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Photo-Induced Cross-Dehydrogenative Alkylation of Heteroarenes with Alkanes under Aerobic Conditions

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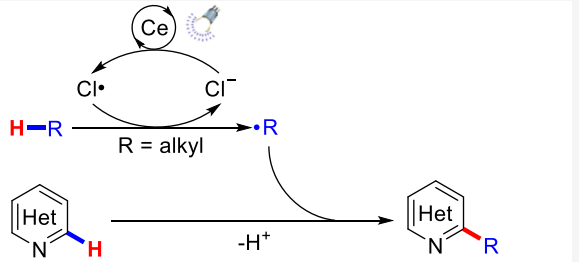
ABSTRACT: We report a Minisci-type cross-dehydrogenative alkylation in an aerobic atmosphere using abundant and inexpensive cerium chloride as a photocatalyst and air as an oxidant. This photoreaction exhibits excellent tolerance to functional groups and is suitable for both heteroarene and alkane substrates under mild conditions, generating the corresponding products in moderate-to-good yields. Our method provides an alternative approach for the late-stage functionalization of valuable substrates.



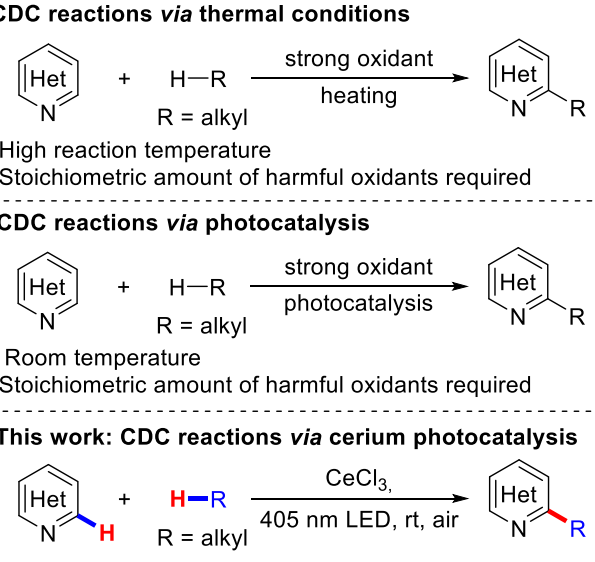
(+) Cerium-photocatalyzed cross-dehydrogenative alkylation
(+) Air acts as a green oxidant
(+) Wide substrate scope with mild conditions

INTRODUCTION

Heteroarenes are important structural motifs in coordination complexes, natural products, advanced materials, and pharmaceuticals.[1] The development of synthetic methods that allow their rapid derivatization and direct structural modification at a late stage through C−H functionalization is of great value and significance.[2−4] Minisci-type reactions provide a powerful tool for the construction of $C(sp^2)-C(sp^3)$ bonds between heteroarenes and alkyl radicals. In recent decades, considerable effort has been made to develop new Minisci-type alkylations that allow efficient, environmentally friendly formation of alkyl radicals. Much has been reported on the generation of alkyl radicals from alkyl carboxylic acids,[5] boronic acids,[6] alkyl halides,[7] and others;[8,9] however, these methods often suffer from high cost and low atom economy. In contrast, alkanes are abundant and inexpensive. They represent ideal alkylation reagents as no prefunctionalization is required, allowing for atom- and step-economical synthesis. In this context, the direct generation of alkyl radicals from alkanes for Minisci-type reactions has recently received considerable attention.[10,11]

The key to successful cross-dehydrogenative alkylation lies in the effective activation of the $C(sp^3)$-H bonds of the alkane to form active open-shell species. A straightforward way to produce alkyl radicals is through oxidative C−H activation, which usually requires expensive, strong oxidants. Among them, thermal cleavage to generate the desired radicals is the most common approach (Scheme 1a).[12,13] Such a process requires a high reaction temperature, which not only degrades the selectivity of the reaction but also increases the safety risk, especially for large-scale syntheses. Recently, photocatalyzed cross-dehydrogenative coupling (CDC) reactions have opened up tremendous opportunities for the sustainable modification

Scheme 1. Cross-Dehydrogenative Alkylation of Heteroarenes with Alkanes



or synthesis of various heteroarenes (Scheme 1b).[14−16] Although the reaction temperature was lowered to room

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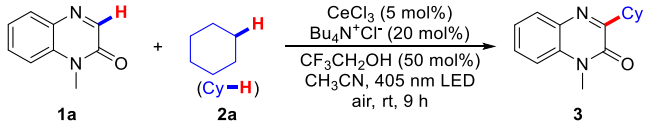
temperature, expensive photocatalysts and stoichiometric strong oxidants were still required, which not only drove up the cost but also made downstream purification difficult. Therefore, it would be desirable to develop CDC reactions under milder conditions by employing cheaper photocatalysts and more environmentally friendly oxidants.

Rare-earth metals have been used as powerful tools for the development of breakthrough technologies.[17] Indeed, related technologies have been applied in many fields, such as optogenetics, biosensing, photothermal therapy, super-resolution imaging, aggregation-induced emission, and organocatalysis.[18] Recent studies have shown that rare-earth metals can also act as a unique platform for photocatalytic reactions due to their unique physical and chemical properties.[19,20] On the other hand, the photocatalytic CDC reactions using chlorine radicals as a reagent for hydrogen atom transfer have attracted considerable attention.[21,22] For example, Li's group recently reported a cobalt-photocatalyzed cross-dehydrogenative heteroarylation of C(sp^3)-H bonds.[21a] In this transformation, chlorine radicals produced *in situ* are used to generate alkyl radicals, and cobalt catalysts are used to enable H_2 evolution for catalytic turnover, providing a practical protocol for the modification of heteroarenes. In sharp contrast, the CDC reaction facilitated by cerium photocatalysis has rarely been reported. During the preparation of our article, Schelter's groups have made a revolutionary discovery enabling the C−H amination of alkanes by a cerium-photocatalyzed ligand-to-metal charge-transfer (LMCT) process.[20a] While investigating the mechanism, they gave an example for the C−H alkylation of heteroarenes using stoichiometric amounts of $(NH_4)_2S_2O_8$ as an oxidant. Although significant progress has been made, they are far from achieving green synthesis and atom economy due to the requirements of strong oxidants. Compared with harmful oxidants, abundant molecular oxygen (O_2) is considered a clean and cheap oxidant for cerium-photocatalyzed organic transformations due to its inexpensive and environmentally friendly properties.[23] For example, in 2020, Mashima and co-workers photocatalyzed the aerobic decarboxylative oxygenation of aliphatic carboxylic acids and lactonization of 2-isopropylbenzoic acids with cerium.[23a] Based on our previous work on C−H functionalization,[24] we report here a cerium-photocatalyzed cross-dehydrogenative alkylation of heteroarenes with simple alkanes using air as the green terminal oxidant (Scheme 1c). The chlorine radical generated *in situ* serves as a hydrogen atom-transfer reagent. The coupling between a wide range of heteroarenes and simple nonfunctionalized alkanes proceeded smoothly and gave the corresponding products in moderate-to-good yields.

RESULTS AND DISCUSSION

The reaction conditions of CDC were optimized by evaluating the photocatalyst, additive, proton source, solvent, and reaction time (Table 1 and the Supporting Information, Table S1−S6). The target product (**3**) was obtained in 87% yield by reacting quinoxalin-2(1*H*)-one (**1a**)[25] (0.2 mmol) with cyclohexane (**2a**) (15 equiv), $CeCl_3$ (5 mol %), $Bu_4N^+Cl^-$ (20 mol %), CF_3CH_2OH (50 mol %), and CH_3CN (1.0 mL) under 405 nm light-emitting diode (LED) (10 W) irradiation for 9 h (Table 1, entry 1). In the absence of $CeCl_3$ or visible light, no desired product was generated (Table 1, entries 2 and 3). It should be noted that the reaction did not proceed without CF_3CH_2OH, probably because protonation of the nitrogen atom with CF_3CH_2OH can activate heteroarenes in Minisci transformations (Table 1, entry 4).[26] It should be noted that $Bu_4N^+Cl^-$ was used because it is a convenient and organically soluble source of chloride ions. The yield decreased to 18% without $Bu_4N^+Cl^-$ (Table 1, entry 5). Other quaternary ammonium salts such as $Bu_4N^+F^-$, $Bu_4N^+F^-$, and $Bu_4N^+OAc^-$ were tested and gave low yields (Table S2, entries 2−4). These results show the importance of the chloride ion in the reaction. Reducing the stoichiometric amount of cyclohexane or increasing the reaction time did not improve the yield (Table 1, entries 6 and 7). The reaction did not proceed under a nitrogen atmosphere, indicating that O_2 involved in this transformation (Table 1, entry 8). Further investigation of the proton source and solvent did not improve the product yield (Tables S3−S5).

Table 1. Evaluation of Reaction Conditions for Cerium-Photocatalyzed CDC Reaction[a,b]



1a 2a 3

entry	variation from given conditions	yield (%)[b]
1	none	87
2	no $CeCl_3$	0
3	no light	0
4	no CF_3CH_2OH	trace
5	no $Bu_4N^+Cl^-$	18
6	10 equiv of **2a** was used	78
7	reaction time,12 h	86
8	under a N_2 atmosphere	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (3.0 mmol), $CeCl_3$ (5 mol %), $Bu_4N^+Cl^-$ (20 mol %), CF_3CH_2OH (50 mol %), CH_3CN (1 mL), 405 nm LED (10 W), rt, air, 9 h. [b]Yield of the isolated product. Note: Cy = cyclohexyl.

Under the optimal reaction conditions (Table 1, entry 1), we investigated the substrate scope of the quinoxalin-2(1*H*)-one derivatives (Table 2). The quinoxalin-2(1*H*)-ones, comprising a series of *N*-substituted methyl, ethyl, isopropyl, *n*-butyl, cyclopropylmethyl and ester groups, were well tolerated and gave the corresponding products (**3**−**9**) in good yields. It is worth noting that the labile allyl group, which could be further functionalized, was also compatible with standard conditions and afforded the target product (**10**) in 69% yield. The reactions of a wide range of quinoxalin-2(1*H*)-ones with different *N*-benzyl groups, bearing electron-donating or electron-withdrawing substituents at the *ortho*-, *meta*-, or *para*-position, gave the corresponding products (**11**−**24**) in 53−78% yield. CDC reactions of cyclohexane with quinoxalin-2(1*H*)-ones bearing both electron-donating and electron-withdrawing groups at the C5- or C6-position gave alkylated products (**25**−**29**) in 55−72% yield.

We next investigated the substrate scope of the simple alkanes. Alkanes are difficult to subject to selective C−H functionalization because they contain different types of inert C (sp^3)−H bonds that have similar bond dissociation energies.[27] In our catalytic system, a variety of cycloalkanes reacted with quinoxalin-2(1*H*)-one to give products (**30**−**33**) in 70−84% yield. The adamantane containing both secondary and tertiary C−H bonds in the molecule was tested. The reaction took place at the tertiary C−H bond and afforded the target product (**34**) in 78% yield. *n*-Pentane reacted with quinoxalin-2(1*H*)-one and afforded a mixture of regioisomers

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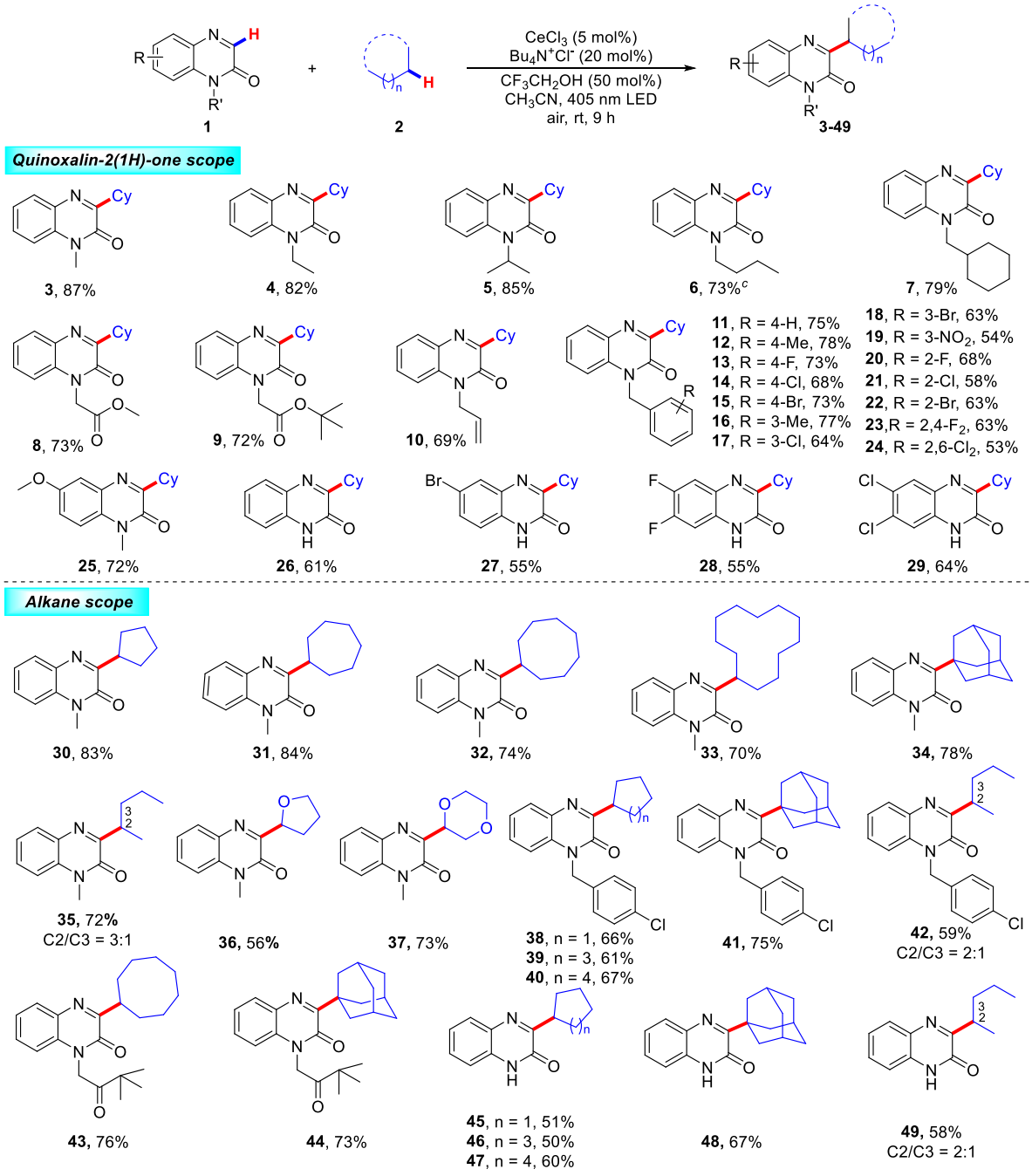
Table 2. Substrate Scope of the Cerium-Photocatalyzed CDC Reaction of Quinoxalin-2(1*H*)-ones with Alkanes[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (3.0 mmol), $CeCl_3$ (5.0 mol %), $Bu_4N^+Cl^-$ (20.0 mol %), CF_3CH_2OH (50.0 mol %), CH_3CN (1.0 mL), 405 nm LED (10 W), rt, air, 9 h. [b]Yield of the isolated product. [c]Reaction was performed on a 1 mmol scale.

(**35**) with a ratio of C2/C3 = 3:1 in 72% combined yield, probably due to more stable alkyl radicals and abundant C−H bonds at the secondary carbon positions. Ethers, such as tetrahydrofuran and 1,4-dioxane, also underwent the CDC reaction, affording **36** and **37** in 56% and 73% yields, respectively. Moreover, reactions between *N*-substituted or N-free quinoxalin-2(1*H*)-ones and simple alkanes can proceed, giving the corresponding products (**38**−**49**) in 50−76% yield.

We further performed gram-scale synthesis of product **26** (51% yield), which was subsequently chlorinated with $POCl_3$ to give product **50**. Cross-coupling of compound **50** with phenylboronic acid or phenylacetylene or treatment with nucleophilic reagents such as morpholine, sodium methoxide, thiophenol, and benzenesulfonyl chloride gave a broad range of quinoxaline derivatives (**51**−**56**) in good yield (Scheme 2).

The success of the cerium-photocatalyzed CDC reactions of quinoxalin-2(1*H*)-ones with alkanes prompted us to evaluate the scope of heteroarenes. Reaction of isoquinoline with cyclohexane under standard conditions yielded only 15% of the product (**57**), probably because the reactivity of isoquinoline is lower than that of quinoxalin-2(1*H*)-ones (see the Supporting Information, Table S7, entry 1). Further optimization of the reaction conditions was performed by replacing CF_3CH_2OH (TFE) with trifluoroacetic acid (TFA) as the proton source,

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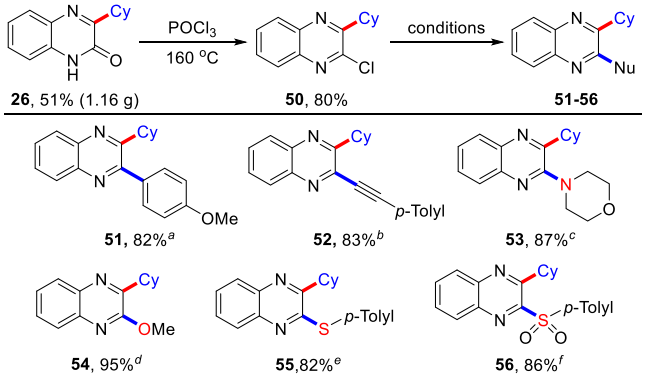
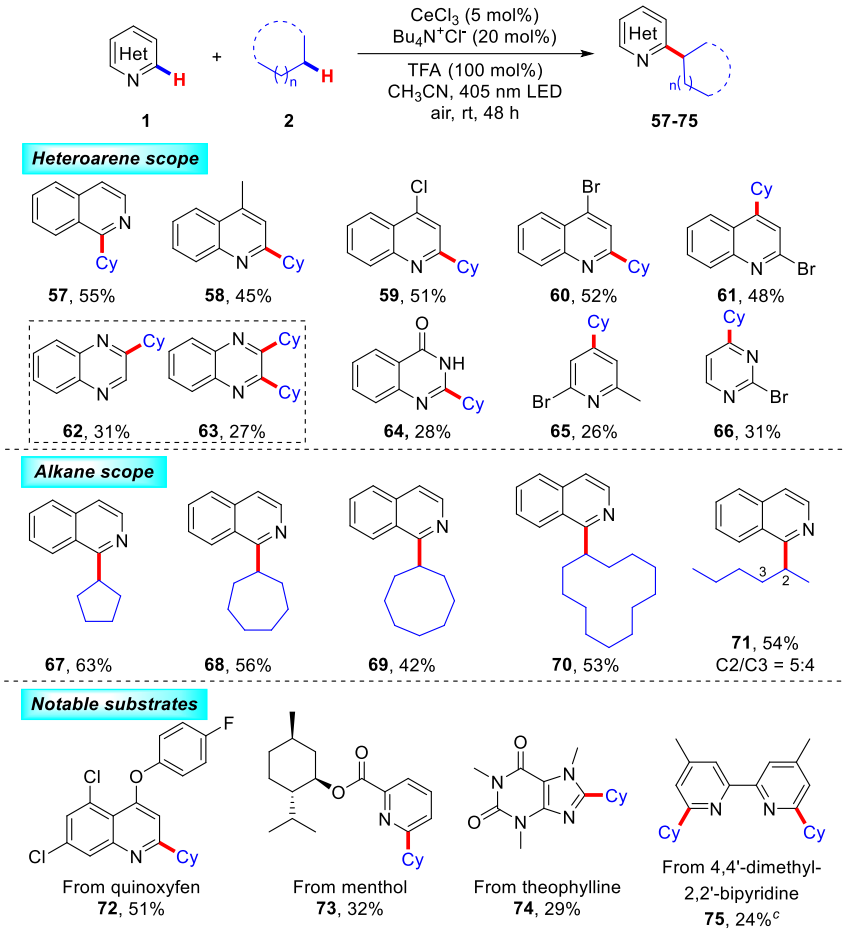
Scheme 2. Gram-Scale Synthesis and Further Derivatization[a]



[a]Reaction conditions: (a) **50** (0.2 mmol), (4-methoxyphenyl)boronic acid (1.5 equiv), $Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (2 M in water, 1.1 mL), toluene (1.5 mL), EtOH (0.5 mL), 115 °C, N_2, 12 h; (b) **50** (0.2 mmol), *p*-tolylacetylene (1.2 equiv), $PdCl_2(PPh_3)_2$ (5 mol %), CuI (7 mol %), Et_3N (1 mL), 90 °C, N_2, 18 h; (c) **50** (0.2 mmol), morpholine (1.5 equiv), K_2CO_3 (1.5 equiv), MeCN (1.5 mL), 85 °C, 12 h; (d) **50** (0.2 mmol), MeONa (5.0 equiv), MeOH (1.5 mL), 80 °C, 4 h; (e) **50** (0.2 mmol), *p*-methylthiophenol (1.1 equiv), H_2O (1 mL), 100 °C, 6 h; (f) **50** (0.2 mmol), tosyl chloride (2 equiv), Zn (1 equiv), H_2O (1 mL), 100 °C, 12 h.

and the product (**57**) was obtained in 55% yield by extending the reaction time to 48 h (Table S7, entry 2). This result shows that the replacement of TFE with TFA leads to an increase in yield. Further evaluation of the reaction conditions did not improve the yield (Table S7, entries 3−10). We then examined the substrate scope in the presence of TFA as a proton source (Table 3). CDC reactions of cyclohexane with a wide range of heteroarenes, including isoquinolines, quinolines, quinoxaline, quinazoline, and pyridine as well as pyrimidine, afforded the desired products (**57**−**66**) in 26−55% yield. Interestingly, both mono- and bifunctionalized products (**62** and **63**) were generated by using quinoxaline as a substrate. Other heteroarenes such as indol (**1ca**), benzoxazole (**1cb**), and benzothiazole (**1cc**) were also tested under optimized conditions, but no corresponding product was obtained (see the Supporting Information, Scheme S2). Several cycloalkanes, including cyclopentane, cycloheptane, cyclooctane, and cyclododecane, also afforded the corresponding products in moderate yields (42−63%, **67**−**70**). Notably, the isomers (**71**) were obtained in 54% yield with a ratio of C2/C3 = 5:4 when *n*-hexane was used as a starting material. Our method was also successfully applied to the late-stage functionalization of complex pharmaceutical compounds, and the corresponding alkylation products (**72**−**75**) were obtained in 24−51% yield.

Table 3. Substrate Scope of the Cerium-Photocatalyzed CDC Reaction of Heteroarenes with Alkanes[a,b]



[a]Reaction conditions: **1** (0.2 mmol), **2** (3.0 mmol), $CeCl_3$ (5 mol %), $Bu_4N^+Cl^-$ (20 mol %), TFA (100 mol %), CH_3CN (1 mL), 405 nm LED (10 W), rt, air, 48 h. [b]Yield of the isolated product. [c]The reaction was performed for 72 h.

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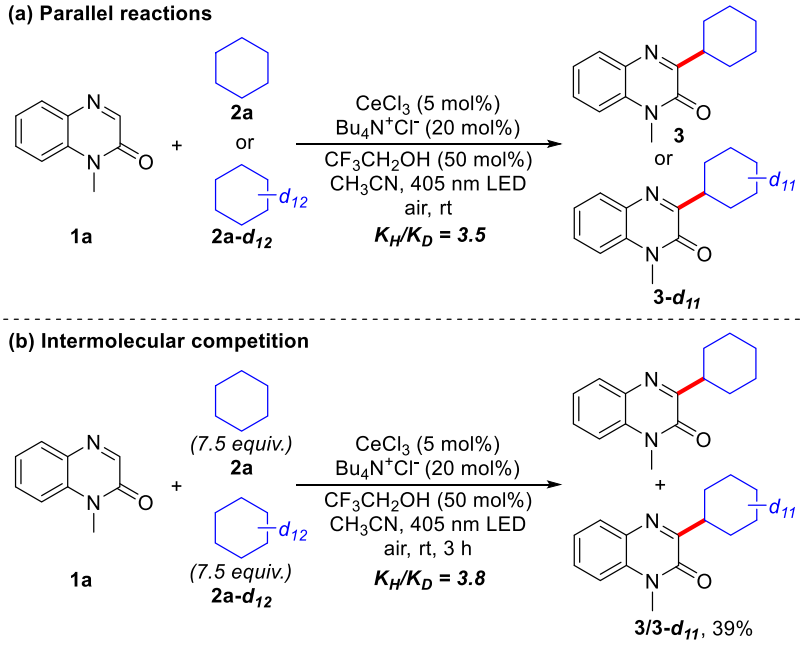
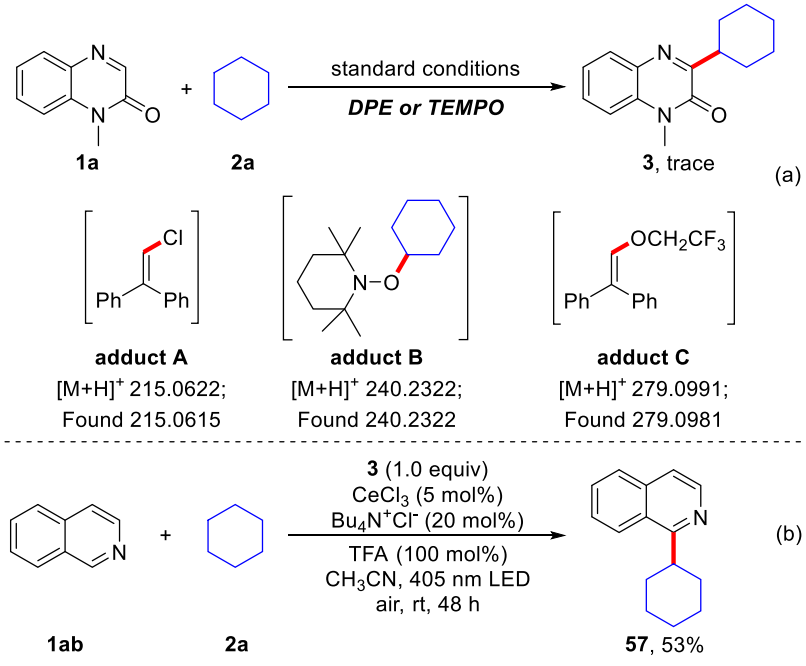
Scheme 3. KIE Study of the Cerium-Photocatalyzed CDC Reaction



Scheme 4. Control Experiments of the Cerium-Photocatalyzed CDC Reaction



We next performed control experiments to elucidate the reaction mechanism. Performing cerium photocatalysis with cyclohexane (**2a**) and cyclohexane-d_{12} (**2a**–d_{12}) independently in separate reactors gave a kinetic isotope effect (KIE) of 3.5 (Scheme 3a). A competing experiment with cyclohexane (**2a**) and cyclohexane-d_{12} (**2a**–d_{12}) gave a ratio of 3.8 (Scheme 3b). Both methods show that a kinetically relevant isotope effect is involved in the reaction, suggesting that cleavage of the C(sp^3)-H bond may be the rate-determining step.[28] The transformation was completely inhibited when two equivalents of radical scavengers, such as 1,1-diphenylethylene (DPE) or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), were added (Scheme 4a). The formation of adducts (**A**) and (**B**) indicates the generation of chlorine and cyclohexyl radicals. In addition, adduct **C** was also detected, probably because a radical adduct [Cl–$OHCH_2CF_3$]$^{\bullet}$, formed from the chlorine radical and CF_3CH_2OH, was eventually trapped by DPE.[20a,22] Overall, a radical pathway appears to be involved. Since the reaction did not occur under a nitrogen atmosphere and superoxide radicals were detected under standard conditions by using electron spin resonance (ESR) spectroscopy (Figure 1a), O_2 in air plays a central role in this transformation. Moreover, the results of fluorescence spectroscopy (Figure S3), UV–visible absorption (Figure S4), and ESR spectroscopy (Figure 1b) of the substrate (**1a**) suggest that singlet oxygen ($^1O_2$) may play an important role in the catalytic system.[29] However, it was found

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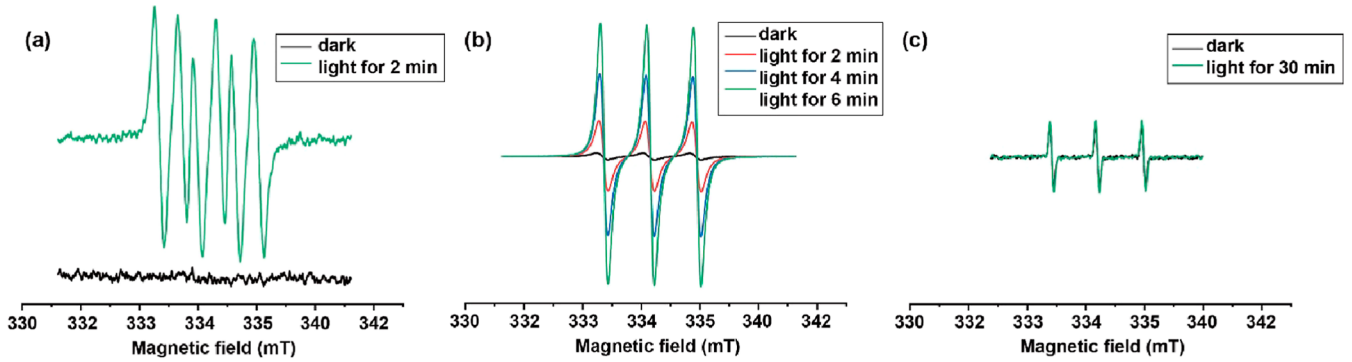


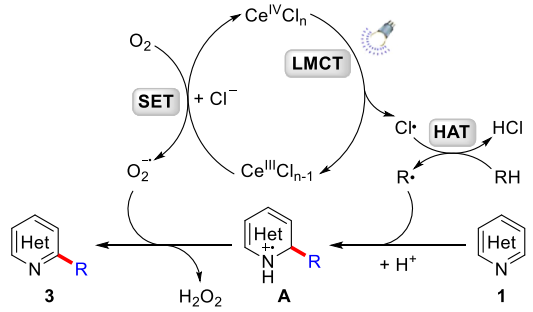
Figure 1. Determination of reactive species by ESR spectroscopy of cerium-photocatalyzed cross-dehydrogenative alkylation. (a) ESR spectra of superoxide radicals; (b) ESR spectra of singlet oxygens photosensitized by substrate **1a**; and (c) ESR spectra of singlet oxygens photosensitized by substrate **1ab**.

that isoquinoline derivatives do not absorb 405 nm LED light to sensitize oxygen,[30] which was also confirmed by ESR (Figure 1c).

On the other hand, oxygen in the ground state is known to auto-oxidize cerium(III) complexes to cerium(IV) complexes.[20d] In this regard, we hypothesized that the transformation is mainly mediated by oxygen, and singlet oxygen ($^1O_2$) would likely accelerate this process. To test this assumption, cross-dehydrogenative alkylation of isoquinoline (**1ab**) with cyclohexane (**2a**) was conducted with one equivalent of compound **3** (Scheme 4b), which proved as a singlet oxygen ($^1O_2$) sensitizer (Figure S6c). However, the absence of any change in product yield indicates that singlet oxygen ($^1O_2$) is insignificant for the transformation.

Based on the experimental results, a possible mechanism for cerium-photocatalyzed CDC reactions was proposed (Scheme 5). First, oxygen reacts with $Ce^{III}Cl_{n-1}$ by a single-electron

Scheme 5. Plausible Mechanism of the Cerium-Photocatalyzed CDC Reaction



transfer to form $Ce^{IV}Cl_n$, which undergoes a photoinduced LMCT to generate a chlorine radical with simultaneous regeneration of $Ce^{III}Cl_{n-1}$.[20b] Meanwhile, protonation of the nitrogen atom with a proton source activates the heteroarene (**1**). The chlorine radical then undergoes hydrogen-atom transfer with an alkane to form an alkyl radical, which subsequently attaches to a protonated heteroarene to form an intermediate (**A**).[22] Subsequent aromatization-driven single-electron oxidation and deprotonation yield the target product (**3**) and H_2O_2.[31]

CONCLUSIONS

In summary, we have reported a cerium-photocatalyzed strategy for facile cross-dehydrogenative alkylation of heteroarenes with simple alkanes. A variety of heteroarenes can be alkylated with simple alkanes in moderate-to-good yields. This protocol offers many advantages, including an excellent step sequence from abundant alkanes, inexpensive catalysts, the use of air as a green oxidant, ambient conditions, and a wide range of substrates.

EXPERIMENTAL SECTION

General Information. All reagents and deuterated solvents were commercially available and used without further purification. All alkanes and heteroarenes in Table 3 were purchased from Energy Chemical. All quinoxalin-2(1*H*)-ones are known compounds and were prepared according to the corresponding literature.[25,32] All products were purified by silica gel (200−300 mesh) column chromatography using petroleum ether (PE) (60−90 °C) and ethyl acetate (EA) as the eluent.[33] ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded using a Bruker ADVANCE 500 spectrometer at room temperature with $CDCl_3$ and CD_3SOCD_3 as solvents and tetramethylsilane as an internal standard. Melting points were determined on an X-5 Data microscopic melting point apparatus. Analytical thin-layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. Compounds for high-resolution mass spectrometry (HRMS) were analyzed by positive mode electrospray ionization (ESI) using an Agilent 6530 QTOF mass spectrometer. ESR spectra were recorded using a JES X320 spectrometer (JEOL Co). Fluorescence quenching experiments were recorded using an F-7000 FL spectrophotometer. The photoreactor (PL-SX100A) was purchased from Beijing Princess Technology Co., Ltd. The Schlenk tube used for photocatalysis was purchased from Beijing Synthware Glass.

General Procedure for the Synthesis of Quinoxalin-2(1*H*)-ones. A mixture of 1,2-phenylenediamines (5.0 mmol, 1.0 equiv), ethyl glyoxalate (6.0 mmol, 1.2 equiv), and ethanol (40.0 mL) was stirred under reflux until the crude material disappeared. Then, the mixture was filtered and washed by ethanol. The solid was dried in vacuo. For further alkylation, the corresponding haloalkane (4.8 mmol, 1.6 equiv) was added to a suspension of quinoxalin-2(1*H*)-one (3.0 mmol, 1.0 equiv) and potassium carbonate (3.6 mmol, 1.2 equiv) in DMF (15.0 mL). The mixture was stirred overnight at room temperature. After the reaction was complete, brine was added and the mixture was extracted with DCM. The collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the residue obtained was further purified by silica gel column chromatography (200−300 mesh silica gel).

1-Methylquinoxalin-2(1H)-one (***1a***).[31a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.89 (dd, J = 8.0, 1.2 Hz, 1H), 7.64−7.58 (m, 1H), 7.39−7.34 (m, 2H), 3.70 (s, 3H).

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1-Ethylquinoxalin-2(1H)-one (**1b**).[31a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.64−7.57 (m, 1H), 7.40−7.34 (m, 2H), 4.33 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H).

1-Butylquinoxalin-2(1H)-one (**1d**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.32), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.89 (dd, J = 8.3, 1.4 Hz, 1H), 7.62−7.56 (m, 1H), 7.38−7.33 (m, 2H), 4.27−4.22 (m, 2H), 1.75 (tt, J = 7.9, 6.7 Hz, 2H), 1.49 (dd, J = 15.1, 7.5 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H).

1-(Cyclohexylmethyl)quinoxalin-2(1H)-one (**1e**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.89 (dd, J = 8.2, 1.4 Hz, 1H), 7.61−7.55 (m, 1H), 7.38−7.32 (m, 2H), 4.14 (d, J = 7.3 Hz, 2H), 1.97−1.85 (m, 1H), 1.78−1.64 (m, 5H), 1.18 (t, J = 7.8 Hz, 5H).

Methyl-2-(2-oxoquinoxalin-1(2H)-yl)acetate (**1f**).[32a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.27), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.95−7.88 (m, 1H), 7.60−7.53 (m, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 5.04 (s, 2H), 3.79 (s, 3H).

tert-Butyl-2-(2-oxoquinoxalin-1(2H)-yl)acetate (**1g**).[31a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.25), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.83 (dd, J = 8.0, 1.4 Hz, 1H), 7.53−7.46 (m, 1H), 7.34−7.25 (m, 1H), 7.04 (dd, J = 8.4, 0.7 Hz, 1H), 4.86 (s, 2H), 1.38 (s, 9H).

1-Allylquinoxalin-2(1H)-one (**1h**).[31a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.35), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.90 (dd, J = 8.0, 1.4 Hz, 1H), 7.60−7.52 (m, 1H), 7.38−7.31 (m, 2H), 5.94 (ddt, J = 17.2, 10.3, 5.1 Hz, 1H), 5.28 (d, J = 10.4 Hz, 1H), 5.17 (d, J = 17.2 Hz, 1H), 4.90 (dt, J = 5.0, 1.6 Hz, 2H).

1-Benzylquinoxalin-2(1H)-one (**1i**).[31a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.28 (ddd, J = 19.2, 14.0, 7.3 Hz, 7H), 5.49 (s, 2H).

1-(4-Methylbenzyl)quinoxalin-2(1H)-one (**1j**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.49−7.43 (m, 1H), 7.32 (dd, J = 11.9, 4.4 Hz, 2H), 7.13 (q, J = 8.3 Hz, 4H), 5.45 (s, 2H), 2.30 (s, 3H).

1-(4-Fluorobenzyl)quinoxalin-2(1H)-one (**1k**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.33), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.90 (dd, J = 8.0, 1.3 Hz, 1H), 7.51−7.47 (m, 1H), 7.36−7.32 (m, 1H), 7.28 (s, 1H), 7.26−7.22 (m, 2H), 7.01 (t, J = 8.6 Hz, 2H), 5.46 (s, 2H).

1-(4-Chlorobenzyl)quinoxalin-2(1H)-one (**1l**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.90 (dd, J = 8.0, 1.2 Hz, 1H), 7.51−7.46 (m, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.3 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 5.45 (s, 2H).

1-(3-Methylbenzyl)quinoxalin-2(1H)-one (**1n**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.47 (dd, J = 11.5, 4.2 Hz, 1H), 7.31 (dd, J = 16.7, 8.2 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.05 (dd, J = 17.8, 7.7 Hz, 3H), 5.45 (s, 2H), 2.30 (s, 3H).

1-(3-Chlorobenzyl)quinoxalin-2(1H)-one (**1o**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.33), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.91 (dd, J = 8.0, 1.4 Hz, 1H), 7.52−7.46 (m, 1H), 7.37−7.32 (m, 1H), 7.27−7.22 (m, 4H), 7.16−7.10 (m, 1H), 5.46 (s, 2H).

1-(3-Nitrobenzyl)quinoxalin-2(1H)-one (**1q**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.23), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.18−8.14 (m, 2H), 7.94 (dd, J = 8.0, 1.3 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.52 (ddd, J = 8.5, 3.4, 1.9 Hz, 2H), 7.40−7.35 (m, 1H), 7.21 (d, J = 8.4 Hz, 1H), 5.58 (s, 2H).

1-(2-Fluorobenzyl)quinoxalin-2(1H)-one (**1r**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.90 (dd, J = 8.0, 1.2 Hz, 1H), 7.53−7.46 (m, 1H), 7.36−7.32 (m, 1H), 7.30−7.26 (m, 2H), 7.15−7.09 (m, 1H), 7.03 (d, J = 4.3 Hz, 2H), 5.55 (s, 2H).

1-(2-Chlorobenzyl)quinoxalin-2(1H)-one (**1s**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (s, 1H), 7.92 (dd, J = 8.0, 1.4 Hz, 1H), 7.51−7.43 (m, 2H), 7.38−7.31 (m, 1H), 7.22 (td, J = 8.0, 1.4 Hz, 1H), 7.14−7.05 (m, 2H), 6.77 (d, J = 7.5 Hz, 1H), 5.58 (s, 2H).

1-(2-Bromobenzyl)quinoxalin-2(1H)-one (**1t**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.32), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (s, 1H), 7.92 (d, J = 7.3 Hz, 1H), 7.68−7.60 (m, 1H), 7.51−7.43 (m, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.19−7.11 (m, 2H), 7.06 (d, J = 8.4 Hz, 1H), 6.77−6.68 (m, 1H), 5.54 (s, 2H).

1-(2,4-Difluorobenzyl)quinoxalin-2(1H)-one (**1u**).[2b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.25), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.52 (dd, J = 11.5, 4.1 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.08 (dd, J = 14.9, 8.5 Hz, 1H), 6.92−6.83 (m, 1H), 6.78 (dd, J = 11.5, 4.9 Hz, 1H), 5.49 (s, 2H).

6-Methoxy-1-methylquinoxalin-2(1H)-one (**1w**).[32e] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.27), white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.35 (d, J = 2.8 Hz, 1H), 7.27 (d, J = 4.9 Hz, 1H), 7.22 (dd, J = 9.1, 2.8 Hz, 1H), 3.90 (s, 3H), 3.69 (s, 3H).

Quinoxalin-2(1H)-one (**1x**).[32a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 2:1, R_f = 0.26), white solid. ^{1}H NMR (500 MHz, DMSO): δ 12.45 (s, 1H), 8.19 (s, 1H), 7.79 (dd, J = 8.0, 1.1 Hz, 1H), 7.59−7.54 (m, 1H), 7.35−7.30 (m, 2H).

General Procedure for Cerium-Photocatalyzed, Cross-Dehydrogenative Alkylation of Quinoxalinone with Alkane. A mixture of quinoxalinone (**1**) (0.2 mmol), alkane (**2**) (3.0 mmol, 15.0 equiv), $CeCl_3$ (5.0 mol %), $Bu_4N^+Cl^-$ (20.0 mol %), CF_3CH_2OH (50.0 mol %), and CH_3CN (1.0 mL) in a 15 mL tube was stirred under the irradiation of 405 nm LED (10 W) for 9 h. After completing the reaction as indicated by TLC, a saturated $NaHCO_3$ solution was added to the residue to neutralize the acidic compounds. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

Procedure for the Synthesis of Product 6 on a 1 mmol Scale. A mixture of quinoxalinone (**1d**) (1.0 mmol), cyclohexane (**2a**) (15.0 mmol, 15.0 equiv), $CeCl_3$ (5.0 mol %), $Bu_4N^+Cl^-$ (20.0 mol %), CF_3CH_2OH (50.0 mol %), and CH_3CN (5.0 mL) in a 15 mL tube was stirred under the irradiation of 405 nm LED (10 W) for 9 h. After completing the reaction as indicated by TLC, a saturated $NaHCO_3$ solution was added to the residue to neutralize the acidic compounds. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

Procedure for the Gram-Scale Synthesis of Product 26. A mixture of quinoxalinone (**1h**) (10.0 mmol), alkane (**2a**) (150.0 mmol, 15.0 equiv), $CeCl_3$ (5.0 mol %), $Bu_4N^+Cl^-$ (20.0 mol %), CF_3CH_2OH (50.0 mol %), and CH_3CN (30.0 mL) in a 100 mL flask was stirred under the irradiation of 405 nm LED (10 W) for 9 h. After completion of the reaction as indicated by TLC, a saturated $NaHCO_3$ solution was added to the residue to neutralize the acidic compounds. The mixture was then extracted with DCM, and the collected organic

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layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

3-Cyclohexyl-1-methylquinoxalin-2(1H)-one ***(3)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), white solid (42 mg, 87% yield), mp 92−93 °C (lit.[12c] 91−92 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (dd, J = 8.0, 1.4 Hz, 1H), 7.48 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 7.33−7.28 (m, 1H), 7.26 (dd, J = 8.4, 0.7 Hz, 1H), 3.68 (s, 3H), 3.34 (tt, J = 11.6, 3.3 Hz, 1H), 1.98−1.93 (m, 2H), 1.90−1.83 (m, 2H), 1.80−1.73 (m, 1H), 1.58 (ddd, J = 24.3, 12.5, 2.9 Hz, 2H), 1.51−1.42 (m, 2H), 1.37−1.28 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.2, 154.5, 132.9, 132.9, 129.8, 129.3, 123.3, 113.4, 40.8, 30.5, 29.0, 26.3, 26.2.

3-Cyclohexyl-1-ethylquinoxalin-2(1H)-one ***(4)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.33), white solid (42 mg, 82% yield), mp 113−114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 8.2, 0.9 Hz, 1H), 7.52−7.46 (m, 1H), 7.30 (dd, J = 7.6, 6.8 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 3.35 (tt, J = 11.6, 3.2 Hz, 1H), 1.96 (d, J = 11.8 Hz, 2H), 1.90−1.83 (m, 2H), 1.79−1.74 (m, 1H), 1.58 (ddd, J = 24.3, 12.5, 2.8 Hz, 2H), 1.51−1.42 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.35−1.27 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.3, 154.0, 133.2, 131.8, 130.1, 129.3, 123.2, 113.3, 40.7, 37.3, 30.6, 26.4, 26.2, 12.4; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{20}N_2ONa$, 279.1468; found, 279.1459.

3-Cyclohexyl-1-isopropylquinoxalin-2(1H)-one ***(5)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.33), white solid (46 mg, 85% yield), mp 107−108 °C ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (dd, J = 8.1, 0.9 Hz, 1H), 7.74 (dd, J = 8.1, 0.7 Hz, 1H), 7.57−7.51 (m, 1H), 7.50−7.44 (m, 1H), 5.55 (dt, J = 12.4, 6.2 Hz, 1H), 3.16 (tt, J = 11.8, 3.3 Hz, 1H), 1.96 (d, J = 11.9 Hz, 2H), 1.92−1.87 (m, 2H), 1.77 (d, J = 12.6 Hz, 1H), 1.69 (qd, J = 12.6, 3.1 Hz, 2H), 1.48 (dt, J = 12.7, 3.3 Hz, 2H), 1.43 (d, J = 6.2 Hz, 6H), 1.38−1.31 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 155.1, 155.1, 139.6, 138.5, 128.5, 128.4, 126.6, 125.8, 68.8, 40.7, 30.7, 26.6, 26.2, 21.9; HRMS (ESI−TOF) m/z: [M + H]$^+$ Calcd for $C_{17}H_{23}N_2O$, 271.1805; found, 271.1806.

1-Butyl-3-cyclohexylquinoxalin-2(1H)-one ***(6)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), white solid (208 mg, 73% yield), mp 118−119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 7.9, 1.4 Hz, 1H), 7.52−7.45 (m, 1H), 7.29 (td, J = 8.5, 2.7 Hz, 2H), 4.27−4.22 (m, 2H), 3.34 (tt, J = 11.6, 3.2 Hz, 1H), 1.96 (d, J = 11.8 Hz, 2H), 1.90−1.84 (m, 2H), 1.79−1.71 (m, 3H), 1.58 (ddd, J = 24.4, 12.5, 2.9 Hz, 2H), 1.51−1.42 (m, 4H), 1.36−1.28 (m, 1H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.2, 154.2, 133.1, 132.0, 130.0, 129.3, 123.2, 113.5, 42.1, 40.7, 30.5, 29.3, 26.4, 26.2, 20.3, 13.8; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{24}N_2ONa$, 307.1781; found, 307.1786.

3-Cyclohexyl-1-(cyclohexylmethyl)quinoxalin-2(1H)-one ***(7)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.32), yellow solid (51 mg, 79% yield), mp 111−112 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 7.9, 1.3 Hz, 1H), 7.53−7.43 (m, 1H), 7.28 (dd, J = 14.4, 8.0 Hz, 2H), 4.13 (d, J = 7.1 Hz, 2H), 3.34 (tt, J = 11.6, 3.2 Hz, 1H), 1.96 (d, J = 11.7 Hz, 2H), 1.93−1.84 (m, 3H), 1.79−1.63 (m, 6H), 1.57 (ddd, J = 24.3, 12.5, 2.8 Hz, 2H), 1.51−1.42 (m, 2H), 1.36−1.28 (m, 1H), 1.18 (d, J = 6.2 Hz, 5H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.3, 154.7, 133.1, 132.5, 130.0, 129.1, 123.1, 113.9, 48.1, 40.8, 36.6, 31.0, 30.5, 26.4, 26.2, 25.8; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{28}N_2ONa$, 347.2094; found, 347.2085.

Methyl 2-(3-Cyclohexyl-2-oxoquinoxalin-1(2H)-yl)acetate ***(8)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), white solid (44 mg, 73% yield), mp 118−119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (dd, J = 8.0, 1.4 Hz, 1H), 7.46 (ddd, J = 8.5, 7.4, 1.5 Hz, 1H), 7.36−7.29 (m, 1H), 7.04 (dd, J = 8.3, 0.8 Hz, 1H), 5.03 (s, 2H), 3.77 (s, 3H), 3.32 (tt, J = 11.6, 3.3 Hz, 1H), 2.01−1.95 (m, 2H), 1.90−1.84 (m, 2H), 1.79−1.74 (m, 1H), 1.58 (ddd, J = 24.5, 12.6, 3.0 Hz, 2H), 1.50−1.41 (m, 2H), 1.36−1.28 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 167.8, 164.1, 154.1, 133.0, 132.0, 130.2, 129.6, 123.7, 112.9, 52.8, 43.5, 40.8, 30.5, 26.3, 26.1; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{17}H_{20}N_2O_3Na$, 323.1366; found, 323.1365.

tert-Butyl 2-(3-Cyclohexyl-2-oxoquinoxalin-1(2H)-yl)acetate ***(9)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), white solid (49 mg, 72% yield), mp 113−114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 8.0 Hz, 1H), 7.49−7.43 (m, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 4.93 (s, 2H), 3.33 (tt, J = 11.6, 3.0 Hz, 1H), 1.97 (d, J = 12.5 Hz, 2H), 1.86 (d, J = 12.9 Hz, 2H), 1.76 (d, J = 12.8 Hz, 1H), 1.58 (dt, J = 12.2, 10.1 Hz, 2H), 1.49−1.42 (m, 11H), 1.35−1.28 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.3, 164.1, 154.1, 132.9, 132.1, 130.0, 129.5, 123.6, 112.9, 83.0, 44.3, 40.8, 30.5, 28.0, 26.3, 26.1; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{26}N_2O_3Na$, 365.1836; found, 365.1817.

1-Allyl-3-cyclohexylquinoxalin-2(1H)-one ***(10)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.36), white solid (37 mg, 69% yield), mp 89−90 °C (lit.[32b] 87−89 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, J = 8.0, 1.4 Hz, 1H), 7.50−7.44 (m, 1H), 7.33−7.29 (m, 1H), 7.27 (s, 1H), 5.94 (ddt, J = 17.1, 10.4, 5.2 Hz, 1H), 5.26 (d, J = 10.4 Hz, 1H), 5.17 (d, J = 17.2 Hz, 1H), 4.94−4.86 (m, 2H), 3.36 (tt, J = 11.6, 3.2 Hz, 1H), 1.97 (d, J = 11.6 Hz, 2H), 1.90−1.84 (m, 2H), 1.77 (d, J = 12.8 Hz, 1H), 1.62−1.54 (m, 2H), 1.51−1.42 (m, 2H), 1.32 (ddd, J = 12.6, 8.1, 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.4, 154.1, 133.0, 132.1, 130.8, 129.8, 129.4, 123.4, 118.0, 114.0, 44.6, 40.8, 30.5, 26.3, 26.2.

1-Benzyl-3-cyclohexylquinoxalin-2(1H)-one ***(11)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.29), white solid (48 mg, 75% yield), mp 132−133 °C (lit.[32b] 134−135 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 7.9, 1.0 Hz, 1H), 7.39−7.35 (m, 1H), 7.32−7.28 (m, 2H), 7.28−7.21 (m, 5H), 5.49 (s, 2H), 3.40 (tt, J = 11.6, 3.2 Hz, 1H), 2.01 (d, J = 11.8 Hz, 2H), 1.93−1.86 (m, 2H), 1.78 (d, J = 12.8 Hz, 1H), 1.61 (ddd, J = 24.6, 12.6, 3.0 Hz, 2H), 1.53−1.43 (m, 2H), 1.37−1.30 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.4, 154.6, 135.5, 133.2, 132.2, 129.9, 129.4, 128.9, 127.6, 126.9, 123.5, 114.3, 46.0, 40.9, 30.6, 26.4, 26.2.

3-Cyclohexyl-1-(4-methylbenzyl)quinoxalin-2(1H)-one ***(12)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.29), yellow solid (52 mg, 78% yield), mp 145−146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90−7.74 (m, 1H), 7.41−7.32 (m, 1H), 7.27−7.23 (m, 2H), 7.15−7.09 (m, 4H), 5.44 (s, 2H), 3.40 (tt, J = 11.7, 3.2 Hz, 1H), 2.29 (s, 3H), 2.01 (d, J = 11.9 Hz, 2H), 1.91−1.85 (m, 2H), 1.77 (d, J = 12.8 Hz, 1H), 1.60 (ddd, J = 24.5, 12.6, 2.9 Hz, 2H), 1.52−1.44 (m, 2H), 1.37−1.28 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.4, 154.6, 137.3, 133.2, 132.5, 132.3, 129.9, 129.6, 129.3, 127.0, 123.4, 114.3, 45.7, 40.9, 30.6, 26.4, 26.2, 21.1; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{24}N_2ONa$, 355.1781; found, 355.1777.

3-Cyclohexyl-1-(4-fluorobenzyl)quinoxalin-2(1H)-one ***(13)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), yellow solid (50 mg, 73% yield), mp 160−161 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 8.0, 1.4 Hz, 1H), 7.43−7.34 (m, 1H), 7.30−7.26 (m, 1H), 7.25−7.17 (m, 3H), 7.02−6.97 (m, 2H), 5.44 (s, 2H), 3.39 (tt, J = 11.6, 3.2 Hz, 1H), 2.00 (d, J = 11.8 Hz, 2H), 1.91−1.85 (m, 2H), 1.80−1.74 (m, 1H), 1.60 (ddd, J = 24.5, 12.6, 3.0 Hz, 2H), 1.52−1.43 (m, 2H), 1.33 (ddt, J = 12.8, 9.2, 4.6 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.4, 162.2 (d, J = 247.0 Hz), 154.5, 133.2, 132.1, 131.3 (d, J = 3.8 Hz), 130.0, 129.4, 128.8 (d, J = 8.8 Hz), 123.6, 115.8 (d, J = 21.4 Hz), 114.0, 45.3, 40.9, 30.6, 26.3, 26.2; ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$): δ −114.5. HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{21}FN_2ONa$, 359.1530; found, 359.1521.

1-(4-Chlorobenzyl)-3-cyclohexylquinoxalin-2(1H)-one ***(14)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), yellow solid (48 mg, 68% yield), mp 157−158 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (dd, J = 8.0, 1.4 Hz, 1H), 7.42−7.36 (m, 1H), 7.31−7.26 (m, 3H), 7.18 (dd, J = 7.9, 5.8 Hz, 3H), 5.44 (s, 2H), 3.38 (tt, J = 11.6, 3.2 Hz, 1H), 2.00 (d, J = 11.8 Hz, 2H), 1.92−1.86 (m, 2H), 1.78 (d, J = 12.8 Hz, 1H), 1.60 (ddd, J

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= 24.5, 12.6, 3.0 Hz, 2H), 1.52−1.43 (m, 2H), 1.34 (ddd, J = 12.7, 8.1, 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.4, 154.5, 134.0, 133.6, 133.2, 132.0, 130.0, 129.5, 129.1, 128.4, 123.6, 114.0, 45.4, 40.9, 30.6, 26.3, 26.2; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}ClN_2O$, 353.1415; found, 353.1413.

1-(4-Bromobenzyl)-3-cyclohexylquinoxalin-2(1H)-one ***(15)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), yellow solid (58 mg, 73% yield), mp 152−153 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 7.5 Hz, 1H), 7.40 (dt, J = 15.7, 8.1 Hz, 3H), 7.30−7.25 (m, 1H), 7.16 (d, J = 8.3 Hz, 1H), 7.12 (d, J = 7.4 Hz, 2H), 5.42 (s, 2H), 3.37 (dd, J = 12.7, 10.5 Hz, 1H), 2.00 (d, J = 11.8 Hz, 2H), 1.88 (d, J = 12.3 Hz, 2H), 1.77 (d, J = 12.6 Hz, 1H), 1.60 (dd, J = 25.0, 12.7 Hz, 2H), 1.47 (dd, J = 23.8, 12.2 Hz, 2H), 1.37−1.29 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.4, 154.5, 134.6, 133.2, 132.0, 132.0, 130.1, 129.5, 128.8, 123.6, 121.6, 114.0, 45.4, 40.9, 30.6, 26.3, 26.2; HRMS (ESI−TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{21}BrN_2ONa$, 419.0729; found, 419.0719.

3-Cyclohexyl-1-(3-methylbenzyl)quinoxalin-2(1H)-one ***(16)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), white solid (51 mg, 77% yield), mp 134−135 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 7.9, 1.3 Hz, 1H), 7.40−7.35 (m, 1H), 7.29−7.22 (m, 2H), 7.18 (t, J = 7.7 Hz, 1H), 7.04 (dd, J = 16.8, 7.6 Hz, 3H), 5.45 (s, 2H), 3.41 (tt, J = 11.6, 3.2 Hz, 1H), 2.29 (s, 3H), 2.01 (d, J = 11.8 Hz, 2H), 1.92−1.86 (m, 2H), 1.78 (d, J = 12.8 Hz, 1H), 1.61 (ddd, J = 24.6, 12.6, 3.0 Hz, 2H), 1.53−1.44 (m, 2H), 1.34 (ddt, J = 12.7, 9.2, 4.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.4, 154.6, 138.7, 135.5, 133.1, 132.3, 129.8, 129.4, 128.8, 128.4, 127.6, 124.0, 123.4, 114.3, 46.0, 40.8, 30.6, 26.4, 26.2, 21.5; HRMS (ESI−TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{24}N_2ONa$, 355.1781; found, 355.1789.

1-(3-Chlorobenzyl)-3-cyclohexylquinoxalin-2(1H)-one ***(17)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), yellow solid (45 mg, 64% yield), mp 152−153 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.85 (dd, J = 7.9, 1.2 Hz, 1H), 7.41−7.36 (m, 1H), 7.28 (dd, J = 11.2, 4.0 Hz, 1H), 7.22 (d, J = 4.0 Hz, 3H), 7.16 (d, J = 8.3 Hz, 1H), 7.10 (dd, J = 6.4, 3.5 Hz, 1H), 5.44 (s, 2H), 3.39 (tt, J = 11.6, 3.2 Hz, 1H), 2.01 (d, J = 11.8 Hz, 2H), 1.91−1.86 (m, 2H), 1.77 (d, J = 12.8 Hz, 1H), 1.65−1.57 (m, 2H), 1.48 (tdd, J = 12.9, 9.7, 3.2 Hz, 2H), 1.33 (ddt, J = 12.7, 9.2, 4.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.4, 154.5, 137.6, 134.9, 133.2, 132.0, 130.2, 130.1, 129.5, 128.0, 127.1, 125.1, 123.7, 114.0, 45.5, 40.9, 30.6, 26.4, 26.2; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}ClN_2O$, 353.1415; found, 353.1413.

1-(3-Bromobenzyl)-3-cyclohexylquinoxalin-2(1H)-one ***(18)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), white solid (50 mg, 63% yield), mp 148−149 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, J = 8.0, 1.3 Hz, 1H), 7.47−7.36 (m, 3H), 7.32−7.28 (m, 1H), 7.21−7.10 (m, 3H), 5.45 (s, 2H), 3.39 (tt, J = 11.6, 3.2 Hz, 1H), 2.01 (d, J = 11.8 Hz, 2H), 1.92−1.86 (m, 2H), 1.78 (d, J = 12.8 Hz, 1H), 1.61 (dt, J = 12.6, 9.6 Hz, 2H), 1.53−1.44 (m, 2H), 1.34 (ddd, J = 12.7, 8.1, 3.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.4, 154.5, 137.9, 133.2, 132.0, 130.9, 130.5, 130.1, 130.0, 129.5, 125.5, 123.7, 123.0, 114.0, 45.4, 40.9, 30.6, 26.3, 26.2; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}BrN_2O$, 397.0910; found, 397.0914.

3-Cyclohexyl-1-(3-nitrobenzyl)quinoxalin-2(1H)-one ***(19)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.22), white solid (39 mg, 54% yield), mp 203−204 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J = 9.0 Hz, 2H), 7.88 (dd, J = 8.0, 1.4 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.45−7.38 (m, 1H), 7.36−7.29 (m, 1H), 7.20−7.12 (m, 1H), 5.57 (s, 2H), 3.38 (tt, J = 11.6, 3.2 Hz, 1H), 2.01 (d, J = 11.6 Hz, 2H), 1.93−1.86 (m, 2H), 1.81−1.76 (m, 1H), 1.64 (dd, J = 12.8, 3.2 Hz, 2H), 1.53−1.44 (m, 2H), 1.34 (ddd, J = 12.7, 8.2, 3.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.4, 154.5, 148.6, 137.7, 133.2, 133.0, 131.8, 130.3, 130.1, 129.7, 123.9, 122.9, 122.1, 113.6, 45.3, 40.9, 30.6, 26.3, 26.2; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}N_3O_3$, 364.1656; found, 364.1647.

3-Cyclohexyl-1-(2-fluorobenzyl)quinoxalin-2(1H)-one ***(20)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.32), yellow solid (46 mg, 68% yield), mp 139−140 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 7.9 Hz, 1H), 7.38 (dd, J = 11.5, 4.1 Hz, 1H), 7.23 (ddd, J = 18.6, 14.3, 8.2 Hz, 3H), 7.11−7.07 (m, 1H), 7.03−6.96 (m, 2H), 5.53 (s, 2H), 3.40 (tt, J = 11.6, 3.1 Hz, 1H), 2.02 (d, J = 13.2 Hz, 2H), 1.88 (d, J = 12.9 Hz, 2H), 1.77 (d, J = 12.7 Hz, 1H), 1.65−1.57 (m, 2H), 1.52−1.44 (m, 2H), 1.37−1.29 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.3, 160.4 (d, J = 245.7 Hz), 154.7, 133.2, 131.9, 130.0, 129.6, 129.4 (d, J = 8.8 Hz), 128.5 (d, J = 2.5 Hz), 124.7 (d, J = 3.8 Hz), 123.6, 122.6 (d, J = 13.9 Hz), 115.5 (d, J = 21.4 Hz) 113.9 (d, J = 1.3 Hz), 40.9, 39.4 (d, J = 5.0 Hz), 30.6, 26.4, 26.2; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$): δ −118.3; HRMS (ESI−TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{21}FN_2ONa$, 359.1530; found, 359.1538.

1-(2-Chlorobenzyl)-3-cyclohexylquinoxalin-2(1H)-one ***(21)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), yellow solid (41 mg, 58% yield), mp 136−137 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 5.55 (s, 2H), 3.40 (tt, J = 11.7, 3.1 Hz, 1H), 2.02 (d, J = 10.2 Hz, 2H), 1.88 (d, J = 13.0 Hz, 2H), 1.77 (d, J = 12.6 Hz, 1H), 1.62 (ddd, J = 24.9, 12.7, 2.9 Hz, 2H), 1.52−1.43 (m, 2H), 1.37−1.29 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.3, 154.6, 133.2, 132.7, 132.5, 132.0, 129.9, 129.7, 129.6, 128.8, 127.3, 126.9, 123.7, 114.1, 43.6, 40.9, 30.6, 26.4, 26.2; HRMS (ESI−TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{21}ClN_2ONa$, 375.1235; found, 375.1228.

1-(2-Bromobenzyl)-3-cyclohexylquinoxalin-2(1H)-one ***(22)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), white solid (50 mg, 63% yield), mp 179−180 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.97 (dd, J = 8.1, 1.4 Hz, 1H), 7.82 (dd, J = 8.2, 1.3 Hz, 1H), 7.64−7.56 (m, 3H), 7.55−7.49 (m, 1H), 7.34 (td, J = 7.6, 0.9 Hz, 1H), 7.20 (td, J = 7.7, 1.5 Hz, 1H), 5.63 (s, 2H), 3.29−3.21 (m, 1H), 2.01 (d, J = 11.9 Hz, 2H), 1.92−1.86 (m, 2H), 1.79−1.67 (m, 3H), 1.51−1.41 (m, 2H), 1.39−1.31 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 155.0, 154.7, 139.3, 139.0, 136.3, 132.9, 129.7, 129.4, 128.8, 128.5, 127.5, 126.8, 126.4, 123.4, 67.5, 40.7, 30.8, 26.5, 26.2; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}BrN_2O$, 397.0910; found, 397.0919.

3-Cyclohexyl-1-(2,4-difluorobenzyl)quinoxalin-2(1H)-one ***(23)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.21), yellow solid (45 mg, 63% yield), mp 151−152 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.85 (dd, J = 8.0, 1.4 Hz, 1H), 7.41 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 7.32−7.27 (m, 1H), 7.20 (dd, J = 8.4, 0.8 Hz, 1H), 7.05 (td, J = 8.6, 6.3 Hz, 1H), 6.89−6.83 (m, 1H), 6.79−6.71 (m, 1H), 5.48 (s, 2H), 3.39 (tt, J = 11.7, 3.3 Hz, 1H), 2.03−1.98 (m, 2H), 1.91−1.86 (m, 2H), 1.78 (ddd, J = 6.3, 3.1, 1.5 Hz, 1H), 1.64−1.56 (m, 2H), 1.48 (dtd, J = 13.0, 9.5, 3.3 Hz, 2H), 1.37−1.29 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.3, 163.4 (d, J = 11.3 Hz), 161.4 (t, J = 11.3 Hz), 159.4 (d, J = 12.6 Hz), 154.7, 133.2, 131.8, 130.1, 129.8 (q, J = 5.0 Hz), 129.6, 123.7, 118.6 (dd, J = 3.8 Hz) 113.6 (d, J = 2.5 Hz), 112.0 (dd, J = 3.8 Hz), 104.0 (t, J = 25.2 Hz), 40.9, 38.9 (d, J = 3.8 Hz), 30.6, 26.3, 26.2; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$): δ −110.3 (d, J = 4.7 Hz), −114.0 (d, J = 4.7 Hz); HRMS (ESI−TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}F_2N_2ONa$, 377.1436; found, 377.1431.

3-Cyclohexyl-1-(2,6-dichlorobenzyl)quinoxalin-2(1H)-one ***(24)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.20), white solid (41 mg, 53% yield), mp 157−158 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, J = 7.8 Hz, 1H), 7.36−7.22 (m, 4H), 7.13 (dt, J = 15.6, 7.2 Hz, 2H), 5.80 (s, 2H), 3.38 (dd, J = 15.3, 7.2 Hz, 1H), 1.97 (d, J = 10.7 Hz, 2H), 1.86 (d, J = 12.2 Hz, 2H), 1.76 (d, J = 11.6 Hz, 1H), 1.63−1.54 (m, 2H), 1.52−1.43 (m, 2H), 1.36−1.29 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.9, 155.2, 135.5, 133.4, 131.9, 131.2, 130.0, 129.4, 129.3, 129.1, 123.3, 114.1, 42.1, 40.8, 30.4, 26.3, 26.2; HRMS (ESI−TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}Cl_2N_2ONa$, 409.0845; found, 409.0833.

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3-Cyclohexyl-6-methoxy-1-methylquinoxalin-2(1H)-one ***(25)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.31), white solid (39 mg, 72% yield), mp 166−167 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 8.8 Hz, 1H), 6.91 (dd, J = 8.8, 2.2 Hz, 1H), 6.70 (d, J = 2.2 Hz, 1H), 3.92 (s, 3H), 3.66 (s, 3H), 3.30 (ddd, J = 11.6, 8.6, 3.0 Hz, 1H), 1.93 (d, J = 11.9 Hz, 2H), 1.86 (d, J = 12.9 Hz, 2H), 1.76 (d, J = 12.7 Hz, 1H), 1.62−1.54 (m, 2H), 1.45 (dt, J = 12.9, 7.9 Hz, 2H), 1.34−1.29 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 160.8, 160.7, 154.8, 134.3, 130.9, 127.6, 110.3, 98.0, 55.8, 40.6, 30.6, 29.2, 26.4, 26.2; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{20}N_2O_2Na$, 295.1417; found, 295.1431.

3-Cyclohexylquinoxalin-2(1H)-one ***(26)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1), white solid (28 mg, 61% yield, R_f = 0.25), mp 174−175 °C (lit.[32a] 177−178 °C); ^{1}H NMR (500 MHz, DMSO): δ 12.29 (s, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.26 (t, J = 7.4 Hz, 2H), 3.18 (t, J = 11.2 Hz, 1H), 1.87 (d, J = 12.1 Hz, 2H), 1.81 (d, J = 12.4 Hz, 2H), 1.72 (d, J = 12.3 Hz, 1H), 1.46 (dd, J = 25.2, 12.4 Hz, 2H), 1.41−1.33 (m, 2H), 1.27 (d, J = 12.5 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, DMSO): δ 165.3, 154.6, 132.1, 132.0, 129.8, 128.6, 123.5, 115.6, 30.5, 26.3, 26.2.

6-Bromo-3-cyclohexylquinoxalin-2(1H)-one ***(27)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1, R_f = 0.29), white solid (34 mg, 55% yield), mp 226−227 °C. ^{1}H NMR (500 MHz, DMSO): δ 12.40 (s, 1H), 7.87 (d, J = 2.2 Hz, 1H), 7.63 (dd, J = 8.7, 2.2 Hz, 1H), 7.22 (d, J = 8.7 Hz, 1H), 3.17 (ddd, J = 11.2, 8.1, 3.2 Hz, 1H), 1.86 (d, J = 13.0 Hz, 2H), 1.81 (d, J = 12.6 Hz, 2H), 1.71 (d, J = 12.8 Hz, 1H), 1.46−1.35 (m, 4H), 1.23 (s, 1H); ^{13}C{^{1}H} NMR (126 MHz, DMSO): δ 166.8, 154.4, 133.1, 132.4, 131.3, 130.7, 117.6, 114.8, 30.4, 26.2, 26.2; HRMS (ESI−TOF) m/z: [M + H]$^+$ Calcd for $C_{14}H_{16}BrN_2O$, 307.0441; found, 307.0444.

3-Cyclohexyl-6,7-difluoroquinoxalin-2(1H)-one ***(28)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1, R_f = 0.32), yellow solid (29 mg, 55% yield), mp 246−247 °C. ^{1}H NMR (500 MHz, DMSO): δ 12.42 (s, 1H), 7.78 (dd, J = 11.1, 8.2 Hz, 1H), 7.18 (dd, J = 11.1, 7.6 Hz, 1H), 3.13 (ddd, J = 11.2, 7.2, 3.0 Hz, 1H), 1.85 (d, J = 12.0 Hz, 2H), 1.80 (d, J = 12.3 Hz, 2H), 1.71 (d, J = 12.7 Hz, 1H), 1.46−1.24 (m, 5H); ^{13}C{^{1}H} NMR (126 MHz, DMSO): δ 166.0, 154.3, 150.3 (dd, J = 15.1 Hz), 146.0 (dd, J = 2.5 Hz), 129.3 (d, J = 10.1 Hz), 128.5 (d, J = 7.6 Hz), 116.4 (d, J = 18.9 Hz), 103.4 (d, J = 22.7 Hz), 30.4, 26.2, 26.2; ^{19}F{^{1}H} NMR (471 MHz, DMSO): δ −134.6 (d, J = 23.4 Hz), −143.8 (d, J = 23.4 Hz); HRMS (ESI−TOF) m/z: [M + H]$^+$ Calcd for $C_{14}H_{15}F_2N_2O$, 265.1147; found, 265.1145.

6,7-Dichloro-3-cyclohexylquinoxalin-2(1H)-one ***(29)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1, R_f = 0.30), white solid (38 mg, 64% yield), mp 280−281 °C. ^{1}H NMR (500 MHz, DMSO): δ 12.43 (s, 1H), 7.94 (s, 1H), 7.41 (s, 1H), 3.15 (ddd, J = 11.2, 7.3, 3.1 Hz, 1H), 1.86 (d, J = 12.1 Hz, 2H), 1.81 (d, J = 12.5 Hz, 2H), 1.71 (d, J = 12.7 Hz, 1H), 1.47−1.24 (m, 5H); ^{13}C{^{1}H} NMR (126 MHz, DMSO): δ 167.3, 154.2, 131.9, 131.8, 131.6, 129.6, 125.2, 116.7, 30.4, 26.2, 26.2; HRMS (ESI−TOF) m/z: [M + H]$^+$ Calcd for $C_{14}H_{15}Cl_2N_2O$, 297.0556; found, 297.0565.

3-Cyclopentyl-1-methylquinoxalin-2(1H)-one ***(30)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), white solid (38 mg, 83% yield), mp 91−92 °C (lit.[32e] 89−91 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (dd, J = 8.0, 1.4 Hz, 1H), 7.53−7.46 (m, 1H), 7.34−7.27 (m, 2H), 3.73−3.67 (m, 4H), 2.10−2.03 (m, 2H), 1.96−1.89 (m, 2H), 1.86−1.79 (m, 2H), 1.75−1.67 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.7, 155.0, 133.0, 132.7, 129.7, 129.3, 123.4, 113.4, 42.7, 30.8, 29.0, 25.9.

3-Cycloheptyl-1-methylquinoxalin-2(1H)-one ***(31)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), yellow solid (43 mg, 84% yield), mp 99−100 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (dd, J = 7.9, 0.9 Hz, 1H), 7.52−7.47 (m, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 8.3 Hz, 1H), 3.69 (s, 3H), 3.52−3.45 (m, 1H), 2.01−1.94 (m, 2H), 1.87−1.78 (m, 4H), 1.70 (dd, J = 7.5, 5.3 Hz, 2H), 1.66−1.58 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.4, 154.5, 132.9, 132.8, 129.7, 129.3, 123.4, 113.4, 42.4, 32.3, 29.1, 28.2, 27.1; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{20}N_2ONa$, 279.1468; found, 279.1471.

3-Cyclooctyl-1-methylquinoxalin-2(1H)-one ***(32)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), yellow solid (40 mg, 74% yield), mp 112−113 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (dd, J = 8.0, 1.2 Hz, 1H), 7.53−7.46 (m, 1H), 7.34−7.30 (m, 1H), 7.28 (d, J = 8.4 Hz, 1H), 3.70 (s, 3H), 3.59−3.53 (m, 1H), 1.89 (dd, J = 11.8, 5.8 Hz, 4H), 1.82 (dd, J = 12.6, 6.7 Hz, 2H), 1.71−1.62 (m, 8H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.8, 154.5, 132.9, 132.8, 129.8, 129.3, 123.4, 113.4, 40.5, 30.6, 29.1, 26.7, 26.6, 26.0; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{17}H_{22}N_2ONa$, 293.1624; found, 293.1618.

3-Cyclododecyl-1-methylquinoxalin-2(1H)-one ***(33)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), white solid (46 mg, 70% yield), mp 119−120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 8.0, 1.3 Hz, 1H), 7.52−7.46 (m, 1H), 7.33−7.25 (m, 2H), 3.73−3.67 (m, 4H), 1.83−1.73 (m, 4H), 1.61 (dd, J = 12.6, 5.4 Hz, 2H), 1.56−1.41 (m, 7H), 1.35 (ddd, J = 21.0, 15.1, 8.2 Hz, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.4, 154.9, 132.9, 132.8, 129.8, 129.3, 123.3, 113.4, 36.2, 29.1, 28.1, 24.0, 23.8, 23.6, 23.3, 23.1; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{30}N_2ONa$, 349.2250; found, 349.2253.

3-((3r,5r,7r)-Adamantan-1-yl)-1-methylquinoxalin-2(1H)-one ***(34)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), yellow solid (46 mg, 78% yield), mp 173−174 °C (lit.[14d] 169−186 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, J = 7.3 Hz, 1H), 7.49 (dd, J = 11.4, 4.1 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H), 3.65 (s, 3H), 2.25 (d, J = 2.4 Hz, 6H), 2.11 (s, 3H), 1.85−1.77 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.8, 153.7, 133.1, 132.5, 130.1, 129.4, 123.1, 113.2, 42.0, 38.9, 37.0, 28.6, 28.6.

Mixture of 3-(Pentan-2-yl)-1-methylquinoxalin-2(1H)-one and 3-(Pentan-3-yl)-1-methylquinoxalin-2(1H)-one ***(35)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), yellow liquid (ratio C2:C3 = 3:1, 33 mg, 72% yield); data for the C2 product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 7.9, 1.4 Hz, 1H), 7.52−7.49 (m, 1H), 7.34−7.30 (m, 1H), 0.88 (t, J = 7.4 Hz, 1H), δ 3.70 (s, 3H), 3.55 (h, J = 6.9 Hz, 1H), δ 1.87 (ddd, J = 16.5, 9.4, 4.4 Hz, 2H), 1.59−1.50 (m, 1H), 1.40−1.26 (m, 4H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.8, 154.7, 132.9, 132.8, 129.8, 129.4, 123.4, 113.5, 36.9, 29.7, 29.1, 20.7, 18.2, 14.2; data for the C3 product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88−7.84 (m, 1H), δ 7.55−7.49 (m, 1H), δ 7.34−7.28 (m, 2H), δ 3.70 (s, 3H), δ 3.35 (tt, J = 8.0, 5.8 Hz, 1H), δ 1.94−1.80 (m, 1H), 1.70 (ddd, J = 13.4, 7.4, 5.9 Hz, 1H), 1.56 (ddd, J = 7.6, 6.0, 4.2 Hz, 1H), 1.46−1.29 (m, 4H), δ 0.88 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.8, 155.1, 132.9, 132.8, 129.8, 129.4, 123.4, 113.5, 44.6, 35.9, 29.1, 25.8, 18.2, 12.0; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{18}N_2ONa$, 253.1311; found, 253.1303.

1-Methyl-3-(tetrahydrofuran-2-yl)quinoxalin-2(1H)-one ***(36)***.[12c] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.33), yellow liquid (26 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (dd, J = 8.0, 1.2 Hz, 1H), 7.58−7.53 (m, 1H), 7.37−7.33 (m, 1H), 7.32 (d, J = 8.4 Hz, 1H), 5.40 (dd, J = 7.4, 6.0 Hz, 1H), 4.26−4.21 (m, 1H), 4.04−3.99 (m, 1H), 3.71 (s, 3H), 2.54−2.47 (m, 1H), 2.06−2.03 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 159.5, 154.1, 133.2, 132.5, 130.5, 130.2, 123.7, 113.5, 77.6, 69.2, 30.5, 28.8, 25.7.

3-(1,4-Dioxan-2-yl)-1-methylquinoxalin-2(1H)-one ***(37)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), yellow solid (36 mg, 73% yield), mp 135−136 °C (lit.[12c] 136−138 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (dd, J = 8.0, 1.2 Hz, 1H), 7.62−7.56 (m, 1H), 7.39−7.35 (m, 1H), 7.33 (d, J = 8.4 Hz, 1H), 5.30 (dd, J = 9.5, 2.6 Hz, 1H), 4.27 (dd, J = 11.2, 2.6 Hz, 1H), 4.12 (d, J = 11.6 Hz, 1H), 3.99 (ddd, J = 11.8, 8.0, 6.1 Hz, 1H), 3.84 (dd, J = 8.1, 2.3 Hz, 2H), 3.71 (s, 3H), 3.66 (dd, J = 11.2, 9.6 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 155.1, 153.7, 133.1, 132.6, 130.8, 130.7, 123.9, 113.6, 74.6, 69.4, 67.5, 66.3, 29.0.

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1-(4-Chlorobenzyl)-3-cyclopentylquinoxalin-2(1H)-one ***(38)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.31), yellow solid (45 mg, 66% yield), mp 148−149 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 8.1 Hz, 3H), 7.20−7.13 (m, 3H), 5.45 (s, 2H), 3.86−3.69 (m, 1H), 2.16−2.04 (m, 2H), 1.96 (dd, J = 12.3, 7.4 Hz, 2H), 1.87−1.80 (m, 2H), 1.73 (dd, J = 6.9, 4.5 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.9, 155.0, 134.0, 133.5, 133.0, 132.1, 130.0, 129.4, 129.1, 128.4, 123.6, 114.0, 45.3, 42.7, 30.9, 26.0; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{19}ClN_2ONa$, 361.1078; found, 361.1076.

1-(4-Chlorobenzyl)-3-cycloheptylquinoxalin-2(1H)-one ***(39)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), yellow solid (45 mg, 61% yield), mp 116−117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 7.9, 1.3 Hz, 1H), 7.42−7.36 (m, 1H), 7.29 (dd, J = 12.7, 4.8 Hz, 3H), 7.17 (dd, J = 7.9, 4.9 Hz, 3H), 5.45 (s, 2H), 3.53 (tt, J = 9.7, 3.5 Hz, 1H), 2.05−1.98 (m, 2H), 1.90−1.79 (m, 4H), 1.71 (dd, J = 7.8, 5.4 Hz, 2H), 1.67−1.61 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.5, 154.4, 134.0, 133.5, 133.1, 132.0, 130.0, 129.4, 129.1, 128.4, 123.6, 114.0, 45.4, 42.4, 32.4, 28.2, 27.2; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{23}ClN_2ONa$, 389.1391; found, 389.1388.

1-(4-Chlorobenzyl)-3-cyclooctylquinoxalin-2(1H)-one ***(40)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), yellow solid (51 mg, 67% yield), mp 112−113 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 8.0, 1.4 Hz, 1H), 7.41−7.36 (m, 1H), 7.33−7.26 (m, 3H), 7.23−7.13 (m, 3H), 5.45 (s, 2H), 3.61 (dq, J = 12.8, 4.4 Hz, 1H), 1.91 (td, J = 7.9, 3.5 Hz, 4H), 1.87−1.81 (m, 2H), 1.68 (dt, J = 18.4, 8.0 Hz, 8H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.9, 154.5, 134.0, 133.5, 133.0, 132.0, 130.0, 129.4, 129.1, 128.3, 123.6, 114.0, 45.4, 40.5, 30.7, 26.7, 26.6, 26.0; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{23}H_{25}ClN_2ONa$, 403.1548; found, 403.1545.

3-((3r,5r,7r)-Adamantan-1-yl)-1-(4-chlorobenzyl)quinoxalin-2(1H)-one ***(41)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.32), white solid (61 mg, 75% yield), mp 179−180 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (dd, J = 7.9, 1.4 Hz, 1H), 7.41−7.35 (m, 1H), 7.28 (dd, J = 10.9, 4.7 Hz, 3H), 7.14 (t, J = 8.1 Hz, 3H), 5.42 (s, 2H), 2.27 (d, J = 2.6 Hz, 6H), 2.13 (s, 3H), 1.86−1.78 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.0, 153.5, 134.2, 133.4, 132.7, 132.2, 130.3, 129.6, 129.1, 128.2, 123.4, 113.7, 44.9, 42.1, 38.9, 37.0, 28.6; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{25}H_{25}ClN_2ONa$, 427.1548; found, 427.1541.

Mixture of 1-(4-Chlorobenzyl)-3-(pentan-2-yl)quinoxalin-2(1H)-one [C2] and 1-(4-Chlorobenzyl)-3-(pentan-3-yl)quinoxalin-2(1H)-one [C3] ***(42)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), yellow liquid (ratio C2:C3 = 2:1, 40 mg, 59% yield); data for the C2 product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 1H), 7.39 (dd, J = 8.3, 1.1 Hz, 1H), 7.30−7.22 (m, 3H), 7.18 (d, J = 4.6 Hz, 3H), 5.46 (s, 2H), 3.60 (dd, J = 13.7, 6.9 Hz, 1H), 1.95−1.85 (m, 1H), 1.63−1.53 (m, 1H), 1.44 (ddd, J = 9.9, 5.0, 2.2 Hz, 1H), 1.39−1.29 (m, 3H), 0.94 (t, J = 5.9 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.9, 154.6, 134.0, 133.5, 133.0, 132.0, 130.0, 129.6, 129.1, 128.3, 123.7, 114.0, 45.3, 37.0, 29.7, 20.8, 18.0, 14.2; data for the C3 product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 15.7 Hz, 1H), 7.44−7.34 (m, 1H), 7.33−7.27 (m, 3H), 7.16 (d, J = 7.7 Hz, 3H), 5.46 (s, 2H), 3.45−3.36 (m, 1H), 1.94−1.85 (m, 1H), 1.79−1.70 (m, 1H), 1.44 (ddd, J = 9.9, 5.0, 2.2 Hz, 1H), 1.39−1.32 (m, 3H), 0.91 (t, J = 5.9 Hz, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.1, 155.0, 134.0, 133.5, 132.9, 132.0, 130.0, 129.6, 129.1, 128.3, 123.7, 114.0, 45.3, 44.7, 36.0, 25.9, 18.2, 12.1; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{21}ClN_2ONa$, 363.1235; found, 363.1230.

3-Cyclooctyl-1-(3,3-dimethyl-2-oxobutyl)quinoxalin-2(1H)-one ***(43)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.30), white solid (54 mg, 76% yield), mp 136−137 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 8.0, 1.3 Hz, 1H), 7.43−7.38 (m, 1H), 7.31−7.27 (m, 1H), 6.81 (t, J = 8.7 Hz, 1H), 5.26 (s, 2H), 3.52 (tt, J = 8.5, 4.1 Hz, 1H), 1.89 (dt, J = 12.9, 7.3 Hz, 4H), 1.80 (d, J = 5.6 Hz, 2H), 1.70−1.60 (m, 8H), 1.36 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 206.7, 165.4, 154.1, 132.9, 132.3, 130.0, 129.3, 123.5, 112.8, 47.0, 43.8, 40.4, 30.6, 26.6, 26.6, 26.5, 26.0; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{30}N_2O_2Na$, 377.2199; found, 377.2204.

3-((3r,5r,7r)-Adamantan-1-yl)-1-(3,3-dimethyl-2-oxobutyl)-quinoxalin-2(1H)-one ***(44)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.35), yellow solid (55 mg, 73% yield), mp 219−220 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 8.0, 1.3 Hz, 1H), 7.43−7.37 (m, 1H), 7.28 (dd, J = 10.9, 3.8 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 5.24 (s, 2H), 2.23 (d, J = 2.6 Hz, 6H), 2.10 (s, 3H), 1.84−1.76 (m, 6H), 1.36 (s, 9H).; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 206.7, 164.4, 153.2, 132.5, 132.5, 130.4, 129.4, 123.2, 112.6, 46.6, 43.8, 41.9, 38.9, 37.0, 28.6, 26.6; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{24}H_{30}N_2O_2Na$, 401.2199; found, 401.2205.

3-Cyclopentylquinoxalin-2(1H)-one ***(45)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1, R_f = 0.26), white solid (22 mg, 51% yield), mp 214−215 °C. ^{1}H NMR (500 MHz, DMSO): δ 12.28 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.49−7.44 (m, 1H), 7.29−7.24 (m, 2H), 3.57 (p, J = 8.1 Hz, 1H), 1.99−1.92 (m, 2H), 1.87−1.79 (m, 2H), 1.76−1.69 (m, 2H), 1.68−1.61 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, DMSO): δ 164.8, 155.1, 132.1, 131.9, 129.8, 128.6, 123.5, 115.6, 41.8, 30.7, 25.9; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{13}H_{14}N_2ONa$, 237.0998; found, 237.1005.

3-Cycloheptylquinoxalin-2(1H)-one ***(46)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1, R_f = 0.25), yellow solid (24 mg, 50% yield), mp 188−189 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.36 (s, 1H), 7.83 (dd, J = 8.0, 0.9 Hz, 1H), 7.52−7.45 (m, 1H), 7.36−7.29 (m, 2H), 3.56−3.48 (m, 1H), 2.04−2.00 (m, 2H), 1.88−1.83 (m, 4H), 1.77−1.71 (m, 2H), 1.67−1.63 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.9, 156.2, 132.9, 130.7, 129.4, 128.8, 124.0, 115.5, 41.8, 32.3, 28.3, 27.1; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{18}N_2ONa$, 265.1311; found, 265.1309.

3-Cyclooctylquinoxalin-2(1H)-one ***(47)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1, R_f = 0.25), white solid (31 mg, 60% yield), mp 190−191 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.31 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.51−7.44 (m, 1H), 7.32 (t, J = 8.0 Hz, 2H), 3.66−3.52 (m, 1H), 1.94 (dd, J = 11.3, 5.9 Hz, 4H), 1.84 (d, J = 8.6 Hz, 3H), 1.69 (ddd, J = 16.0, 11.0, 5.9 Hz, 7H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.3, 156.2, 132.9, 130.7, 129.4, 128.8, 123.9, 115.5, 39.9, 30.5, 26.8, 26.6, 25.9; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{20}N_2ONa$, 279.1468; found, 279.1469.

3-((3r,5r,7r)-Adamantan-1-yl)quinoxalin-2(1H)-one ***(48)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 6:1, R_f = 0.29), white solid (37 mg, 67% yield), mp 164−165 °C. ^{1}H NMR (500 MHz, DMSO): δ 12.20 (s, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.46 (dd, J = 11.4, 3.9 Hz, 1H), 7.35−7.18 (m, 2H), 2.16 (s, 6H), 2.06 (s, 3H), 1.75 (s, 6H); ^{13}C{^{1}H} NMR (126 MHz, DMSO): δ 165.7, 154.1, 132.2, 131.6, 130.0, 128.9, 123.4, 115.2, 41.5, 38.7, 37.0, 28.3; HRMS (ESI−TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{21}N_2O$, 281.1648; found, 281.1648.

Mixture of 3-(Pentan-2-yl)quinoxalin-2(1H)-one [C2] and 3-(Pentan-3-yl)quinoxalin-2(1H)-one [3] ***(49)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1, R_f = 0.26), white solid (ratio C2:C3 = 2:1, 25 mg, 58% yield), mp 148−149 °C. Data for the C2 product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.37 (s, 1H), 7.86 (t, J = 7.1 Hz, 1H), 7.52−7.45 (m, 1H), 7.34 (ddd, J = 3.7, 3.1, 1.9 Hz, 2H), 3.60 (dd, J = 13.8, 6.9 Hz, 1H), 1.99−1.85 (m, 2H), 1.48−1.40 (m, 2H), 1.34 (d, J = 6.9 Hz, 2H), 0.95 (t, J = 7.4 Hz, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.3, 156.5, 132.9, 130.7, 129.5, 128.8, 124.0, 115.5, 37.0, 29.7, 20.7, 18.3, 14.3; data for the C3 product: ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.37 (s, 1H), 7.86 (t, J = 6.9 Hz, 1H), 7.53−7.44 (m, 1H), 7.35−7.30 (m, 2H), 3.44−3.35 (m, 1H), 1.77 (ddd, J = 13.4, 7.3, 5.9 Hz, 2H), 1.65−1.54 (m, 2H), 1.34 (t, J = 6.5 Hz, 2H), 0.94−0.89 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.5, 156.9, 133.0, 130.7, 129.6, 128.9,

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124.0, 115.5, 44.1, 35.4, 25.9, 18.3, 12.0; HRMS (ESI−TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}N_2ONa$, 239.1155; found, 239.1150.

Procedure for the Synthesis of 2-Chloro-3-cyclohexylquinoxaline 50. A mixture of 3-cyclohexylquinoxalinone (**26**) (6.0 mmol), $POCl_3$ (7.2 mmol, 1.2 equiv), and pyridine (6.0 mmol, 1.0 equiv) in a 15 mL pressure tube was stirred at 160 °C in an oil bath for 2 h. After reaction completion confirmed by TLC, the mixture was cooled down to room temperature and a saturated $NaHCO_3$ solution was added to the residue to neutralize the acidic compounds. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

2-Chloro-3-cyclohexylquinoxaline (50). Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.52), white solid (1.18 g, 80% yield), mp 89−90 °C (lit.[33d] 94−96 °C); ^1H NMR (500 MHz, $CDCl_3$): δ 8.07−8.03 (m, 1H), 8.01−7.92 (m, 1H), 7.74−7.67 (m, 2H), 3.34 (tt, J = 11.6, 3.3 Hz, 1H), 2.03 (d, J = 12.1 Hz, 2H), 1.96−1.90 (m, 2H), 1.84−1.78 (m, 1H), 1.71 (dd, J = 17.2, 7.7 Hz, 2H), 1.53−1.44 (m, 2H), 1.41−1.33 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 159.2, 147.5, 141.2, 140.6, 129.8, 128.8, 128.1, 42.6, 31.3, 26.4, 26.0.

Procedure for the Synthesis of Compound 51. A mixture of 2-chloro-3-cyclohexylquinoxaline (**50**) (0.2 mmol), (4-methoxyphenyl)boronic acid (0.3 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (5.0 mol %), K_2CO_3 (2.0 M in water, 1.1 mL), toluene (1.5 mL), and EtOH (0.5 mL) in a 15 mL pressure tube was stirred at 115 °C in an oil bath for 12 h under a N_2 atmosphere. After reaction completion (as indicated by TLC), the mixture was cooled down to room temperature and water (5 mL) was added to the residue. The mixture was extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

2-Cyclohexyl-3-(4-methoxyphenyl)quinoxaline (51). Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.35), white solid (52 mg, 82% yield), mp 135−136 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.07 (dd, J = 6.9, 1.8 Hz, 2H), 7.69 (ddd, J = 8.4, 7.0, 1.5 Hz, 2H), 7.58−7.50 (m, 2H), 7.05 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H), 3.22−3.12 (m, 1H), 1.86−1.79 (m, 6H), 1.71 (d, J = 12.7 Hz, 1H), 1.38−1.27 (m, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 160.1, 160.1, 154.4, 141.6, 140.6, 131.7, 130.3, 129.2, 129.1, 129.0, 128.7, 114.0, 55.4, 42.3, 32.5, 26.4, 25.9; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}N_2O$, 319.1805; found, 319.1802.

Procedure for the Synthesis of Compound 52. A mixture of 2-chloro-3-cyclohexylquinoxaline (**50**) (0.2 mmol), *p*-tolylacetylene (0.24 mmol, 1.2 equiv), $PdCl_2(PPh_3)_2$ (5.0 mol %), CuI (7.0 mol %), and Et_3N (1.0 mL) in a 15 mL pressure tube was stirred at 90 °C in an oil bath for 18 h under a N_2 atmosphere. After completion of the reaction (as indicated by TLC), the mixture was cooled down to room temperature and water (5 mL) was added to the residue. The mixture was extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

2-Cyclohexyl-3-(p-tolylethynyl)quinoxaline (52). Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.35), colorless liquid (54 mg, 83% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 8.11−7.97 (m, 2H), 7.74−7.65 (m, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 3.54 (tt, J = 11.7, 3.2 Hz, 1H), 2.41 (s, 3H), 2.13 (d, J = 12.3 Hz, 2H), 2.01−1.92 (m, 2H), 1.85−1.74 (m, 3H), 1.58−1.48 (m, 2H), 1.45−1.35 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 162.0, 140.8, 140.7, 140.1, 139.4, 132.2, 130.0, 129.4, 129.3, 128.9, 128.7, 118.8, 95.3, 86.4, 43.7, 31.5, 26.7, 26.1, 21.7; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}N_2$, 327.1856; found, 327.1863.

Procedure for the Synthesis of Compound 53. A mixture of 2-chloro-3-cyclohexylquinoxaline (**50**) (0.2 mmol), morpholine (0.3 mmol, 1.5 equiv), K_2CO_3 (0.3 mmol, 1.5 equiv), and MeCN (1.5 mL) in a 15 mL pressure tube was stirred at 85 °C in an oil bath for 12 h. After completion of the reaction as indicated by TLC, the mixture was cooled down to room temperature and water (5 mL) was added to the residue. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

4-(3-Cyclohexylquinoxalin-2-yl)morpholine (53). Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), colourless liquid (52 mg, 87% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (dd, J = 8.1, 1.4 Hz, 1H), 7.82 (dd, J = 8.2, 1.2 Hz, 1H), 7.55 (dtd, J = 15.0, 7.0, 1.4 Hz, 2H), 3.95−3.90 (m, 4H), 3.33−3.28 (m, 4H), 3.06 (ddd, J = 15.0, 9.9, 4.8 Hz, 1H), 1.88 (ddd, J = 50.2, 13.8, 8.5 Hz, 7H), 1.45−1.37 (m, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 157.6, 155.5, 139.7, 139.5, 128.7, 128.2, 127.4, 126.9, 66.8, 51.0, 41.4, 32.5, 26.8, 25.9; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}N_3O$, 298.1914; found, 298.1916.

Procedure for the Synthesis of Compound 54. A mixture of 2-chloro-3-cyclohexylquinoxaline (**50**) (0.2 mmol), MeONa (1.0 mmol, 5.0 equiv), and MeOH (1.5 mL) in a 15 mL pressure tube was stirred at 80 °C in an oil bath for 4 h. After completion of the reaction (as indicated by TLC), the mixture was cooled down to room temperature and water (5 mL) was added to the residue. The mixture was extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

2-Cyclohexyl-3-methoxyquinoxaline (54). Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.36), colorless liquid (46 mg, 95% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 7.97 (dd, J = 8.2, 1.2 Hz, 1H), 7.79 (dd, J = 8.2, 1.1 Hz, 1H), 7.60−7.53 (m, 1H), 7.53−7.45 (m, 1H), 4.09 (s, 3H), 3.22−3.12 (m, 1H), 1.96 (dd, J = 13.4, 1.5 Hz, 2H), 1.93−1.86 (m, 2H), 1.78 (ddd, J = 12.6, 4.6, 2.4 Hz, 1H), 1.70 (qd, J = 12.6, 3.0 Hz, 2H), 1.50−1.40 (m, 2H), 1.39−1.31 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 156.0, 154.8, 139.5, 138.7, 128.7, 128.4, 126.6, 126.2, 53.7, 40.5, 30.7, 26.5, 26.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}N_2O$, 243.1492; found, 243.1495.

Procedure for the Synthesis of Compound 55. A mixture of 2-chloro-3-cyclohexylquinoxaline (**50**) (0.2 mmol), *p*-methylthiophenol (0.22 mmol, 1.1 equiv), and H_2O (1.0 mL) in a 15 mL pressure tube was stirred at 100 °C in an oil bath for 6 h. After completion of the reaction (as indicated by TLC), the mixture was cooled down to room temperature and water (5 mL) was added to the residue. The mixture was extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

2-Cyclohexyl-3-(p-tolylthio)quinoxaline (55). Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.35), white solid (55 mg, 82% yield), mp 129−130 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (dd, J = 8.1, 1.3 Hz, 1H), 7.64 (dd, J = 8.1, 1.4 Hz, 1H), 7.55−7.44 (m, 4H), 7.27−7.22 (m, 2H), 3.20 (tt, J = 11.5, 3.2 Hz, 1H), 2.41 (s, 3H), 2.07 (d, J = 12.1 Hz, 2H), 1.97−1.90 (m, 2H), 1.83−1.73 (m, 3H), 1.55−1.45 (m, 2H), 1.43−1.34 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 158.6, 155.5, 141.2, 140.2, 139.1, 135.4, 129.9, 128.7, 128.6, 128.0, 128.0, 125.6, 42.5, 31.4, 26.6, 26.1, 21.4; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}N_2S$, 335.1576; found, 335.1578.

Procedure for the Synthesis of Compound 56. A mixture of 2-chloro-3-cyclohexylquinoxaline (**50**) (0.2 mmol), tosyl chloride (0.4 mmol, 2.0 equiv), zinc powder (0.2 mmol, 1.0 equiv), and H_2O (1.0 mL) in a 15 mL pressure tube was stirred at 100 °C in an oil bath for 12 h. After completion of the reaction (as indicated by TLC), the mixture was cooled down to room temperature and a saturated $NaHCO_3$ solution was added to the residue to neutralize the acidic compounds. The mixture was extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further

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purified by silica gel column chromatography (200−300 mesh silica gel).

2-Cyclohexyl-3-tosylquinoxaline ***(56)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid (63 mg, 86% yield), mp 165−166 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.87 (dd, J = 8.4, 0.7 Hz, 1H), 7.83−7.76 (m, 1H), 7.72−7.65 (m, 1H), 7.39 (d, J = 8.1 Hz, 2H), 3.92 (tt, J = 11.5, 3.3 Hz, 1H), 2.49 (s, 3H), 1.95 (d, J = 11.7 Hz, 2H), 1.92−1.86 (m, 2H), 1.81 (td, J = 12.1, 3.1 Hz, 3H), 1.58−1.47 (m, 2H), 1.43−1.33 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 158.9, 152.7, 145.0, 142.9, 138.4, 135.4, 132.1, 130.0, 129.8, 129.7, 129.5, 128.6, 42.0, 32.3, 26.4, 25.9, 21.8; HRMS (ESI−TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{22}N_2O_2SNa$, 389.1294; found, 389.1299.

General Procedure for Cerium-Photocatalyzed, Cross-Dehydrogenative Alkylation of Heteroarene with Alkane. A mixture of heteroarene (**1**) (0.2 mmol), alkane (**2**) (3.0 mmol, 15.0 equiv), $CeCl_3$ (5.0 mol %), $Bu_4N^+Cl^-$ (20.0 mol %), TFA (100.0 mol %), and CH_3CN (1.0 mL) in a 15 mL tube was stirred under the irradiation of 405 nm LED (10 W) for 48 h. After completion of the reaction (as indicated by TLC), a saturated $NaHCO_3$ solution was added to the residue to neutralize the acidic compounds. The mixture was then extracted with DCM, and the collected organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the obtained residue was further purified by silica gel column chromatography (200−300 mesh silica gel).

1-Cyclohexylisoquinoline ***(57)***.[10d] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.33), colorless liquid (23 mg, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (d, J = 5.7 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.71−7.64 (m, 1H), 7.63−7.58 (m, 1H), 7.51 (d, J = 5.7 Hz, 1H), 3.58 (tt, J = 11.7, 3.2 Hz, 1H), 1.96 (ddd, J = 12.7, 11.6, 8.9 Hz, 4H), 1.86 (ddd, J = 22.0, 12.3, 6.2 Hz, 3H), 1.58−1.49 (m, 2H), 1.46−1.38 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.6, 141.3, 136.5, 129.9, 127.6, 127.0, 126.2, 124.9, 119.1, 41.5, 32.6, 26.9, 26.2.

2-Cyclohexyl-4-methylquinoline ***(58)***.[10d] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.33), colorless liquid (20 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.61−7.57 (m, 1H), 7.44−7.39 (m, 1H), 2.81 (tt, J = 12.0, 3.3 Hz, 1H), 2.60 (s, 3H), 1.96−1.90 (m, 2H), 1.81 (d, J = 13.1 Hz, 2H), 1.71 (d, J = 12.8 Hz, 1H), 1.55 (dd, J = 12.5, 3.1 Hz, 2H), 1.39 (dt, J = 12.9, 3.2 Hz, 2H), 1.30−1.24 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.5, 147.5, 144.5, 129.4, 129.0, 127.1, 125.4, 123.6, 120.3, 47.5, 32.8, 26.6, 26.1, 18.9.

4-Bromo-2-cyclohexylquinoline ***(59)***.[10d] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.32), colorless liquid (25 mg, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.74−7.69 (m, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.42 (s, 1H), 2.89 (tt, J = 12.0, 3.4 Hz, 1H), 2.04−2.01 (m, 2H), 1.90−1.88 (m, 2H), 1.80−1.77 (m, 1H), 1.65−1.57 (m, 2H), 1.50−1.41 (m, 2H), 1.36−1.31 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.80, 148.58, 142.73, 130.22, 129.25, 126.63, 125.14, 123.90, 119.81, 47.35, 32.69, 26.44, 26.01.

4-Bromo-2-cyclohexylquinoline ***(60)***.[5d] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.33), yellow liquid (30 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (dd, J = 18.4, 7.6 Hz, 2H), 7.74 (t, J = 7.6 Hz, 1H), 7.65 (s, 1H), 7.59 (t, J = 7.6 Hz, 1H), 2.95 (t, J = 10.7 Hz, 1H), 2.05−2.02 (m, 2H), 1.92−1.89 (m, 2H), 1.81−1.78 (m, 1H), 1.66−1.58 (m, 2H), 1.51−1.43 (m, 2H), 1.37−1.31 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 166.61, 130.96, 130.54, 128.96, 128.90, 127.11, 126.61, 126.55, 123.72, 46.93, 32.69, 26.38, 25.96.

2-Bromo-4-cyclohexylquinoline ***(61)***.[10b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.35), yellow liquid (28 mg, 48% yield). ^{1}H NMR (500 MHz, DMSO): δ 8.23 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.49 (s, 1H), 3.38 (s, 1H), 1.90−1.81 (m, 4H), 1.77 (d, J = 13.1 Hz, 1H), 1.54 (t, J = 10.4 Hz, 4H), 1.31 (dd, J = 9.3, 6.1 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, DMSO): δ 157.3, 148.7, 142.5, 130.9, 129.3, 127.6, 125.8, 124.4, 122.4, 38.6, 33.2, 26.6, 26.0.

2-Cyclohexylquinoxaline ***(62)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.36), white solid (13 mg, 31% yield), mp 47−48 °C (lit.[33c] 43−44 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.10−8.01 (m, 2H), 7.71 (ddd, J = 12.7, 8.0, 1.3 Hz, 2H), 2.97 (tt, J = 12.0, 3.4 Hz, 1H), 2.04 (d, J = 11.8 Hz, 2H), 1.93 (d, J = 13.3 Hz, 2H), 1.81 (d, J = 12.8 Hz, 1H), 1.76−1.68 (m, 2H), 1.48 (dd, J = 25.8, 12.8 Hz, 2H), 1.37 (t, J = 12.7 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 161.1, 145.0, 142.2, 141.4, 129.8, 129.1, 129.0, 128.9, 45.1, 32.3, 26.4, 25.9.

2,3-Dicyclohexylquinoxaline ***(63)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.25), white solid (16 mg, 27% yield), mp 66−67 °C (lit.[33c] 68−69 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (dd, J = 6.3, 3.4 Hz, 2H), 7.62 (dd, J = 6.4, 3.4 Hz, 2H), 3.09 (td, J = 11.1, 5.4 Hz, 2H), 1.98−1.90 (m, 5H), 1.89−1.78 (m, 11H), 1.51−1.37 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 159.7, 140.9, 128.6, 128.4, 41.7, 32.4, 26.7, 26.0.

2-Cyclohexylquinazolin-4(3H)-one ***(64)***. Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), white solid (13 mg, 28% yield), mp 210−211 °C (lit.[32c] 214−215 °C); ^{1}H NMR (500 MHz, DMSO): δ 12.10 (s, 1H), 8.10−8.05 (m, 1H), 7.80−7.74 (m, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 2.58 (t, J = 11.8 Hz, 1H), 1.91 (d, J = 12.0 Hz, 2H), 1.80 (d, J = 12.9 Hz, 2H), 1.69 (d, J = 11.8 Hz, 1H), 1.63−1.56 (m, 2H), 1.29 (dd, J = 20.9, 7.7 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.6, 154.8, 151.2, 133.7, 126.2, 125.4, 125.2, 119.8, 43.7, 29.6, 24.9, 24.7.

2-Bromo-4-cyclohexyl-6-methylpyridine ***(65)***.[10b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.40), colorless liquid (13 mg, 26% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (s, 1H), 6.86 (s, 1H), 2.42 (s, 3H), 2.38−2.32 (m, 1H), 1.77 (d, J = 7.2 Hz, 4H), 1.69 (d, J = 12.5 Hz, 1H), 1.55 (s, 1H), 1.30 (t, J = 10.2 Hz, 4H); ^{13}C{^{1}H} NMR (126 MHz, DMSO): δ 160.7, 159.9, 141.2, 123.8, 121.8, 43.2, 33.1, 26.4, 25.8, 24.0.

2-Bromo-4-cyclohexylpyrimidine ***(66)***.[32d] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.38), colorless liquid (15 mg, 31% yield). ^{1}H NMR (500 MHz, DMSO): δ 8.58 (d, J = 5.0 Hz, 1H), 7.50 (d, J = 5.1 Hz, 1H), 2.67 (tt, J = 11.6, 3.2 Hz, 1H), 1.85 (d, J = 11.5 Hz, 2H), 1.78 (dd, J = 12.6, 3.0 Hz, 2H), 1.69 (d, J = 12.6 Hz, 1H), 1.45 (ddd, J = 23.9, 12.1, 2.4 Hz, 2H), 1.34 (ddd, J = 12.7, 7.7, 2.9 Hz, 2H), 1.24 (t, J = 9.0 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, DMSO): δ 178.4, 160.7, 152.6, 119.1, 45.2, 31.7, 26.0, 25.7.

1-Cyclopentylisoquinoline ***(67)***.[33a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.35), yellow liquid (25 mg, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (d, J = 5.7 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 5.6 Hz, 1H), 4.11−3.95 (m, 1H), 2.12 (ddd, J = 14.4, 12.1, 8.0 Hz, 4H), 1.93 (dt, J = 13.6, 8.0 Hz, 2H), 1.79 (ddd, J = 10.5, 8.3, 3.4 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.7, 141.5, 136.4, 129.8, 127.4, 127.2, 126.9, 125.3, 119.1, 43.0, 32.8, 26.1.

1-Cycloheptylisoquinoline ***(68)***.[33a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.36), yellow liquid (25 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (d, J = 5.8 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.69 (t, J = 7.2 Hz, 1H), 7.65−7.59 (m, 1H), 7.51 (d, J = 5.7 Hz, 1H), 3.75 (dt, J = 13.9, 6.6 Hz, 1H), 2.05 (dt, J = 9.5, 5.3 Hz, 4H), 1.96−1.89 (m, 2H), 1.80−1.65 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 167.1, 136.7, 130.1, 130.1, 127.7, 127.2, 125.9, 125.1, 119.1, 43.2, 34.6, 28.0, 27.6.

1-Cyclooctylisoquinoline ***(69)***.[33a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.35), yellow liquid (20 mg, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (d, J = 5.7 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 11.0, 3.9 Hz, 1H), 7.62−7.55 (m, 1H), 7.46 (d, J = 5.7 Hz, 1H), 3.89−3.80 (m, 1H), 2.12−2.04 (m, 2H), 2.00 (ddd, J =

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14.5, 7.8, 3.5 Hz, 2H), 1.89 (dd, J = 7.3, 3.4 Hz, 2H), 1.79−1.63 (m, 8H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 167.9, 141.7, 136.6, 129.6, 127.6, 126.9, 125.9, 124.9, 118.8, 41.1 33.1, 26.8, 26.8, 26.3.

1-Cyclododecylisoquinoline (70).[33b] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.33), yellow liquid (31 mg, 53% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 8.51 (d, J = 5.7 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 5.7 Hz, 1H), 3.89 (dd, J = 12.4, 6.2 Hz, 1H), 2.03−1.96 (m, 2H), 1.92−1.86 (m, 2H), 1.62−1.46 (m, 10H), 1.38 (d, J = 12.5 Hz, 7H), 1.22 (d, J = 6.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.7, 141.3, 136.5, 129.9, 127.6, 127.1, 127.0, 124.8, 119.0, 36.7, 29.8, 23.9, 23.8, 23.7, 23.6, 23.0.

Mixture of 1-(Hexan-2-yl)isoquinoline [C2] and 1-(Hexan-3-yl)isoquinoline [C3] (71).[33a] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.30), yellow liquid (ratio C2:C3 = 5:4, 23 mg, 54% yield). Data for the C2 product: ^1H NMR (500 MHz, $CDCl_3$): δ 8.51 (d, J = 5.0 Hz, 1H), 8.23 (d, J = 10.0 Hz, 1H), 7.82 (d, J = 10.0 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.50 (d, J = 5.0 Hz, 1H), 3.83−3.76 (m, 1H), 2.01−1.98 (m, 2H), 1.78−1.76 (m, 1H), 1.42 (d, J = 10.0 Hz, 3H), 1.33−1.3 (m, 3H), 0.87−0.85 (m, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.1, 141.8, 136.4, 129.7, 127.6, 126.9, 124.8, 118.9, 37.6, 36.5, 30.1, 22.9, 20.5, 14.1. Data for the C3 product: ^1H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, J = 5.0 Hz, 1H), 8.26 (d, J = 10.0 Hz, 1H), 7.82 (d, J = 10.0 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.50 (d, J = 5.0 Hz, 1H), 3.66−3.61 (m, 1H), 1.87−1.83 (m, 1H), 1.76−1.74 (m, 1H), 1.42 (d, J = 10.0 Hz, 3H), 1.14−1.11 (m, 1H), 0.85−0.83 (m, 3H), 0.78 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.3, 141.8, 136.3, 128.0, 127.5, 126.8, 125.0, 118.8, 42.9, 36.1, 28.6, 21.0, 14.3, 12.3.

5,7-Dichloro-2-cyclohexyl-4-(4-fluorophenoxy)quinoline (72).[10d] Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 10:1, R_f = 0.25), yellow liquid (40 mg, 51% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.50 (d, J = 2.1 Hz, 1H), 7.18−7.14 (m, 2H), 7.12−7.09 (m, 2H), 6.52 (s, 1H), 2.72 (t, J = 10.6 Hz, 1H), 1.88 (d, J = 12.9 Hz, 2H), 1.82 (d, J = 12.7 Hz, 2H), 1.72 (d, J = 12.9 Hz, 1H), 1.46−1.35 (m, 4H), 1.25 (t, J = 10.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 169.5, 162.6, 160.9, 158.9, 151.0, 150.2, 150.2, 135.0, 130.0, 128.8, 127.2, 122.0, 121.9, 117.2, 117.0, 105.6, 47.0, 32.3, 26.3, 25.8.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 6-Cyclohexylpicolinate (73). Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1, R_f = 0.28), yellow liquid (22 mg, 32% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 8.68 (d, J = 4.4 Hz, 1H), 7.96 (s, 1H), 7.30 (d, J = 4.1 Hz, 1H), 5.05 (td, J = 10.8, 4.2 Hz, 1H), 2.59 (s, 1H), 2.11 (d, J = 11.8 Hz, 1H), 1.90 (d, J = 10.2 Hz, 4H), 1.70 (d, J = 22.1 Hz, 6H), 1.47−1.39 (m, 4H), 1.26 (d, J = 11.4 Hz, 3H), 1.15−1.10 (m, 1H), 0.92 (dd, J = 9.8, 6.8 Hz, 6H), 0.80 (d, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.2, 158.0, 149.9, 148.3, 125.3, 123.9, 75.8, 46.8, 43.9, 40.8, 34.3, 33.5, 31.5, 26.5, 26.3, 25.8, 23.5, 22.1, 20.8, 16.3; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{34}NO_2$, 344.2584; found, 344.2585.

8-Cyclohexyl-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione (74). Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 3:1, R_f = 0.30), white solid (16 mg, 29% yield), mp 216−217 °C (lit.[32c] 215−216 °C); ^1H NMR (500 MHz, $CDCl_3$): δ 3.86 (s, 3H), 3.51 (s, 3H), 3.32 (s, 3H), 2.70−2.60 (m, 1H), 1.81 (t, J = 14.7 Hz, 4H), 1.72−1.56 (m, 3H), 1.30 (dd, J = 16.5, 8.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 157.0, 154.5, 150.8, 147.1, 106.0, 34.8, 30.4, 29.9, 28.7, 26.8, 25.0, 24.5.

6,6′-Dicyclohexyl-4,4′-dimethyl-2,2′-bipyridine (75). Purified by silica gel column chromatography (200−300 mesh silica gel, PE/EA = 1:2, R_f = 0.25), yellow liquid (17 mg, 24% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 2H), 7.32 (s, 2H), 3.38 (tt, J = 11.9, 3.1 Hz, 2H), 2.53 (s, 6H), 2.23 (d, J = 11.6 Hz, 4H), 1.89−1.83 (m, 4H), 1.63 (dd, J = 26.0, 12.9 Hz, 6H), 1.41 (dt, J = 12.4, 9.4 Hz, 4H), 1.31−1.26 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.8, 152.1, 147.6, 123.6, 119.0, 46.6, 32.3, 25.0, 24.9, 20.8; HRMS (ESI−TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{33}N_2$, 349.2638; found, 349.2627.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c02125.

Optimization of reaction conditions, mechanistic studies, and NMR and HRMS spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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