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吡唑化提高喹喔啉酮敏化效率: 氮杂环丁烷的合成及进一步开环反应

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摘要 在温和条件下利用吡唑作为合适的辅助基促进喹喔啉酮类化合物被光催化剂敏化, 通过分子间 aza Paternò-Büchi 反应制备功能化的氮杂环丁烷. 总体而言, 吡唑基具有降低喹喔啉酮类化合物的三线态激发态能量、改变氧化还原电位及作为良好的离去基进行后续转化等关键作用. 研究涉及交叉脱氢偶联(CDC)-胺化、aza Paternò-Büchi 反应和消除反应.
关键词 可见光催化; 需氧氧化; 光环加成; aza Paternò-Büchi 反应; 能量转移

Improving the Efficiency of Sensitized Quinoxlin-2(1*H*)-ones via Pyrazolylation: Synthesis of Azetidines and Further Ring-Opening Reaction

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Abstract A mild approach to prepare functionalized azetidines by intermolecular aza Paternò-Büchi reaction using suitable auxochrome (pyrazole) to promote 3-pyrazolyl quinoxalin-2(1*H*)-ones into its excited state has been developed. Overall, pyrazolyl plays a key role in reducing the excited state energy of the triplet state of quinoxalinones, changing the redox potential and subsequent transformation as a good leaving group. The cross-dehydrogenative coupling (CDC)-amination, aza Paternò-Büchi reaction, and elimination reaction were also investigated.
Keywords visible light catalysis; aerobic oxidation; photocycloaddition; Paternò-Buchi reaction; energy transfer

1 Introduction

The aza Paternò-Buchi (PB) reaction, the [2+2] photocycloaddition reaction between an imine and an alkene component, is one of the most efficient ways to synthesize functionalized azetidines (Scheme 1).[1] Traditionally, the aza PB cycloadditions often proceed under high-energy UV radiation,[2] which can lead to the problems including the special equipment for UV irradiation, practical limitations in assembling structurally complex azetidines and the undesired parallel pathways of the excited imines.[3] Recently, visible-light-mediated energy transfer (EnT) pathway has served as a powerful strategy for cycloadditions.[4-5] Compared to activation of the alkene component[6-8] to its corresponding triplet state to accomplish the aza PB reaction, visible-light-enabled intermolecular cycloadditions of alkenes with triplet state imines are rare. The high triplet state energy of imines seriously restricts the scope of triplet sensitizers to activate imines. So far, the reported sensitizers are either noble metal complexes[4] or hard-to-excite ketones.[5a,5m] Consequently, developing a protocol for aza PB reactions relying on a commonly available and highly efficient organo-ensitizer would be highly desirable.

Herein, we try to modify the imine moiety of quinoxalin-2(1*H*)-ones[4] with pyrazole, a reversible directing group in photocycloadditions, to decrease their first triplet energies and enable efficient aza PB reactions with a commonly available sensitizer. In this regard, we successfully developed an efficient visible-light-induced 4CzIPN-catalyzed direct C—H amination[9] with pyrazole leading to 3-pyrazol-quinoxalinones. The pyrazole-modified quinoxalinones could be easily activated by many photocatalysts due to their dramatically decreased triplet ener-

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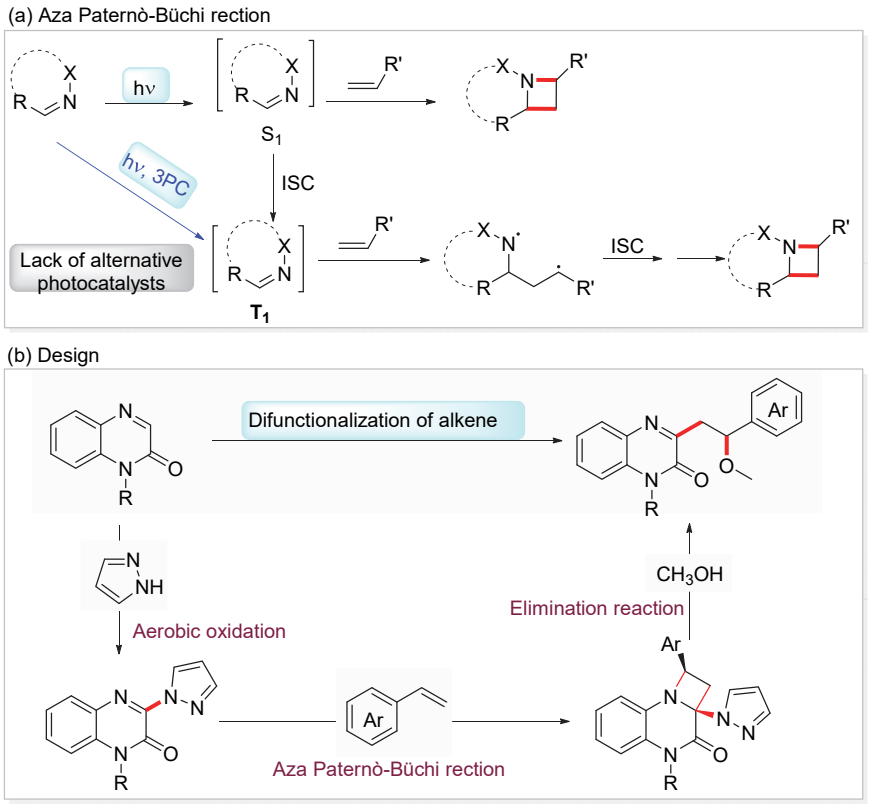
gies.[8] As a result, the aza PB reaction between 3-pyrazol-quinoxalinones and alkenes could be achieved efficiently under blue LEDs irradiation. In addition, the removal of pyrazole moiety of the azetidine products could obtain 3-alkylated quinoxalinones (Scheme 1).

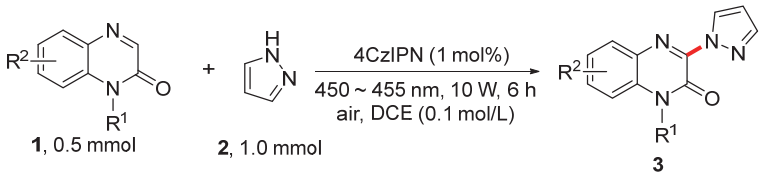
2 Results and discussion

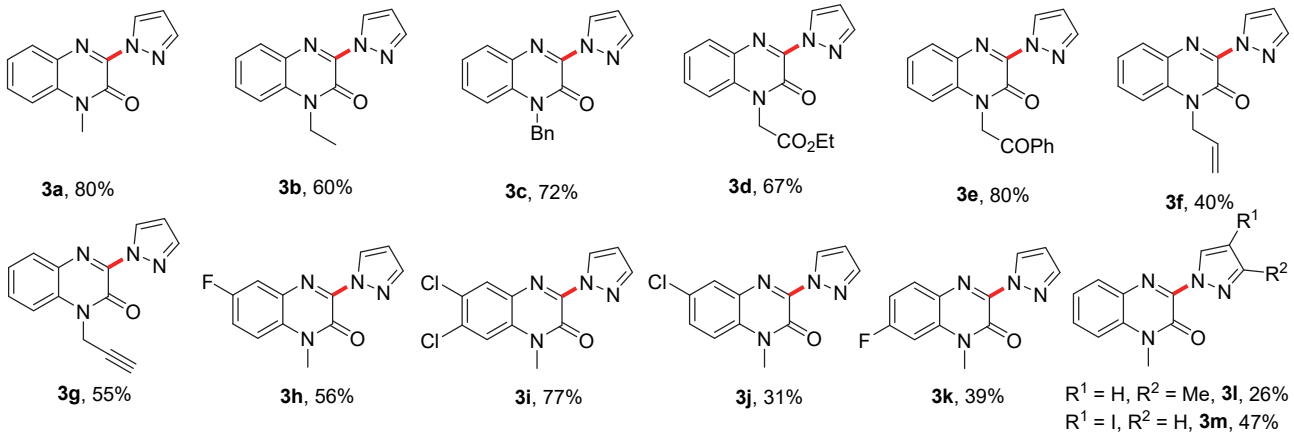
To this end, the generality of the C3-amination of quinoxalin-2(1*H*)-ones with azoles was examined (Table 1). A variety of functional groups were tolerated under the



Scheme 1 Strategies for the functionalization of quinoxalin-2(1*H*)-ones

Table 1 Scope of C-3 amination of quinoxalinones[a,b]





[a] Reation conditions: **1** (0.5 mmol), **2** (2 equiv.), catalyst (1 mol%) were added in 1,2-dichloroethene (DCE, 0.1 mol/L) under air atmosphere and irradiation of 10 W blue LED for 6 h at room temperature. [b] Isolated yield.

optimized reaction conditions, including *N*-ethyl, *N*-benzyl, *N*-esteryl, *N*-2-oxo-2-phenylethyl and *N*-allylic, affording 3-pyrazol-quinoxalinones (Table 1, **3a**～**3g**). Furthermore, a series of substituted quinoxalin-2-ones with halo groups at the phenyl ring reacted smoothly to produce the corresponding products **3h**～**3j**. Finally, substituted azoles **3l** and **3m** were attempted under the standard conditions, and the C3-aminated quinoxalin-2(1*H*)-ones could also be obtained with a decreased efficiency.

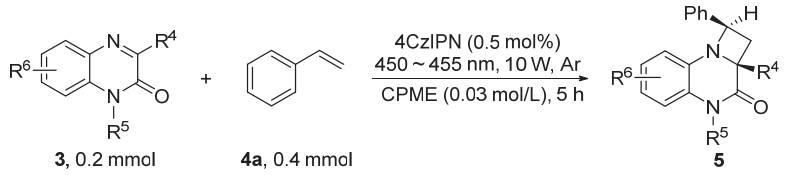
As shown in Table 2, the reaction aza Paternò-Buchi of 3-pyrazol-quinoxalinones and styrene occurred smoothly by using the organic dye 4CzIPN as photocatalyst and blue LEDs as the light source. Quinoxalinones with the functional groups at N atom (Table 2, **5a**～**5f**) and phenyl ring reacted (**5g**～**5j**) with styrene giving high to excellent yields of the desired azetidines with moderate diastereoselectivity. The scope of [2＋2] photocycloadditions could be successfully explored to quinoxalinone bearing substituted pyrazole such as 3-methylpyrazole (**5k**) and 4-iodopyrazole (**5l**) without significant influence on yield.

We next targeted to extend [2＋2] cycloadditions to various alkenes (Table 3). To our delight, both electron-deficient and electron-rich vinylarenes were tolerated, affording the corresponding adducts in high yields (**6a**～**6i**, **6m**, **6z** and **6ab**). Vinyl heteroarenes were used as good coupling partners in this transformation, such as vinyl pyridines (**6j**～**6k**) and vinyl indole (**6ab**). At the same time, [2＋2]-cycloadducts with vinyl naphthalene (**6o**) and 2-substituted vinylarenes (**6q**～**6r**) were achieved. In addition, terminal alkenes like buta-1,3-diene (**6s**), acrylonitrile (**6t**) and *N*-vinylpyrrolidin-2-one (**6y**), also conducted well leading to desired products. Moreover, internal alkenes, such as prop-1-en-1-ylbenzene (**6n**), dihydrofuran (**6u**), 1*H*-indene (**6v**), 1,2-dihydronaphthalene (**6x**) and *N*-methylmaleimide (**6w**), were appropriate for this cyclization resulting in desired azetidines. It should be noted that polycyclic skeletons could be formed from 3-pyrazol-quinoxalinones and cycloalkenes (**6u**～**6w**).

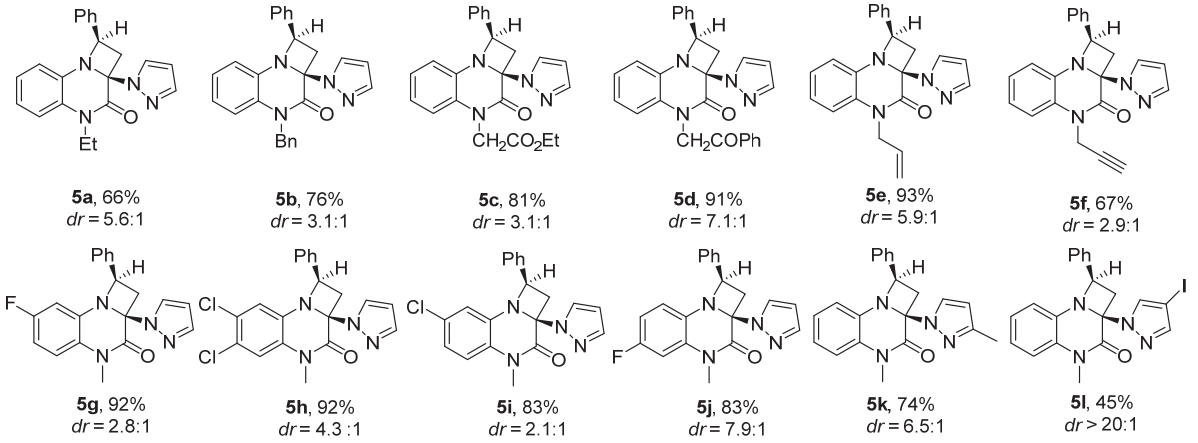
The removal of pyrazole moiety of the photoadducts was accompanied by ring opening of azetidine rings in a methanol solution containing acetic acid. As a consequence, 3-alkylated-quinoxalinones were formed from pyrazole-containing azetidines in excellent yield. The photocycloddition and subsequent pyrazole removal were successfully extended to a one-pot process and accomplished 3-(2-methoxy-2-arylethyl)quinoxalin-2(1*H*)-one using simple quinoxalin-2(1*H*)-ones and vinylarenes as starting materials. As shown in Table 4, a cyclopentyl methyl ether (CPME) solution containing quinoxalin-2(1*H*)-ones **3**, vinylarenes **4** and a catalytic amount of 4CzIPN were irradiated by blue LEDs irradiation for 5 h. After the removal of CPME, methanol and acetic acid were added to the reaction mixture, followed by stirring at 35 ℃ for 5 h. Gratifyingly, a series of representative quinoxalin-2(1*H*)-one substrates smoothly underwent the one-pot process, providing a diverse library of 3-alkylated quinoxalin-2(1*H*)-ones (**7a**～**7f**, with 55%～84% yields).

The low-temperature phosphorescence of quinoxalinone **1a** and 3-pyrazol-quinoxalinone **3a** (Figure 1, A) indicates that the first triplet energy of **3a** is much lower than that of **1a** [E_T(**1a**)＝250.3 kJ•mol^{-1} (77 K, CPME), while E_T(**3a**)＝236.5 kJ•mol^{-1}]. In addition, the phosphorescence of the photocatalyst 4CzIPN could be quenched efficiently in the presence of **3a**, while the quenching of the phosphoresc-

Table 2 Substrate scope with respect to quinoxalinones derivatives[a,b]

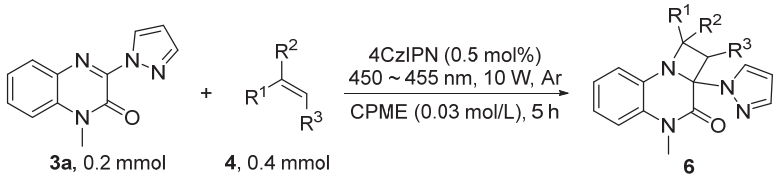


3, 0.2 mmol + **4a**, 0.4 mmol → **5**

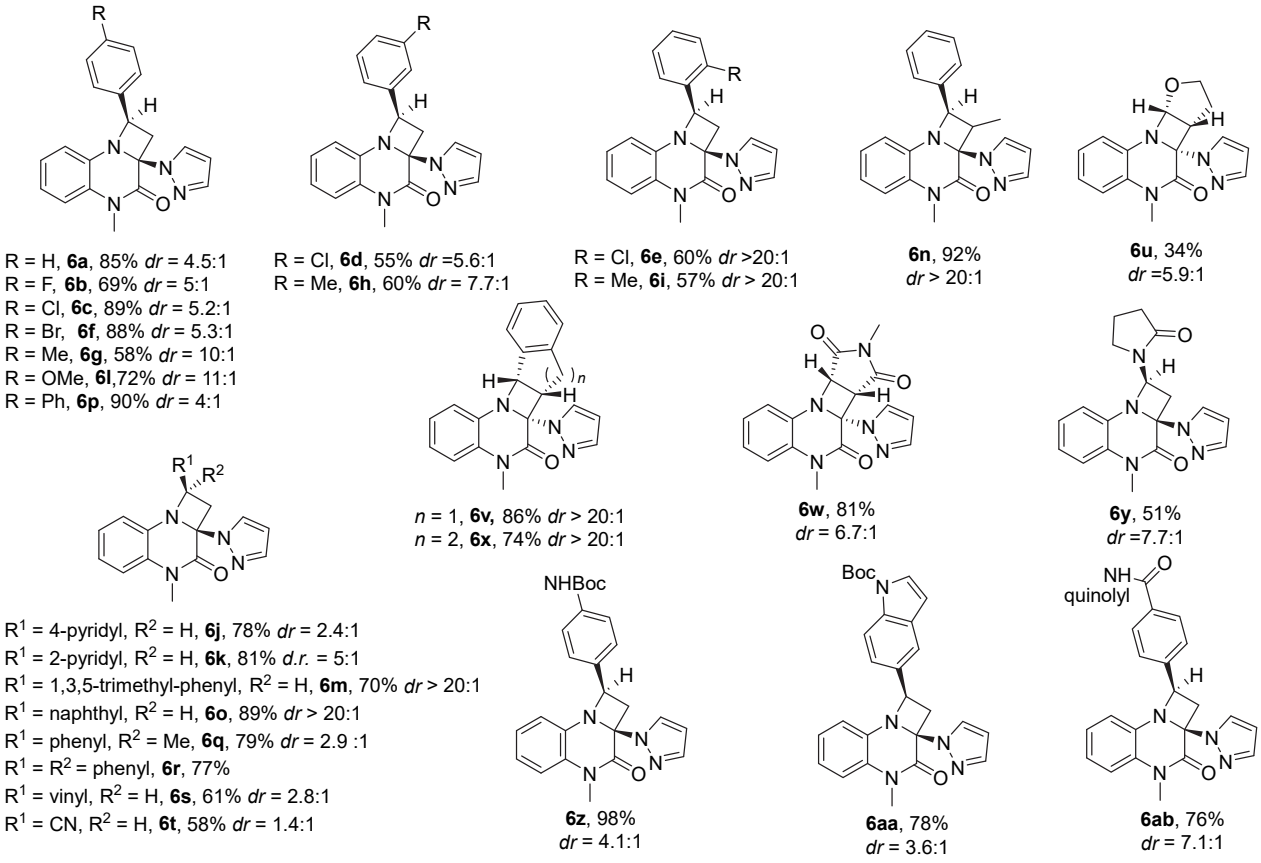


[a] Standard condition: **3** (0.2 mmol), **4a** (2 equiv.), **PC** (0.5 mol%), Ar atmosphere, solvent (0.03 mol/L), irradiated by 10 W 450～455 nm for 5 h at room temperature. [b] Isolated yield.

Table 3 Scope alkenes of aza-Paternò-Büchi reaction[a,b]



3a, 0.2 mmol **4**, 0.4 mmol **6**



R = H, **6a**, 85% *dr* = 4.5:1
R = F, **6b**, 69% *dr* = 5:1
R = Cl, **6c**, 89% *dr* = 5.2:1
R = Br, **6f**, 88% *dr* = 5.3:1
R = Me, **6g**, 58% *dr* = 10:1
R = OMe, **6l**,72% *dr* = 11:1
R = Ph, **6p**, 90% *dr* = 4:1

R = Cl, **6d**, 55% *dr* =5.6:1
R = Me, **6h**, 60% *dr* = 7.7:1

R = Cl, **6e**, 60% *dr* >20:1
R = Me, **6i**, 57% *dr* > 20:1

6n, 92%
dr > 20:1

6u, 34%
dr =5.9:1

n = 1, **6v**, 86% *dr* > 20:1
n = 2, **6x**, 74% *dr* > 20:1

6w, 81%
dr = 6.7:1

6y, 51%
dr =7.7:1

R^1 = 4-pyridyl, R^2 = H, **6j**, 78% *dr* = 2.4:1
R^1 = 2-pyridyl, R^2 = H, **6k**, 81% *d.r.* = 5:1
R^1 = 1,3,5-trimethyl-phenyl, R^2 = H, **6m**, 70% *dr* > 20:1
R^1 = naphthyl, R^2 = H, **6o**, 89% *dr* > 20:1
R^1 = phenyl, R^2 = Me, **6q**, 79% *dr* = 2.9 :1
R^1 = R^2 = phenyl, **6r**, 77%
R^1 = vinyl, R^2 = H, **6s**, 61% *dr* = 2.8:1
R^1 = CN, R^2 = H, **6t**, 58% *dr* = 1.4:1

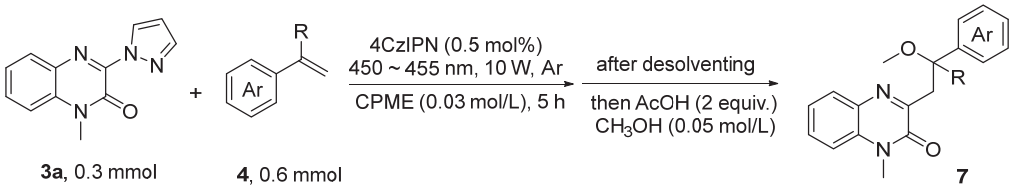
6z, 98%
dr = 4.1:1

6aa, 78%
dr = 3.6:1

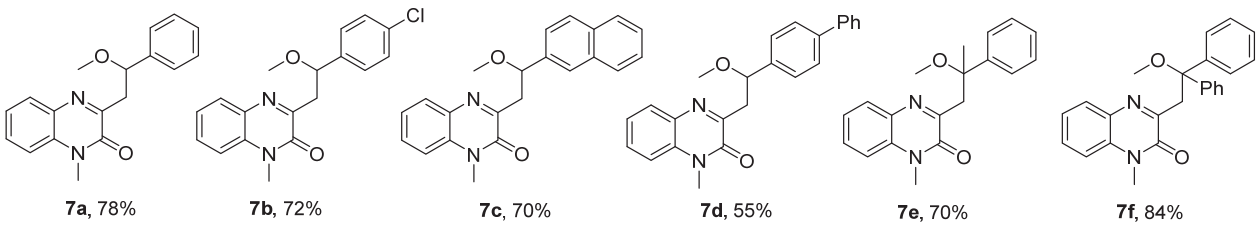
6ab, 76%
dr = 7.1:1

[a] Standard condition: **3a** (0.2 mmol), **4** (2 equiv.), **PC** (0.5 mol%), Ar atmosphere, cyclopentyl methyl ether (CPME, 0.03 mol/L), irradiated by 10 W 450～455 nm for 5 h at room temperature. [b] Isolated yield.

Table 4 Scope of the difunctionalization of vinyl arenes[a,b]



3a, 0.3 mmol **4**, 0.6 mmol **7**



7a, 78% **7b**, 72% **7c**, 70% **7d**, 55% **7e**, 70% **7f**, 84%

[a] Standard condition: **3a** (0.3 mmol), **4** (2 equiv.), **PC** (0.5 mol%), Ar atmosphere, CPME (0.03 mol/L), irradiated by 10 W 450～455 nm for 5 h at room temperature. After completion of the reaction as indicated by thin layer chromatography (TLC), CPME was replaced by MeOH (6 mL), and AcOH (0.6 mmol) was added. The mixture was stirred in 35 ℃ until the disappearance of **3a**. [b] Isolated yield.

ence of 4CzIPN is very slight with unmodified quinoxalinone **1a**. These results indicate that the pyrazolated

quinoxalinone could be activated by 4CzIPN in the triplet state. Moreover, the activation is unlikely to result from an electron-transfer process between **3a** and 4CzIPN based on the insufficient redox potentials of 4CzIPN [E_{red}(**T1**)＝＋1.35 V vs SCE; E_{ox}(**T1**)＝－1.04 V vs SCE][10] to oxidize or reduce **3a** (E_{red}＝－1.31 V, E_{ox}＝＋1.79 V vs SCE). Therefore, the activation of 3-pyrazol-quinoxalinones should be attributed to triplet-triplet energy transfer from the excited 4CzIPN to 3-pyrazol-quinoxalinones.

On the basis of the performed mechanistic experiments and previous mechanistic studies, a reasonable mechanistic hypothesis was put forth as described in Scheme 1. We propose a mechanism that relies on an efficient triplet energy transfer from 4CzIPN to **3a**. Subsequently, the ^{3}**3a** (**A**) undergoes stepwise [2＋2] cycloaddition with the alkene to intermediate **B** (Scheme 2).[8] The 1,4-biradicals (**B**) undergo intersystem crossing to the corresponding singlet 1,4-biradicals followed by ring closure leading to the desired azetidine product **6**.

3 Conclusions

In summary, we have reported the development of visible light-mediated multi-step reactions of quinoxalin-2(1*H*)-ones. Our current understanding of pyrozole effects observed in this strategy now enables access to three classes of divergent reactivity: (a) visible-light-promoted aerobic oxidation, (b) aza Paternò-Büchi reaction, and (c) elimination reaction. As a result, the approach developed herein the functionalization of imines and activating of imines. We expect that this strategy will provide a new platform for the synthesis of azetidines and will enable further advancements in other conversions.

4 Experimental section

4.1 General experimental information

Unless otherwise stated, all reactions were set up in clear pyrex glassware and were stirred with a Teflon-coated magnetic stir bar. Analytical grade solvents and commercially available reagents were used to conduct the reactions. All other reagents were purchased from commercial suppliers and used without additional purification. Except in the case of aqueous reactions, all reaction glassware was oven-dried prior to use. Reactions were monitored by thin layer chromatography (TLC), and the products were obtained by column chromatography on neutral alumina (Al_2O_3). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker AM-400 MHz spectrometer. ^{1}H NMR spectra were internally referenced to tetramethyl silane (δ 0.00) or the residual proton-solvent peak in $CDCl_3$ (δ 7.26), and ^{13}C NMR spectra were internally referenced to $CDCl_3$ (δ 77.16). Mass spectra were reported in units of *m*/*z* and were obtained with esquire6000, TRACE DSQ and ORBITRAP ELITE mass spectrometers. UV-Vis absorption spectra were recorded on UV-2600 UV-Vis spectrophotometers. Phosphorescence spectra were measured using a combined fluorescence lifetime & steady state spectrometer (FLS920). Infrared spectra (IR) were recorded with a Bruker TENSOR27 fourier transform infrared

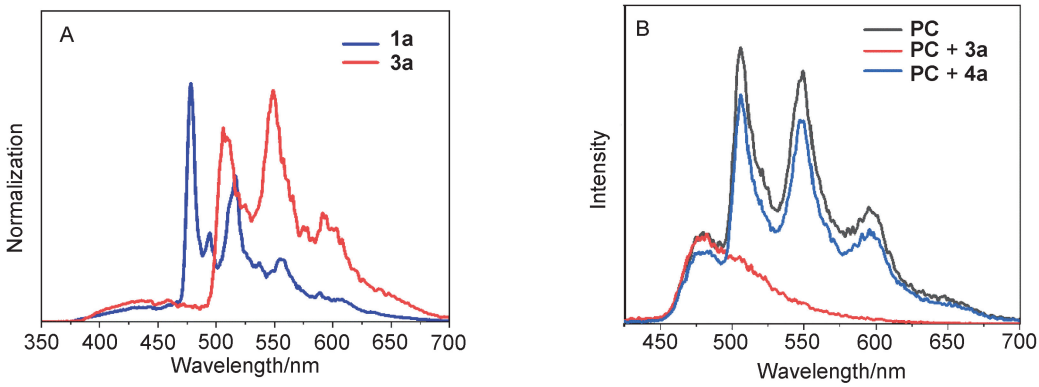
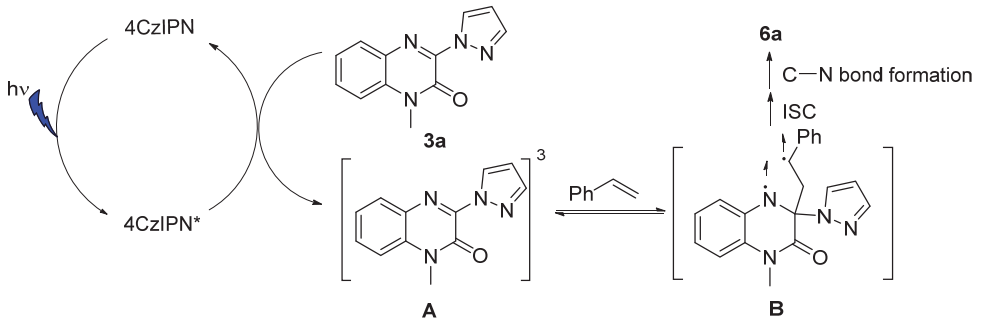


Figure 1 (A) Normalized phosphorescence emission of **1a** and **3a** (λ_{ex}＝300 nm,150 μs delay) and (B) emission spectrum of **PC** (black line), luminescence quenching of 4CzIPN by **3a** and **4a** (λ_{ex}＝340 nm, 500 μs delay) in deoxygenated CPME at 77 K



Scheme 2 Proposed reaction mechanism for aza Paternò-Buchi reaction

spectrometer. The melting point was measured by a WRX® X-4B melting point system.

4.2 General procedure for the synthesis of C-3 amination of quinoxalin-2(1*H*)-ones.

1a (0.5 mmol, 1.0 equiv.), pyrazole substrate (1.0 mmol, 2.0 equiv.) and photosensitizer **PC** (1 mol%) were added to a 10 mL Pyrex tube equipped with a magnetic stir bar. The combined materials were dissolved in DCE (5 mL) under an air atmosphere. The reaction mixture was irradiated by 10 W LEDs (450～455 nm) for 5 h at room temperature (maintained with cooling water). After completion of the reaction as indicated by TLC, the organic layer was washed with saturated NH_4Cl (15 mL×1) and deionized water (15 mL×1), and then dried over Na_2SO_4. The solvent was removed *in vacuo* to give a solid that was purified by flash chromatography (SiO_2) using hexane/EtOAc mixtures of increasing polarity as the eluent to give the corresponding 1-substituted quinoxalin-2(1*H*)-ones.

1-Methyl-3-(1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3a**):[11] White solid, yield 80% (90.4 mg). m.p. 153～155 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.11 (dd, *J*=2.7, 0.6 Hz, 1H), 8.05 (dd, *J*=8.1, 1.5 Hz, 1H), 7.91～7.90 (m, 1H), 7.59 (ddd, *J*=8.6, 7.3, 1.5 Hz, 1H), 7.44～7.37(m, 2H), 6.53 (dd, *J*=2.8, 1.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 150.7, 143.4, 142.6, 133.2, 132.6, 131.3, 130.2, 130.1, 124.6, 113.7, 108.3, 29.9; IR (thin film) *v*: 3169, 1661, 1601, 1476, 1392, 1196, 1094, 1039, 930, 754 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{10}N_4ONa$ $[M+Na]^+$ 249.0747, found 249.0744.

1-Ethyl-3-(1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3b**):[11] White solid, yield 60% (72 mg). m.p. 101～103 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.10 (d, *J*=2.2 Hz, 1H), 8.04 (d, *J*=7.9 Hz, 1H), 7.89 (s, 1H), 7.59～7.55 (m, 1H), 7.41～7.37 (m, 2H), 6.51 (t, *J*=2.1 Hz, 1H), 4.44 (q, *J*=7.1 Hz, 2H), 1.44 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 150.3, 143.5, 142.7, 133.3, 131.7, 131.6, 130.6, 130.2, 124.5, 113.6, 108.3, 38.4, 12.5; IR (thin film) *v*: 2921, 1749, 1659, 1604, 1509, 1394, 1218, 1098, 1040, 933, 771, 668 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{12}N_4ONa$ $[M+Na]^+$ 263.0903, found 263.0907.

1-Benzyl-3-(1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3c**):[11] Pale yellow solid, yield 72% (108.8 mg). m.p. 124～126 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.11 (s, 1H), 8.01 (d, *J*=7.8 Hz, 1H), 7.91 (s, 1H), 7.43～7.39 (m, 1H), 7.34～7.24 (m, 7H), 6.50 (s, 1H), 5.57 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 150.7, 143.4, 142.5, 134.6, 133.2, 131.8, 131.4, 130.1, 130.0, 128.9, 127.8, 126.7, 124.6, 114.4, 108.3, 46.5; IR (thin film) *v*: 3031, 2921, 2852, 1661, 1475, 1392, 1194, 1040, 926, 753, 668 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{14}N_4ONa$ $[M+Na]^+$ 325.1060, found 325.1068.

Ethyl 2-(2-oxo-3-(1*H*-pyrazol-1-yl)quinoxalin-1(2*H*)-yl)acetate (**3d**):[11] Pale yellow solid, yield 67% (99.9 mg). m.p. 162～164 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.03 (s, 1H), 8.03 (d, *J*=8.0 Hz, 1H), 7.88 (s, 1H), 7.54～7.50 (m, 1H), 7.39 (t, *J*=7.6 Hz, 1H), 7.12 (d, *J*=8.4 Hz, 1H), 6.49 (s, 1H), 5.11 (s, 2H), 4.25 (q, *J*=7.1 Hz, 2H), 1.26 (t, *J*=7.1 Hz, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 166.7, 150.5, 143.6, 142.5, 133.2, 131.8, 131.4, 130.6, 130.3, 125.0, 113.2, 108.5, 62.4, 44.3, 14.2; IR (thin film) *v*: 2982, 2922, 2850, 1747, 1666, 1601, 1393, 1213, 1105, 1039, 925, 756, 667 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{14}N_4O_3Na$ $[M+Na]^+$ 321.0958, found 321.0966.

1-(2-Oxo-2-phenylethyl)-3-(1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3e**):[11] Pale yellow solid, yield 80% (132 mg). m.p. 208～210 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.00 (s, 1H), 8.06～8.00 (m, 3H), 7.88 (s, 1H), 7.67～7.63 (m, 1H), 7.54～7.50 (m, 2H), 7.42～7.38 (m, 1H), 7.35～7.31 (m, 1H), 6.96 (d, *J*=8.2 Hz, 1H), 6.47 (s, 1H), 5.79 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 190.6, 150.5, 143.5, 142.4, 134.6, 134.4, 133.2, 132.0, 131.4, 130.4, 130.2, 129.5, 128.2, 124.7, 113.5, 108.4, 49.2; IR (thin film) *v*: 2924, 2851, 1699, 1663, 1603, 1475, 1393, 1227, 1105, 1040, 917, 752, 688 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{14}N_4O_2Na$ $[M+Na]^+$ 353.1009, found 353.1015.

1-Allyl-3-(1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3f**):[11] Pale yellow solid, yield 40% (50.4 mg). m.p. 111～113 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.09 (s, 1H), 8.02 (d, *J*=7.8 Hz, 1H), 7.89 (s, 1H), 7.55～7.51 (m, 1H), 7.38 (t, *J*=7.4 Hz, 1H), 7.33 (d, *J*=8.3 Hz, 1H), 6.50 (s, 1H), 6.00～5.91 (m, 1H), 5.30 (d, *J*=10.4 Hz, 1H), 5.20 (d, *J*=17.3 Hz, 1H), 5.01 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 150.4, 143.5, 142.7, 133.3, 131.9, 131.6, 130.4, 130.2, 130.1, 124.7, 118.6, 114.3, 108.4, 45.4; IR (thin film) *v*: 3133, 2980, 1662, 1604, 1475, 1394, 1197, 1103, 1043, 929, 756, 670 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{12}N_4ONa$ $[M+Na]^+$ 275.0903, found 275.0907.

1-(Prop-2-yn-1-yl)-3-(1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3g**):[11] Pale yellow solid, yield 55% (68.8 mg). m.p. 189～191 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.06 (s, 1H), 8.02 (d, *J*=7.6 Hz, 1H), 7.88 (s, 1H), 7.60～7.56 (m, 1H), 7.49 (d, *J*=8.0 Hz, 1H), 7.42～7.39 (m, 1H), 6.50 (s, 1H), 5.14 (s, 2H), 2.32 (s, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 149.9, 143.6, 142.4, 133.3, 131.5, 131.2, 130.4, 130.3, 125.0, 114.2, 108.5, 76.3, 73.8, 32.4; IR (thin film) *v*: 2920, 2851, 1664, 1603, 1474, 1393, 1298, 1195, 1105, 1040, 916, 770, 668 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{10}N_4ONa$ $[M+Na]^+$ 273.0747, found 273.0756.

6-Fluoro-1-methyl-3-(1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3h**):[11] Pale yellow solid, yield 56% (68.3 mg). m.p. 184～186 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.11 (d, *J*=2.7 Hz, 1H), 7.89 (s, 1H), 7.69 (d, *J*=8.8 Hz, 1H), 7.31～7.29 (m, 2H), 6.52 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 159.17 (d, *J*=244.9 Hz), 150.2, 143.7, 143.4, 133.4, 132.0 (d, *J*=11.8 Hz), 129.2, 117.8 (d, *J*=24.1 Hz), 115.4 (d, *J*=23.1 Hz), 114.82 (d, *J*=9.0 Hz), 108.58, 30.18; ^{19}F NMR (376 MHz, chloroform-*d*) *δ*: −117.29; IR (thin film) *v*: 3184, 3097, 3041, 2924, 1662, 1501, 1392, 1305, 1164, 1034, 929, 808, 756, 637 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_9FN_4ONa$ $[M+Na]^+$ 267.0653, found 267.0658.

6,7-Dichloro-1-methyl-3-(1*H*-pyrazol-1-yl)quinoxalin-

2(1*H*)-one (**3i**):[11] Pale yellow solid, yield 77% (113.2 mg). m.p. 190～192 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.06 (d, *J*=2.2 Hz, 1H), 8.07 (s, 1H), 7.89 (s, 1H), 7.43 (s, 1H), 6.51 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 150.2, 144.1, 143.3, 134.2, 133.5, 131.9, 130.8, 130.5, 128.6, 115.3, 108.9, 30.3; IR (thin film) *v*: 2919, 2850, 1672, 1560, 1527, 1382, 1300, 1099, 931, 768, 669 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_8Cl_2N_4ONa$ [M+Na]$^+$ 316.9967, found 316.9974.

6-Chloro-1-methyl-3-(1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3j**):[11] White solid, yield 31% (40.3 mg). m.p. 190～192 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.09 (d, *J*=2.4 Hz, 1H), 7.97 (d, *J*=2.1 Hz, 1H), 7.90 (s, 1H), 7.49 (dd, *J*=8.9, 2.2 Hz, 1H), 7.27 (d, *J*=8.9 Hz, 1H), 6.52 (d, *J*=0.9 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 150.3, 143.8, 143.3, 133.4, 131.9, 131.2, 130.0, 130.0, 129.3, 114.9,108.7, 30.1; IR (thin film) *v*: 3171, 2925, 1721, 1665, 1586, 1488, 1388, 1302, 1100, 1039, 933, 759, 648 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_9ClN_4ONa$ [M+Na]$^+$ 283.0357, found 283.0365.

7-Fluoro-1-methyl-3-(1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3k**):[11] Pale yellow solid, yield 39% (47.6 mg). m.p. 174～176 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.05 (d, *J*=2.5 Hz, 1H), 8.02～7.98 (m, 1H), 7.89 (d, *J*=0.6 Hz, 1H), 7.12 (dt, *J*=8.5, 2.5 Hz, 1H), 7.04 (dd, *J*=9.8, 2.4 Hz, 1H), 6.52～6.51 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.3 (d, *J*=251.3 Hz), 150.6, 143.4, 141.8, 134.0 (d, *J*=11.7 Hz), 133.2, 132.1 (d, *J*=10.3 Hz), 127.9 (d, *J*=12 Hz), 112.7 (d, *J*=23.5 Hz), 108.4, 100.8 (d, *J*=28.1 Hz), 30.2; ^{19}F NMR (376 MHz, chloroform-*d*) *δ*: −106.83; IR (thin film) *v*: 3173, 2923, 2854, 1665, 1616, 1594, 1471, 1391, 1242, 1194, 1090, 941, 760 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_9FN_4ONa$ [M+Na]$^+$ 267.0653, found 267.0660.

1-Methyl-3-(3-methyl-1*H*-pyrazol-1-yl)quinoxalin-2(1*H*)-one (**3l**):[12] Pale yellow solid, yield 26% (31.2 mg). m.p. 114～116 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.04 (d, *J*=2.3 Hz, 1H), 8.04 (d, *J*=7.2 Hz, 1H), 7.56～7.52 (m, 1H), 7.38 (t, *J*=7.7 Hz, 1H), 7.34 (d, *J*=8.6 Hz, 1H), 6.32 (d, *J*=2.4 Hz, 1H), 3.81 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 153.5, 150.7, 142.4, 134.2, 132.4, 131.4, 130.2, 129.7, 124.5, 113.6, 109.0, 29.9, 14.2; IR (thin film) *v*: 3171, 2926, 2853, 1658, 1661, 1545, 1477, 1360, 1206, 1046, 937, 772, 669 cm^{-1}; HRMS (ESI) calcd for [$C_{13}H_{12}N_4ONa$ [M+Na]$^+$ 263.0903, found 263.0909.

3-(4-Iodo-1*H*-pyrazol-1-yl)-1-methyl quinoxaline-2(1*H*)-one (**3m**):[12] Pale yellow solid, yield 47% (82.8 mg). m.p. 157～159 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 9.17 (s, 1H), 7.99 (d, *J*=8.0 Hz, 1H), 7.86 (s, 1H), 7.61～7.57 (m, 1H), 7.41 (t, *J*=7.7 Hz, 1H), 7.36 (d, *J*=8.4 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 150.4, 147.9, 141.6, 137.4, 132.7, 131.0, 130.6, 130.3, 124.9, 113.8, 60.4, 30.0; IR (thin film) *v*: 3223, 3163, 2983, 1660, 1602, 1476, 1390, 1313, 1177, 943, 754 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_9IN_4ONa$ [M+Na]$^+$ 374.9713, found 374.9721.

4.3 General procedure for the synthesis of azetidines

3a (0.2 mmol, 1.0 equiv.), styrene (**4a**) (0.4 mmol, 2.0 equiv.) and photosensitizer **PC** (0.001 mmol,0.5 mol%) were added to a 10 mL Pyrex tube equipped with a magnetic stir bar. The combined materials were dissolved in cyclopentyl methyl ether (6 mL). This system was bubbled with Ar for 10 min, then sealed and irradiated by 10 W LEDs (450～455 nm) for 5 h at room temperature (maintained with cooling water). After completion of the reaction as indicated by TLC, the solution was concentrated under reduced pressure. The residue was purified by flash column chromatography on aluminum oxide gel [unless otherwise specified, petroleumether/ethyl acetate (*V*∶*V*=5∶1) was used as eluent] to give the target product.

4-Ethyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**5a**, **5a'**): Pale yellow solid (R_f=0.5), yield 66% (45.4 mg, 5.6∶1 *dr*). m.p. 52～54 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 7.71～7.67 (m, 1.2H), 7.62～7.58 (m, 3.3H), 7.43～7.39 (m, 2H), 7.36～7.32 (m, 1.1H), 7.20～7.14 (m, 1H), 7.10～7.03 (m, 2.2H), 6.92～6.75 (m, 1.8H), 6.70 (d, *J*=7.8 Hz, 1H), 6.59 (d, *J*=7.8 Hz, 0.2H), 6.29 (t, *J*=2.3 Hz, 1H), 6.26 (t, *J*=2.2 Hz, 0.2H), 5.54 (dd, *J*=7.7, 4.8 Hz, 0.2H), 4.73 (t, *J*=7.5 Hz, 1H), 4.33～4.21 (m, 1.3H), 4.14～4.05 (m, 1.2H), 3.88 (dd, *J*=12.9, 7.7 Hz, 0.2H), 3.66 (dd, *J*=12.0, 7.7 Hz, 1H), 3.55 (dd, *J*=12.9, 4.8 Hz, 0.2H), 3.35(dd, *J*=12.0, 7.4 Hz, 1H), 1.37 (t, *J*=7.1 Hz, 3H), 1.29 (t, *J*=7.1 Hz, 0.8H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.40, 161.12, 141.49, 140.67, 140.57, 137.66, 132.53, 131.85, 130.42, 128.81, 128.64, 128.47, 128.36, 127.88, 127.21, 127.09, 127.05, 125.20, 123.74, 123.61, 122.80, 122.52, 120.26, 115.16, 115.13, 106.47, 106.38, 77.67, 74.98, 64.21, 63.31, 41.43, 40.21, 37.68, 37.47, 12.57, 12.20; IR (thin film) *v*: 3065, 2977, 2867, 1672, 1597, 1548, 1498, 1395, 1262, 1101, 1045, 913, 749, 700 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}N_4ONa$ [M+Na]$^+$ 367.1529, found 367.1537.

4-Benzyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**5b**, **5b'**): Pale yellow solid (R_f=0.5), yield 76% (61.7 mg, 3.1∶1 *dr*). m.p. 145～147 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 7.77 (d, *J*=2.5 Hz, 1H), 7.67 (d, *J*=2.4 Hz, 0.3H), 7.62～7.59 (m, 3H), 7.41～7.15 (m, 10.4H), 6.89 (d, *J*=3.7 Hz, 2H), 6.83～6.80 (m, 0.3H), 6.77～6.68 (m, 2.4H), 6.55 (dd, *J*=7.3, 2.1 Hz, 0.2H), 6.31～6.27 (m, 1.1H), 5.77 (d, *J*=16.1 Hz, 1H), 5.60～5.52 (m, 0.4H), 5.03 (d, *J*=15.9 Hz, 0.2H), 4.94 (d, *J*=16.1 Hz, 1H), 3.81 (dd, *J*=13.0, 7.6 Hz, 0.2H), 3.73 (dd, *J*=12.1, 7.7 Hz, 1H), 3.59 (dd, *J*=13.0, 5.0 Hz, 0.2H), 3.28 (dd, *J*=12.1, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.32, 161.97, 141.35, 140.69, 140.57, 137.48, 136.14, 136.09, 132.61, 132.43, 129.38, 128.84, 128.82, 128.75, 128.69, 128.47, 128.38, 127.84, 127.35, 127.30, 127.10, 127.06, 126.94, 126.58, 125.12, 123.88, 123.72, 122.39, 122.29, 119.64, 116.16, 115.99, 77.80, 75.23, 64.18, 63.32, 46.48, 46.35, 41.42, 39.96; IR (thin film) *v*: 3032, 2920, 2851, 1750, 1677,

1596, 1498, 1394, 1217, 1044, 772, 670, 664 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{22}N_4ONa$ $[M+Na]^+$ 429.1686, found 429.1692.

Ethyl-2-(3-oxo-1-phenyl-2a-(1*H*-pyrazol-1-yl)-1,2,2a,3-tetrahydro-4*H*-azeto[1,2-*a*]quinoxalin-4-yl)acetate (**5c**, **5c'**): Pale yellow solid (R_f=0.5), yield 81% (65.1 mg, 3.1∶1 *dr*). m.p. 159～161 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.84 (d, *J*=2.5 Hz, 1H), 7.79 (d, *J*=2.5 Hz, 0.3H), 7.68～7.64 (m, 3.1H), 7.45～7.34 (m, 3H), 7.29～7.17 (m, 1.7H), 7.09～7.05 (m, 1H), 6.92～6.76 (m, 2.5H), 6.72～6.68 (m, 1H), 6.56～6.50 (m, 1.2H), 6.54～6.52 (m, 0.3H), 6.31～6.27 (m, 1.2H), 5.66 (dd, *J*=7.5, 5.2 Hz, 0.25H), 5.11 (d, *J*=17.5 Hz, 1.2H), 4.82～4.65 (m, 2.3H), 4.34～4.23 (m, 2.5H), 4.09 (dd, *J*=12.8, 7.6 Hz, 0.3H), 3.70～3.56 (m, 2H), 3.50 (dd, *J*=12.8, 5.2 Hz, 0.3H), 1.33～1.26 (m, 4.5H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 168.10, 163.74, 161.99, 141.45, 140.84, 140.70, 137.74, 132.43, 132.30, 129.31, 128.83, 128.57, 128.44, 128.11, 127.98, 127.88, 127.49, 125.39, 124.47, 124.26, 123.26, 122.22, 119.56, 114.79, 114.57, 77.48, 75.35, 64.54, 63.31, 62.05, 61.99, 44.37, 44.25, 41.18, 40.75, 29.75, 14.22; IR (thin film) *v*: 3736, 3609, 3567, 3398, 2919, 2851, 1784, 1682, 1598, 1499, 1389, 1212, 1109, 1016, 921, 770, 688 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}N_4O_3Na$ $[M+Na]^+$ 425.1584, found 425.1593.

4-(2-Oxo-2-phenylethyl)-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinox-alin-3(4*H*)-one (**5d**, **5d'**): Pale yellow solid (R_f=0.5), yield 91% (80 mg, 7.1∶1 *dr*). m.p. 147～149 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 8.10～7.99 (m, 3.4H), 7.71～7.64 (m, 4.4H), 7.54 (t, *J*=7.6 Hz, 2.4H), 7.43 (t, *J*=7.4 Hz, 1H), 7.39～7.26 (m, 1.7H), 7.24 (s, 0.7H), 6.98～6.94 (m, 1H), 6.82 (t, *J*=7.6 Hz, 1H), 6.75～6.67 (m, 2.3H), 6.65～6.50 (m, 0.3H), 6.32 (t, *J*=2.1 Hz, 1.1H), 5.85 (d, *J*=17.8 Hz, 0.2H), 5.79 (d, *J*=17.8 Hz, 1H), 5.67 (dd, *J*=7.7, 5.2 Hz, 0.2H), 5.47 (d, *J*=17.8 Hz, 1H), 5.34 (d, *J*=17.8 Hz, 0.2H), 4.87 (t, *J*=7.6 Hz, 1.0H), 4.11 (dd, *J*=12.0, 7.5 Hz, 1H), 3.70 (dd, *J*=12.0, 7.5 Hz, 0.2H), 3.61 (dd, *J*=12.0, 7.7 Hz, 1H), 3.52 (dd, *J*=12.9, 5.1 Hz, 0.2H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 192.36, 192.22, 163.98, 162.29, 141.56, 140.82, 140.69, 137.85, 134.65, 134.63, 134.29, 132.47, 132.43, 130.64, 129.38, 129.11, 128.85, 128.80, 128.55, 128.52, 128.40, 128.20, 128.19, 128.17, 128.07, 127.54, 125.34, 124.31, 124.12, 123.30, 122.19, 119.64, 115.11, 114.92, 106.83, 106.71, 77.91, 75.45, 64.55, 63.20, 49.47, 49.30, 41.19, 40.77; IR (thin film) *v*: 2920, 2851, 1677, 1597, 1498, 1395, 1226, 1109, 1003, 921, 772, 669 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{22}N_4O_2Na$ $[M+Na]^+$ 435.1816, found 435.1818.

4-Allyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**5e**, **5e'**): Pale yellow solid (R_f=0.5), yield 93% (66.2 mg, 5.9∶1 *dr*). m.p. 78～80 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.73 (d, *J*=2.5 Hz, 1H), 7.64 (d, *J*=2.5 Hz, 0.2H), 7.62～7.57 (m, 3H), 7.47～7.38 (m, 2H), 7.44～7.40 (m, 1H), 7.37～7.32 (m, 1H), 7.20～7.15 (m, 1H), 7.08～6.99 (m, 2.2H), 6.89～6.75 (m, 1.7H), 6.71 (dd, *J*=7.8, 1.4 Hz, 1H), 6.59 (dd, *J*=7.8, 1.4 Hz, 0.2H), 6.30 (t, *J*=2.1 Hz, 1H), 6.27 (t, *J*=2.1 Hz, 0.2H), 6.00～5.81 (m, 1.2H), 5.55 (dd, *J*=7.7, 4.9 Hz, 0.2H), 5.37 (dd, *J*=17.3, 1.3 Hz, 1H), 5.26 (dd, *J*=10.5, 1.3 Hz, 1H), 5.23～5.18 (m, 0.2H), 5.11～5.04 (m, 1H), 5.00～4.93 (m, 0.2H), 4.77 (t, *J*=7.5 Hz, 1H), 4.53～4.40 (m, 1.2H), 3.83 (dd, *J*=12.0, 7.7 Hz, 0.2H), 3.67 (dd, *J*=12.0, 7.7 Hz, 1H), 3.56 (dd, *J*=13.0, 4.9 Hz, 0.2H), 3.56 (dd, *J*=13.0, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, chloroform-*d*) *δ*: 162.83, 161.51, 141.41, 140.75, 140.63, 132.44, 132.37, 131.36, 131.31, 128.84, 128.71, 128.54, 128.40, 128.16, 127.91, 127.15, 127.11, 125.15, 123.91, 123.77, 122.55, 122.41, 117.65, 117.38, 116.00, 115.86, 106.51, 106.41, 77.79, 75.14, 64.18, 63.23, 45.06, 45.00, 41.47, 39.94; IR (thin film) *v*: 3031, 2967, 2922, 2852, 1676, 1597, 1498, 1389, 1346, 1218, 1106, 1043, 920, 700, 668 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{20}N_4ONa$ $[M+Na]^+$ 379.1529, found 379.1537.

1-Phenyl-4-(prop-2-yn-1-yl)-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**5f**, **5f'**): Pale yellow solid (R_f=0.5), yield 67% (47.4 mg, 2.9∶1 *dr*). m.p. 70～72 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.67 (d, *J*=2.5 Hz, 1H), 7.64～7.57 (m, 3.6H), 7.46～7.39 (m, 2H), 7.38～7.33 (m, 1H), 7.26～7.05 (m, 5.4H), 6.90～6.86 (m, 1H), 6.83～6.79 (m, 0.4H), 6.71 (dd, *J*=7.8, 1.5 Hz, 1H), 6.57 (dd, *J*=7.8, 1.5 Hz, 0.3H), 6.33～6.27 (m, 1H), 5.55 (dd, *J*=7.7, 4.9 Hz, 0.3H), 5.03～4.97 (m, 1.4H), 4.88～4.83 (m, 1.3H), 4.75 (t, *J*=7.5 Hz, 1H), 3.91 (dd, *J*=13.0, 7.7 Hz, 0.4H), 3.69 (s, 0.8H), 3.65 (dd, *J*=12.1, 7.4 Hz, 1H), 3.52 (dd, *J*=13.0, 4.9 Hz, 0.4H), 3.40 (dd, *J*=12.1, 7.4 Hz, 1H), 2.33～2.26 (m, 1.3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.60, 141.37, 140.85, 140.76, 132.45, 131.39, 130.15, 129.59, 128.88, 128.81, 128.55, 128.47, 127.89, 127.27, 127.20, 125.20, 124.40, 124.27, 122.65, 122.50, 119.94, 115.92, 115.84, 106.69, 106.60, 77.71, 75.25, 72.93, 72.58, 64.42, 63.49, 41.25, 40.29, 32.06, 31.97; IR (thin film) *v*: 3283, 2920, 2851, 1679, 1598, 1450, 1389, 1317, 1218, 1107, 1045, 920, 771, 668 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{18}N_4ONa$ $[M+Na]^+$ 377.1313, found 377.1384.

7-Fluoro-4-methyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**5g**, **5g'**): Pale yellow solid (R_f=0.5), yield 92% (64 mg, 2.8∶1 *dr*). m.p. 6365 ℃; ^1H NMR (400 MHz, Chloroform-*d*) *δ*: 7.72 (d, *J*=2.5 Hz, 1H), 7.64～7.56 (m, 3.5H), 7.45～7.35 (m, 3.1H), 7.27～7.21 (m, 1.3H), 7.14 (d, *J*=6.3 Hz, 1H), 6.98 (dd, *J*=9.1, 4.9 Hz, 1H), 6.86～6.77 (m, 1.4H), 6.56 (td, *J*=8.5, 2.8 Hz, 0.4H), 6.42 (dd, *J*=8.8, 2.9 Hz, 1H), 6.33～6.29 (m, 1.2H), 6.26 (dd, *J*=8.8 Hz, 2.9 Hz, 0.3H), 5.55 (dd, *J*=7.6, 5.1 Hz, 0.3H), 4.80 (t, *J*=7.6 Hz, 1H), 3.83 (dd, *J*=13.0, 7.9 Hz, 0.4H), 3.69 (dd, *J*=12.2, 7.9 Hz, 1H), 3.55 (s, 3H), 3.53 (s, 1H), 3.29 (dd, *J*=12.2, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) *δ*: 162.57, 161.38, 160.22, 157.79, 141.00, 140.96, 140.88, 137.12, 133.71, 133.60, 129.57, 129.03, 128.96, 128.84, 128.65, 127.84, 127.22, 127.04, 116.40, 116.31, 116.17, 111.70, 111.47, 109.39, 109.15, 108.87, 106.71, 106.64, 106.44, 74.97, 64.60, 63.68, 41.35, 40.31, 30.11, 30.03; IR (thin

film) *v*: 3032, 2923, 2852, 1675, 1591, 1505, 1387, 1172, 858, 700, 689 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}FN_4ONa$ $[M+Na]^+$ 371.1279, found 371.126.

6,7-Dichloro-4-methyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxal-in-3(4*H*)-one (**5h**, **5h'**): Pale yellow solid (R_f=0.5), yield 92% (73 mg, 4.3∶1 *dr*). m.p. 136～138 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.73 (d, *J*=2.5 Hz, 1H), 7.65 (d, *J*=2.5 Hz, 0.3H), 7.61～7.52 (m, 3.2H), 7.46～7.36 (m, 3H), 7.31～7.24 (m, 1.1H), 7.14～7.12 (m, 1.5H), 6.97 (s, 0.3H), 6.76 (s, 1H), 6.62 (s, 0.2H), 6.35～6.31 (m, 1.2H), 5.52 (dd, *J*=7.7, 5.0 Hz, 0.2H), 4.78 (t, *J*=7.5 Hz, 1H), 3.81 (dd, *J*=13.1, 7.7 Hz, 0.3H), 3.67 (dd, *J*=12.2, 7.9 Hz, 1H), 3.54 (s, 3H), 3.50 (s, 0.8H), 3.25 (dd, *J*=12.2, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.85, 161.67, 141.16, 141.09, 140.70, 136.69, 133.01, 131.96, 129.16, 129.14, 129.11, 128.82, 128.68, 127.80, 127.23, 127.15, 127.04, 126.94, 123.50, 120.79, 117.05, 116.89, 106.91, 106.87, 74.87, 64.75, 63.77, 41.40, 39.95, 30.12, 30.05; IR (thin film) *v*: 2920, 1683, 1490, 1392, 1102, 1025, 938, 771, 668 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{16}Cl_2N_4ONa$ $[M+Na]^+$ 421.0593, found 421.0603.

7-Chloro-4-methyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**5i**, **5i'**): Pale yellow solid (R_f=0.5), yield 83% (60.4 mg, 2.1:1 *dr*). m.p. 56～58 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.72 (d, *J*=2.5 Hz, 1H), 7.64 (d, *J*=2.5 Hz, 1H), 7.60～7.56 (m, 3H), 7.47～7.33 (m, 3.1H), 7.28～7.19 (m, 2.2H), 7.14～7.12 (m, 1H), 7.06 (dd, *J*=8.8, 2.3 Hz, 1H), 6.95 (d, *J*=8.7 Hz, 1H), 6.81 (d, *J*=1.4 Hz, 1H), 6.68 (d, *J*=2.3 Hz, 1H), 6.54 (t, *J*=1.4 Hz, 0.5H), 6.63～6.29 (m, 1.4H), 5.54 (dd, *J*=7.6, 5.1 Hz, 0.5H), 4.80 (t, *J*=7.5 Hz, 1H), 3.82 (dd, *J*=13.0, 7.7 Hz, 0.5H), 3.68 (dd, *J*=12.2, 7.9 Hz, 1H), 3.54 (s, 3H), 3.51 (s, 1H), 3.26 (dd, *J*=12.2, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.74, 161.56, 141.01, 140.95, 140.88, 137.05, 133.48, 131.94, 130.75, 130.50, 129.05, 128.97, 128.86, 128.64, 127.77, 127.20, 127.14, 126.95, 125.02, 122.40, 122.04, 119.42, 116.45, 116.27, 106.74, 106.67, 77.56, 74.99, 64.59, 63.67, 41.48, 40.21, 30.02, 29.94; IR (thin film) *v*: 2920, 1748, 1680, 1593, 1375, 1218, 1044, 772, 669 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}ClN_4ONa$ $[M+Na]^+$ 387.0983, found 387.0991.

6-Fluoro-4-methyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1H-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**5j**): Pale yellow solid (R_f=0.5), yield 83% (57.8 mg, 7.9∶1 *dr*). m.p. 80～82 ℃; ^1H NMR (600 MHz, chloroform-*d*) *δ*: 7.75 (d, *J*=2.0 Hz, 1H), 7.58 (d, *J*=5.9 Hz, 3H), 7.43 (t, *J*=7.5 Hz, 2H), 7.38～7.35 (m, 1H), 6.79 (dd, *J*=10.2, 2.2 Hz, 1H), 6.68～6.66 (m, 1H), 6.57 (dt, *J*=2.3, 8.3 Hz, 1H), 6.33 (s, 1H), 4.70 (t, *J*=7. 6 Hz, 1H), 3.64 (dd, *J*=12.0, 7.7 Hz, 1H), 3.55 (s, 3H), 3.25 (dd, *J*=12.0, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.45, 160.44 (d, *J*=242.6 Hz), 141.18, 140.88, 134.76 (d, *J*=10.3 Hz), 128.99, 128.61, 128.27 (d, *J*=2.8 Hz), 127.25, 127.19, 123.97 (d, *J*=9.5 Hz), 110.19 (d, *J*=22.3 Hz), 106.73, 103.38 (d, *J*=28.0 Hz), 75.09, 63.42, 41.59, 30.04; IR (thin film) *v*: 3032, 2921, 1682, 1509, 1364, 1219, 1091, 1025, 847, 772, 669 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}FN_4ONa$ $[M+Na]^+$ 371.1279, found 371.1286.

4-Methyl-2a-(3-methyl-1*H*-pyrazol-1-yl)-1-phenyl-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**5k**): Pale yellow solid (R_f=0.5), yield 74% (50.9 mg, 6.5∶1 *dr*). m.p. 142～144 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.60 (d, *J*=7.4 Hz, 2H), 7.58 (d, *J*=2.3 Hz, 1H), 7.43 (t, *J*=7.3 Hz, 2H), 7.36 (d, *J*=7.2 Hz, 1H), 7.10 (t, *J*=7.7 Hz, 1H), 7.04 (d, *J*=7.8 Hz, 1H), 6.88 (t, *J*=7.2 Hz, 1H), 6.72 (d, *J*=7.4 Hz, 1H), 6.08 (d, *J*=2.1 Hz, 1H), 4.75 (t, *J*=7.6 Hz, 1H), 3.64 (dd, *J*=12.1, 7.8 Hz, 1H), 3.56 (s, 3H), 3.29 (dd, *J*=12.1, 7.4 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.20, 149.93, 141.63, 133.28, 132.56, 128.86, 128.40, 127.78, 127.26, 125.08, 123.88, 122.33, 115.41, 106.48, 74.90, 63.59, 41.41, 29.88, 14.02; IR (thin film) *v*: 3032, 2924, 1676, 1596, 1473, 1219, 771, 668 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}N_4ONa$ $[M+Na]^+$ 367.1529, found 367.1537.

2a-(4-Iodo-1*H*-pyrazol-1-yl)-4-methyl-1-phenyl-2,2a-dihydro-1*H*-azeto[1,2-*a*]quin-oxalin-3(4*H*)-one (**5l**): Pale yellow solid (R_f=0.5), yield 45% (41 mg, >20∶1 *dr*). m.p. 79～81 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.75 (s, 1H), 7.59 (d, *J*=6.0 Hz, 3H), 7.44 (t, *J*=7.3 Hz, 2H), 7.38 (d, *J*=7.2 Hz, 1H), 7.15～7.11 (m, 1H), 7.06 (d, *J*=8.2 Hz, 1H), 6.90 (t, *J*=7.5 Hz, 1H), 6.74～6.72 (m, 1H), 4.77 (t, *J*=7.5 Hz, 1H), 3.67 (dd, *J*=12.1, 7.8 Hz, 1H), 3.57 (s, 3H), 3.24 (dd, *J*=12.1, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.48, 145.64, 141.17, 133.06, 132.06, 131.72, 129.00, 128.61, 127.17, 125.47, 124.22, 122.43, 115.60, 75.59, 63.59, 57.97, 41.49, 29.95; IR (thin film) *v*: 2921, 1679, 1598, 1376, 1218, 1128, 1041, 939, 772, 669 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}IN_4ONa$ $[M+Na]^+$ 479.0339, found 479.0347.

4-Methyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6a**, **6a'**): White solid (R_f=0.4), yield 85% (56.1 mg, 4.5∶1 *dr*). m.p. 58～60 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.73 (d, *J*=2.5 Hz, 1H), 7.63 (d, *J*=2.5 Hz, 0.3H), 7.61～7.58 (m, 3H), 7.61～7.58 (m, 2H), 7.38～7.33 (m, 1.1H), 7.23～7.00 (m, 3.2H), 6.91～6.82 (m, 1.5H), 6.91～6.82 (m, 0.3H), 6.71 (dd, *J*=7.8, 1.5 Hz, 1H), 6.57 (dd, *J*=7.8, 1.5 Hz, 0.2H), 6.31 (t, *J*=2.1 Hz, 1H), 6.27 (t, *J*=2.1 Hz, 0.2H), 5.54 (dd, *J*=7.7, 4.9 Hz, 0.2H), 4.76 (t, *J*=7.5 Hz, 1H), 3.84 (dd, *J*=13.0, 7.7 Hz, 0.3H), 3.68 (dd, *J*=12.1, 7.8 Hz, 1H), 3.57 (s, 3H), 3.53 (s, 0.7H), 3.28 (dd, *J*=12.1, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.06, 161.87, 141.49, 140.78, 140.69, 137.53, 133.23, 132.41, 132.06, 129.38, 128.89, 128.76, 128.56, 128.43, 127.89, 127.19, 127.16, 125.23, 123.98, 123.82, 122.56, 122.38, 119.85, 115.44, 115.29, 106.55, 106.46, 77.85, 75.21, 64.36, 63.49, 41.52, 40.14, 29.91, 29.84; IR (thin film) *v*: 2954, 2924, 2853, 1683, 1598, 1500, 1378, 1305, 1096, 1043, 921, 750, 710 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{18}N_4ONa$ $[M+Na]^+$ 353.1373, found 353.1376.

1-(4-Fluorophenyl)-4-methyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6b**, **6b'**):

Pale yellow solid (R_f=0.4), yield 69% (48 mg, 5∶1 *dr*). m.p. 134～136 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 7.67 (d, *J*=2.5 Hz, 1H), 7.64～7.54 (m, 3.4H), 7.13～7.04 (m, 4.3H), 6.93～6.87 (m, 1.8H), 6.84～7.80 (m, 0.2H), 6.69～6.66 (m, 1H), 6.58～6.56 (m, 0.2H), 6.31 (t, *J*=2.1 Hz, 1H), 6.28 (t, *J*=2.2 Hz, 0.2H), 5.53 (dd, *J*=7.7, 4.9 Hz, 0.2H), 4.73 (t, *J*=7.5 Hz, 1H), 3.86 (dd, *J*=12.1, 7.7 Hz, 0.2H), 3.66 (dd, *J*=12.1, 7.7 Hz, 1H), 3.57 (s, 3H), 3.56～7.50 (m, 0.8H), 3.31 (dd, *J*=12.1, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 164.08, 163.08, 161.93, 161.62, 140.82, 137.41, 137.38, 133.21, 132.28, 129.73, 129.65, 129.09, 129.01, 127.20, 125.40, 124.08, 123.94, 122.87, 122.36, 120.04, 115.91, 115.70, 115.53, 115.40, 106.63, 106.55, 77.76, 75.14, 63.62, 62.85, 41.61, 40.18, 29.94, 29.88; IR (thin film) *v*: 3118, 3065, 2920, 2852, 1671, 1601, 1510, 1379, 1223, 1094, 1043, 840, 749, 669 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}FN_4ONa$ [M+Na]$^+$ 371.1279, found 371.1284.

1-(4-Chlorophenyl)-4-methyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6c**, **6c**): Pale yellow solid (R_f=0.4), yield 89 % (64.8 mg, 5.2∶1 *dr*). m.p. 152～154 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 7.67 (d, *J*=2.4 Hz, 1H), *δ*: 7.62 (d, *J*=2.4 Hz, 0.2H), 7.42～7.33 (m, 3.2H), 7.45～7.33 (m, 2.4H), 7.27～7.25 (m, 0.4H), 7.20～7.18 (m, 0.4H), 7.15～7.02 (m, 2.5H), 6.94～6.79 (m, 1.7H), 6.68 (dd, *J*=7.8, 1.5 Hz, 1H), 6.60～6.53 (m, 0.2H), 6.31～6.28 (m, 1.3H), 5.51 (dd, *J*=7.7, 4.9 Hz, 0.2H), 4.73 (t, *J*=7.5 Hz, 1H), 3.86 (dd, *J*=13.0, 7.7 Hz, 0.2H), 3.66 (dd, *J*=12.1, 7.8 Hz, 1H), 3.57 (s, 3H), 3.53～3.48 (m, 0.9H), 3.29 (dd, *J*=12.1, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.95, 140.77, 140.03, 134.19, 133.13, 132.14, 129.47, 129.21, 129.03, 128.96, 128.61, 128.22, 127.14, 125.39, 124.04, 123.95, 122.89, 122.28, 119.90, 115.49, 115.40, 106.60, 106.51, 75.09,63.54, 62.75, 41.39, 39.97, 29.91, 29.82; IR (thin film) *v*: 2920, 1674, 1599, 1499, 1473, 1378, 1318, 1218, 1091, 1013, 833, 750, 668 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}ClN_4ONa$ [M+Na]$^+$ 387.0983, found 387.0991.

1-(3-Chlorophenyl)-4-methyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6d**, **6d'**): Pale yellow solid (R_f=0.4), yield 55% (40 mg, 5.6∶1 *dr*). m.p. 88～90 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 7.69～7.68 (m, 1H), 7.62～7.59 (m, 2.2H), 7.51～7.49 (m, 1H), 7.38～7.32 (m, 2H), 7.16～7.09 (m, 1.6H), 7.07～7.04 (m, 1H), 6.93～6.88 (m, 1.3H), 6.85～6.81 (m, 0.2H), 6.72 (dd, *J*=7.7, 1.5 Hz, 1H), 6.59 (dd, *J*=7.7, 1.5 Hz, 0.2H), 6.31 (dd, *J*=2.5, 1.8 Hz, 1H), 6.28 (dd, *J*=2.5, 1.8 Hz, 0.2H), 5.49 (dd, *J*=7.7, 4.8 Hz, 0.2H), 4.73 (t, *J*=7.5 Hz, 1H), 3.87 (dd, *J*=12.1, 7.8 Hz, 0.2H), 3.67 (dd, *J*=12.1, 7.8 Hz, 1H), 3.57 (s, 3H), 3.55 (s, 1H), 3.50 (dd, *J*=13.0, 4.8 Hz, 0.2H), 3.29 (dd, *J*=12.1, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.99, 143.68, 140.88, 140.83, 134.82, 133.23, 132.13, 130.29, 130.12, 128.74, 128.63, 128.20, 127.31, 127.23, 127.19, 125.87, 125.52, 125.40, 124.12, 124.05, 123.07, 122.42, 120.06, 115.54, 115.49, 106.70, 106.58,75.15, 63.74, 62.86, 41.38, 40.03, 29.97, 29.88; IR (thin film) *v*: 2919, 2851, 1676, 1596, 1474, 1378, 1318, 1215, 1128, 1043, 772, 750, 669 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}ClN_4ONa$ [M + Na]$^+$ 387.0983, found 387.0989.

1-(2-Chlorophenyl)-4-methyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6e**): Pale yellow solid (R_f=0.4), yield 60% (43.7 mg, >20∶1 *dr*). m.p. 124～126 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 8.17 (dd, *J*=7.7, 1.5 Hz, 1H), 7.66 (d, *J*=2.3 Hz, 1H), 7.57 (d, *J*=1.40 Hz, 1H), 7.43 (dt, *J*=7.5, 1.0 Hz, 1H), 7.38～7.36 (m, 1H), 7.31～7.27 (m, 1H), 7.15～7.10 (m, 1H), 7.05 (d, *J*=7.4 Hz, 1H), 6.95～6.90 (m, 1H), 6.89～6.87 (m, 1H), 6.30～6.29 (m, 1H), 5.24 (t, *J*=7.4 Hz, 1H), 3.86 (dd, *J*=12.3, 8.1 Hz, 1H), 3.57 (s, 3H), 3.14 (dd, *J*=12.3, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.81, 140.72, 139.48, 132.95, 132.66, 132.05, 129.55, 129.17, 128.09, 127.53, 127.25, 125.12, 124.12, 121.54, 115.60, 106.66, 60.95, 40.68, 29.92; IR (thin film) *v*: 2924, 2852, 1675, 1598, 1502, 1472, 1380, 1034, 1044, 922, 750 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}ClN_4ONa$ [M+Na]$^+$ 387.0983, found 387.0993.

1-(4-Bromophenyl)-4-methyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6f**, **6f'**): Pale yellow solid (R_f=0.4), yield 88% (74.8 mg, 5.3∶1 *dr*). m.p. 151～153 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 7.67 (d, *J*=2.5 Hz, 1H), 7.62 (d, *J*=2.5 Hz, 0.3H), 7.60～7.40 (m, 5.7H), 7.36～7.34 (m, 0.6H), 7.29～7.26 (m, 0.4H), 7.16～6.98 (m, 2.6H), 6.93～6.81 (m, 1.8H), 6.72～6.64 (m, 1H), 6.60～6.53 (m, 0.3H), 6.33～6.24 (m, 1.3H), 5.50 (dd, *J*=7.7, 4.8 Hz, 0.3H), 4.72 (t, *J*=7.5 Hz, 1H), 3.85 (dd, *J*=13.0, 7.7 Hz, 0.3H), 3.66 (dd, *J*=12.1, 7.8 Hz, 1.2H), 3.57 (s, 3H), 3.54～3.45 (m, 1H), 3.29 (dd, *J*=12.1, 7.3 Hz, 1H); ^{13}C NMR (101 MHz, chloroform-*d*) *δ*: 162.57, 161.23, 141.33, 140.84, 140.76, 137.60, 132.40, 131.35, 130.10, 129.55, 128.86, 128.80, 128.54, 128.46, 127.87, 127.25, 127.19, 125.20, 124.39, 124.26, 122.65, 122.50, 119.93, 115.90, 115.83, 106.68, 106.59, 77.73, 77.67, 77.53, 75.20, 72.93, 72.58, 64.40, 63.43, 43.57, 41.25, 40.27, 32.04, 31.94; IR (thin film) *v*: 2919, 2852, 1675, 1597, 1473, 1378, 1216, 1010, 829, 749, 669 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}BrN_4ONa$ [M + Na]$^+$ 431.0478, found 431.0482.

4-Methyl-2a-(1*H*-pyrazol-1-yl)-1-(*p*-tolyl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6g**, **6g'**): Pale yellow solid (R_f=0.4), yield 58% (39.9 mg, 10∶1 *dr*). m.p. 95～97 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) *δ*: 7.65 (d, *J*=2.5 Hz, 1H), 7.55 (d, *J*=2.5 Hz, 0.1H), 7.52 (d, *J*=1.7 Hz, 0.1H), 7.49 (d, *J*=1.8 Hz, 1H), 7.39 (d, *J*=7.8 Hz, 2H), 7.14 (d, *J*=7.7 Hz, 2H), 7.03～6.94 (m, 2H), 6.83～6.76 (m, 1.2H), 6.63 (dd, *J*=7.8, 1.5 Hz, 1H), 6.48 (dd, *J*=7.8, 1.5 Hz, 0.1H), 6.22 (t, *J*=2.0 Hz, 1H), 6.19 (t, *J*=2.0 Hz, 0.1H), 5.43 (dd, *J*=7.7, 5.0 Hz, 0.1H), 4.64 (t, *J*=7.5 Hz, 1H), 3.73 (dd, *J*=12.1, 7.6 Hz, 0.1H), 3.57 (dd, *J*=12.1, 7.6 Hz, 1H), 3.48 (s, 3H), 3.46～3.42 (m, 0.5H), 3.17 (dd, *J*=12.1, 7.4 Hz, 1H), 2.30 (s, 3H), 2.14 (s, 0.3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.08, 140.76, 140.67, 138.54, 138.24, 133.22, 132.45, 129.55, 129.46, 127.82, 127.18, 127.12, 125.17, 123.94, 123.81,

122.40, 119.81, 115.41, 115.26, 106.51, 106.42, 75.14, 64.16, 63.31, 41.63, 40.33, 29.90, 29.82, 21.28; IR (thin film) *v*: 2920, 2851, 1750, 1679, 1595, 1509, 1387, 1218, 773, 669 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}N_4ONa$ $[M+Na]^+$ 367.1529, found 367.1536.

4-Methyl-2a-(1*H*-pyrazol-1-yl)-1-(*m*-tolyl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6h**, **6h'**): Pale yellow solid (R_f=0.4), yield 60% (41.3 mg, 7.7∶1 *dr*). m.p. 50～52 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.74 (d, *J*=2.5 Hz, 1H), 7.68 (d, *J*=2.5 Hz, 0.2H), 7.65～7.58 (m, 1.4H), 7.50 (d, *J*=6.8 Hz, 0.2H), 7.41～7.29 (m, 4H), 7.18～7.03 (m, 3.1H), 7.02～6.98 (m, 0.2H), 6.95～6.83 (m, 1.5H), 6.74 (dd, *J*=7.7, 1.5 Hz, 1H), 6.57 (dd, *J*=7.7, 1.5 Hz, 0.1H), 6.31 (t, *J*=2.1 Hz, 1H), 6.28 (t, *J*=2.1 Hz, 0.1H), 5.50 (dd, *J*=7.7, 4.9 Hz, 0.1H), 4.73 (t, *J*=7.5 Hz, 1H), 3.83 (dd, *J*=12.0, 7.7 Hz, 0.1H), 3.66 (dd, *J*=12.0, 7.7 Hz, 1H), 3.57 (s, 3H), 3.55～3.51 (m, 0.6H), 3.26 (dd, *J*=12.1, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.11, 162.99, 143.70, 141.45, 140.83, 140.70, 138.57, 134.83, 133.25, 132.50, 132.15, 130.29, 129.31, 129.22, 128.83, 128.63, 127.75, 127.32, 127.22, 127.19, 125.52, 125.40, 125.22, 124.85, 124.25, 124.12, 123.97, 123.85, 122.45, 122.42, 115.55, 115.44, 106.70, 106.55, 75.22, 75.16, 63.54, 62.87, 41.52, 41.38, 29.88, 29.85, 21.58, 21.49; IR (thin film) *v*: 3109, 3028, 2919, 1674, 1598, 1499, 1470, 1381, 1306, 1100, 1042, 911, 747 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}N_4ONa$ $[M+Na]^+$ 367.1529, found 367.1538.

4-Methyl-2a-(1*H*-pyrazol-1-yl)-1-(*o*-tolyl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6i**): Pale yellow solid (R_f=0.4), yield 57% (39.2 mg, >20∶1 *dr*). m.p. 102～104 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 8.09 (d, *J*=7.6 Hz, 1H), 7.73 (d, *J*=2.3 Hz, 1H), 7.55 (s, 1H), 7.37 (t, *J*=7.5 Hz, 1H), 7.25 (t, *J*=7.40 Hz, 1H), 7.16 (d, *J*=7.5 Hz, 1H), 7.12～7.09 (m, 1H), 7.06 (d, *J*=7.8 Hz, 1H), 6.95～6.86 (m, 2H), 6.30 (t, *J*=2.0 Hz, 1H), 5.06 (t, *J*=7.5 Hz, 1H), 3.80 (dd, *J*=12.1, 8.0 Hz, 1H), 3.59 (s, 3H), 3.06 (dd, *J*=12.1, 7.0 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 162.86, 140.59, 139.93, 134.50, 133.04, 132.88, 130.41, 127.78, 127.28, 126.73, 126.09, 124.97, 124.07, 121.76, 115.54, 106.65, 75.64, 61.03, 40.95, 29.93, 18.90; IR (thin film) *v*: 2965, 2924, 1674, 1598, 1468, 1381, 1304, 1099, 1041, 752 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}N_4ONa$ $[M+Na]^+$ 367.1529, found 367.1535.

4-Methyl-2a-(1*H*-pyrazol-1-yl)-1-(pyridin-4-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quino-xalin-3(4*H*)-one (**6j**): Pale yellow solid (R_f=0.4, petroleumether/ethyl acetate, *V*∶*V*=3∶1), yield 55% (36.4 mg, 2.4∶1 *dr*). m.p. 178～180 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 8.66 (d, *J*=5.5 Hz, 2H), 7.63 (d, *J*=2.0 Hz, 2H), 7.58 (s, 1H), 7.55 (d, *J*=5.5 Hz, 2H), 7.13 (t, *J*=7.7 Hz, 1H), 7.06 (d, *J*=7.8 Hz, 1H), 6.90 (t, *J*=7.5 Hz, 1H), 6.70 (d, *J*=7.7 Hz, 1H), 6.30 (s, 1H), 4.76 (t, *J*=7.5 Hz, 1H), 3.69 (dd, *J*=12.1, 8.0 Hz, 1H), 3.57 (s, 3H), 3.31 (dd, *J*=12.1, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.85, 140.57, 139.93, 134.48, 133.04, 132.88, 130.40, 127.77, 127.26, 126.73, 126.09, 124.96, 124.05, 121.75, 115.52, 106.63, 75.64, 61.01, 40.94, 29.92, 18.88; IR (thin film) *v*: 3028, 2927, 1673, 1599, 1562, 1501, 1414, 1379, 1303, 1098, 1043, 827 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{17}N_5ONa$ $[M+Na]^+$ 354.1325, found 354.1333.

4-Methyl-2a-(1*H*-pyrazol-1-yl)-1-(pyridin-4-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quin-oxalin-3(4*H*)-one (**6j'**): Pale yellow solid (R_f=0.4, petroleumether/ethyl acetate, *V*∶*V*=3∶1), yield 23% (15.2 mg, 2.4∶1 *dr*). m.p. 178～180 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 8.49～8.48 (m, 1H), 7.62～7.60 (m, 1H), 7.04～7.03 (m, 1H), 6.95～6.93 (m, 1H), 6.88～6.84 (m, 1H), 6.64～6.62 (m, 1H), 6.29 (t, *J*=2.1 Hz, 1H), 5.51 (dd, *J*=7.7, 4.6 Hz, 1H), 3.89 (dd, *J*=13.1, 7.7 Hz, 1H), 3.55～3.49 (m, 4H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 161.84, 150.45, 146.39, 141.03, 132.31, 128.81, 127.25, 124.20, 123.52, 122.60, 120.17, 115.66, 106.73, 77.83, 62.96, 39.16, 30.05; IR (thin film) *v*: 3060, 3037, 2957, 2853, 1664, 1632, 1600, 1466, 1385, 1130, 751 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{17}N_5ONa$ $[M+Na]^+$ 354.1325, found 354.1333.

4-Methyl-2a-(1*H*-pyrazol-1-yl)-1-(pyridin-2-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6k**, **6k'**): Pale yellow solid (R_f=0.4, petroleumether/ethyl acetate, *V*∶*V*=3∶1), yield 81% (53.6 mg, 5∶1 *dr*). m.p. 136～138 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 8.56～8.54 (m, 1H), 8.32～8.30 (m, 0.2H), 7.79 (d, *J*=2.5 Hz, 1H), 7.76～7.69 (m, 2H), 7.63～7.53 (m, 1H), 7.47 (d, *J*=1.8 Hz, 1H), 7.42～7.36 (m, 0.4H), 7.22～7.15 (m, 1.6H), 7.04～6.95 (m, 2.8H), 6.92～6.89 (m, 0.4H), 6.81～6.74 (m, 1.6H), 6.64 (dd, *J*=7.8, 1.5 Hz, 1H), 6.55 (dd, *J*=7.8, 6.4 Hz, 0.3H), 6.22 (t, *J*=2.2 Hz, 1H), 6.18 (t, *J*=2.1 Hz, 0.2H), 5.34 (dd, *J*=7.6, 4.1 Hz, 0.2H), 4.82 (dd, *J*=8.0, 7.0 Hz, 1H), 3.71 (dd, *J*=12.2, 7.6 Hz, 0.2H), 3.62 (dd, *J*=12.2, 8.1 Hz, 1.2H), 3.47 (s, 3H), 3.45～3.38 (m, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.92, 160.53, 157.20, 150.07, 149.68, 140.65, 140.53, 137.24, 136.14, 133.04, 132.28, 127.62, 127.28, 125.18, 124.00, 123.88, 123.13, 123.03, 122.82, 122.01, 121.97, 121.78, 120.37, 115.54, 115.07, 106.65, 106.26, 77.98, 75.48, 64.67, 64.12, 39.48, 37.86, 29.87, 29.80; IR (thin film) *v*: 3032, 2919, 2851, 1678, 1591, 1474, 1390, 1213, 1042, 922, 772, 669 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{17}N_5ONa$ $[M+Na]^+$ 354.1325, found 354.1332.

1-(4-Methoxyphenyl)-4-methyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxal-in-3(4*H*)-one (**6l**, **6l'**): Pale yellow solid (R_f=0.4), yield 72% (52 mg, 11∶1 *dr*). m.p. 86～88 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.72 (d, *J*=2.5 Hz, 1H), 7.63 (d, *J*=2.5 Hz, 0.1H), 7.58 (d, *J*=1.8 Hz, 1H), 7.51 (d, *J*=8.6 Hz, 2H), 7.13～7.02 (m, 2.2H), 6.95 (d, *J*=8.7 Hz, 2H), 6.87 (td, *J*=7.5, 1.4 Hz, 1H), 6.80 (td, *J*=7.4, 1.8 Hz, 0.1H), 6.74 (d, *J*=8.7 Hz, 0.2H), 6.69 (dd, *J*=7.8, 1.5 Hz, 1H), 6.57 (dd, *J*=7.7, 1.5 Hz, 0.1H), 6.30 (t, *J*=2.2 Hz, 1H), 6.27 (t, *J*=2.2 Hz, 0.1H), 5.49 (dd, *J*=7.7, 4.9 Hz, 0.1H), 4.70 (t, *J*=7.5 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 0.3H), 3.64 (dd, *J*=12.1, 7.7 Hz, 1H), 3.56 (s, 3H), 3.53 (s, 0.3H), 3.28 (dd, *J*=12.1, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.13,

159.81, 140.76, 140.70, 133.61, 133.21, 132.45, 129.21, 128.57, 127.17, 125.17, 123.95, 123.82, 122.50, 122.41, 115.42, 115.27, 114.22, 114.10, 106.50, 106.42, 75.09, 63.10, 55.41, 55.23, 41.70, 40.38, 29.90, 29.83; IR (thin film) *v*: 2919, 1750, 1676, 1601, 1513, 1376, 1303, 1250, 1175, 1036, 771, 668, cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}NO_2Na$ $[M+Na]^+$ 354.1325, found 354.1333.

1-Mesityl-4-methyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6m**): Pale yellow solid (R_f=0.4), yield 70% (52.1 mg, >20∶1 *dr*). m.p. 146～148 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.59 (d, *J*=4.3 Hz, 2H), 7.12 (t, *J*=7.6 Hz, 1H), 7.07 (d, *J*=7.5 Hz, 1H), 6.92 (t, *J*=7.5 Hz, 1H), 6.86 (s, 2H), 6.69 (d, *J*=7.7 Hz, 1H), 6.29 (s, 1H), 5.28 (t, *J*=8.2 Hz, 1H), 3.61 (d, *J*=8.2 Hz, 2H), 3.54 (s, 3H), 2.41 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.15, 140.66, 137.68, 133.45, 132.86, 131.48, 126.99, 124.84, 124.23, 121.82, 115.38, 106.33, 75.39, 60.61, 37.23, 29.75, 20.90, 20.77; IR (thin film) *v*: 2920, 1673, 1599, 1500, 1472, 1376, 1302, 1095, 1041, 853, 748, 668 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}N_4ONa$ $[M+Na]^+$ 95.1842, found 395.1849.

2,4-Dimethyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxal-in-3(4*H*)-one (**6n**): Pale yellow solid (R_f=0.4), yield 92% (63.3 mg, >20∶1 *dr*). m.p. 109～111 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.63 (d, *J*=1.8 Hz, 1H), 7.61 (s, 1H), 7.56 (d, *J*=7.2 Hz, 2H), 7.42 (t, *J*=7.3 Hz, 2H), 7.36 (t, *J*=7.2 Hz, 1H), 7.11 (t, *J*=7.6 Hz, 1H), 7.06 (d, *J*=7.5 Hz, 1H), 6.89 (t, *J*=7.4 Hz, 1H), 6.74 (d, *J*=7.6 Hz, 1H), 6.31 (t, *J*=2.1 Hz, 1H), 4.32 (d, *J*=6.7 Hz, 1H), 3.62 (q, *J*=7.1 Hz, 1H), 3.56 (s, 3H), 1.46 (d, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 161.44, 141.09, 140.70, 132.80, 132.60, 128.91, 128.44, 127.22, 127.11, 124.95, 124.04, 122.12, 115.12, 106.32, 73.74, 49.97, 29.42, 15.34; IR (thin film) *v*: 3397, 2966, 2926, 2853, 1685, 1591, 1457, 1388, 1255, 1215, 1011, 858, 749, 708 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}N_4ONa$ $[M+Na]^+$ 367.1529, found 367.1534.

4-Methyl-1-(naphthalen-2-yl)-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6o**): Pale yellow solid (R_f=0.4), yield 89% (67.6 mg, >20∶1 *dr*). m.p. 123～125 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.96 (d, *J*=8.2 Hz, 2H), 7.91～7.84 (m, 3H), 7.79 (d, *J*=1.9 Hz, 1H), 7.65 (s, 1H), 7.53 (d, *J*=3.2 Hz, 1H), 7.52 (d, *J*=3.3 Hz, 1H), 7.12 (t, *J*=7.6 Hz, 1H), 7.08 (d, *J*=7.1 Hz, 1H), 6.86 (td, *J*=7.3, 1.2 Hz, 1H), 6.73 (dd, *J*=7.7, 0.6 Hz, 1H), 6.36 (s, 1H), 4.95 (t, *J*=7.5 Hz, 1H), 3.76 (dd, *J*=12.2, 7.8 Hz, 1H), 3.62 (s, 3H), 3.42 (dd, *J*=12.1, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.11, 140.80, 138.79, 133.48, 133.27, 133.23, 132.40, 129.03, 128.13, 127.89, 127.27, 126.50, 126.39, 126.36, 125.29, 124.80, 124.02, 122.44, 115.48, 106.62, 75.34, 63.71, 41.38, 29.88; IR (thin film) *v*: 3118, 3080, 3012, 1750, 1684, 1550, 1509, 1362, 1339, 1219, 773, 669 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{20}N_4ONa$ $[M+Na]^+$ 403.1529, found 403.1536.

1-([1,1'-Biphenyl]-4-yl)-4-methyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinox-alin-3(4*H*)-one (**6p**, **6p'**): Pale yellow solid (R_f=0.4), yield 90% (73.1 mg, 4∶1 *dr*). m.p. 123～125 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.74 (d, *J*=2.5 Hz, 1H), 7.69～7.59 (m, 7.6H), 7.50～7.42 (m, 3.5H), 7.41～7.26 (m, 2.1H), 7.23～7.18 (m, 0.8H), 7.12～7.03 (m, 2.1H), 6.92～6.76 (m, 2.8H), 6.61 (dd, *J*=7.7, 1.6 Hz, 0.3H), 6.32～6.27 (m, 1.2H), 5.58 (dd, *J*=7.7, 4.9 Hz, 0.2H), 4.80 (t, *J*=7.6 Hz, 1H), 3.86 (dd, *J*=13.0, 7.7 Hz, 0.3H), 3.70 (dd, *J*=12.1, 7.8 Hz, 1H), 3.57 (s, 3H), 3.54 (s, 1H), 3.33 (dd, *J*=12.1, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.06, 161.88, 141.36, 140.80, 140.73, 140.68, 140.49, 140.19, 136.59, 133.20, 132.39, 132.05, 128.91, 128.83, 128.33, 127.62, 127.54, 127.37, 127.22, 127.16, 127.00, 125.26, 124.03, 123.92, 122.62, 122.41, 119.86, 115.47, 115.36, 106.58, 106.48, 77.83, 75.21,64.03, 63.22, 41.54, 40.25, 29.94, 29.85; IR (thin film) *v*: 3029, 1673, 1598, 1472, 1378, 1306, 1095, 1043, 750, 698 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{22}N_4ONa$ $[M+Na]^+$ 429.1686, found 429.1687.

1,4-Dimethyl-1-phenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6q**, **6q'**): Pale yellow solid (R_f=0.4), yield 79% (54.4 mg, 2.9∶1 *dr*). m.p. 71～73 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.70～7.63 (m, 3.4H), 7.58～7.53 (m, 1.6H), 7.44～7.40 (m, 2H), 7.36～7.24 (m, 1.7H), 7.23～7.03 (m, 5.2H), 6.98～6.87 (m, 4.4H), 6.86～6.83 (m, 1H), 6.81～6.78 (m, 0.6H), 6.27～6.26 (m, 1.5H), 3.94 (d, *J*=16.0 Hz, 0.6H), 3.56 (s, 2.7H), 3.51 (d, *J*=12.4 Hz, 1H), 3.46 (d, *J*=12.7 Hz, 0.6H), 3.33 (d, *J*=12.4 Hz, 1H), 3.27 (s, 1.8H), 2.08 (s, 2H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 162.90, 162.70, 146.70, 140.65, 140.49, 140.02, 133.61, 133.27, 129.84, 128.82, 128.15, 127.78, 127.49, 127.22, 127.07, 126.14, 125.34, 124.22, 124.02, 123.92, 123.75, 122.31, 121.39, 115.63, 115.43, 106.51, 106.42, 75.16,74.87, 67.71, 66.64, 47.88, 44.92, 30.80, 29.91, 29.66, 23.99; IR (thin film): *v* 2970, 2927, 1673, 1597, 1499, 1473, 1378, 1318, 1110, 1043, 923, 748, 701 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}N_4ONa$ $[M+Na]^+$ 367.1529, found 367.1535.

4-Methyl-1,1-diphenyl-2a-(1*H*-pyrazol-1-yl)-2,2a-dihydro-1*H*-azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6r**): Pale yellow solid (R_f=0.4), yield 77% (62.5mg). m.p. 119～121 ℃; ^1H NMR (400 MHz, chloroform-*d*) *δ*: 7.71 (d, *J*=2.3 Hz, 1H), 7.63 (d, *J*=7.4 Hz, 2H), 7.53 (d, *J*=0.8 Hz, 1H), 7.42 (t, *J*=7.5 Hz, 2H), 7.35 (t, *J*=7.8 Hz, 1H), 7.12 (s, 5H), 7.06 (dd, *J*=7.7, 0.9 Hz, 1H), 6.97～6.93 (m, 1H), 6.86 (t, *J*=7.2 Hz, 1H), 6.75 (d, *J*=8.1 Hz, 1H), 6.28 (t, *J*=1.9 Hz, 1H), 4.43 (d, *J*=12.9 Hz, 1H), 3.49 (d, *J*=12.9 Hz, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) *δ*: 163.00, 147.25, 140.39, 138.48, 134.34, 129.83, 128.61, 128.31, 127.96, 127.65, 127.49, 127.36, 126.66, 124.89, 123.62, 123.41, 115.44, 106.70, 75.19, 73.68, 45.78, 29.67; IR (thin film) *v*: 3057, 3028, 1672, 1599, 1470, 1381, 1317, 1103, 1043, 749, 700 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{22}N_4ONa$ $[M+Na]^+$ 429.1686, found 429.1690.

4-Methyl-2a-(1*H*-pyrazol-1-yl)-1-vinyl-2,2a-dihydro-1*H*-

azeto[1,2-*a*]quinoxalin-3(4*H*)-one (**6s**, **6s'**): Pale yellow oil (R_f=0.5), yield 61% (34.2 mg, 2.8∶1 *dr*). ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.67～7.59 (m, 1H), 7.56～7.53 (m, 1H), 7.14～6.82 (m, 4H), 6.27～6.24 (m, 1H), 6.22～5.62 (m, 1H), 5.40～5.17 (m, 2H), 4.84～4.17 (m, 1H), 3.70～3.47 (m, 4H), 3.20～3.10 (m, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 162.85, 140.73, 140.61, 139.28, 136.28, 133.11, 132.32, 129.85, 127.08, 125.04, 124.01, 123.91, 123.61, 122.49, 121.54, 121.01, 118.10, 115.44, 115.30, 106.49, 106.44, 75.49, 62.89, 62.62, 39.02, 38.39, 29.93, 29.81; IR (thin film) *v*: 3118, 2920, 2853, 1646, 1508, 1474, 1379, 1219, 1043, 772, 669 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{16}N_4ONa$ [M+Na]$^+$ 303.1216, found 303.1220.

4-Methyl-3-oxo-2a-(1*H*-pyrazol-1-yl)-2,2a,3,4-tetrahydro-1*H*-azeto[1,2-*a*]quinoxaline-1-carbonitrile (**6t**, **6t'**): Pale yellow solid (R_f=0.5, petroleumether/ethyl acetate, *V*∶*V*=3∶1), yield 58% (32.4 mg, 1.4∶1 *dr*). m.p. 82～84 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J*=4.0 Hz, 1H), 7.57 (dd, *J*=14.0, 4.0 Hz, 1.5H), 7.49 (d, *J*=4.0 Hz, 0.8H), 7.26～7.18 (m, 3.5H), 7.14～7.01 (m, 4.6H), 6.33 (t, *J*=4.0 Hz, 1H), 6.27 (t, *J*=4.0 Hz, 0.8H), 4.9 (dd, *J*=8.0, 4.0 Hz, 0.8H), 4.44 (dd, *J*=8.0, 8.0 Hz,1H), 3.96 (dd, *J*=12.0, 8.0 Hz, 0.8H), 3.72 (dd, *J*=12.0, 8.0 Hz, 1H), 3.64 (dd, *J*=12.0, 8.0 Hz, 0.8H), 3.59 (s, 2.2H), 3.54 (s, 3H), 3.50 (dd, *J*=12.0, 4.0 Hz, 1H); ^{13}C NMR (101 MHz, chloroform-*d*) δ: 161.77, 161.67, 141.32, 141.13, 134.45, 133.30, 129.82, 128.05, 127.50, 127.25, 126.94, 124.77, 124.71, 123.42, 123.21, 118.07, 116.17, 115.83, 107.41, 107.13, 77.76,76.05, 47.98, 46.70, 36.99, 36.64, 30.25, 30.05; IR (thin film) *v*: 3398, 3118, 2923, 2851, 1675, 1601, 1473, 1380, 1307, 1129, 1044, 752, 664 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_5ONa$ [M+Na]$^+$ 302.1012, found 302.1018.

5-Methyl-6a-(1*H*-pyrazol-1-yl)-6b,7,8,9a-tetrahydro-5*H*-furo[3',2':3,4]azeto[1,2-*a*]quinoxalin-6(6a*H*)-one (**6u**, **6u'**): Pale yellow oil (R_f=0.5, petroleumether/ethyl acetate, *V*∶*V*=2∶1), yield 34% (20.1 mg, 5.9∶1 *dr*). ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.90～7.85 (m, 1.2H), 7.70 (d, *J*=1.7 Hz, 0H), 7.66 (d, *J*=2.4 Hz, 1H), 7.60～7.54 (m, 2.4H), 7.42 (d, *J*=2.4 Hz, 0.2H), 7.39～7.30 (m, 2.6H), 6.70 (d, *J*=6.6 Hz, 0.2H), 6.53 (d, *J*=3.6 Hz, 1H), 6.28 (t, *J*=2.1 Hz, 1H), 5.95 (t, *J*=2.1 Hz, 0.2H), 4.73～4.68 (m, 1H), 4.59～4.54 (m, 0.2H), 4.38～4.33 (m, 1.1H), 4.26～4.18 (m, 1.5H), 3.70 (s, 3H), 3.63 (s, 0.5H), 2.84～2.76 (m, 1H), 2.45～2.37 (m, 1.2H); ^{13}C NMR (101 MHz, chloroform-*d*) δ: 158.02, 154.64, 140.45, 139.54, 133.35, 132.48, 130.46, 130.38, 130.25, 130.02, 128.86, 128.78, 123.87, 123.54, 113.74, 113.54, 105.83, 104.80, 92.18, 90.59, 69.73, 69.41, 48.86, 48.43, 30.56, 29.82, 29.28, 29.12; IR (thin film) *v*: 2919, 2851, 1716, 1654, 1602, 1473, 1396, 1214, 931, 771, 669 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{16}N_4O_2Na$ [M+Na]$^+$ 319.1165, found 319.1170.

5-Methyl-6a-(1*H*-pyrazol-1-yl)-6a,6b,7,11b-tetrahydro-indeno[2',1':3,4]azeto[1,2-*a*]quinoxalin-6(5*H*)-one (**6v**): White solid (R_f=0.5, petroleumether/ethyl acetate, *V*∶*V*=3∶1), yield 86% (58.8 mg, >20∶1 *dr*). m.p. 228～230 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.60 (s, 1H), 7.51～4.89 (m, 1H), 7.46 (d, *J*=1.9 Hz, 1H), 7.32～7.29 (m, 2H), 7.23～7.22 (m, 1H), 7.13～7.05 (m, 3H), 6.96～6.94 (m, 1H), 6.12 (s, 1H), 5.25 (d, *J*=6.8 Hz, 1H), 4.39～4.34 (m, 1H), 3.49 (s, 3H), 3.12 (dd, *J*=18.0, 10.3 Hz, 1H), 2.59～2.54 (m, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 161.70, 146.09, 142.25, 141.31, 132.45, 131.33, 129.05, 128.55, 127.20, 125.78, 124.26, 124.16, 123.97, 120.22, 115.44, 105.42, 78.55, 71.42, 46.17, 32.01, 30.06; IR (thin film) *v*: 2920, 1750, 1680, 1603, 1550, 1457, 1213, 1036, 772, 669 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{18}N_4ONa$ [M+Na]$^+$ 365.1373, found 365.1380.

5,8-Dimethyl-6a-(2*H*-pyrrol-2-yl)-6b,9a-dihydropyrrolo-[3',4':3,4]azeto[1,2-*a*]quinoxaline-6,7,9(5*H*,6a*H*,8*H*)-trione (**6w**, **6w'**): Pale yellow solid (R_f=0.5, petroleumether/ethyl acetate, *V*∶*V*=3∶1), yield 81% (54.6 mg, 6.7∶1 *dr*). m.p. 158～160 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.68 (d, *J*=2.6 Hz, 0.2H), 7.66 (d, *J*=1.8 Hz, 1H), 7.55 (d, *J*=1.7 Hz, 0.2H), 7.52 (d, *J*=2.6 Hz, 1H), 7.21～7.10 (m, 3.2H), 7.04～6.98 (m, 1.2H), 6.30 (dd, *J*=2.6, 1.7 Hz, 1H), 6.26 (dd, *J*=2.6, 1.7 Hz, 0.2H), 5.06 (d, *J*=5.5 Hz, 1H), 4.68 (d, *J*=5.4 Hz, 1H), 4.46 (d, *J*=6.0 Hz, 0.2H), 4.42 (d, *J*=6.0 Hz,0.2H), 3.54 (s, 0.4H), 3.47 (s, 3H), 3.11 (s, 0.4H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 171.69, 170.81, 158.50, 141.84, 132.43, 131.58, 129.61, 128.45, 128.12, 127.89, 125.96, 125.24, 124.97, 124.85, 122.60, 122.13, 115.74, 115.59, 107.34, 107.21, 61.48, 60.52, 50.20, 47.30, 30.43, 30.07, 25.63, 25.24; IR (thin film) *v*: 2922, 2851, 1712, 1501, 1474, 1376, 1278, 1132, 1042, 751, 669 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}N_5O_3Na$ [M+Na]$^+$ 360.1067, found 360.1074.

5-Methyl-6a-(1*H*-pyrazol-1-yl)-6b,7,8,12b-tetrahydro-5*H*-naphtho[2',1':3,4]azeto[1,2-*a*]quinoxalin-6(6a*H*)-one (**6x**): White solid (R_f=0.5, petroleumether/ethyl acetate, *V*∶*V*=3∶1), yield 74% (52.7 mg, >20∶1 *dr*). m.p. 214～216 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.63 (d, *J*=0.7 Hz, 1H), 7.57 (d, *J*=1.8 Hz, 1H), 7.31 (t, *J*=7.4 Hz, 1H), 7.23 (t, *J*=7.1 Hz, 1H), 7.17 (d, *J*=7.7 Hz, 2H), 7.15～7.10 (m, 1H), 7.05～6.94 (m, 2H), 6.85～6.80 (m, 1H), 6.20 (s, 1H), 4.86 (d, *J*=7.6 Hz, 1H), 3.96 (td, *J*=7.2, 2.2 Hz, 1H), 3.45 (s, 3H), 2.70～2.62 (m, 1H), 2.55 (dt, *J*=15.4, 3.9 Hz, 1H), 2.15 (dd, *J*=14.2, 2.8 Hz, 1H), 1.70～1.61 (m, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 163.16, 141.01, 140.11, 134.99, 133.52, 131.73, 128.91, 128.79, 128.69, 127.71, 126.42, 125.33, 123.96, 122.82, 115.38, 105.43, 77.26, 61.83, 41.44, 29.82, 27.07, 21.51; IR (thin film) *v*: 2928, 2853, 1679, 1499, 1473, 1373, 1310, 1127, 1041, 750, 669 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{20}N_4ONa$ [M+Na]$^+$ 379.1529, found 379.1536.

4-Methyl-1-(2-oxopyrrolidin-1-yl)-2a-(1*H*-pyrazol-1-yl)-2,2a,4,8b-tetrahydrocyclobuta[*c*]quinolin-3(1*H*)-one (**6y**, **6y'**): Pale yellow solid (R_f=0.5, petroleumether/ethyl acetate, *V*∶*V*=4∶1), yield 51% (34.3 mg, 7.7∶1 *dr*). m.p. 102～104 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.68 (d, *J*=2.4 Hz, 0.2H), 7.58 (d, *J*=1.7 Hz, 1H), 7.50 (d, *J*=2.6 Hz, 1.2H), 7.16～7.12 (m, 1H), 7.07～6.98 (m, 2.3H), 6.76 (dd, *J*=7.8, 1.5 Hz, 1H), 6.26 (t, *J*=2.2 Hz, 1H), 6.22

(t, J=2.1 Hz, 0.1H), 5.81 (dd, J=7.5, 6.3 Hz, 1H), 4.08～4.00 (m, 1.1H), 3.73～3.69 (m, 1.6H), 3.69～3.63 (m, 1.3H), 3.53 (s, 3H), 3.52～3.47 (m, 1.3H), 2.50 (t, J=8.0 Hz, 2H), 2.27 (t, J=8.1 Hz, 0.3H), 2.19～2.11 (m, 2H); ^{13}C NMR (101 MHz, chloroform-*d*) δ: 175.34, 155.16, 154.66, 140.76, 139.66, 133.22, 132.56, 130.34, 130.21, 130.06, 127.06, 125.62, 124.51, 123.75, 122.26, 115.50, 113.75, 106.73, 105.59, 64.69, 63.64, 43.39, 42.58, 36.98, 34.97, 32.19, 31.20, 29.91, 29.22, 18.37, 18.10; IR (thin film) *v*: 2920, 2852, 1690, 1653, 1602, 1473, 1418, 1268, 1215, 1091, 1041, 756, 669 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}N_5O_2Na$ [M+Na]$^+$ 360.1431, found 360.1437.

tert-Butyl(4-(4-methyl-3-oxo-2a-(1*H*-pyrazol-1-yl)-2,2a,3,4-tetrahydro-1*H*-azeto[1,2-*a*]quino-xalin-1-yl)-phenyl)carbamate (**6z**, **6z'**): Pale yellow solid (R_f=0.5), yield 98% (87.2 mg, 4.2∶1 *dr*). m.p. 190～192 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.72 (d, J=4.0 Hz, 1H), 7.63 (d, J=4.0 Hz,1H), 7.60～7.57 (m, 1.3H), 7.53～7.45 (m, 2H), 7.42 (d, J=8.0 Hz, 2.0H), 7.26～7.22 (m, 2H), 7.11～7.02 (m, 2.6H), 6.88～6.78 (m, 2.9H), 6.70～ 6.67 (m, 1.3H), 6.31～7.27 (m, 1.2H), 5.48 (dd, J=8.0, 4.0 Hz, 0.2H), 4.69 (t, J=8.0 Hz, 1H), 3.82 (dd, J=16.0, 8.0 Hz, 0.2H), 3.64 (dd, J=12.0, 8.0 Hz,1H), 3.56 (s, 3H), 3.52 (s, 0.8H), 3.64 (dd, J=12.0, 4.0 Hz, 1H), 1.52 (s, 9H), 1.46 (s, 2H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 163.09, 162.37, 152.86, 140.73, 140.67, 138.68, 135.84, 133.14, 132.34, 132.02, 131.79, 128.61, 127.94, 127.19, 125.20, 123.96, 122.55, 122.41, 119.92, 118.85, 118.37, 115.41, 115.29, 106.52, 106.42, 80.65,77.73, 77.34,75.08, 63.89, 63.05, 41.50, 40.25, 29.89, 29.81, 28.39, 28.33; IR (thin film) *v*: 3309, 3118, 2921, 2851, 1600, 1528, 1417, 1318, 1217, 1160, 1048, 772, 669 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{27}N_5O_3Na$ [M+Na]$^+$ 468.2006, found 468.2013.

tert-Butyl-5-(4-methyl-3-oxo-2a-(1*H*-pyrazol-1-yl)-2,2a,3,4-tetrahydro-1*H*-azeto[1,2-*a*]quino-xalin-1-yl)-1*H*-indole-1-carboxylate (**6aa**, **6aa'**): Pale yellow solid (R_f= 0.5), yield 78% (73.2 mg, 3.6∶1 *dr*). m.p. 104～106 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 8.19 (d, J=8.5 Hz, 1H), 7.98 (d, J=8.5 Hz, 0.26H), 7.78 (t, J=2.7 Hz, 2H), 7.66～7.60 (m, 2.5H), 7.57～7.53 (m, 1.4H),7.39 (d, J= 1.6 Hz, 0.3H), 7.25 (s, 0.7H), 7.12～7.03 (m, 2.4H), 6.90～6.69 (m, 2.9H), 6.60～6.57 (m, 1.3H), 6.47 (d, J= 4.0 Hz, 0.3H), 6.32(t, J=4.0 Hz, 1H), 6.29 (d, J=4.0 Hz, 0.3H), 5.64 (dd, J=7.6, 5.4 Hz, 0.3H), 4.85 (t, J=8.0 Hz, 1H), 3.89 (dd, J=12.0, 8.0 Hz, 0.3H), 3.71 (dd, J=12.0, 8.0 Hz, 1H), 3.65～3.61 (m, 0.3H), 3.58 (s, 3H), 3.55 (s, 0.8H), 3.34 (dd, J=12.0, 8.0 Hz, 1H), 1.68 (s, 9H), 1.62 (s, 2.4H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 163.16, 161.98, 149.72, 140.72, 135.91, 135.23, 133.24, 132.48, 130.96, 127.26, 127.18, 125.20, 123.93, 123.82, 123.68, 123.49, 122.45, 120.87, 119.80, 119.72, 115.55, 115.42, 115.30, 107.41, 107.20, 106.54, 106.43, 83.97, 77.88, 75.16, 64.63, 63.74, 41.96, 40.63, 29.94, 29.84, 28.26, 28.20; IR (thin film) *v*: 3118, 2978, 2932, 1732, 1674, 1599, 1501, 1473, 1359, 1161, 1084, 852, 751 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{27}N_5O_3Na$ [M + Na]$^+$ 492.2006, found 492.2014.

4-Methyl-3-oxo-2a-(1*H*-pyrazol-1-yl)-2,2a,3,4-tetrahydro-1*H*-azeto[1,2-*a*]quino-xalin-1-yl)-*N*-(quinolin-7-yl)benzamide (**6ab**): Pale yellow solid (R_f=0.5), yield 76% (76 mg, 7.1∶1 *dr*). m.p. 115～117 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 10.79 (s, 1H), 8.95 (d, J=7.4 Hz, 1H), 8.85 (d, J=2.7 Hz, 1H), 8.19 (d, J=8.5 Hz, 1H), 8.16 (d, J= 8.1 Hz, 2H), 7.81 (d, J=8.1 Hz, 2H), 7.72 (d, J=1.9 Hz, 1H), 7.62 (s, 1H), 7.59 (d, J=7.6 Hz, 1H), 7.55 (d, J=8.1 Hz, 1H), 7.48 (dd, J=8.2, 4.2 Hz, 1H), 7.13 (t, J=7.6 Hz, 1H), 7.07 (d, J=7.8 Hz, 1H), 6.91 (t, J=7.1 Hz, 1H), 6.75 (d, J=7.7 Hz, 1H), 6.34 (s, 1H), 4.87 (t, J=7.5 Hz, 1H), 3.74 (dd, J=12.2, 7.9 Hz, 1H), 3.60 (s, 3H), 3.38 (dd, J= 12.1, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 165.15, 163.01, 148.44, 145.46, 140.87, 138.87, 136.53, 135.35, 134.62, 133.24, 132.23, 128.11, 128.02, 127.68, 127.57, 127.27, 125.50, 124.18, 122.39, 121.90, 121.84, 116.68, 115.57, 106.73, 75.30, 63.09, 41.44, 29.93; IR (thin film) *v*: 3351, 2920, 2851, 1671, 1597, 1532, 1484, 1386, 1328, 1268, 1125, 1044, 752, 669 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{24}N_6O_2Na$ [M+Na]$^+$ 523.1853, found 523.1859.

4.4 General procedure for the synthesis of 3-alkylated quinoxalin-2(1*H*)-ones

3a (0.3 mmol, 1.0 equiv.), styrene substrate (**4**) (0.6 mmol, 2.0 equiv.) and photosensitizer **PC** (0.0015 mmol, 0.5 mol%) were dissolved in dry and deoxygenated cyclopentyl methyl ether (9 mL) under argon atmosphere. The reaction mixture was irradiated by 10 W LEDs (450～455 nm) for 5 h at room temperature (maintained with cooling water). After completion of the reaction as indicated by TLC, cyclopentyl methyl ether (9 mL) was replaced by MeOH (6 mL), and AcOH (35 μL, 0.6 mmol) was added at 35 ℃. After completion of the reactions, the solvent was removed under reduced pressure and the residues purified by flash column chromatography (petroleumether/ethyl acetate, V∶V=5∶1) to give the target product **7**.

3-(2-Methoxy-2-phenylethyl)-1-methylquinoxalin-2(1*H*)-one (**7a**): Pale yellow solid (R_f=0.5), yield 78% (68.8 mg). m.p. 118～120 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.89 (dd, J=8.0, 1.5 Hz, 1H), 7.55～7.51 (m, 1H), 7.49～7.46 (m, 2H), 7.38～7.25 (m, 5H), 4.98 (dd, J=9.3, 4.4 Hz, 1H), 3.70 (s, 3H), 3.41 (dd, J=14.7, 9.3 Hz, 1H), 3.30～3.23 (m, 1H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 158.03, 155.09,141.91, 133.30, 132.91, 130.10, 129.91, 128.55, 127.81, 126.97, 123.66, 113.68, 81.04, 56.89, 43.45, 29.16; IR (thin film) *v*: 2980, 2932, 2821, 1653, 1602, 1472, 1312, 1096, 1000, 754, 702 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}N_2O_2Na$ [M + Na]$^+$ 317.1259, found 317.1260.

3-(2-(4-Chlorophenyl)-2-methoxyethyl)-1-methylquinoxalin-2(1*H*)-one (**7b**): Pale yellow solid (R_f=0.5), yield 72% (70.8 mg). m.p. 90～92 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.87 (d, J=8.0 Hz, 1H), 7.53 (t, J=7.8 Hz, 1H), 7.41 (d, J=8.0 Hz, 2H), 7.42～7.27 (m, 4H), 4.97 (dd, J=9.0, 4.8 Hz, 1H), 3.69 (s, 3H), 3.38 (dd, J= 14.8, 9.0 Hz, 1H), 3.23 (dd, J=14.9, 5.0 Hz, 1H), 3.18 (s,

3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 157.54, 154.96, 140.41, 133.40, 133.21, 132.77, 129.99, 129.97, 128.68, 128.34, 123.66, 113.66, 80.34, 56.86, 43.15, 29.11; IR (thin film) *v*: 2982, 2933, 2821, 1654, 1602, 1473, 1411, 1305, 1093, 1014, 827, 753 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}ClN_2O_2Na$ $[M+Na]^+$ 351.0871, found 351.0869.

3-(2-Methoxy-2-(naphthalen-2-yl)ethyl)-1-methylquinoxalin-2(1*H*)-one (**7c**): Pale yellow solid (R_f=0.5), yield 70% (72.3 mg). m.p. 35～37 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.92～7.82 (m, 5H), 7.66～7.64 (m, 1H), 7.47～7.45 (m, 3H), 7.32～7.28 (m, 1H), 7.21～7.19 (m, 1H), 5.16 (dd, *J*=9.2, 4.4 Hz, 1H), 3.64 (s, 3H), 3.50 (dd, *J*=14.7, 9.3 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 157.82, 154.98, 139.26, 133.27, 133.18, 133.16, 132.78, 129.95, 129.84, 128.43, 127.96, 127.74, 126.11, 126.09, 125.86, 124.67, 123.57, 113.61, 81.09, 56.89, 43.31, 29.04; IR (thin film) *v*: 3053, 2934, 2821, 1652, 1602, 1472, 1095, 821, 751, 665 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{20}N_2O_2Na$ $[M+Na]^+$ 367.1417, found 367.1416.

3-(2-([1,1'-Biphenyl]-4-yl)-2-methoxyethyl)-1-methylquinoxalin-2(1*H*)-one (**7d**): Pale yellow solid (R_f=0.5), yield 55% (61.1.7 mg). m.p. 165～167 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.89 (d, *J*=8.0 Hz, 1H), 7.60～7.48 (m, 7H), 7.42 (t, *J*=7.6 Hz, 2H), 7.34～7.25 (m, 3H), 5.04 (dd, *J*=9.2, 4.5 Hz, 1H), 3.68 (s, 3H), 3.45 (dd, *J*=14.7, 9.2 Hz, 1H), 3.31 (dd, *J*=14.6, 4.7 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 157.90, 155.03, 140.94, 140.63, 133.25, 132.85, 130.02, 129.87, 128.80, 127.40, 127.29, 127.25, 127.12, 123.62, 113.64, 80.76, 56.90, 43.32, 29.10; IR (thin film) *v*: 3028, 2931, 2821, 1653, 1601, 1472, 1310, 1095, 1006, 839, 753, 698 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}N_2O_2Na$ $[M+Na]^+$ 393.1573, found 393.1573.

3-(2-Methoxy-2-phenylpropyl)-1-methylquinoxalin-2(1*H*)-one (**7e**): Pale yellow solid (R_f=0.5), yield 70% (64.7 mg). m.p. 105～107 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.81～7.79 (m, 1H), 7.50～7.44 (m, 3H), 7.33～7.27 (m, 3H), 7.24～7.20 (m, 2H), 3.58 (s, 3H), 3.52～3.44 (m, 2H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 157.72, 155.20, 144.60, 133.17, 132.58, 130.01, 129.82, 128.02, 127.00, 126.53, 123.36, 113.46, 79.93, 50.72, 44.53, 29.19, 23.11; IR (thin film) *v*: 3057, 2978, 2936, 2824, 1654, 1602, 1472, 1315, 1154, 1094, 1071, 755, 701 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}N_2O_2Na$ $[M+Na]^+$ 331.1417, found 331.1416.

3-(2-Methoxy-2,2-diphenylethyl)-1-methylquinoxalin-2(1*H*)-one (**7f**): Pale yellow solid (R_f=0.5), yield 84% (93.3 mg). m.p. 53～55 ℃; ^{1}H NMR (400 MHz, chloroform-*d*) δ: 7.60 (d, *J*=7.9 Hz, 1H), 7.46～7.39 (m, 1H), 7.33～7.31 (m, 4H), 7.25～7.12 (m, 8H), 7.13 (d, *J*=8.3 Hz, 1H), 4.03 (s, 2H), 3.41 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ: 157.18, 154.73, 144.91, 132.98, 132.50, 129.98, 129.71, 127.70, 127.62, 126.91, 123.21, 113.35, 83.81, 51.41, 36.97, 29.02; IR (thin film) *v*: 3057, 3022, 2937, 2827, 1654, 1602, 1472, 1194, 1076, 1036, 895, 753, 699 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}N_2O_2Na$ $[M+Na]^+$ 393.1573, found 393.1571.

Supporting Information Experimental procedures, the synthesis method of the starting materials, the mechanistic study and compound characterization data. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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