Article

O-Perfluoropyridin-4-yl Oximes: Iminyl Radical Precursors for Photo- or Thermal-Induced N-O Cleavage in C(sp2)-C(sp3) Bond Formation

Peng-Ju Xia, Yuan-Zhuo Hu, Zhi-Peng Ye, Xu-Jie Li, Hao-Yue Xiang, and Hua Yang

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b03251 • Publication Date (Web): 23 Jan 2020

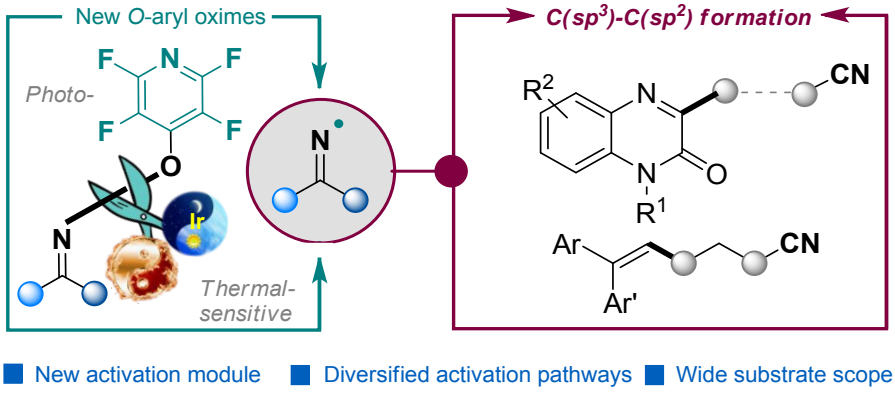
O-Perfluoropyridin-4-yl Oximes: Iminyl Radical Precursors for Photo- or Thermal-Induced *N*−*O* Cleavage in *C(sp²)-C(sp³)* Bond Formation

Peng-Ju Xia,[†,#] Yuan-Zhuo Hu,[†,#] Zhi-Peng Ye,[†] Xu-Jie Li,[†] Hao-Yue Xiang,*[,†] and Hua Yang*[,†,§]

[†]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China

[§]Key Laboratory of Hunan Province for Water Environment and Agriculture Product Safety, Central South University, Changsha 410083, P. R. China

e-mail: hyangchem@csu.edu.cn, xianghaoyue@csu.edu.cn



ABSTRACT: *O*-Perfluoropyridin-4-yl group was firstly installed onto cycloketone oximes as a new electrophore, which were proven to be efficient iminyl radical precursors under photocatalytic and thermal conditions. A range of *O*-perfluoropyridin-4-yl oximes were successfully utilized in *C(sp²)-C(sp³)* bond formations of quinoxalin-2(*1H*)-ones and alkenes, providing facile accesses to a range of functionalized alkylnitriles.

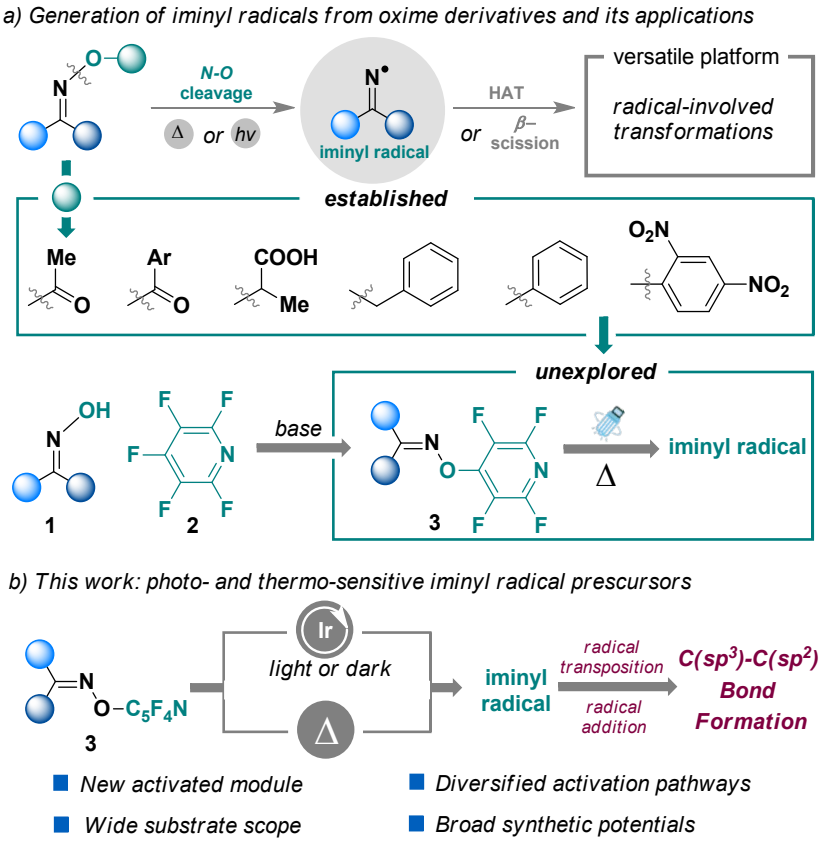
INTRODUCTION

Over the last decade, iminyl radical chemistry[1] has garnered intensive efforts due to its unique reactivity in *C-C* bond-forming events. In general, iminyl radicals are

prone to proceeding radical transposition to generate *C*-centered alkyl radicals *via* the classical Norrish type-1 fragmentation[2] or intramolecular hydrogen-atom abstraction[3] (i.e., 1,5-HAT) (Scheme 1a), providing alternative accesses to *C*-centered alkyl radicals. Pioneered by Forrester's group,[4] oxime derivatives have been extensively utilized in the generation of iminyl radicals,[5] owing to their readily cleavable *N*-*O* bond. To date, three major activation modes for *N*-*O* bond cleavage of oximes, including homolytic bond cleavage under harsh conditions,[6] transition-metal-catalyzed[7] or visible-light-driven[8,9] SET-mediated *N*-*O* bond cleavage of redox-active oximes, have progressively evolved. In particular, visible-light-driven photoredox catalysis has significantly boosted the advance of this field.[1c] In general, introducing an electrophore to oxime is usually necessitated to modulate its redox potential, matching that of the visible-light-excited photocatalyst. To this end, various oxime esters and oxime ethers have been designed and used in a range of radical-involved transformations, thus offering new synthetic opportunities in modern organic chemistry.

Previous reports disclosed that oxime ethers usually deliver the corresponding iminyl radicals under harsh conditions, such as microwave and elevated temperature.[6a,6b] Specifically, electron-poor oxime ethers possess lower reduction potentials, compatible with single electron transfer (SET) reduction by visible-light-excited photocatalysts.[1c] Following this rationale, a range of aromatic moieties bearing strong electron-withdrawing groups were installed onto the oxime skeletons to tailor their redox properties. *O*-2,4-dinitrophenyl oximes[9] possessing low reduction potentials and LUMO energies were found to be suitable for the SET process with the commonly used photocatalysts. Despite these advances, new readily available electrophore is still highly desirable to broadly tune the redox potentials of the oxime derivatives, facilitating the extension of the boundary of the iminyl radical chemistry.

Scheme 1. Synthetic Profiles of *O*-aryl Oximes as Iminyl Radical Precursors



Pentafuoropyridine,[10] a readily available multifluorinated arene (1.35 $/g), is highly electron-deficient and thus susceptible to nucleophilic attack due to the presence of high electronegative fluorine atoms. Realizing this fact, we envisaged that installing perfluoropyridin-4-yl moiety onto oximes might offer an effective pathway to markedly modulate their redox potentials, therefore facilitating the generation of the corresponding iminyl radicals. Based on our previous work on the radical-mediated *N-O* cleavage of strained cycloketone oximes,[11] we designed a series of *O*-perfluoropyridin-4-yl cycloketone oximes and evaluated their behaviors under both thermal- and photocatalytic conditions. Interestingly, it turned out that *O*-perfluoropyridin-4-yl oximes are able to serve as reliable iminyl racial precursors under photocatalytic and thermal conditions, enabling the subsequent radical-involved *C-C* bond formations (Scheme 1b).

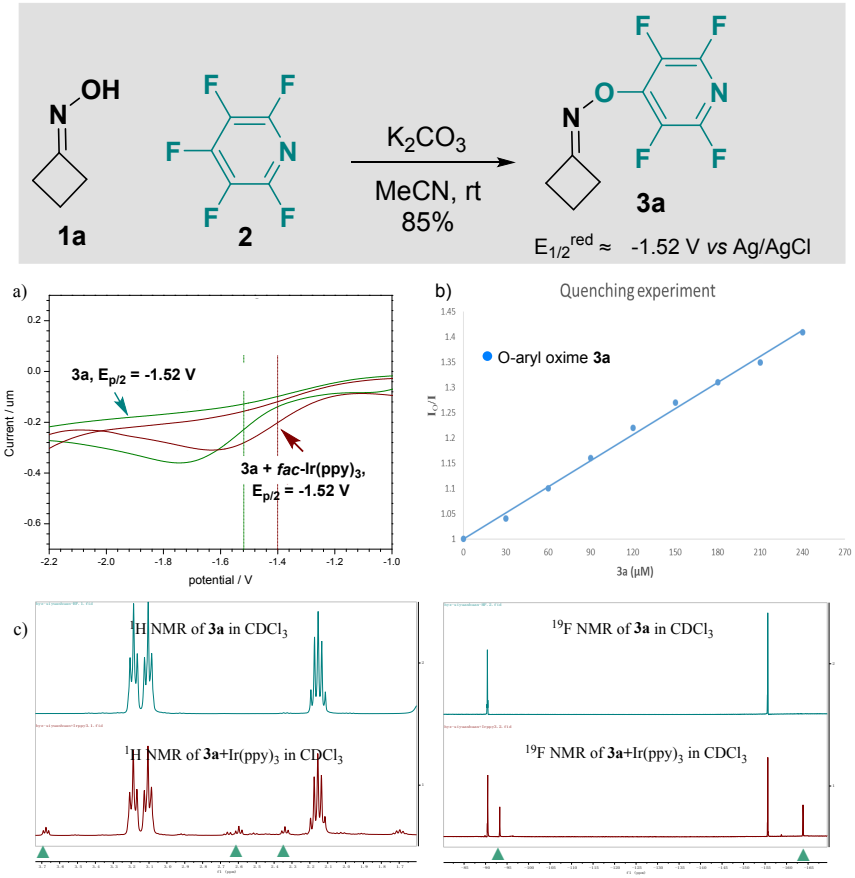


Figure 1. Preliminary studies on the properties of *O*-perfluoropyridin-4-yl oxime 3a: a) CV studies; b) quenching experiments; c) ^{1}H NMR and ^{19}F NMR studies.

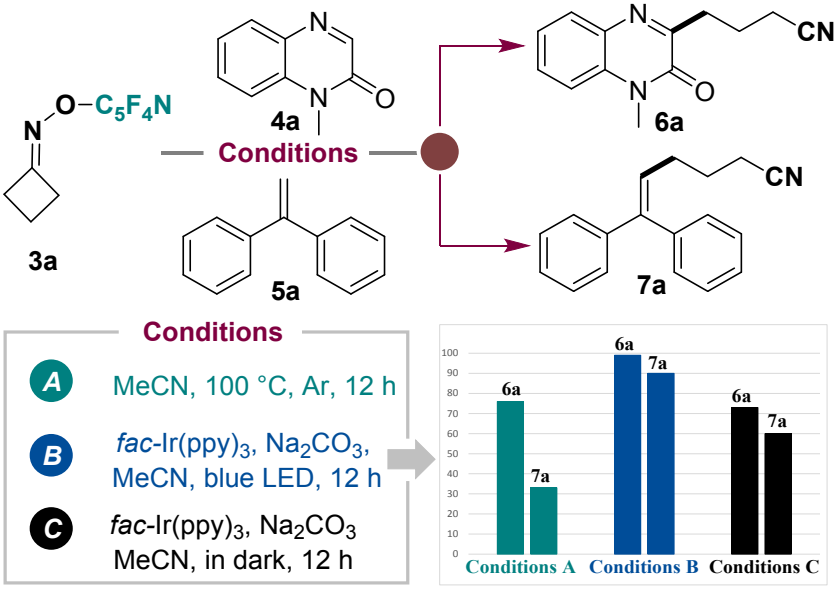
RESULTS AND DISSUSSION

Initially, in order to verify the viability of our hypothesis, *O*-perfluoropyridin-4-yl cyclobutanone oxime **3a** was prepared *via* a straightforward one-step process in high yield. The reduction potential of **3a** was then examined by cyclic voltammetry, which would be crucial for the studies on its photochemical behaviors (Figure 1a, see SI for details). It was found that a reduction wave was recorded at -1.52 V *vs.* Ag/AgCl ($E_{red}^{p/2}$ = -1.45 V *vs.* SCE. in MeCN, see SI for details). Interestingly, adding 1 mol% of *fac*-Ir(ppy)$_3$ resulted in a significant positive-shift for the E_{red} value, suggesting that *fac*-Ir(ppy)$_3$ could enhance the oxidizing ability of **3a**. At this stage, we realized that the photocatalyst *fac*-Ir(ppy)$_3$ (E_{red} = -1.73 V *vs.* SCE. in MeCN)[12] could serve as an electron donor to directly reduce *O*-perfluoropyridin-4-yl cyclobutanone oxime **3a** from its excited state, which was further confirmed by the Stern−Volmer plot

measurements (k_q = 8.95*10^2 mL^{-1}·s^{-1}, Figure 1b, see SI for details). The low kq value indicates that a reaction-controlled process might be involved in this photocatalytic transformation. Furthermore, ^{1}H NMR and ^{19}F NMR experiments were also carried out to further examine the interaction of *fac*-Ir(ppy)$_3$ with **3a** (Figure 1c, see SI for details). Upon mixing **3a** with 5 mol% of *fac*-Ir(ppy)$_3$, new distinct peaks in ^{1}H and ^{19}F spectra were observed immediately, suggesting that the *N-O* bond cleavage of **3a** might occur in the presence of *fac*-Ir(ppy)$_3$.

Once understanding the inherent features of **3a**, we next investigated its reactivity as an iminyl precursor for the functionalization of *C=N* or *C=C* bonds (Scheme 2). As a result, quinoxalin-2(*1H*)-ones and alkenes were employed as the radical trapping reagents to explore the reactivity of **3a**. Gratifyingly, under the optimized reaction conditions (see SI for details), the resulting *C(sp^2)-C(sp^3)* coupling products **6a** and **7a** were furnished through a homolytic process under elevated temperature (conditions a), or a photocatalytic SET process (conditions b). Interestingly, **6a** and **7a** were also accessible without blue-LED irradiation (conditions c). Based on these results, incomparable features of *O*-perfluoropyridin-4-yl oximes can be obviously identified in the context of radical generation as well as radical-involved transformations.

Scheme 2. Reactivities of *O*-Perfluoropyridin-4-yl Oxime 3a



To gain better mechanistic understanding on the process, additional control experiments were also carried out (Figure 2). On/off and off/on experiments on the reaction of **3a** and **4a** demonstrate that the corresponding product **6a** can be formed upon constant irradiation and in the dark, though a much slower reaction was achieved in the dark. This suggests a photochemical pathway and a redox process might be effective concurrently in the process of the title reaction. Radical inhibition experiments were also conducted by adding 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) under the corresponding reaction conditions, and all the reactions were significantly inhibited (Figure 2c). These results indicate that a free-radical pathway might be involved in the transformations. Additionally, we also studied the spin-trapping reactions of the involved radicals by adding *N*-benzylidene-*tert*-butylamine *N*-oxide (PBN) under the standard reaction conditions (see the Supporting Information). Under irradiation with blue LED, a EPR signal for $CN(CH_2)_3$•/PBN adduct was clearly observed,[13] which was also identified by HRMS analysis. On the other hand, upon heating the reaction system, the superposition of EPR signals for radical $CN(CH_2)_3$•/PBN and C_5F_4NO•/PBN adducts were detected, and their molecular ions were detected in HRMS analysis as well. The observation of PBN adducts derived from *C*- and *O*-centered radicals shows the difference in the pathway for the photo- and thermal-induced *N*-*O* bond cleavage of **3a** (please see structures 10 & 11 in the SI).

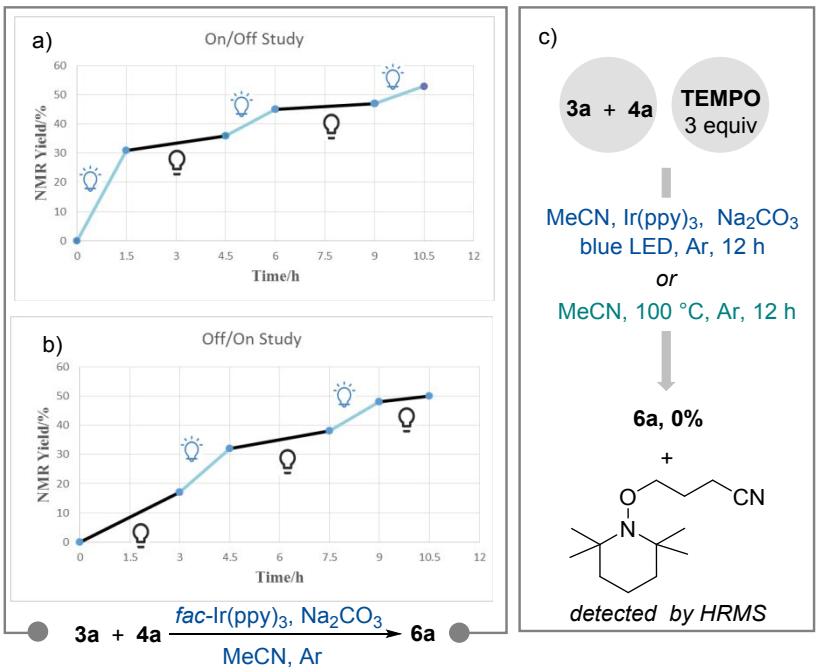
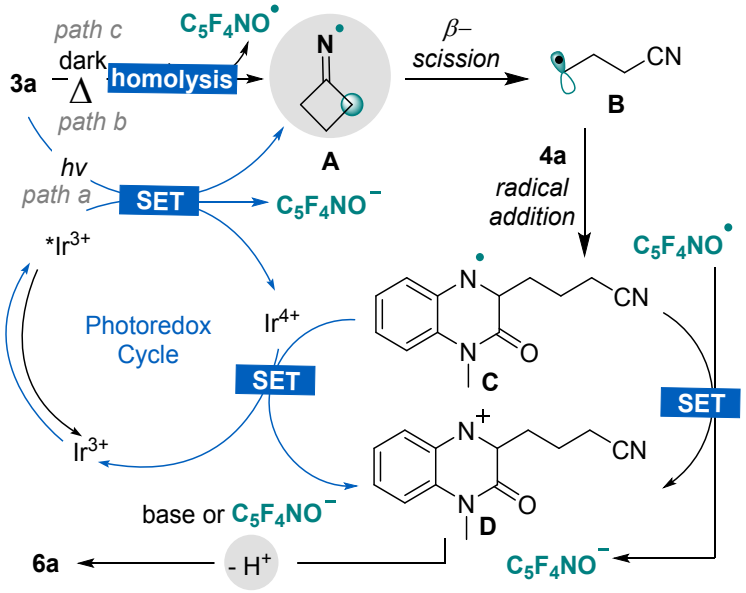


Figure 2. Control experiments. a) On/off experiments; b) Off/on experiments; c) Radical trapping experiments.

On the basis of previous reports and the above-mentioned results, a plausible mechanism for this process is proposed in Scheme 3. In the case of photocatalytic pathway (Scheme 3, path a), photocatalyst *fac*-Ir(ppy)$_3$ was converted to a highly reducing excited **fac*-Ir(ppy)$_3$ ($E_{1/2}(Ir_{IV}/*Ir_{III}) = -1.73$ V *vs* SCE)[12] under the irradiation of blue light, which was subsequently oxidatively quenched by oxime **3a**. As a result, a reductive *N–O* bond cleavage of **3a** occurred *via* a single-electron-transfer process to deliver iminyl radical **A**. Alternatively, promoted by *fac*-Ir(ppy)$_3$ without irradiation (path b) or heating (path c), iminyl radical **A** could be generated *via* a homolytic *N–O* bond fragmentation. A facile radical transposition through a strain relieved *C–C* single bond cleavage delivered a cyanoalkyl radical species **B**, which could be rapidly intercepted by quinoxalin-2(*1H*)-one **1** and alkene **2** through a radical addition process to yield a new radical intermediate **C**. This radical was further oxidized to cation **D** by *fac*-Ir(IV) species (or oxime **3a**, or C_5F_4NO•) *via* a SET process, thus completing the photocatalytic cycle with releasing the ground state *fac*-Ir(ppy)$_3$. In the presence of base or $C_5F_4NO^-$, the subsequent deprotonation of intermediate **D** gave the final *C(sp^2)-C(sp^3)* coupling product.

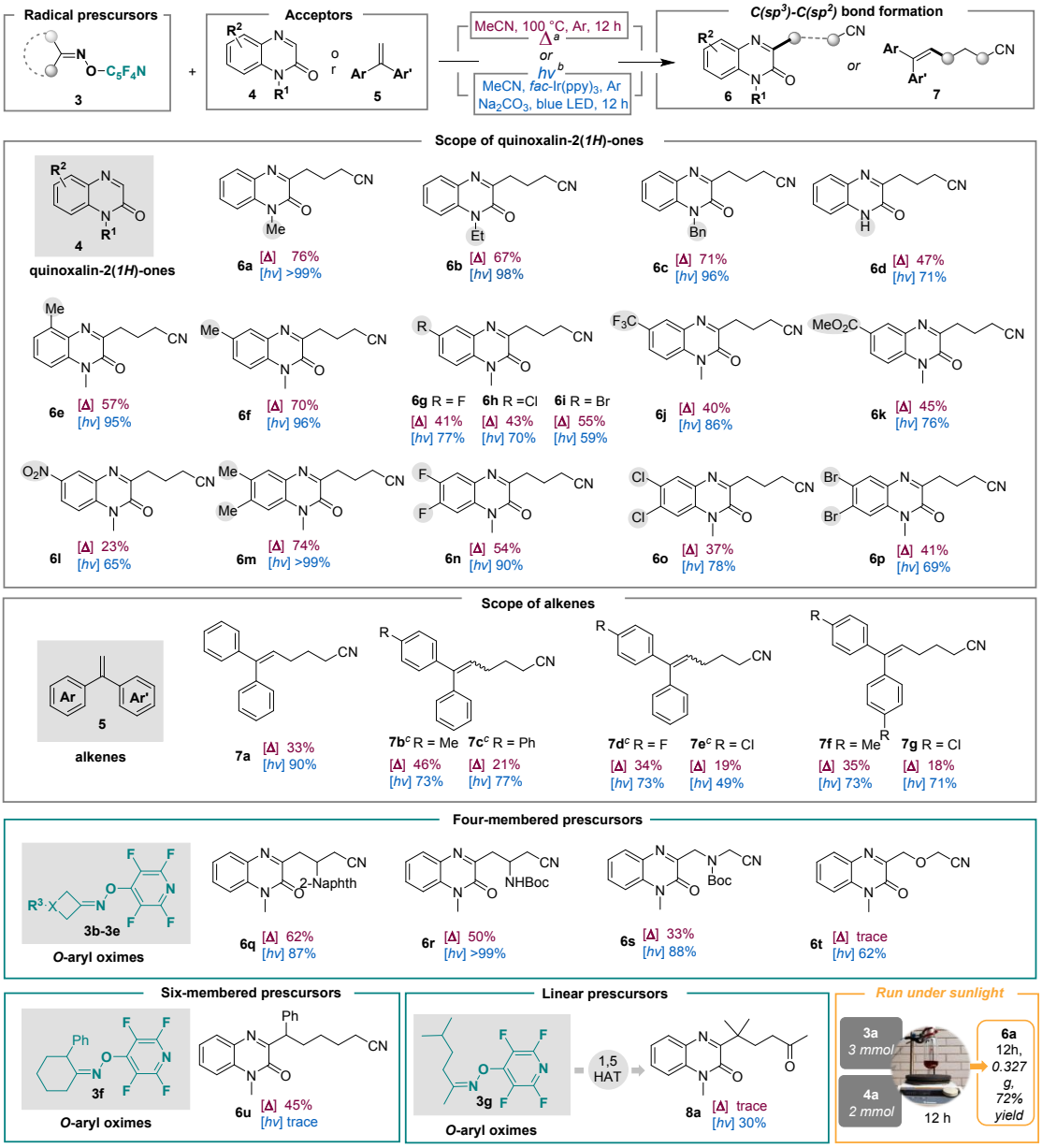
Scheme 3. Proposed Mechanism



Ultimately, the versatility and reliability of this developed strategy as well as the compatibility of the reaction conditions were extensively evaluated in various transformations (Scheme 4). A wide range of quinoxalin-2(*1H*)-ones and alkenes bearing various substituents were proven to be suitable partners for this transformation, giving the corresponding $C(sp^2)$-$C(sp^3)$ coupling products in good to excellent yields. It is worth mentioning that the photocatalytic conditions usually gave superior results, especially for the alkene substrates. As for the thermal processes, unidentified by-products were also observed at the elevated reaction temperature, resulting in lower chemical yields. Interestingly, unprotected quinoxa-lin-2(1*H*)-one also delivered the desired product **6d** in good yield. Noticeably, this newly developed activation module is also amenable to other ring systems such as *N- or O*-heterocyclobutane and cyclohexane, delivering the corresponding products (**6q-6u**) in satisfactory yields. It is noteworthy that oxime ester **3f** was unable to furnish the desired product under the photocatalytic conditions, possibly due to its lower strain of the six-membered ring. Encouragingly, this strategy was further extended to linear oxime **3g**, successfully giving **8a** *via* a 1,5-HAT process. However, other simple alkenes including styrene and cyclohexene only rendered a fairly complex reaction, and the corresponding products was unable to be isolated. Impressively, the practicality and scalability of this protocol

were demonstrated by running the title reaction of **3a** with **4a** on a large scale under sunlight for 12 h, which also proceeded smoothly to give **6a** in 72% yield.

Scheme 4. Scope of the Construction of $C(sp^3)$-$C(sp^2)$ Bonds based on *O*-Perfluoropyridin-4-yl Oximes



[a]Conditions A: **3** (0.3 mmol), **4** or **5** (0.2 mmol), CH_3CN (2 mL), 100 ℃, Ar, 12 h, isolated yields; [b]Conditions B: **3** (0.3 mmol), **4** or **5** (0.2 mmol), Na_2CO_3 (0.4 mmol), *fac*-Ir(ppy)$_3$ (5 mol%), CH_3CN (2 mL), blue LED, Ar, 12 h, isolated yields. [c]As mixture of inseparable *Z*/*E* isomers.

CONCLUSIONS

In summary, a range of readily prepared, bench-stable *O*-perfluoropyridin-4-yl oximes served as effective iminyl radical precursors for the first time. These newly developed precursors were demonstrated to be compatible with photocatalytic and thermal reaction conditions. A variety of quinoxalin-2(1*H*)-ones and alkenes were functionalized through facile radical-involved $C(sp^2)-C(sp^3)$ bond-forming processes. This research opens a door for the synthetic applications of *O*-perfluoropyridin-4-yl moiety as an activation module in the generation of radicals, thus building up a platform for broadly exploring radical-involved transformations.

EXPERIMENTAL SECTION

General Experimental Methods. Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. And the light source used for illuminating the reaction vessel (commercial supplier: Synthware) consisted of blue LEDs (λ_{max} = 460 nm) purchased from Taobao (https://gpiled.taobao.com). ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. UV–Vis spectra were recorded using a Shimadzu UV-2600. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ mass spectrometer and acetonitrile was used to dissolve the sample. Cyclic Voltammetry (CV) experiments were recorded on a CHI650D electrochemical workstation. Emission intensities were recorded using Perkin-Elemer LS 55 Fluorescence Spectrometer. Continuous-wave (CW) electron paramagnetic resonance (EPR) measurements were performed on a JEOL JES-FA200 X-band spectrometer. Column chromatography was carried out on silica gel (200-300 mesh).

General procedure for the preparation of 3a-3g. Step1: To a mixture of ketone (5 mmol, 1.0 equiv.) and hydroxylamine hydrochloride (6 mmol, 1.2 equiv.) in MeOH (30 mL) was added NaOAc (7.5 mmol, 1.5 equiv.). The mixture was heated to reflux until the reaction was monitored

to be completed by TLC analysis. Methanol was then removed under vacuum, and ethyl acetate and saturated solution of $NaHCO_3$ were added. The aqueous layer was extracted once with EtOAc (100 mL). The combined organic layers were washed twice with water (20 mL), dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to afford crude product oxime. Step2: A mixture of oxime (3.8 mmol, 1.0 equiv.), potassium carbonate (7.6 mmol, 2.0 equiv.) and MeCN (20 mL) were stirred at room temperature for 3 h. Then pentafluoropyridine (3.8 mmol, 1.0 equiv) was added and the obtained mixture was stirred overnight at room temperature. Afterwards, brine was added, and the mixture was diluted with EtOAc (100 mL). The organic layer was washed twice with water (30 mL), dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (PE/EtOAc = 100:1 or 25:1) to afford the corresponding *O*-aryl oximes.

General procedure for the preparation of 4a-4q. The starting materials **4a-4q** were prepared according to the previously described method.[14] The data of known compounds are consistent with the previously reports[14,15] and the copies of their ^{1}HNMR spectra are included in the Supporting Information. The characterization data of new compounds **4b**, **4e**, **4f**, **4j**, **4m**, **4n** and **4p** are also provided herein.

General procedure for the synthesis of compound 5a-5g. Compound **5a** was purchased from Energy Chemistry Company and used without any further purification. The starting materials **5b-5g** were prepared according to the previously described method.[16] The data of known compounds are consistent with the previously reports[16,17] and the copies of their ^{1}HNMR spectra are included in the Supporting Information.

General procedure for the synthesis of compound 6a-6u, 7a-7g, 8a. Conditions A [Δ]: To an oven-dried 15 mL Schleck flask equipped with a magnetic stir bar, *o*-aryl oximes **3** (0.3 mmol, 1.5 equiv.), quinoxalin-2(*1H*)-ones **4** or alkenes **5** (0.20 mmol, 1.0 equiv.) and MeCN (2 mL) were added. The vessel was evacuated and backfilled with Ar. The tube was screw-capped and stirred at 100 ℃ (oil bath) for 12 h. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE/EtOAc = 4:1 or 20:1) to afford the desired products **6** or **7**. Conditions B [*hv*] : To an oven-dried 15 mL Schleck flask equipped with a magnetic stir bar, *o*-aryl oximes **3** or **3a** (0.3 mmol, 1.5 equiv.), quinoxalin-2(*1H*)-ones **4** or alkenes **5** (0.20 mmol, 1.0 equiv.) *fac*-$Ir(ppy)_3$ (5% mmol), Na_2CO_3 (0.4 mmol, 2 equiv.) and MeCN (2 mL) were added. The vessel was evacuated and backfilled with Ar. The tube was screw-capped and stirred at

room temperature under irradiation of 30 W blue LEDs (distance app. 5 cm) for 12 h. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE/EtOAc = 4:1 or 20:1) to afford the desired products **6**, **7** or **8**.

Scale-up Reaction. To an oven-dried 100 mL Schleck flask equipped with a magnetic stir bar, *o*-aryl oximes **3a** (3 mmol, 1.5 equiv.), quinoxalin-2(*1H*)-ones **4a** (2 mmol, 1.0 equiv.), *fac*-$Ir(ppy)_3$ (5% mmol), Na_2CO_3 (4 mmol, 2 equiv.) and MeCN (20 mL) were added. The vessel was evacuated and backfilled with Ar. The tube was screw-capped and stirred at room temperature under sunlight for 12 h. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE/EtOAc = 4:1) to afford the desired products **6a** (327mg, 72 yield).

Characterization Data of Compound 3a-3g, 4b, 4e, 4f, 4j, 4m, 4n, 4p, 6a-6u, 7a-7g, 8a.

*Cyclobutanone O-perfluoropyridin-4-yl oxime (**3a**)*. Yellow oil, 755.8 mg, yield 85%; IR (neat) *v* 1636, 1473, 1412, 1068, 981, 822 cm^{-1}; ^1H NMR (400 MHz, Chloroform-*d*) δ 3.11 (t, *J* = 8.0 Hz, 2H), 3.02 (t, *J* = 8.0 Hz, 2H), 2.03 – 2.12 (m, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.51 – -90.34 (m), -155.72 – -155.55 (m); $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 167.7, 147.4 – 147.7 (m), 145.0 – 145.4 (m), 142.6 – 142.9 (m), 136.0 – 136.3 (m), 133.4 – 133.7 (m), 31.4, 31.2, 14.3; HRMS (ESI): $C_9H_6F_4N_2NaO^+$ $[M+Na]^+$ Calcd 257.0308, Found 257.0308.

*3-(Naphthalen-2-yl)cyclobutan-1-one O-perfluoropyridin-4-yl oxime (**3b**)*. White solid, 1.067 g, yield 78%, m.p. 114-116 ℃; IR (neat) *v* 1469, 1400, 1062, 965, 809, 750, 723, 471 cm^{-1}; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.86 (m, 3H), 7.69 (s, 1H), 7.45 – 7.52 (m, 2H), 7.38 – 7.40 (m, 1H), 3.83 – 3.91 (m, 1H), 3.68 – 3.61 (m, 1H), 3.53 – 3.61 (m, 1H), 3.27 – 3.38 (m, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.26 – -90.09 (m), -155.55 – -155.38 (m); $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 164.5, 148.0 – 146.7 (m), 145.9 – 144.3 (m), 143.6 – 142.0 (m), 139.9, 137.1 – 135.5 (m), 134.0 – 133.4 (m), 133.3, 132.4, 128.8, 127.7, 127.7, 126.6, 126.0, 124.8, 124.5, 39.0, 38.8, 32.8. HRMS (ESI): $C_{19}H_{12}F_4N_2NaO^+$ $[M+Na]^+$ Calcd 383.0778, Found 383.0776.

*tert-Butyl (3-(((perfluoropyridin-4-yl)oxy)imino)cyclobutyl)carbamate (**3c**)*. White solid, 1.061 g, yield 80%, m.p. 155-156 ℃; IR (neat) *v* 1680, 1528, 1467, 1275, 1162, 1065, 984, 833 cm^{-1}; ^1H NMR (400 MHz, Chloroform-*d*) δ 5.02 (s, 1H), 4.31 (s, 1H), 3.56 – 3.62 (m, 1H), 3.42 – 3.48 (m, 1H), 3.05 – 3.15 (m, 2H), 1.47 (s, 9H); ^{19}F NMR (375 MHz, Chloroform-*d*) δ -90.23 – -90.06 (m), -155.57 – -157.40 (m); $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 162.1, 154.9, 147.1 – 147.4 (m), 145.0 – 145.4 (m), 142.6 – 142.9 (m), 136.0 – 136.3 (m), 133.4 – 133.7 (m), 80.4, 40.2,

40.0, 39.8, 28.3; HRMS (ESI): $C_{14}H_{15}F_4N_3NaO_3^+$ [M+Na]$^+$ Calcd 372.0942, Found 372.0969.

tert-Butyl 3-(((perfluoropyridin-4-yl)oxy)imino)azetidine-1-carboxylate ***(3d)***. White solid, 967.5 mg, yield 76%, m.p. 146-147 ℃; IR (neat) *v* 1688, 1473, 1401, 1123, 1061, 972, 839 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.85 – 4.87 (m, 2H), 4.78 – 4.79 (m, 2H), 1.49 (s, 9H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.34 – -89.16 (m), -155.26 – -155.09 (m); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 157.5, 155.9, 146.5 – 146.8 (m), 145.0 – 145.3 (m), 142.5 – 142.9 (m), 136.0 – 136.3 (m), 133.4 – 133.7 (m), 81.3, 58.1, 57.2, 28.2; HRMS (ESI): $C_{13}H_{13}F_4N_3NaO_3^+$ [M+Na]$^+$ Calcd 358.0785, Found 358.0796.

Oxetan-3-one O-perfluoropyridin-4-yl oxime ***(3e)***. Pale yellow oil, 672.8 mg, yield 75%; IR (neat) *v* 1639, 1469, 1063, 959, 865, 835, 723 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.41 – 5.42 (m, 2H), 5.33 – 5.35 (m, 2H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.00 – -89.84 (m), -155.70 – -155.54 (m); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.9, 146.4 – 146.7 (m), 144.9 – 145.3 (m), 142.5 – 142.9 (m), 135.9 – 136.3 (m), 133.3 – 133.7 (m), 78.0, 77.8; HRMS (ESI): $C_8H_4F_4N_2NaO_2^+$ [M+Na]$^+$ Calcd 259.0101, Found 259.0114.

5-Methylhexan-2-one O-perfluoropyridin-4-yl oxime ***(3f)***. Yellow oil, 1.066 g, yield 83%; as an inseparable mixture of *Z/E* isomers (0.66/1.00); IR (neat) *v* 1637, 1494, 1471, 1068, 973, 819, 698 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.38 (m, 8H), 4.95 (*br* s, 0.66H), 3.71 (dd, *J* = 5.2, 8.0 Hz, 1H), 2.80 – 2.86 (m, 1H), 2.62 – 2.69 (m, 1H), 2.48 – 2.55 (m, 1H), 2.06 – 1.80 (m, 10.41H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.50 – -90.33 (m, 1.48F), -90.85 – -90.68 (m, 2.26F), -155.02 – -155.85 (m, 1.28F), -155.59 – -155.42 (m, 2.00F); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 169.7^{M} (169.3^{m}), 147.5 – 147.8$^{M/m}$ (m), 145.0 – 145.4 (m), 142.6 – 143.0 (m), 138.7^{M} (137.6^{m}), 136.0 – 136.7 (m), 133.4 – 134.1 (m), 129.0^{m} (128.5^{M}), 128.0^{M} (127.2^{m}), 126.9^{M} (126.8^{m}), 46.8^{M} (38.3^{m}), 32.6^{M}, 26.1^{M}, 25.1^{M}, (29.0^{m}, 28.8^{m}, 26.8 ^{m}), 23.5^{M} (20.7 ^{m}); HRMS (ESI): $C_{17}H_{14}F_4N_2NaO^+$ [M+Na]$^+$ Calcd 361.0934, Found 361.0933.

Oxetan-3-one O-perfluoropyridin-4-yl oxime ***(3g)***. Colorless liquid, 709.1 mg, yield 85%; as an inseparable mixture of *Z/E* isomers (0.77/2.01); IR (neat) *v* 1638, 1496, 1471, 1074, 976, 837 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.53 – 2.58 (m, 0.77H), 2.31 – 2.35 (m, 2.01H), 2.11 (s, 3.03H), 2.11 (s, 1.07H), 1.57 – 1.60 (m, 1.68H), 1.44 – 1.48 (m, 2.80H), 0.93 (d, *J* = 6.4 Hz, 8.21H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.71 – -90.49 (m), -155.57 – -155.40 (m); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 167.0^{m} (166.3^{M}), 147.43 – 147.67 (m), 145.03 – 145.36 (m), 142.62 –

142.95 (m), 136.11 – 136.47 (m), 133.52 – 133.88 (m), 34.7^{M}, 34.5^{m}, 33.3^{M}, 28.2^{m}, 28.1^{m}, 27.7^{M}, 22.25^{M}, 22.23^{m}, 19.37^{m}, 14.73^{M}; HRMS (ESI): $C_{12}H_{15}F_4N_2O^+$ $[M+H]^+$ Calcd 279.1115, Found 279.1115.

*1-Ethylquinoxalin-2(1H)-one (**4b**)*. White solid, 219 mg, yield 42%; m.p. 80-82℃; IR (neat) *v* 1656, 1593, 1449, 1316, 1150, 1058, 760; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.39 (m, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 154.6, 150.3, 133.7, 132.2, 131.0, 130.8, 123.6, 113.6, 37.0, 12.5; HRMS (ESI): $C_{10}H_{10}N_2NaO^+$ $[M+Na]^+$ Calcd 197.0686, Found 197.0709.

*1,5-Dimethylquinoxalin-2(1H)-one (**4e**)*. White solid, 378 mg, yield 72%; m.p. 144-146℃; IR (neat) *v* 1653, 1531, 1461, 1309, 1062, 934, 763; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.48 (t, *J* = 8.0, 1H), 7.17 – 7.23 (m, 2H), 3.68 (s, 3H), 2.68 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 155.0, 148.4, 139.2, 133.3, 132.0, 130.8, 125.1, 111.7, 28.9, 17.6; HRMS (ESI): $C_{10}H_{10}N_2NaO^+$ $[M+Na]^+$ Calcd 197.0685, Found 197.0703.

*1,6-Dimethylquinoxalin-2(1H)-one (**4f**)*. White solid, 280 mg, yield 54%; m.p. 133-135℃; IR (neat) *v* 1646, 1445, 1311, 1058, 805, 579, 477; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 18.8 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 0.5 H), 7.67 (s, 0.5H), 7.41 – 7.43 (m, 0.5H), 7.24 (d, *J* = 8.4 Hz, 0.5H), 7.18 (d, *J* = 8.4 Hz, 0.5H), 7.13 (s, 0.5H), 3.68 (s, 3H), 2.50 (d, *J* = 26.8 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 155.2, 155.0, 150.1, 148.9, 142.0, 133.7, 133.3, 133.1, 132.2, 131.6, 131.0, 130.3, 130.2, 125.1, 113.9, 113.5, 28.7, 28.7, 22.2, 20.6; HRMS (ESI): $C_{10}H_{10}N_2NaO^+$ $[M+Na]^+$ Calcd 197.0685, Found 197.0698.

*1-Methyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (**4j**)*. White solid, 242 mg, yield 35%; m.p. 105-107℃; IR (neat) *v* ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.17 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 154.8, 151.7, 135.6, 132.7, 128.0 (q, $J_{C\text{-}F}$ = 3.9 Hz), 127.43 (q, $J_{C\text{-}F}$ = 3.5 Hz), 126.1 (q, $J_{C\text{-}F}$ = 33.8 Hz), 123.6 (q, $J_{C\text{-}F}$ = 271.8 Hz), 114.5, 29.0; HRMS (ESI): $C_{10}H_7N_2F_3NaO^+$ $[M+Na]^+$ Calcd 251.0403, Found 251.0431.

*1,6,7-Trimethylquinoxalin-2(1H)-one (**4m**)*. Pale yellow solid, 538 mg, yield 95%; m.p. 175-177℃; IR (neat) *v* 1644, 1532, 1447, 1032, 992, 930, 583; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.61 (s, 1H), 7.09 (s, 1H), 3.66 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 Hz, Chloroform-*d*) δ 155.1, 148.9, 141.0, 132.7, 131.8, 131.2, 130.4, 114.3, 28.6, 20.6, 19.1; HRMS

(ESI): $C_{11}H_{12}N_2NaO^+$ $[M+Na]^+$ Calcd 211.0842, Found 211.0861.

*6,7-Difluoro-1-methylquinoxalin-2(1H)-one (**4n**)*. White solid, 438 mg, yield 74%; m.p. 124-126℃; IR (neat) *v* 1667, 1601, 1452, 1308, 1119, 887, 828, 522; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (s, 1H), 7.68 – 7.73 (m, 1H), 7.14 – 7.19 (m, 2H), 3.66 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 154.5, 152.0 (dd, J_{C-F} = 254.7, 14.3 Hz), 150.5 (d, J_{C-F} = 3.6 Hz), 146.7 (dd, J_{C-F} = 247.8, 14.0 Hz), 130.6 (dd, J_{C-F} = 9.1, 1.7 Hz), 129.6 (dd, J_{C-F} = 9.2, 2.9 Hz), 118.2 (dd, J_{C-F} = 18.1, 2.3 Hz), 102.5 (d, J_{C-F} = 23.2 Hz), 29.3; HRMS (ESI): $C_9H_6F_2N_2NaO^+$ $[M+Na]^+$ Calcd 219.0340, Found 219.0340.

*6,7-Dibromo-1-methylquinoxalin-2(1H)-one (**4p**)*. Pale yellow solid, 249 mg, yield 26%; m.p. 262-264℃; IR (neat) *v* 1659, 1525, 1447, 1392, 1285, 921, 799; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 8.12 (s, 1H), 7.62 (s, 1H), 3.65 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 154.3, 151.5, 134.4, 133.1, 133.0, 127.7, 119.0, 118.5, 29.0; HRMS (ESI): $C_9H_6Br_2N_2NaO^+$ $[M+Na]^+$ Calcd 338.8739, Found 338.8728.

*4-(4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (**6a**)*.[6d] Pale yellow solid, 34.5 mg, yield: 76% [Δ]; 45.2mg, yield >99% [*hv*]; m.p. 110-111 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.42 (m, 2H), 3.70 (s, 3H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.19 – 2.26 (m, 2H); HRMS (ESI): $C_{13}H_{13}N_3NaO^+$ $[M+Na]^+$ Calcd 250.0951, Found 250.0955.

*4-(4-Ethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (**6b**)*. Pale yellow solid, 32.2 mg, yield: 67% [Δ]; 47.3mg, yield 98% [*hv*]; m.p. 102-103 ℃; IR (neat) *v* 2921, 1645, 1596, 1463, 1165, 1092, 759, 712 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.33 – 7.36 (m, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.20 – 2.27 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-d) δ 158.5, 154.2, 132.8, 132.0, 130.1, 130.0, 123.5, 119.6, 113.5, 37.4, 32.2, 22.1, 16.8, 12.4; HRMS (ESI): $C_{14}H_{15}N_3NaO^+$ $[M+Na]^+$ Calcd 264.1107, Found 264.1115.

*4-(4-Benzyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (**6c**)*.[6d] Pale yellow solid, 42.9 mg, yield: 71% [Δ]; 58.3mg, yield 96% [*hv*]; m.p. 116-117 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.23 – 7.33 (m, 7H), 5.50 (s, 2H), 3.15 (t, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.24 – 2.31 (m, 2H); HRMS (ESI): $C_{19}H_{17}N_3NaO^+$ $[M+Na]^+$ Calcd 326.1264, Found 326.1272.

4-(3-oxo-3,4-Dihydroquinoxalin-2-yl)butanenitrile (**6d**).[6d] Pale yellow solid, 20.1 mg, yield: 47% [Δ]; 30.3mg, yield 71% [*hv*]; m.p. 190-192 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.34 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.30 (m, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.00 – 2.07 (m, 2H); HRMS (ESI): $C_{12}H_{11}N_3NaO^+$ [M+Na]$^+$ Calcd 236.0794, Found 236.0809.

*4-(4,8-Dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (**6e**)*.[8g] Pale yellow solid, 27.5 mg, yield: 57% [Δ]; 45.7mg, yield 95% [*hv*]; m.p. 128-130 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 3H), 3.10 (t, *J* = 6.8 Hz, 2H), 2.67 (s, 3H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.22 – 2.29 (m, 2H); HRMS (ESI): $C_{14}H_{15}N_3NaO^+$ [M+Na]$^+$ Calcd 264.1107, Found 264.1120.

*4-(4,7-Dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile(**6f**)*.[6d] Pale yellow solid, 33.7 mg, yield: 70% [Δ]; 46.2 mg, yield 96% [*hv*]; m.p. 112-114 ℃; as an inseparable (1:1) mixture of 6-methyl and 7-methylquinoxalin-2(1*H*)-ones was used as the substrate; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 0.5H), 7.63 (s, 0.5H), 7.37 (d, *J* = 8.4 Hz, 0.5H), 7.16 – 7.22 (m, 1H), 7.10 (s, 0.5H), 3.69 (s, 3H), 3.07 (q, *J* = 6.8 Hz, 2H), 2.52 – 2.56 (m, 3.5H), 2.46 (s, 1.5H), 2.23 (m, 2H); HRMS (ESI): $C_{14}H_{15}N_3NaO^+$ [M+Na]$^+$ Calcd 264.1107, Found 264.1102.

*4-(7-Fluoro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (**6g**)*.[6d] Pale yellow solid, 20.1 mg, yield: 41% [Δ]; 37.9 mg, yield 77% [*hv*]; m.p. 101-103 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.28 – 7.33 (m, 2H), 3.71 (s, 3H), 3.10 (t, *J* = 6.8 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.18 – 2.26 (m, 2H); HRMS (ESI): $C_{13}H_{12}FN_3NaO^+$ [M+Na]$^+$ Calcd 268.0857, Found 268.0859.

*4-(7-Chloro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (**6h**)*.[6d] Pale yellow solid, 22.2 mg, yield: 43% [Δ]; 36.8 mg, yield 70% [*hv*]; m.p. 112-114 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 2.4 Hz, 1H), 7.51 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.26 (d, *J* = 8.9 Hz, 1H), 3.69 (s, 3H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.18 – 2.25 (m, 2H); HRMS (ESI): $C_{13}H_{12}ClN_3NaO^+$ [M+Na]$^+$ Calcd 284.0561, Found 284.0574.

*4-(7-Bromo-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (**6i**)*.[6d] Pale yellow solid, 33.7 mg, yield: 55% [Δ]; 35.8mg, yield 59% [*hv*]; m.p. 100-102 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.63 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 3.68 (s, 3H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.18 – 2.25 (m, 2H); HRMS (ESI):

$C_{13}H_{12}BrN_3NaO^+$ $[M+Na]^+$ Calcd 328.0056, Found 328.0074.

4-(4-Methyl-3-oxo-7-(trifluoromethyl)-3,4-dihydroquinoxalin-2-yl)butanenitrile ***(6j)***. Pale yellow solid, 23.6 mg, yield: 40% [Δ]; 50.8mg, yield 86% [*hv*]; m.p. 110-112 ℃; IR (neat) *v* 1663, 1618, 1312, 1218, 1169, 1106, 831, 655 cm^{-1}; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 3H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.20 – 2.27 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 160.3, 154.5, 135.4, 131.8, 127.2 (q, J_{C-F} = 4.0 Hz,), 126.4 (q, J_{C-F} = 3.5 Hz), 126.0 (q, J_{C-F} = 33.7 Hz), 123.7 (q, J_{C-F} = 271.8 Hz), 119.5, 114.3, 32.2, 29.4, 21.7, 16.7; HRMS (ESI): $C_{14}H_{12}F_3N_3NaO^+$ $[M+Na]^+$ Calcd 318.0825, Found 318.3008.

Methyl 3-(3-cyanopropyl)-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carboxylate ***(6k)***.[6d] Pale yellow solid, 25.6 mg, yield: 45% [Δ]; 43.2 mg, yield 76% [*hv*]; m.p. 134-136 ℃; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 8.02 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H), 3.75 (s, 3H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.21 – 2.28 (m, 2H); HRMS (ESI): $C_{15}H_{15}N_3NaO_3^+$ $[M+Na]^+$ Calcd 308.1006, Found 308.1018.

4-(4-Methyl-7-nitro-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile ***(6l)***.[6d] Pale yellow solid, 12.5 mg, yield: 23% [Δ]; 35.1 mg, yield 65% [*hv*]; m.p. 127-129 ℃; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 2.4 Hz, 1H), 8.41 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.42 (d, *J* = 9.2 Hz, 1H), 3.76 (s, 3H), 3.15 (t, *J* = 6.8 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.21 – 2.28 (m, 2H); HRMS (ESI): $C_{13}H_{12}N_4NaO_3^+$ $[M+Na]^+$ Calcd 295.0802, Found 295.0821.

4-(4,6,7-Trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile ***(6m)***. Pale yellow solid, 37.6 mg, yield: 74% [Δ]; 50.8 mg, yield >99% [*hv*]; m.p. 162-164 ℃; IR (neat) *v* 1614, 1583, 1463, 1172, 1088, 1013, 502 cm^{-1}; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.07 (s, 1H), 3.67 (s, 3H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 2.17 – 2.24 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-d) δ 157.1, 154.8, 139.8, 132.7, 131.1, 130.9, 129.9, 119.7, 114.2, 32.3, 29.0, 22.2, 20.5, 19.2, 16.8; HRMS (ESI): $C_{15}H_{17}N_3NaO^+$ $[M+Na]^+$ Calcd 278.1264, Found 278.1260.

4-(6,7-Difluoro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile ***(6n)***. Pale yellow solid, 28.3 mg, yield: 54% [Δ]; 47.1 mg, yield 90% [*hv*]; m.p. 136-138 ℃; IR (neat) *v* 1648, 1603, 1366, 1255, 918, 780 cm^{-1}; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 9.9, 8.4 Hz, 1H), 7.12 (dd, *J* = 11.2, 7.0 Hz, 1H), 3.66 (s, 3H), 3.08 (t, *J* = 7.1 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.36

– 1.90 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 159.1 (d, J_{C-F} = 3.5 Hz), 154.3, 151.3 (dd, J_{C-F} = 253.3, 14.4 Hz), 146.7 (dd, J_{C-F} = 247.3, 13.9 Hz), 130.3 (dd, J_{C-F} = 8.8, 1.7 Hz), 128.7 (dd, J_{C-F} = 9.3, 2.9 Hz), 119.5, 117.5 (dd, J_{C-F} = 18.0, 2.0 Hz), 102.4 (d, J_{C-F} = 23.1 Hz), 32.2, 29.6, 21.8, 16.7; HRMS (ESI): $C_{13}H_{11}F_2N_3NaO^+$ $[M+Na]^+$ Calcd 286.0762, Found 286.0763.

*4-(6,7-Dichloro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (**6o**)*.[6d] Pale yellow solid, 21.6 mg, yield: 37% [Δ]; 46 mg, yield 78% [*hv*]; m.p. 143-145 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.41 (s, 1H), 3.66 (s, 3H), 3.08 (t, *J* = 6.8 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.17 – 2.24 (m, 2H); HRMS (ESI): $C_{13}H_{11}Cl_2N_3NaO^+$ $[M+Na]^+$ Calcd 318.0171, Found 318.0182.

*4-(6,7-Dibromo-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (**6p**)*. Pale yellow solid, 31.2 mg, yield: 41% [Δ]; 52.5 mg, yield 69% [*hv*]; m.p. 143-145 ℃; IR (neat) *v* 2919, 1657, 1456, 1393, 1102, 406 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.58 (s, 1H), 3.65 (s, 3H), 3.07 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.17 – 2.24 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 160.3, 154.1, 133.8, 133.0, 132.2, 126.3, 119.4, 118.9, 118.4, 32.3, 29.3, 21.7, 16.7; HRMS (ESI): $C_{13}H_{11}Br_2N_3NaO^+$ $[M+Na]^+$ Calcd 405.9161, Found 405.9185.

*4-(4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-3-(naphthalen-2-yl)butanenitrile (**6q**)*. Pale yellow solid, 43.9 mg, yield: 62% [Δ]; 61.6 mg, yield 87% [*hv*]; m.p. 170-172 ℃; IR (neat) *v* 2978, 2905, 1649, 1405, 1063, 750 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.83 (m, 5H), 7.40 – 7.52 (m, 4H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 4.8 Hz, 1H), 4.06 (p, *J* = 7.2, 1H), 3.62 (s, 3H), 3.56 (dd, *J* = 16.4, 6.3 Hz, 1H), 3.44 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.83 – 2.94 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 157.3, 154.8, 139.1, 133.5, 133.0, 132.8, 132.5, 130.2, 129.8, 128.7, 127.9, 127.6, 126.3, 126.2, 125.9, 125.5, 123.7, 118.5, 113.7, 39.0, 38.6, 29.1, 24.4; HRMS (ESI): $C_{23}H_{19}N_3NaO^+$ $[M+Na]^+$ Calcd 376.1420, Found 376.1425.

*tert-Butyl (1-cyano-3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propan-2-yl)carbamate (**6r**)*.[6d] Pale yellow solid, 36.7 mg, yield: 50% [Δ]; 67.7 mg, yield >99% [*hv*]; m.p. 151-153 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.60 (m, 1H), 7.32 – 7.39 (m, 2H), 5.56 (d, *J* = 6.4 Hz, 1H), 4.46 (d, *J* = 5.2 Hz, 1H), 3.72 (s, 3H), 3.28 (d, *J* = 6.4 Hz, 2H), 2.95 (dd, *J* = 16.7, 5.1 Hz, 1H), 2.84 (dd, *J* = 16.6, 4.2 Hz, 1H), 1.37 (s, 9H); HRMS (ESI): $C_{18}H_{22}N_4NaO_3^+$ $[M+Na]^+$ Calcd 365.1584, Found 365.1568.

*tert-Butyl (cyanomethyl)((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)carbamate (**6s**)*.

Pale yellow solid, 21.6 mg, yield: 33% [Δ]; 58.0 mg, yield 88% [*hv*]; m.p. 153-155 ℃, as an inseparable mixture of atropisomers; IR (neat) *v* 1708, 1647, 1456, 1256, 1159, 1130, 757, 727 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*,) δ 7.86 $^{M/m}$ (d, *J* = 7.6 Hz, 1H), 7.55 – 7.61$^{M/m}$ (m, 1H), 7.30 – 7.39$^{M/m}$ (m, 2H), 4.77 – 4.79$^{M/m}$ (m, 2H), 4.45 ^{M} (s, 1.11H), 4.32 ^{m} (s, 0.88H), 3.72^{M} (s, 1.66H), 3.68^{m} (s, 1.33H), 1.56^{m} (s, 4.00H), 1.39^{M} (s, 5.00H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 155.2^{M}, 154.4^{m}, 154.1, 153.8, 153.7^{M}, 133.1 , 132.4^{m}, (132.3^{M}), 130.6^{M} (130.5^{m}), 130.22$^{M/m}$, 124.0^{M} (123.8^{m}), 116.1$^{M/m}$, 113.8^{M} (113.7^{m}), 82.1^{m} (81.7 ^{M}), 49.9^{m} (49.5^{M}), 37.34^{m} (36.29^{M}), 28.91^{M} (28.85^{m}), 28.2^{m} (28.1^{M}); HRMS (ESI): $C_{17}H_{20}N_4NaO_3^+$ $[M+Na]^+$ Calcd 351.1428, Found 351.1454.

2-((4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methoxy)acetonitrile ***(6t)***.[6d] Pale red solid, 28.5 mg, yield 62% [*hv*]; m.p. 112-113 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.42 (m, 2H), 4.95 (s, 2H), 4.58 (s, 2H), 3.72 (s, 3H); HRMS (ESI): $C_{12}H_{11}N_3NaO_2^+$ $[M+Na]^+$ Calcd 252.0743, Found 252.0764.

6-(4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-6-phenylhexanenitrile ***(6u)***.[8g] Pale yellow solid, 29.8 mg, yield: 45% [Δ]; m.p. 111-112 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.29 (m, 3H), 7.18 (t, *J* = 7.6 Hz, 1H), 4.67 (t, *J* = 7.6 Hz, 1H), 3.62 (s, 3H), 2.32 (t, *J* = 7.2 Hz, 3H), 2.04 – 2.13 (m, 1H), 1.67 – 1.76 (m, 2H), 1.40 – 1.54 (m, 2H); HRMS (ESI): $C_{21}H_{21}N_3NaO^+$ $[M+Na]^+$ Calcd 354.1577, Found 354.1566.

6,6-Diphenylhex-5-enenitrile ***(7a)***.[8b] Colorless oil, 16.4 mg, yield: 33% [Δ]; 44.4 mg, yield 90% [*hv*]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.39 (m, 3H), 7.20 – 7.27 (m, 5H), 7.15 (d, *J* = 6.8 Hz, 2H), 6.01 (t, *J* = 7.2 Hz, 1H), 2.22 – 2.30 (m, 4H), 1.74 – 1.81 (m, 2H); HRMS (ESI): $C_{18}H_{17}NNa^+$ $[M+Na]^+$ Calcd 270.1253, Found 270.1273.

6-Phenyl-6-(p-tolyl)hex-5-enenitrile ***(7b)***.[8b] Colorless oil, 24.0 mg, yield: 46% [Δ]; 38.3mg, yield 73% [*hv*]; as an inseparable mixture of *Z/E* isomers; IR (neat) *v* 1648, 1597, 1464, 1312, 752, 703 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 – 7.39 (m, 9H), 5.97 (t, *J* = 7.2 Hz, 1H), 2.22 – 2.38 (m, 7H), 1.75 – 1.83 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 143.74 (143.65), 142.4, 139.8 (139.34), 137.1 (136.9), 136.61, 129.68 (129.60), 129.07 (128.89), 128.34 (128.15), 127.24 (127.19), 127.07, 126.5, 125.7, 119.59 (119.58), 28.77 (28.68), 25.82, 21.26 (21.08), 16.71 (16.69); HRMS (ESI): $C_{19}H_{19}NNa^+$ $[M+Na]^+$ Calcd 284.1410, Found 284.1424.

6-([1,1'-Biphenyl]-4-yl)-6-phenylhex-5-enenitrile ***(7c)***. Colorless oil, 13.6 mg, yield: 21% [Δ];

50.0mg, yield 77% [*hv*]; as an inseparable mixture of *Z/E* isomers (0.28/0.68); IR (neat) *v* 1487, 1445, 840, 762, 736, 696 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.64 (m, 3.5H), 7.32 – 7.51 (m, 4.5H), 7.18 – 7.30 (m, 6H), 6.01 – 6.10 (m, 1H), 2.25 – 2.36 (m, 4H), 1.79 – 1.86 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 143.5^{M} (143.4^{m}), 142.2, 141.0^{m} (140.7^{M}), 140.1^{M} (139.5^{m}), 138.6, 130.2^{M} (129.7^{m}), 128.81^{M} (128.77^{m}), 128.5^{m} (128.2^{M}), 127.5^{m} (127.4^{M}), 127.3, 127.1^{M} (127.0^{m}), 126.9^{M} (126.6^{m}), 119.53^{M} (119.51^{m}), 28.84^{M} (28.78^{m}), 25.83^{M} (25.78^{m}), 16.74^{M} (16.72^{m}); HRMS (ESI): $C_{24}H_{21}NNa^{+}$ $[M+Na]^{+}$ Calcd 346.1566, Found 346.1570.

*6-(4-Fluorophenyl)-6-phenylhex-5-enenitrile (**7d**)*. Colorless oil, 18.1 mg, yield: 34% [Δ]; 38.7 mg, yield 73% [*hv*]; as an inseparable mixture of *Z/E* isomers (0.41:0.49); IR (neat) *v* 1503, 1223, 1158, 835, 764, 701 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 – 7.41 (m, 8H), 6.93 – 6.97 (m, 1H), 5.93 – 6.03 (m, 1H), 2.23 – 2.34 (m, 4H), 1.76 – 1.84 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.2 (d, $J_{C\text{-}F}$ = 246.5.2 Hz) [162.0 (d, $J_{C\text{-}F}$ = 246.3 Hz)], 142.8, 142.0 (139.43), 138.29 (d, $J_{C\text{-}F}$ = 3.3 Hz) [135.45 (d, $J_{C\text{-}F}$ = 3.5 Hz)], 131.3 (d, $J_{C\text{-}F}$ = 7.9 Hz) [128.8, (d, $J_{C\text{-}F}$ = 7.9 Hz)], 129.6 (128.5), 128.3 (127.2), 127.41 (127.40), 127.0, 126.47 (126.46), 119.46 (119.43), 115.4 (d, $J_{C\text{-}F}$ = 21.3 Hz) [115.0 (d, $J_{C\text{-}F}$ = 21.4 Hz)], 28.72 (28.70), 25.71 (25.69), 16.7; HRMS (ESI): $C_{18}H_{16}FNNa^{+}$ $[M+Na]^{+}$ Calcd 288.1159, Found 288.1171.

*6-(4-Chlorophenyl)-6-phenylhex-5-enenitrile (**7e**)*. Colorless oil, 10.8 mg, yield: 19% [Δ]; 27.5 mg, yield 49% [*hv*]; as an inseparable mixture of *Z/E* isomers; IR (neat) *v* 1590, 1562, 1445, 1419, 1078, 775, 699 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.05 – 7.41 (m, 9H), 6.00 – 6.05 (m, 1H), 2.23 – 2.34 (m, 4H), 1.76 – 1.84 (m, 2H), 1.57 – 1.58 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 142.6^{M}, 141.47^{M}, 141.44^{M} (144.0^{m}, 142.7^{m}, 138.9^{m}), 134.3^{M} (134.2^{m}), 129.71^{m} (129.65^{M}), 129.6^{M} (129.4^{m}), 128.6^{m} (128.3^{M}), 127.93^{M} (127.89^{m}), 127.6^{m} (127.5^{M}), 127.4, 127.24, 127.21, 127.1^{M} 125.4, 119.4, 28.73^{M} (28.70^{m}), 25.66^{M} (25.63^{m}), 16.7; HRMS (ESI): $C_{18}H_{16}ClNNa^{+}$ $[M+Na]^{+}$ Calcd 304.0863, Found 304.0888.

*6-(4-Chlorophenyl)-6-phenylhex-5-enenitrile (**7f**)*.[8b] Colorless oil, 19.1 mg, yield: 35% [Δ]; 40.4mg, yield 73% [*hv*]; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 7.6 Hz, 2H), 7.02 – 7.12 (m, 6H), 5.94 (t, *J* = 7.6 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H), 2.23 – 2.29 (m, 4H), 1.78 (q, *J* = 7.2 Hz, 2H); HRMS (ESI): $C_{20}H_{21}NNa^{+}$ $[M+Na]^{+}$ Calcd 298.1566, Found 298.1572.

*6,6-Bis(4-chlorophenyl)hex-5-enenitrile (**7g**)*. Colorless oil, 11.3 mg, yield: 18% [Δ]; 44.7 mg, yield 71% [*hv*]; IR (neat) *v* 2916, 1488, 1089, 1012, 823, 516 cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-

d) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.26 (m, 2H), 7.07 – 7.23 (m, 4H), 6.01 (t, *J* = 7.6 Hz, 1H), 2.23 – 2.33 (m, 4H), 1.76 – 1.83 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 141.6, 140.2, 137.5, 133.5, 133.4, 131.0, 128.8, 128.44, 128.42, 127.7, 119.3, 28.8, 25.6, 16.8; HRMS (ESI): $C_{18}H_{15}Cl_2NNa^+$ $[M+Na]^+$ Calcd 338.0474, Found 338.0501.

*1-Methyl-3-(2-methyl-5-oxohexan-2-yl)quinoxalin-2(1H)-one (**8a**)*.[17] Pale yellow solid, 16.2 mg, yield 30% [*hv*]; m.p. 71-72 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.25 (m, 2H), 3.60 (s, 3H), 2.20 – 2.27 (m, 4H), 2.03 (s, 3H), 1.39 (s, 6H); HRMS (ESI): $C_{16}H_{20}N_2NaO_2^+$ $[M+Na]^+$ Calcd 295.1417, Found 295.1410.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.xxxxxxx

The setup for the photocatalytic procedure.
Reaction optimization and mechanistic studies.
^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra for compounds **3.**

^{1}H NMR spectra for compounds **4a**, **4c-4d**, **4g-4i**, **4k**, **4o**, **5b-5g**, **6a**, **6c-6i**, **6k**, **6o**, **6r**, **6t-6u**, **7a**, **7f** and **8a**.

^{1}H NMR and ^{13}C NMR spectra for compounds **4b, 4e-4f, 4j, 4m-4n, 4p, 6b, 6j, 6m-6n, 6p-6q, 6s, 7b-7e** and **7g.**

AUTHOR INFORMATION

Corresponding Author

* Email: hyangchem@csu.edu.cn (H. Yang)
* Email: xianghaoyue@csu.edu.cn (H. Y. Xiang)

Author Contributions

# These authors contributed equally.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENT

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (21576296, 21776318, 21676302 & 81703365), and the Fundamental Research Funds for Central South University (grant number 2019zzts222).

REFERENCES

(1) (a) Zard, S. Z. Recent Progress in the Generation and Use of Nitrogen-centred Radicals. *Chem. Soc. Rev.* **2008**, *37*, 1603–1618. (b) Karkas, M. D. Photochemical Generation of Nitrogen-Centered Amidyl, Hydrazonyl, and Imidyl Radicals: Methodology Developments and Catalytic Applications. *ACS Catal.* **2017**, *7*, 4999–5022. (c) Davies, J.; Morcillo, S. P.; Douglas, J. J.; Leonori, D. Hydroxylamine Derivatives as Nitrogen-Radical Precursors in Visible-Light Photochemistry. *Chem. Eur. J.* **2018**, *24*, 12154–12163. (d) Yin, W.; Wang, X. Recent Advances in Iminyl Radical-Mediated Catalytic Cyclizations and Ring-opening Reactions. *New J. Chem.*, **2019**, *43*, 3254−3264.

(2) (a) Lu, B.; Cheng, Y.; Chen, L.-Y.; Chen, J.-R.; Xiao, W.-J. Photoinduced Copper-Catalyzed Radical Aminocarbonylation of Cycloketone Oxime Esters. *ACS Catal.* **2019**, 9, 8159−8164. (b) Li, L.; Chen, H.; Mei, M.; Zhou, L. Visible-light Promoted γ-Cyanoalkyl Radical Generation: Three-component Cyanopropylation/etherification of Unactivated Alkenes. *Chem. Commun.* **2017**, 53, 11544−11547. (c) Yin, Z.; Rabeah, J.; Brückner, A.; Wu, X. F. Gallic Acid-Promoted SET Process for Cyclobutanone Oximes Activation and (Carbonylative-)Alkylation of Olefins. *ACS Catal.* **2018**, 8, 10926−10930.

(3) (a) Shu, W.; Nevado, C. Visible-Light-Mediated Remote Aliphatic C−H Functionalizations through a 1,5-Hydrogen Transfer Cascade. *Angew. Chem. Int. Ed.* **2017**, 56, 1881−1884. (b) Jiang, H.; Studer, A. α-Aminoxy-Acid-Auxiliary-Enabled Intermolecular Radical γ-C(sp^3)-H Functionalization of Ketones. *Angew. Chem. Int. Ed.* **2018**, 57, 1692−1696.

(4) Atmaram, S.; Forrester, A. R.; Gill, M.; Thomson, R. H. Iminyls. Part 9. Intramolecular Addition of an lminyl to an Alkene. *J. Chem. Soc. Perkin Trans. 1.* **1981**, *1*, 1721−1724.

(5) (a) Faulkner, A.; Scott, J. S.; Bower, J. F. An Umpolung Approach to Alkene Carboamination: Palladium Catalyzed 1,2-Amino-Acylation, -Carboxylation, -Arylation, -Vinylation, and –Alkynylation. *J. Am. Chem. Soc.* **2015**, *137*, 7224–7230. (b) Chen, C.; Hou, L.-L.; Cheng, M.; Su, J.-H.; Tong X.-F. Palladium(0)-Catalyzed Iminohalogenation of Alkenes: Synthesis of 2-Halomethyl Dihydropyrroles and Mechanistic Insights into the Alkyl Halide Bond Formation.

Angew. Chem. Int. Ed. **2015**, *54*, 3092–3096. (c) Ai, W.-Y.; Liu, Y.-Q.; Wang, Q.; Lu, Z.-L.; Liu, Q. Cu-Catalyzed Redox-Neutral Ring Cleavage of Cycloketone O-Acyl Oximes: Chemodivergent Access to Distal Oxygenated Nitriles. *Org. Lett.* **2018**, *20*, 409–412. (d) An, Z.-Y.; Jiang, Y.; Guan, X.; Yan, R.-L. Copper-catalyzed Tandem Aerobic Oxidative Cyclization for the Synthesis of 4-Cyanoalkylpyrrolo[1,2-a]quinoxalines from 1-(2-Aminophenyl)pyrroles and Cyclobutanone Oxime Esters. *Chem. Commun.* **2018**, *54*, 10738–10741. (e) Yu, X.-Y.; Zhao, Q.-Q.; Chen, J.; Chen, J.-R.; Xiao, W.-J. Copper-Catalyzed Radical Cross-Coupling of Redox-Active Oxime Esters, Styrenes, and Boronic Acids. *Angew. Chem. Int. Ed.* **2018**, *57*, 15505–15509. (f) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. Visible Light Photoredox-controlled Reactions of *N*-Radicals and Radical Ions. *Chem. Soc. Rev.* **2016**, *45*, 2044–2056.

(6) (a) Jackman, M. M.; Im, S.; Bohman, S. R.; Lo, C. C. L.; Garrity, A. L.; Castle, S. L. Synthesis of Functionalized Nitriles by Microwave-Promoted Fragmentations of Cyclic Iminyl Radicals. *Chem. Eur. J.* **2018**, *24*, 594–598. (b) Cai. Y; Jalan, A.; Kubosumi, A. R.; Castle, S. L. Microwave-Promoted Tin-Free Iminyl Radical Cyclization with TEMPO Trapping: A Practical Synthesis of 2-Acylpyrroles. *Org. Lett.* **2015**, *17*, 488–491. (c) Yin, Z.; Rabeah, J.; Brückner, A.; Wu, X. F. Vinylboron Self-Promoted Carbonylative Coupling with Cyclobutanone Oxime Esters. *Org. Lett.* **2019**, *21*, 1766–1769. (d) Yang, L.; Gao, P.; Duan, X.-H.; Gu, Y.-R.; Guo, L.-N. Direct C–H Cyanoalkylation of Quinoxalin-2(1*H*)-ones *via* Radical C–C Bond Cleavage. *Org. Lett*. **2018**, *20*, 1034-1037.

(7) (a) Ding, D.; Wang, C. Nickel-Catalyzed Reductive Electrophilic Ring Opening of Cycloketone Oxime Esters with Aroyl Chlorides. *ACS Catal.* **2018**, *8*, 11324–11329. (b) Yang, H.-B.; Pathipati, R. S.; Selander, N. Nickel-Catalyzed 1,2-Aminoarylation of Oxime Ester-Tethered Alkenes with Boronic Acids. *ACS Catal.* **2017**, *7*, 8441–8445. (c) Zhao, J.-F.; Duan, X.-H.; Gu, Y.-R.; Gao, P.; Guo, L.-N. Iron-Catalyzed Decarboxylative Olefination of Cycloketone Oxime Esters with α,β-Unsaturated Carboxylic Acids via C–C Bond Cleavage. *Org. Lett.* **2018**, *20*, 4614–4617. (d) Zhao, B,-L.; Shi, Z.-Z. Copper-Catalyzed Intermolecular Heck-Like Coupling of Cyclobutanone Oximes Initiated by Selective C−C Bond Cleavage. *Angew. Chem. Int. Ed.* **2017**, *56*, 12727–12731. (e) Gu, Y.-R.; Duan, X.-H.; Yang, L.; Guo, L.-N. Direct C–H Cyanoalkylation of Heteroaromatic N-Oxides and Quinones via C–C Bond Cleavage of Cyclobutanone Oximes. *Org. Lett.* **2017**, *19*, 5908–5911.

(8) (a) Narasaka, K. Synthesis of Azaheterocycles from Oxime Derivatives. *Pure Appl. Chem.* **2003**, *75*, 19–28. (b) Yu, X.-Y.; Chen, J.-R.; Wang, P.-Z.; Yang, M.-N.; Liang, D.; Xiao, W.-J. A Visible-Light-Driven Iminyl Radical-Mediated C−C Single Bond Cleavage/Radical Addition Cascade of Oxime Esters. *Angew. Chem. Int. Ed.* **2018**, *57*, 738–743. (c) Vaillant, F. L.; Garreau, M.; Nicolai, S.; Grynova, G.; Corminboeuf, C.; Waser, J. Fine-tuned Organic Photoredox Catalysts for Fragmentation-alkynylation Cascades of Cyclic Oxime Ethers. *Chem. Sci*. **2018**, *9*, 5883–5889. (d) Dauncey, E. M.; Morcillo, S. P.; Douglas, J. J.; Sheikh, N. S.; Leonori, D. Photoinduced Remote Functionalisations by Iminyl Radical Promoted C-C and C-H Bond Cleavage Cascades. *Angew. Chem. Int. Ed*. **2018**, *57*, 744–748. (e) Svejstrup, T. D.; Ruffoni, A.; Julia, F.; Aubert, V. M.; Leonori , D. Synthesis of Arylamines *via* Aminium Radicals . *Angew. Chem. Int. Ed.* **2017**, *56*, 14948–14952. (f) Davies, J.; Booth, S. G.; Essafi, S.; Dryfe, R. A. W.; Leonori, D. Visible-Light-Mediated Generation of Nitrogen-Centered Radicals: Metal-Free Hydroimination and Iminohydroxylation Cyclization Reactions. *Angew. Chem. Int. Ed.* **2015**, 54, 14017–14021. (g) Dauncey, E. M.; Morcillo, S. P.; Douglas, J. J.; Sheikh, N. S.; Leonori, D. Photoredox Imino Functionalizations of Olefins. *Angew. Chem. Int. Ed*. **2017**, *56*, 13361–13365. (h) Li, J.; Zhang, P.; Jiang, M.; Yang, H.; Zhao, Y.; Fu, H.; Visible Light as a Sole Requirement for Intramolecular C(sp^3)–H Imination. *Org. Lett.* **2017**, *19*, 1994–1997. (i) Wang, P.-Z.; He, B.-Q.; Cheng, Y.; Chen, Y.; Xiao, W.-J. Radical C–C Bond Cleavage/Addition Cascade of Benzyl Cycloketone Oxime Ethers Enabled by Photogenerated Cyclic Iminyl Radicals. *Org. Lett.* **2019**, *21*, 6924–6929.

(9) (a) He, Y.-W.; Anand, D.; Sun, Z.-C.; Zhou, L. Visible-Light-Promoted Redox Neutral *γ,γ*-Difluoroallylation of Cycloketone Oxime Ethers with Trifluoromethyl Alkenes via C–C and C–F Bond Cleavage. *Org. Lett.* **2019**, *21*, 3769–3773. (b) Zhang, W.; Pan, Y.-L.; Yang, C.; Chen, L.; Li, X.; Cheng J.-P. Metal-Free Direct C−H Cyanoalkylation of Quinoxalin-2(1H)-Ones by Organic Photoredox Catalysis. *J. Org. Chem.* **2019**, *84*, 7786−7795. (c) Jelier, B. J.; Tripet, P. F.; Pietrasiak, E.; Franzoni, I.; Jeschke, G.; Togni, A. Radical Trifluoromethoxylation of Arenes Triggered by a VisibleLight-Mediated N-O Bond Redox Fragmentation. *Angew. Chem. Int. Ed.* **2018**, *57*, 13784–13789.

(10) (a) Arora, A.; Weaver, J. D. Visible Light Photocatalysis for the Generation and Use of Reactive Azolyl and Polyfluoroaryl Intermediates. *Acc. Chem. Res.* **2016**, *49*, 2273–2283. (b) Singh, A.; Kubik, J. J.; Weaver, J. D. Photocatalytic C–F Alkylation: Facile Access to Multifluorinated

Arenes. *Chem. Sci.* **2015**, *6*, 7206–7212. (c) Matsunami, A.; Kuwata, S.; Kayaki, Y. Hydrodefluorination of Fluoroarenes Using Hydrogen Transfer Catalysts with a Bifunctional Iridium/NH Moiety. *ACS Catal.* **2016**, 6, 5181−5185.

(11) Xia, P.-J.; Ye, Z.-P.; Hu, Y.-Z.; Song, D. Xiang, H.-Y.; Chen, X.-Q.; Yang, H. Photocatalytic, Phosphoranyl Radical-Mediated N–O Cleavage of Strained Cycloketone Oximes. *Org. Lett.* **2019**, *21*, 2658–2662.

(12) Arias-Rotondo, D. M.; McCusker, J. K. The Photophysics of Photoredox Catalysis: a Roadmap for Catalyst Design. *Chem. Soc. Rev.* **2016**, 45, 5803-5820.

(13) (a) Stoyanovsky, D. A.; Cederbaum, A. I.; Metabolism of Carbon Tetrachloride to Trichloromethyl Radical: An ESR and HPLC-EC Study. *Chem. Res. Toxicol.* **1999,** *12,* 730-736. (b) Zhao. B.; Liang, H.-W.; Yang, J.; Yang, Z.; Wei, Y. Copper-Catalyzed Intermolecular Cyclization between Oximes and Alkenes: A Facile Access to Spiropyrrolines. *ACS Catal*. **2017**, *7*, 5612−5617.

(14) (a) Dhameliya, T. M.; Chourasiya, S. S.; Mishra, E.; Jadhavar, P. S.; Bharatam, P. V.; Chakraborti, A. K. Rationalization of Benzazole-2-carboxylate versus Benzazine-3-one/Benzazine-2,3-dione Selectivity Switch during Cyclocondensation of 2-Aminothiophenols/Phenols/Anilines with 1,2-Biselectrophiles in Aqueous Medium. *J. Org. Chem.* **2017**, *82*, 10077−10091.(b) Carrer, A.; Brion, J.-D.; Messaoudi, S.; Alami, M. Palladium(II)-Catalyzed Oxidative Arylation of Quinoxalin-2(1*H*)-ones with Arylboronic Acids. *Org. Lett.* **2013**, *15*, 5606-5609.

(15) (a) Chen, D.-B.; Wang, Z.-J.; B, W.-L. Copper-catalyzed Cascade Syntheses of 2H-benzo[*b*][1,4]thiazin-3(4*H*)-ones and Quinoxalin-2(1*H*)-ones through Capturing S and N Atom respectively from AcSH and TsNH2. *J. Org. Chem.* **2010**, *75*, 5768–5771. (b) Li, Z.-S.; Wang, W.-X.; Yang, J.-D.; Wu, Y.-W.; Zhang, W. Photoinduced and *N*-Bromosuccinimide Mediated Cyclization of 2-Azido-*N*-phenylacetamides. **2013**, *15*, 3820–3823.

(16) Onuigbo, L.; Raviola, C.; Fonzo, A. D.; Protti, S.; Fagnoni, M. Sunlight-Driven Synthesis of Triarylethylenes (TAEs) via Metal-Free Mizoroki–Heck-Type Coupling. *Eur. J. Org. Chem*. **2018**, *38*, 5297–5303.

(17) (a) Tang, J.; Hackenberger, D.; Goossen, L. J. Branched Arylalkenes from Cinnamates: Selectivity Inversion in Heck Reactions by Carboxylates as Deciduous Directing Groups. *Angew. Chem. Int. Ed.* **2016**, *55*, 11296–11299. (b) Shen, R.-W.; Yang, J.-J.; Zhu, S.-G.; Chen, C.; Wu,

L.-L. Gold(I)-Catalyzed Decarboxylation of Propargyl Carbonates: Reactivity Reversal of the Gold Catalyst from π-Lewis Acidity to σ-Lewis Acidity. *Adv. Synth. Catal.* **2015**, *6*, 1259–1269.

(18) Gu, Y.-R.; Duan, X.-H.; Chen, L.; Ma, Z.-Y.; Gao, P.; Guo, L.-N. Iminyl Radical-Triggered Intermolecular Distal C(sp^3)-H Heteroarylation via 1,5-Hydrogen-Atom Transfer (HAT) Cascade. *Org. Lett*. **2019**, *21*, 917-920.