benign hypervalent organoiodine reagent make this protocol very simple, practical, and easy to handle.

Results and discussion

Hypervalent organoiodine reagents (I^{III}) have been widely used in organic transformations, serving as advanced oxidants features of their nontoxicity, ready availability, environmentally benign and ease of handling characteristics.[7] And the I^{III}-promoted Hofmann rearrangements of amides for the construction of various *N*-containing functional organic molecules has been benefits for green synthetic chemistry, chemicobiology, and pharmaceutical chemistry etc.[8] In general, these processes afforded primary amines via Hofmann degradation by releasing carbonyl moiety, or generated urea and carbamate derivatives via a process of *N*-, *O*-nucleophilic attack to the *C* atom in the isocyanate group, which is an incomplete rearrangement intermediate forming from corresponding primary amides (Scheme 2a). To date, amines, alcohols, even water had been used as the nucleophiles in the Hofmann rearrangement involved cascade transformation via an inter- or intramolecular process. In the absence of additional nucleophilic reagent, however, the primary amides always generated symmetric urea derivatives with the amino group, which is generated in situ, serving as the nucleophile (Scheme 2b).[9] Accordingly, we envisioned that readily available primary *o*-(pyridin-2-yl)aryl carboxamide **1** mediated by a hypervalent organoiodine reagent (e.g. PIFA) might be give an iodoimidate intermediate **A** via an intermolecular nucleophilic attack of **1** to PIFA, then **A** rearrangement yielded isocyanate **B** by losing a molecule PhI and TfOH. Next, ring closure of **B** via an intramolecular nucleophilic attack of the pyridyl N atom to the *C* atom of isocyanate group and the electron reorganization might give pyridoquinazolinones **2** (Scheme 3). The aromaticity of the extended conjugated π-systems **2** might provide a means for driving the selective formation of **2** instead of the formation of corresponding amines and ureas.



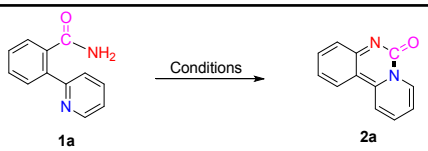
Scheme 2. I^{III}-promoted Hofmann reactions of amides.



Scheme 3. Proposed mechanism.

In recent years, we concerning on the hypervalent organoiodine compounds promoted the construction of the *N*-containing fused-heterocycles.[10] These ring closure procedures proceeded generally in high yield and allowed to access various *N*-containing five-, six-membered fused or spiro-heterocycles. Based on our experiences with hypervalent iodine reagents-promoted oxidative coupling reactions, we began our evaluation with *o*-(pyridin-2-yl)benzamide (**1a**) as a model substrate (Table 1), which was readily prepared by Suzuki reaction and nitrile hydrolysis,[11] and a series of hypervalent organoiodine reagents were first investigated. To our delight, the desired product **2a** was formed in 91% yield in the presence of 1.1 equiv of PIFA at room temperature after 30 min in MeCN solvent (entry 1). The experiment showed that upon reducing the PIFA loading from 1.1 equiv to 0.5 equiv, the yield of **2a** dropped from 91% to 66%, and **1a** was recovered in 30% (entry 2). It was found that the yield of **2a** was not significantly improved when we increased the PIFA loading from 1.1 equiv to 1.5 equiv (entry 3). Other organoiodine reagents including diacetoxyiodobenzene (III) (PIDA), iodosylbenzene (III) (PhIO), and 2-iodoxybenzoic acid (V) (IBX) were screened and they were found to be not as efficient as PIFA, especially for IBX which was ineffective to the transformation and 91% of substrate **1a** was recovered (entries 4-6). When the solvent was switched to THF, MeOH, DMSO, and DMF, product **2a** was obtained in lower yields (31-83%) than that in MeCN (entry 1 vs. 7-10). After screening, the optimal reaction conditions eventually emerged as **1a** (0.2 mmol) and PIFA (1.1 equiv) in MeCN (2 mL) at room temperature.

Table 1 Optimization of the reaction conditions[a]

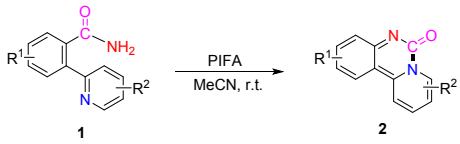


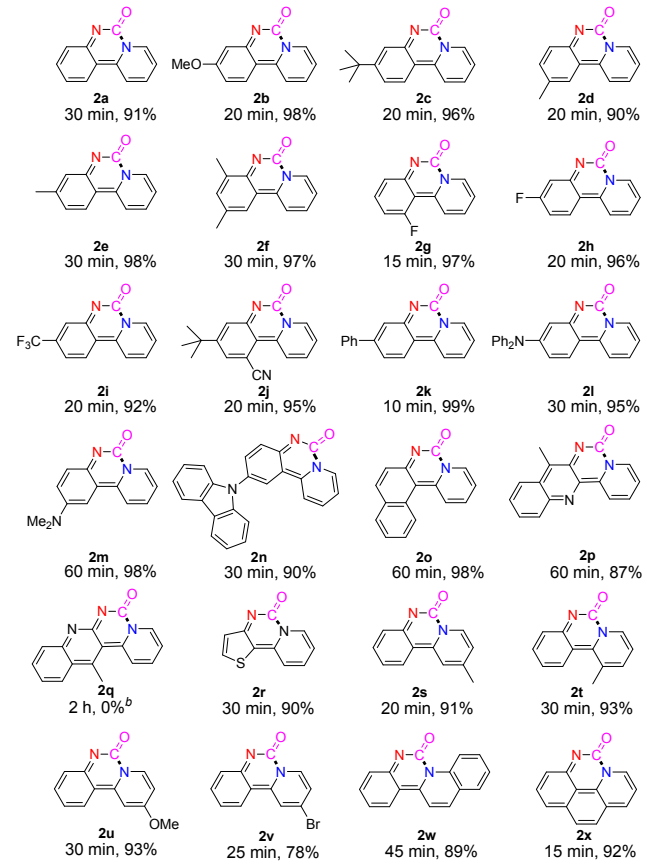
Entry	Catalyst (equiv)	Solvent	Yields[b] of **2a** /%	**1a** (Recovery)
1	PIFA (1.1)	MeCN	91	0
2	PIFA (0.5)	MeCN	66	30
3	PIFA (1.5)	MeCN	92	0
4	PIDA (1.1)	MeCN	53	30
5	PhIO (1.1)	MeCN	56	35
6	IBX (1.1)	MeCN	trace	91
7	PIFA (1.1)	THF	83	0
8	PIFA (1.1)	MeOH	64	9
9	PIFA (1.1)	DMSO	70	0
10	PIFA (1.1)	DMF	31	55

[a]Reaction conditions: **1a** (0.2 mmol), PIFA (1,1 equiv), in MeCN (2 mL) at room temperature for 30 min. [b]Isolated yield of the pure product **2a**.

With the optimized conditions in hand (Table 1, entry 1), we investigated the substrate scope of this PIFA-promoted Hofmann rearrangement-involved tandem reaction (Table 2). Firstly, various R^1 substituents were investigated, and the results indicated that a number of functional groups including –Me, –OMe, –^{t}Bu, –CF_3, –F, –CN, –Ph, –$N(Ph)_2$, –$N(Me)_2$, and 9*H*-carbazol-9-yl at the 3-, 4-, 5-, and/or 6-positions were tolerated well to the reaction, regardless of the electronic effect. The target products **2b–n** were isolated in excellent to almost quantitative yields (90–99%). It is worth mentioning that there is a nitrile group in compound **2j**, which is useful for further derivatization. Compounds **2l** and **2n** bearing a *N*,*N*-diphenyl group and 9*H*-carbazol-9-yl, respectively, should be especially popular with people who are engaged in optoelectronic materials. To our delight, α-pyridyl-β-naphthamide **1o** also underwent well to produce polycyclic compound **2o** in 98% yields. Similarly, the reaction of aza- or thia-heteroaryl amides **1p** and **1r** gave corresponding products **2p** and **2r** in yields of 87% and 90%, respectively. However, compound **1q** failed to the desired product **2q** under the optimized conditions, and a complex mixture was observed. Compared with the starting materials **1p** and **1q**, the nitrogen atom at the *ortho*-position of primary amide group inhibited the Hofmann rearrangement process of **1q** obviously. Unfortunately, we don't know why such a small change on the substrate structure has so big impact on the reaction at present. Then, a limited diversity of R^2 substituents was tested due to the inherent limitations of substrate synthesis. Preliminary investigation indicated that the methyl substituted pyridyl (**2s** and **2t**), Methoxyl pyridyl (**2u**), bromopyridyl (**2v**), and quinoline group (**2w**) can be tolerated to the transformation. The substrates bearing an electron-donating group in pyridyl moiety (**1s**-**u**) gave corresponding products (**2s**-**u**) in excellent yields, which were obviously higher than that of the product bearing an electron-withdrawing bromo group (**2v**). To our delight, the expected product 5*H*-pyrido[1,2,3-*cd*]perimidin-5-one (**2x**) was obtained in 92% yield after 15 min when benzo[*h*]quinoline-10-carboxamide (**1x**) was used as the starting material.

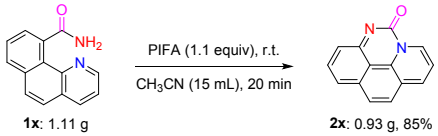
Table 2 Reaction extension[a]





[a]Reaction conditions: **1a** (0.2 mmol) and PIFA (1,1 equiv) in MeCN (2 mL) at room temperature under air atmosphere, isolated yield of the pure product **2**. [b]Complex mixture.

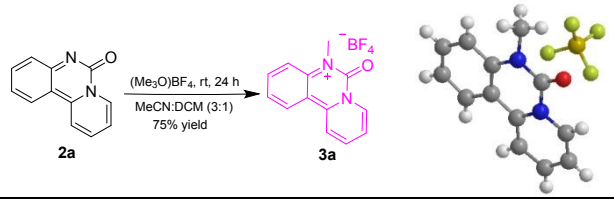
Furthermore, to demonstrate the productive practicability of this reaction, a gram-scale preparation of benzo[*h*]quinoline-10-carboxamide **2x** also got a satisfied result (Scheme 4).



Scheme 4. Gram-scale preparation of **2x**

The excitation and emission spectra for fluorescence compounds **2** were detrmined (Figure S2). As the basic backbone structure of pyridoquinazolinones **2**, **2a** was selected to investigate the potential applications in photocatalytic chemistry. Its fluorescence emission spectra were measured in MeCN at room temperature and shown in table 3. Upon excitation at 416 nm, linear *N*-embedded triacene **2a** emitted fluorescence in the green to yellow region (λ_{em} = 507 nm), and has an excited state lifetime τ (7.2 ns). Inspired by Fukuzumi's pioneering work of 9-mesityl-10-methylacridinium perchlorate[12] that has been utilized effectively in a variety of transformations,[3f,13] we initially considered introducing a methyl group at N^5 position of **2a** into a methylated pyridoquinazolinonium salt **3a** for improving its photocatalytic properties (Table 3). As depicted in table 3, 75% yield of **3a** was obtained when **2a** was reacted with $(Me_3O)BF_4$ in a mixed solvent of acetonitrile and dichloromethane (DCM). The structure of **3a** was unequivocally determined by single-crystal X-ray diffraction (Figure S1). Gratifyingly, **3a** has a longer excited state lifetime τ (9.4 ns), a positive excited state reduction potential ($E^*_{1/2}$ = +2.32 V vs SCE), and a negative ground state reduction potential ($E_{1/2}$(C/C−) = −0.65 V vs SCE) (Table 3), and show its comparability to the well-known 9-mesityl-10-methylacridinium perchlorate.

Table 3 The preparation of **3a** from **2a**[a] and their Photophysical Properties



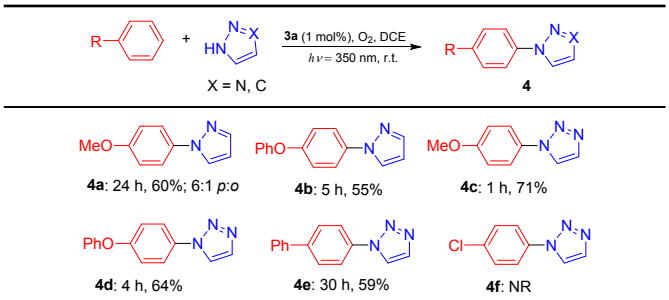
	$E_{1/2}(C^*/C^-)$[b] (V)	$E_{1/2}(C/C^-)$[c] (V)	τ (ns)	λ_{ex} (nm)	λ_{em} (nm)
2a	/	/	7.2	416	507
3a	**2.32**	**-0.65**	9.4	382	474

[a]Reaction conditions: **2a** (0.2 mmol) and $(Me_3O)BF_4$ (3.0 equiv) in MeCN/CH_2Cl_2 (2 mL) at room temperature. [b]Excited state reduction potentials were estimated from ground state redox potentials and the intersection of the absorption and emission bands. [c]Determined by cyclic voltammetry in acetonitrile versus saturated calomel electrode (SCE).

With these promising results in hand, we next investigated the photocatalytic reactivity of **3a** in several metal-free organic transformations.

Direct cross-coupling between arenes and heterocyclic amines under mild and metal-free conditions is undoubtedly important for C–N bonds formation. Selective C(sp2)-H amination under mild and metal-free conditions is more valuable and challenge.[14] Recently, Nicewicz reported an acridinium photocatalyst-promoted site-selective amination of aromatics with heteroaromatic azoles, without the need for prefunctionalization of the aromatic component.[14] In our initial investigations for photocatalysis activity of **3a**, we selected pyrazole and triazole as representative nucleophiles to conduct the cross couplings with substituted arenes. Under the conditions given in table 4, **3a** can effectively catalyze the oxidative C(sp2)-H amination of arenes bearing electron-donating groups gave good yields (**4a**-**4e**) but ineffective to electron-deficient arenes (e.g.**4f**).

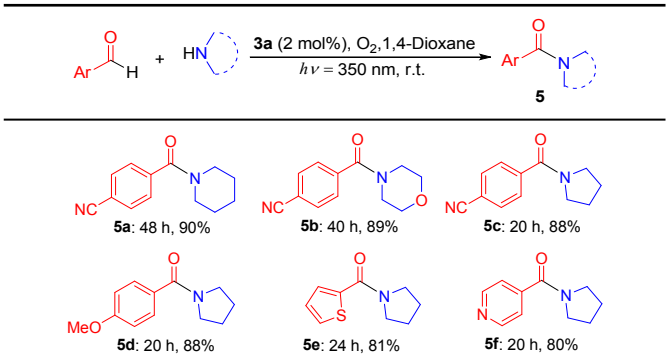
Table 4 Photocatalytic site-selective oxidative C–H/N–H cross-coupling between arenes and azoles[a]



[a]Reaction conditions: arenes (0.2 mmol), azoles (0.4 mmol) and **3a** (0.002 mmol) in dichloroethane (DCE, 2 mL) under O_2 atmosphere, irradiation by 350 nm cobalt lamps, isolated yield of the pure product **4.**

Traditionally, amides are prepared from the condensation of acylating agents with amines, which needs either coupling agents or conversion into more reactive derivatives. The direct oxidative addition of amines to aromatic aldehydes under mild and metal-free conditions provided a more economic and eco-friendly method for accessing amides.[15] Inspired by the good results of applying in oxidative cross-coupling between arenes and azoles, **3a** was applied for the oxidative cross-couplings between aromatic aldehydes and secondary amines (Table 5). To our delight, the aromatic aldehydes bearing electron-donating or withdrawing groups all underwent the direct amidation smoothly to give the desired amides in high yields (**5a–5f**, 80%–90%).

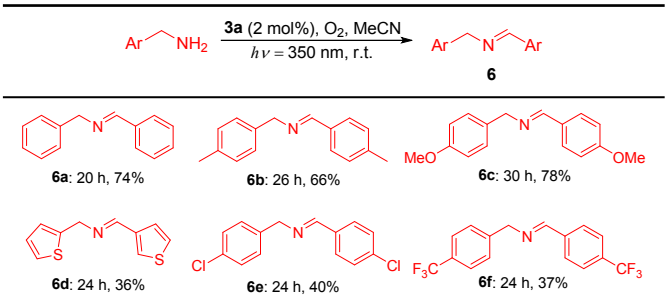
Table 5 Photocatalytic oxidative C–H/N–H cross-coupling between aryl aldehydes and amines[a]



[a]Reaction conditions: aryl aldehyde (0.2 mmol), amine (0.8 mmol) and **3a** (0.004 mmol) in dioxane (2 mL) under O_2 atmosphere, irradiation by 350 nm cobalt lamps, isolated yield of the pure product **5.**

The selective oxidation of benzylamine and its derivatives to imines, which are regarded as useful and active electrophilic intermediates for organic transformations, is an important laboratory and commercial procedure, and is often used as a model organic reaction for testing photocatalyst activity.[3h,16] The above results encouraged us to investigate the application of **3a** in the photocatalytic aerobic oxidative self-coupling of benzylamines under irradiation by 350 nm cobalt lamps. Under the conditions given in table 6, **3a** is effective to the selective oxidations to give the desired imines in moderate to good yields (**6a–6f**, 37%–78%).

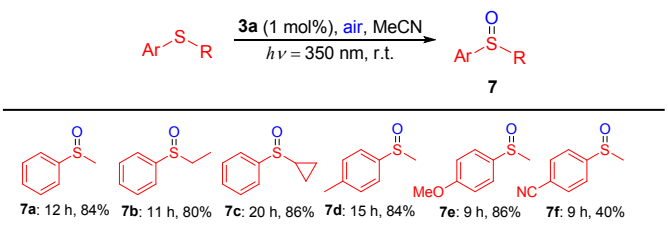
Table 6 Photocatalytic oxidative self-couplings of benzylamines[a]



[a]Reaction conditions: benzylamines (0.2 mmol) and **3a** (0.004 mmol) in MeCN (2 mL) under O_2 atmosphere, irradiation by 350 nm cobalt lamps, isolated yield of the pure product **6.**

Photocatalytic selective oxidation of thioethers into sulfoxides without using additives was the most straightforward, environmentally friendly, atom-economical approach to sulfoxides.[3h,17] To further investigate its photocatalytic activity, **3a** was subjected to the sulfides transformation. Under the conditions given in table 6, **3a** could effectively catalyze the sulfide transformation with excellent selectivity without obtaining the unwished sulfone caused by overoxidation. Various thioether substrates bearing methyl, ethyl, cyclopropyl, and methoxy functionalities could be selectively oxidized with high yields (**7a–7e**, 80%–86%), except for the substrate bearing a strong electron-withdrawing cyano group which was converted to sulfoxide **7f** with a moderate yield.

Table 7 Photocatalytic selective oxidation of sulfides[a]



[a]Reaction conditions: thioether (0.2 mmol) and **3a** (0.002 mmol) in MeCN (2 mL) under air atmosphere, irradiation by 350 nm cobalt lamps, isolated yield of the pure product **7.**

Experimental

General information. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400/600 MHz NMR spectrometer (^{1}H NMR, 400/600 MHz; ^{13}C NMR, 100/150 MHz at 25 °C). Coupling constants are reported in Hz. All high-resolution mass spectra (HRMS) were measured on a mass spectrometer (ESI-oa-TOF). All reagents were purchased from commercial sources and used without further treatment. All reactions were monitored by thin layer chromatography (TLC).

General procedure for synthesis of compound 2 (**2a** as an example)**.** To a round-bottom flask (25 mL) was added **1a** (39.6 mg, 0.2 mmol), PIFA (94.6 mg, 0.22 mmol), the reaction was allowed to stir for 30 min in CH_3CN (2 mL) at room temperature until completion. The reaction mixture was treated with saturated $NaHCO_3$ solution (5 mL), and extracted with DCM (3×10 mL). The combined organic layer was dried over anhydrous $MgSO_4$, and concentrated on a rotary evaporator. The crude product was further purified by recrystallized with ethyl ether to produce the desired **2a** as a yellow solid (35.6 mg, 91%).

Preparation procedure of compound 3a. To a round-bottom flask (25 mL) was added **2a** (59.0 mg, 0.3 mmol), $(Me_3O)BF_4$ (133.0 mg, 0.9 mmol), the reaction was allowed to stir for 24 h in a mixed solvent of CH_3CN and DCM (3 : 1, 3 mL) at room temperature until completion. The reaction was quenched with water (10 mL), and extracted with DCM (3×15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and concentrated on a rotary evaporator. The crude product was further purified by recrystallized with ethyl ether to produce the desired **3a** as a yellow solid (67.0 mg, 75%).

General procedure for synthesis of compound 4-7 (**4d** as an example)**.** In a sealed quartz tube with a magnetic stir bar were placed anisole (21.6 mg, 0.2 mmol), 1*H*-1,2,3-triazole (27.6 mg, 0.4 mmol), **3a** (0.6 mg, 0.002 mmol), and DCE (2 mL) under O_2 atmosphere. The reaction was stirred for 10 h under the irradiation by 350 nm cobalt lamps at room temperature. TLC was used to monitor the progress of the reaction. After the reaction was complete, the reaction mixture was concentrated and the crude product was further purified by column chromatography (petroleum ether/ethyl acetate) to give the desired **4d** (24.8 mg, 71%).

Conclusions

In summary, we have developed an efficient and straightforward method to rapid construct the diverse 6*H*-Pyrido[1,2-*c*]quinazolin-6-ones in excellent yields under mild reaction conditions via a novel intramolecular Hofmann rearrangement reaction of readily available primary *o*-(pyridin-2-yl)aryl carboxamide mediated by PIFA. The simple

procedure, high chemoselectivity and excellent yields, short reaction time, mild reaction condition, the use of nontoxic and environmentally benign hypervalent organoiodine reagent, and broad substrate scope and high functional group tolerance make this protocol very simple, practical, and easy to handle. Furthermore, the N^5-methylated derivative **3a** exhibits a good photocatalytic activity in the photocatalyses of site-selective oxidative C–H/N–H cross-coupling between arenes and azoles, oxidative C–H/N–H cross-coupling between aryl aldehydes and amines, oxidative self-couplings of benzylamines, and selective oxidation of sulfides. Further modifications on the promising pyrido[1,2-*c*]quinazolin-6-one structure to find novel photocatalysts with a superior activity are ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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