有机化学 DOI: 10.6023/cjoc202201025 研究论文
Chinese Journal of Organic Chemistry ARTICLE

光氧化还原催化串联自由基加成反应构建 1,4-二酮官能团化喹喔啉-2(1*H*)-酮衍生物

孙 鑫[†,a] 屈超凡[†,a] 马超蕊[a] 赵筱薇[a,b]
柴国璧*[,c] 江智勇*[,a,b]
([a]河南大学 河南省手性化学国际联合基地 开封 475004)
([b]河南师范大学化学化工学院 新乡 453007)
([c]中国烟草总公司郑州烟草研究院 烟草香料基础研究重点实验室 郑州 450001)

摘要 喹喔啉-2(1*H*)-酮的生物学重要性激发了开发高效简便合成方法学的持续追求. 其中, 对其 C3—H 官能团化已成为近年的研究热点, 尤其是利用光催化平台. 目前除了光催化产生的自由基直接加成喹喔啉-2(1*H*)-酮, 已有零星三组分串联反应策略被报道, 这一手段是基于烯烃优先接受自由基加成, 由所产生的自由基物种随后加成到喹喔啉-2(1*H*)-酮. 鉴于多组分反应能够有效丰富该化合物类型, 发展新的策略成为必然. 报道了 *α*-溴代芳基乙酮与喹喔啉-2(1*H*)-酮的光氧化还原催化反应, 用于构建重要的 1,4-二酮官能团化衍生物. 这是一个新的串联反应策略: 自由基首先加成到喹喔啉-2(1*H*)-酮, 所产生的中间体进一步接受溴代物产生的自由基加成或与溴代物发生 S_N2 反应.

关键词 可见光; 光氧化还原催化; 自由基加成; 串联反应; 2-羟基喹喔啉

Photoredox Catalytic Cascade Radical Addition to Construct 1,4-Diketone-Functionalized Quinoxalin-2(1*H*)-one Derivatives

Sun, Xin[†,a] Qu, Chaofan[†,a] Ma, Chaorui[a] Zhao, Xiaowei[a,b]
Chai, Guobi*[,c] Jiang, Zhiyong*[,a,b]
([a] *International Scientific and Technological Cooperation Base of Chiral Chemistry, Henan University, Kaifeng, Henan 475004*)
([b] *School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007*)
([c] *Key Laboratory of Tobacco Flavor Basic Research of China National Tobacco Corporation, Zhengzhou Tobacco Research Institute of China National Tobacco Corporation, Zhengzhou 450001*)

Abstract The biological importance of quinoxalin-2(1*H*)-ones has inspired increasing pursuit for the development of efficient and expedient synthetic methods to access these entities. Among them, C3—H functionalization of quinoxalin-2(1*H*)-ones has been a sought-after strategy in recent years, especially using photocatalysis platform to trigger radical intermediates. Besides the direct addition of photocatalysis-yielding radicals to 3-position of quinoxalin-2(1*H*)-ones, a handful of three-component cascade reactions have been described, wherein olefins were used to preferentially accept radicals to generate new radical intermediates to experience the second addition process. Given the robust ability of cascade strategy to enrich the varieties of quinoxalin-2(1*H*)-ones, the exploration of new protocols remains a highly attractive task. Herein, we report photoredox catalytic reactions of quinoxalin-2(1*H*)-ones with 2-bromo-1-arylethan-1-ones as the partners, leading to a series of valuable 1,4-diketone-functionalized quinoxalin-2(1*H*)-one derivatives with satisfactory results. This is an unprecedented cascade reaction strategy, involving radical addition to quinoxalin-2(1*H*)-ones and the resultant intermediates to accept a second addition of radicals generated from bromide substrates or to experience S_N2 reaction with bromides.

Keywords visible light; photoredox catalysis; radical addition; cascade reaction; quinoxalin-2(1*H*)-ones

* Corresponding authors. E-mail: chaigb@ztri.com.cn; jiangzhiyong@htu.edu.cn
Received January 17, 2022; revised January 26, 2022; published online January 28, 2022.
Project supported by the National Natural Science Foundation of China (No. 21925103) and the Young Elite Scientists Sponsorship Program by China Association for Science and Technology (No. 2017QNRC001).
国家自然科学基金(No. 21925103)和中国科协青年人才托举工程(No. 2017QNRC001)资助项目.
† 共同第一作者(These authors contributed equally to this work).

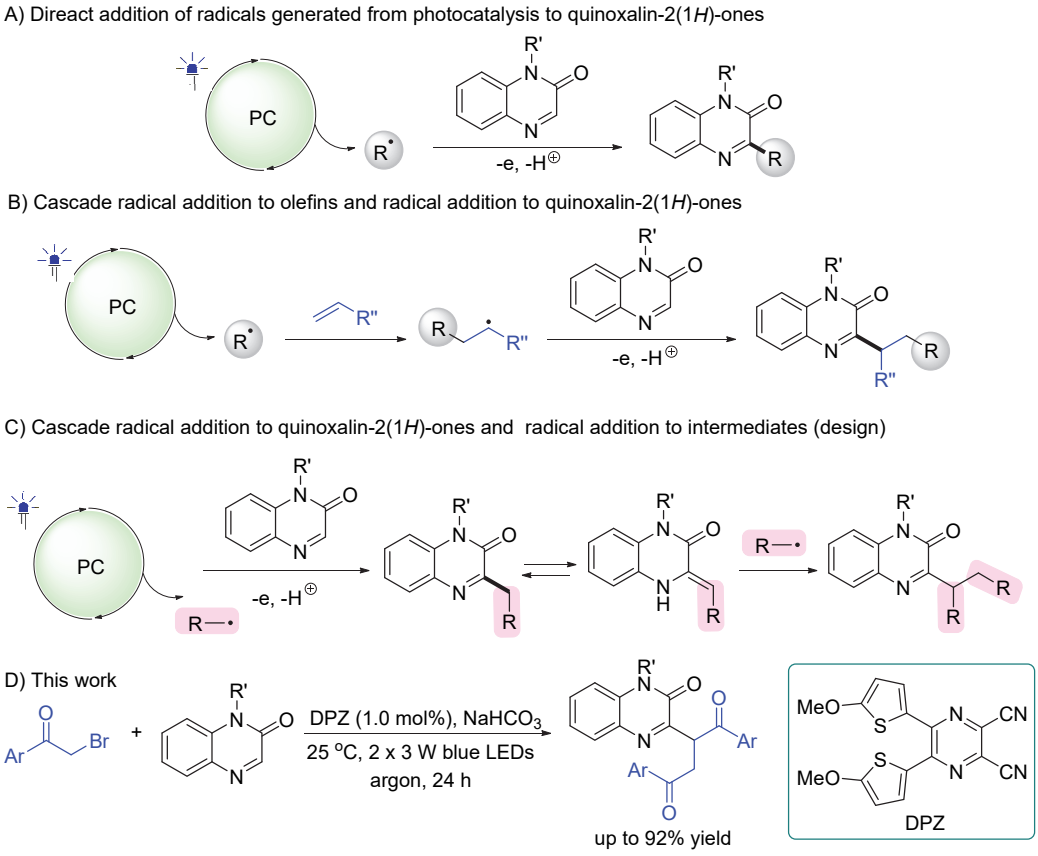
1 Introduction

Quinoxalin-2(1*H*)-ones that contain functional groups on the 3-position are a kind of attractive N-heterocyclic compounds due to their diverse significant biological activities.[1] In this context, the development of efficient and convenient methods to access these entities featuring known or new structures has attracted increasing attention of chemists. Among the numerous established protocols,[2-6] C3—H functionalization of quinoxalin-2(1*H*)-ones via visible-light-driven photocatalysis[7] has been appreciated as a powerful tool, given the ability to use simple and readily accessible feedstocks, the sustainable manner of producing radical species, mild reaction conditions and good functional group tolerance.[4-6] The most popular approach is the direct addition of radical species that are generated through photocatalysis to the 3-position of quinoxalin-2(1*H*)-ones (Scheme 1A).[5] A handful of three-component reactions by using alkenes to first accept the addition of radicals and manipulating the resultant radical intermediates to perform addition to 3-position of quinoxalin-2(1*H*)-ones have also been developed (Scheme 1B).[6] Inarguably, the cascade synthetic methods can effectively enrich the varieties of quinoxalin-2(1*H*)-one derivatives, thus providing more kinds of promising drug candidates to prompt the advance in pharmaceutical industry.[3c-3d,6] Accordingly, exploring new multi-component methodologies remains highly desirable.

As an extension of our current research interest towards photocatalytic synthesis of the important imine-containing azaarene derivatives,[7] we were intrigued in developing conceptually new cascade reaction strategies. We wondered whether the resultant *α*-methylene-containing products from radical addition to quinoxalin-2(1*H*)-ones could facilitate tautomerization to generate exocyclic olefins, thereby offering a chance to further experience radical addition (Scheme 1C). Mechanistically, to enable tautomerization, the substituent of methylene should be electron-deficient, which would lead to the foreseeable difficulty to both radical addition processes owing to the electrophilicity of alkyl radicals at *α* position of electron-withdrawing groups.

Herein, we demonstrate the viability of this scenario by using 2-bromo-1-arylethan-1-ones as the reaction partners of quinoxalin-2(1*H*)-ones (Scheme 1D). When in the presence of DPZ[7-8] as the photoredox catalyst and $NaHCO_3$ as base, the transformations produced an array of attractive 1,4-diketone-based quinoxalin-2(1*H*)-one variants in high yields.

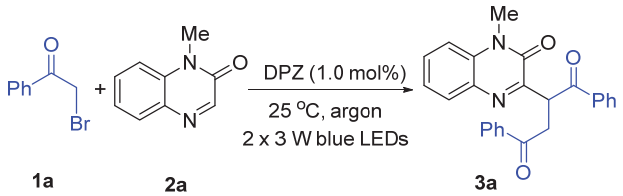
Our study began by selecting 2-bromoacetophenone (**1a**) and 1-methylquinoxalin-2(1*H*)-one (**2a**) as the model substrates (Table 1). Initially, the transformation was attempted by using 1.0 mol% dicyanopyrazine-derived chromophore (DPZ) and 3.0 equiv. of $NaHCO_3$ in 1.5 mL of CH_2Cl_2 as the solvent at 25 °C and under irradiation with two 3 W blue



Scheme 1 Development of photocatalytic strategies for the construction of quinoxalin-2(1*H*)-one derivatives

LEDs (Entry 1). To our delight, the desired product **3a** was obtained in 58% yield within 24 h. Notably, prolonging the reaction time to 36 h could not promote the yield (Entry 2). A variety of solvents were evaluated (Entries 3～6). It was found that no reaction was observed when tetrahydrofuran (THF) was used as the solvent (Entry 3). Other solvents with either the lower (Entry 4) or higher polarity (Entry 5) could not increase the yield. Moreover, methanol as protic solvent rendered **3a** in only 27% yield (Entry 6). Lowering concentration was found to make transformation more sluggish (Entry 7). To improve the reactivity, the equivalent of **1a** was increased to 4.0, but the yield of **3a** was decreased to 45% (Entry 8). The dilemma prompted us to test other inorganic bases, such as $KHCO_3$ (Entry 9) and Na_2CO_3 (Entry 10), but all yields were not satisfactory. In previous works, Brønsted acid was usually employed to promote chemical transformations of azaarene- based substrates. Hence, diphenylphosphate instead of $NaHCO_3$ was added into the reaction system (Entry 11). Disappointedly, roughly no product **3a** was obtained, suggesting the inapplicability of Brønsted acids. We had to attempt the effect of the amounts of $NaHCO_3$ to the reaction (Entries 12～14). As a result, the yield of **3a** was improved to 61% when 5.0 equiv. of $NaHCO_3$ was used (Entry 14).

Table 1 Reaction conditions optimizations[a]



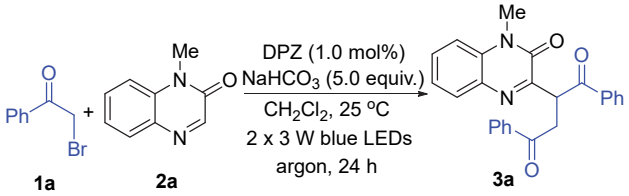
1a 2a 3a

Entry	Base (equiv.)	Solvent (mL)	*t*/h	Yield[b]%
1	$NaHCO_3$ (3.0)	CH_2Cl_2 (1.5)	24	58
2	$NaHCO_3$ (3.0)	CH_2Cl_2 (1.5)	36	55
3	$NaHCO_3$ (3.0)	THF (1.5)	24	N.R.
4	$NaHCO_3$ (3.0)	PhCl (1.5)	24	46
5	$NaHCO_3$ (3.0)	Ethyl acetate (1.5)	24	28
6	$NaHCO_3$ (3.0)	MeOH (1.5)	24	27
7	$NaHCO_3$ (3.0)	CH_2Cl_2 (3.0)	24	48
8[c]	$NaHCO_3$ (3.0)	CH_2Cl_2 (1.5)	24	45
9	$KHCO_3$ (3.0)	CH_2Cl_2 (1.5)	24	42
10	Na_2CO_3 (3.0)	CH_2Cl_2 (1.5)	24	44
11	Diphenylphosphate (1.0)	CH_2Cl_2 (1.5)	24	＜5
12	$NaHCO_3$ (1.0)	CH_2Cl_2 (1.5)	24	24
13	$NaHCO_3$ (2.0)	CH_2Cl_2 (1.5)	24	45
14	$NaHCO_3$ (5.0)	CH_2Cl_2 (1.5)	24	61

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.1 mmol). [b] Isolated yields. [c] 0.4 mmol of **1a** was used. N.R.＝no reaction.

To better understand the role of other important reaction parameters, several control experiments were performed (Table 2). First, the transformation was attempted without $NaHCO_3$, leading to **3a** in ＜10% yield (Entry 1). The poor yield was originated from the reaction being considerably sluggish. When in the absence of photosensitizer DPZ, roughly no **3a** was obtained, demonstrating the importance of DPZ to transformation proceeding (Entry 2). Evaluations towards both light source and the reaction atmosphere were subsequently carried out (Entries 3～4), and the results indicated that the visible light and the oxygen-free environment are indispensable to the success of the reaction.

Table 2 Evaluation of reaction conditions[a]



1a 2a 3a

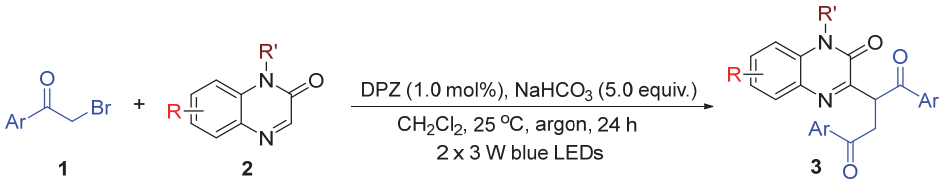
Entry	Variation from the standard conditions	Yield[b]%
1	No $NaHCO_3$	＜10
2	No DPZ	＜5
3	No light	N.R.
4	Under air	N.R.

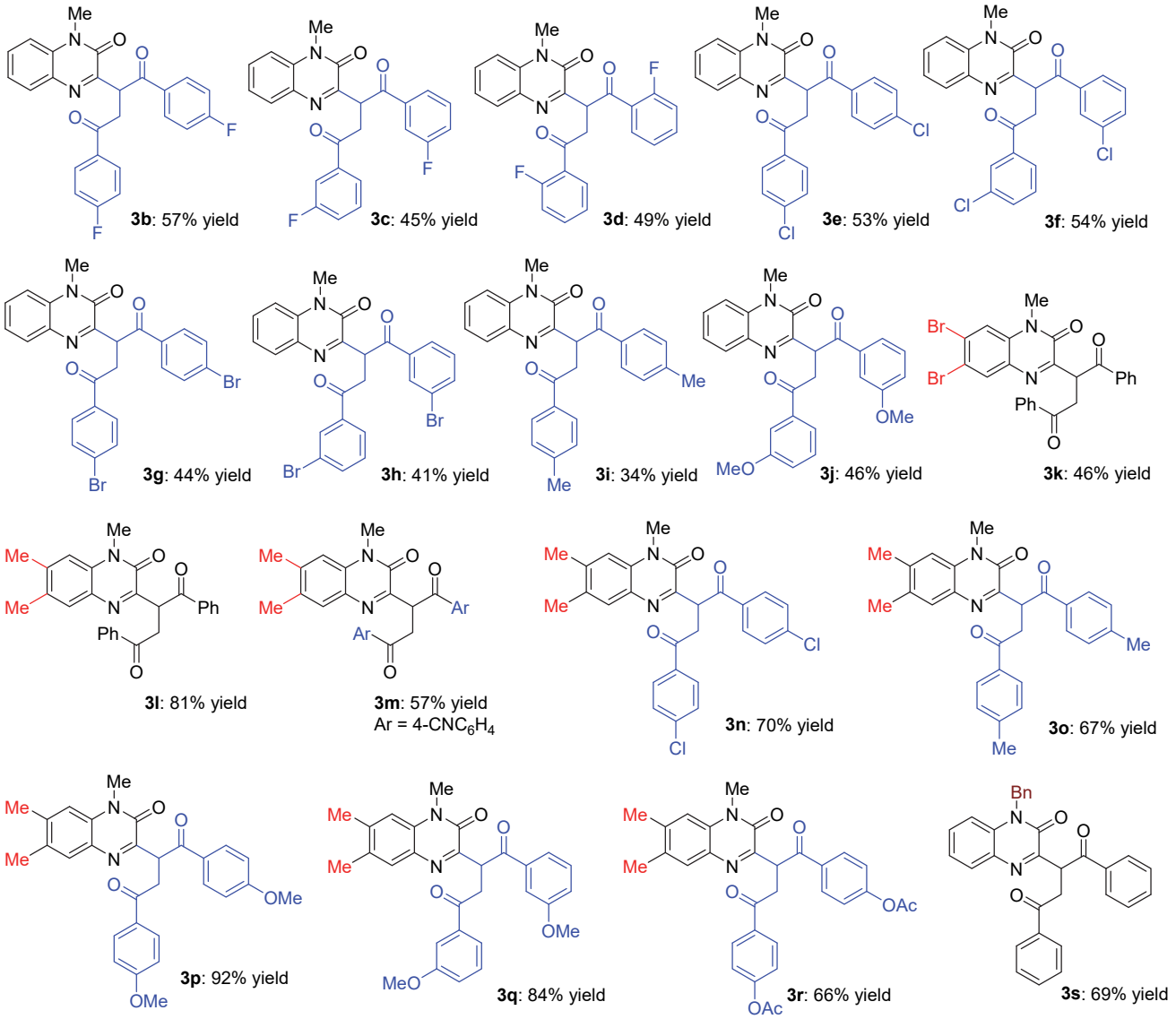
[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.1 mmol) in CH_2Cl_2 (1.5 mL). [b] Isolated yields.

With the optimal reaction conditions in hand, the scope of this tandem radical addition protocol was examined (Table 3). From the reactions of **2a** with diverse 2-bromo-1-arylethan-1-ones **1** that feature different substituents on the aryl rings, products **3b**～**3j** were obtained in 34%～57% yields. Notably, electron-withdrawing substituents offered slightly higher yields than electron-donating substituents, due to the higher reactivity. The substituent effect on the aromatic rings of 1-methylquinoxalin-2(1*H*)-ones was then evaluated. It was found that bromo as a representative of the electron-deficient groups (**3k**) presented moderate yield. However, quinoxalin-2(1*H*)-one containing 6,7-dimethyl groups led to adduct **3l** in good yield. The result prompted us to use such a quinoxalin-2(1*H*)-one substrate to react with distinct 2-bromo-1-arylethan-1-ones. A series of corresponding products **3m**～**3r** were obtained in 57%～92% yields, underscoring the generality of this method. The effect of *N*-substituent of quinoxalin-2(1*H*)-one was also evaluated. As a result, product **3s** with *N*-benyl was achieved in 69% yield. It is worth mentioning that other electron-withdrawing groups, such as esters and amides, instead of ketone **1** could not afford the corresponding adducts. Furthermore, when bromide of **1** was changed as chloride or iodine, the reaction became highly sluggish, and roughly no product was obtained.

Due to the high reactivity, the radical-based transformations are usually difficult to achieve precise chemoselectivity, thus compromising yields. In quite a few examples of our reactions, moderate and even poor yields were obtained, which are mainly stemmed from not chemoselectivity but reactivity. In these cases, roughly just one byproduct with a small amount was detected. As an example, in the reaction of producing **3a**, byproduct **4a** was isolated in only 4.2% yield, which was determined as an exocyclic olefin derivative (Scheme 2A). According to the structure, we speculated that such an olefin might be an intermediate

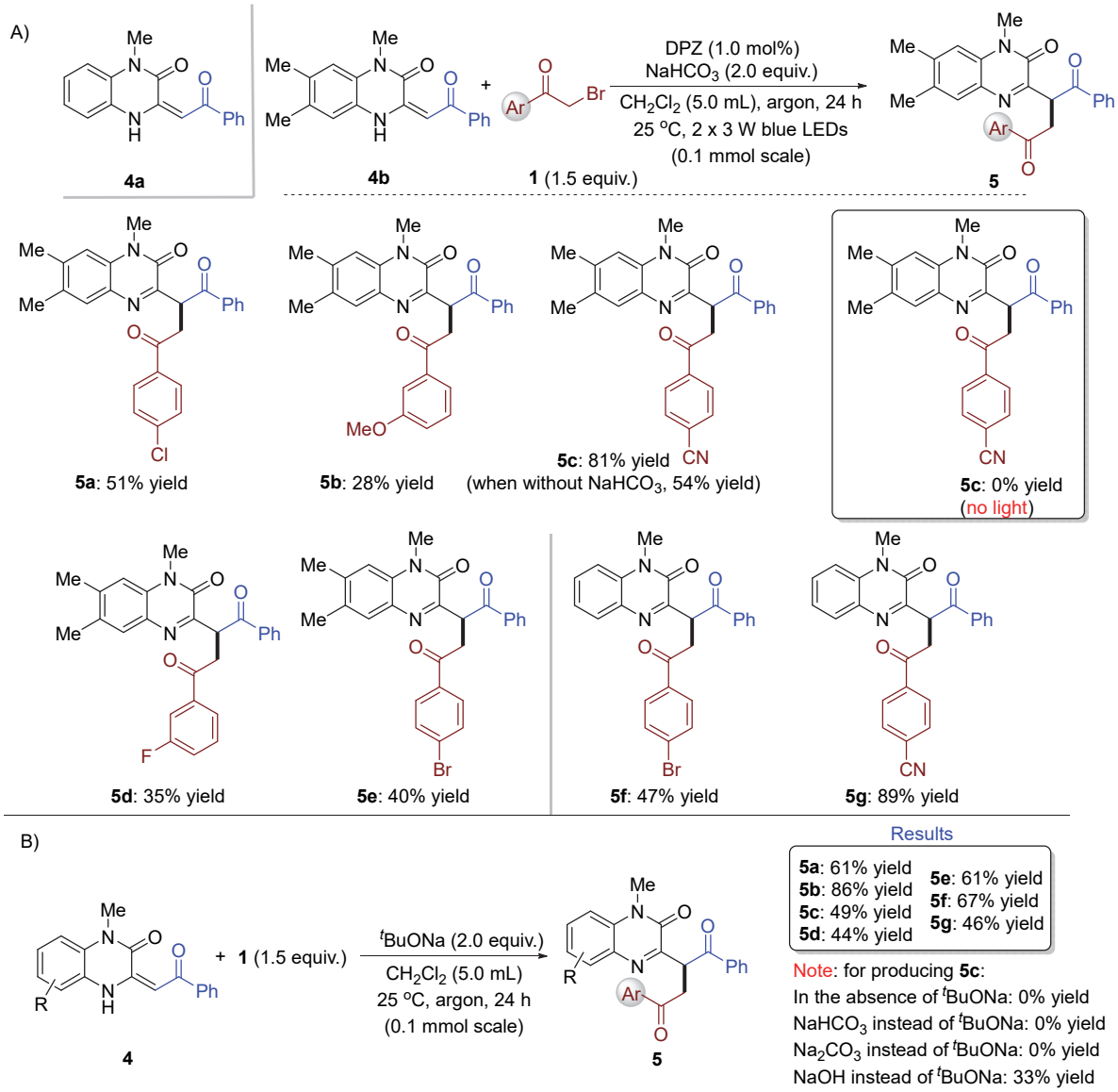
Table 3 Substrate scope [a]





[a] Reaction conditions: **1** (0.25 mmol), **2** (0.1 mmol) in CH_2Cl_2 (1.5 mL).

of the reaction. In this context, we attempted this reaction by changing the ratio of **1a** ∶ **2a** from 2.5 ∶ 1 to 1 ∶ 2 to attain **4a** in a larger amount. However, **3a** was obtained in 49% yield, and trace **4a** was still detected, likely due to high reactivity of the subsequent process. Then the viability of reaction between **4a** and bromides **1** was explored under the established reaction conditions wherein 2.0 equiv. of $NaHCO_3$ was employed as the acid-binding agent. Likely due to the considerably higher concentration of **4a** than alkyl radicals produced from bromides, several unknown by-products were observed. Nevertheless, trace desired diketone-based products were found, which prompted us to further evaluate the viability of **4b** given the good reactivity of the original reaction (see the result of product **3l**, Table 3). It is worth mentioning that **4b** was synthesized through the established method[9] but not isolated from the reaction of producing **3l**, since roughly no **4b** was found in the reaction system. To our delight, product **5a** was obtained from transformation of **4b** with 4-chlorophenacyl bromide in 51% yield when under the photoredox catalytic conditions. In view of two different aryls as the substituents of ketones in the structure of **5a**, we were intrigued in exploring the

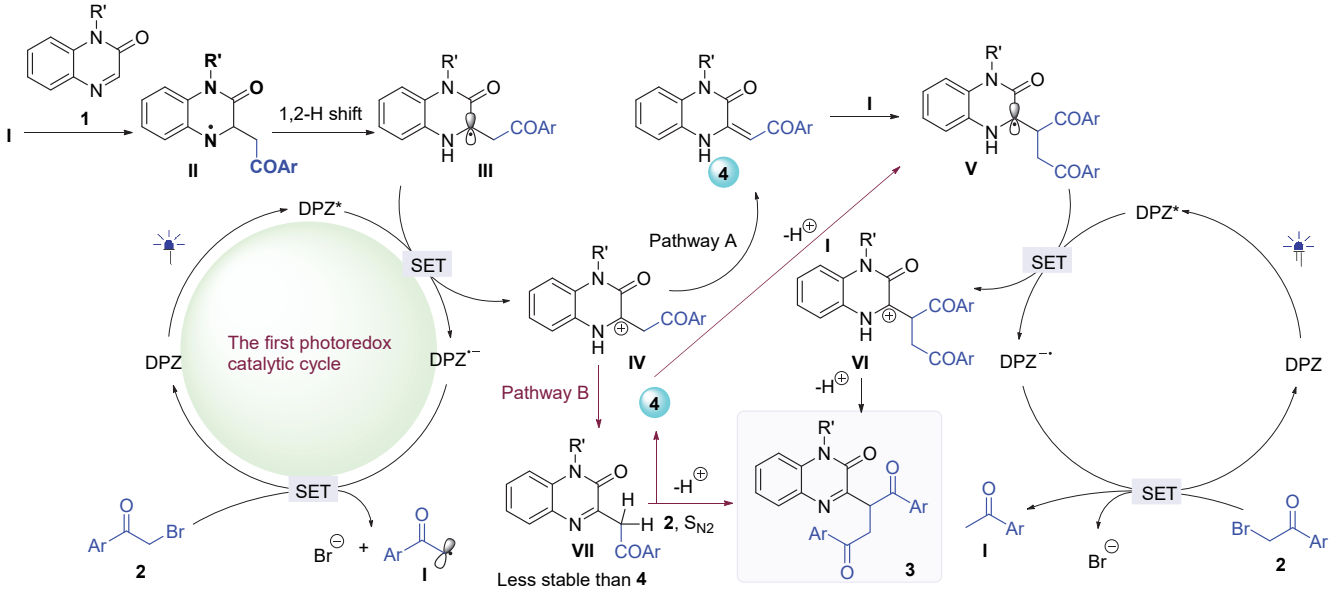


Scheme 2 Exploration of constructing unsymmetrical 1,4-diketone-functionalized quinoxalin-2(1*H*)-ones

substrate scope, to further enrich the patterns of such attractive quinoxalin-2(1*H*)-one variants. As a result, a series of the desired products **5b**～**5e** were obtained in 28%～81% yields. It is worth noting that in the absence of $NaHCO_3$, product **5c** was achieved in 54% yield, suggesting that the transformation could proceed even without inorganic base. In addition, visible light is crucial to the transformation, since no reaction was observed in the dark. Then transformations of **4a** with bromides **1** that contain strong electron-withdrawing groups (*e.g.*, Br and CN) were evaluated, leading to the corresponding products **5f** and **5g** in 47% and 89% yields, respectively.

Notably, olefins **4** are the isomers of methylene-substituted quinoxalin-2(1*H*)-ones (see the structure in Scheme 1C). Despite not detected in the reaction system, the strong electron-withdrawing ability of ketones would lead to facile isomerization of these methylene-containing compounds to **4**, thus offering a chance to experience S_N2 reaction with **1** to render products **3**. In this context, the reactions between **4** and **1** were carried out in the presence of 2.0 equiv. of sodium *tert*-butoxide (^{t}BuONa, Scheme 2B). It was found that corresponding products **5a**～**5g** were obtained in 44%～86% yields. When without such a strong inorganic base or using tremendously weaker bases such as $NaHCO_3$ and Na_2CO_3, no reaction was observed. Moreover, 33% yield of **5c** was obtained when using NaOH instead of ^{t}BuONa. The results suggested the viability of α-anions of ketones to experience S_N2 reaction with **1**.

Combined the results in Scheme 2 and Stern-Volmer experiments[10] with the previous reports,[6,11] a plausible mechanism was proposed. As depicted in Scheme 3, after addition of radicals **I**, that are generated from bromides **2** via single-electron reduction, to quinoxalin-2(1*H*)-ones, radials **II** are formed, which can further deliver radical species **III** via 1,2-H shift.[3c-3d,3l-3n,5a-5b] The subsequent single-electron oxidation of **III** by the photo-excited DPZ (*DPZ) leads to cations **IV**. Given the acidity of α-proton of ketones, exocyclic olefin intermediates **4** are readily prod-



Scheme 3 Proposed mechanism

uced (Pathway A). Under the sequential addition by radicals **I**, single-electron oxidation and deprotonation, products **3** are obtained. Certainly, given the probability of deprotonation of **IV** to furnish methylene-containing intermediates **VII** and the viability of S_N2 reaction between **VII** and bromides **1**, an ionic-based approach after the generation of cations **IV** is also possible (Pathway B).

3 Conclusions

In summary, a new photocatalytic cascade reaction strategy to access quinoxalin-2(1*H*)-ones has been developed. By using DPZ as a photoredox catalyst and $NaHCO_3$ as base, the transformations of 2-bromo-1-arylethan-1-ones with quinoxalin-2(1*H*)-ones could offer a series of structurally novel 1,4-diketone-based quinoxalin-2(1*H*)-one derivatives. Exocyclic olefins generated via the first radical addition of quinoxalin-2(1*H*)-ones are proposed as the intermediates, which can further accept the addition of the resultant *α*-ketone radicals from bromides via single-electron reduction. Furthermore, strong inorganic base enables S_N2 reaction of the intermediates with bromides. Two approaches could effectively improve the utility of the current method, which also represents two plausible pathways in the reaction system. We anticipate that this work would inspire more kinds of cascade reactions by exploiting this unprecedented strategy of assembling the versatile exocyclic olefin intermediates.

4 Experimental section

4.1 General procedures and methods

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. Reaction mixtures were stirred in 10 mL Schlenk tube with Teflon-coated magnetic stirring bars unless otherwise stated. Moisture in non-volatile reagents/compounds was removed in high *vacuo* by means of an oil pump and subsequent purging with nitrogen. Solvents were removed *in vacuo* under *ca.* 4.0 kPa and heated with a water bath at 30～35 ℃ using rotary evaporator with aspirator. The condenser was cooled with running water at 0 ℃.

All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, 60 F_{254}. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining 2,4-dinitrofenylhydrazine (DNP) and phosphomolybdic acid solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

Columns for flash chromatography (FC) contained silica gel 200～300 mesh. Columns were packed as slurry of silica gel in petroleum ether and equilibrated solution using the appropriate solvent system. The elution was assisted by applying pressure of about 202 kPa with an air pump.

4.2 Instruments

Proton nuclear magnetic resonance (^{1}H NMR) and carbon NMR (^{13}C NMR) were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$, unless otherwise stated. Chemical shifts are reported using the residual solvent signal as an internal standard: $CDCl_3$ (^{1}H NMR: δ 7.26, singlet; ^{13}C NMR: δ 77.0, triplet). HRMS (Analyzer: TOF) was reported in units of mass of charge ratio (*m/z*).

4.3 Materials

All commercial reagents were purchased with the highest purity grade. They were used without further purification unless specified. All solvents used, mainly petroleum ether (PE) and ethyl acetate (EtOAc) were distilled. Anhydrous

dichloromethane (DCM) and $CHCl_3$ were freshly distilled from CaH_2 and stored under N_2 atmosphere. THF and toluene were freshly distilled from sodium/benzophenone before use. All compounds synthesized were stored in a −20 ℃ freezer and light-sensitive compounds were protected with aluminium foil.

4.4 General experiment produces

71.0 μL (0.001 mmol, 0.01 equiv.) of DPZ solution (1.0 mg of DPZ in 200 μL of toluene) was added into a 10 mL Schlenk tube, and then solvent was removed *in vacuo*. Subsequently, **1** (0.25 mmol, 2.5 equiv.), **2** (0.1 mmol, 1.0 equiv.), $NaHCO_3$ (0.5 mmol, 5.0 equiv.) and CH_2Cl_2 (1.5 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at 25 °C, then irradiated by two 3 W blue LED (λ_{max}=450 nm) from a 1.0 cm distance for 24 h. After that, the mixture was directly loaded onto a short silica gel column, followed by elution with CH_2Cl_2 and then CH_2Cl_2/ethyl acetate (V∶V=50∶1). The solvent was removed *in vacuo* to obtain product **3**.

4.5 Characterization of adducts

2-(4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-1,4-diphenylbutane-1,4-dione **(3a)**: 24.1 mg, 61% yield. Yellow solid, m.p. 174.2～176.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.19 (d, J=7.1 Hz, 2H), 8.05 (d, J=7.1 Hz, 2H), 7.66 (d, J=8.3 Hz, 1H), 7.61～7.44 (m, 7H), 7.27 (d, J=7.8 Hz, 2H), 6.08 (dd, J=8.0, 5.4 Hz, 1H), 4.06 (dd, J=17.6, 8.1 Hz, 1H), 3.69 (s, 3H), 3.55 (dd, J=17.5, 5.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.3, 197.5, 157.2, 154.5, 137.0, 136.2, 133.4, 133.3, 132.7, 130.4, 130.3, 129.1, 128.9, 128.7, 128.4, 123.7, 113.7, 46.4, 38.5, 29.4; HRMS (ESI) calcd for $C_{25}H_{21}N_2O_3$ ($M+H^+$) 397.1547, found 397.1548.

1,4-Bis(4-fluorophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3b)**: 24.6 mg, 57% yield. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.28～8.17 (m, 2H), 8.13～8.02 (m, 2H), 7.68 (dd, J=8.3, 1.3 Hz, 1H), 7.58～7.47 (m, 1H), 7.34～7.24 (m, 2H), 7.14 (t, J=8.5 Hz, 4H), 6.02 (dd, J=7.3, 6.1 Hz, 1H), 3.96 (dd, J=17.5, 7.5 Hz, 1H), 3.69 (s, 3H), 3.57 (dd, J=17.5, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.6, 196.0, 166.03 (d, J=255.0 Hz), 165.95 (d, J=254.8 Hz), 156.9, 154.4, 133.3 (d, J=3.0 Hz), 133.3, 132.7 (d, J=3.0 Hz), 132.6, 131.7 (d, J=9.4 Hz), 131.0 (d, J=9.3 Hz), 130.6, 130.3, 123.9, 116.0 (d, J=21.9 Hz), 115.82 (d, J=21.8 Hz), 113.8, 46.2, 38.5, 29.5; HRMS (ESI) calcd for $C_{25}H_{19}F_2N_2O_3$ ($M+H^+$) 433.1358, found 433.1359.

1,4-Bis(3-fluorophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3c)**: 19.4 mg, 45% yield. Yellow solid, m.p. 127.1～128.3 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.98 (d, J=7.7 Hz, 1H), 7.90～7.80 (m, 2H), 7.75～7.64 (m, 2H), 7.59～7.42 (m, 3H), 7.36～7.25 (m, 4H), 5.98 (dd, J=7.3, 6.0 Hz, 1H), 3.94 (dd, J=17.6, 7.4 Hz, 1H), 3.70 (s, 3H), 3.57 (dd, J=17.6, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.9 (d, J=2.2 Hz), 196.2 (d, J=2.2 Hz), 163.1 (d, J=247.9 Hz), 162.9 (d, J=247.9 Hz), 156.7, 154.3, 138.9 (d, J=6.2 Hz), 138.4 (d, J=6.3 Hz), 133.3, 132.6, 130.7, 130.5 (d, J=11.9 Hz), 130.4 (d, J=12.1 Hz), 130.4, 124.8 (d, J=3.0 Hz), 124.2 (d, J=2.9 Hz), 123.9, 120.5 (d, J=21.5 Hz), 120.4 (d, J=21.4 Hz), 115.6 (d, J=22.5 Hz), 115.1 (d, J=22.4 Hz), 113.8, 46.5, 38.6, 29.5; HRMS (ESI) calcd for $C_{25}H_{19}F_2N_2O_3$ ($M+H^+$) 433.1358, found 433.1361.

1,4-Bis(2-fluorophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3d)**: 21.2 mg, 49% yield. Yellow solid, m.p. 162.4～163.7 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06 (td, J=7.7, 1.8 Hz, 1H), 7.90 (td, J=7.6, 1.8 Hz, 1H), 7.64 (dd, J=8.0, 1.5 Hz, 1H), 7.58～7.44 (m, 3H), 7.33～7.19 (m, 4H), 7.12 (ddd, J=16.6, 11.3, 8.3 Hz, 2H), 5.85 (t, J=6.6 Hz, 1H), 3.86 (ddd, J=18.1, 6.9, 3.1 Hz, 1H), 3.70 (s, 3H), 3.65 (ddd, J=6.4, 3.2, 1.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 195.7 (d, J=4.1 Hz), 195.5 (d, J=4.0 Hz), 162.2 (d, J=254.9 Hz), 161.8 (d, J=255.2 Hz), 157.5, 154.40, 134.8 (d, J=7.5 Hz), 134.7 (d, J=7.3 Hz), 133.4, 132.5, 131.6 (d, J=2.3 Hz), 130.9 (d, J=2.6 Hz), 130.4, 130.3, 125.6 (d, J=33.3 Hz), 125.4 (d, J=32.1 Hz), 124.7 (d, J=3.4 Hz), 124.5 (d, J=3.3 Hz), 123.7, 116.9 (d, J=23.9 Hz), 116.8 (d, J=23.7 Hz), 113.73, 51.0 (dd, J=6.7, 2.0 Hz), 42.2 (d, J=8.2 Hz), 29.4; HRMS (ESI) calcd for $C_{25}H_{19}F_2N_2O_3$ ($M+H^+$) 433.1358, found 433.1360.

1,4-Bis(4-chlorophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3e)**: 24 mg, 53% yield. Yellow solid, m.p. 162.4～163.7 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.11 (d, J=8.5 Hz, 2H), 7.97 (d, J=8.5 Hz, 2H), 7.66 (dd, J=8.2, 1.5 Hz, 1H), 7.51 (td, J=7.7, 7.2, 1.6 Hz, 1H), 7.43 (dd, J=8.6, 1.8 Hz, 4H), 7.33～7.24 (m, 2H), 5.99 (dd, J=7.3, 6.1 Hz, 1H), 3.92 (dd, J=17.6, 7.3 Hz, 1H), 3.67 (s, 3H), 3.58 (dd, J=17.6, 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.8, 196.2, 156.7, 154.3, 139.8, 139.7, 135.1, 134.6, 133.1, 132.5, 130.6, 130.3, 130.2, 129.7, 129.1, 128.9, 123.8, 113.7, 46.2, 38.5, 29.4; HRMS (ESI) calcd for $C_{25}H_{19}Cl_2N_2O_3$ ($M+H^+$) 465.0767, found 465.0769.

1,4-Bis(3-methoxyphenyl)-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3f)**: 25.1 mg, 54% yield. Yellow solid, m.p. 62.9～ 64.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.12 (t, J=1.9 Hz, 1H), 8.07 (d, J=7.9 Hz, 1H), 8.01 (t, J=1.9 Hz, 1H), 7.91 (d, J=7.7 Hz, 1H), 7.67 (dd, J=8.2, 1.5 Hz, 1H), 7.597.49 (m, 3H), 7.42 (t, J=7.8 Hz, 2H), 7.31～7.27 (m, 2H), 5.96 (dd, J=7.4, 6.0 Hz, 1H), 3.94 (dd, J=17.5, 7.4 Hz, 1H), 3.68 (s, 3H), 3.55 (dd, J=17.5, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.8, 196.2, 156.6, 154.3, 138.3, 137.9, 135.2, 135.0, 133.4, 133.3, 133.2, 132.5, 130.7, 130.3, 130.2, 130.1, 129.0, 128.5, 127.1, 126.5, 123.9, 113.8, 46.5, 38.5, 29.4; HRMS (ESI) calcd for $C_{25}H_{19}Cl_2N_2O_3$ ($M+H^+$) 465.0767, found 465.0770.

1,4-Bbis(4-bromophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3g)**: 24.3 mg, 44% yield. Yellow solid, m.p. 174.1～175.7 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.04 (d, J=8.6 Hz, 2H), 7.90 (d, J=8.6 Hz, 2H), 7.64 (ddd, J=18.3, 8.5, 2.2 Hz, 5H), 7.53 (td, J=7.7, 7.1, 1.5 Hz, 1H), 7.31～7.27 (m, 2H), 5.98 (dd, J=7.2,

6.1 Hz, 1H), 3.91 (dd, *J*=17.5, 7.3 Hz, 1H), 3.69 (s, 3H), 3.57 (dd, *J*=17.5, 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 197.1,196.5, 156.7, 154.4, 135.6, 135.1, 133.2, 132.6, 132.2, 132.0, 130.7, 130.6, 130.3, 129.9, 128.7, 128.6, 123.9, 113.8, 46.3, 38.5, 29.5; HRMS (ESI) calcd for $C_{25}H_{19}Br_2N_2O_3$ (M+H$^+$) 552.9757, found 552.9759.

1,4-Bis(3-bromophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3h)**: 22.6 mg, 41% yield. Yellow solid, m.p. 87.3～89.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.27 (t, *J*=1.9 Hz, 1H), 8.17 (t, *J*=1.8 Hz, 1H), 8.12 (d, *J*=7.8 Hz, 1H), 7.96 (d, *J*=7.8 Hz, 1H), 7.76～7.63 (m, 3H), 7.54 (td, *J*=7.7, 1.5 Hz, 1H), 7.36 (t, *J*=7.9 Hz, 2H), 7.30 (dd, *J*=7.7, 1.9 Hz, 2H), 5.95 (dd, *J*=7.5, 5.9 Hz, 1H), 3.94 (dd, *J*=17.5, 7.5 Hz, 1H), 3.69 (s, 3H), 3.54 (dd, *J*=17.5, 5.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 196.8, 196.1, 156.6, 154.4, 138.6, 138.1, 136.3, 136.2, 133.3, 132.6, 131.9, 131.5, 130.7, 130.5, 130.4, 130.3, 127.6, 126.9, 124.0, 123.2, 123.1, 113.8, 46.5, 38.5, 29.5; HRMS (ESI) calcd for $C_{25}H_{19}Br_2N_2O_3$ (M+H$^+$) 552.9757, found 552.9761.

2-(4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-1,4-di-*p*-tolylbutane-1,4-dione **(3i)**: 14.4 mg, 34% yield. Yellow solid, m.p. 173.6～174.9 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.09 (d, *J*=8.2 Hz, 2H), 7.95 (d, *J*=8.2 Hz, 2H), 7.67 (dd, *J*=8.4, 1.4 Hz, 1H), 7.49 (td, *J*=7.8, 7.2, 1.6 Hz, 1H), 7.27 (dd, *J*=6.9, 2.7 Hz, 6H), 6.05 (dd, *J*=8.3, 5.1 Hz, 1H), 4.05 (dd, *J*=17.5, 8.3 Hz, 1H), 3.67 (s, 3H), 3.50 (dd, *J*=17.5, 5.2 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 198.1, 197.1, 157.4, 154.5, 144.2, 144.0, 134.5, 133.72 , 133.3, 132.7, 130.3, 130.3, 129.6, 129.3, 129.2, 128.5, 123.6, 113.7, 46.2, 38.5, 29.4, 21.8; HRMS (ESI) calcd for $C_{27}H_{25}N_2O_3$ (M+H$^+$) 425.1860, found 425.1859.

1,4-Bis(3-methoxyphenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3j)**: 21 mg, 46% yield. Yellow solid, m.p. 57.3～58.8 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 7.80 (d, *J*=7.7 Hz, 1H), 7.73～7.62 (m, 3H), 7.56～7.46 (m, 2H), 7.38 (td, *J*=8.0, 1.3 Hz, 2H), 7.32～7.22 (m, 2H), 7.11 (ddd, *J*=8.1, 5.6, 2.5 Hz, 2H), 6.05 (dd, *J*=7.8, 5.5 Hz, 1H), 4.01 (dd, *J*=17.6, 7.8 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.69 (s, 3H), 3.59 (dd, *J*=17.6, 5.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 197.9, 197.3, 160.0, 159.9, 157.2, 154.4, 138.3, 137.6, 133.3, 132.7, 130.4, 130.4, 129.9, 129.7, 123.7, 121.7, 121.1, 120.3, 120.0, 113.7, 112.8, 112.3, 55.6, 46.4, 38.8, 29.4; HRMS (ESI) calcd for $C_{27}H_{25}N_2O_5$ (M+H$^+$) 457.1758, found 457.1760.

2-(6,7-Dibromo-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-1,4-diphenylbutane-1,4-dione **(3k)**: 25.4 mg, 46% yield. Yellow solid, m.p. 212.4～213.9 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.16 (d, *J*=7.0 Hz, 2H), 8.03 (d, *J*=7.4 Hz, 2H), 7.90 (s, 1H), 7.65～7.54 (m, 3H), 7.53～7.44 (m, 4H), 6.03 (dd, *J*=8.7, 4.6 Hz, 1H), 4.09 (dd, *J*=17.8, 8.8 Hz, 1H), 3.63 (s, 3H), 3.49 (dd, *J*=17.7, 4.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 198.1, 197.0, 159.0, 154.0, 136.7, 135.9, 134.1, 133.7, 133.5, 133.2, 132.3, 129.0, 129.0, 128.8, 128.4, 126.7, 118.9, 118.4, 46.4, 38.3, 29.6; HRMS (ESI) calcd for $C_{25}H_{19}Br_2$- N_2O_3 (M + H$^+$) 552.9757, found 552.9756.

1,4-Diphenyl-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3l)**: 34.3 mg, 81% yield. Yellow solid, m.p. 217.3～218.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.17 (d, *J*=7.3 Hz, 2H), 8.04 (d, *J*=7.3 Hz, 2H), 7.64～7.40 (m, 7H), 7.03 (s, 1H), 6.06 (dd, *J*=7.3, 6.0 Hz, 1H), 3.97 (dd, *J*=17.6, 7.4 Hz, 1H), 3.74～3.49 (m, 4H), 2.36 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 198.3, 197.5, 155.8, 154.4, 140.3, 137.0, 136.4, 133.2, 133.2, 132.6, 131.3, 131.1, 130.3, 129.0, 128.8, 128.6, 128.4, 114.2, 46.1, 38.6, 29.3, 20.7, 19.2; HRMS (ESI) calcd for $C_{27}H_{25}N_2O_3$ (M+H$^+$) 425.1860, found 425.1862.

4,4'-(2-(4,6,7-Trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)succinyl)dibenzonitrile **(3m)**: 27 mg, 57% yield. Yellow solid, m.p. 184.3～185.6 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.22 (d, *J*=8.4 Hz, 2H), 8.11 (d, *J*=8.4 Hz, 2H), 7.77 (dd, *J*=11.1, 8.4 Hz, 4H), 7.43 (s, 1H), 7.07 (s, 1H), 5.95 (t, *J*=6.7 Hz, 1H), 3.78 (dd, *J*=6.6, 1.9 Hz, 2H), 3.67 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 196.6, 196.3, 154.8, 154.3, 141.2, 139.7, 133.3, 132.7, 132.7, 131.3, 131.1, 130.3, 129.3, 128.8, 118.2, 118.1, 116.7, 116.4, 114.4, 46.6, 39.1, 29.5, 20.8, 19.3; HRMS (ESI) calcd for $C_{29}H_{23}N_4O_3$ (M+H$^+$) 475.1765, found 475.1763.

1,4-Bis(4-chlorophenyl)-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3n)**: 34.4 mg, 70% yield. Yellow solid, m.p. 180.3～181.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.09 (d, *J*=8.6 Hz, 2H), 7.97 (d, *J*=8.5 Hz, 2H), 7.48～7.39 (m, 5H), 7.04 (s, 1H), 5.96 (t, *J*=6.7 Hz, 1H), 3.84 (dd, *J*=17.6, 6.7 Hz, 1H), 3.71～3.58 (m, 4H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 196.9, 196.4, 155.4, 154.4, 140.7, 139.7, 135.2, 134.8, 132.9, 131.2, 131.1, 130.4, 130.4, 129.8, 129.1, 129.0, 114.3, 46.1, 38.7, 29.4, 20.7, 19.2; HRMS (ESI) calcd for $C_{27}H_{23}Cl_2N_2O_3$ (M+H$^+$) 493.1080, found 493.1083.

1,4-Di-*p*-tolyl-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3o)**: 30.3 mg, 67% yield. Yellow solid, m.p. 201.2～202.0 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.07 (d, *J*=8.2 Hz, 2H), 7.94 (d, *J*=8.2 Hz, 2H), 7.44 (s, 1H), 7.28～7.23 (m, 4H), 7.02 (s, 1H), 6.02 (dd, *J*=7.6, 5.7 Hz, 1H), 3.96 (dd, *J*=17.6, 7.7 Hz, 1H), 3.65 (s, 3H), 3.57 (dd, *J*=17.6, 5.7 Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H), 2.37 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 198.0, 197.2, 156.1, 154.5, 144.0, 143.9, 140.1, 134.5, 133.9, 132.5, 131.3, 131.2, 130.4, 129.5, 129.3, 129.2, 128.5, 114.2, 46.0, 38.6, 29.3, 21.8, 20.7, 19.2; HRMS (ESI) calcd for $C_{29}H_{29}N_2O_3$ (M+H$^+$) 453.2173, found 453.2175.

1,4-Bis(4-methoxyphenyl)-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3p)**: 44.5 mg, 92% yield. Yellow solid, m.p. 202.1～203.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.17 (d, *J*=8.8 Hz, 2H), 8.02 (d, *J*=8.8 Hz, 2H), 7.46 (s, 1H), 7.02 (s, 1H), 6.93 (d, *J*=8.6 Hz, 4H), 6.01 (dd, *J*=7.6, 5.7 Hz, 1H), 3.96 (dd, *J*=17.5, 7.7 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.65 (s, 3H), 3.55 (dd, *J*=17.5, 5.7 Hz, 1H), 2.37 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 197.0, 196.2, 163.7, 163.6, 156.1,

154.5, 140.1, 132.5, 131.4, 131.3, 131.2, 130.7, 130.4, 130.1, 129.4, 114.2, 114.0, 113.8, 55.6, 45.7, 38.5, 29.3, 20.7, 19.2; HRMS (ESI) calcd for $C_{29}H_{29}N_2O_5$ ($M+H^+$) 485.2071, found 485.2070.

1,4-Bis(3-methoxyphenyl)-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(3q)**: 40.7 mg, 84% yield. Yellow solid, m.p. 60.2～62.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.78 (d, J=7.7 Hz, 1H), 7.69 (d, J=2.2 Hz, 1H), 7.65 (d, J=8.0 Hz, 1H), 7.53 (t, J=2.0 Hz, 1H), 7.46 (s, 1H), 7.36 (td, J=7.9, 5.5 Hz, 2H), 7.16～7.03 (m, 2H), 7.03 (s, 1H), 6.02 (t, J=6.7 Hz, 1H), 3.92 (dd, J=17.7, 7.3 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.71～3.60 (m, 4H), 2.37 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.9, 197.3, 160.0, 159.8, 155.8, 154.4, 140.3, 138.3, 137.7, 132.7, 131.3, 131.2, 130.4, 129.8, 129.6, 121.7, 121.1, 120.2, 119.9, 114.2, 112.8, 112.3, 55.5, 46.2, 38.9, 29.3, 20.7, 19.2; HRMS (ESI) calcd for $C_{29}H_{29}N_2O_5$ ($M+H^+$) 485.2071, found 485.2073.

(2-(4,6,7-Trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-succinyl)bis(4,1-phenylene) diacetate **(3r)**: 35.6 mg, 66% yield. Yellow solid, m.p. 211.7～213.4 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.21 (d, J=8.7 Hz, 2H), 8.07 (d, J=8.7 Hz, 2H), 7.45 (s, 1H), 7.19 (dd, J=8.5, 5.9 Hz, 4H), 7.04 (s, 1H), 6.01 (dd, J=7.3, 6.0 Hz, 1H), 3.91 (dd, J=17.5, 7.4 Hz, 1H), 3.66 (s, 3H), 3.61 (dd, J=17.6, 6.1 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.9, 196.3, 169.0, 169.0, 155.5, 154.5, 154.5, 154.5, 140.5, 134.5, 133.9, 132.8, 131.3, 131.2, 130.7, 130.4, 130.0, 122.0, 121.9, 114.3, 46.1, 38.6, 29.4, 21.3, 20.7, 19.2; HRMS (ESI) calcd for $C_{31}H_{29}N_2O_7$ ($M+H^+$) 541.1969, found 541.1971.

2-(4-Benzyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-1,4-diphenylbutane-1,4-dione **(3s)**: 32.7 mg, 69% yield. Yellow solid, m.p. 192.7～194.3 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.21 (d, J=7.3 Hz, 2H), 8.08 (d, J=7.0 Hz, 2H), 7.67 (dd, J=8.3, 1.5 Hz, 1H), 7.63～7.54 (m, 2H), 7.52～7.44 (m, 4H), 7.40～7.10 (m, 8H), 6.15 (dd, J=8.2, 5.2 Hz, 1H), 5.61～5.32 (m, 2H), 4.09 (dd, J=17.5, 8.2 Hz, 1H), 3.61 (dd, J=17.5, 5.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.3, 197.5, 157.4, 154.6, 137.0, 136.3, 135.1, 133.4, 133.3, 132.9, 132.6, 130.4, 130.4, 129.1, 129.0, 128.9, 128.7, 128.4, 127.8, 126.9, 123.8, 114.5, 46.6, 46.2, 38.6; HRMS (ESI) calcd for $C_{31}H_{25}N_2O_3$ ($M+H^+$) 473.1860, found 473.1861.

(*E*)-1-Methyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one **(4a)**: 387.6 mg, 33% yield. Yellow solid, m.p. 149.5～151.2 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 14.01 (s, 1H), 8.03 (d, J=6.2 Hz, 2H), 7.59～7.40 (m, 3H), 7.22～7.15 (m, 4H), 7.01 (s, 1H), 3.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.1, 156.3, 144.7, 138.9, 131.9, 128.6, 128.4, 127.5, 125.3, 124.4, 124.1, 116.7, 114.5, 91.0, 29.9; HRMS (ESI) calcd for $C_{17}H_{15}N_2O_2$ ($M+H^+$) 279.1128, found 279.1129.

(*E*)-1,6,7-Trimethyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one **(4b)**: 500.0 mg, 38% yield. Yellow solid, m.p. 207.4～209.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 14.09 (s, 1H), 8.06～7.98 (m, 2H), 7.57～7.40 (m, 3H), 7.00～6.87 (m, 3H), 3.61 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.2, 156.2, 145.1, 139.1, 133.2, 131.7, 128.5, 127.4, 126.5, 123.1, 117.8, 115.4, 90.4, 29.8, 20.0, 19.4; HRMS (ESI) calcd for $C_{19}H_{19}N_2O_2$ ($M+H^+$) 307.1441, found 307.1440.

4-(4-Chlorophenyl)-1-phenyl-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(5a)**: 23.4 mg, 51% yield (photocatalysis); 28 mg, 61% yield (ionic-type reaction). Yellow solid, m.p. 245.3～247.2 ℃;^{1}H NMR (300 MHz, CD_2Cl_2) δ: 8.09 (d, J=7.3 Hz, 2H), 7.98 (d, J=8.6 Hz, 2H), 7.56 (t, J=7.3 Hz, 1H), 7.50～7.39 (m, 5H), 7.10 (s, 1H), 5.95 (t, J=6.7 Hz, 1H), 3.78 (dd, J=17.6, 6.6 Hz, 1H), 3.71～3.55 (m, 4H), 2.39 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 198.0, 196.7, 156.3, 154.6, 141.0, 139.7, 136.7, 135.7, 133.5, 133.2, 131.7, 131.2, 130.1, 130.0, 129.2, 129.1, 114.7, 53.8, 46.5, 38.9, 29.5, 20.7, 19.20; HRMS (ESI) calcd for $C_{27}H_{24}ClN_2O_3$ ($M+H^+$) 459.1470, found 459.1472.

4-(3-Methoxyphenyl)-1-phenyl-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(5b)**: 12.5 mg, 28% yield (photocatalysis); 38.9 mg, 86% yield (ionic-type reaction). Yellow solid, m.p. 167.6～169.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.21～8.12 (m, 2H), 7.65 (d, J=7.7 Hz, 1H), 7.53 (dd, J=4.6, 2.3 Hz, 2H), 7.47 (d, J=7.7 Hz, 3H), 7.37 (t, J=7.9 Hz, 1H), 7.12 (dd, J=8.1, 2.2 Hz, 1H), 7.04 (s, 1H), 6.04 (dd, J=7.4, 6.0 Hz, 1H), 3.96 (dd, J=17.7, 7.4 Hz, 1H), 3.84 (s, 3H), 3.71～3.56 (m, 4H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.3, 197.4, 159.9, 155.8, 154.5, 140.3, 138.3, 136.4, 133.3, 132.7, 131.3, 131.2, 130.4, 129.7, 129.0, 128.8, 121.1, 120.0, 114.3, 112.3, 55.6, 46.1, 38.8, 29.3, 20.7, 19.2. HRMS (ESI) calcd for $C_{28}H_{27}N_2O_4$ ($M+H^+$) 455.1965, found 455.1968.

4-(4-Oxo-4-phenyl-3-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanoyl)benzonitrile **(5c)**: 38.2 mg, 81% yield (photocatalysis); 23.1 mg, 49% yield (ionic-type reaction). Yellow solid, m.p. 221.7～222.4 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.16～8.09 (m, 4H), 7.78 (d, J=8.4 Hz, 2H), 7.62～7.51 (m, 1H), 7.47 (q, J=7.0, 5.6 Hz, 2H), 7.39 (s, 1H), 7.05 (s, 1H), 6.03 (t, J=6.7 Hz, 1H), 3.84 (dd, J=17.5, 7.1 Hz, 1H), 3.70～3.54 (m, 4H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.8, 196.6, 155.5, 154.4, 140.7, 140.1, 136.2, 133.4, 132.9, 132.6, 131.3, 131.1, 130.3, 129.0, 128.9, 128.8, 118.2, 116.4, 114.3, 46.5, 38.9, 29.4, 20.7, 19.2; HRMS (ESI) calcd for $C_{28}H_{23}N_3O_3Na$ ($M+Na^+$) 472.1632, found 472.1620.

4-(Fluorophenyl)-1-phenyl-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione **(5d)**: 15.5 mg, 35% yield (photocatalysis); 19.6 mg, 44% yield (ionic-type reaction). Yellow solid, m.p. 174.2～176.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.16 (d, J=7.7 Hz, 2H), 7.83 (d, J=7.7 Hz, 1H), 7.71 (d, J=9.4 Hz, 1H), 7.58～7.50 (m, 1H), 7.50～7.39 (m, 4H), 7.31～7.22 (m, 1H), 7.04 (s, 1H), 6.03 (t, J=6.7 Hz, 1H), 3.89 (dd, J=17.6, 7.2 Hz, 1H), 3.72～3.52 (m, 4H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.1, 196.4 (d, J=2.1 Hz), 162.9(d, J=247.6 Hz), 155.7, 154.4, 140.4, 139.1 (d, J=6.1 Hz), 136.3,

133.3, 132.8, 131.2 (d, J=12.4 Hz), 130.4, 130.3 (d, J=7.4 Hz), 129.0, 128.8, 124.2(d, J=3.0 Hz), 120.2(d, J=21.5 Hz), 115.1(d, J=22.4 Hz), 114.3, 46.2, 38.8, 29.4, 20.7, 19.2; HRMS (ESI) calcd for $C_{27}H_4FN_2O_3$ ($M+H^+$) 443.1765, found 443.1755.

4-(4-Bromophenyl)-1-phenyl-2-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butane-1,4-dione (**5e**): 20.1 mg, 40% yield (photocatalysis); 30.4 mg, 61% yield (ionic-type reaction). Yellow solid, m.p. 243.9～244.8 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.15 (d, J=7.2 Hz, 3H), 7.90 (d, J=8.5 Hz, 2H), 7.61 (d, J=8.5 Hz, 2H), 7.58～7.51 (m, 1H), 7.50～7.39 (m, 4H), 7.04 (s, 1H), 6.02 (dd, J=7.3, 6.1 Hz, 1H), 3.88 (dd, J=17.5, 7.3 Hz, 1H), 3.66 (s, 3H), 3.58 (dd, J=17.5, 6.1 Hz, 1H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.1, 196.7, 155.8, 154.5, 140.4, 136.3, 135.8, 133.3, 132.8, 132.0, 131.3, 131.2, 130.4, 130.0, 129.0, 128.9, 128.4, 114.3, 46.3, 38.6, 29.4, 20.7, 19.2; HRMS (ESI) calcd for $C_{27}H_{24}BrN_2O_3$ ($M+H^+$) 503.0965, found 503.0956.

4-(4-Mromophenyl)-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-1-phenylbutane-1,4-dione (**5f**): 22.3 mg, 47% yield (photocatalysis); 31.6 mg, 67% yield (ionic-type reaction). Yellow solid, m.p. 68.3～70.2 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.17 (d, J=7.3 Hz, 2H), 7.91 (d, J=8.5 Hz, 2H), 7.63 (t, J=8.8 Hz, 3H), 7.56 (d, J=7.2 Hz, 1H), 7.53～7.44 (m, 3H), 7.31～7.24 (m, 2H), 6.06 (dd, J=7.9, 5.5 Hz, 1H), 3.96 (dd, J=17.4, 7.9 Hz, 1H), 3.69 (s, 3H), 3.51 (dd, J=17.4, 5.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.1, 196.6, 157.1, 154.4, 136.2, 135.7, 133.5, 133.3, 132.6, 132.0, 130.5, 130.3, 123.0, 129.0, 128.9, 128.5, 123.8, 113.8, 46.4, 38.4, 29.4; HRMS (ESI) calcd for $C_{25}H_{20}BrN_2O_3$ ($M+H^+$) 475.0652, found 475.0644.

4-(3-(4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-4-oxo-4-phenylbutanoyl)benzonitrile (**5g**): 37.5 mg, 89% yield (photocatalysis); 19.2 mg, 46% yield (ionic-type reaction). Yellow solid, m.p. 96.2～98.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.15 (t, J=7.9 Hz, 4H), 7.79 (d, J=8.3 Hz, 2H), 7.65～7.43 (m, 5H), 7.33～7.23 (m, 2H), 6.06 (dd, J=7.7, 5.9 Hz, 1H), 3.93 (dd, J=17.4, 7.7 Hz, 1H), 3.69 (s, 3H), 3.58 (dd, J=17.4, 5.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.8, 196.5, 156.9, 154.4, 140.0, 136.1, 133.6, 133.3, 132.6, 132.6, 130.7, 130.2, 129.0, 129.0, 128.8, 123.9, 118.1, 116.5, 113.8, 46.6, 38.7, 29.5; HRMS (ESI) calcd for $C_{26}H_{20}N_3O_3$ ($M+H^+$) 422.1499, found 422.1492.

Supporting Information Mechanistic studies and NMR spectra. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

References

[1] (a) Shi, L.-L.; Zhou, H.; Wu, J.-F.; Li, X. *Mini-Rev. Org. Chem.* **2015**, *12*, 96.
(b) Carta, A.; Piras, S.; Loriga, G.; Paglietti, G. *Mini-Rev. Med. Chem.* **2006**, *6*, 1179.
(c) Li, X.; Yang, K.; Li, W.; Xu, W. *Drugs Future* **2006**, *31*, 979.
(d) Akins, P. T.; Atkinson, R. P. *Curr. Med. Res. Opin.* **2002**, *18*, 9.

[2] For selected reviews, see: (a) Ke, Q.; Yan, G.; Yu, J.; Wu, X. *Org. Biomol. Chem.* **2019**, *17*, 5863.
(b) Monika, M.; Selvakumar, S. *Synthesis* **2019**, 4113.
(c) Ghosh, P.; Das, S. *Synth. Commun.* **2020**, *50*, 2266.
(d) Meng, W.; Xu, K.; Guo, B.; Zeng, C. *Chin. J. Org. Chem.* **2021**, *41*, 2621 (in Chinese).
(孟薇, 徐坤, 郭兵冰, 曾程初, 有机化学, **2021**, *41*, 2621.)
(e) Liu, X.; Li, W.; Zhuang, C.; Cao, H. *Chin. J. Org. Chem.* **2021**, *41*, 3459 (in Chinese).
(刘想, 李文, 庄灿展, 曹华, 有机化学, **2021**, *41*, 3459.)
(f) Li, D.; Wang, X.; Li, S.; Fu, C.; Li, Q.; Xu, D.; Ma, Y. *Chin. J. Org. Chem.* **2021**, *41*, 4610 (in Chinese).
(李丹丹, 王晓辰, 李闪闪, 付晨雨, 李倩倩, 许东涛, 马莹莹, 有机化学, **2021**, *41*, 4610.)

[3] For selected recent examples of direct functionalization except of photocatalytic reactions, see: (a) Liu, S.; Huang, Y.; Qing, F.-L.; Xu, X.-H. *Org. Lett.* **2018**, *20*, 5497.
(b) Dutta, H. S.; Ahmad, A.; Khan, A. A.; Kumar, M.; Raziullah; Koley, D. *Adv. Synth. Catal.* **2019**, *361*, 5534.
(c) Zheng, D.; Studer, A. *Org. Lett.* **2019**, *21*, 325.
(d) Shen, J.; Xu, J.; Huang, L.; Zhu, Q.; Zhang, P. *Adv. Synth. Catal.* **2020**, *362*, 230.
(e) Lu, J.; He, X.-K.; Cheng, X.; Zhang, A.-J.; Xu, G.-Y.; Xuan, J. *Adv. Synth. Catal.* **2020**, *362*, 2178.
(f) Su, H.-Y.; Zhu, X.-L.; Huang, Y.; Xu, X.-H.; Qing, F.-L. *Chem. Commun.* **2020**, *56*, 12805.
(g) Wang, J.; Sun, B.; Zhang, L.; Xu, T.; Xie, Y.; Jin, C. *Org. Chem. Front.* **2020**, *7*, 113.
(h) Yuan, J.-W.; Zhu, J.-L.; Zhu, H.-L.; Peng, F.; Yang, L.-Y.; Mao, P.; Zhang, S.-R.; Li, Y.-C.; Qu, L.-B. *Org. Chem. Front.* **2020**, *7*, 273.
(i) Xu, J.; Zhang, H.; Zhao, J.; Ni, Z.; Zhang, P.; Shi, B.-F.; Li, W. *Org. Chem. Front.* **2020**, *7*, 4031.
(j) Meng, N.; Wang, L.; Liu, Q.; Li, Q.; Lv, Y.; Yue, H.; Wang, X.; Wei, W. *J. Org. Chem.* **2020**, *85*, 6888.
(k) Xu, J.; Yang, H.; He, L.; Huang, L.; Shen, J.; Li, W.; Zhang, P. *Org. Lett.* **2021**, *23*, 195.
(l) Wen, J.; Yang, X.; Yan, K.; Qin, H.; Ma, J.; Sun, X.; Yang, J.; Wang, H. *Org. Lett.* **2021**, *23*, 1081.
(m) He, X.-K.; Lu, J.; Zhang, A.-J.; Zhang, Q.-Q.; Xu, G.-Y.; Xuan, J. *Org. Lett.* **2020**, *22*, 5984.
(n) Niu, K.; Song, L.; Hao, Y.; Liu, Y.; Wang, Q. *Chem. Commun.* **2020**, *56*, 11673.
(o) Clinton, C. D.; Prasad, C. D.; Thombal, R. S.; Lee, Y. R. *Adv. Synth. Catal.* **2021**, *363*, 776.

[4] For a review on photocatalytic functionalization, see: Rostoll-Berenguer, J.; Blay, G.; Pedro, J. R.; Vila, C. *Eur. J. Org. Chem.* **2020**, 6148.

[5] (a) Bao, P.; Liu, F.; Lv, Y.; Yue, H.; Li, J.-S.; Wei. W. *Org. Chem. Front.* **2020**, *7*, 492. (b) Dai, C.; Zhan, Y.; Liu, P.; Sun, P. *Green Chem.* **2021**, *23*, 314. (c) Aganda, K. C. C.; Hong, B.; Lee, A. *Adv. Synth. Catal.* **2021**, *363*, 1443.

[6] (a) Meng, N.; Lv, Y.; Liu, Q.; Liu, R.; Zhao, X.; Wei, W. *Chin. Chem. Lett.* **2021**, *32*, 258.
(b) Yang, X.; Meng, W.-D.; Xu, X.-H.; Huang, Y. *Org. Chem. Front.* **2021**, *8*, 6597.

[7] For selected reviews, see: (a) Lv, X.; Xu, H.; Yin, Y.; Zhao, X.; Jiang, Z. *Chin. J. Chem.* **2020**, *38*, 1480.
(b) Yin, Y.; Zhao, X.; Qiao, B.; Jiang, Z. *Org. Chem. Front.* **2020**, *7*, 1283.
(c) Yin, Y.; Zhao, X.; Jiang, Z. *ChemCatChem* **2020**, *12*, 4471.
For selected examples, see: (d) Shao, T.; Yin, Y.; Lee, R.; Zhao, X.; Chai, G.; Jiang, Z. *Adv. Synth. Catal.* **2018**, *360*, 1754.
(e) Li, J.; Gu, Z.; Zhao, X.; Qiao, B.; Jiang, Z. *Chem. Commun.* **2019**, *55*, 12916.
(f) Qiao, B.; Li, C.; Zhao, X.; Yin, Y.; Jiang, Z. *Chem. Commun.* **2019**, *55*, 7534.
(g) Yin, Y.; Dai, Y.; Jia, H.; Li, J.; Bu, L.; Qiao, B.; Zhao, X.; Jiang, Z. *J. Am. Chem. Soc.* **2018**, *140*, 6083.
(h) Cao, K.; Tan, S. M.; Lee, R.; Yang, S.; Jia, H.; Zhao, X.; Qiao,

B.; Jiang, Z. *J. Am. Chem. Soc.* **2019**, *141*, 5437.
(i) Yin, Y.; Li, Y.; Gonçalves, T. P.; Zhan, Q.; Wang, G.; Zhao, X.; Qiao, B.; Huang, K.-W.; Jiang, Z. *J. Am. Chem. Soc.* **2020**, *142*, 19451.
(j) Kong, M.; Tan, Y.; Zhao, X.; Qiao, B.; Tan, C.-H.; Cao, S.; Jiang, Z. *J. Am. Chem. Soc.* **2021**, *143*, 4024.
(k) Guo, Z.; Chen, X.; Fang, H.; Zhao, X.; Jiang, Z. *Sci. China Chem.* **2021**, *64*, 1522.
(l) Hu, W.; Zhan, Q.; Zhou, H.; Cao, S.; Jiang, Z. *Chem. Sci.* **2021**, *12*, 6543.
(m) Chen, X.; Wei, W.; Li, C.; Zhou, H.; Qiao, B.; Jiang, Z. *Org. Lett.* **2021**, *23*, 8744.
(n) Chai, X.; Hu, X.; Zhao, X.; Yin, Y.; Cao, S.; Jiang, Z. *Angew. Chem. Int. Ed.* **2022**, *61*, e202115110.
(o) Tan, Y.; Yin, Y.; Cao, S.; Zhao, X.; Qu, G.; Jiang, Z. *Chin. J. Catal.* **2022**, *43*, 558.

[8] (a) Zhao, Y.; Zhang, C.; Chin, K. F.; Pytela, O.; Wei, G.; Liu, H.; Bureš, F.; Jiang, Z. *RSC Adv.* **2014**, *4*, 30062.
(b) Liu, X.; Ye, X.; Bureš, F.; Liu, H.; Jiang, Z. *Angew. Chem. Int. Ed.* **2015**, *54*, 11443.
(c) Shao, T.; Jiang, Z. *Acta Chim. Sinica* **2017**, *75*, 70 (in Chinese).
(邵天举, 江智勇, 化学学报, **2017**, *75*, 70.)
(d) Jia, H.; Qiao, B.; Jiang, Z. *Acta Chim. Sinica* **2021**, *79*, 1477 (in Chinese).
(贾红绍, 乔保坤, 江智勇, 化学学报, **2021**, *79*, 1477.)
(e) Yang, H.; Li, H.; Wei, G.; Jiang, Z. *Angew. Chem. Int. Ed.* **2021**, *60*, 19696.
[9] Badawy, M. A.; Mohamed, G. G.; Omar, M. M.; Nassar, M. M.; Kamel, A. B. *Eur. J. Chem.* **2010**, *4*, 282.
[10] See the Supporting Information for the details.
[11] Li, J.; Kong, M.; Qiao, B.; Lee, R.; Zhao, X.; Jiang, Z. *Nat. Commun.* **2018**, *9*, 2445.

(Li, L.)

