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Visible-Light-Induced C(sp^2)−C(sp^3) Cross-Dehydrogenative-Coupling Reaction of *N*-Heterocycles with *N*-Alkyl-*N*-methylanilines under Mild Conditions

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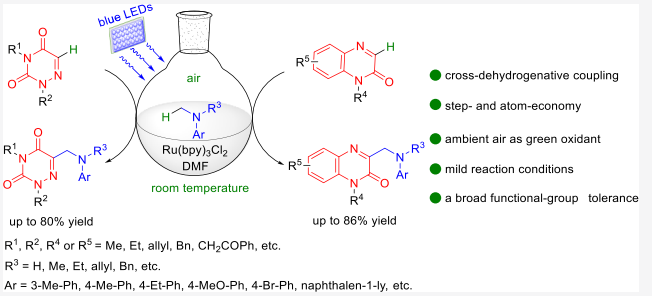
ABSTRACT: Disclosed herein is a cross-dehydrogenative-coupling reaction of *N*-heterocycles including 1,2,4-triazine-3,5(2*H*,4*H*)-diones and quinoxaline-2(1*H*)-ones with *N*-methylanilines to form C(sp^2)−C(sp^3) under visible-light illumination and ambient air at room temperature. In this process, easily available $Ru(bpy)_3Cl_2·6H_2O$ serves as the catalyst, and air acts as the green oxidant. This method features high atom economy, environmental friendliness, and convenient operation and provides an efficient and practical access to aminomethyl-substituted *N*-heterocycles with extensive functional group compatibility in 40−86% yields.



INTRODUCTION

N-Heterocycles, such as 1,2,4-triazine-3,5(2*H*,4*H*)-dione (6-azauracil) and quinoxalin-2(1*H*)-one, are privileged scaffolds and commonly found in a wide range of biologically active molecules, natural products, and synthetic pharmaceuticals.[1,2] As shown in Figure 1, diclazuril is a broad-spectrum anticoccidial drug on the market and applicable to treat coccidiosis in chicken.[2a] Furthermore, 6-azauridine which is an analogue of uridine shows effective antiviral activity and is utilized in clinics against pathogenic flaviviruses.[2b] Other examples shown in Figure 1 also exhibit distinct bioactivity and medicinal properties, such as the c-MeT kinase inhibitor, 5-HT_{2C} receptor agonist, and cannabinoid CB_2 receptor agonist.[2c−e]

Although 1,2,4-triazine-3,5(2*H*,4*H*)-dione derivatives are of interest in pharmaceutical chemistry, the direct and efficient synthesis methods for 1,2,4-triazine-3,5(2*H*,4*H*)-dione derivatives have not been well established. The traditional methods are based on the nucleophilic substitution or cross-coupling reactions of 3-halo-1,2,4-triazine-3,5(2*H*,4*H*)-dione, which suffer from limitations such as the requirement of prefunctionalized substrates, low atom economy, and harsh conditions.[3] The newly developed C−H functionalization strategy shows its superiority in short steps, high atom economy, and mild conditions,[4] but only a few of the examples of direct functionalization of 1,2,4-triazine-3,5(2*H*,4*H*)-dione have been achieved.[5−7] In 2018, the Xu group gave a pioneering example for the C−H functionalization of 1,2,4-triazine-3,5(2*H*,4*H*)-dione to synthesize $C(CH_3)_2CF_3$-substituted 1,2,4-triazine-3,5(2*H*,4*H*)-dione in a moderate yield (Scheme 1, equation a).[5] In 2020, Meng and Li groups cooperatively disclosed an elegant C−H difluoromethylation of heterocycles, and 1,2,4-triazine-3,5(2*H*,4*H*)-dione was selected as a substrate providing 6-(difluoromethyl)-1,2,4-triazine-3,5-(2*H*,4*H*)-dione in a good yield (Scheme 1, equation b).[6] Recently, the Kim group described a novel C−H methylation of heterocycles with sulfur ylides and found that a range of 1,2,4-triazine-3,5(2*H*,4*H*)-diones matched well with the standard conditions (Scheme 1, equation c).[7] In view of the conflict between the significance of 1,2,4-triazine-3,5(2*H*,4*H*)-dione derivatives and the scarcity of synthesis methods for them, it is in urgent demand to develop the convenient and direct C−H functionalization of 1,2,4-triazine-3,5(2*H*,4*H*)-diones.

In addition, over the past decade, various protocols for the C−H functionalization of quinoxalin-2(1*H*)-ones, including alkylation,[8] arylation,[9] acylation,[10] amination,[11] alkoxylation,[12] phosphorylation,[13] sulfenylation,[14] and so forth,[15] have been accomplished, but the direct introduction of diverse aminomethyl groups into quinoxalin-2(1*H*)-ones *via* C−H functionalization is extremely rare. In 2020, Chen and Yu groups cooperatively reported a visible-light-induced addition reaction of quinoxalin-2(1*H*)-ones with *N*-aryl glycines achieving 3-aminomethyl-substituted 3,4-dihydroquinoxalin-2(1*H*)-ones (Scheme 1, equation d).[16] This hydro-aminomethyl addition transformation features the utilization of recyclable g-C_3N_4 as

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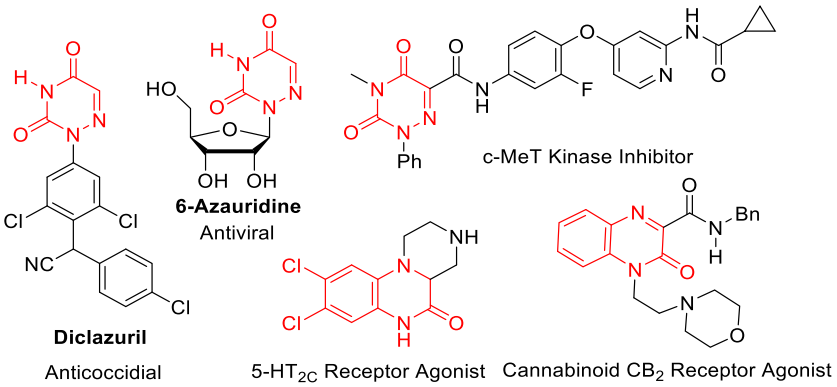
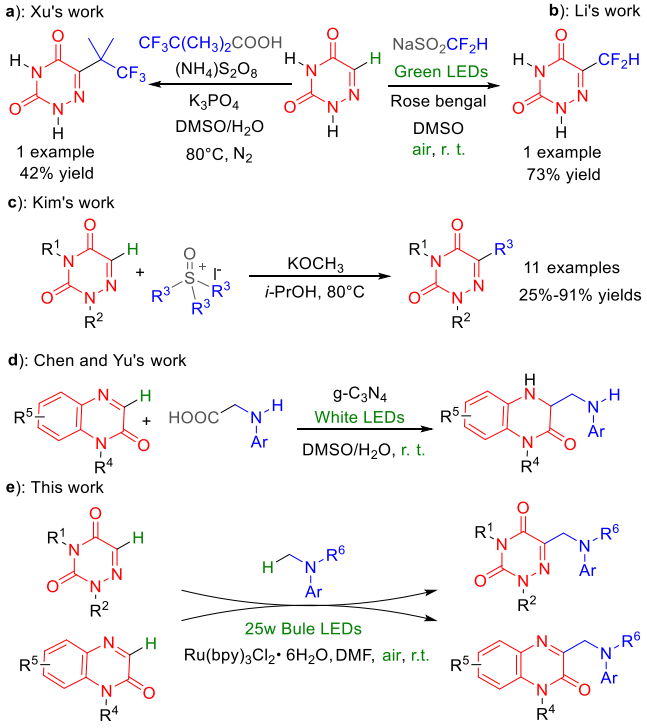


Figure 1. Representation of 1,2,4-triazine-3,5(2*H*,4*H*)-dione and quinoxalin-2(1*H*)-one derivatives with bioactivity.

Scheme 1. C−H Functionalization of 1,2,4-Triazine-3,5(2*H*,4*H*)-diones and Hydro-aminomethyl Addition of Quinoxalin-2(1*H*)-ones



the catalyst, mild conditions, and easy operation. However, compared with *N*-aryl glycines which have to undergo decarboxylation to generate aminomethyl radicals, *N*-methylaniline derivatives are regarded as more environmentally friendly and higher atom-economic aminomethyl radical precursors.[17] Therefore, the exploration of C−H aminomethylation of quinoxalin-2(1*H*)-ones with *N*-methylanilines is still meaningful and challenging. Over the past years, the visible-light-induced cross-dehydrogenative coupling (CDC) reaction has emerged as a popular and ideal strategy for the step- and atom-economical construction of C−C bonds due to the advantages such as high efficiency, mild reaction conditions, and low energy consumption.[18] Herein, we disclose the first visible-light-induced CDC reactions of *N*-heterocycles including 1,2,4-triazine-3,5(2*H*,4*H*)-diones and quinoxalin-2(1*H*)-ones with *N*-methylanilines (Scheme 1, equation e). Thanks to the features of low catalyst loading, using molecular oxygen in ambient air as an oxidant and a wide range of functional tolerance, this method offers an environmentally benign and synthetically efficient protocol to potentially pharmacoactive 3-aminomethyl-substituted 1,2,4-triazine-3,5-(2*H*,4*H*)-dione or quinoxalin-2(1*H*)-one derivatives in moderate to high yields.

RESULTS AND DISCUSSION

Our investigation was started by employing 1-methylquinoxalin-2(1*H*)-one (**1a**) and *N*,*N*-dimethylaniline (**2a**) as the model substrates to optimize the reaction conditions (Table 1). Initially, diverse solvents, such as CH_3CN, dimethylformamide (DMF), dimethyl ether (DME), acetone, and *N*-methyl-2-pyrrolidone (NMP), were tested in the presence of rose bengal (5 mol %) as the photocatalyst under blue light irradiation and ambient air at room temperature (Table 1, entries 1−5). Fortunately, DMF was found to be the effective solvent, and the expected product (**3a**) was obtained in 18% yield. Subsequently, a series of other photocatalysts including eosin B, eosin Y, *fac*-Ir(ppy)$_3$, and Ru(bpy)$_3$Cl$_2$·6H$_2$O were examined (Table 1, entries 6−9). Among them, Ru(bpy)$_3$Cl$_2$·6H$_2$O was proved to be the most suitable and delivered product **3a** in 24% yield. In addition, the yield of product **3a** increased to 32% in the presence of 3 equiv of *N*,*N*-dimethylaniline, but a further increase in the amount of *N*,*N*-dimethylaniline was slightly helpful (Table 1, entry 10). Next, various oxidants, including O_2, $K_2S_2O_8$, di-*tert*-butyl peroxide (DTBP), *tert*-butyl hydroperoxide (TBHP), and cumene hydroperoxide (CHP), were employed instead of air (Table 1, entries 11−15). Fortunately, the reaction with CHP as the oxidant provided the target product in a yield of 58%. Changing the loading of CHP or Ru(bpy)$_3$Cl$_2$·6H$_2$O did not enhance the reaction efficiency (Table 1, entries 16−19). Subsequently, we investigated the dosage of the solvent and found that 1 mL of DMF was appropriate offering the desired product in a yield of 64% (Table 1, entries 20−21). Next, a number of bases including K_2CO_3, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), Et_3N, and CH_3COOK were investigated, and DBU was found to be the best one with the yield of **3a** increasing from 64 to 72% (Table 1, entries 22−25). However, the yield of **3a** was not further increased by using 0.5 or 1.5 equiv of DBU (Table 1, entries 26 and 27). To our great surprise, the yield of **3a** dramatically increased to 83% under an air atmosphere without CHP (Table 1, entry 28). Therefore, the optimal reaction conditions were achieved, which are blue light as the light source, 2 mol % of Ru(bpy)$_3$Cl$_2$·6H$_2$O as the photocatalyst, and 1.0 equiv of DBU as the additive in 1.0 mL of DMF under ambient air at room temperature.

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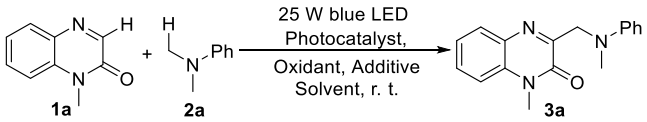
Table 1. Selected Reaction Condition Optimization[a]



entry	photocatalyst	oxidant	solvent	yield (%)[b]
1[c,d,e]	rose bengal	air	CH_3CN	17
2[c,d,e]	rose bengal	air	DMF	18
3[c,d,e]	rose bengal	air	DME	13
4[c,d,e]	rose bengal	air	acetone	15
5[c,d,e]	rose bengal	air	NMP	trace
6[c,d,e]	eosin B	air	DMF	18
7[c,d,e]	eosin Y	air	DMF	15
8[c,e]	*fac*-Ir(ppy)$_3$	air	DMF	12
9[c,e]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	air	DMF	24
10[e]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	air	DMF	32(29[f])
11[e]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	O_2	DMF	11
12[e]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	$K_2S_2O_8$	DMF	n.d.
13[e]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DTBP[g]	DMF	trace
14[e]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	TBHP[h]	DMF	51(50[i])
15[e]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP[j]	DMF	58
16[e,k]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	53
17[e,l]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	36
18[e,m]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	50
19[e,d]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	45
20	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	64
21[n]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	61
22[o]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	65
23[p]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	72
24[q]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	59
25[r]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	64
26[s]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	70
27[t]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	CHP	DMF	69
28[p]	**Ru(bpy)$_3$Cl$_2$·6H$_2$O**	**air**	**DMF**	**83**

[a]Unless specifically noted otherwise, reaction conditions are **1a** (0.3 mmol), **2a** (3.0 equiv), catalyst (2 mol %), oxidant (1.0 equiv., except for an air or O_2 atmosphere), and solvent (1.0 mL), stirring at room temperature under an argon atmosphere about 12 h. [b]Yield of the isolated product. [c]**2a** (2.0 equiv). [d]Photocatalyst (5 mol %). [e]Solvent (1.5 mL). [f]stirring for 28 h. [g]Di-*tert*-butyl peroxide. [h]*tert*-Butyl hydroperoxide (70% in water). [i]TBHP 5.5 M in decane. [j]CHP (contains *ca.* 20% aromatic hydrocarbon). [k]Oxidant (1.5 equiv). [l]Oxidant (0.5 equiv). [m]Photocatalyst (1 mol %). [n]Solvent (0.5 mL). [o]K_2CO_3 as the additive (1.0 equiv). [p]DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene) as the additive (1.0 equiv). [q]Et_3N as the additive (1.0 equiv). [r]CH_3COOK as the additive (1.0 equiv). [s]DBU as the additive (0.5 equiv). [t]DBU as the additive (1.5 equiv).

With the optimal reaction conditions established, the scope of the present transformation was further investigated by employing different quinoxalin-2(1*H*)-ones as substrates and *N*-methylanilines as aminomethyl radical precursors (Table 2). First, several quinoxalin-2(1*H*)-ones with different *N*-substituent groups such as ethyl, benzyl, allyl, and ester groups were examined to react with *N*,*N*-dimethylaniline (**3b**−**3f**). As expected, *N*-ethyl-substituted quinoxalin-2(1*H*)-one was also well compatible with the optimal reaction conditions and gave the corresponding product **3b** in a good yield of 72%. However, for the other N-substituted quinoxalin-2(1*H*)-ones, CHP was utilized as the oxidant instead of ambient air in order to obtain the corresponding products in moderate to good yields. Quinoxalin-2(1*H*)-ones with electron-donating groups could provide the expected products in good yields (**3g**−**3i**). Next, we continued to explore the substrate range with a series of *N*,*N*-dimethylanilines bearing the electron-donating or electron-withdrawing groups on the benzene ring. *N*,*N*-Dimethylanilines with electron-donating methyl, ethyl, or methoxy groups at the *para* or *meta* position on the benzene ring reacted well to give the target products in good to excellent yields (**3j**−**3m**). On the other hand, *N*,*N*-dimethylanilines with electron-withdrawing bromine atoms at the *para* position on the benzene ring offered the corresponding product **3n** in a moderate yield of 49%. It was assumed that the reaction became more challenging in the cases where one methyl was replaced by ethyl, *n*-butyl, allyl, or even benzyl in *N*,*N*-dimethylaniline. Fortunately, the reaction exclusively took place on the *N*-methyl group and afforded the corresponding in moderate yields (**3o**−**3r**). Other aminomethyl sources including 4-dimethylaminopyridine, 2-phenyl-1,2,3,4-tetrahydroisoquinoline, and so forth, were also tested in the reaction with 1-methylquinoxalin-2(1*H*)-one, but no corresponding products were detected (Figure S6, Supporting Information).

In consideration of the significance of 1,2,4-triazine-3,5-(2*H*,4*H*)-dione derivatives, we further verified the feasibility of this methodology for the modification of 1,2,4-triazine-3,5(2*H*,4*H*)-diones (Table 3). To our delight, 1,2,4-triazine-3,5(2*H*,4*H*)-diones with diverse *N*-substituent groups including methyl, benzyl, 4-fluorobenzyl, allyl, and acetophenone groups matched with the present transformation well, and the target products were received in good to high yields (**5a**−**5e**). The reaction with **4b** as the substrate could be readily scaled up to 1.5 mmol, and the target product **5b** was obtained in a satisfactorily isolated yield of 78%. Subsequently, a variety of *N*,*N*-dimethylanilines with electron-donating groups, such as methyl, ethyl, or methoxy groups on the benzene ring, progressed successfully under the optimal conditions and afforded the corresponding products in good yields (**5f**−**5i**). Furthermore, the reaction was also investigated with other dialkylanilines having two different *N*-alkyl groups, for instance, *N*-butyl-*N*-methylaniline, *N*-allyl-*N*-methylaniline, and *N*-benzyl-*N*-methylaniline. Satisfyingly, C−C bond formation highly selectively took place on the *N*-methyl carbon, and the aminomethyl-substituted products were obtained in moderate to good yields (**5j**−**5l**). Besides, *N*,*N*-dimethylnaphthalen-1-amine and *N*,*N*-diethylaniline were attempted as special substrates and offered the corresponding products in good yields of 75 and 78%, respectively (**5m**−**5n**). What surprised us was the reaction of *N*-methylaniline with free NH groups was also carried out smoothly under the standard conditions and provided the corresponding C−C cross-coupling product **5o** in a satisfactory yield of 53%.

After studying the range of substrates, several control experiments were carried out to clarify the mechanism of the reaction (Scheme 2). When 3.0 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added under the standard reaction conditions, the reaction was completely inhibited and a TEMPO-adduct **6a** was detected by high-resolution mass spectrometry (HRMS) (Scheme 2, equation A). This result suggested that the transformation might involve a single-electron transfer. When 3.0 equiv of 1,4-diazabicyclo[2.2.2]-octane as singlet oxygen scavengers was added in the model reaction, the target product was obtained in 45% yield, which excluded the possibility that the singlet oxygen might be a reactive intermediate in this transformation (Scheme 2, equation B). Besides, an iminium ion species **7a** was observed

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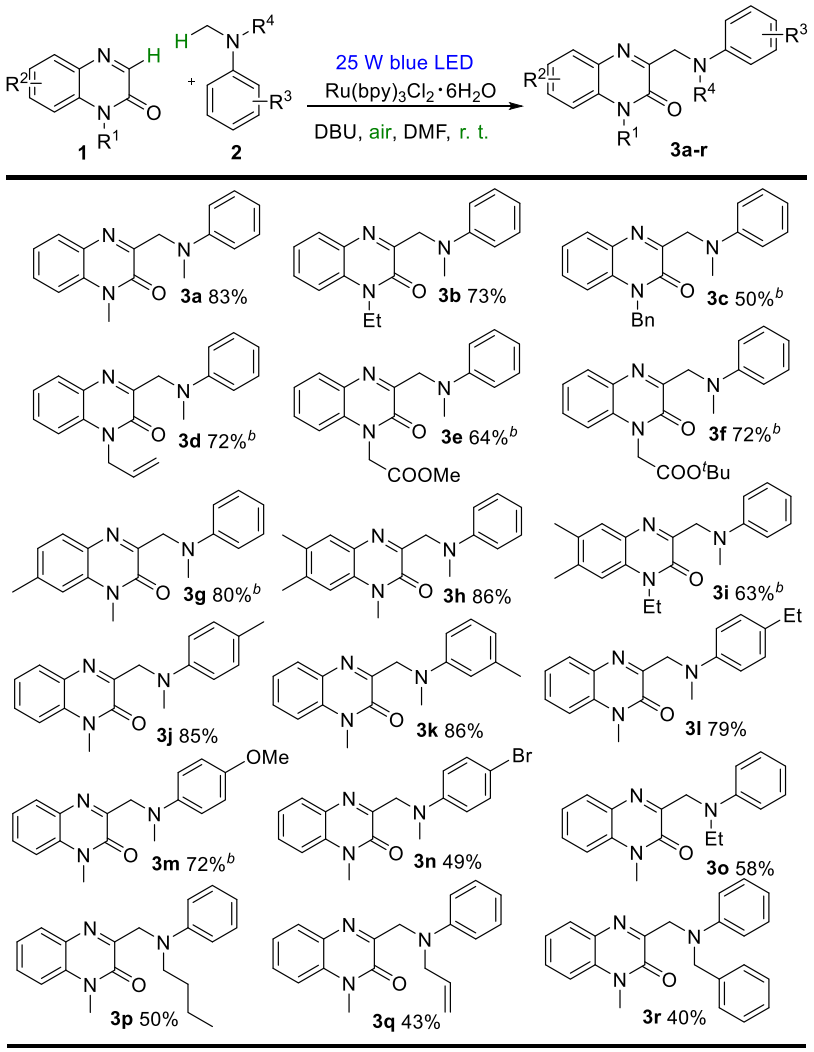
Table 2. Substrate Scope of Various Quinoxalin-2(1*H*)-ones[a]



[a]General conditions: **1** (0.3 mmol), **2** (0.9 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (2.0 mol %), and DBU (1.0 equiv) in 1.0 mL of DMF irradiated with a 25 W blue LED under an air atmosphere for 12 h; yield of the isolated product. [b]CHP was used as the oxidant under an argon atmosphere.

when the model reaction was stopped at 4 h (Scheme 2, equation C). When the reaction was performed in the absence of the photocatalyst, hardly any desired product was detected, suggesting that the photocatalyst played an important role in the process of electron transfer (Scheme 2, equation D). In addition, the formation of the product did not take place in the dark (Scheme 2, equation E). This indicated that visible-light irradiation was essential to initiate catalytic reactions. Moreover, the on/off visible-light irradiation experiments also confirmed the great influence of continuous illumination (Figure 2).

On the basis of the aforementioned results and previous literature studies,[19] a plausible mechanism pathway is proposed in Scheme 3. Initially, $Ru(bpy)_3^{2+}$ is photoexcited by visible-light irradiation to generate excited $*Ru(bpy)_3^{2+}$. Subsequently, a single-electron-transfer process between excited $*Ru(bpy)_3^{2+}$ and *N*,*N*-dimethylaniline (**2a**) takes place to furnish $Ru(bpy)_3^{+}$ and the cation radical of *N*,*N*-dimethylaniline (**8a**).[19b] Then, $Ru(bpy)_3^{+}$ is oxidized by aerial oxygen or CHP to regenerate ground-state $Ru(bpy)_3^{2+}$.[19e] Meanwhile, with the assistance of DBU, **8a** undergoes deprotonation to generate α-amino radical **9a** which is sequentially oxidized to iminium ion species **7a**.[19c] Next, the electrophilic addition of **7a** to 1-methylquinoxalin-2(1*H*)-one (**1a**) provides the cation intermediate **10a**.[19f] Finally, the target product **3a** is obtained through H^+ elimination from intermediate **10a** with the aid of DBU.

In conclusion, we have developed, for the first time, an efficient and atom-economic visible-light-induced $C(sp^3)$–$C(sp^2)$ cross-dehydrogenation-coupling reaction between 1,2,4-triazine-3,5(2*H*,4*H*)-diones/quinoxalin-2(1*H*)-ones and *N*,*N*-dimethylanilines. The method was also applicable to other *N*-methylaniline derivatives such as *N*,*N*-diethylaniline, dialkylanilines with two different *N*-alkyl groups, and even *N*-methylaniline. This protocol had the advantages of cheap and easily available starting materials and catalysts, ambient air as the green oxidant, eco-friendly energy source, mild reaction conditions, a broad functional-group tolerance in good yields, high scalability, and operational simplicity, so it is promising to provide an ideal method for organic synthesis and pharmaceutical chemistry.

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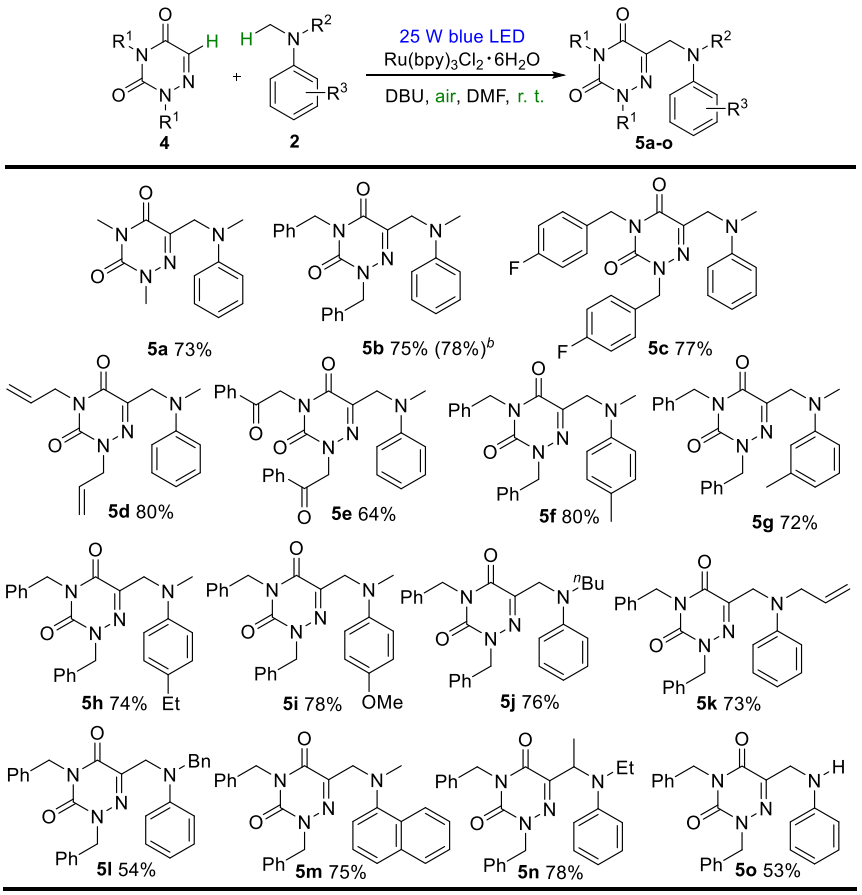
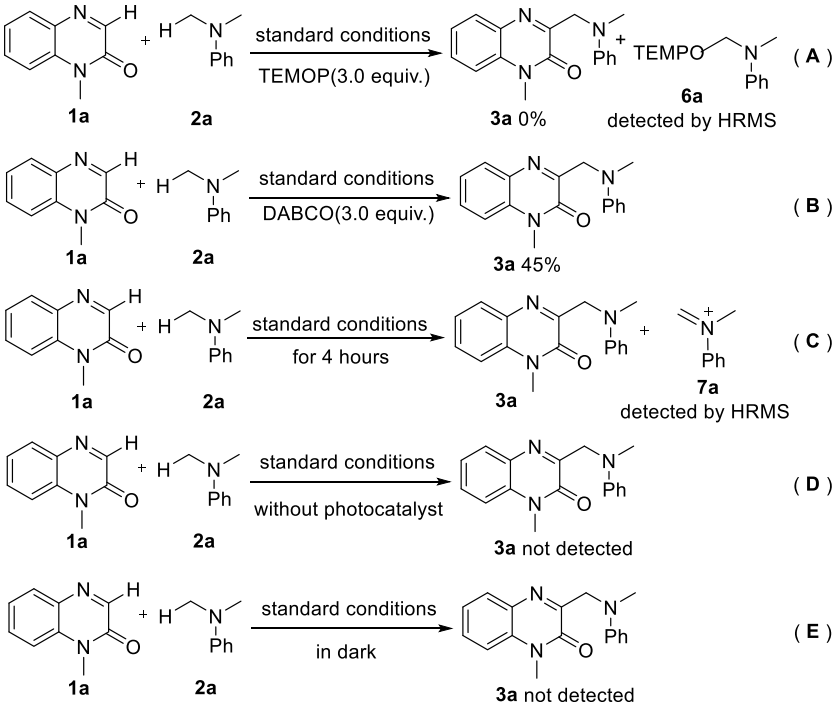
Table 3. Substrate Scope of Various 1,2,4-Triazine-3,5(2*H*, 4*H*)-diones[a]



[a]General conditions: **4** (0.3 mmol), **2** (0.9 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (2.0 mol %), and DBU (1.0 equiv) in 1.0 mL of DMF irradiated with a 25 W blue LED under an air atmosphere for 12 h; yield of the isolated product. [b]Scaled up to 1.5 mmol **4b**.

Scheme 2. Control Experiments



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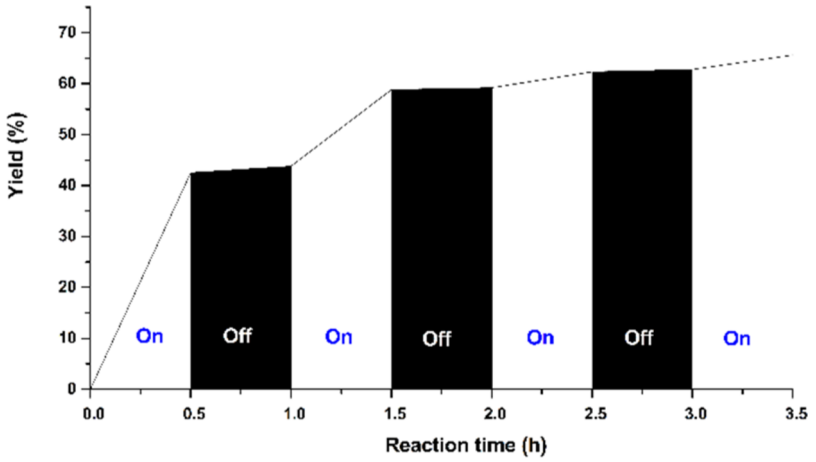
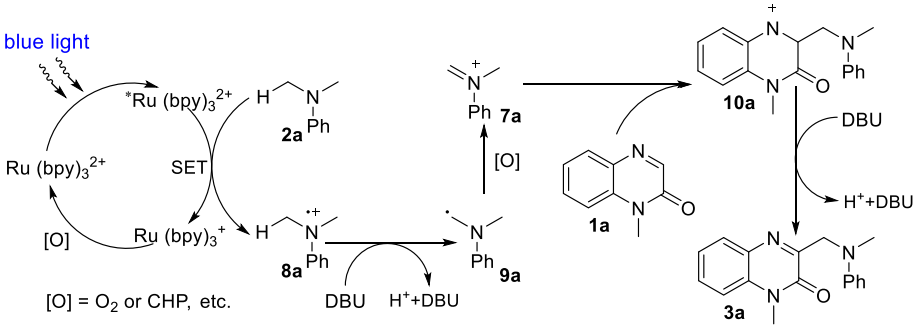


Figure 2. On/off visible-light irradiation experiments.

Scheme 3. Proposed Reaction Mechanism



EXPERIMENTAL SECTION

General. All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a Bruker AC-P 400 spectrometer (400 MHz for ^{1}H, 100 MHz for $^{13}C\{^{1}H\}$, and 376 MHz for $^{19}F\{^{1}H\}$) in $CDCl_3$ [with trimethylsilyl (TMS) as the internal standard]. Chemical shifts (δ) were measured in parts per million relative to TMS $\delta = 0$ for ^{1}H or to chloroform $\delta = 77.0$ for ^{13}C as the internal standard. Coupling constants, J, are reported in Hertz. Mass data were measured using a Thermo Scientific DSQ II mass spectrometer. High-resolution mass spectra were recorded on a quadrupole time-of-flight mass spectrometer using electrospray ionization (ESI) as an ionization method. Melting points were obtained using a Shanghai Inesa WRS-3 melting point apparatus. The starting materials were purchased from Energy Chemical or J&K Chemicals and used without further purification. Solvents were dried and purified according to the procedure from the "Purification of Laboratory Chemicals" book. The reaction procedure was monitored through thin-layer chromatography (TLC), which was performed using 0.25 mm silica gel plates (60 F254) and was visualized using a UV lamp (254 nm). As for cyclic voltammetry experiments, a CHI760E electrochemical workstation was used. The crude products were purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent, and the reported yields are the actual isolated yields of pure products. The purity of products was determined by high-performance liquid chromatography (HPLC) with a Shimadzu LC-20AD system.

General Procedure for the Preparation of Various Quinoxalin-2(1*H*)-ones. The substrates of various quinoxalin-2(1*H*)-ones **1** were synthesized according to procedures described in the previous literature studies.[9a,20]

General Procedure for the Preparation of Various 1,2,4-Triazine-3,5(2*H*,4*H*)-diones. The substrates of various 1,2,4-triazine-3,5(2*H*,4*H*)-diones **4** were synthesized according to procedures described in the previous literature studies.[21]

General Procedure for the Preparation of Various *N*-Methylanilines. To a stirred solution of *N*-methylaniline (30 mmol) and Et_3N (75 mmol) in MeCN (30 mL), various halogenoalkanes (51 mmol) were added, and the mixture was heated to reflux for 16 h. Then, the solution was added with brine (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure to obtain a crude product, which was purified by column chromatography on silica gel to afford the alkylated *N*-methylanilines **2**.

General Procedure of Aminomethylation of *N*-Heterocycles (Condition for 3a−3b, 3h, 3j−3l, 3n−3r, and 5a−o). *N*-Heterocycle derivatives (**1** and **4**) (0.3 mmol) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.02 equiv., 0.006 mmol) were added to an oven-dried reaction vessel (dimension: 20 mL) equipped with a magnetic stir bar. Subsequently, anhydrous DMF (1.0 mL), DBU (1.0 equiv., 0.3 mmol), and *N*-methylaniline derivatives (**2**) (3.0 equiv., 0.9 mmol) were added successively through respective syringes. The mixture was stirred at room temperature under an air atmosphere and irradiated with a 25 W blue light-emitting diode (LED) lamp until the substrate was consumed completely (TLC monitoring, about 12 h). Then, the reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (20 mL × 3). The organic layer was separated, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure to obtain a crude product, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to afford the pure product.

General Procedure of Aminomethylation of Quinoxalin-2(1*H*)-ones (Condition for 3c−3g, 3i, and 3m). Quinoxalin-2(1*H*)-one derivatives (**1**) (0.3 mmol) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.02 equiv., 0.006 mmol) were added to an oven-dried reaction vessel (dimension: 20 mL) equipped with a magnetic stir bar. Then, the vessel was evacuated and backfilled with argon three times.

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Subsequently, anhydrous DMF (1.0 mL), DBU (1.0 equiv., 0.3 mmol), CHP (1.0 equiv., 0.3 mmol), and *N*-methylaniline derivatives (**2**) (3.0 equiv., 0.9 mmol) were added successively through respective syringes. The mixture was stirred at room temperature under an argon atmosphere and irradiated with a 25 W blue LED lamp until the substrate was consumed completely (TLC monitoring, about 12 h). Then, the reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (20 mL × 3). The organic layer was separated, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure to obtain a crude product, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to afford the pure product.

Scaled-Up Reaction Condition for 5b. 2,4-Dibenzyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (1.5 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.02 equiv., 0.03 mmol) were added to an oven-dried reaction vessel (dimension: 120 mL) equipped with a magnetic stir bar. Subsequently, anhydrous DMF (5.0 mL), DBU (1.0 equiv., 1.5 mmol), and *N*,*N*-dimethylaniline (3.0 equiv., 4.5 mmol) were added successively through respective syringes. The mixture was stirred at room temperature under an air atmosphere and irradiated with a 25 W blue LED lamp until the substrate was consumed completely (TLC monitoring, about 12 h). Then, the reaction mixture was quenched with water (100 mL) and extracted with ethyl acetate (100 mL × 3). The organic layer was separated, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure to obtain a crude product, which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5b** (78% yield, 483.1 mg) as a white solid.

Control Experiment A. 1-Methylquinoxalin-2(1*H*)-one (**1a**) (0.3 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.02 equiv., 0.006 mmol), and 2,2,6,6-tetramethyl-1-piperidinyloxy (3.0 equiv., 0.9 mmol) were added to an oven-dried reaction vessel (dimension: 20 mL) equipped with a magnetic stir bar. Subsequently, anhydrous DMF (1.0 mL), DBU (1.0 equiv., 0.3 mmol), and *N*,*N*-dimethylaniline (**2a**) (3.0 equiv., 0.9 mmol) were added successively through respective syringes. The mixture was stirred at room temperature under an air atmosphere and irradiated with a 25 W blue LED lamp for 12 h. However, no target product **3a** was detected by TLC (petroleum ether/ethyl acetate = 4:1 as a spread solvent). Compound **6a** was detected by HRMS (ESI) *m*/*z*: calcd for $C_{17}H_{28}KN_2O^+$ $[M + K]^+$, 315.1833; found, 315.1837.

Control Experiment B. 1-Methylquinoxalin-2(1*H*)-one (**1a**) (0.3 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.02 equiv., 0.006 mmol), and 1,4-diazabicyclo[2.2.2]octane (3.0 equiv., 0.9 mmol) were added to an oven-dried reaction vessel (dimension: 20 mL) equipped with a magnetic stir bar. Subsequently, anhydrous DMF (1.0 mL), DBU (1.0 equiv., 0.3 mmol), and *N*,*N*-dimethylaniline (**2a**) (3.0 equiv., 0.9 mmol) were added successively through respective syringes. The mixture was stirred at room temperature under an air atmosphere and irradiated with a 25 W blue LED lamp for 12 h. Then, the reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (20 mL × 3). The organic layer was separated, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure to obtain a crude product, which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3a** in 45% yield.

Control Experiment C. 1-Methylquinoxalin-2(1*H*)-one (**1a**) (0.3 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.02 equiv., 0.006 mmol) were added to an oven-dried reaction vessel (dimension: 20 mL) equipped with a magnetic stir bar. Subsequently, anhydrous DMF (1.0 mL), DBU (1.0 equiv., 0.3 mmol), and *N*,*N*-dimethylaniline (**2a**) (3.0 equiv., 0.9 mmol) were added successively through respective syringes. The mixture was stirred at room temperature under an air atmosphere and irradiated with a 25 W blue LED lamp for 4 h. The target product **3a** was detected by TLC (petroleum ether/ethyl acetate = 4:1 as a spread solvent). Compound **7a** was detected by HRMS (ESI) *m*/*z*: calcd for $C_8H_{10}N^+$ $[M]^+$, 120.0808; found, 120.0815.

Control Experiment D. 1-Methylquinoxalin-2(1*H*)-one (**1a**) (0.3 mmol) was added to an oven-dried reaction vessel (dimension: 20 mL) equipped with a magnetic stir bar. Subsequently, anhydrous DMF (1 mL), DBU (1.0 equiv., 0.3 mmol), and *N*, *N*-dimethylaniline (**2a**) (3.0 equiv., 0.9 mmol) were added successively through respective syringes. The mixture was stirred at room temperature under an air atmosphere and irradiated with a 25 W blue LED lamp for 12 h. The target product **3a** was not detected by TLC (petroleum ether/ethyl acetate = 4:1 as a spread solvent).

Control Experiment E. 1-Methylquinoxalin-2(1*H*)-one (**1a**) (0.3 mmol) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.02 equiv., 0.006 mmol) were added to an oven-dried reaction vessel (dimension: 20 mL) which was equipped with a magnetic stir bar and wrapped in tinfoil. Subsequently, anhydrous DMF (1 mL), DBU (1.0 equiv., 0.3 mmol), and *N*,*N*-dimethylaniline (**2a**) (3.0 equiv., 0.9 mmol) were added successively through respective syringes. The mixture was stirred in the dark at room temperature under an air atmosphere for 12 h. The target product **3a** was not detected by TLC (petroleum ether/ethyl acetate = 4:1 as a spread solvent).

Characterization of the Products. *1-Methyl-3-((methyl(phenyl)amino)methyl)quinoxalin-2(1H)-one (**3a**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3a** (83% yield, 69.3 mg) as a yellow solid, mp 86−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.0 Hz, 1H), 7.51 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 7.28 (dd, J = 8.0 Hz, J = 8.0 Hz, 2H), 7.20 (dd, J = 8.0 Hz, J = 8.0 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 6.70 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 4.74 (s, 2H), 3.68 (s, 3H), and 3.20 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.5, 154.8, 149.7, 133.2, 132.6, 130.4, 130.2, 129.0, 123.6, 116.5, 113.6, 112.6, 55.3, 39.7, and 28.9; and HRMS (ESI) *m*/*z*: calcd for $C_{17}H_{18}N_3O^+$ $[M + H]^+$, 280.1444; found, 280.1444. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 80:20, flow rate = 1 mL/min, λ = 254 nm, and t_R = 7.369 min).

*1-Ethyl-3-((methyl(phenyl)amino)methyl)quinoxalin-2(1H)-one (**3b**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3b** (73% yield, 64.3 mg) as a yellow solid, mp 106−107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8 Hz, 1H), 7.51 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 7.29 (dd, J = 8.0 Hz, J = 8.0 Hz, 2H), 7.24−7.19 (m, 2H), 6.90 (d, J = 8 Hz, 2H), 6.68 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 4.75 (s, 2H), 4.31 (q, J = 8.0 Hz, 2H), 3.20 (s, 3H), and 1.38 (t, J = 8.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.5, 154.3, 149.7, 132.9, 132.1, 130.7, 130.2, 129.0, 123.4, 116.5, 113.5, 112.6, 55.2, 39.6, 37.2, and 12.5; and HRMS (ESI) *m*/*z*: calcd for $C_{18}H_{20}N_3O^+$ $[M + H]^+$, 294.1601; found, 294.1599. Purity: 98% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 80:20, flow rate = 1 mL/min, λ = 254 nm, and t_R = 17.679 min).

*1-Benzyl-3-((methyl(phenyl)amino)methyl)quinoxalin-2(1H)-one (**3c**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3c** (50% yield, 53.4 mg) as a yellow solid, mp 141−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8 Hz, 1H), 7.39 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.33−7.22 (m, 9H), 6.93 (d, J = 8 Hz, 2H), 6.70 (dd, J = 8 Hz, J = 8 Hz, 1H), 5.49 (s, 2H), 4.81 (s, 2H), and 3.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.7, 154.9, 149.7, 135.1, 132.9, 132.5, 130.5, 130.19, 129.0, 129.0, 127.8, 126.9, 123.7, 116.6, 114.4, 112.6, 55.2, 45.8, and 39.7; and HRMS (ESI) *m*/*z*: calcd for $C_{23}H_{22}N_3O^+$ $[M + H]^+$, 356.1757; found, 356.1755. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 80:20, flow rate = 1 mL/min, λ = 254 nm, and t_R = 11.958 min).

*1-Allyl-3-((methyl(phenyl)amino)methyl)quinoxalin-2(1H)-one (**3d**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3d** (72% yield, 66.2 mg) as a yellow solid, mp 115−116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8 Hz, 1H), 7.48 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.31−7.19 (m, 4H), 6.90 (d, J = 8 Hz, 2H), 6.69 (dd, J = 8 Hz, J = 8 Hz, 1H), 5.98−5.89 (m, 1H), 3.76 (s, 3H), 3.36 (s, 3H), and 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.6, 154.4, 149.7, 132.8, 132.4, 130.6, 130.5, 130.1, 129.0, 123.6, 118.2, 116.6, 114.2, 112.6, 55.2, 44.4, and 39.6; and HRMS (ESI) *m*/*z*: calcd for $C_{19}H_{20}N_3O^+$ $[M + H]^+$, 306.1601; found, 306.1591. Purity: 99% (HPLC: a Shim-pack VP-ODS column,

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MeOH/H_2O = 90:10, flow rate = 1 mL/min, λ = 254 nm, and t_R = 5.181 min).

*Methyl 2-(3-((methyl(phenyl)amino)methyl)-2-oxoquinoxalin-1(2H)-yl)acetate (**3e**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3e** (64% yield, 65.0 mg) as a yellow solid, mp 113−115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8 Hz, 1H), 7.49 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.31 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.22 (dd, J = 8 Hz, J = 8 Hz, 2H), 7.05 (d, J = 8 Hz, 1H), 6.90 (d, J = 8 Hz, 2H), 6.69 (dd, J = 8 Hz, J = 8 Hz, 1H), 5.03 (s, 2H), 4.76 (s, 2H), 3.78 (s, 3H), and 3.19 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.6, 156.4, 154.3, 149.6, 132.7, 132.3, 130.8, 130.4, 129.0, 124.0, 116.6, 113.0, 112.6, 55.2, 53.0, 43.3, and 39.5; and HRMS (ESI) m/z: calcd for $C_{19}H_{20}N_3O_3^+$ [M + H]$^+$, 338.1499; found, 338.1499. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 80:20, flow rate = 1 mL/min, λ = 254 nm, and t_R = 6.037 min).

*tert-Butyl 2-(3-((methyl(phenyl)amino)methyl)-2-oxoquinoxalin-1(2H)-yl)acetate (**3f**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3f** (72% yield, 81.4 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8 Hz, 1H), 7.48 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.29 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.21 (dd, J = 8 Hz, J = 8 Hz, 2H), 7.03 (d, J = 8 Hz, 1H), 6.88 (d, J = 8 Hz, 2H), 6.68 (dd, J = 8 Hz, J = 8 Hz, 1H), 4.93 (s, 2H), 4.75 (s, 2H), 3.18 (s, 3H), and 1.46 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.1, 156.3, 154.2, 149.6, 132.6, 132.3, 130.6, 130.2, 129.0, 123.8, 116.5, 113.0, 112.5, 83.2, 55.1, 44.0, 39.5, and 28.0; and HRMS (ESI) m/z: calcd for $C_{22}H_{26}N_3O_3^+$ [M + H]$^+$, 380.1969; found, 380.1969. Purity: 98% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 80:20, flow rate = 1 mL/min, λ = 254 nm, and t_R = 9.773 min).

*1,7-Dimethyl-3-((methyl(phenyl)amino)methyl)quinoxalin-2(1H)-one (**3g**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3g** (80% yield, 70.1 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8 Hz, 1H), 7.20 (dd, J = 8 Hz, J = 8 Hz, 2H), 7.12 (d, J = 8 Hz, 1H), 7.07 (s, 1H), 6.90 (d, J = 8 Hz, 2H), 6.68 (dd, J = 8 Hz, J = 8 Hz, 1H), 4.71 (s, 2H), 3.67 (s, 3H), 3.19 (s, 3H), and 2.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.2, 154.9, 149.7, 140.9, 133.1, 130.8, 130.0, 128.9, 124.9, 116.4, 113.7, 112.6, 55.3, 39.6, 28.8, and 22.1; and HRMS (ESI) m/z: calcd for $C_{18}H_{20}N_3O^+$ [M + H]$^+$, 294.1601; found, 294.1593. Purity: 98% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 80:20, flow rate = 1 mL/min, λ = 254 nm, and t_R = 9.120 min).

*1,6,7-Trimethyl-3-((methyl(phenyl)amino)methyl)quinoxalin-2(1H)-one (**3h**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3h** (86% yield, 79.2 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.20 (dd, J = 8 Hz, J = 8 Hz, 2H), 7.04 (s, 1H), 6.90 (d, J = 8 Hz, 2H), 6.68 (dd, J = 8 Hz, J = 8 Hz, 1H), 4.71 (s, 2H), 3.67 (s, 3H), 3.19 (s, 3H), 2.39 (s, 3H), and 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 154.8, 149.7, 140.0, 132.5, 131.2, 131.0, 130.4, 128.9, 116.4, 114.1, 112.6, 55.3, 39.5, 28.8, 20.6, and 19.1; and HRMS (ESI) m/z: calcd for $C_{19}H_{22}N_3O^+$ [M + H]$^+$, 308.1757; found, 308.1751. Purity: >99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 90:10, flow rate = 1 mL/min, λ = 254 nm, and t_R = 6.298 min).

*1-Ethyl-6,7-dimethyl-3-((methyl(phenyl)amino)methyl)-quinoxalin-2(1H)-one (**3i**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3i** (63% yield, 60.9 mg) as a yellow solid, mp 133−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.20 (dd, J = 8 Hz, J = 8 Hz, 2H), 7.06 (s, 1H), 6.90 (d, J = 8 Hz, 2H), 6.68 (dd, J = 8 Hz, J = 8 Hz, 1H), 4.71 (s, 2H), 4.29 (q, J = 8 Hz, 2H), 3.19 (s, 3H), 2.40 (s, 3H), 2.31 (s, 3H), and 1.37 (t, J = 8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.2, 154.4, 149.8, 140.0, 132.4, 131.4, 130.7, 130.1, 129.0, 116.4, 113.9, 112.6, 55.3, 39.6, 37.1, 20.7, 19.1, and 12.6; and HRMS (ESI) m/z: calcd for $C_{20}H_{24}N_3O^+$ [M + H]$^+$, 322.1914; found, 322.1919. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 70:30, flow rate = 1 mL/min, λ = 254 nm, and t_R = 36.525 min).

*1-Methyl-3-((methyl(p-tolyl)amino)methyl)quinoxalin-2(1H)-one (**3j**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3j** (85% yield, 74.6 mg) (conditions[b]) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8 Hz, 1H), 7.51 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.32−7.25 (m, 2H), 7.01 (d, J = 8 Hz, 2H), 6.83 (d, J = 8 Hz, 2H), 4.70 (s, 2H), 3.68 (s, 3H), 3.16 (s, 3H), and 2.22 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.7, 154.7, 147.6, 133.2, 132.6, 130.3, 130.1, 129.5, 125.7, 123.5, 113.5, 112.9, 55.5, 39.7, 28.9, and 20.2; and HRMS (ESI) m/z: calcd for $C_{18}H_{20}N_3O^+$ [M + H]$^+$, 294.1601; found, 294.1605. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 90:10, flow rate = 1 mL/min, λ = 254 nm, and t_R = 5.555 min).

*1-Methyl-3-((methyl(m-tolyl)amino)methyl)quinoxalin-2(1H)-one (**3k**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3k** (86% yield, 75.3 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8 Hz, 1H), 7.53−7.49 (m, 1H), 7.31−7.24 (m, 2H), 7.09 (dd, J = 8 Hz, J = 8 Hz, 1H), 6.71 (d, J = 8 Hz, 2H), 6.51 (d, J = 8 Hz, 1H), 4.73 (s, 2H), 3.68 (s, 3H), 3.18 (s, 3H), and 2.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.6, 154.8, 149.7, 138.7, 133.2, 132.6, 130.4, 130.2, 128.9, 123.6, 117.5, 113.6, 113.3, 109.8, 55.3, 39.7, 28.9, and 22.0; and HRMS (ESI) m/z: calcd for $C_{18}H_{20}N_3O^+$ [M + H]$^+$, 294.1601; found, 294.1595. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 90:10, flow rate = 1 mL/min, λ = 254 nm, and t_R = 3.059 min).

*3-(((4-Ethylphenyl) (methyl)amino)methyl)-1-methylquinoxalin-2(1H)-one (**3l**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3l** (79% yield, 69.7 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8 Hz, 1H), 7.50 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.31−7.24 (m, 2H), 7.05 (d, J = 8 Hz, 2H), 6.86 (d, J = 8 Hz, 2H), 4.70 (s, 2H), 3.67 (s, 3H), 3.17 (s, 3H), 2.52 (q, J = 8 Hz, 2H), and 1.17 (t, J = 8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.8, 154.8, 147.8, 133.2, 132.6, 132.4, 130.4, 130.2, 128.4, 123.6, 113.6, 55.6, 39.7, 28.9, 27.8, and 16.0; and HRMS (ESI) m/z: calcd for $C_{19}H_{22}N_3O^+$ [M + H]$^+$, 308.1757; found, 308.1759. Purity: 98% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 8.447 min).

*3-(((4-Methoxyphenyl)(methyl)amino)methyl)-1-methylquinoxalin-2(1H)-one (**3m**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3m** (72% yield, 66.8 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8 Hz, 1H), 7.54−7.51 (m, 1H), 7.33−7.26 (m, 2H), 6.92 (d, J = 8 Hz, 2H), 6.81 (d, J = 8 Hz, 2H), 4.65 (s, 2H), 3.73 (s, 3H), 3.70 (s, 3H), and 3.11 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.8, 154.8, 151.8, 144.7, 133.2, 132.6, 130.4, 130.2, 123.6, 114.6, 114.6, 113.6, 56.4, 55.8, 39.9, and 29.0; and HRMS (ESI) m/z: calcd for $C_{18}H_{20}N_3O_2^+$ [M + H]$^+$, 310.1550; found, 310.1540. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 80:20, flow rate = 1 mL/min, λ = 254 nm, and t_R = 3.733 min).

*3-(((4-Bromophenyl) (methyl)amino)methyl)-1-methylquinoxalin-2(1H)-one (**3n**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3n** (49% yield, 52.3 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8 Hz, 1H), 7.56−7.52 (m, 1H), 7.34−7.24 (m, 4H), 6.75 (d, J = 8 Hz, 2H), 4.72 (s, 2H), 3.70 (s, 3H), and 3.17 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.0, 154.7, 148.6, 133.2, 132.5, 131.6, 130.4, 130.4, 123.7, 114.2, 113.6, 108.4, 55.1, 39.8, and 29.0; and HRMS (ESI) m/z: calcd for $C_{17}H_{17}BrN_3O^+$ [M + H]$^+$, 358.0550; found, 358.0550. Purity: 97% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 90:10, flow rate = 1 mL/min, λ = 254 nm, and t_R = 4.892 min).

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*3-((Ethyl(phenyl)amino)methyl)-1-methylquinoxalin-2(1H)-one (**3o**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3o** (58% yield, 51.1 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8 Hz, 1H), 7.50 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.31−7.24 (m, 2H), 7.18 (dd, J = 8 Hz, J = 8 Hz, 2H), 6.83 (d, J = 8 Hz, 2H), 6.64 (dd, J = 8 Hz, J = 8 Hz, 1H), 4.72 (s, 2H), 3.69−3.64 (m, 5H), and 1.25 (t, J = 8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.6, 154.8, 148.4, 133.2, 132.7, 130.4, 130.1, 129.1, 123.6, 116.0, 113.6, 112.4, 52.6, 45.8, 28.9, and 12.1; and HRMS (ESI) m/z: calcd for $C_{18}H_{20}N_3O^+$ [M + H]$^+$, 294.1601; found, 294.1608. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 90:10, flow rate = 1 mL/min, λ = 254 nm, and t_R = 3.498 min).

*3-((Butyl(phenyl)amino)methyl)-1-methylquinoxalin-2(1H)-one (**3p**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3p** (50% yield, 48.0 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8 Hz, 1H), 7.49 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.27 (dd, J = 8 Hz, J = 8 Hz, 2H), 7.16 (dd, J = 8 Hz, J = 8 Hz, 2H), 6.80 (d, J = 8 Hz, 2H), 6.62 (dd, J = 8 Hz, J = 8 Hz, 1H), 4.73 (s, 2H), 3.68 (s, 3H), 3.58 (t, J = 8 Hz, 2H), 1.72−1.64 (m, 2H), 1.44−1.35 (m, 2H), and 0.96 (t, J = 8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.4, 154.7, 148.5, 133.0, 132.6, 130.3, 130.0, 129.0, 123.5, 115.8, 113.5, 112.2, 53.0, 51.5, 29.2, 28.8, 20.4, and 14.1; HRMS (ESI) m/z: calcd for $C_{20}H_{24}N_3O^+$ [M + H]$^+$, 322.1914; found, 322.1913. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 90:10, flow rate = 1 mL/min, λ = 254 nm, and t_R = 6.812 min).

*3-((Allyl(phenyl)amino)methyl)-1-methylquinoxalin-2(1H)-one (**3q**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3q** (43% yield, 39.5 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13−8.11 (m, 3H), 7.88−7.81 (m, 2H), 7.52−7.37 (m, 5H), 3.66 (s, 3H), 3.39 (s, 3H), and 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.5, 154.7, 148.8, 134.2, 133.1, 132.6, 130.4, 130.1, 128.9, 123.6, 116.4, 116.1, 113.5, 112.5, 53.9, 52.6, and 28.9; and HRMS (ESI) m/z: calcd for $C_{19}H_{20}N_3O^+$ [M + H]$^+$, 306.1601; found, 306.1601. Purity: 98% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 70:30, flow rate = 1 mL/min, λ = 254 nm, and t_R = 21.005 min).

*3-((Benzyl(phenyl)amino)methyl)-1-methylquinoxalin-2(1H)-one (**3r**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1 as an eluent) to afford the product **3r** (40% yield, 42.1 mg) as a yellow solid, mp 106−108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8 Hz, 1H), 7.52 (dd, J = 8 Hz, J = 8 Hz, 1H), 7.31−7.21 (m, 6H), 7.14 (dd, J = 8 Hz, J = 8 Hz, 2H), 6.81 (d, J = 8 Hz, 2H), 6.66 (dd, J = 8 Hz, J = 8 Hz, 1H), 4.89 (s, 2H), 4.86 (s, 2H), and 3.68 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.4, 154.7, 149.0, 139.2, 133.2, 132.7, 130.4, 130.2, 129.1, 128.6, 126.8, 123.7, 116.6, 113.6, 112.6, 55.4, 53.1, and 28.9; and HRMS (ESI) m/z: calcd for $C_{23}H_{22}N_3O^+$ [M + H]$^+$, 356.1757; found, 356.1752. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 80:20, flow rate = 1 mL/min, λ = 254 nm, and t_R = 13.461 min).

*2,4-Dimethyl-6-((methyl(phenyl)amino)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5a**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5a** (73% yield, 57.6 mg) as a white solid, mp 108−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, J = 8 Hz, J = 8 Hz, 2H), 6.86 (d, J = 8 Hz, 2H), 6.73 (dd, J = 8 Hz, J = 8 Hz, 1H), 4.42 (s, 2H), 3.59 (s, 3H), 3.34 (s, 3H), and 3.09 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.4, 149.1, 148.9, 140.6, 129.1, 117.0, 112.6, 52.1, 39.7, 39.4, and 27.1; and HRMS (ESI) m/z: calcd for $C_{13}H_{17}N_4O_2^+$ [M + H]$^+$, 261.1346; found, 261.1343. Purity: >99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 14.716 min).

*2,4-Dibenzyl-6-((methyl(phenyl)amino)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5b**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5b** (75% yield, 92.8 mg) as a white solid, mp 130−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8 Hz, 2H), 7.31−7.19 (m, 10H), 6.78 (dd, J = 8 Hz, J = 8 Hz, 3H), 5.04 (s, 2H), 4.99 (s, 2H), 4.45 (s, 2H), and 3.06 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.9, 148.8, 148.7, 140.9, 135.4, 135.3, 129.5, 129.1, 128.9, 128.6, 128.6, 128.2, 128.1, 116.9, 112.6, 55.4, 51.9, 44.2, and 39.5; and HRMS (ESI) m/z: calcd for $C_{25}H_{25}N_4O_2^+$ [M + H]$^+$, 413.1972; found, 413.1977. Purity: >99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 24.488 min).

*2,4-Bis(4-fluorobenzyl)-6-((methyl(phenyl)amino)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5c**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5c** (77% yield, 103.2 mg) as a white solid, mp 131−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49−7.45 (m, 2H), 7.20 (dd, J = 8 Hz, J = 8 Hz, 2H), 7.16−7.14 (m, 2H), 7.01−6.96 (m, 2H), 6.91 (dd, J = 8 Hz, J = 8 Hz, 2H), 6.76 (dd, J = 8 Hz, J = 8 Hz, 3H), 5.00 (s, 2H), 4.94 (s, 2H), 4.47 (s, 2H), and 3.07 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.77 (d, J = 72 Hz), 161.31 (d, J = 68 Hz), 155.8, 148.7, 148.6, 140.9, 131.5 (d, J = 80 Hz), 131.2 (d, J = 29 Hz), 131.0 (d, J = 35 Hz), 130.8 (d, J = 80 Hz), 129.1, 117.0, 115.6 (d, J = 89 Hz), 115.4 (d, J = 88 Hz), 112.5, 54.6, 51.7, 43.4, and 39.6; ^{19}F{1H} NMR (376 MHz, $CDCl_3$): δ −113.5 (d, J = 13 Hz, 1F) and −113.6 (d, J = 14 Hz, 1F); and HRMS (ESI) m/z: calcd for $C_{25}H_{23}F_2N_4O_2^+$ [M + H]$^+$, 449.1784; found, 449.1781. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 11.913 min).

*2,4-Diallyl-6-((methyl(phenyl)amino)methyl)-1,2,4-triazine-3,5-(2H,4H)-dione (**5d**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5d** (80% yield, 74.7 mg) as a white solid, mp 113−115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, J = 8 Hz, J = 8 Hz, 2H), 6.86 (d, J = 8 Hz, 2H), 6.73 (dd, J = 8 Hz, J = 8 Hz, 1H), 5.90−5.81 (m, 1H), 5.32−5.21 (m, 2H), 4.53−4.50 (m, 4H), 4.44 (s, 2H), and 3.09 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.8, 148.9, 148.4, 141.2, 131.3, 130.3, 129.1, 119.4, 119.3, 117.1, 112.8, 54.0, 52.3, 43.0, and 39.5; and HRMS (ESI) m/z: calcd for $C_{17}H_{21}N_4O_2^+$ [M + H]$^+$, 313.1659; found, 313.1655. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 6.382 min).

*6-((Methyl(phenyl)amino)methyl)-2,4-bis(2-oxo-2-phenylethyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5e**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5e** (64% yield, 89.5 mg) as a yellow solid, mp 67−69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, J = 8 Hz, J = 8 Hz, 4H), 7.62 (dd, J = 8 Hz, J = 8 Hz, 2H), 7.50(dd, J = 8 Hz, J = 8 Hz, 4H), 7.25−7.21 (m, 2H), 6.86 (d, J = 8 Hz, 2H), 6.74 (dd, J = 8 Hz, J = 8 Hz, 1H), 5.39−5.38 (m, 4H), 4.47 (s, 2H), and 3.03 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.4, 190.3, 155.8, 149.1, 149.1, 141.9, 134.5, 134.4, 134.2, 134.2, 129.1, 129.0, 128.9, 128.2, 128.1, 117.3, 112.9, 57.6, 52.4, 46.6, and 38.9; and HRMS (ESI) m/z: calcd for $C_{27}H_{25}N_4O_4^+$ [M + H]$^+$, 469.1870; found, 469.1867. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 90:10, flow rate = 1 mL/min, λ = 254 nm, and t_R = 4.552 min).

*2,4-Dibenzyl-6-((methyl(p-tolyl)amino)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5f**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5f** (80% yield, 102.1 mg) as a yellow solid, mp 88−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7 Hz, 2H), 7.29−7.22 (m, 8H), 7.01 (d, J = 8 Hz, 2H), 6.72 (d, J = 8 Hz, 2H), 5.02 (s, 2H), 4.97 (s, 2H), 4.41 (s, 2H), 3.02 (s, 3H), and 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.9, 148.7, 146.7, 141.1, 135.5, 135.3, 129.6, 129.4, 128.8, 128.6, 128.5, 128.1, 128.1, 126.1 112.9, 55.3, 52.1, 44.1, 39.5, and 20.3; and HRMS (ESI) m/z: calcd for $C_{26}H_{27}N_4O_2^+$ [M + H]$^+$, 427.2129; found, 427.2122. Purity: >99% (HPLC: a Shim-pack VP-ODS column,

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MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 27.237 min).

*2,4-Dibenzyl-6-((methyl(m-tolyl)amino)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5g**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5g** (72% yield, 91.9 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 6 Hz, 2H), 7.32−7.22 (m, 8H), 7.09 (dd, J = 8 Hz, J = 8 Hz, 1H), 6.60 (dd, J = 8 Hz, J = 8 Hz, 3H), 5.04 (s, 2H), 4.99 (s, 2H), 4.44 (s, 2H), 3.05 (s, 3H), and 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.0, 149.0, 148.8, 141.1, 138.8, 135.6, 135.4, 129.6, 129.1, 128.9, 128.7, 128.7, 128.3, 128.2, 118.0, 113.4, 109.9, 55.5, 51.9, 44.2, 39.6, and 22.0; and HRMS (ESI) m/z: calcd for $C_{26}H_{27}N_4O_2^+$ $[M + H]^+$, 427.2129; found, 427.2126. Purity: 98% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 14.372 min).

*2,4-Dibenzyl-6-(((4-ethylphenyl) (methyl)amino)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5h**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5h** (74% yield, 97.3 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 6 Hz, 2H), 7.31−7.25 (m, 8H), 7.04 (d, J = 8 Hz, 2H), 6.75 (d, J = 8 Hz, 2H), 5.03 (s, 2H), 4.99 (s, 2H), 4.41 (s, 2H), 3.03 (s, 3H), 2.57 (q, J = 8 Hz, 2H), and 1.21 (t, J = 8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.9, 148.7, 146.9, 141.2, 135.5, 135.3, 132.7, 129.4, 128.9, 128.6, 128.6, 128.4, 128.2, 128.1, 112.8, 55.3, 52.1, 44.1, 39.5, 27.8, and 16.0; and HRMS (ESI) m/z: calcd for $C_{27}H_{29}N_4O_2^+$ $[M + H]^+$, 441.2285; found, 441.2285. Purity: 98% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 19.486 min).

*2,4-Dibenzyl-6-(((4-methoxyphenyl) (methyl)amino)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5i**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5i** (78% yield, 103.8 mg) as a yellow solid, mp 76−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 7 Hz, 2H), 7.32−7.23 (m, 8H), 6.80 (d, J = 4 Hz, 4H), 5.05 (s, 2H), 5.00 (s, 2H), 4.37 (s, 2H), 3.76 (s, 3H), and 2.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.0, 152.0, 148.8, 143.7, 141.3, 135.5, 135.4, 129.5, 128.9, 128.7, 128.6, 128.3, 128.2, 114.7, 114.6, 55.8, 55.4, 52.9, 44.2, and 39.8; and HRMS (ESI) m/z: calcd for $C_{26}H_{27}N_4O_3^+$ $[M + H]^+$, 443.2078; found, 443.2075. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 9.756 min).

*2,4-Dibenzyl-6-((butyl(phenyl)amino)methyl)-1,2,4-triazine-3,5-(2H,4H)-dione (**5j**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5j** (76% yield, 104.2 mg) as a yellow solid, mp 63−64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 6 Hz, 2H), 7.32−7.23 (m, 8H), 7.18 (dd, J = 8 Hz, J = 8 Hz, 2H), 6.72 (dd, J = 8 Hz, J = 8 Hz, 3H), 5.05 (s, 2H), 4.99 (s, 2H), 4.44 (s, 2H), 3.42 (t, J = 8 Hz, 2H), 1.60 (m, 2H), 1.34 (m, 2H), and 0.93 (t, J = 8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.0, 148.8, 147.8, 141.0, 135.5, 135.3, 129.5, 129.2, 129.0, 128.7, 128.6, 128.2, 128.2, 116.4, 112.4, 55.4, 51.5, 50.1, 44.2, 29.4, 20.3, and 14.1; and HRMS (ESI) m/z: calcd for $C_{28}H_{31}N_4O_2^+$ $[M + H]^+$, 455.2442; found, 455.2438. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 90:10, flow rate = 1 mL/min, λ = 254 nm, and t_R = 5.048 min).

*6-((Allyl(phenyl)amino)methyl)-2,4-dibenzyl-1,2,4-triazine-3,5-(2H,4H)-dione (**5k**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5k** (73% yield, 96.5 mg) as a yellow solid, mp 72−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 6 Hz, 2H), 7.31−7.24 (m, 8H), 7.17 (dd, J = 8 Hz, J = 8 Hz, 2H), 6.77−6.71 (m, 3H), 5.87−5.78 (m, 1H), 5.16−5.02 (m, 6H), 4.45 (s, 2H), and 4.07 (d, J = 4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.9, 148.7, 148.0, 141.1, 135.4, 135.3, 133.9, 129.5, 129.1, 128.9, 128.7, 128.6, 128.2, 128.1, 116.9, 116.2, 112.6, 55.3, 53.7, 49.7, and 44.2; and HRMS (ESI) m/z: calcd for $C_{27}H_{27}N_4O_2^+$ $[M + H]^+$, 439.2129; found, 439.2137. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 15.126 min).

*2,4-Dibenzyl-6-((benzyl(phenyl)amino)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5l**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5l** (54% yield, 78.4 mg) as a white solid, mp 113−115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 6 Hz, 2H), 7.31−7.26 (m, 10H), 7.21−7.14 (m, 5H), 6.76 (dd, J = 8 Hz, J = 8 Hz, 3H), 5.03 (s, 2H), 5.01 (s, 2H), 4.69 (s, 2H), and 4.54 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.9, 148.7, 148.4, 141.1, 138.7, 135.5, 135.4, 129.5, 129.2, 129.0, 128.7, 128.6, 128.6, 128.3, 128.2, 126.9, 126.7, 117.2, 112.9, 55.4, 55.2, 50.2, and 44.2; and HRMS (ESI) m/z: calcd for $C_{31}H_{29}N_4O_2^+$ $[M + H]^+$, 489.2285; found, 489.2279. Purity: 98% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 20.023 min).

*2,4-Dibenzyl-6-((methyl(naphthalen-1-yl)amino)methyl)-1,2,4-triazine-3,5(2H,4H)-dione (**5m**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5m** (75% yield, 103.8 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31−8.29 (m, 1H), 7.83−7.81 (m, 1H), 7.56 (d, J = 8 Hz, 1H), 7.47−7.43 (m, 4H), 7.37−7.21 (m, 9H), 7.15 (d, J = 8 Hz, 1H), 5.04 (s, 2H), 5.00 (s, 2H), 4.30 (s, 2H), and 2.92 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.8, 149.0, 148.8, 141.6, 135.6, 135.5, 134.8, 129.6, 129.5, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 125.9, 125.6, 125.6, 123.9, 123.9, 116.6, 55.5, 55.0, 44.2, and 43.1; and HRMS (ESI) m/z: calcd for $C_{29}H_{27}N_4O_2^+$ $[M + H]^+$, 463.2129; found, 463.2128. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 5.450 min).

*2,4-Dibenzyl-6-(1-(ethyl(phenyl)amino)ethyl)-1,2,4-triazine-3,5-(2H,4H)-dione (**5n**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 as an eluent) to afford the product **5n** (78% yield, 103.4 mg) as yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.42 (m, 2H), 7.31−7.24 (m, 8H), 7.22−7.18 (m, 2H), 6.86 (d, J = 8 Hz, 2H), 6.72 (dd, J = 7 Hz, J = 7 Hz, 1H), 6.86 (q, J = 7 Hz, 1H), 5.16−5.00 (m, 4H), 3.39−3.22 (m, 2H), 1.44 (d, J = 7 Hz, 3H), and 0.98 (t, J = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.5, 148.8, 147.8, 144.7, 135.6, 135.6, 129.4, 129.2, 128.8, 128.7, 128.6, 128.3, 128.1, 117.3, 114.1, 55.4, 52.3, 44.3, 39.3, 15.0, and 14.5; and HRMS (ESI) m/z: calcd for $C_{27}H_{29}N_4O_2^+$ $[M + H]^+$, 441.2285; found, 441.2285. Purity: >99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 85:15, flow rate = 1 mL/min, λ = 254 nm, and t_R = 15.515 min).

*2,4-Dibenzyl-6-((phenylamino)methyl)-1,2,4-triazine-3,5-(2H,4H)-dione (**5o**).* The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 as an eluent) to afford the product **5o** (53% yield, 63.8 mg) as a yellow solid, mp 127−128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 2 Hz, 2H), 7.44−7.24 (m, 8H), 7.16 (dd, J = 8 Hz, J = 8 Hz, 2H), 6.74 (dd, J = 8 Hz, J = 8 Hz, 1H), 6.69−6.67 (m, 2H), 5.08 (s, 2H), 5.05 (s, 2H), 4.44 (t, J = 6 Hz, 1H), and 4.29 (d, J = 6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.7, 148.8, 146.9, 141.6, 135.4, 135.4, 129.4, 129.3, 128.8, 128.8, 128.7, 128.3, 128.2, 118.3, 113.5, 55.4, 44.3, and 43.5; and HRMS (ESI) m/z: calcd for $C_{24}H_{23}N_4O_2^+$ $[M + H]^+$, 399.1816; found, 399.1816. Purity: 99% (HPLC: a Shim-pack VP-ODS column, MeOH/H_2O = 70:30, flow rate = 1 mL/min, λ = 254 nm, and t_R = 31.705 min).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01207.

Details of the photoreaction setup, cyclic voltammetry, copies of ^{1}H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra for all products, and copies of HPLC chromatograms for all products (PDF)

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Notes

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